Supporting Information

Transition Metal-free Regioselective Aza-Michael Approach to Access Spiro-heterocycles through [3+2]/[4+2] spiro-annulation using haloamines

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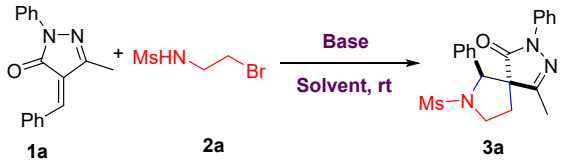
1. General Information

Unless otherwise noted, all commercially available components, as well as reagents, and solvents, were obtained from suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed using a Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness). After elution, plates were visualized using UV radiation (254 nm). Further visualization was possible by staining with a basic solution of potassium permanganate or an acidic solution of ceric molybdate. Column chromatography was carried out through silica gel (100-200 mesh) using EtOAc/n-Hexane as an eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100MHz) spectra were measured on Bruker AMX 400 spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.00 ppm. All coupling constants (J values) were reported in Hertz (Hz). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets), coupling constants (Hz) and integration. Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. HRMS (ESI) spectra were recorded using a Bruker Impact HD quadrupole plus ion trap at the CIF, S. P. Pune University. Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and were uncorrected. An oil bath was used as a heating source. The starting compounds **1**[1], **2a**[2], **4a**[3], **6a**[4], and **9a**[5] have been synthesized using the reported procedure.

Table S1: Optimisation of reaction conditions for synthesis of *spiro*-pyrrolidine derivatives using alkylidine pyrazolones[a]

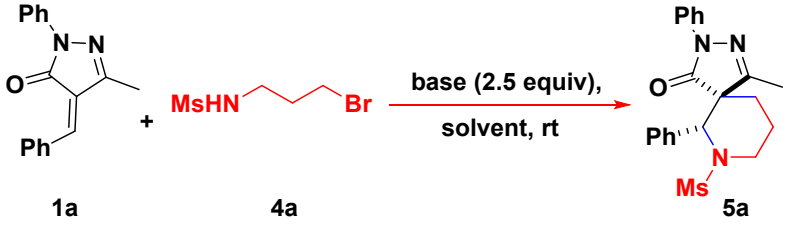


1a 2a 3a

sr. no	**2a** (equiv.)	base	solvent	yield (%)[b]	*dr*[c]
1	1.5	K_2CO_3	MeCN	80	5:1
2	1.5	Cs_2CO_3	MeCN	70	5:1
3	1.5	K_3PO_4	MeCN	78	5:1
4	1.5	Et_3N	MeCN	74	5:1
5	1.5	DBU	MeCN	69	3:1
6	1.5	NaH	MeCN	76	5:1
7	1.5	*t*-BuOK	MeCN	75	5:1
8	1.5	K_2CO_3	Toluene	15	4:1
9	1.5	K_2CO_3	THF	35	11:1
10	1.5	K_2CO_3	1,4-dioxane	10	11:1
11	1.5	K_2CO_3	DMF	54	10:1
12	1.5	K_2CO_3	DCE	35	9:1
13	**1.5**	**K_2CO_3**	**Acetone**	**86**	**10:1**
14	1.5	K_2CO_3	DMSO	nr	-
15	1.5	K_2CO_3	EtOAc	30	8:1
16	1	K_2CO_3	Acetone	79	10:1
17	2	K_2CO_3	Acetone	86	10:1
18	1.5	K_2CO_3	Acetone	81[d]	10:1
19	1.5	K_2CO_3	Acetone	83[e]	10:1

[a]All reactions were performed with **1a** (0.19 mmol, 1.0 equiv.), **2a** (0.29 mmol, 1.5 equiv.), and base (0.48 mmol, 2.5 equiv.) in solvent (2.0 mL) at room temperature (rt) for 6 h. [b]isolated yields, [c]determined by ^{1}H NMR of the crude reaction mixture, [d]K2CO3 (0.53 mmol, 2.0 equiv.). [e]K2CO3 (0.80 mmol, 3.0 equiv.), nr = no reaction.

Table S2: Optimisation of reaction conditions for synthesis of *spiro*-piperidine derivatives using alkylidine pyrazolone[a]

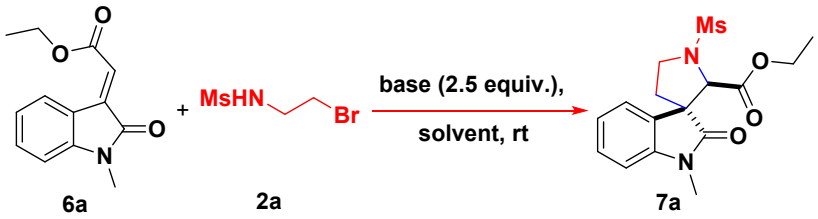


1a 4a 5a

sr.no	base	solvent	time t (h)	yield (%)[b]	*dr*[c]
1	K_2CO_3	MeCN	14	35	1.3:1
2	DBU	MeCN	1	15	1.6:1
3	K_3PO_4	MeCN	2	70	1:1
7	*t*-BuOK	MeCN	18	64	1.8:1
5	**Cs_2CO_3**	**MeCN**	**1**	**72**	**1.6:1**
6	NaH	MeCN	16	60	1.8:1
7	Et_3N	MeCN	24	nr	-
8	Cs_2CO_3	Acetone	1	65	1.5:1
9	Cs_2CO_3	DMF	2	32	1.2:1
9	Cs_2CO_3	DMSO	24	nr	-
10	Cs_2CO_3	THF	12	54	1.3:1
11	Cs_2CO_3	DCM	12	44	1.4:1
12	Cs_2CO_3	toluene	12	21	1.2:1

[a]All reactions were performed with **1a** (0.19 mmol, 1.0 equiv.), **4a** (0.29 mmol, 2.0 equiv.), and base (0.48 mmol, 2.5 equiv.) in solvent (2 mL) at room temperature (rt), [b]isolated yields for both distereomers, [c]determined by ^{1}H NMR of the crude reaction mixture, nr= no reaction.

Table S3. Optimization of Reaction Conditions for the synthesis of *spiro*-pyrrolidine using methyleneindolinone[a]

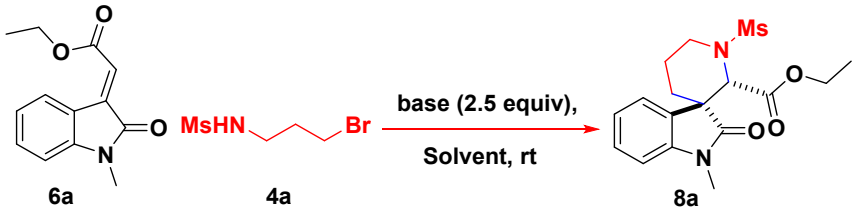


6a 2a 7a

sr. no	base	solvent	time (h)	yield (%)[b]	*dr*[c]
1	K_2CO_3	MeCN	12	22	5.8:1
2	**DBU**	**MeCN**	**3**	**42**	**7:1**
3	Cs_2CO_3	MeCN	12	15	5.6:1
4	Et_3N	MeCN	12	18	5:1
5	NaH	MeCN	12	20	4.5:1
6	K_3PO_4	MeCN	12	27	6:1
7	t-BuOK	MeCN	12	32	8.5:1
8	DBU	1,4-dioxane	12	15	-
9	DBU	DMF	12	nr	-
10	DBU	DMSO	12	nr	3.4:1
11	DBU	THF	12	35	6:1
12	DBU	DCE	12	trace	-
13	DBU	toluene	12	23	6:1
14	DBU	EtOAc	12	20	5.5:1
15	DBU	acetone	12	36	3:1

[a]All reactions were performed with **6a** (0.22 mmol, 1.0 equiv.), **2a** (0.32 mmol, 1.5 equiv.), and base (0.54 mmol, 2.5 equiv.) in solvent (2 mL) at room temperature (rt), [b]isolated yields. [c]determined by ^{1}H NMR of the crude reaction mixture, nr= no reaction.

Table S4. Optimization of Reaction Conditions for the synthesis of *spiro*-piperidine using methyleneindolinone[a]

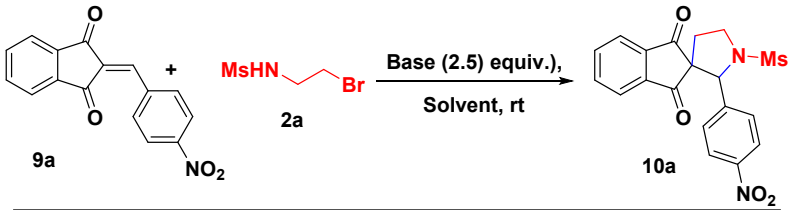


6a 4a 8a

sr. no	base	solvent	time t (h)	yield (%)[b]	*dr*[c]
1	**Cs_2CO_3**	**MeCN**	**18**	**82**	**1.4:1**
2	DBU	MeCN	3	41	2.5:1
3	K_3PO_4	MeCN	48	58	2:1
7	*t*-BuOK	MeCN	12	trace	-
5	K_2CO_3	MeCN	48	68	1.4:1
6	NaH	MeCN	12	nr	-
7	Et_3N	MeCN	12	nr	-
8	Cs_2CO_3	acetone	2	63	1.4:1
9	Cs_2CO_3	DMF	12	32	1.4:1
9	Cs_2CO_3	DMSO	3	36	1.3:1
10	Cs_2CO_3	THF	12	31	2:1
11	Cs_2CO_3	DCM	12	38	1.3:1
12	Cs_2CO_3	toluene	12	32	1.4:1

[a]All reactions were performed with **6a** (0.22 mmol, 1.0 equiv.), **4a** (0.32 mmol, 2.0 equiv.), and base (0.54 mmol, 2.5 equiv.) in solvent (2 mL) at room temperature (rt), [b]isolated yields for both distereomers, [c]determined by ^{1}H NMR of the crude reaction mixture, nr= no reaction.

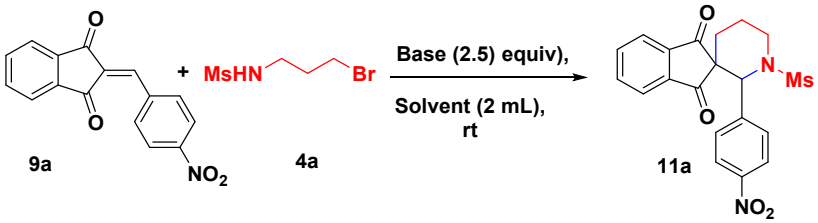
Table S5: Optimisation of reaction conditions for synthesis of *spiro*-pyrrolidine 1,3-indandione derivatives[a]



sr. no	**2a** (equiv.)	base	solvent	time (h)	yield (%)[b]
1	1.5	K_2CO_3	MeCN	3	97
2	1.5	DBU	MeCN	1	25
3	**1.5**	**Cs_2CO_3**	**MeCN**	**2**	**99**
4	1.5	Et_3N	MeCN	3	95
5	1.5	NaH	MeCN	4	94
6	1.5	K_3PO_4	MeCN	2	98
7	1.5	t-BuOK	MeCN	4	42
8	1.5	Cs_2CO_3	1,4-dioxane	2	60
9	1.5	Cs_2CO_3	DMF	2	50
10	1.5	Cs_2CO_3	DMSO	6	40
11	1.5	Cs_2CO_3	THF	2	92
12	1.5	Cs_2CO_3	DCE	1	90
13	1.5	Cs_2CO_3	toluene	5	40
14	1.5	Cs_2CO_3	EtOAc	3	65
15	1.5	Cs_2CO_3	acetone	2	85
17	1	Cs_2CO_3	MeCN	2	80
18	2	Cs_2CO_3	MeCN	2	92
19	1.5	Cs_2CO_3	MeCN	2	99[c]

[a]All reactions were performed with **9a** (0.21 mmol, 1.0 equiv.), **2a** (0.32 mmol, 1.5 equiv.), and base (0.53 mmol, 2.5 equiv.) in solvent (2 mL) at room temperature (i.e., 25 °C) (rt), [b]isolated yields, [c]base (0.64 mmol, 3.0 equiv.), nr= no reaction.

Table S6: Optimisation of reaction conditions for synthesis of *spiro*-pyrrolidine 1,3-indandione derivatives[a]

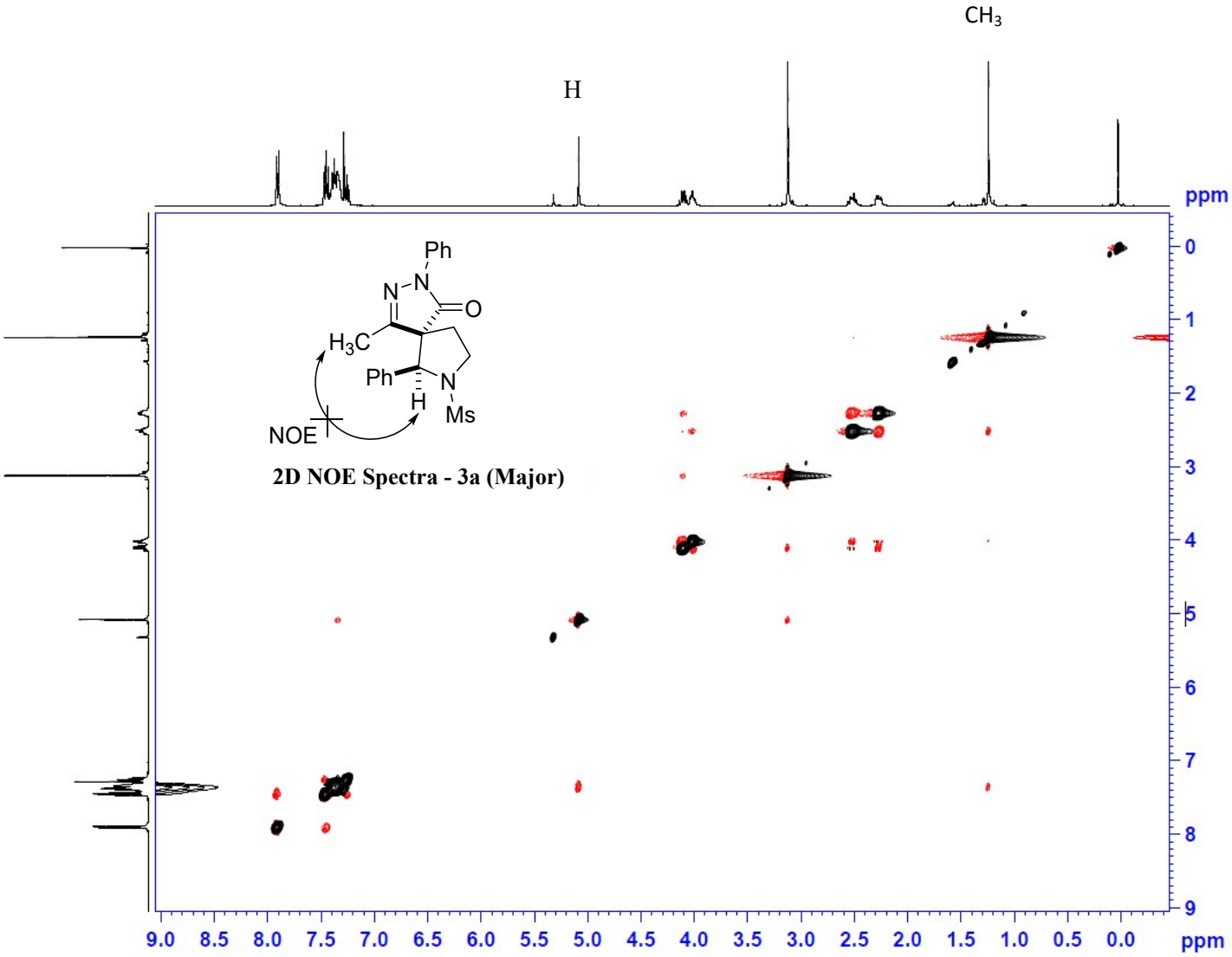


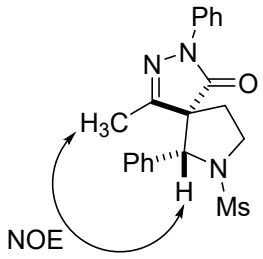
sr.no	base	solvent	time t (h)	yield (%)[b]
1	**Cs_2CO_3**	**MeCN**	**4**	**91**
2	DBU	MeCN	1	42
3	K_3PO_4	MeCN	4	90
7	*t*-BuOK	MeCN	5	85
5	K_2CO_3	MeCN	8	89
6	NaH	MeCN	6	80
7	Et_3N	MeCN	nr	nr
8	Cs_2CO_3	acetone	4	63
9	Cs_2CO_3	DMF	5	40
9	Cs_2CO_3	DMSO	8	35
10	Cs_2CO_3	THF	6	75
11	Cs_2CO_3	DCM	2	68
12	Cs_2CO_3	toluene	9	27

[a]All reactions were performed with **9a** (0.21 mmol, 1.0 equiv.), **4a** (0.32 mmol, 1.5 equiv.), and base (0.53 mmol, 2.5 equiv.) in solvent (2 mL) at room temperature (i.e., 25 °C) (rt), [b]isolated yields, nr= no reaction.

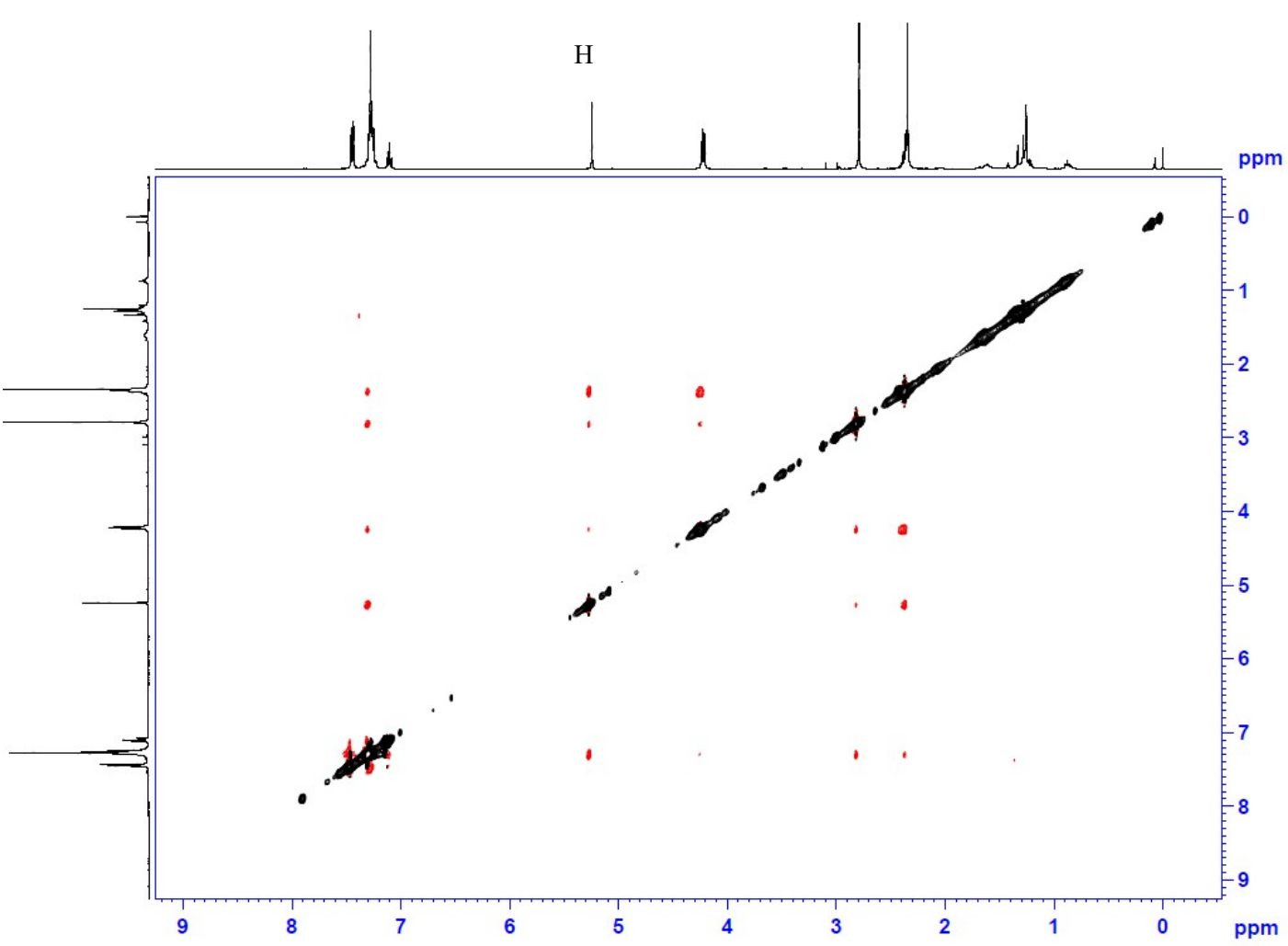
2. Relative configuration determination

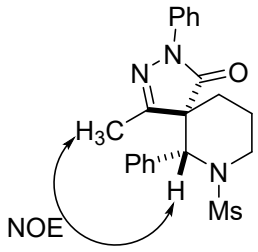
The relative configuration of diastereomers **3a/3a', 5a/5a', 7a**, and **8n/8n'** was determined by 2D NOE and 1D NOE spectra of the isolated compound. For diastereomers **3a, 5a**', **7a,** and **8n'**, there are no significant cross-peaks between H-CH_3 (**3a,** and **5a**') and H_a-H_b (**7a,** and **8n')** as shown in 2D NOE spectra. Whereas, in the case of diastereomers **3a'** and **5a,** there are significant cross-peaks between H-CH_3 (**3a'** and **5a**) and H_a-H_b (**8n)** as shown in 2D NOE spectra. Also, the relative configuration of the diastereomers **7a** was determined by 1D NOE spectra, which did not show significant cross-peaks between H_a-H_b.



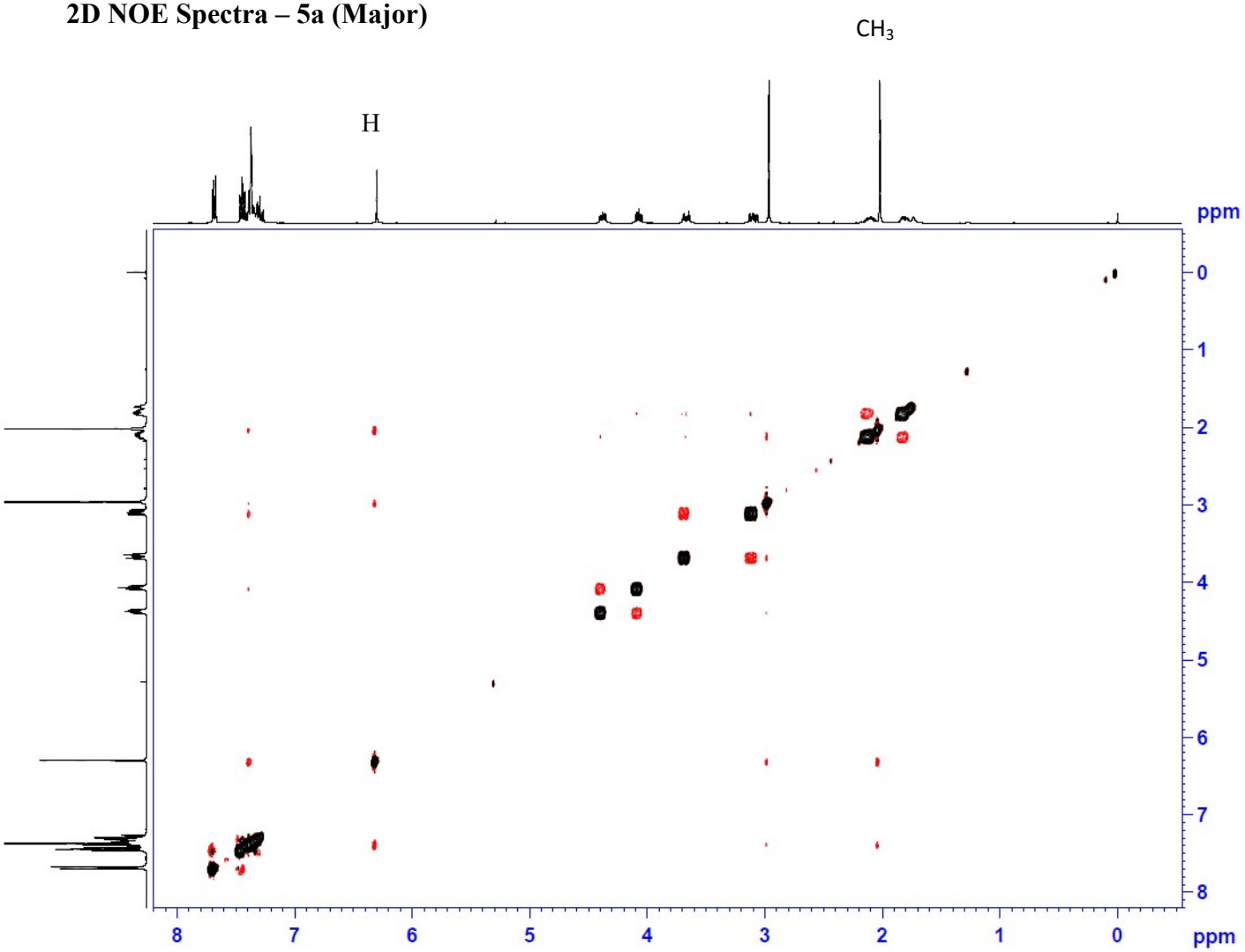


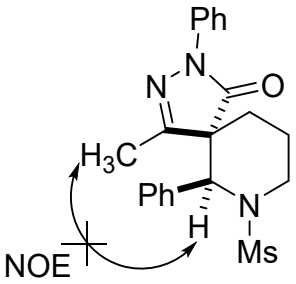
2D NOE Spectra - 3a' (Minor)



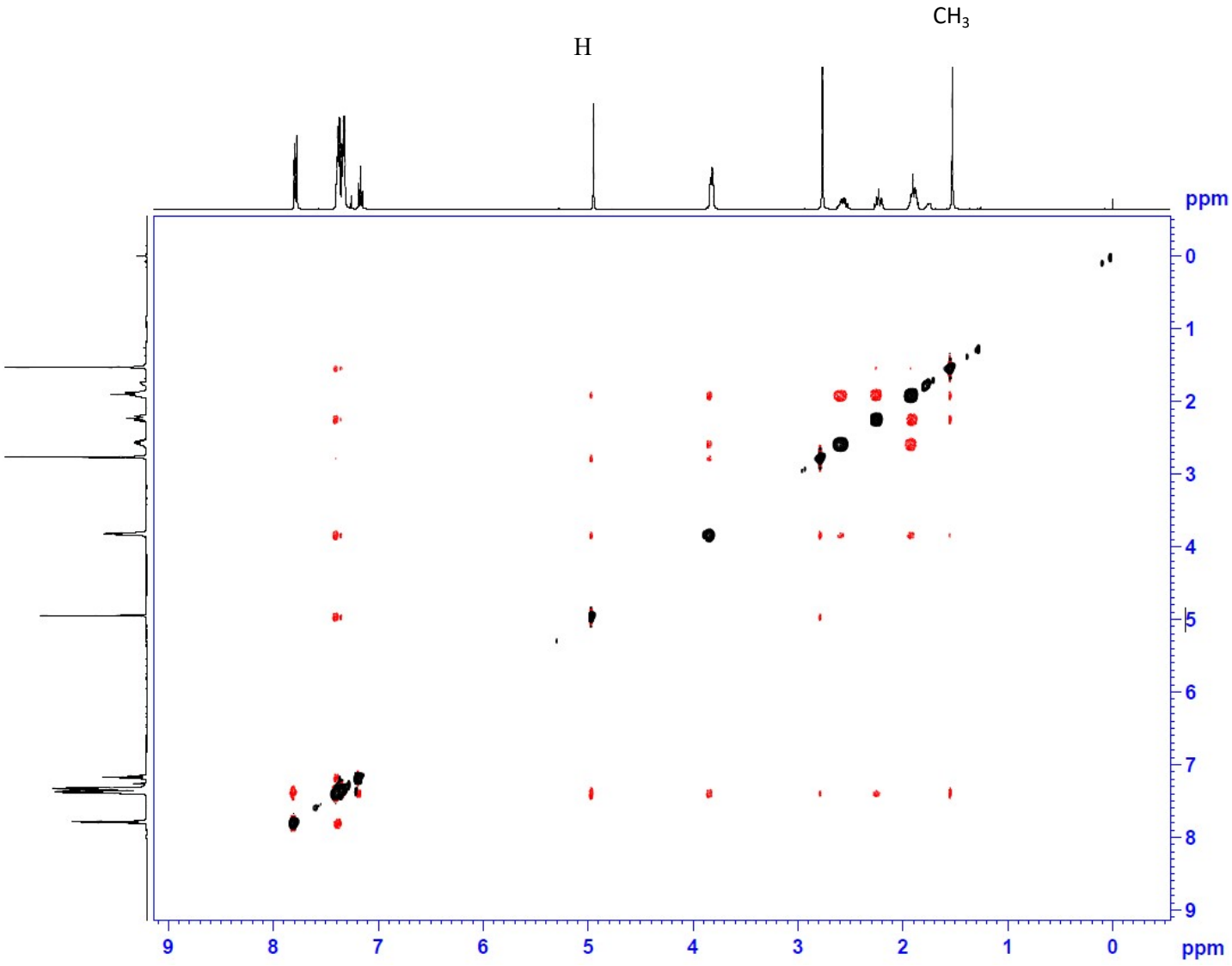


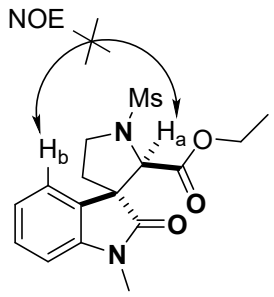
2D NOE Spectra – 5a (Major)



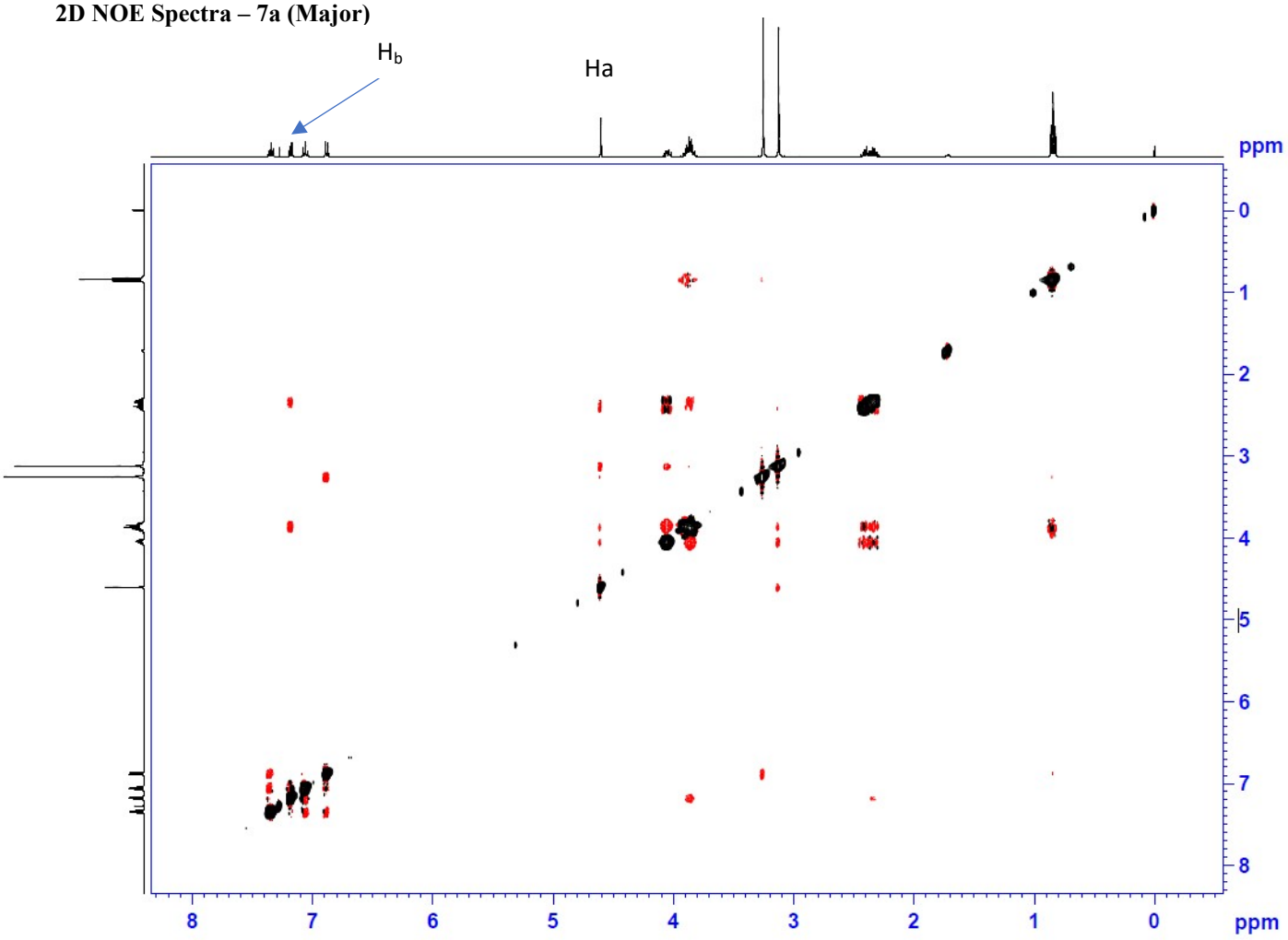


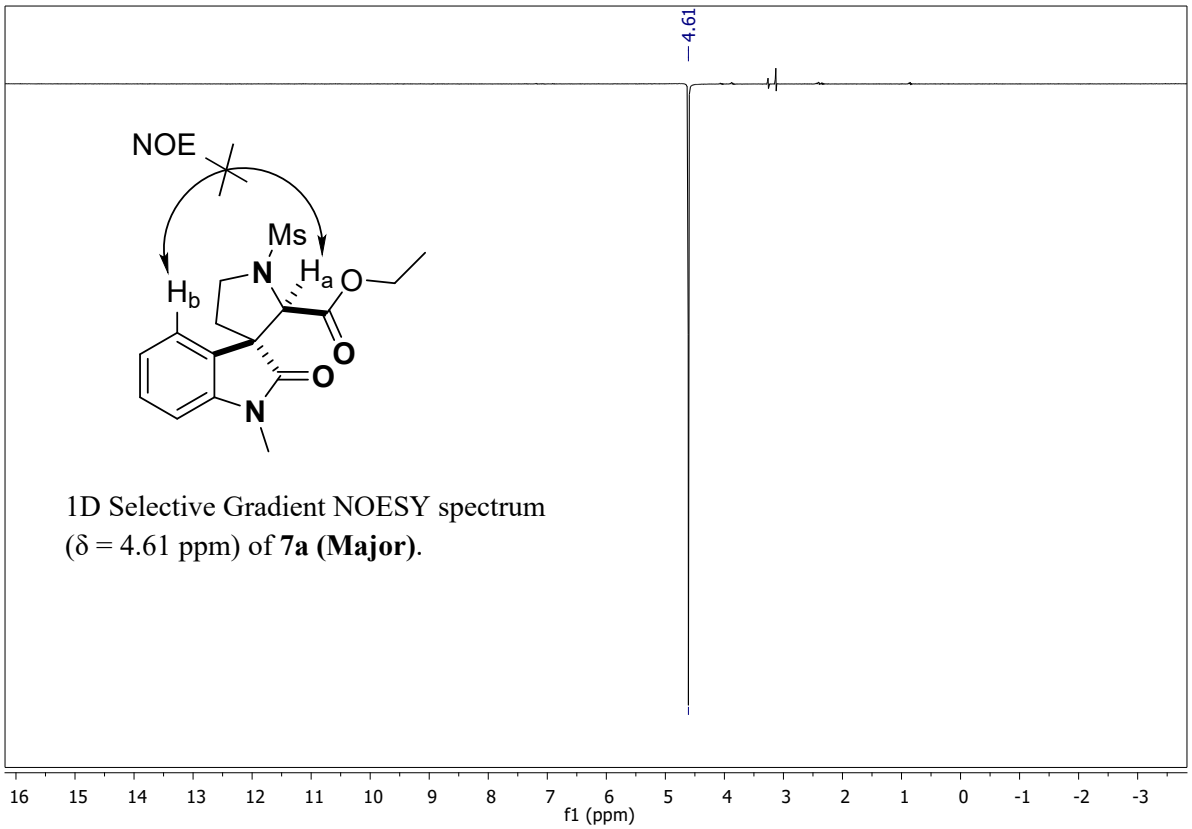
2D NOE Spectra – 5a' (Minor)



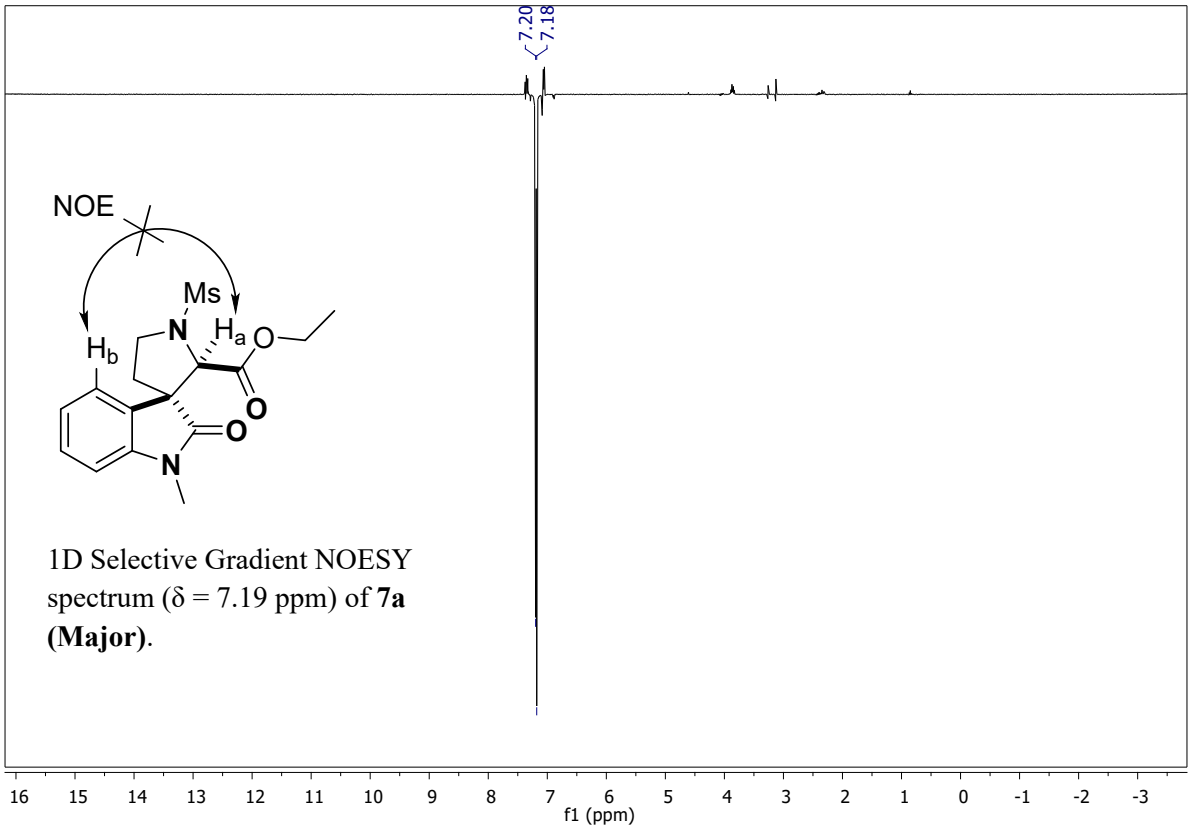


2D NOE Spectra – 7a (Major)

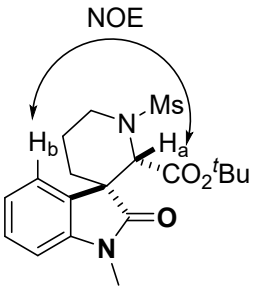




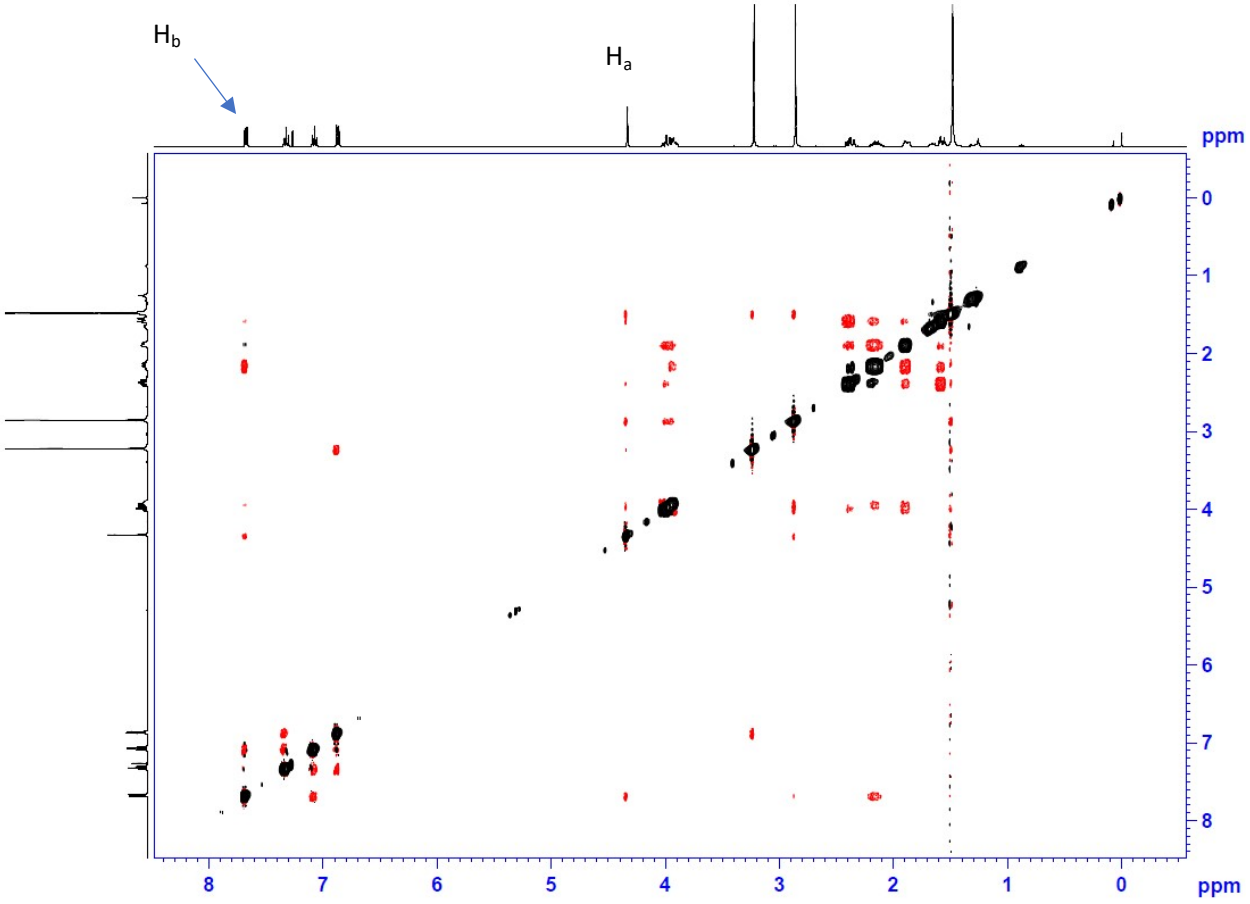
1D Selective Gradient NOESY spectrum (δ = 4.61 ppm) of **7a (Major)**.

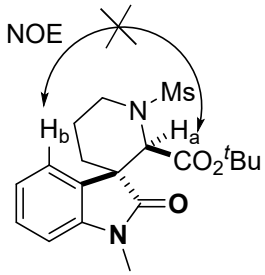


1D Selective Gradient NOESY spectrum (δ = 7.19 ppm) of **7a (Major)**.

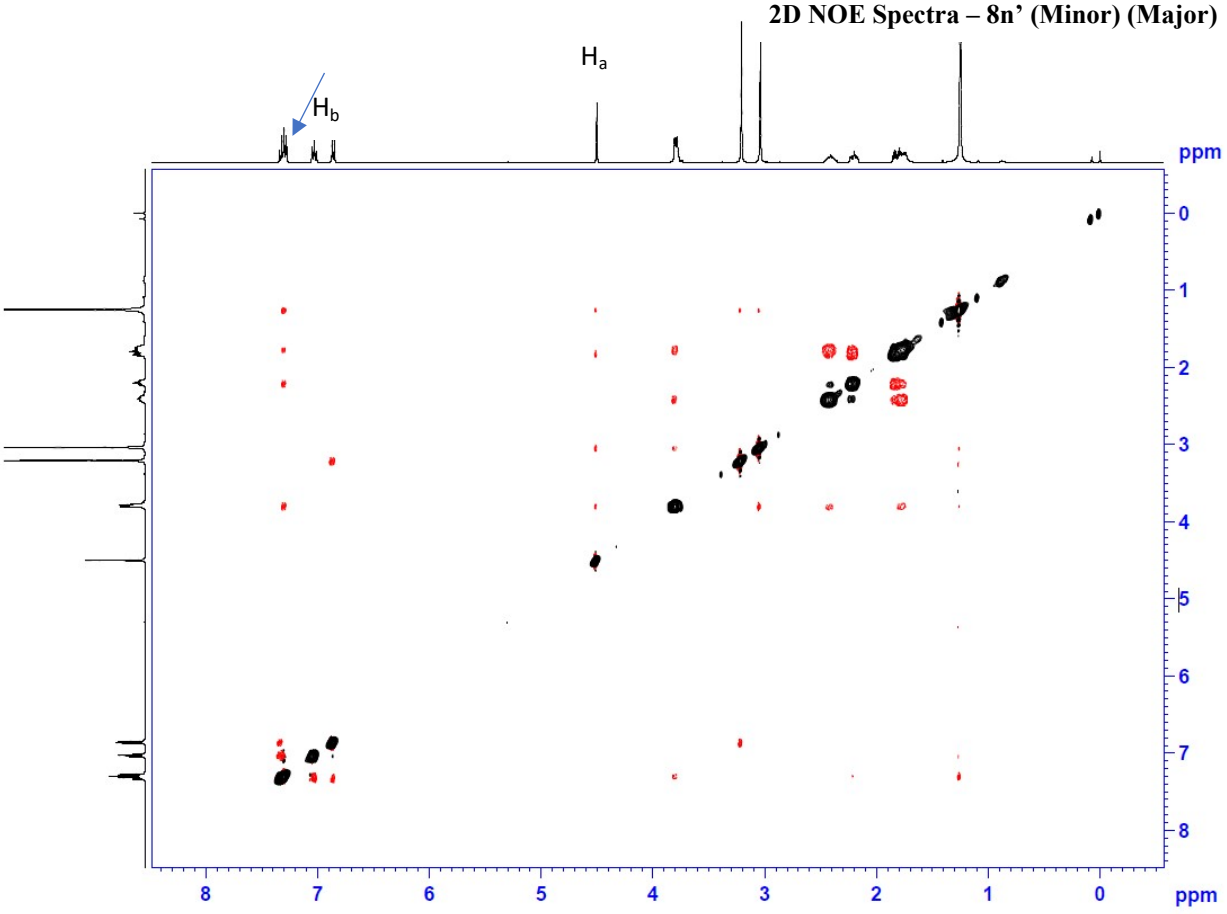


2D NOE Spectra – 8n (Major)

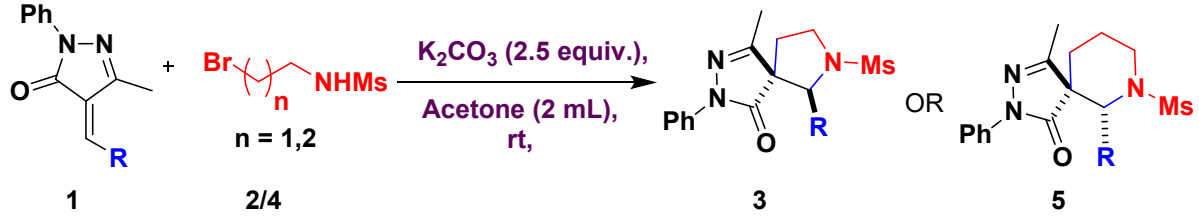




2D NOE Spectra – 8n' (Minor) (Major)

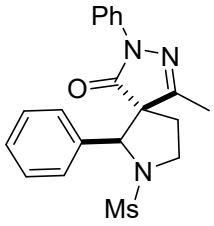


4. General experimental procedures and characterization data for the synthesis of compounds 3 and 5

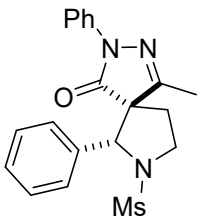


General experimental procedure: To an oven-dried 50 mL round bottom flask was added alkylidene pyrazolone (0.19 mmol, 1.0 equiv.), haloamines (0.29 mmol, 1.5 equiv.), and base (0.48 mmol, 2.5 equiv.) in solvent (2.0 mL), and the resulting solution was stirred at room temperature until the starting completely consumed. After completion of the reaction, the reaction mass was diluted with water (10.0 mL) and extracted with EtOAc (3×10 mL). The organic layers were collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent.

Characterization of the products:

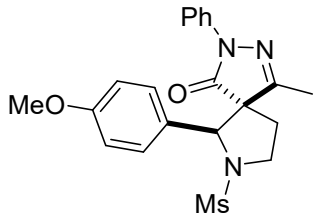


(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2,6-diphenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3a);** Pinkish solid, 63 mg, 86% yield, 10:1 *dr*, *Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 162−164°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 8.08 – 7.69 (m, 2H), 7.42 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 3H), 7.26 (s, 2H), 7.22 (s, 1H), 5.05 (s, 1H), 4.06 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.99 (dd, *J* = 7.7, 3.7 Hz, 1H), 3.09 (s, 3H), 2.48 (ddd, *J* = 13.1, 8.9, 7.8 Hz, 1H), 2.24 (ddd, *J* = 13.0, 6.9, 3.7 Hz, 1H), 1.21 (s, 3H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 159.1, 138.8, 137.7, 129.1, 129.1, 128.8, 126.5, 125.7, 118.9, 68.6, 63.4, 47.3, 35.6, 31.3, 14.9; **HRMS (ESI)** calcd for: $C_{20}H_{22}N_3O_3S$: [M + H]+, 384.1376 found: 384.1373.

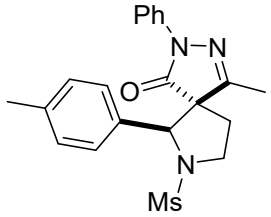


(*5R*,6R**)-4-methyl-7-(methylsulfonyl)-2,6-diphenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3a') (minor);** White solid, 6 mg, 8% yield, 10:1 *dr*, *Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 166−168°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.37 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.25 – 7.15 (m, 7H), 7.07 – 6.99 (m, 1H), 5.16 (s, 1H), 4.18 – 4.09 (m, 2H),

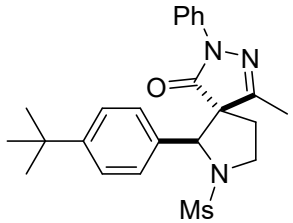
2.71 (s, 3H), 2.34 – 2.23 (m, 5H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.8, 158.8, 137.3, 135.4, 128.9, 128.8, 128.6, 126.9, 125.4, 119.2, 67.2, 64.6, 47.9, 41.5, 32.8, 13.8.;**HRMS (ESI)** calcd for: $C_{20}H_{22}N_3O_3S$: [M + H]+, 384.1376 found: 384.1373.



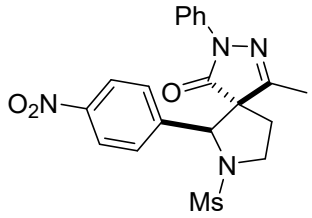
(*5R*,6S**)-6-(4-methoxyphenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3b);** Yellow solid, 56 mg, 79% yield, 10.5:1 *dr*, *Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 158−160°C;**^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.94 – 7.79 (m, 2H), 7.42 (dd, *J* = 11.4, 4.6 Hz, 2H), 47.27 – 7.17 (m, 3H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.01 (s, 1H), 4.04 (dd, *J* = 9.2, 7.0 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.79 (s, 3H), 3.07 (s, 3H), 2.48 (dt, *J* = 13.0, 8.4 Hz, 1H), 2.23 (ddd, *J* = 13.0, 6.9, 3.6 Hz, 1H), 1.29 (s, 3H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 159.9, 159.2, 137.7, 130.8, 129.1, 127.7, 125.6, 118.9, 114.5, 68.2, 63.5, 55.4, 47.2, 35.5, 31.2, 15.1; **HRMS (ESI)** calcd for: $C_{22}H_{26}N_3O_4S$: [M + H]+, 414.1482 found: 414.1494.



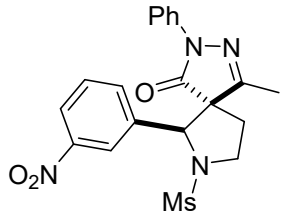
(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3c);** White solid, 60 mg, 83% yield, 10:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 136−138°C;**^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.99 – 7.75 (m, 2H), 7.42 (dd, *J* = 8.5, 7.6 Hz, 2H), 7.25 – 7.09 (m, 5H), 5.02 (s, 1H), 4.14 – 3.88 (m, 2H), 3.07 (s, 3H), 2.47 (ddd, *J* = 13.0, 8.8, 7.9 Hz, 1H), 2.33 (s, 3H), 2.23 (ddd, *J* = 13.0, 6.9, 3.7 Hz, 1H), 1.25 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.9, 159.2, 138.6, 137.7, 135.8, 129.8, 129.1, 126.4, 125.6, 118.9, 68.4, 63.5, 47.2, 35.6, 31.3, 21.3, 15.1; **HRMS (ESI)** calcd for: $C_{21}H_{24}N_3O_3S$: [M + H]+, 398.1533 found: 398.1539.



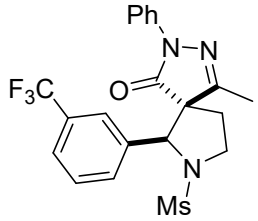
(*5R*,6S**)-6-(4-(tert-butyl)phenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3d);** White solid, 49 mg, 71% yield, 3:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 156−158°C;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.47 – 7.32 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 3H), 5.04 (s, 1H), 4.02 (dtd, *J* = 12.7, 9.9, 5.2 Hz, 2H), 3.08 (s, 3H), 2.54 – 2.42 (m, 1H), 2.27 – 2.17 (m, 1H), 1.30 (s, 9H), 1.17 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.9, 159.2, 151.9, 137.7, 135.7, 129.1, 126.2, 125.9, 125.6, 118.9, 68.3, 63.4, 47.2, 35.6, 34.7, 31.4, 31.3, 14.7; **HRMS (ESI)** calcd for: $C_{24}H_{30}N_3O_3S$: [M + H]+, 440.2002 found: 440.2012.



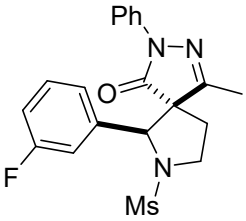
(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-6-(4-nitrophenyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3e);** White solid, 51 mg, 73% yield, 3.3:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 188−190°C;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.97 – 7.78 (m, 2H), 7.44 (dd, *J* = 8.5, 7.6 Hz, 4H), 7.26 (dt, *J* = 12.8, 4.3 Hz, 1H), 5.13 (s, 1H), 4.15 – 3.94 (m, 2H), 3.11 (s, 3H), 2.51 – 2.40 (m, 1H), 2.39 – 2.29 (m, 1H), 1.36 (s, 3H).; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 157.9, 148.1, 145.7, 137.4, 129.2, 127.5, 125.9, 124.3, 118.9, 68.2, 63.6, 47.7, 35.2, 31.9, 15.4; **HRMS (ESI)** calcd for: $C_{20}H_{21}N_4O_5S$: [M + H]+, 429.1227 found: 429.1236.



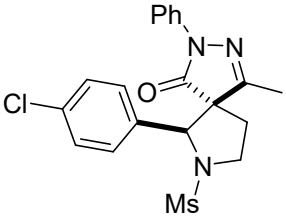
(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-6-(3-nitrophenyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3f);** White solid, 54 mg, 77% yield, 7:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 184−186°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.35 – 8.08 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.62 (s, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.20 (m, 1H), 5.13 (s, 1H), 4.06 (ddd, *J* = 9.9, 8.8, 2.6 Hz, 2H), 3.11 (s, 3H), 2.47 (dt, *J* = 13.3, 7.7 Hz, 1H), 2.39 – 2.28 (m, 1H), 1.35 (s, 3H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 157.9, 148.7, 141.0, 137.4, 132.5, 130.2, 129.2, 125.9, 123.8, 121.5, 119.1, 68.1, 63.5, 47.6, 35.3, 31.7, 15.4; **HRMS (ESI)** calcd for: $C_{20}H_{21}N_4O_5S$: [M + H]+, 429.1227 found: 429.1229.



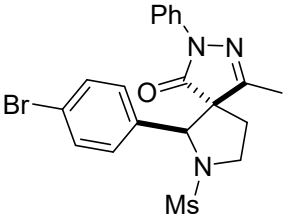
(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(3-(trifluoromethyl)phenyl)-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3g);** White solid, 54 mg, 79% yield, 4.8:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 128−130°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.93 – 7.79 (m, 2H), 7.74 – 7.47 (m, 4H), 7.47 – 7.39 (m, 2H), 7.24 (dd, *J* = 10.7, 4.3 Hz, 1H), 5.10 (s, 1H), 4.16 – 3.94 (m, 2H), 3.11 (s, 3H), 2.53 – 2.40 (m, 1H), 2.34 – 2.24 (m, 1H), 1.28 (d, *J* = 7.7 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.3, 158.3, 139.9, 137.5, 131.7, 131.4, 129.9, 129.7, 129.2, 125.9, 125.7 (d, *J* = 3.7 Hz), 123.3 (d, *J* = 3.8 Hz), 119.0, 68.3, 63.5, 47.5, 35.4, 31.5, 15.0**; ^{19}F NMR (377 MHz, $CDCl_3$):** δ -62.66; **HRMS (ESI)** ca3lcd for: $C_{21}H_{21}F_3N_3O_3S$: [M + H]+, 452.1250 found: 452.1261.



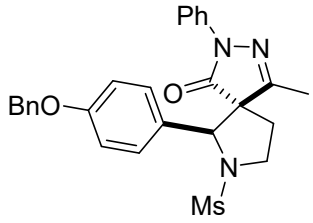
(*5R*,6S**)-6-(3-fluorophenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3h);** White solid, 55 mg, 77% yield, 6:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 150−152°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.73 (m, 2H), 7.50 – 7.37 (m, 2H), 7.33 (td, *J* = 8.0, 5.8 Hz, 1H), 7.23 (ddd, *J* = 8.5, 2.5, 1.5 Hz, 1H), 7.04 (dt, *J* = 8.3, 5.3 Hz, 3H), 5.03 (s, 1H), 4.12 – 3.91 (m, 2H), 3.10 (s, 3H), 2.61 – 2.36 (m, 1H), 2.25 (ddd, *J* = 13.1, 6.9, 3.8 Hz, 1H), 1.29 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.6, 164.5, 161.9, 158.5, 141.5 (d, *J* = 6.8 Hz), 137.6, 130.8 (d, *J* = 8.2 Hz), 129.2, 125.8, 122.2 (d, *J* = 2.9 Hz), 118.9, 115.8 (d, *J* = 21.2 Hz), 113.8 (d, *J* = 22.7 Hz), 67.9 (d, *J* = 1.8 Hz), 63.3, 47.3, 35.5, 31.5, 14.9; **^{19}F NMR (377 MHz, $CDCl_3$):** δ -111.25; **HRMS (ESI)** calcd for: $C_{20}H_{21}FN_3O_3S$: [M + H]+, 402.1282 found: 402.1291.



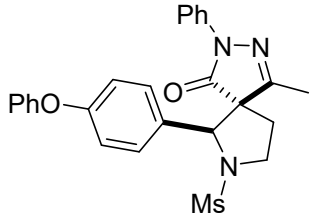
(*5R*,6S**)-6-(4-chlorophenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3i);** White solid, 55 mg, 78% yield, 6.8:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 150−152°C;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.77 (m, 2H), 7.43 (dd, *J* = 10.8, 5.2 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.24 (dd, *J* = 12.9, 5.7 Hz, 3H), 5.01 (s, 1H), 4.12 – 3.93 (m, 2H), 3.08 (s, 3H), 2.44 (dt, *J* = 14.0, 8.0 Hz, 1H), 2.33 – 2.20 (m, 1H), 1.33 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.5, 158.6, 137.6, 137.3, 134.7, 129.3, 129.2, 127.9, 125.8, 118.9, 68.1, 63.5, 47.4, 35.4, 31.5, 15.2; **HRMS (ESI)** calcd for: $C_{20}H_{21}ClN_3O_3S$: [M + H]+, 418.0987 found: 418.0998.



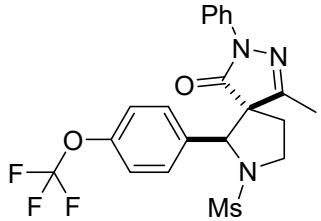
(*5R*,6S**)-6-(4-bromophenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3j);** White solid, 54 mg, 80% yield, 6:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 170−172°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.87 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.29 – 7.14 (m, 3H), 5.00 (s, 1H), 4.12 – 3.89 (m, 2H), 3.08 (s, 3H), 2.44 (dt, *J* = 13.1, 8.0 Hz, 1H), 2.26 (ddd, *J* = 13.0, 7.0, 4.2 Hz, 1H), 1.33 (s, 3H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.5, 158.6, 137.8, 137.6, 132.3, 129.2, 128.2, 125.8, 122.8, 118.9, 68.2, 63.4, 47.4, 35.4, 31.5, 15.3; **HRMS (ESI)** calcd for: $C_{20}H_{21}BrN_3O_3S$: [M + H]+, 462.0482 found: 462.0492.



(*5R*,6S**)-6-(4-(benzyloxy)phenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3k);** Yellow solid, 48 mg, 72% yield, 4:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 150−152°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.87 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.50 – 7.28 (m, 7H), 7.26 – 7.16 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.05 (s, 2H), 5.00 (s, 1H), 4.13 – 3.90 (m, 2H), 3.07 (s, 3H), 2.56 – 2.38 (m, 1H), 2.22 (ddd, *J* = 12.9, 6.8, 3.5 Hz, 1H), 1.27 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.8, 159.2, 159.1, 137.7, 136.8, 131.2, 129.1, 128.7, 128.2, 127.7, 127.7, 125.6, 118.9, 115.5, 70.3, 68.2, 63.5, 47.2, 35.5, 31.2, 15.1; **HRMS (ESI)** calcd for: $C_{27}H_{28}N_3O_4S$: [M + H]+, 490.1795 found: 490.1798.

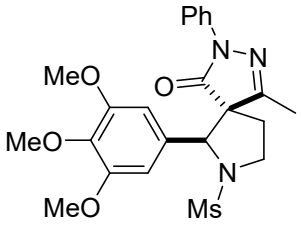


(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-6-(4-phenoxyphenyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3l);** White solid, 50 mg, 75% yield, 8.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 180−182°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 – 7.80 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.24 (dq, *J* = 14.9, 7.3 Hz, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.05 – 6.91 (m, 4H), 5.04 (s, 1H), 4.11 – 4.01 (m, 1H), 4.00 – 3.90 (m, 1H), 3.09 (s, 3H), 2.47 (dt, *J* = 13.1, 8.2 Hz, 1H), 2.24 (ddd, *J* = 12.9, 6.8, 3.7 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.7, 158.9, 157.8, 156.7, 137.6, 133.4, 129.9, 129.1, 127.9, 125.7, 123.9, 119.3, 119.1, 118.9, 68.2, 63.5, 47.3, 35.5, 31.3, 15.1; **HRMS (ESI)** calcd for: $C_{26}H_{26}N_3O_4S$: [M + H]+, 476.1639 found: 476.1645.

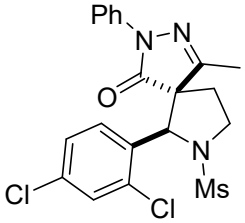


(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(4-(trifluoromethoxy)phenyl)-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3m);** White solid, 54 mg, 80% yield, 5.8:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 176−178°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.99 – 7.76 (m, 2H), 7.53 – 7.40 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.19 (m, 3H), 5.05 (s, 1H), 4.21 – 3.89 (m, 2H), 3.11 (s, 3H), 2.46 (dt, *J* = 13.1, 8.1 Hz, 1H), 2.28 (ddd, *J* = 13.1, 6.9, 4.1 Hz, 1H), 1.29 (s, 3H**); ^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.5, 158.5, 149.5 (q, *J* = 1.9 Hz), 137.6, 137.4, 129.2, 128.0, 125.9, 121.5, 118.9, 68.0, 63.5, 47.4, 35.4, 31.5, 15.1;**^{19}F NMR (377 MHz, $CDCl_3$)** δ -57.90.;**HRMS (ESI)** calcd for: $C_{21}H_{21}F_3N_3O_4S$: [M + H]+, 468.1199 found: 468.1199.

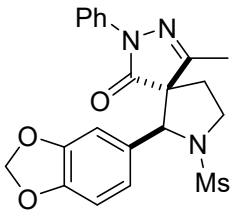
(*5R*,6S**)-6-(3,4-dimethoxyphenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3n);** Yellow solid, 52 mg, 76% yield, 9.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 148−150°C; **^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.89 (dd, *J* = 29.1, 8.1 Hz, 2H), 6.71 (s, 1H), 5.01 (s, 1H), 4.15 – 4.02 (m, 1H), 3.98 (dt, *J* = 9.9, 5.0 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.09 (s, 3H), 2.55 – 2.39 (m, 1H), 2.26 (ddd, *J* = 12.8, 6.8, 4.2 Hz, 1H), 1.35 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.7, 159.3, 149.5, 149.4, 137.7, 131.1, 129.2, 125.7, 118.8, 118.7, 111.5, 109.4, 68.6, 63.7, 56.1, 56.1, 47.4, 35.5, 31.4, 15.2; **HRMS (ESI)** calcd for: $C_{22}H_{26}N_3O_4S$: [M + H]+, 444.1588 found: 444.1593.



(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(3,4,5-trimethoxyphenyl)-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3o);** White solid, 56 mg, 83% yield, 10.3:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 104−106°C; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{P}δ 7.88 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.51 – 7.35 (m, 2H), 7.26 – 7.17 (m, 1H), 6.50 (s, 2H), 5.00 (s, 1H), 4.07 (ddd, *J* = 9.9, 8.2, 7.2 Hz, 1H), 3.97 (ddd, *J* = 10.2, 7.4, 4.6 Hz, 1H), 3.81 (d, *J* = 11.3 Hz, 9H), 3.11 (s, 3H), 2.53 – 2.38 (m, 1H), 2.34 – 2.20 (m, 1H), 1.37 (d, *J* = 19.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.6, 159.3, 153.8, 138.3, 137.6, 134.1, 129.2, 125.7, 118.8, 103.3, 68.9, 63.8, 61.1, 56.4, 47.7, 35.3, 31.6, 15.1; **HRMS (ESI)** calcd for: $C_{23}H_{28}N_3O_6S$: [M + H]+, 474.1693 found: 474.1699.

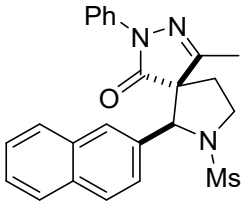


(*5R*,6R**)-6-(2,4-dichlorophenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3p);** White solid, 51 mg, 75% yield, 4:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 110−112°C;**^{1}H NMR (400 MHz, $CDCl_3$) :** δ 7.94 – 7.77 (m, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.42 (dd, *J* = 17.1, 8.8 Hz, 4H), 7.23 (d, *J* = 7.4 Hz, 1H), 5.34 (s, 1H), 4.11 – 3.89 (m, 2H), 3.15 (s, 3H), 2.45 (ddd, *J* = 13.0, 10.2, 8.1 Hz, 1H), 2.21 (ddd, *J* = 13.0, 6.0, 2.3 Hz, 1H), 1.30 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) :** δ 174.9, 157.6, 137.5, 135.4, 135.3, 133.1, 130.1, 129.6, 129.2, 127.9, 125.9, 119.21, 64.6, 62.3, 46.8, 34.9, 31.9, 14.6; **HRMS (ESI)** calcd for: $C_{20}H_{20}Cl_2N_3O_3S$: [M + H]+, 452.0597 found: 452.0599.

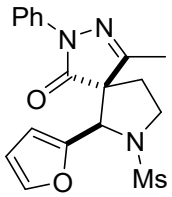


(*5R*,6S**)-6-(benzo[d][1,3]dioxol-5-yl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3q);** Yellow solid, 56 mg, 80% yield, 7.7:1 *dr, Rf* = 0.5,

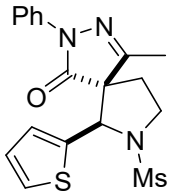
column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 – 7.80 (m, 2H), 7.42 (dd, *J* = 8.5, 7.6 Hz, 2H), 7.26 – 7.18 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 3H), 5.97 (s, 2H), 4.95 (s, 1H), 4.08 – 3.92 (m, 2H), 3.08 (s, 3H), 2.54 – 2.43 (m, 1H), 2.27 – 2.16 (m, 1H), 1.36 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 158.9, 148.4, 147.9, 137.6, 132.9, 129.1, 125.7, 119.9, 118.9, 108.9, 107.1, 101.6, 68.2, 63.4, 47.1, 35.5, 31.1, 15.1; **HRMS (ESI)** calcd for: $C_{21}H_{22}N_3O_5S$: [M + H]+, 428.1275 found: 428.1284.



(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-6-(naphthalen-2-yl)-2-phenyl-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3r);** White solid, 52 mg, 75`% yield, 10.6:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 178−180°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 – 7.71 (m, 6H), 7.58 – 7.40 (m, 4H), 7.37 – 7.19 (m, 2H), 5.23 (s, 1H), 4.26 – 3.93 (m, 2H), 3.13 (s, 3H), 2.62 – 2.47 (m, 1H), 2.35 – 2.21 (m, 1H), 1.16 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.8, 158.9, 137.6, 136.1, 133.4, 133.2, 129.2, 129.1, 128.4, 127.9, 126.8, 126.7, 125.7, 125.7, 124.1, 118.9, 68.7, 63.6, 47.4, 35.5, 31.6, 15.2; **HRMS (ESI)** calcd for: $C_{24}H_{24}N_3O_3S$: [M + H]+, 434.1533 found: 434.1541.

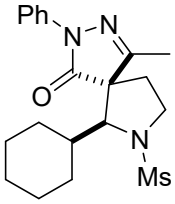


(*5R*,6R**)-6-(furan-2-yl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3s);** White solid, 48mg, 65% yield, 15.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 130−132°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 – 7.80 (m, 2H), 7.47 – 7.35 (m, 3H), 7.24 – 7.15 (m, 1H), 6.42 (d, *J* = 3.3 Hz, 1H), 6.38 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.99 (s, 1H), 4.00 (td, *J* = 9.3, 7.1 Hz, 1H), 3.90 (ddd, *J* = 9.3, 8.2, 2.9 Hz, 1H), 3.00 (s, 3H), 2.64 (ddd, *J* = 12.9, 9.3, 8.2 Hz, 1H), 2.27 (ddd, *J* = 12.9, 7.0, 2.9 Hz, 1H), 1.52 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 158.6, 150.9, 142.7, 137.6, 129.1, 125.6, 118.9, 111.3, 109.6, 62.1, 61.5, 46.2, 36.4, 31.5, 13.9; **HRMS (ESI)** calcd for: $C_{18}H_{20}N_3O_4S$: [M + H]+, 374.1169 found: 374.1175.

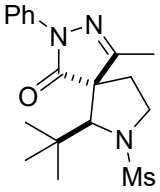


(*5R*,6R**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(thiophen-2-yl)-2,3,7-triazaspiro [4.4]non-3-en-1-one **(3t);** White solid, 52mg, 72% yield, 14:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 166−168°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 7.68 (m, 2H), 7.41 (dd, *J* = 11.5, 4.6 Hz, 2H), 7.28 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.21 (dd, *J* = 10.7, 4.2 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.97 – 6.86 (m, 1H), 5.28 (s,

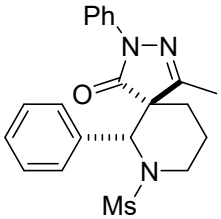
1H), 4.10 – 3.86 (m, 2H), 3.06 (s, 3H), 2.62 (dt, *J* = 13.0, 8.6 Hz, 1H), 2.27 (ddd, *J* = 13.0, 6.8, 3.1 Hz, 1H), 1.43 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.3, 158.9, 143.4, 137.6, 129.1, 127.7, 125.8, 125.8, 125.3, 118.9, 64.3, 63.3, 46.7, 36.2, 31.3, 14.6; **HRMS (ESI)** calcd for: $C_{18}H_{20}N_3O_3S_2$: [M + H]+, 390.0941 found: 390.0951.



(*5R*,6S**)-6-cyclohexyl-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3u);** White solid, 46 mg, 63% yield, 2:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 102−104°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.33 (dd, *J* = 11.4, 4.6 Hz, 2H), 7.18 – 7.07 (m, 1H), 4.15 (d, *J* = 10.3 Hz, 1H), 3.77 – 3.57 (m, 2H), 2.98 (s, 3H), 2.13 (s, 3H), 2.04 (dd, *J* = 11.8, 4.0 Hz, 2H), 1.79 (d, *J* = 12.3 Hz, 1H), 1.69 (d, *J* = 12.9 Hz, 1H), 1.57 – 1.45 (m, 2H), 1.20 – 0.95 (m, 6H), 0.78 – 0.68 (m, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.0, 161.9, 137.9, 129.0, 125.3, 119.1, 67.8, 61.2, 47.9, 41.3, 39.1, 37.8, 31.2, 30.2, 26.1, 25.9, 25.6; **HRMS (ESI)** calcd for: $C_{20}H_{28}N_3O_3S$: [M + H]+, 390.1846 found: 390.1854.

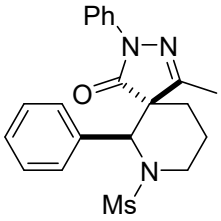


(*5R*,6S**)-6-(tert-butyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.4]non-3-en-1-one **(3v);** White solid, 48 mg, 64% yield, 10:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 120−122°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 – 7.71 (m, 2H), 7.40 (dd, *J* = 11.5, 4.5 Hz, 2H), 7.25 – 7.12 (m, 1H), 4.42 (s, 1H), 3.95 – 3.81 (m, 1H), 3.71 (td, *J* = 11.9, 4.7 Hz, 1H), 3.09 (s, 3H), 2.26 (d, *J* = 6.7 Hz, 1H), 2.24 (s, 3H), 2.13 (dd, *J* = 12.4, 4.5 Hz, 1H), 1.10 – 0.99 (m, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 174.9, 162.3, 138.1, 129.1, 125.3, 119.1, 72.6, 61.8, 50.2, 42.2, 38.9, 37.8, 27.5, 13.6; **HRMS (ESI)** calcd for: $C_{18}H_{26}N_3O_3S$: [M + H]+, 364.1689 found: 364.1696.

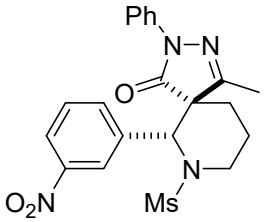


(*5R*,6R**)-4-methyl-7-(methylsulfonyl)-2,6-diphenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5a);** White solid, 55 mg, 72% yield, 1.2:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 – 7.59 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.38 (dd, *J* = 7.1, 1.5 Hz, 4H), 7.34 – 7.26 (m, 2H), 6.30 (s, 1H), 4.44 – 4.31 (m, 1H), 4.14 – 4.01 (m, 1H), 3.67 (dt, *J* = 15.5, 4.4 Hz, 1H), 3.10 (ddd, *J* = 15.4, 10.2, 3.4 Hz, 1H), 2.97 (s, 3H), 2.19 – 2.07 (m, 1H), 2.02 (s, 3H), 1.81 (dddd, *J* = 15.5, 7.2, 3.6, 1.7 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 151.5, 147.6, 138.6, 129.1, 129.0, 128.6,

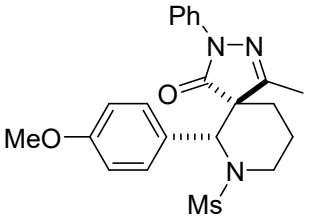
128.3, 126.7, 122.4, 103.0, 74.5, 56.2, 42.3, 40.9, 28.5, 13.5; **HRMS (ESI)** calcd for: $C_{21}H_{24}N_3O_3S$: [M + H]+, 398.1533 found: 398.1542.



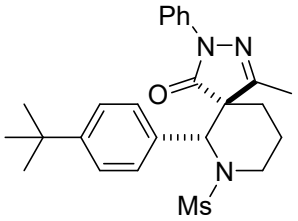
(*5R*,6S**)-4-methyl-7-(methylsulfonyl)-2,6-diphenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5a') (minor);** White solid, 55 mg, 72% yield, 1.2:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 178−180°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.43 – 7.28 (m, 7H), 7.18 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.95 (s, 1H), 3.91 – 3.75 (m, 2H), 2.78 (s, 3H), 2.65 – 2.49 (m, 1H), 2.31 – 2.16 (m, 1H), 1.97 – 1.82 (m, 2H), 1.53 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 160.8, 137.7, 129.1, 128.9, 128.9, 128.6, 125.3, 119.1, 60.8, 55.8, 43.1, 39.2, 25.4, 18.5, 16.6; **HRMS (ESI)** calcd for: $C_{21}H_{24}N_3O_3S$: [M + H]+, 398.1533 found: 398.1542.



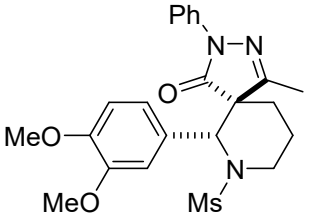
(*5R*,6R**)-4-methyl-7-(methylsulfonyl)-6-(3-nitrophenyl)-2-phenyl-2,3,7-triazaspiro [4.5]dec-3-en-1-one **(5b);** White solid, 52 mg, 72% yield, 1.3:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 170−172°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (t, *J* = 1.8 Hz, 1H), 8.15 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 7.83 – 7.66 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.40 – 7.29 (m, 2H), 7.21 – 7.11 (m, 1H), 4.95 (s, 1H), 4.02 – 3.88 (m, 1H), 3.69 (dt, *J* = 13.6, 5.3 Hz, 1H), 2.91 (s, 3H), 2.44 (qd, *J* = 8.5, 4.9 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.06 – 1.96 (m, 2H), 1.82 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.4, 159.9, 147.9, 139.2, 137.3, 134.6, 129.7, 128.9, 125.7, 123.9, 123.1, 119.1, 61.7, 56.6, 44.6, 38.5, 26.7, 18.8, 17.5; **HRMS (ESI)** calcd for: $C_{21}H_{23}N_4O_5S$: [M + H]+, 443.1384 found: 443.1392.



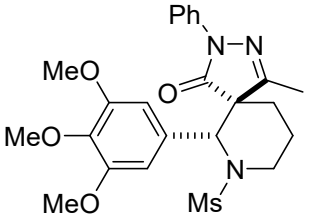
(*5R*,6R**)-6-(4-methoxyphenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.5]dec-3-en-1-one **(5c);** White solid, 53 mg, 72% yield, 1.2:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 98−100°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.41 – 7.28 (m, 4H), 7.22 – 7.11 (m, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.85 (s, 1H), 3.90 – 3.81 (m, 1H), 3.76 (s, 3H), 3.73 – 3.67 (m, 1H), 2.72 (s, 3H), 2.61 – 2.47 (m, 1H), 2.28 – 2.15 (m, 1H), 1.97 – 1.85 (m, 2H), 1.65 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.7, 160.9, 159.9, 137.7, 130.1, 129.2, 128.8, 125.2, 119.1, 114.1, 60.9, 56.1, 55.30, 43.4, 38.9, 25.7, 18.8, 16.8; **HRMS (ESI)** calcd for: $C_{22}H_{26}N_3O_4S$: [M + H]+, 428.1639 found: 428.1643.



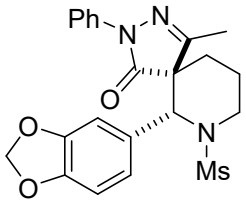
(*5R*,6R**)-6-(4-(*tert*-butyl)phenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro [4.5]dec-3-en-1-one **(5d);** White solid, 54 mg, 76% yield, 1.4:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 150−152°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 13.0, 7.9 Hz, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 3.99 (ddd, *J* = 16.3, 11.8, 6.7 Hz, 2H), 2.55 (s, 3H), 2.39 (s, 3H), 2.09 (dt, *J* = 13.3, 8.1 Hz, 4H), 1.23 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.3, 162.2, 151.7, 137.6, 133.1, 128.8, 127.0, 125.6, 125.5, 119.8, 58.9, 56.9, 40.8, 40.5, 34.7, 31.3, 25.4, 18.6, 15.5; **HRMS (ESI)** calcd for: $C_{25}H_{32}N_3O_3S$: [M + H]+, 454.2159 found: 454.2168.



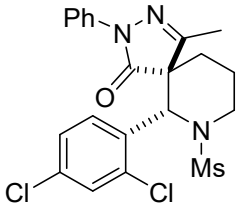
(*5R*,6R**)-6-(3,4-dimethoxyphenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5e);** White solid, 53 mg, 74% yield, 1.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.13 (dd, *J* = 10.8, 3.9 Hz, 1H), 6.92 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.77 (dd, *J* = 15.8, 5.1 Hz, 2H), 5.07 (s, 1H), 3.91 (dd, *J* = 12.4, 5.8 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H), 2.14 (ddd, *J* = 15.8, 10.7, 5.3 Hz, 3H), 2.01 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.2, 162.4, 149.2, 148.9, 137.7, 128.9, 128.3, 125.3, 120.4, 119.1, 111.0, 110.9, 59.4, 56.8, 56.0, 55.9, 41.1, 40.3, 25.9, 18.8, 15.8; **HRMS (ESI)** calcd for: $C_{23}H_{28}N_3O_3S$: [M + H]+, 458.1744 found: 458.1751.



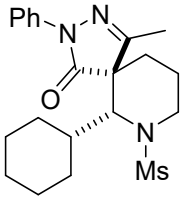
(*5R*,6R**)-4-methyl-7-(methylsulfonyl)-2-phenyl-6-(3,4,5-trimethoxyphenyl)-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5f);** White solid, 51 mg, 73% yield, 1.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 144−146°C**; ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 – 7.61 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.58 (s, 2H), 6.23 (s, 1H), 4.51 – 4.31 (m, 1H), 4.08 (ddd, *J* = 11.5, 8.1, 3.1 Hz, 1H), 3.82 (s, 9H), 3.76 – 3.60 (m, 1H), 3.14 (ddd, *J* = 13.9, 10.2, 3.2 Hz, 1H), 2.96 (s, 3H), 2.12 (d, *J* = 5.9 Hz, 1H), 2.08 (s, 3H), 1.83 (ddd, *J* = 11.8, 5.0, 3.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 153.7, 151.4, 147.7, 138.5, 138.1, 134.2, 129.2, 126.8, 122.3, 105.8, 102.7, 74.6, 60.9, 56.5, 56.2, 42.3, 41.2, 28.4, 13.6; **HRMS (ESI)** calcd for: $C_{24}H_{30}N_3O_6S$: [M + H]+, 488.1850 found: 488.1861.



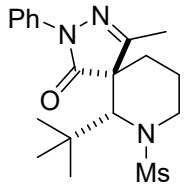
(*5R*,6R**)-6-(benzo[d][1,3]dioxol-5-yl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5g);** White solid, 47 mg, 65% yield, 1.3:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 144−146°C**; ^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.29 (dd, *J* = 14.4, 7.0 Hz, 1H), 6.89 (s, 1H), 6.79 (d, *J* = 0.6 Hz, 2H), 6.19 (s, 1H), 5.99 (s, 2H), 4.46 – 4.31 (m, 1H), 4.17 – 4.01 (m, 1H), 3.67 (ddd, *J* = 14.8, 10.4, 5.2 Hz, 1H), 3.21 – 3.03 (m, 1H), 2.95 (s, 3H), 2.12 (ddd, *J* = 10.7, 7.3, 4.0 Hz, 1H), 2.03 (s, 3H), 1.81 (ddd, *J* = 15.2, 7.3, 4.1 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 151.5, 148.5, 147.7, 147.6, 138.5, 132.4, 129.1, 126.7, 122.5, 122.2, 108.9, 108.4, 103.2, 101.5, 74.8, 56.1, 42.2, 41.1, 28.5, 13.5; **HRMS (ESI)** calcd for: $C_{22}H_{24}N_3O_5S$: [M + H]+, 442.1431found: 442.1441.



(*5R*,6S**)-6-(2,4-dichlorophenyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5h);** White solid, 52 mg, 74% yield, 1.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 182−184°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.28 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.57 (s, 1H), 3.98 – 3.85 (m, 2H), 3.01 (s, 3H), 2.51 (ddd, *J* = 15.6, 11.8, 5.2 Hz, 1H), 2.09 (ddd, *J* = 8.2, 6.9, 4.5 Hz, 1H), 1.95 – 1.82 (m, 2H), 1.59 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.9, 160.1, 137.7, 136.0, 135.2, 134.1, 130.0, 129.0, 127.8, 125.7, 119.3, 55.1, 54.7, 44.6, 39.6, 26.5, 18.2, 15.8; **HRMS (ESI)** calcd for: $C_{21}H_{22}Cl_2N_3O_3S$: [M + H]+, 466.0753 found: 466.0761.

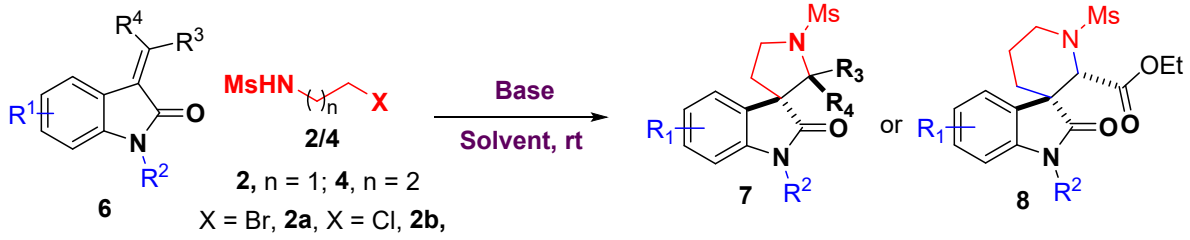


(*5R*,6R**)-6-cyclohexyl-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5i);** White solid, 68 mg, 90% yield, 1.5:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 182−184°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 11.1, 4.5 Hz, 2H), 7.20 (dd, *J* = 6.4, 4.8 Hz, 1H), 4.09 (d, *J* = 10.7 Hz, 1H), 3.55 (d, *J* = 4.0 Hz, 2H), 3.17 – 2.80 (m, 3H), 2.35 – 2.19 (m, 3H), 2.15 (dd, *J* = 21.4, 10.5 Hz, 1H), 2.10 – 1.88 (m, 3H), 1.74 (d, *J* = 11.1 Hz, 2H), 1.57 (dd, *J* = 23.7, 10.3 Hz, 3H), 1.38 – 0.86 (m, 5H), 0.70 (d, *J* = 11.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$:** δ 173.45, 164.36, 138.14, 129.01, 125.37, 119.35, 60.88, 55.53, 40.73, 39.18, 37.66, 31.43, 29.34, 27.82, 26.14, 25.77, 25.50, 16.62, 13.91.;**HRMS (ESI)** calcd for: $C_{21}H_{30}N_3O_3S$: [M + H]+, 404.2002 found: 404.2016.



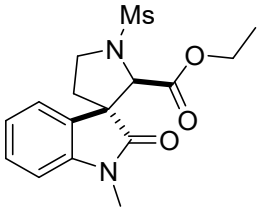
(*5R*,6R**)-6-(*tert*-butyl)-4-methyl-7-(methylsulfonyl)-2-phenyl-2,3,7-triazaspiro[4.5]dec-3-en-1-one **(5j);** White solid, 72 mg, 92% yield, 1.4:1 *dr, Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 182−184°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 11.1, 4.5 Hz, 2H), 7.20 (dd, *J* = 6.4, 4.8 Hz, 1H), 4.09 (d, *J* = 10.7 Hz, 1H), 3.55 (d, *J* = 4.0 Hz, 2H), 3.17 – 2.80 (m, 3H), 2.35 – 2.19 (m, 3H), 2.15 (dd, *J* = 21.4, 10.5 Hz, 1H), 2.10 – 1.88 (m, 3H), 1.74 (d, *J* = 11.1 Hz, 2H), 1.57 (dd, *J* = 23.7, 10.3 Hz, 3H), 1.38 – 0.86 (m, 5H), 0.70 (d, *J* = 11.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.45, 164.36, 138.14, 129.01, 125.37, 119.35, 60.88, 55.53, 40.73, 39.18, 37.66, 31.43, 29.34, 27.82, 26.14, 25.77, 25.50, 16.62, 13.91; **HRMS (ESI)** calcd for: $C_{19}H_{28}N_3O_3S$: [M + H]+, 378.1846 found: 378.1852.

5. General experimental procedures and characterization data for the synthesis of compounds 7 and 8:

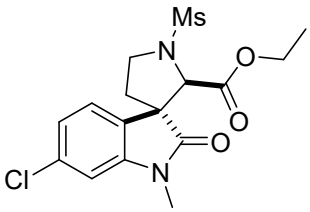


General experimental procedure: To an oven-dried 50 mL round-bottom flask was charged the corresponding methyleneindolinones **6** (0.22 mmol, 1.0 equiv.), and haloamines **2/4** (0.42 mmol, 1.5 equiv.) were dissolved in anhydrous solvent (2.0 mL). Then base (0.54 mmol, 2.5 equiv.) was added to the reaction mixture, and the resulting solution was stirred for 3 h at room temperature. After completion of the reaction, it was extracted with EtOAc (3×10 mL). The organic layer was collected and dried over Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using EtOAc/*n*-hexane as an eluent.

Characterization of the products:

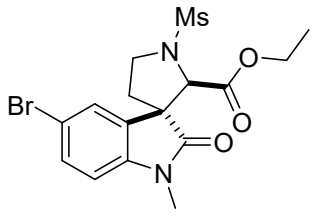


ethyl (*2'R*,3S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7a***)*; White solid, 64 mg, 42% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 122-124°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.18 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.06 (td, *J* = 7.6, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.60 (s, 1H), 4.05 (ddd, *J* = 9.5, 7.4, 6.2 Hz, 1H), 3.94 – 3.80 (m, 3H), 3.25 (s, 3H), 3.12 (s, 3H), 2.43 – 2.26 (m, 2H), 0.85 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 176.9, 169.2, 143.6, 129.6, 127.2, 123.9, 123.0, 108.6, 66.9, 61.4, 55.9, 47.5, 38.5, 36.06, 26.7, 13.7; **HRMS (ESI)** calcd for: $C_{16}H_{21}N_2O_5S$: $[M+H]^+$, 353.1166 found: 353.1205.

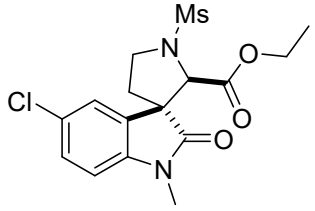


ethyl (2'*R**,3*S**)-6-chloro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate **(7b).** White solid, 51 mg, 35% yield, 6:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 134-136°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.09 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.88 (d, *J* = 1.7 Hz, 1H), 4.58 (s, 1H), 4.04

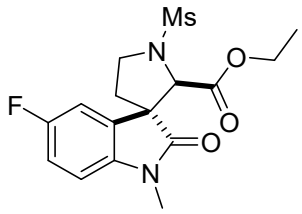
(ddd, J = 9.4, 7.4, 6.3 Hz, 1H), 3.99 – 3.79 (m, 3H), 3.22 (d, J = 9.5 Hz, 3H), 3.11 (s, 3H), 2.43 – 2.27 (m, 2H), 0.92 (t, J = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.7, 169, 144.8, 135.5, 125.4, 124.8, 122.7, 109.3, 66.6, 61.4, 55.4, 47.8, 38.4, 35.8, 26.7, 13.7; **HRMS (ESI)** calcd for: $C_{16}H_{20}ClN_2O_5S$: $[M + H]^+$, 387.0776 found: 387.0783.



ethyl (2'*R**,3*S**)-5-bromo-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate(**7c**). White solid, 56 mg, 40% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 132-134°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.48 (dd, J = 8.3, 1.9 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.76 (d, J = 8.3 Hz, 1H), 4.55 (s, 1H), 4.07 – 3.93 (m, 3H), 3.85 (dt, J = 9.4, 6.6 Hz, 1H), 3.23 (s, 3H), 3.11 (s, 3H), 2.37 (td, J = 7.0, 1.7 Hz, 2H), 0.94 (t, J = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.4, 169.1, 142.7, 132.4, 129, 127.2, 115.6, 110, 66.6, 61.7, 55.7, 47.3, 38.4, 35.7, 26.8, 13.9; **HRMS (ESI)** calcd for: $C_{16}H_{20}BrN_2O_5S$: $[M + H]^+$, 431.0271 found: 431.0276.

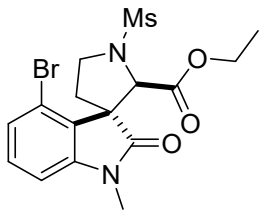


ethyl (2'*R**,3*S**)-5-chloro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7d**). White solid, 44 mg, 30% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 136-138°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.33 (dd, J = 8.3, 2.1 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 4.57 (s, 1H), 4.08 – 4.01 (m, 1H), 3.96 (qd, J = 7.1, 3.7 Hz, 2H), 3.85 (ddd, J = 13.2, 8.2, 4.7 Hz, 1H), 3.24 (s, 3H), 3.12 (s, 3H), 2.42 – 2.30 (m, 2H), 0.92 (td, J = 7.1, 3.4 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.4, 169.1, 142.2, 129.5, 128.6, 128.4, 124.4, 109.5, 66.6, 61.6, 55.8, 47.3, 38.4, 35.7, 26.8, 13.8; **HRMS (ESI)** calcd for: $C_{16}H_{20}ClN_2O_5S$: $[M + H]^+$, 387.0776 found: 387.0783.

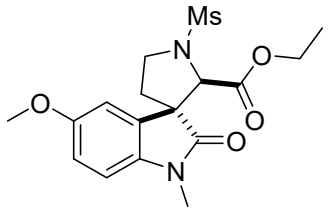


ethyl (2'*R**,3*S**)-5-fluoro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7e**). White solid, 48 mg, 32% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 96-98°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.06 (td,

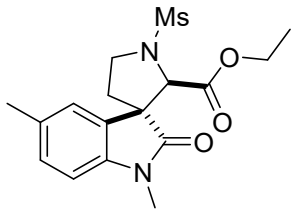
J = 8.8, 2.5 Hz, 1H), 6.95 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.5, 4.1 Hz, 1H), 4.59 (s, 1H), 4.08 – 4.01 (m, 1H), 3.94 (dt, *J* = 13.6, 6.7 Hz, 2H), 3.83 (dt, *J* = 9.4, 6.7 Hz, 1H), 3.24 (s, 3H), 3.12 (s, 3H), 2.45 – 2.30 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 176.5, 169.1, 159.2 (d, *J* = 241.9 Hz), 139.6 (d, *J* = 2.0 Hz), 128.6 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 23.4 Hz), 112.3 (d, *J* = 25.5 Hz), 109.1 (d, *J* = 8.1 Hz), 66.7, 61.5, 56, 47.3, 38.5, 35.9, 26.8, 13.8; **^{19}F NMR (377 MHz, $CDCl_3$):** δ -119.3, -119.4; **HRMS (ESI)** calcd for: $C_{16}H_{20}FN_2O_5S$: $[M + H]^+$, 371.1071 found: 371.1079.



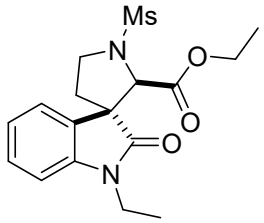
ethyl (2'*R**,3*S**)-4-bromo-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7f**). White solid, 45 mg, 32% yield, 5:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 132-134°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.27 – 7.19 (m, 2H), 6.81 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.54 (s, 1H), 4.20 – 4.06 (m, 2H), 3.99 – 3.87 (m, 2H), 3.25 (s, 3H), 3.18 (s, 3H), 2.91 (td, *J* = 12.1, 8.1 Hz, 1H), 2.02 (dd, *J* = 12.5, 5.2 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 177, 169.6, 145.5, 130.6, 127.5, 127.1, 118.8, 107.4, 64, 61.6, 58.6, 47, 42.1, 34.4, 26.5, 14; **HRMS (ESI)** calcd for: $C_{16}H_{20}BrN_2O_5S$: $[M + H]^+$, 431.0271 found: 431.0278.



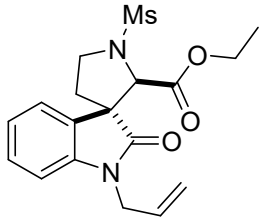
ethyl (2'*R**,3*S**)-5-methoxy-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7g**). White solid, 50 mg, 35% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 118-120°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.85 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.78 (dd, *J* = 8.1, 5.5 Hz, 2H), 4.57 (s, 1H), 4.08 – 3.94 (m, 2H), 3.93 – 3.81 (m, 2H), 3.77 (s, 3H), 3.22 (s, 3H), 3.11 (s, 3H), 2.44 – 2.23 (m, 2H), 1.63 (s, 1H), 0.90 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 176.7, 169.2, 156.3, 137.1, 128.3, 113.5, 111.8, 108.9, 66.8, 61.4, 56.1, 56, 47.5, 38.2, 35.9, 26.7, 13.8; **HRMS (ESI)** calcd for: $C_{17}H_{23}N_2O_6S$: $[M + H]^+$, 383.1271 found: 383.1278.



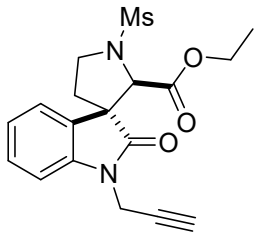
ethyl (2'*R**,3*S**)-1,5-dimethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7h**). White solid, 51 mg, 34% yield, 7:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 134-138°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.13 (t, *J* = 6.7 Hz, 1H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.82 – 6.67 (m, 1H), 4.54 (d, *J* = 6.3 Hz, 1H), 4.02 (dq, *J* = 9.4, 6.8 Hz, 1H), 3.96 – 3.80 (m, 3H), 3.22 (d, *J* = 6.3 Hz, 3H), 3.11 (d, *J* = 6.4 Hz, 3H), 2.46 – 2.33 (m, 2H), 2.31 (d, *J* = 6.3 Hz, 3H), 0.86 (q, *J* = 6.9 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$):** δ 177, 169.3, 141.2, 132.6, 129.8, 127, 124.7, 108.3, 66.7, 61.3, 55.8, 47.5, 38.1, 35.9, 26.7, 21.2, 13.8; **HRMS (ESI)** calcd for: $C_{17}H_{23}N_2O_5S$: $[M + H]^+$, 367.1322 found: 367.1327.



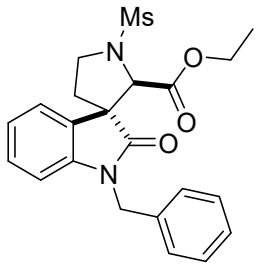
ethyl (2'*R**,3*S**)-1-ethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7i**); Yellow liquid, 69 mg, 46% yield, 7.5:1 dr, *Rf* = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25); **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.31 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.62 (s, 1H), 4.04 (ddd, *J* = 9.5, 7.6, 5.6 Hz, 1H), 3.88 – 3.74 (m, 5H), 3.11 (s, 3H), 2.40 (dt, *J* = 12.8, 7.4 Hz, 1H), 2.25 (dt, *J* = 12.4, 6.1 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.3, 169.1, 142.6, 129.4, 127.6, 124, 122.7, 108.6, 77.4, 77.1, 76.8, 66.8, 61.3, 55.8, 47.5, 38.6, 36.1, 35.1, 13.6, 12.6; **HRMS (ESI)** calcd for: $C_{17}H_{23}N_2O_5S$: $[M + H]^+$, 367.1322 found: 367.1327.



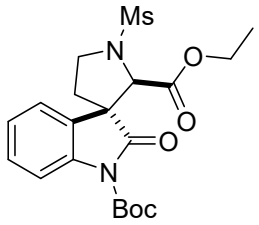
ethyl (2'*R**,3*S**)-1-allyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7j**). Yellow semisolid, 56 mg, 38% yield, 7:1 dr, Rf = 0.3, column chromatography on silica gel (n-hexane/EtOAc 75:25); **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.32 – 7.27 (m, 1H), 7.19 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.90 – 5.80 (m, 1H), 5.27 (t, *J* = 1.4 Hz, 1H), 5.23 (dd, *J* = 7.4, 1.0 Hz, 1H), 4.65 (s, 1H), 4.42 – 4.30 (m, 2H), 4.06 (ddd, *J* = 9.6, 7.5, 5.7 Hz, 1H), 3.95 – 3.81 (m, 3H), 3.13 (s, 3H), 2.44 (dt, *J* = 12.6, 7.3 Hz, 1H), 2.36 – 2.28 (m, 1H), 0.83 (t, *J* = 7.1 Hz, 3H): **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.7, 169.2, 142.8, 131, 129.4, 127.4, 124, 123, 118, 109.4, 67, 61.5, 55.9, 47.6, 42.7, 38.6, 36.4, 13.7; **HRMS (ESI)** calcd for: $C_{18}H_{23}N_2O_5S$: $[M + H]^+$, 379.1322 found: 379.1329.



Ethyl (2'*R**,3*S**)-1'-(methylsulfonyl)-2-oxo-1-(prop-2-yn-1-yl)spiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7k**). Yellow liquid, 47 mg, 32% yield, 6.5:1 dr, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25); **^{1}H NMR (400 MHz, CDCl$_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 7.25 – 7.16 (m, 2H), 7.01 (td, *J* = 7.6, 0.9 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.77 (s, 1H), 4.10 (ddd, *J* = 9.7, 7.7, 5.1 Hz, 1H), 3.94 – 3.71 (m, 3H), 3.15 (s, 3H), 2.51 (dt, *J* = 12.5, 7.7 Hz, 1H), 2.35 – 2.16 (m, 1H), 0.75 – 0.54 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 175.8, 169, 141.7, 129.5, 127.3, 124, 123.4, 109.6, 76.5, 72.9, 67, 61.5, 56, 47.5, 38.9, 36.2, 29.7, 13.6.; **HRMS (ESI)** calcd for: $C_{18}H_{21}N_2O_5S$: $[M + H]^+$, 377.1166 found: 377.1166.

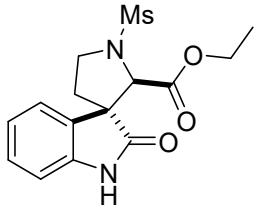


ethyl (2'*R**,3*S**)-1-benzyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7l**). White solid, 59 mg, 42% yield, 7:1 dr, Rf = 0.3, column chromatography on silica gel (n-hexane/EtOAc 75:25), mp 118-120°C; 1H NMR (400 MHz, CDCl3): δ 7.41 – 7.27 (m, 5H), 7.25 – 7.16 (m, 2H), 7.01 (td, J = 7.6, 0.9 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.77 (s, 1H), 4.10 (ddd, *J* = 9.7, 7.7, 5.1 Hz, 1H), 3.94 – 3.71 (m, 3H), 3.15 (s, 3H), 2.51 (dt, *J* = 12.5, 7.7 Hz, 1H), 2.35 – 2.16 (m, 1H), 0.75 – 0.54 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.8, 169, 142.6, 135.4, 129.3, 128.9, 127.9, 127.6, 127.4, 123.9, 122.9, 109.5, 67.1, 61.3, 56, 47.6, 44.1, 38.8, 36.5, 13.3; **HRMS (ESI)** calcd for: $C_{22}H_{25}N_2O_5S$: $[M + H]^+$, 429.1479 found: 429.1485.

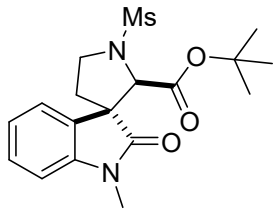


1-(*tert*-butyl) 2'-ethyl (2'*R**,3*S**)-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-1,2'-dicarboxylate (**7m**). White solid, 48 mg, 35% yield, 7.5:1 dr, Rf = 0.3, column chromatography on silica gel (n-hexane/EtOAc 75:25), mp 122-124°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.25 – 7.13 (m, 2H), 4.68 (s, 1H), 4.07 (ddd, *J* = 9.6, 7.6, 6.1 Hz, 1H), 3.88 (dddd, *J* = 27.3, 14.3, 7.2, 3.6 Hz, 3H), 3.14 (s, 3H),

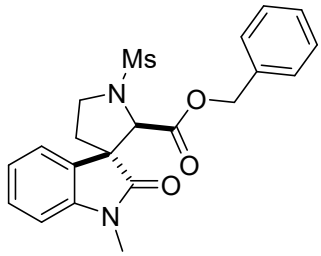
2.55 – 2.46 (m, 1H), 2.37 (dt, *J* = 12.9, 6.6 Hz, 1H), 1.68 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 175.6, 168.8, 148.9, 139.6, 129.8, 126.2, 124.8, 123.7, 115.3, 85.3, 67.7, 61.6, 56.4, 47.5, 38.8, 36.8, 28.2, 13.6; **HRMS (ESI)** calcd for: $C_{20}H_{27}N_2O_7S$: [M + H]$^+$, 429.1533 found: 429.1538.



ethyl (2'*R**,3*S**)-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7n**). Yellow semisolid, 31 mg, 20% yield, 7:1 dr, R_f = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30); **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.63 (s, 1H), 7.29 – 7.25 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.03 (td, *J* = 7.6, 0.9 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.71 (s, 1H), 4.07 (ddd, *J* = 9.6, 7.6, 5.6 Hz, 1H), 3.93 – 3.82 (m, 3H), 3.14 (s, 3H), 2.46 (dt, *J* = 12.6, 7.4 Hz, 1H), 2.36 – 2.28 (m, 1H), 0.84 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 177, 169.2, 140.8, 129.6, 127.9, 124.2, 123, 110.4, 66.9, 61.5, 56.4, 47.6, 38.9, 36.2, 13.7; **HRMS (ESI)** calcd for: $C_{15}H_{19}N_2O_5S$: [M + H]$^+$, 339.1009 found: 339.1009.

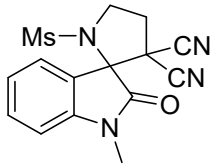


tert-butyl (2'*R**,3*S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7o**). White solid, 41 mg, 28% yield, 6:1 dr, *Rf* = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 146-148°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.34 (td, *J* = 7.8, 1.0 Hz, 1H), 7.27 (s, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.72 (s, 1H), 4.16 – 4.07 (m, 1H), 3.79 (td, *J* = 9.8, 6.2 Hz, 1H), 3.26 (s, 3H), 3.17 (s, 3H), 2.49 (ddd, *J* = 12.3, 9.3, 8.5 Hz, 1H), 2.10 (ddd, *J* = 12.3, 6.1, 3.1 Hz, 1H), 1.02 (s, 9H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 176.3, 167.8, 143.7, 129.4, 128.6, 124.4, 122.9, 108.3, 82.3, 67.7, 56.5, 47.9, 40, 36.6, 27.5, 26.7; **HRMS (ESI)** calcd for: $C_{18}H_{25}N_2O_5S$: [M + H]$^+$, 381.1479 found: 381.1484.

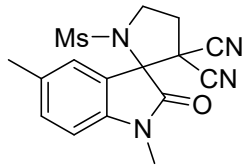


benzyl (2'*R**,3*S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-pyrrolidine]-2'-carboxylate (**7p**). White solid, 42 mg, 30% yield, 7:1 dr, *Rf* = 0.3, column chromatography on

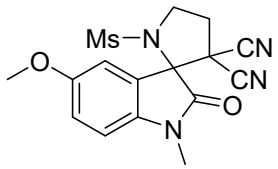
silica gel (*n*-hexane/EtOAc 75:25), mp 148-150°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 – 7.28 (m, 1H), 7.26 (dt, *J* = 3.5, 1.6 Hz, 2H), 7.23 (dt, *J* = 5.8, 2.3 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.06 – 6.98 (m, 1H), 6.98 – 6.91 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.78 – 4.62 (m, 2H), 4.06 (ddd, *J* = 9.5, 7.5, 5.9 Hz, 1H), 3.86 (dt, *J* = 9.5, 6.9 Hz, 1H), 3.12 (s, 3H), 3.04 (s, 3H), 2.40 (dt, *J* = 12.7, 7.2 Hz, 1H), 2.33 – 2.25 (m, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 176.6, 169.1, 143.5, 134.7, 129.5, 128.6, 128.6, 128.5, 127.1, 123.8, 123, 108.7, 67.3, 66.9, 55.9, 47.5, 38.6, 35.9, 26.5; **HRMS (ESI)** calcd for: $C_{21}H_{23}N_2O_5S$: $[M + H]^+$, 415.1322 found: 415.1326.



1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7r**). White solid, 107 mg, 68% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 156-158°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 13.3, 5.7 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 4.28 (t, *J* = 9.4 Hz, 1H), 3.97 (td, *J* = 9.7, 6.6 Hz, 1H), 3.54 (dd, *J* = 20.5, 10.5 Hz, 1H), 3.28 (s, 3H), 2.89 (s, 3H), 2.80 (ddd, *J* = 12.7, 6.5, 2.2 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 171.8, 144.4, 132.5, 125.1, 123.7, 121.3, 112.4, 111, 110, 72, 46.4, 44.8, 41.7, 33, 27.2; **HRMS (ESI)** calcd for: $C_{15}H_{15}N_4O_3S$: $[M + H]^+$, 331.0859 found: 331.0865.

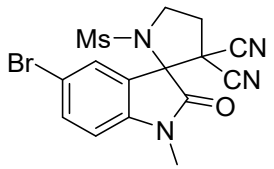


1,5-dimethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'- dicarbonitrile (**7s**). White solid, 100 mg, 65% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 188-190°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (s, 1H), 7.31 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.25 (ddd, *J* = 9.8, 9.1, 2.5 Hz, 1H), 3.98 (td, *J* = 9.6, 6.5 Hz, 1H), 3.53 (dt, *J* = 12.7, 9.1 Hz, 1H), 3.26 (s, 3H), 2.92 (s, 3H), 2.80 (ddd, *J* = 12.7, 6.5, 2.4 Hz, 1H), 2.41 (s, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 171.6, 141.9, 133.6, 132.8, 125.8, 121.5, 112.4, 111, 109.7, 72.1, 46.4, 44.9, 41.5, 33.1, 27.2, 21.4; **HRMS (ESI)** calcd for: $C_{16}H_{17}N_4O_3S$: $[M + H]^+$, 345.1016 found: 345.1019.

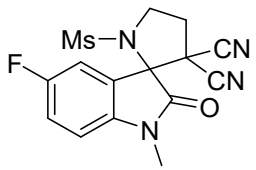


5-methoxy-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7t**). White solid, 99 mg, 66% yield, *Rf* = 0.4, column chromatography on silica

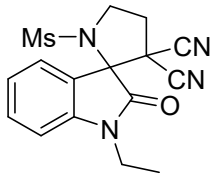
gel (*n*-hexane/EtOAc 80:20), mp 168-170°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (s, 1H), 7.31 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.25 (ddd, *J* = 9.8, 9.1, 2.5 Hz, 1H), 3.98 (td, *J* = 9.6, 6.5 Hz, 1H), 3.53 (dt, *J* = 12.7, 9.1 Hz, 1H), 3.26 (s, 3H), 2.92 (s, 3H), 2.80 (ddd, *J* = 12.7, 6.5, 2.4 Hz, 1H), 2.41 (s, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 171.6, 141.9, 133.6, 132.8, 125.8, 121.5, 112.4, 111, 109.7, 72.1, 46.4, 44.9, 41.5, 33.1, 27.2, 21.4; **HRMS (ESI)** calcd for: $C_{16}H_{17}N_4O_4S$: $[M + H]^+$, 361.0965 found: 361.0965.



5-bromo-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7u**). White solid, 108 mg, 76% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 232-234°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 1.9 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.28 (ddd, *J* = 9.9, 9.0, 2.5 Hz, 1H), 4.00 (td, *J* = 9.6, 6.5 Hz, 1H), 3.54 (dt, *J* = 12.8, 9.1 Hz, 1H), 3.30 (s, 3H), 2.97 (s, 3H), 2.85 (ddd, *J* = 12.8, 6.5, 2.5 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 171.2, 143.3, 135.4, 128.1, 123.7, 116.4, 112, 111.4, 110.6, 71.9, 46.4, 44.7, 41.8, 33.2, 27.4; **HRMS (ESI)** calcd for: $C_{15}H_{14}BrN_4O_3S$: $[M + H]^+$, 408.9965 found: 408.9969.

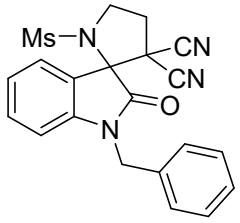


5-fluoro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7v**), White solid, 100 mg, 65% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 200-202°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (dd, *J* = 7.5, 2.5 Hz, 1H), 7.25 – 7.15 (m, 1H), 6.92 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.98 (td, *J* = 9.7, 6.5 Hz, 1H), 3.54 (dt, *J* = 12.7, 9.2 Hz, 1H), 3.28 (s, 3H), 2.95 (s, 3H), 2.81 (ddd, *J* = 12.8, 6.4, 2.3 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)**: δ 171.5, 159.5 (d, *J* = 244.4 Hz), 140.2 (d, *J* = 2.2 Hz), 123.2 (d, *J* = 7.8 Hz), 119 (d, *J* = 23.5 Hz), 113.4 (d, *J* = 26.1 Hz), 112.1, 110.8 (d, *J* = 8.0 Hz), 110.7, 72.1, 46.4, 44.7, 41.5, 33.1, 27.4;**^{19}F NMR (377 MHz, $CDCl_3$):** δ -117.16; **HRMS (ESI)** calcd for: $C_{15}H_{14}FN_4O_3S$: $[M + H]^+$, 349.0765 found: 349.0768.

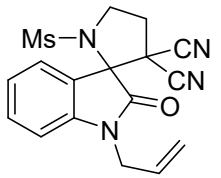


1-ethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7w**). White solid, 123 mg, 80% yield, *Rf*= 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 148-150°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.6 Hz,

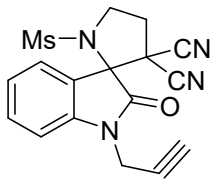
1H), 7.50 (td, *J* = 7.8, 1.0 Hz, 1H), 7.23 (dd, *J* = 16.8, 9.2 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 4.28 (td, *J* = 9.7, 1.9 Hz, 1H), 4.01 – 3.71 (m, 3H), 3.55 (dt, *J* = 12.6, 9.4 Hz, 1H), 3.01 – 2.72 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 171.5, 143.6, 132.4, 125.4, 123.4, 121.4, 112.4, 111, 110.1, 71.6, 46.4, 44.8, 41.7, 35.7, 32.9, 11.9; **HRMS (ESI)** calcd for: $C_{16}H_{17}N_4O_3S$: $[M + H]^+$, 345.1016 found: 345.1022.



11-benzyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7x**). White solid, 100 mg, 70% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 152-154°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.39 (s, 1H), 7.37 (s, 2H), 7.35 – 7.27 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 5.01 (d, *J* = 15.9 Hz, 1H), 4.94 (d, *J* = 15.9 Hz, 1H), 4.33 (td, *J* = 9.5, 1.9 Hz, 1H), 3.99 (td, *J* = 9.7, 6.5 Hz, 1H), 3.61 (dt, *J* = 12.5, 9.4 Hz, 1H), 2.89 (s, 3H), 2.82 (ddd, *J* = 12.7, 6.4, 1.9 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 172.1, 143.9, 134.4, 132.4, 129.1, 128.1, 127.5, 125.2, 123.7, 121.2, 112.4, 111.2, 111.1, 71.9, 46.4, 45.1, 44.9, 41.9, 33.1; **HRMS (ESI)** calcd for: $C_{21}H_{19}N_4O_3S$: $[M + H]^+$, 407.1172 found: 407.1178.

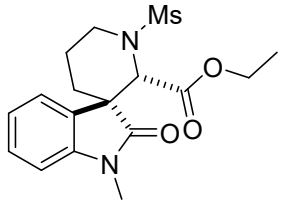


1-allyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbonitrile (**7y**). White solid, 113 mg, 75% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 158-160°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.68 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.48 (td, *J* = 7.8, 1.2 Hz, 1H), 7.22 (td, *J* = 7.7, 0.8 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 5.83 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 1H), 5.32 (ddd, *J* = 13.8, 11.2, 0.8 Hz, 2H), 4.43 – 4.35 (m, 1H), 4.31 – 4.23 (m, 1H), 3.97 (td, *J* = 9.7, 6.4 Hz, 1H), 3.55 (dt, *J* = 11.5, 9.3 Hz, 1H), 2.89 (s, 3H), 2.86 – 2.71 (m, 2H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 171.7, 143.7, 132.4, 130.2, 125.2, 123.6, 121.2, 118.8, 112.4, 111, 111, 71.8, 46.4, 44.9, 43.4, 41.7, 33; **HRMS (ESI)** calcd for: $C_{17}H_{17}N_4O_3S$: $[M + H]^+$, 357.1016 found: 357.1022.

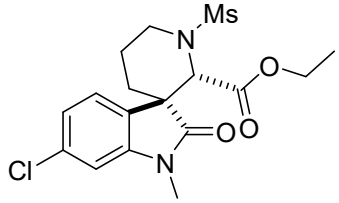


1'-(methylsulfonyl)-2-oxo-1-(prop-2-yn-1-yl)spiro[indoline-3,2'-pyrrolidine]-3',3'-dicarbo nitrile (**7z**). White solid, 104 mg, 68% yield, *R*f = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 80:20), mp 196-198°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.68 (dd, *J* = 7.6, 0.6

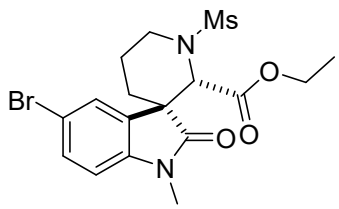
Hz, 1H), 7.48 (td, *J* = 7.8, 1.2 Hz, 1H), 7.22 (td, *J* = 7.7, 0.8 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 5.83 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 1H), 5.32 (ddd, *J* = 13.8, 11.2, 0.8 Hz, 2H), 4.43 – 4.35 (m, 1H), 4.31 – 4.23 (m, 1H), 3.97 (td, *J* = 9.7, 6.4 Hz, 1H), 3.55 (dt, *J* = 11.5, 9.3 Hz, 1H), 2.89 (s, 3H), 2.86 – 2.71 (m, 2H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$)**: δ 171.0, 142.6, 132.4, 125.2, 123.9, 120.9, 118.3, 112.3, 110.9, 110.6, 75.2, 73.5, 55.6, 46.3, 44.7, 41.7, 32.9, 30.2; **HRMS (ESI)** calcd for: $C_{17}H_{15}N_4O_3S$: $[M + H]^+$, 355.0859 found: 355.0865.



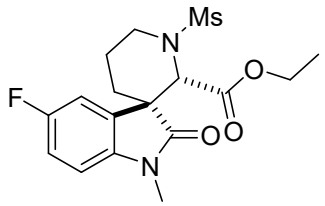
ethyl (2'*S**,3*S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8a);** White solid, 130 mg, 82% yield, 1.4:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 170-172°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.41 (s, 1H), 4.29 – 4.18 (m, 2H), 3.99 (qd, *J* = 11.8, 4.6 Hz, 2H), 3.22 (s, 3H), 2.81 (s, 3H), 2.41 (td, *J* = 13.5, 4.4 Hz, 1H), 2.25 – 2.10 (m, 1H), 1.95 – 1.81 (m, 1H), 1.54 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$):** δ 175.7, 169.6, 142.5, 131.8, 128.8, 125.2, 123.0, 108.5, 61.4, 58.2, 48.3, 41.1, 37.9, 27.8, 26.5, 19.6, 14.1; **HRMS (ESI)** calcd for: $C_{17}H_{23}N_2O_5S$: $[M + H]^+$, 367.1322 found: 367.1328.



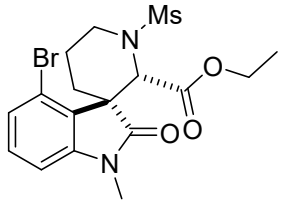
ethyl (2'*S**,3*S**)-6-chloro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8b);** White solid, 108 mg, 72% yield, 1.3:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 160-162°C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.63 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.89 (s, 1H), 4.39 (s, 1H), 4.30 – 4.11 (m, 2H), 4.06 – 3.84 (m, 2H), 3.20 (d, *J* = 1.1 Hz, 3H), 2.81 (d, *J* = 1.2 Hz, 3H), 2.40 (td, *J* = 13.5, 3.6 Hz, 1H), 2.19 – 2.01 (m, 1H), 1.89 (d, *J* = 13.6 Hz, 1H), 1.52 (d, *J* = 13.6 Hz, 1H), 1.27 (td, *J* = 7.1, 1.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$):** δ 175.7, 169.2, 143.8, 134.9, 130.1, 126.1, 122.7, 109.2, 61.5, 58.1, 48.1, 40.9, 37.9, 27.7, 26.6, 19.6, 14.1; **HRMS (ESI)** calcd for: $C_{17}H_{22}ClN_2O_5S$: $[M + H]^+$, 401.0932 found: 401.0939.



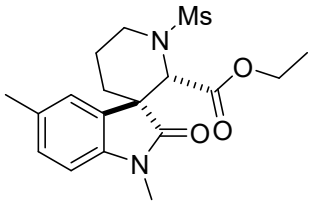
ethyl (2'*S**,3*S**)-5-bromo-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8c);** White solid, 108 mg, 75% yield, 1.4:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 174-176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.38 (m, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 4.40 (s, 1H), 4.28 – 4.07 (m, 2H), 4.05 – 3.80 (m, 2H), 3.20 (s, 3H), 2.83 (s, 3H), 2.39 (td, *J* = 13.4, 4.5 Hz, 1H), 2.20 – 2.02 (m, 1H), 1.91 (d, *J* = 14.3 Hz, 1H), 1.61 – 1.53 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.3, 169.3, 141.7, 133.7, 131.8, 128.2, 115.6, 109.9, 61.6, 58.1, 48.6, 41.0, 38.1, 27.7, 26.7, 19.5, 14.1; **HRMS (ESI)** calcd for: $C_{17}H_{22}BrN_2O_5S$: $[M + H]^+$, 445.0427 found: 445.0432.



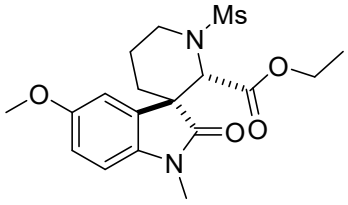
ethyl (2'*S**,3*S**)-5-fluoro-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8d);** White solid, 125 mg, 81% yield, 1.5:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 146-148°C; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.05 (td, *J* = 8.7, 1.9 Hz, 1H), 6.81 (dd, *J* = 8.5, 4.2 Hz, 1H), 4.40 (s, 1H), 4.30 – 4.13 (m, 2H), 4.06 – 3.85 (m, 2H), 3.21 (s, 3H), 2.82 (s, 3H), 2.42 (td, *J* = 13.5, 4.5 Hz, 1H), 2.08 (ddd, *J* = 13.2, 11.8, 6.9 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.55 (t, *J* = 6.8 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H);**^{13}C NMR (101 MHz, $CDCl_3$)**: δ 175.3, 169.2, 159.0 (d, *J* = 241.5 Hz), 145.3, 138.4 (d, *J* = 2.1 Hz), 133.1, 133.0(d, *J* = 8.3 Hz), 115.0 (d, *J* = 23.6 Hz), 113.5 (d, *J* = 25.8 Hz), 108.7 (d, *J* = 8.5 Hz), 61.4, 57.9, 48.6, 40.8, 37.8, 27.5, 26.5, 19.4, 14.0; **HRMS (ESI)** calcd for: $C_{17}H_{22}FN_2O_5S$: $[M + H]^+$, 385.1228 found: 385.1231.



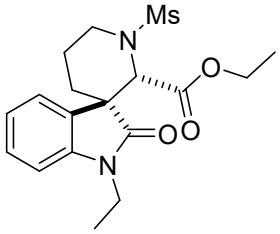
ethyl (2'*S**,3*S**)-4-bromo-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8e);** White solid, 92 mg, 64% yield, >20:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 166-168°C;**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 – 7.08 (m, 2H), 6.78 (dd, *J* = 7.6, 1.0 Hz, 1H), 5.61 (d, *J* = 1.2 Hz, 1H), 4.14 – 3.99 (m, 1H), 3.98 – 3.83 (m, 2H), 3.66 (m, 1H), 3.18 (s, 3H), 3.11 (s, 3H), 2.76 (ddd, *J* = 14.0, 12.1, 7.4 Hz, 1H), 2.15 – 2.04 (m, 1H), 2.04 – 1.92 (m, 1H), 1.51 (dd, *J* = 14.1, 5.7 Hz, 1H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 176.5, 169.7, 144.9, 130.1, 129.8, 127.5, 118.7, 107.2, 61.5, 58.7, 51.2, 40.5, 39.9, 26.4, 25.5, 17.6, 13.8; **HRMS (ESI)** calcd for: $C_{17}H_{22}BrN_2O_5S$: $[M + H]^+$, 445.0427 found: 445.0433.



ethyl (2'*S**,3*S**)-1,5-dimethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8f);** White solid, 109 mg, 70% yield, 1.4:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 150-152°C; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.40 (s, 1H), 4.30 – 4.11 (m, 2H), 4.06 – 3.85 (m, 2H), 3.19 (s, 3H), 2.81 (s, 3H), 2.43 – 2.36 (m, 1H), 2.35 (s, 3H), 2.24 – 2.07 (m, 1H), 1.96 – 1.82 (m, 1H), 1.53 (d, *J* = 13.6 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.7, 169.7, 140.2, 132.5, 132.0, 129.0, 126.0, 108.1, 61.4, 58.3, 48.4, 41.1, 38.0, 27.9, 26.5, 21.5, 19.6, 14.1; **HRMS (ESI)** calcd for: $C_{18}H_{25}N_2O_5S$: $[M + H]^+$, 381.1479 found: 381.1482.

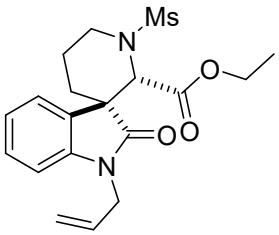


ethyl (2'*S**,3*S**)-5-methoxy-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8g);** White solid, 114 mg, 75% yield, 1.4:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 152-154 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 4.42 (s, 1H), 4.22 (tdd, *J* = 11.2, 7.2, 3.6 Hz, 2H), 4.09 – 3.90 (m, 2H), 3.79 (s, 3H), 3.19 (s, 3H), 2.81 (s, 3H), 2.41 (td, *J* = 13.5, 4.4 Hz, 1H), 2.16 (tdd, *J* = 18.3, 13.2, 5.3 Hz, 1H), 1.97 – 1.81 (m, 1H), 1.54 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.4, 169.5, 156.0, 135.98, 133.0, 113.4, 112.6, 108.7, 61.4, 58.1, 56.0, 48.6, 41.0, 38.1, 27.7, 26.6, 19.6, 14.1; **HRMS (ESI)** calcd for: $C_{18}H_{25}N_2O_6S$: $[M + H]^+$, 397.1428 found: 397.1433.

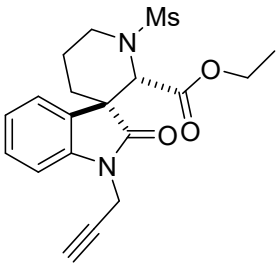


ethyl (2'*S**,3*S**)-1-ethyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8h);** White solid, 124 mg, 80% yield, 1.3:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 138-140°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 6.9 Hz, 1H), 7.32 (td, *J* = 7.8, 1.1 Hz, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.40 (s, 1H), 4.26 – 4.14 (m, 2H), 4.03 – 3.93 (m, 2H), 3.76 (ddt, *J* = 25.0, 14.1, 7.1 Hz, 2H), 2.81 (s, 3H), 2.40 (td, *J* = 13.6, 4.3 Hz, 1H), 2.29 – 2.12 (m, 1H), 1.93 – 1.84 (m,

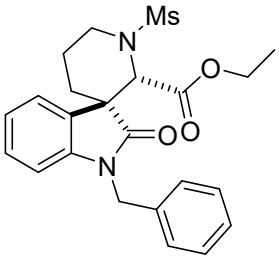
1H), 1.53 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.26 (t, *J* = 5.8 Hz, 6H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.3, 169.7, 141.6, 132.1, 128.8, 125.4, 122.8, 108.6, 61.4, 58.2, 48.2, 41.2, 37.9, 35.0, 27.8, 19.7, 14.1, 12.8; **HRMS (ESI)** calcd for: $C_{18}H_{25}N_2O_5S$: $[M + H]^+$, 381.1479 found: 381.1480.



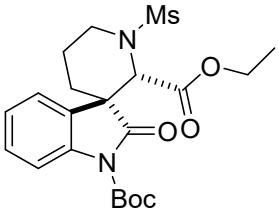
ethyl (2'*S**,3*S**)-1-allyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8i);** White solid, 119 mg, 78% yield, 1.2:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 134-136°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 7.5 Hz, 1H), 7.30 (td, *J* = 7.8, 1.2 Hz, 1H), 7.08 (td, *J* = 7.6, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.83 (ddt, *J* = 17.0, 10.3, 5.1 Hz, 1H), 5.21 (ddd, *J* = 11.8, 7.0, 1.2 Hz, 2H), 4.42 (s, 1H), 4.41 – 4.24 (m, 2H), 4.24 – 4.12 (m, 2H), 4.07 – 3.91 (m, 2H), 2.82 (s, 3H), 2.42 (td, *J* = 13.6, 4.3 Hz, 1H), 2.27 – 2.12 (m, 1H), 1.97 – 1.84 (m, 1H), 1.57 (dd, *J* = 10.2, 6.7 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.5, 169.6, 141.6, 131.9, 131.0, 128.8, 125.3, 123.0, 117.6, 109.3, 61.5, 58.3, 48.3, 42.4, 41.2, 37.9, 28.0, 19.7, 14.1; **HRMS (ESI)** calcd for: $C_{19}H_{25}N_2O_5S$: $[M + H]^+$, 393.1479 found: 393.1483.



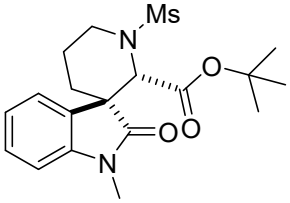
ethyl (2'*S**,3*S**)-1'-(methylsulfonyl)-2-oxo-1-(prop-2-yn-1-yl)spiro[indoline-3,3'-piperidine]-2'-carboxylate **(8j);** White solid, 124 mg, 81% yield, 1.2:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 172-174°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 7.1 Hz, 1H), 7.36 (td, *J* = 7.8, 1.1 Hz, 1H), 7.15 – 7.07 (m, 2H), 4.50 (d, *J* = 2.5 Hz, 2H), 4.45 (s, 1H), 4.21 (qd, *J* = 7.2, 3.0 Hz, 2H), 3.98 (dt, *J* = 11.1, 3.6 Hz, 2H), 2.82 (s, 3H), 2.39 (td, *J* = 13.4, 4.4 Hz, 1H), 2.24 (t, *J* = 2.5 Hz, 1H), 2.15 (tdd, *J* = 13.2, 6.8, 3.9 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.62 – 1.56 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 174.8, 169.4, 140.5, 131.6, 128.7, 125.2, 123.3, 109.3, 72.4, 61.4, 58.1, 50.3, 48.2, 41.0, 37.9, 29.4, 27.8, 19.5, 13.9; **HRMS (ESI)** calcd for: $C_{19}H_{23}N_2O_5S$: $[M + H]^+$, 391.1322 found: 391.1329.



ethyl (2'*S**,3*S**)-1-benzyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8k);** White solid, 135 mg, 84% yield, 1.3:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 178-180°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 – 7.63 (m, 1H), 7.34 – 7.25 (m, 5H), 7.21 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.82 (d, *J* = 15.7 Hz, 1H), 4.47 (s, 1H), 4.31 – 4.16 (m, 2H), 4.12 – 3.93 (m, 2H), 2.83 (s, 3H), 2.47 (td, *J* = 13.6, 4.3 Hz, 1H), 2.28 – 2.07 (m, 1H), 2.00 – 1.84 (m, 1H), 1.62 (dd, *J* = 13.1, 3.7 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.9, 169.7, 141.5, 135.6, 131.9, 129.0, 128.8, 127.9, 127.2, 125.3, 123.0, 109.5, 61.5, 58.3, 48.4, 43.9, 41.2, 37.9, 28.0, 19.7, 14.0; **HRMS (ESI)** calcd for: $C_{23}H_{27}N_2O_5S$: $[M + H]^+$, 443.1635 found: 443.1637.

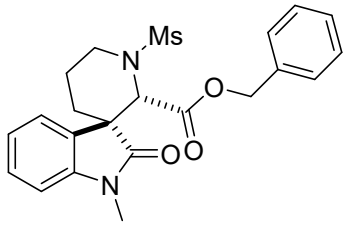


1-(tert-butyl) 2'-ethyl (2'*S**,3*S**)-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-1,2'-dicarboxylate **(8l);** White solid, 88 mg, 62% yield, 7:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 144-146°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 – 7.81 (m, 1H), 7.79 – 7.68 (m, 1H), 7.42 – 7.30 (m, 1H), 7.19 (td, *J* = 7.6, 1.1 Hz, 1H), 4.53 (s, 1H), 4.30 – 4.10 (m, 2H), 3.97 (dd, *J* = 18.7, 5.4 Hz, 2H), 2.84 (s, 3H), 2.34 (td, *J* = 13.3, 4.5 Hz, 1H), 2.14 (ddd, *J* = 18.4, 12.2, 6.3 Hz, 1H), 1.89 (d, *J* = 13.8 Hz, 1H), 1.71 (d, *J* = 15.5 Hz, 1H), 1.64 (s, 8H), 1.32 – 1.20 (m, 3H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 174.5, 169.3, 149.0, 138.4, 130.9, 129.0, 124.9, 124.8, 115.1, 84.8, 61.6, 58.8, 48.7, 40.9, 38.2, 29.0, 28.2, 19.0, 13.9; **HRMS (ESI)** calcd for: $C_{21}H_{28}KN_2O_7S$: $[M +H]^+$, 453.1690 found: 453.1695.



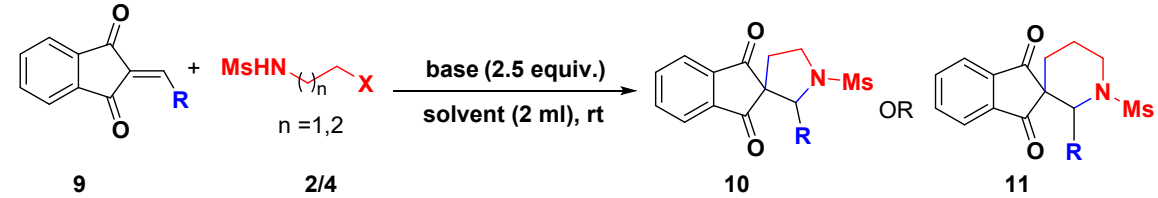
tert-butyl (2'*S**,3*S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8n);** White solid, 116 mg, 76% yield, 1.4:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 172-174°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz,

1H), 4.34 (s, 1H), 3.96 (dtd, *J* = 17.4, 12.0, 5.1 Hz, 2H), 3.22 (s, 3H), 2.86 (s, 3H), 2.38 (td, *J* = 13.0, 4.6 Hz, 1H), 2.25 – 2.04 (m, 1H), 1.87 (dd, *J* = 8.8, 6.8 Hz, 1H), 1.57 (dt, *J* = 13.9, 4.1 Hz, 1H), 1.48 (s, 9H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.8, 168.4, 142.6, 132.1, 128.7, 125.1, 122.8, 108.3, 83.0, 59.3, 48.5, 40.9, 38.5, 28.1, 27.9, 26.4, 19.6; **HRMS (ESI)** calcd for: $C_{19}H_{27}N_2O_5S$: $[M + H]^+$, 395.1635 found: 395.1639.



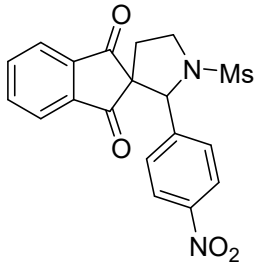
benzyl (2'*S**,3*S**)-1-methyl-1'-(methylsulfonyl)-2-oxospiro[indoline-3,3'-piperidine]-2'-carboxylate **(8o);** White solid, 110 mg, 75% yield, 1.5:1 *dr*, R_f = 0.3, column chromatography on silica gel (*n*-hexane/EtOAc 75:25), mp 158-160°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.70 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.28 (m, 6H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.28 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 4.46 (s, 1H), 4.04 – 3.91 (m, 2H), 3.18 (s, 3H), 2.62 (s, 3H), 2.43 (tt, *J* = 10.5, 5.3 Hz, 1H), 2.23 – 2.08 (m, 1H), 1.94 – 1.83 (m, 1H), 1.56 (dt, *J* = 13.5, 3.5 Hz, 1H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 175.8, 169.4, 142.5, 135.3, 131.7, 128.9, 128.8, 128.6, 128.6, 125.1, 123.0, 108.5, 67.3, 58.2, 48.3, 41.0, 37.8, 27.8, 26.5, 19.6; **HRMS (ESI)** calcd for: $C_{22}H_{25}N_2O_5S$: $[M + H]^+$, 429.1479 found: 429.1482.

6. General experimental procedures and characterization data for the synthesis of compounds 10 and 11

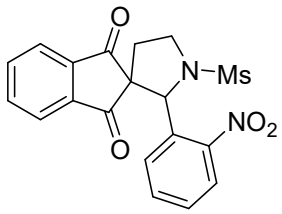


General experimental procedure: To an oven-dried 50 mL round bottom flask was added arylidene 1,3 Indandione (0.21 mmol, 1.0 equiv.), haloamines (0.32 mmol, 1.5 equiv.), and Cs_2CO_3 (0.53 mmol, 2.5 equiv.) in solvent (2.0 mL), and the resulting solution was stirred at room temperature until starting completely consumed (based on TLC analysis). After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with EtOAc (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent.

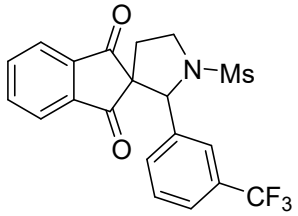
Characterization of the products:



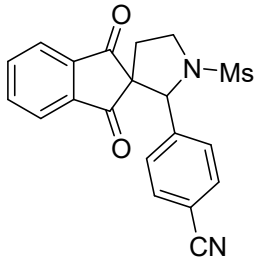
1'-(methylsulfonyl)-2'-(4-nitrophenyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10a);** White solid, 71 mg, 99% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 200−202°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 – 7.95 (m, 3H), 7.86 (dd, *J* = 22.5, 1.2 Hz, 2H), 7.76 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 4.22 – 4.11 (m, 1H), 4.04 (dd, *J* = 11.7, 5.5 Hz, 1H), 3.03 (s, 3H), 2.39 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.9, 197.4, 147.7, 145.2, 141.7, 140.8, 137.1, 136.7, 127.8, 124.1, 123.9, 123.7, 67.9, 63.6, 48.9, 36.6, 33.2; **HRMS (ESI)** calcd for: $C_{19}H_{17}N_2O_6S$: [M + H]+, 401.0802 found: 401.0815.



1'-(methylsulfonyl)-2'-(2-nitrophenyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10b);** White solid, 70 mg, 98% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 194−196°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 7.98 (m, 3H), 7.94 – 7.74 (m, 4H), 7.57 – 7.48 (m, 1H), 5.46 (s, 1H), 4.08 (t, *J* = 8.3 Hz, 1H), 3.84 (ddd, *J* = 11.7, 9.1, 6.3 Hz, 1H), 3.16 (s, 3H), 2.55 (ddd, *J* = 13.1, 11.8, 8.1 Hz, 1H), 2.16 (dd, *J* = 13.3, 6.0 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.4, 195.9, 146.4, 141.9, 139.2, 136.7, 136.5, 136.2, 134.4, 130.6, 129.1, 125.3, 123.9, 123.6, 64.3, 61.7, 47.6, 35.2, 32.7;**HRMS (ESI)** calcd for: $C_{19}H_{17}N_2O_6S$: [M + H]+, 401.0802 found: 401.0816.

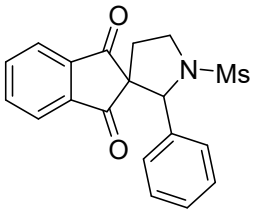


1'-(methylsulfonyl)-2'-(3-(trifluoromethyl)phenyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10c);** White solid, 69 mg, 98% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 120−122°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.91 – 7.82 (m, 1H), 7.79 (td, *J* = 7.4, 1.1 Hz, 1H), 7.74 – 7.63 (m, 1H), 7.46 – 7.30 (m, 3H), 7.27 (d, *J* = 4.5 Hz, 1H), 5.19 (s, 1H), 4.11 (dqd, *J* = 10.6, 8.6, 7.0 Hz, 2H), 2.99 (s, 3H), 2.38 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.1, 197.7, 141.9, 140.9, 138.7, 136.8, 136.4, 130.2, 128.9, 125.2, 125.01 (q, *J* = 3.1 Hz), 123.8, 123.5, 123.48 (q, *J* = 3.5 Hz), 122.5, 68.5, 63.8, 49.0, 36.9, 32.5; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.72; **HRMS (ESI)** calcd for: $C_{20}H_{17}F_3NO_4S$: [M + H]+, 424.0825 found: 424.0834.

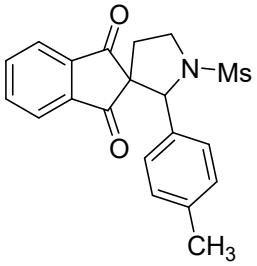


4-(1'-(methylsulfonyl)-1,3-dioxo-1,3-dihydrospiro[indene-2,3'-pyrrolidin]-2'-yl)benzonitrile **(10d);** Pinkish solid, 72 mg, 98% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 186−188°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 7.4 Hz, 1H), 7.87 (dtd, *J* = 19.9, 7.3, 1.2 Hz, 2H), 7.76 (dd, *J* = 6.8, 0.7 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 5.17 (s, 1H), 4.15 (dd, *J* = 12.5, 5.3 Hz, 1H), 4.08 – 3.97 (m, 1H), 3.03 (s, 3H), 2.38 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.9, 197.5,

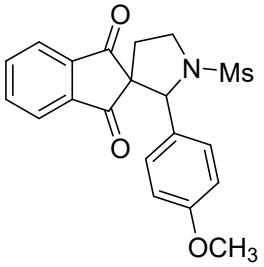
143.1, 141.8, 140.8, 137.0, 136.7, 132.2, 127.6, 123.9, 123.9, 118.5, 112.2, 68.2, 63.6, 48.9, 36.6, 33.1; **HRMS (ESI)** calcd for: $C_{20}H_{17}N_2O_4S$: [M + H]+, 381.0904 found: 381.0904.



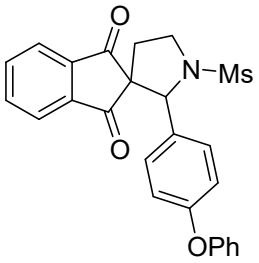
1'-(methylsulfonyl)-2'-phenylspiro[indene-2,3'-pyrrolidine]-1,3-dione **(10e);** Brown solid, 73 mg, 96% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 194−196°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 – 7.93 (m, 1H), 7.80 (dtd, *J* = 22.5, 7.2, 1.2 Hz, 2H), 7.74 – 7.62 (m, 1H), 7.25 – 7.14 (m, 3H), 7.14 – 7.00 (m, 2H), 5.17 (s, 1H), 4.24 – 4.05 (m, 2H), 2.93 (s, 3H), 2.38 (dd, *J* = 10.2, 4.4 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.4, 198.2, 142.2, 141.1, 137.2, 136.5, 136.1, 128.5, 128.,4 126.9, 123.7, 123.6, 69.4, 64.2, 48.9, 37.8, 32.4;**HRMS (ESI)** calcd for: $C_{19}H_{18}NO_4S$: [M + H]+, 356.0951 found: 356.0964.



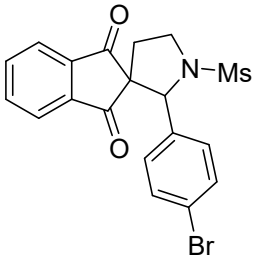
1'-(methylsulfonyl)-2'-(p-tolyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10f);** Pinkish solid, 69 mg, 93% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 134−136°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 – 7.93 (m, 1H), 7.87 – 7.71 (m, 3H), 6.98 (s, 4H), 5.13 (s, 1H), 4.11 (dd, *J* = 7.0, 2.4 Hz, 2H), 2.91 (s, 3H), 2.36 (t, *J* = 6.9 Hz, 2H), 2.23 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.5, 198.2, 142.2, 1411., 138.1, 136.5, 136.1, 134.2, 129.2, 126.9, 123.7, 123.6, 69.2, 64.2, 48.9, 37.9, 32.3, 21.2; **HRMS (ESI)** calcd for: $C_{22}H_{20}NO_4S$: [M + H]+, 370.1108 found: 370.1115.



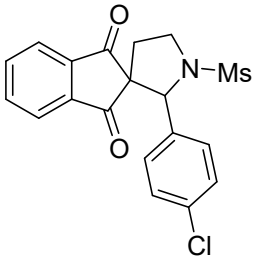
2'-(4-methoxyphenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10g);** White solid, 69 mg, 94% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 98−100°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 – 7.92 (m, 1H), 7.86 – 7.71 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 5.11 (s, 1H), 4.12 (ddd, *J* = 7.4, 6.2, 4.0 Hz, 2H), 3.71 (s, 3H), 2.89 (s, 3H), 2.43 – 2.29 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.4, 198.4, 159.4, 142.2, 141.1, 136.5, 136.1, 129.0, 128.2, 123.7, 123.6, 113.8, 69.1, 64.3, 55.2, 48.9, 37.8, 32.2; **HRMS (ESI)** calcd for: $C_{20}H_{20}NO_5S$: [M + H]+, 386.1057 found: 386.1068.



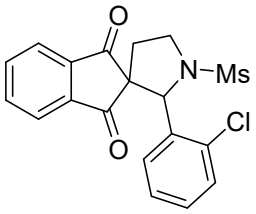
1'-(methylsulfonyl)-2'-(4-phenoxyphenyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10h);** White solid, 64 mg, 93% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 160−162°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (dd, *J* = 6.5, 1.2 Hz, 1H), 7.88 – 7.72 (m, 3H), 7.32 – 7.25 (m, 2H), 7.08 (dd, *J* = 11.3, 4.8 Hz, 3H), 6.95 – 6.84 (m, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.14 (s, 1H), 4.20 – 4.04 (m, 2H), 2.95 (s, 3H), 2.44 – 2.29 (m, 2H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.3, 198.3, 157.2, 156.9, 142.2, 141.2, 136.5, 136.2, 131.8, 129.8, 128.4, 123.8, 123.6, 123., 119.1, 118.5, 69.0, 64.3, 48., 37.63, 32.2.; **HRMS (ESI)** calcd for: $C_{25}H_{22}NO_5S$: [M + H]+, 448.1213 found: 448.1219.



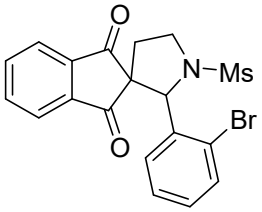
2'-(4-bromophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10i);** White solid, 68 mg, 98% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 130−132°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.2 Hz, 1H), 7.93 – 7.79 (m, 2H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.11 (s, 1H), 4.20 – 4.01 (m, 2H), 2.96 (s, 3H), 2.45 – 2.26 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.2, 197.9, 142.1, 140.9, 136.8, 136.5, 136.4, 131.6, 128.6, 123.8, 123.8, 122.4, 68.6, 63.9, 48.9, 37.4, 32.8; **HRMS (ESI)** calcd for: $C_{19}H_{17}BrNO_4S$: [M + H]+, 434.0056 found: 434.0067.



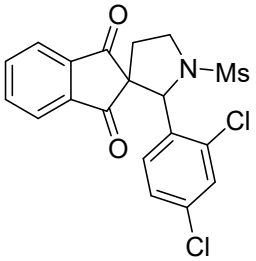
2'-(4-chlorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10j);** White solid, 70 mg, 96% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 110−112°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 7.92 (m, 1H), 7.92 – 7.79 (m, 2H), 7.79 – 7.67 (m, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.13 (s, 1H), 4.24 – 4.00 (m, 2H), 2.96 (s, 3H), 2.47 – 2.27 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.2, 197.9, 141.9, 140.9, 136.8, 136.4, 135.9, 134.1, 128.7, 128.3, 123.8, 123.8, 68.5, 63.9, 48.9, 37.3, 32.7; **HRMS (ESI)** calcd for: $C_{19}H_{17}ClNO_4S$: [M + H]+, 390.0561 found: 390.0572.



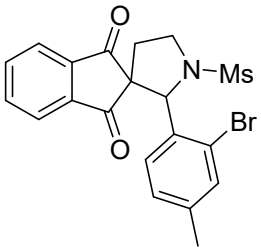
2'-(2-chlorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10k);** White solid, 69 mg, 95% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 7.3 Hz, 1H), 7.93 – 7.76 (m, 3H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 5.38 (s, 1H), 4.16 – 4.00 (m, 1H), 3.94 (dt, *J* = 16.5, 8.2 Hz, 1H), 3.11 (s, 3H), 2.50 (dt, *J* = 13.1, 8.8 Hz, 1H), 2.19 (ddd, *J* = 13.0, 6.6, 2.8 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.9, 196.2, 142.4, 139.8, 136.6, 136.3, 136.2, 132.2, 129.5, 129.4, 128.9, 127.2, 123.7, 123.6, 64.9, 61.6, 48.1, 35.9, 32.7; **HRMS (ESI)** calcd for: $C_{19}H_{17}ClNO_4S$: [M + H]+, 390.0561 found: 390.0565.



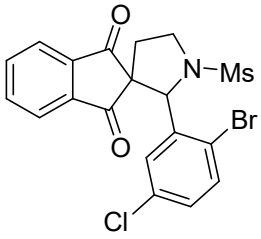
2'-(2-bromophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10l);** White solid, 67 mg, 96% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 194−196°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 – 7.97 (m, 1H), 7.91 – 7.82 (m, 3H), 7.69 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.17 (td, *J* = 7.6, 1.6 Hz, 1H), 5.35 (s, 1H), 4.07 (ddd, *J* = 9.5, 7.9, 2.4 Hz, 1H), 3.91 (td, *J* = 9.9, 6.6 Hz, 1H), 3.12 (s, 3H), 2.53 (ddd, *J* = 13.1, 10.3, 7.9 Hz, 1H), 2.18 (ddd, *J* = 13.1, 6.6, 2.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.1, 196.0, 142.5, 139.7, 137.9, 136.6, 136.2, 132.2, 129.9, 129.7, 127.8, 123.7, 123.6, 122.9, 67.2, 61.5, 48.1, 35.8, 32.7;**HRMS (ESI)** calcd for: $C_{19}H_{17}BrNO_4S$: [M + H]+, 434.0056 found: 434.0068.



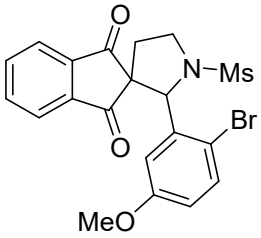
2'-(2,4-dichlorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10m);** White solid, 69 mg, 98% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 182−184°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 – 7.97 (m, 1H), 7.94 – 7.82 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.30 (m, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 5.29 (s, 1H), 4.05 (ddd, *J* = 9.7, 7.7, 2.9 Hz, 1H), 3.90 (td, *J* = 9.7, 6.7 Hz, 1H), 3.12 (s, 3H), 2.53 – 2.41 (m, 1H), 2.20 (ddd, *J* = 13.1, 6.7, 2.9 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.7, 196.1, 142.2, 139.7, 136.8, 136.4, 135.2, 134.6, 132.6, 130.5, 128.8, 127.6, 123.8, 123.7, 64.5, 61.5, 48.1, 35.7, 32.9;**HRMS (ESI)** calcd for: $C_{19}H_{16}Cl_2NO_4S$: [M + H]+, 424.0172 found: 424.0185.



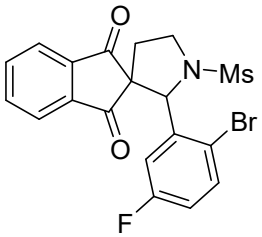
2'-(2-bromo-4-methylphenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione
(10n); White solid, 63 mg, 92% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 210−212°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 – 7.96 (m, 1H), 7.93 – 7.80 (m, 3H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.22 (ddd, *J* = 11.7, 6.4, 0.9 Hz, 2H), 5.31 (s, 1H), 4.06 (ddd, *J* = 9.6, 7.9, 2.4 Hz, 1H), 3.90 (td, *J* = 9.9, 6.6 Hz, 1H), 3.11 (s, 3H), 2.59 – 2.46 (m, 1H), 2.31 (s, 3H), 2.22 – 2.11 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.2, 196.2, 142.6, 139.9, 139.7, 136.6, 136.1, 134.8, 132.7, 129.6, 128.7, 123.7, 123.6, 122.6, 67.1, 61.5, 47.9, 35.8, 32.6, 20.9 ;**HRMS (ESI)** calcd for: $C_{20}H_{19}BrNO_4S$: [M + H]+, 448.0213 found: 448.0224.



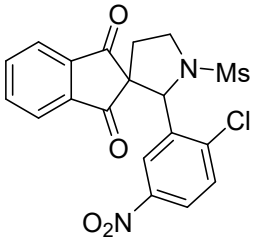
2'-(2-bromo-5-chlorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione
(10o); White solid, 65 mg, 96% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 188−190°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 – 7.98 (m, 1H), 7.93 – 7.82 (m, 3H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.16 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.26 (s, 1H), 4.06 (ddd, *J* = 9.7, 7.8, 2.1 Hz, 1H), 3.87 (ddd, *J* = 10.5, 9.6, 6.5 Hz, 1H), 3.14 (s, 3H), 2.53 (ddd, *J* = 13.2, 10.6, 7.8 Hz, 1H), 2.18 (ddd, *J* = 13.2, 6.5, 2.1 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.9, 195.7, 142.4, 139.9, 139.5, 136.8, 136.3, 134.2, 133.2, 129.9, 129.9, 123.8, 123.7, 120.6, 66.8, 61.3, 47.9, 35.6, 32.9; **HRMS (ESI)** calcd for: $C_{19}H_{16}BrClNO_4S$: [M + H]+, 467.9666 found: 467.9675.



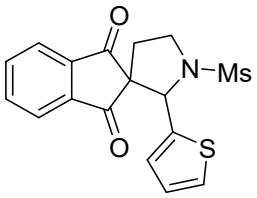
2'-(2-bromo-5-methoxyphenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione
(10p); White solid, 64 mg, 94% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 182−184°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08 – 7.95 (m, 1H), 7.93 – 7.77 (m, 3H), 7.57 (d, *J* = 8.7 Hz, 1H), 6.96 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 5.30 (s, 1H), 4.05 (ddd, *J* = 9.7, 7.8, 2.7 Hz, 1H), 3.91 (td, *J* = 9.8, 6.7 Hz, 1H), 3.78 (s, 3H), 3.10 (s, 3H), 2.51 (ddd, *J* = 13.1, 10.0, 7.8 Hz, 1H), 2.26 – 2.12 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.2, 196.4, 159.8, 142.6, 139.9, 136.6, 136.1, 130.4, 129.7, 123.7, 123.6, 122.9, 117.6, 113.7, 66.9, 61.7, 55.6, 48.1, 35.8, 32.5;**HRMS (ESI)** calcd for: $C_{20}H_{19}BrNO_5S$: [M + H]+, 464.0162 found: 464.0179.



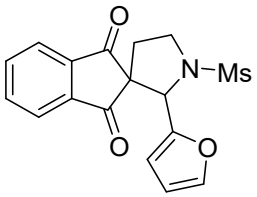
2'-(2-bromo-5-fluorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10q);** White solid, 64 mg, 93% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 194−196°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14 – 7.97 (m, 1H), 7.96 – 7.64 (m, 3H), 7.44 (dd, *J* = 9.4, 3.0 Hz, 1H), 7.33 (dd, *J* = 8.7, 5.1 Hz, 1H), 6.91 (ddd, *J* = 8.7, 7.8, 3.1 Hz, 1H), 5.26 (s, 1H), 4.06 (ddd, *J* = 9.8, 7.8, 2.1 Hz, 1H), 3.87 (ddd, *J* = 10.5, 9.5, 6.5 Hz, 1H), 3.14 (s, 3H), 2.52 (ddd, *J* = 13.2, 10.6, 7.8 Hz, 1H), 2.19 (ddd, *J* = 13.2, 6.5, 2.1 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.9, 195.8, 163.5, 161.1, 142.4, 140.4 (d, *J* = 7.2 Hz), 139.5, 136.8, 136.3, 133.4 (d, *J* = 8.0 Hz), 123.8 (d, *J* = 13.0 Hz), 117.5, 117.2 (d, *J* = 13.1 Hz), 116.9 (d, *J* = 12.7 Hz), 66.9, 61.3, 47.9, 35.6, 32.9; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -112.98;**HRMS (ESI)** calcd for: $C_{19}H_{16}BrFNO_4S$: [M + H]+, 451.9962 found: 451.9979.



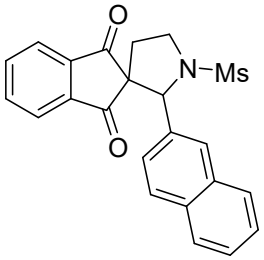
2'-(2-chloro-5-nitrophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10r);** Yellow solid, 67 mg, 97% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 220−222°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.57 (d, *J* = 2.6 Hz, 1H), 8.13 (dd, *J* = 8.7, 2.7 Hz, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.90 (ddt, *J* = 11.5, 10.3, 4.2 Hz, 3H), 7.37 (d, *J* = 8.7 Hz, 1H), 5.34 (s, 1H), 4.14 (ddd, *J* = 9.8, 7.8, 2.2 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 1H), 3.16 (s, 3H), 2.59 – 2.46 (m, 1H), 2.32 – 2.19 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.4, 195.9, 147.1, 141.9, 139.5, 139.1, 138.7, 136.9, 136.7, 130.1, 124.8, 124.3, 124.1, 123.8, 64.3, 61.3, 48.0, 35.6, 33.3.;**HRMS (ESI)** calcd for: $C_{19}H_{16}ClN_2O_6S$: [M + H]+, 435.0412 found: 435.0423.



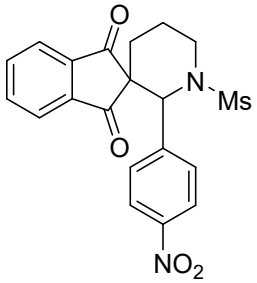
1'-(methylsulfonyl)-2'-(thiophen-2-yl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10s);** Brown solid, 72 mg, 95% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 156−158°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 – 7.96 (m, 1H), 7.91 – 7.79 (m, 3H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.72 (ddd, *J* = 3.6, 1.2, 0.8 Hz, 1H), 5.43 (s, 1H), 4.14 – 4.03 (m, 2H), 2.92 (s, 3H), 2.51 – 2.33 (m, 2H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.9, 197.6, 142.2, 141.1, 141.1, 136.6, 136.2, 126.9, 126.1, 125.81, 123.9, 123.7, 64.8, 63.9, 48.3, 38.7, 32.1;**HRMS (ESI)** calcd for: $C_{17}H_{16}NO_4S_2$: [M + H]+, 362.0515 found: 362.0524.



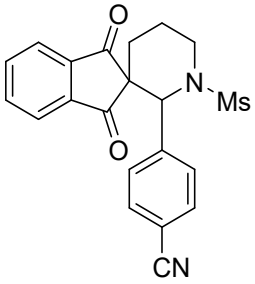
2'-(furan-2-yl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10t);** White solid, 74 mg, 96% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 154−156°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 – 7.98 (m, 1H), 7.92 – 7.84 (m, 3H), 7.28 (t, *J* = 1.3 Hz, 1H), 6.29 (d, *J* = 1.3 Hz, 2H), 5.08 (s, 1H), 4.00 (dd, *J* = 7.3, 6.5 Hz, 2H), 2.89 (s, 3H), 2.60 (dt, *J* = 12.9, 7.5 Hz, 1H), 2.29 (dt, *J* = 12.8, 6.4 Hz, 1H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.2, 196.8, 150.2, 142.8, 142.1, 140.8, 136.6, 136.3, 123.9, 123.8, 110.8, 109.5, 62.2, 62.1, 47.9, 37.7, 31.7.;**HRMS (ESI)** calcd for: $C_{17}H_{16}NO_5S$: [M + H]+, 346.0744 found: 346.0756.



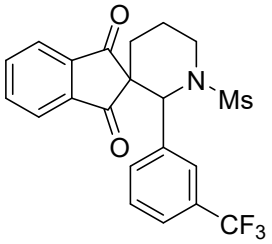
1'-(methylsulfonyl)-2'-(naphthalen-2-yl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(10u);** White solid, 61 mg, 86% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 176−178°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.68 (ddd, *J* = 22.5, 10.9, 5.5 Hz, 5H), 7.57 (s, 1H), 7.45 – 7.35 (m, 2H), 7.26 (d, *J* = 5.7 Hz, 1H), 5.35 (s, 1H), 4.28 – 4.13 (m, 2H), 2.93 (s, 3H), 2.42 (dd, *J* = 10.1, 4.2 Hz, 2H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.4, 198.1, 142.1, 141.1, 136.5, 136.2, 134.7, 133.2, 133.0, 128.3, 128.2, 127.8, 126.3, 126.3, 124.7, 123.7, 123.7, 69.4, 64.4, 49.1, 37.8, 32.8.;**HRMS (ESI)** calcd for: $C_{23}H_{20}NO_4S$: [M + H]+, 406.1108 found: 406.1116.



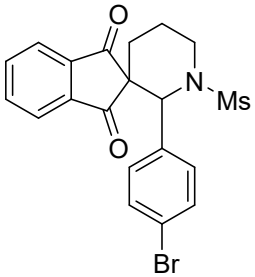
1'-(methylsulfonyl)-2'-(p-tolyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11a);** White solid, 64 mg, 86% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 144−146°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.7 Hz, 3H), 7.85 (dtd, *J* = 21.2, 7.2, 1.2 Hz, 2H), 7.79 – 7.65 (m, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.55 (s, 1H), 4.18 – 3.98 (m, 2H), 2.92 (s, 3H), 2.33 – 2.16 (m, 1H), 2.11 – 1.99 (m, 2H), 1.95 – 1.79 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.7, 198.9, 147.5, 145.9, 141.1, 140.1, 136.7, 136.5, 127.7, 124.2, 123.9, 123.9, 59.2, 57.5, 41.5, 40.2, 26.8, 19.3.;**HRMS (ESI)** calcd for: $C_{20}H_{19}N_2O_6S$: [M + H]+, 415.0958 found: 415.0969.



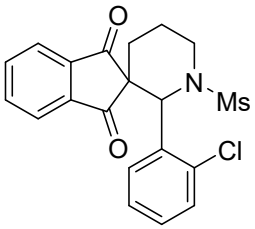
4-(1'-(methylsulfonyl)-1,3-dioxo-1,3-dihydrospiro[indene-2,3'-piperidin]-2'-yl)benzonitrile **(11b);** White solid, 65 mg, 85% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 158−160°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08 – 7.95 (m, 1H), 7.85 (dtd, *J* = 18.9, 7.2, 1.2 Hz, 2H), 7.77 (ddd, *J* = 7.3, 1.3, 0.8 Hz, 1H), 7.55 – 7.36 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.48 (s, 1H), 4.20 – 3.93 (m, 2H), 2.90 (s, 3H), 2.31 – 2.17 (m, 1H), 2.09 – 1.96 (m, 2H), 1.95 – 1.85 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.7, 198.9, 143.8, 141.1, 140.2, 136.7, 136.4, 132.4, 127.6, 124.1, 123.9, 118.3, 112.0, 59.5, 57.4, 41.5, 40.1, 26.6, 19.3.;**HRMS (ESI)** calcd for: $C_{21}H_{19}N_2O_4S$: [M + H]+, 395.1060 found: 395.1074.



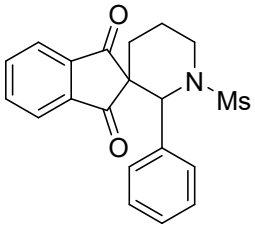
1'-(methylsulfonyl)-2'-(3-(trifluoromethyl)phenyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11c);** White solid, 62 mg, 85% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 118−120°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 – 7.93 (m, 1H), 7.89 – 7.76 (m, 2H), 7.76 – 7.67 (m, 1H), 7.34 (dd, *J* = 23.6, 12.0 Hz, 4H), 5.47 (s, 1H), 4.12 – 3.94 (m, 2H), 2.84 (s, 3H), 2.36 – 2.18 (m, 1H), 2.12 – 2.00 (m, 2H), 1.94 (dddd, *J* = 8.8, 7.2, 5.7, 2.8 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** 201.0, 199.3, 141.3, 140.3, 139.3, 136.5, 136.3, 131.0, 130.7, 130.4, 129.2, 124.96 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 3.8 Hz), 123.7, 59.7, 57.3, 41.6, 40.3, 26.2, 19.4;**^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.95.;**HRMS (ESI)** calcd for: $C_{21}H_{19}F_3NO_4S$: [M + H]+, 438.0981 found: 438.0992.



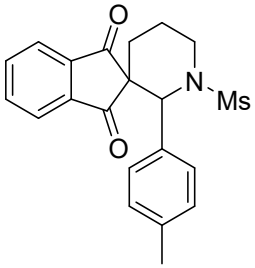
2'-(4-bromophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11d);** White solid, 60 mg, 84% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 142−144°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (dd, *J* = 4.6, 3.4 Hz, 1H), 7.92 – 7.64 (m, 3H), 7.33 – 7.26 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 1H), 4.09 – 3.93 (m, 2H), 2.78 (s, 3H), 2.27 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.03 (dd, *J* = 8.1, 5.4 Hz, 2H), 1.95 – 1.84 (m, 1H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.8, 199.3, 141.3, 140.3, 137.2, 136.4, 136.2, 131.8, 128.9, 124.2, 123.8, 122.3, 59.5, 57.3, 41.4, 40.3, 26.2, 19.6.;**HRMS (ESI)** calcd for: $C_{20}H_{19}BrNO_4S$: [M + H]+, 448.0213 found: 448.0212.



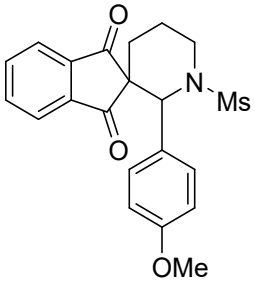
2'-(2-chlorophenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11e);** White solid, 61 mg, 81% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 196−198°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 6.9 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.19 (d, *J* = 3.9 Hz, 2H), 5.73 (s, 1H), 4.12 – 3.93 (m, 2H), 2.90 (s, 3H), 2.41 – 2.26 (m, 1H), 2.12 (ddd, *J* = 14.4, 10.0, 4.2 Hz, 1H), 2.01 – 1.85 (m, 2H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.1, 198.9, 141.3, 139.9, 137.6, 136.2, 136.1, 132.8, 129.7, 129.3, 129.1, 127.1, 123.8, 123.5, 54.6, 54.6, 43.1, 39.8, 25.7, 19.2;**HRMS (ESI)** calcd for: $C_{20}H_{19}ClNO_4S$: [M + H]+, 404.0718 found: 404.0729.



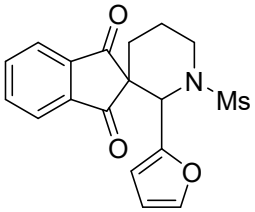
1'-(methylsulfonyl)-2'-phenylspiro[indene-2,3'-piperidine]-1,3-dione **(11f);** White solid, 57 mg, 72% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 188−190°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 – 7.91 (m, 1H), 7.90 – 7.65 (m, 3H), 7.23 – 7.08 (m, 5H), 5.38 (s, 1H), 4.09 – 3.92 (m, 2H), 2.70 (s, 3H), 2.38 – 2.22 (m, 1H), 2.12 – 1.99 (m, 2H), 1.94 (dddd, *J* = 13.0, 7.8, 5.2, 2.6 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.1, 199.5, 141.3, 140.4, 137.7, 136.2, 136.1, 128.6, 128.3, 127.3, 123.9, 123.6, 60.1, 57.3, 41.5, 40.2, 25.9, 19.7;**HRMS (ESI)** calcd for: $C_{20}H_{20}NO_4S$: [M + H]+, 370.1108 found: 370.1119.



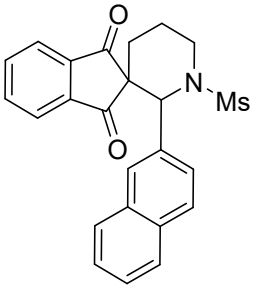
1'-(methylsulfonyl)-2'-(p-tolyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11g);** White solid, 60 mg, 77% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 206−208°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (dd, *J* = 7.3, 0.6 Hz, 1H), 7.88 – 7.67 (m, 3H), 7.12 – 7.01 (m, 2H), 7.01 – 6.86 (m, 2H), 5.32 (s, 1H), 4.05 – 3.89 (m, 2H), 2.66 (s, 3H), 2.40 – 2.28 (m, 1H), 2.22 (s, 3H), 2.14 – 2.06 (m, 1H), 2.02 (dd, *J* = 14.3, 7.4 Hz, 1H), 1.93 (dtd, *J* = 10.0, 7.1, 3.0 Hz, 1H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.9, 199.6, 141.3, 140.4, 138.1, 136.1, 135.9, 134.6, 129.3, 127.5, 124.0, 123.6, 59.9, 57.2, 41.4, 40.1, 25.7, 21.2, 19.8.;**HRMS (ESI)** calcd for: $C_{21}H_{22}NO_4S$: [M + H]+, 384.1264 found: 384.1278.



2'-(4-methoxyphenyl)-1'-(methylsulfonyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11h);** White solid, 60 mg, 79% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 130−132°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.05 – 7.87 (m, 1H), 7.81 (dd, *J* = 7.4, 3.0 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.19 – 7.05 (m, 2H), 6.79 – 6.61 (m, 2H), 5.25 (s, 1H), 4.05 – 3.87 (m, 2H), 3.70 (s, 3H), 2.64 (s, 3H), 2.33 (ddd, *J* = 12.5, 10.1, 6.6 Hz, 1H), 2.17 – 1.92 (m, 3H);**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.9, 199.7, 159.4, 141.3, 140.5, 136.1, 135.9, 129.5, 129.1, 123.9, 123.6, 113.9, 59.8, 57.2, 55.2, 41.5, 40.0, 25.6, 19.9.;**HRMS (ESI)** calcd for: $C_{21}H_{22}NO_5S$: [M + H]+, 400.1213 found: 400.1221.



2'-(furan-2-yl)-1'-(methylsulfonyl)spiro[indene-2,3'-piperidine]-1,3-dione **(11i);** White solid, 57 mg, 71% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 190−192°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.02 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.91 – 7.79 (m, 3H), 7.48 (d, *J* = 1.2 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.19 (dd, *J* = 3.3, 0.7 Hz, 1H), 5.12 (s, 1H), 3.87 (dd, *J* = 13.7, 3.9 Hz, 1H), 3.61 (dd, *J* = 14.0, 10.6 Hz, 1H), 2.57 (s, 3H), 2.56 – 2.39 (m, 2H), 1.93 – 1.80 (m, 2H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.3, 198.9, 150.7, 143.3, 140.6, 140.5, 136.3, 136.1, 124.3, 123.7, 110.3, 110.3, 54.6, 52.1, 41.7, 38.4, 24.1, 19.9.;**HRMS (ESI)** calcd for: $C_{18}H_{18}NO_5S$: [M + H]+, 360.0900 found: 360.0916.



1'-(methylsulfonyl)-2'-(naphthalen-2-yl)spiro[indene-2,3'-piperidine]-1,3-dione **(11j);** White solid, 51 mg, 69% yield, *Rf* = 0.4, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 162−164°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 10.1, 4.2 Hz, 1H), 7.74 – 7.57 (m, 6H), 7.39 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.33 – 7.25 (m, 1H), 5.57 (s, 1H), 4.16 (ddd, *J* = 14.0, 10.7, 5.5 Hz, 1H), 4.10 – 3.99 (m, 1H), 2.69 (s, 3H), 2.33 (dd, *J* = 11.1, 5.9 Hz, 1H), 2.15 – 2.03 (m, 2H), 2.01 – 1.92 (m, 1H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 201.1, 199.4, 141.3, 140.3, 136.2, 136.0, 135.3, 133.1, 132.9, 128.4, 128.2, 127.6, 126.7, 126.4, 124.9, 123.9, 123.6, 60.3, 57.5, 41.6, 40.2, 26.2, 19.8.;**HRMS (ESI)** calcd for: $C_{24}H_{22}NO_4S$: [M + H]+, 420.1264 found: 420.1279.

7. Experimental procedure for gram-scale synthesis of 3a

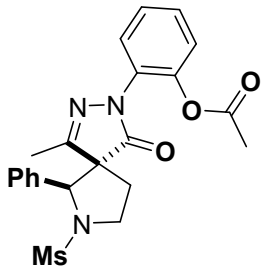
To an oven-dried 50 mL round-bottom flask was added arylidene pyrazolone **1a** (3.8 mmol, 1.0 equiv.), haloamine **2a** (5.7 mmol, 1.5 equiv.), and K_2CO_3 (9.7 mmol, 2.5 equiv.) in acetone (10 mL), and the resulting solution was stirred at room temperature until starting completely consumed. After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with DCM (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane /EtOAc as eluent (1.13 gm, 77% yield.

8. Experimental procedure for gram-scale synthesis of 10i

To an oven-dried 50 mL round-bottom flask was added arylidene 1,3 indandione **9a** (3.2 mmol, 1.0 equiv.), haloamine **2a** (4.8 mmol, 1.5 equiv.), and Cs_2CO_3 (7.9 mmol, 2.5 equiv.) in MeCN (10 mL), and the resulting solution was stirred at room temperature until starting completely consumed (based on TLC analysis). After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with DCM (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane /EtOAc as eluent (1.21 gm, 87% yield).

9. General experimental procedures and characterization data for the transformation of compounds

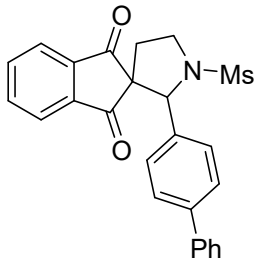
a) General experimental procedure for oxyacylation of 3a: Solution containing **3a** (0.13 mmol, 1.0 equiv.), (diacetoxyiodo)benzene (0.16 mmol, 1.2 equiv.), and $Pd(OAc)_2$ (0.013 mmol, 0.1 equiv.) in AcOH (0.3ml) and acetic anhydride (0.3ml) was refluxed (110^0C) for 2 hours. The reaction mixture was quenched with water and extracted with DCM. The organic layer was dried with anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent (*n*-hexane/EtOAc 70:30) to afford **12** (49 mg) as a white solid in 85% yield.



2-((*5R*,6S**)-4-methyl-7-(methylsulfonyl)-1-oxo-6-phenyl-2,3,7-triazaspiro[4.4]non-3-en-2-yl)phenyl acetate **(12);** White solid, 49 mg, 85% yield, *Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 230−232°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.36 – 7.19 (m, 7H), 7.16 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.96 (s, 1H), 4.02 – 3.87 (m, 2H), 2.98 (s, 3H), 2.42 (dt, *J* = 13.0, 8.3 Hz, 1H), 2.25 – 2.08 (m, 4H), 1.10 (s, 3H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 175.2, 168.4, 159.1, 144.2, 138.8, 129.1, 128.9, 128.7, 128.4, 126.5, 126.4, 126.1, 124.3, 68.5, 62.1, 47.2, 35.5, 31.2, 21.2, 14.8.;**HRMS (ESI)** calcd for: $C_{22}H_{22}N_3O_5S$: [M + H]+, 442.1431 found: 442.1439.

b) Synthetic Transformations of the Product 11i (Suzuki Coupling Reaction): In a 10 mL oven-dried sealed tube charged with a magnetic bar, aryl halide **11i** (0.12 mmol, 1.0 equiv.), phenylboronic acid (0.17 mmol, 1.5 equiv.), $Pd(OAc)_2$ (3.0 mg, 10 mol %), PPh_3 (0.05 mmol,

0.4 equiv.), and K_2CO_3 (3.0 equiv.) were added sequentially in 1,4-dioxane (1 mL), and the reaction mixture was heated in an oil bath at 80°C. After 12 h, the reaction mixture was cooled at room temperature, quenched with H_2O, and extracted with EtOAc (5 mL × 3). Organic layers were collectively washed with brine and dried over Na_2SO_4. After evaporation under vacuum, the crude product obtained was purified by silica gel column chromatography to afford **13** (19 mg) as a white solid in 38% yield. (*n*-hexane/EtOAc 70:30).

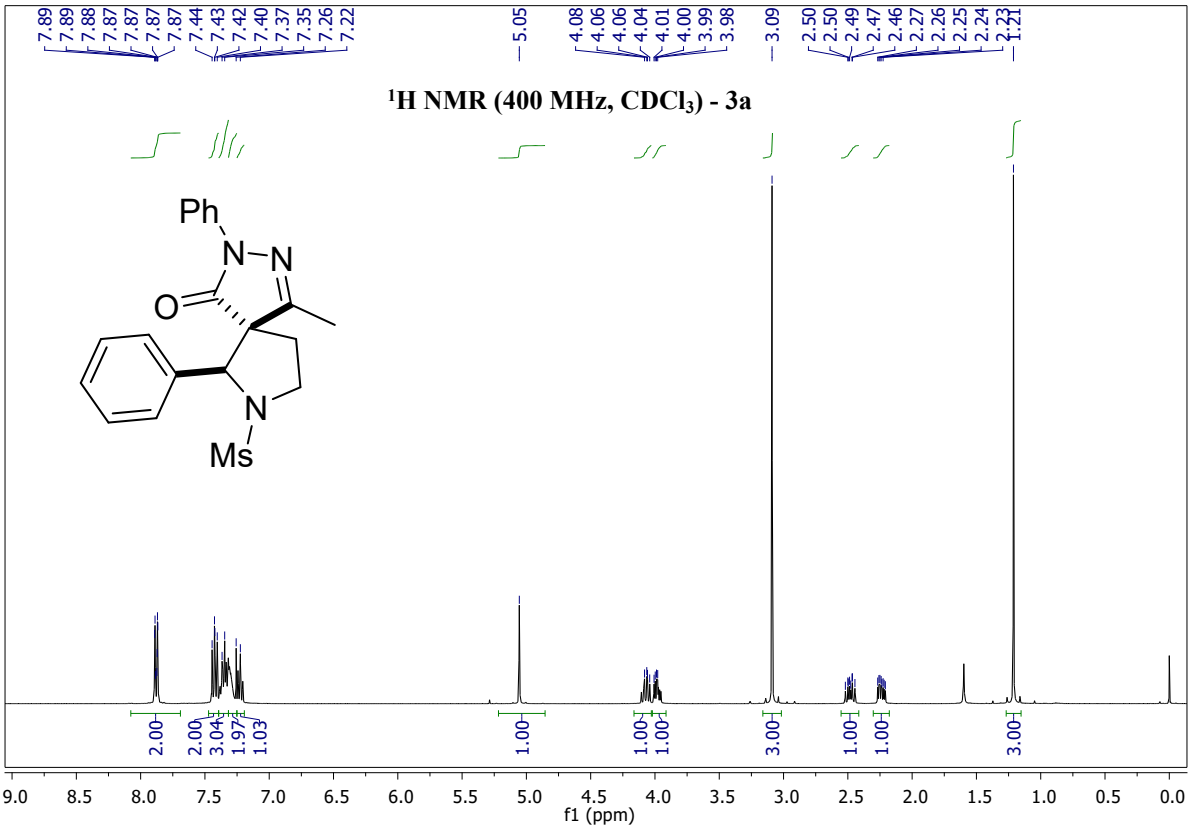


2'-([1,1'-biphenyl]-4-yl)-1'-(methylsulfonyl)spiro[indene-2,3'-pyrrolidine]-1,3-dione **(13);** White solid, 19 mg, 38% yield, *Rf* = 0.5, column chromatography on silica gel (*n*-hexane/EtOAc 70:30), mp 158−160°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.79 – 7.63 (m, 3H), 7.51 – 7.37 (m, 2H), 7.37 – 7.24 (m, 4H), 7.20 (d, *J* = 13.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.14 (s, 1H), 4.16 – 4.01 (m, 2H), 2.89 (s, 3H), 2.35 – 2.28 (m, 2H).;**^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.3, 198.2, 142.2, 141.1, 141.0, 140.5, 136.6, 136.2, 128.8, 127.5, 127.3, 127.1, 123.7, 123.7, 69.1, 64.3, 49.0, 37.7, 32.5; **HRMS (ESI)** calcd for: $C_{25}H_{21}NO_4S$: [M + H]+, 432.1264 found: 432.1269.

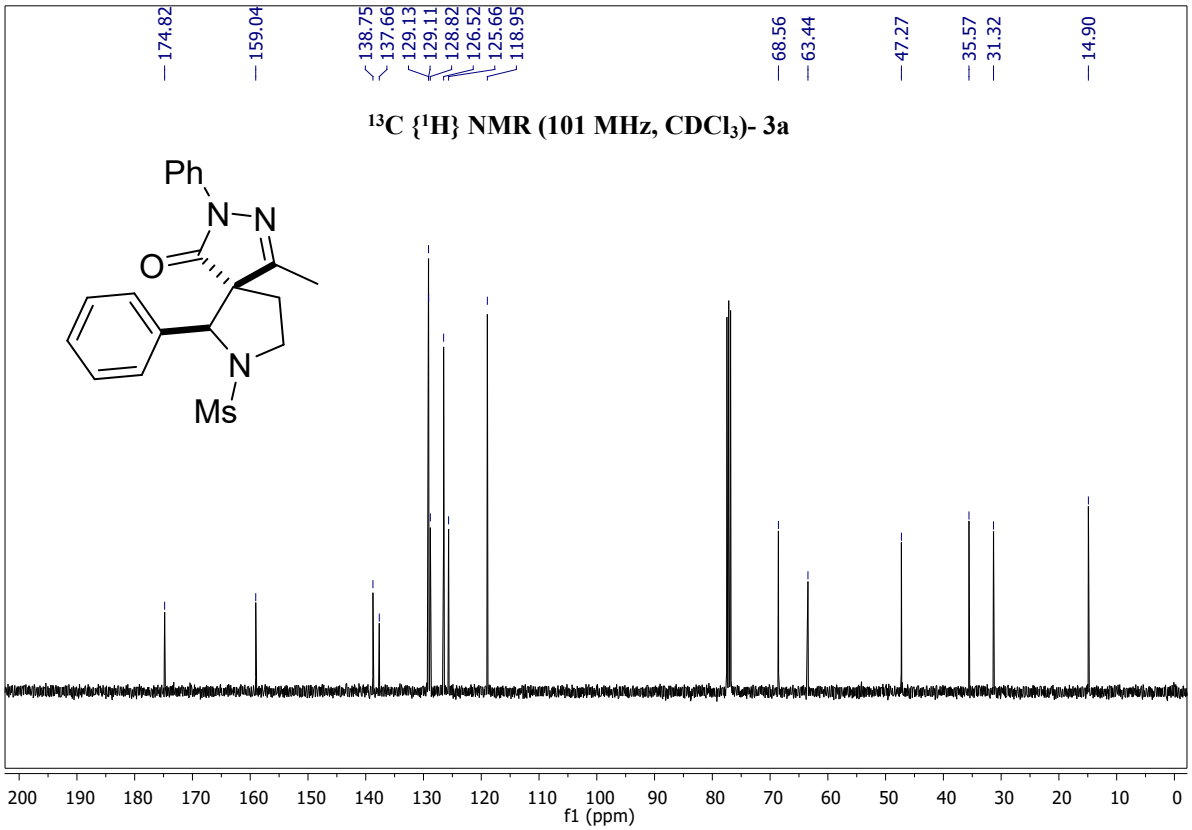
10. References:

1. D. S. Ji, X. Zhang, P. Zhang, X. Bao, Y. Yuan, C. Huo, P. F. Xu, *Org. Lett.* 2025, ***27*** (2), 709–714.
2. J. Nomme, Z. Li, R. M. Gipson, J. Wang, A. L. Armijo, T. Le, S. Poddar, T. Smith, B. D. Santarsiero, H. A. Nguyen, J. Czernin, A. N. Alexandrova, M. E. Jung, C. G. Radu and A. Lavie, *J. Med. Chem.*, 2014, **57**, 9480–9494.
3. C. B. Zartman, I. M. Bell, S. N. Gallicchio, S. L. Graham, S. A. Kane, J. J. Mallee, R. Z. Rutledge, C. A. Salvatore, J. P. Vacca and T. M. Williams, *Bioorganic Med. Chem. Lett.*, 2011, **21**, 6705–6708.
4. (a) A. Vopálenská, V. Dočekal, S. Petrželová, I. Císařová, J. Veselý, *J. Org. Chem.* 2023, *88* (12), 7724–7735; (b) M. Eskandari, K. Jadidi, B. Notash, *J. Org. Chem.* 2023, *88* (9), 5254–5274; (c) C. B. Nichinde, B. R. Patil, S. S. Chaudhari, B. P. Mali, R. G. Gonnade, A. K. Kinage, *RSC Adv. 2023*, ***13*** (19), 13206–13212.
5. P. Suresh, S. Prasanna Kumari, S. M. Krishna Reddy, S. P. Anthony, S. Thamotharan, and S. Selva Ganesan, *New J. Chem., 2022*, **46**, 20951–20956.

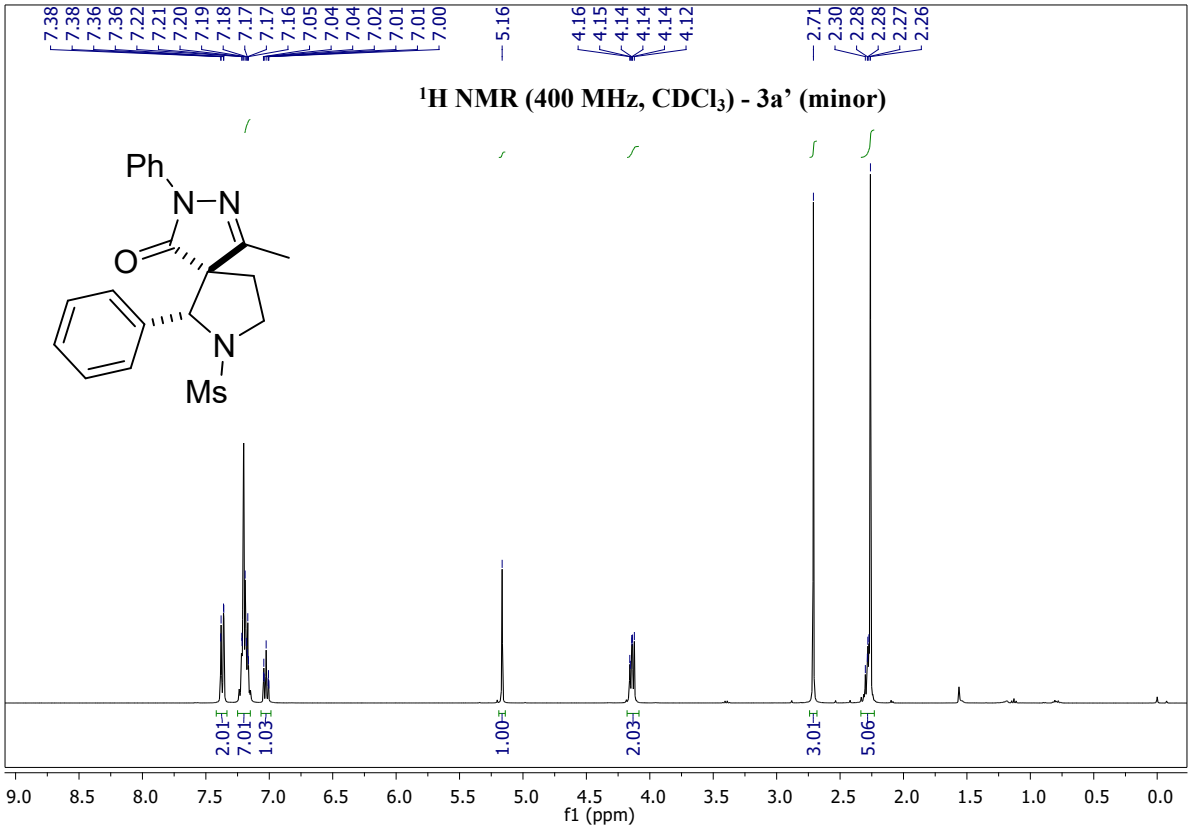
11.^{1}H NMR, ^{13}C NMR and ^{19}F Spectra of Products:

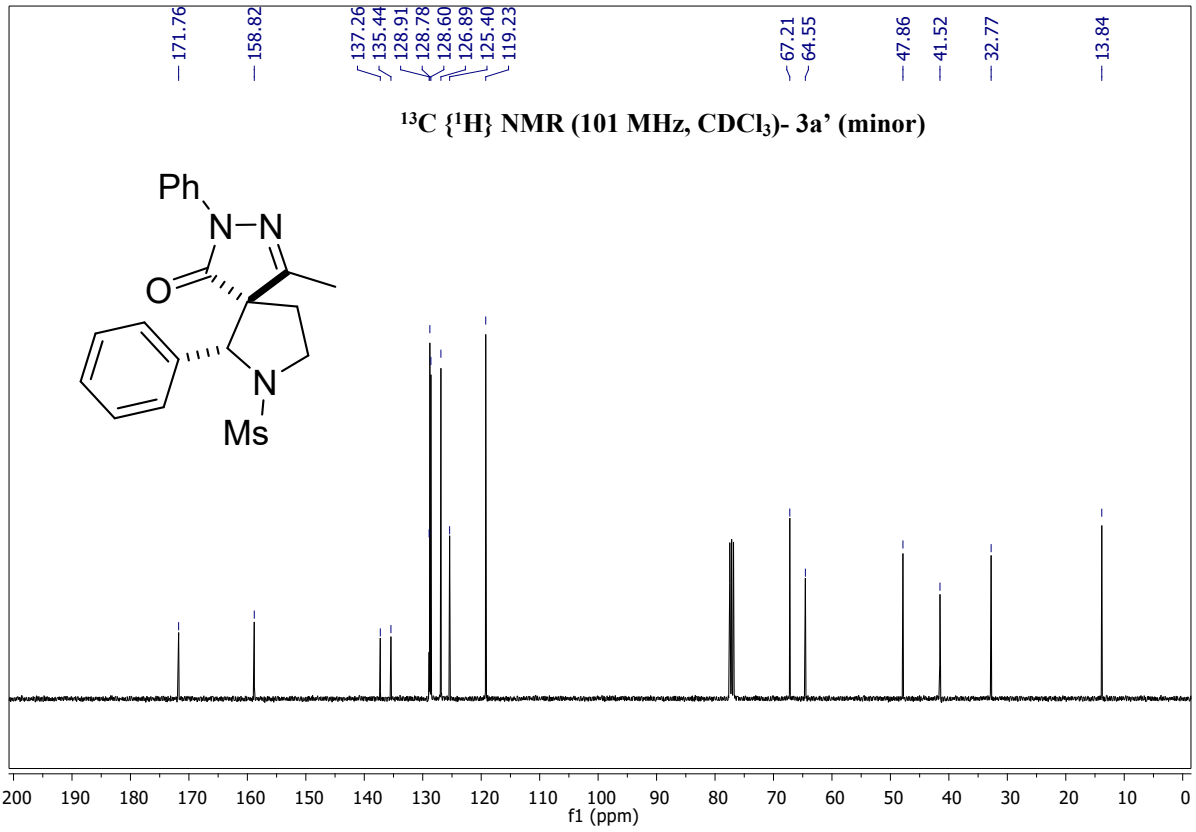


^{1}H NMR (400 MHz, $CDCl_3$) - 3a

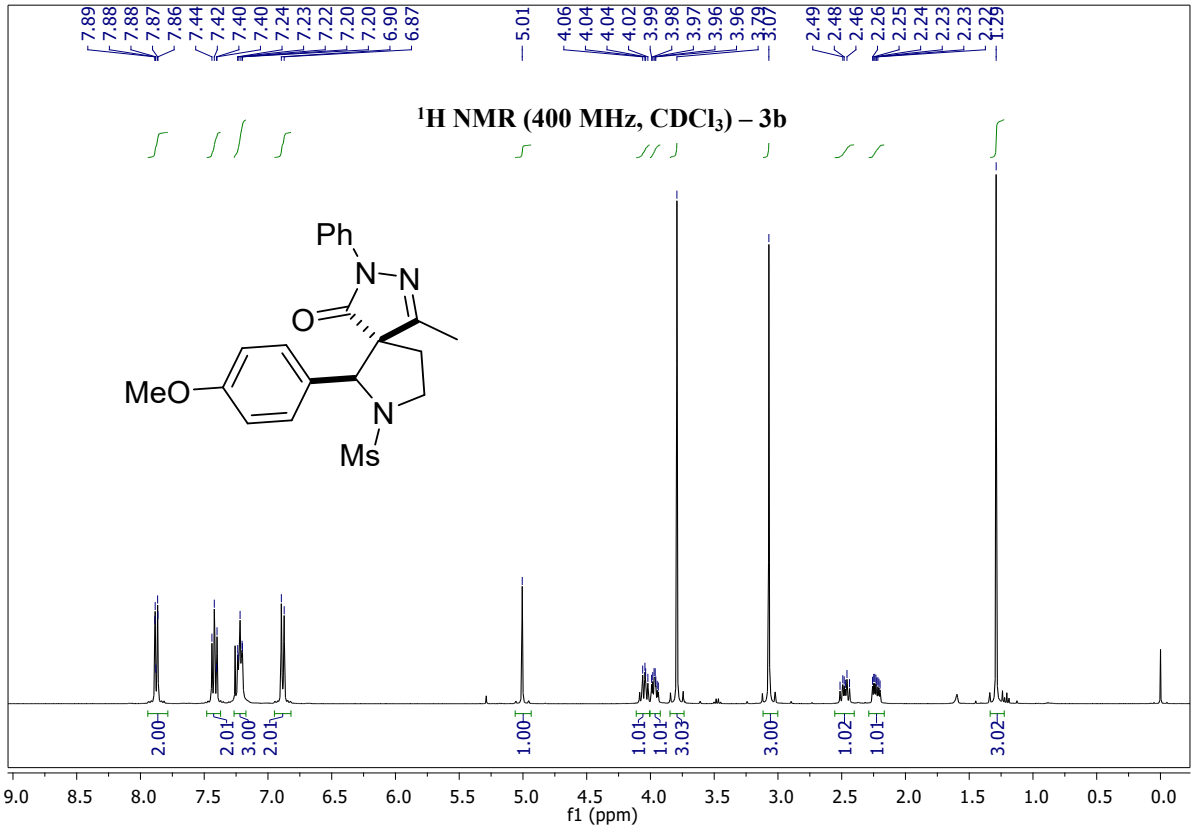


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3a

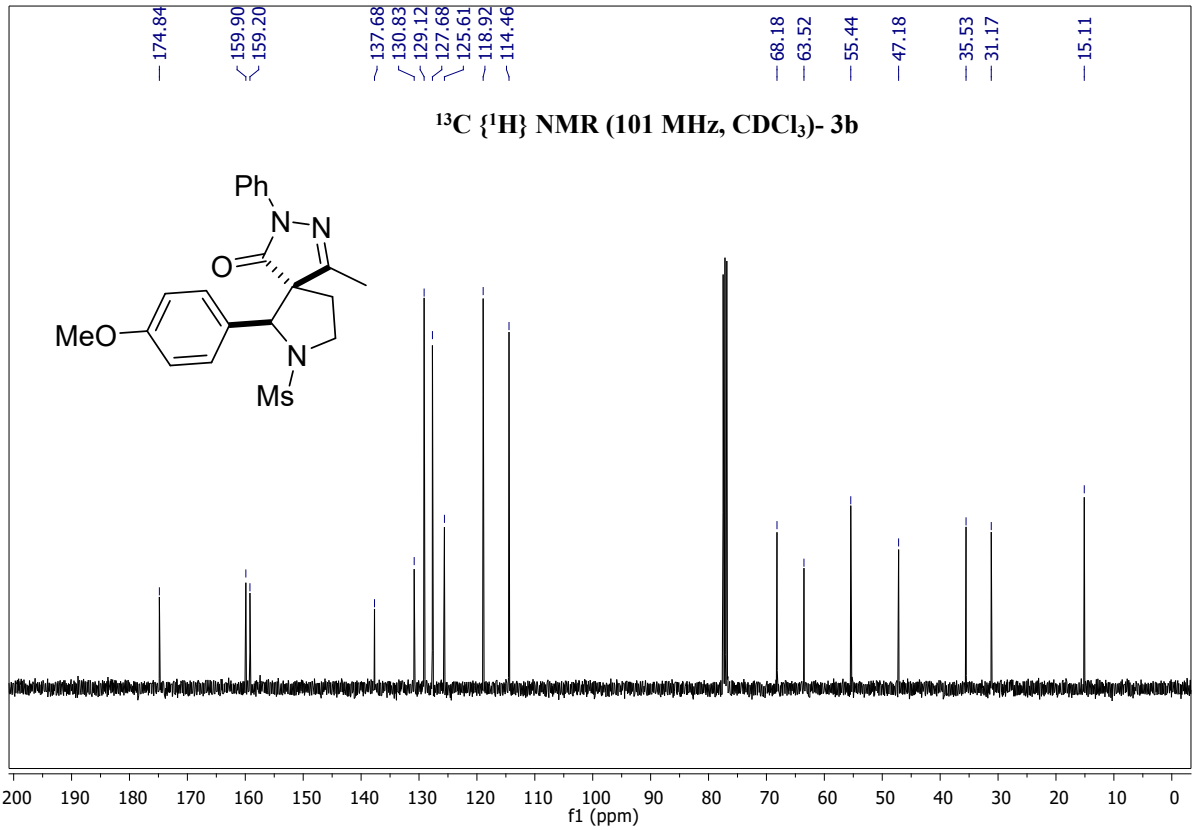

7.38
7.38
7.36
7.36
7.22
7.21
7.20
7.19
7.18
7.17
7.17
7.16
7.05
7.04
7.04
7.02
7.01
7.01
7.00
5.16
4.16
4.15
4.14
4.14
4.14
4.12
2.71
2.30
2.28
2.28
2.27
2.26
1H NMR (400 MHz, CDCl3) - 3a' (minor)
Ph
N
N
O
N
Ms
2.01
7.01
1.03
1.00
2.03
3.01
5.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



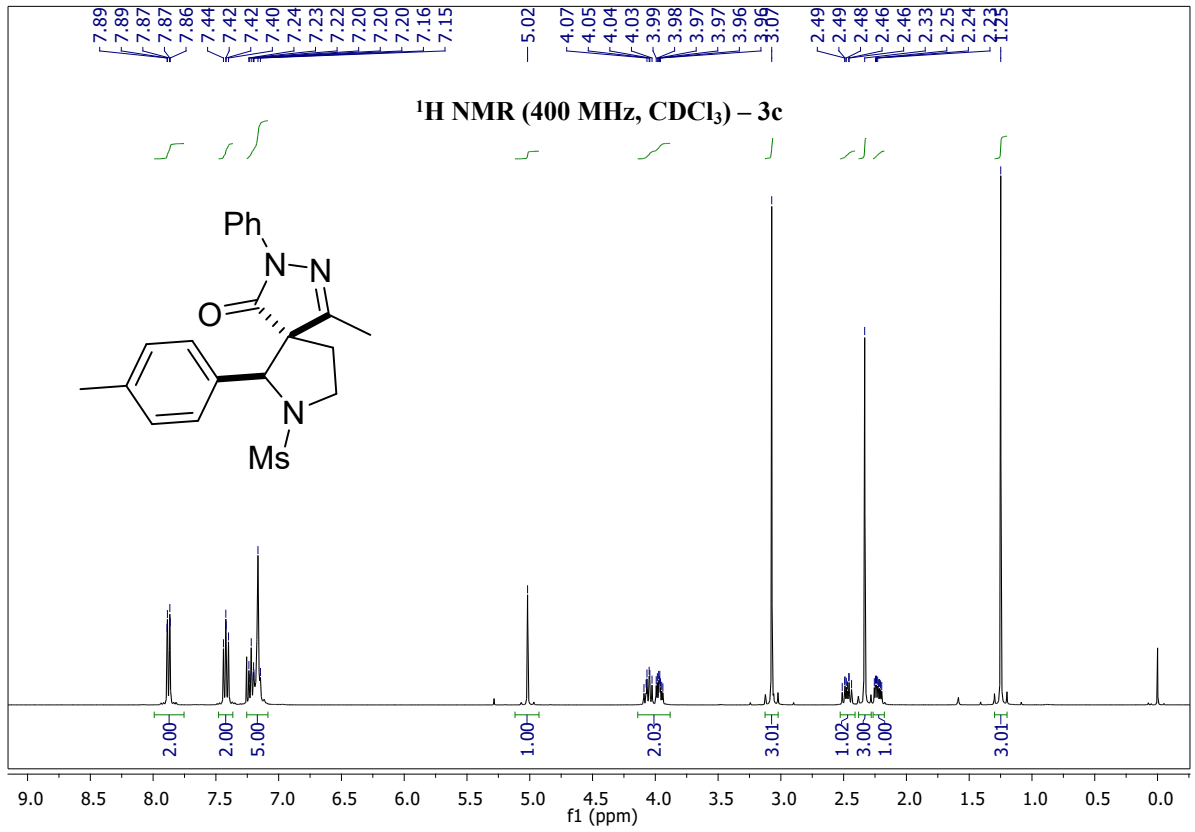
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3a' (minor)



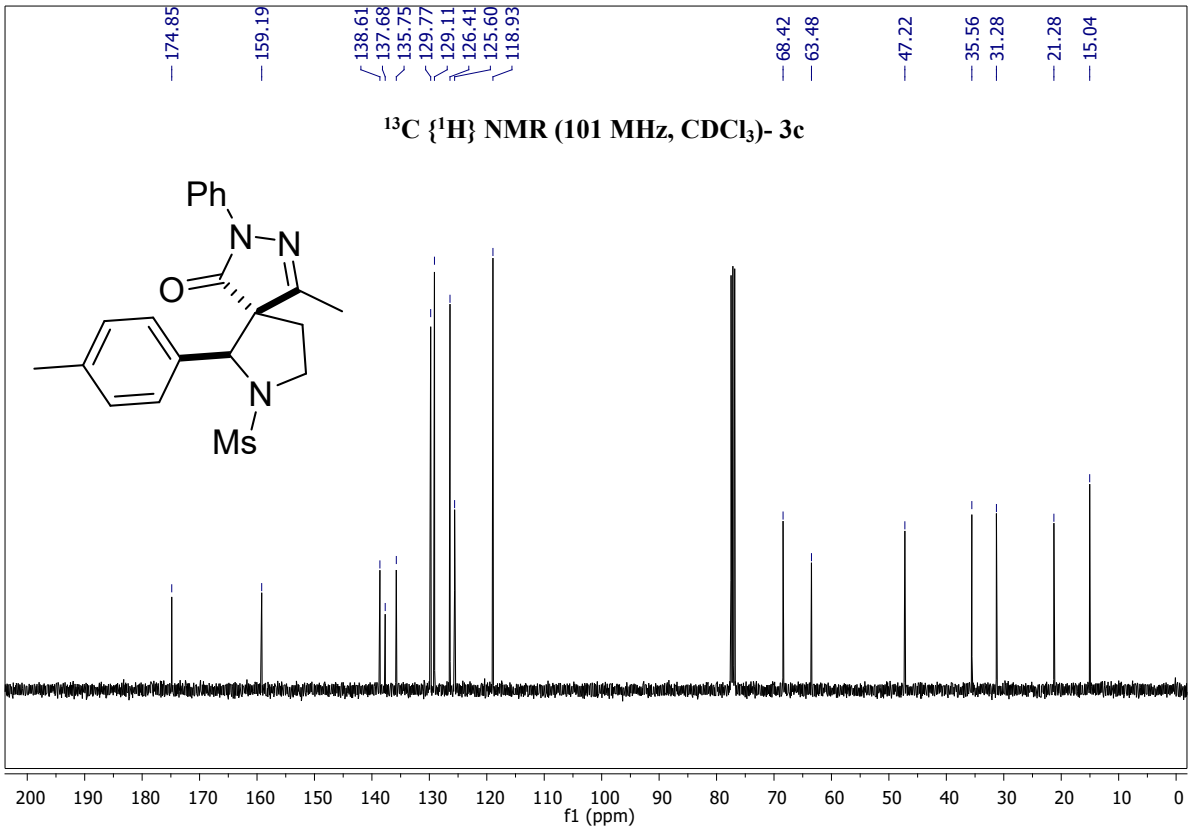
^{1}H NMR (400 MHz, $CDCl_3$) – 3b



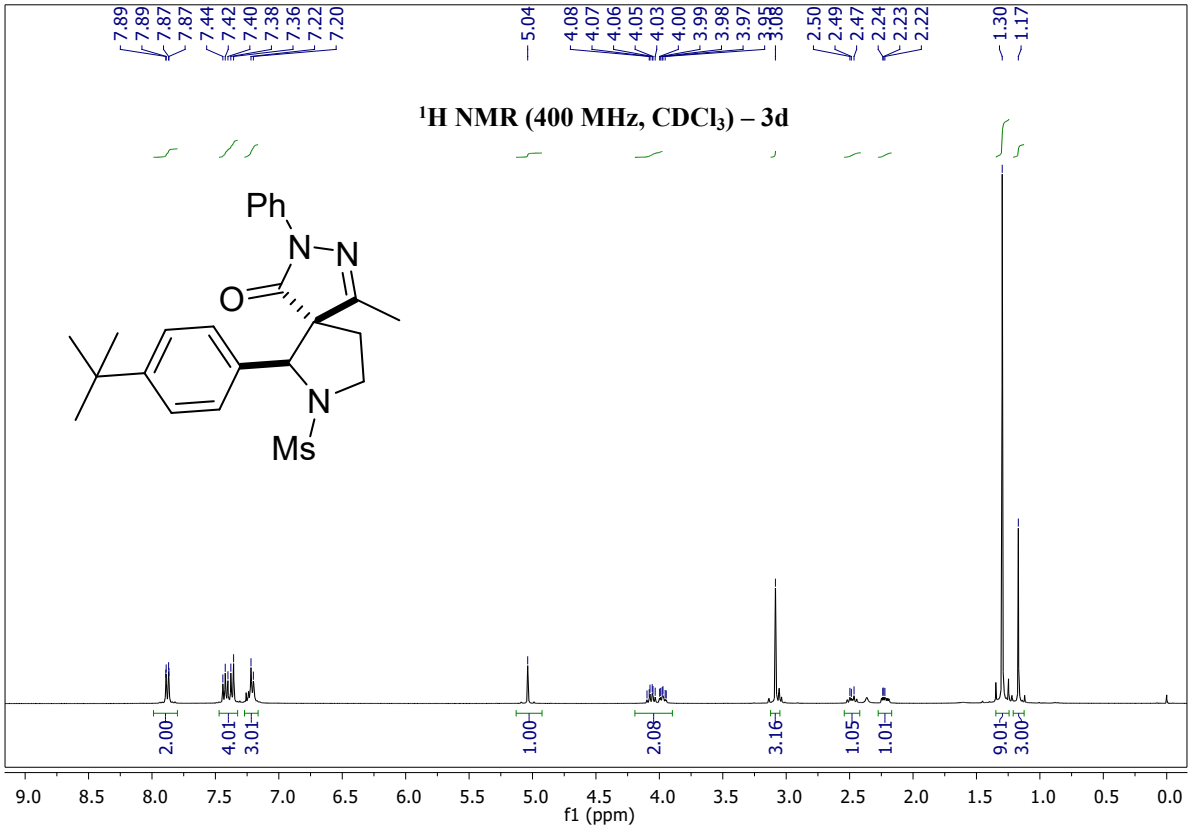
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3b



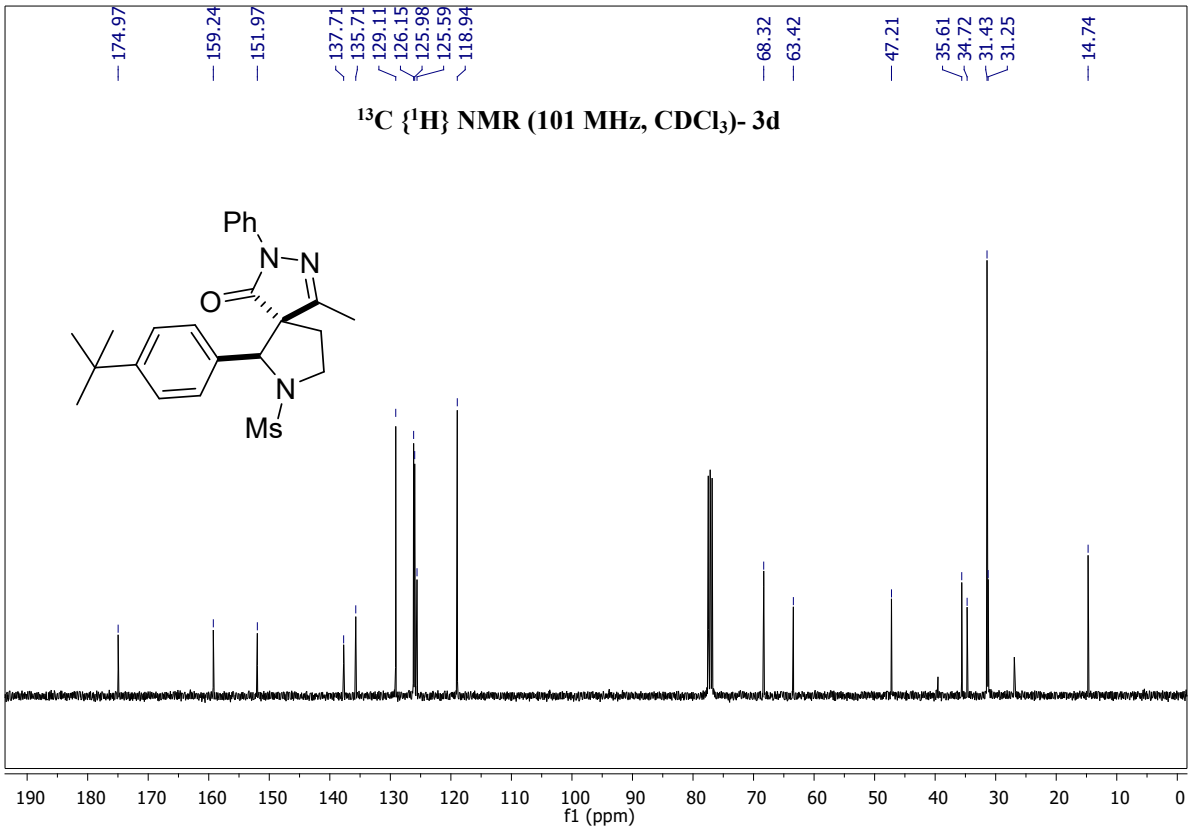
^{1}H NMR (400 MHz, $CDCl_3$) – 3c



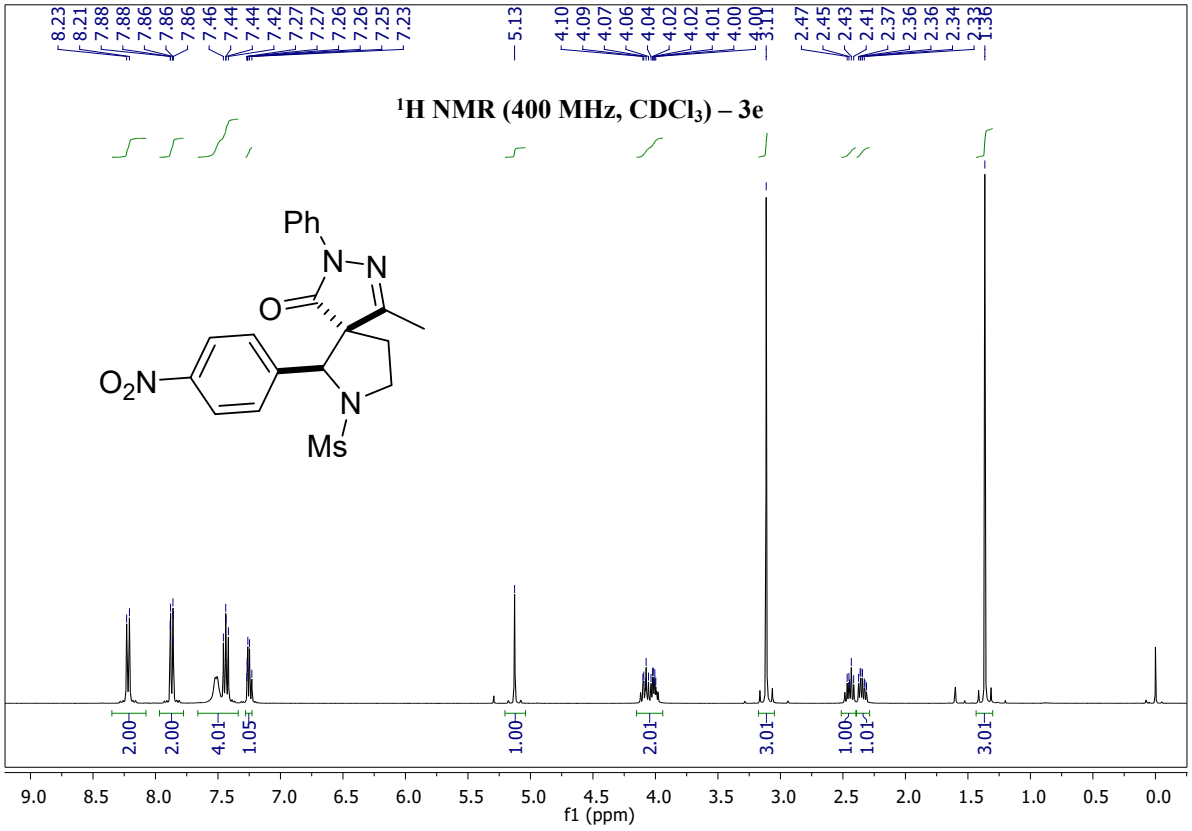
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3c



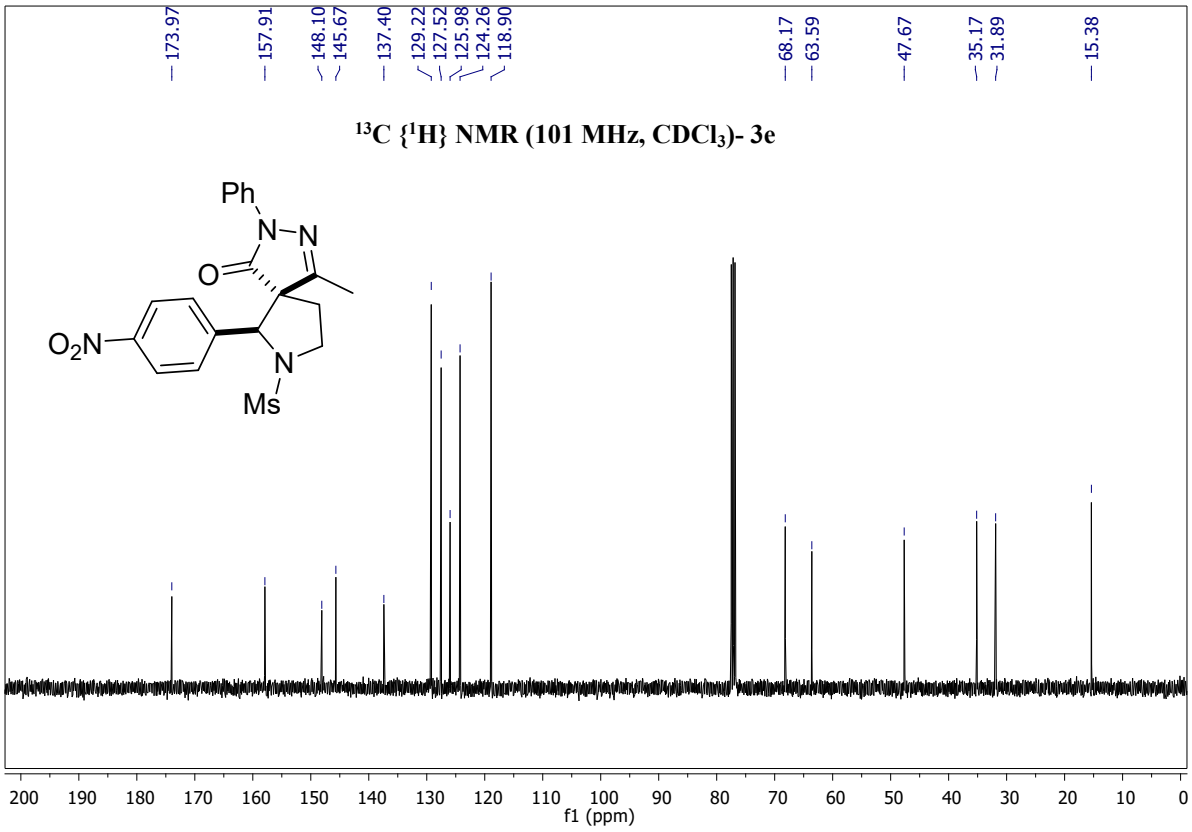
^{1}H NMR (400 MHz, $CDCl_3$) – 3d



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



^{1}H NMR (400 MHz, $CDCl_3$) – 3e



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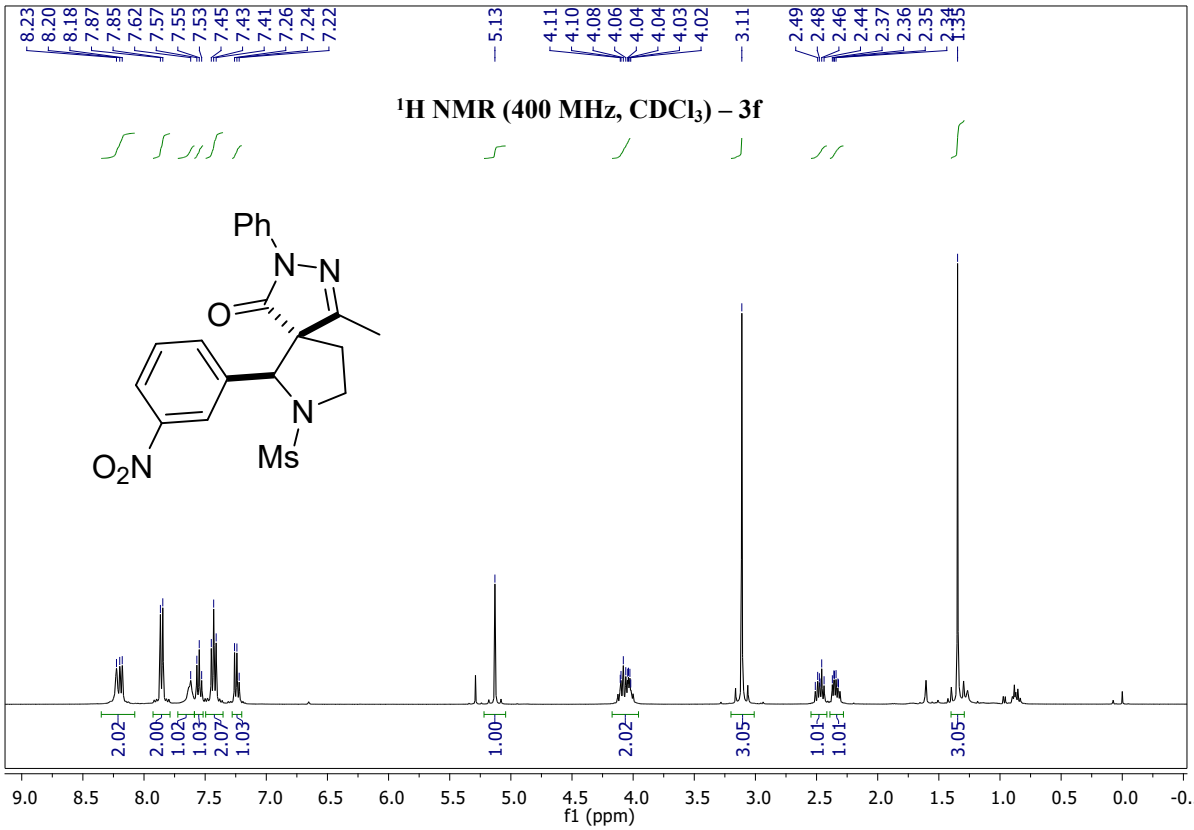
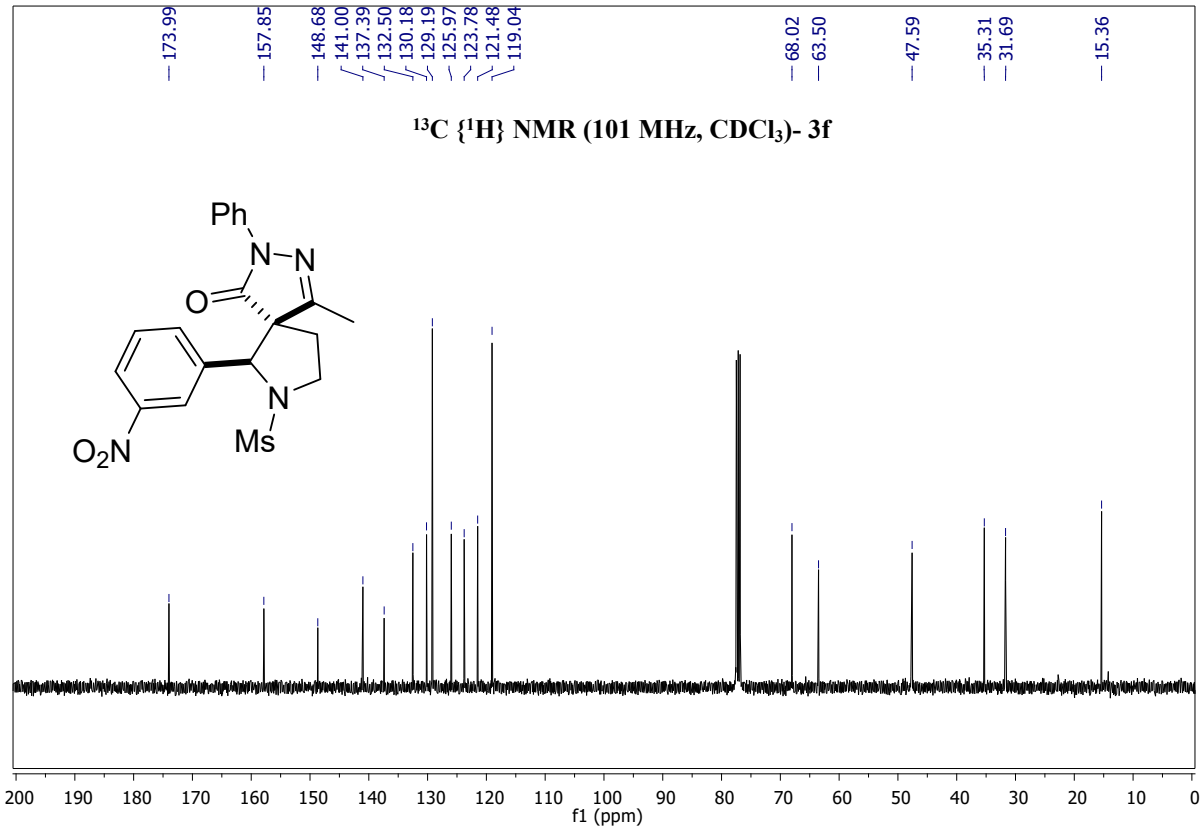
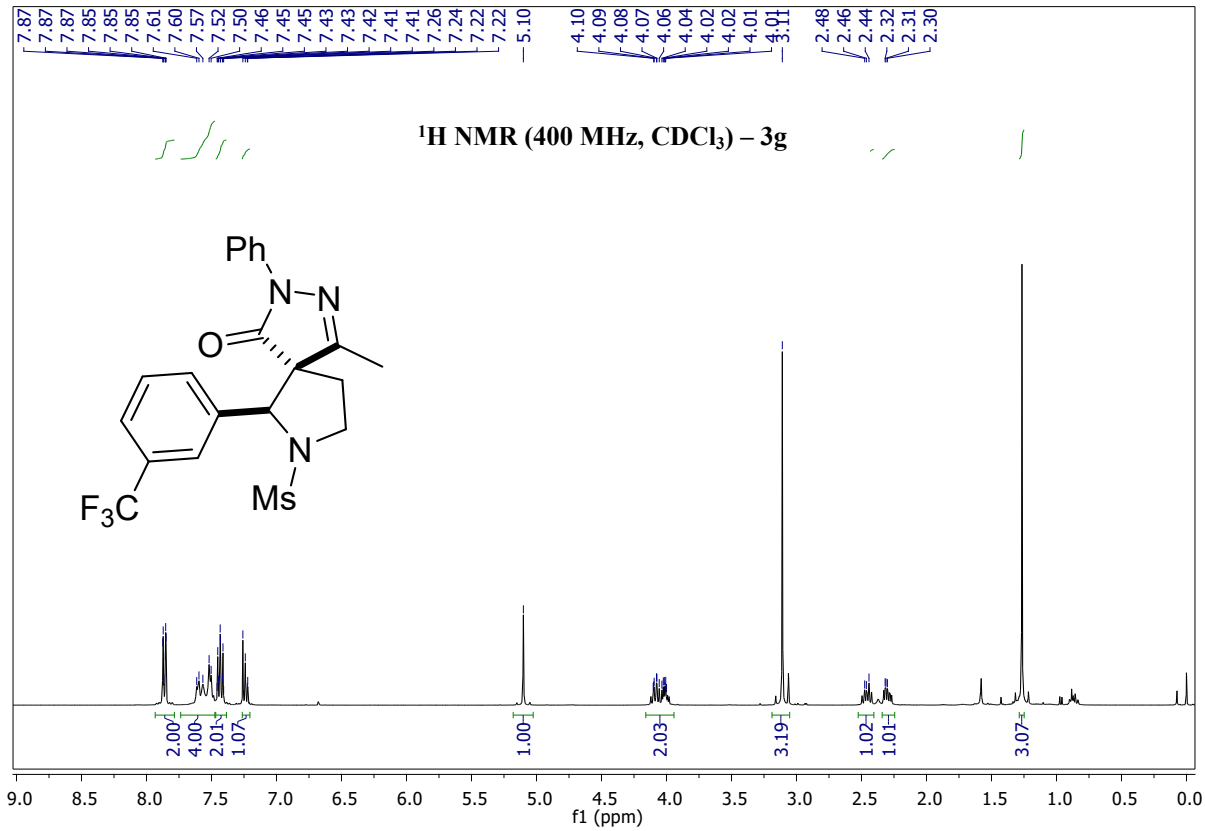


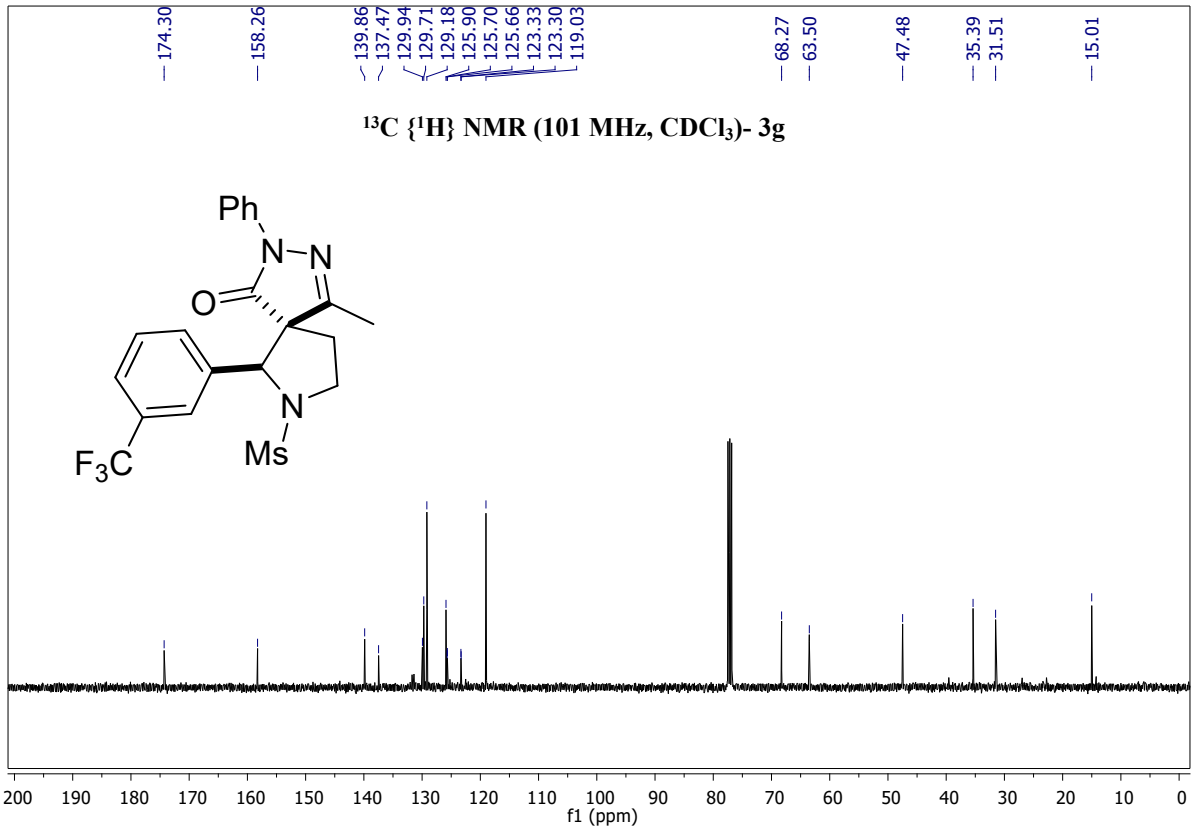
^{1}H NMR (400 MHz, $CDCl_3$) – 3f



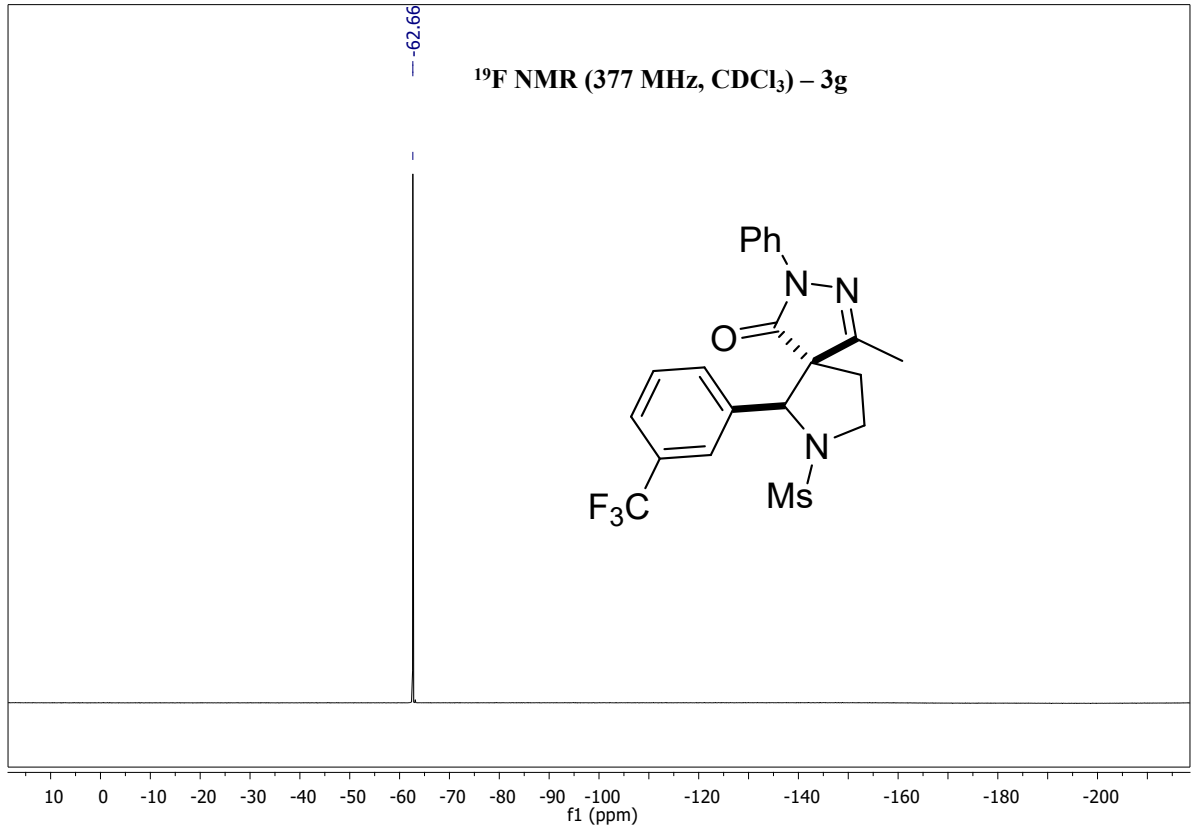
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3f



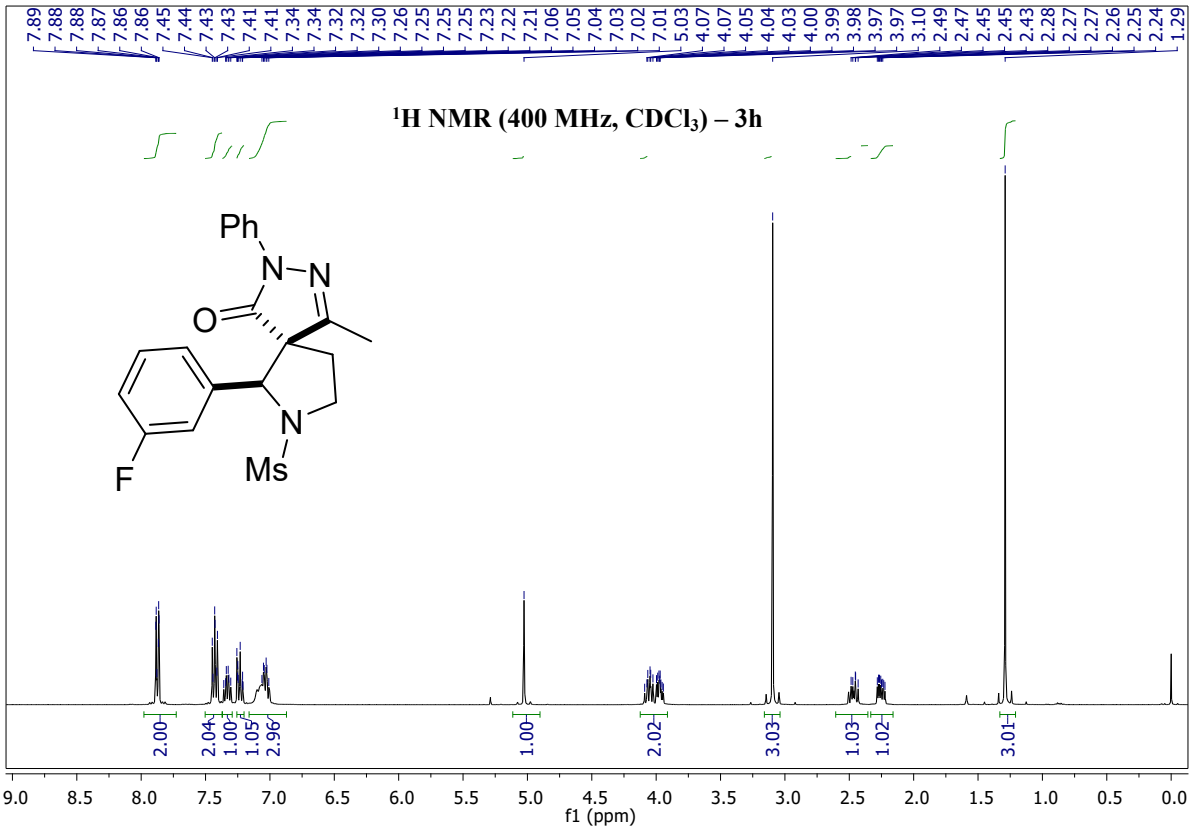
^{1}H NMR (400 MHz, $CDCl_3$) – 3g



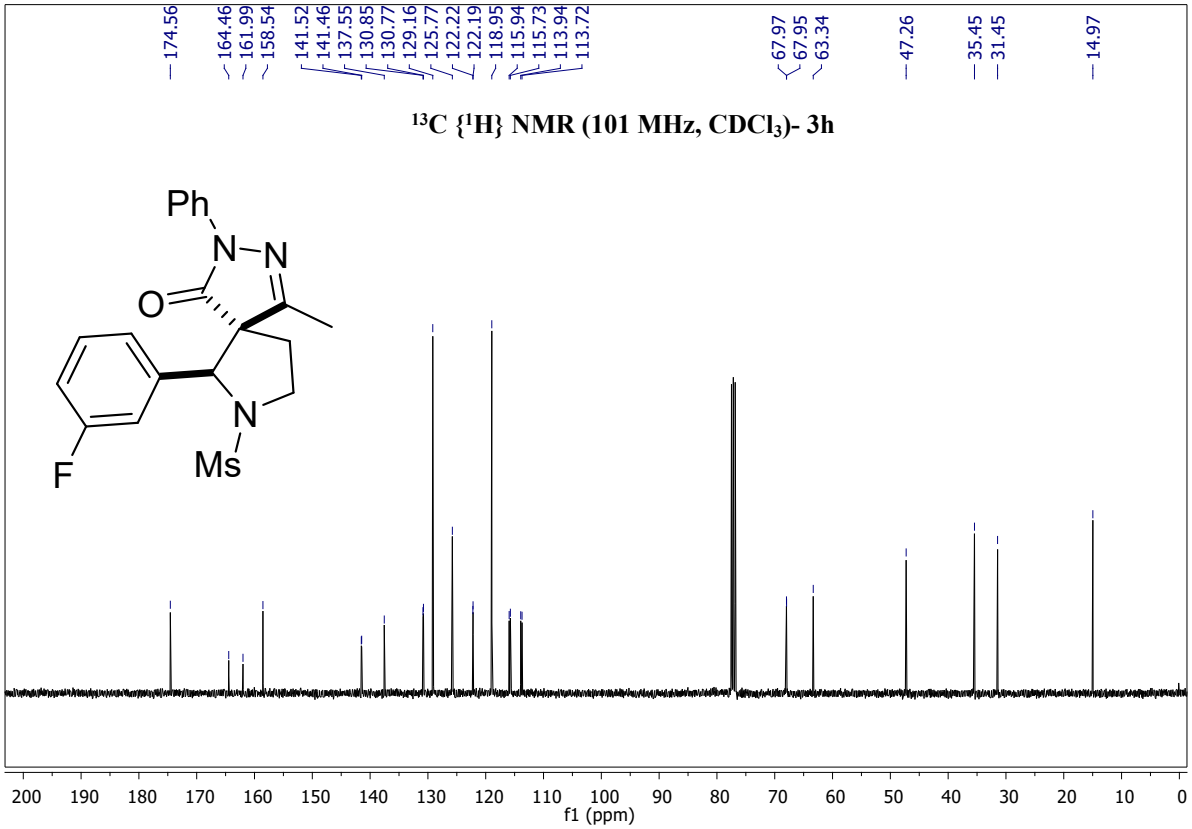
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 3g



^{19}F NMR (377 MHz, $CDCl_3$) – 3g



^{1}H NMR (400 MHz, $CDCl_3$) – 3h



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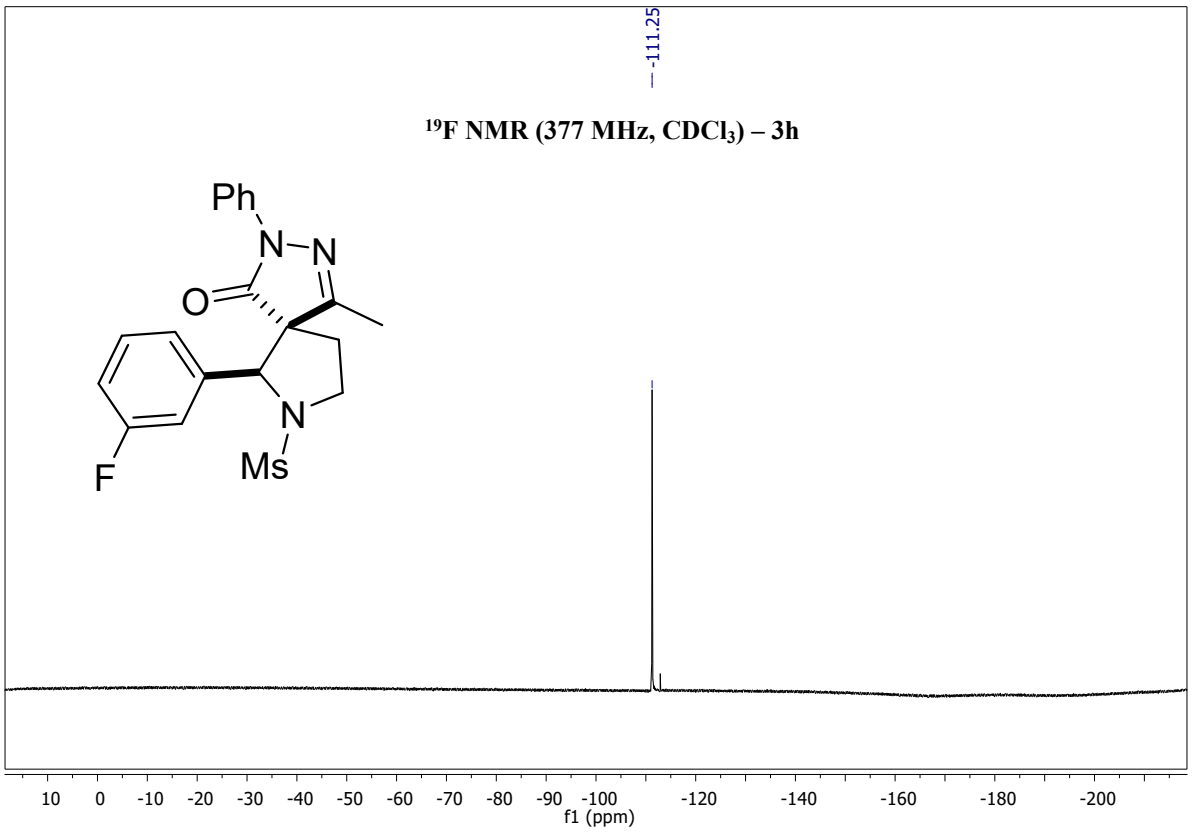
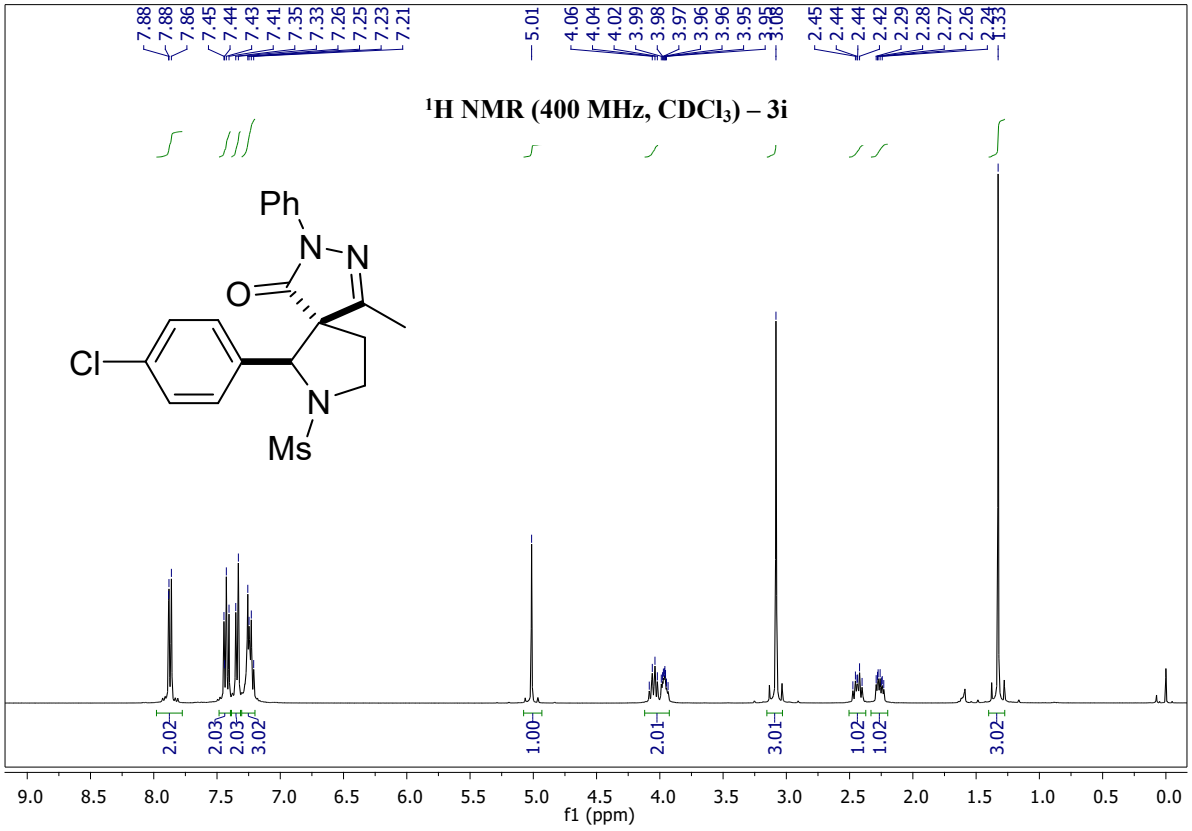
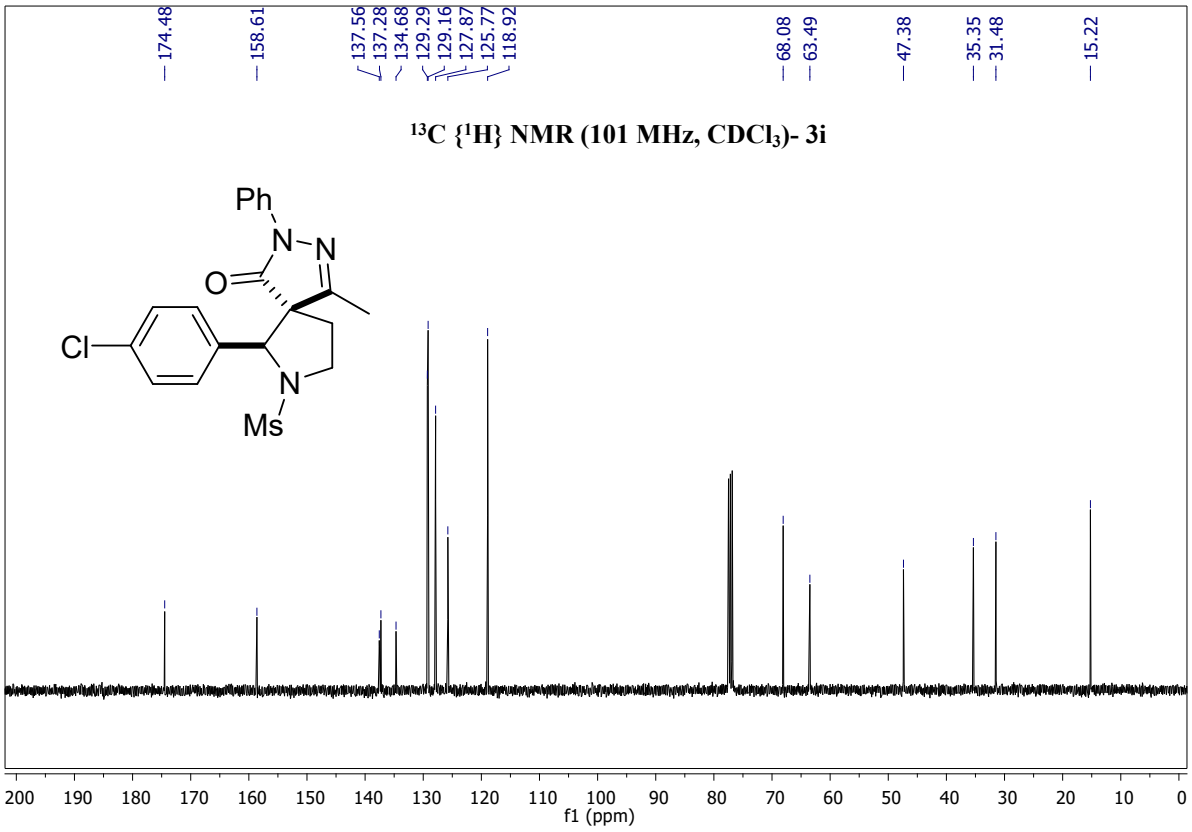


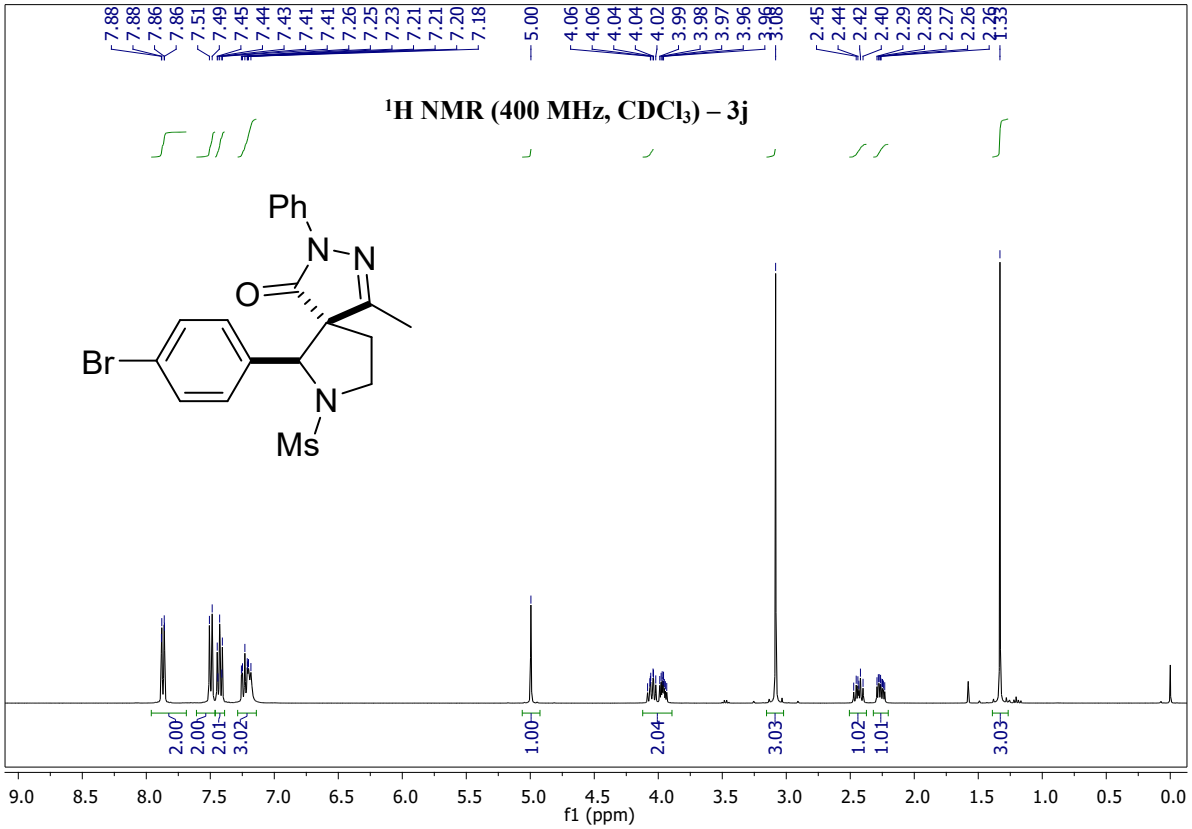
^{19}F NMR (377 MHz, $CDCl_3$) – 3h



^{1}H NMR (400 MHz, $CDCl_3$) – 3i



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



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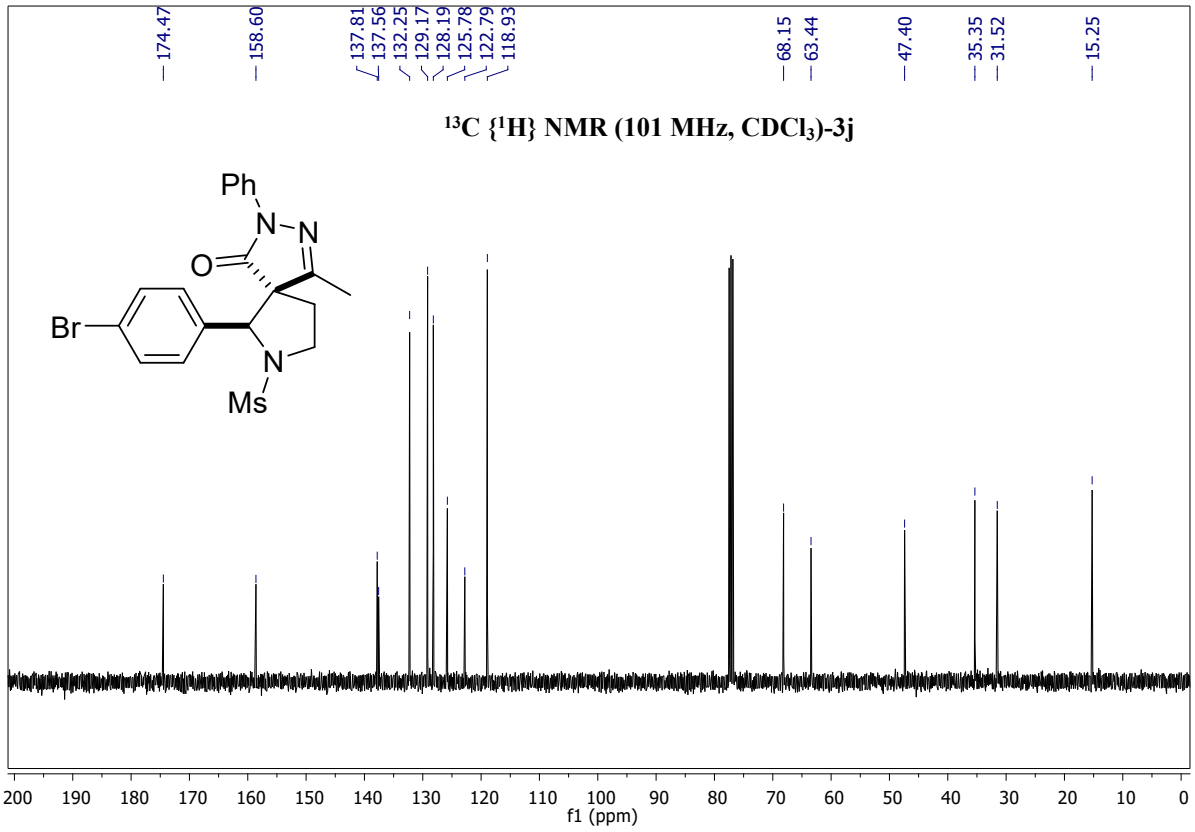

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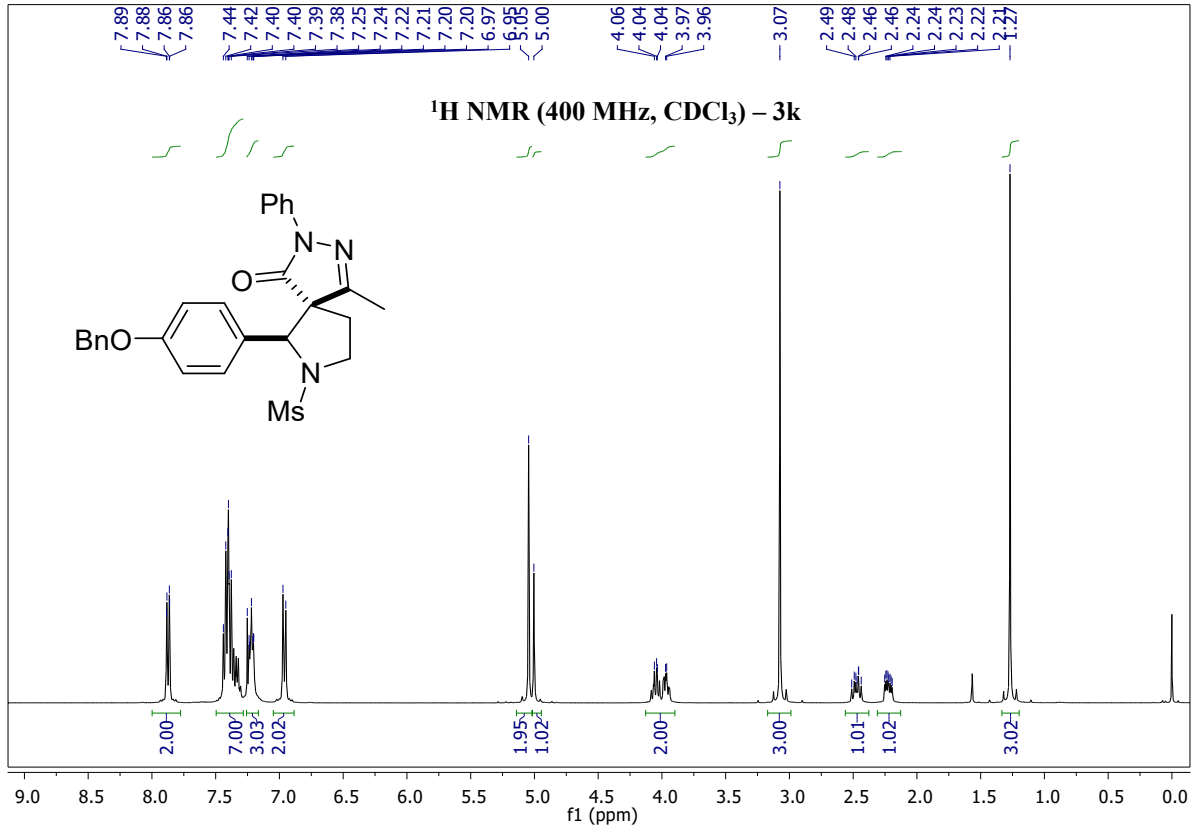

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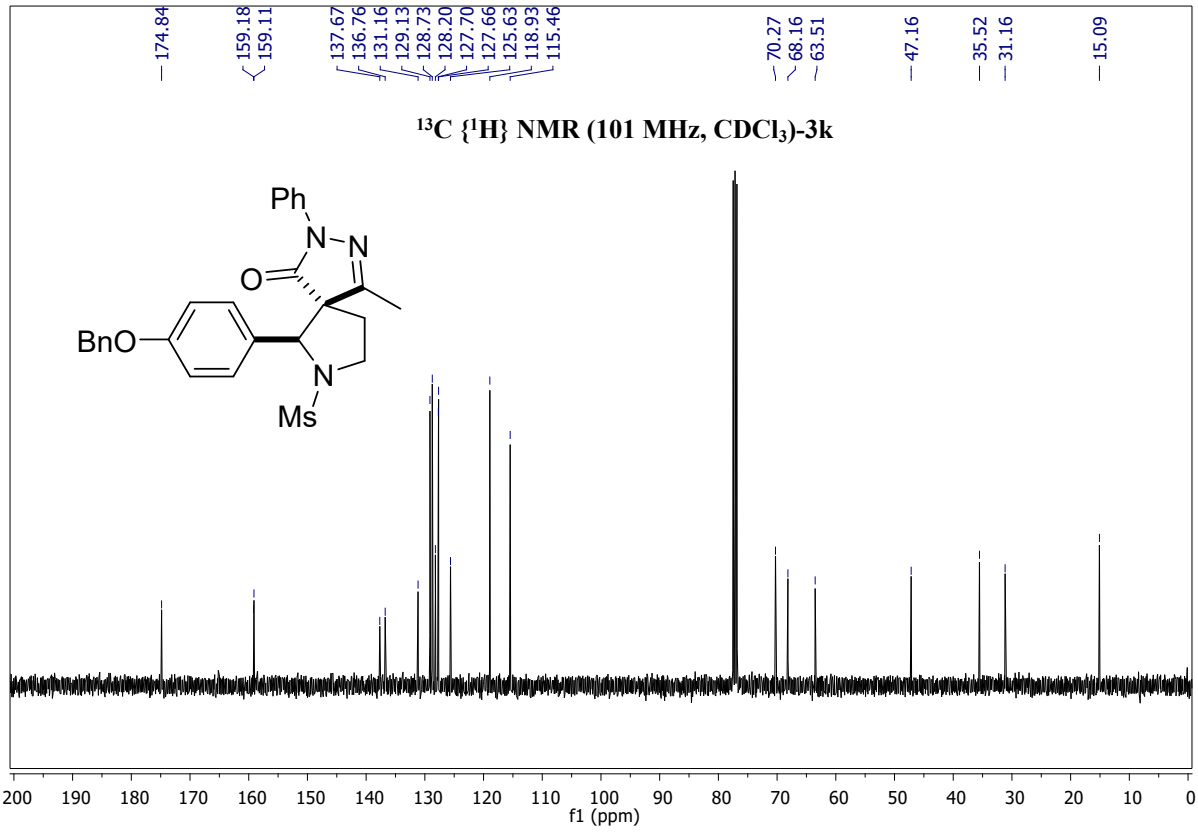

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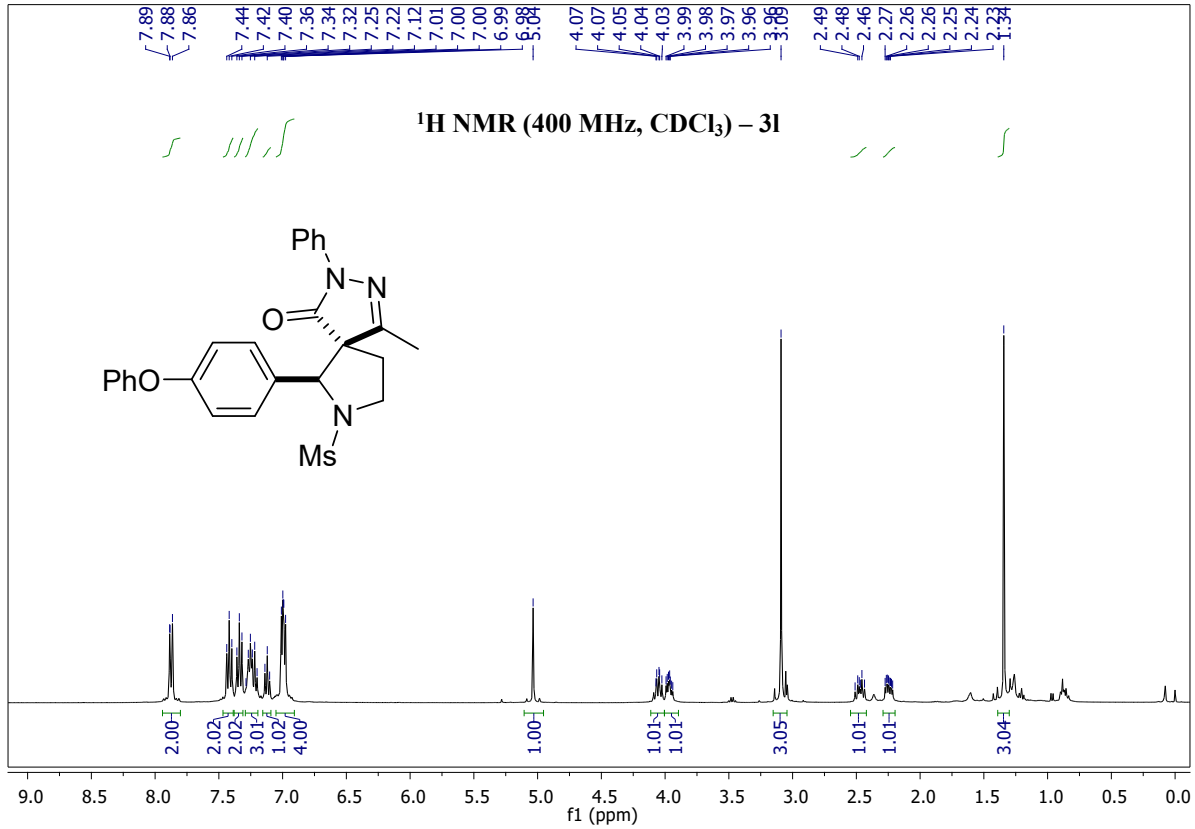
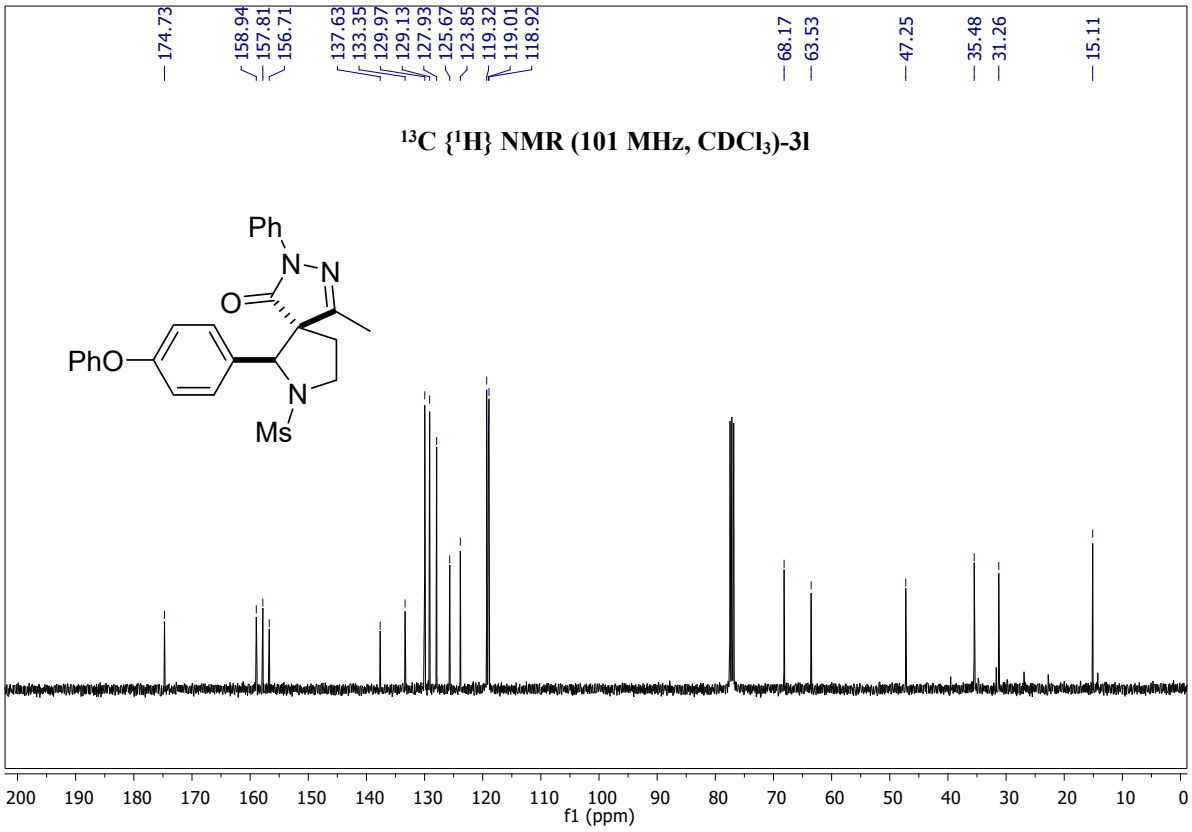


^{1}H NMR (400 MHz, $CDCl_3$) – 3l



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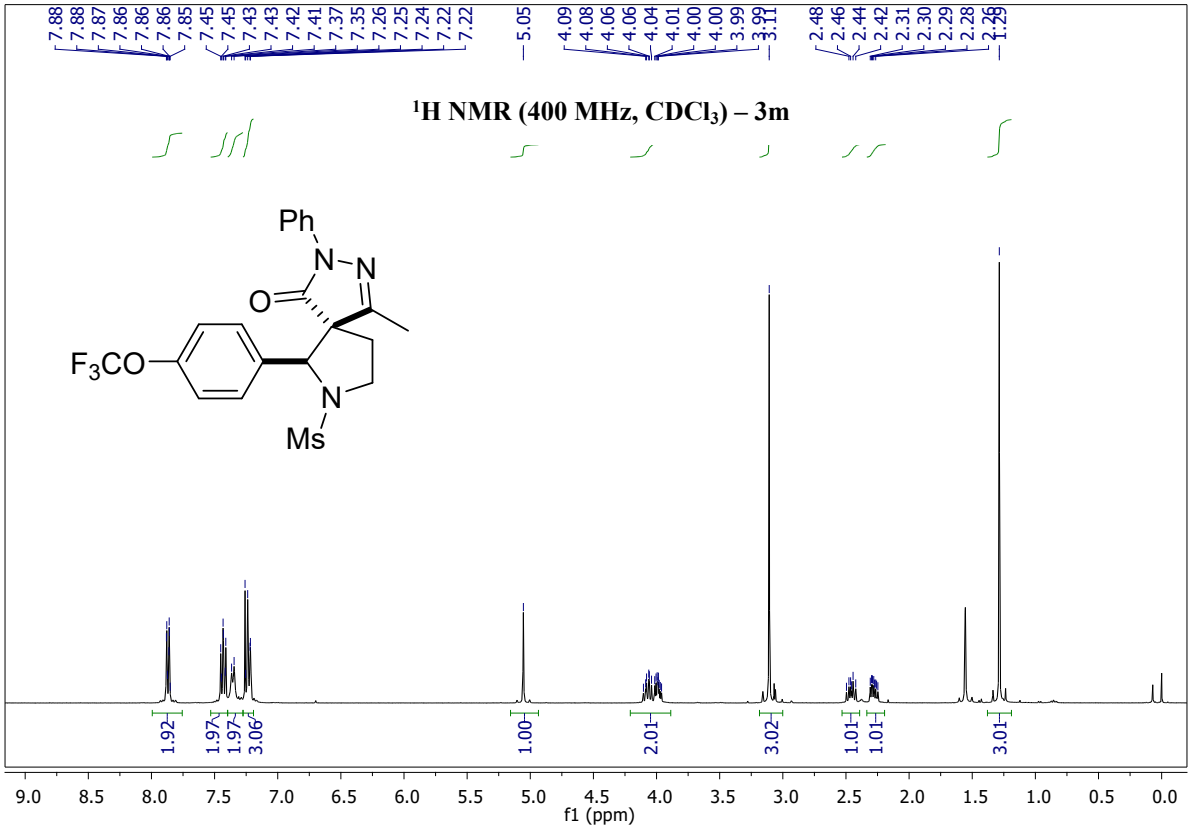
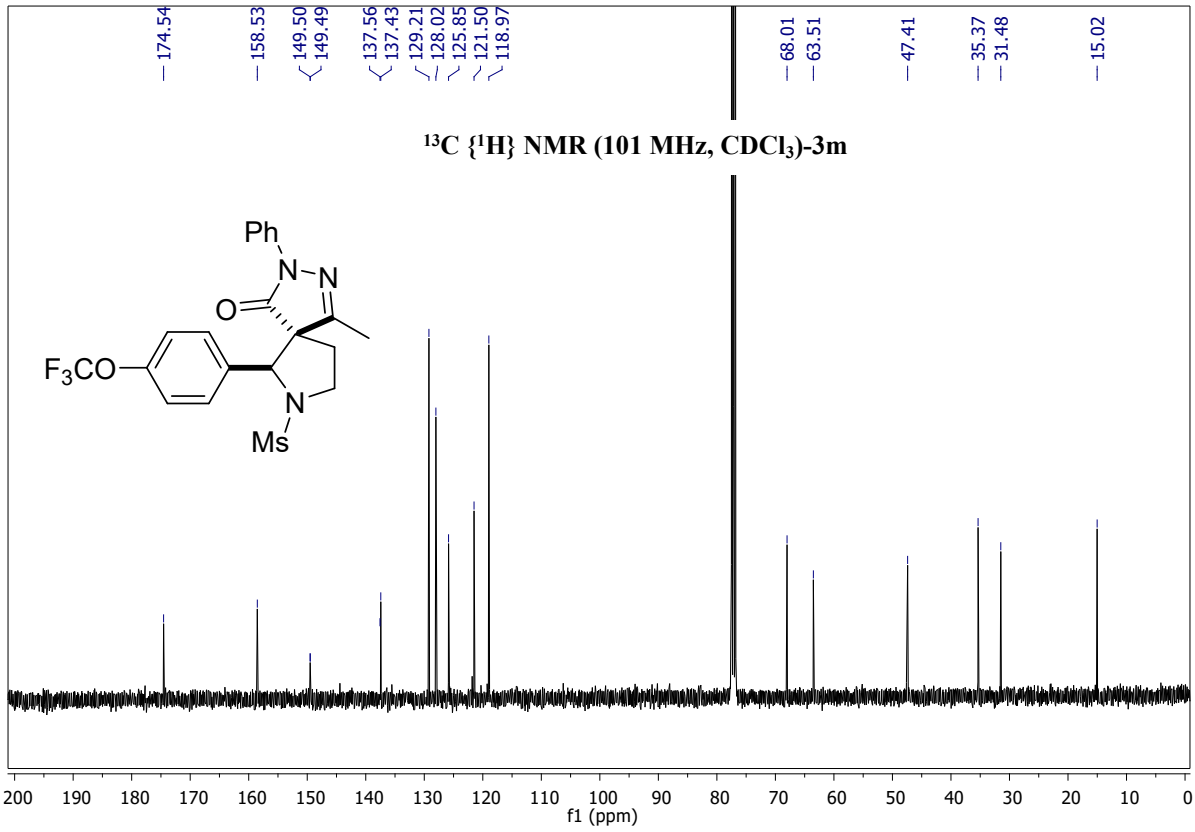
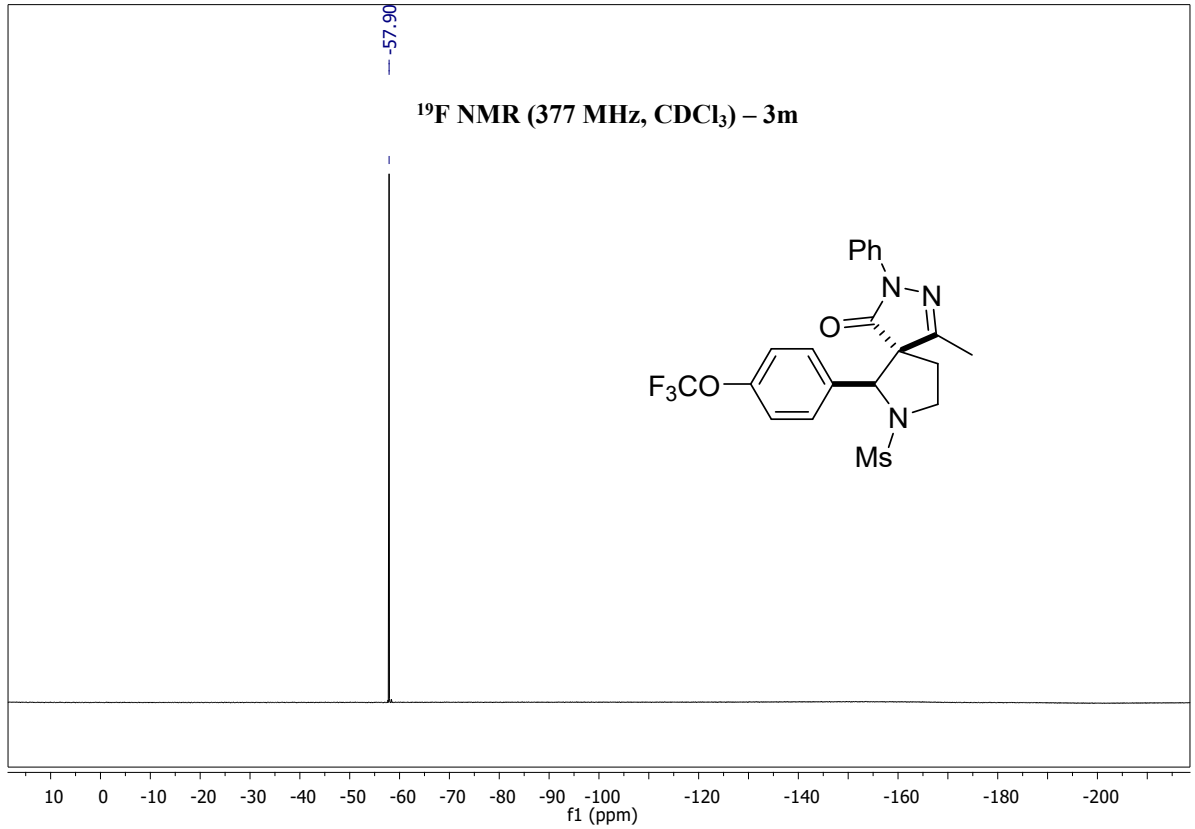


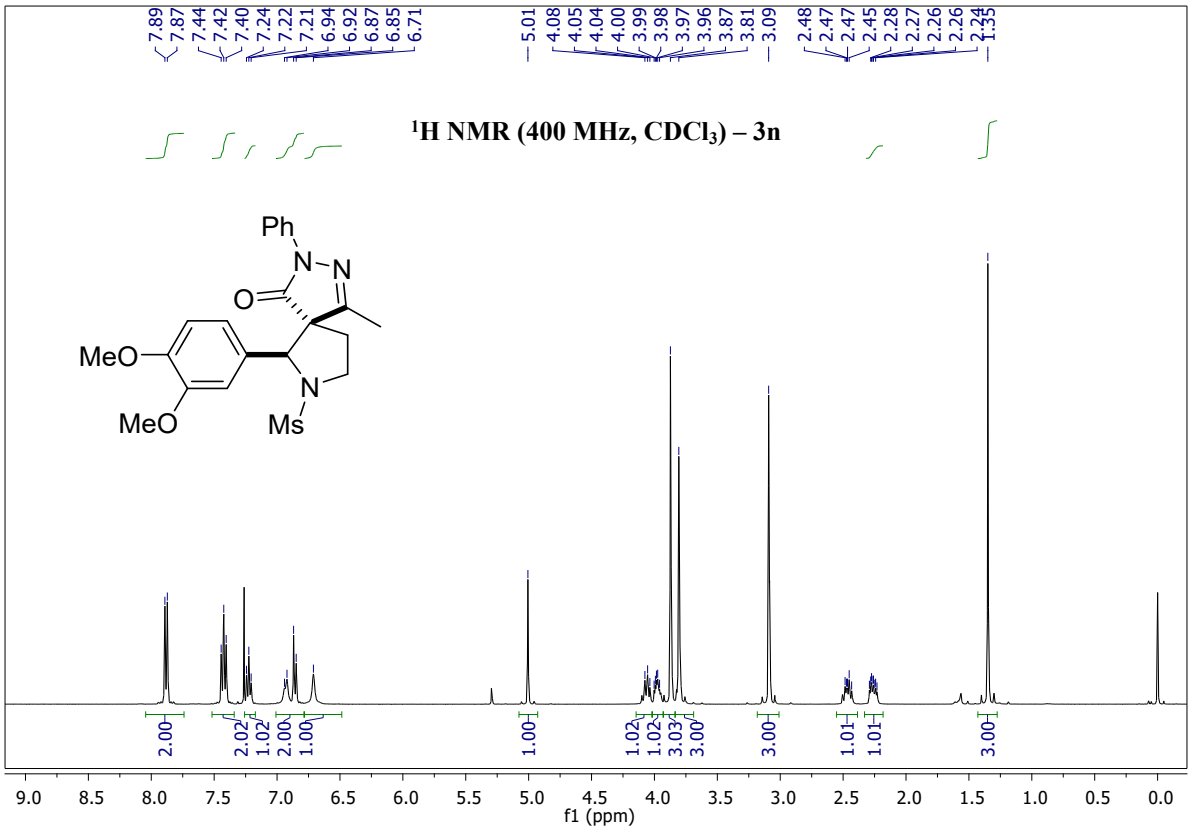
^{1}H NMR (400 MHz, $CDCl_3$) – 3m



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



^{19}F NMR (377 MHz, $CDCl_3$) – 3m



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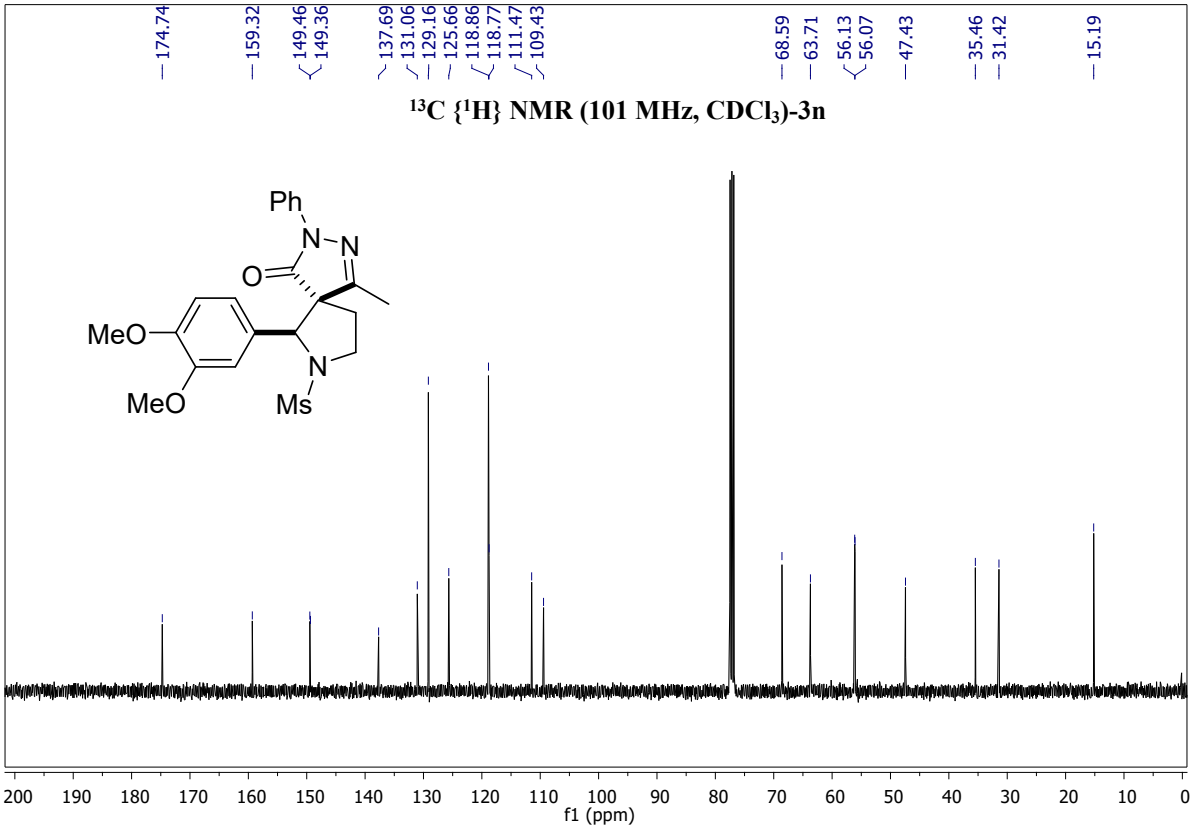

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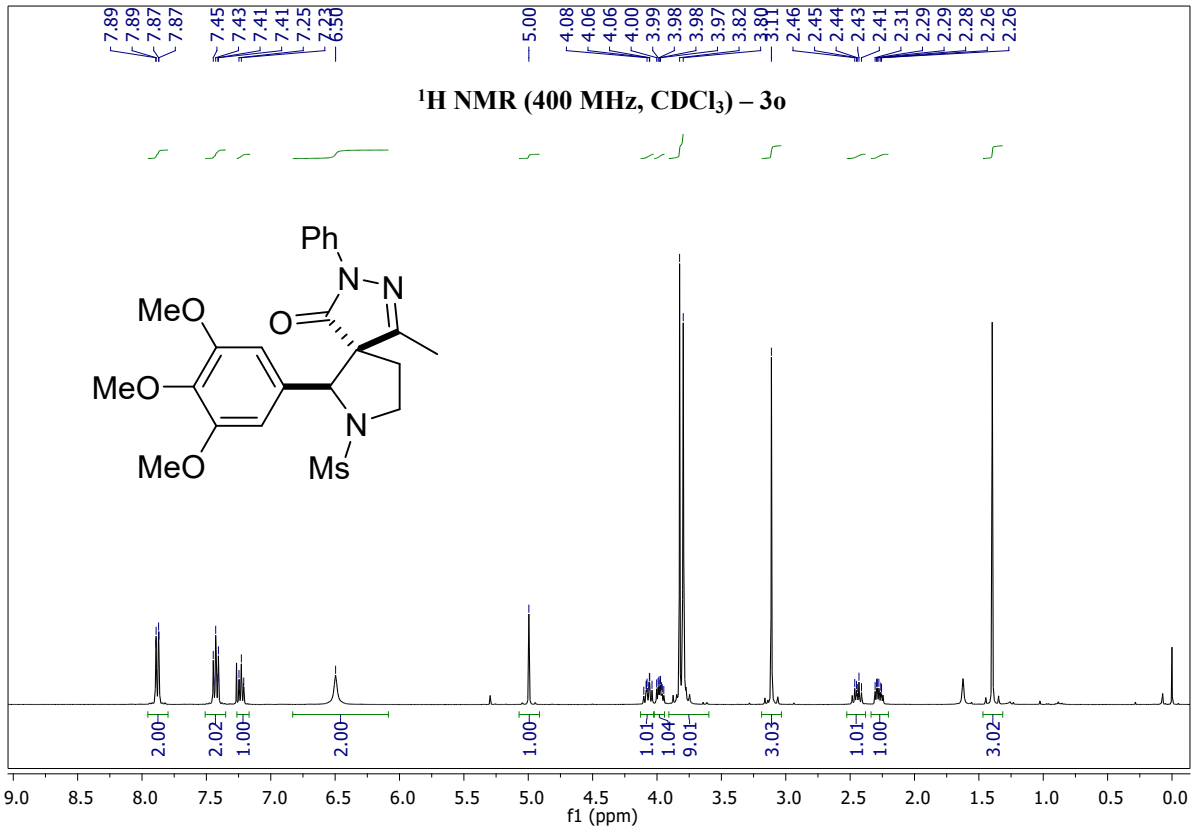

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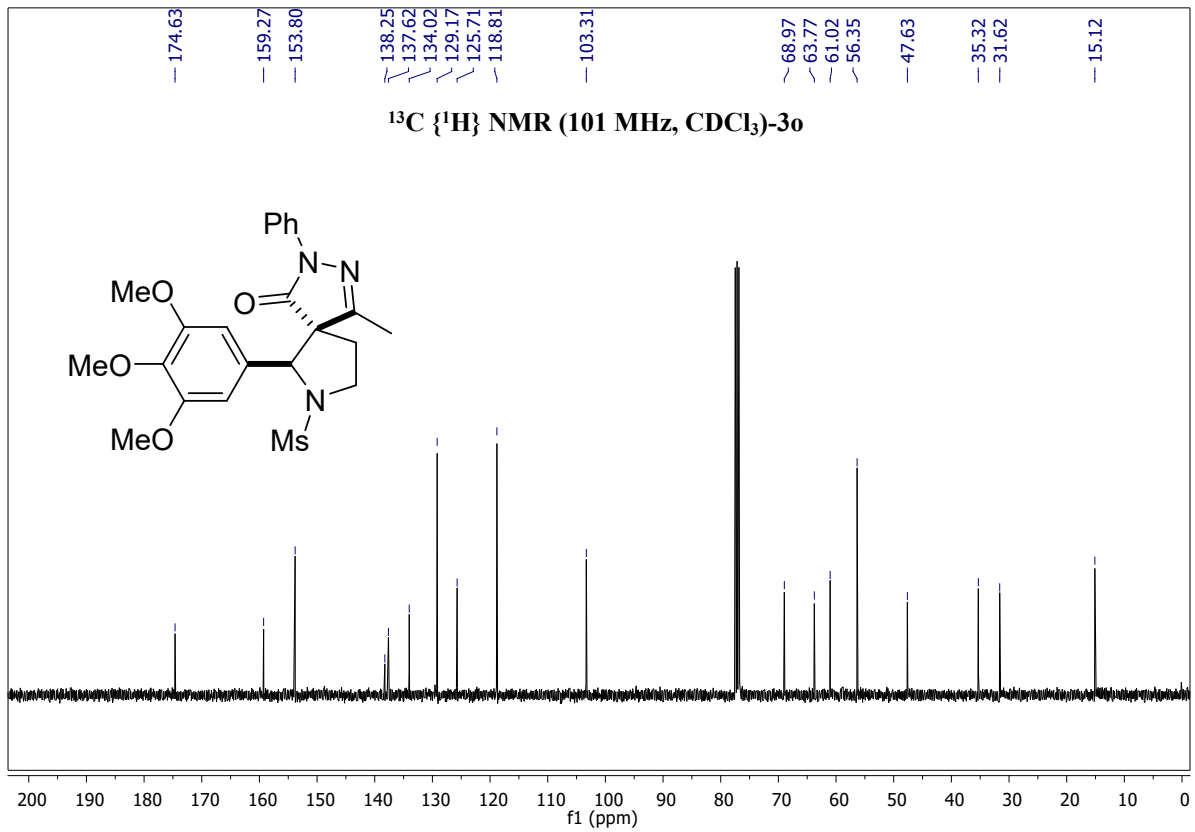
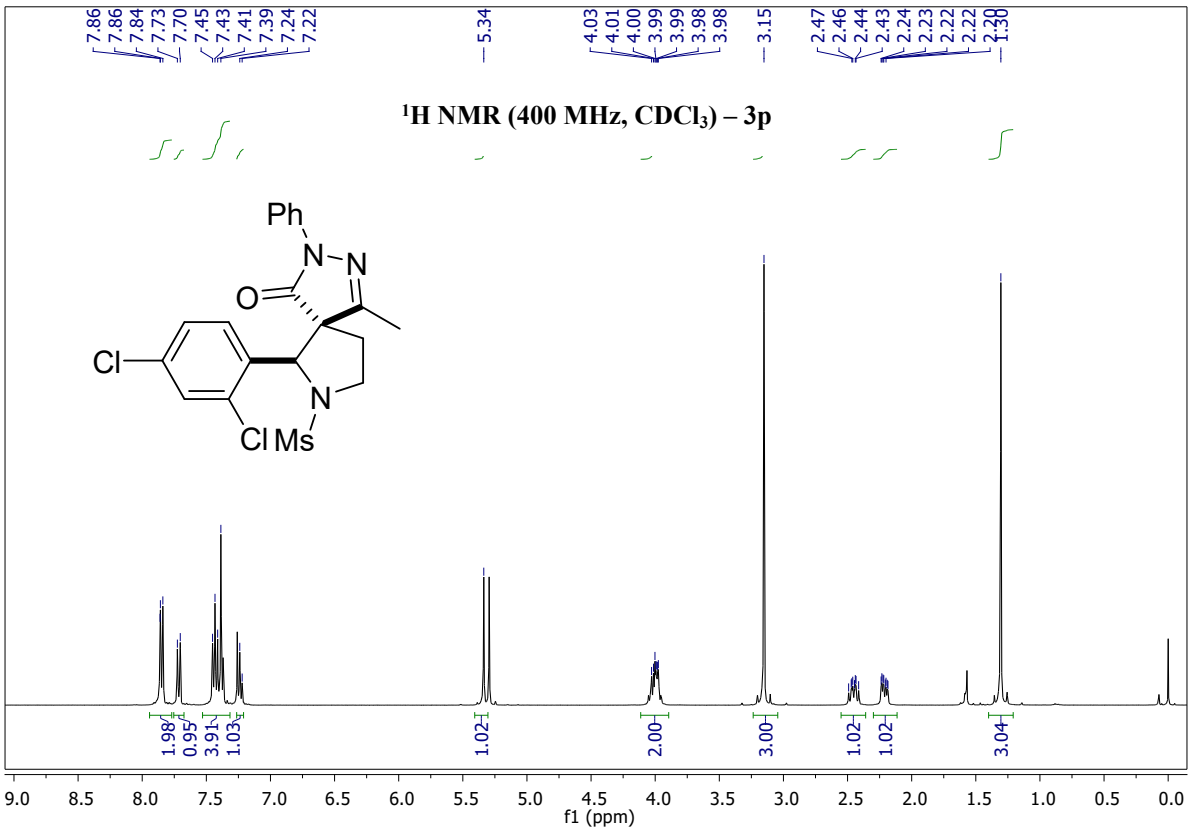
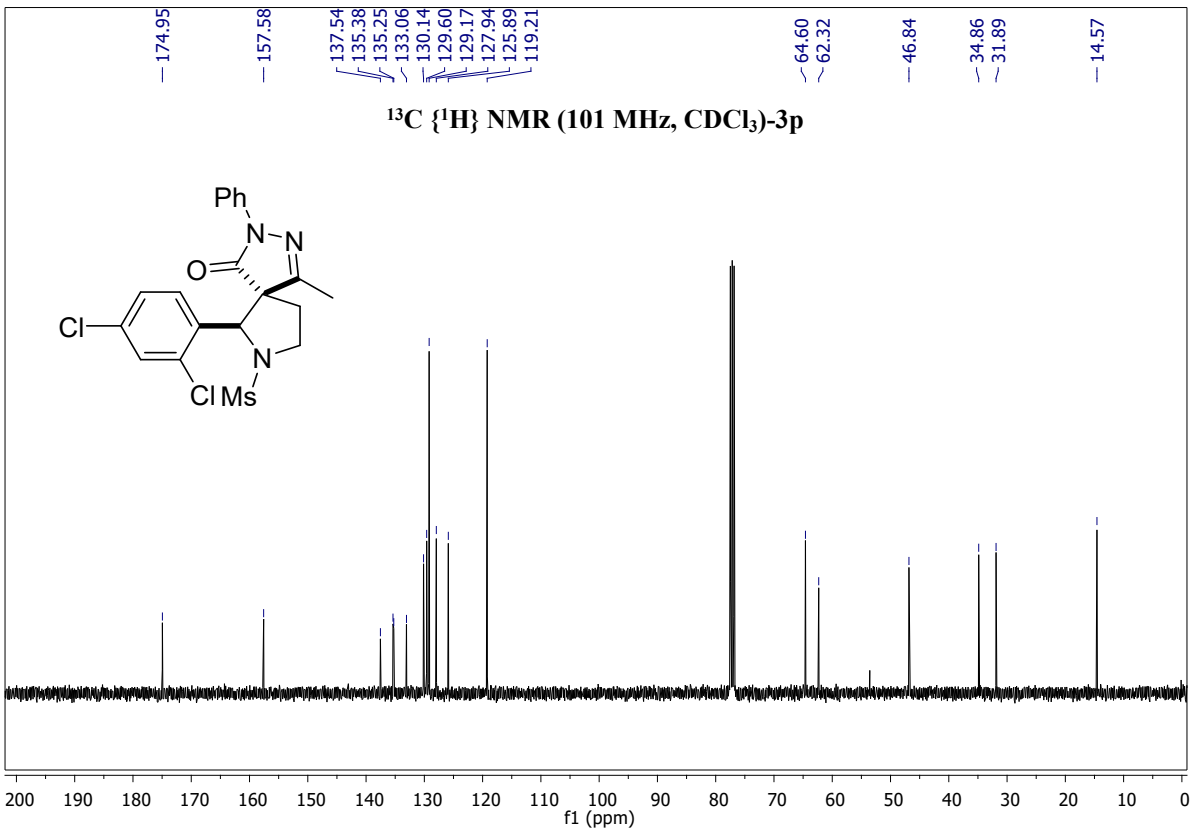


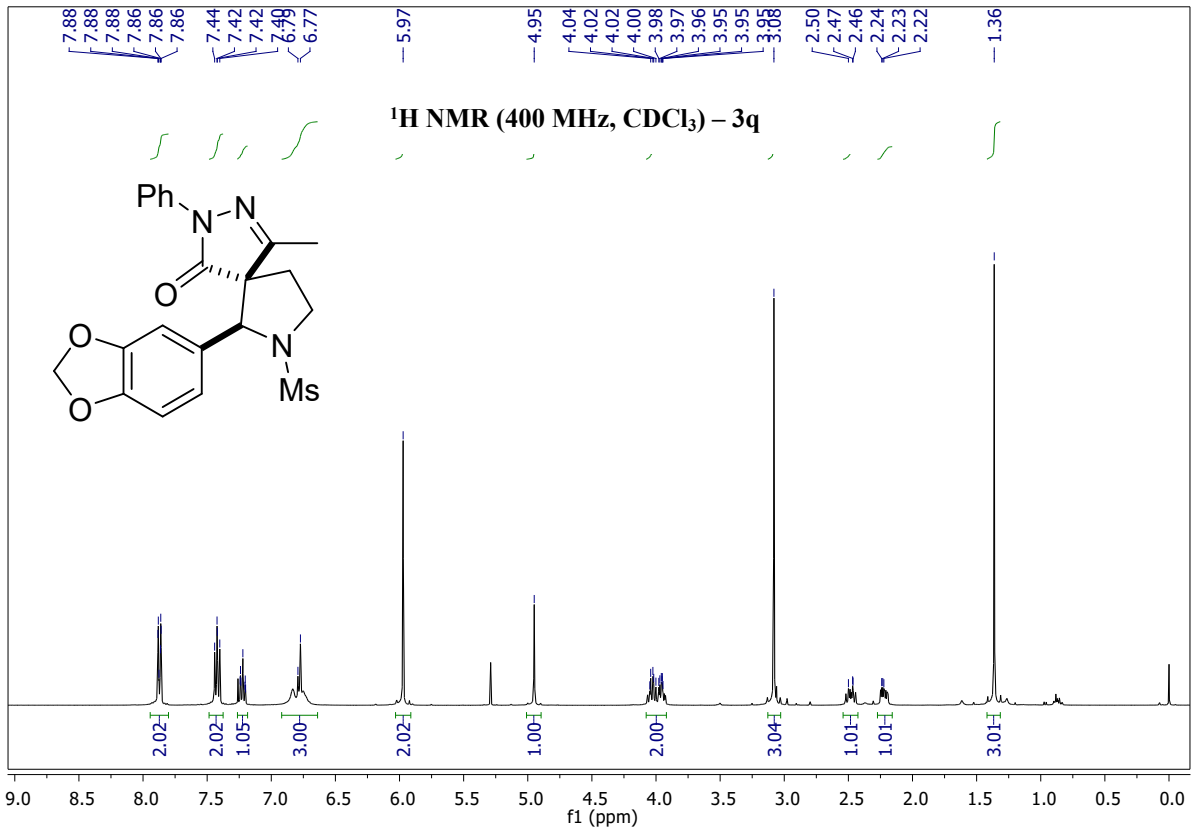
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3o



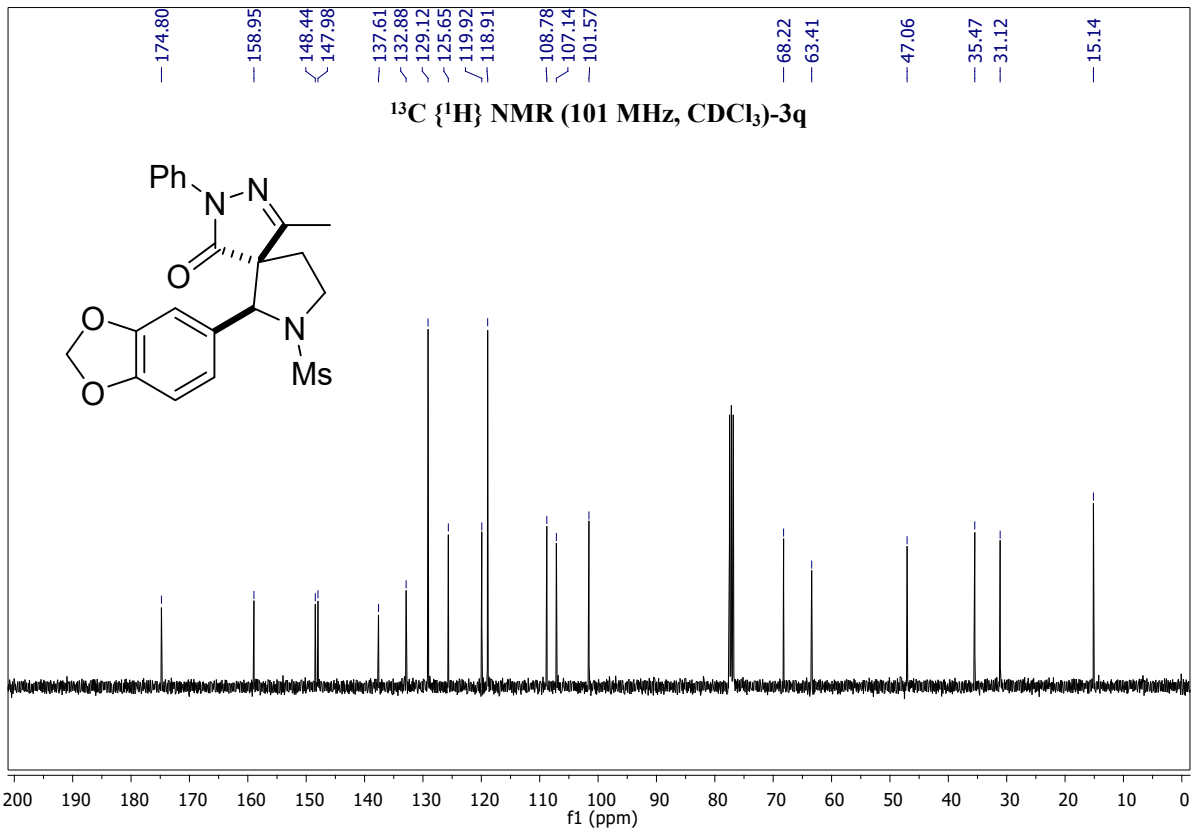
^{1}H NMR (400 MHz, $CDCl_3$) – 3p



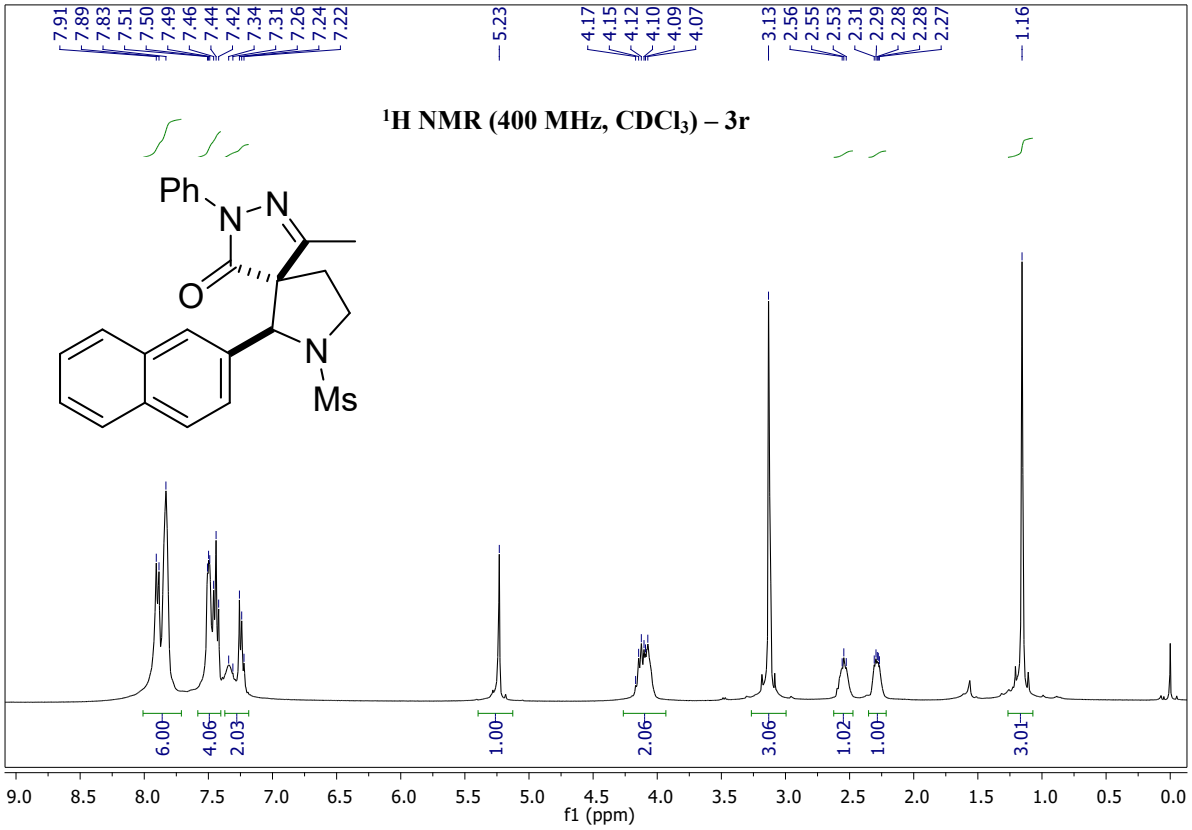
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3p



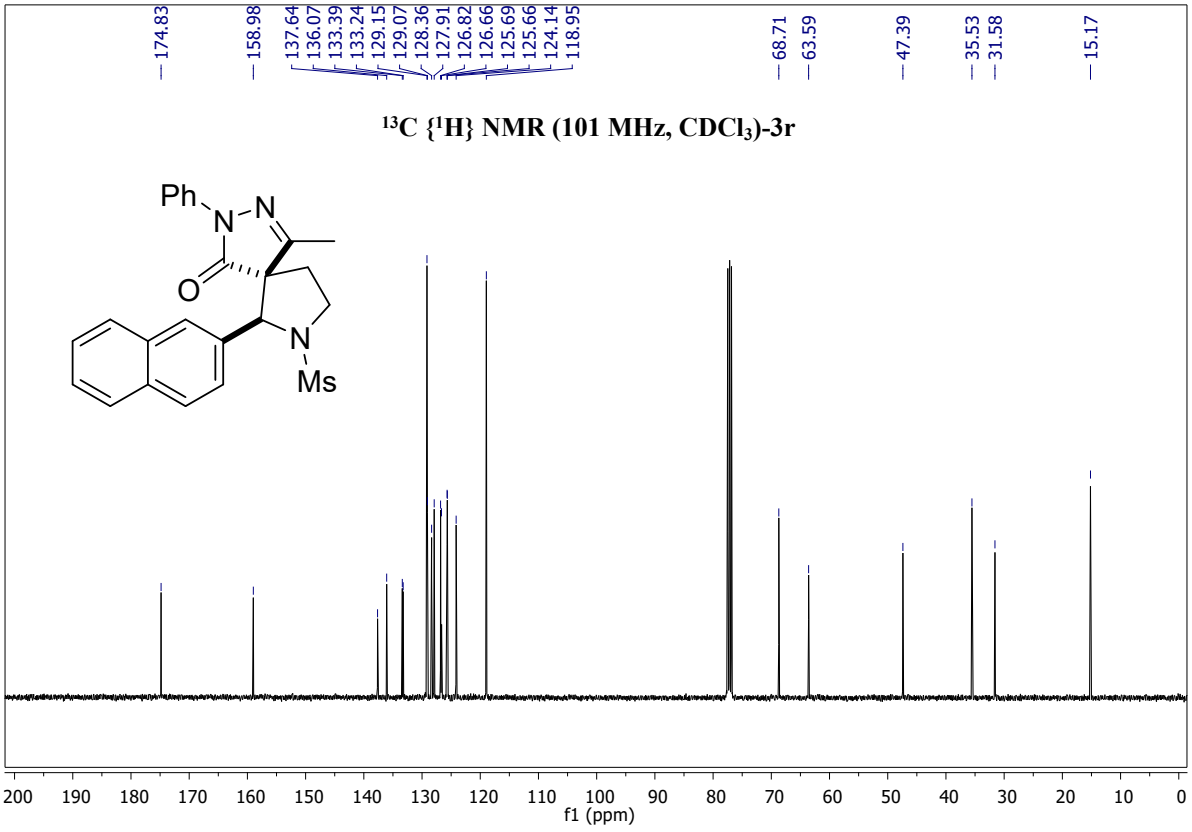
^{1}H NMR (400 MHz, $CDCl_3$) – 3q



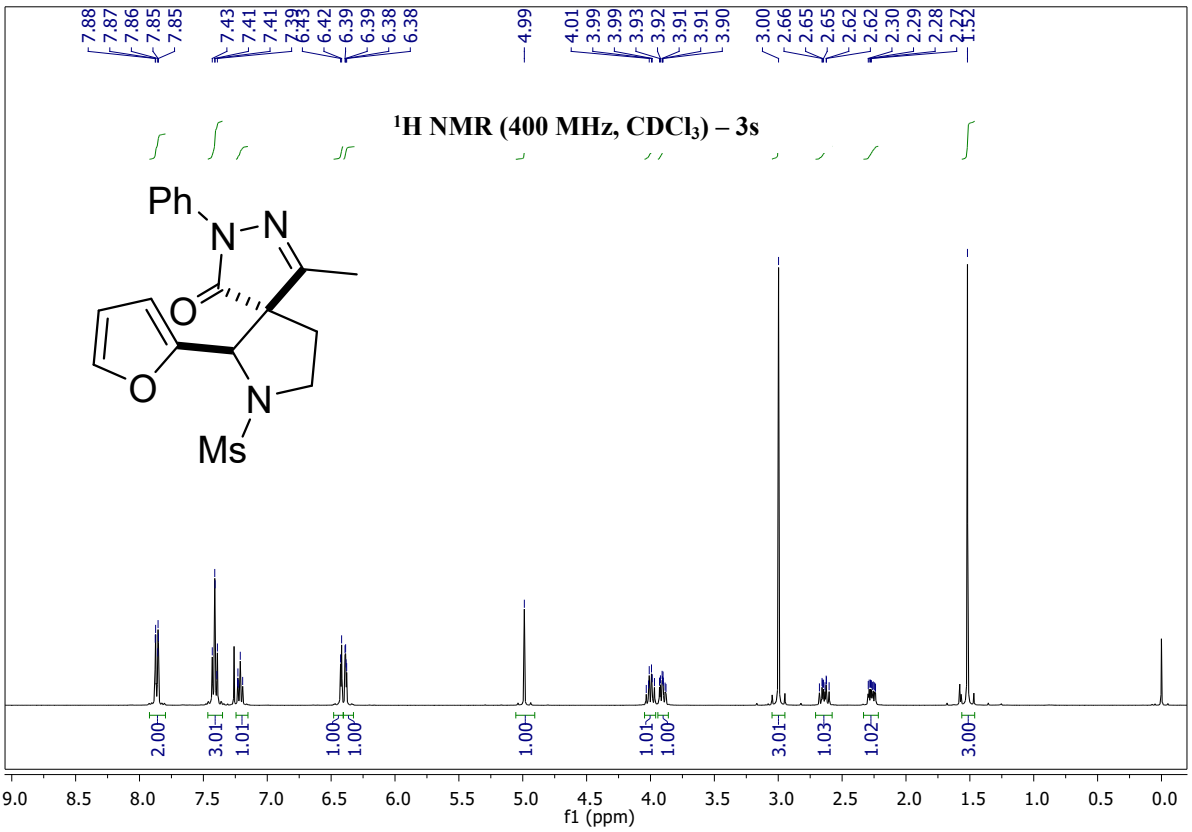
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3q



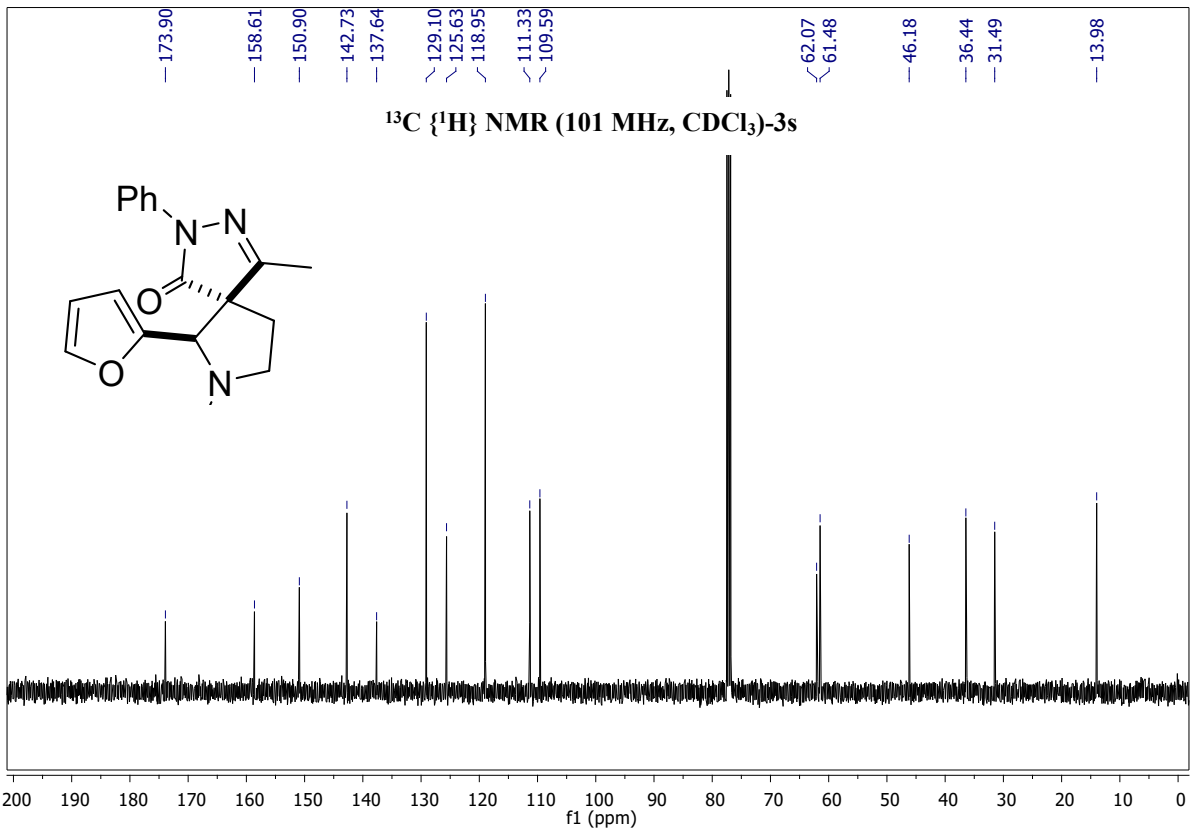
^{1}H NMR (400 MHz, $CDCl_3$) – 3r



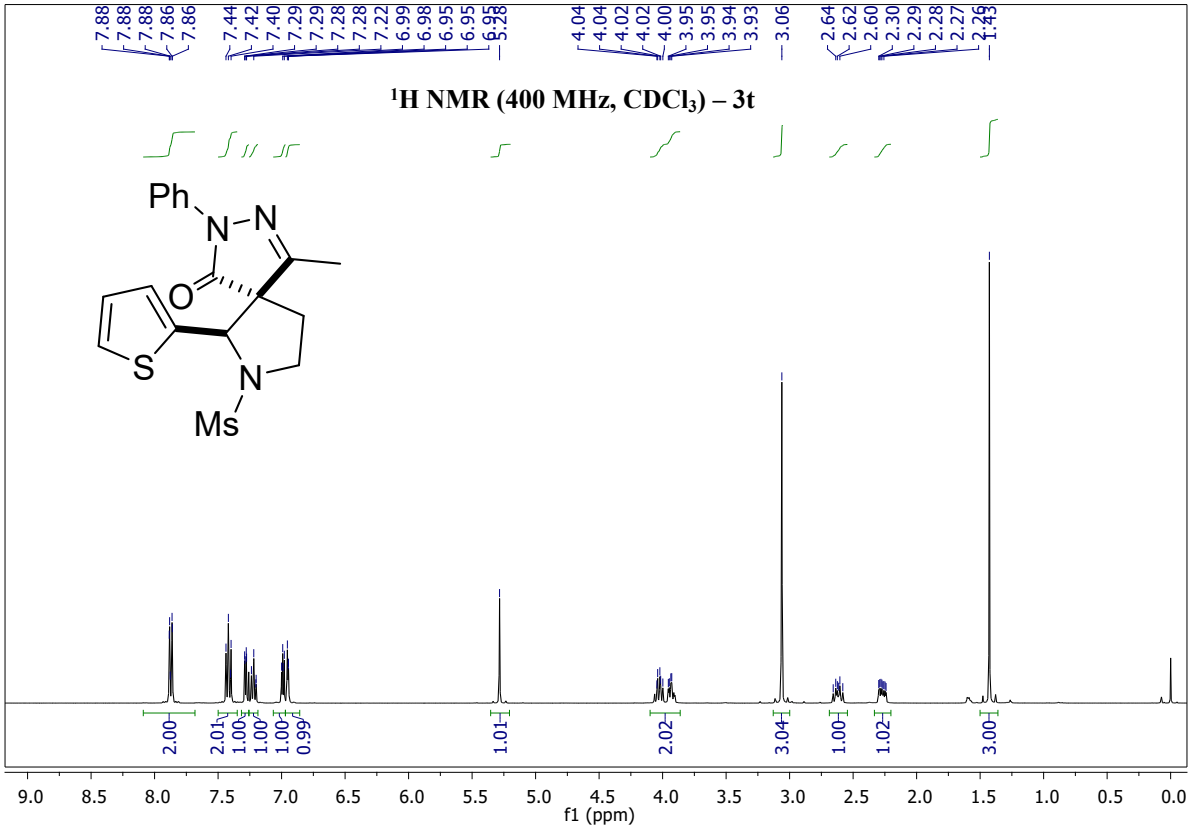
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3r



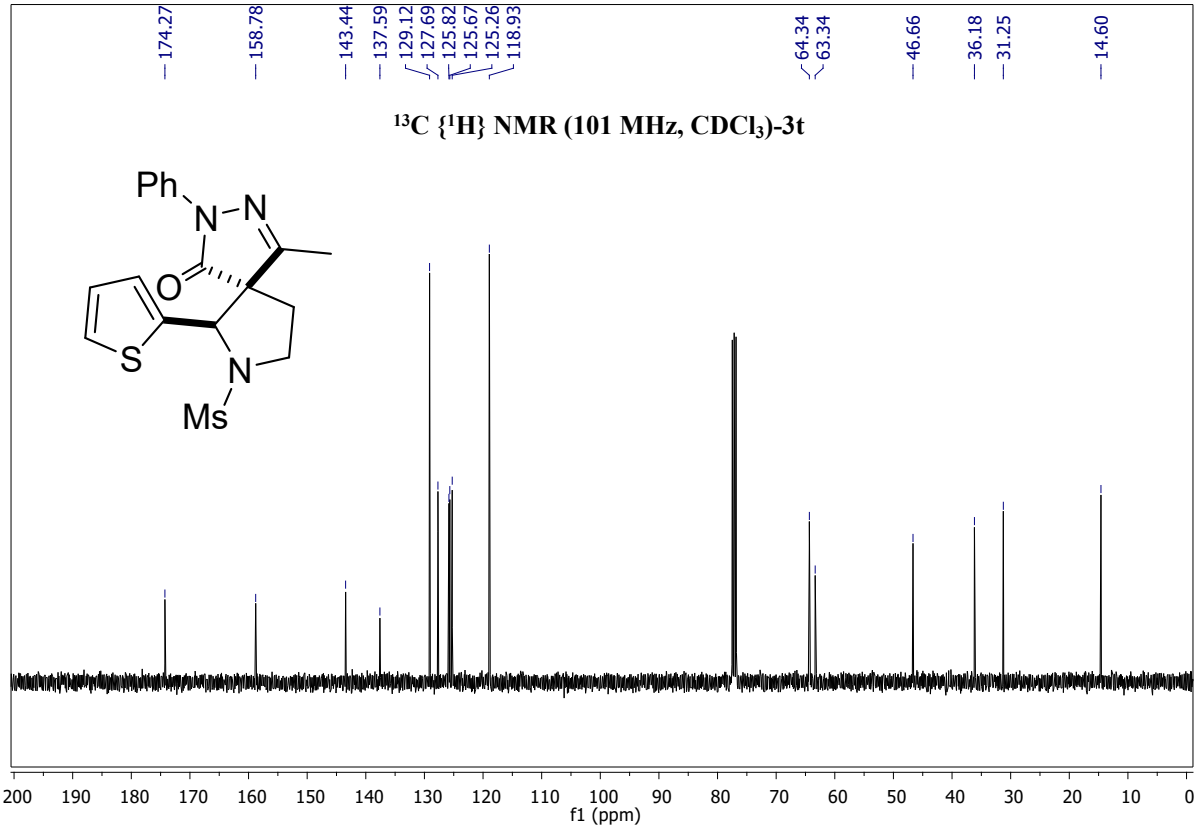
^{1}H NMR (400 MHz, $CDCl_3$) – 3s



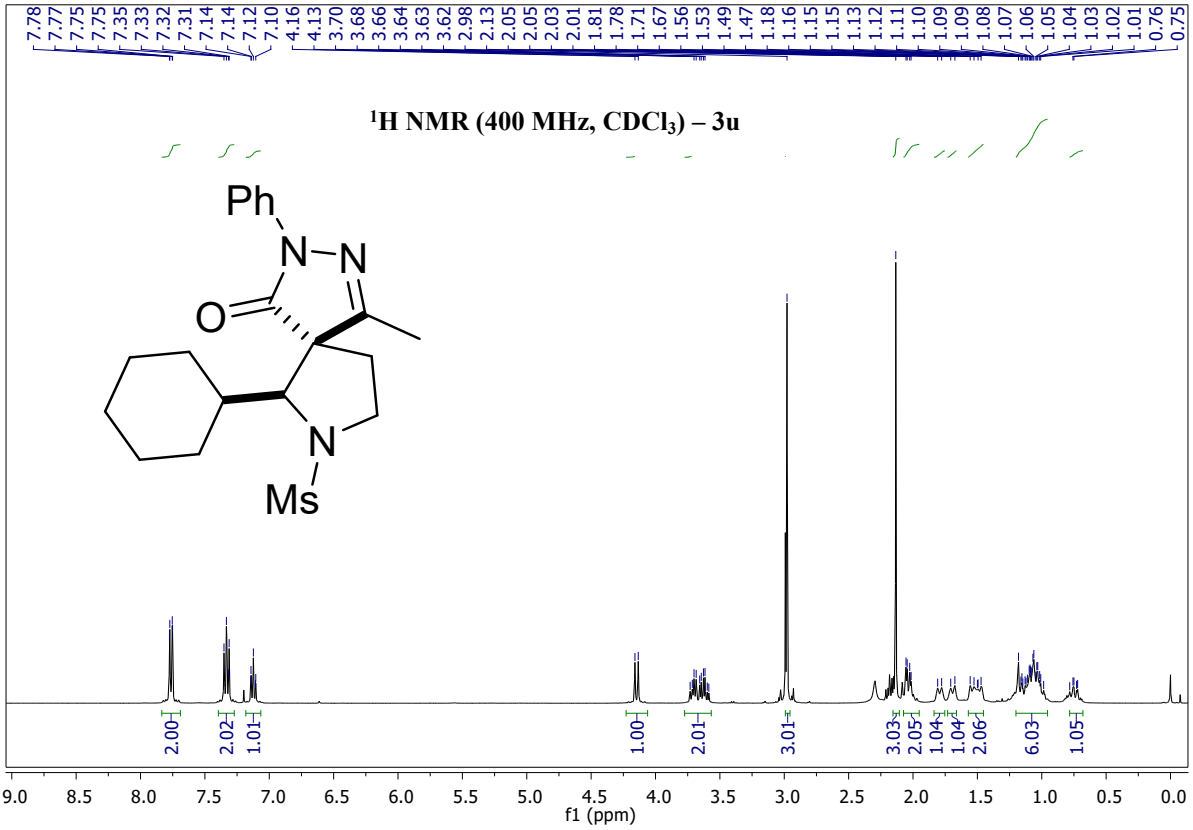
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3s



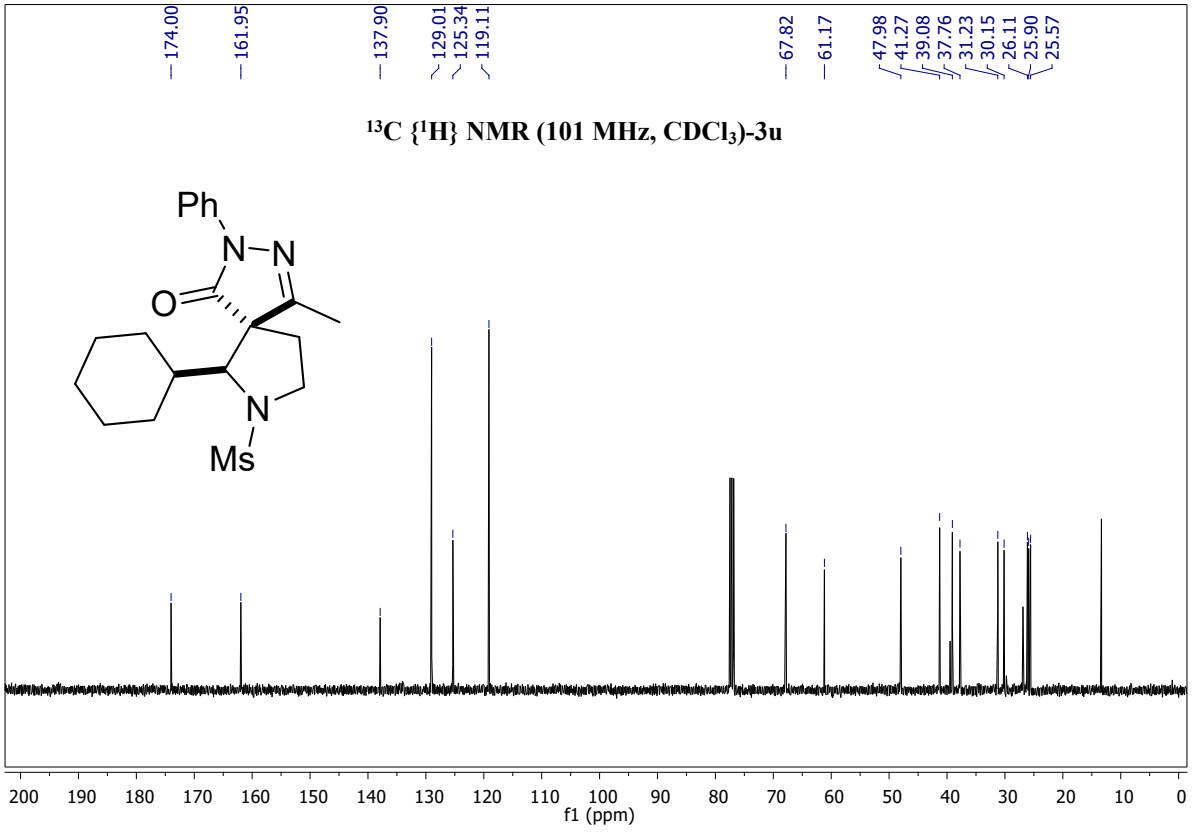
^{1}H NMR (400 MHz, $CDCl_3$) – 3t



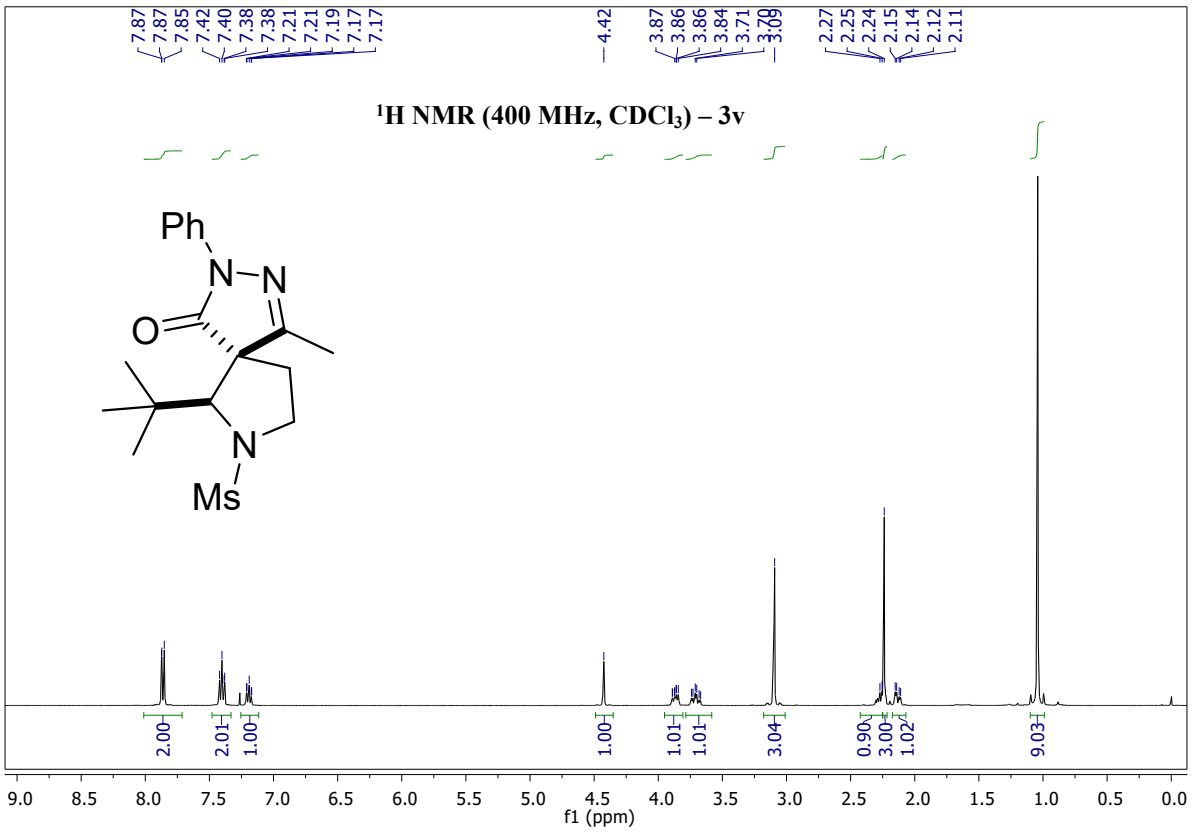
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3t



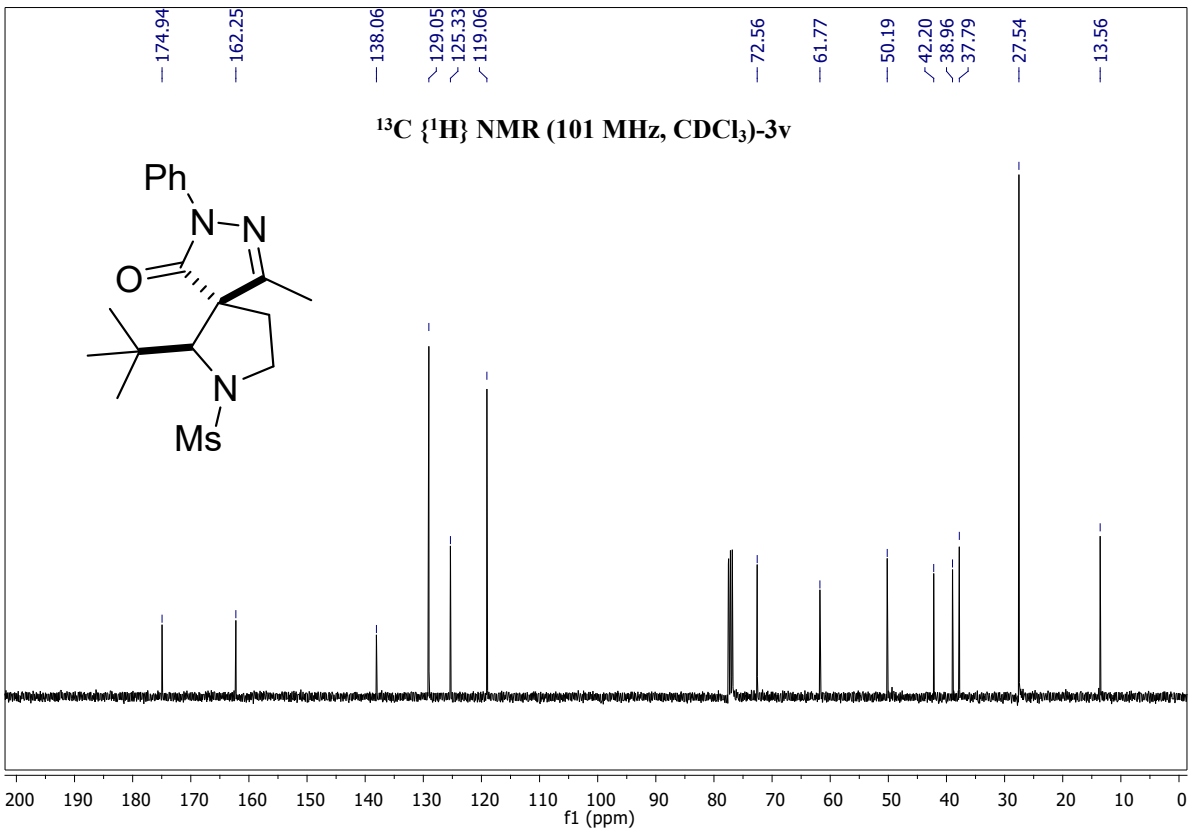
^{1}H NMR (400 MHz, $CDCl_3$) – 3u



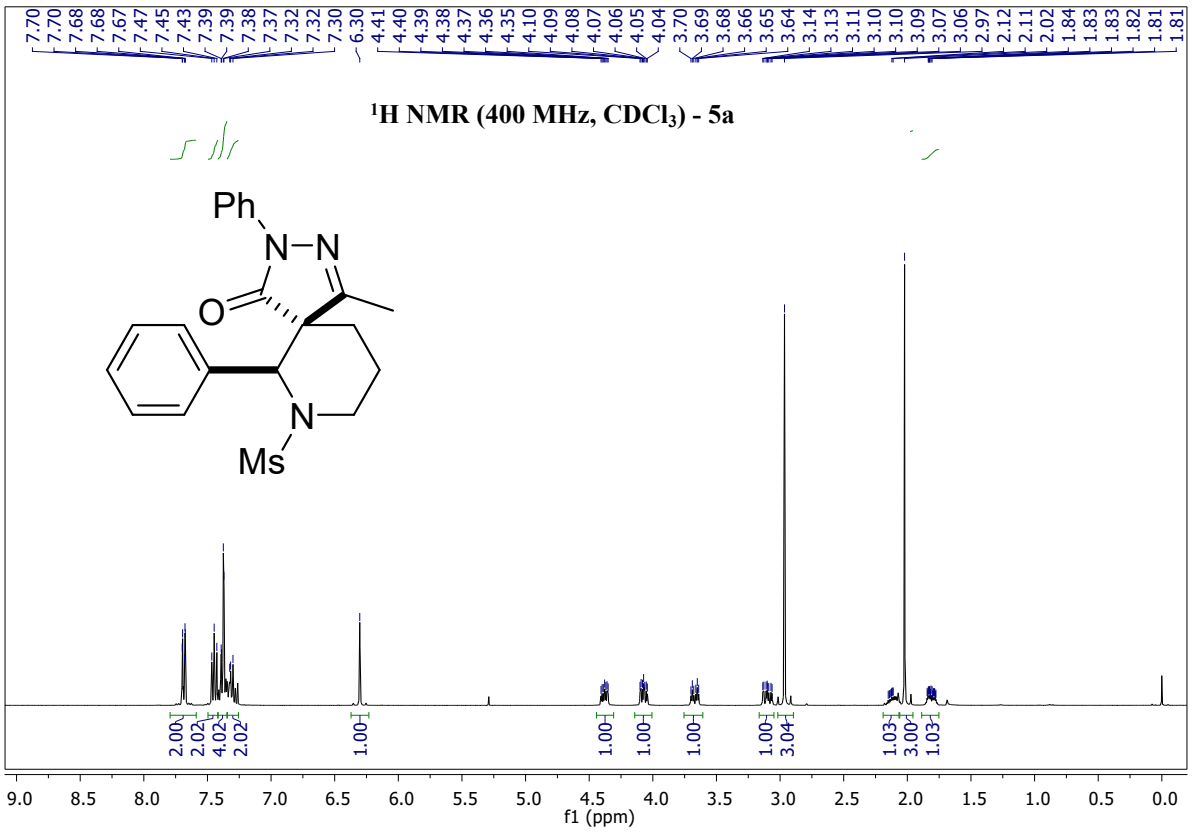
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3u

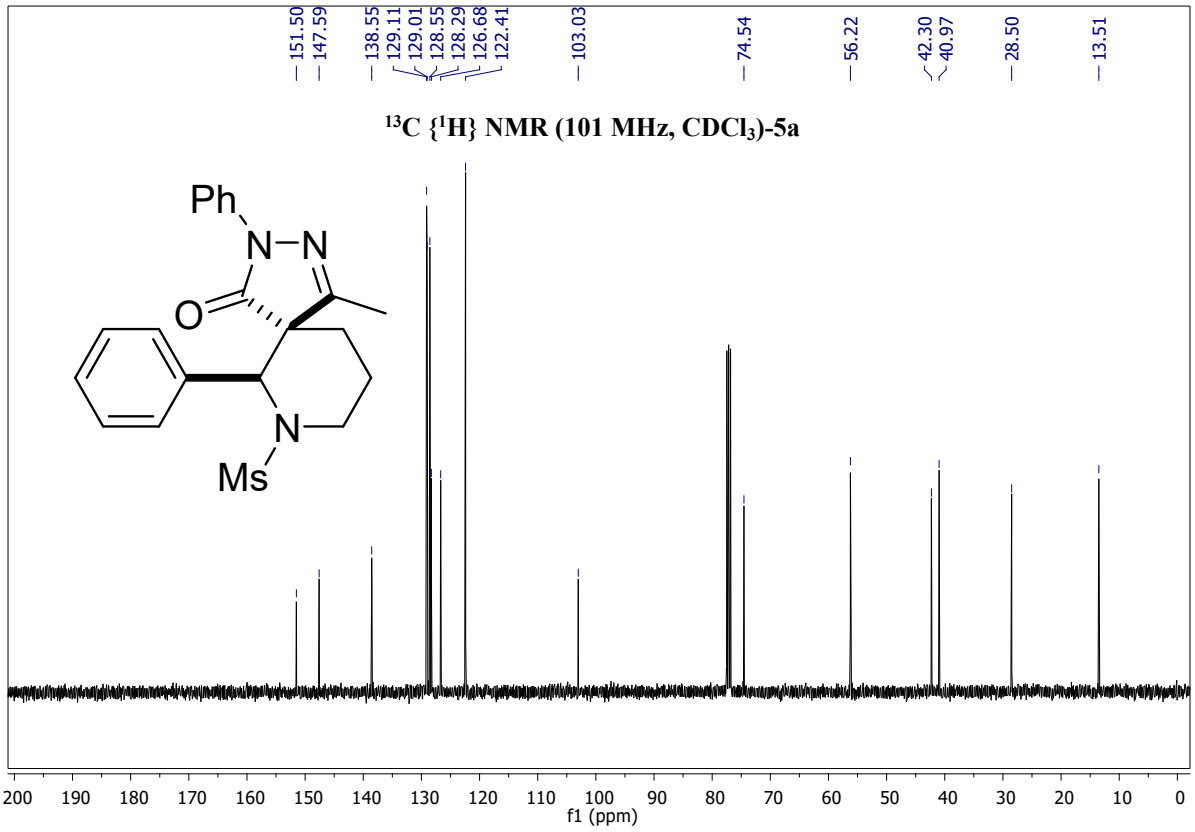


^{1}H NMR (400 MHz, $CDCl_3$) – 3v

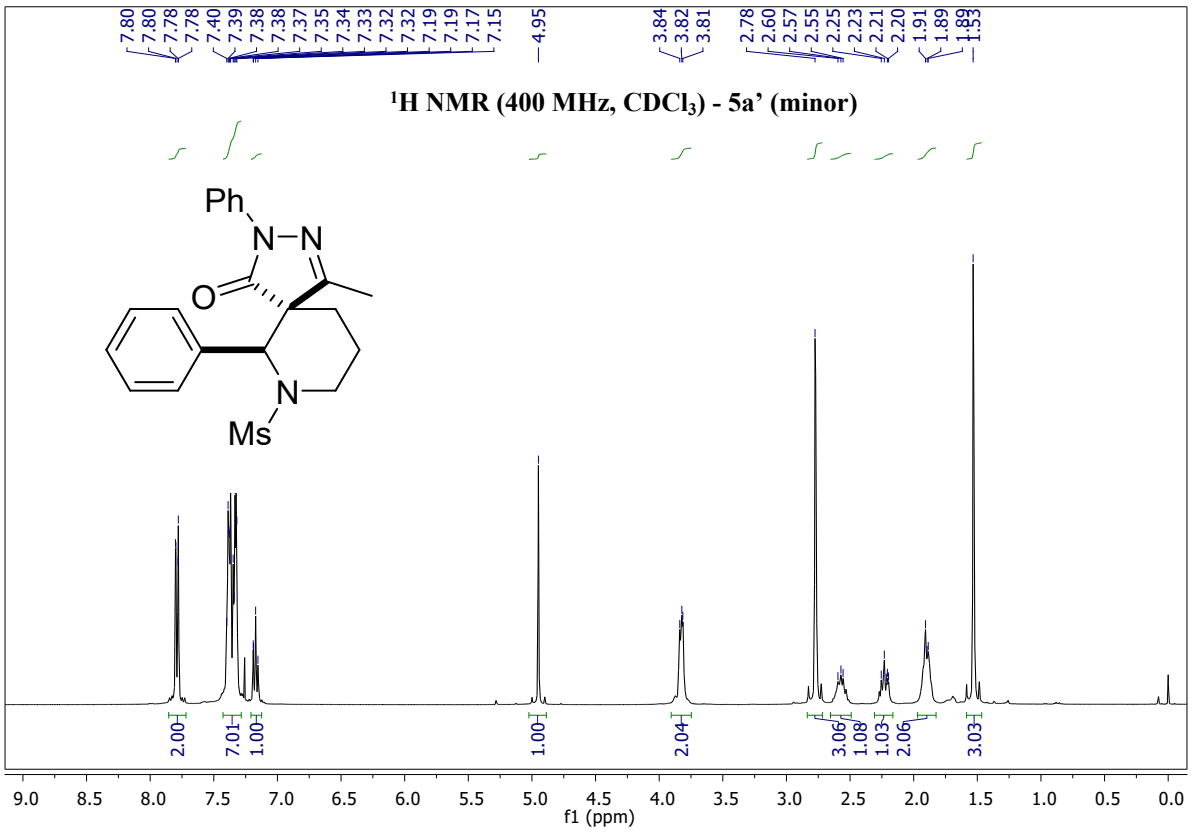


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3v

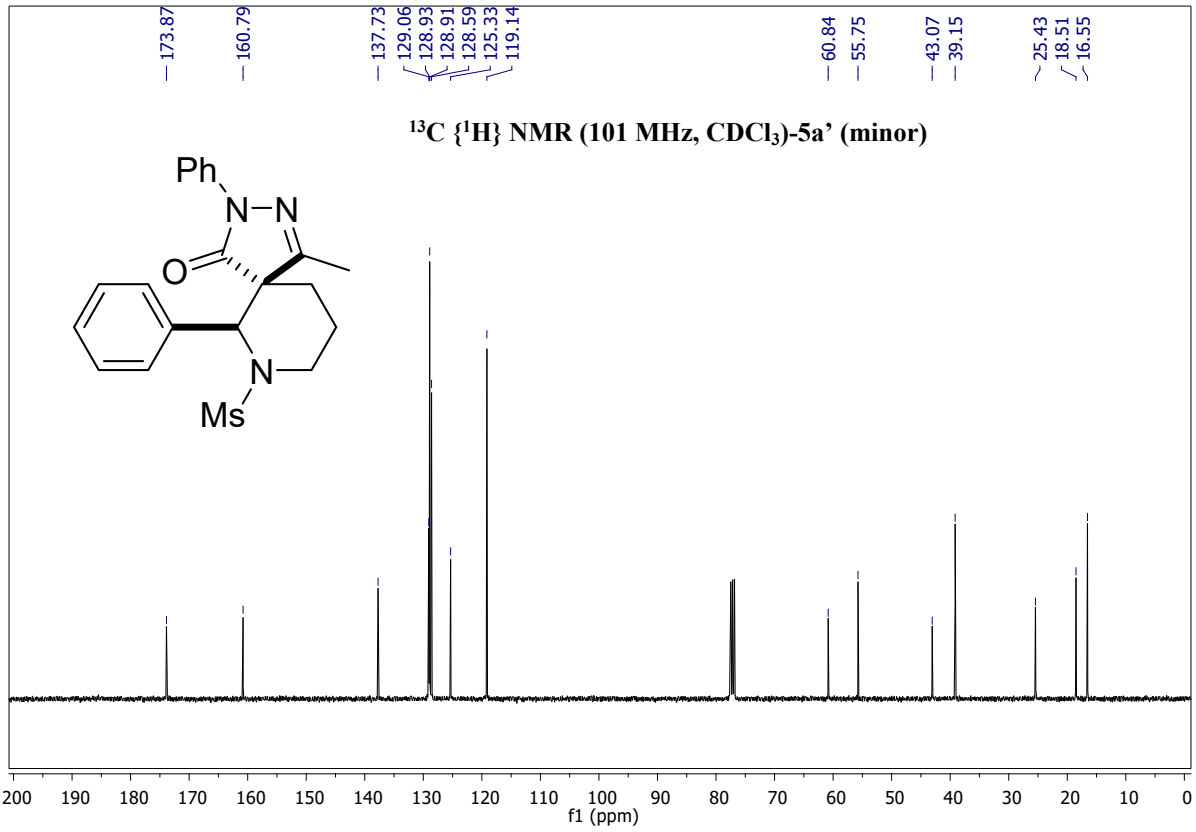

7.70 7.70 7.68 7.68 7.67 7.47 7.45 7.43 7.39 7.39 7.38 7.37 7.32 7.30 6.30 4.41 4.40 4.39 4.38 4.37 4.36 4.35 4.10 4.09 4.08 4.07 4.06 4.05 4.04 3.70 3.69 3.68 3.66 3.65 3.64 3.14 3.13 3.11 3.10 3.10 3.09 3.07 3.06 2.97 2.12 2.11 2.02 1.84 1.83 1.83 1.82 1.81 1.81
1H NMR (400 MHz, CDCl3) - 5a
Ph
N–N
O
N
Ms
2.00 2.02 4.02 2.02 1.00 1.00 1.00 1.00 1.00 3.04 1.03 3.00 1.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



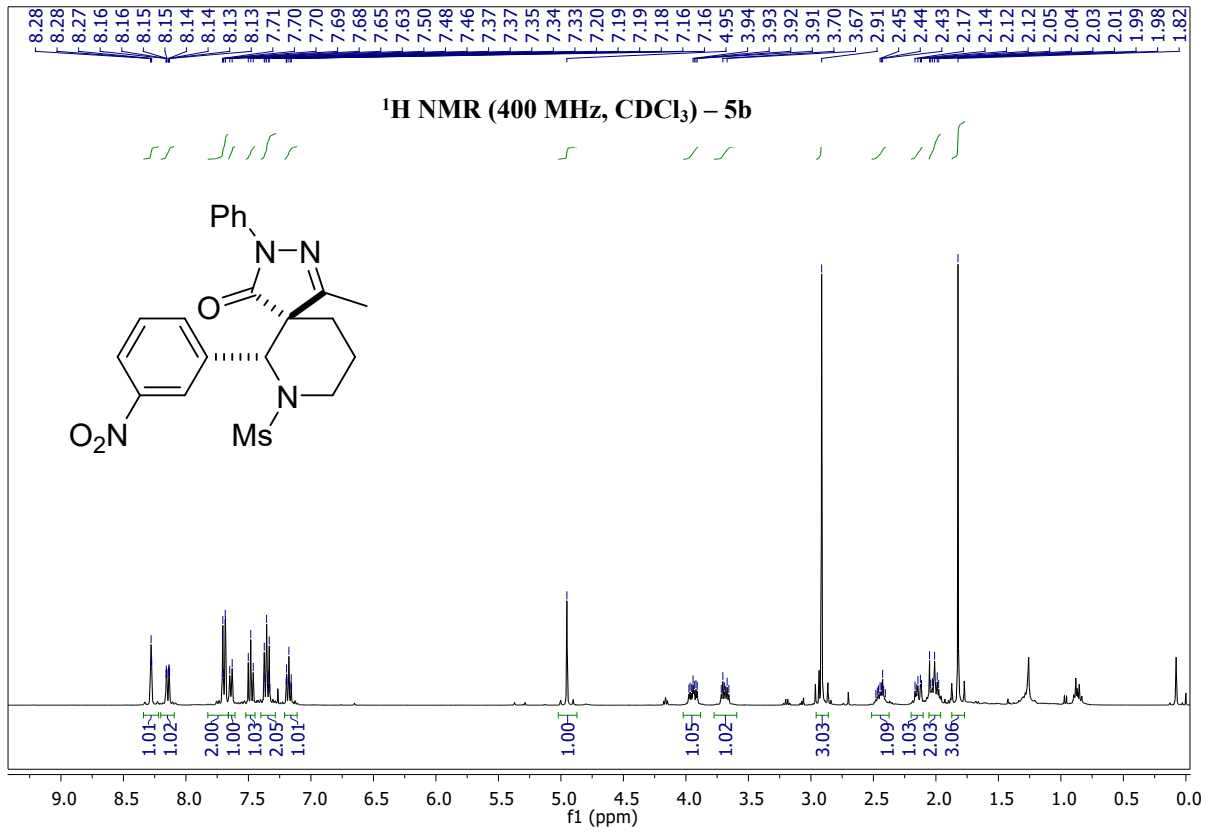
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5a



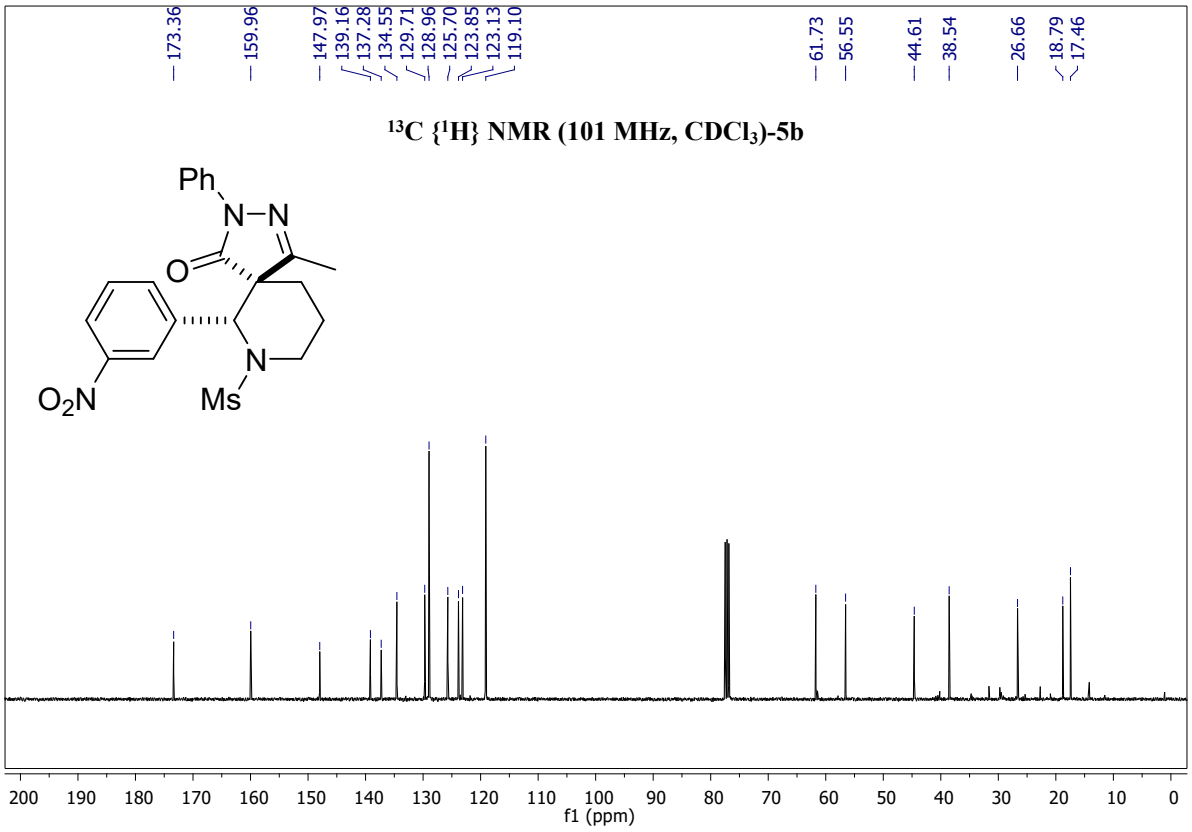
^{1}H NMR (400 MHz, $CDCl_3$) - 5a' (minor)



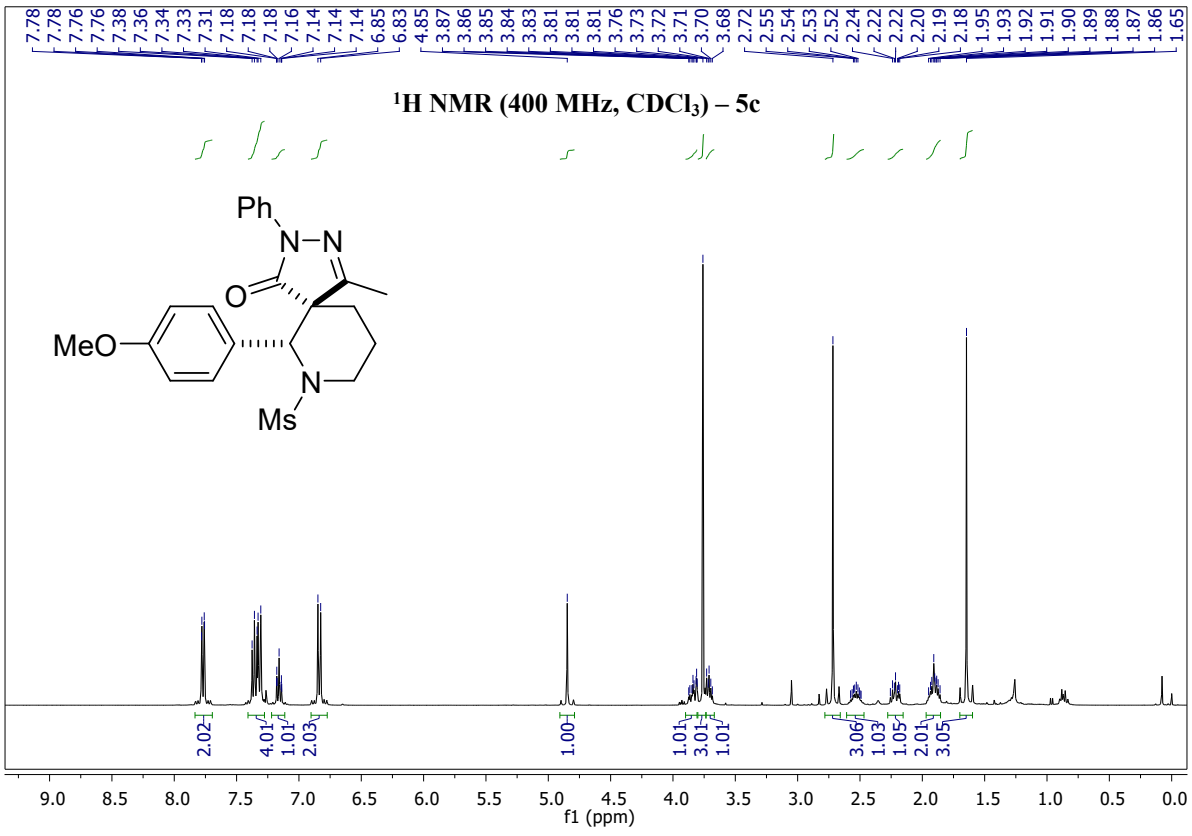
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5a' (minor)



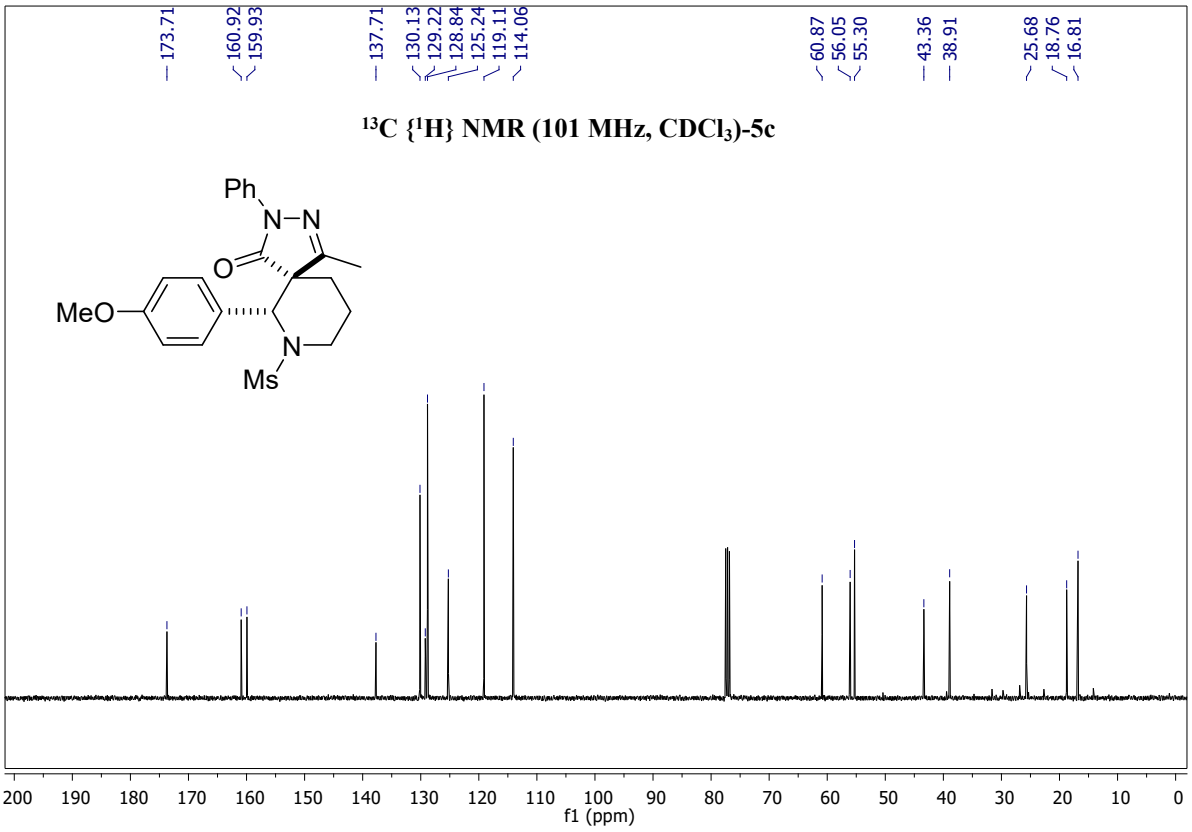
^{1}H NMR (400 MHz, $CDCl_3$) – 5b



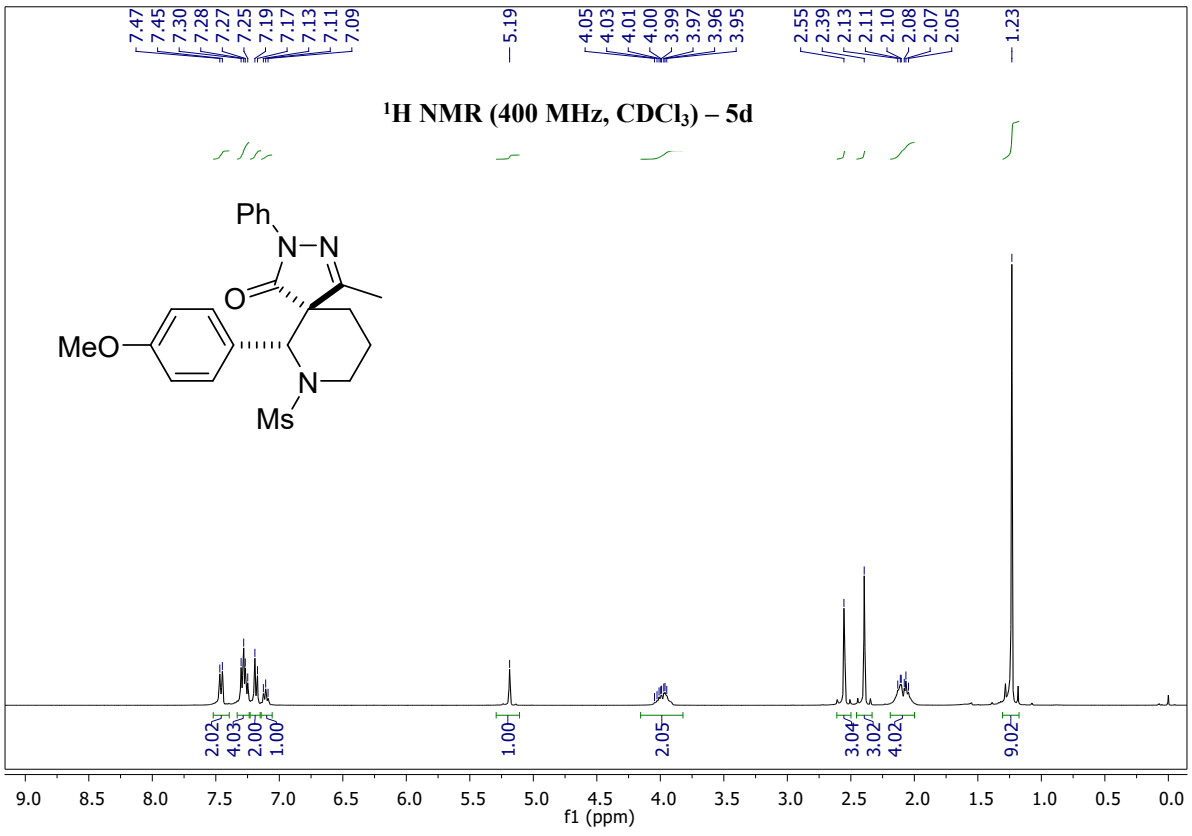
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5b



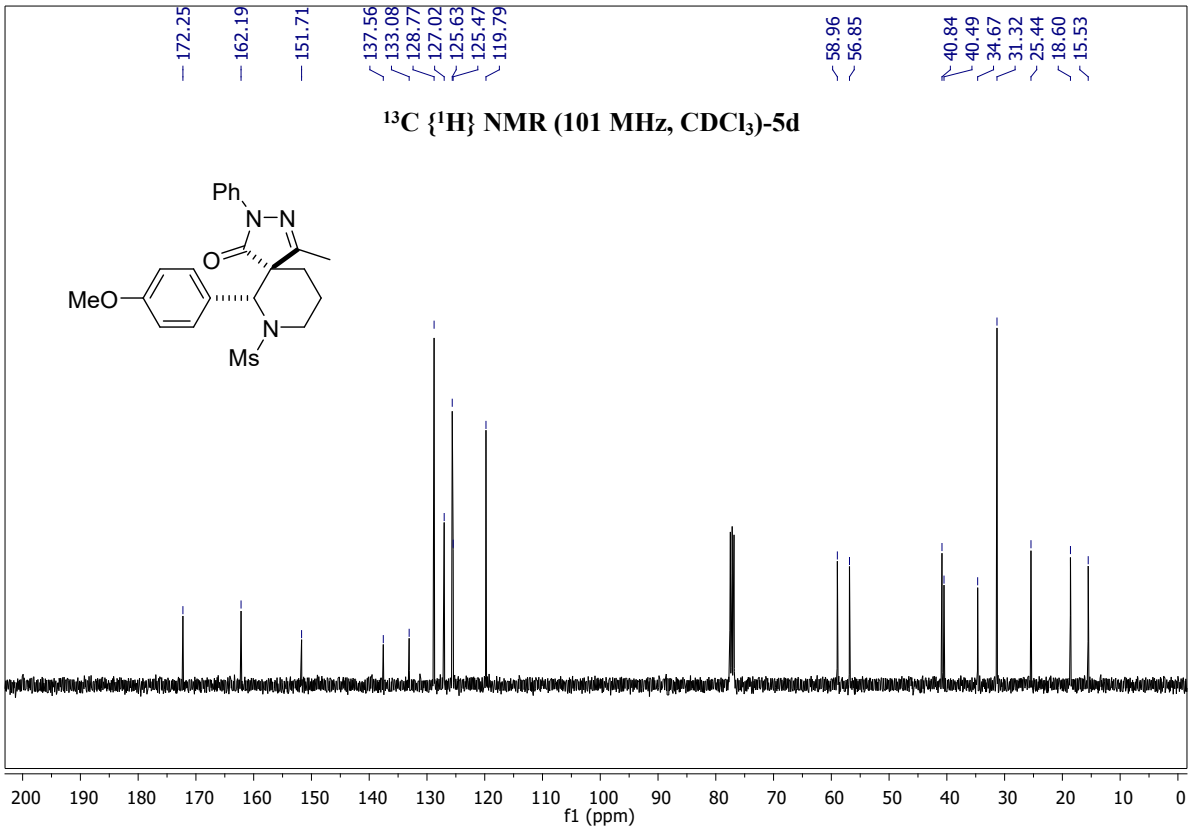
^{1}H NMR (400 MHz, $CDCl_3$) – 5c



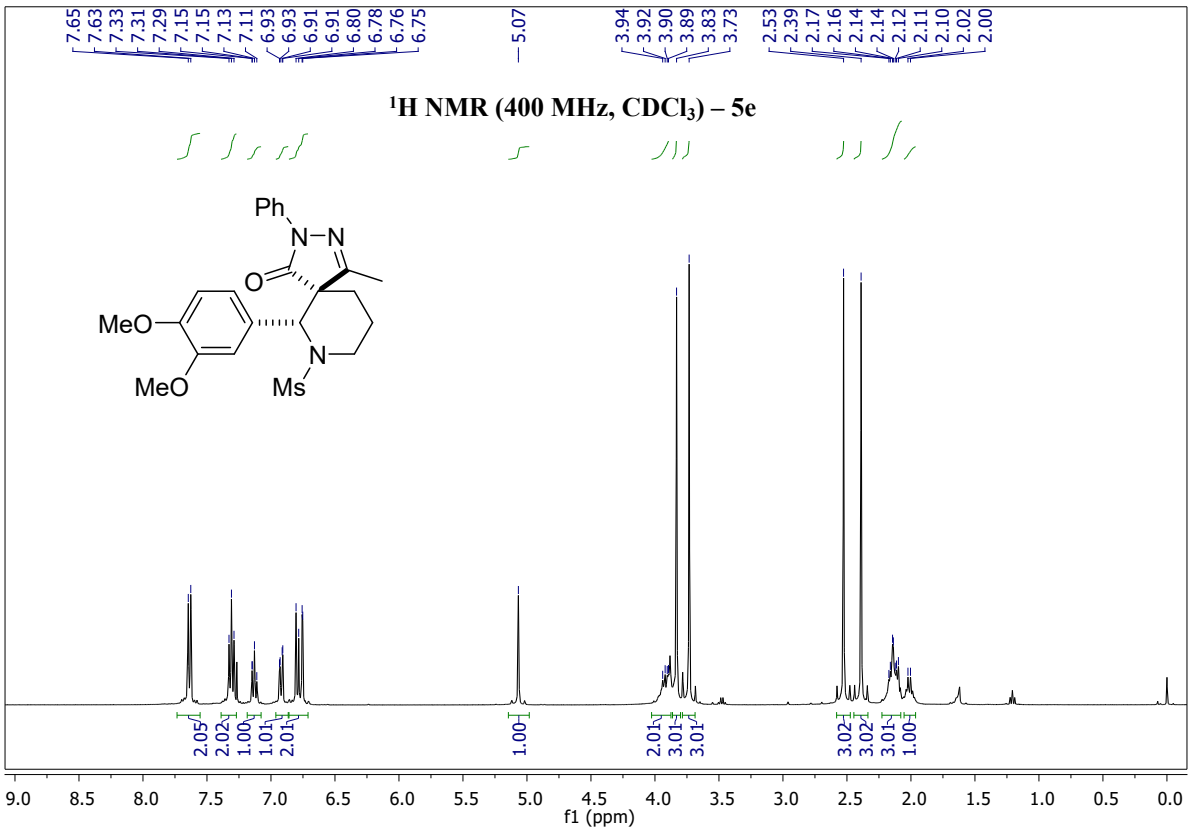
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5c



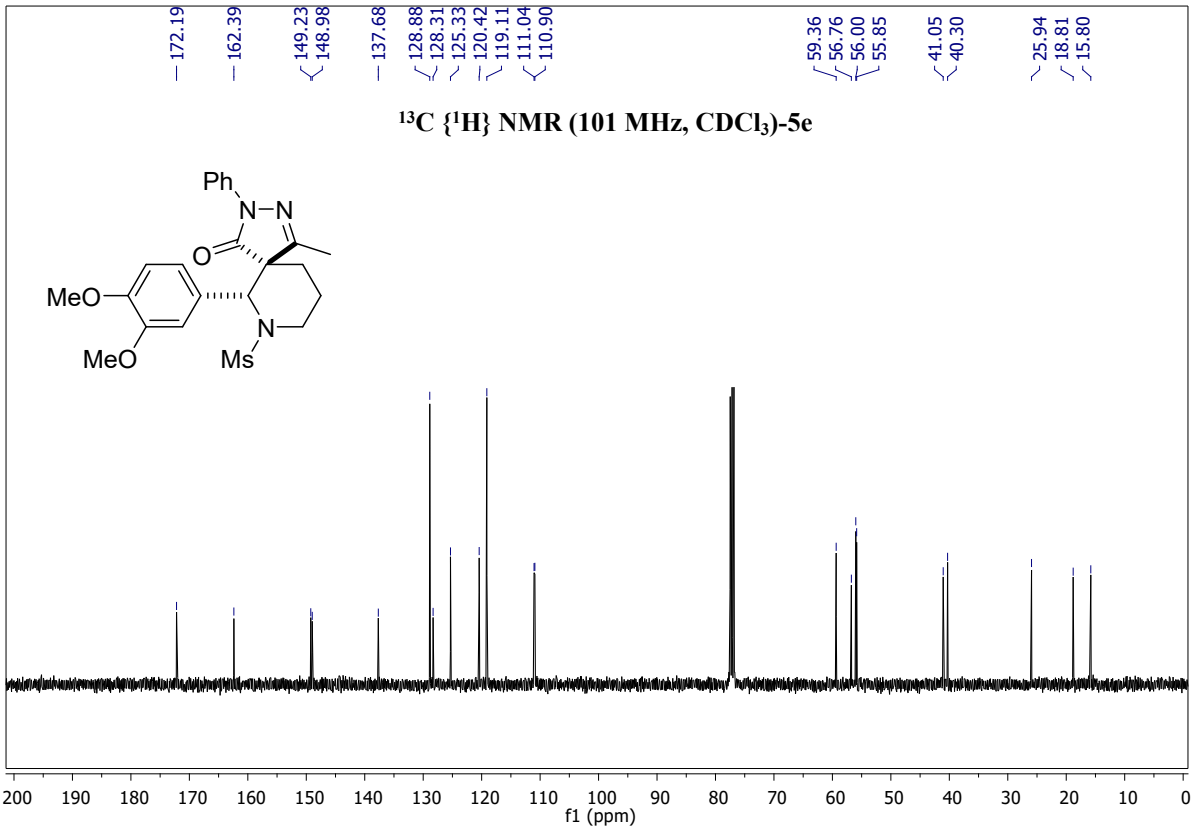
^{1}H NMR (400 MHz, $CDCl_3$) – 5d



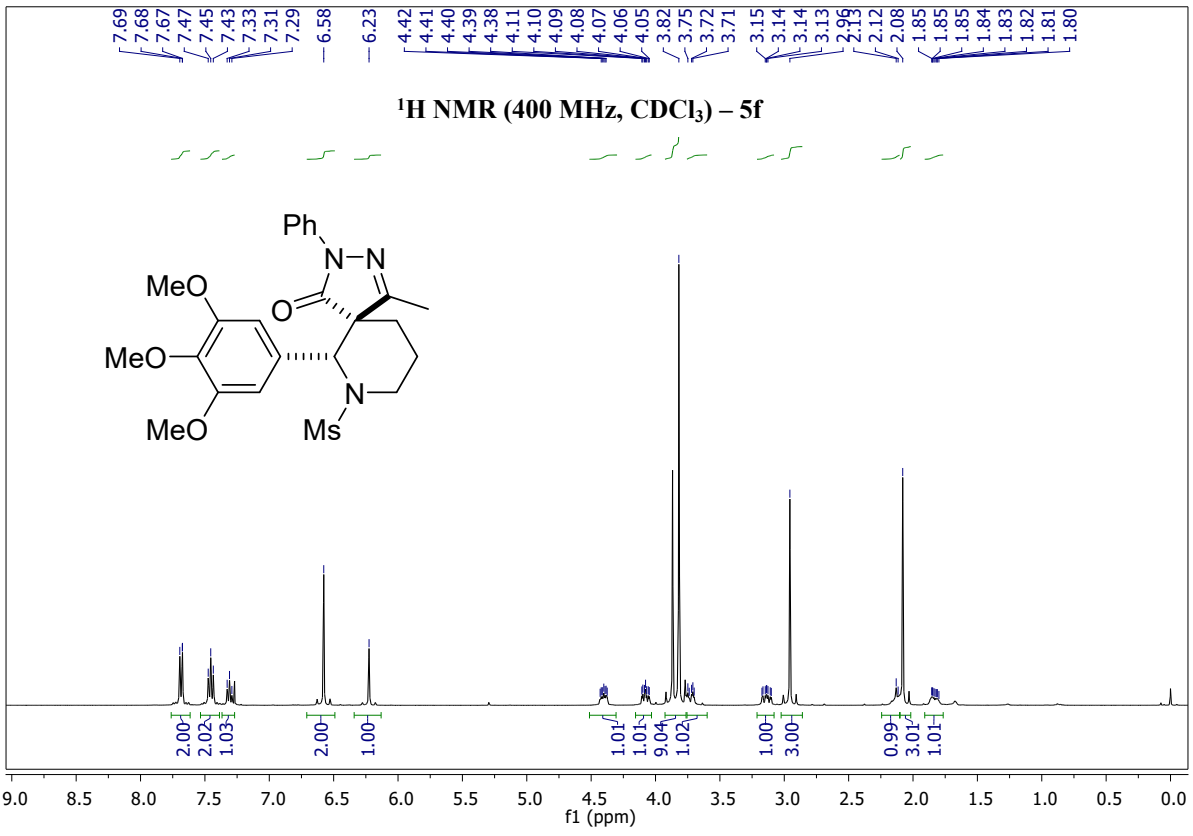
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5d



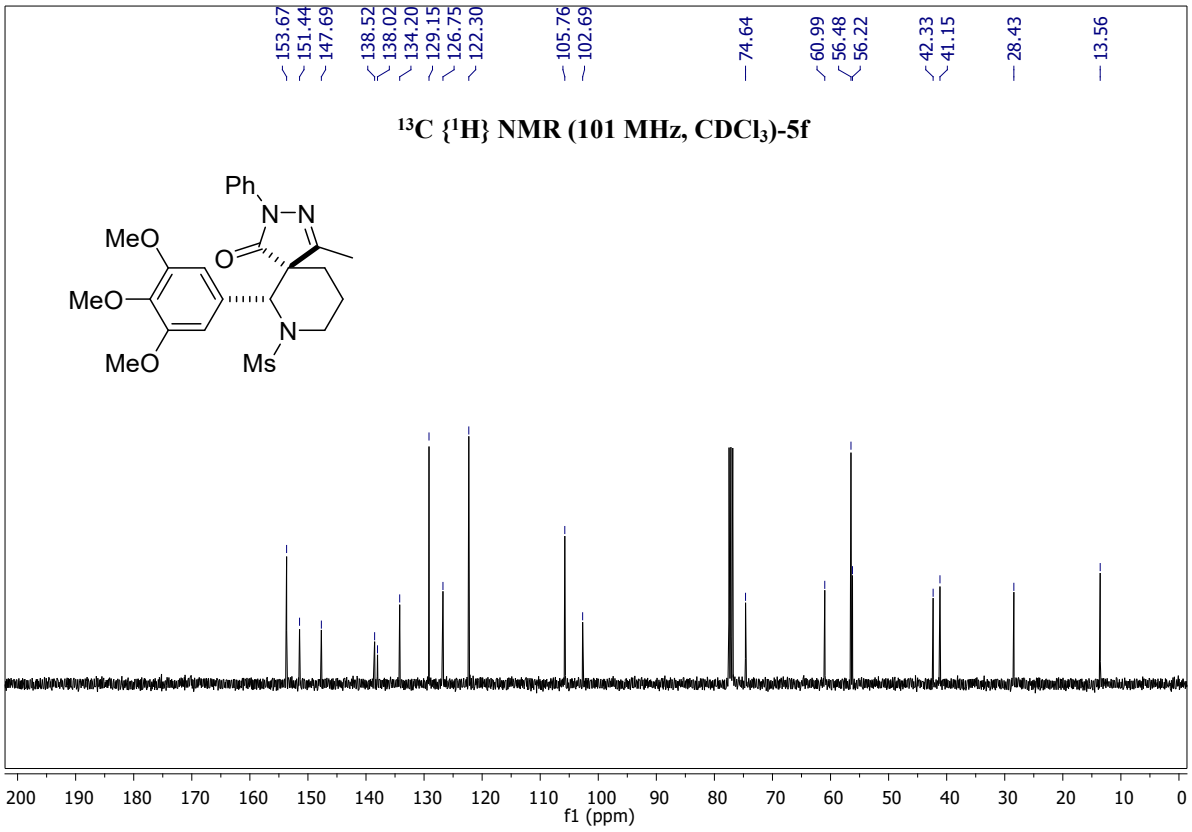
^{1}H NMR (400 MHz, $CDCl_3$) – 5e



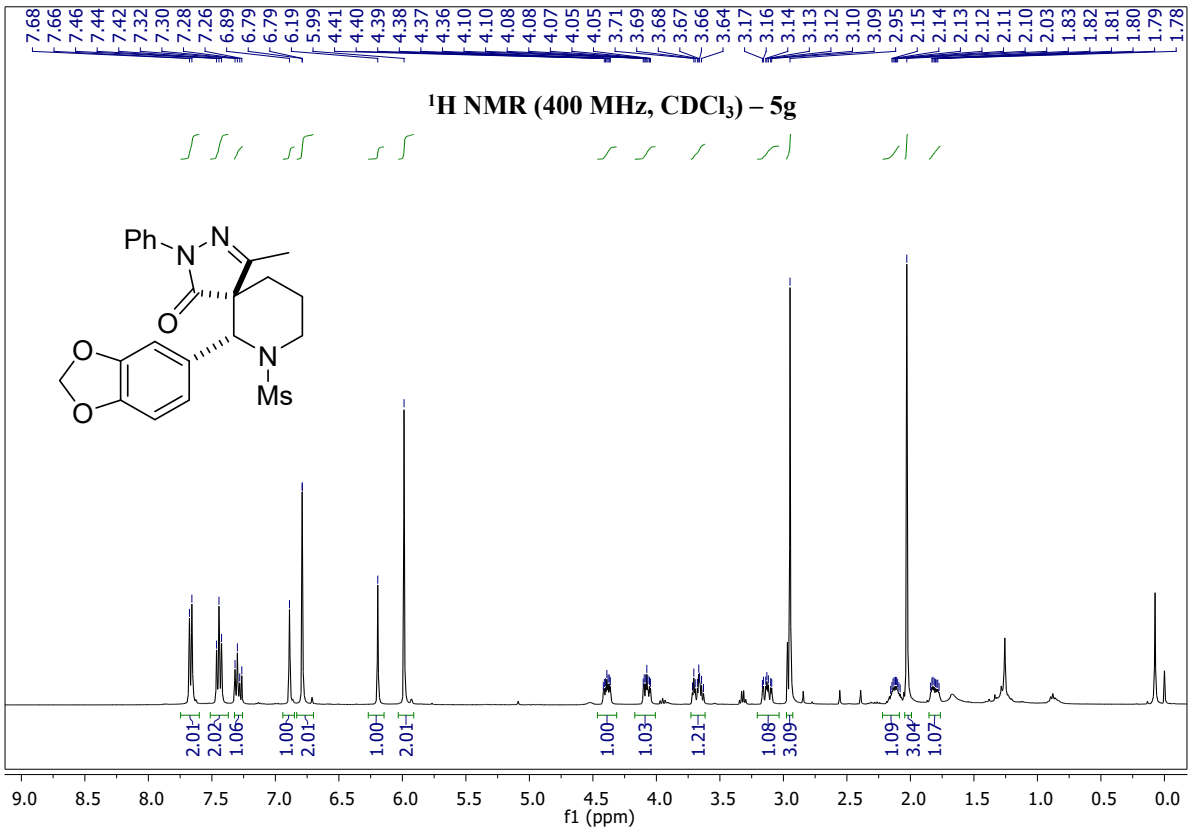
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5e



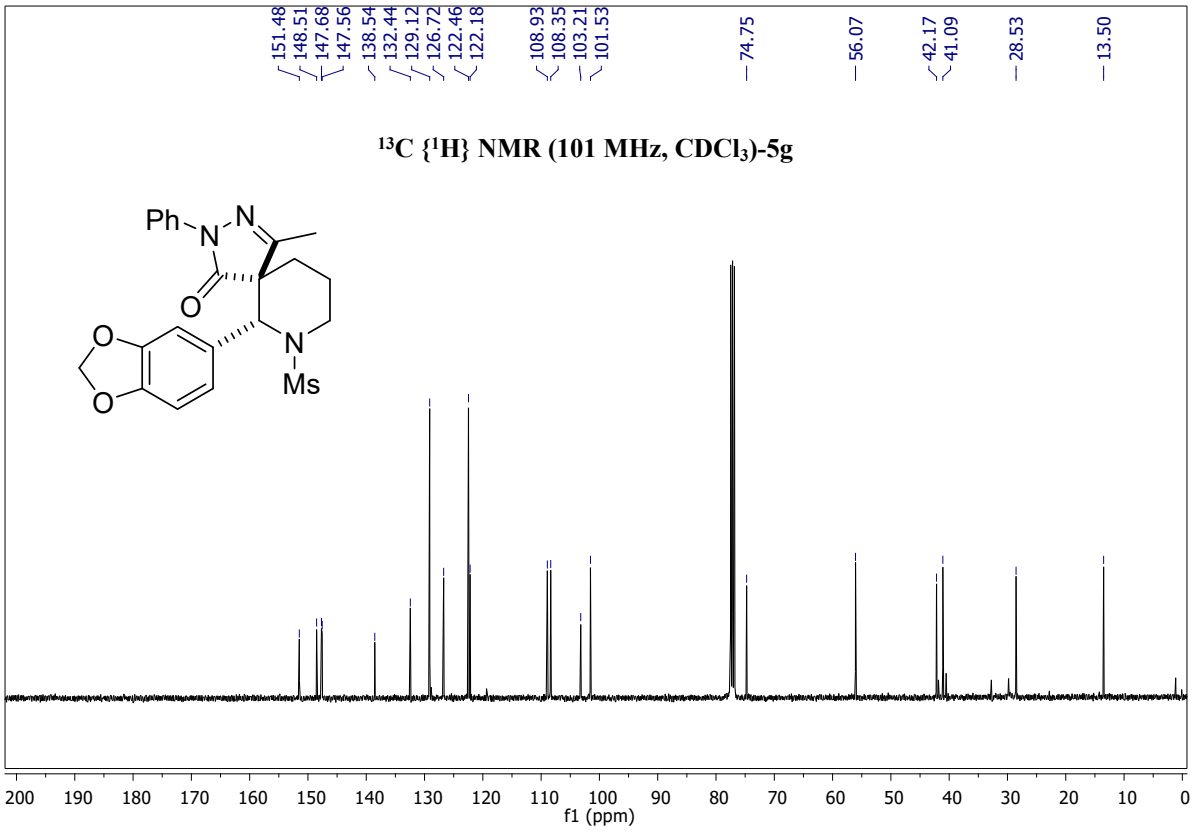
^{1}H NMR (400 MHz, $CDCl_3$) – 5f



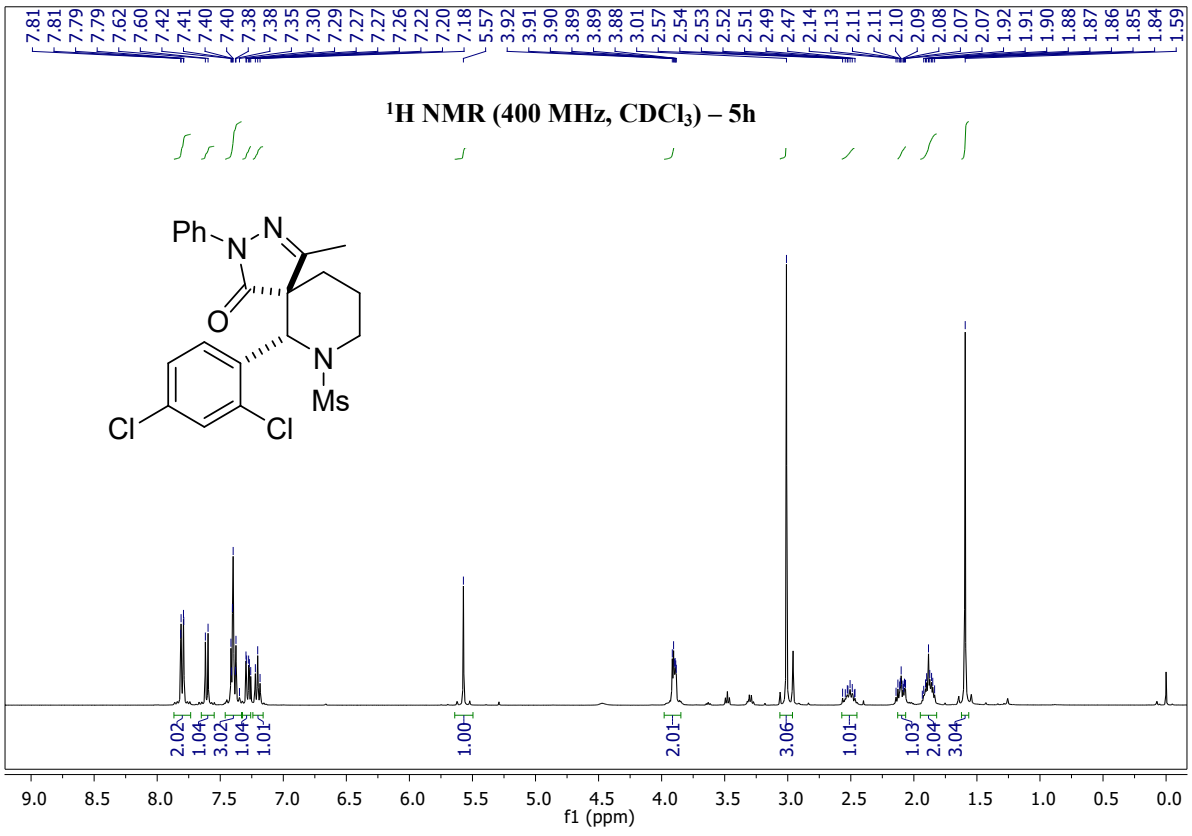
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5f



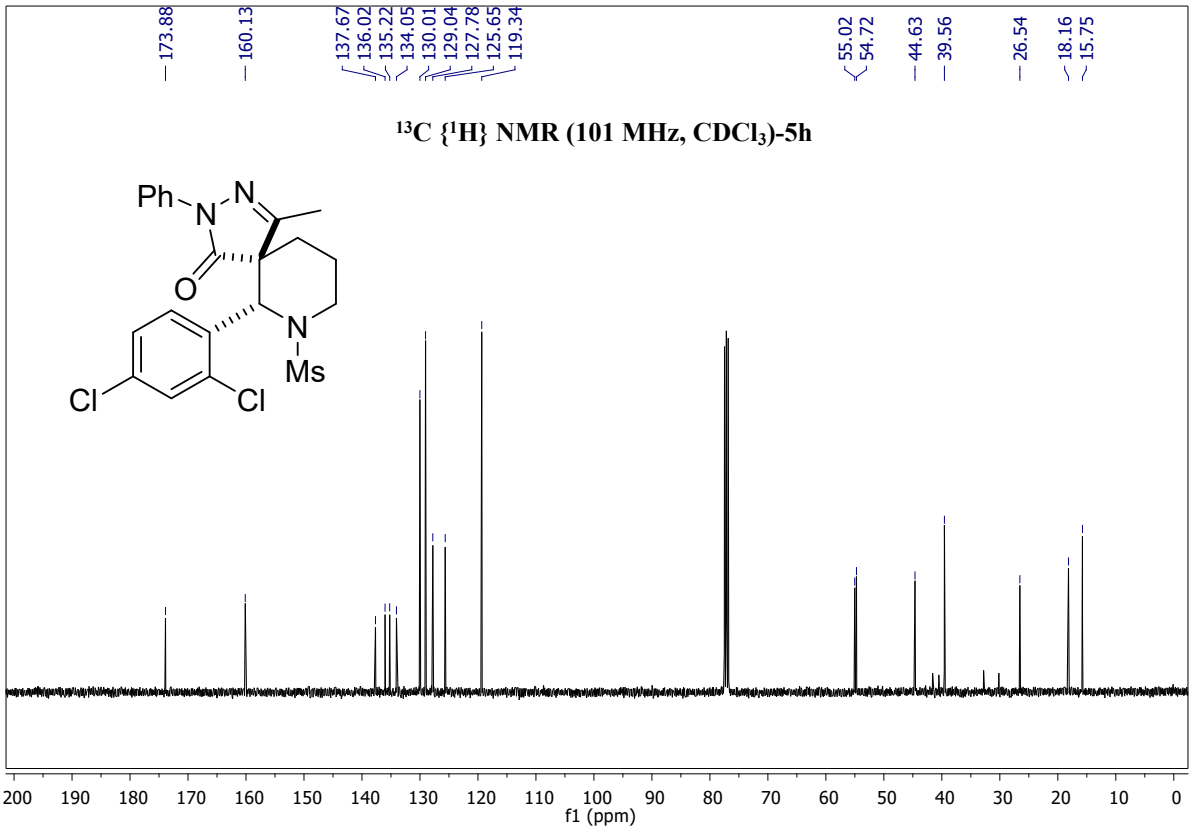
^{1}H NMR (400 MHz, $CDCl_3$) – 5g



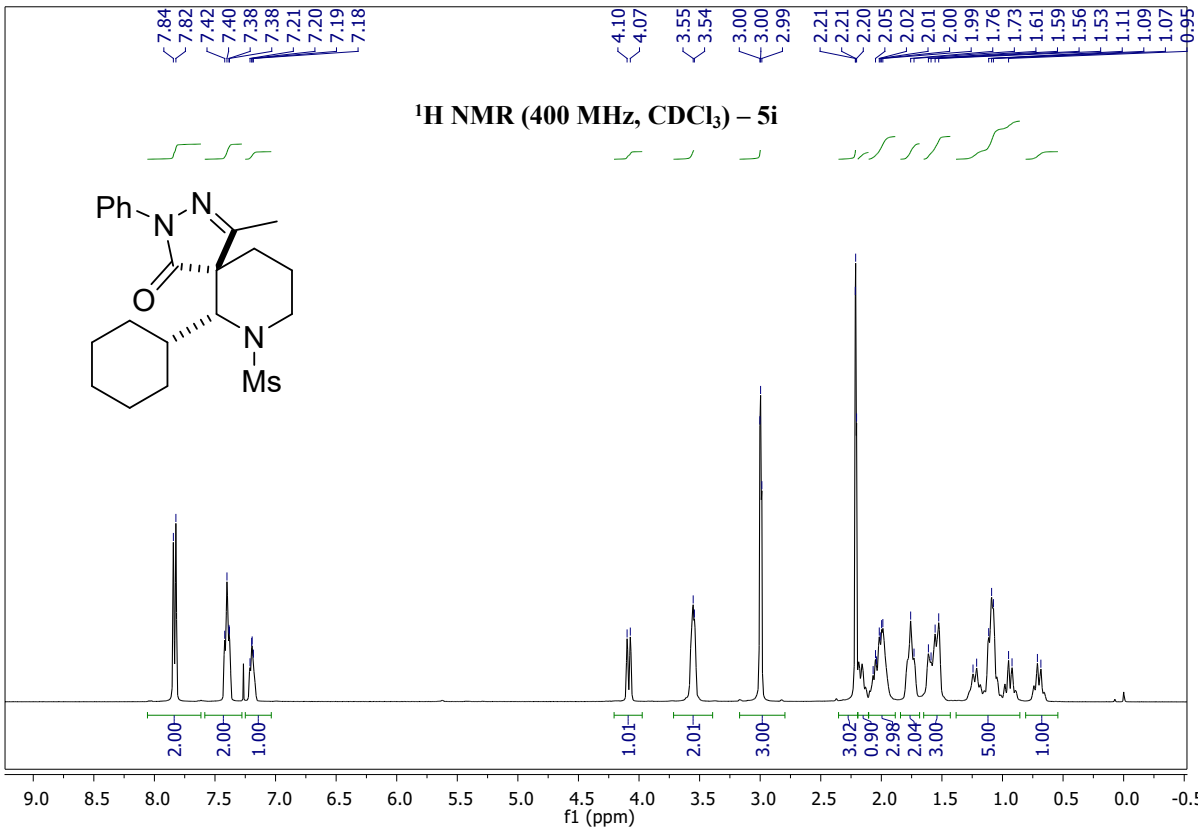
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5g



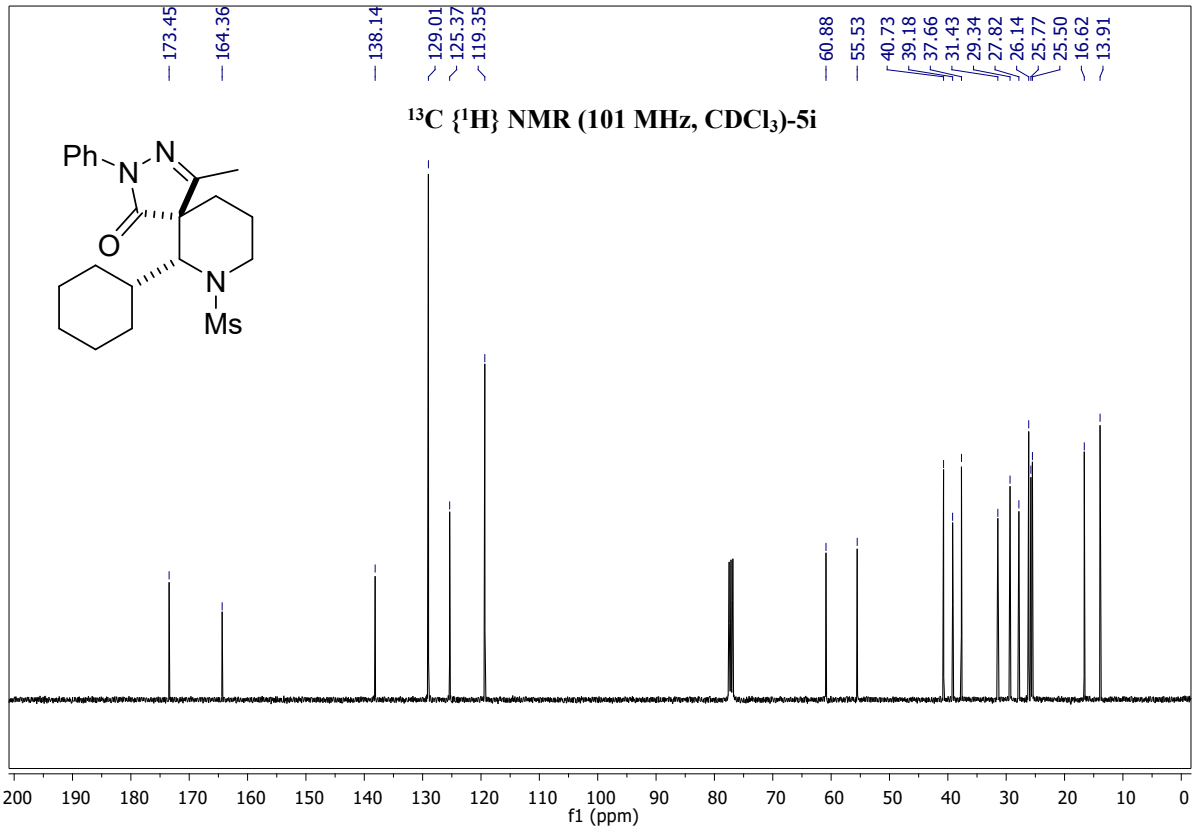
^{1}H NMR (400 MHz, $CDCl_3$) – 5h



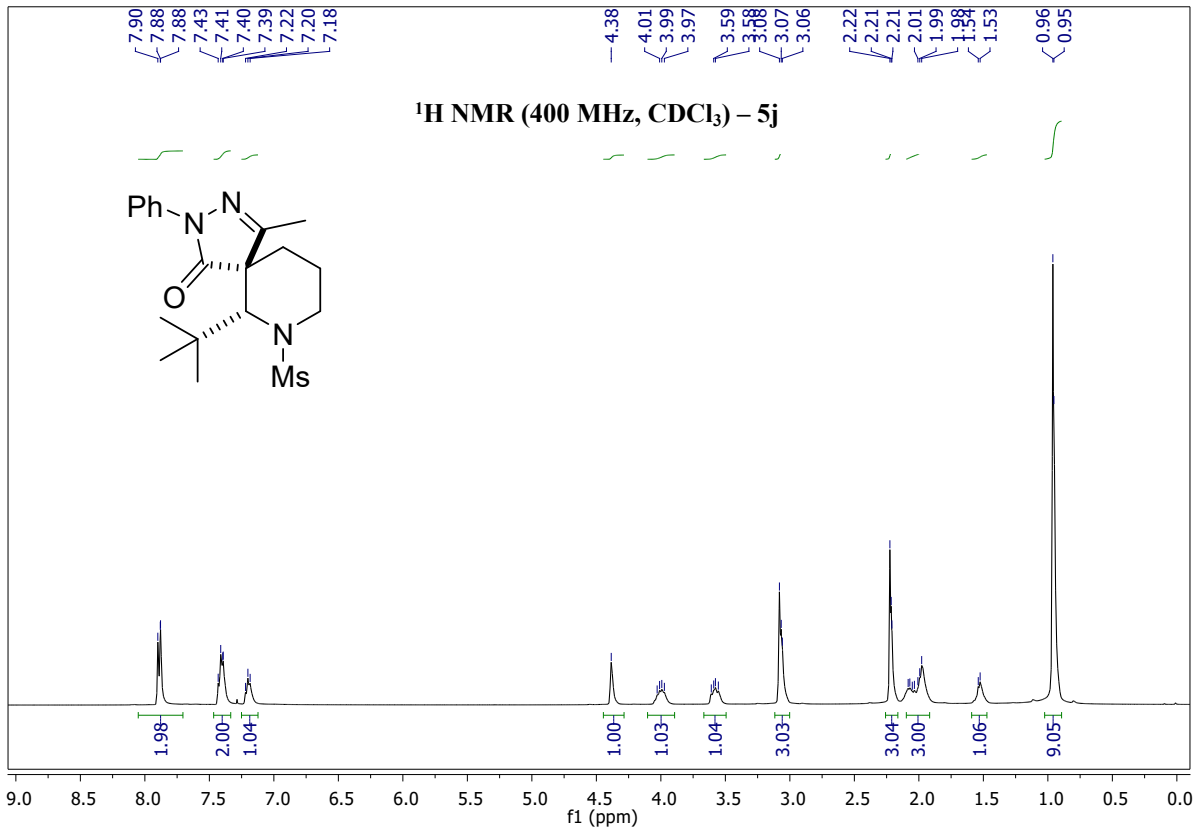
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5h



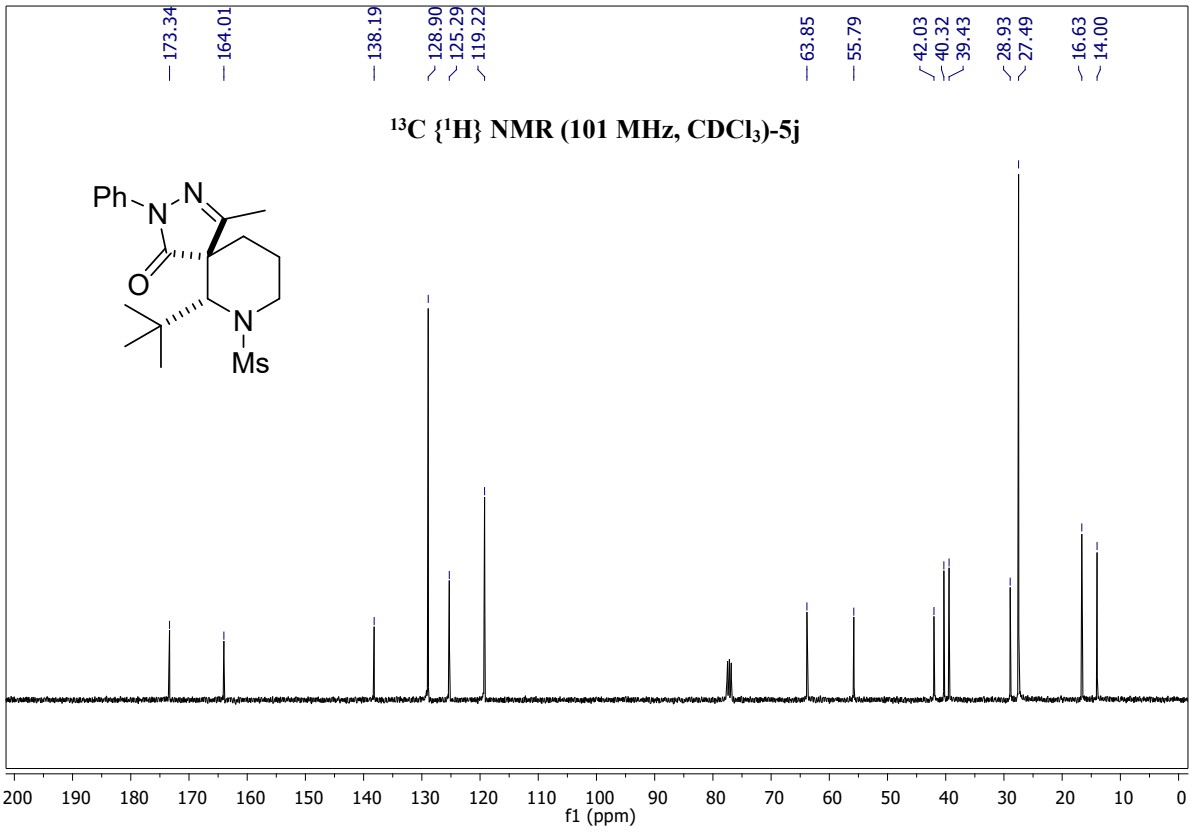
^{1}H NMR (400 MHz, $CDCl_3$) – 5i



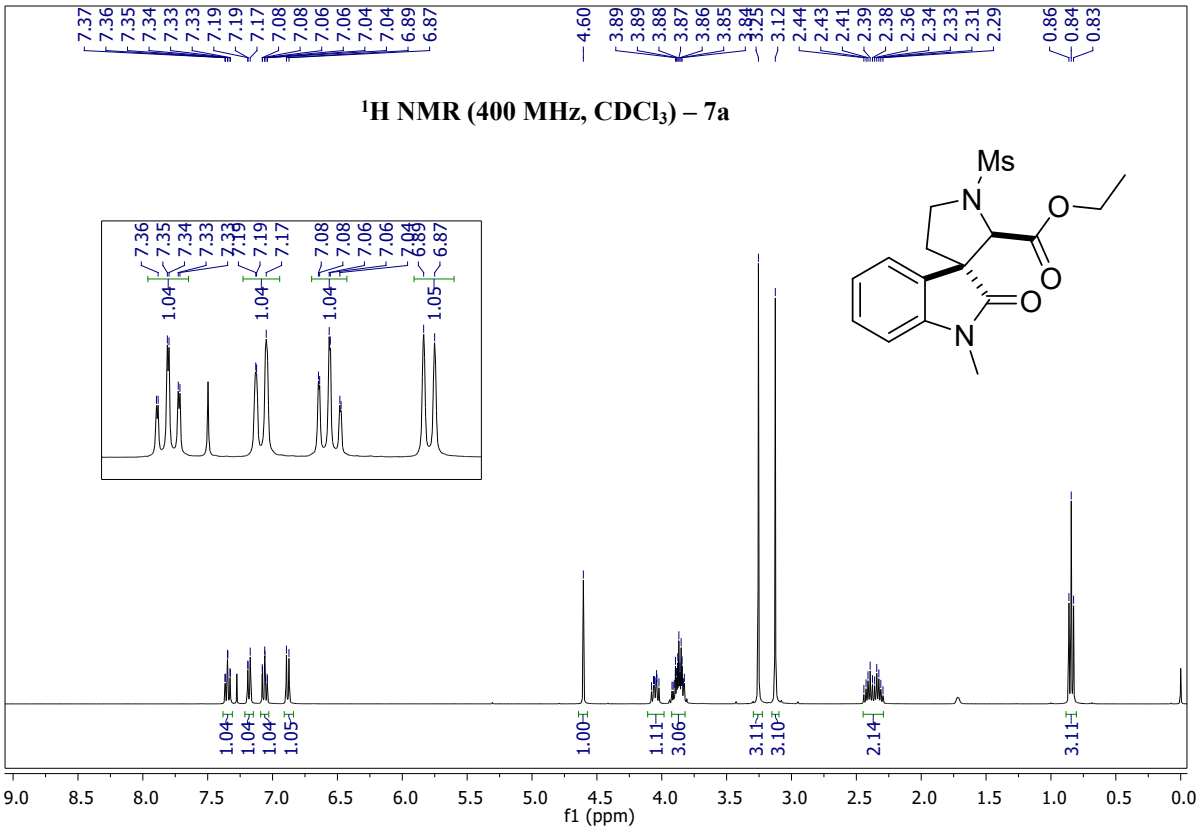
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5i



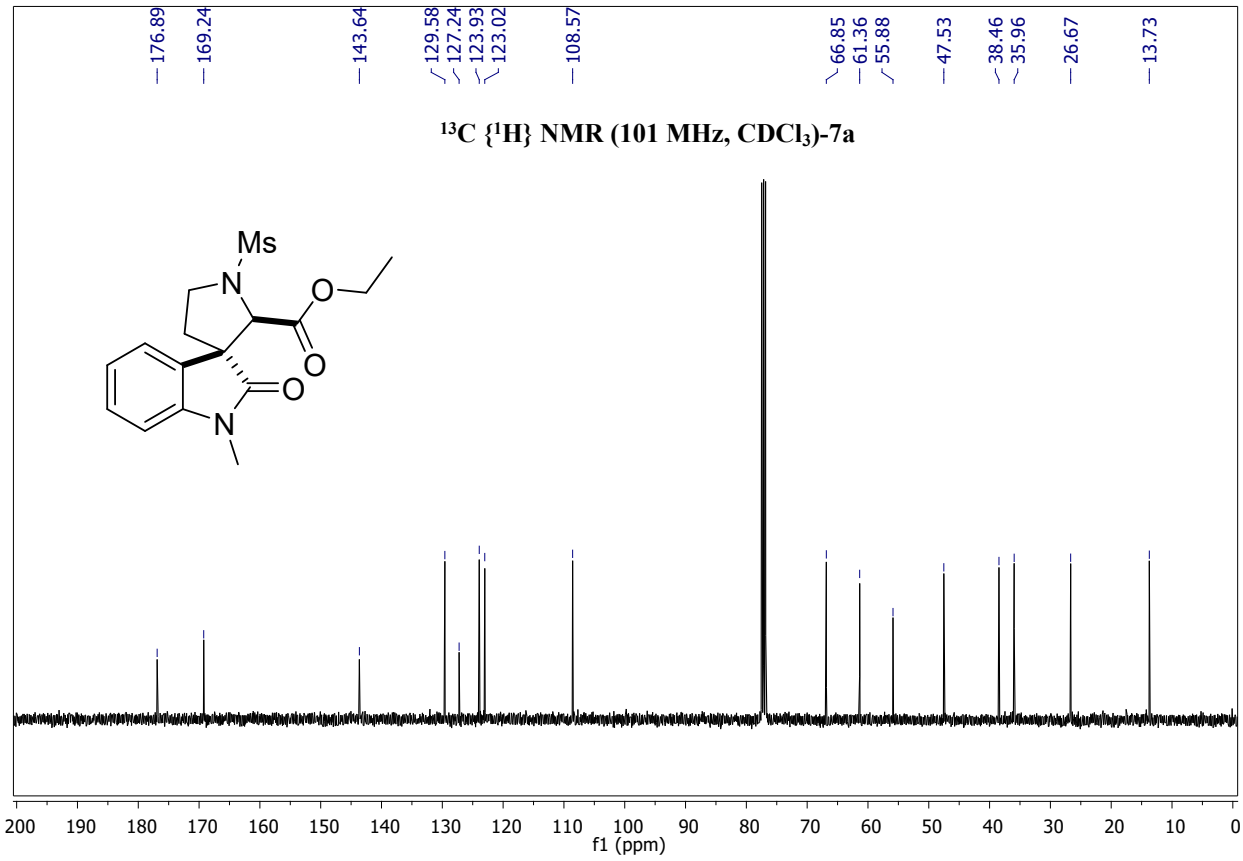
^{1}H NMR (400 MHz, $CDCl_3$) – 5j



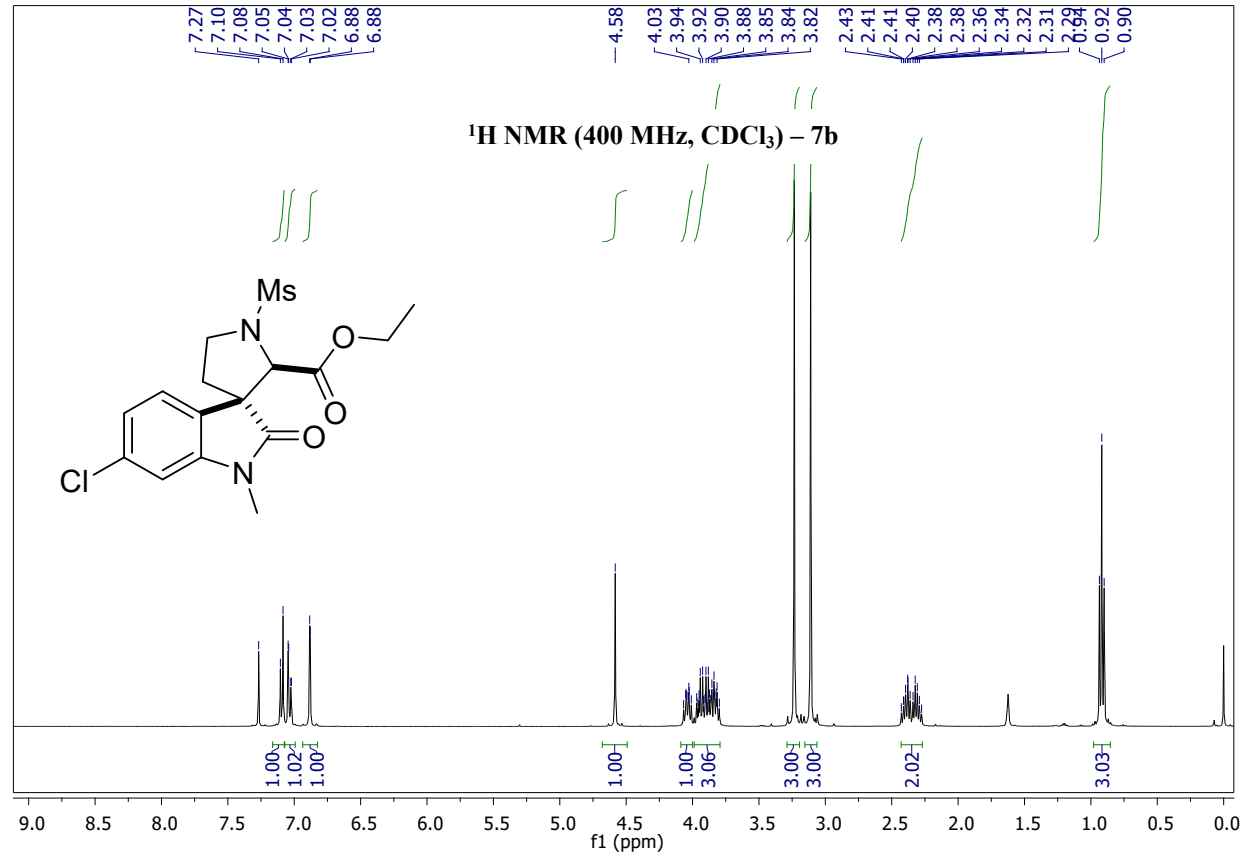
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-5j



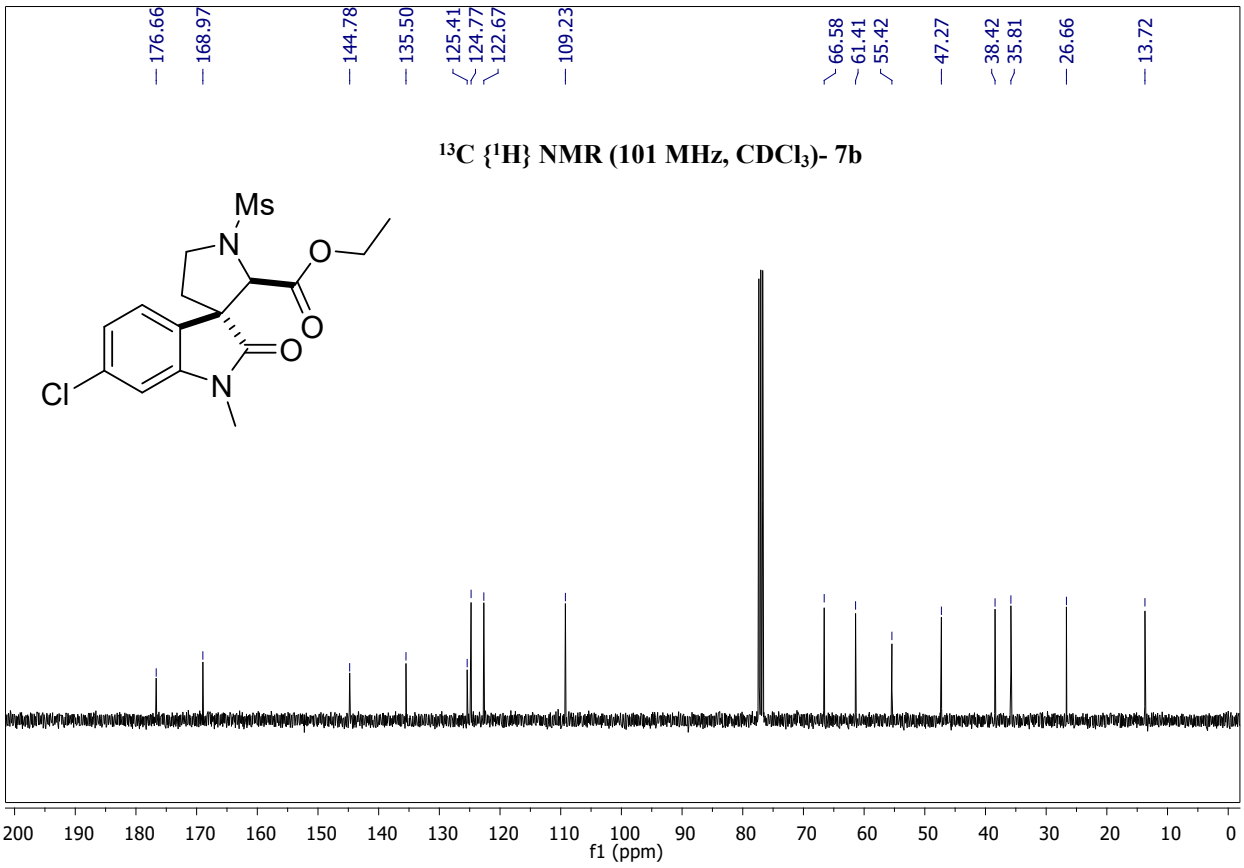
^{1}H NMR (400 MHz, $CDCl_3$) – 7a



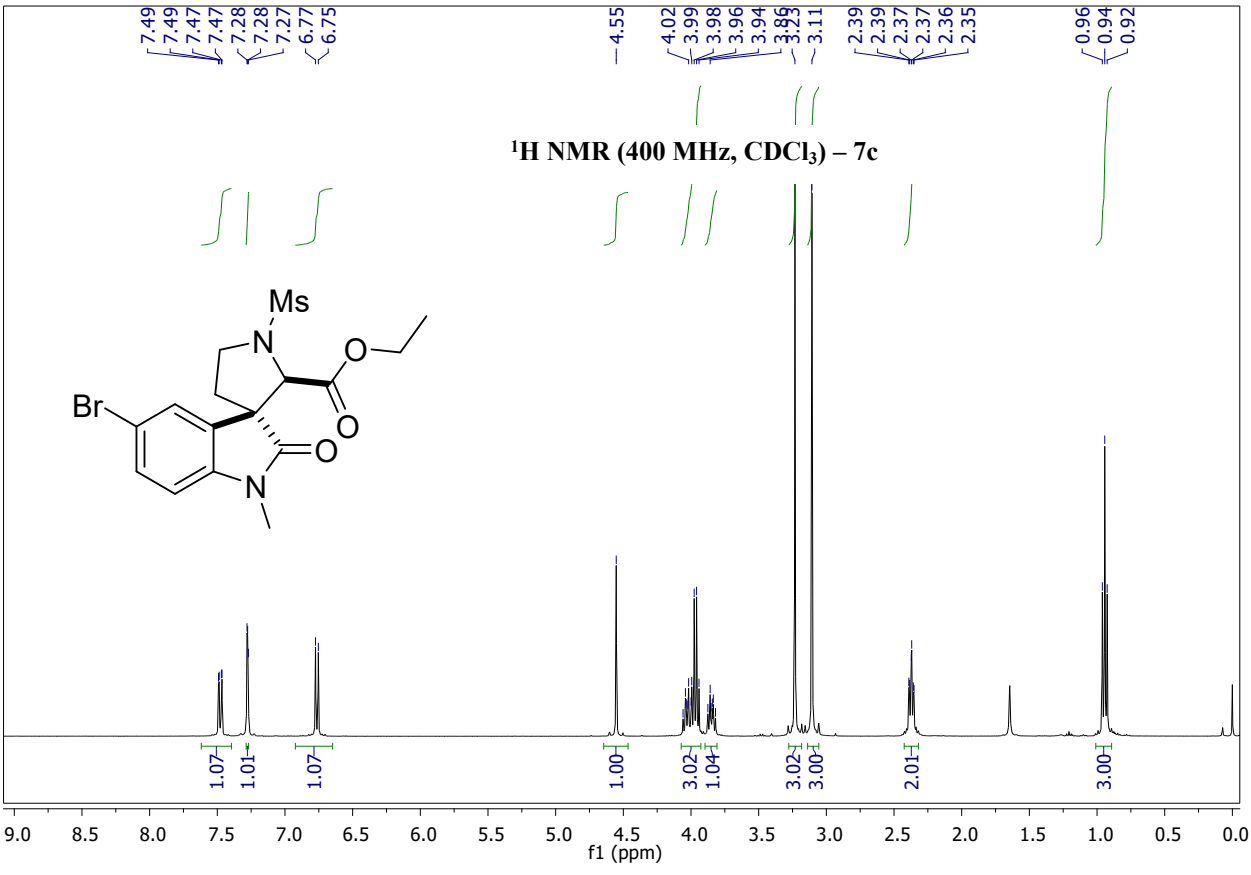
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-7a



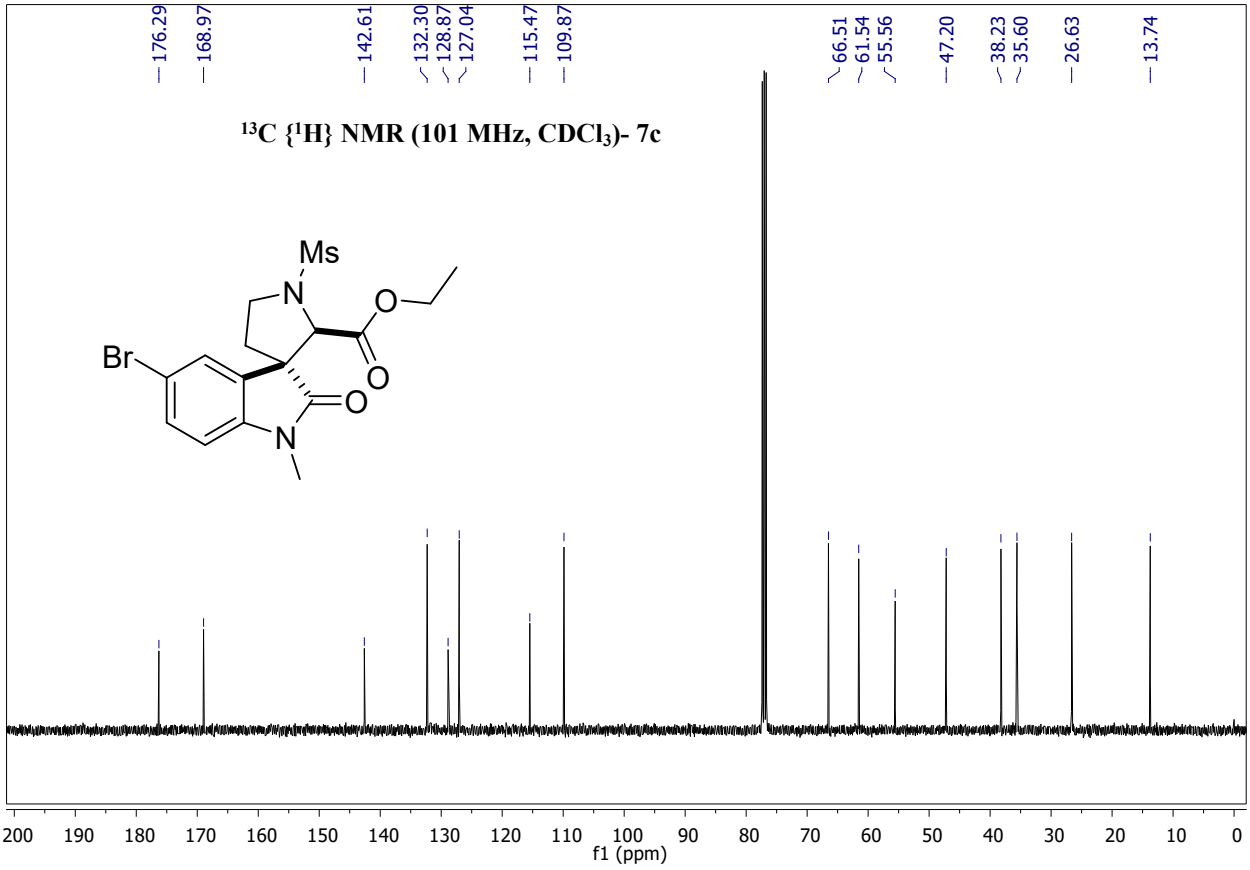
^{1}H NMR (400 MHz, $CDCl_3$) – 7b



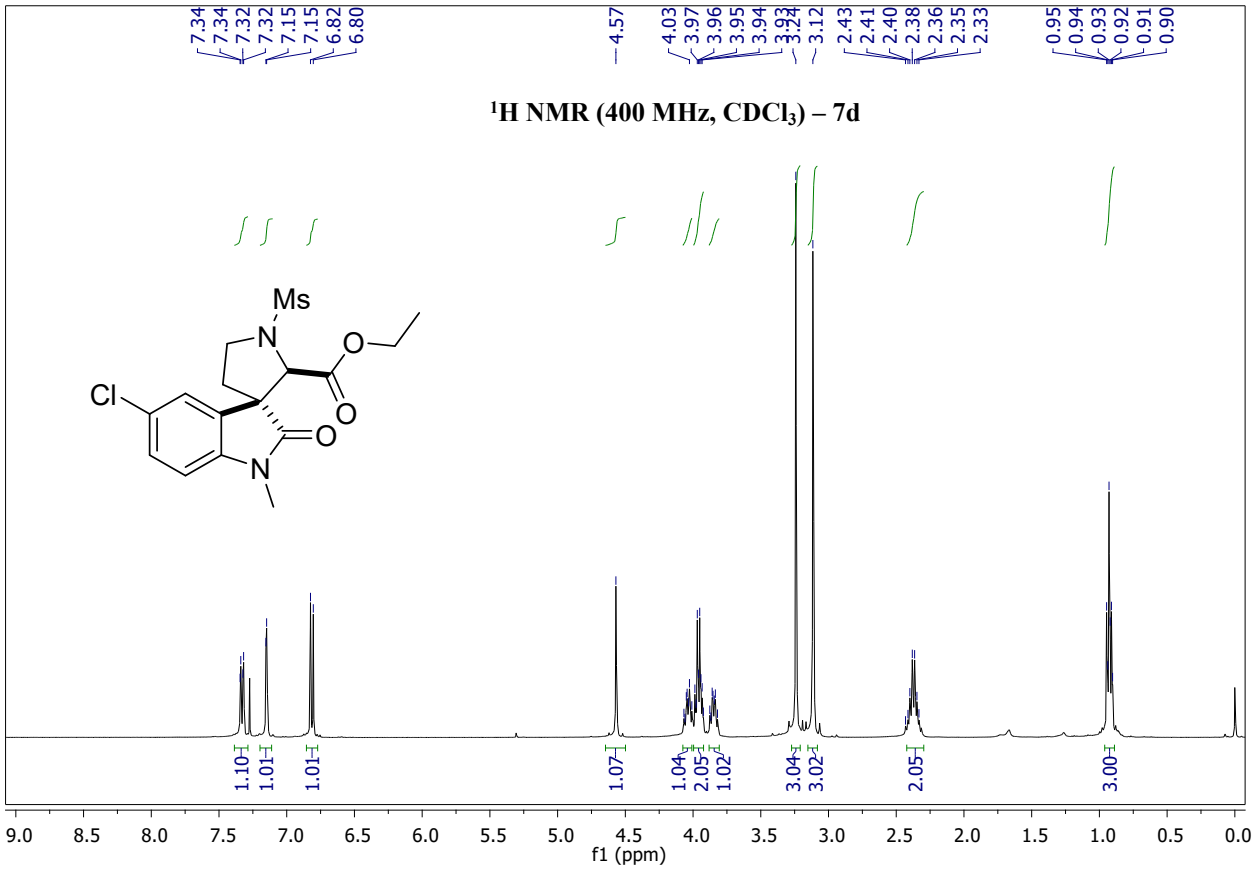
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7b



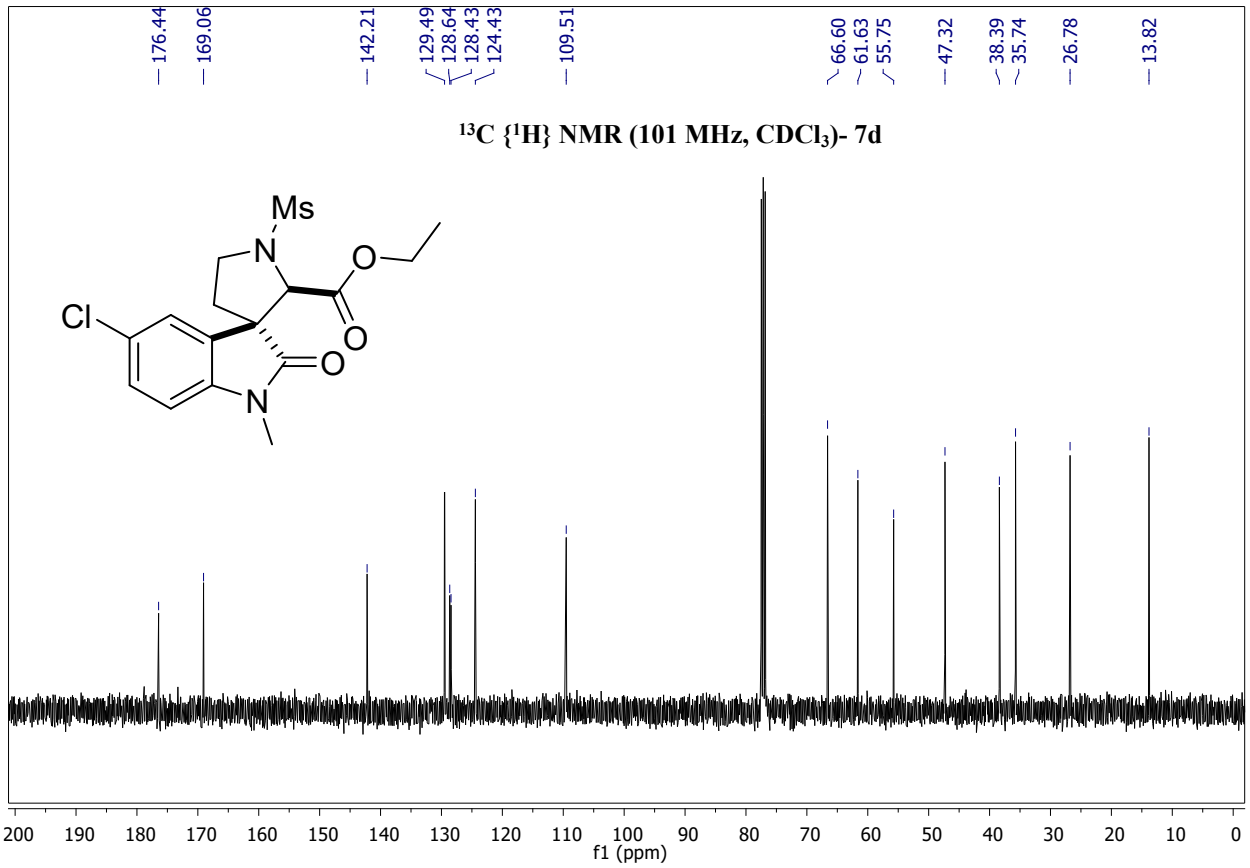
^{1}H NMR (400 MHz, $CDCl_3$) – 7c



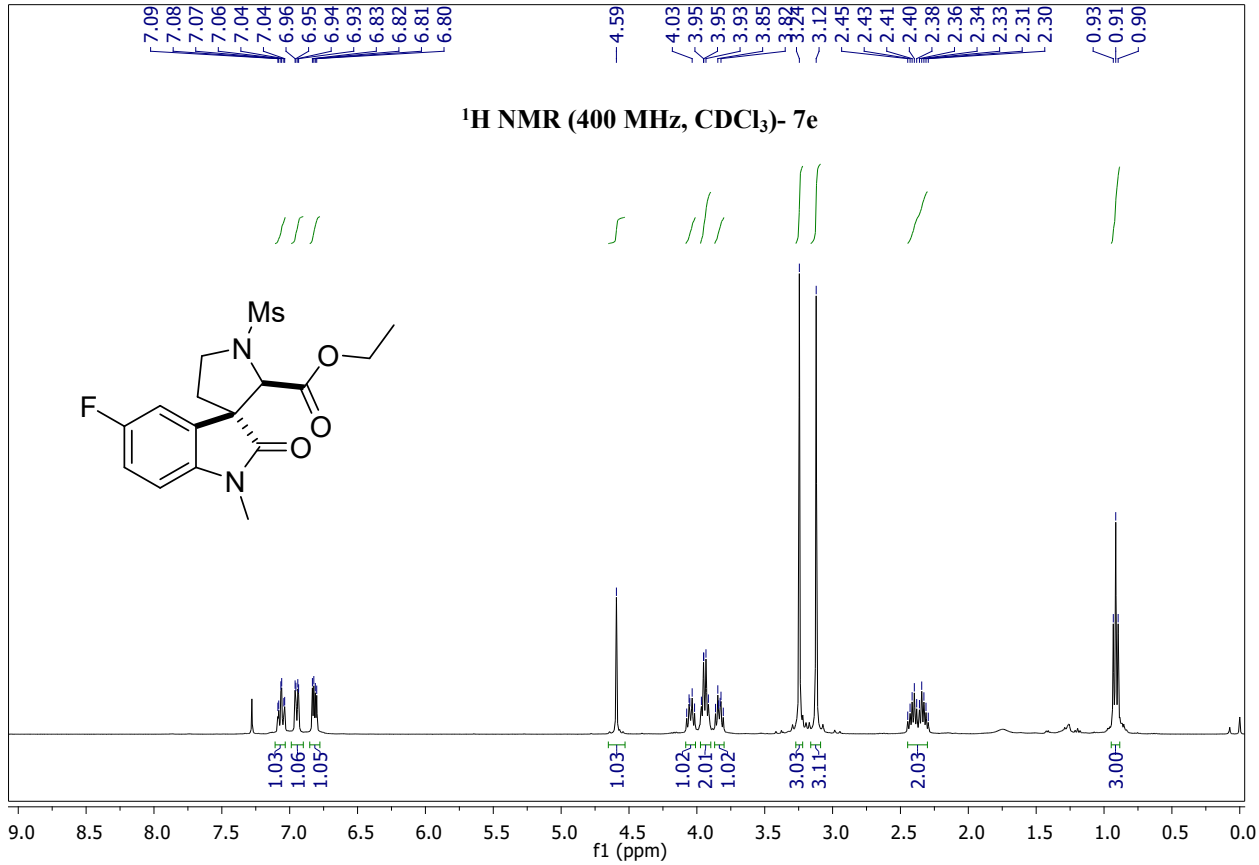
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7c



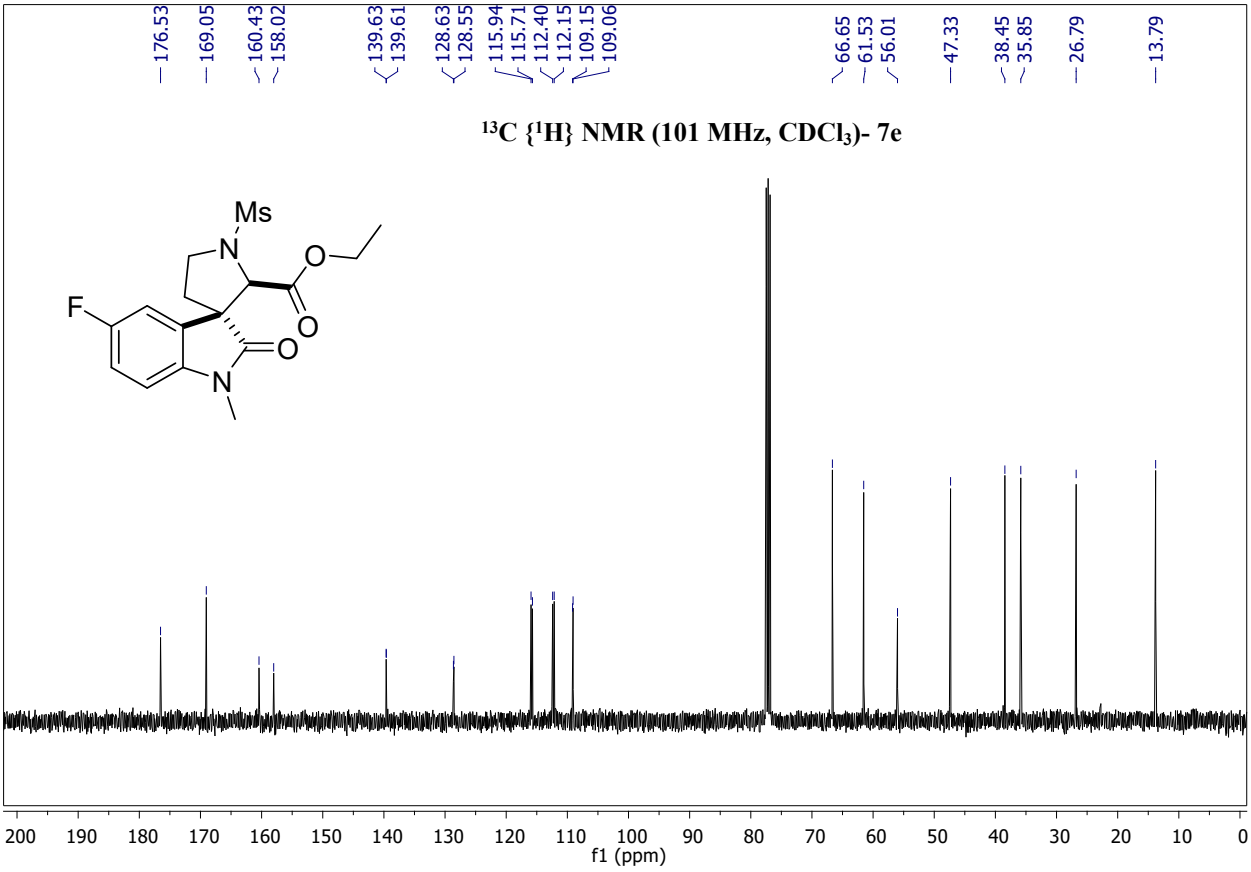
^{1}H NMR (400 MHz, $CDCl_3$) – 7d



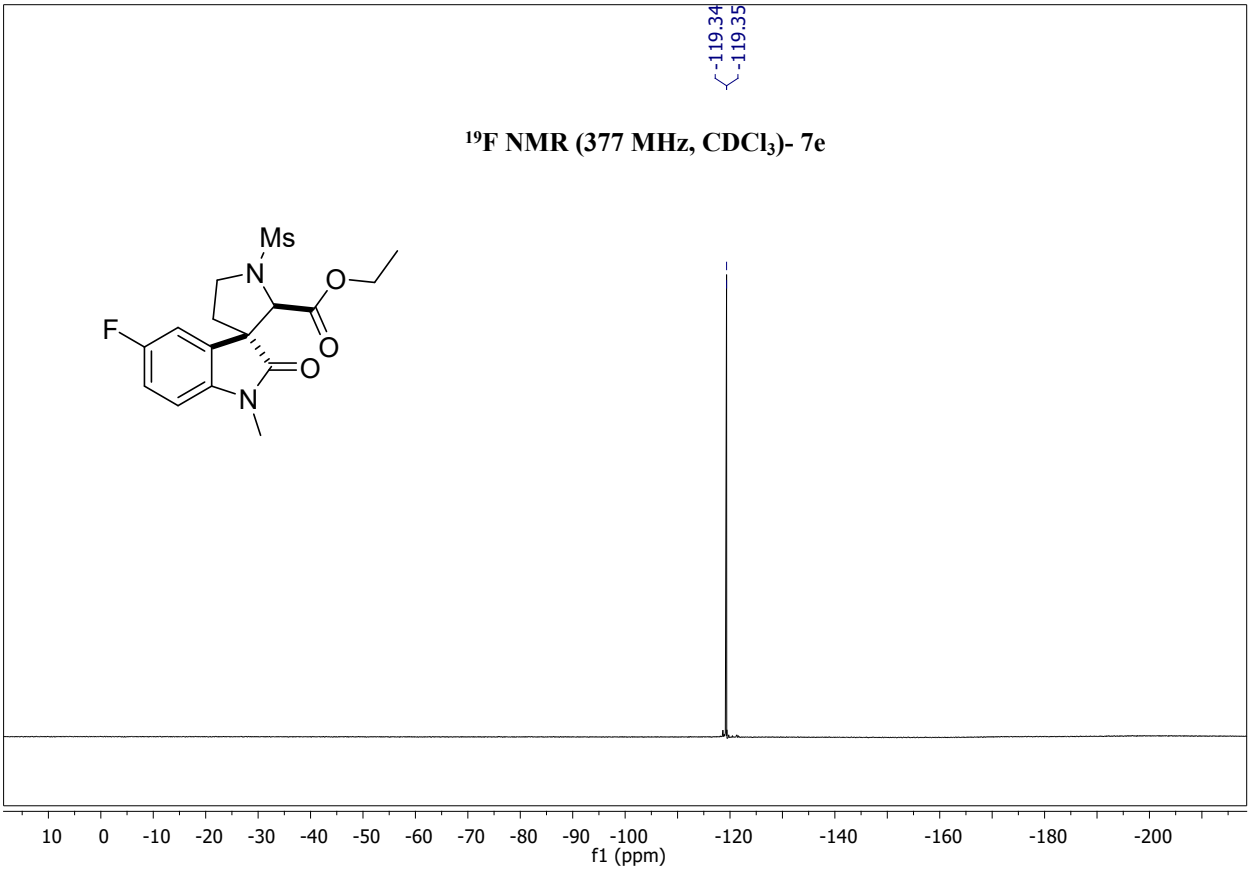
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7d



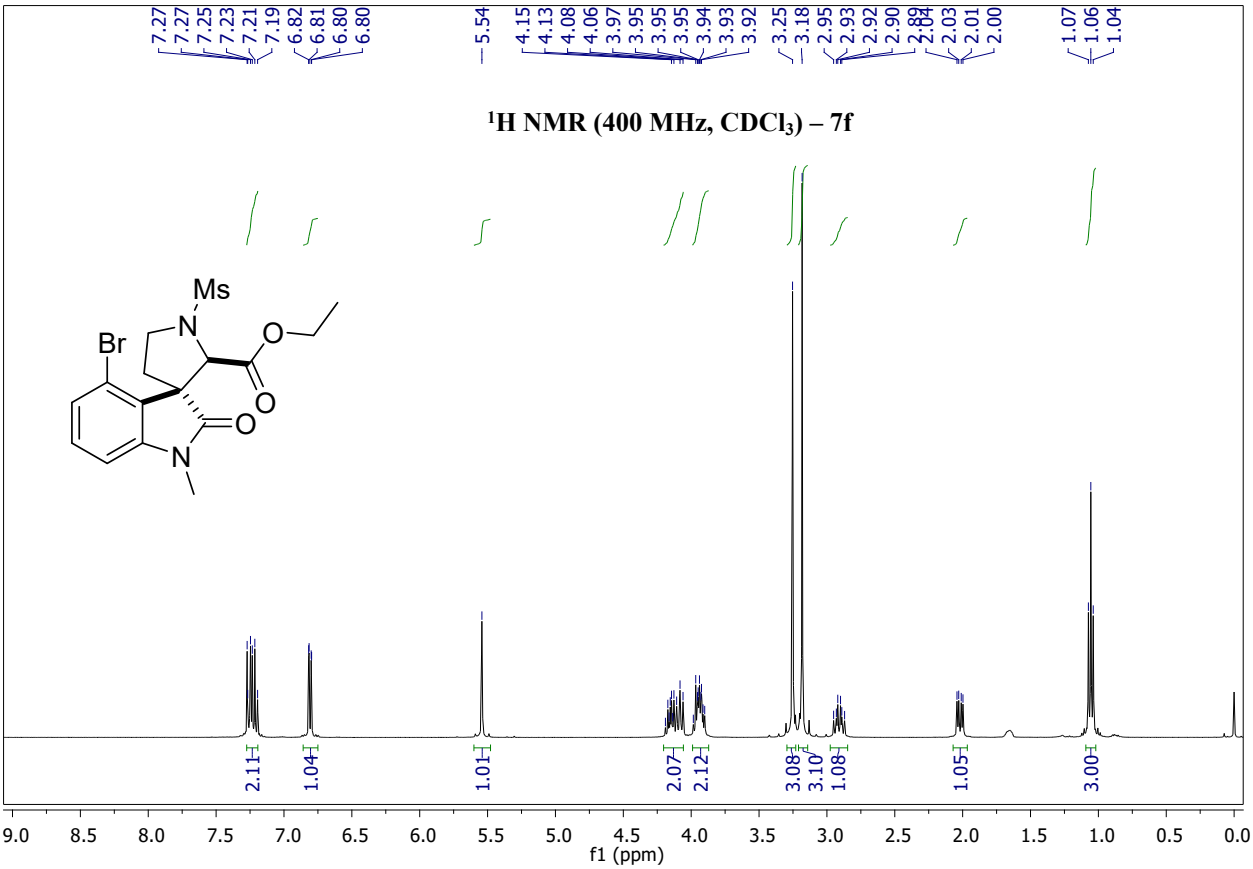
^{1}H NMR (400 MHz, $CDCl_3$)- 7e



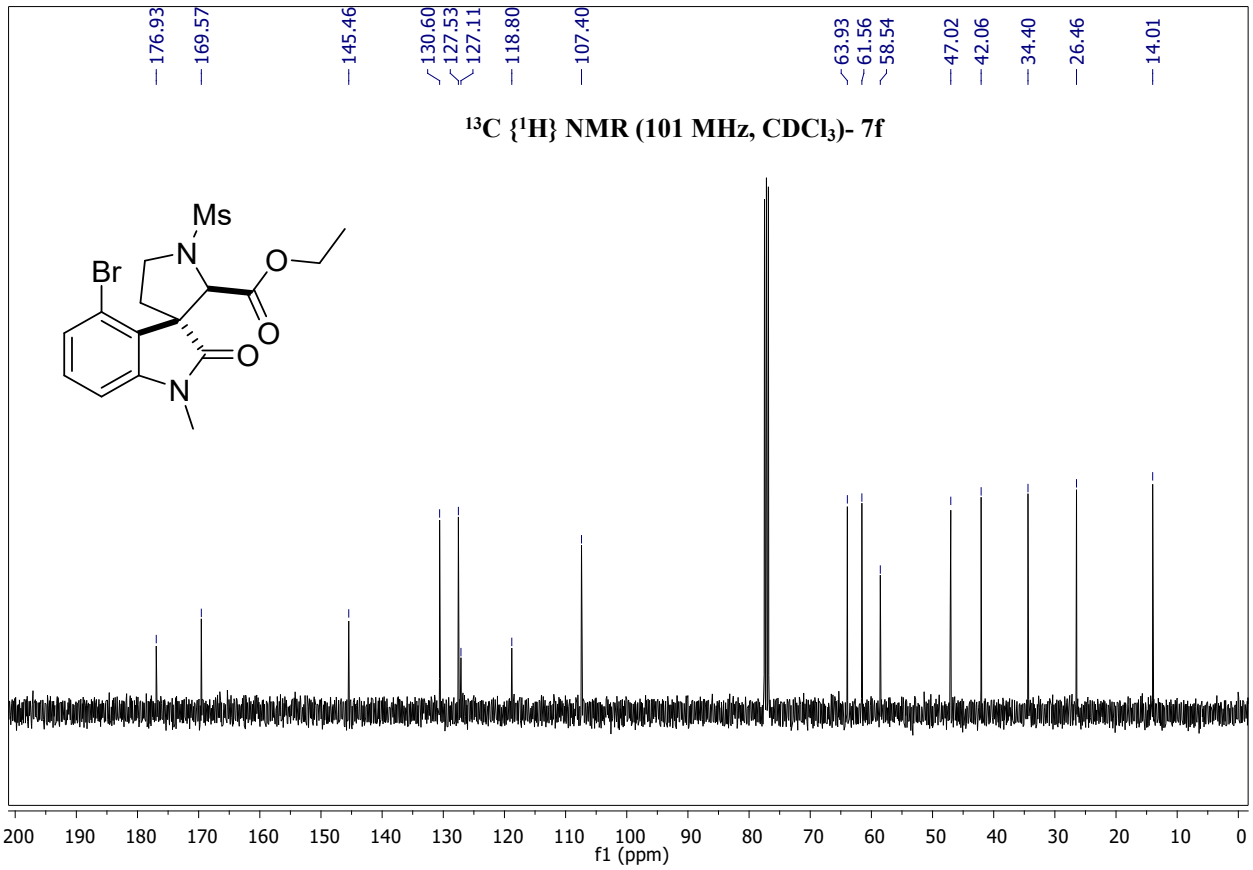
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7e



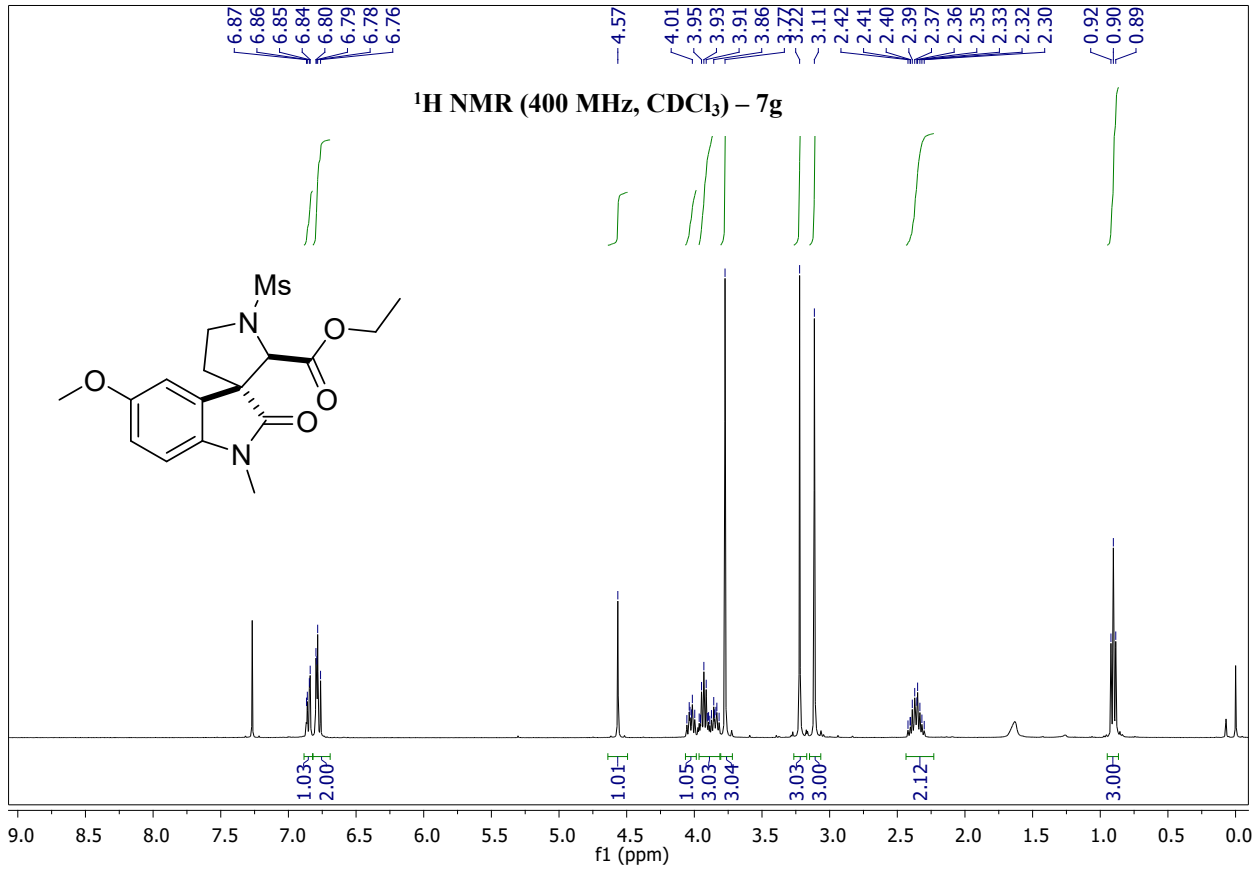
^{19}F NMR (377 MHz, $CDCl_3$)- 7e



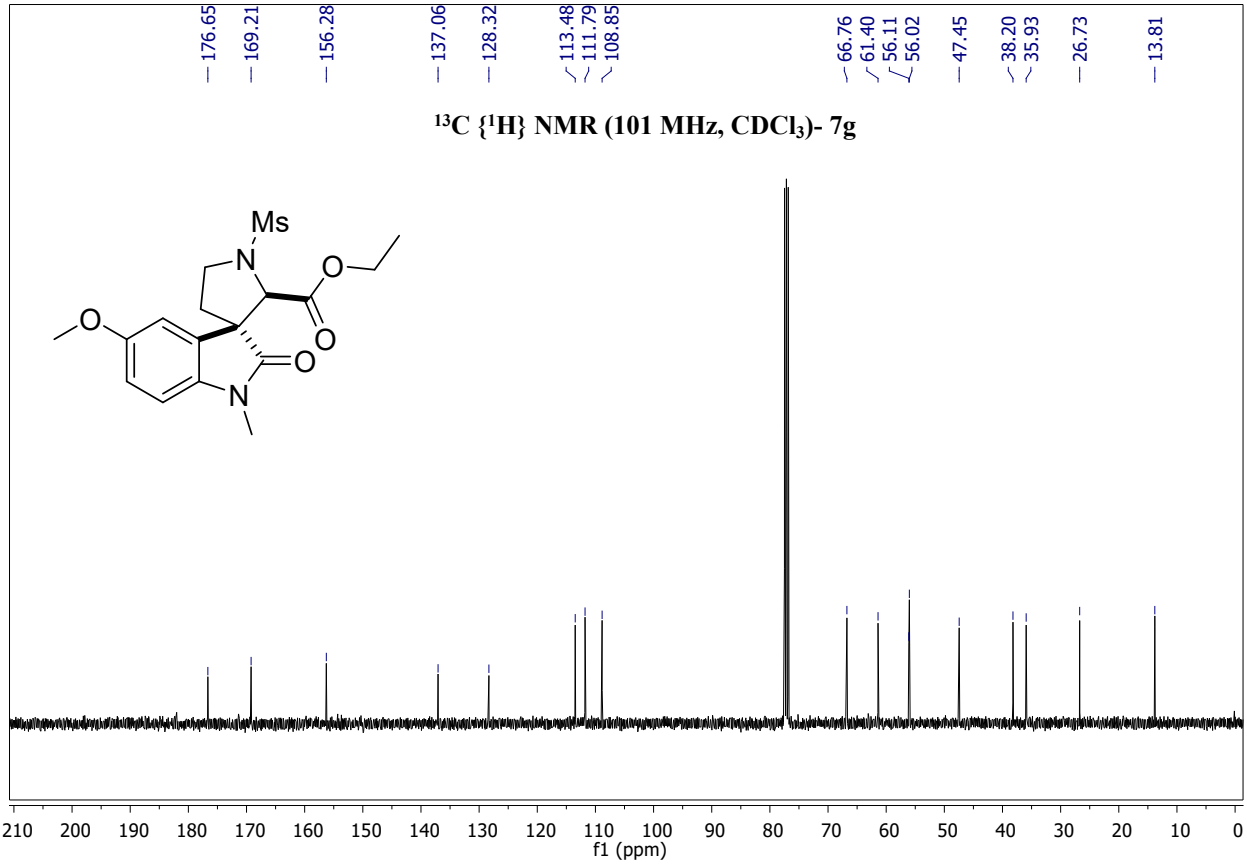
^{1}H NMR (400 MHz, $CDCl_3$) – 7f



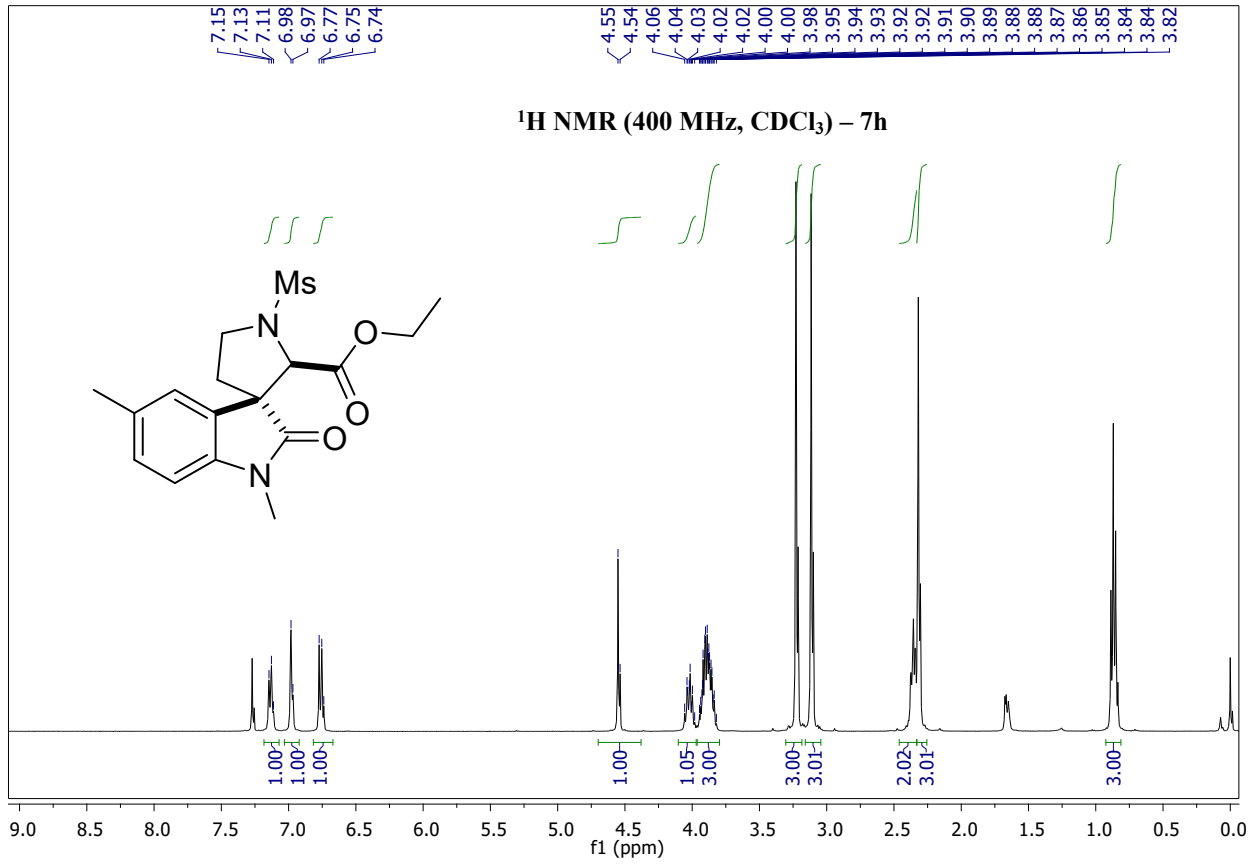
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7f



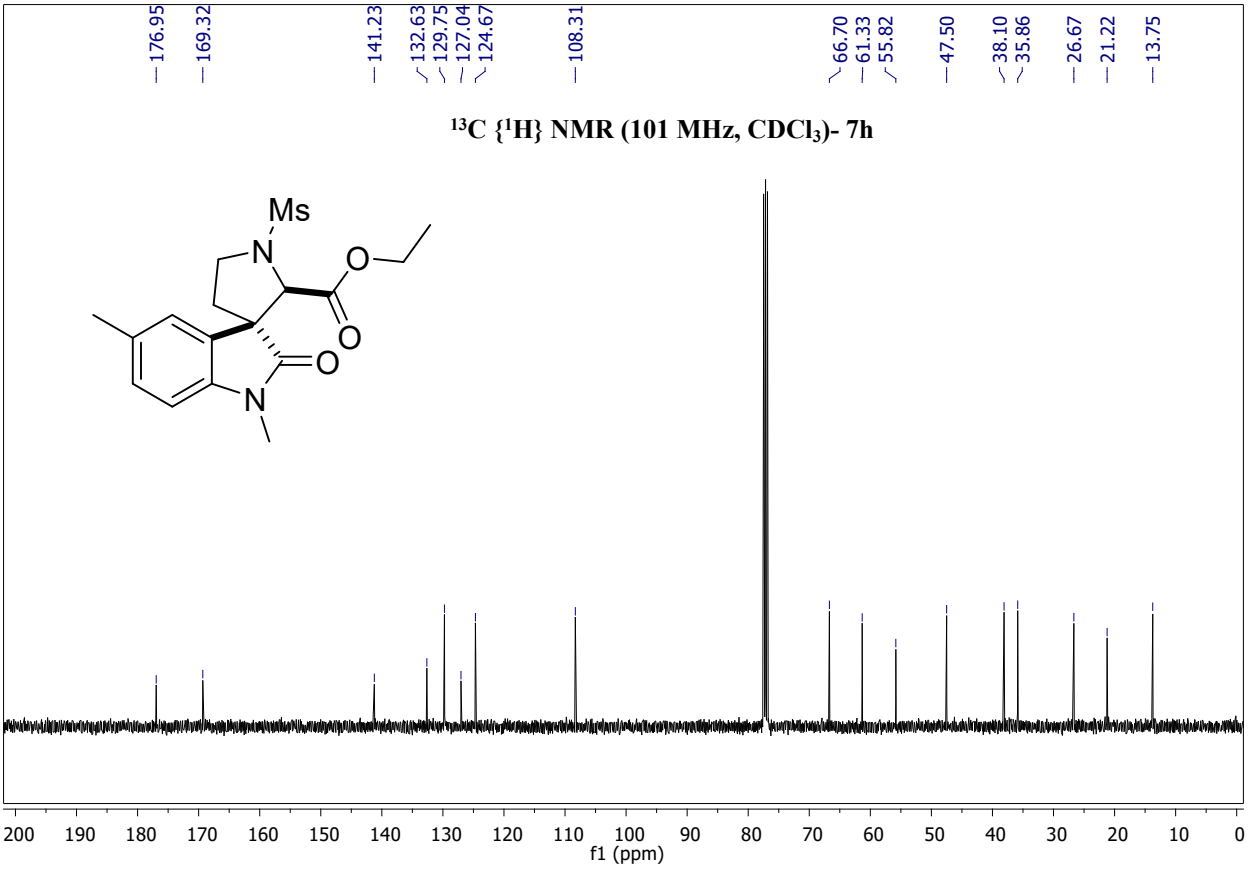
^{1}H NMR (400 MHz, $CDCl_3$) – 7g



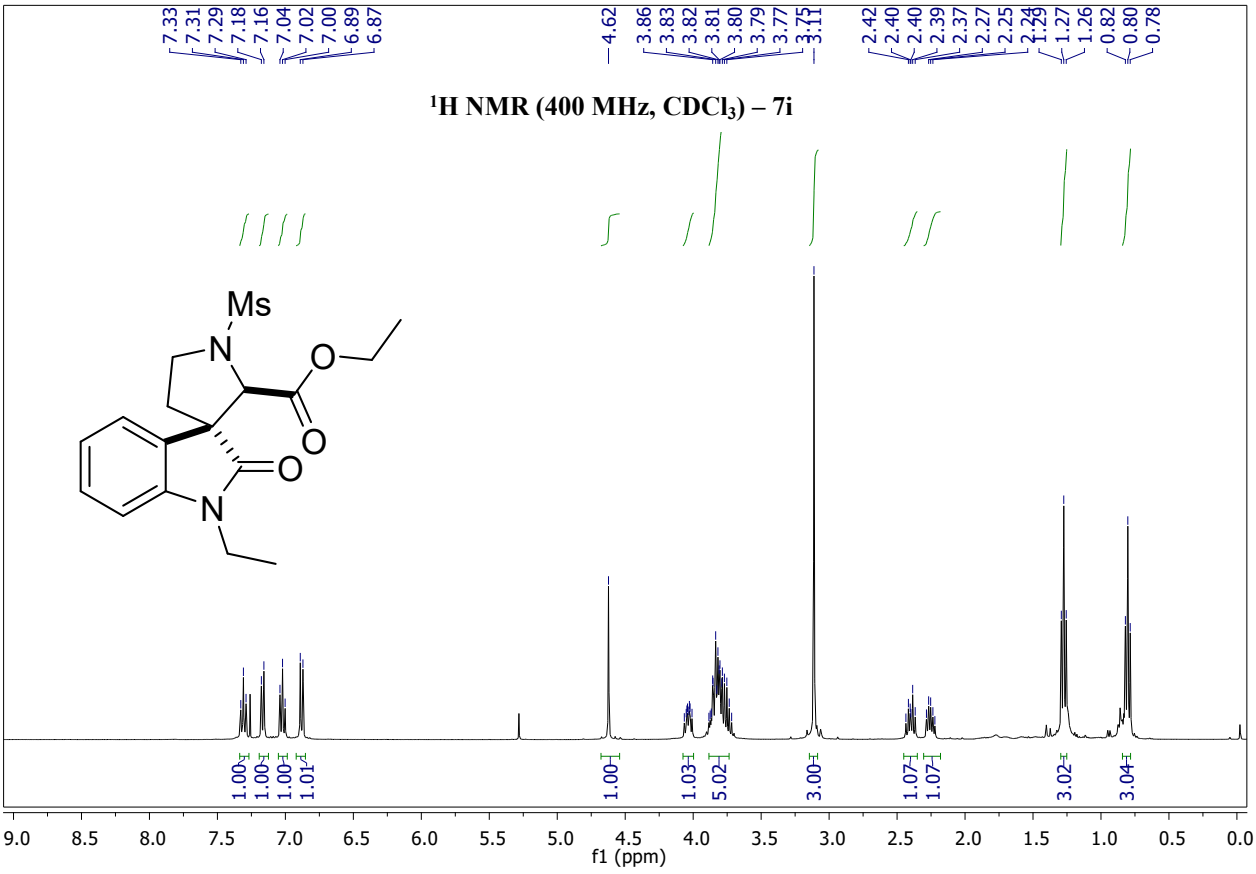
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7g



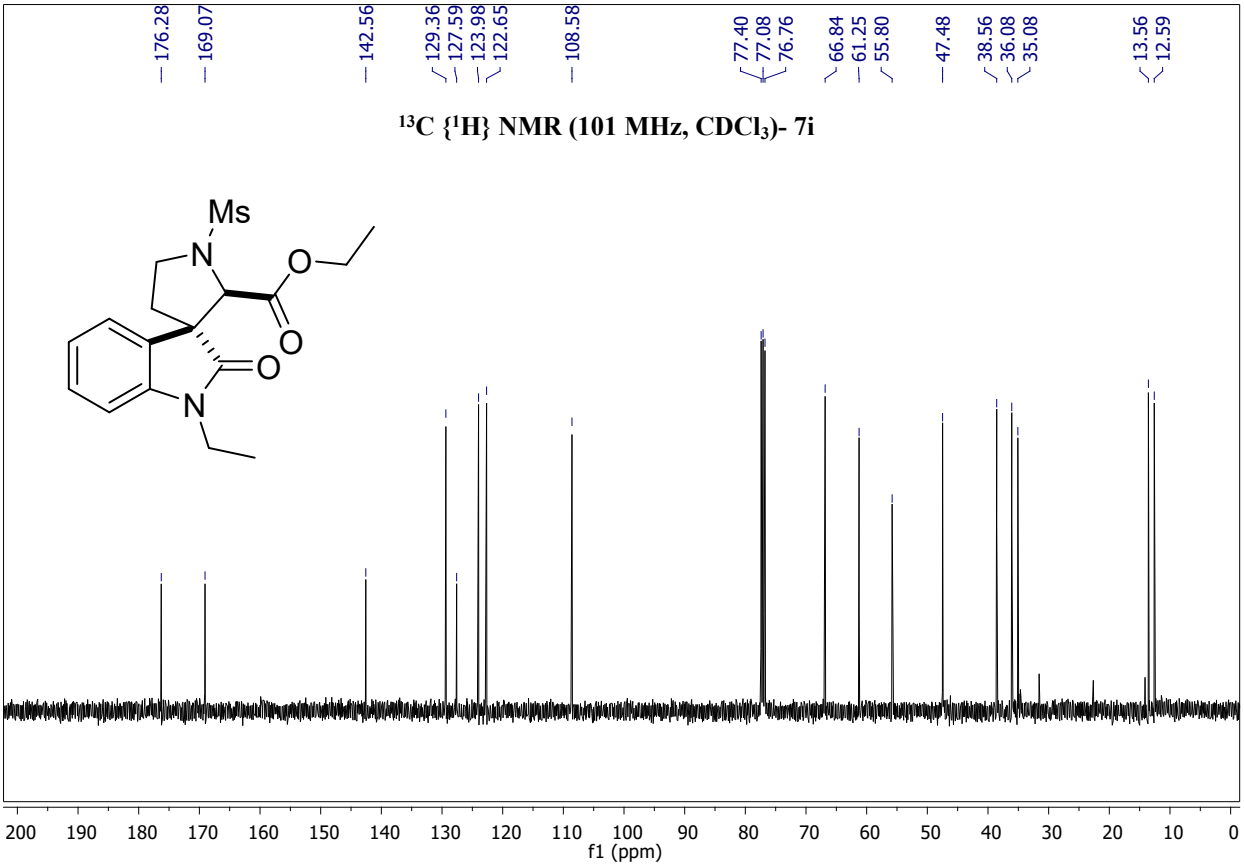
^{1}H NMR (400 MHz, $CDCl_3$) – 7h



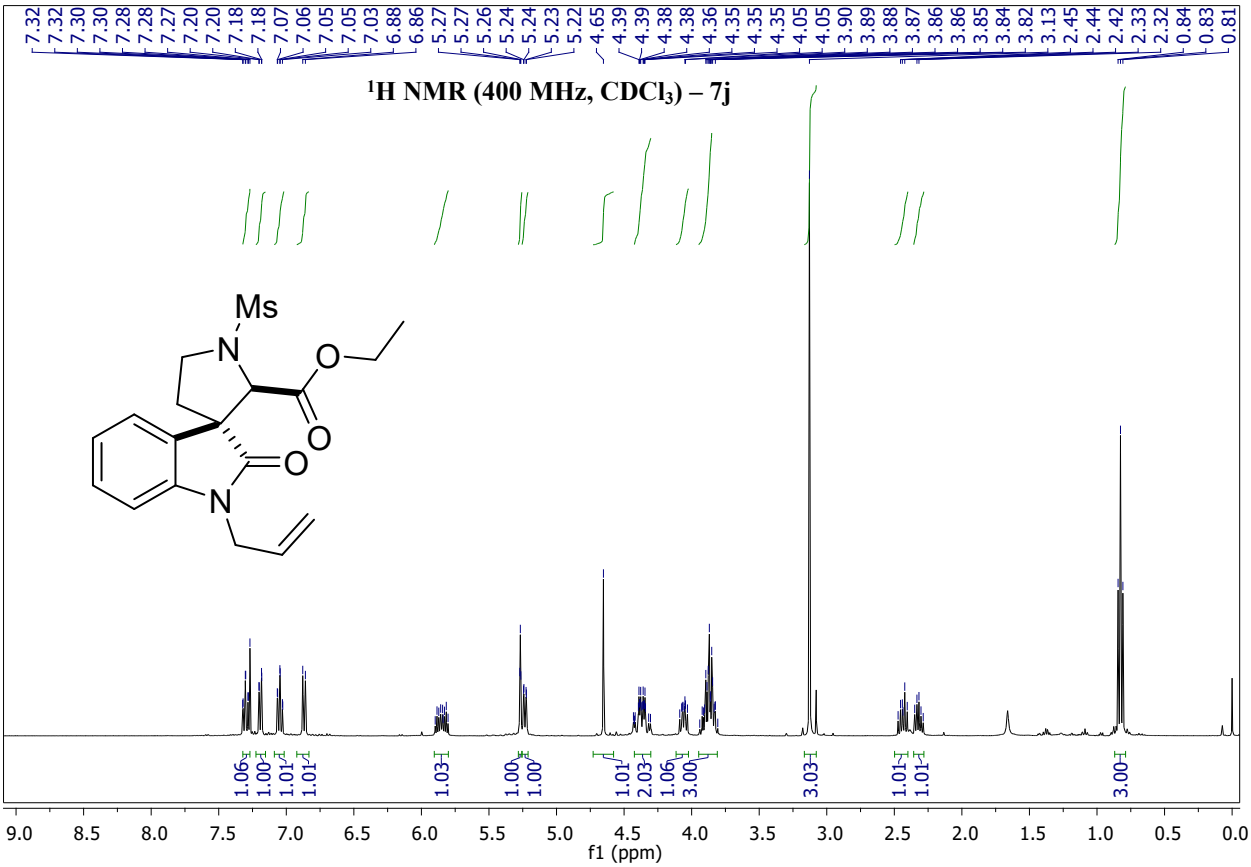
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7h



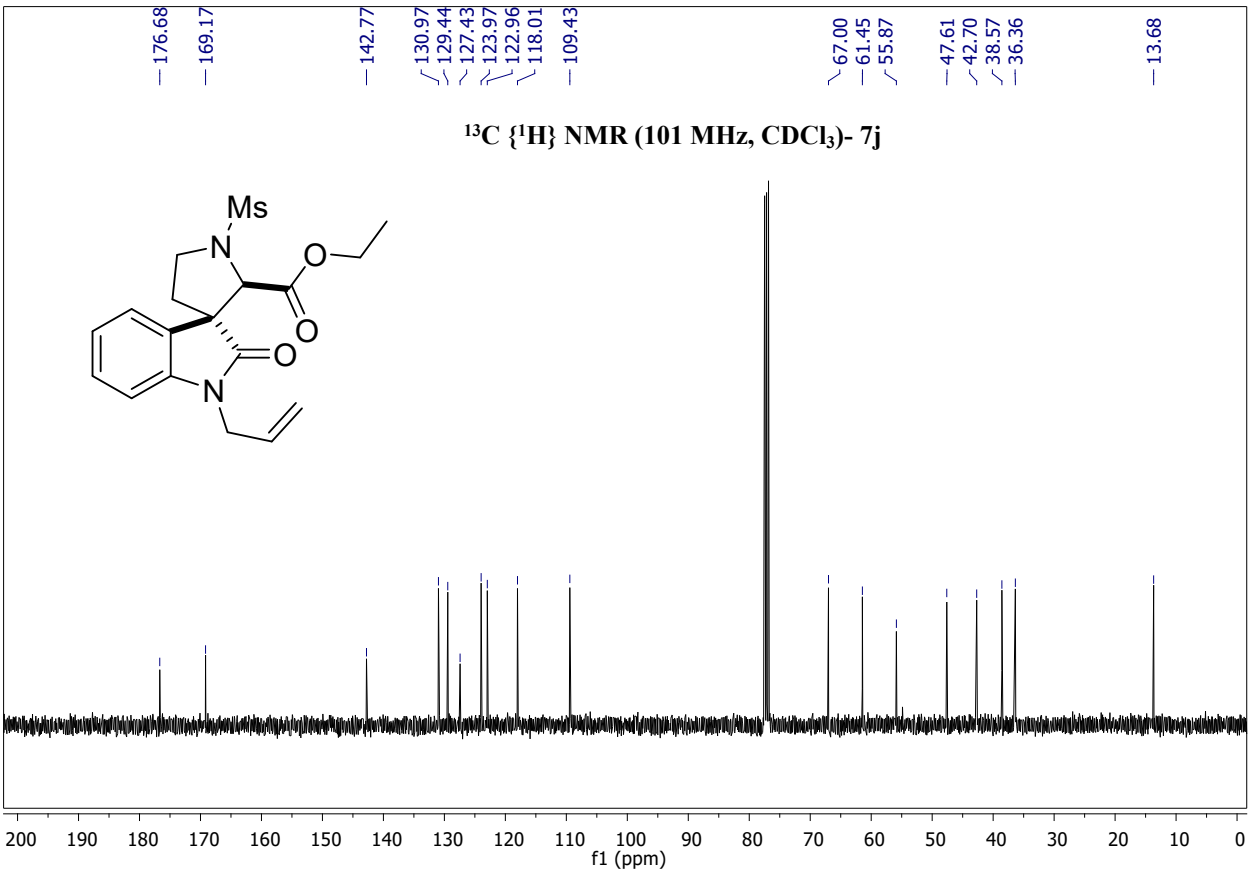
^{1}H NMR (400 MHz, $CDCl_3$) – 7i



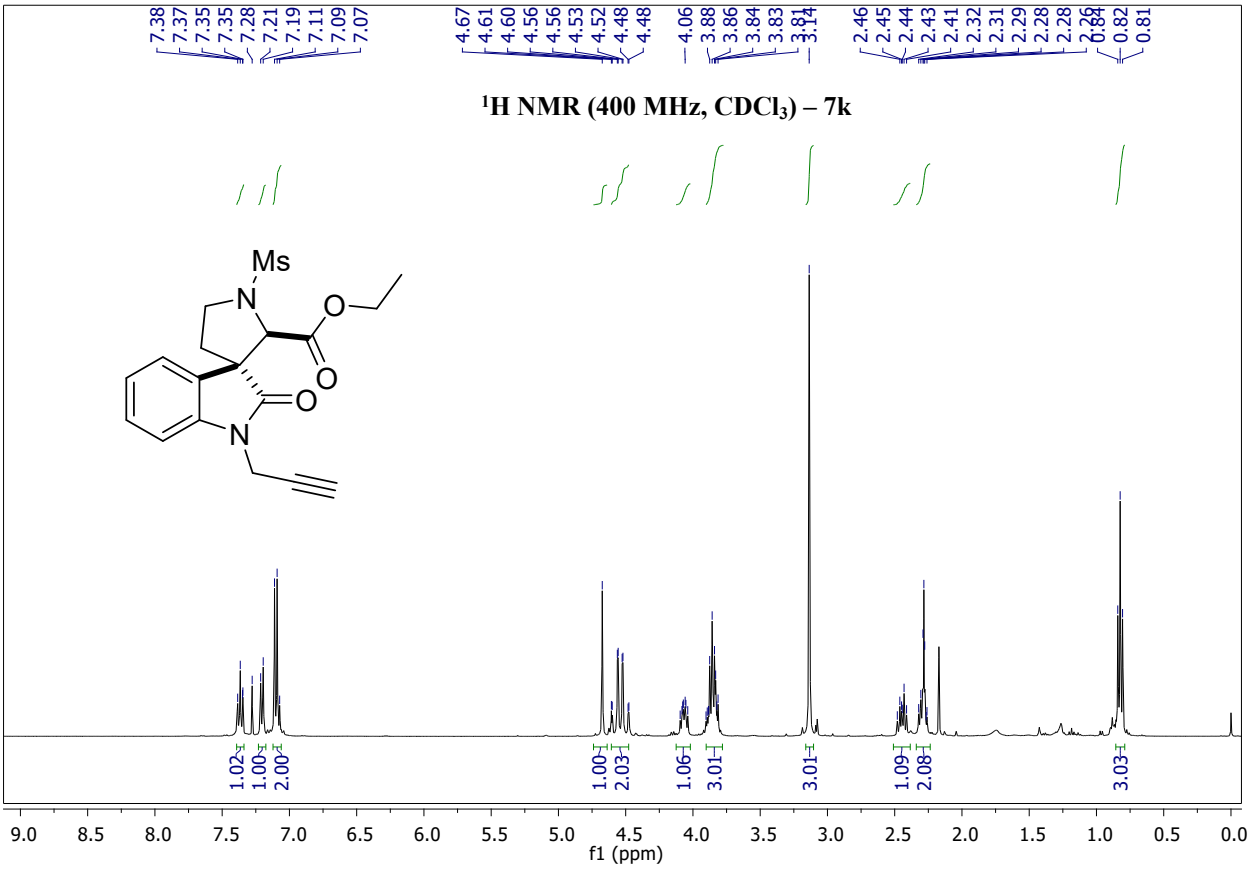
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7i



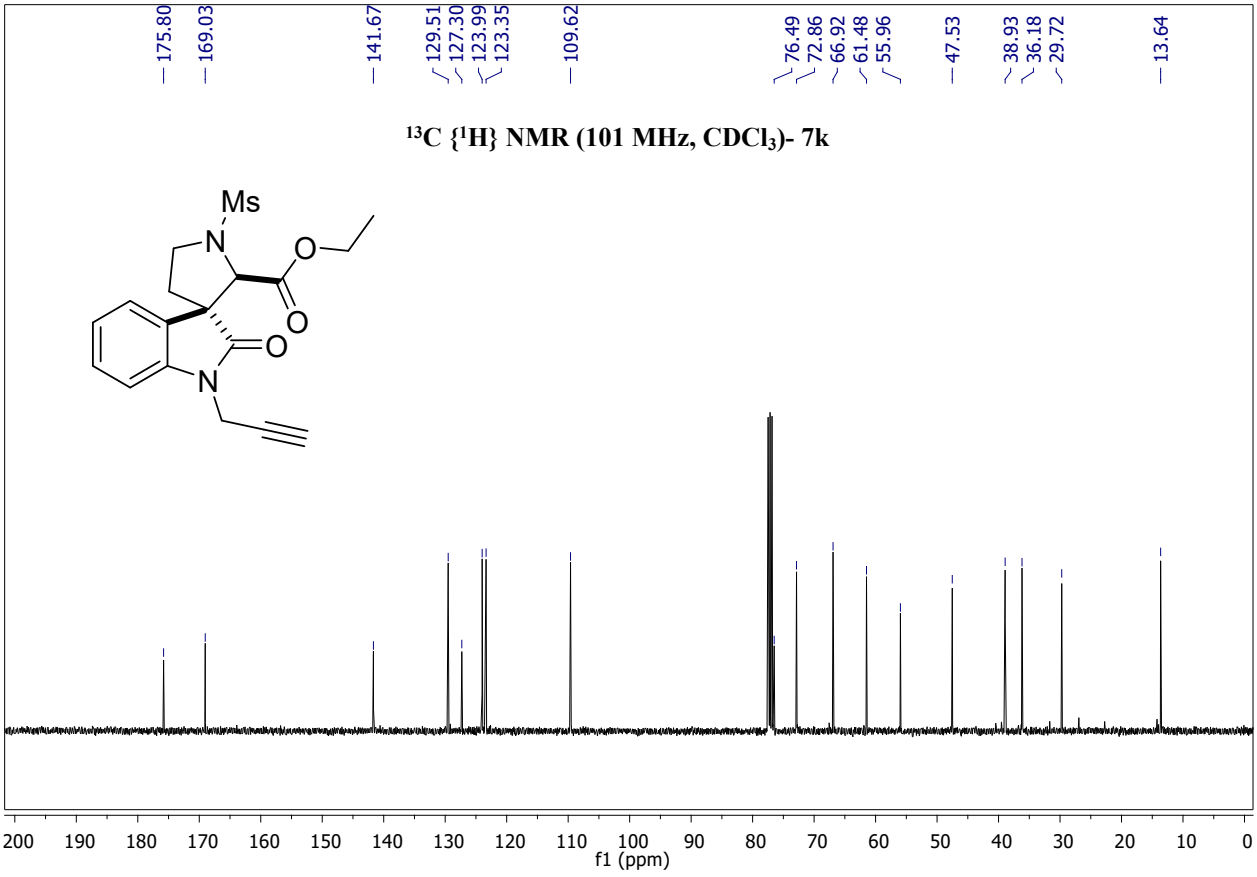
^{1}H NMR (400 MHz, $CDCl_3$) – 7j



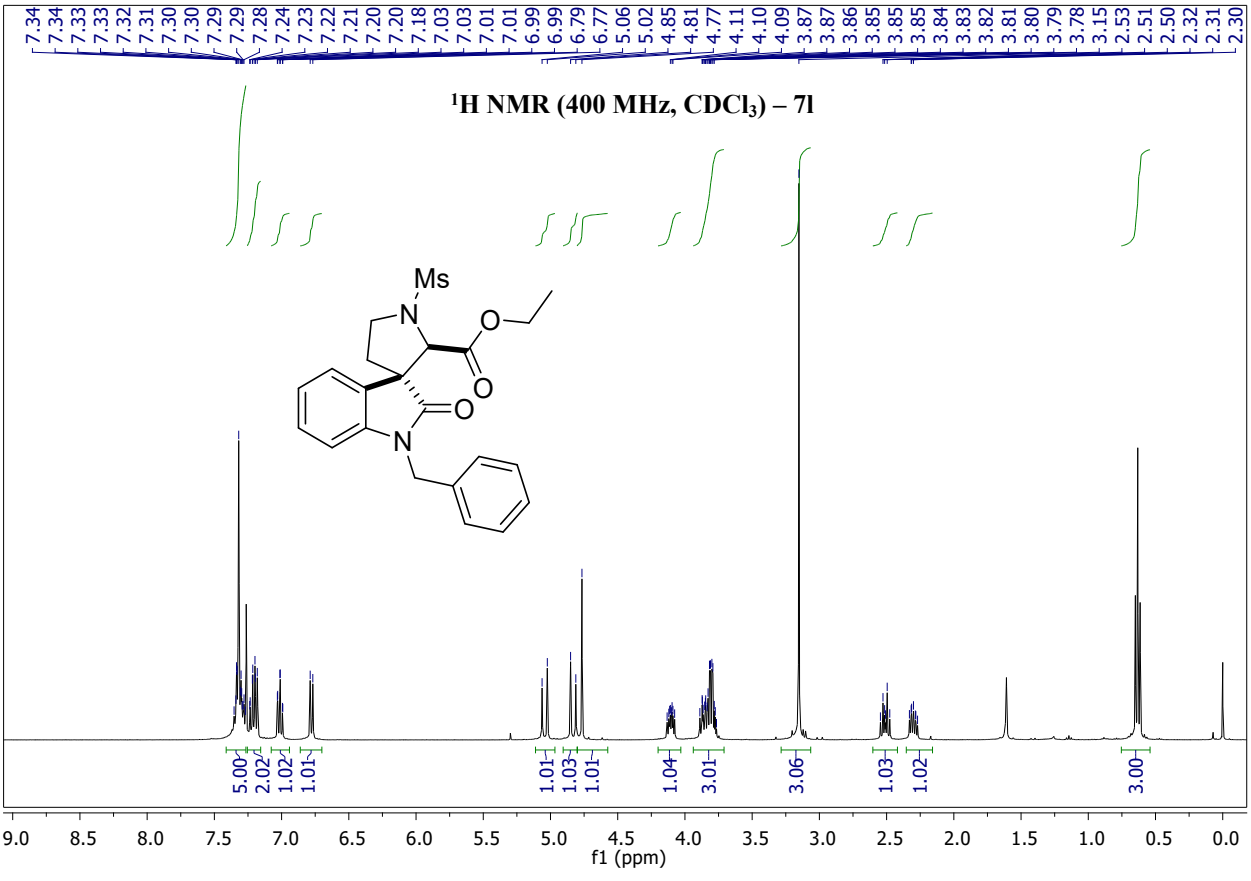
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7j



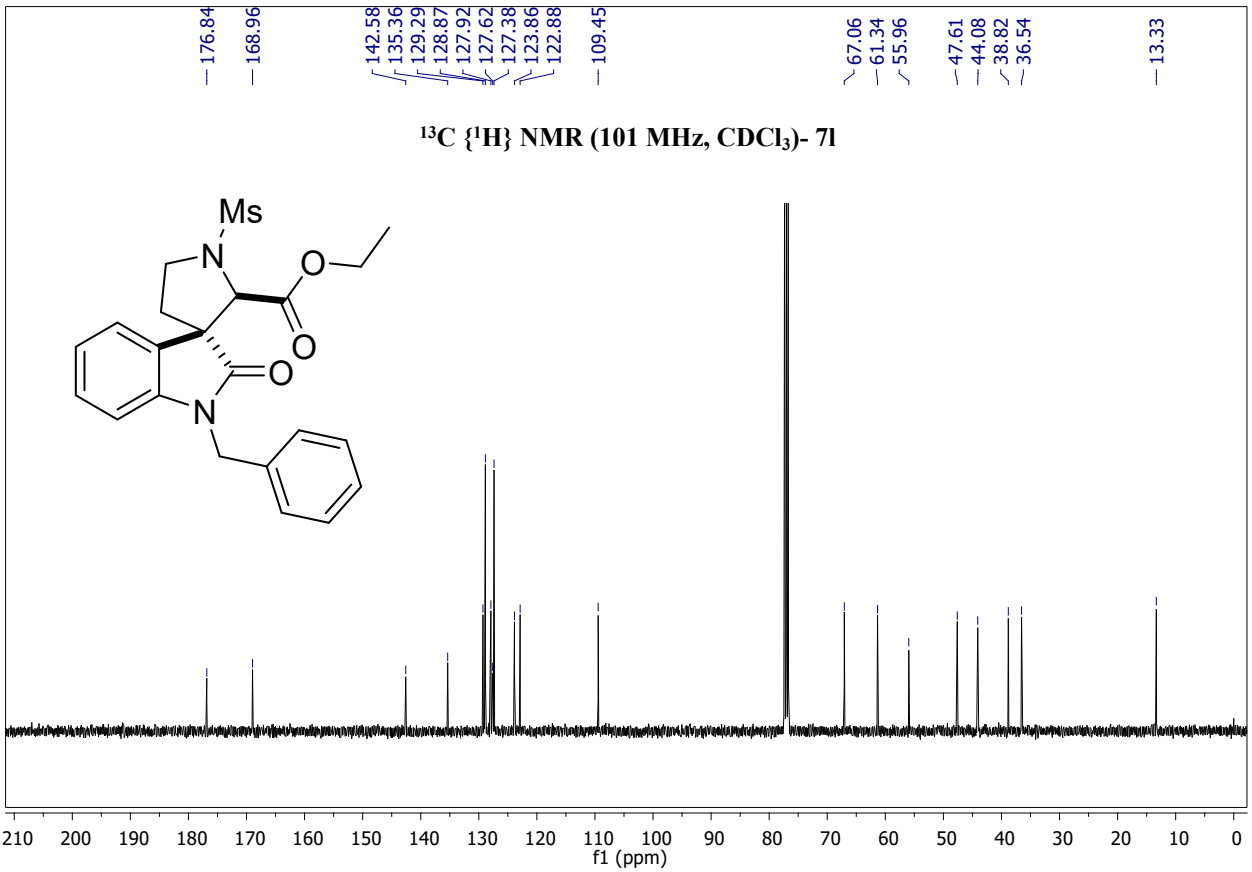
^{1}H NMR (400 MHz, $CDCl_3$) – 7k



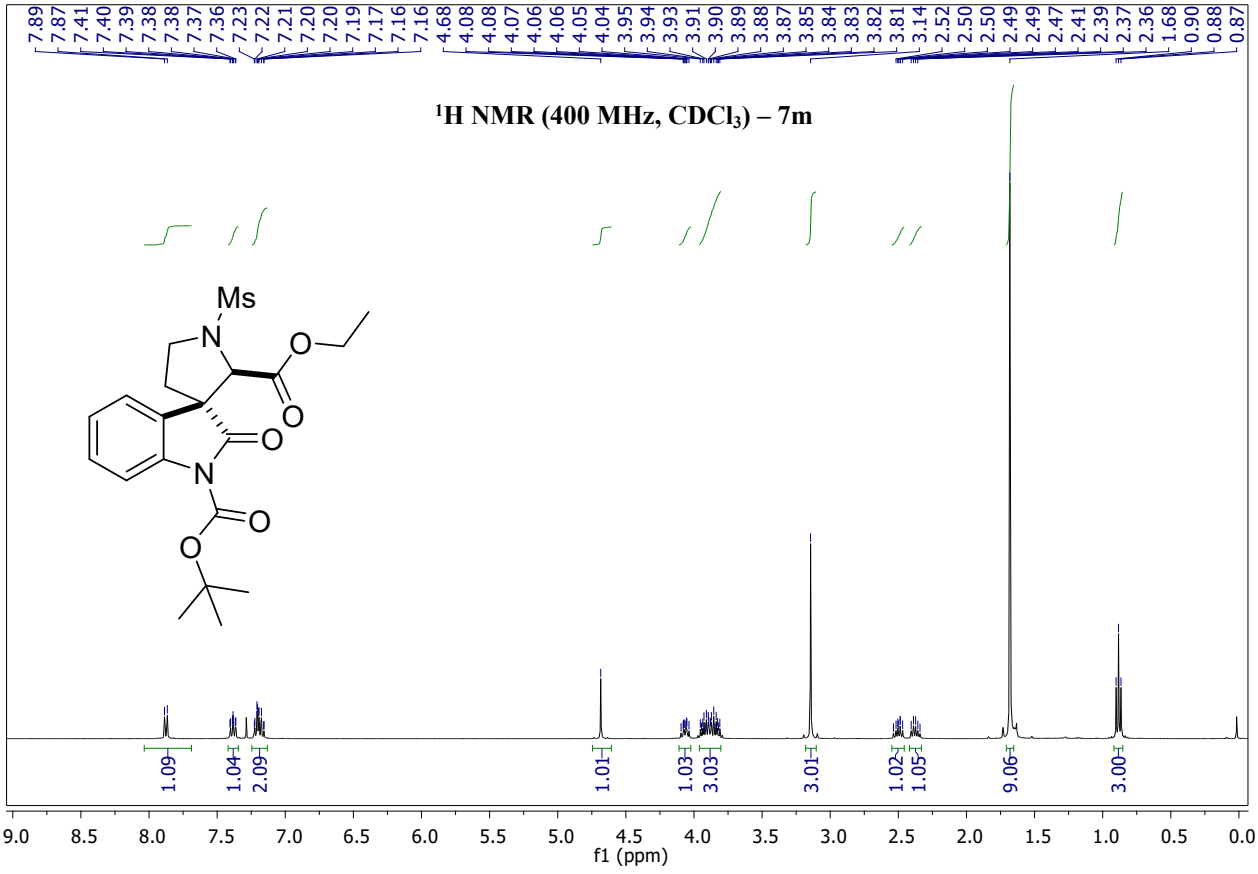
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7k



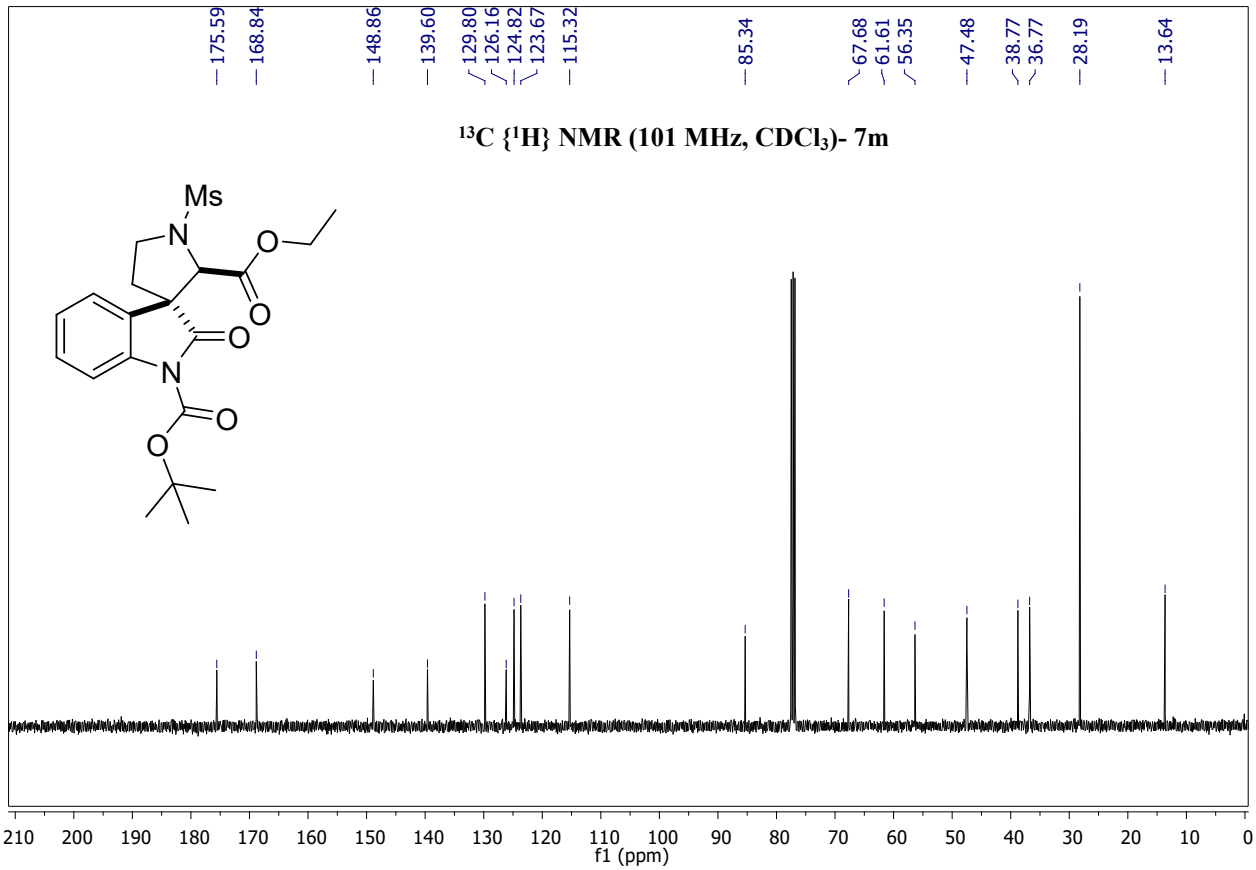
^{1}H NMR (400 MHz, $CDCl_3$) – 7l



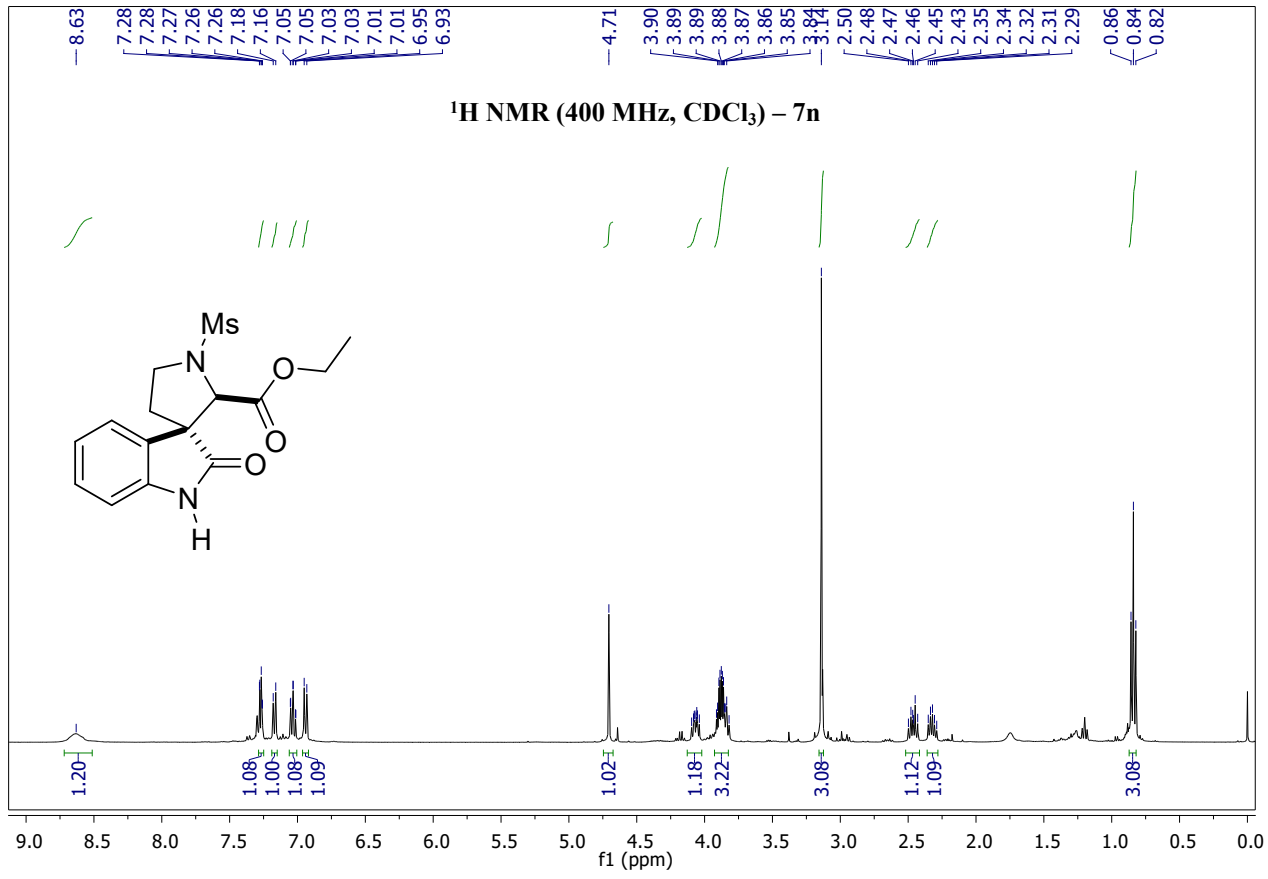
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7l



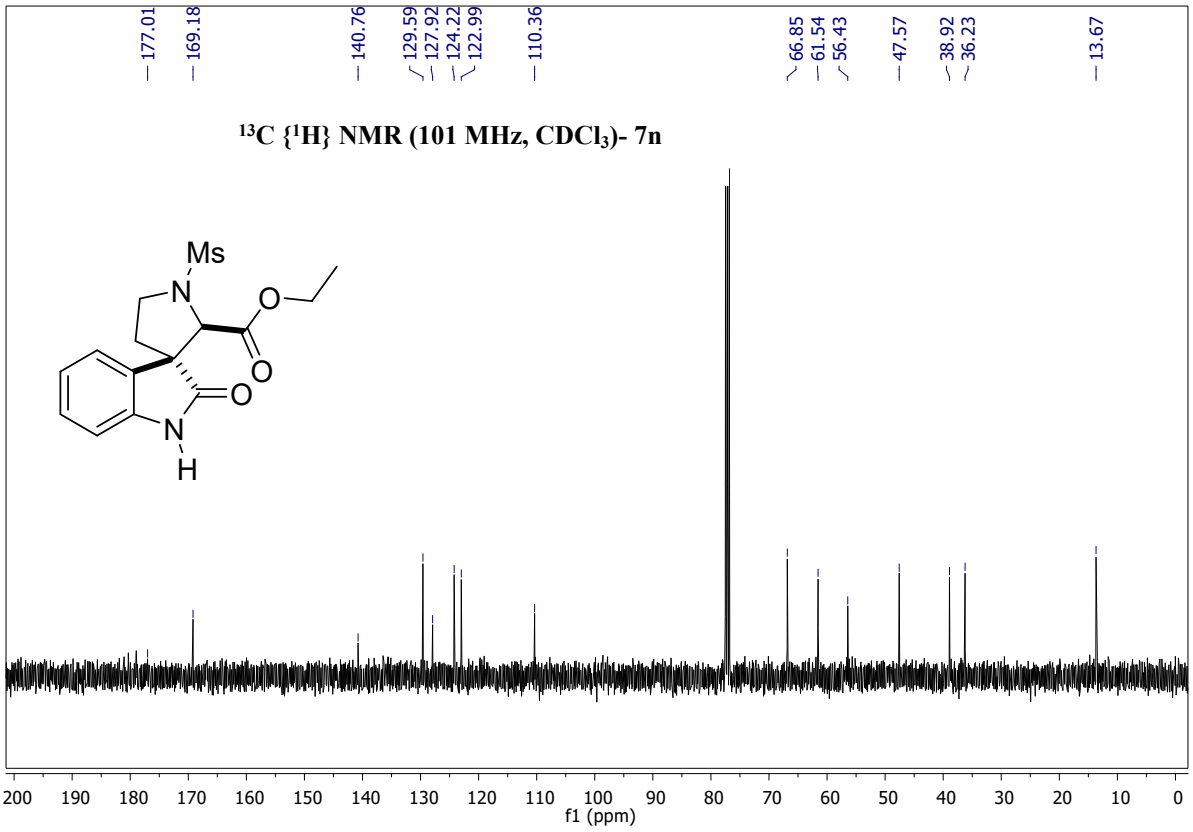
^{1}H NMR (400 MHz, $CDCl_3$) – 7m



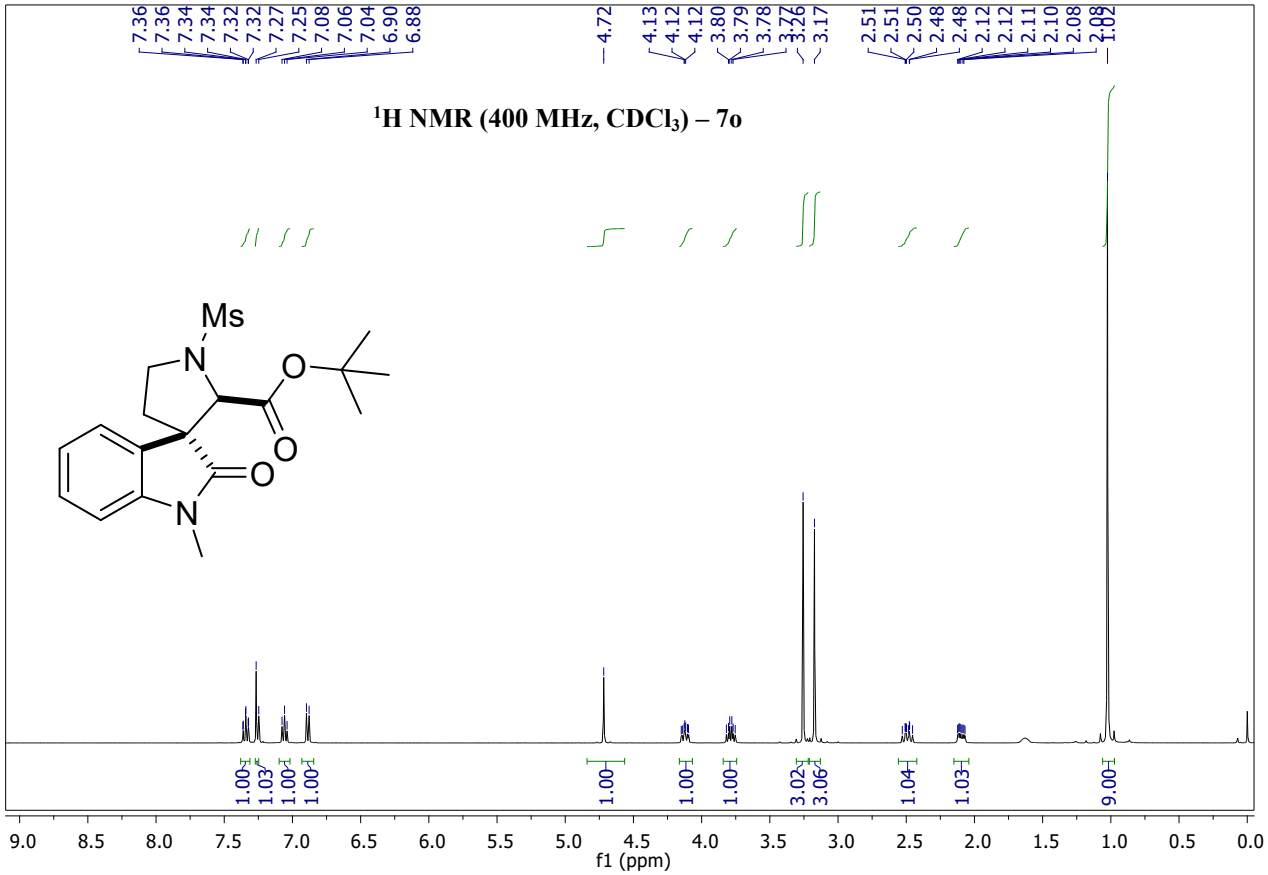
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7m



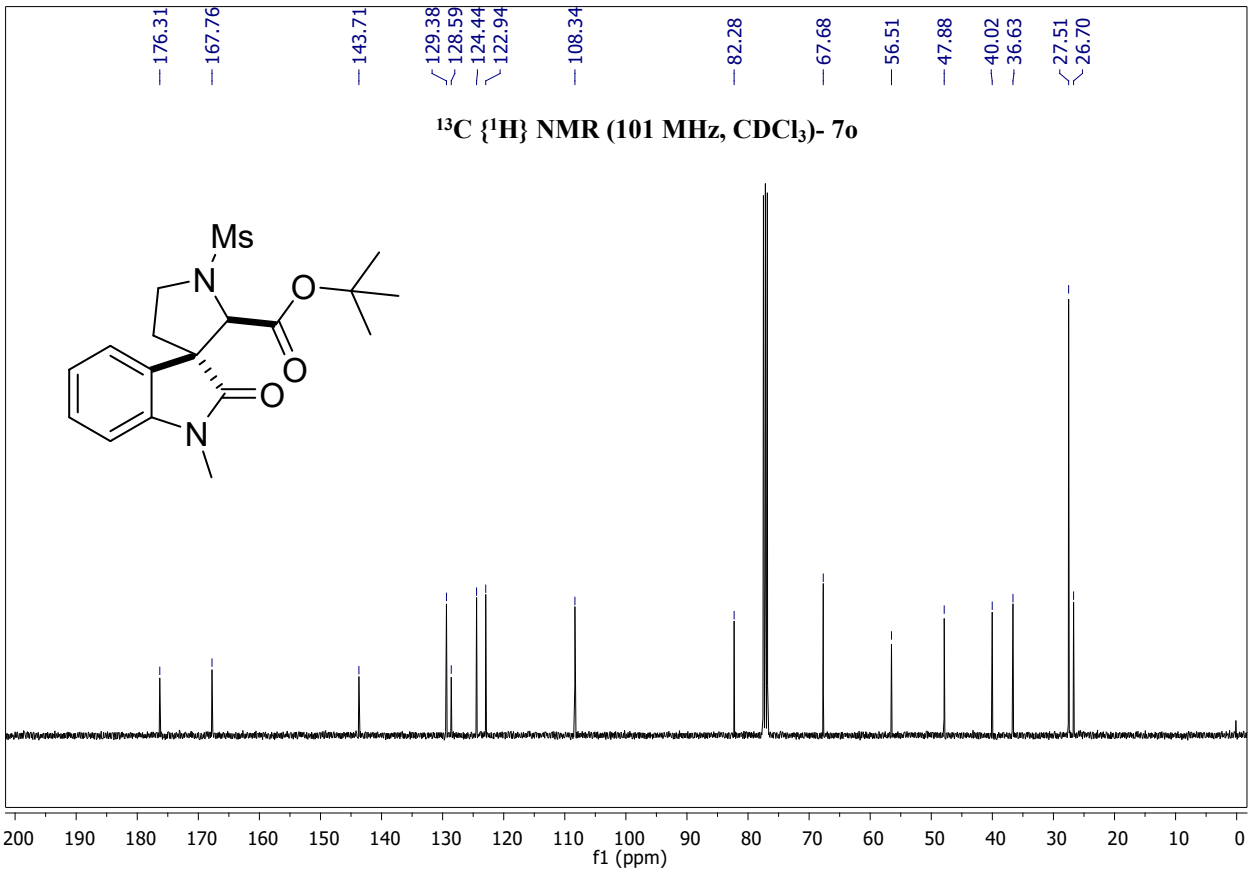
^{1}H NMR (400 MHz, $CDCl_3$) – 7n



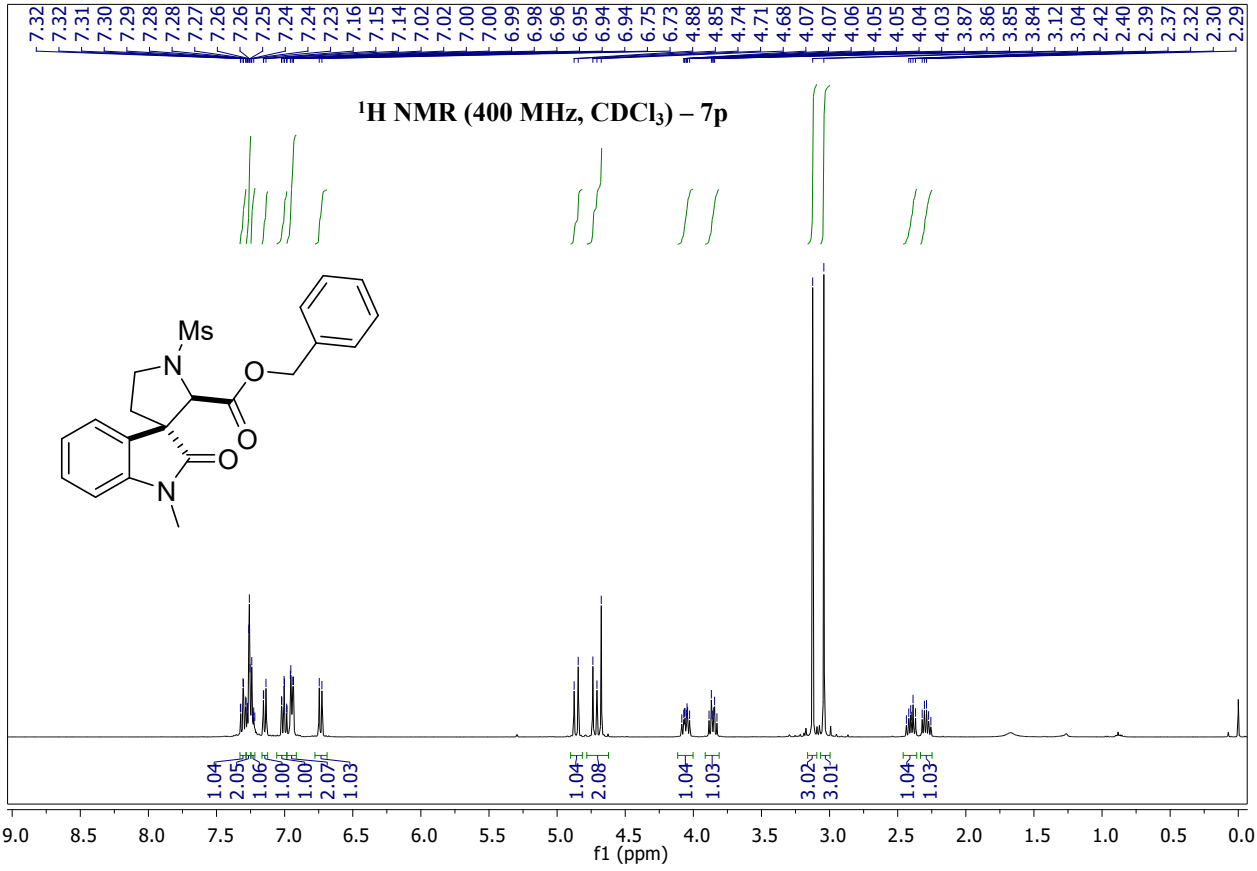
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7n



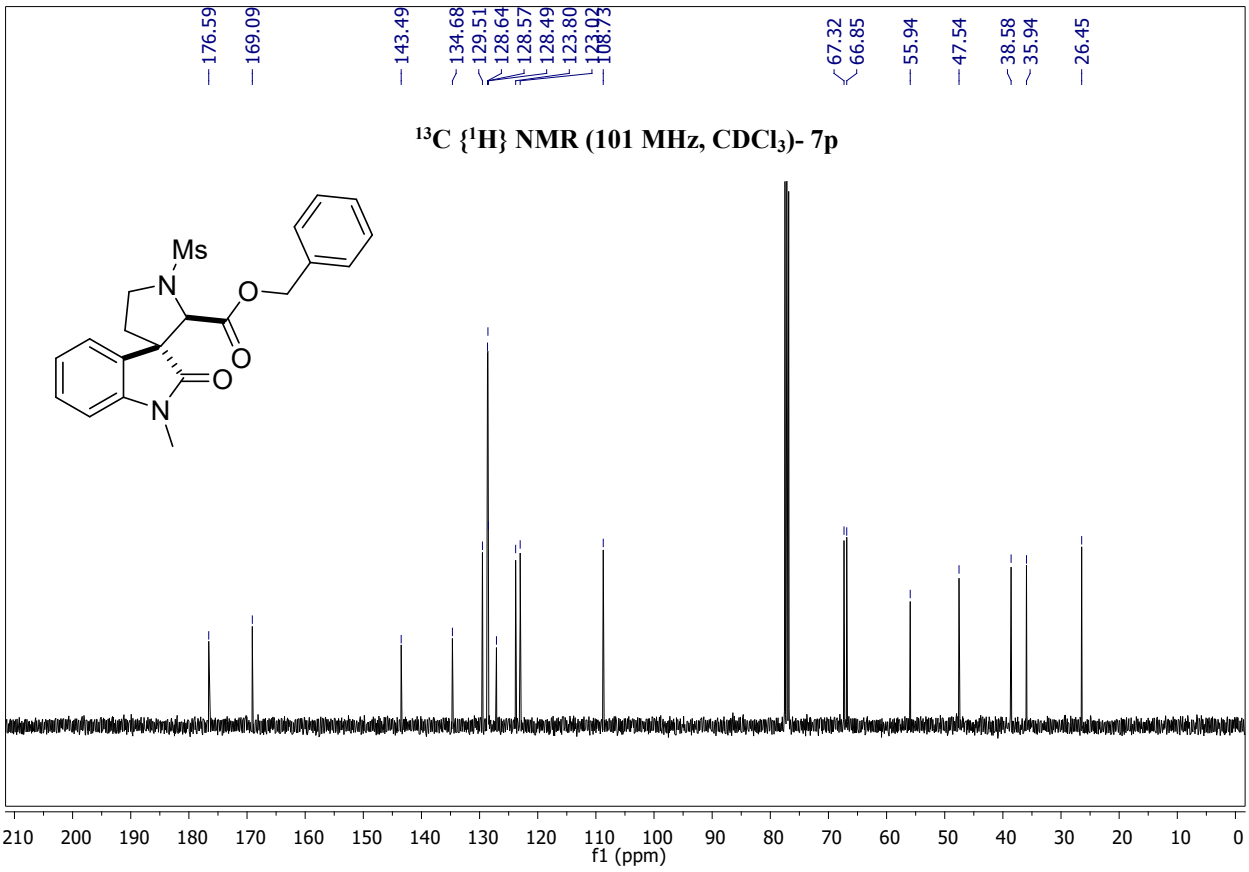
^{1}H NMR (400 MHz, $CDCl_3$) – 7o



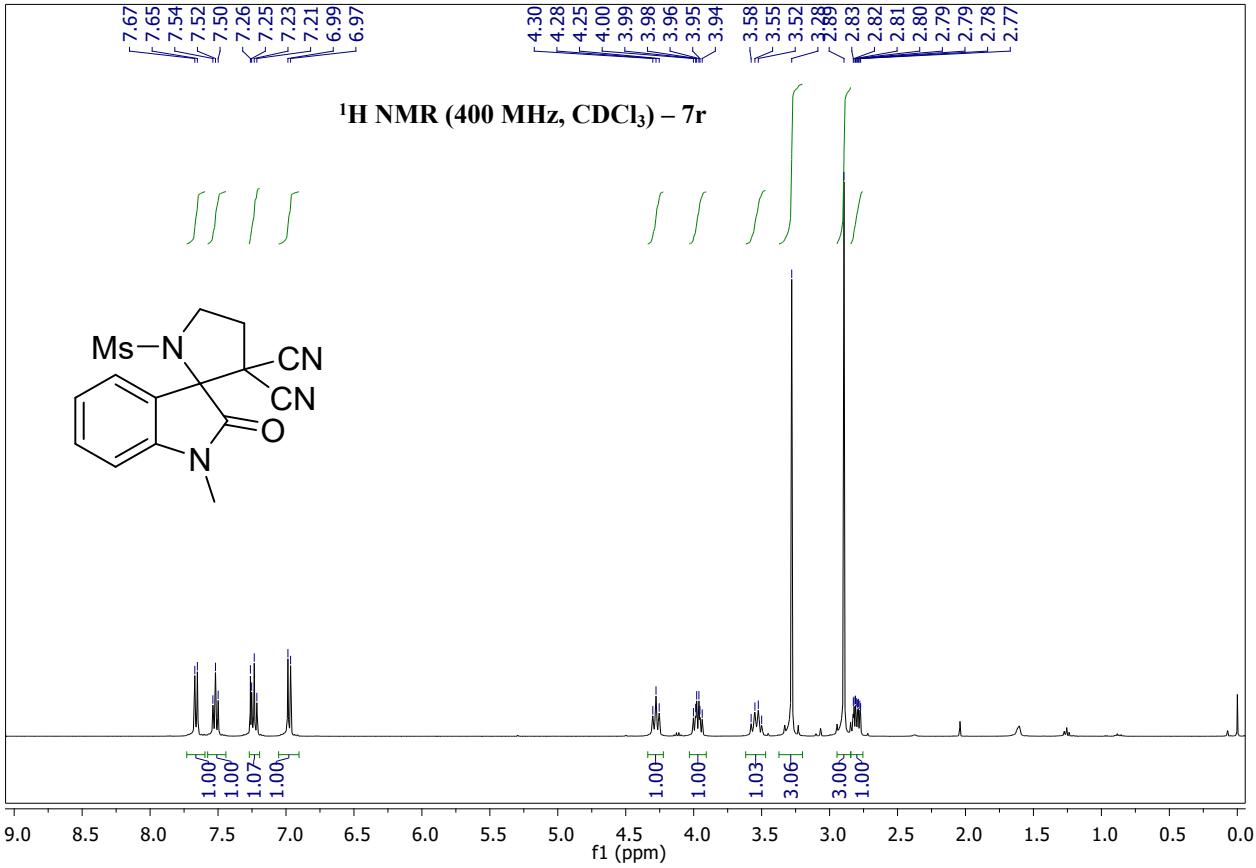
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7o



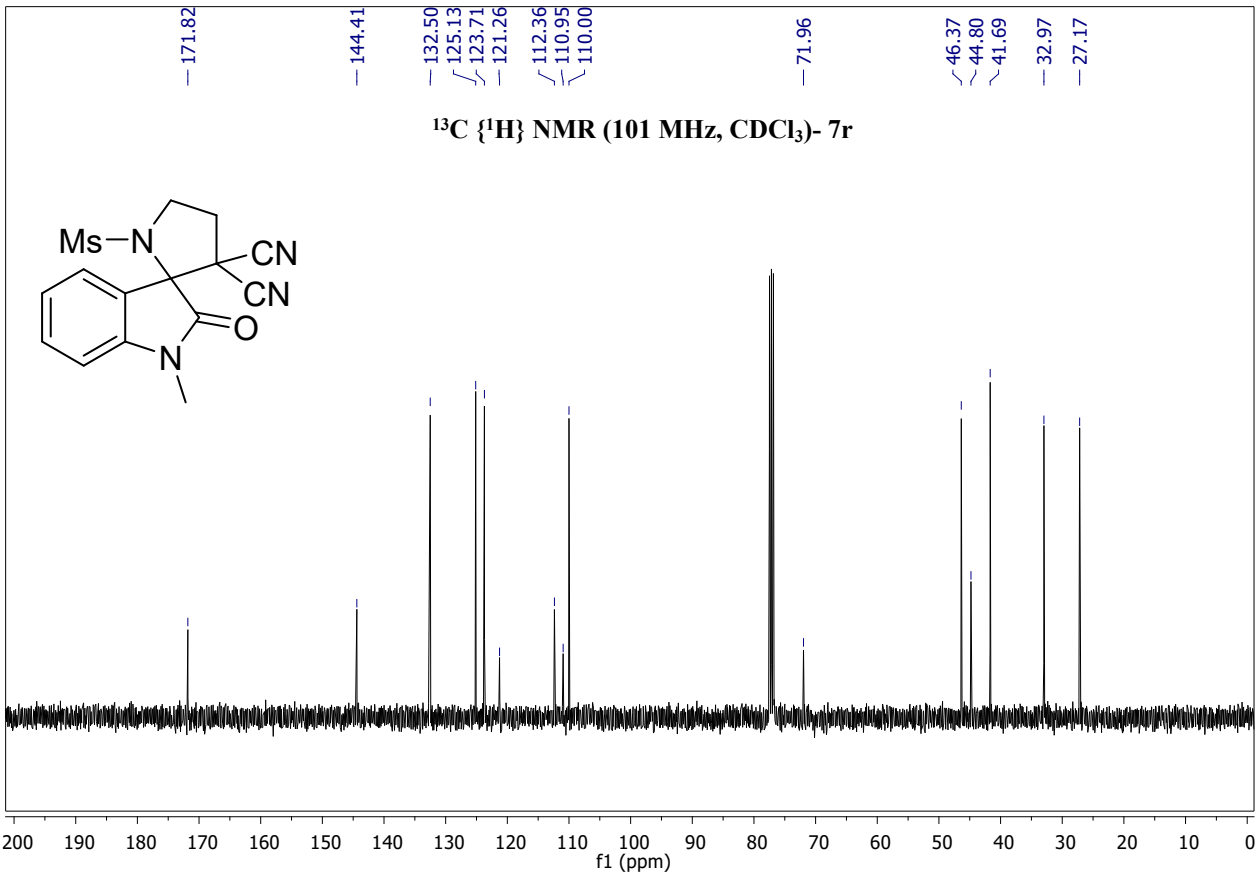
^{1}H NMR (400 MHz, $CDCl_3$) – 7p



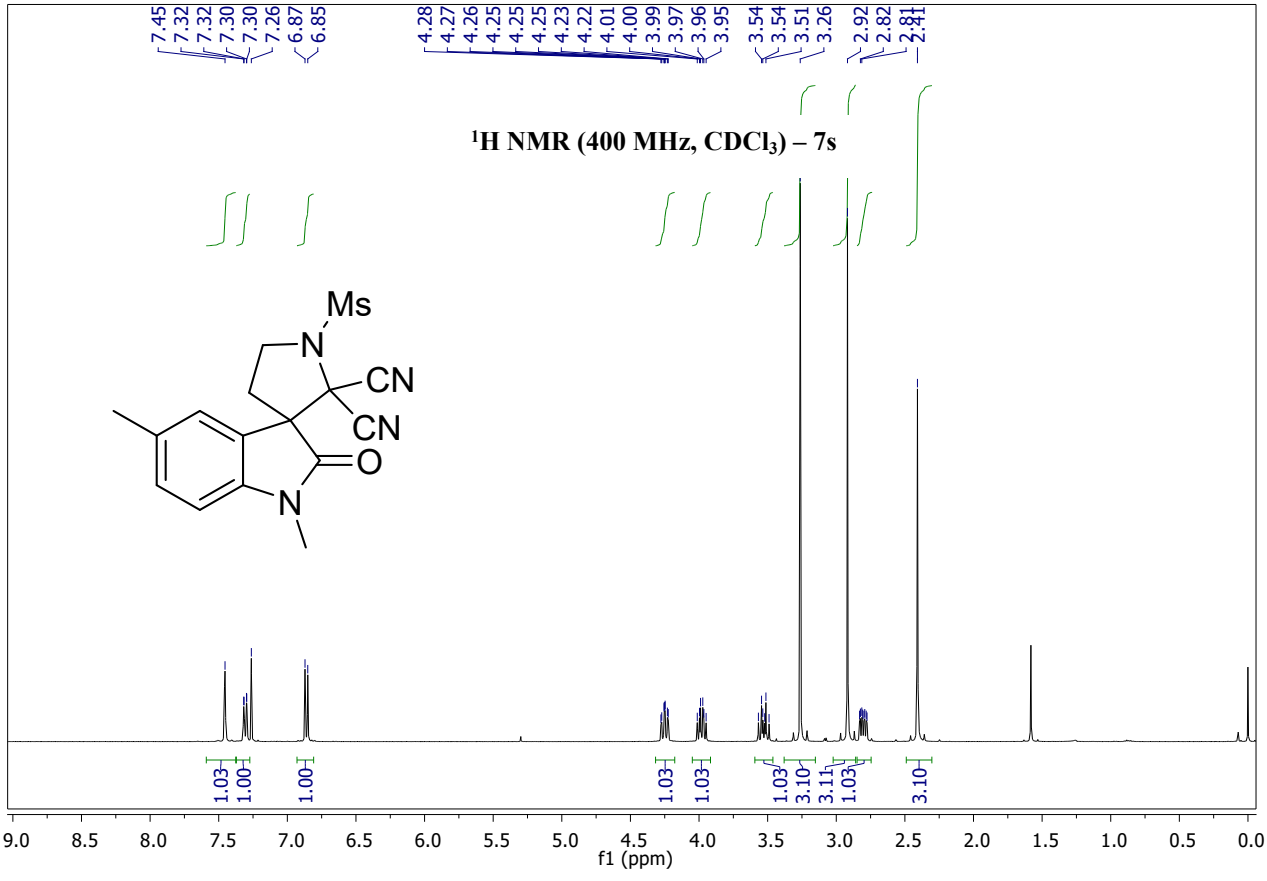
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7p



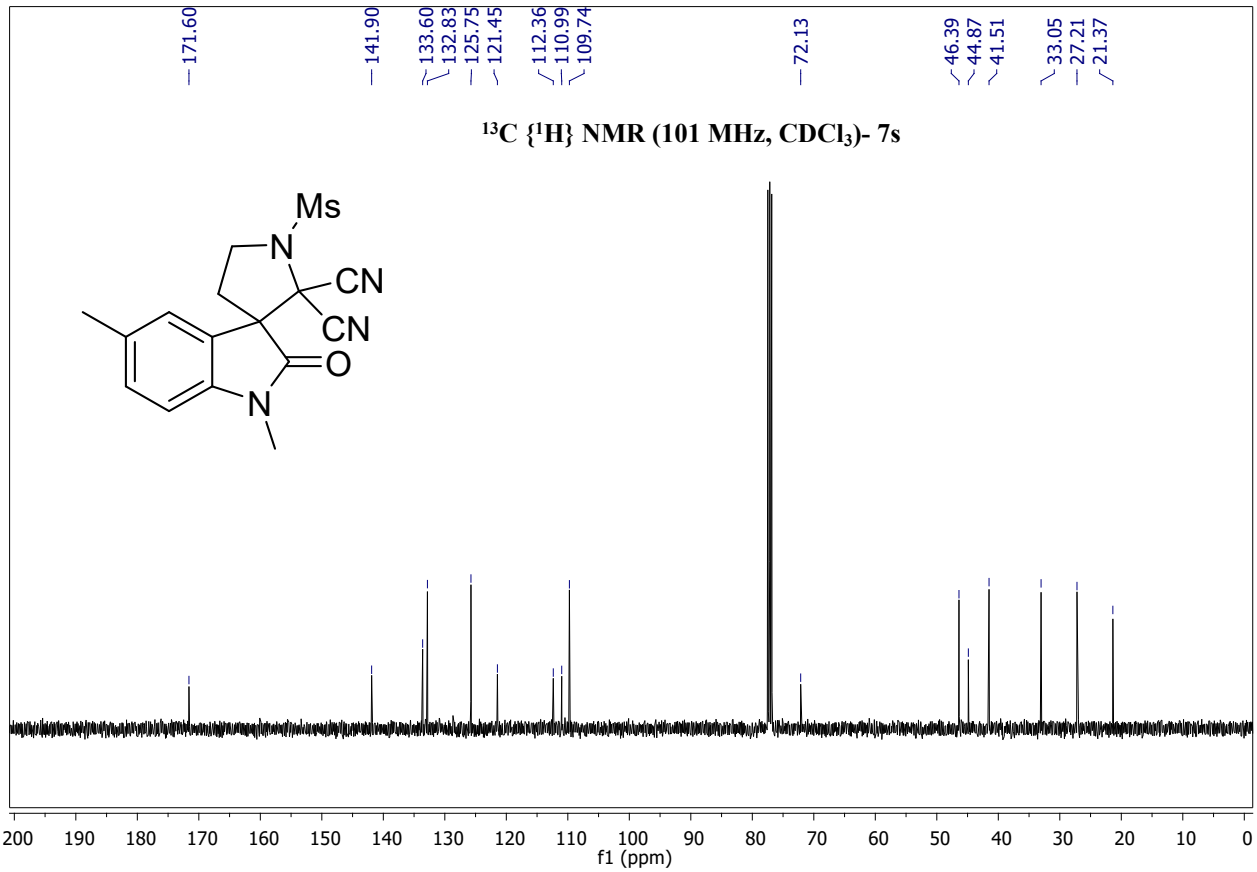
^{1}H NMR (400 MHz, $CDCl_3$) – 7r



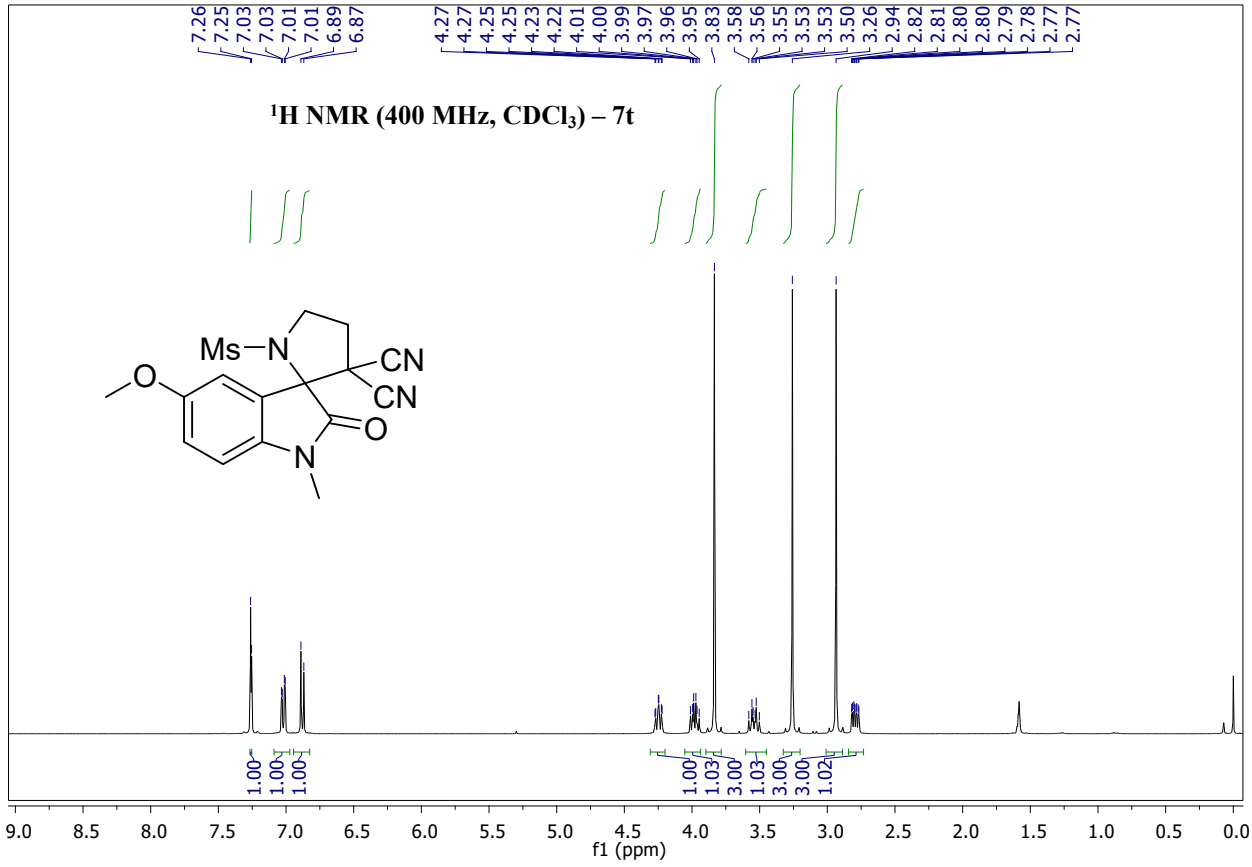
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7r



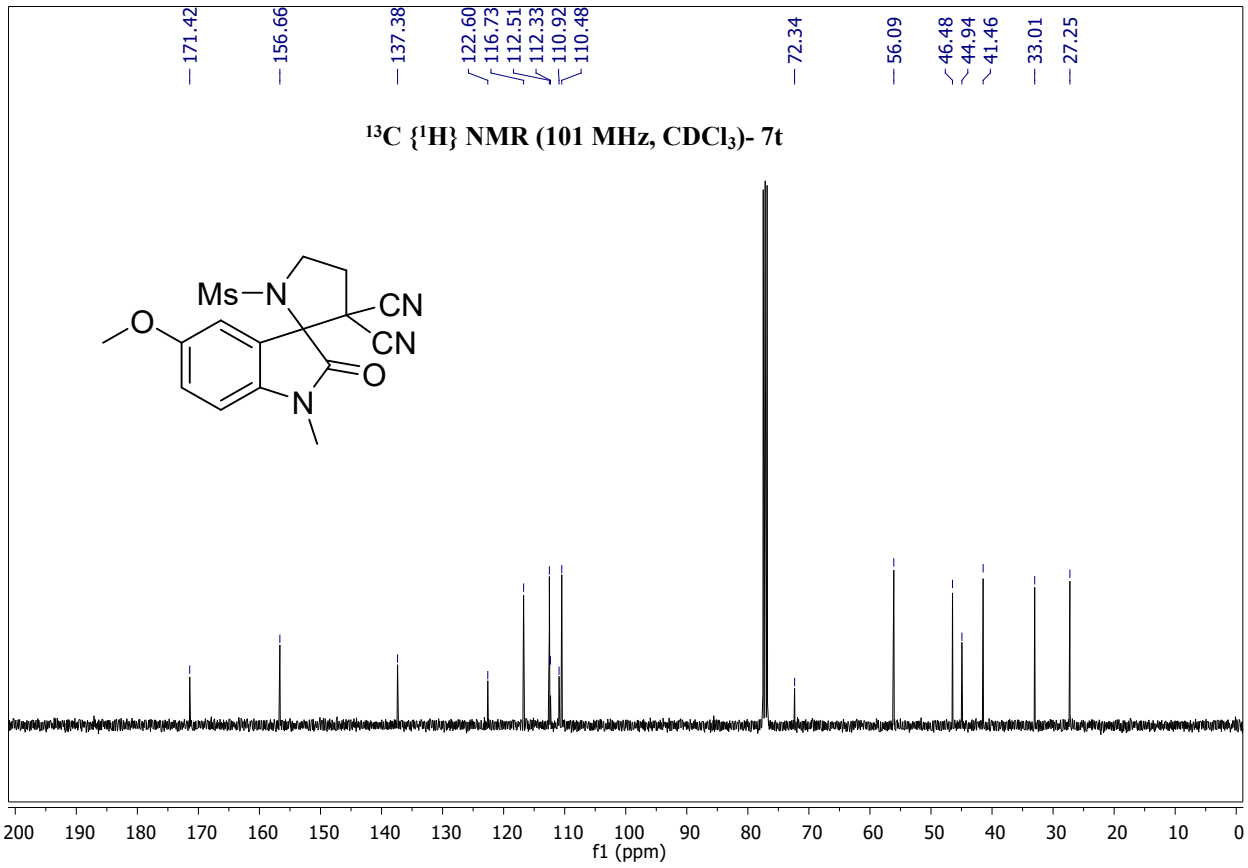
^{1}H NMR (400 MHz, $CDCl_3$) – 7s



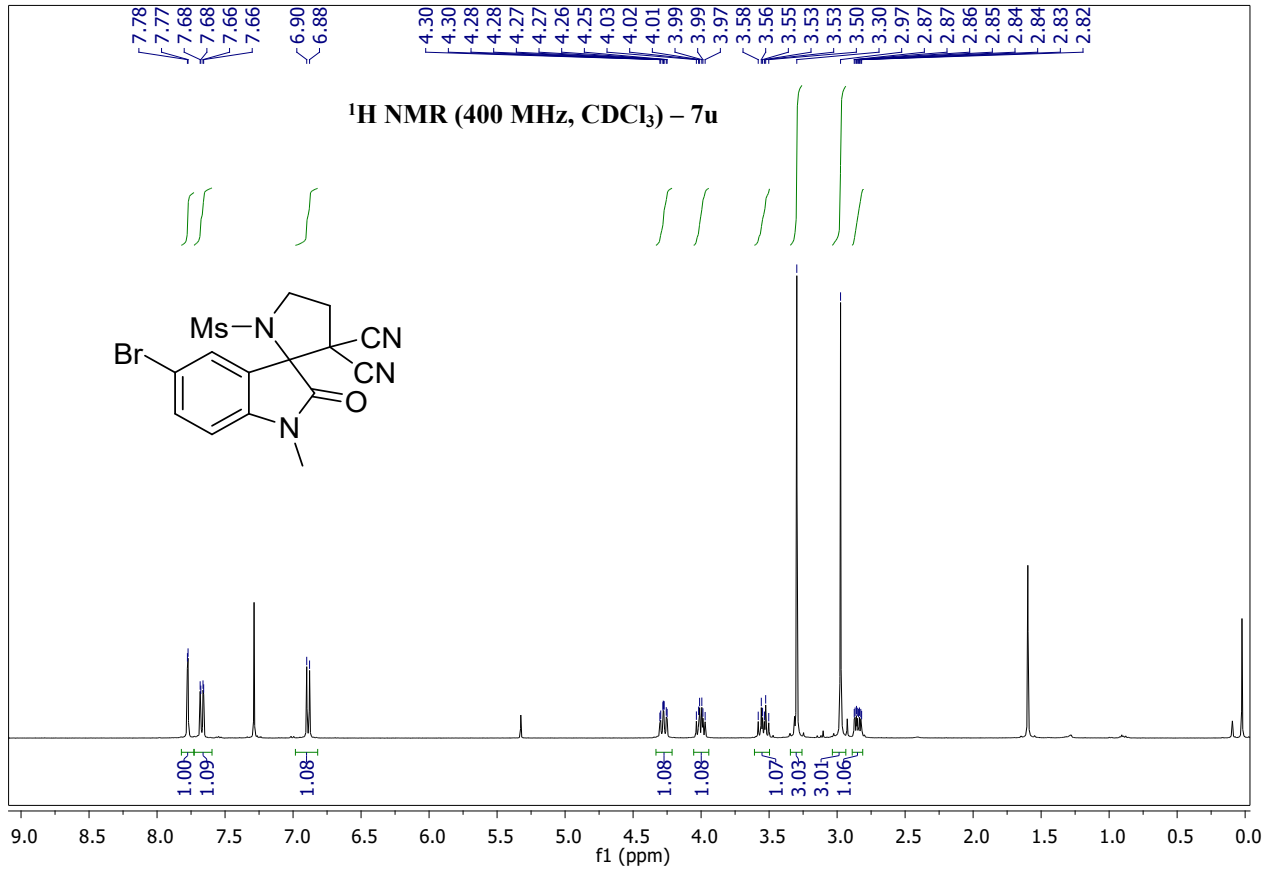
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7s



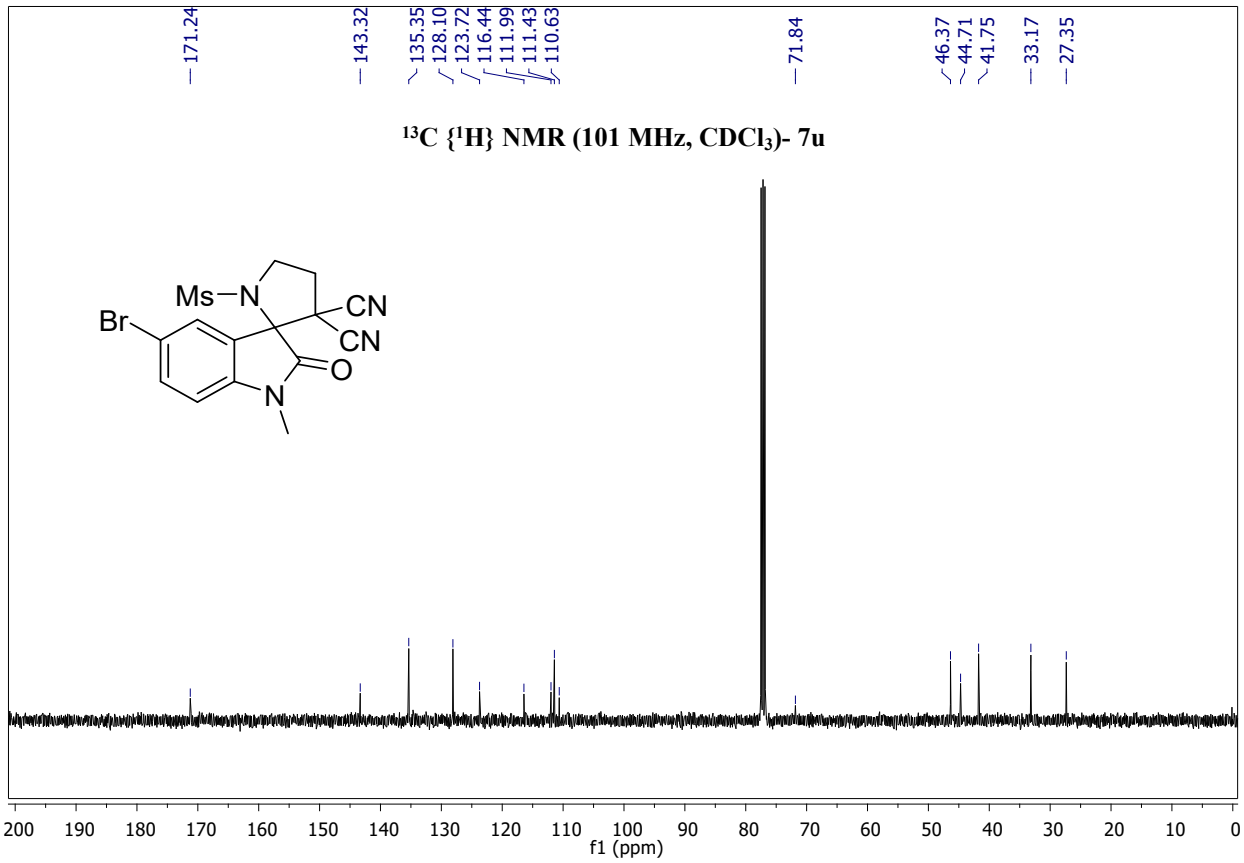
^{1}H NMR (400 MHz, $CDCl_3$) – 7t



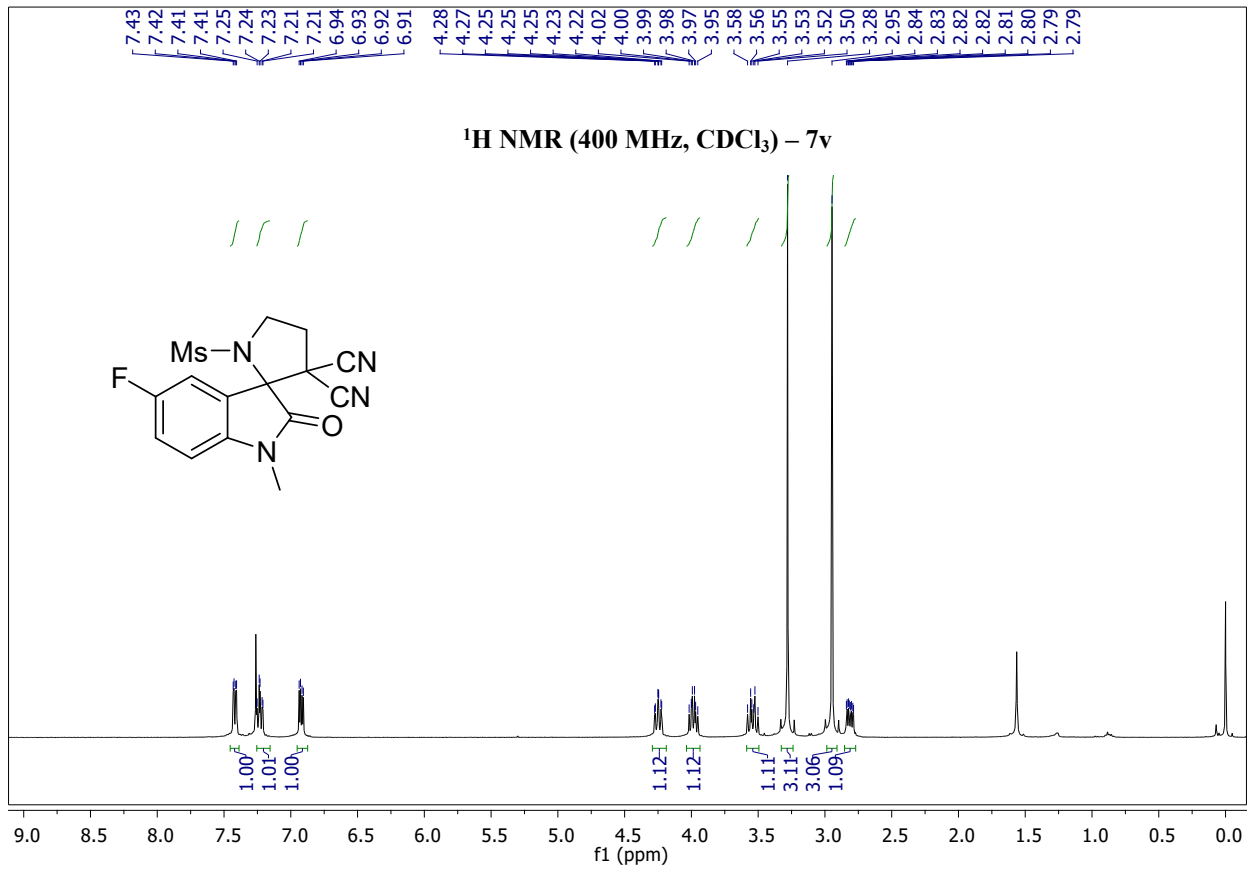
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7t



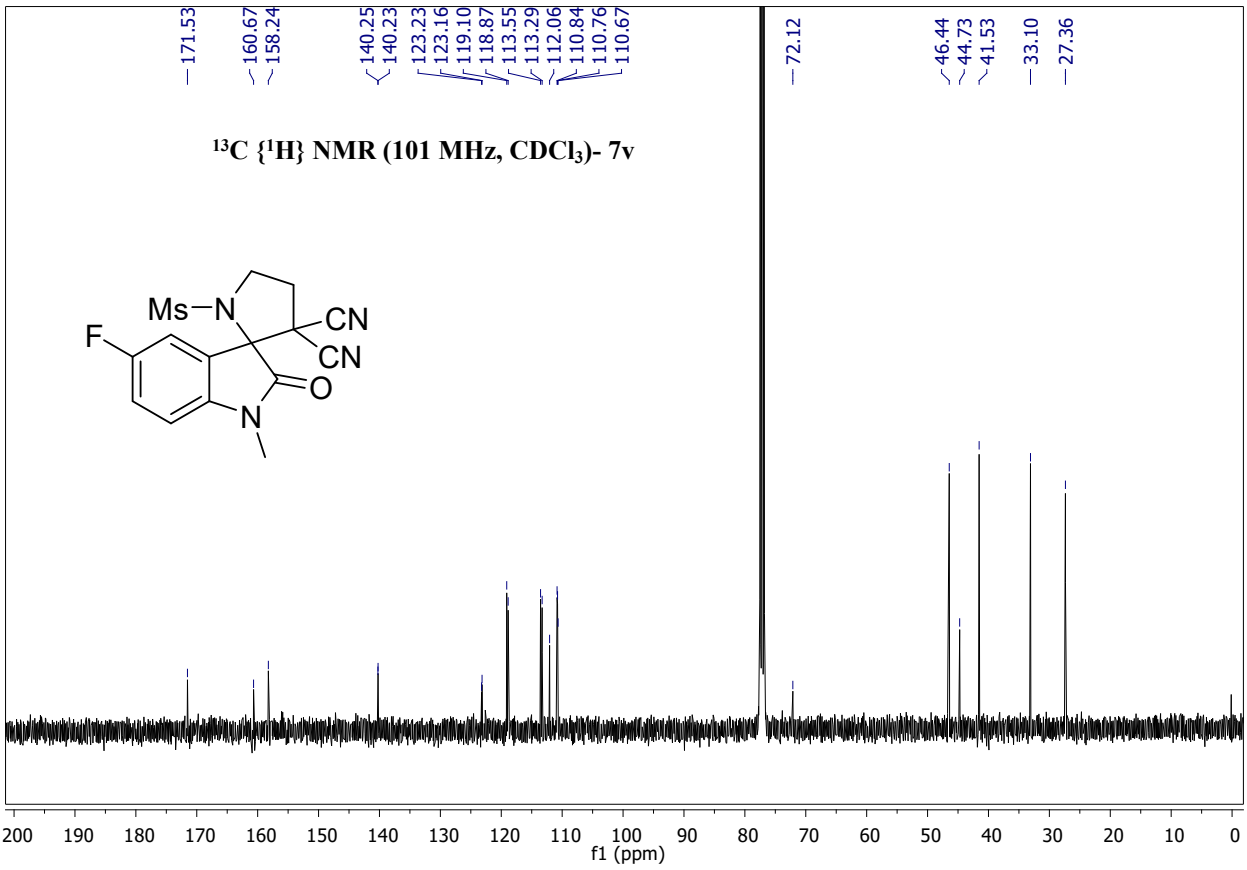
^{1}H NMR (400 MHz, $CDCl_3$) – 7u



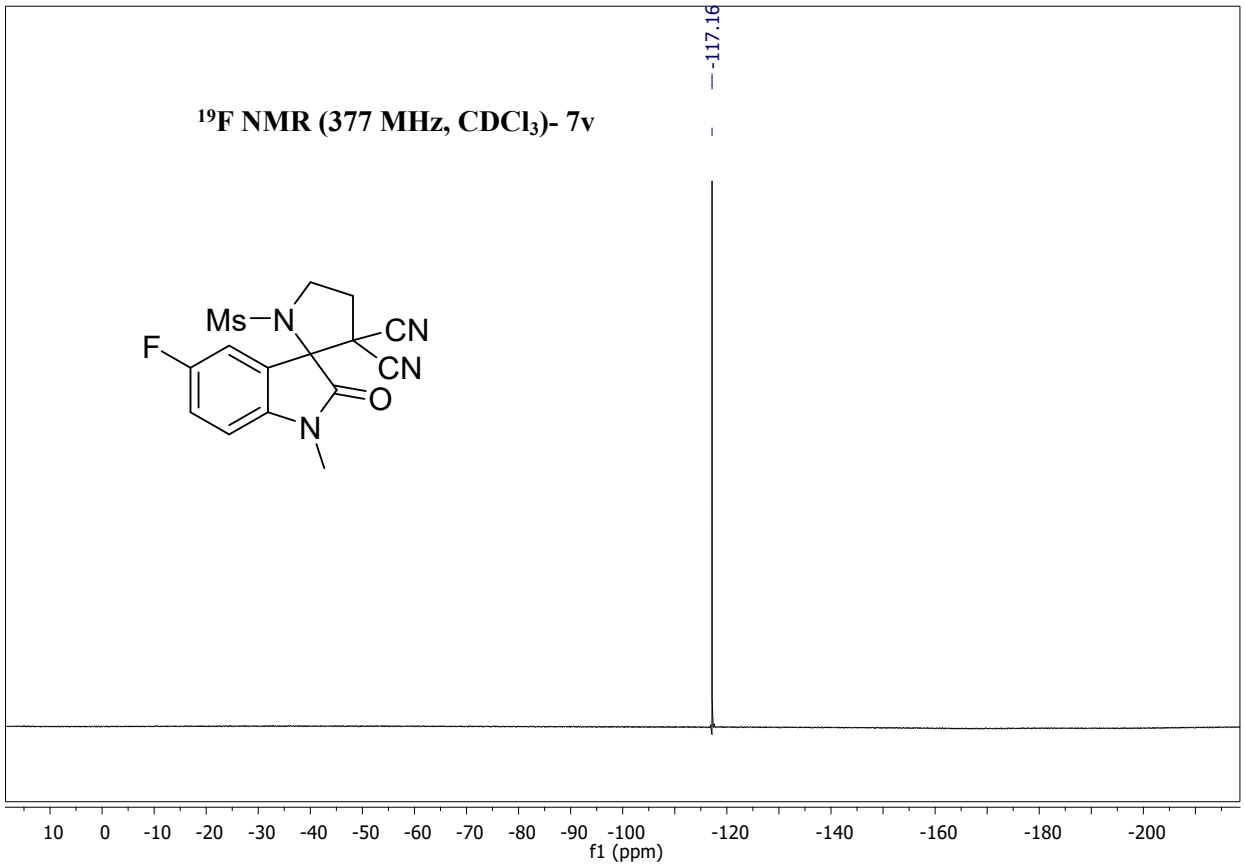
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7u



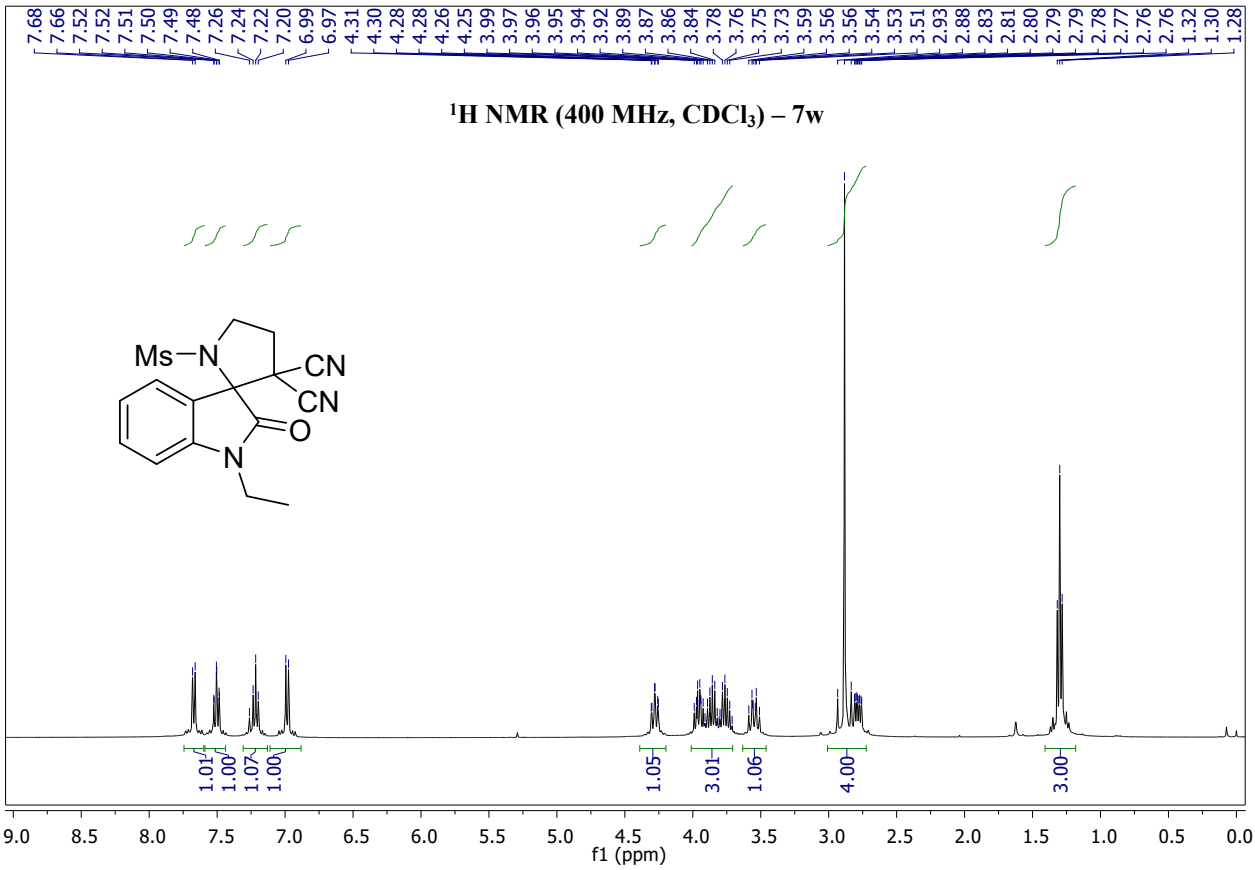
^{1}H NMR (400 MHz, $CDCl_3$) – 7v



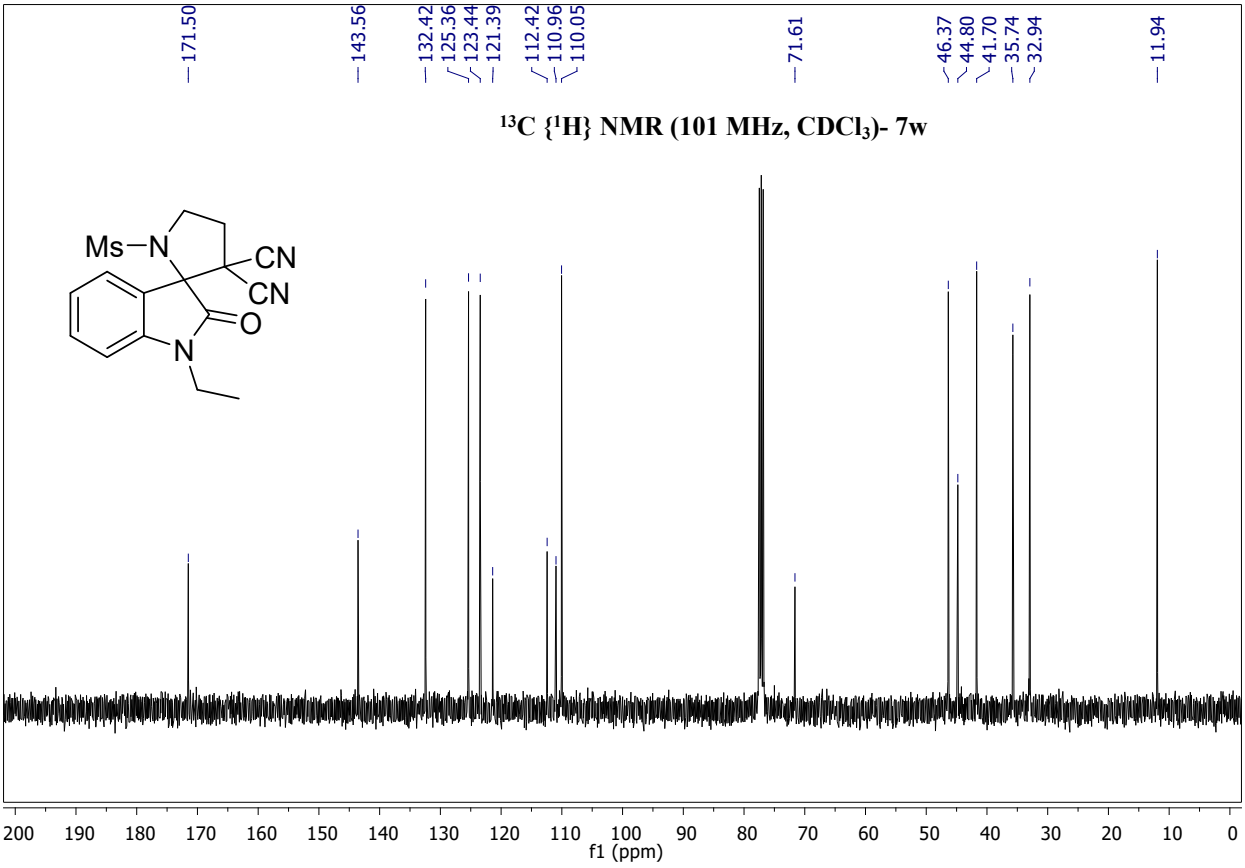
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7v



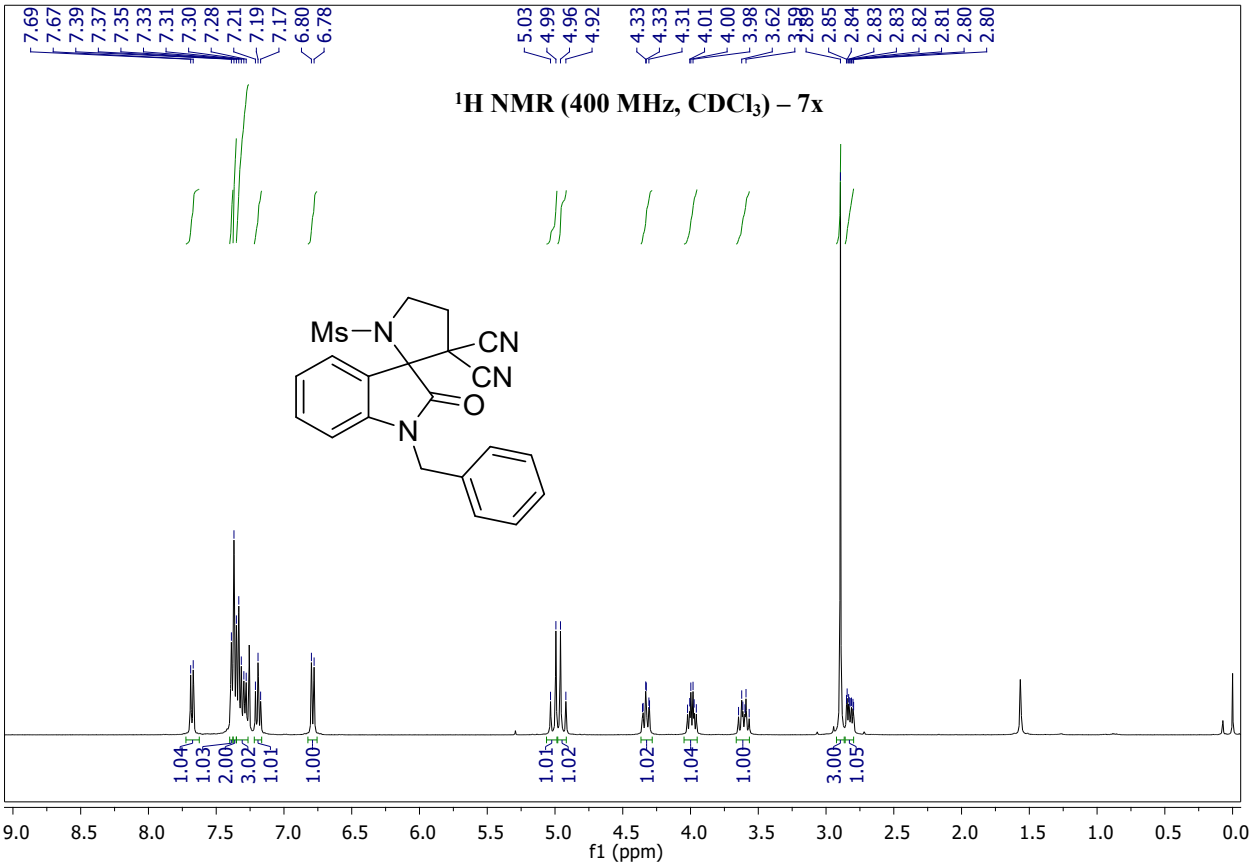
^{19}F NMR (377 MHz, $CDCl_3$)- 7v



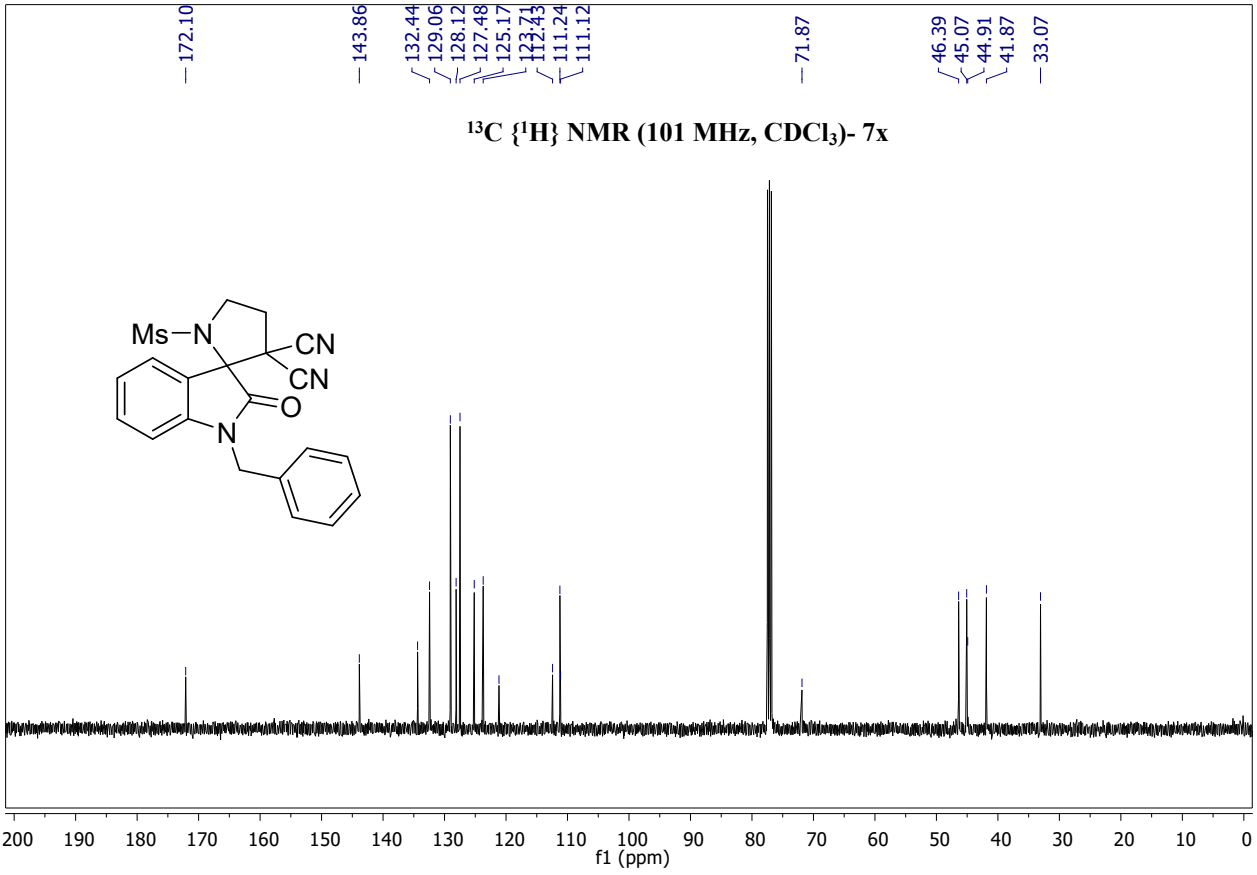
^{1}H NMR (400 MHz, $CDCl_3$) – 7w



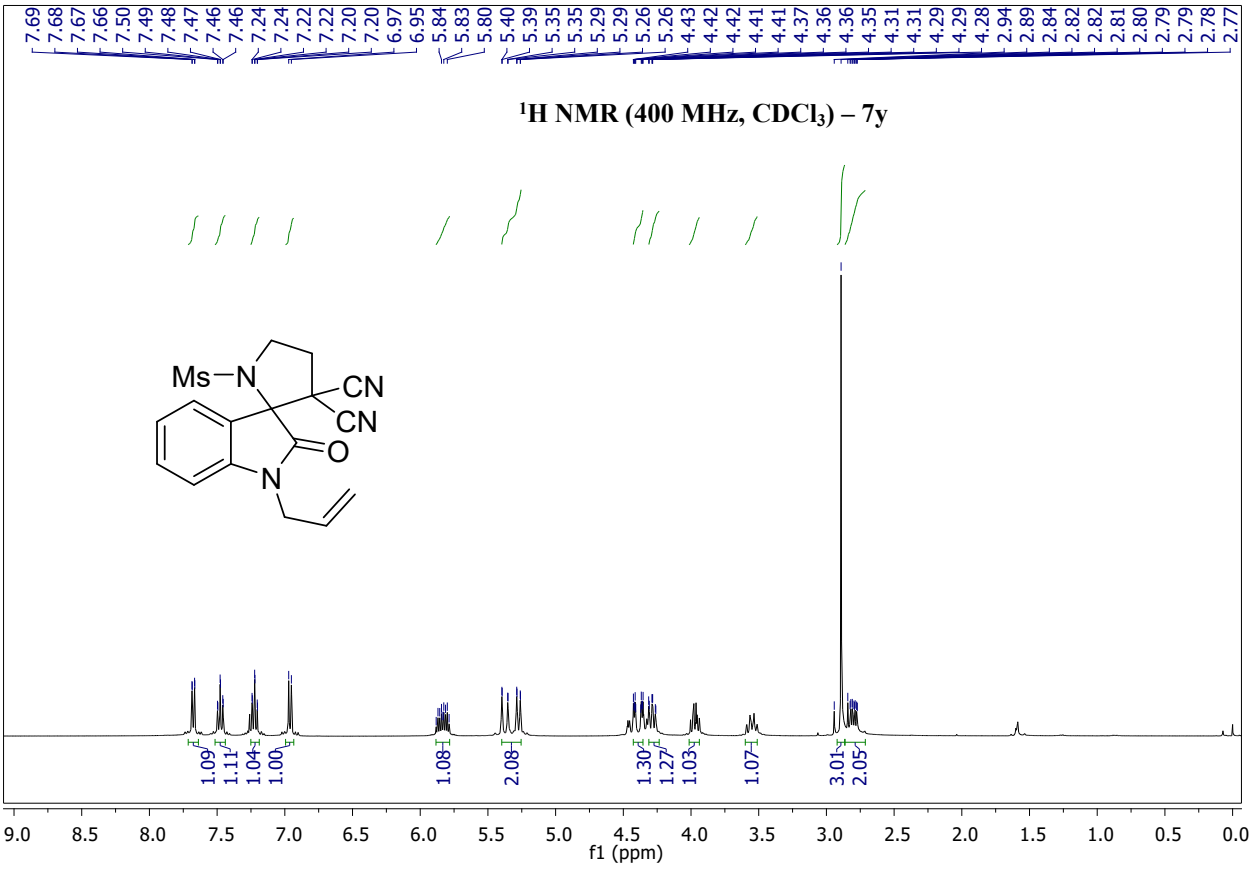
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7w



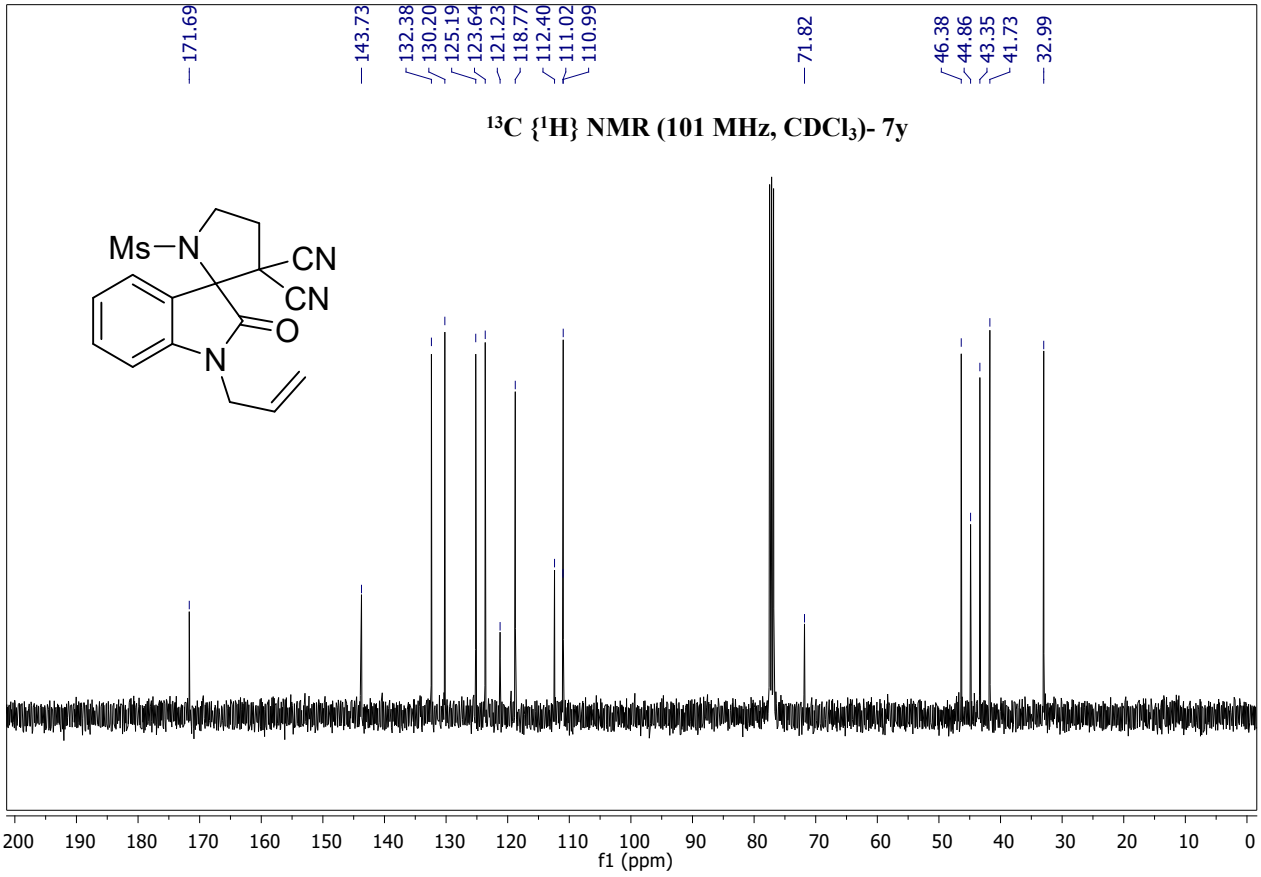
^{1}H NMR (400 MHz, $CDCl_3$) – 7x



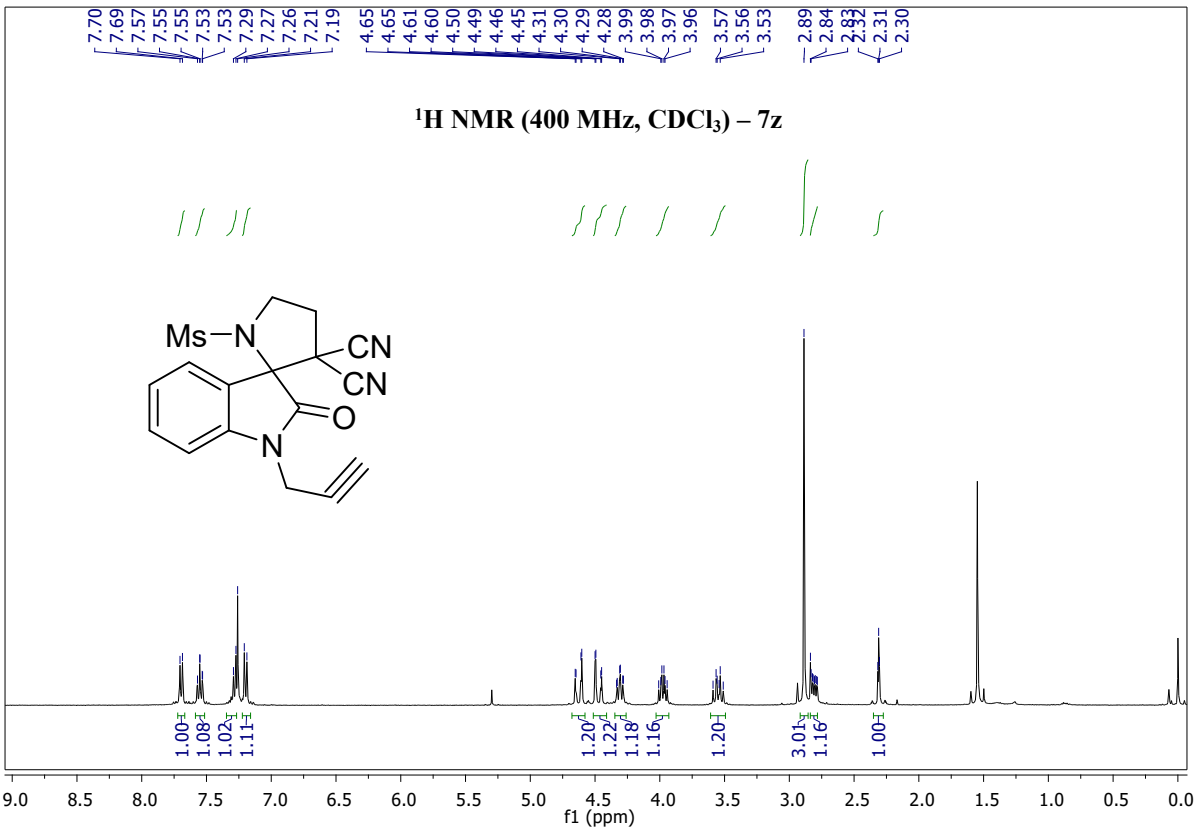
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7x



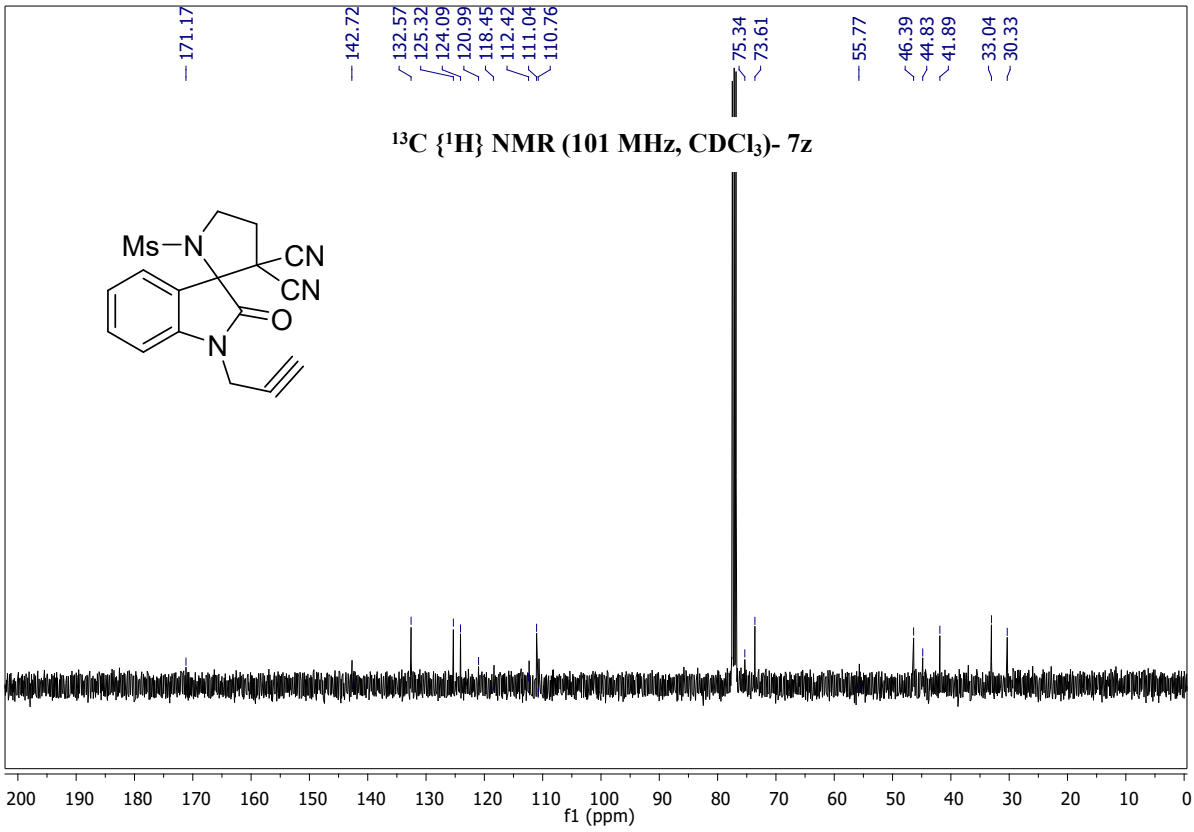
^{1}H NMR (400 MHz, $CDCl_3$) – 7y



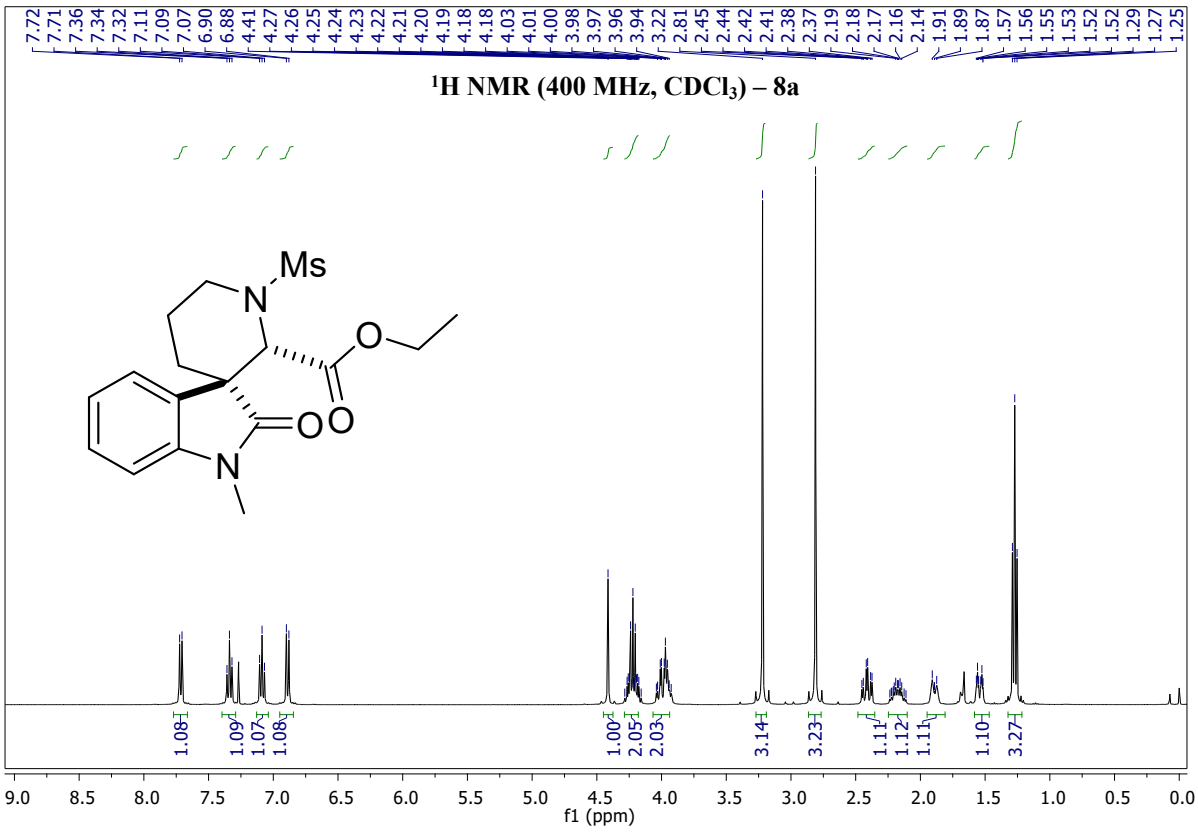
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7y



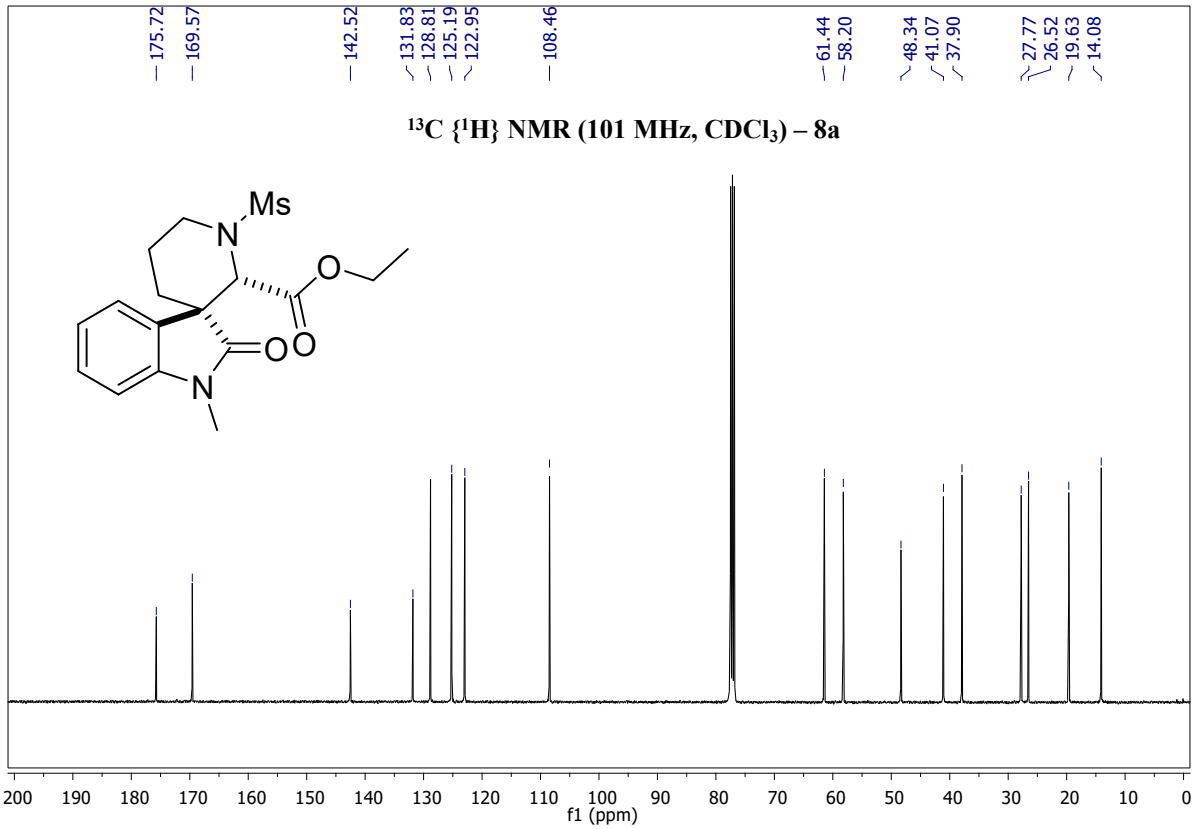
^{1}H NMR (400 MHz, $CDCl_3$) – 7z



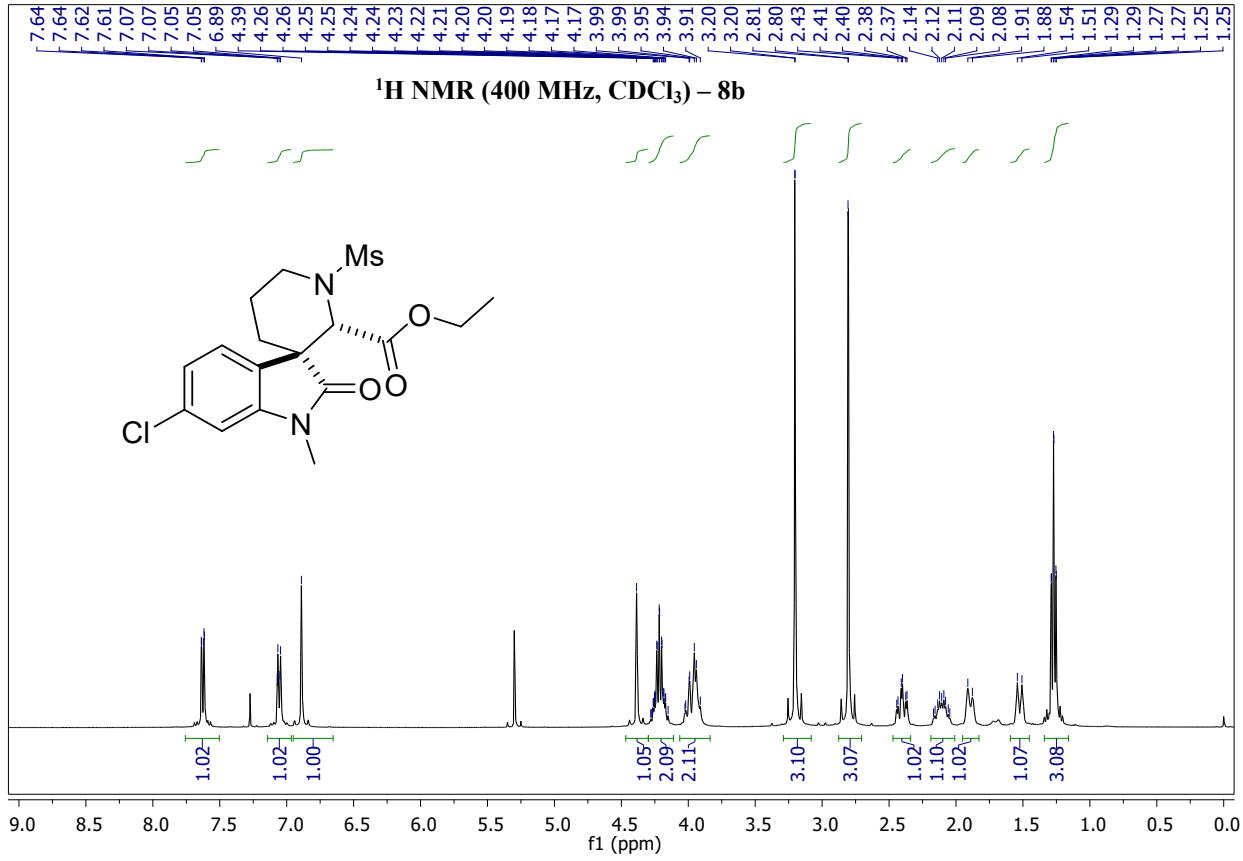
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 7z



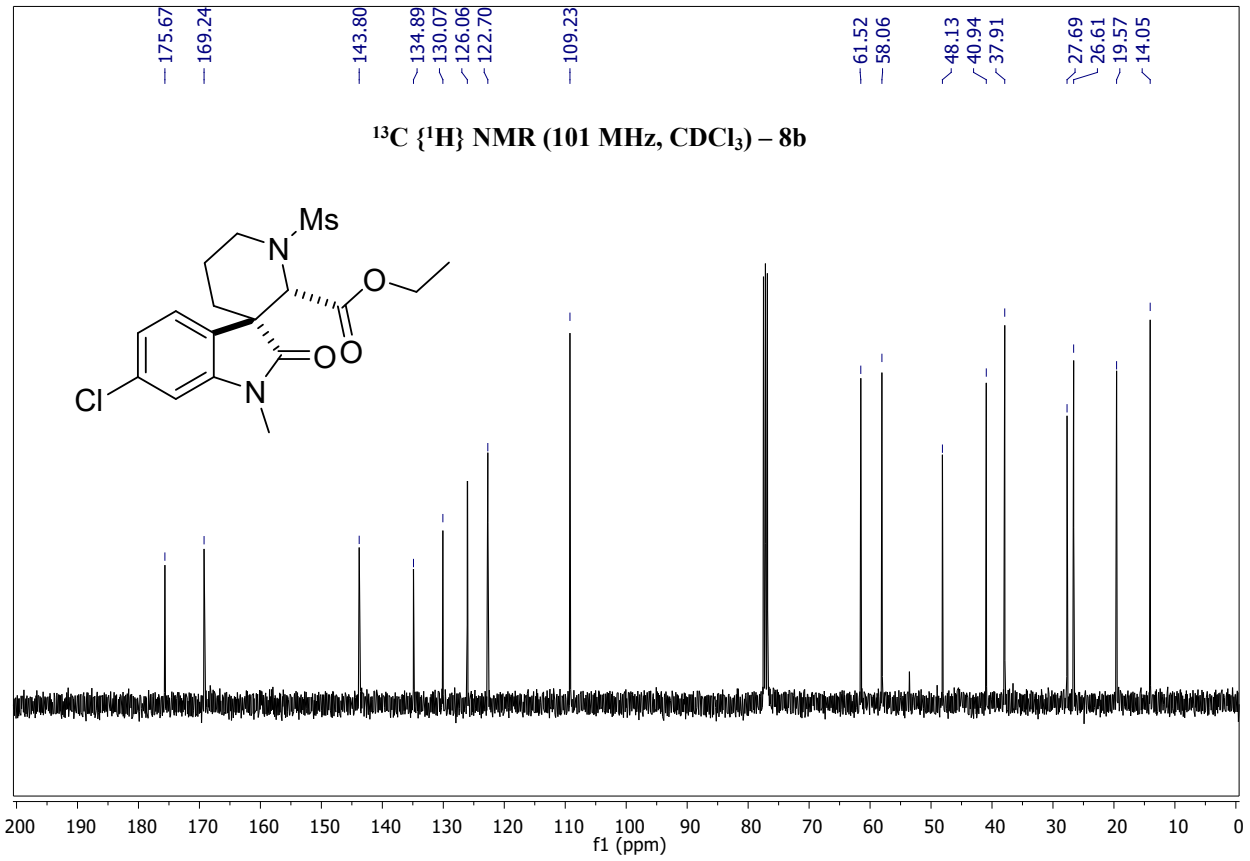
^{1}H NMR (400 MHz, $CDCl_3$) – 8a



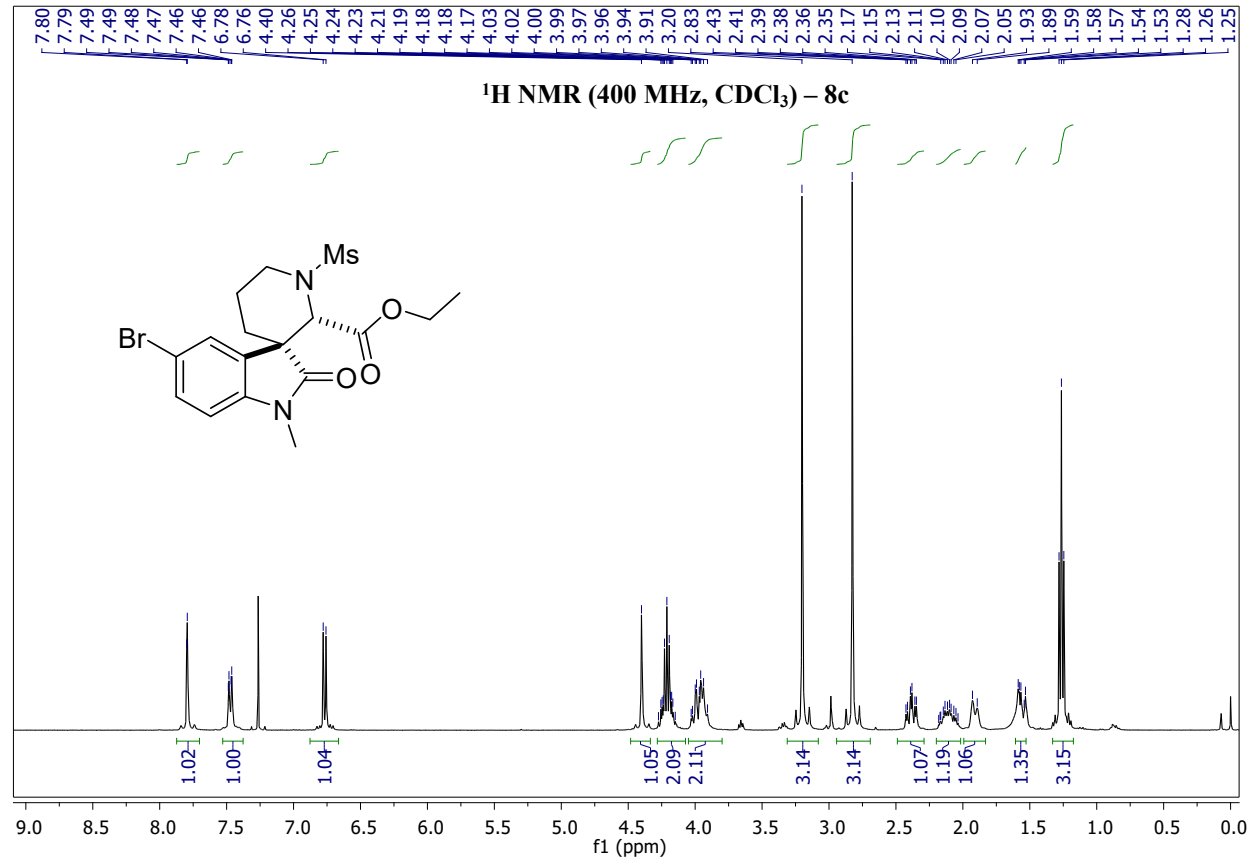
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8a



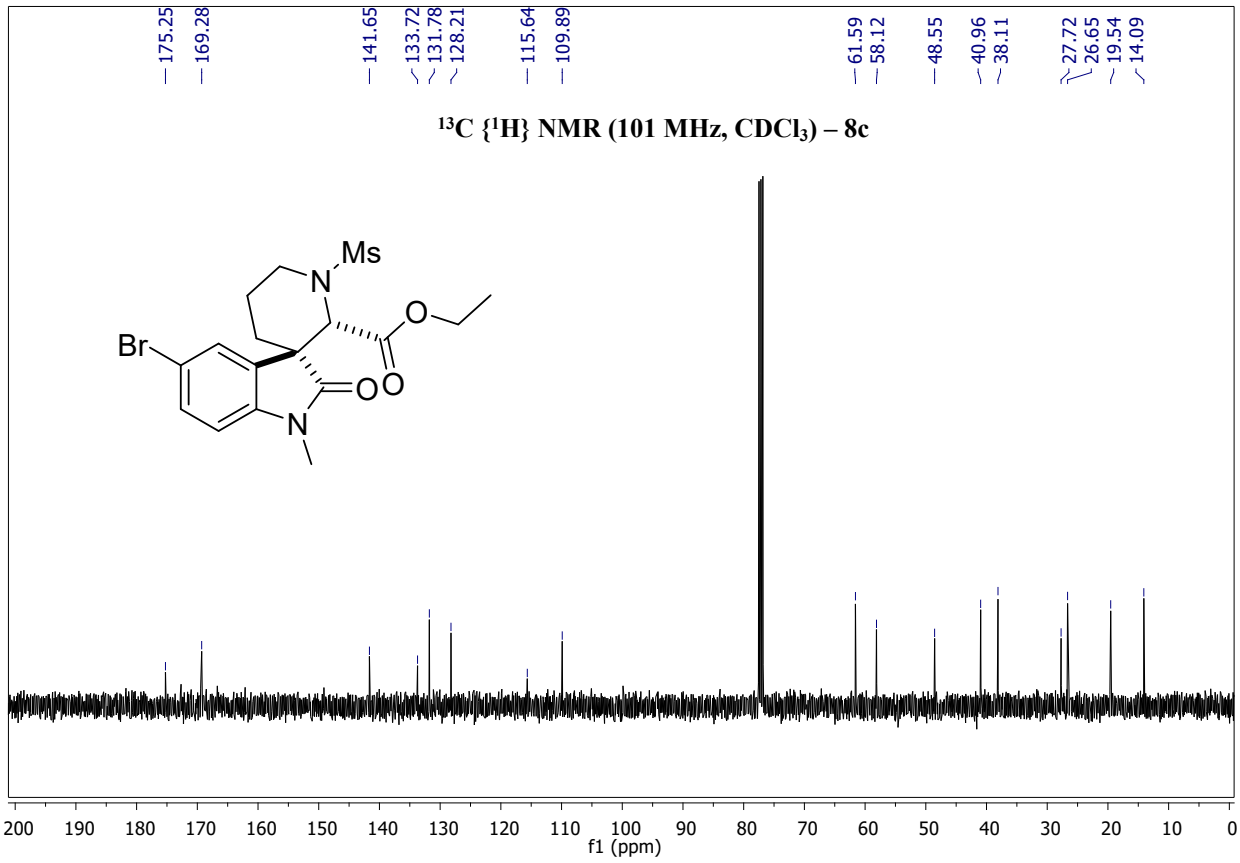
^{1}H NMR (400 MHz, $CDCl_3$) – 8b



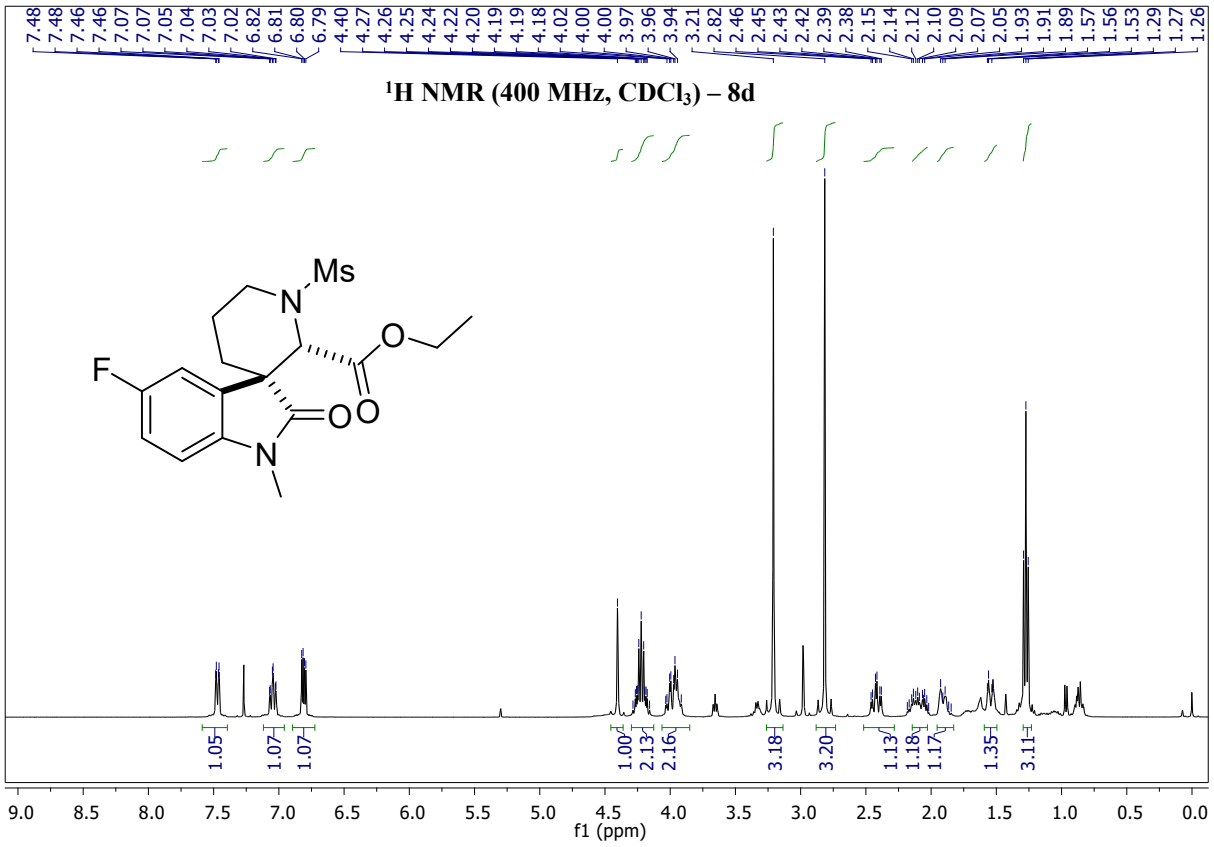
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8b



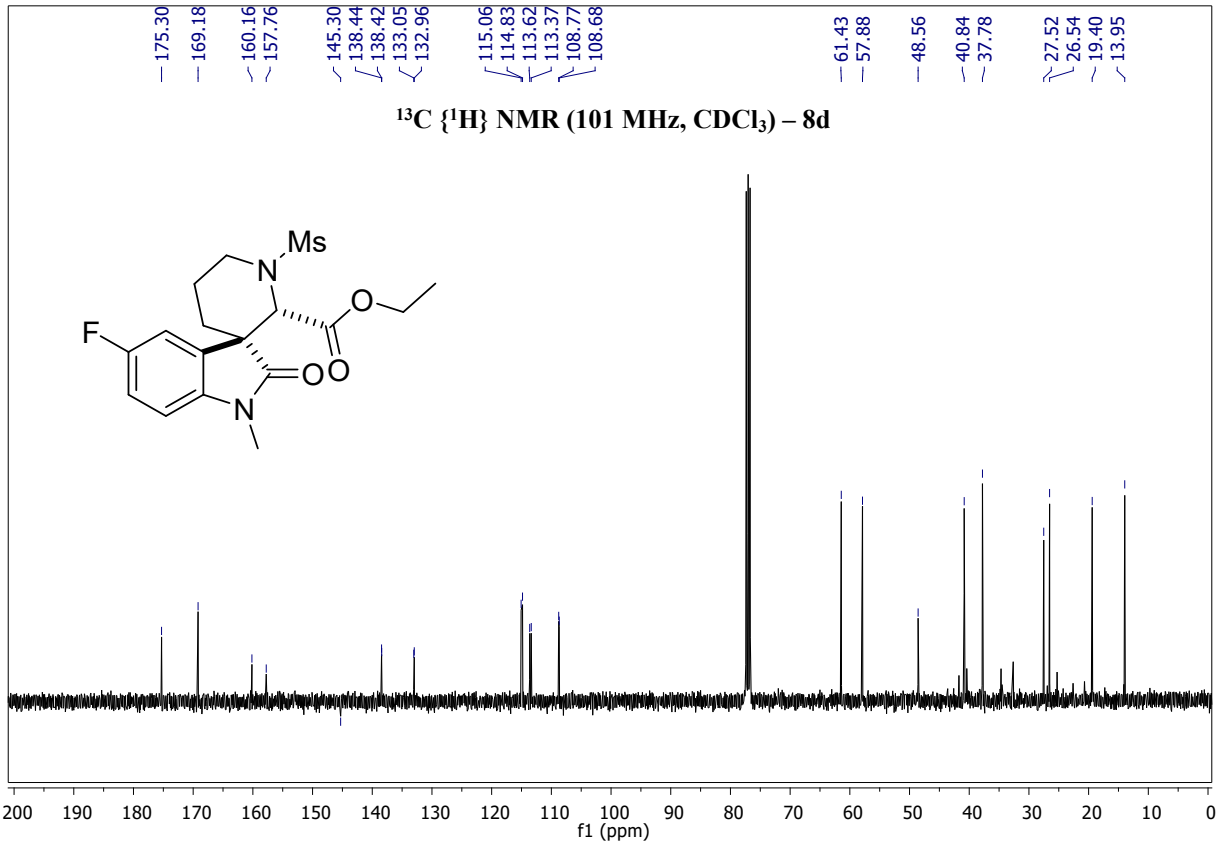
^{1}H NMR (400 MHz, $CDCl_3$) – 8c



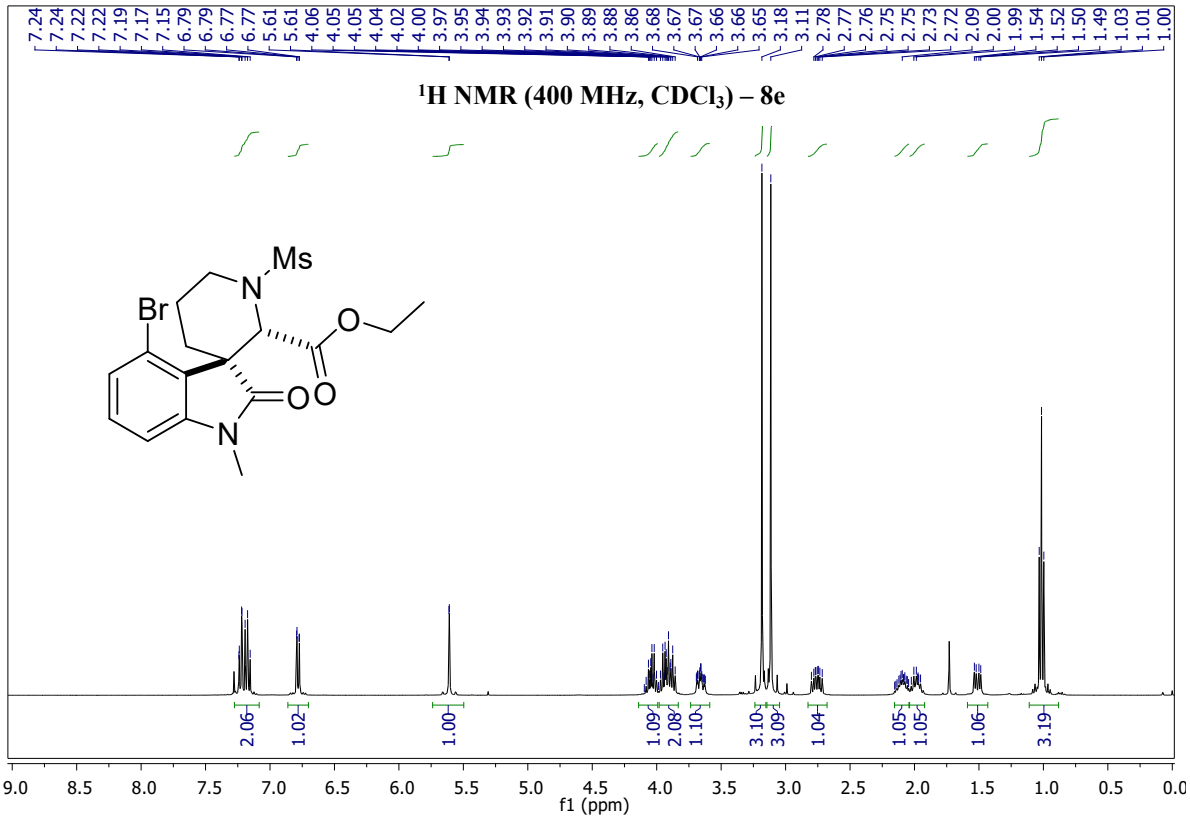
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8c



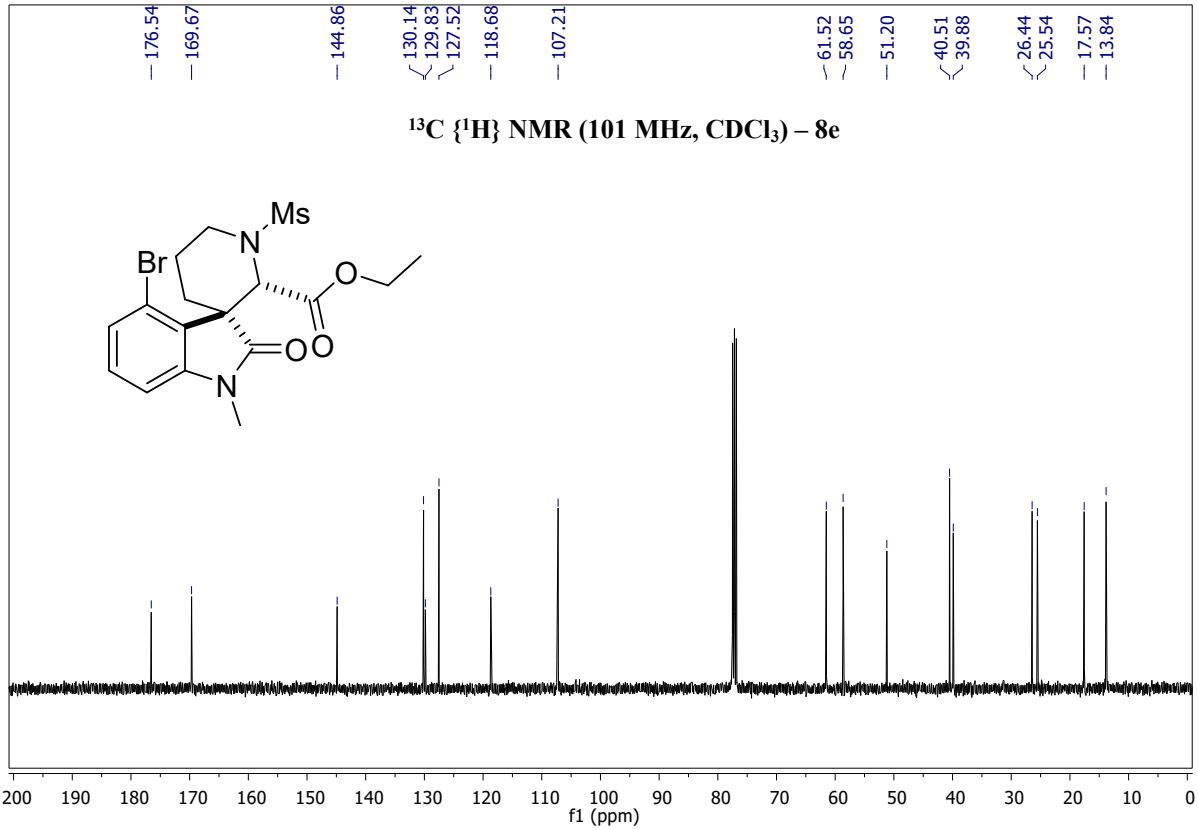
^{1}H NMR (400 MHz, $CDCl_3$) – 8d



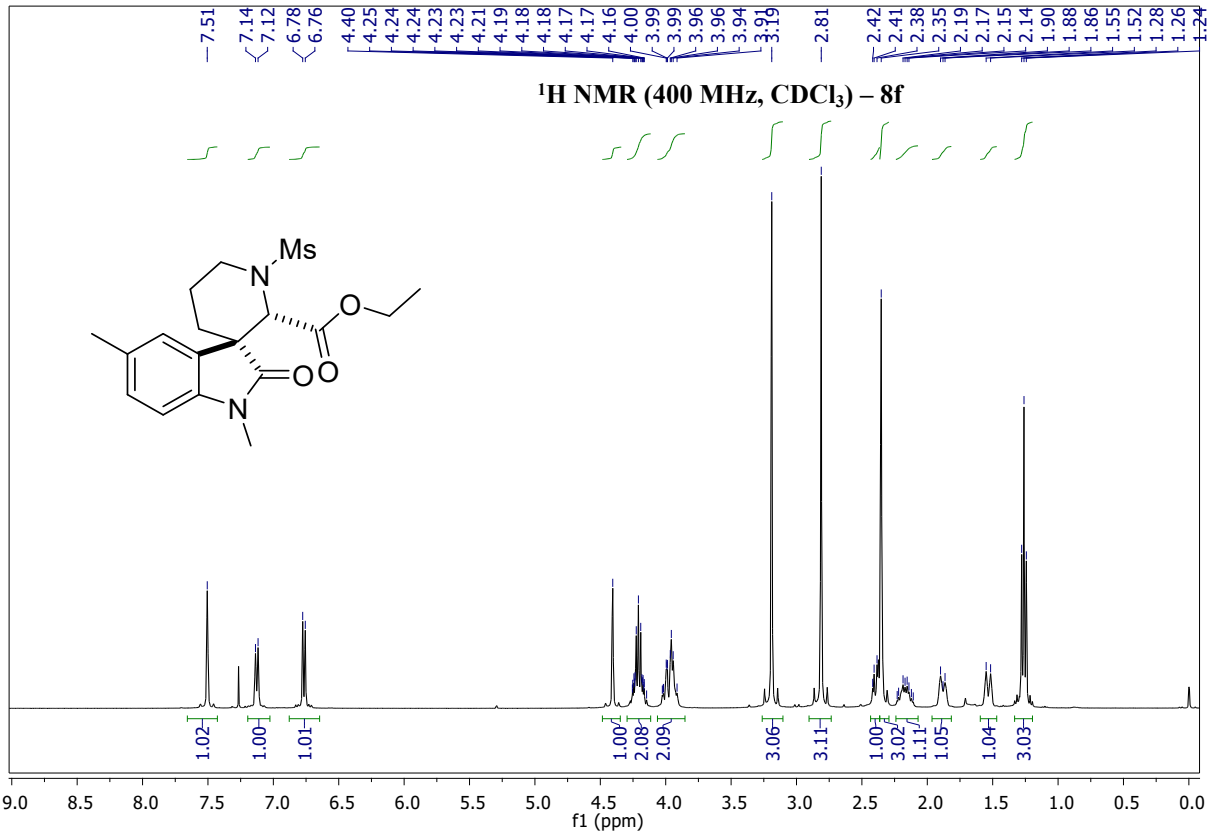
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8d



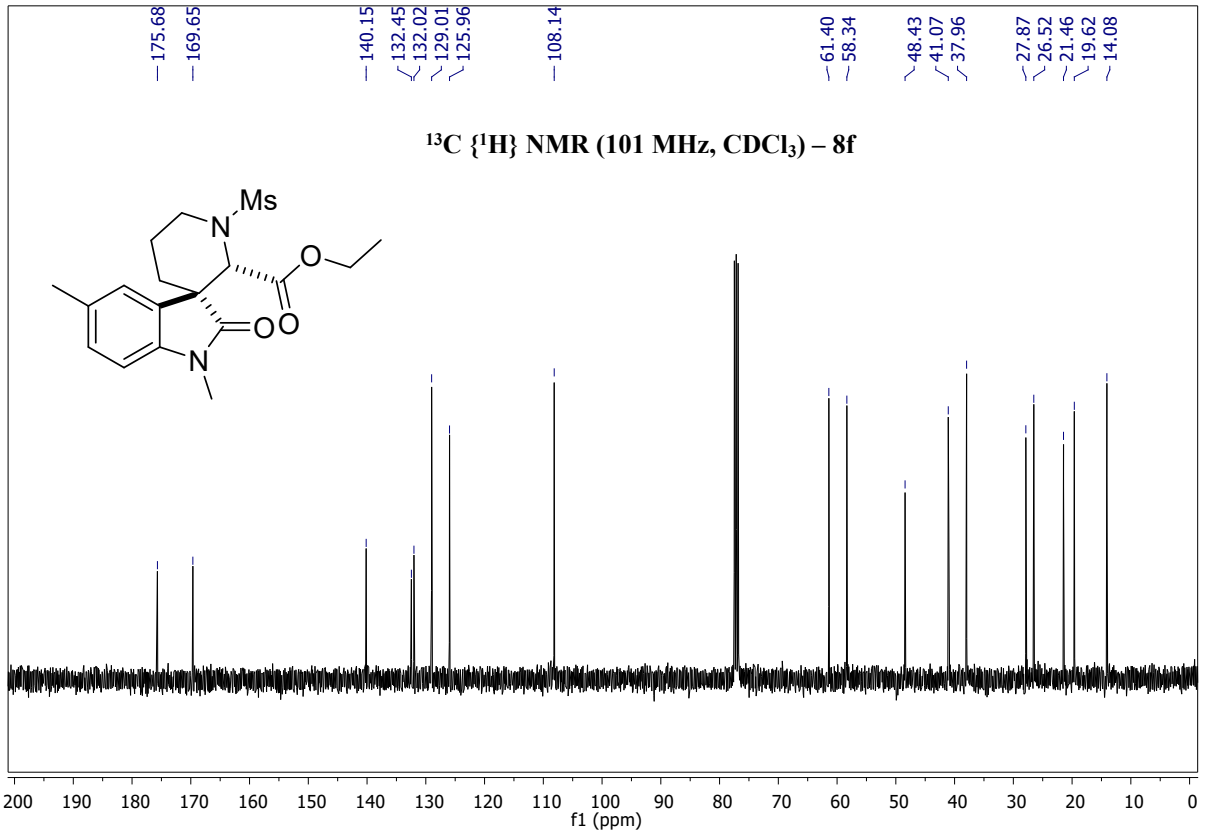
^{1}H NMR (400 MHz, $CDCl_3$) – 8e



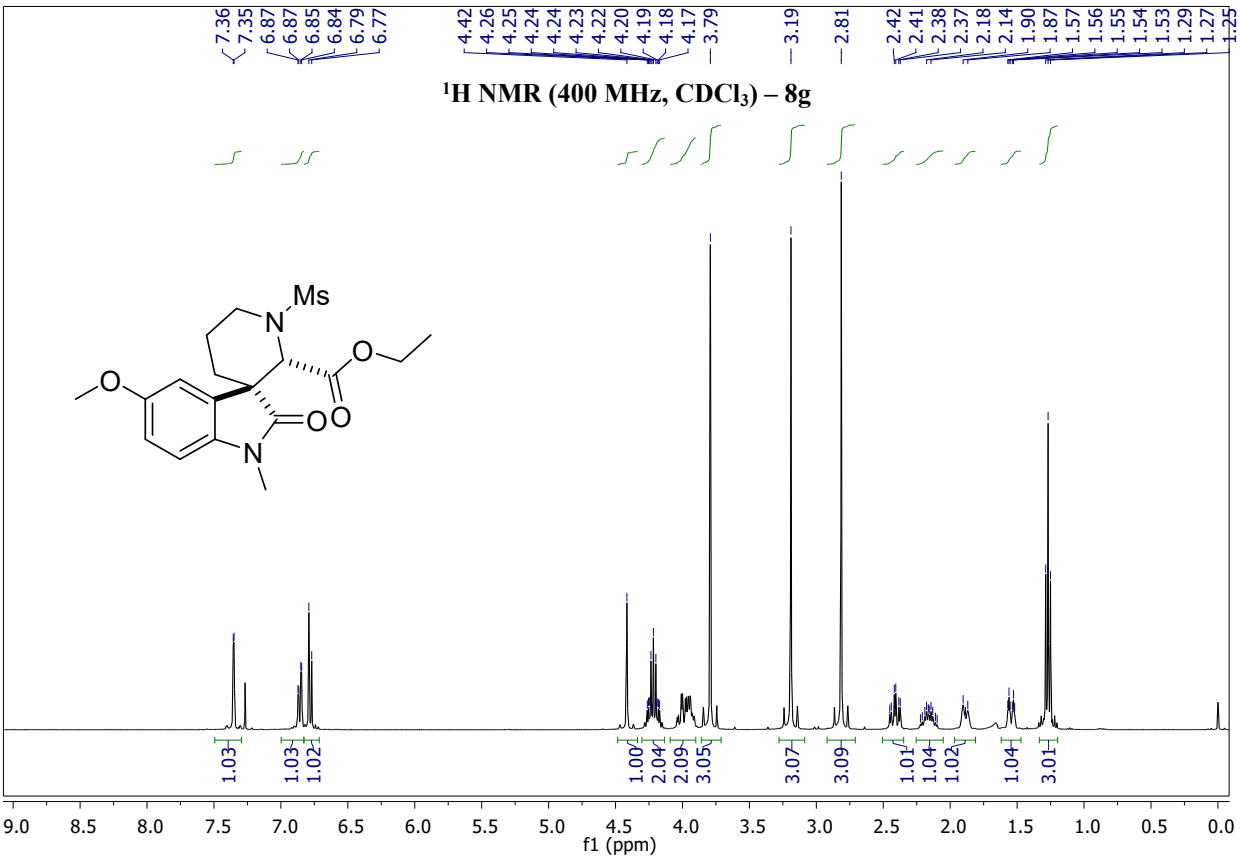
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8e



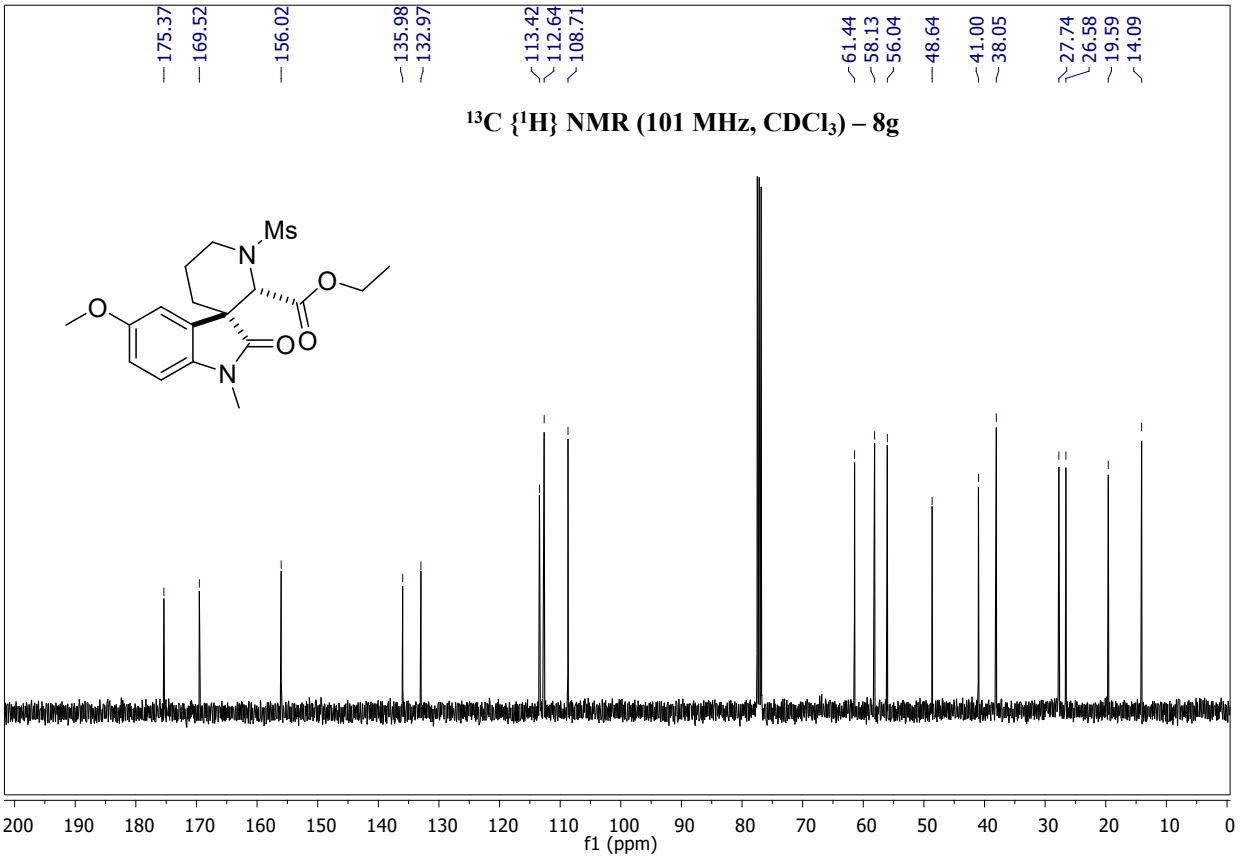
^{1}H NMR (400 MHz, $CDCl_3$) – 8f



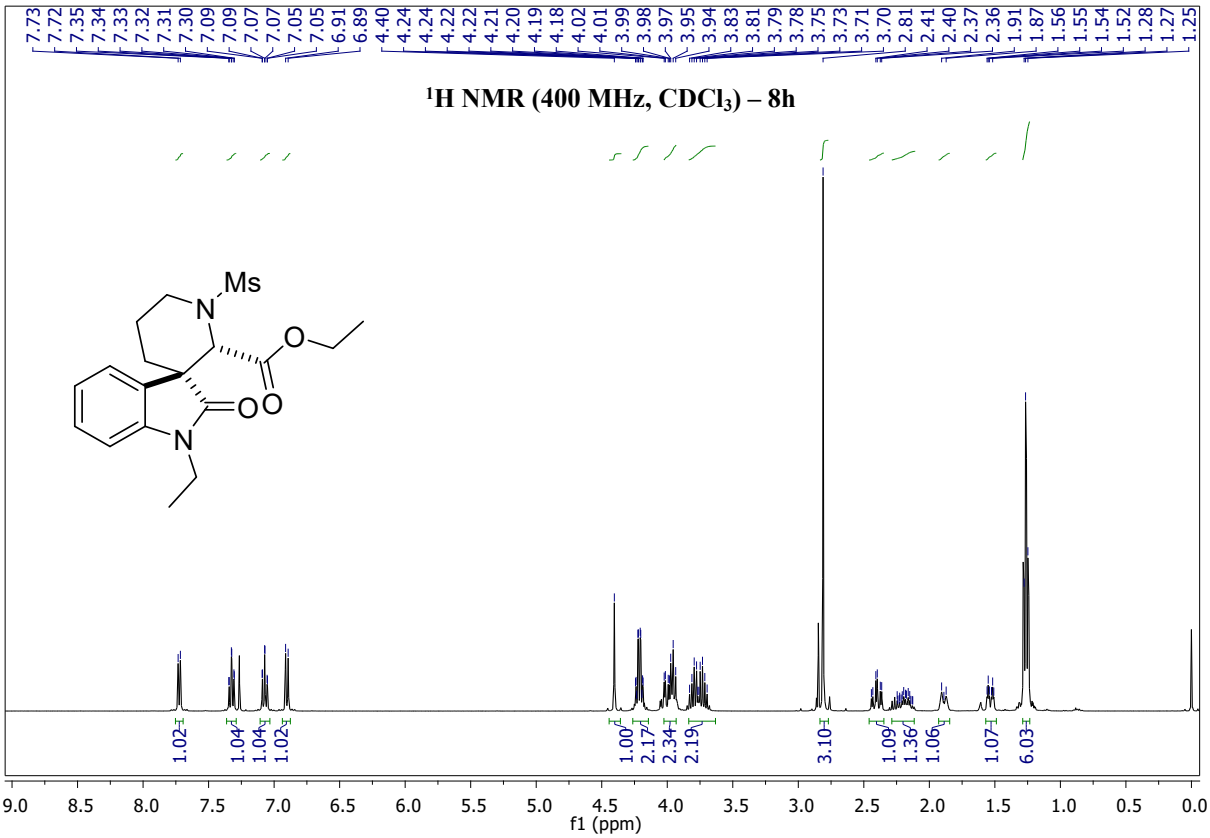
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8f



^{1}H NMR (400 MHz, $CDCl_3$) – 8g



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8g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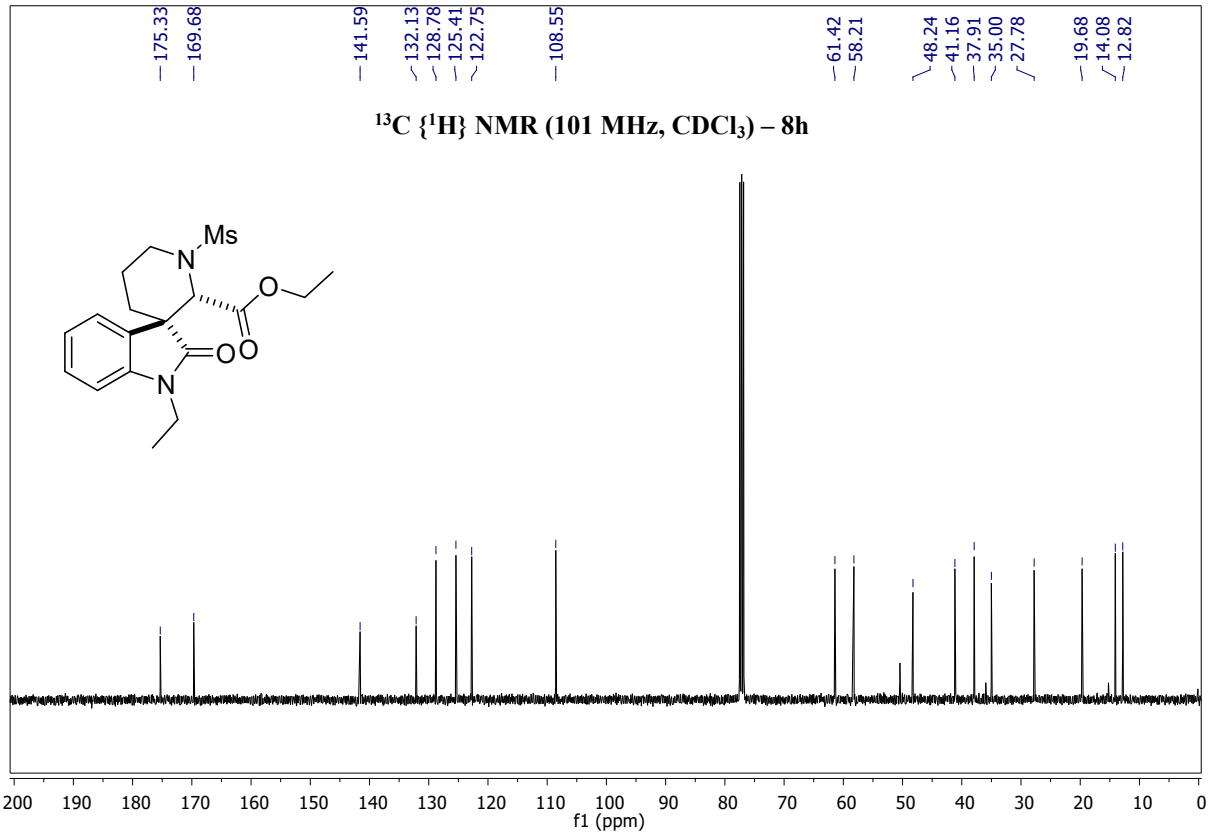
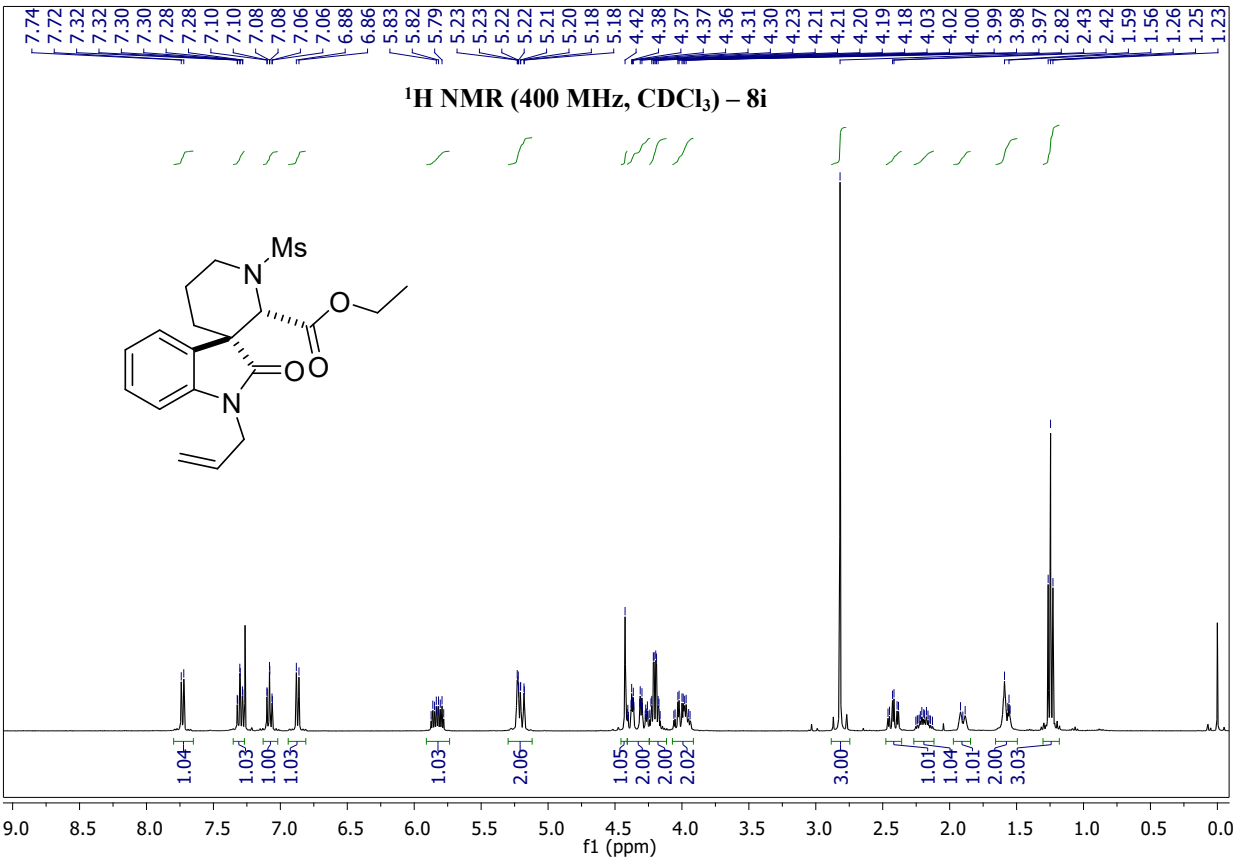
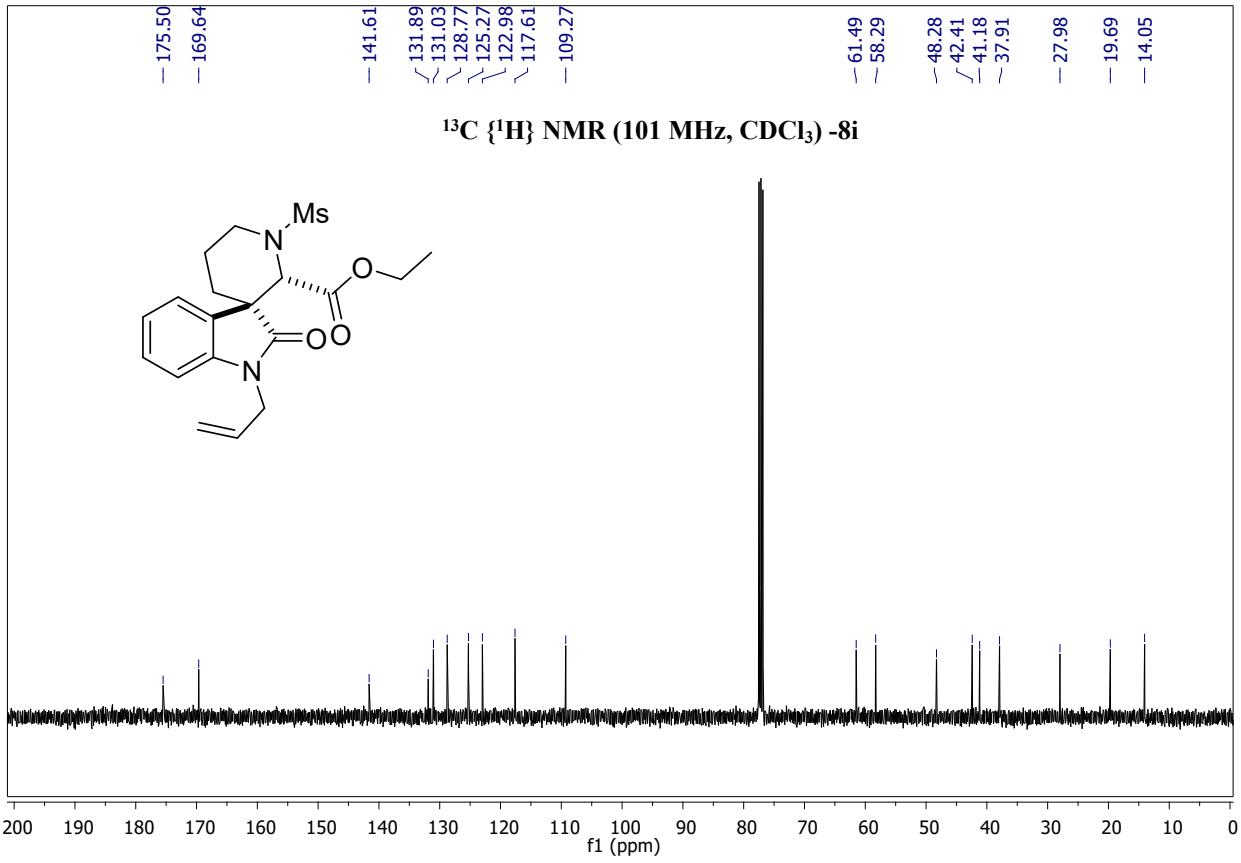
1H NMR (400 MHz, CDCl3) – 8h
Ms
N
O
O
O
N
1.02 1.04 1.04 1.02 1.00 2.17 2.34 2.19 3.10 1.09 1.36 1.06 1.07 6.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

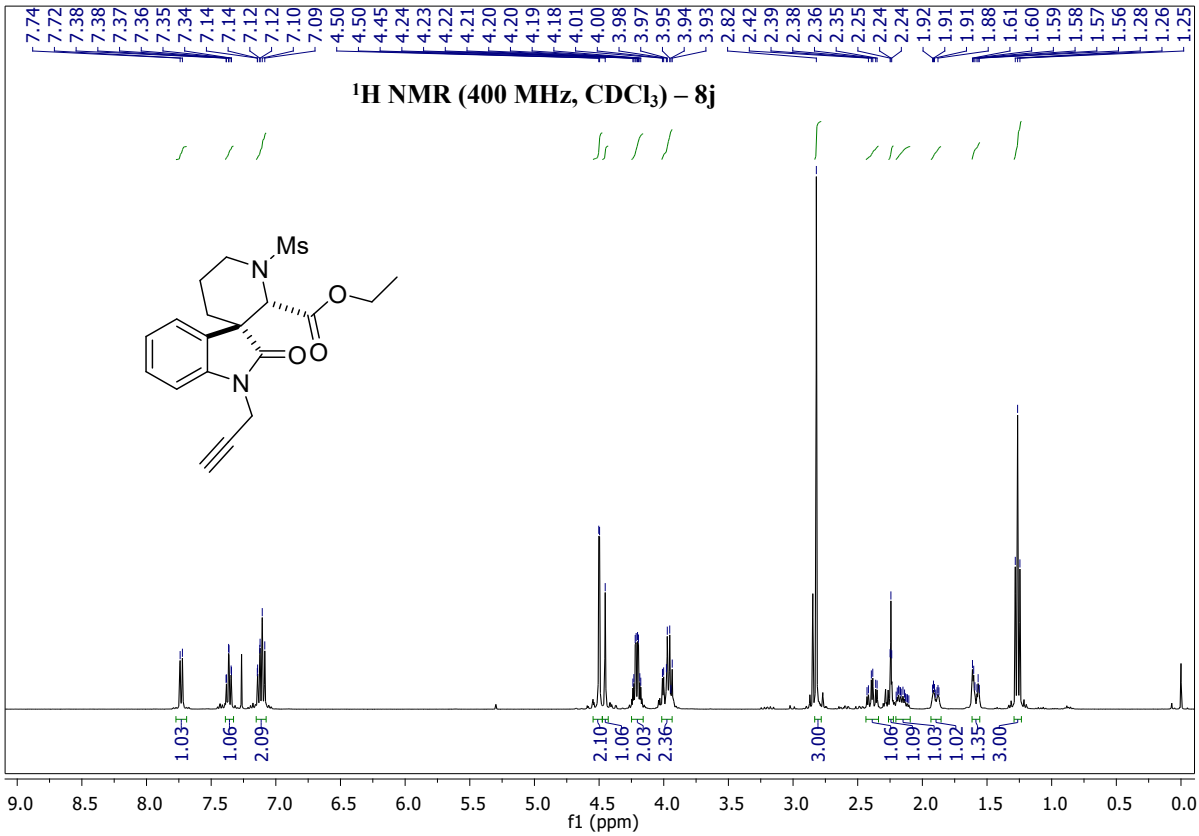

175.33 169.68 141.59 132.13 128.78 125.41 122.75 108.55 61.42 58.21 48.24 41.16 37.91 35.00 27.78 19.68 14.08 12.82
13C {1H} NMR (101 MHz, CDCl3) – 8h
Ms
N
O
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



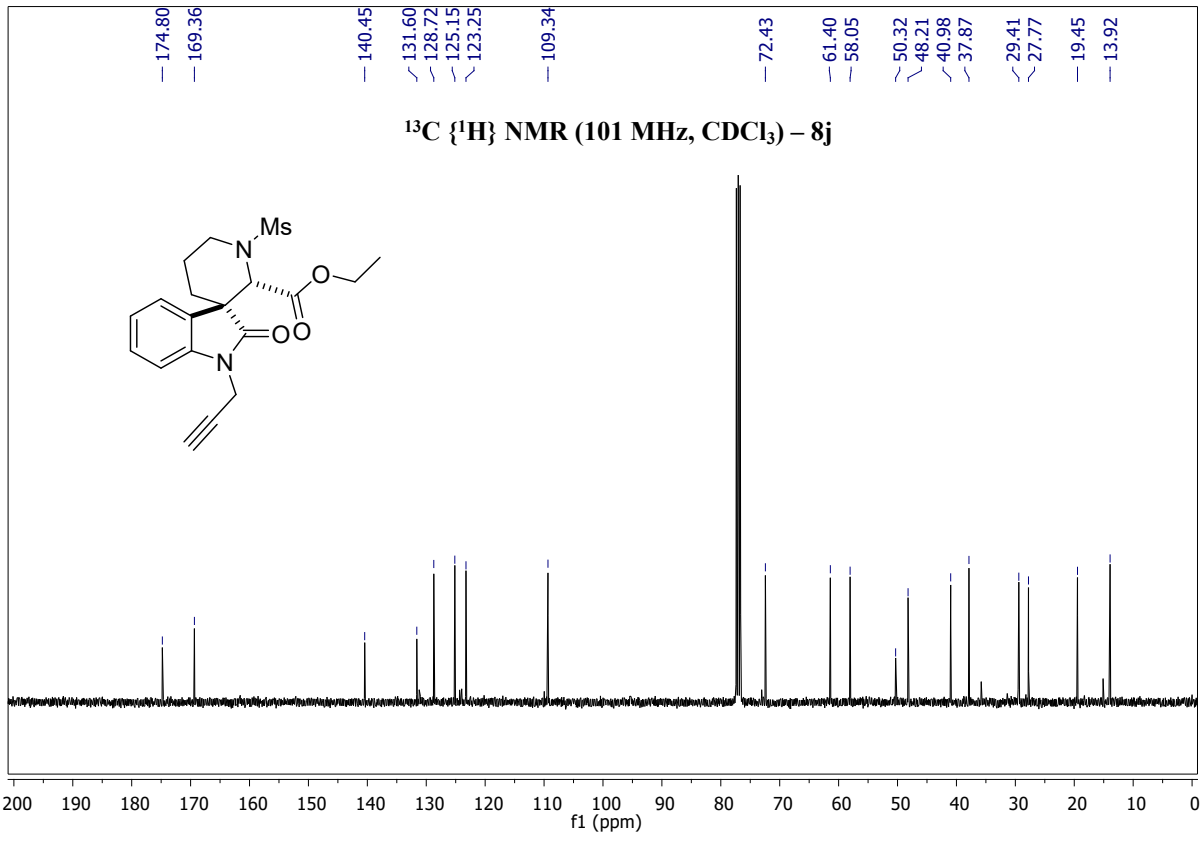
^{1}H NMR (400 MHz, $CDCl_3$) – 8i



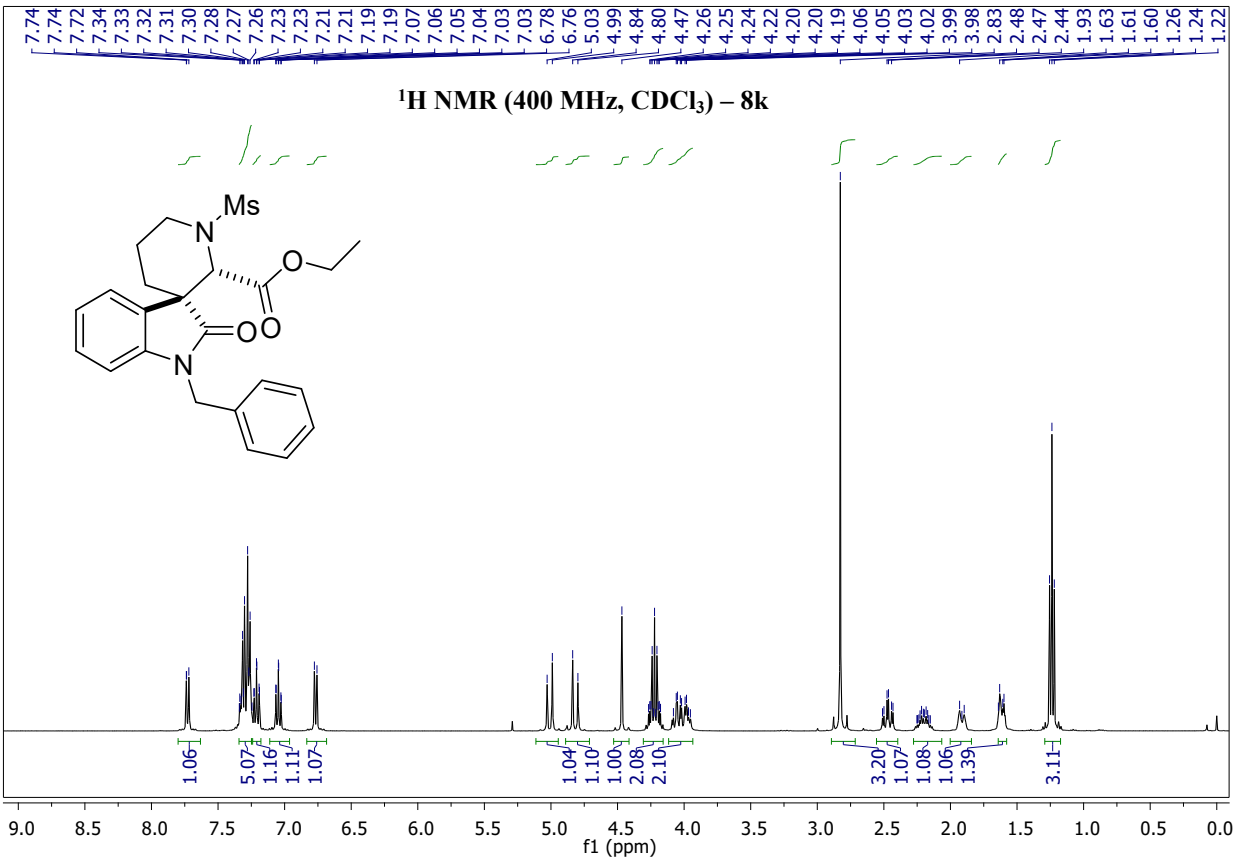
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) -8i



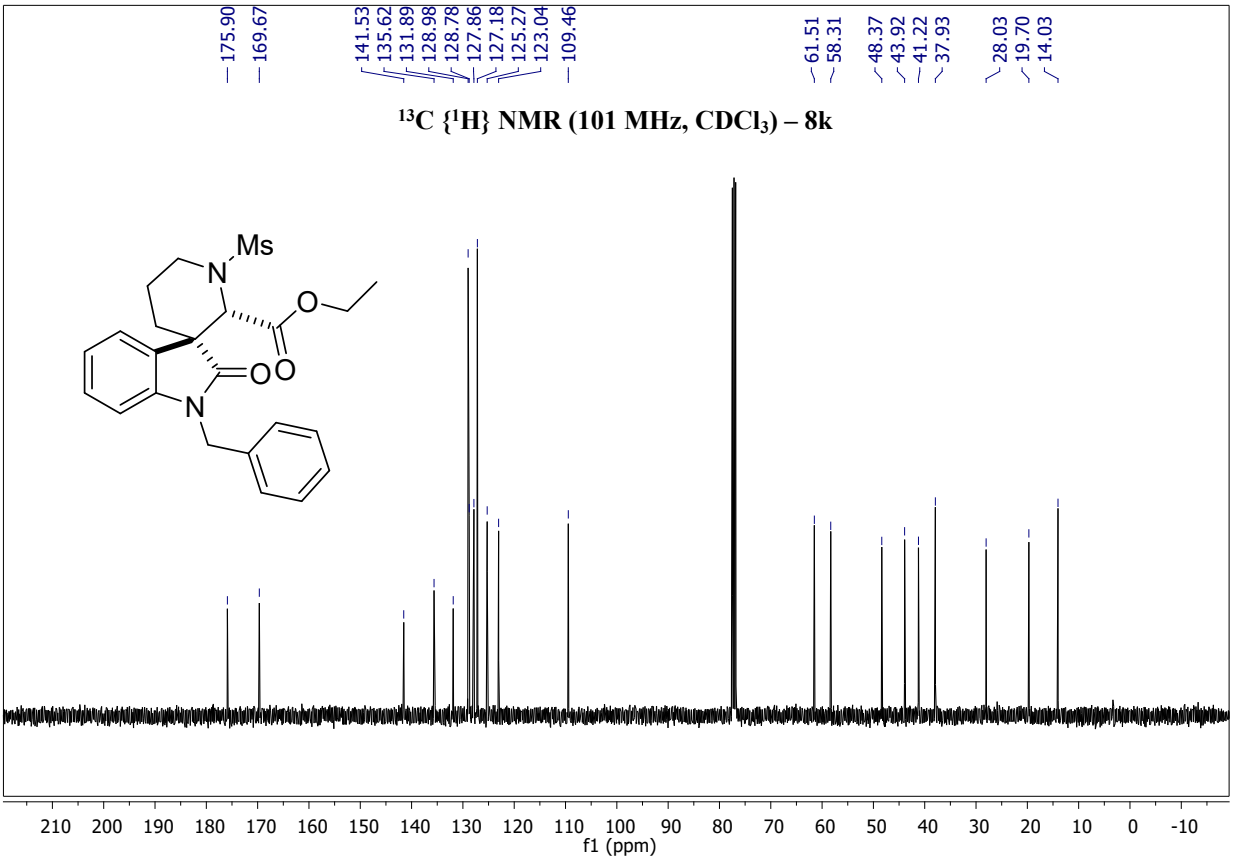
^{1}H NMR (400 MHz, $CDCl_3$) – 8j



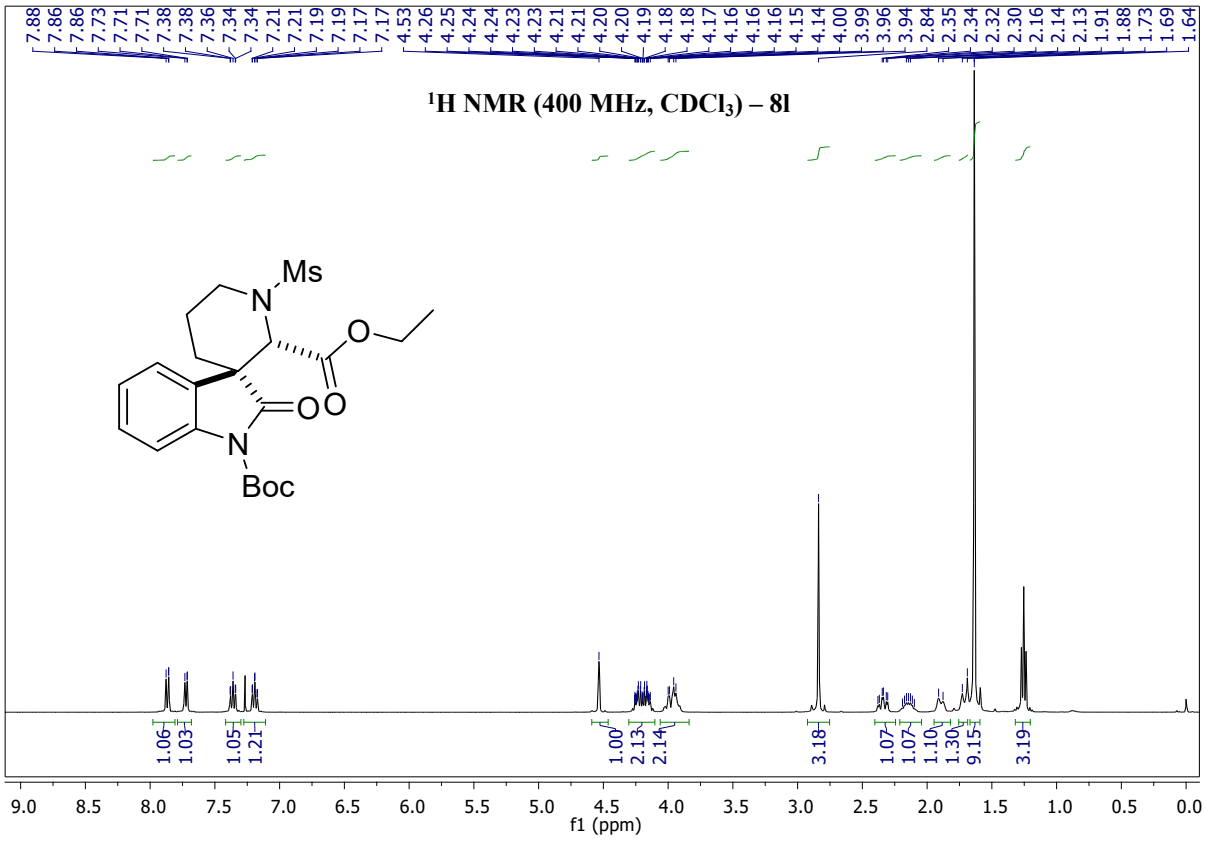
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8j

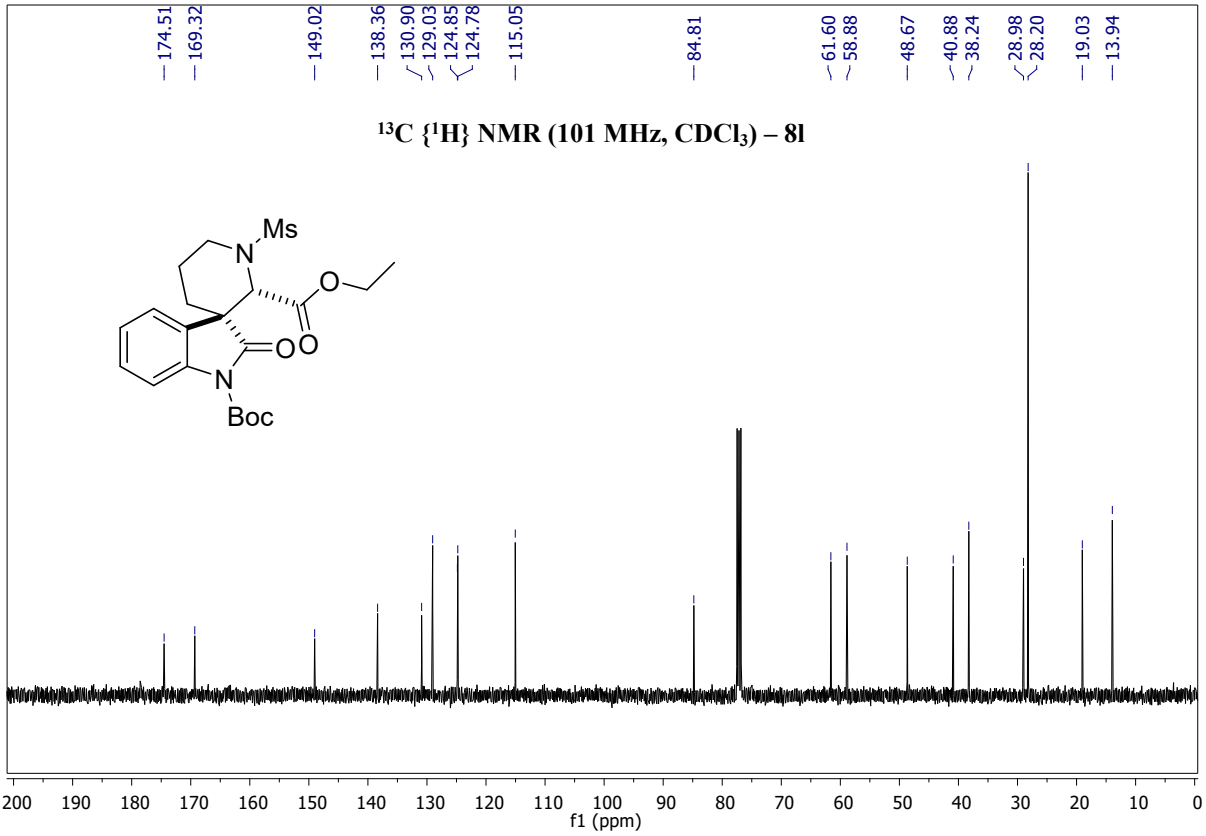


^{1}H NMR (400 MHz, $CDCl_3$) – 8k

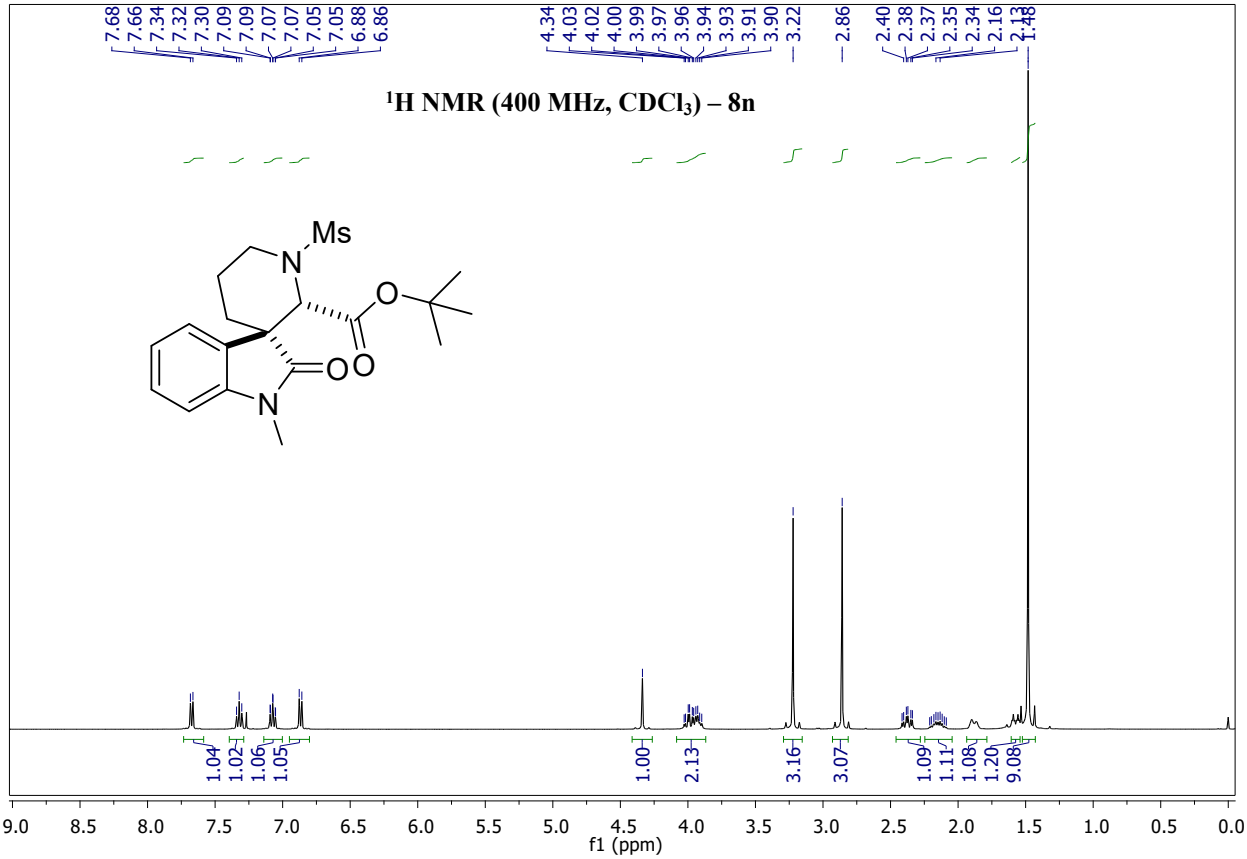


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8k

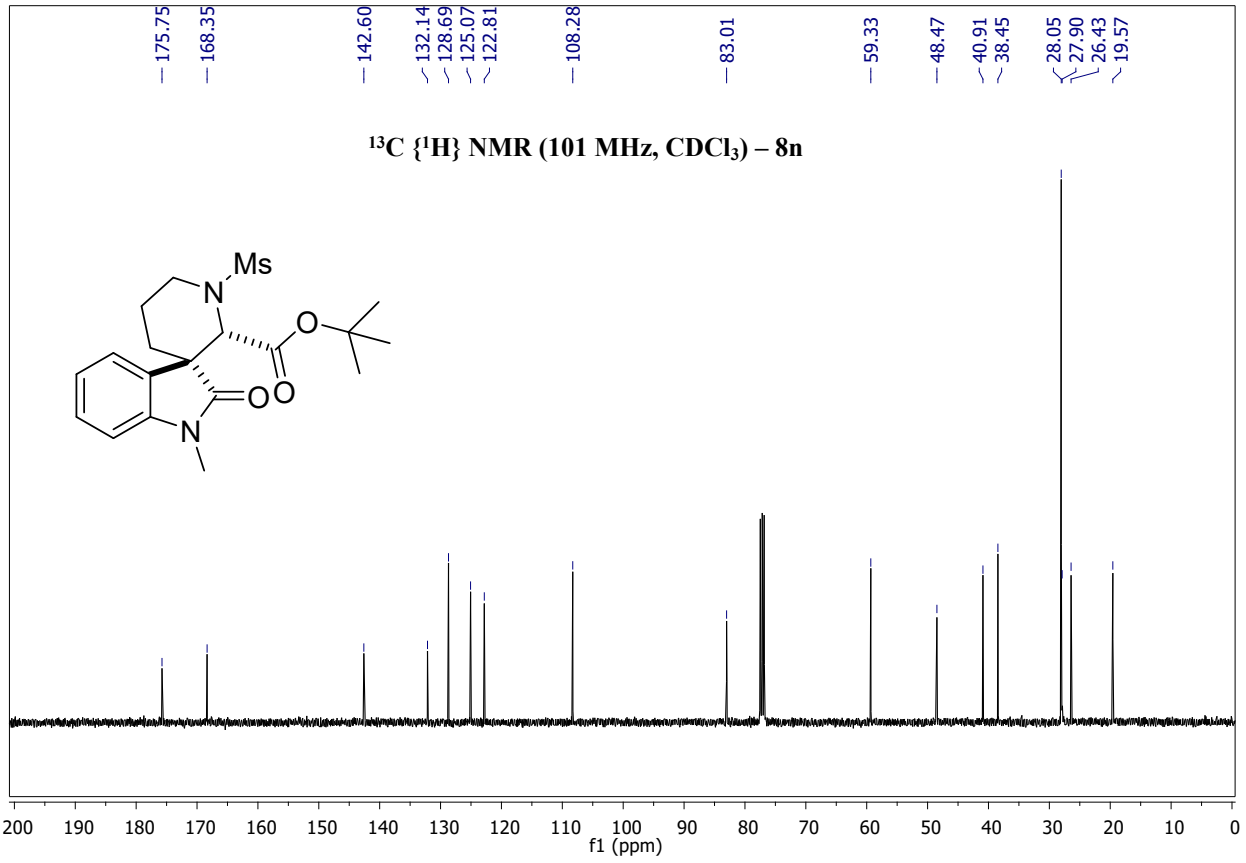

7.88 7.86 7.86 7.73 7.71 7.71 7.38 7.38 7.36 7.34 7.34 7.21 7.21 7.19 7.19 7.17 7.17 4.53 4.26 4.25 4.24 4.24 4.23 4.21 4.21 4.20 4.20 4.19 4.18 4.18 4.17 4.16 4.16 4.16 4.15 4.14 4.00 3.99 3.96 3.94 2.84 2.35 2.34 2.32 2.30 2.16 2.14 2.13 1.91 1.88 1.73 1.69 1.64
1H NMR (400 MHz, CDCl3) – 8l
Ms
N
O
O
O
N
Boc
1.06 1.03 1.05 1.21 1.00 2.13 2.14 3.18 1.07 1.07 1.10 1.30 9.15 3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

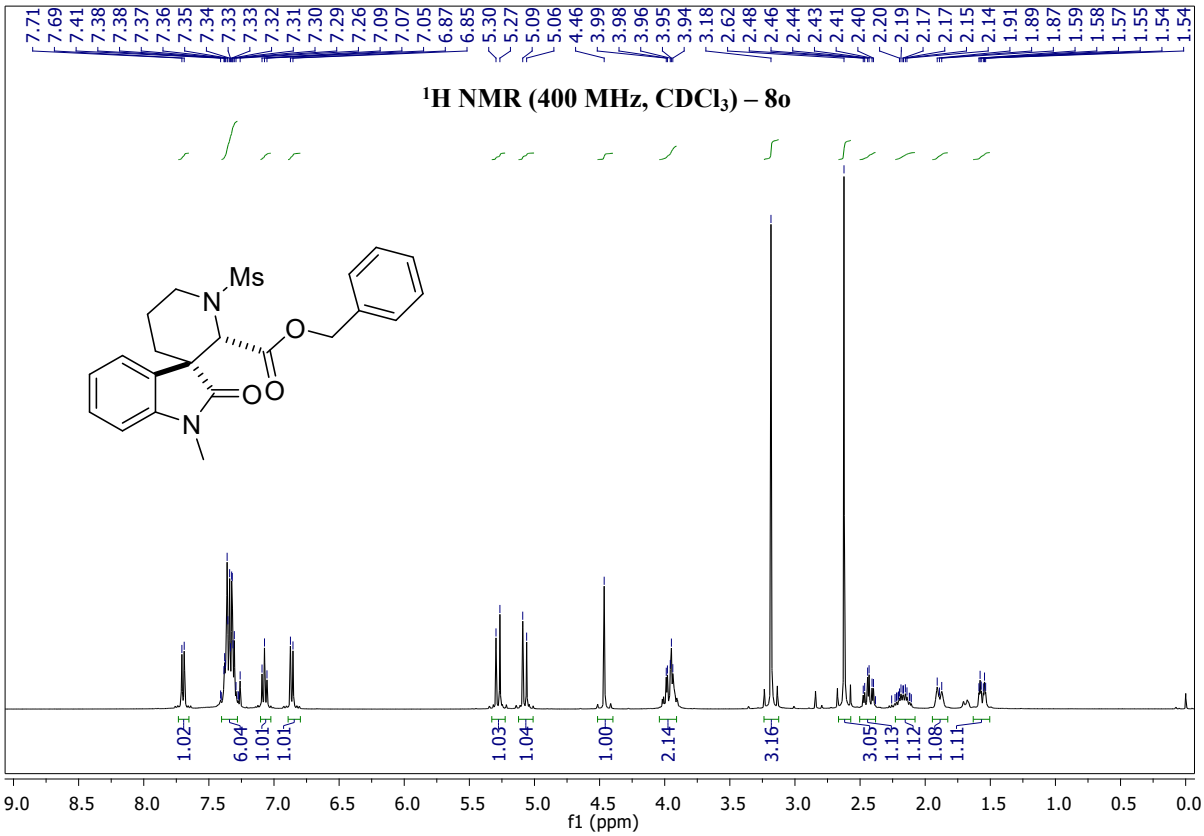

174.51 169.32 149.02 138.36 130.90 129.03 124.85 124.78 115.05 84.81 61.60 58.88 48.67 40.88 38.24 28.98 28.20 19.03 13.94
13C {1H} NMR (101 MHz, CDCl3) – 8l
Ms
N
O
O
O
N
Boc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$) – 8n

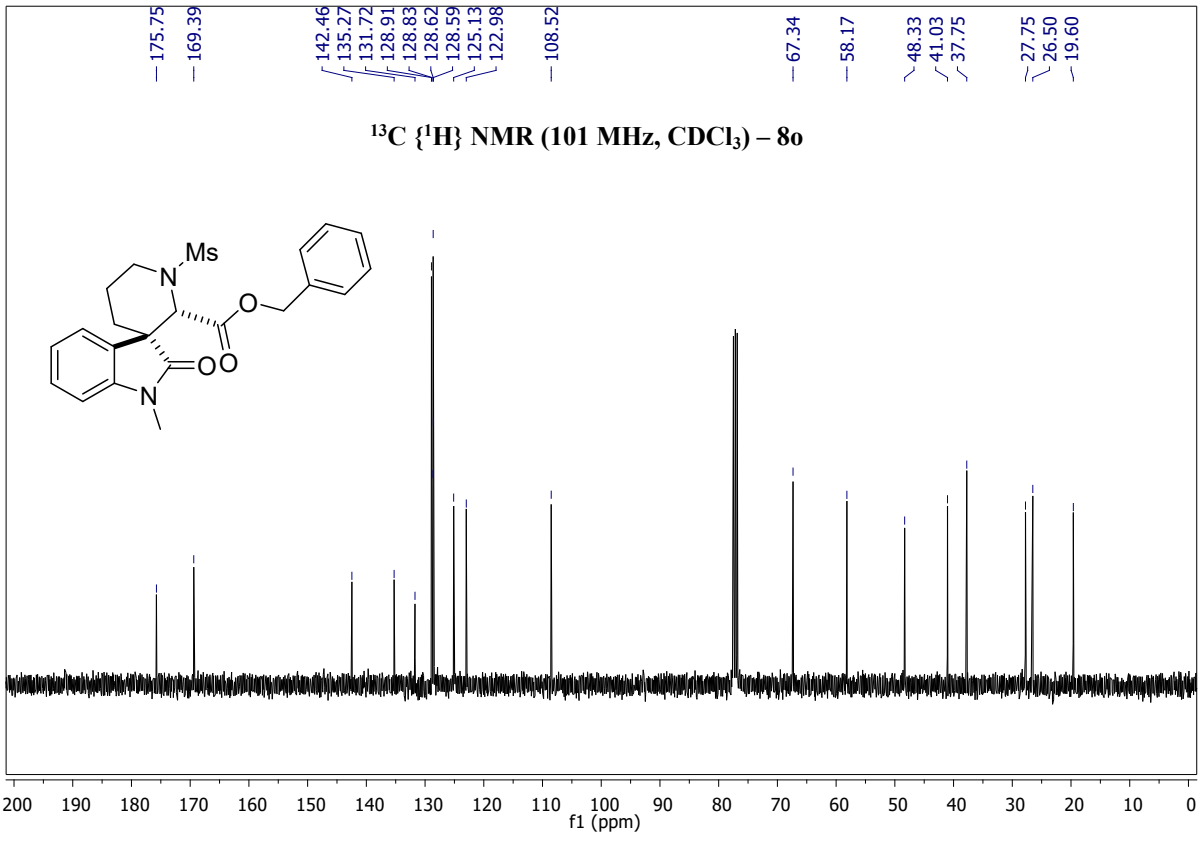


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8n

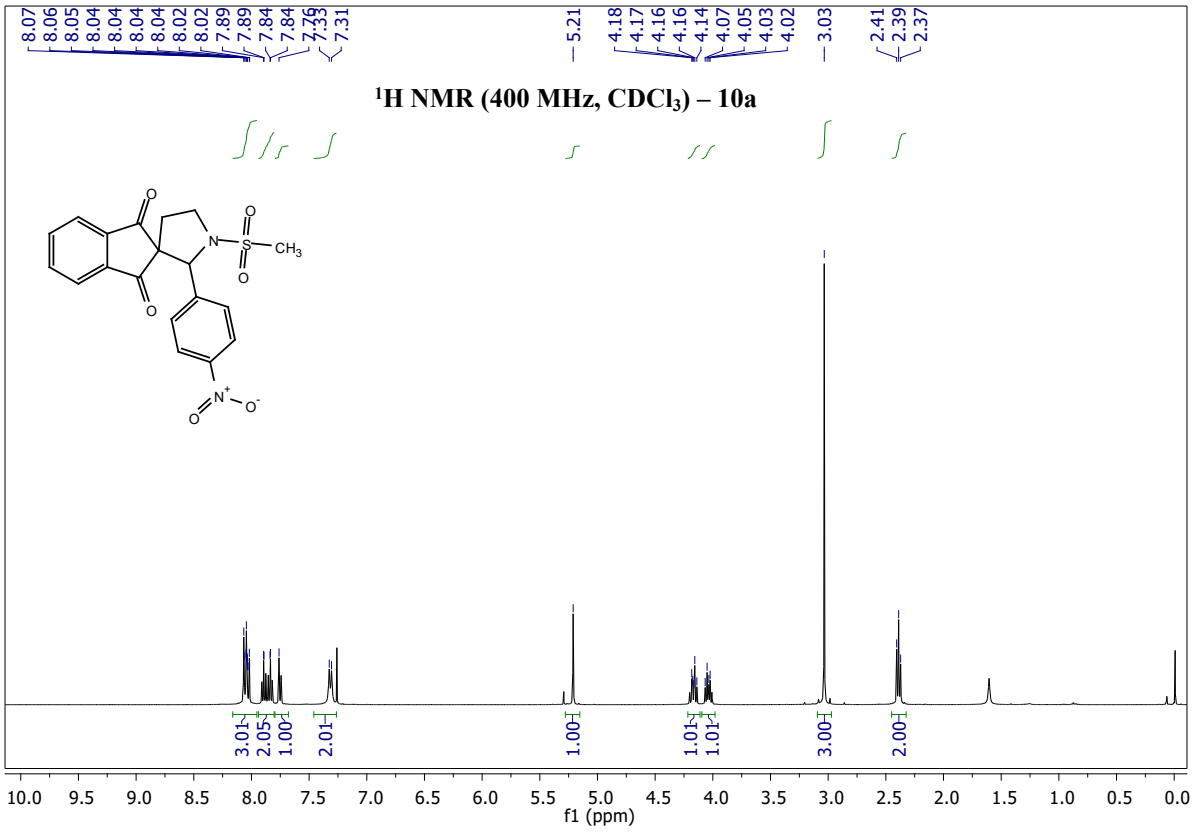




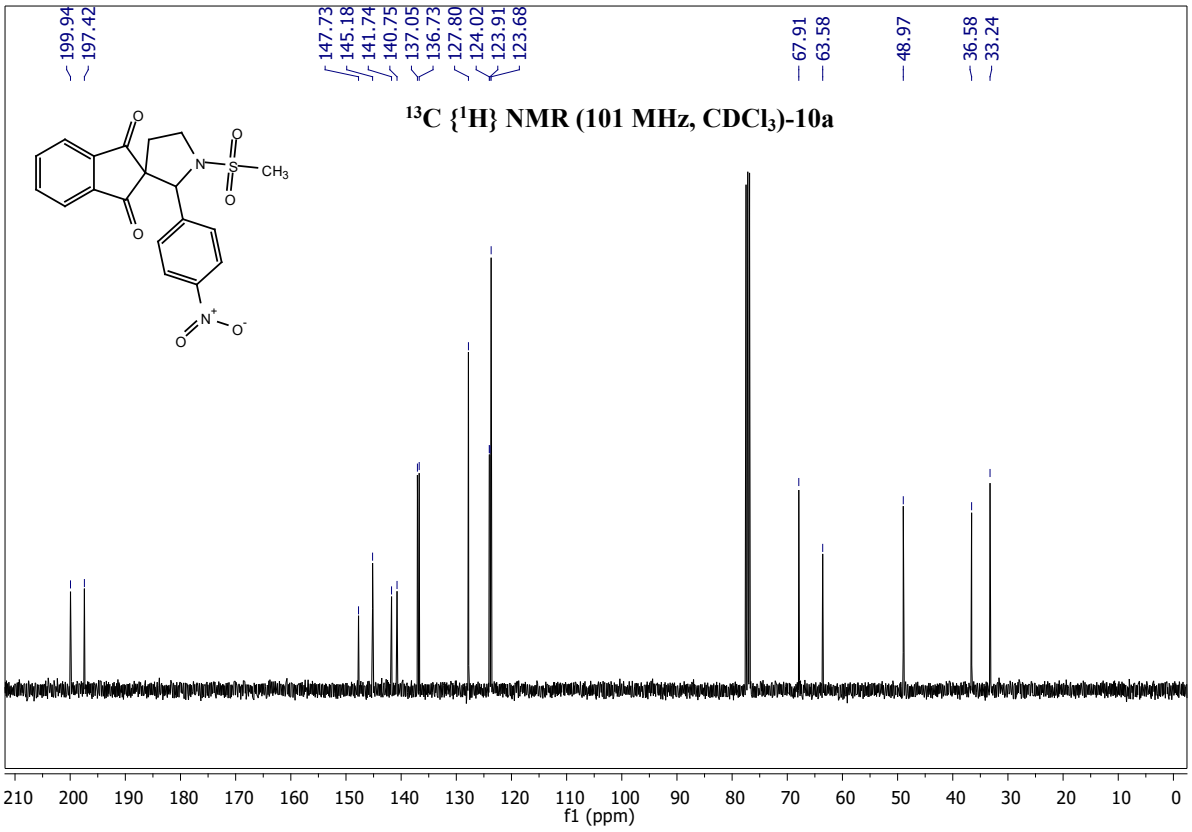
^{1}H NMR (400 MHz, $CDCl_3$) – 8o



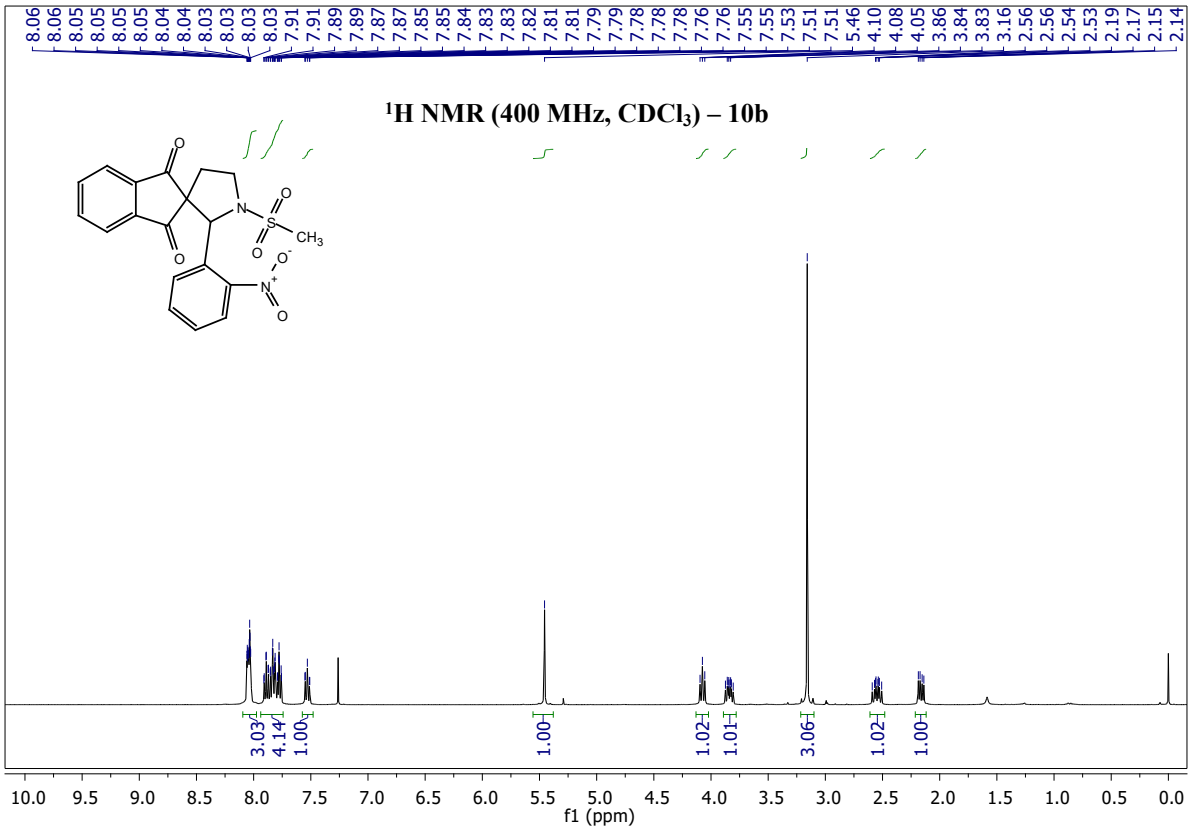
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 8o



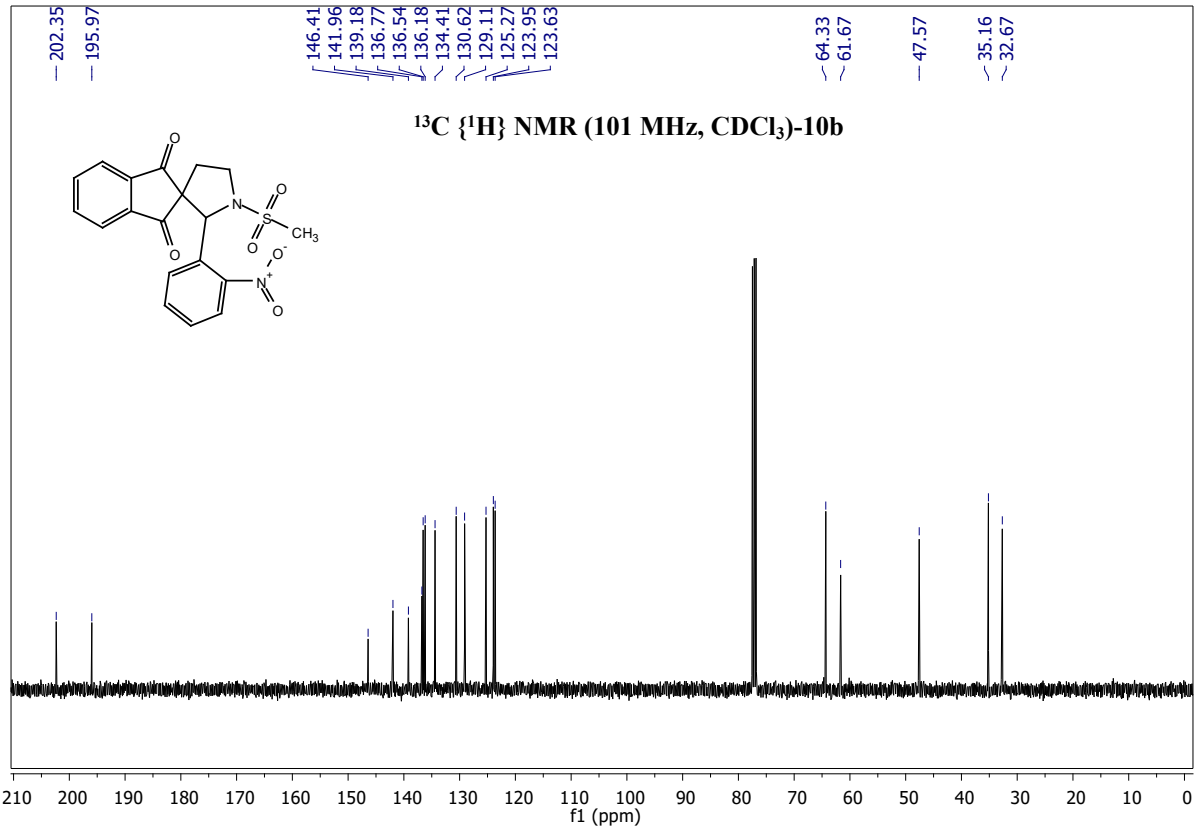
^{1}H NMR (400 MHz, $CDCl_3$) – 10a



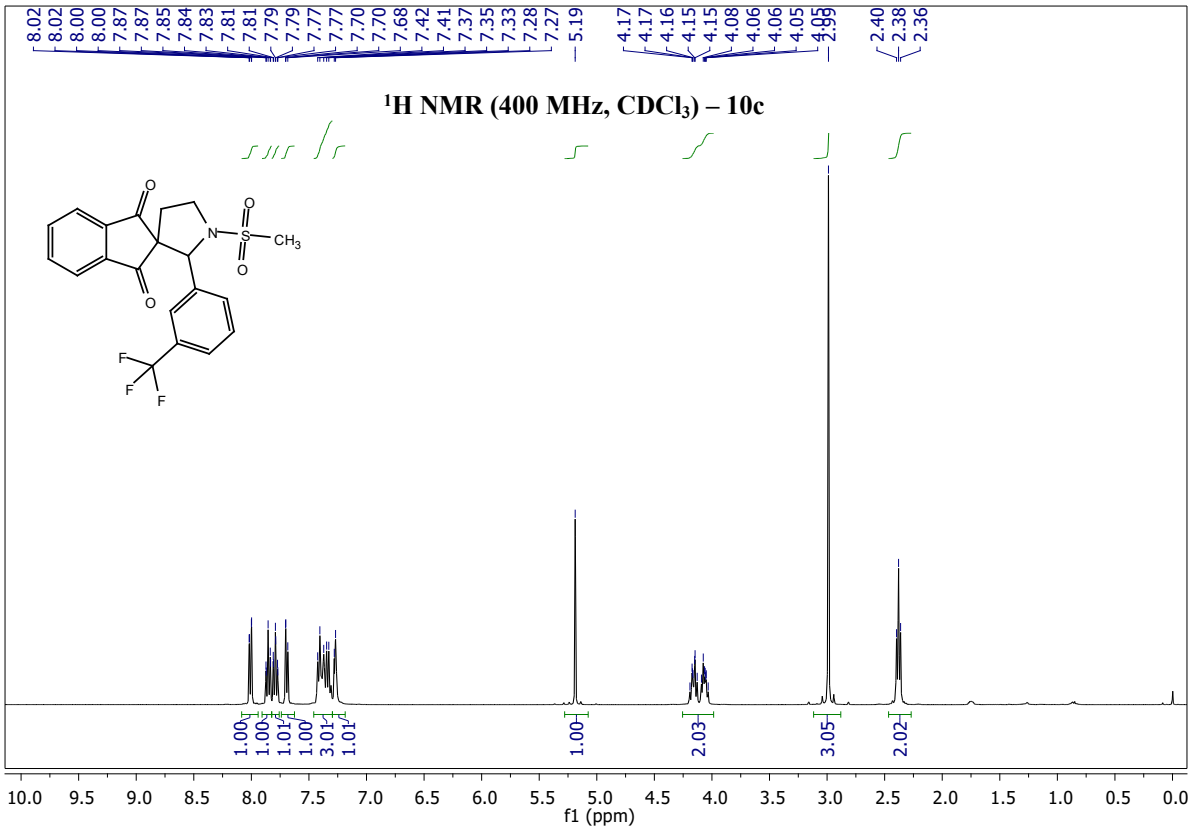
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10a



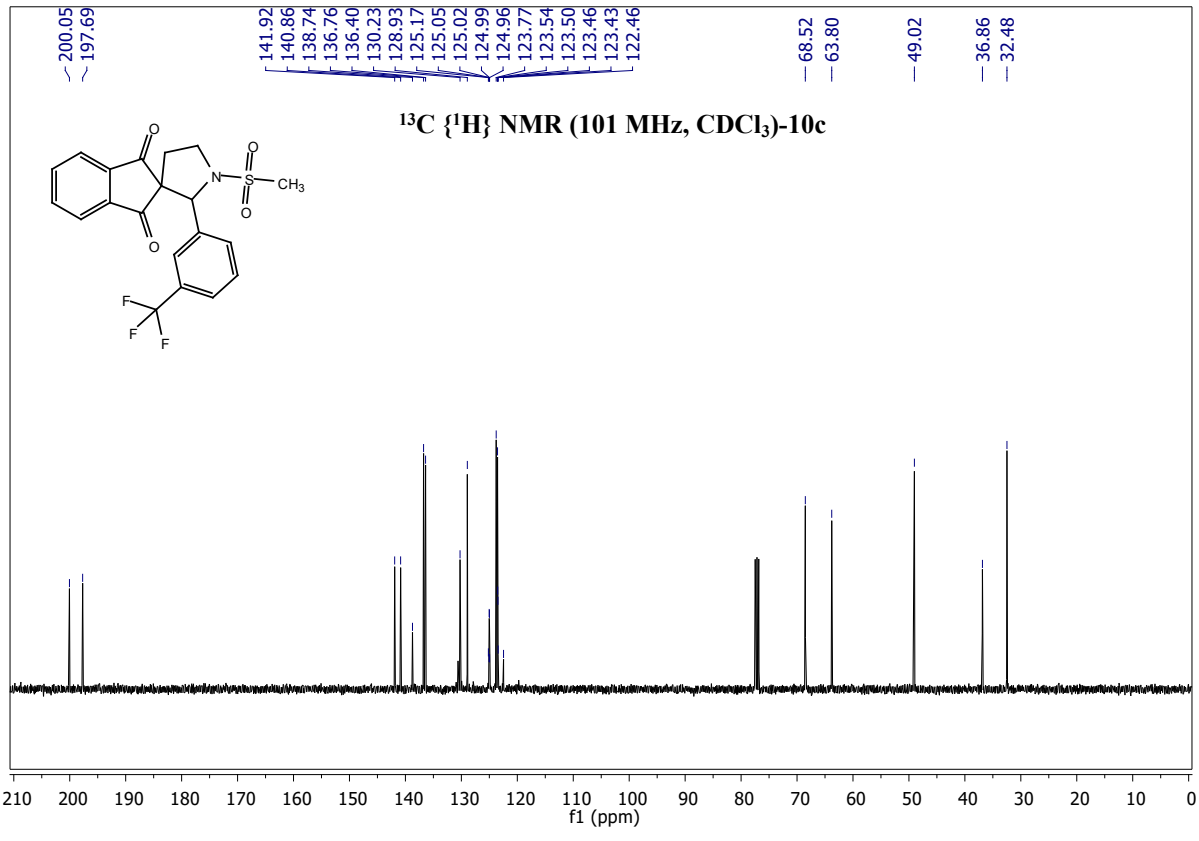
^{1}H NMR (400 MHz, $CDCl_3$) – 10b



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10b

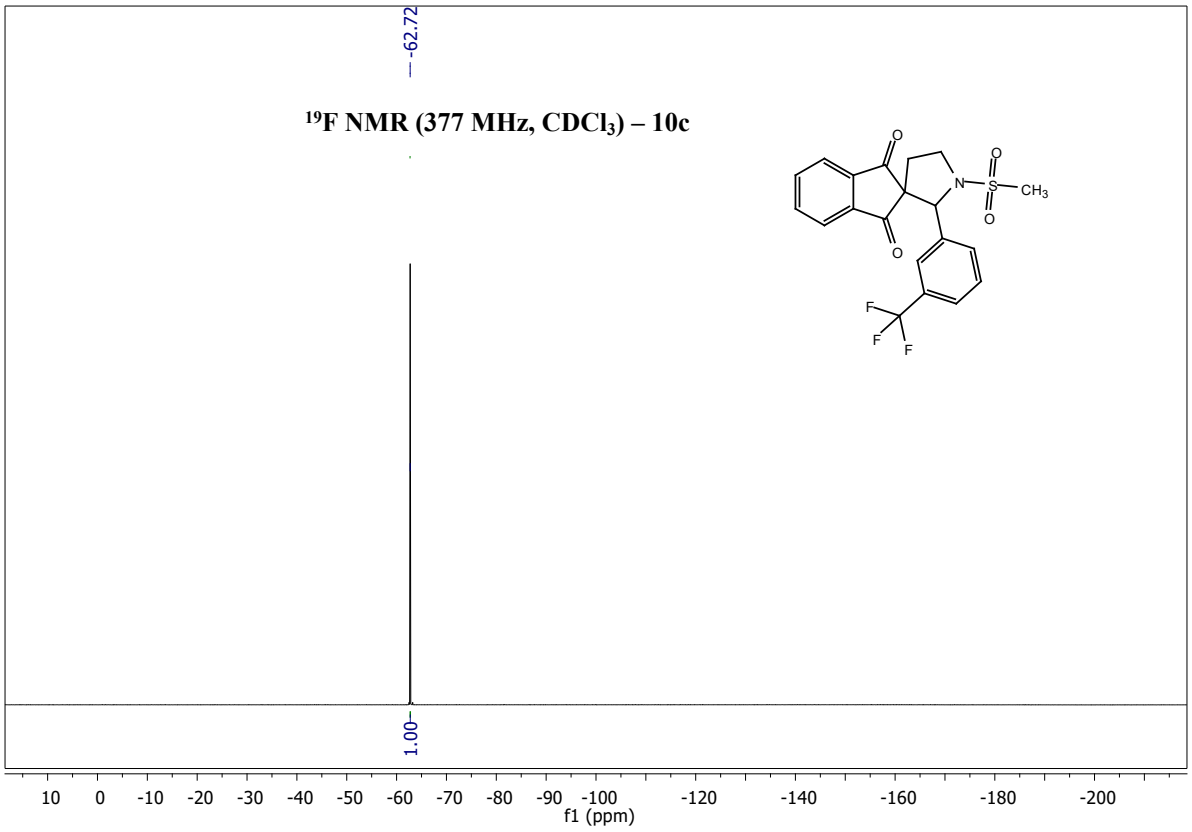


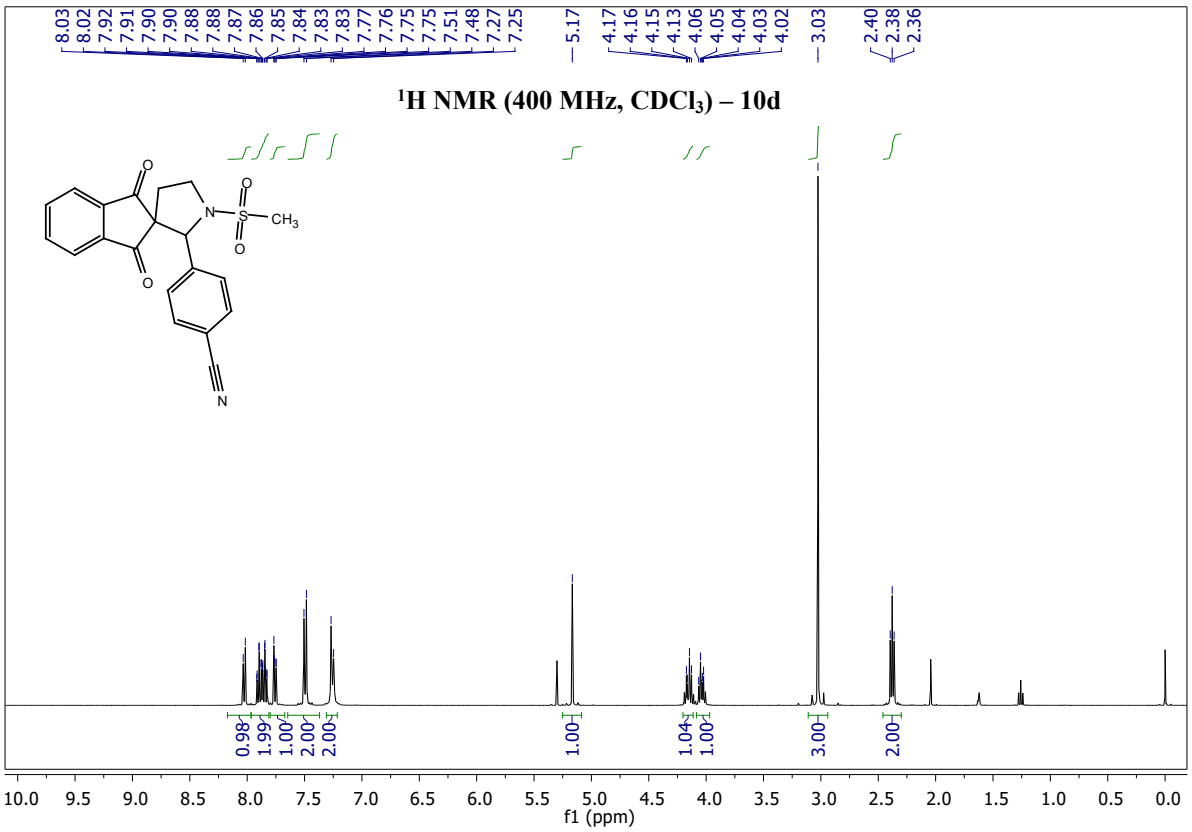
^{1}H NMR (400 MHz, $CDCl_3$) – 10c



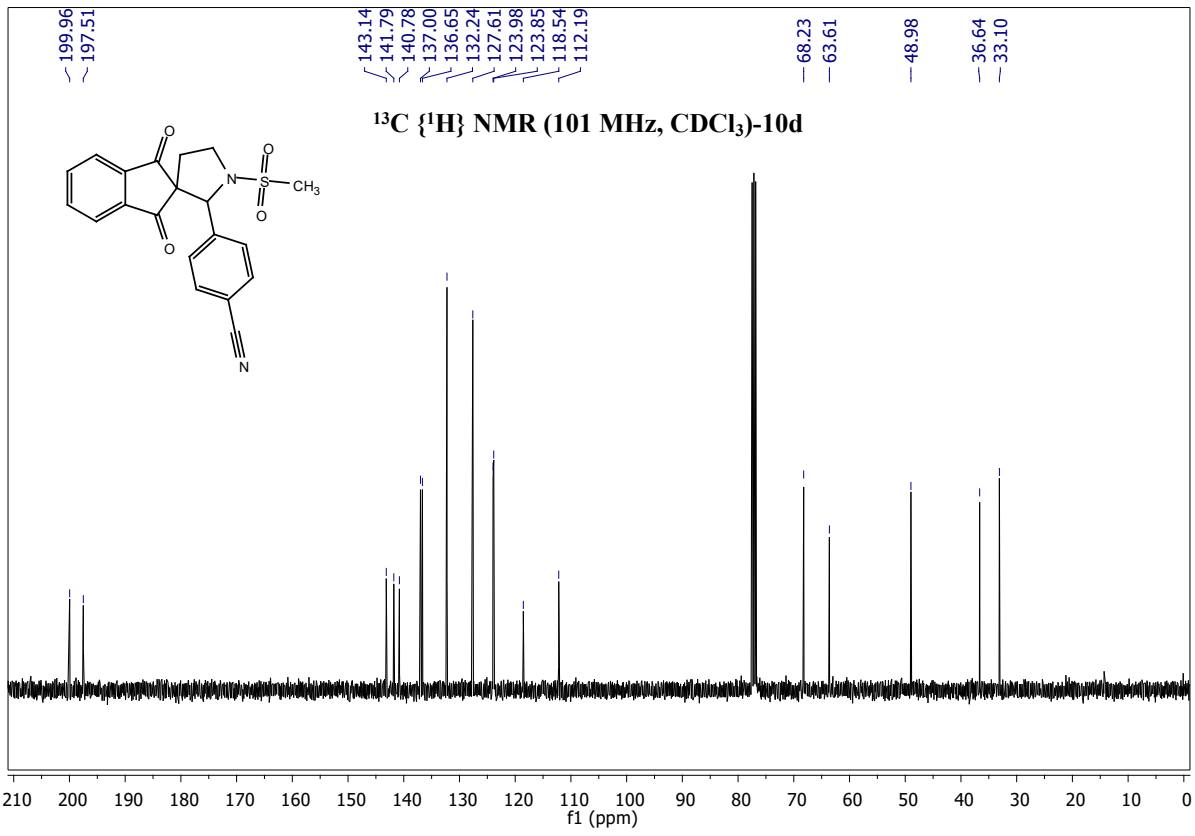
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10c

^{19}F NMR (377 MHz, $CDCl_3$) – 10c

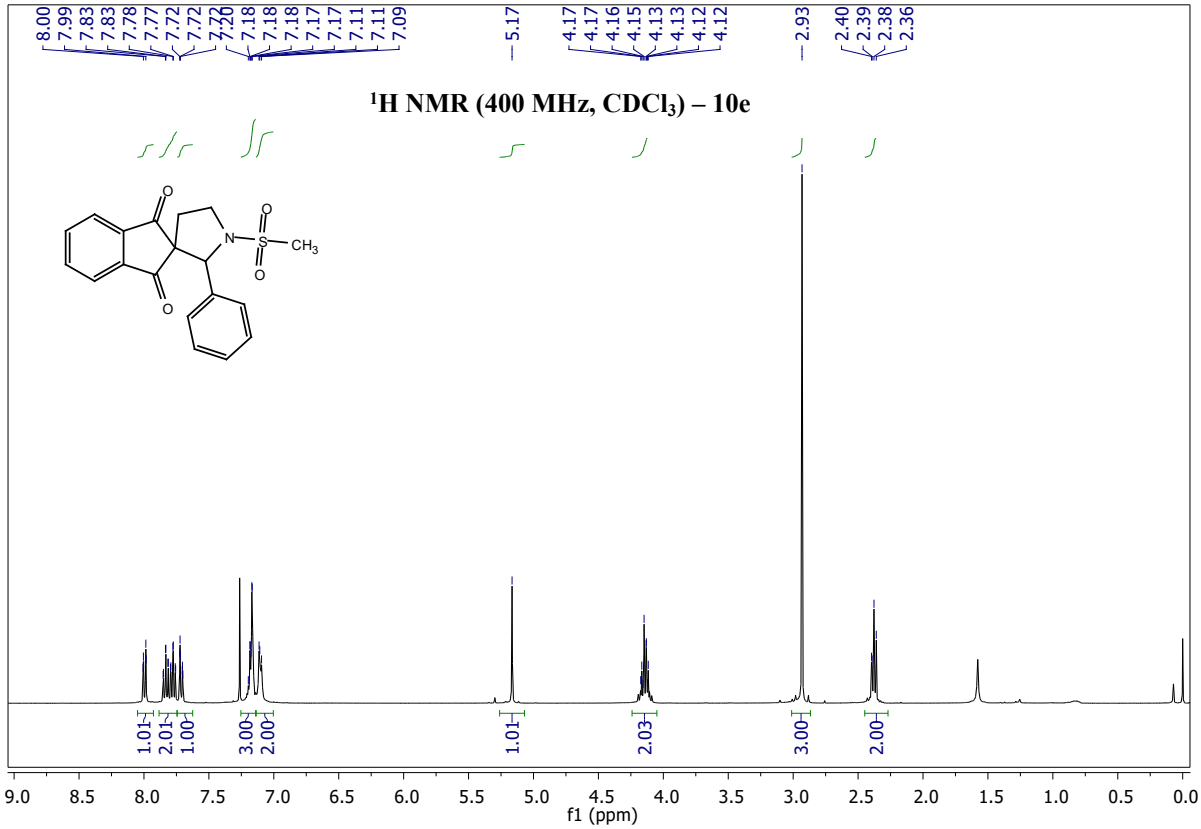


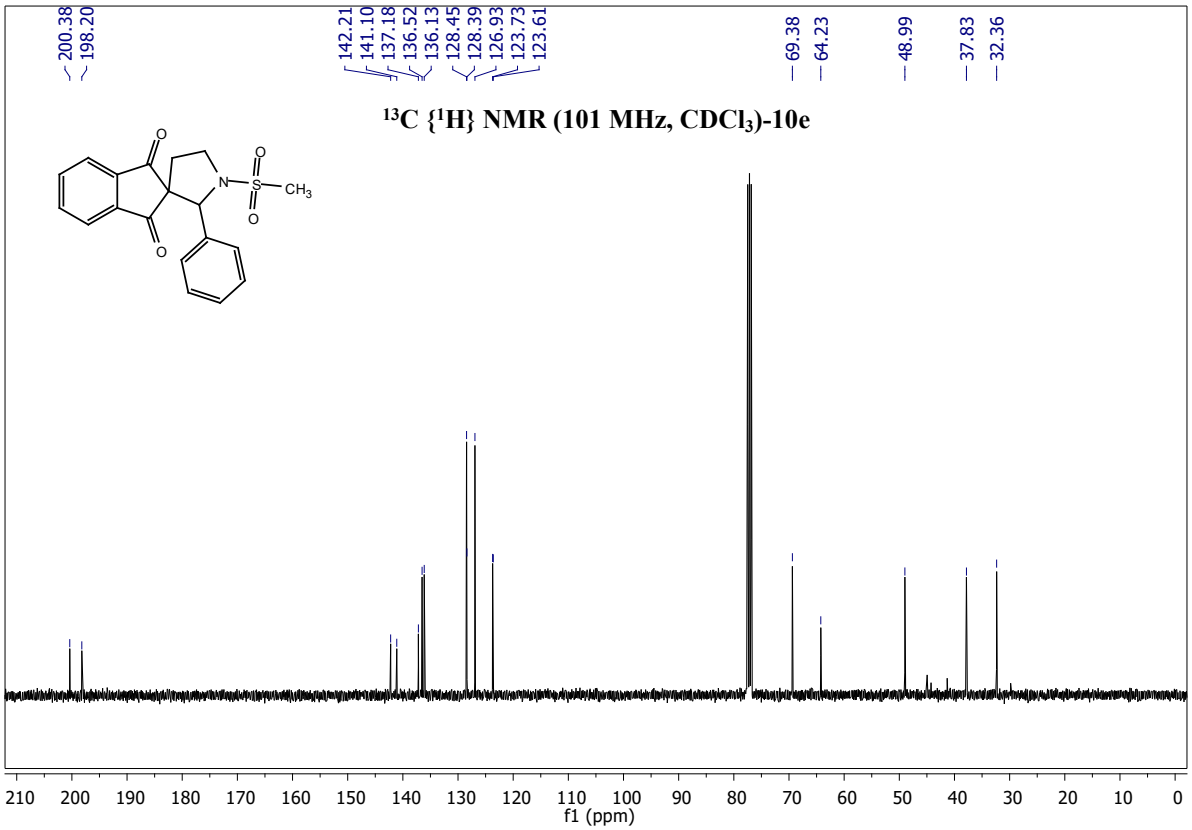


^{1}H NMR (400 MHz, $CDCl_3$) – 10d

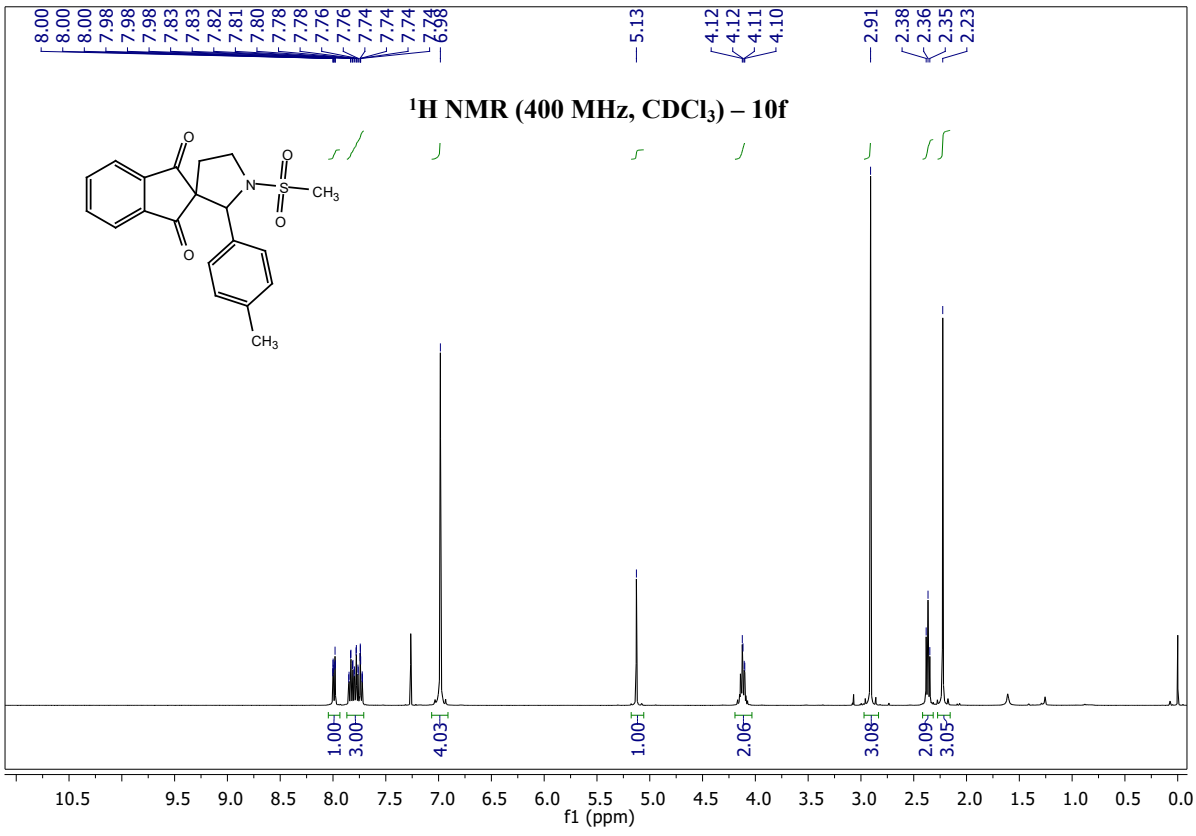


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10d

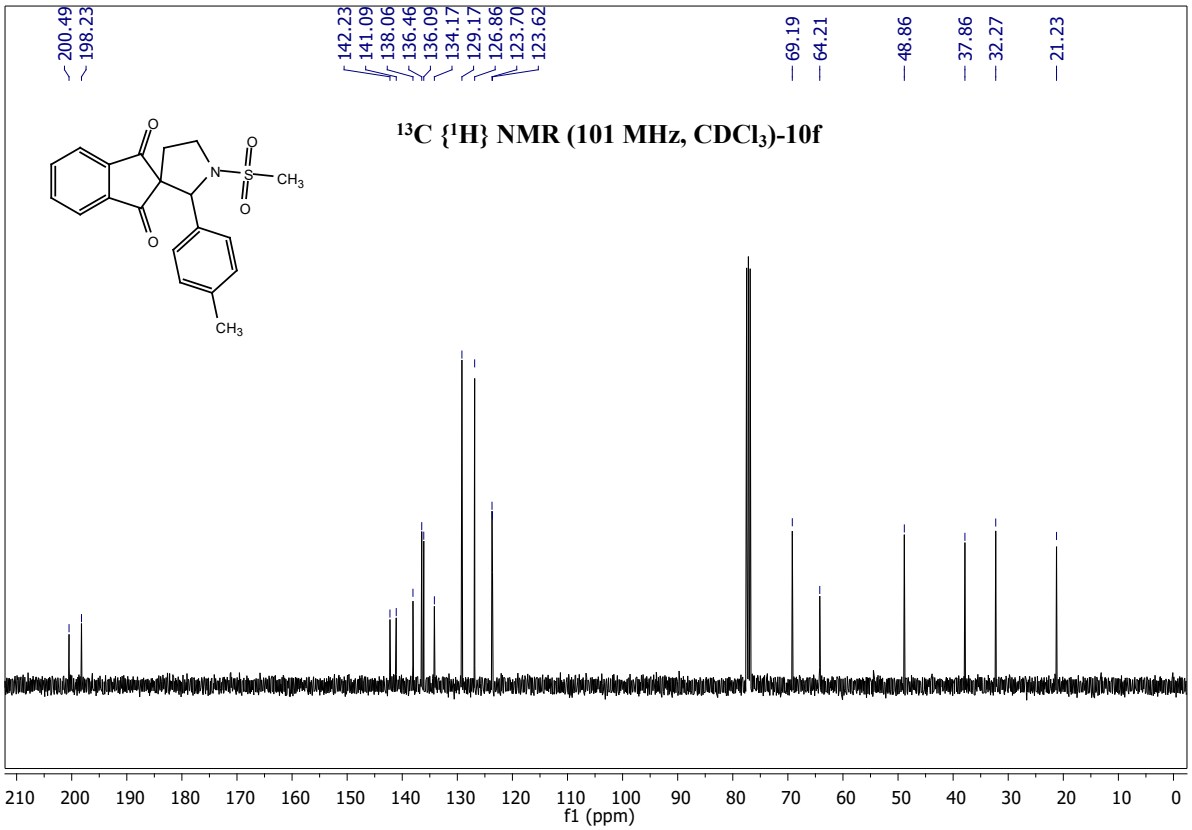

8.00
7.99
7.83
7.83
7.78
7.77
7.72
7.72
7.20
7.18
7.18
7.18
7.17
7.17
7.11
7.11
7.09
5.17
4.17
4.17
4.16
4.15
4.13
4.13
4.12
4.12
2.93
2.40
2.39
2.38
2.36
1H NMR (400 MHz, CDCl3) – 10e
O
O
N
S
O
O
CH3
1.01
2.01
1.00
3.00
2.00
1.01
2.03
3.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



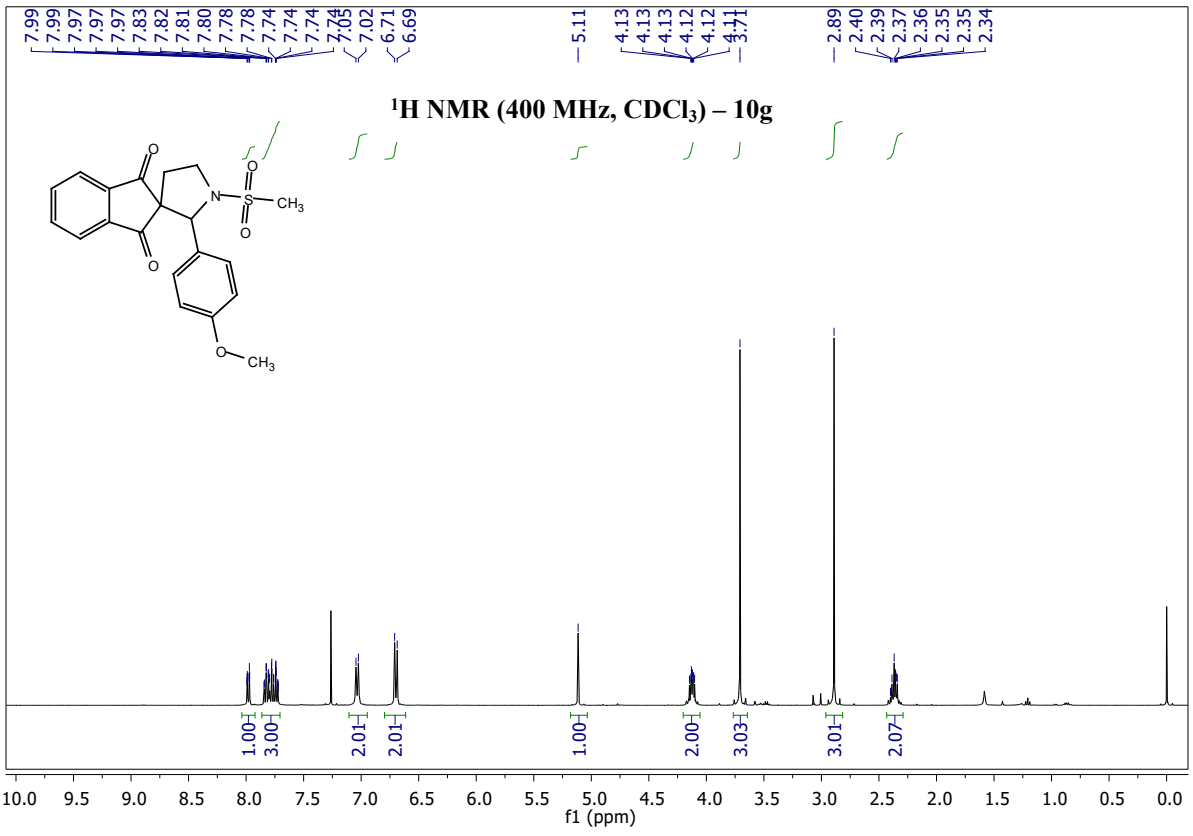
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10e



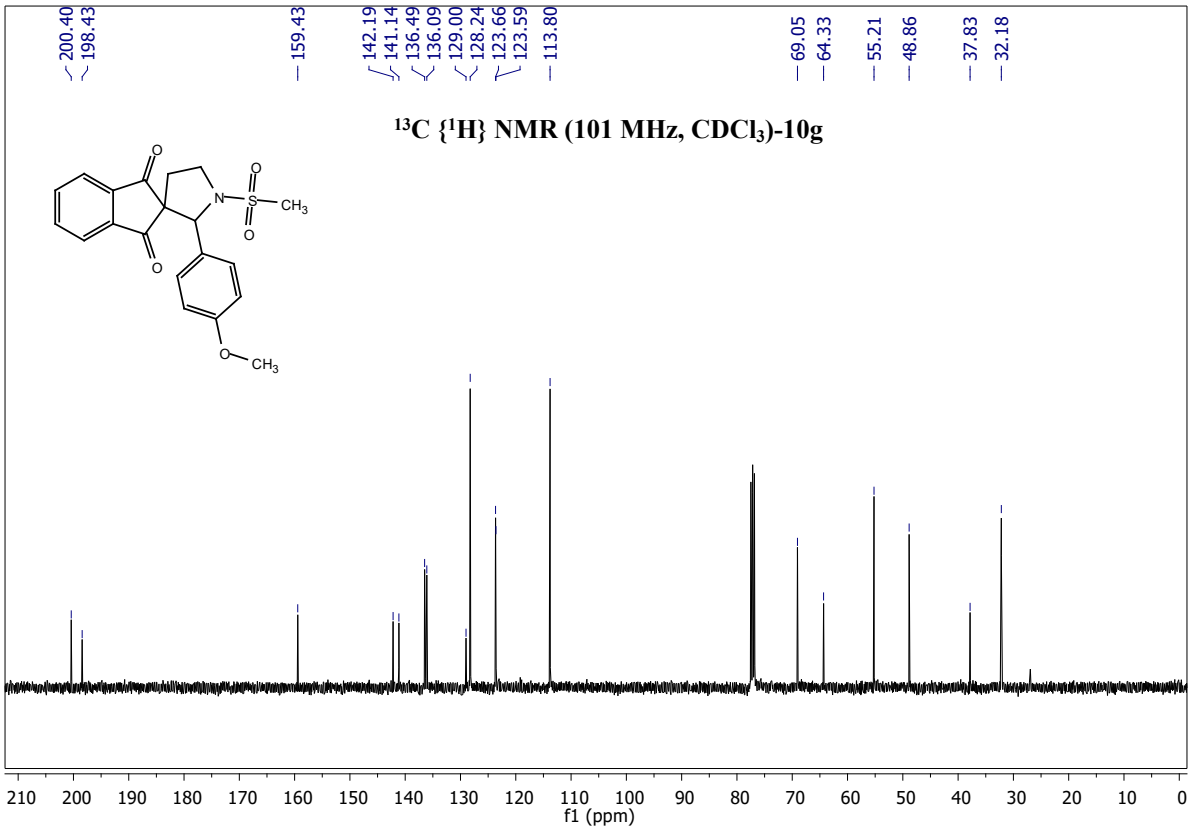
^{1}H NMR (400 MHz, $CDCl_3$) – 10f



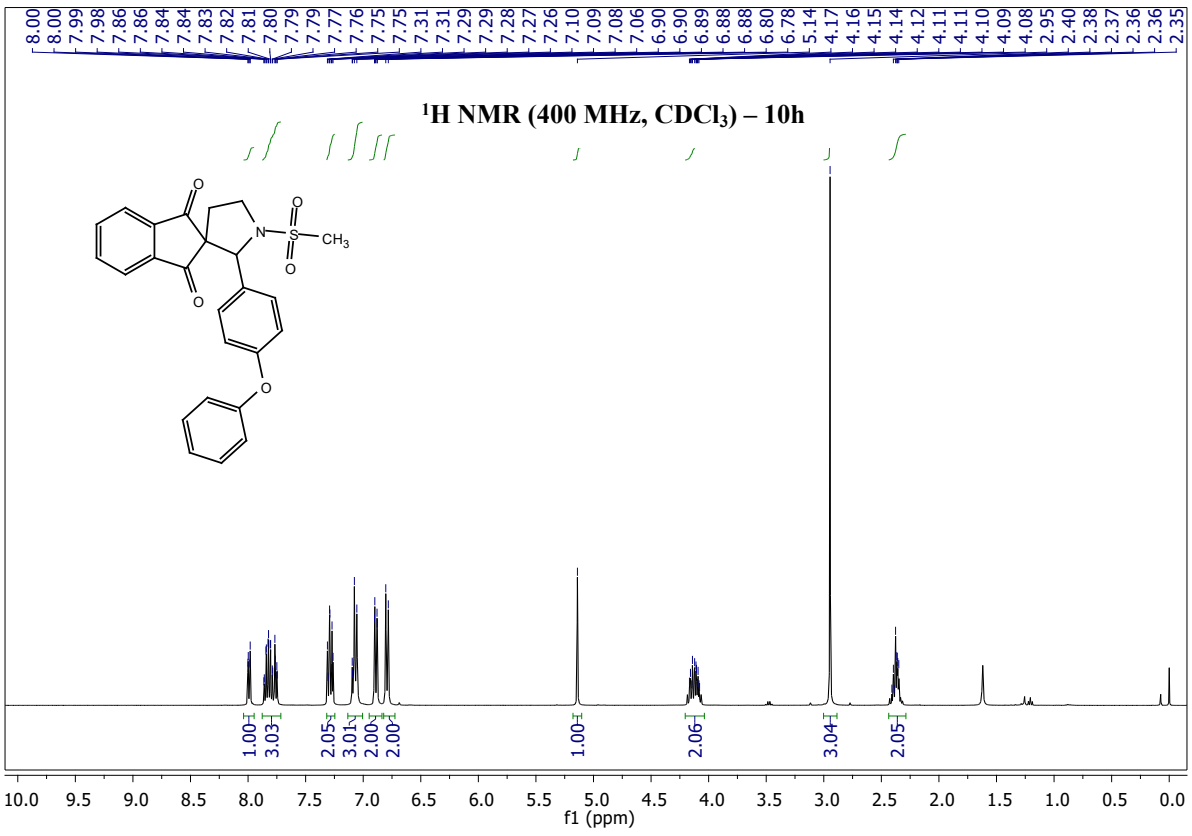
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10f



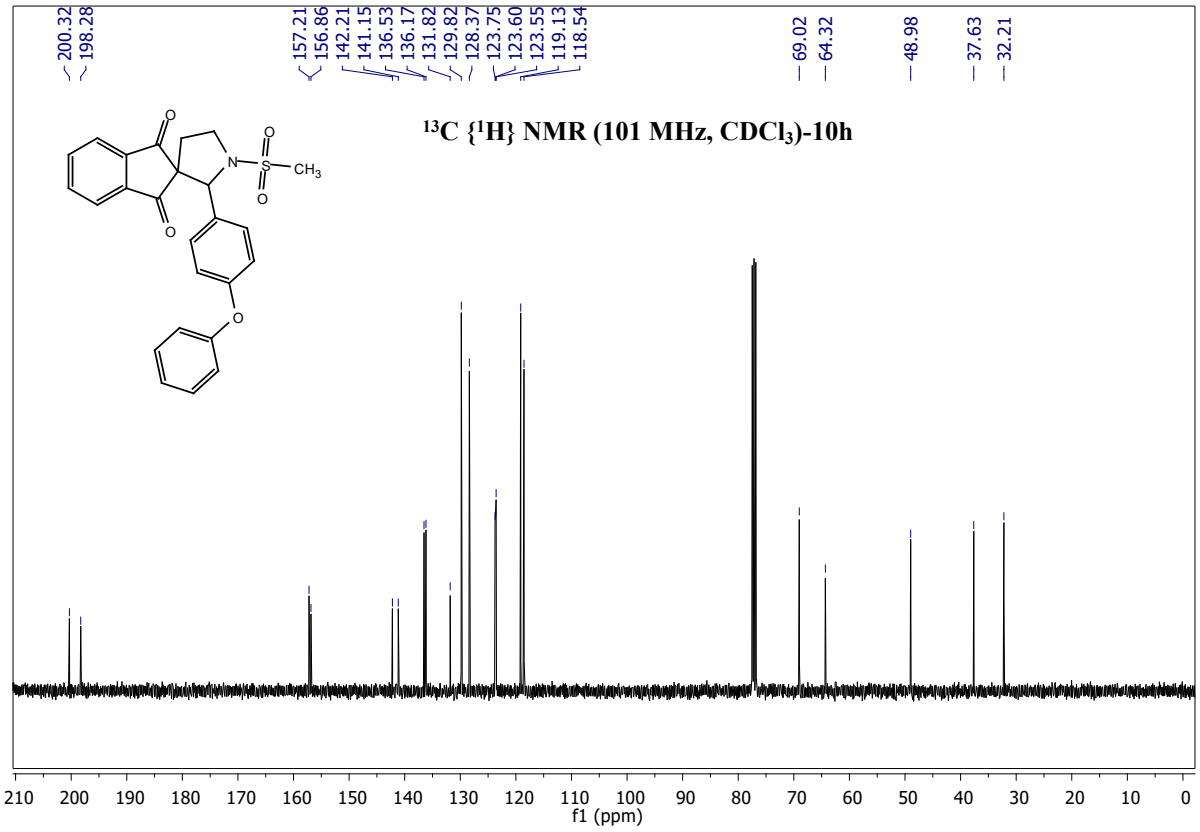
^{1}H NMR (400 MHz, $CDCl_3$) – 10g



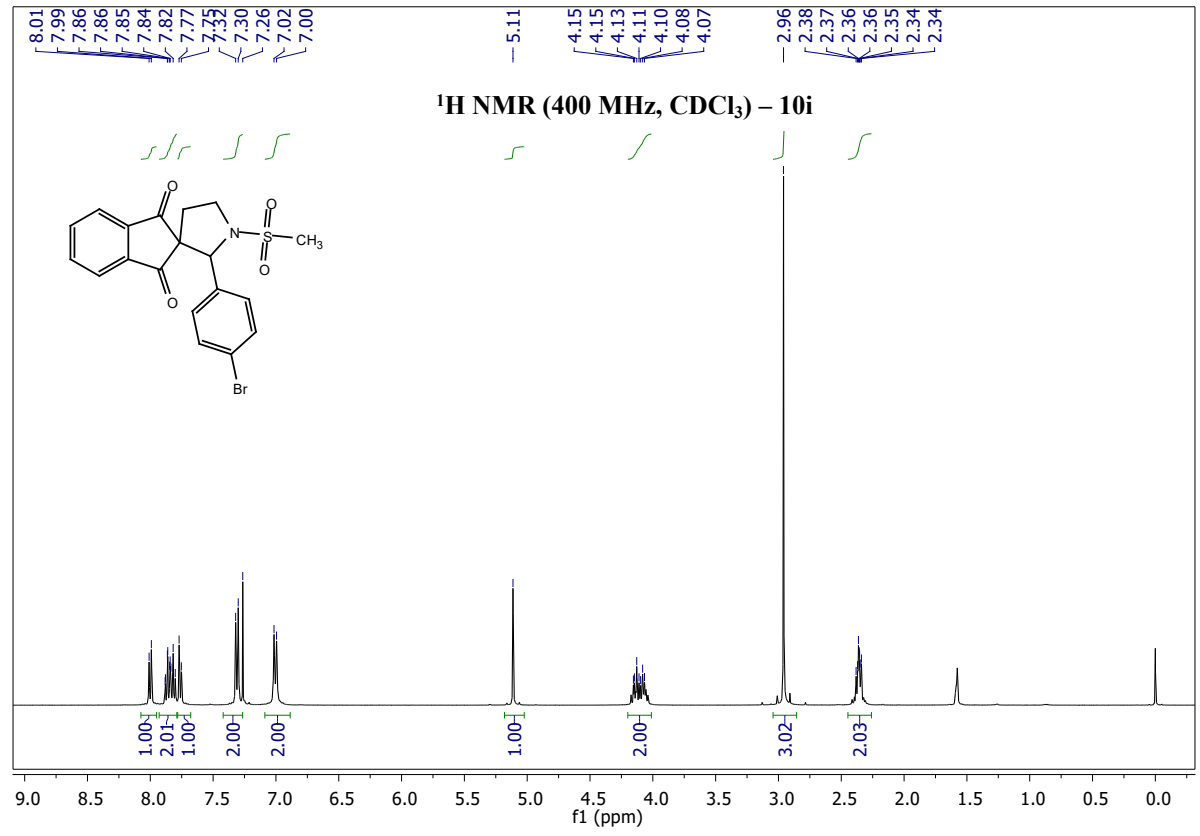
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10g



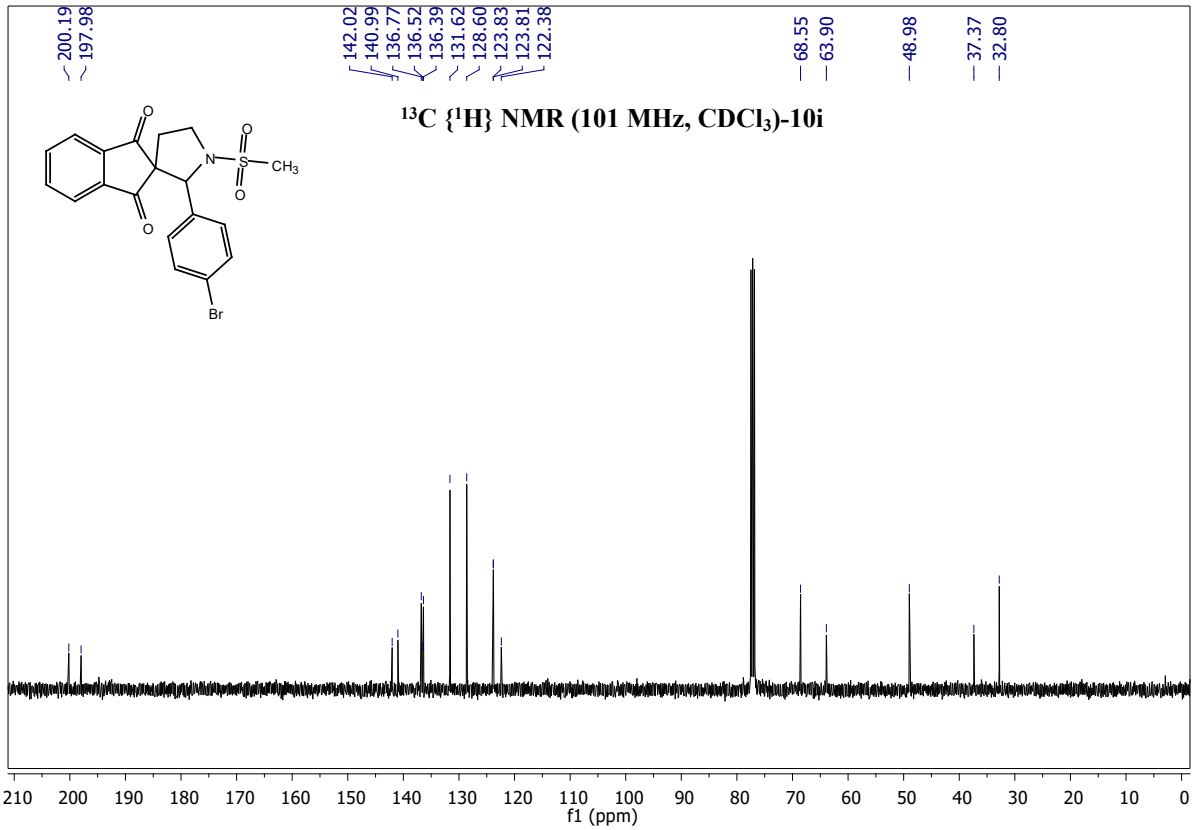
^{1}H NMR (400 MHz, $CDCl_3$) – 10h



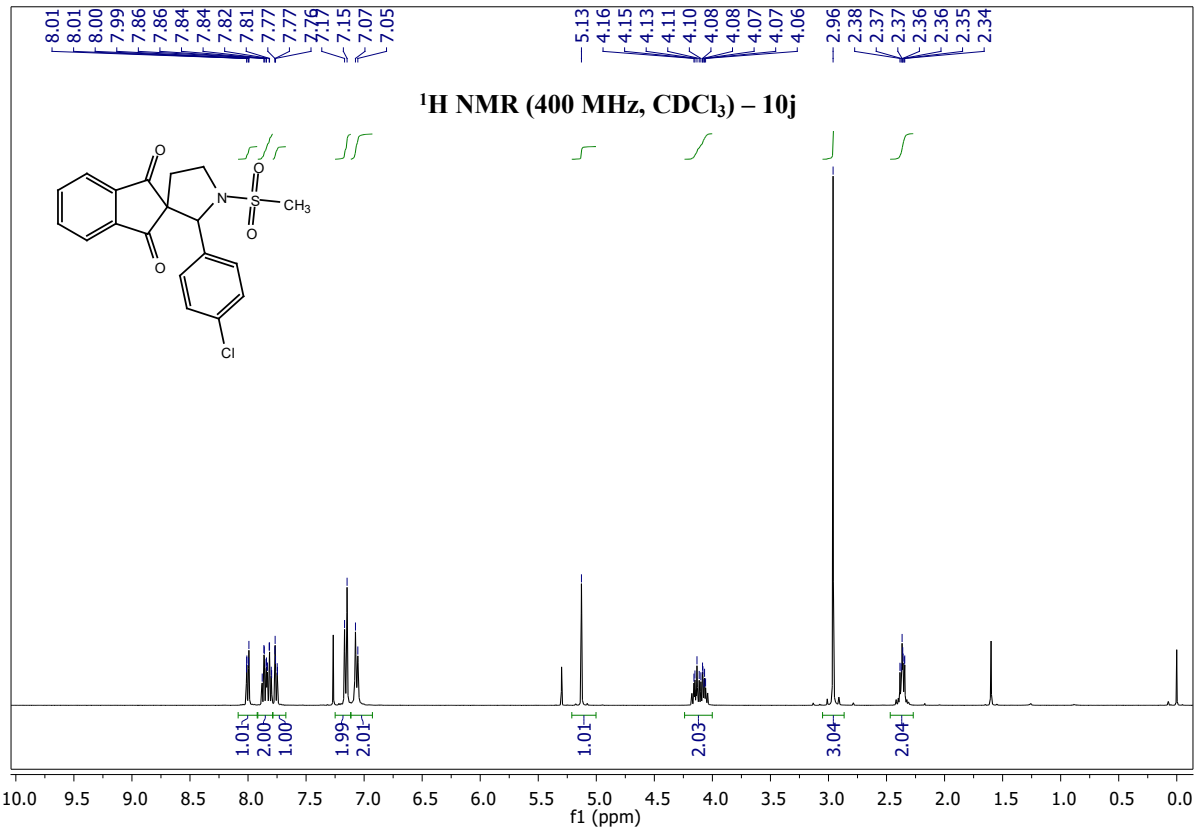
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10h



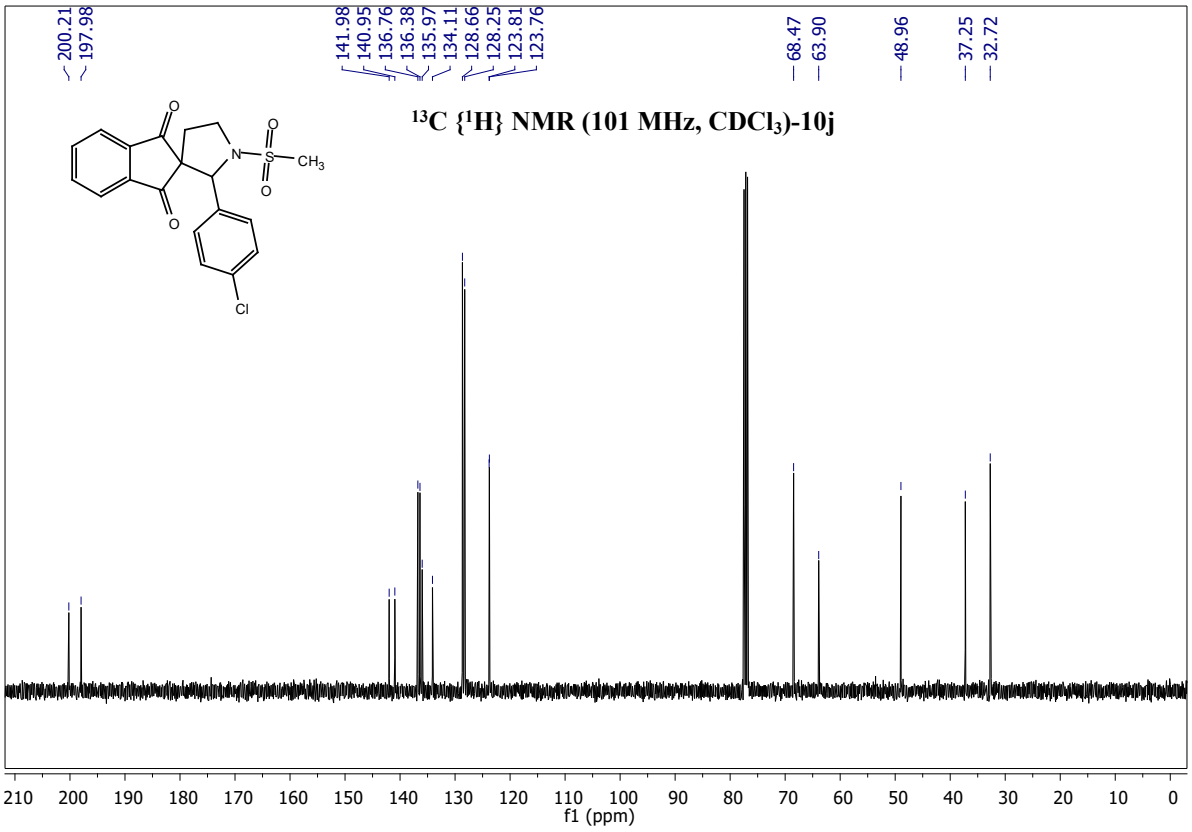
^{1}H NMR (400 MHz, $CDCl_3$) – 10i



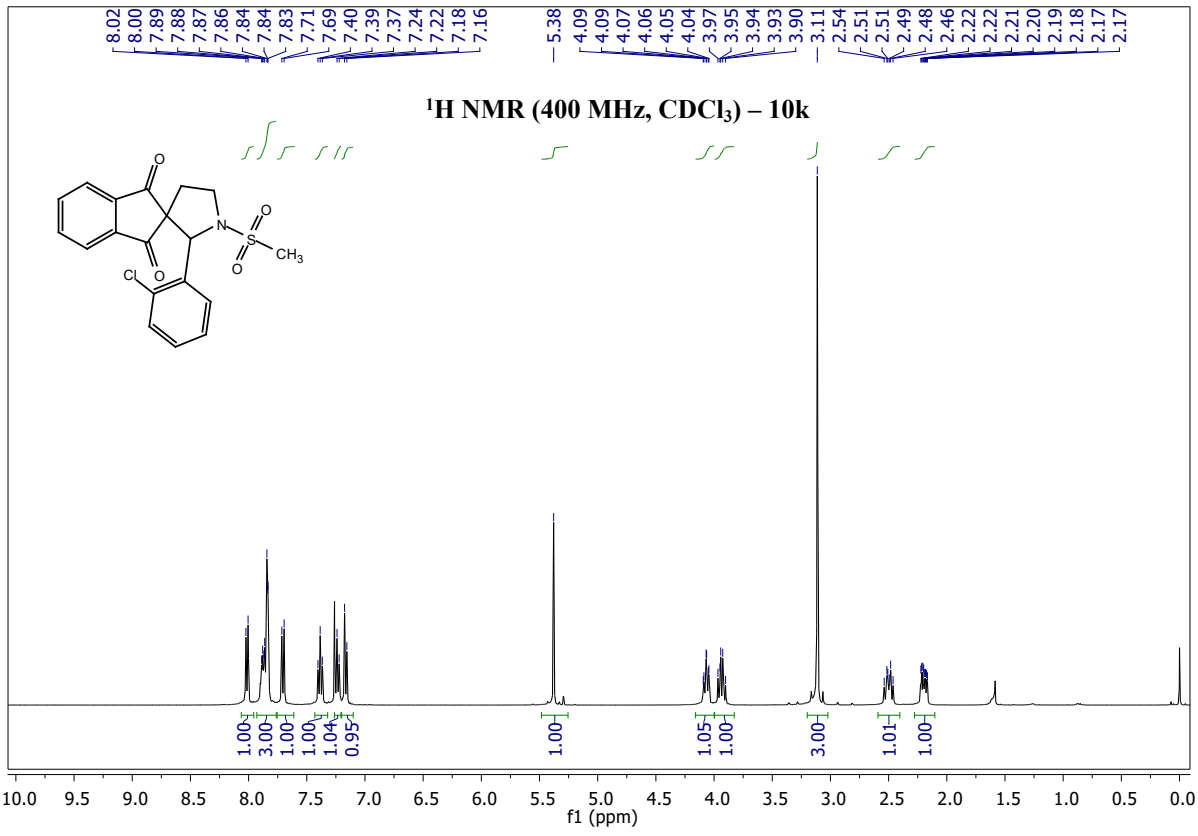
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10i



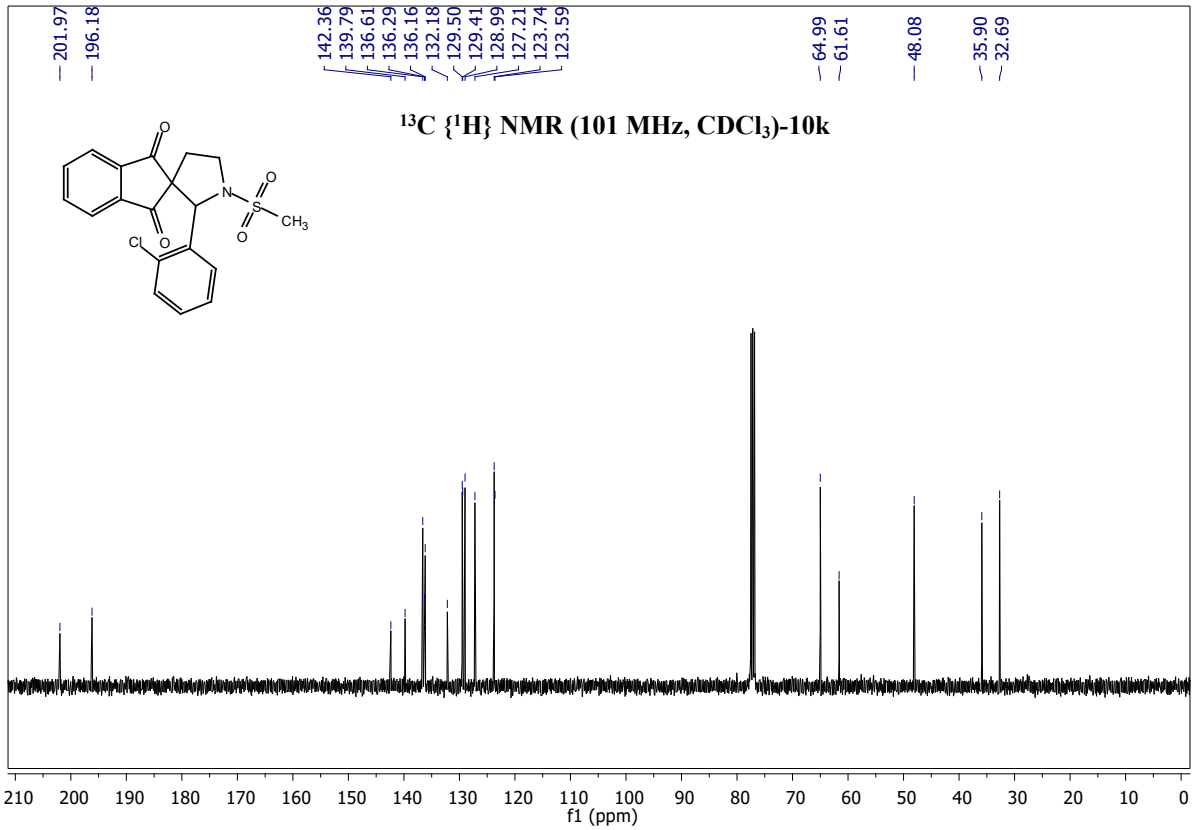
^{1}H NMR (400 MHz, $CDCl_3$) – 10j



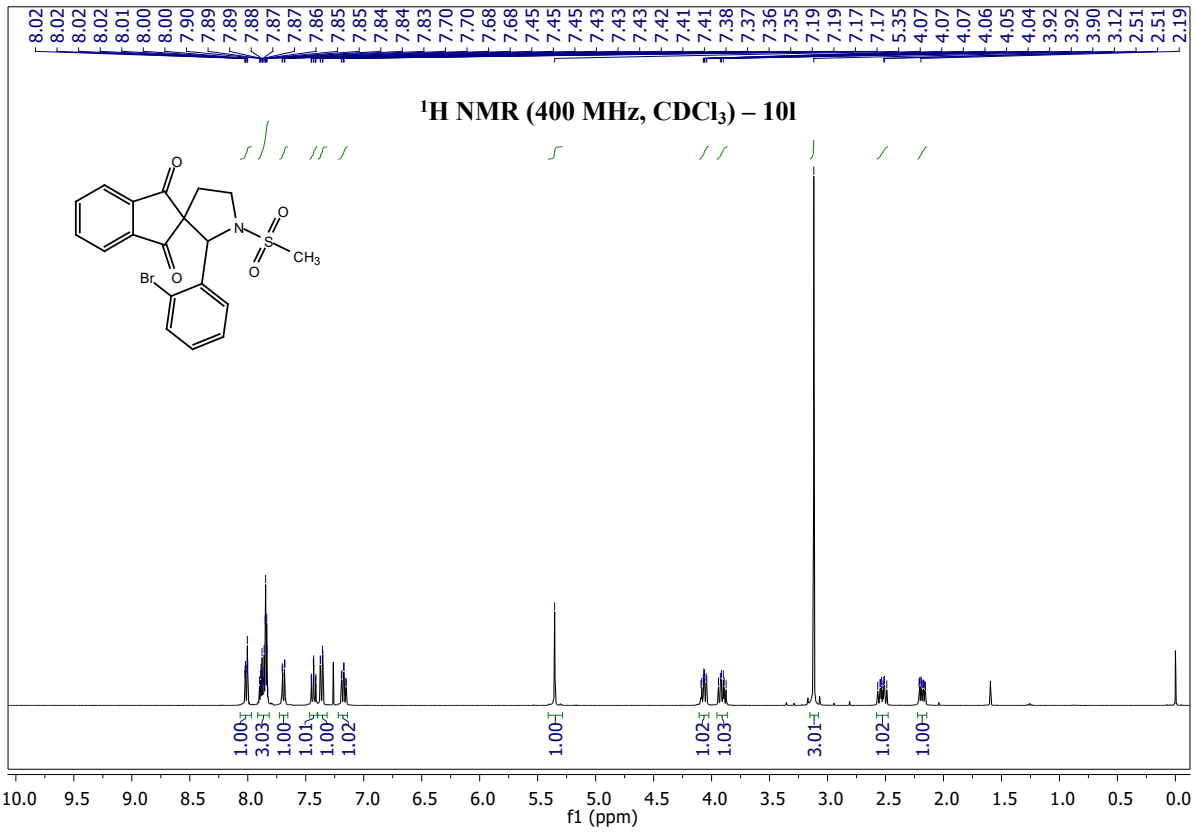
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10j



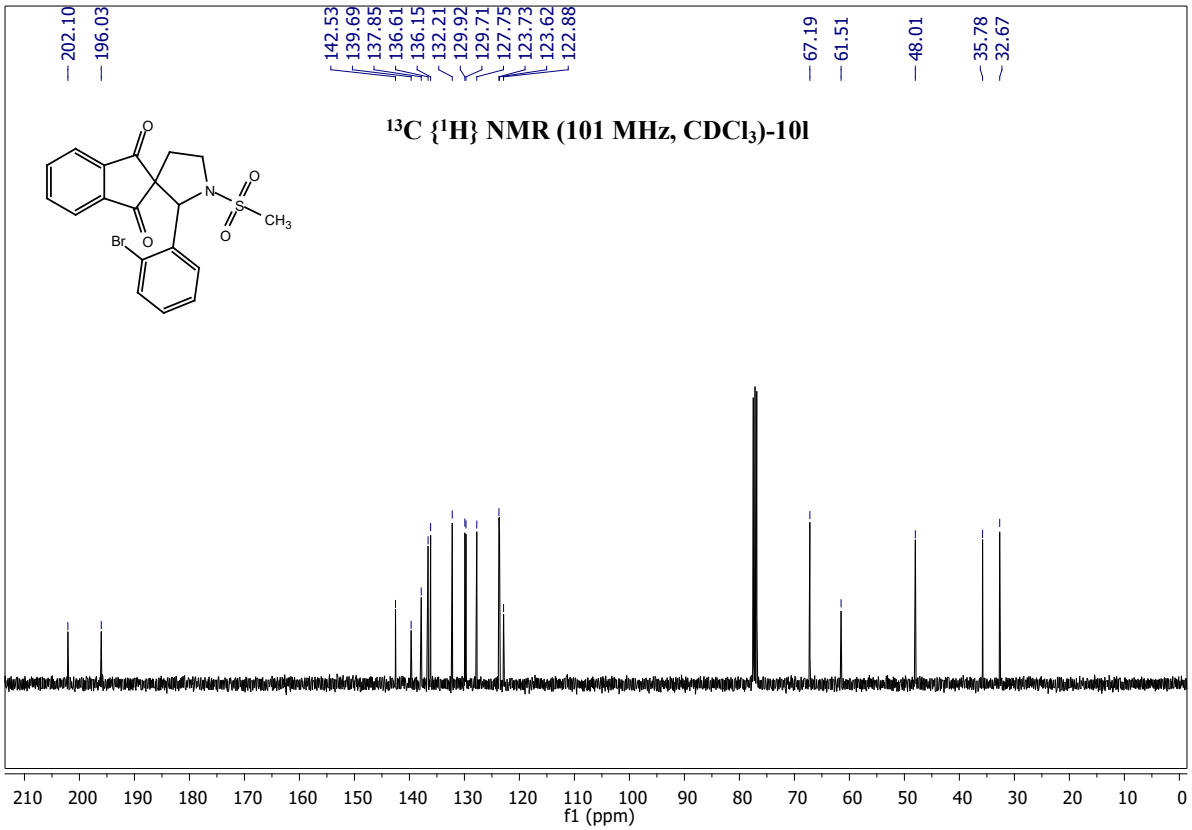
^{1}H NMR (400 MHz, $CDCl_3$) – 10k



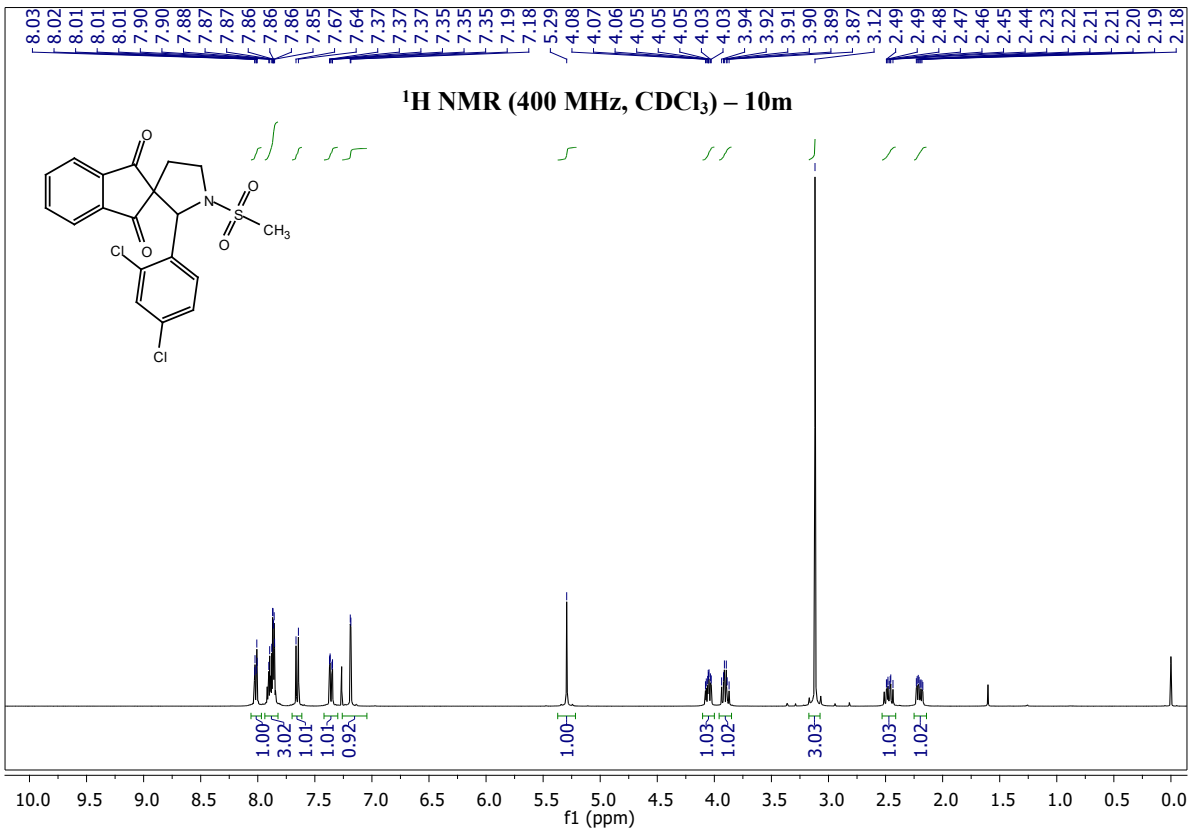
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10k



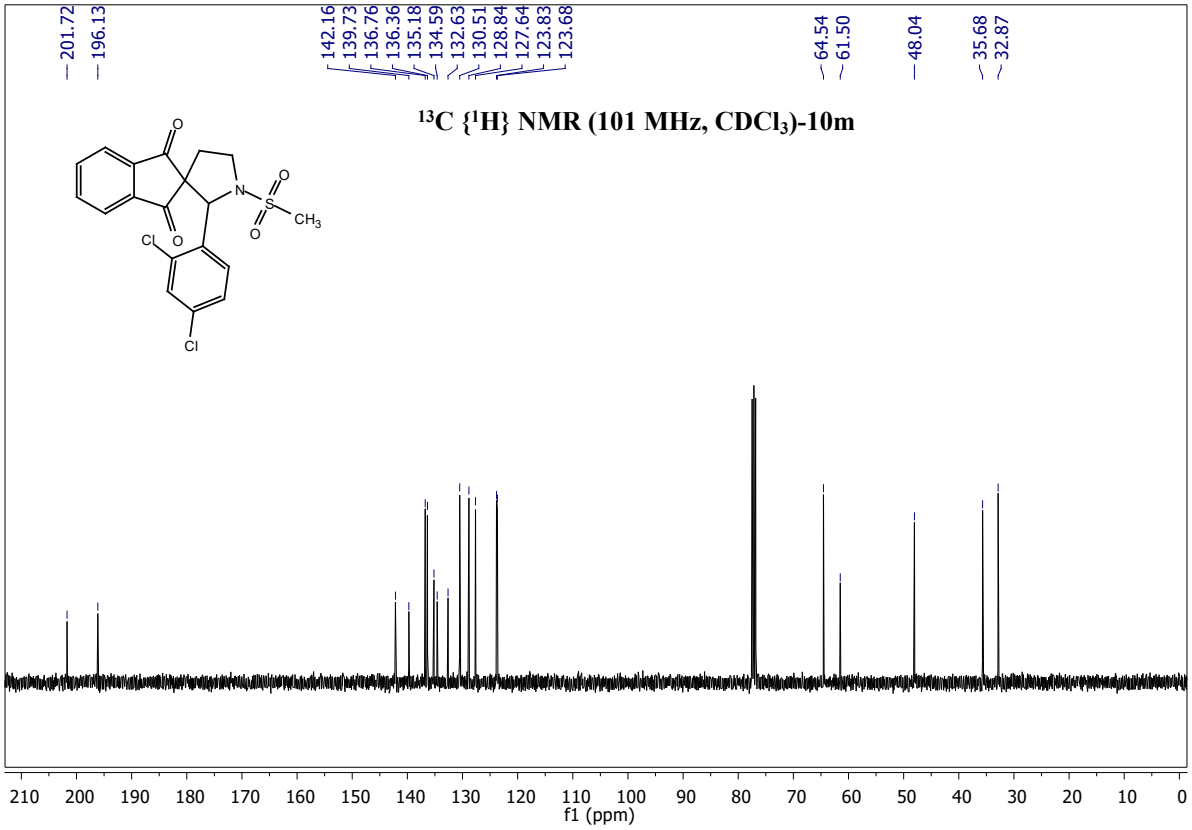
^{1}H NMR (400 MHz, $CDCl_3$) – 10l



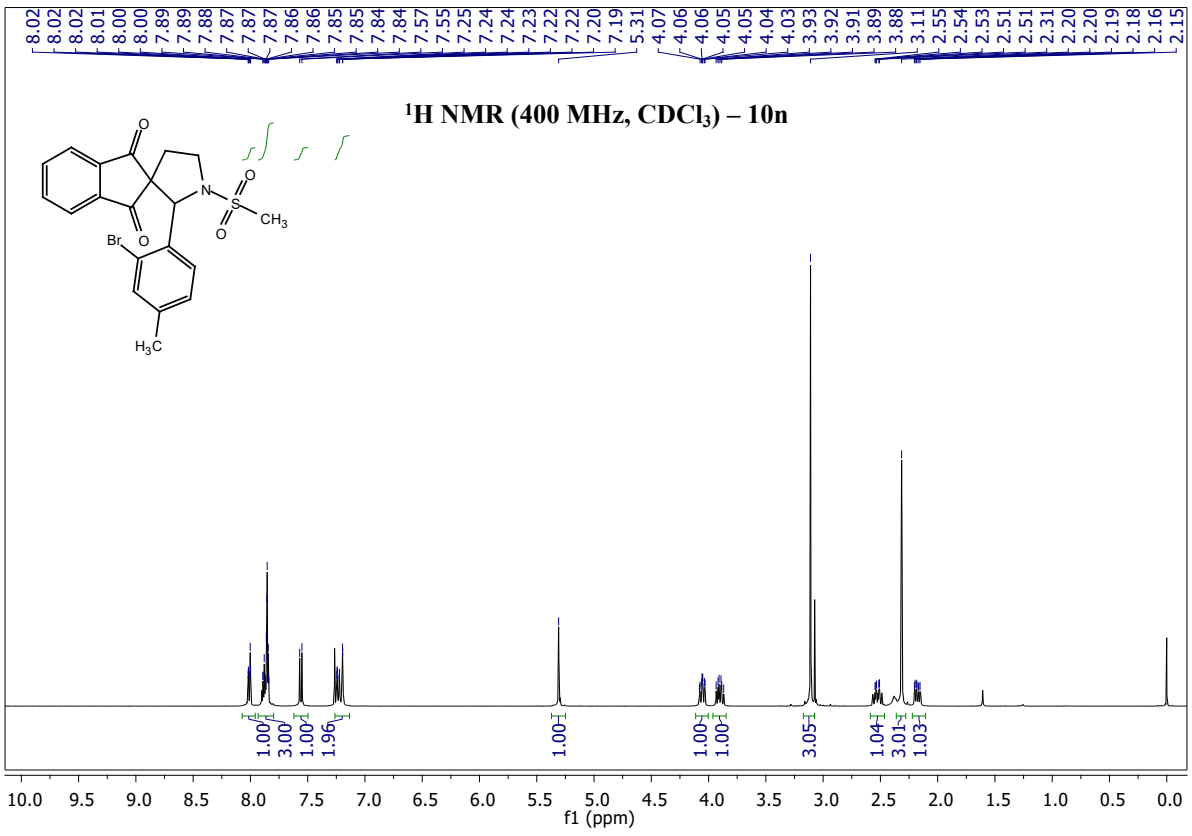
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10l



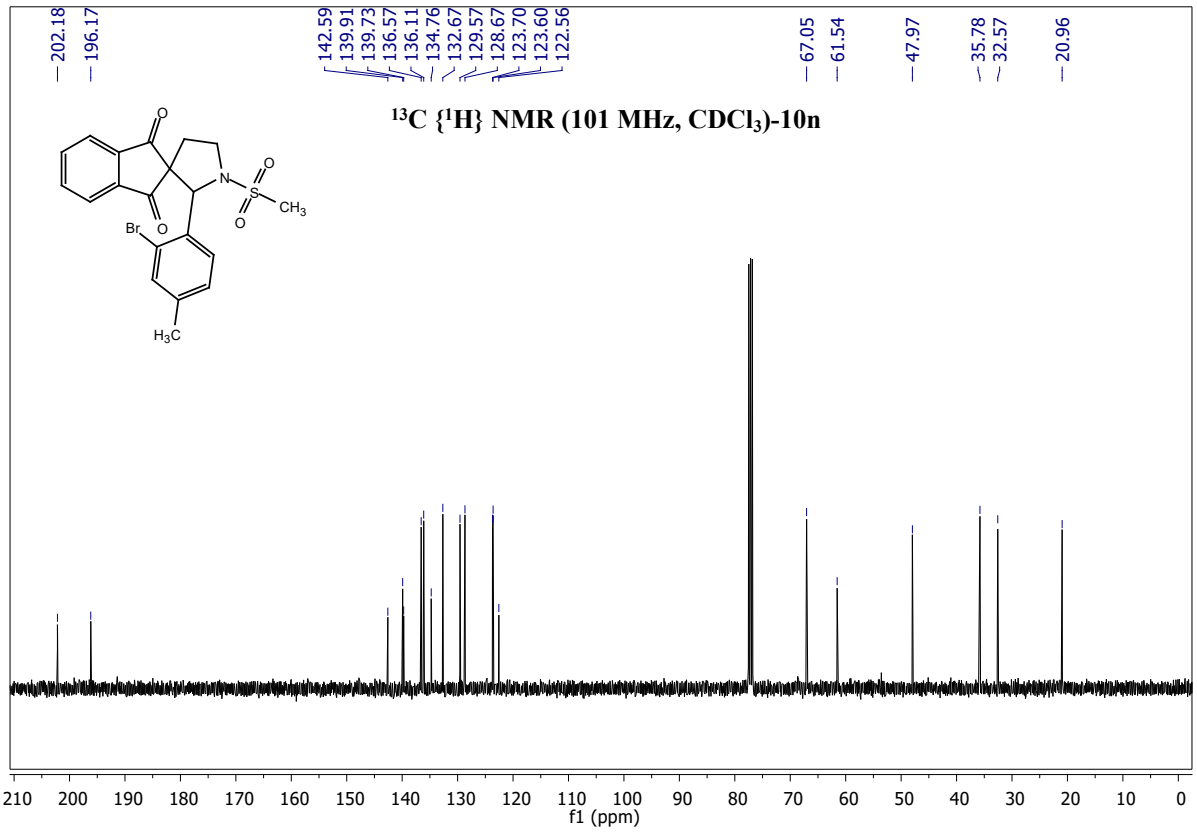
^{1}H NMR (400 MHz, $CDCl_3$) – 10m



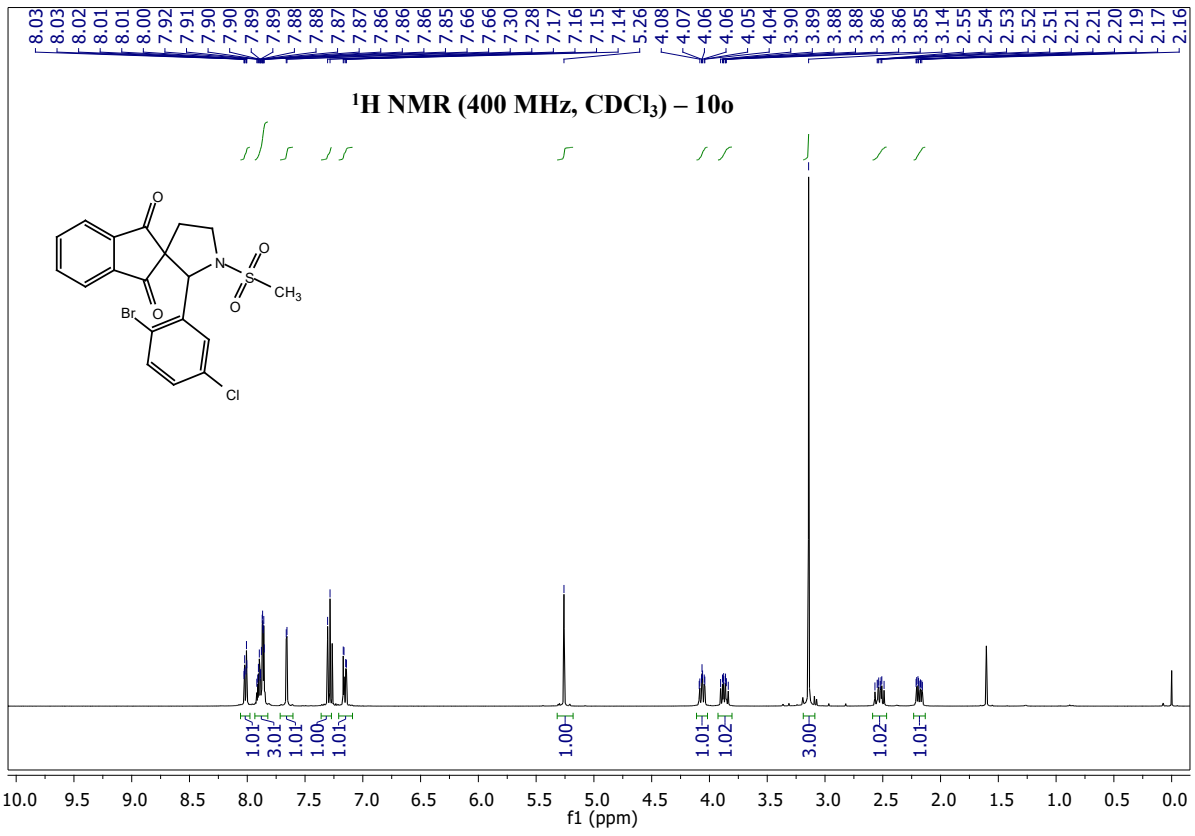
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10m



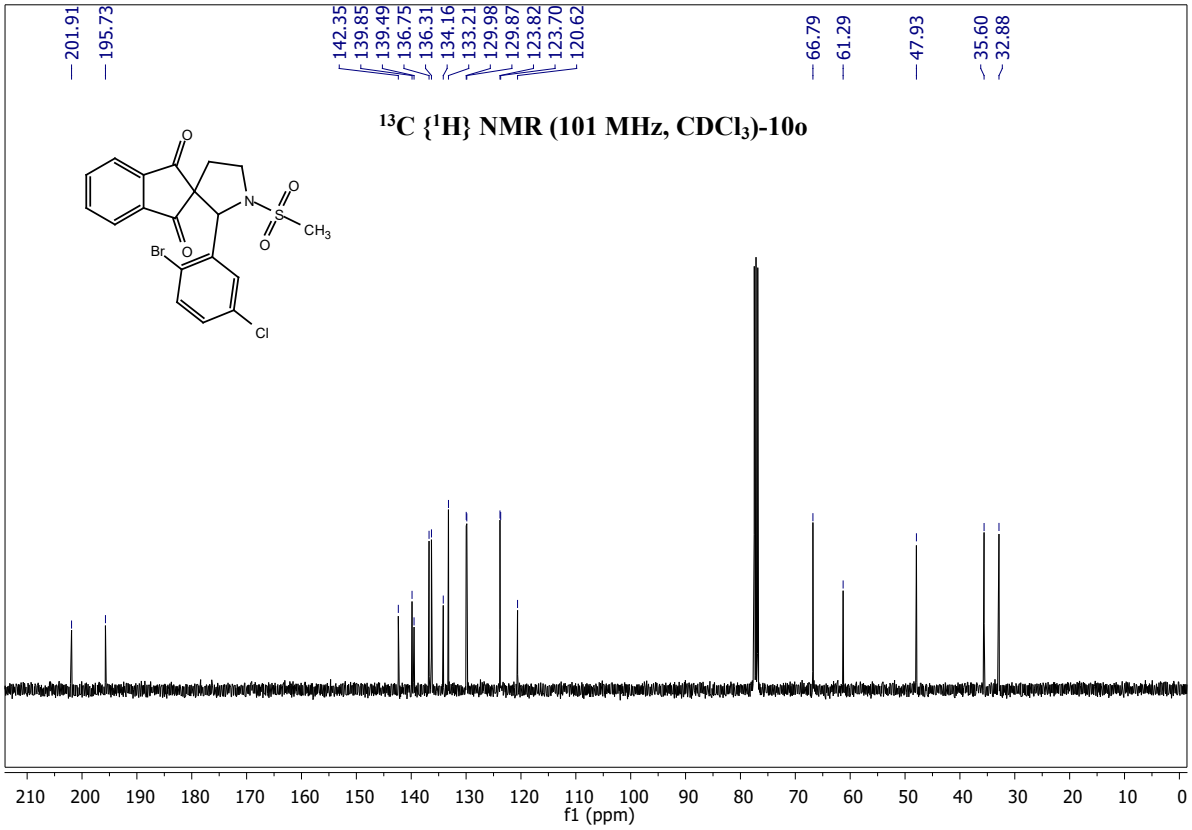
^{1}H NMR (400 MHz, $CDCl_3$) – 10n



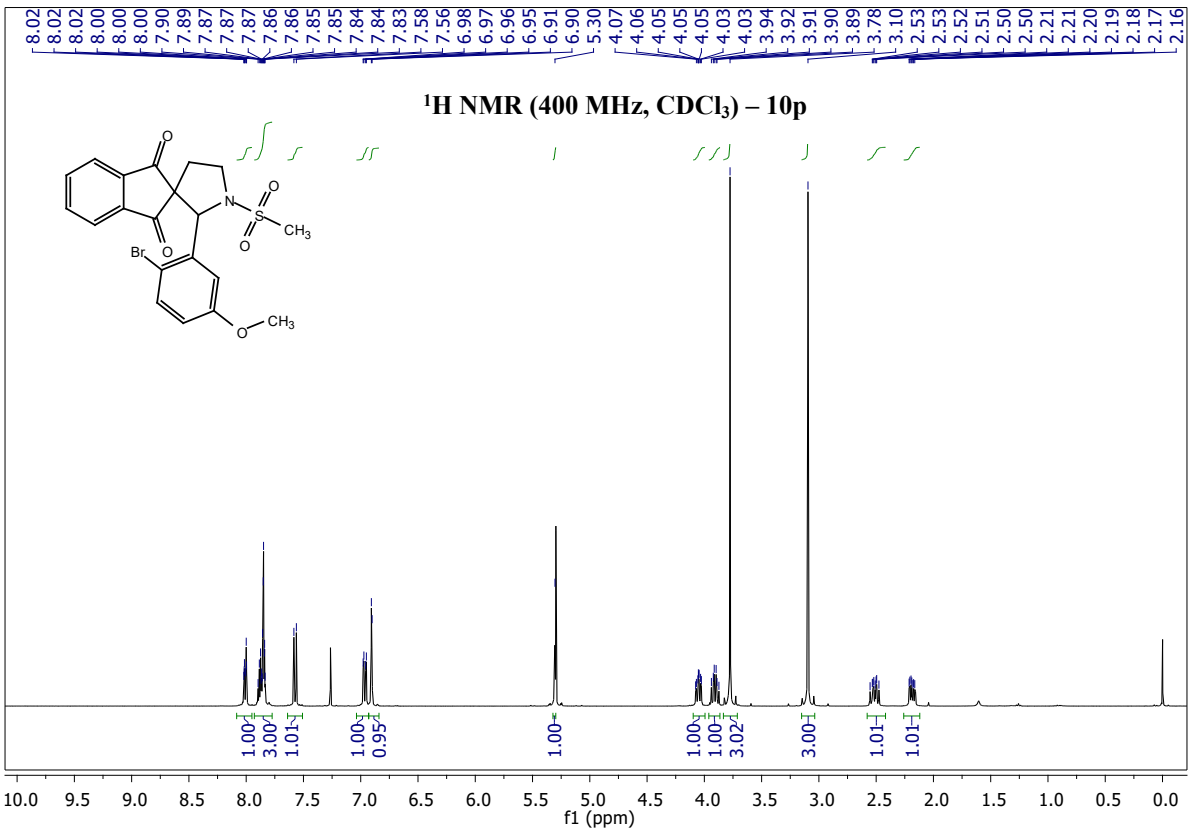
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10n



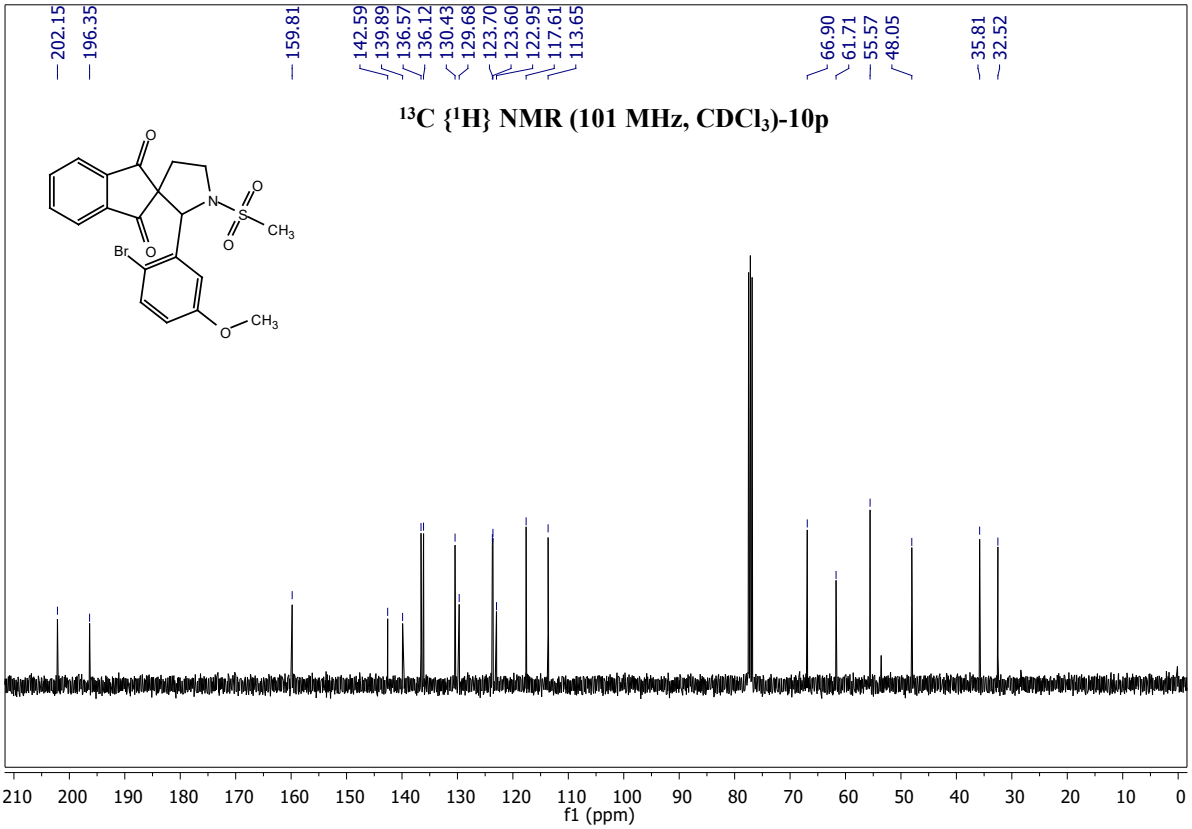
^{1}H NMR (400 MHz, $CDCl_3$) – 10o

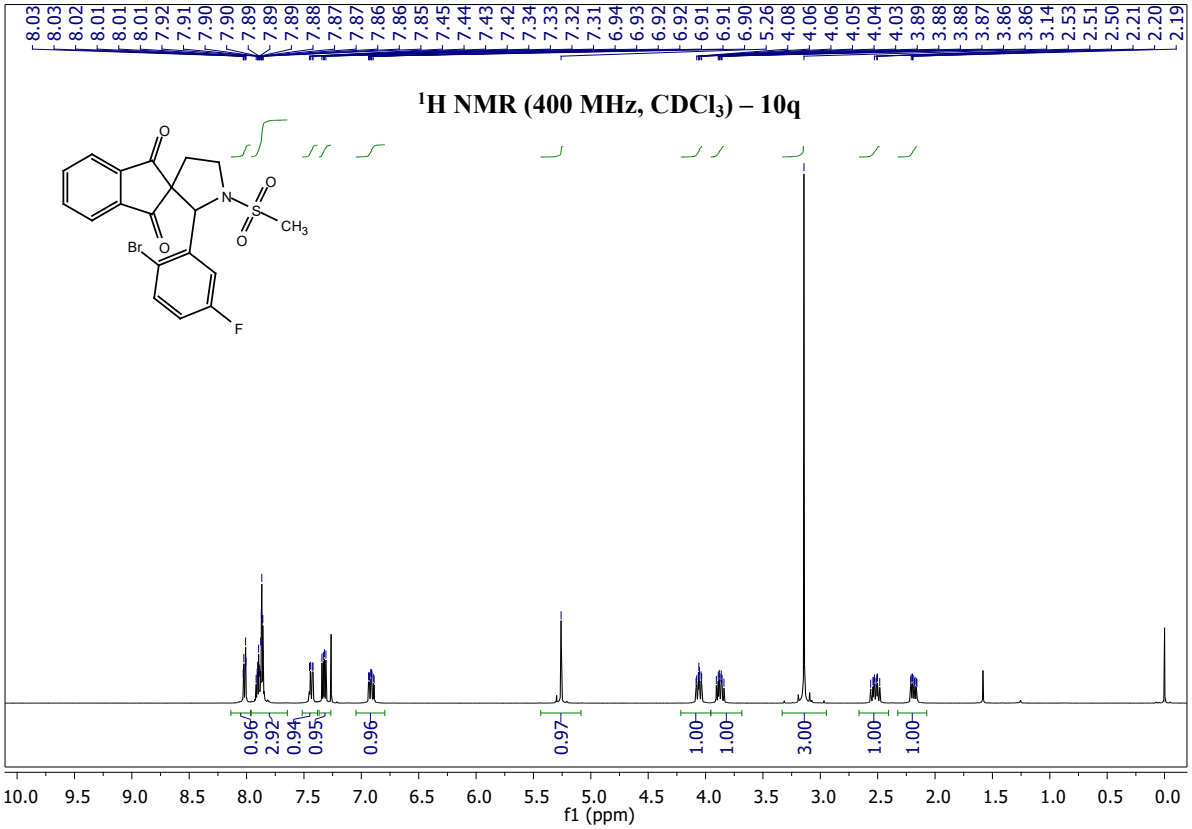


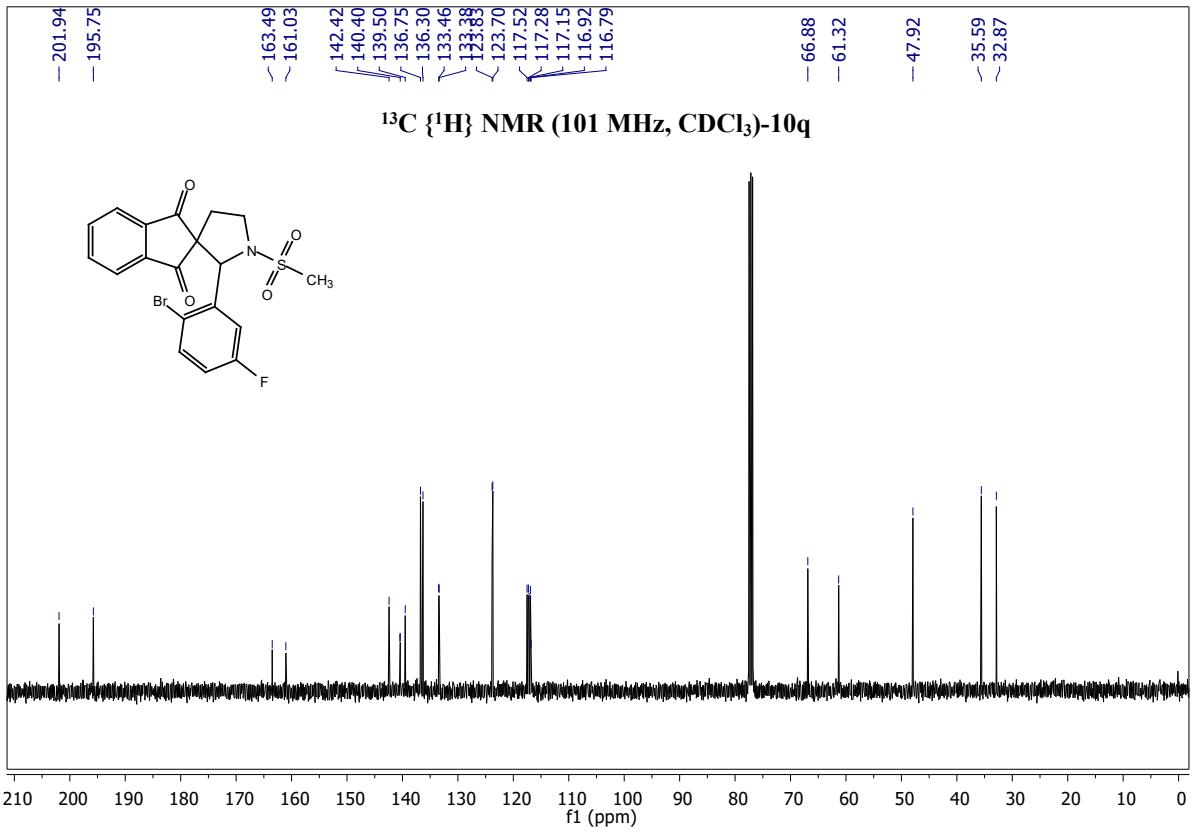
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10o



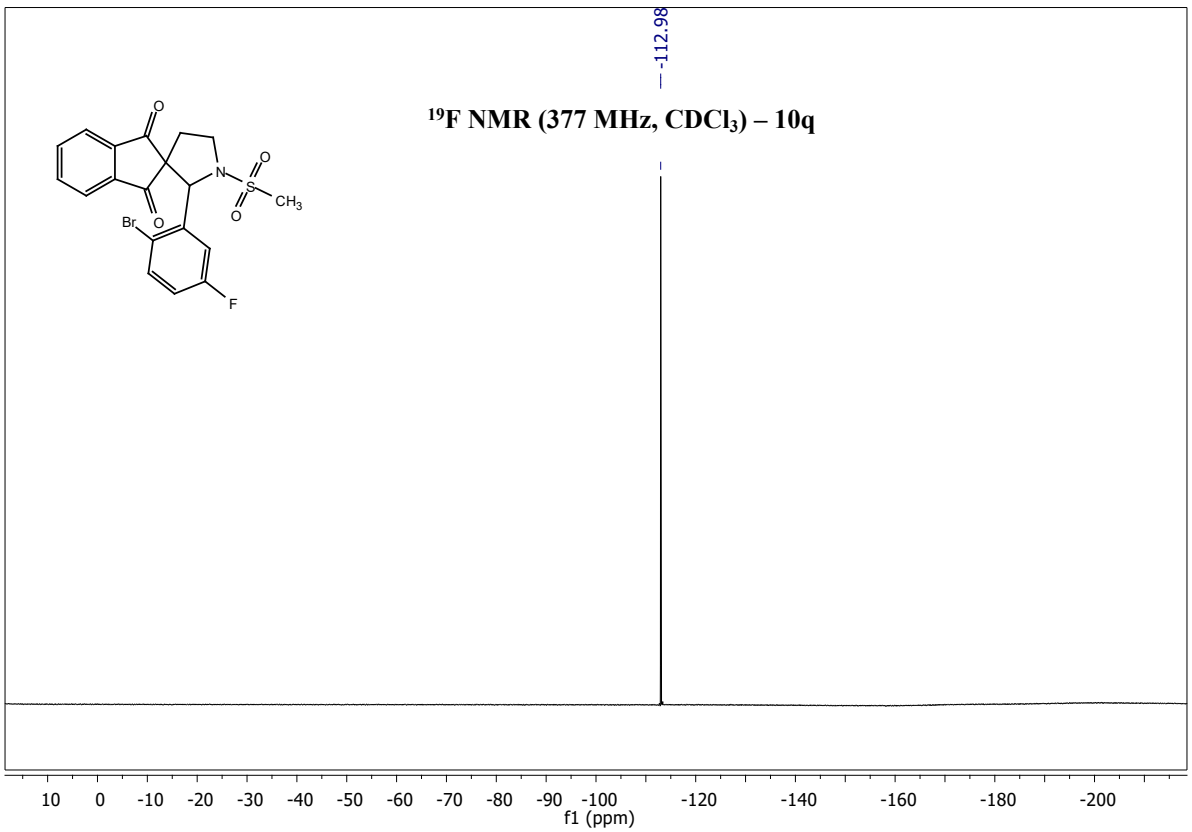
^{1}H NMR (400 MHz, $CDCl_3$) – 10p


202.15
196.35
159.81
142.59
139.89
136.57
136.12
130.43
129.68
123.70
123.60
122.95
117.61
113.65
66.90
61.71
55.57
48.05
35.81
32.52
13C {1H} NMR (101 MHz, CDCl3)-10p
f1 (ppm)

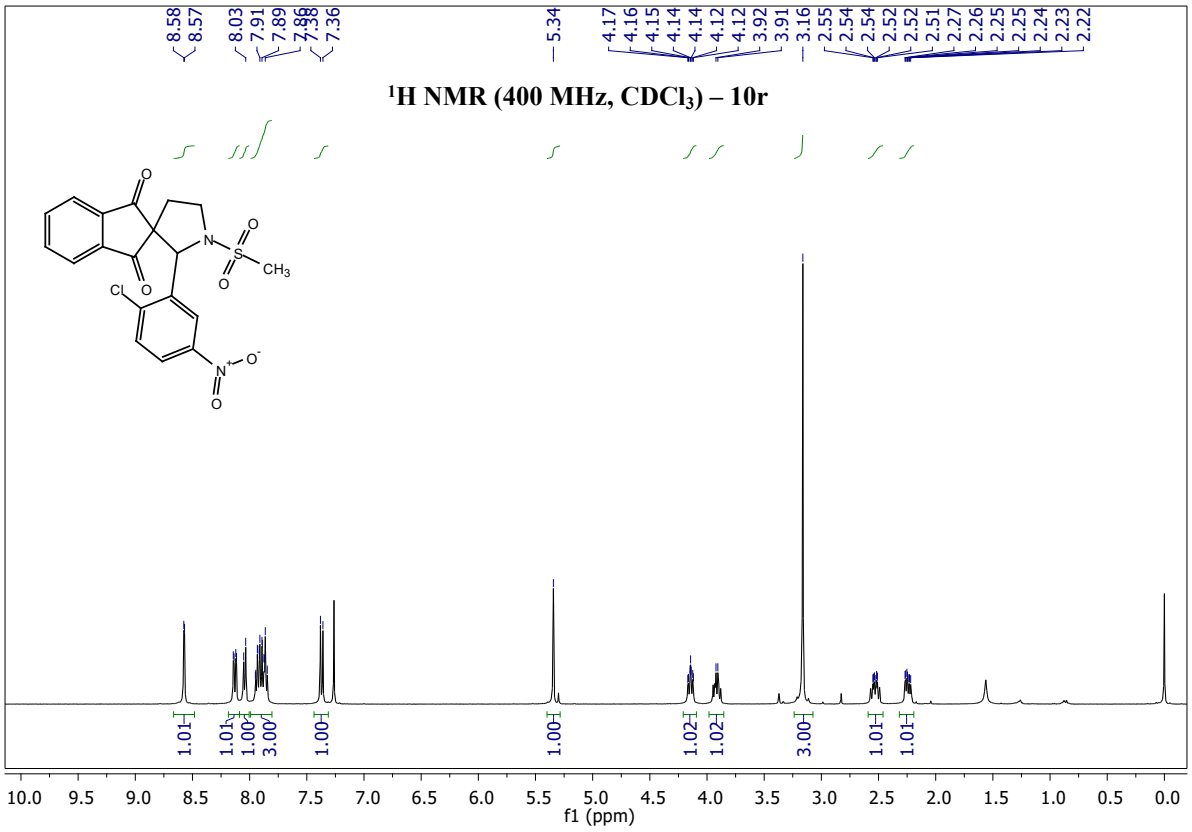

1H NMR (400 MHz, CDCl3) – 10q
f1 (ppm)



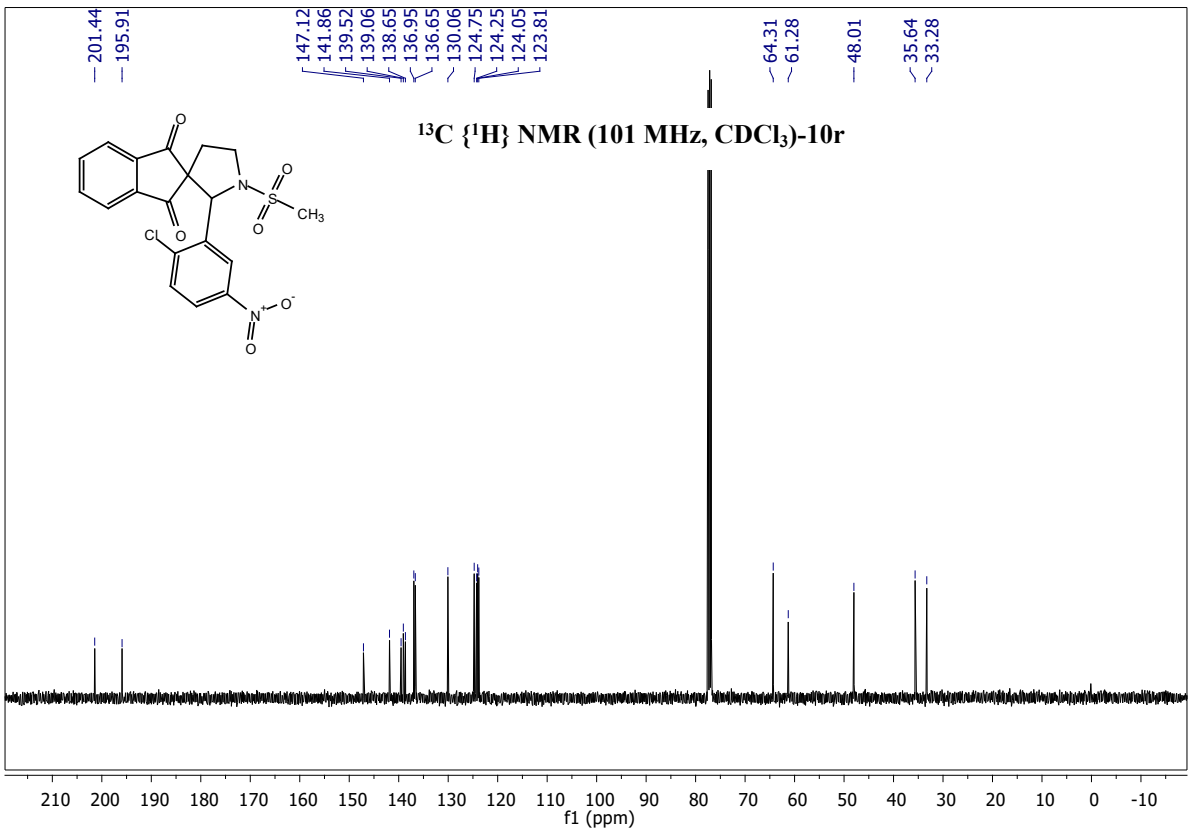
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10q



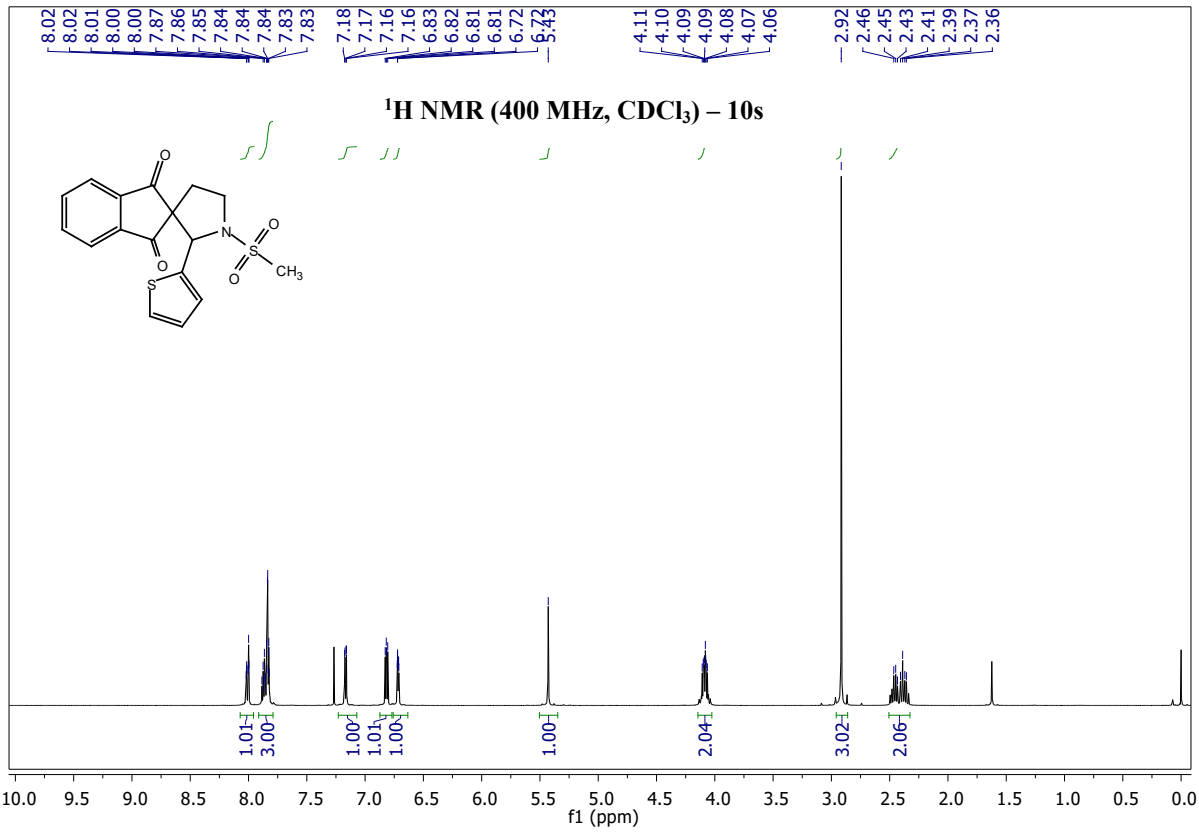
^{19}F NMR (377 MHz, $CDCl_3$) – 10q



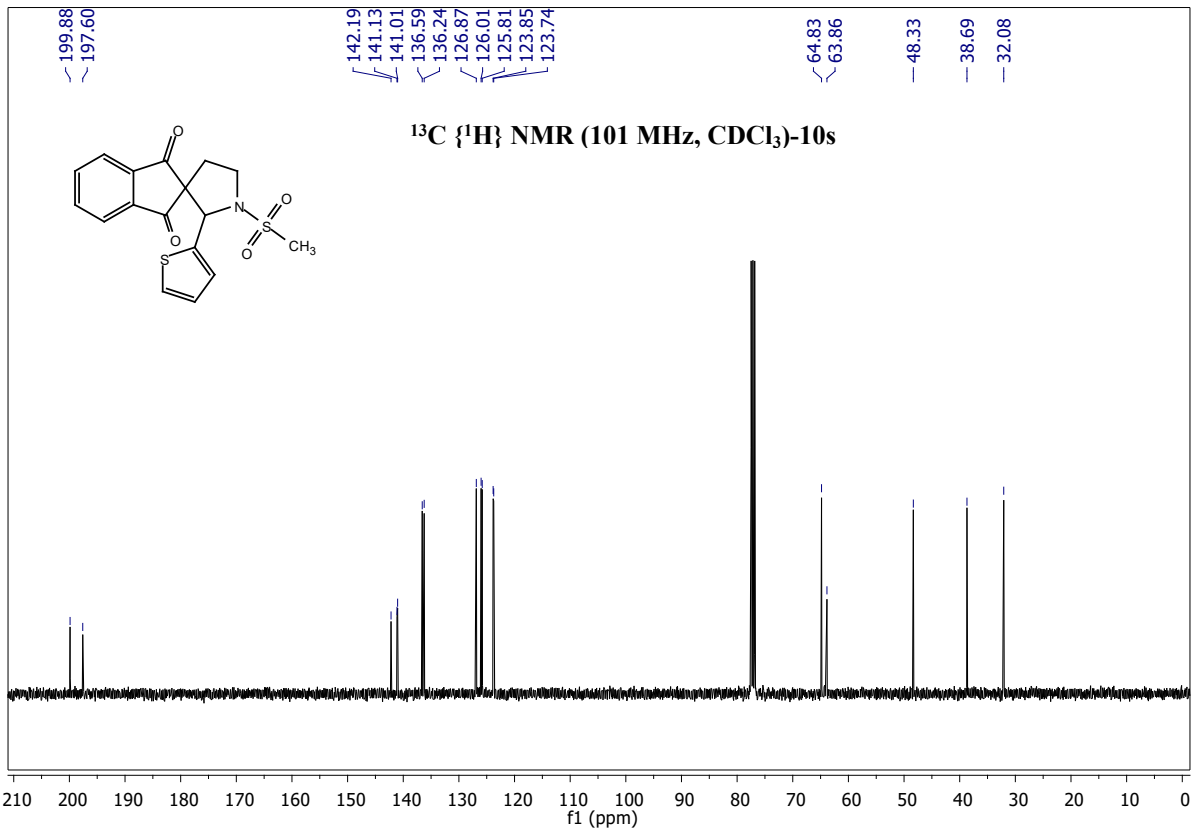
^{1}H NMR (400 MHz, $CDCl_3$) – 10r



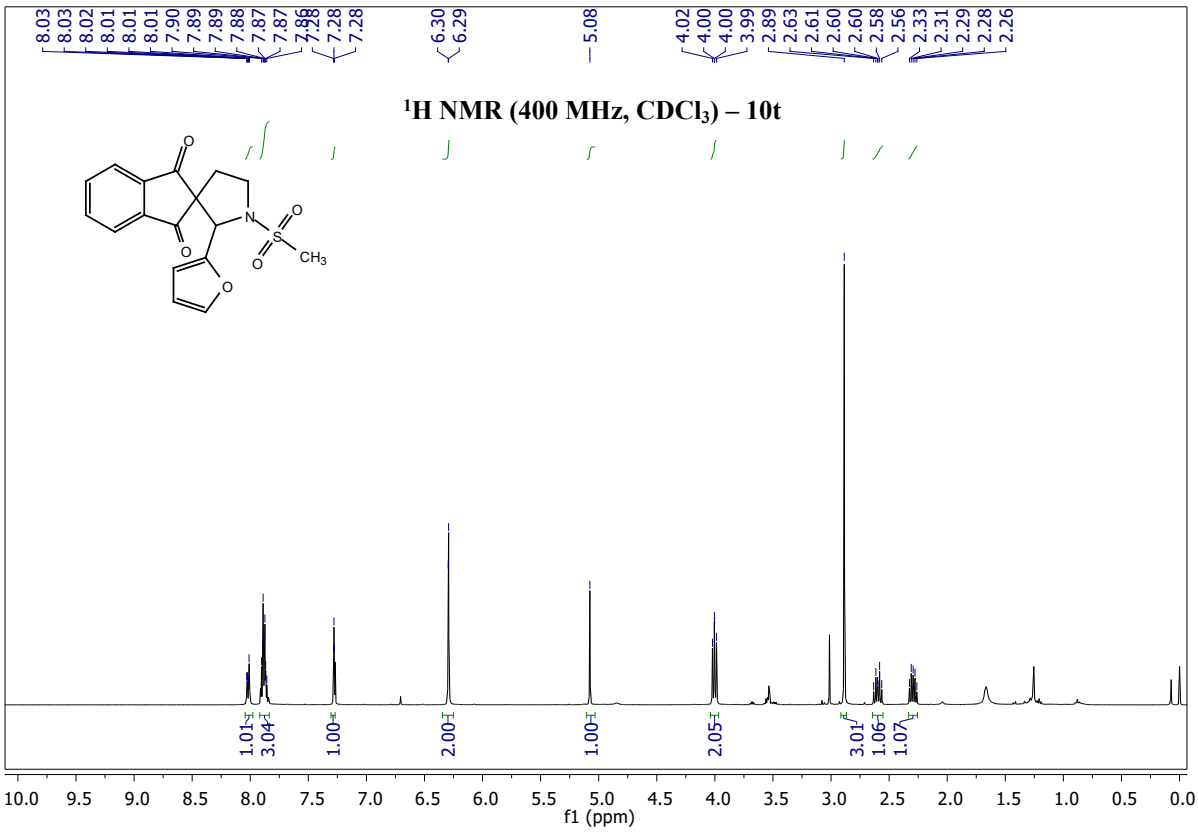
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10r



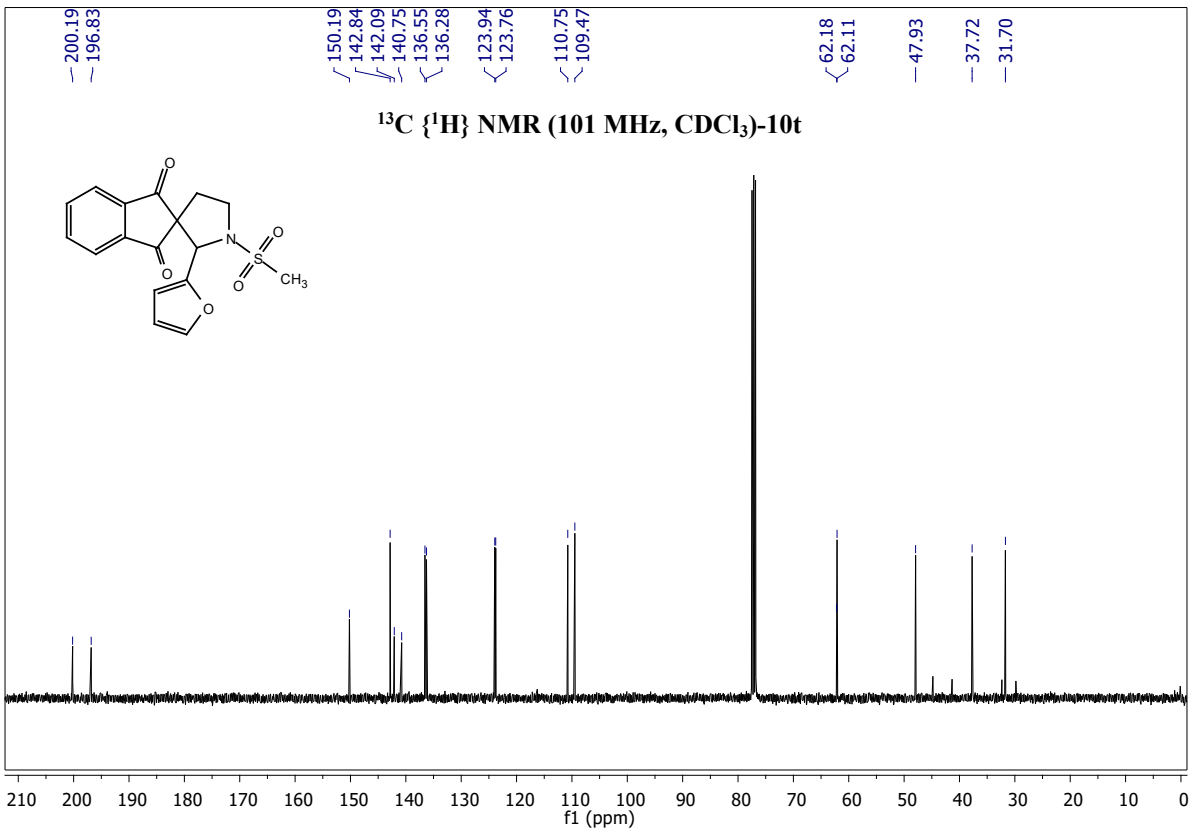
^{1}H NMR (400 MHz, $CDCl_3$) – 10s



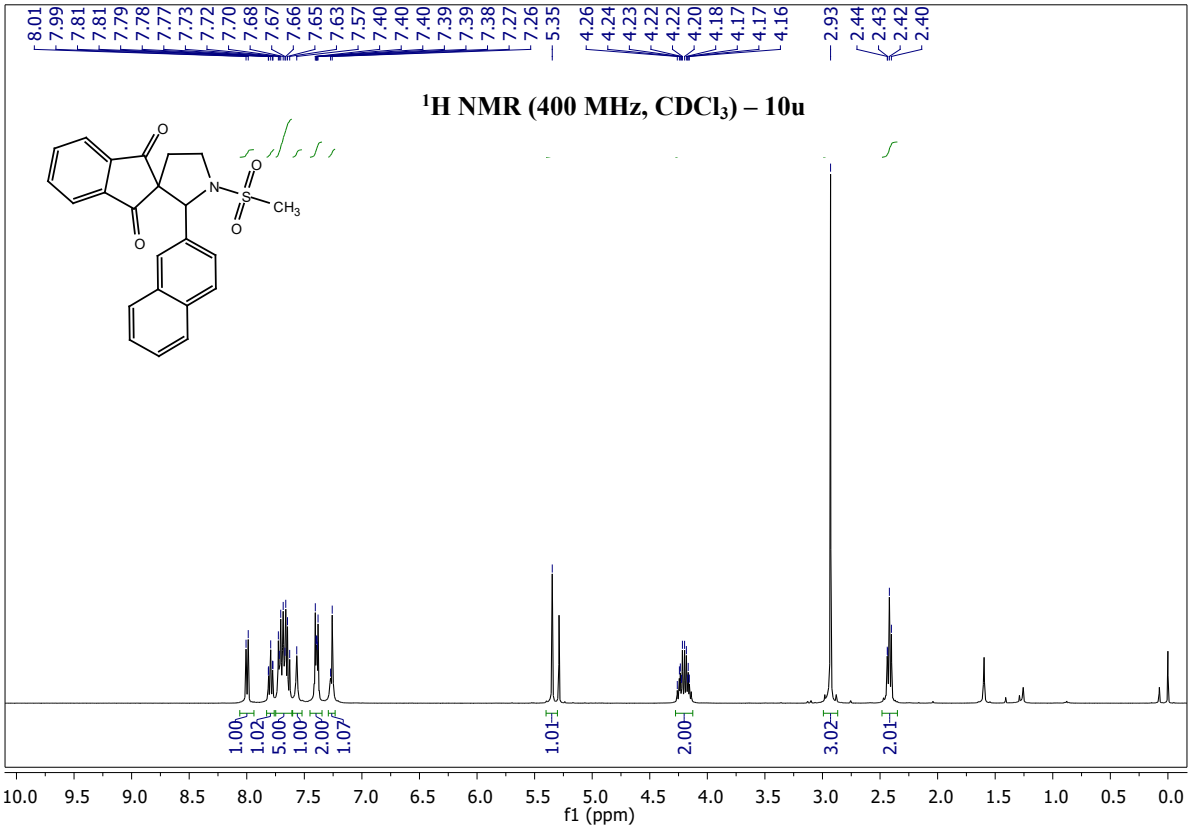
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10s



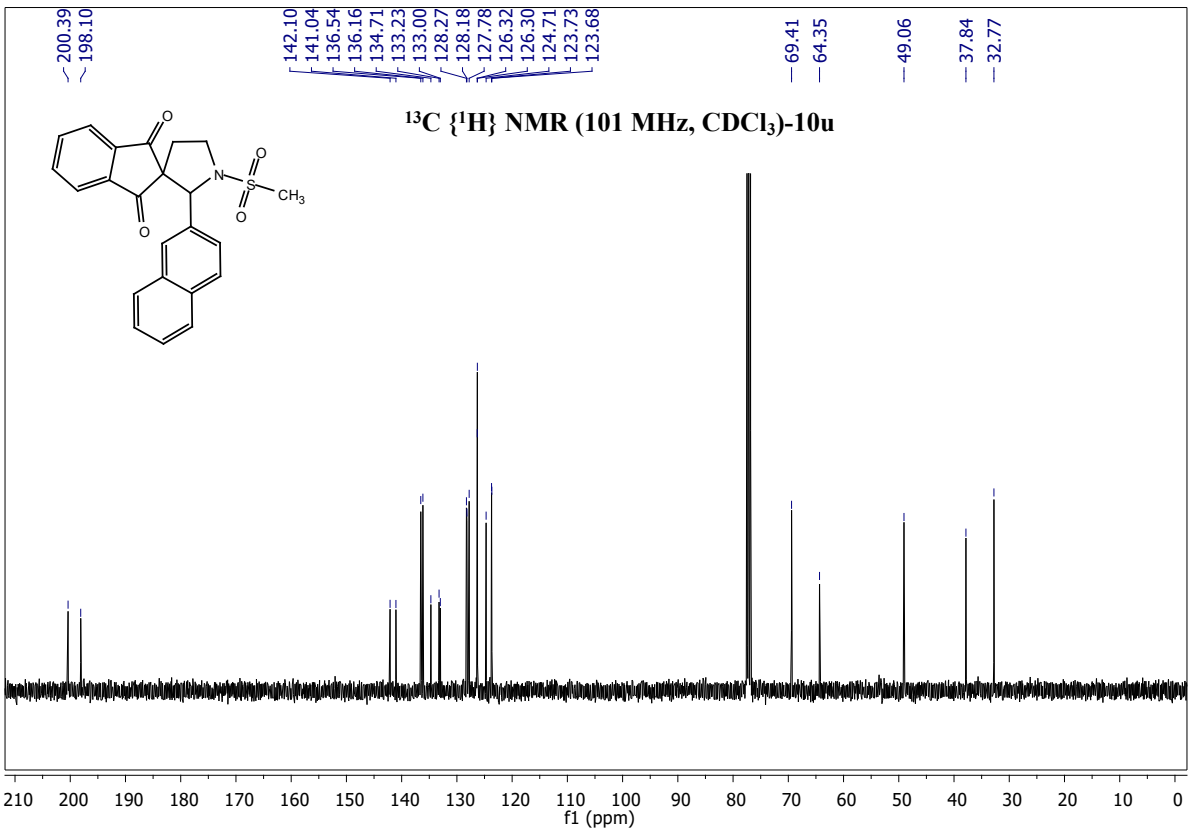
^{1}H NMR (400 MHz, $CDCl_3$) – 10t



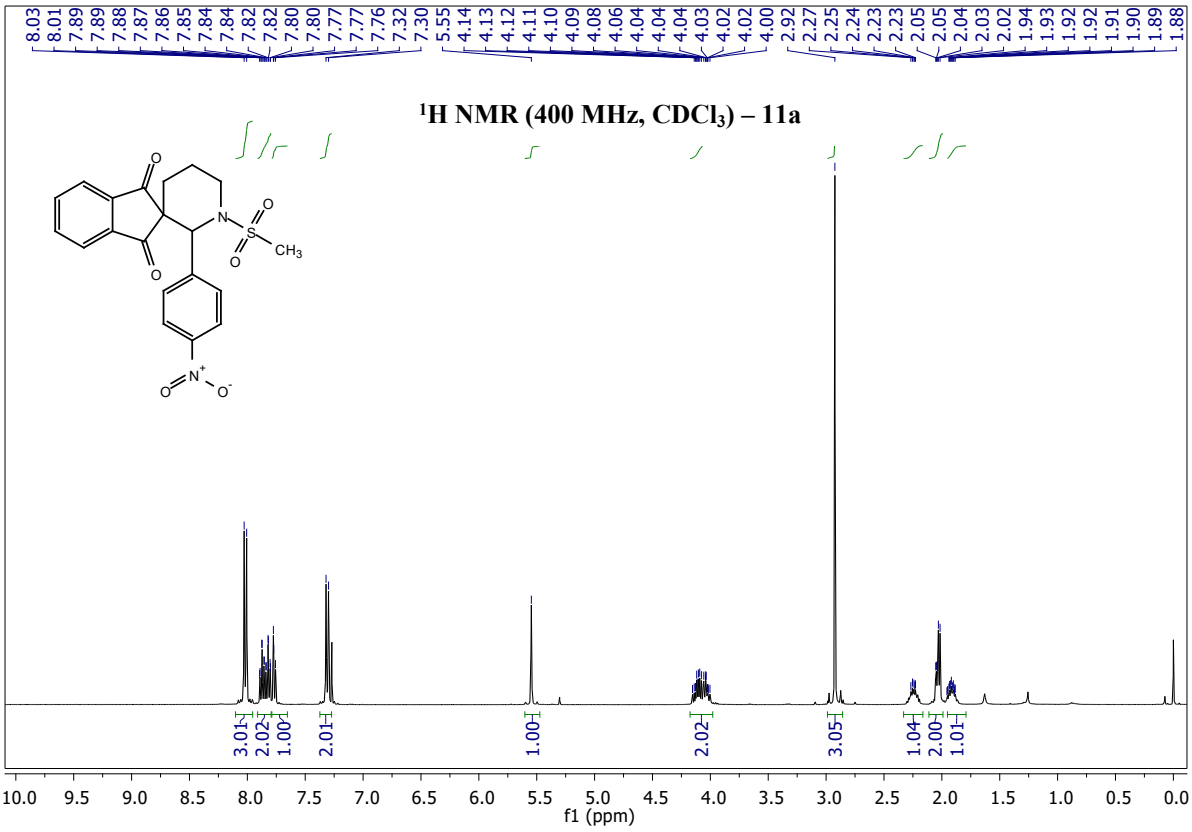
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10t



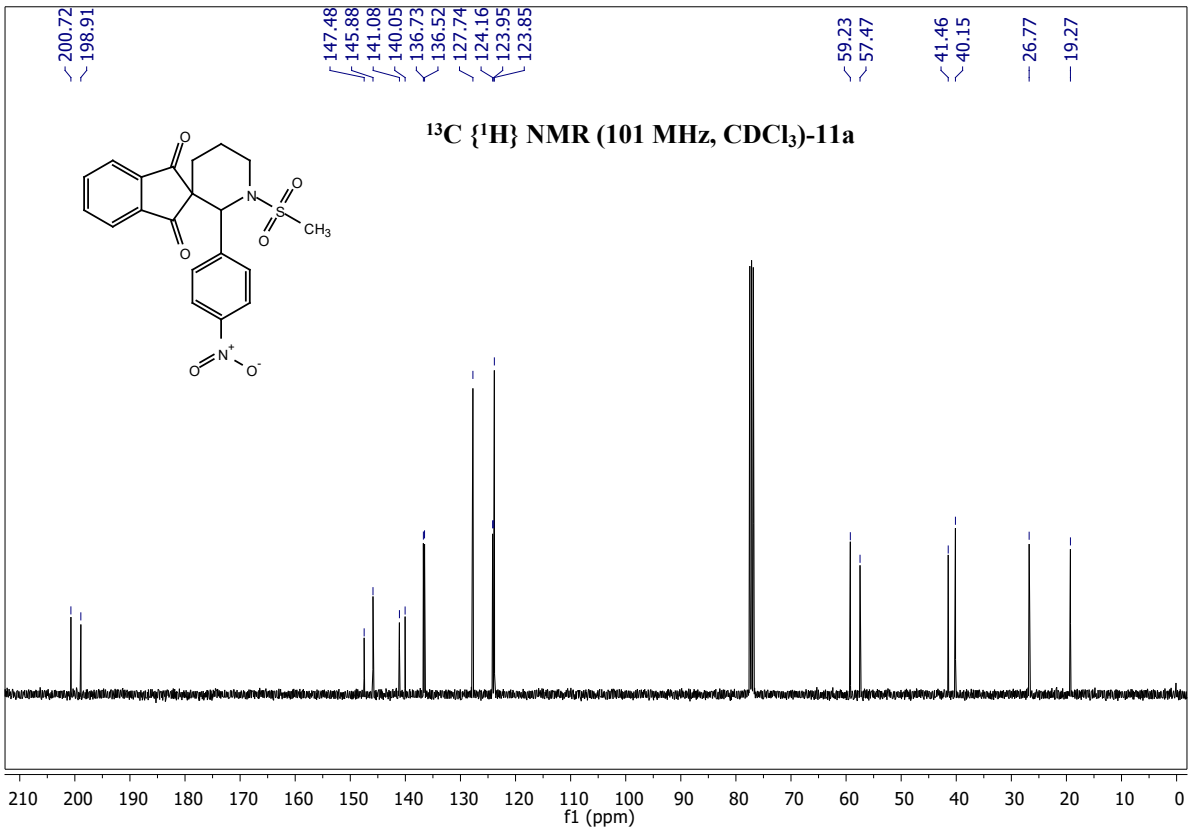
^{1}H NMR (400 MHz, $CDCl_3$) – 10u



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-10u

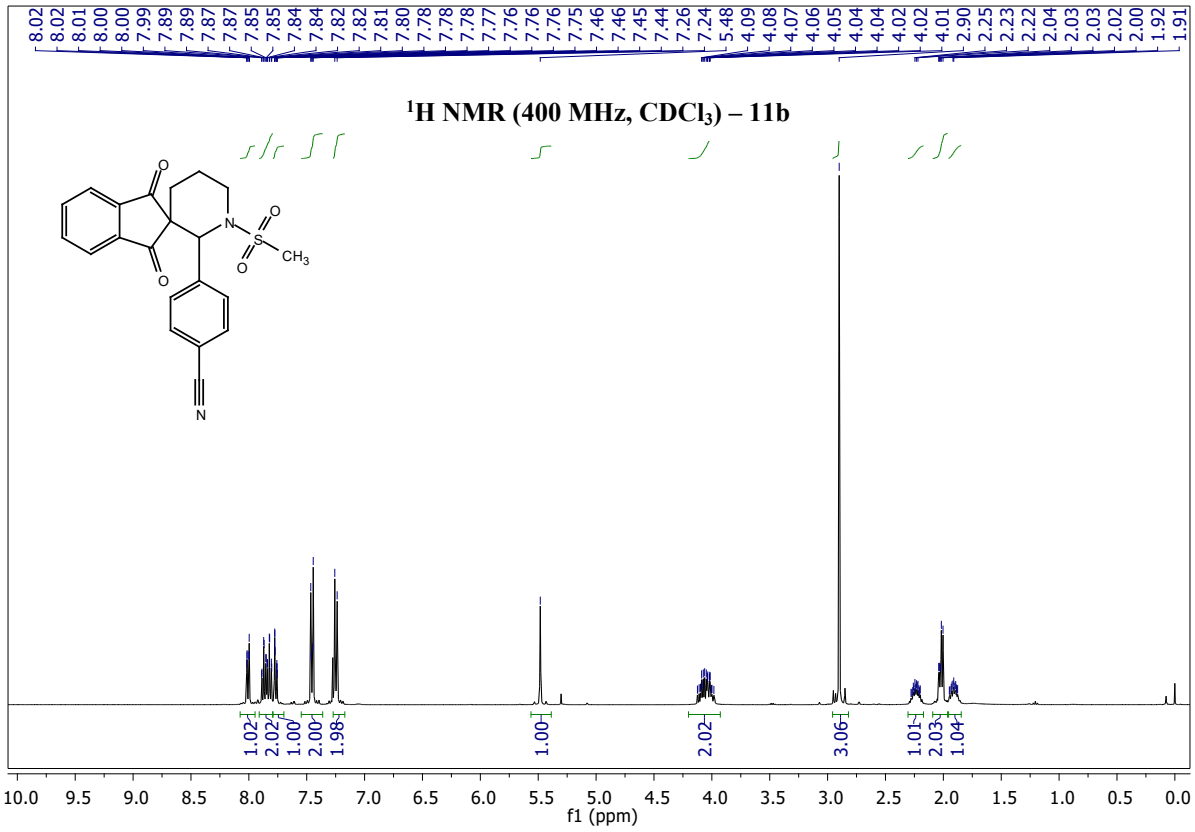


^{1}H NMR (400 MHz, $CDCl_3$) – 11a

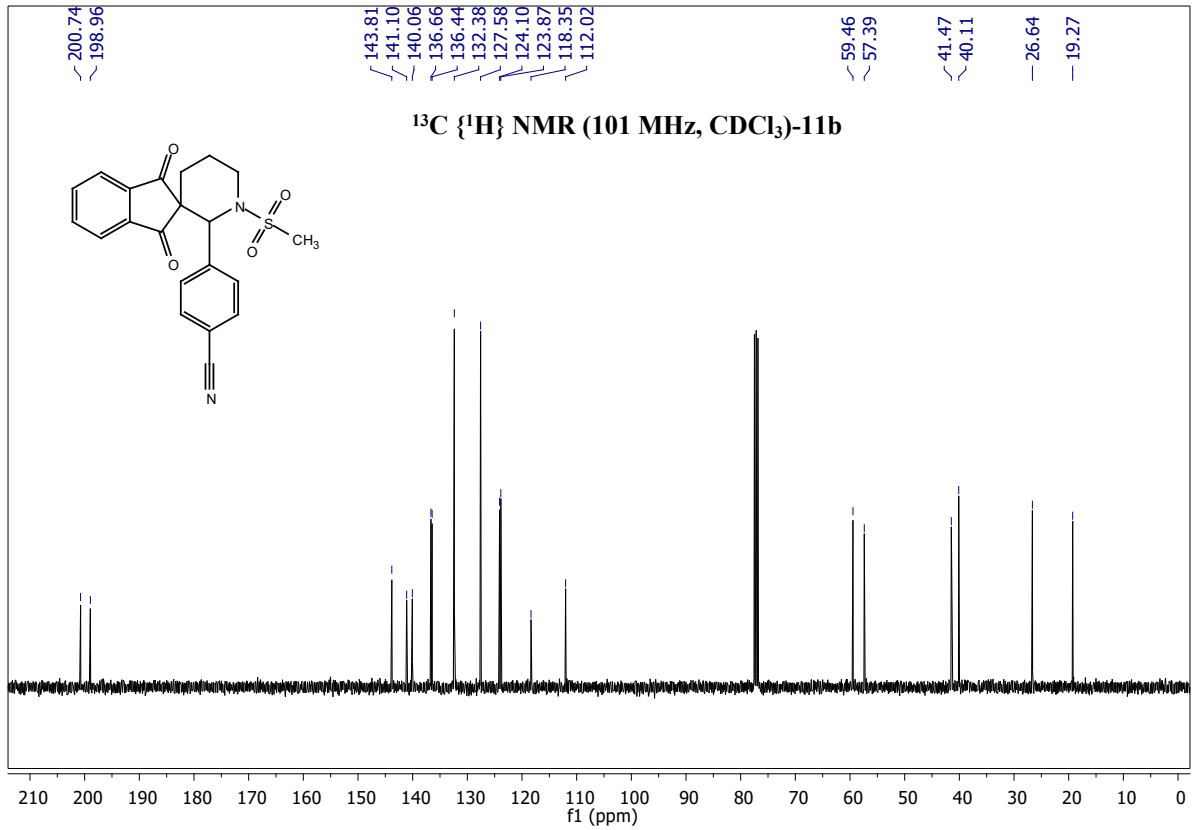


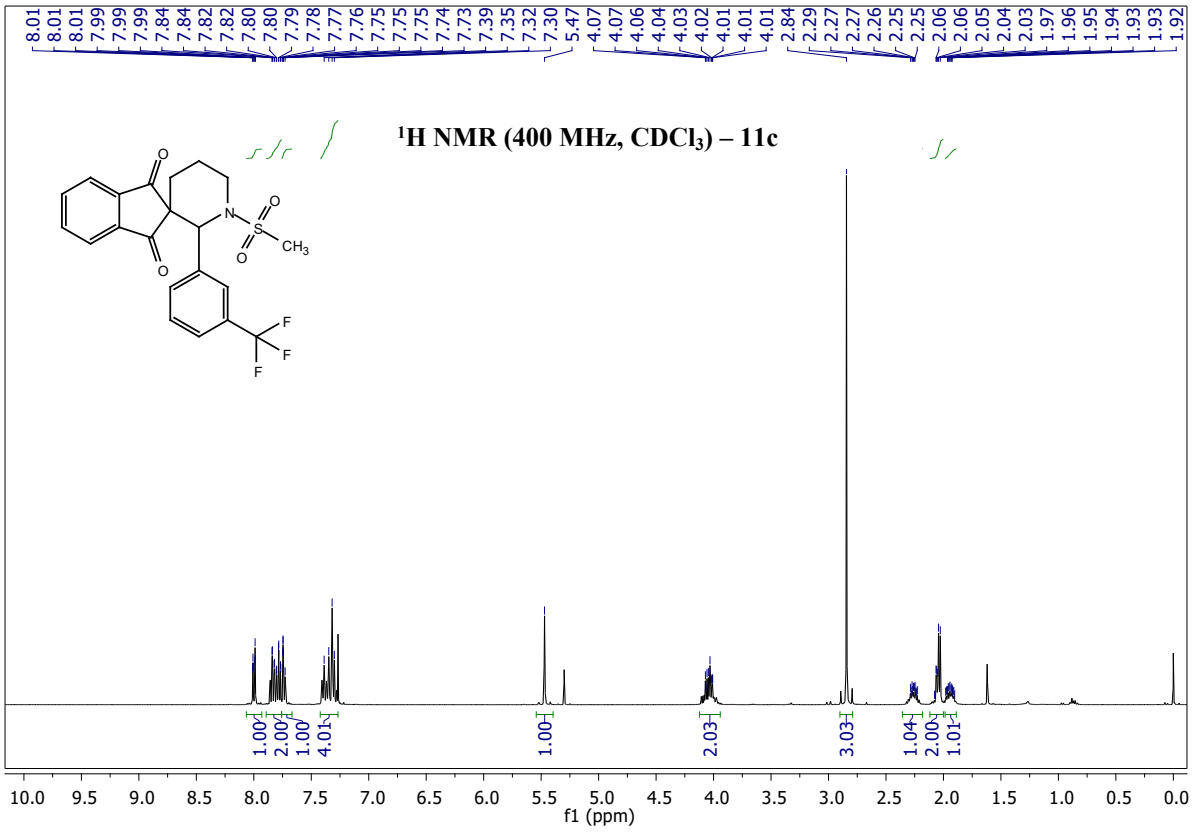
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11a

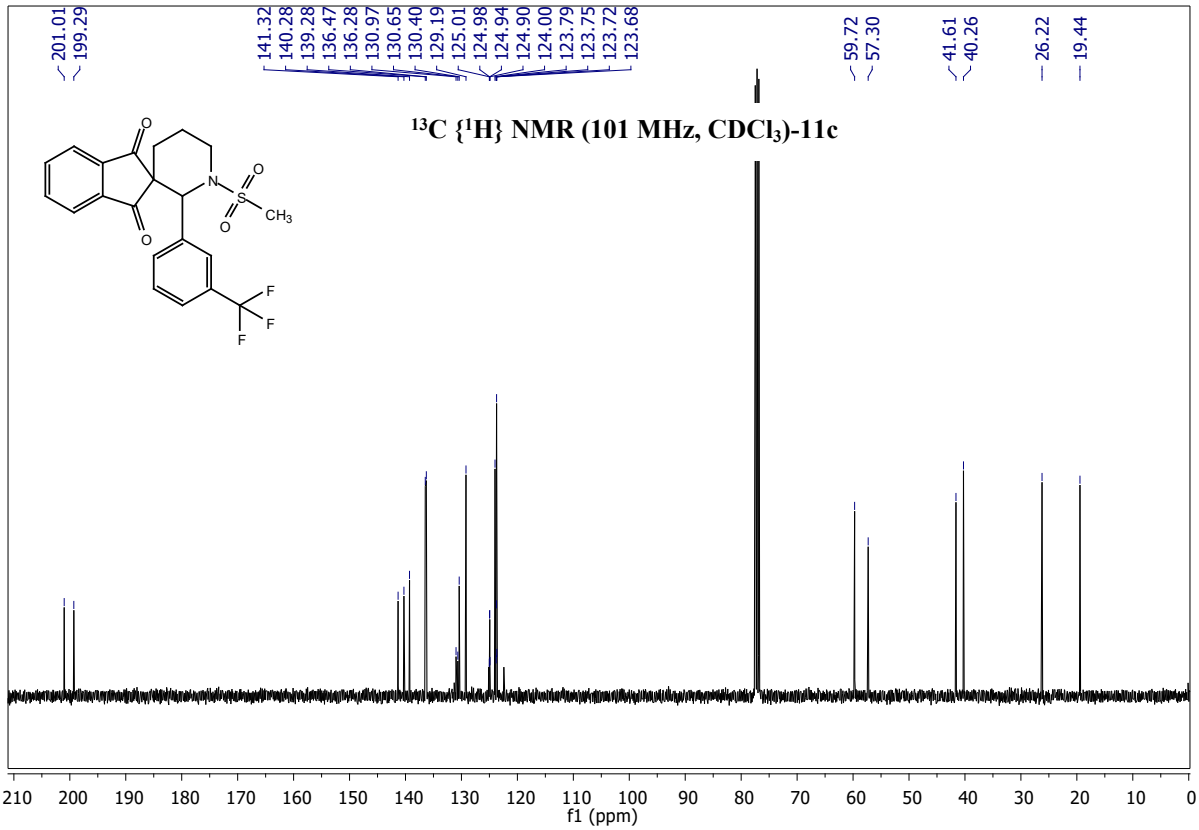
^{1}H NMR (400 MHz, $CDCl_3$) – 11b

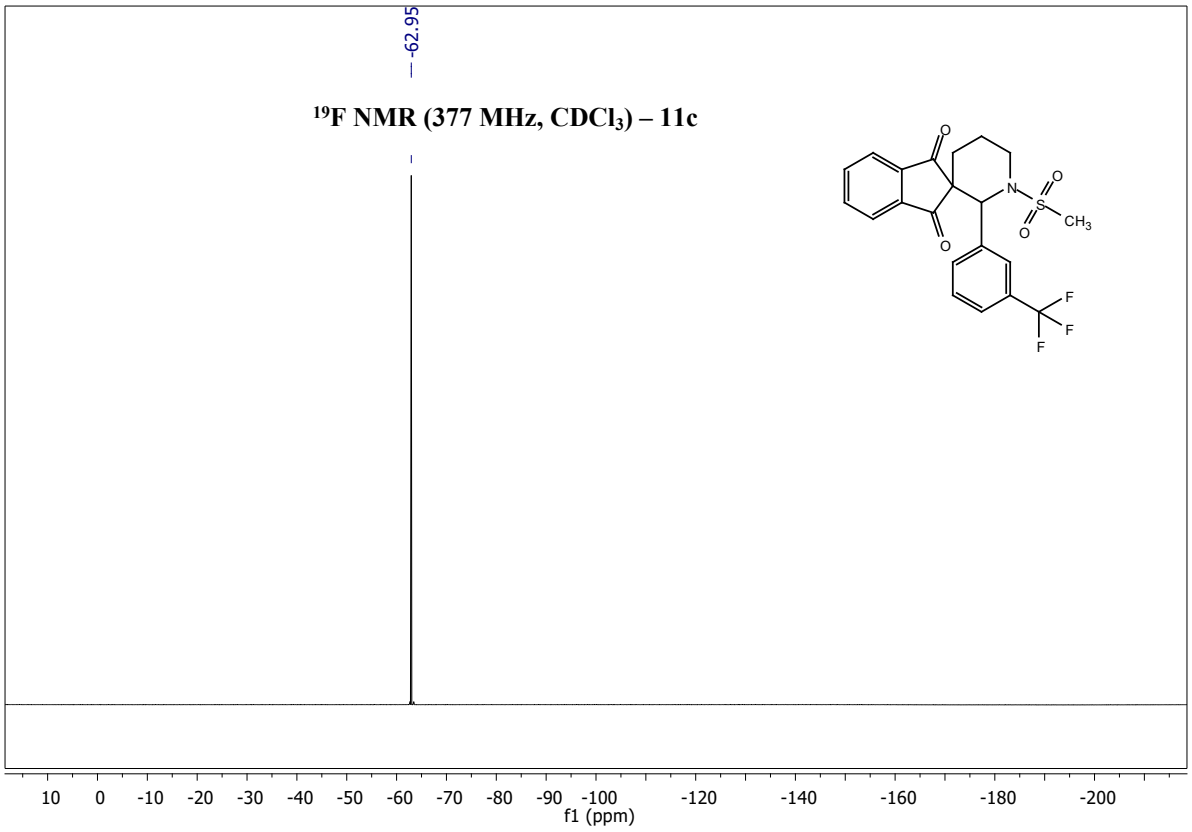


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11b

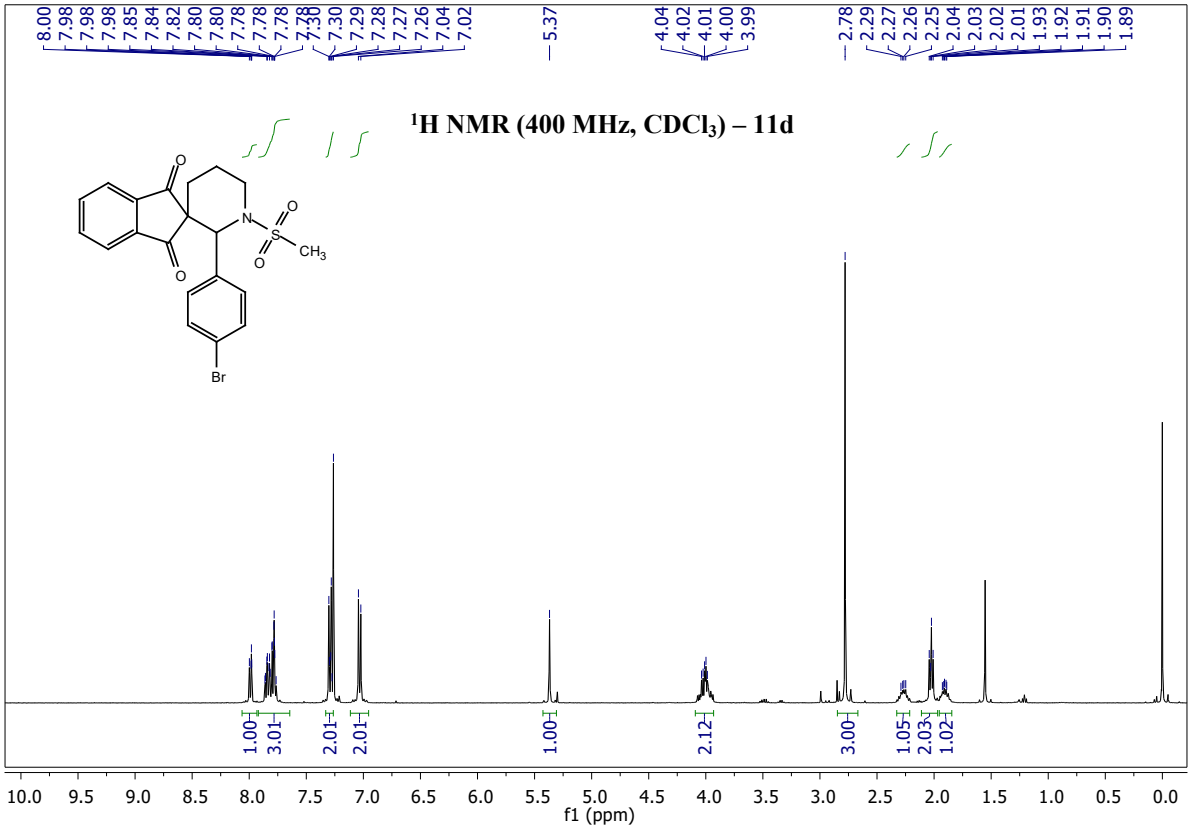



8.01 8.01 8.01 7.99 7.99 7.99 7.84 7.84 7.82 7.82 7.80 7.80 7.79 7.78 7.77 7.76 7.75 7.75 7.75 7.74 7.73 7.39 7.35 7.32 7.30 5.47 4.07 4.07 4.06 4.04 4.03 4.02 4.01 4.01 4.01 2.84 2.29 2.27 2.27 2.26 2.25 2.25 2.06 2.06 2.05 2.04 2.03 1.97 1.96 1.95 1.94 1.93 1.93 1.92
1H NMR (400 MHz, CDCl3) – 11c
1.00 2.00 1.00 4.01 1.00 2.03 3.03 1.04 2.00 1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

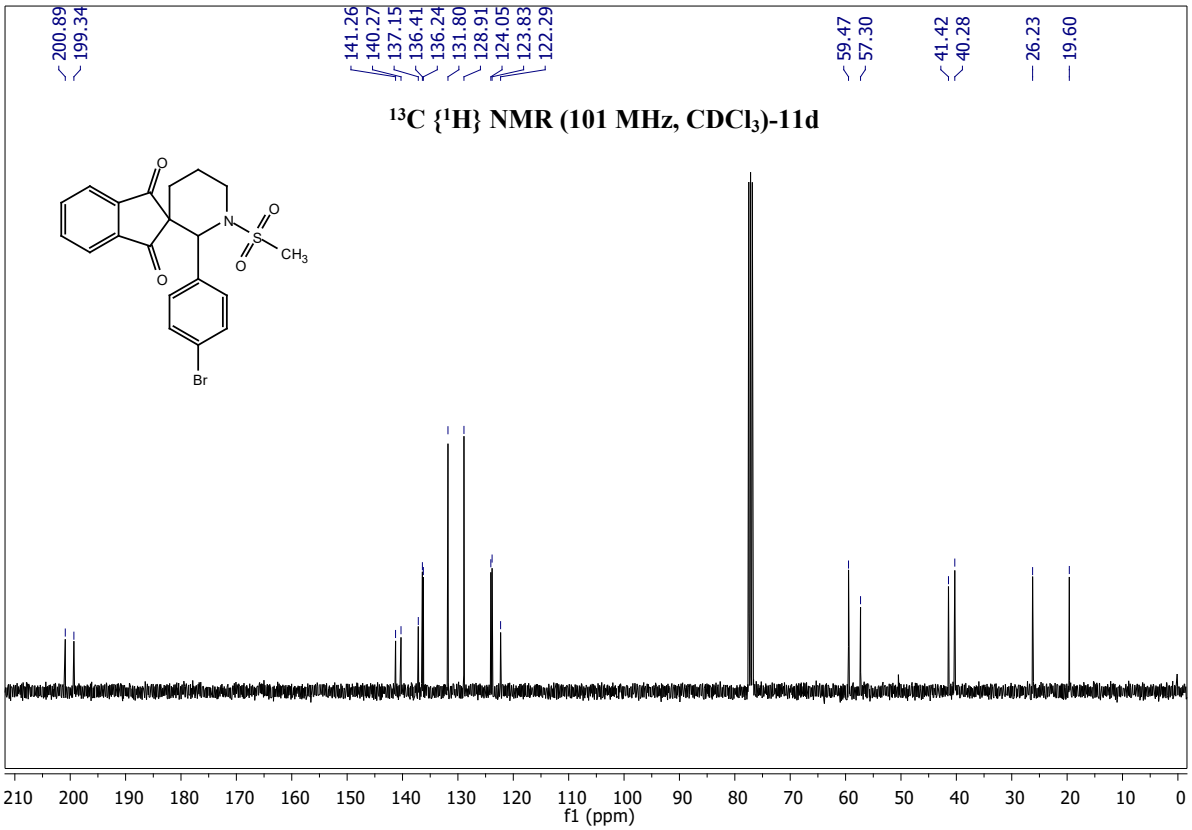

201.01 199.29 141.32 140.28 139.28 136.47 136.28 130.97 130.65 130.40 129.19 125.01 124.98 124.94 124.90 124.00 123.79 123.75 123.72 123.68 59.72 57.30 41.61 40.26 26.22 19.44
13C {1H} NMR (101 MHz, CDCl3)-11c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



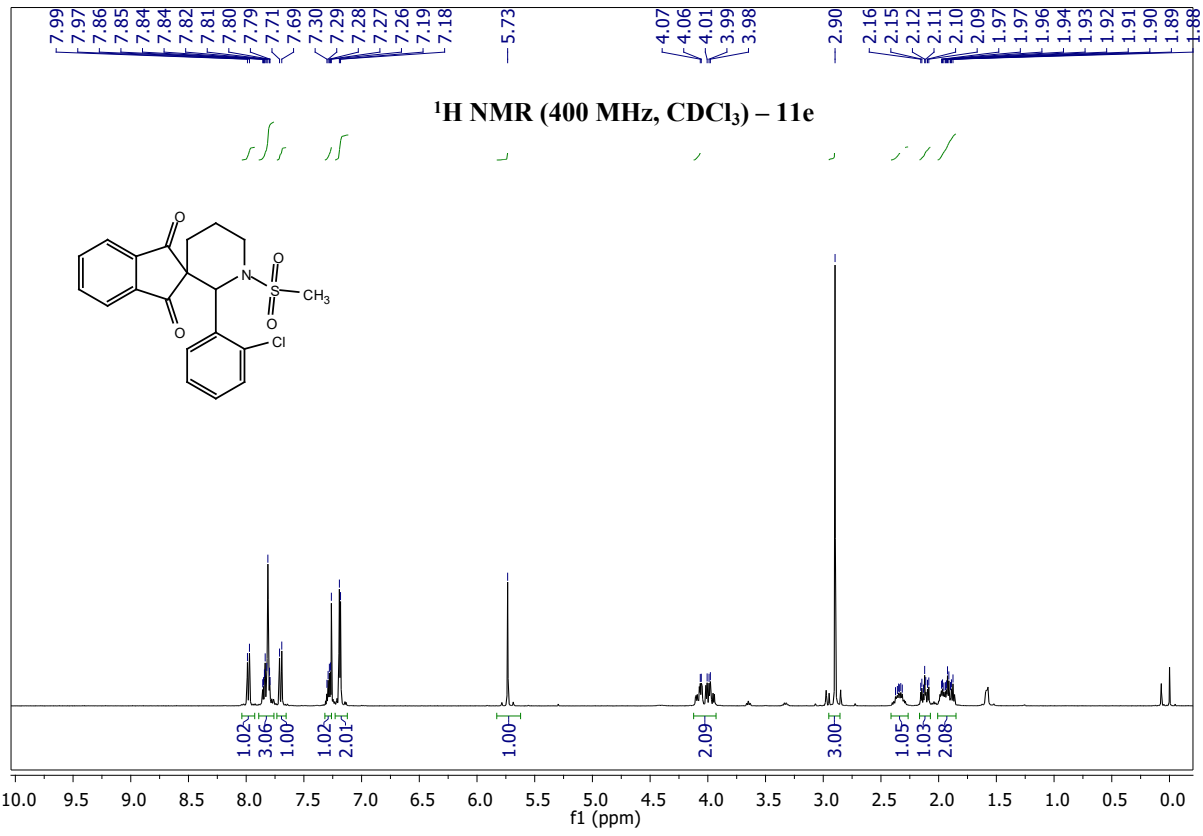
^{19}F NMR (377 MHz, $CDCl_3$) – 11c



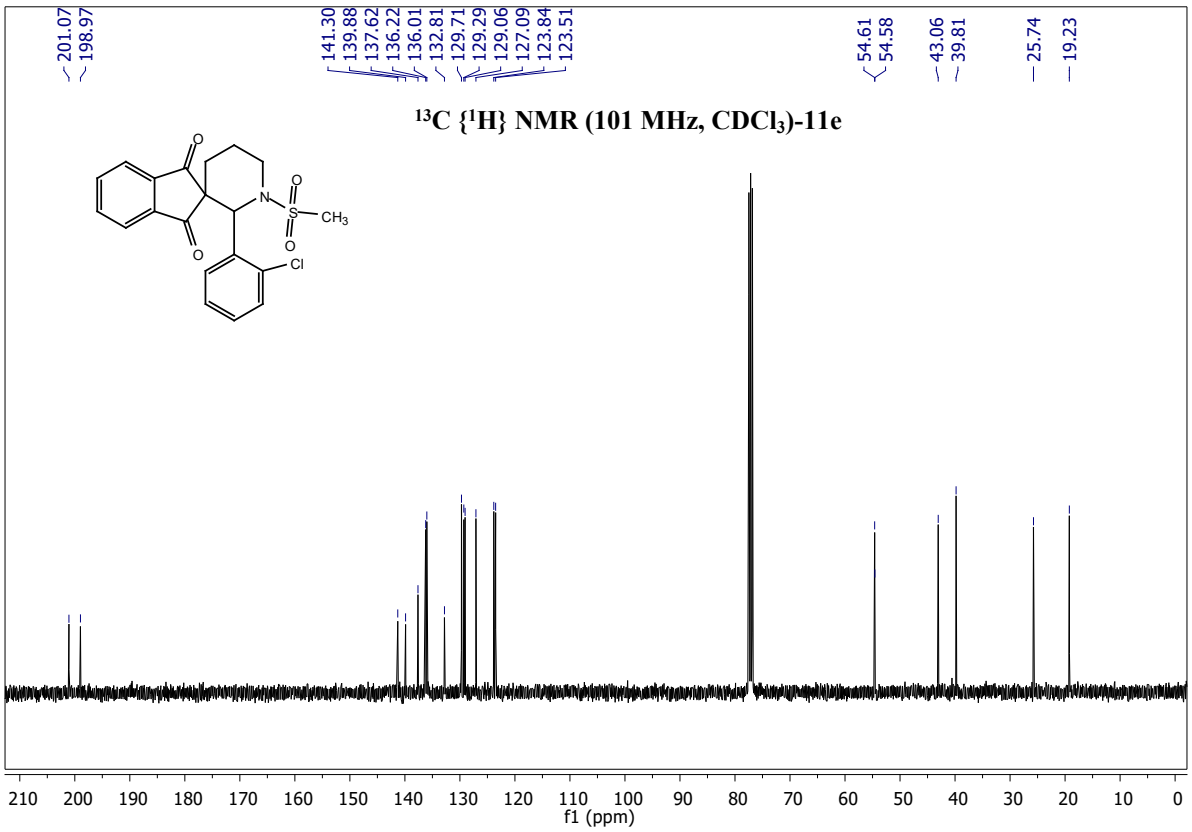
^{1}H NMR (400 MHz, $CDCl_3$) – 11d



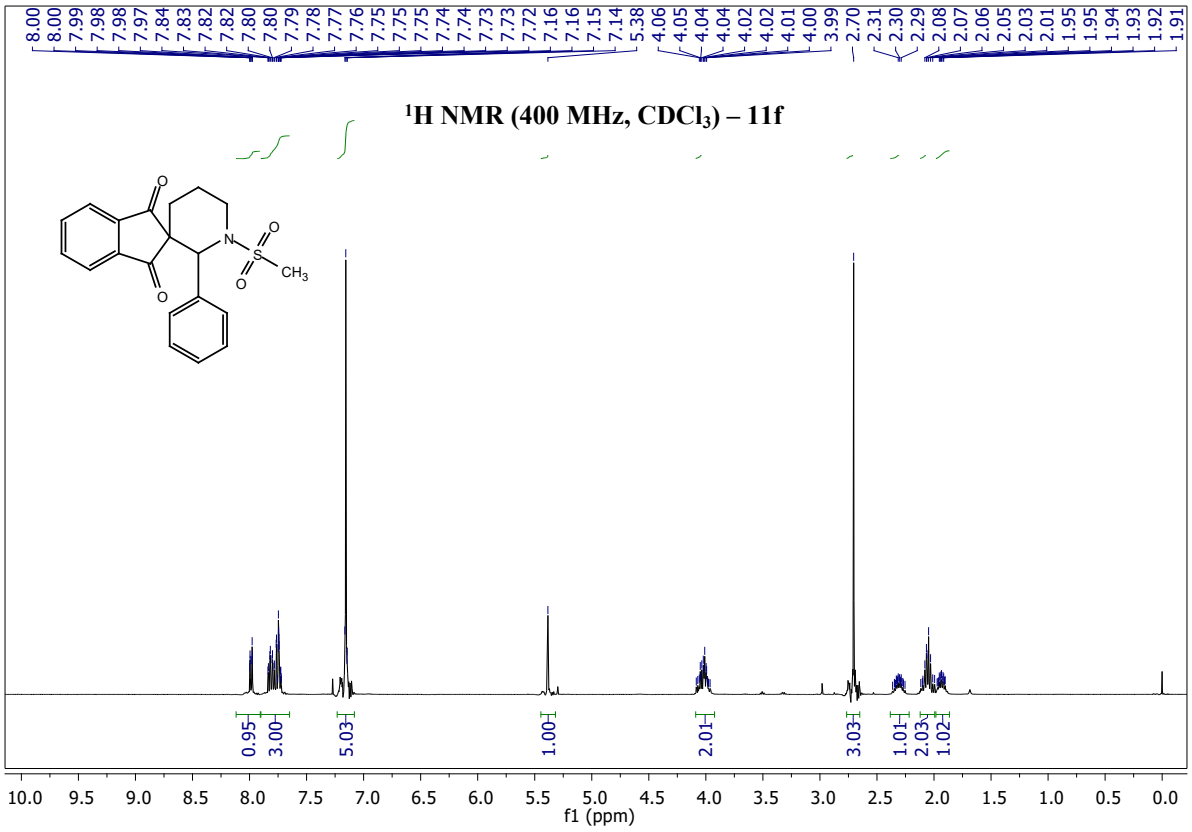
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11d



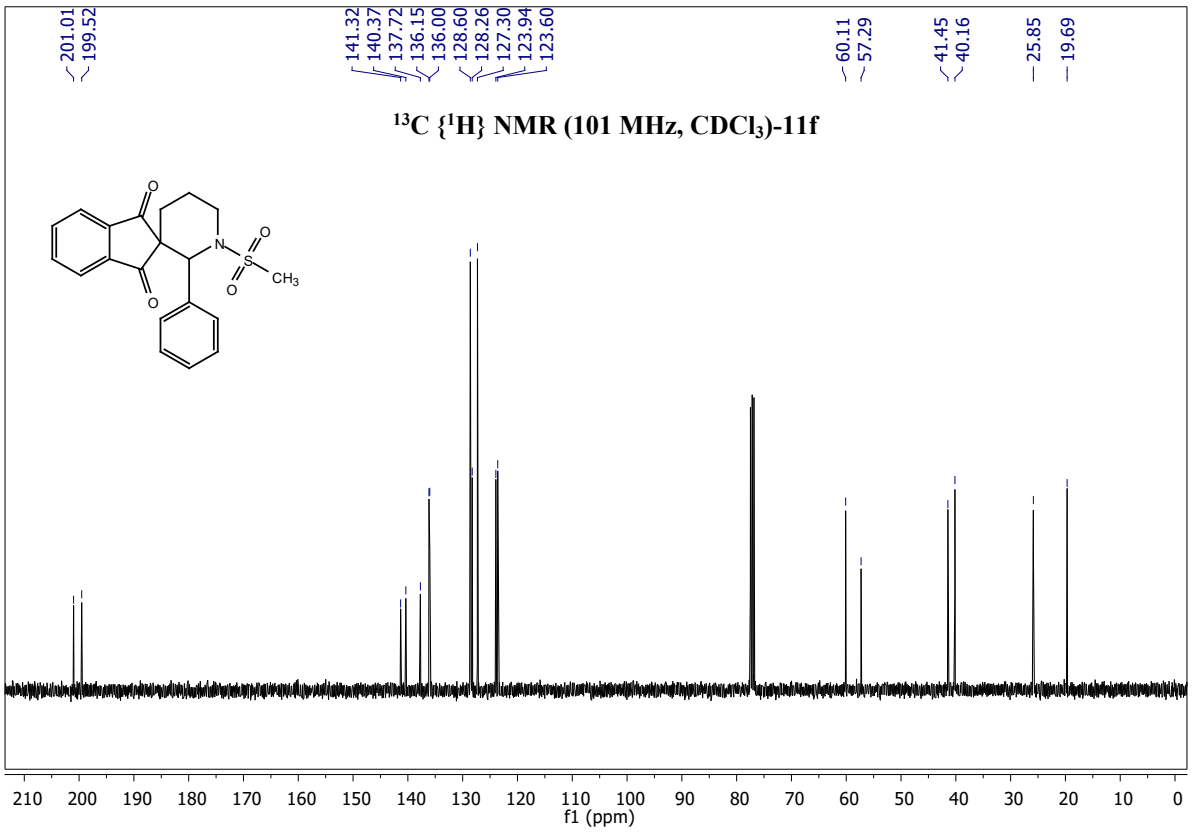
^{1}H NMR (400 MHz, $CDCl_3$) – 11e



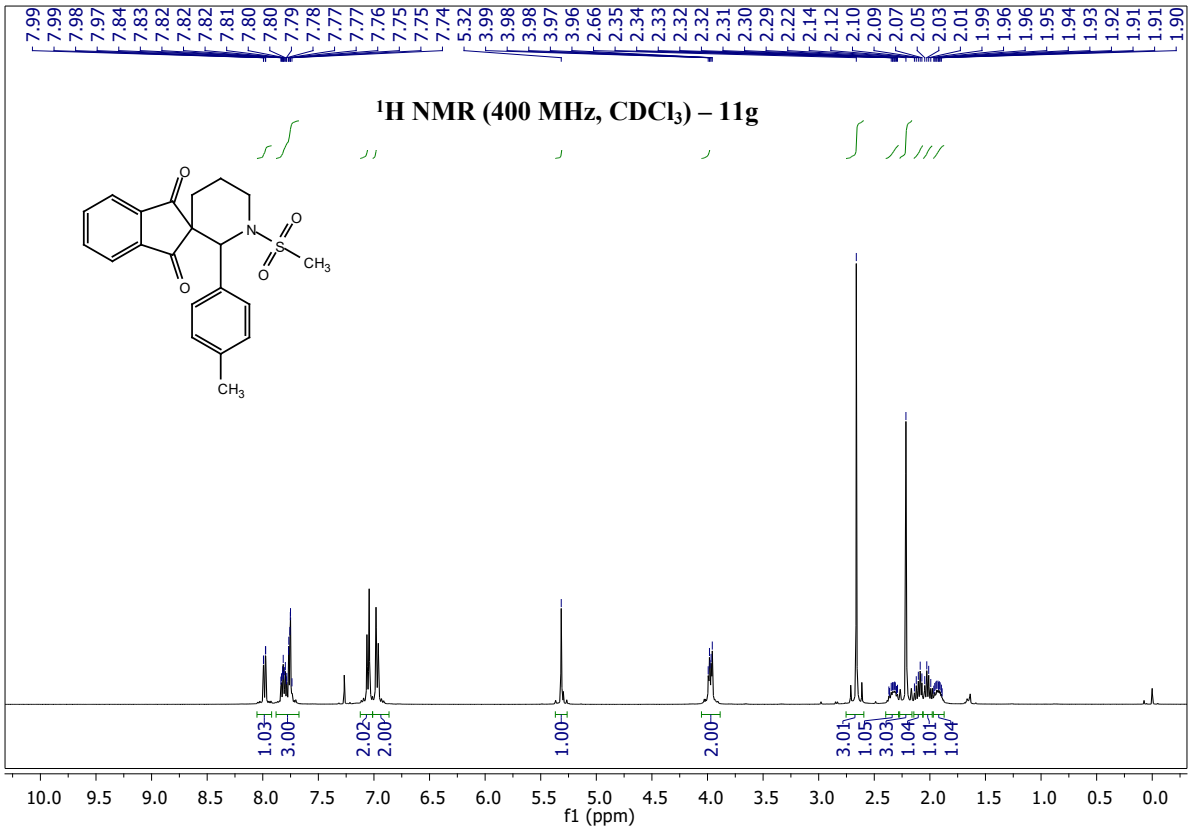
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11e



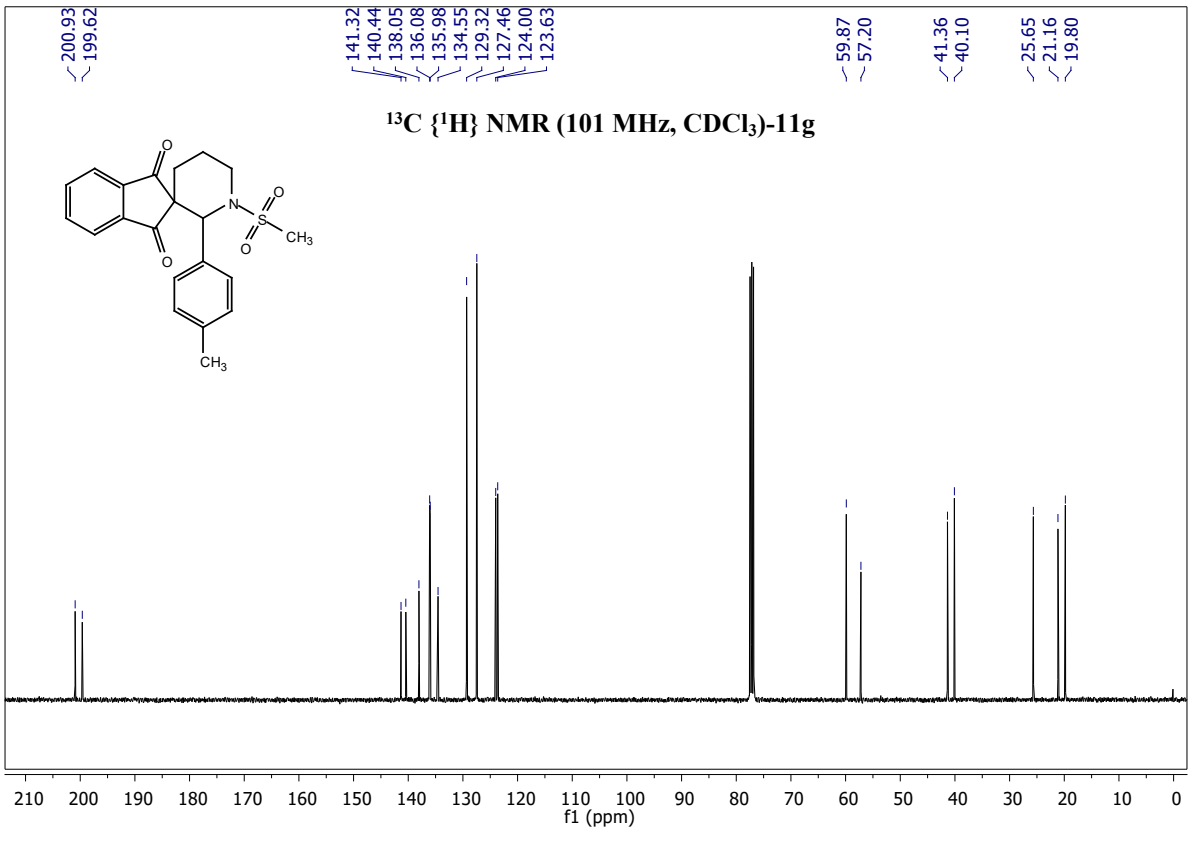
^{1}H NMR (400 MHz, $CDCl_3$) – 11f



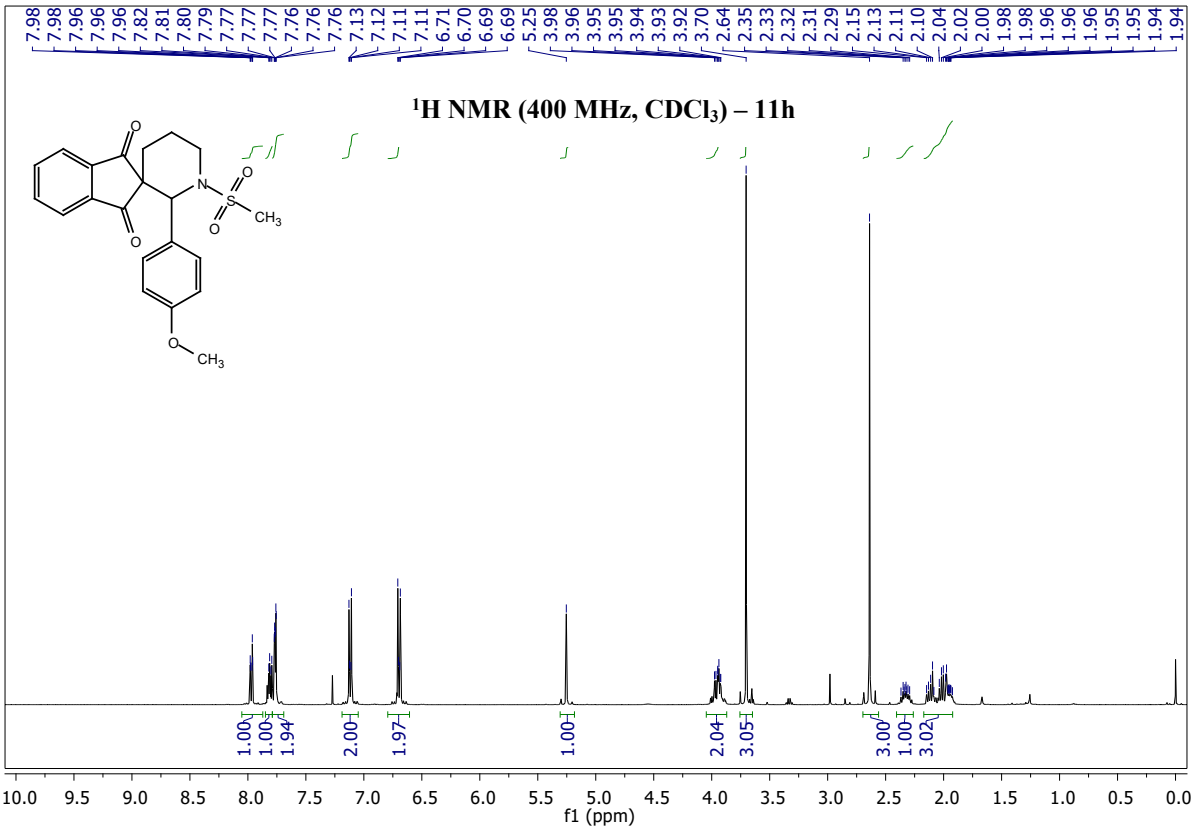
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11f



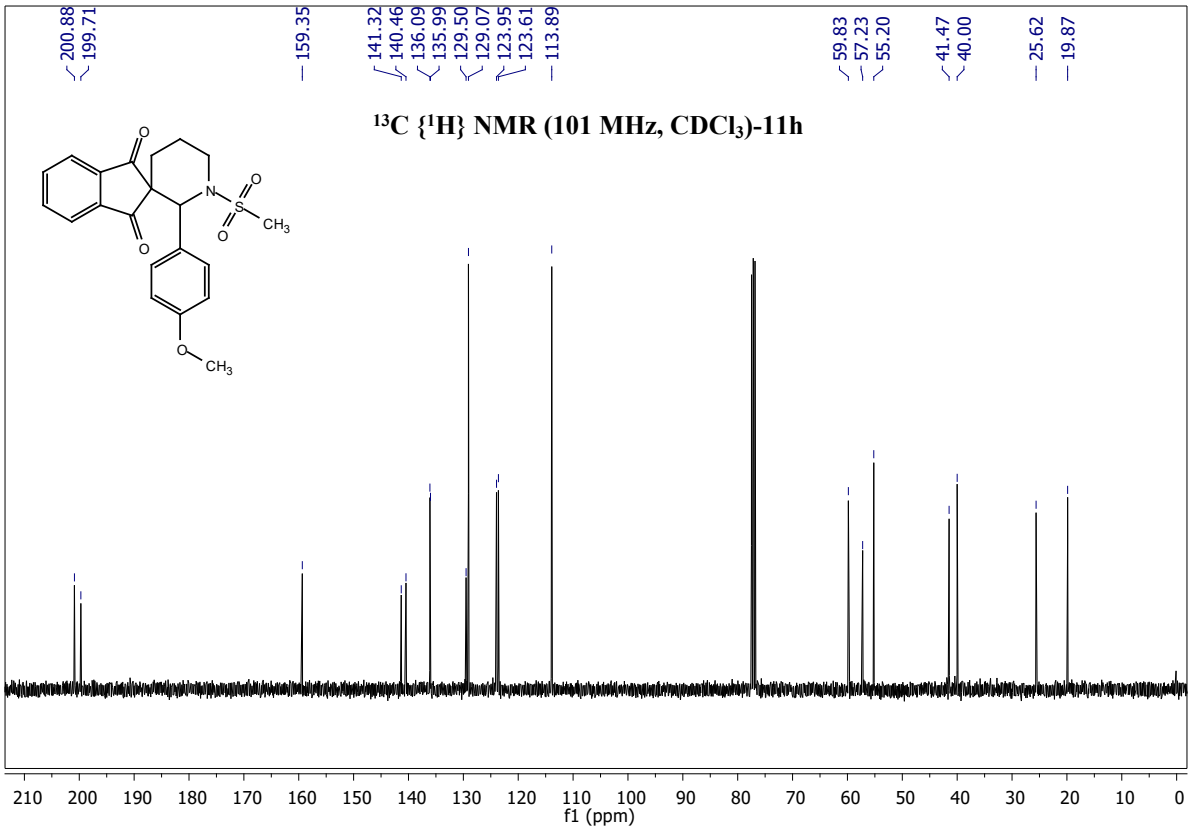
^{1}H NMR (400 MHz, $CDCl_3$) – 11g



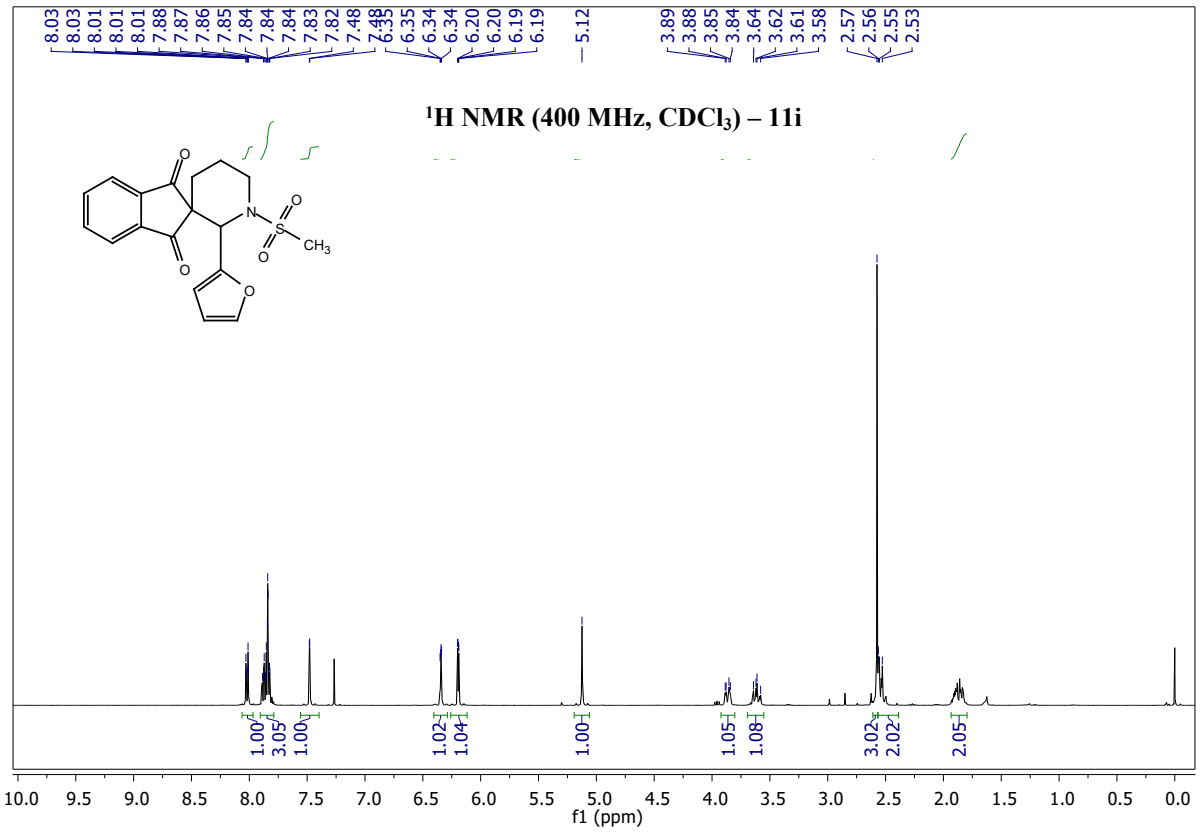
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11g



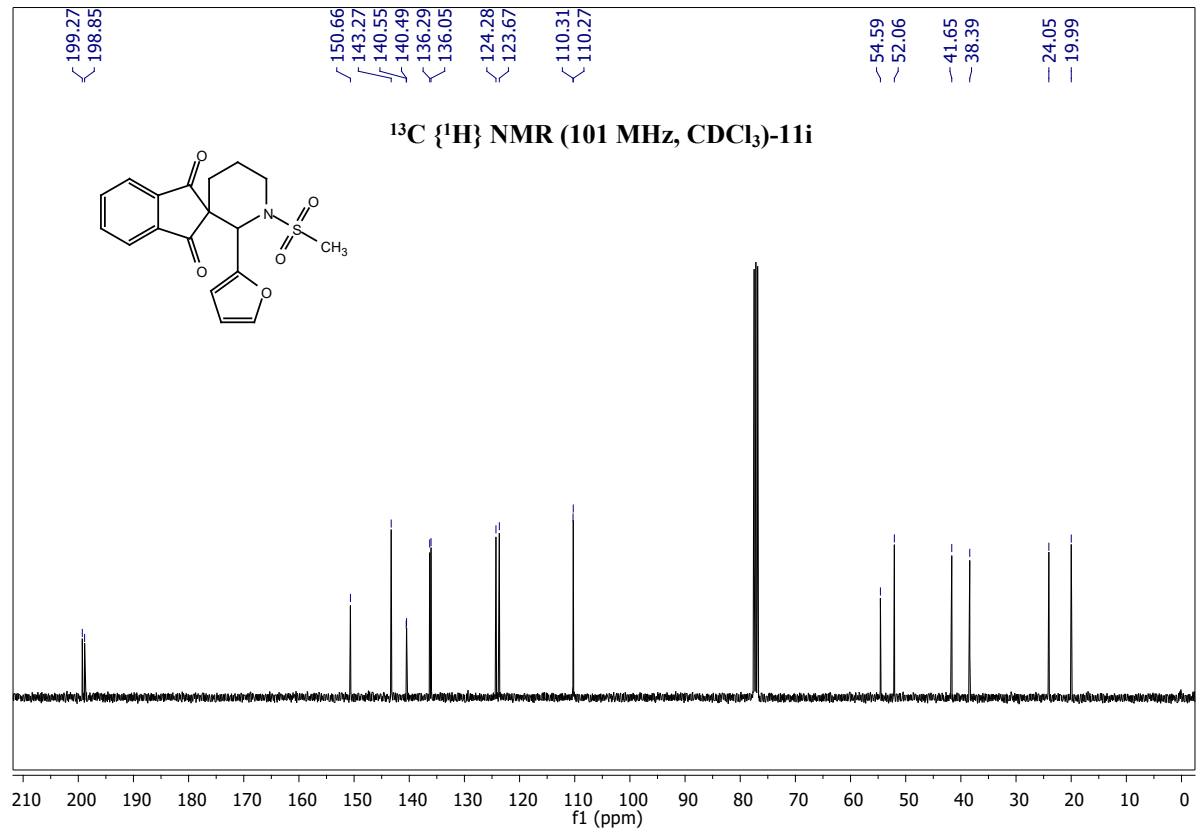
^{1}H NMR (400 MHz, $CDCl_3$) – 11h



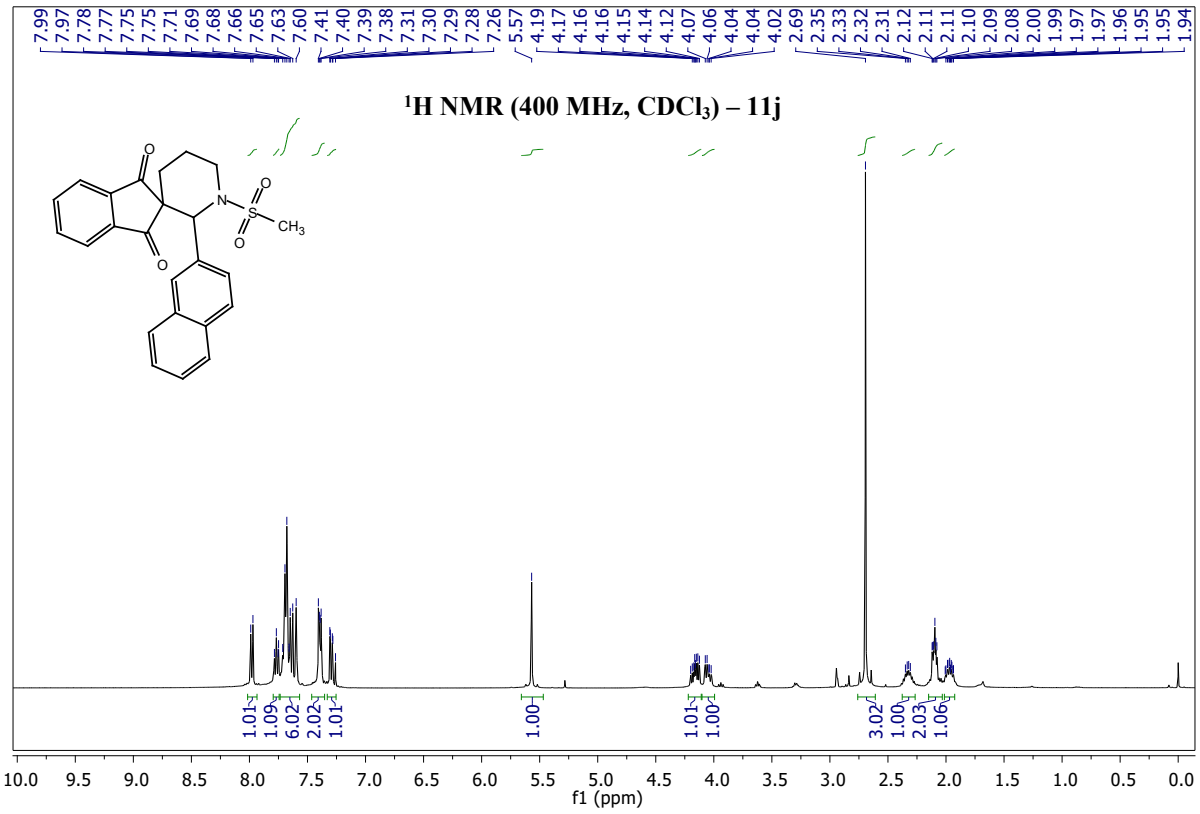
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11h



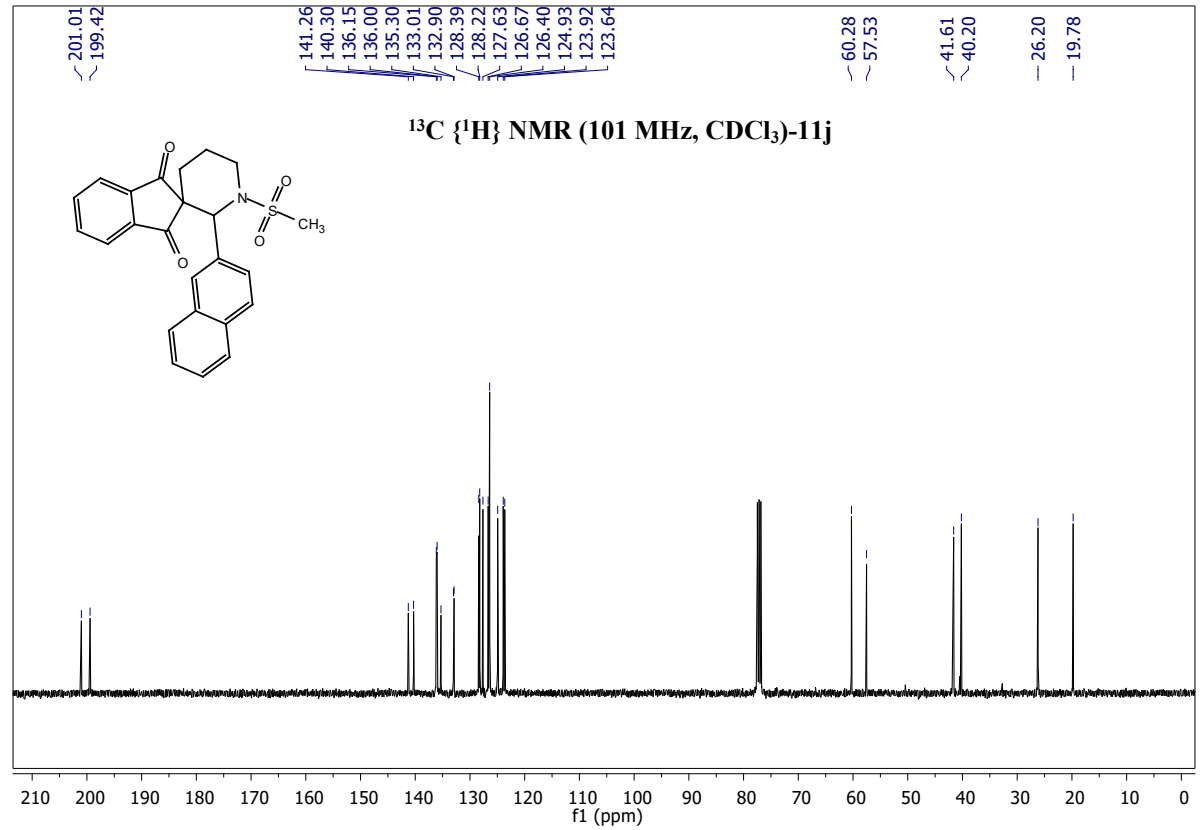
^{1}H NMR (400 MHz, $CDCl_3$) – 11i



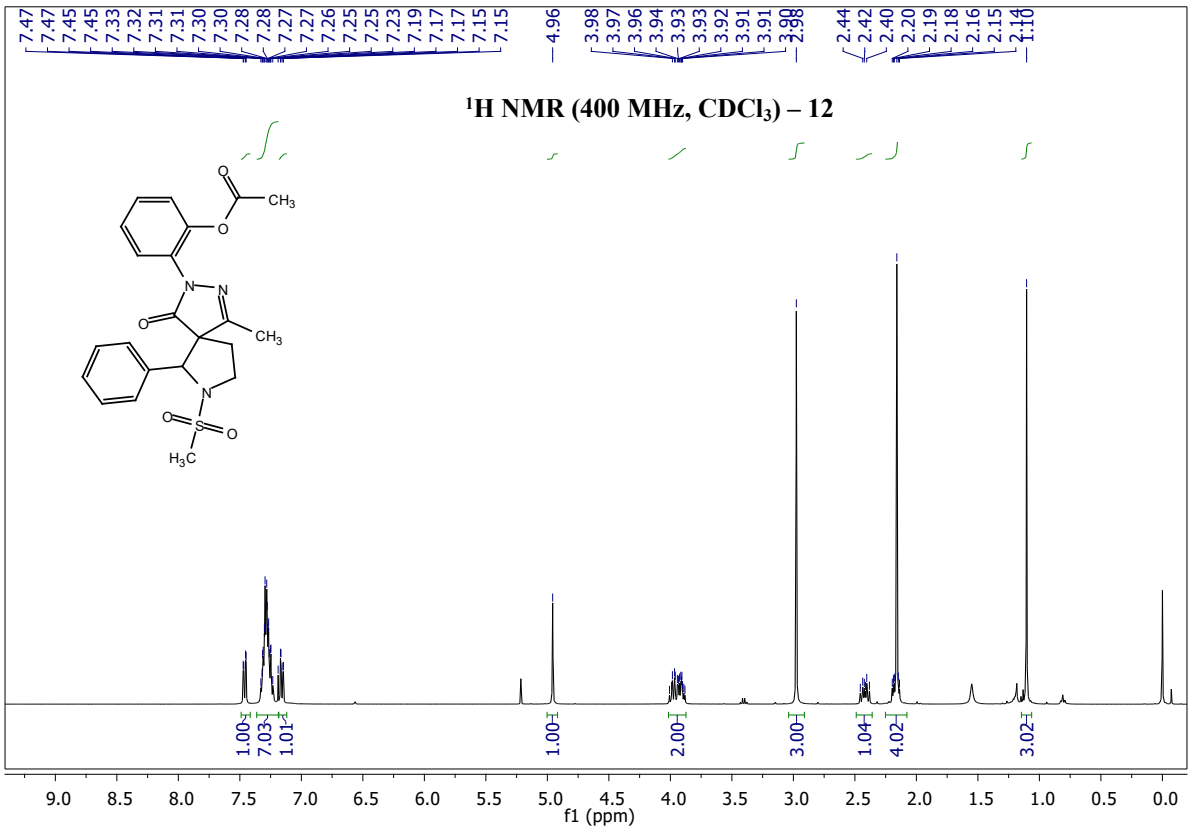
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11i



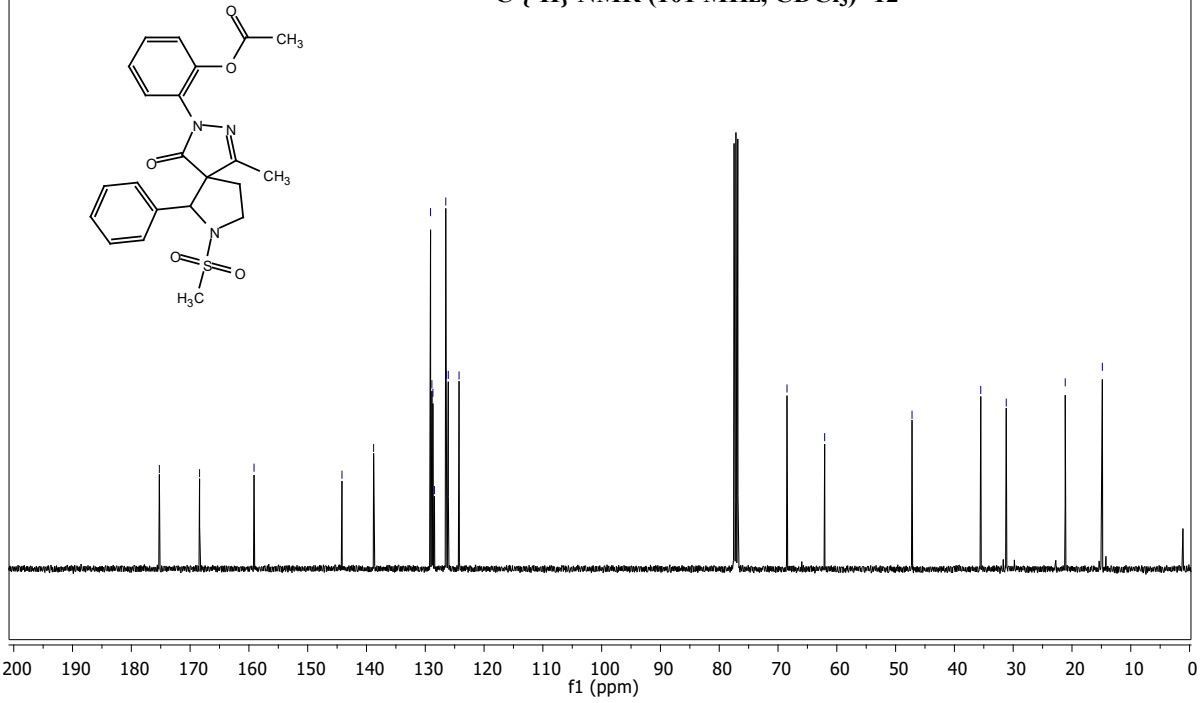
^{1}H NMR (400 MHz, $CDCl_3$) – 11j



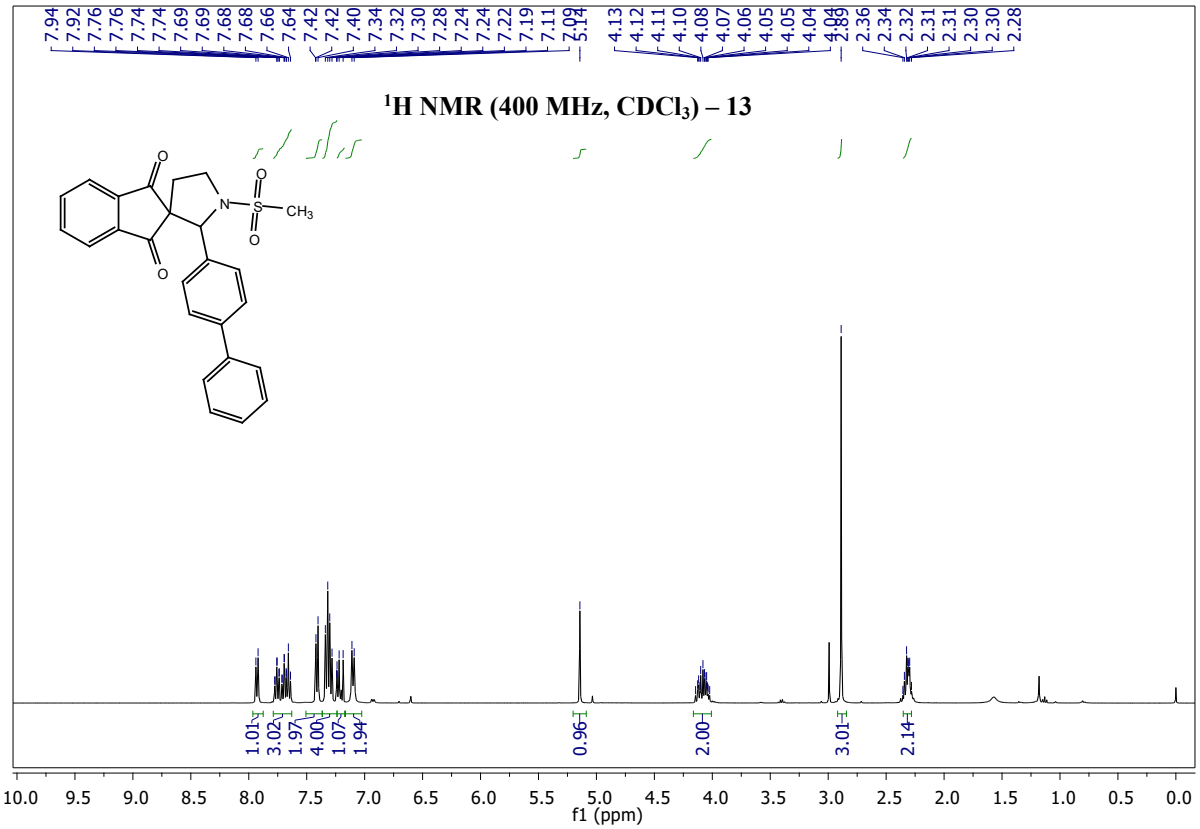
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-11j



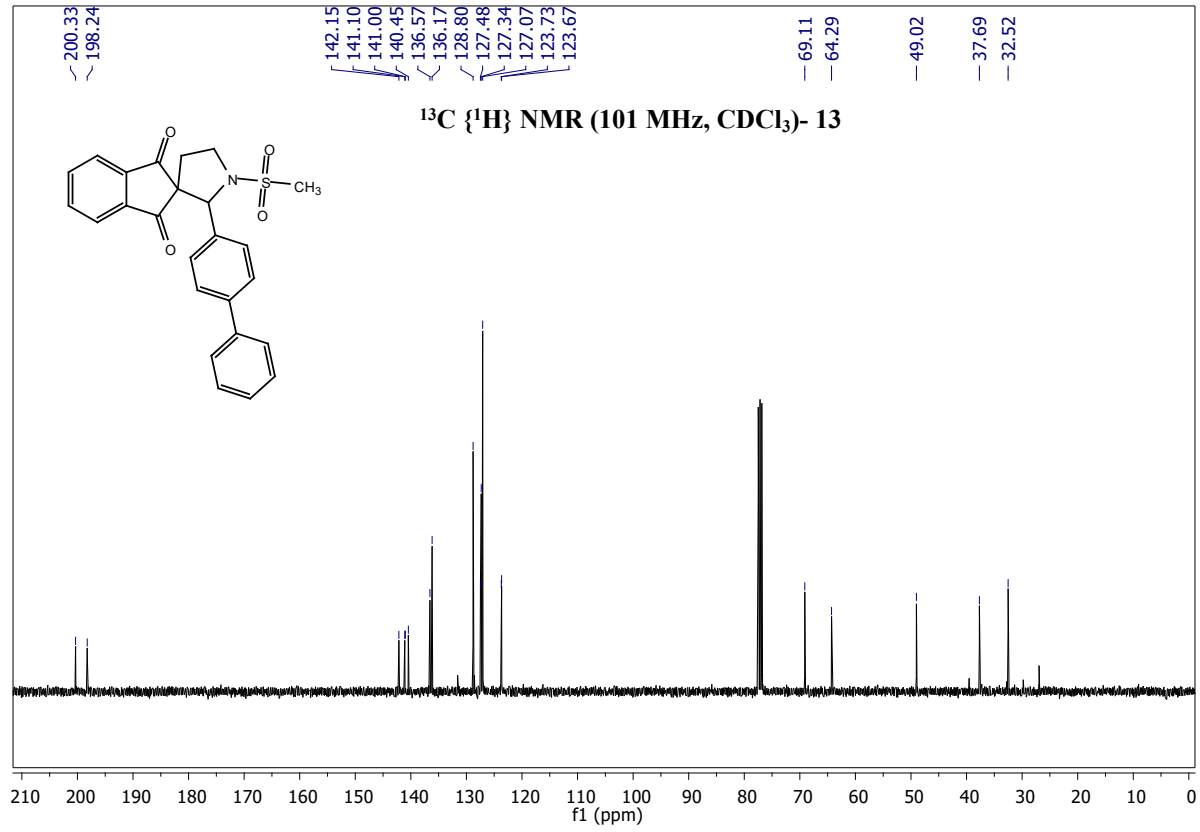
^{1}H NMR (400 MHz, $CDCl_3$) – 12



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 12



^{1}H NMR (400 MHz, $CDCl_3$) – 13



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 13