Electronic Supplementary Material (ESI) for ChemComm.

SUPPLEMENTARY INFORMATION

A Tethering Directing Group Strategy for Ruthenium-Catalyzed Intramolecular Alkene Hydroarylation

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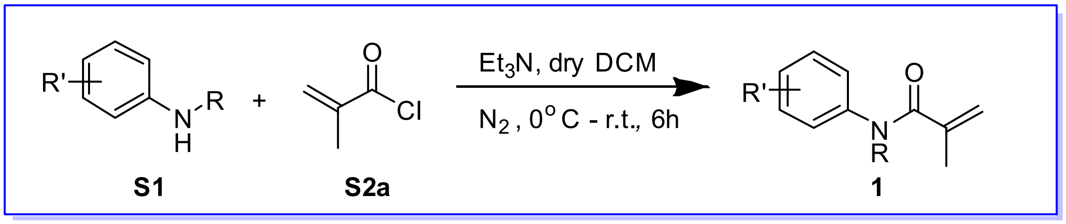
General Experimental Procedures and Reagent Availability

Unless otherwise noted, all manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line or glove box techniques. All glassware was oven-dried for at least 1 h prior to use. Toluene and hexane solvents were degassed by purging with nitrogen for 45 min and dried with a solvent purification system (MBraun MB-SPS). THF and dichloromethane were dried over activated 3Å molecular sieves and degassed by purging with nitrogen. Other reagents and starting materials for substrate synthesis were purchased from commercial vendors and used as received. TLC plates were visualized by exposure to ultraviolet light.

Organic solutions were concentrated by rotary evaporation at ~10 torr. Flash column chromatography was performed with 40–63 microns silica gel. ^{1}H NMR and ^{13}C NMR spectra were obtained on a 400 MHz spectrometer, and chemical shifts were recorded relative to residual protiated solvent. Both ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million downfield from tetramethylsilane (δ = 0 ppm). ^{19}F NMR spectra were obtained at 282.4 MHz, and all chemical shifts were reported in parts per million upfield of CF_3COOH (δ = -78.5 ppm). High resolution mass spectra were obtained at a Waters HRMS spectrometer.

Experimental Procedure for Preparation of Acrylamide Substrates

- **General Procedure for Preparation of Substrates 1a-1g and 1i-1n**[1,2]

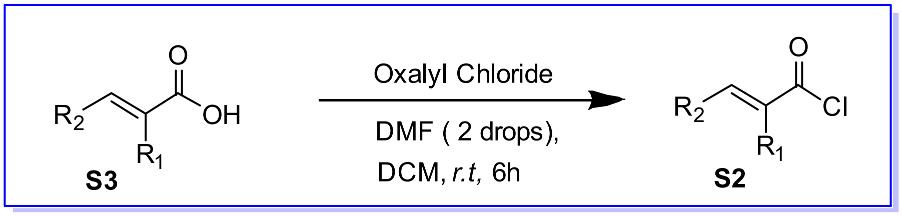


R = Me
R' = *p*-H **1a -** 84% (white solid)
R' = *p*-Me **1b -** 87% (yellow liquid)
R' = *p*-OMe **1c** - 94% (Yellow liquid)
R' = *p*-F **1d** - 79% (Yellow liquid)
R' = *p*-Cl **1e -** 81% (white solid)
R' = *p*-Br **1f -** 85% (white solid)
R' = *p*-CF_3 **1g -** 76% (yellow liquid)
R' = *p*-COMe **1i** - 78% (yellow liquid)
R' = *p*-CO_2Et **1j** - 75% (yellow liquid)
R' = *o*-F **1k -** 73% (yellow liquid)
R' = *m*-F **1l** - 79% (yellow liquid)

R' = *p*-H R = Ph **1m -** 92% (white solid)
R' = *p*-H R = Bn **1n** - 94% (white solid)

Into a 250 mL round-bottom flask equipped with a magnetic stir-bar was added solution of aniline **S1** (1.0 g, 1 equiv) in DCM (60 mL) and triethylamine (2 equiv). The mixture was stirred at 0° C, and methacryloyl chloride **S2a** (1.5 equiv) was added under nitrogen atmosphere. The resulting solution was allowed to warm up to room temperature and stirred for 6 hours, followed by the addition of H_2O (150 mL) to quench excess acyl chloride. The mixture was settled in a separation funnel, and the organic layer was extracted, washed with brine (3 x 100 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (0 to 6% ethyl acetate in hexanes).

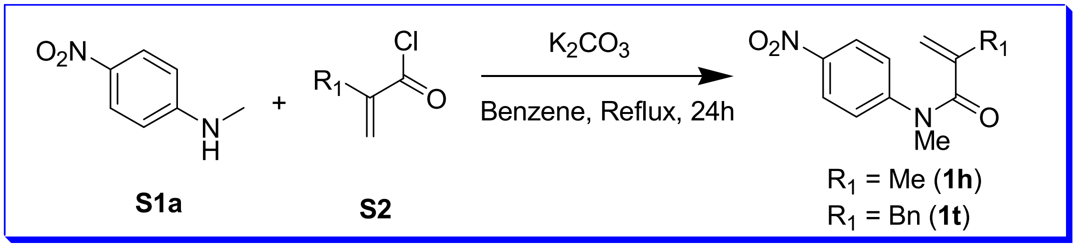
- **Preparation of Substrates 1o and 1u**
  - ➢ Synthesis of corresponding acryloyl chlorides (**S2**)[2]



Into a 50 mL round-bottom flask equipped with a magnetic stir-bar was added solution of acrylic acid **S3** (1.5 g, 1 equiv) in dichloromethane (DCM, 20 mL), followed by dropwise addition of oxalyl chloride (2 equiv) and 2 drops of DMF under nitrogen atmosphere. The mixture was stirred at room temperature for 6 hours before removing all volatiles under reduced pressure. The crude product was used for the next step without purification.

- ➢ The general procedure for acrylamide synthesis was applied for the reaction between corresponding N-methylaniline and crude acryloyl amide compounds.
- ➢ Compound **1o** is isolated in 76% yield as a white solid.
- ➢ Compound **1u** is isolated in 71% yield as a white solid.

- **Preparation of Substrates 1h and 1t**[3]

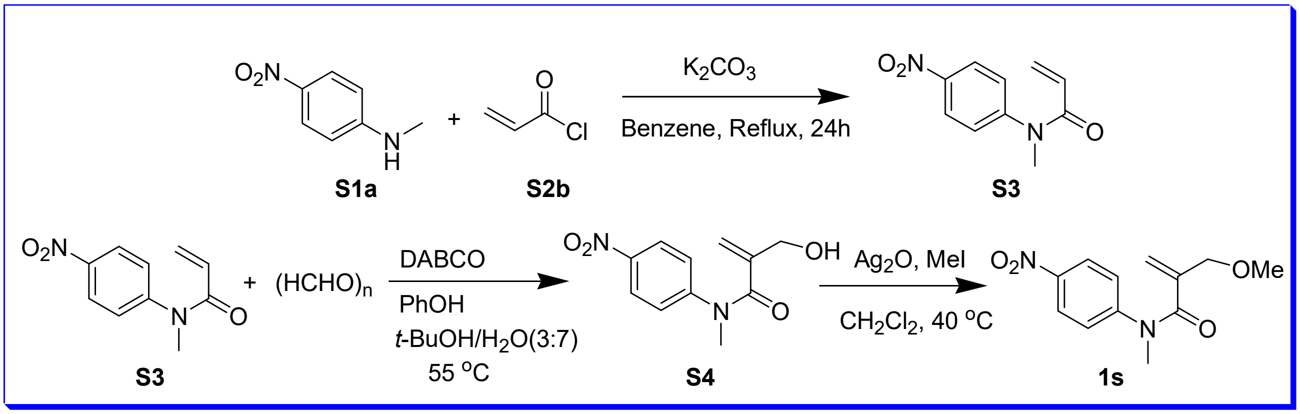


Into a 250 mL round-bottom flask equipped with Liebig condenser and a magnetic stir-bar was added a solution of N-methyl- 4-nitroaniline **S1a** (1.0 g, 1 equiv) in benzene (100 mL) and potassium carbonate (1.82 g, 2 equiv). Under N_2 atmosphere, the reaction mixture was added with acryloyl chloride **S2** (1.5 equiv), transferred to an oil bath, and refluxed under stirring for 24h. After cooling to room temperature, the reaction mixture was added with water (150 mL) and continued to with stirring for 30 min. The reaction mixture was then extracted with ethyl acetate (3 x 100 mL), and the combined organic phases were evaporated under reduced pressure to remove all volatiles. The resulting crude product was purified by column chromatography (0 to 8% ethyl acetate in hexanes).

The compound **1h** is isolated in 69% yield as a yellow solid.

The compound **1t** is isolated in 63% yield as a yellow solid.

- **Preparation of Substrate 1s**[4]



- Synthesis of intermediate **S3**: the synthetic procedure for substrate **1h** and **1t** was applied for the reaction between **S1a** and parent acryloyl chloride (**S2b**) to obtain **S3**.

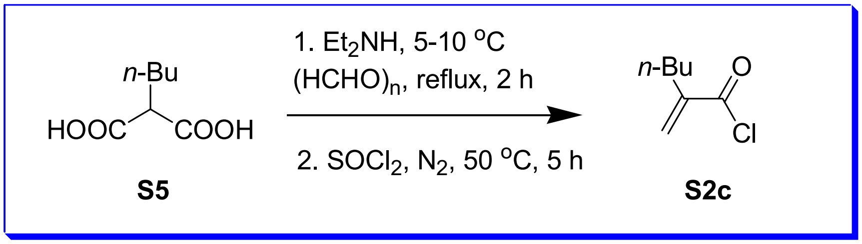
- Synthesis of intermediate **S4**

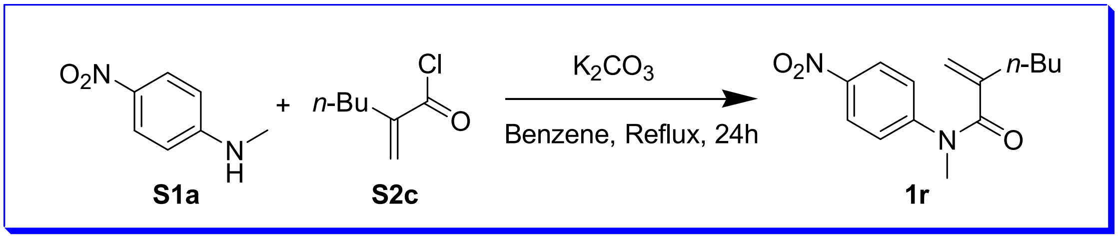
Into a 10 mL Schlenk tube equipped with a magnetic stir-bar was added paraformaldehyde (5 equiv), DABCO (1 equiv), phenol (0.25 equiv) and 4 mL of mixed solvent (3:7 *t*-BuOH/H_2O). The mixture was stirred at 55 °C until all reactants were dissolved. Intermediate **S3** (1.0 g, 1 equiv) was then added slowly for 5 min, and the reaction mixture was stirred at 55 °C for three days. After cooling to room temperature, the mixture was evaporated under reduced pressure to remove *t*-BuOH and extracted with ethyl acetate (3 x 100 mL). The combined organic phases was dried over anhydrous sodium sulfate and concentrated over rotary evaporator to remove all volatiles. The resulting crude mixture was subjected to column chromatography (0 to 17% ethyl acetate in hexanes) to obtain the desired intermediate **S4** in 45% yield as light yellow oil.

- Methylation of **S4** to synthesize substrate **1s**

Into a 100 mL round-bottom flask equipped with a magnetic stir-bar was added a solution of intermediate **S4** (1.5 g, 1 equiv) in DCM (40 mL), Ag_2O (2 equiv), and iodomethane (3 equiv). The resulting mixture was stirred at 40 °C and monitored by TLC to ensure the complete conversion of **S4**. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure to remove all volatiles. The resulting crude mixture was purified by column chromatography (0 to 10% ethyl acetate in hexanes) to afford compound **1s** in 71% yield as a yellow solid.

- **Preparation of Substrate 1r**



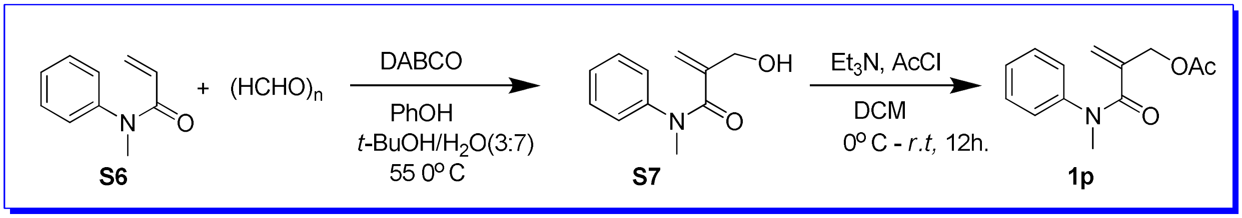


- Synthesis of 2-butyl acryloyl chloride **S2c**[2,5]

Into a 100 mL round-bottom flask equipped with a magnetic stir-bar was added a solution of butyl malonic acid **S5** (2.0 g, 1 equiv) in dry ethyl acetate (50 mL). The solution was cooled to 5 °C and added with diethyl amine (1.5 equiv) under nitrogen atmosphere. After stirring the mixture for 5 min, paraformaldehyde (1.5 equiv) was added slowly and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and quenched with water (100 mL). The p^H value of the solution was brought to ~1 by adding concentrated HCl before being extracted with ethyl acetate (3 x 75 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated at rotary evaporator to remove all volatiles. The crude **S2c** was acquired as a pale-yellow liquid and used for the next step without purification.

- Synthesis of substrate **1r**: the synthetic procedure for substrate **1h** and **1t** was applied for the reaction between **S1a** and **S2c** to obtain **1r**. The compound **1r** is purified by column chromatography (0 to 8% ethyl acetate in hexanes) in 65% yield as yellow solid.

- **Preparation of Substrate 1p**[4]

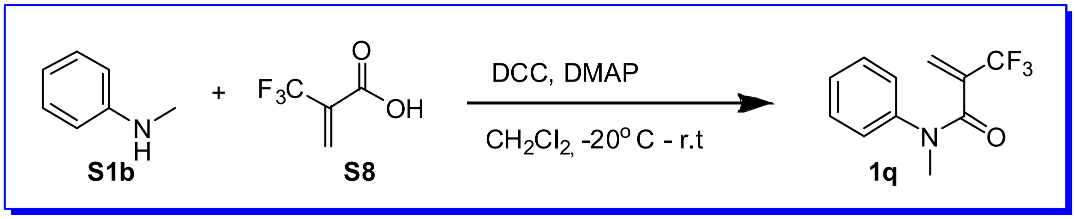


- Synthesis of intermediate **S7**: the synthetic procedure for intermediate **S4** was applied for the reaction with N-methyl-N-phenyl acrylamide (**S6**) to afford intermediate **S7**.

- Acetylation of **S7** to synthesize substrate **1p**

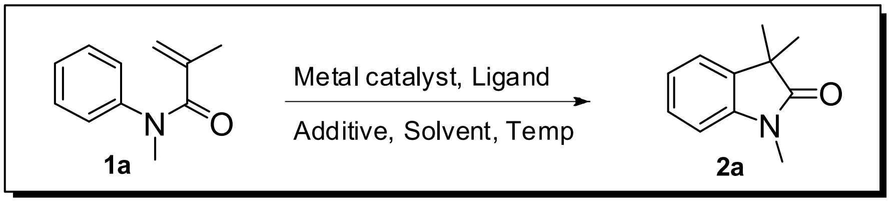
Into a 100 mL round-bottom flask equipped with a magnetic stir-bar was added a solution of **S7** (1.0 g, 1 equiv) in DCM (30 mL) and triethylamine (2 equiv). The mixture was cooled to 0 °C and added with acetyl chloride (1.5 equiv) under nitrogen atmosphere, then stirred at room temperature for 12h. The reaction mixture was then added with water (100 mL) to quench the excess acetyl chloride and settled in a separation funnel. The organic layer was collected, washed with brine (3 x 50 mL), and dried over anhydrous sodium sulfate. All volatiles were removed under reduced pressure and the resulting crude product was purified by column chromatography (0 to 10% ethyl acetate in hexanes) to afford the compound **1p** in yield 55% as a white solid.

- **Preparation of Substrate 1q**



Into a 100 mL round-bottom flask equipped with a magnetic stir-bar was added N-methyl aniline **S1b** (2 equiv), acrylic acid **S8** (1.0 g, 1 equiv) and dichloromethane (40 mL). The mixture was cooled to -20 °C before the addition of a solution of DCC (1.3 equiv) and DMAP (0.2 equiv) in dichloromethane (10 mL). The resulting mixture was stirred overnight at room temperature, and then evaporated under reduced pressure to remove all volatiles. The crude product was subjected to column chromatography (6% ethyl acetate in hexanes) to obtain compound **1q** in 62% yield as a white solid.

Table S1: Development of Catalytic Reaction Conditions (Part I)

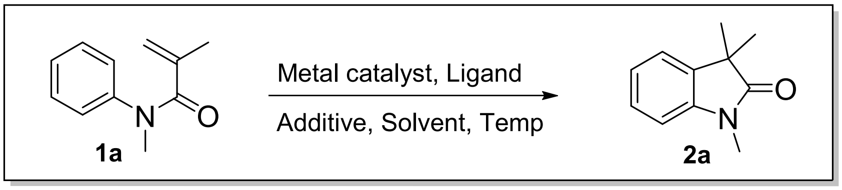


Catalyst	Additive	Solvent	Temp(^{o} C)	Yield (%)
$[RuH_2(CO)(PPh_3)_3]$	-	Dioxane	120	0
$[Ru_3(CO)_{12}]$	-	Dioxane	120	0
$[RuCl_2(p\text{-cymene})]_2$	-	Dioxane	120	0
$[Ru(COD)(Methallyl)_2]$	NaOAc	Dioxane	120	0
$[RuCl_2(cod)]_2$	NaOAc	Dioxane	120	43^a
$[RuCl_2(cod)]_2$	AgOAc	Dioxane	120	20^b
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	Dioxane	120	61^a
$[RuCl_2(p\text{-cymene})]_2^c$	AgOAc	Dioxane	120	55^a
$[RuCl_2(p\text{-cymene})]_2$	K_2CO_3	Dioxane	120	20^b
$[RuCl_2(p\text{-cymene})]_2^c$	$AgSbF_6$ + Pivalic aicd	Dioxane	120	10^b
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	Toluene	120	60^a
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	THF	120	30^b
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	DCE	120	$<20^b$
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	DME	120	$<20^b$
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	DMF	120	$<10^b$
$[RuCl_2(p\text{-cymene})]_2^c$	NaOAc	CH_3CN	120	$<5^b$

0.17mmol of Substarte, 10mol% Catalyst, 20 mol% additive, 1mL of Solvent.

a = Isolated yield; b = estimated based on TLC. c = 5mol% of the catalyst

Table S2: Development of Catalytic Reaction Conditions (Part II)



Catalyst	Additive	Ligand	Solvent	Temp(^{o} C)	Yield (%)
[RuCl$_2$(p-cymene)]$_2$	NaOAc(20mol%)	-	Dioxane	140	$73^{a,c}$
[RuCl$_2$(p-cymene)]$_2$	NaOAc(20mol%)	Phen	Dioxane	140	$82^{a,c}$
[Ru(COD)(Methallyl)$_2$]			Dioxane	120	0^b
[Ru(COD)(Methallyl)$_2$]		PPh$_3$	Dioxane	120	$<5^b$
[Ru(COD)(Methallyl)$_2$]		PCy$_3$	Dioxane	120	<10
[Ru(COD)(Methallyl)$_2$]		PMe$_3$	Dioxane	120	0^b
[Ru(COD)(Methallyl)$_2$]		Phen	Dioxane	120	0^b
[Ru(COD)(Methallyl)$_2$]		IPr	Dioxane	120	28^a
[Ru(COD)(Methallyl)$_2$]		SIPr	Dioxane	120	25^a
[Ru(COD)(Methallyl)$_2$]	AcOH (1equiv)	IPr	Dioxane	120	46^a
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IPr	Dioxane	120	$\mathbf{81^a}$
-	AcOH(2equiv))	-	Dioxane	120	0
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	SIPr	Dioxane	120	80^a
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	SIMes	Dioxane	120	78^a
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IMes	Dioxane	120	75^a
[Ru(COD)(Methallyl)$_2$]	Pivalic acid(2equiv)	IMes	Dioxane	120	$<50^b$
[Ru(COD)(Methallyl)$_2$]	CF$_3$COOH(2equiv)	IMes	Dioxane	120	$<70^b$
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IPr	Dioxane	120	54^c
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IPr	Toluene	120	79^a
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IPr	DCE	120	$<60^b$
[Ru(COD)(Methallyl)$_2$]	AcOH(2equiv)	IPr	THF	120	$<60^b$

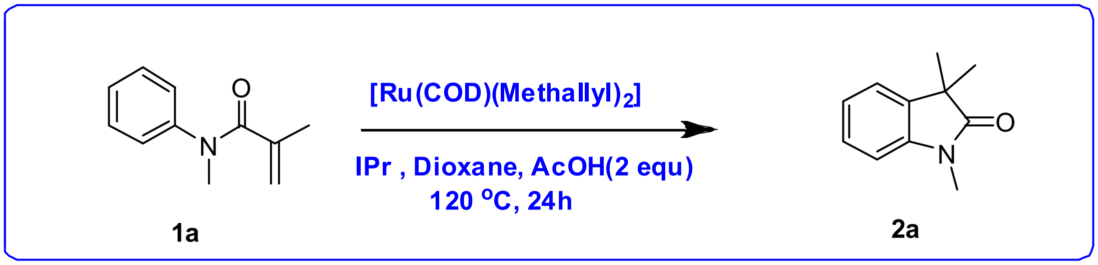
0.17mmol of Substarte, 10mol% Catalyst, 20 mol% additive, 1mL of Solvent.

a = Isolated yield   b = estimated based on TLC   c = 5mol% catalyst and Ligand

General Procedure for Ru-Catalyzed Intramolecular Alkene Hydroarylation

Into a 4 mL scintillation vial equipped with a magnetic stir bar was placed $[Ru(cod)(\eta^3\text{-}C_4H_7)_2]$ (0.017 mmol), IPr (0.017 mmol), and N-aryl acrylamide substrate (0.17 mmol). Dioxane (1.0 mL) and acetic acid (0.34 mmol) were subsequently added. The reaction mixture was stirred at room temperature for 5 minutes and the vial was sealed with a silicone-lined screw-cap and electrical tape before being transferred out of the glovebox and stirred at 120 °C for 24 hours. The reaction mixture was cooled to room temperature and evaporated under reduced pressure to remove all volatiles. Further purification was achieved by flash-column chromatography on silica.

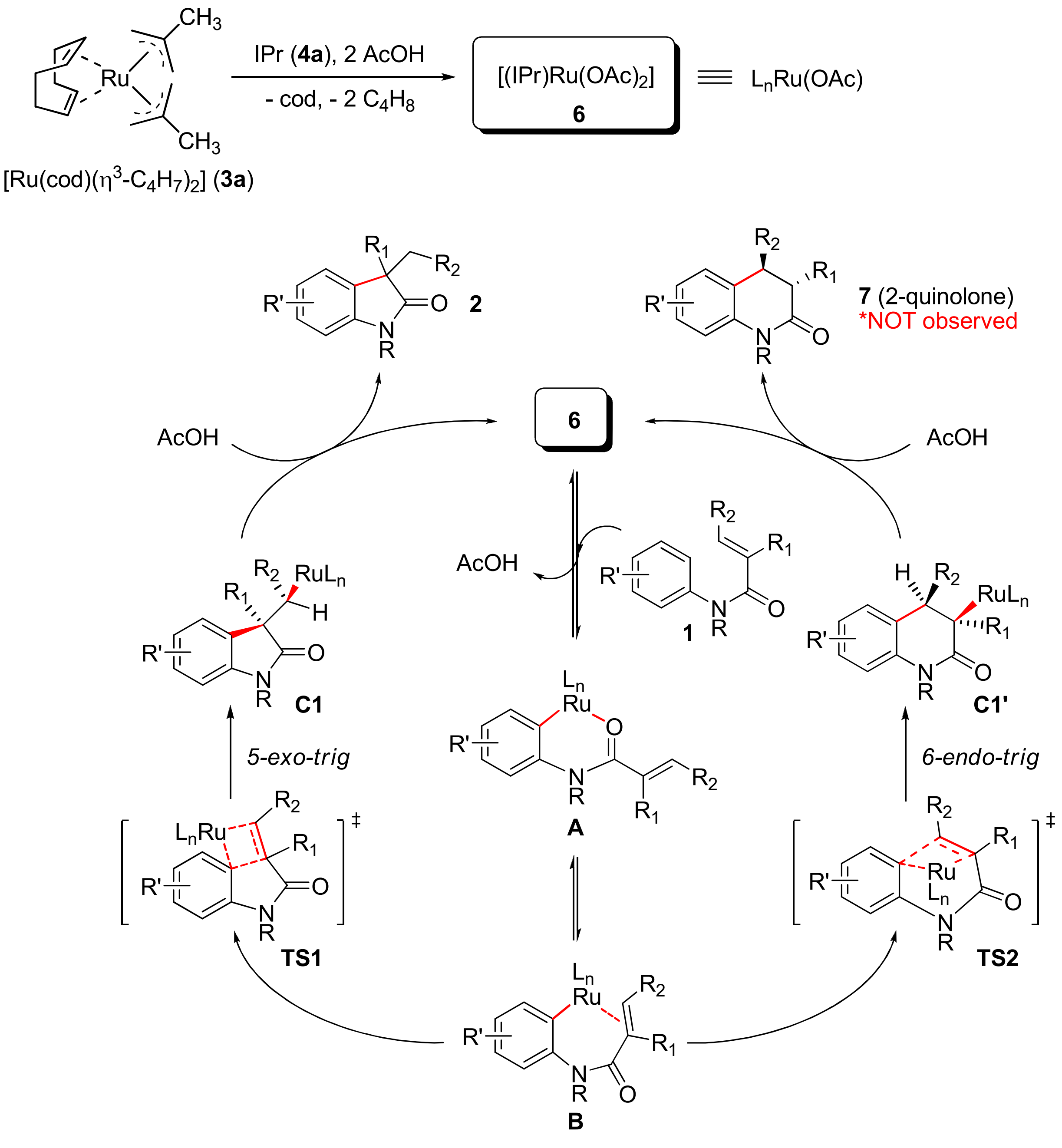
Table S3: Evaluation of Scale-Up Reaction Conditions



Amount	Solvent	Concentration	Catalyst loading	Yield[e]
30mg	1mL	0.17mM	10 mol%	81%
300mg	10mL	0.17mM	10mol%	66%
300mg	5mL	0.34mM	10mol%	85%
300mg	5mL	0.34mM	5mol%	82%
300mg	5mL	0.34mM	2.5mol%	59%
1g	8.1	0.70mM	2.5mol%	80%
1g	8.1	0.70mM	5mol%	92%

e = Isolated yield

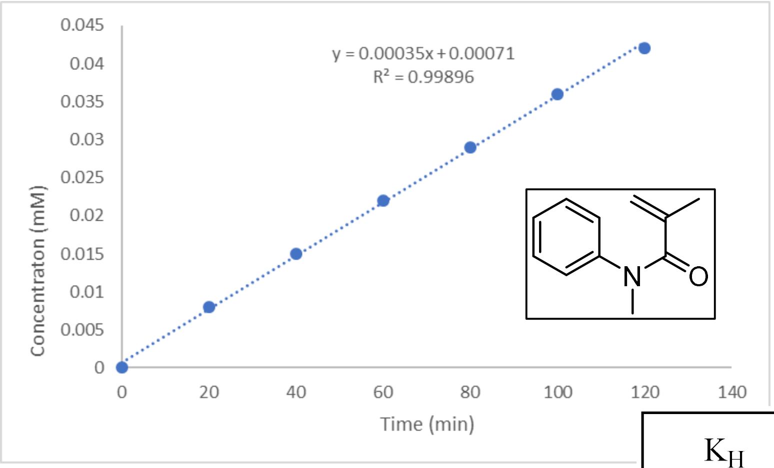
Scheme S1. Proposed Catalyst Activation Process and Catalytic Cycles



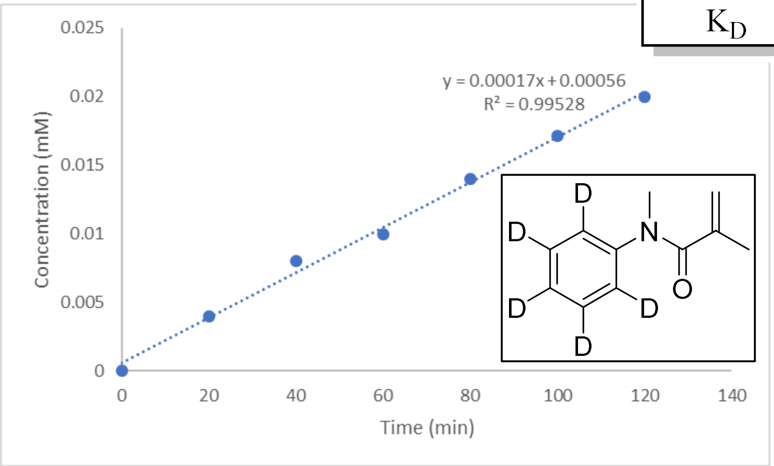
^{1}H NMR-Based Initial-Rate Kinetic Studies

General Procedure. Into a 4 mL scintillation vial equipped with a magnetic stir bar was placed [Ru(cod)(η^3-C_4H_7)$_2$] (0.017 mmol), IPr (0.017 mmol), acrylamide substrate (0.17 mmol), and triphenylmethane (internal standard, 41.5 mg). Deuterated toluene (C_7D_8, 99.94% D, 1.0 mL) and acetic acid (2 equiv) was subsequently added, and the mixture was stirred at room temperature for 5-10 minutes to get a homogeneous solution. The reaction mixture was transferred into a screw-cap NMR tube and analyzed by ^{1}H NMR to determine initial substrate concentration. The NMR tube was placed in a 120 ^{o}C oil bath and the reaction progress was monitored by ^{1}H NMR by taking the NMR tube out of the oil bath every 20 minutes, immediately transferring to a cold water bath to cool to room temperature, and analyzed by ^{1}H NMR to get relative integration values of substrate and product signals against the internal standard. The resulting product concentrations were plotted against time to determine the reaction rates at early conversions (<25% conversion).

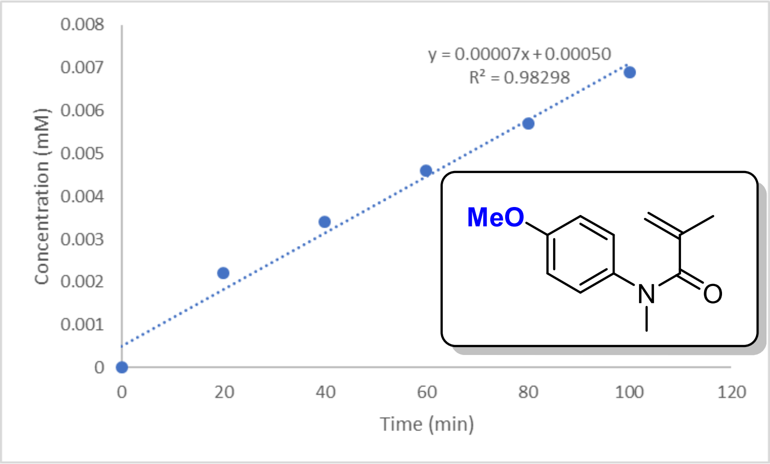
- **Kinetic isotope effect measurement**

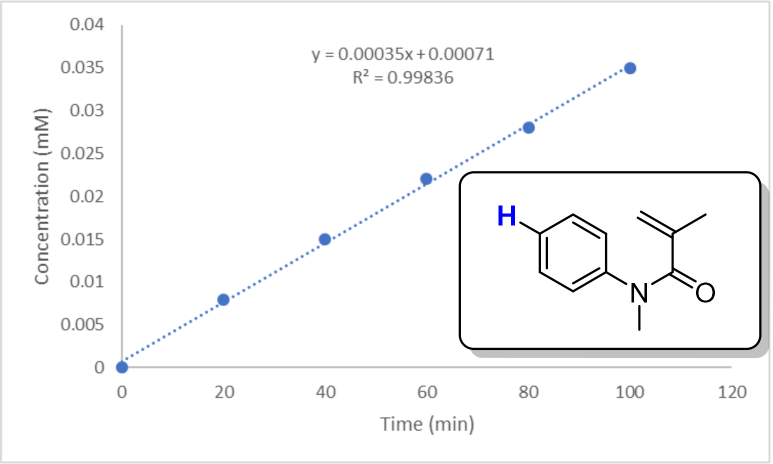


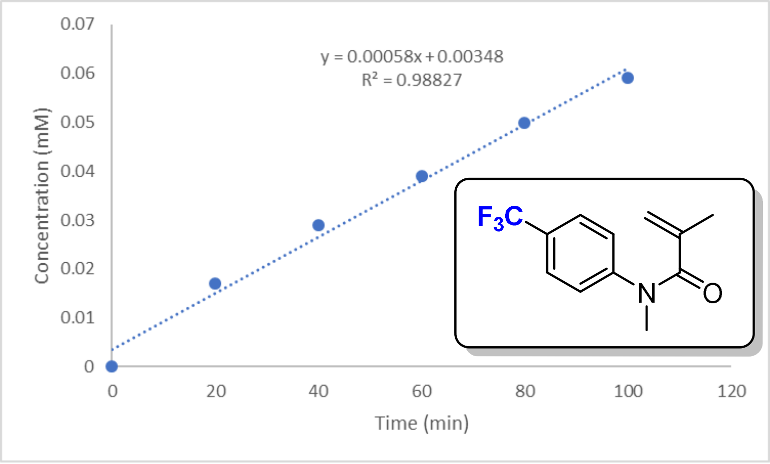
$$\frac{K_H}{K_D} = \frac{0.00035}{0.00017} = 2.1$$



- **Reactivity comparison by intermolecular competition**



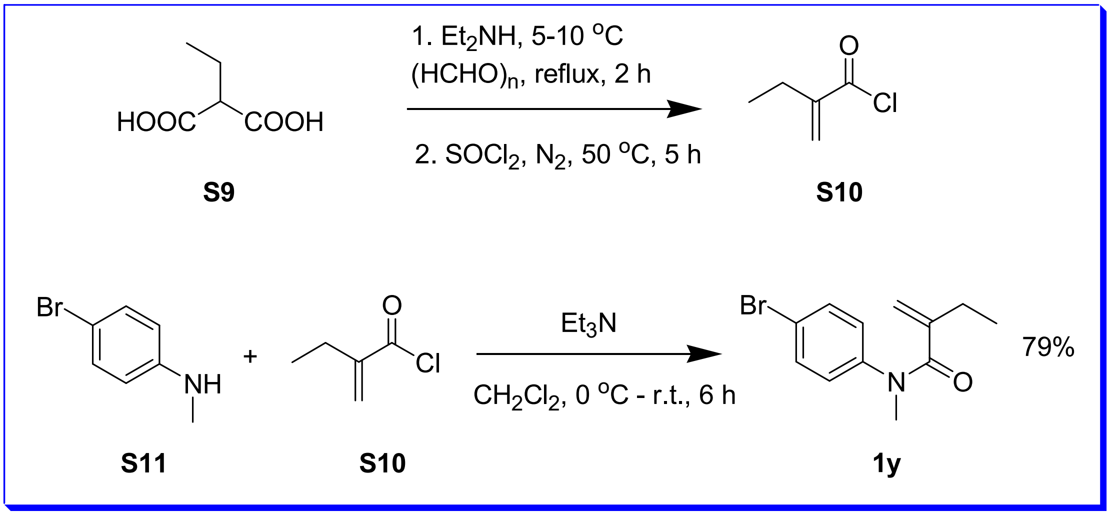




$$\boxed{K_{OMe} : K_H : K_{CF_3} = 1 : 5.0 : 8.3}$$

Synthesis of the Progesterone Receptor Antagonist 5

➢ Synthesis of N-Aryl Acrylamide Compound 1y



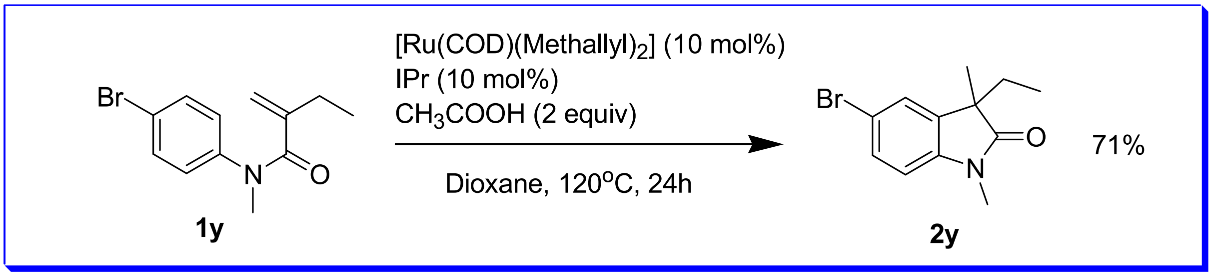
➢ Synthesis of acyl chloride intermediate S10

In a 250 mL round bottom flask equipped with a magnetic stir bar was placed ethylmalonic acid **S9** (2.0 g, 1 equiv) and dry ethyl acetate (50 mL). Diethylamine (1.5 equiv) was subsequently added at 5 °C under nitrogen atmosphere. After stirring the mixture at 5 °C for 5 min, paraformaldehyde (1.5 equiv) was slowly added over 5 min and then the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and quenched with water (150 mL). The PH value of the solution was brought to ~1 by adding concentrated HCl, and the resulting mixture was settled in a separation funnel and extracted with ethyl acetate (3 x 75 mL). The combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure to remove all volatiles. The crude compound **S10** was acquired as a pale-yellow liquid and used for the next step without further purification.

➢ Synthesis of 1y by N-acylation with S10

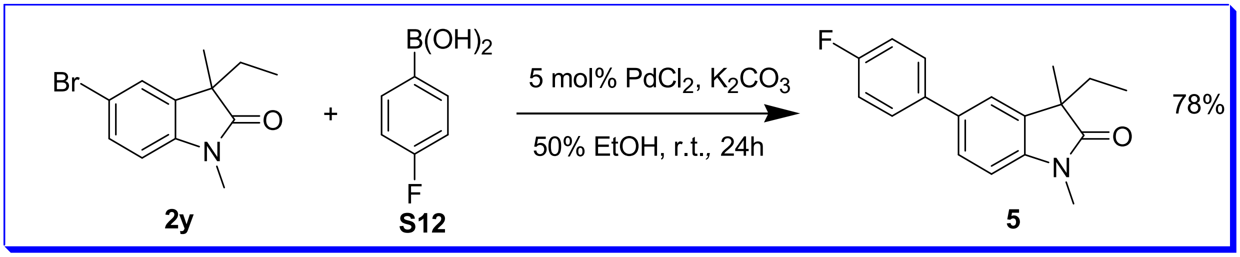
In a 250 mL round bottom flask equipped with a magnetic stir bar was placed 4–bromo-N-methylaniline **S11** (1.0 g, 1 equiv), dichloromethane (60 mL) and triethylamine (2 equiv). A solution of crude 2-ethylacryloyl chloride **S10** (~2 equiv) in dry dichloromethane (10 mL) was subsequently added dropwise at 0 °C under nitrogen atmosphere. The resulting solution was stirred at room temperature for 6 hours, followed by addition of water (150 mL) to quench the excess acryl chloride. The mixture was settled in a separation funnel and extracted with dichloromethane (3 x 50 mL). The combined organic layers was washed with brine (3 x 100 mL) and then dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the crude product was purified by column chromatography (0 to 5% ethyl acetate in hexanes) to give **1y** as white solid in 79% yield.

➢ Synthesis of Oxindole 2y by Intramolecular Hydroarylation with 1y



In a 20 mL scintillation vial equipped with a magnetic stir-bar was placed [Ru(COD)(methallyl)$_2$] (0.10 equiv), IPr (0.10 equiv) and **1y** (300 mg, 1.0 equiv, 1.12 mmol). Dioxane (5 mL) was added, followed by the addition of acetic acid (2 equiv). The reaction mixture was stirred at room temperature for five minutes and the vial was sealed with a silicone-lined screw-cap before transferring out of the glove box. The mixture was stirred in a 120^{o} C oil bath for 24 hours. After the reaction mixture was cooled to room temperature, all volatiles were removed under reduced pressure. Further purification was achieved by column chromatography (0 to 4% ethyl acetate in hexanes) to give **2y** as colorless oil in 71% yield.

➢ Synthesis of Compound 5 by Suzuki Coupling with 2y



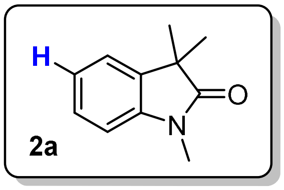
In a 10 mL round bottom flask equipped with a magnetic stir bar was placed **2y** (213 mg, 1.0 equiv), 50% ethanol (4 mL), and PdCl$_2$ (0.05 equiv). The mixture was stirred at room temperature for 5 min to give a homogeneous solution, and subsequently added with potassium carbonate (2.0 equiv) and 4-FC$_6$H$_5$B(OH)$_2$ **S12** (1.0 equiv). The mixture was stirred at room temperature under air for 24 hours, mixed with brine (50 mL), and settled in a separation funnel. After extraction with dichloromethane (3 x 50 mL), the combined organic layers were dried over sodium sulfate and evaporated under reduced pressure to remove all volatiles. Further purification by column chromatography (0 to 3% ethyl acetate in hexanes) gave **5** as colorless oil in 78% yield.

References:

1. Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J.; *Chem. Eur. J.* **2007**, *13*, 961.
2. Raghunathan, R.; Kumarasamy, E.; Akila, I.; Ugrinov, A.; Sivaguru, J. *Chem. Commun.,* **2013**, *49,* 8713.
3. Ayitou, A. J.; J. Sivaguru; *J. Am. Chem. Soc.*, **2009**, *131*, 5036.
4. Mu, X.; Wu, T.; Wang, H.; Guo, Y.; Liu, G.; *J. Am. Chem. Soc.*, **2012**, *134* , 878.
5. Kuang, Y-Y.; Chen, F-E.; *Org. Prep. Proc. Int.,* **2005,** *37,* 184**.**

Spectral Data for Reported Compounds

1, 3, 3-trimethylindolin-2-one (2a)



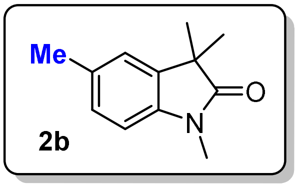
The compound **2a** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 81% yield as a light-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.24 – 7.16 (m, 2H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 3.18 (s, 3H), 1.34 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.23, 142.59, 135.74, 127.65, 122.45, 122.20, 108.01, 77.60, 77.28, 76.96, 44.09, 26.13, 24.36.

HRMS: m/z calcd for $C_{11}H_{13}NO$: 176.1075; found: 176.1076

1,3,3,5-tetramethylindolin-2-one (2b)



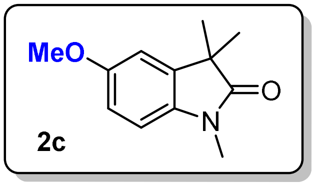
The compound **2b** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 61% yield as a light-yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.09 – 7.05 (m, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.36 (s, 3H), 1.38 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.78, 140.02, 135.88, 132.28, 127.92, 123.16, 107.94, 77.43, 77.12, 76.80, 44.40, 26.31, 24.31, 21.11.

HRMS: m/z calcd for $C_{12}H_{15}NO$: 190.1232; found: 190.1239

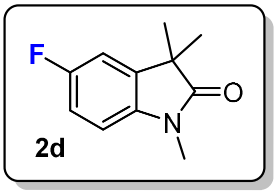
5-methoxy-1, 3, 3-trimethylindolin-2-one (2c)



The compound **2c** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 65% yield as a light-yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.82 – 6.81 (m, 1H), 6.78 – 6.72 (m, 2H), 3.79 (s, 3H), 3.18 (s, 3H), 1.35 (s, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 180.98, 156.07, 137.20, 136.13, 111.57, 110.04, 108.22, 77.45, 77.13, 76.82, 55.78, 44.58, 26.24, 24.39.
HRMS: m/z calcd for $C_{12}H_{16}NO_2$: 206.1181; found: 206.1181

5-fluoro-1, 3, 3-trimethylindolin-2-one (2d)

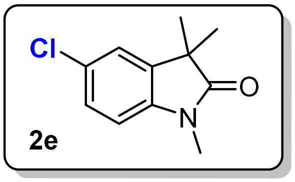


2d

The compound **2d** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 88% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.95 – 6.90 (m, 2H), 6.74 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.18 (s, 3H), 1.34 (s, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 180.87, 160.54, 158.15, 138.49, 137.48, 137.40, 113.80, 113.57, 110.59, 110.34, 108.44, 108.36, 77.44, 77.12, 76.80, 44.61, 44.60, 29.66, 26.27, 24.22.
^{19}F NMR (376 MHz, CDCl$_3$): δ -120.92.
HRMS: m/z calcd for $C_{11}H_{12}FNO$: 194.0981; found: 194.0989

5-chloro-1, 3, 3-trimethylindolin-2-one (2e)

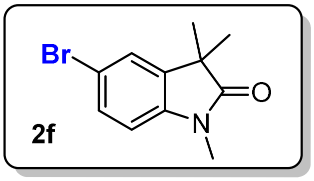


2e

The compound **2e** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 86% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.21 – 7.15 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.18 (s, 3H), 1.34 (s, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 180.70, 141.19, 137.44, 127.78, 127.53, 122.88, 108.94, 77.46, 77.15, 76.83, 44.39, 29.67, 26.28, 24.23.
HRMS: m/z calcd for $C_{11}H_{12}ClNO$: 210.0686; found: 210.0690

5-bromo-1, 3, 3-trimethylindolin-2-one (2f)



2f

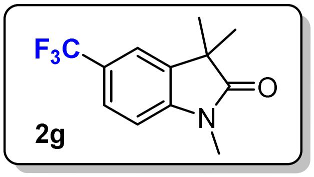
The compound **2f** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 79% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 3.17 (s, 3H), 1.34 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.58, 141.68, 137.82, 130.45, 125.63, 115.11, 109.49, 77.47, 77.16, 76.84, 44.37, 26.28, 24.26.

HRMS: m/z calcd for $C_{11}H_{12}BrNO$: 254.0181; found: 254.0180

1, 3, 3-trimethyl-5-(trifluoromethyl)indolin-2-one (2g)



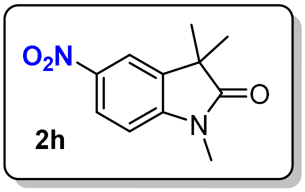
The compound **2g** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 89% yield as a light-yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (ddd, *J* = 8.2, 1.7, 0.8 Hz, 1H), 7.43 – 7.32 (m, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.24 (s, 3H), 1.38 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.14, 145.64, 136.28, 128.52, 125.83, 125.54, 125.50, 125.46, 125.42, 125.15, 124.82, 124.50, 124.18, 123.13, 120.43, 119.34, 119.30, 119.27, 119.23, 107.74, 77.40, 77.08, 76.76, 44.12, 29.65, 26.30, 24.14.

HRMS: m/z calcd for $C_{12}H_{12}F_3NO$: 244.0949; found: 244.0953

1,3,3-trimethyl-5-nitroindolin-2-one (2h)



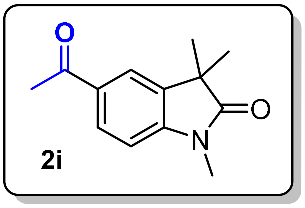
The compound **2h** was prepared according to the general method described above and purified by flash column chromatography (0 to 6% ethyl acetate in hexanes) in 91% yield as a yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.07 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 3.27 (s, 3H), 1.40 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.22, 148.40, 143.40, 136.42, 125.14, 118.23, 107.65, 77.46, 77.14, 76.83, 44.17, 26.62, 24.09.

HRMS: m/z calcd for $C_{11}H_{12}N_2O_3$: 221.0926; found: 221.0929

5-acetyl-1, 3, 3-trimethylindolin-2-one (2i)



2i

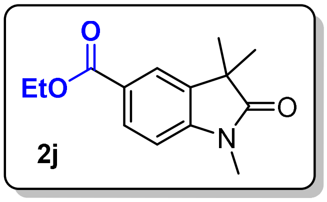
The compound **2i** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 83% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.83 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.75 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.15 (s, 3H), 2.47 (s, 3H), 1.28 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 196.72, 181.40, 146.95, 135.83, 132.01, 129.80, 122.05, 107.44, 77.59, 77.27, 76.95, 43.86, 26.33, 26.30, 24.15.

HRMS: m/z calcd for $C_{13}H_{15}NO_2$: 218.1181; found: 218.1190.

Ethyl 1, 3, 3-trimethyl-2-oxoindoline-5-carboxylate (2j)



2j

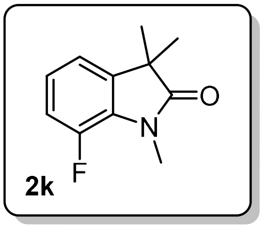
The compound **2j** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 84% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.82 (d, *J* = 1.4 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.18 (s, 3H), 1.37 – 1.29 (m, 9H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.43, 166.35, 146.67, 135.55, 130.37, 124.68, 123.43, 107.48, 77.51, 77.19, 76.87, 60.76, 43.92, 26.31, 24.18, 14.36.

HRMS: m/z calcd for $C_{14}H_{17}NO_3$: 248.1287; found: 248.1292

7-fluoro-1,3,3-trimethylindolin-2-one (2k)



2k

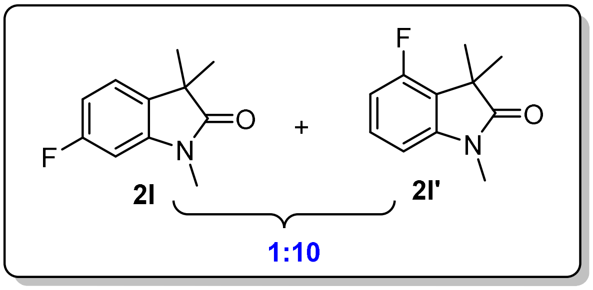
The compound **2k** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 73% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.97 – 6.90 (m, 3H), 3.39 (d, *J* = 2.7 Hz, 3H), 1.34 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.77, 148.88, 146.46, 138.73, 138.70, 129.15, 129.08, 122.98, 122.92, 118.06,

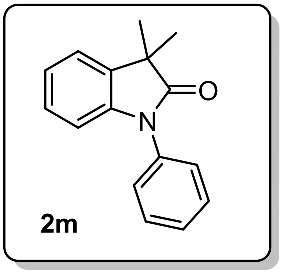
118.03, 115.63, 115.44, 77.47, 77.15, 76.83, 44.44, 44.42, 28.56, 28.50, 24.48.
^{19}F NMR (376 MHz, CDCl$_3$): δ -136.96.
HRMS: m/z calcd for $C_{11}H_{12}FNO$: 194.0981; found: 194.0978

6-fluoro-1,3,3-trimethylindolin-2-one + 4-fluoro-1,3,3-trimethylindolin-2-one (2l and 2l’)



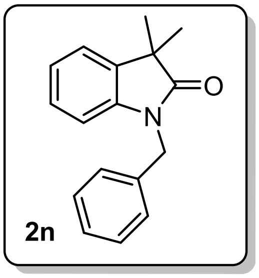
The product mixture of **2l/2l’** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 84% yield as a white solid. The product ratio was determined by ^{1}H NMR.
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.21 – 7.16 (m, 0.09H) **(2l’)** 7.08 (dd, *J* = 8.1, 5.3 Hz, 0.91H) (**2l**), 6.70 – 6.61 (m, 1.09H), **(2l + 2l’)** 6.55 (dd, *J* = 8.9, 2.3 Hz, 0.90H) **(2l),** 3.16 (d, *J* = 6.1 Hz, 3H) **(2l+2l’),** 1.42 (s, 0.53H) (**2l**), 1.31 (s, 5.49H) **(2l).**
^{13}C NMR (100 MHz, CDCl$_3$): δ 181.46, 180.54, 163.92, 161.49, 144.11, 143.99, 131.01, 130.98, 129.28, 129.19, 123.10, 123.00, 110.14, 109.93, 108.33, 108.10, 104.14, 104.11, 96.94, 96.66, 77.48, 77.16, 76.84, 44.06, 43.73, 29.65, 26.52, 26.22, 24.37, 22.74.
^{19}F NMR (376 MHz, CDCl$_3$): δ -113.22, -121.95.
HRMS: m/z calcd for $C_{11}H_{12}FNO$: 194.0981; found: 194.0986

3,3-dimethyl-1-phenylindolin-2-one (2m)



The compound **2m** was prepared according to the general method described above and purified by flash column chromatography (0 to 2% ethyl acetate in hexanes) in 90% yield as a white solid.
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 – 7.09 (m, 8H), 6.91 (d, *J* = 7.8 Hz, 1H), 1.56 (s, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 180.67, 142.52, 135.65, 134.76, 129.59, 127.90, 127.66, 126.57, 123.05, 122.70, 109.42, 77.66, 77.34, 77.02, 44.33, 24.86.
HRMS: m/z calcd for $C_{16}H_{13}NONa$: 260.1051; found: 260.1058

1-benzyl-3,3-dimethylindolin-2-one (2n)



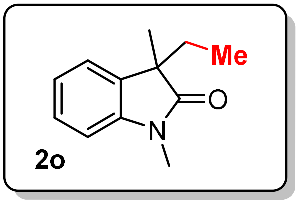
The compound **2n** was prepared according to the general method described above and purified by flash column chromatography (0 to 2% ethyl acetate in hexanes) in 84% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 – 7.23 (m, 6H), 7.17 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 4.97 (s, 2H), 1.50 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.43, 141.72, 136.20, 135.82, 128.82, 127.65, 127.58, 127.22, 122.58, 122.39, 109.14, 77.60, 77.28, 76.96, 44.21, 43.56, 24.63.

HRMS: m/z calcd for $C_{17}H_{17}NONa$: 274.1208; found: 274.1221.

3-ethyl-1,3-dimethylindolin-2-one (2o)



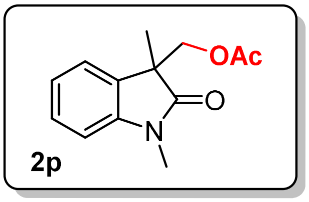
The compound **2o** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 59% yield as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.22 (s, 3H), 1.93 (dd, *J* = 13.6, 7.1 Hz, 1H), 1.77 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.35 (s, 3H), 0.59 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.68, 143.47, 133.91, 127.61, 122.49, 122.39, 107.82, 77.47, 77.15, 76.83, 48.91, 31.47, 26.06, 23.32, 8.85.

HRMS: m/z calcd for $C_{12}H_{15}NO$: 190.1232; found: 190.1234

(1,3-dimethyl-2-oxoindolin-3-yl) methyl acetate (2p)



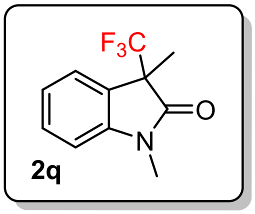
The compound **2p** was prepared according to the general method described above and purified by flash column chromatography (0 to 6% ethyl acetate in hexanes) in 74% yield as a light yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 – 7.20 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.46 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 10.8 Hz, 1H), 3.21 (s, 3H), 1.83 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 178.12, 170.31, 143.39, 131.28, 128.37, 123.06, 122.59, 108.10, 77.51, 77.19, 76.87, 67.47, 47.95, 26.29, 20.53, 19.67.

HRMS: m/z calcd for $C_{13}H_{13}NO_3Na$: 256.0950; found: 256.0962

1,3-dimethyl-3-(trifluoromethyl) indolin-2-one (2q)



The compound **2q** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 61% yield as a light yellow oil.

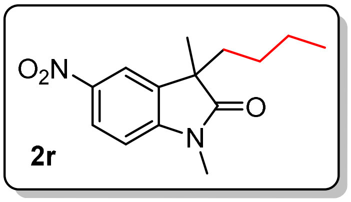
^{1}H NMR (400 MHz, CDCl3): δ 7.37 – 7.36 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 3.22 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 172.19, 143.65, 129.90, 129.20, 126.39, 126.11, 124.45, 123.60, 123.13, 108.64, 77.48, 77.16, 76.85, 52.47, 52.20, 51.93, 51.65, 29.68, 26.44, 17.67, 17.65.

^{19}F NMR (376 MHz, CDCl$_3$): δ -73.65.

HRMS: m/z calcd for C11H10F$_3$NO: 230.0793; found: 230.0803

3-butyl-1,3-dimethyl-5-nitroindolin-2-one (2r)



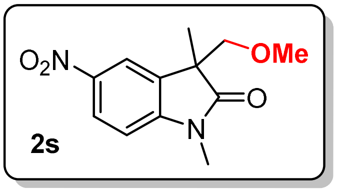
The compound **2r** was prepared according to the general method described above and purified by flash column chromatography (0 to 6% ethyl acetate in hexanes) in 82% yield as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.26 (s, 3H), 1.90 (td, *J* = 12.9, 12.4, 4.7 Hz, 1H), 1.76 (td, *J* = 13.4, 12.9, 4.5 Hz, 1H), 1.36 (s, 3H), 1.15 (ddd, *J* = 14.8, 7.6, 3.0 Hz, 2H), 0.89 (ddd, *J* = 10.7, 7.5, 5.4 Hz, 1H), 0.81 – 0.69 (m, 4H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.76, 149.05, 143.38, 135.04, 125.10, 118.29, 107.49, 77.48, 77.16, 76.85, 48.46, 38.08, 26.48, 26.46, 23.48, 22.63, 13.70.

HRMS: m/z calcd for $C_{14}H_{18}N_2O_3$: 263.1396; found: 263.1408

3-(methoxymethyl)-1, 3-dimethyl-5-nitroindolin-2-one (2s)



2s

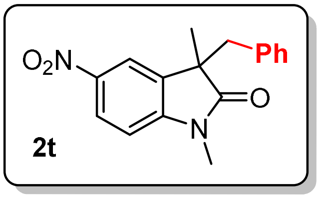
The compound **2s** was prepared according to the general method described above and purified by flash column chromatography (0 to 8% ethyl acetate in hexanes) in 78% yield as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.21 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.11 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.72 – 3.57 (m, 2H), 3.25 (s, 3H), 3.18(s, 3H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): 179.11, 149.38, 143.36, 133.56, 125.40, 118.71, 107.59, 77.52, 77.20, 76.88, 76.57, 59.38, 49.39, 26.64, 19.34.

HRMS: m/z calcd for $C_{12}H_{14}N_2O_4$: 251.1032; found: 251.1036

3-benzyl-1, 3-dimethyl-5-nitroindolin-2-one (2t)



2t

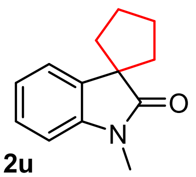
The compound **2t** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 69% yield as a yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.14 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.81 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 1H), 3.20 (d, *J* = 13.1 Hz, 1H), 3.05 (d, *J* = 15.7 Hz, 4H), 1.54 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 179.96, 148.85, 143.09, 135.19, 133.86, 129.55, 127.80, 126.91, 125.21, 119.07, 107.31, 77.49, 77.17, 76.86, 50.12, 44.51, 26.25, 22.48.

HRMS: m/z calcd for $C_{17}H_{16}N_2O_3$: 297.1239; found: 297.1238.

1-methylspiro(cyclopentane-1')-indolin-2-one (2u)



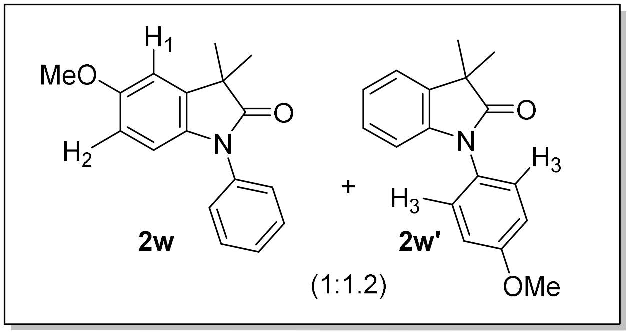
2u

The compound **2u** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 38% yield as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 – 7.23 (m, 2H), 7.08 – 7.04 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.23 (s, 3H), 2.20 – 1.86 (m, 6H), 1.85 (ddd, *J* = 12.1, 7.0, 4.2 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 181.91, 142.91, 136.87, 127.34, 122.51, 122.22, 107.69, 77.40, 77.09, 76.77, 53.92, 38.34, 26.65, 26.25.
HRMS: m/z calcd for $C_{11}H_{13}NO$: 202.1232; found: 202.1242

5-methoxy-3,3-dimethyl-1-phenylindolin-2-one + 1-(4-methoxyphenyl)-3,3-dimethylindolin-2-one (2w and 2w')

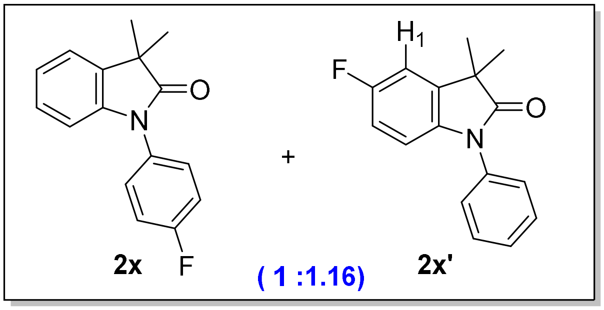


The product mixture of **2w/2w'** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 79% yield as a white solid. The product ratio was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.54 – 7.46 (m, 3.42H), 7.40 – 7.28 (m, 4.48H), 7.21 – 7.17 (m, 1.18H), 7.04 – 7.12 (m, 3.51H), 6.94 (d, *J* = 2.4 Hz, 0.82H) **(H$_1$),** 6.82 (d, *J* = 8.3 Hz, 2H) **(H$_3$),** 6.74 (dd, *J* = 8.6, 2.5 Hz, 0.82H) **(H$_2$),** 3.84 (s, 3.44H), 3.81 (s, 2.42H), 1.52 (s, 12.28H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.86, 180.31, 159.06, 156.40, 142.99, 137.03, 135.89, 135.57, 135.00, 129.50, 127.94, 127.64, 127.33, 126.29, 122.86, 122.59, 114.87, 111.85, 109.98, 109.83, 109.27, 77.69, 77.37, 77.05, 55.79, 55.50, 44.70, 44.22, 24.87, 24.79.

1-(4-fluorophenyl)-3,3-dimethylindolin-2-one + 5-fluoro-3,3-dimethyl-1-phenylindolin-2-one (2x and 2x')

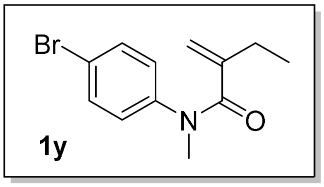


The product mixture of **2x/2x'** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 87% combined yield as a white solid. The product ratio was determined by ^{1}H NMR.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 – 7.41 (m, 6.52H), 7.31 (d, *J* = 7.2 Hz, 1H) **(H$_1$)**, 7.24 – 7.19 (m, 2.73H), 7.13 (t, *J* = 7.4 Hz,0.931H), 7.05 (dd, *J* = 7.8, 2.3 Hz, 0.94H), 6.90 – 6.79 (m, 2.75H), 1.56 – 1.47 (d, 10.68H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.73, 180.22, 162.96, 160.75, 160.50, 158.36, 142.38, 138.38, 137.36, 137.29, 135.54, 134.63, 130.67, 130.64, 129.63, 128.50, 128.42, 127.97, 127.69, 126.42, 123.15, 122.74, 116.64, 116.41, 113.93, 113.70, 110.78, 110.54, 110.04, 109.96, 109.18, 77.60, 77.28, 76.96, 44.73, 44.72, 44.27, 24.77, 24.67.

N-(4-bromophenyl)-N-methyl-2-methylenebutanamide (1y)

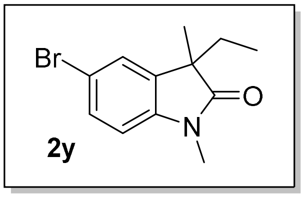


1y

The compound **1y** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 79% yield as a white solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, J = 8 Hz 2H), 7.01 (d, J = 8 Hz, 2H), 5.01 (d, J = 30.9 Hz, 2H), 3.31 (s, 3H), 2.12 (q, J = 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 171.66, 146.16, 143.60, 132.30, 128.23, 120.30, 117.36, 77.46, 77.14, 76.82, 37.67, 26.51, 11.75.

5-bromo-3-ethyl-1,3-dimethylindolin-2-one (2y)

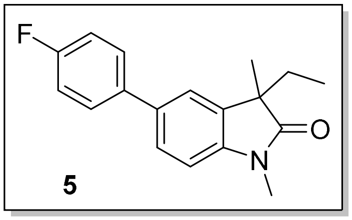


2y

The compound **2y** was prepared according to the general method described above and purified by flash column chromatography (0 to 4% ethyl acetate in hexanes) in 71% yield as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (dd, J = 8.2, 1.9 Hz, 1H), 7.25 (d, J = 1.9 Hz, 1H), 6.70 (d, J = 8.2 Hz, 1H), 3.17 (s, 3H), 1.90 (dq, J = 14.8, 7.4 Hz, 1H), 1.72 (dq, J = 14.8, 7.4 Hz, 1H), 1.31 (s, 3H), 0.56 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 179.94, 142.53, 136.04, 130.44, 125.78, 115.11, 109.28, 77.47, 77.15, 76.83, 49.18, 31.39, 26.14, 23.23, 8.82.

3-ethyl-5-(4-fluorophenyl)-1,3-dimethylindolin-2-one (5)



5

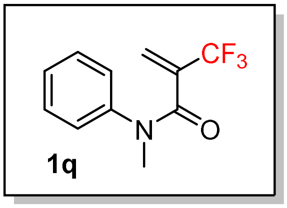
The compound **5** was prepared according to the general method described above and purified by flash column chromatography (0 to 3% ethyl acetate in hexanes) in 78% yield as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 – 7.34 (m, 4H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 2.06 – $_3$1.70 (m, 2H), 1.38 (s, 3H), 0.62 (t, *J* = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 180.54, 163.39, 160.95, 142.94, 137.28, 137.25, 134.81, 134.60, 128.39, 128.31, 126.41, 121.23, 115.70, 115.48, 108.10, 49.05, 31.51, 26.08, 23.34, 8.92.

^{19}F NMR (376 MHz, CDCl$_3$): δ -116.01.

N-methyl-N-phenyl-2-(trifluoromethyl) Acrylamide (1q)



1q

The compound **1q** was prepared according to the general method described above and purified by flash column chromatography (0 to 5% ethyl acetate in hexanes) in 62% yield as a white solid.

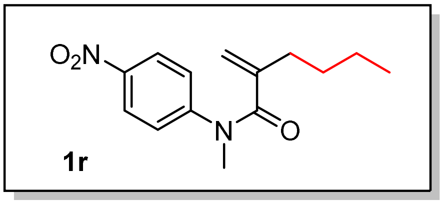
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.83 (s, 1H), 5.38 (s, 1H), 3.39 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 163.79, 143.53, 134.73, 134.42, 134.10, 129.64, 127.76, 126.82, 125.57, 122.85, 120.13, 117.41, 77.43, 77.11, 76.79, 37.76.

^{19}F NMR: (376 MHz, CDCl$_3$) δ -64.70.

HRMS: m/z calcd for $C_{11}H_{10}F_3NONa$: 252.0612; found: 252.0618

N-methyl-N-phenyl-2-(*n*-butyl) Acrylamide (1r)



1r

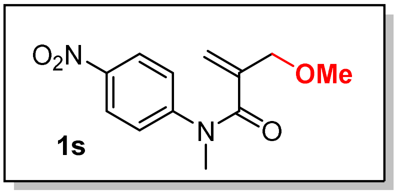
The compound **1r** was prepared according to the general method described above and purified by flash column chromatography (0 to 8% ethyl acetate in hexanes) in 65% yield as a yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 – 8.15 (m, 2H), 7.36 – 7.29 (m, 2H), 5.20 – 5.11 (m, 1H), 5.08 – 5.00 (m, 1H), 3.40 (s, 3H), 2.19 – 2.08 (m, 2H), 1.44 – 1.35 (m, 2H), 1.28 (dq, *J* = 14.3, 7.1 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 171.61, 150.24, 145.39, 144.68, 126.32, 124.56, 119.16, 77.47, 77.15, 76.83, 37.57, 33.24, 29.68, 22.27, 13.80

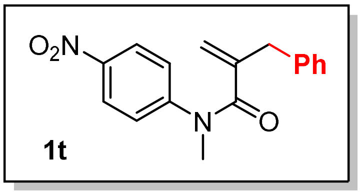
HRMS: m/z calcd for $C_{14}H_{18}N_2O_3Na$: 285.1215; found: 285.1227

N-methyl-N-phenyl-2-(methoxy methyl) Acrylamide (1s)



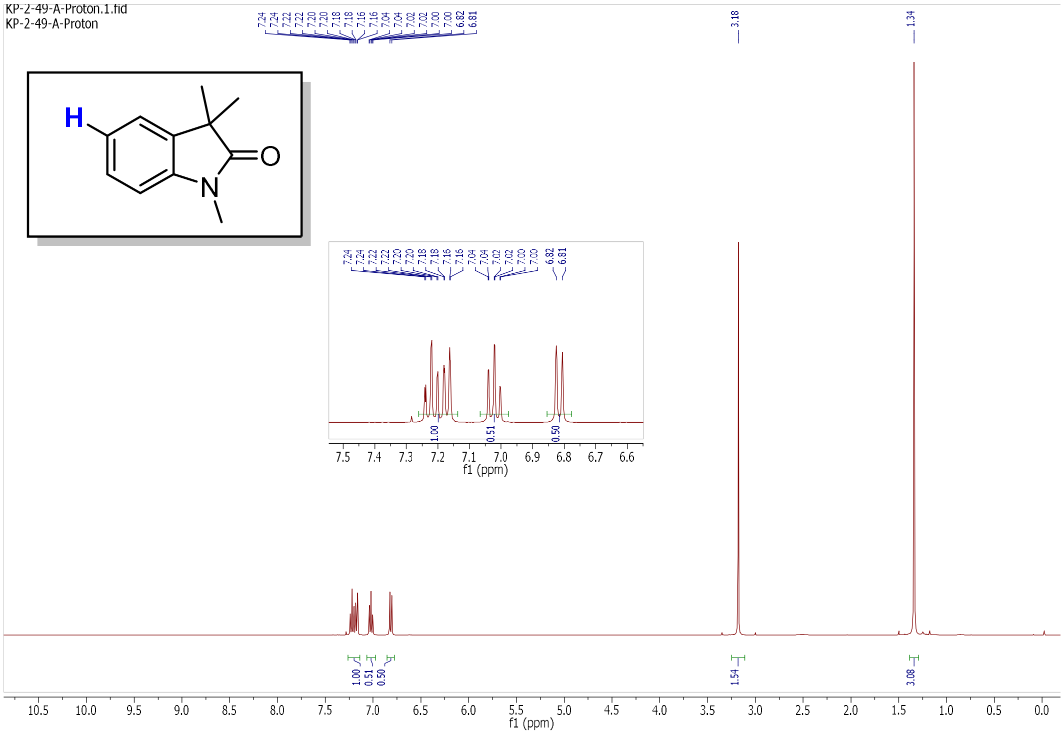
The compound **1s** was prepared according to the general method described above and purified by flash column chromatography (0 to 10% ethyl acetate in hexanes) in 71% yield as a yellow solid.
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.23 – 8.11 (m, 2H), 7.47 – 7.36 (m, 2H), 5.31 (s, 1H), 4.98 (s, 1H), 4.10 – 4.00 (m, 2H), 3.46 – 3.29 (m, 6H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 169.62, 150.24, 145.44, 141.08, 126.72, 124.50, 120.82, 77.48, 77.16, 76.84, 73.23, 58.84, 37.38.
HRMS: m/z calcd for $C_{12}H_{14}N_2O_4Na$: 273.0851; found: 273.0863

N-methyl-N-phenyl-2-(benzyl) Acrylamide (1t)

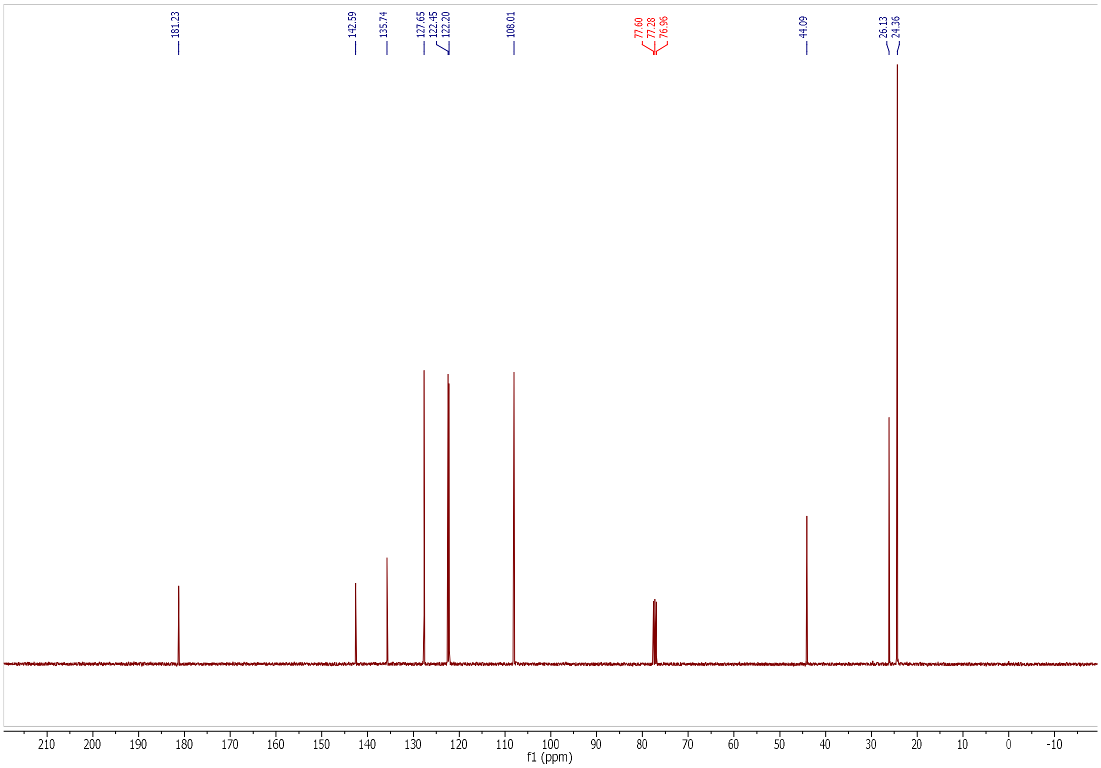


The compound **1t** was prepared according to the general method described above and purified by flash column chromatography (0 to 8% ethyl acetate in hexanes) in 63% yield as a yellow solid.
^{1}H NMR (400 MHz, CDCl$_3$): 8.11 – 8.01 (m, 2H), 7.39 – 7.24 (m, 3H), 7.22 – 7.12 (m, 2H), 6.92 – 6.82 (m, 2H), 5.20 – 5.14 (m, 1H), 4.98 – 4.90 (m, 1H), 3.60 (s, 2H), 3.32 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$): δ 170.65, 150.16, 145.52, 143.63, 137.42, 129.33, 128.74, 126.92, 126.52, 124.49, 120.29, 77.46, 77.14, 76.83, 40.52, 37.62.
HRMS: m/z calcd for $C_{17}H_{16}N_2O_3Na$: 319.1059; found: 319.1066.

^{1}H NMR



^{13}C NMR



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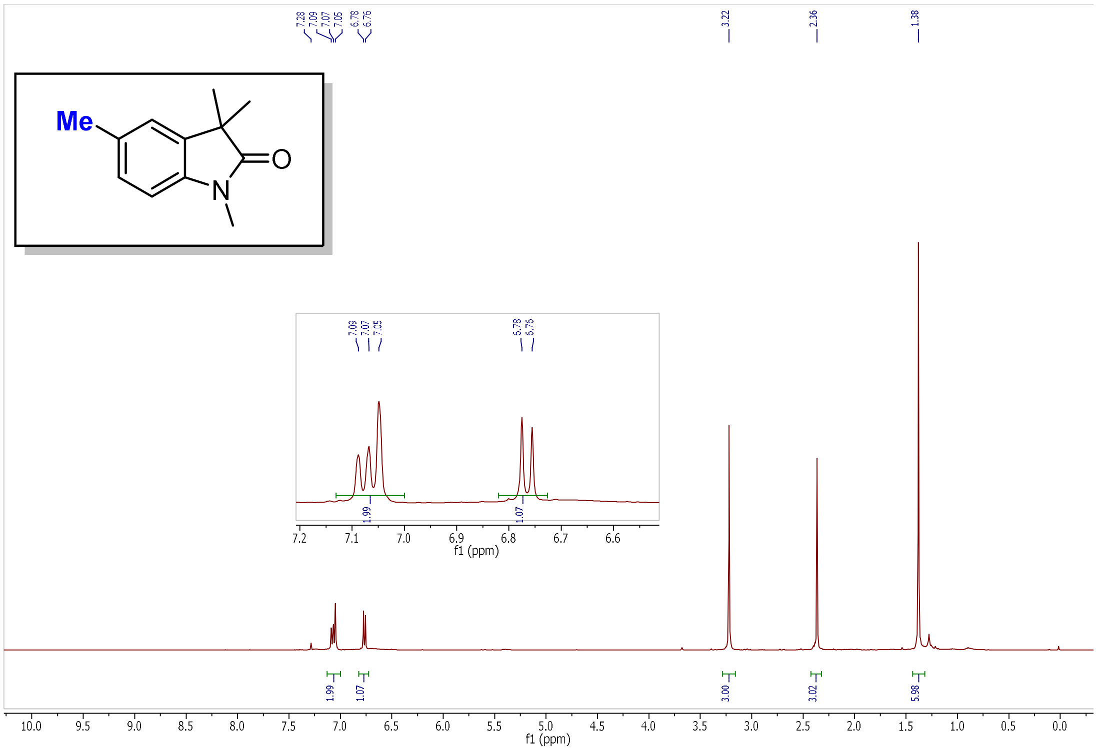

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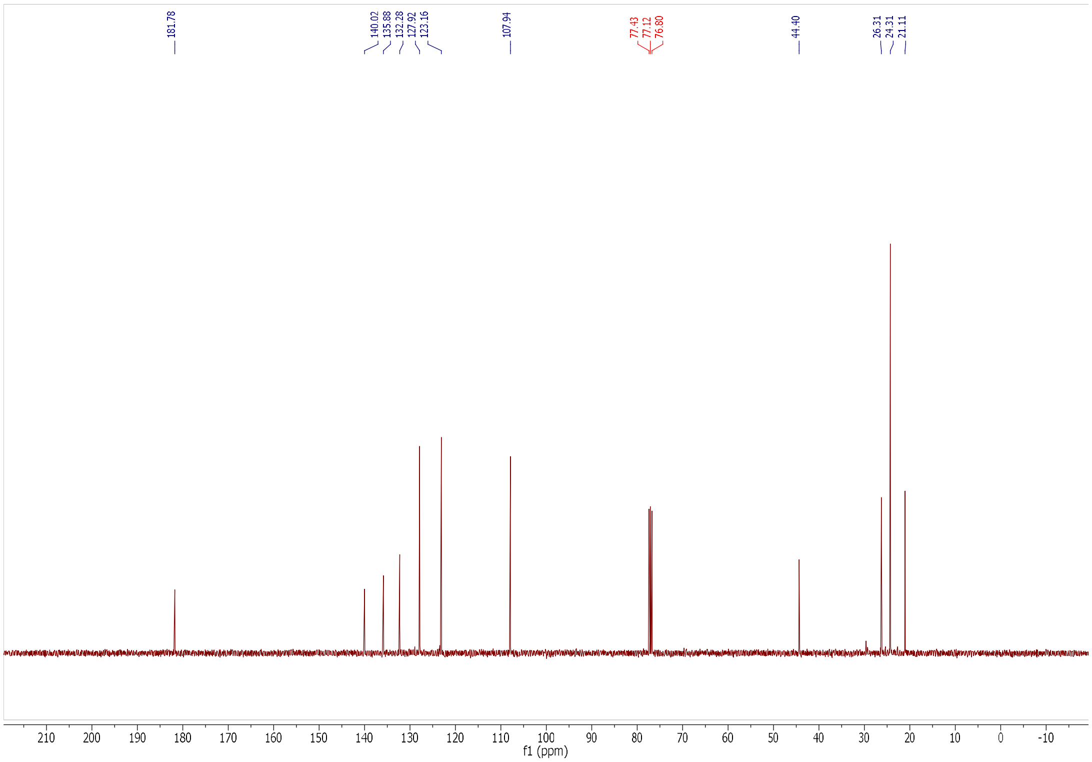

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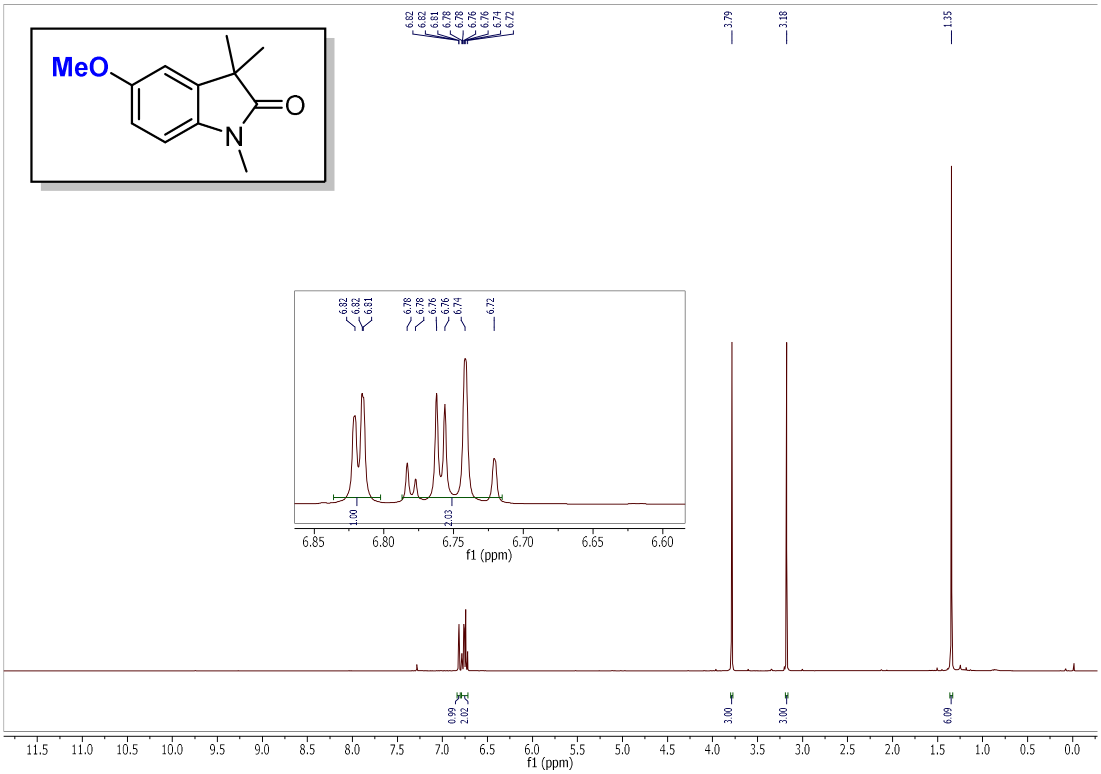

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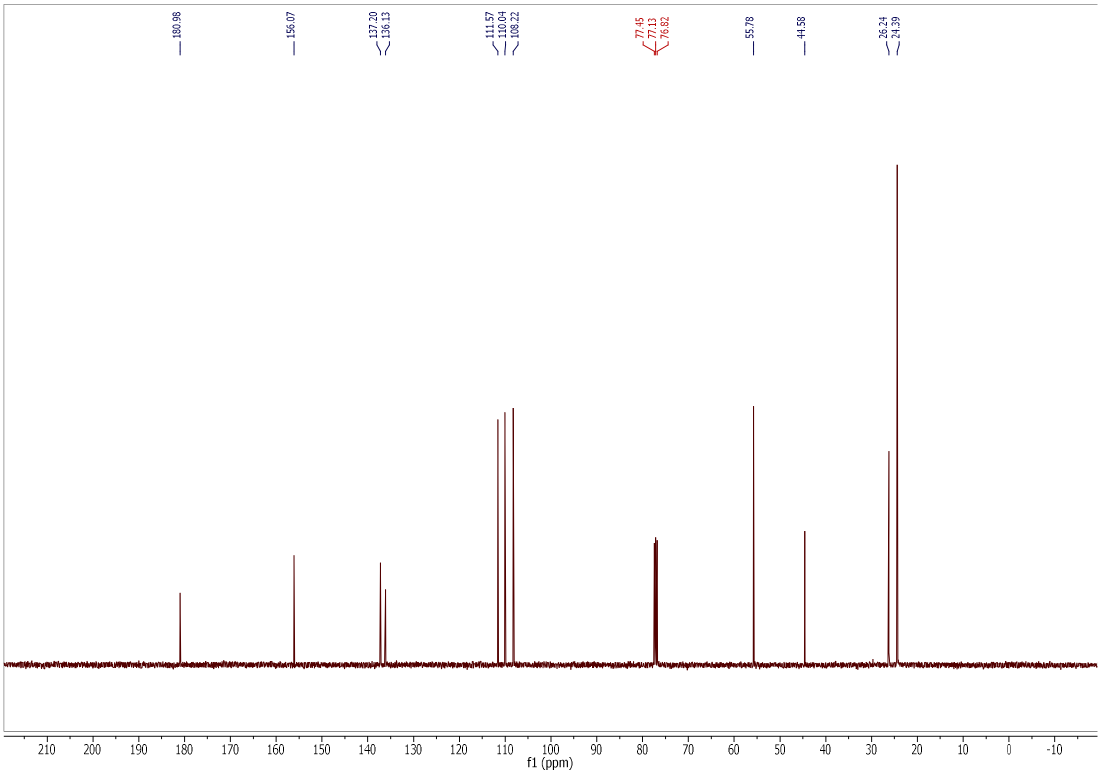

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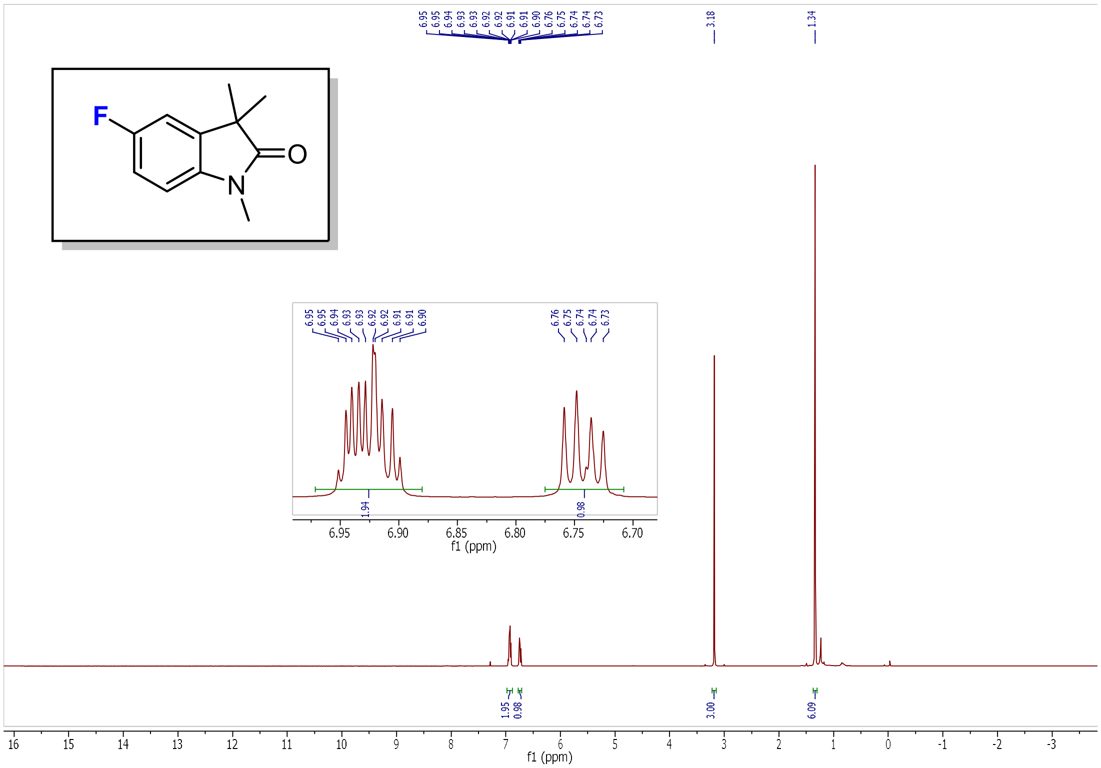

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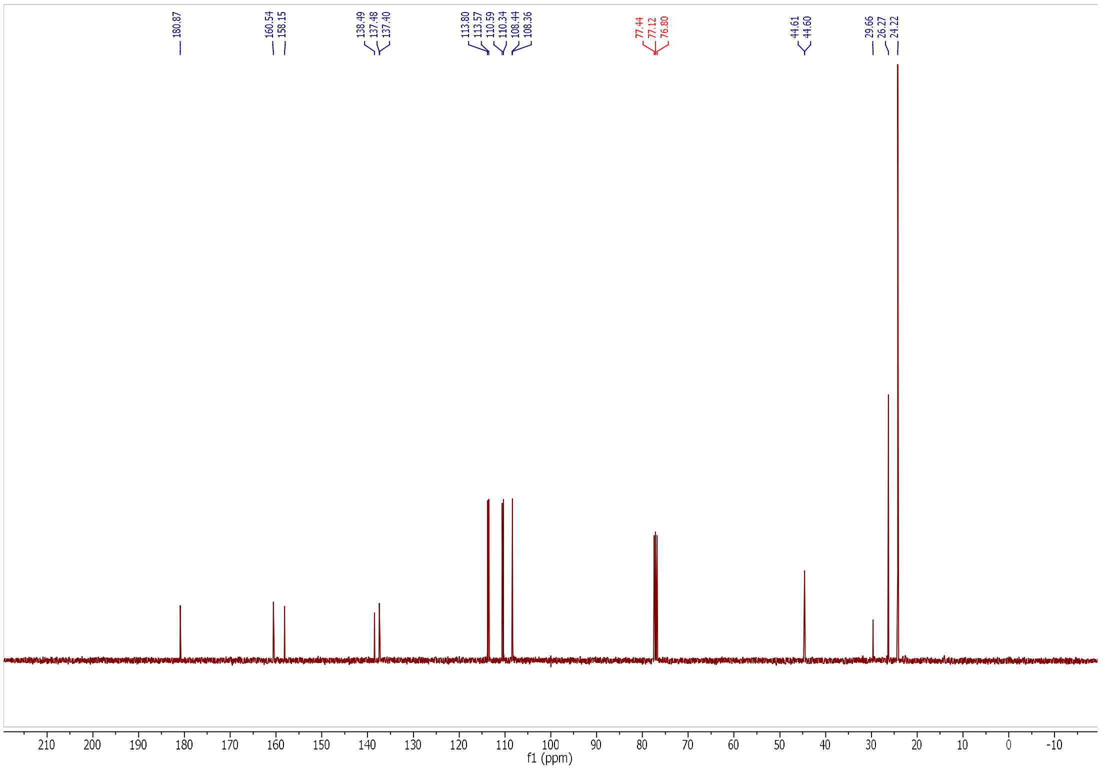

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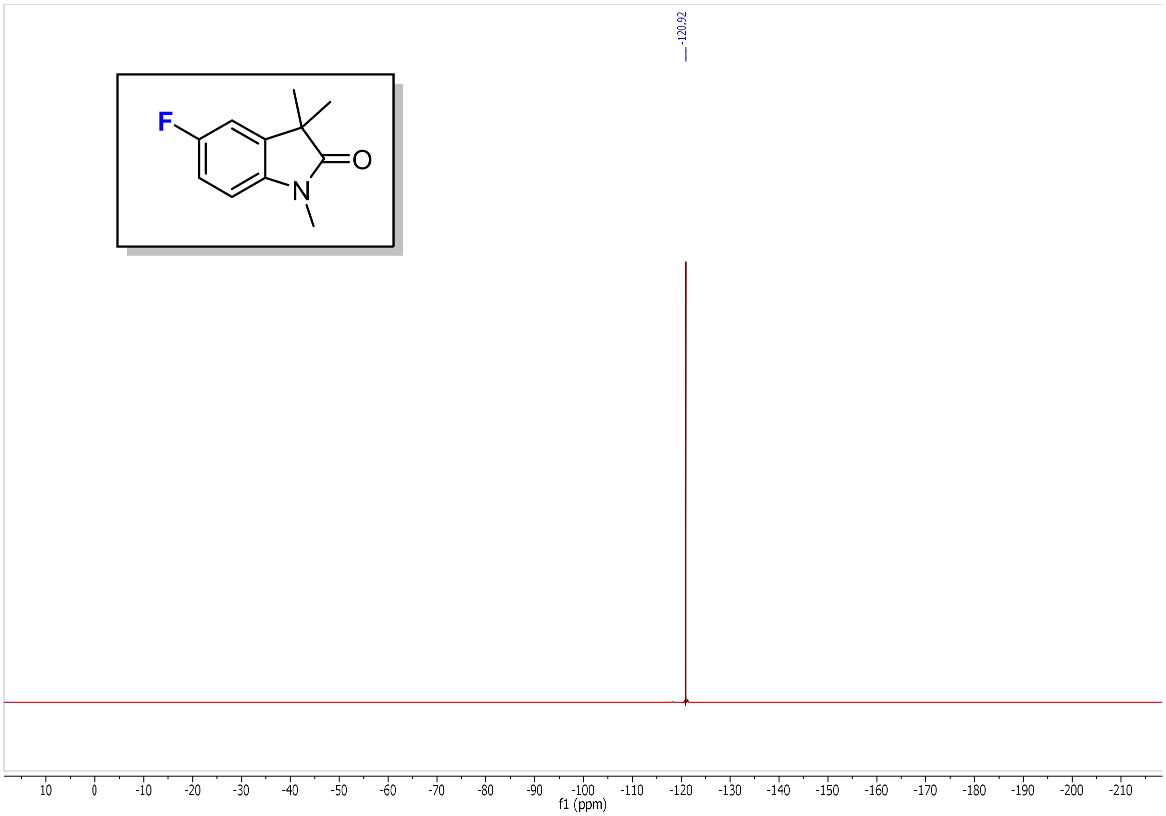
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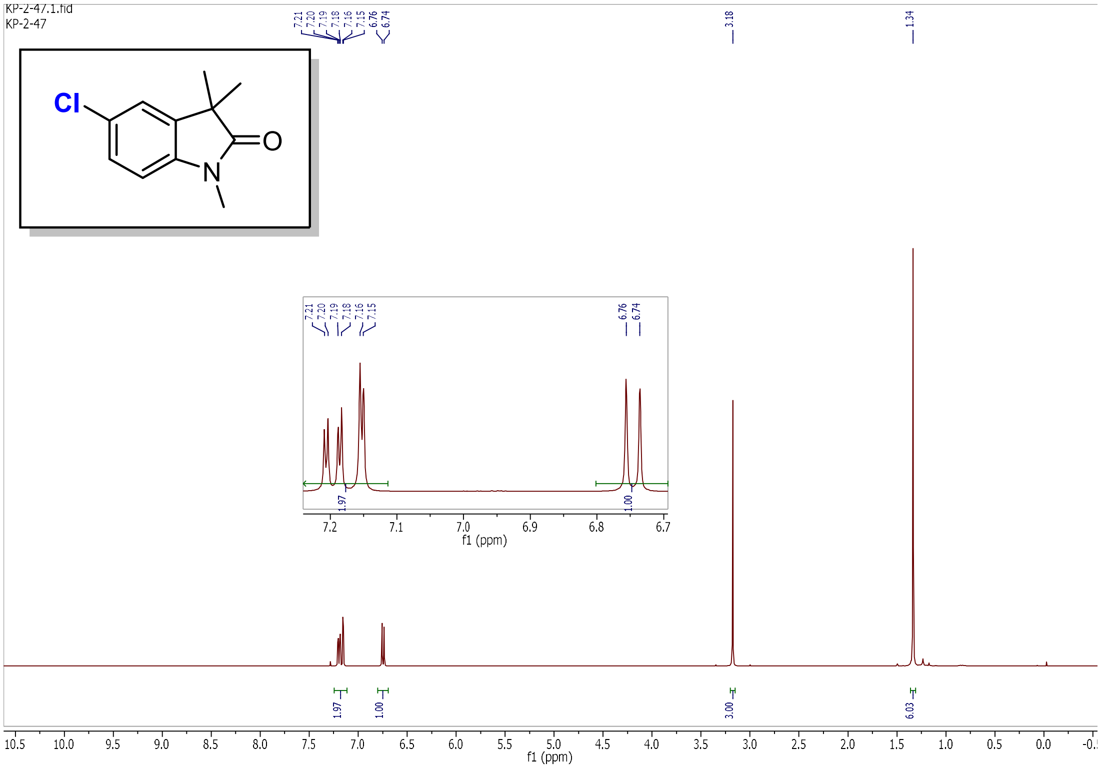
f1 (ppm)

^{1}H NMR



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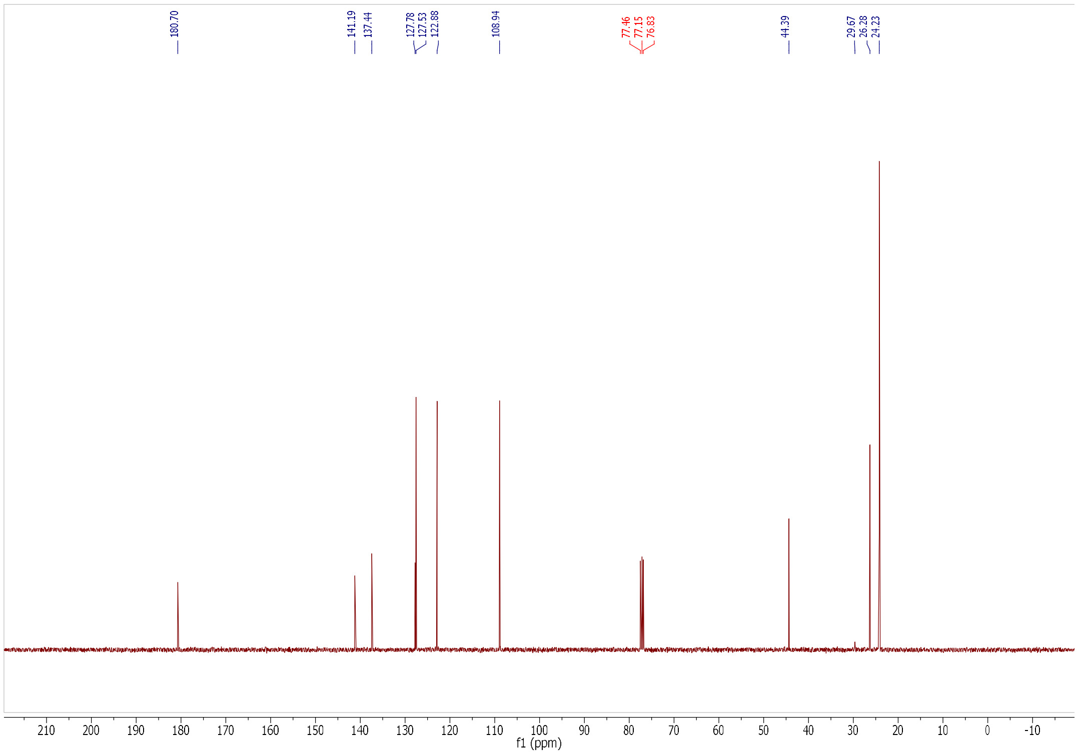

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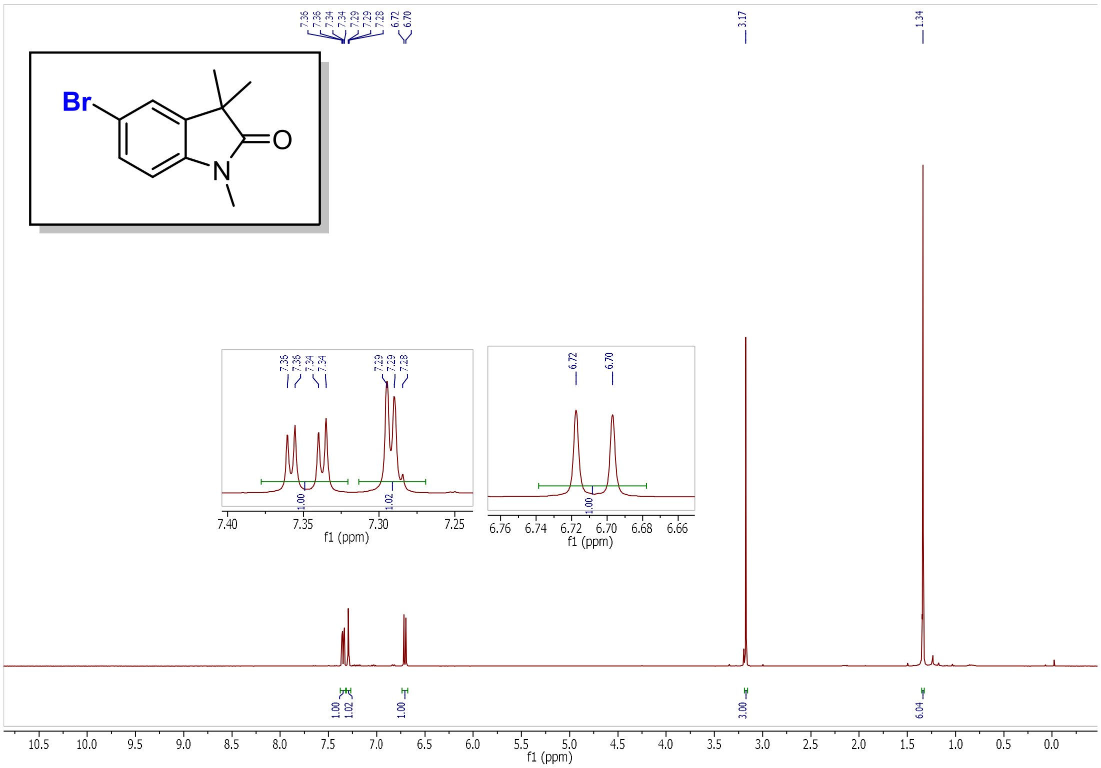

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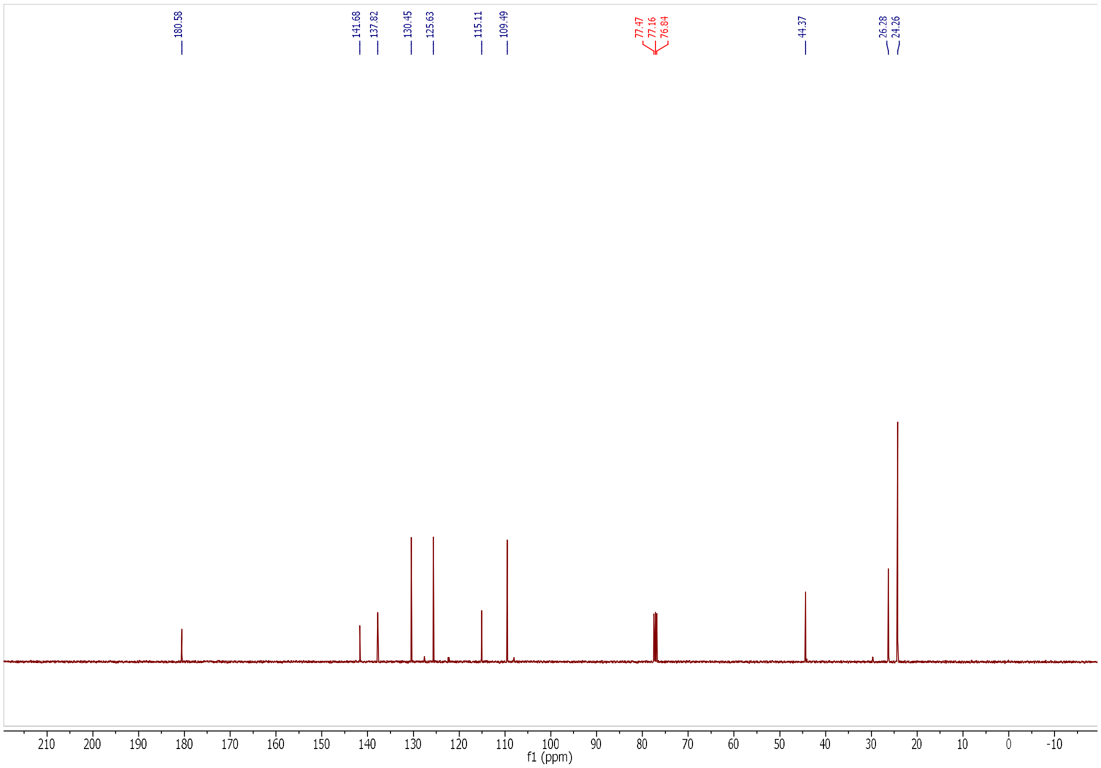

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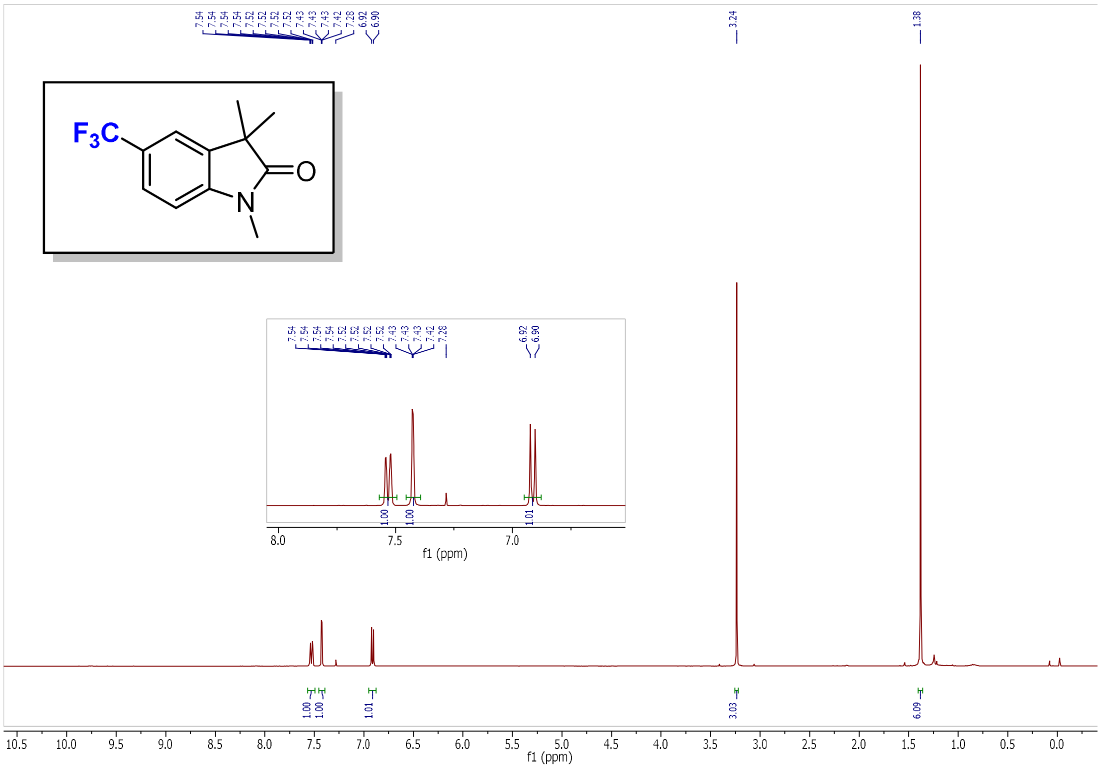

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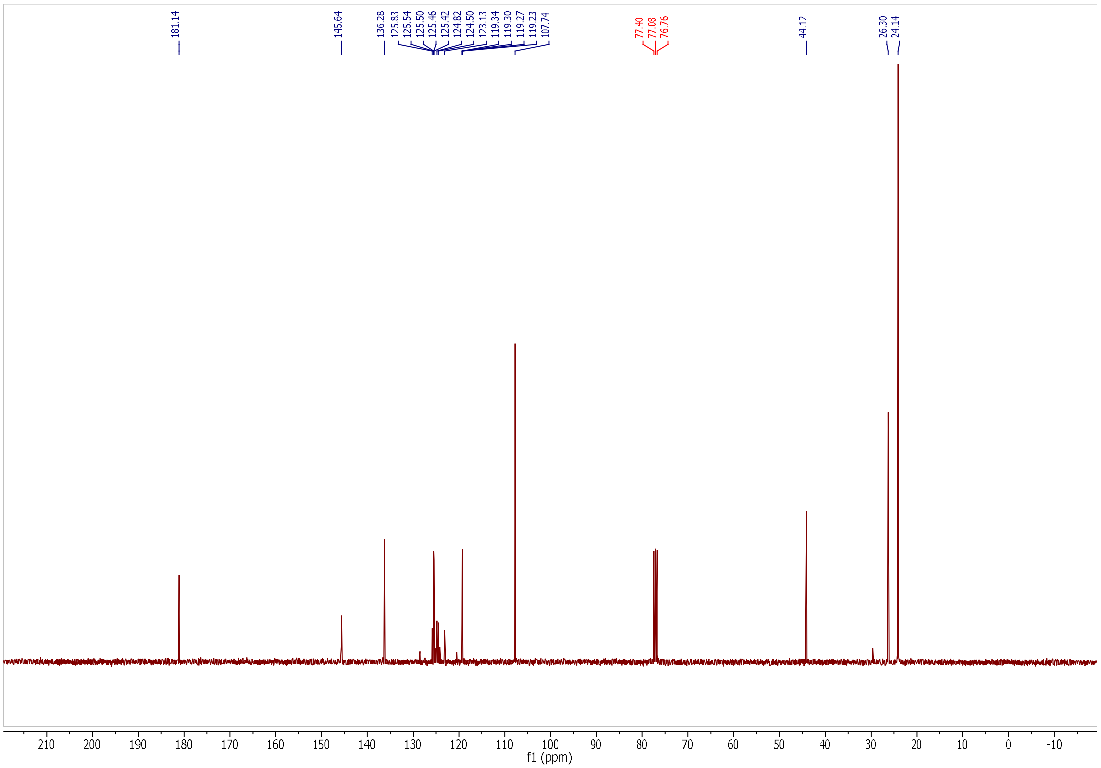
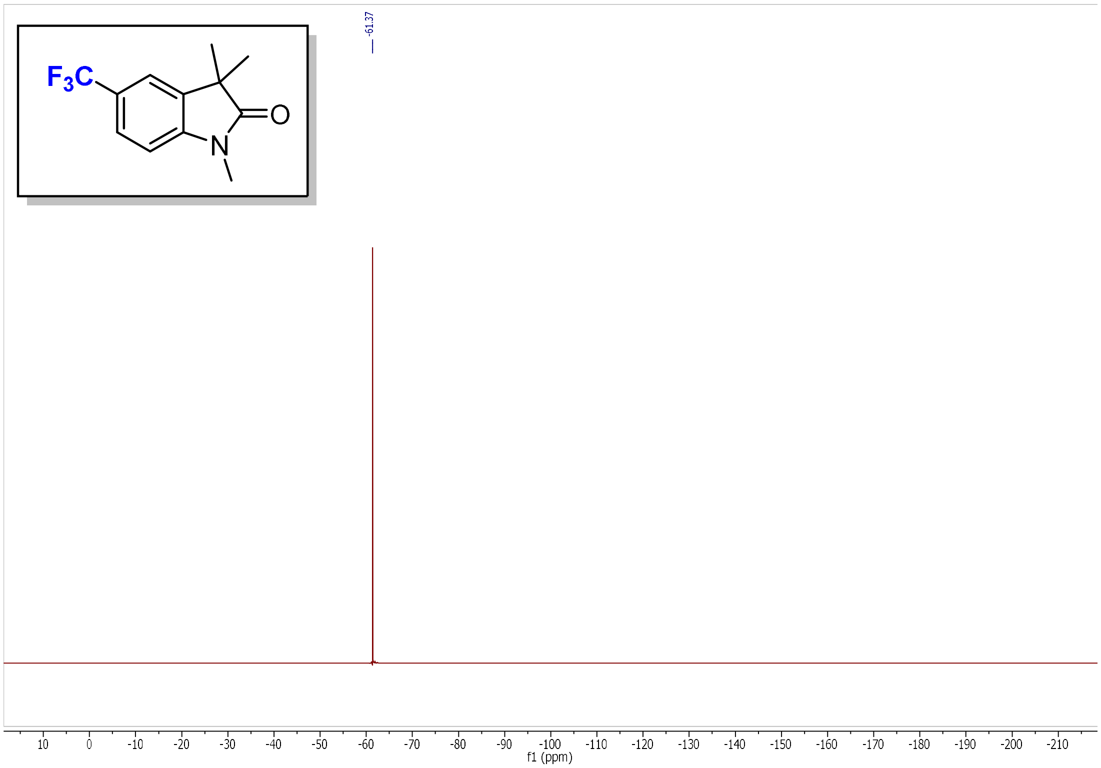


^{19}F NMR



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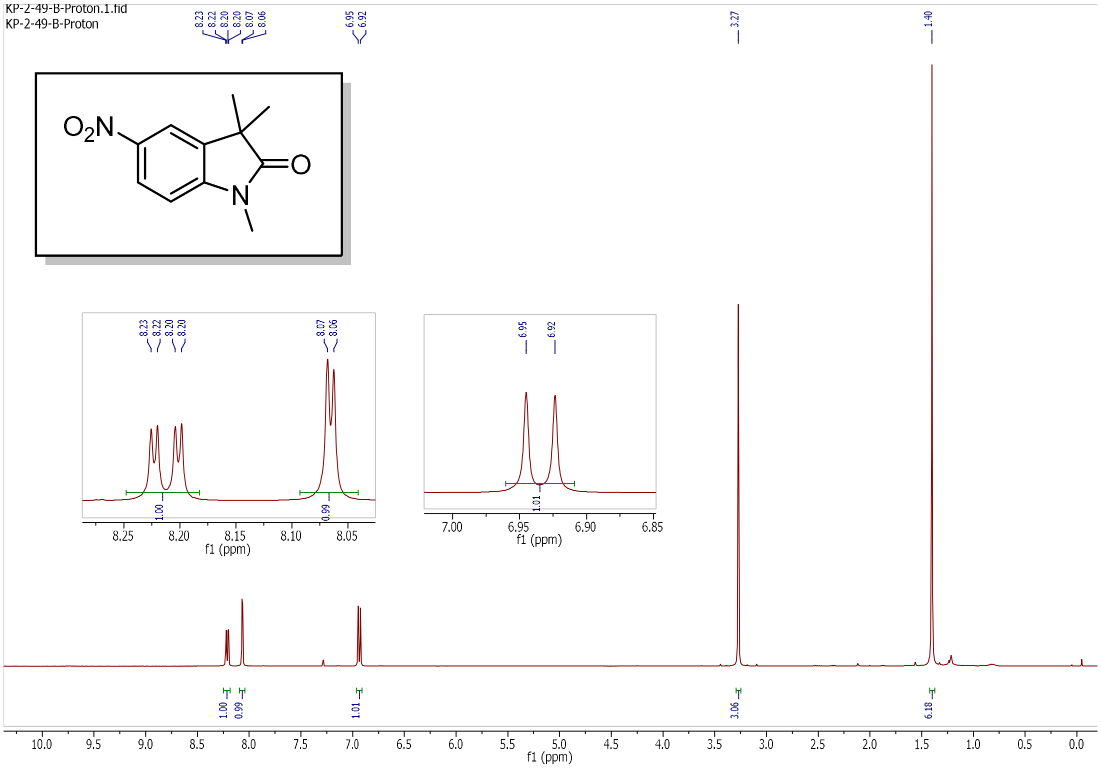
f1 (ppm)

^{1}H NMR



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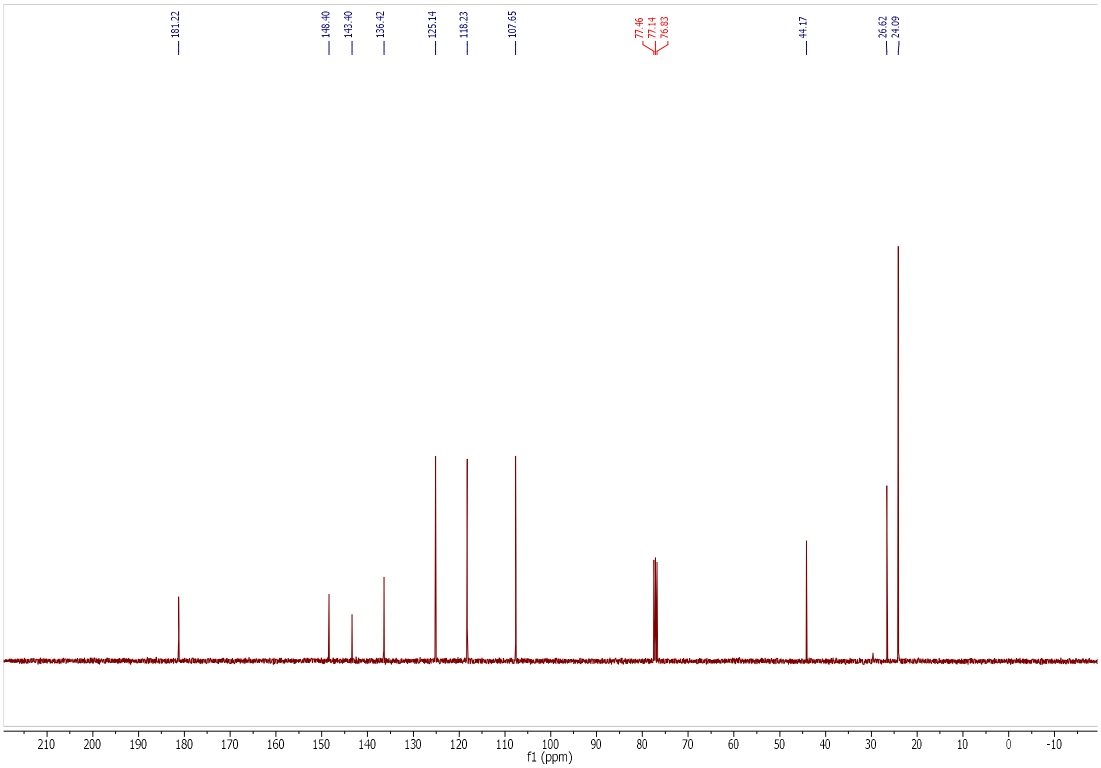

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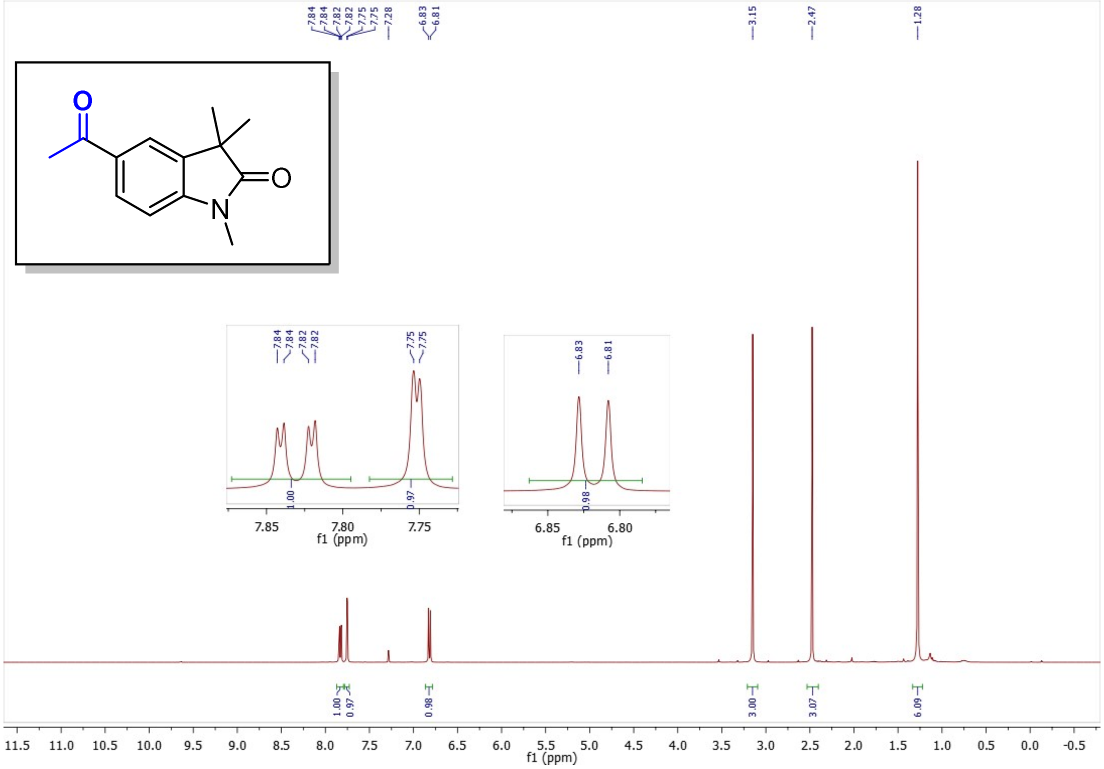

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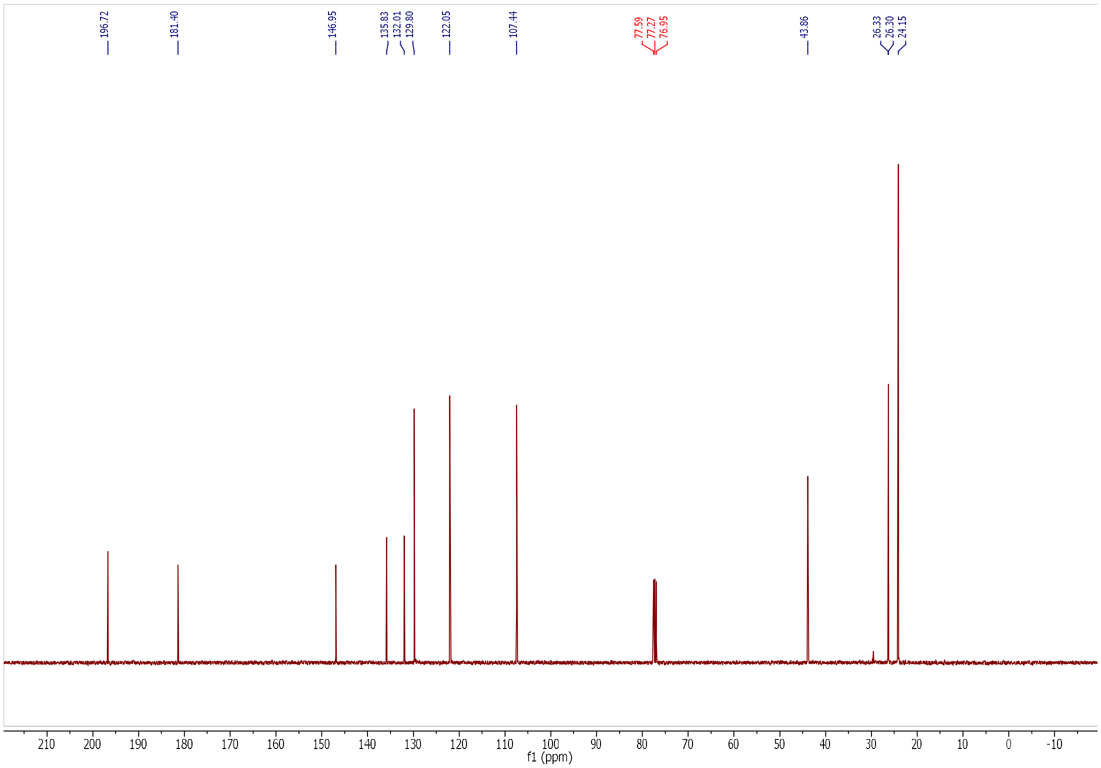

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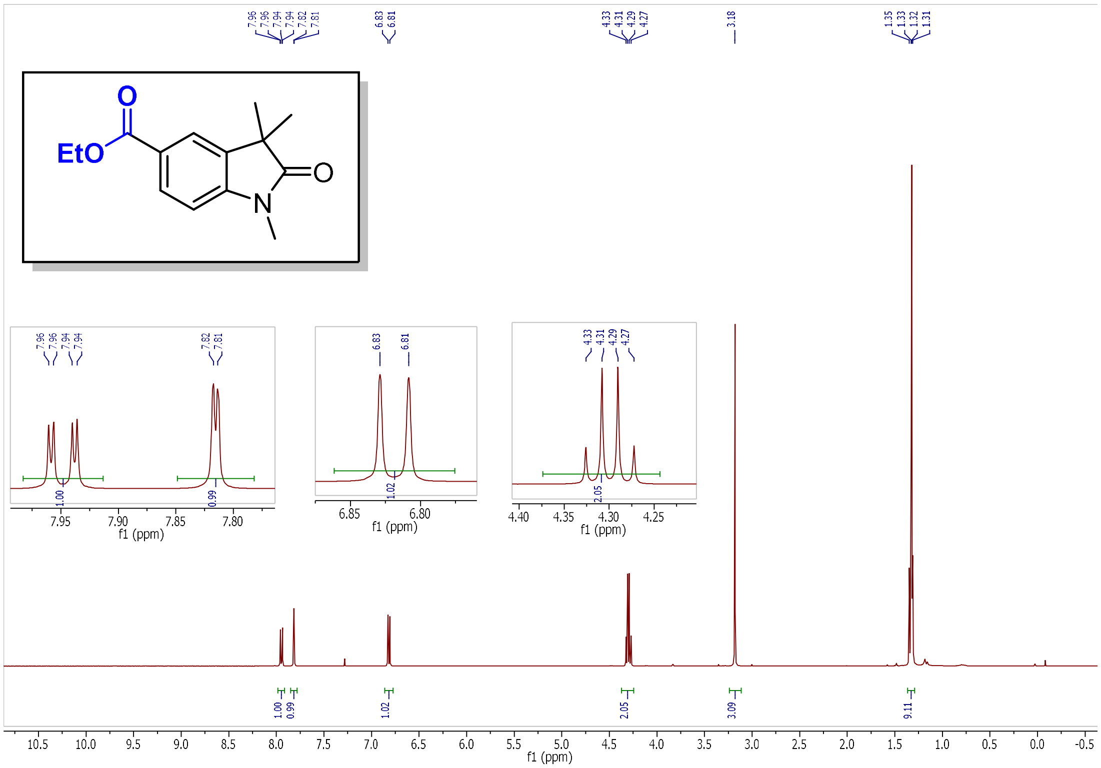
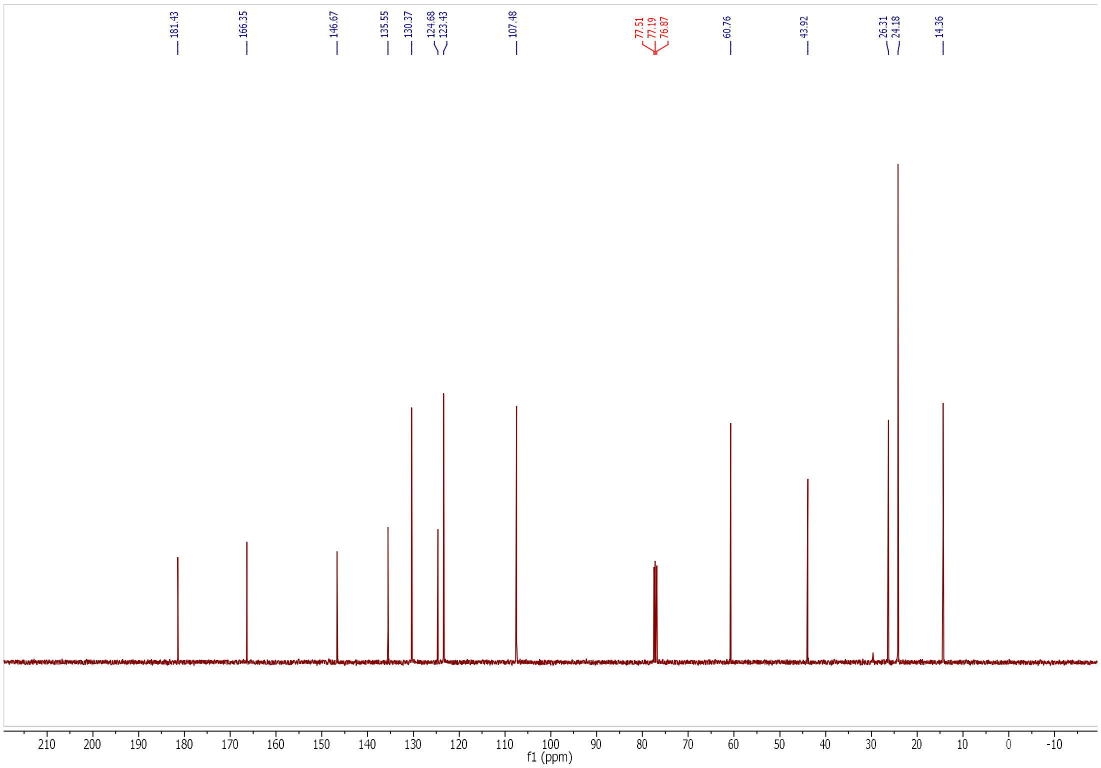


^{13}C NMR



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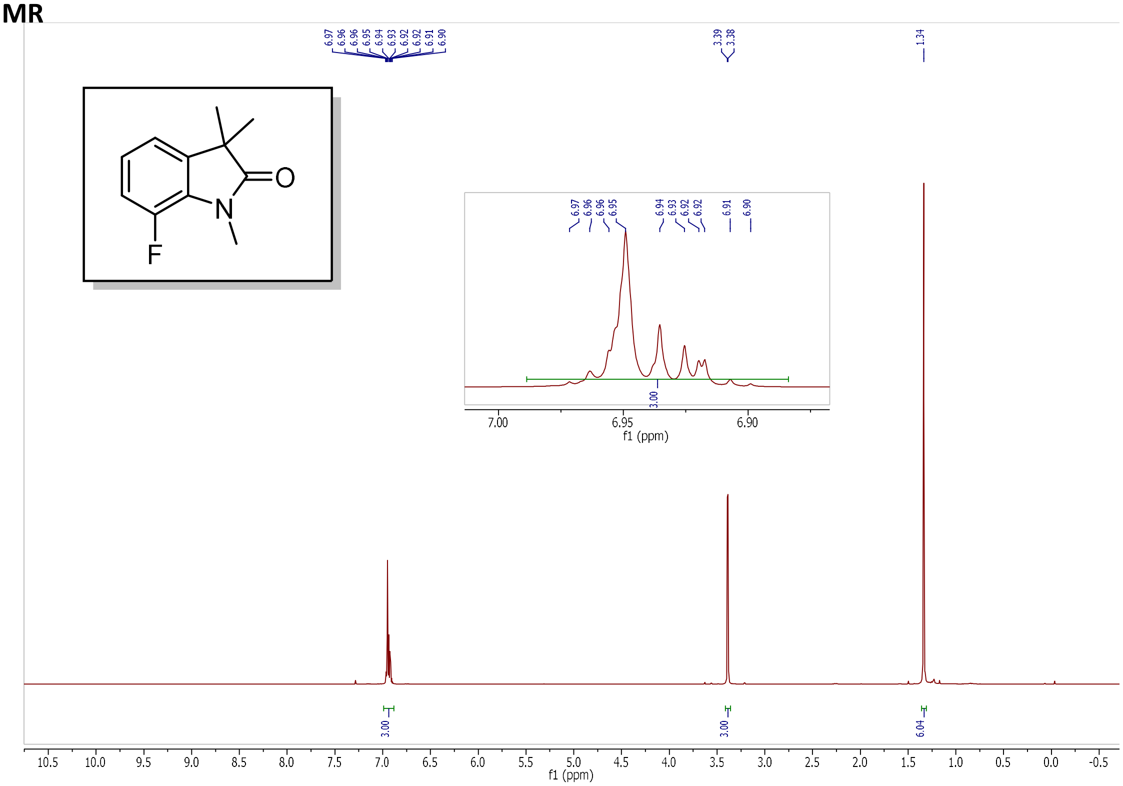

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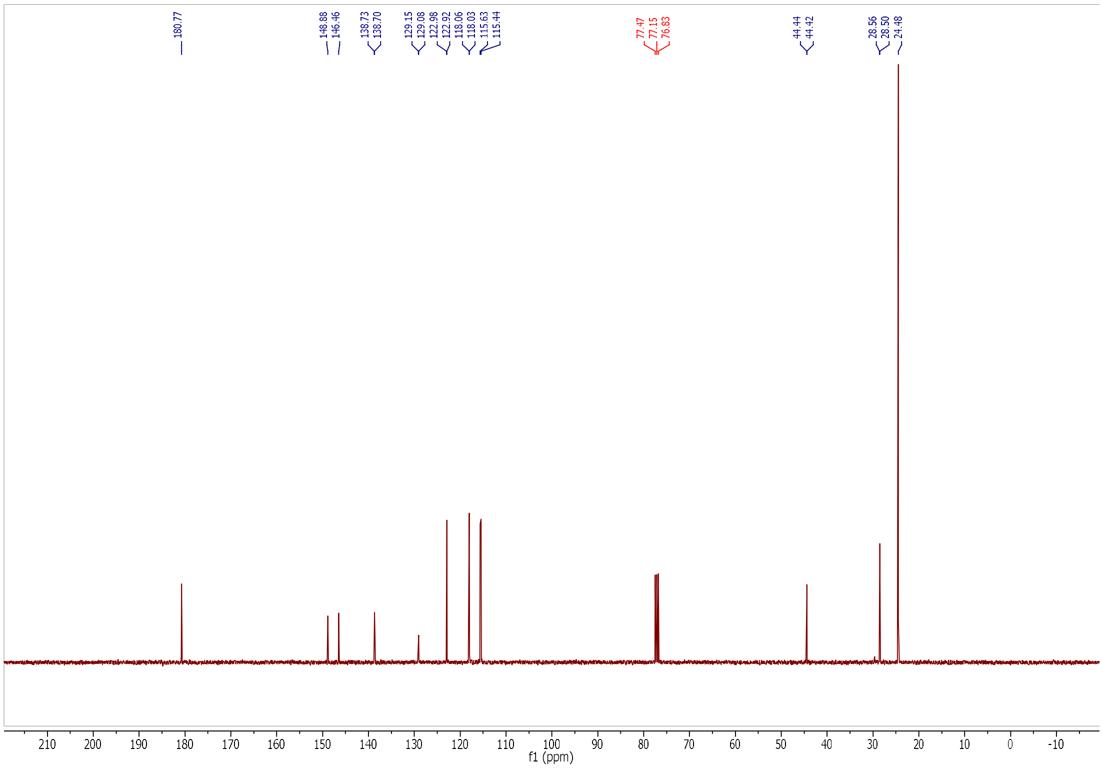

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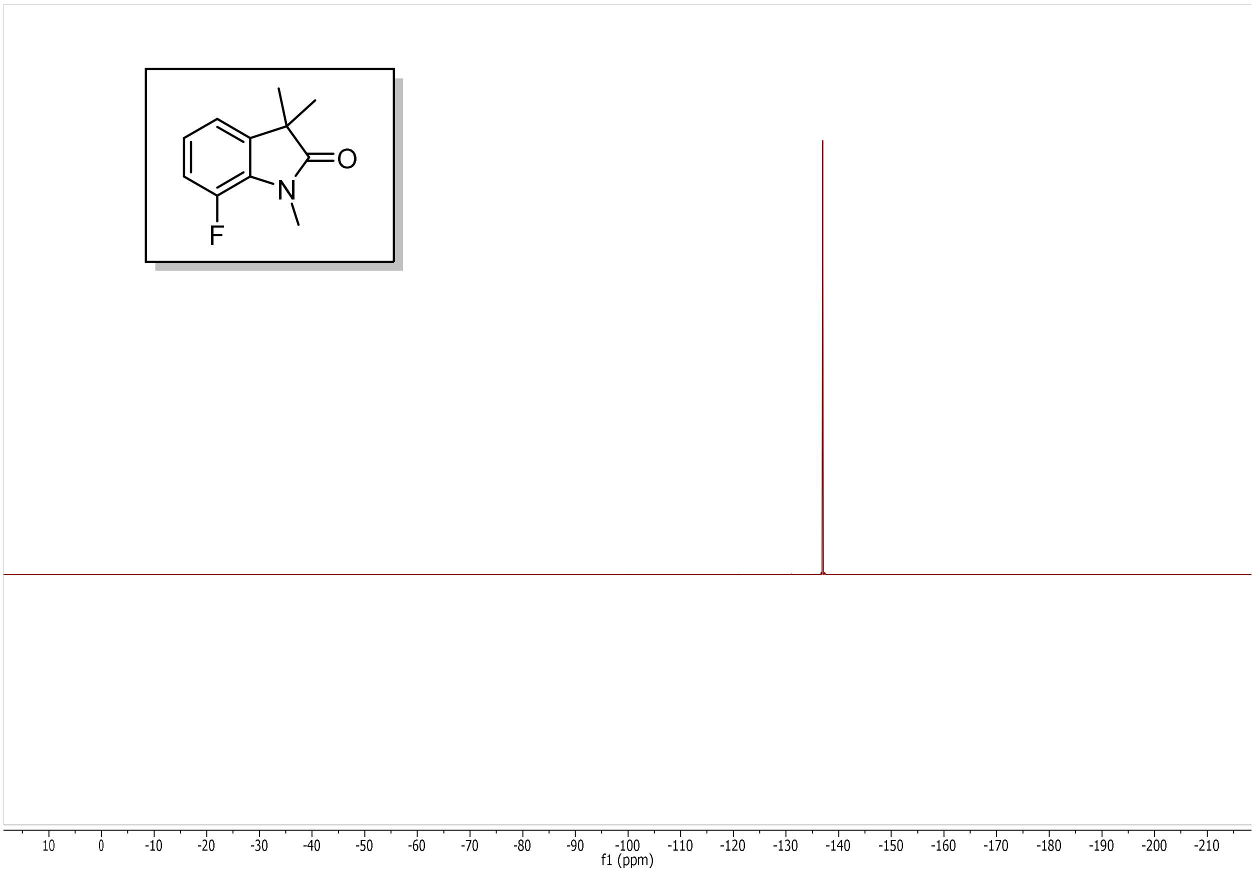

O
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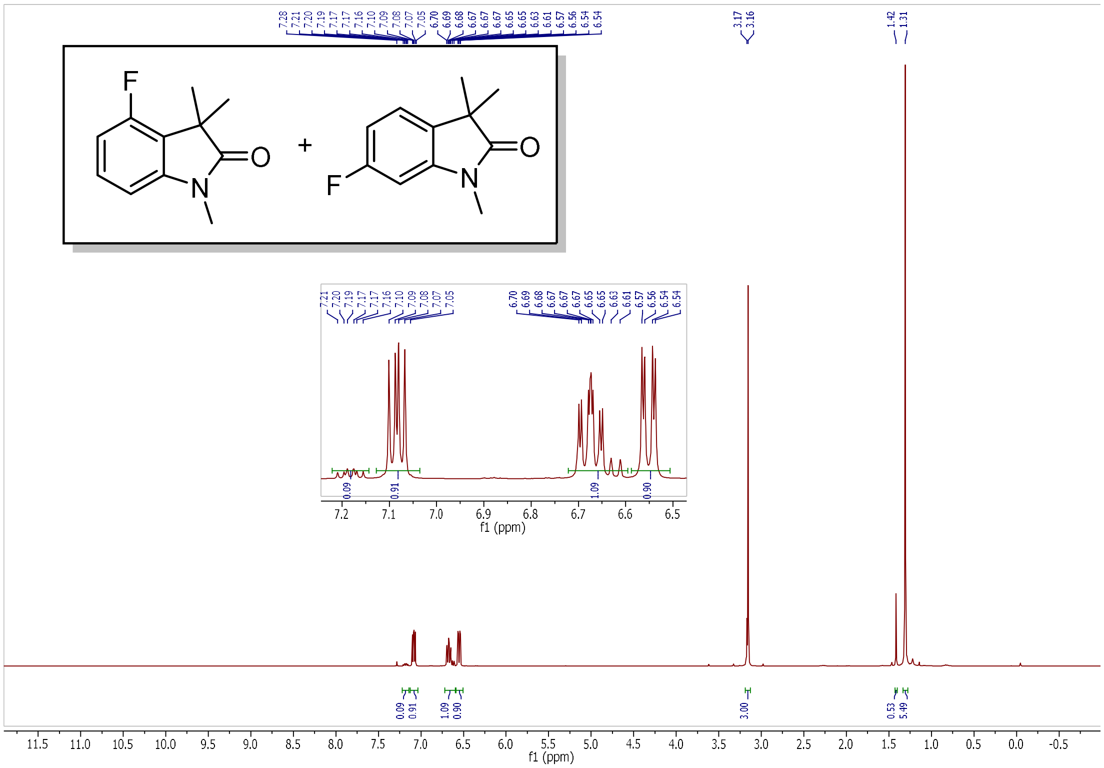
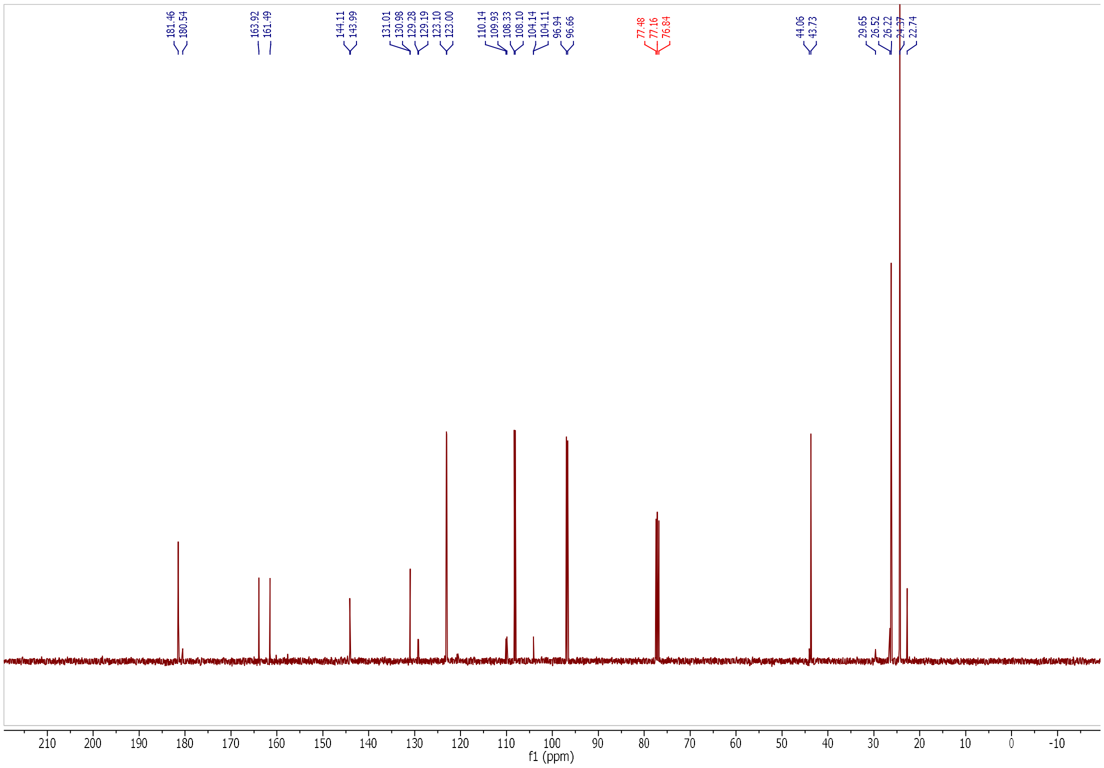
f1 (ppm)

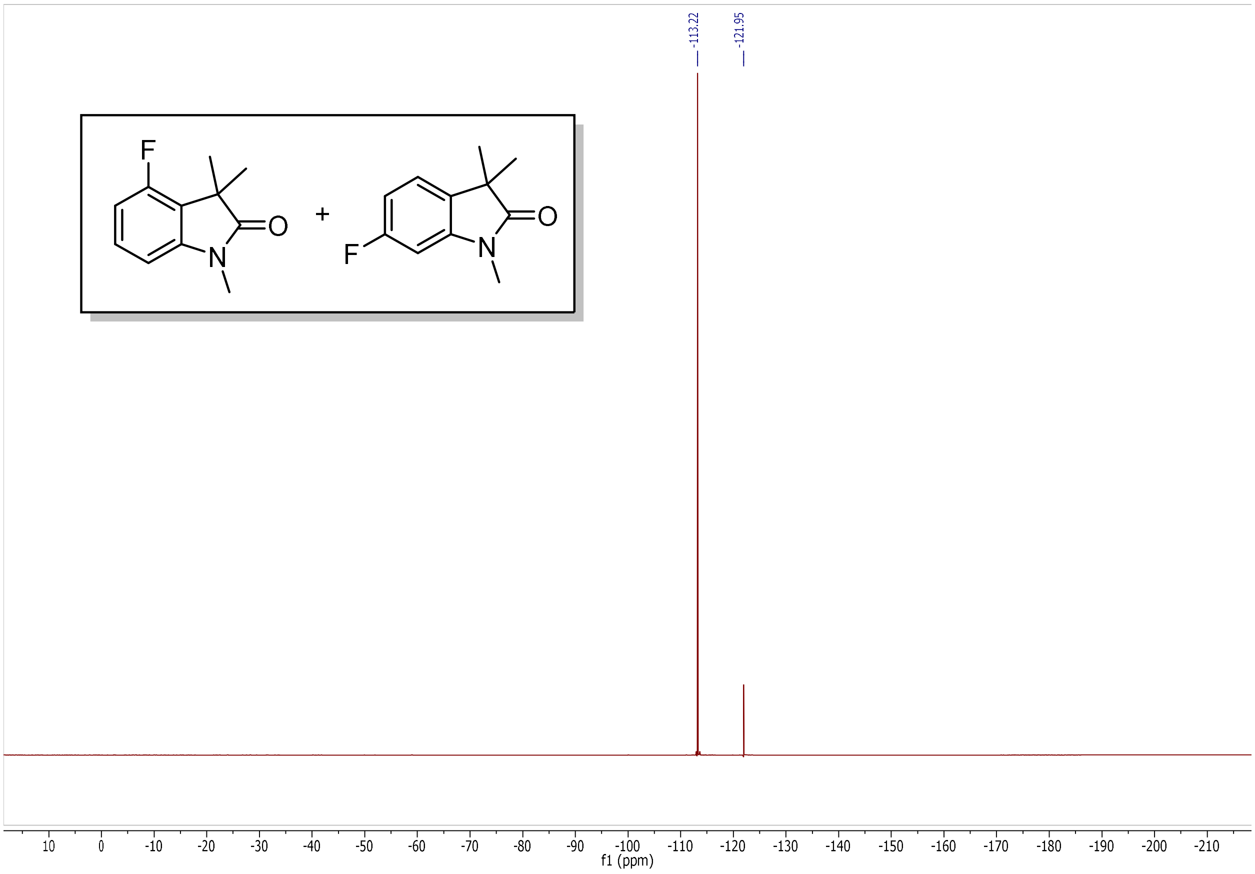
^{1}H NMR



13C NMR



^{19}F NMR



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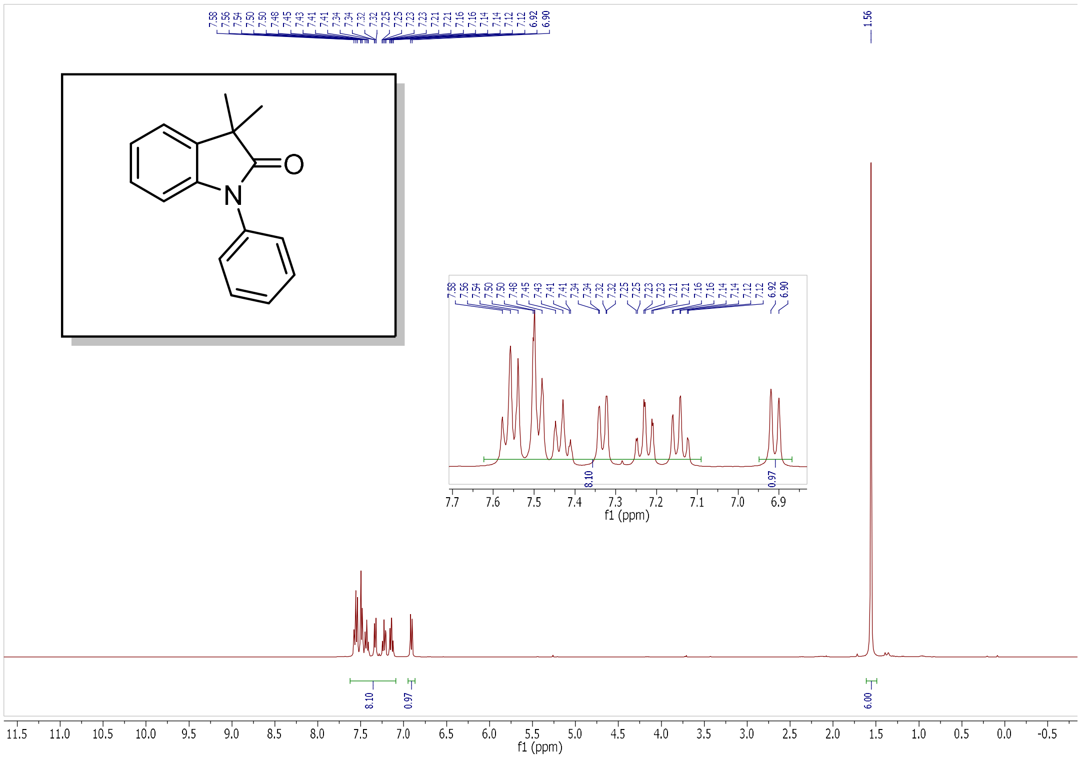
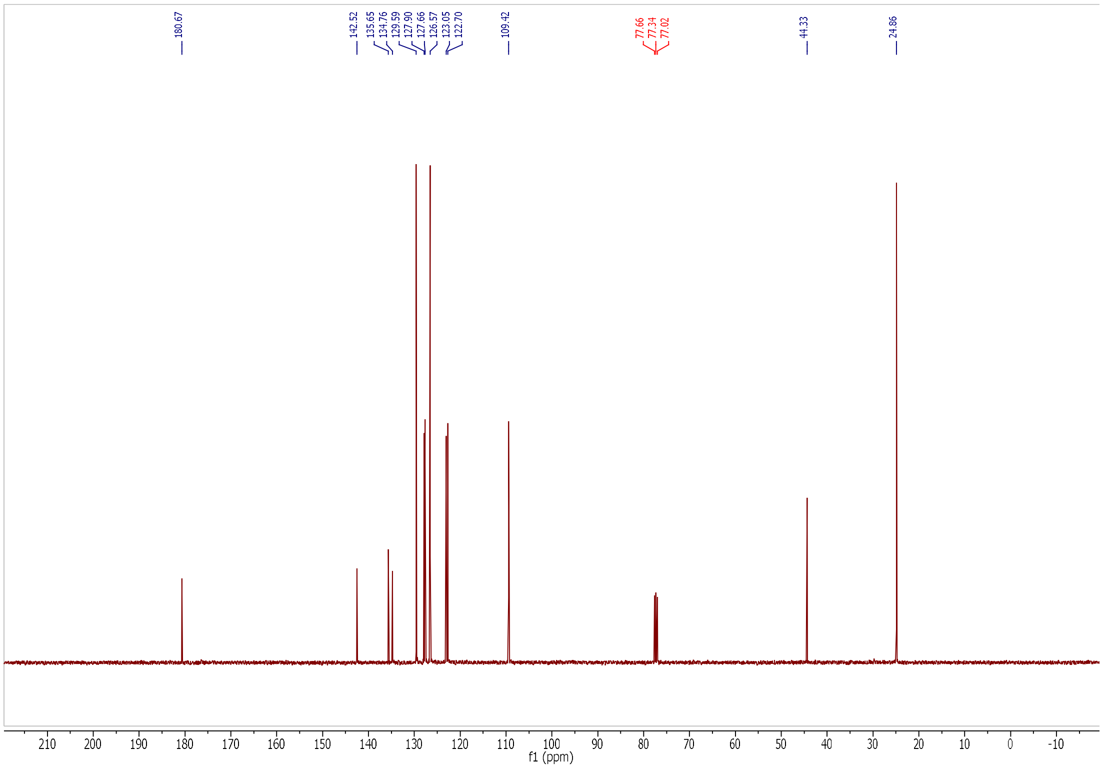
-210
f1 (ppm)

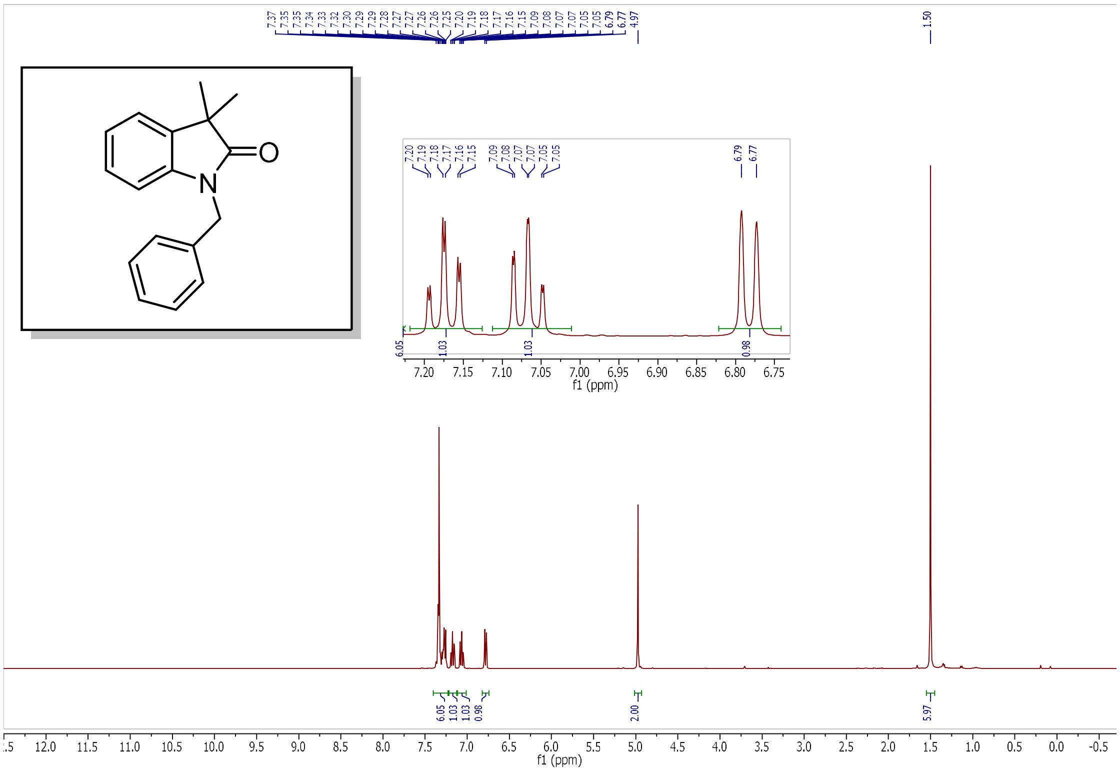
^{1}H NMR



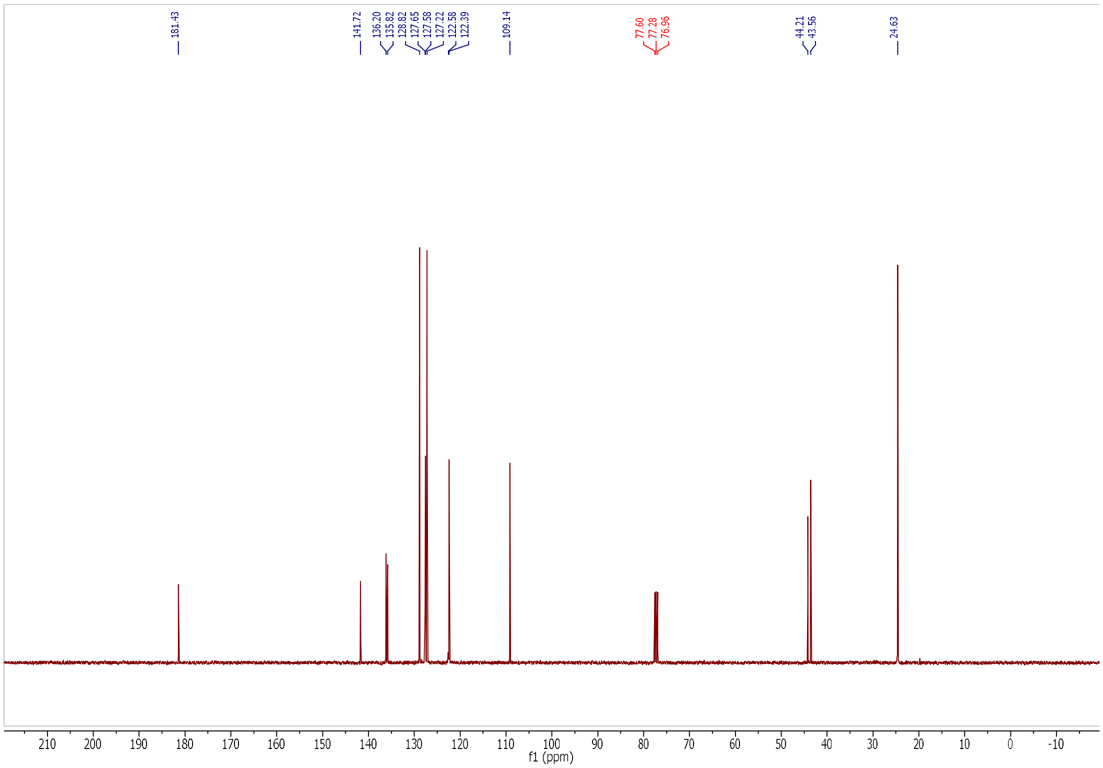
^{13}C NMR



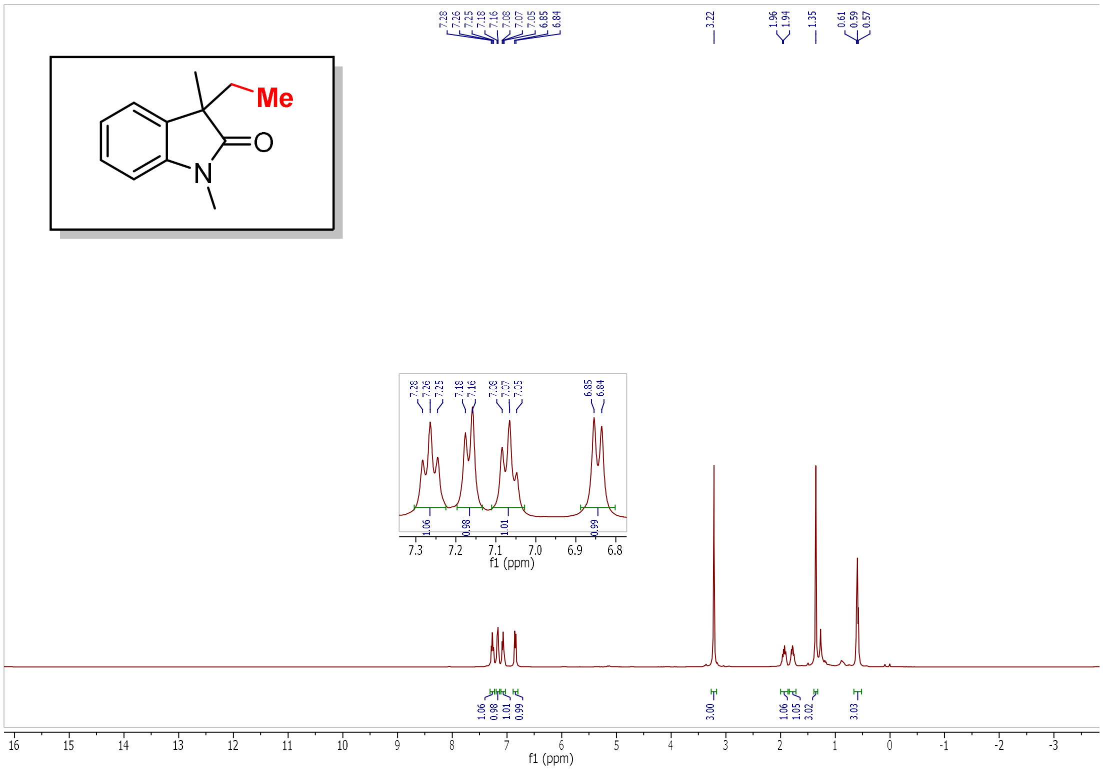
^{1}H NMR



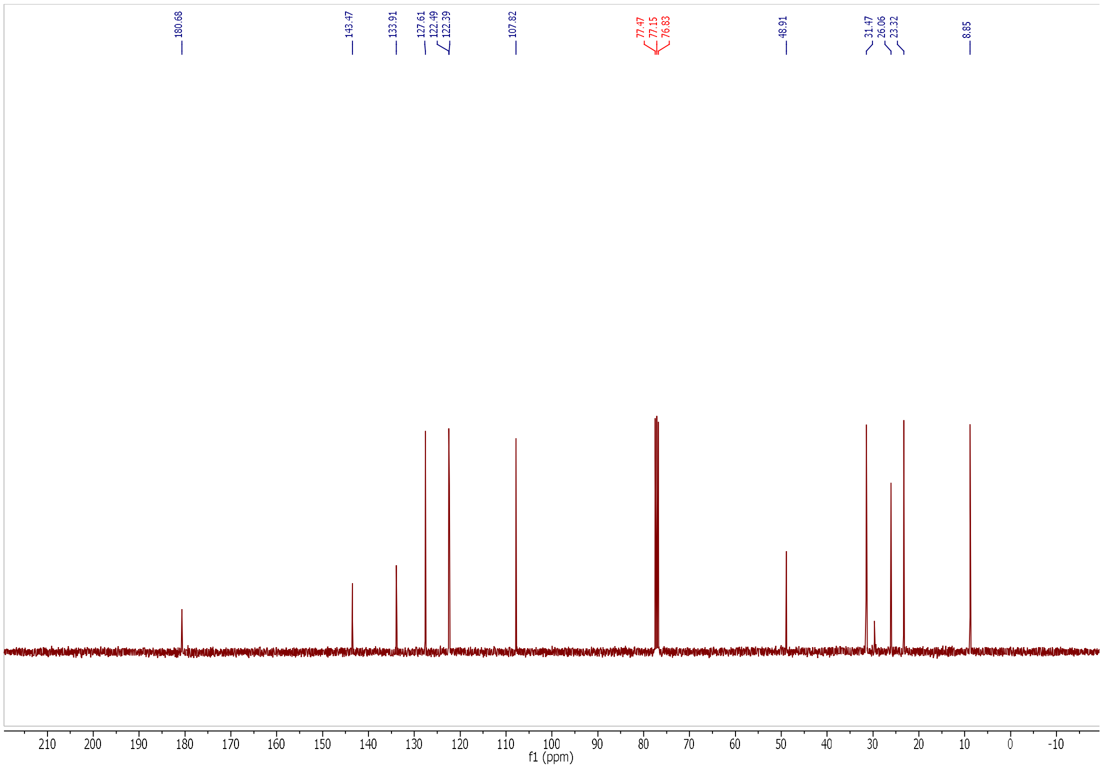
^{13}C NMR



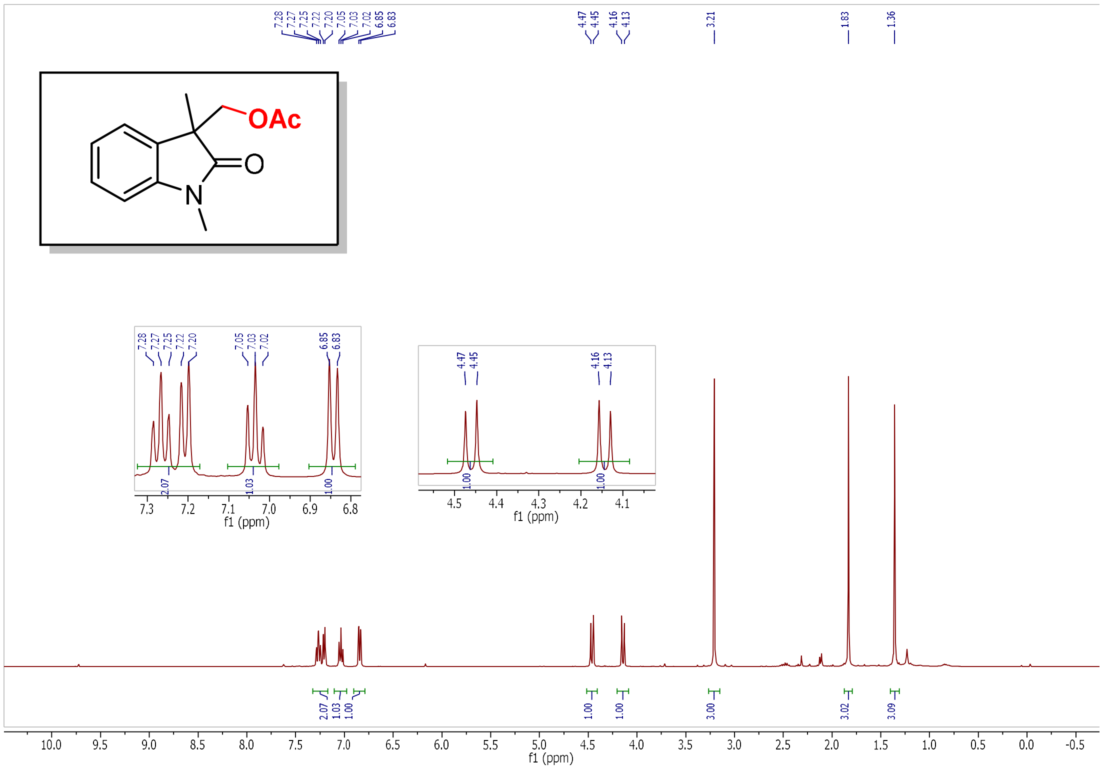
^{1}H NMR



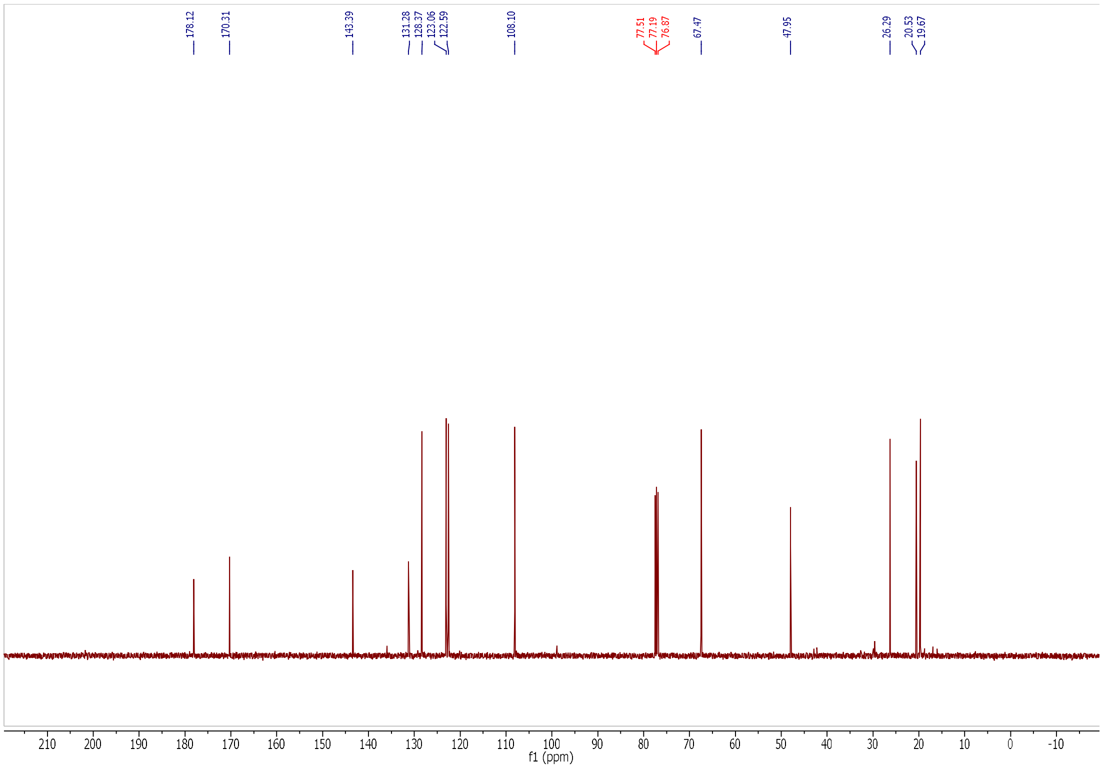
^{13}C NMR



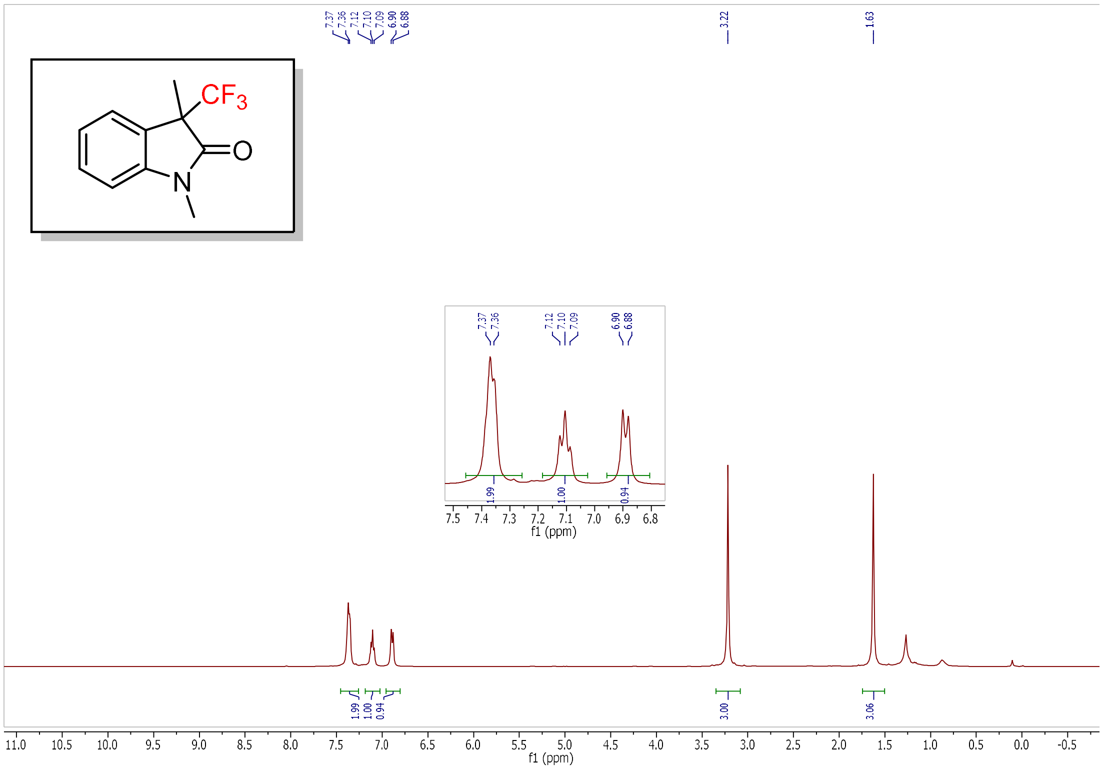
^{1}H NMR



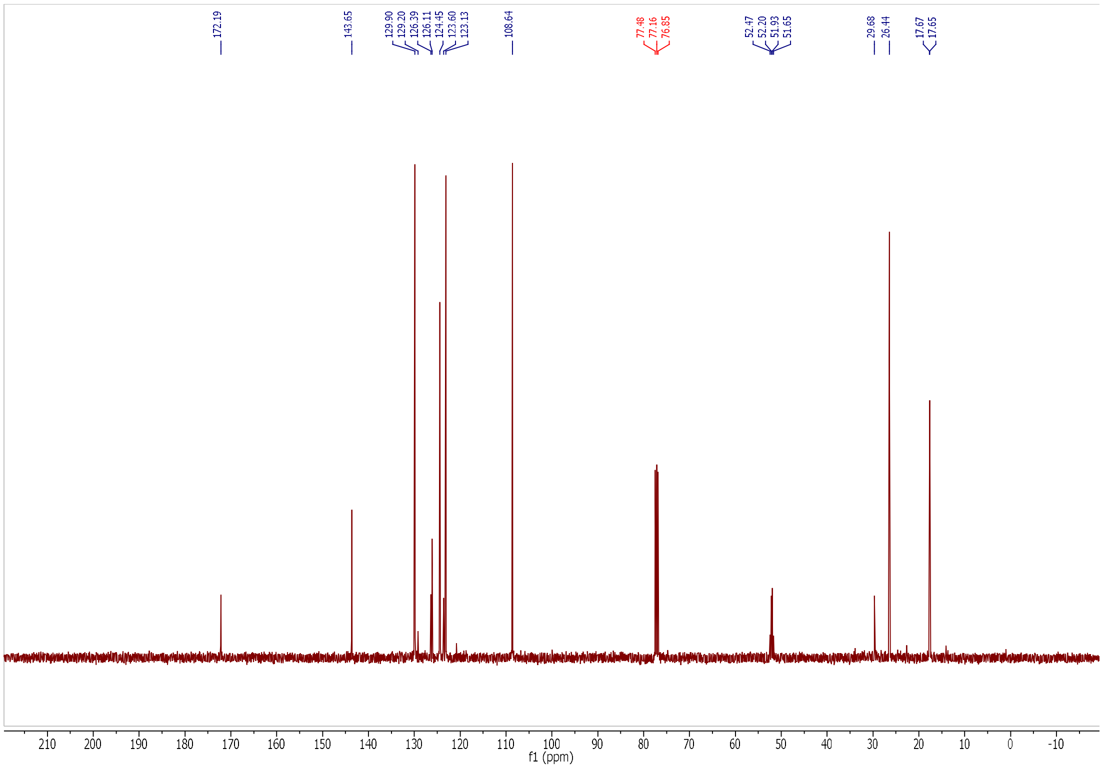
^{13}C NMR



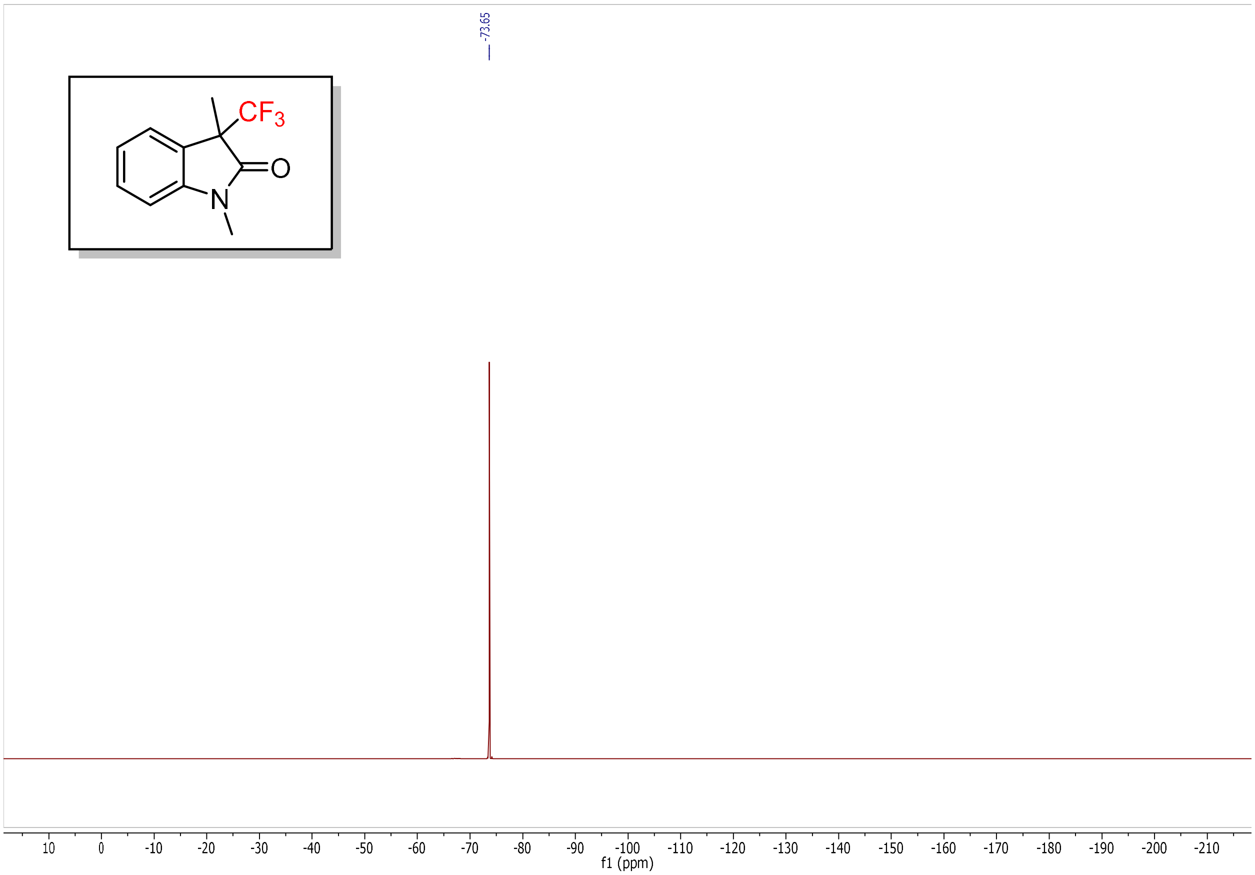
^{1}H NMR



^{13}C NMR



^{19}F NMR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CF3
O
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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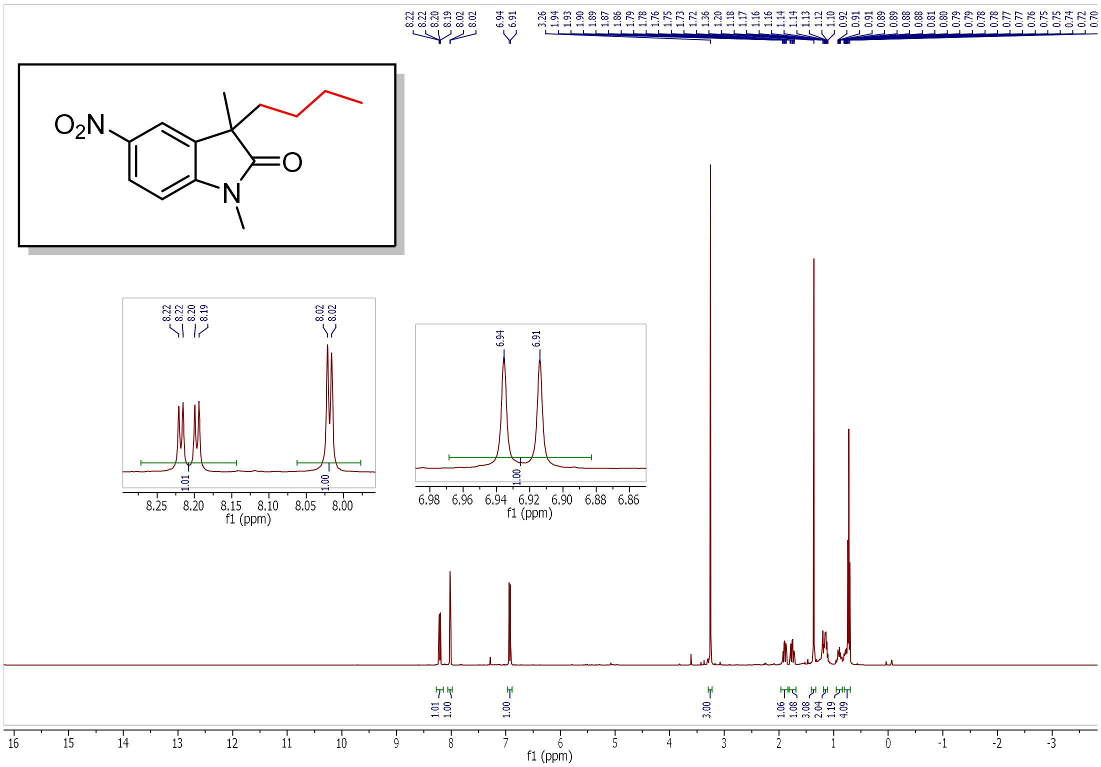
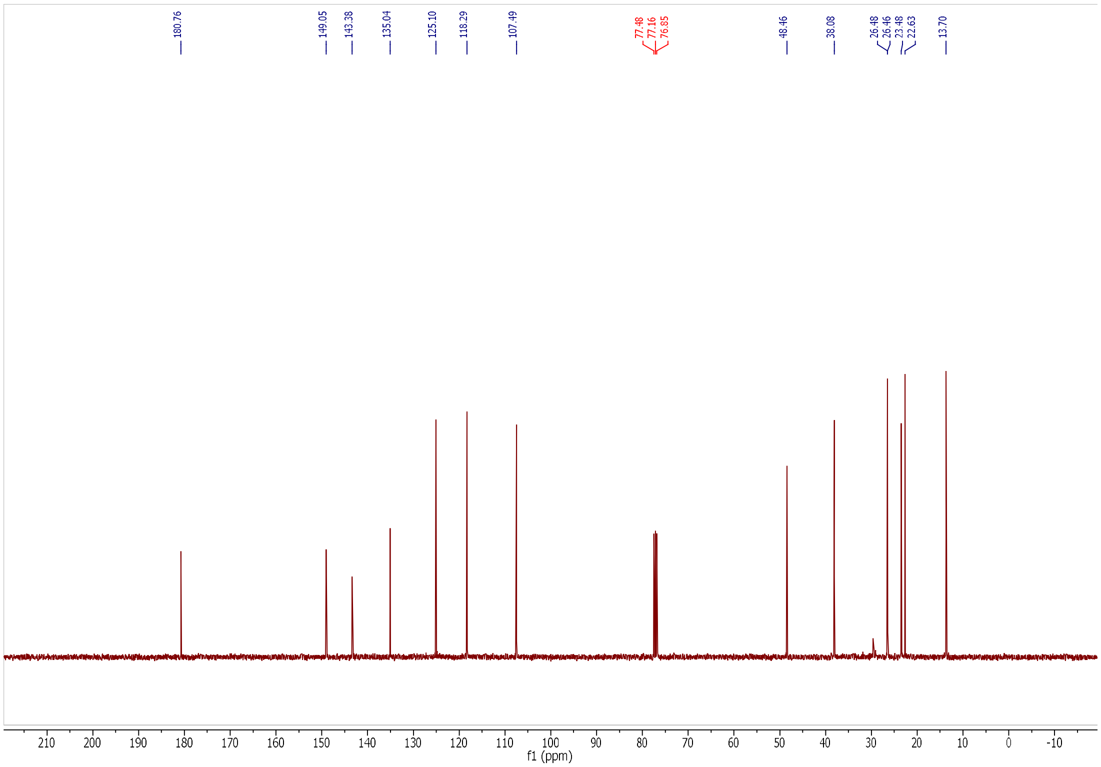
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

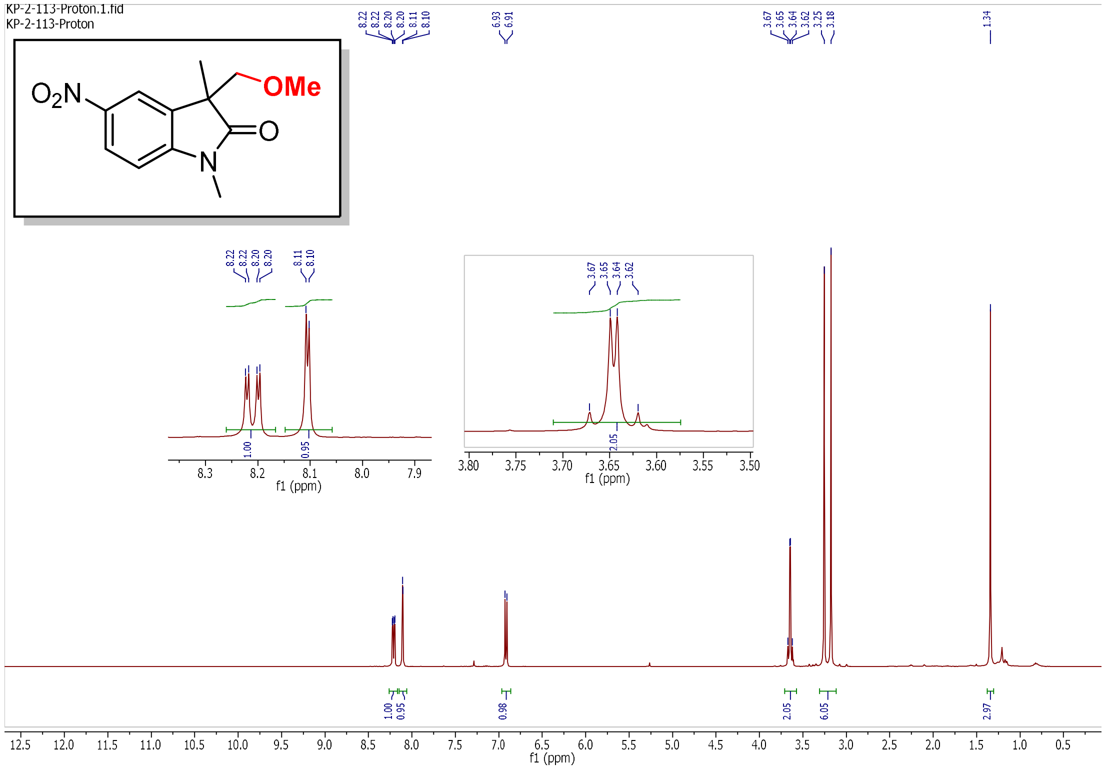
^{1}H NMR



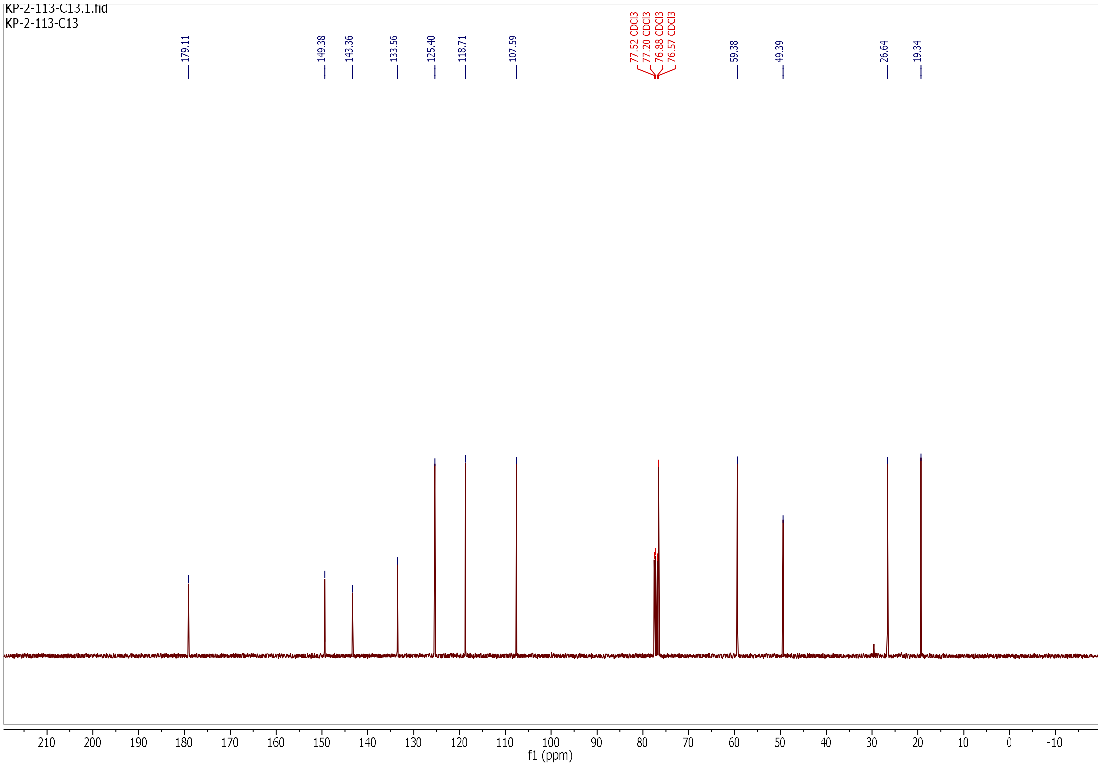
^{13}C NMR



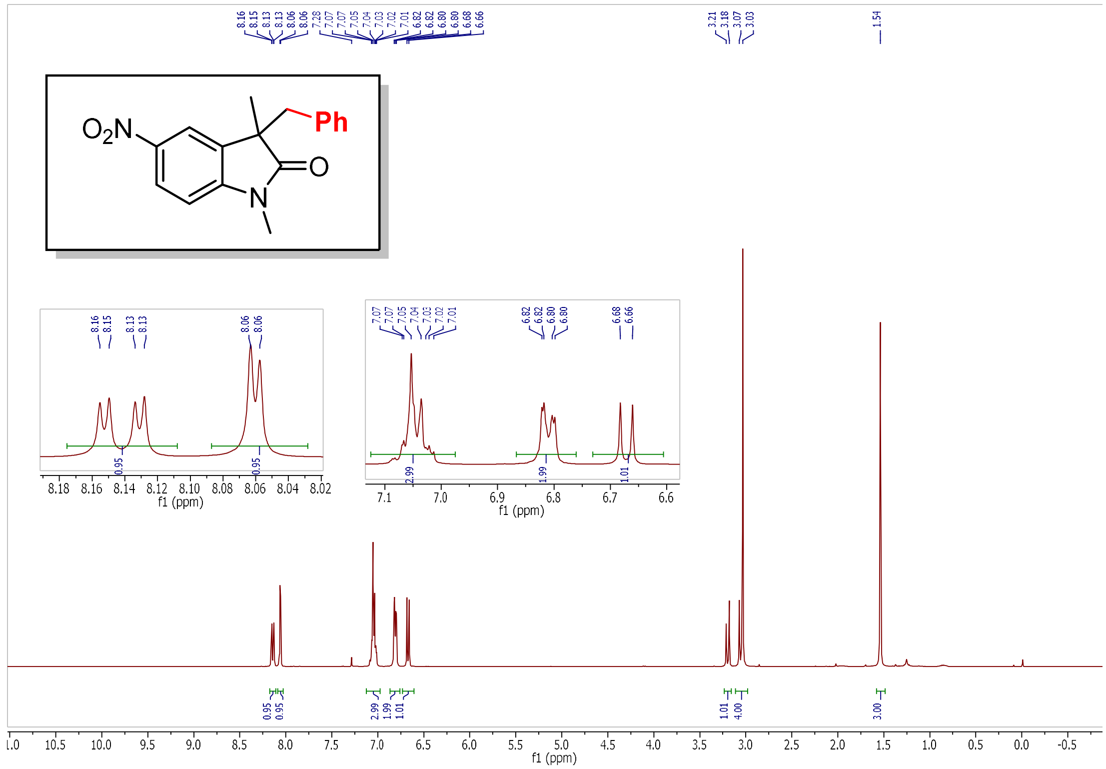
^{1}H NMR



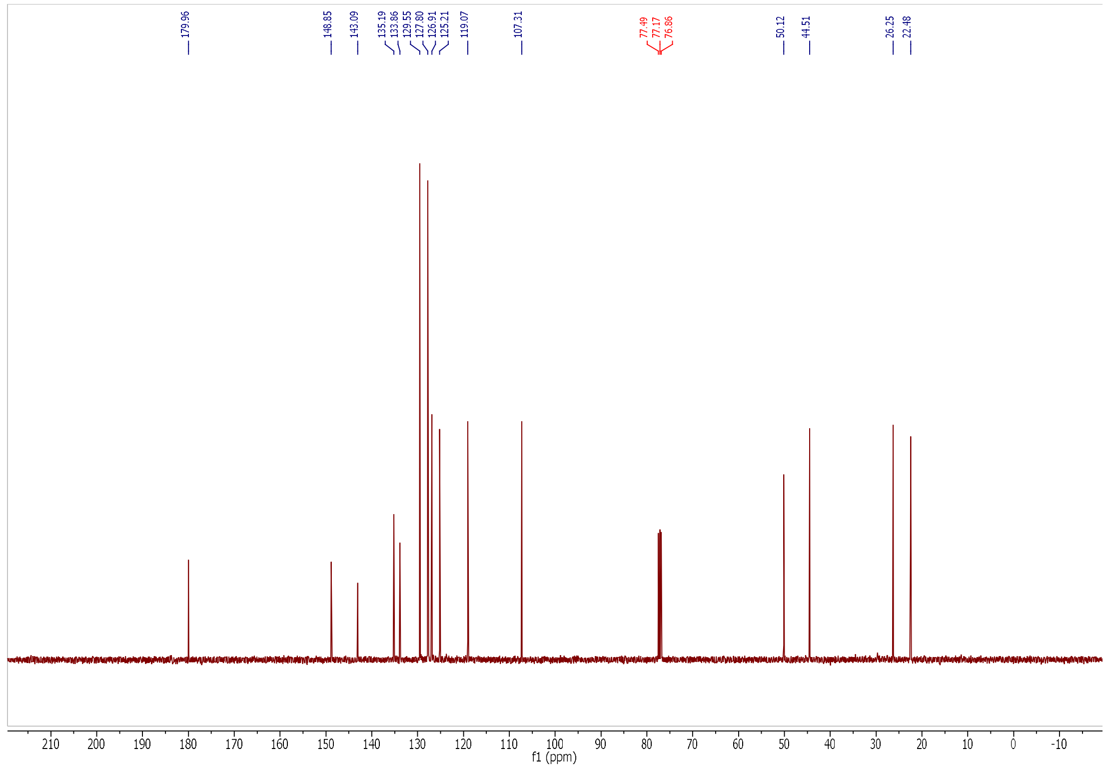
^{13}C NMR



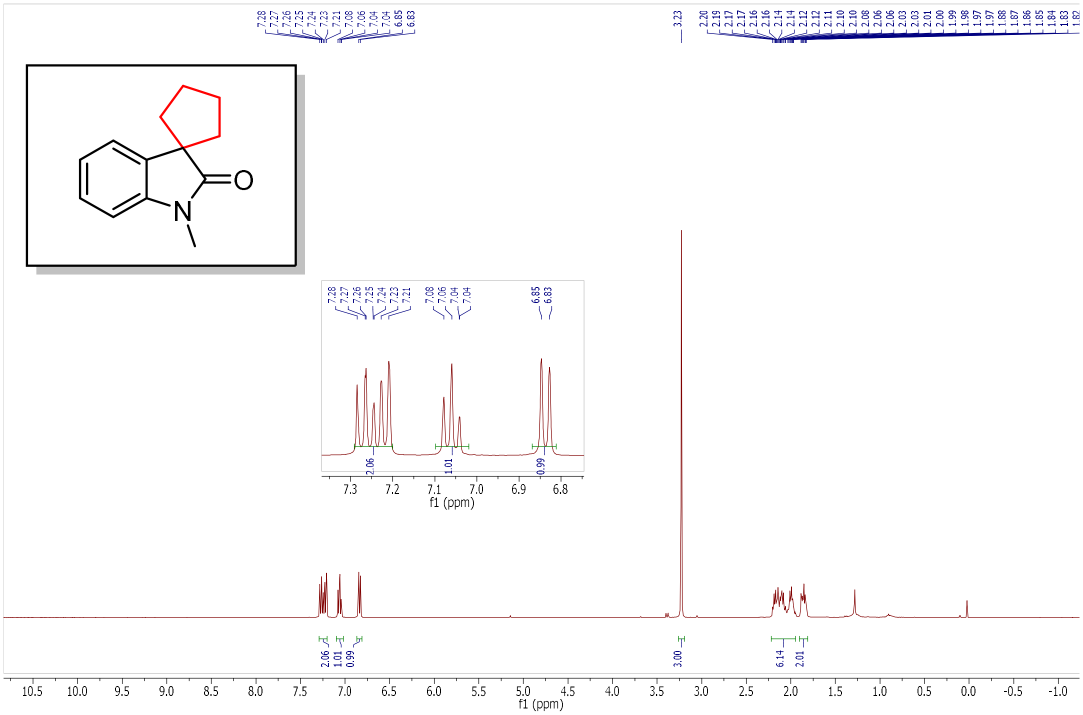
^{1}H NMR



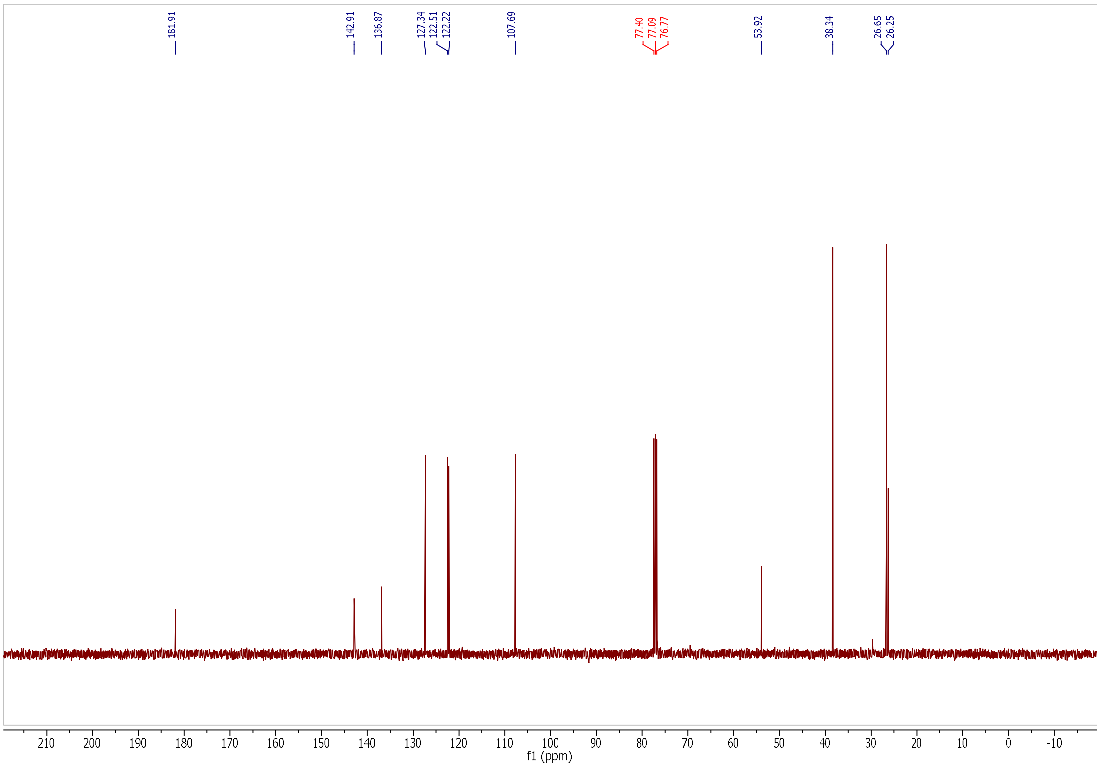
^{13}C NMR



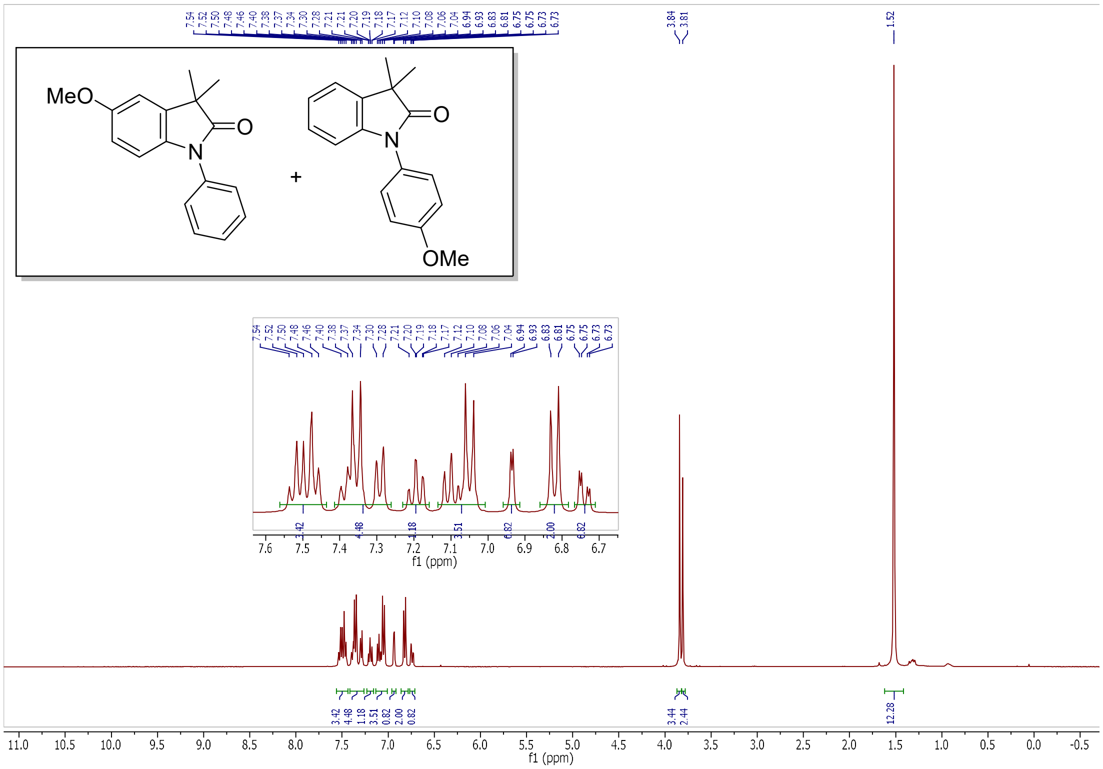
^{1}H NMR



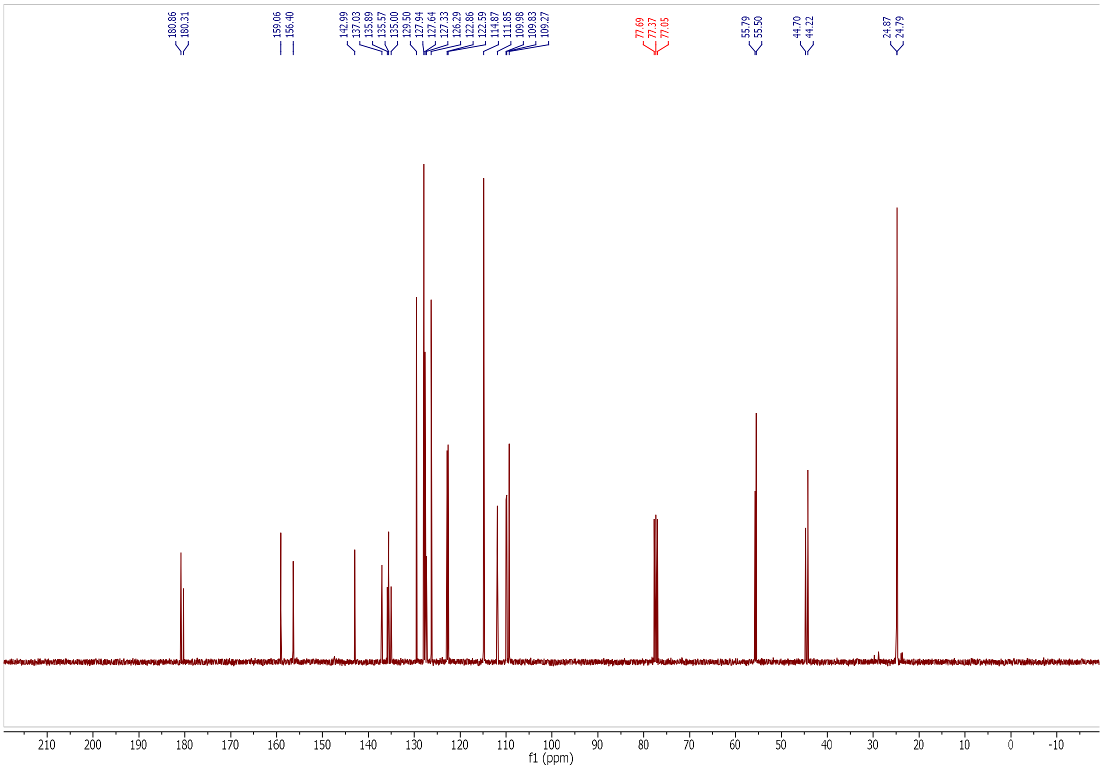
^{13}C NMR



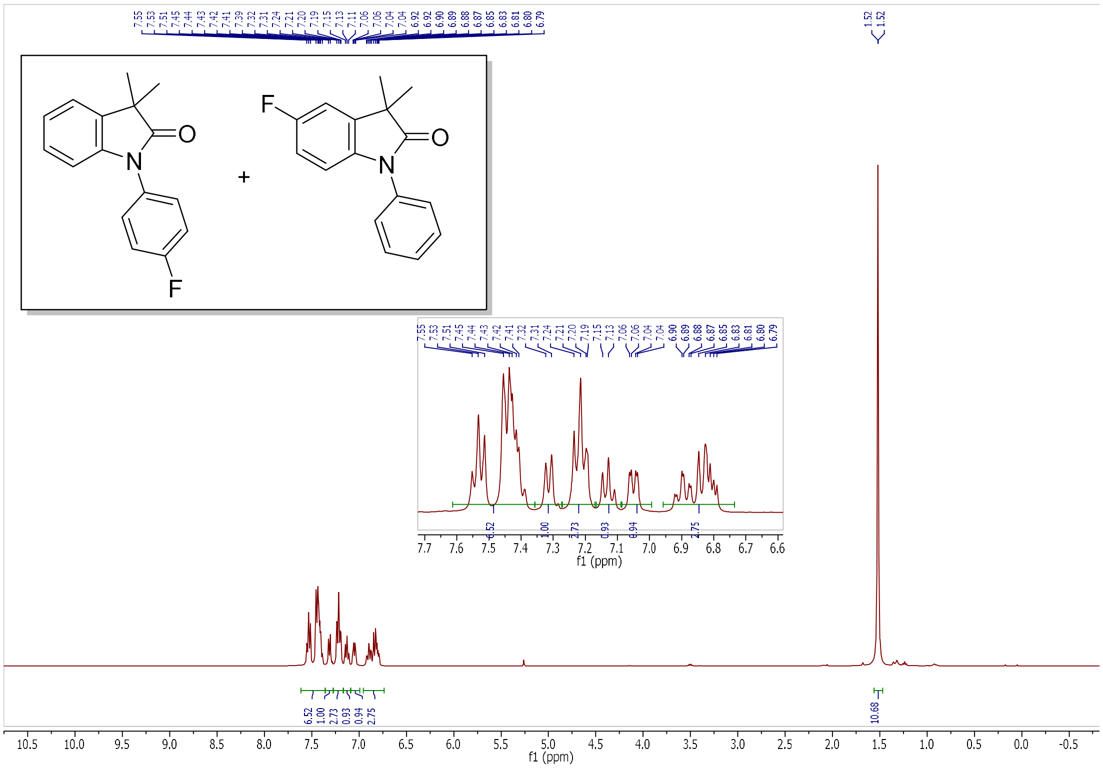
^{1}H NMR



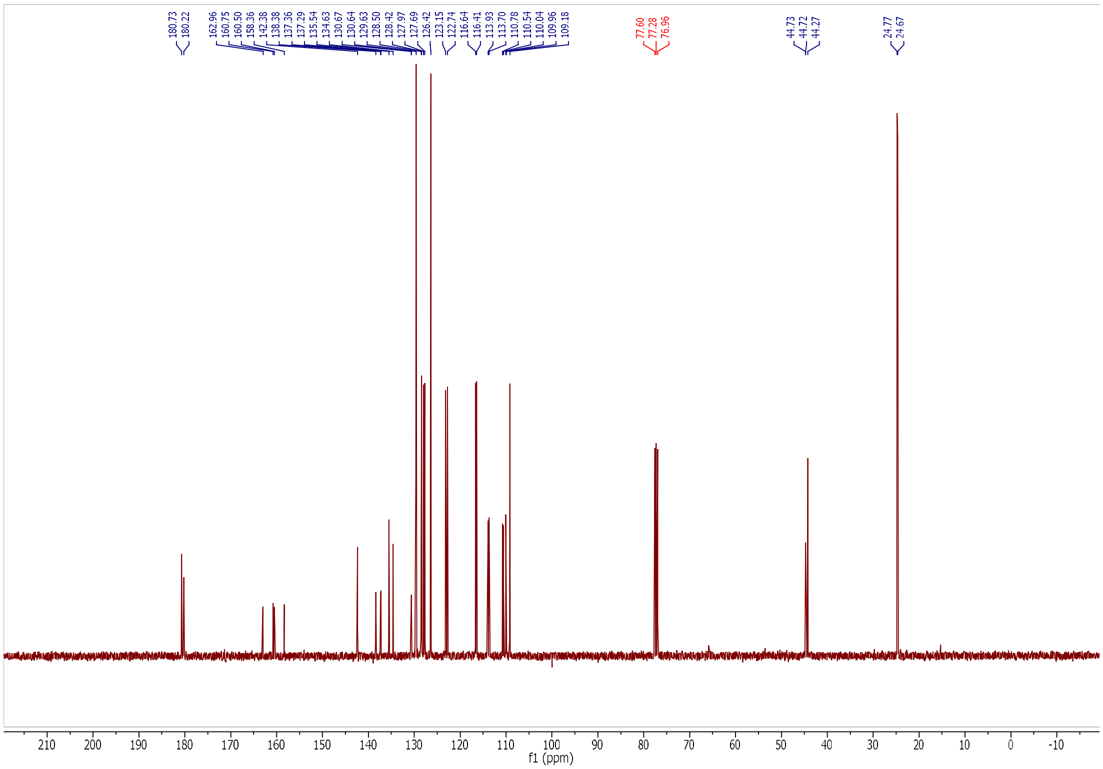
^{13}C NMR



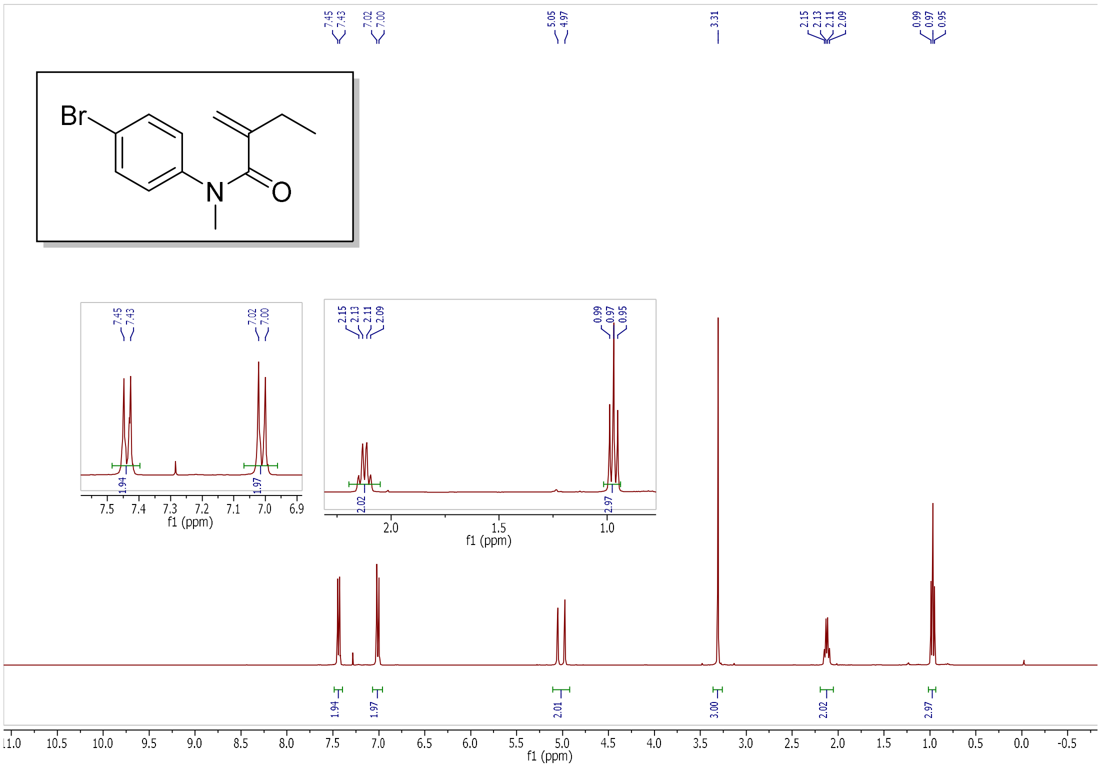
^{1}H NMR



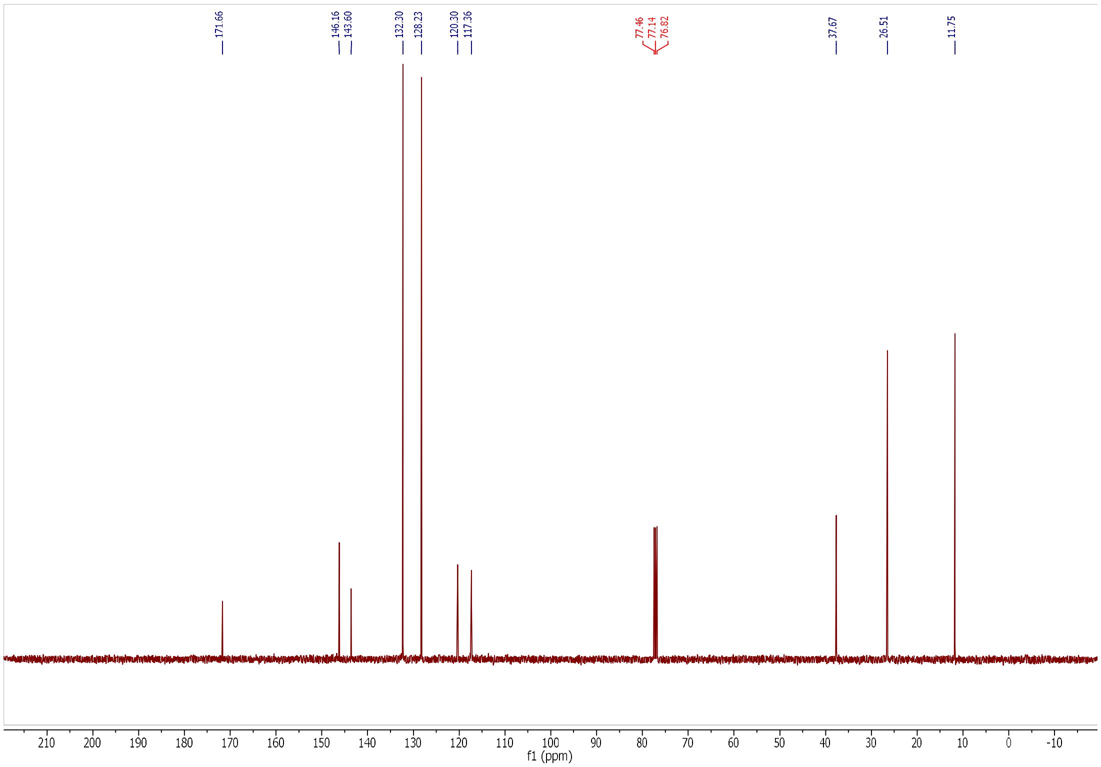
^{13}C NMR



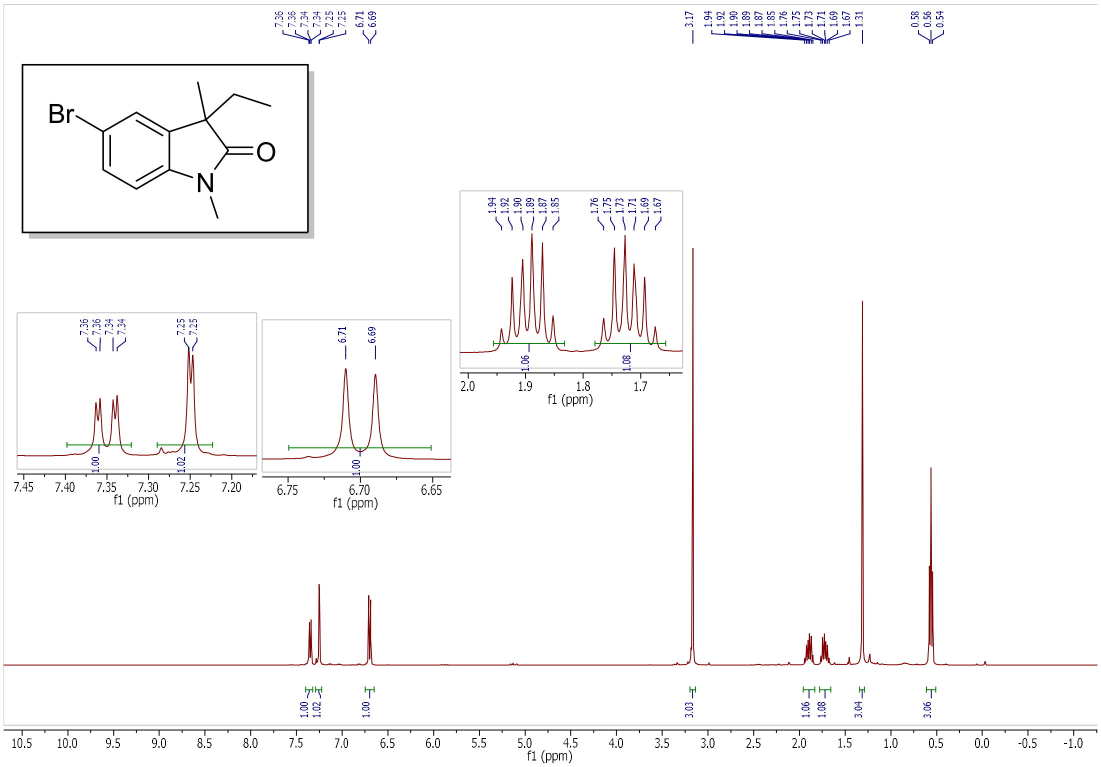
^{1}H NMR



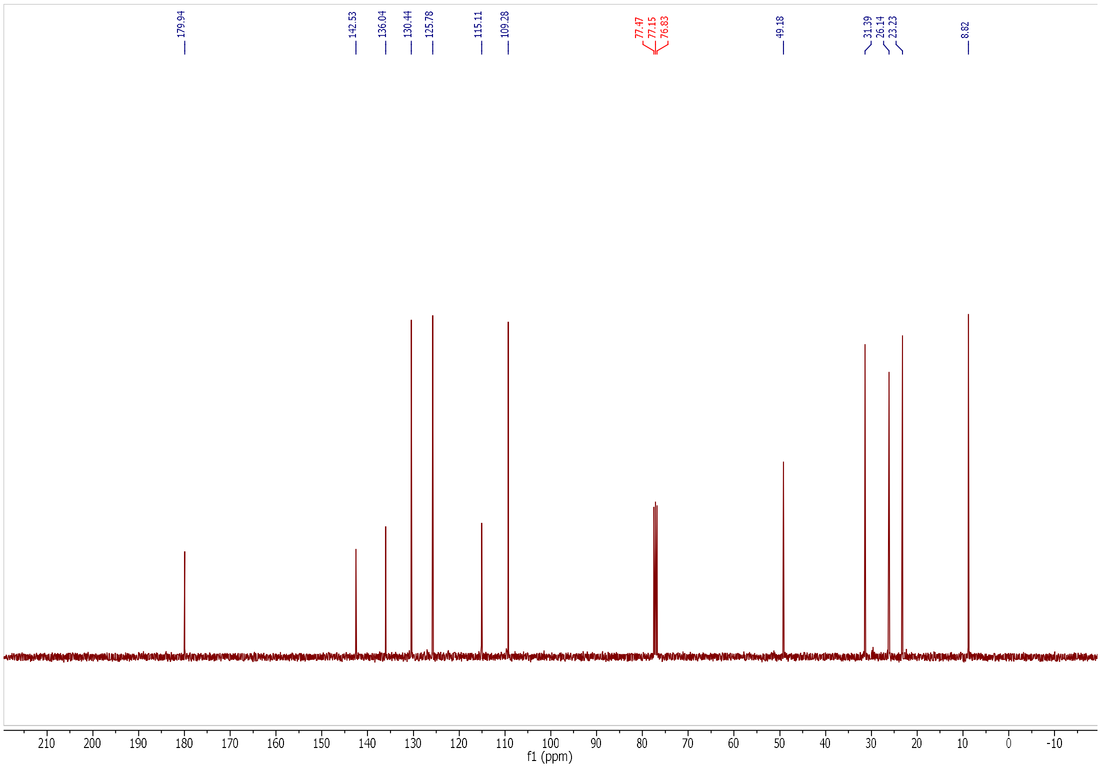
^{13}C NMR



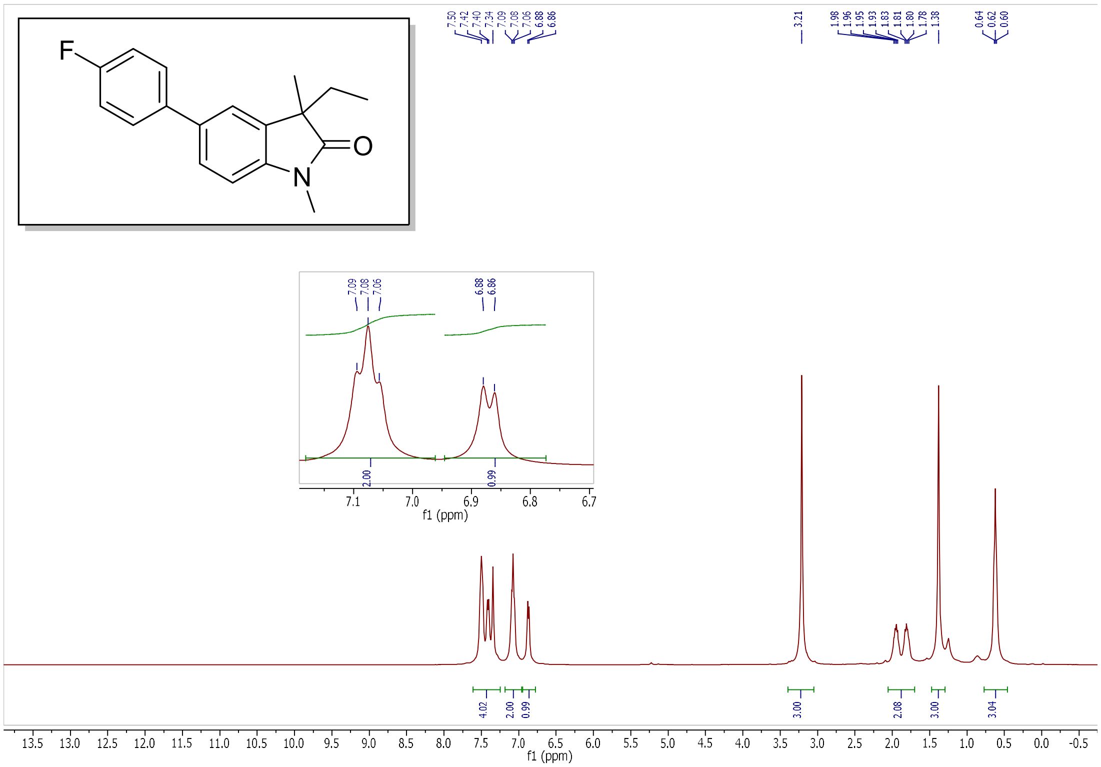
^{1}H NMR



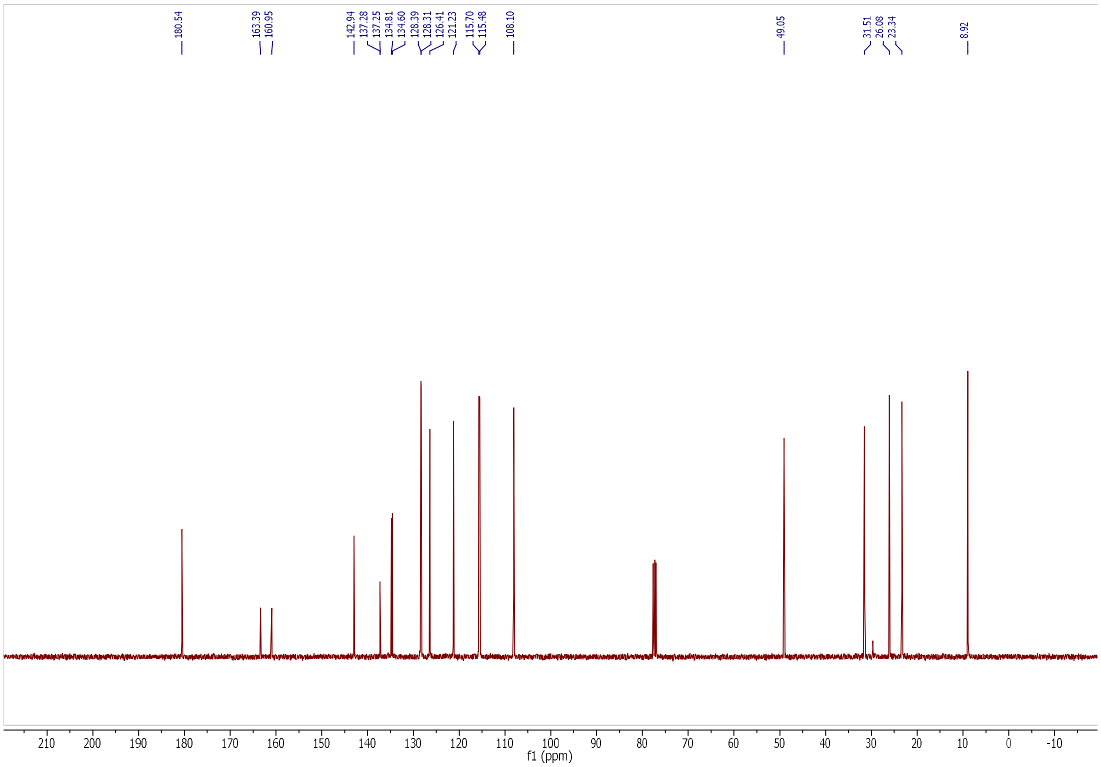
^{13}C NMR



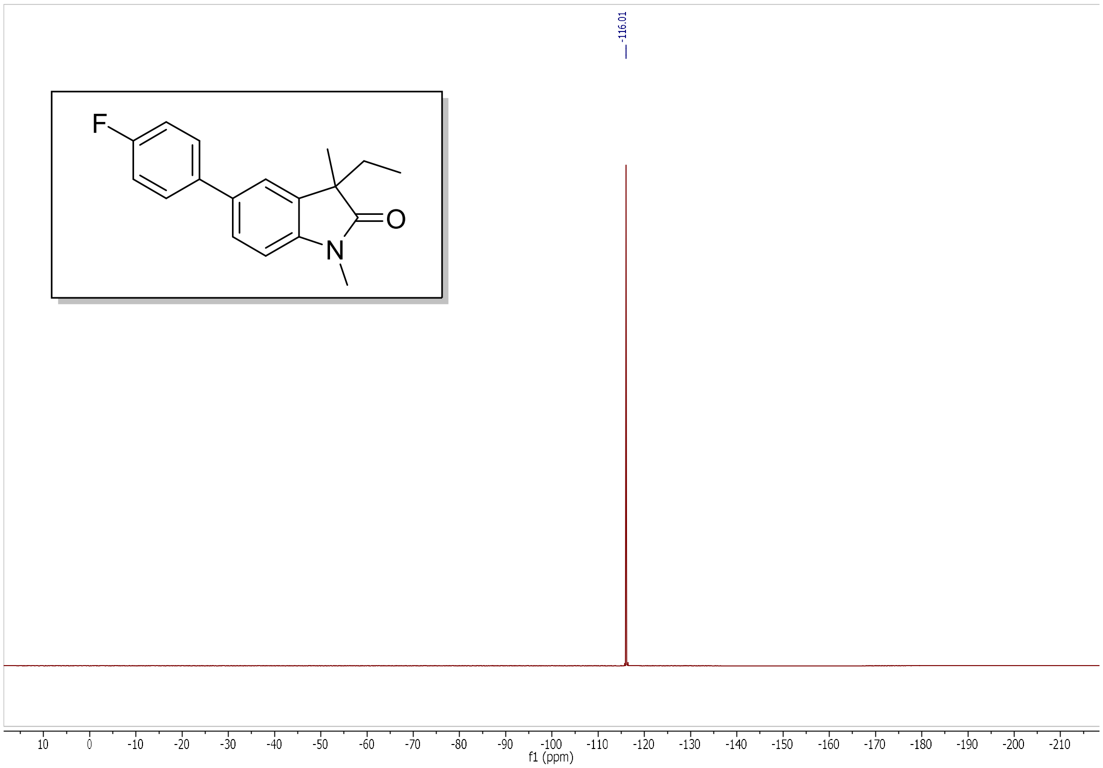
^{1}H NMR



^{13}C NMR



^{19}F NMR


-116.01
F
O
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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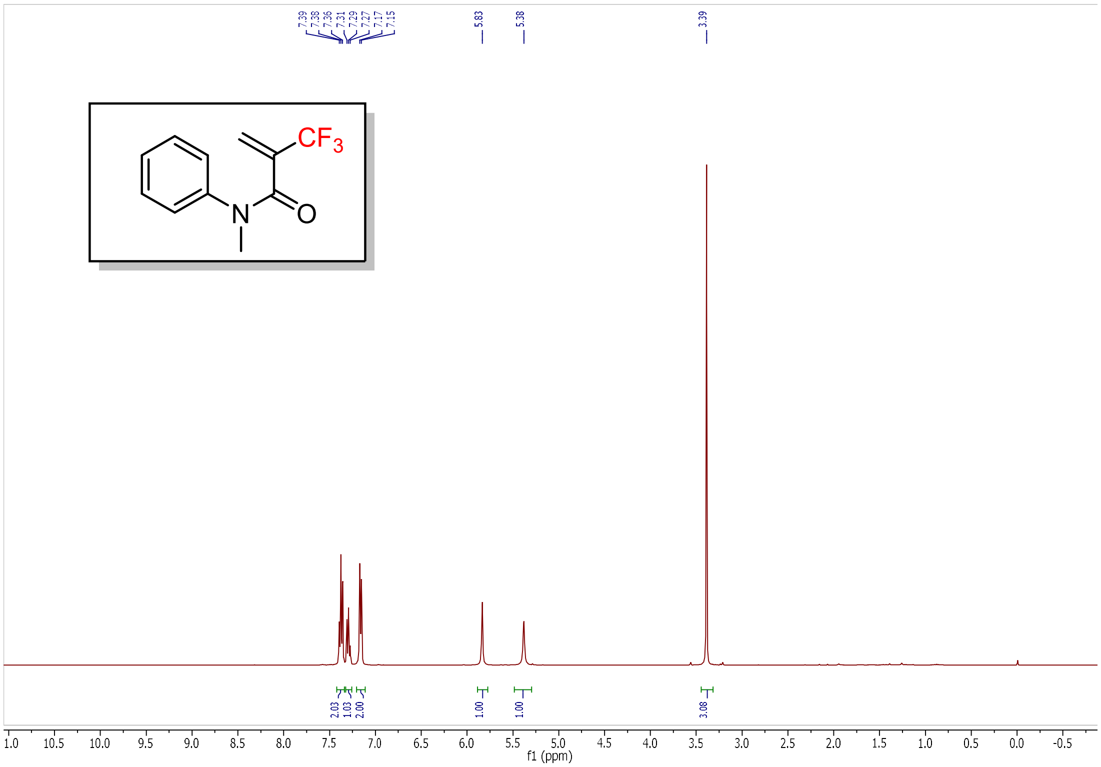
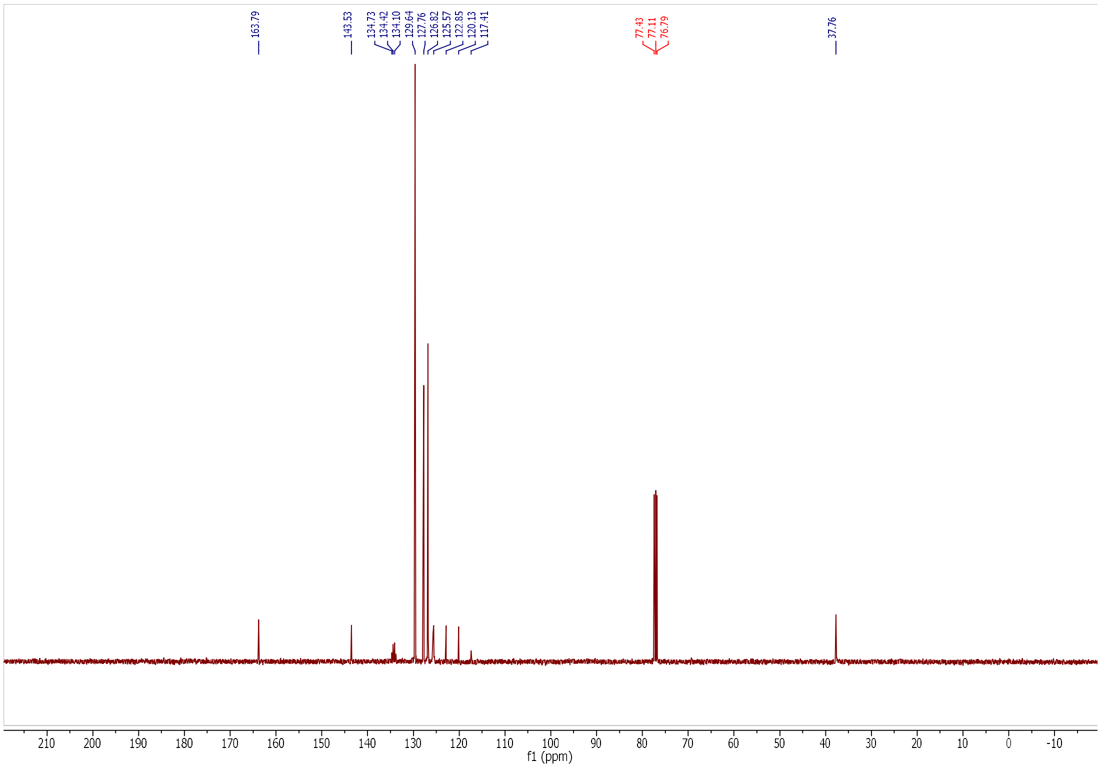
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

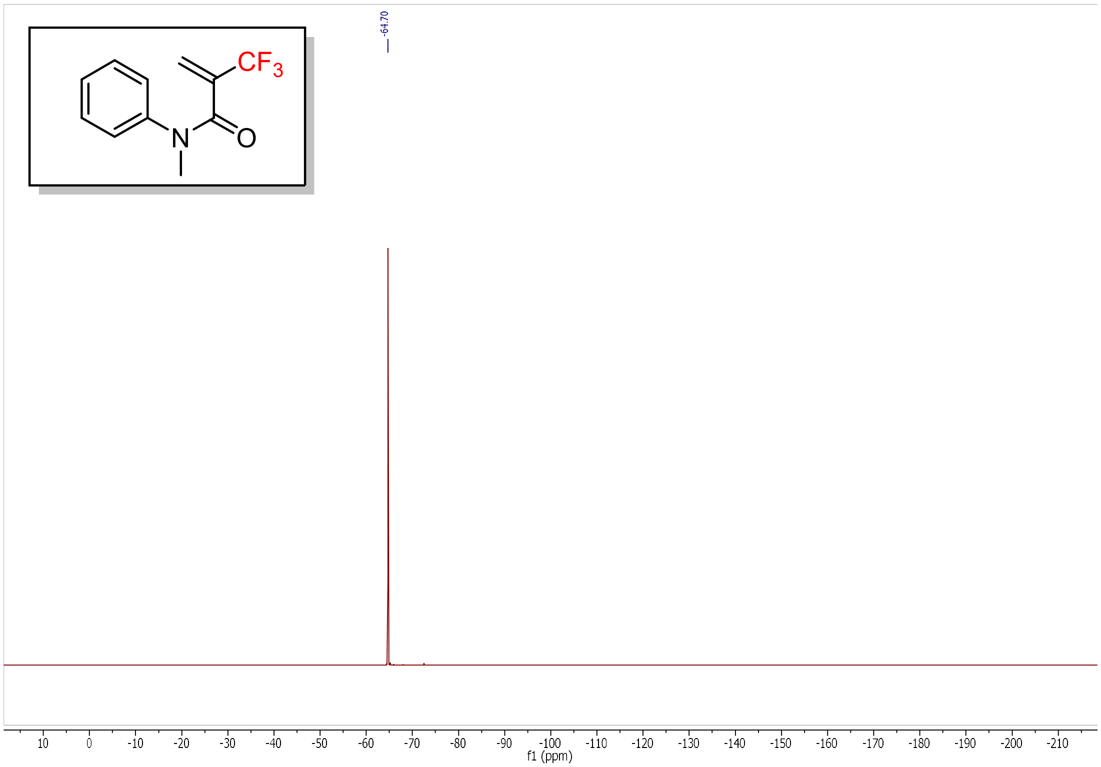
^{1}H NMR



^{13}C NMR



^{19}F NMR


-64.70
CF3
N
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-160
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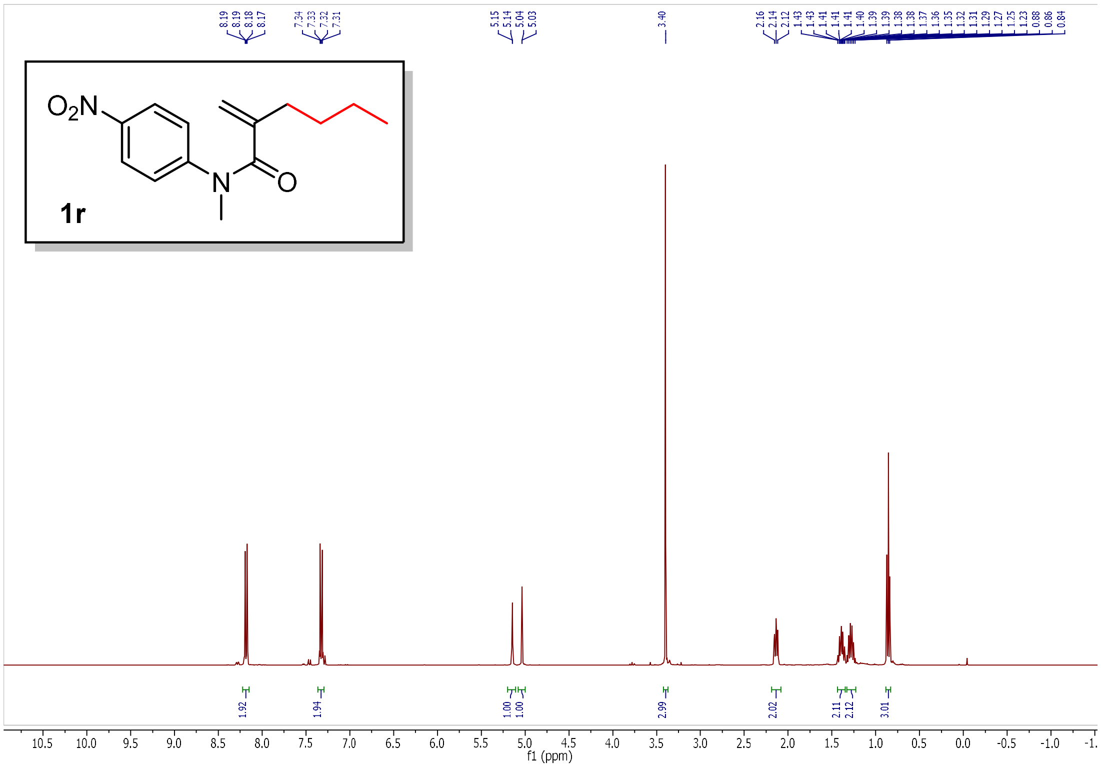
-200
-210
f1 (ppm)

^{1}H NMR



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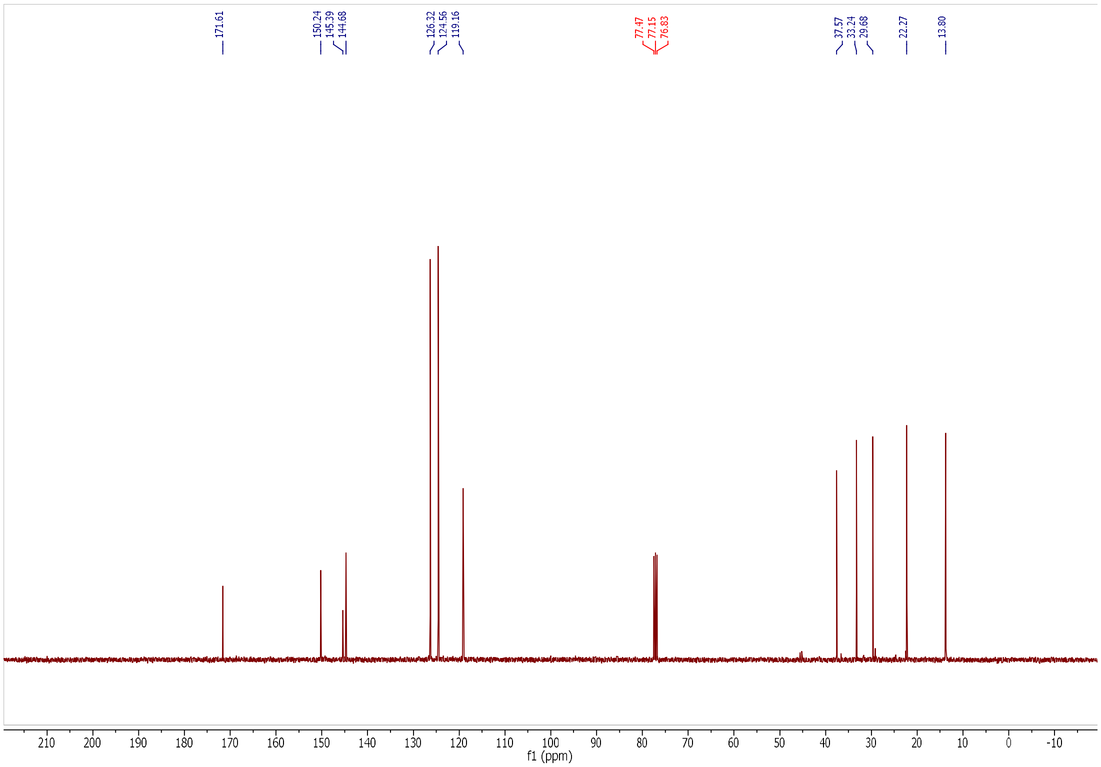

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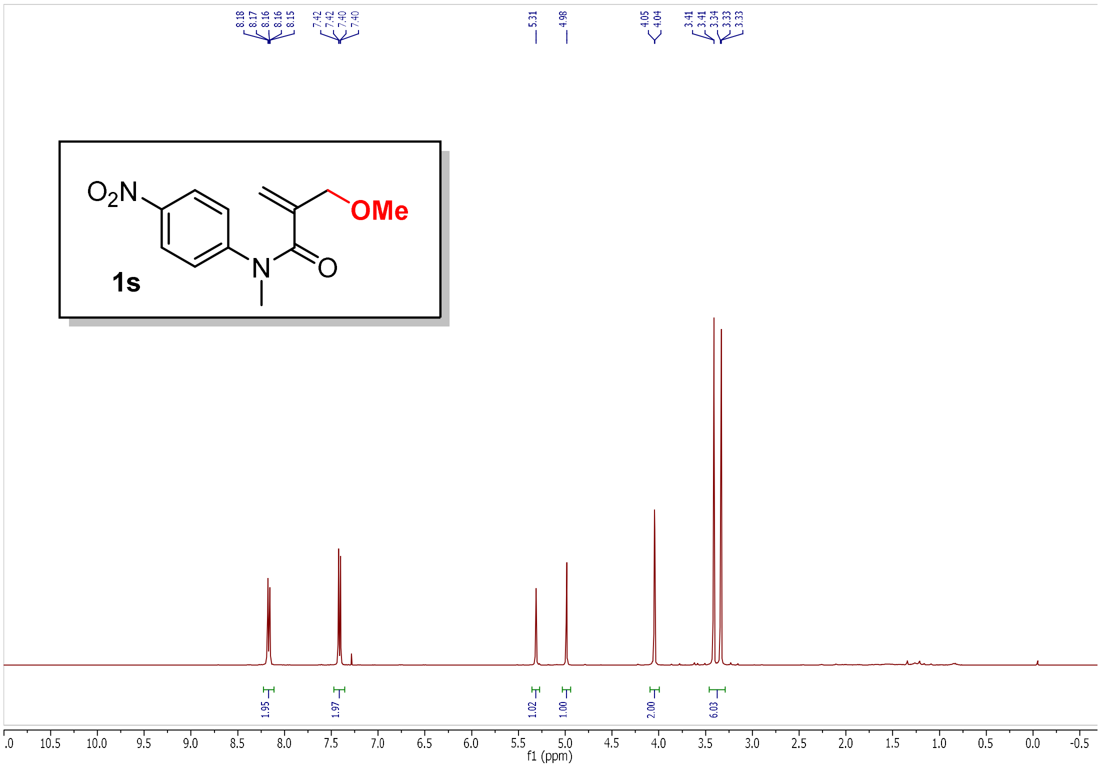
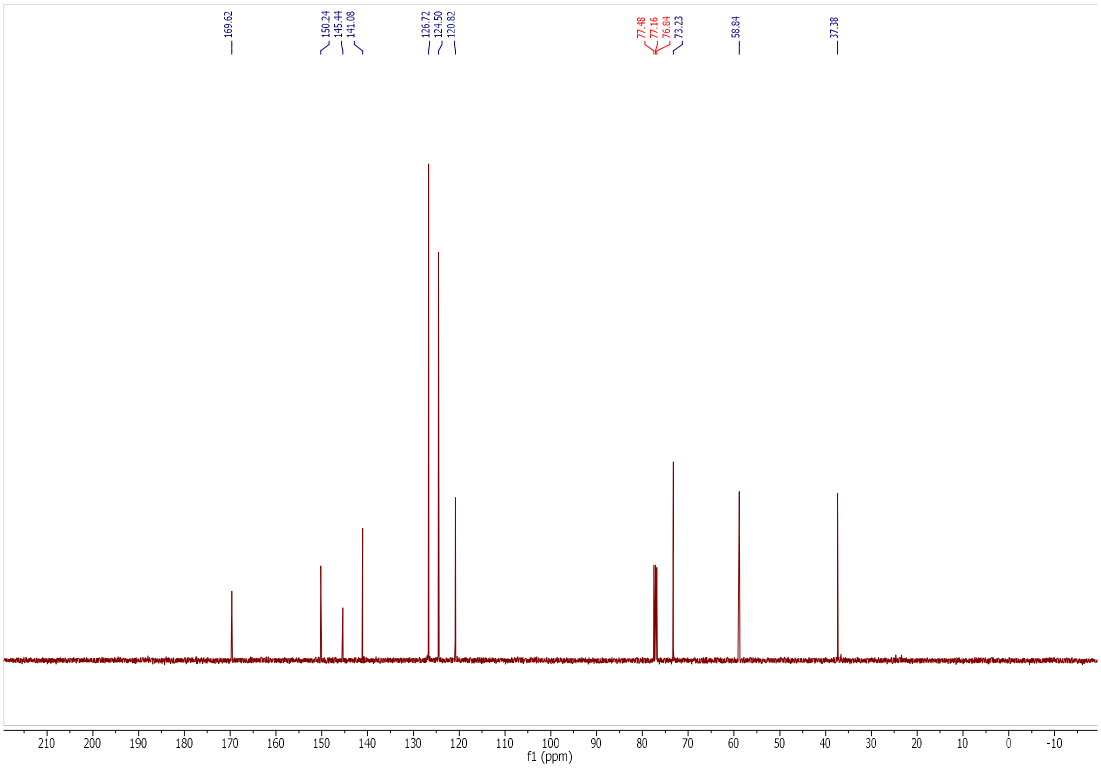
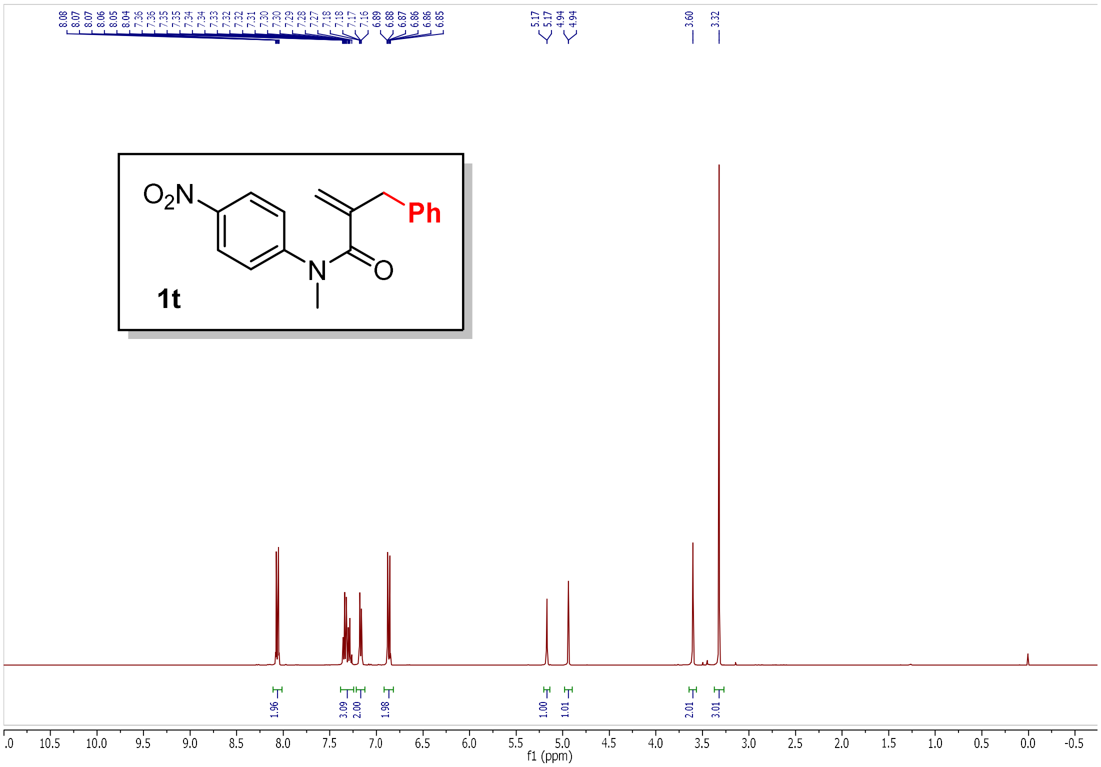


^{13}C NMR



^{1}H NMR



^{13}C NMR