Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

Ruthenium-catalyzed synthesis of vinylamides at low acetylene pressures

Elena Semina, Pavel Tuzina, Frank Bienewald, A. Stephen K. Hashmi, Thomas Schaub

Supporting information

Table of content

S1. General Information 2
S2: ICP MS analysis 4
S3: General Procedure for the Ligand Screening (Chem Speed) 5
S4: General procedures and optimization table 6
S5: A limitation of the catalytic system 14
S6. The optimization table of the vinylation of 5-methyl-2-oxazolidinone 2b using $RuCl_3$ as a catalyst source 16
S7: Synthesis and characterization 17
S8: ^{1}H and ^{13}C Spectra 21
S9: References 43

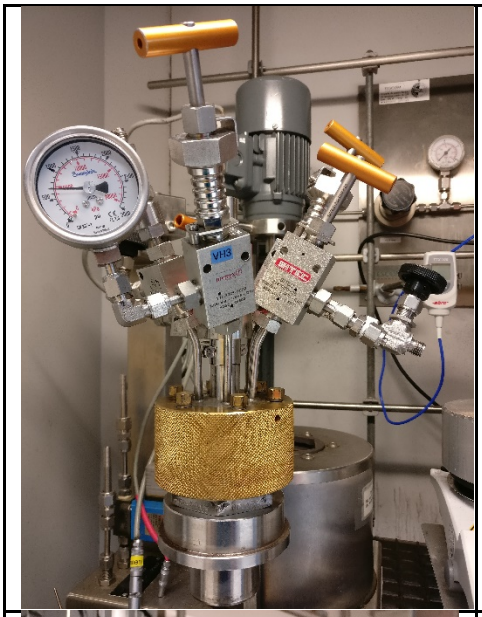
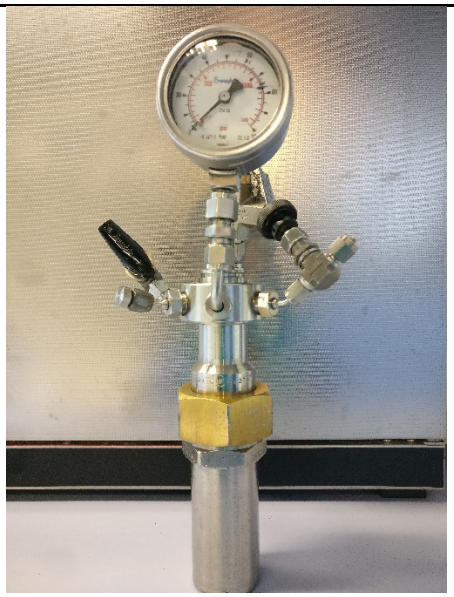
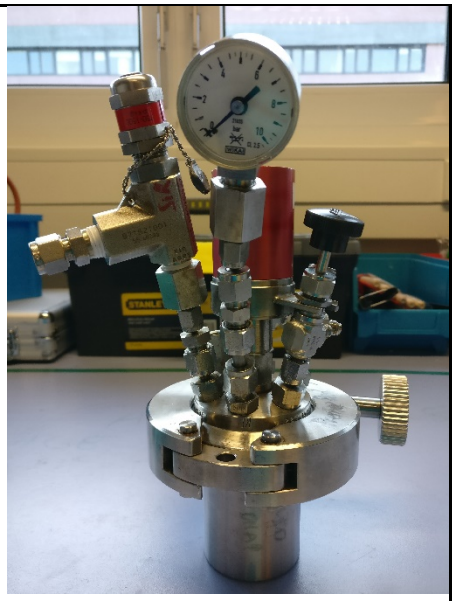
S1. General Information

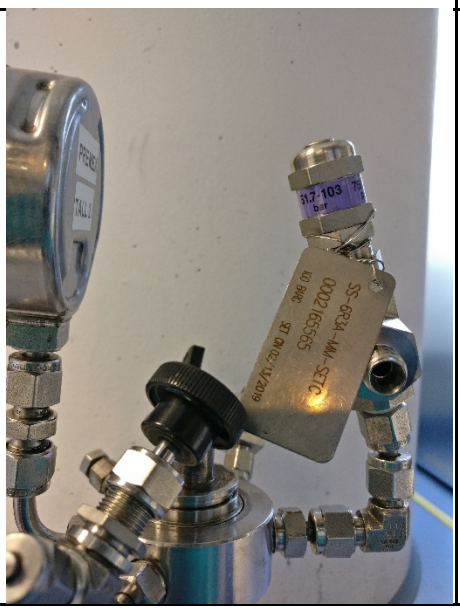
All chemicals and solvents were purchased from Sigma-Aldrich, ABCR, Acros, Fisher Scientific and used without further purification. Solvents for extractions and chromatography were reagent grade and used as received. Extracts were dried over technical grade Na_2SO_4 or $MgSO_4$. Analytical thin layer chromatography (TLC) was performed on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 polyester sheets. Visualization was achieved using UV lamp (check) or potassium permanganate stain [$KMnO_4$ (10 g), K_2CO_3 (65 g), and aqueous NaOH solution (1N, 15 mL) in water (1000 mL)] followed by heating. Column chromatography was carried out using Biotage ® SNAP Cartridge KP-Sil on Isolera.
^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Avance III 300, Avance III 400, Avance III 500, a Bruker Avance DRX 300, or a Bruker Fourier 300 spectrometer at ambient temperature. Chemical shifts δ are reported in ppm relative to either the residual solvent peak (CD_3CN: δ = 1.94 ppm, $CDCl_3$: δ = 7.26 ppm, CD_2Cl_2 = 5.32). Coupling constants *J* are reported in Hz. The multiplicities are reported as: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, td = triplet of doublets, tt = triplet of triplets, qd = quartet of doublets.
GC analysis were performed on an Agilent Technologies 6890N gas chromatography system equipped with a FID detector and an Agilent Technologies DB-1 capillary column (30 m x 0.250 mm / 1.0 µm) or an Agilent Technologies Rtx-5 Amine Capillary Column (30m x 0.32mm / 1.50µm). GC-MS analyses were performed on an Agilent Technologies 6890N gas chromatography system coupled with an Agilent Technologies 5975B mass spectrometer and equipped with an Agilent Technologies HP-5MS capillary column (30 m x 0.250 mm / 0.25 µm).
Mass spectra were recorded on a Vacuum Generators ZAB- 2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. IR spectra (in cm^{-1}) were recorded on a Varian 2000, Scimitar Series, FTS2000, as KBr pellets at room temperature. Elemental Analysis measurements were performed by the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg. Melting points were measured with a Büchi Melting Point B-540 apparatus.
All experiments were carried out in Premex or Hastelloy C type reactors with 40 mL nominal volumes (see table below).

***Caution**: Reactions must be carried out in a well ventilated fume hood. The used reactors must tolerate up to at least 12 times greater pressure than the working pressure. The equipment must be copper- or silver-free, since the acetylides of these elements are especially prone to explosion.*[1]

Table: Types of autoclaves

Hastelloy C	Premex (tall)	Premex
Material		
Nickel-chromium alloy	Stainless steel	Stainless steel
Pressure tolerance		
Up to 1000 bar	51.7 - 103	50 - 100
Sealing		
Metal-to-metal	Kalrez (O-ring)	Kalrez (O-ring)

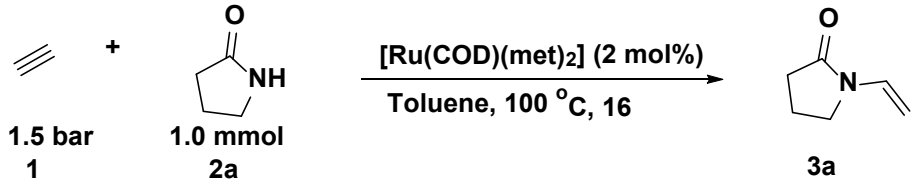

VH3



premex
SITEC
720.1433-HC22
2000 bar - DN13
HC22 - 2.4602

31.7-103
bar
SS-6BA-M-SEIC
0002165565

T8
EX RED 7

S2: ICP MS analysis

ICP MS analysis of the reaction solution after filtration via Rotilabo ® Spritzenfilter, PTFE, 0.20 µm-Filter was performed in the certified central analytical department of BASF SE in Ludwigshafen, Germany:



Procedure (entry 1): An approximately 40 mL Premex autoclave was charged with [Ru(COD)(met)$_2$] (0.02 mmol, 6.5 mg), 2-pyrrolidinone (1.00 mmol, 88.0 mg), toluene (5.0 mL), and tri-n-butylphosphine (0.1 mmol, 21.0 mg) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times . Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 °C. The mixture was then stirred at the specified temperature for 16 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was filtered via Rotilabo ® Spritzenfilter, PTFE, 0.20 µm-Filter giving 4509.4 g of crude reaction solution. The aliquot (1.3 mL, 1185.2 mg) of the crude mixture was taken and given for the analysis. The determined content of Ru was 420 mg/kg.

Procedure (entry 2): An approximately 40 mL Premex autoclave was charged with [Ru(COD)(met)$_2$] (0.02 mmol, 6.4 mg), 2-pyrrolidinone (1.00 mmol, 89.0 mg), toluene (5.0 mL), tri-n-butylphosphine (0.06 mmol, 14.0 mg) and DMAP (0.04 mmol, 5.0 mg) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 °C. The mixture was then stirred at the specified temperature for 16 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was filtered via Rotilabo ® Spritzenfilter, PTFE, 0.20 µm-Filter giving 4187.1 g of crude reaction solution. The aliquot (1.3 mL, 1166.5 mg) of the crude mixture was taken and given for the analysis. The determined content of Ru was 500 mg/kg.

Entry	P(nBu)$_3$ (mol%)	DMAP (mol%)	m of the crude reaction mixture, mg	m of the aliquot for the analysis, mg	Determined content of Ru, mg/kg	ICP-Ms result (Ru content)
1	10	none	4509.4	1185.2	420	95 %
2	6	4	4187.1	1166.5	500	105 %

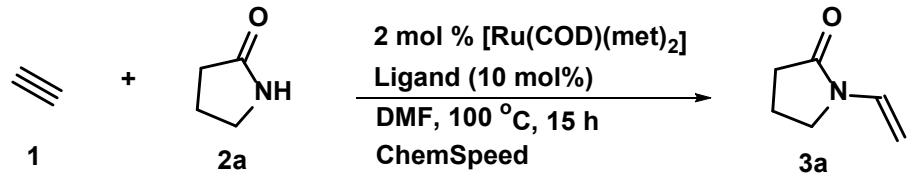
Conclusion: The analysis of the crude reaction mixtures by ICP MS from both aforementioned experiments revealed that about 100% of the used Ruthenium remains in the filtered crude reaction solution. This indicates that the catalyst is not precipitating as ruthenium-black during the reaction.

S3: General Procedure for the Ligand Screening (Chem Speed)

(description of the setup)

Screening reactions with 2-pyrrolidinone **2a** were performed in a ChemSpeed Accelerator SLT 106 high-throughput robot system. Acetylene in DMF (0.4 M) 2-Pyrrolidinone **2a** (1.00 mmol), [Ru(COD)(met)$_2$] catalyst (2 mol%) and ligand (6 mol%) in DMF (3 mL) were pressurized with N_2 (10 bar) and stirred at 100 °C for 16 h. After releasing the pressure and cooling to room temperature, the reaction mixture was analyzed by GC to determine the conversion of the starting material **2a** to product **3a**.

Preparation of the stock solution of acetylene in DMF: anhydrous DMF was filled into Premex (40 mL) autoclave in the glovebox. Subsequently, the autoclave with DMF was charged under 1.5 bar of acetylene (gas station) at room temperature for 15 min. The mixture was stirred for another 15 min at room temperature and subsequently was depressurized. The autoclave was placed into the glovebox and the solution was transferred into the flask suitable for the ChemSpeed setup. The concentration of acetylene in DMF was determined by analyzing of ^{1}H-NMR of the freshly prepared solution using DMF as an internal standard.

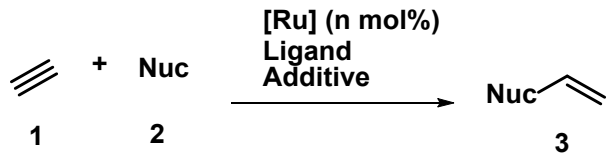


0.4 M Stock solution in DMF

Entry	Ligand	Product, GC[a]	Separate run
1	P(*n*Bu)$_3$	26,2	100 [b]
2	P(Oct)$_3$	16,9	100 [b]
3	PCy$_3$	17,5	35 [b]
4	P(*t*Bu)$_3$	2,0	-
5	P(Me)$_3$	0	0 [b]
6	depe	0,1	-
7	dcpe	1,9	-
8	dmpe	0	-
9	dppe	0	-
10	*t*bpmb	1,2	-
11	P(OMe)$_3$	0	-
12	P(OPh)$_3$	0	-
13	triphos	0,4	-
14	Imes	0,7	-
15	Ipr	5,3	14 [b]

[a] The reactions were run with ChemSpeed. [b] The reaction was run in a separate reactor following the General procedure A in toluene (*vide infra*, S4)

S4: General procedures and optimization table



A) General procedure A for the synthesis of (entry 1, 9, 10, 11, 12, 13, 14, 15, 19, 23, 28, 30, 32, 33, 35, 37, 38, 39, 45, 47, 49, 50) An approximately 40 mL autoclave (Premex, Hastelloy C) was charged with [Ru(COD)(met)$_2$] (0.001-0.060 mmol), *N*-nucleophile (amide) (1.00 mmol), toluene (5.0 -10.0 mL, entries 1, 10, 11, 12, 13, 15, 19, 23, 30, 32, 33, 35, 39, 45, 47, 49) or dichloromethane (10.0 ml, entry 9) or dimethylformamide (5.0 ml, entries 28, 37, 38, 40, 50) or in absence of the solvent (entry 14) and tri-n-butylphosphine (0.005 – 0.18 mmol) or trioctylphosphine (0.10 mmol) or tricyclohexylphosphine (0.10 mmol) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 - 140 °C. The mixture was then stirred at the specified temperature for 14 - 18 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. Subsequently, it was dissolved in 1.0 mL of CH_2Cl_2 and coated on silica. The product was isolated by column chromatography (petroleum ether/ethyl: acetate 8/2 or hexane/ diethyl ether 1/1 – for different products the system ratio was slightly varied). When the reaction was performed in DMF, the product was either extracted with dichloromethane from aqueous solution of the reaction mixture, organic layer was washed with water minimum 5 times (entries 40, 41) or collected in a round bottom flask and concentrated under vacuum followed by column chromatography isolation (petroleum ether/ethyl acetate, entries 20, 36, 37).

B) General procedure B for the synthesis of (entry 24, 25, 26, 27, 29, 31, 34, 36, 41, 42, 43, 44, 46, 48) An approximately 40 mL autoclave (Premex, Hastelloy) was charged with [Ru(COD)(met)$_2$] (0.02 - 0.06 mmol), *N*-nucleophile (1.00 mmol), toluene (5.0 mL, entries 24, 25, 26, 27, 29, 31, 34, 36, 42, 46, 48) or dimethylformamide (5.0 - 8.0 mL, entries 41, 43, 44), DMAP (0.04 – 0.12 mmol) and tri-*n*-butylphosphine (0.06 – 0.18 mmol) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 - 150 °C. The mixture was then stirred at the specified temperature for 14 - 18 h. **Note**: *At this temperature the internal pressure rises to 4 - 6 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. Subsequently, it was dissolved in 1.0 mL of CH_2Cl_2 and coated on silica. The product was isolated by column chromatography (petroleum ether/ethyl: acetate 8/2 – for different products the system ratio was slightly varied).

C) General procedure C for the synthesis of (entry 2, 3) An approximately 40 mL autoclave (Premex, Hastelloy C) was charged with Ruthenium 5 % on activated charcoal (100 mg), 2-pyrrolidinone (13.10 mmol, 1120 mg), and diglyme (for entry 2) or toluene (for entry 3) (8.0 mL) under argon atmosphere in the Glovebox. After

closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 170 °C. The mixture was then stirred at the specified temperature for 14 h. **Note**: *At this temperature the internal pressure rises to 5 (diglyme)/7 (toluene) bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. The crude mixture was analyzed by GC and/or NMR. Product was not isolated.

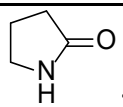
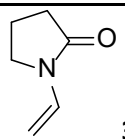
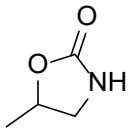
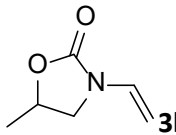
D) **General procedure D for the synthesis of (entry 4)** An approximately 40 mL autoclave (Premex, Hastelloy C) was charged with Ruthenium 5% on activated charcoal (10 mg), 2-pyrrolidinone (1.00 mmol, 85 mg), and toluene (10.0 mL) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 170°C. The mixture was then stirred at the specified temperature for 14 h. **Note**: *At this temperature the internal pressure rises to 7 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. The crude mixture was analyzed by GC and/or NMR. Product was not isolated.

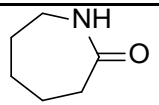
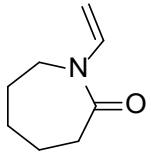
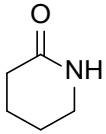
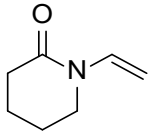
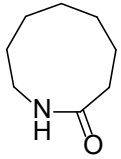
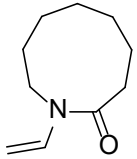
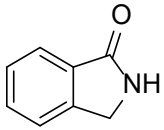
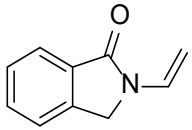
E) **General procedure E for the synthesis of (entry 5, 6, 7, 8)** An approximately 40 mL autoclave (Premex, Hastelloy C) was charged with 2 mol % Ruthenium catalyst ($RuCl_3 \cdot 3H_2O$ – entry 5; $Ru(acac)_3$ – entry 6; $Ru_3(CO)_{12}$ – entry 7; $[Ru(COD)(met)_2]_2$ – entry 8), 2-pyrrolidinone (1.00 mmol, 85 mg), and toluene (5.0 mL) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 °C. The mixture was then stirred at the specified temperature for 16.-.19 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. The crude mixture was analyzed by GC. Product was not isolated.

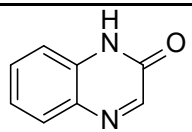
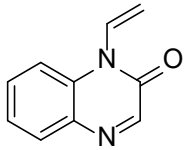
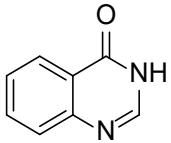
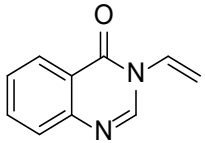
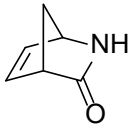
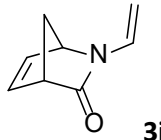
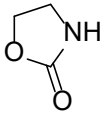
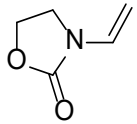
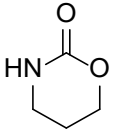
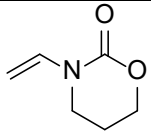
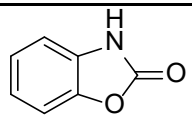
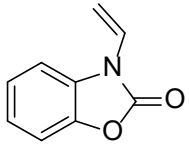
F) **General procedure F for the synthesis of (entry 16)** An approximately 40 mL autoclave (Premex) was charged with 20 mol% of tri-*n*-butylphosphine (0.20 mmol, 42 mg), 2-pyrrolidinone (1 mmol, 85 mg), and toluene (10.0 mL) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 °C. The mixture was then stirred at the specified temperature for 16 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. The crude mixture was analyzed by GC. Product was not formed.

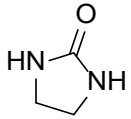
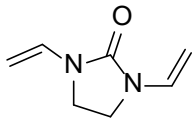
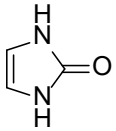
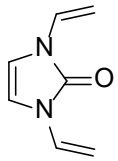
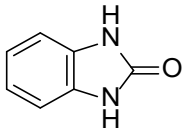
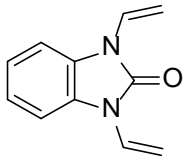
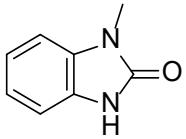
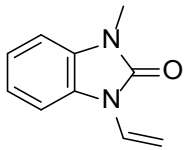
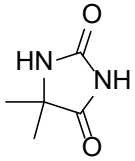
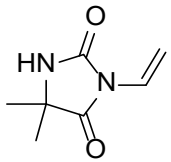
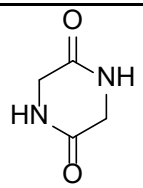
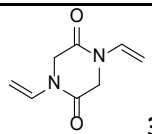
G) **General procedure G for the synthesis of (entry 17, 18, 20, 21, 22)** An approximately 40 mL autoclave (Premex, Hastelloy C) was charged with anhydrous ruthenium (III) chloride (0.03 mmol, entry 26) or ruthenium (III) chloride hydrate (0.03-0.09 mmol, entries 17, 18, 20, 21, 22), 5-methyl-1,3-oxazolidin-2-one (1.00 mmol, 101 mg), toluene (5.0 mL), and tri-n-butylphosphine (0.06 – 0.12 mmol, entries 17, 18, 20, 21) or triphenylphosphine (0.10 mmol, entry 22) under argon atmosphere in the Glovebox. After closing the reaction vessel, the system was purged with acetylene (three times). Finally, the autoclave was pressurized with

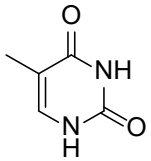
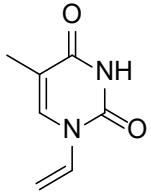
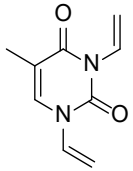
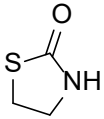
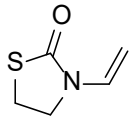
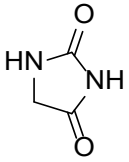
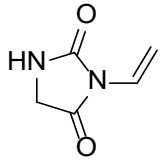
acetylene (at 1.5 bar for 15 min at room temperature) and heated at 100 °C. The mixture was then stirred at the specified temperature for 14 - 16 h. **Note**: *At this temperature the internal pressure rises to 3 - 4 bar*. Then, the reaction was cooled down on a water bath and depressurized carefully. The crude mixture was collected in a round bottom flask and concentrated under vacuum. The crude mixture was analyzed by GC and/or NMR. Product was not isolated.

Entry	Procedure	Nuc **2**	Cat/ mol %	Ligand/ mol%	Additive/ mol%	Solvent	T, °C	t, h	Product **3**	Yield, % (isolated)	Conversion of starting material to product (area ratio %, GC)
1	A	 **2a**	$[Ru(COD)(met)_2]/2$	$PnBu_3$/ 10	-	Tol	100	15	 **3a**	89	100
2	C		Ru/C /5	-	-	Diglyme	170	14		-	6
3	C		Ru/C /5	-	-	Tol	170	16		-	10
4	D		Ru/C /5	-	-	Tol	170	16		-	<1
5	E		$RuCl_3$-$3H_2O$/ 2	-	-	Tol	100	19		-	5
6	E		$Ru(AcAc)_3$/ 2	-	-	Tol	100	19		-	0
7	E		$Ru_3(CO)_{12}$/ 2	-	-	Tol	100	19		-	8
8	E		$[Ru(COD)(met)_2]/2$	-	-	Tol	100	16		-	0,9
9	A		$[Ru(COD)(met)_2]/2$	$PnBu_3$/ 10	-	DCM	100	17		-	28
10	A		$[Ru(COD)(met)_2]/1$	$PnBu_3$/ 10	-	Tol	100	17		78 (IS, NMR) [a]	100
11	A		$[Ru(COD)(met)_2]/0,1$	$PnBu_3$/ 0,5	-	Tol	100	17		26 (IS, NMR) [a]	30
12	A		$[Ru(COD)(met)_2]/2$	$P(Oct)_3$/ 10	-	Tol	100	17		79 (IS, NMR) [a]	100
13	A		$[Ru(COD)(met)_2]/2$	PCy_3	-	Tol	100	17		35 (IS, NMR) [a]	35
14	A		$[Ru(COD)(met)_2]/2$	$PnBu_3$/ 10	-	-	100	17		-	95
15	A	 **2b**	$[Ru(COD)(met)_2]/2$	$PnBu_3$/ 10	-	Tol	100	16	 **3b**	84	100
16	F		-	$PnBu_3$/ 20	-	Tol	100	16		-	0
17	G		$RuCl_{3(anhyd)}$/3	$PnBu_3$/ 10	-	Tol	100	16		-	50

18	G		$RuCl_3$-H_2O/3	$PnBu_3$/ 10	-	Tol	100	16		-	67
19	A		[Ru(COD)(met)$_2$]/2	PPh_3/ 10	-	Tol	100	16		17	20
20	G		$RuCl_3$-H_2O/3	$PnBu_3$/ 6	DMAP/4	Tol	100	15		-	13
21	G		$RuCl_3$-H_2O/9	$PnBu_3$/ 12	-	Tol	100	14.5		-	100
22	G		$RuCl_3$-H_2O/3	PPh_3/ 10	-	Tol	100	14		-	0
23	A	 **2c**	[Ru(COD)(met)$_2$]/2	$PnBu_3$/ 10	-	Tol	100	17,5	 **3c**	33	33
24	B		[Ru(COD)(met)$_2$]/2	$PnBu_3$/ 6	DMAP/4	Tol	100	16		80	100
25	B	 **2d**	[Ru(COD)(met)$_2$]/2	$PnBu_3$/ 6	DMAP/4	Tol	100	6	 **3d**	85	100
26	B	 **2e**	[Ru(COD)(met)$_2$]/2	$PnBu_3$/ 6	DMAP/4	Tol	100	14,5	 **3e**	60	74
27	B	 **2f**	[Ru(COD)(met)$_2$]/2	$PnBu_3$/ 6	DMAP/4	Tol	150	15	 **3f**	75	100

28	A	 **2g**	[Ru(COD)(met)$_2$]/4	PnBu$_3$/ 6	-	DMF	140	17	 **3g**	13	NA
29	B	 **2h**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	Tol	140	16	 **3h**	58	NA
30	A	 **2i**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	Tol	100	16	 **3i**	57	82
31	B	 **2j**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	Tol	100	16	 **3j**	9	100
32	A		[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	-	Tol	100	16		29	100
33	A	 **2k**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	-	Tol	100	16	 **3k**	82	100
34	B	 **2l**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	Tol	100	16	 **3l**	10	NA
35	A		[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	Tol	100	15		25	NA

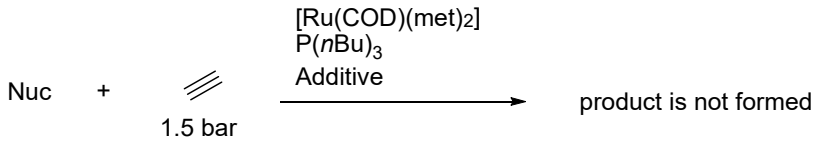
36	B	 **2m**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	Tol	120	16	 **3m**	15	NA
37	A	 **2n**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	-	DMF	140	16	 **3n**	25	57
38	A	 **2o**	[Ru(COD)(met)$_2$]/6	PnBu$_3$/ 18	-	DMF	140	16	 **3o**	27	N/A
39	A	 **2p**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	-	Tol	130	16	 **3p**	37	N/A
40	A	 **2q**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	DMF	100	18	 **3q**	38	NA
41	B		[Ru(COD)(met)$_2$]/6	PnBu$_3$/ 18	DMAP/12	DMF	130	18		30	NA
42	B	 **2r**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	Tol	140	14	 **3r**	99	

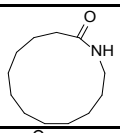
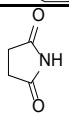
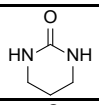
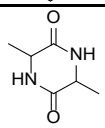
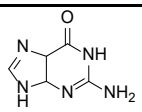
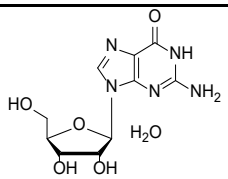
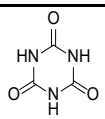
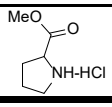
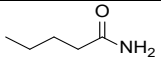
43	B	 **2s**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/4	DMF	150	16	 **3s**	20 (vinyl) + traces divinyl	NA
44	**B**		[Ru(COD)(met)$_2$]/6	PnBu$_3$/ 18	DMAP/12	DMF	150	16	 **3t**	11	NA
45	A	 **2u**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	-	Tol	100	15	 **3u**	22	64
46	B		[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 6	DMAP/ 4	Tol	100	15		-	82
47	A		[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	Tol	100	15		-	51
48	B		[Ru(COD)(met)$_2$]/3	PnBu$_3$/ 6	DMAP/ 4	Tol	100	15		49	97
49	A	 **2v**	[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	Tol	100	16	 **3v**	-	5
50	A		[Ru(COD)(met)$_2$]/2	PnBu$_3$/ 10	-	DMF	100	16		56 (not isolated)	NA

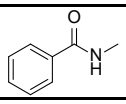
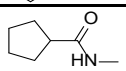
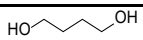
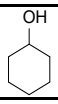
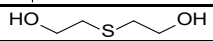
[a] Mesitylene was used as an internal standard for the yield determination

S5: A limitation of the catalytic system

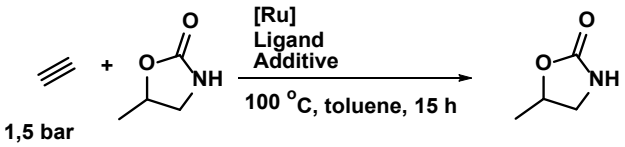
All reactions were performed following the general procedures A or B. The desired vinylated substrates were not obtained when nucleophiles (see table below) were treated with acetylene.



Entry	Nuc	mol % of [Ru(COD)(met)$_2$]	mol% of P(nBu)$_3$	Additive/ mol%	Solvent	T, °C	t, h
Cyclic amides							
1		2	6	DMAP/4	Toluene	100	15
2		2	6	-	DMF	130	
3		4	6	-	DMF	140	17
4		2	10	-	DMF	100	16
5		2	6	DMAP/4	Toluene	100	16
6		2	6	Yb(OTf)$_3$/4	DMF	120	16
7		4	12	-	DMF	140	16
8		2	6	DMAP/4	DMF	150	14
9		2	6	DMAP/4	Toluene	190	16
10		6	18	DMAP/12	DMF	190	16
11		2	6	-	DMF	130	16
12		2	6	-	DMSO	130	16
13		6	18	DMAP/12	DMF	150	16
14		2	6	DMAP/ 4	Toluene	140	4
15		2	6	-	Toluene	100	15
16		2	6	DMAP/ 4	Toluene	140	16
17		4	12	DMAP/ 8	DMF	140	16
18		4	12	Pyridine/8	DMF		
Acyclic amides							
19		2	10	-	Toluene	100	15
20		2	10	-	Toluene	100	15
21		2	10	-	Toluene	100	15
22		2	6	DMAP/4	Toluene	150	16
23		2	10	-	DMF	100	15

24		2	10	-	DMF	100	15
25		2	6	DMAP/ 4	Toluene	120	15
Cyclic amines							
26		2	10	DMAP/ 4	Toluene	120	15
27		2	10	-	Toluene	100	15
Alcohols							
28		2	6	DMAP/4	Toluene	100	16
29		2	10	-	Toluene	100	15
30		2	10	-	Toluene	100	15
31		2	10	-	Toluene	100	15

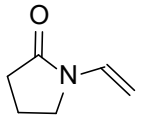
S6. The optimization table of the vinylation of 5-methyl-2-oxazolidinone 2b using $RuCl_3$ as a catalyst source



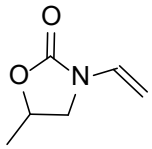
Entry	[Ru] (mol %)	Ligand (mol %)	Additive (mol %)	Conversion to product (NMR, %)[a]
1	$RuCl_{3(anhydrous)}$ (3)	P*n*Bu_3 (10)	-	52
2	$RuCl_3 \cdot H_2O$ (3)	P*n*Bu_3 (10)	-	67
3	$RuCl_3 \cdot H_2O$ (3)	P*n*Bu_3 (6)	DMAP (4)	13
4	$RuCl_3 \cdot H_2O$ (6)	P*n*Bu_3 (12)	-	100
5	$RuCl_3 \cdot H_2O$ (3)	PPh_3 (10)	-	0

[a] Mesitylene was used as an internal standard for NMR analysis.

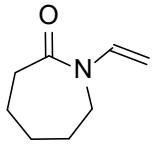
S7: Synthesis and characterization



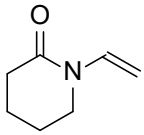
1-Vinylpyrrolidin-2-one **(3a)**. Synthesized following the general procedure "A" (Solvent – toluene). Yield: 89 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.14). Yellow oil. The spectroscopic data is in correspondence with the spectra of the commercial source (Sigma Aldrich, CAS Number 88-12-0). **^{1}H NMR** (301 MHz, CD_2Cl_2) δ 7.04 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.40 (d, *J* = 9.1 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 3.48 (t, *J* = 8.1 Hz, 2H), 2.42 (t, *J* = 8.1 Hz, 2H), 2.20 – 1.95 (m, 2H). **^{13}C NMR** (76 MHz, CD_2Cl_2) δ 173.5, 129.8, 93.9, 44.8, 31.6, 17.7.



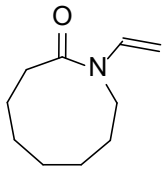
5-methyl-3-vinyloxazolidin-2-one **(3b)**. Synthesized following the general procedure "A" (solvent – toluene). Yield: 84 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.23). Pale yellow oil. The spectroscopic data is in correspondence with the spectra of the commercial source (BASF, CAS Number 3395-98-0).**^{1}H NMR** (301 MHz, CD_3CN) δ 6.80 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.74 (dp, *J* = 8.6, 6.5 Hz, 1H), 4.37 (dd, *J* = 9.0, 0.9 Hz, 1H), 4.31 (dd, *J* = 15.8, 0.9 Hz, 1H), 3.78 (t, *J* = 8.6 Hz, 1H), 3.23 (dd, *J* = 9.3, 6.5 Hz, 1H), 1.40 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, CD_3CN) δ 155.9, 130.9, 93.4, 72.0, 49.3, 20.9. **IR (film)**: 1063, 1094, 1246, 1431, 1467, 1637, 1758, 2890, 2934, 2983. **HRMS (EI)**: m/z calcd. for $C_6H_9NO_2$ [M$^+$]: 127.06278, found: 127.06303.



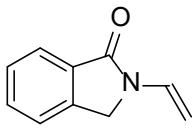
1-Vinylazepan-2-one **(3c)**. Synthesized following the general procedure "B" (Solvent – toluene). Yield: 80 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.20). Pale yellow oil. The spectroscopic data is in correspondence with the spectra of the commercial source (Sigma Aldrich, CAS Number 2235-00-9). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 16.1, 9.4 Hz, 1H), 4.44 (dd, *J* = 16.1, 1.3 Hz, 1H), 4.37 (dd, *J* = 9.4, 1.3 Hz, 1H), 3.62 – 3.49 (m, 2H), 2.68 – 2.53 (m, 2H), 1.78 – 1.57 (m, 6H).



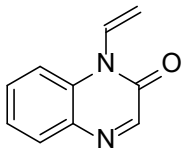
1-Vinylpiperidin-2-one **(3d)**: Synthesized following the general procedure "B" (Solvent – toluene). Yield: 85 % (column chromatography hexane/ diethyl ether 8/2, R_f 0.16). Pale yellow oil. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.53 (dd, *J* = 16.2, 9.4 Hz, 1H), 4.48 (d, *J* = 16.2 Hz, 1H), 4.35 (d, *J* = 9.4 Hz, 1H), 3.37 (t, *J* = 6.2 Hz, 2H), 2.38 (t, *J* = 6.5 Hz, 2H), 1.86 (p, *J* = 6.1 Hz, 2H), 1.76 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR** (126 MHz, CD_3CN) δ 169.3, 133.3, 93.3, 45.1, 33.5, 23.1, 21.2. **IR** (film): 1089, 1169, 1249, 1297, 1348, 1410, 1430, 1627, 1667, 2874, 2950. **HRMS** (EI): m/z calcd. for $C_7H_{11}NO$ [M$^+$]: 125.08352, found: 125.08448.



1-Vinylazonan-2-one **(3e)**. Synthesized following the general procedure "B" (Solvent – toluene). Yield: 60 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.3). Yellow oil. **^{1}H NMR** (301 MHz, CD_3CN) δ 7.38 (dd, *J* = 16.4, 9.5 Hz, 1H), 4.51 (d, *J* = 16.4 Hz, 1H), 4.39 (d, *J* = 9.5 Hz, 1H), 3.82 – 3.72 (m, 2H), 2.63 – 2.49 (m, 2H), 1.83 – 1.59 (m, 4H), 1.59 – 1.36 (m, 6H). **^{13}C NMR** (76 MHz, CD_3CN) δ 174.9, 131.9, 94.4, 45.3, 35.6, 29.0, 26.2, 26.0, 25.8, 23.2. **IR (film)**: 1030, 1182, 1254, 1346, 1385, 1421, 1449, 1626, 1659, 2865, 2928, 3021, 3109. **HRMS** (EI): m/z calcd. for $C_{10}H_{17}NO$ [M$^+$]: 167.13047, found: 167.13088.

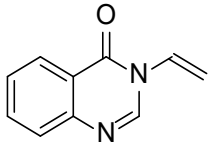


2-vinylisoindolin-1-one **(3f)**. Synthesized following the general procedure "B" (Solvent – toluene). Yield: 75 % (column chromatography hexane/ diethyl ether 8/2, R_f 0.27). White solid, T_{melt} = 48 °C. **^{1}H NMR** (301 MHz, CD_2Cl_2) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.64 – 7.44 (m, 3H), 7.30 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.65 (dd, *J* = 16.0, 0.9 Hz, 1H), 4.53 (s, 2H), 4.52 (dd, *J* = 9.0, 0.9 Hz, 1H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 166.5, 141.4, 132.7, 132.5, 129.4, 128.6, 124.2, 123.4, 93.6, 47.9. **IR (film)**: 1332, 1377, 1451, 1634, 1699, 2918. **HRMS** (EI): m/z calcd. for $C_{10}H_9NO$ [M$^+$]: 159.06787, found: 159.06735.

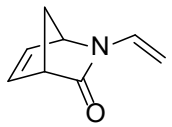


1-vinylquinoxalin-2(1H)-one **(3g)**. Synthesized following the general procedure "A" (Reaction temperature – 140 °C, solvent – DMF). Yield: 13 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.19). Pale yellow crystals, T_{melt} = 72 °C. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.22 (s, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.36 (ddd, *J* = 8.3, 6.7, 1.9 Hz, 1H), 6.68 (dd, *J* = 15.9, 8.5 Hz, 1H), 5.81 (dd, *J* = 8.5, 0.7 Hz, 1H), 5.76 (dd, *J* = 15.9, 0.7 Hz, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ

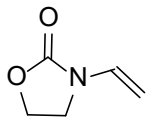
154.4, 151.2, 133.8, 132.6, 131.2, 130.7, 128.9, 124.4, 119.0, 115.4. **IR (film)**: 755, 1461, 1601, 1671, 2928, 3041. **HRMS** (EI): m/z calcd. for $C_{10}H_8N_2O$ [M⁺]: 172.06311, found: 172.06240.



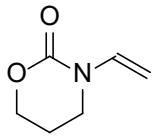
3-vinylquinazolin-4(3H)-one **(3h)**. Synthesized following the general procedure "B" (Reaction temperature – 140 °C, solvent – toluene). Yield: 58 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.09). Brown oil. **^{1}H NMR** (301 MHz, CD_2Cl_2) δ 8.32 – 8.23 (m, 1H), 8.28 (s, 1H), 7.84 – 7.66 (m, 2H), 7.52 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H), 7.40 (dd, *J* = 16.1, 9.1 Hz, 1H), 5.48 (dd, *J* = 16.1, 1.8 Hz, 1H), 5.20 (dd, *J* = 9.1, 1.8 Hz, 1H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 159.9, 147.9, 143.1, 134.9, 130.5, 128.0, 127.9, 127.2, 122.2, 106.1. **IR (film)**: 771, 1166, 1247, 1332, 1475, 1604, 1690, 3000, 3079. **HRMS** (EI): m/z calcd. for $C_{10}H_8N_2O$ [M⁺]: 172.06311, found: 172.06228.



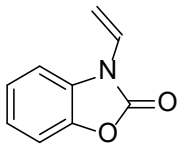
2-vinyl-2-azabicyclo[2.2.1]hept-5-en-3-one **(3i)**. Synthesized following the general procedure "A" (solvent – toluene). Yield: 57 % (column chromatography cexane/ diethyl ether 8/2, R_f 0.22). Viscous yellow oil. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 6.92 – 6.88 (m, 1H), 6.67 (dd, *J* = 16.3, 9.3 Hz, 1H), 6.64 – 6.58 (m, 1H), 4.64 (s, 1H), 4.41 (d, *J* = 16.3 Hz, 1H), 4.27 (d, *J* = 9.3 Hz, 1H), 3.35 (s, 1H), 2.28 (d, *J* = 8.1 Hz, 1H), 2.21 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 176.6, 139.0, 138.7, 129.8, 91.4, 60.3, 56.9, 53.6. **IR (film)**: 758, 838, 1015, 1082, 1228, 1393, 1450, 1561, 1709, 2951, 2985. **HRMS** (EI): m/z calcd. for C_8H_9NO [M⁺]: 135.06787, found: 135.06741.



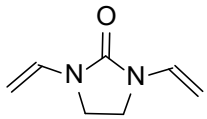
3-vinyloxazolidin-2-one **(3j)**. Synthesized following the general procedure "A" (solvent – toluene). Yield: 29 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.08). Yellow oil. The spectroscopic data is in correspondence with the literature data.[2] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 15.8, 8.9 Hz, 1H), 4.47 (t, *J* = 8.3 Hz, 2H), 4.43 (dd, *J* = 8.9, 1.3 Hz, 1H), 4.29 (dd, *J* = 15.8, 1.3 Hz, 1H), 3.72 (t, *J* = 8.3, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.5, 130.0, 93.6, 62.3, 42.0. **IR (film)**: 763, 1055, 1249, 1425, 1484, 1747, 2885, 2932. **HRMS (EI)**: m/z calcd. for $C_5H_7NO_2$ [M⁺]: 113.04713, found: 113. 04736**.**



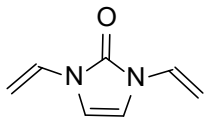
3-vinyl-1,3-oxazinan-2-one **(3k)**. Synthesized following the general procedure "A" (solvent – toluene). Yield: 82 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.05). Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 16.4, 9.1 Hz, 1H), 4.40 - 4.35 (m, 2H), 4.27 (t, *J* = 5.2 Hz, 2H), 3.43 (t, *J* = 6.4 Hz, 2H), 2.13 (qd, *J* = 6.4, 5.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 134.3, 92.9, 66.2, 42.1, 21.5. **IR (film)**: 1117, 1282, 1480, 1601, 1698, 2906, 2975. **HRMS (EI)**: m/z calcd. for $C_6H_9NO_2$ [M⁺]: 127.06278, found: 127.06217.



2-vinylbenzo[d]isoxazol-3(2H)-one **(3l)**. Synthesized following the general procedure "A" (solvent – toluene). Yield: 25 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.46). White solid, T_{melt} = 53 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.37 – 7.13 (m, 4H), 6.88 (dd, *J* = 16.1, 9.5 Hz, 1H), 5.64 (d, *J* = 16.1 Hz, 1H), 5.11 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 152.7, 142.8, 129.6, 126.9, 124.5, 123.7, 110.5, 110.3, 103.1. **IR (film)**: 753, 1255, 1397, 1486, 1649, 1780, 2927, 2959. **HRMS (EI)**: m/z calcd. for $C_9H_7NO_2$ [M⁺]: 161.04713, found: 161.04692.

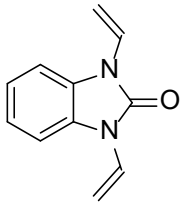


1,3-divinylimidazolidin-2-one **(3m)**. Synthesized following the general procedure "B" (the reaction temperature 120 °C, solvent - toluene). Yield: 15 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.3). Yellow oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.98 (dd, *J* = 15.9, 9.0 Hz, 2 x 1H), 4.28 (dd, *J* = 9.1, 0.9 Hz, 2 x 1H), 4.20 (dd, *J* = 15.9, 0.9 Hz, 2 x 1H), 3.60 (s, 2 x 2H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 153.6, 130.6 (2 x C), 90.4 (2 x C), 39.8 (2 x C). **IR (film)**: 1265, 1428, 1488, 1699, 2881, 2966. **HRMS (EI)**: m/z calcd. for $C_7H_{10}N_2O$ [M⁺]: 138.07876, found: 138.07781.

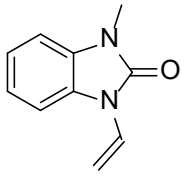


1,3-divinyl-1,3-dihydro-2H-imidazol-2-one **(3n)**. Synthesized following the general procedure "A" (the reaction temperature 140 °C, solvent - DMF). Yield: 25 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.27). Brown oil. **^{1}H NMR**(400 MHz, CD_2Cl_2) δ 6.89 (dd, *J* = 16.1, 9.1 Hz, 2 x 1H), 6.61 (s, 2 x 1H), 4.96 (dd, *J* = 16.1, 1.4 Hz, 2 x 1H), 4.67 (dd, *J* = 9.1, 1.4 Hz, 2 x 1H). **^{13}C NMR**

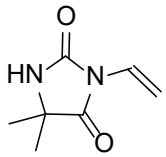
(101 MHz, CD_2Cl_2) δ 150.0, 127.6, 108.6, 96.6. **IR (film)**: .972, 1249, 1435, 1643, 1707. **HRMS (EI)**: m/z calcd. for $C_7H_8N_2O$ [M⁺]: 136.06311, found: 136.06331.



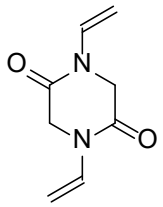
1,3-divinyl-1,3-dihydro-2H-benzo[d]imidazol-2-one **(3o)**. Synthesized following the general procedure "A" (the reaction temperature 140 °C, solvent - DMF). Yield: 27 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.6). Brown oil. **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.36 (dd, *J* = 6.0, 3.3 Hz, 2 x 1H), 7.19 (dd, *J* = 6.0, 3.3 Hz, 2 x 1H), 6.99 (dd, *J* = 16.2, 9.6 Hz, 2 x 1H), 5.67 (d, *J* = 16.2 Hz, 2 x 1H), 5.05 (d, *J* = 9.6 Hz, 2 x 1H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 151.6, 128.1 (2 x C), 127.2 (2 x C), 122.9 (2 x C), 109.9 (2 x C), 102.2 (2 x C). **IR (film)**: 732, 880, 962, 1080, 1142, 1186, 1240, 1303, 1408, 1492, 1606, 1647, 1762, 2964, 3062. **HRMS (EI)**: m/z calcd. for $C_{11}H_{10}N_2O$ [M⁺]: 186.07876, found: 186.07939.



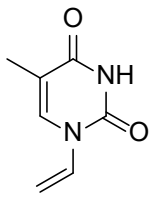
1-methyl-3-vinyl-1,3-dihydro-2H-benzo[d]imidazol-2-one **(3p)**. Synthesized following the general procedure "A" (the reaction temperature 130 °C, solvent - toluene). Yield: 37 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.26). White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.18 – 7.09 (m, 2H), 7.05 (dd, *J* = 16.3, 9.6 Hz, 1H), 6.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 5.56 (dd, *J* = 16.3, 1.1 Hz, 1H), 4.97 (dd, *J* = 9.6, 1.1 Hz, 1H), 3.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.13, 130.29 (2 x C_{arom}), 127.5, 122.4, 121.8, 109.7, 107.8, 100.8, 27.2. **IR (film)**: 751, 1078, 1129, 1182, 1399, 1435, 1497, 1618, 1647, 1716, 2938, 3062. **HRMS (EI)**: m/z calcd. for $C_{10}H_{10}N_2O$ [M⁺]: 174.07876, found: 174.07873.



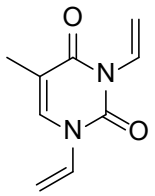
5,5-dimethyl-1-vinylimidazolidine-2,4-dione **(3q)**. Synthesized following the general procedure "A" (the reaction temperature 130 °C, solvent - DMF). Yield: 38 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.25). White crystals. **^{1}H NMR** (301 MHz, $CDCl_3$) δ 6.65 (dd, *J* = 16.4, 9.8 Hz, 1H), 6.35 (s, 1H), 6.00 (d, *J* = 16.4 Hz, 1H), 4.99 (d, *J* = 9.8 Hz, 1H), 1.46 (s, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 175.6, 154.7, 124.2, 104.7, 58.0, 25.3 (2 x C). **IR (film)**: 1087, 1135, 1210, 1390, 1497, 1628, 1647, 1718, 2938, 3062, 3361, 3448. **HRMS (EI)**: m/z calcd. for $C_7H_{10}N_2O_2$ [M⁺]: 154.07368, found: 154.07246.



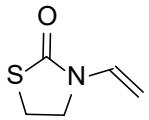
1,4-divinylpiperazine-2,5-dione **(3r)**. Synthesized following the general procedure "B" (the reaction temperature 150 °C, solvent - toluene). Yield: 99 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.1). Pale yellow crystals, T_{melt} = 167 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 16.2, 9.3 Hz, 2 x 1H), 4.68 (dd, *J* = 9.3, 1.9 Hz, 2 x 1H), 4.61 (dd, *J* = 16.2, 1.9 Hz, 2 x 1H), 4.21 (s, 2 x 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7 (2 x C), 129.7 (2 x C), 97.1 (2 x C), 46.9 (2 x C). **IR (film)**: 1260, 1340, 1416, 1456, 1632, 1667, 2900, 3004, 3113. **HRMS (EI)**: m/z calcd. for $C_8H_{10}N_2O_2$ [M⁺]: 166.07368, found: 166.07305.



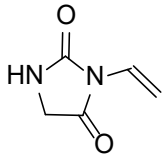
5-methyl-1-vinylpyrimidine-2,4(1*H*,3*H*)-dione **(3s)**. Synthesized following the general procedure "B" (the reaction temperature 150 °C, solvent - DMF). Yield: 20 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.06). White crystals, T_{melt} = 195 °C. The spectroscopic data is in correspondence with the literature data.[3] **^{1}H NMR** (301 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.34 (d, *J* = 1.3 Hz, 1H), 7.20 (dd, *J* = 16.0, 9.0 Hz, 1H), 5.07 (dd, *J* = 16.0, 2.2 Hz, 1H), 4.92 (dd, *J* = 9.0, 2.2 Hz, 1H), 1.99 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.4, 149.3, 134.6, 129.7, 112.2, 100.7, 12.7. **IR (film)**: 690, 769, 843, 909, 974, 1128, 1275, 1341, 1416, 1457, 1520, 1680, 2821, 3068, 3183. **HRMS (EI)**: m/z calcd. for $C_7H_8N_2O_2$ [M⁺]: 152.05803, found: 152.05740.



5-methyl-1,3-divinylpyrimidine-2,4(1H,3H)-dione **(3t)**. Synthesized following the general procedure "B" (the reaction temperature 150 °C, solvent - DMF). Yield: 11 % (column chromatography petroleum ether/ ethyl acetate 8/2, R_f 0.24). Viscous yellow oil. The spectroscopic data is in correspondence with the literature data.[4-5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 1.3 Hz, 1H), 7.25 (dd, *J* = 16.0, 9.0 Hz, 1H), 6.89 (dd, *J* = 16.1, 9.5 Hz, 1H), 5.97 (d, *J* = 16.1 Hz, 1H), 5.36 (d, *J* = 9.5 Hz, 1H), 5.08 (dd, *J* = 16.0, 2.2 Hz, 1H), 4.93 (dd, *J* = 9.0, 2.2 Hz, 1H), 2.01 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 149.3, 132.9, 130.7, 127.1, 112.7, 111.5, 101.1, 13.5. **IR (film)**: 769, 898, 969, 1147, 1279, 1369, 1436, 1667, 1714, 2931, 2961, 3092, 3278. **HRMS (EI)**: m/z calcd. for $C_9H_{10}N_2O_2$ [M$^+$]: 178.07368, found: 178.07454.



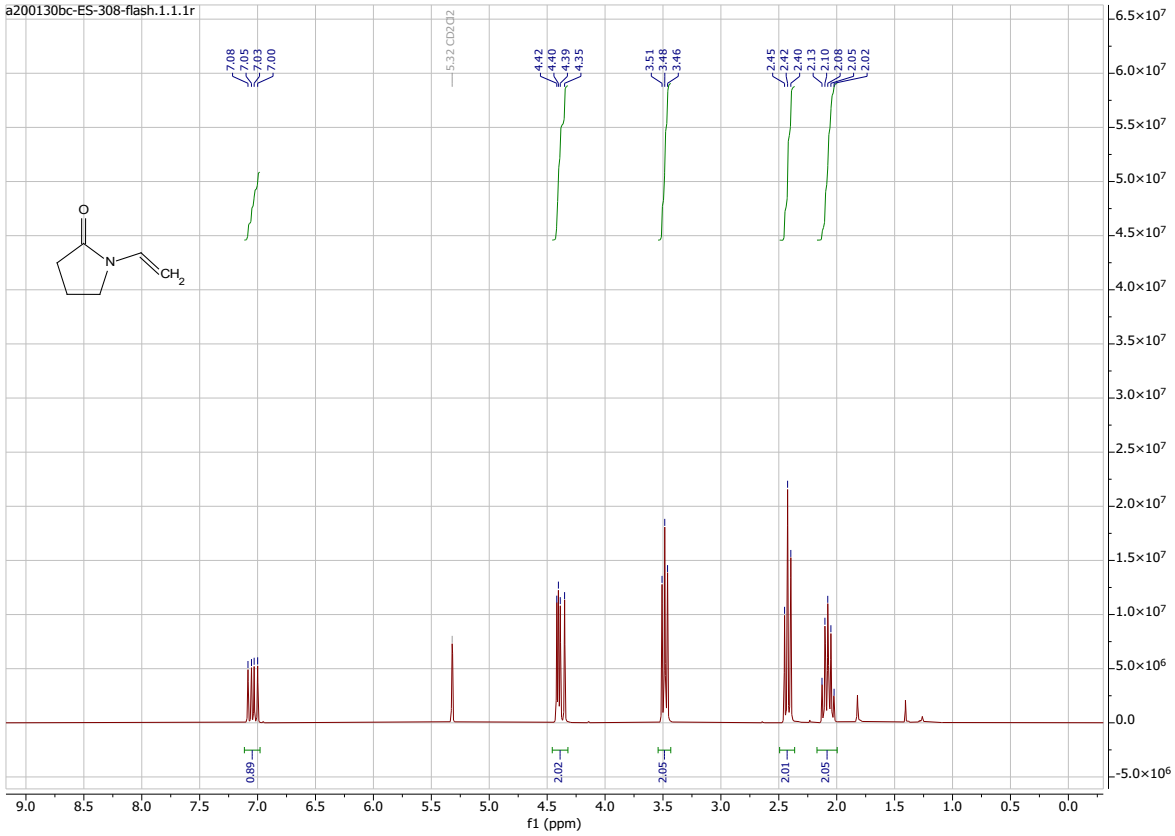
3-vinylthiazolidin-2-one **(3u)**. Synthesized following the general procedure "B" (Solvent – toluene). Yield: 49 % (Column chromatography Petroleum ether/ ethyl acetate 8/2, R_f 0.32). Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 16.0, 9.1 Hz, 1H), 4.47 (dd, *J* = 9.1, 1.3 Hz, 1H), 4.34 (dd, *J* = 16.0, 1.3 Hz, 1H), 3.79 (dd, *J* = 8.3, 6.7 Hz, 2H), 3.40 – 3.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 130.0, 94.5, 45.6, 25.0. **IR (film)**: 732, 1069, 1188, 1232, 1409, 1444, 1676, 2882, 2942, 2986. **HRMS (EI)**: m/z calcd. for C_5H_7NOS [M$^+$]: 129.02429, found: 129.02527.



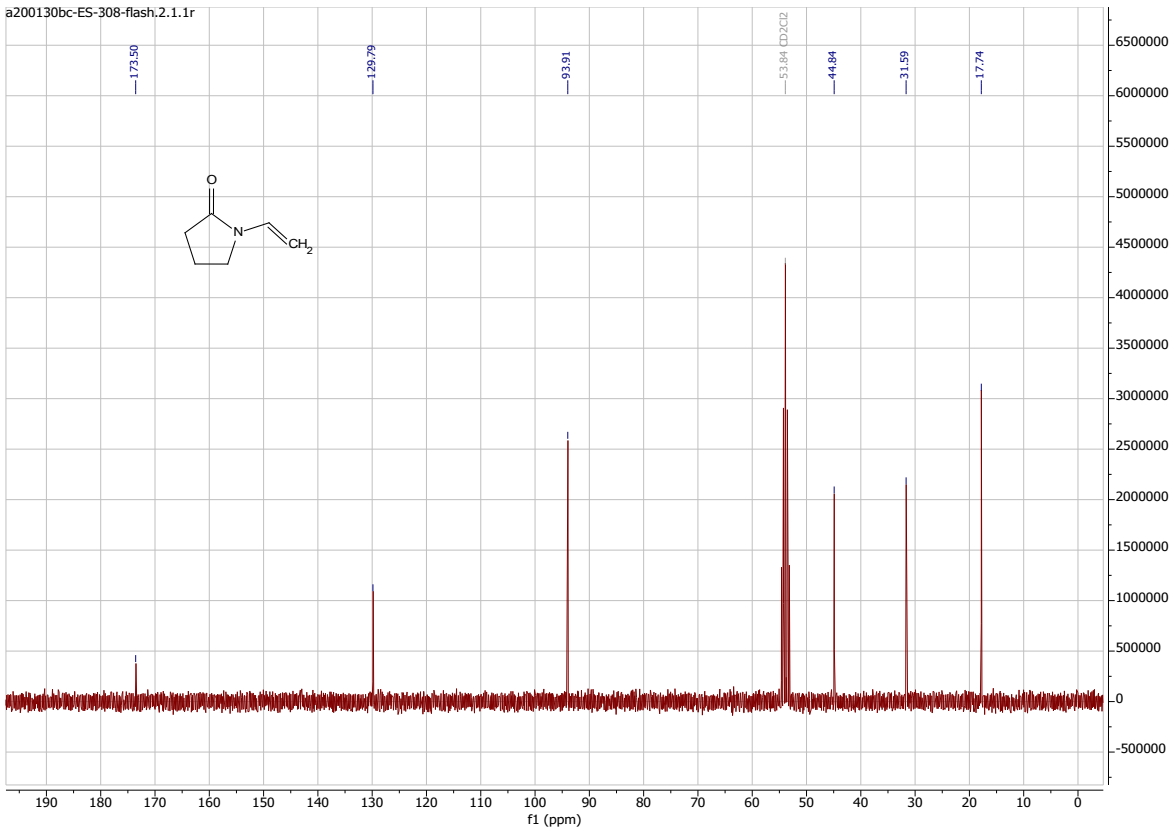
1-vinylimidazolidine-2,4-dione **(3v)**. Synthesized following the general procedure "A" (Solvent – DMF). Pure compound is not isolated, the product is decomposed during purification via column chromatography. **^{1}H NMR** (crude mixture) (200 MHz, $CDCl_3$) δ 6.66 (dd, *J* = 16.4, 9.8 Hz, 1H), 6.02 (d, *J* = 16.4 Hz, 1H), 5.01 (d, *J* = 9.8 Hz, 1H), 3.97 (s, 1H, 2H).

S8: ^{1}H and ^{13}C Spectra

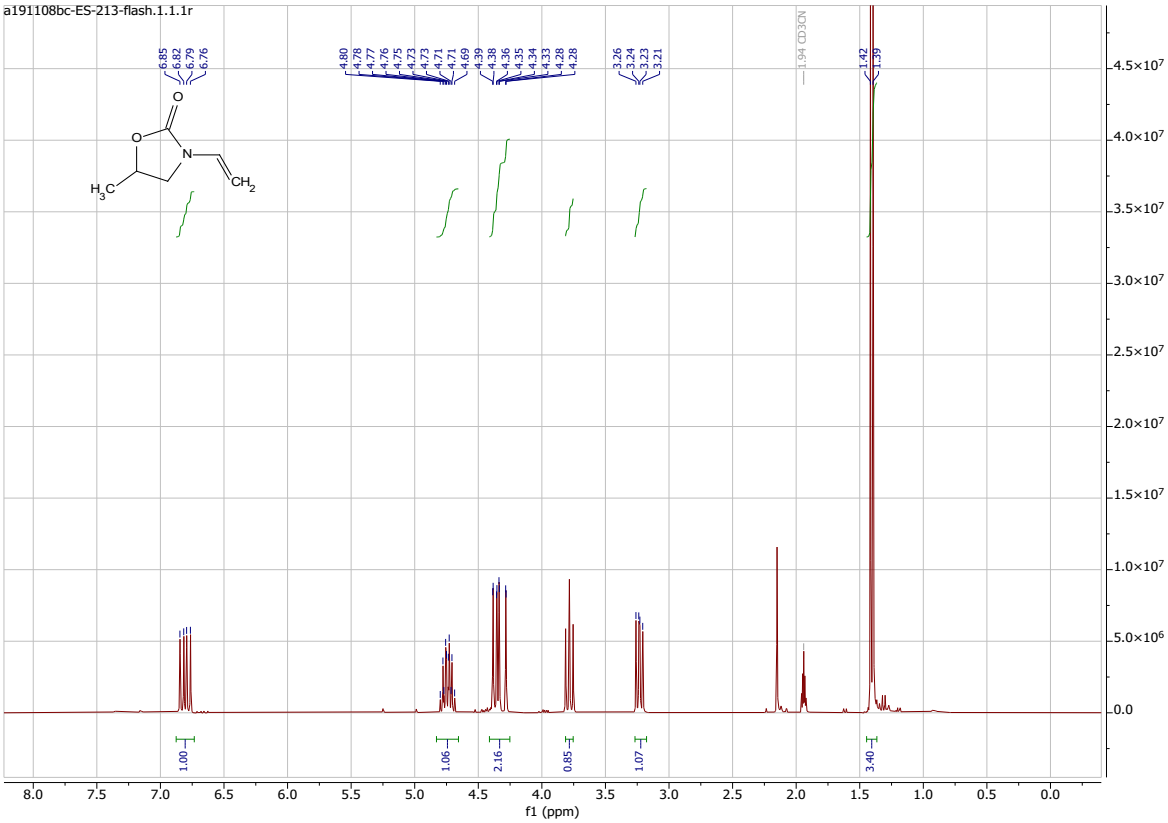
^{1}H NMR of **3a**:



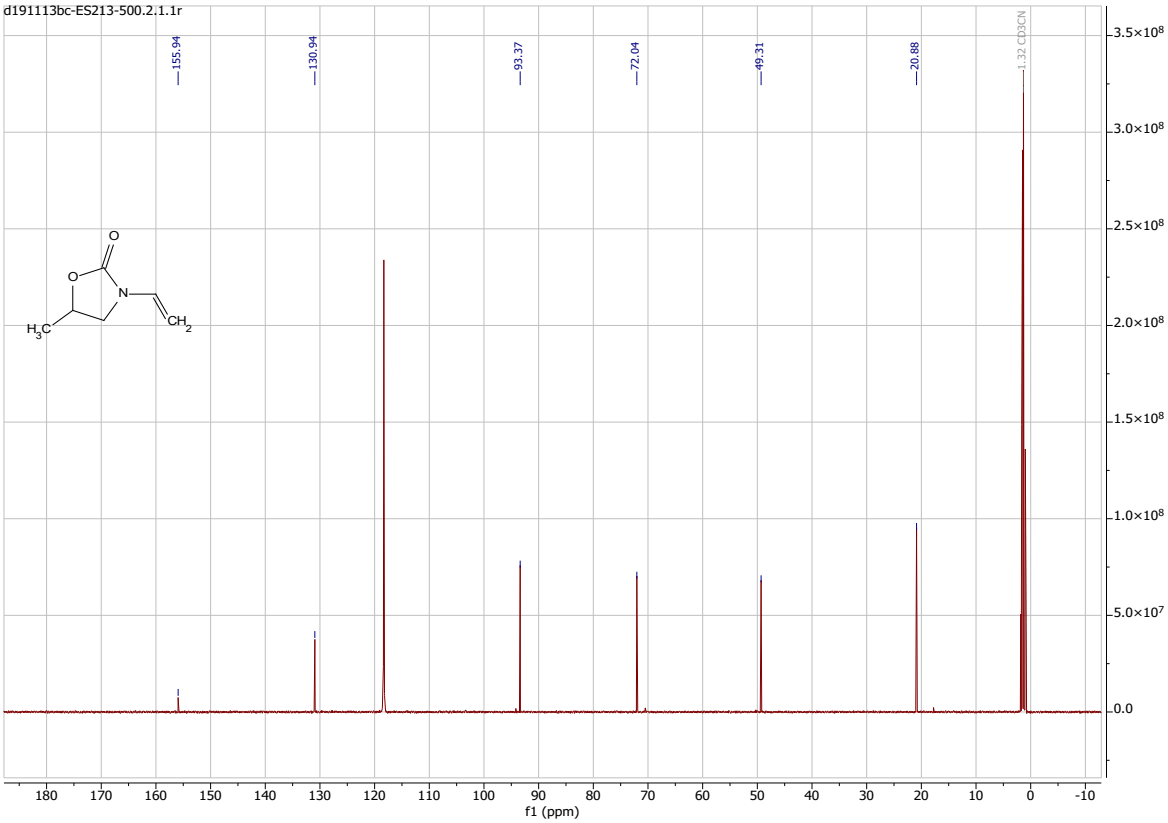
^{13}C of **3a**:



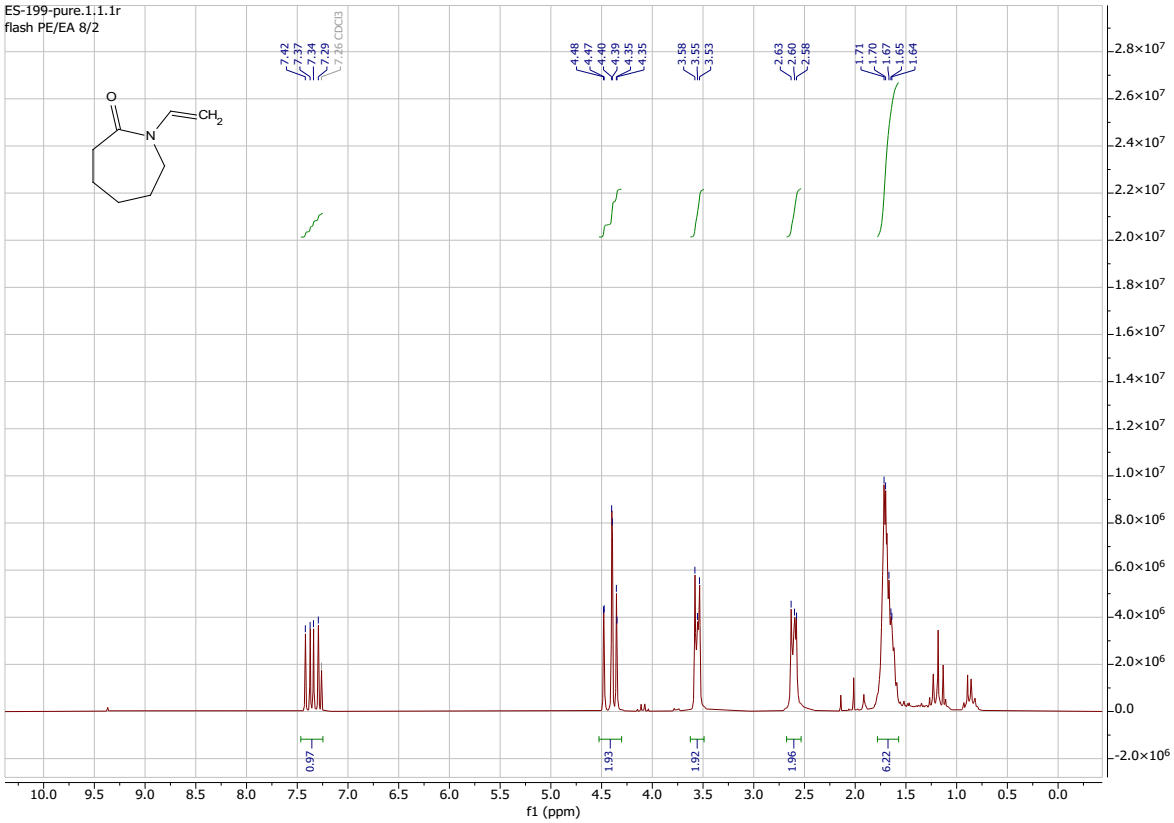
^{1}H NMR of **3b**:



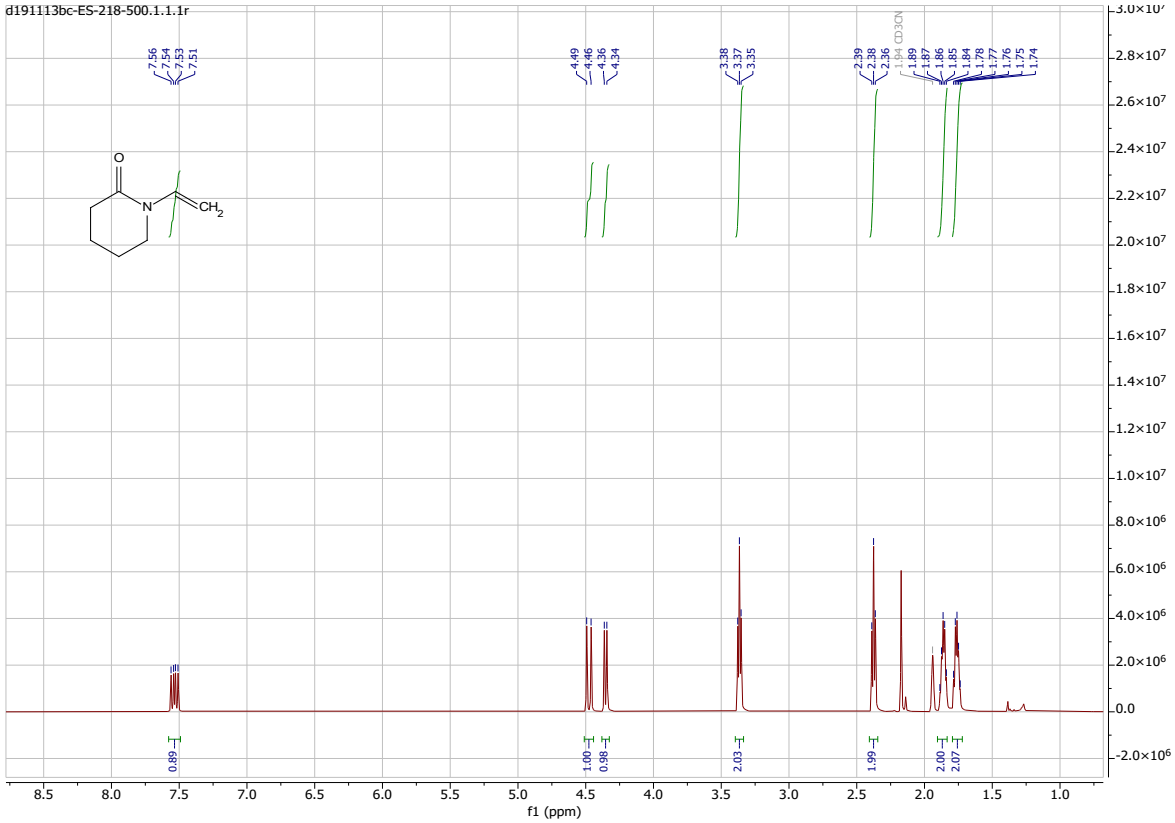
^{13}C of **3b**:



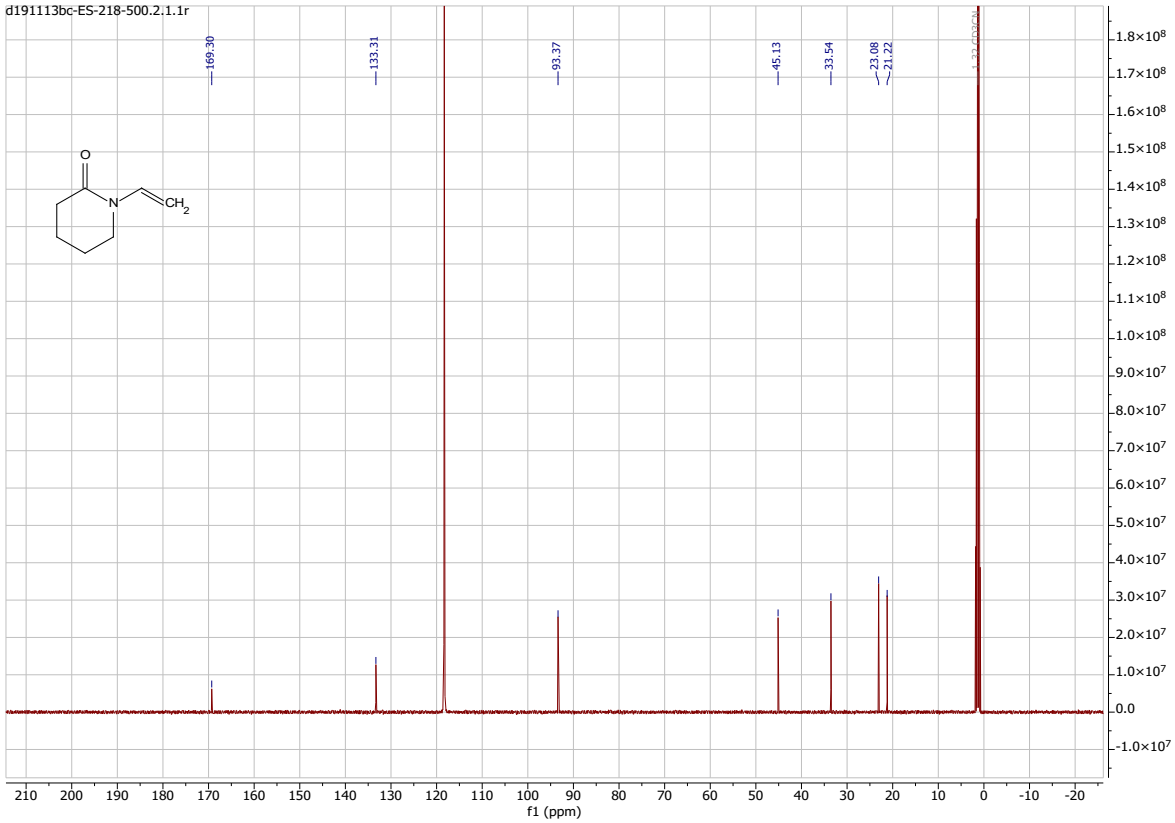
^{1}H NMR of **3c**:


ES-199-pure.1.1.1r
flash PE/EA 8/2
7.42
7.37
7.34
7.29
7.26 CDCl3
4.48
4.47
4.40
4.39
4.35
4.35
3.58
3.55
3.53
2.63
2.60
2.58
1.71
1.70
1.67
1.65
1.64
O
N
CH2
0.97
1.93
1.92
1.96
6.22
f1 (ppm)

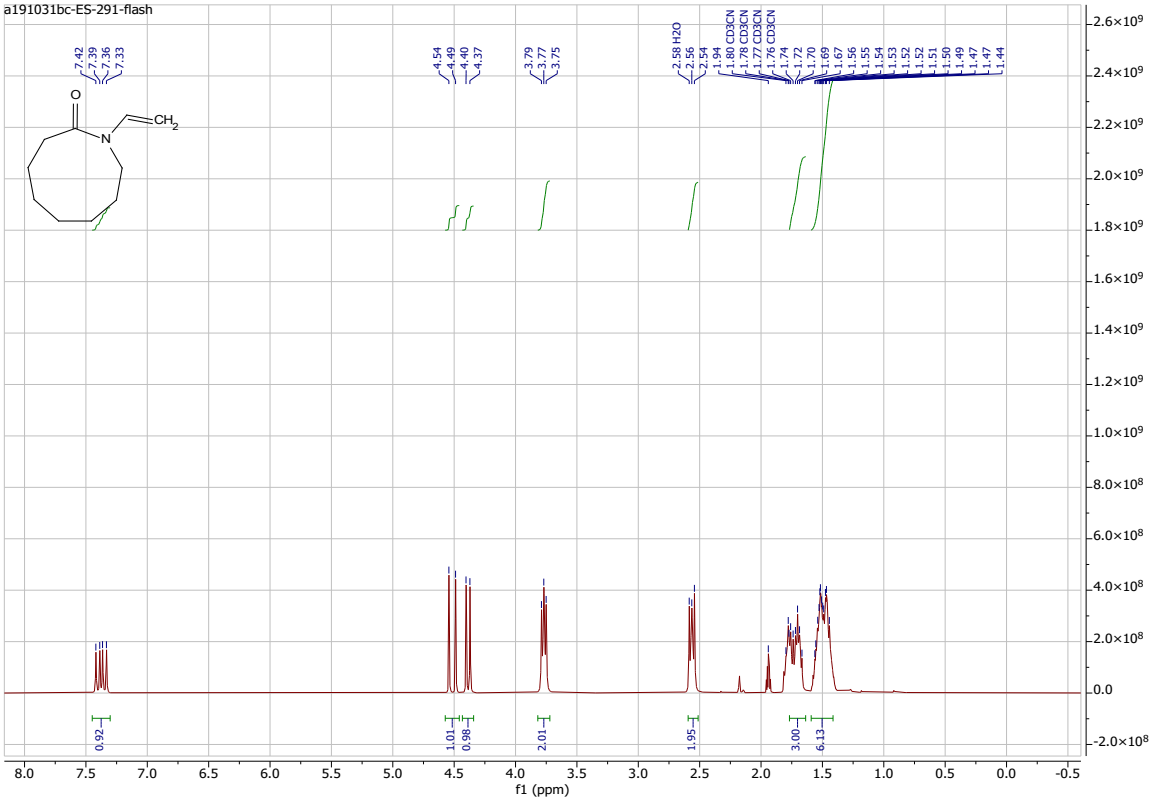
^{1}H NMR of **3d**:



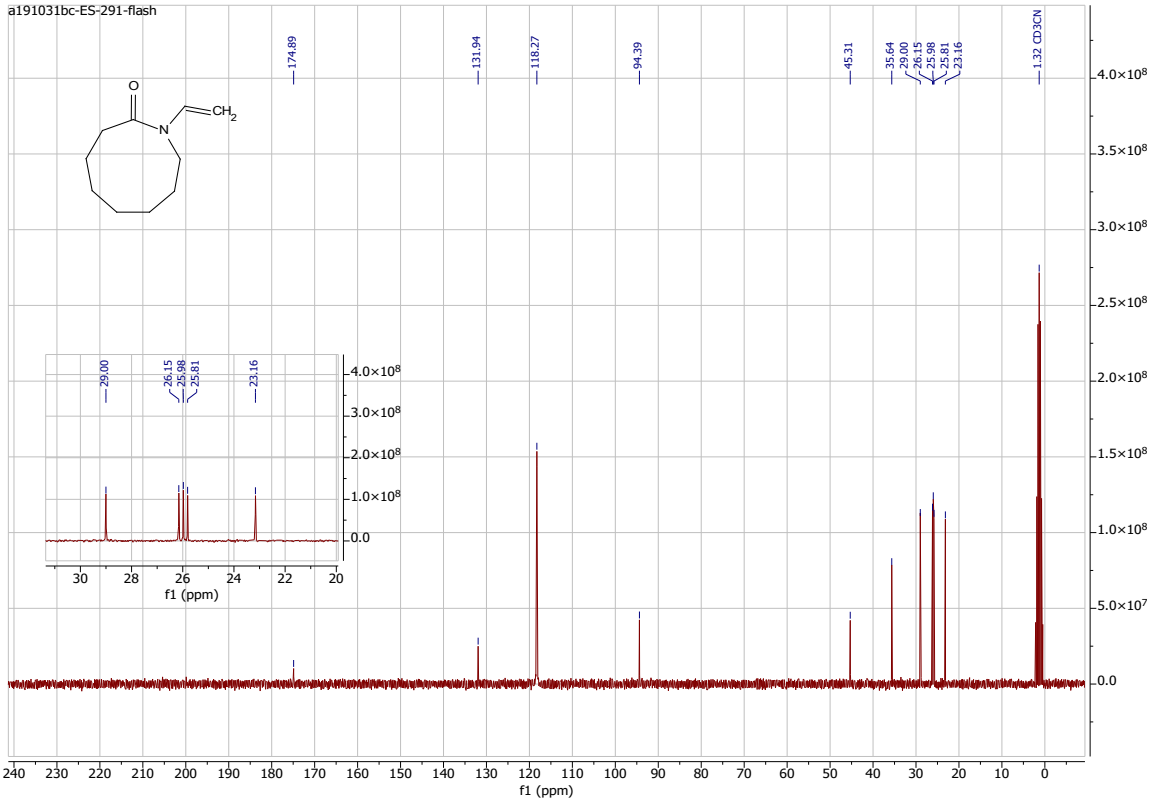
^{13}C of **3d**:



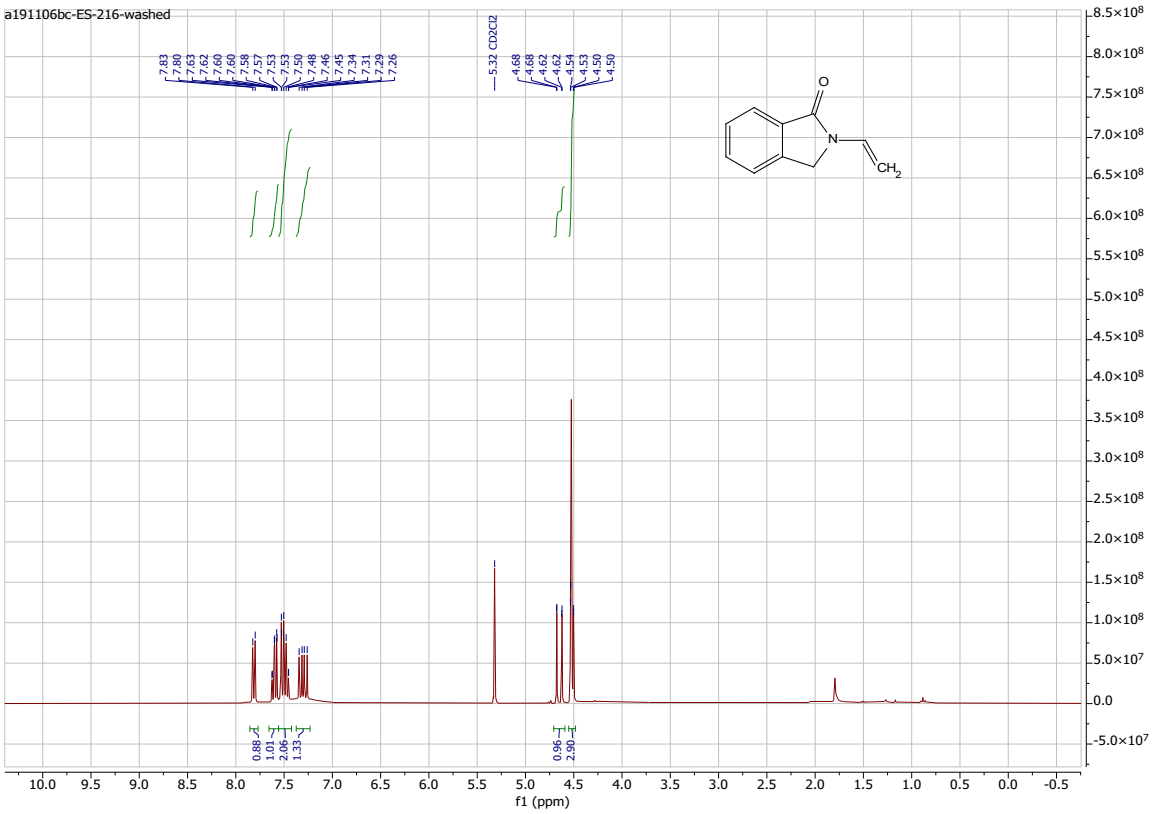
^{1}H NMR of **3e**:



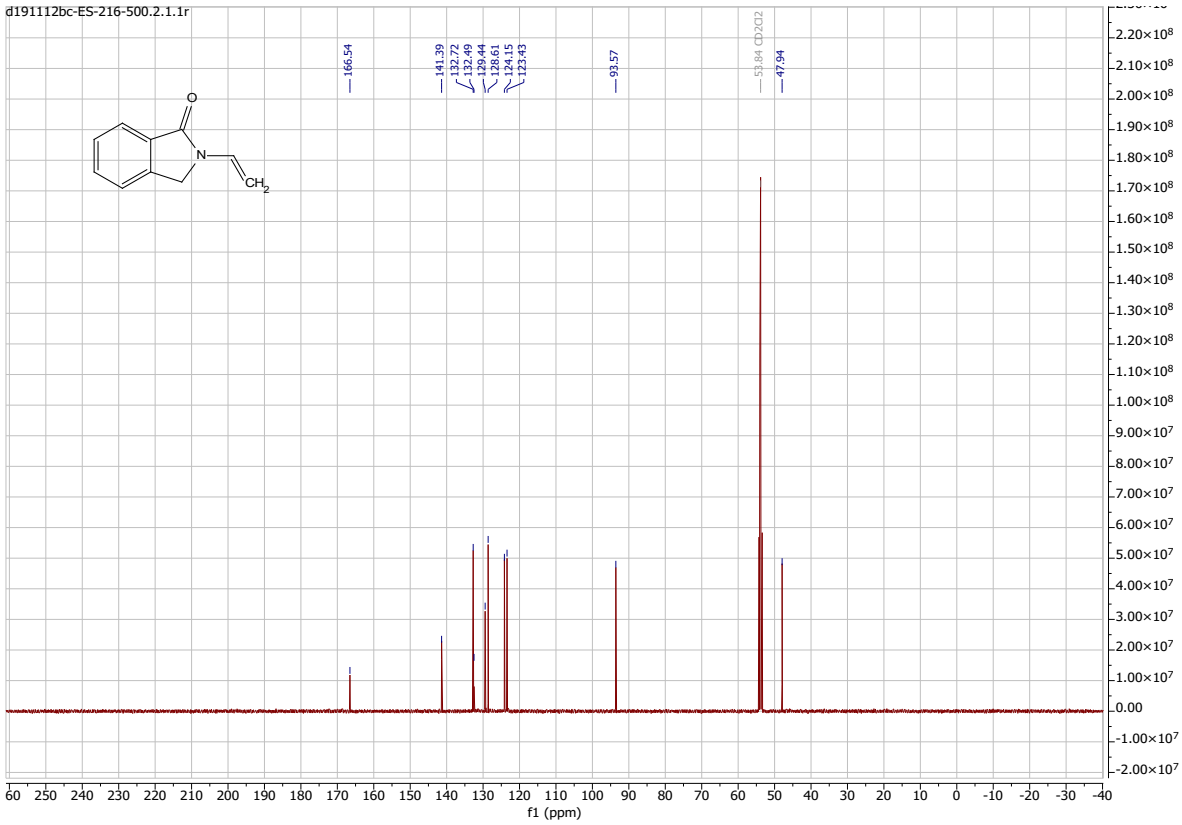
^{13}C of **3e**:



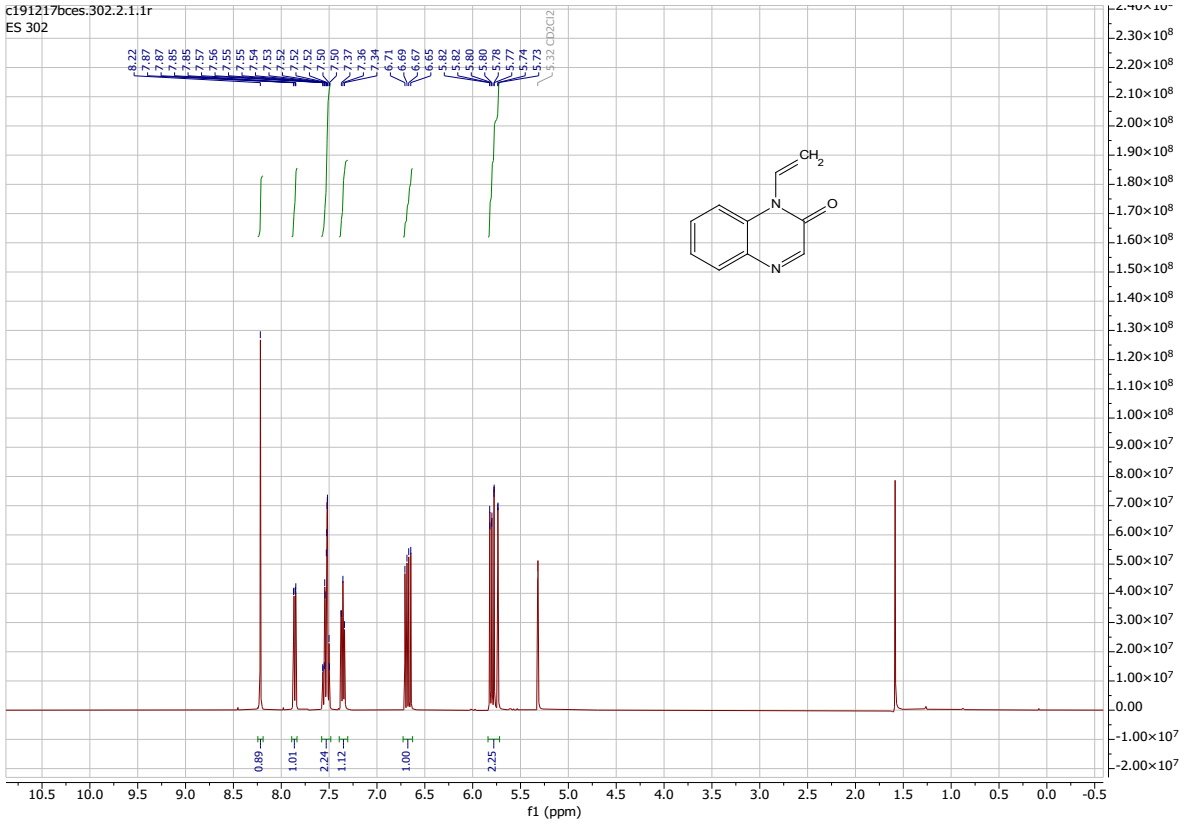
^{1}H NMR of **3f**:



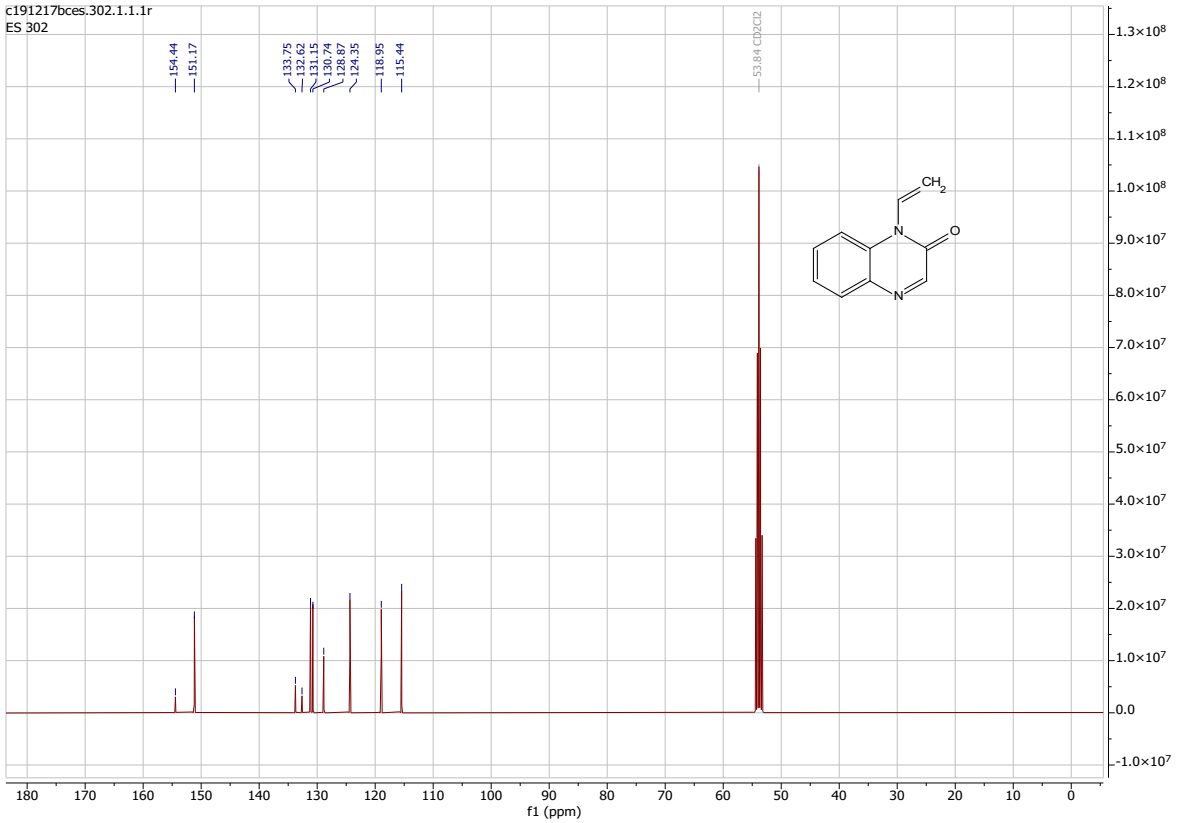
^{13}C of **3f**:



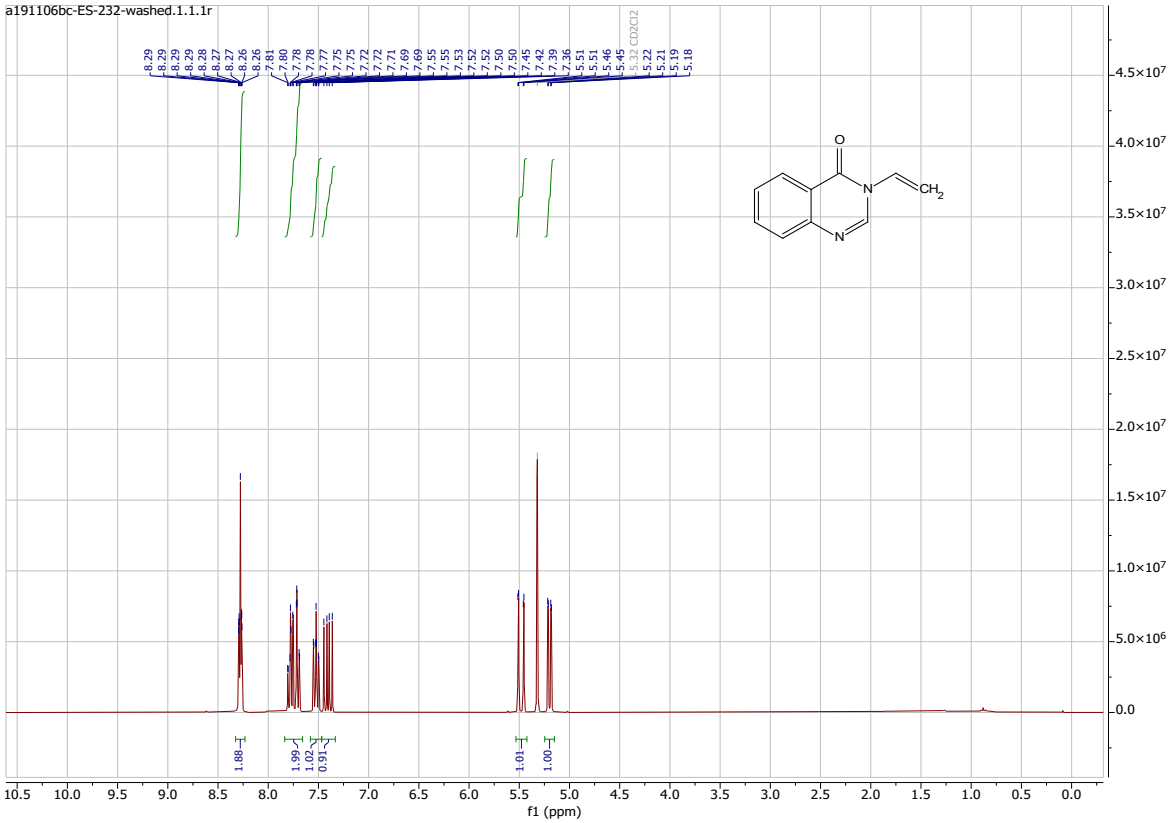
^{1}H NMR of **3g**:



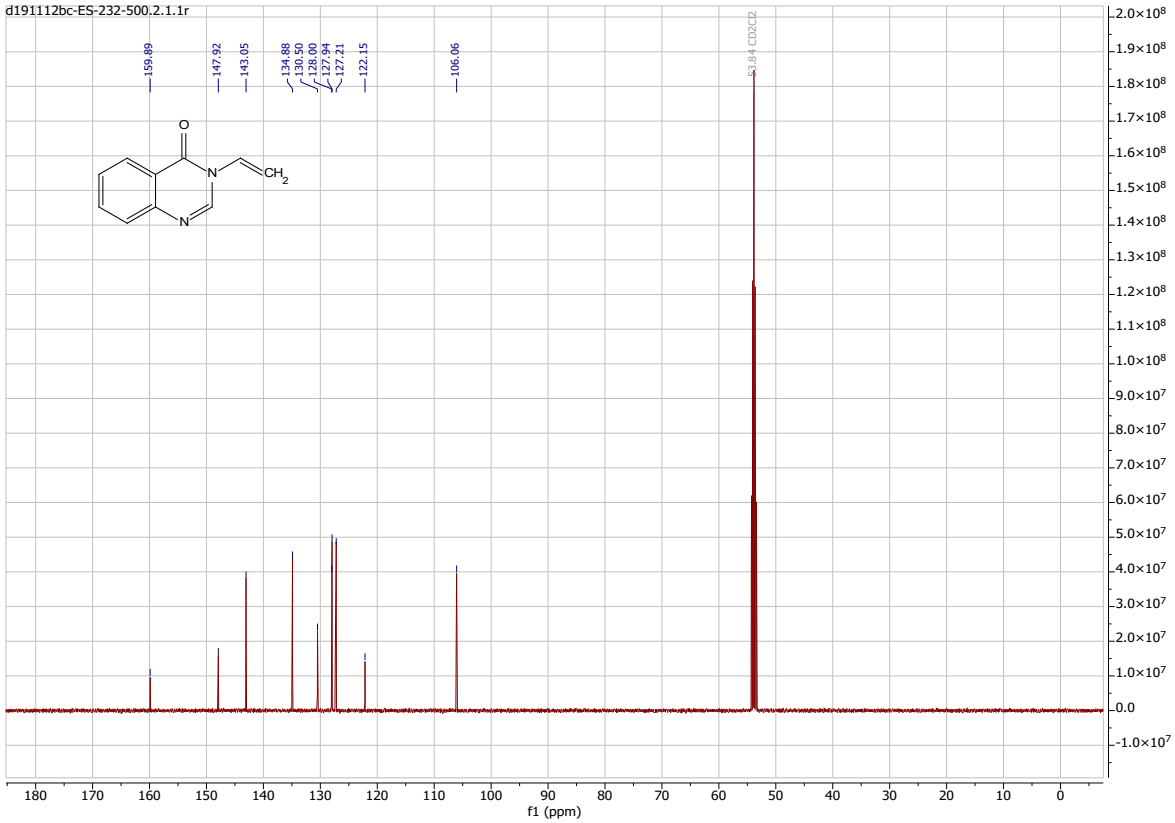
^{13}C of **3g**:



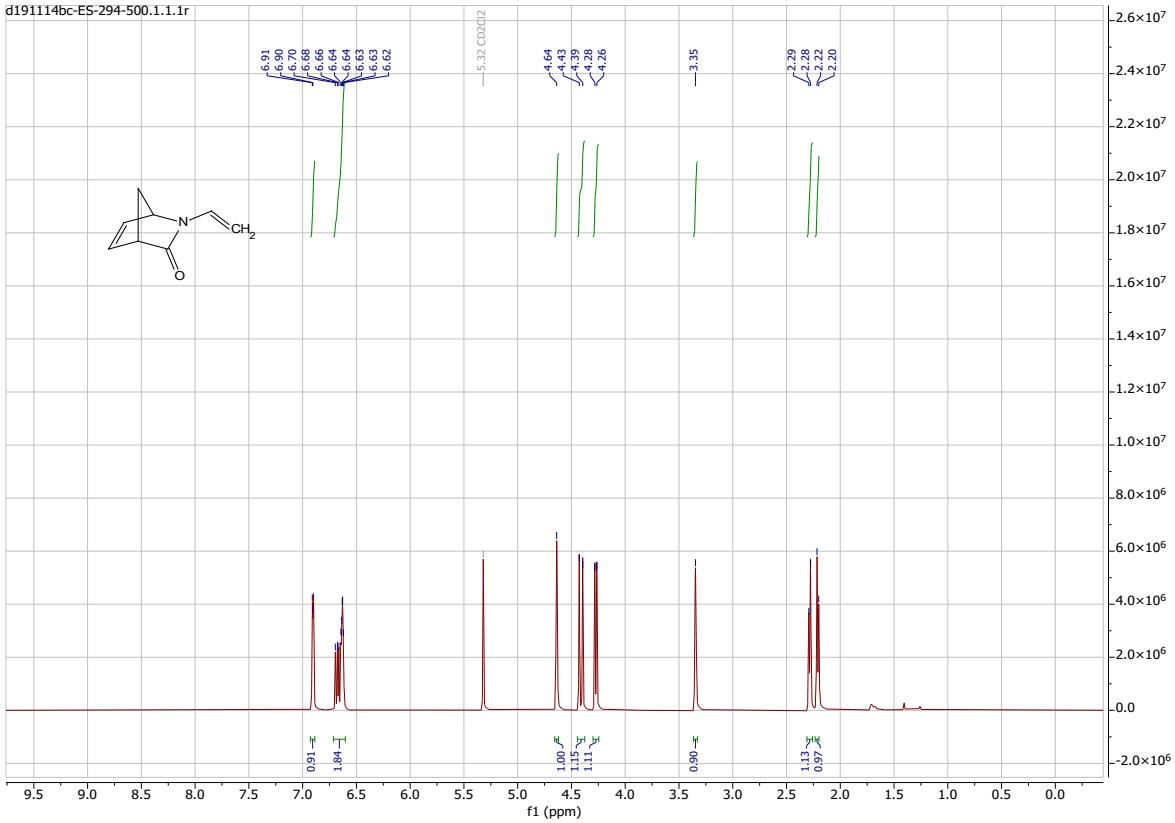
^{1}H NMR of **3h**:



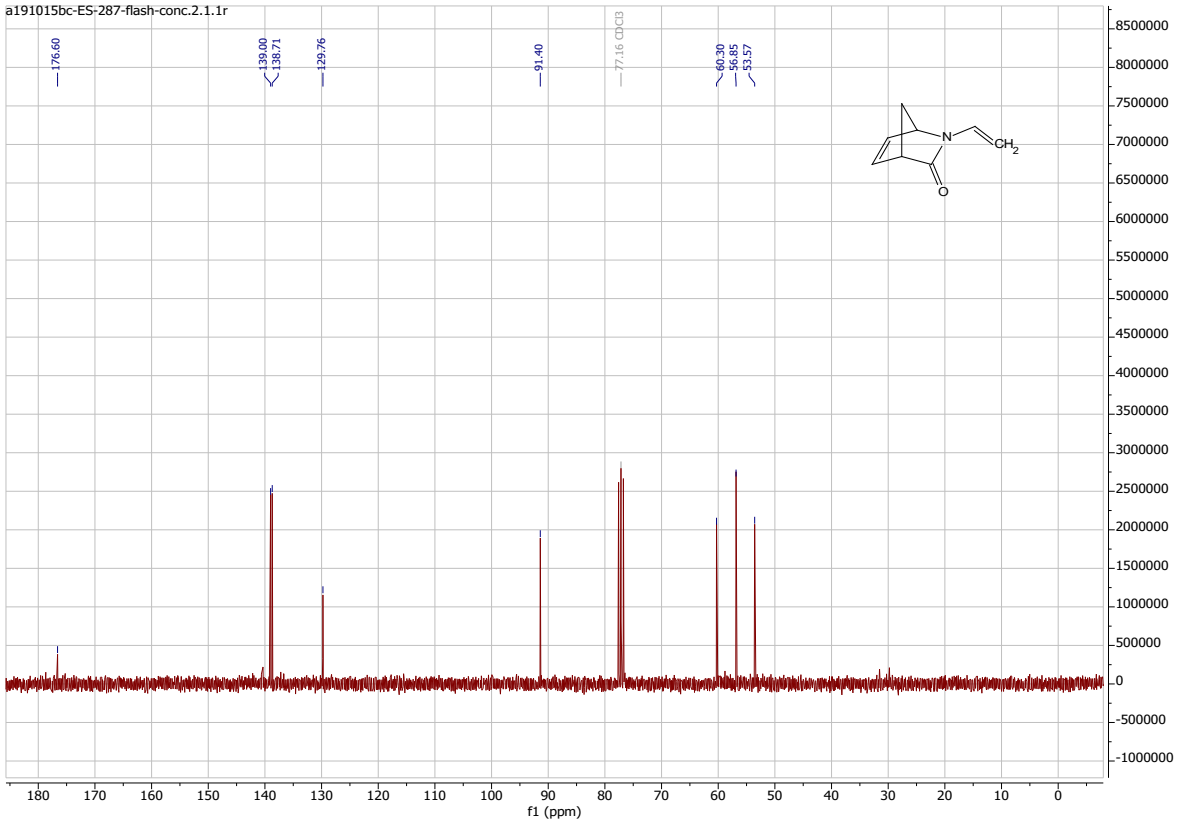
^{13}C of **3h**:



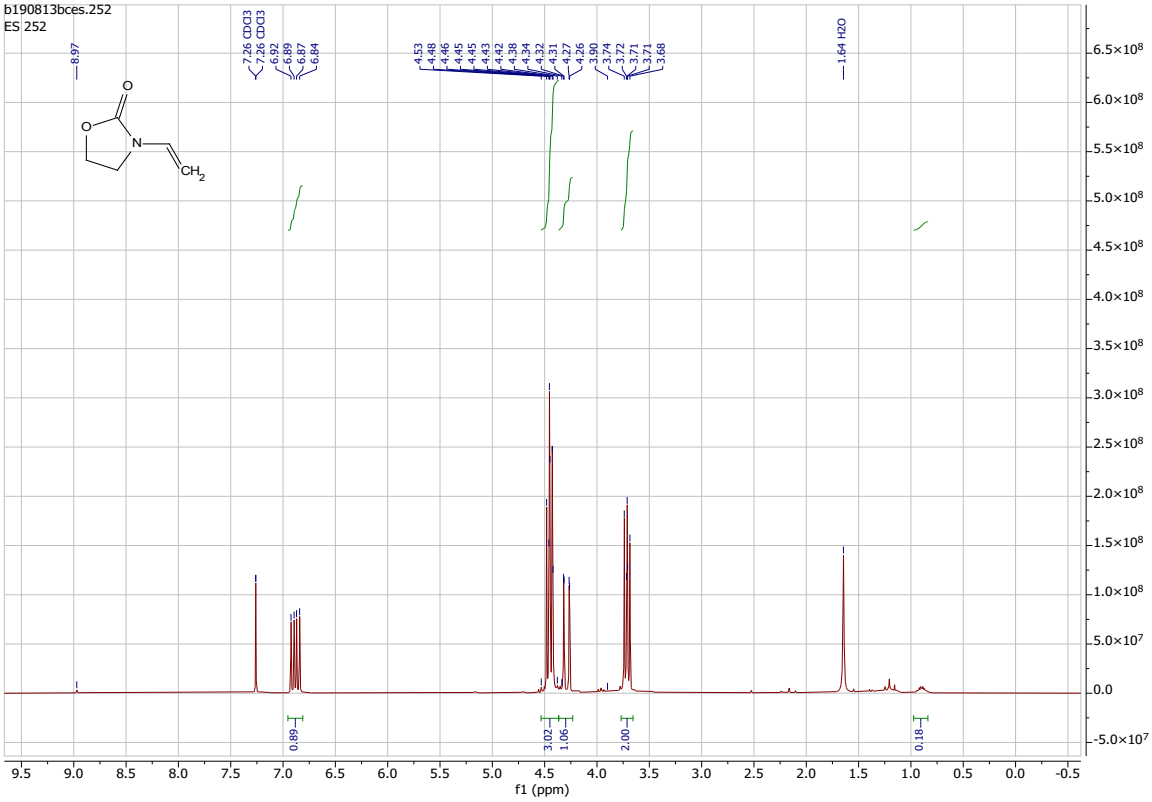
^{1}H NMR of **3i**:



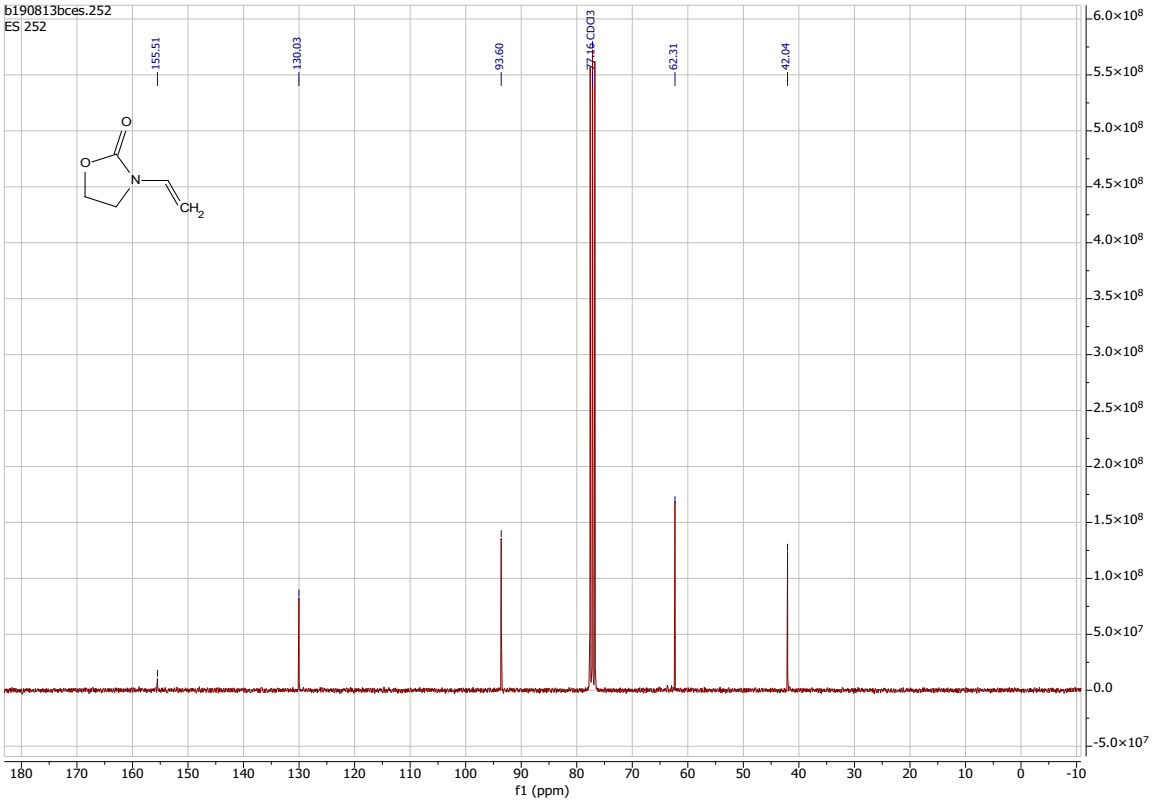
^{13}C of **3i**:



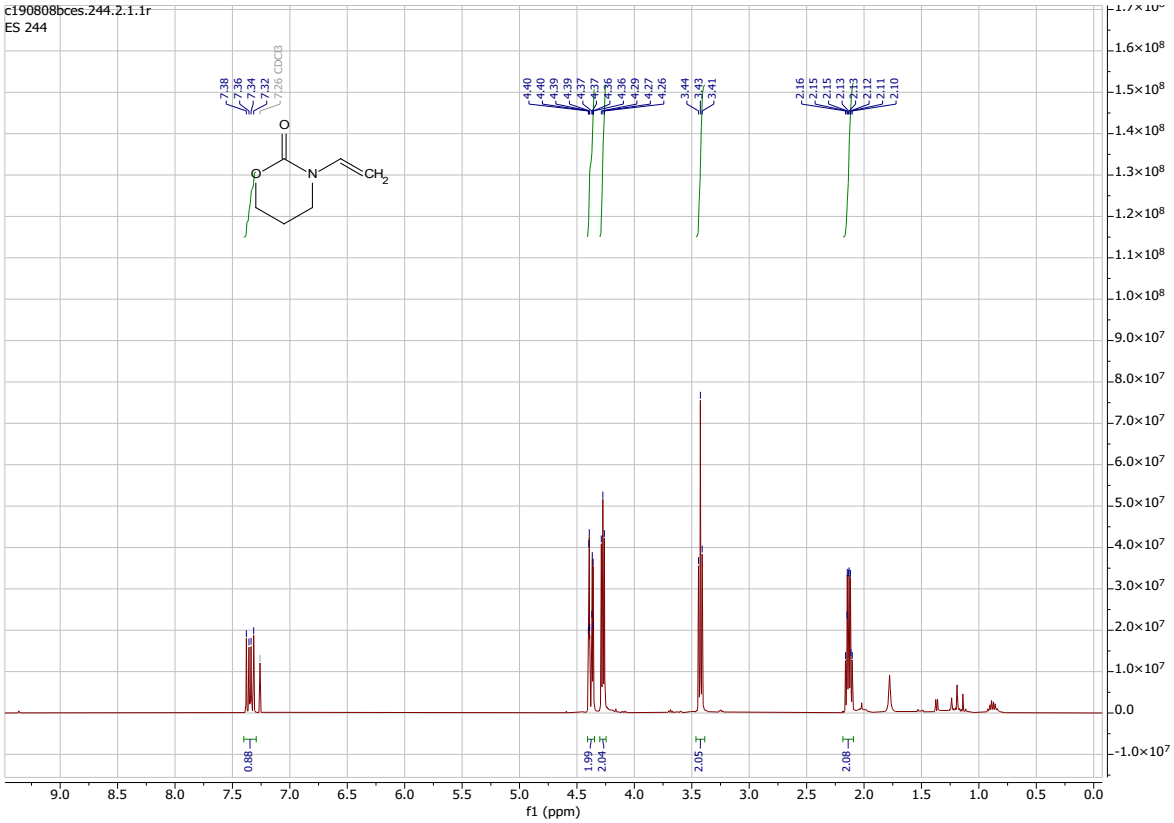
^{1}H NMR of **3j**:



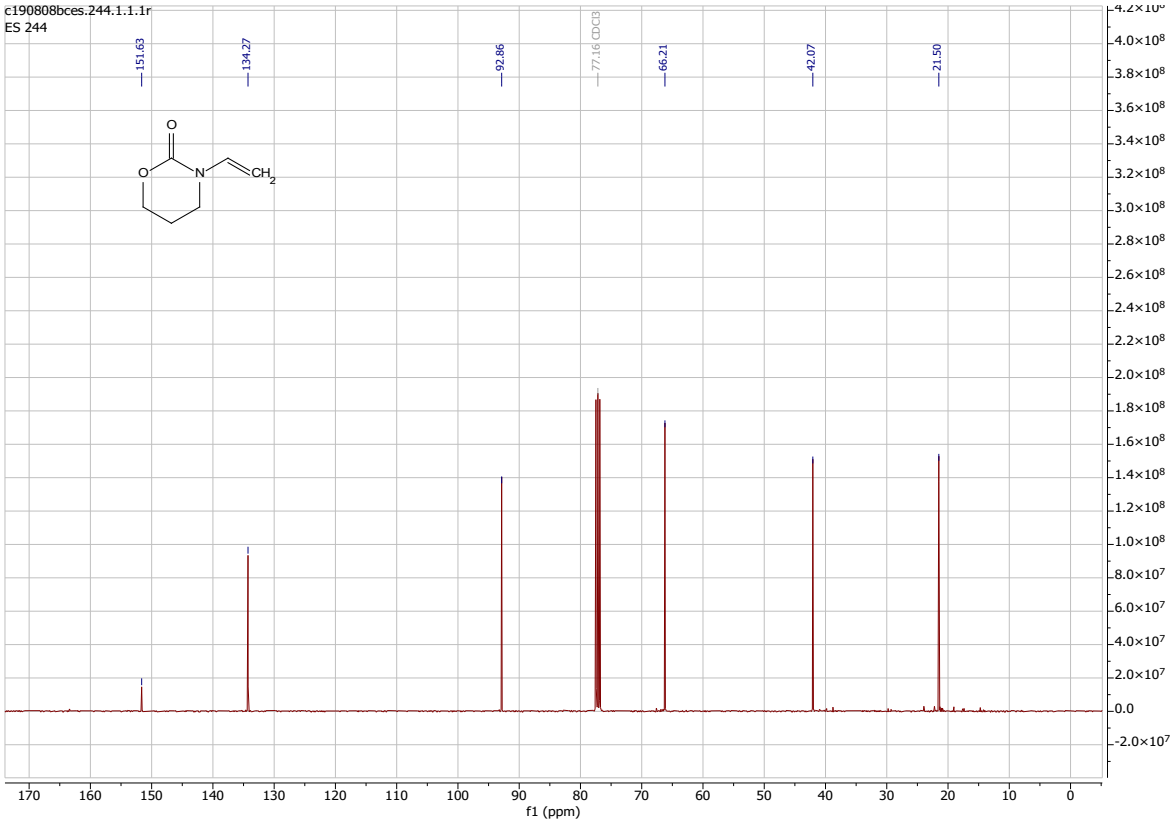
^{13}C of **3j**:



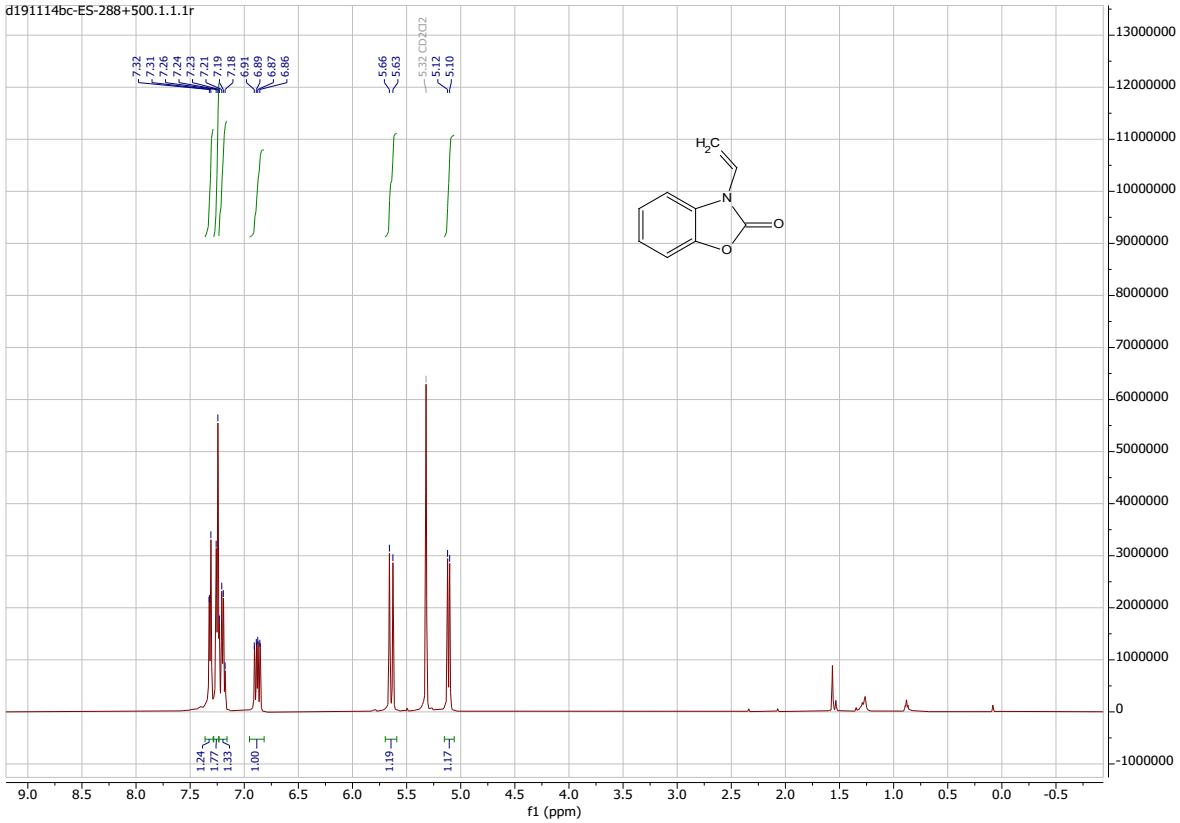
^{1}H NMR of **3k**:



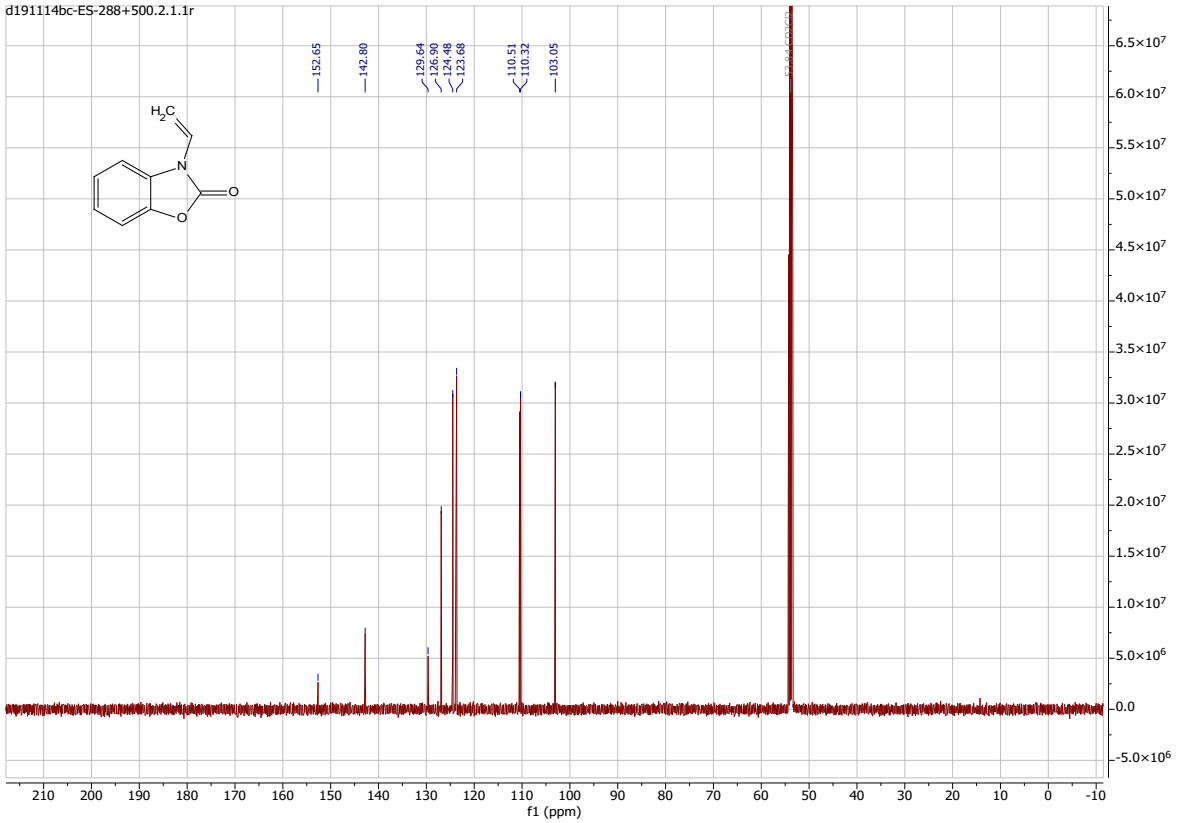
^{13}C of **3k**:



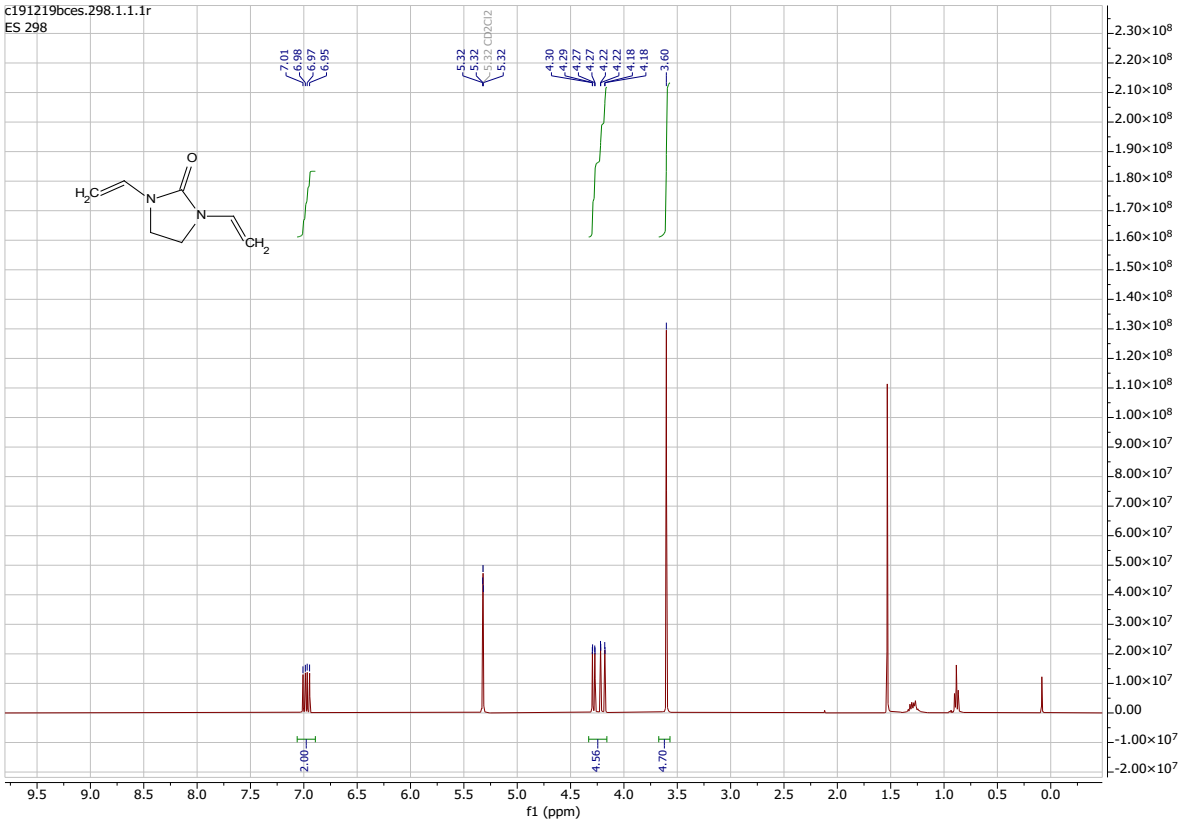
^{1}H NMR of **3l**:



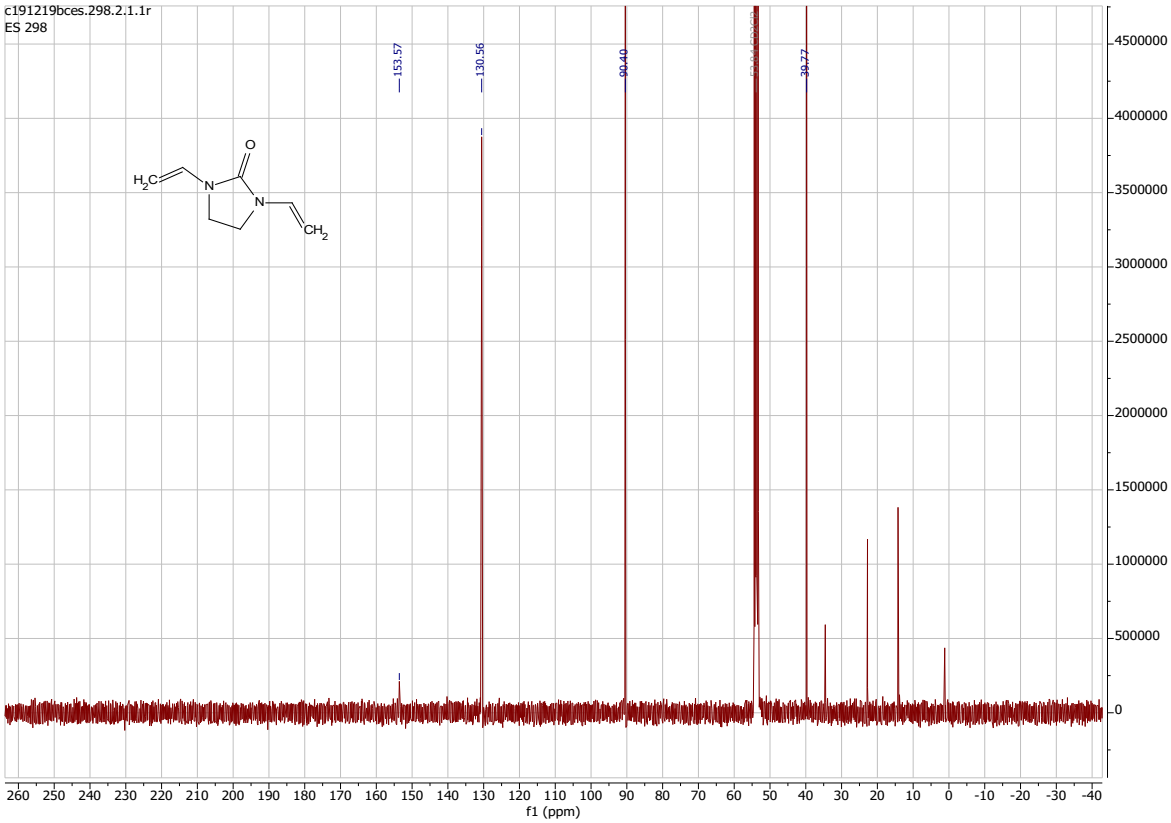
^{13}C of **3l**:



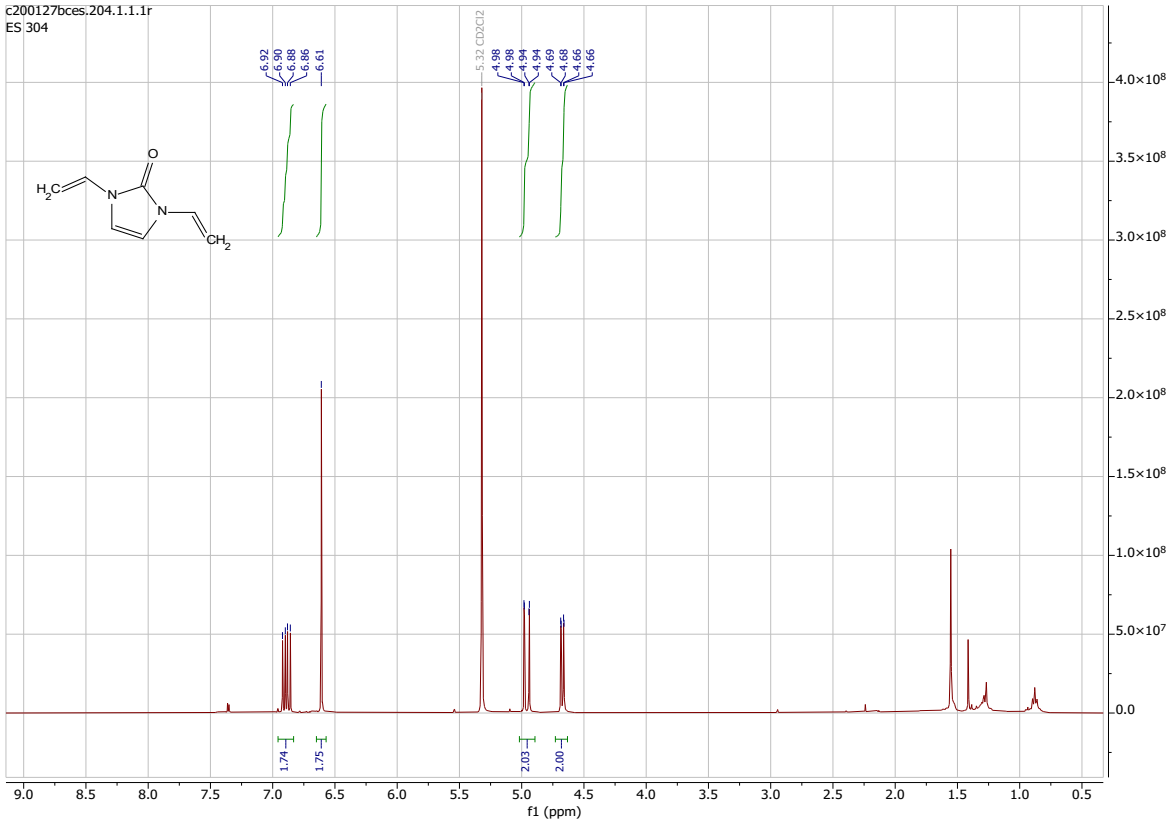
^{1}H NMR of **3m**:



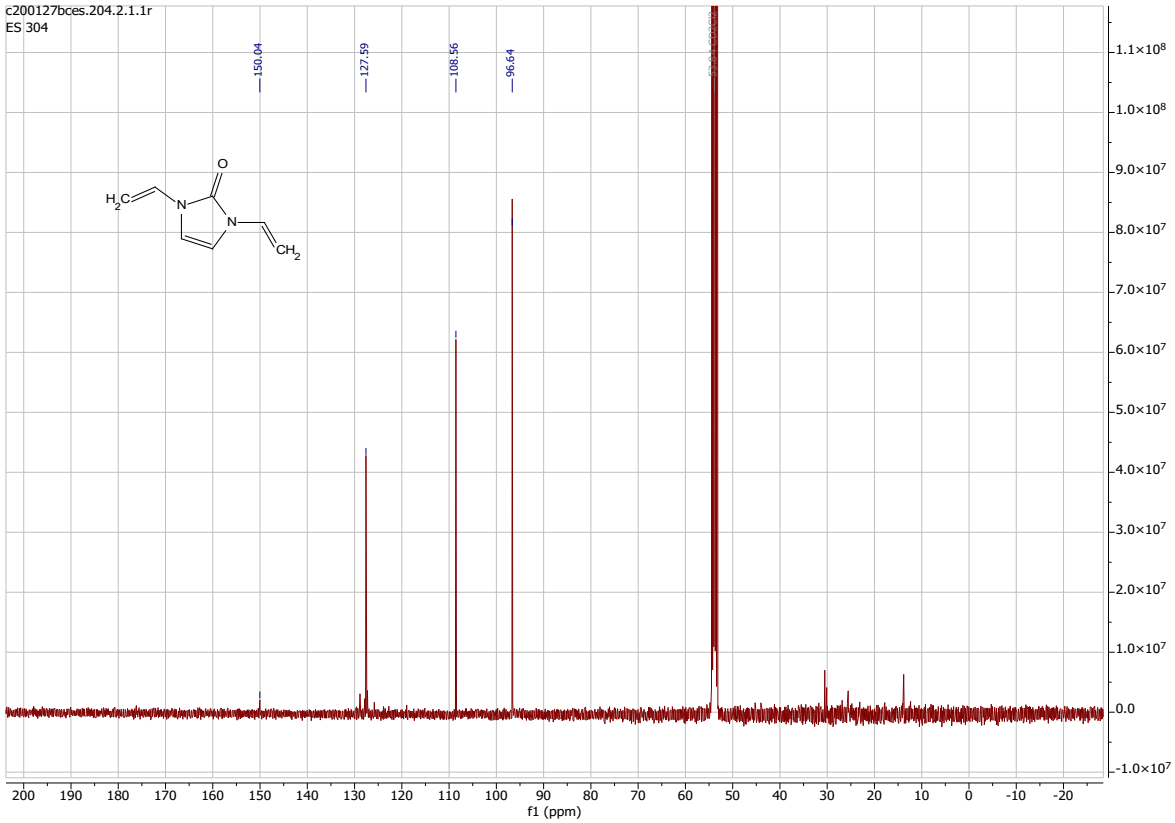
^{13}C of **3m**:



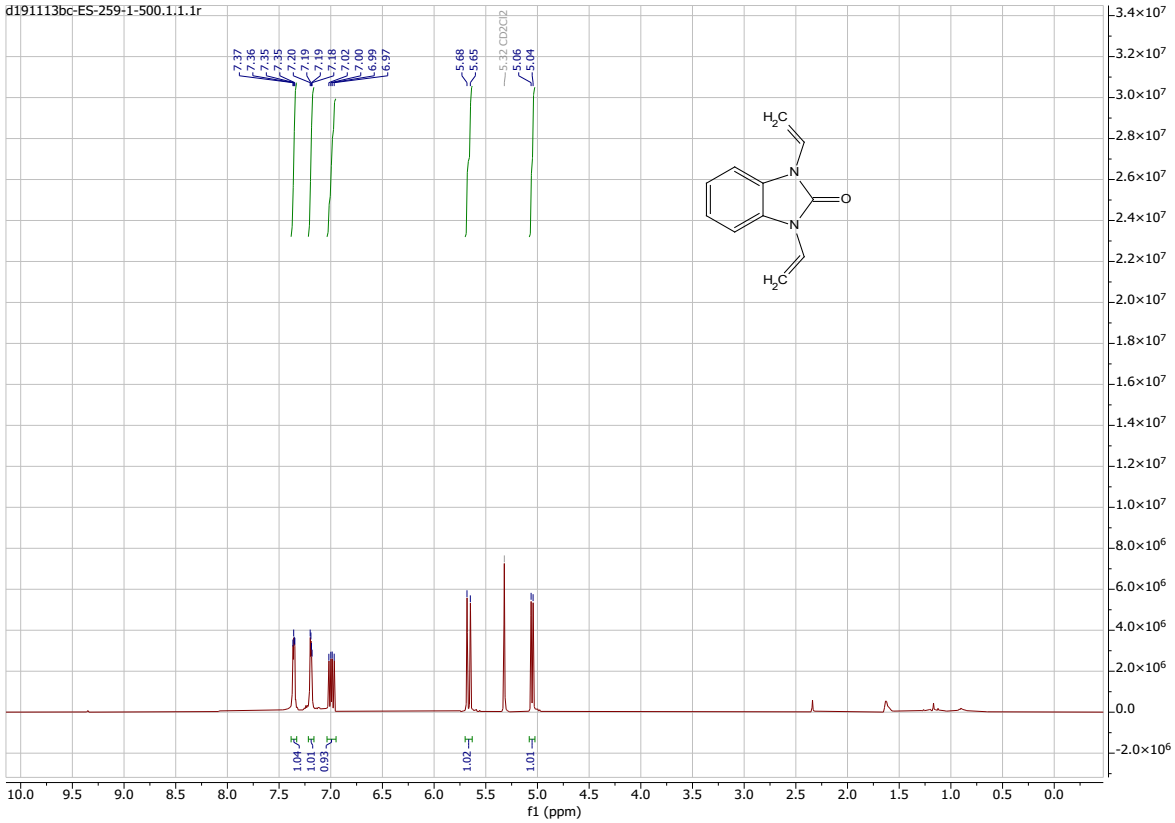
^{1}H NMR of **3n**:



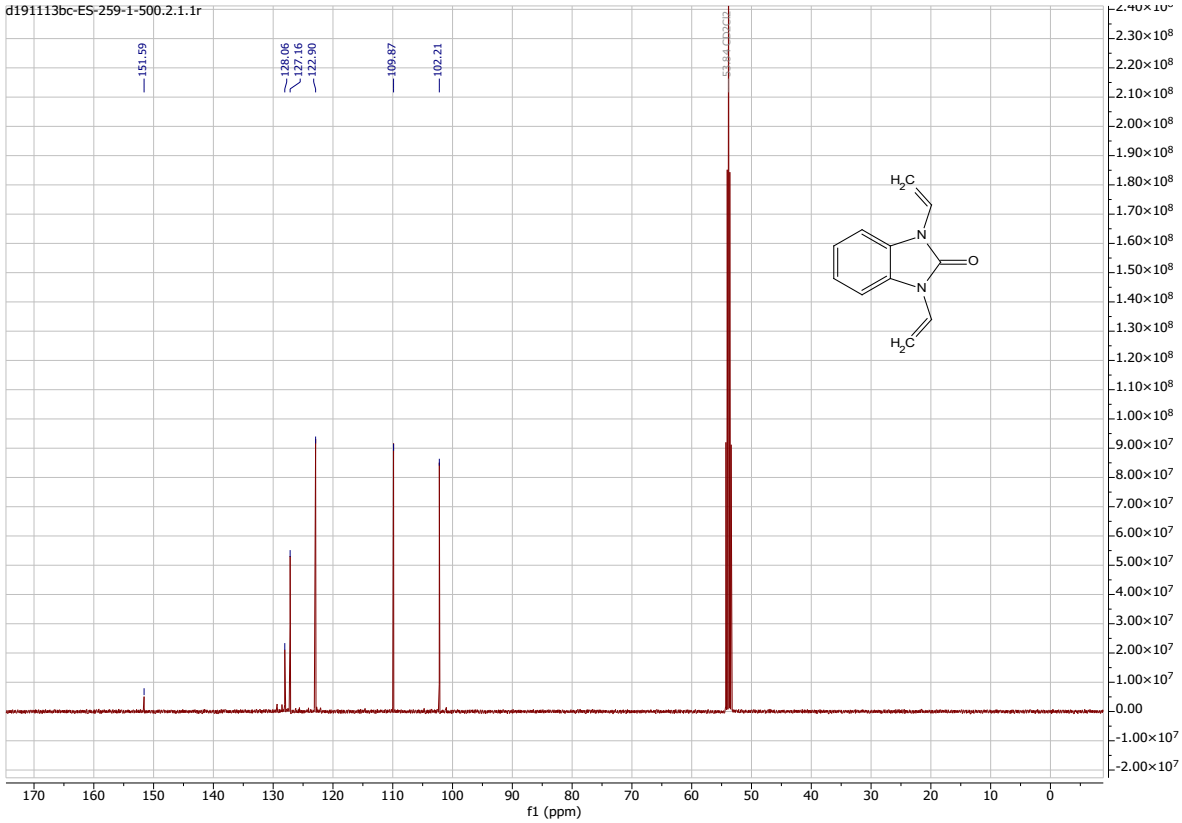
^{13}C of **3n**:



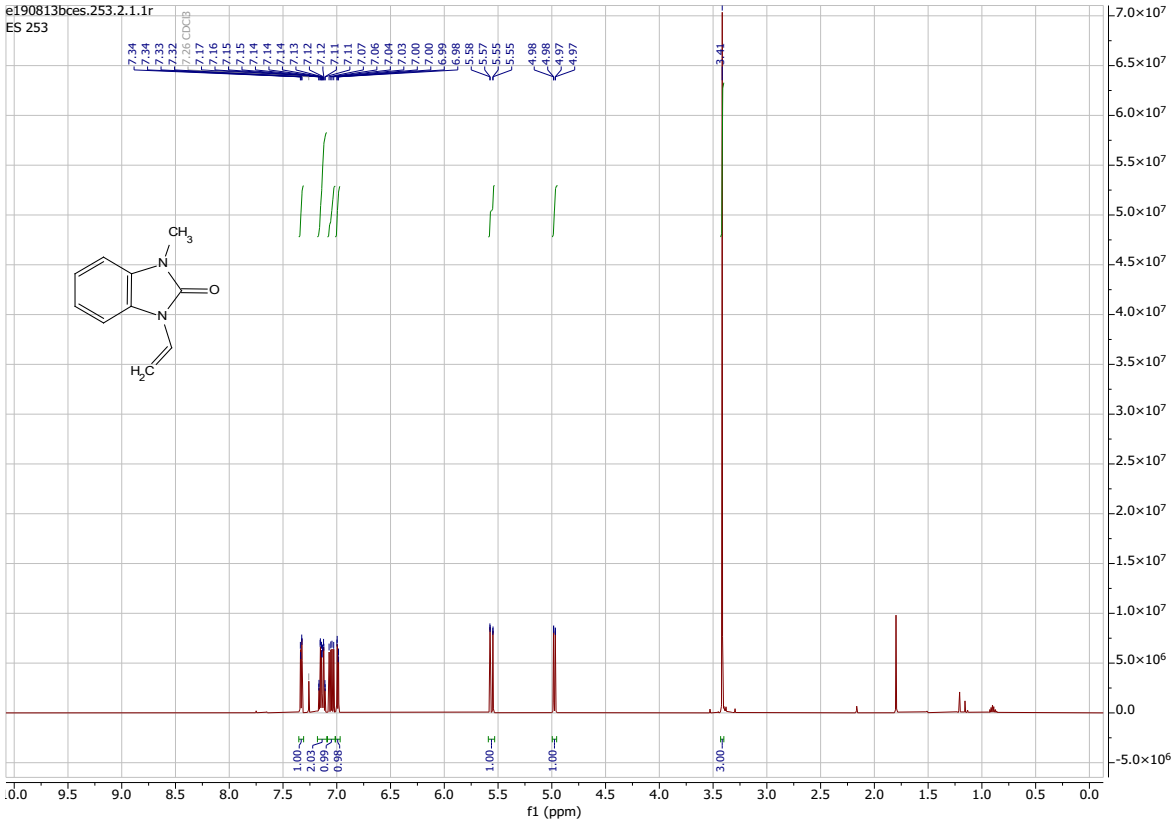
^{1}H NMR of **3o**:



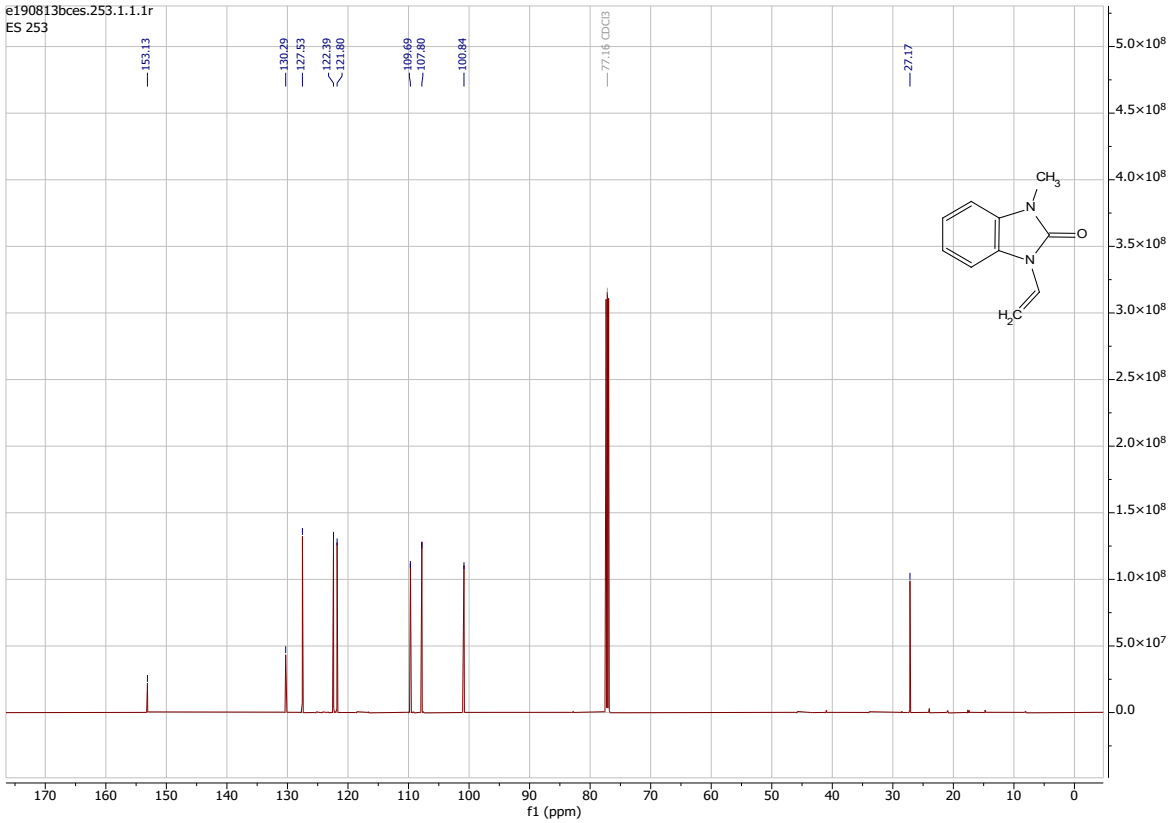
^{13}C of **3o**:



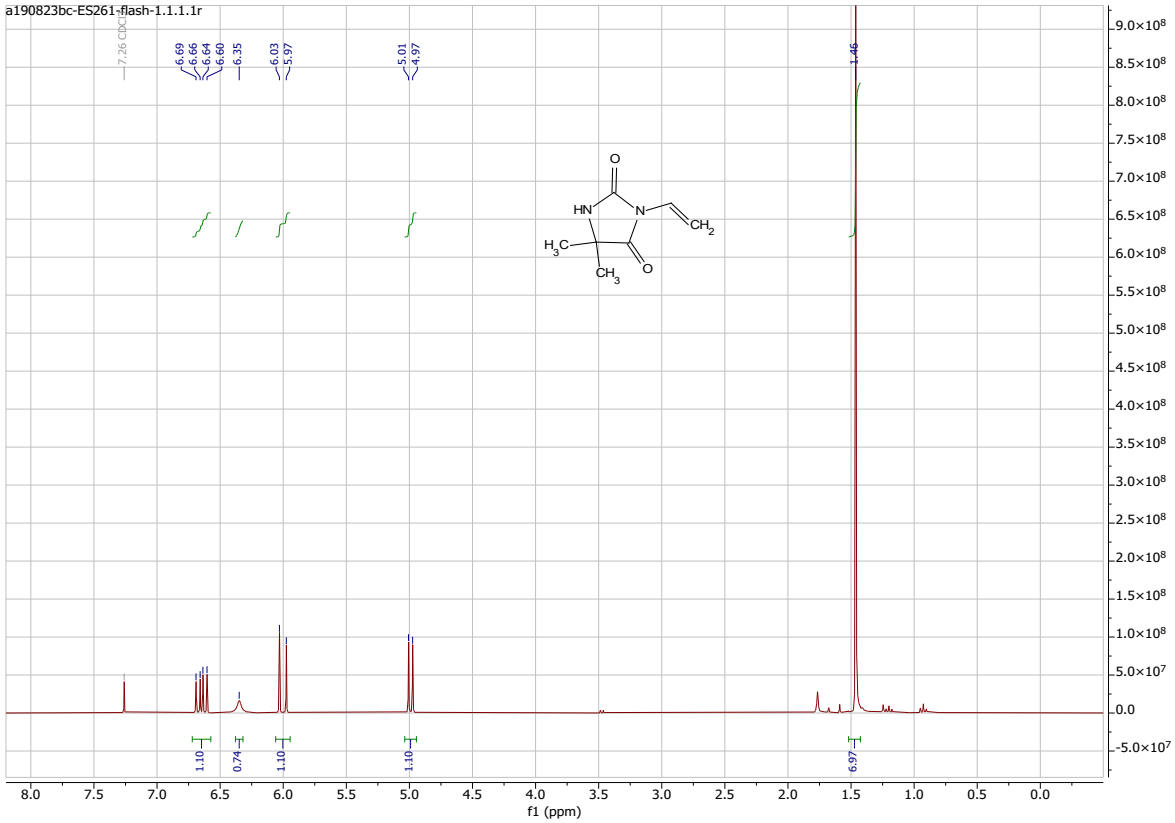
^{1}H NMR of **3p**:



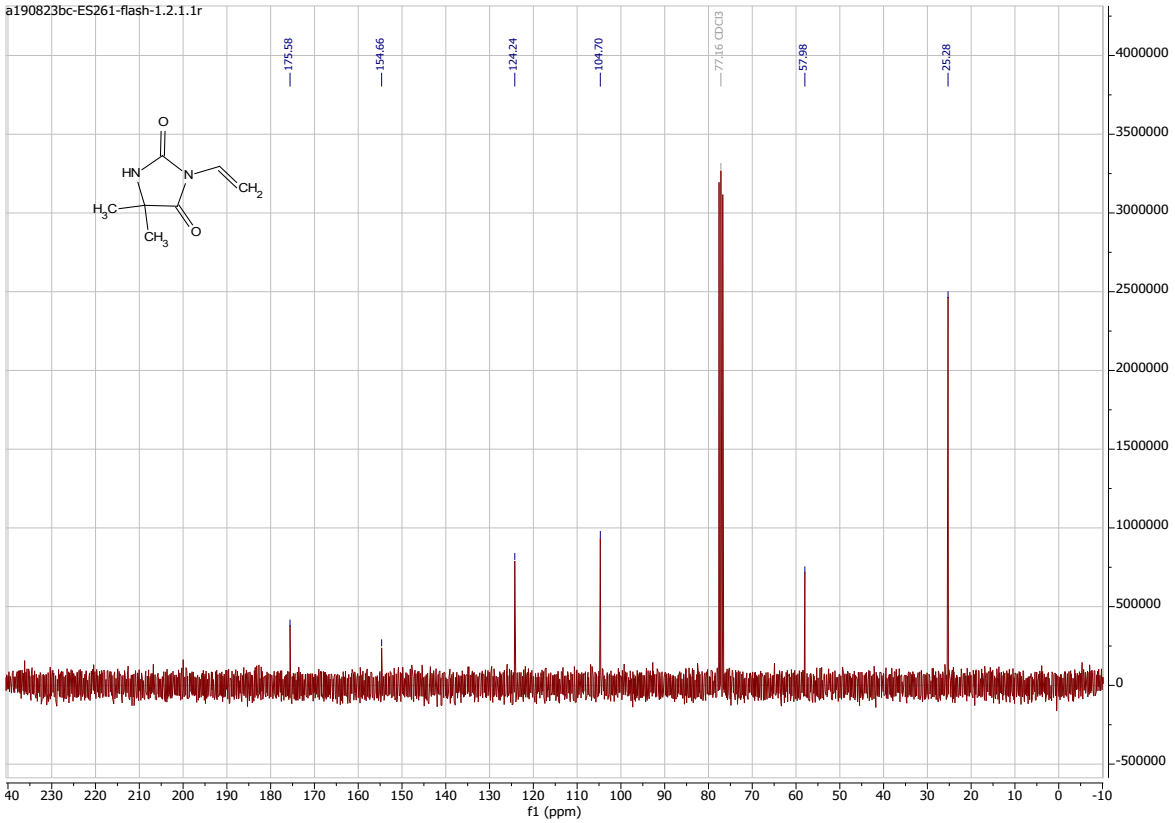
^{13}C of **3p**:



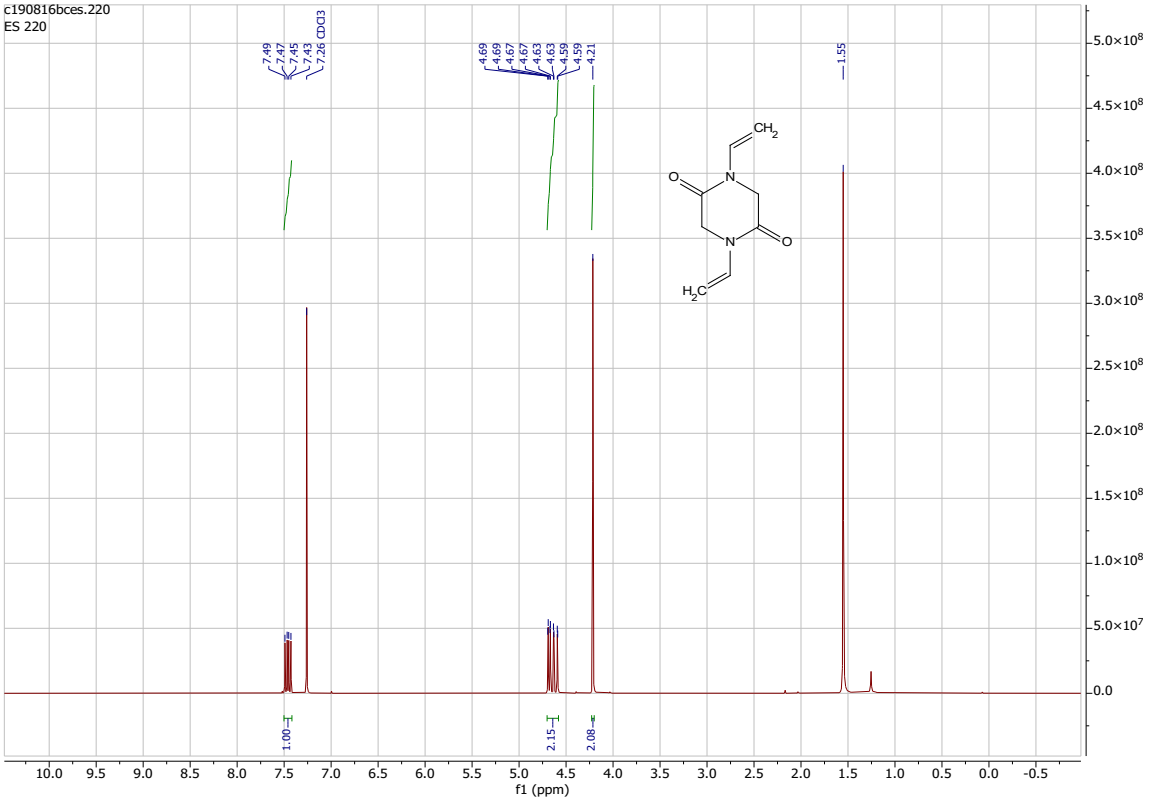
^{1}H NMR of **3q**:



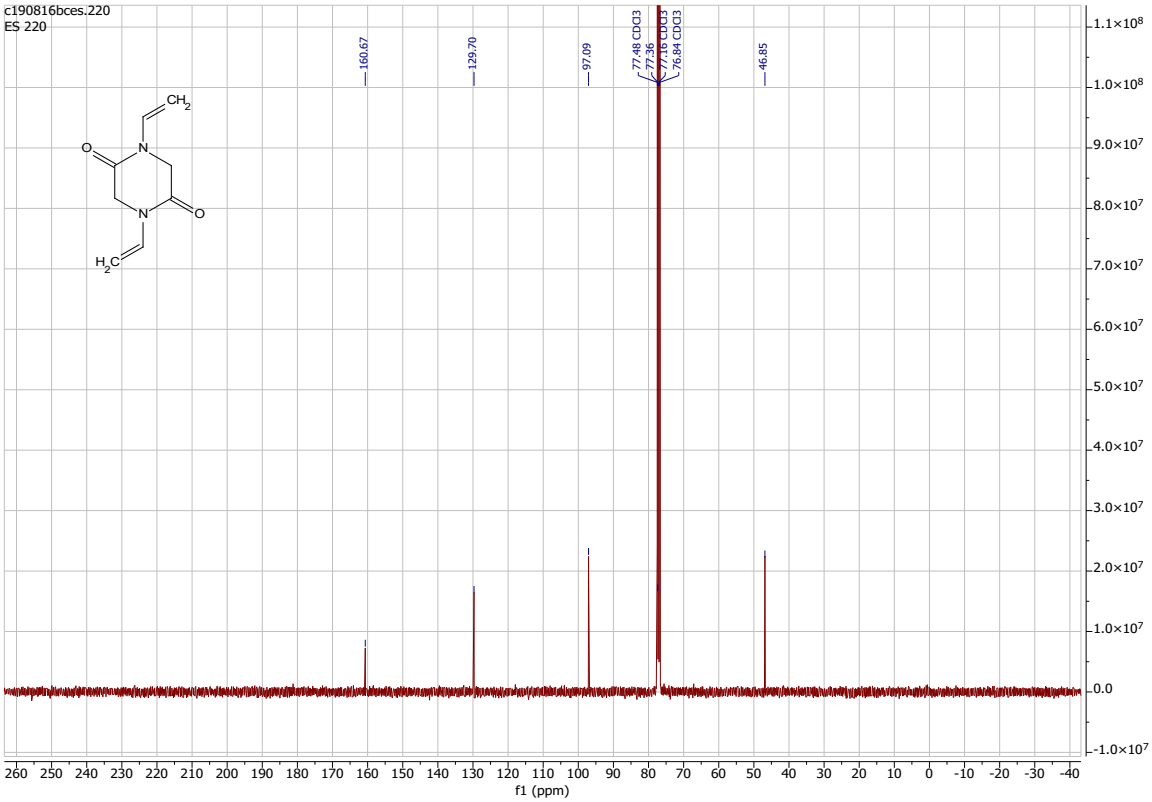
^{13}C of **3q**:



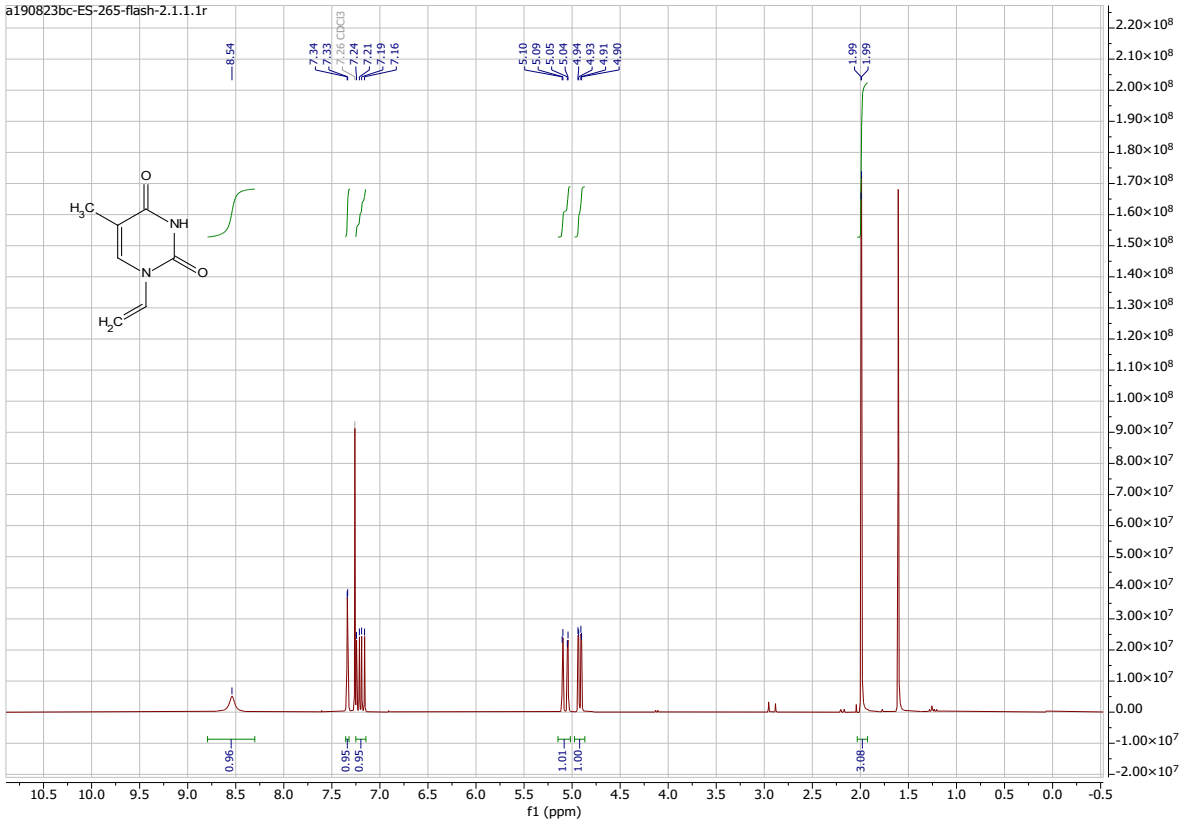
^{1}H NMR of **3r**:



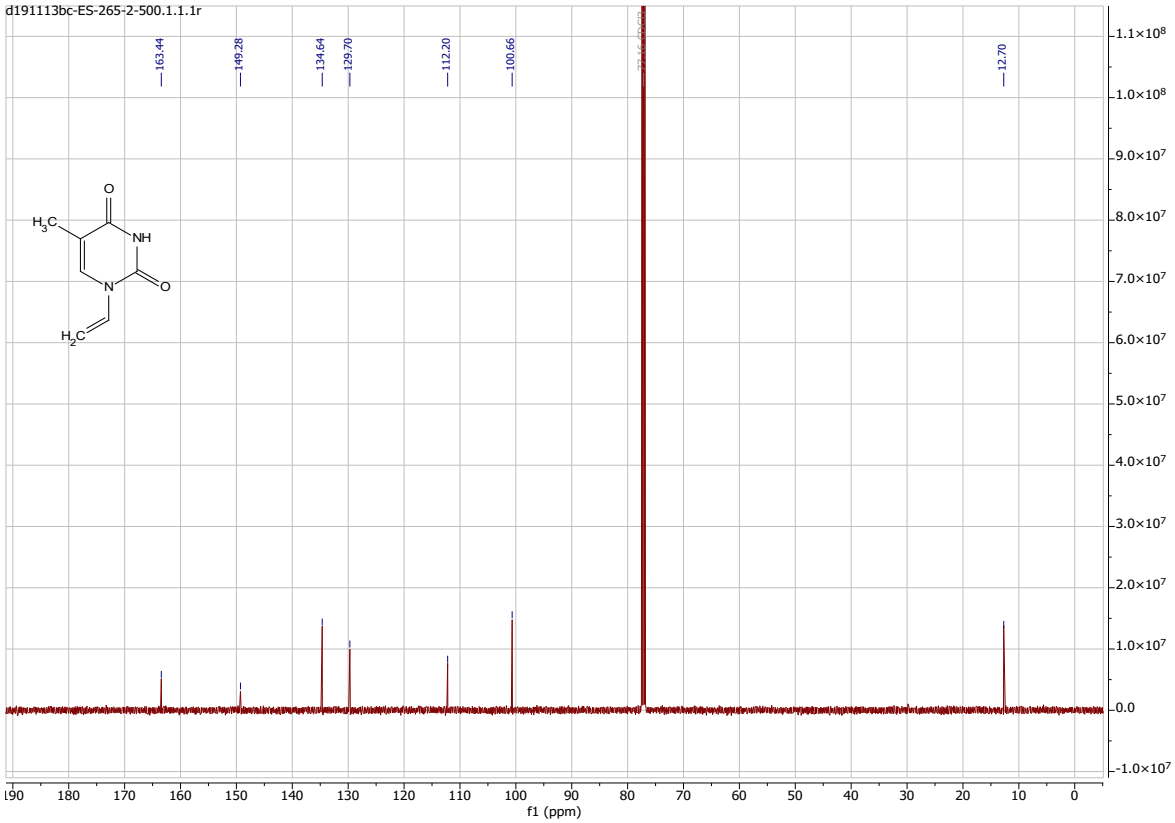
^{13}C of **3r**:



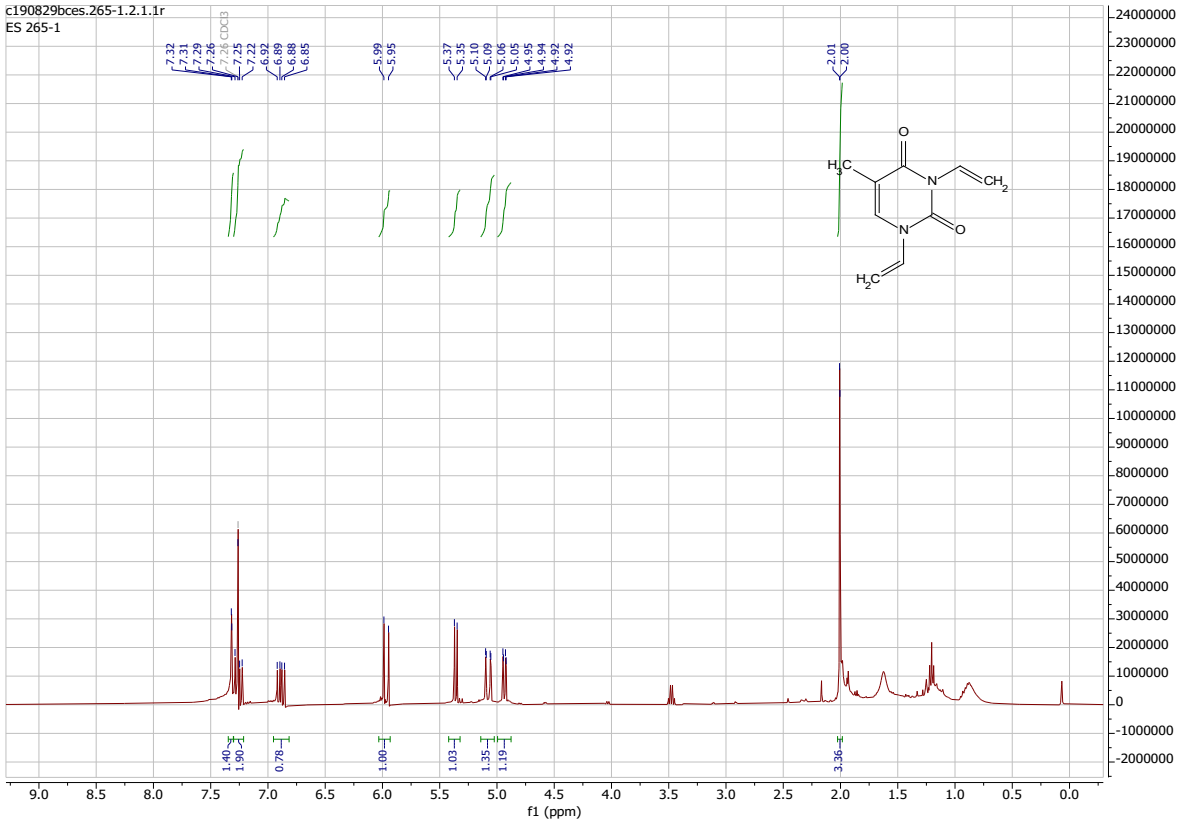
^{1}H NMR of **3s**:



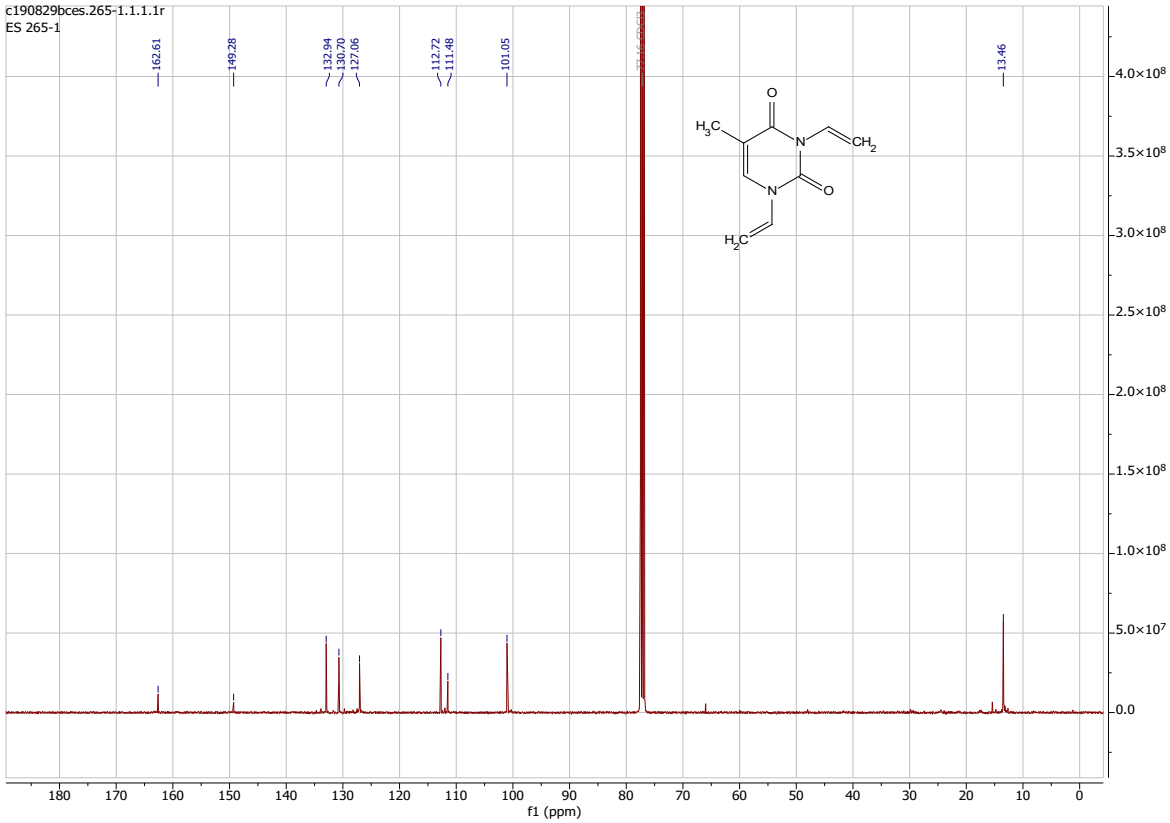
^{13}C of **3s**:



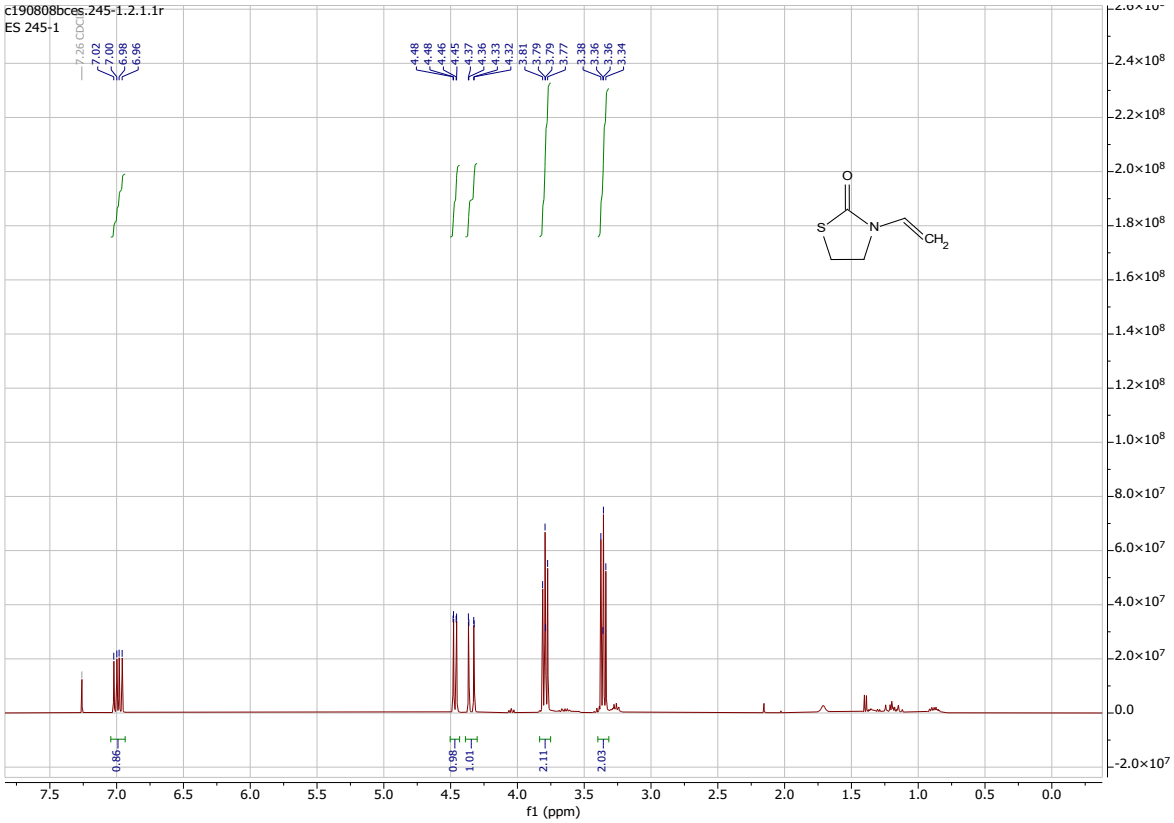
^{1}H NMR of **3t**:



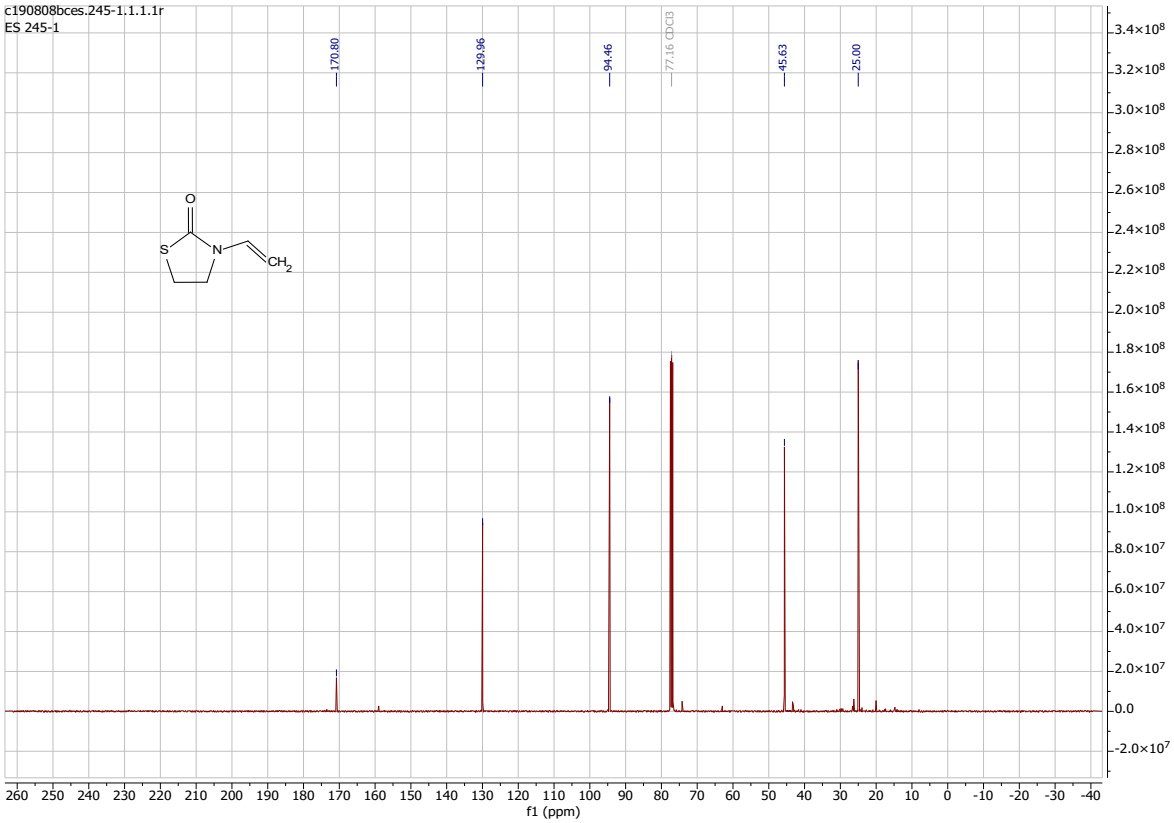
^{13}C of **3t**:



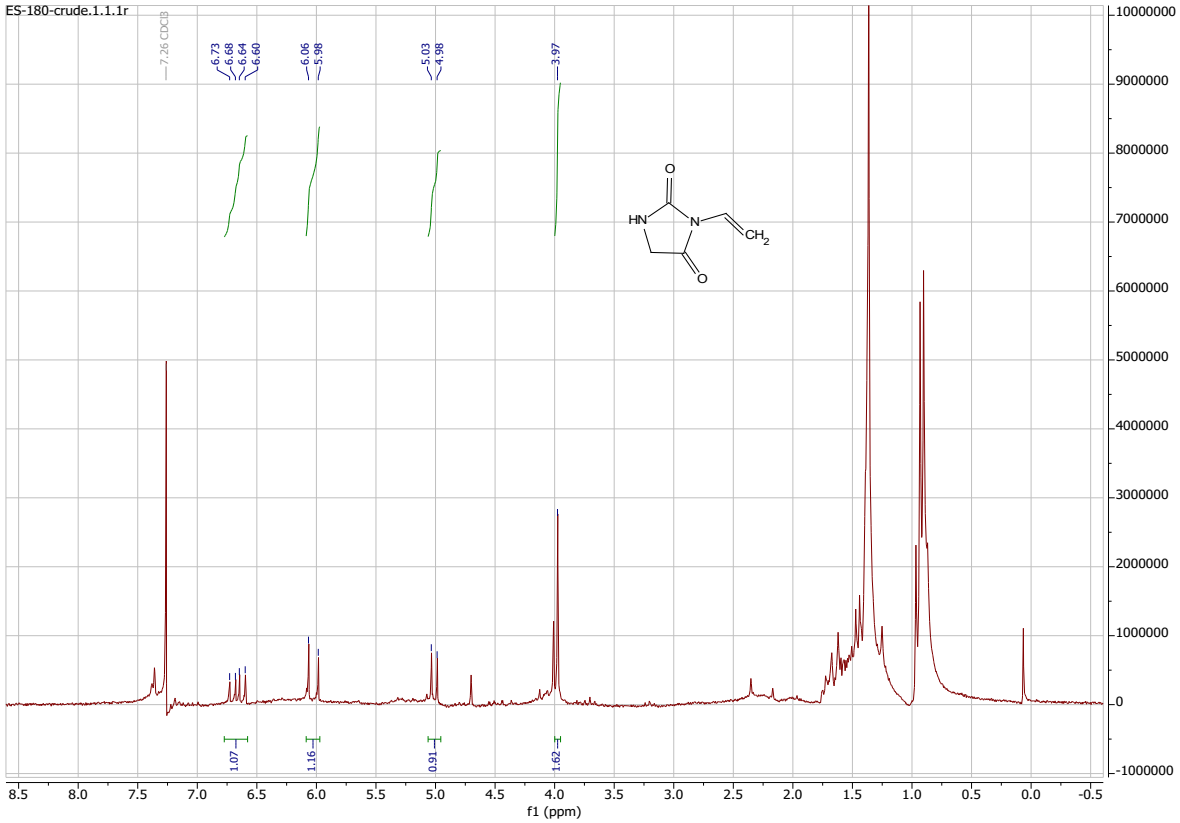
^{1}H NMR of **3u**:



^{13}C of **3u**:



^{1}H NMR of **3v** (1H NMR of the crude compound):



S9: References

1 I. T. Trotus, T. Zimmermann, F. Schuth, *Chem. Rev.*, 2014, **114**, 1761.
2 C. Gaulon, P. Gizecki, R. Dhal, G. Dujardin, *Synlett*, 2002, 952.
3 R. Dalpozzo, A. De Nino, L. Maiuolo, A. Procopio, R. Romeo, G. Sindona, *Synthesis-Stuttgart*, 2002, 172.
4 P. Arsenyan, A. Petrenko, E. Paegle, S. Belyakov, *Mendeleev Commun*, 2011, **21**, 326.
5 Z. V. Stepanova, G. G. Skvortsova, V. K. Voronov, A. V. Afonin, *Khim. Geterotsikl. Soedin.*, 1986, 567.