Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

gem-Bromonitrocyclobutane induced radical cyclization of acrylanilide to construct 2-oxindole via photoredox catalysis

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1. General information

All the solvents and reagents were obtained from commercial sources and used without purification unless stated otherwise. THF, Et_2O and 1,4-dioxane were distilled over CaH_2 and $LiAlH_4$ under N_2 atmosphere. Toluene, CH_2Cl_2 and CH_3CN were distilled over CaH_2 under N_2. Acetone, AcOEt, DMSO, DMA, DMF, DME, $CHCl_3$, $C_2H_5NO_2$, CH_3NO_2 and DBU were dried over activated 4A molecular sieves. All glassware was dried overnight at 100°C prior to use. All visible light induced photocatalytic reactions were performed in a Schlenk tube under N_2 atmosphere. Thin-layer chromatography (TLC) was performed on silica gel plates (0.2–0.25 mm thickness). Visualization of TLC was achieved by the use of UV light (254 nm). Flash column chromatography was performed on a silica gel (Qingdao Haiyang, 200–300 mesh) column. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECZ 400 MHz or 600 MHz spectrometer. The chemical shift (δ) values are given in ppm and are referenced to TMS or residual solvent peaks. Chemical shifts of ^{19}F NMR are referred to $CFCl_3$ (δ = 0). Infrared spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRX-4 (Shanghai Yice) micro melting point apparatus. Mass spectra were obtained on an AB Sciex TripleTOF 5600+ mass spectrometer. X-ray diffraction experiment was performed on a Rigaku XtaLAB Synergy diffractometer using Cu Kα radiation. For reactions that require heating, a silicone oil bath was used.

1.1 Photochemical set-up in our lab

Synthware® glassware made from borosilicate glass 3.3 and strips of 2835 light-emitting diode (120 LEDs/m, DC 12 V, 10 watt/m) surface-mounted on bare printed circuit board from Shenzhen Jinhongyan Lighting Co., Ltd. were used for photochemical reactions. A LED tube (inner diameter and height of 10 cm) was used as the lighting device for all photochemical reactions. The length of blue LED strip is 1.5 meters and the power is 15 W. The reaction temperature is controlled at about 25 °C by a small desk fan.

Figure S1 Photochemical set-up in our lab.

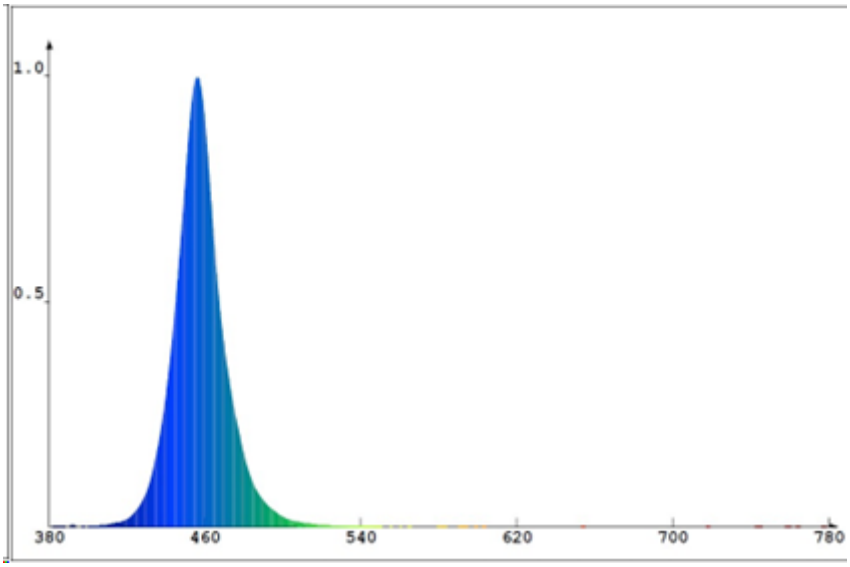
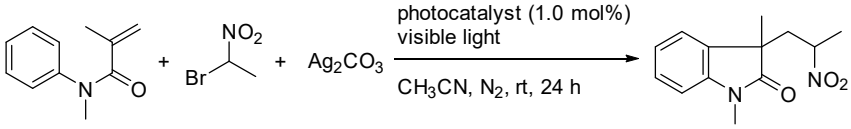


Figure S2 Luminous spectrum of blue LED (λ_p = 456 nm).

1.2 Optimization of reaction conditions

Table S1 Effect of photocatalyst.

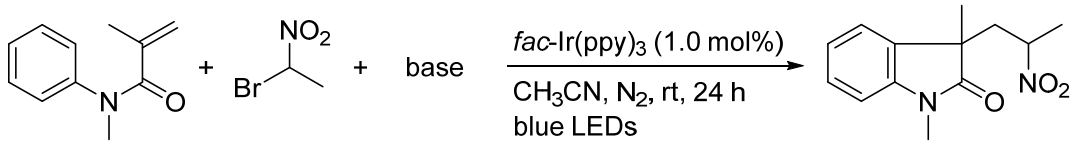


1a **2a** (2.0 equiv) (2.0 equiv) **3aa**

Entry	Photocatalyst	Light source	**3aa** Yield (%)
1	*fac*-Ir(ppy)$_3$	blue LEDs (15 W)	61
2	[Ru(bpy)$_3$](PF$_6$)$_2$		10
3	[Ru(bpy)$_3$]Cl$_2$		trace

4	$[Ru(bpy)_3]Cl_2·6H_2O$		5
5	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$		trace
6	4CzIPN (10 mol%)		10
7	PDI (10 mol%)		0
8	none		5
9	PTh (10 mol%)	purple LEDs	0
10	*fac*-Ir(ppy)$_3$	ambient light	0

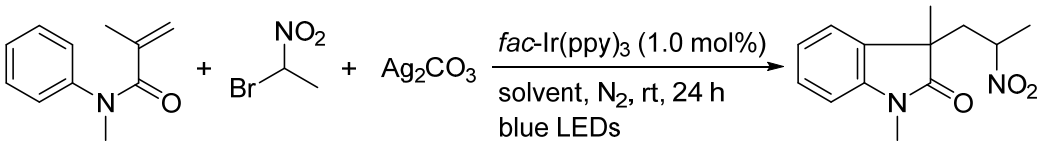
Table S2 Effect of base.



1a **2a** (2.0 equiv) (2.0 equiv) **3aa**

Entry	Base	Yield (%)	Entry	Base	Yield (%)
1	Na_2CO_3	5	11	Ag_2CO_3	83
2	Cs_2CO_3	4	12	AgF	20
3	$CsHCO_3$	trace	13	$AgPF_6$	trace
4	$KF·2H_2O$		14	$AgNO_2$	
5	$K_3PO_4·7H_2O$		15	$AgNO_3$	
6	2,6-lutidine	0	16	Ag_2O	
7	pyridine		17	AgOAc	0
8	Et_3N		18	Ag_2SO_4	
9	DBU		19	AgOTf	
10	TBD	13	20	none	

Table S3 Effect of solvent.



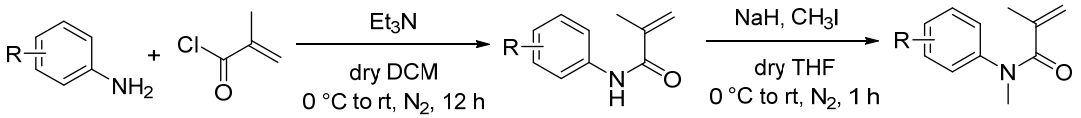
1a **2a** (2.0 equiv) (2.0 equiv) **3aa**

Entry	Solvent	Yield (%)	Entry	Solvent	Yield (%)
1	CH_3CN	61	7	1,2-dichloroethane	32
2	THF	41	8	ethyl acetate	0
3	DME	62	9	acetone	88
4	1,4-dioxane	0	10	DMSO	trace
5	toluene	0	11	DMF	43
6	DCM	42	12	CH_3OH	0

2. Preparation of acrylamides

2.1 Preparation of acrylamides

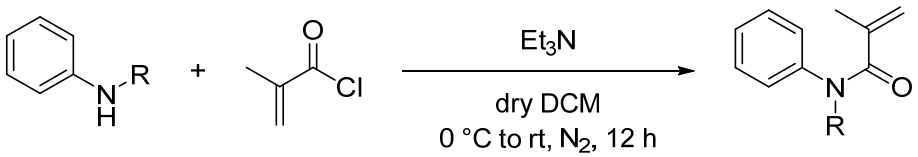
General procedure A[1]



In a 100 mL Schlenk tube, the corresponding aniline (21 mmol) and triethylamine (4.19 g, 42 mmol, 2 equiv) were dissolved in anhydrous DCM (50 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, and methacryloyl chloride (2.4 g, 23 mmol, 1.1 equiv) was added slowly under N_2 atmosphere. The resulting solution was stirred at room temperature for 12 h, quenched with H_2O (10 mL), extracted with DCM (50 mL × 3). The combined organic layer was washed with saturated brine (50 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by recrystallization.

In a 100 mL Schlenk tube, the corresponding *N*-phenylmethacrylamide (6.0 mmol) was dissolved in anhydrous THF (50 mL) under N_2 atmosphere. Then NaH (60% in mineral oil, 480 mg, 12 mmol, 2.0 equiv) was added in portions to the solution. The mixture was stirred at 0 °C for 20 min, then CH_3I (1.70 g, 12 mmol, 2.0 equiv) was added dropwise under N_2 atmosphere. The resulting solution was stirred at room temperature for 1 h, quenched carefully with H_2O (10 mL), extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with saturated brine (30 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give the corresponding *N*-phenyl methacrylamide.

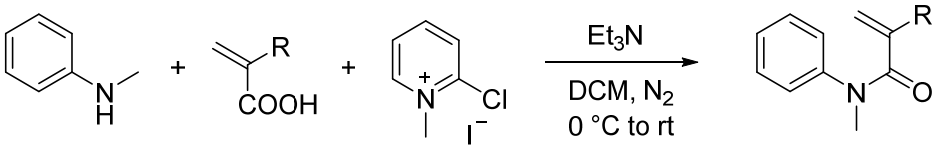
General procedure B[1]



In a 100 mL Schlenk tube, *N*-substituted aniline (21 mmol) and triethylamine (4.19 g, 42 mmol, 2 equiv) were dissolved in anhydrous DCM (50 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, and methacryloyl chloride (2.6 g, 24 mmol, 1.2 equiv) was added slowly under N_2 atmosphere. The resulting solution was stirred at room temperature for 12 h, quenched with H_2O (10 mL), extracted with DCM (50 mL × 3). The combined organic layer was washed with saturated brine (50 mL × 3), dried over Na_2SO_4,

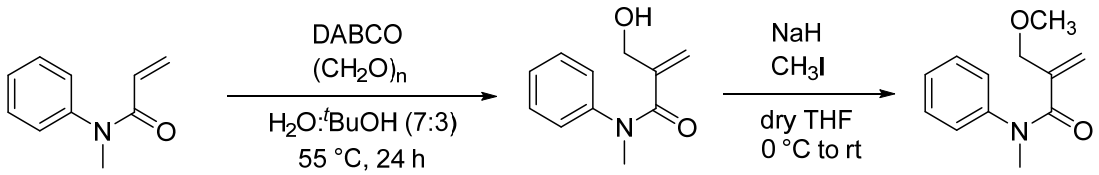
and concentrated. The residue was purified by flash chromatography on silica gel to give the corresponding product.

General procedure C[2]



In a 100 mL Schlenk tube, *N*-methylaniline (14 mmol), Mukaiyama reagent (4.3 g,1.5 equiv) and triethylamine (4.25 g, 42 mmol, 3 equiv) were dissolved in anhydrous DCM (20 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, and the corresponding acrylic acid (1.2 equiv) was added slowly under N_2 atmosphere. The resulting solution was stirred at room temperature for 12 h, quenched with H_2O (10 mL), extracted with DCM (50 mL × 3). The combined organic layer was washed with saturated brine (50 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give the corresponding product.

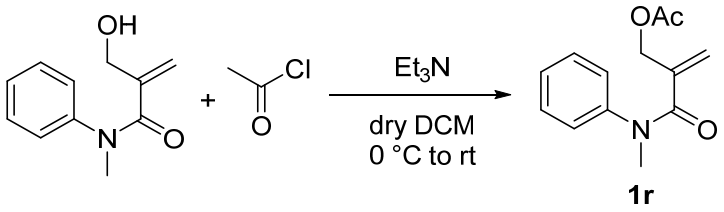
General procedure D[3]



In a 100 mL Schlenk tube, paraformaldehyde (3.0 g, 5.0 equiv), DABCO (2.24 g, 1.0 equiv) and phenol (0.47 g, 0.25 equiv) were dissolved in a mixture of *t*-butanol and water (7 mL, 3:7). The mixture was stirred at 55 ºC until dissolution is complete. *N*-Methyl-*N*-phenylacrylamide (3.22 g, 20 mmol) was added and the mixture was stirred at 55 ºC for 24 h. Then, the organic solvent was removed under reduced pressure and the residue was extracted with chloroform (20 mL × 3). The organic phase was collected and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography on silica gel to give 2-(hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide (white solid, 84% yield).

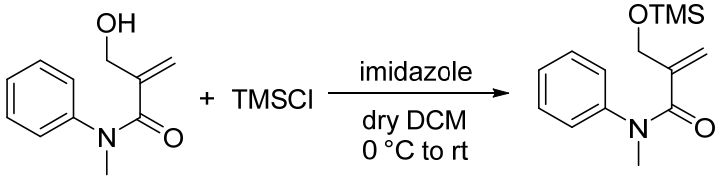
In a 100 mL Schlenk tube, 2-(hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide (0.30 g, 1.57 mmol) was dissolved in anhydrous THF (50 mL) under N_2 atmosphere. Then NaH (60% in mineral oil, 130 mg, 3.14 mmol, 2.0 equiv) was added in portions to the solution. The mixture was stirred at 0 °C for 20 min, then CH_3I (0.45 g, 3.14 mmol, 2.0 equiv) was added dropwise under N_2 atmosphere. The resulting solution was stirred at room temperature until the reaction was completed, quenched carefully with H_2O (10 mL),

extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with saturated brine (30 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give the corresponding product as a colorless oil (300 mg, 82% yield).



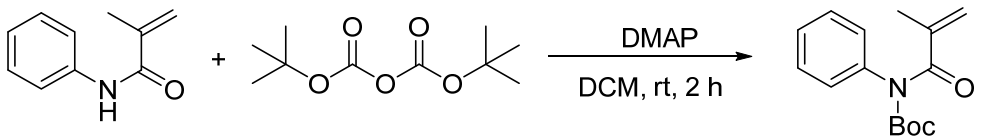
1r

In a 100 mL Schlenk tube, 2-(hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide (2.0 g, 1.0 equiv) and Et_3N (2.1 g, 2.0 equiv) were dissolved in anhydrous CH_2Cl_2 (50 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, then acetyl chloride (1.6 g, 2.0 equiv) was added dropwise under N_2 atmosphere. The resulting solution was stirred at room temperature until the reaction was completed, quenched carefully with H_2O (10 mL), extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with saturated brine (30 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give **1r** as a pale yellow oil (2.44 g, 86% yield).



In a 100 mL Schlenk tube, 2-(hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide (2.0 g, 1.0 equiv) and imidazole (2.14 g, 3.0 equiv) were dissolved in anhydrous CH_2Cl_2 (50 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, then TMSCl (2.3 g, 2.0 equiv) was added dropwise under N_2 atmosphere. The resulting solution was stirred at room temperature until the reaction was completed, quenched with H_2O (10 mL), extracted with ethyl acetate (30 mL × 3). The combined organic layer was washed with saturated brine (30 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel to give the corresponding product as a yellow oil (2.5 g, 91% yield).

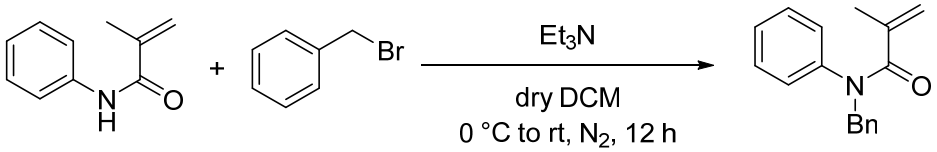
***tert*-Butyl methacryloyl(phenyl)carbamate**[4]



To a stirred solution of *N*-phenyl methacrylamide (2.25 g, 14 mmol) in 50 mL DCM were added DMAP (30 mg, 0.25 mmol) and Boc_2O (3.91 g, 21 mmol) successively. The resulting solution was stirred at

room temperature for 2 h, after which the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel to give a white solid (3.3 g, 90% yield).

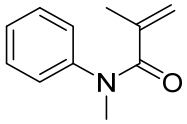
***N*-Benzyl-*N*-phenyl methacrylamide**[1]



In a 100 mL Schlenk tube, *N*-phenyl methacrylamide (1.5 g, 14 mmol) and triethylamine (2.8 g, 28 mmol, 2.0 equiv) were dissolved in anhydrous DCM (50 mL) under N_2 atmosphere. The mixture was stirred at 0 °C, and benzyl bromide (4.18 g, 21 mmol, 1.5 equiv) was added slowly under N_2 atmosphere. The resulting solution was stirred at room temperature for 12 h, after which the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel to give a light yellow oil (3.5 g, 86% yield).

2.2 Physical data

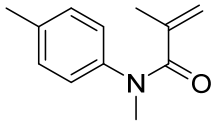
***N*-Methyl-*N*-phenylmethacrylamide (1a)** [1]



General procedure A

White solid (2.1 g, 97% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.30 – 7.21 (m, 1H), 7.17 – 7.10 (m, 2H), 5.03 (t, *J* = 1.5 Hz, 1H), 4.99 (t, *J* = 1.1 Hz, 1H), 3.35 (s, 3H), 1.76 (dd, *J* = 1.6, 1.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.9, 144.6, 140.7, 129.2, 126.8, 126.5, 119.3, 37.6, 20.2 ppm.

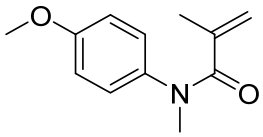
***N*-Methyl-*N*-(*p*-tolyl)methacrylamide (1b)** [1]



General procedure A

Yellow oil (2.0 g, 95% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (t, *J* = 6.7 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 4.96 (d, *J* = 11.5 Hz, 2H), 3.28 (d, *J* = 1.4 Hz, 3H), 2.30 (s, 3H), 1.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 141.9, 140.7, 136.6, 129.7, 126.2, 118.9, 37.5, 20.8 ppm.

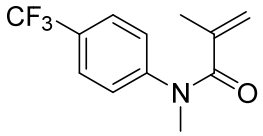
***N*-(4-Methoxyphenyl)-*N*-methylmethacrylamide (1c)** [1]



General procedure A

Yellow oil (1.6 g ,86% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.02 – 6.95 (m, 2H), 6.83 – 6.77 (m, 2H), 4.94 (d, J = 17.7 Hz, 2H), 3.74 (s, 3H), 3.24 (s, 3H), 1.68 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.8, 158.0, 140.6, 127.4, 118.6, 114.1, 55.1, 37.5, 20.1 ppm.

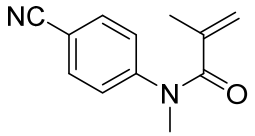
***N*-Methyl-*N*-(4-(trifluoromethyl) phenyl)methacrylamide (1d)** [1]



General procedure A

Yellow oil (2.0 g, 95% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.67 – 6.59 (m, 2H), 6.28 (dt, *J* = 7.7, 1.0 Hz, 2H), 4.35 – 3.87 (m, 2H), 2.39 (s, 3H), 0.83 (d, *J* = 0.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 147.8, 140.1, 128.8 (q, *J*=0.32 Hz), 126.4, 120.1, 37.4, 20.1 ppm.

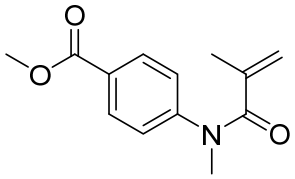
***N*-(4-Cyanophenyl)-*N*-methylmethacrylamide (1e)** [1]



General procedure A

White solid (1.9 g, 94% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.62 – 6.26 (m, 2H), 6.01 (d, *J* = 8.7 Hz, 2H), 4.23 – 3.58 (m, 2H), 2.13 (s, 3H), 0.59 (dd, *J* = 1.7, 1.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.6, 148.6, 140.0, 133.1, 126.4, 120.4, 118.1, 110.1, 37.3, 20.0 ppm.

Methyl 4-(*N*-methylmethacrylamido) benzoate (1f) [1]

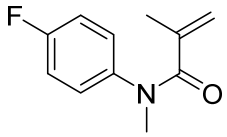


General procedure A

White solid (1.5 g, 80% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 7.93 (m, 2H), 7.39 – 7.07 (m, 2H), 5.02 (ddd, *J* = 36.3, 1.8, 0.9 Hz, 2H), 3.91 (d, *J* = 0.6 Hz, 3H), 3.37 (d, *J* = 0.6 Hz, 3H), 1.79 (t,

J = 0.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 166.2, 148.7, 140.3, 130.6, 128.2, 125.9, 120.1, 52.2, 37.4, 20.1 ppm.

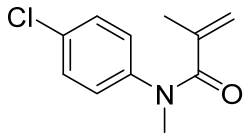
***N*-(4-Fluorophenyl)-*N*-methylmethacrylamide (1g)** [1]



General procedure A

White solid (1.9 g, 90% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 6.80 (m, 4H), 4.99 (dt, *J* = 30.4, 1.4 Hz, 2H), 3.30 (s, 3H), 1.74 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 161.1 (d, *J* = 247.0 Hz), 140.5, 128.1 (d, *J* = 8.6 Hz), 119.3, 116.0 (d, *J* = 22.7 Hz), 37.7, 20.2 ppm.

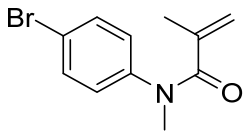
***N*-(4-Chlorophenyl)-*N*-methylmethacrylamide (1h)** [1]



General procedure A

White solid (1.8 g, 92% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.28 (m, 2H), 7.08 – 7.04 (m, 2H), 5.05 (p, *J* = 1.6 Hz, 1H), 4.96 (p, *J* = 1.1 Hz, 1H), 3.30 (s, 3H), 1.76 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.8, 143.1, 140.3, 132.5, 129.3, 127. 7, 119.6, 37.6, 20.2 ppm.

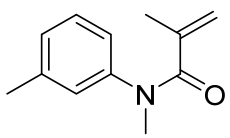
***N*-(4-Bromophenyl)-*N*-methylmethacrylamide (1i)** [1]



General procedure A

White solid (2.1 g, 96% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.99 (dt, *J* = 36.5, 1.2 Hz, 2H), 3.29 (s, 3H), 1.75 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.6, 143.6, 140.3, 132.3, 127.9, 120.3, 119.6, 37.5, 20.1 ppm.

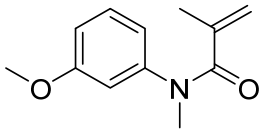
***N*-Methyl-*N*-(*m*-tolyl) methacrylamide (1j)** [1]



General procedure A

Yellow oil (1.9 g, 93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.7 Hz, 1H), 7.02 – 6.93 (m, 1H), 6.91 – 6.82 (m, 2H), 4.93 (dt, *J* = 9.5, 1.3 Hz, 2H), 3.25 (s, 3H), 2.42 – 2.17 (m, 3H), 1.82 – 1.64 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 144.4, 140.6, 139.0, 128.8, 127.5, 126.9, 123.4, 119.0, 37.5, 21.1, 20.2 ppm.

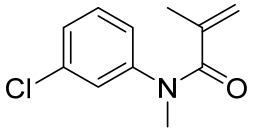
***N*-(3-Methoxyphenyl)-*N*-methylmethacrylamide (1k)** [1]



General procedure A

Yellow oil (1.8 g, 91% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (ddd, *J* = 8.1, 6.7, 2.2 Hz, 1H), 6.73 – 6.55 (m, 3H), 5.13 – 4.78 (m, 2H), 3.68 (d, *J* = 2.5 Hz, 3H), 3.22 (d, *J* = 2.4 Hz, 3H), 1.78 – 1.55 (m, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.8, 160.1, 145.7, 140. 7, 129.8, 119.1, 118.7, 112.5, 112.1, 55.3, 37.5, 20.2 ppm.

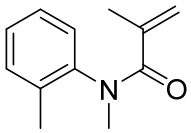
***N*-(3-Chlorophenyl)-*N*-methylmethacrylamide (1l)** [1]



General procedure A

Yellow oil (1.5 g, 85% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 6.93 (m, 4H), 5.64 – 4.86 (m, 2H), 3.34 (s, 3H), 1.80 (d, *J* = 1.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 145.8, 140.2, 134.6, 130.1, 127.0, 126.6, 124.6, 119.8, 37.6, 20.2 ppm.

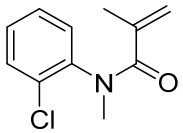
***N*-Methyl-*N*-(*m*-tolyl) methacrylamide (1m)** [1]



General procedure A

Yellow oil (2.1 g, 95% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 6.80 (m, 4H), 4.95 (s, 2H), 3.22 (s, 3H), 2.26 (s, 3H), 1.74 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 143.0, 140.4, 134.7, 131.1, 128.0, 127.7, 126.7, 118.3, 36.5, 20.1, 17.5 ppm.

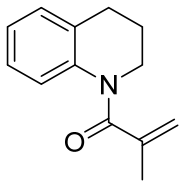
***N*-(2-Chlorophenyl)-*N*-methylmethacrylamide (1n)** [1]



General procedure A

Yellow oil (2.0 g, 93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 1H), 7.24 – 7.06 (m, 3H), 4.87 (d, *J* = 8.0 Hz, 2H), 3.15 (s, 3H), 1.71 (s, 3H) ppm.

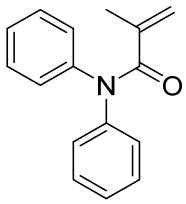
1-(3,4-Dihydroquinolin-1(*2H*)-yl)-2-methylprop-2-en-1-one (1o) [1]



General procedure B

Colorless oil (1.8 g, 89% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.17 (m, 1H), 7.15 – 6.99 (m, 3H), 5.42 – 4.97 (m, 2H), 3.79 (t, *J* = 6.5 Hz, 2H), 2.76 (t, *J* = 6.7 Hz, 2H), 1.97 (p, *J* = 6.6 Hz, 2H), 1.87 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 141.0, 138.7, 131.1, 128.1, 125.6, 124.6, 123.9, 118.8, 43.7, 26.5, 23.7, 19.6 ppm.

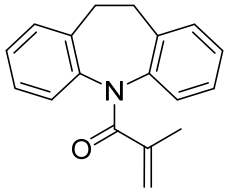
3-Methyl-1,1-diphenylbut-3-en-2-one (1p) [1]



General procedure B

White solid (2.2 g, 95% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dd, *J* = 10.9, 4.7 Hz, 4H), 7.28 – 7.13 (m, 6H), 5.20 (d, *J* = 25.0 Hz, 2H), 1.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 143.5, 141.2, 129.1, 127.1, 126.5, 120.9, 19.9 ppm.

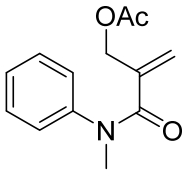
1-(10,11-Dihydro-*5H*-dibenzo[*b*,*f*]azepin-5-yl)-2-methylprop-2-en-1-one (1q) [1]



General procedure B

White solid (2.3 g, 93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.00 (m, 8H), 5.12 (dt, *J* = 19.0, 1.3 Hz, 2H), 3.46 (q, *J* = 7.8, 7.4 Hz, 2H), 2.87 (td, *J* = 9.4, 8.9, 4.2 Hz, 2H), 1.84 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.0, 140.6, 135.6, 130.1, 128.0, 127.8, 126.7, 118.8, 30.7, 20.3 ppm.

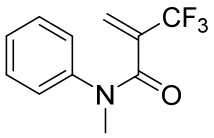
2-(Methyl(phenyl) carbamoyl) allyl acetate (1r) [3]



General procedure D

Colorless oil (0.5 g, 80% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 2H), 7.24 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.18 – 7.13 (m, 2H), 5.31 (s, 1H), 5.10 (s, 1H), 4.68 – 4.50 (m, 2H), 3.35 (s, 3H), 2.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 168.7, 144.2, 139.1, 129.3, 127.1, 126.7, 122.0, 64.7, 37.8, 20.8 ppm.

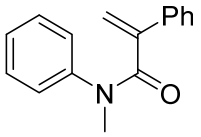
***N*-Methyl-*N*-phenyl-2-(trifluoromethyl) acrylamide (1s)** [2]



General procedure C

Colorless oil (1.4 g, 85% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 7.21 – 7.15 (m, 2H), 5.84 (s, 1H), 5.39 (s, 1H), 3.39 (d, *J* = 1.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 143.4, 134.0 (q, *J* = 31.6 Hz), 129.5, 127.6, 126.7, 125.5, 121.3 (q, *J* = 273.7 Hz), 37.6 ppm.

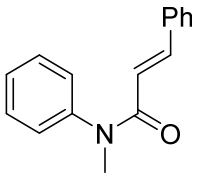
***N*-Methyl-*N*,2-diphenylacrylamide (1t)** [2]



General procedure C

White solid (1.9 g, 93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.80 (m, 10H), 5.41 (d, *J* = 40.2 Hz, 2H), 3.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 145.6, 143.5, 136.7, 128.7, 128.1, 127.8, 126.7, 125.9, 117.6, 37.2 ppm.

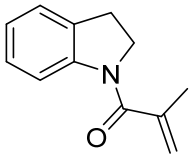
***N*-Methyl-*N*-phenylcinnamamide (1u)** [2]



General procedure C

Colorless oil (1.9 g, 89% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 15.6, 1.5 Hz, 1H), 7.42 (td, *J* = 7.9, 7.4, 1.6 Hz, 2H), 7.35 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.25 (tdd, *J* = 15.4, 5.5, 2.0 Hz, 7H), 6.36 (d, *J* = 15.4 Hz, 1H), 3.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.0, 143.6, 141.6, 135.1, 129.5, 129.4, 128.6, 127.7, 127.5, 127.2, 118.7, 37.4 ppm.

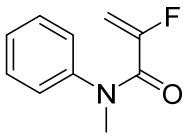
1-(Indolin-1-yl)-2-methylprop-2-en-1-one [1]



General procedure B

White solid (1.3 g, 84% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.39 – 5.16 (m, 2H), 4.09 (t, *J* = 8.3 Hz, 2H), 3.11 (t, *J* = 8.4 Hz, 2H), 2.04 (t, *J* = 1.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.8, 141.7, 132.3, 127.2, 124.8, 123.8, 116.6, 49.6, 27.8, 19.7 ppm.

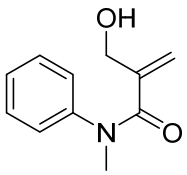
2-Fluoro-*N*-methyl-*N*-phenylacrylamide [2]



General procedure C

Colorless oil (0.7 g, 92% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (dddd, *J* = 9.2, 8.0, 3.1, 1.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.17 – 7.13 (m, 2H), 5.21 (d, *J* = 45.8 Hz, 1H), 4.92 (dd, *J* = 15.8, 3.4 Hz, 1H), 3.31 (d, *J* = 3.2 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 161.6, 161.4, 158.0, 156.2, 143.3, 129.33, 127.4, 125.7, 100.6, 100.5, 38.3 ppm.

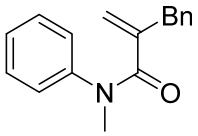
2-(Hydroxymethyl)-*N*-methyl-*N*-phenylacrylamide [3]



General procedure D

Colorless oil (2.4 g, 92% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 1H), 7.21 – 7.17 (m, 2H), 5.29 (s, 1H), 4.97 (s, 1H), 4.20 (s, 2H), 3.38 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 165.3, 164.6, 141.0, 139.6, 137.6, 137.5, 129.0, 128.9, 128.9, 125.1, 124.6, 124.5, 123.4, 120.4, 120.3, 120.3, 70.5, 63.6 ppm.

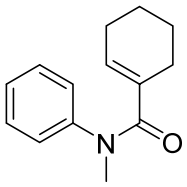
2-Benzyl-*N*-methyl-*N*-phenylacrylamide [2]



General procedure C

Colorless oil (1.6 g, 90% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.28 – 7.18 (m, 6H), 7.11 – 7.03 (m, 2H), 6.84 – 6.79 (m, 2H), 5.32 – 4.67 (m, 2H), 3.45 (s, 2H), 3.27 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 170.9, 144.3, 144.2, 137.7, 129.4, 129.0, 128.3, 126.8, 126.7, 126.4, 119.3, 77.2, 77.0, 76.8, 40.2, 37.7 ppm.

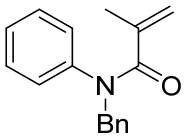
***N*-Methyl-*N*-phenylcyclohex-1-ene-1-carboxamide** [2]



General procedure C

Colorless oil (1.8 g, 88% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.18 (tdd, *J* = 7.6, 2.3, 1.1 Hz, 1H), 7.08 (ddd, *J* = 7.3, 2.5, 1.3 Hz, 2H), 5.79 (dt, *J* = 3.7, 2.0 Hz, 1H), 3.34 – 3.29 (m, 3H), 1.98 – 1.80 (m, 4H), 1.39 (dtt, *J* = 29.1, 5.7, 3.0 Hz, 4H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 172.5, 144.9, 134.5, 132.4, 128.9, 126.4, 126.3, 77.2, 77.0, 76.8, 37.5, 25.8, 24. 8, 21.9, 21.3 ppm.

***N*-Benzyl-*N*-phenylmethacrylamide** [1]

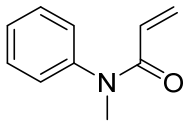


General procedure B

White solid (1.3 g, 74% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (dddd, *J* = 11.7, 8.5, 4.4, 2.3 Hz, 9H), 7.02 – 6.90 (m, 2H), 5.01 (dt, *J* = 7.6, 1.3 Hz, 2H), 4.96 (s, 2H), 1.77 (s, 3H) ppm; ^{13}C NMR

(150 MHz, Chloroform-*d*) δ 171.8, 143.2, 140.7, 137.5, 129.0, 128.4, 127.4, 127.3, 127.1, 119.4, 53.1, 20.4 ppm.

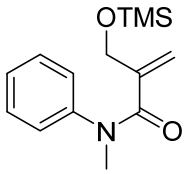
_N_-Methyl-_N_-phenylacrylamide [1]



General procedure B

White solid (2.8 g, 97% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 7.21 – 7.13 (m, 2H), 6.36 (dd, *J* = 16.8, 2.1 Hz, 1H), 6.07 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.51 (dd, *J* = 10.3, 2.1 Hz, 1H), 3.35 (d, *J* = 1.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.7, 143.4, 129.6, 128.5, 127.6, 127.4, 127.3, 37.4 ppm.

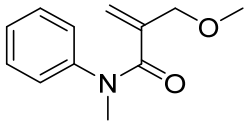
_N_-Methyl-_N_-phenyl-2-(((trimethylsilyl)oxy)methyl)acrylamide



General procedure D

Yellow oil (2.5 g, 91% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dd, *J* = 8.2, 6.7 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.16 – 7.10 (m, 2H), 5.28 – 5.15 (m, 1H), 4.88 (d, *J* = 1.3 Hz, 1H), 4.16 (s, 2H), 3.29 (s, 3H), 0.03 (d, *J* = 0.6 Hz, 9H) ppm.

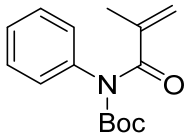
2-(Methoxymethyl)-_N_-methyl-_N_-phenylacrylamide [3]



General procedure D

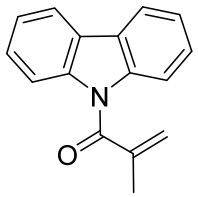
Colorless oil (0.23 g, 61% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (ddq, *J* = 7.9, 4.6, 2.0 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.18 – 7.15 (m, 2H), 5.23 (dt, *J* = 2.6, 1.3 Hz, 1H), 5.04 (d, *J* = 3.3 Hz, 1H), 3.91 (t, *J* = 1.6 Hz, 2H), 3.38 – 3.31 (m, 3H), 3.25 (dd, *J* = 3.3, 1.8 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 169.5, 144.2, 141.4, 129.1, 126.8, 126.7, 119.8, 72.9, 58.3, 37.6 ppm.

***tert*-Butyl methacryloyl(phenyl)carbamate**



White solid (1.8 g, 94% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 7.19 – 7.13 (m, 2H), 5.97 – 5.07 (m, 2H), 2.06 (d, *J* = 1.2 Hz, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 153.2, 142.9, 138.6, 129.0, 127.6, 127.6, 118.6, 83.5, 27.8, 27.7, 19.0 ppm.

1-(9*H*-Carbazol-9-yl)-2-methylprop-2-en-1-one [1]

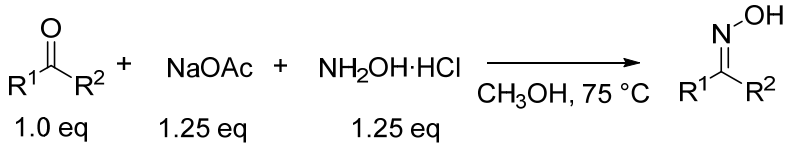


General procedure B

Yellow oil (0.7 g, 71% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.27 – 7.89 (m, 4H), 7.54 – 7.32 (m, 4H), 5.77 – 5.51 (m, 2H), 2.26 (dd, *J* = 3.1, 1.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 141.5, 138.6, 126.8, 125.9, 123.4, 122.3, 119.7, 115.7, 19.2 ppm.

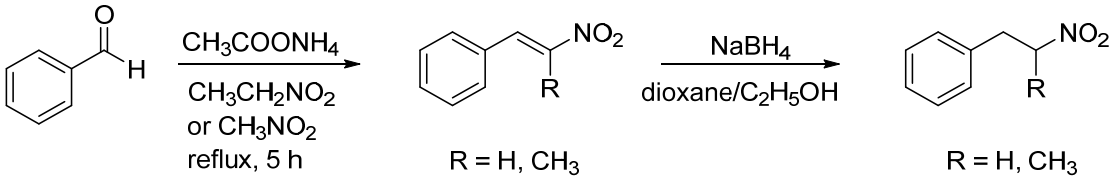
3. Preparation of gem-bromonitroalkanes

3.1 Preparation of oximes[5,6]



In a round-bottom flask, the ketone (50 mmol) was dissolved in CH_3OH (100 mL) under N_2 atmosphere, then sodium acetate (5.12 g, 62.5 mmol) and hydroxylamine hydrochloride (4.35 g, 62.5 mmol) were added. The solution was heated at 75 °C to reflux and stirred overnight. After cooling to room temperature, methanol was evaporated and H_2O (50 mL) was added followed by AcOEt (100 mL). Then the organic layer was washed with saturated brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated to give a white solid.

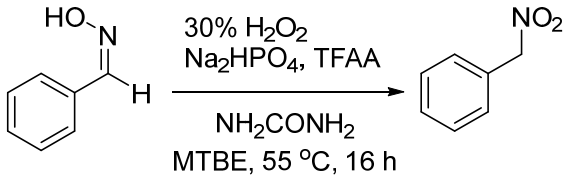
3.2 Preparation of nitro compounds[7-9]



Step 1: Benzaldehyde (5.0 g, 47 mmol) and ammonium acetate (0.5 g, 6.5 mmol) were added to nitroethane (20 mL) and the mixture was refluxed for 5 h. After cooling to room temperature, the mixture was partially evaporated with a rotary evaporator, diluted with diethyl ether, and washed twice with water. The organic layer was dried over anhydrous magnesium sulphate, filtered, and concentrated. The remaining residue was recrystallized from petroleum ether to afford (2-nitroprop-1-en-1-yl)benzene.

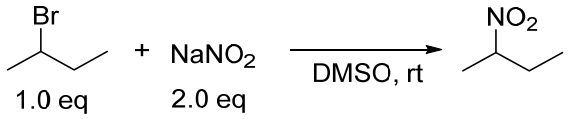
Step 2: A solution of (2-nitroprop-1-en-1-yl)benzene (3.9 g, 24 mmol) in dioxane (40 mL) was added dropwise to an efficiently stirred suspension of sodium borohydride (2.0 g, 52 mmol) in a mixture of dioxane (40 mL) and ethanol (12.5 mL) over a period of 45 min while maintaining a temperature of 30 °C. After the addition was over, stirring was continued for 45 min. The resultant slurry was diluted with ice/water (100 mL) and the excess metal hydride decomposed with 50% aqueous acetic acid. The solution was concentrated under reduced pressure and extracted with chloroform (3 × 50 mL). The organic layer

was washed successively with water (3 × 50 mL) and brine (100 mL) and dried with anhydrous sodium sulfate. The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel.



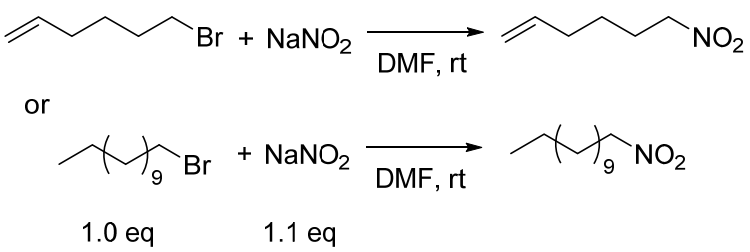
H_2O_2 (30% in H_2O, 10.6 g, 93.5 mmol) was slowly added to a cooled (ice-water bath) solution of trifluoracetic anhydride (14.0 g, 66.8 mmol) in MTBE (50 mL). After further stirring for 15 min, the mixture was poured to a suspension of benzaldoxime (1.63 g, 13.4 mmol), urea (0.4 g, 6.68 mmol) and $Na_2HPO_4 \cdot 2\ H_2O$ (13.6 g, 76.1 mmol) in MTBE (50 mL). The resulting mixture was stirred at 55 °C for 16 h. After cooling to ambient temperature, the mixture was filtered, diluted with saturated aqueous NH_4Cl solution (50 mL) and extracted with MTBE (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated in vacuo to furnish the compound (1.75 g, 95%) as yellow oil, which did not require further purification.

2-Nitrobutane[10]



2-Bromobutane (5.5 mL, 40 mmol) was added to a stirred mixture of $NaNO_2$ (5.5 g, 80 mmol) and DMSO (100 mL). After stirring for 6 h, the reaction mixture was poured into ice-water (60 mL) and layered with hexanes (100 mL). The aq. phase was extracted with hexanes. Then the organic layers were washed with water (2 × 50 mL), dried over anhydrous Na_2SO_4, filtered, concentrated at 30 °C under vacuum (20 Torr) to afford the product as blue oil (2.5 g, 61% yield).

6-Nitro-1-hexene or 1-Nitrododecane[10]

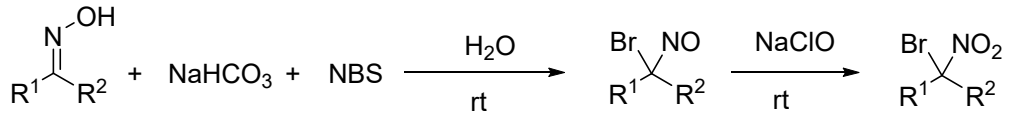


To a stirred solution of sodium nitrite (1.42 g, 20.56 mmol) in DMF (40 mL) was added 6-bromohex-1-ene (2.50 mL, 18.7 mmol), and the reaction mixture was stirred at room temperature for 2 hours. The pale yellow solution was then partitioned between ice-water (100 mL) and diethyl ether (50 mL), and the

organic phase was separated. The aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic extracts were subsequently washed with water (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography (petroleum ether) afforded the product as a pale yellow oil (1.0 g, 42% yield).

3.3 Preparation of *gem*-bromonitroalkanes

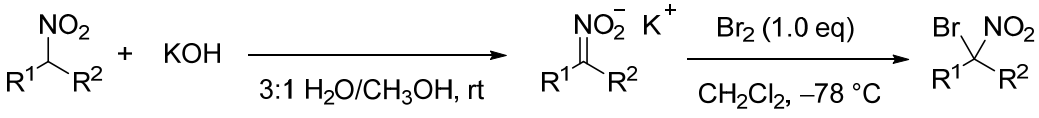
General procedure E[11]



1.0 equiv 2.3 equiv 2.3 equiv

The corresponding oxime (25.0 mmol) was added to a solution of sodium bicarbonate (4.80 g, 57.5 mmol) in 150 mL of water followed by *N*-bromosuccinimide (10.2 g, 57.5 mmol). The reaction mixture was stirred at rt overnight and extracted with AcOEt, and the organic layers were washed with brine and dried over Na_2SO_4. After evaporation of solvents, the residue of bromonitrosoalkane was diluted with benzene (50 mL). To the benzene solution were added tetrabutylammonium hydrogensulfate (4.25 g, 12.5 mmol) and sodium hypochlorite solution (ca. 1.3 M, 60 mL) in portions. Stirring was continued until blue or green color of the reaction mixture faded. After separation and concentration of the organic phase, the crude product was purified by flash column chromatography on silica gel (petroleum ether).

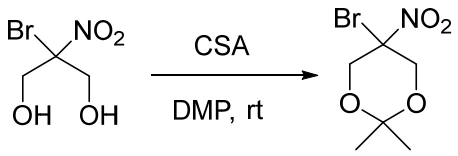
General procedure F[12]



1.0 eq 1.0 eq

The respective nitro compound (30.0 mmol) was added to a mixture of solid KOH (85%, 2.0 g, 30.0 mmol), CH_3OH (25 mL) and H_2O (75 mL) at room temperature. The mixture was vigorously stirred until complete dissolution of the starting nitro compound (ca. 30 min), and then cooled to 0 °C. Bromine (1.52 mL, 30 mmol) in CH_2Cl_2 (50 mL, precooled to −78 °C) was added in one pot. The cooling bath was removed, and the mixture was vigorously stirred for 5 min. After separation and concentration of the organic phase, the crude product was chromatographed on silica gel (petroleum ether).

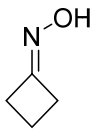
5-Bromo-2,2-dimethyl-5-nitro-1,3-dioxane[13]



To a solution of 2-bromo-2-nitro-1,3-propanediol (20.0 g, 0.101 mol) in 2,2-dimethoxypropane (80 mL) was added *L*-camphor-10-sulfonic acid (1.62 g, 8.09 mmol). The mixture was stirred for 3 d at rt under a nitrogen atmosphere. The solvent was evaporated with a rotary evaporator and the residual solid was purified by chromatography on silica gel (petroleum ether) to give a white solid (70% yield).

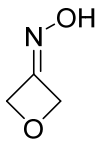
3.4 Physical data

Cyclobutanone oxime[14]



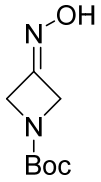
White solid (3.6 g, 87% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 2.95 (t, *J* = 8.1 Hz, 2H), 2.90 (t, *J* = 8.1 Hz, 2H), 2.00 (p, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 159.8, 31.4, 30.5, 14.4 ppm.

Oxetan-3-one oxime[14]



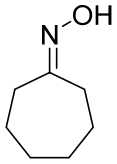
White solid (2.4 g, 80% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 5.35 – 5.33 (m, 2H), 5.30 – 5.27 (m, 2H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 153.6, 78.9 ppm.

***tert*-Butyl 3-(hydroxyimino)azetidine-1-carboxylate**[14]



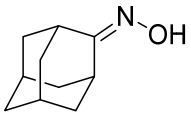
White solid (4.8 g, 90% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 4.81 – 4.21 (m, 4H), 1.46 (q, *J* = 1.3 Hz, 9H) ppm.

Cycloheptanone oxime[15]



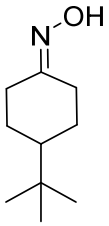
White solid (3.6 g, 79% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.93 (br, 1H), 2.55 (s, 2H), 2.35 (s, 2H), 1.78 – 1.41 (m, 8H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 164.1, 33.6, 30.3, 30.2, 28.5, 27.4, 24.4 ppm.

Adamantan-2-one oxime[15]



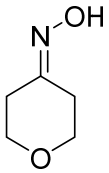
White solid (3.7 g, 82% yield);^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 3.57 (s, 1H), 2.57 (s, 1H), 2.00 – 1.90 (m, 6H), 1.87 – 1.81 (m, 6H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 166.8, 38.9, 37.4, 36.5, 36.2, 28.7, 27.8 ppm.

4-(*tert*-Butyl)cyclohexan-1-one oxime[15]



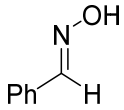
White solid (4.0 g, 91% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 3.37 (d, *J* = 12.3 Hz, 1H), 2.44 (d, *J* = 13.9 Hz, 1H), 2.06 (td, *J* = 13.4, 4.8 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.69 (td, *J* = 14.0, 5.3 Hz, 1H), 1.31 – 1.07 (m, 3H), 0.86 (s, 9H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 160.8, 32.5, 31.9, 27.5, 26.3, 24.3 ppm.

Tetrahydro-4*H*-pyran-4-one oxime[16]



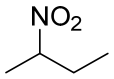
White solid (4.0 g, 87% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.04 (s, 1H), 3.81 (t, *J* = 5.7 Hz, 2H), 3.76 (t, *J* = 5.8 Hz, 2H), 2.67 (t, *J* = 5.8 Hz, 2H), 2.37 (t, *J* = 5.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 68.2, 66.7, 32.2, 25.9 ppm.

(*E*)-Benzaldehyde oxime



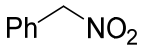
Yellow solid (90% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 8.18 (s, 1H), 7.57 (ddt, *J* = 3.9, 2.7, 1.6 Hz, 2H), 7.45 – 7.21 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.4, 131,8, 130.0, 128.7, 127.0 ppm.

2-Nitrobutane



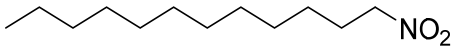
Blue oil (2.5 g, 61%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.41 (d, *J* = 6.7 Hz, 1H), 1.95 – 1.64 (m, 2H), 1.47 – 1.34 (m, 3H), 0.90 – 0.81 (m, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 84.6, 28.1, 18.4, 9.7 ppm.

(Nitromethyl)benzene



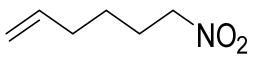
Yellow oil (1.85 g, 45%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.53 – 7.49 (m, 1H), 7.47 – 7.44 (m, 2H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 139.0, 137.1, 132.1, 130.1, 129.4, 129.1 ppm.

1-Nitrododecane



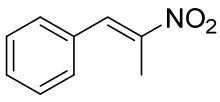
Yellow oil (2.2 g, 63%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.37 (t, *J* = 7.1 Hz, 2H), 2.23 – 1.89 (m, 2H), 1.25 (s, 18H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm.

6-Nitrohex-1-ene



Yellow oil (1.0 g, 42%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.76 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.17 – 4.90 (m, 2H), 4.38 (td, *J* = 7.0, 2.5 Hz, 2H), 2.43 – 1.91 (m, 4H), 1.49 (tt, *J* = 7.4, 6.4 Hz, 2H) ppm.

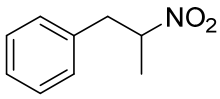
(2-Nitroprop-1-en-1-yl)benzene



White solid (3.6 g, 85% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.48 – 7.41 (m, 5H), 2.46 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 147.8, 133.5, 132.4, 129.9, 129.9, 128.9, 14.0

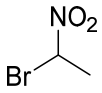
ppm.

(2-Nitropropyl)benzene



White solid (4.1 g, 83% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.24 – 7.21 (m, 1H), 7.15 – 7.12 (m, 2H), 4.78 – 4.70 (m, 1H), 3.26 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.97 (dd, *J* = 14.0, 6.6 Hz, 1H), 1.48 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 135.4, 128.8, 128.6, 127.2, 84.3, 40.9, 18.6 ppm.

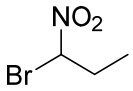
1-Bromo-1-nitroethane (2a)[17,18]



General procedure F

Yellow oil (4.3 g, 94% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.04 (q, *J* = 6.4 Hz, 1H), 2.14 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 74.5, 24.2 ppm.

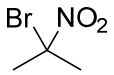
1-Bromo-1-nitropropane (2b)[17,18]



General procedure F

Yellow oil (4.2 g, 86% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.93 – 5.80 (m, 1H), 2.53 – 2.19 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 81.2, 31.0, 10.4 ppm.

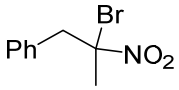
2-Bromo-2-nitropropane (2d)[19]



General procedure F

Yellow oil (3.5 g, 93% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.26 (d, *J* = 7.6 Hz, 6H) ppm.

(2-Bromo-2-nitropropyl)benzene (2e)

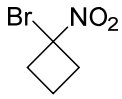


General procedure F

White solid (1.0 g, 75% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (q, *J* = 2.5, 1.8 Hz, 2H), 7.19 (dd, *J* = 6.6, 3.1 Hz, 2H), 3.87 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.3 Hz, 1H), 2.17 (s, 3H) ppm; ^{13}C

NMR (150 MHz, Chloroform-*d*) δ 133.1, 130.3, 128.7, 128.2, 93.6, 77.2, 77.0, 76.8, 49.4, 29.0 ppm.

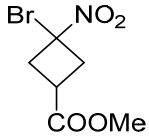
1-Bromo-1-nitrocyclobutane (2f)



General procedure E

Yellow oil (3.5 g, 72% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.29 – 3.17 (m, 2H), 2.92 – 2.77 (m, 2H), 2.30 – 2.12 (m, 1H), 1.97 (dtt, *J* = 11.3, 9.6, 5.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 84.4, 39.6, 13.6 ppm.

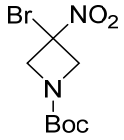
Methyl 3-bromo-3-nitrocyclobutane-1-carboxylate (2g)



General procedure E

Yellow oil (2.0 g, 60% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.63 (d, *J* = 21.9 Hz, 3H), 3.51 – 3.42 (m, 1H), 3.39 – 3.31 (m, 1H), 3.28 – 3.17 (m, 1H), 3.17 – 3.11 (m, 1H), 3.02 – 2.94 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 172.0, 81.6, 79.5, 52.2, 52.2, 42.3, 42.1, 31.9, 28.4 ppm.

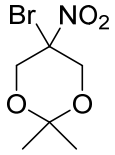
***tert*-Butyl 3-bromo-3-nitroazetidine-1-carboxylate (2h)**



General procedure E

Blue solid (2.5 g, 83% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.89 (dd, *J* = 11.3, 1.6 Hz, 2H), 4.50 (dd, *J* = 11.3, 1.6 Hz, 2H), 1.45 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 81.6, 75.9, 64.5, 28.1 ppm; IR (film) ν_{max} 1697, 1582, 1366, 1157, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^{+}$ Calcd for $C_8H_{14}N_2O_4Br$ 281.0131; Found 281.0127.

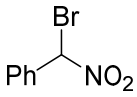
5-Bromo-2,2-dimethyl-5-nitro-1,3-dioxane (2i)



White solid (16.1g, 70% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.77 (dd, *J* = 13.3, 1.6 Hz, 2H), 4.26 (d, *J* = 13.4 Hz, 2H), 1.53 (s, 3H), 1.37 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 99.4,

66.1, 27.8, 18.4 ppm.

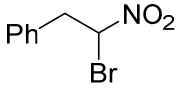
(Bromo(nitro)methyl)benzene[20]



General procedure F

Yellow oil (329 mg, 38% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.49 – 7.41 (m, 3H), 6.91 (s, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 132.8, 131.4, 129.2, 128.2, 80.4 ppm.

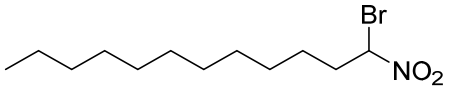
(2-Bromo-2-nitroethyl)benzene[21]



General procedure F

Yellow oil (1.1 g, 75% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 3H), 7.21 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.06 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.76 (dd, *J* = 14.5, 8.2 Hz, 1H), 3.52 (dd, *J* = 14.5, 6.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.2, 129.1, 129.0, 128.3, 79.2, 43.4 ppm.

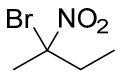
1-Bromo-1-nitrododecane



General procedure F

Colorless oil (2.3 g, 84% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.87 – 2.79 (m, 2H), 1.60 (q, *J* = 7.6 Hz, 2H), 1.48 – 1.18 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 87.9, 49.1, 31.9, 29.5, 29.5, 29.3, 29.3, 29.1, 28.3, 27.2, 22.7, 14.1 ppm.

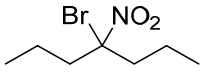
2-Bromo-2-nitrobutane[22]



General procedure F

Yellow oil (1.2 g, 75% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.55 – 2.34 (m, 2H), 2.21 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 96.1, 37.9, 29.4, 9.9 ppm.

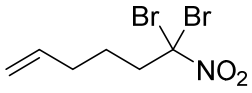
4-Bromo-4-nitroheptane



General procedure E

Yellow oil (2.7 g, 78% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.50 – 2.20 (m, 4H), 1.63 – 1.27 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H) ppm.

6,6-Dibromo-6-nitrohex-1-ene



General procedure F

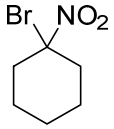
Yellow oil (2.5 g, 56% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.91 – 5.64 (m, 1H), 5.23 – 4.78 (m, 2H), 2.97 – 2.63 (m, 2H), 2.18 (d, *J* = 9.8 Hz, 2H), 1.77 – 1.57 (m, 2H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 136.6, 116.2, 87.7, 48.3, 32.1, 26.3 ppm.

1-Bromo-1-nitrocyclopentane

General procedure E

Yellow oil (3.5 g, 72% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.86 (dtdd, *J* = 12.0, 5.9, 3.2, 1.5 Hz, 2H), 2.50 (dddd, *J* = 14.5, 7.1, 3.8, 1.5 Hz, 2H), 2.05 – 1.75 (m, 4H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 96.4, 42.6, 22.8 ppm.

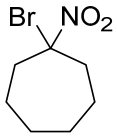
1-Bromo-1-nitrocyclohexane



General procedure E

Yellow oil (2.5 g, 71% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.52 – 2.20 (m, 4H), 1.82 – 1.54 (m, 5H), 1.36 (dd, *J* = 9.2, 4.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 103.7, 38.6, 23.8, 22.9 ppm.

1-Bromo-1-nitrocycloheptane

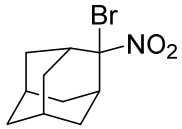


General procedure E

Yellow oil (3.8 g, 70% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.74 (dt, *J* = 14.2, 7.5 Hz, 1H), 2.51 (d, *J* = 7.9 Hz, 1H), 2.39 (s, 2H), 1.59 (d, *J* = 28.5 Hz, 8H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ

99.3, 43.0, 27.9, 23.0 ppm.

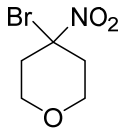
(1*r*,3*r*,5*r*,7*r*)-2-Bromo-2-nitroadamantane



General procedure E

Colorless oil (1.2 g, 43% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 2.90 (s, 2H), 2.37 (d, *J* = 13.7 Hz, 2H), 1.98 (d, *J* = 14.6 Hz, 2H), 1.95 – 1.75 (m, 8H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 102.5, 38.3, 37.6, 35.0, 34.5, 26.1, 25.6 ppm.

4-Bromo-4-nitrotetrahydro-2*H*-pyran

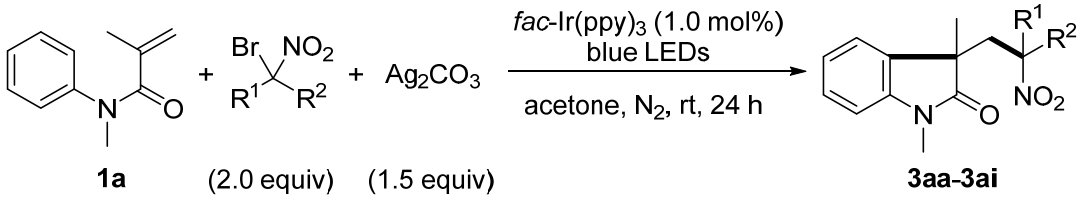


General procedure E

Yellow oil (2.5 g, 71% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 4.53 (tt, *J* = 9.9, 4.7 Hz, 1H), 4.01 (dt, *J* = 12.1, 4.0 Hz, 2H), 3.46 (ddd, *J* = 12.1, 10.4, 2.9 Hz, 2H), 2.25 – 2.05 (m, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ = 80.7, 65.3, 30.5 ppm.

4. Photocatalytic radical reactions

4.1 Typical procedure

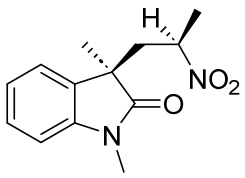


1a (2.0 equiv) (1.5 equiv) **3aa-3ai**

A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). *N*-Methyl-*N*-phenylmethacrylamide (**1a**, 80 mg, 0.45 mmol), 1-bromo-1-nitrocyclobutane (**2f**, 0.15 mL, 0.90 mmol), Ag_2CO_3 (250 mg, 0.90 mmol) and anhydrous acetone (8.0 mL) were added under N_2 atmosphere followed by *fac*-Ir(ppy)$_3$ (5.0 mg, 1.0 mol%). The reaction mixture was degassed by freeze-pump-thaw method and then stirred under irradiation with blue LEDs (456 nm, approximately 3.0 cm distance from the tube). The mixture was maintained at approximately 25 °C by a desk fan in air-conditioned room. The reaction was monitored by TLC. Upon completion (24 h), the mixture was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (10:1 hexanes/AcOEt) to give **3af**.

4.2 Physical data

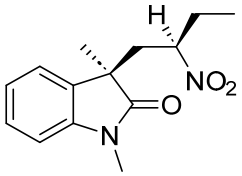
(3*R)-1,3-Dimethyl-3-((*R**)-2-nitropropyl)indolin-2-one (3aa)**



Yellow oil; R_f = 0.3 (5:1 hexanes/AcOEt, less polar); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 1H), 7.14 (dd, *J* = 7.4, 2.6 Hz, 1H), 7.07 (dddd, *J* = 8.6, 7.5, 2.8, 1.5 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 4.17 (ttq, *J* = 8.2, 4.2, 2.0, 1.4 Hz, 1H), 3.33 – 3.20 (m, 3H), 2.74 (ddt, *J* = 14.9, 8.3, 2.0 Hz, 1H), 2.30 (ddt, *J* = 14.9, 4.2, 2.0 Hz, 1H), 1.41 – 1.37 (m, 6H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.2, 143.0, 130.6, 128.7, 123.3, 122.9, 108.4, 80.6, 47.0, 41.6, 26.3, 25.0, 20.7 ppm; IR (film) ν_{max} 1605, 1366, 1103, 748, 594 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_3$ 249.1233; Found 249.1235.

Note: A 1:1 mixture of two diastereomers was obtained as a yellow oil (94 mg, 88% total yield).

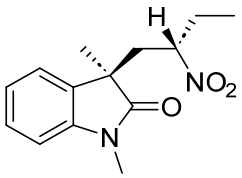
(3*R)-1,3-Dimethyl-3-((2*R**)-2-nitrobutyl)indolin-2-one (3ab)**



Yellow oil; R_f = 0.3 (5:1 hexanes/AcOEt, less polar); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 7.7, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 6.86 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.99 (tdd, *J* = 9.4, 4.8, 2.6 Hz, 1H), 3.26 (s, 3H), 2.70 (dd, *J* = 15.1, 9.5 Hz, 1H), 2.28 (dd, *J* = 15.1, 2.6 Hz, 1H), 1.82 (ddq, *J* = 14.6, 9.3, 7.3 Hz, 1H), 1.67 (dqd, *J* = 14.7, 7.4, 4.7 Hz, 1H), 1.37 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.2, 143.0, 130.6, 128.5, 123.3, 122.8, 108.2, 86.9, 47.1, 40.1, 26.2, 24.7, 9.7 ppm; IR (film) ν_{max} 2955, 1705, 1589, 1466, 1358, 1265, 1111, 748 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{19}N_2O_3$ 263.1390; Found 263.1392.

Note: A 1:1 mixture of two diastereomers was obtained as a yellow oil (80 mg, 67% total yield).

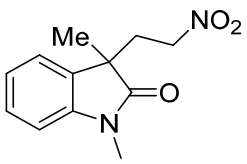
(3*R)-1,3-Dimethyl-3-((2*S**)-2-nitrobutyl)indolin-2-one (3ab)**



Yellow oil; R_f = 0.3 (5:1 hexanes/AcOEt, more polar); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.27 (m, 1H), 7.19 – 7.05 (m, 2H), 6.90 (dt, *J* = 7.8, 1.0 Hz, 1H), 4.26 (tddd, *J* = 6.5, 4.9, 2.5, 1.0 Hz, 1H), 3.35 – 3.13 (m, 3H), 2.91 – 2.69 (m, 1H), 2.01 (ddd, *J* = 15.3, 2.6, 1.1 Hz, 1H), 1.82 (dtt, *J* = 14.2, 7.1, 2.0 Hz, 1H), 1.58 (dddd, *J* = 14.4, 7.2, 5.1, 1.9 Hz, 1H), 1.46 – 1.29 (m, 3H), 0.93 – 0.72 (m, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 143.1, 132.2, 128.5, 122.7, 122.3, 108.4, 86.1, 46.3, 40.4, 28.4, 26.0, 23.4, 9.8 ppm; IR (film) ν_{max} 2963, 1713, 1612, 1474, 1366, 1119, 748 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{19}N_2O_3$ 263.1390; Found 263.1392.

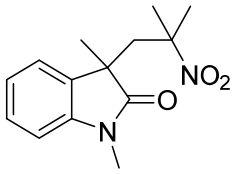
Note: A 1:1 mixture of two diastereomers was obtained as a yellow oil (80 mg, 67% total yield).

1,3-Dimethyl-3-(2-nitroethyl)indolin-2-one (3ac)



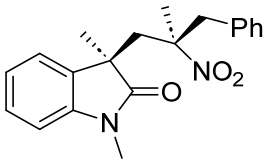
Yellow oil (66 mg, 62% yield); R_f = 0.3 (5:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 1H), 7.26 – 7.01 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.15 (dddd, *J* = 55.5, 13.4, 9.8, 5.8 Hz, 2H), 3.23 (s, 3H), 2.74 – 2.39 (m, 2H), 1.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.7, 142.8, 131.6, 128.7, 123.0, 122.6, 108.5, 71.3, 46.0, 34.4, 26.2, 23.5 ppm; IR (film) ν_{max} 2947, 1605, 1366, 1103, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{15}N_2O_3$ 235.1077; Found 235.1080.

1,3-Dimethyl-3-(2-methyl-2-nitropropyl)indolin-2-one (3ad)



White solid (70 mg, 60% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 93.6–94.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 1H), 7.12 – 7.01 (m, 2H), 6.86 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.23 (s, 3H), 2.98 (d, *J* = 15.4 Hz, 1H), 2.56 (d, *J* = 15.3 Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.8, 142.8, 130.1, 128.4, 124.1, 122.8, 108.3, 86.7, 46.5, 45.8, 30.0, 27.8, 26.4, 22.5 ppm; IR (film) ν_{max} 1713, 1605, 1474, 1358, 1119, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{19}N_2O_3$ 263.1390; Found 263.1392.

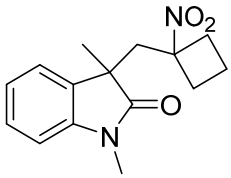
(3*R)-1,3-Dimethyl-3-((2*R**)-2-methyl-2-nitro-3-phenylpropyl)indolin-2-one (3ae)**



White solid; R_f = 0.2 (10:1 hexanes/AcOEt, less polar); m.p. 184.0–185.2 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.16 (m, 5H), 7.12 – 6.88 (m, 4H), 3.39 – 3.12 (m, 5H), 2.85 (ddt, *J* = 32.1, 13.7, 2.5 Hz, 1H), 2.65 (dddd, *J* = 15.8, 10.3, 5.1, 2.3 Hz, 1H), 1.37 (dt, *J* = 23.5, 2.4 Hz, 3H), 1.18 – 0.97 (m, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 180.0, 178.7, 142.8, 142.6, 134.5, 133.6, 131.8, 130.2, 130.0, 129.6, 128.5, 128.4, 128.4, 128.3, 127.6, 127.3, 124.3, 123.3, 122.8, 122.6, 108.5, 108.3, 90.7, 90.1, 77.2, 77.0, 76.8, 48.6, 46.7, 46.5, 46.4, 45.4, 45.3, 27.9, 27.7, 26.4, 26.3, 26.3, 21.5, 18.1 ppm; IR (film) ν_{max} 2940, 1713, 1605, 1551, 1474, 1358, 1126, 910, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{23}N_2O_3$ 339.1703; Found 339.1701.

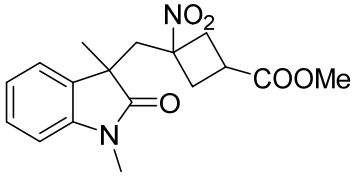
Note: A 1:1 mixture of two diastereomers was obtained as a white solid (50 mg, 30% total yield).

1,3-Dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3af)



White solid (100 mg, 80% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 101.7–102.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.19 (m, 1H), 7.12 – 6.95 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.41 – 3.05 (m, 3H), 2.97 – 2.66 (m, 2H), 2.58 – 2.43 (m, 1H), 2.38 – 2.12 (m, 3H), 1.86 – 1.70 (m, 2H), 1.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 143.1, 130.2, 128.4, 123.7, 122.5, 108.1, 87.8, 46.3, 43.8, 36.4, 29.4, 26.3, 26.2, 14.1 ppm; IR (film) ν_{max} 3241, 1613, 1366, 1103, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{18}N_2O_3$ 275.1390; Found 275.1391.

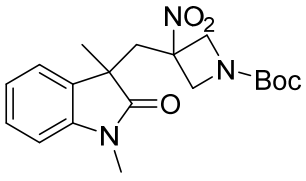
Methyl 3-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-3-nitrocyclobutane-1-carboxylate (3ag)



Yellow oil (70 mg, 66% yield); R_f = 0.1 (5:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.7 Hz, 1H), 7.13 – 6.98 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 3H), 3.21 (s, 3H), 2.99 (p, *J* = 9.0 Hz, 1H), 2.88 (d, *J* = 15.1 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.62 – 2.49 (m, 3H), 1.35 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.8, 173.7, 143.1, 128.6, 123.7, 122.5, 108.2, 86.8, 52.1, 46.1, 44.6, 38.1, 34.3, 32.2, 26.3, 26.0 ppm; IR (film) ν_{max} 3017, 2963, 1736, 1566, 1435, 1358, 1204, 1080, 1011, 841, 741, 609 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{21}N_2O_5$ 333.1444; Found 333.1440.

Note: A single diastereomer was obtained. But the *cis*- or *trans*- configuration was not determined.

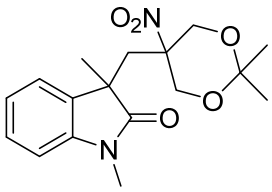
***tert*-Butyl 3-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-3-nitroazetidine-1-carboxylate (3ah)**



Yellow oil (73 mg, 65% yield); R_f = 0.1 (5:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.23 – 7.20 (m, 1H), 7.11 – 7.03 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.25 (d, *J* = 10.3 Hz, 1H), 4.03 (dd, *J* = 10.2, 1.0 Hz, 1H), 3.94 (dd, *J* = 10.2, 1.0 Hz, 1H), 3.34 (d, *J* = 6.4 Hz, 1H), 3.22 (s, 3H), 2.87 (d, *J* = 3.4 Hz, 2H), 1.39 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.3, 143.1, 129.4, 128.9, 126.5,

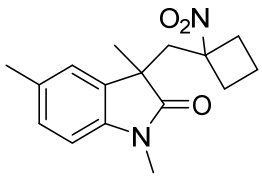
123.3, 122.7, 108.4, 88.2, 81.8, 60.4, 46.0, 42.3, 31.5, 28.2, 28.2, 26.3 ppm; IR (film) ν_{max}, 1635, 1366, 1080, 741 cm^{-1}.

3-((2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)methyl)-1,3-dimethylindolin-2-one (3ai)



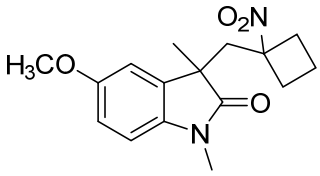
White solid (100 mg, 70% yield); R_f = 0.1 (5:1 hexanes/AcOEt); m.p. 185.6–186.1 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (ddd, *J* = 7.8, 6.9, 2.0 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.87 (dt, *J* = 7.8, 0.9 Hz, 1H), 4.10 (ddd, *J* = 13.5, 5.7, 2.7 Hz, 2H), 3.90 – 3.68 (m, 2H), 3.24 (d, *J* = 2.4 Hz, 3H), 2.48 (t, *J* = 1.3 Hz, 2H), 1.37 – 1.29 (m, 6H), 1.22 (d, *J* = 2.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.6, 142.6, 129.9, 128.9, 123.0, 122.9, 108.6, 98.7, 85.0, 65.6, 62.5, 45.5, 39.6, 27.6, 27.4, 26.4, 19.0 ppm; IR (film) ν_{max} 1604, 1366, 1103 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{23}N_2O_5$ 335.1601; Found 335.1603.

1,3,5-Trimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3bf)



Yellow oil (45 mg, 40% yield); R_f = 0.3 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.07 (t, *J* = 6.0 Hz, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.71 (t, *J* = 6.0 Hz, 1H), 3.19 (d, *J* = 4.1 Hz, 3H), 2.93 – 2.68 (m, 2H), 2.49 (t, *J* = 10.2 Hz, 1H), 2.37 – 2.18 (m, 6H), 1.76 (t, *J* = 7.7 Hz, 2H), 1.34 (d, *J* = 4.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 140.7, 132.1, 130.3, 128.6, 124.6, 107.8, 87.8, 46.3, 43.7, 36.3, 29.5, 26.3, 21.1, 14.1 ppm; IR (film) ν_{max} 2955, 2831, 1605, 1366, 1088, 764, 617 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2O_3$ 289.1546; Found 289.1544.

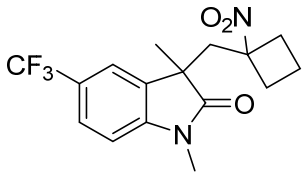
5-Methoxy-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3cf)



Yellow oil (46 mg, 36% yield); R_f = 0.1 (10:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.81 (dtd, *J* = 7.8, 3.5, 1.8 Hz, 1H), 6.73 (ddd, *J* = 8.5, 3.4, 1.7 Hz, 1H), 6.68 (dt, *J* = 4.1, 2.0 Hz, 1H),

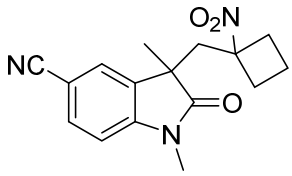
3.78 (d, *J* = 1.7 Hz, 3H), 3.19 (d, *J* = 1.7 Hz, 3H), 2.94 – 2.71 (m, 2H), 2.58 – 2.46 (m, 1H), 2.38 – 2.18 (m, 3H), 1.79 – 1.76 (m, 2H), 1.35 (d, *J* = 1.7 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 179.0, 156.0, 136.5, 131.4, 113.2, 110.9, 108.5, 87.7, 55.9, 46.7, 43.6, 36.4, 29.3, 26.3, 26.3, 14.1 ppm; IR (film) ν_{max} 1612, 1366, 1103, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2O_4$ 305.1495; Found 305.1494.

1,3-Dimethyl-3-((1-nitrocyclobutyl)methyl)-5-(trifluoromethyl)indolin-2-one (3df)



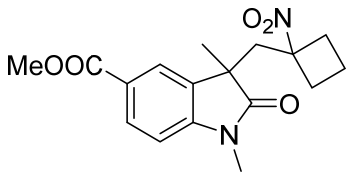
White solid (40 mg, 33% yield); R_f = 0.2 (10:1 hexanes/AcOEt); m.p. 134.1–134.6 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 6.5 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 3.37 – 3.14 (m, 2H), 2.58 – 2.49 (m, 1H), 2.39 – 2.30 (m, 1H), 2.29 – 2.18 (m, 1H), 1.78 (dddd, *J* = 15.7, 9.3, 4.9, 1.9 Hz, 1H), 1.39 (q, *J* = 5.4, 4.4 Hz, 2H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 179.1, 146.1, 130.9, 126.2 (d, *J* = 4.2 Hz), 125.5 – 124.2 (m), 120.8 (d, *J* = 3.7 Hz), 107.9, 87.5, 46.2, 43.6, 36.0, 30.1, 26.5, 26.2, 14.0 ppm; ^{19}F NMR (565 MHz, Chloroform-*d*) δ 61.2 ppm; IR (film) ν_{max} 1605, 1373, 1103, 764 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}N_2O_3F_3$ 343.1264; Found 343.1265.

1,3-Dimethyl-3-((1-nitrocyclobutyl)methyl)-2-oxoindoline-5-carbonitrile (3ef)



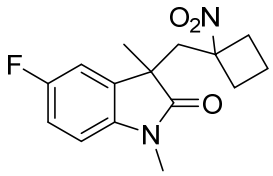
White solid (68 mg, 61% yield); R_f = 0.1 (10:1 hexanes/AcOEt); m.p. 139.7–140.9 °C; ^{1}H NMR (400 MHz, C`hloroform-*d*) δ 7.71 – 7.56 (m, 1H), 7.33 – 7.30 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.24 (s, 3H), 2.85 – 2.71 (m, 2H), 2.59 – 2.48 (m, 1H), 2.42 – 2.17 (m, 3H), 1.79 (h, *J* = 7.6, 6.9 Hz, 2H), 1.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.7, 147.0, 133.8, 131.3, 126.9, 119.0, 108.6, 105.7, 87.3, 46.1, 43.5, 36.0, 30.0, 26.5, 26.2, 14.0 ppm; IR (film) ν_{max} 2831, 1605, 1366, 1080, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}N_3O_3$ 300.1342; Found 300.1339.

Methyl 1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)-2-oxoindoline-5-carboxylate (3ff)



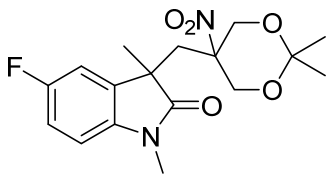
White solid (61 mg, 55% yield); R_f = 0.1 (10:1 hexanes/AcOEt); m.p. 132.1 –132.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.76 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.23 (s, 3H), 2.79 (q, *J* = 15.1 Hz, 2H), 2.52 (ddt, *J* = 11.0, 8.5, 4.2 Hz, 1H), 2.38 – 2.08 (m, 3H), 1.75 (p, *J* = 9.5, 8.7 Hz, 2H), 1.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.3, 166.7, 147.2, 131.2, 130.3, 124.8, 124.4, 107.7, 87.5, 52.0, 46.1, 43.6, 35.7, 30.5, 26.4, 26.3, 14.0 ppm; IR (film) ν_{max} 1589, 1373, 1088, 779 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{21}N_2O_5$ 333.1444; Found 333.1452.

5-Fluoro-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3gf)



White solid (59 mg, 55% yield); R_f = 0.2 (10:1 hexanes/AcOEt); m.p. 122.6–123.7 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.98 (td, *J* = 8.8, 2.6 Hz, 1H), 6.81 (dd, *J* = 7.9, 2.6 Hz, 1H), 6.73 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.20 (s, 3H), 2.88 – 2.71 (m, 2H), 2.57 – 2.49 (m, 1H), 2.39 – 2.31 (m, 1H), 2.24 (dddd, *J* = 11.9, 8.5, 6.9, 2.0 Hz, 2H), 1.77 (dddd, *J* = 16.1, 8.3, 6.9, 2.8 Hz, 2H), 1.35 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.9, 160.0, 158.4, 139.0, 131.9, 131.9, 114.8, 114.7, 111.9, 111.8, 108.6, 108.6, 87.6, 46.8, 43.6, 36.3, 29.6, 26.4, 26.2, 14.1 ppm; IR (film) ν_{max} 1597, 1381, 1088, 772 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{17}N_2O_3F$ 293.1295; Found 293.1298.

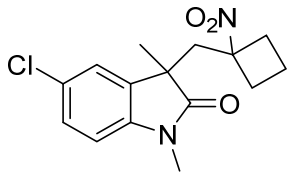
3-((2,2-Dimethyl-5-nitro-1,3-dioxan-5-yl)methyl)-5-fluoro-1,3-dimethylindolin-2-one (3gi)



White solid (90 mg, 55% yield); R_f = 0.2 (10:1 hexanes/AcOEt); m.p. 145.3–146.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 6.97 (m, 1H), 6.88 – 6.75 (m, 2H), 4.19 – 4.03 (m, 2H), 3.93 – 3.68 (m, 2H), 3.23 (d, *J* = 0.8 Hz, 3H), 2.54 – 2.38 (m, 2H), 1.35 (s, 3H), 1.32 (s, 3H), 1.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.2, 160.5, 158.1, 138.6, 131.6, 131.5, 115.3, 115.1, 111.3, 111.1, 109.2,

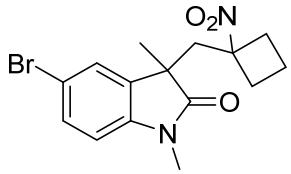
109.1, 98.8, 84.7, 65.5, 62.6, 46.0, 39.4, 27.6, 27.2, 26.5, 19.1 ppm; IR (film) ν_{max} 2963, 1597, 1366, 1103, 733, 571 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{22}N_2O_5F$ 353.1507; Found 353.1508.

5-Chloro-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3hf)



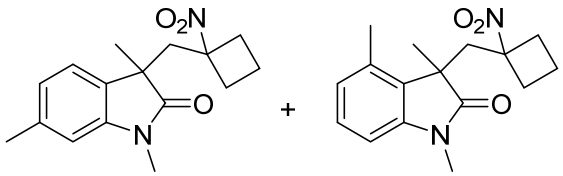
White solid (92 mg, 73% yield); R_f = 0.2 (10:1 hexanes/AcOEt); m.p. 129.6–130.7 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.03 (d, *J* = 2.2 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.18 (s, 3H), 2.89 – 2.70 (m, 2H), 2.52 (dt, *J* = 16.0, 8.8 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.29 – 2.13 (m, 2H), 1.80 – 1.73 (m, 2H), 1.34 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.6, 141.6, 132.0, 128.3, 127.9, 124.1, 109.0, 87.5, 46.5, 43.6, 36.0, 29.9, 26.3, 26.2, 14.0 ppm; IR (film) ν_{max}3387, 1613, 1374, 1088, 772 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}N_2O_3Cl$ 309,1000; Found 309.1005.

5-Bromo-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3if)



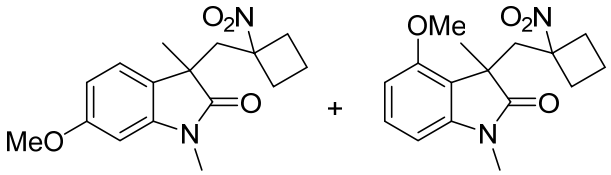
White solid (104 mg, 78% yield); R_f = 0.2 (10:1 hexanes/AcOEt); m.p. 154.2–155.4 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 3.17 (s, 3H), 2.75 (q, *J* = 15.2 Hz, 2H), 2.57 – 2.46 (m, 1H), 2.38 – 2.29 (m, 1H), 2.22 (dq, *J* = 19.0, 10.9, 9.8 Hz, 2H), 1.75 (ddtd, *J* = 14.5, 11.0, 8.4, 4.1 Hz, 2H), 1.33 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.4, 142.1, 132.4, 131.2, 126.8, 115.1, 109.5, 87.5, 46.4, 43.5, 35.9, 30.0, 26.3, 26.1, 14.0 ppm; IR (film) ν_{max} 2955, 1697, 1612, 1358, 1103, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{18}N_2O_3Br$ 353.0495; Found 353.0492.

1,3,6-Trimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one and 1,3,4-trimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3jf)



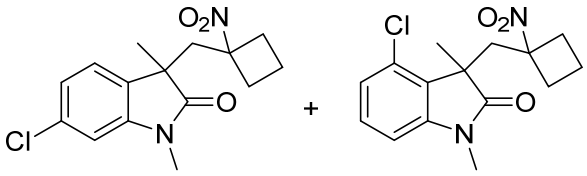
Yellow oil (41mg, 38% total yield); R_f = 0.3 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.90 (m, 1H), 6.81 (dd, *J* = 16.7, 7.7 Hz, 1H), 6.71 – 6.63 (m, 1H), 3.19 (s, 3H), 3.07 – 2.63 (m, 2H), 2.56 – 2.45 (m, 1H), 2.34 (d, *J* = 26.1 Hz, 6H), 1.82 – 1.70 (m, 2H), 1.35 – 1.21 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.7, 179.0, 143.5, 143.1, 138.6, 135.2, 128.4, 127.5, 127.1, 125.2, 123.4, 123.1, 109.1, 105.8, 88.0, 87.8, 46.8, 46.1, 43.7, 42.6, 36.4, 29.7, 29.5, 29.3, 26.3, 26.3, 26.2, 23.6, 21.8, 18.3, 14.3, 14.1 ppm; IR (film) v_{max} 1598, 1373, 1088, 771 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{21}N_2O_3$ 289.1546; Found 289.1544.

6-Methoxy-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one and 4-methoxy-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3kf)



Yellow oil (34 mg, 31% total yield); R_f = 0.2 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.23 (m, 1H), 6.53 (dd, *J* = 25.8, 8.1 Hz, 2H), 3.84 (d, *J* = 0.9 Hz, 3H), 3.19 (d, *J* = 0.9 Hz, 3H), 3.10 (d, *J* = 14.9 Hz, 1H), 2.64 (d, *J* = 15.0 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.25 (ddddd, *J* = 21.9, 19.8, 12.7, 7.6, 2.3 Hz, 3H), 1.77 – 1.70 (m, 2H), 1.41 (d, *J* = 0.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 156.4, 144.3, 130.5, 129.8, 128.9, 127.8, 105.5, 101.5, 88.0, 55.1, 46.3, 42.0, 35.6, 30.5, 29.7, 26.4, 23.7, 20.1, 14.0 ppm; IR (film) v_{max} 1598, 1373, 1088, 772 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{21}N_2O_4$ 305.1495; Found 305.1502.

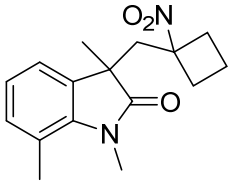
6-Chloro-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one and 4-Chloro-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3lf)



Yellow oil (35 mg, 38% total yield); R_f = 0.2 (10:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.8 Hz, 1.73H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1.67H), 6.72

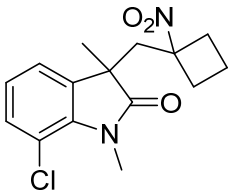
– 6.62 (m, 2.63H), 3.19 (s, 8.11H), 3.03 (d, *J* = 15.2 Hz, 1.74H), 2.87 (d, *J* = 15.2 Hz, 1H), 2.73 (d, *J* = 15.2 Hz, 1H), 2.67 (d, *J* = 15.1 Hz, 1.78H), 2.51 (t, *J* = 10.1 Hz, 2.89H), 2.31 (s, 7.88H), 2.24 (d, *J* = 9.8 Hz, 3.87H), 1.76 (q, *J* = 7.8, 7.1 Hz, 5.71H), 1.44 (s, 5.81H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.7, 179.0, 143.5, 143.1, 138.6, 135.2, 128.4, 127.5, 127.1, 125.2, 123.4, 123.1, 109.1, 105.8, 88.0, 87.7, 46.8, 46.1, 43.7, 42.6, 36.4, 29.7, 29.5, 29.3, 26.4, 26.3, 26.2, 23.5, 21.8, 18.3, 14.3, 14.1 ppm; R (film) ν_{max}3387, 1613, 1374, 1088, 772 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{17}N_2O_3Cl$ 309,1000; Found 309.1005.

1,3,7-Trimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3mf)



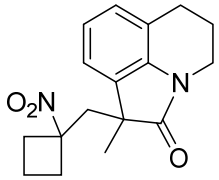
Yellow oil (54 mg, 60% yield); R_f = 0.3 (10:1 hexanes/AcOEt); ^{1}H NMR ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.00 – 6.87 (m, 2H), 3.59 (s, 3H), 2.84 (dd, *J* = 15.2, 1.1 Hz, 1H), 2.74 (d, *J* = 15.2 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.40 – 2.33 (m, 1H), 2.29 – 2.18 (m, 2H), 1.84 – 1.74 (m, 2H), 1.34 (s, 3H), 1.27 – 1.24 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.6, 139.0, 133.0, 130.8, 123.2, 122.1, 115.6, 87.6, 46.1, 43.9, 36.5, 29.7, 29.3, 26.6, 14.1 ppm; IR (film) ν_{max} 1605, 1366, 1088, 764 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{21}N_2O_3$ 289.1546; Found 289.1544.

7-Chloro-1,3-dimethyl-3-((1-nitrocyclobutyl)methyl)indolin-2-one (3nf)



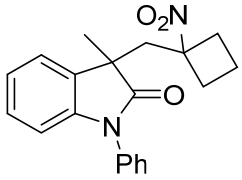
Yellow oil (51 mg, 62% yield); R_f = 0.3 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (dd, *J* = 6.4, 3.0 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.58 (s, 3H), 2.84 (dd, *J* = 15.2, 1.1 Hz, 1H), 2.74 (d, *J* = 15.2 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.43 – 2.32 (m, 1H), 2.29 – 2.17 (m, 2H), 1.84 – 1.72 (m, 2H), 1.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.5, 139.0, 132.9, 130.7, 123.3, 122.1, 115.5, 87.6, 46.1, 43.8, 36.5, 29.7, 29.6, 29.3, 26.6, 14.1 ppm; IR (film) ν_{max} 1720, 1535, 1466, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{17}N_2O_3Cl$ 309,1000; Found 309.0997.

1-Methyl-1-((1-nitrocyclobutyl)methyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2(1*H*)-one (3of)



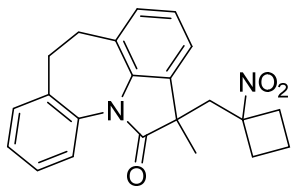
Yellow oil (64 mg, 43% yield); R_f = 0.1 (10:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.03 – 6.99 (m, 1H), 6.92 – 6.87 (m, 2H), 3.75 – 3.64 (m, 2H), 2.87 (dd, *J* = 15.2, 1.1 Hz, 1H), 2.81 (dt, *J* = 16.3, 6.0 Hz, 1H), 2.76 – 2.71 (m, 2H), 2.54 (dtt, *J* = 12.2, 8.1, 1.4 Hz, 1H), 2.38 – 2.21 (m, 3H), 2.00 (p, *J* = 6.0 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.35 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 178.1, 138.9, 128.7, 127.1, 121.9, 121.6, 120.1, 87.8, 77.2, 77.0, 76.8, 47. 6, 43.7, 39.0, 36.3, 29.5, 25.9, 24.5, 21.1, 14.1 ppm; IR (film) ν_{max} 2940, 1705, 1605, 1612, 1450, 1366, 1080, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{21}N_2O_3$ 301.1546; Found 301.1542.

3-Methyl-3-((1-nitrocyclobutyl)methyl)-1-phenylindolin-2-one (3pf)



Yellow oil (66 mg, 45% yield); R_f = 0.2 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.39 (m, 5H), 7.23 – 6.98 (m, 3H), 6.78 (d, *J* = 7.9 Hz, 1H), 3.00 – 2.81 (m, 2H), 2.73 – 2.63 (m, 1H), 2.48 – 2.26 (m, 3H), 1.85 – 1.74 (m, 2H), 1.49 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.7, 143.0, 134.3, 129.8, 129.6, 128.3, 128.1, 126.3, 123.9, 122.9, 109.4, 87.7, 46.4, 43.8, 36.6, 29.5, 26.9, 14.0 ppm; IR (film) ν_{max} 1605, 1366, 1080, 771, 610, 555 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1546; Found 337.1543.

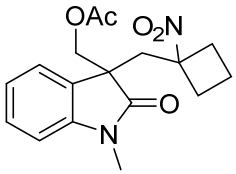
7-Methyl-7-((1-nitrocyclobutyl)methyl)-11,12-dihydrobenzo[6,7]azepino[3,2,1-*hi*]indol-6(7*H*)-one (3qf)



White solid (124 mg, 93% yield); R_f = 0.3 (10:1 hexanes/AcOEt); m.p. 134.4 –134.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.16 (m, 3H), 7.06 – 6.90 (m, 3H), 3.16 – 2.83 (m, 6H), 2.69 – 2.55 (m, 1H), 2.43 – 2.26 (m, 3H), 1.77 (p, *J* = 7.8 Hz, 2H), 1.48 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.6, 140.1, 136.8, 135.7, 130.3, 130.2, 129.5, 126.5, 126.4, 126.2, 124.9,

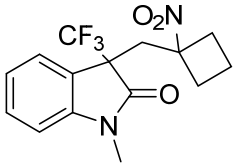
122.2, 121.4, 87.6, 46.2, 43.9, 36.6, 33.9, 33.7, 27.6, 14.0 ppm; IR (film) ν_{max} 1605, 1373, 1103 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_3$ 363.1703; Found 363.1705.

(1-Methyl-3-((1-nitrocyclobutyl)methyl)-2-oxoindolin-3-yl)methyl acetate (3rf)



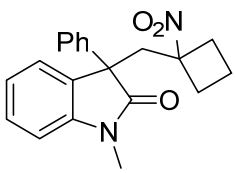
Yellow oil (42 mg, 30% yield); R_f = 0.1 (10:1 hexanes/AcOEt); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.8 Hz, 1H), 7.13 – 6.97 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.22 (ddd, *J* = 150.8, 10.7, 1.7 Hz, 2H), 3.23 (d, *J* = 1.7 Hz, 3H), 3.09 – 2.69 (m, 2H), 2.61 – 2.45 (m, 1H), 2.27 (dtd, *J* = 28.5, 16.0, 14.3, 7.6 Hz, 3H), 1.91 (d, *J* = 1.7 Hz, 3H), 1.84 – 1.76 (m, 2H), 1.25 (s, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 176.1, 170.2, 143.9, 129.2, 125.8, 124.8, 122.6, 108.2, 87.4, 77.2, 77.0, 76.8, 67.9, 50.2, 39.1, 36.5, 29.6, 29.5, 26.4, 20.5, 14.2 ppm; IR (film) ν_{max} 2831, 1605, 1366, 1088, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_5$ 333.1444; Found 333.1441.

1-Methyl-3-((1-nitrocyclobutyl)methyl)-3-(trifluoromethyl)indolin-2-one (3sf)



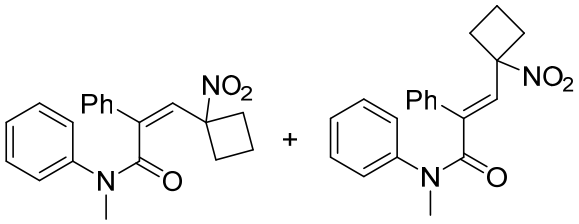
Yellow oil (54 mg, 50% yield); R_f = 0.1 (10:1 hexanes/AcOEt); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.41 (tt, *J* = 7.8, 1.3 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.08 (tt, *J* = 7.6, 1.2 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 3.30 – 3.26 (m, 1H), 3.25 (d, *J* = 1.3 Hz, 3H), 3.07 (dd, *J* = 15.1, 1.3 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.41 – 2.30 (m, 2H), 2.29 – 2.21 (m, 1H), 1.85 (dtdd, *J* = 12.8, 7.4, 3.8, 2.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 143.3, 134.0 (q, *J* = 31.8 Hz), 129.4, 127.6, 126.6, 125.5, 121.3 (q, *J* = 273.7 Hz), 37.5 ppm; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -73.8 ppm; IR (film) ν_{max} 1612, 1366, 1157, 764 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{15}N_2O_3F_3Na$ 351.0927; Found 351.0926.

1-Methyl-3-((1-nitrocyclobutyl)methyl)-3-phenylindolin-2-one (3tf)



White solid (24 mg, 26% yield); R_f = 0.1 (10:1 hexanes/AcOEt); m.p. 160.6–161.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.21 (m, 6H), 7.16 – 7.04 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.31 (dt, *J* = 16.1, 15.1 Hz, 2H), 3.22 (d, *J* = 1.0 Hz, 3H), 2.61 – 2.49 (m, 1H), 2.43 – 2.26 (m, 3H), 1.89 – 1.76 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.4, 143.8, 140.2, 129.0, 128. 7, 128.1, 127.6, 126.4, 126.4, 122.6, 108.4, 88.1, 54.1, 43.9, 37.0, 29.3, 26.5, 14.5 ppm; IR (film) v_{max} 1713, 1614, 1538, 1493, 1467, 1346, 750, 693 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1546; Found 337.1543.

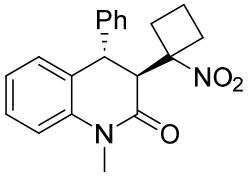
(*Z*)-*N*-Methyl-3-(1-nitrocyclobutyl)-*N*,2-diphenylacrylamide and (*E*)-*N*-methyl-3-(1-nitrocyclobutyl)-*N*,2-diphenylacrylamide (3tf′′)



(*Z*) (*E*)

Yellow oil (88 mg, 82% total yield); R_f = 0.2 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.30 (m, 5H), 7.23 – 6.97 (m, 9H), 6.76 (d, *J* = 7.2 Hz, 2H), 6.31 (s, 0.41H), 5.90 (s, 1H), 3.34 (s, 3H), 3.08 (s, 1.38H), 3.02 – 2.73 (m, 6.36H), 2.22 – 1.96 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.6, 142.2, 142.1, 141.9, 141.6, 137.4, 135.0, 129.3, 129.2, 129.1, 128.7, 128.3, 128.2, 127.9, 127.3, 127.1, 126.6, 126.1, 125.9, 125.7, 125.3, 89.1, 88.5, 38.7, 37.0, 33.9, 14.9, 14.6 ppm; IR (film) v_{max} 1647,1597, 1540, 1495, 1384, 1126, 766, 698 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1546; Found 337.1542.

***trans*-1-Methyl-3-(1-nitrocyclobutyl)-4-phenyl-3,4-dihydroquinolin-2(1*H*)-one (3uf)**



White solid (62 mg, 58% yield); R_f = 0.1 (10:1 hexanes/AcOEt); m.p. 86.1–86.9 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (ddd, *J* = 8.0, 6.6, 2.5 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.18 (m, 1H), 7.09 – 7.03 (m, 3H), 6.99 – 6.94 (m, 2H), 4.10 (d, *J* = 2.1 Hz, 1H), 3.53 (d, *J* = 2.1 Hz, 1H), 3.44 (s, 3H), 2.69 (dd, *J* = 8.5, 7.5 Hz, 2H), 2.61 – 2.51 (m, 1H), 2.42 (ddt, *J* = 9.6, 8.2, 5.9 Hz, 1H), 1.98 – 1.84 (m, 1H), 1.81 – 1.67 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.8, 141.4, 139.4, 129.6, 129.0, 128.7,

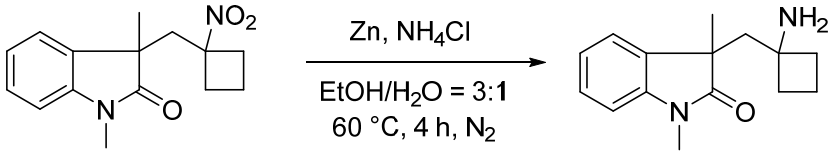
127.3, 127.0, 124.6, 124.0, 114.7, 90.9, 53.8, 43.2, 32.7, 30.9, 30.0, 14.2 ppm; IR (film) ν_{max} 1628, 1366, 1134, 786 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1546; Found 337.1541.

5. Gram-scale reaction

A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). *N*-Methyl-*N*-phenylmethacrylamide (**1a**, 1.6 g, 9.0 mmol), 1-bromo-1-nitrocyclobutane (**2f**, 3.0 mL, 18 mmol), Ag_2CO_3 (12.5 g, 18.0 mmol) and anhydrous acetone (50 mL) were added under N_2 atmosphere followed by *fac*-Ir(ppy)$_3$ (20 mg, 1.0 mol%). The reaction mixture was degassed by freeze-pump-thaw method and then stirred under irradiation with blue LEDs (456 nm, approximately 3.0 cm distance from the tube). The mixture was maintained at approximately 25 °C by a desk fan in air-conditioned room. The reaction was monitored by TLC. Upon completion (24 h), the mixture was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (10:1 hexanes/AcOEt) to give **3af** (light yellow oil, 1.72 g, 71% yield).

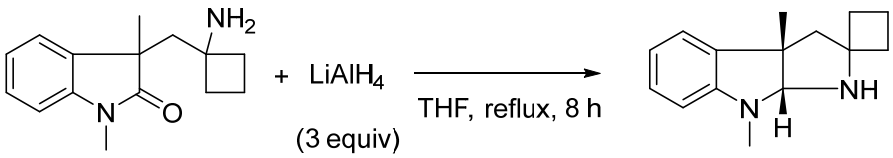
6. Conversions of 3af

6.1 Conversions of 3af [23,24]



3af

Zn dust was stirred with 1 M HCl (10.0 mL) for 5 minutes, filtered and washed with H_2O. **3af** (137 mg, 0.5 mmol), NH_4Cl (294 mg, 5.5 mmol, 11 equiv) and activated Zn dust (325 mg, 5.0 mmol, 10.0 equiv) were added to a mixture of EtOH and water (3:1, 20 mL). The Schlenk tube was purged with N_2 and the mixture was stirred at 60 °C for 4 h. The reaction was monitored by TLC. After cooling to rt, the mixture was filtered. The filtrate was diluted with H_2O and extracted with CH_2Cl_2. The crude product was purified by flash chromatography on silica gel (5:1 CH_2Cl_2/MeOH) to give 3-((1-aminocyclobutyl)methyl)-1,3-dimethylindolin-2-one as a light yellow oil (102 mg, 86% yield).



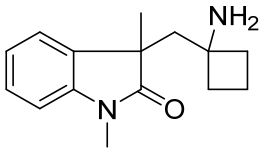
(±)

A Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). 3-((1-Aminocyclobutyl)methyl)-1,3-dimethylindolin-2-one (98 mg, 0.40 mmol) and anhydrous THF (10 mL)

were added followed by $LiAlH_4$ (115 mg, 3.0 equiv). The reaction was refluxed (oil bath: 80 °C) for 8 h and monitored by TLC. After cooling to rt, water was added slowly and the mixture was extracted with ethyl acetate. The ethyl acetate extracts were combined, dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography on silica gel (5:1 CH_2Cl_2/MeOH) to give 3a',8'-dimethyl-3',3a',8',8a'-tetrahydro-1'H-spiro[cyclobutane-1,2'-pyrrolo[2,3-*b*]indole] as a brown oil (99 mg, 90% yield).

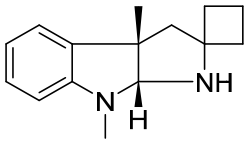
6.2 Physical data

3-((1-Aminocyclobutyl)methyl)-1,3-dimethylindolin-2-one



Yellow oil, R_f = 0.1 (5:1 CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 6.6 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.19 (s, 5H), 2.38 (d, *J* = 14.6 Hz, 1H), 2.21 (d, *J* = 14.6 Hz, 1H), 2.03 (q, *J* = 10.1, 7.8 Hz, 1H), 1.87 – 1.66 (m, 3H), 1.59 (qd, *J* = 8.4, 5.4, 4.2 Hz, 1H), 1.44 (dt, *J* = 14.4, 6.3 Hz, 1H), 1.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.5, 142.9, 133.8, 127.8, 123.3, 122.2, 108.2, 56.8, 47.8, 46.9, 36.7, 35.9, 29.6, 26.4, 26.3, 14.3 ppm; IR (film) ν_{max} 1705, 1612, 1466, 1381, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{21}N_2O$ 245.1653; Found 245.1653.

3a',8'-Dimethyl-3',3a',8',8a'-tetrahydro-1'H-spiro[cyclobutane-1,2'-pyrrolo[2,3-*b*]indole]



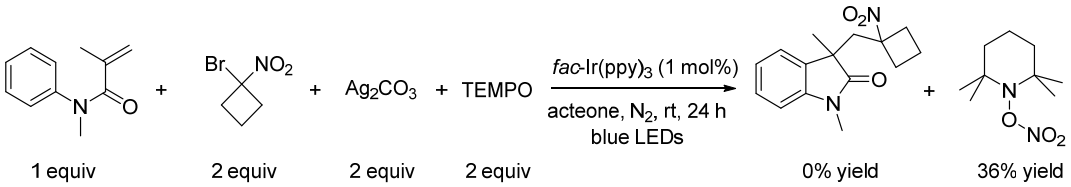
(±)

Brown oil, R_f = 0.3 (5:1 CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 6.98 (m, 2H), 6.62 (td, *J* = 7.4, 1.0 Hz, 1H), 6.28 (dd, *J* = 7.8, 0.9 Hz, 1H), 4.54 (s, 1H), 2.83 (s, 3H), 2.32 (d, *J* = 12.2 Hz, 1H), 2.15 (dt, *J* = 11.6, 9.0 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.91 (dd, *J* = 12.3, 0.7 Hz, 1H), 1.79 – 1.70 (m, 1H), 1.64 – 1.58 (m, 1H), 1.57 – 1.45 (m, 2H), 1.43 (s, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 136.5, 127.7, 122.2, 116.7, 105.2, 91.1, 64.9, 52.3, 52.3, 37.5, 35.1, 31.7, 26.6, 14.3 ppm; IR (film)

ν_{max} 2970, 1088, 1049, 880, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{21}N_2$ 229.1699; Found 229.1706.

7. Mechanism experiments

7.1 Radical-trapping experiment



A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). *N*-Methyl-*N*-phenylmethacrylamide (**1a**, 80 mg, 0.45 mmol), 1-bromo-1-nitrocyclobutane (**2f**, 0.15 mL, 0.90 mmol), Ag_2CO_3 (250 mg, 0.90 mmol), TEMPO (141 mg, 0.90 mmol) and anhydrous acetone (8.0 mL) were added under N_2 atmosphere followed by *fac*-Ir(ppy)$_3$ (5 mg, 1 mol%). The reaction mixture was degassed by freeze-pump-thaw method and then stirred under irradiation with blue LEDs (456 nm, app. 3.0 cm distance from the tube). The mixture was maintained at approximately 25 °C by a desk fan in air-conditioned room. The reaction was monitored by TLC. Upon completion (24 h), the mixture was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (20:1 hexanes/AcOEt) to give TEMPONO_2 (65 mg, 36% yield, based on **2f**).

7.2 X-ray diffraction experiment

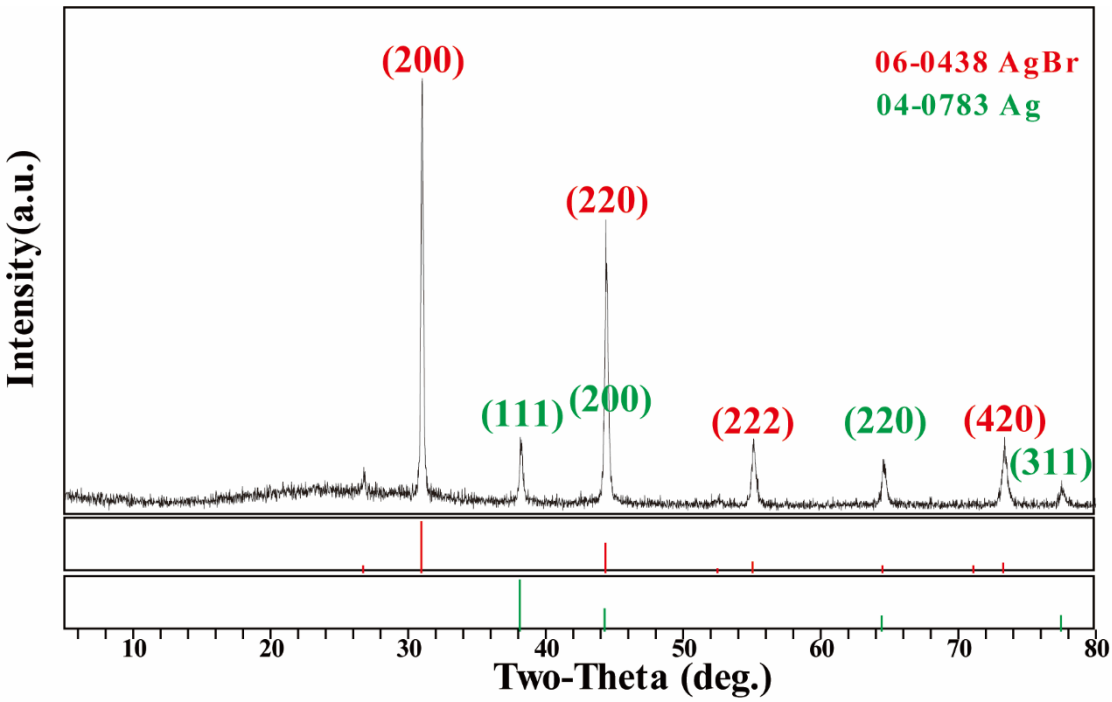


Figure S3 XRD patterns of the precipitate in the mechanism experiment.

7.3 Stern–Volmer plot

Stern–Volmer luminescence quenching analysis was conducted at room temperature using an Agilent spectrofluorometer. The excitation wavelength was 420 nm and the emission was collected across a range of 450–750 nm. The samples were placed in a screw-capped quartz cuvette (H × W × D = 60 × 12.5 × 12.5 mm) of 3.5 mL.

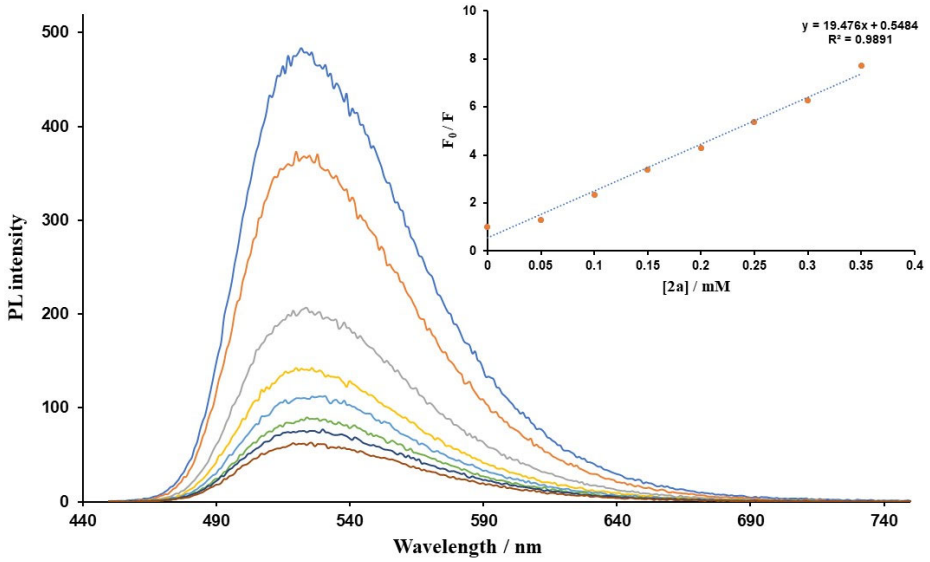
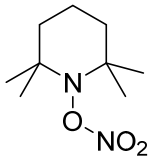


Figure S4 Luminescence spectra of *fac*-Ir(ppy)$_3$ (0.5 mM in deaerated CH_3CN) quenched with varying concentrations (0.05 mM to 0.4 mM) of 1-bromo-1-nitrocyclobutane **2f** at 25 °C. Inset is the corresponding Stern–Volmer plot.

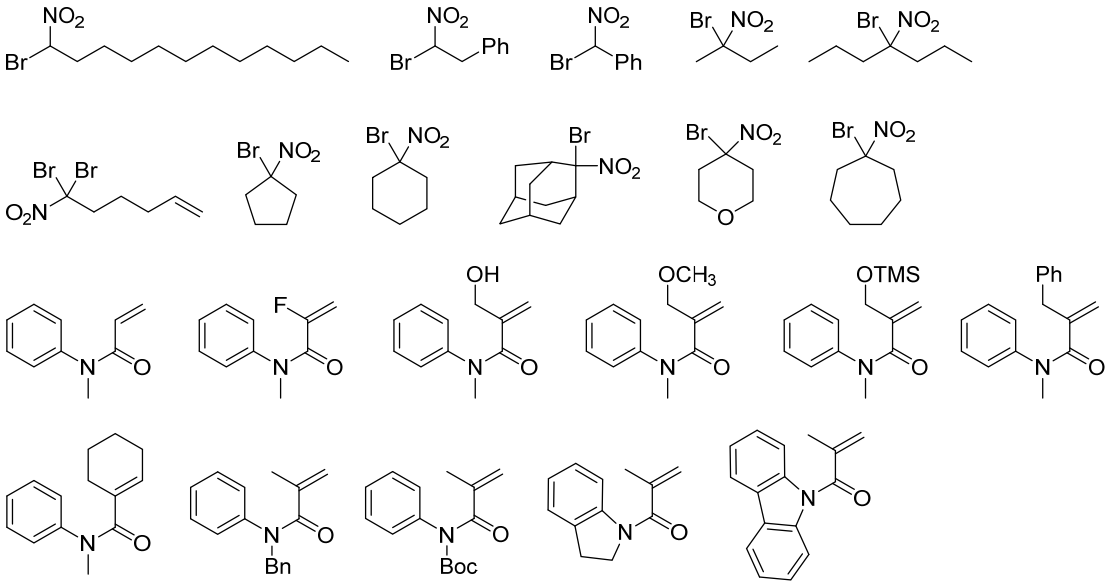
7.4 Physical data

2,2,6,6-Tetramethylpiperidin-1-yl nitrate[25]



Orange oil (36% yield, based on **2f**); R_f = 0.6 (10:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 1.79 (dq, *J* = 6.2, 2.3 Hz, 2H), 1.65 (dddd, *J* = 7.6, 5.8, 3.6, 2.1 Hz, 2H), 1.58 (d, *J* = 2.8 Hz, 8H), 1.38 (d, *J* = 3.0 Hz, 6H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 41.4, 38.8, 31.8, 26.0, 16.1 ppm; IR (film) ν_{max} 2947, 1790, 1605, 1450, 1366, 1258, 1134, 1049 cm^{-1}.

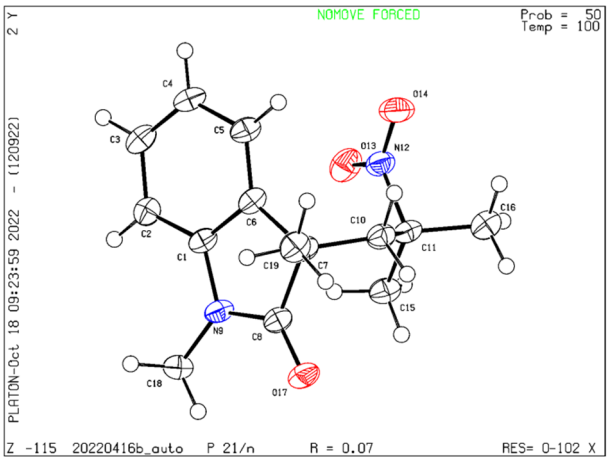
8. Unsuccessful reactants



9. Crystal data

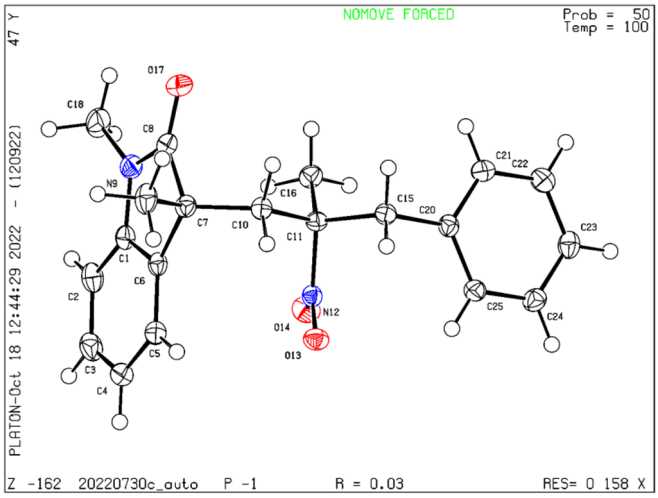
CCDC numbers: 2235177; 2235178; 2235872; 2236062; 2235193; 2238530.

Single crystals of **3aa**, **3ae** and **3uf** were obtained by layering a CH_2Cl_2 solution with *n*-hexane and subsequent slow evaporation of the solvents at rt. Single crystals of **3ai**, **3tf**, **3tf′** were obtained by layering an AcOEt solution with *n*-hexane and subsequent slow evaporation of the solvents at rt. The ellipsoid contour probability level is 50%.



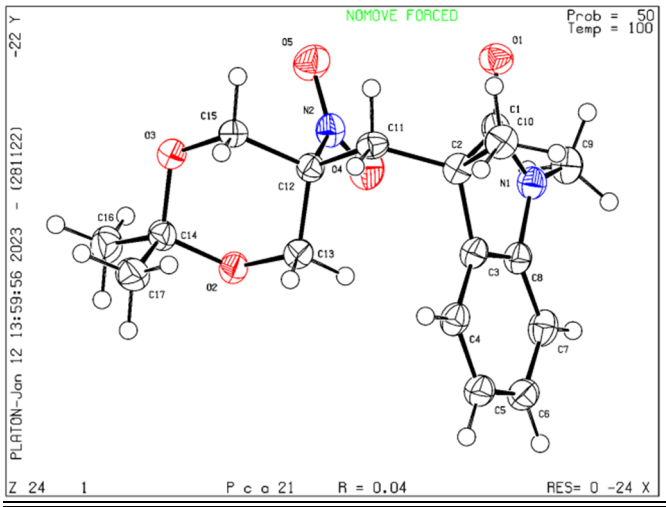
Crystal data and structure refinement for **3ad**.

Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.3740(4)
b/Å	6.6672(3)
c/Å	15.1512(6)
α/°	90
β/°	98.804(4)
γ/°	90
Volume/Å^3	1335.07(9)
Z	4
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	0.758
F(000)	560.0
Crystal size/mm^3	0.500 × 0.500 × 0.400
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.218 to 152.7
Index ranges	$-16 \le h \le 16$, $-7 \le k \le 7$, $-18 \le l \le 19$
Reflections collected	11615
Independent reflections	2637 [R_{int} = 0.0880, R_{sigma} = 0.0693]
Data/restraints/parameters	2637/0/176
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0698, wR_2 = 0.1849
Final R indexes [all data]	R_1 = 0.0977, wR_2 = 0.2162
Largest diff. peak/hole / e Å^{-3}	0.43/-0.32



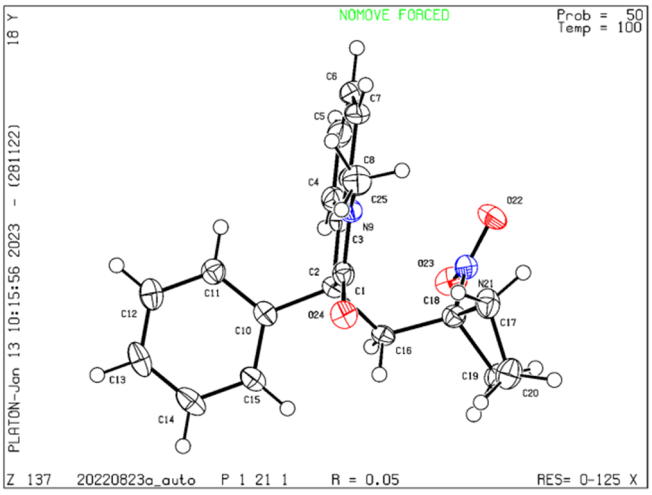
Crystal data and structure refinement for **3ae**.

Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.1551(9)
b/Å	11.4451(13)
c/Å	11.4726(13)
α/°	62.610(11)
β/°	70.408(10)
γ/°	87.885(9)
Volume/Å^3	886.86(19)
Z	2
ρ_{calc}g/cm^3	1.267
μ/mm^{-1}	0.692
F(000)	360.0
Crystal size/mm^3	0.400 × 0.300 × 0.100
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.788 to 151.67
Index ranges	-10 ≤ h ≤ 9, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	32637
Independent reflections	3536 [R_{int} = 0.0406, R_{sigma} = 0.0164]
Data/restraints/parameters	3536/0/230
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0872
Largest diff. peak/hole / e Å^{-3}	0.25/-0.22

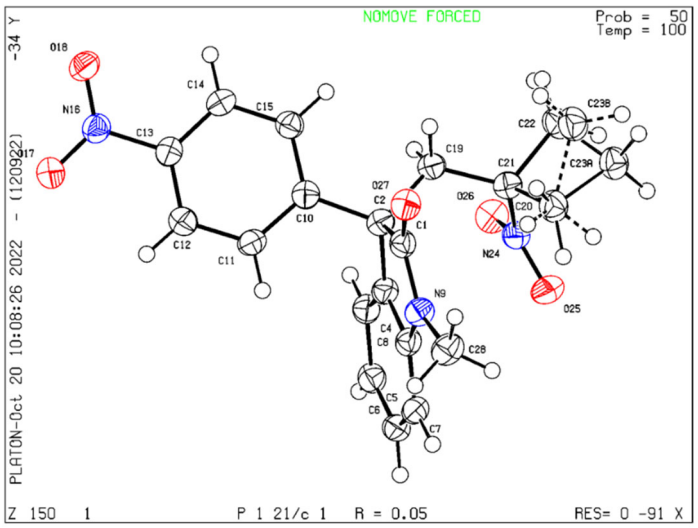


Crystal data and structure refinement for **3ai**.

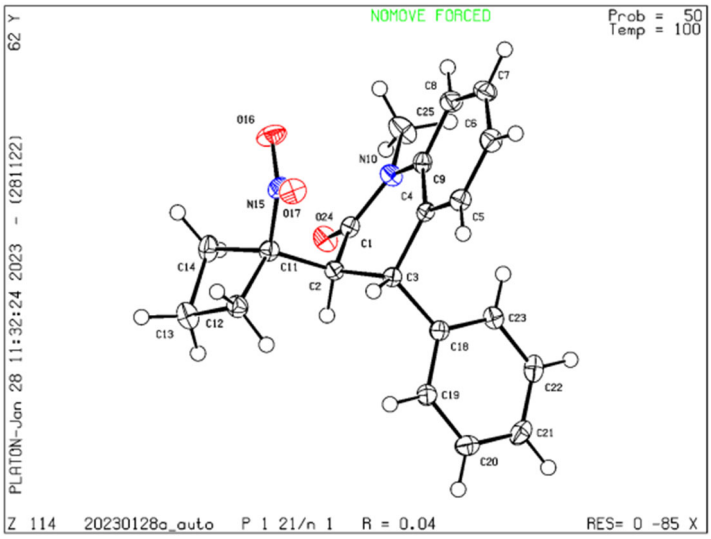
Temperature/K	99.99(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	10.2000(3)
b/Å	12.8987(3)
c/Å	12.6329(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1662.07(8)
Z	4
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.820
F(000)	712.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.852 to 153.262
Index ranges	-12 ≤ h ≤ 10, -16 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	10868
Independent reflections	3147 [R_{int} = 0.0759, R_{sigma} = 0.0754]
Data/restraints/parameters	3147/1/221
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1004
Final R indexes [all data]	R_1 = 0.0555, wR_2 = 0.1072
Largest diff. peak/hole / e Å^{-3}	0.16/-0.18
Flack parameter	0.0(2)



Crystal data and structure refinement for **3tf**.	
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.3516(6)
b/Å	8.7894(3)
c/Å	10.7156(7)
α/°	90
β/°	118.800(8)
γ/°	90
Volume/Å^3	854.35(10)
Z	2
ρ_{calc}g/cm^3	1.308
μ/mm^{-1}	0.718
F(000)	356.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.418 to 153.336
Index ranges	-13 ≤ h ≤ 12, -10 ≤ k ≤ 11, -13 ≤ l ≤ 11
Reflections collected	8156
Independent reflections	3052 [R_{int} = 0.0626, R_{sigma} = 0.0633]
Data/restraints/parameters	3052/1/228
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.1112
Largest diff. peak/hole / e Å^{-3}	0.18/-0.21
Flack parameter	0.1(3)



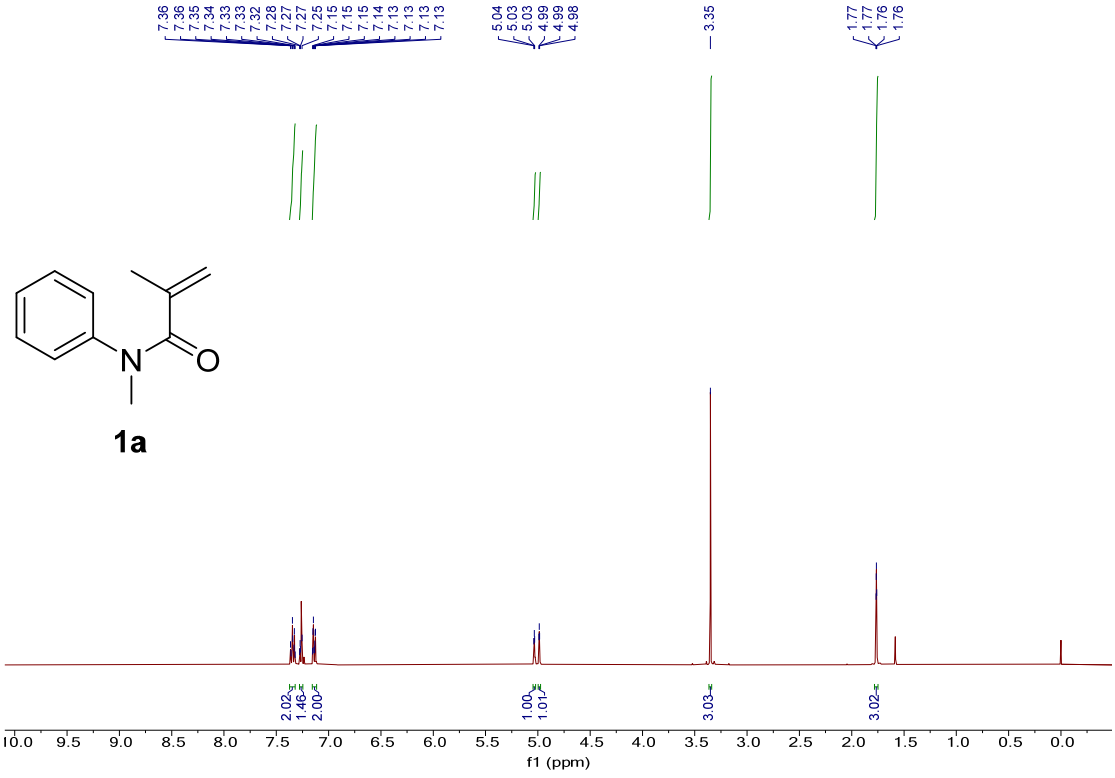
Crystal data and structure refinement for **3tf'**.	
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.2829(10)
b/Å	8.1950(5)
c/Å	12.6580(7)
α/°	90
β/°	106.083(6)
γ/°	90
Volume/Å^3	1822.30(19)
Z	4
ρ_{calc}g/cm^3	1.390
μ/mm^{-1}	0.845
F(000)	800.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.07 to 153.482
Index ranges	$-22 \le h \le 22$, $-10 \le k \le 10$, $-15 \le l \le 15$
Reflections collected	31943
Independent reflections	3709 [R_{int} = 0.1376, R_{sigma} = 0.0640]
Data/restraints/parameters	3709/12/264
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1310
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1429
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21

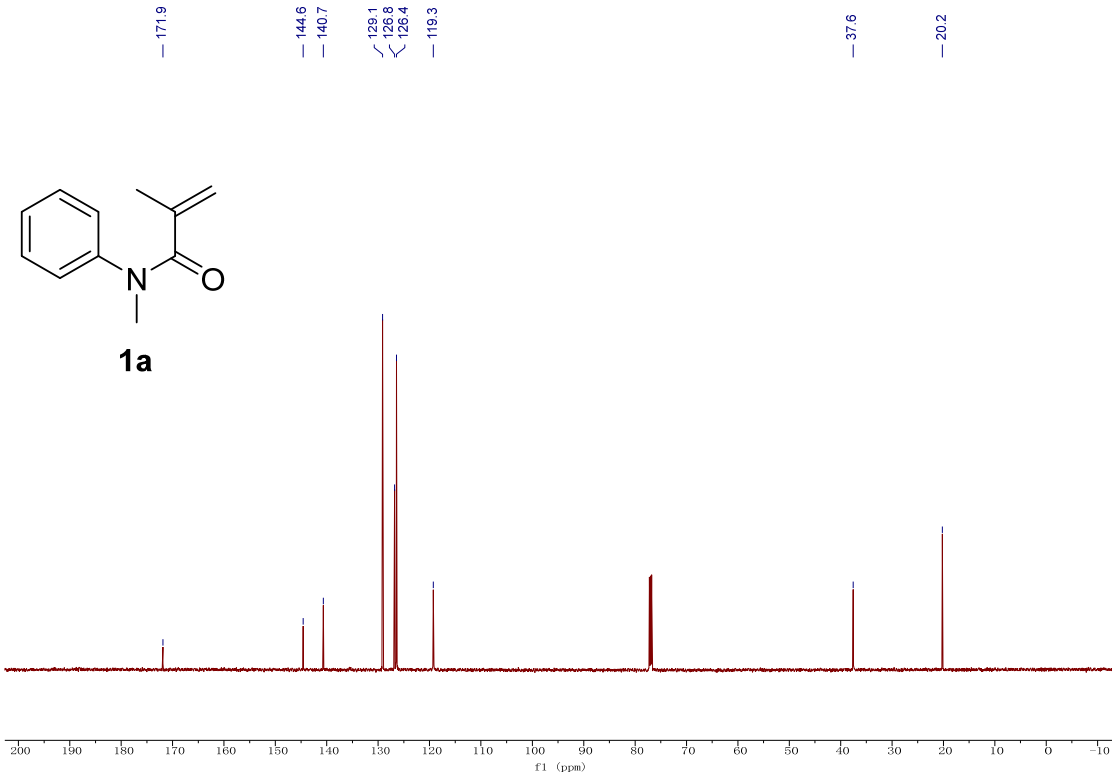


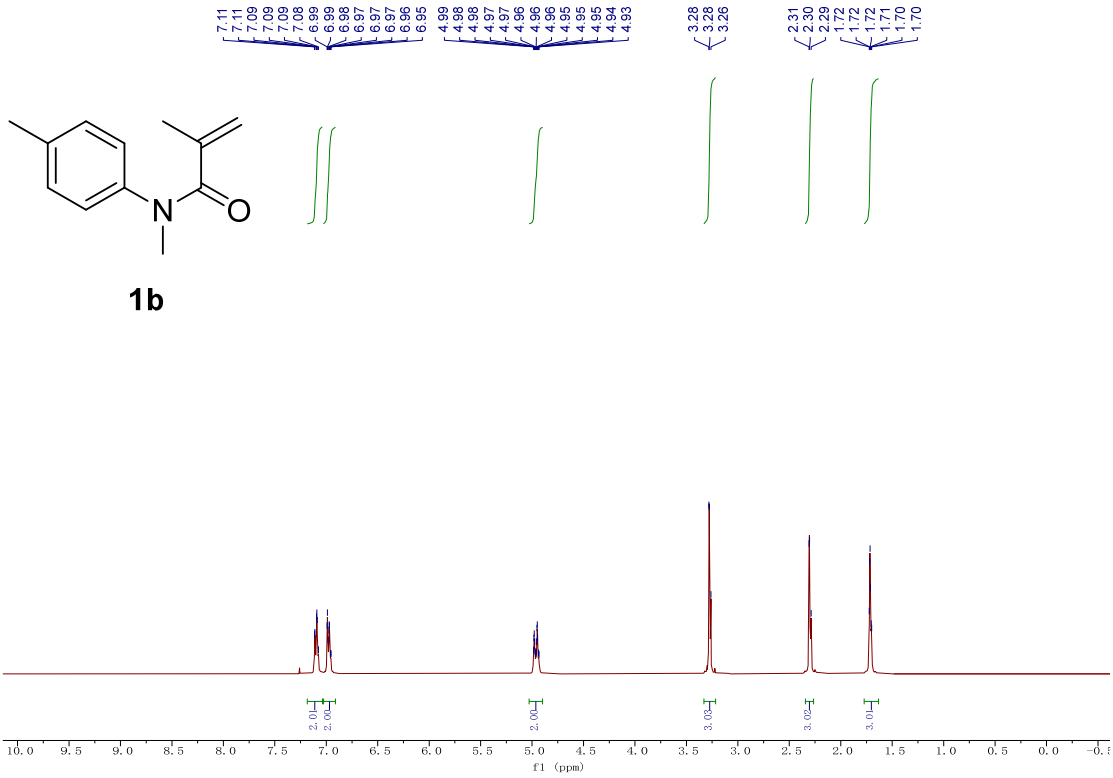
Crystal data and structure refinement for **3uf**.

Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.9343(3)
b/Å	19.1994(7)
c/Å	11.1708(2)
α/°	90
β/°	90.627(3)
γ/°	90
Volume/Å^3	1701.59(10)
Z	4
ρ_{calc}g/cm^3	1.313
μ/mm^{-1}	0.721
F(000)	712.0
Crystal size/mm^3	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.16 to 153.302
Index ranges	-10 ≤ h ≤ 8, -24 ≤ k ≤ 22, -13 ≤ l ≤ 14
Reflections collected	16238
Independent reflections	3413 [R_{int} = 0.0614, R_{sigma} = 0.0390]
Data/restraints/parameters	3413/0/228
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1132
Largest diff. peak/hole / e Å^{-3}	0.27/-0.21

10. NMR spectra



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7.08
6.99
6.99
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6.95
4.99
4.98
4.98
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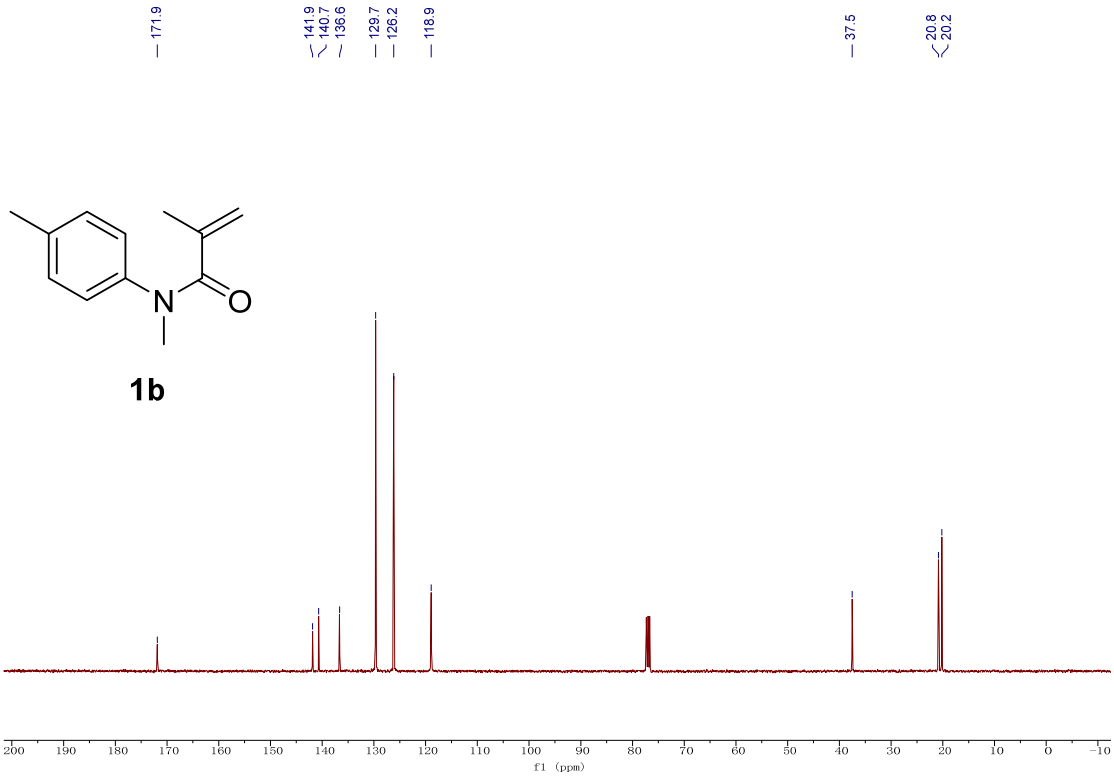
4.95
4.94
4.93
3.28
3.28
3.26
2.31
2.30
2.29
1.72
1.72
1.71
1.70
1.70
N
O
1b
2.01
2.00
2.00
3.03
3.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.9
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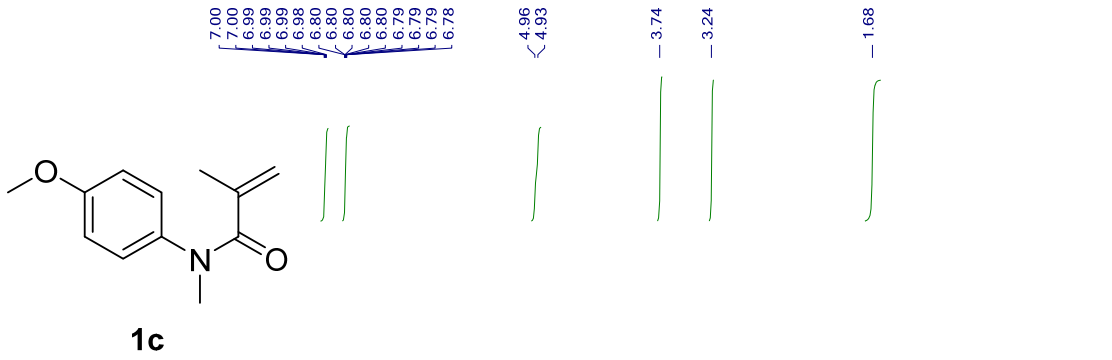
136.6
129.7
126.2
118.9
37.5
20.8
20.2
N
O
1b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.96
4.93
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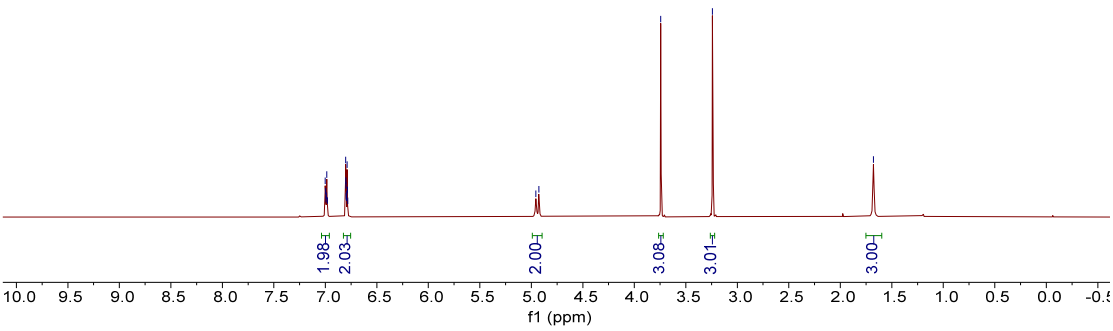
3.24
1.68
O
N
O

1c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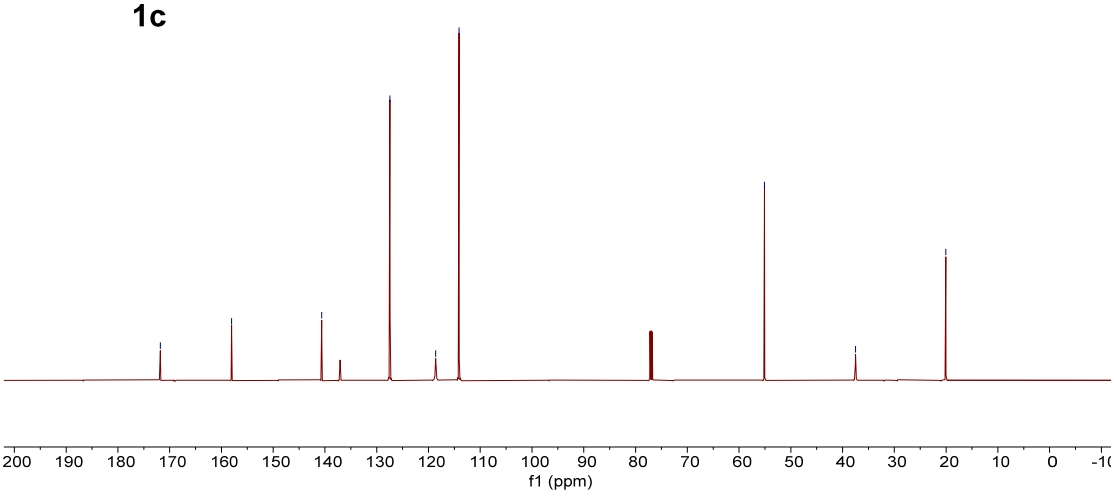
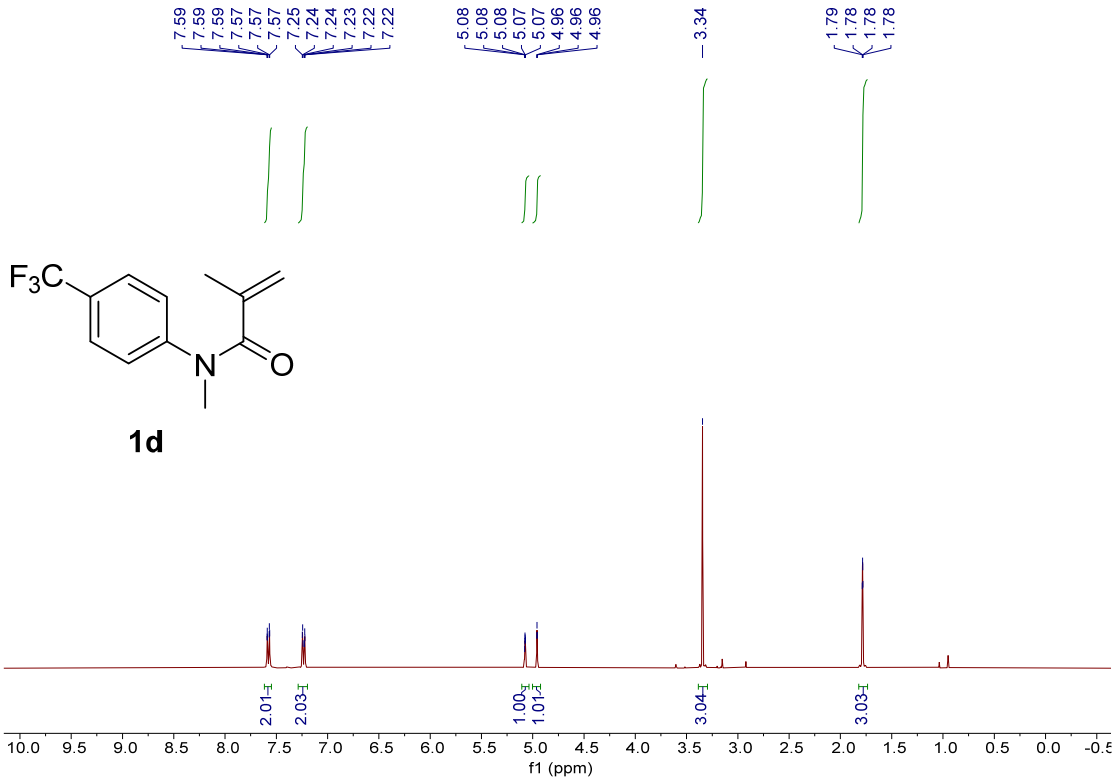
2.00
3.08
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.8
158.0
140.6
127.5
118.6
114.1
55.1
37.5
20.1

O
N
O

1c


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.59
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F3C
N
O
1d
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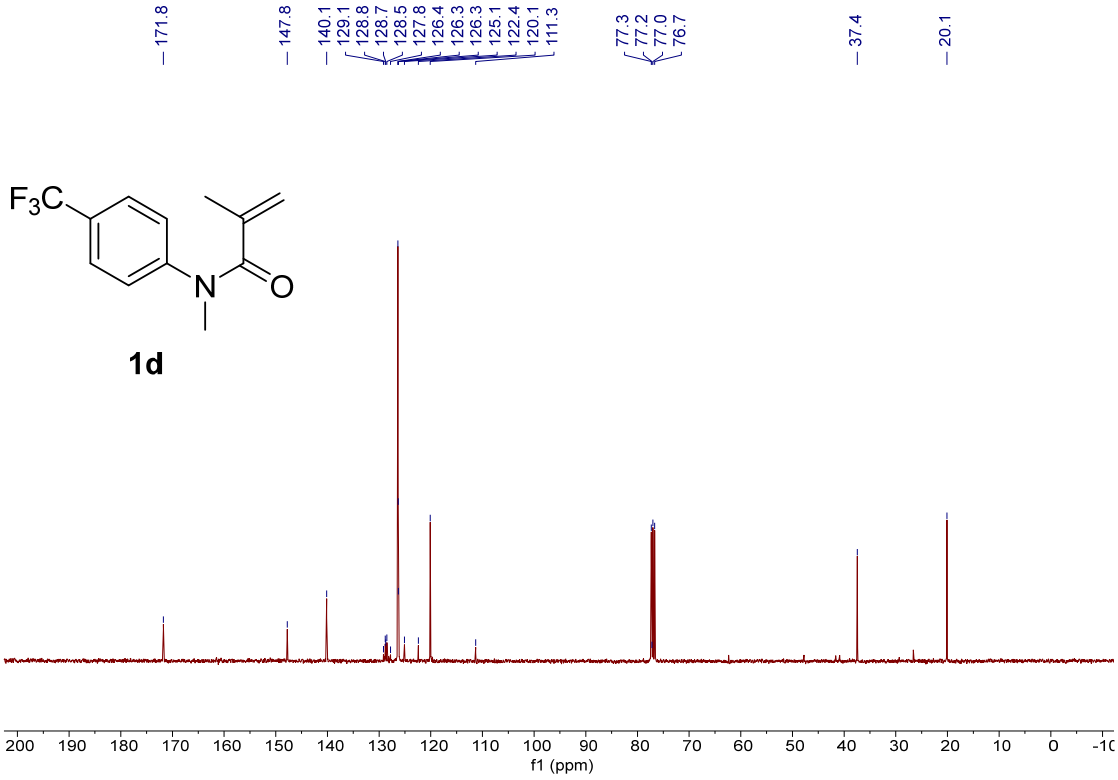
2.03
1.00
1.01
3.04
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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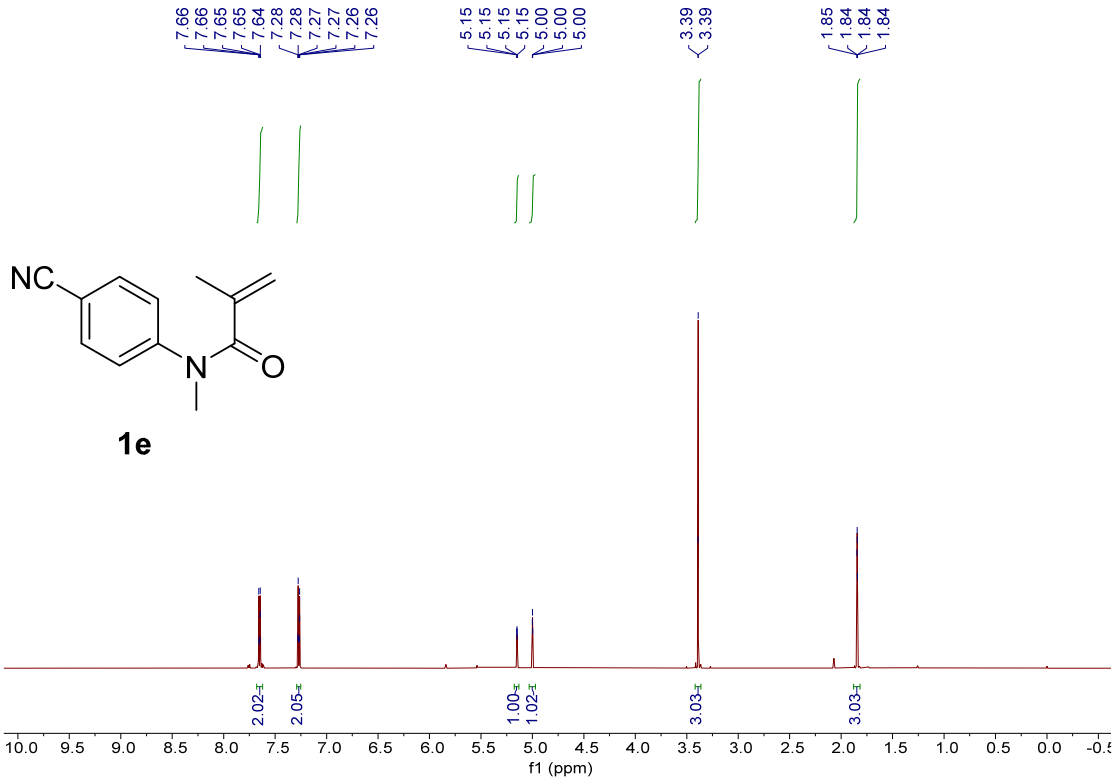
128.7
128.5
127.8
126.4
126.3
126.3
125.1
122.4
120.1
111.3
77.3
77.2
77.0
76.7
37.4
20.1
F3C
N
O
1d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.27
7.26
7.26
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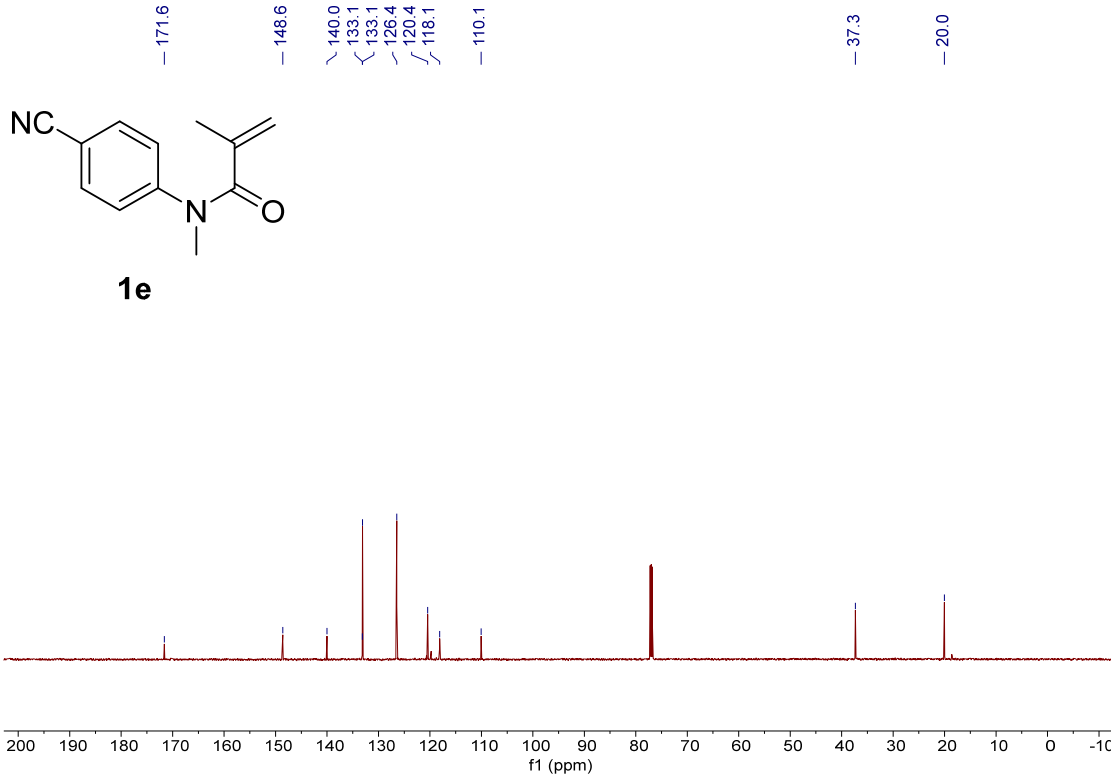
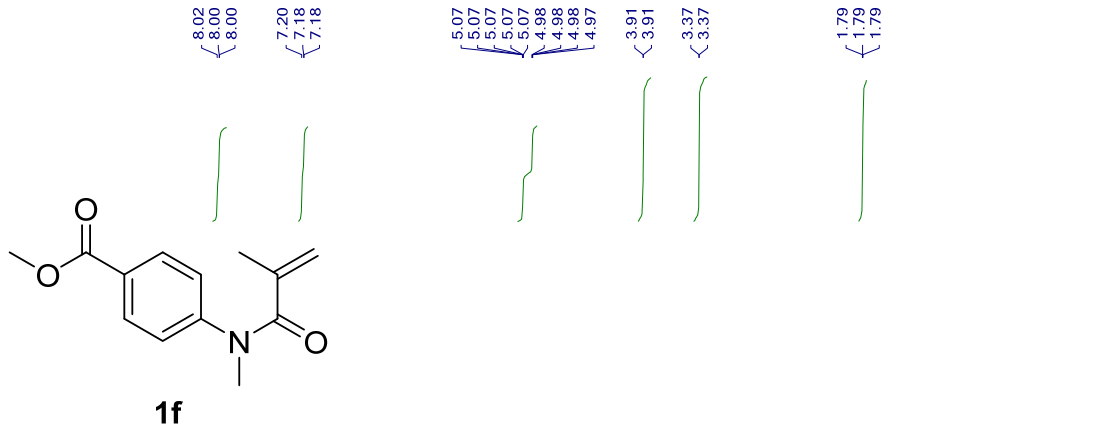
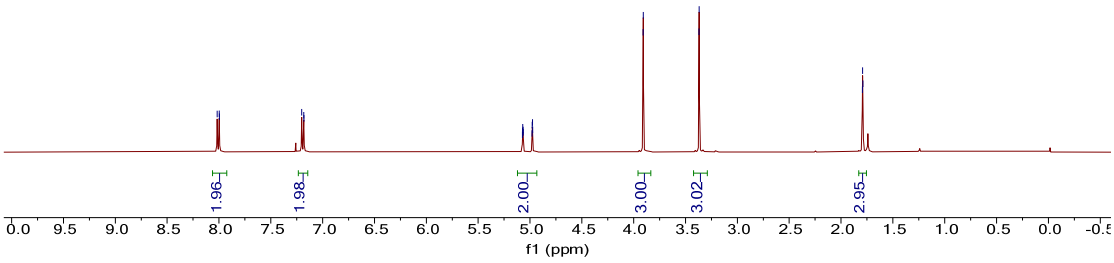
5.15
5.00
5.00
5.00
3.39
3.39
1.85
1.84
1.84
1.84
NC
N
O
1e
2.02
2.05
1.00
1.02
3.03
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.6
148.6
140.0
133.1
133.1
126.4
120.4
118.1
110.1
37.3
20.0
NC
N
O
1e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

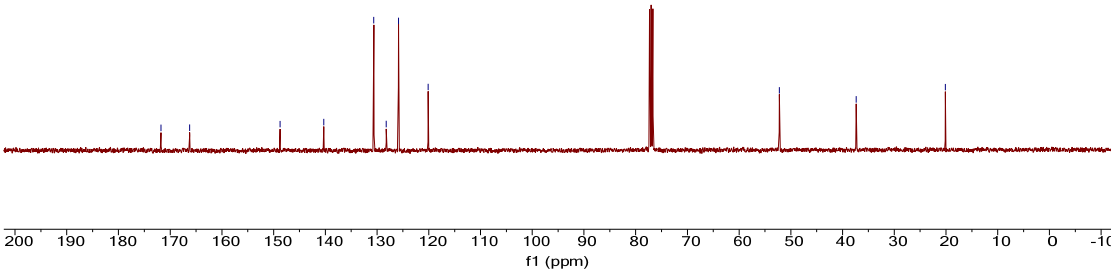

8.02
8.00
8.00
7.20
7.18
7.18
5.07
5.07
5.07
5.07
4.98
4.98
4.98
4.97
3.91
3.91
3.37
3.37
1.79
1.79
1.79
O
O
N
O

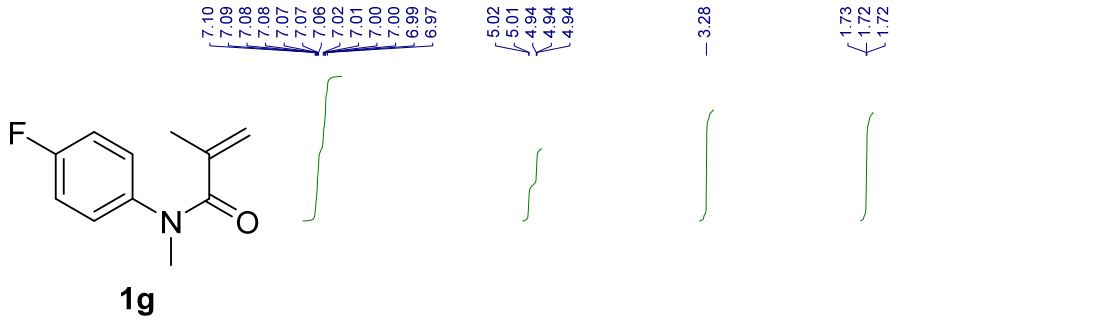
1f


1.96
1.98
2.00
3.00
3.02
2.95
f1 (ppm)

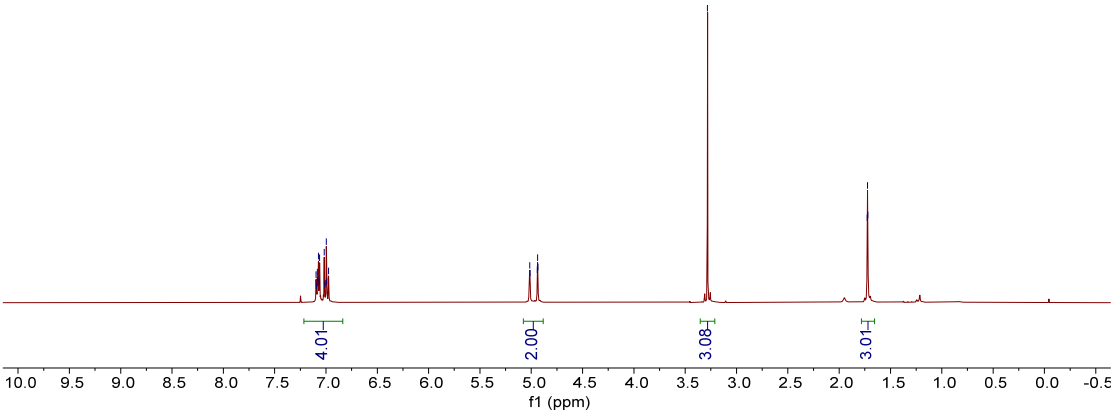

171.8
166.2
148.8
140.3
130.6
128.2
125.9
120.1
52.2
37.4
20.1
O
O
N
O

1f


f1 (ppm)

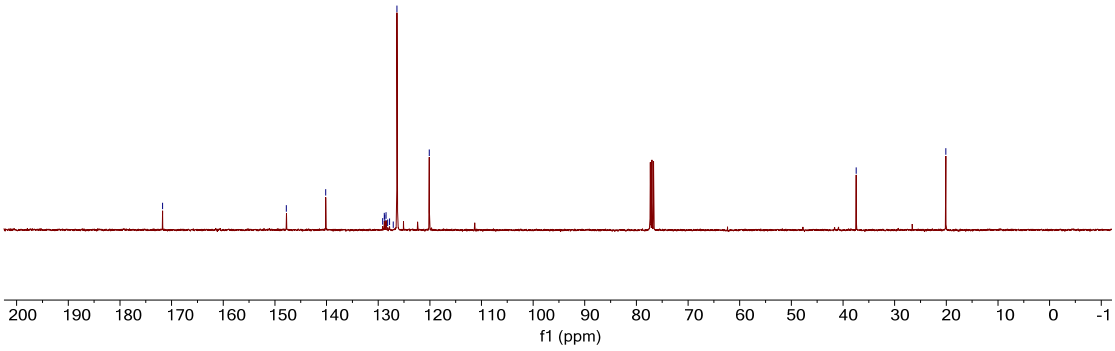

7.10
7.09
7.08
7.08
7.07
7.07
7.06
7.02
7.01
7.00
7.00
6.99
6.97
5.02
5.01
4.94
4.94
4.94
3.28
1.73
1.72
1.72
F
N
O

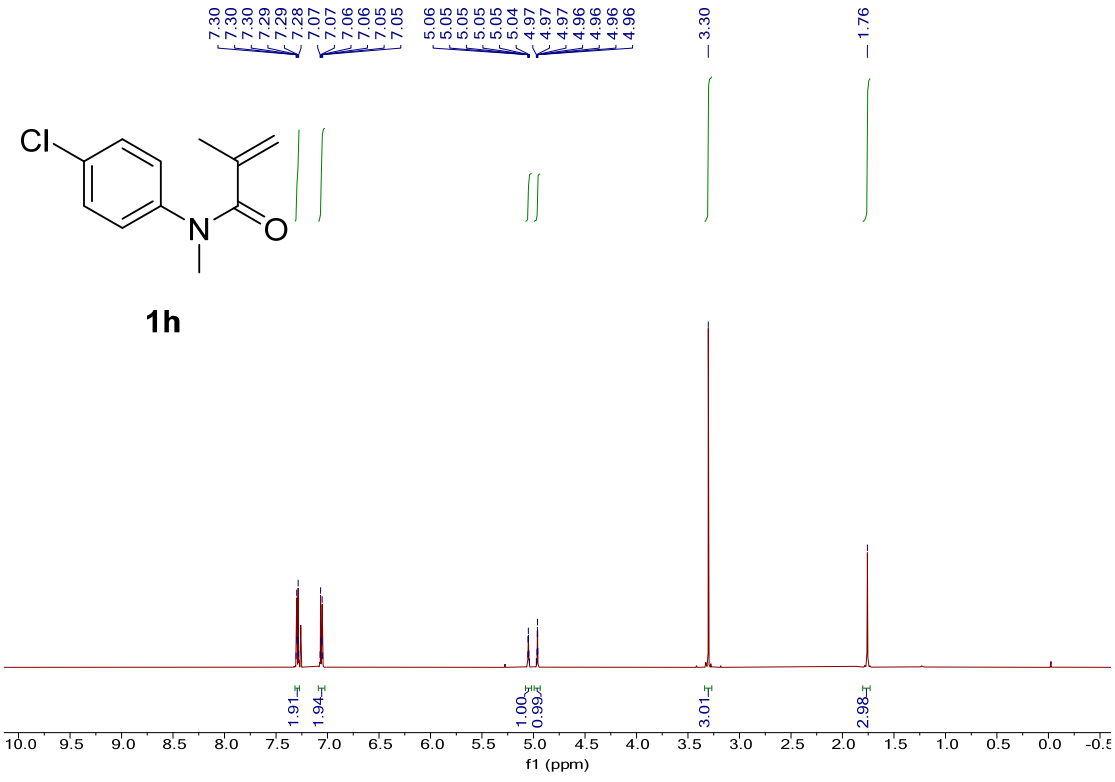
1g

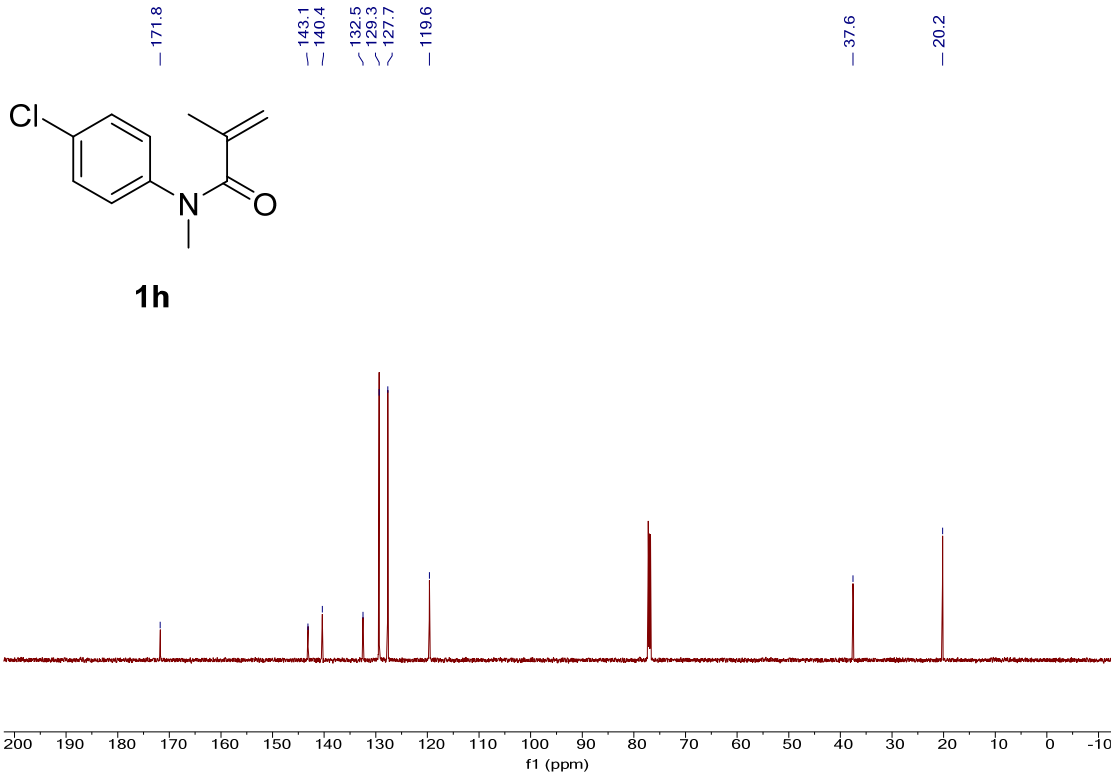

4.01
2.00
3.08
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

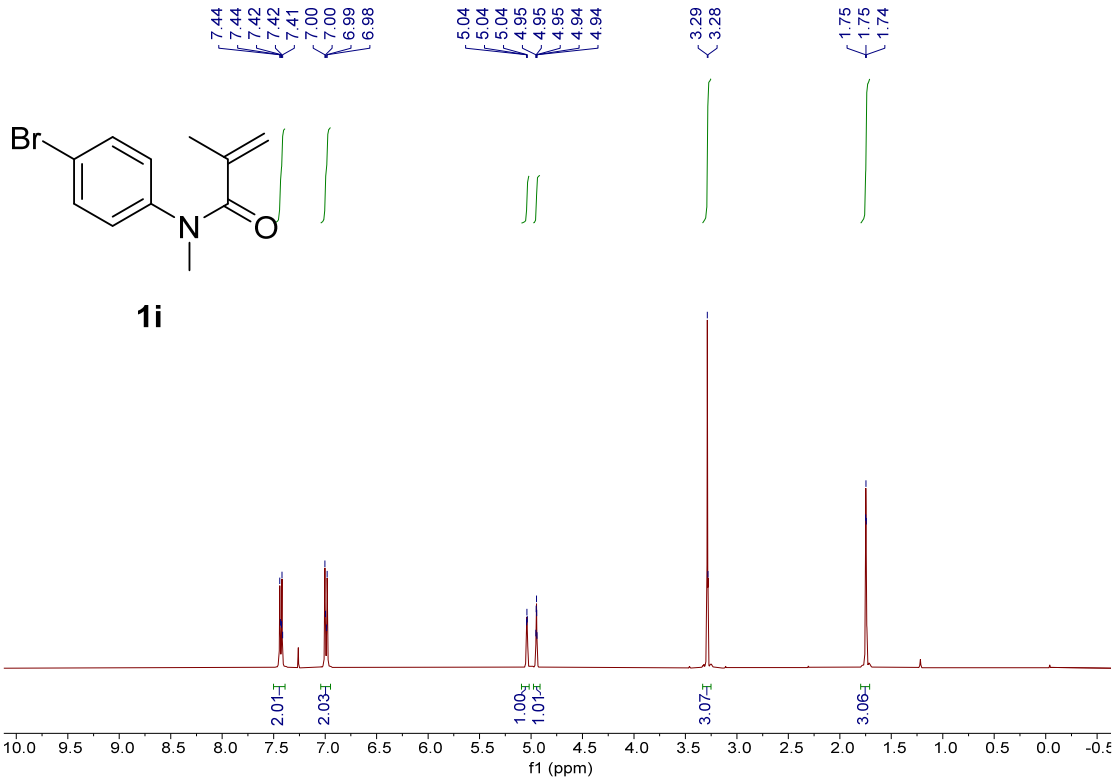

171
147
140
129
128
128
128
128
127
127
126
120
37.4
20.1
F
N
O

1g

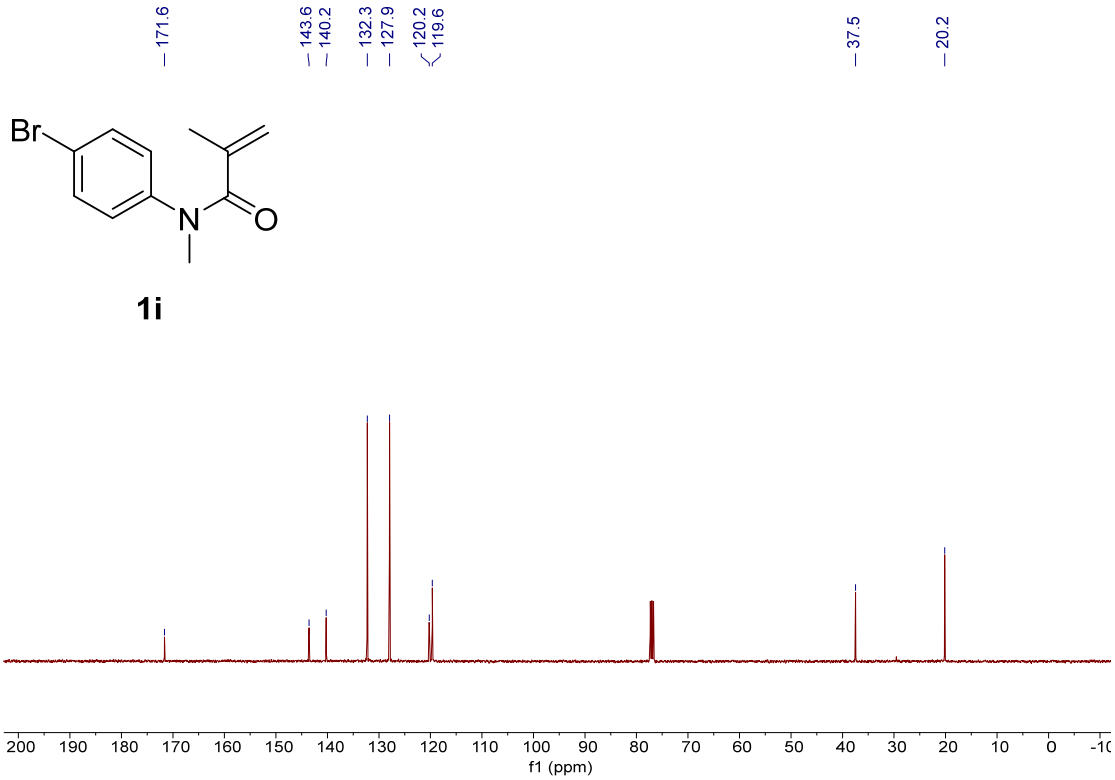

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.30
7.30
7.30
7.29
7.29
7.28
7.07
7.07
7.06
7.06
7.05
7.05
5.06
5.05
5.05
5.05
5.05
5.04
4.97
4.97
4.97
4.96
4.96
4.96
4.96
3.30
1.76
Cl
N
O
1h
1.91
1.94
1.00
0.99
3.01
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

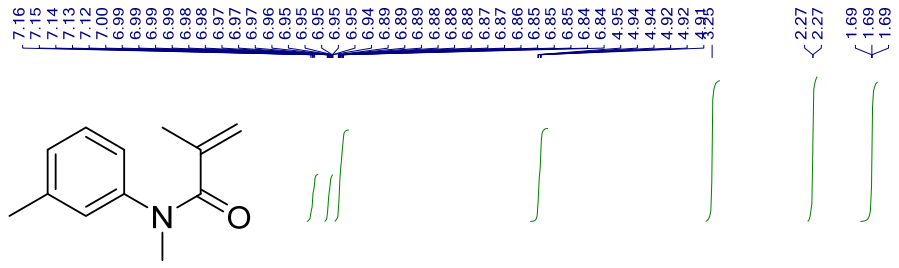

171.8
143.1
140.4
132.5
129.3
127.7
119.6
37.6
20.2
Cl
N
O
1h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.44
7.44
7.42
7.42
7.41
7.00
7.00
6.99
6.98
5.04
5.04
5.04
4.95
4.95
4.95
4.94
4.94
3.29
3.28
1.75
1.75
1.74
Br
N
O
2.01
2.03
1.00
1.01
3.07
3.06
f1 (ppm)

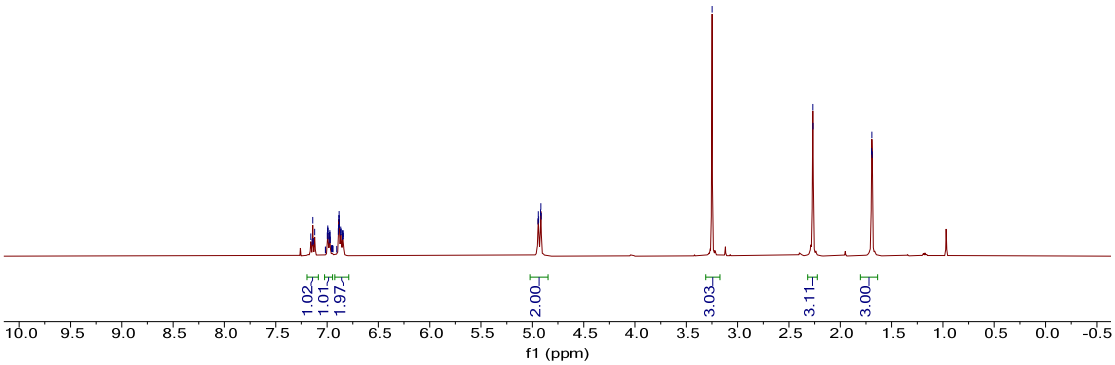
1i

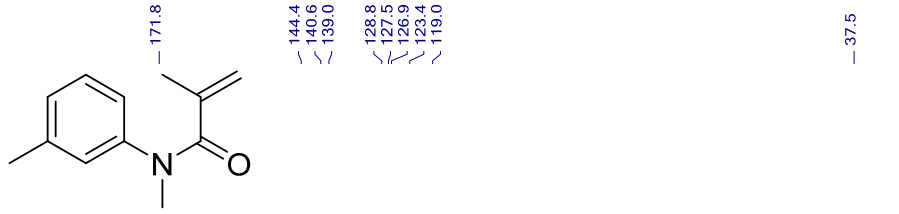

171.6
143.6
140.2
132.3
127.9
120.2
119.6
37.5
20.2
Br
N
O
f1 (ppm)

1i

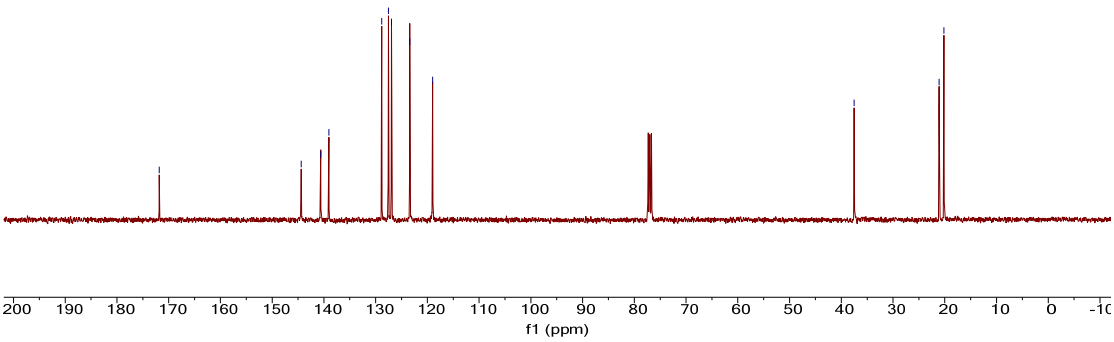

7.16
7.15
7.14
7.13
7.12
7.00
6.99
6.99
6.99
6.98
6.98
6.97
6.97
6.97
6.96
6.95
6.95
6.95
6.95
6.94
6.89
6.89
6.89
6.88
6.88
6.88
6.87
6.87
6.86
6.85
6.85
6.84
6.84
4.95
4.94
4.94
4.92
4.92
4.91
2.27
2.27
1.69
1.69
1.69
N
O

1j


1.02
1.01
1.97
2.00
3.03
3.11
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.8
144.4
140.6
139.0
128.8
127.5
126.9
123.4
119.0
37.5
21.1
20.2
N
O

1j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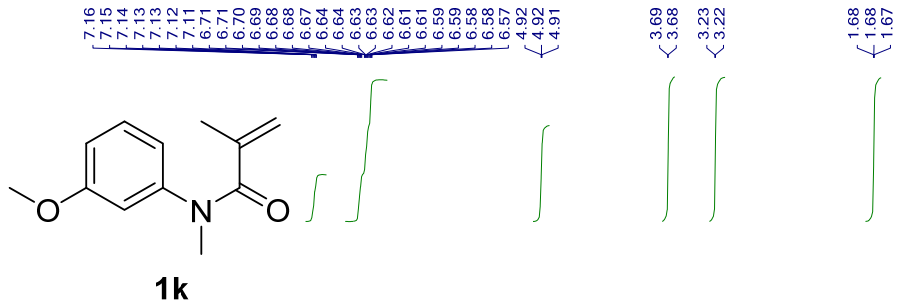
f1 (ppm)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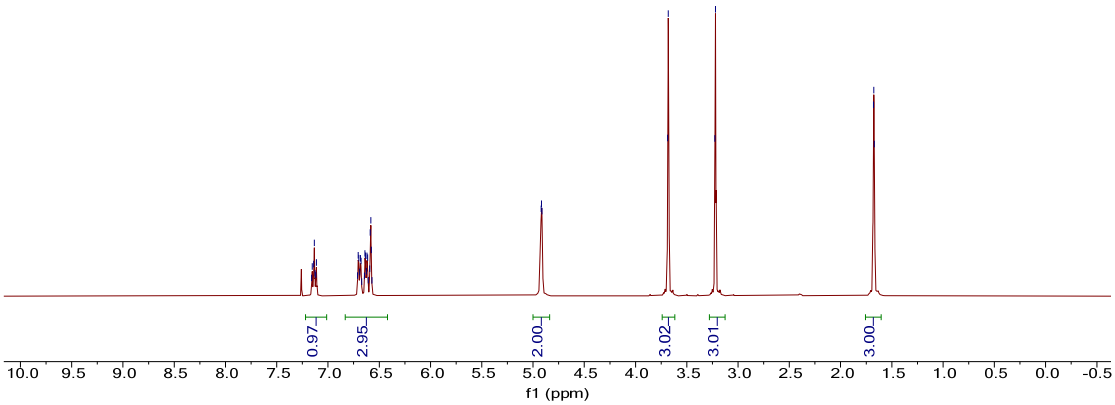
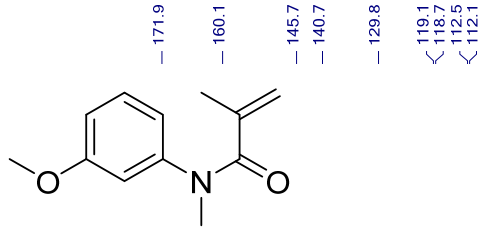
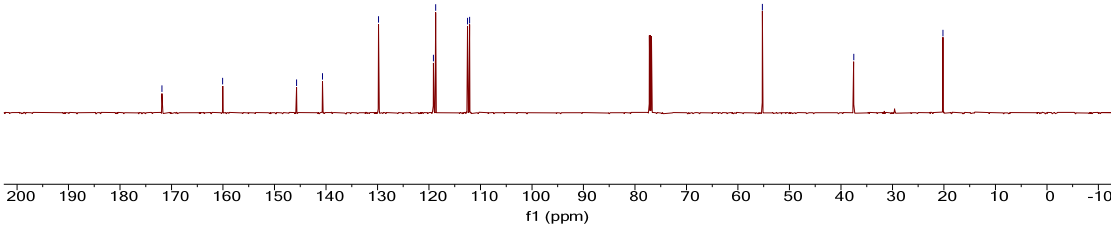
7.15
7.14
7.13
7.13
7.12
7.11
6.71
6.70
6.69
6.68
6.68
6.67
6.64
6.64
6.63
6.63
6.62
6.61
6.61
6.59
6.59
6.58
6.58
6.57
4.92
4.92
4.91
3.69
3.68
3.23
3.22
1.68
1.68
1.67
O
N
O

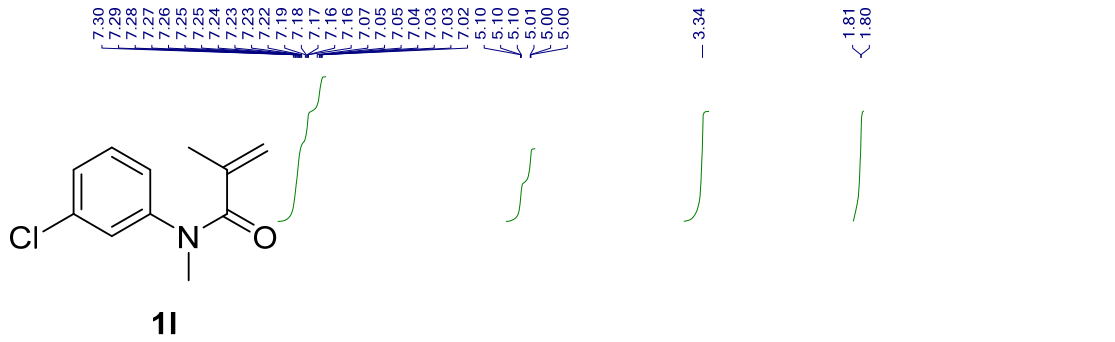
1k


0.97
2.95
2.00
3.02
3.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.9
160.1
145.7
140.7
129.8
119.1
118.7
112.5
112.1
55.3
37.5
20.2
O
N
O

1k


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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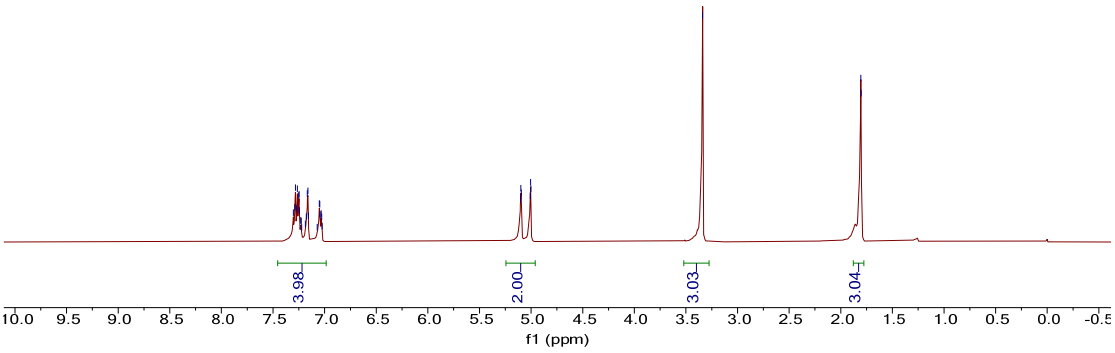
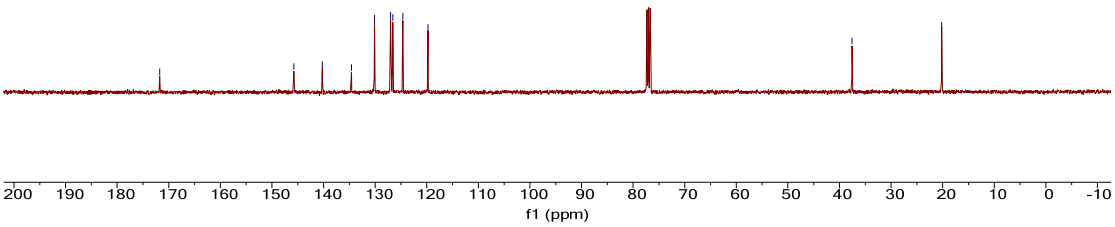
7.25
7.24
7.23
7.23
7.22
7.19
7.18
7.17
7.16
7.16
7.07
7.05
7.05
7.04
7.03
7.03
7.02
5.10
5.10
5.01
5.00
5.00
3.34
1.81
1.80
Cl
N
O

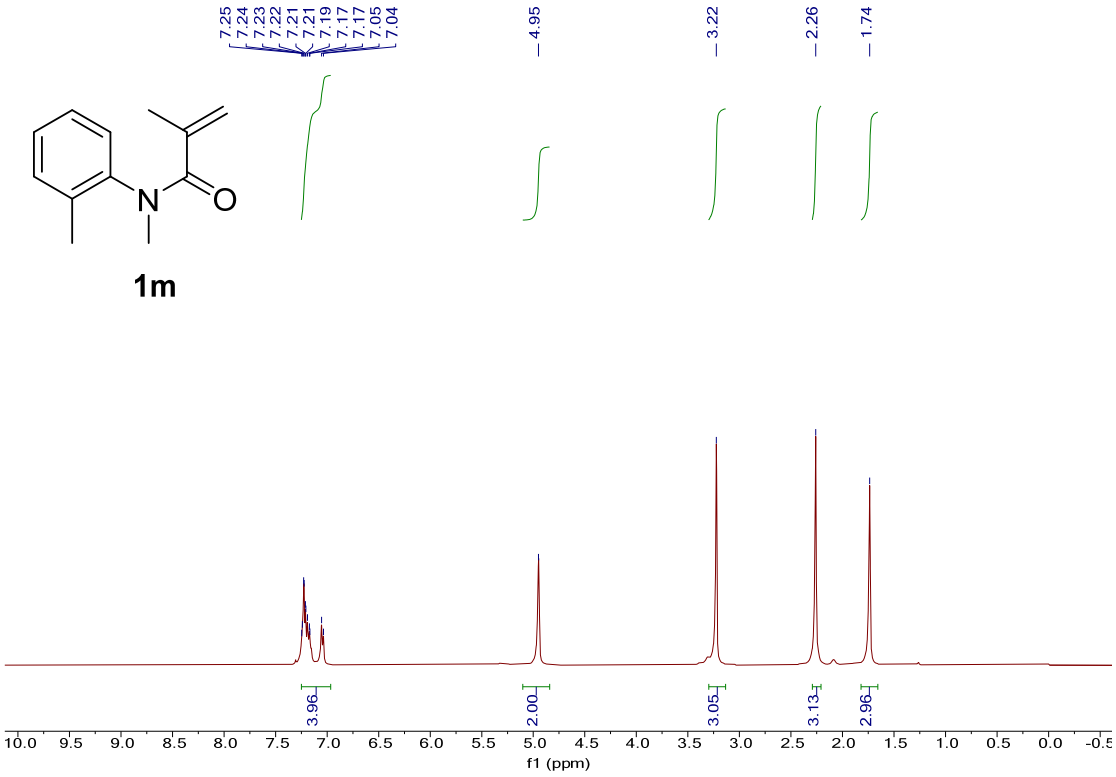
1l


3.98
2.00
3.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.8
145.8
140.2
134.6
130.1
127.0
126.6
124.6
119.8
37.6
20.2
Cl
N
O

1l


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.24
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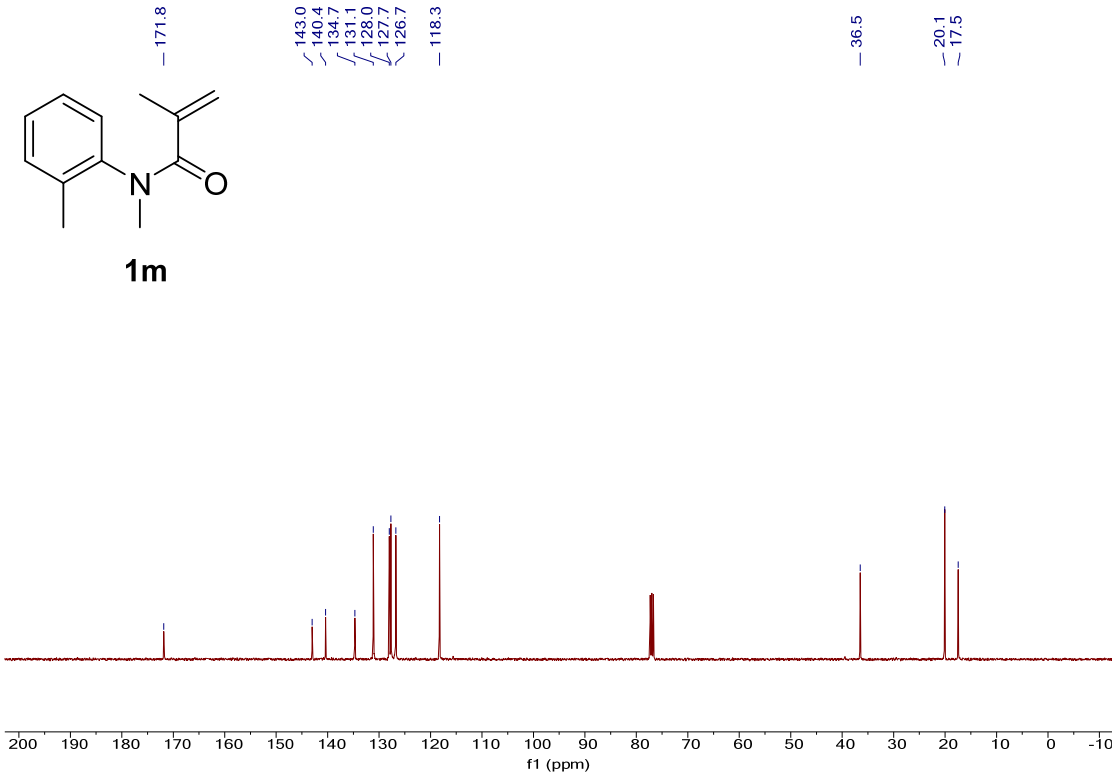
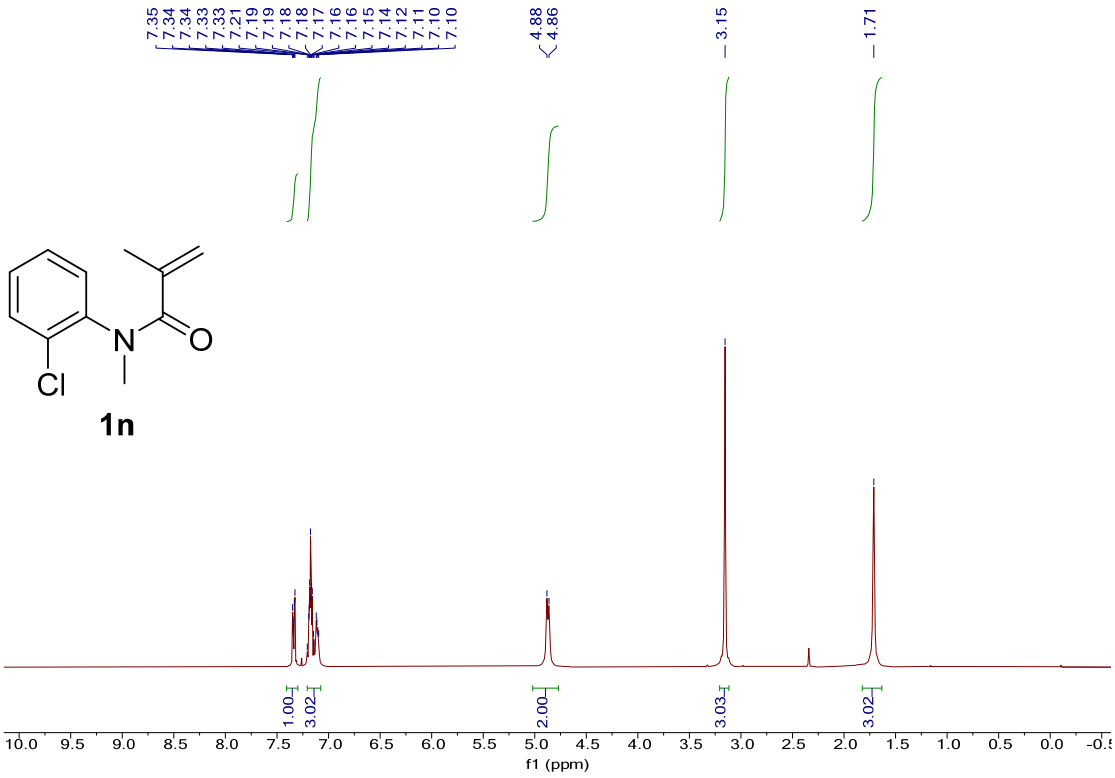
7.22
7.21
7.21
7.19
7.17
7.17
7.05
7.04
4.95
3.22
2.26
1.74
N
O
3.96
2.00
3.05
3.13
2.96
f1 (ppm)

1m


171.8
143.0
140.4
134.7
131.1
128.0
127.7
126.7
118.3
36.5
20.1
17.5
N
O
f1 (ppm)

1m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7.34
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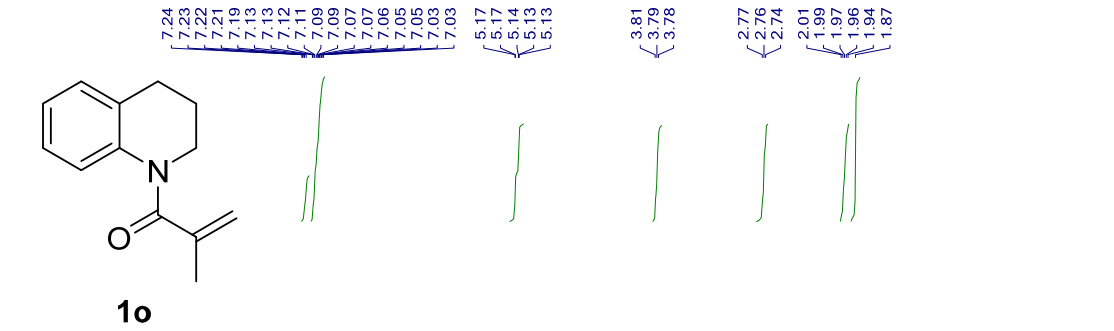
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.12
7.11
7.10
7.10
4.88
4.86
3.15
1.71
N
O
Cl
1n
1.00
3.02
2.00
3.03
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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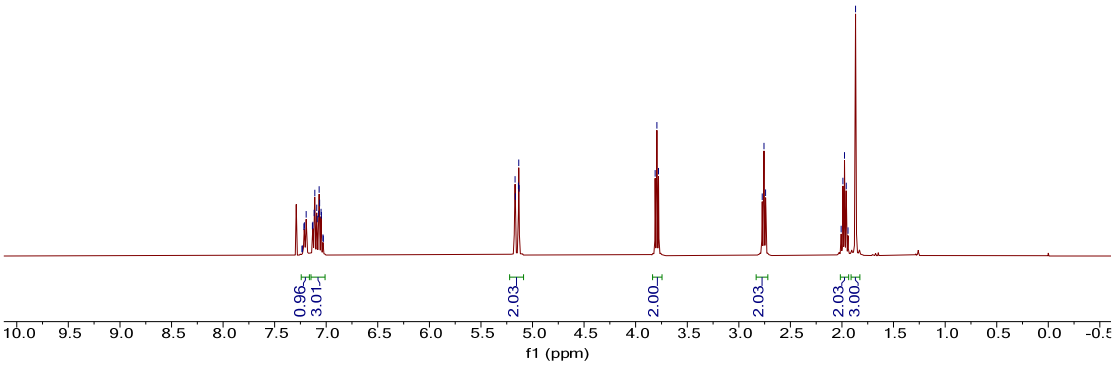
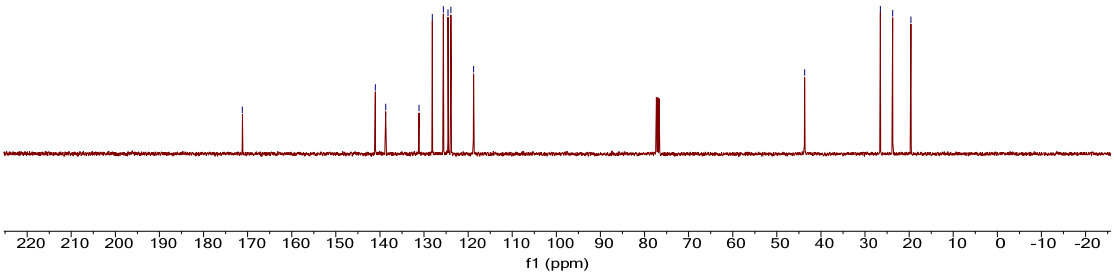
7.23
7.22
7.21
7.19
7.13
7.13
7.12
7.11
7.09
7.09
7.07
7.07
7.06
7.05
7.05
7.03
7.03
5.17
5.17
5.14
5.13
5.13
3.81
3.79
3.78
2.77
2.76
2.74
2.01
1.99
1.97
1.96
1.94
1.87
N
O

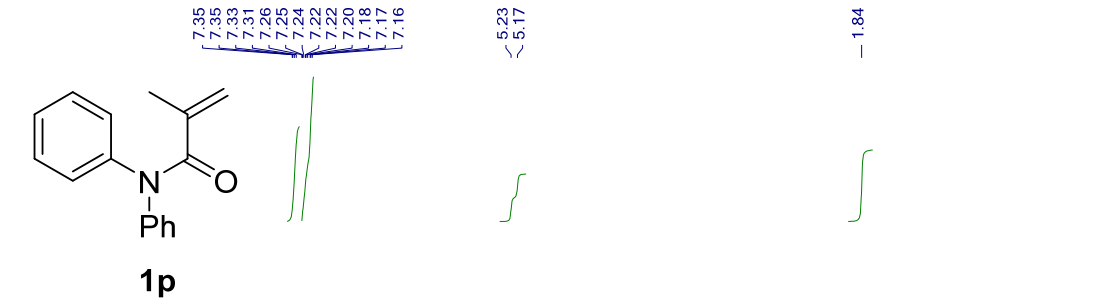
1o


0.96
3.01
2.03
2.00
2.03
2.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

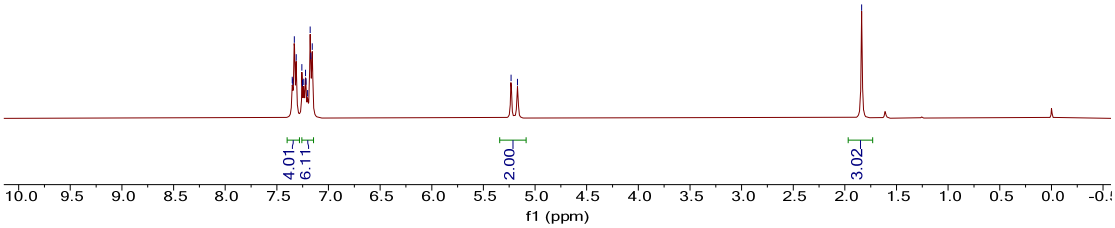

171.2
141.0
138.7
131.1
128.1
125.6
124.6
123.9
118.8
43.7
26.5
23.7
19.6
N
O

1o


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

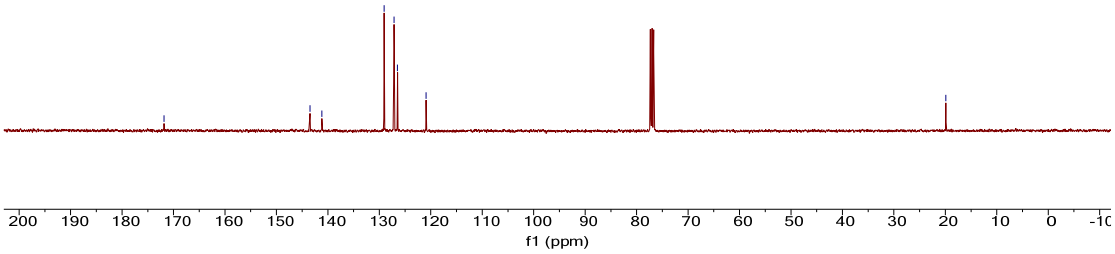

7.35
7.35
7.33
7.31
7.26
7.25
7.24
7.22
7.22
7.20
7.18
7.17
7.16
5.23
5.17
1.84
N
O
Ph

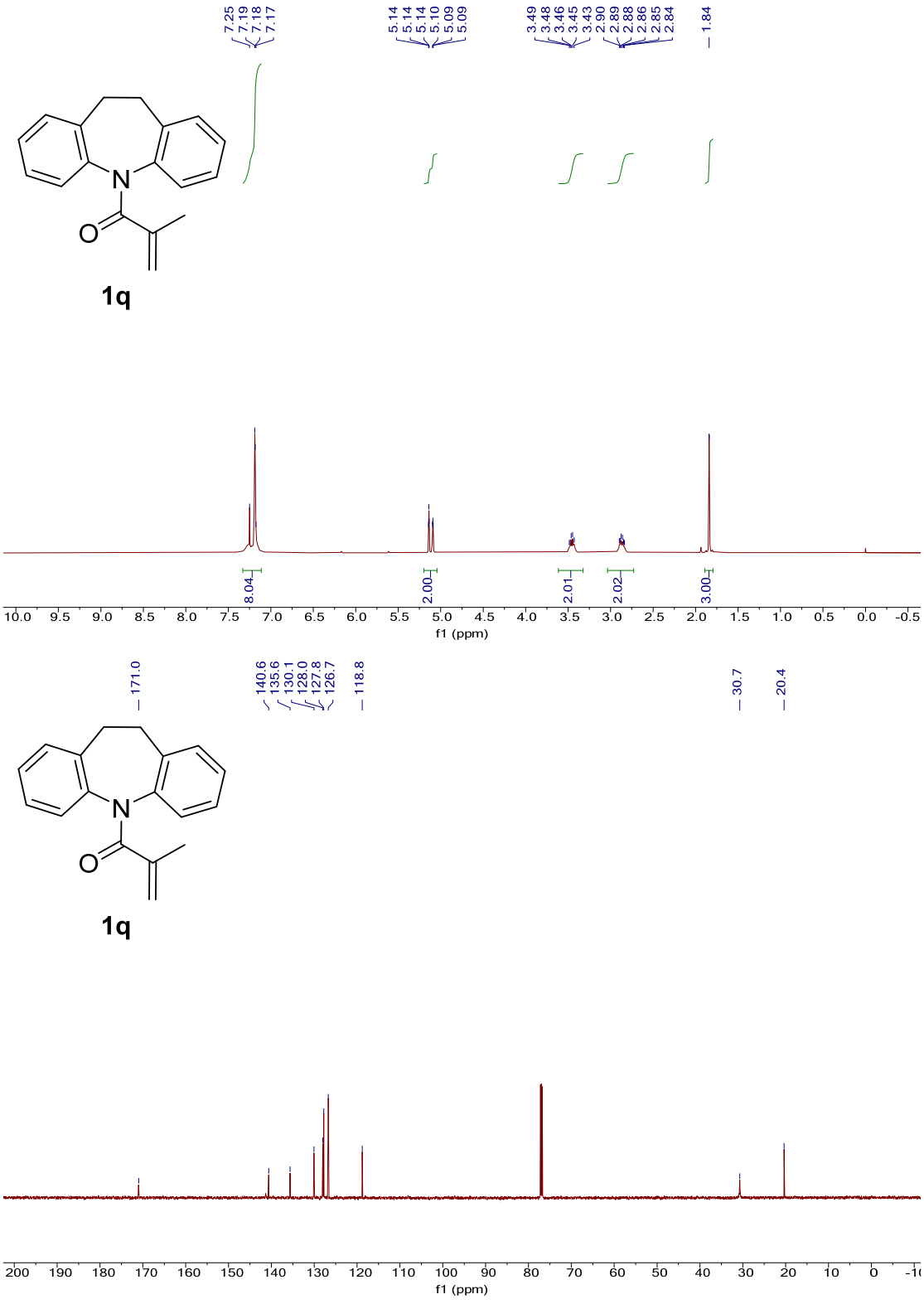
1p

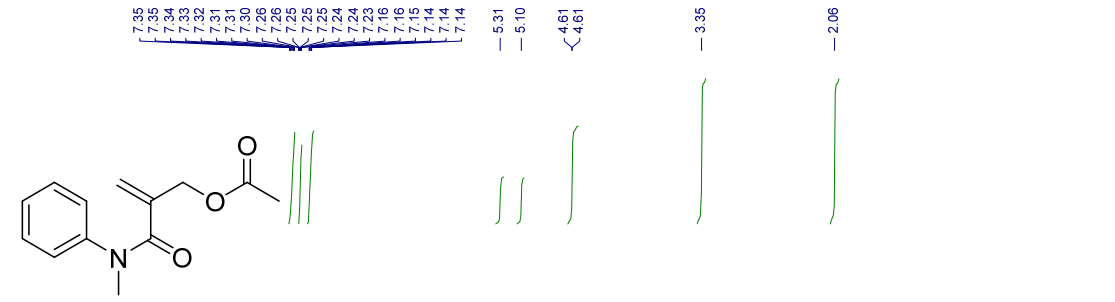

4.01
6.11
2.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.9
143.5
141.2
129.1
127.1
126.5
120.9
19.9
N
O
Ph

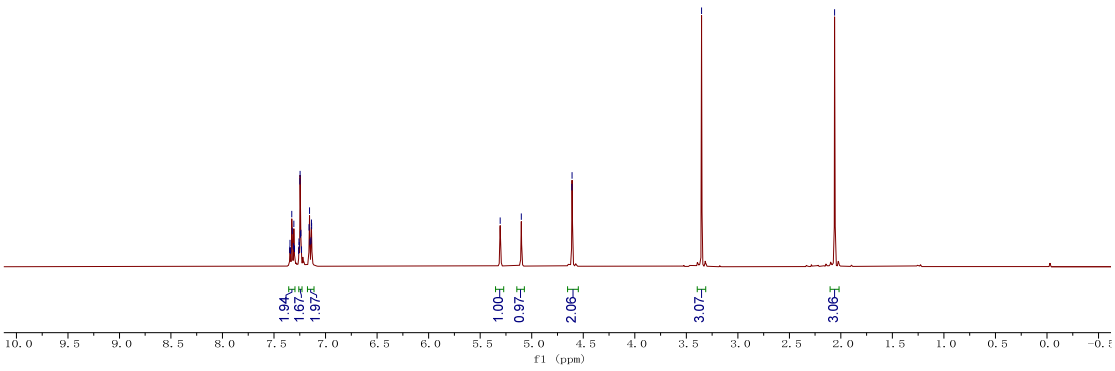
1p


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.25
7.19
7.18
7.17
5.14
5.14
5.14
5.10
5.09
5.09
3.49
3.48
3.46
3.45
3.43
2.90
2.89
2.88
2.86
2.85
2.84
1.84
N
O
1q
8.04
2.00
2.01
2.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
171.0
140.6
135.6
130.1
128.0
127.8
126.7
118.8
30.7
20.4
N
O
1q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.16
7.16
7.15
7.14
7.14
7.14
5.31
5.10
4.61
4.61
3.35
2.06
O
O
N
O

1r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3.07
3.06
f1 (ppm)


170.2
168.7
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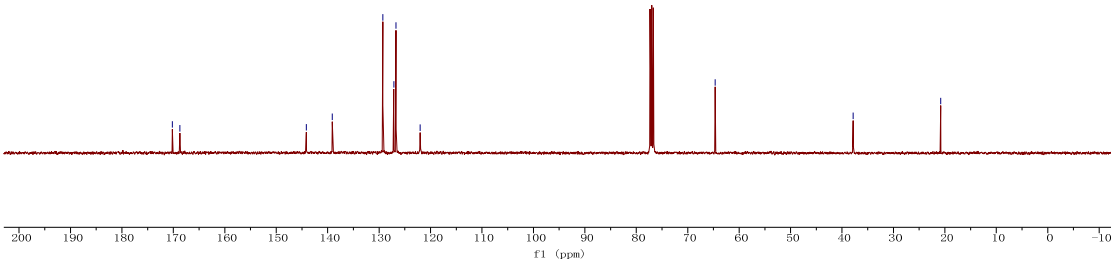
127.1
126.7
122.0
64.7
37.8
20.8
O
O
N
O

1r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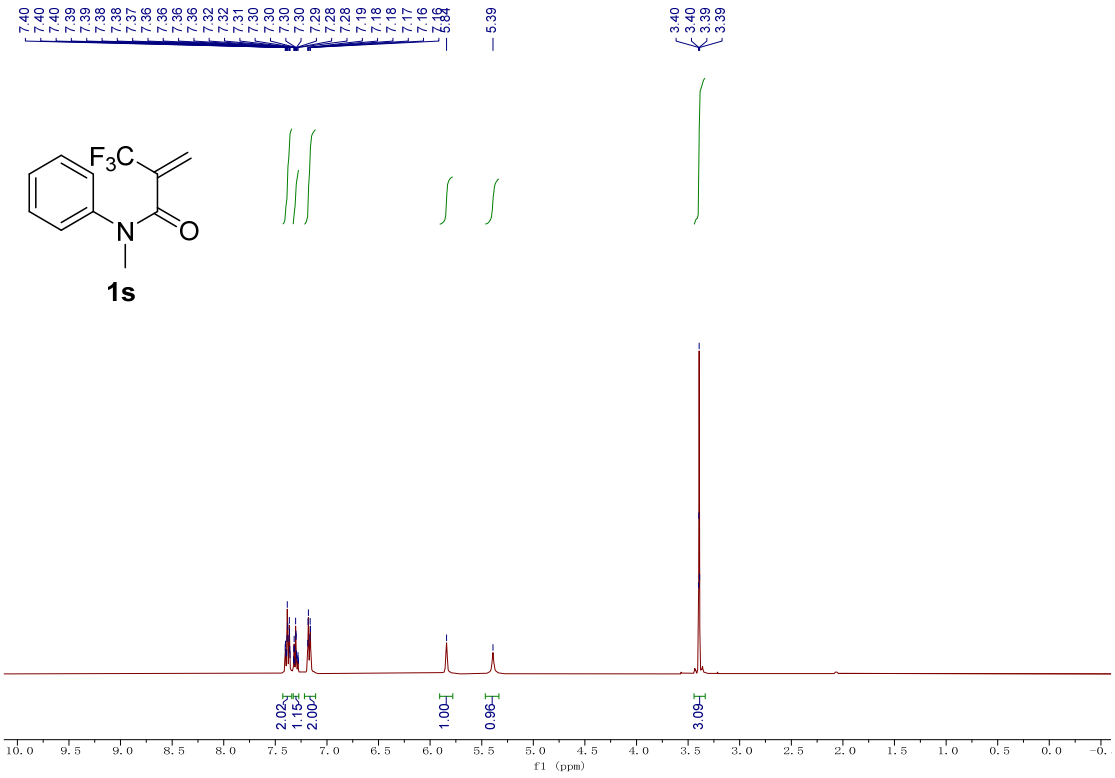
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7.31
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7.30
7.29
7.28
7.28
7.19
7.18
7.18
7.17
7.16
5.40
5.39
3.40
3.40
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3.39
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N
O
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1.00
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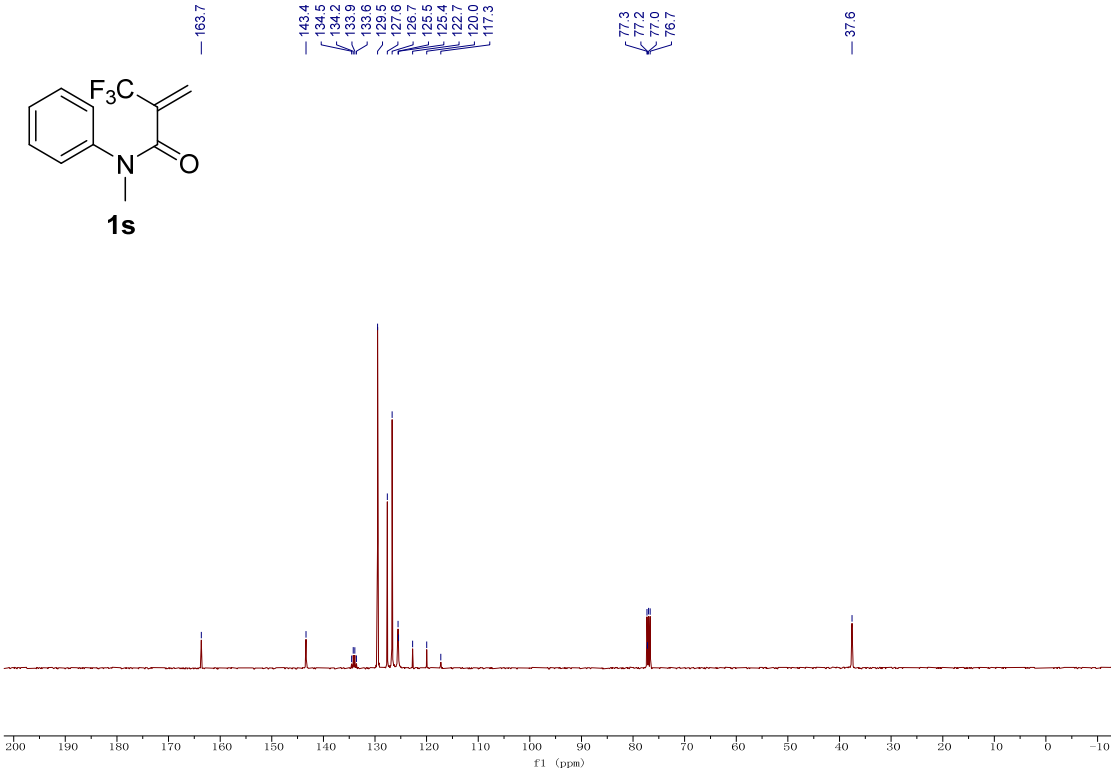
3.09
f1 (ppm)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129.5
127.6
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125.4
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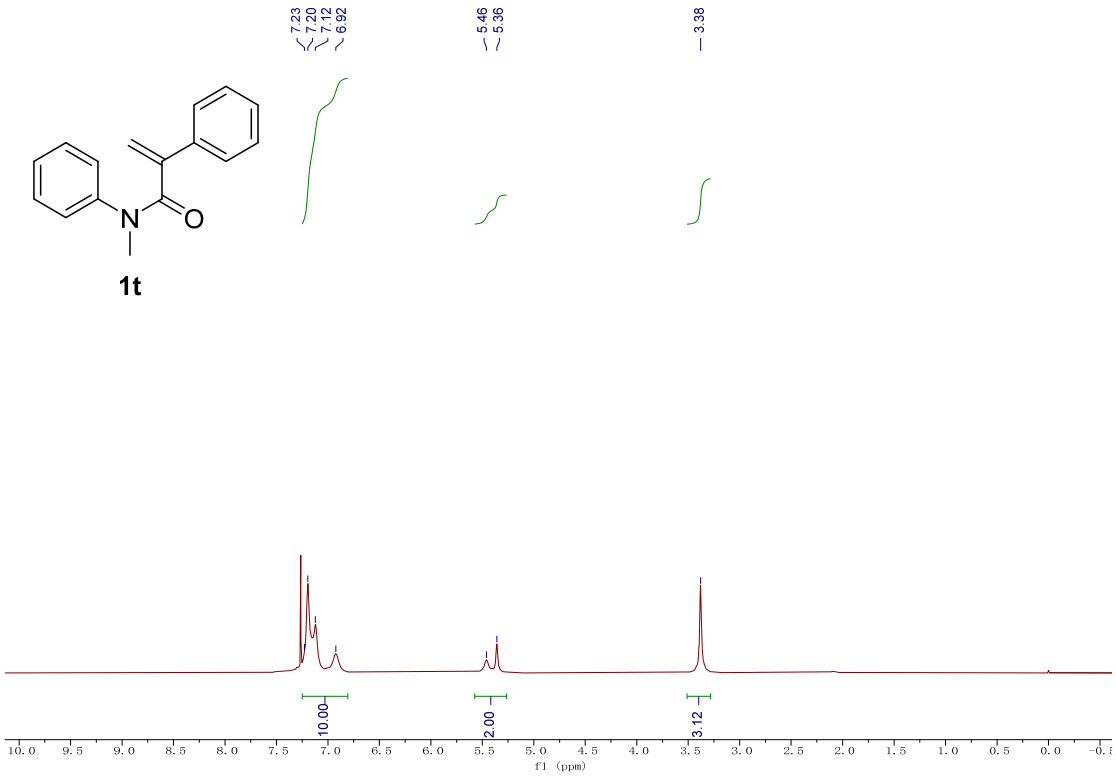
77.3
77.2
77.0
76.7
37.6
F3C
N
O
1s
f1 (ppm)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5.36
3.38
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O
1t
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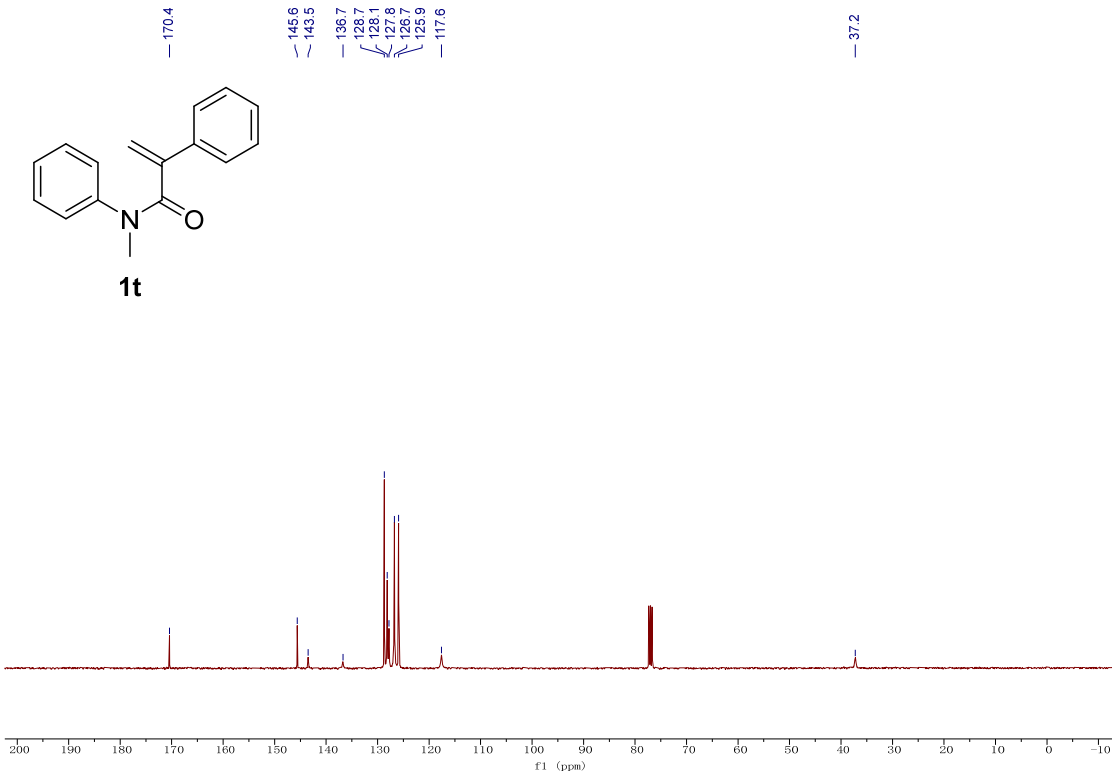
3.12
f1 (ppm)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145.6
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126.7
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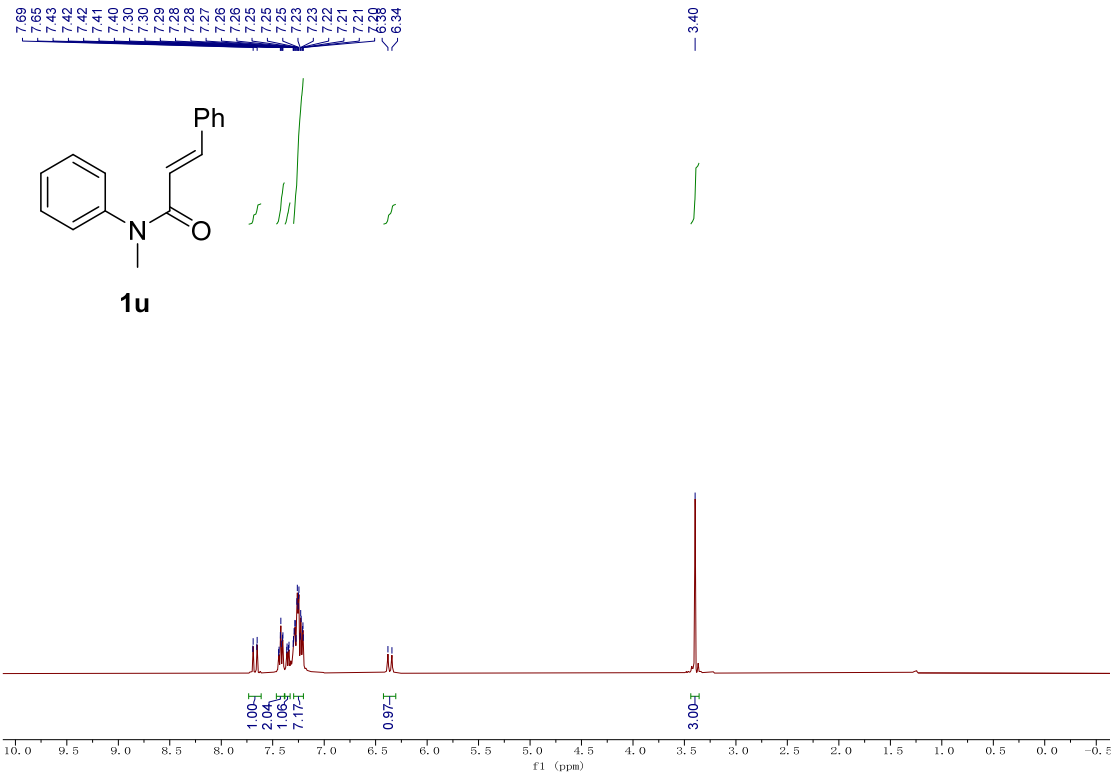
37.2
N
O
1t
f1 (ppm)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7.25
7.23
7.23
7.22
7.21
7.21
7.20
6.38
6.34
3.40
Ph
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O
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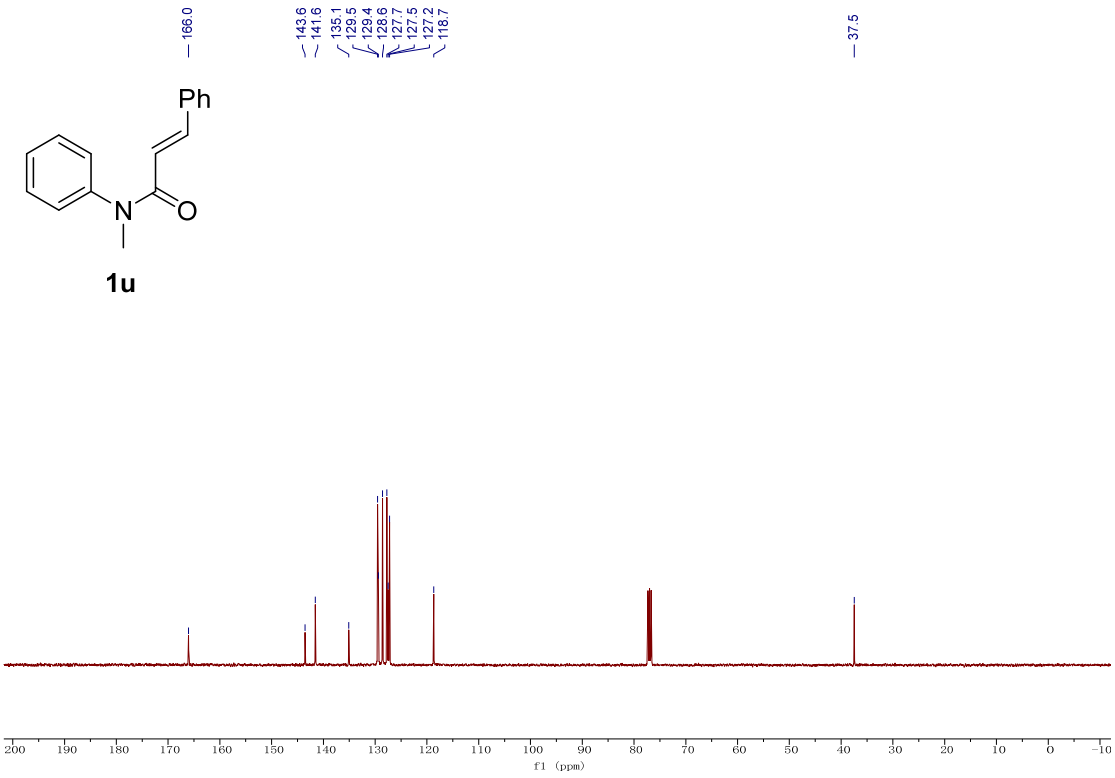
2.04
1.06
7.17
0.97
3.00
f1 (ppm)

1u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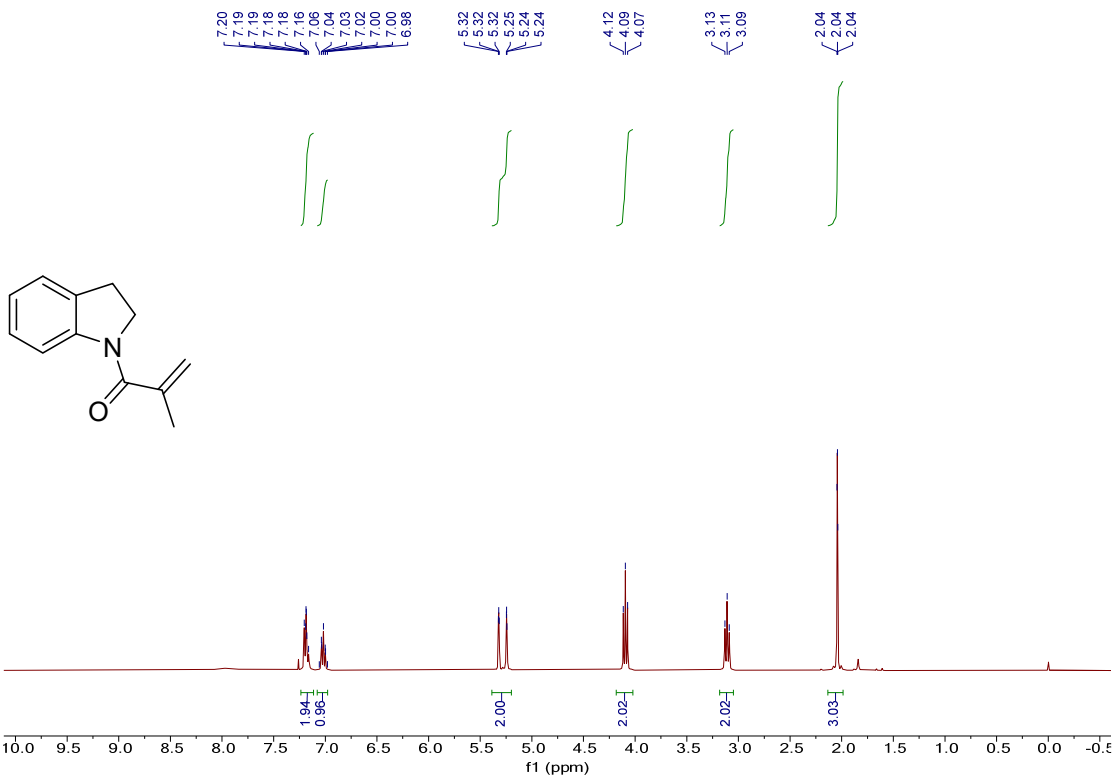
Ph
N
O
f1 (ppm)

1u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7.02
7.00
7.00
6.98
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5.32
5.32
5.25
5.24
5.24
4.12
4.09
4.07
3.13
3.11
3.09
2.04
2.04
2.04
N
O
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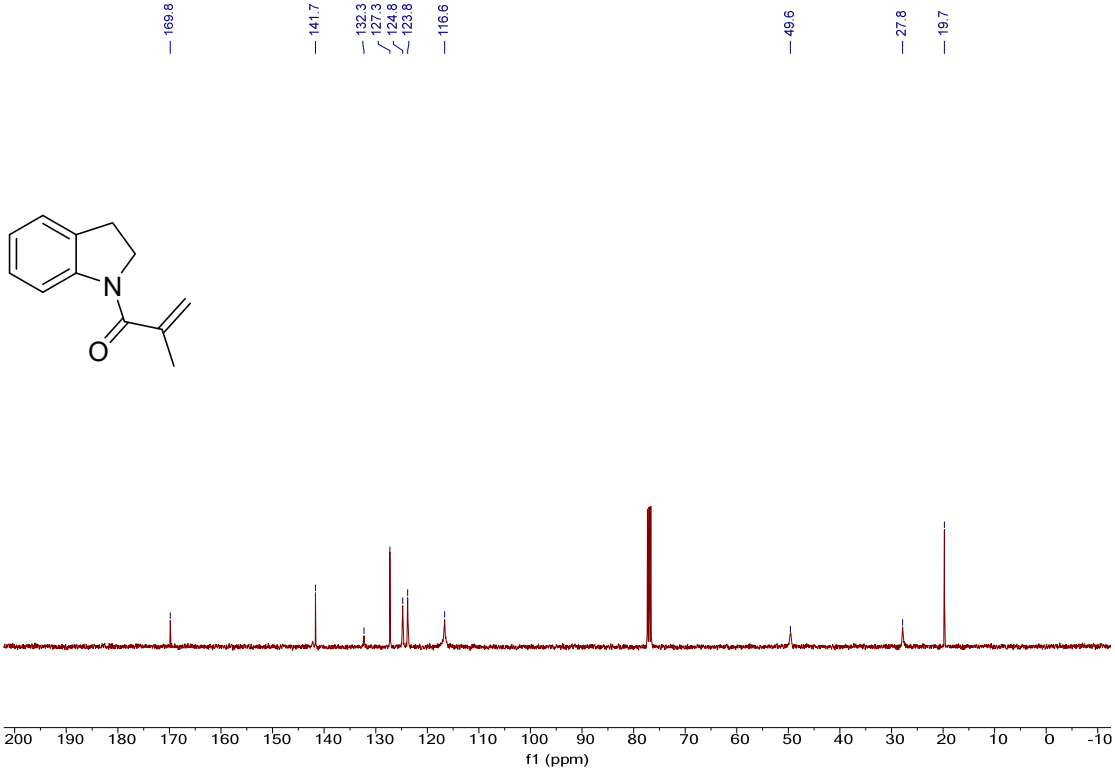
0.96
2.00
2.02
2.02
3.03
f1 (ppm)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123.8
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49.6
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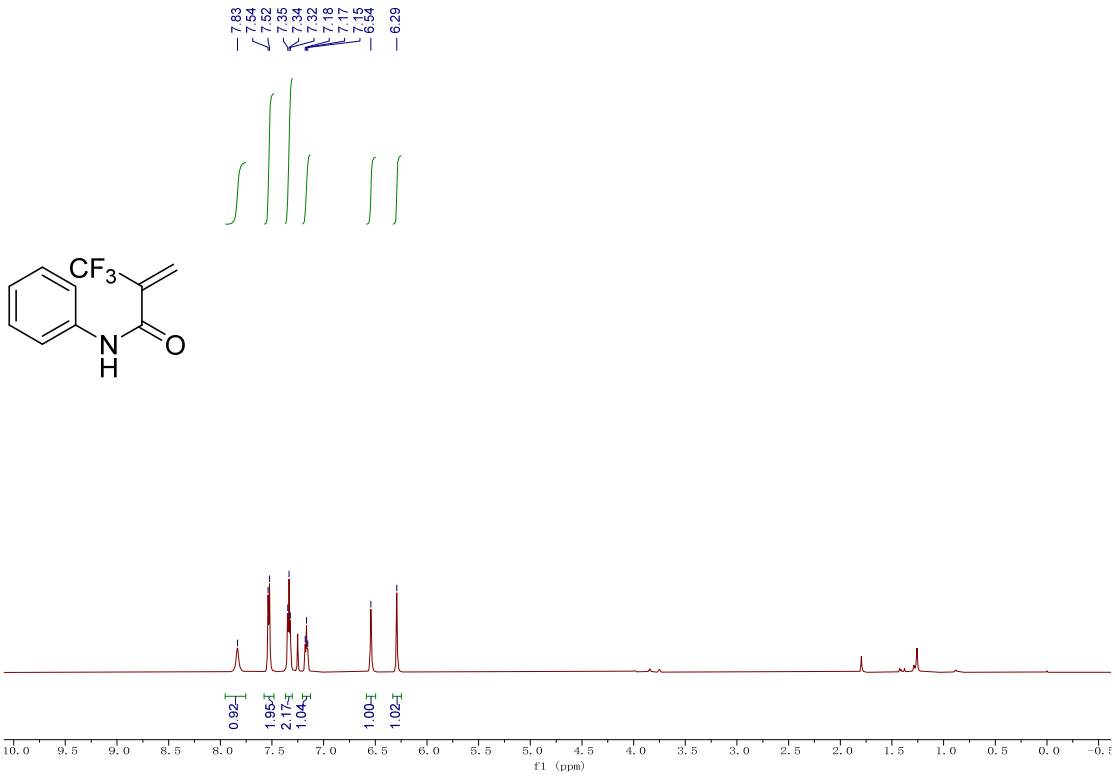
19.7
N
O
f1 (ppm)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7.18
7.17
7.15
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CF3
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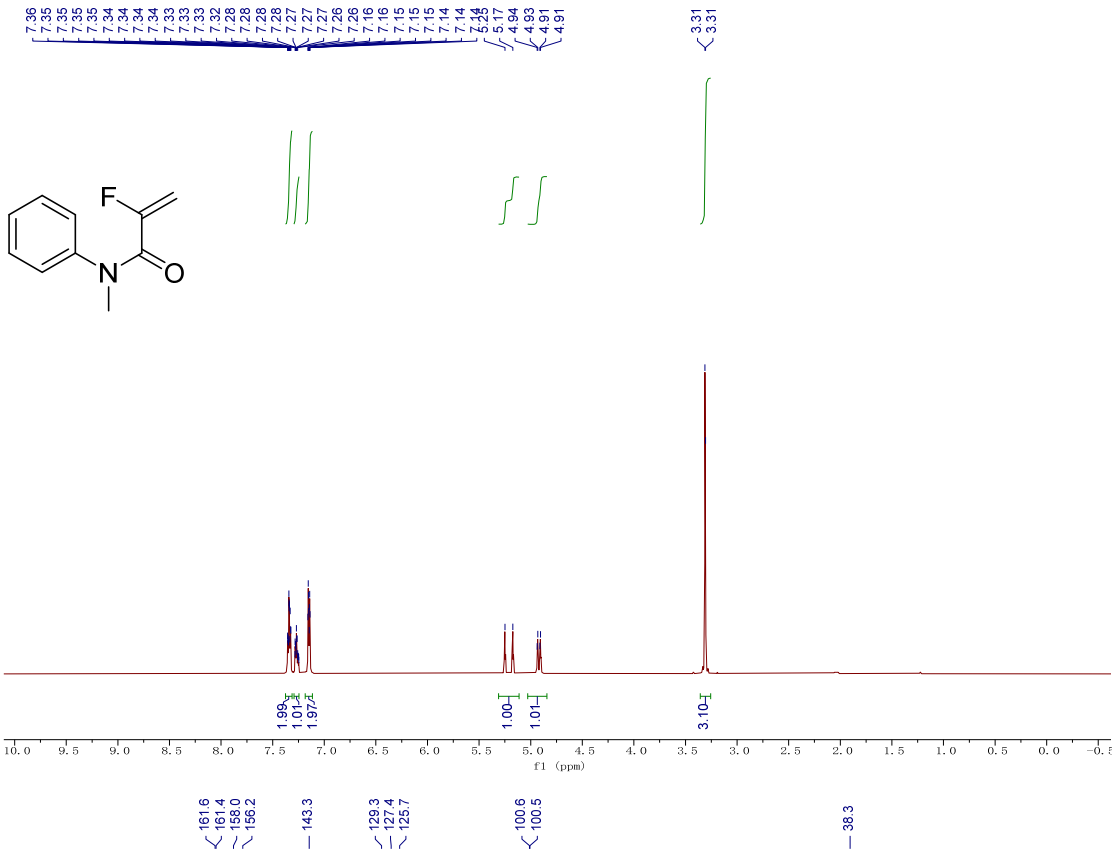
H
O
0.92
1.95
2.17
1.04
1.00
1.02
f1 (ppm)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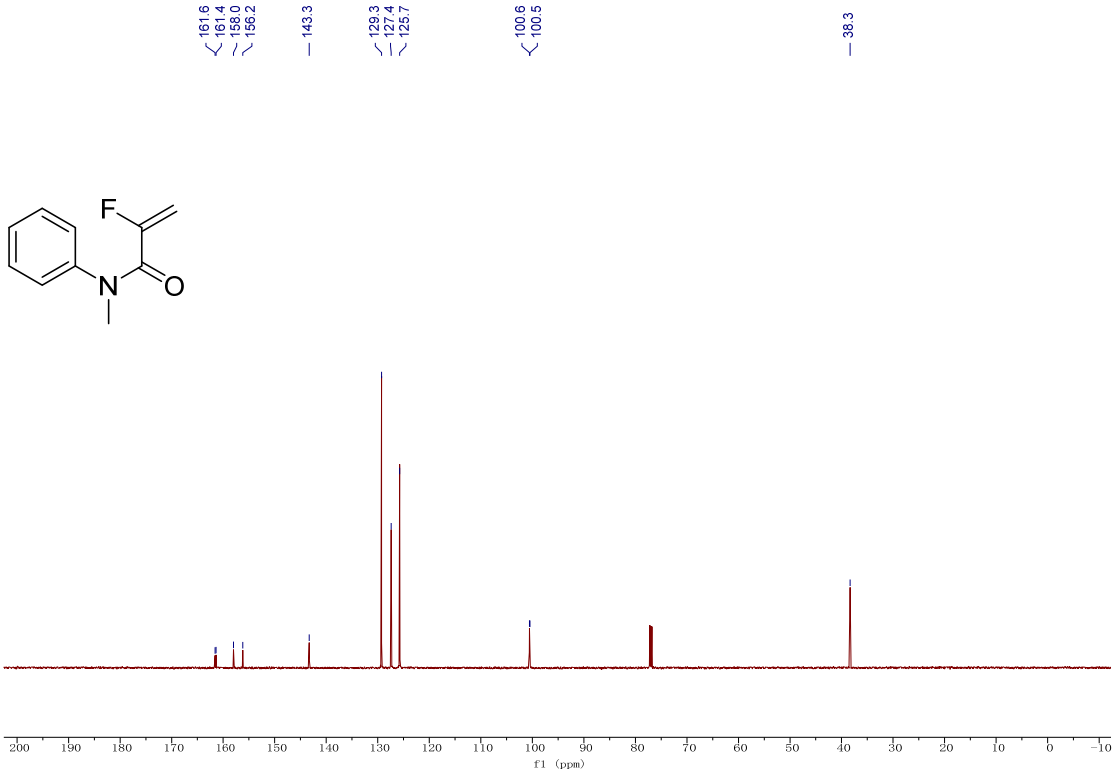
7.15
7.15
7.14
7.14
5.25
5.17
4.94
4.93
4.91
4.91
3.31
3.31
F
N
O
1.99
1.01
1.97
1.00
1.01
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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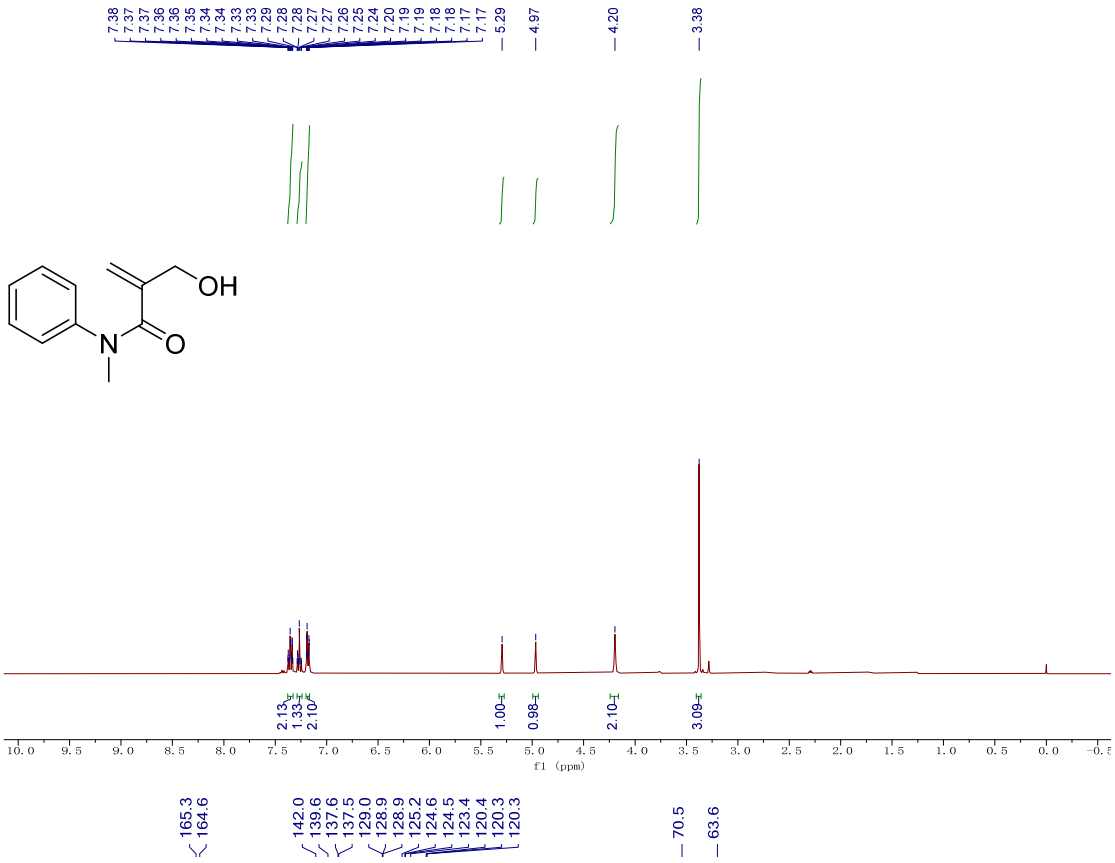
161.4
158.0
156.2
143.3
129.3
127.4
125.7
100.6
100.5
38.3
F
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.24
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7.19
7.19
7.18
7.18
7.17
7.17
5.29
4.97
4.20
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OH
N
O
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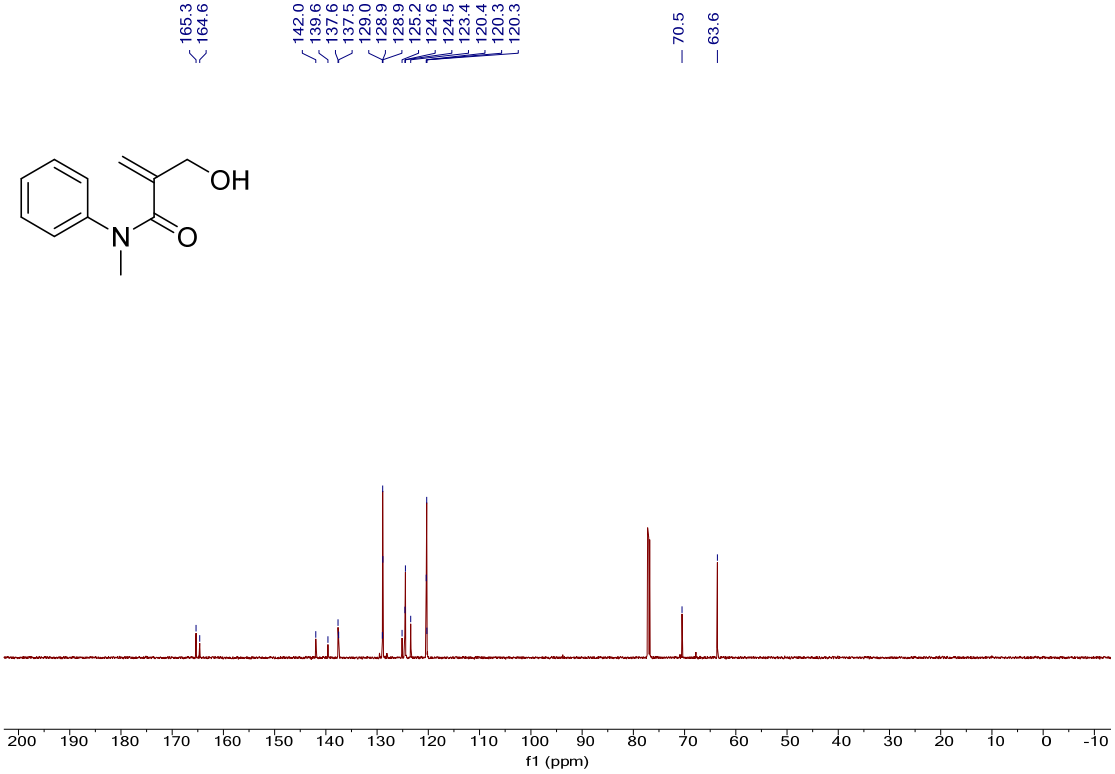
1.33
2.10
1.00
0.98
2.10
3.09
f1 (ppm)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123.4
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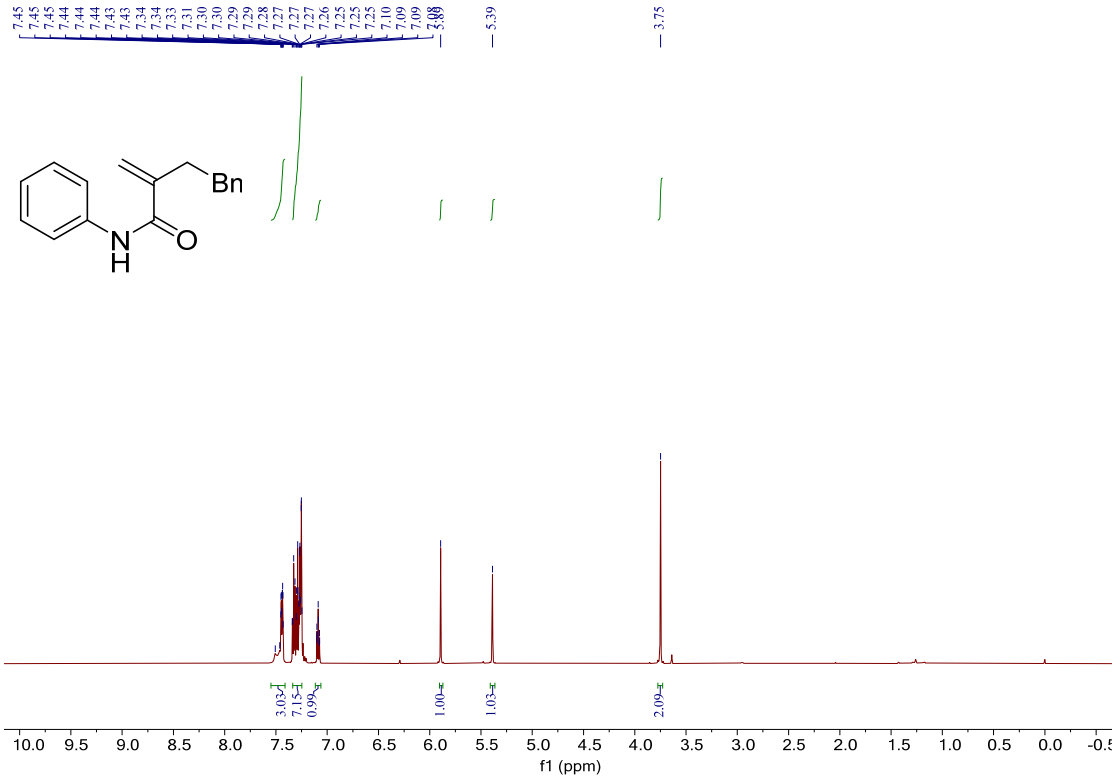
120.3
120.3
70.5
63.6
OH
N
O
f1 (ppm)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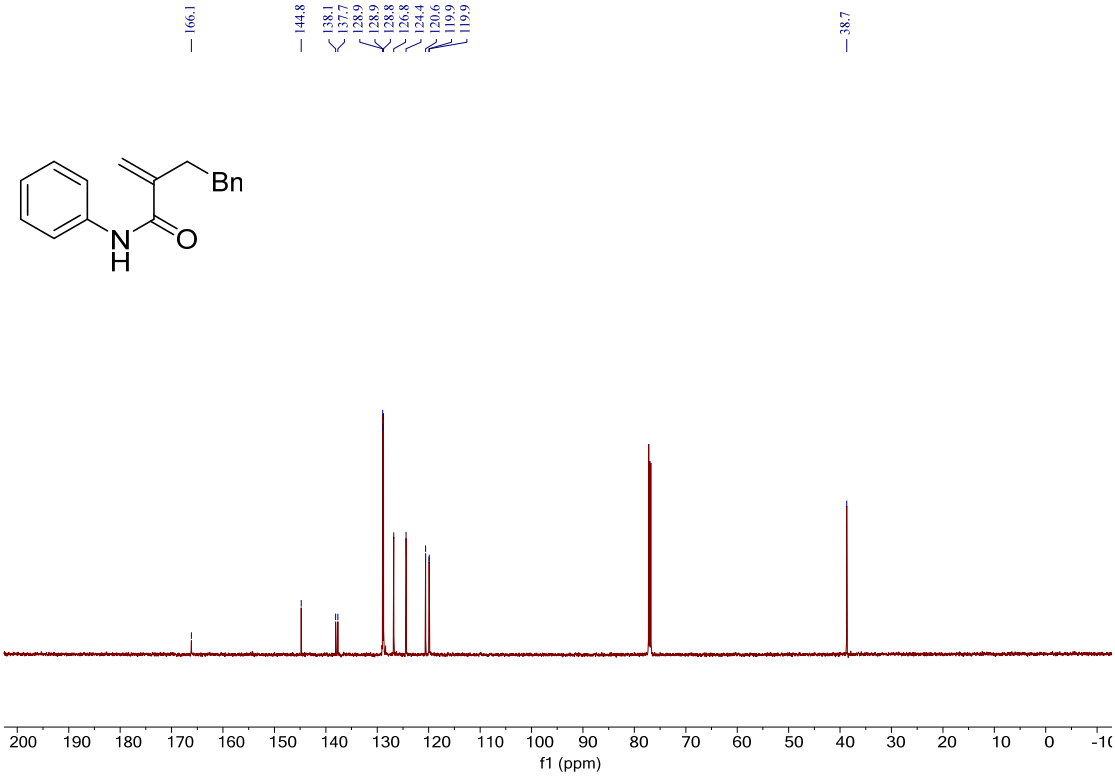
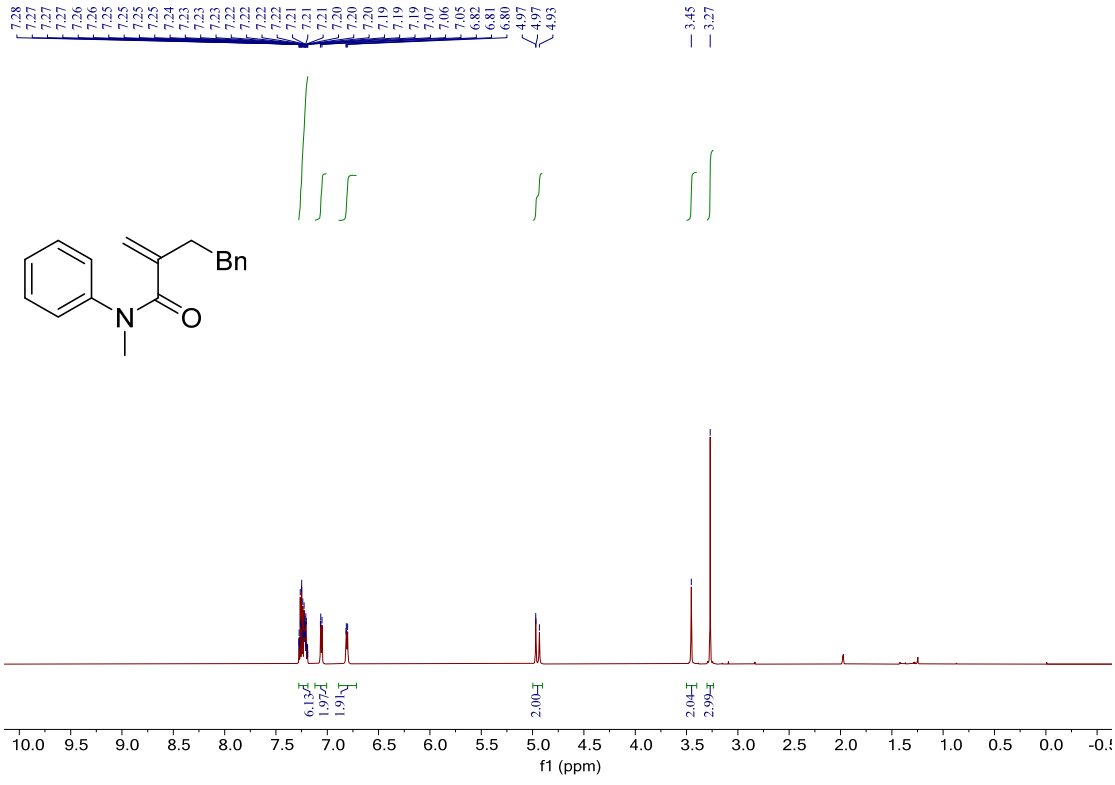

Bn
N
H
O
f1 (ppm)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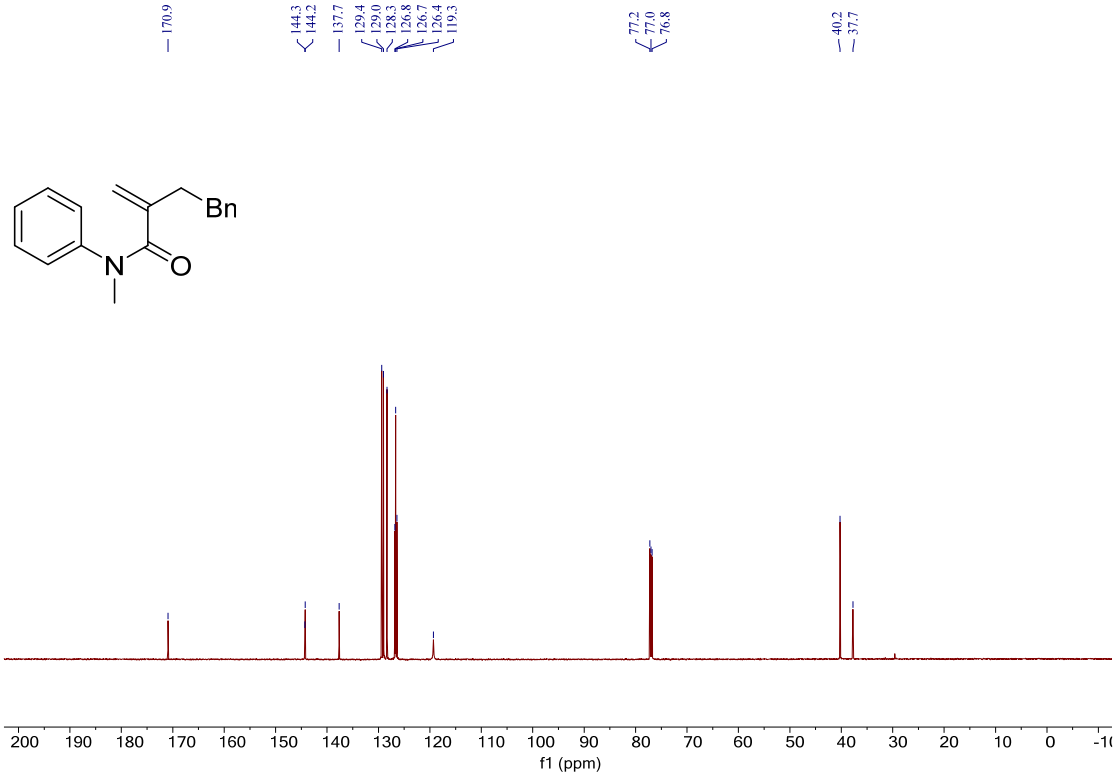
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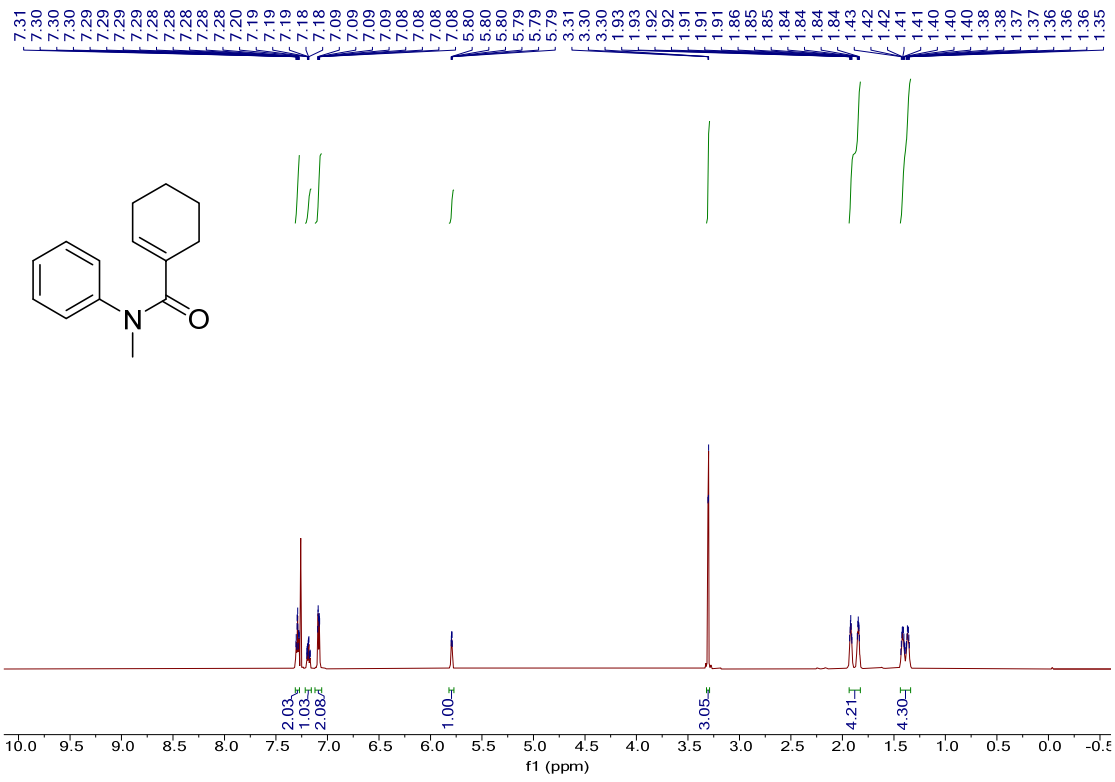
7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.28 7.28 7.20 7.19 7.19 7.19 7.18 7.18 7.09 7.09 7.09 7.09 7.08 7.08 7.08 7.08 5.80 5.80 5.80 5.79 5.79 5.79
3.31 3.30 3.30 1.93 1.93 1.92 1.92 1.91 1.91 1.91 1.86 1.85 1.85 1.84 1.84 1.84 1.84 1.43 1.42 1.41 1.41 1.40 1.40 1.40 1.38 1.37 1.37 1.36 1.36 1.36 1.35
N
O
2.03
1.03
2.08
1.00
3.05
4.21
4.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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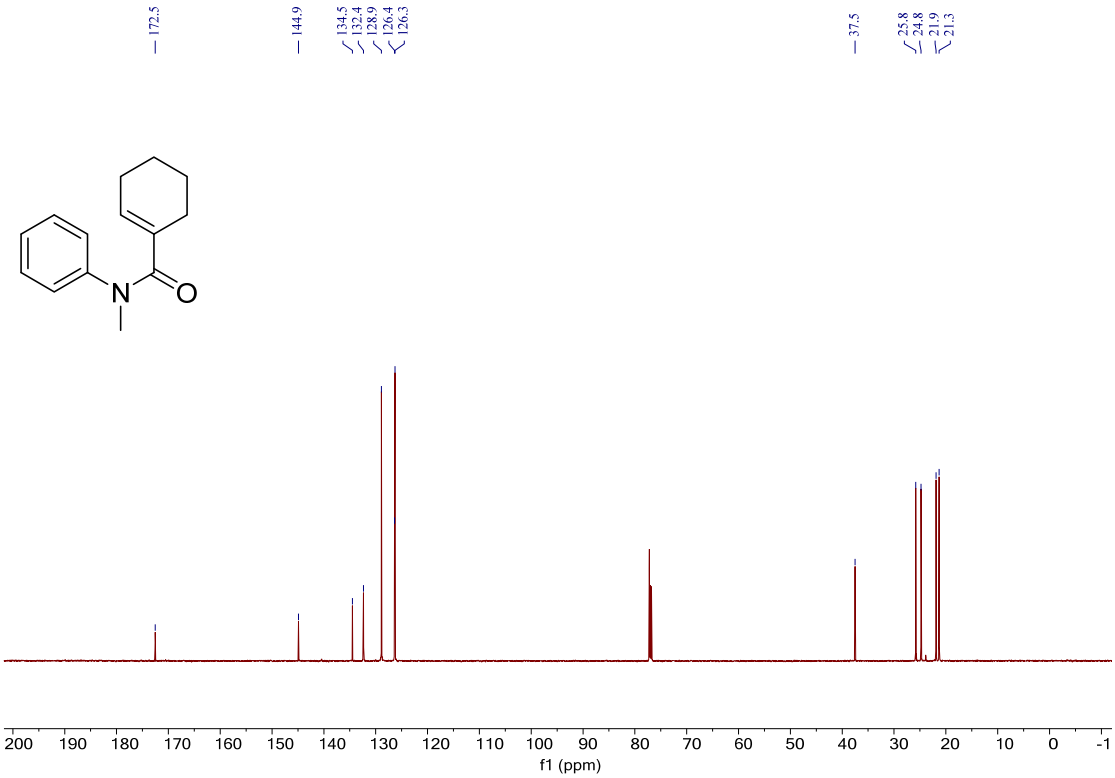
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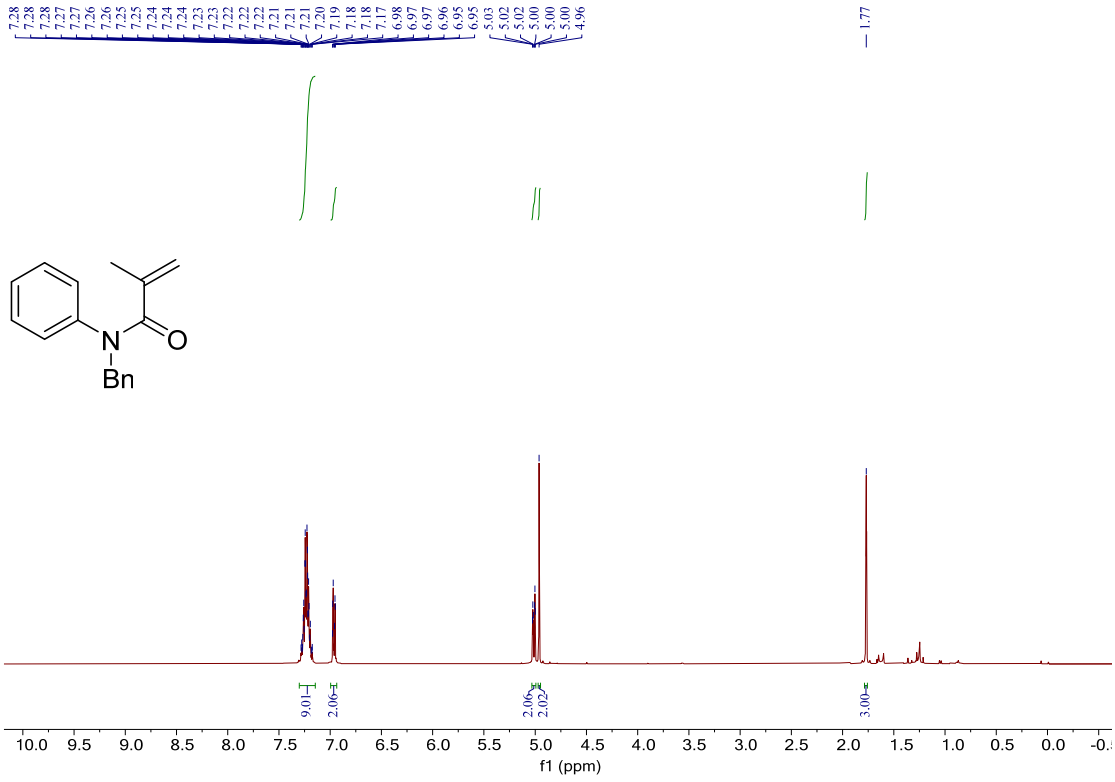
f1 (ppm)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5.02
5.00
5.00
5.00
4.96
1.77
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2.06
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2.02
3.00
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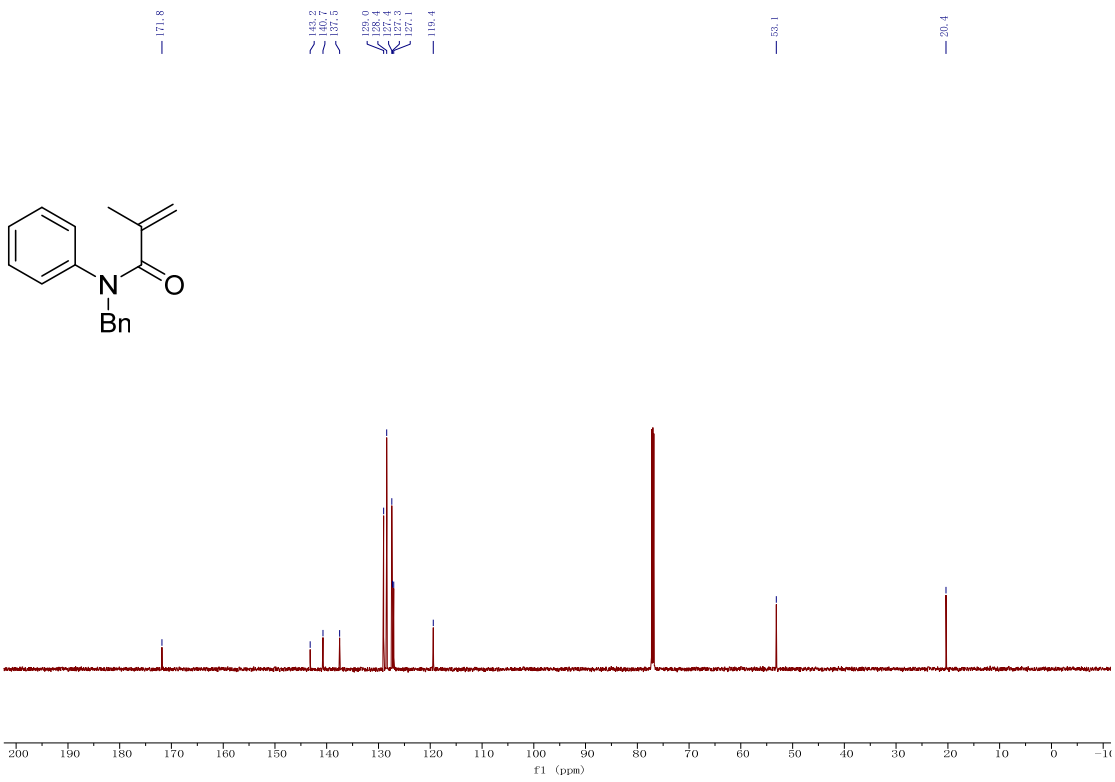
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Bn
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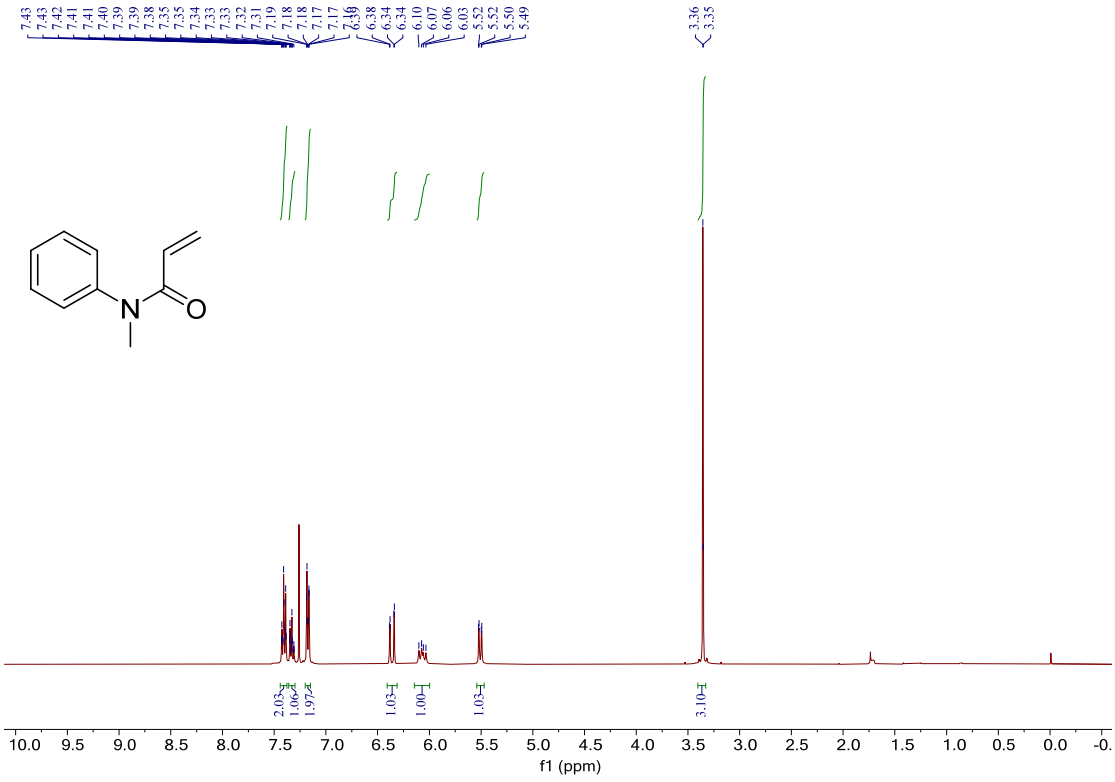
f1 (ppm)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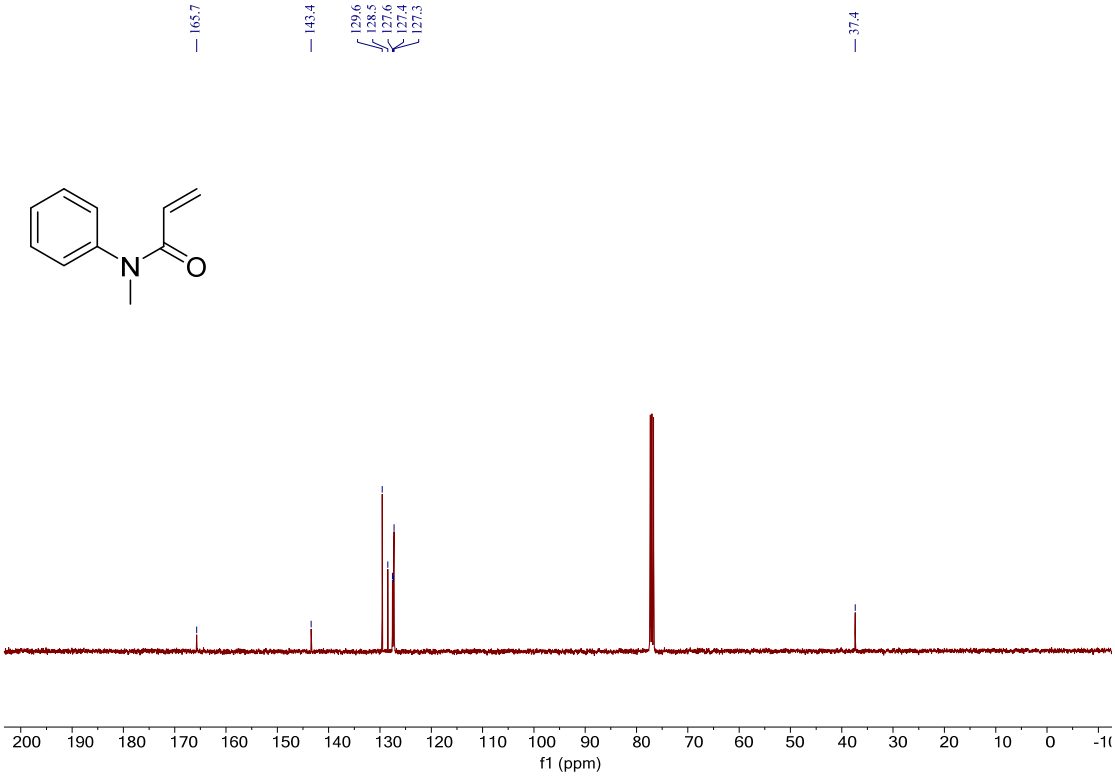
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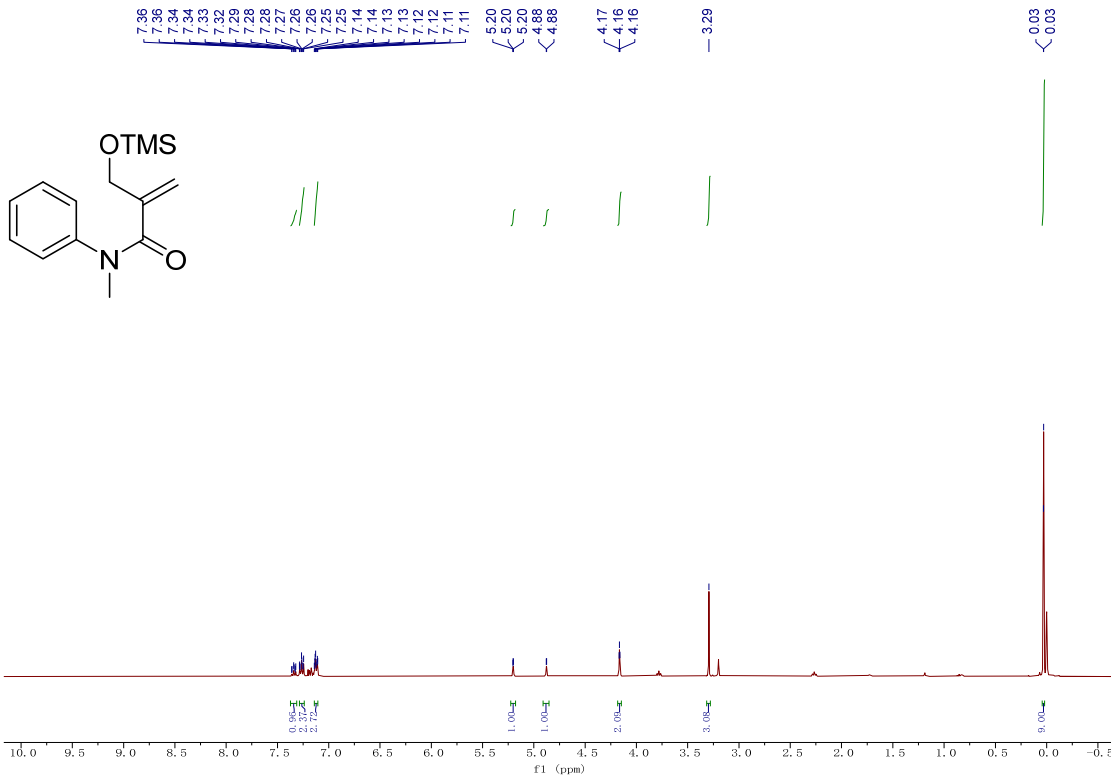
f1 (ppm)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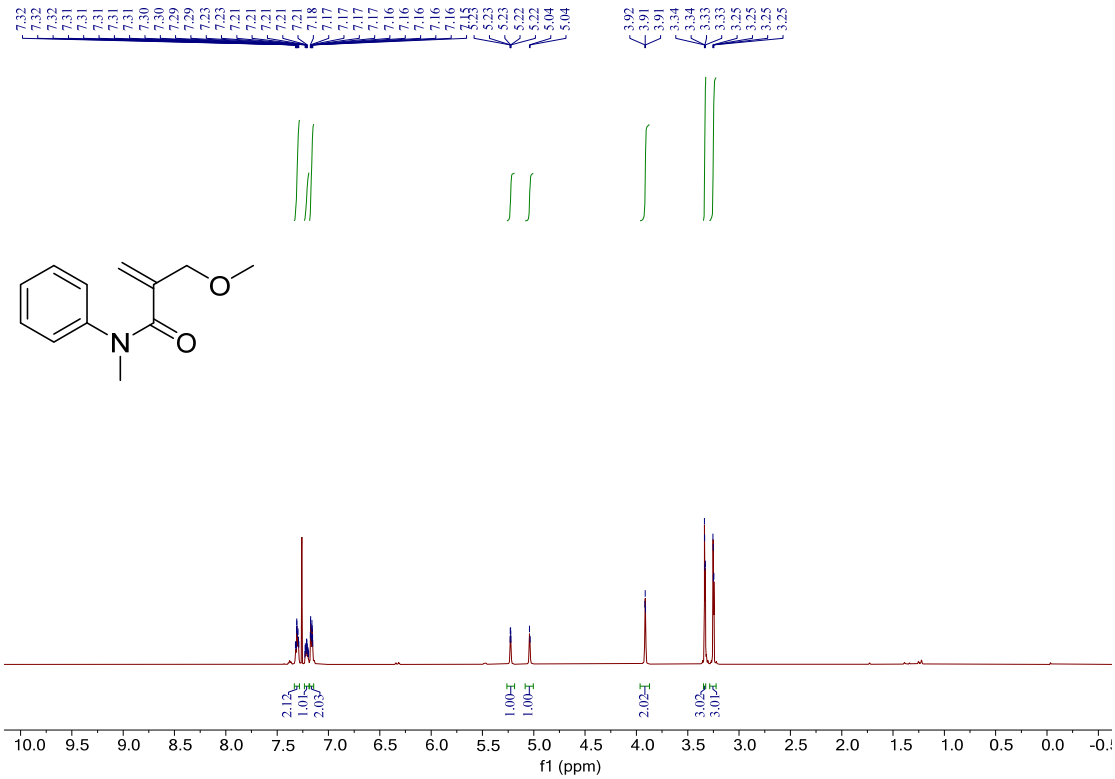
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5.04
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1.00
2.02
3.02
3.01
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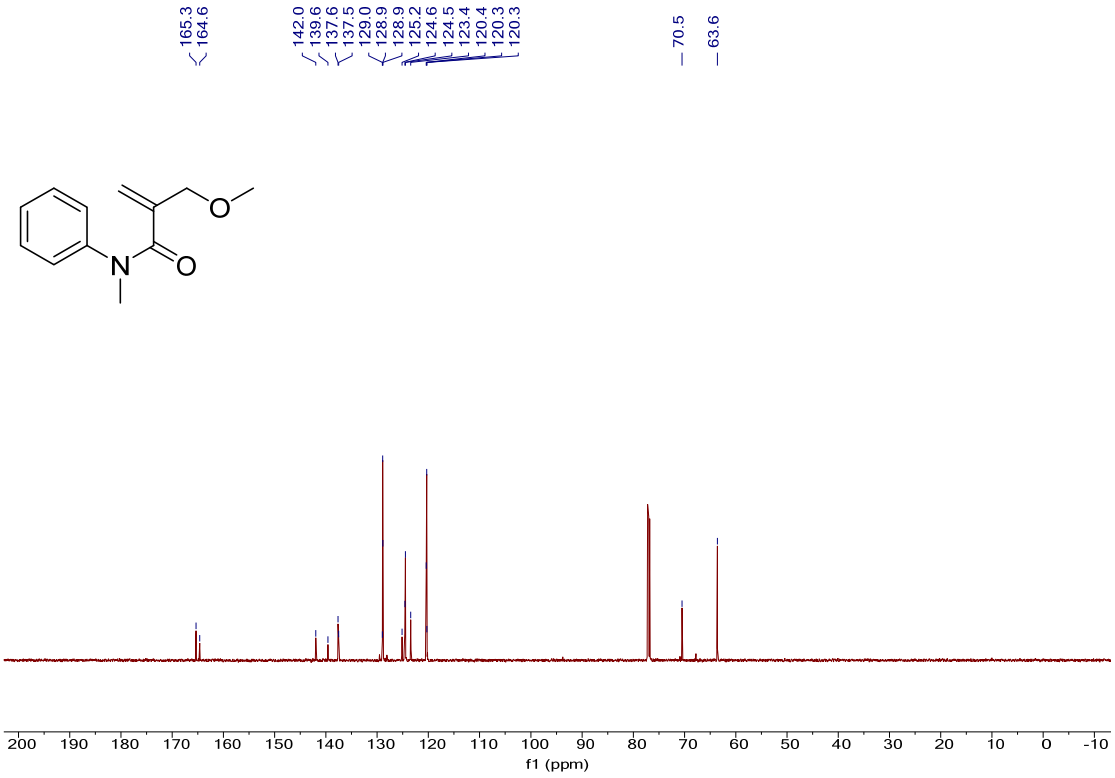
f1 (ppm)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128.9
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124.6
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123.4
120.4
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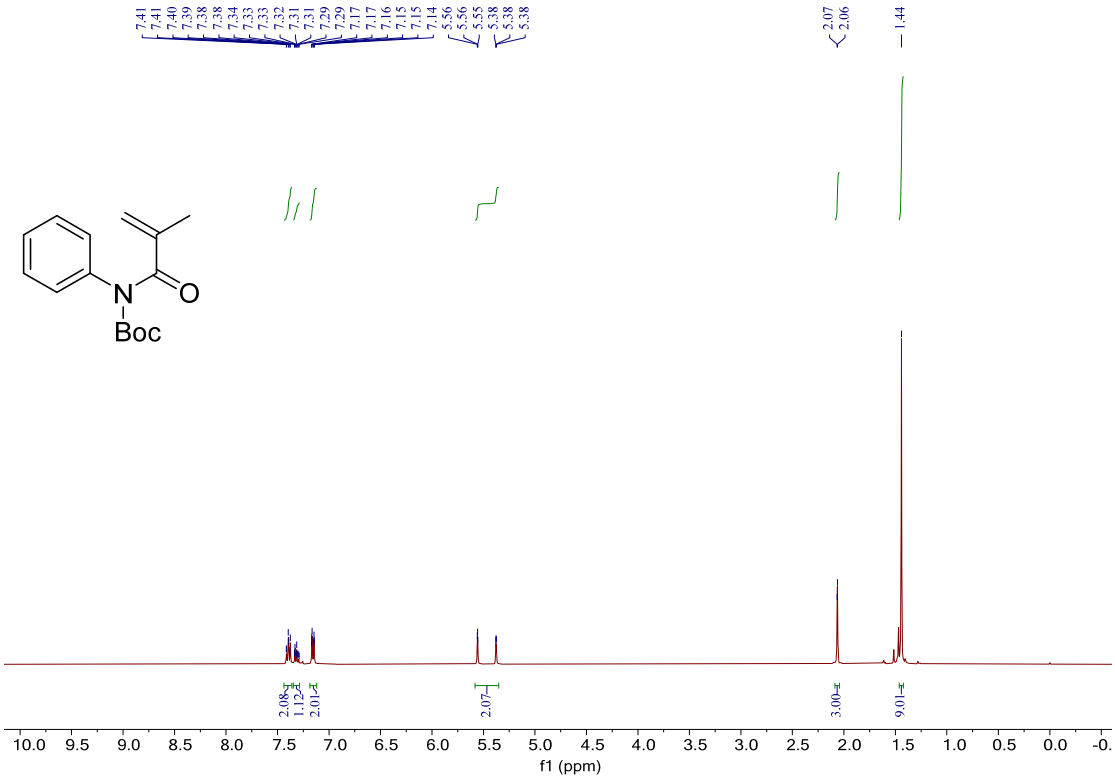
f1 (ppm)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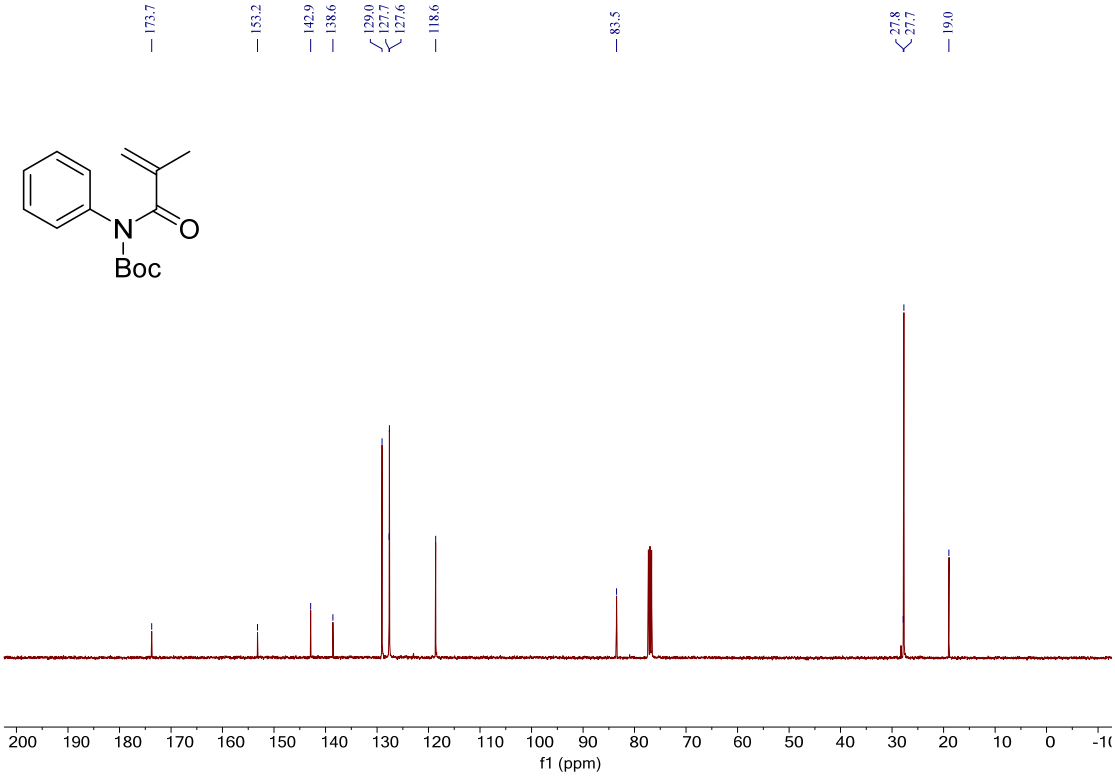
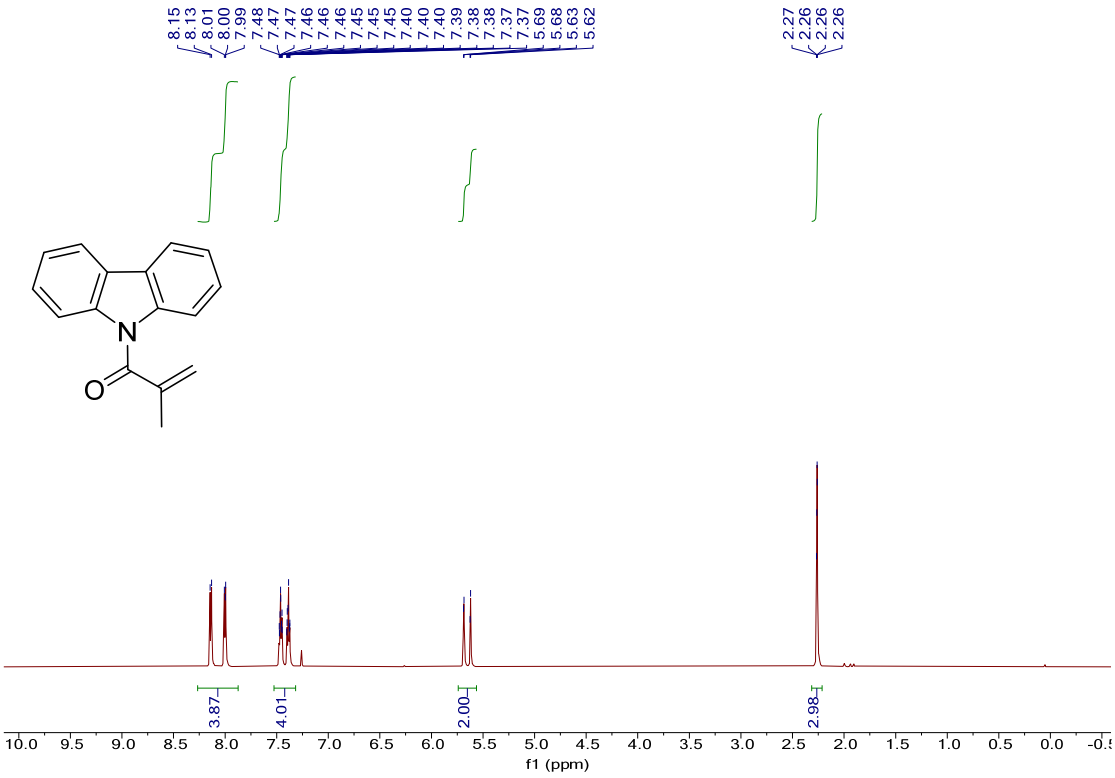
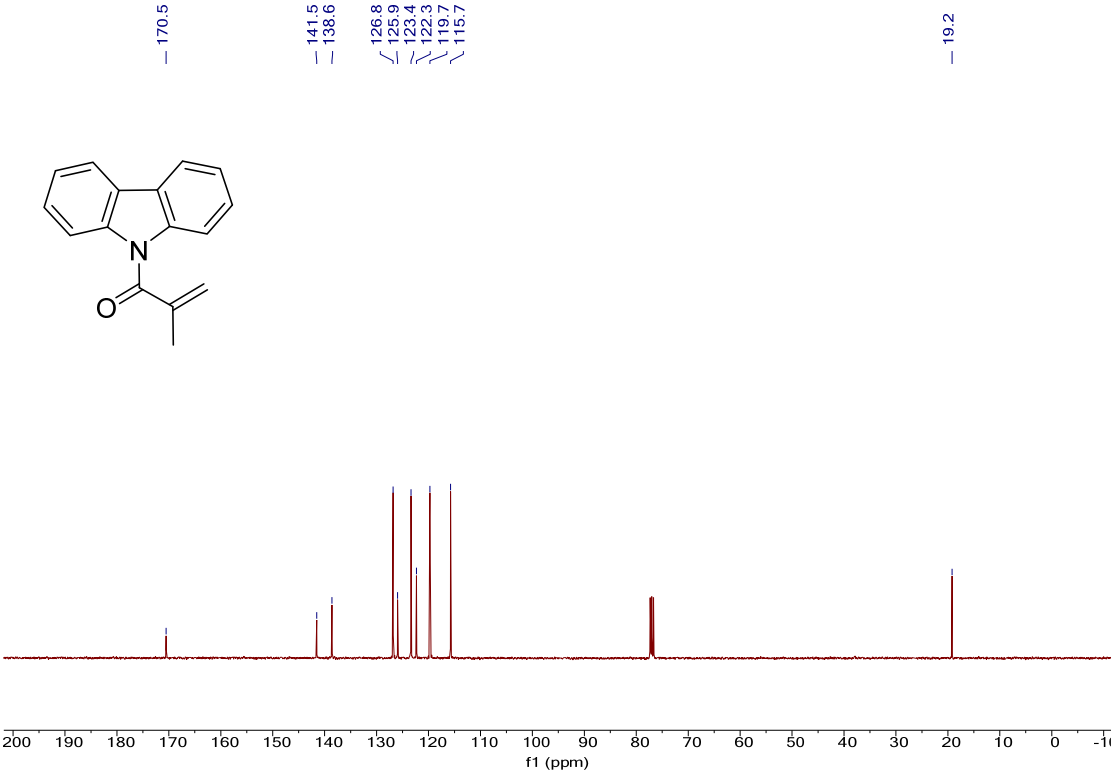
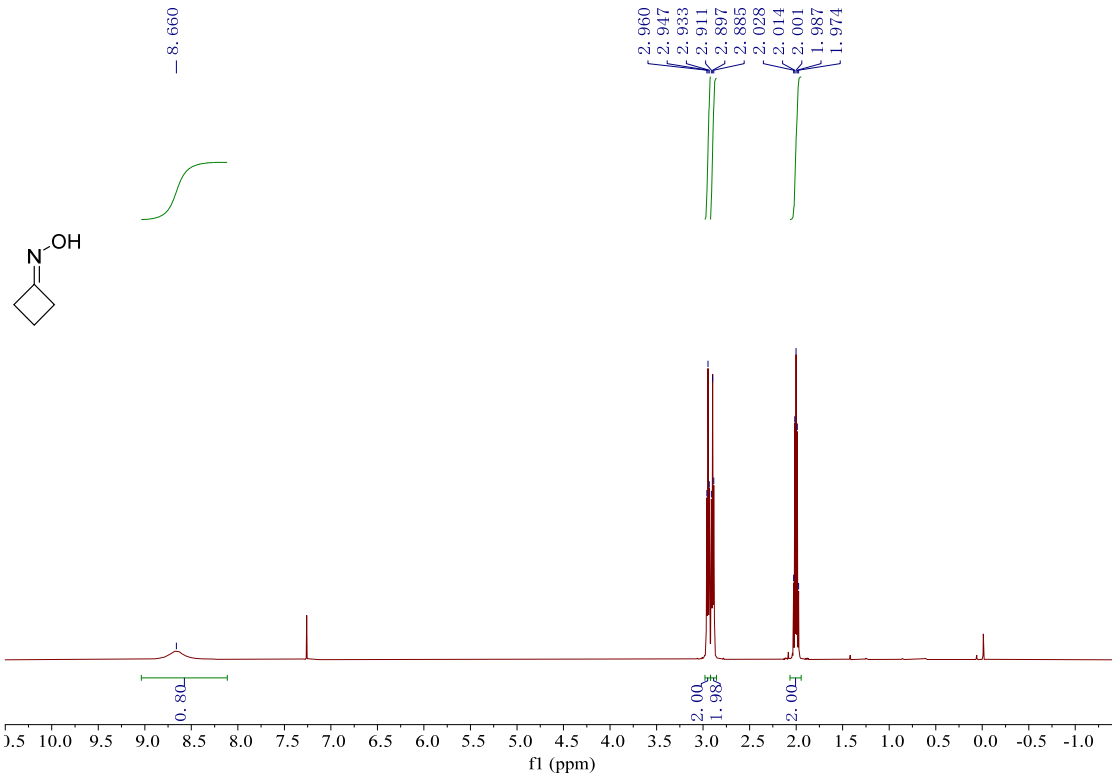
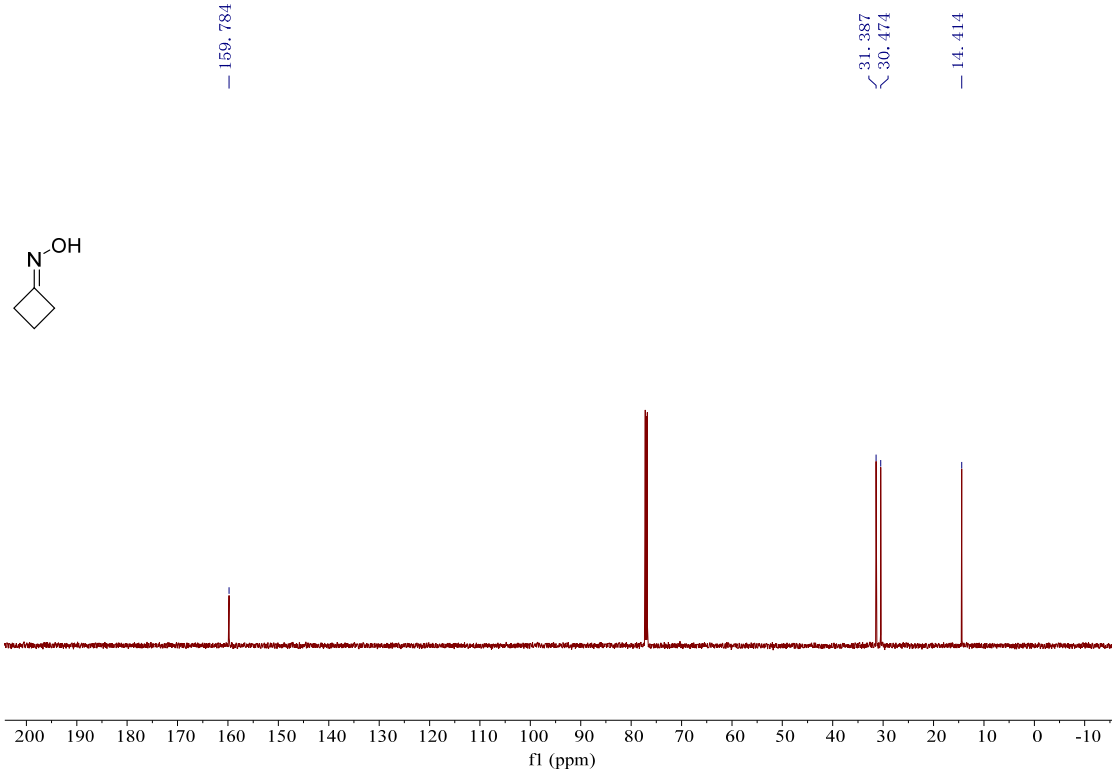
7.15
7.14
5.56
5.56
5.55
5.38
5.38
5.38
2.07
2.06
1.44
N
O
Boc
2.08
1.12
2.01
2.07
3.00
9.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

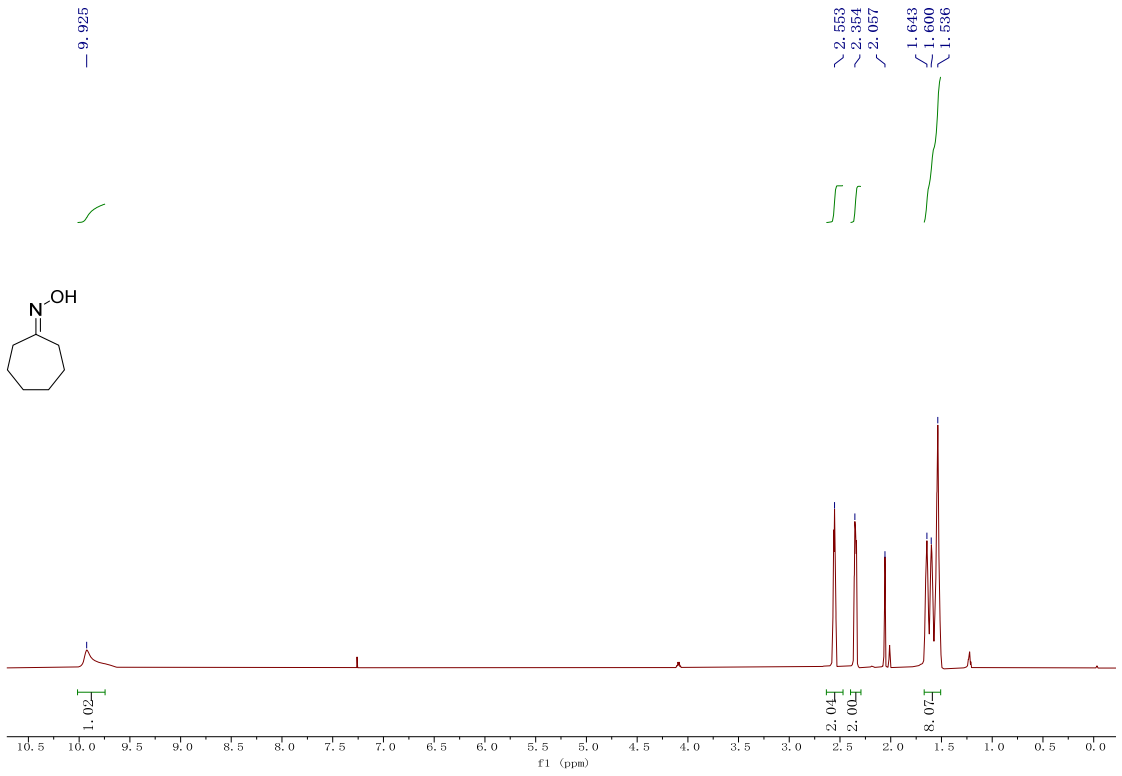

173.7
153.2
142.9
138.6
129.0
127.7
127.6
118.6
83.5
27.8
27.7
19.0
N
O
Boc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

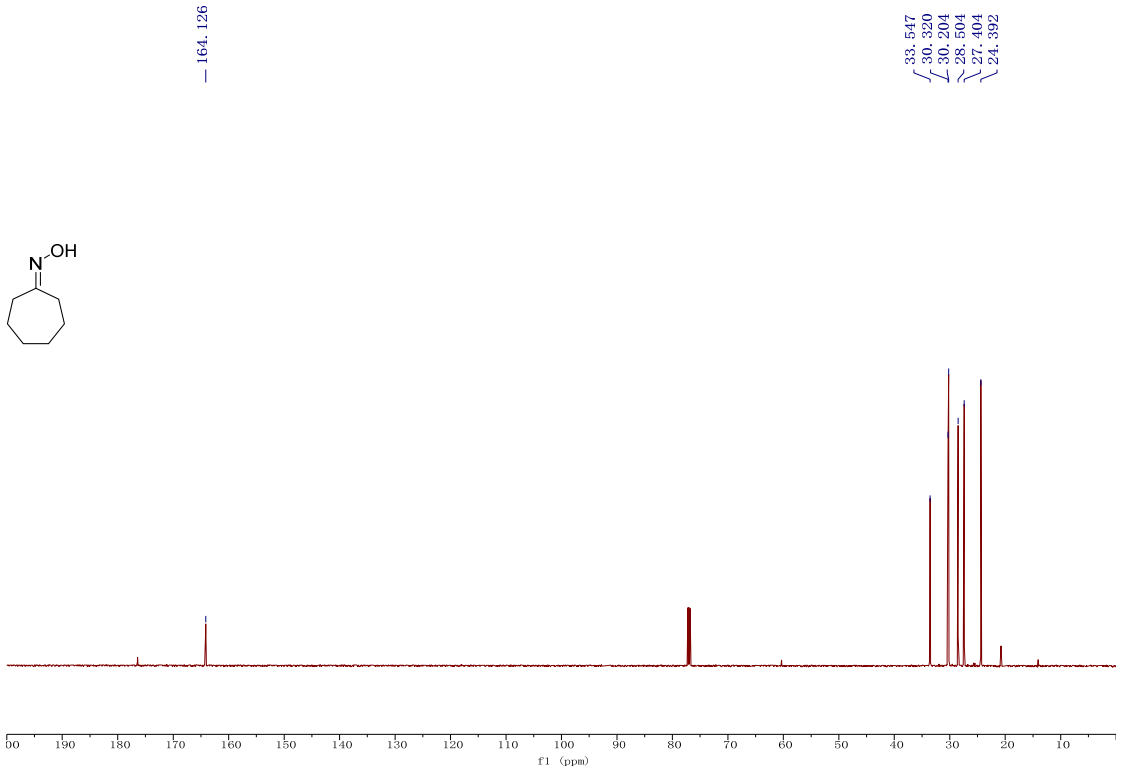

8.15
8.13
8.01
8.00
7.99
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.40
7.40
7.40
7.39
7.38
7.38
7.37
7.37
5.69
5.68
5.63
5.62
2.27
2.26
2.26
2.26
N
O
3.87
4.01
2.00
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

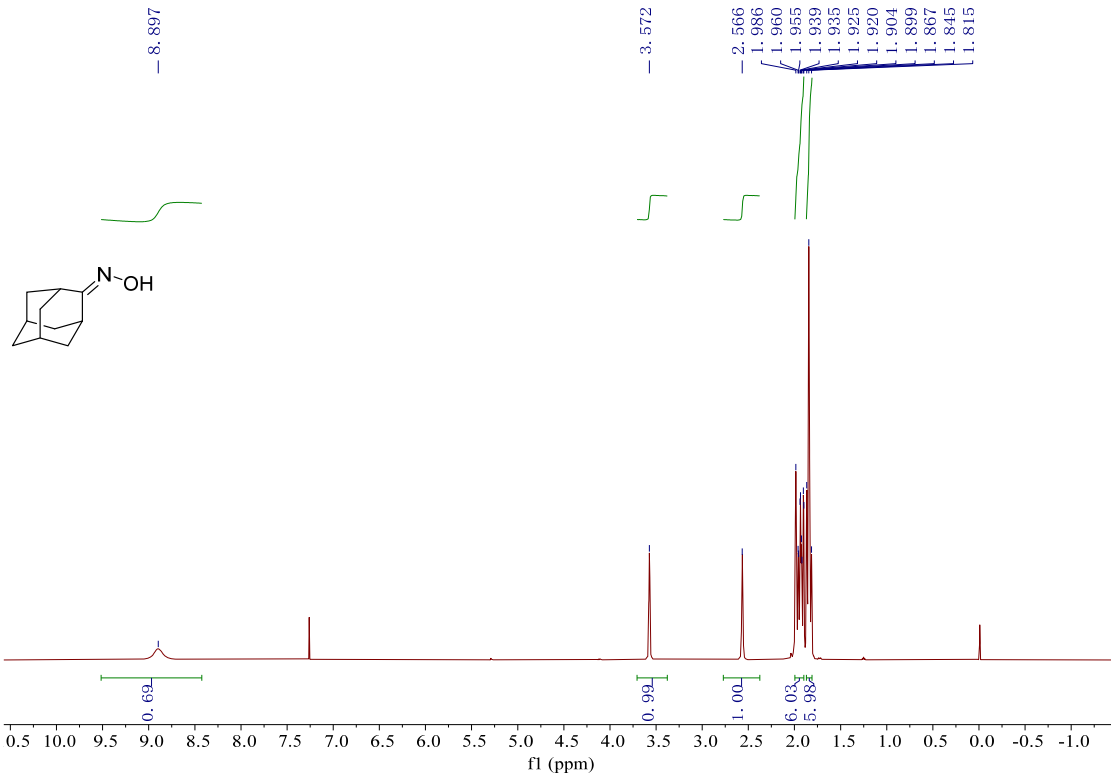

170.5
141.5
138.6
126.8
125.9
123.4
122.3
119.7
115.7
19.2
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

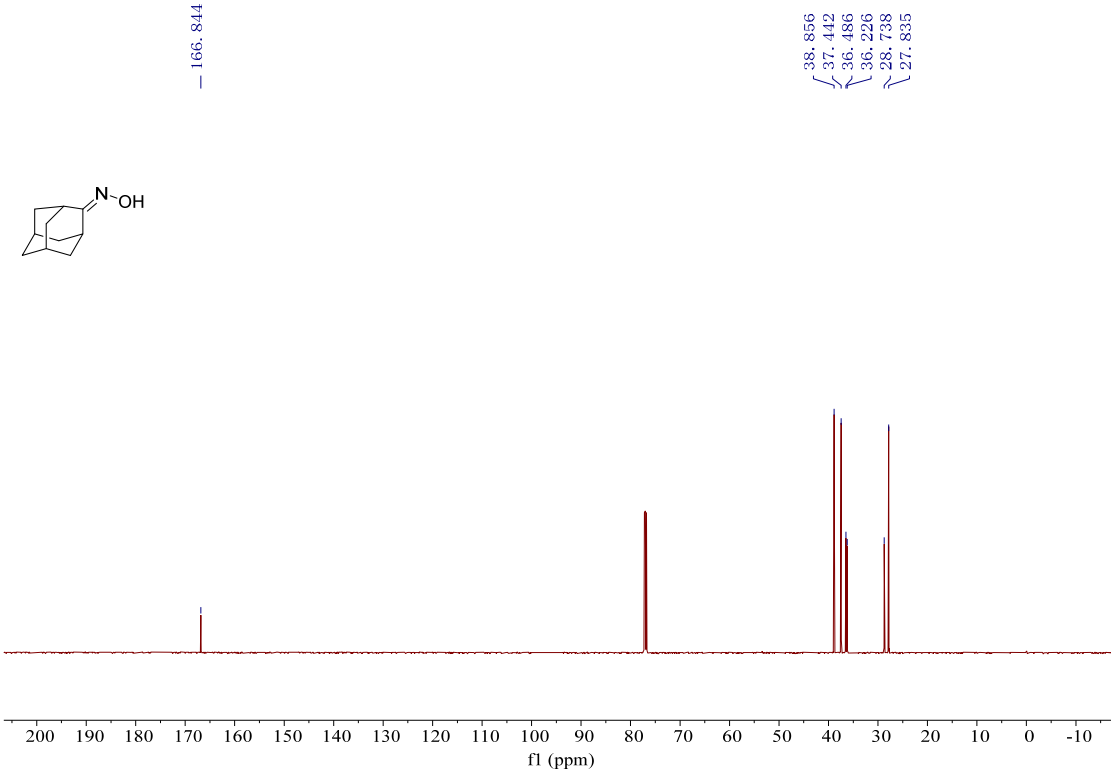

8.660
2.960
2.947
2.933
2.911
2.897
2.885
2.028
2.014
2.001
1.987
1.974
N
OH
0.80
2.00
1.98
2.00
f1 (ppm)

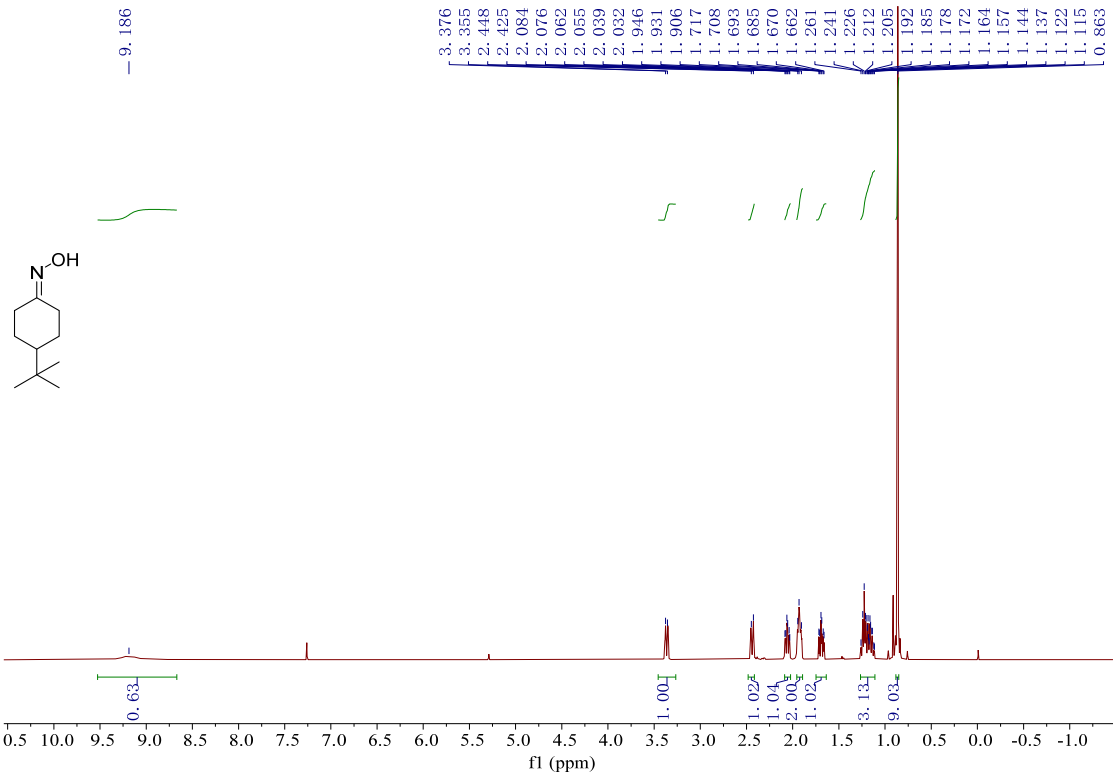

159.784
31.387
30.474
14.414
N
OH
f1 (ppm)

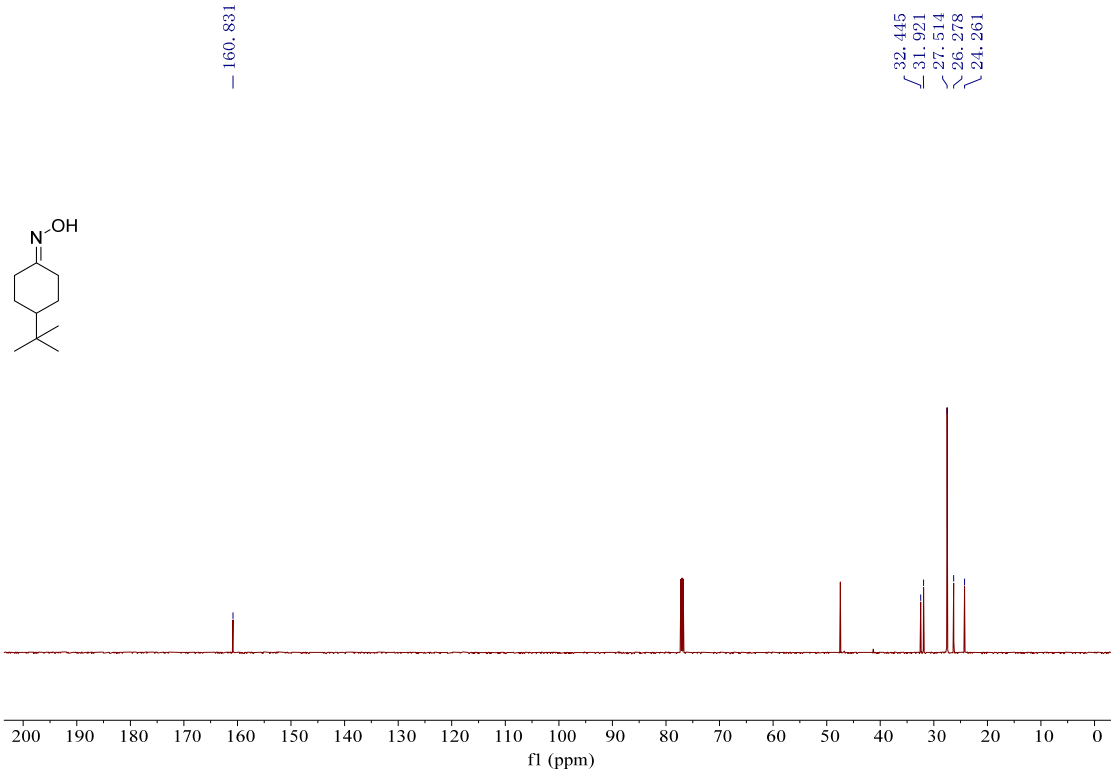

9.925
2.553
2.354
2.057
1.643
1.600
1.536
N
OH
1.02
2.04
2.00
8.07
f1 (ppm)

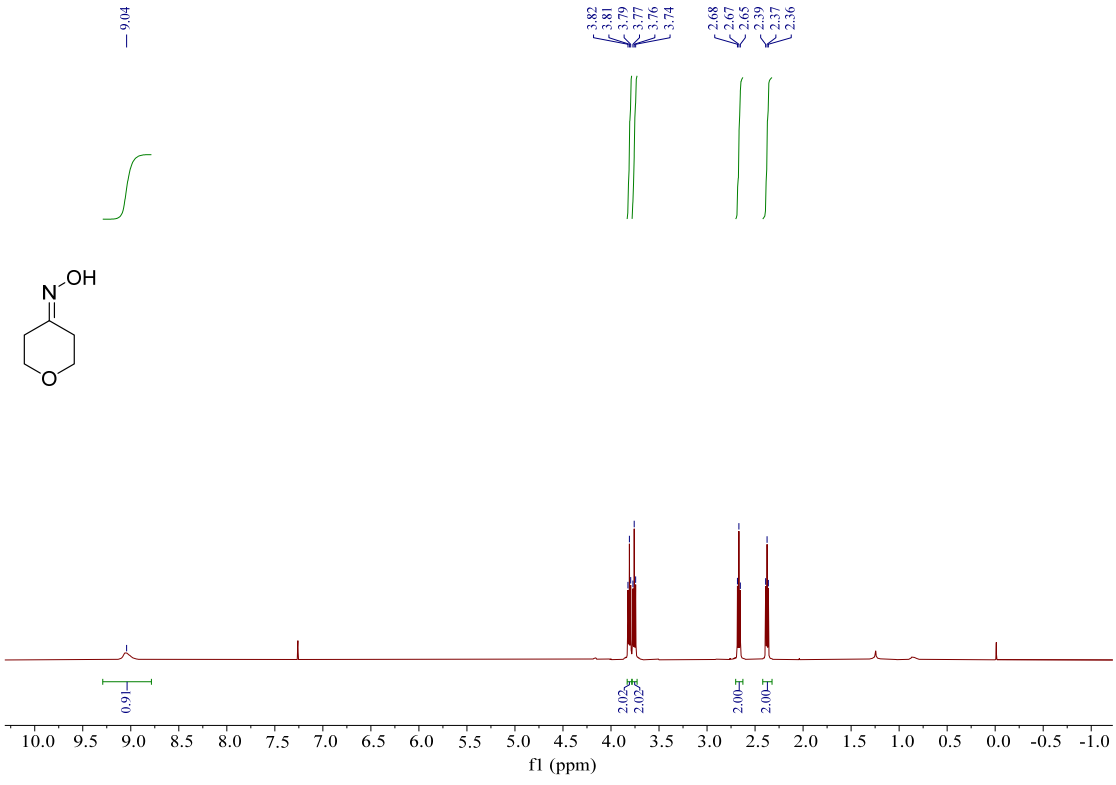

164.126
33.547
30.320
30.204
28.504
27.404
24.392
N
OH
f1 (ppm)

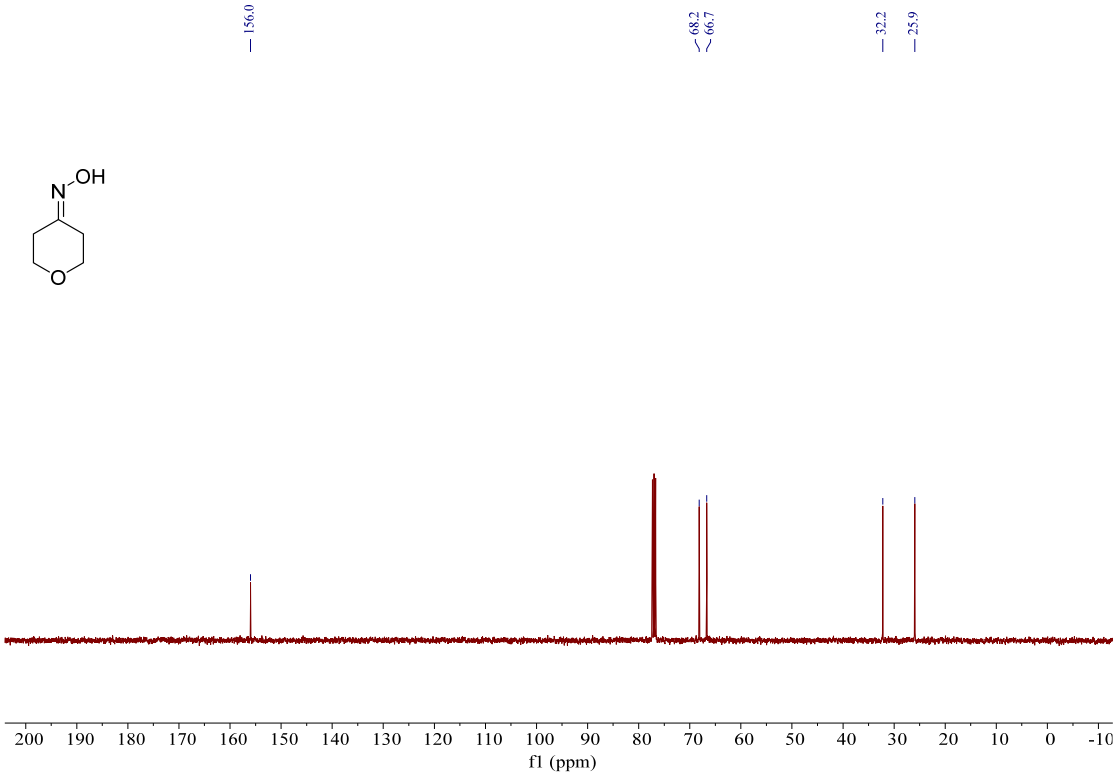

8.897
3.572
2.566
1.986
1.960
1.955
1.939
1.935
1.925
1.920
1.904
1.899
1.867
1.845
1.815
N
OH
0.69
0.99
1.00
6.03
5.98
f1 (ppm)

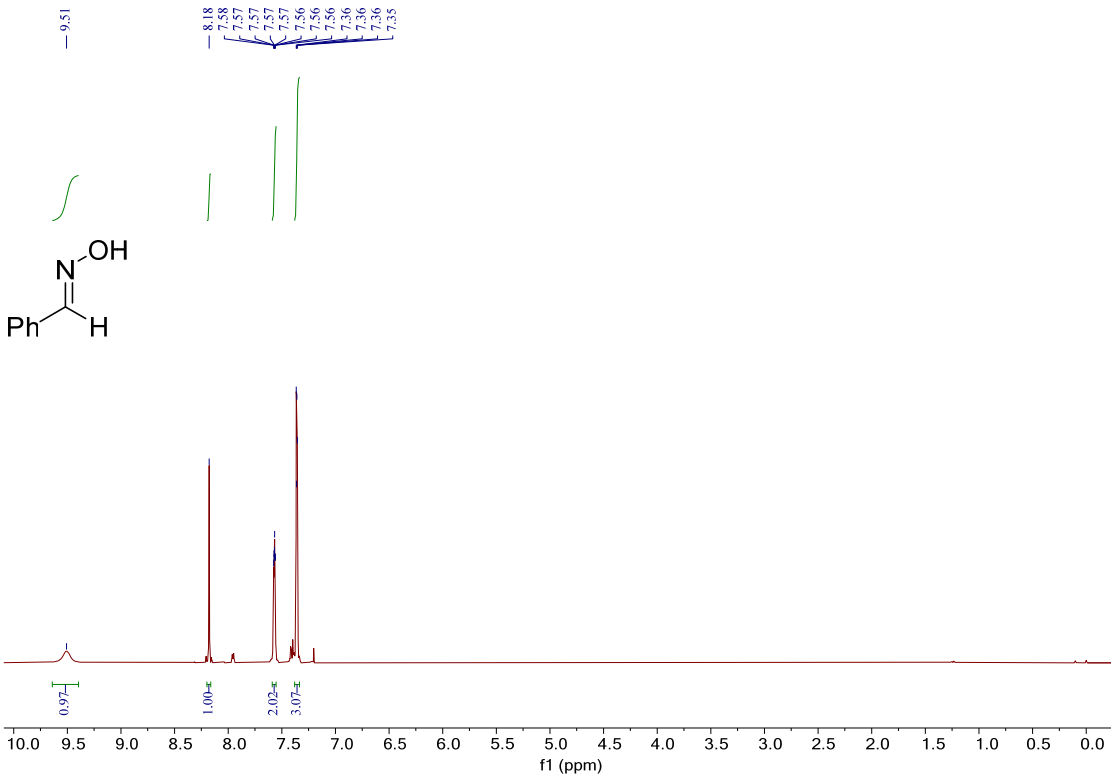

166.844
38.856
37.442
36.486
36.226
28.738
27.835
N
OH
f1 (ppm)

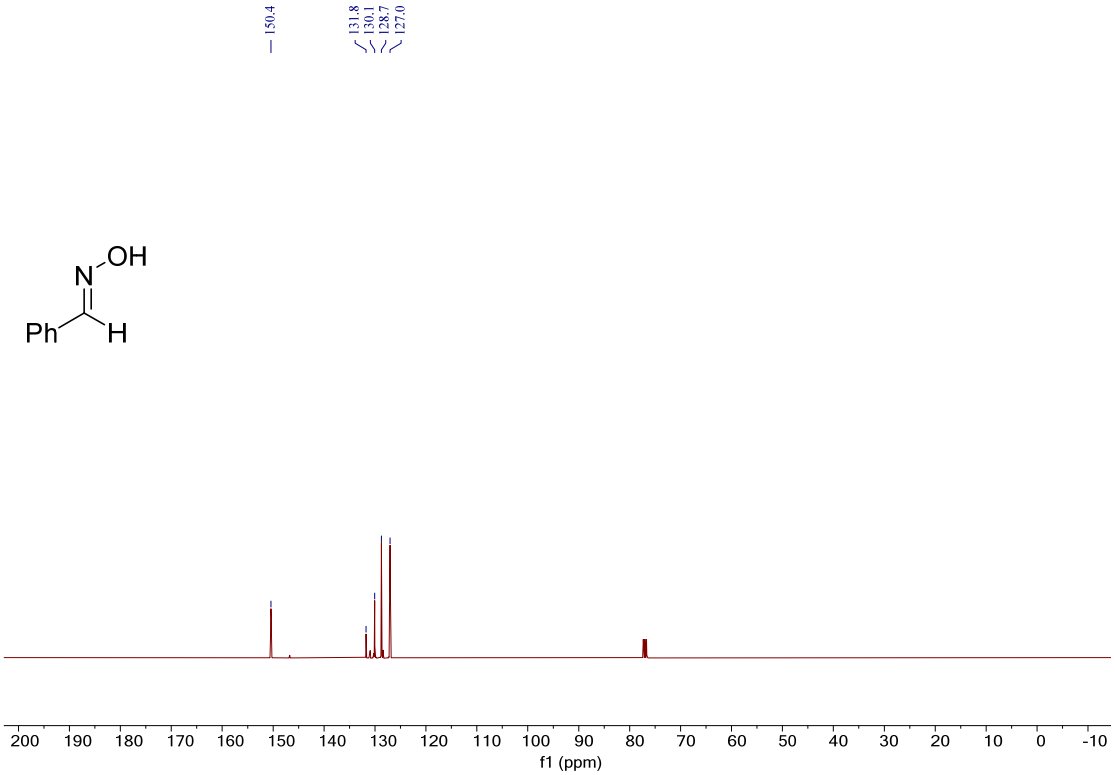

9.186
3.376
3.355
2.448
2.425
2.084
2.076
2.062
2.055
2.039
2.032
1.946
1.931
1.906
1.717
1.708
1.693
1.685
1.670
1.662
1.261
1.241
1.226
1.212
1.205
1.192
1.185
1.178
1.172
1.164
1.157
1.144
1.137
1.122
1.115
0.863
OH
N
0.63
1.00
1.02
1.04
2.00
1.02
3.13
9.03
f1 (ppm)

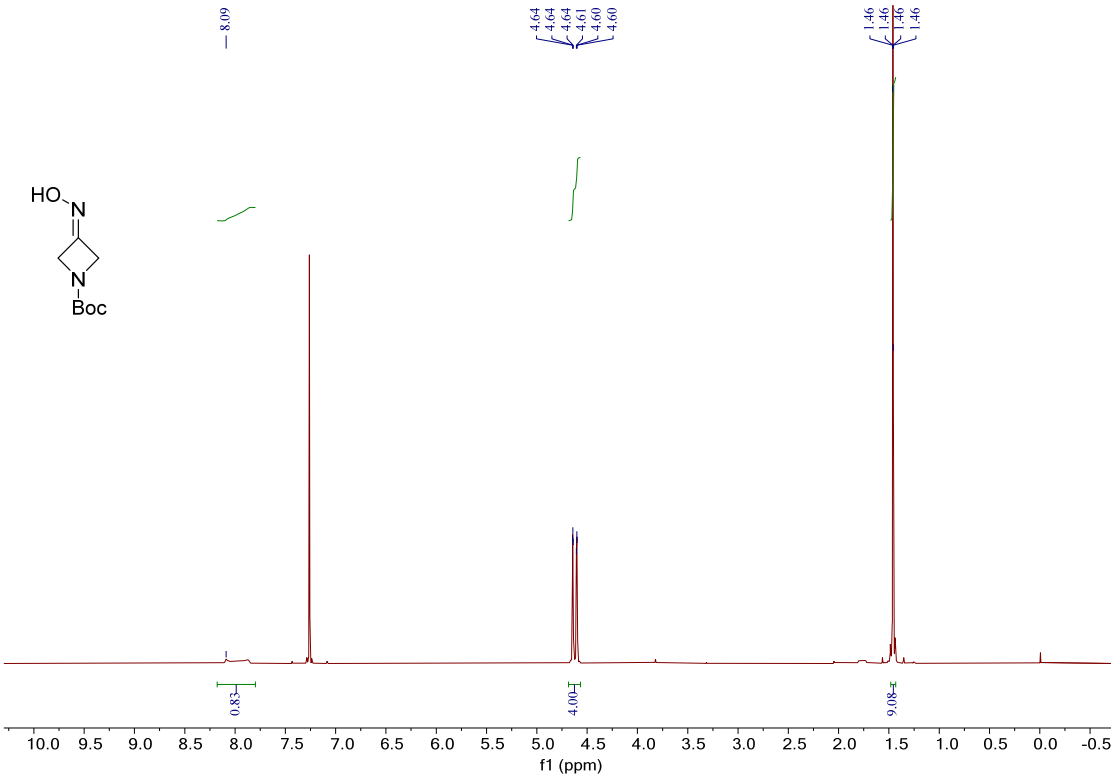

160.831
32.445
31.921
27.514
26.278
24.261
OH
N
f1 (ppm)

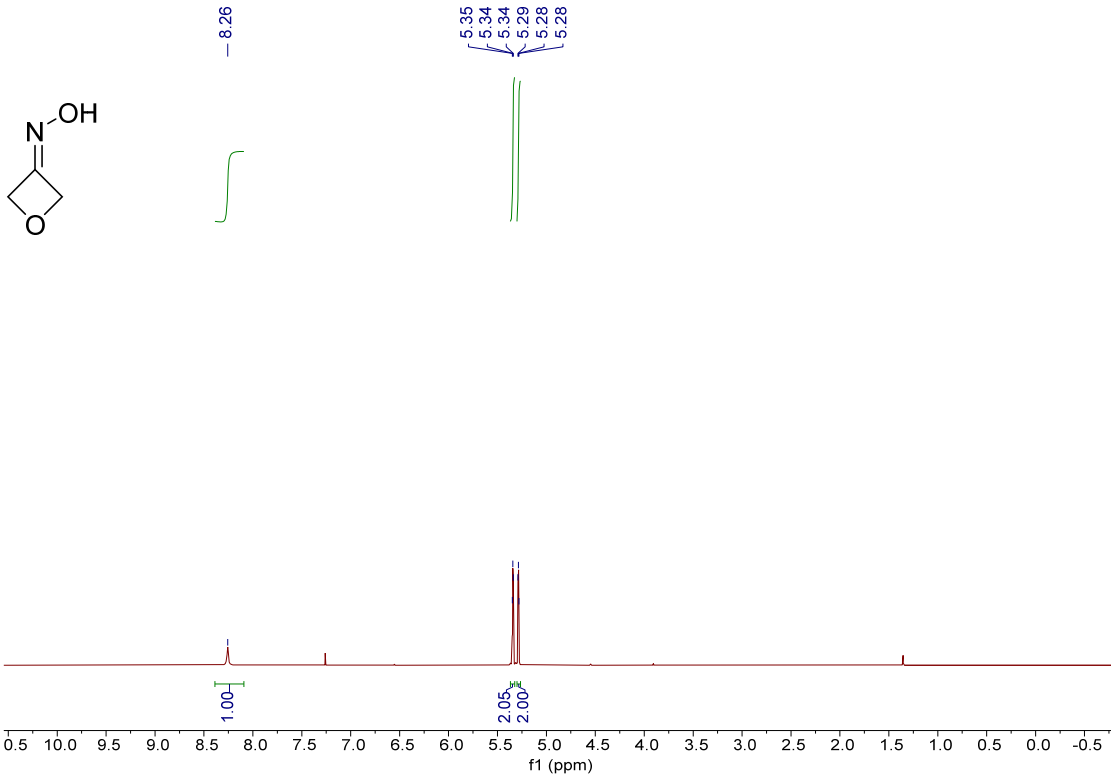

9.04
3.82
3.81
3.79
3.77
3.76
3.74
2.68
2.67
2.65
2.39
2.37
2.36
N
OH
O
0.91
2.02
2.02
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

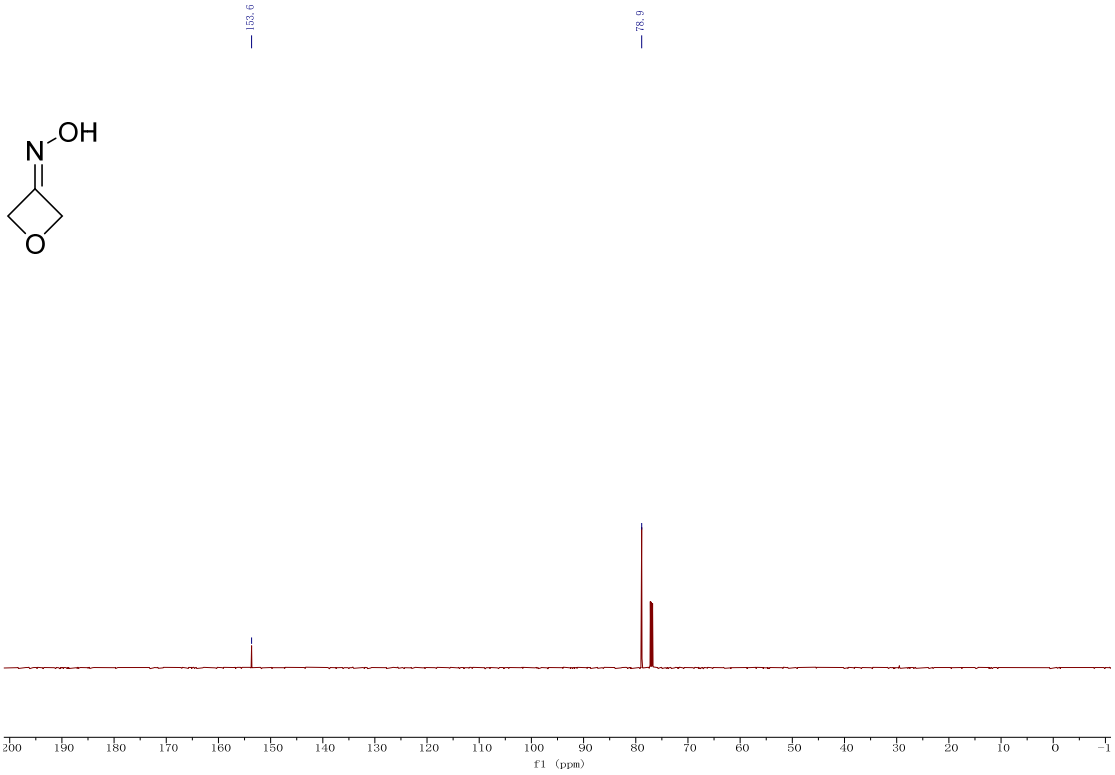

156.0
68.2
66.7
32.2
25.9
N
OH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

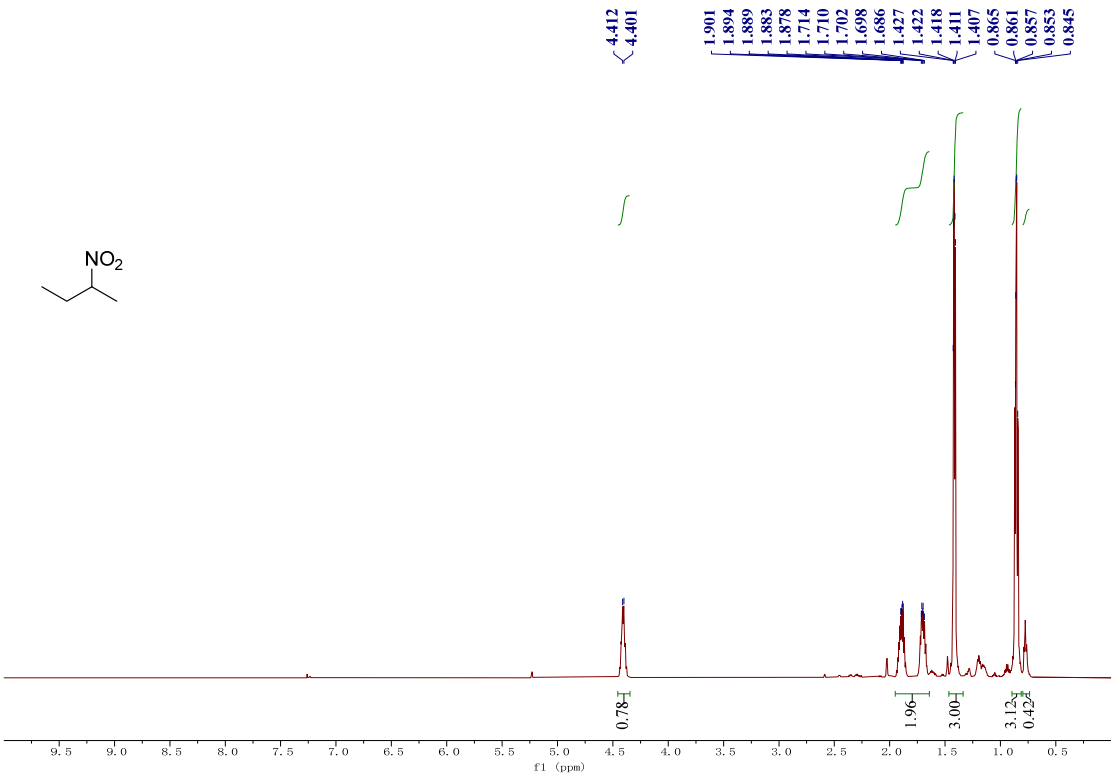

9.51
8.18
7.58
7.57
7.57
7.57
7.57
7.56
7.56
7.56
7.36
7.36
7.36
7.35
OH
N
Ph
H
0.97
1.00
2.02
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

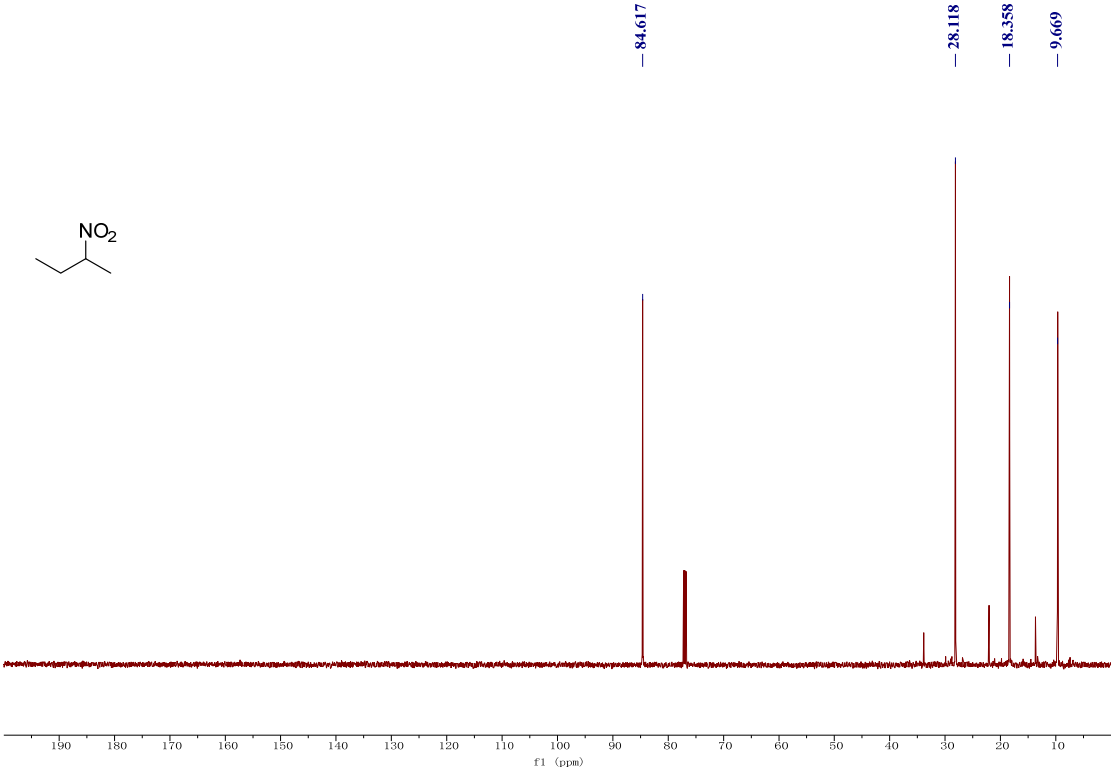

150.4
131.8
130.1
128.7
127.0
OH
N
Ph
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

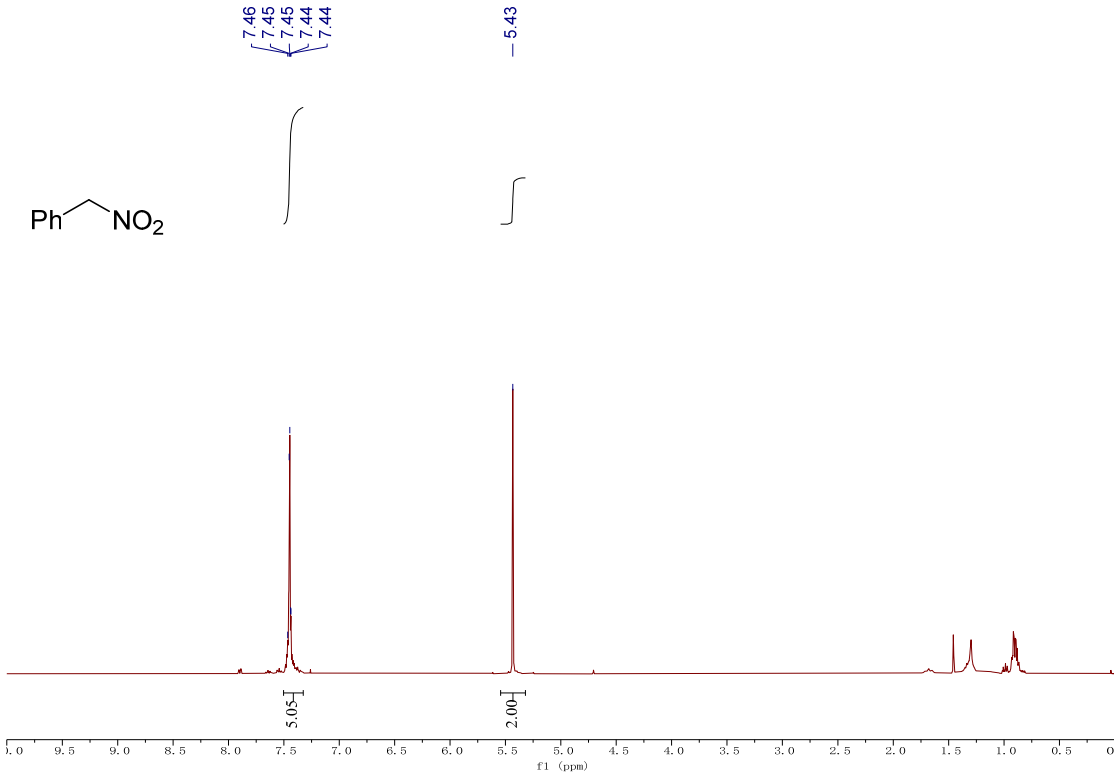

8.09
4.64
4.64
4.64
4.61
4.60
4.60
1.46
1.46
1.46
1.46
HO
N
N
Boc
0.83
4.00
9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

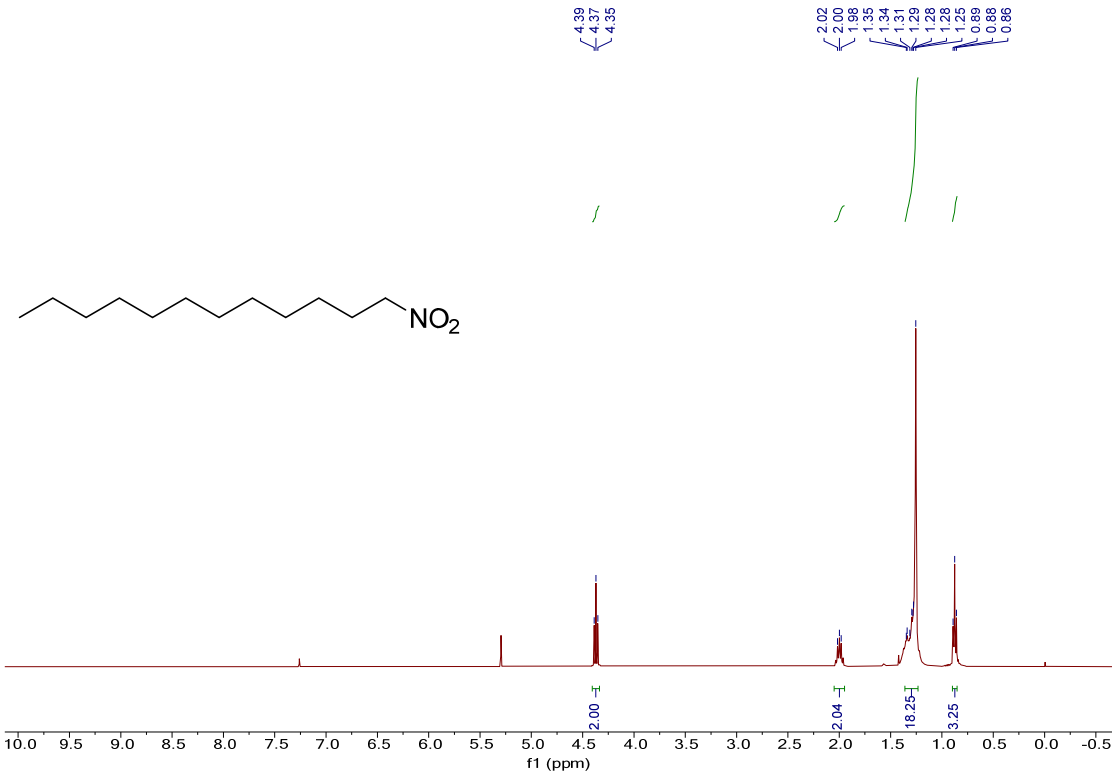

8.26
5.35
5.34
5.34
5.29
5.28
5.28
OH
N
O
1.00
2.05
2.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

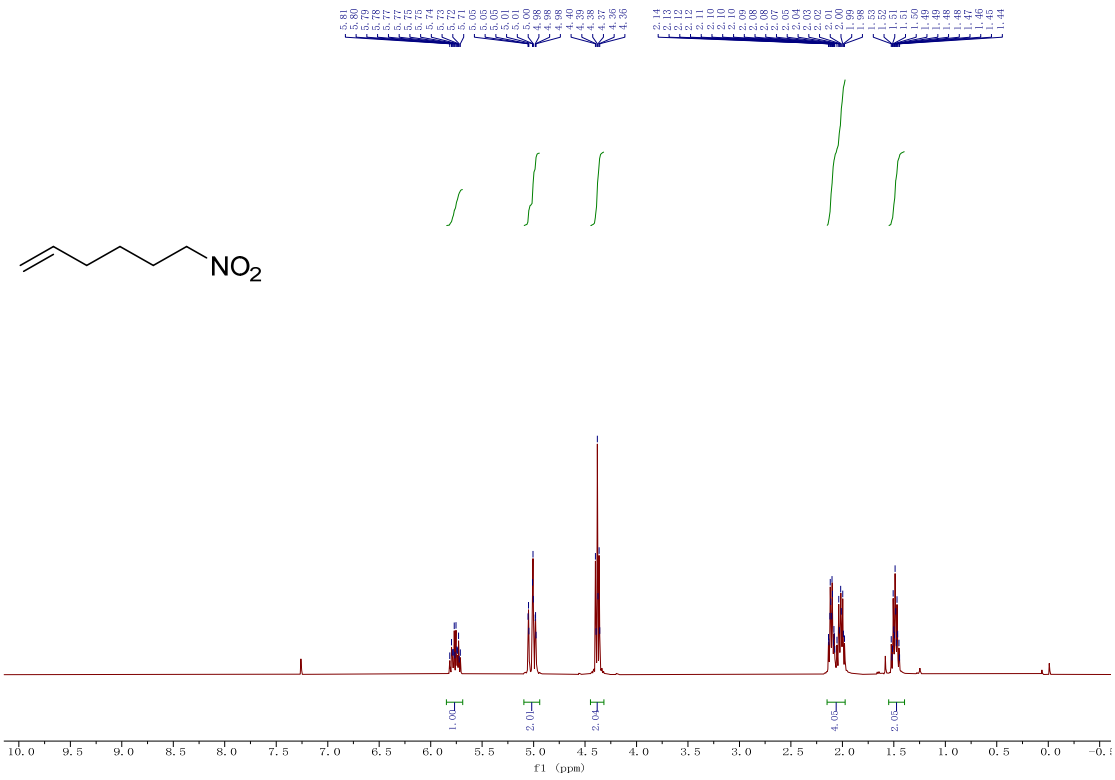

153.6
78.9
OH
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

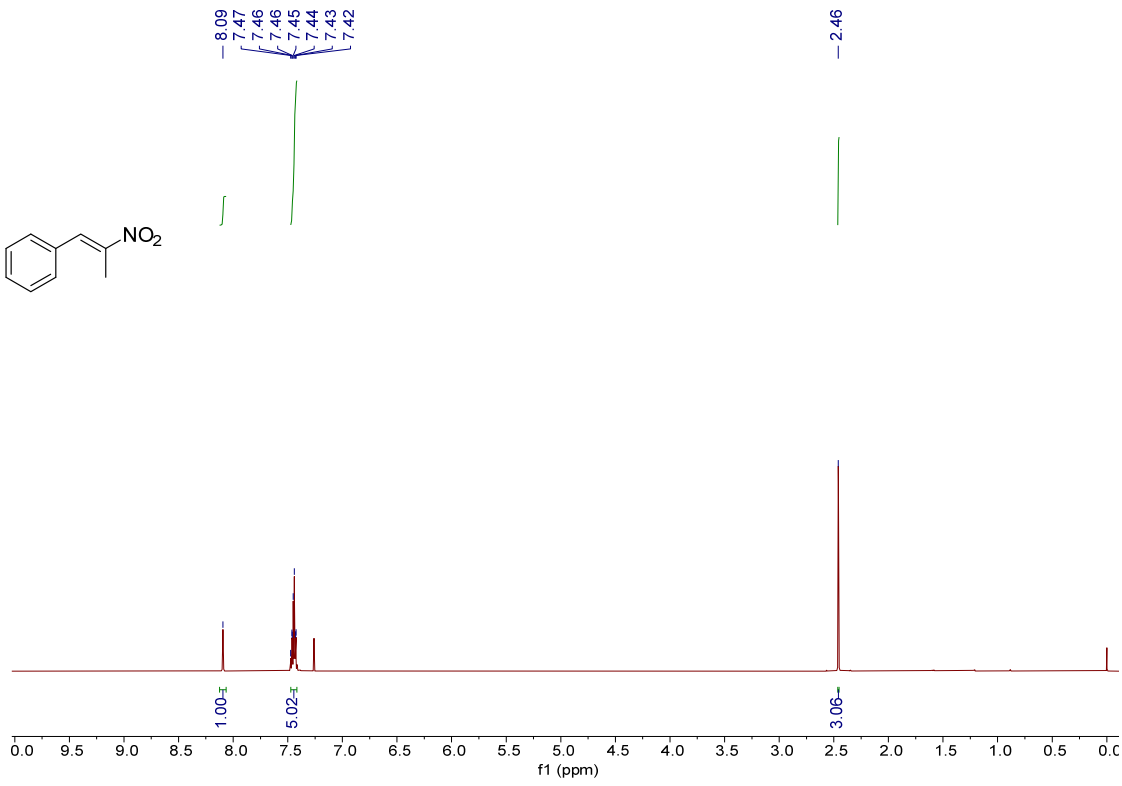

4.412
4.401
1.901
1.894
1.889
1.883
1.878
1.714
1.710
1.702
1.698
1.686
1.427
1.422
1.418
1.411
1.407
0.865
0.861
0.857
0.853
0.845
NO2
0.78
1.96
3.00
3.12
0.42
f1 (ppm)

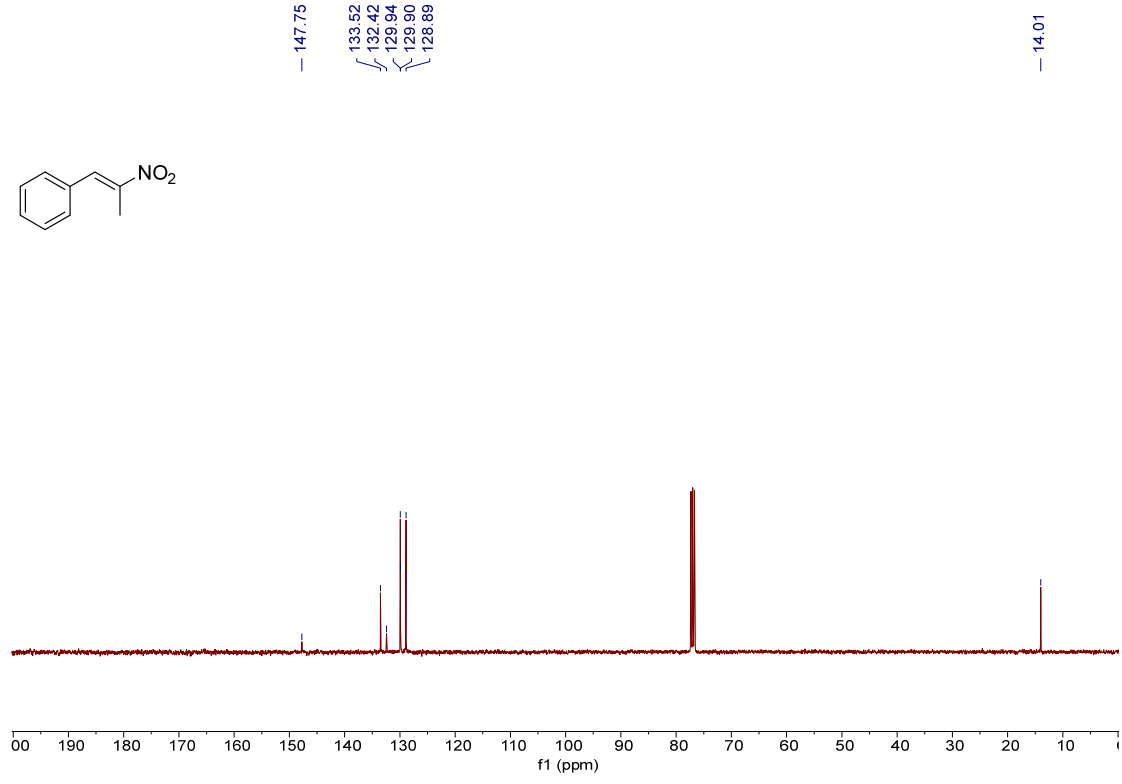

84.617
28.118
18.358
9.669
NO2
f1 (ppm)

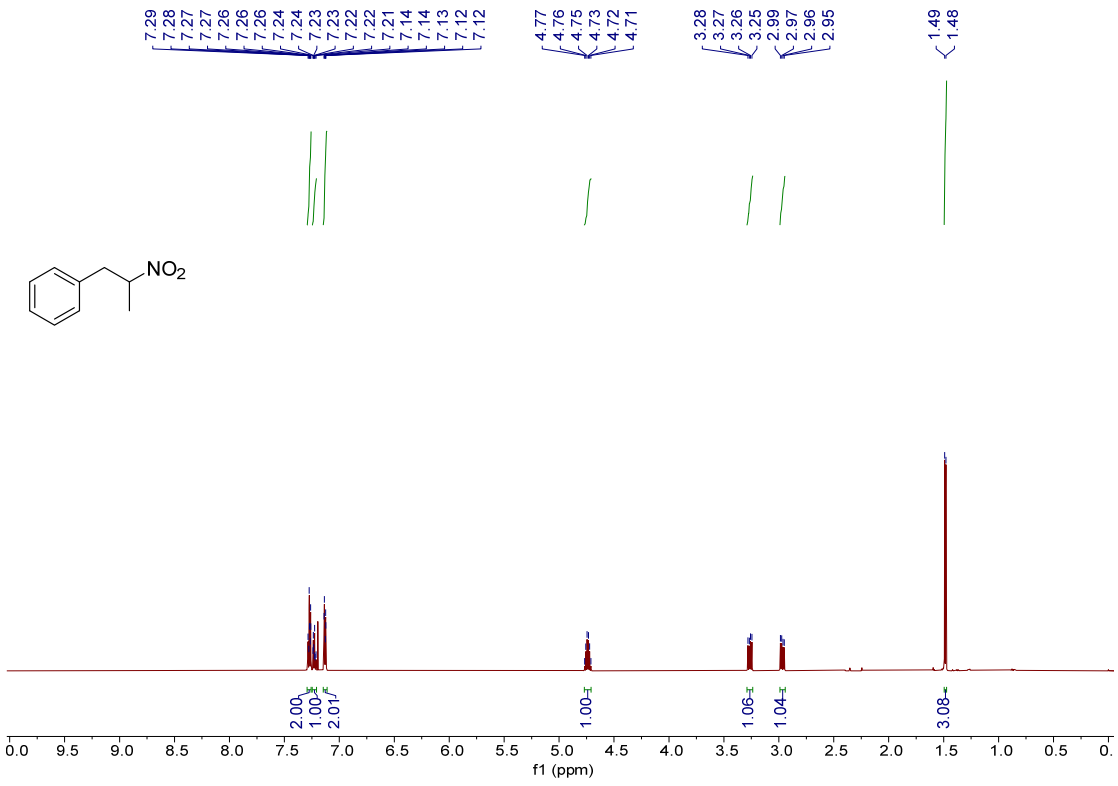

7.46
7.45
7.45
7.44
7.44
5.43
Ph
NO2
5.05
2.00
f1 (ppm)

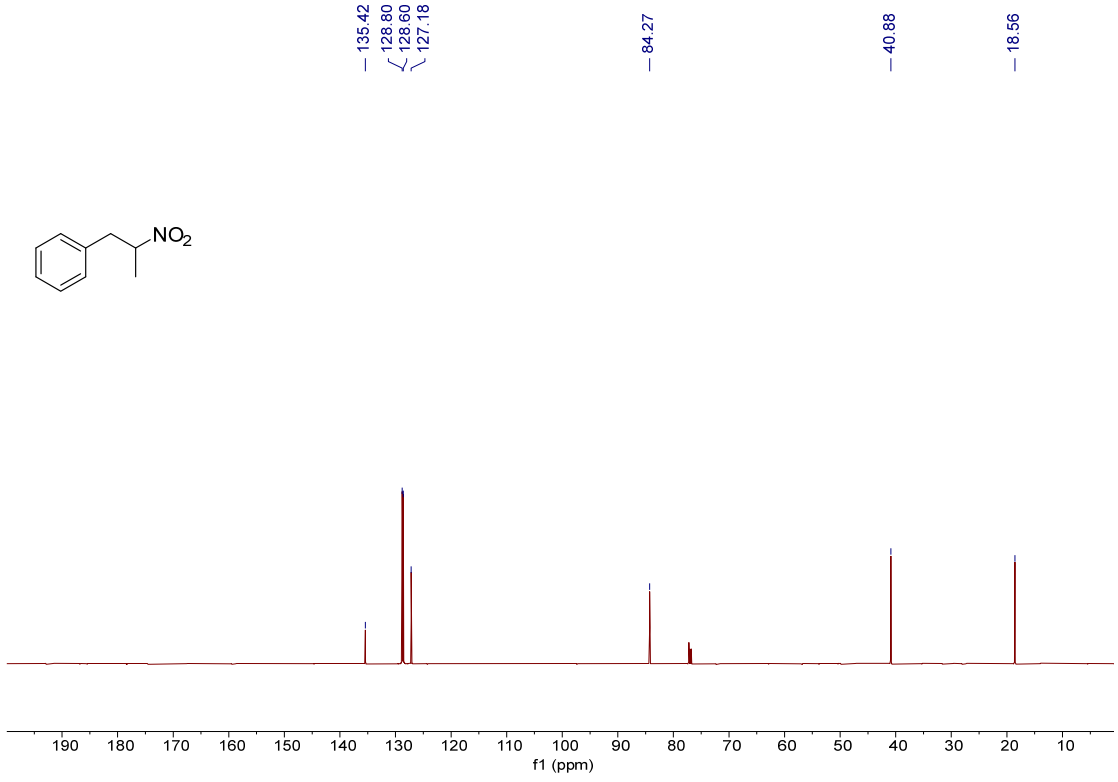

4.39
4.37
4.35
2.02
2.00
1.98
1.35
1.34
1.31
1.29
1.28
1.28
1.25
0.89
0.88
0.86
NO2
2.00
2.04
18.25
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

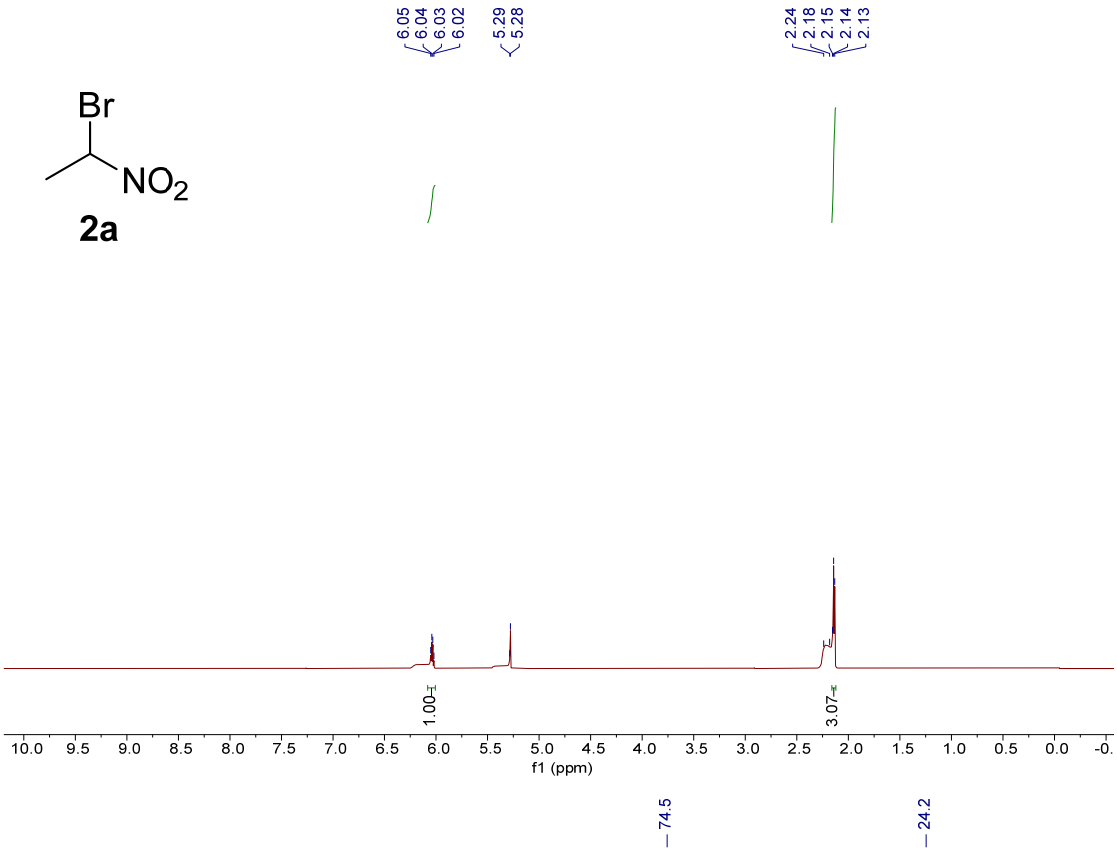

NO2
1.00
2.01
2.04
4.05
2.05
f1 (ppm)

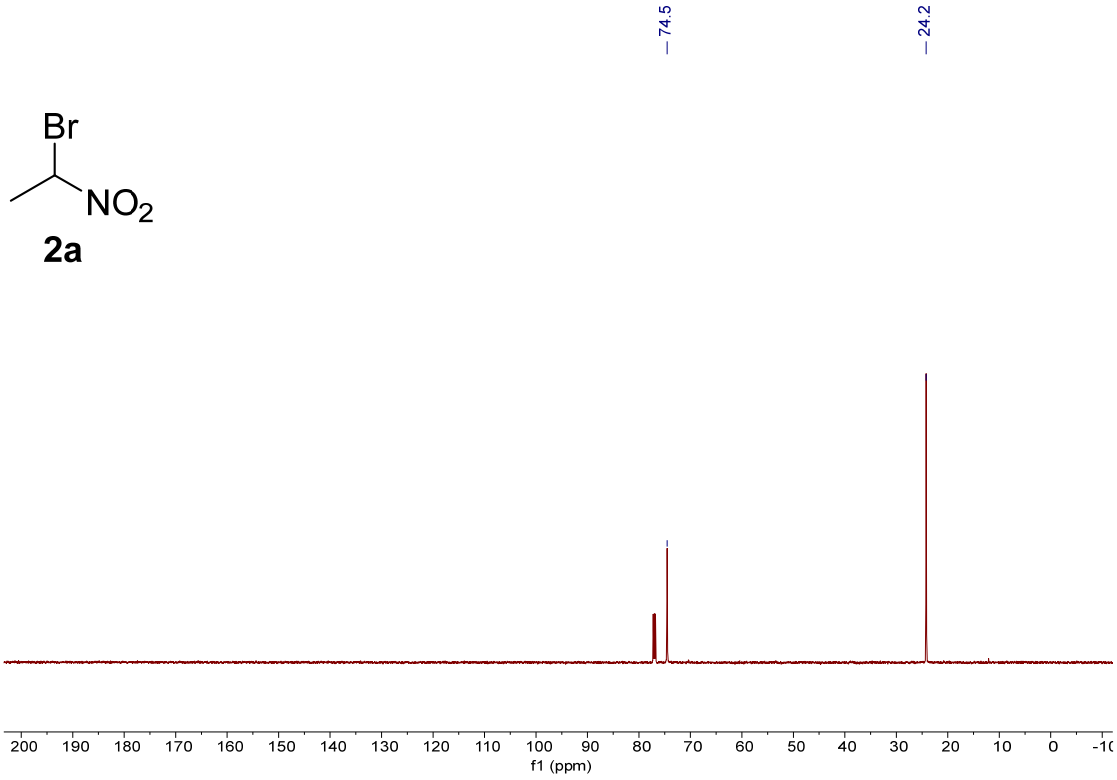

8.09
7.47
7.46
7.46
7.45
7.44
7.43
7.42
2.46
NO2
1.00
5.02
3.06
f1 (ppm)

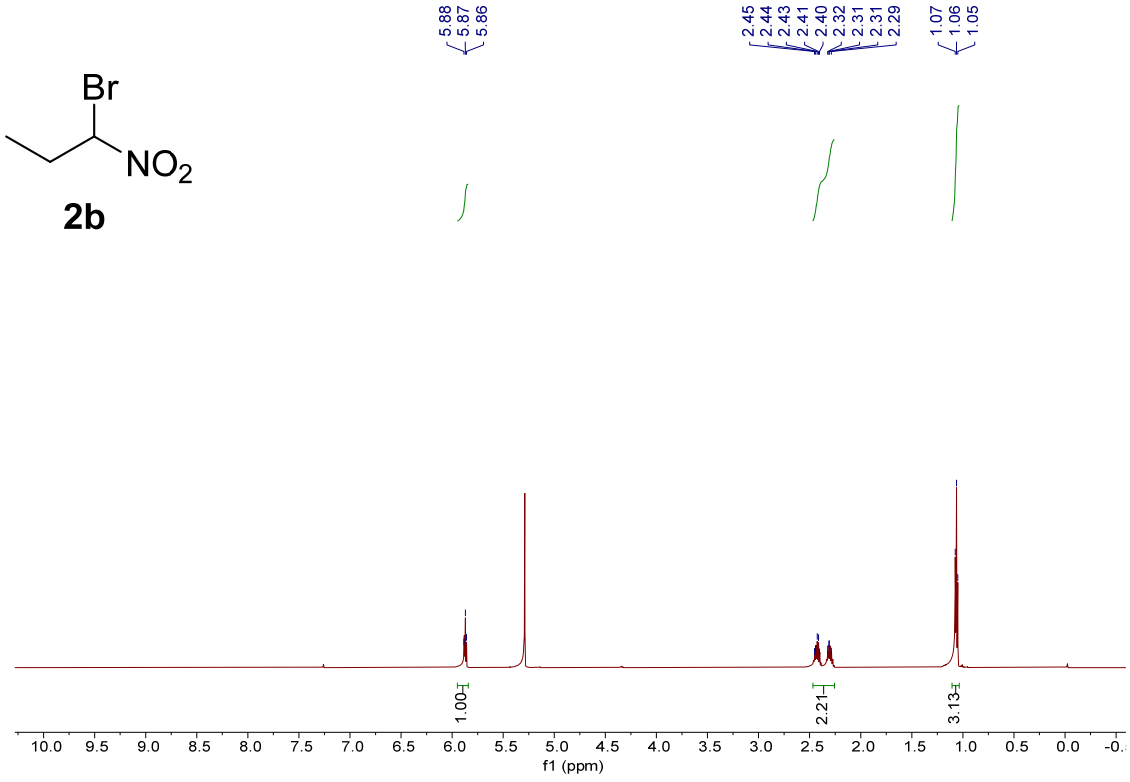

147.75
133.52
132.42
129.94
129.90
128.89
14.01
NO2
f1 (ppm)

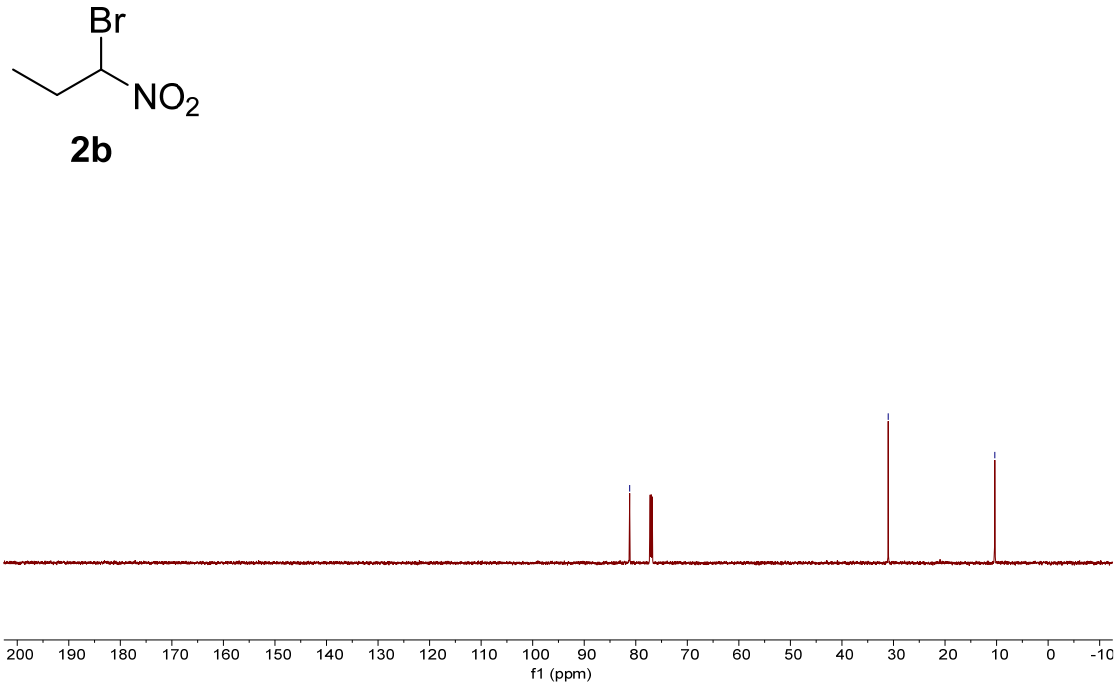

7.29
7.28
7.27
7.27
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.14
7.14
7.13
7.12
7.12
4.77
4.76
4.75
4.73
4.72
4.71
3.28
3.27
3.26
3.25
2.99
2.97
2.96
2.95
1.49
1.48
NO2
2.00
1.00
2.01
1.00
1.06
1.04
3.08
f1 (ppm)

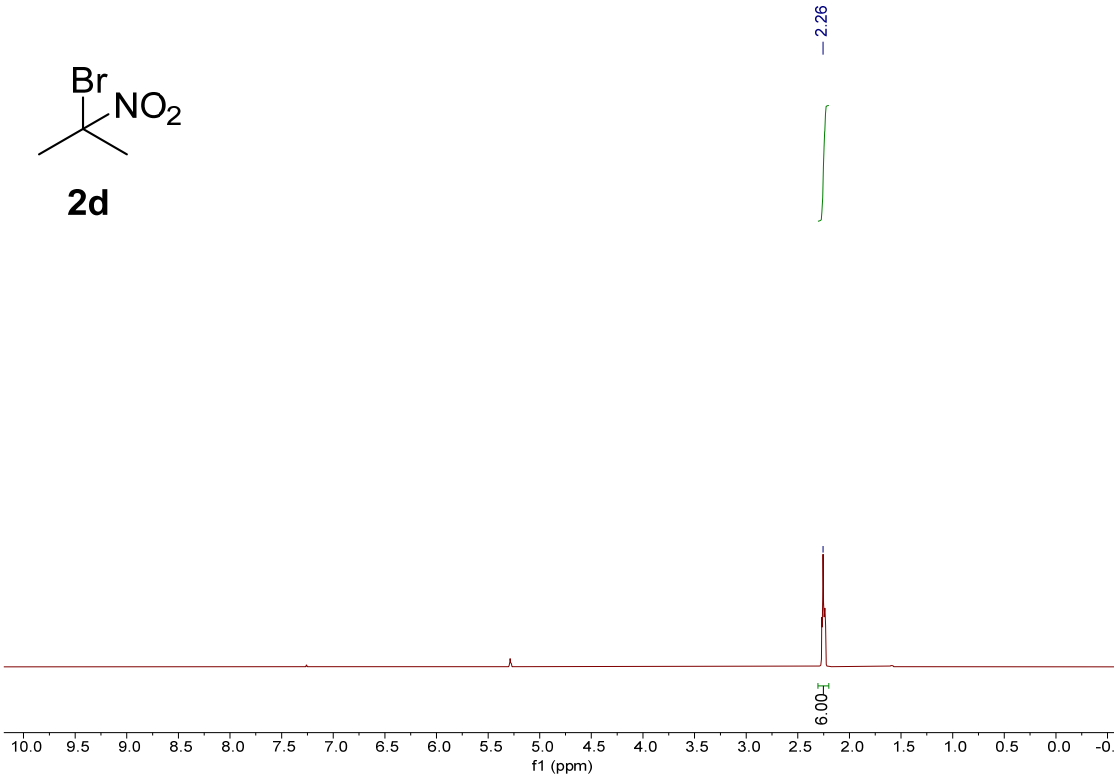

135.42
128.80
128.60
127.18
84.27
40.88
18.56
NO2
f1 (ppm)

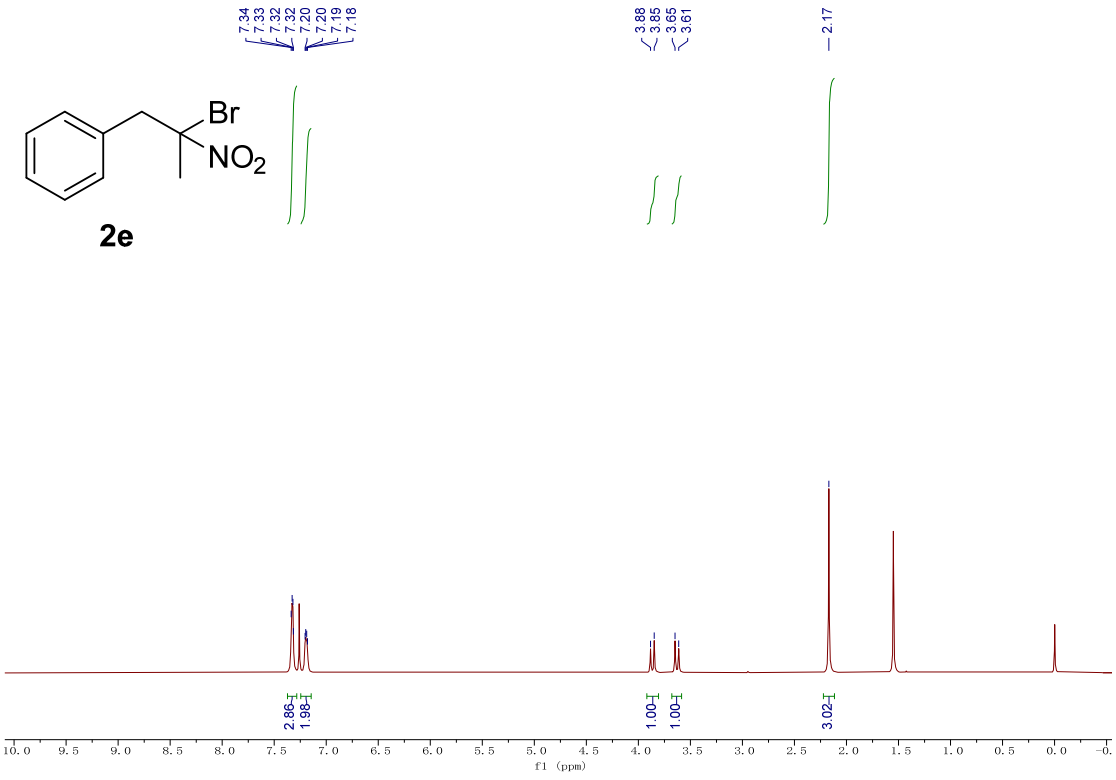

6.05
6.04
6.03
6.02
5.29
5.28
2.24
2.18
2.15
2.14
2.13
Br
NO2
2a
1.00
3.07
f1 (ppm)

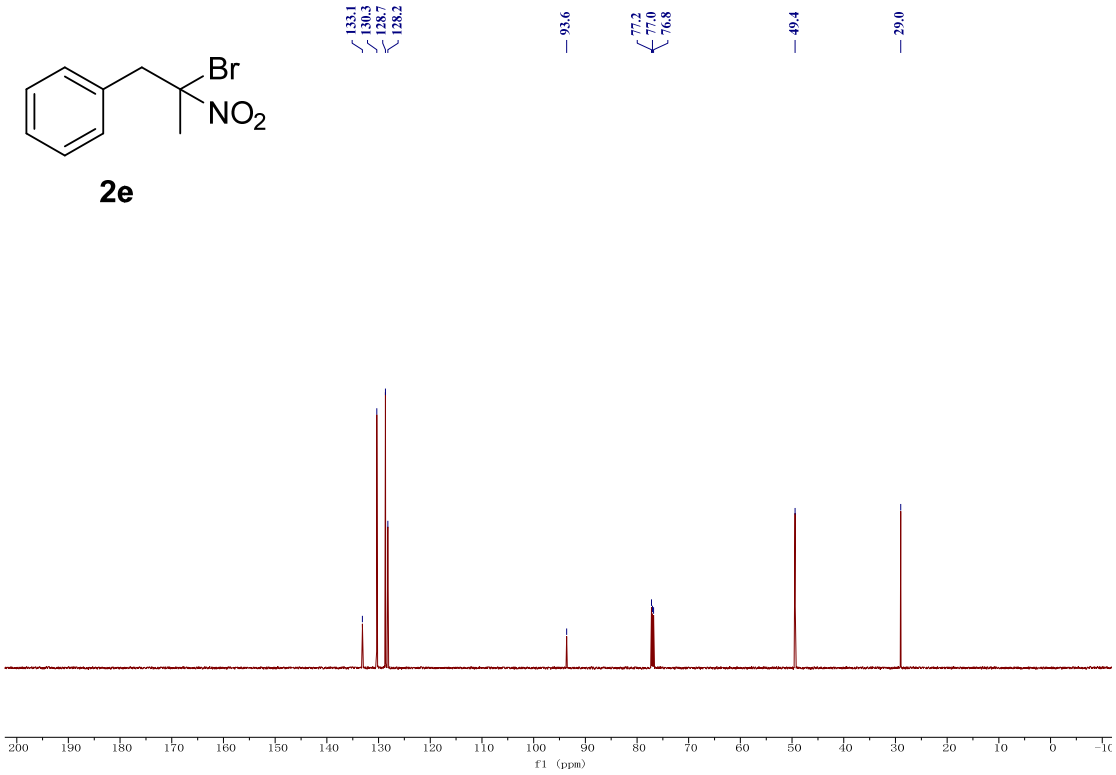

74.5
24.2
Br
NO2
2a
f1 (ppm)

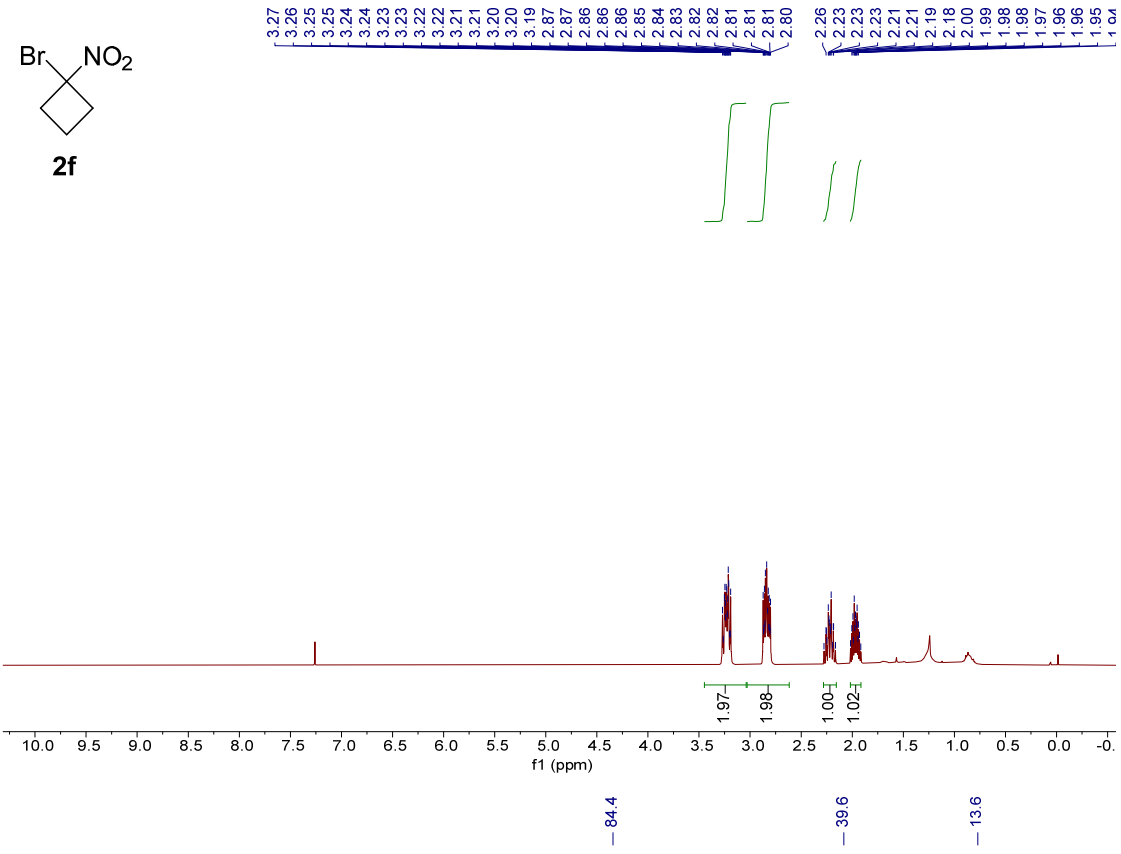

Br
NO2
2b
5.88
5.87
5.86
2.45
2.44
2.43
2.41
2.40
2.32
2.31
2.31
2.29
1.07
1.06
1.05
1.00
2.21
3.13
f1 (ppm)

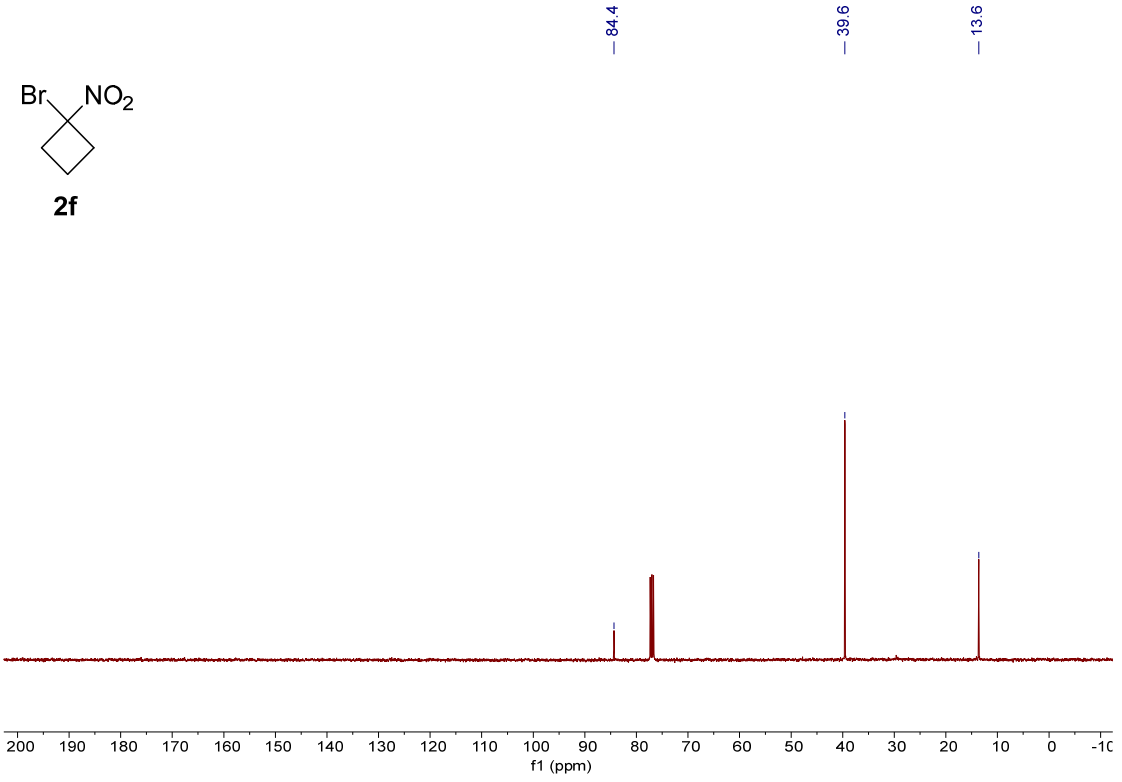

81.2
31.0
10.3
Br
NO2
2b
f1 (ppm)

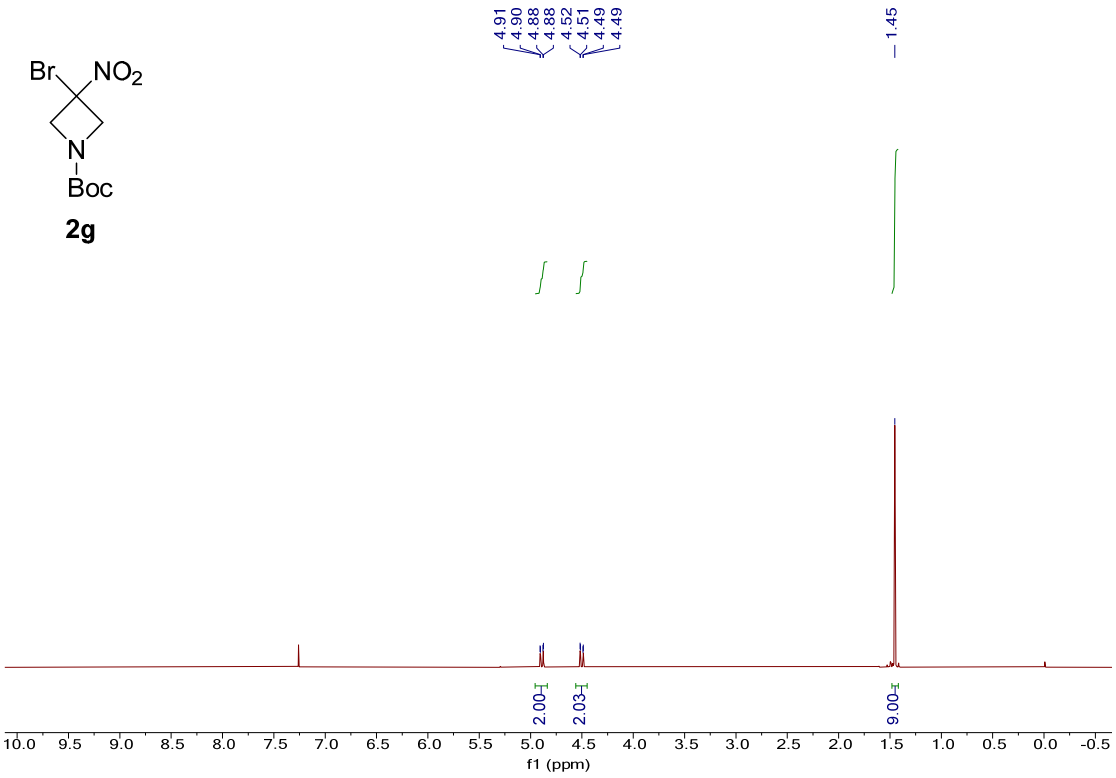

Br
NO2
2d
2.26
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

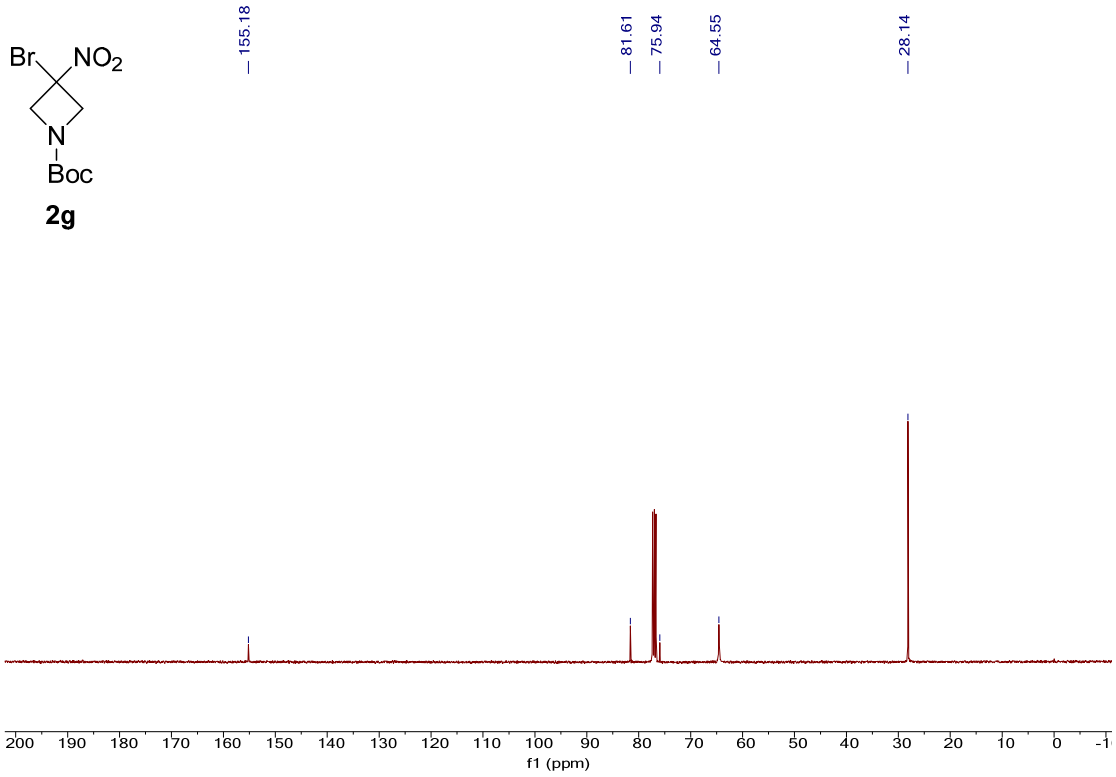

7.34
7.33
7.32
7.32
7.20
7.20
7.19
7.18
3.88
3.85
3.65
3.61
2.17
Br
NO2
2e
2.86
1.98
1.00
1.00
3.02
f1 (ppm)

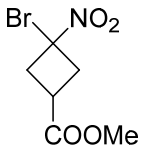

133.1
130.3
128.7
128.2
93.6
77.2
77.0
76.8
49.4
29.0
Br
NO2
2e
f1 (ppm)


Br
NO2
2f
3.27 3.26 3.25 3.25 3.24 3.24 3.23 3.23 3.22 3.21 3.21 3.20 3.20 3.19 2.87 2.87 2.86 2.86 2.86 2.85 2.84 2.83 2.82 2.82 2.81 2.81 2.80
2.26 2.23 2.23 2.23 2.21 2.21 2.19 2.18 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.95
1.97 1.98 1.00 1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

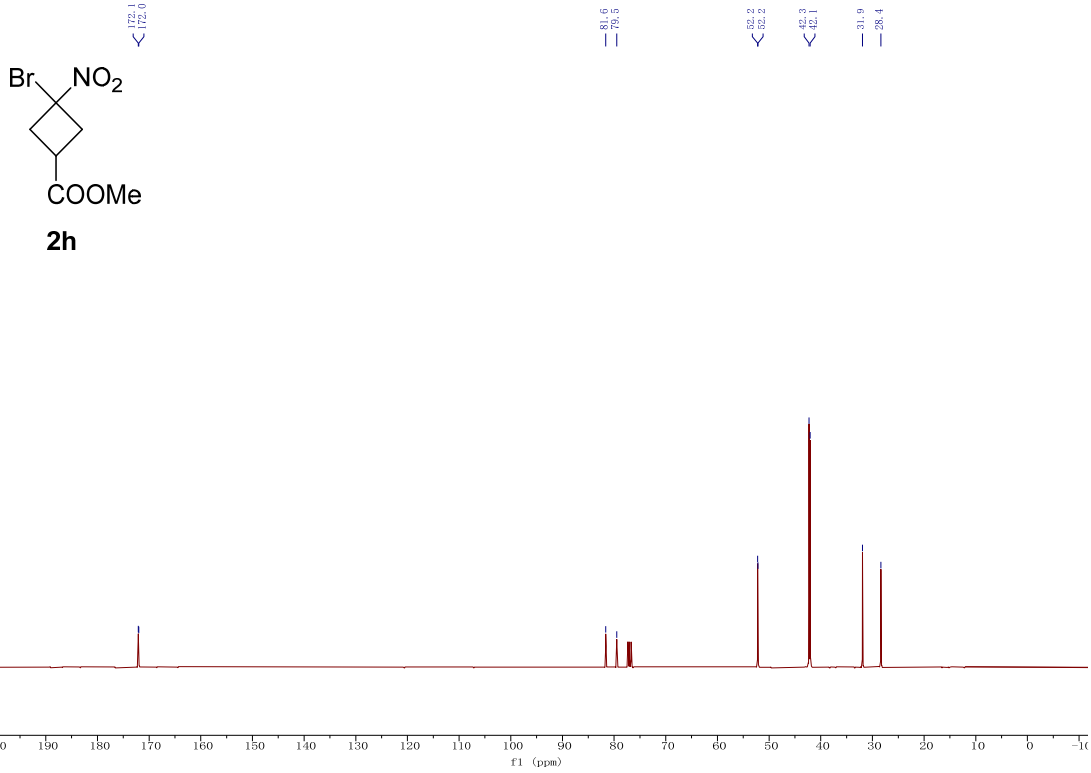

84.4
39.6
13.6
Br
NO2
2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
NO2
N
Boc
2g
4.91
4.90
4.88
4.88
4.52
4.51
4.49
4.49
1.45
2.00
2.03
9.00
f1 (ppm)

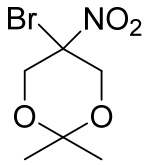

Br
NO2
N
Boc
2g
155.18
81.61
75.94
64.55
28.14
f1 (ppm)



2h

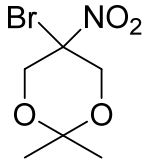


2h


Br
NO2
O
O

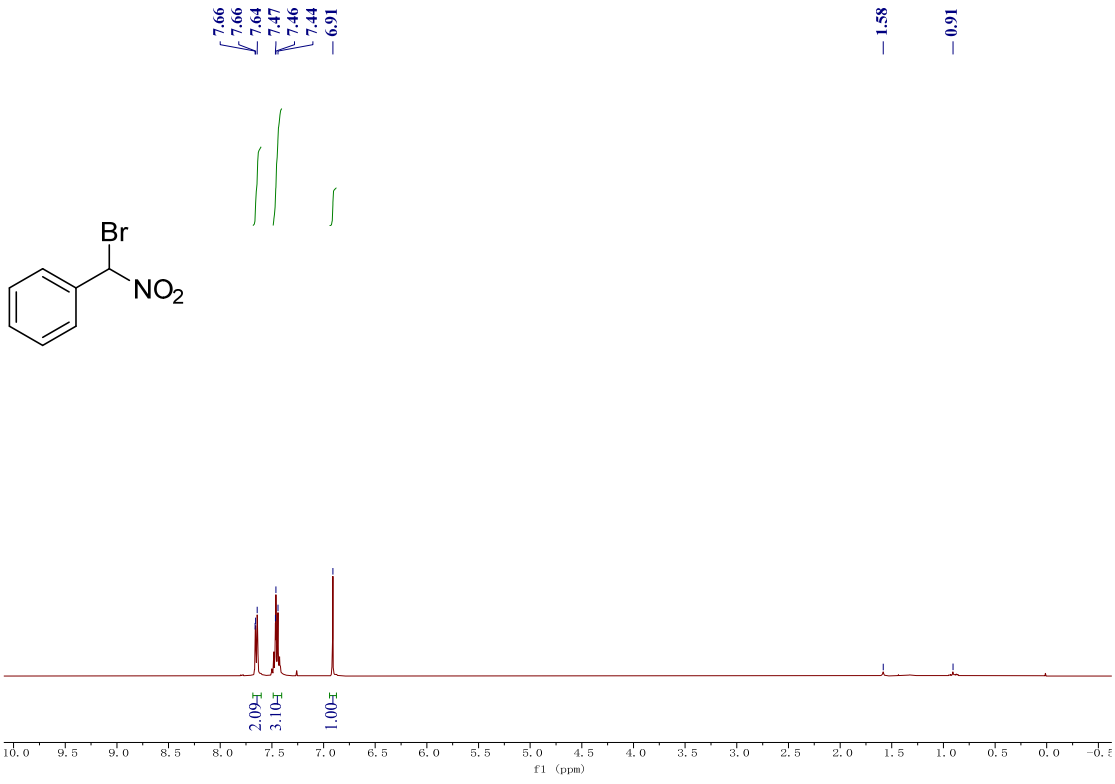
2i

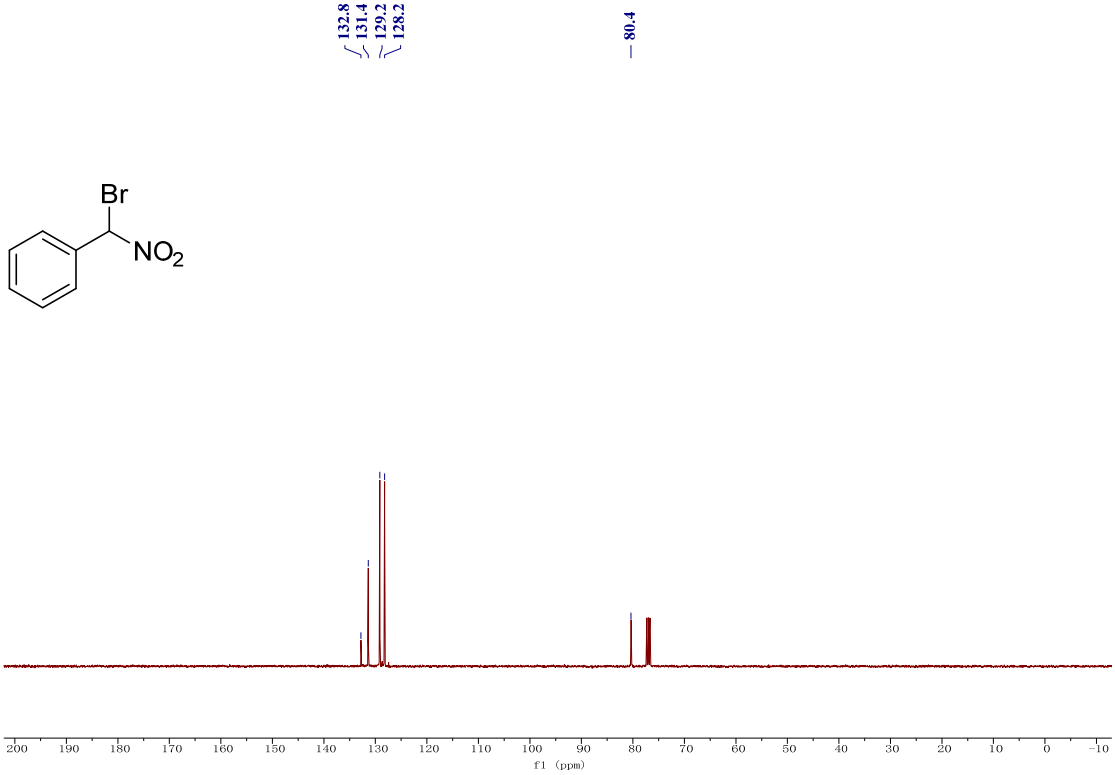
4.80
4.79
4.79
4.79
4.78
4.77
4.76
4.76
4.75
4.75
4.28
4.28
4.28
4.25
1.54
1.53
1.52
1.38
1.37
1.36
2.00
2.04
3.20
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

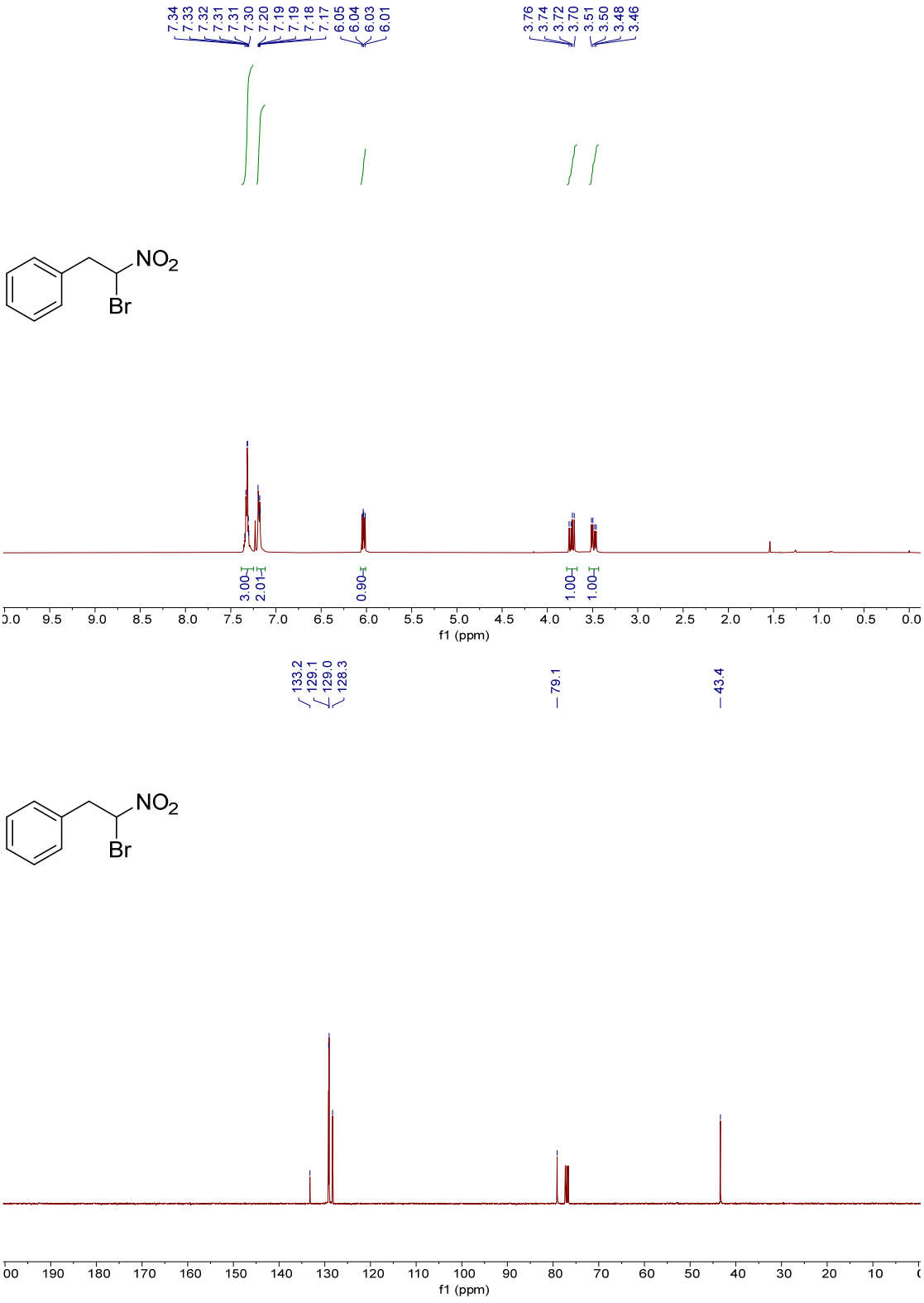

Br
NO2
O
O

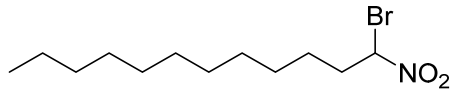
2i

99.4
66.1
27.8
18.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

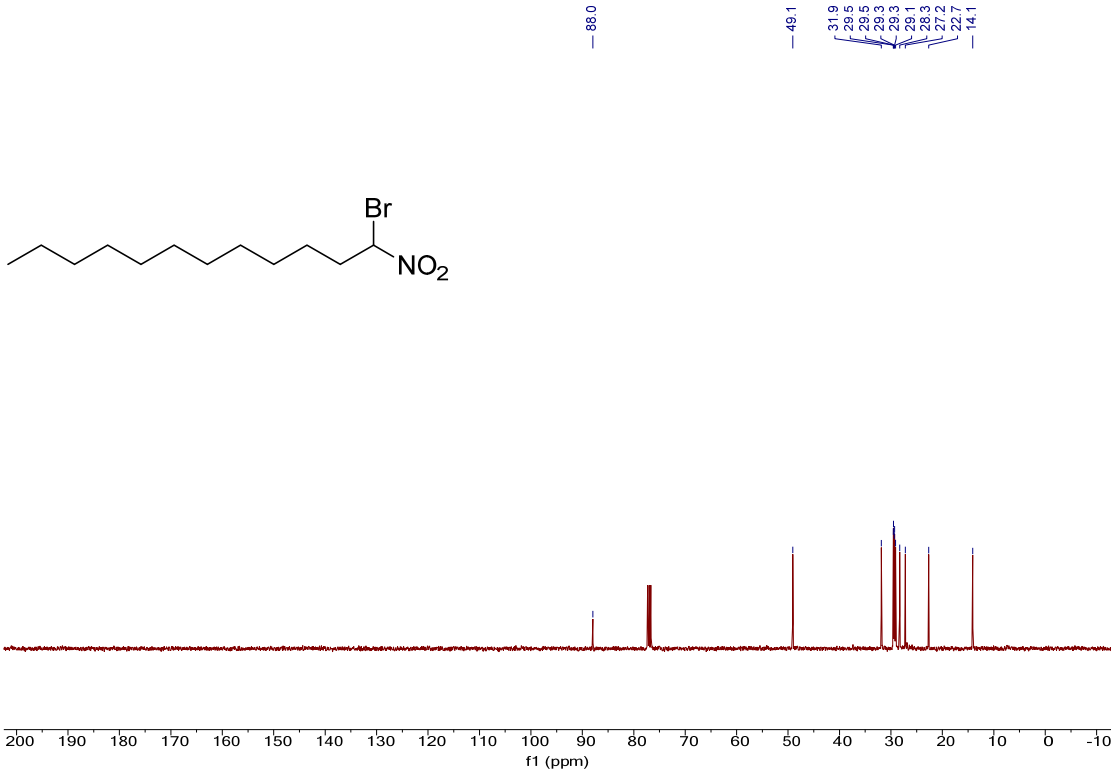

7.66
7.66
7.64
7.47
7.46
7.44
6.91
1.58
0.91
Br
NO2
2.09
3.10
1.00
f1 (ppm)


132.8
131.4
129.2
128.2
80.4
Br
NO2
f1 (ppm)

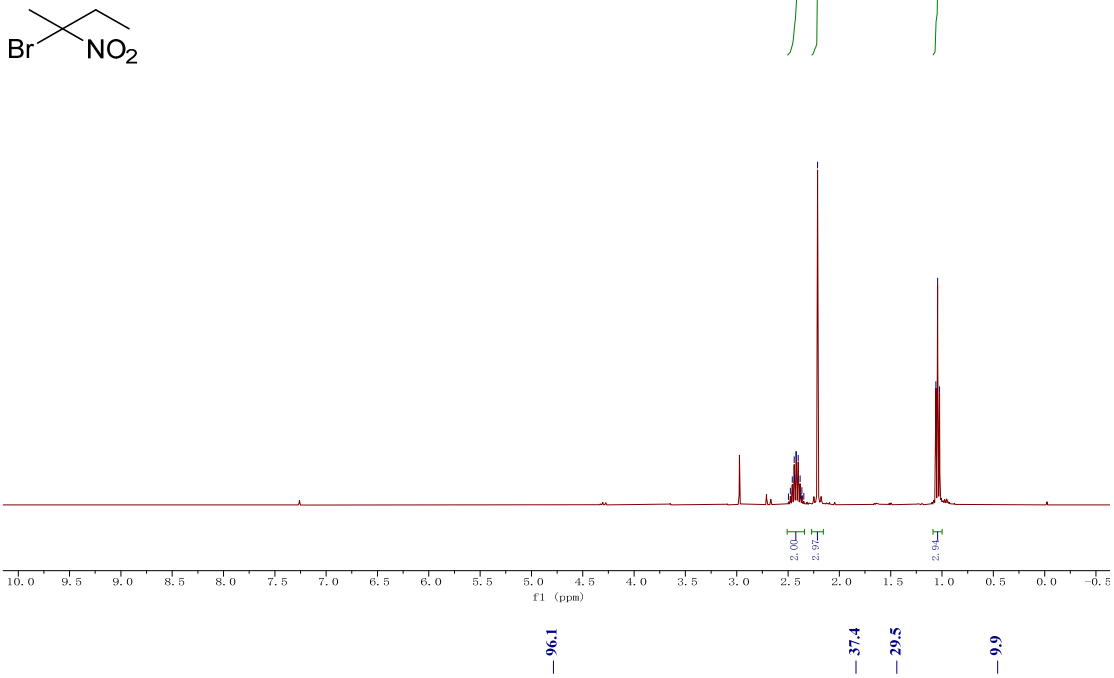

7.34
7.33
7.32
7.31
7.31
7.30
7.20
7.19
7.19
7.18
7.17
6.05
6.04
6.03
6.01
3.76
3.74
3.72
3.70
3.51
3.50
3.48
3.46
NO2
Br
3.00
2.01
0.90
1.00
1.00
f1 (ppm)
133.2
129.1
129.0
128.3
79.1
43.4
NO2
Br
f1 (ppm)

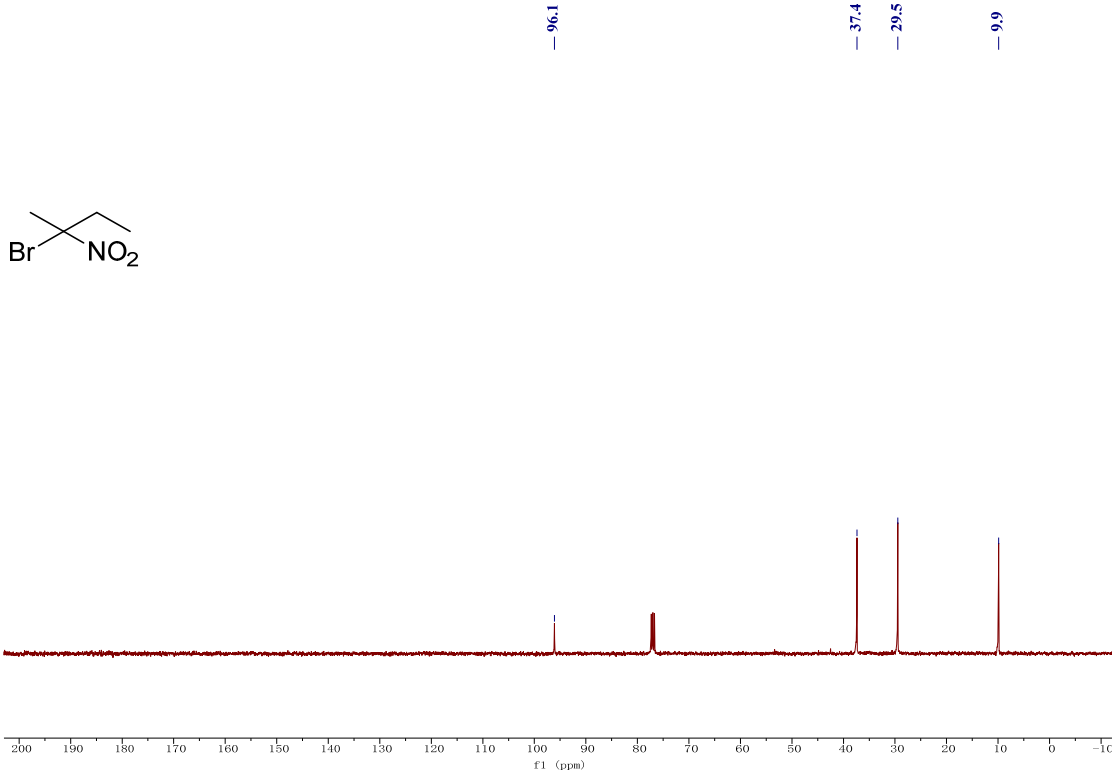

Br
NO2

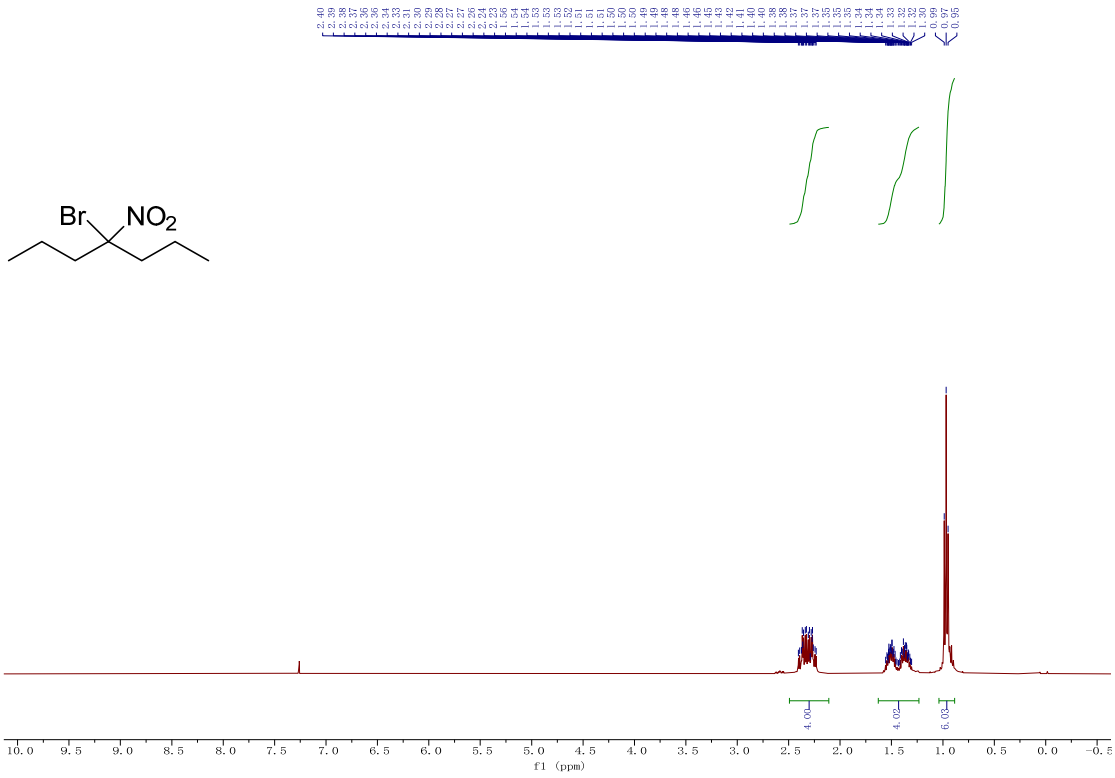
2.85
2.83
2.81
1.63
1.61
1.59
1.57
1.43
1.41
1.39
1.34
1.32
1.30
1.27
0.90
0.88
0.87
2.00
2.15
18.03
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

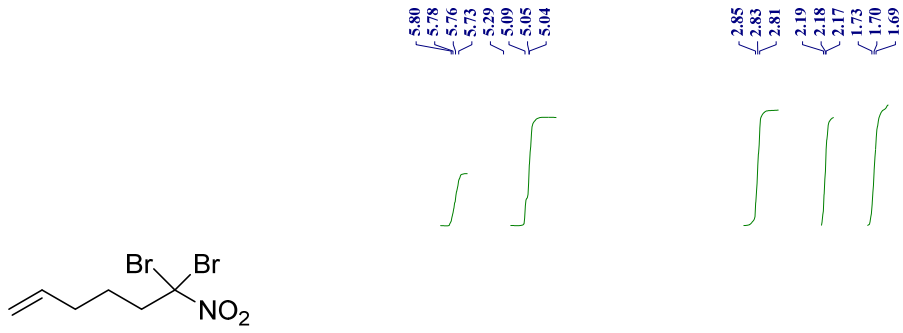

88.0
49.1
31.9
29.5
29.5
29.3
29.3
29.1
28.3
27.2
22.7
14.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Br
NO2

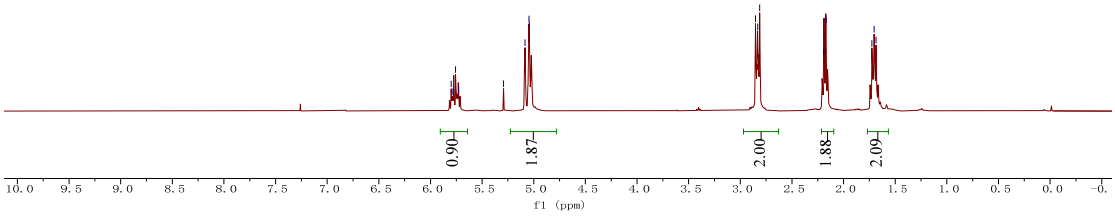

Br
NO2
2.50
2.48
2.46
2.44
2.42
2.40
2.38
2.37
2.35
2.33
2.21
1.06
1.04
1.02
2.00
2.97
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Br
NO2
96.1
37.4
29.5
9.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

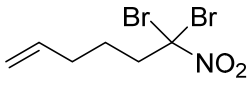

Br
NO2
4.00
4.02
6.03
f1 (ppm)

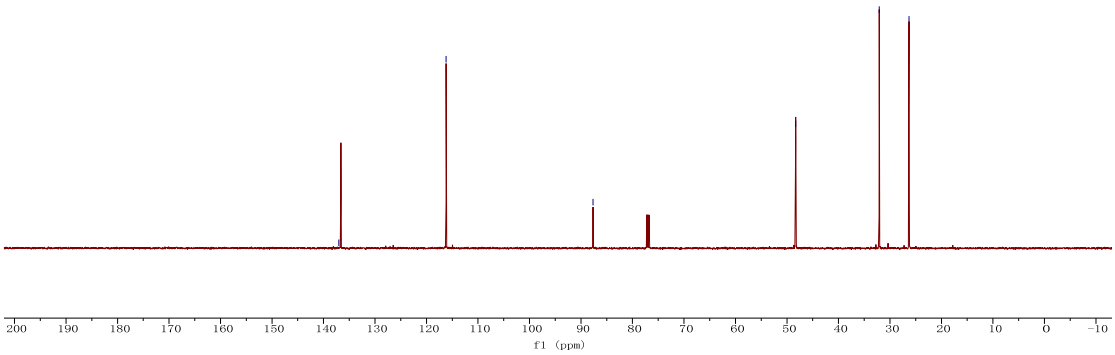

5.80
5.78
5.76
5.73
5.29
5.09
5.05
5.04
2.85
2.83
2.81
2.19
2.18
2.17
1.73
1.70
1.69

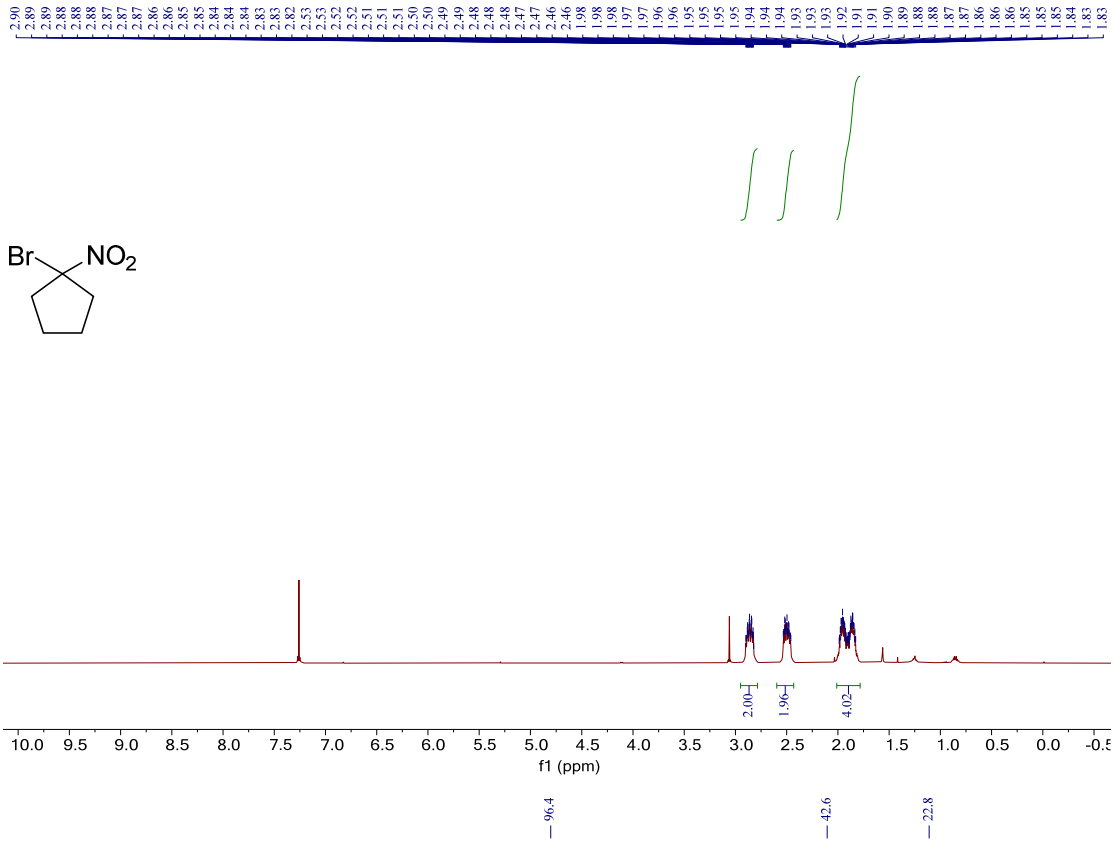
Br
Br
NO2

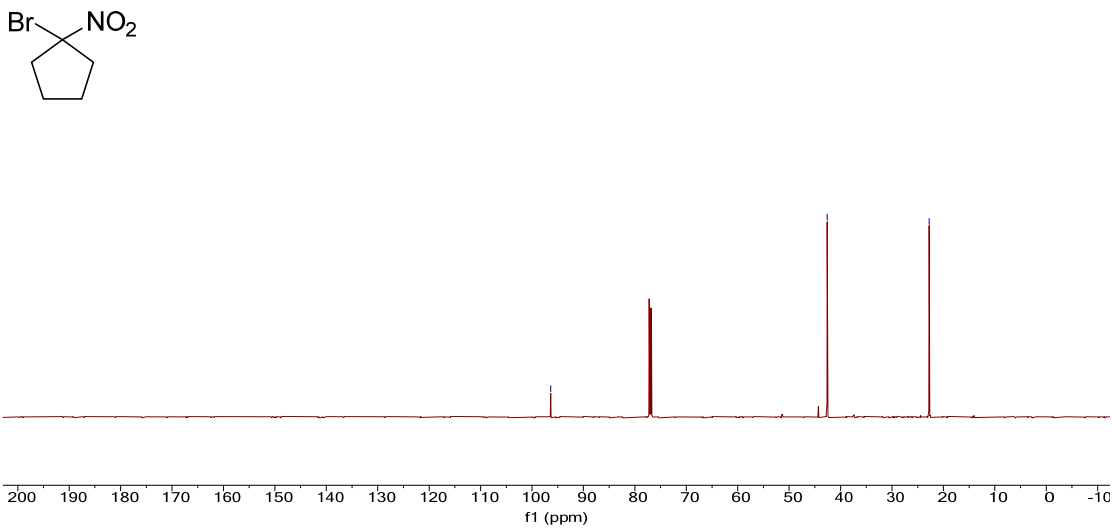

0.90
1.87
2.00
1.88
2.09
f1 (ppm)

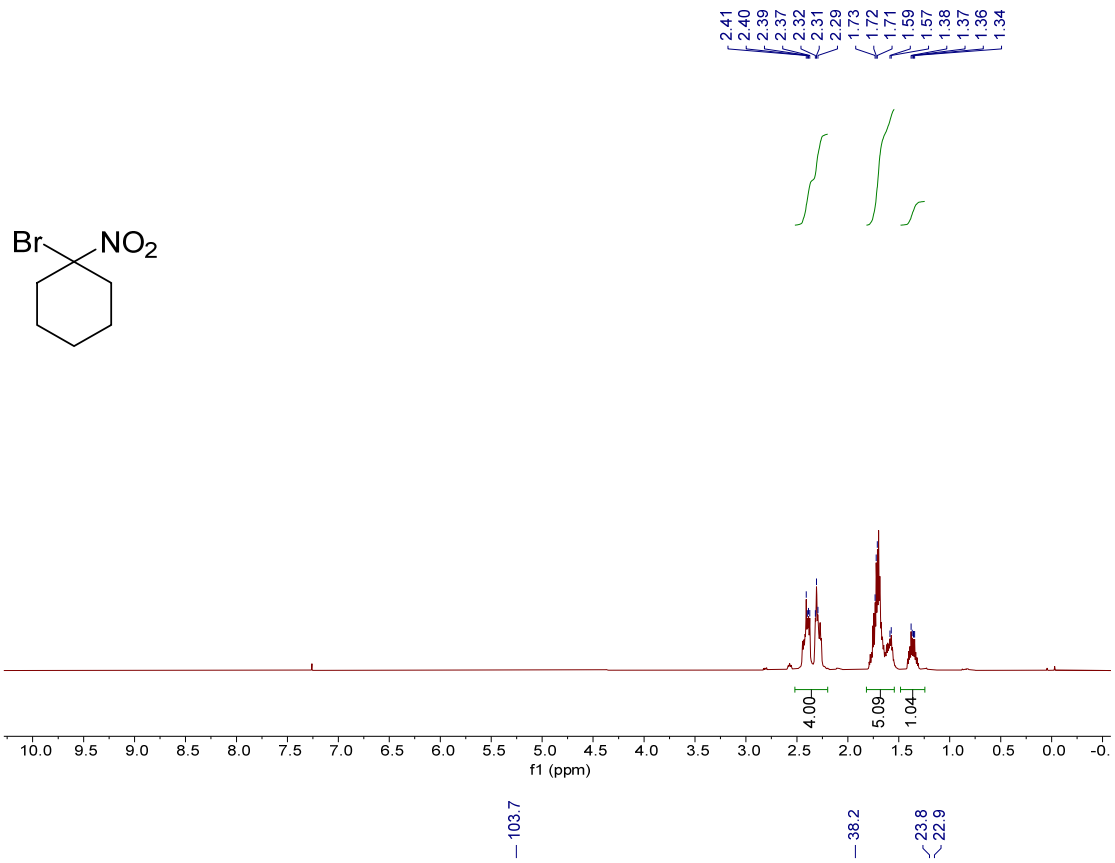

137.0
116.2
87.7
48.3
32.1
26.3

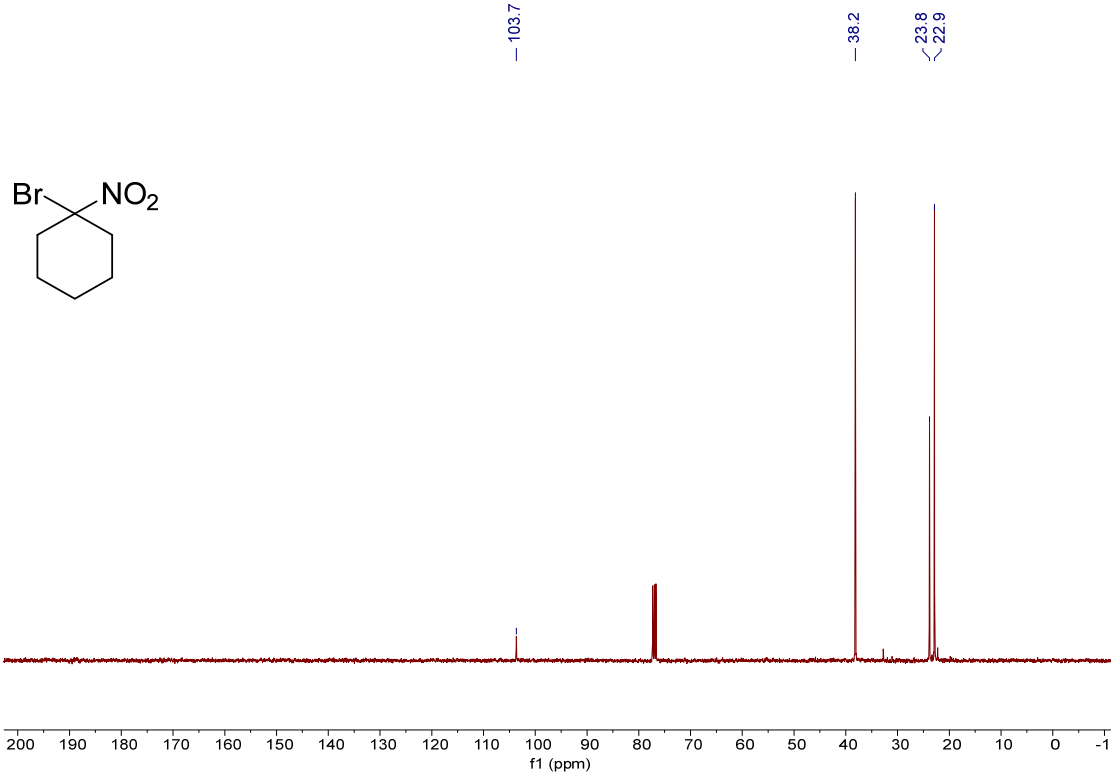

Br
Br
NO2

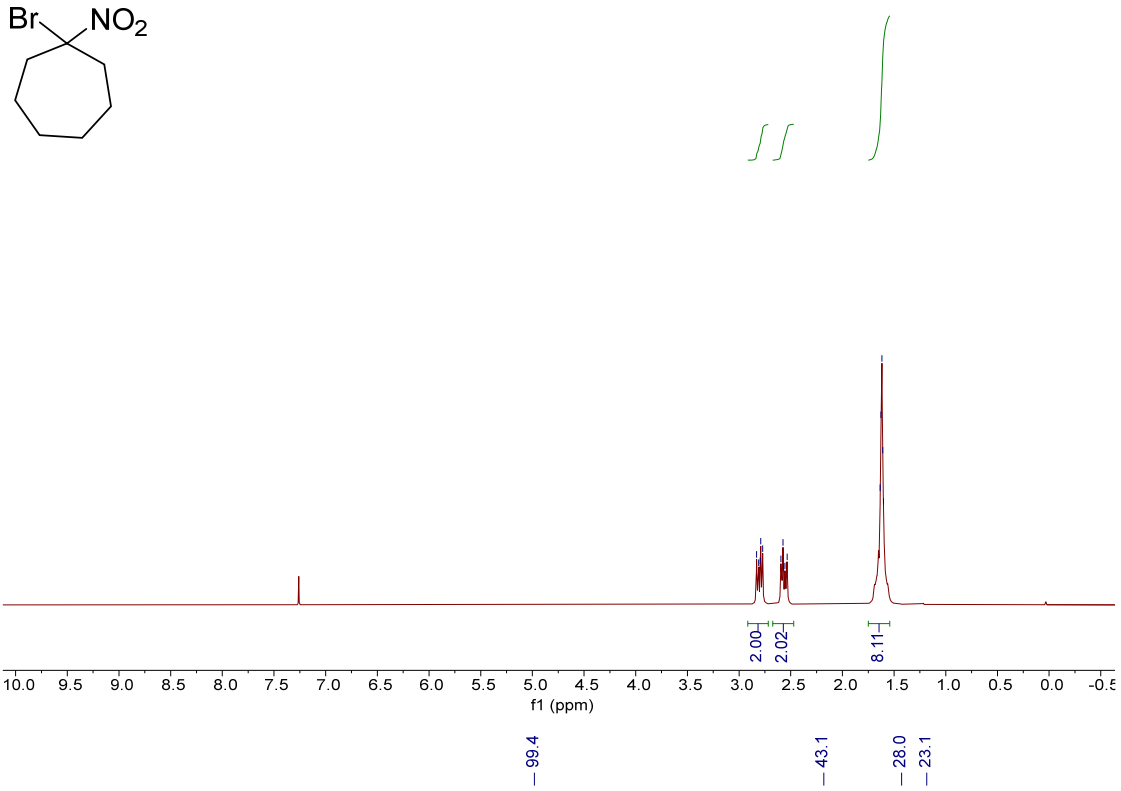

f1 (ppm)

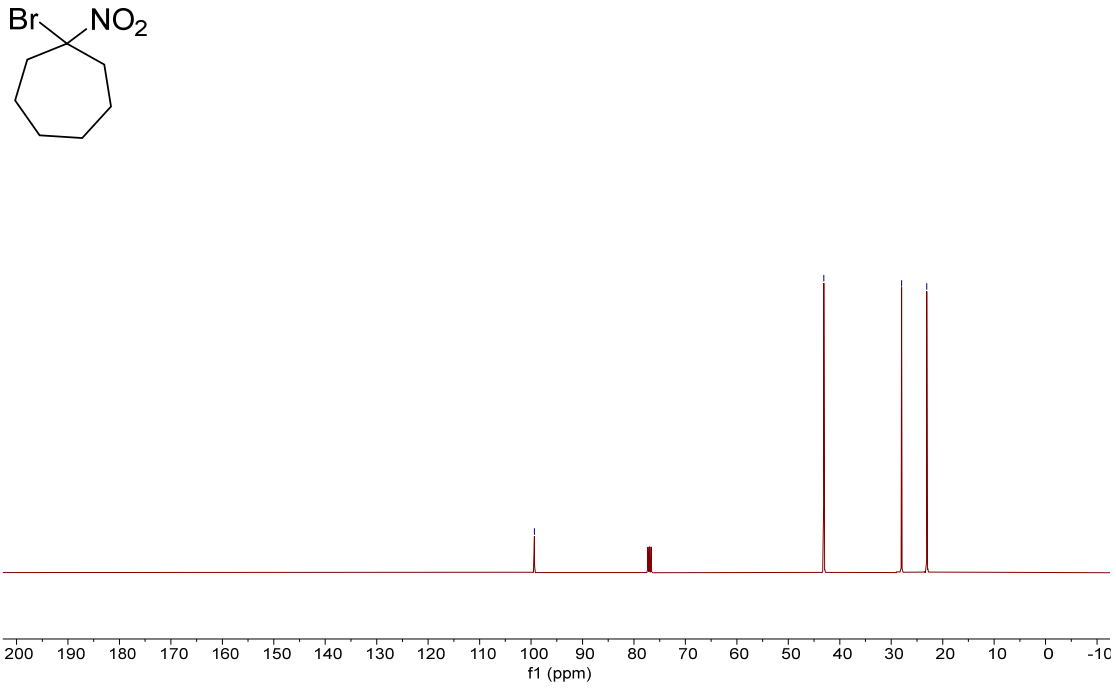

Br
NO2
2.00
1.96
4.02
f1 (ppm)

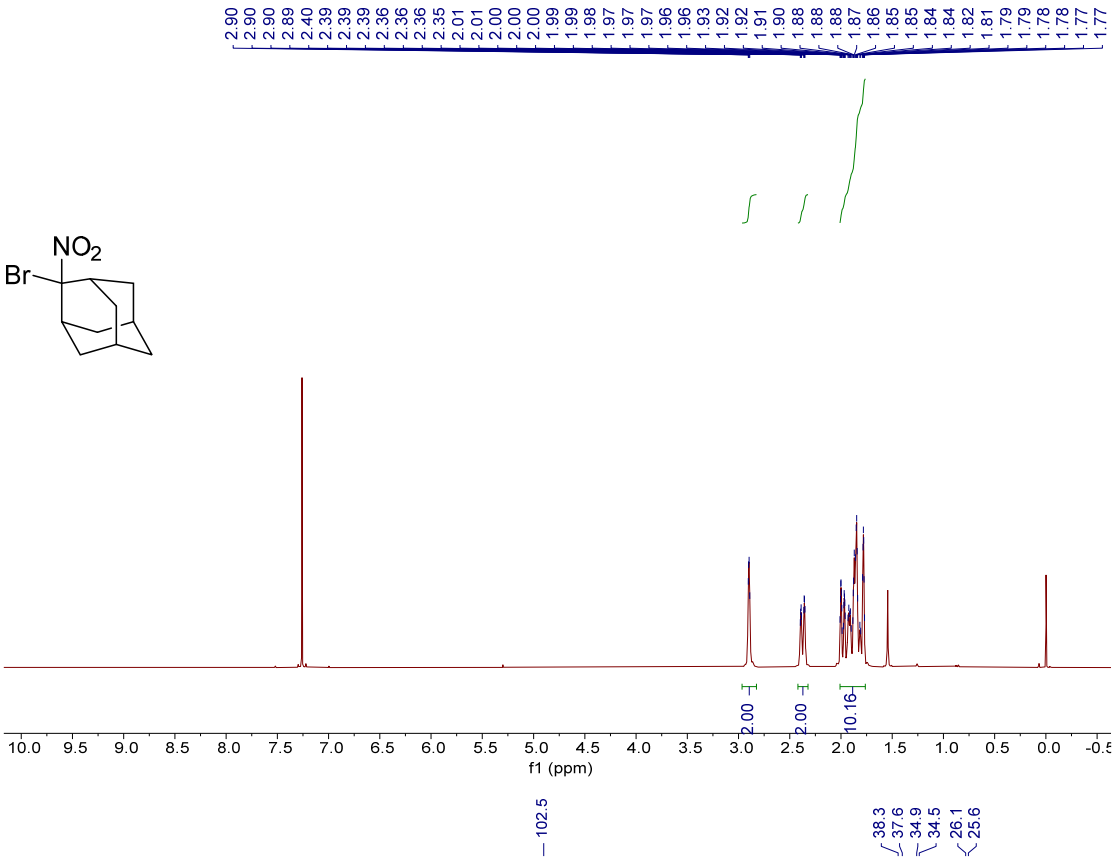

96.4
42.6
22.8
f1 (ppm)

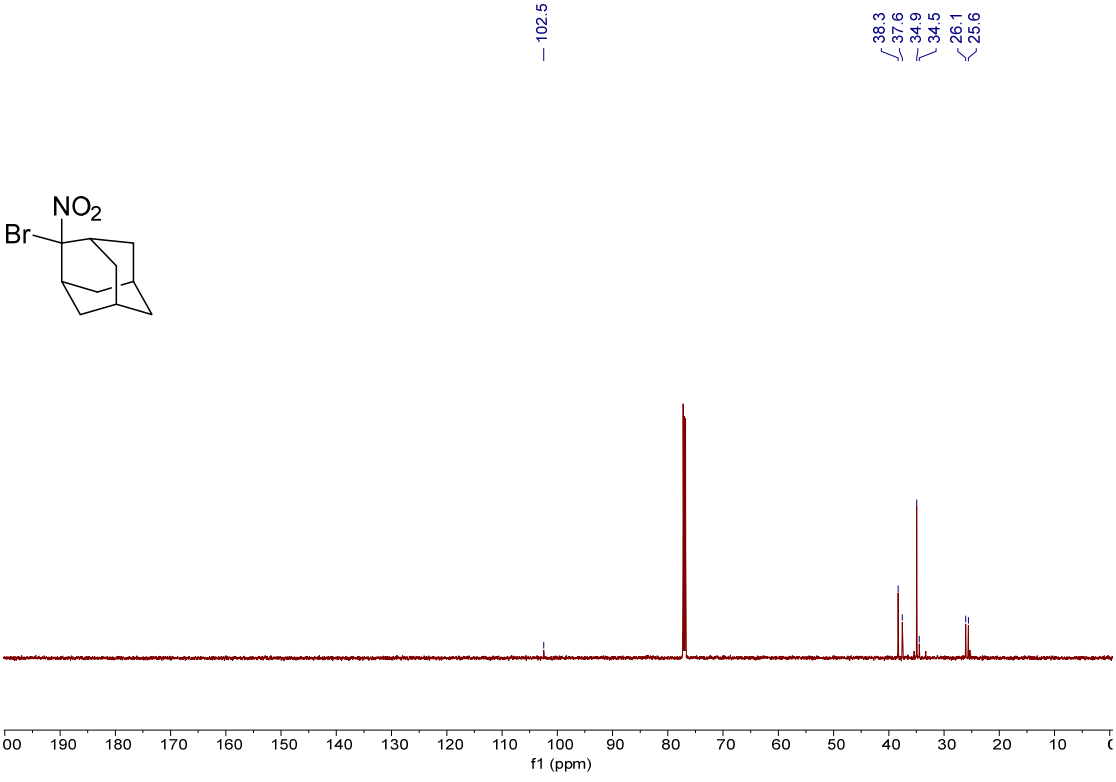

2.41
2.40
2.39
2.37
2.32
2.31
2.29
1.73
1.72
1.71
1.59
1.57
1.38
1.37
1.36
1.34
Br
NO2
4.00
5.09
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

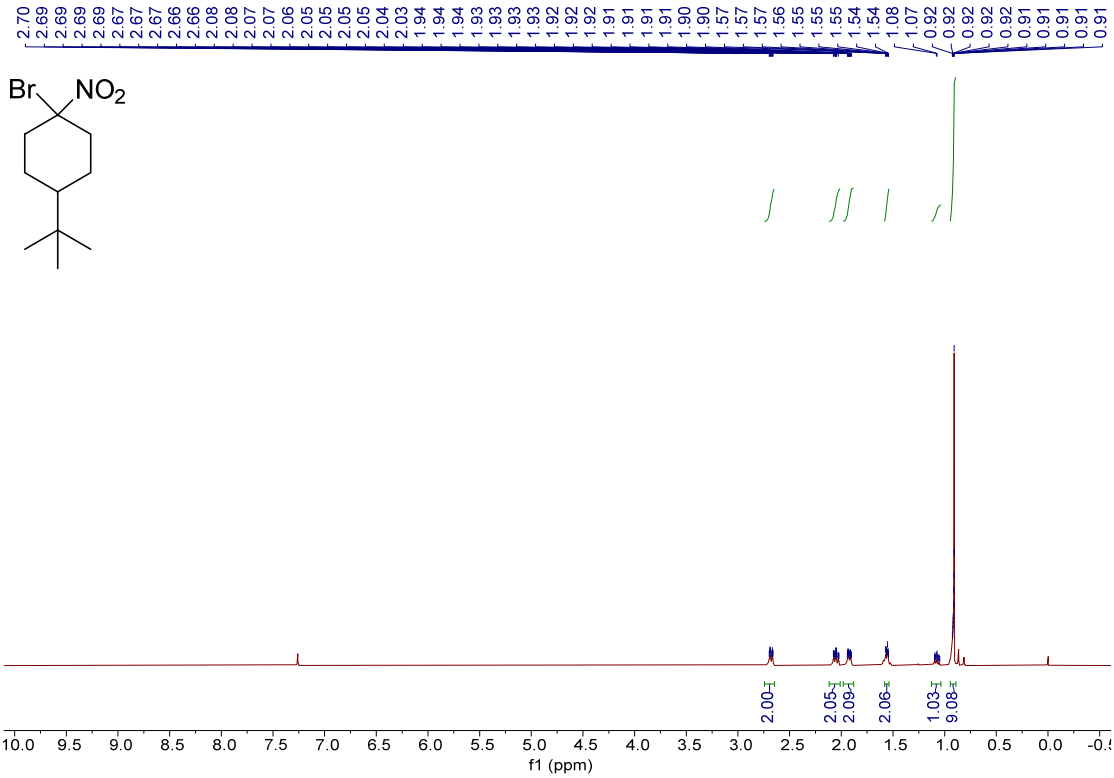

103.7
38.2
23.8
22.9
Br
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

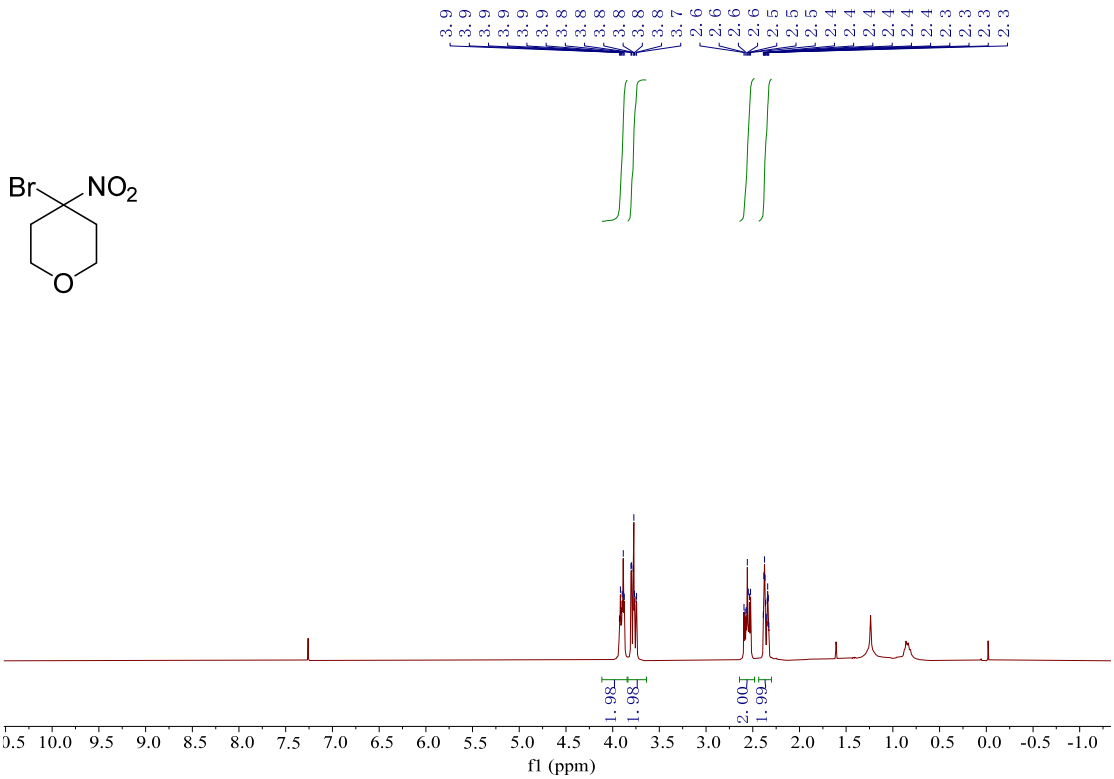

Br
NO2
2.83
2.81
2.80
2.79
2.77
2.59
2.58
2.57
2.56
2.54
1.63
1.62
1.61
1.60
2.00
2.02
8.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

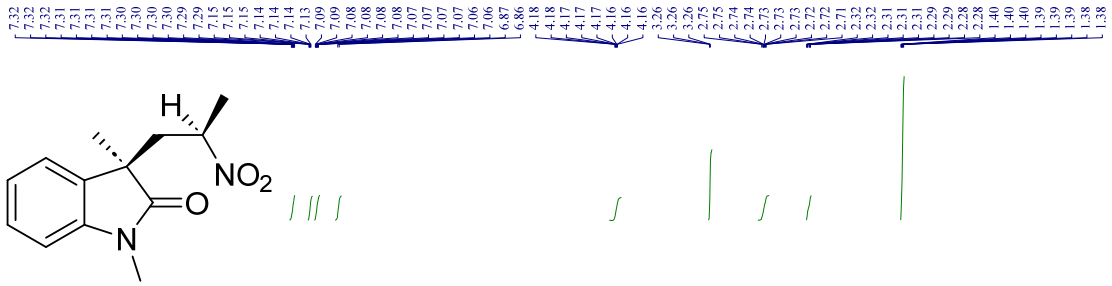

Br
NO2
99.4
43.1
28.0
23.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2.90 2.90 2.90 2.89 2.40 2.39 2.39 2.39 2.36 2.36 2.36 2.35 2.01 2.01 2.00 2.00 2.00 1.99 1.99 1.98 1.97 1.97 1.97 1.96 1.96 1.93 1.92 1.92 1.91 1.90 1.88 1.88 1.87 1.86 1.85 1.85 1.84 1.84 1.82 1.81 1.79 1.79 1.78 1.78 1.77 1.77
NO2
Br
2.00
2.00
10.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

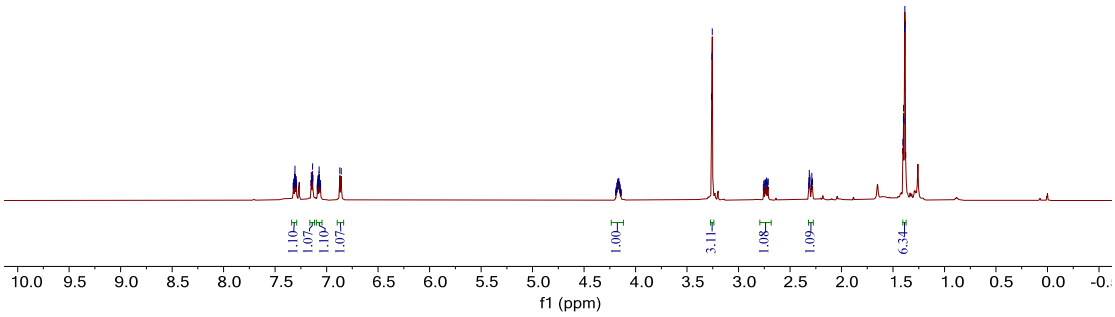

102.5
38.3
37.6
34.9
34.5
26.1
25.6
NO2
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Br
NO2
2.00
2.05
2.09
2.06
1.03
9.08
f1 (ppm)

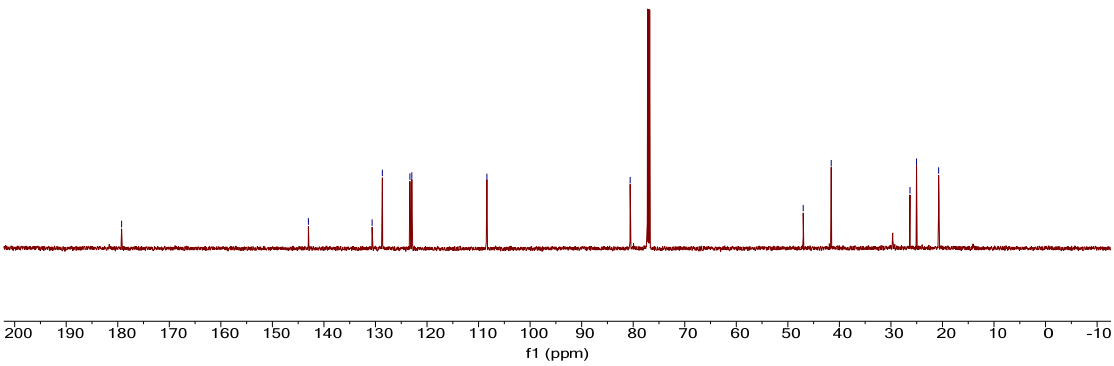

Br
NO2
O
1.98
1.98
2.00
1.99
f1 (ppm)

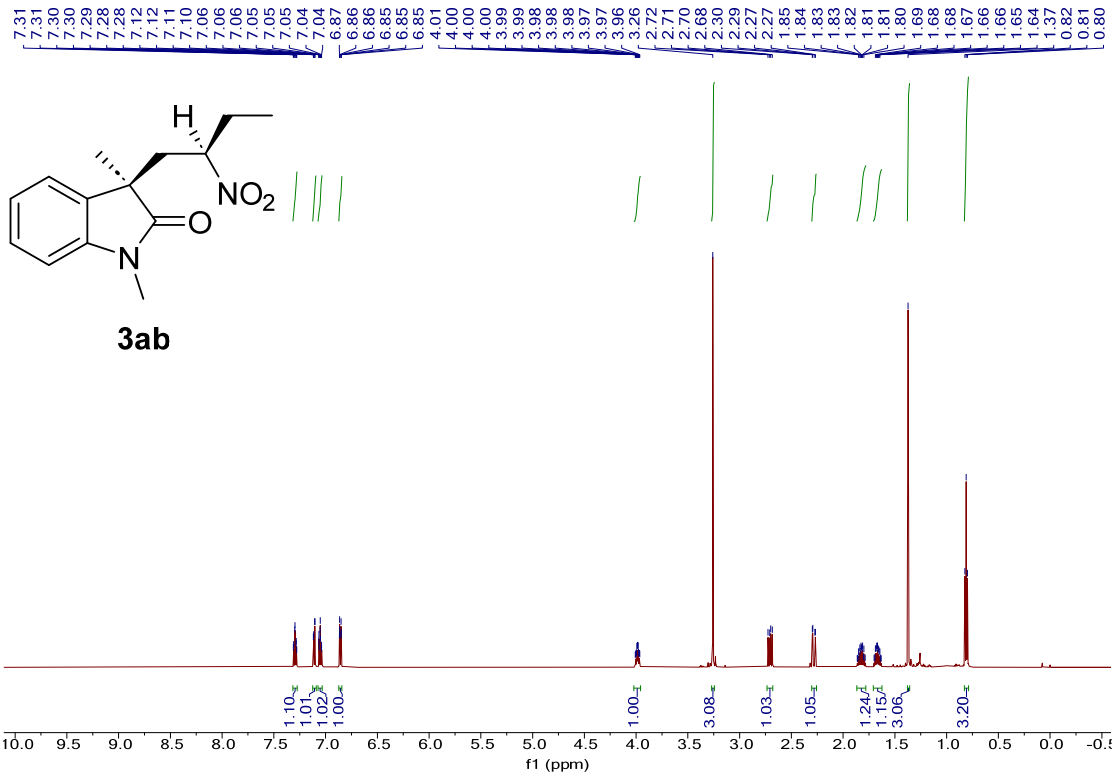


3aa

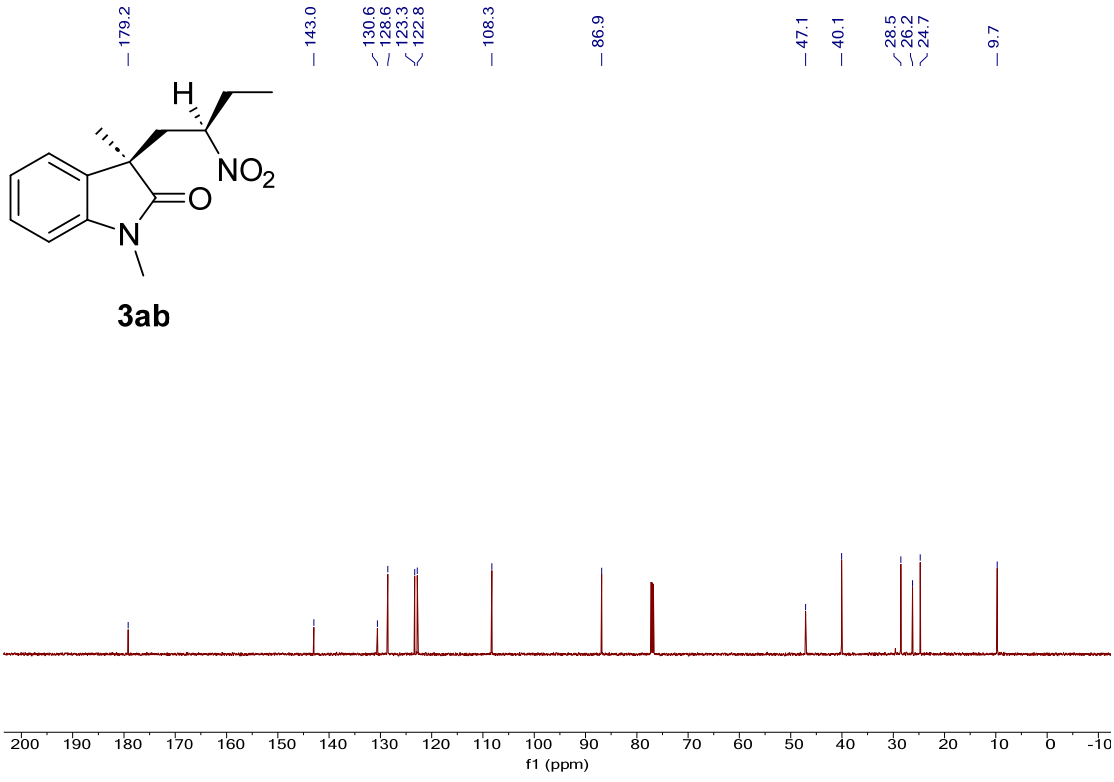


3aa

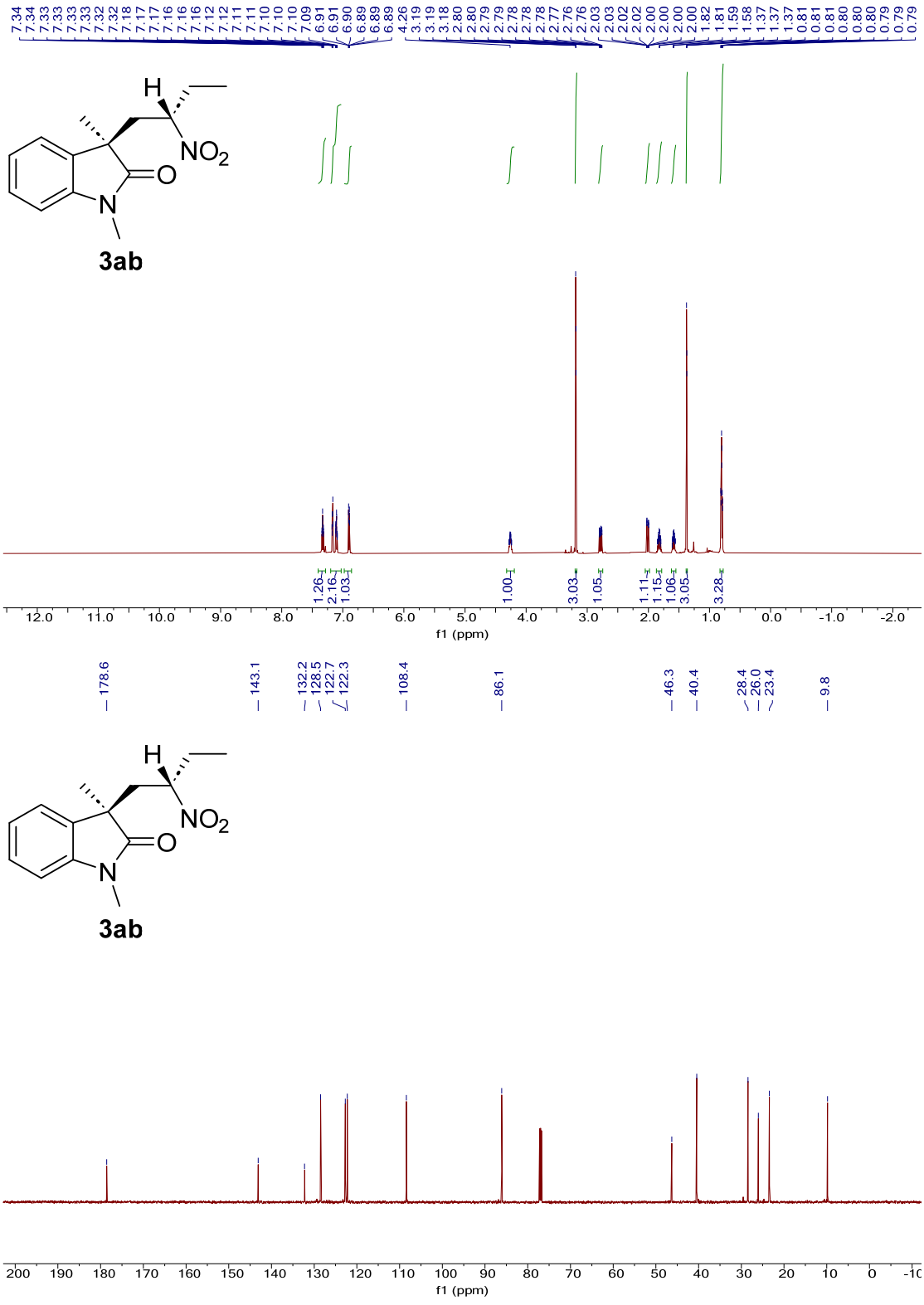


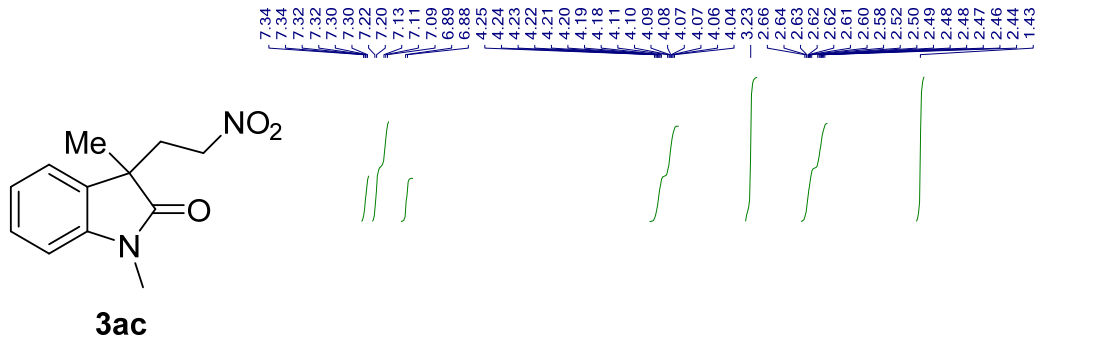

7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.12 7.12 7.11 7.10 7.06 7.06 7.06 7.05 7.05 7.04 7.04 6.87 6.86 6.86 6.85 6.85 6.85 4.01 4.00 4.00 4.00 3.99 3.99 3.98 3.98 3.97 3.97 3.96 3.26 2.72 2.71 2.70 2.68 2.30 2.29 2.27 2.27 1.85 1.84 1.83 1.82 1.81 1.81 1.80 1.69 1.68 1.68 1.67 1.66 1.66 1.65 1.64 1.37 0.82 0.81 0.80
H
NO2
O
N
1.10 1.01 1.02 1.00 1.00 3.08 1.03 1.05 1.24 1.15 3.06 3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ab

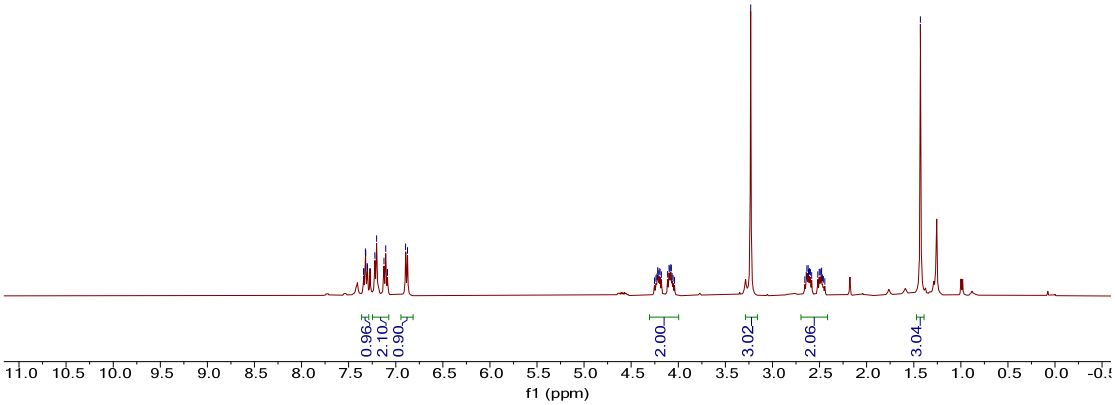

179.2 143.0 130.6 128.6 123.3 122.8 108.3 86.9 47.1 40.1 28.5 26.2 24.7 9.7
H
NO2
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ab

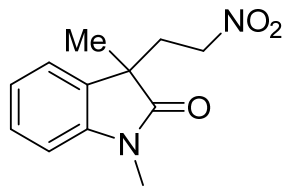

7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.18 7.17 7.17 7.16 7.16 7.16 7.12 7.11 7.11 7.10 7.10 7.10 7.09 6.91 6.91 6.90 6.89 6.89 6.89 4.26 3.19 3.19 3.18 2.80 2.80 2.79 2.79 2.78 2.78 2.78 2.77 2.76 2.76 2.03 2.03 2.02 2.02 2.00 2.00 2.00 2.00 1.82 1.81 1.59 1.58 1.37 1.37 1.37 0.81 0.81 0.81 0.80 0.80 0.80 0.80 0.79 0.79 0.79
H
NO2
O
N
3ab
1.26 2.16 1.03 1.00 3.03 1.05 1.11 1.15 1.06 3.05 3.28
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)
178.6 143.1 132.2 128.5 122.7 122.3 108.4 86.1 46.3 40.4 28.4 26.0 23.4 9.8
H
NO2
O
N
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.34
7.34
7.32
7.30
7.30
7.22
7.20
7.13
7.11
7.09
6.89
6.88
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.11
4.10
4.09
4.08
4.07
4.07
4.06
4.04
3.23
2.66
2.64
2.63
2.62
2.62
2.61
2.60
2.58
2.52
2.50
2.49
2.48
2.48
2.47
2.46
2.44
1.43
Me
NO2
O
N

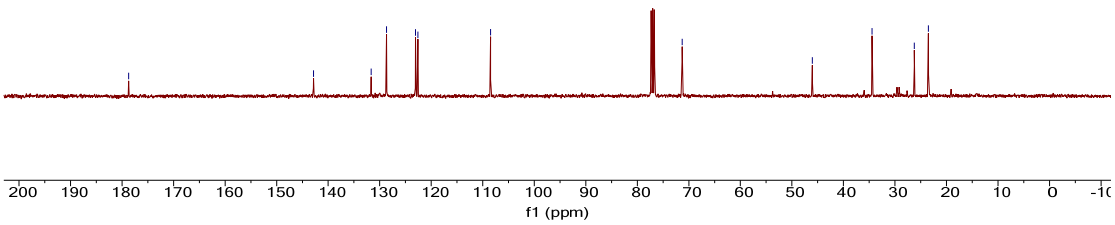
3ac


0.96
2.10
0.90
2.00
3.02
2.06
3.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.7
142.8
131.7
128.7
123.1
122.6
108.5
71.3
46.0
34.4
26.2
23.5


Me
NO2
O
N

3ac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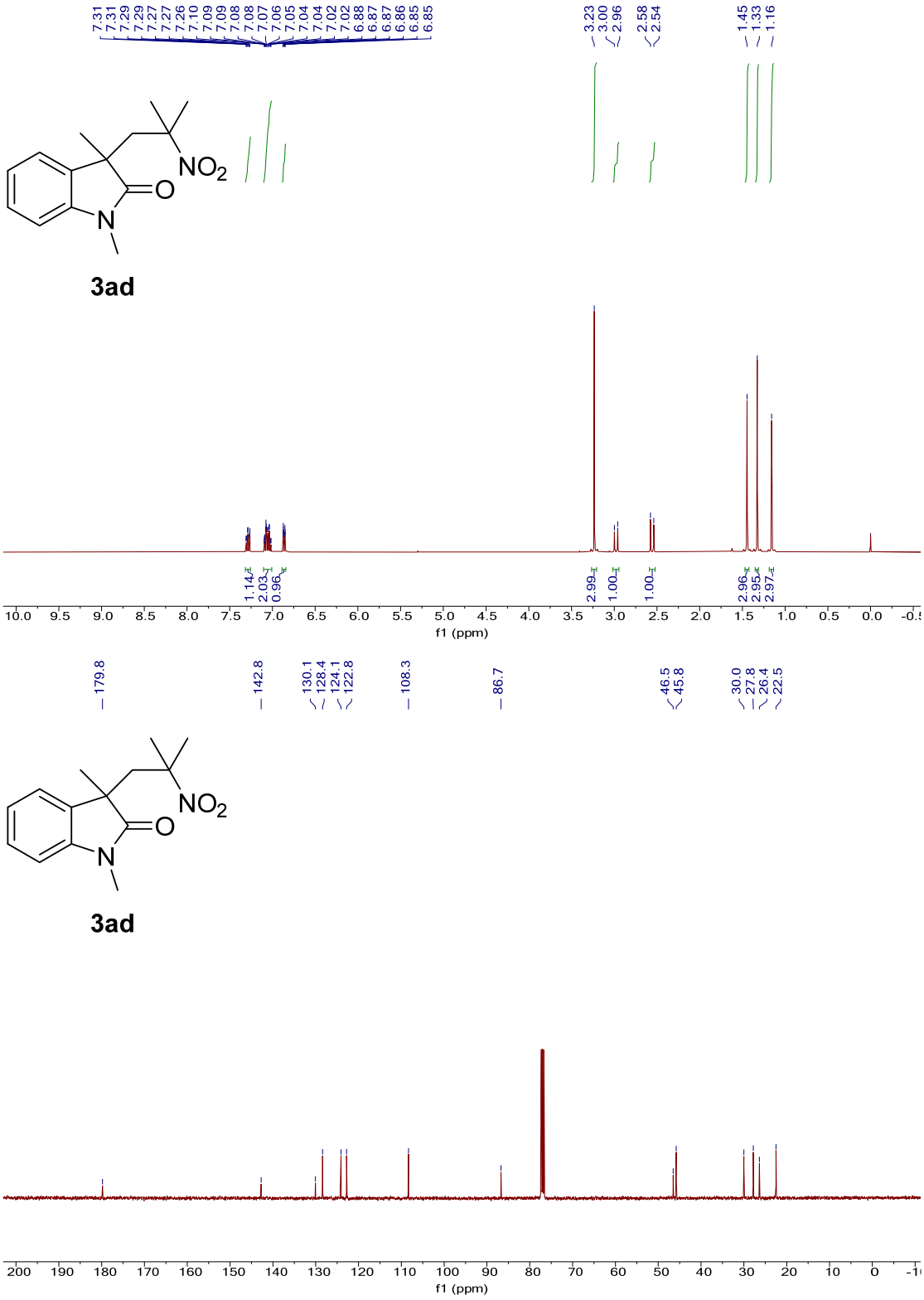
f1 (ppm)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7.10
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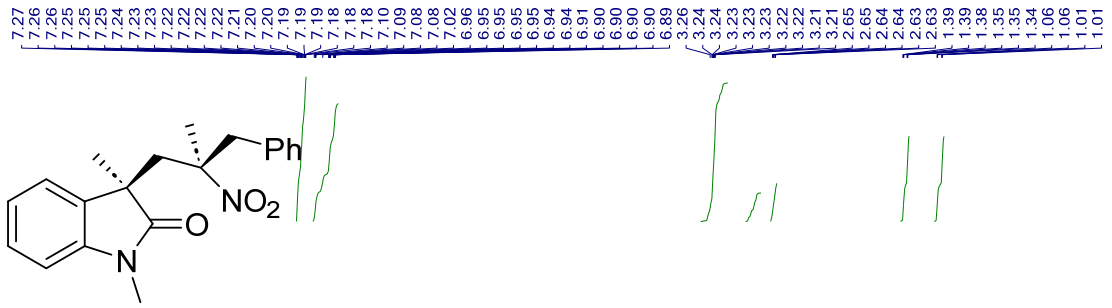
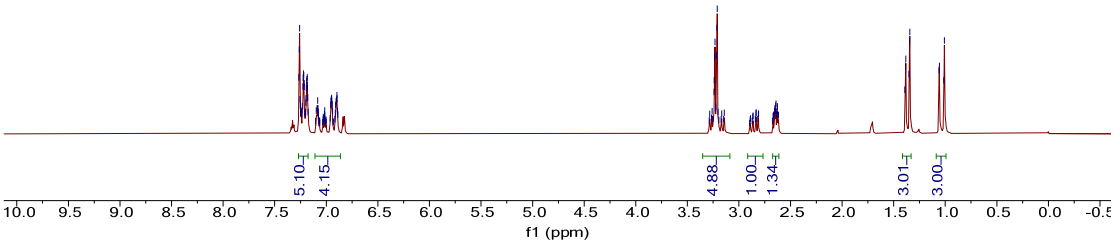
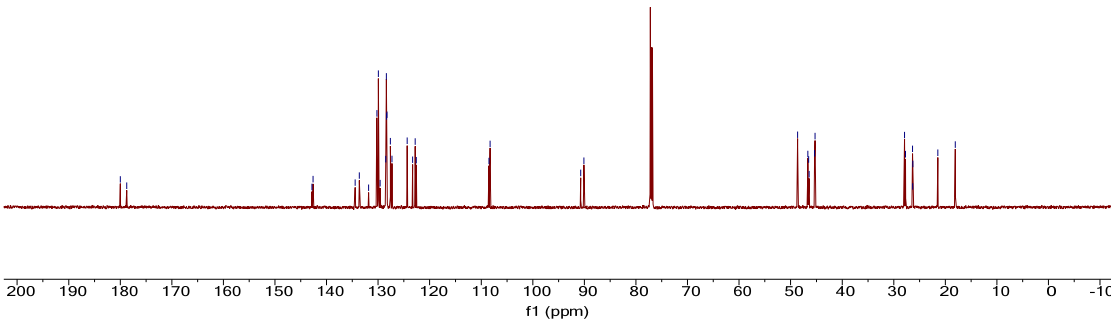
7.09
7.08
7.08
7.07
7.06
7.05
7.04
7.04
7.02
7.02
6.88
6.87
6.86
6.85
6.85
3.23
3.00
2.96
2.58
2.54
1.45
1.33
1.16
NO2
O
N
3ad
1.14
2.03
0.96
2.99
1.00
1.00
2.96
2.95
2.97
f1 (ppm)
179.8
142.8
130.1
128.4
124.1
122.8
108.3
86.7
46.5
45.8
30.0
27.8
26.4
22.5
NO2
O
N
3ad
f1 (ppm)

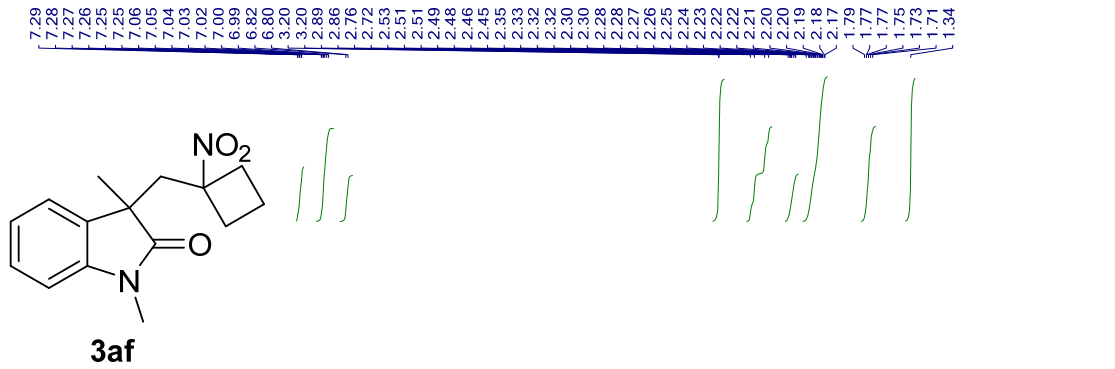


3ae



3ae

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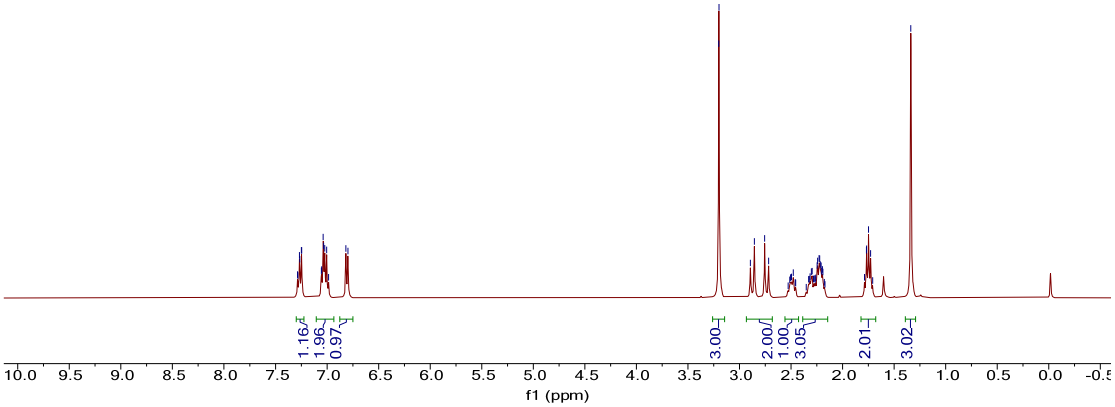
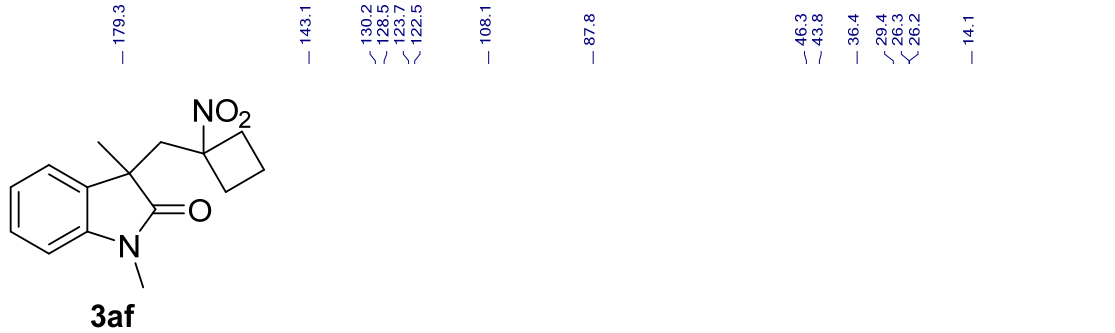
7.05
7.04
7.03
7.02
7.00
6.99
6.82
6.80
3.20
2.89
2.86
2.76
2.72
2.53
2.51
2.49
2.48
2.46
2.45
2.35
2.33
2.32
2.30
2.30
2.28
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.22
2.21
2.20
2.20
2.19
2.18
2.17
1.79
1.77
1.77
1.75
1.73
1.71
1.34
NO2
O
N

3af


1.16
1.96
0.97
3.00
2.00
1.00
3.05
2.01
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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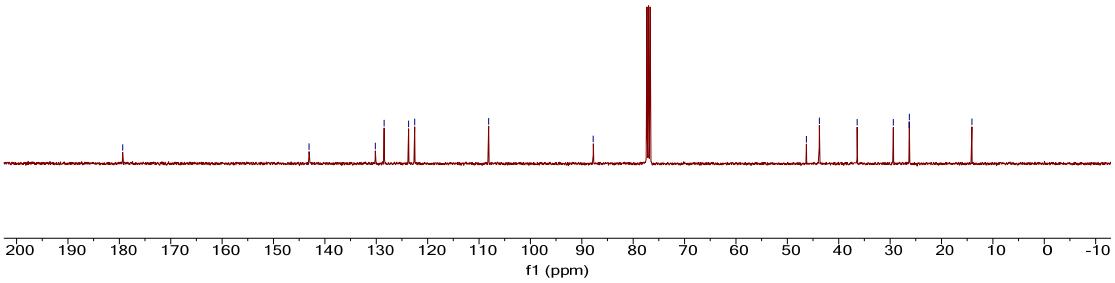
143.1
130.2
128.5
123.7
122.5
108.1
87.8
46.3
43.8
36.4
29.4
26.3
26.2
14.1
NO2
O
N

3af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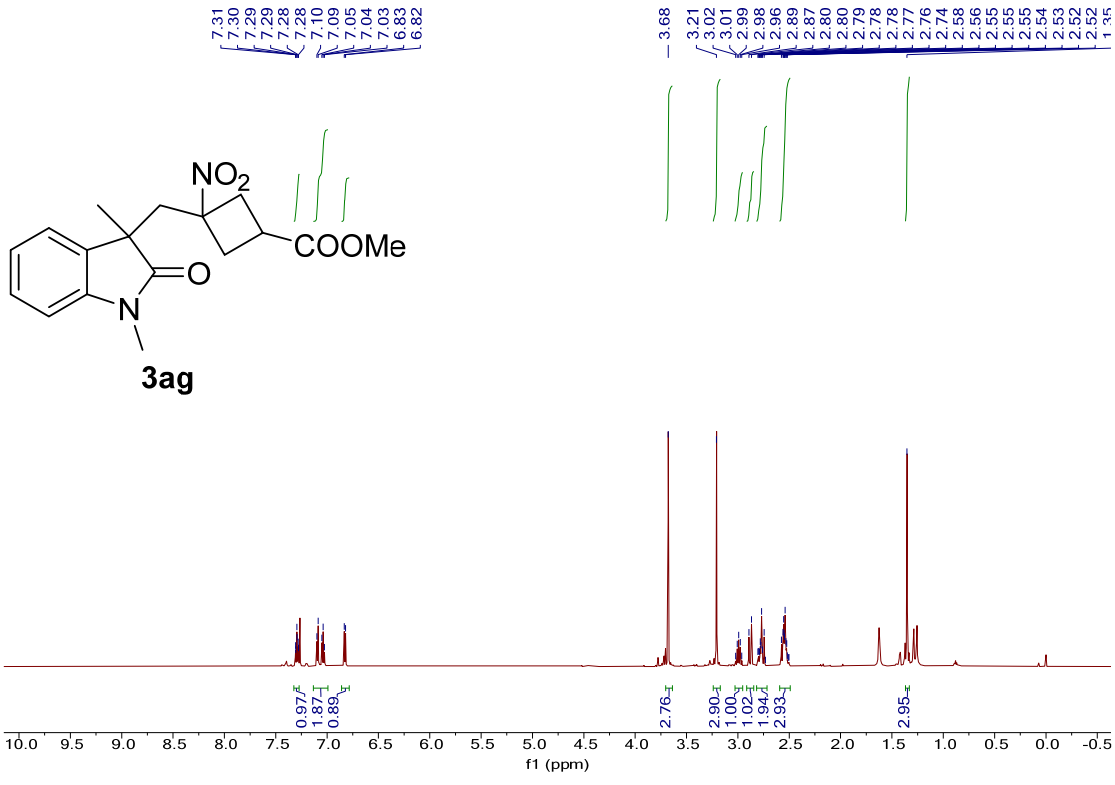
f1 (ppm)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7.30
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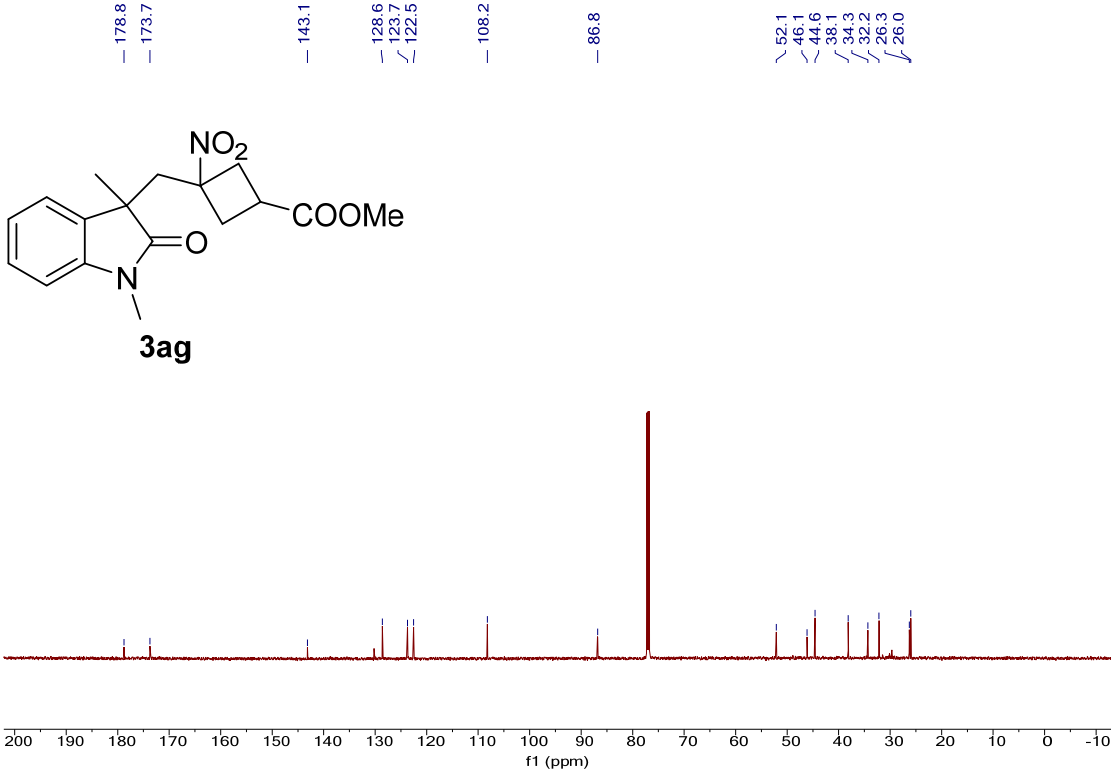
7.29
7.28
7.10
7.09
7.05
7.04
7.03
6.83
6.82
3.68
3.21
3.02
3.01
2.99
2.98
2.96
2.89
2.87
2.80
2.80
2.79
2.78
2.78
2.77
2.76
2.74
2.58
2.56
2.55
2.55
2.54
2.53
2.52
2.52
NO2
COOMe
O
N
0.97
1.87
0.89
2.76
2.90
1.00
1.02
1.94
2.93
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3ag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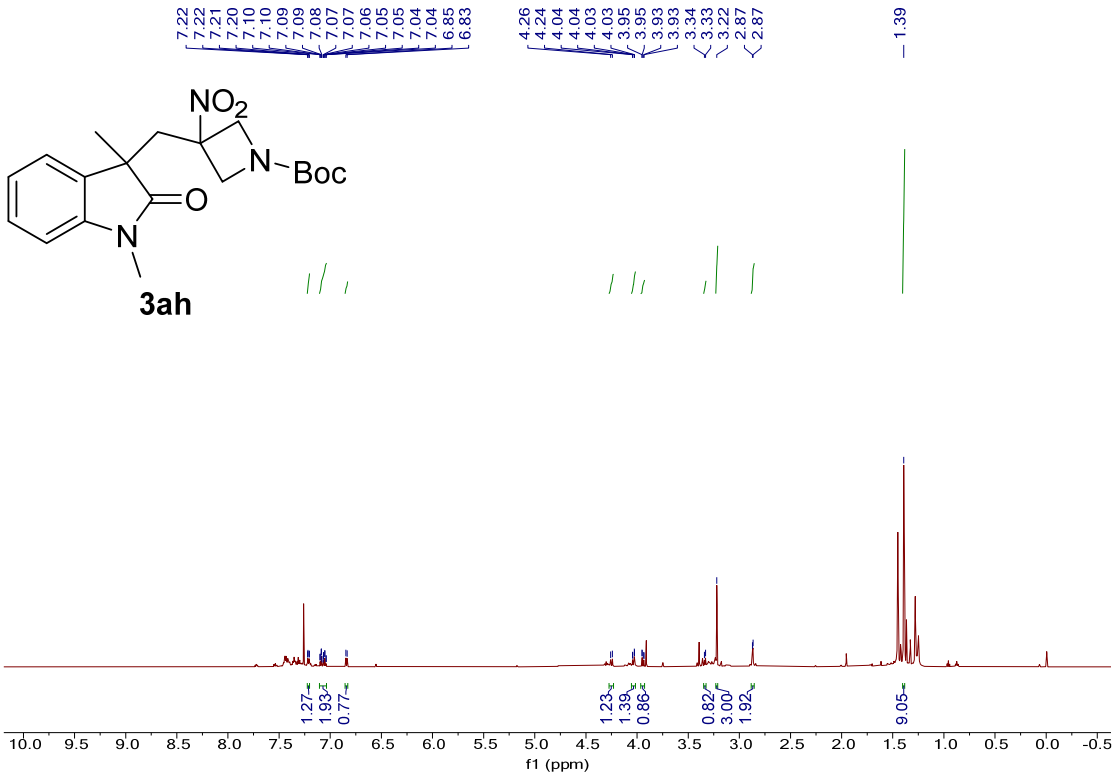
173.7
143.1
128.6
123.7
122.5
108.2
86.8
52.1
46.1
44.6
38.1
34.3
32.2
26.3
26.0
NO2
COOMe
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ag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7.09
7.09
7.08
7.07
7.07
7.06
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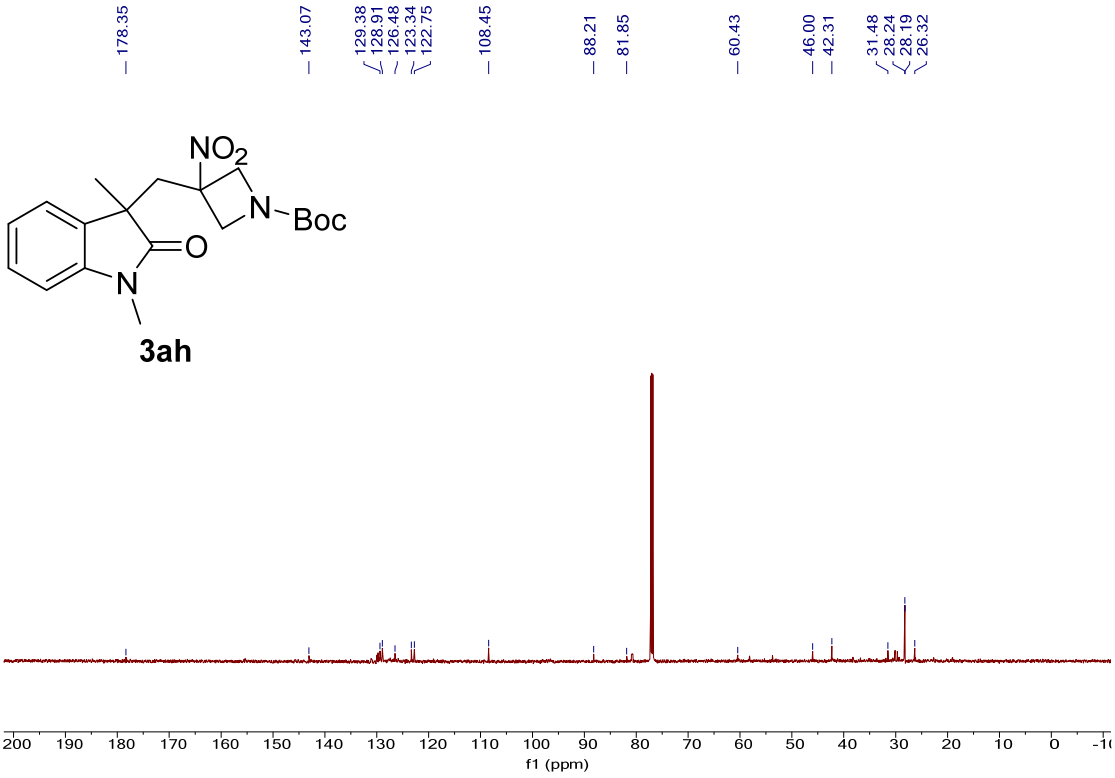
7.05
7.04
7.04
6.85
6.83
4.26
4.24
4.04
4.04
4.03
4.03
3.95
3.95
3.93
3.93
3.34
3.33
3.22
2.87
2.87
1.39
NO2
N
Boc
O
N
3ah
1.27
1.93
0.77
1.23
1.39
0.86
0.82
3.00
1.92
9.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.38
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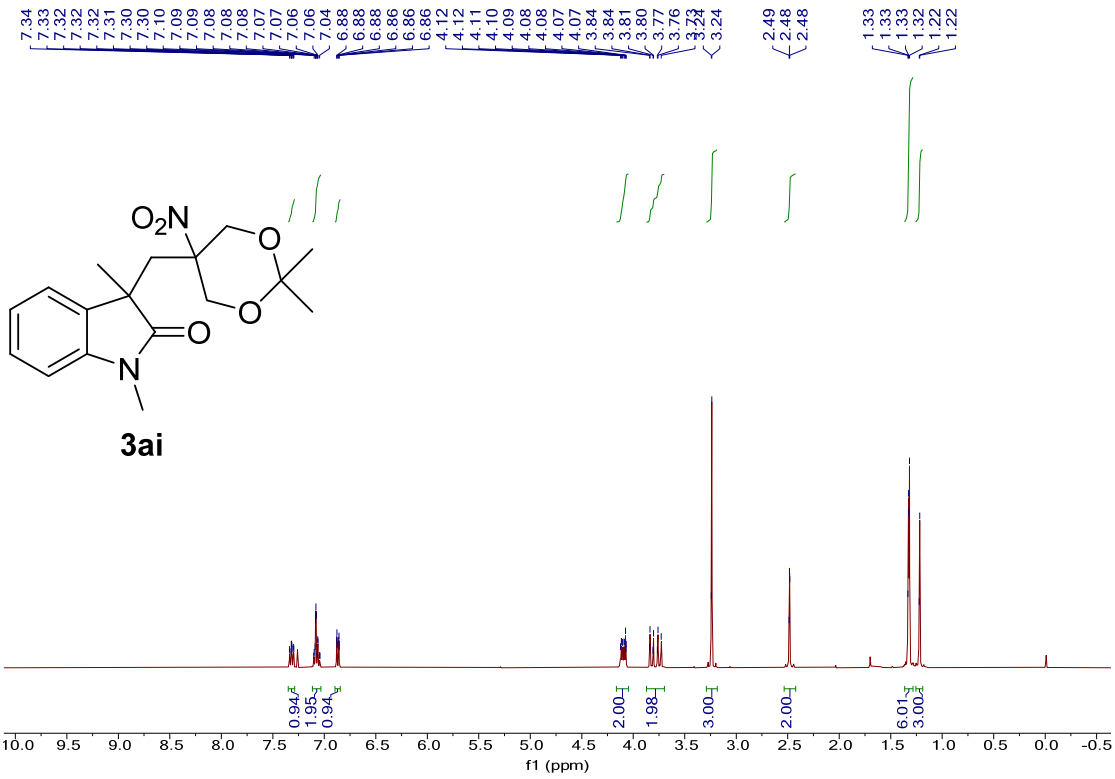
126.48
123.34
122.75
108.45
88.21
81.85
60.43
46.00
42.31
31.48
28.24
28.19
26.32
NO2
N
Boc
O
N
3ah
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.30
7.10
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7.09
7.08
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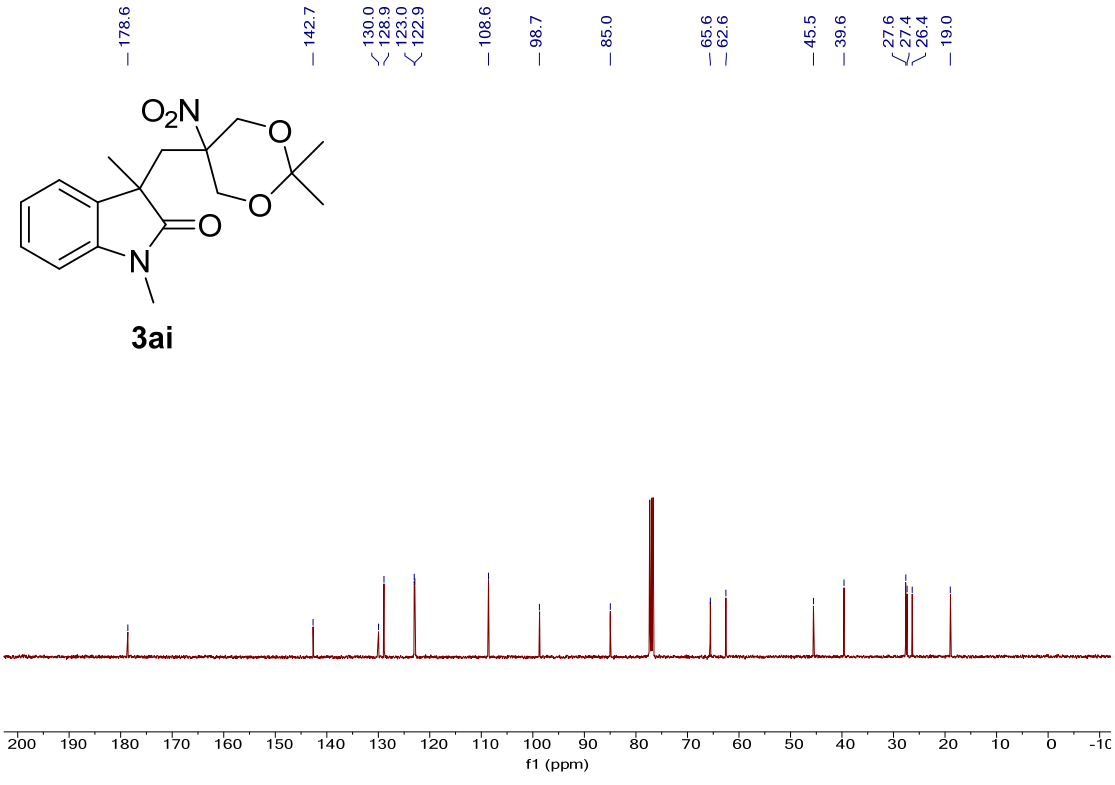
7.07
7.07
7.06
7.06
7.04
6.88
6.88
6.88
6.86
6.86
6.86
4.12
4.12
4.11
4.10
4.09
4.08
4.08
4.07
4.07
3.84
3.84
3.81
3.80
3.77
3.76
3.24
3.24
2.49
2.48
2.48
1.33
1.33
1.33
1.32
1.22
1.22
O2N
O
O
O
N
3ai
0.94
1.95
0.94
2.00
1.98
3.00
2.00
6.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


178.6
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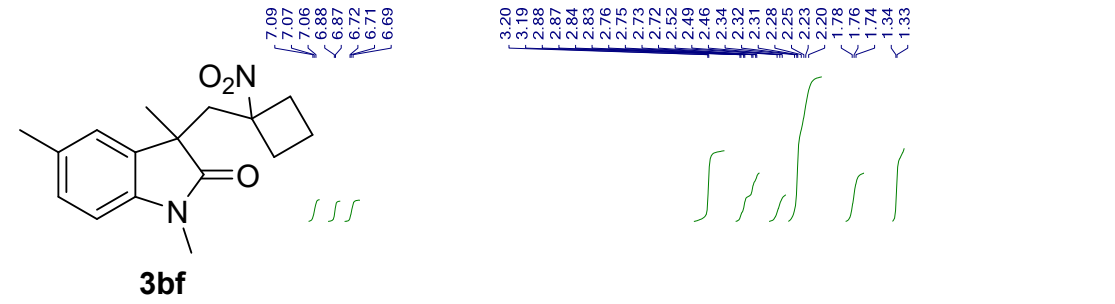
130.0
128.9
123.0
122.9
108.6
98.7
85.0
65.6
62.6
45.5
39.6
27.6
27.4
26.4
19.0
O2N
O
O
O
N
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.09
7.07
7.06
6.88
6.87
6.72
6.71
6.69
3.20
3.19
2.88
2.87
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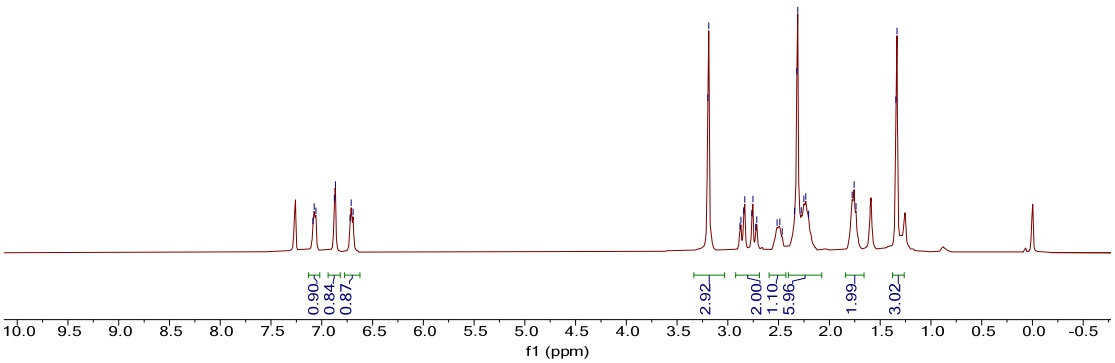
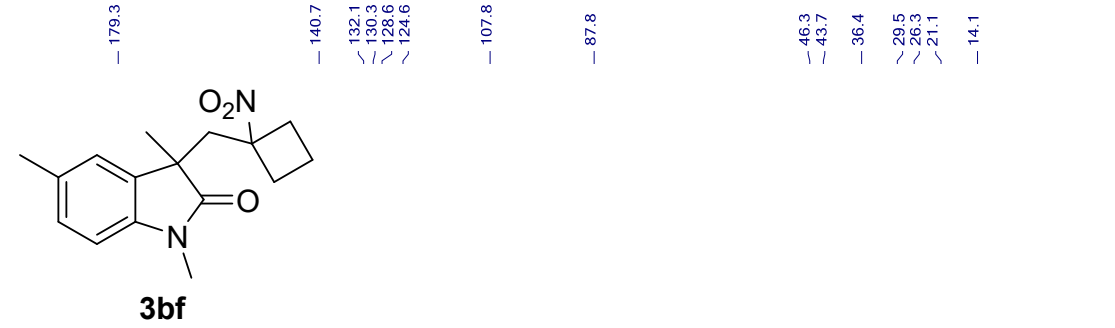
2.83
2.76
2.75
2.73
2.72
2.52
2.49
2.46
2.34
2.32
2.31
2.28
2.25
2.23
2.20
1.78
1.76
1.74
1.34
1.33
O2N
O
N

3bf


0.90
0.84
0.87
2.92
2.00
1.10
5.96
1.99
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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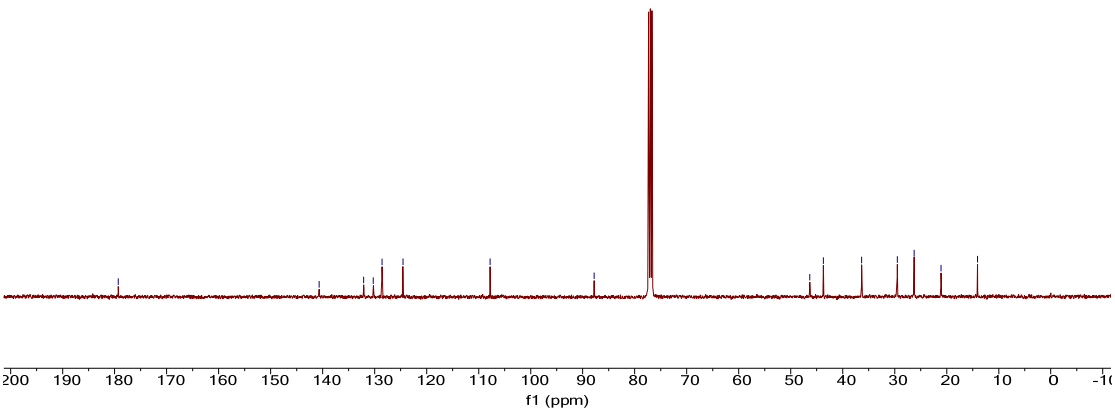
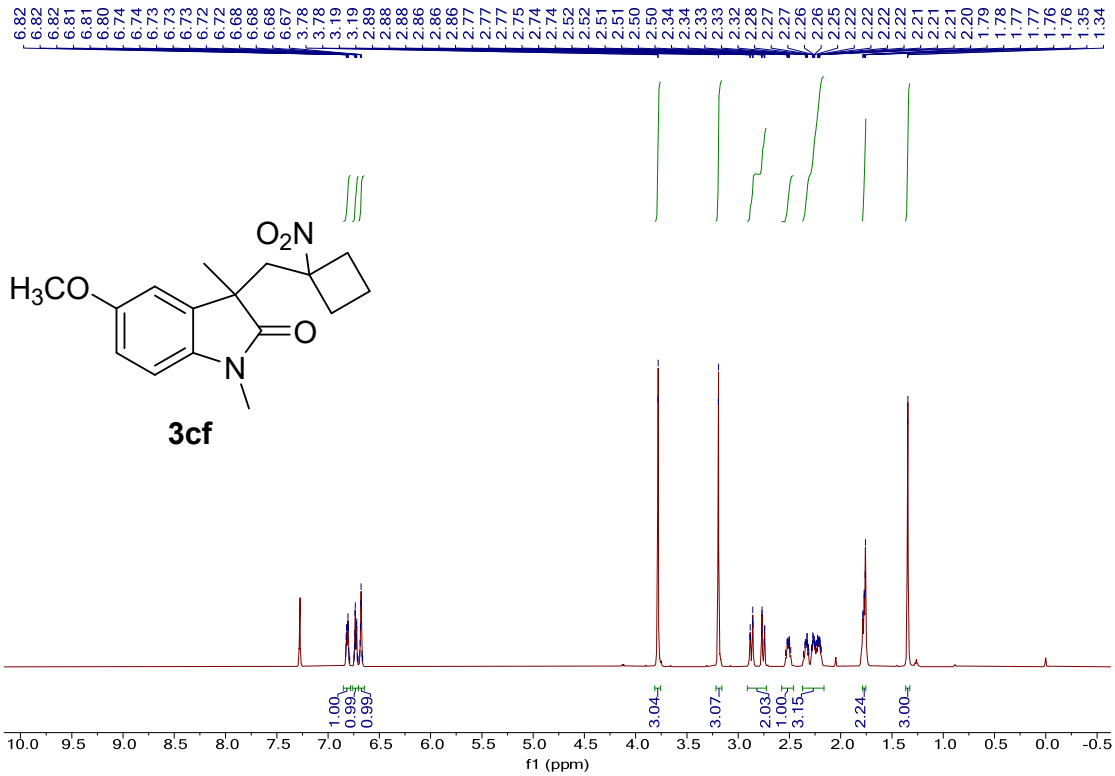
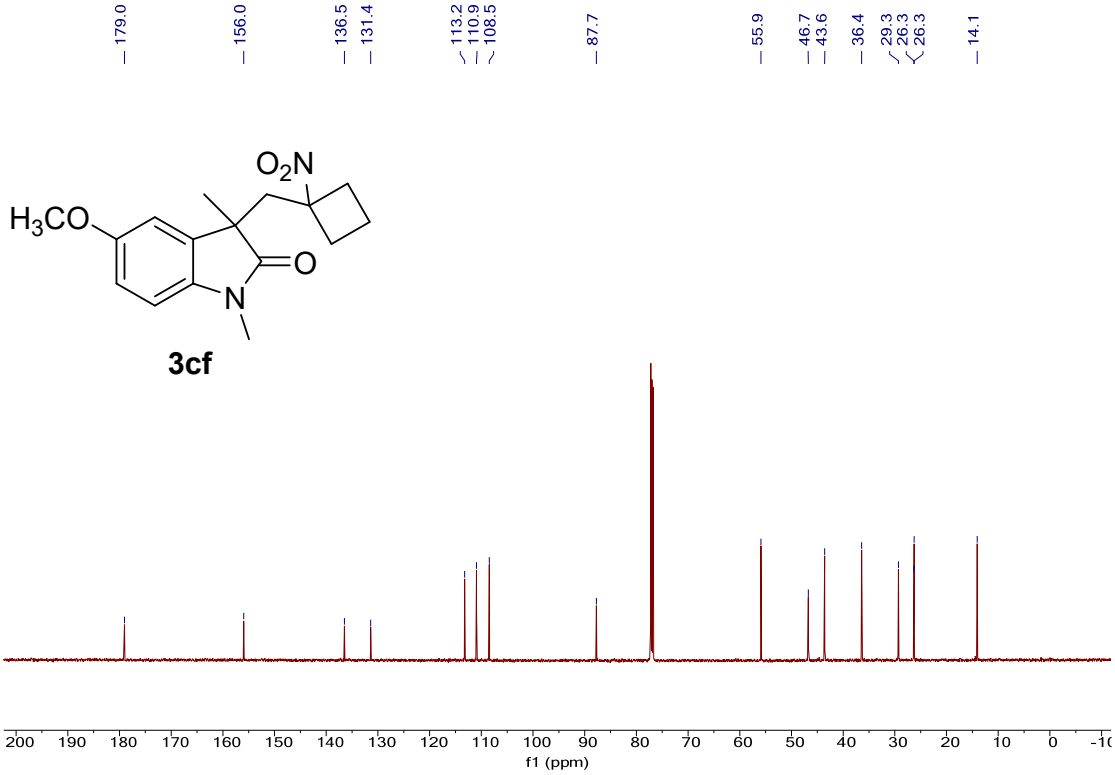
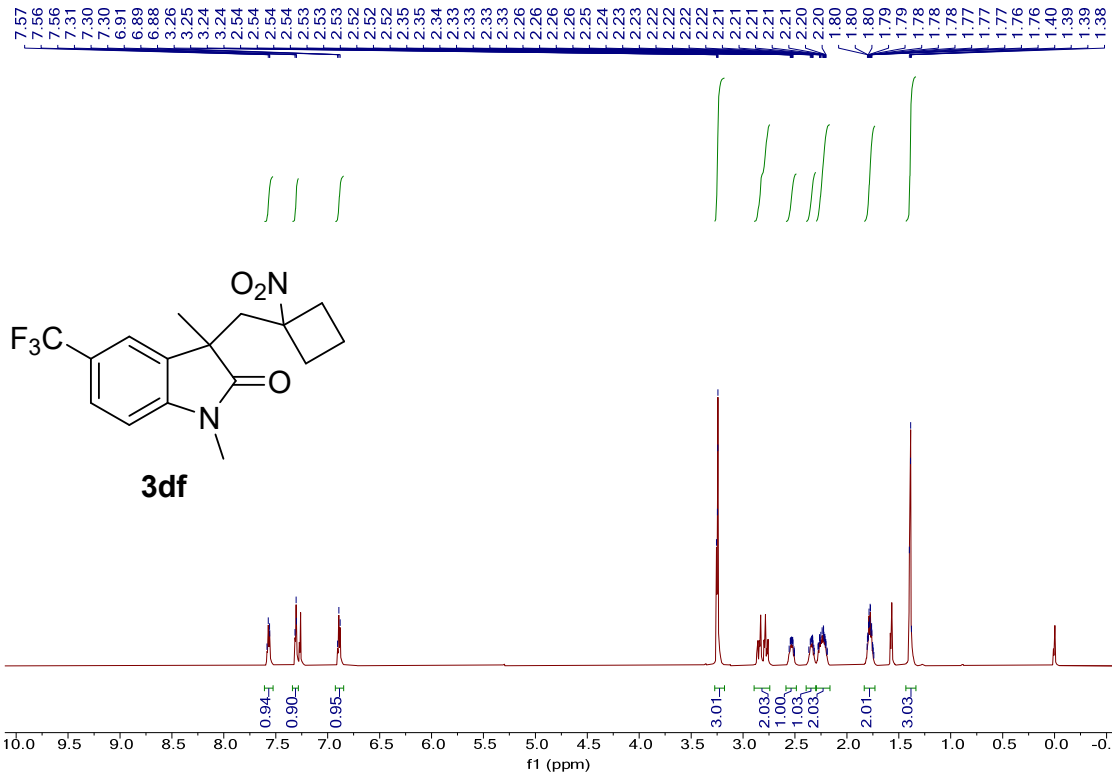
140.7
132.1
130.3
128.6
124.6
107.8
87.8
46.3
43.7
36.4
29.5
26.3
21.1
14.1
O2N
O
N

3bf


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.82 6.82 6.82 6.81 6.81 6.80 6.74 6.74 6.73 6.73 6.72 6.72 6.68 6.68 6.68 6.67 3.78 3.78 3.19 3.19 2.89 2.88 2.88 2.86 2.86 2.86 2.77 2.77 2.77 2.75 2.74 2.74 2.52 2.52 2.51 2.51 2.50 2.50 2.34 2.34 2.33 2.33 2.32 2.28 2.27 2.27 2.26 2.26 2.25 2.22 2.22 2.22 2.22 2.21 2.21 2.21 2.20 1.79 1.78 1.77 1.77 1.76 1.76 1.35 1.34
O2N
H3CO
O
N
3cf
1.00 0.99 0.99 3.04 3.07 2.03 1.00 3.15 2.24 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.0 156.0 136.5 131.4 113.2 110.9 108.5 87.7 55.9 46.7 43.6 36.4 29.3 26.3 26.3 14.1
O2N
H3CO
O
N
3cf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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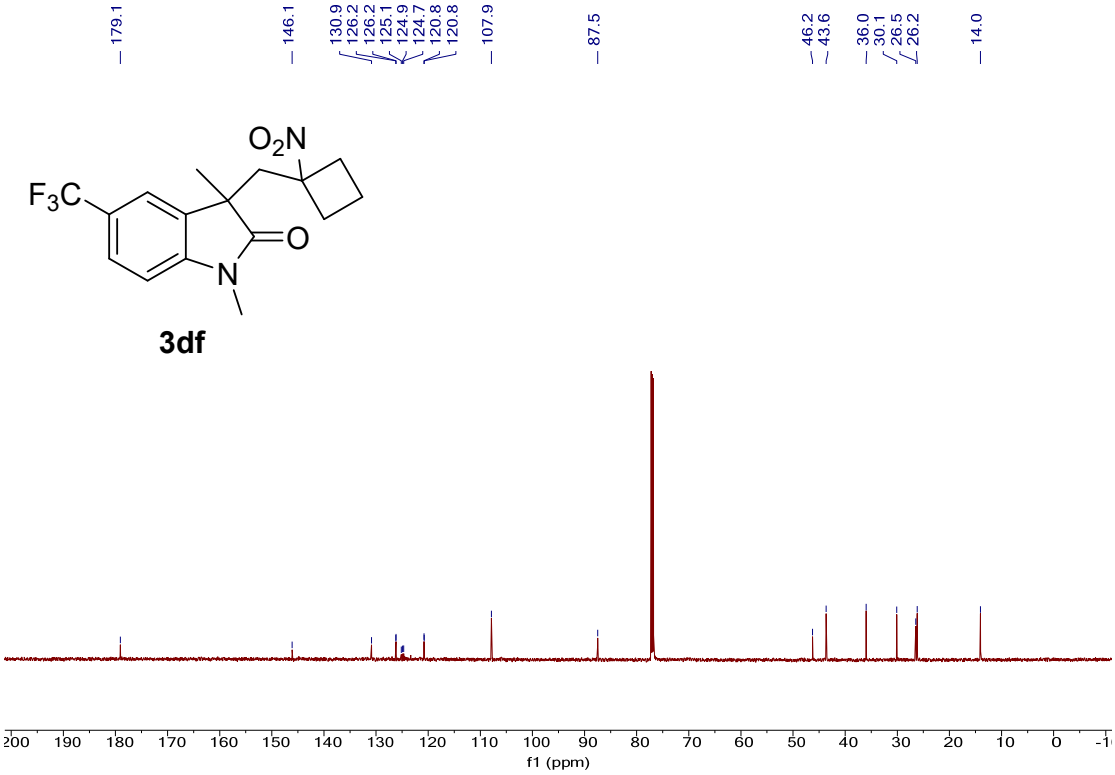
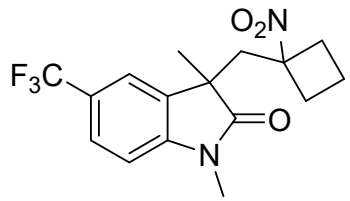
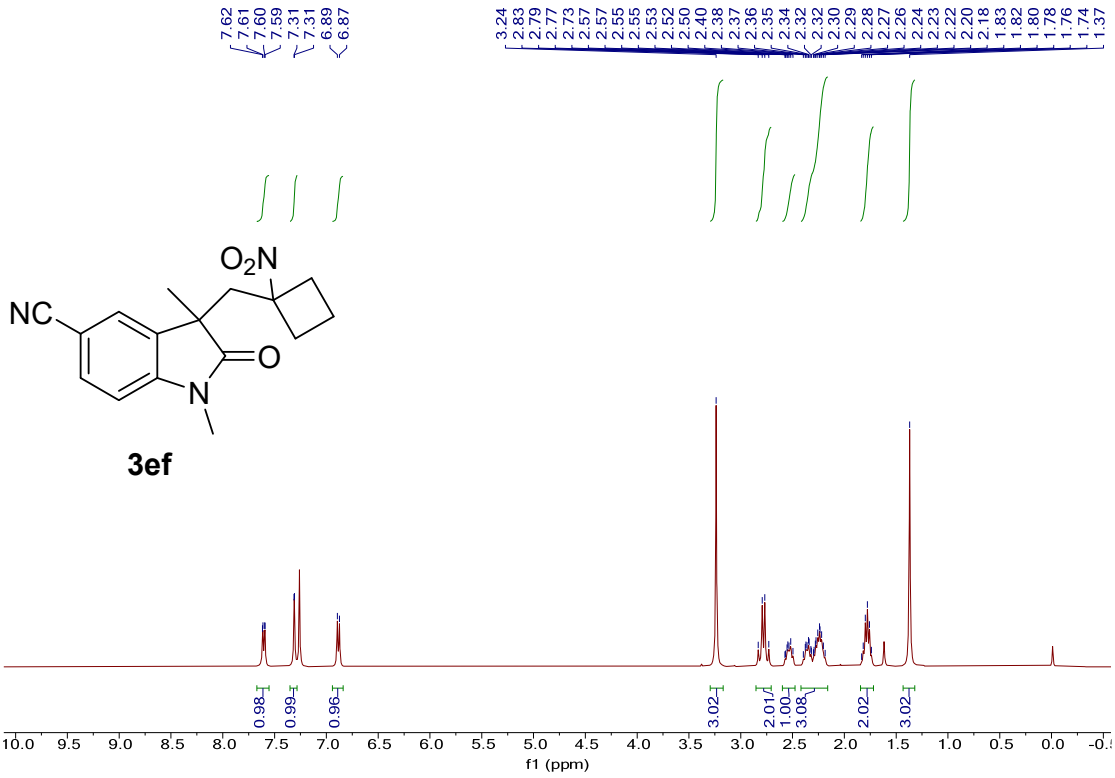
O2N
F3C
O
N
3df
0.94 0.90 0.95 3.01 2.03 1.00 1.03 2.03 2.01 3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


179.1 146.1 130.9 126.2 126.2 125.1 124.9 124.7 120.8 120.8 107.9 87.5 46.2 43.6 36.0 30.1 26.5 26.2 14.0
O2N
F3C
O
N
3df
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O_2N
F_3C
O
N

3df

61.53
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)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7.60
7.59
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6.87
3.24
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2.79
2.77
2.73
2.57
2.57
2.55
2.55
2.53
2.52
2.50
2.40
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2.37
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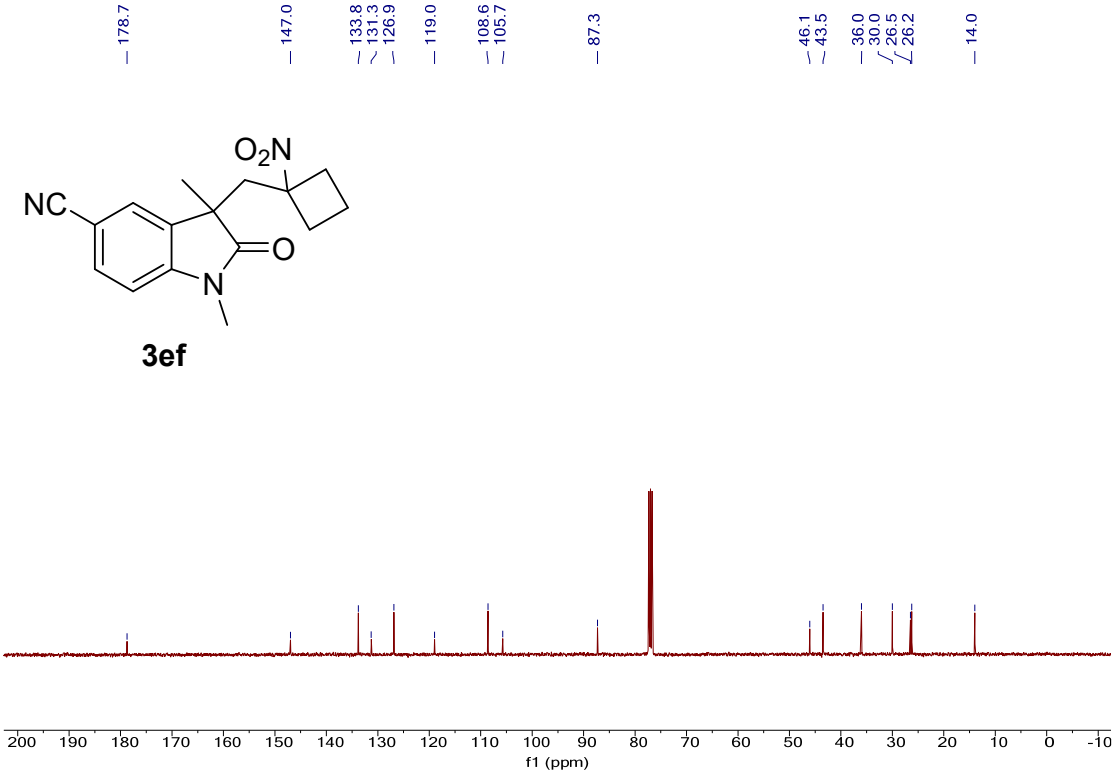
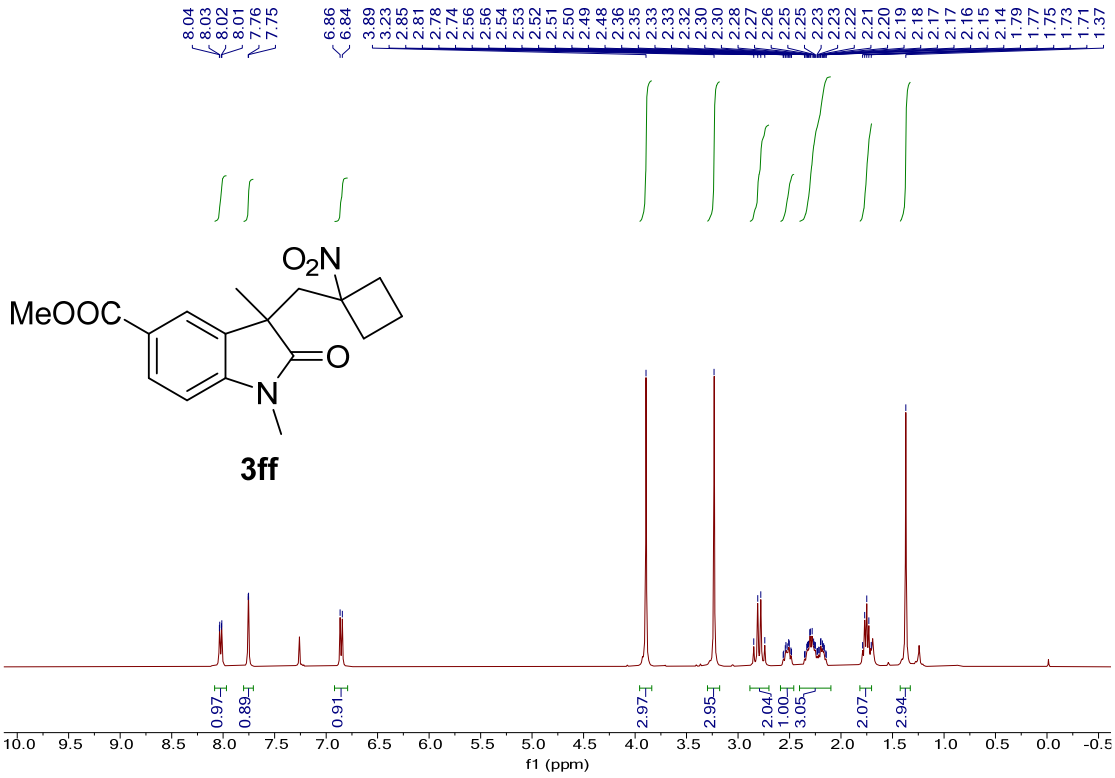
2.34
2.32
2.32
2.30
2.29
2.28
2.27
2.26
2.24
2.23
2.22
2.20
2.18
1.83
1.82
1.80
1.78
1.76
1.74
1.37
O2N
NC
O
N
3ef
0.98
0.99
0.96
3.02
2.01
1.00
3.08
2.02
3.02
f1 (ppm)


178.7
147.0
133.8
131.3
126.9
119.0
108.6
105.7
87.3
46.1
43.5
36.0
30.0
26.5
26.2
14.0
O2N
NC
O
N
3ef
f1 (ppm)


8.04
8.03
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8.01
7.76
7.75
6.86
6.84
3.89
3.23
2.85
2.81
2.78
2.74
2.56
2.54
2.53
2.52
2.51
2.50
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2.48
2.36
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2.32
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2.28
2.27
2.26
2.25
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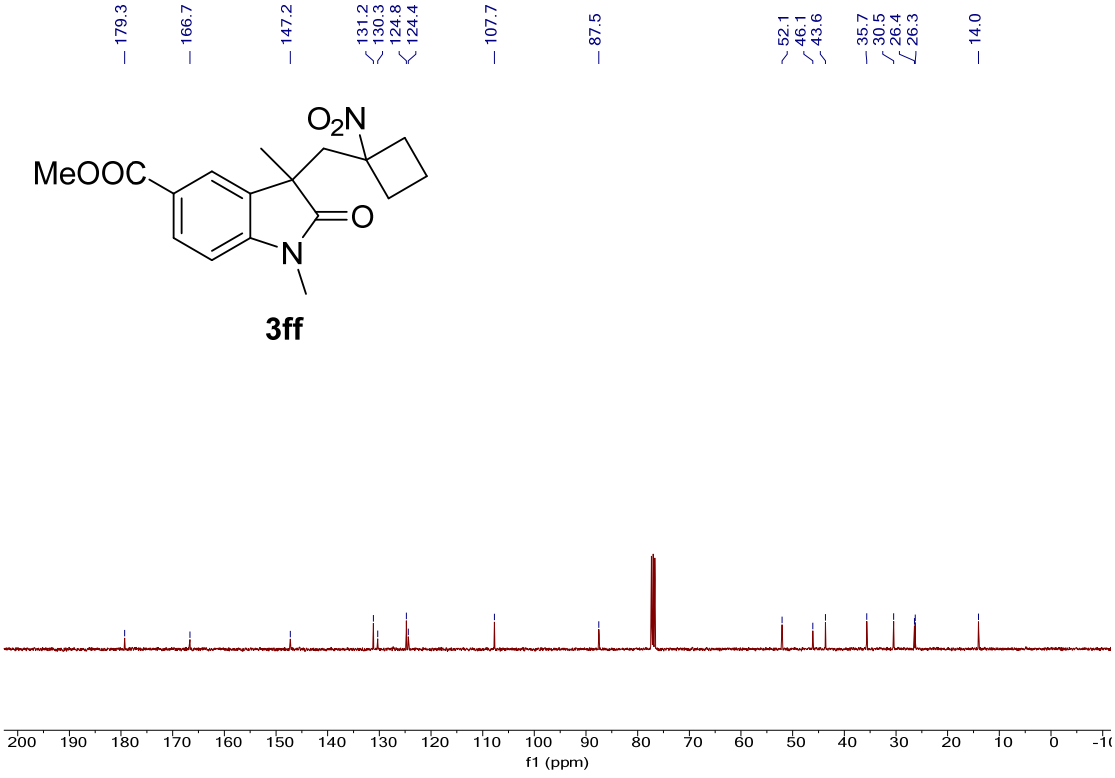
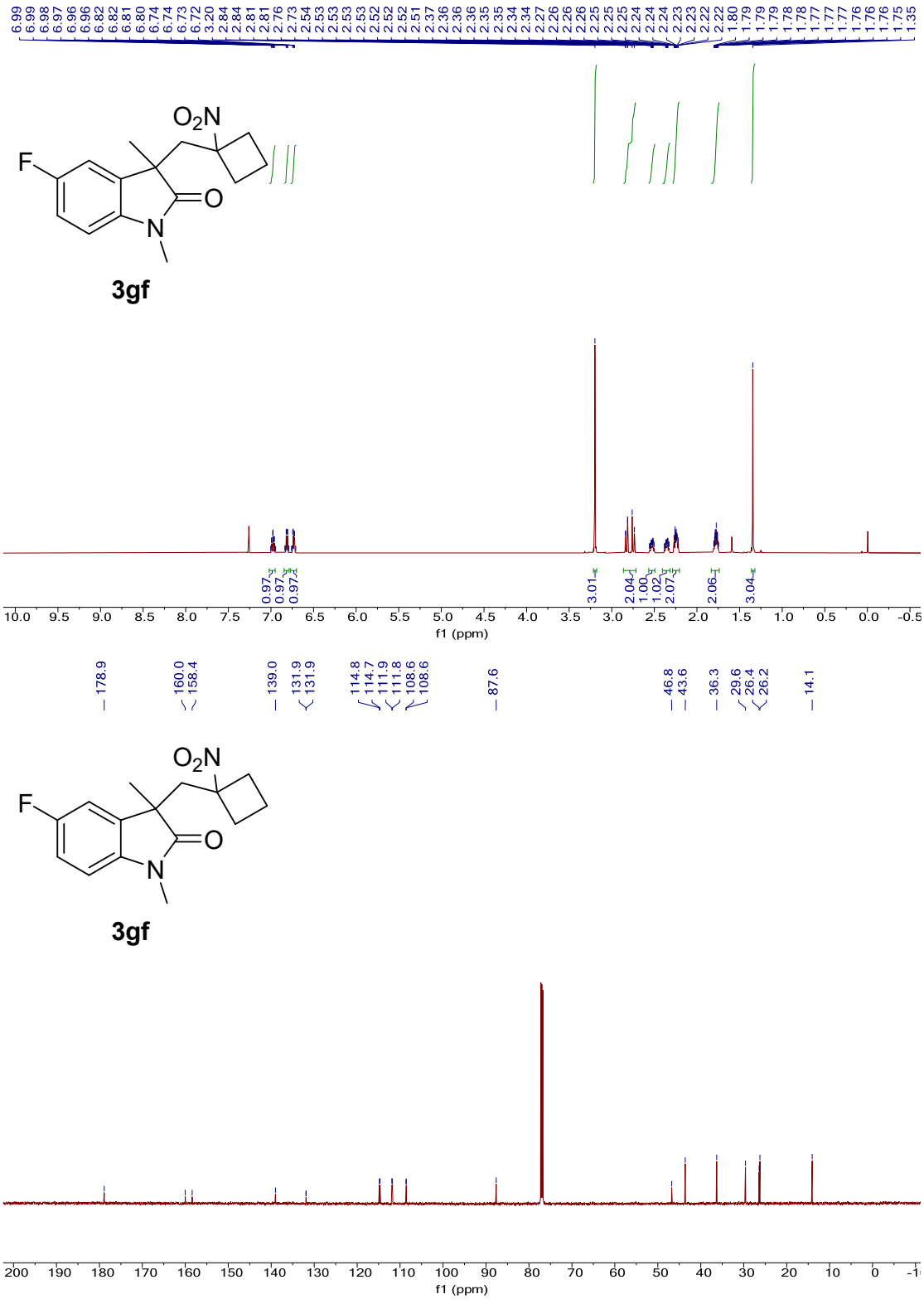
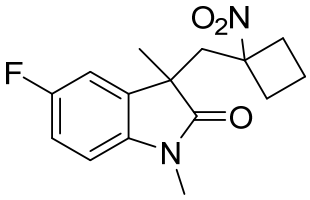
2.23
2.23
2.22
2.21
2.20
2.19
2.18
2.17
2.17
2.16
2.15
2.14
1.79
1.77
1.75
1.73
1.71
1.37
O2N
MeOOC
O
N
3ff
0.97
0.89
0.91
2.97
2.95
2.04
1.00
3.05
2.07
2.94
f1 (ppm)

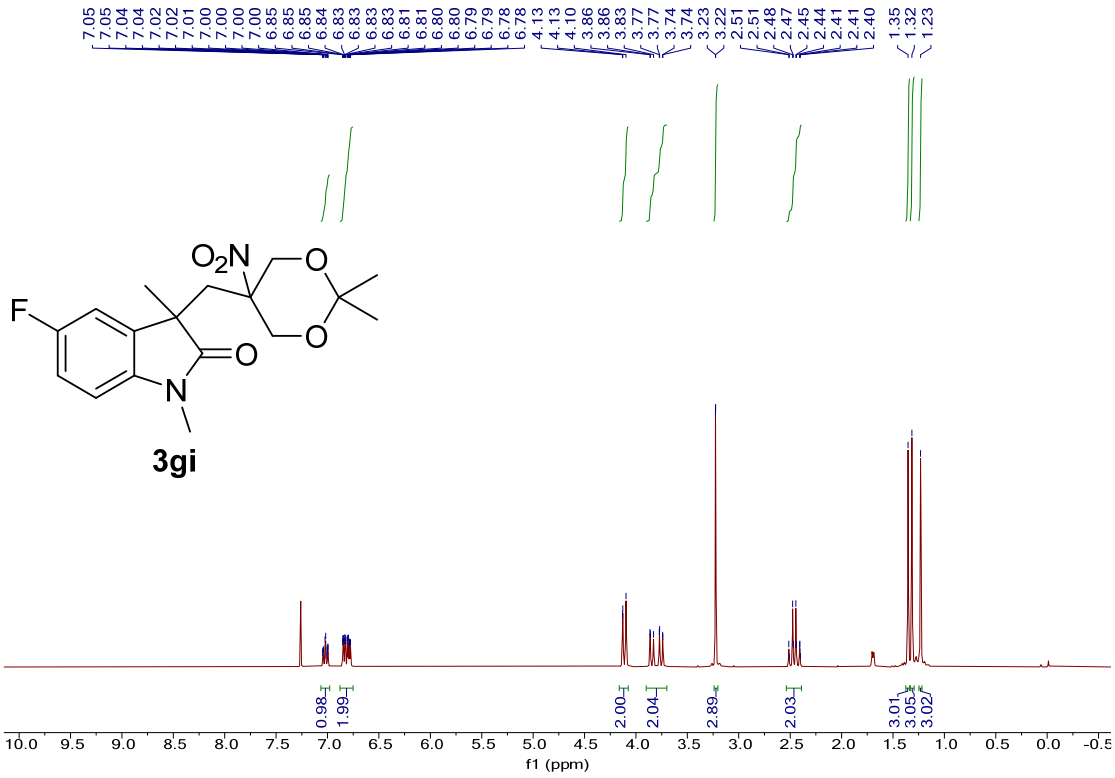

179.3
166.7
147.2
131.2
130.3
124.8
124.4
107.7
87.5
52.1
46.1
43.6
35.7
30.5
26.4
26.3
14.0
O2N
MeOOC
O
N
3ff
f1 (ppm)

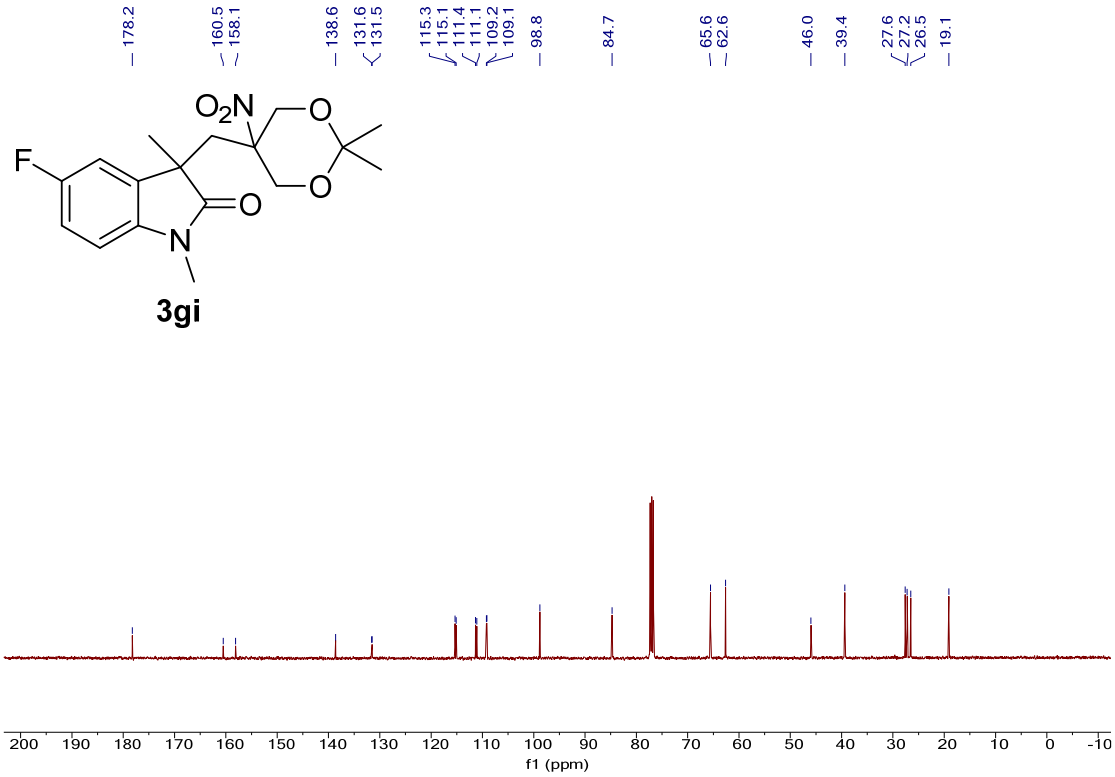

6.99 6.99 6.98 6.97 6.96 6.96 6.82 6.81 6.80 6.74 6.74 6.73 6.72 3.20 2.84 2.84 2.81 2.81 2.76 2.73 2.54 2.53 2.53 2.53 2.52 2.52 2.51 2.37 2.36 2.36 2.35 2.35 2.34 2.34 2.27 2.26 2.26 2.26 2.25 2.25 2.25 2.24 2.24 2.24 2.23 2.23 2.22 2.22 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.77 1.76 1.76 1.76 1.75 1.35
O2N
F
O
N
3gf
0.97 0.97 0.97 3.01 2.04 1.00 1.02 2.07 2.06 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
178.9 160.0 158.4 139.0 131.9 131.9 114.8 114.7 111.9 111.8 108.6 108.6 87.6 46.8 43.6 36.3 29.6 26.4 26.2 14.1
O2N
F
O
N
3gf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

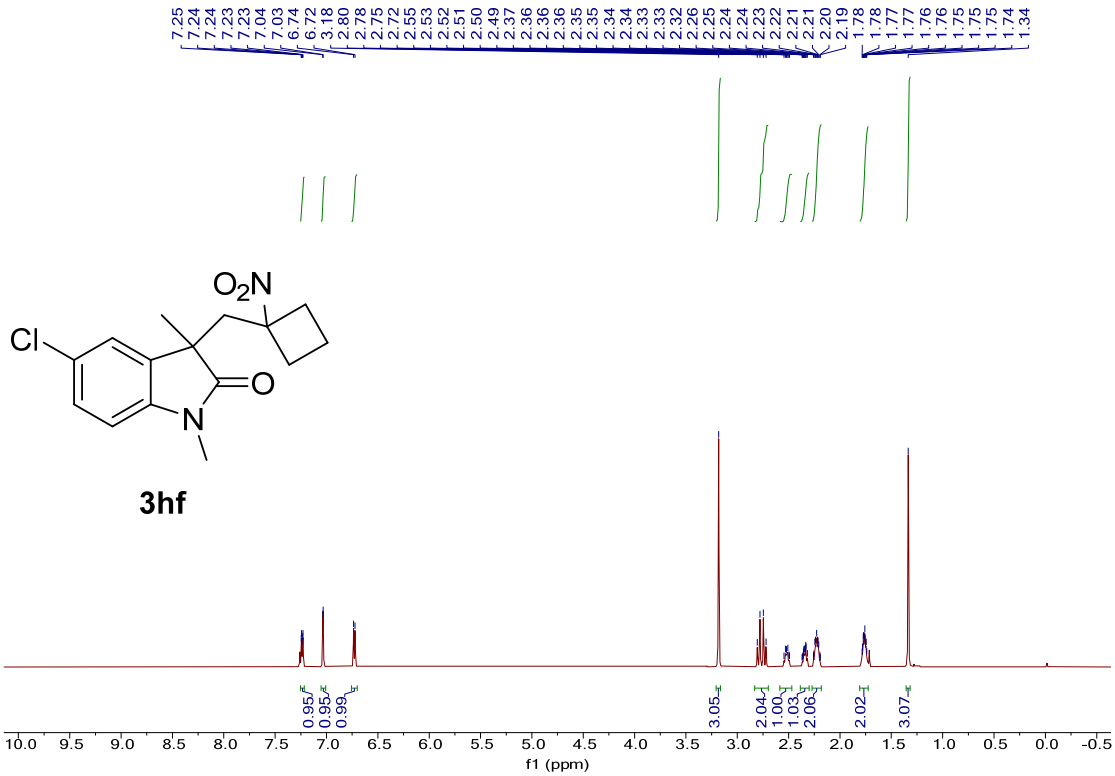

O_2N
F
O
N

3gf

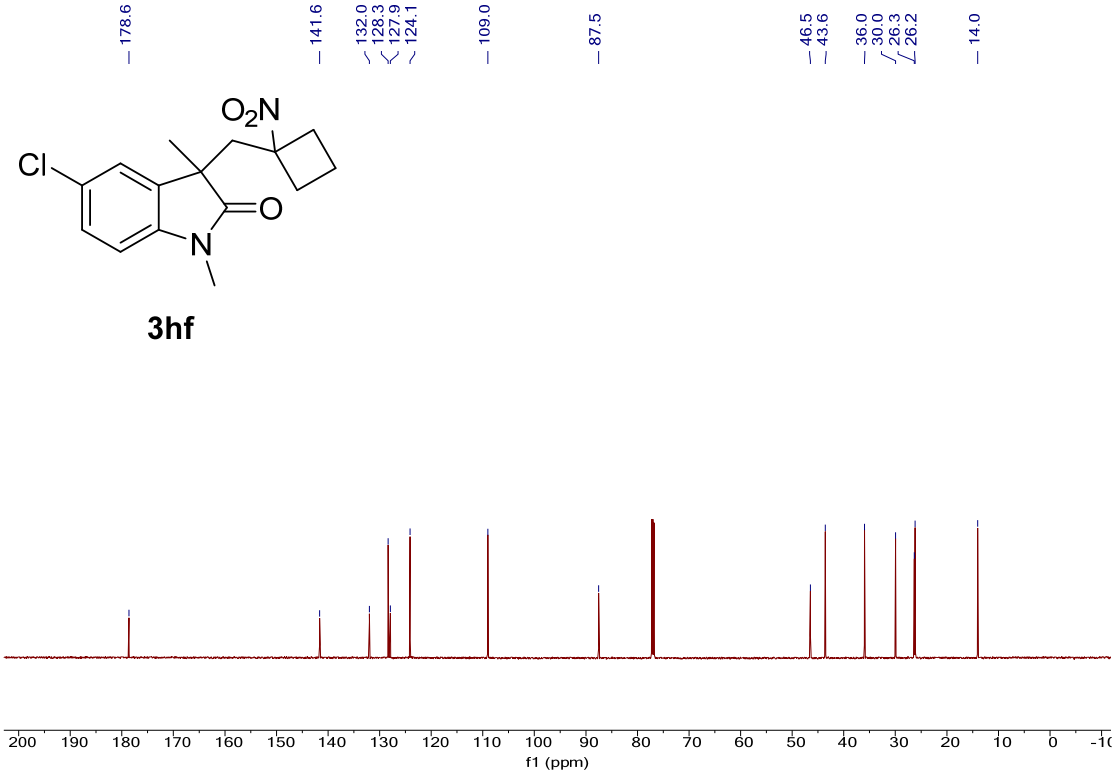
-119.95
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -19
f1 (ppm)


7.05 7.05 7.04 7.04 7.02 7.02 7.01 7.00 7.00 7.00 7.00 6.85 6.85 6.84 6.83 6.83 6.83 6.83 6.81 6.81 6.80 6.80 6.79 6.79 6.78 4.13 4.10 3.86 3.86 3.83 3.77 3.77 3.74 3.74 3.23 2.51 2.51 2.48 2.47 2.45 2.44 2.41 2.41 2.40 1.35 1.32 1.23
O2N
O
O
F
O
N
3gi
0.98 1.99 2.00 2.04 2.89 2.03 3.01 3.05 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

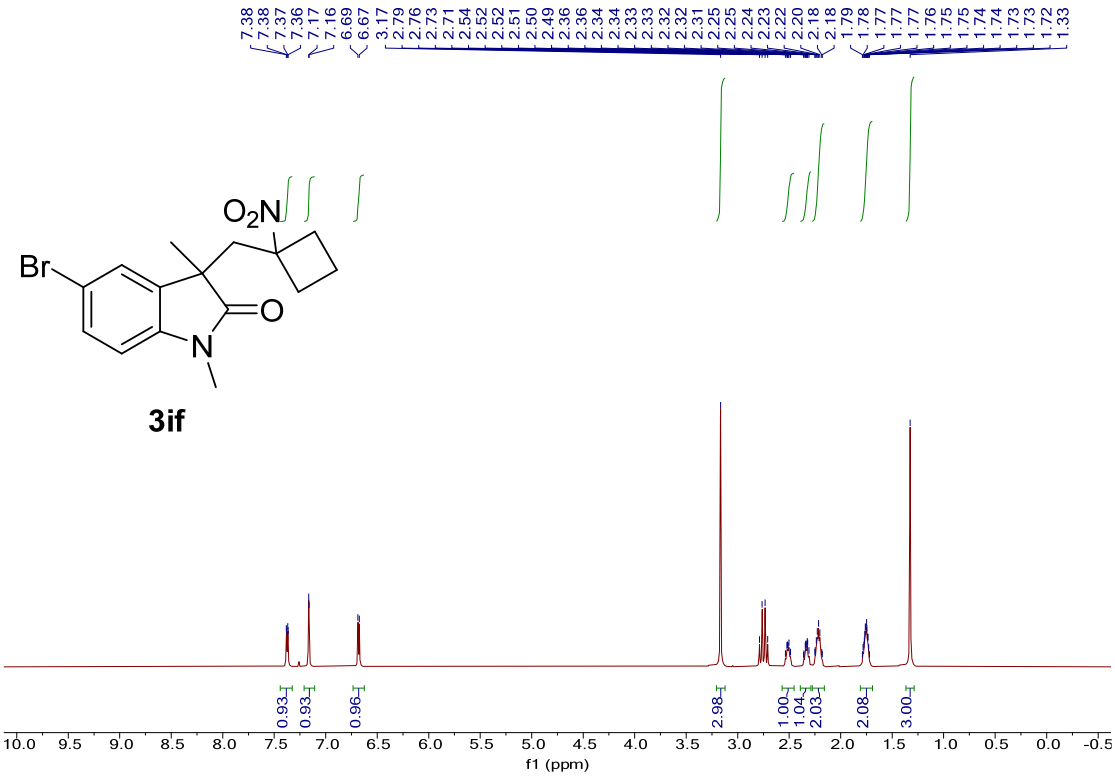

178.2 160.5 158.1 138.6 131.6 131.5 115.3 115.1 111.4 111.1 109.2 109.1 98.8 84.7 65.6 62.6 46.0 39.4 27.6 27.2 26.5 19.1
O2N
O
O
F
O
N
3gi
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.25 7.24 7.24 7.23 7.23 7.04 7.03 6.74 6.72 3.18 2.80 2.78 2.75 2.72 2.55 2.53 2.52 2.51 2.50 2.49 2.37 2.36 2.36 2.35 2.35 2.34 2.34 2.33 2.33 2.32 2.26 2.25 2.24 2.24 2.23 2.22 2.21 2.21 2.20 2.19 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.75 1.75 1.74 1.34
O2N
Cl
O
N
0.95 0.95 0.99 3.05 2.04 1.00 1.03 2.06 2.02 3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

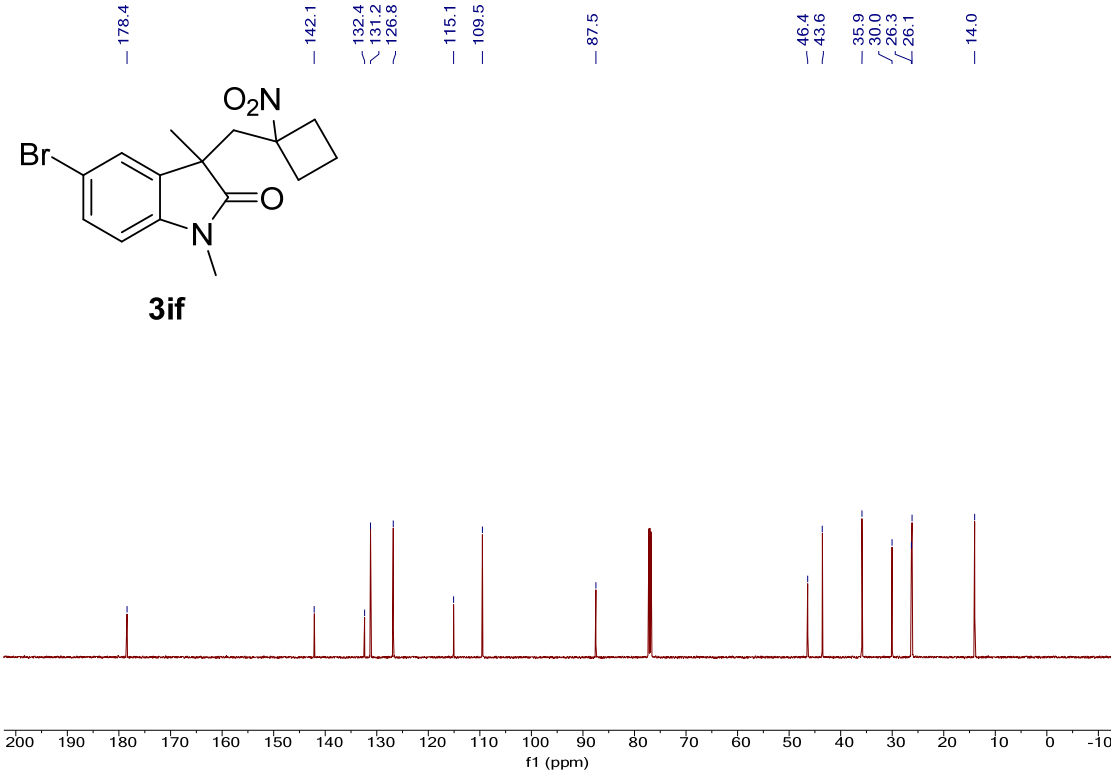
3hf


178.6 141.6 132.0 128.3 127.9 124.1 109.0 87.5 46.5 43.6 36.0 30.0 26.3 26.2 14.0
O2N
Cl
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

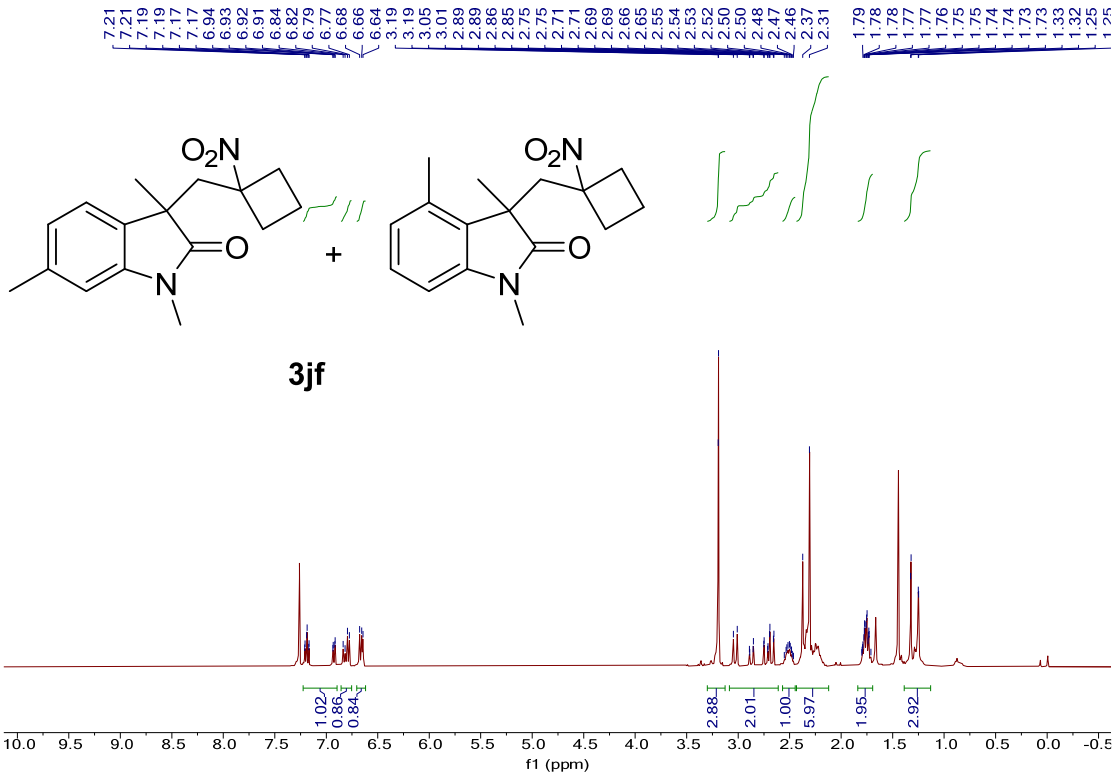
3hf

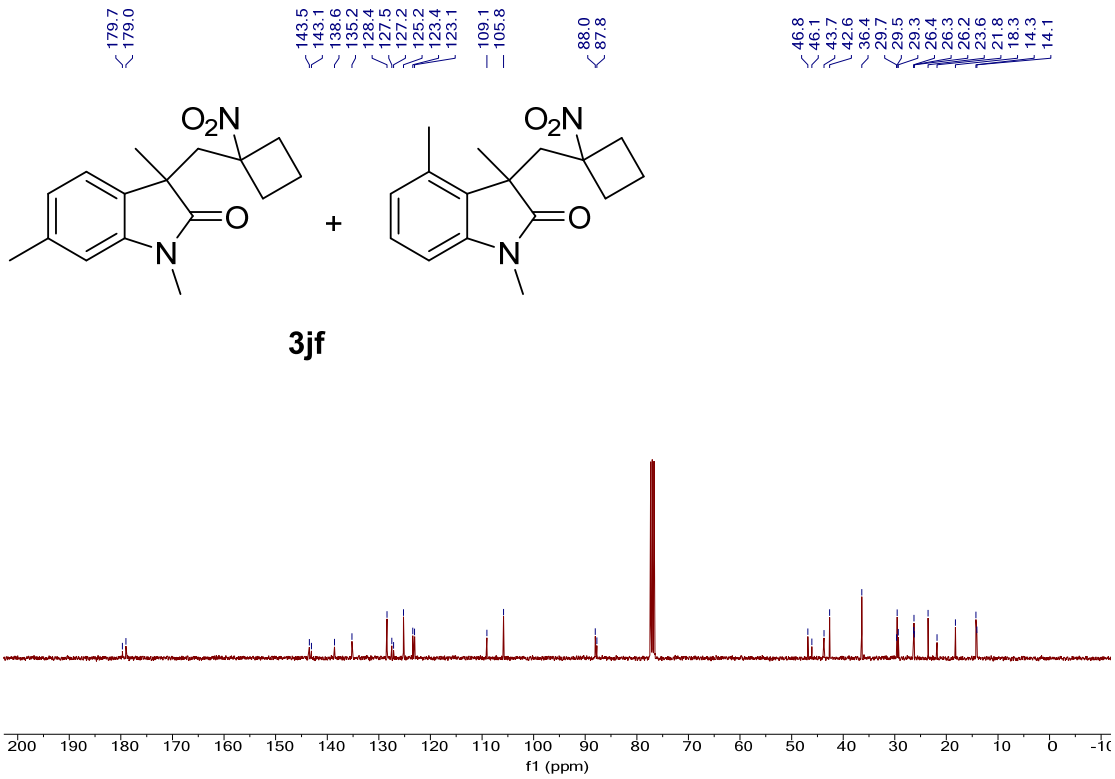

7.38
7.38
7.37
7.36
7.17
7.16
6.69
6.67
3.17
2.79
2.76
2.73
2.71
2.54
2.52
2.52
2.51
2.50
2.49
2.36
2.36
2.34
2.34
2.33
2.33
2.32
2.32
2.31
2.25
2.25
2.24
2.23
2.22
2.20
2.18
2.18
1.79
1.78
1.77
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.33
O2N
Br
O
N
0.93
0.93
0.96
2.98
1.00
1.04
2.03
2.08
3.00
f1 (ppm)

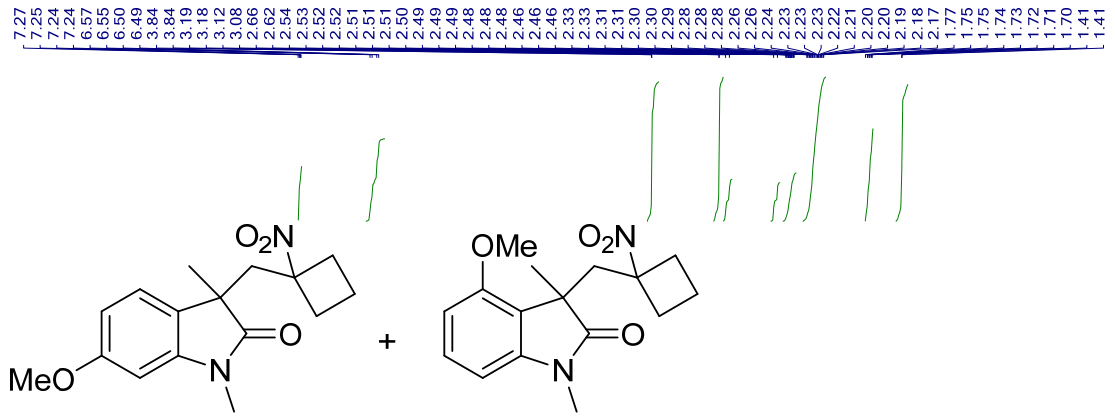
3if


178.4
142.1
132.4
131.2
126.8
115.1
109.5
87.5
46.4
43.6
35.9
30.0
26.3
26.1
14.0
O2N
Br
O
N
f1 (ppm)

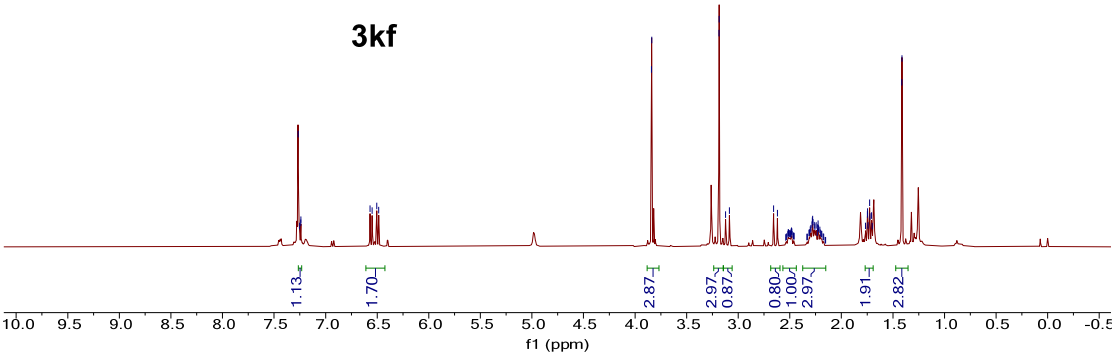
3if

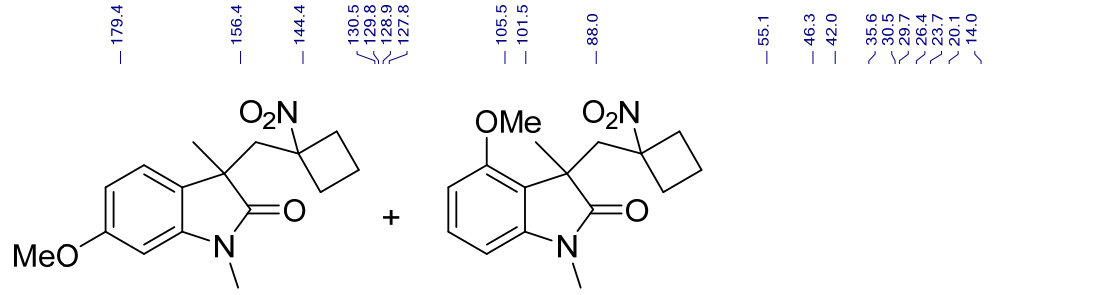

7.21 7.21 7.19 7.19 7.17 7.17 6.94 6.93 6.92 6.91 6.84 6.82 6.79 6.77 6.68 6.66 6.64 3.19 3.19 3.05 3.01 2.89 2.89 2.86 2.85 2.75 2.75 2.71 2.71 2.69 2.69 2.66 2.65 2.55 2.54 2.53 2.52 2.50 2.50 2.48 2.47 2.46 2.37 2.31 1.79 1.78 1.78 1.77 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.33 1.32 1.25
O2N
O
N
+
O2N
O
N
3jf
1.02 0.86 0.84 2.88 2.01 1.00 5.97 1.95 2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.7 179.0 143.5 143.1 138.6 135.2 128.4 127.5 127.2 125.2 123.4 123.1 109.1 105.8 88.0 87.8 46.8 46.1 43.7 42.6 36.4 29.7 29.5 29.3 26.4 26.3 26.2 23.6 21.8 18.3 14.3 14.1
O2N
O
N
+
O2N
O
N
3jf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

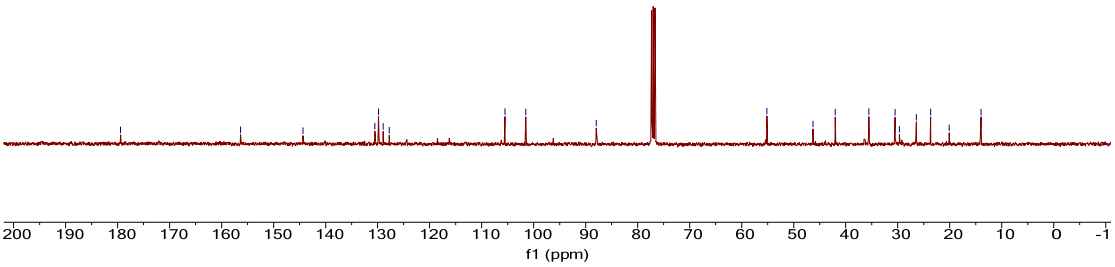

7.27 7.25 7.24 7.24 6.57 6.55 6.50 6.49 3.84 3.84 3.19 3.18 3.12 3.08 2.66 2.62 2.54 2.53 2.52 2.52 2.51 2.51 2.51 2.50 2.49 2.49 2.49 2.48 2.48 2.48 2.46 2.46 2.46 2.33 2.33 2.31 2.31 2.30 2.30 2.29 2.28 2.28 2.26 2.26 2.24 2.23 2.23 2.22 2.21 2.20 2.20 2.19 2.18 2.17 1.77 1.75 1.75 1.74 1.73 1.72 1.71 1.70 1.41 1.41
O2N
MeO
O
N
+
OMe
O2N
O
N

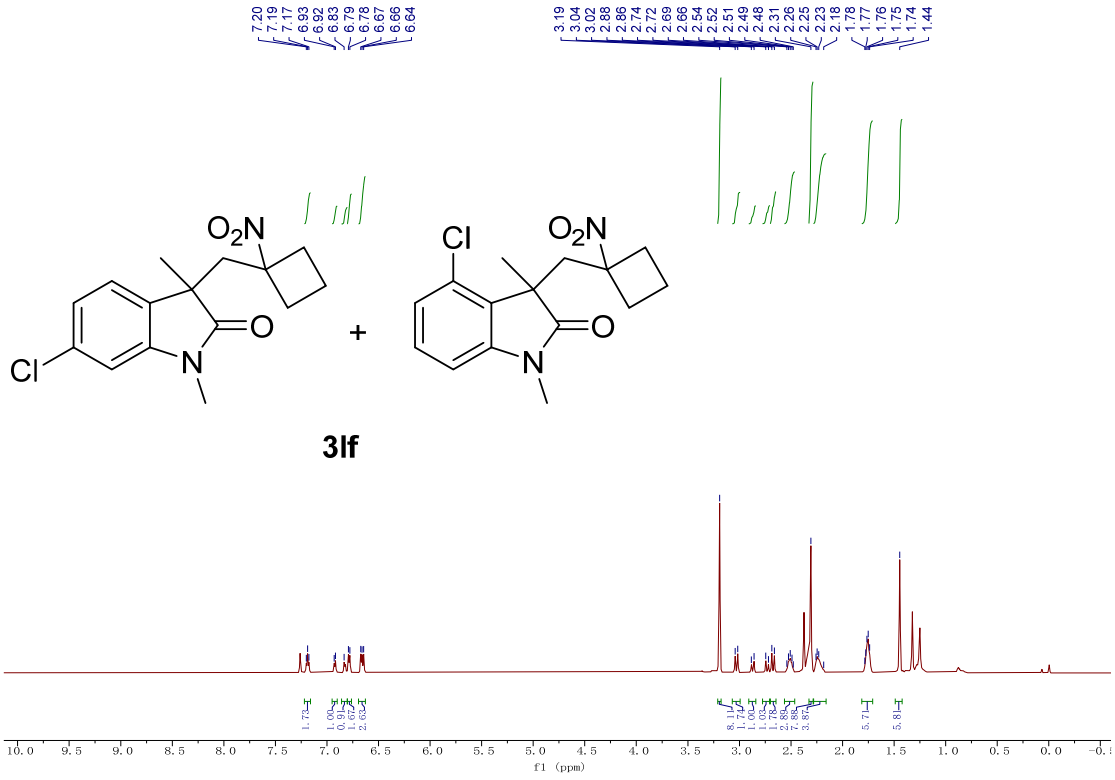
3kf

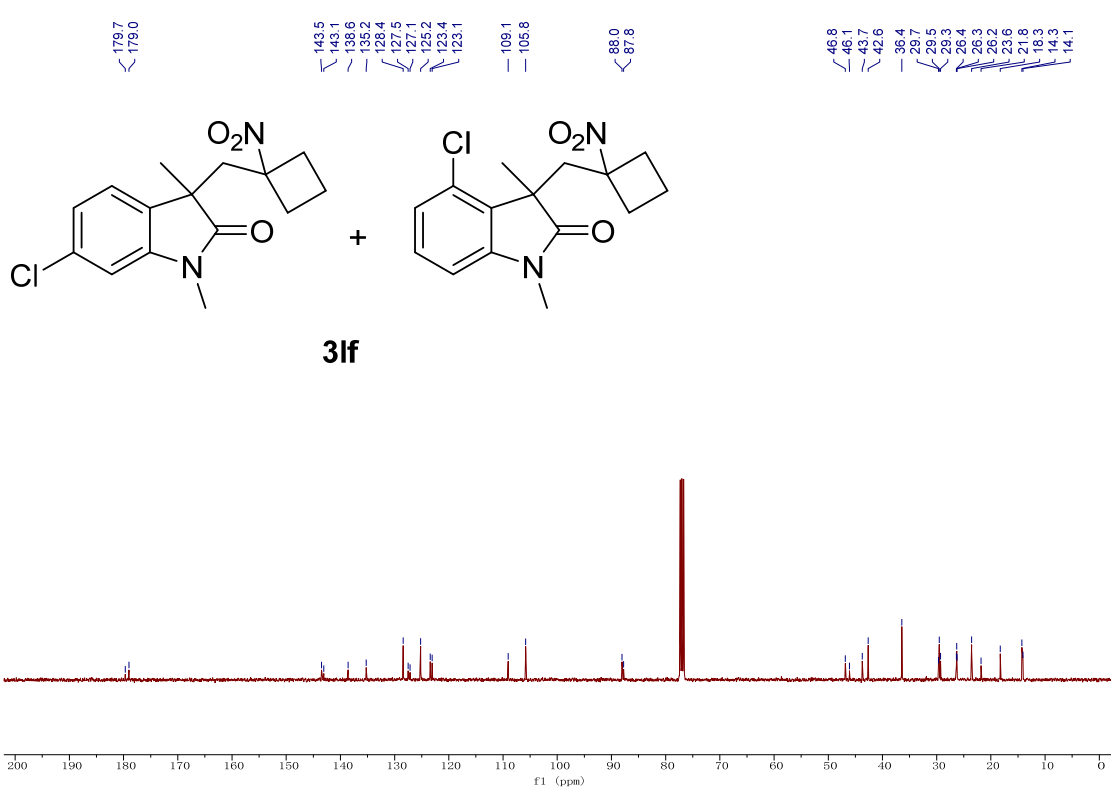

1.13 1.70 2.87 2.97 0.87 0.80 1.00 2.97 1.91 2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

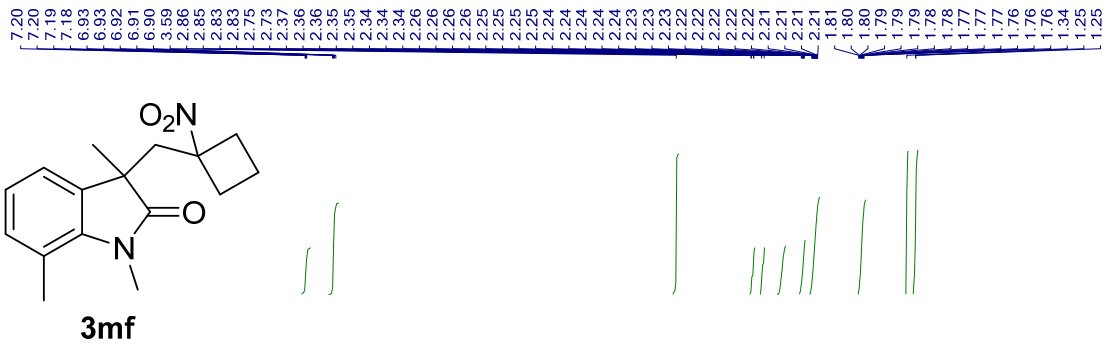

179.4 156.4 144.4 130.5 129.8 128.9 127.8 105.5 101.5 88.0 55.1 46.3 42.0 35.6 30.5 29.7 26.4 23.7 20.1 14.0
O2N
MeO
O
N
+
OMe
O2N
O
N

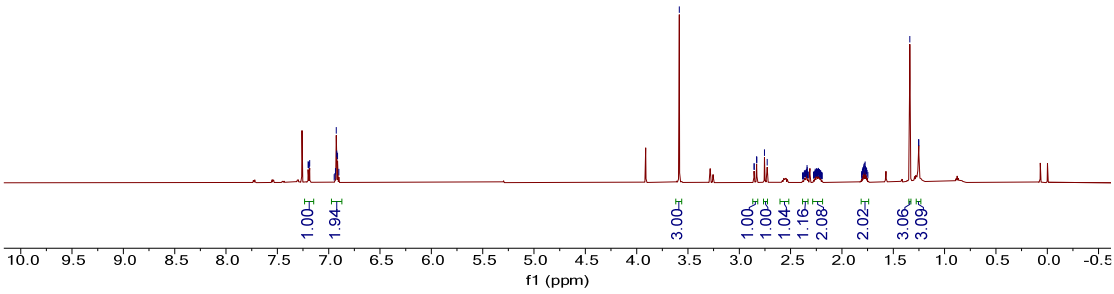
3kf

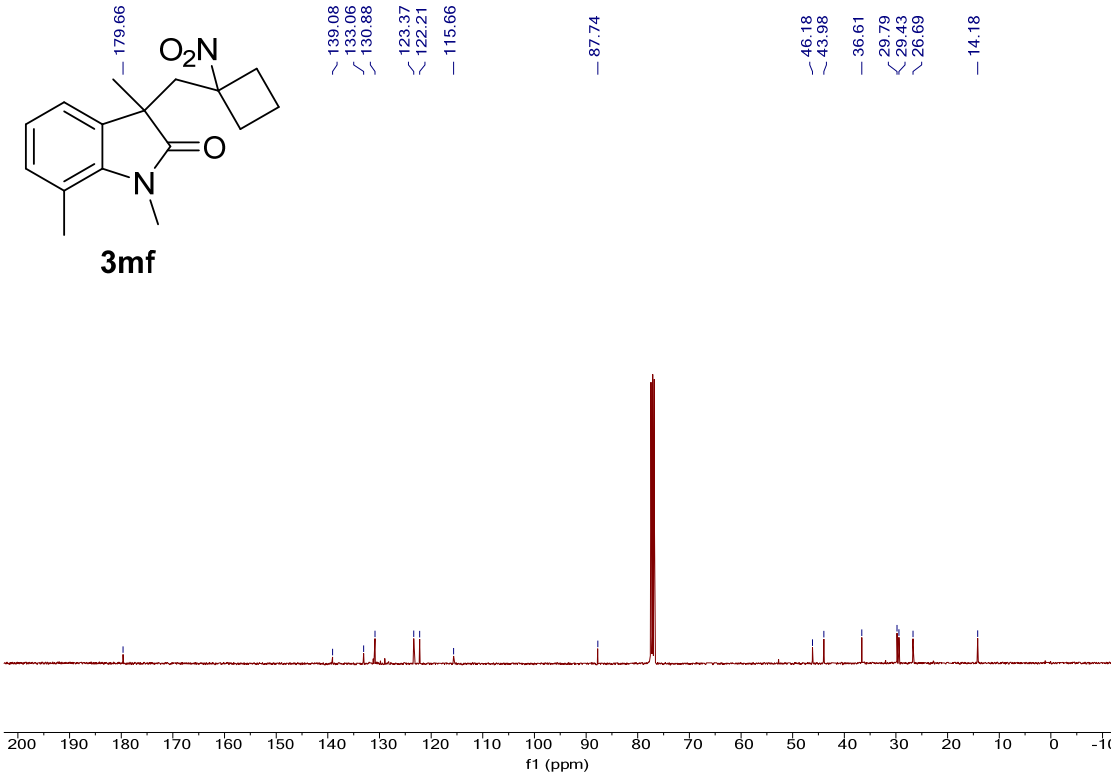

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

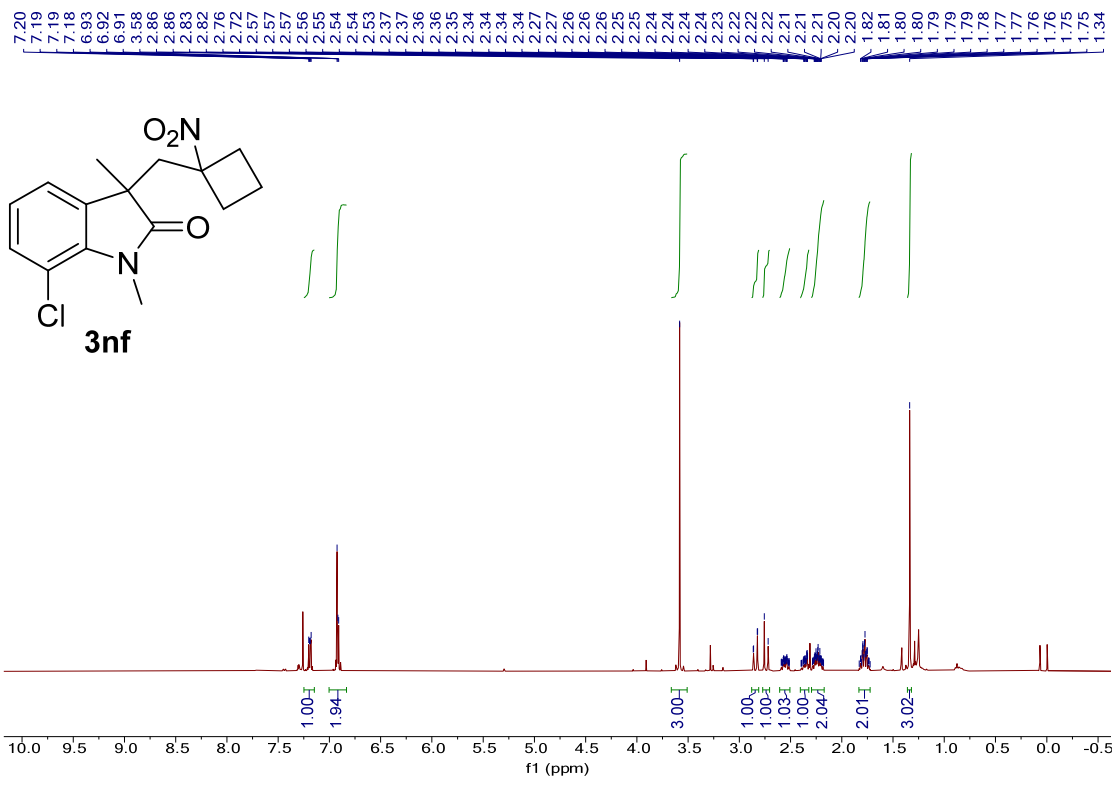

7.20
7.19
7.17
6.93
6.92
6.83
6.79
6.78
6.67
6.66
6.64
3.19
3.04
3.02
2.88
2.86
2.74
2.72
2.69
2.66
2.54
2.52
2.51
2.49
2.48
2.31
2.26
2.25
2.23
2.18
1.78
1.77
1.76
1.75
1.74
1.44
O2N
Cl
O
N
+
3lf
f1 (ppm)

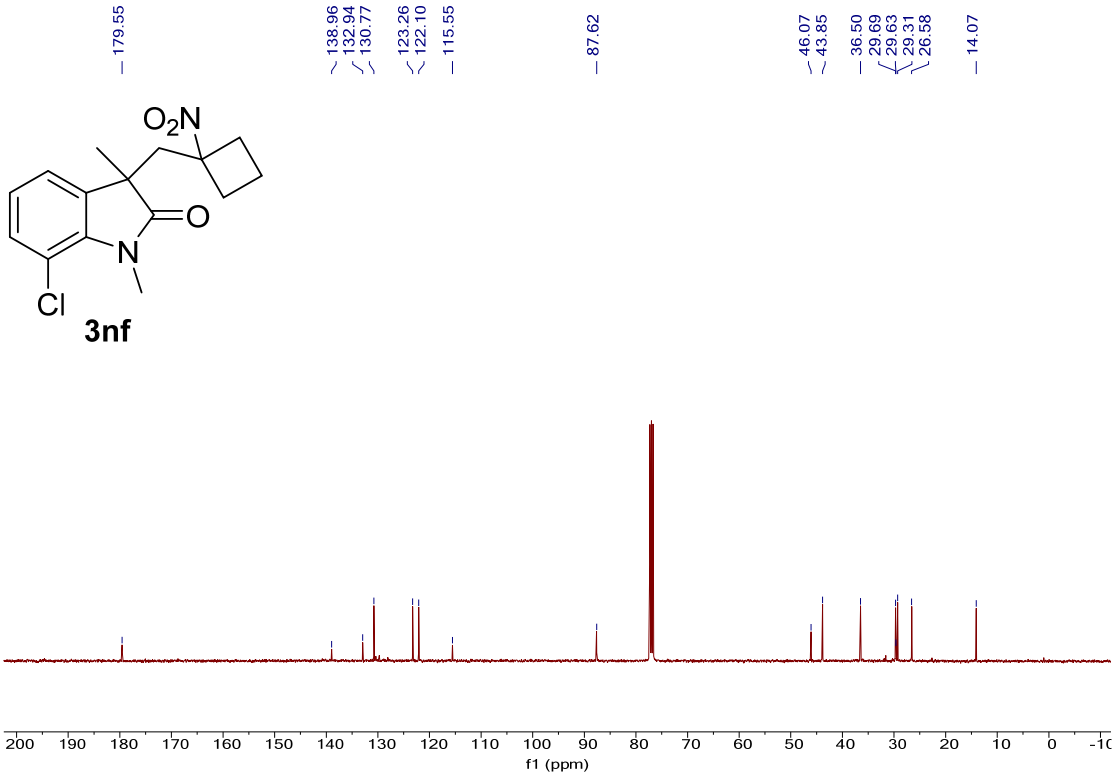

179.7
179.0
143.5
143.1
138.6
135.2
128.4
127.5
127.1
125.2
123.4
123.1
109.1
105.8
88.0
87.8
46.8
46.1
43.7
42.6
36.4
29.7
29.5
29.3
26.4
26.3
26.2
23.6
21.8
18.3
14.3
14.1
O2N
Cl
O
N
+
3lf
f1 (ppm)

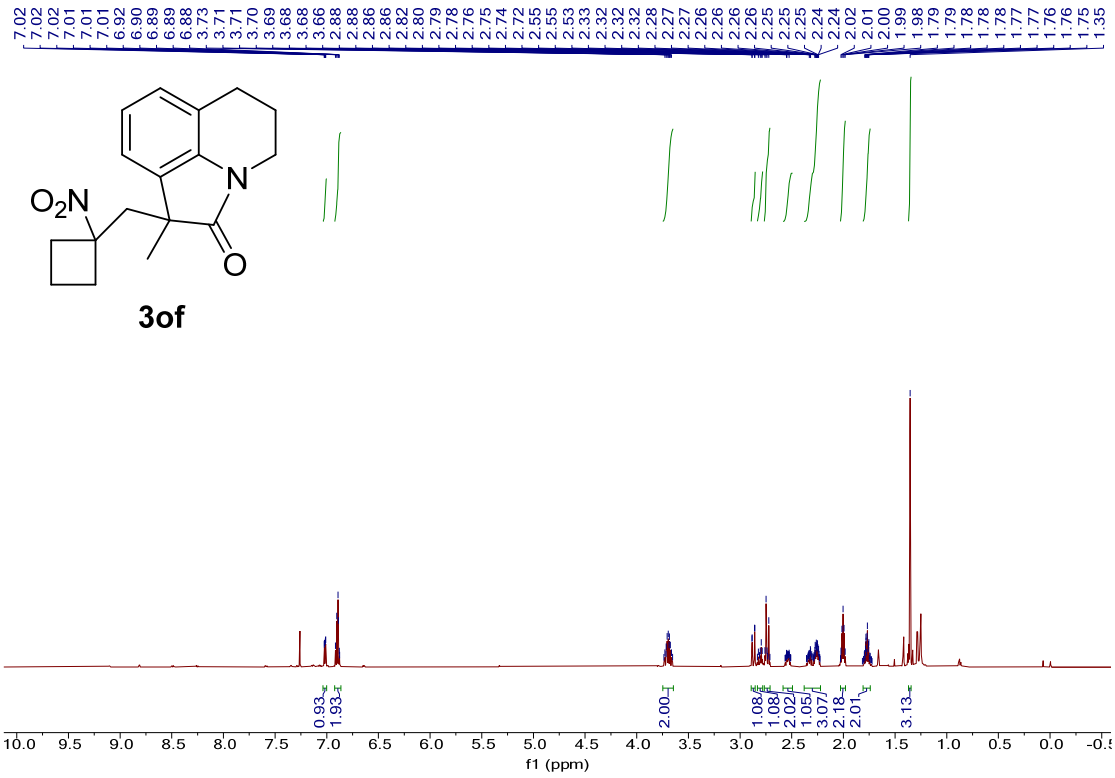

7.20 7.20 7.19 7.18 6.93 6.93 6.92 6.91 6.90 3.59 2.86 2.85 2.83 2.83 2.75 2.73 2.37 2.36 2.36 2.35 2.35 2.34 2.34 2.34 2.26 2.26 2.26 2.25 2.25 2.25 2.25 2.24 2.24 2.24 2.24 2.24 2.23 2.23 2.23 2.22 2.22 2.22 2.22 2.22 2.21 2.21 2.21 2.21 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.77 1.76 1.76 1.76 1.34 1.25 1.25
O2N
O
N
3mf

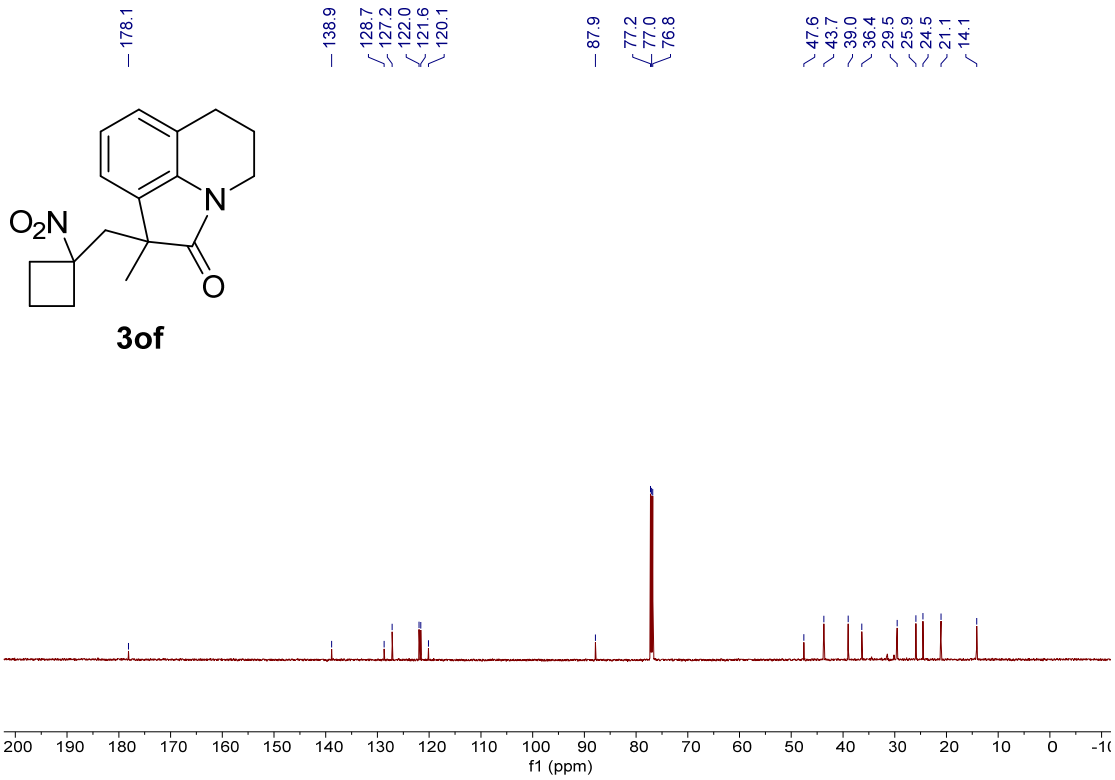

1.00 1.94 3.00 1.00 1.00 1.04 1.16 2.08 2.02 3.06 3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

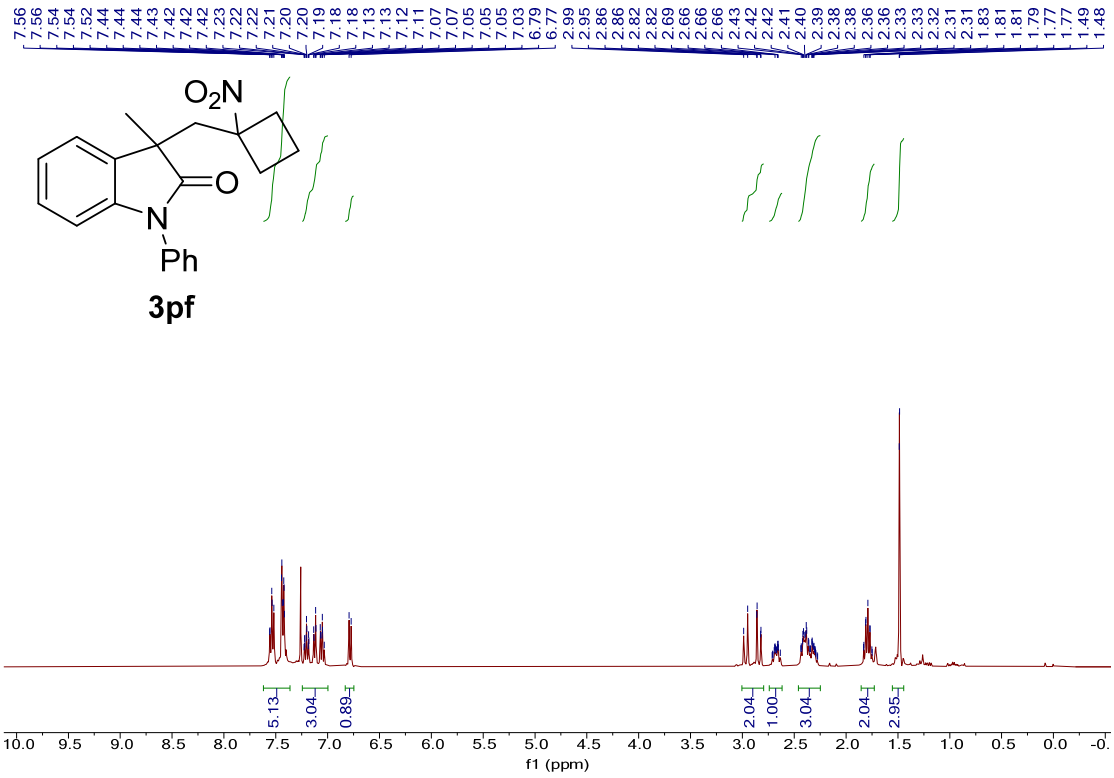

179.66
139.08 133.06 130.88 123.37 122.21 115.66 87.74 46.18 43.98 36.61 29.79 29.43 26.69 14.18
O2N
O
N
3mf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

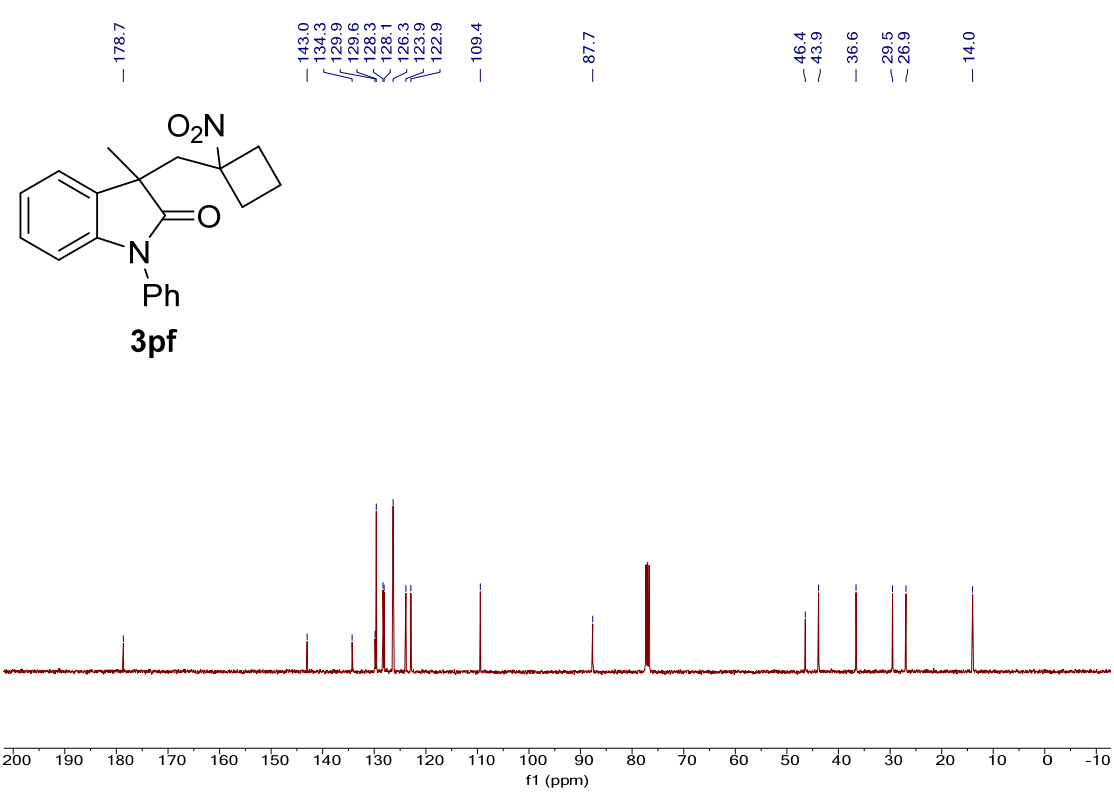

7.20 7.19 7.19 7.18 6.93 6.92 6.91 3.58 2.86 2.86 2.83 2.82 2.76 2.72 2.57 2.57 2.57 2.56 2.55 2.54 2.54 2.53 2.37 2.36 2.36 2.35 2.34 2.34 2.34 2.34 2.27 2.26 2.26 2.26 2.25 2.25 2.24 2.24 2.24 2.24 2.23 2.22 2.22 2.22 2.21 2.21 2.21 2.20 2.20 1.82 1.81 1.80 1.80 1.79 1.79 1.79 1.78 1.77 1.77 1.76 1.76 1.75 1.75 1.34
O2N
O
N
Cl
3nf
1.00 1.94 3.00 1.00 1.00 1.03 1.00 2.04 2.01 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

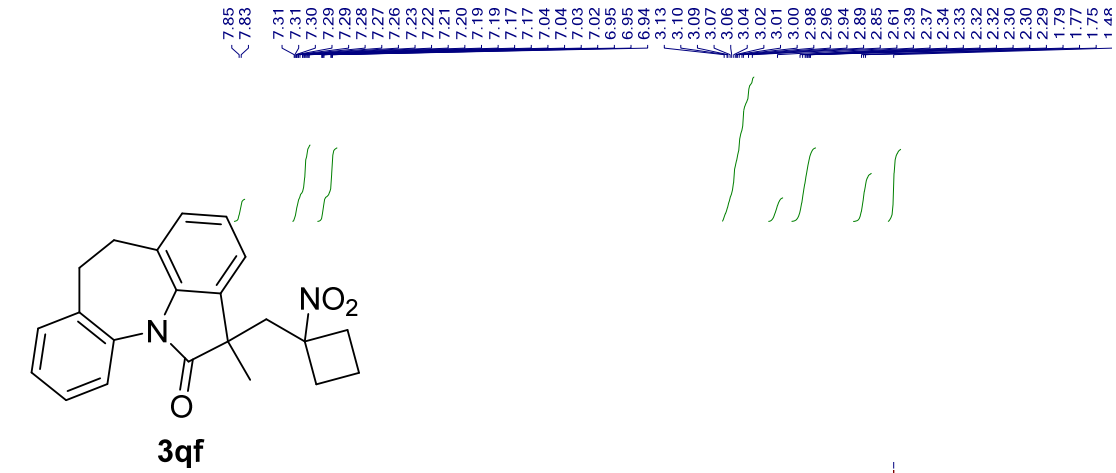

179.55
138.96 132.94 130.77 123.26 122.10 115.55 87.62 46.07 43.85 36.50 29.69 29.63 29.31 26.58 14.07
O2N
O
N
Cl
3nf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.02 7.02 7.02 7.01 7.01 7.01 6.92 6.90 6.89 6.89 6.88 3.73 3.71 3.71 3.70 3.69 3.68 3.68 3.66 2.88 2.88 2.86 2.86 2.82 2.80 2.79 2.78 2.76 2.75 2.74 2.72 2.55 2.55 2.53 2.33 2.32 2.32 2.28 2.27 2.27 2.26 2.26 2.26 2.25 2.25 2.25 2.24 2.24 2.02 2.01 2.00 1.99 1.98 1.79 1.79 1.78 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.35
O2N
N
O
3of
0.93 1.93 2.00 1.08 1.08 2.02 1.05 3.07 2.18 2.01 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


178.1
138.9
128.7
127.2
122.0
121.6
120.1
87.9
77.2
77.0
76.8
47.6
43.7
39.0
36.4
29.5
25.9
24.5
21.1
14.1
O2N
N
O
3of
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56 7.56 7.54 7.54 7.52 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.13 7.13 7.12 7.11 7.07 7.07 7.05 7.05 7.05 7.03 6.79 6.77
2.99 2.95 2.86 2.86 2.82 2.82 2.69 2.66 2.66 2.66 2.43 2.42 2.42 2.41 2.40 2.39 2.38 2.38 2.36 2.36 2.33 2.33 2.32 2.31 2.31 1.83 1.81 1.81 1.79 1.77 1.77 1.49 1.48
O2N
O
N
Ph
3pf
5.13
3.04
0.89
2.04
1.00
3.04
2.04
2.95
f1 (ppm)


178.7
143.0
134.3
129.9
129.6
128.3
128.1
126.3
123.9
122.9
109.4
87.7
46.4
43.9
36.6
29.5
26.9
14.0
O2N
O
N
Ph
3pf
f1 (ppm)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7.83
7.31
7.31
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7.29
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7.28
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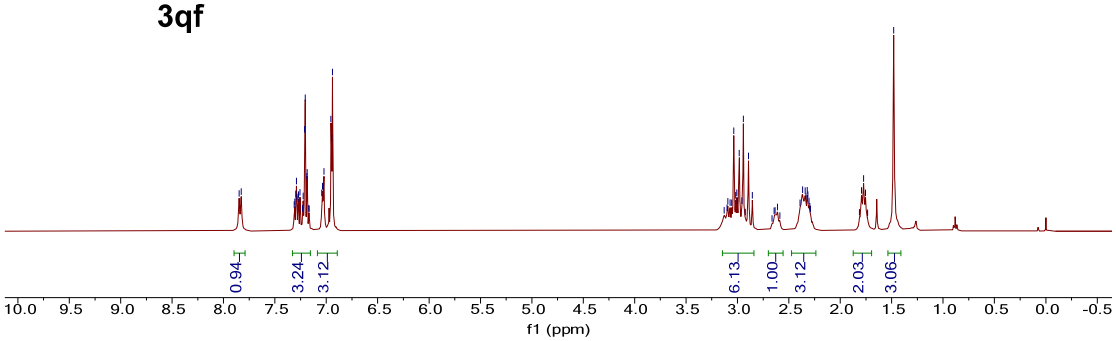
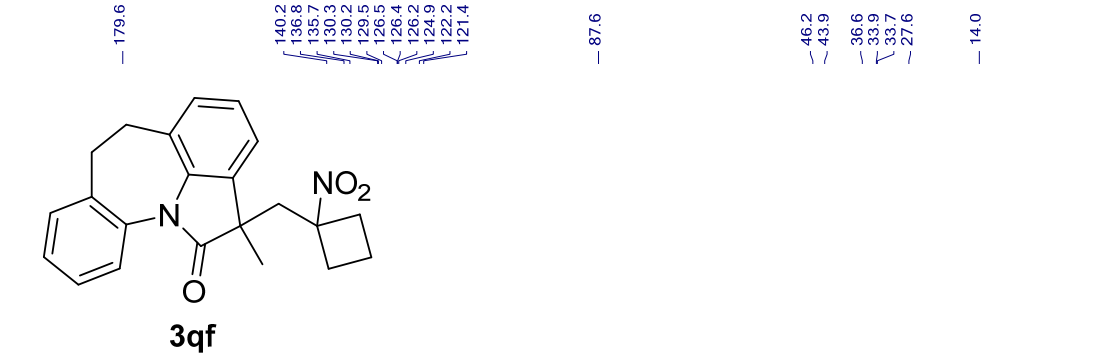
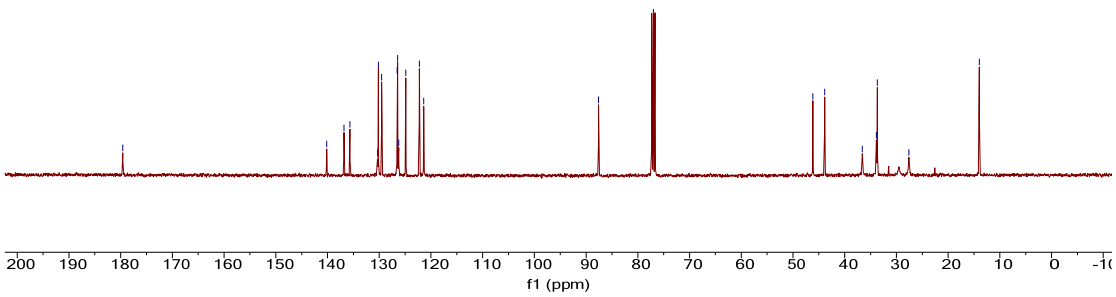
7.23
7.22
7.21
7.20
7.19
7.19
7.17
7.17
7.04
7.04
7.03
7.02
6.95
6.95
6.94
3.13
3.10
3.09
3.07
3.06
3.04
3.02
3.01
3.00
2.98
2.96
2.94
2.89
2.85
2.61
2.39
2.37
2.34
2.33
2.32
2.32
2.30
2.30
2.29
1.79
1.77
1.75
1.48
NO2
N
O

3qf


0.94
3.24
3.12
6.13
1.00
3.12
2.03
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


179.6
140.2
136.8
135.7
130.3
130.2
129.5
126.5
126.4
126.2
124.9
122.2
121.4
87.6
46.2
43.9
36.6
33.9
33.7
27.6
14.0
NO2
N
O

3qf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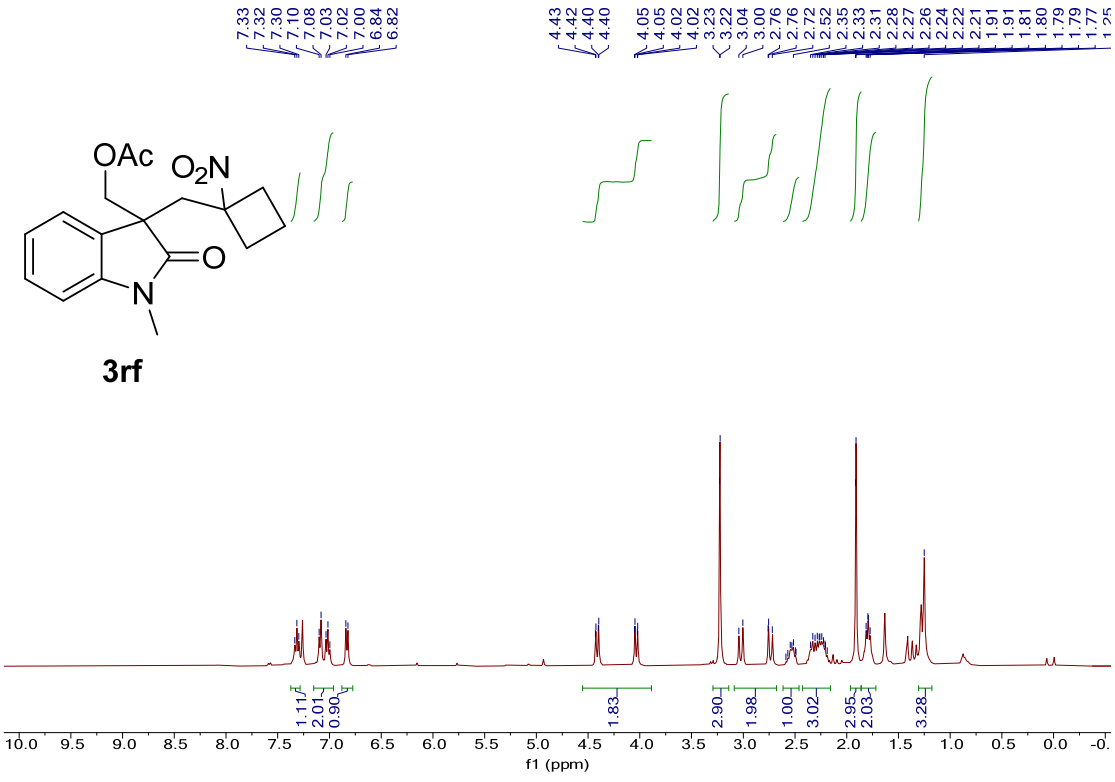
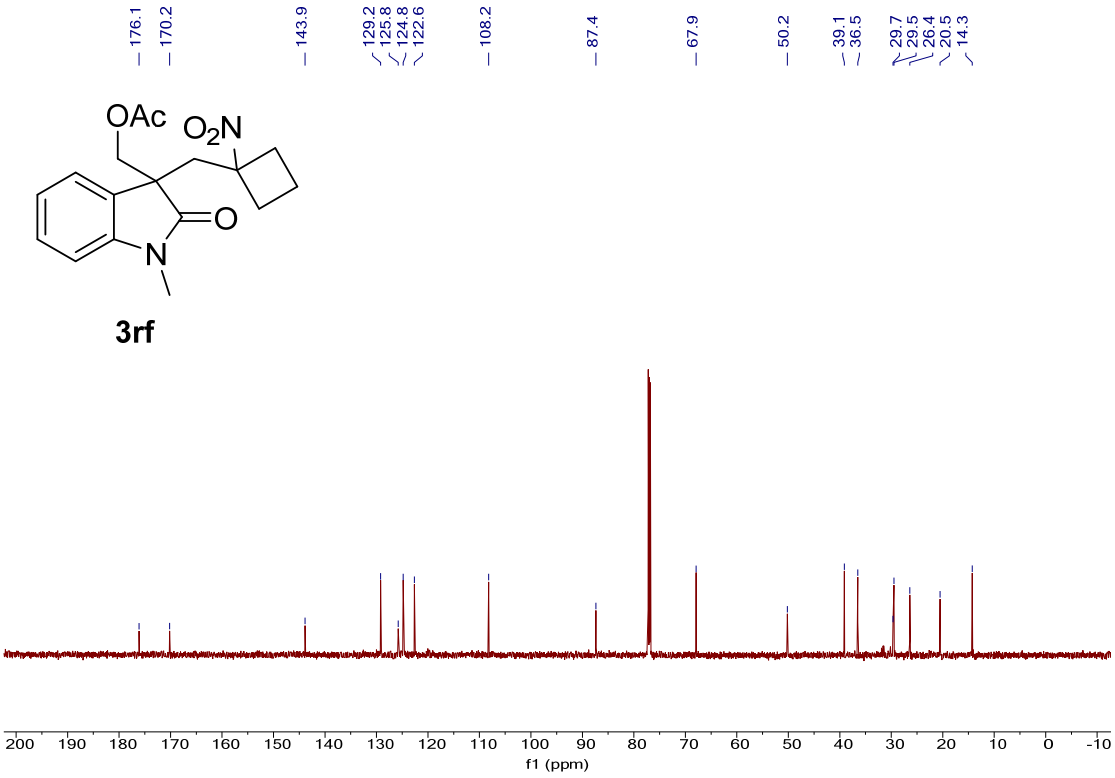
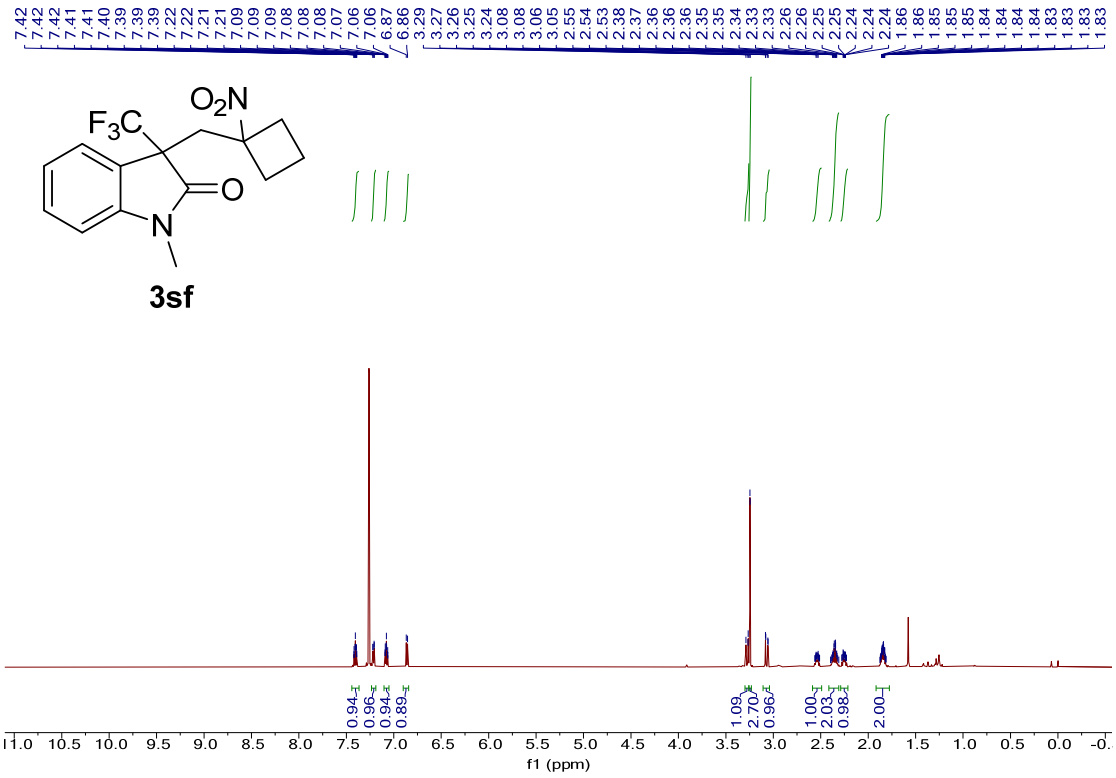
f1 (ppm)


OAc
O2N
O
N
3rf
f1 (ppm)


OAc
O2N
O
N
3rf
f1 (ppm)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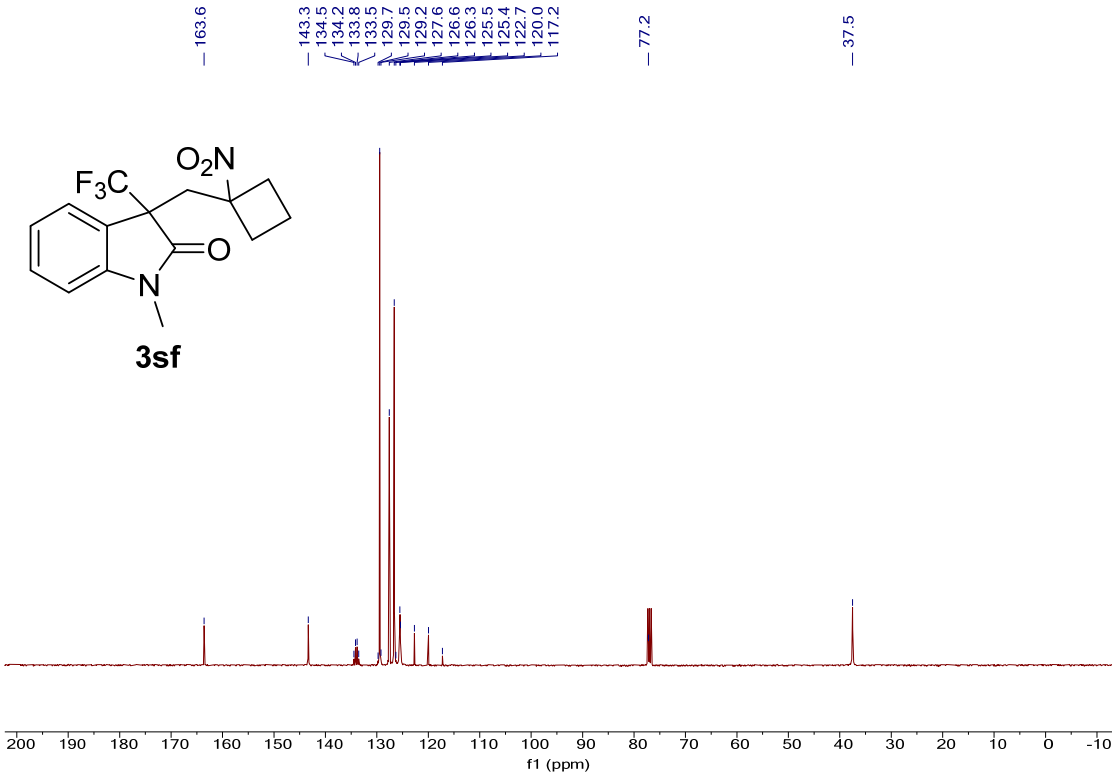
3.29 3.27 3.26 3.25 3.24 3.08 3.08 3.06 3.05 2.55 2.54 2.53 2.38 2.37 2.36 2.36 2.36 2.35 2.35 2.34 2.33 2.33 2.26 2.25 2.25 2.24 2.24 2.24 1.86 1.86 1.85 1.85 1.85 1.84 1.84 1.84 1.84 1.83 1.83 1.83 1.83
F3C
O2N
O
N
3sf
0.94 0.96 0.94 0.89
1.09 2.70 0.96
1.00 2.03 0.98
2.00
f1 (ppm)


163.6
143.3 134.5 134.2 133.8 133.5 129.7 129.5 129.2 127.6 126.6 126.3 125.5 125.4 122.7 120.0 117.2
77.2
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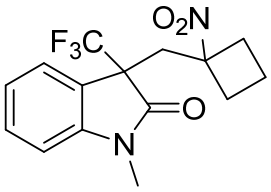
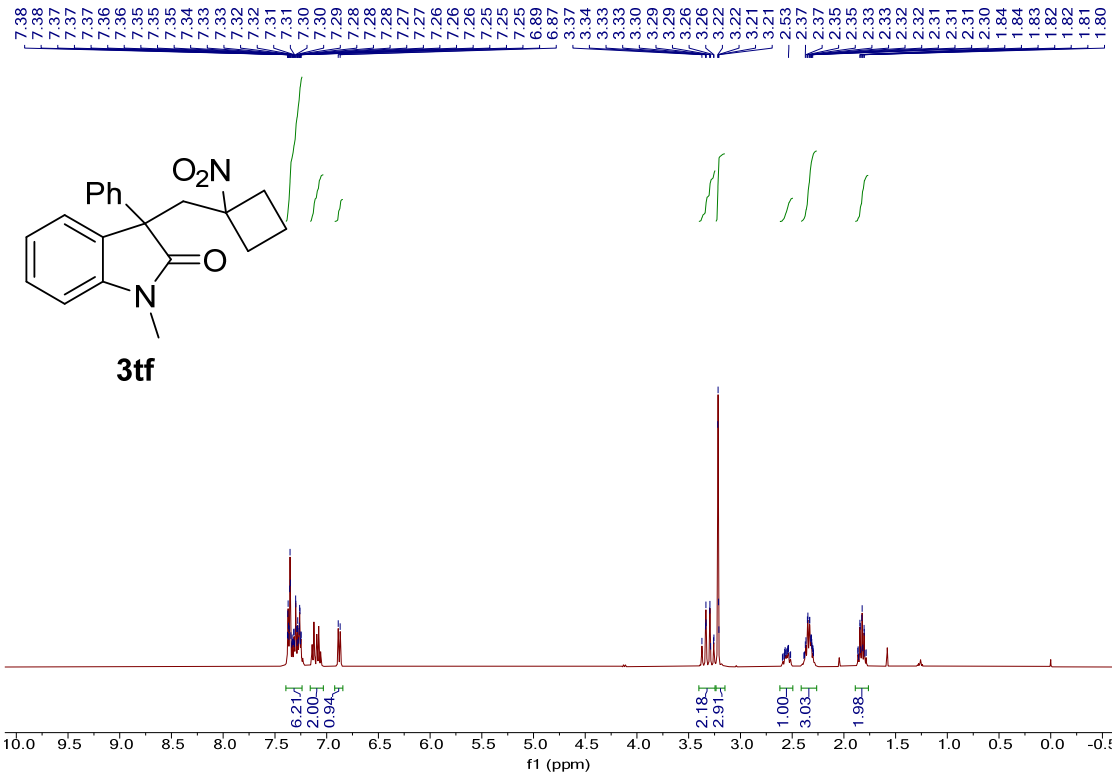
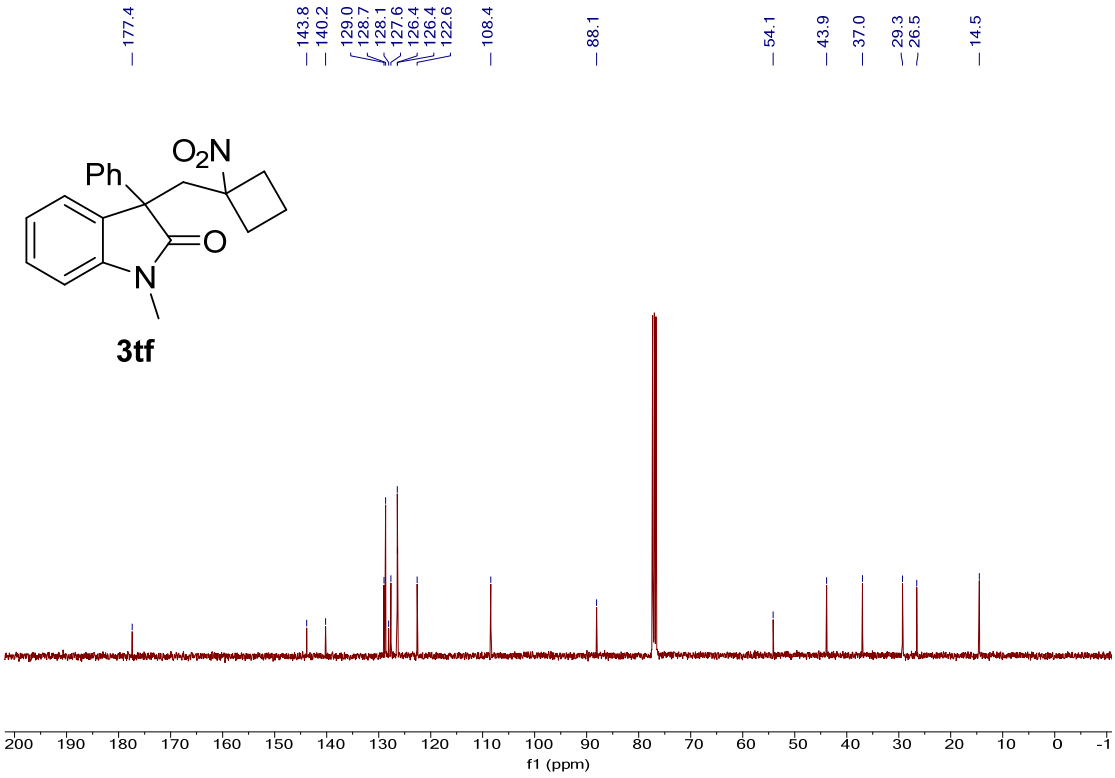
F3C
O2N
O
N
3sf
f1 (ppm)

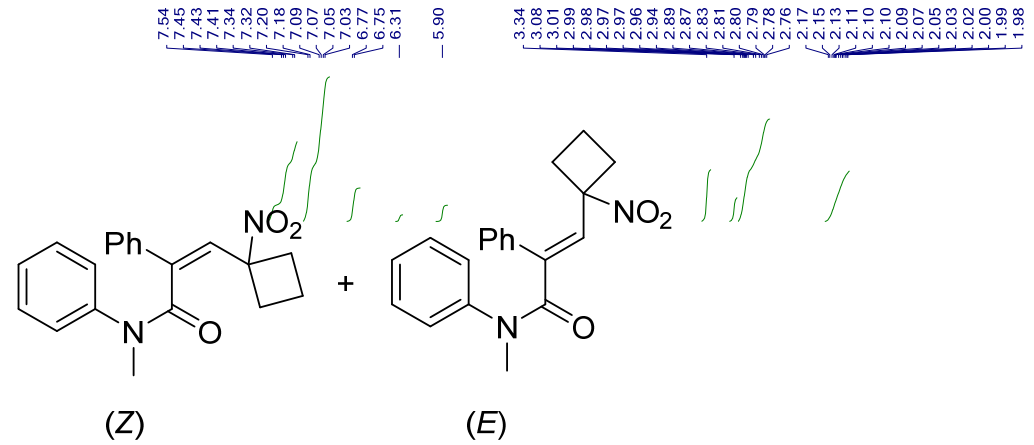

O_2N
F_3C
O
N

3sf

-73.76
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

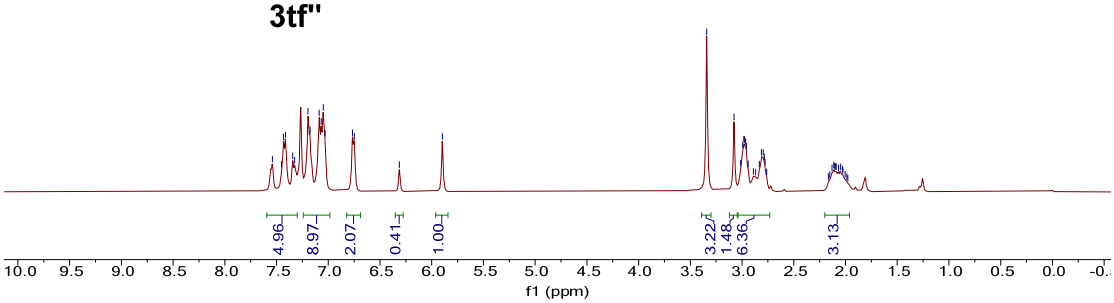

7.38 7.38 7.37 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 6.89 6.87
3.37 3.34 3.33 3.33 3.30 3.29 3.29 3.26 3.26 3.22 3.21 3.21 2.53 2.37 2.37 2.35 2.35 2.33 2.32 2.31 2.31 2.30 1.84 1.84 1.83 1.82 1.82 1.81 1.80
Ph
O2N
O
N
3tf
6.21 2.00 0.94 2.18 2.91 1.00 3.03 1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

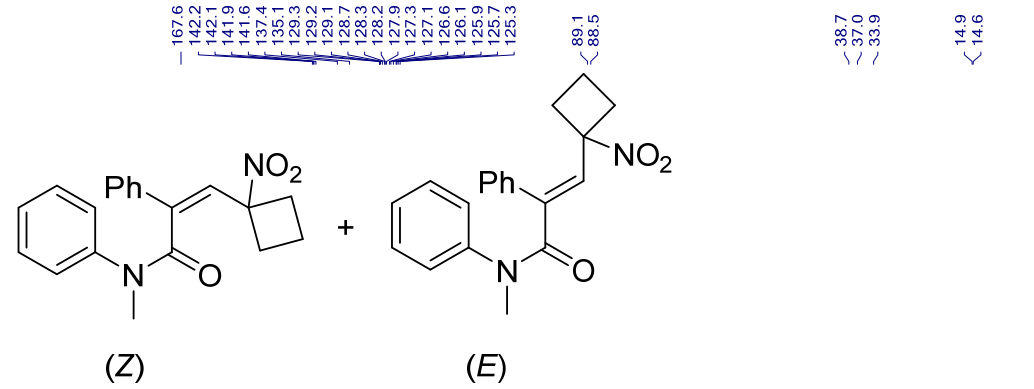

177.4
143.8 140.2 129.0 128.7 128.1 127.6 126.4 126.4 122.6 108.4 88.1 54.1 43.9 37.0 29.3 26.5 14.5
Ph
O2N
O
N
3tf
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.54
7.45
7.43
7.41
7.34
7.32
7.20
7.18
7.09
7.07
7.05
7.03
6.77
6.75
6.31
5.90
3.34
3.08
3.01
2.99
2.98
2.97
2.97
2.96
2.94
2.89
2.87
2.83
2.81
2.80
2.79
2.78
2.76
2.17
2.15
2.13
2.11
2.10
2.10
2.09
2.07
2.05
2.03
2.02
2.00
1.99
1.98
NO2
Ph
N
O
+
NO2
Ph
N
O

(*Z*) (*E*)

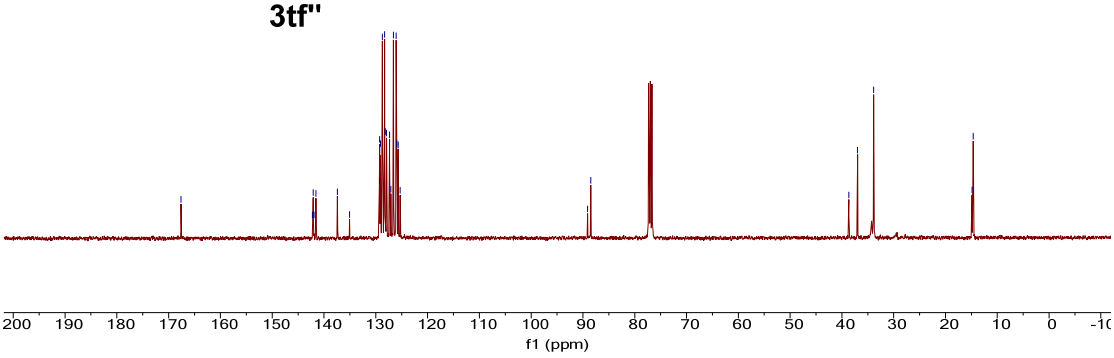
3tf''


4.96
8.97
2.07
0.41
1.00
3.22
1.48
6.36
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.6
142.2
142.1
141.9
141.6
137.4
135.1
129.3
129.2
129.1
128.7
128.3
128.2
127.9
127.3
127.1
126.6
126.1
125.9
125.7
125.3
89.1
88.5
38.7
37.0
33.9
14.9
14.6
NO2
Ph
N
O
+
NO2
Ph
N
O

(*Z*) (*E*)

3tf''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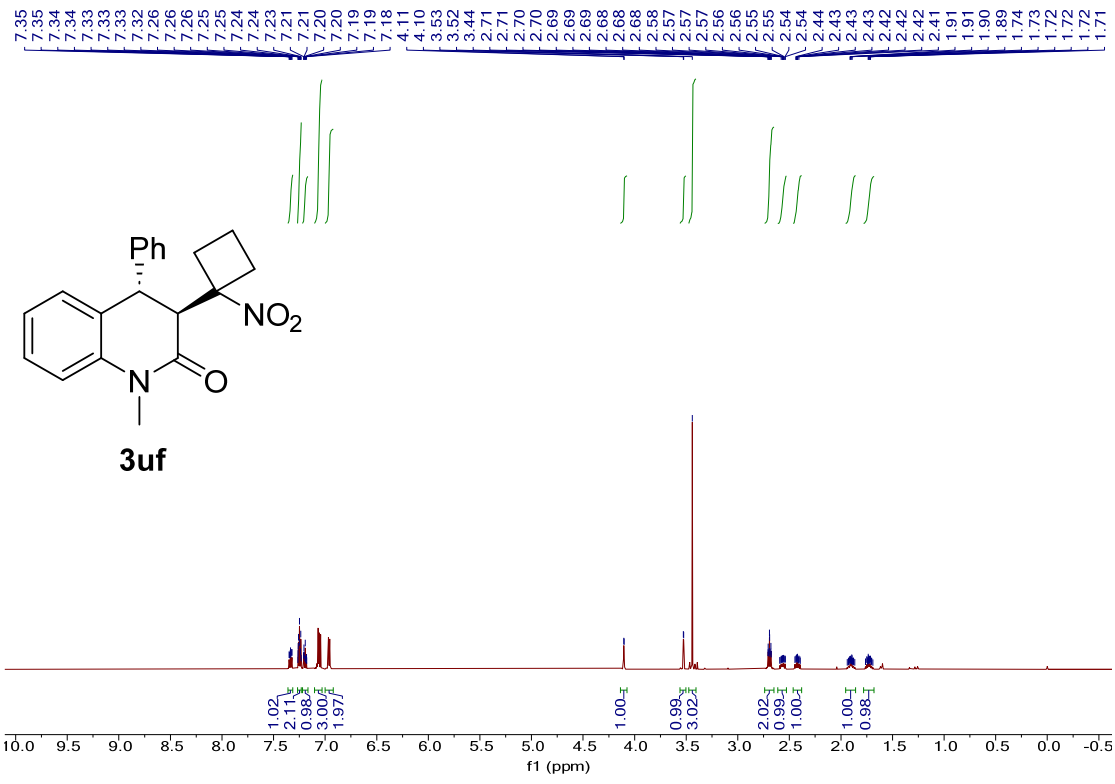
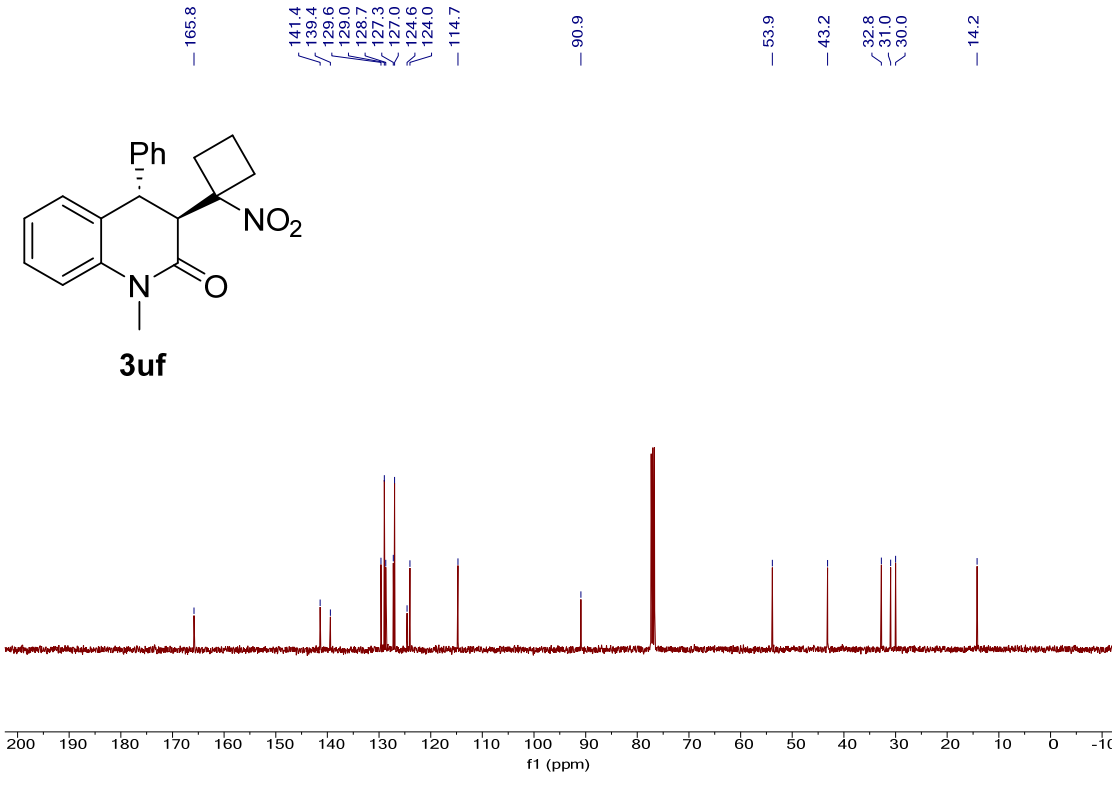
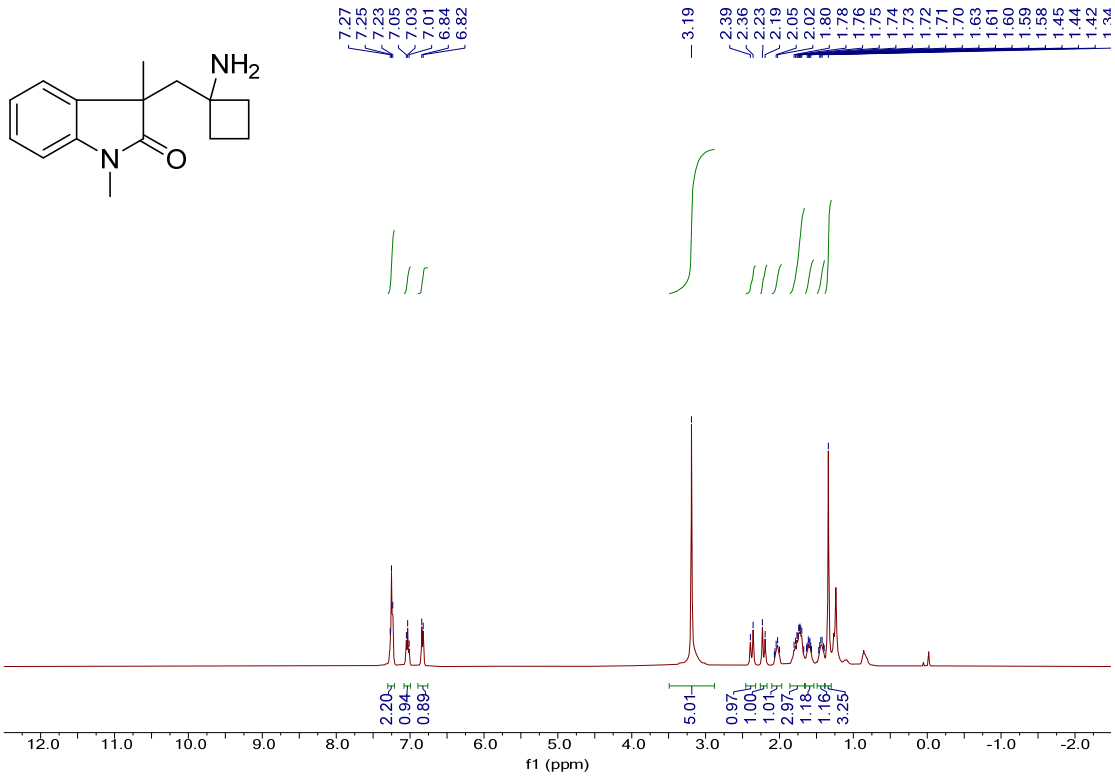
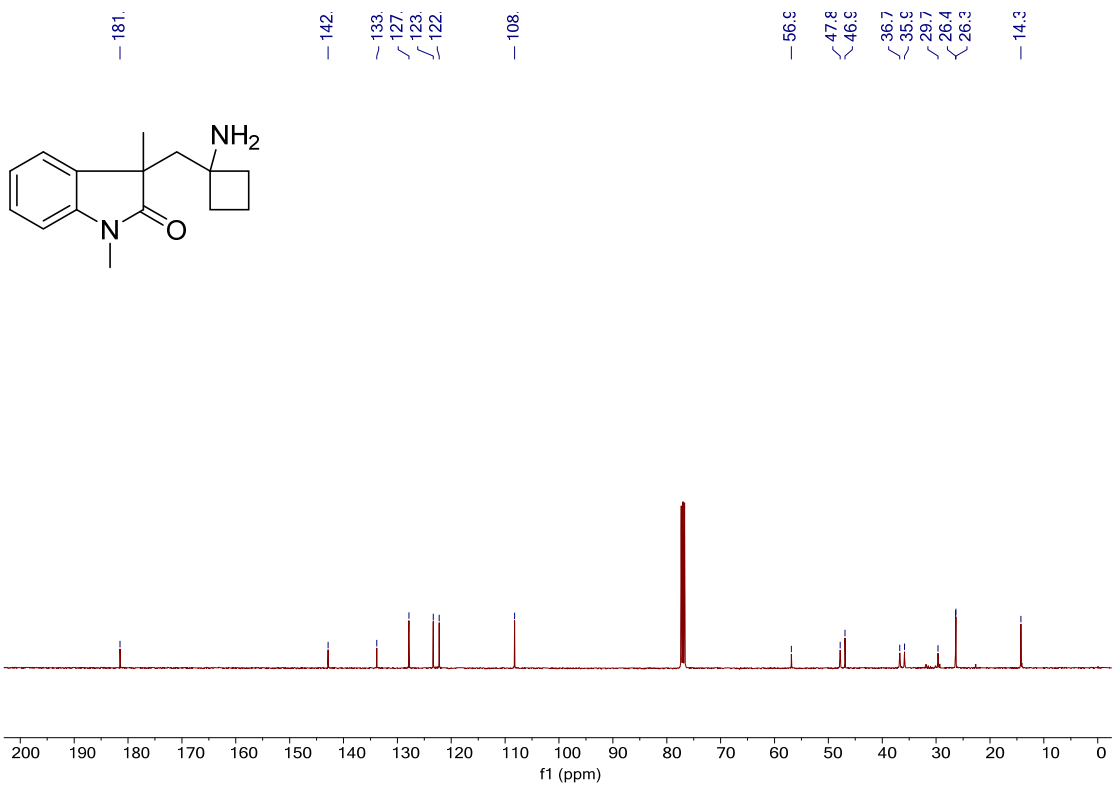
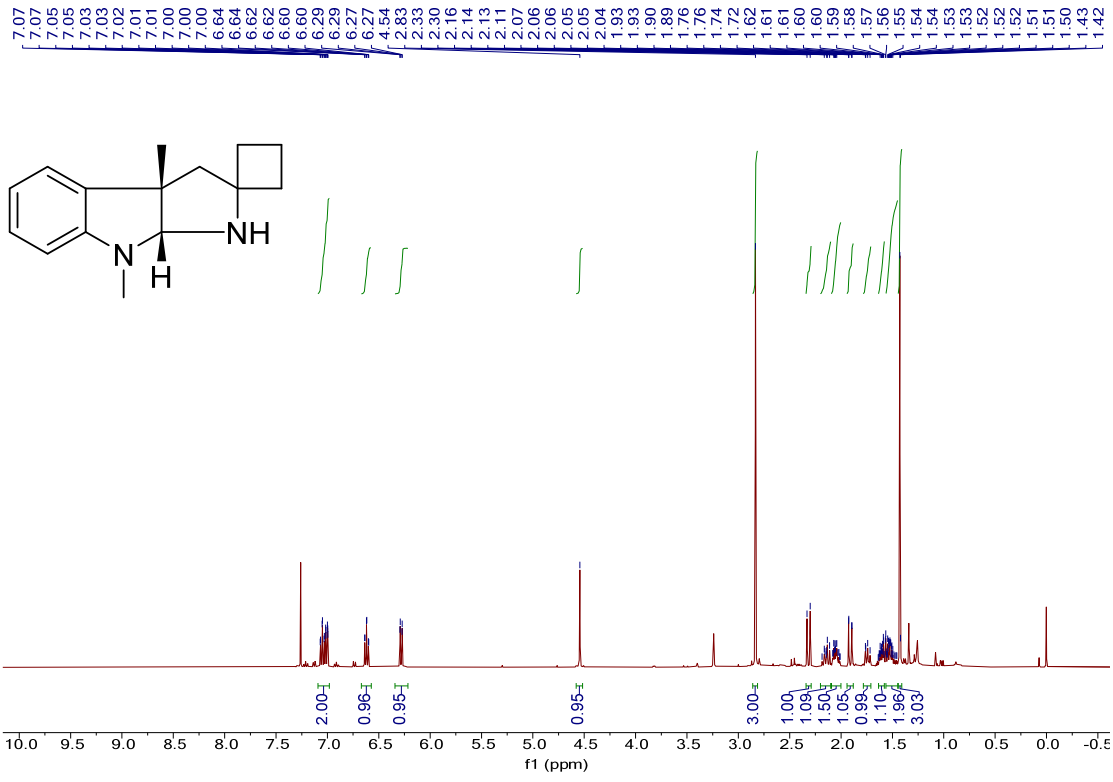
f1 (ppm)

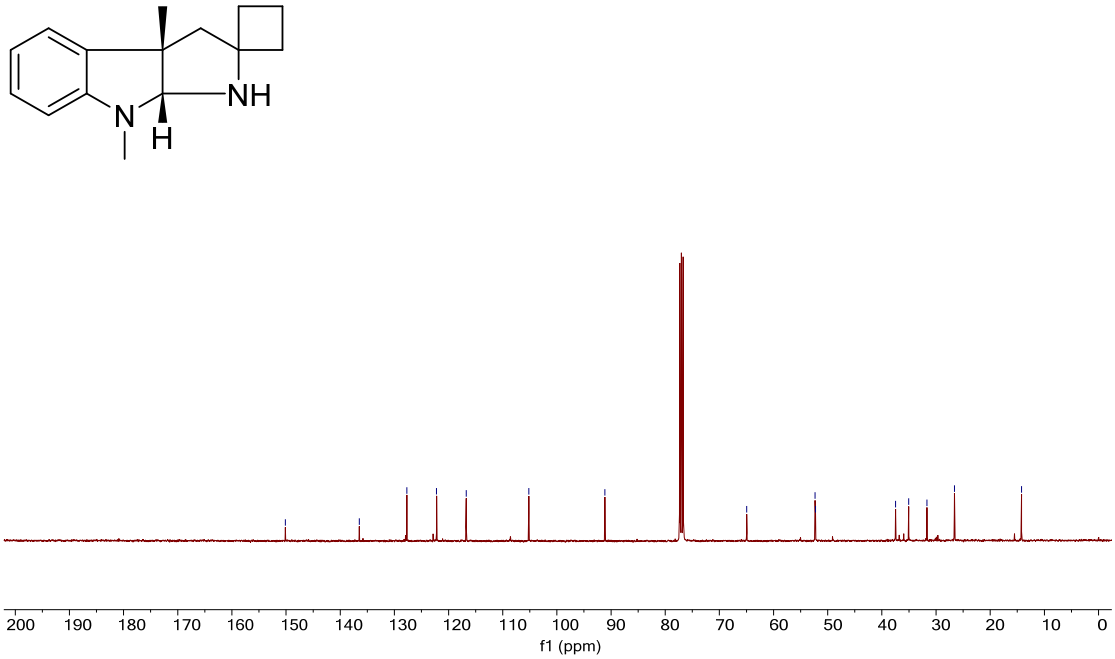

Ph
NO2
N
O
3uf
f1 (ppm)

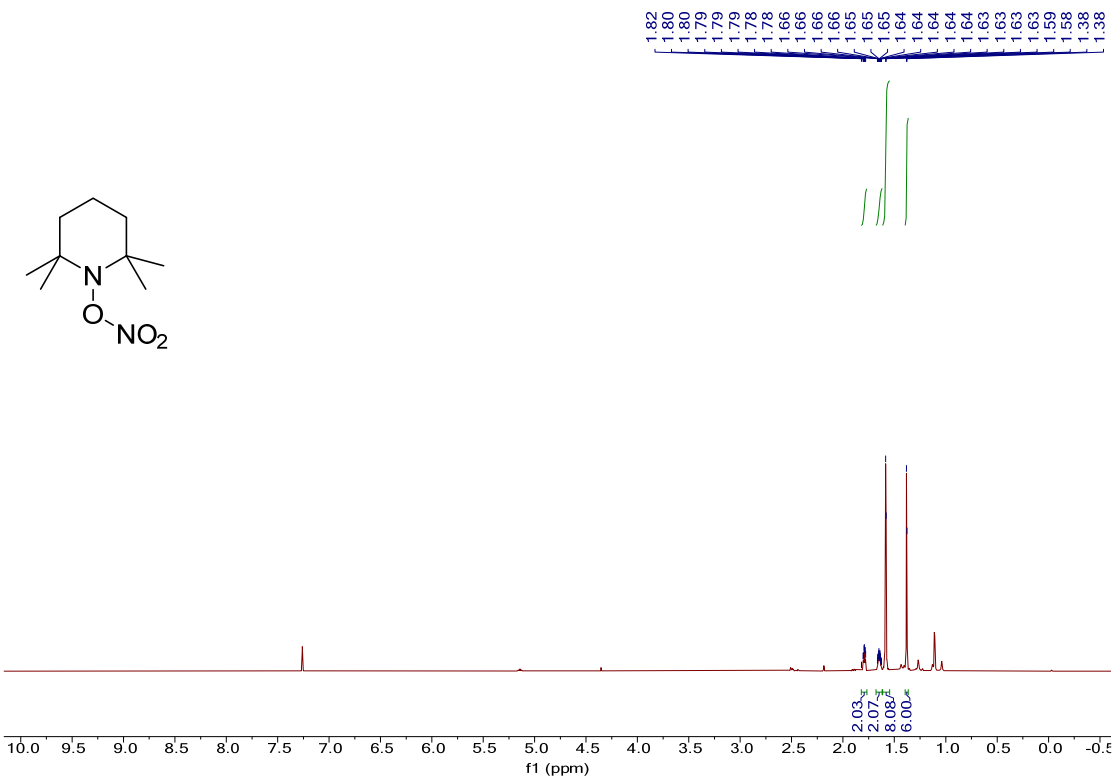

Ph
NO2
N
O
3uf
f1 (ppm)

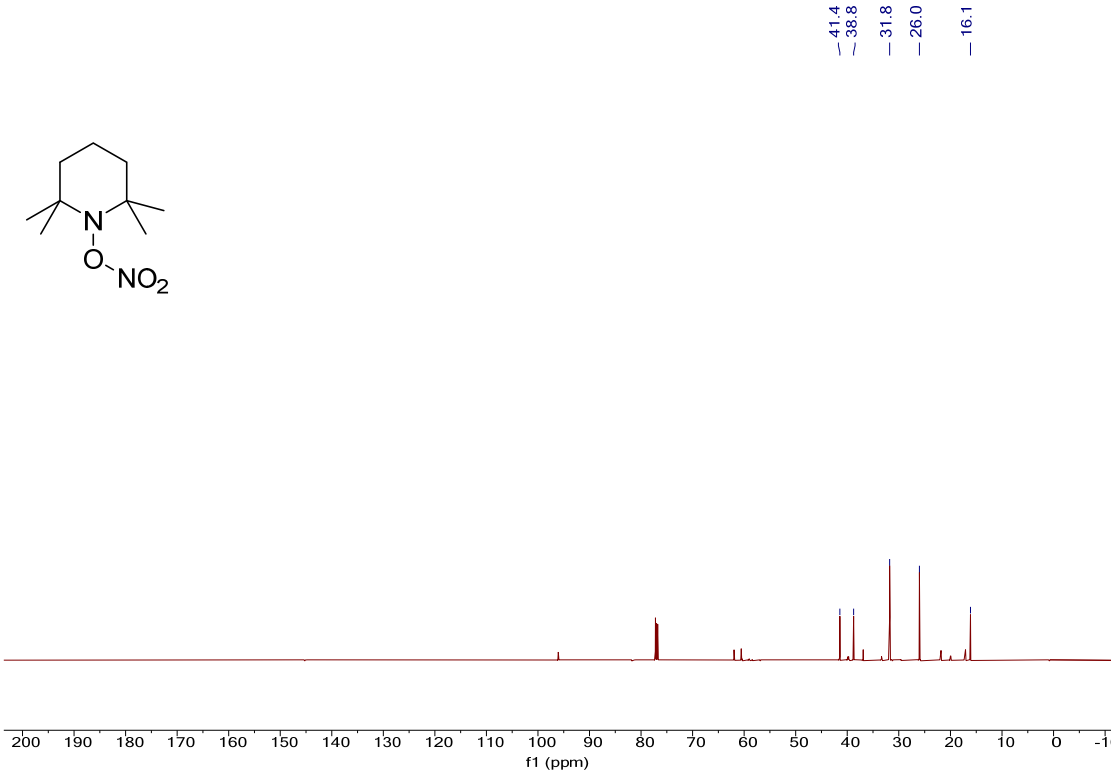

NH2
N
O
7.27
7.25
7.23
7.05
7.03
7.01
6.84
6.82
3.19
2.39
2.36
2.23
2.19
2.05
2.02
1.80
1.78
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.63
1.61
1.60
1.59
1.58
1.45
1.44
1.42
2.20
0.94
0.89
5.01
0.97
1.00
1.01
2.97
1.18
1.16
3.25
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)


NH2
N
O
181.
142.
133.
127.
123.
122.
108.
56.9
47.8
46.9
36.7
35.9
29.7
26.4
26.3
14.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
N
H
f1 (ppm)


NH
N
H
f1 (ppm)


1.82
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.66
1.66
1.66
1.65
1.65
1.65
1.64
1.64
1.64
1.64
1.63
1.63
1.63
1.63
1.59
1.58
1.38
1.38
N
O
NO2
2.03
2.07
8.08
6.00
f1 (ppm)


41.4
38.8
31.8
26.0
16.1
N
O
NO2
f1 (ppm)

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