

Supporting Information

Solvent-Controlled, Tunable β -OAc and β -H Elimination in Rh(III)-Catalyzed Allyl Acetate and Aryl Amides Coupling via C–H Activation

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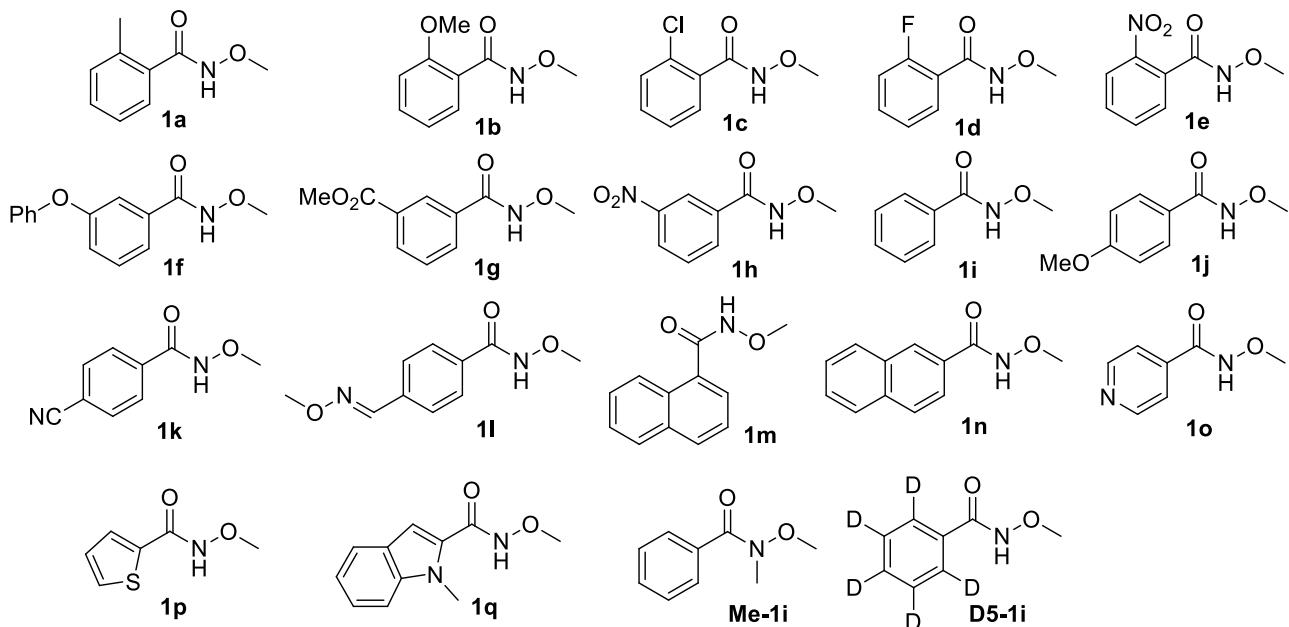
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I. General Remarks

Analytical thin layer chromatography (TLC) was performed on silica gel GF254 plates. Flash column chromatography was undertaken on silica gel (200–300 mesh). ¹H NMR was performed on Bruker DRX 600, 500 or 400 MHz at ambient temperature. Data was recorded as follows: chemical shift in ppm from solvent resonance employed as their internal standard (deuterochloroform at 7.26 ppm) on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; brs = broad singlet), coupling constant (Hz), integration, and assignment. ¹³C NMR was recorded on 150, 125 or 100 MHz at ambient temperature and fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.00 ppm of *d*-chloroform. High resolution mass spectra were measured on Agilent-G6540 UHD Accurate-MassQ-TOF. In experiments that required, THF, ethyl ether, 1,4-dioxane and toluene were refluxed and distilled over sodium/benzophenone under nitrogen; Dichloromethane, DCE and acetonitrile were distilled over CaH₂ under nitrogen; Methanol was distilled over magnesium/iodine under nitrogen. Other simple chemicals were analytical-pure grade and obtained commercially.

II. Preparation of substrates **1a–q**, **Me-1i**, **D5-1i**

Table S1. Prepared Substrates



Compounds **1a–h**, **1m–n**, **1p–q** were prepared following **Method 1**, compound **1o** was prepared

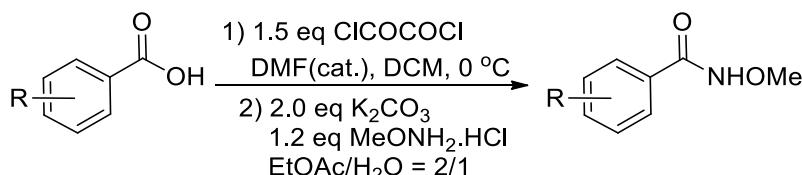
following **Method 2**, compound **1l** was prepared following **Method 3**, compound **Me-1i** was prepared following **Method 4**, compound **D5-1i** was prepared following **Method 5**.

1a-c, 1i, 1m^{S1}, 1h, 1j^{S2}, 1d, 1n, 1p^{S3}, 1g^{S4}, 1h^{S5}, 1q^{S6}, 1k, 1o^{S7}, Me-1i^{S8}, D5-1i^{S9} are known compounds.

1e: White solid. Yield: 715.0 mg, 3.645 mmol, 81%. **¹H NMR** (400 MHz, CDCl₃) δ 8.52 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 3.95 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 164.45, 146.28, 133.90 (2C), 131.04, 129.45, 124.60, 64.06.

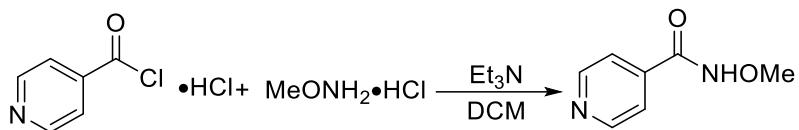
1f: Oil. Yield: 853.8 mg, 3.510 mmol, 78%. **¹H NMR** (500 MHz, CDCl₃) δ 9.97 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 3H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 165.33, 157.50, 156.45, 133.44, 129.89, 129.81, 123.71, 121.96, 121.64, 119.02, 117.38, 64.09.

1l: White solid. Yield: 815.2 mg, 3.915 mmol, 87%. **¹H NMR** (400 MHz, CDCl₃) δ 8.73 (s, 1H), 8.07 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 4.00 (s, 3H), 3.89 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 165.98, 147.35, 135.77, 132.57, 127.47, 127.12, 64.62, 62.28.



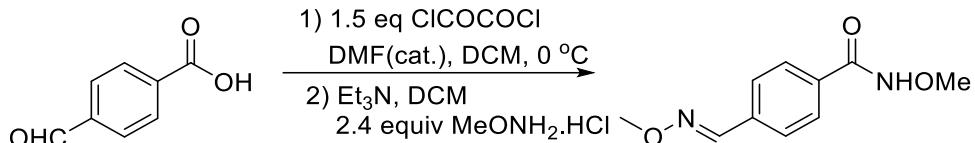
Scheme S1. General Procedure for Preparing Amides Using Method 1

Method 1: A dried round-bottom flask was charged with acid (4.5 mmol), DCM (15 mL), and 2 drops of DMF. Then, oxalyl chloride (0.60 mL, 0.876 g, 6.9 mmol) was added dropwise within 5 min at 0 °C. The resulting mixture was stirred at room temperature for 3.5 h and concentrated under reduced pressure. The residues was dissolved in EtOAc (40 mL) and K₂CO₃ (1.24 g, 9.0 mmol), MeONH₂·HCl (458 mg, 5.4 mmol), water (20 mL) were added sequentially. The resulting mixture was stirred for 20 h at room temperature and extracted with EtOAc (50 mL). The organic layer was washed with saturated aqueous NaHCO₃ (15 mL × 2), brine (15 mL × 2), and dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was recrystallized (EtOAc) to afford the product. In the case of an oil, the crude product was purified by silica gel column chromatography, using EtOAc/hexane as the eluent.



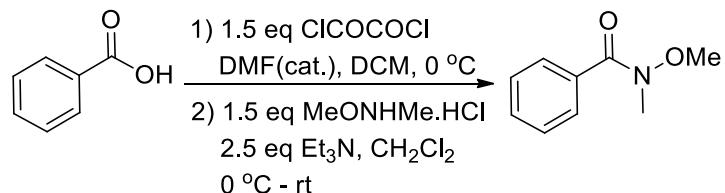
Scheme S2. Preparation of Amide 1o

Method 2: A mixture of methoxylamine hydrochloride (840 mg, 10 mmol) and Et₃N (4.15 mL, 3.03 g, 30 mmol) in DCM (20 mL) was stirred at room temperature for 3 h, and then cooled to 0 °C upon which acyl chloride (10 mmol) was added slowly. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Upon completion, the solvent was removed under reduced pressure. The residue was diluted with acetone (20 mL), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography, using EtOAc/hexane as the eluent.



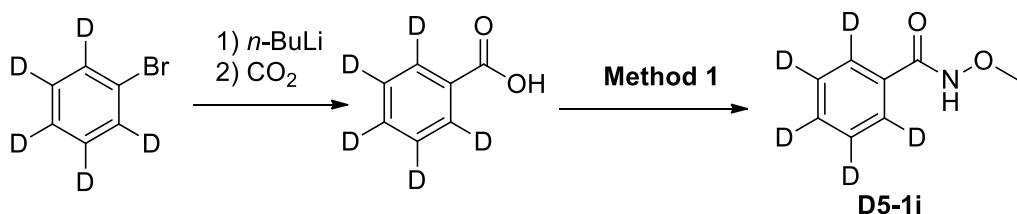
Scheme S3. Preparation of Amide 1l

Method 3: A dried round-bottom flask was charged with 4-formylbenzoic acid (675.0 mg, 4.5 mmol, 1.0 equiv), DCM (15 mL), and 2 drops of DMF. Then, oxalyl chloride (0.60 mL, 0.876 g, 6.9 mmol, 1.5 equiv) was added dropwise within 5 min at 0 °C. The resulting mixture was stirred at room temperature for 3.5 h and concentrated under reduced pressure. The residues was dissolved in DCM (20 mL) and then was added dropwise to the mixture of methoxylamine hydrochloride (916 mg, 10.8 mmol, 2.4 equiv) and Et₃N (2.09 mL, 1.52 g, 15 mmol, 3.3 equiv) in DCM (20 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Upon completion, the solvent was removed under reduced pressure. The residue was diluted with acetone (20 mL), filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography, using EtOAc/hexane as the eluent.



Scheme S4. Preparation of Amide Me-1i

Method 4: (1) A dried round-bottom flask was charged with benzoic acid (549.0 mg, 4.5 mmol, 1.0 equiv), DCM (15 mL), and 2 drops of DMF. Then, oxalyl chloride (0.60 mL, 0.876 g, 6.9 mmol, 1.5 equiv) was added dropwise within 5 min at 0 °C. The resulting mixture was stirred at room temperature for 3.5 h and concentrated under reduced pressure. (2) An oven-dried flask containing a stir bar and fitted with a septum was purged with N₂. The flask was then charged with N,O-dimethylhydroxylamine hydrochloride (0.66 g, 6.75 mmol, 1.5 equiv,) and dry CH₂Cl₂ (100 mL). The mixture was cooled to 0 °C and stirred for 5 min before the addition of Et₃N (1.57 mL, 1.14 g, 11.25 mmol, 2.5 equiv,) and the prepared benzoyl chloride. The resulting mixture was stirred for 30 min before warming to room temperature and stirring for 16 h. The mixture was treated with sat. aq. NaHCO₃ solution (10 mL) and stirred vigorously for 10 min. The phases were separated and the aqueous layer was re-extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phases were dried by passing through a hydrophobic frit and concentrated under reduced pressure to afford a residue that was purified by flash column chromatography (EtOAc/petroleum ether = 1/3) to afford the title compound.

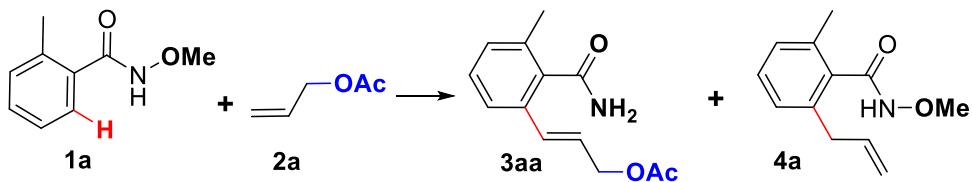


Scheme S5. Preparation of Amide D5-1i

Method 5: To a stirred solution of 2,3,4,5,6-pentadeuteriobromobenzene (500 mg, 3.09 mmol) in anhydrous THF (10 mL), a solution of *n*-BuLi in *n*-hexane (2.2 mL, 1.6M, 3.48 mmol) was added dropwise at -78 °C for 10 min. The mixture was stirred at the same temperature for 30 min, and then CO₂ was bubbled through the mixture at -78 °C for 10 min. The mixture was allowed to warm to ambient temperature, quenched with H₂O (20 mL), acidified to pH = 1 with 1M HCl, and extracted with EtOAc (3 × 30 mL). The combined organic phase was dried over MgSO₄, filtered and the solvents were removed in vacuum to give the product (yield: 319 mg, 2.51 mmol, 81%). **D5-1i** was prepared from the 2,3,4,5,6-pentadeuteriobenzoyl acid according to **Method 1**.

III. Optimization of reaction condition

Table S2. Optimization of Reaction Condition ^a

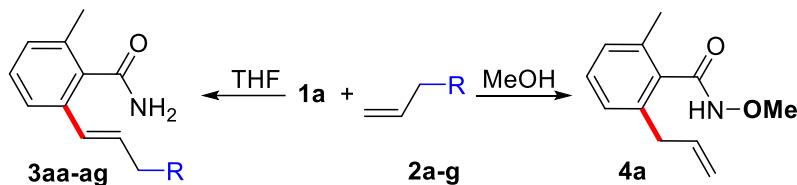


entry	catalyst	solvent	additive	yield (%)	
				3aa	4a
1	[Cp [*] RhCl ₂] ₂	MeOH	AgOAc	-	99
2	-	MeOH	AgOAc	-	-
3	[Cp [*] RhCl ₂] ₂ (0.8 mol %)	MeOH	AgOAc	-	88
4	[Cp [*] RhCl ₂] ₂	THF	AgOAc	46	19
5	[Cp [*] RhCl ₂] ₂	THF	-	-	-
6	[Cp [*] RhCl ₂] ₂	THF	LiOAc	39	23
7	[Cp [*] RhCl ₂] ₂	THF	NaOAc	25	18
8	[Cp [*] RhCl ₂] ₂	THF	KOAc	14	<10
9	[Cp [*] RhCl ₂] ₂	THF	CsOAc	<10	26
10	[Cp [*] RhCl ₂] ₂	THF	Ag ₂ CO ₃	49	15
11	[Cp [*] RhCl ₂] ₂	THF	AgOTf	-	<10
12	[Cp [*] RhCl ₂] ₂	THF	AgBF ₄	-	<10
13	[Cp [*] RhCl ₂] ₂ (3 mol %)	THF	Ag ₂ CO ₃	67	19
14 ^b	[Cp [*] RhCl ₂] ₂ (3 mol %)	THF	Ag ₂ CO ₃	74	18
15	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃	-	98
16	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃ (10 mol %)	-	89
17	[Cp [*] RhCl ₂] ₂ (3 mol %)	THF	Ag ₂ CO ₃ (30 mol %)	64	17
18 ^c	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃	-	85
19 ^c	[Cp [*] RhCl ₂] ₂ (3 mol %)	THF	Ag ₂ CO ₃	63	17
20 ^d	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃	-	88
21 ^e	[Cp [*] RhCl ₂] ₂	THF	Ag ₂ CO ₃	53	15
22 ^f	[Cp [*] RhCl ₂] ₂	THF	Ag ₂ CO ₃	<10	<10

23 ^g	[Cp [*] RhCl ₂] ₂	THF	Ag ₂ CO ₃	73	16
24 ^f	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃	-	47
25 ^g	[Cp [*] RhCl ₂] ₂	MeOH	Ag ₂ CO ₃	-	97

^a The reactions were carried out when the dry solvents (2 mL) refluxing using **1a** (0.2 mmol), **2a** (43 μ L), catalyst (1.5 mol %) and silver additive (20 mol %) for 12 hours. Isolated yield. ^b 200% 4 \AA molecular sieves was added. ^c 8 h. ^d 50 $^{\circ}\text{C}$. ^e rt. ^f The solvent is not dried in advance. ^g In O₂.

Table S3. Scope of Allyl Resources^a



entry	R	yield (%)	
		3aa-ag _(THF)	4a _(MeOH)
1	OAc, 2a	74	98
2	OBz, 2b	18	54
3	OCOCF ₃ , 2c	<10	23
4	OCOOMe, 2d	23	99
5	OTf, 2e	0	<10
6	OPO(OEt) ₂ , 2f	0	47
7	Br, 2g	0	17

^a The reactions were carried out at 70 $^{\circ}\text{C}$ using **1a** (33.0 mg, 0.2 mmol), **2a-g** (2.5 equiv), and Ag₂CO₃ (20 mol %) for 12 hours. Isolated yield. (1) In MeOH, [Cp^{*}RhCl₂]₂: 1.5 mol %; (2) in THF, [Cp^{*}RhCl₂]₂: 3 mol % and 60 mg 4 \AA molecular sieves.

IV. General procedures for 3aa-pa preparation

A 10 mL dried sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate (0.20 mmol, 1.0 equiv), [Cp^{*}RhCl₂]₂ (3.7 mg, 0.006 mmol, 3.0 mol %), Ag₂CO₃ (11.0 mg, 0.04 mmol, 20 mol %), 200% 4 \AA molecular sieves and anhydrous THF (2.0 mL), allyl reagent (43 μ L, 0.4 mmol, 2.0 equiv). The tube was then capped and submerged into a pre-heated 70 $^{\circ}\text{C}$ oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The

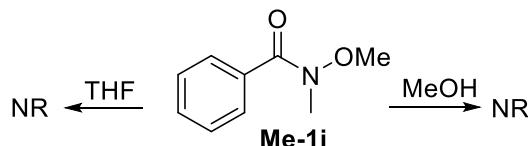
resulting residue was purified by chromatography (petrol ether/ethyl acetate = 3/1).

V. General procedures for 4a-q preparation

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate (0.20 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (1.9 mg, 0.003 mmol, 1.5 mol %), Ag_2CO_3 (11.0 mg, 0.04 mmol, 20 mol %) and anhydrous CH_3OH (2.0 mL), allyl reagent (43 μL , 0.4 mmol, 2.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The resulting residue was purified by chromatography (petrol ether/ethyl acetate = 5/1).

VI. Mechanistic study of the reactions

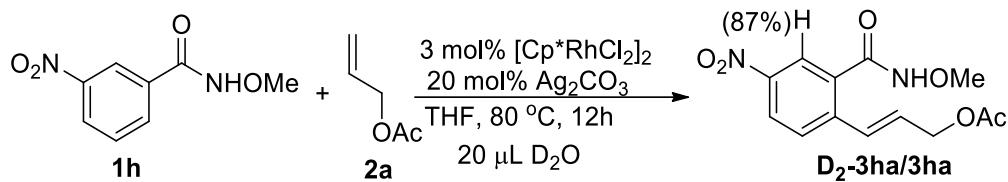
Followed the standard conditions of THF reaction and methanol reaction respectively, using **Me-1i** as the starting material. After the reactions finished, they was monitored by TLC analysis. Nonetheless, no product was observed but the reactant, elucidating that the directing atom is the anionic nitrogen. (Scheme S6)



Scheme S6. Activity of Me-1i in the Solvent-Controlled Reaction

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate **1h** (39.2 mg, 0.20 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.6 mg, 0.006 mmol, 3 mol %), Ag_2CO_3 (11.0 mg, 0.04 mmol, 20 mol %), THF (2.0 mL), allyl acetate **2a** (43 μL , 0.4 mmol, 2.0 equiv) and D_2O (20 μL) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The resulting residue was purified by chromatography (petrol ether/ethyl acetate = 3/1). The deuterium ratio of the product was determined by ^1H NMR.

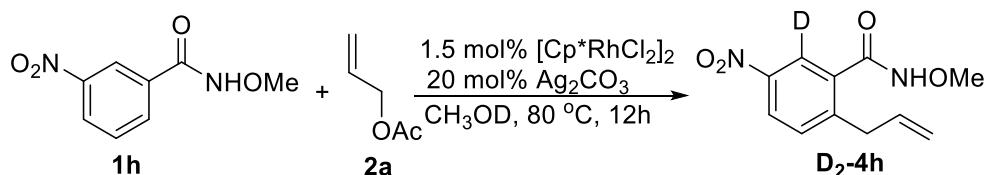
Since H/D scrambling was observed at the 2-site of the product **3ha** (Scheme S7), the C–H bond activation is reversible.



Scheme S7. 3ha Preparation in D₂O-Contained THF

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate **1h** (39.2 mg, 0.20 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (1.8 mg, 0.003 mmol, 1.5 mol %), Ag₂CO₃ (11.0 mg, 0.04 mmol, 20 mol %) and CH₃OD (2.0 mL), allyl acetate **2a** (43 μL, 0.4 mmol, 2.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The resulting residue was purified by chromatography (petrol ether/ethyl acetate = 5/1). (Note: the CH₃OD was obtained commercially and directly used without pre-procedures.) The deuterium ratio of the product was determined by ¹H NMR.

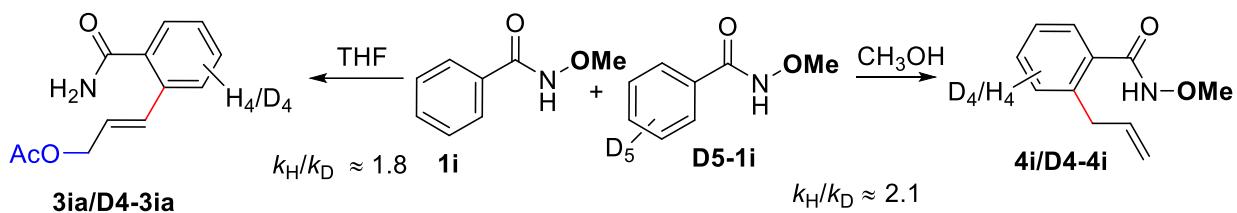
Since H/D scrambling was observed at the 2-site of the product **4h** (Scheme S8), the C–H bond activation is reversible.



Scheme S8. 4h Preparation in CH₃OD

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate (**1i**: 15.1 mg, 0.10 mmol; **D5-1i**: 15.6 mg, 0.10 mmol), [Cp*RhCl₂]₂ (1.8 mg, 0.003 mmol, 1.5 mol %), Ag₂CO₃ (11.0 mg, 0.04 mmol, 20 mol %) and CH₃OH or THF (2.0 mL), allyl acetate **2a** (43 μL, 0.4 mmol, 2.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The resulting residue was purified by chromatography. The values of the kinetic isotopic effect were determined by ¹H NMR.

The kinetic isotopic effect is 1.8 in THF and 2.1 in MeOH, respectively (Scheme S9), indicating the fact that the C–H bond activation is the rate determining step in both reactions.



Scheme S9. Intermolecular Kinetic Isotopic Effect Measurement

VII. Preparation of product 5a

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate **4a** (40.8 mg, 0.20 mmol), Grubbs 2nd catalyst (8.5 mg, 0.01 mmol, 5.0 mol %), DCM (2.0 mL) and 1-hexene (200 μ L, 1.6 mmol, 8.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 50 °C oil bath and stirred for 18 h. After cooled to rt, the solvent was removed under reduced pressure and the resulting residue was purified by chromatography to get product **5a** in the yield of 87% (0.174 mmol, 45.5 mg). (*E* style of alkene: 36.6 mg, 0.14 mmol, 70%)

VIII. Preparation of product 6i

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate **1i** (30.2 mg, 0.20 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.7 mg, 0.006 mmol, 3.0 mol %), Ag_2CO_3 (11.0 mg, 0.04 mmol, 20 mol %) and THF (2.0 mL), allyl acetate **2a** (43 μ L, 0.4 mmol, 2.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. Then $[\text{Cp}^*\text{RhCl}_2]_2$ (1.9 mg, 0.003 mmol, 1.5 mol %), Ag_2CO_3 (11.0 mg, 0.04 mmol, 20 mol %), CH_3OH (2.0 mL) and allyl acetate **2a** (43 μ L, 0.4 mmol, 2.0 equiv) were added to the tube under Argon. Closed the tube and kept the tube in a 70 °C oil bath for another 12 h. After cooled to rt, the solvent was removed under reduced pressure and the resulting residue was purified by chromatography to get product **6i** in the yield of 42% (0.084 mmol, 21.8 mg).

IX. Preparation of product 7a

To a 10 mL sealed tube (with a Teflon cap) which was charged with **3aa** (46.6 mg, 0.20 mmol), NaN_3 (14.3 mg, 0.22 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (11.1 mg, 5 mol %), THF (1.5 mL) and H_2O (0.5 mL) were added under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure. The

mixture was purified by chromatography to get product **7a** in the yield of 96% (0.192 mmol, 41.5 mg).

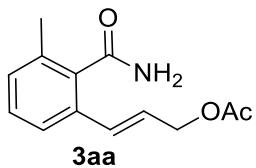
X. Preparation of product **8a**

To a 10 mL sealed tube (with a Teflon cap) which was charged with **3aa** (46.6 mg, 0.20 mmol) and DMF (2 mL) under Argon and in ice-water bath, NaH (10 mg, 0.25 mmol, 60% in mineral oil) was added. The mixture was stirred at 0 °C for 5 minutes and then Pd(PPh₃)₄ (11.1 mg, 5 mol %) was added. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, the solvent was removed under reduced pressure and the resulting residue was purified by chromatography to get product **8a** in the yield of 81% (0.162 mmol, 28.1 mg).

XI. Preparation of product **9aa-9ac**

A 10 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with substrate **1a** (0.20 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (1.9 mg, 0.003 mmol, 1.5 mol %), Ag₂CO₃ (11.0 mg, 0.04 mmol, 20 mol %), anhydrous CH₃OH (2.0 mL) and allyl reagent (43 µL, 0.4 mmol, 2.0 equiv) under Argon. The tube was then capped and submerged into a pre-heated 70 °C oil bath and stirred overnight. After cooled to rt, halogen reagent (NCS, NBS, NIS) (0.22 mmol, 1.1 equiv) was added and the closed tube was submerged into the 70 °C oil bath and stirred for another 1 h. After cooled to rt, the solvent was removed under reduced pressure and the resulting residue was purified by chromatography to get product **9aa-9ac**.

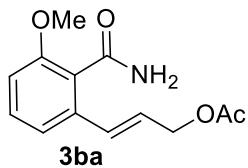
XII. Characterization of products **3aa-3pa**, **3aa-3ab**, **3ad**, **4a-4q**, **5i**, **6a-8a**, **9aa-ac**



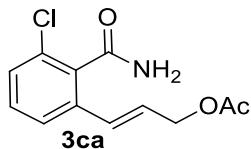
3aa (E)-3-(2-carbamoyl-3-methylphenyl)allyl acetate

Yield: 34.5 mg, 0.148 mmol, 74%. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.23 (s, 1H), 5.80 (s, 1H), 4.70 (dd, *J* = 6.3, 1.3 Hz, 2H), 2.38 (s, 3H), 2.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.64, 170.77, 135.77, 134.48, 132.91, 130.83, 129.78, 129.03, 125.90,

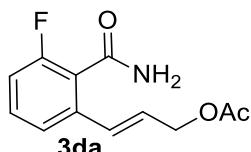
123.07, 64.91, 20.90, 19.18. **HRMS** (ESI) m/z calcd for $C_{13}H_{15}NNaO_3$ ($[M+Na]^+$): 256.0944, found: 256.0941.



Yield: 34.4 mg, 0.138 mmol, 69%. White solid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.31 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 15.8 Hz, 1H), 6.85 (d, J = 7.2 Hz, 1H), 6.27 (dt, J = 6.2, 15.8 Hz, 1H), 5.99 (s, 1H), 5.90 (s, 1H), 4.71 (d, J = 6.2 Hz, 2H), 3.85 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.79, 169.21, 156.13, 135.64, 130.74, 130.34, 126.20, 124.64, 118.41, 110.31, 64.90, 55.93, 20.94. **HRMS** (ESI) m/z calcd for $C_{13}H_{15}NNaO_4$ ($[M+Na]^+$): 272.0893, found: 272.0889.

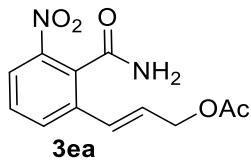


Yield: 29.9 mg, 0.118 mmol, 59%. White solid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 6.9, 2.0 Hz, 1H), 7.31 (t, J = 6.9, 2.0 Hz, 1H), 7.30 (d, J = 6.9 Hz, 1H), 6.78 (d, J = 15.8 Hz, 1H), 6.32 (dt, J = 15.8, 6.2 Hz, 1H), 6.08 (s, 1H), 5.78 (s, 1H), 4.72 (dd, J = 6.2, 1.4 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.72, 168.41, 135.50, 134.82, 130.69, 130.17, 129.47, 128.80, 127.60, 124.15, 64.56, 20.90. **HRMS** (ESI) m/z calcd for $C_{12}H_{12}ClNNaO_3$ ($[M+Na]^+$): 276.0398, found: 276.0400.



Yield: 27.0 mg, 0.114 mmol, 57%. White solid. **1H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 2H), 7.03 (ddd, J = 9.3, 7.0, 2.3 Hz, 1H), 6.92 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.9, 6.2 Hz, 1H), 6.25 (s, 1H), 5.95 (s, 1H), 4.72 (dd, J = 6.2, 1.2 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.74, 166.32, 159.25 (d, J_{C-F} = 247.6 Hz), 137.03 (d, J_{C-F} = 3.4 Hz), 131.02 (d, J_{C-F} = 9.0 Hz), 129.83 (d,

$J_{C-F} = 2.9$ Hz), 127.33, 122.79 (d, $J_{C-F} = 17.7$ Hz), 122.08 (d, $J_{C-F} = 3.1$ Hz), 114.96 (d, $J_{C-F} = 22.4$ Hz), 64.64, 20.89. **HRMS** (ESI) m/z calcd for $C_{12}H_{12}FNNaO_3$ ($[M+Na]^+$): 260.0693, found: 260.0688.



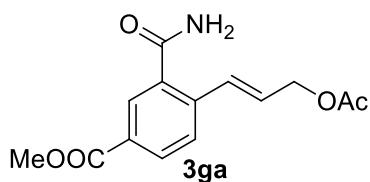
3ea (E)-3-(2-carbamoyl-3-nitrophenyl)allyl acetate

Yield: 24.3 mg, 0.092 mmol, 46%. White solid. **¹H NMR** (400 MHz, Acetone) δ 8.06 (d, $J = 8.0$ Hz, 1H), 8.02 (dd, $J = 8.0, 0.7$ Hz, 1H), 7.63 (t, $J = 8.0$ Hz, 1H), 7.45 (s, 1H), 7.13 (s, 1H), 6.94 (d, $J = 15.9$ Hz, 1H), 6.53 (dt, $J = 15.9, 5.8$ Hz, 1H), 4.75 (dd, $J = 5.8, 1.6$ Hz, 2H), 2.06 (s, 3H). **¹³C NMR** (100 MHz, Acetone) δ 170.65, 167.58, 147.65, 136.62, 133.14, 131.82, 130.23, 129.80, 128.85, 124.10, 64.74, 20.72. **HRMS** (ESI) m/z calcd for $C_{12}H_{12}N_2NaO_5$ ($[M+Na]^+$): 287.0638, found: 287.0633.



3fa⁶ (E)-3-(2-carbamoyl-4-phenoxyphenyl)allyl acetate

Yield: 28.6 mg, 0.092 mmol, 46%. White solid. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, $J = 8.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 2.5$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.07 – 7.00 (m, 4H), 6.18 (dt, $J = 15.8, 6.3$ Hz, 1H), 5.82 (s, 2H), 4.73 (dd, $J = 6.3, 1.2$ Hz, 2H), 2.10 (s, 3H). **¹³C NMR** (100 MHz, $CDCl_3$) δ 170.90, 170.07, 157.23, 156.23, 135.53, 130.80, 129.98, 129.52, 128.53, 125.53, 124.06, 120.67, 119.36, 117.30, 65.04, 20.98. **HRMS** (ESI) m/z calcd for $C_{18}H_{17}NNaO_4$ ($[M+Na]^+$): 334.1050, found: 334.1052.

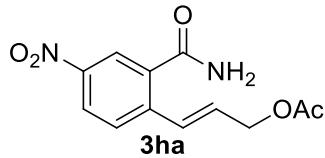


3ga (E)-methyl 4-(3-acetoxyprop-1-enyl)-3-carbamoylbenzoate

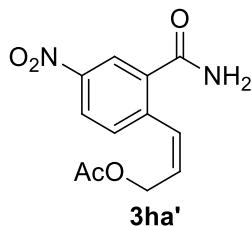
Yield: 37.2 mg, 0.134 mmol, 67%. White solid. **¹H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, $J = 1.6$ Hz, 1H), 8.05 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.63 (d, $J = 8.2$ Hz, 1H), 7.13 (d, $J = 16.0$ Hz, 1H), 6.34 (dt, $J =$

16.0, 6.1 Hz, 1H), 6.08 (s, 1H), 6.02 (s, 1H), 4.75 (dd, $J = 6.1, 1.3$ Hz, 2H), 3.92 (s, 3H), 2.10 (s, 3H).

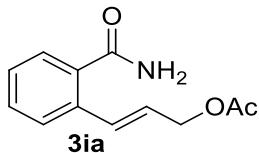
^{13}C NMR (100 MHz, CDCl_3) δ 170.83, 170.01, 166.01, 139.34, 134.13, 131.47, 130.21, 129.39, 128.95, 128.62, 126.98, 64.66, 52.36, 20.92. **HRMS** (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{NNaO}_5$ ($[\text{M}+\text{Na}]^+$): 300.0842, found: 300.0845.



Yield: 16.9 mg, 0.064 mmol, 32%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.42 (d, $J = 2.4$ Hz, 1H), 8.25 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.13 (d, $J = 15.9$ Hz, 1H), 6.40 (dt, $J = 15.9, 5.9$ Hz, 1H), 6.05 (s, 2H), 4.78 (dd, $J = 5.9, 1.5$ Hz, 2H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 170.80, 168.47, 146.76, 141.26, 134.95, 130.77, 128.96, 127.92, 125.26, 123.17, 64.35, 20.88. **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 287.0638, found: 287.0642.

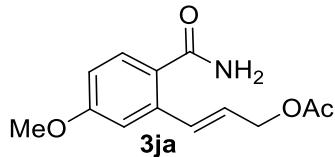


Yield: 8.5 mg, 0.032 mmol, 16%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.56 (d, $J = 2.4$ Hz, 1H), 8.27 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 1H), 6.93 (d, $J = 11.6$ Hz, 1H), 6.54 (s, 1H), 6.11 (s, 1H), 5.99 (dt, $J = 11.6, 6.7$ Hz, 1H), 4.68 (dd, $J = 6.7, 1.5$ Hz, 2H), 2.03 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 171.40, 168.18, 147.22, 140.31, 135.96, 131.32, 130.54, 129.76, 124.83, 123.87, 61.20, 20.86. **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{NaO}_5$ ($[\text{M}+\text{Na}]^+$): 287.0638, found: 287.0641.



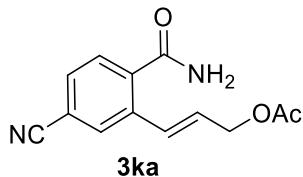
Yield: 31.1 mg, 0.142 mmol, 71%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.0$ Hz, 2H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 15.8$ Hz, 1H), 6.24 (dt, $J = 15.8,$

6.2 Hz, 1H), 6.17 (s, 1H), 5.93 (s, 1H), 4.74 (dd, $J = 6.2, 1.1$ Hz, 2H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 171.09, 170.86, 134.78, 134.17, 131.38, 130.65, 127.92, 127.73, 126.85, 126.36, 64.94, 20.94. **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 242.0788, found: 242.0790.



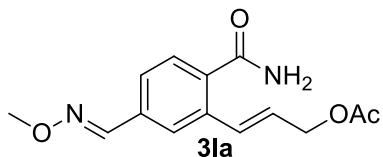
3ja (E)-3-(2-carbamoyl-5-methoxyphenyl)allyl acetate

Yield: 40.4 mg, 0.162 mmol, 81%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 7.55 (d, $J = 8.5$ Hz, 1H), 7.14 (d, $J = 15.8$ Hz, 1H), 6.99 (d, $J = 2.1$ Hz, 1H), 6.82 (dd, $J = 8.5, 2.1$ Hz, 1H), 6.19 (dt, $J = 15.8, 6.2$ Hz, 1H), 6.13 (s, 1H), 5.91 (s, 1H), 4.73 (d, $J = 6.2$ Hz, 2H), 3.84 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 170.86, 170.73, 161.28, 137.17, 131.79, 129.91, 126.51, 126.48, 113.34, 112.13, 64.85, 55.37, 20.91. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_4$ ($[\text{M}+\text{Na}]^+$): 272.0893, found: 272.0894.



3ka (E)-3-(2-carbamoyl-5-cyanophenyl)allyl acetate

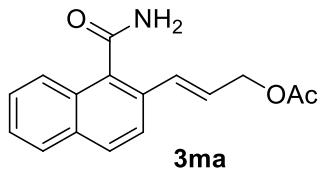
Yield: 28.8 mg, 0.118 mmol, 59%. White solid. **^1H NMR** (500 MHz, CDCl_3) δ 7.82 (s, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 15.6$ Hz, 1H), 6.30 (dt, $J = 15.6, 5.8$ Hz, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 4.76 (d, $J = 5.8$ Hz, 2H), 2.11 (s, 3H). **^{13}C NMR** (125 MHz, CDCl_3) δ 170.78, 168.87, 137.79, 136.02, 131.03, 130.62, 129.38, 128.90, 128.65, 117.75, 114.71, 64.36, 20.89. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 267.0740, found: 267.0745.



3la (E)-3-(2-carbamoyl-5-((E)-(methoxyimino)methyl)phenyl)allyl acetate

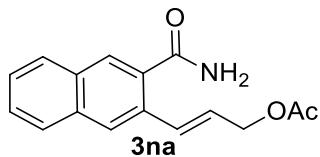
Yield: 34.8 mg, 0.126 mmol, 63%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.03 (s, 1H), 7.71 (s, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 15.8$ Hz, 1H), 6.35 (s, 1H), 6.27 (dt, $J = 15.8, 6.2$ Hz, 1H), 6.03 (s, 1H), 4.73 (dd, $J = 6.2, 1.0$ Hz, 2H), 3.99 (s, 3H), 2.08 (s, 3H). **^{13}C**

NMR (100 MHz, CDCl₃) δ 170.89, 170.63, 147.32, 135.31, 134.92, 134.38, 130.73, 128.24, 127.11, 126.23, 125.20, 64.80, 62.23, 20.92. **HRMS** (ESI) m/z calcd for C₁₄H₁₆N₂NaO₄ ([M+Na]⁺): 299.1002, found: 299.1000.



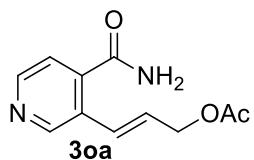
3ma (E)-3-(1-carbamoylnaphthalen-2-yl)allyl acetate

Yield: 32.9 mg, 0.122 mmol, 61%. White solid. **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.54 (ddd, *J* = 8.5, 6.9 Hz, 1.5 Hz, 1H), 7.50 (ddd, *J* = 8.0, 6.9, 1.3 Hz, 1H), 7.02 (d, *J* = 15.8 Hz, 1H), 6.44 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.16 (s, 1H), 5.88 (s, 1H), 4.78 (dd, *J* = 6.3, 1.4 Hz, 2H), 2.11 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 170.87, 170.78, 132.96, 132.87, 130.62, 130.11, 129.74, 129.53, 128.05, 127.44, 126.62, 126.61, 125.34, 122.68, 64.97, 20.96. **HRMS** (ESI) m/z calcd for C₁₆H₁₅NNaO₃ ([M+Na]⁺): 292.0944, found: 292.0947.



3na (E)-3-(3-carbamoylnaphthalen-2-yl)allyl acetate

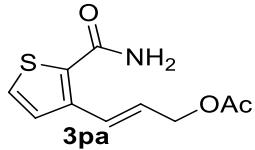
Yield: 49.0 mg, 0.182 mmol, 91%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.50 (*J* = 6.9 Hz, 1H), 7.19 (d, *J* = 15.8 Hz, 1H), 6.33 (dt, *J* = 15.8, 6.0 Hz, 1H), 6.17 (s, 1H), 6.09 (s, 1H), 4.78 (d, *J* = 6.0 Hz, 2H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 171.04, 170.95, 134.04, 132.22, 132.11, 132.02, 131.88, 128.18, 128.03, 127.81, 127.80, 126.87, 126.36, 126.30, 65.05, 20.99. **HRMS** (ESI) m/z calcd for C₁₆H₁₅NNaO₃ ([M+Na]⁺): 292.0944, found: 292.0946.



3oa (E)-3-(4-carbamoylpyridin-3-yl)allyl acetate

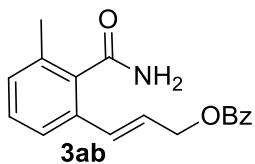
Yield: 11.9 mg, 0.054 mmol, 27%. White solid. **¹H NMR** (600 MHz, CDCl₃) δ 8.79 (s, 1H), 8.60 (d, *J* = 5.5 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 5.5 Hz, 1H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 15.8 Hz, 1H), 6.17 (s, 1H), 6.09 (s, 1H), 4.78 (d, *J* = 6.0 Hz, 2H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 171.04, 170.95, 134.04, 132.22, 132.11, 132.02, 131.88, 128.18, 128.03, 127.81, 127.80, 126.87, 126.36, 126.30, 65.05, 20.99. **HRMS** (ESI) m/z calcd for C₁₆H₁₅NNaO₃ ([M+Na]⁺): 292.0944, found: 292.0946.

J = 5.0 Hz, 1H), 7.44 (d, *J* = 5.0 Hz, 1H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.32 (dt, *J* = 16.1, 5.9 Hz, 1H), 5.92 (s, 1H), 5.86 (s, 1H), 4.77 (dd, *J* = 5.9, 1.5 Hz, 2H), 2.12 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.83, 168.31, 149.21, 148.66, 140.31, 129.53, 128.94, 127.76, 121.19, 64.60, 20.93. HRMS (ESI) m/z calcd for C₁₁H₁₂N₂NaO₃ ([M+Na]⁺): 243.0740, found: 243.0741.



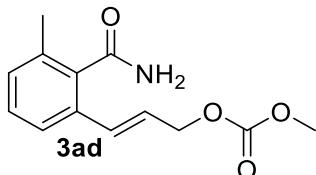
3pa (E)-3-(2-carbamoylthiophen-3-yl)allyl acetate

Yield: 14.4 mg, 0.064 mmol, 32%. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 16.1 Hz, 1H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.24 (d, *J* = 5.0 Hz, 1H), 6.25 (dt, *J* = 16.1, 6.2 Hz, 1H), 5.72 (s, 2H), 4.74 (dd, *J* = 6.2, 1.2 Hz, 2H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.89, 164.20, 141.40, 130.94, 127.73, 127.64, 127.29, 126.94, 64.83, 20.96. HRMS (ESI) m/z calcd for C₁₀H₁₁NNaO₃S ([M+Na]⁺): 248.0352, found: 248.0357.



3ab (E)-3-(2-carbamoyl-3-methylphenyl)allyl benzoate

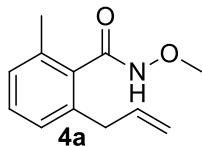
Yield: 10.6 mg, 0.036 mmol, 18%. White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.57 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.42 (d, 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.40 (dt, *J* = 15.8, 6.3 Hz, 1H), 5.92 (s, 1H), 5.68 (s, 1H), 4.97 (dd, *J* = 6.3, 1.3 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.37, 166.34, 135.72, 134.59, 133.03, 133.00, 131.02, 130.11, 129.86, 129.65, 129.13, 128.39, 126.10, 123.18, 65.41, 19.24. HRMS (ESI) m/z calcd for C₁₈H₁₇NNaO₃ ([M+Na]⁺): 318.1101, found: 318.1104.



3ad (E)-3-(2-carbamoyl-3-methylphenyl)allyl methyl carbonate

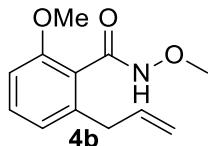
Yield: 11.5 mg, 0.046 mmol, 23%. White solid. ¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, *J* = 7.7 Hz,

1H), 7.26 (t, J = 7.7 Hz, 1H), 7.14 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 15.8 Hz, 1H), 6.28 (dt, J = 15.8, 6.4 Hz, 1H), 5.92 (s, 1H), 5.66 (s, 1H), 4.78 (dd, J = 6.4, 1.3 Hz, 2H), 3.80 (s, 3H), 2.39 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 171.34, 155.58, 135.75, 134.60, 132.83, 131.63, 129.99, 129.15, 125.26, 123.22, 68.31, 54.86, 19.22. **HRMS** (ESI) m/z calcd for C₁₃H₁₅NNaO₄ ([M+Na]⁺): 272.0893, found: 272.0898.



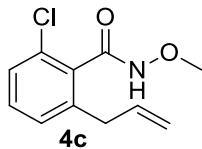
4a 2-allyl-N-methoxy-6-methylbenzamide

Yield (From allyl acetate): 40.2 mg, 0.196 mmol, 98%. Oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.76 (s, 1H), 7.22 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 2H), 5.95 (ddt, J = 16.8, 10.1, 6.4 Hz, 1H), 5.06 (d, J = 10.1 Hz, 1H), 5.00 (dd, J = 16.8, 1.5 Hz, 1H), 3.84 (s, 3H), 3.35 (d, J = 6.3 Hz, 2H), 2.29 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.20, 137.26, 137.03, 135.63, 133.06, 129.59, 128.02, 126.88, 116.15, 64.23, 37.16, 18.94. **HRMS** (ESI) m/z calcd for C₁₂H₁₅NNaO₂ ([M+Na]⁺): 228.0995, found: 228.0100.



4b 2-allyl-N,6-dimethoxybenzamide

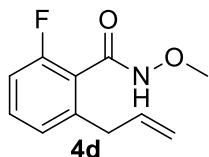
Yield: 43.4 mg, 0.196 mmol, 98%. Oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.30 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 5.96 (ddt, J = 16.8, 10.1, 6.6 Hz, 1H), 5.06 (d, J = 10.1 Hz), 5.06 (d, J = 16.8 Hz), 3.88 (s, 3H), 3.81 (s, 3H), 3.45 (d, J = 6.6 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 165.91, 156.70, 140.30, 136.78, 130.91, 122.25, 122.17, 116.15, 108.80, 64.34, 55.80, 37.12. **HRMS** (ESI) m/z calcd for C₁₂H₁₅NNaO₃ ([M+Na]⁺): 244.0944, found: 244.0942.



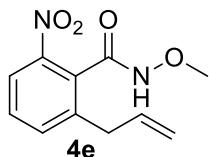
4c 2-allyl-6-chloro-N-methoxybenzamide

Yield: 44.2 mg, 0.196 mmol, 98%. Oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.77 (s, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.4 Hz, 1H), 5.91 (ddt, J = 17.2, 10.1, 6.3 Hz, 1H),

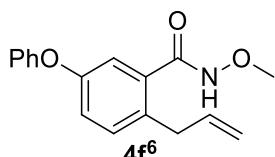
5.09 (d, $J = 10.1$ Hz), 5.05 (d, $J = 17.2$ Hz), 3.88 (s, 3H), 3.40 (d, $J = 6.3$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 164.27, 140.14, 136.13, 132.45, 131.64, 130.77, 127.96, 127.29, 116.88, 64.34, 37.20. **HRMS** (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{ClINaO}_2$ ($[\text{M}+\text{Na}]^+$): 248.0449, found: 248.0452.



Yield: 33.9 mg, 0.162 mmol, 81%. Oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.69 (s, 1H), 7.31 (td, $J = 8.0, 5.9$ Hz, 1H), 7.04 (d, $J = 7.7$ Hz, 1H), 6.94 (t, $J = 8.8$ Hz, 1H), 5.92 (ddt, $J = 16.8, 10.1, 6.6$ Hz, 1H), 5.08 (dd, $J = 10.1, 1.5$ Hz, 1H), 5.05 (d, $J = 16.8$ Hz, 1H), 3.87 (s, 3H), 3.47 (d, $J = 6.6$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 162.64, 159.57 (d, $J_{\text{C}-\text{F}} = 247.0$ Hz), 141.29, 136.26, 131.51 (d, $J_{\text{C}-\text{F}} = 8.7$ Hz), 125.70, 121.04 (d, $J_{\text{C}-\text{F}} = 17.8$ Hz), 116.72, 113.52 (d, $J_{\text{C}-\text{F}} = 22.2$ Hz), 64.57, 36.95 (d, $J_{\text{C}-\text{F}} = 1.9$ Hz). **HRMS** (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{FNNaO}_2$ ($[\text{M}+\text{Na}]^+$): 232.0744, found: 232.07442.

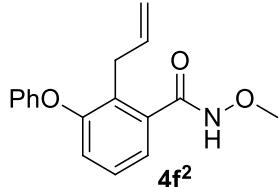


Yield: 29.8 mg, 0.126 mmol, 63%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.45 (s, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.71 – 7.58 (m, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 5.95 (ddt, $J = 16.7, 10.1, 6.6$ Hz, 1H), 5.16 (dd, $J = 10.1, 1.4$ Hz, 1H), 5.08 (d, $J = 15.6$ Hz, 1H), 3.95 (br, 2H), 3.53 (d, $J = 6.6$ Hz, 2H), 3.41 (br, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ 163.96, 146.52, 140.85, 135.59, 130.37, 129.90, 128.54, 122.63, 117.68, 64.09, 36.69. **HRMS** (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{NaO}_4$ ($[\text{M}+\text{Na}]^+$): 259.0689, found: 259.0686.



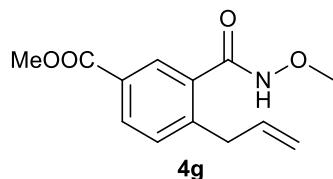
Yield: 24.4 mg, 0.086 mmol, 43%. Oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.48 (s, 1H), 7.34 (dd, $J = 8.5, 7.5$ Hz, 2H), 7.25 – 7.18 (m, 1H), 7.12 (t, $J = 7.4$ Hz, 1H), 7.07 – 7.01 (m, 2H), 6.99 (d, $J = 8.6$ Hz,

2H), 5.99 (ddt, $J = 16.5, 10.1, 6.3$ Hz, 1H), 5.10 (dd, $J = 10.1, 1.5$ Hz, 1H), 5.03 (dd, $J = 17.1, 1.5$ Hz, 1H), 3.85 (s, 3H), 3.53 (d, $J = 6.3$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 166.91, 156.69, 155.57, 137.37, 133.88, 132.97, 132.04, 129.87, 123.68, 120.98, 118.93, 117.84, 116.27, 64.60, 36.61. **HRMS** (ESI) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 306.1101, found: 306.1102.



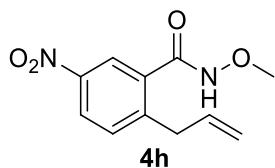
4f² 2-allyl-N-methoxybenzamide

Yield: 30.0 mg, 0.106 mmol, 53%. Oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.66 (s, 1H), 7.32 (dd, $J = 8.5, 7.5$ Hz, 2H), 7.23 – 7.15 (m, 2H), 7.10 (t, $J = 7.4$ Hz, 1H), 7.00 – 6.90 (m, 3H), 6.02 (ddt, $J = 16.5, 10.3, 6.2$ Hz, 1H), 5.08 – 4.96 (m, 2H), 3.89 (s, 3H), 3.60 (d, $J = 6.2$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 167.06, 157.13, 155.55, 136.68, 134.99, 129.80, 129.54, 127.66, 123.29, 122.96, 121.14, 118.35, 115.82, 64.59, 31.17. **HRMS** (ESI) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 306.1101, found: 306.1103.



4g methyl 4-allyl-3-(methoxycarbamoyl)benzoate

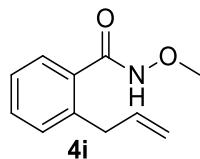
Yield: 44.4 mg, 0.178 mmol, 89%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.04 (s, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 5.97 (ddt, $J = 16.6, 10.1, 6.4$ Hz, 1H), 5.11 (d, $J = 10.1$ Hz, 1H), 5.04 (d, $J = 17.1$ Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.62 (d, $J = 6.4$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 166.58, 166.16, 144.20, 136.10, 132.81, 131.56, 130.66, 128.69, 128.14, 116.96, 64.54, 52.24, 37.25. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_4$ ($[\text{M}+\text{Na}]^+$): 272.0893, found: 272.0897.



4h 2-allyl-N-methoxy-5-nitrobenzamide

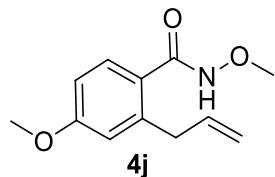
Yield: 39.2 mg, 0.166 mmol, 83%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.59 (s, 1H), 8.26 (s, 1H), 7.98 (d, $J = 8.5$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 5.97 (ddt, $J = 16.6, 10.1, 6.4$ Hz, 1H), 5.11 (d, $J = 10.1$ Hz, 1H), 5.04 (d, $J = 17.1$ Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.62 (d, $J = 6.4$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 166.58, 166.16, 144.20, 136.10, 132.81, 131.56, 130.66, 128.69, 128.14, 116.96, 64.54, 52.24, 37.25. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_4$ ($[\text{M}+\text{Na}]^+$): 272.0893, found: 272.0897.

1H), 8.24 (d, J = 9.1 Hz, 1H), 7.48 (d, J = 9.1 Hz, 1H), 5.96 (ddt, J = 16.7, 10.1, 6.4 Hz, 1H), 5.17 (dd, J = 10.1, 1.1 Hz, 1H), 5.08 (d, J = 17.1 Hz, 1H), 3.92 (s, 3H), 3.67 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.30, 146.52, 146.11, 135.34, 133.75, 131.71, 125.39, 122.79, 117.85, 64.82, 37.24. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{NaO}_4$ ($[\text{M}+\text{Na}]^+$): 259.0689, found: 259.0695.



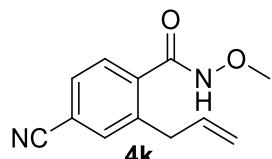
4i 2-allyl-N-methoxybenzamide

Yield: 26.8 mg, 0.140 mmol, 70%. White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.51 (s, 1H), 7.42 – 7.35 (m, 2H), 7.29 – 7.21 (m, 2H), 6.00 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.09 (dd, J = 10.1, 1.6 Hz, 1H), 5.02 (dd, J = 17.1, 1.6 Hz, 1H), 3.87 (s, 3H), 3.56 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.67, 138.39, 137.29, 132.64, 130.80, 130.58, 127.64, 126.33, 116.32, 64.60, 37.29. HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{NNaO}_2$ ($[\text{M}+\text{Na}]^+$): 214.0838, found: 214.0837.



4j 2-allyl-N,4-dimethoxybenzamide

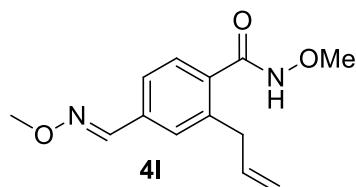
Yield: 29.2 mg, 0.132 mmol, 66%. Oil. ^1H NMR (400 MHz, CDCl_3) δ 8.50 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 2.5 Hz, 1H), 6.74 (dd, J = 8.4, 2.5 Hz, 1H), 5.99 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.09 (dd, J = 10.1, 1.6 Hz, 1H), 5.04 (dd, J = 17.1, 1.6 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.56 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.81, 161.34, 140.87, 137.14, 129.44, 124.89, 116.40, 116.18, 111.30, 64.52, 55.27, 37.52. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{NNaO}_3$ ($[\text{M}+\text{Na}]^+$): 244.0944, found: 244.0946.



4k 2-allyl-4-cyano-N-methoxybenzamide

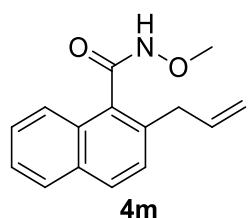
Yield: 33.7 mg, 0.156 mmol, 78%. White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.58 (s, 1H), 7.56 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 5.94 (ddt, J = 16.7, 10.1, 6.3 Hz, 1H), 5.17

(dd, $J = 10.1, 1.1$ Hz, 1H), 5.06 (d, $J = 17.0$ Hz, 1H), 3.89 (s, 3H), 3.57 (d, $J = 6.3$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 165.77, 140.08, 136.88, 135.57, 133.96, 130.02, 128.36, 117.83, 114.59, 99.96, 64.78, 36.82. **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{NaO}_2$ ($[\text{M}+\text{Na}]^+$): 239.0791, found: 239.0792.



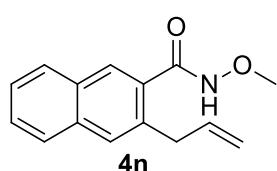
4l (E)-2-allyl-N-methoxy-4-((methoxyimino)methyl)benzamide

Yield: 36.2 mg, 0.146 mmol, 73%. Solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.51 (s, 1H), 8.03 (s, 1H), 7.47 (s, 1H), 7.46 (d, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 7.7$ Hz, 1H), 5.99 (ddt, $J = 16.6, 10.1, 6.3$ Hz, 1H), 5.11 (dd, $J = 1.4, 10.1$ Hz, 1H), 5.03 (dd, $J = 1.4, 17.1$ Hz, 1H), 3.99 (s, 3H), 3.88 (s, 3H), 3.57 (d, $J = 6.3$ Hz, 2H). **^{13}C NMR** (125 MHz, CDCl_3) δ 166.99, 147.51, 139.08, 136.90, 134.58, 133.65, 129.00, 128.14, 124.91, 116.72, 64.67, 62.22, 37.23. **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{NaO}_3$ ($[\text{M}+\text{Na}]^+$): 271.1053, found: 271.1058.



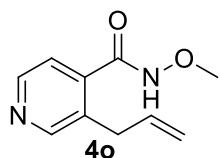
4m 2-allyl-N-methoxy-1-naphthamide

Yield: 46.8 mg, 0.194 mmol, 97%. White solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.43 (s, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.6$ Hz, 1H), 7.82 (d, $J = 8.6$ Hz, 1H), 7.53 (t, $J = 8.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.34 (d, $J = 8.6$ Hz, 1H), 6.06 (ddt, $J = 16.5, 10.1, 6.3$ Hz, 1H), 5.13 (dd, $J = 10.1, 1.4$ Hz, 1H), 5.05 (dd, $J = 17.1, 1.4$ Hz, 1H), 4.00 (s, 3H), 3.58 (d, $J = 6.3$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 166.72, 136.92, 135.03, 131.75, 130.55, 129.89, 129.52, 127.90, 127.24, 127.11, 125.83, 124.35, 116.44, 64.41, 37.57. **HRMS** (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_2$ ($[\text{M}+\text{Na}]^+$): 264.0995, found: 264.0997.



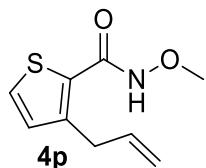
4n 3-allyl-N-methoxy-2-naphthamide

Yield: 46.8 mg, 0.194 mmol, 97%. White solid. **1H NMR** (400 MHz, CDCl_3) δ 8.54 (s, 1H), 7.87 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.69 (s, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 6.05 (ddt, J = 16.6, 10.1, 6.4 Hz, 1H), 5.12 (dd, J = 10.1, 1.5 Hz, 1H), 5.07 (dd, J = 17.1, 1.5 Hz, 1H), 3.92 (s, 3H), 3.73 (d, J = 6.4 Hz, 2H). **13C NMR** (100 MHz, CDCl_3) δ 167.79, 137.19, 135.20, 134.31, 131.12, 131.09, 129.15, 127.97, 127.81, 127.63, 127.38, 126.34, 116.52, 64.64, 37.29. **HRMS** (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NNaO}_2$ ($[\text{M}+\text{Na}]^+$): 264.0995, found: 264.1000.



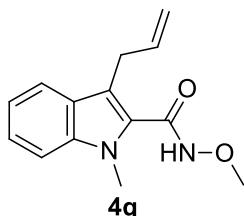
4o 3-allyl-N-methoxyisonicotinamide

Yield: 21.5 mg, 0.112 mmol, 56%. Oil. **1H NMR** (400 MHz, CDCl_3) δ 9.31 (s, 1H), 8.48 (s, 1H), 8.45 (d, J = 4.8 Hz, 1H), 7.25 (d, J = 4.8 Hz, 1H), 5.95 (ddt, J = 16.6, 10.1, 6.3 Hz, 1H), 5.12 (dd, J = 10.1, 1.0 Hz, 1H), 5.02 (d, J = 17.1 Hz, 1H), 3.88 (s, 3H), 3.55 (d, J = 5.0 Hz, 2H). **13C NMR** (100 MHz, CDCl_3) δ 164.96, 151.68, 147.89, 140.14, 135.89, 133.07, 121.54, 117.34, 64.66, 34.55. **HRMS** (ESI) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{NaO}_2$ ($[\text{M}+\text{Na}]^+$): 215.0791, found: 215.0798.



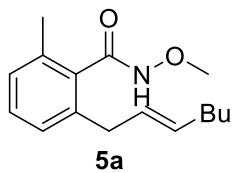
4p 3-allyl-N-methoxythiophene-2-carboxamide

Yield: 18.5 mg, 0.094 mg, 47%. Oil. **1H NMR** (400 MHz, CDCl_3) δ 8.52 (s, 1H), 7.37 (d, J = 5.0 Hz, 1H), 6.96 (d, J = 5.0 Hz, 1H), 6.02 (ddt, J = 16.6, 10.1, 6.2 Hz, 1H), 5.13 (dd, J = 10.1, 1.5 Hz, 1H), 5.06 (dd, J = 17.1, 1.5 Hz, 1H), 3.86 (s, 3H), 3.71 (d, J = 6.2 Hz, 2H). **13C NMR** (100 MHz, CDCl_3) δ 162.51, 144.40, 136.31, 130.89, 128.20, 127.55, 116.52, 64.77, 33.84. **HRMS** (ESI) m/z calcd for $\text{C}_9\text{H}_{11}\text{NNaO}_2\text{S}$ ($[\text{M}+\text{Na}]^+$): 220.0403, found: 220.0410.

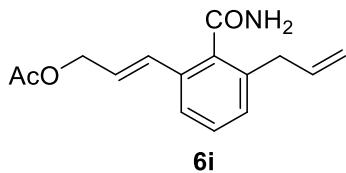


4q 3-allyl-N-methoxy-1-methyl-1H-indole-2-carboxamide

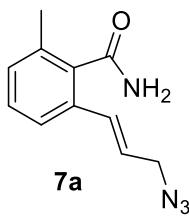
Yield: 19.1 mg, 0.078 mmol, 39%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.80 (s, 1H), 7.58 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.16 (ddt, *J* = 15.5, 10.7, 5.4 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.00 (dd, *J* = 17.2, 1.5 Hz, 1H), 3.92 (s, 6H), 3.69 (d, *J* = 5.4 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 161.25, 138.32, 137.88, 127.30, 126.49, 124.47, 120.11, 120.06, 116.15, 114.49, 109.98, 64.95, 31.26, 29.03. **HRMS** (ESI) m/z calcd for C₁₄H₁₆N₂NaO₂ ([M+Na]⁺): 267.1104, found: 267.1105.

**(E)-2-(hept-2-en-1-yl)-N-methoxy-6-methylbenzamide**

Yield: 36.6 mg, 0.14 mmol, 70%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.39 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 5.55 (dt, *J* = 15.2, 6.0 Hz, 1H), 5.45 (dt, *J* = 15.2, 6.5 Hz, 1H), 3.89 (s, 3H), 3.32 (d, *J* = 6.0 Hz, 2H), 2.32 (s, 3H), 2.00 (q, *J* = 6.5 Hz, 2H), 1.44 – 1.28 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 167.55, 138.10, 135.69, 132.94, 132.59, 129.69, 128.62, 127.92, 126.90, 64.47, 36.18, 32.13, 31.54, 22.21, 19.04, 13.90. **HRMS** (ESI) m/z calcd for C₁₆H₂₃NNaO₂ ([M+Na]⁺): 284.1621, found: 284.1623.

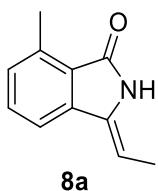
**6i (E)-3-(3-allyl-2-carbamoylphenyl)allyl acetate**

Yield: 21.8 mg, 0.084 mmol, 42%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 15.8 Hz, 1H), 6.28 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.00 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.87 (s, 1H), 5.69 (s, 1H), 5.08 (dd, *J* = 10.1, 3.1 Hz, 1H), 5.02 (dd, *J* = 16.6, 3.1 Hz, 1H), 4.72 (d, *J* = 6.3 Hz, 2H), 3.47 (d, *J* = 6.3 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 171.03, 170.79, 137.21, 136.38, 135.37, 133.36, 130.84, 129.38, 129.33, 126.11, 123.78, 116.28, 64.93, 37.35, 20.97. **HRMS** (ESI) m/z calcd for C₁₄H₁₆N₂NaO₂ ([M+Na]⁺): 267.1104, found: 267.1105.



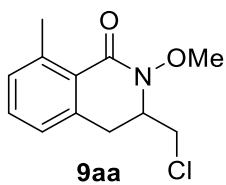
(E)-2-(3-azidoprop-1-en-1-yl)-6-methylbenzamide

Yield: 41.5 mg, 0.192 mmol, 96%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.22 (dt, *J* = 15.6, 6.6 Hz, 1H), 6.22 (s, 1H), 5.77 (s, 1H), 3.92 (d, *J* = 6.6 Hz, 2H), 2.38 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 171.60, 135.81, 134.52, 132.73, 131.69, 129.90, 129.10, 125.07, 123.18, 52.86, 19.17. **HRMS** (ESI) m/z calcd for C₁₁H₁₂N₄NaO ([M+Na]⁺): 239.0903, found: 239.0901.



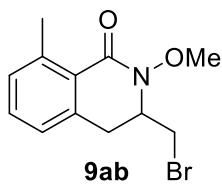
(Z)-3-ethylidene-7-methylisoindolin-1-one

Yield: 28.1 mg, 0.162 mmol, 81%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 9.36 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 5.62 (q, *J* = 7.4 Hz, 1H), 2.72 (s, 3H), 2.01 (d, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.14, 138.15, 137.44, 134.20, 131.44, 130.22, 126.82, 116.75, 101.84, 17.35, 12.43. **HRMS** (ESI) m/z calcd for C₁₁H₁₁NNaO ([M+Na]⁺): 196.0733, found: 196.0730.



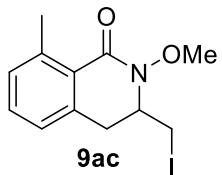
3-(chloromethyl)-2-methoxy-8-methyl-3,4-dihydroisoquinolin-1(2H)-one

Yield: 21.6 mg, 0.090 mmol, 45%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 4.40 (dd, *J* = 9.2, 7.6, 4.8, 3.2 Hz, 1H), 3.95 (s, 3H), 3.82 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.62 (dd, *J* = 11.2, 7.6 Hz, 1H), 3.09 (dd, *J* = 15.8, 3.2 Hz, 1H), 2.99 (dd, *J* = 15.8, 9.2 Hz, 1H), 2.59 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 149.45, 138.16, 134.63, 130.97, 129.28, 125.63, 123.83, 75.20, 62.79, 44.30, 32.57, 23.47. **HRMS** (ESI) m/z calcd for C₁₂H₁₄ClNNaO₂ ([M+Na]⁺): 262.0605, found: 262.0600.



3-(bromomethyl)-2-methoxy-8-methyl-3,4-dihydroisoquinolin-1(2H)-one

Yield: 44.3 mg, 0.156 mmol, 78%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 4.42 (dddd, *J* = 9.1, 7.9, 4.6, 3.2 Hz, 1H), 3.95 (s, 3H), 3.66 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.45 (dd, *J* = 10.4, 7.9 Hz, 1H), 3.14 (dd, *J* = 15.7, 3.2 Hz, 1H), 3.00 (dd, *J* = 15.7, 9.1 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 149.40, 138.08, 134.54, 130.94, 129.25, 125.63, 123.73, 74.94, 62.74, 33.25, 31.93, 23.44. **HRMS** (ESI) *m/z* calcd for C₁₂H₁₄BrNNaO₂ ([M+Na]⁺): 306.0100, found: 306.0102.



3-(iodomethyl)-2-methoxy-8-methyl-3,4-dihydroisoquinolin-1(2H)-one

Yield: 57.0 mg, 0.172 mmol, 86%. White solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 4.33 (dddd, *J* = 9.0, 8.4, 4.6, 3.0 Hz, 1H), 3.95 (s, 3H), 3.49 (dd, *J* = 10.2, 4.6 Hz, 1H), 3.26 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.20 (dd, *J* = 15.7, 3.0 Hz, 1H), 2.98 (dd, *J* = 15.7, 9.0 Hz, 1H), 2.58 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 149.52, 138.03, 134.55, 130.94, 129.22, 125.64, 123.66, 75.37, 62.73, 34.44, 23.44, 5.00. **HRMS** (ESI) *m/z* calcd for C₁₂H₁₄INNaO₂ ([M+Na]⁺): 353.9961, found: 353.9960.

IX. References

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- [S2] Guimond, N.; Gouliaras, C. and Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6908.
- [S3] Rakshit, S.; Grohmann, C.; Basset, T. and Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350.
- [S4] Zhang, S.-S.; Wu, J.-Q.; Lao, Y.-X.; Liu, X.-G.; Liu, Y.; Lv, W.-X.; Tan, D.-H.; Zeng, Y.-F. and Wang, H.-G. *Org. Lett.* **2014**, *16*, 6412.

[S5] Guimond, N.; Gorelsky, S.-I. and Fagnou, K. *J. Am. Chem. Soc.* **2011**, *133*, 6449.

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[S7] Liu, Y.-J.; Xu, H.; Kong, W.-J.; Shang, M.; Dai, H.-X. and Yu, J.-Q. *Nature*, **2014**, *515*, 389.

[S8] Muir, C. W.; Kennedy, A. R.; Redmond, J. M. and Watson, A. J. B. *Org. Biomol. Chem.* **2013**, *11*, 3337.

[S9] Karthikeyan, J.; Haridharan, R. and Cheng, C.-H. *Angew. Chem. Int. Ed.* **2012**, *51*, 12343.

XIII. NMR Spectra of products 3-9

Figure S1. Compound 3aa-¹H NMR (400M, CDCl₃)

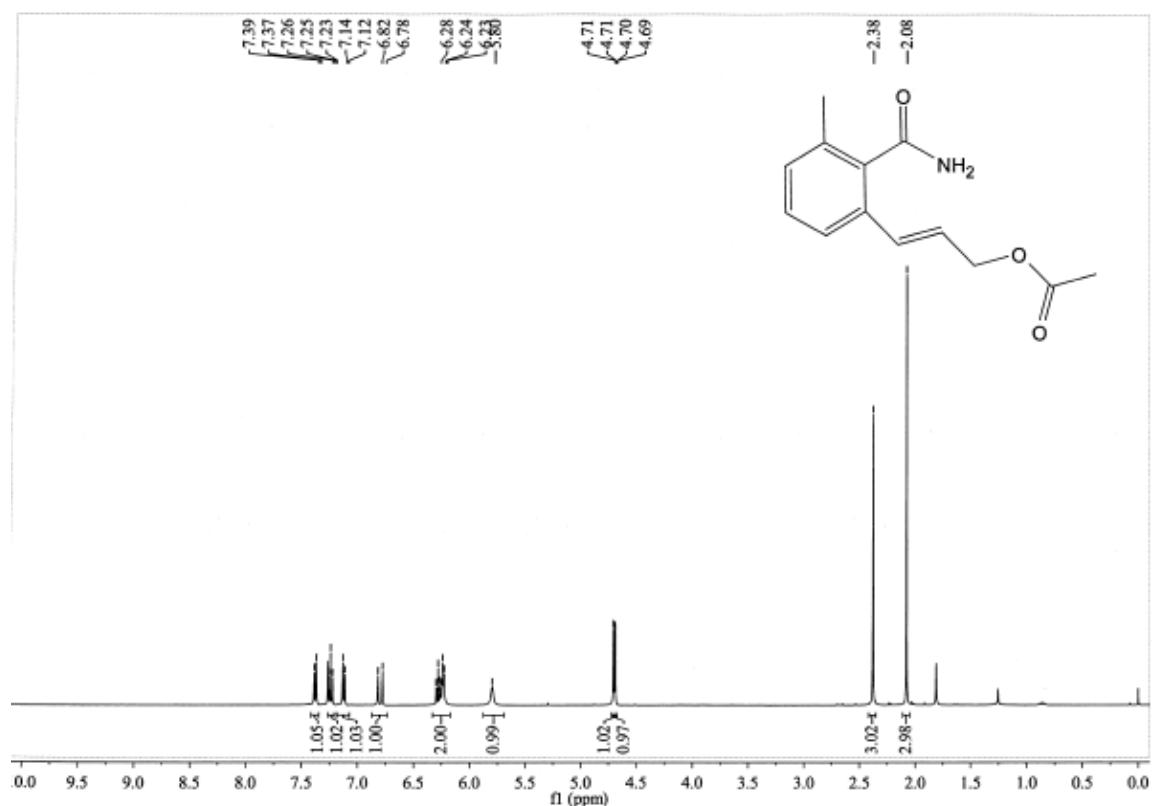


Figure S2. Compound 3aa-¹³C NMR (100M, CDCl₃)

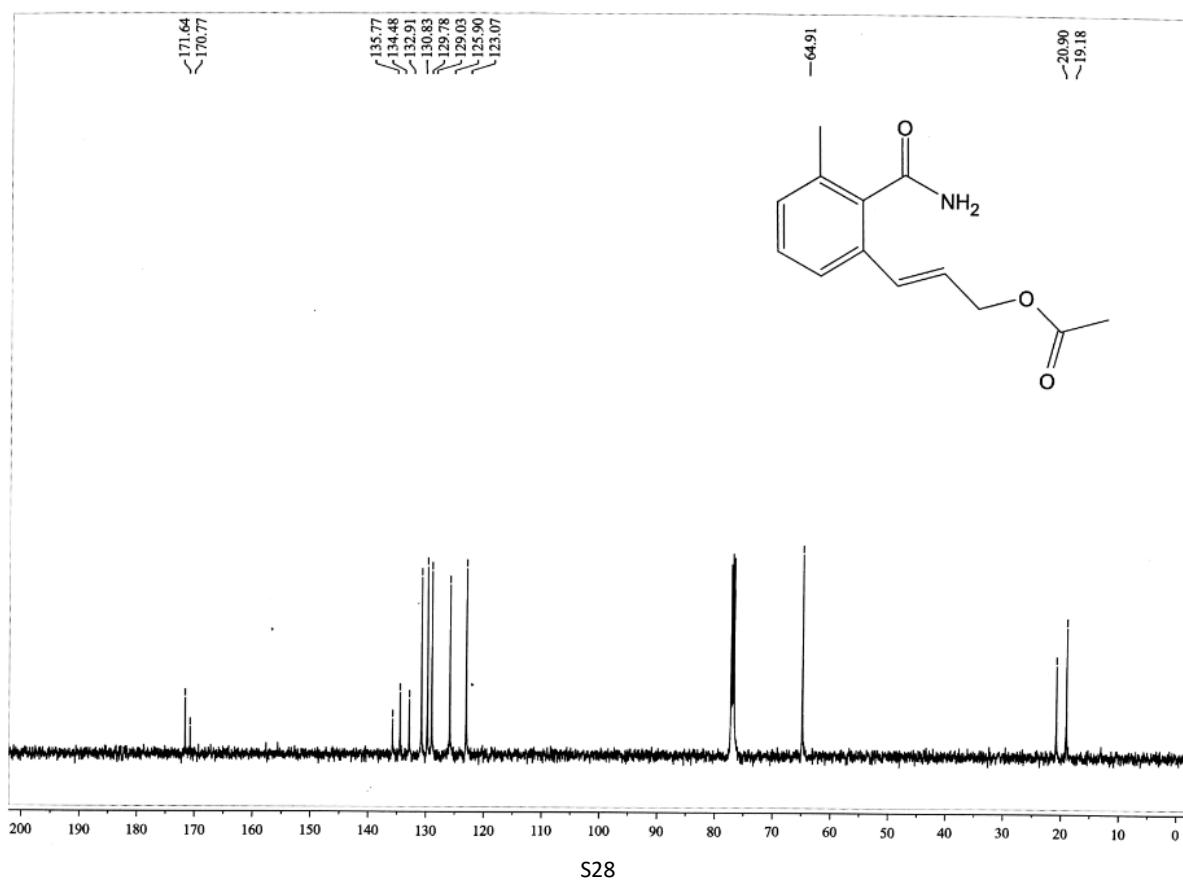


Figure S3. Compound 3ba-¹H NMR (400M, CDCl₃)

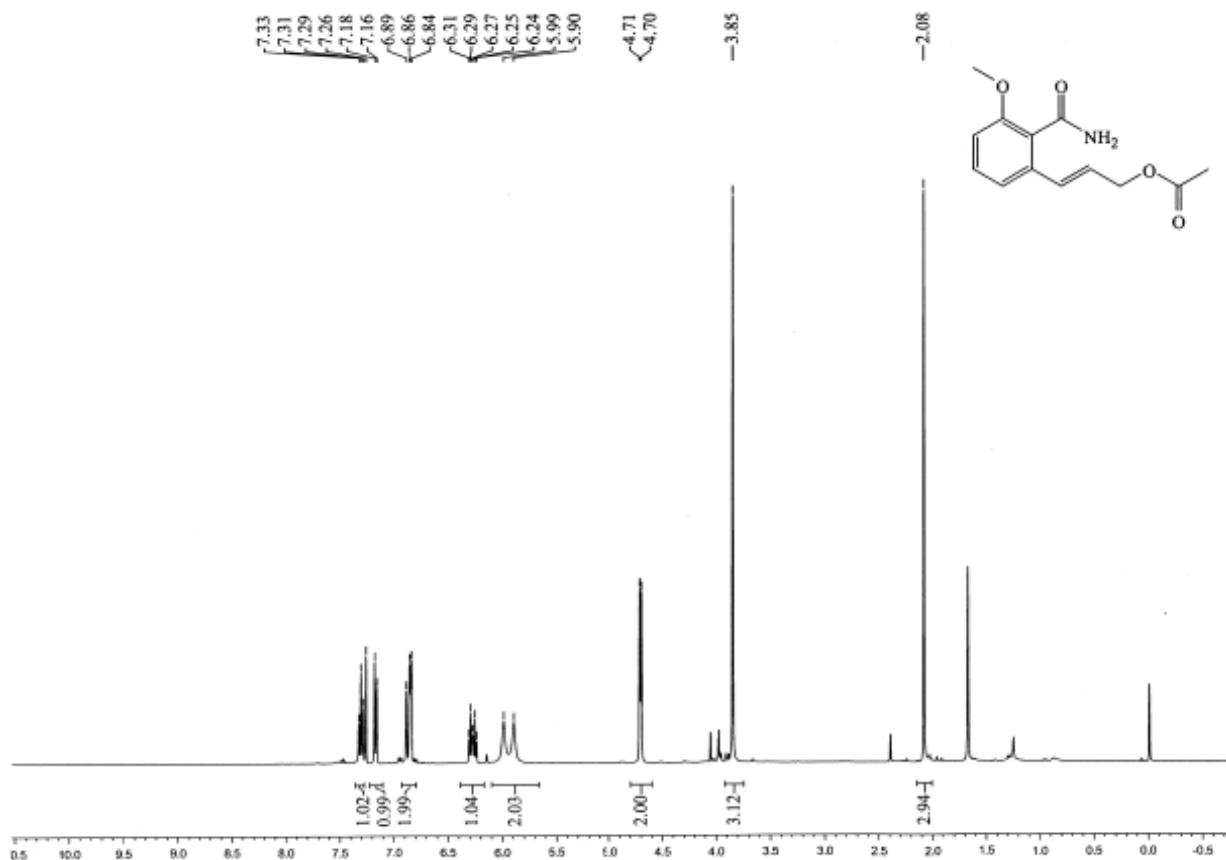


Figure S4. Compound 3ba-¹³C NMR (100M, CDCl₃)

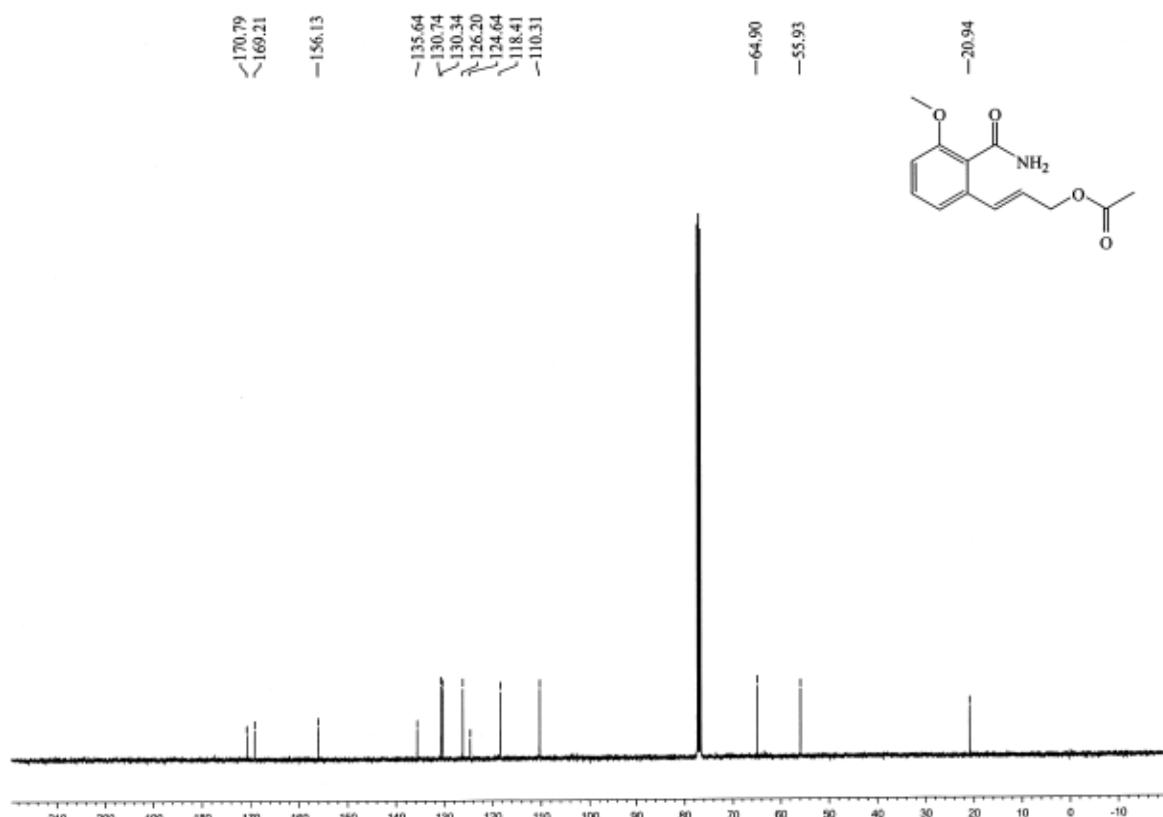


Figure S5. Compound 3ca-¹H NMR (400M, CDCl₃)

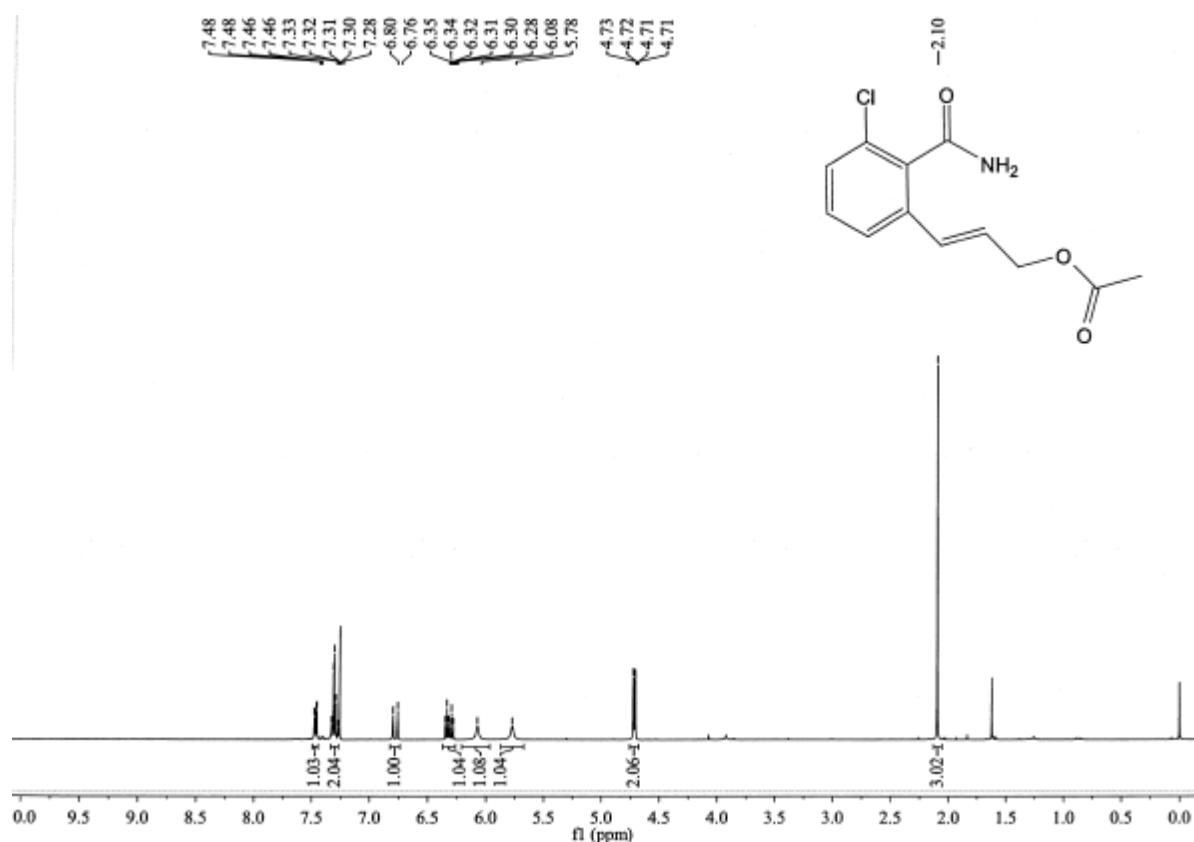


Figure S6. Compound 3ca-¹³C NMR (100M, CDCl₃)

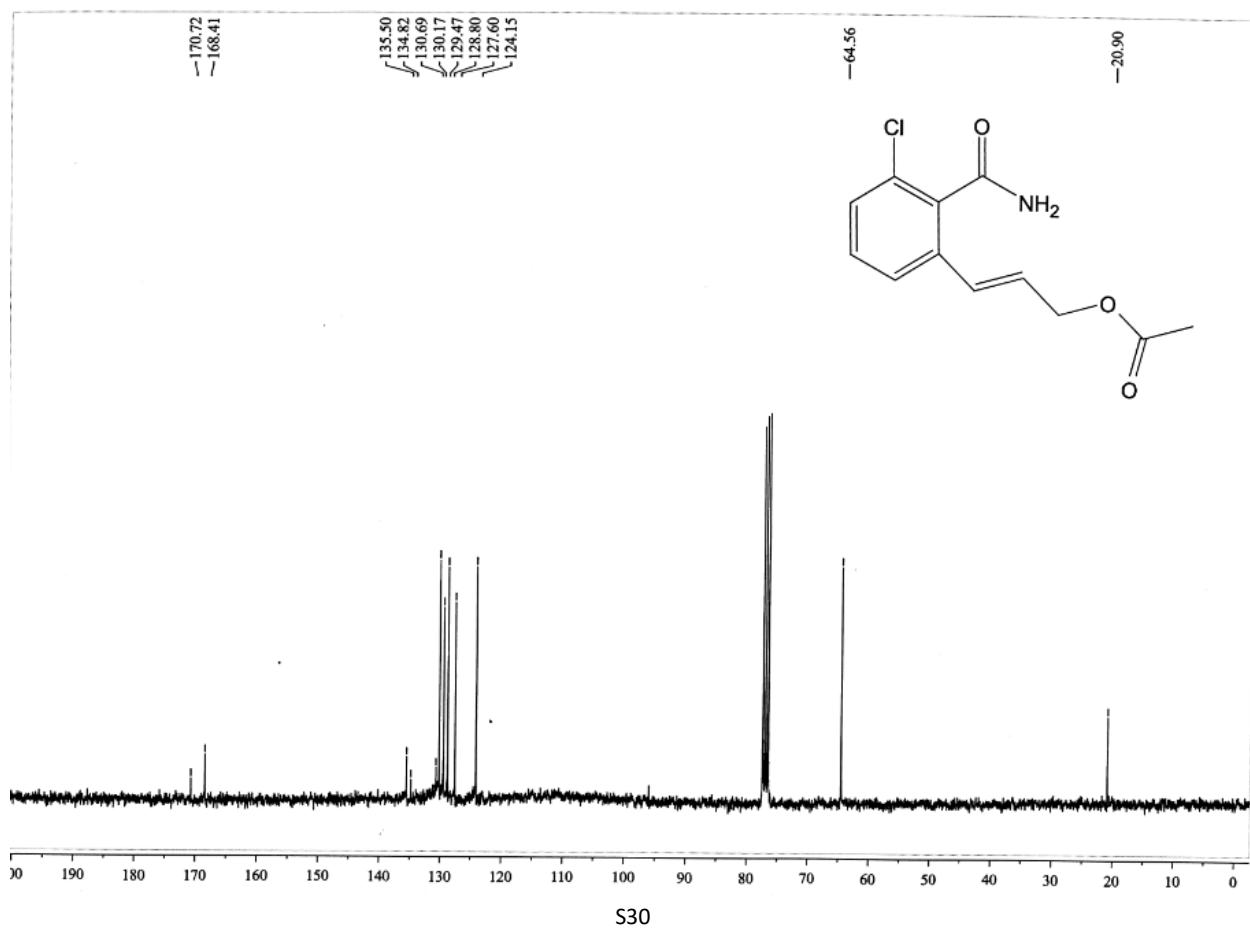


Figure S7. Compound **3da**- ^1H NMR (400M, CDCl_3)

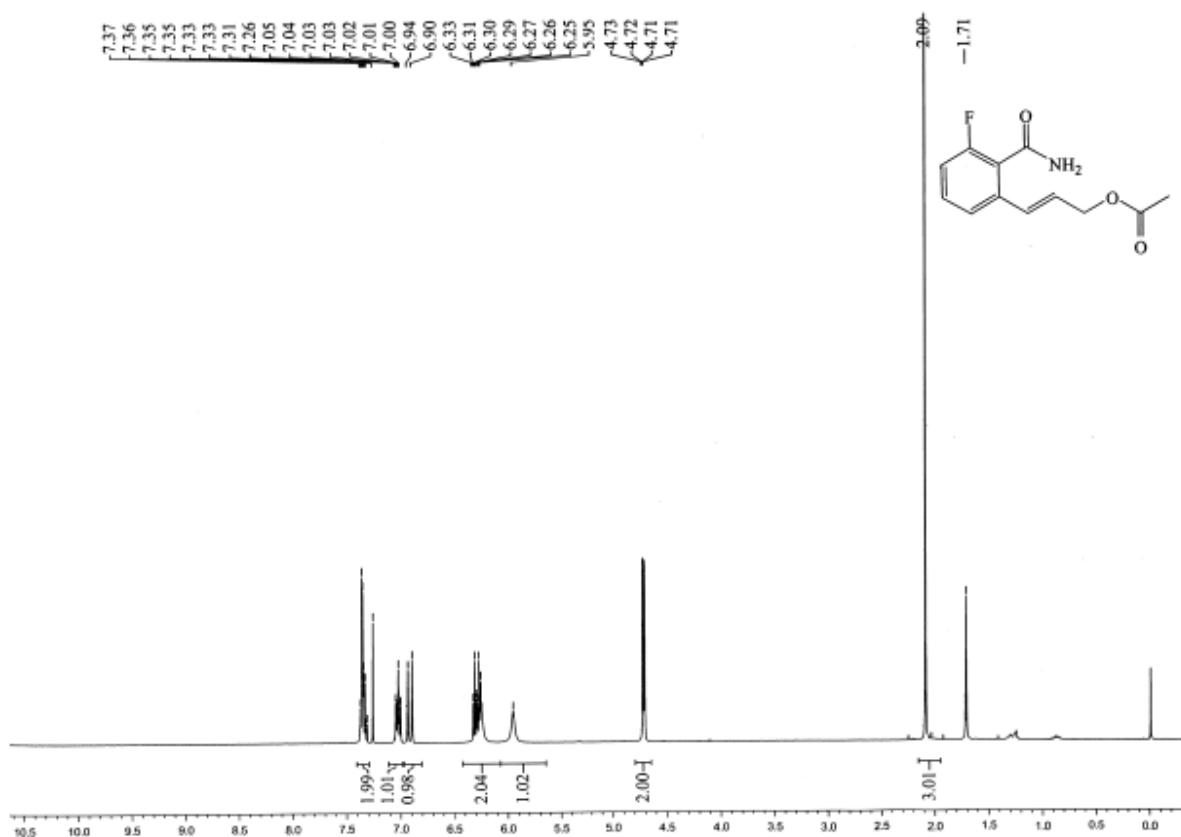


Figure S8. Compound **3da**-¹³C NMR (100M, CDCl₃)

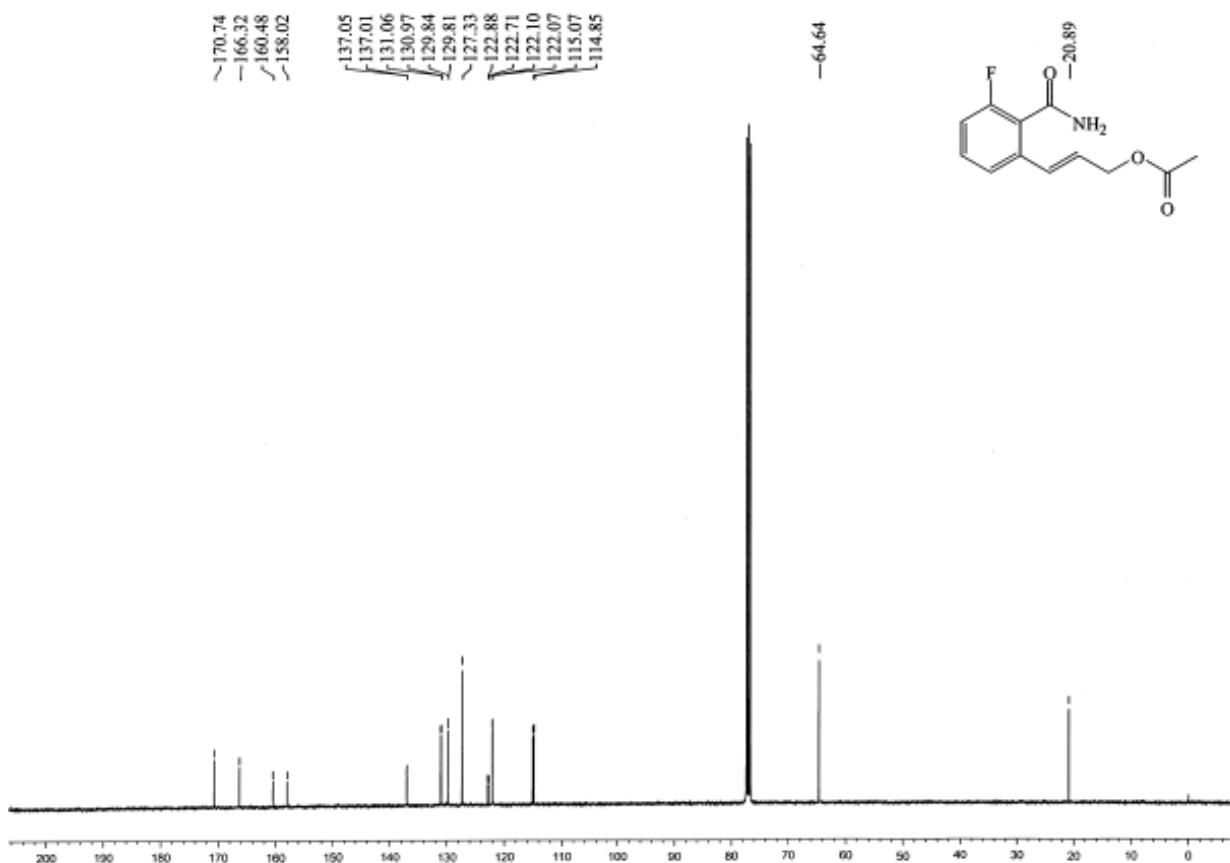


Figure S9. Compound 3ea-¹H NMR (400M, Acetone)

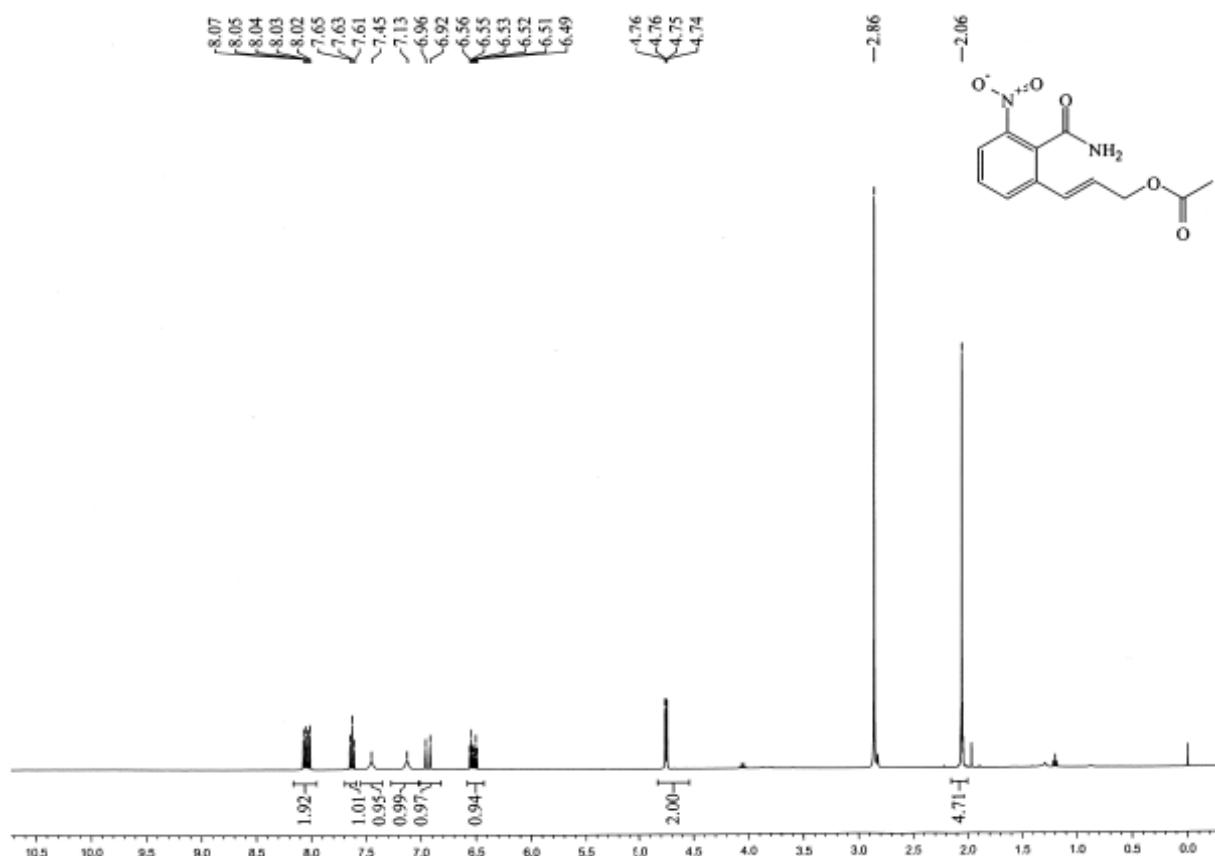


Figure S10. Compound 3ea-¹³C NMR (100M, Acetone)

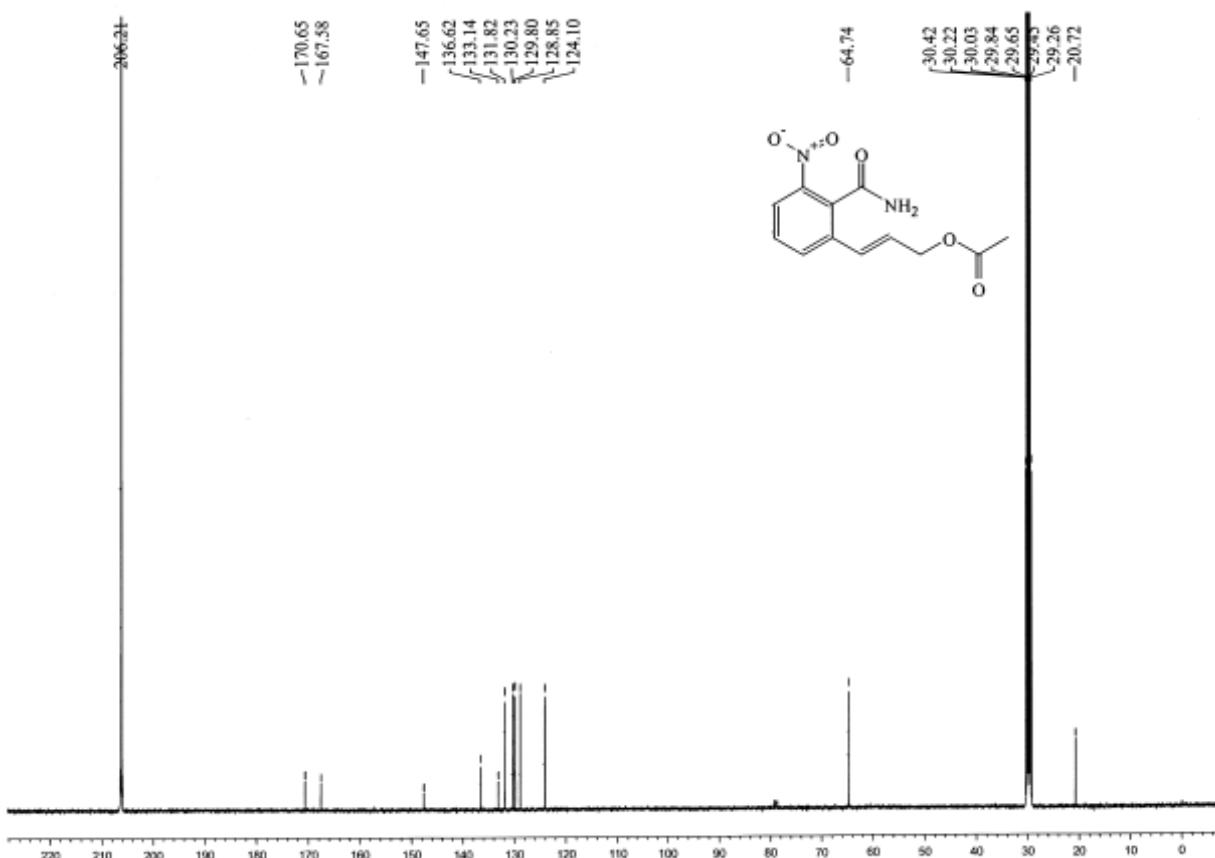


Figure S11. Compound 3fa-¹H NMR (400M, CDCl₃)

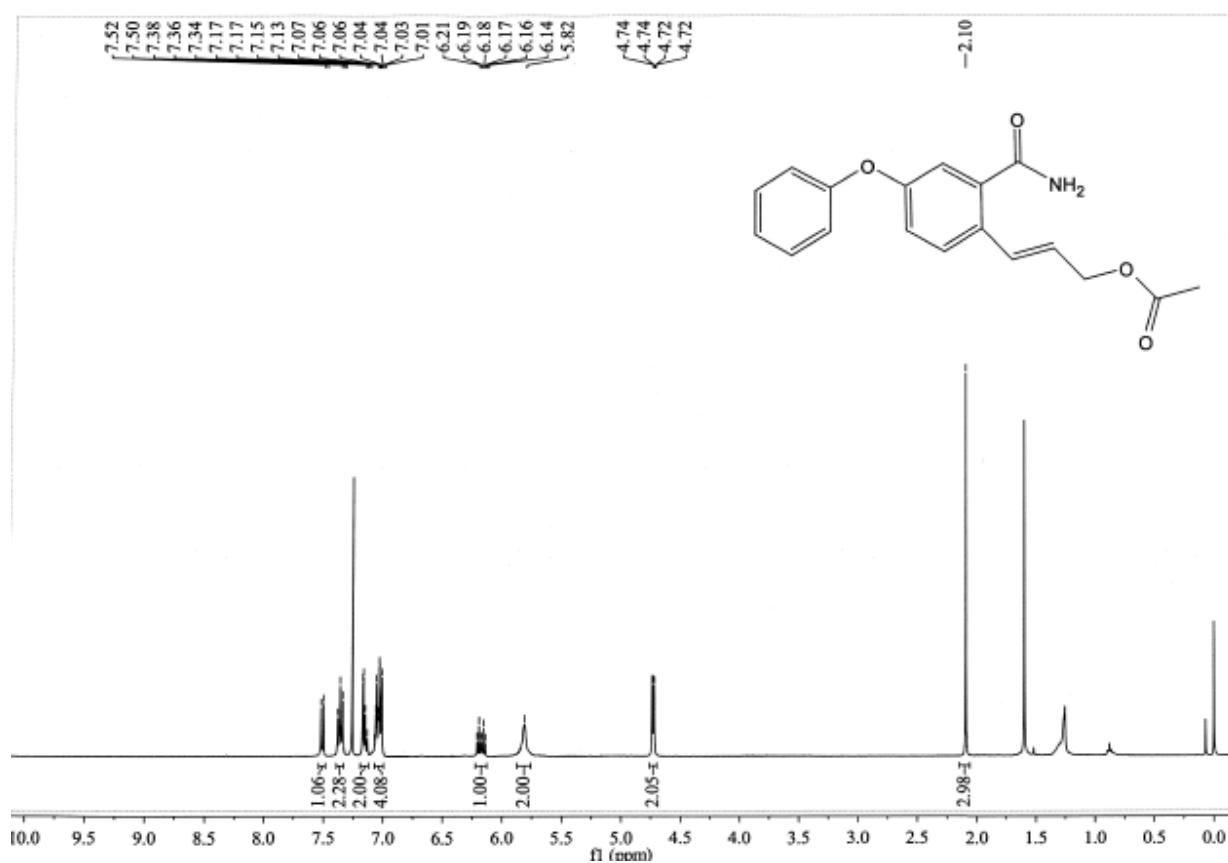


Figure S12. Compound 3fa-¹³C NMR (100M, CDCl₃)

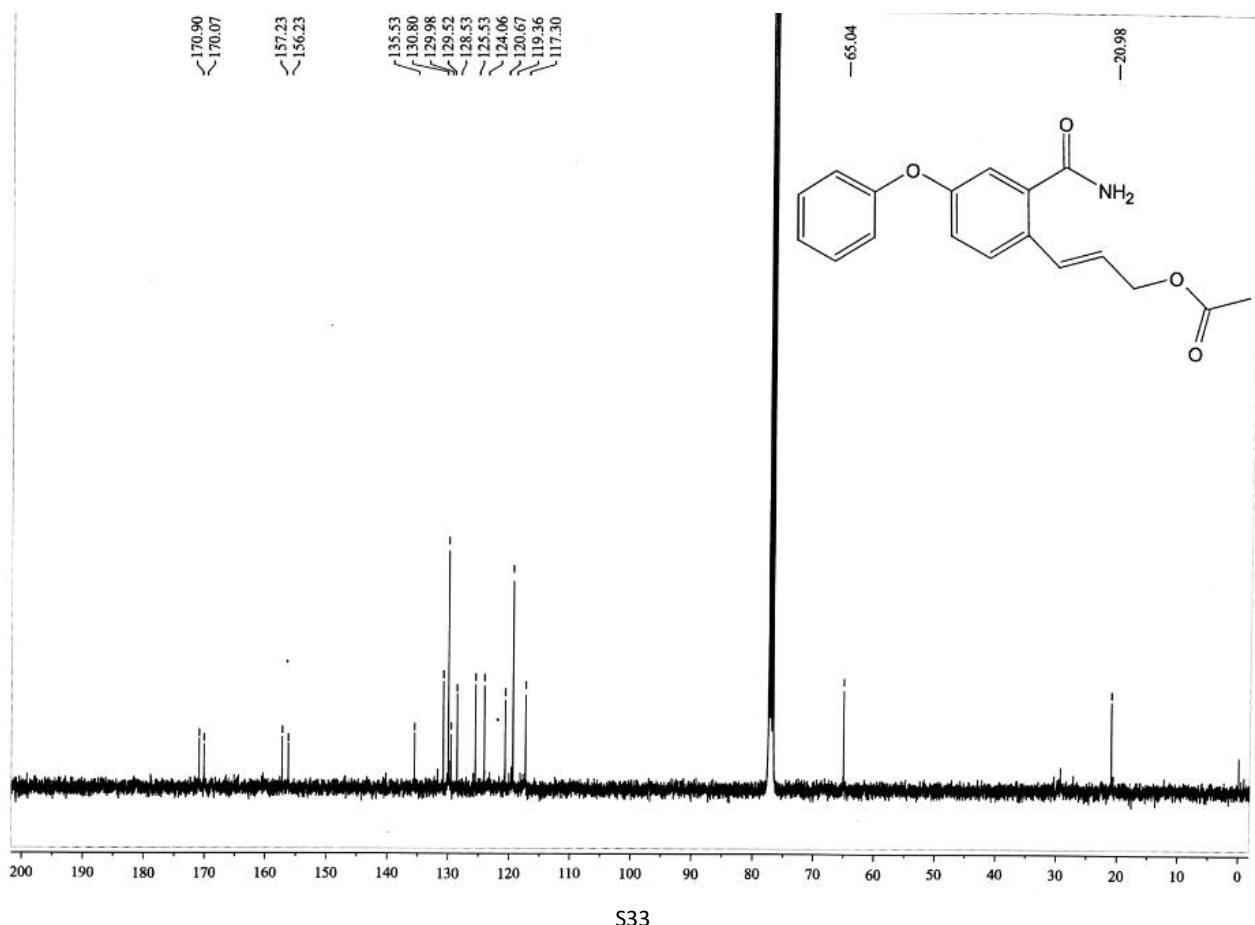


Figure S13. Compound **3ga**-¹H NMR (400M, CDCl₃)

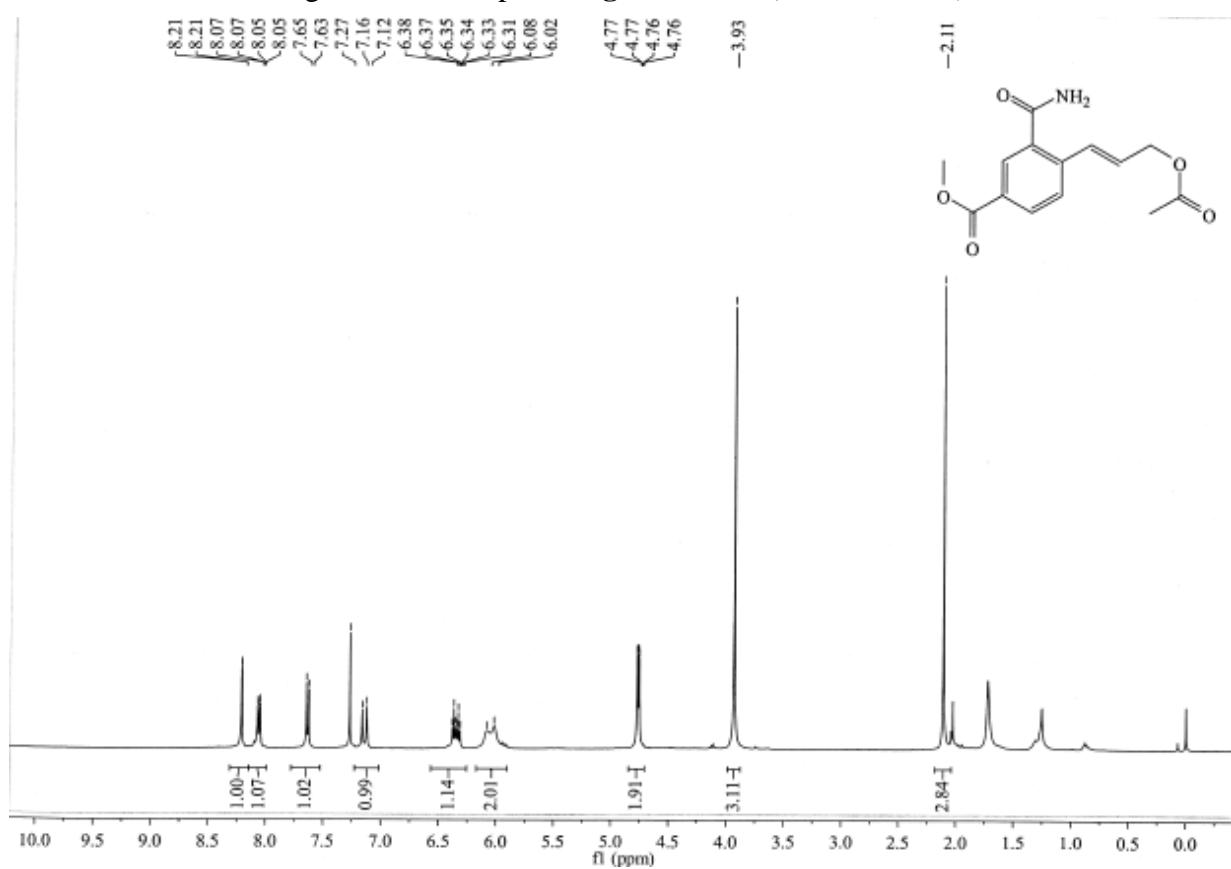


Figure S14. Compound **3ga**-¹³C NMR (100M, CDCl₃)

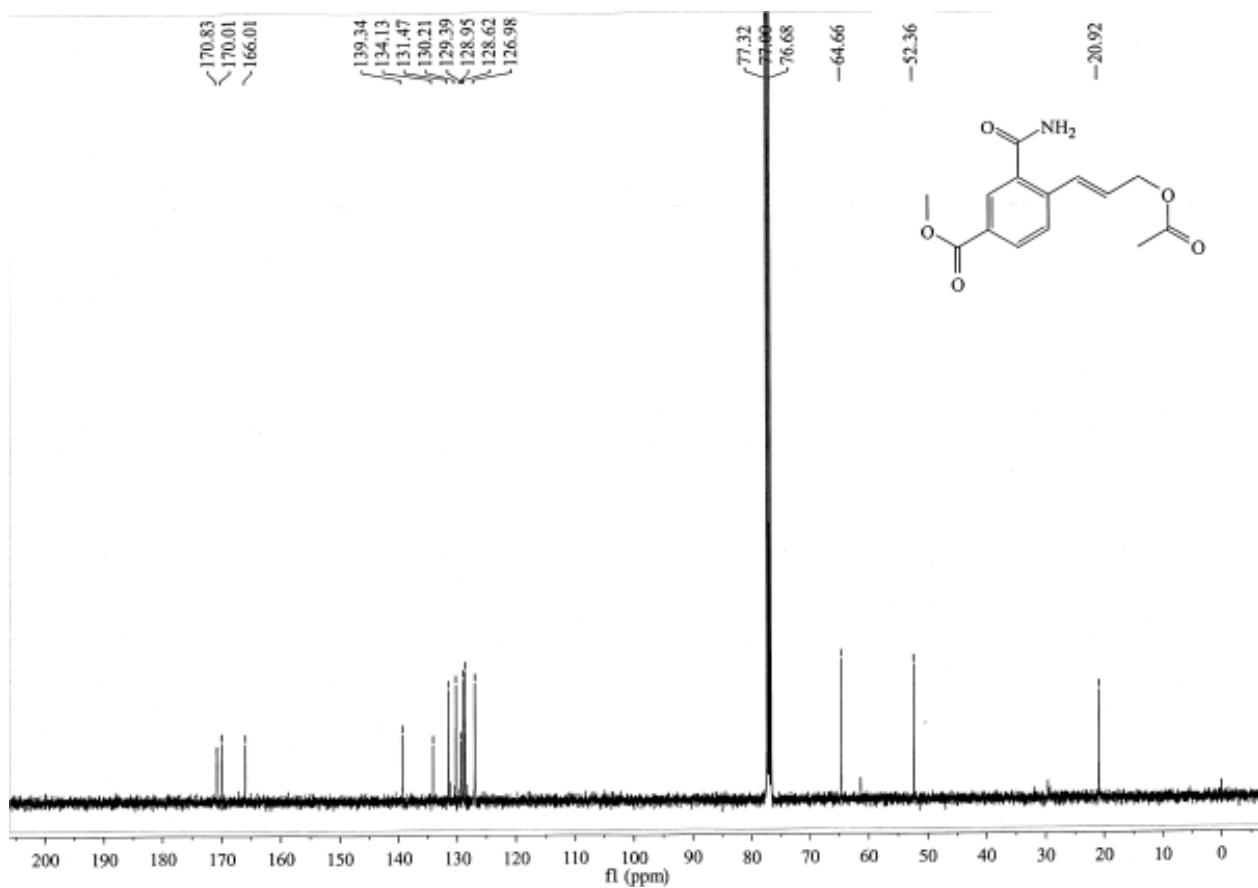


Figure S15. Compound **3ha** (E-isomer) & **3ha'** (Z-isomer)-¹H NMR (400M, CDCl₃)

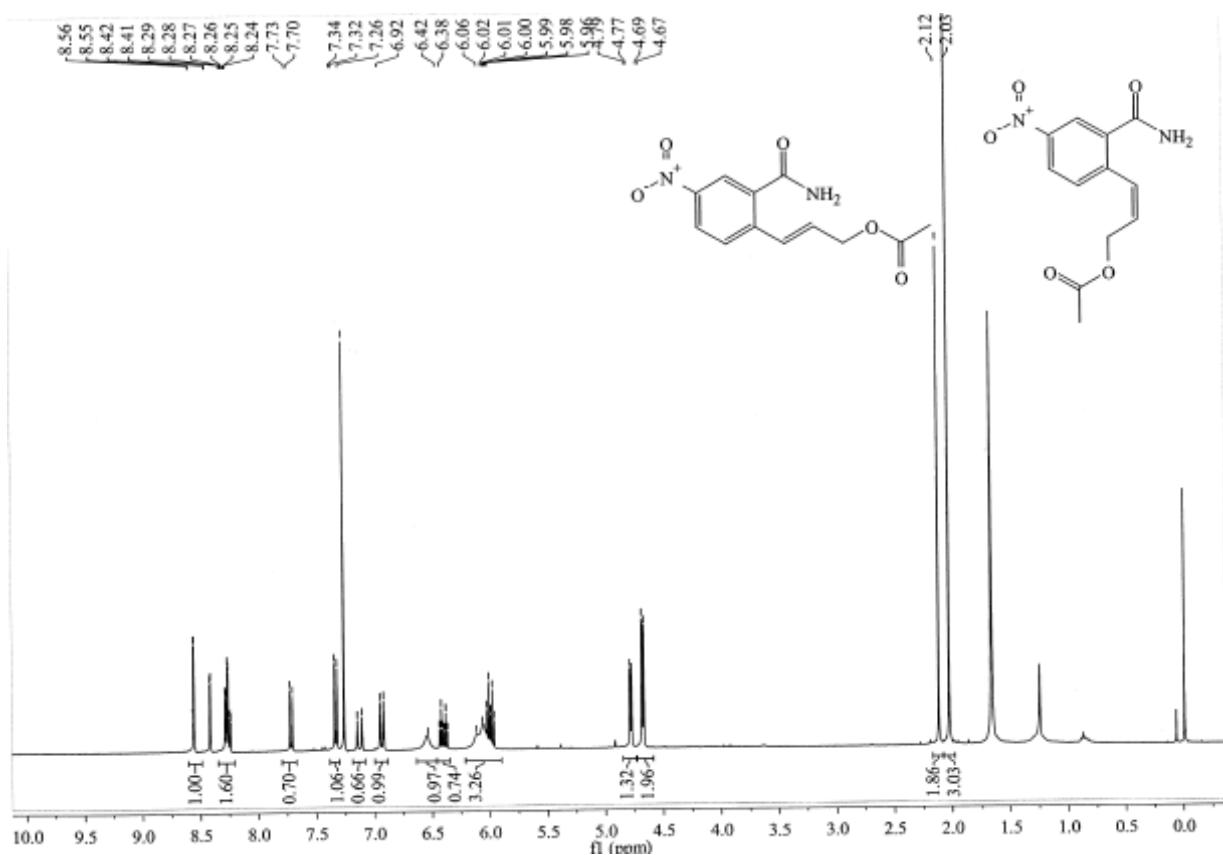


Figure S16. Compound **3ha** (E-isomer) & **3ha'** (Z-isomer)-¹³C NMR (100M, CDCl₃)

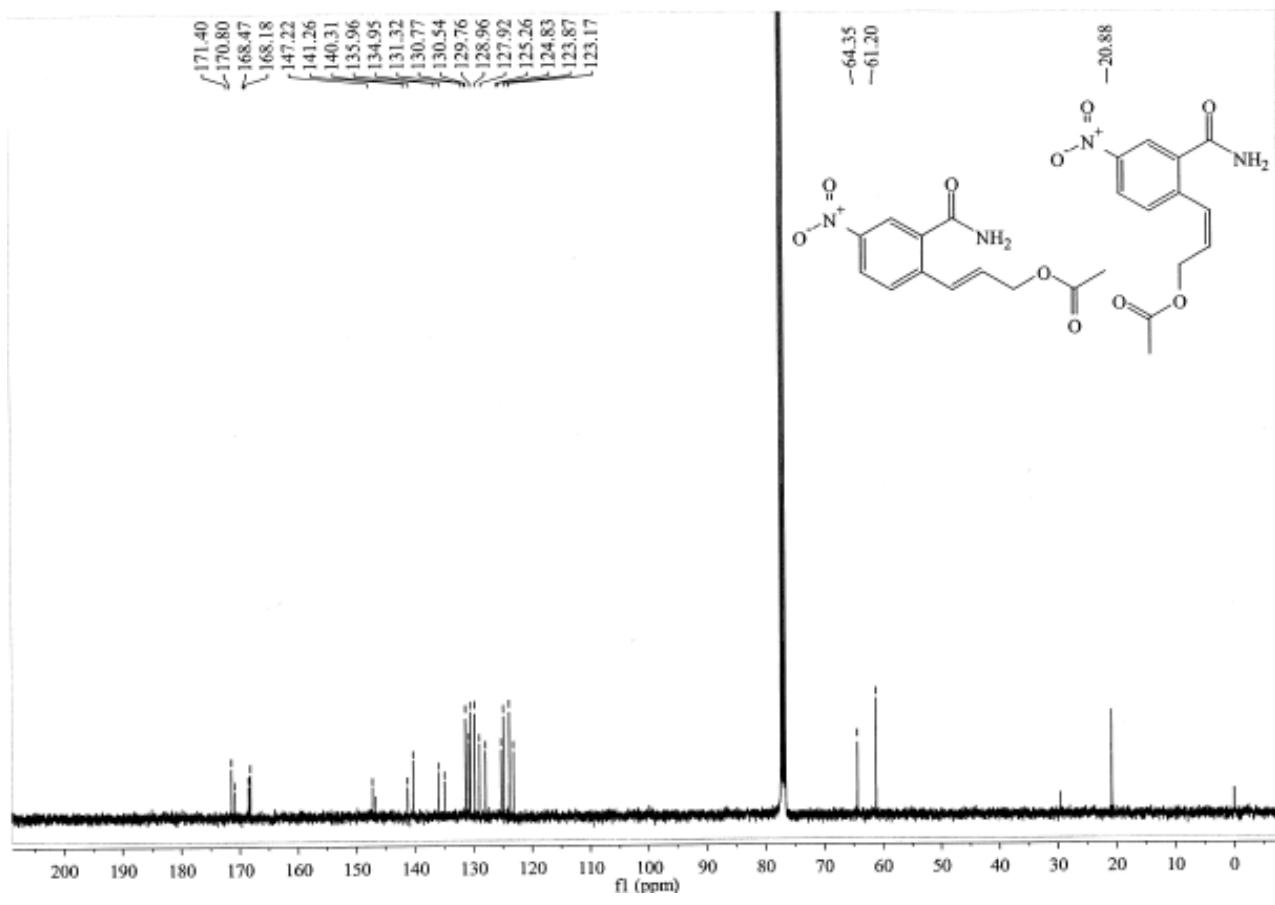


Figure S17. Compound 3ia-¹H NMR (400M, CDCl₃)

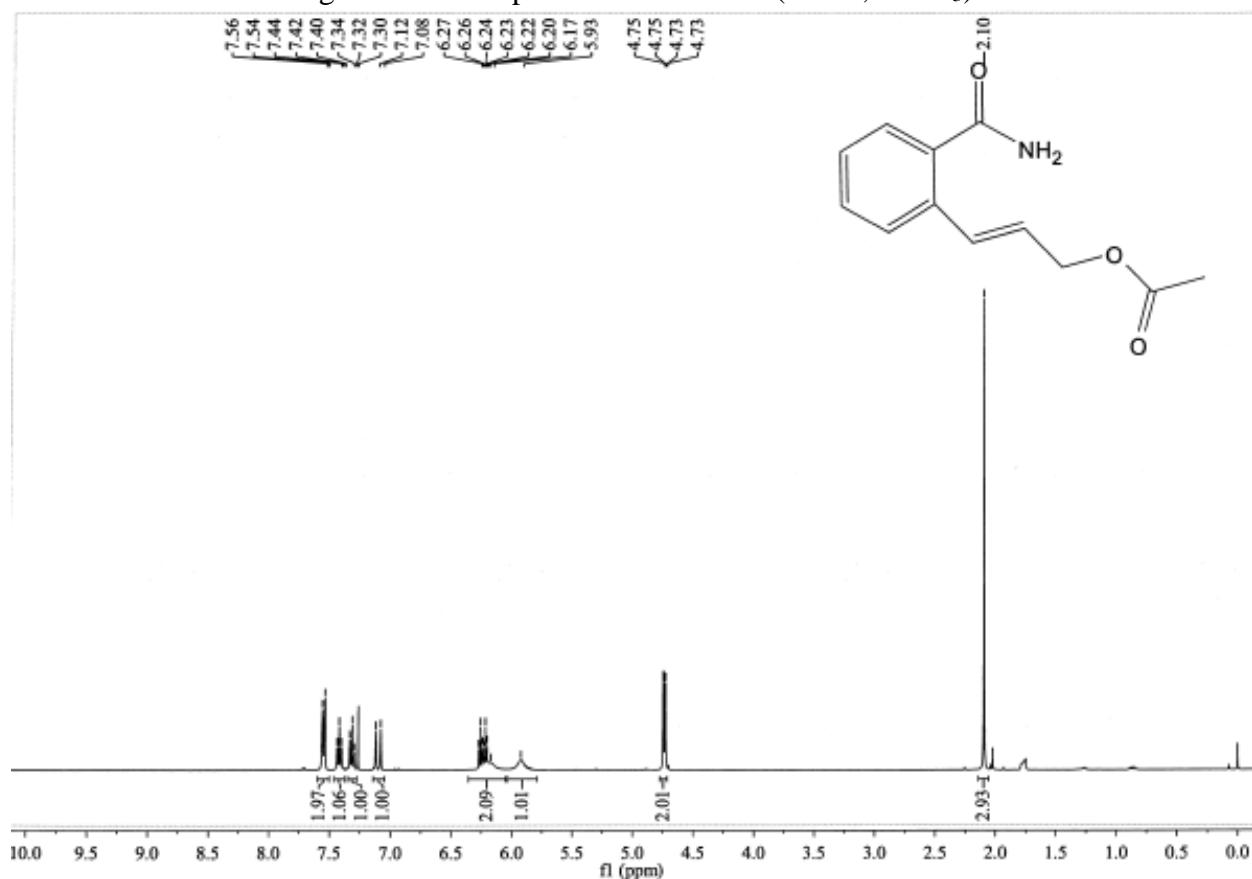


Figure S18. Compound 3ia-¹³C NMR (100M, CDCl₃)

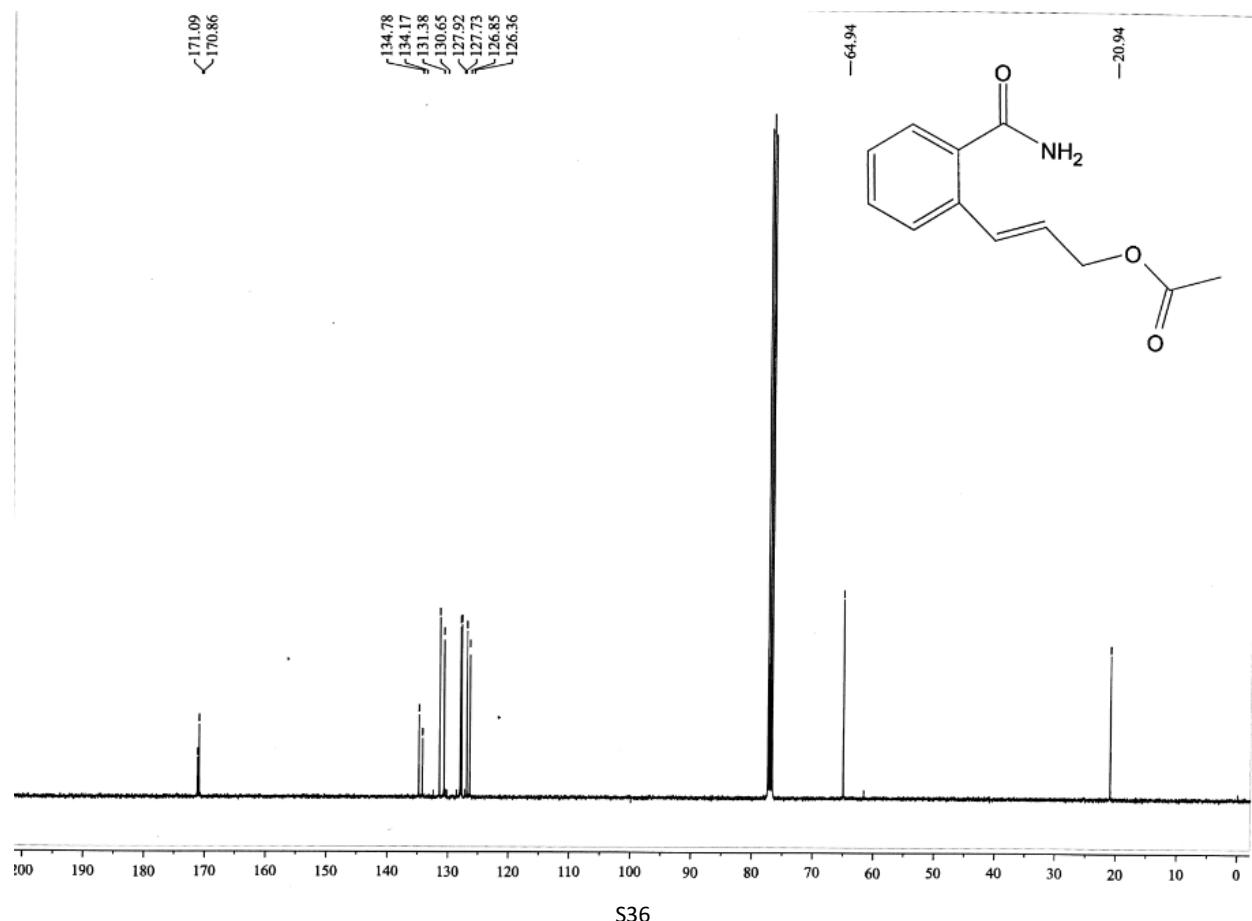


Figure S19. Compound 3ja-¹H NMR (400M, CDCl₃)

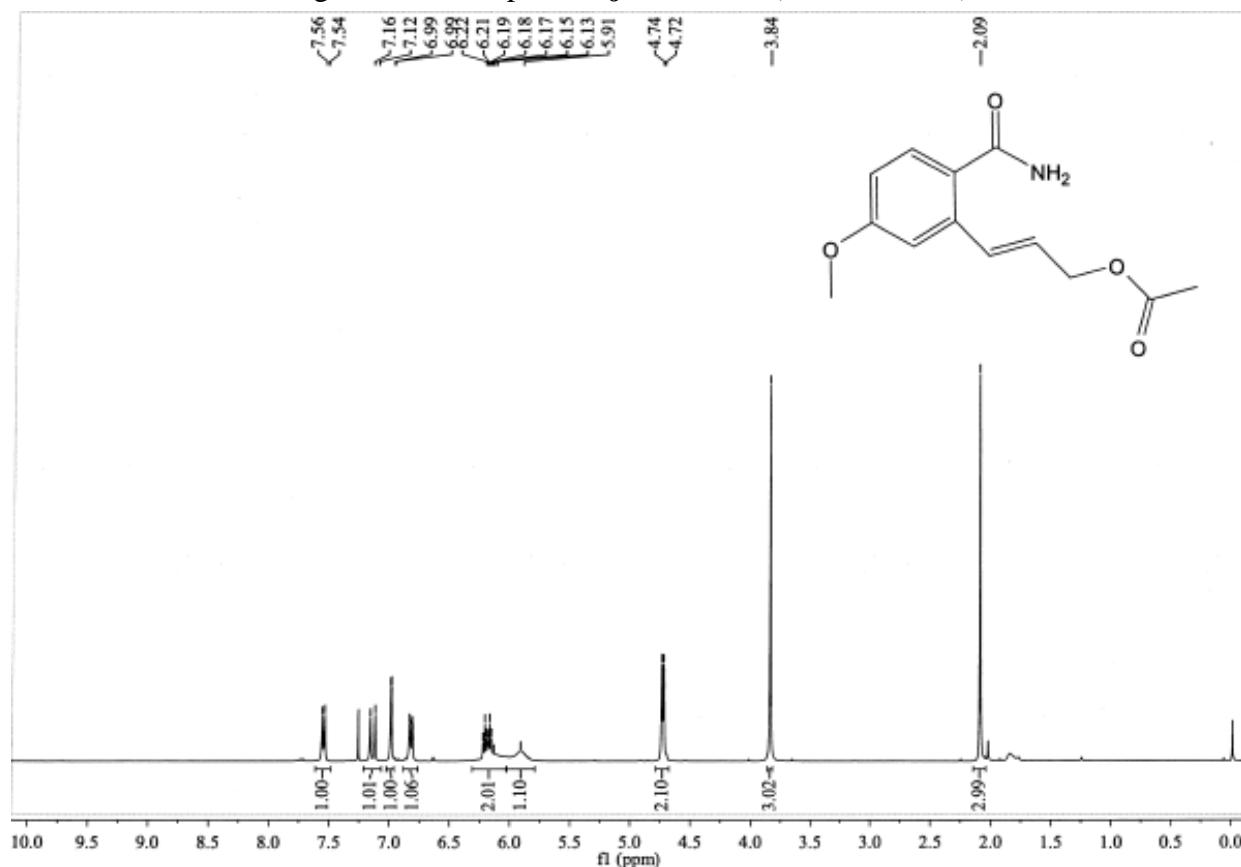


Figure S20. Compound 3ja-¹³C NMR (100M, CDCl₃)

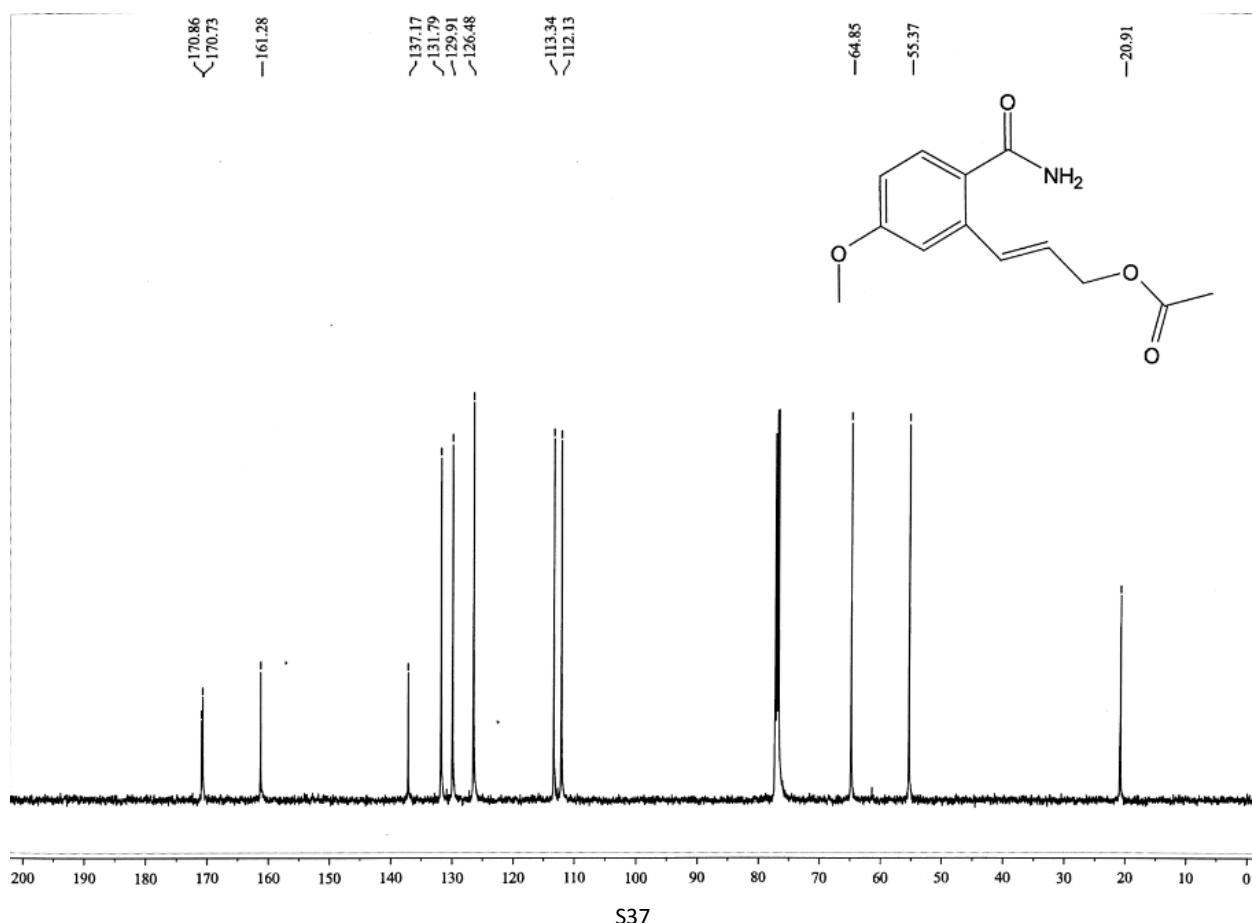


Figure S21. Compound 3ka-¹H NMR (500M, CDCl₃)

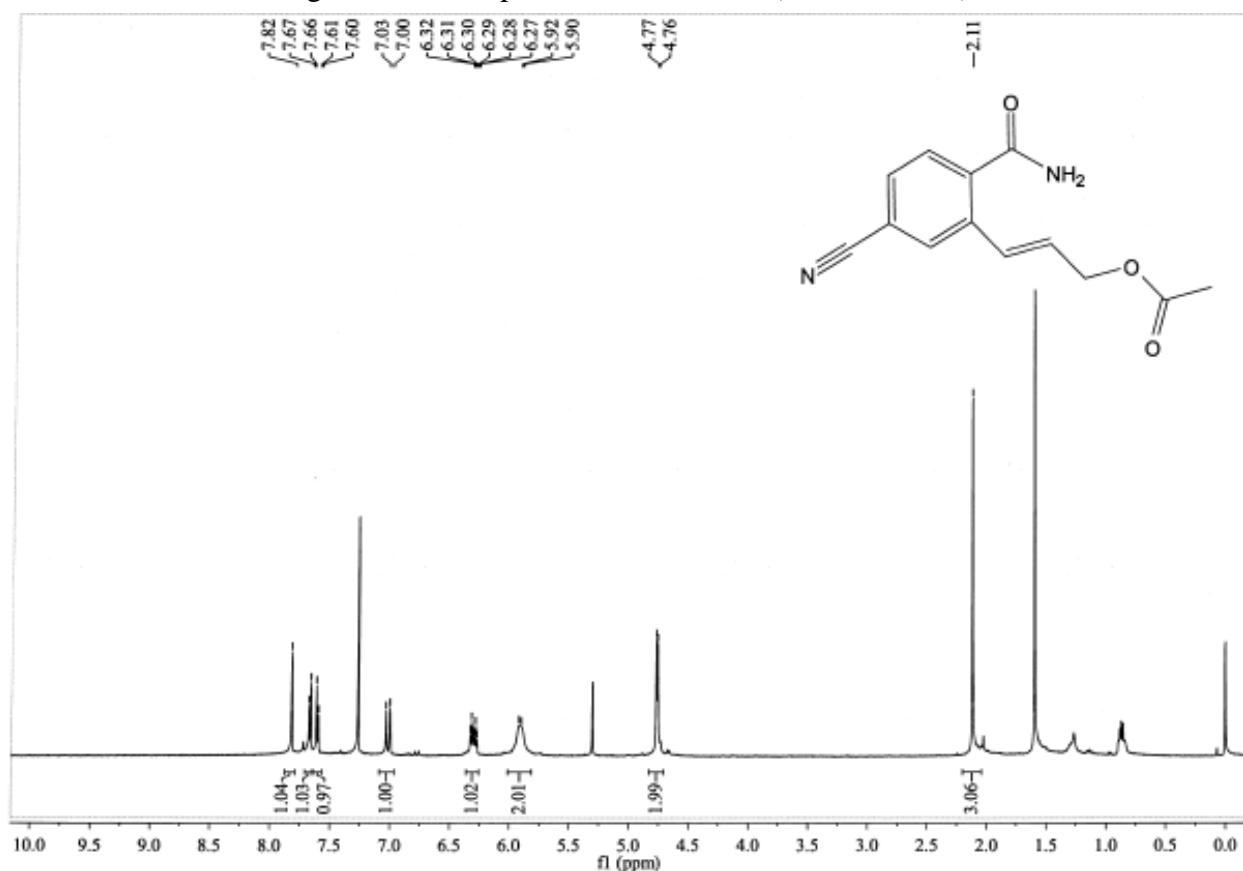


Figure S22. Compound 3ka-¹³C NMR (125M, CDCl₃)

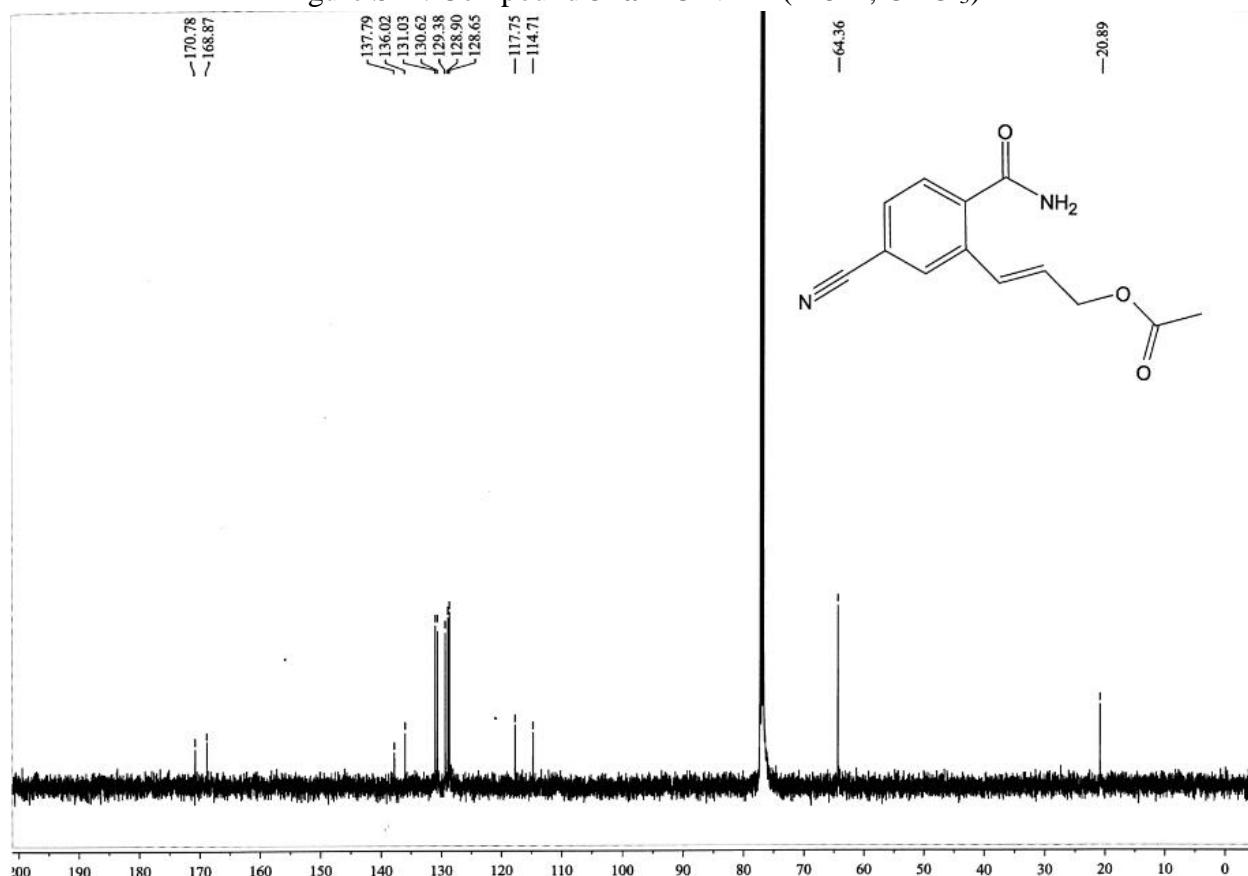


Figure S23. Compound 3la-¹H NMR (400M, CDCl₃)

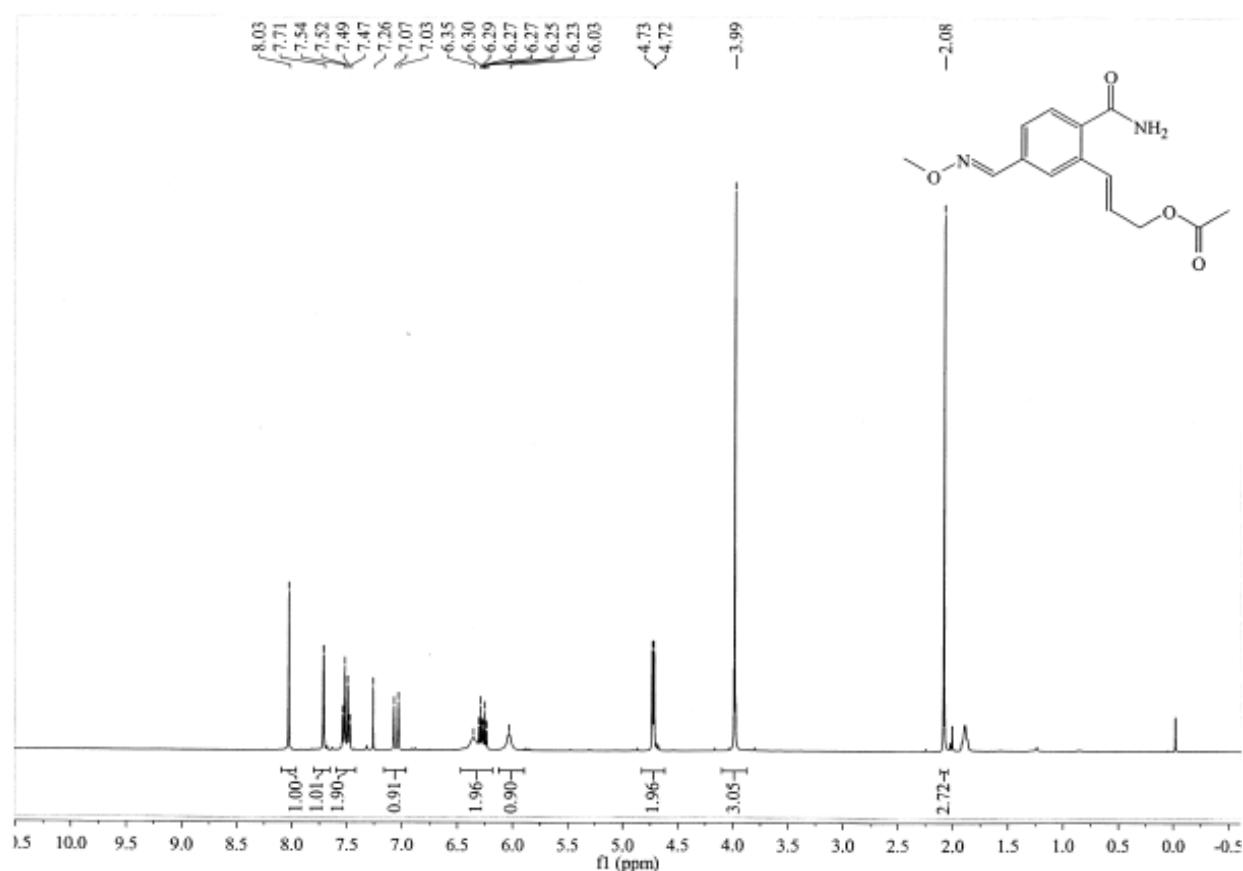


Figure S24. Compound 3la-¹³C NMR (100M, CDCl₃)

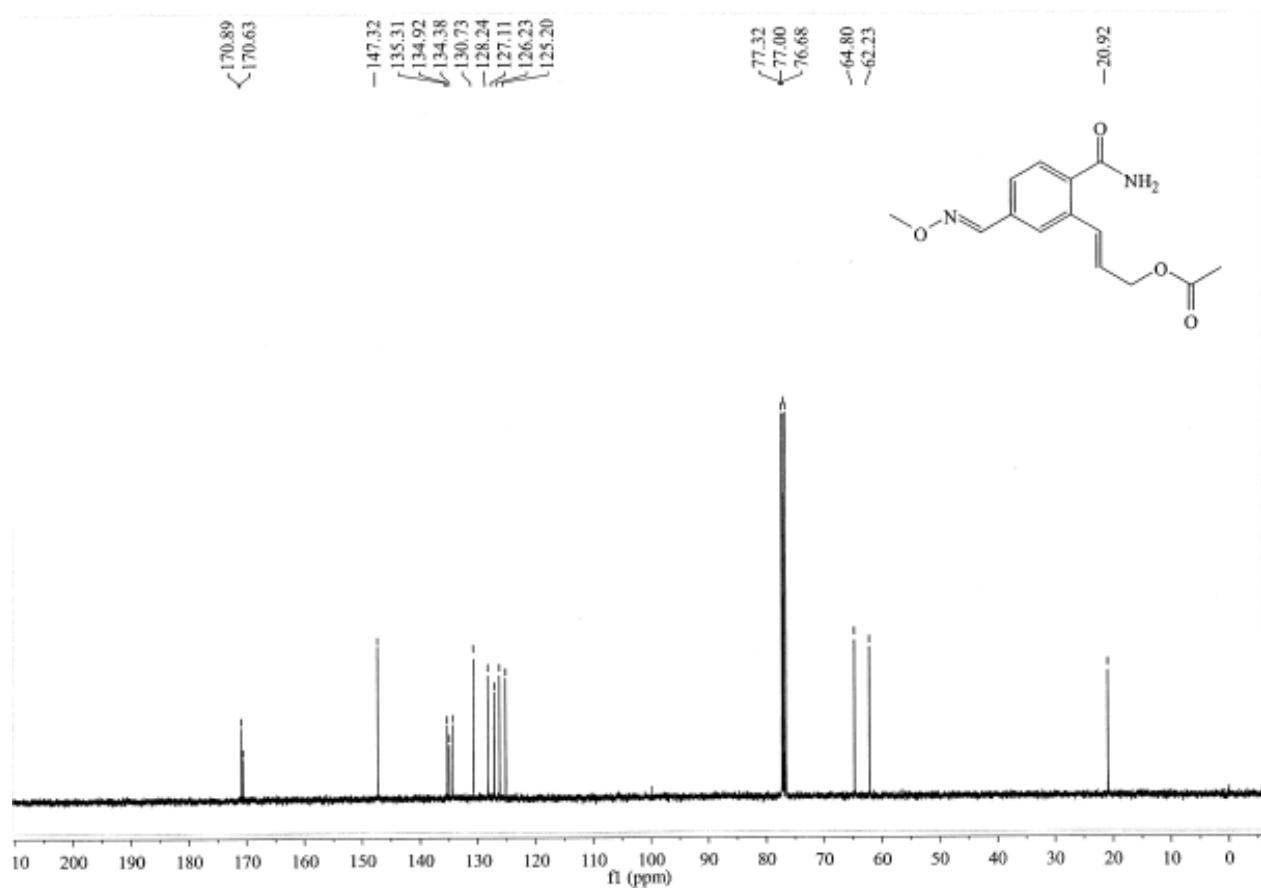


Figure S25. Compound 3ma-¹H NMR (500M, CDCl₃)

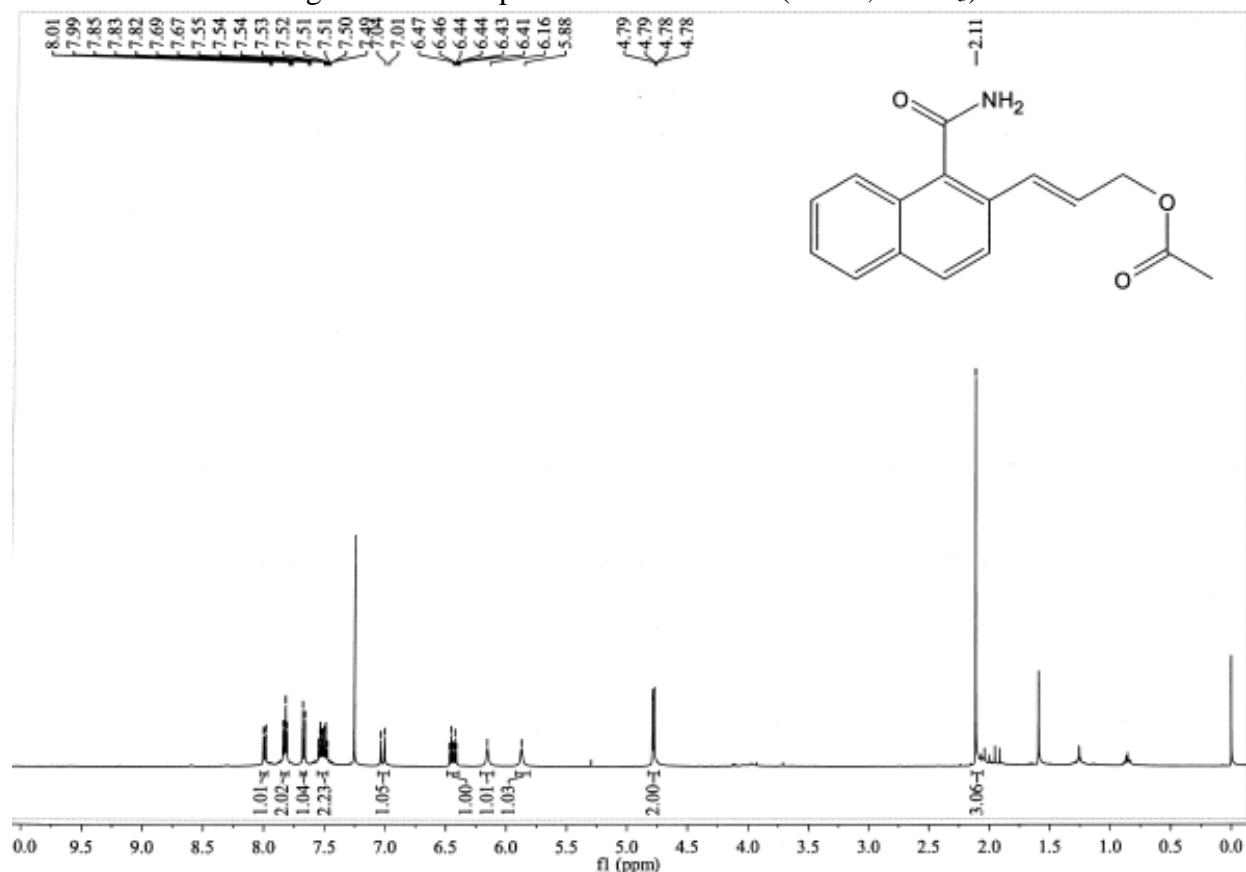


Figure S26. Compound 3ma-¹³C NMR (125M, CDCl₃)

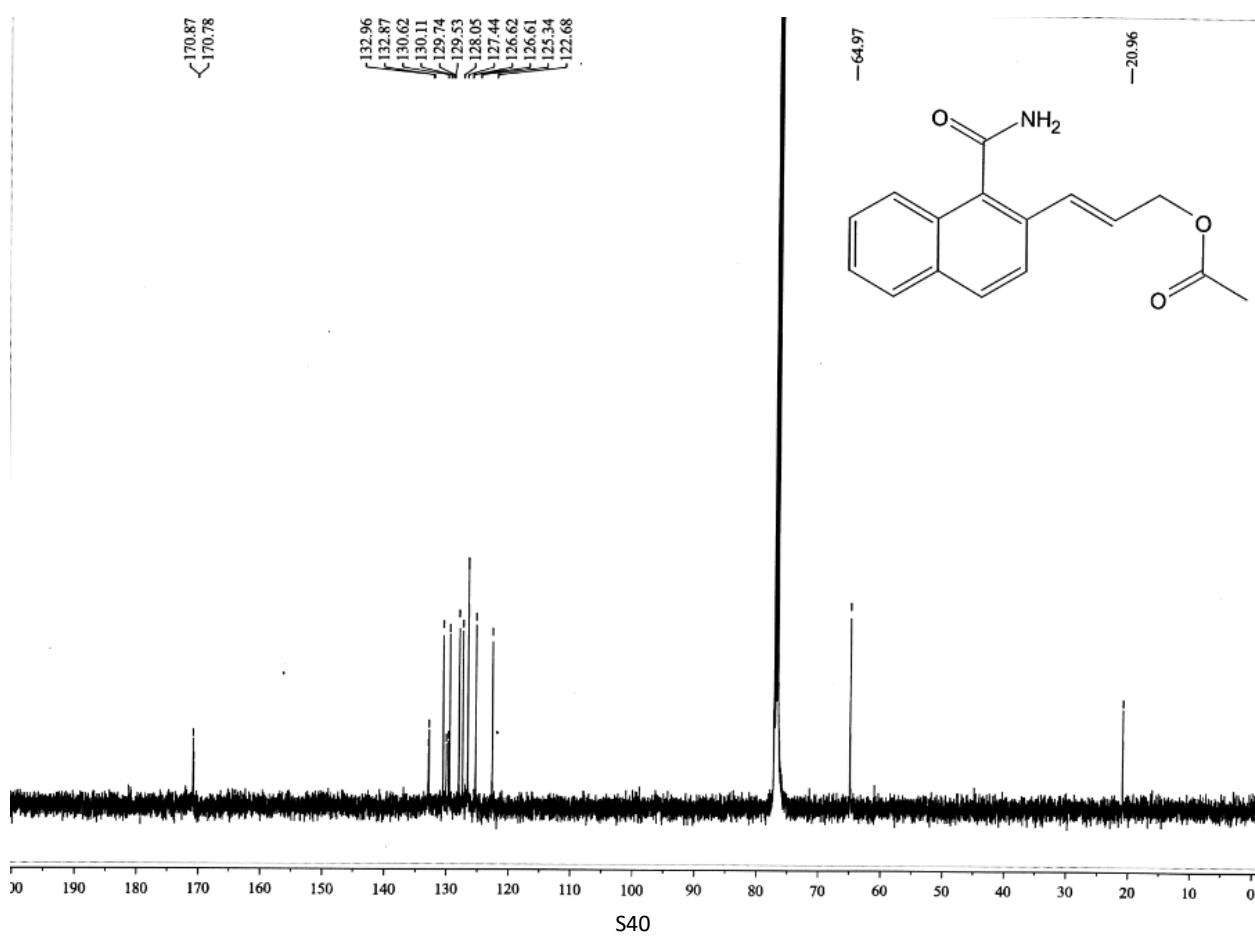


Figure S27. Compound 3na-¹H NMR (400M, CDCl₃)

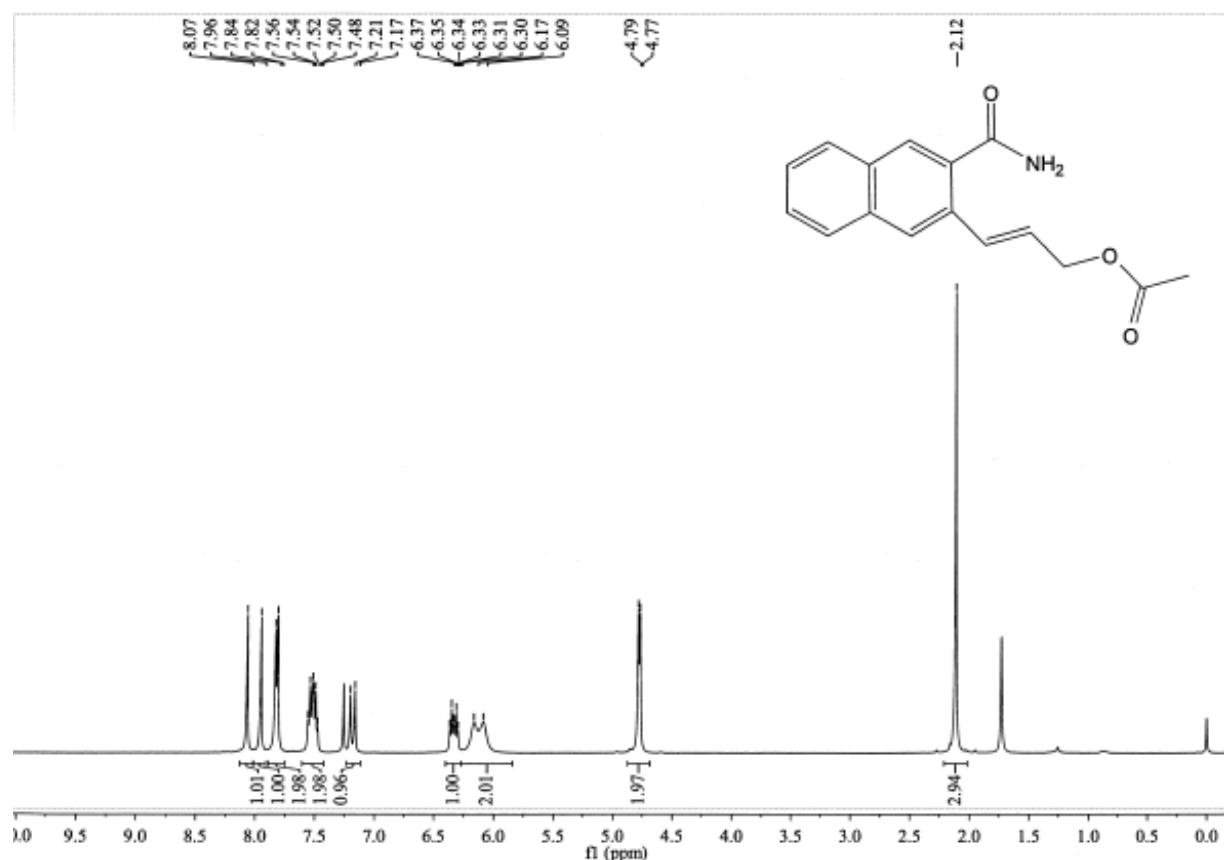


Figure S28. Compound 3na-¹³C NMR (100M, CDCl₃)

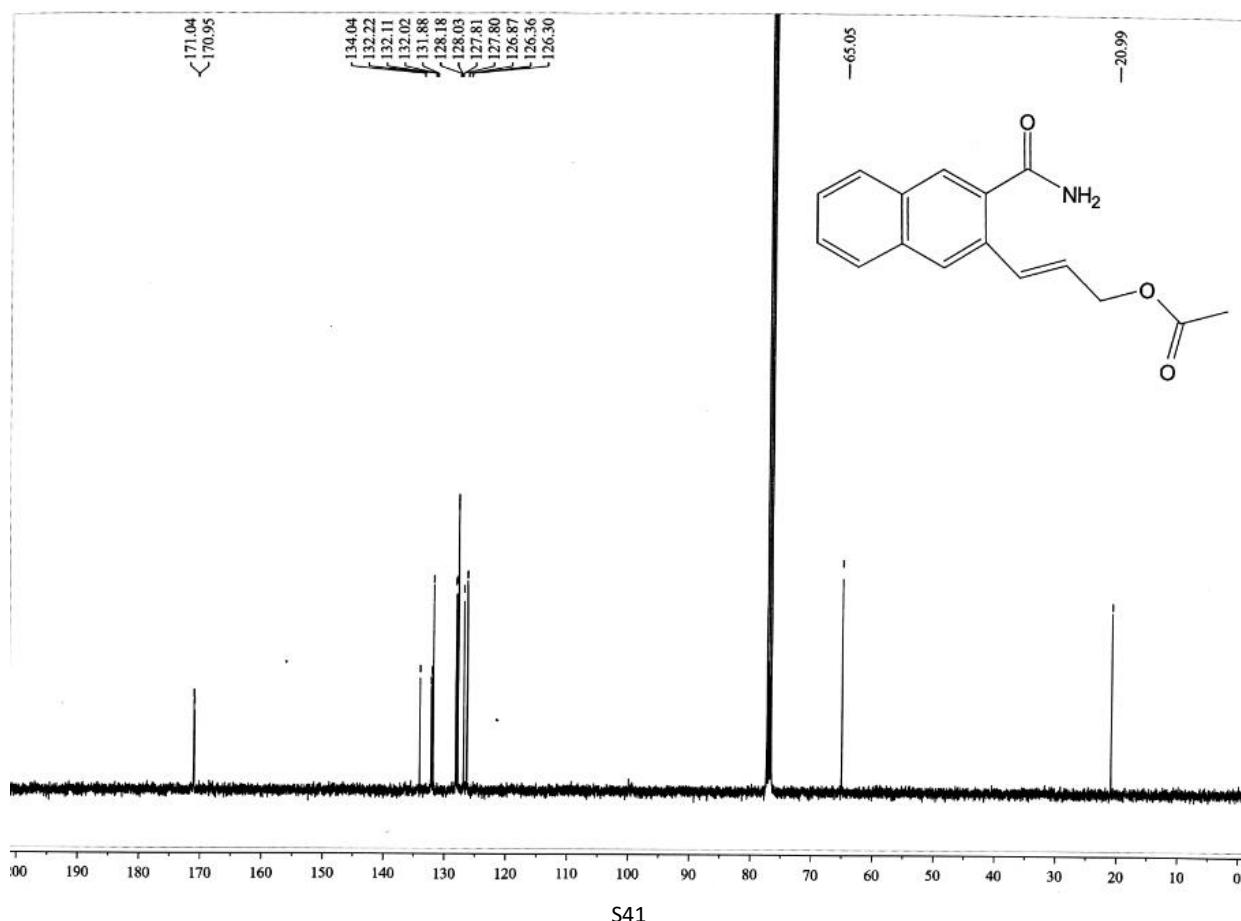


Figure S29. Compound 3oa-¹H NMR (600M, CDCl₃)

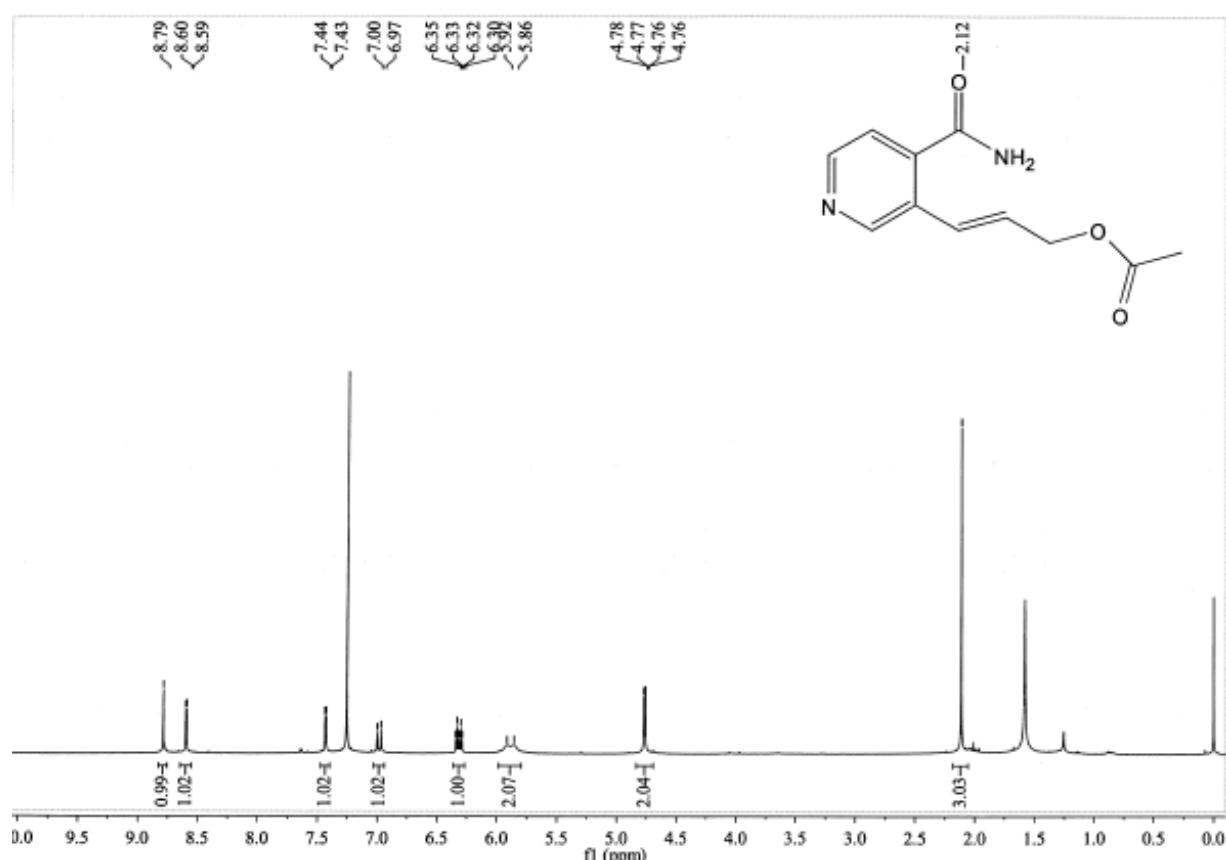


Figure S30. Compound 3oa-¹³C NMR (150M, CDCl₃)

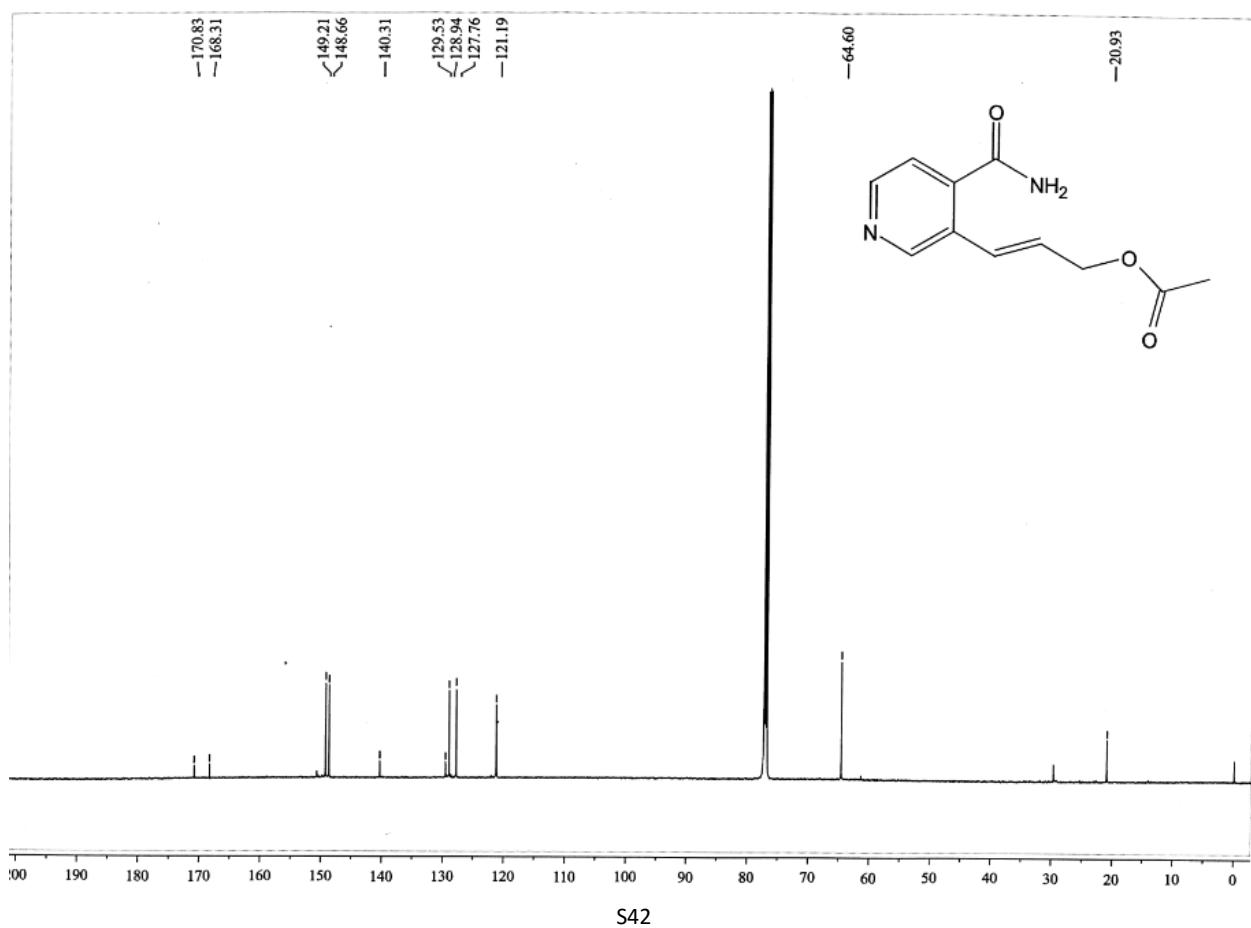


Figure S31. Compound 3pa-¹H NMR (400M, CDCl₃)

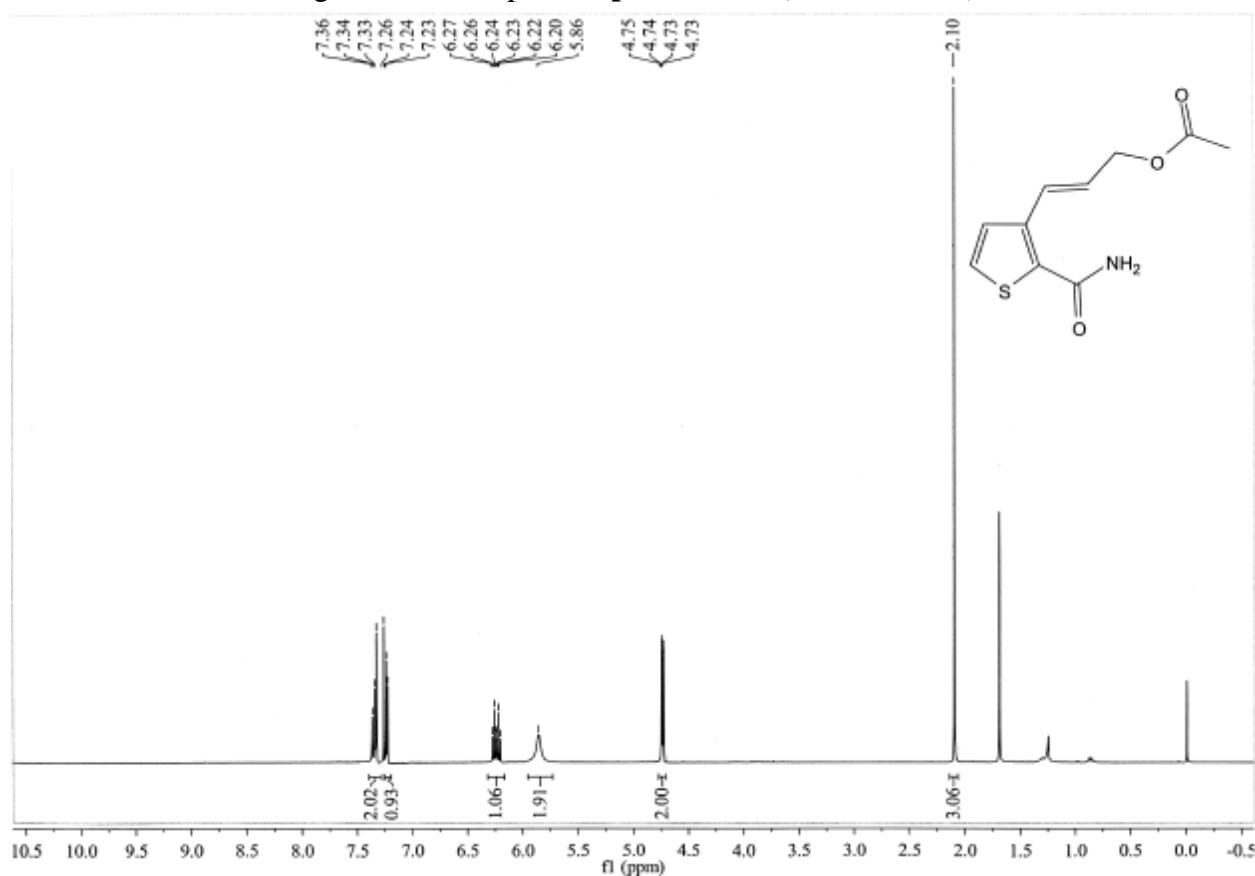


Figure S32. Compound 3pa-¹³C NMR (100M, CDCl₃)

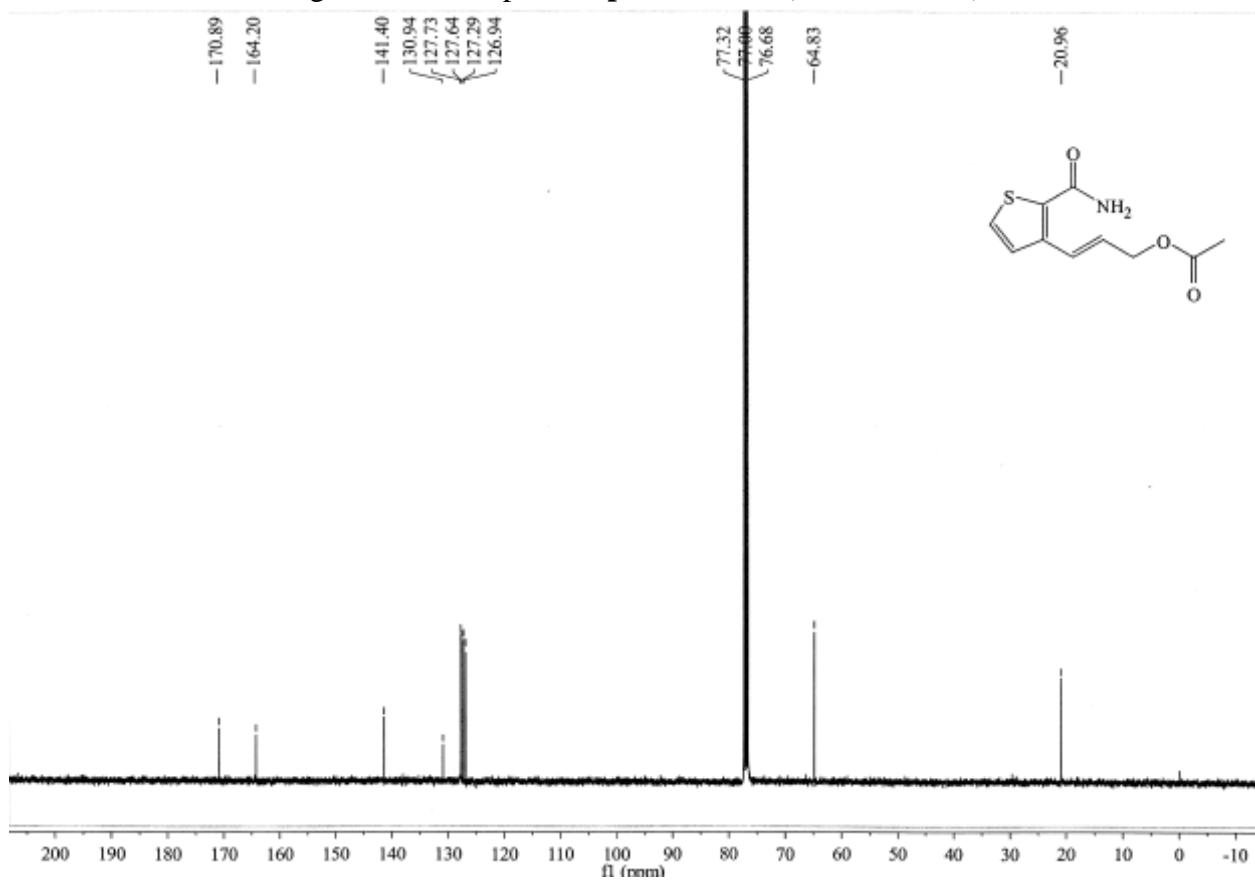


Figure S33. Compound 3ab-¹H NMR (400M, CDCl₃)

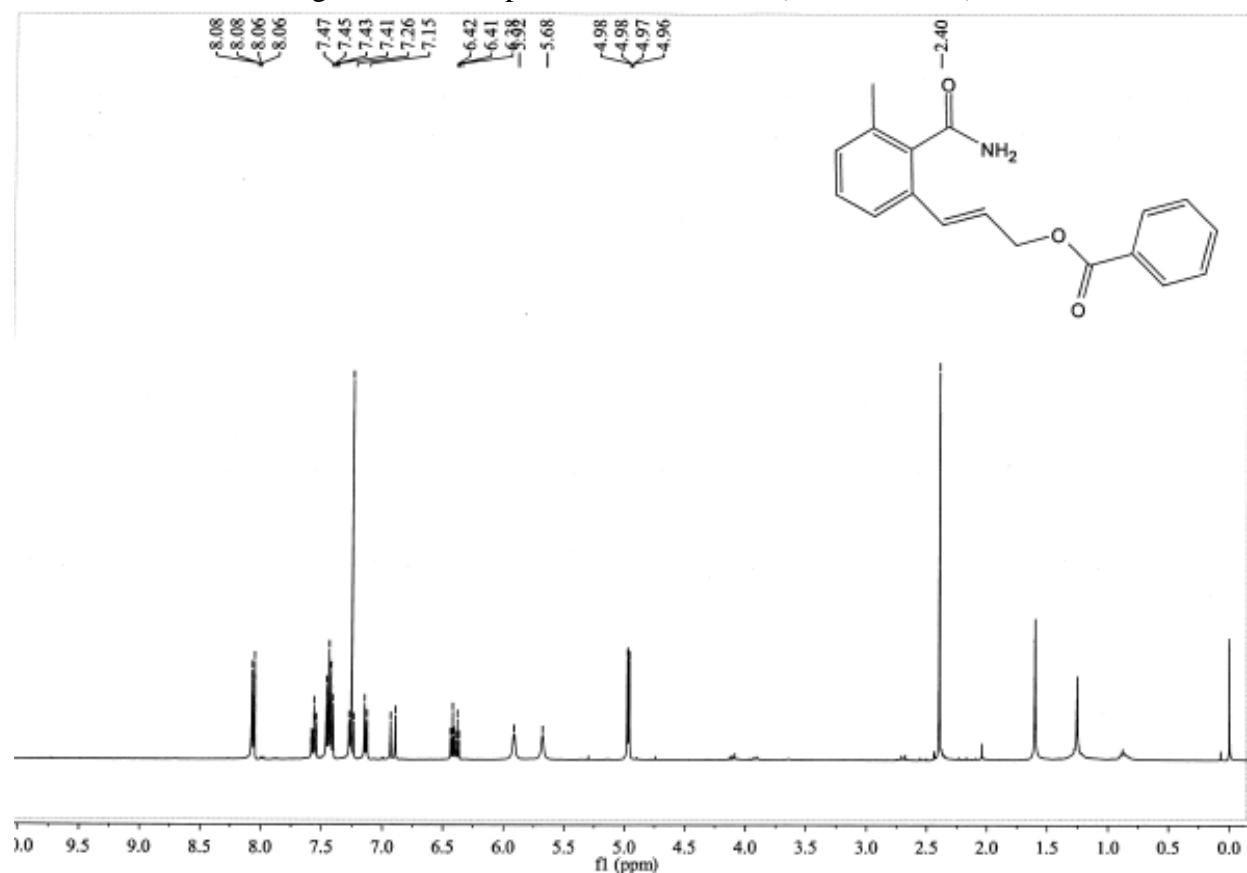


Figure S34. Compound 3ab-¹³C NMR (100M, CDCl₃)

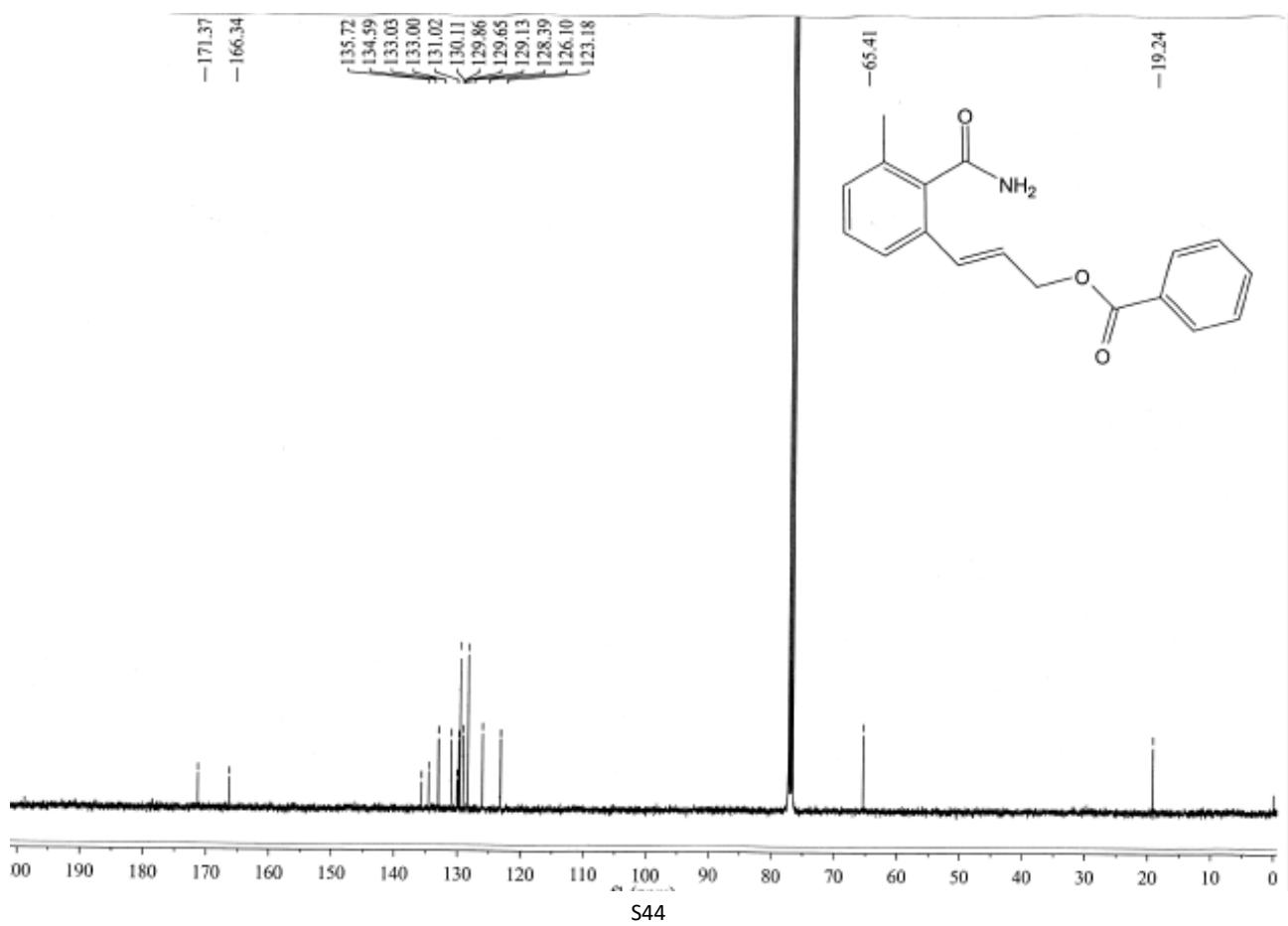


Figure S35. Compound 3ad-¹H NMR (600M, CDCl₃)

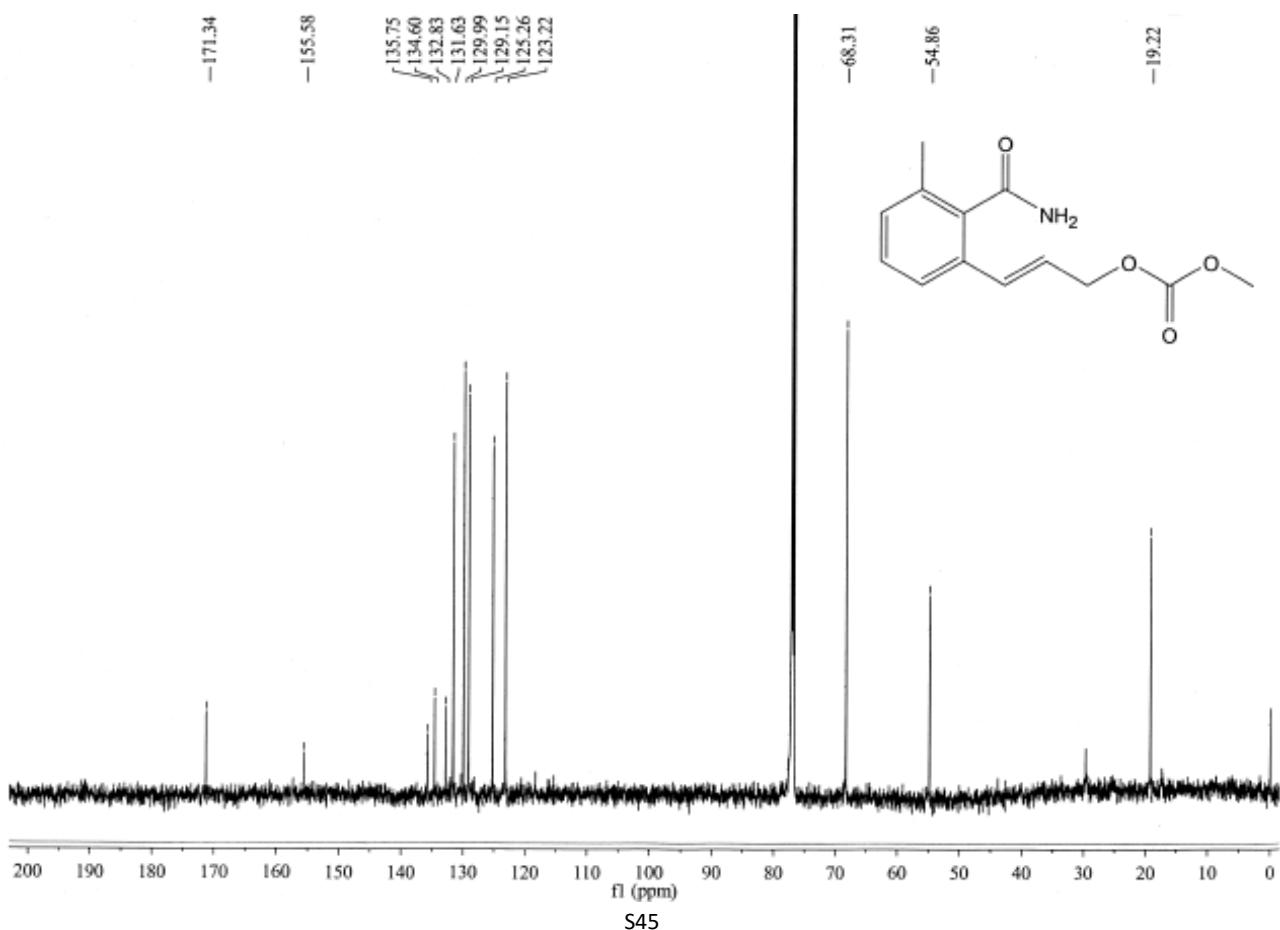
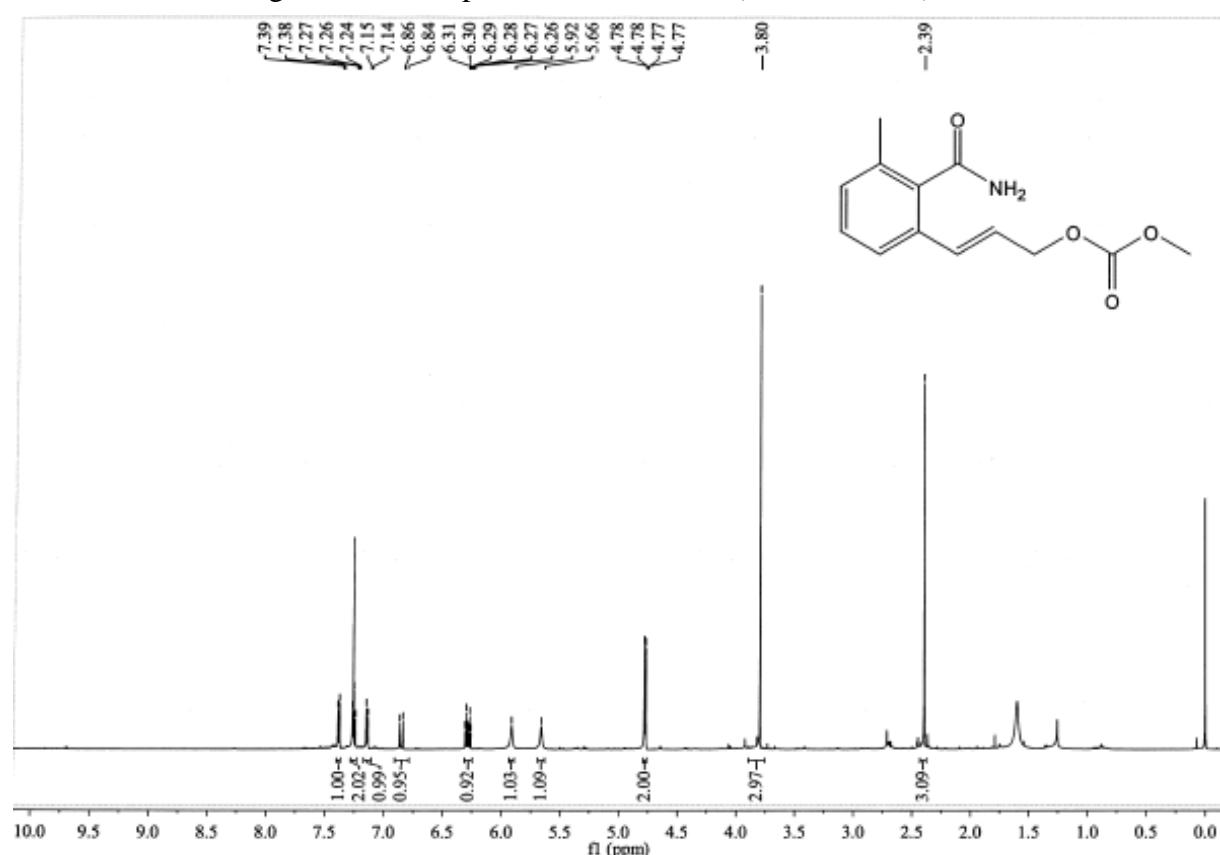


Figure S37. Compound 4a-¹H NMR (400M, CDCl₃)

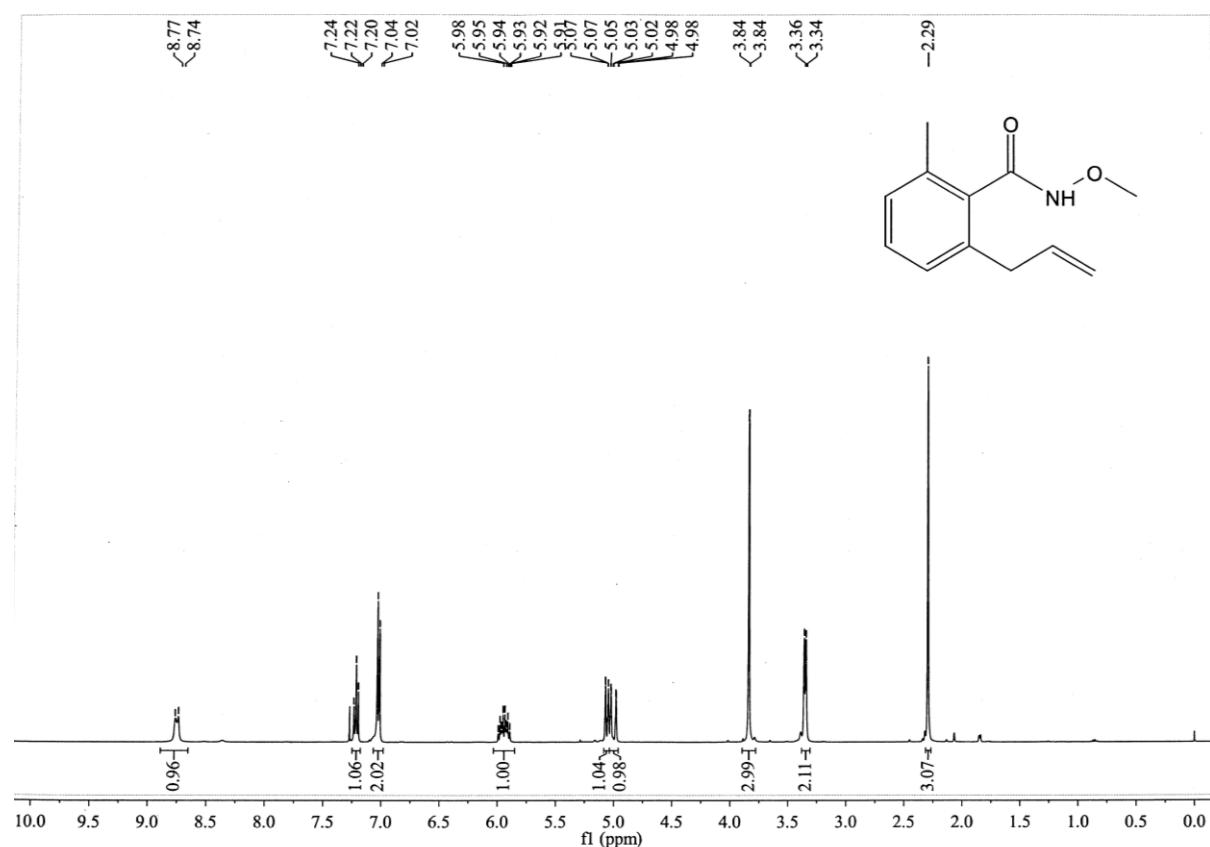


Figure S38. Compound 4a-¹³C NMR (100M, CDCl₃)

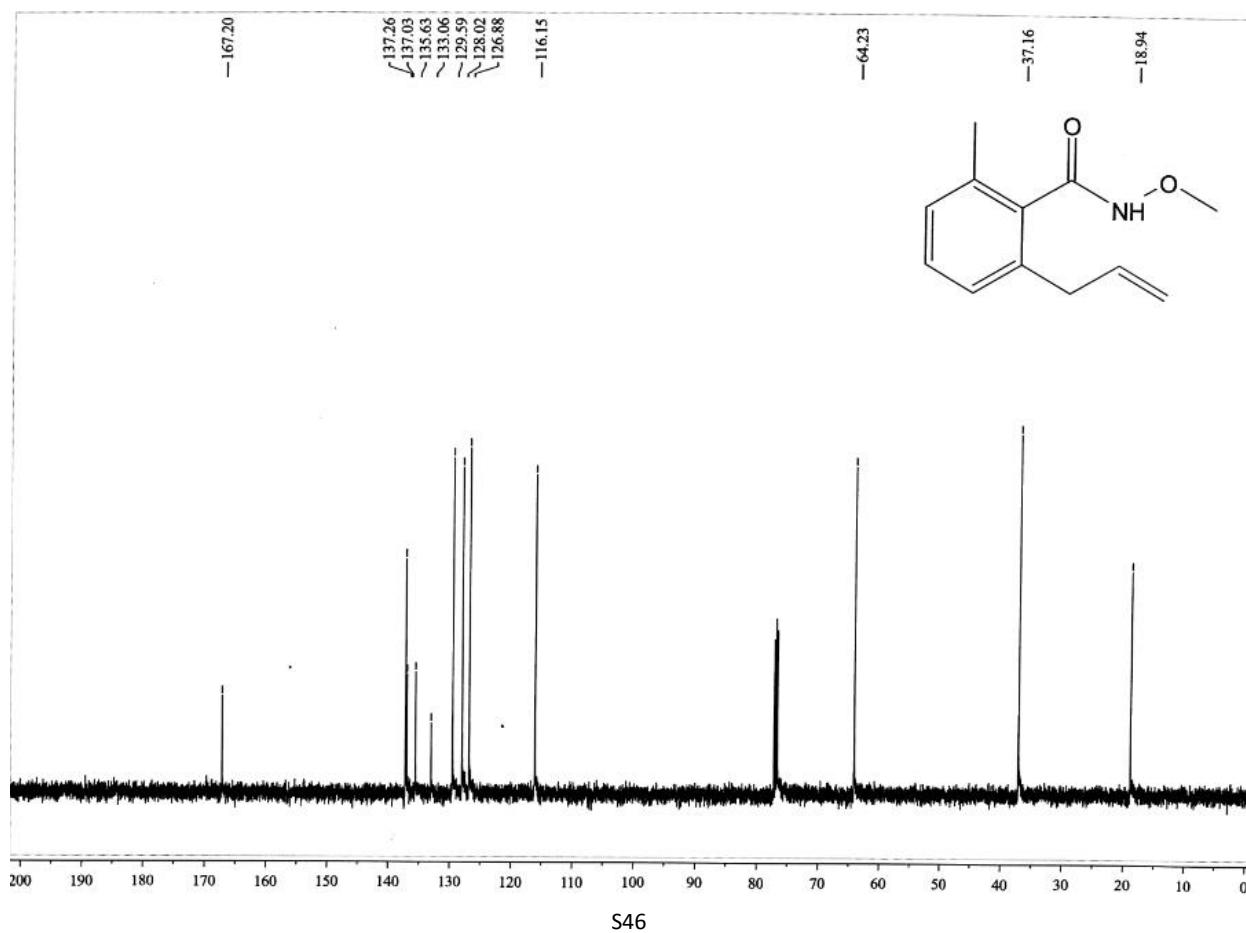


Figure S39. Compound 4b-¹H NMR (400M, CDCl₃)

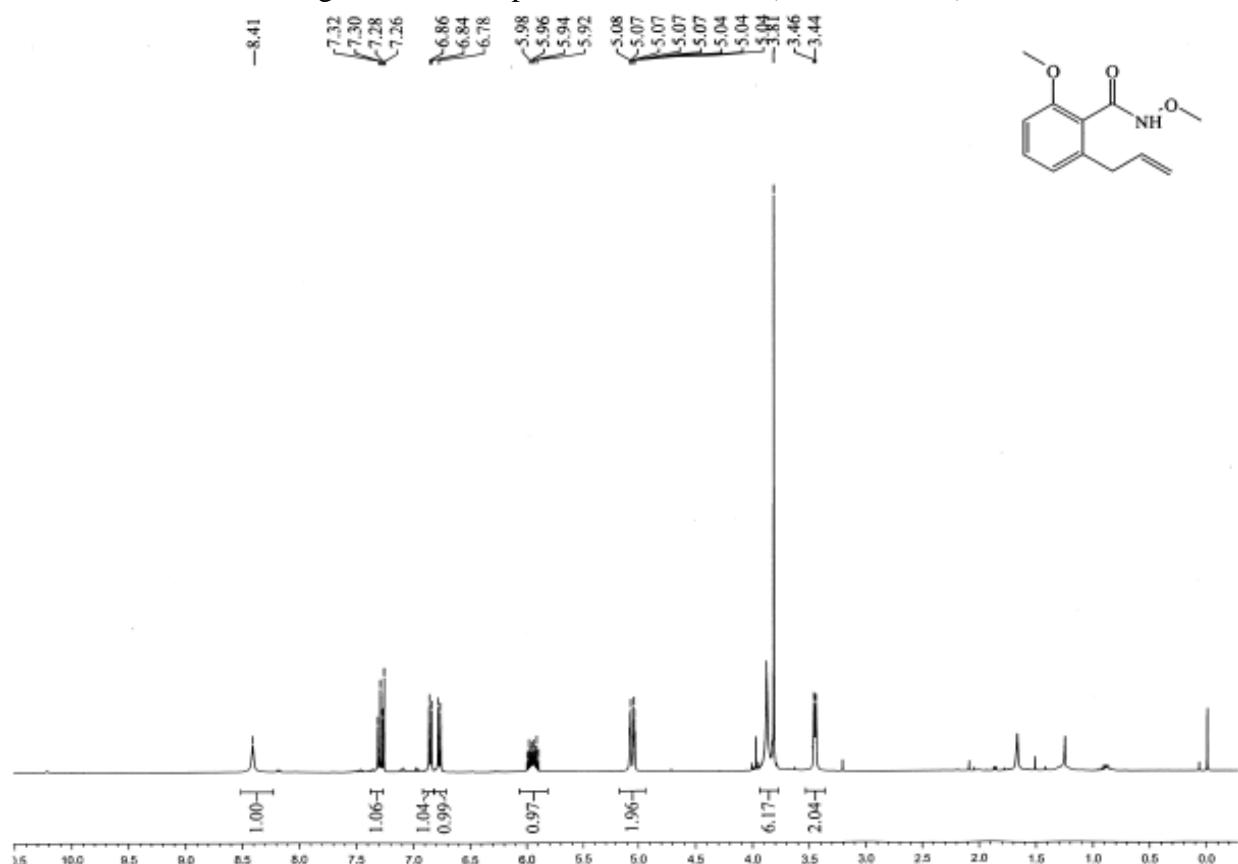


Figure S40. Compound 4b-¹³C NMR (100M, CDCl₃)

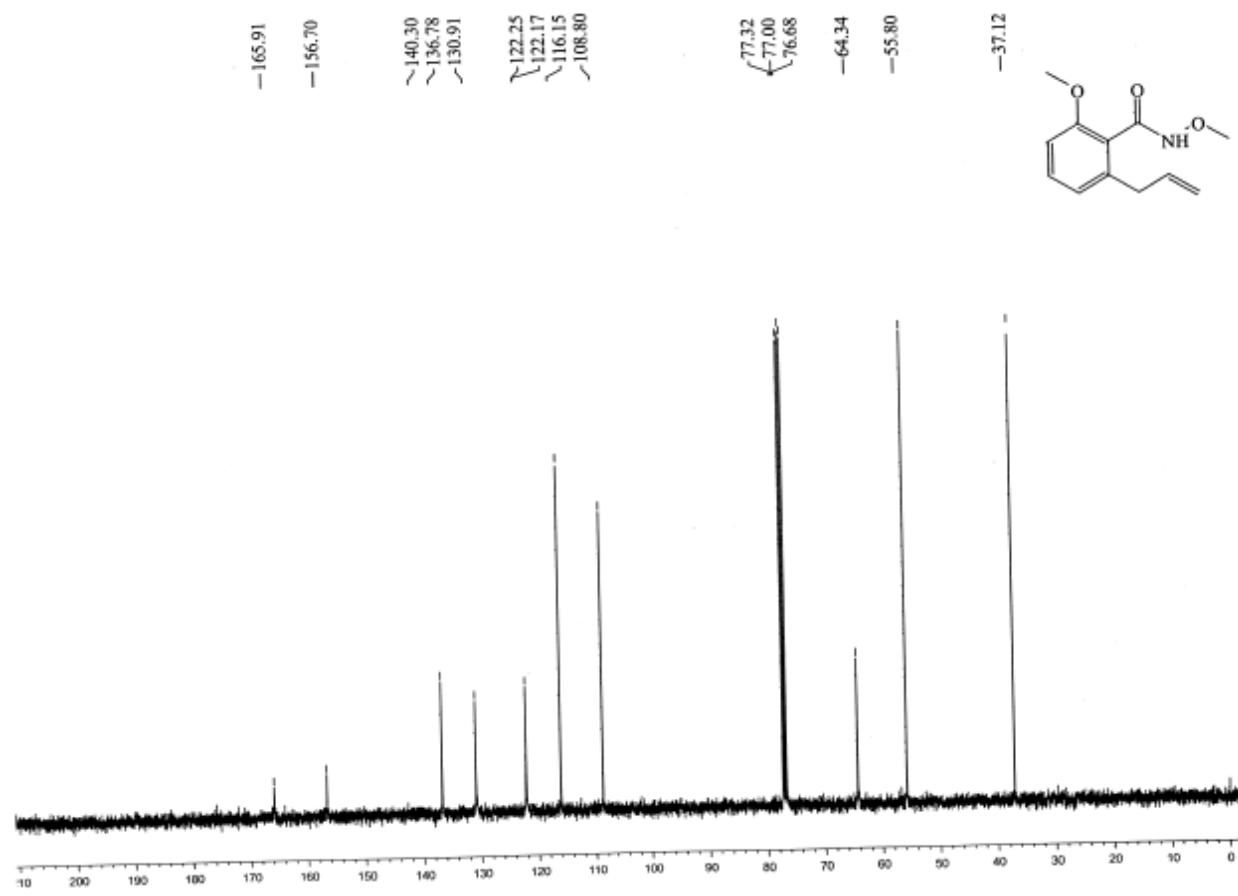


Figure S41. Compound 4c-¹H NMR (400M, CDCl₃)

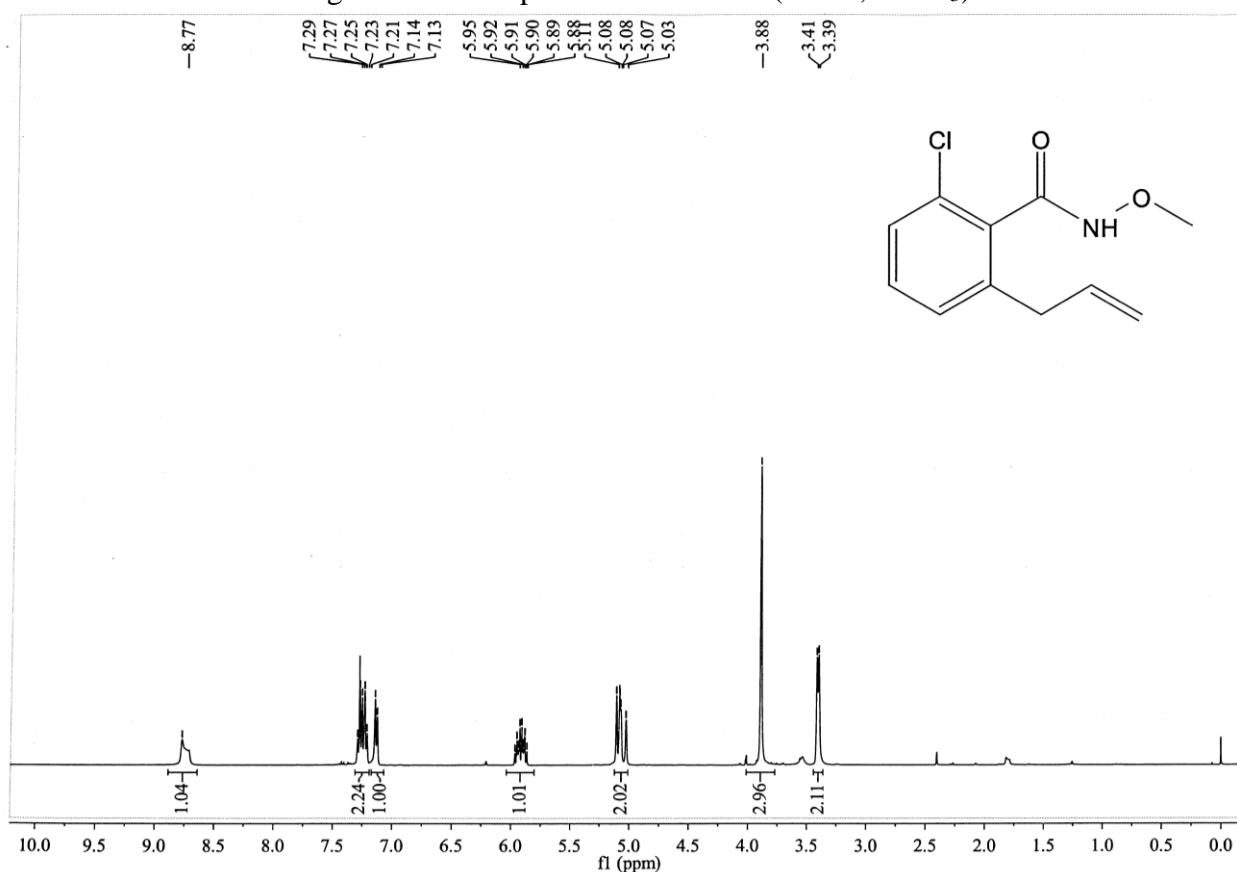


Figure S42. Compound 4c-¹³C NMR (100M, CDCl₃)

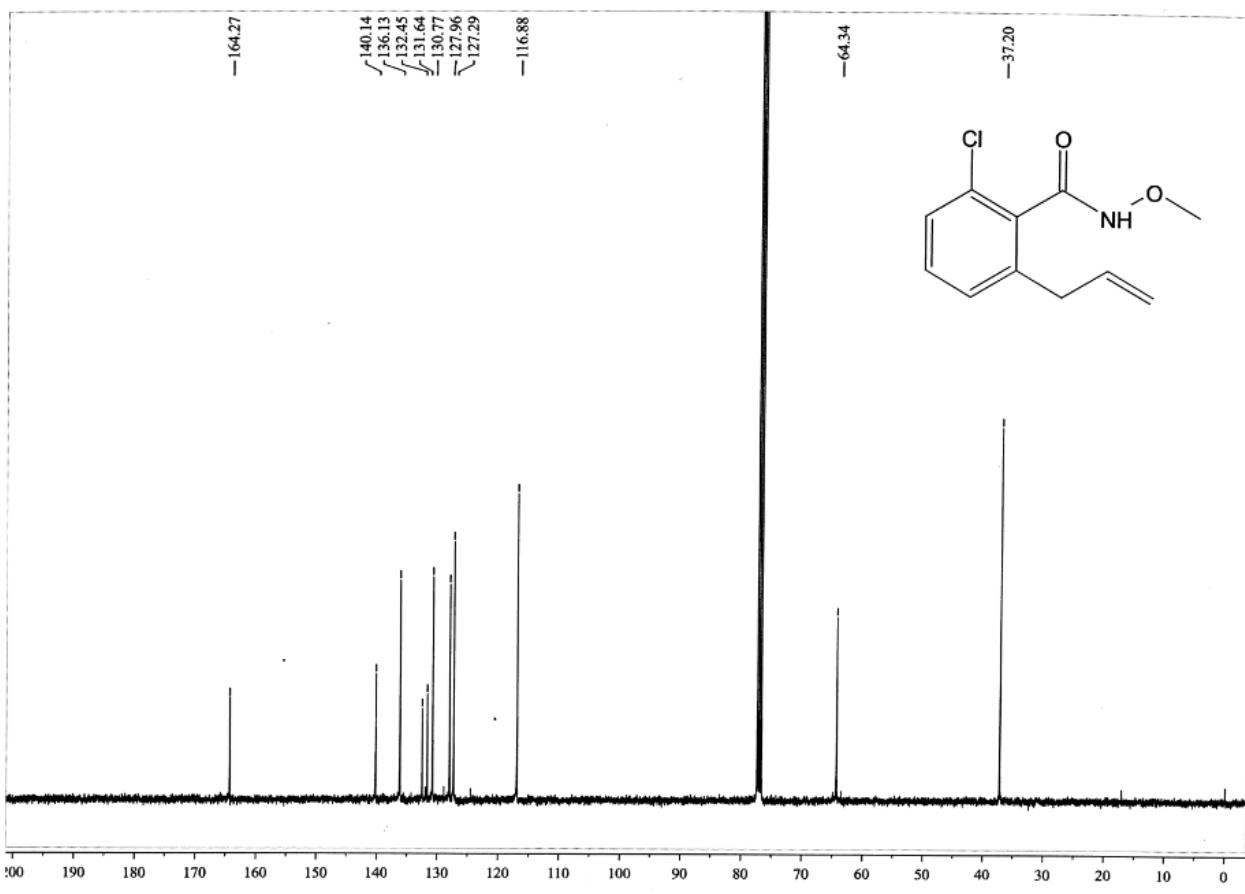


Figure S43. Compound **4d** ^1H NMR (400M, CDCl_3)

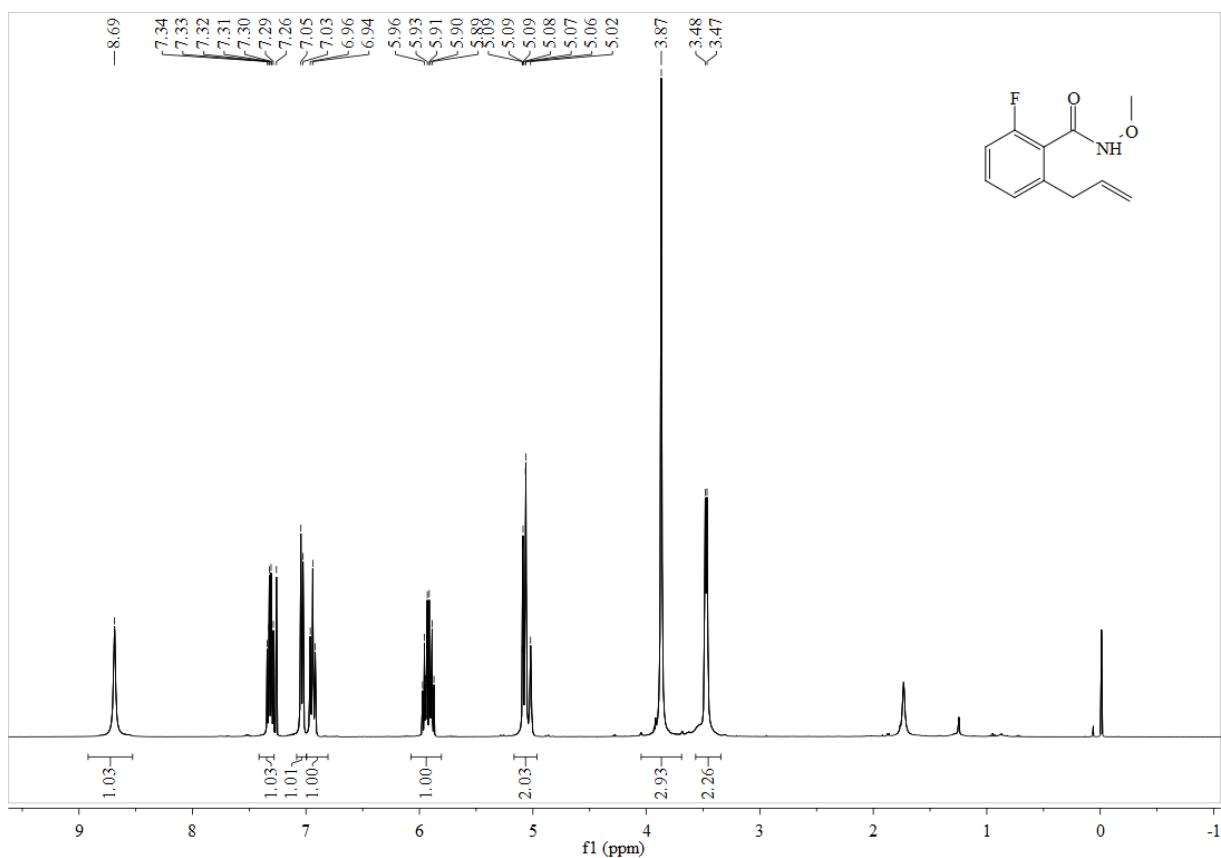


Figure S44. Compound **4d**- ^{13}C NMR (100M, CDCl_3)

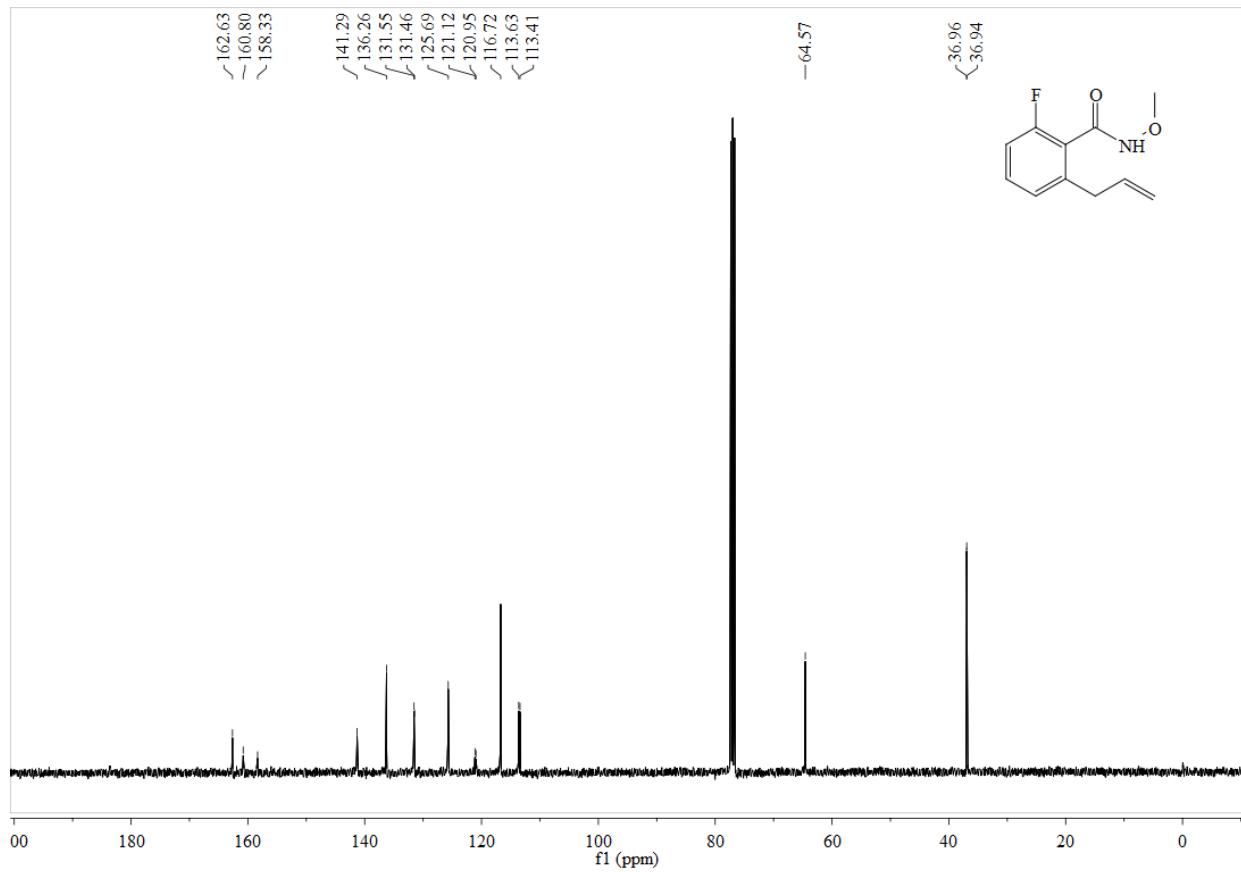


Figure S45. Compound 4e- ^1H NMR (400M, CDCl_3)

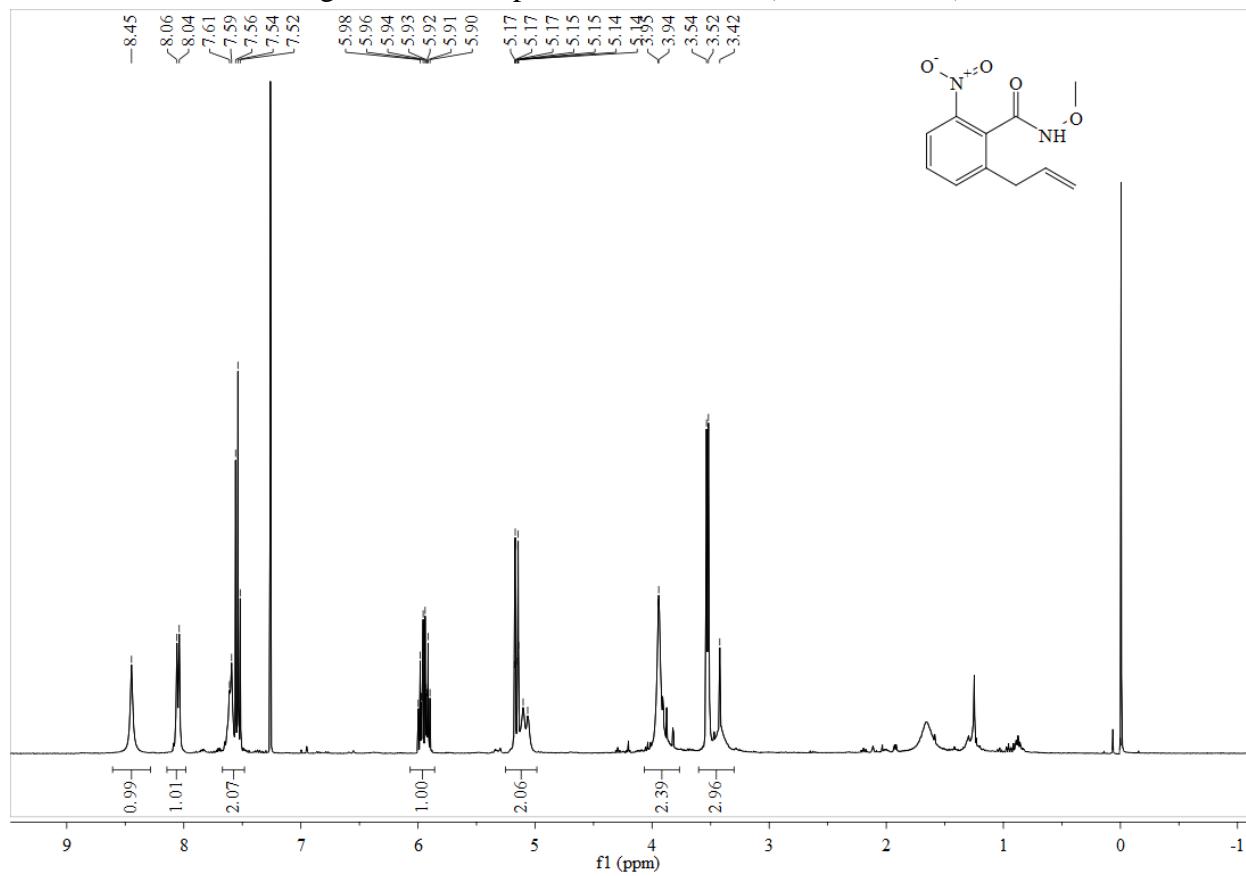


Figure S46. Compound 4e- ^{13}C NMR (100M, CDCl_3)

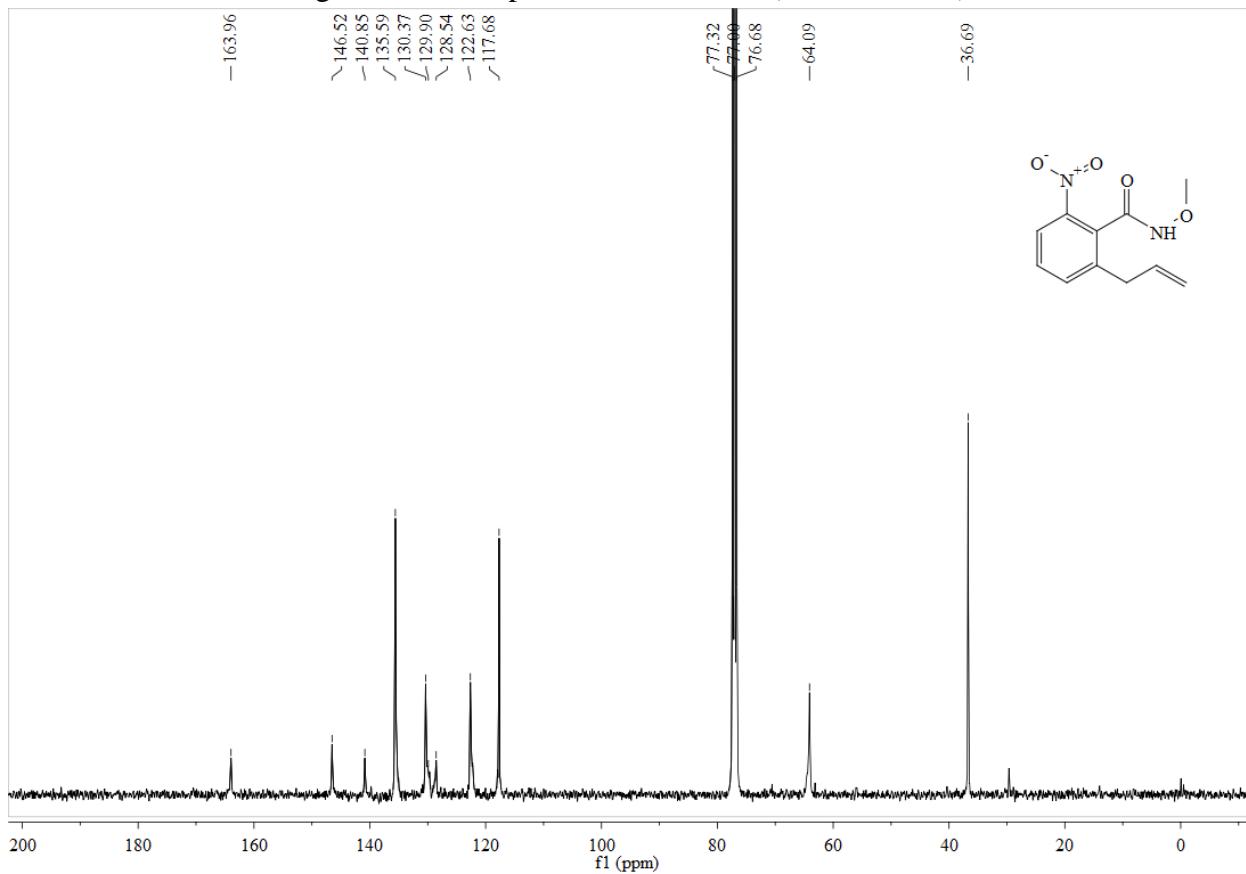


Figure S47. Compound 4f²-¹H NMR (400M, CDCl₃)

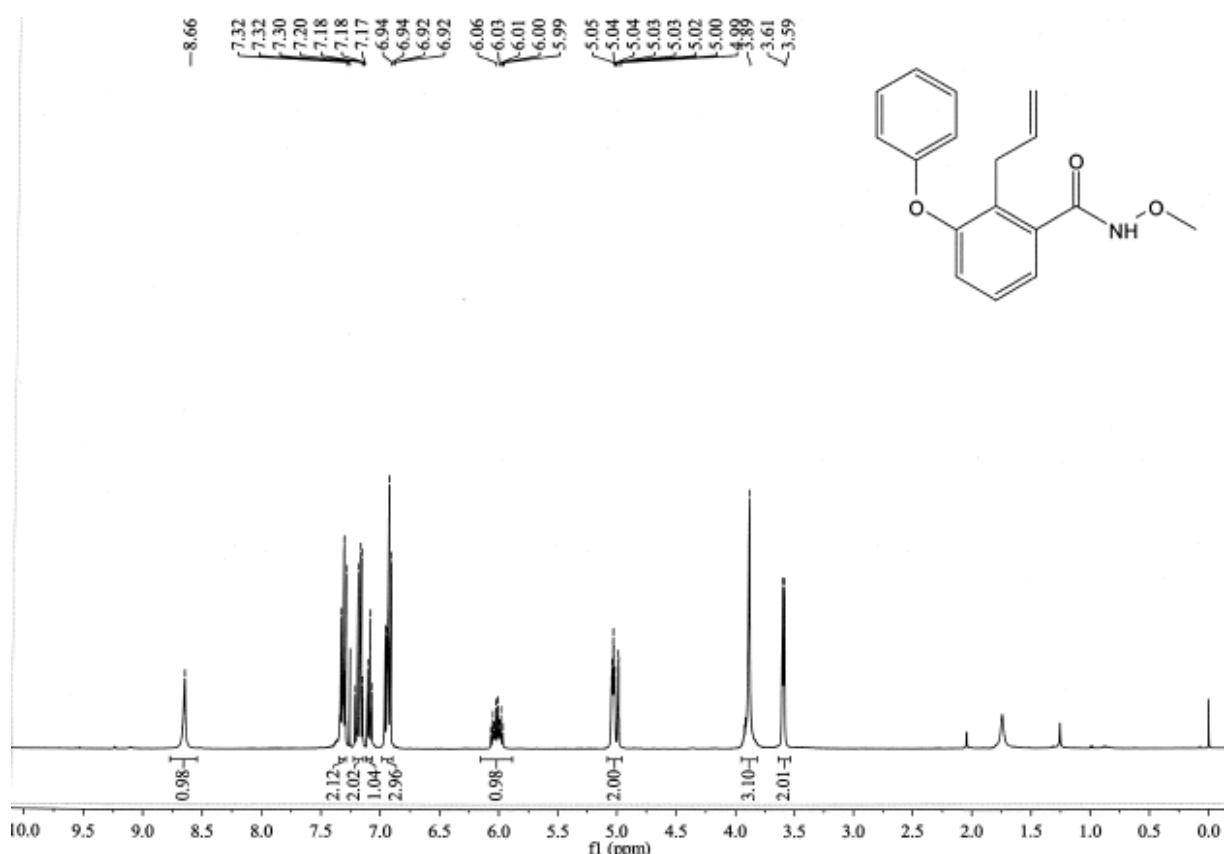


Figure S48. Compound 4f²-¹³C NMR (100M, CDCl₃)

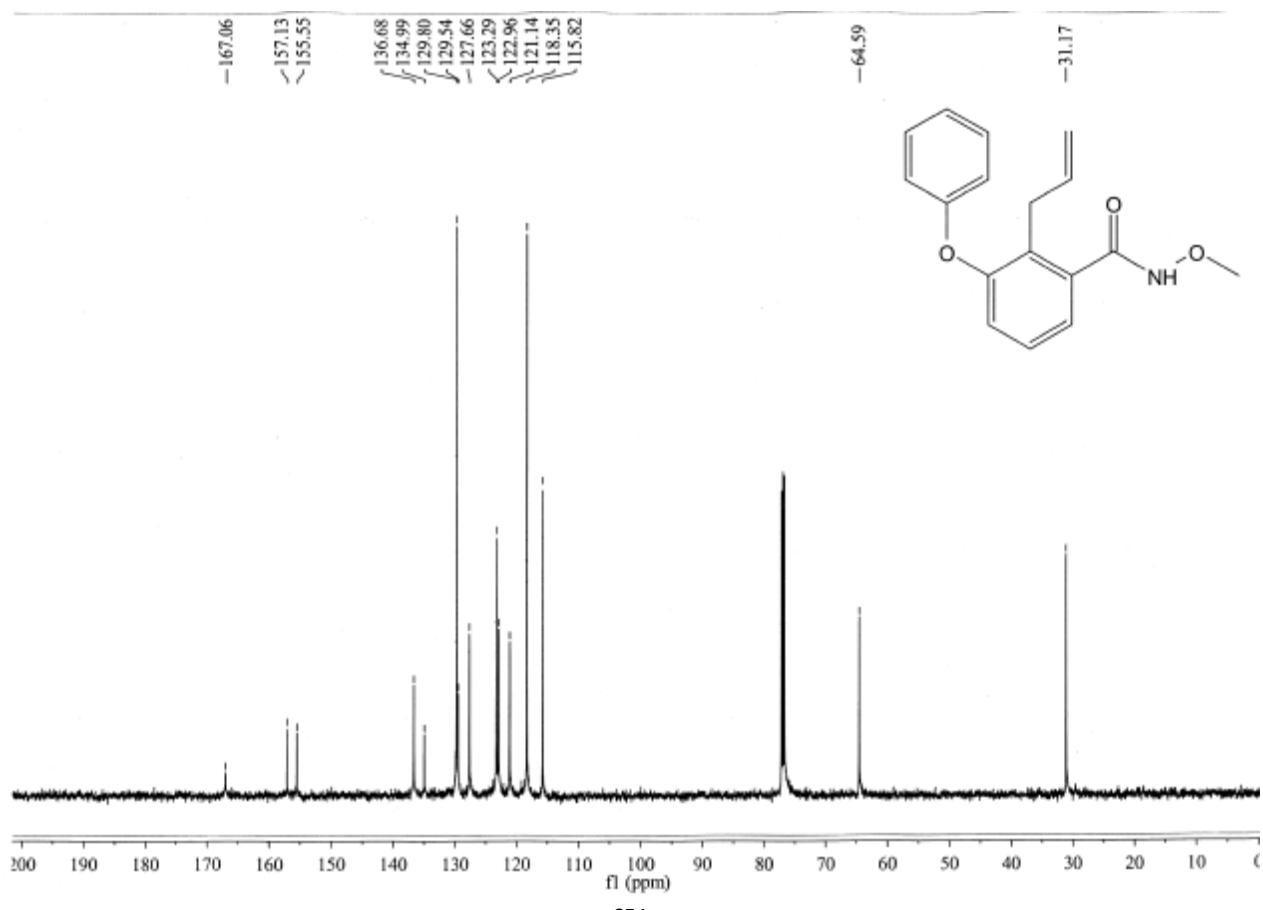


Figure S49. Compound 4f⁶-¹H NMR (400M, CDCl₃)

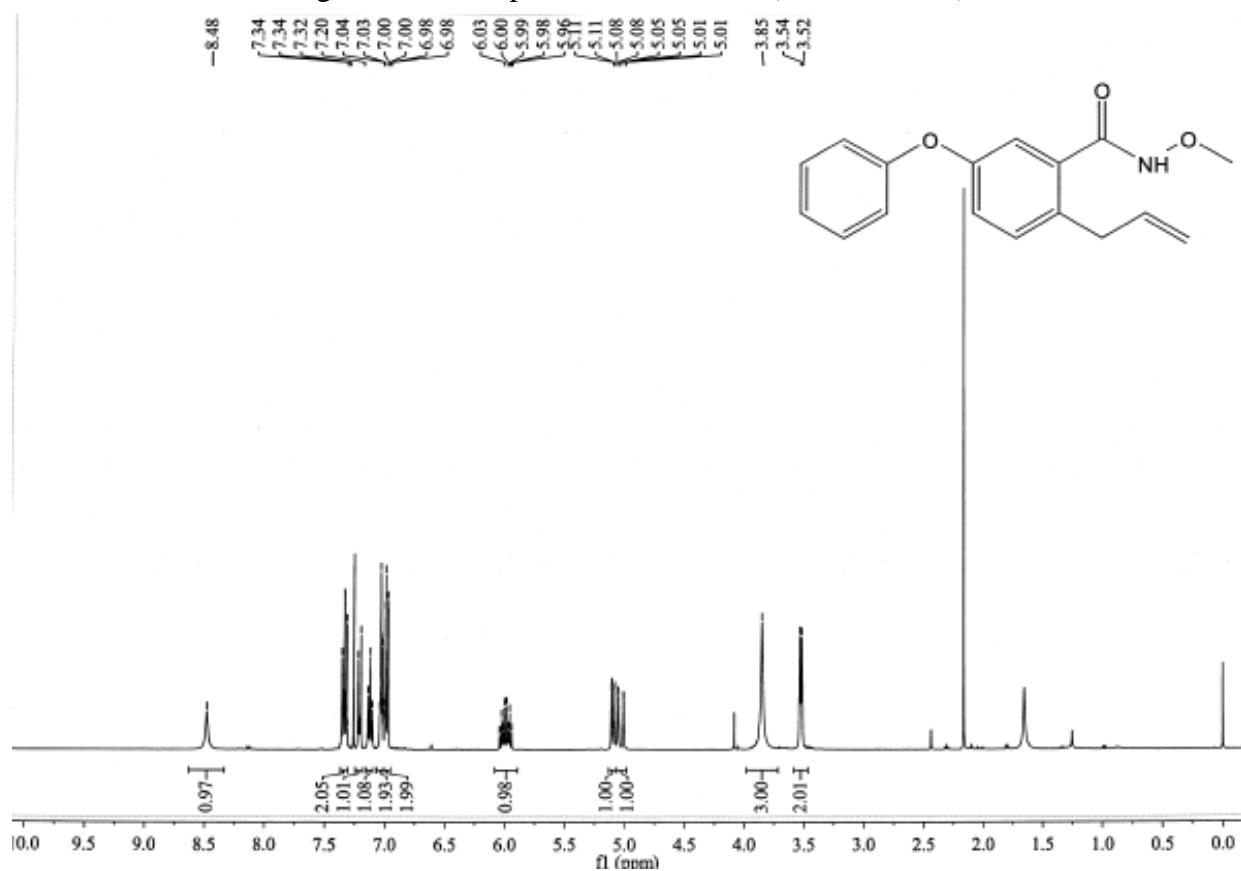


Figure S50. Compound 4f⁶-¹³C NMR (100M, CDCl₃)

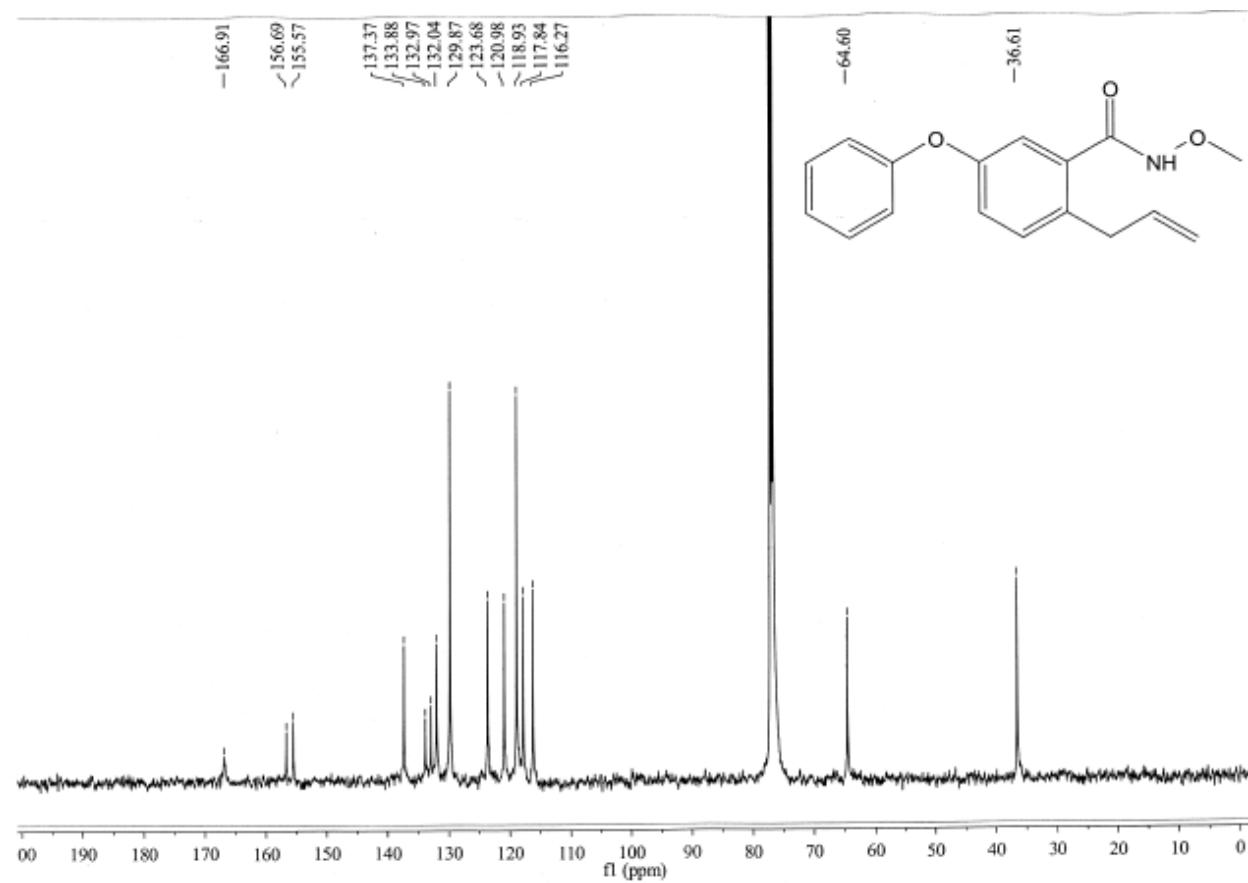


Figure S51. Compound **4g** ^1H NMR (400M, CDCl_3)



Figure S52. Compound **4g**- ^{13}C NMR (100M, CDCl_3)

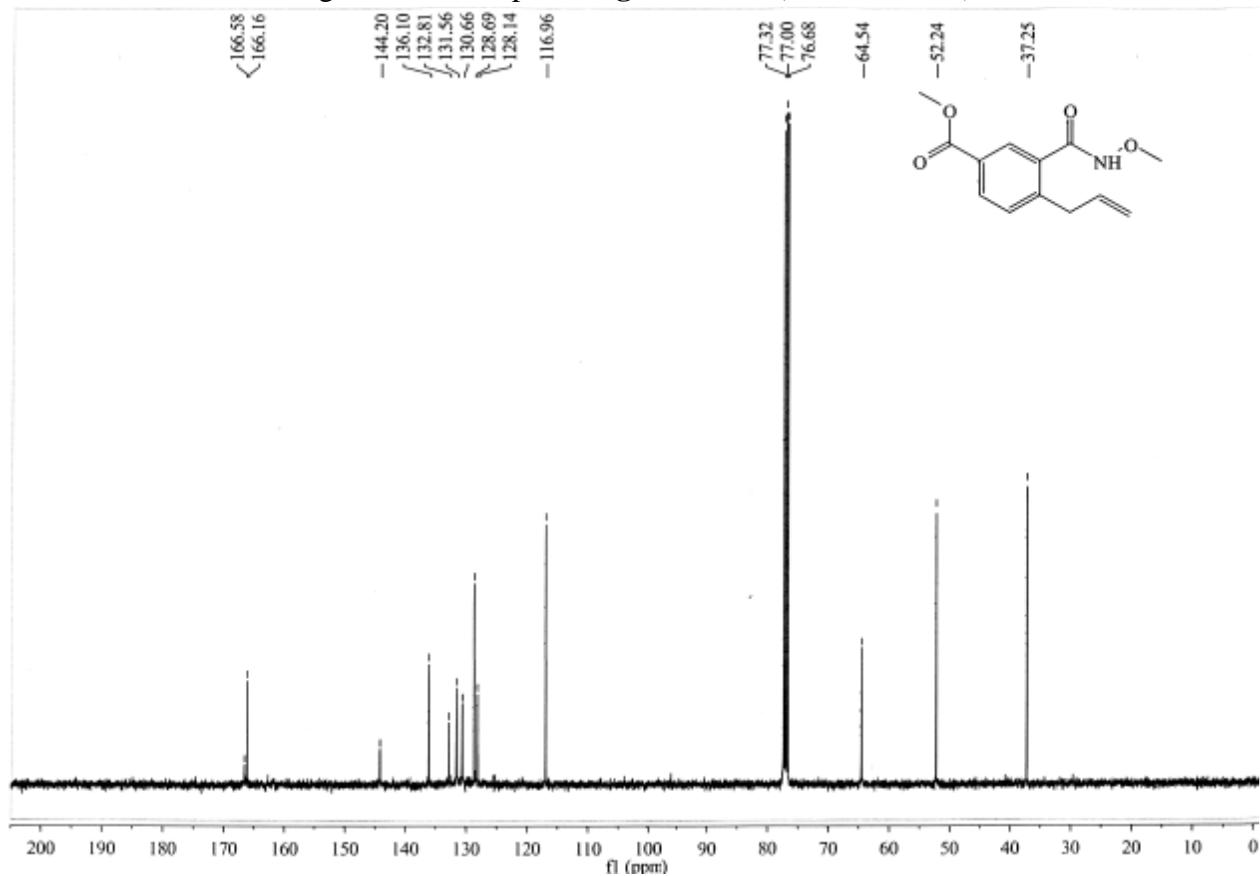


Figure S53. Compound **4h**- ^1H NMR (400M, CDCl_3)

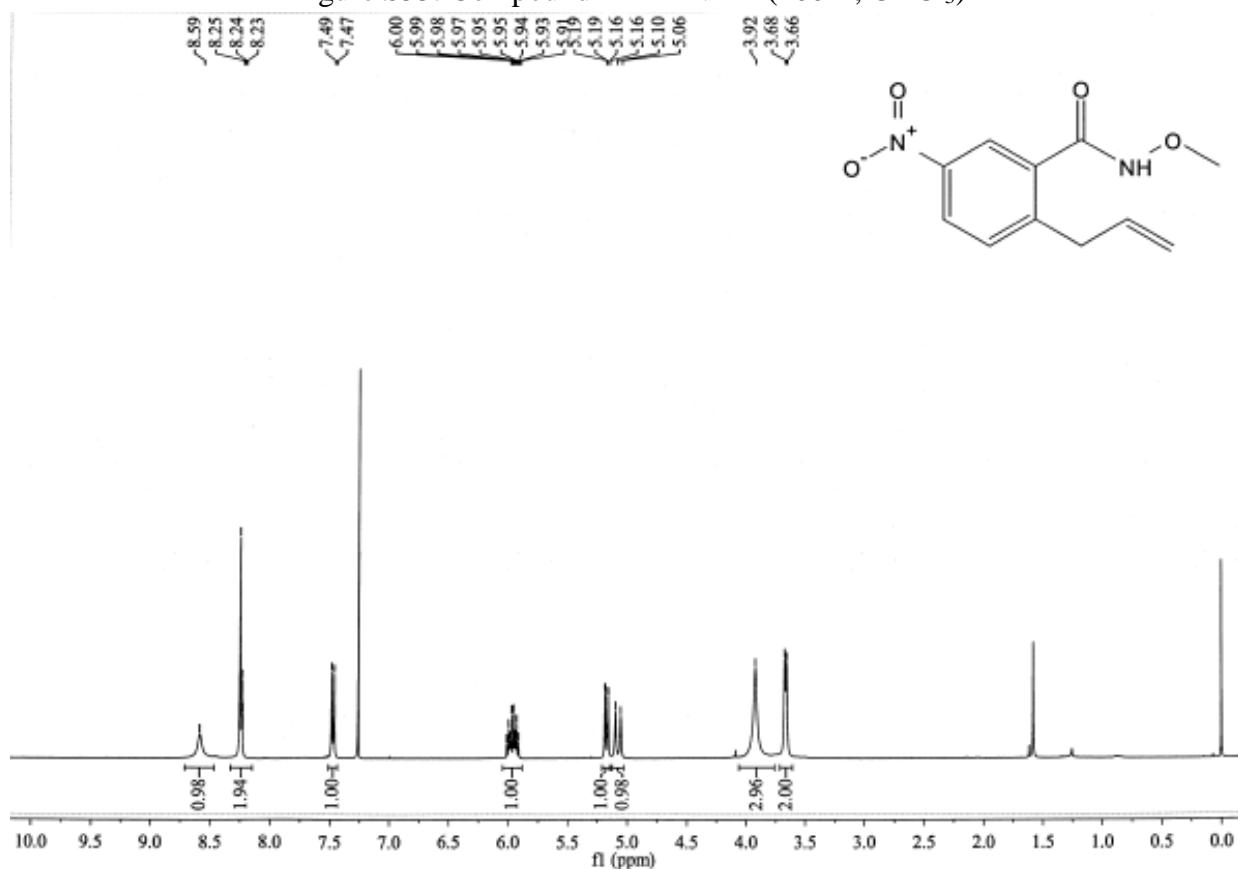


Figure S54. Compound **4h**- ^{13}C NMR (100M, CDCl_3)

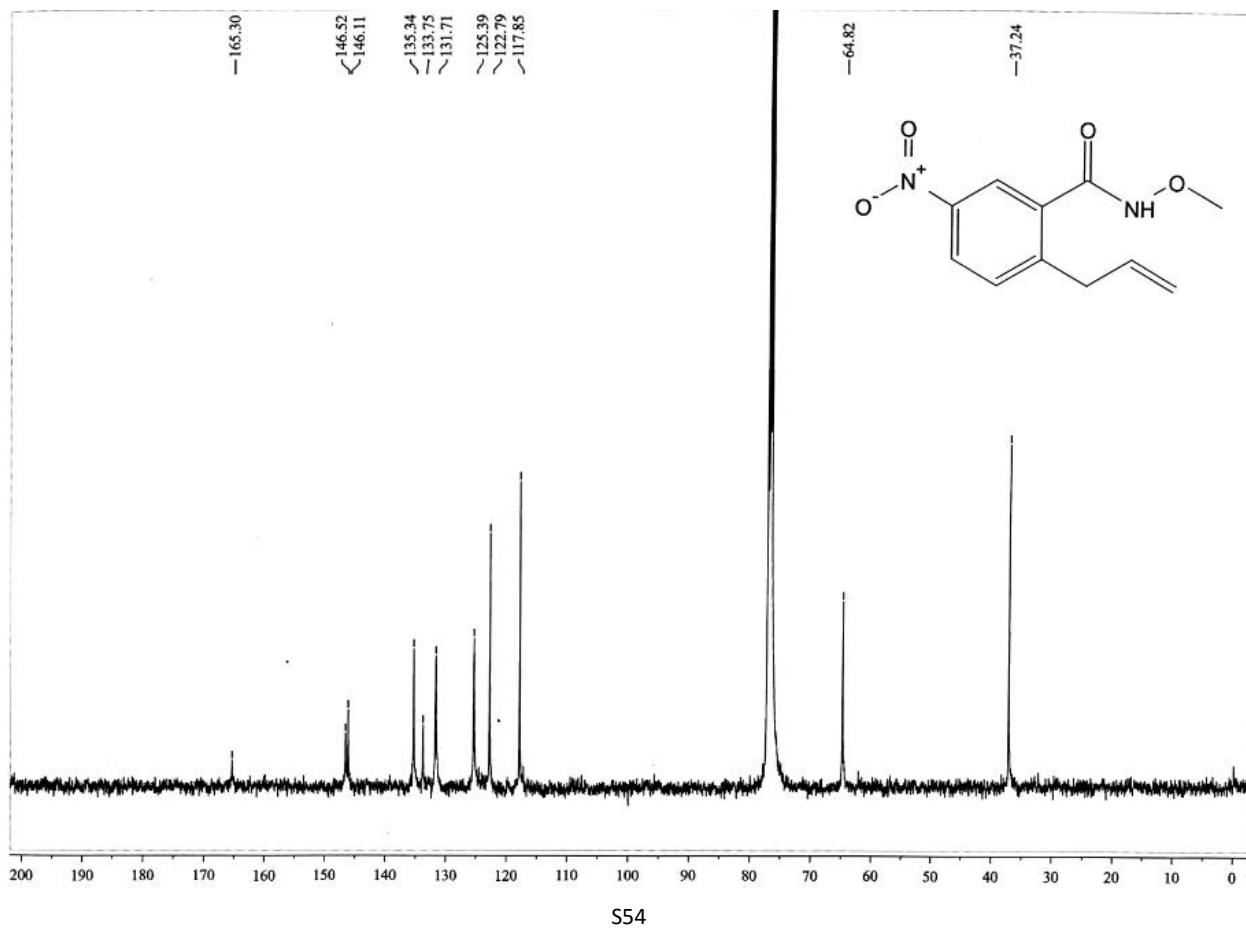


Figure S55. Compound **4i**-¹H NMR (400M, CDCl₃)

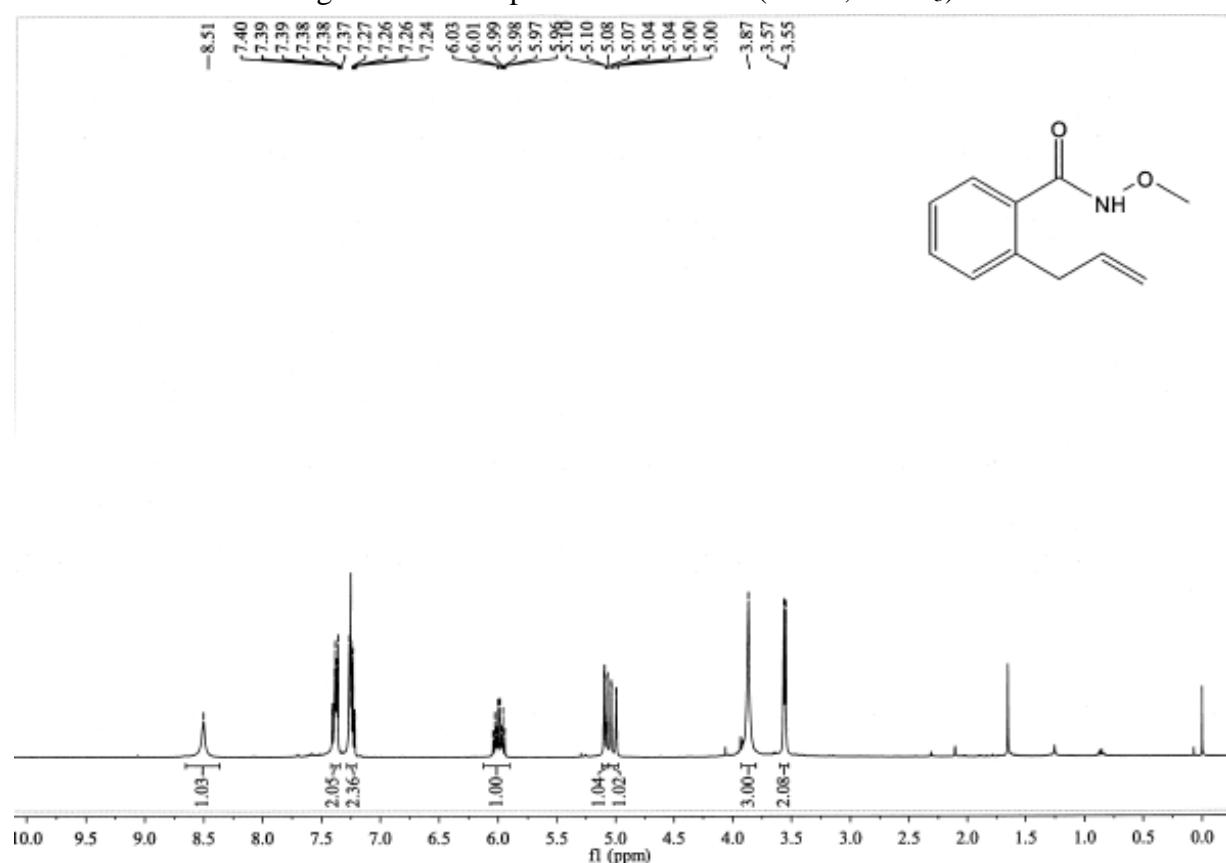


Figure S56. Compound **4i**-¹³C NMR (100M, CDCl₃)

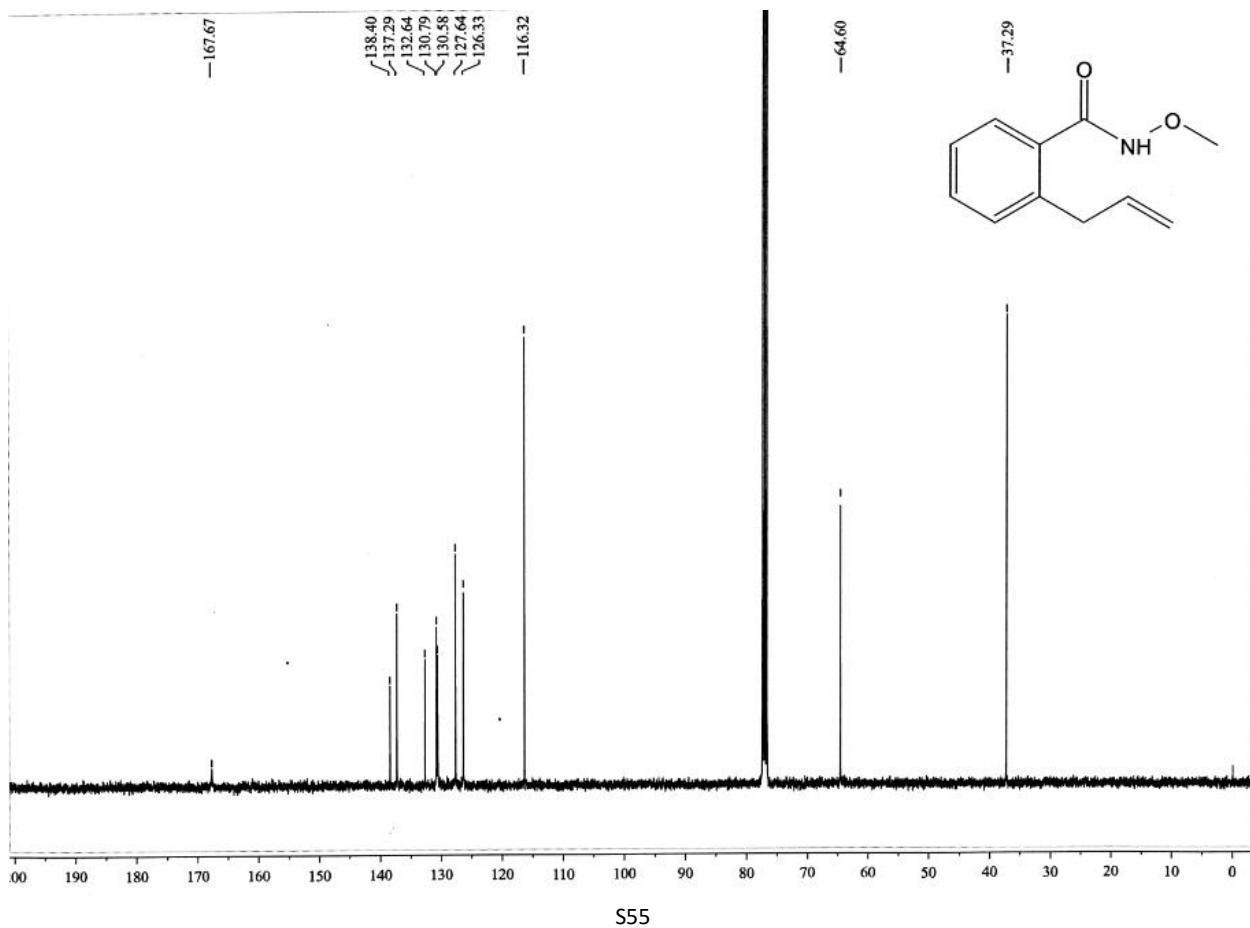


Figure S57. Compound **4j**-¹H NMR (400M, CDCl₃)

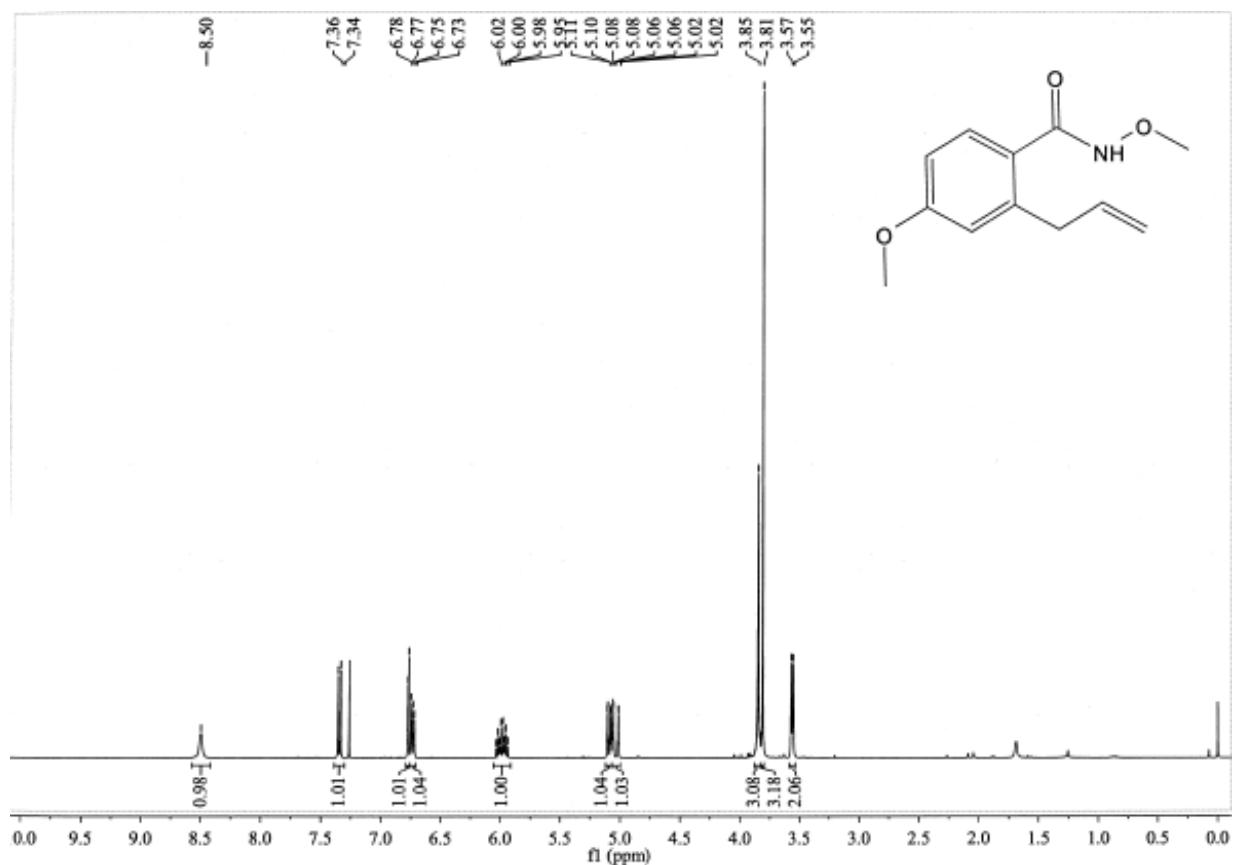


Figure S58. Compound **4j**-¹³C NMR (100M, CDCl₃)

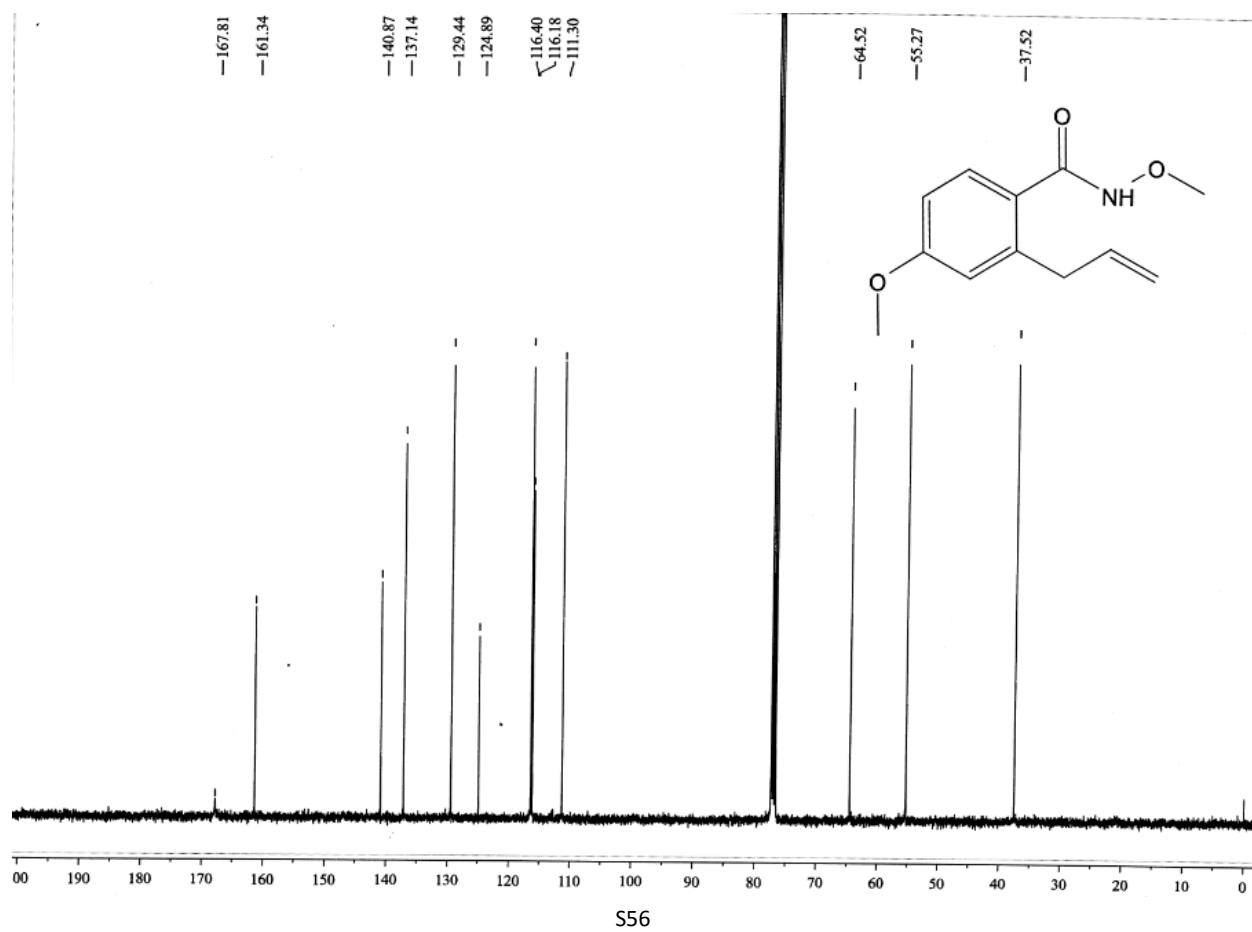


Figure S59. Compound **4k**-¹H NMR (400M, CDCl₃)

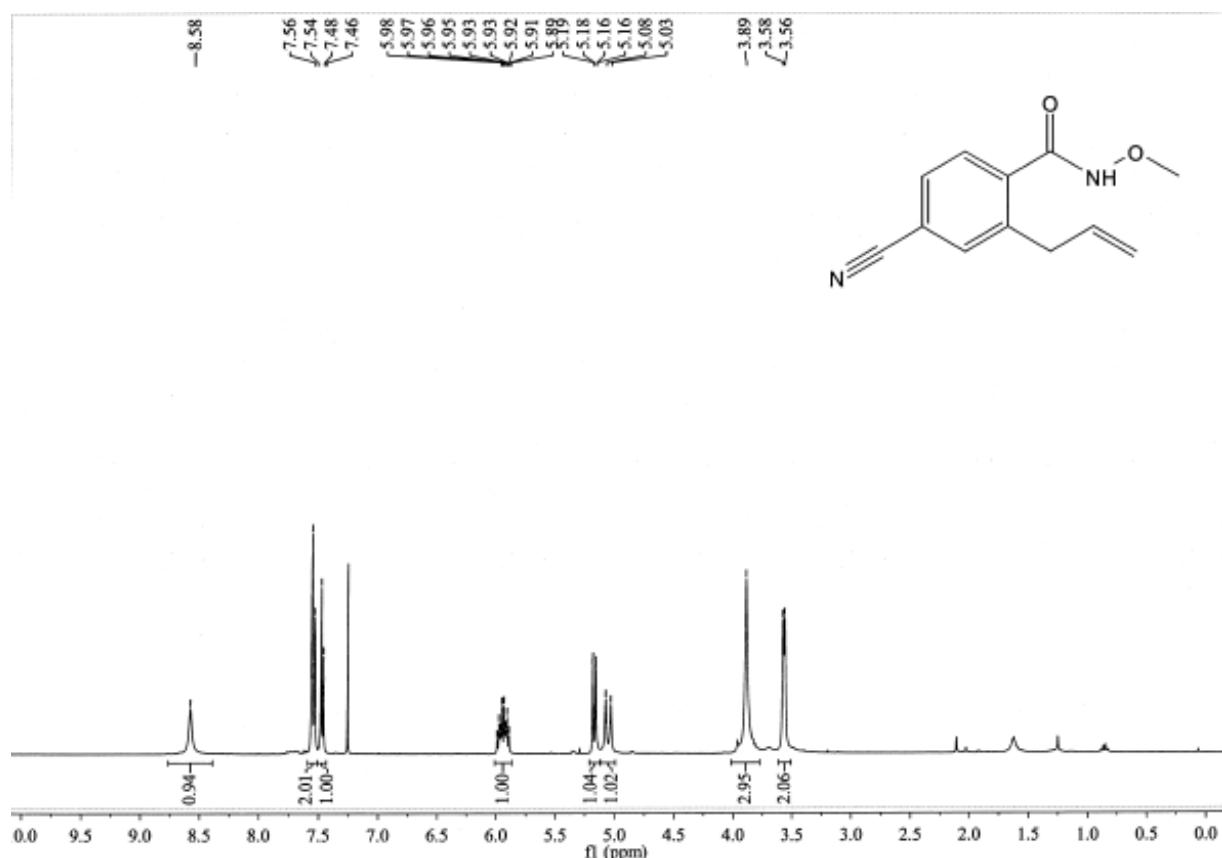


Figure S60. Compound **4k**-¹³C NMR (100M, CDCl₃)

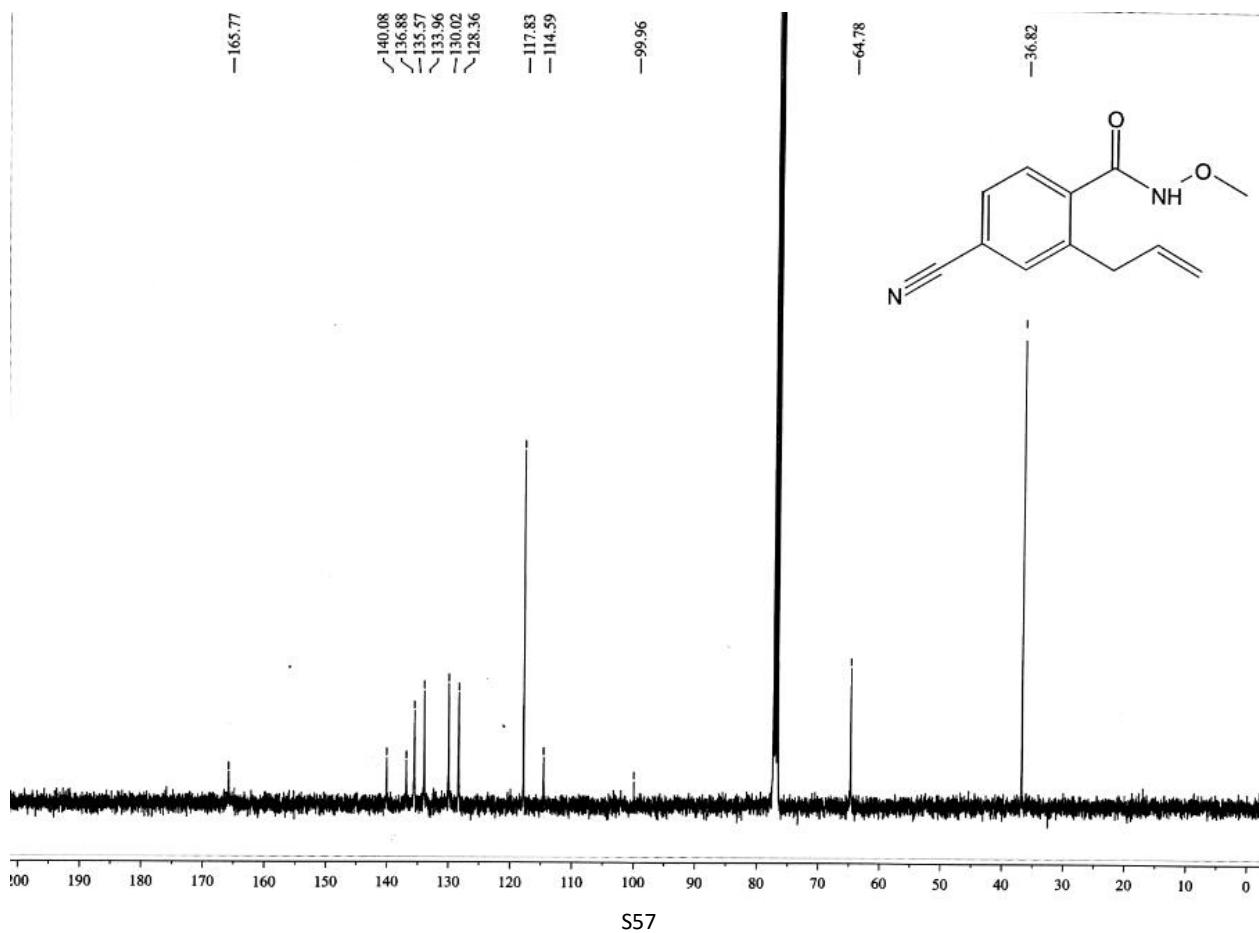


Figure S61. Compound 4l-¹H NMR (400M, CDCl₃)

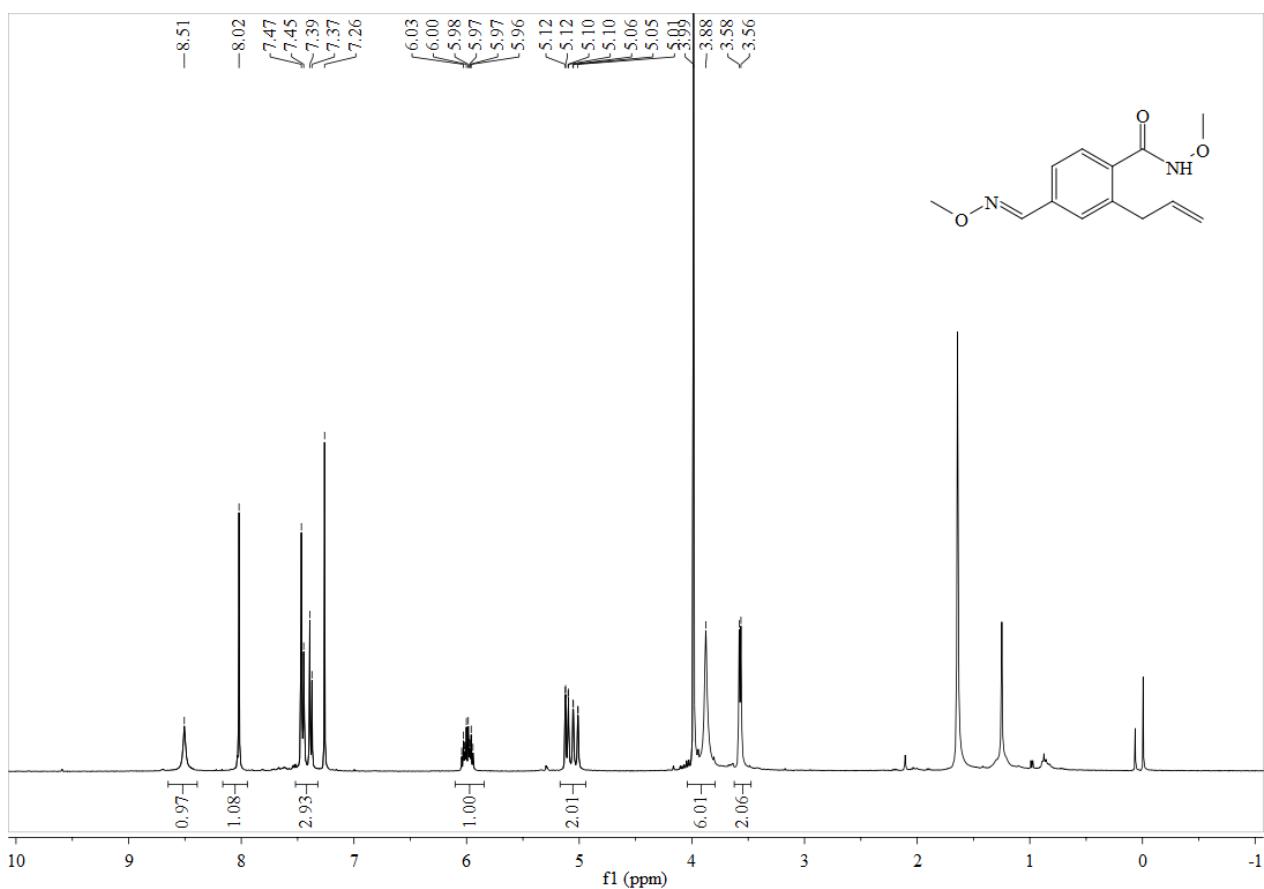


Figure S62. Compound 4l-¹³C NMR (125M, CDCl₃)

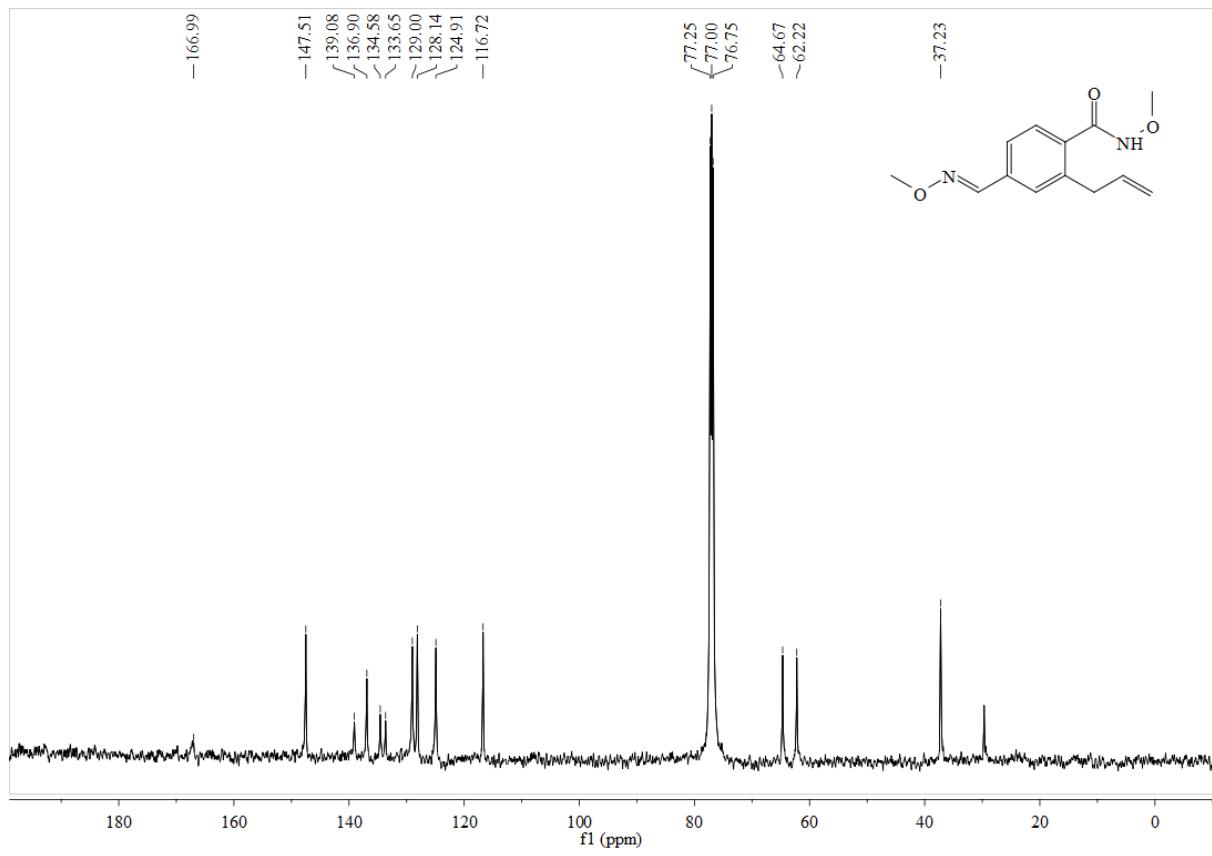


Figure S63. Compound **4m**- ^1H NMR (400M, CDCl_3)

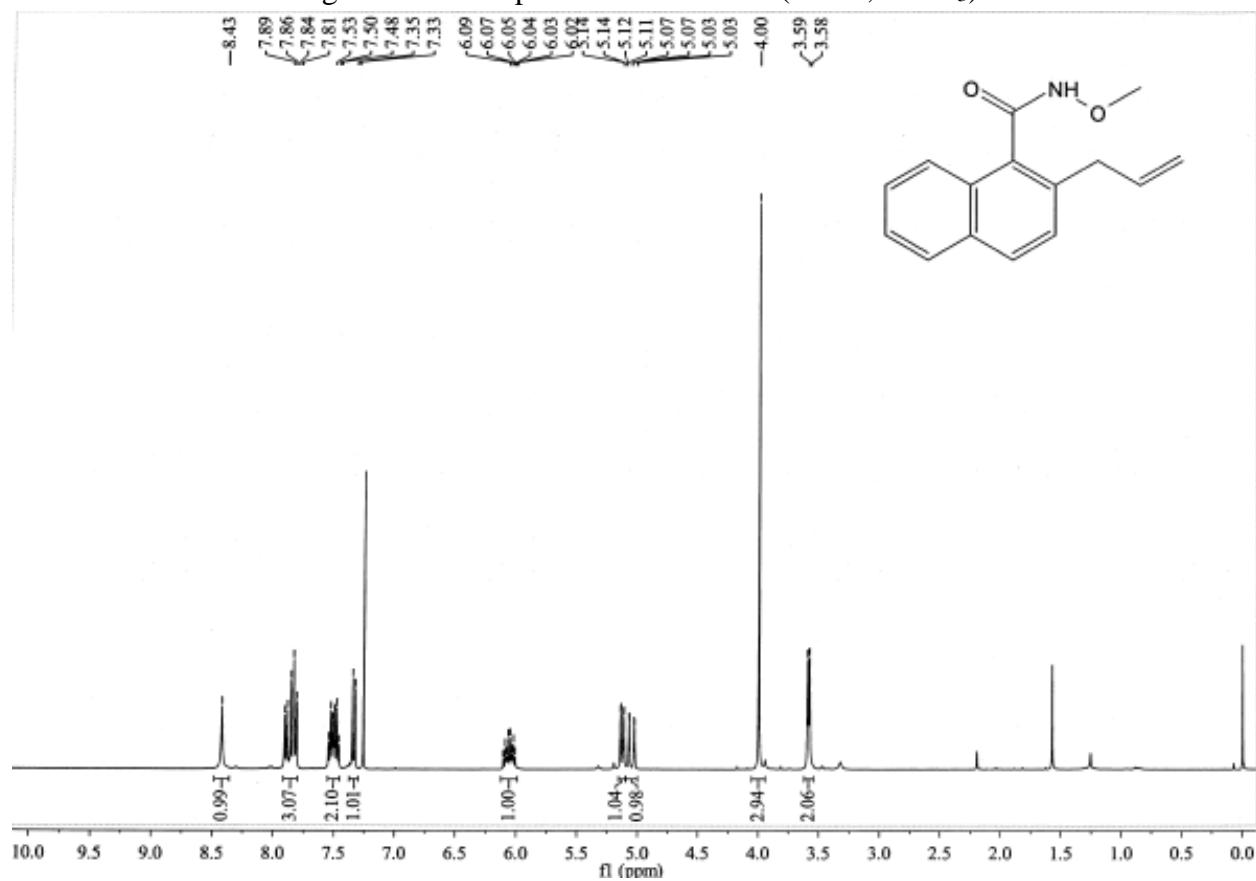


Figure S64. Compound **4m**- ^{13}C NMR (100M, CDCl_3)

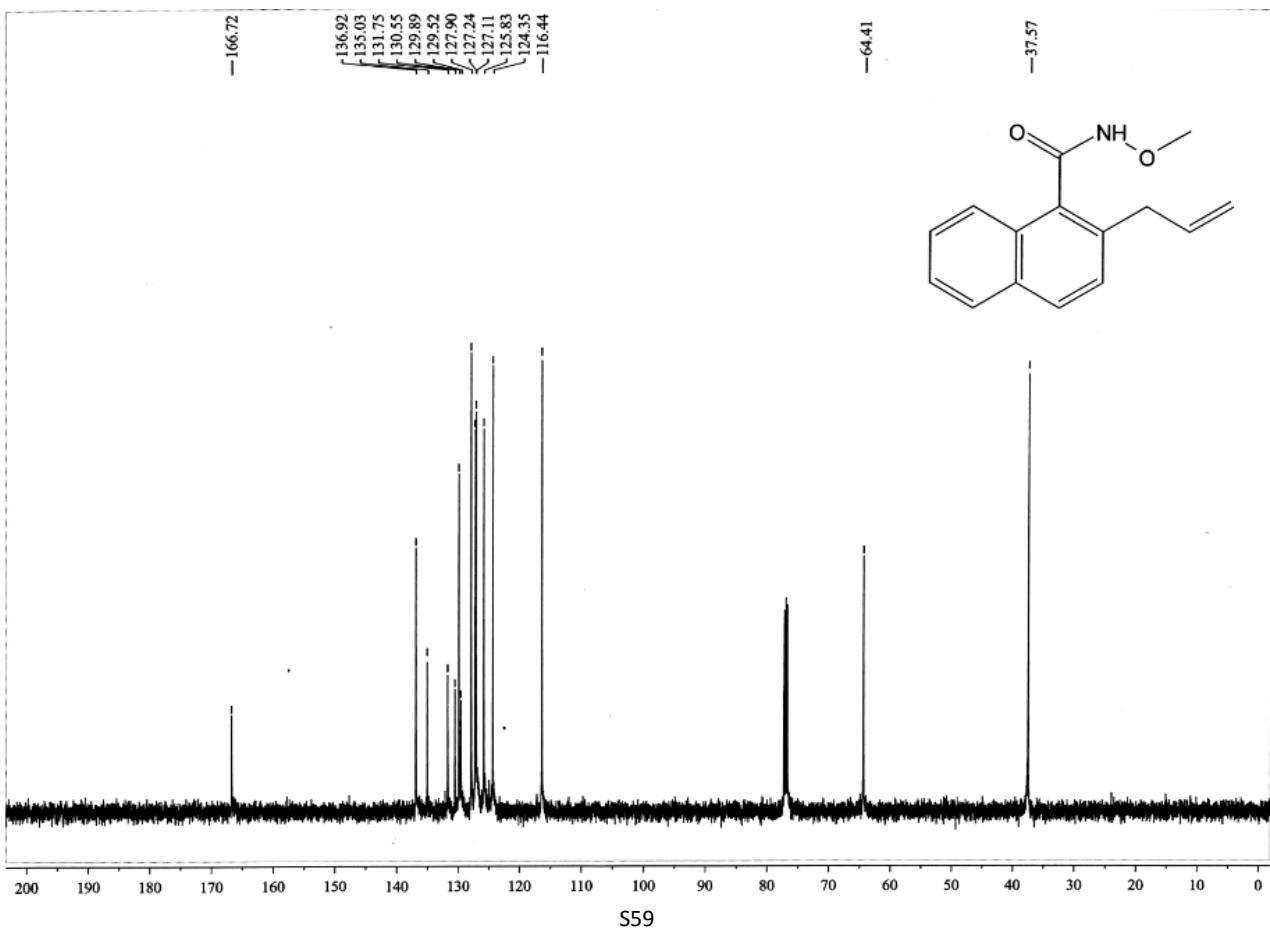


Figure S65. Compound **4n**-¹H NMR (400M, CDCl₃)

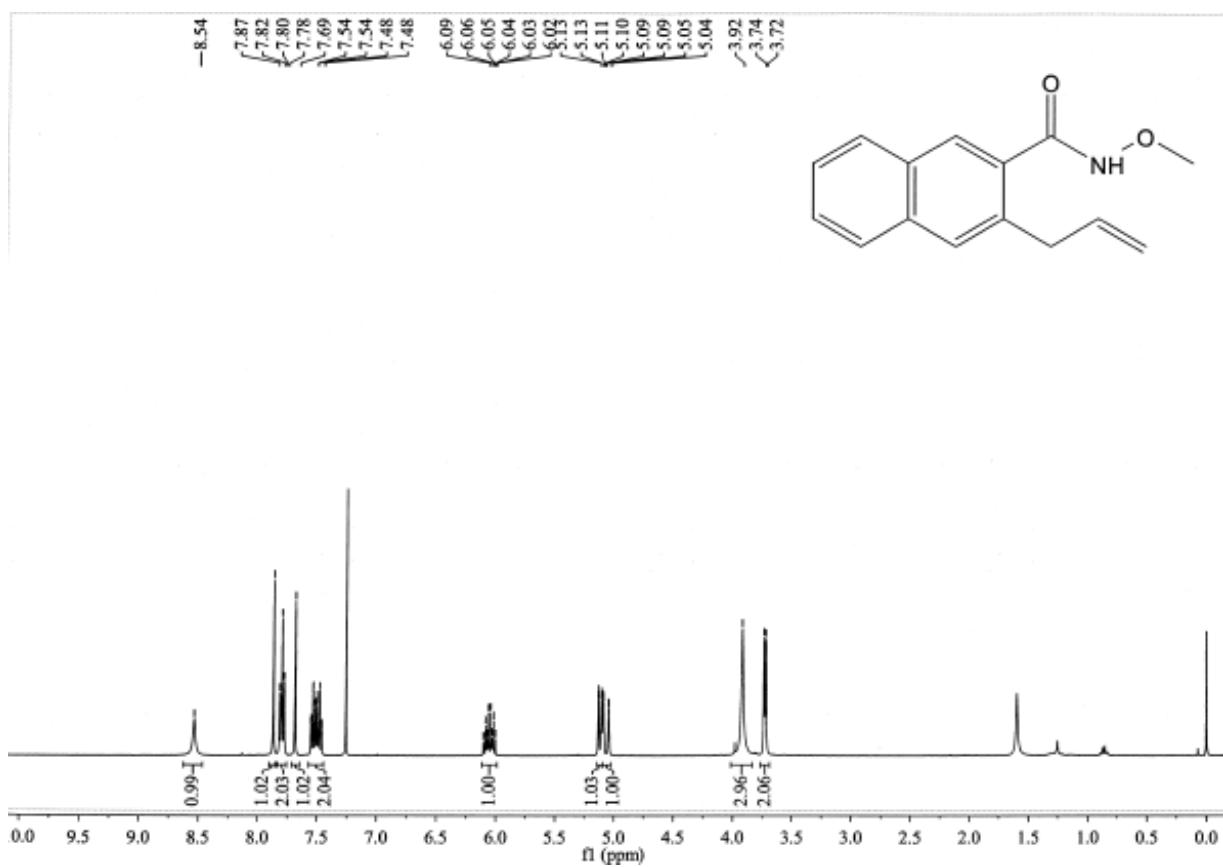


Figure S66. Compound **4n**-¹³C NMR (100M, CDCl₃)

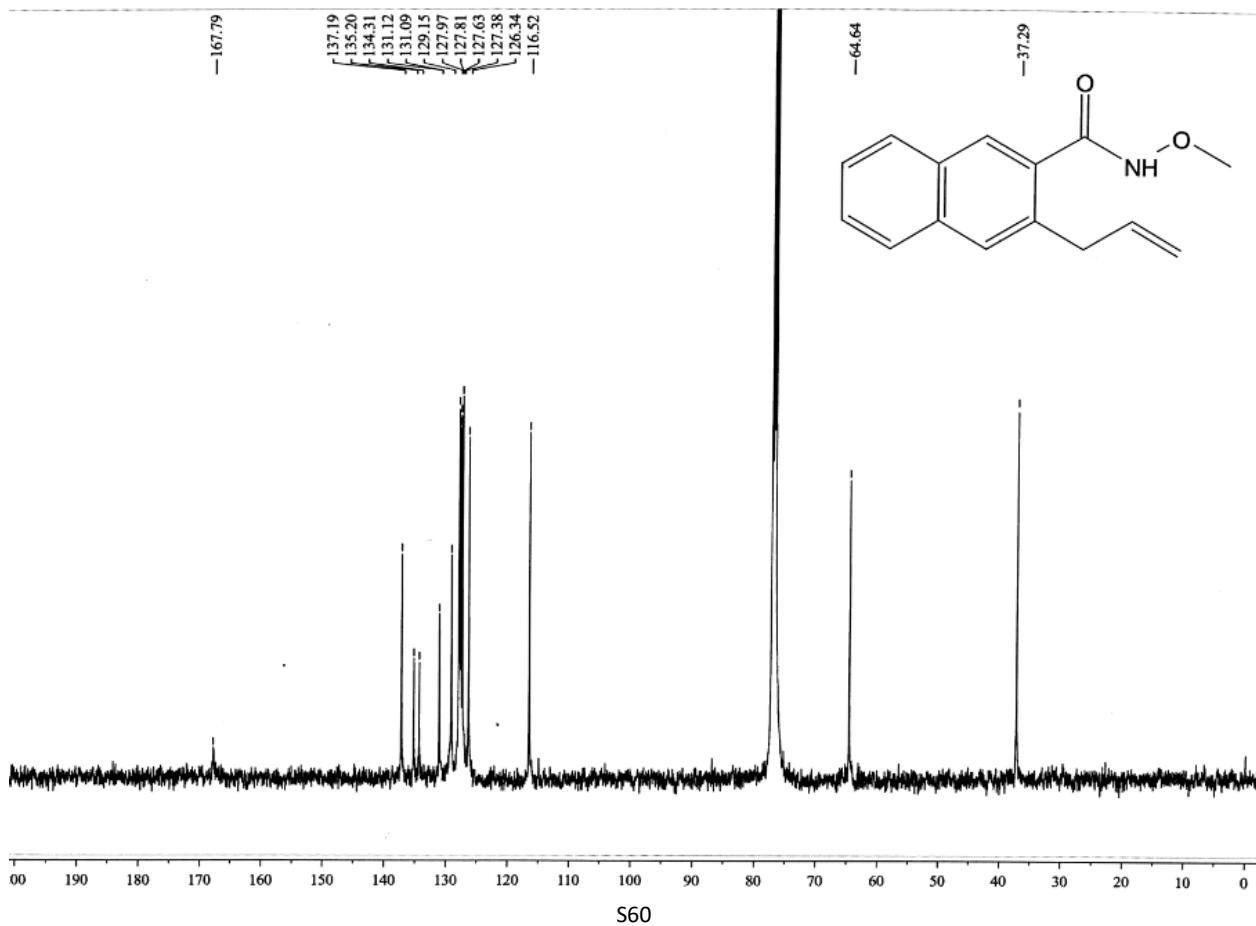


Figure S67. Compound **4o**- ^1H NMR (400M, CDCl_3)

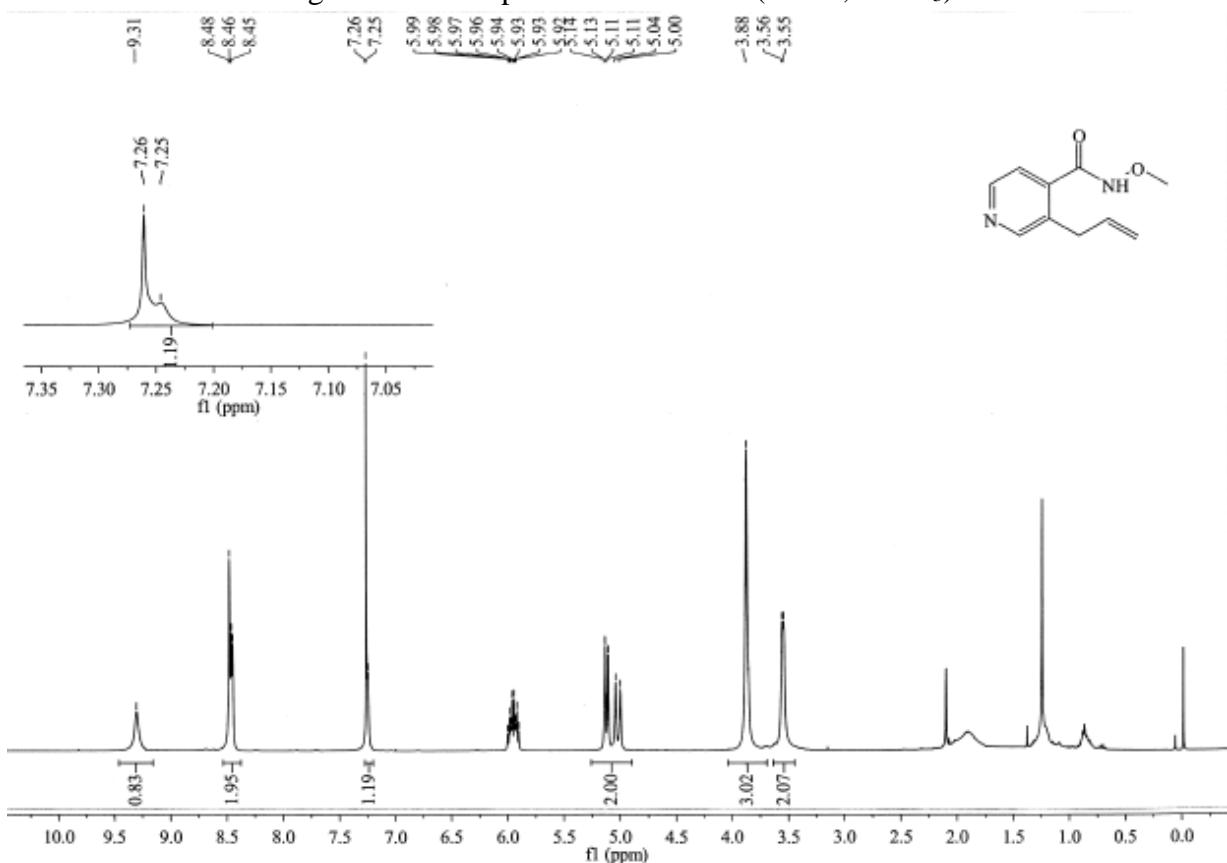


Figure S68. Compound **4o**- ^{13}C NMR (100M, CDCl_3)

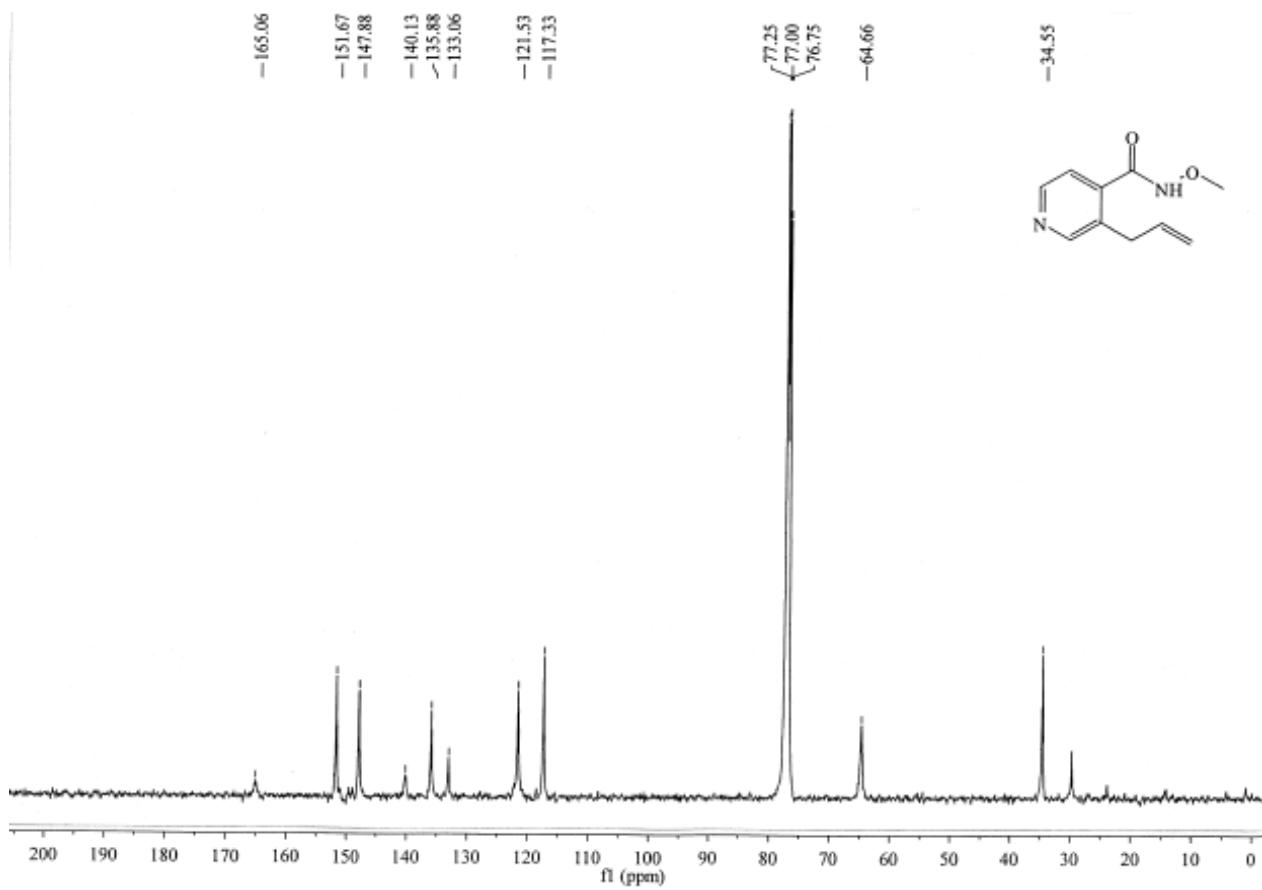


Figure S69. Compound 4p- ^1H NMR (400M, CDCl_3)

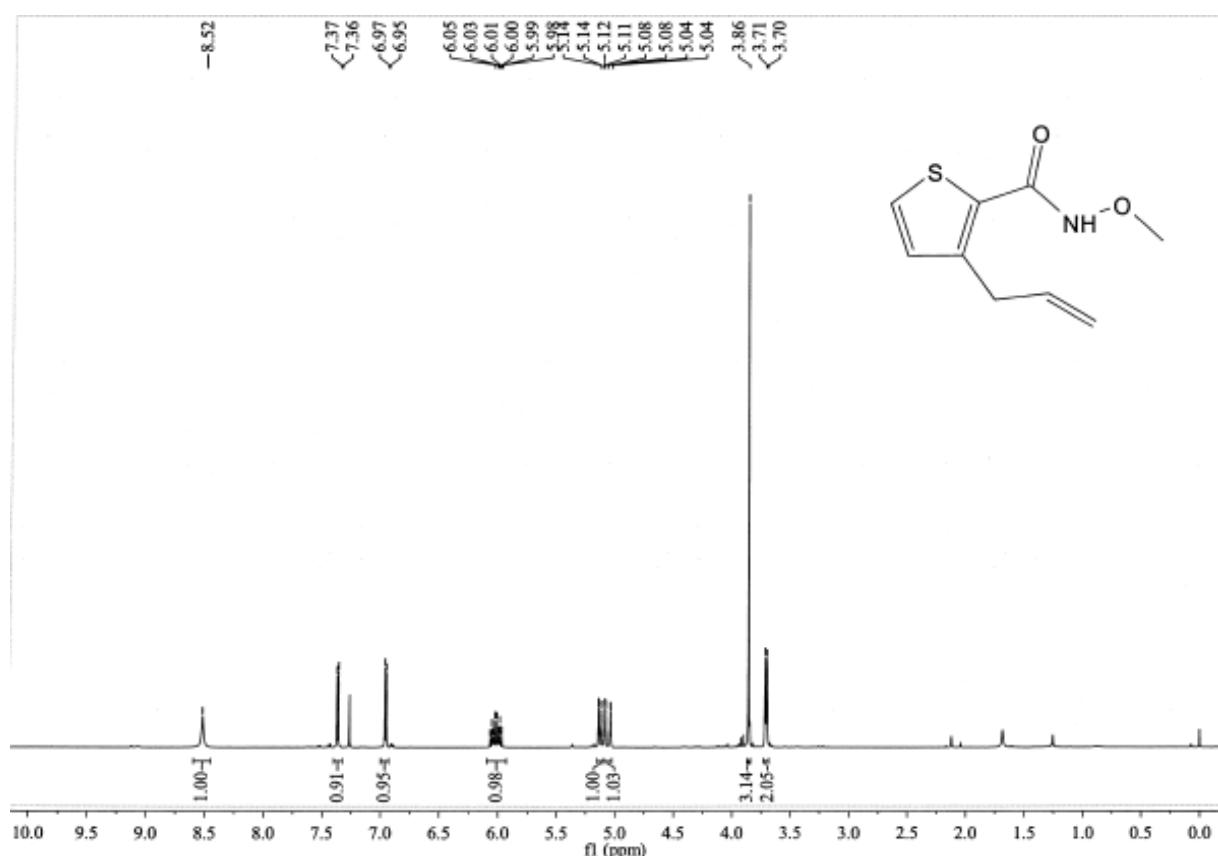


Figure S70. Compound 4p- ^{13}C NMR (100M, CDCl_3)

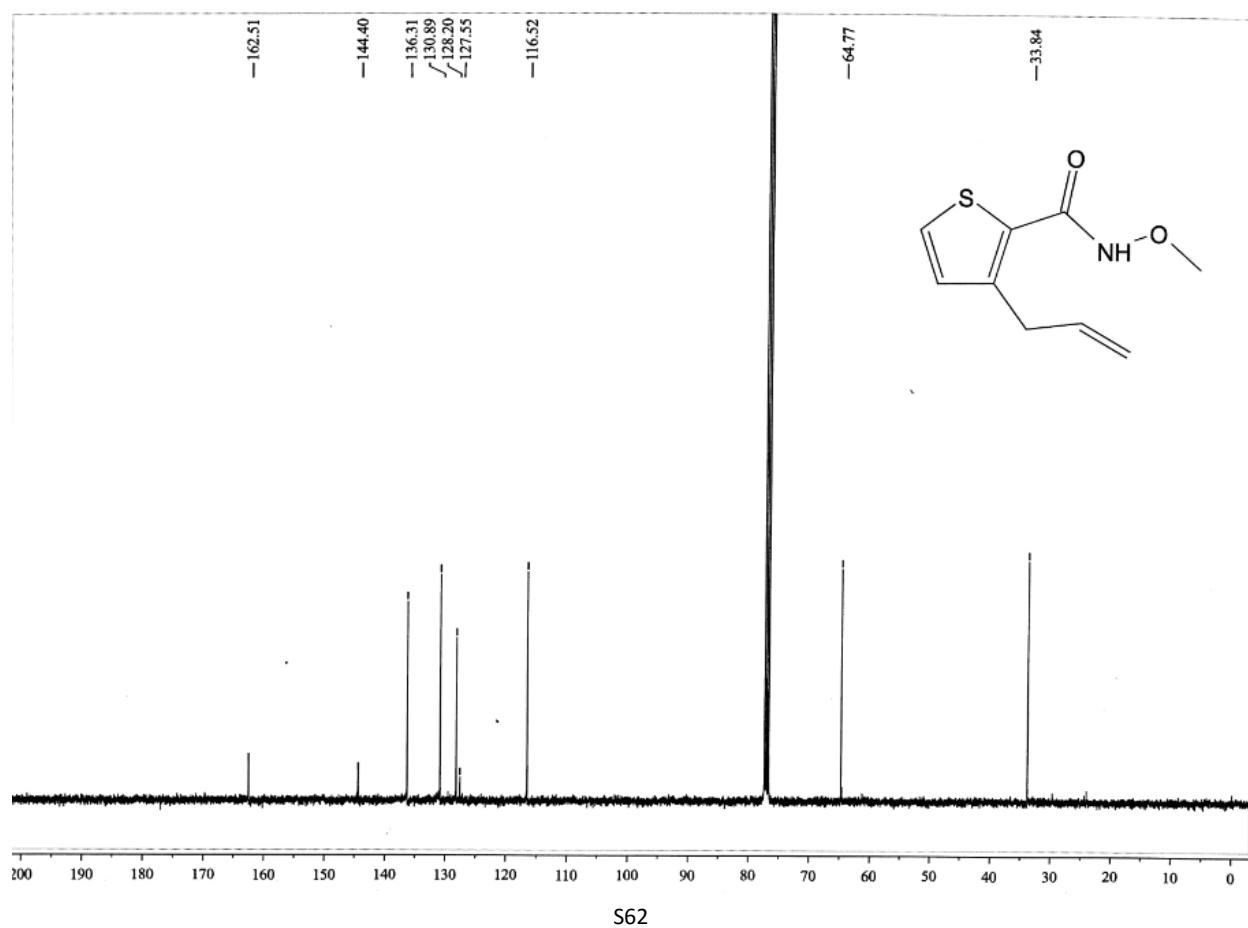


Figure S71. Compound 4q-¹H NMR (400M, CDCl₃)

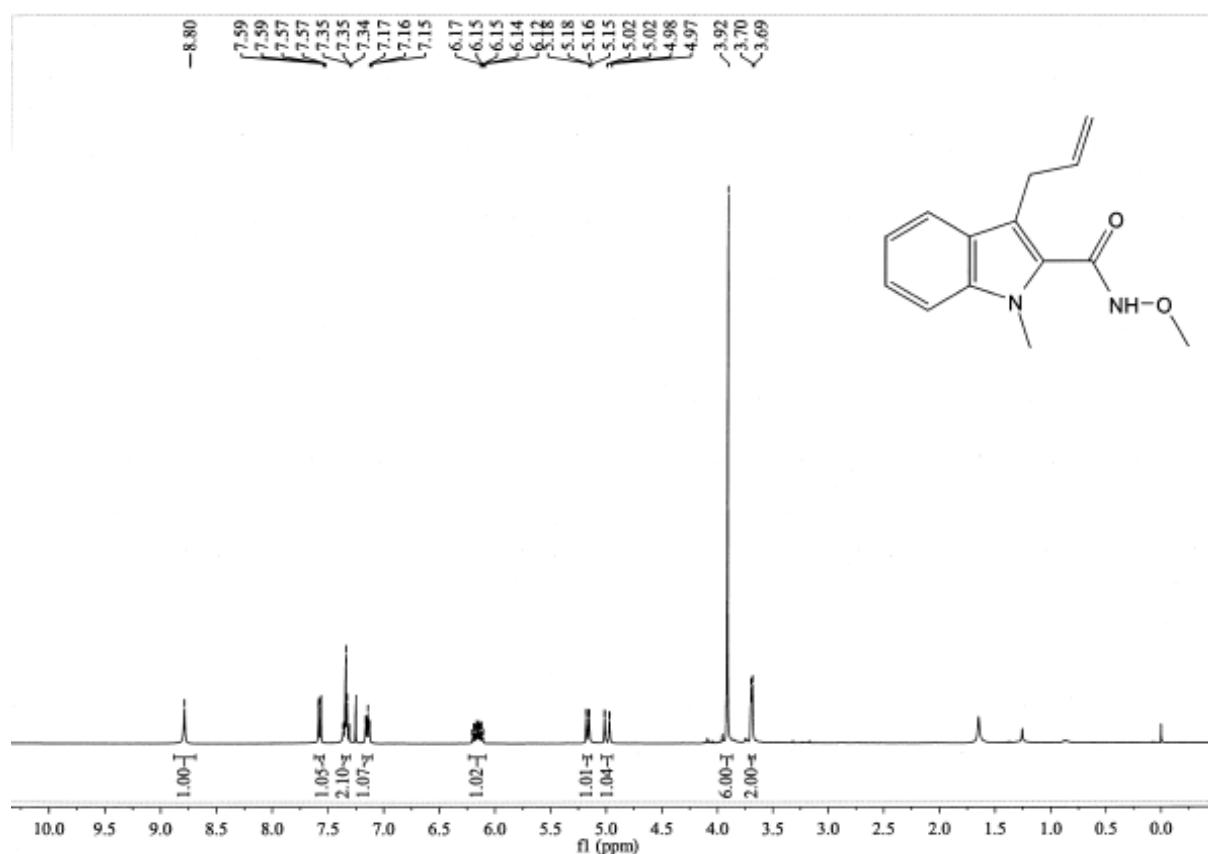


Figure S72. Compound 4q-¹³C NMR (100M, CDCl₃)

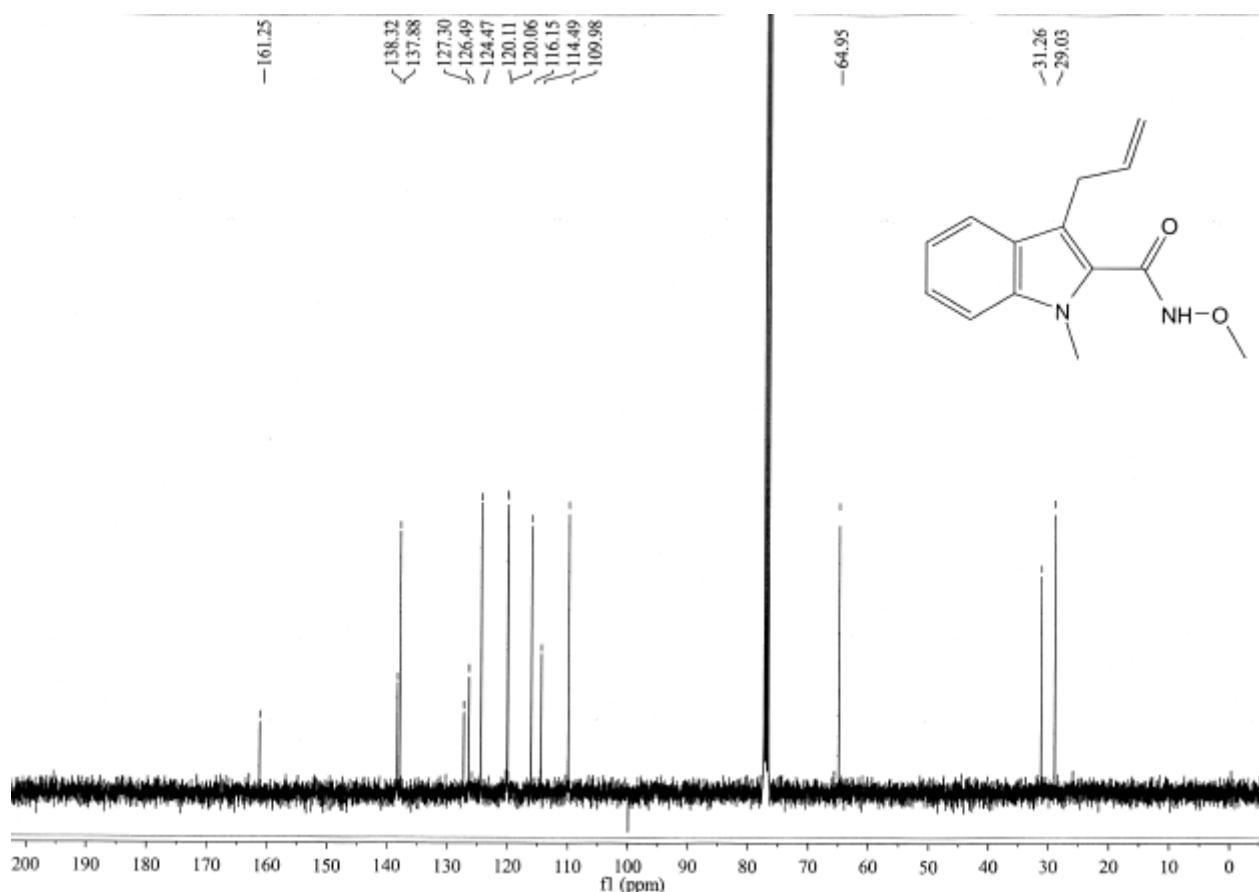


Figure S73. Compound 5a-¹H NMR (400M, DCCl_3)

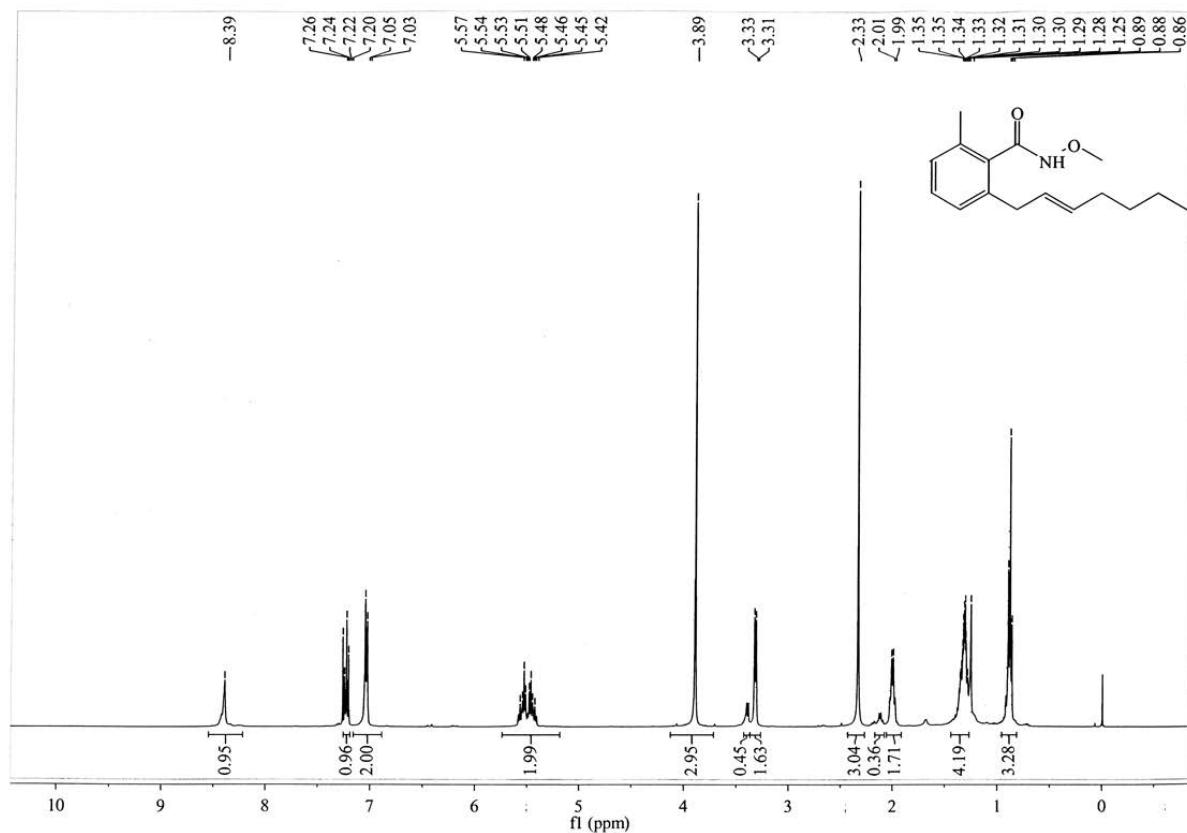


Figure S74. Compound 5a-¹³C NMR (100M, DCCl_3)

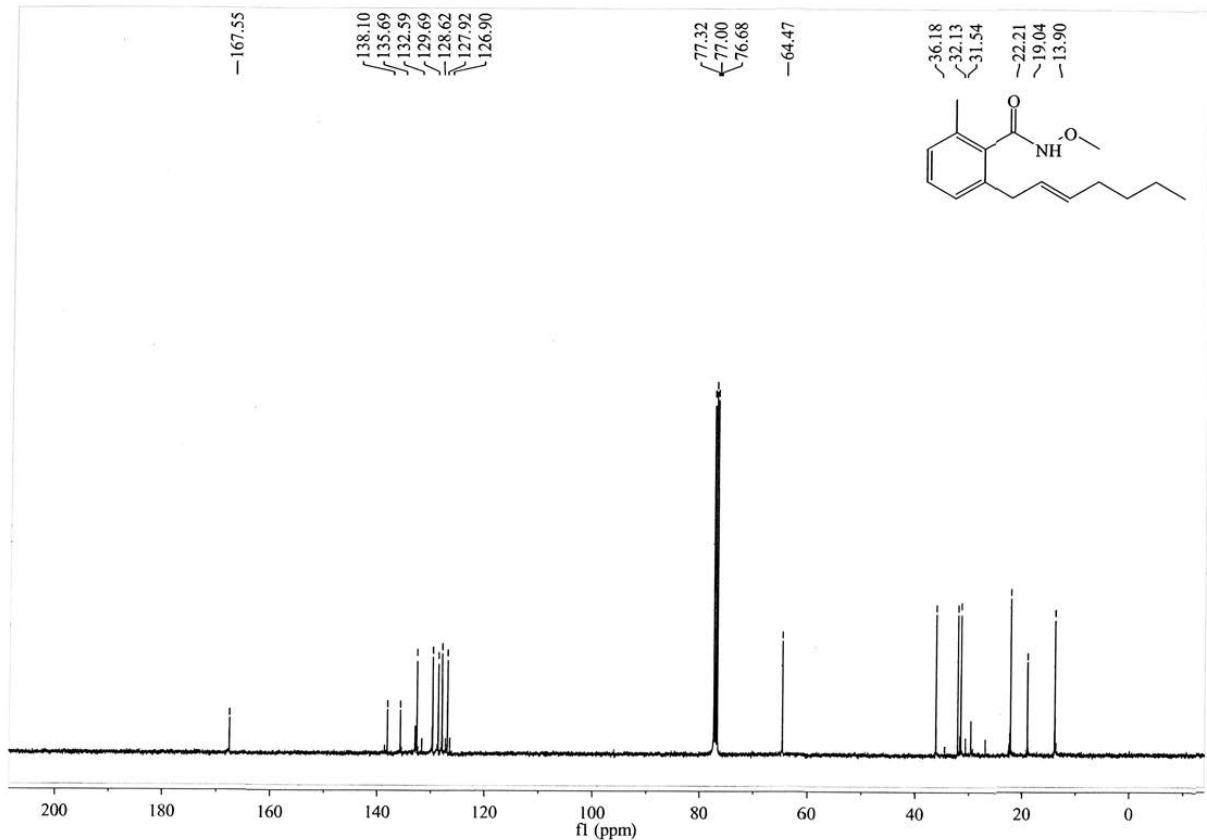


Figure S75. Compound **6i**-¹H NMR (400M, CDCl₃)

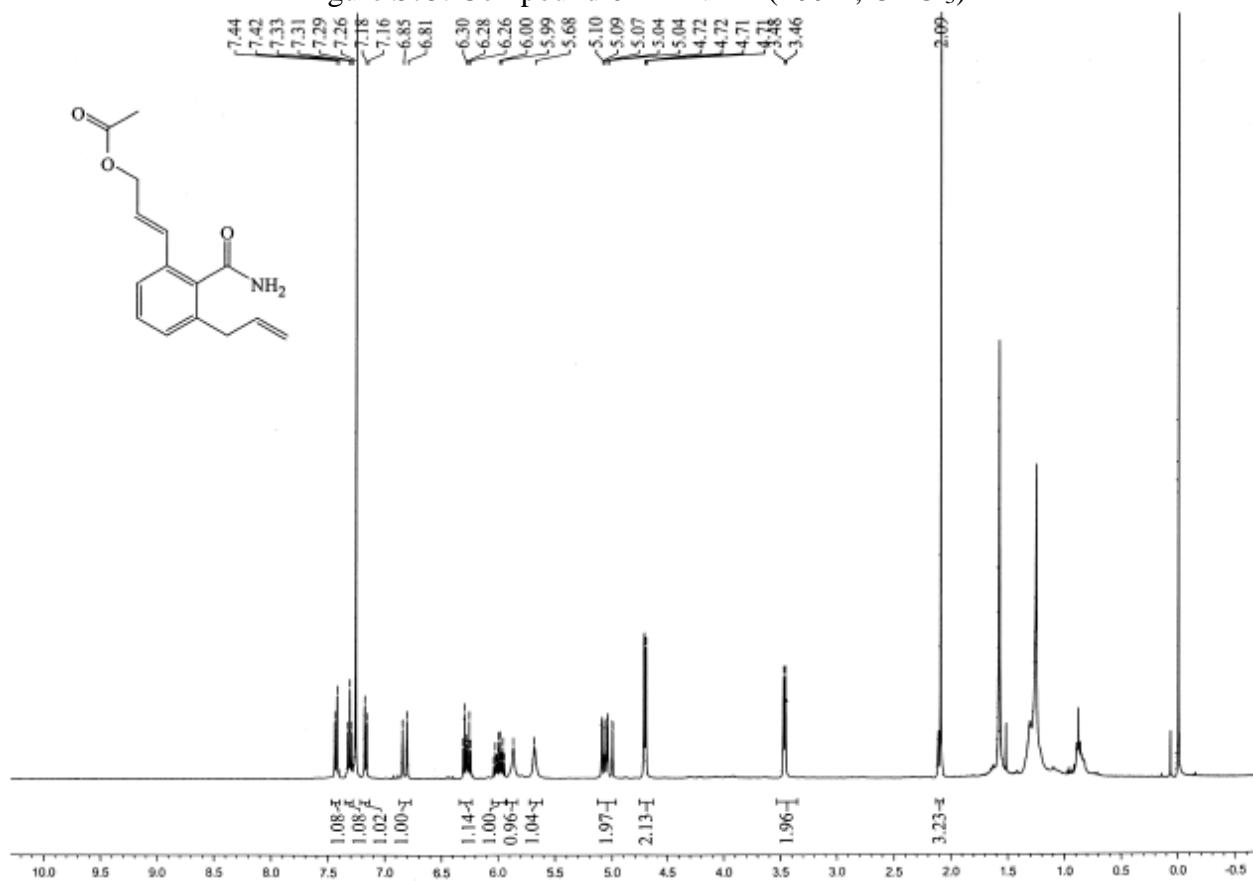


Figure S76. Compound **6i**-¹³C NMR (100M, CDCl₃)

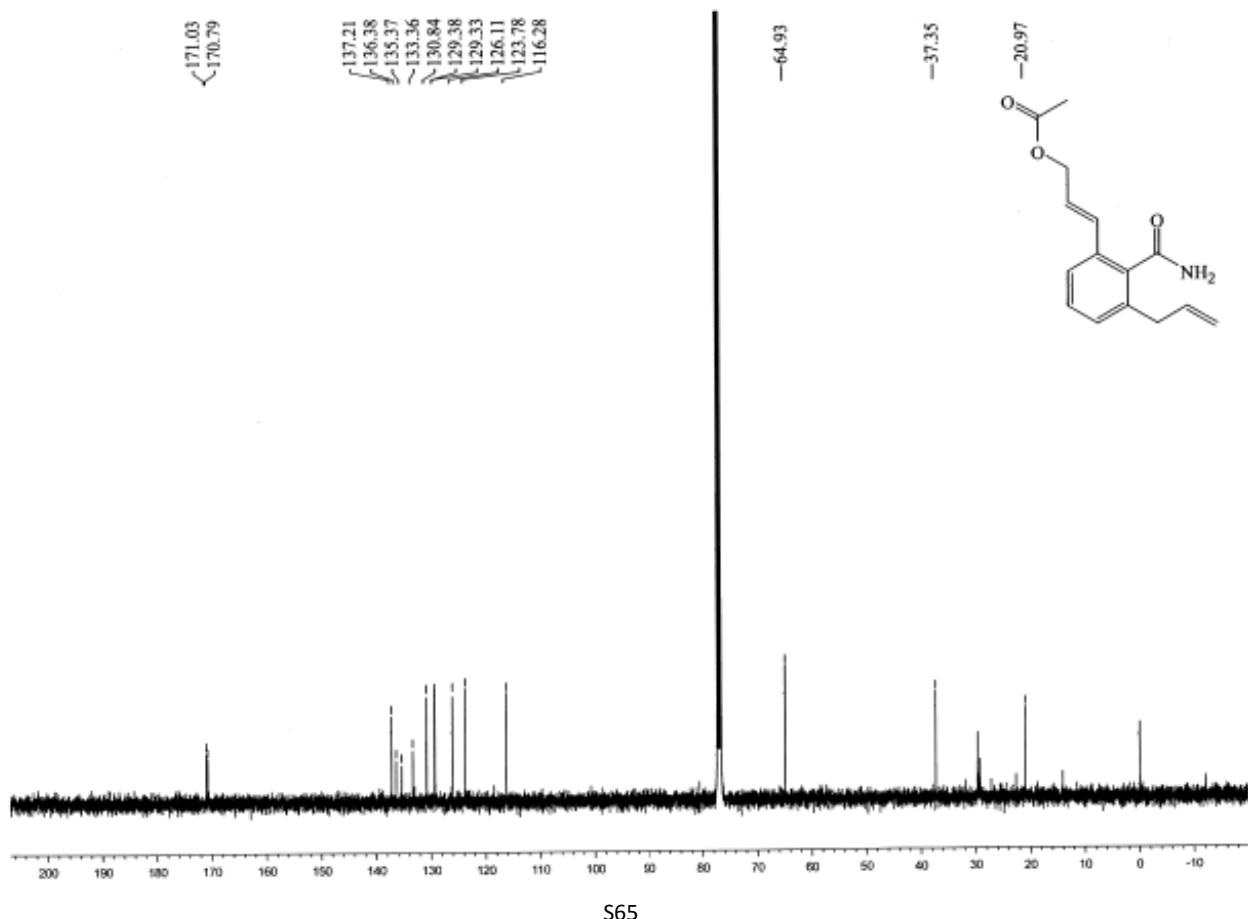


Figure S77. Compound 7a-¹H NMR (400M, DCCl_3)

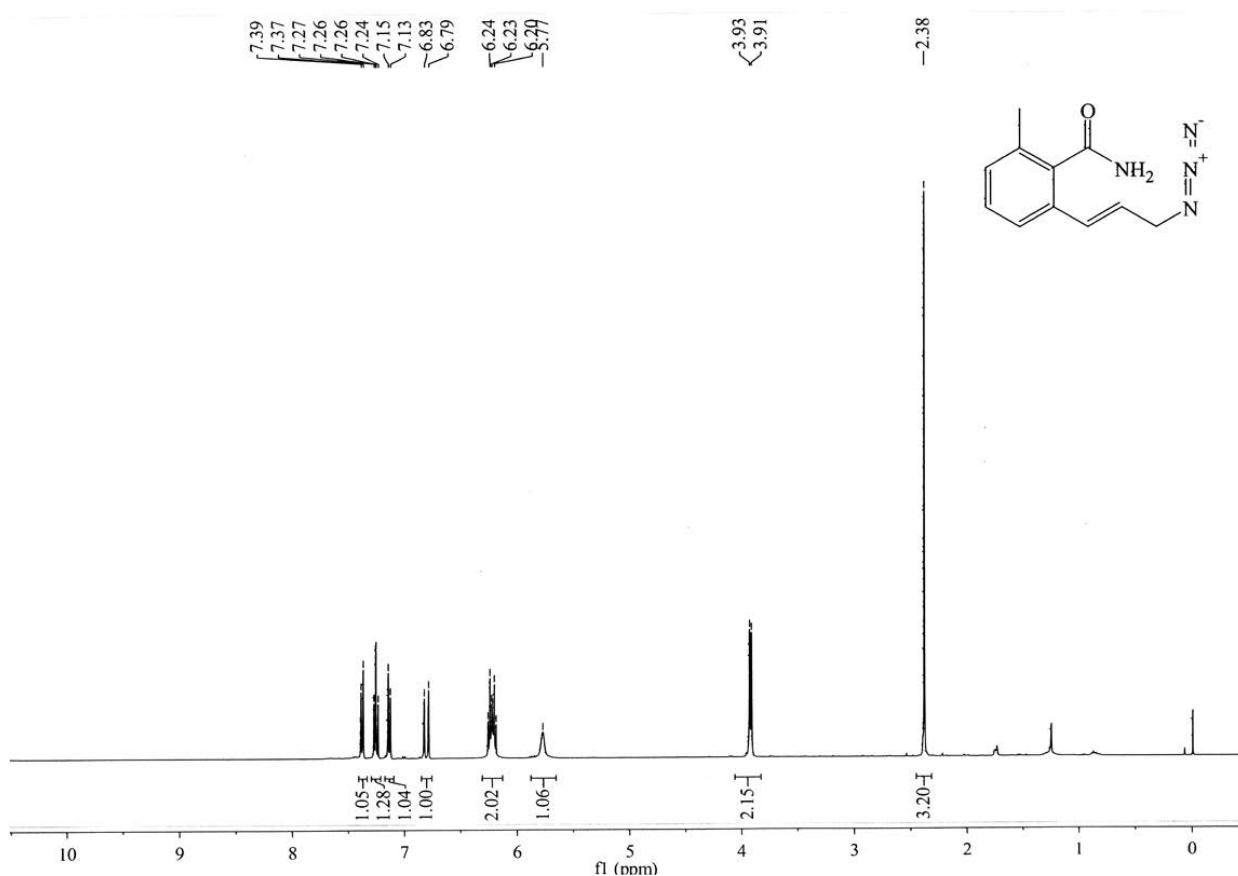


Figure S78. Compound 7a-¹³C NMR (100M, DCCl_3)

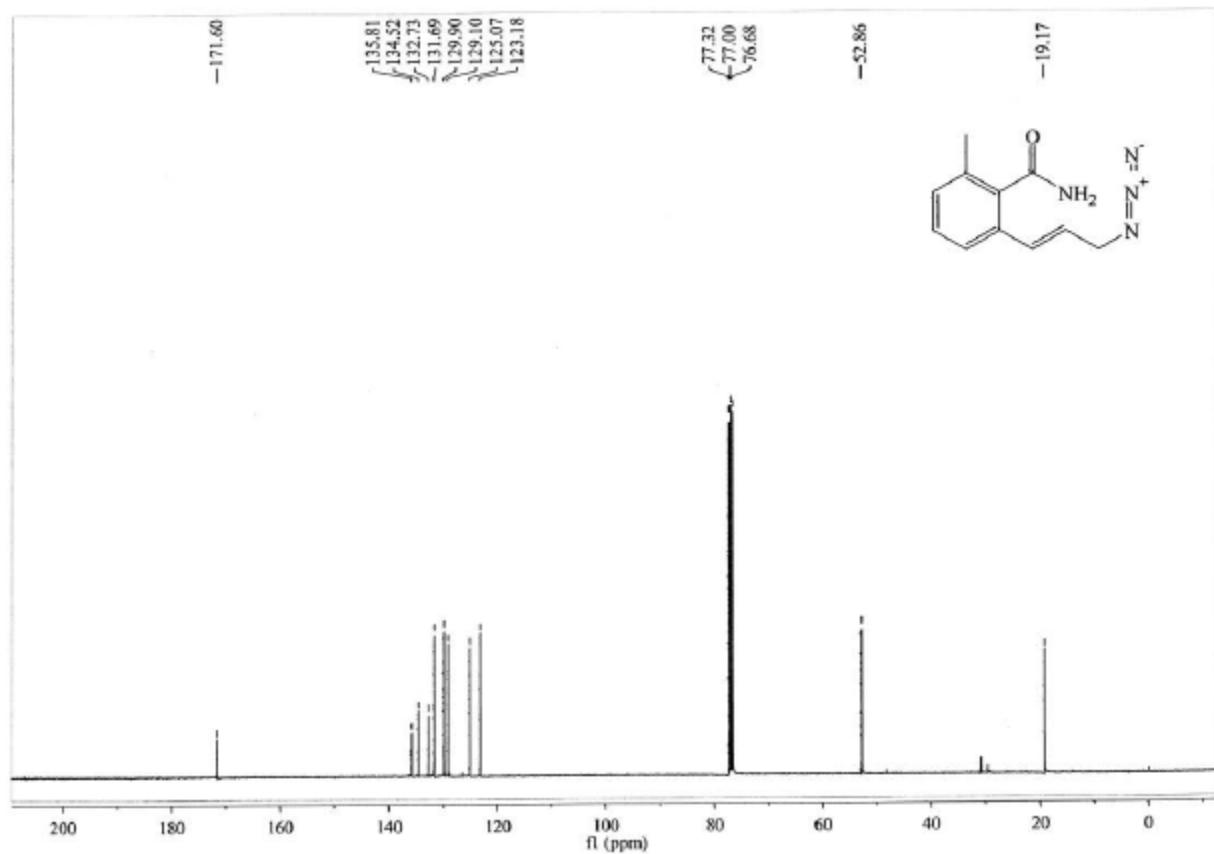


Figure S79. Compound **8a**- ^1H NMR (400M, DCCl_3)

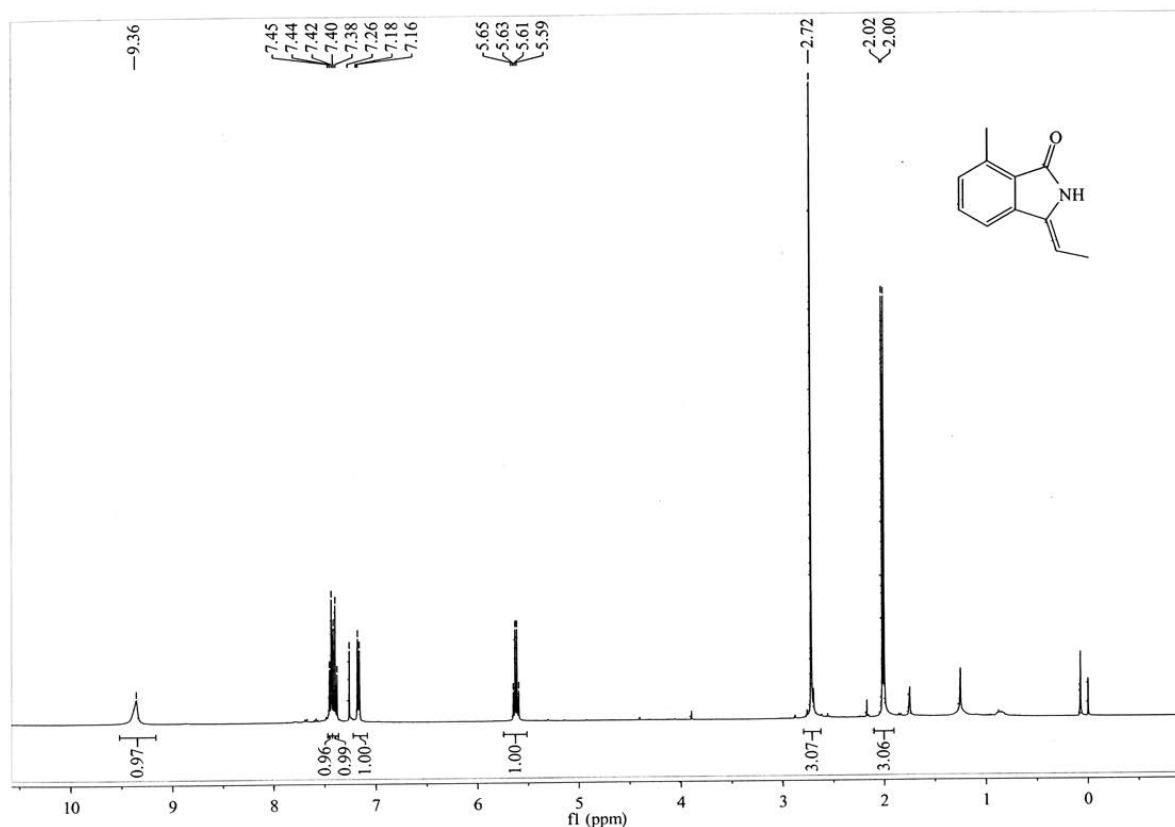


Figure S80. Compound **8a**- ^{13}C NMR (100M, DCCl_3)

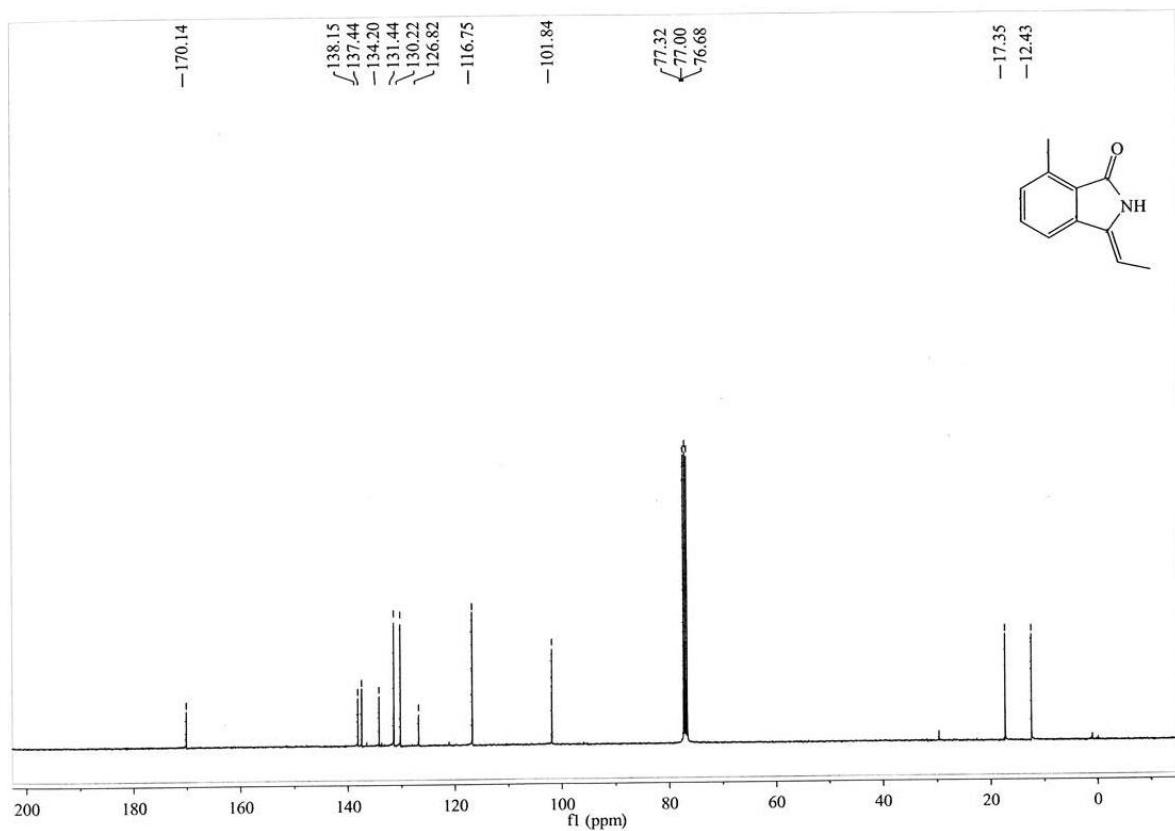


Figure S81. Compound **8a**-NOESY spectrum (400M, DCCl_3)

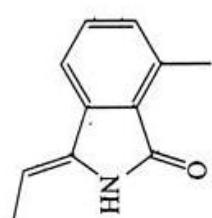
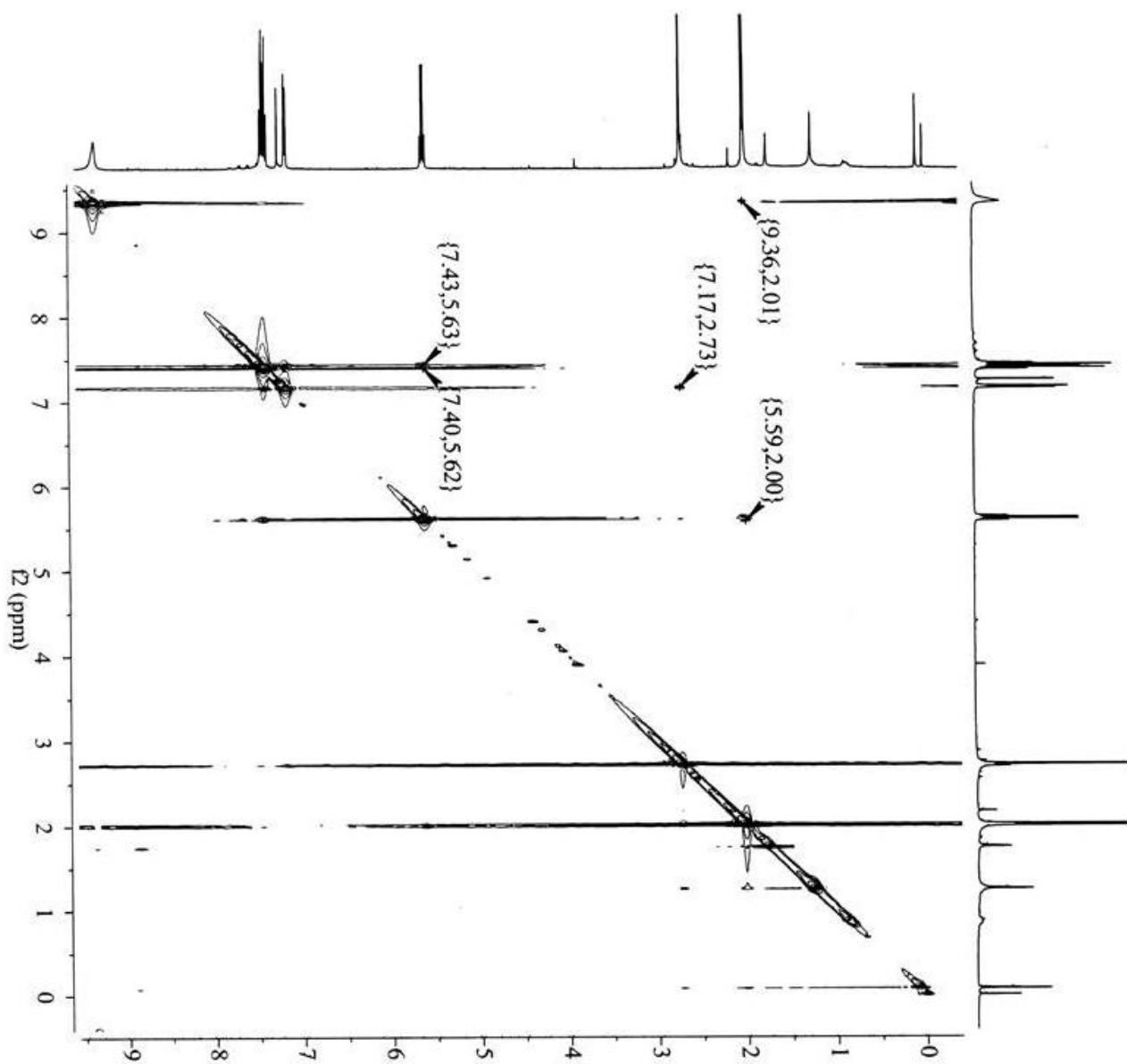


Figure S82. Compound 9aa-¹H NMR (400M, DCCl₃)

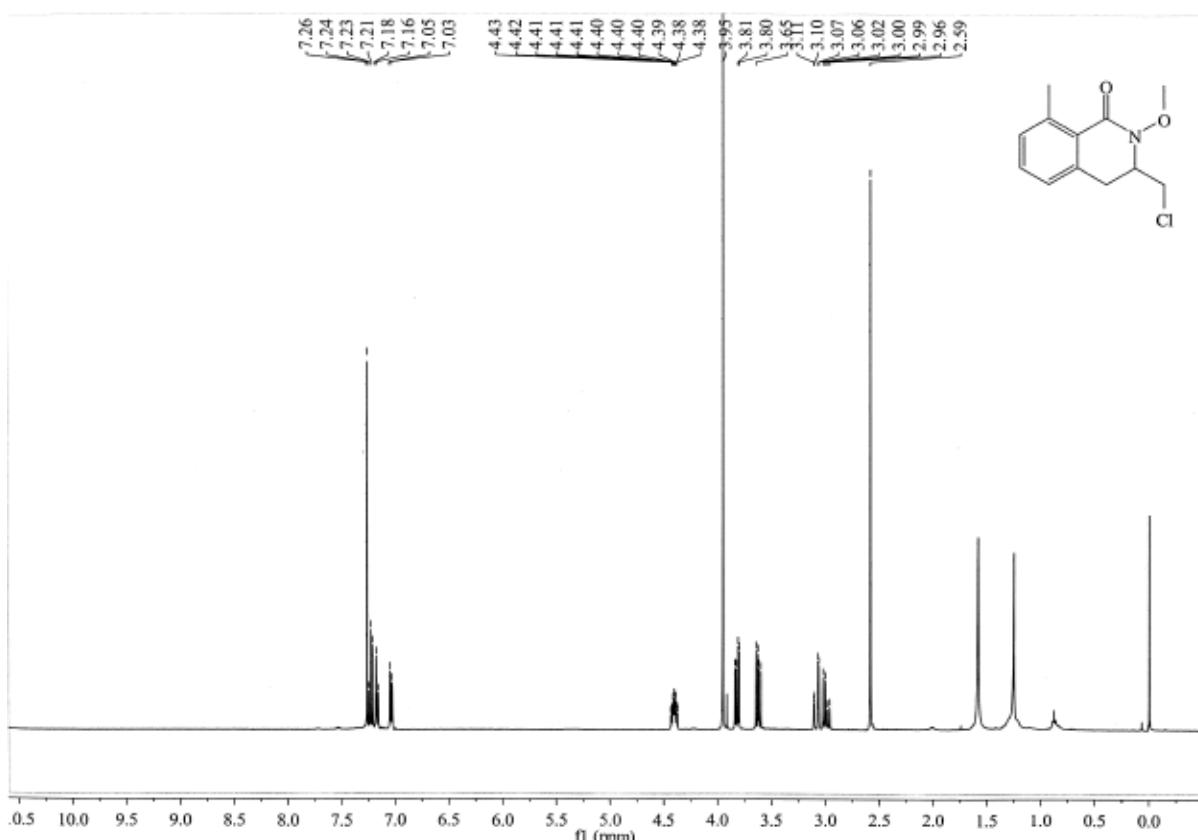


Figure S83. Compound 9aa-¹³C NMR (100M, DCCl₃)

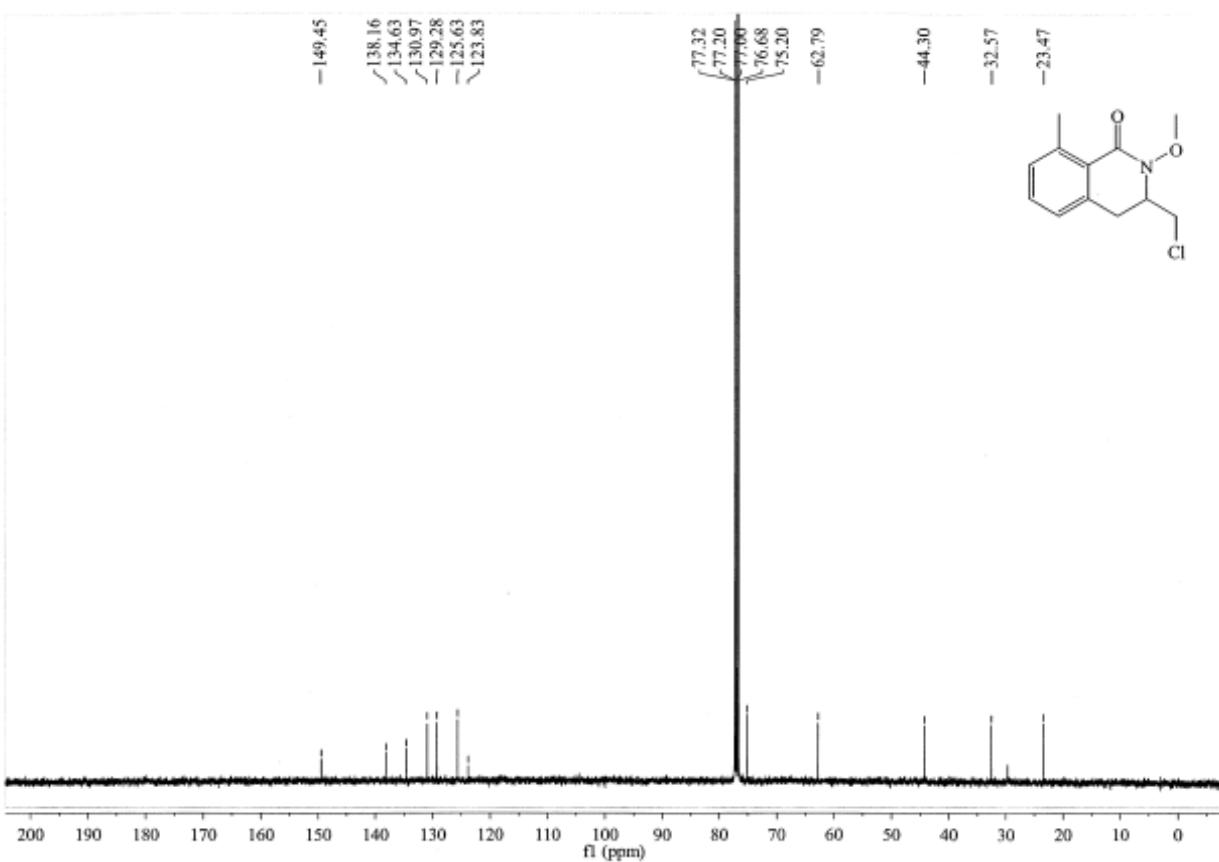


Figure S84. Compound 9ab-¹H NMR (400M, DCCl₃)

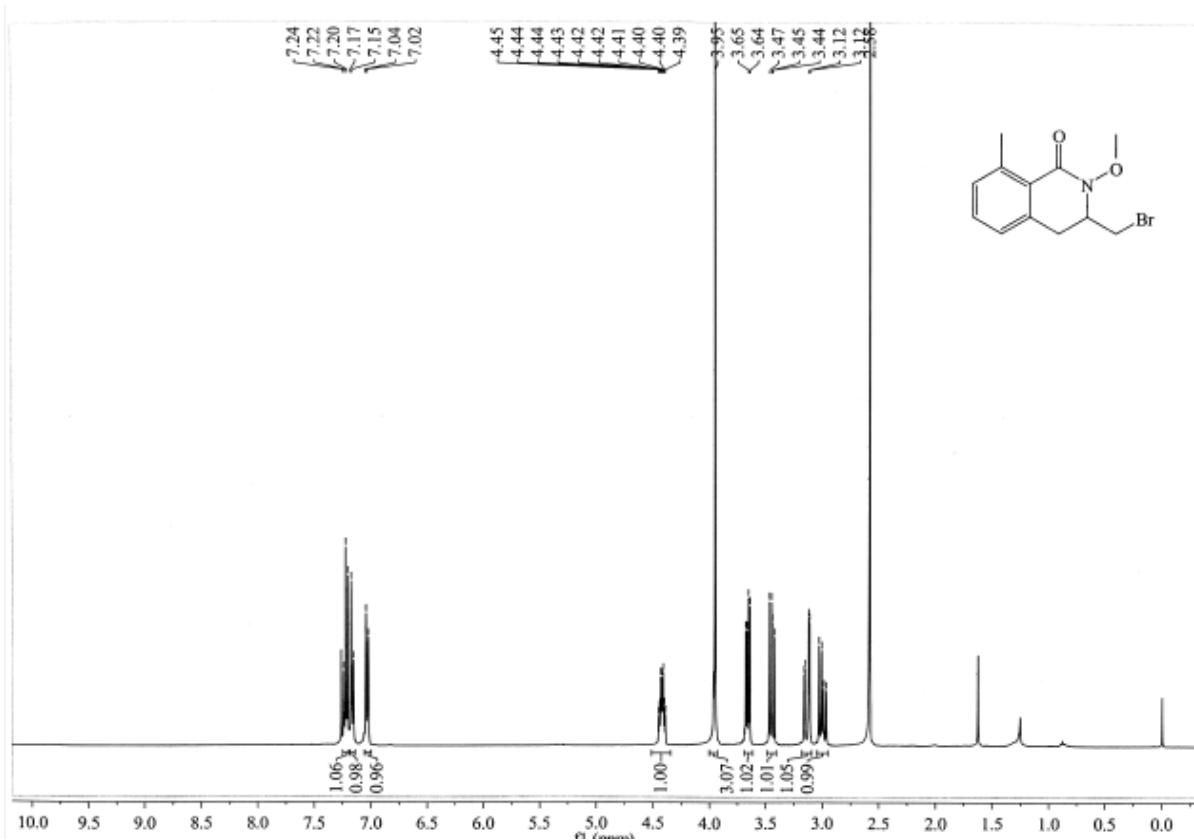


Figure S85. Compound 9ab-¹³C NMR (100M, DCCl₃)

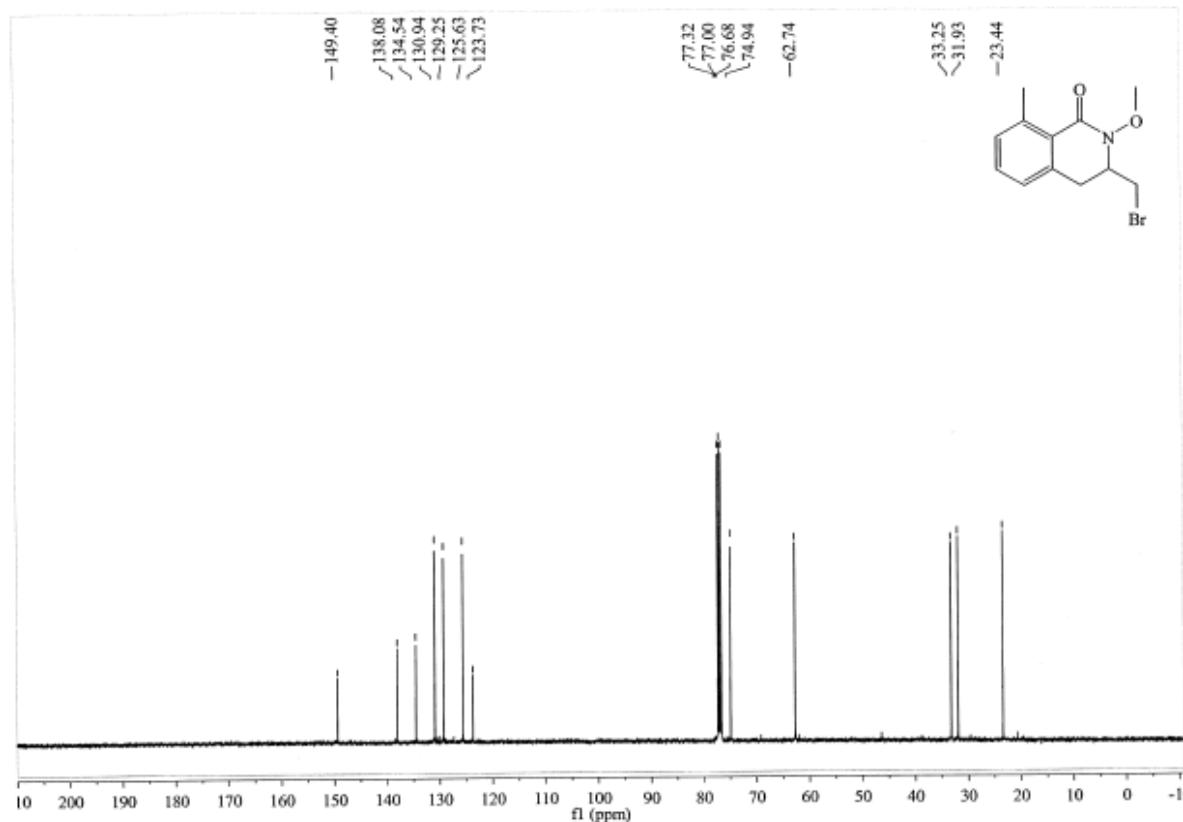


Figure S86. Compound 9ac-¹H NMR (400M, DCCl₃)

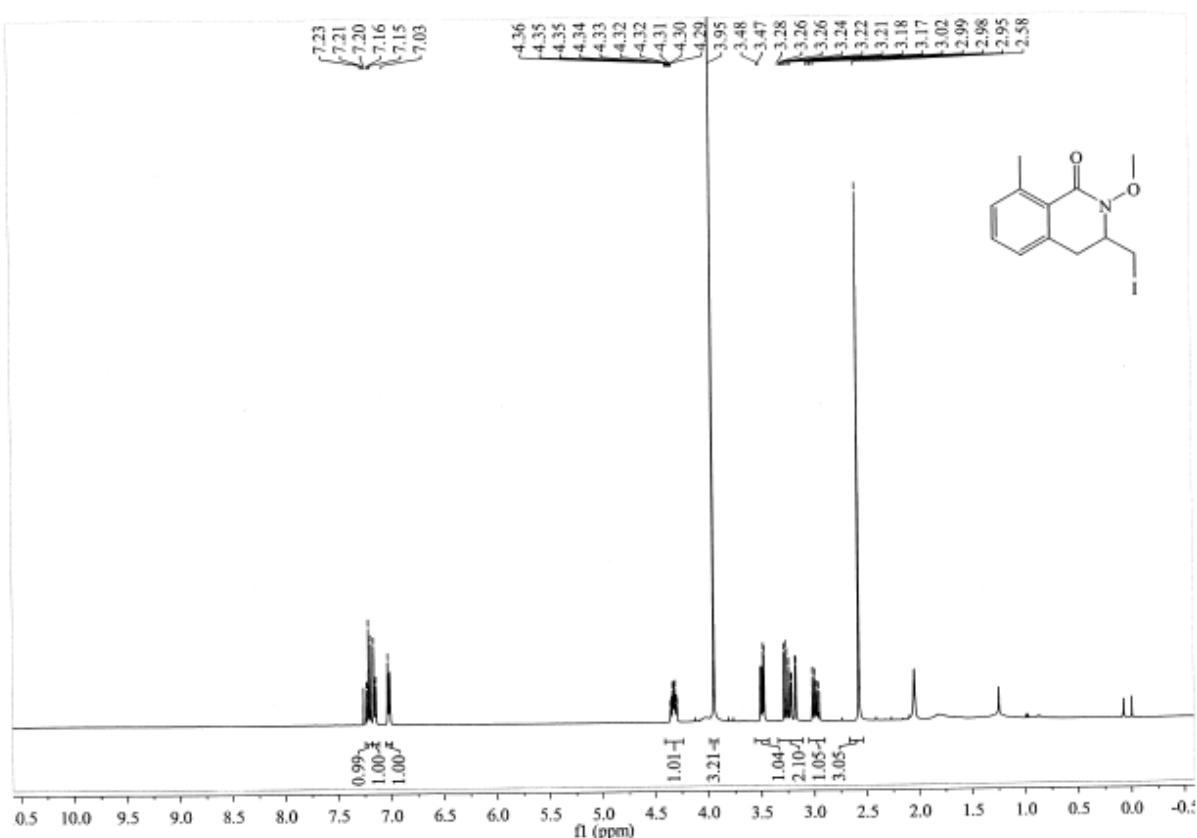


Figure S87. Compound 9ac-¹³C NMR (100M, DCCl₃)

