Supporting Information

Rh(III)-catalyzed regioselective C(sp^2)-H alkenylation of isoquinolones with methoxyallene: A facile access to aldehyde bearing isoquinolones

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1. General information

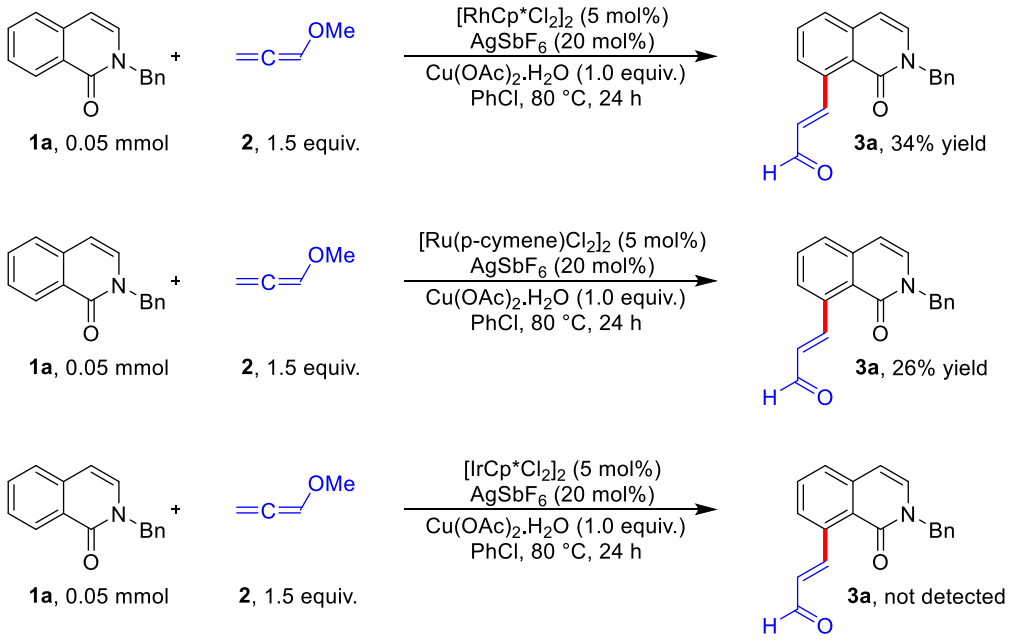
Unless otherwise mentioned, all reactions were performed in clean screw cap vials (10 ml) under air. All Chemicals were purchased from the Sigma-Aldrich, TCI and AVRA chemicals until described otherwise. TLC plates (Aluminium Sheet Silica gel 60 F254) were purchased from Merck. Column chromatography was performed over silica gel (230−400 mesh) using *n*-hexane and ethyl acetate as eluents. All the reactions were carried out using IKA magnetic hot plate stirrers. All products were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and high-resolution mass spectrometry (HRMS) and melting points. NMR spectra were recorded in on Bruker Advance at 600 & 500 MHz (^{1}H) and 150 & 125 MHz (^{13}C) respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δH = 7.26 and δC =77.16) and coupling constants (J) are given in Hz. High-Resolution Mass spectra were recorded on Water Q-ToF Micromass, maXis Impact mass spectrometers, and a high-resolution 6560 Ion Mobility Q-TOF LC/MS (Agilent, Santa Clara, USA). The melting points were recorded on a Brønsted Electrothermal 9100 and Labindia visual melting range.

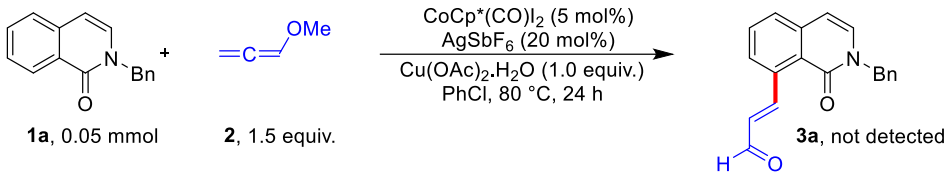
2. Preparation of *N*-substituted isoquinolone substrates

Isoquinolone were prepared according to known reported literature method.[1]

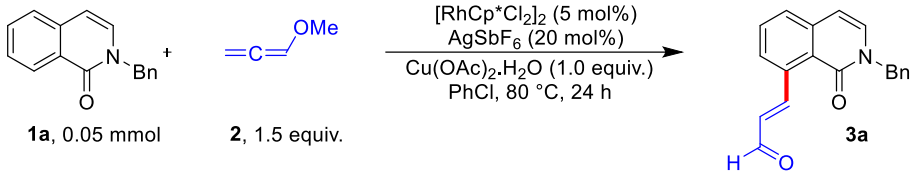
3. Optimization studies

3.1 Screening of Catalyst





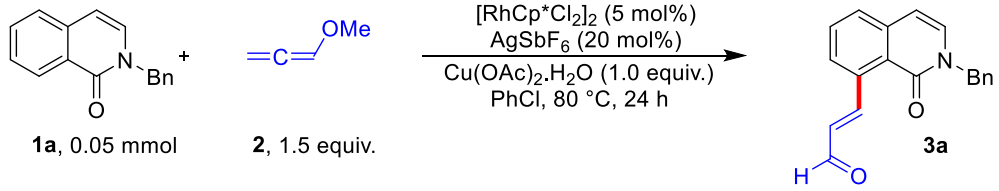
3.2 Screening of solvents



S.No.	Variation in above condition	Yield[a]
1	DCE instead of PhCl	36%
2	TFE instead of PhCl	48%
3	THF instead of PhCl	n.d.
4	**HFIP instead of PhCl**	**54%**
5	Toluene instead of PhCl	50%
6	DMF instead of PhCl	n.d.
7	DME instead of PhCl	21%
8	EtOAc instead PhCl	n.d.
9	H_2O instead of PhCl	n.d.
10	$CHCl_3$ instead of PhCl	n.d.
11	DCM instead of PhCl	32%
12	1,4-dioxane instead of PhCl	25%
13	Benzene instead of PhCl	39%

[a]GC yield are calculated using *n*-decane as internal standard, n.d. = not detected.

3.3 Screening of additives

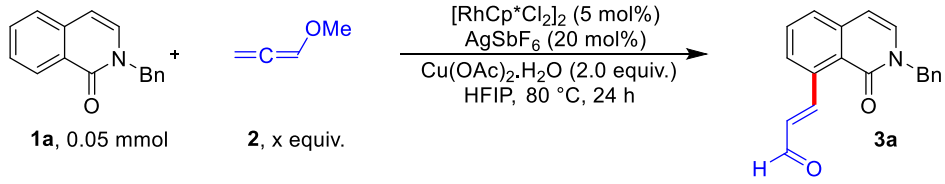


S.No.	Variation in above condition	Yield[a]
1.	AgOAc instead of $Cu(OAc)_2.H_2O$	n.d.
2.	AgCl (1.0 equiv.) instead of $Cu(OAc)_2.H_2O$	n.d.
3.	Ag_2O instead of $Cu(OAc)_2.H_2O$	n.d.
4.	Ag_2CO_3 instead of $Cu(OAc)_2.H_2O$	n.d.
5.	$AgBF_4$ instead of $Cu(OAc)_2.H_2O$	n.d.
6.	NaOAc instead of $Cu(OAc)_2.H_2O$	n.d.
7.	CsOAc instead of $Cu(OAc)_2.H_2O$	n.d.
8.	Anhydrous $Cu(OAc)_2$ instead of $Cu(OAc)_2.H_2O$	44%
9.	PivOH instead of $Cu(OAc)_2.H_2O$	31%

10.	AcOH instead of $Cu(OAc)_2.H_2O$	27%
11.	1-AdCOOH instead of $Cu(OAc)_2.H_2O$	29%
12.	Anhydrous $Cu(OAc)_2$ (2.0 equiv.) instead of $Cu(OAc)_2.H_2O$	51%
13.	**$Cu(OAc)_2.H_2O$ (2.0 equiv.)**	**62%**

[a]GC yield are calculated using *n*-decane as internal standard, n.d. = not detected.

3.4 Screening of methoxyallene loading

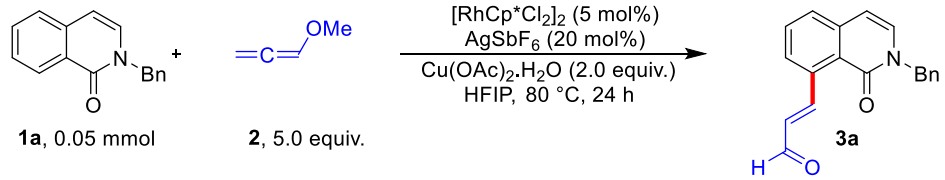


1a, 0.05 mmol **2**, x equiv. **3a**

S.No.	Variation in above condition	Yield[a]
1	1.0 equiv.	53%
2	1.5 equiv.	62%
3	2.0 equiv.	63%
4	2.5 equiv.	66%
5	3.0 equiv.	78%
6	4.0 equiv.	81%
7	**5.0 equiv.**	**92%**

[a]GC yield are calculated using *n*-decane as internal standard.

3.5 Variation in temperature

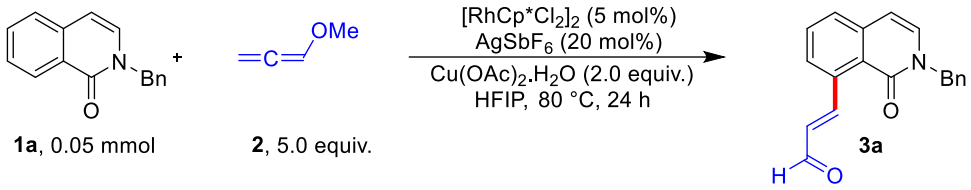


1a, 0.05 mmol **2**, 5.0 equiv. **3a**

S.No.	Variation in above condition	Yield[a]
1	RT instead of 80°C	n.d.
2	40°C instead of 80°C	n.d.
3	60°C instead of 80°C	37%
4	100°C instead of 80°C	72%
5	120°C instead of 80°C	52%
6	140°C instead of 80°C	43%

[a]GC yield are calculated using *n*-decane as internal standard, n.d. = not detected.

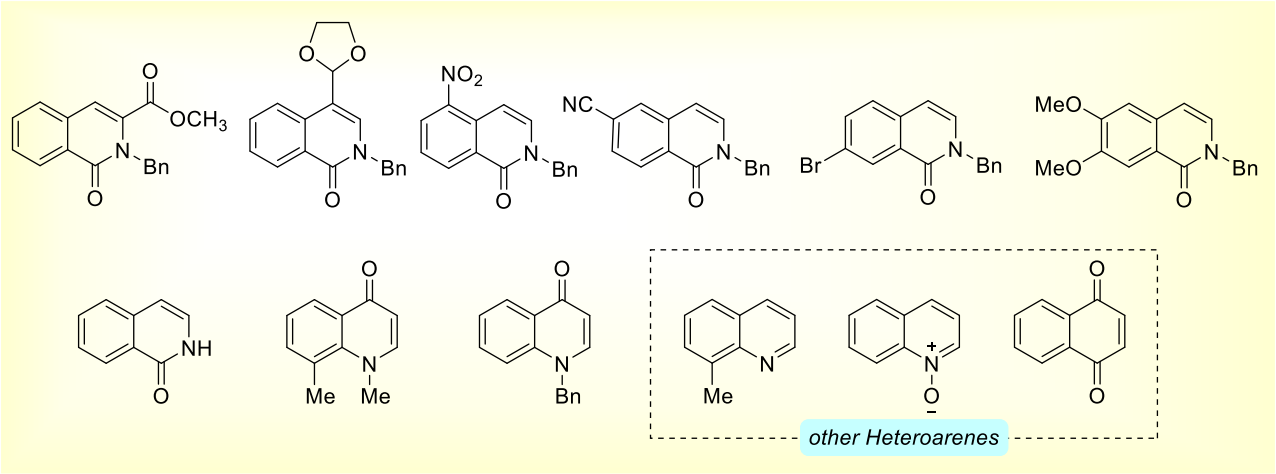
3.6 Variation in time



S.No.	Variation in above condition	Yield[a]
1	6 h instead of 24 h	48
2	12 h instead of 24 h	62
3	18 h instead of 24 h	78
4	20 h instead of 24 h	82
5	30 h instead of 24 h	79
6	36 h instead of 24 h	66

[a]GC yield are calculated using *n*-decane as internal standard.

Failure Substrates



4. Procedure for the scale-up synthesis and post-transformations

4.1. Scale-up synthesis: In a round-bottom flask, equipped with a magnetic stir bar were added *N*-benzylisoquinolone **1a** (706 mg, 3.0 mmol), methoxyallene **2** (1.26 mL, 5.0 equiv.), $[RhCp^*Cl_2]_2$ (92.7 mg, 5.0 mol%), $AgSbF_6$ (206.2 mg, 20 mol%) and $Cu(OAc)_2.H_2O$ (1.2 g, 2.0 equiv.) in HFIP (15 mL, 0.2 M). The reaction mixture was stirred at 80 °C for 24 h. After completion, the solvent from reaction mixture was removed under reduced pressure. The product was isolated from crude mixture by column chromatography (20% EtOAc:*n*-hexane) on silica gel (230−400) to obtain 703 mg of **3a**, yield 81%.

4.2. Post synthetic transformation of 3a

4.2.1. Synthesis of *2-benzyl-8-(3-hydroxyprop-1-en-1-yl)isoquinolin-1(2H)-one* (4a): To a reaction vial equipped with magnetic stir bar were added synthesized alkenylated product **3a** (0.2 mmol) which dissolved in MeOH (0.2 M). After that, $NaBH_4$ (1.2 equiv.) was added at 0 °C slowly to the reaction mixture and continue stirring for 2h at room temperature. After completion, the solvent was evaporated under reduced pressure. Product was then extracted with DCM and purified by flash chromatography using silica gel (230−400 mesh size) and EtOAc/n-hexane as the eluent. The isolated yield of desired transformed product **4a** was 78% as white solid.

4.2.2. Synthesis of *5-(2-benzyl-1-oxo-1,2-dihydroisoquinolin-8-yl)-3-hydroxy-2-methylenepent-4-enenitrile* (4b): To a reaction vial equipped with magnetic stir bar were added synthesized alkenylated product **3a** (0.2 mmol), DABCO (30 mol%), acrylonitrile (1.5 equiv.). The subsequent reaction mixture was stirred at room temperature for 12h. After completion, reaction mixture was diluted with ethyl acetate and evaporated under reduced pressure. Finally, the crude mixture was purified by column chromatography using silica gel (230−400 mesh size) and EtOAc:*n*-hexane as the eluent. The isolated yield of desired Baylis-Hillman adduct **4b** was 74% as light yellow solid.

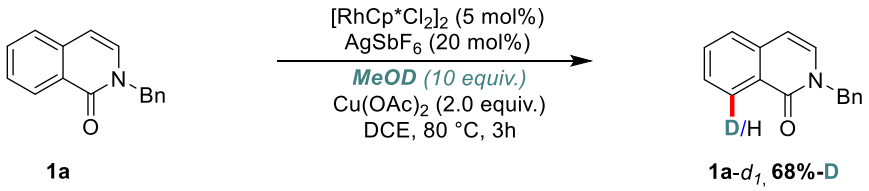
5. Mechanistic study

5.1. Reversibility (Deuterium Scrambling) experiments

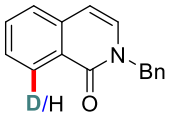
5.1.1. Without coupling partner

The substrate **1a** (0.1 mmol), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2.H_2O$ or anhydrous $Cu(OAc)_2$ (2.0 equiv.), MeOD (10.0 equiv.) in DCE (0.5 mL) were added to a screw-cap reaction vial equipped with magnetic stirring bar and then the mixture was stirred at 80 °C for 3h. The reaction mixture was then allowed to cool to room temperature. The residue was purified by silica gel column chromatography. Finally, deuterium incorporation was determined by ^1H NMR.

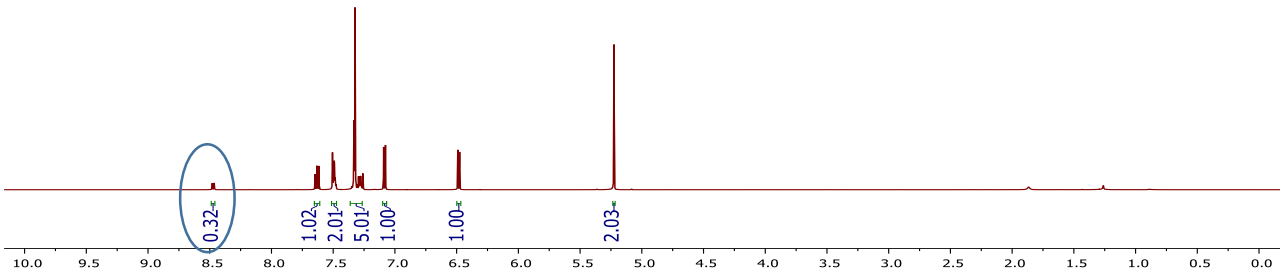
In the presence of anhydrous $Cu(OAc)_2$:



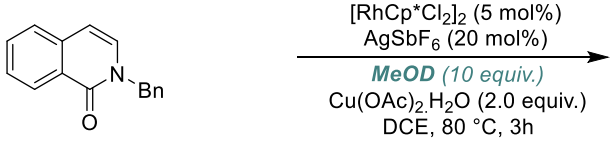
1a **1a-d_1, 68%-D**



1a-d_1, 68% Deuteration

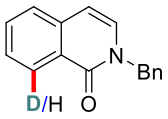


In the presence of anhydrous $Cu(OAc)_2.H_2O$:

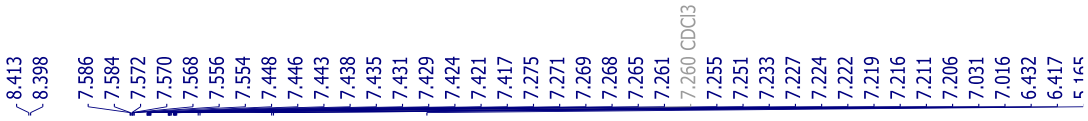


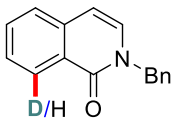
1a

$[RhCp^*Cl_2]_2$ (5 mol%)
$AgSbF_6$ (20 mol%)
MeOD *(10 equiv.)*
$Cu(OAc)_2.H_2O$ (2.0 equiv.)
DCE, 80 °C, 3h

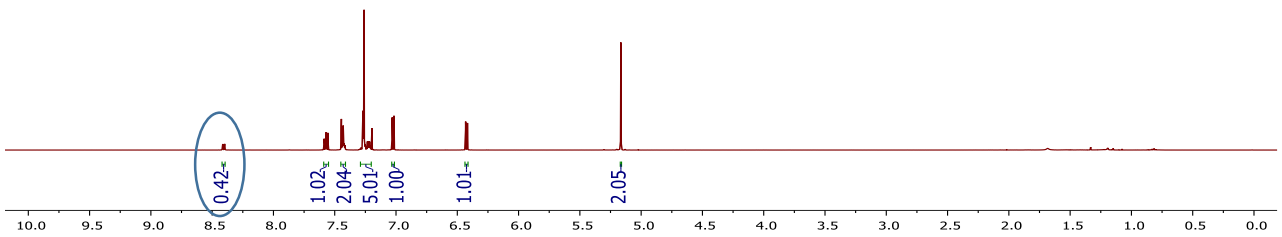


1a-d_1, 58%-D



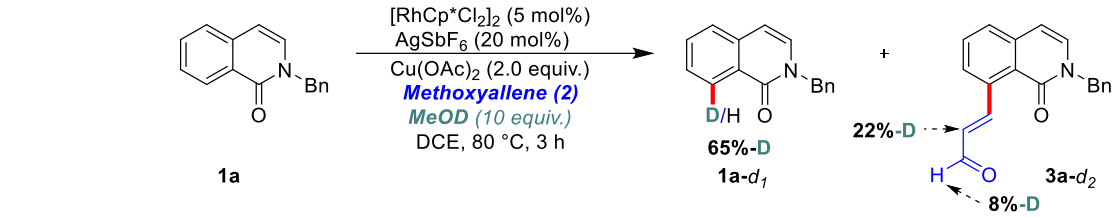


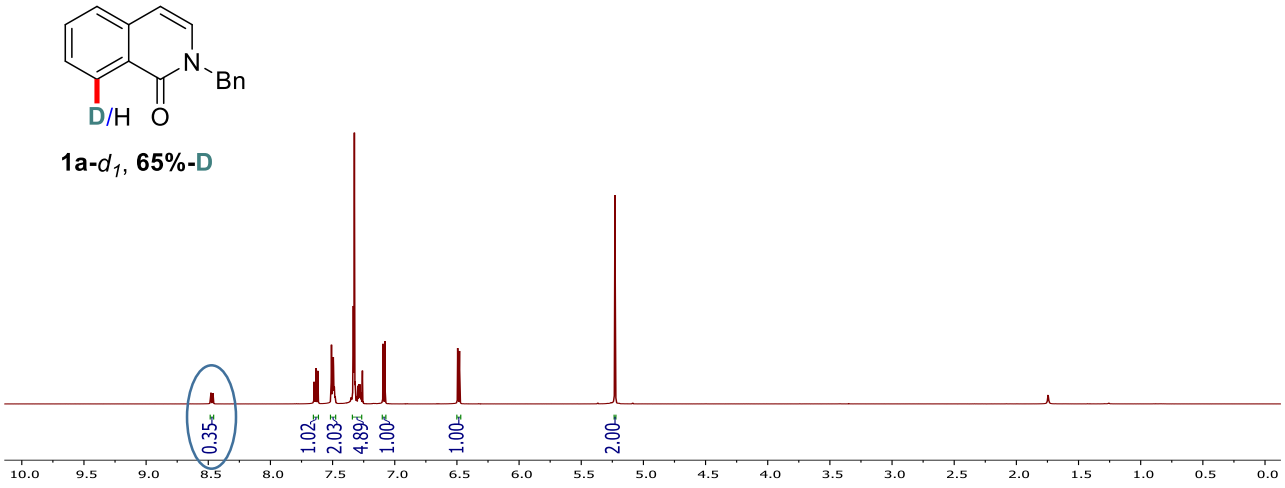
1a-d_1, 58% Deuteration

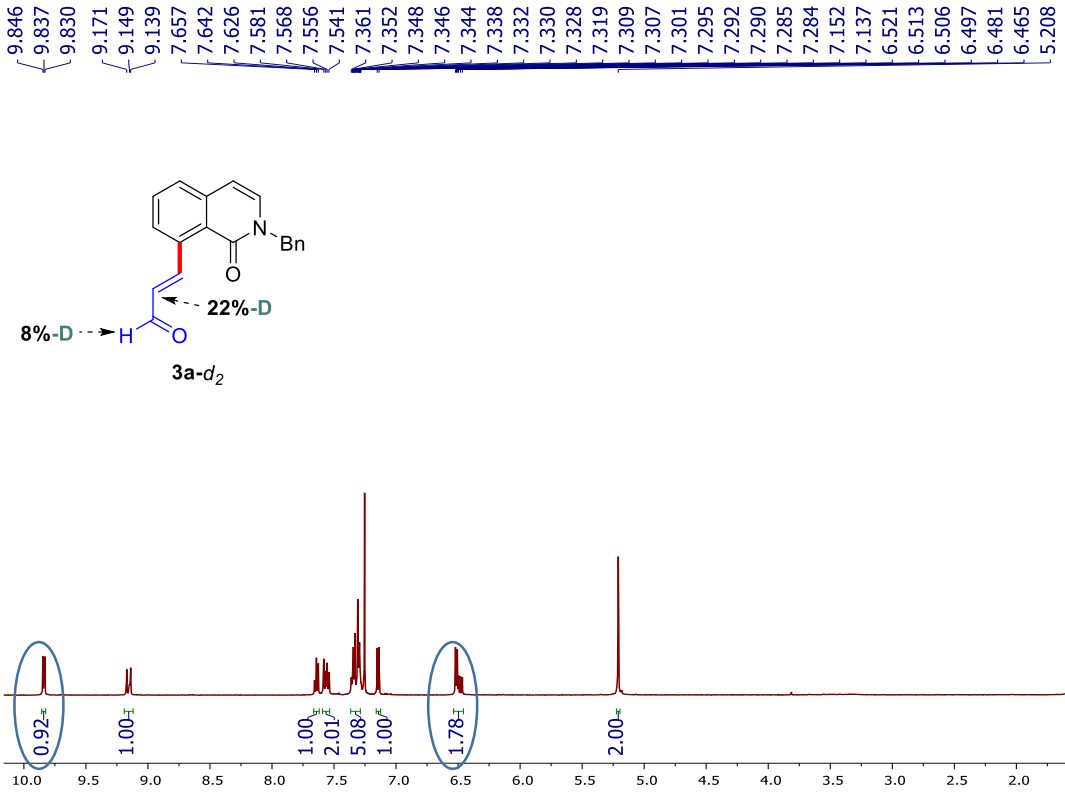


5.1.2. With coupling partner (Standard Reaction)

The substrate **1a** (0.1 mmol), **2** (5.0 equiv.), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (2.0 equiv.) and MeOD (10.0 equiv.) in DCE (0.5 mL) were added to a screw-cap reaction vial equipped with magnetic stirring bar and then the mixture was stirred at 80 °C for 3h. The reaction mixture was then allowed to cool to room temperature. The residue was purified by silica gel column chromatography to give **1a**-d_1 and **3a**-d_2. Finally, deuterium incorporation was determined by ^{1}H NMR.







Conclusion: From the results obtained in the above sets of deuterium scrambling experiments, we conclude that:

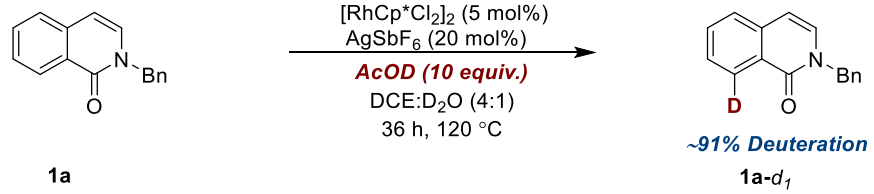
(i) The step accompanied C-H metalation is reversible in nature.

(ii) H/D exchange at the *β*-position of **3a** suggest that the reaction proceeds *via* 1,2 migratory insertion.

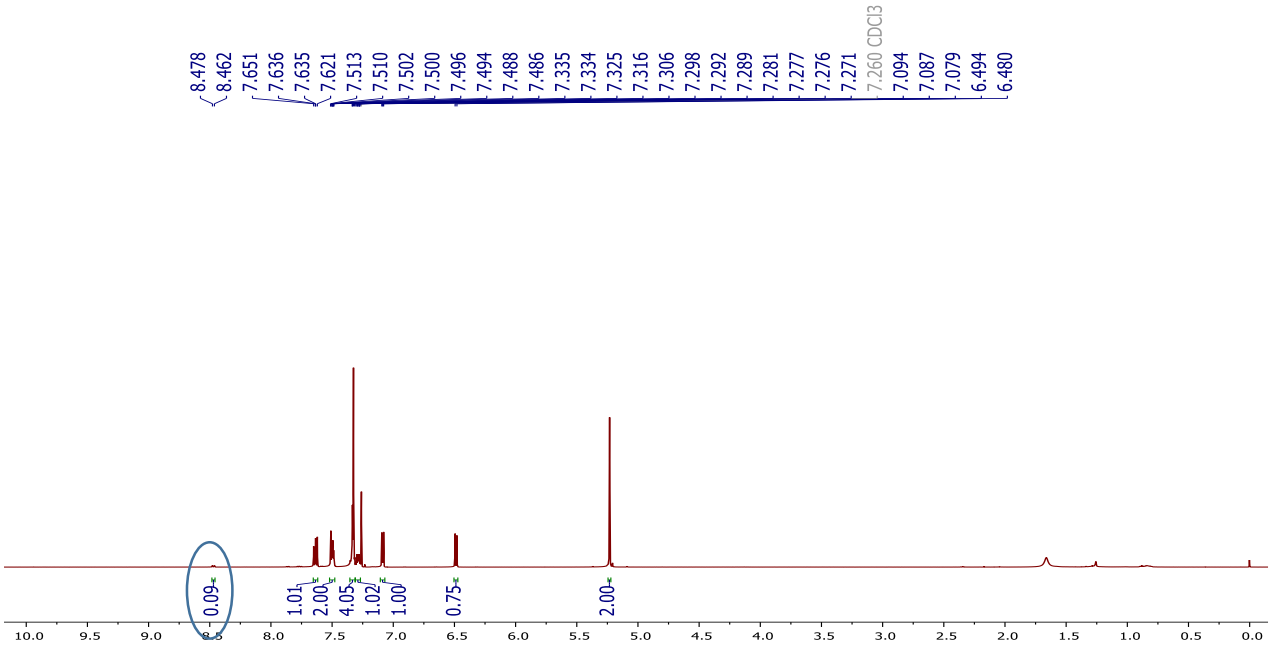
5.2. Kinetic isotope effect experiments for alkenylation

5.2.1. Synthesis of 1a-d_1

1a (0.1 mmol × 5) was taken in 10 mL screw cap vial equipped with magnetic stirrer and dissolved in mixture of 0.5 ml of DCE: D_2O (4:1) and AcOD (10 equiv). $[Cp^*RhCl_2]_2$ (5 mol%), followed by $AgSbF_6$ (20 mol%) were added to the solution. The reaction mixture was stirred for 36 h at 120 °C. Next the reaction mixture was filtered through a short pad of silica gel, Deuterium incorporation was measured with help of ^{1}H NMR of isolated **1a**-d_1 isoquinolone.

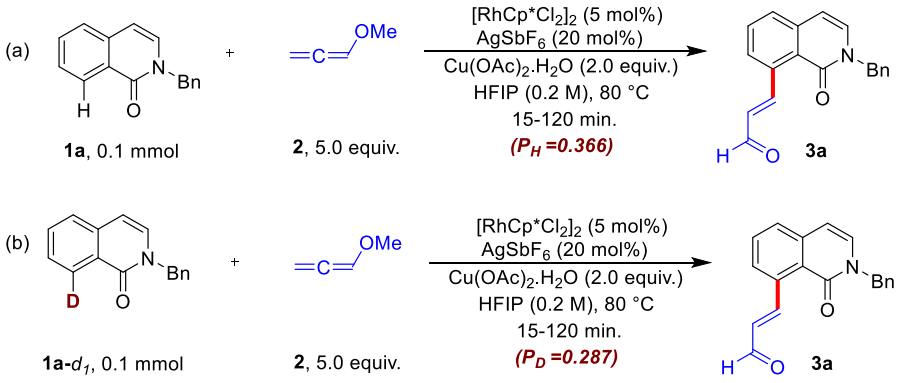


1a **1a**-d_1



5.2.2. Determination of Kinetic Isotope Effect through parallel reactions:

KIE study was carried out by initial rate method. In two different screw capped vials with a stir bar separately placed **1a** and **1a**-d_1 (0.1 mmol), were reacted with methoxyallene **2** (5.0 equiv.) under standard reaction conditions. Yield of product in both the reactions were analysed at various time interval by GC-FID.



Time (min)	15	30	45	60	75	90	105	120
Product Yield (%) with (**1a**)	11	18	22	30	36	45	42	49
Product Yield (%) with (**1a**-d_1)	9	15	19	23	30	33	34	40

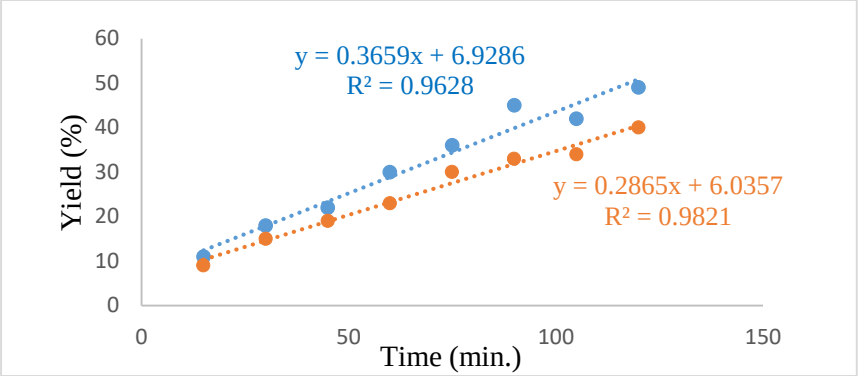
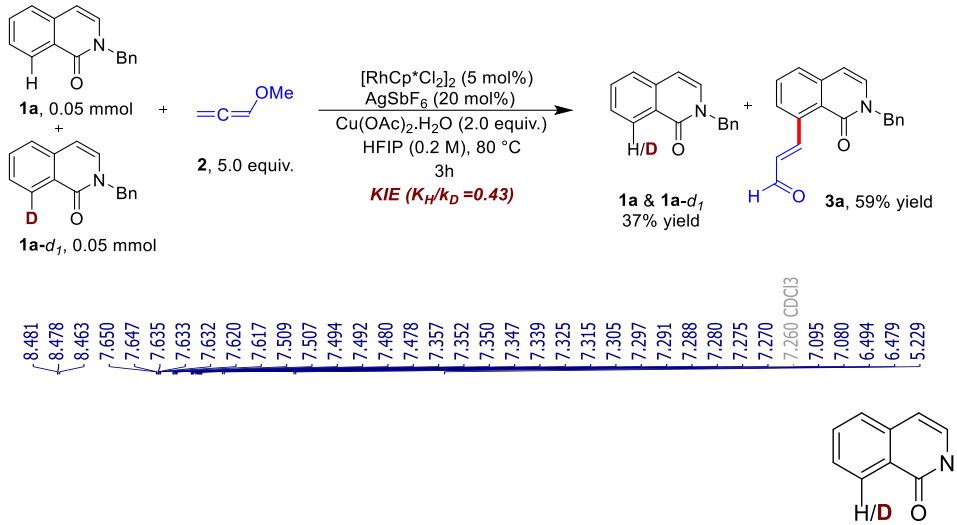


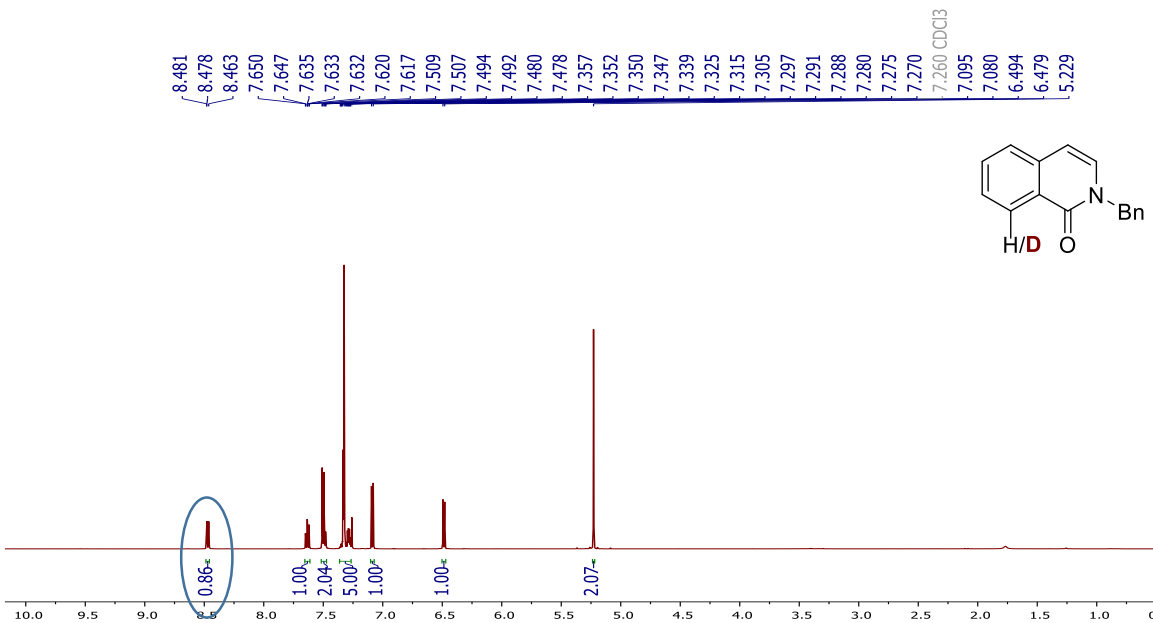
Fig S1: rate constant w.r.t to 1a and 1a-d_1

Conclusion: P_H/P_D=1.28 for parallel reactions

5.2.3. Determination of Kinetic Isotope Effect from competition experiment:

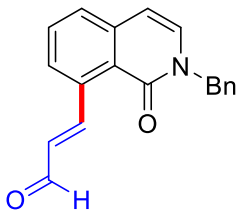
1a and **1a-d_1** (1:1) (total 0.1 mmol), were reacted with methoxyallene **2** (5.0 equiv.) under standard reaction conditions. After 3 h, starting materials (mixture of **1a** and **1a-d_1**) were recovered in 37% isolated yield and product in 59% yield. ^{1}H NMR of recovered starting material shows 14% deuteration at C8 of **1a**. The k_H/k_D = 0.43 was calculated on the basis of isolated yields.





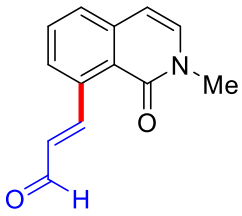
6. Characterization data

3-(2-benzyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3a).



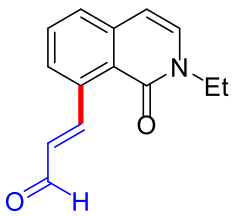
Light yellow solid. yield = 52.6 mg (91%). Mp = 132–134 °C. Isolated from flash chromatography (15% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.84 (d, J = 8.0 Hz, 1H), 9.15 (d, J = 15.5 Hz, 1H), 7.65 –7.62 (m, 1H), 7.58 – 7.53 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 3H), 7.15 (d, J = 7.0 Hz, 1H), 6.52 (d, J = 7.0 Hz, 1H), 6.50 – 6.46 {m, 1H(merged)}, 5.20 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 194.7, 162.5, 155.3, 138.9, 137.9, 136.6, 132.1, 132.0, 130.7, 129.0, 128.8, 128.1, 127.9, 127.4, 123.6, 106.7, 52.0. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{19}H_{15}NNaO_2$, 312.0995; found, 312.0995.

3-(2-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3b).



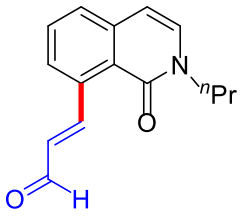
Yellow solid. yield = 34.1 mg (80%). Mp = 141–144 °C. Isolated from flash chromatography (7% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.83 (d, J = 8.0 Hz, 1H), 9.15 (d, J = 16.0 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.58 (dd, J = 8.0, 1.5 Hz, 1H), 7.52 (dd, J = 7.5, 1.0 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.52 (d, J = 7.0 Hz, 1H), 6.48 (dd, J = 15.5, 7.5 Hz, 1H), 3.59 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 194.6, 162.9, 155.3, 139.1, 137.6, 133.2, 131.9, 130.7, 128.7, 127.3, 123.3, 106.3, 37.6. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{13}H_{11}NNaO_2$, 236.0682; found, 236.0680.

3-(2-ethyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3c).



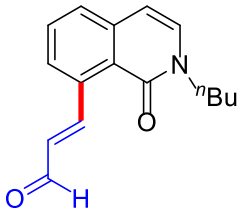
Yellow solid. yield = 34.9 mg (77%). Mp = 138–139 °C. Isolated from flash chromatography (13% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.82 (d, J = 8.0 Hz, 1H), 9.13 (d, J = 16.0 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.55 (dd, J = 8.0, 1.5 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.51 (d, J = 7.0 Hz, 1H), 6.45 (dd, J = 15.5, 8.0 Hz, 1H), 4.02 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.6, 162.2, 155.4, 138.9, 137.5, 131.9, 131.7, 130.4, 128.7, 127.1, 123.5, 106.5, 44.8, 14.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{14}NO_2$, 228.1019; found, 228.1020.

3-(1-oxo-2-propyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3d).



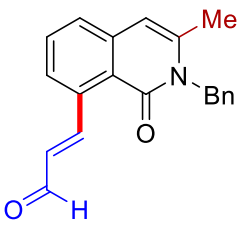
Yellow solid. yield = 34.7 mg (72%). Mp = 140–141 °C. Isolated from flash chromatography (11% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.84 (d, J = 8.0 Hz, 1H), 9.13 (d, J = 15.5 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.57 – 7.55 (m, 1H), 7.52 – 7.50 (m, 1H), 7.12 (d, J = 7.0 Hz, 1H), 6.50 (d, J = 7.0 Hz, 1H), 6.47 (dd, J = 16.0, 8.0 Hz, 1H), 3.94 – 3.91 (m, 2H), 1.85 – 1.77 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.6, 162.4, 155.5, 138.9, 137.7, 132.5, 131.8, 130.5, 128.6, 127.2, 123.6, 106.1, 51.5, 22.5, 11.3. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{16}NO_2$, 242.1176; found, 242.1177.

3-(2-butyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3e).



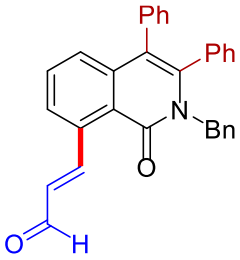
Yellow solid. yield = 32.1 mg (63%). Mp = 135–137 °C. Isolated from flash chromatography (8% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.83 (d, J = 8.0 Hz, 1H), 9.13 (d, J = 16.0 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.56 (dd, J = 8.0, 1.5 Hz, 1H), 7.51 – 7.49 (m, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.50 (d, J = 7.0 Hz, 1H), 6.46 (dd, J = 16.0, 8.0 Hz, 1H), 3.97 – 3.94 (m, 2H), 1.78 – 1.72 (m, 2H), 1.44 – 1.36 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.6, 162.3, 155.4, 138.9, 137.6, 132.4, 131.7, 130.5, 128.6, 127.2, 123.5, 106.2, 49.8, 31.3, 20.1, 13.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{18}NO_2$, 256.1332; found, 256.1341.

3-(2-benzyl-3-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3f).



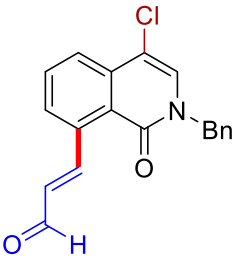
Yellow solid. yield = 50.9 mg (84%). Mp = 135–137 °C. Isolated from flash chromatography (13% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.81 (d, J = 8.0 Hz, 1H), 9.14 (d, J = 16.0 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.52 – 7.49 (m, 2H), 7.32 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 7.15 – 7.13 (m, 2H), 6.50 (dd, J = 16.0, 8.0 Hz, 1H), 6.41 (s, 1H), 5.41 (s, 2H), 2.36 (d, J = 1.0 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.7, 155.4, 163.6, 140.6, 138.6, 137.7, 136.7, 132.1, 130.5, 129.0, 128.0, 127.4, 126.5, 126.1, 121.6, 106.5, 47.3, 20.6. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_2$, 326.1151; found, 326.1151.

3-(2-benzyl-1-oxo-3,4-diphenyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3g).



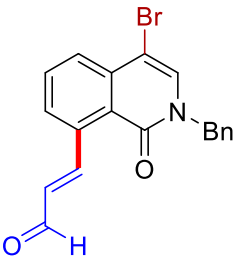
Light yellow solid. yield = 72.4 mg (82%). Mp = 150–152 °C. Isolated from flash chromatography (22% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.86 (d, J = 8.0 Hz, 1H), 9.20 (d, J = 15.5 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.27 – 7.25 (m, 1H), 7.20 – 7.11 (m, 8H), 7.06 – 7.02 (m, 3H), 6.90 – 6.88 (m, 4H), 6.52 (dd, J = 15.5, 8.0 Hz, 1H), 5.19 (s (broad), 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.8, 162.8, 156.0, 142.4, 139.2, 137.9, 137.4, 136.4, 134.1, 132.0, 131.6, 130.6, 130.2, 128.4, 128.27, 128.21, 127.8, 127.4, 127.18, 127.12, 126.7, 122.6, 119.5, 49.5. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{31}H_{24}NO_2$, 442.1802; found, 442.1798.

3-(2-benzyl-4-chloro-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3h).



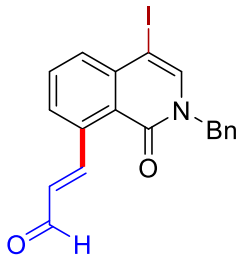
Yellow solid. yield = 58.2 mg (90%). Mp = 145–148 °C. Isolated from flash chromatography (18% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.84 (d, J = 7.5 Hz, 1H), 9.05 (d, J = 16.0 Hz, 1H), 7.97 (dd, J = 8.0, 1.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.60 (dt, J = 7.5, 1.0 Hz, 1H), 7.38 – 7.31 (m, 5H), 7.30 (s, 1H), 6.47 (dd, J = 15.5, 8.0 Hz, 1H), 5.18 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.4, 161.3, 154.7, 138.3, 136.3, 135.9, 132.7, 131.0, 130.0, 129.1, 128.5, 128.4, 128.0, 125.9, 123.5, 111.5, 52.0. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{19}H_{14}ClNNaO_2$, 346.0605; found, 346.0603.

3-(2-benzyl-4-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3i).



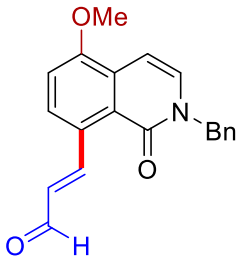
Light yellow solid. yield = 64.1 mg (87%). Mp = 156–158 °C. Isolated from flash chromatography (12% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.85 (d, J = 7.8 Hz, 1H), 9.04 (d, J = 15.6 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.43 (s, 1H), 7.39 – 7.36 (m, 2H), 7.34 – 7.31 (m, 3H), 6.48 (dd, J = 15.6, 7.8 Hz, 1H), 5.18 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 194.4, 161.6, 154.7, 138.4, 137.1, 136.0, 132.9, 132.7, 131.1, 129.2, 128.6, 128.4, 128.0, 123.9, 100.1, 52.1. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{19}H_{14}BrNNaO_2$, 390.0100; found, 390.0101.

3-(2-benzyl-4-iodo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3j).



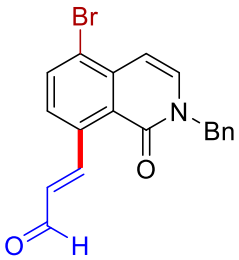
Light yellow solid. yield = 73.9 mg (89%). Mp = 176–177 °C. Isolated from flash chromatography (15% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.84 (d, J = 8.0 Hz, 1H), 9.02 (d, J = 16.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 6.46 (dd, J = 15.5, 8.0 Hz, 1H), 5.17 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.5, 161.8, 154.9, 138.6, 138.5, 138.4, 136.0, 133.4, 133.0, 131.0, 129.1, 128.6, 128.4, 127.9, 123.9, 72.0, 52.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{15}INO_2$, 416.0142; found, 416.0146.

3-(2-benzyl-5-methoxy-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3k).



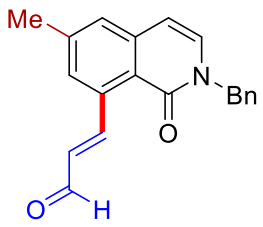
Light yellow solid. yield = 54.9 mg (86%). Mp = 174–175 °C. Isolated from flash chromatography (12% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.79 (d, J = 8.0 Hz, 1H), 9.19 (d, J = 16.0 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.14 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.46 (dd, J = 15.5, 8.0 Hz, 1H), 5.20 (s, 2H), 3.97 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.8, 162.3, 156.3, 155.3, 136.5, 131.6, 129.9, 129.1, 129.0, 128.1, 128.0, 127.8, 124.4, 111.0, 100.7, 56.1, 52.1. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_3$, 342.1101; found, 342.1103.

3-(2-benzyl-5-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3l).



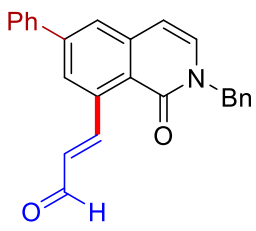
Yellow solid. yield = 59.6 mg (81%). Mp = 171–173 °C. Isolated from flash chromatography (13% EtOAc/*n*-hexane). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 9.84 (d, J = 7.8 Hz, 1H), 9.16 (d, J = 16.2 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.31 (d, J = 7.2 Hz, 3H), 7.15 (d, J = 7.2 Hz, 1H), 6.52 – 6.48 (m, 2H), 5.21 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ): 194.7, 162.5, 155.2, 138.9, 137.9, 136.6, 132.1, 132.0, 130.7, 129.0, 128.8, 128.1, 127.9, 127.4, 123.6, 106.7, 52.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{15}BrNO_2$, 368.0281; found, 368.0280.

3-(2-benzyl-6-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3m).



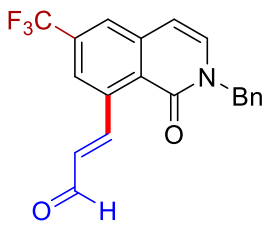
Light yellow solid. yield = 53.4 mg (88%). Mp = 133–136 °C. Isolated from flash chromatography (9% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.82 (d, J = 8.0 Hz, 1H), 9.15 (d, J = 16.0 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.30 – 7.27 (m, 3H), 7.11 (d, J = 7.5 Hz, 1H), 6.48 (dd, J = 16.0, 8.0 Hz, 1H), 6.44 (d, J = 7.0 Hz, 1H), 5.18 (s, 2H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.7, 162.4, 155.4, 142.5, 139.0, 137.6, 136.7, 132.1, 130.5, 129.0, 128.9, 128.5, 128.0, 127.8, 121.4, 106.5, 51.8, 21.6. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{20}H_{17}NNaO_2$, 326.1151; found, 326.1151.

3-(2-benzyl-1-oxo-6-phenyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3n).



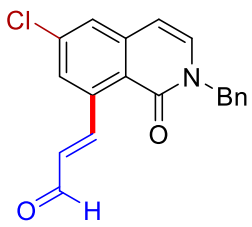
Light yellow solid. yield = 65.8 mg (90%). Mp = 174–175 °C. Isolated from flash chromatography (12% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.87 (d, J = 8.0 Hz, 1H), 9.20 (d, J = 16.0 Hz, 1H), 7.76 – 7.75 (m, 2H), 7.68 – 7.65 (m, 2H), 7.52 – 7.49 (m, 2H), 7.46 – 7.42 (m, 1H), 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.17 (d, J = 7.5 Hz, 1H), 6.59 – 6.54 (m, 2H), 5.22 (s, 2H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.6, 162.4, 155.2, 144.7, 139.4, 139.1, 138.4, 136.6, 132.5, 130.9, 129.2, 129.0, 128.8, 128.1, 127.8, 127.4, 126.6, 126.5, 122.3, 106.9, 51.9. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{25}H_{19}NNaO_2$, 388.1308; found, 388.1308.

3-(2-benzyl-1-oxo-6-(trifluoromethyl)-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3o).



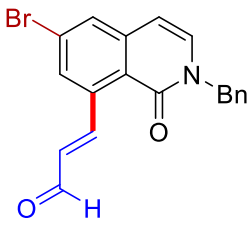
Light yellow solid. yield = 64.3 mg (90%). Mp = 149–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.86 (dd, J = 8.0, 1.0 Hz, 1H), 9.07 (d, J = 16.0 Hz, 1H), 7.83 (s, 1H), 7.69 (s, 1H), 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 3H), 7.25 – 7.24 (m, 1H), 6.58 (d, J = 7.5 Hz, 1H), 6.52 (ddd, J = 16.0, 8.0, 1.0 Hz, 1H), 5.21 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.1, 161.8, 153.4, 139.3, 139.0, 136.1, 133.8 (q, $J_{C–F}$ = 33.75 Hz, 1C), 133.5, 131.6, 129.1, 128.3, 127.9, 125.4, 123.3 (q, $J_{C–F}$ = 271.2 Hz, 1C), 123.1, 106.3, 52.3. ^{19}F NMR (471 MHz, $CDCl_3$, δ): -63.17 (s, 3F). HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{20}H_{14}F_3NNaO_2$, 380.0869; found, 380.0863.

3-(2-benzyl-6-chloro-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3p).



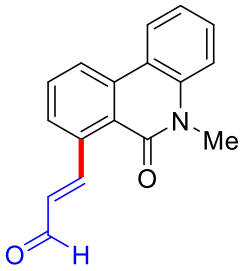
Light yellow solid. yield = 56.3 mg (87%). Mp = 148–150 °C. 1H NMR (500 MHz, $CDCl_3$, δ): 9.83 (d, J = 7.5 Hz, 1H), 9.03 (d, J = 15.5 Hz, 1H), 7.55 (d, J = 2.5 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.32 – 7.28 (m, 3H), 7.17 (d, J = 7.0 Hz, 1H), 6.47 (dd, J = 15.5, 8.0 Hz, 1H), 6.43 (d, J = 7.0 Hz, 1H), 5.18 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ): 194.3, 162.0, 153.5, 140.1, 139.8, 138.3, 136.3, 133.3, 131.3, 129.1, 128.2, 127.9, 127.5, 127.4, 121.9, 105.7, 52.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$, 324.0786; found, 324.0776.

3-(2-benzyl-6-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (Table 2, Entry 3q).



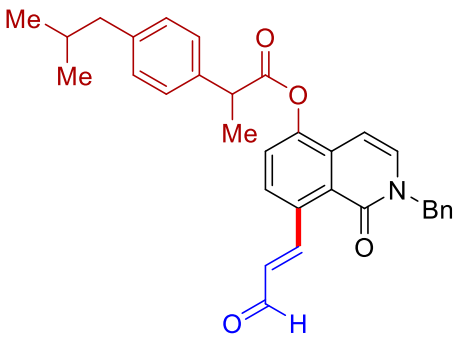
Light yellow solid. yield = 60.4 mg (82%). Mp = 194–195 °C. Isolated from flash chromatography (12% EtOAc/*n*-hexane). ^1H NMR (500 MHz, $CDCl_3$, δ): 9.83 (d, J = 8.0 Hz, 1H), 9.02 (d, J = 16.0 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.62 (d, J = 2.5 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 3H), 7.17 (d, J = 7.5 Hz, 1H), 6.46 (dd, J = 15.5, 7.5 Hz, 1H), 6.42 (d, J = 7.5 Hz, 1H), 5.18 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ): 194.2, 162.1, 153.4, 140.1, 139.8, 136.2, 133.3, 131.4, 130.7, 130.1, 129.1, 128.2, 127.9, 126.8, 122.2, 105.6, 52.1. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{19}H_{14}BrNNaO_2$, 390.0100; found, 390.0100.

3-(5-methyl-6-oxo-5,6-dihydrophenanthridin-7-yl)acrylaldehyde (Table 2, Entry 3r).



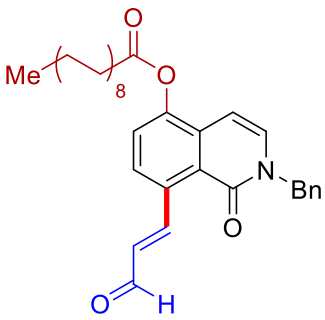
Light yellow solid. yield = 42.7 mg (81%). Mp = 197–198 °C. Isolated from flash chromatography (10% EtOAc/*n*-hexane). ^1H NMR (500 MHz, $CDCl_3$, δ): 9.86 (d, J = 8.0 Hz, 1H), 8.97 (d, J = 16.0 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.28 (dd, J = 8.0, 1.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.41 (dd, J = 8.5, 1.0 Hz, 1H), 7.34 (ddd, J = 8.0, 7.5, 1.0 Hz, 1H), 6.44 (dd, J = 15.5, 8.0 Hz, 1H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, δ): 194.6, 161.8, 156.2, 138.5, 138.0, 135.2, 132.2, 130.3, 130.2, 128.8, 124.0, 123.8, 123.1, 122.9, 118.8, 115.1, 30.2. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{17}H_{13}NNaO_2$, 286.0838; found, 286.0837.

2-benzyl-1-oxo-8-(3-oxoprop-1-en-1-yl)-1,2-dihydroisoquinolin-5-yl 2-(4 isobutylphenyl)propanoate (Table 2, Entry 3s).



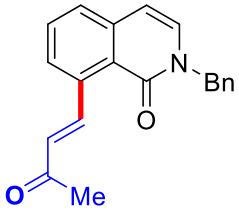
Light yellow solid. yield = 76.0 mg (77%). Mp = 130–132 °C. Isolated from flash chromatography (17% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.81 (d, J = 8.0 Hz, 1H), 9.06 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.32 – 7.29 (m, 3H), 7.25 – 7.22 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.45 (dd, J = 15.5, 8.0 Hz, 1H), 5.93 (d, J = 7.5 Hz, 1H), 5.17 – 5.09 (m, 2H), 4.05 (q, J = 7.0 Hz, 1H), 2.48 (d, J = 7.0 Hz, 2H), 1.88 – 1.77 (m, 1H), 1.66 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.5, 172.7, 161.8, 154.6, 147.0, 141.4, 136.8, 136.2, 135.5, 132.5, 132.1, 130.7, 129.8, 129.0, 128.2, 127.9, 127.5, 127.2, 124.9, 124.6, 99.6, 52.0, 45.4, 45.0, 30.3, 22.4, 18.0. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{32}H_{31}NNaO_4$, 516.2145; found, 516.2149.

2-benzyl-1-oxo-8-(3-oxoprop-1-en-1-yl)-1,2-dihydroisoquinolin-5-yl stearate (Table 2, Entry 3t).



Light yellow solid. yield = 90.3 mg (79%). Mp = 92–94 °C. Isolated from flash chromatography (10% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.83 (d, J = 8.0 Hz, 1H), 9.09 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.31 – 7.28 (m, 3H), 7.17 (d, J = 7.5 Hz, 1H), 6.51 (d, J = 7.5 Hz, 1H), 6.47 (dd, J = 16.0, 8.0 Hz, 1H), 5.20 (s, 2H), 2.67 (t, J = 7.5 Hz, 2H), 1.80 (p, J = 7.5 Hz, 2H), 1.46 – 1.34 (m, 5H), 1.29 – 1.25 (m, 23H), 0.87 (t, J = 7.5 Hz, 3H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 194.6, 171.8, 161.9, 154.6, 147.1, 136.2, 135.5, 132.8, 132.1, 130.8, 129.1, 128.2, 127.9, 127.3, 125.0, 124.7, 99.9, 52.1, 34.4, 32.0, 29.8, 29.7, 29.58, 29.50, 29.3, 29.2, 25.0, 22.8, 14.2. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{37}H_{49}NNaO_4$, 594.3554; found, 594.3554.

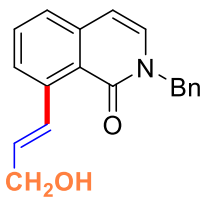
2-benzyl-8-(3-oxobut-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3, 3aa).



White solid. yield = 37 mg (61%). Mp = 146–147 °C. Isolated from flash chromatography (40% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.07 (d, J = 16.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 3H), 7.10 (d, J = 7.5 Hz, 1H), 6.49 (d, J = 7.5 Hz, 1H),

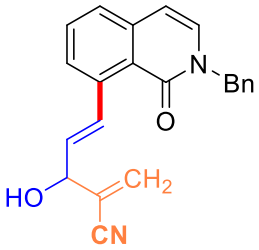
6.40 (d, J = 16.5 Hz, 1H), 5.21 (s, 2H), 2.49 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ): 199.9, 162.5, 146.9, 138.7, 138.6, 136.7, 132.0, 131.9, 130.1, 129.0, 128.1, 128.0, 127.9, 127.4, 123.8, 106.7, 51.6, 26.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{20}H_{18}NO_2$, 304.1332; found, 304.1332.

2-benzyl-8-(3-hydroxyprop-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 4, 4a).



White solid. yield = 45.5 mg (78%). Mp = 94–98 °C. Isolated from flash chromatography (35% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.98 (d, J = 15.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.38 (dd, J = 8.0, 1.0 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.26 – 7.24 (m, 3H), 7.03 (d, J = 7.0 Hz, 1H), 6.43 (d, J = 7.0 Hz, 1H), 6.11 (dt, J = 15.5, 6.0 Hz, 1H), 5.14 (s, 2H), 4.37 (dd, J = 6.0, 1.5 Hz, 2H), 3.07 {s (broad: O-H), 1H}. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ): 162.7, 141.1, 138.5, 136.9, 133.1, 131.9, 131.3, 130.7, 128.8, 127.8, 127.3, 125.9, 123.2, 106.9, 63.8, 51.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{18}NO_2$, 292.1332; found, 292.1334.

5-(2-benzyl-1-oxo-1,2-dihydroisoquinolin-8-yl)-3-hydroxy-2-methylenepent-4-enenitrile (Scheme 4, 4b).



White solid. yield = 50.7 mg (74%). Mp = 101–103 °C. Isolated from flash chromatography (40% EtOAc/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.06 (d, J = 15.5 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.28 – 7.26 (m, 1H), 7.24 – 7.22 (m, 2H), 7.05 (d, J = 7.0 Hz, 1H), 6.47 (d, J = 7.0 Hz, 1H), 6.14 (d, J = 1.5 Hz, 1H), 5.99 (d, J = 1.0 Hz, 1H), 5.94 (dd, J = 15.5, 7.0 Hz, 1H), 5.16 – 5.09 (m, 2H), 5.00 (dq, J = 7.0, 1.5 Hz, 1H), 4.38 (s (broad: O-H),1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ): 162.6, 140.0, 138.5, 136.7, 135.9, 132.1, 131.4, 130.1, 128.9, 127.9, 127.7, 126.6, 125.5, 123.3, 117.5, 107.1, 72.7, 51.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{22}H_{19}N_2O_2$, 343.1441; found, 343.1436.

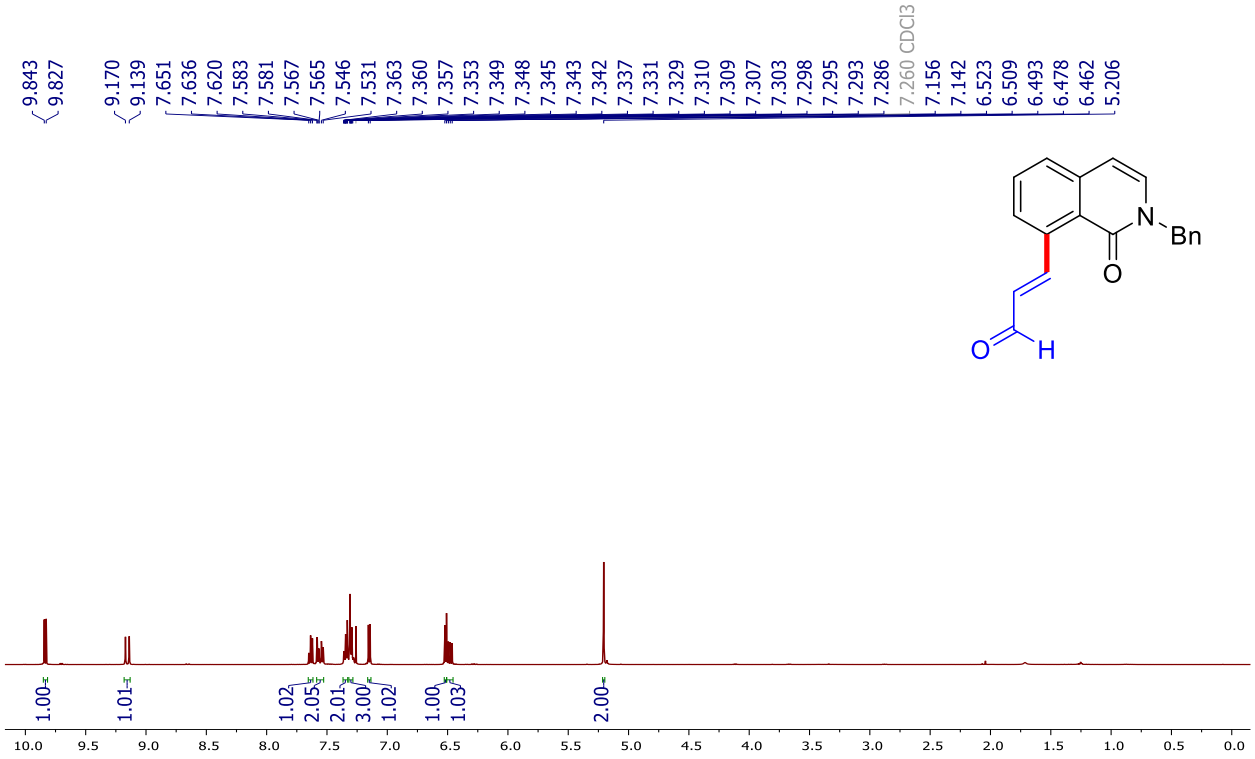
7. References

1. (a) Zhao, P.; Niu, R.; Wang, F.; Han, K.; Li, X., Rhodium(III)-and ruthenium(II)-catalyzed olefination of isoquinolones. *Org. Lett.* **2012,** *14*, 4166-4169; (b) Das, D.; Samanta, R., Iridium (III)-catalyzed regiocontrolled direct amidation of isoquinolones and pyridones. *Adv. Synth. Catal.* **2018,** *360* (2), 379-384; (c) Chandra, D.; Kumar, N.; Parmar, D.; Gupta, P.; Sharma, U., Co(III)-catalyzed regioselective linear C(8)-H olefination of isoquinolone with terminal aromatic and aliphatic alkynes. *ChemComm* **2021,** *57*, 11613-11616; (d) Manisha, Chandra, D.; Sharma, U., Rhodium-catalyzed C8-alkenylation of isoquinolones with maleimides. *Eur. J. Org. Chem.* **2023,** *26*, e202300411.

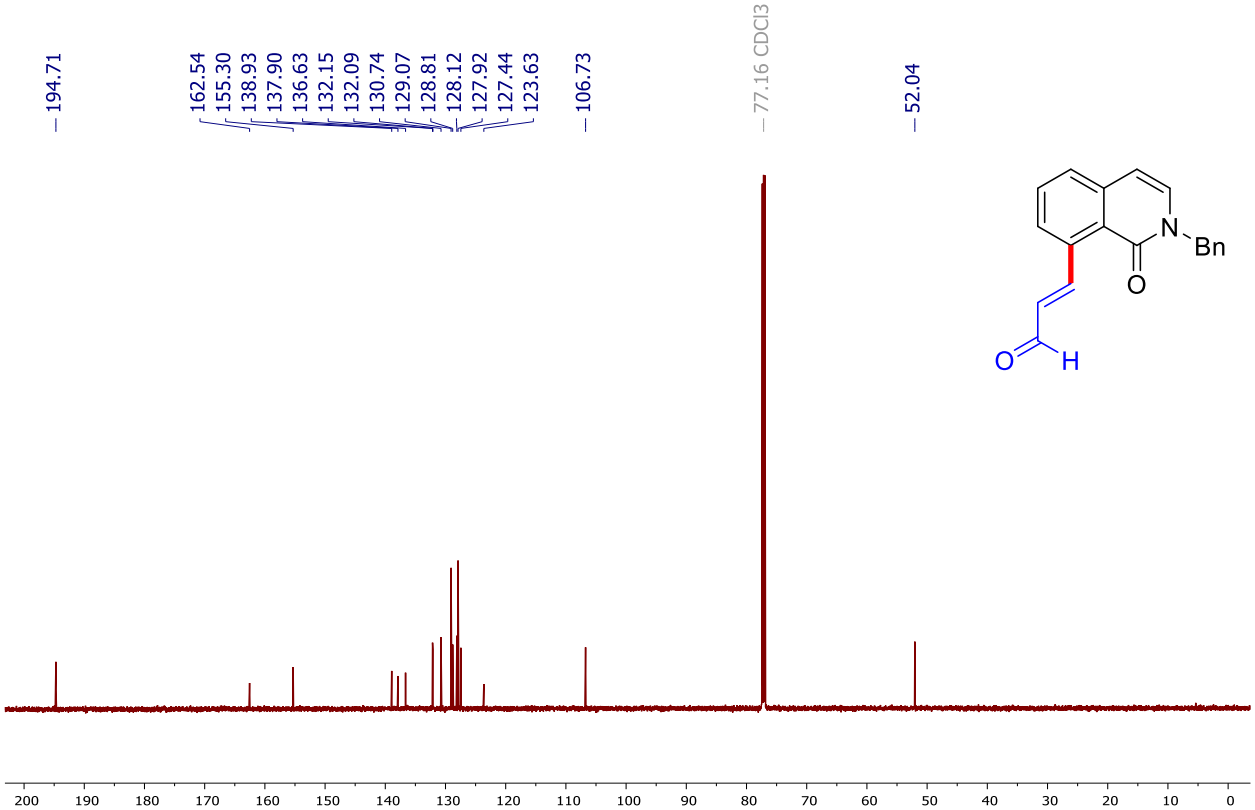
8. Copy of ^{1}H, ^{13}C and ^{19}F NMR spectra

*3-(2-benzyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3a**)*

^{1}H NMR (500 MHz)

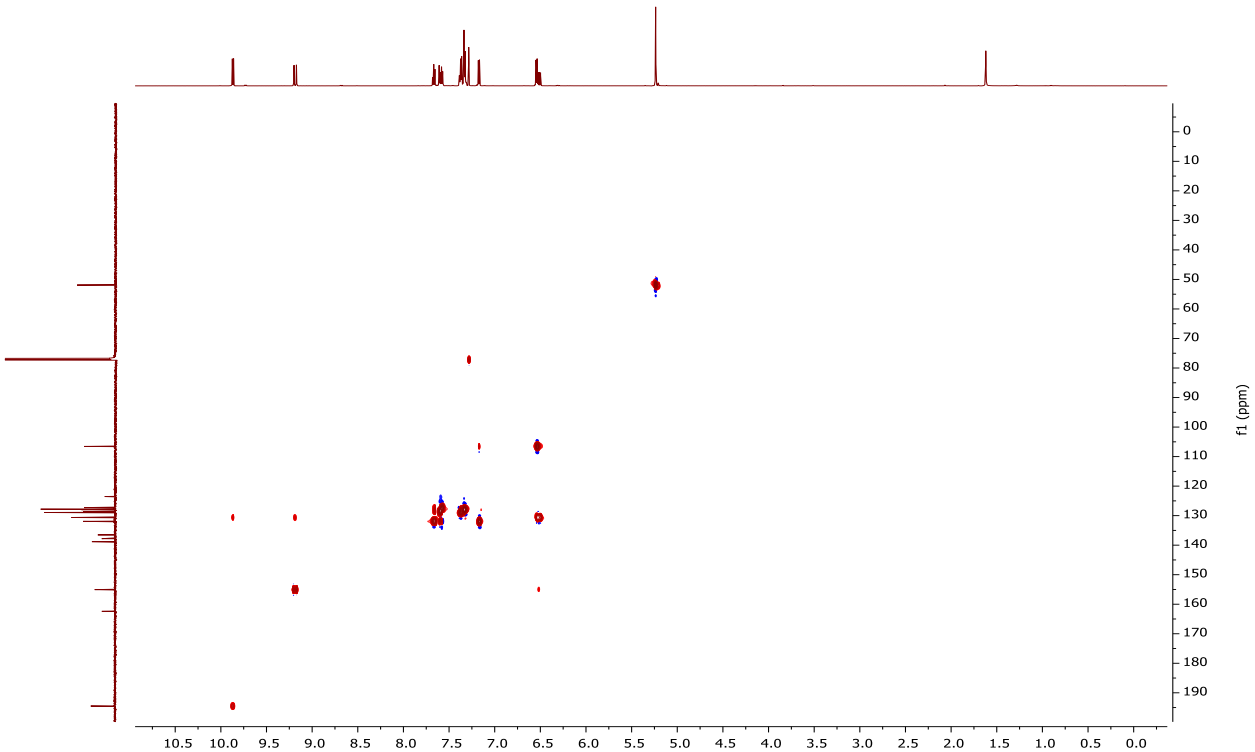


$^{13}C\{^{1}H\}$ NMR (150 MHz)

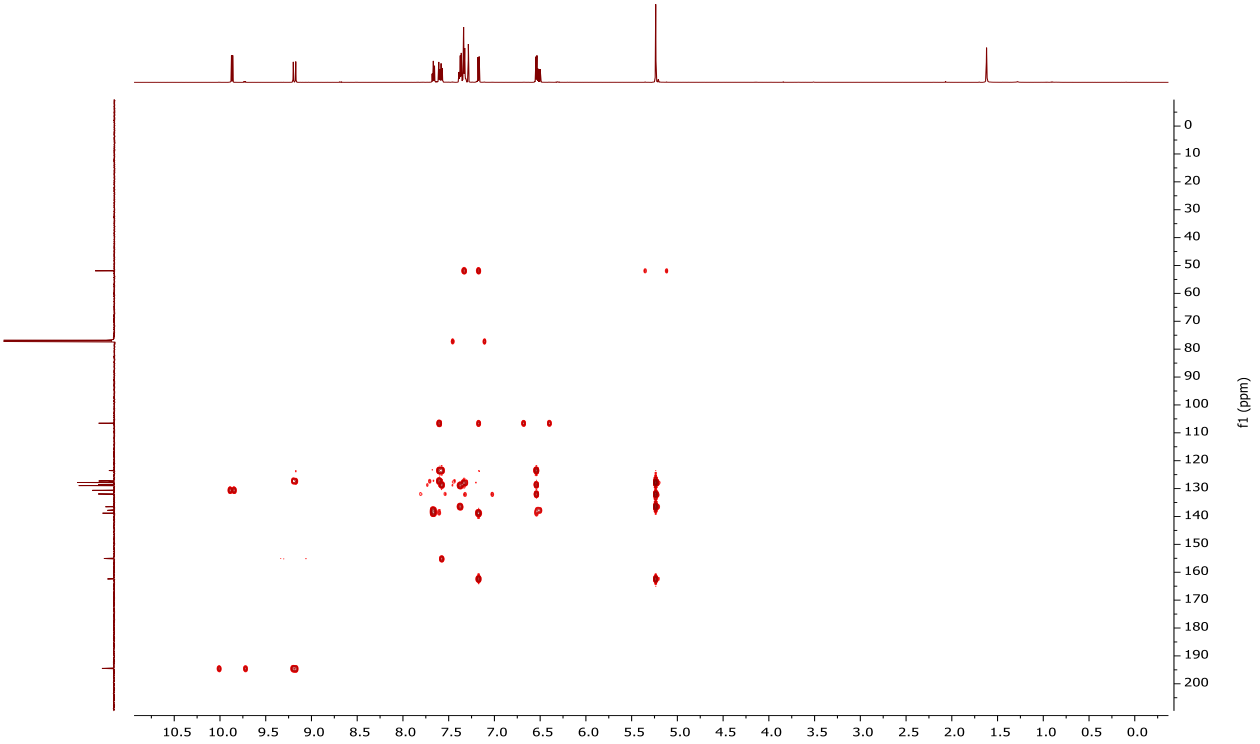


DEPT-135

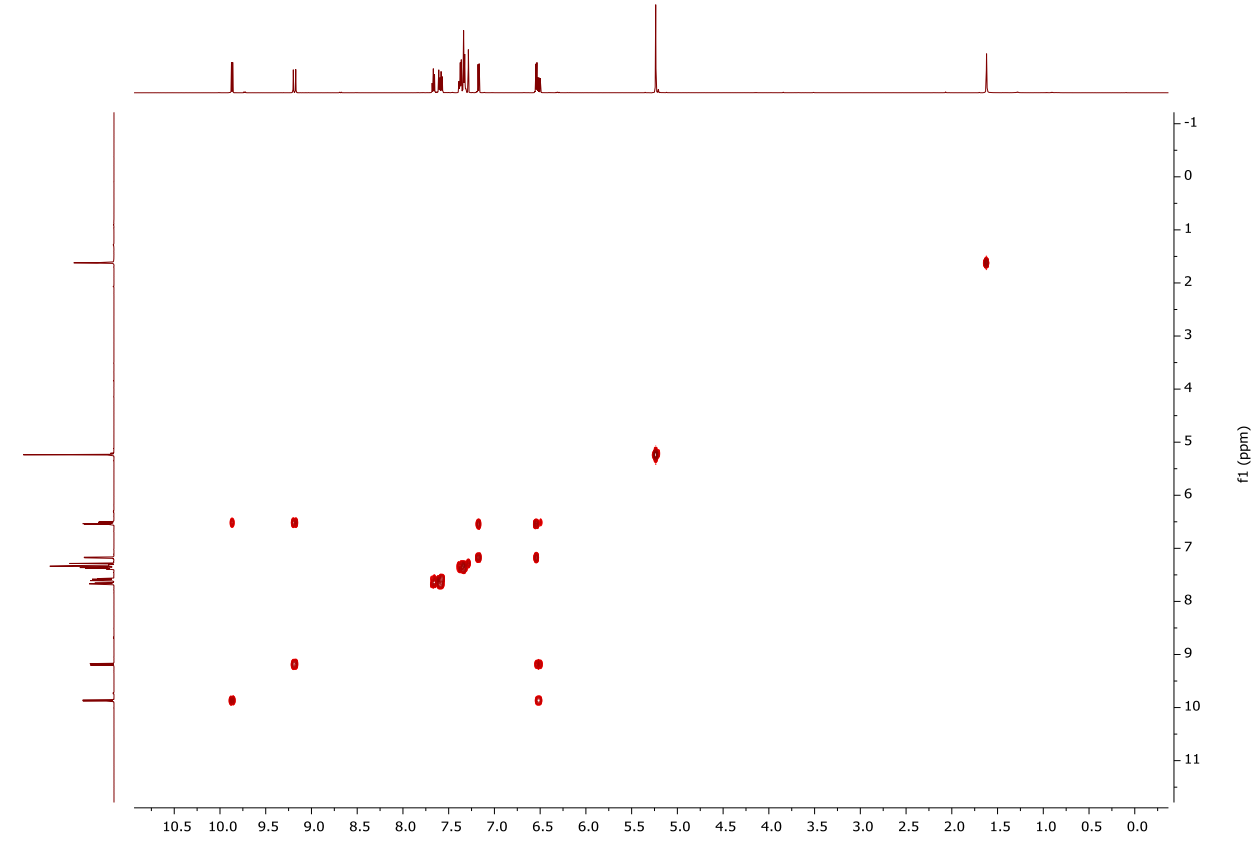
HSQC



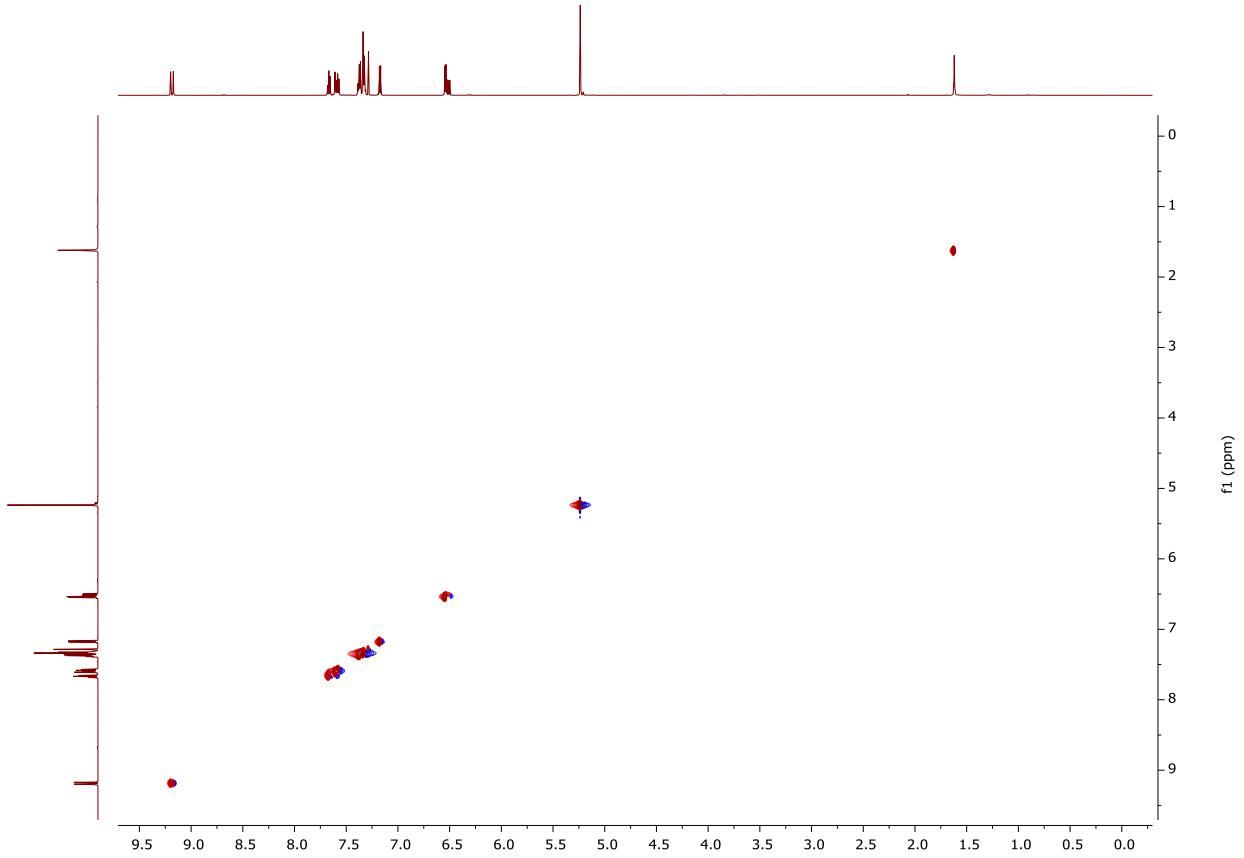
HMBC


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

COSY

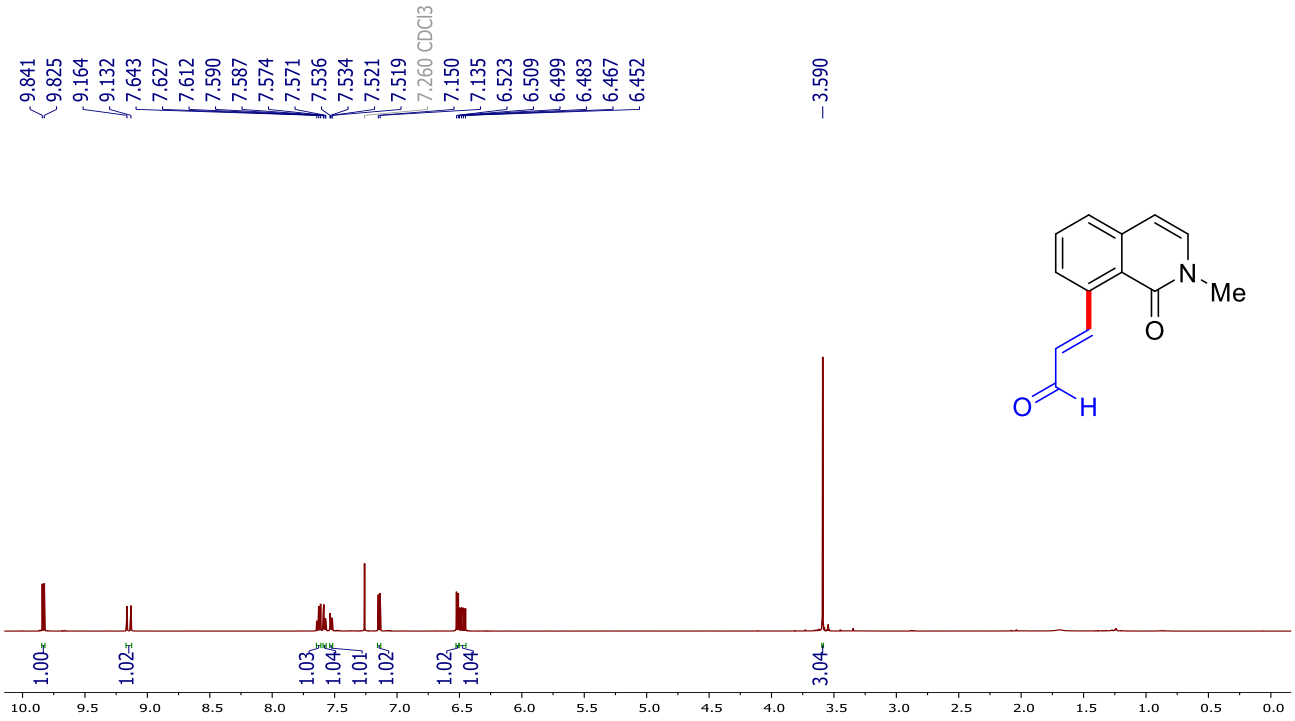

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
-1 0 1 2 3 4 5 6 7 8 9 10 11
f1 (ppm)

NOESY

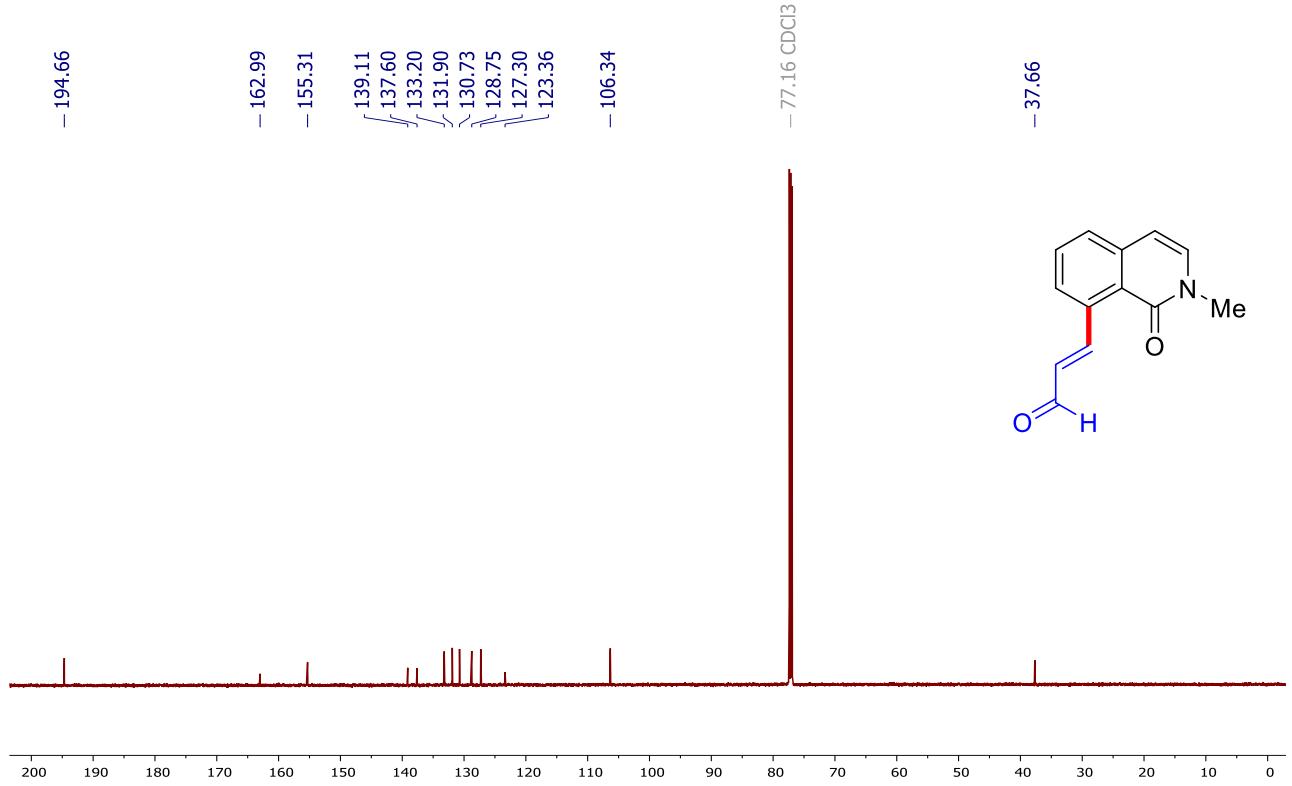


*3-(2-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3b**)*

^{1}H NMR (500 MHz)

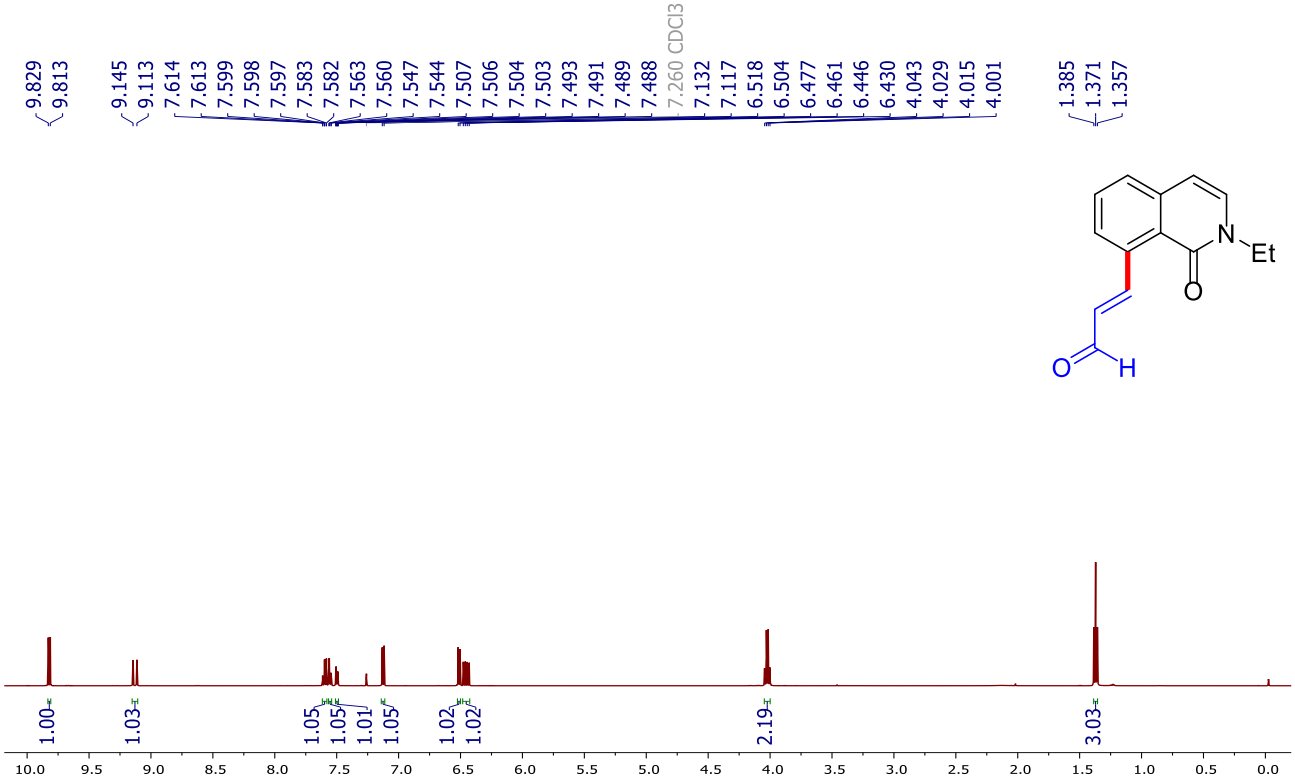


$^{13}C\{^{1}H\}$ NMR (150 MHz)

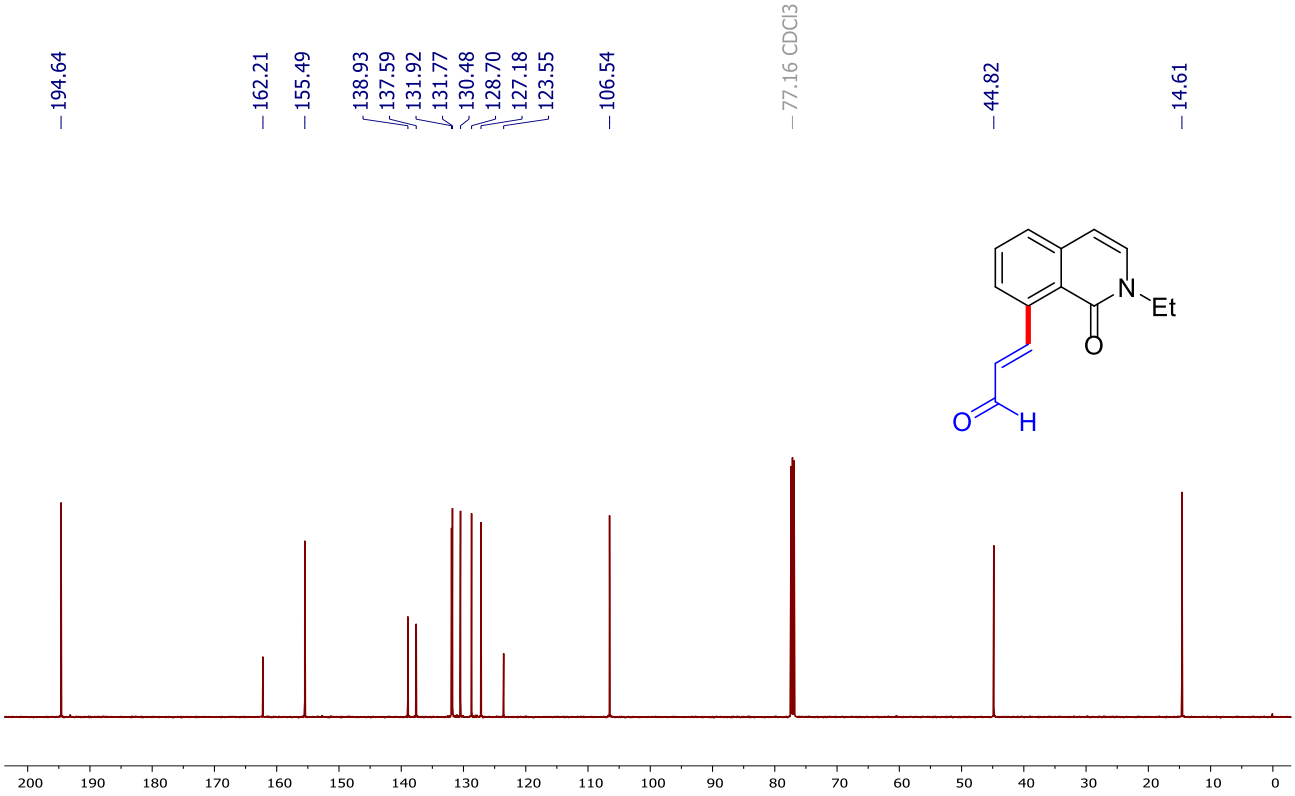


*3-(2-ethyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3c**)*

^{1}H NMR (500 MHz)

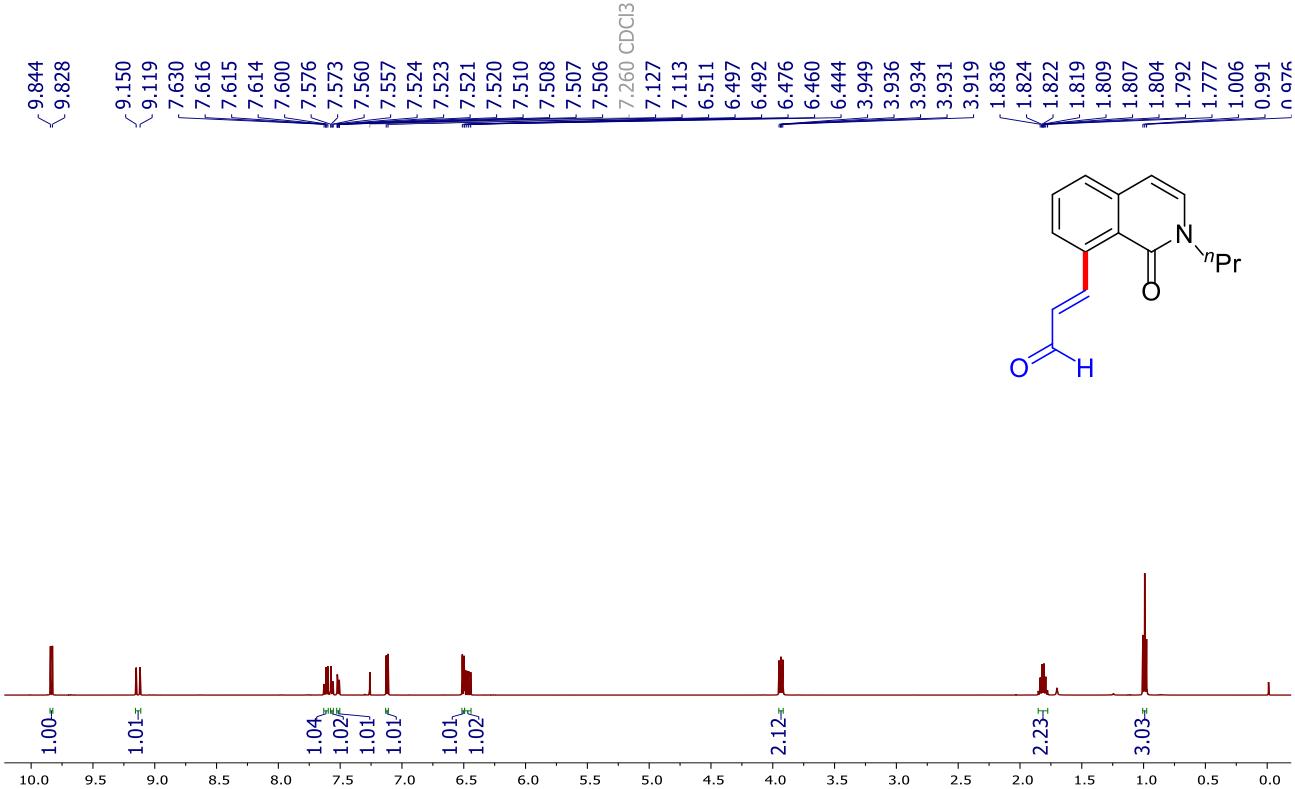


$^{13}C\{^{1}H\}$ NMR (125 MHz)

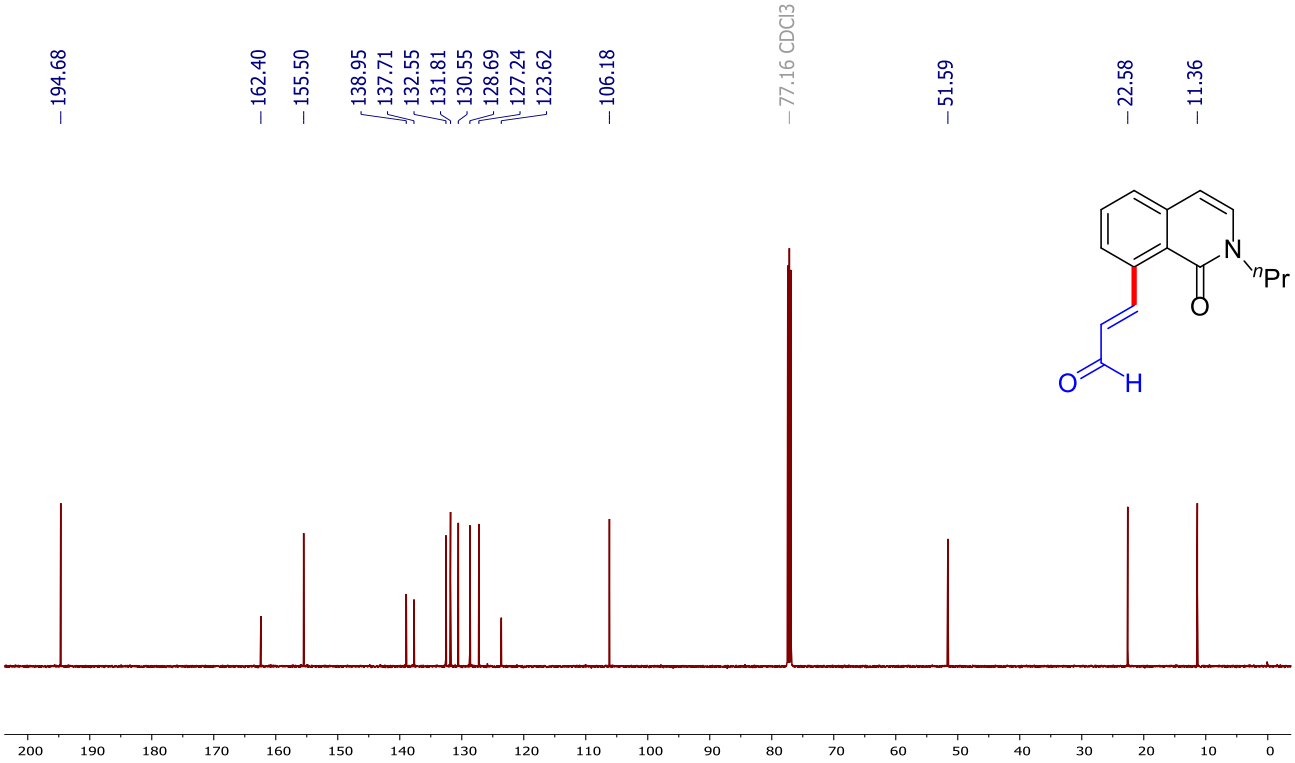


*3-(1-oxo-2-propyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3d**)*

^{1}H NMR (500 MHz)

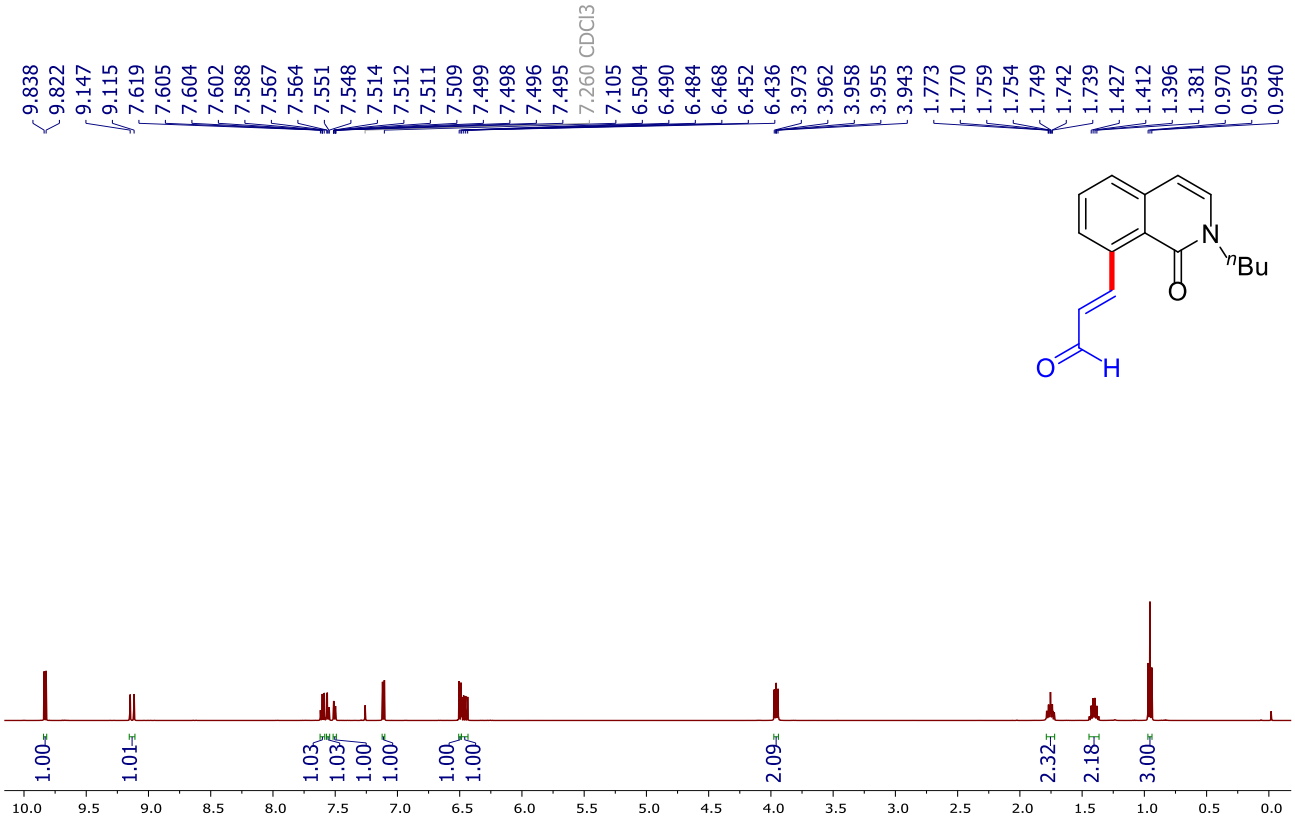


$^{13}C\{^{1}H\}$ NMR (125 MHz)

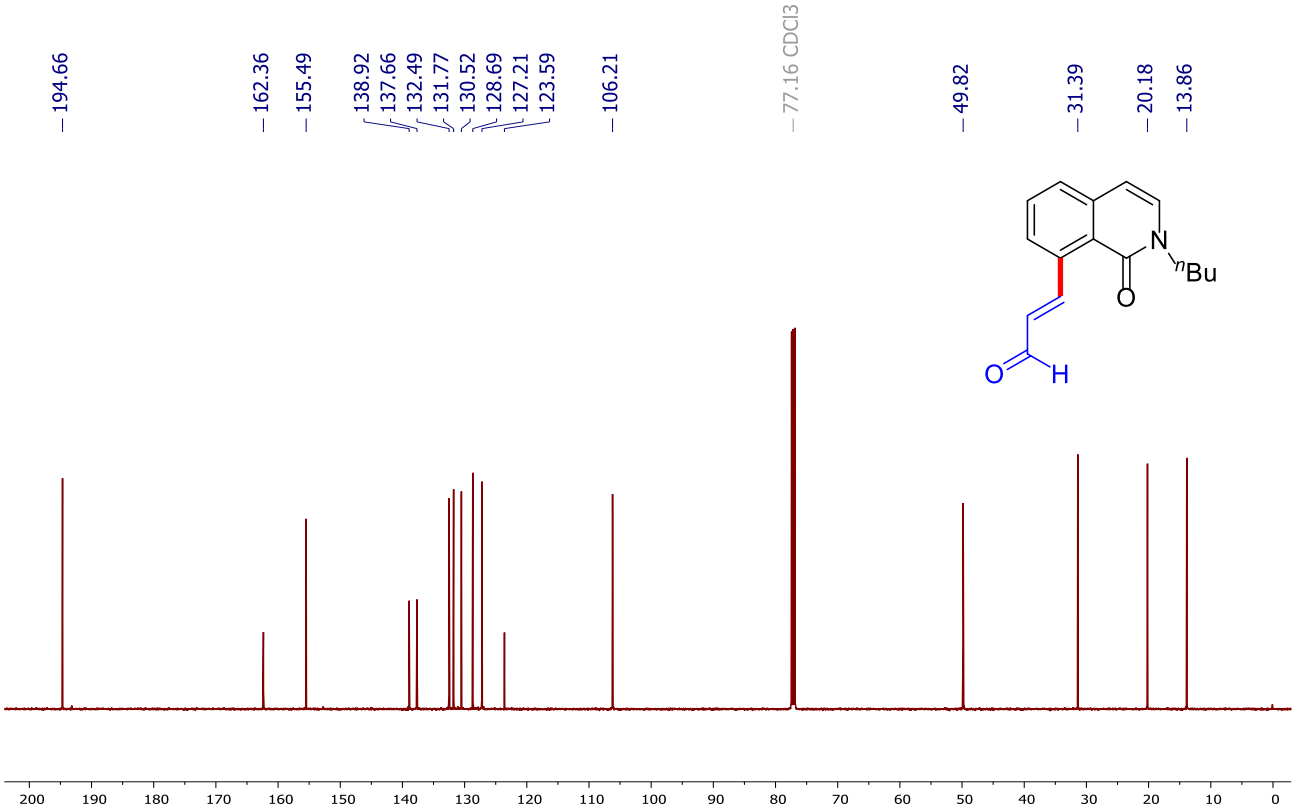


*3-(2-butyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3e**)*

^{1}H NMR (500 MHz)

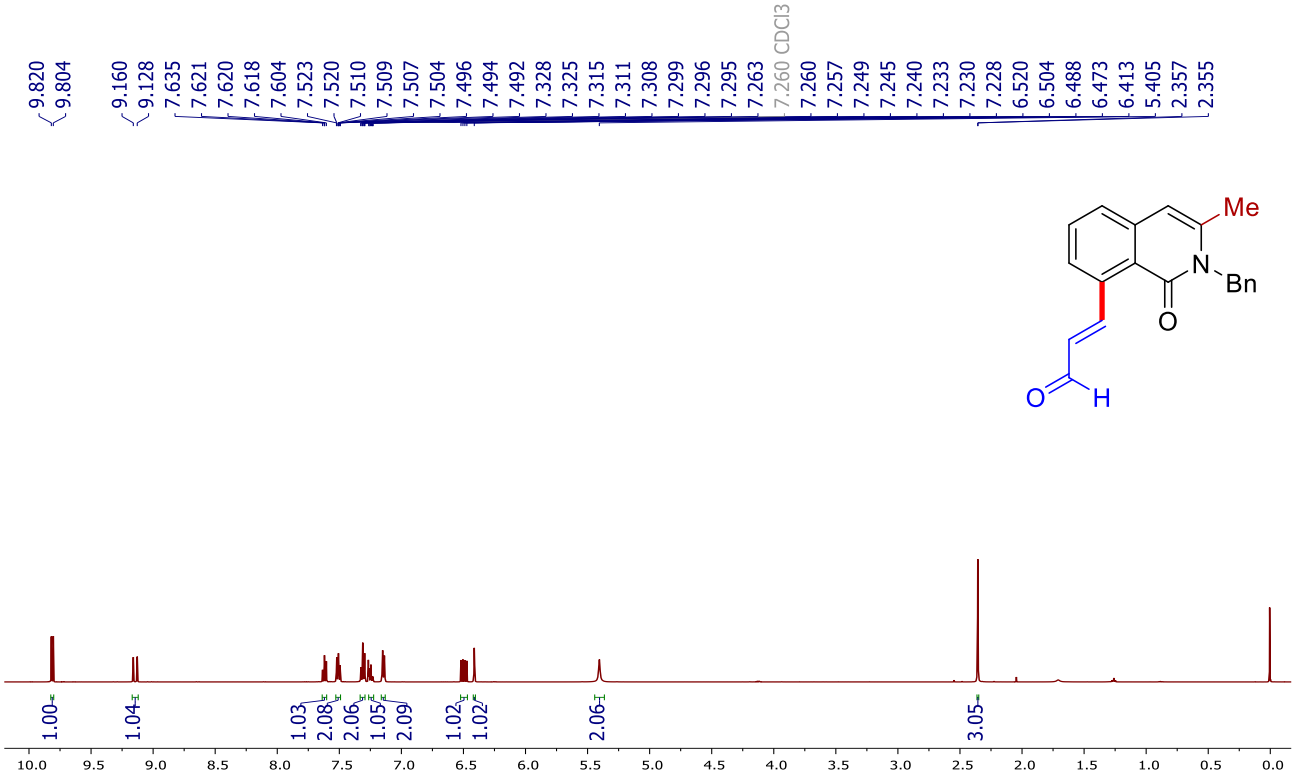


$^{13}C\{^{1}H\}$ NMR (125 MHz)

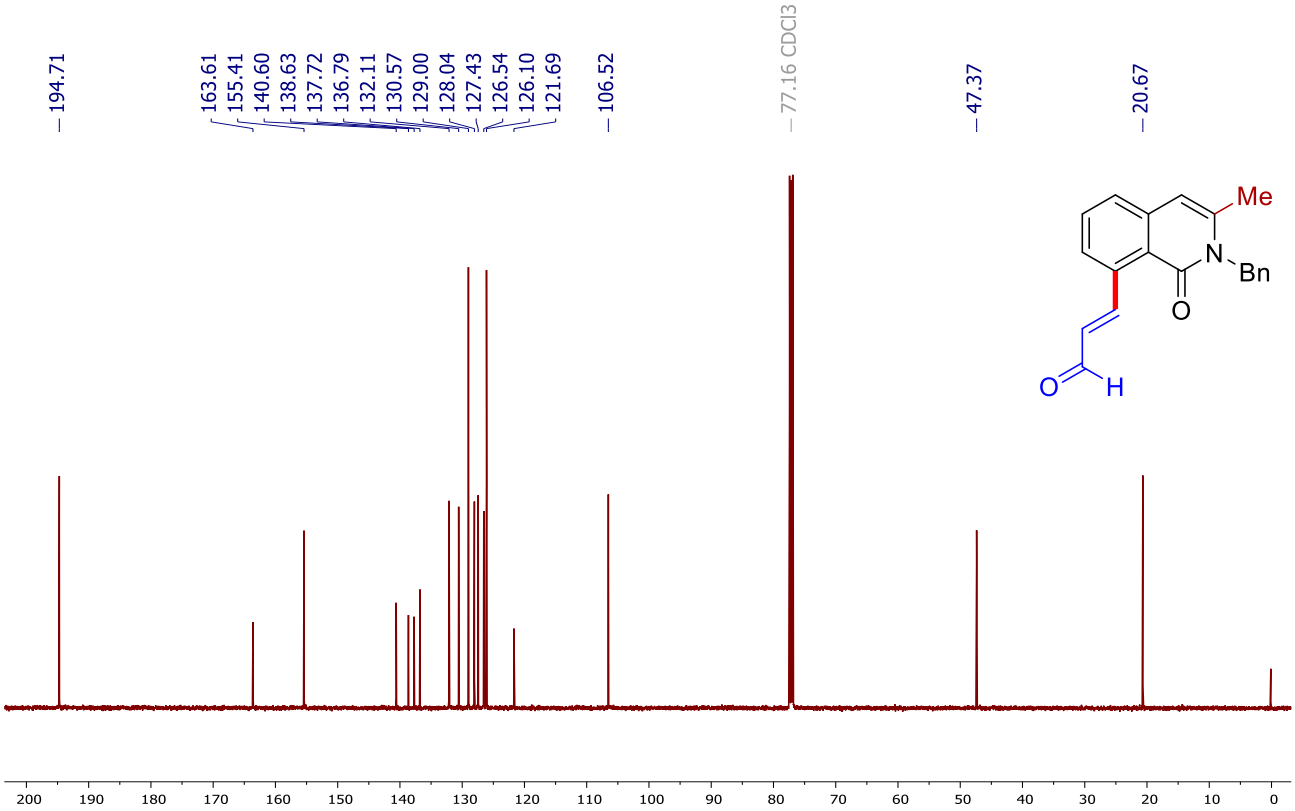


*3-(2-benzyl-3-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3f**)*

^{1}H NMR (500 MHz)

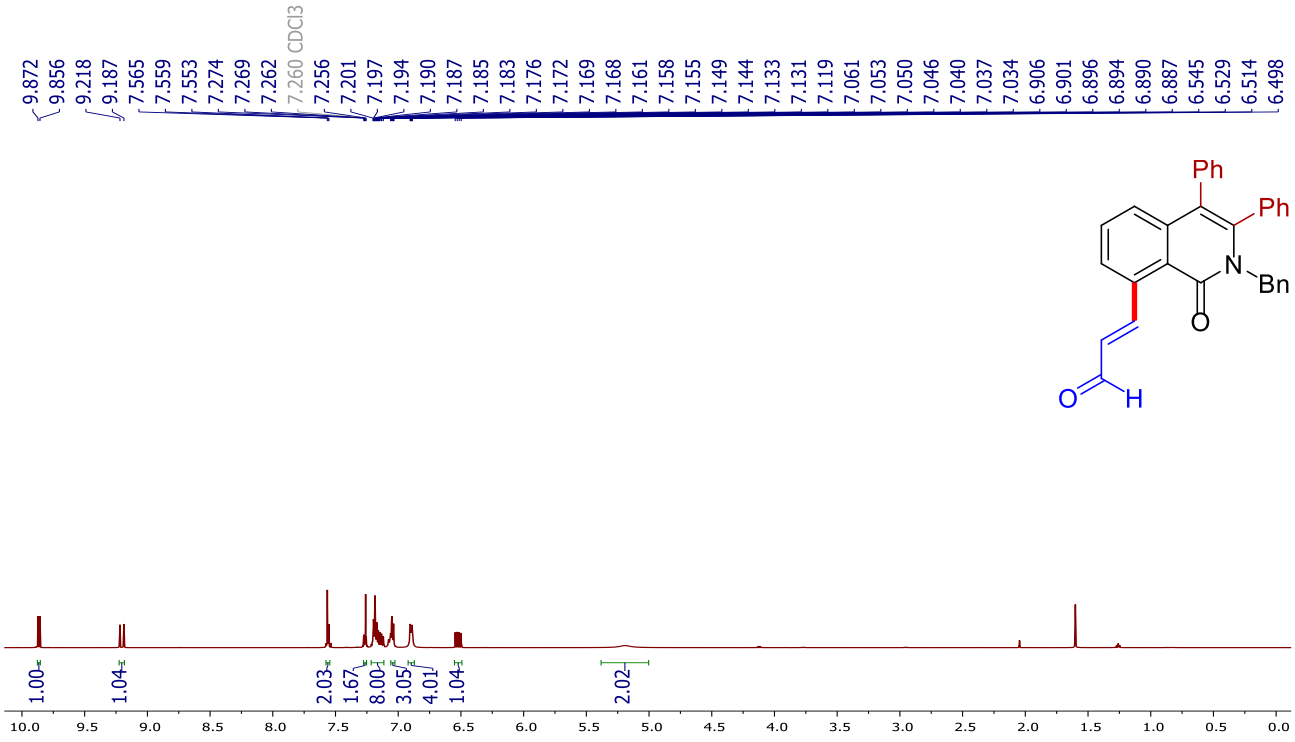


$^{13}C\{^{1}H\}$ NMR (150 MHz)

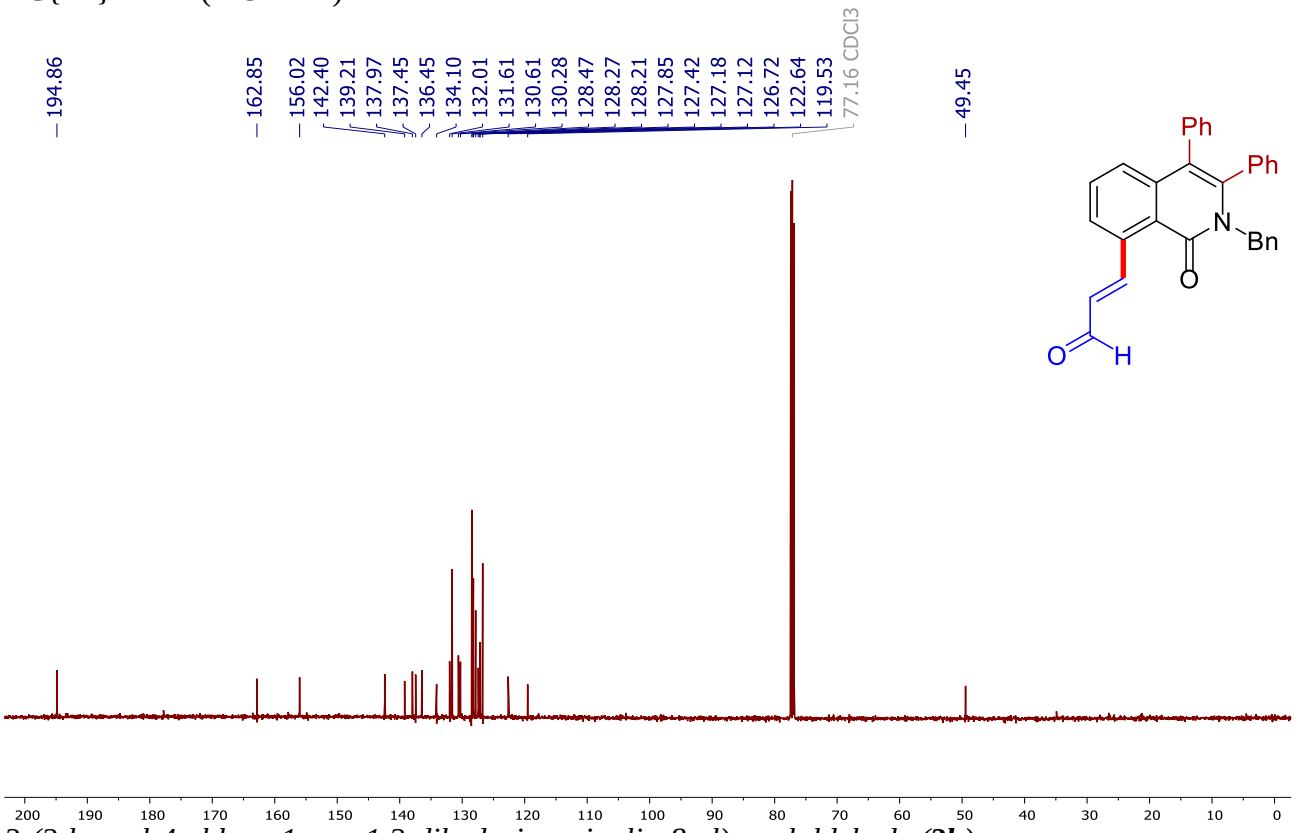


*3-(2-benzyl-1-oxo-3,4-diphenyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3g**)*

^{1}H NMR (500 MHz)

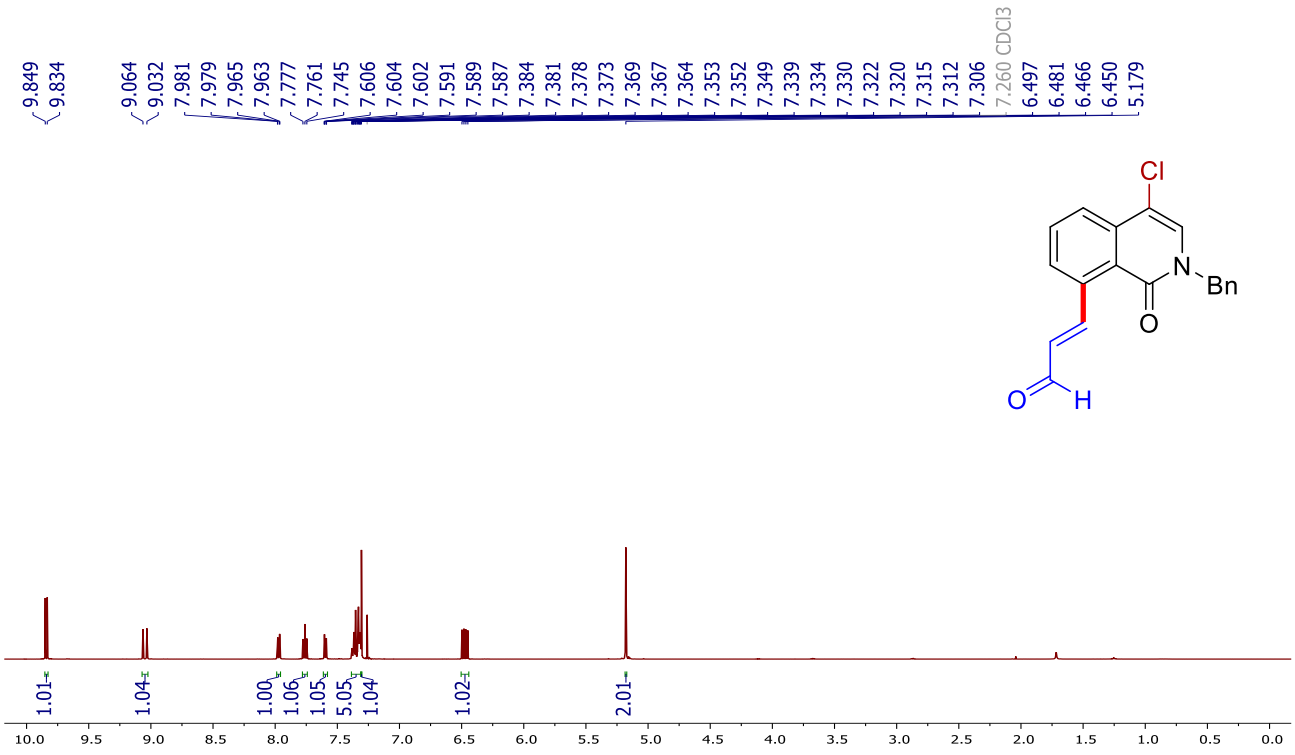


$^{13}C\{^{1}H\}$ NMR (125 MHz)

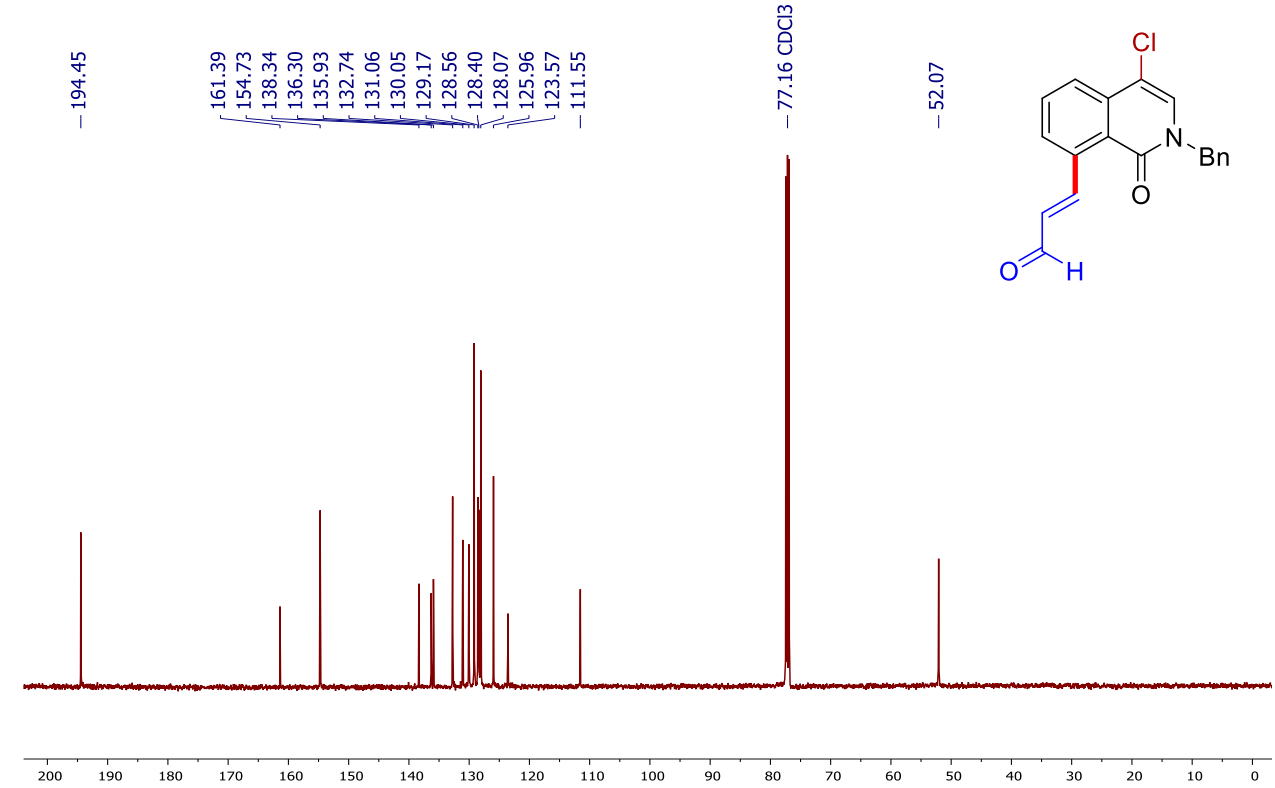


*3-(2-benzyl-4-chloro-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3h**)*

^{1}H NMR (500 MHz)

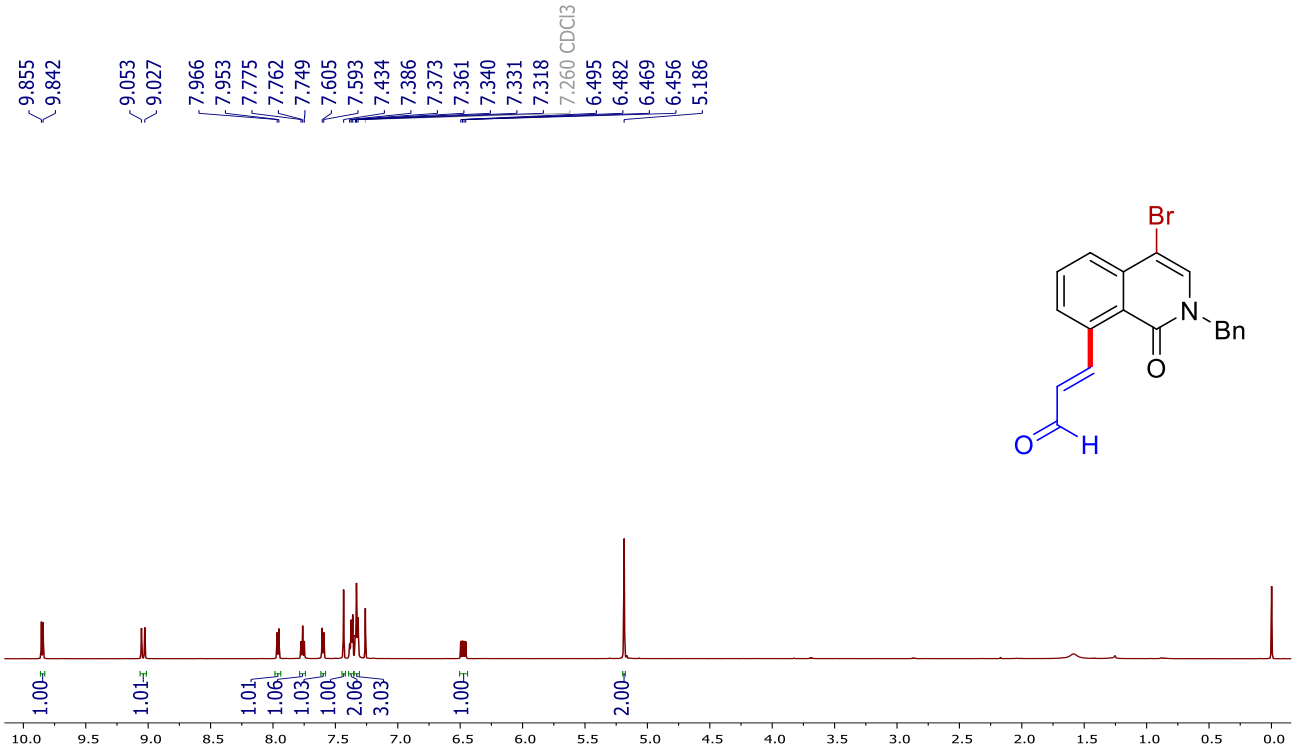


$^{13}C\{^{1}H\}$ NMR (125 MHz)

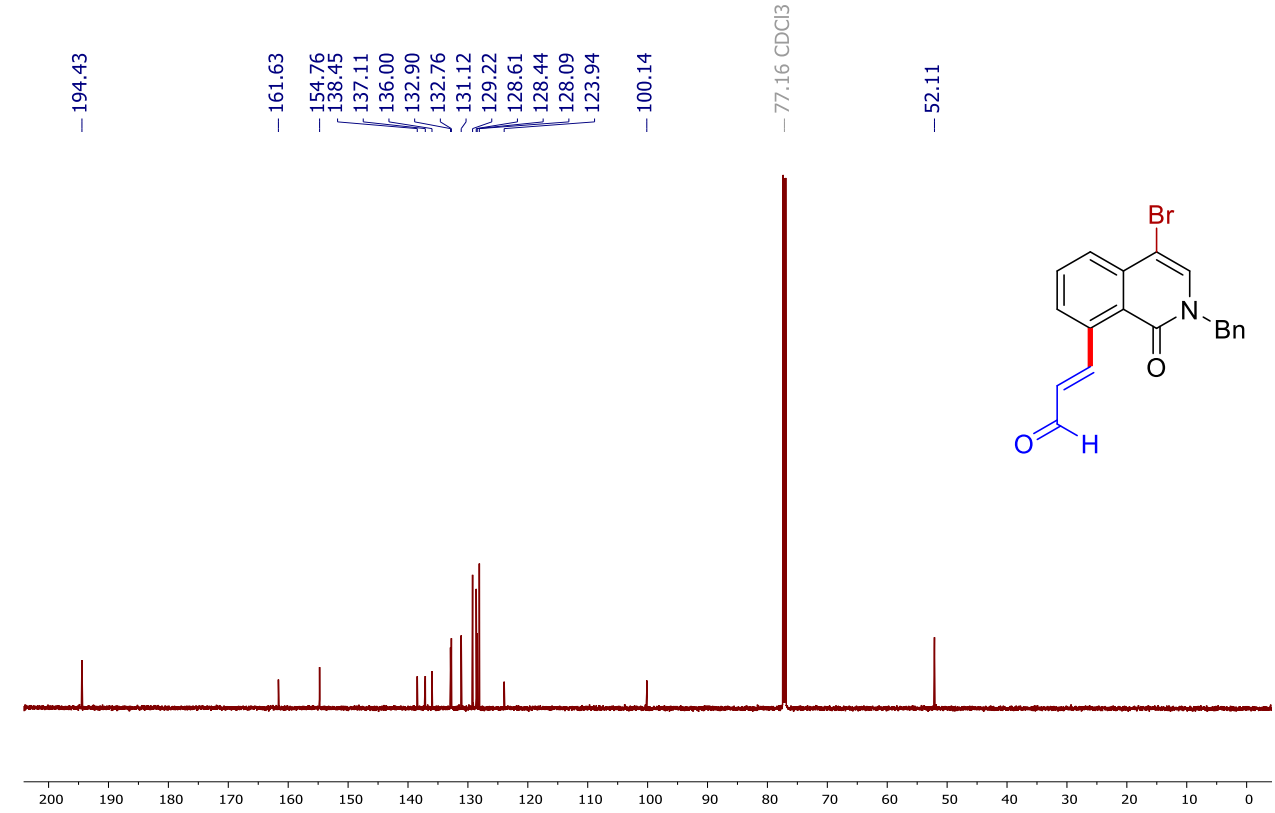


*3-(2-benzyl-4-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3i**)*

^{1}H NMR (600 MHz)

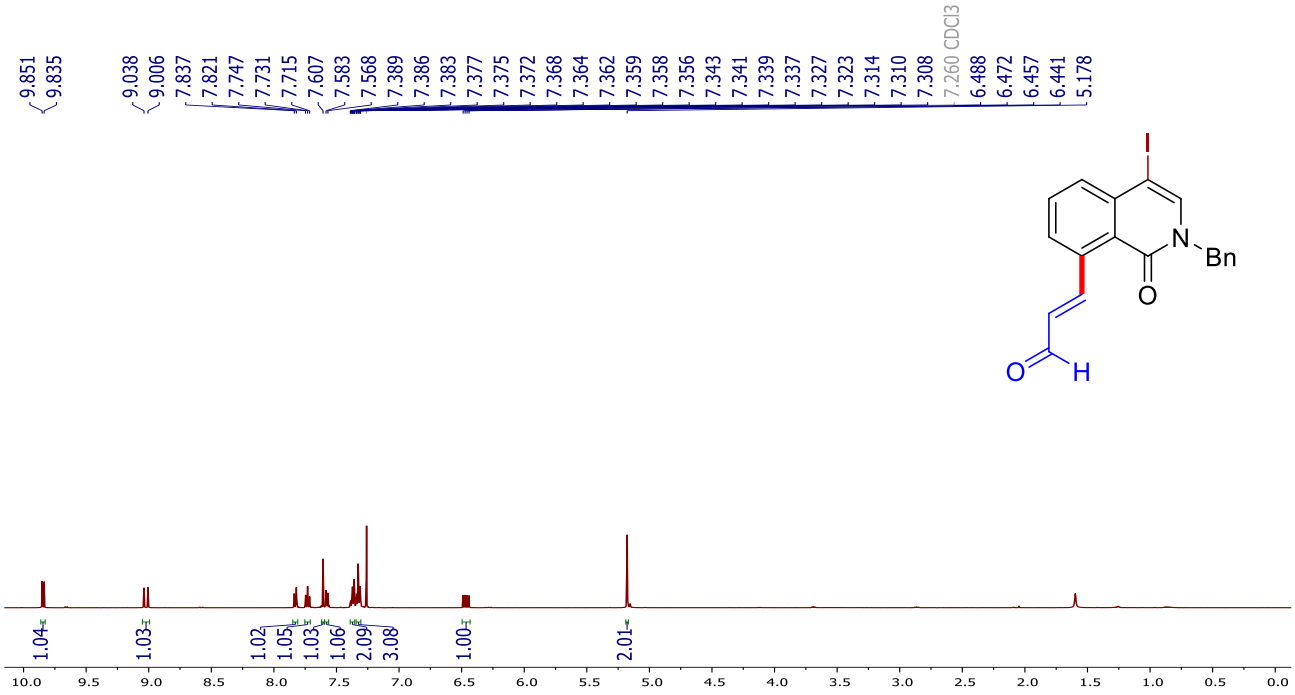


$^{13}C\{^{1}H\}$ NMR (150 MHz)

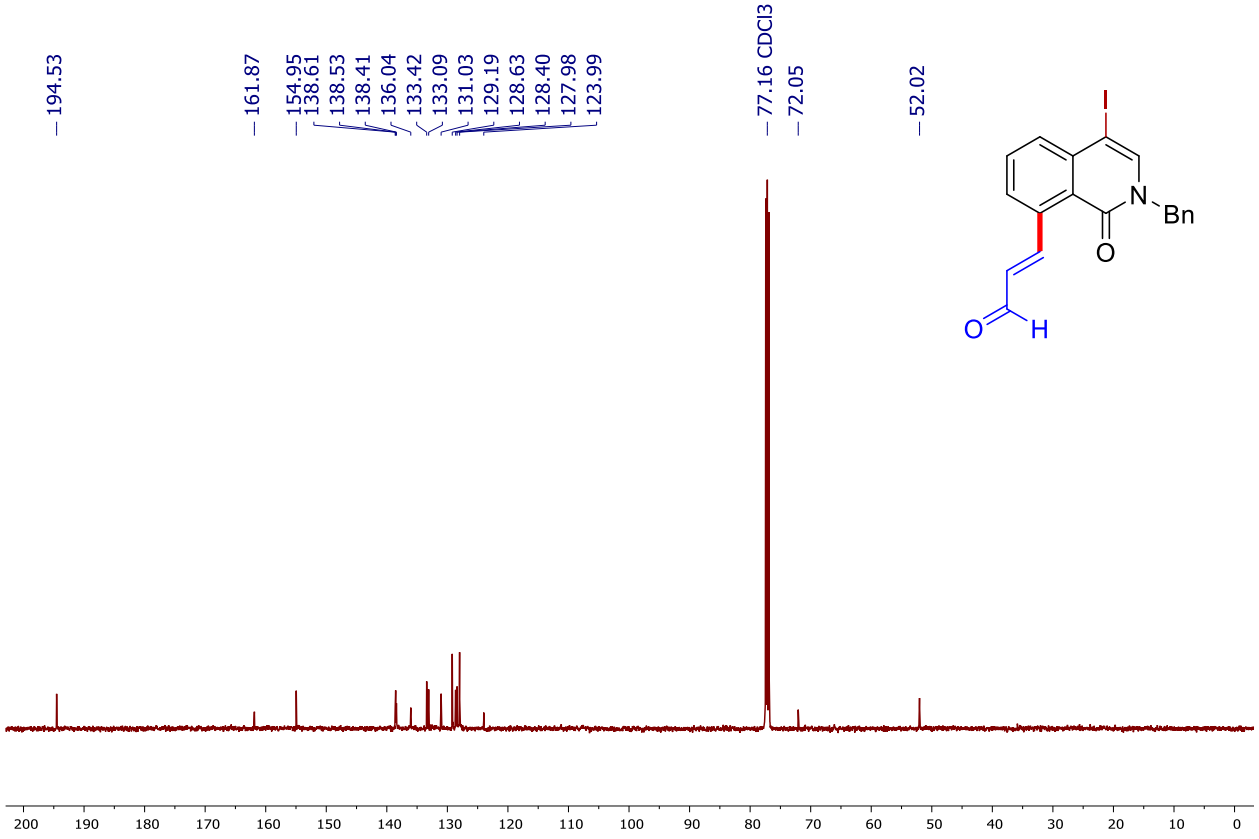


*3-(2-benzyl-4-iodo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3j**)*

^{1}H NMR (500 MHz)

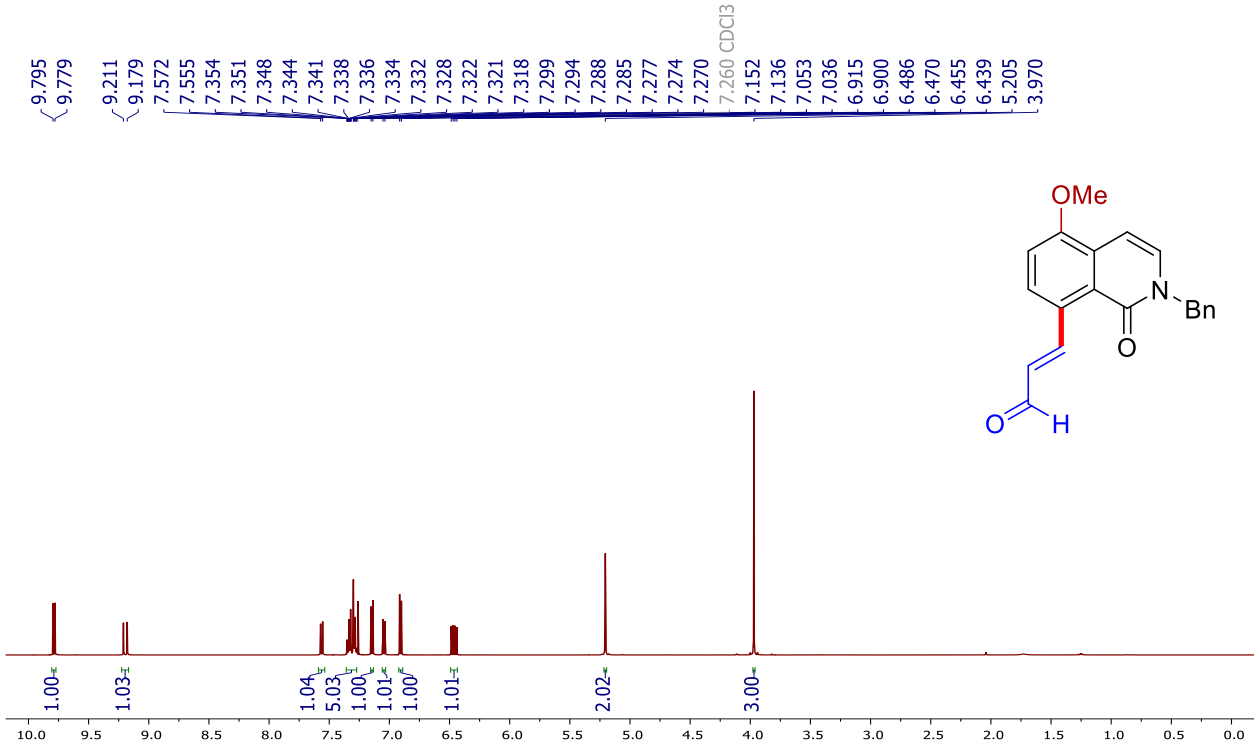


$^{13}C\{^{1}H\}$ NMR (125 MHz)

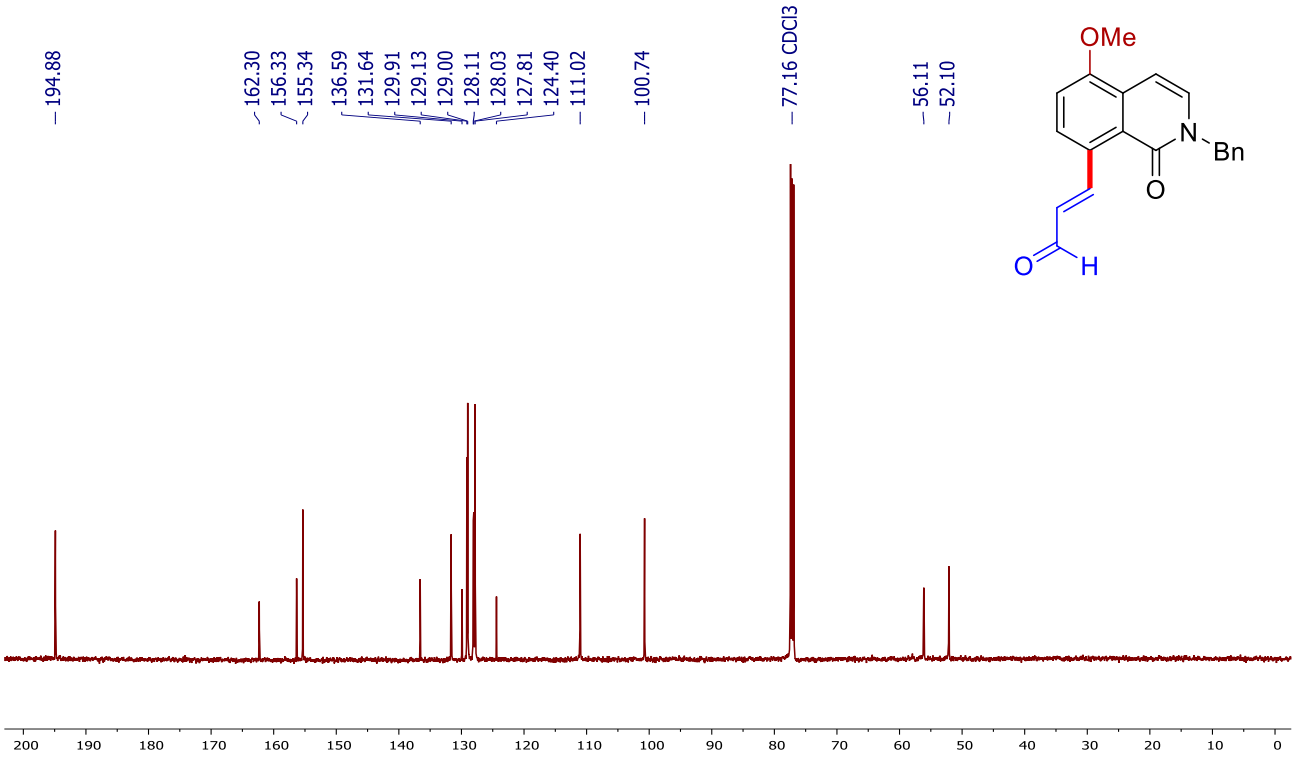


*3-(2-benzyl-5-methoxy-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3k**)*

^{1}H NMR (500 MHz)

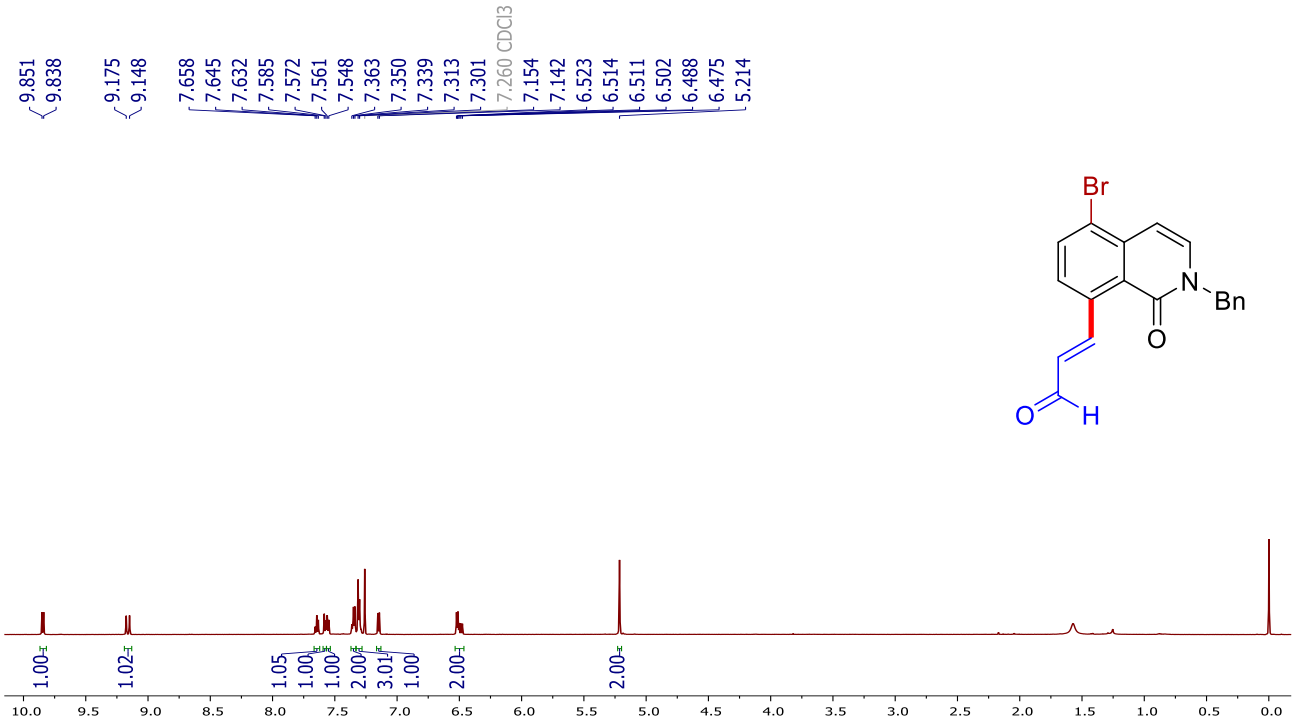


$^{13}C\{^{1}H\}$ NMR (125 MHz)

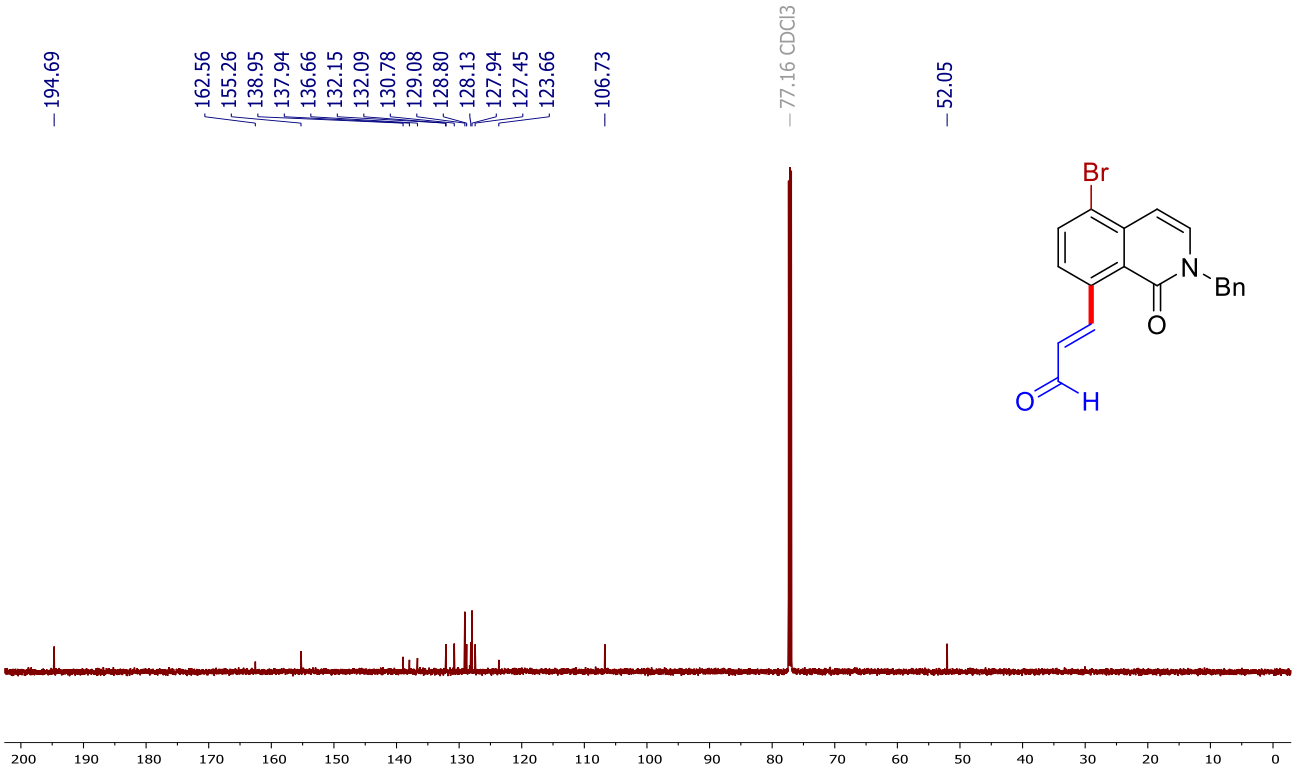


*3-(2-benzyl-5-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3l**)*

^{1}H NMR (600 MHz)

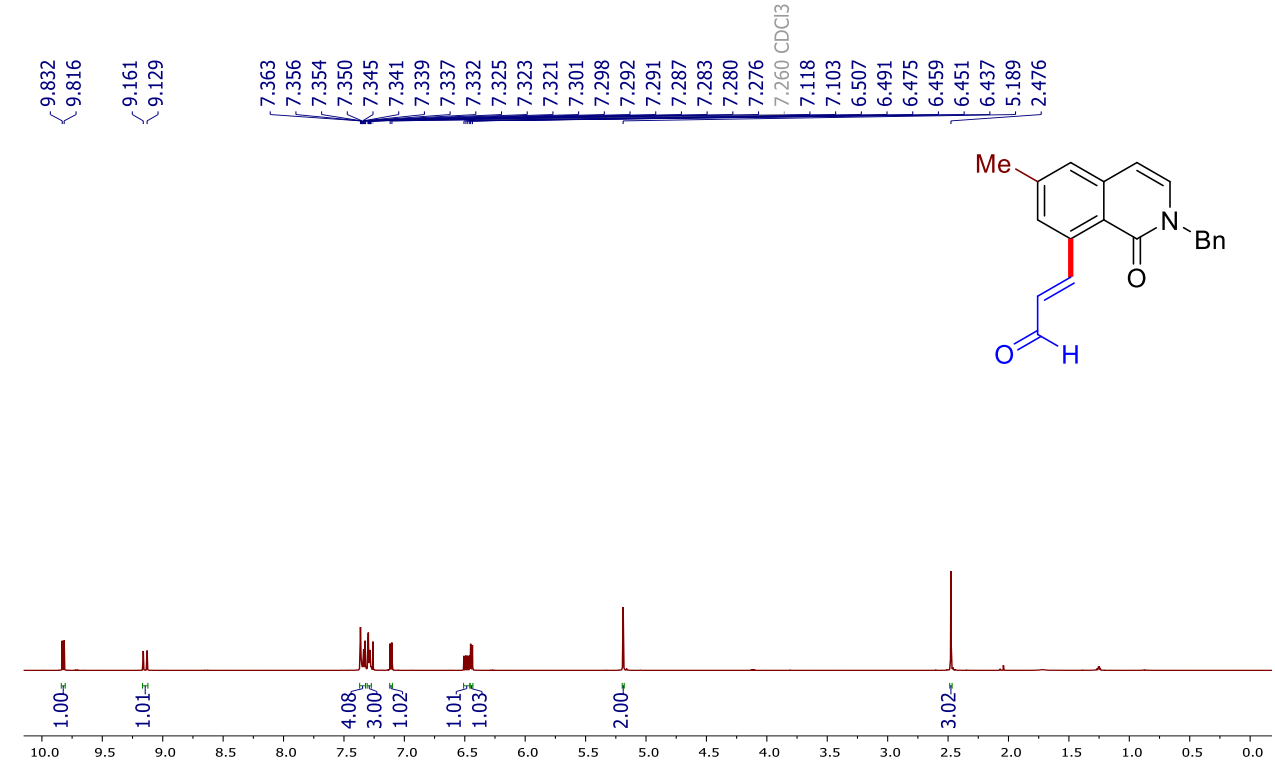


$^{13}C\{^{1}H\}$ NMR (150 MHz)

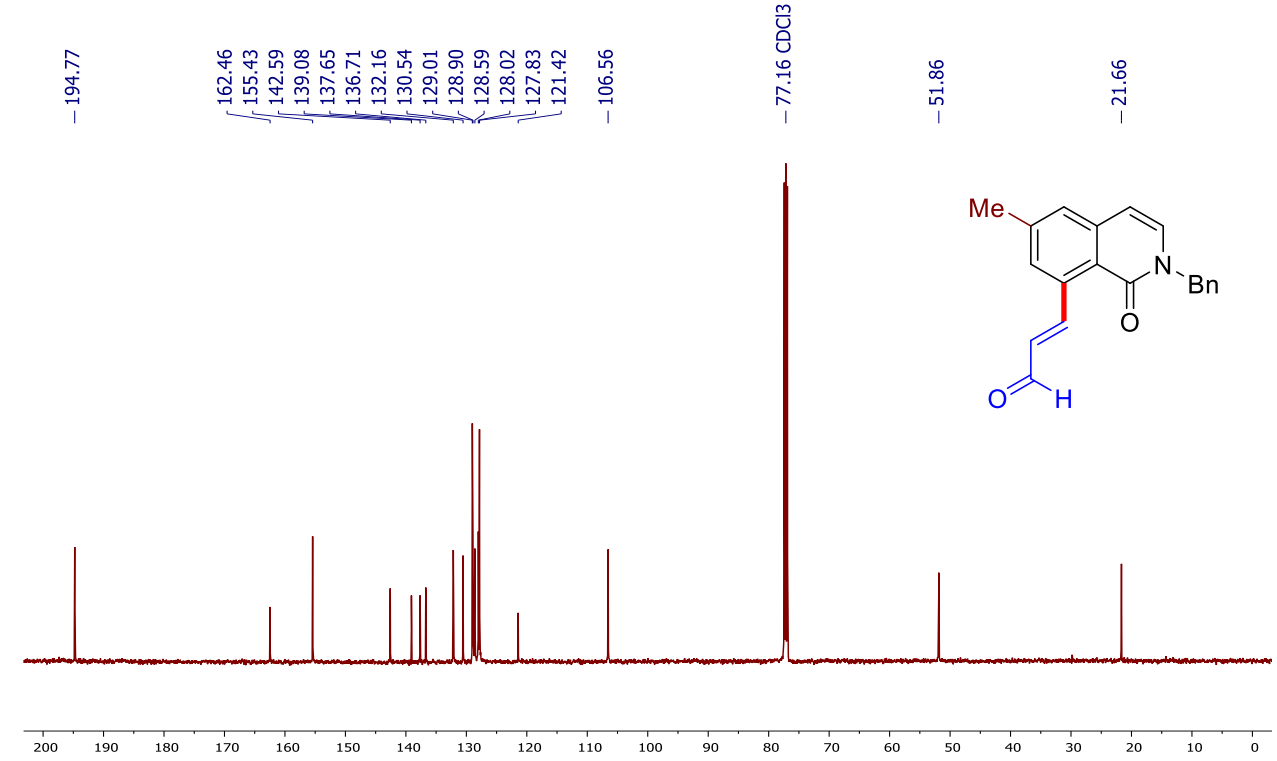


*3-(2-benzyl-6-methyl-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3m**)*

^{1}H NMR (500 MHz)

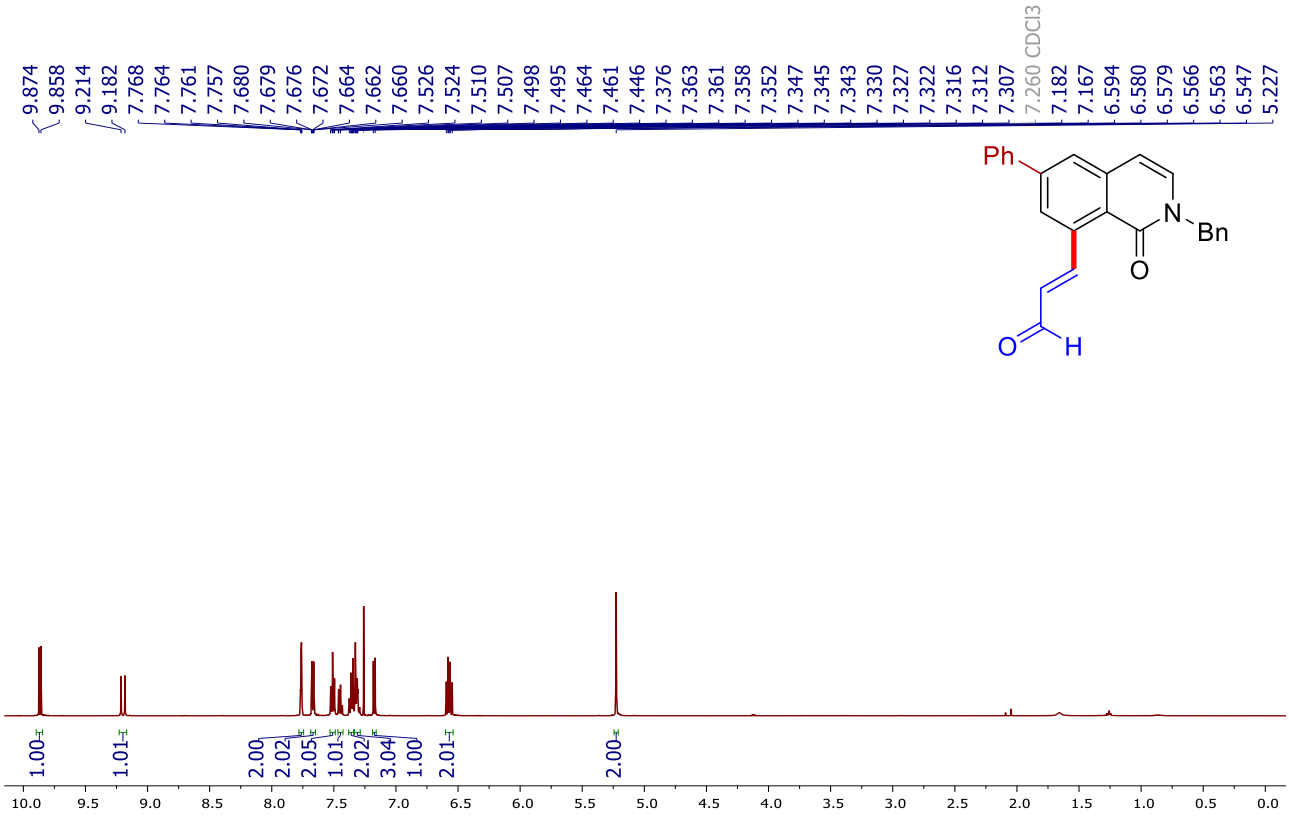


$^{13}C\{^{1}H\}$ NMR (125 MHz)

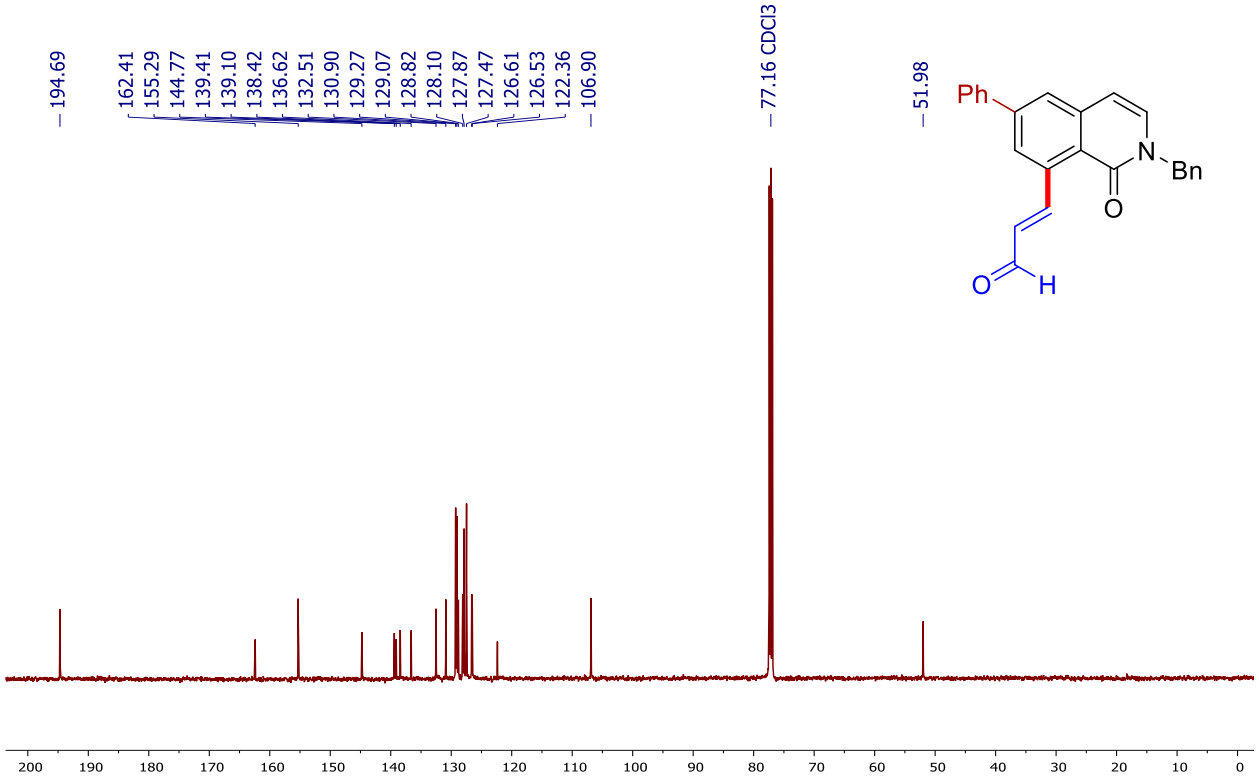


*3-(2-benzyl-1-oxo-6-phenyl-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3n**)*

^{1}H NMR (500 MHz)

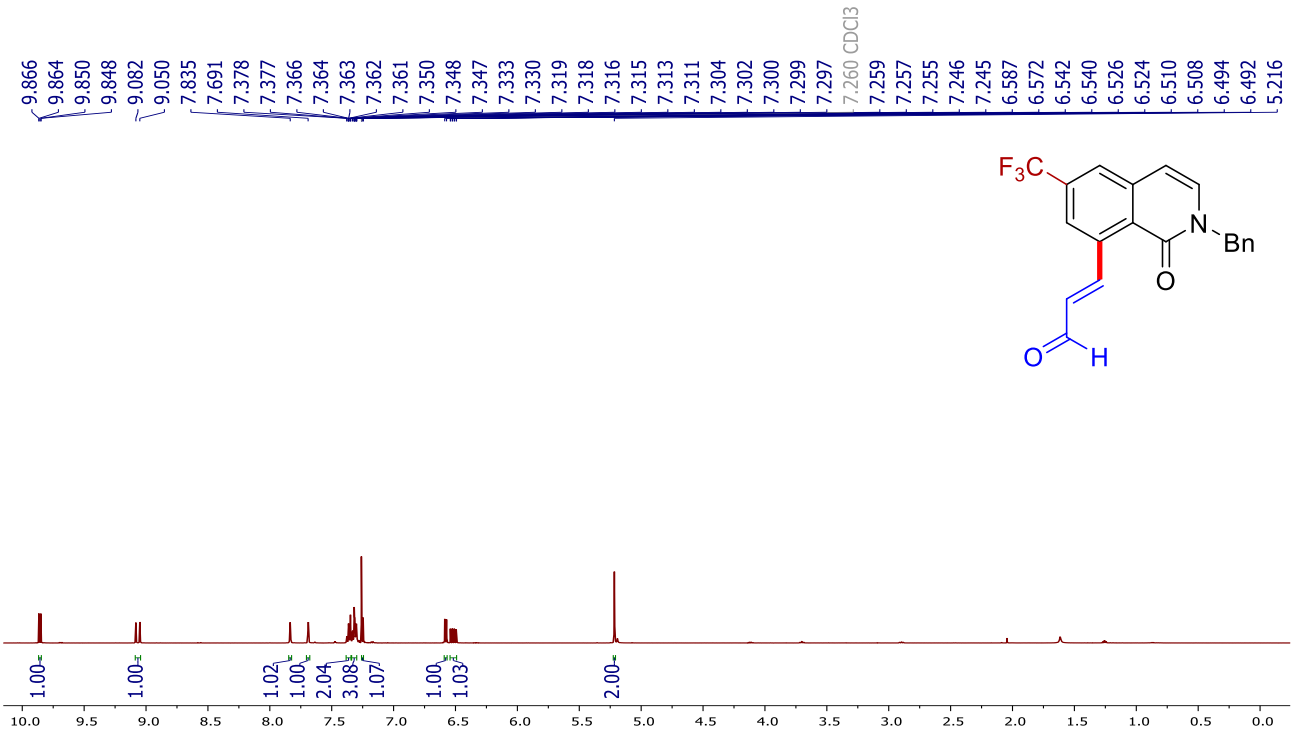


$^{13}C\{^{1}H\}$ NMR (125 MHz)

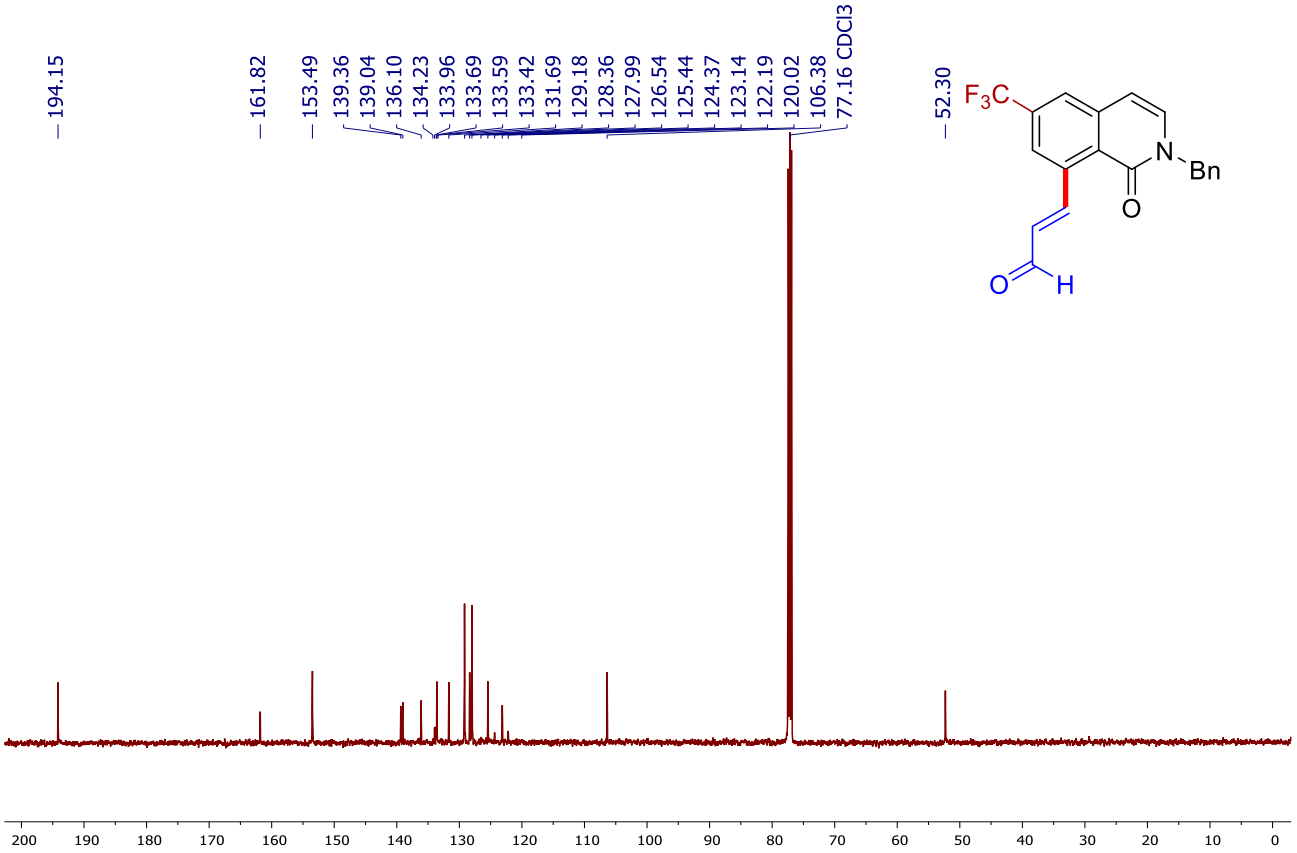


*3-(2-benzyl-1-oxo-6-(trifluoromethyl)-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3o**)*

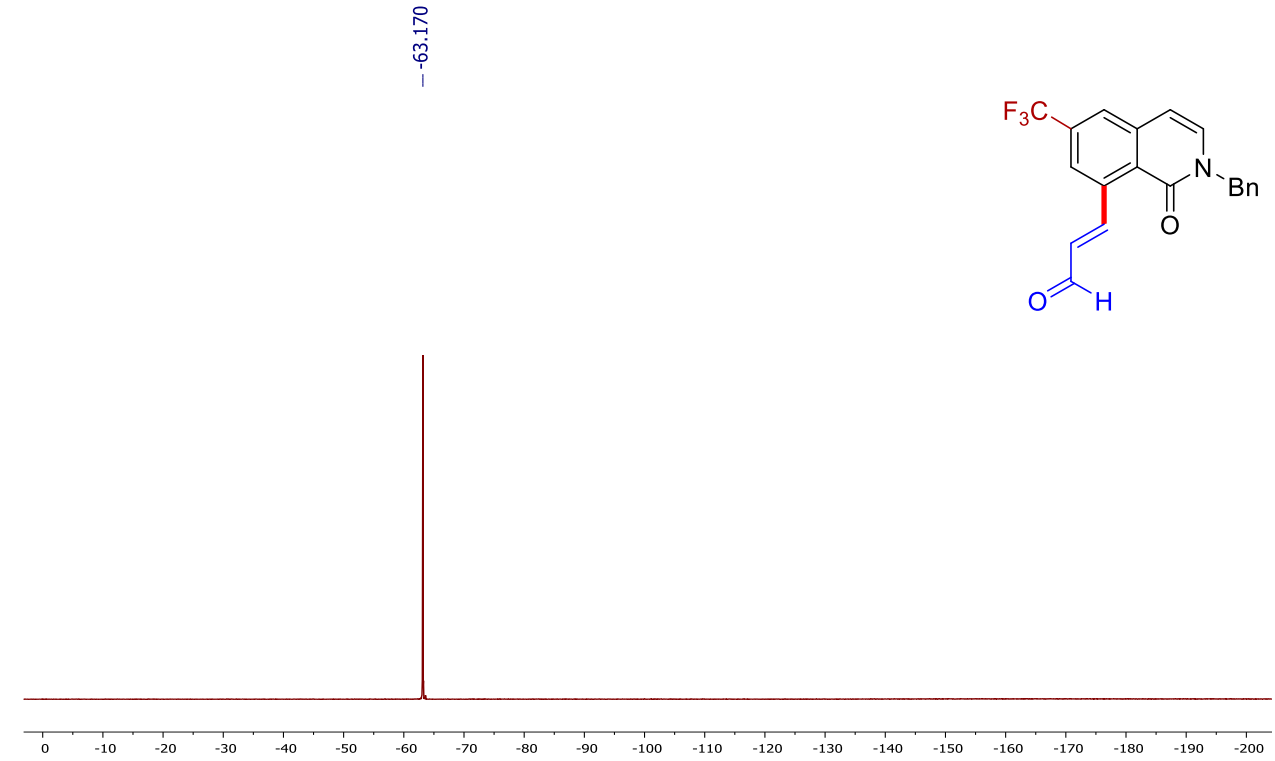
^{1}H NMR (500 MHz)



$^{13}C\{^{1}H\}$ NMR (125 MHz)

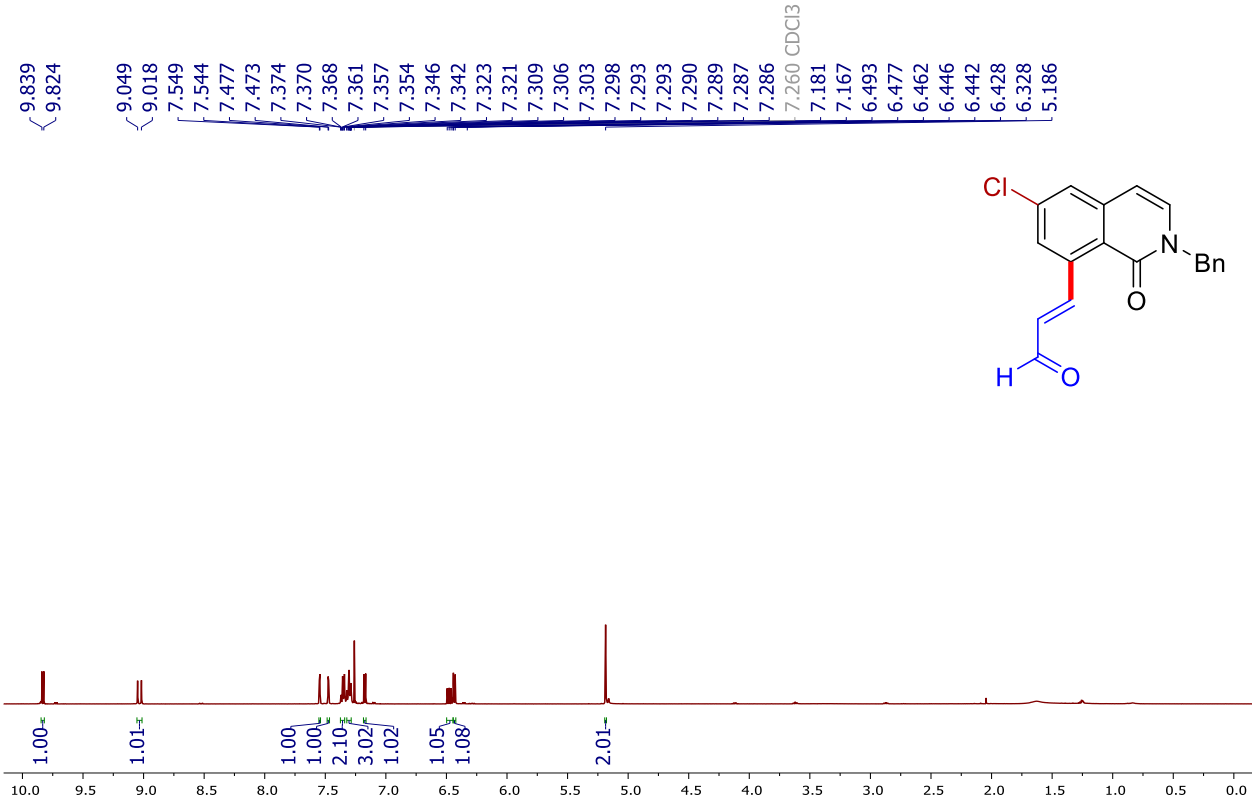


^{19}F NMR (471 MHz)

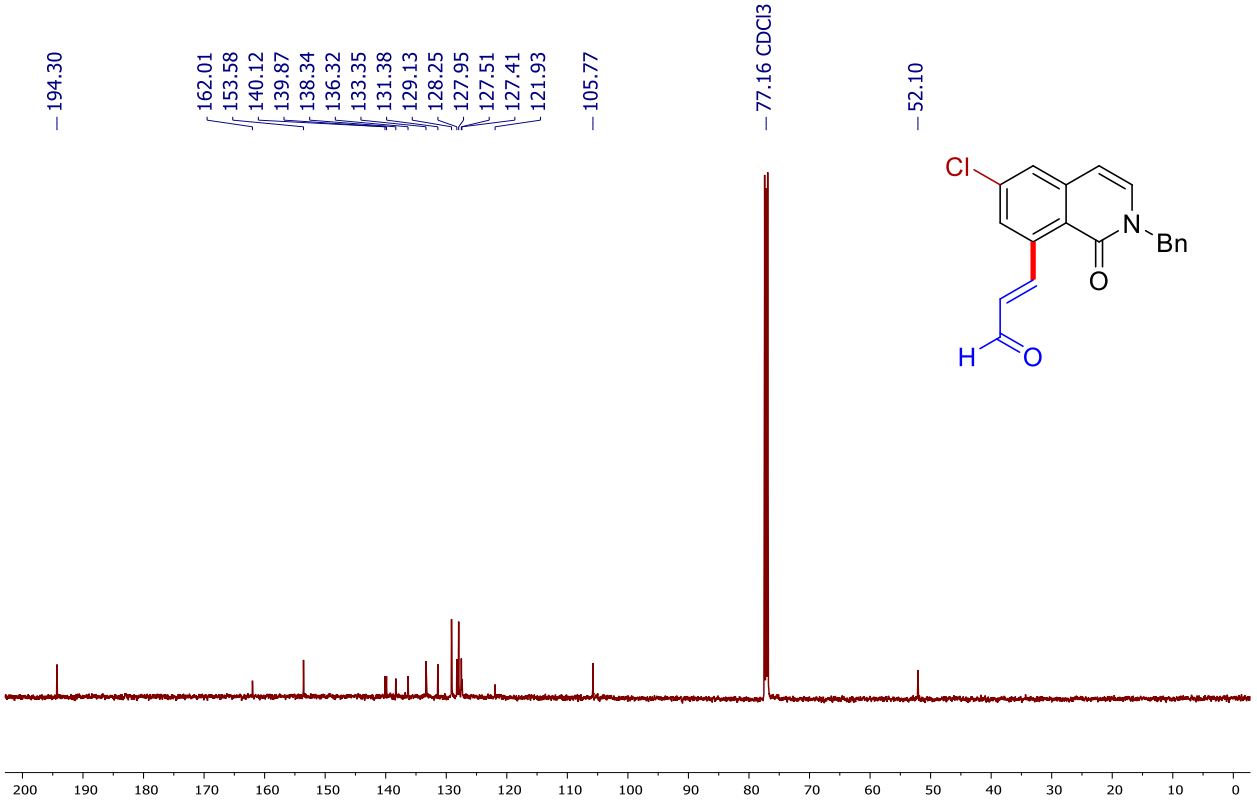


*3-(2-benzyl-6-chloro-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3p**)*

^{1}H NMR (500 MHz)

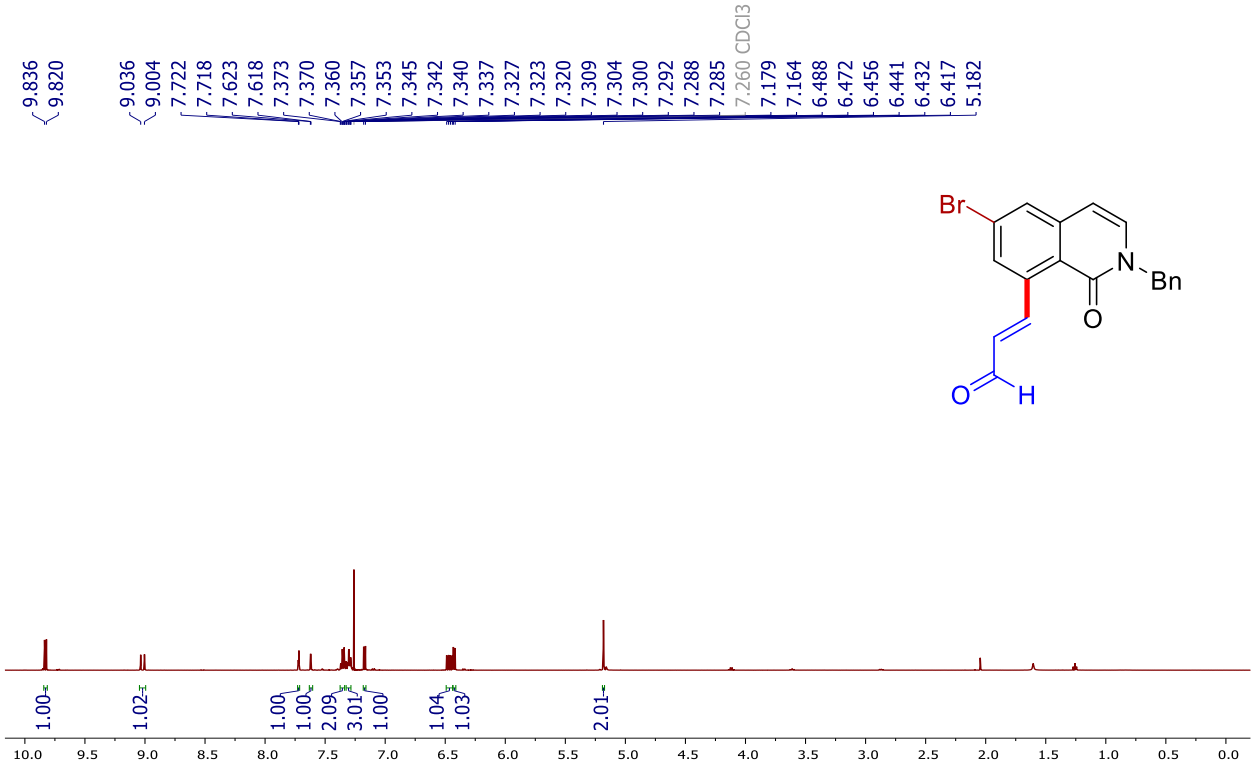


^{13}C{^{1}H} NMR (125 MHz)

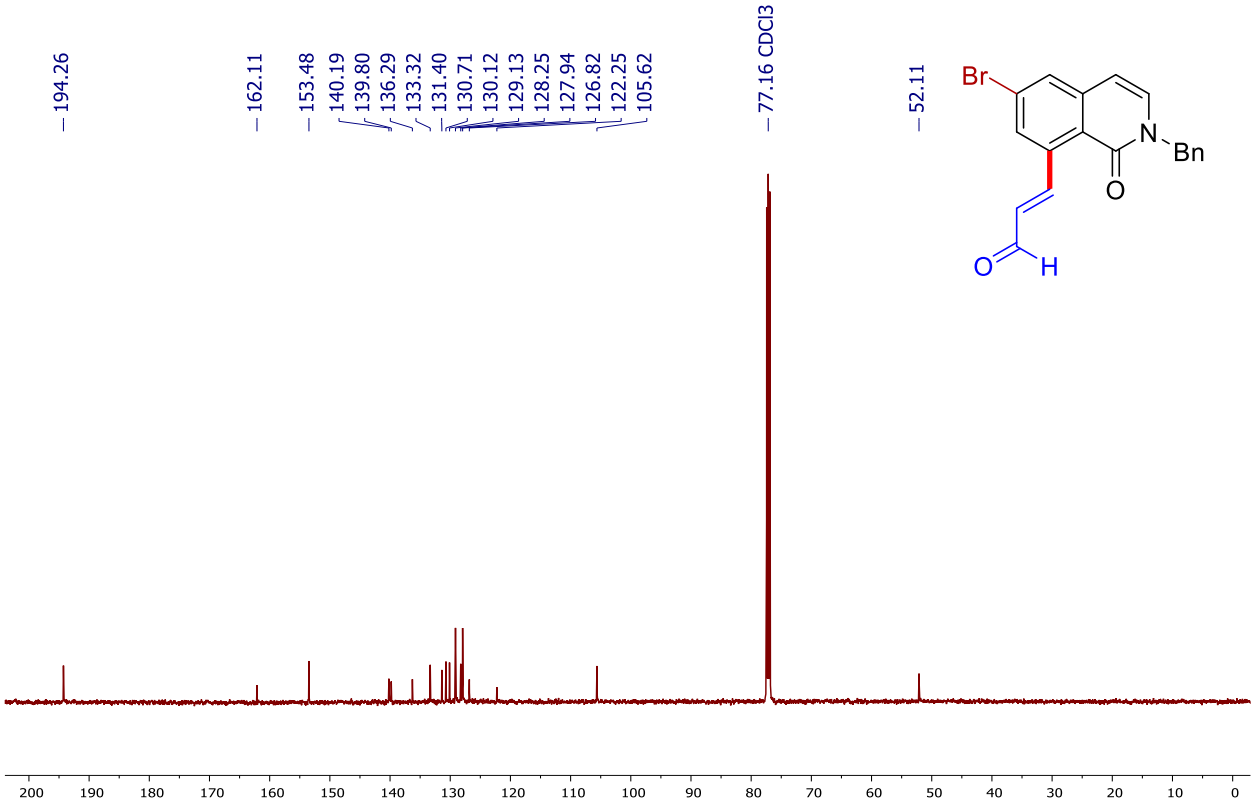


*3-(2-benzyl-6-bromo-1-oxo-1,2-dihydroisoquinolin-8-yl)acrylaldehyde (**3q**)*

^{1}H NMR (500 MHz)

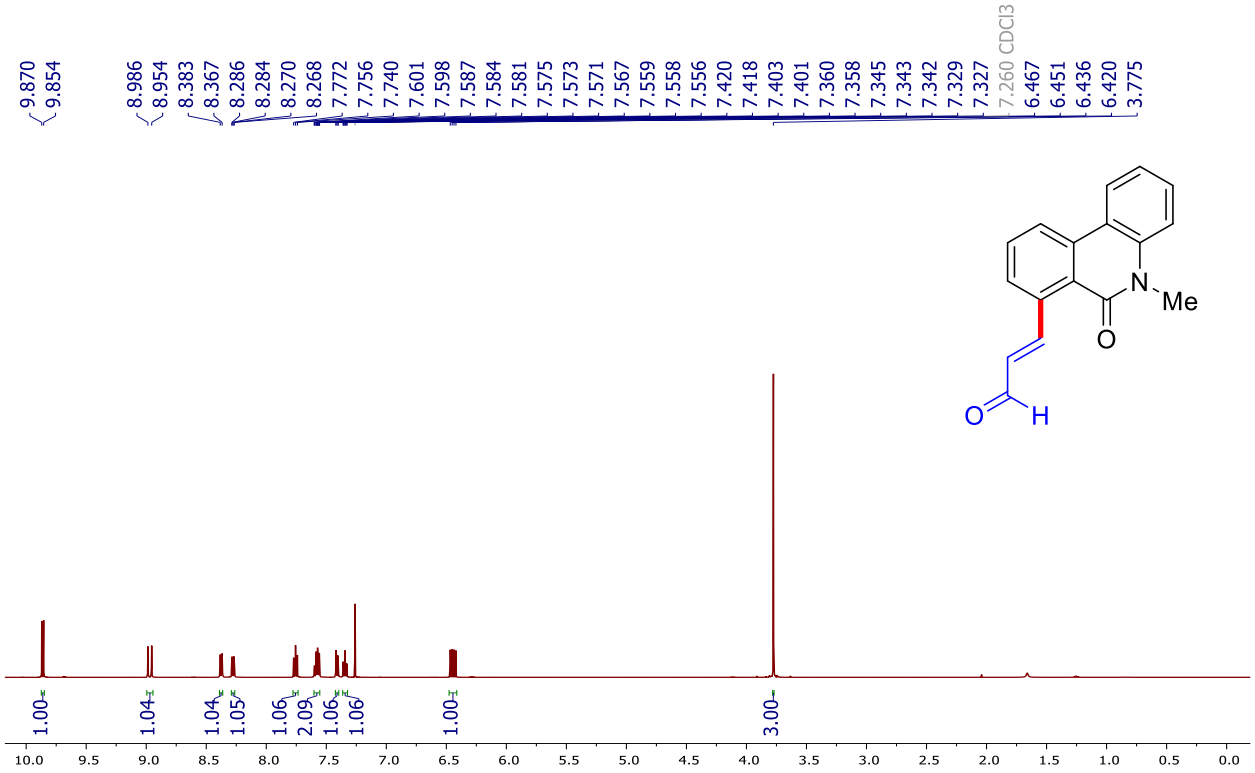


^{13}C{^{1}H} NMR (125 MHz)

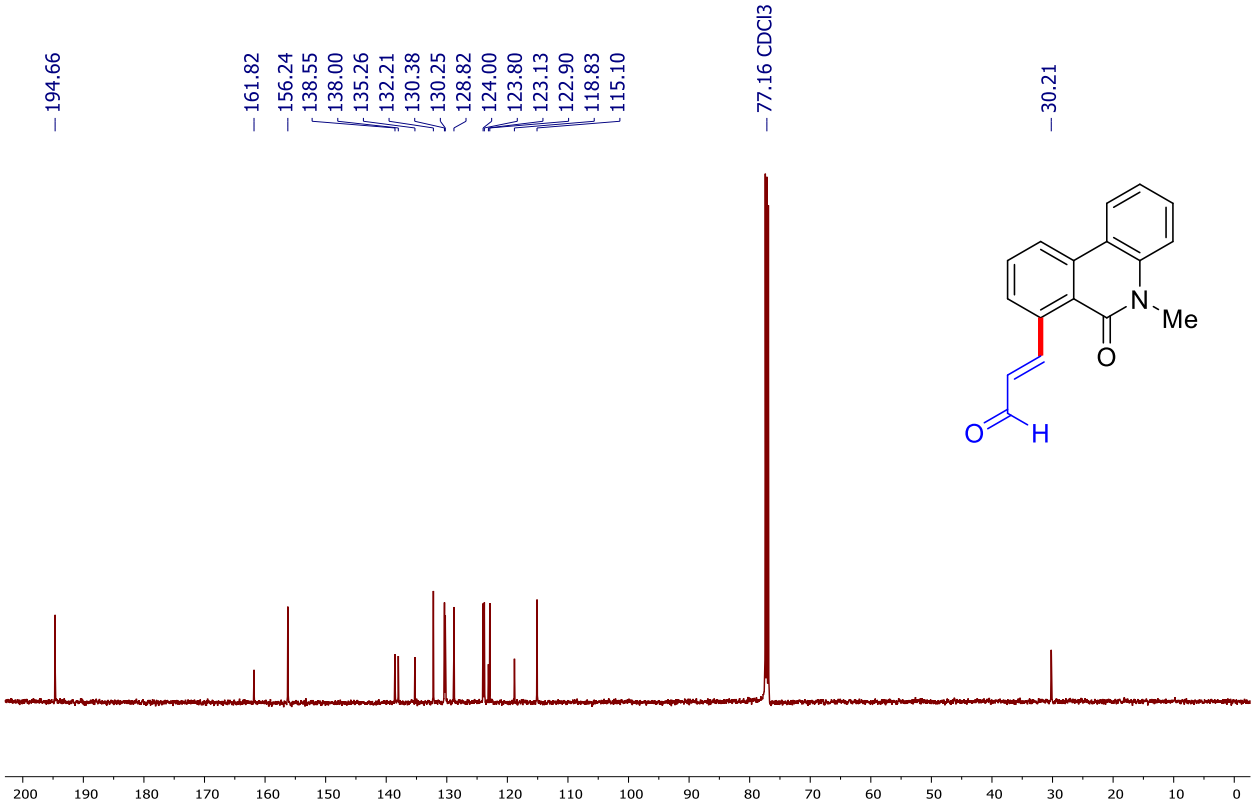


*3-(5-methyl-6-oxo-5,6-dihydrophenanthridin-7-yl)acrylaldehyde (**3r**)*

^{1}H NMR (500 MHz)

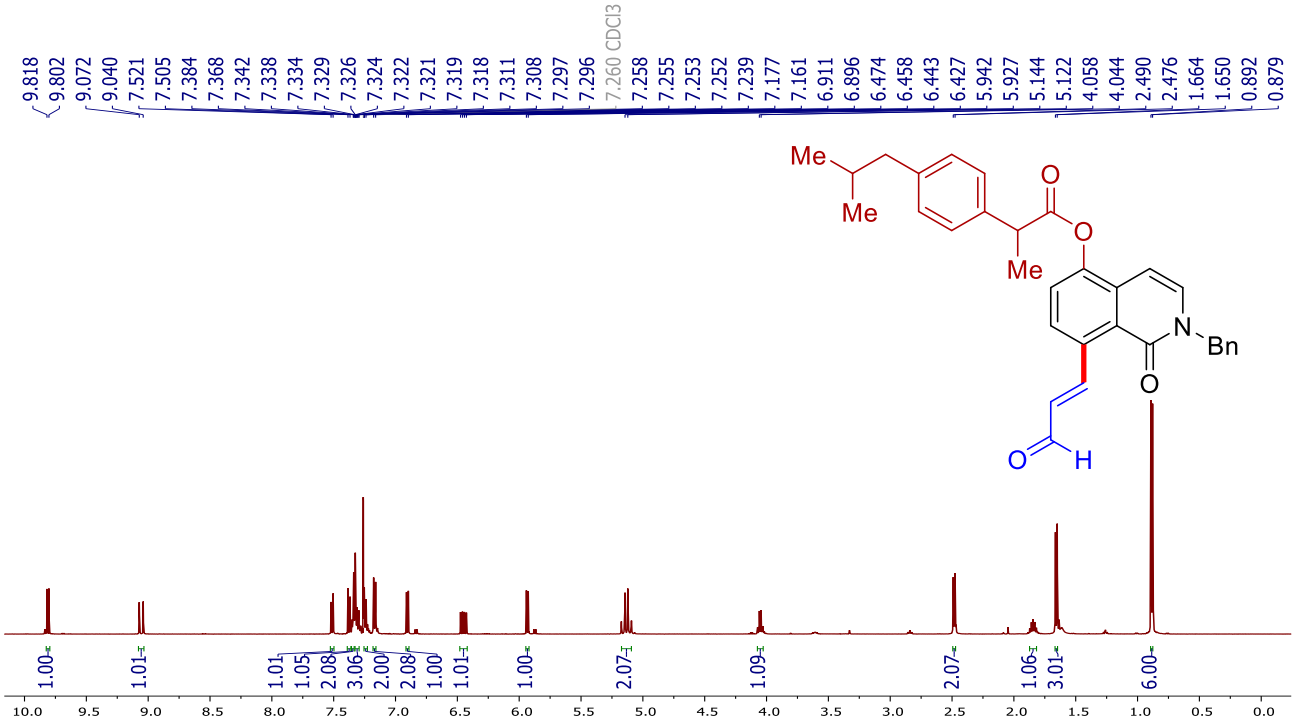


^{13}C{^{1}H} NMR (125 MHz)

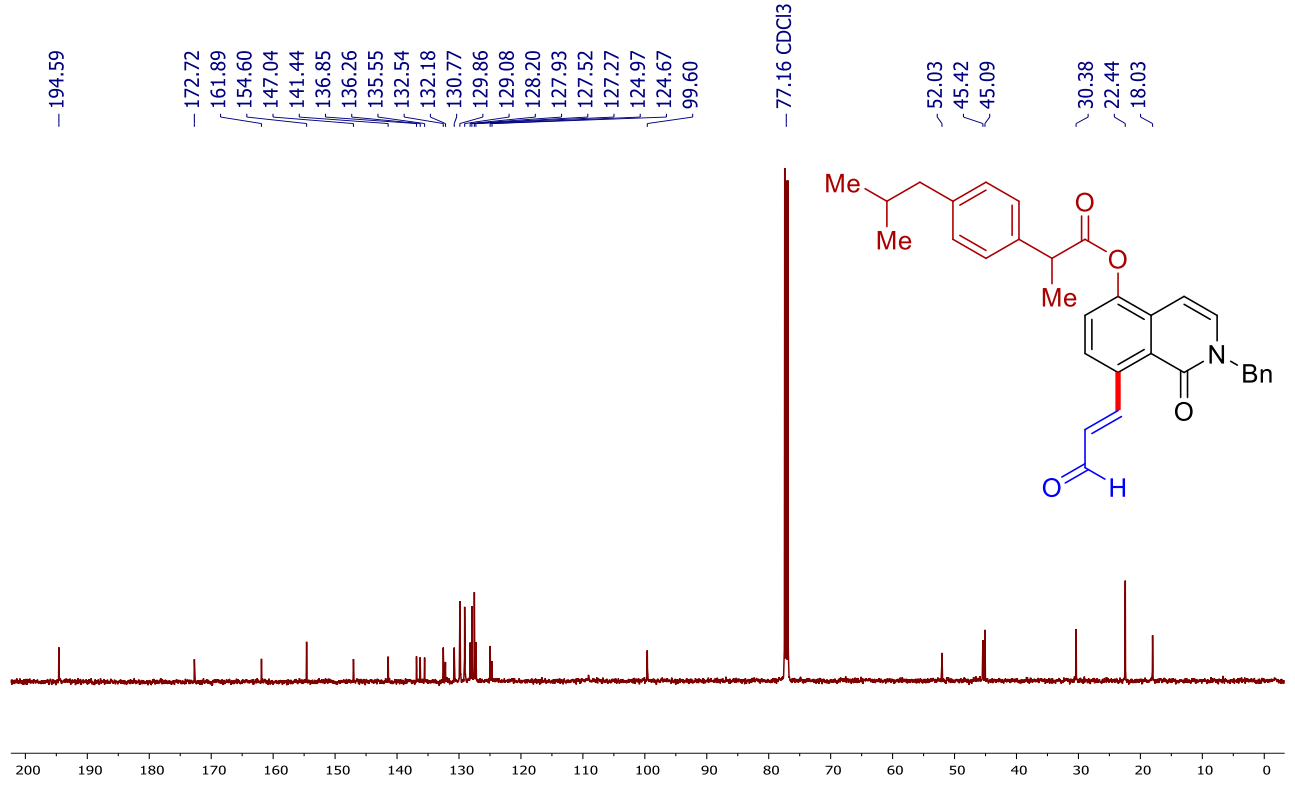


*2-benzyl-1-oxo-8-(3-oxoprop-1-en-1-yl)-1,2-dihydroisoquinolin-5-yl 2-(4-isobutylphenyl)propanoate (**3s**)*

^{1}H NMR (500 MHz)

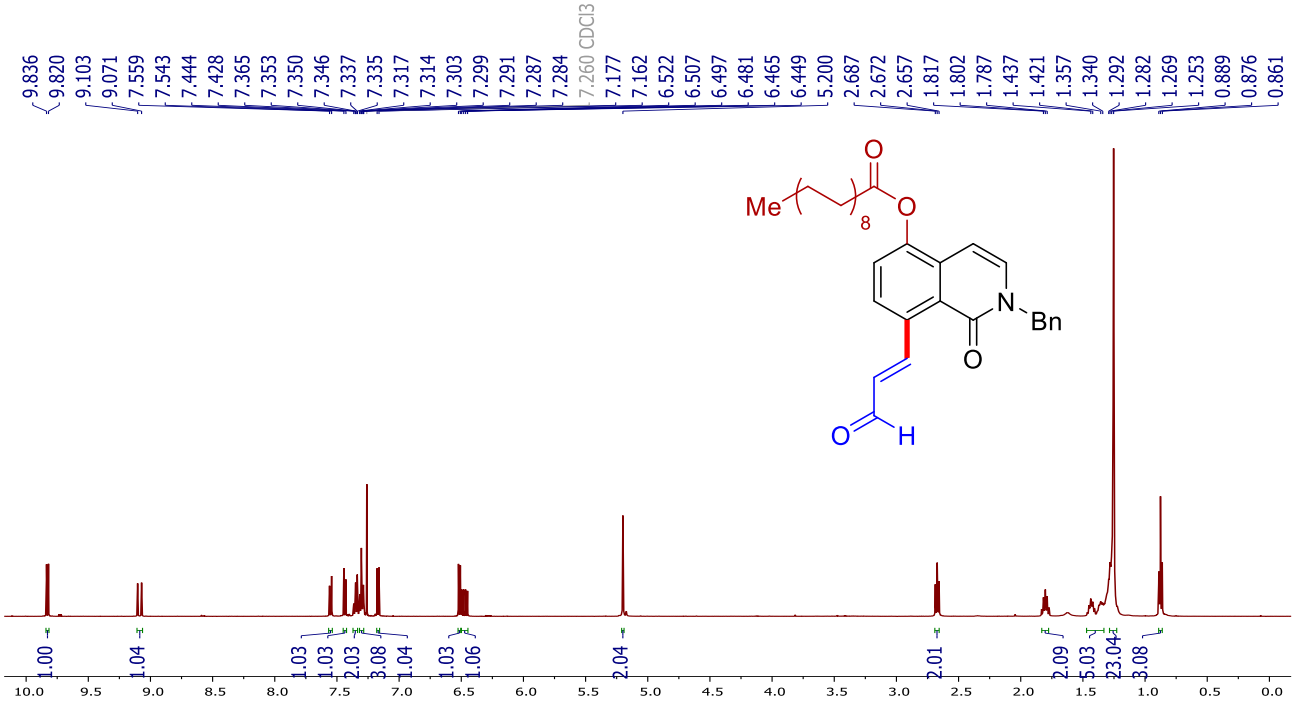


^{13}C{^{1}H} NMR (125 MHz)

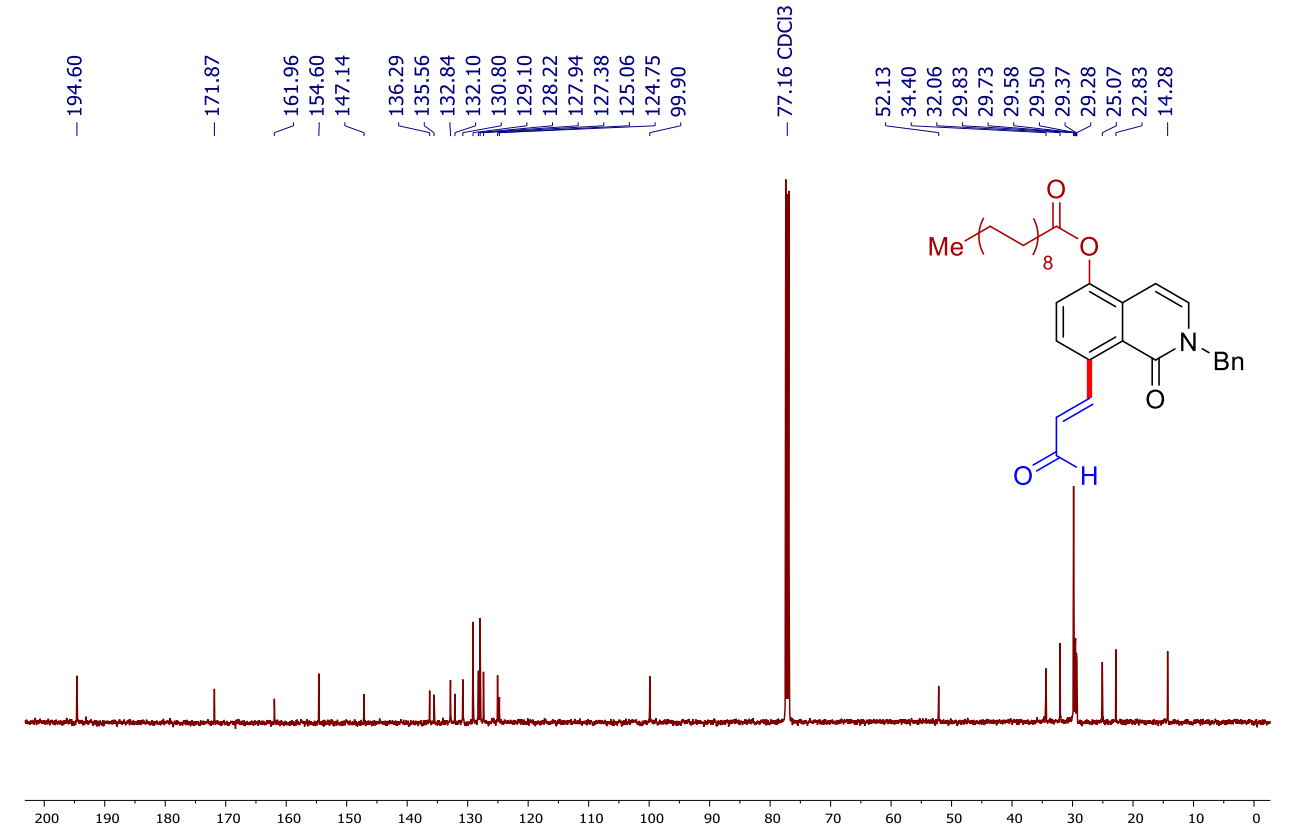


*2-benzyl-1-oxo-8-(3-oxoprop-1-en-1-yl)-1,2-dihydroisoquinolin-5-yl stearate (**3t**)*

^{1}H NMR (500 MHz)

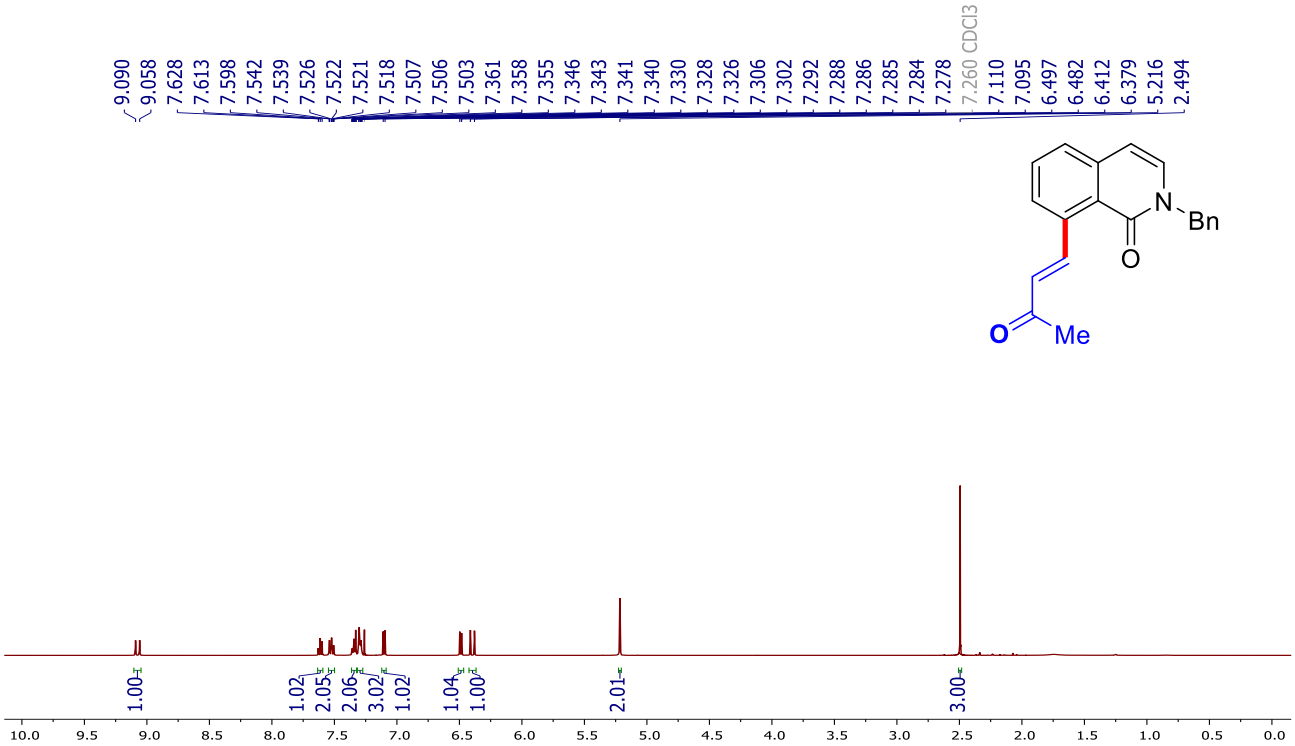


^{13}C{^{1}H} NMR (125 MHz)

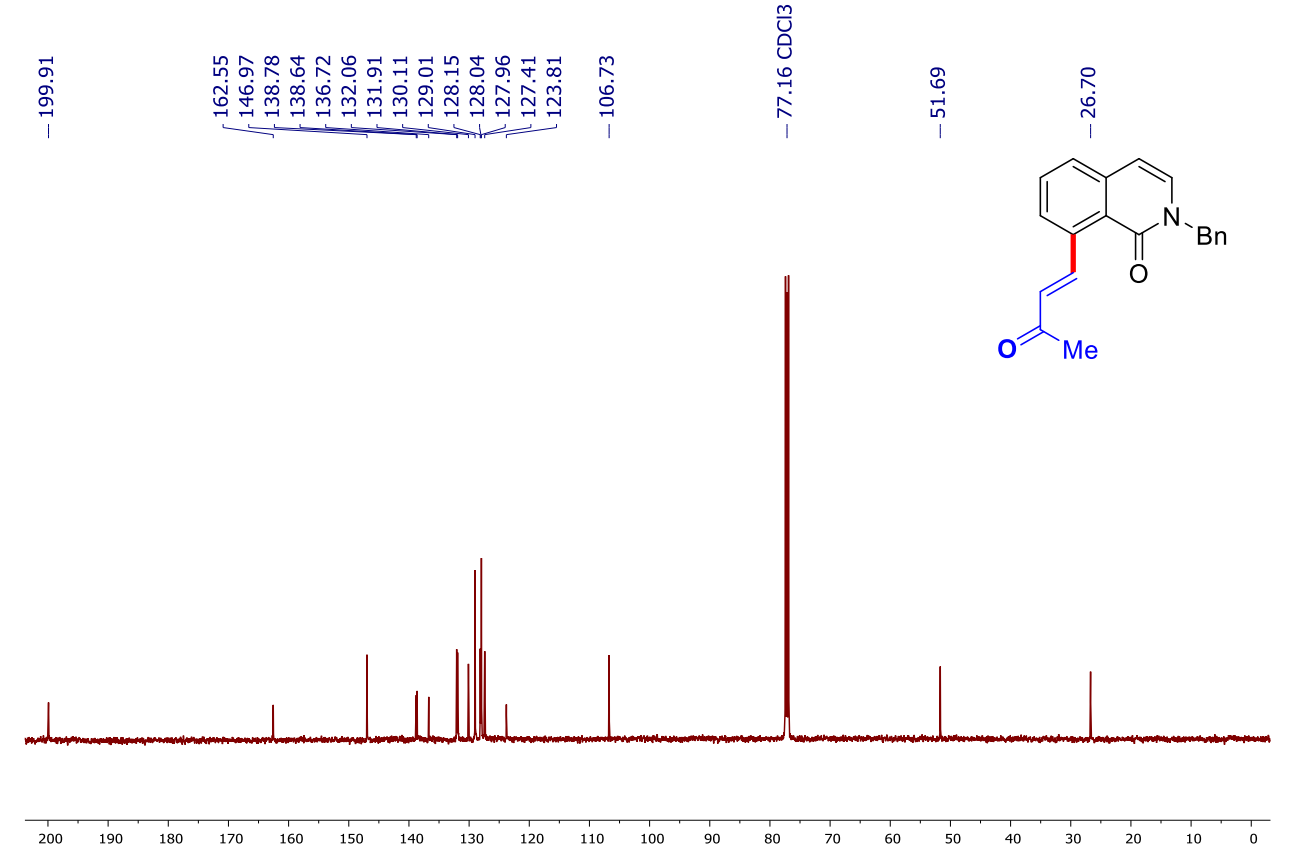


*2-benzyl-8-(3-oxobut-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3, **3aa**)*

^{1}H NMR (500 MHz)

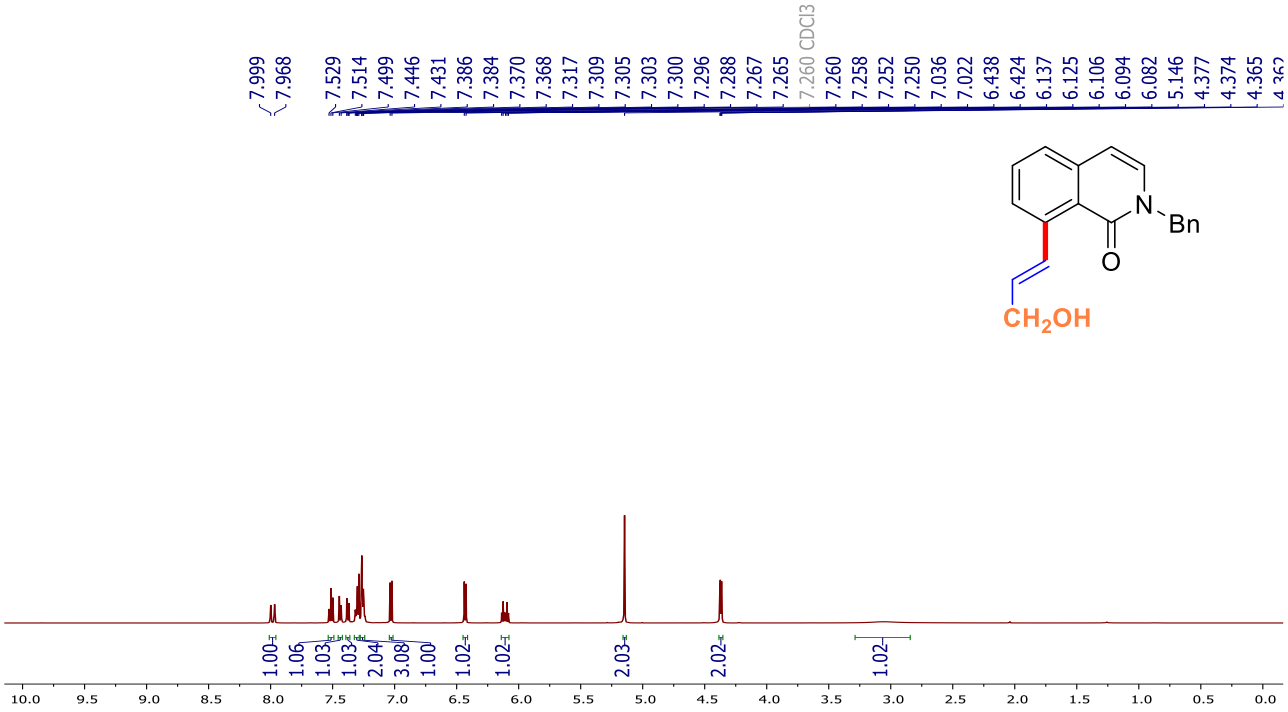


^{13}C{^{1}H} NMR (125 MHz)

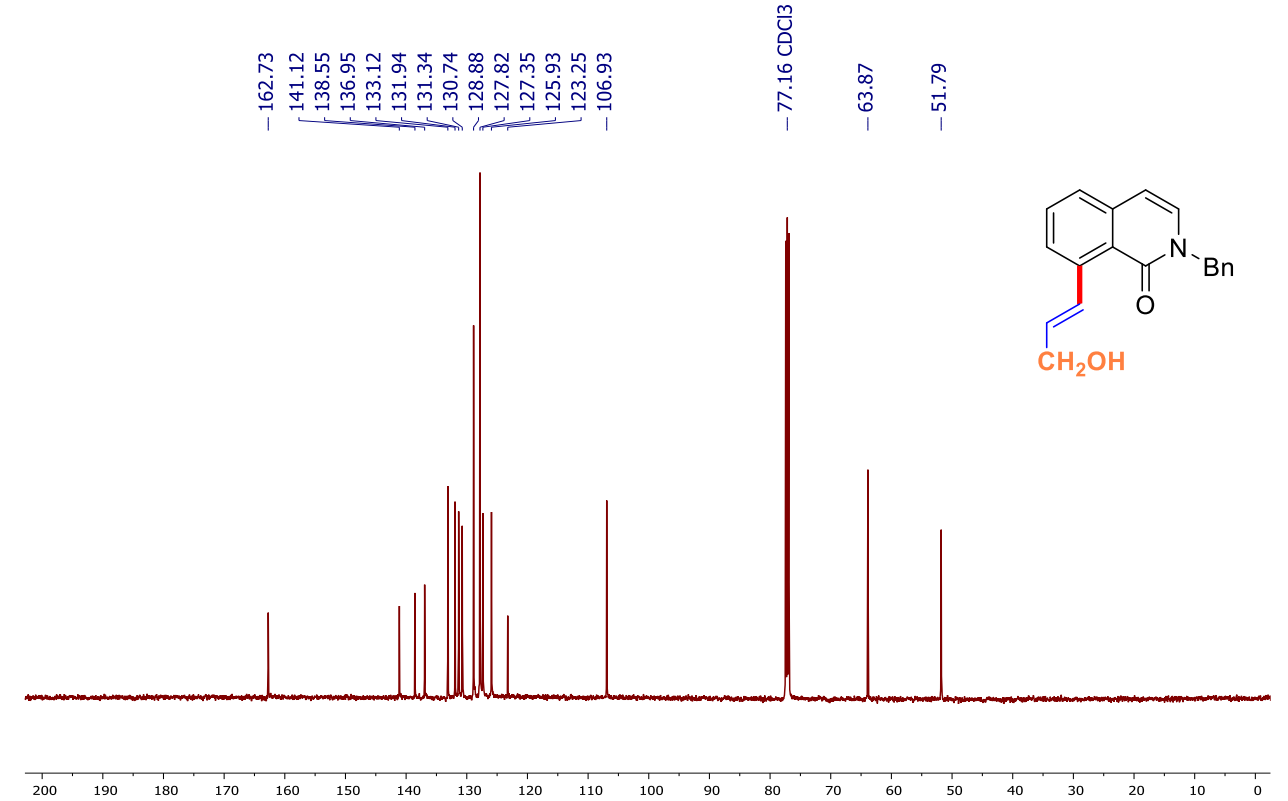


*2-benzyl-8-(3-hydroxyprop-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 5, **4a**)*

^{1}H NMR (500 MHz)

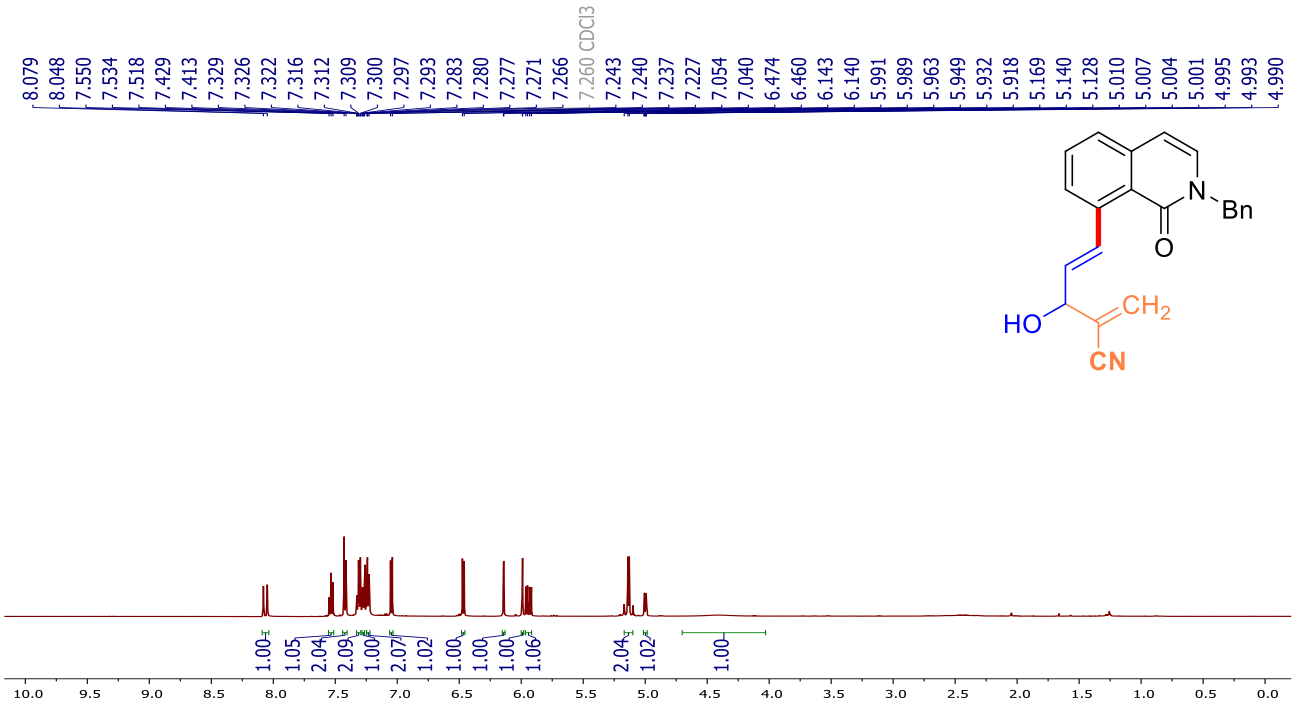


^{13}C{^{1}H} NMR (125 MHz)



*5-(2-benzyl-1-oxo-1,2-dihydroisoquinolin-8-yl)-3-hydroxy-2-methylenepent-4-enenitrile (Scheme 5, **4b**)*

^{1}H NMR (500 MHz)



^{13}C{^{1}H} NMR (125 MHz)