Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Co(III)-Catalyzed *N*-Chloroamide-Directed C-H Activation for 3,4-Dihydroisoquinolone Synthesis

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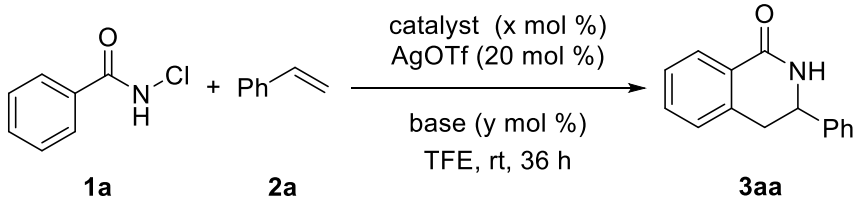
1. General Information

All reactions were carried out under a dry nitrogen atmosphere. All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under an argon atmosphere. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsing dao silica gel (60, particle size 0.040 - 0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR in $CDCl_3$ or DMSO with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR were recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR were reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometric data were obtained using Bruker Apex IV RTMS. Column conditions are reported in the experimental section below.

2. Optimization of Reaction Conditions

Table S1. Optimization of reaction conditions[a]

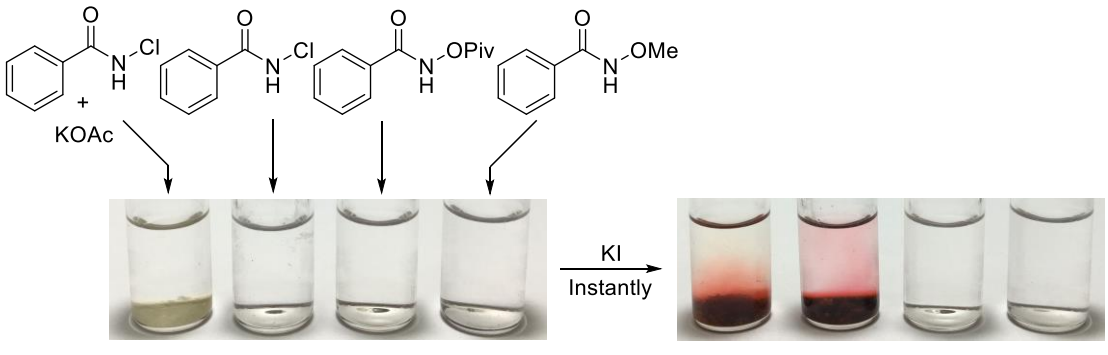


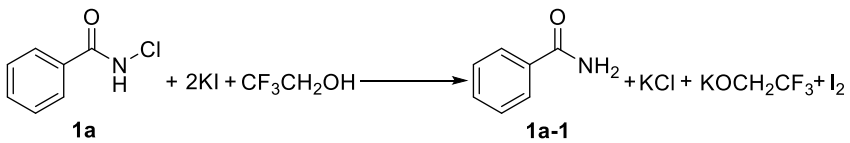
1a **2a** **3aa**

entry	catalyst (x mol %)	base (y mol %)	yield[b] (%)
1	$[RuCp^*Cl_2]_2$ (5)	KOAc (120)	-
2	$Co(acac)_2$ (10)	KOAc (120)	-
3	$[CoCp^*(CO)I_2]$ (10)	KOAc (120)	58[c]
4	$[CoCp^*(CO)I_2]$ (10)	NaOAc (120)	65
5	$[CoCp^*(CO)I_2]$ (10)	KO^{t}Bu (120)	58
6	$[CoCp^*(CO)I_2]$ (10)	KOAc (20)	11
7	$[CoCp^*(CO)I_2]$ (10)	KOAc (50)	25

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), TFE (1.0 mL), N_2. [b]Isolated yields are shown. [c]Air.

3. Oxidizing Reactivity of N-Cl Bond Experiments





1a **1a-1**

To four 1.5 ml sample bottles were respectively added *N*-chlorobenzamide (0.2 mmol, 32 mg) and KOAc (0.24 mmol, 24 mg) in CF_3CH_2OH (1 mL) under air, *N*-chlorobenzamide (0.2 mmol, 32 mg) in CF_3CH_2OH (1 mL) under air, *N*-pivaloyloxybenzamide (0.2 mmol, 44 mg) in CF_3CH_2OH (1 mL) under air, and *N*-methoxybenzamide (0.2 mmol, 30 mg) in CF_3CH_2OH (1 mL) under air. And KI (0.4 mmol, 66.4 mg) was added respectively.

The high oxidizing power of *N*-chlorobenzamides is evidenced by upon mixing of *N*-chlorobenzamide (**1a**) with KI in trifluoroethanol (TFE; in the absence or presence of KOAc), an instant color change to reddish brown characteristic of the generation of I_2. The same color change is not observed by the replacement of **1a** with *N*-pivaloyloxybenzamide or *N*-methoxybenzamide, indicating that N-Cl bond is more oxidizing than N-O bond.

Cyclic voltammetry (CV) was carried out on a CHI 660D electrochemical workstation (Shanghai Chen Hua Instrument Co. Ltd., China) with a conventional three-electrode system composed of a glassy carbon electrode as the working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The higher oxidizing capability of N-Cl bond is also evidenced by cyclic voltammetry measurement.

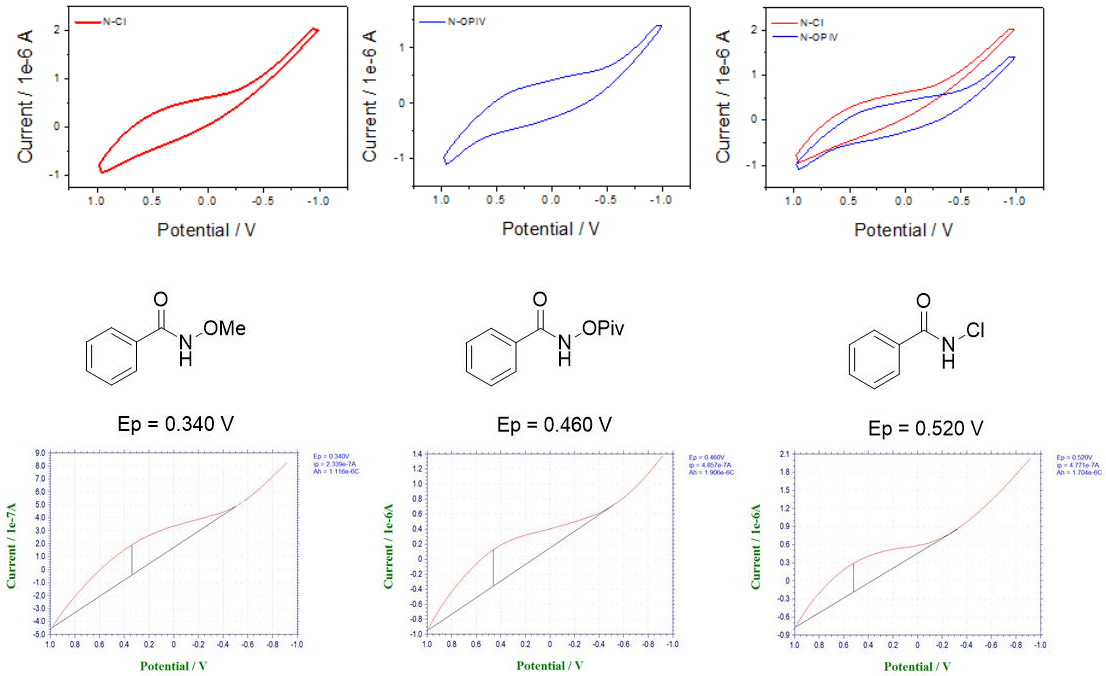
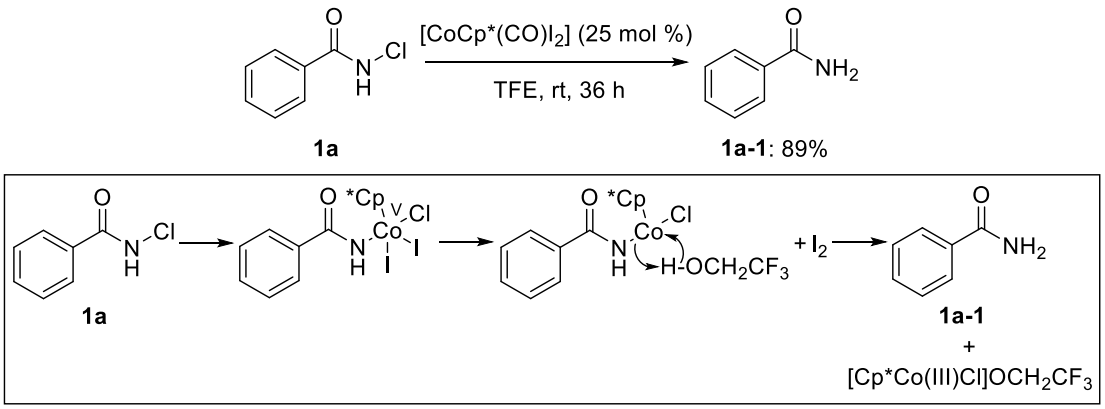


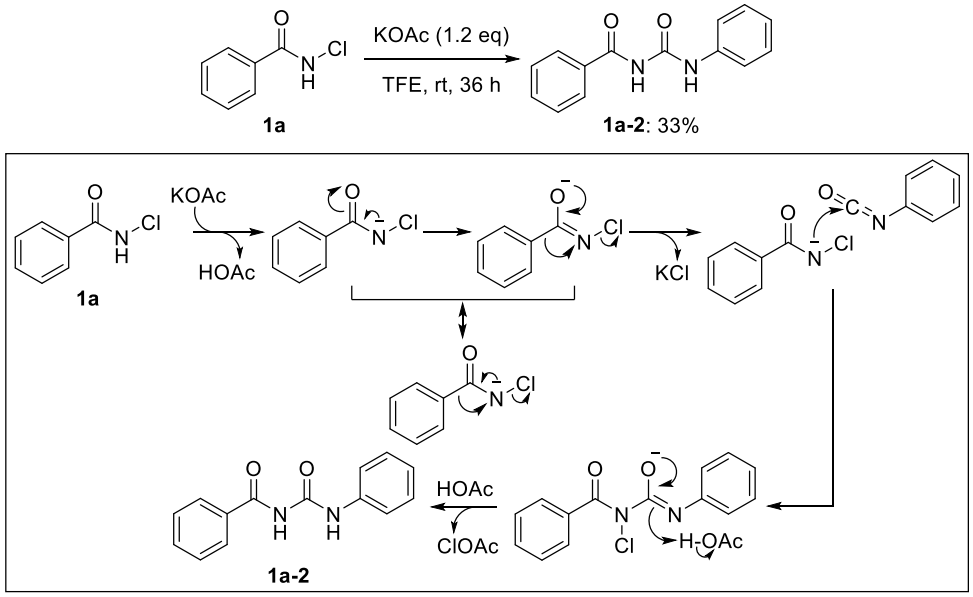
Figure S1. Cyclic voltammetry data (CF_3CH_2OH, 0.2 mmol/mL, 100 mV/s) for complexes **1a** (N-Cl), *N*-pivaloyloxybenzamide (N-OPiv) and *N*-methoxybenzamide



To a 13 × 150 mm test tube equipped with magnetic stir bar were added

N-chlorobenzamide (31.2 mg, 0.2 mmol), [CoCp*(CO)I_2] (25 mg, 25 mol %) under nitrogen. Then, 1 mL of CF_3CH_2OH was injected into the tube through a syringe. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 3:1). The corresponding product was obtained as a white solid (22 mg, 89%).

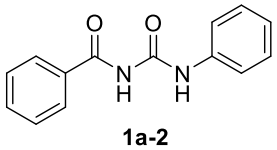
The oxidizing power of *N*-chlorobenzamides can translate to smooth conversion of **1a** to benzamide (**1a-1**, 89% yield) under [CoCp*(CO)I_2] catalysis at rt, with N-Cl bond oxidative addition and concomitant Co^{III}-to-Co^{V} transformation[1] as the critical step.



To a 13 × 150 mm test tube equipped with magnetic stir bar were added *N*-chlorobenzamide (31 mg, 0.2 mmol) and KOAc (24 mg, 120 mol %) under nitrogen. Into the tube was then injected 1 mL of CF_3CH_2OH via syringe. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 3:1). The corresponding product was obtained as a white solid (8 mg, 33%).

Switching of [CoCp*(CO)I_2] to KOAc results in the exhibition of nitrene-like reactivity and generation of group-migrated *N*-(phenylcarbamoyl)benzamide (**1a-2**) through initial deprotonation of **1a**. In fact, the group migration process can also be viewed as a formal oxidation of C atoms by the N-Cl bond.

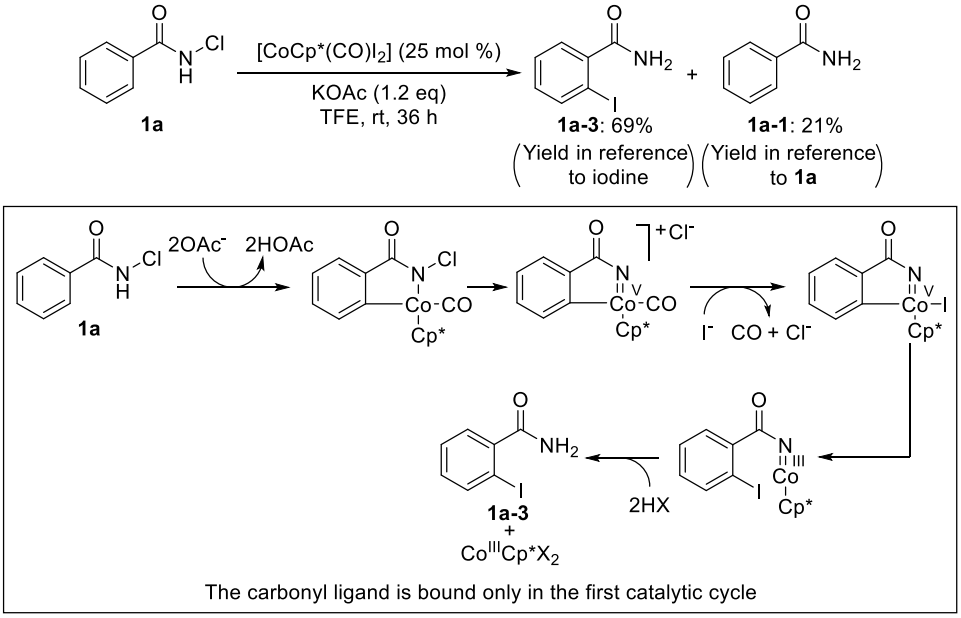
_N_-(phenylcarbamoyl)benzamide (1a-2)[2]



1a-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 (s, 1H), 10.04 (s, 1H), 8.17 – 8.01 (m, 2H), 7.69 – 7.57 (m, 3H), 7.52 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.41 – 7.32 (m, 2H), 7.20 – 7.10 (m, 1H).

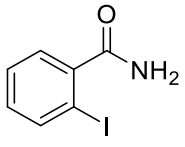
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.68, 152.13, 137.24, 133.35, 132.16, 129.01, 128.86, 128.06, 124.45, 120.47.



To a 13 × 150 mm test tube equipped with magnetic stir bar were added *N*-chlorobenzamide (31 mg, 0.2 mmol), [$CoCp^*(CO)I_2$] (25 mg, 25 mol %) and KOAc (24 mg, 120 mol %) under nitrogen. Into the tube was then injected 1 mL of CF_3CH_2OH via syringe. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 3:1). The corresponding products were obtained as white solids: 2-iodobenzamide (8.5 mg, 69%, the yield is calculated according to the amount of iodine ion) and benzamide (5 mg, 21%).

The combination of [$CoCp^*(CO)I_2$] with KOAc enables complete suppression of group migration pathway and elicitation of C-H activation capability for cobalt. Indeed, the formation of 2-iodobenzamide (**1a-3**) under this condition supports the following mechanistic sequence: N-H deprotonation, cobalt coordination, C-H activation, oxidative addition of N-Cl bond and simultaneous oxidation of Co^{III} to Co^{V} (in the form of Co^{V}-nitrenoid), I^- coordination, C-I reductive elimination and proto-demetalation to regenerate Co^{III}.

2-iodobenzamide (1a-3)

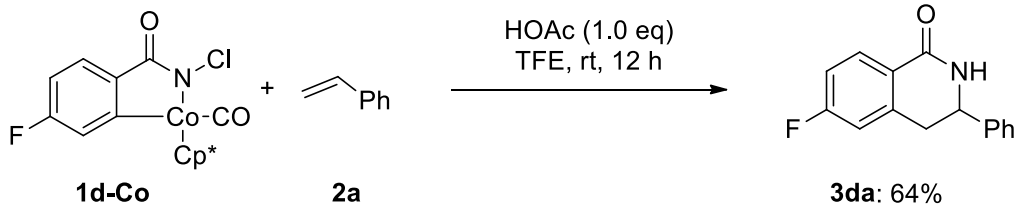


1a-3

^{1}H NMR (400 MHz, DMSO) δ 7.87 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.81 (s, 1H), 7.51 (s,

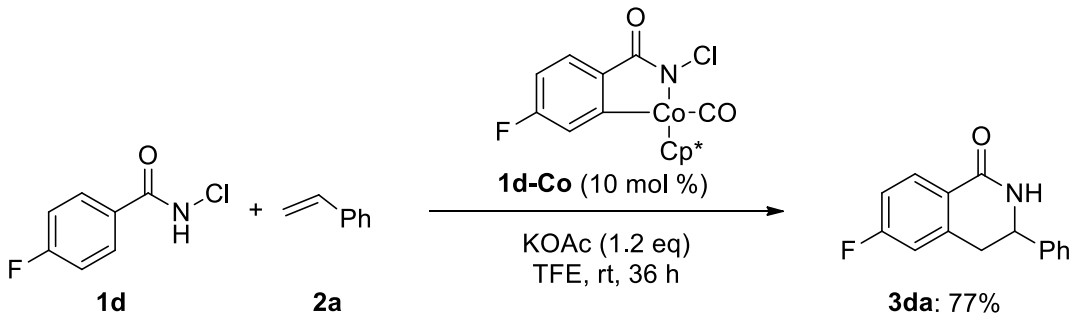
1H), 7.42 (td, *J* = 7.5, 1.1 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.19 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 170.66, 143.11, 139.12, 130.54, 127.82 (d, *J* = 15.0 Hz), 93.09.
HRMS (EI) m/z calcd. for C_7H_6INO $[M]^+$ 246.9494, found 246.9496.

4. Mechanism Experiments



1d-Co **2a** **3da**: 64%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1d-Co** (43 mg, 0.11 mmol), **2a** (18 mg, 150 mol %) and AcOH (7.0 mg, 100 mol %) in CF_3CH_2OH (1 mL) under nitrogen. The resulting solution was stirred at rt for 20 h. The reaction was concentrated in vacuo, the residue was purified by column chromatography (silica gel, PE:EtOAc = 3:1). **3da** was obtained as white solid (17 mg, 64%).

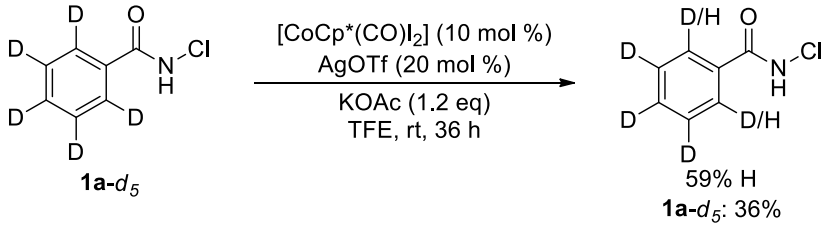


1d **2a** **3da**: 77%

To a 13 × 150 mm test tube equipped with magnetic stir bar were added **1d** (35 mg, 0.2 mmol), **1d-Co** (8 mg, 10 mol %), **2a** (32 mg, 150 mol %) and KOAc (24 mg, 120 mol%) in CF_3CH_2OH (1 mL) under nitrogen. The resulting solution was stirred at rt for 36 h. The reaction was concentrated in vacuo, the residue was purified by column chromatography (silica gel, PE:EtOAc = 3:1). **3da** was obtained as white solid (37 mg, 77%).

5. Deuterium Exchange Experiments

General procedure for the catalytic deuterium exchange experiments:



To a 13 × 150 mm test tube equipped with magnetic stir bar were added *N*-chlorobenzamide **1a**-d_5 (32 mg, 0.2 mmol), [CoCp*(CO)I_2] (10 mg, 10 mol %), KOAc (24 mg, 120 mol %) and AgOTf (10 mg, 20 mol %) under nitrogen. Then, 1 mL of CF_3CH_2OH was injected into the tube through a syringe. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 4:1). The reaction mixture was subjected to ^{1}H NMR measurement. **1a**-d_5 was obtained as white solid (12 mg, 36%).

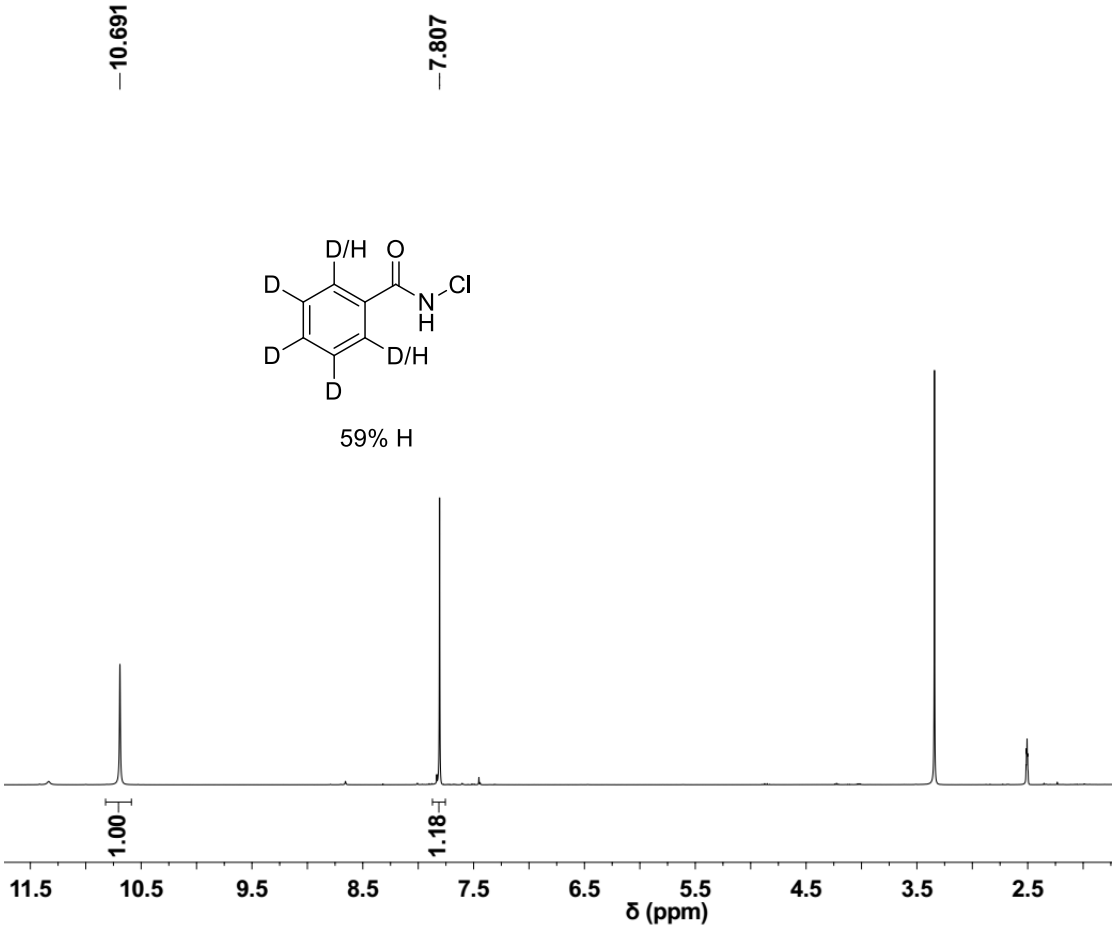
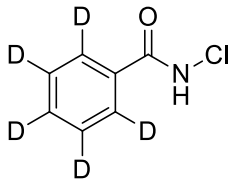


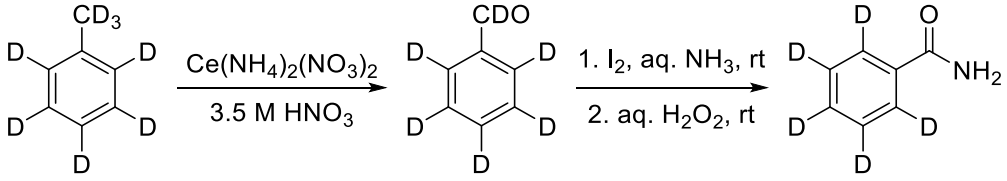
Figure S2. ^{1}H NMR spectrum for the product of equation above

6. Kinetic Isotope Effect Experiment

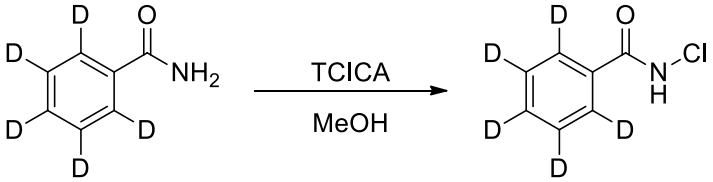
Preparation of deuterated 3-phenyl-1,2,4-oxadiazol-5(4*H*)-one:



1a-d_5

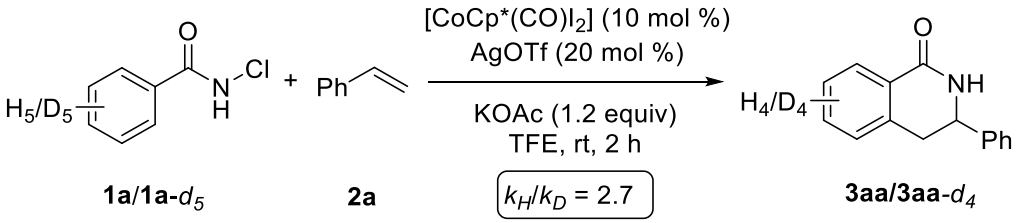


To d_8-toluene (2.5 g, 25 mmol) in 3.5 M HNO_3 (50 mL) was added $Ce(NH_4)_2(NO_3)_2$ (54.8 g, 100 mmol) in 3.5 M HNO_3 (200 mL). After stirring for 2.5 h at 80 ℃, the solution was cooled to room temperature, extracted with chloroform (3×50 mL), and the combined organic layers were washed with water until pH ≈ 7. The orange extract was dried over Na_2SO_4 and the solvent was removed in vacuum. The resulting red residue was distilled to give d_6-benzaldehyde, which was used without purification. A solution of the appropriate aldehyde (5 mmol) and iodine (5.5 mmol) in ammonia water (30 mL of 28% solution) and THF (5 mL) was stirred at room temperature for 1 h. The dark solution became colorless at the end of reaction. Then, aqueous H_2O_2 (3 mL of 35% solution) was added dropwise. The reaction mixture was stirred for 2-4 h and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo without purification.



1a-d_5

In a 100 mL, round-bottom flask were added 30 mL methanol and d_5-benzamide (4 mmol), and the mixture was allowed to stir until the solid dissolved. TCICA (trichloroisocyanuric acid) (1.5 mmol), was added and a precipitate of cyanuric acid formed in 8 min. After stirring for 1 h, the mixture was vacuum filtered and the solid was washed with methylene chloride. The solvent was removed from the filtrate using a rotary evaporator to give crude solid product. Recrystallization from toulene gave *N*-chloro-amide (448 mg, 70%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.51, 131.99 (t, J = 24.4 Hz), 131.61, 128.25 (t, J = 24.3 Hz), 127.29 (t, J = 24.5 Hz).



To a 13 × 150 mm test tube equipped with magnetic stir bar were added *N*-chlorobenzamide **1a** (31 mg, 0.2 mmol), d_5-*N*-chlorobenzamide **1a**-d_5 (32 mg, 0.2 mmol), styrene (21 mg, 0.2 mmol), [CoCp*(CO)I_2] (10 mg, 10 mol %), KOAc (24 mg, 120 mol %) and AgOTf (10 mg, 20 mol %) under nitrogen. Into the tube was then injected 1 mL of CF_3CH_2OH via syringe. The resulting solution was stirred at rt for 2 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 4:1). The corresponding product was obtained as an off-white solid (9 mg, 20%). The reaction mixture was subjected to ^{1}H NMR measurement.

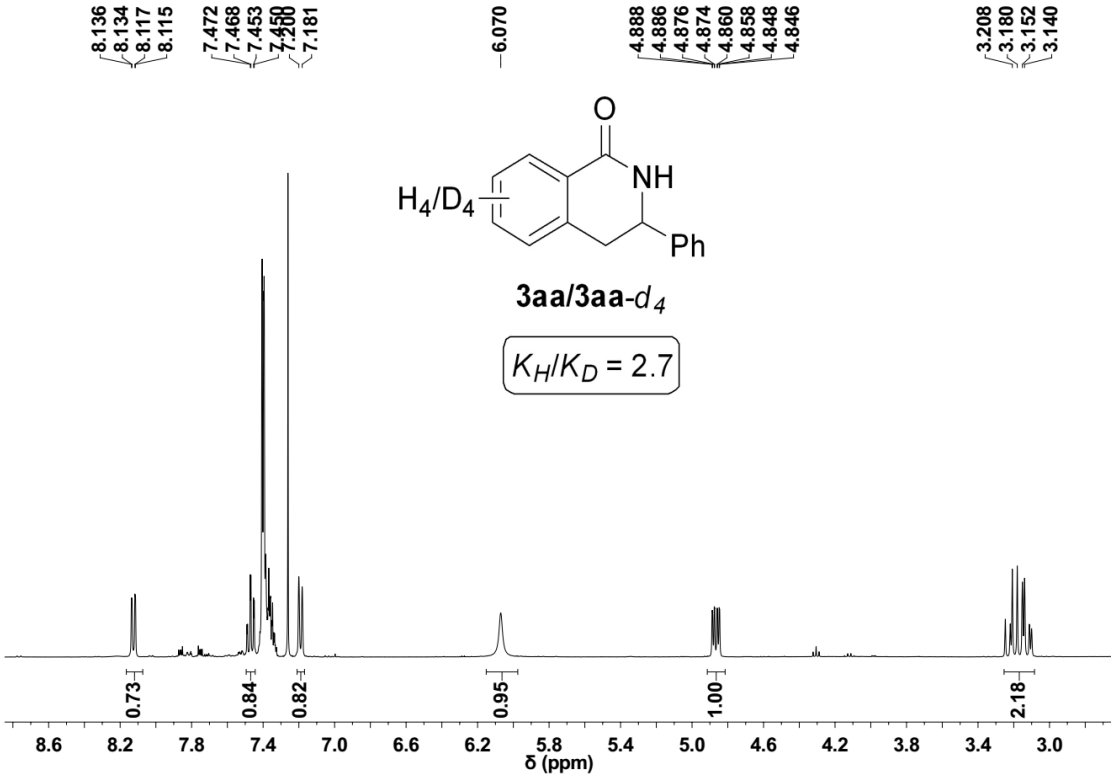
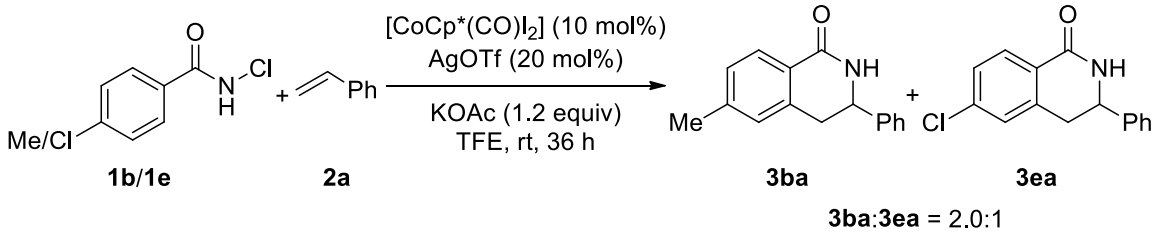


Figure S3. ^{1}H NMR spectrum for the mixture product of the equation above

7. Competition Experiment



To a 13 × 150 mm test tube equipped with magnetic stir bar were added *N*-chloro-4-methylbenzamide **1b** (35 mg, 0.2 mmol), *N*-chloro-4-chlorobenzamide **1e** (39 mg, 0.2 mmol), styrene (21 mg, 0.2 mmol), [CoCp*(CO)I_2] (10 mg, 10 mol %), KOAc (24 mg, 120 mol %) and AgOTf (10 mg, 20 mol %) under nitrogen. Then, 1 mL of CF_3CH_2OH was injected into the tube through a syringe. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo and the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 4:1). The reaction mixture was subjected to ^{1}H NMR measurement.

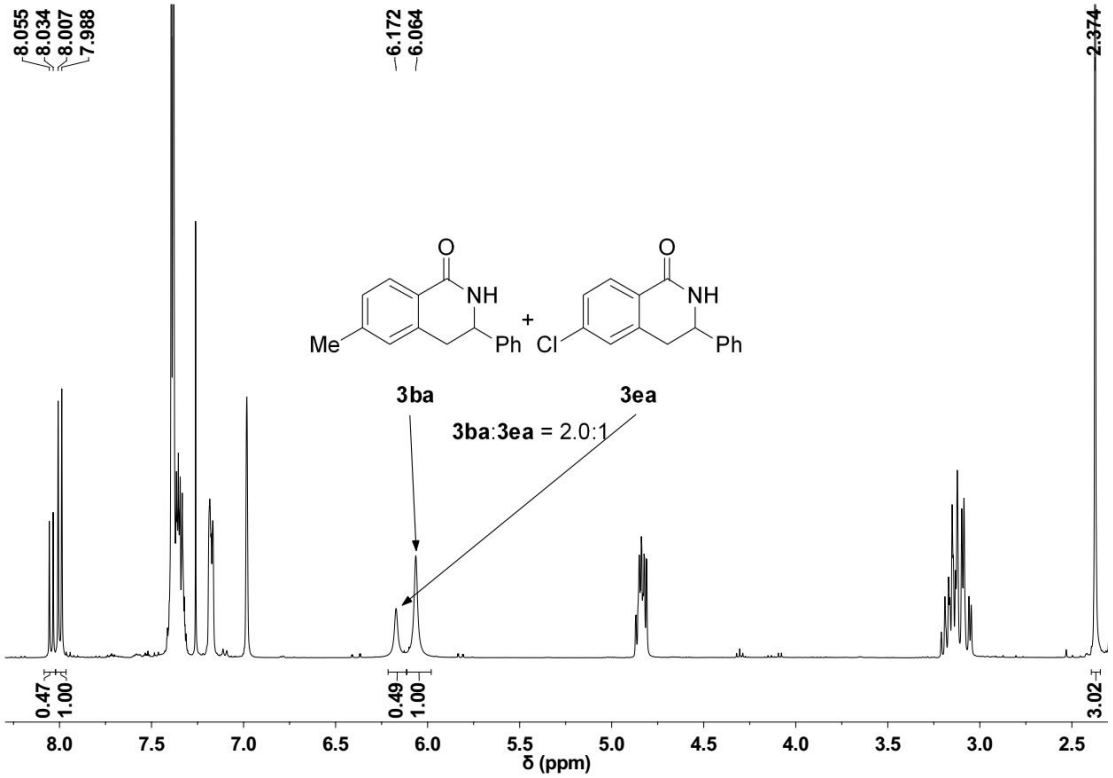
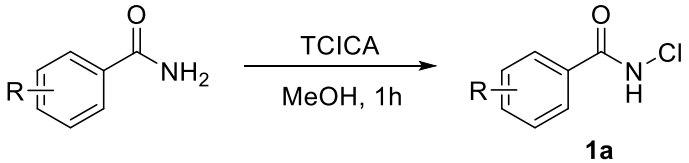


Figure S4. ^{1}H NMR spectrum for the products of equation above

8 Synthesis of Substrates

General procedure for the synthesis of substrates (1a-1j):



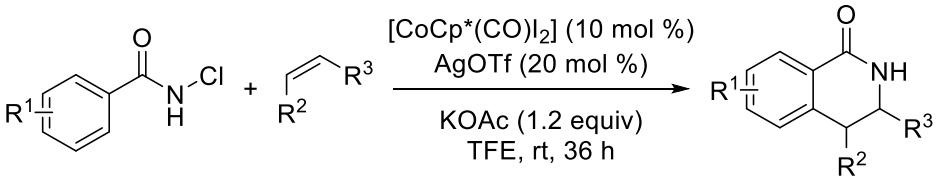
1a

In a 100 mL, round-bottom flask were placed 20 mL of methanol and amide (20 mmol), and the mixture was allowed to stir until the solid dissolved. TCICA (trichloroisocyanuric acid) (7.3 mmol) was added and a precipitate of cyanuric acid formed in 8 min. After stirring for 1 h, the mixture was vacuum filtered and the solid was washed with methylene chloride. The solvent was removed from the filtrate using

a rotary evaporator to give crude solid product. Recrystallization from toulene gave *N*-chloroamide.

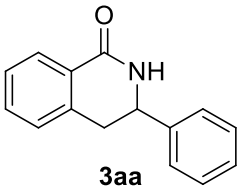
9. Preparation and Characterization Data of Products

General procedure for the synthesis of products



To a 13 × 150 mm test tube equipped with magnetic stir bar were added substituted *N*-chlorobenzamides (0.2 mmol), alkenes (0.3 mmol), [CoCp*(CO)I_2] (10 mg,10 mol %), KOAc (24 mg, 120 mol %) and AgOTf (10 mg, 20 mol %) in CF_3CH_2OH (1 mL) under nitrogen. The resulting solution was stirred at rt for 36 h. The reaction mixture was concentrated in vacuo, the residue was dissolved in methylene chloride and purified by column chromatography (silica gel, PE:EtOAc = 3:1).

3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3aa)[1]



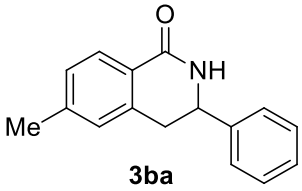
3aa

The corresponding product was obtained as an off-white solid (39 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 – 7.30 (m, 6H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.18 (s, 1H), 6.18 (s, 1H), 4.85 (m, 1H), 3.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 140.98, 137.58, 135.97, 132.53, 129.02, 128.41, 128.07, 127.35, 127.31, 126.45, 56.15, 37.47.

6-methyl-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ba)[2]



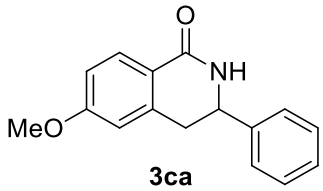
3ba

The corresponding product was obtained as an off-white solid (28 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.30 (m, 5H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 6.08 (s, 1H), 4.86 – 4.79 (m, 1H), 3.11 (qd, *J* = 15.7, 7.9 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 143.16, 141.12, 137.57, 129.00, 128.36, 128.13, 127.97, 126.45, 125.74, 56.22, 37.48, 21.64.

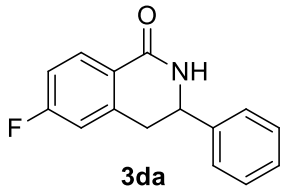
6-methoxy-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ca) [2]



3ca

The corresponding product was obtained as an off-white solid (19 mg, 38%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 1H), 7.44 – 7.31 (m, 5H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.98 (s, 1H), 4.84 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.84 (s, 3H), 3.12 (qd, *J* = 15.7, 7.8 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.46, 162.93, 141.04, 139.73, 130.24, 129.01, 128.39, 126.44, 121.14, 112.67, 112.48, 56.19, 55.44, 37.80.

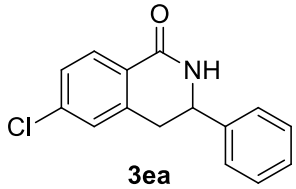
6-fluoro-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3da) [2]



3da

The corresponding product was obtained as an off-white solid (30 mg, 63%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.46 – 7.29 (m, 5H), 7.03 (td, *J* = 8.6, 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.26 (s, 1H), 4.86 (m, 1H), 3.15 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ165.63, 165.21 (d, *J* = 252.0 Hz), 140.60, 140.42 (d, *J* = 9.0 Hz), 130.89 (d, *J* = 10.0 Hz), 129.07, 128.52, 126.41, 124.83, 114.55 (d, *J* = 22.0 Hz), 114.23 (d, *J* = 22.0 Hz), 55.96, 37.40 (d, *J* = 1.0 Hz).

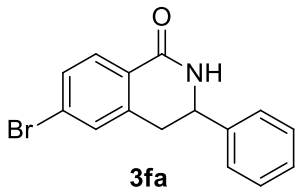
6-chloro-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ea) [2]



3ea

The corresponding product was obtained as an off-white solid (31 mg, 60%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.48 – 7.27 (m, 6H), 7.17 (d, *J* = 14.5 Hz, 1H), 6.46 – 6.18 (m, 1H), 4.87 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.30 – 3.01 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.59, 140.55, 139.41, 138.64, 129.72, 129.10, 128.55, 127.68, 127.51, 126.41, 55.87, 37.14.

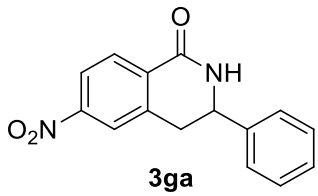
6-bromo-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3fa) [2]



3fa

The corresponding product was obtained as an off-white solid (32 mg, 53%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.44 – 7.28 (m, 6H), 6.29 (s, 1H), 4.85 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.32 – 3.04 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.75, 140.51, 139.38, 130.66, 130.38, 129.80, 129.10, 128.56, 127.23, 126.40, 55.92, 37.06.

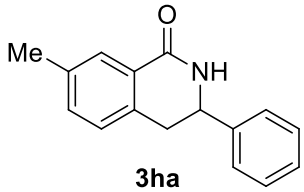
6-nitro-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ga) [2]



3ga

The corresponding product was obtained as an off-white solid (15 mg, 28%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.20 (dd, *J* = 8.5, 2.2 Hz, 1H), 8.07 (d, *J* = 1.9 Hz, 1H), 7.39 (qd, *J* = 7.2, 3.3 Hz, 5H), 6.45 (s, 1H), 4.93 (t, *J* = 7.5 Hz, 1H), 3.30 (d, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.35, 150.10, 139.86, 139.08, 133.79, 129.58, 129.24, 128.83, 126.35, 122.61, 122.30, 55.73, 37.13.

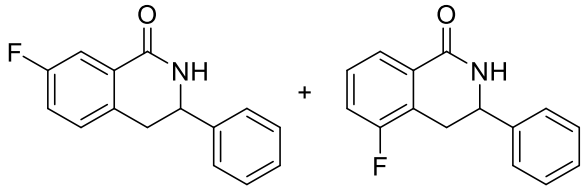
7-methyl-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ha) [2]



3ha

The corresponding product was obtained as an off-white solid (25 mg, 53%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.43 – 7.30 (m, 5H), 7.29 – 7.24 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.12 (s, 1H), 4.90 – 4.75 (m, 1H), 3.11 (m, 2H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.76, 141.08, 137.08, 134.75, 134.60, 133.32, 129.00, 128.43, 128.37, 128.19, 127.28, 126.45, 56.28, 37.11, 21.08.

7-fluoro-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ia)



3ial **3iall**

3ia (3ial:3iall = 1.4:1)

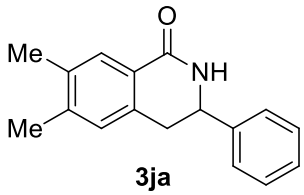
The corresponding product was obtained as an off-white solid (29 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 1H), 7.78 (dd, *J* = 8.7, 1.6 Hz, 0.74 ×1H), 7.44 –7.15 (m, 0.74×7H + 7H), 6.33 (s, 0.74×1H), 6.29 (s, 1H), 4.92 – 4.79 (m, 0.74×1H + 1H), 3.37 – 2.98 (m, 0.74×2H + 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.51, 163.22, 160.78, 160.29, 157.85, 140.63, 140.57, 133.22, 130.43, 129.15, 129.10, 129.06, 128.59, 128.52, 128.14, 128.06, 126.45, 126.43, 124.71, 124.53, 123.76, 123.73, 119.69, 119.47, 119.30, 119.08, 114.84, 114.61, 56.14, 55.60, 36.68, 29.85, 29.83.

HRMS (ESI) m/z calcd. for $C_{15}H_{13}FNO$ $[M+H]^+$ 242.0976, found 242.0975.

6,7-dimethyl-3-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (3ja)



3ja

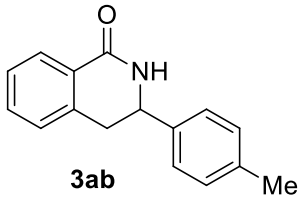
The corresponding product was obtained as an off-white solid (18 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.42 – 7.30 (m, 5H), 6.95 (s, 1H), 6.01 (s, 1H), 4.83 (dd, *J* = 10.6, 5.0 Hz, 1H), 3.08 (qd, *J* = 15.6, 7.9 Hz, 2H), 2.29 (d, *J* = 5.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.94, 141.23, 135.75, 135.11, 128.98, 128.93, 128.60, 128.33, 126.45, 56.36, 37.03, 19.96, 19.39.

HRMS (ESI) m/z calcd. for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1383.

3-(p-tolyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ab) [2]



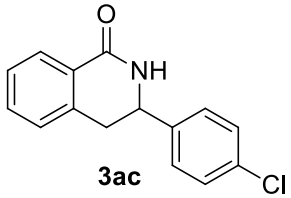
3ab

The corresponding product was obtained as light yellow solid (37 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 11.9 Hz, 2H), 7.18 (dd, *J* = 7.4, 4.8 Hz, 3H), 6.19 (s, 1H), 4.81 (dd, *J* = 11.0, 4.7 Hz, 1H), 3.13 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.44, 138.20, 137.97, 137.72, 132.50, 129.65, 128.41, 128.06, 127.36, 127.26, 126.36, 55.88, 37.50, 21.13.

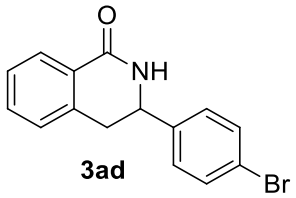
3-(4-chlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ac) [3]



3ac

The corresponding product was obtained as light yellow solid (36 mg, 69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.03 (m, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 7.41 – 7.28 (m, 5H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 4.84 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.22 – 3.09 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.48, 139.54, 137.16, 134.06, 132.65, 129.13, 128.06, 127.84, 127.40, 55.34, 37.21.

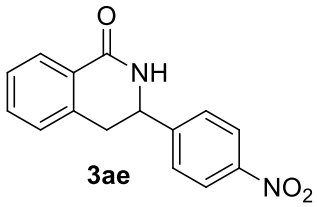
3-(4-bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ad) [4]



3ad

The corresponding product was obtained as light yellow solid (42 mg, 69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 4.83 (dd, *J* = 8.4, 6.5 Hz, 1H), 3.23 – 3.03 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.41, 140.08, 137.11, 132.64, 132.09, 128.25, 128.16, 128.07, 127.42, 127.39, 122.16, 55.41, 37.18.

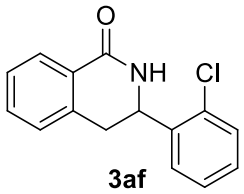
3-(4-nitrophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ae) [5]



3ae

The corresponding product was obtained as light yellow solid (39 mg, 72%).
^{1}H NMR (400 MHz, DMSO) δ 8.51 (d, *J* = 2.6 Hz, 1H), 8.24 – 8.16 (m, 2H), 7.91 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 5.02 (td, *J* = 6.1, 3.0 Hz, 1H), 3.44 – 3.37 (m, 1H), 3.14 (dd, *J* = 16.0, 6.6 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 164.69, 149.95, 146.70, 136.73, 132.15, 128.77, 127.72, 126.99, 126.90, 123.48, 53.00, 35.10.

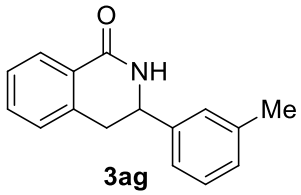
3-(2-chlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3af)



3af

The corresponding product was obtained as light yellow solid (25 mg, 49%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.43 – 7.33 (m, 2H), 7.31 – 7.22 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.26 (s, 1H), 5.36 (m,1H), 3.36 (dd, *J* = 15.8, 5.2 Hz, 1H), 3.12 (dd, *J* = 15.8, 9.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.61, 138.26, 137.00, 132.74, 130.03, 129.27, 128.05, 127.60, 127.50, 127.40, 127.28, 52.11, 34.77.
HRMS (ESI) m/z calcd. for $C_{15}H_{13}ClNO$ $[M+H]^+$ 258.0680, found 258.0680.

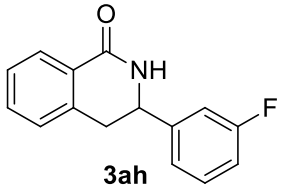
3-(m-tolyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ag)[2]



3ag

The corresponding product was obtained as an off-white solid (37 mg, 77%).
^{1}H NMR (400 MHz, DMSO) δ 8.27 (d, *J* = 1.9 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.45 (td, *J* = 7.4, 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.1 Hz, 1H), 7.26 – 7.14 (m, 3H), 7.08 (dd, *J* = 16.8, 7.6 Hz, 2H), 5.05 – 4.57 (m, 1H), 3.28 (dd, *J* = 15.9, 5.4 Hz, 1H), 3.08 (dd, *J* = 15.9, 7.4 Hz, 1H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 165.30, 142.63, 137.88, 137.86, 132.46, 129.44, 128.70, 128.39, 128.18, 127.51, 127.32, 127.28, 123.91, 54.07, 36.25, 21.55.

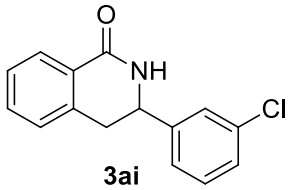
3-(3-fluorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ah)



3ah

The corresponding product was obtained as an off-white solid (29 mg, 59%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.46 (m, 1H), 7.42 – 7.31 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.11 (dd, *J* = 9.6, 1.7 Hz, 1H), 7.03 (dd, *J* = 11.7, 5.0 Hz, 1H), 6.50 (s, 1H), 4.94 – 4.80 (m, 1H), 3.26 – 3.10 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.44, 164.24, 161.78, 143.61, 143.54, 137.12, 132.69, 130.67, 130.58, 128.08, 127.44, 127.39, 122.07, 122.05, 115.40, 115.19, 113.64, 113.42, 55.53, 37.16.
HRMS (ESI) m/z calcd. for $C_{15}H_{13}FNO$ $[M+H]^+$ 242.0976, found 242.0974.

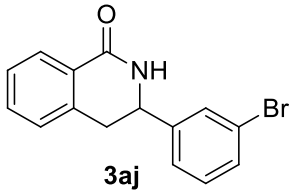
3-(3-chlorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3ai)



3ai

The corresponding product was obtained as light yellow solid (36 mg, 69%).
^{1}H NMR (400 MHz, DMSO) δ 8.39 (d, *J* = 2.2 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.4 Hz, 1H), 7.42 – 7.22 (m, 6H), 4.89 – 4.81 (m, 1H), 3.31 (dd, *J* = 16.0, 5.5 Hz, 1H), 3.12 (dd, *J* = 15.9, 7.1 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 164.71, 144.76, 137.08, 132.98, 132.08, 130.21, 128.83, 127.73, 127.23, 126.89, 126.85, 126.42, 125.10, 52.99, 35.28.
HRMS (ESI) m/z calcd. for $C_{15}H_{13}ClNO$ $[M+H]^+$ 258.0680, found 258.0680.

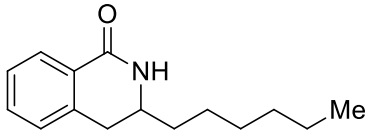
3-(3-bromophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3aj)



3aj

The corresponding product was obtained as an off-white solid (37 mg, 61%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.55 (s, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.83 (t, *J* = 7.6 Hz, 1H), 3.16 (d, *J* = 7.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 143.27, 137.07, 132.72, 131.47, 130.58, 129.66, 128.10, 127.47, 127.38, 125.06, 122.99, 55.46, 37.18.
HRMS (ESI) m/z calcd. for $C_{15}H_{13}BrNO$ $[M+H]^+$ 302.0175, found 302.0173.

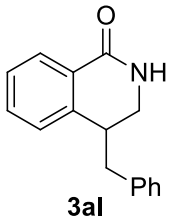
3-hexyl-3,4-dihydroisoquinolin-1(2H)-one (3ak)



3ak

The corresponding product was obtained as an off-white solid (25 mg, 54%).
^{1}H NMR (400 MHz, DMSO) δ 7.93 (s, 1H), 7.86 – 7.80 (m, 1H), 7.46 (td, *J* = 7.4, 1.4 Hz, 1H), 7.37 – 7.26 (m, 2H), 3.57 – 3.47 (m, 1H), 3.00 (dd, *J* = 15.7, 4.6 Hz, 1H), 2.70 (dd, *J* = 15.7, 9.0 Hz, 1H), 1.62 – 1.48 (m, 1H), 1.47 – 1.23 (m, 9H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, DMSO) δ 164.88, 138.73, 132.21, 129.54, 128.22, 127.32, 127.08, 50.73, 35.07, 33.46, 31.68, 29.14, 25.33, 22.49, 14.42.
HRMS (ESI) m/z calcd. for $C_{15}H_{22}NO$ $[M+H]^+$ 232.1696, found 232.1695.

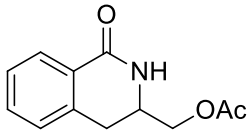
3-benzyl-3,4-dihydroisoquinolin-1(2*H*)-one (3al)[1]



3al

The corresponding product was obtained as an off-white solid (31 mg, 64%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.28 (dt, *J* = 4.9, 2.0 Hz, 1H), 7.23 – 7.16 (m, 3H), 6.03 (s, 1H), 4.15 – 3.77 (m, 1H), 3.32 – 2.58 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.12, 137.73, 136.60, 132.41, 129.21, 128.98, 128.64, 128.04, 127.54, 127.16, 52.48, 41.79, 34.15.

(1-oxo-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl acetate (3am)



3am

The corresponding product was obtained as an off-white solid (33 mg, 75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 4.26 (dd, *J* = 11.1, 4.4 Hz, 1H), 4.10 (dd, *J* = 11.1, 7.8 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.05 (dd, *J* = 15.7, 4.9 Hz, 1H), 2.91 (dd, *J* = 15.7, 9.0 Hz, 1H), 2.08 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.72, 166.07, 136.74, 132.55, 131.94, 128.60, 128.49, 128.05, 127.63, 127.35, 65.95, 49.93, 30.33, 20.74.
HRMS (ESI) m/z calcd. for $C_{12}H_{14}NO_3$ $[M+H]^+$ 220.0968, found 220.0967.

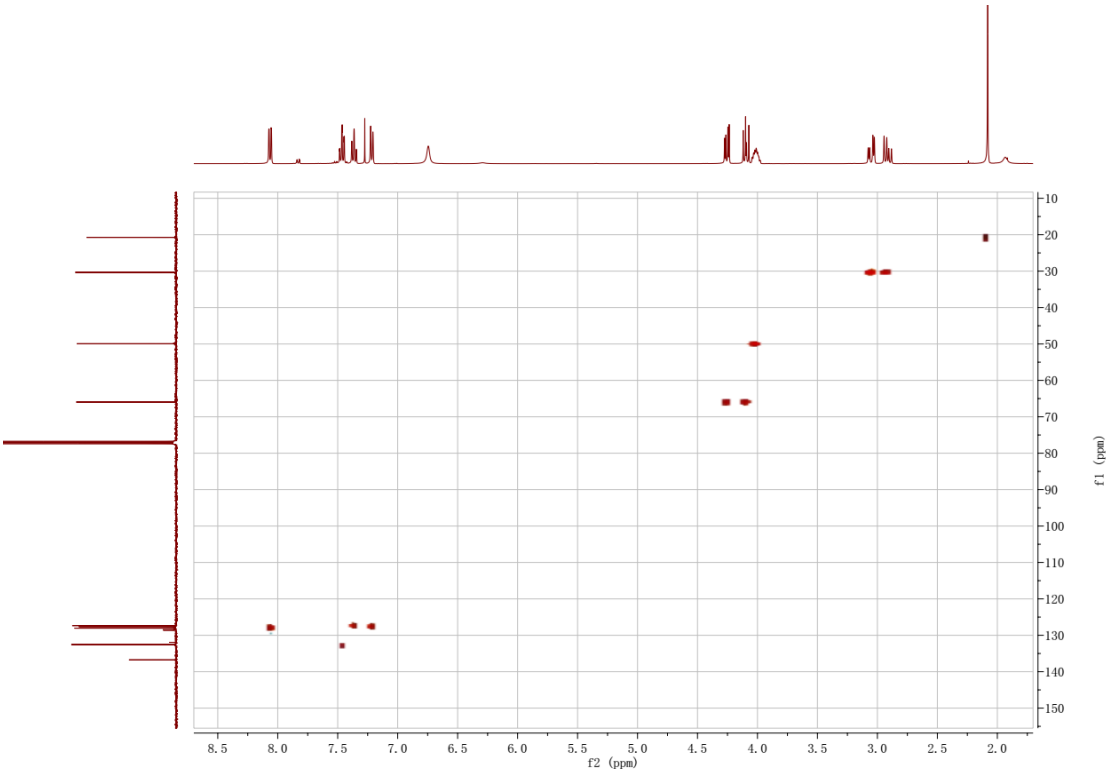


Figure S5. The ^{1}H–^{13}C HSQC (400 MHz, $CDCl_3$) spectrum of **3am**

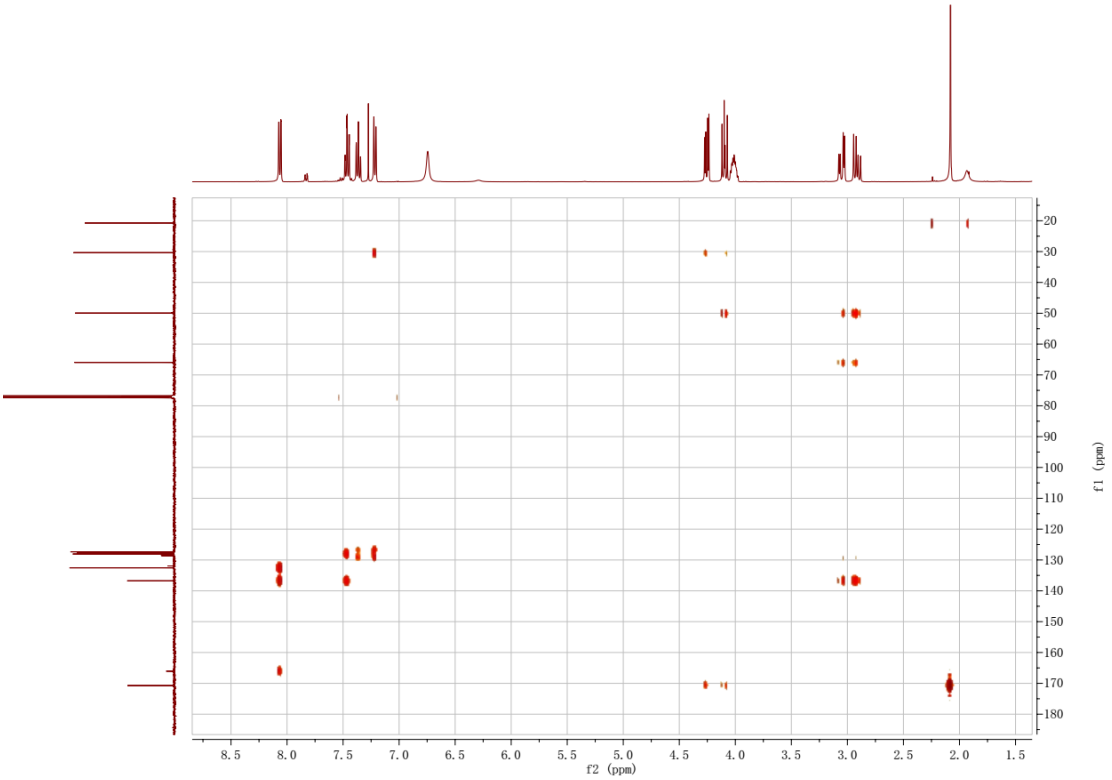
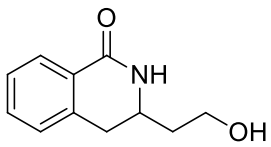


Figure S6. The ^{1}H–^{13}C HMBC (400 MHz, $CDCl_3$) spectrum of **3am**

3-(2-hydroxyethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3anI)



3anI

The corresponding product was obtained as an off-white solid (22 mg, 58%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.64 (s, 1H), 3.81 – 3.70 (m, 2H), 3.65 (ddd, *J* = 10.8, 6.8, 5.9 Hz, 1H), 3.44 (ddd, *J* = 12.6, 4.8, 2.8 Hz, 1H), 3.13 (dt, *J* = 7.3, 3.7 Hz, 1H), 2.12 (s, 1H), 1.93 (dtd, *J* = 7.4, 5.9, 3.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.35, 142.59, 132.32, 128.19, 128.04, 127.25, 60.02, 44.26, 35.83, 34.38.
HRMS (ESI) m/z calcd. for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.1019, found 192.1018.

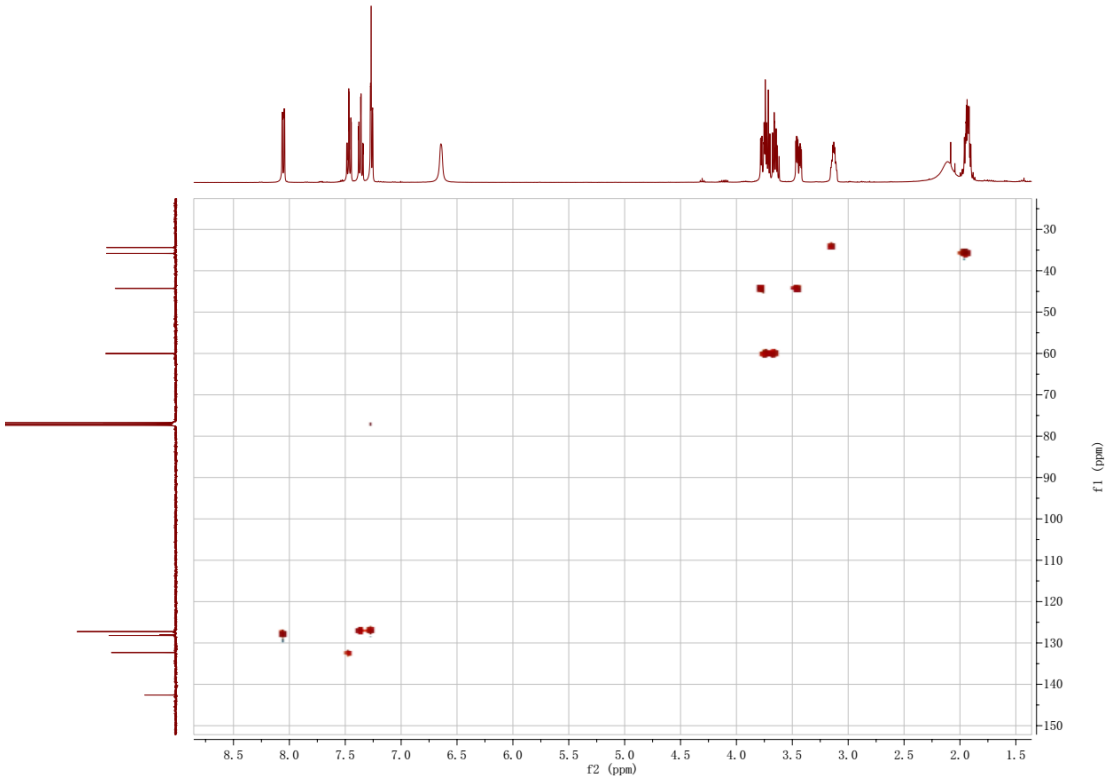


Figure S7. The ^{1}H–^{13}C HSQC (400 MHz, $CDCl_3$) spectrum of **3anI**

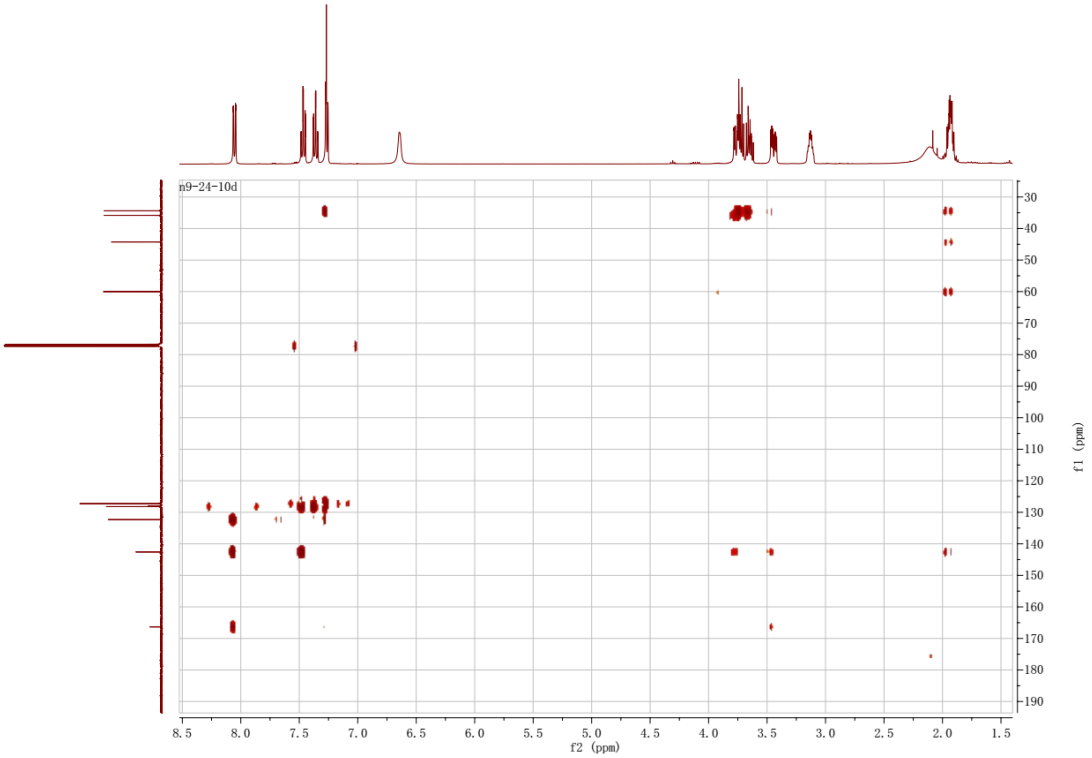
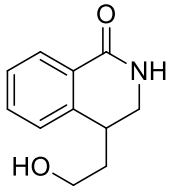


Figure S8. The ^{1}H–^{13}C HMBC (400 MHz, $CDCl_3$) spectrum of **3anI**

4-(2-hydroxyethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (3anII)



3anII

The corresponding product was obtained as an off-white solid (14 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 1H), 7.61 (s, 1H), 7.44 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.04 – 3.91 (m, 2H), 3.88 – 3.80 (m, 1H), 3.05 (s, 1H), 2.98 – 2.84 (m, 2H), 1.92 (ddd, *J* = 13.3, 9.7, 4.6 Hz, 1H), 1.84 – 1.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 138.15, 132.38, 128.28, 127.86, 127.45, 127.09, 60.64, 51.10, 36.86, 34.67.

HRMS (ESI) m/z calcd. for $C_{11}H_{14}NO_2$ $[M+H]^+$ 192.1019, found 192.1018.

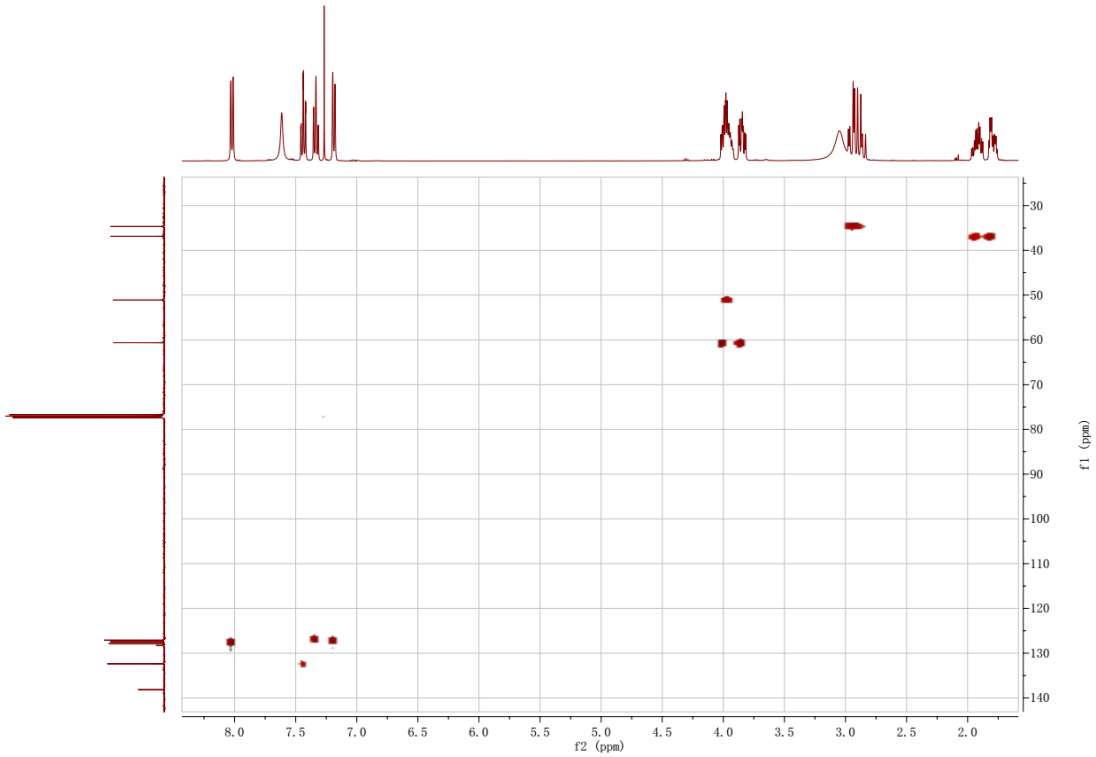


Figure S9. The $^{1}H–^{13}C$ HSQC (400 MHz, $CDCl_3$) spectrum of **3anII**

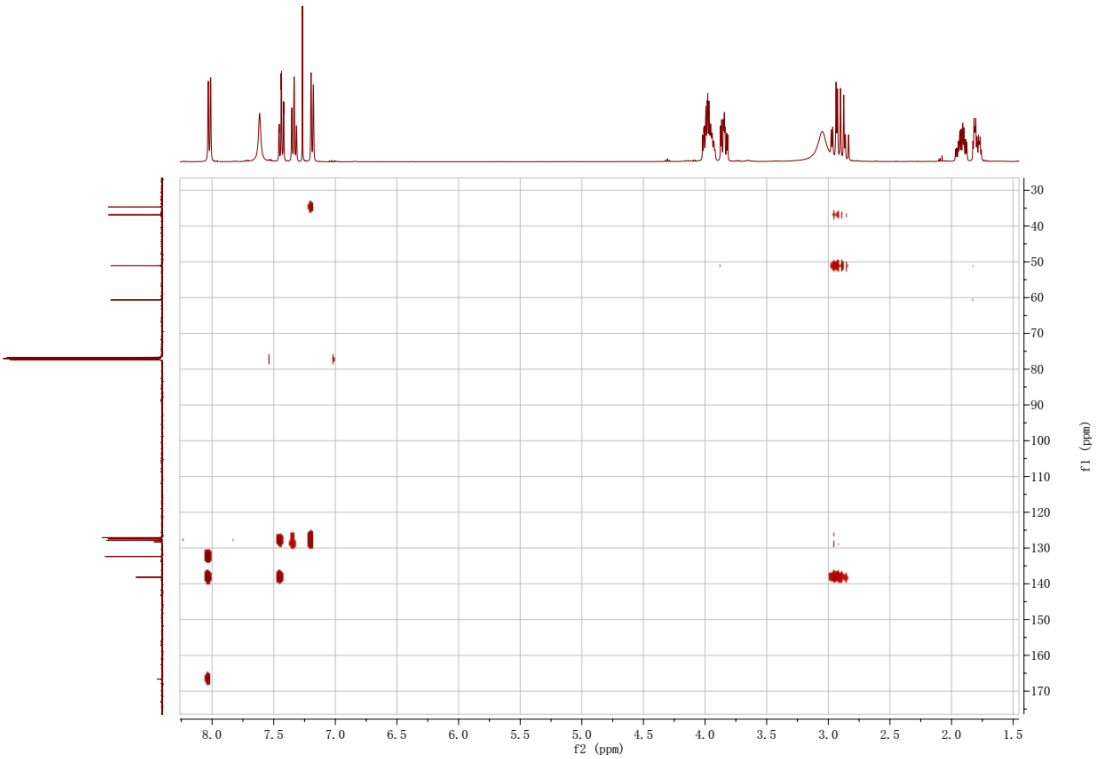
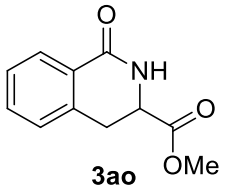


Figure S10. The $^{1}H–^{13}C$ HMBC (400 MHz, $CDCl_3$) spectrum of **3anII**

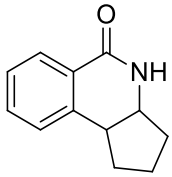
methyl 1-oxo-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (3ao)[1]



3ao

The corresponding product was obtained as an off-white solid (32 mg, 78%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 4.42 (m, 1H), 3.79 (s, 3H), 3.34 (dd, *J* = 15.7, 5.2 Hz, 1H), 3.22 (dd, *J* = 15.7, 9.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.89, 165.26, 136.21, 132.59, 128.42, 128.19, 127.61, 127.47, 53.08, 52.92, 31.15.

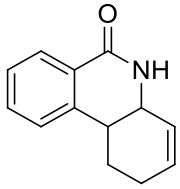
2,3,3a,4-tetrahydro-1H-cyclopenta[c]isoquinolin-5(9b*H*)-one (3ap)[2]



3ap

The corresponding product was obtained as an off-white solid (22 mg, 59%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 5.74 (s, 1H), 4.21 (t, *J* = 5.0 Hz, 1H), 3.11 (td, *J* = 9.2, 5.7 Hz, 1H), 2.20 – 2.11 (m, 1H), 2.10 – 2.01 (m, 1H), 1.98 – 1.90 (m, 1H), 1.87 – 1.77 (m, 3H).
^{13}C NMR (101 MHz, DMSO) δ 164.08, 142.25, 132.28, 128.18, 127.64, 127.48, 127.00, 55.58, 42.38, 33.76, 33.41, 23.12.

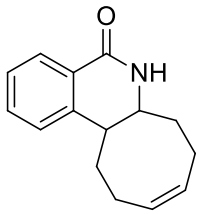
1,4a,5,10b-tetrahydrophenanthridin-6(2*H*)-one (3aq)[1]



3aq

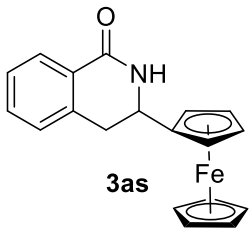
The corresponding product was obtained as an off-white solid (15 mg, 38%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 – 7.21 (m, 1H), 6.04 (dt, *J* = 9.9, 3.7 Hz, 1H), 5.88 (s, 1H), 5.82 – 5.75 (m, 1H), 4.28 (t, *J* = 4.6 Hz, 1H), 2.94 (dt, *J* = 12.2, 3.8 Hz, 1H), 2.31 – 2.13 (m, 2H), 2.06 – 1.85 (m, 1H), 1.76 – 1.62 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.00, 142.79, 132.59, 132.45, 128.06, 127.50, 127.26, 127.14, 124.34, 48.00, 37.84, 25.20, 25.03.

(*Z*)-6,6a,7,8,12,12a-hexahydrocycloocta[c]isoquinolin-5(11*H*)-one (3ar)



3ar

The corresponding product was obtained as an off-white solid (13 mg, 33%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.25 (s, 1H), 5.78 – 5.53 (m, 2H), 4.08 – 3.83 (m, 1H), 3.25 (dt, *J* = 11.9, 3.6 Hz, 1H), 2.90 – 2.72 (m, 1H), 2.70 – 2.54 (m, 1H), 2.54 – 2.38 (m, 1H), 2.26 – 2.15 (m, 1H), 2.12 – 2.05 (m, 1H), 1.87 (m, 2H), 1.57 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.49, 144.96, 132.40, 130.37, 128.31, 128.00, 126.87, 126.67, 125.87, 55.72, 38.95, 29.71, 29.54, 27.52, 25.45.
HRMS (ESI) m/z calcd. for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383, found 228.1382.



3as

The corresponding product was obtained as a brown solid (27 mg, 40%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.4, 6.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.28 (s, 1H), 4.52 (dd, *J* = 10.3, 5.5 Hz, 1H), 4.29 – 4.17 (m, 8H), 3.10 – 2.95 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.01, 138.00, 134.19, 132.42, 128.56, 128.06, 127.25, 127.22, 123.51, 89.38, 68.66, 68.32, 68.31, 66.89, 65.20, 51.05, 37.65.
HRMS (ESI) m/z calcd. for $C_{19}H_{18}FeNO$ $[M+H]^+$ 332.0732, found 332.0732.

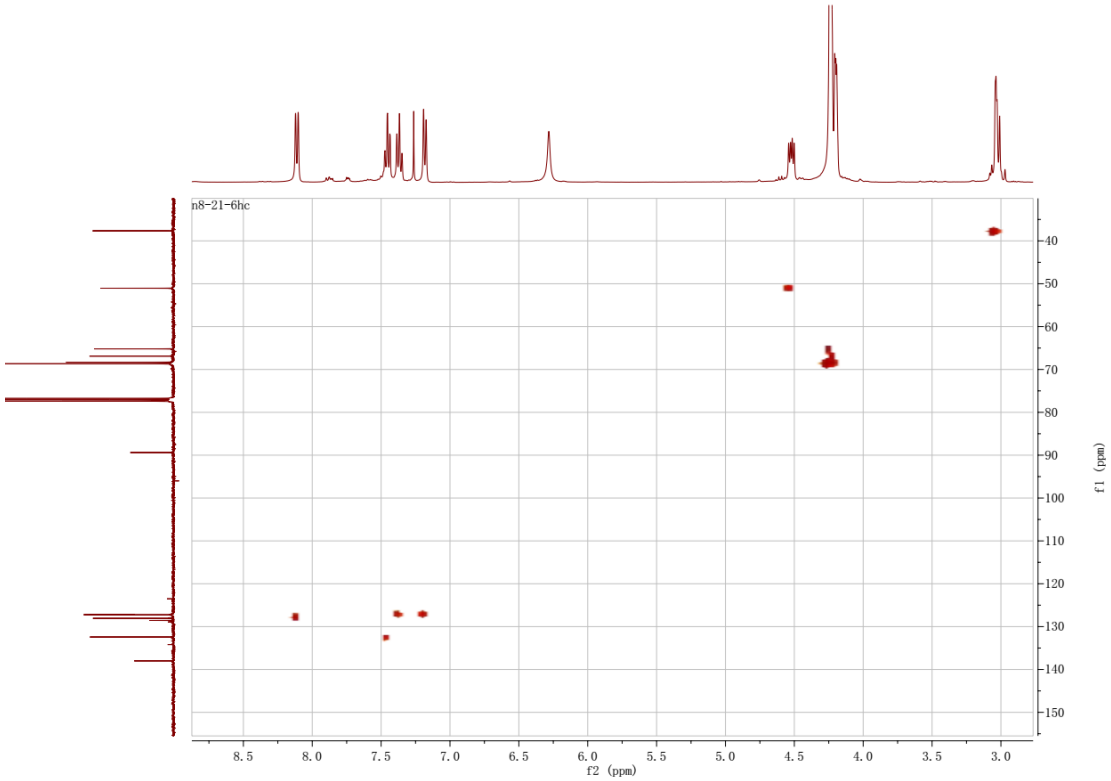


Figure S11. The $^{1}H–^{13}C$ HSQC (400 MHz, $CDCl_3$) spectrum of **3as**

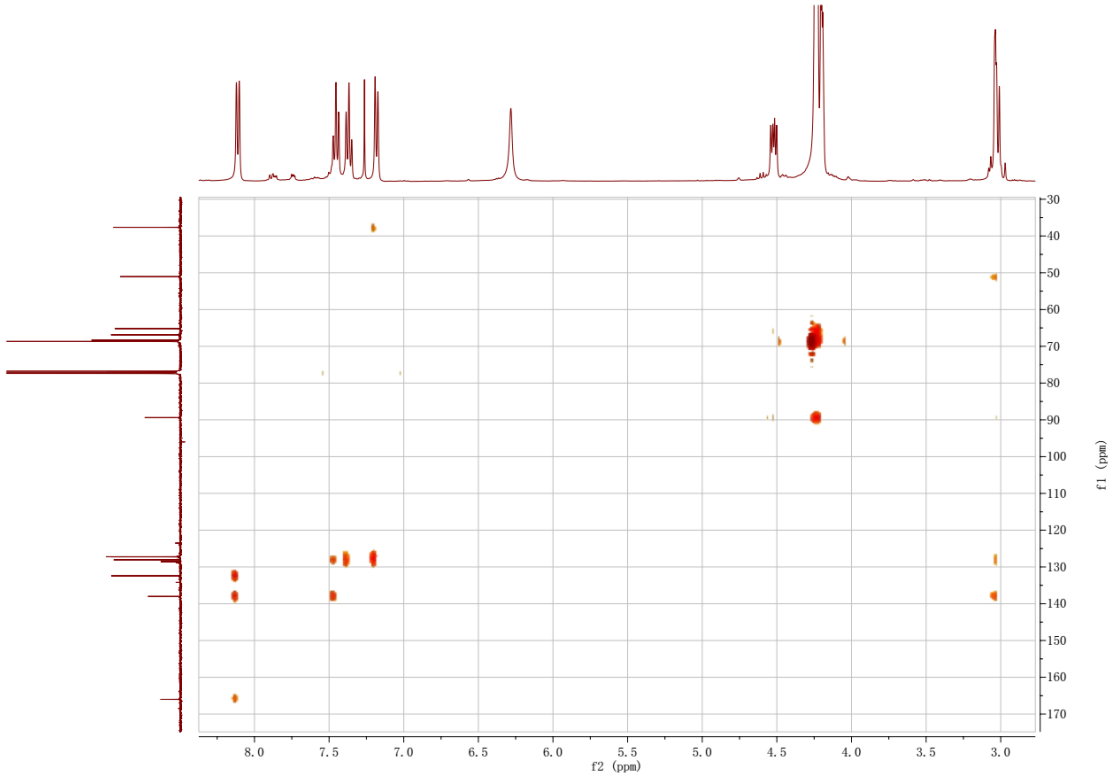
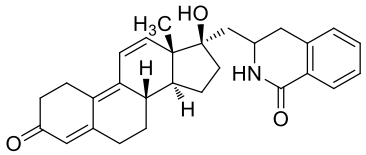


Figure S12. The $^{1}H–^{13}C$ HMBC (400 MHz, $CDCl_3$) spectrum of **3as**



3atI

The corresponding product was obtained as a off-white solid (33 mg, 39%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 9.4, 8.6 Hz, 2H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.50 (s, 2H), 5.79 (s, 1H), 4.07 (dd, *J* = 16.4, 6.7 Hz, 1H), 3.15 (s, 1H), 2.94 – 2.79 (m, 3H), 2.72 (dd, *J* = 15.5, 3.6 Hz, 1H), 2.58 (dd, *J* = 12.8, 2.0 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 3H), 2.15 – 2.04 (m, 1H), 1.94 (m, 3H), 1.72 – 1.54 (m, 4H), 1.34 – 1.25 (m, 1H), 1.10 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.26, 166.12, 156.51, 141.87, 141.72, 138.35, 132.23, 128.48, 127.91, 127.15, 127.09, 124.09, 123.66, 83.20, 49.94, 48.86, 48.02, 41.58, 38.40, 36.70, 35.71, 34.27, 31.49, 27.16, 24.36, 23.16, 16.29.
HRMS (ESI) m/z calcd. for $C_{28}H_{32}NO_3$ $[M+H]^+$ 430.2377, found 430.2376.

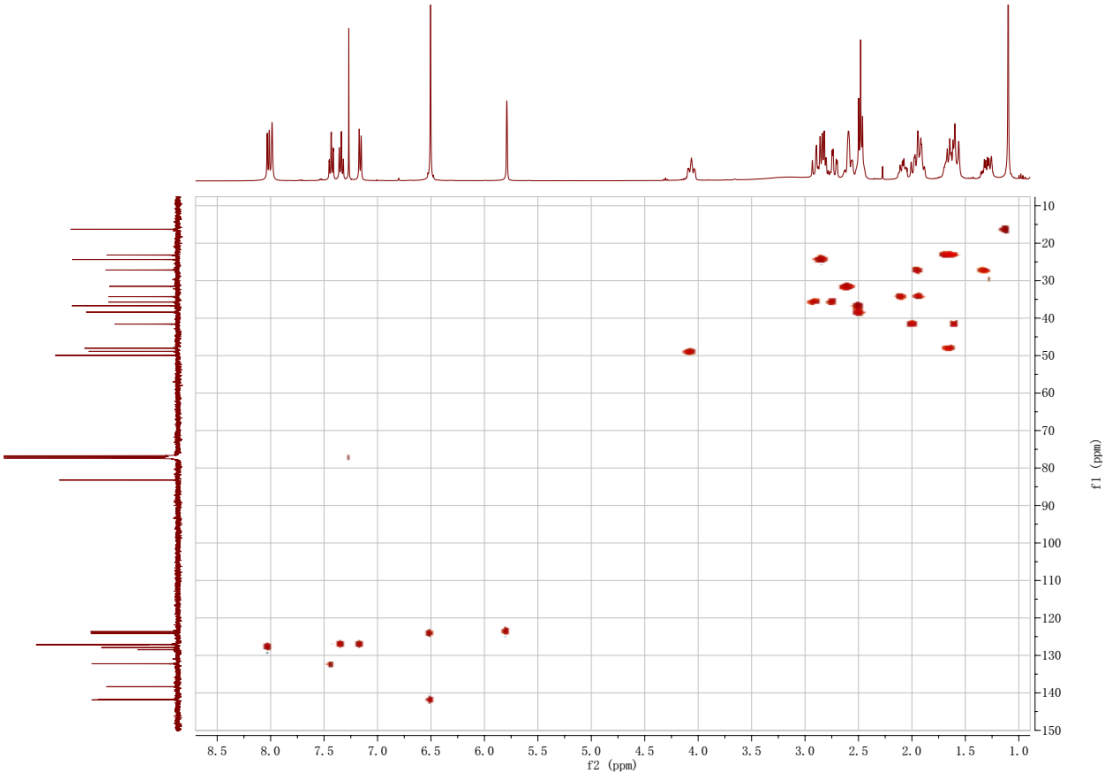


Figure S13. The ^{1}H–^{13}C HSQC (400 MHz, $CDCl_3$) spectrum of **3atI**

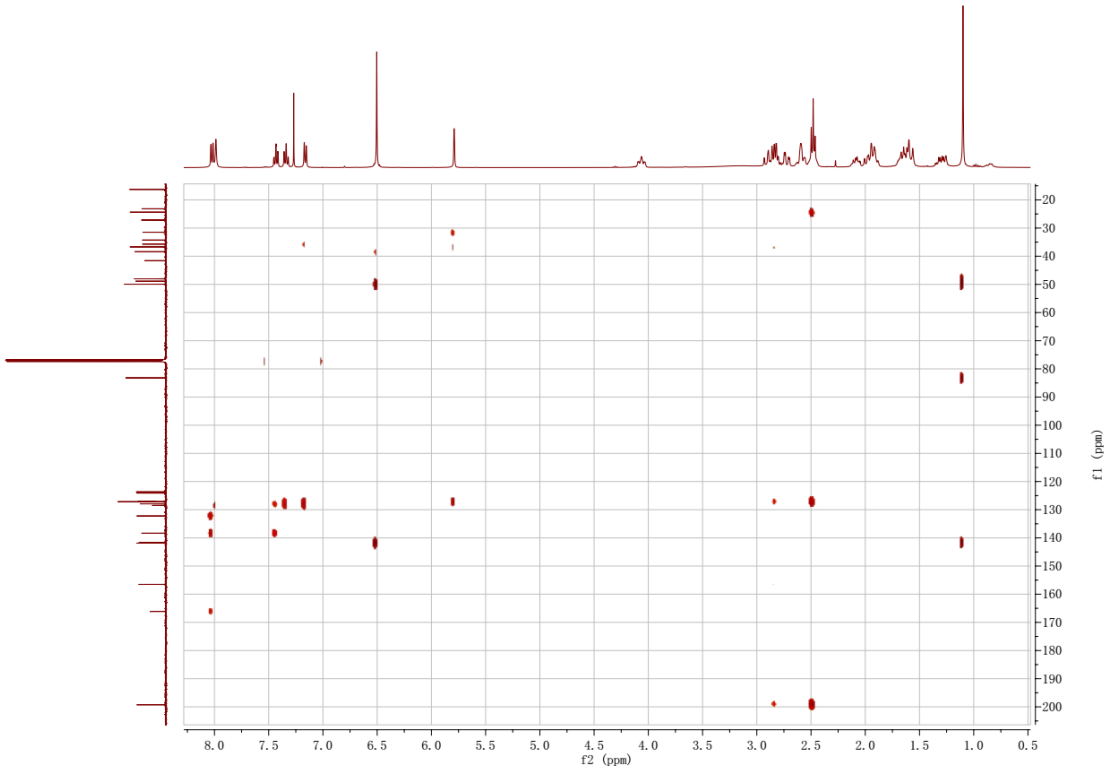
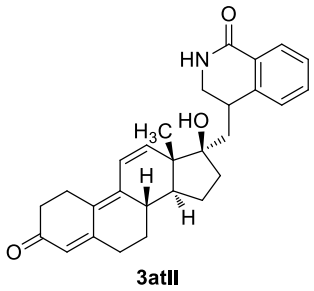


Figure S14. The ^{1}H–^{13}C HMBC (400 MHz, $CDCl_3$) spectrum of **3atI**



3atII

The corresponding product was obtained as a off-white solid (29 mg, 33%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.73 (s, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.42 (s, 2H), 5.78 (s, 1H), 4.16 (td, *J* = 10.3, 5.6 Hz, 1H), 2.91 (dd, *J* = 15.6, 4.4 Hz, 1H), 2.79 (dd, *J* = 17.3, 9.1 Hz, 3H), 2.55 (d, *J* = 17.4 Hz, 2H), 2.47 – 2.37 (m, 3H), 2.00 – 1.82 (m, 5H), 1.70 (dt, *J* = 16.4, 7.4 Hz, 2H), 1.54 – 1.44 (m, 1H), 1.35 – 1.26 (m, 1H), 1.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.18, 166.16, 156.39, 141.43, 141.22, 138.33, 132.28, 128.45, 127.96, 127.39, 127.19, 127.04, 123.90, 123.69, 82.55, 49.62, 49.20, 47.40, 44.28, 39.60, 38.39, 36.64, 35.52, 31.43, 27.02, 24.30, 22.63, 17.03.
HRMS (ESI) m/z calcd. for $C_{28}H_{32}NO_3$ $[M+H]^+$ 430.2377, found 430.2376.

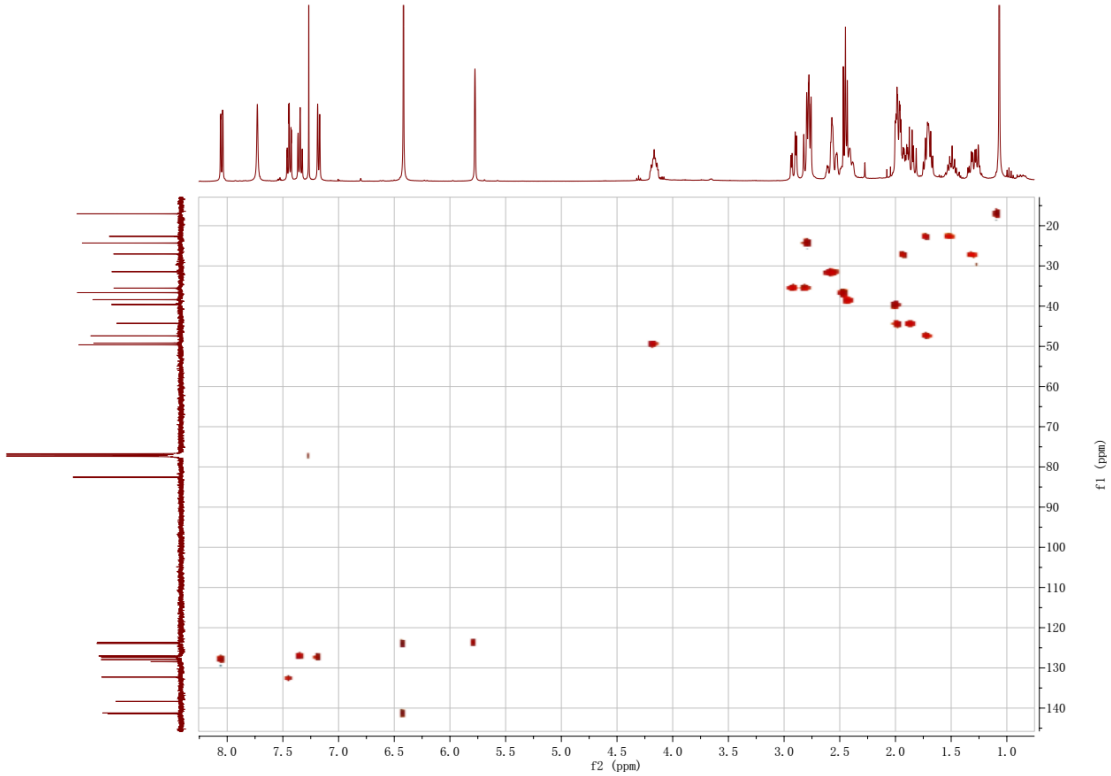


Figure S15. The $^{1}H–^{13}C$ HSQC (400 MHz, $CDCl_3$) spectrum of **3atII**

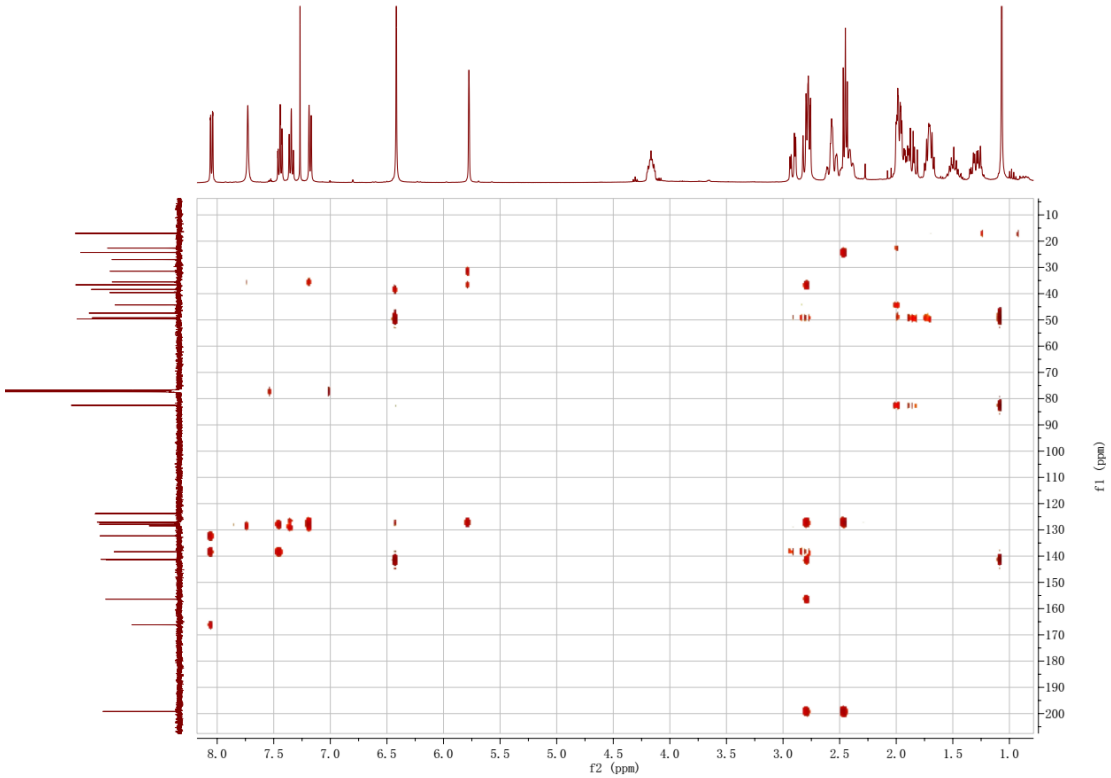


Figure S16. The $^{1}H–^{13}C$ HMBC (400 MHz, $CDCl_3$) spectrum of **3atII**

10. References

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

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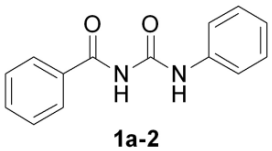
[3] S. Rakshit, C. Grohmann, T. Besset and F. Glorius, *J. Am. Chem. Soc.*, 2011, **133**, 2350.

[4] B. Li, J. Ma, N. Wang, H. Feng, S. Xu and B. Wang, *Org. Lett.*, 2012, **14**, 736.

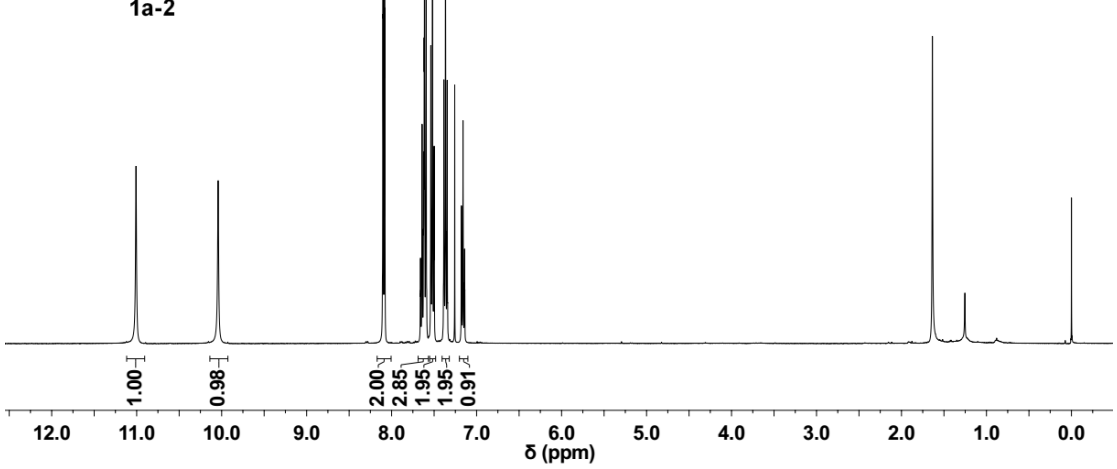
[5] H. Liu, Z. An and J. He, *ACS Catal.*, 2014, **4,** 3543.

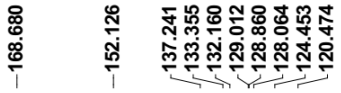
11. NMR Spectra for New Compounds

^{1}H NMR (400 MHz, $CDCl_3$)

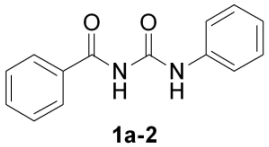


1a-2

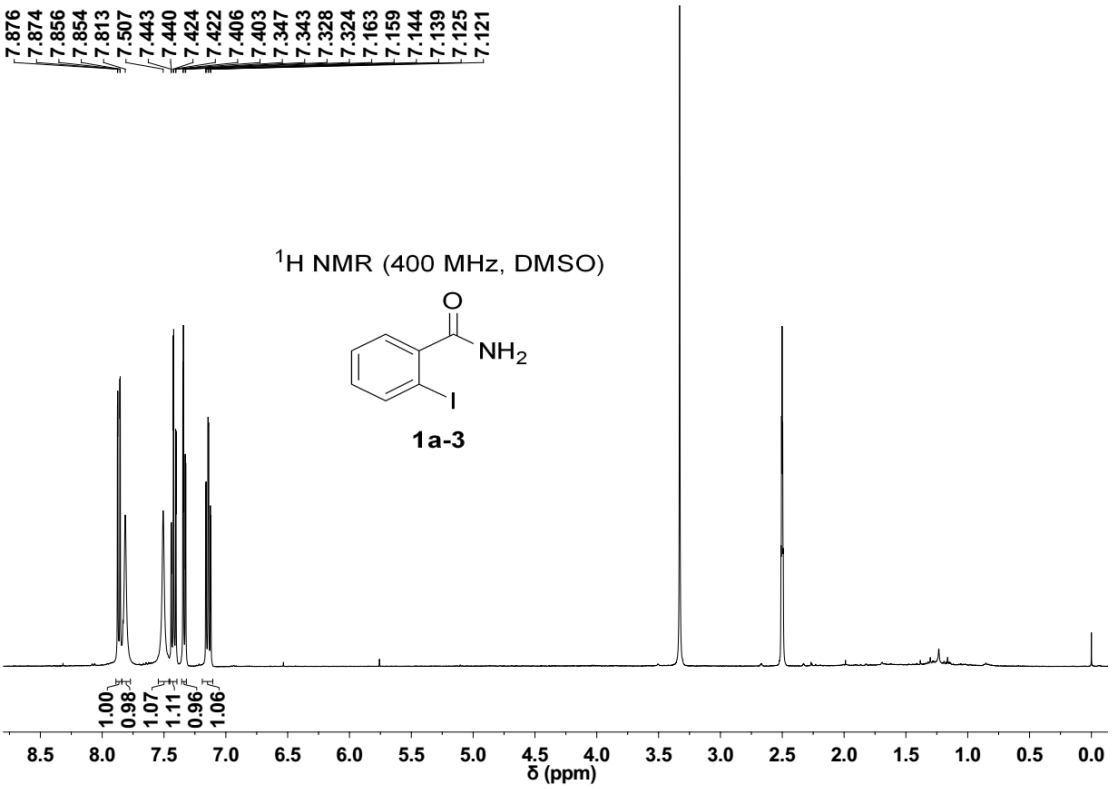


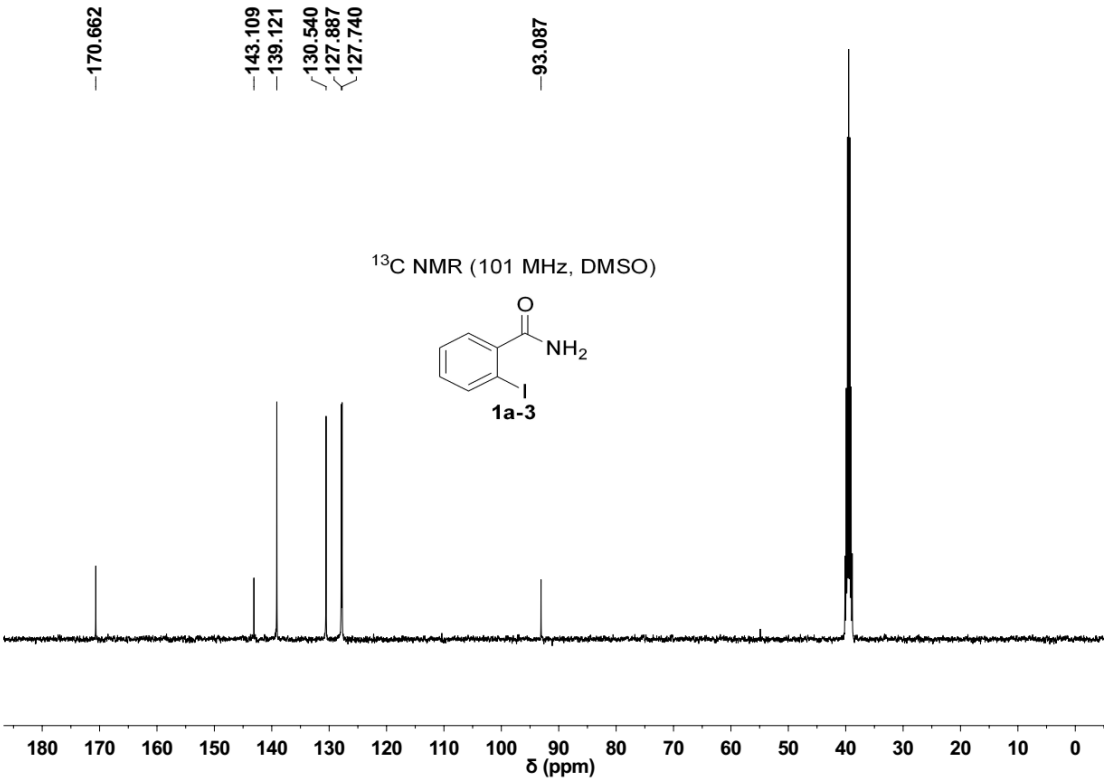


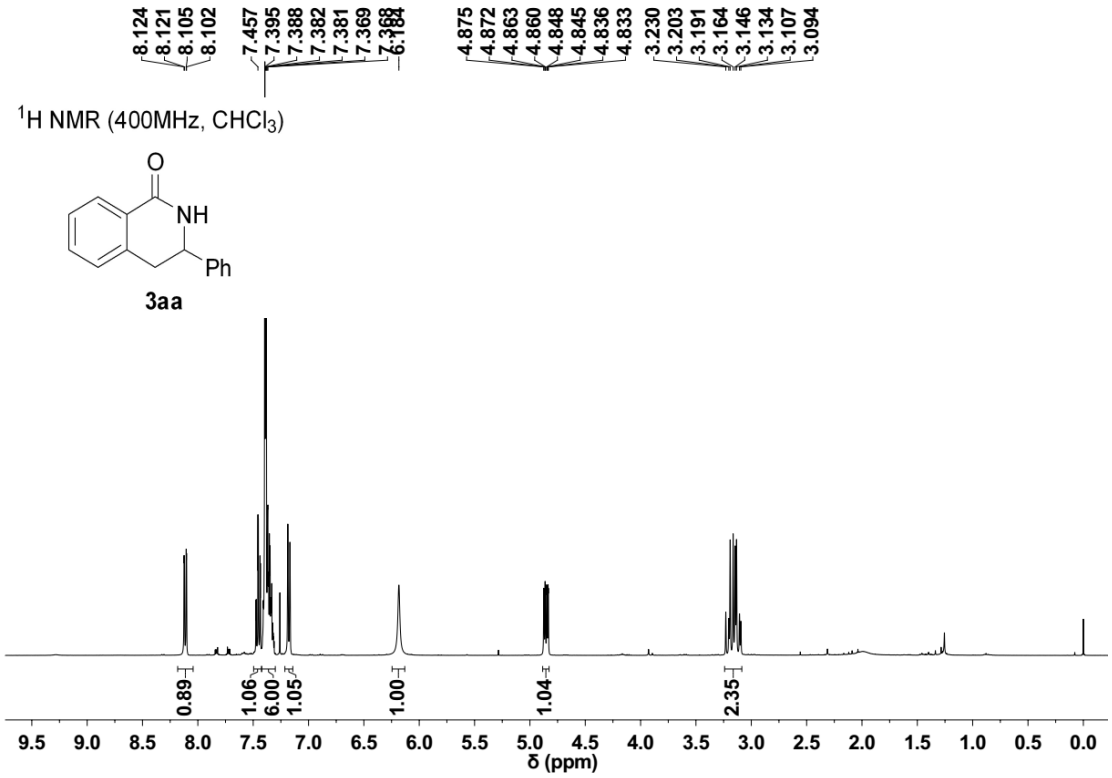
^{13}C NMR (101 MHz, $CDCl_3$)

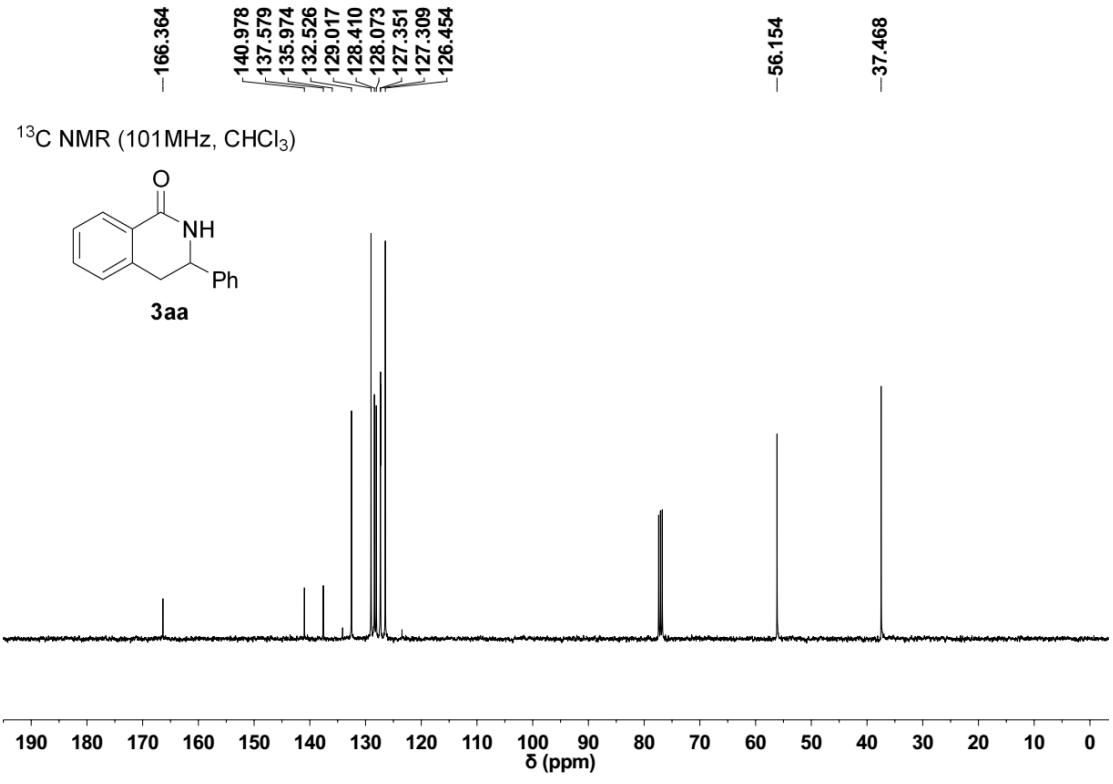


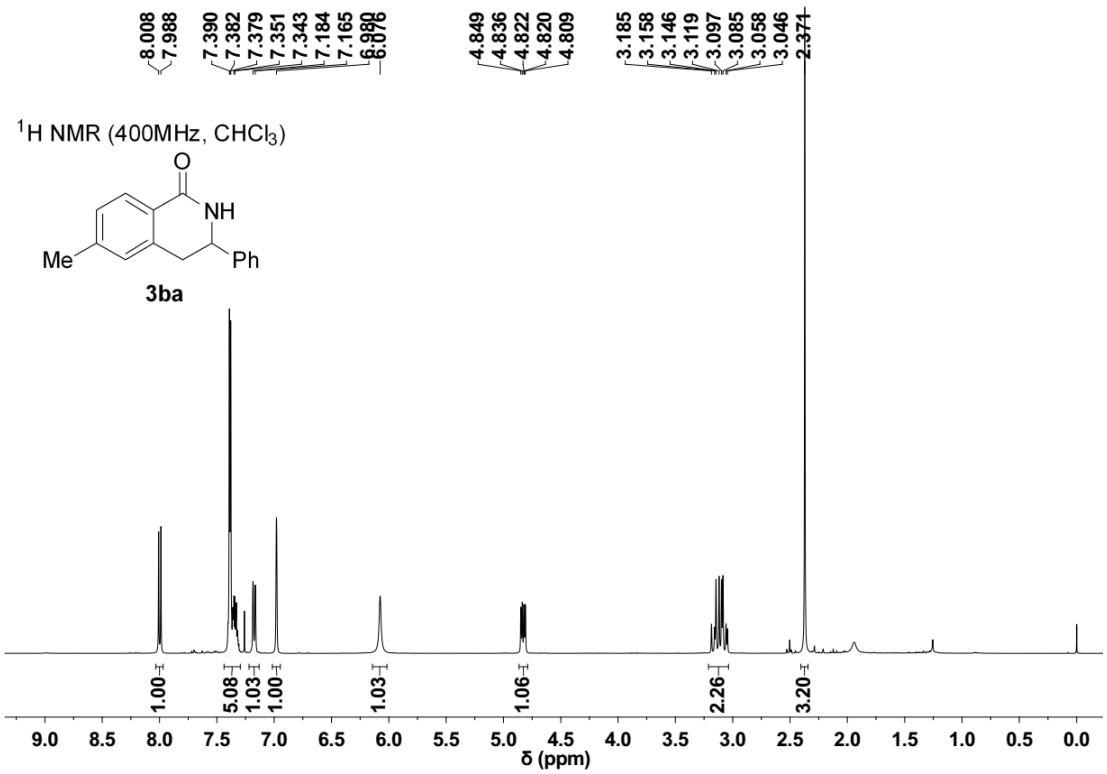
1a-2

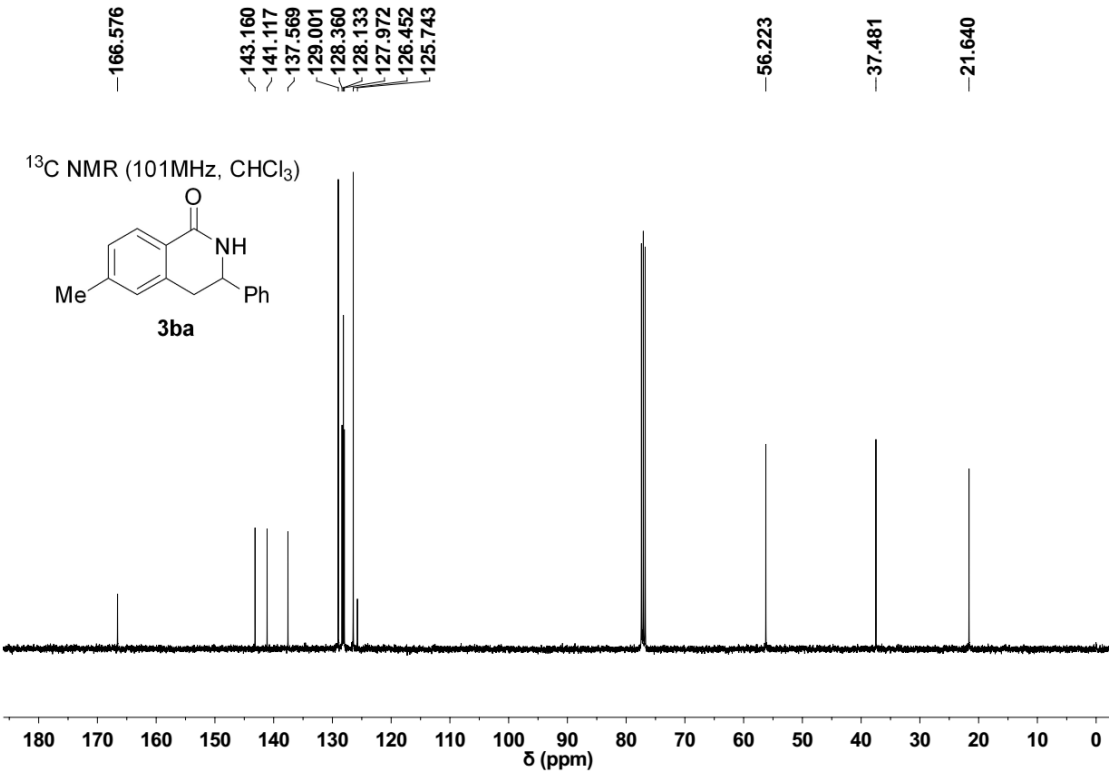

7.876
7.874
7.856
7.854
7.813
7.507
7.443
7.440
7.424
7.422
7.406
7.403
7.347
7.343
7.328
7.324
7.163
7.159
7.144
7.139
7.125
7.121
1H NMR (400 MHz, DMSO)
O
NH2
I
1a-3
1.00
0.98
1.07
1.11
0.96
1.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

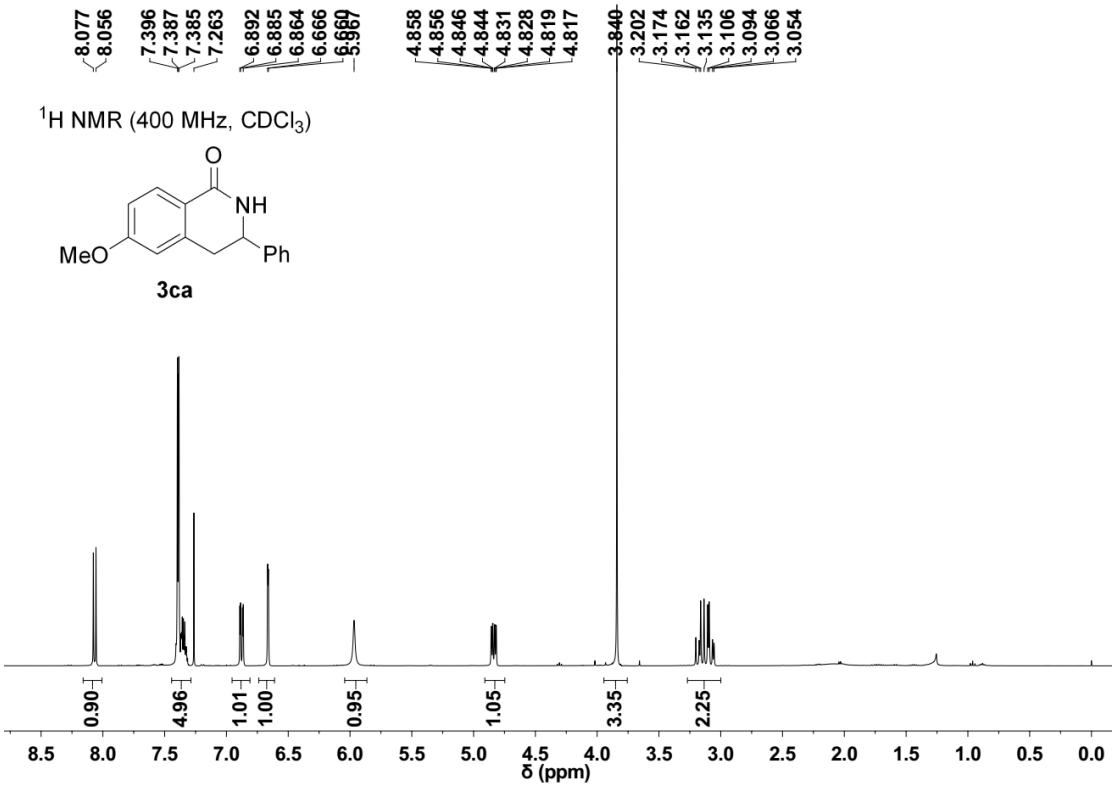

170.662
143.109
139.121
130.540
127.887
127.740
93.087
13C NMR (101 MHz, DMSO)
O
NH2
I
1a-3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

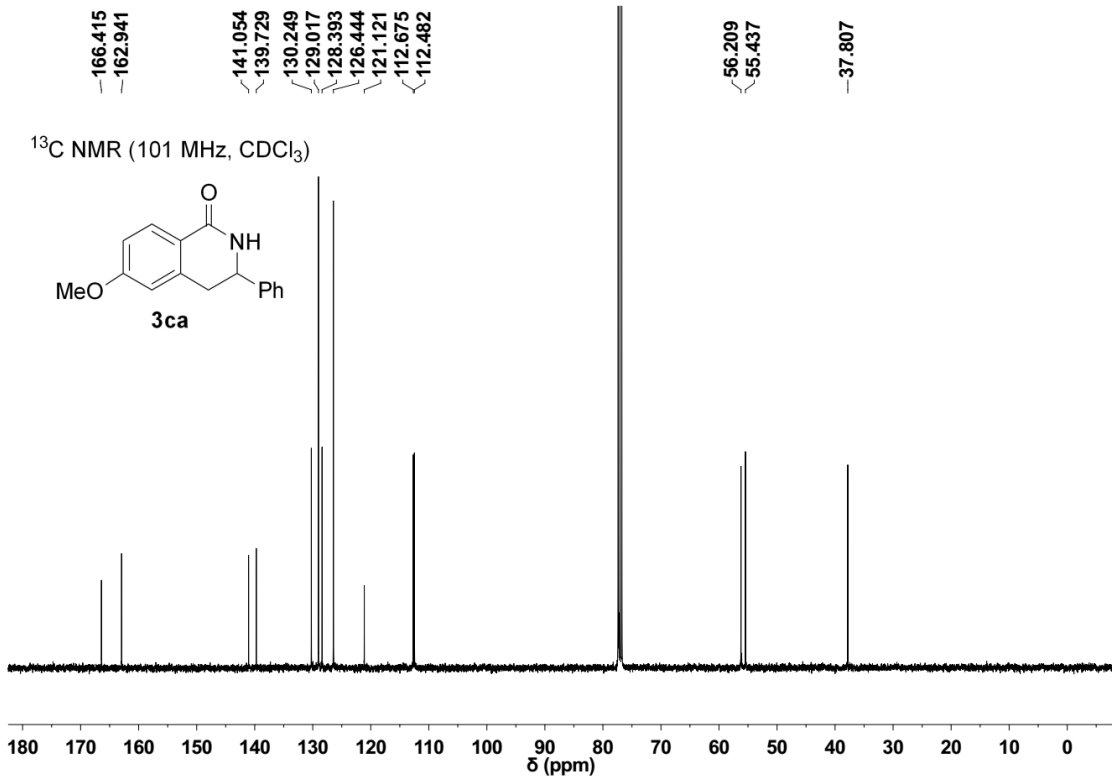

8.124
8.121
8.105
8.102
7.457
7.395
7.388
7.382
7.381
7.369
4.875
4.872
4.863
4.860
4.848
4.845
4.836
4.833
3.230
3.203
3.191
3.164
3.146
3.134
3.107
3.094
1H NMR (400MHz, CHCl3)
O
NH
Ph
3aa
0.89
1.06
6.00
1.05
1.00
1.04
2.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

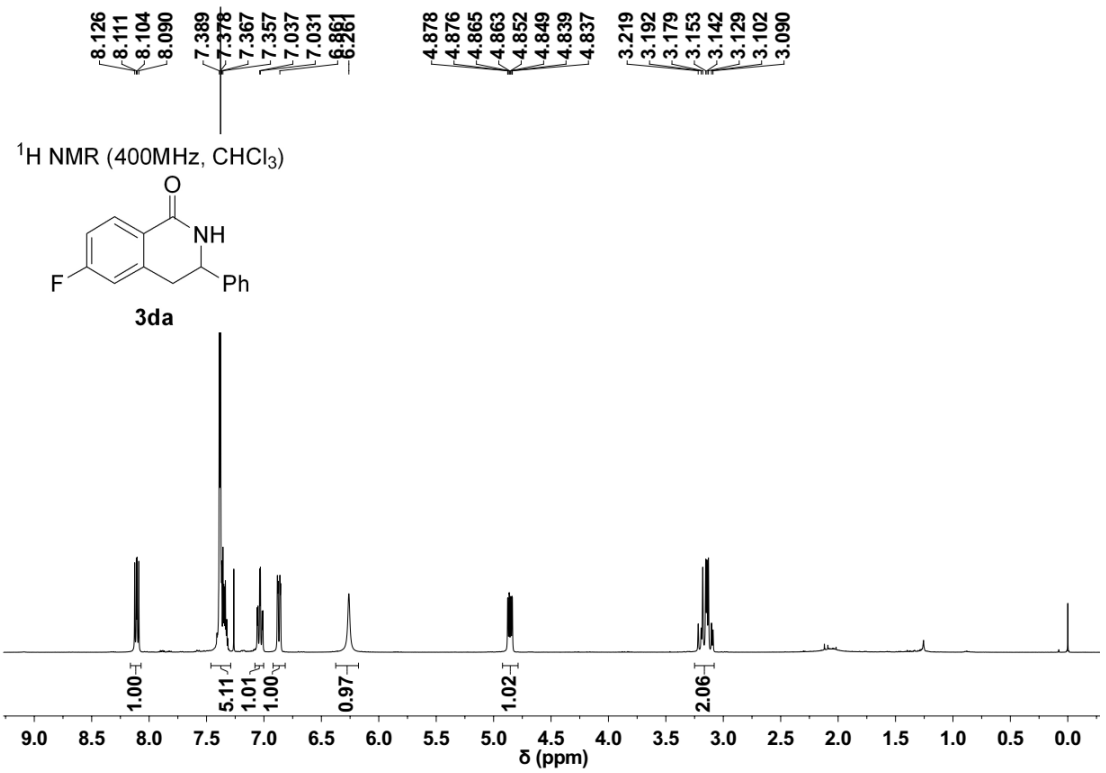

166.364
140.978
137.579
135.974
132.526
129.017
128.410
128.073
127.351
127.309
126.454
56.154
37.468
13C NMR (101MHz, CHCl3)
O
NH
Ph
3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

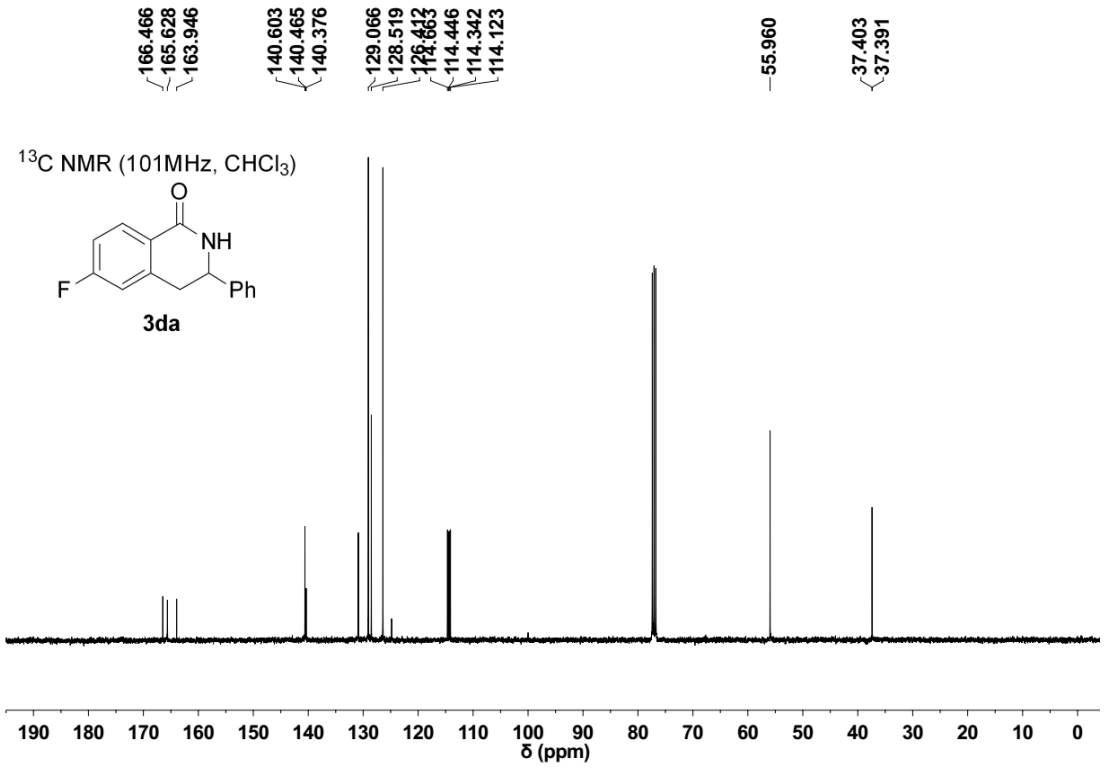

8.008
7.988
7.390
7.382
7.379
7.351
7.343
7.184
7.165
4.849
4.836
4.822
4.820
4.809
3.185
3.158
3.146
3.119
3.097
3.085
3.058
3.046
2.371
1H NMR (400MHz, CHCl3)
O
NH
Me
Ph
3ba
1.00
5.08
1.03
1.00
1.03
1.06
2.26
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

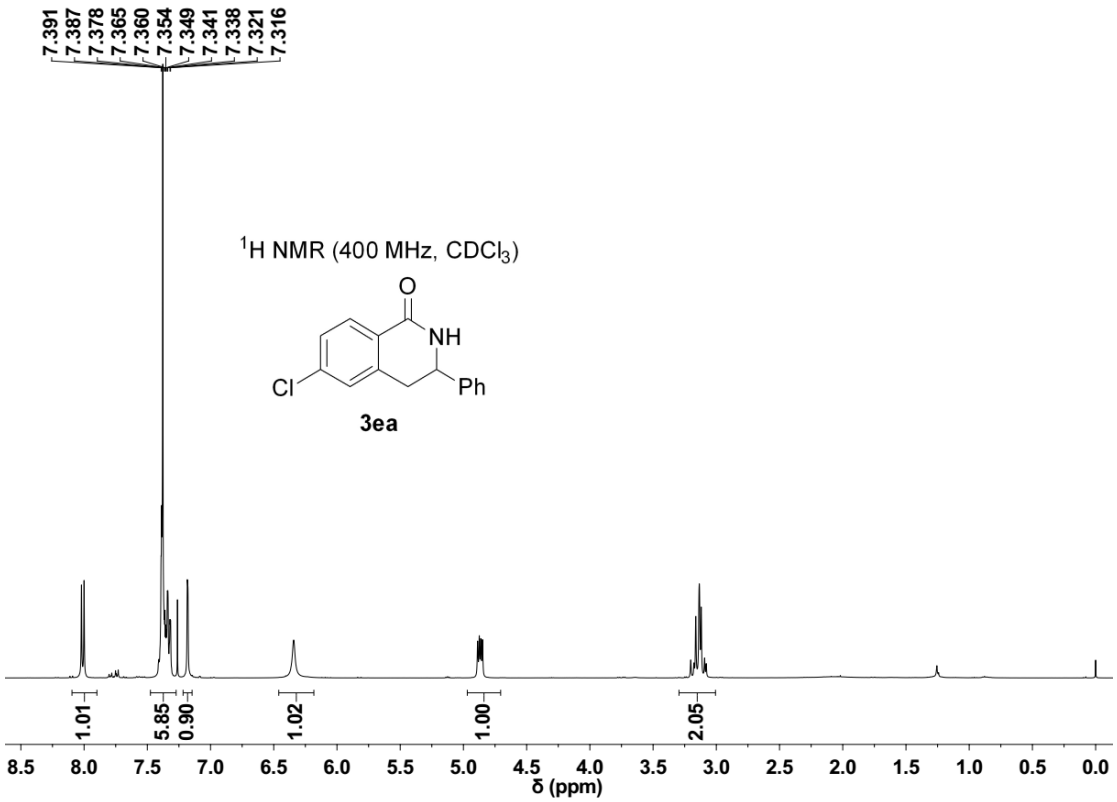

166.576
143.160
141.117
137.569
129.001
128.360
128.133
127.972
126.452
125.743
56.223
37.481
21.640
13C NMR (101MHz, CHCl3)
O
NH
Me
Ph
3ba
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

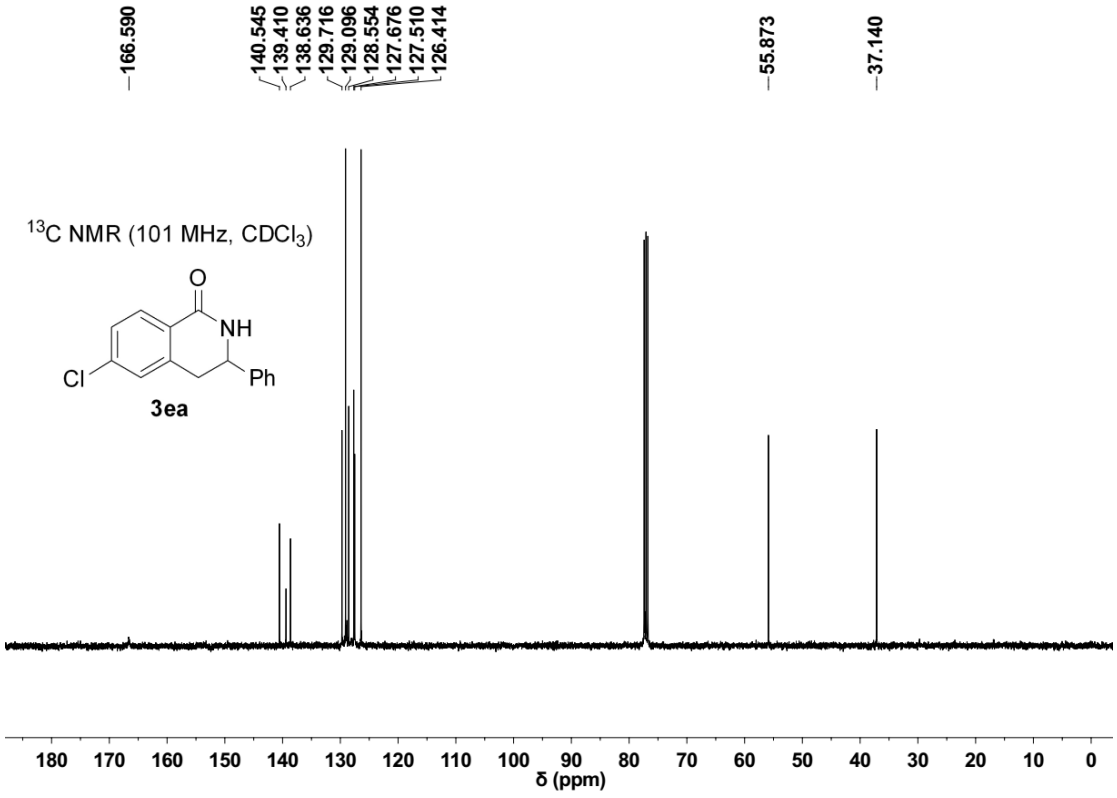

8.077
8.056
7.396
7.387
7.385
7.263
6.892
6.885
6.864
6.666
5.987
4.858
4.856
4.846
4.844
4.831
4.828
4.819
4.817
3.840
3.202
3.174
3.162
3.135
3.106
3.094
3.066
3.054
1H NMR (400 MHz, CDCl3)
O
NH
MeO
Ph
3ca
0.90
4.96
1.01
1.00
0.95
1.05
3.35
2.25
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

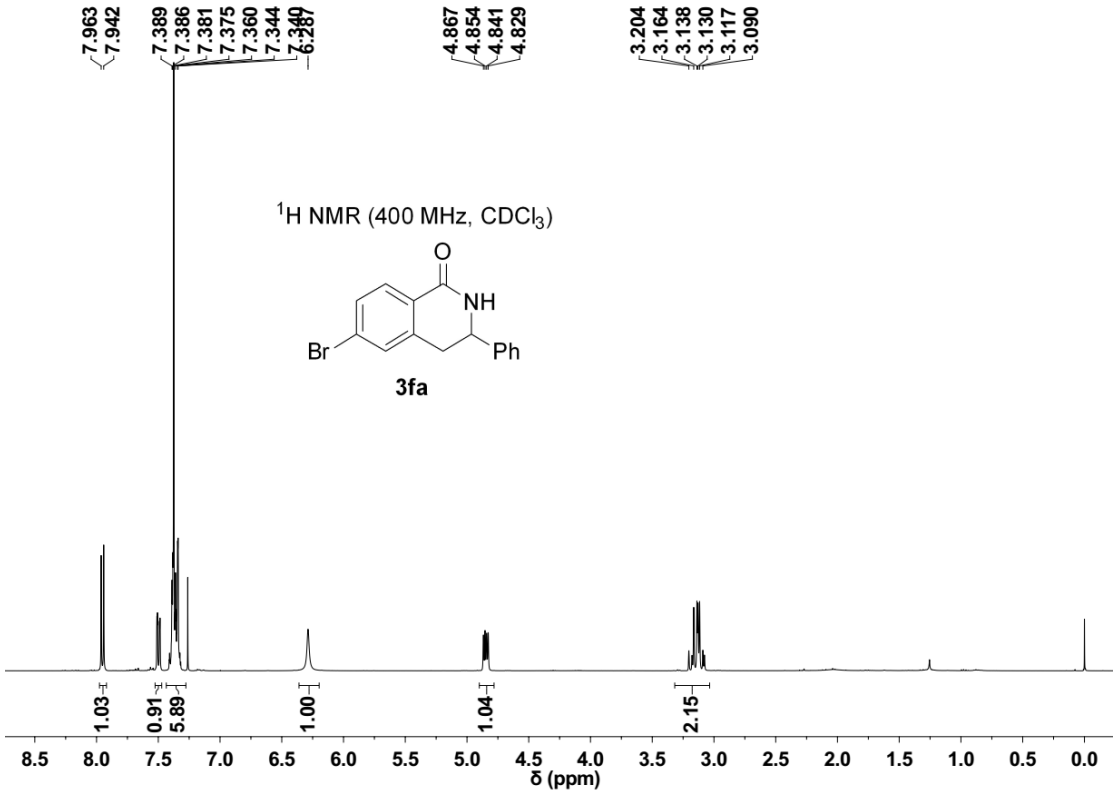

166.415
162.941
141.054
139.729
130.249
129.017
128.393
126.444
121.121
112.675
112.482
56.209
55.437
37.807
13C NMR (101 MHz, CDCl3)
O
NH
MeO
Ph
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

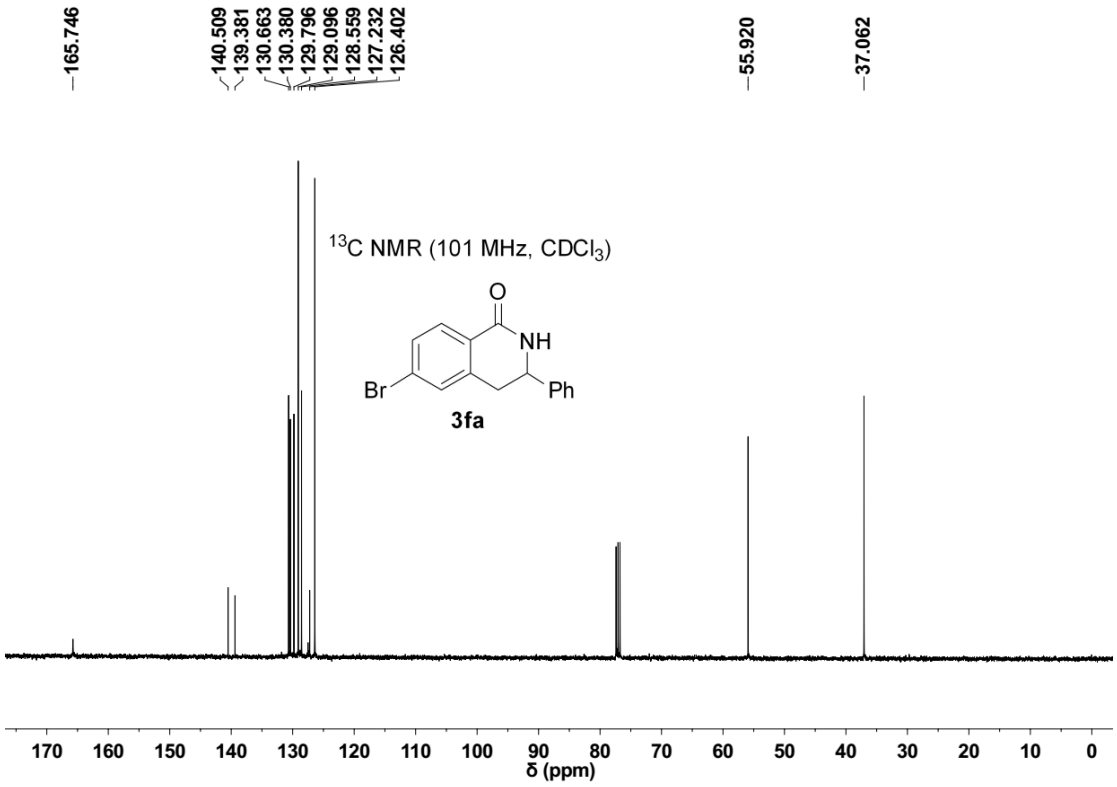

8.126
8.111
8.104
8.090
7.389
7.378
7.367
7.357
7.037
7.031
4.878
4.876
4.865
4.863
4.852
4.849
4.839
4.837
3.219
3.192
3.179
3.153
3.142
3.129
3.102
3.090
1H NMR (400MHz, CHCl3)
O
NH
F
Ph
3da
1.00
5.11
1.01
1.00
0.97
1.02
2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

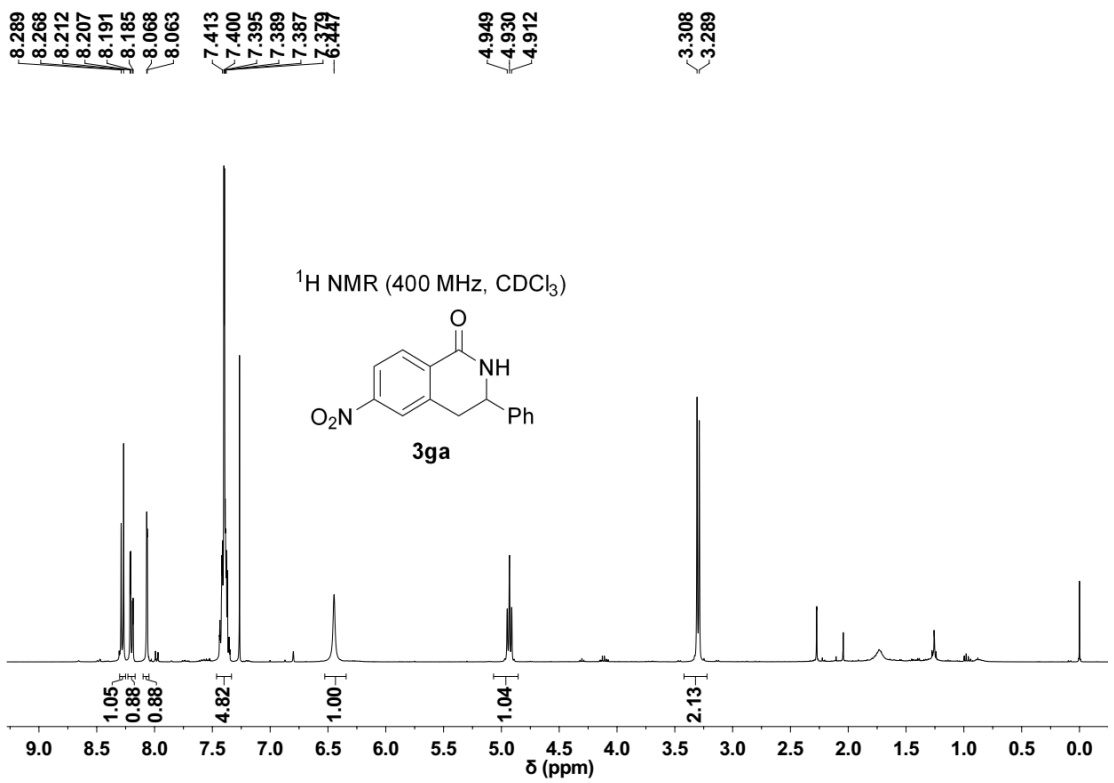

166.466
165.628
163.946
140.603
140.465
140.376
129.066
128.519
114.446
114.342
114.123
55.960
37.403
37.391
13C NMR (101MHz, CHCl3)
O
NH
F
Ph
3da
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

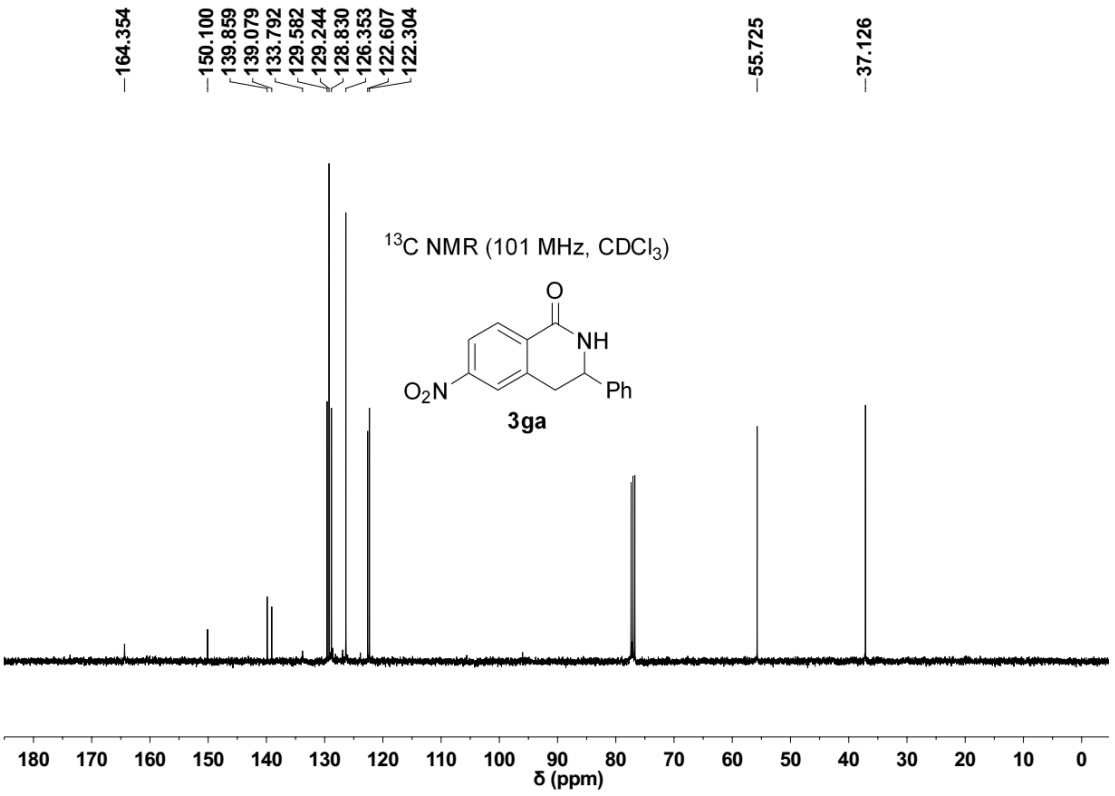

7.391
7.387
7.378
7.365
7.360
7.354
7.349
7.341
7.338
7.321
7.316
1H NMR (400 MHz, CDCl3)
O
NH
Cl
Ph
3ea
1.01
5.85
0.90
1.02
1.00
2.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

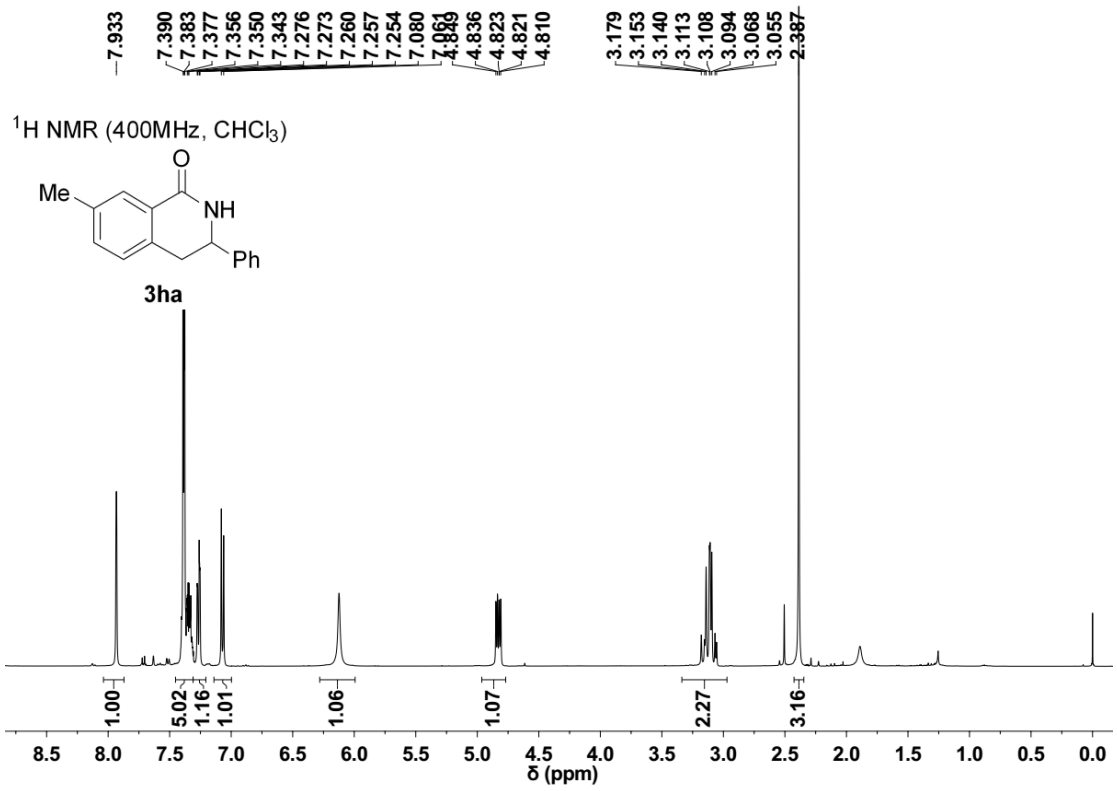

166.590
140.545
139.410
138.636
129.716
129.096
128.554
127.676
127.510
126.414
55.873
37.140
13C NMR (101 MHz, CDCl3)
O
NH
Cl
Ph
3ea
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

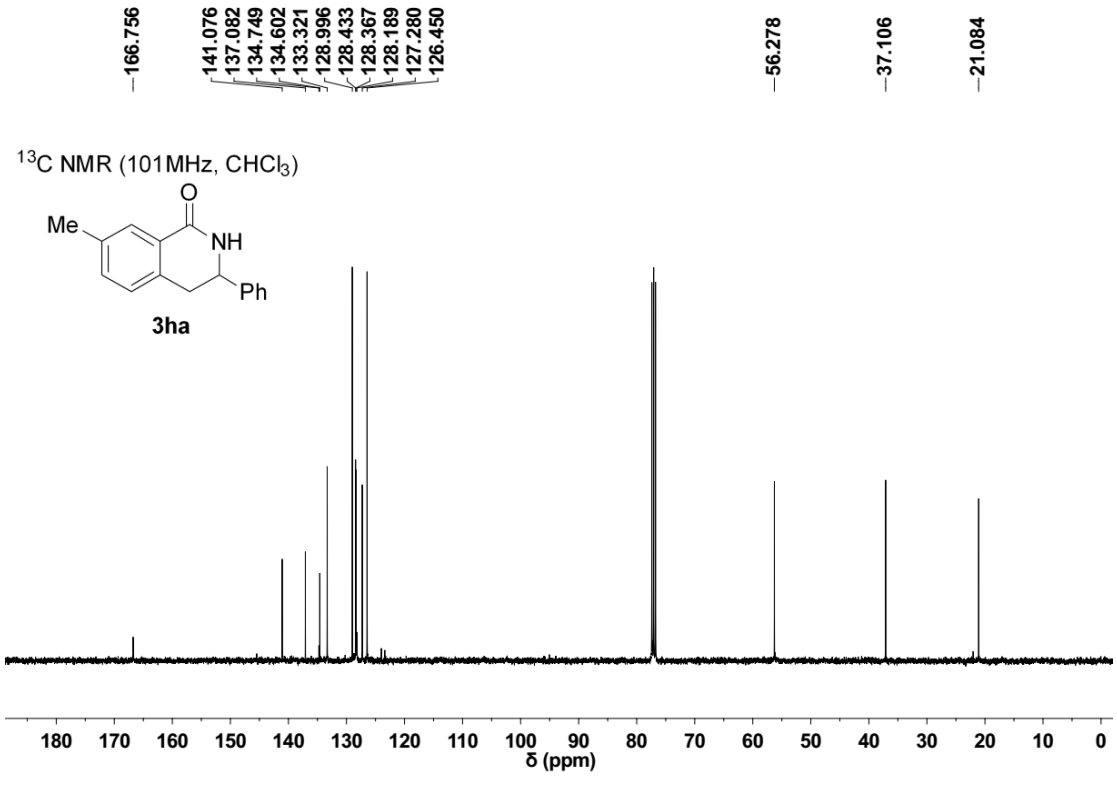

7.963
7.942
7.389
7.386
7.381
7.375
7.360
7.344
6.287
4.867
4.854
4.841
4.829
3.204
3.164
3.138
3.130
3.117
3.090
1H NMR (400 MHz, CDCl3)
O
NH
Br
Ph
3fa
1.03
0.91
5.89
1.00
1.04
2.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

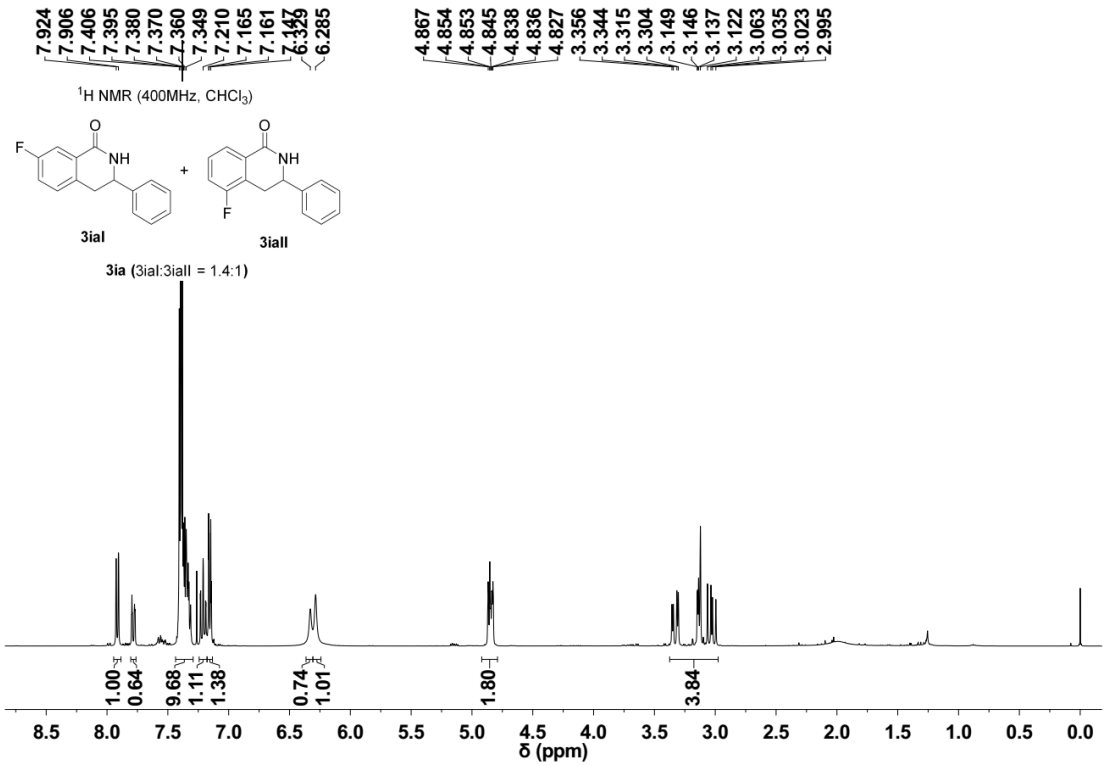

165.746
140.509
139.381
130.663
130.380
129.796
129.096
128.559
127.232
126.402
55.920
37.062
13C NMR (101 MHz, CDCl3)
O
NH
Br
Ph
3fa
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

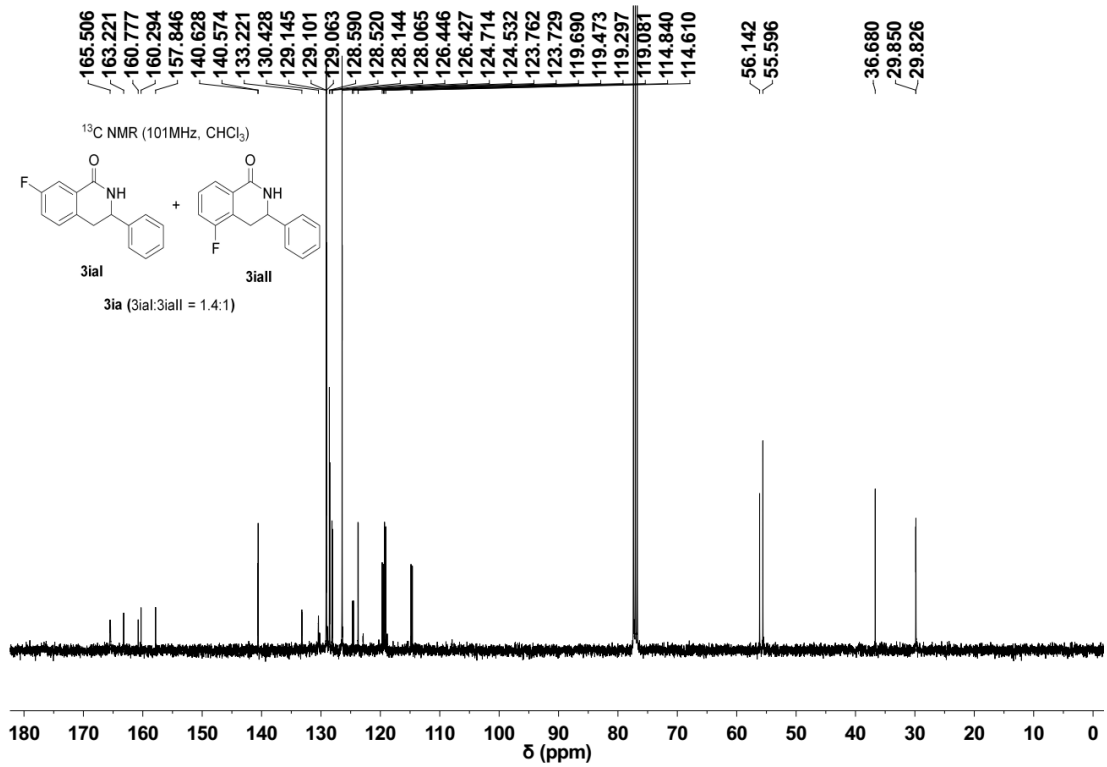

8.289
8.268
8.212
8.207
8.191
8.185
8.068
8.063
7.413
7.400
7.395
7.389
7.387
7.379
7.377
6.447
4.949
4.930
4.912
3.308
3.289
^{1}H NMR (400 MHz, $CDCl_3$)
O
NH
O_2N
Ph
3ga
1.05
0.88
0.88
4.82
1.00
1.04
2.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

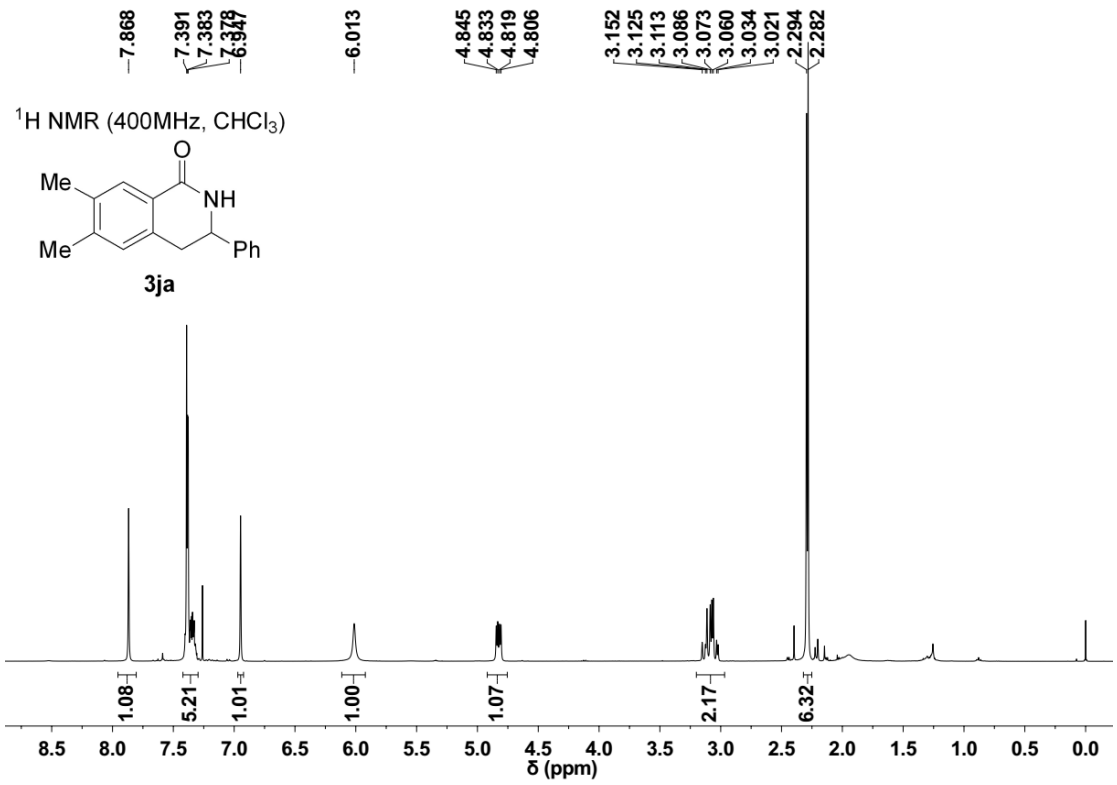

164.354
150.100
139.859
139.079
133.792
129.582
129.244
128.830
126.353
122.607
122.304
55.725
37.126
^{13}C NMR (101 MHz, $CDCl_3$)
O
NH
O_2N
Ph
3ga
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

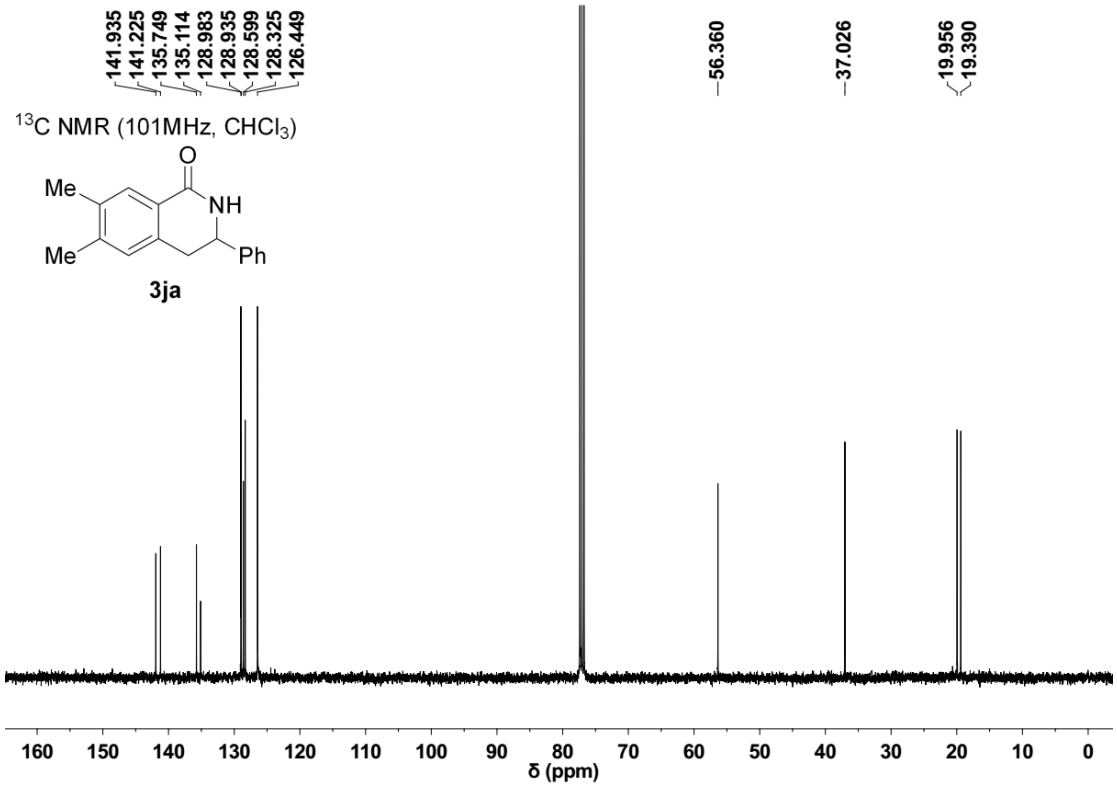

7.933
7.390
7.383
7.377
7.356
7.350
7.343
7.276
7.273
7.260
7.257
7.254
7.080
4.836
4.823
4.821
4.810
3.179
3.153
3.140
3.113
3.108
3.094
3.068
3.055
2.387
1H NMR (400MHz, CHCl3)
Me
NH
Ph
3ha
1.00
5.02
1.16
1.01
1.06
1.07
2.27
3.16
δ (ppm)

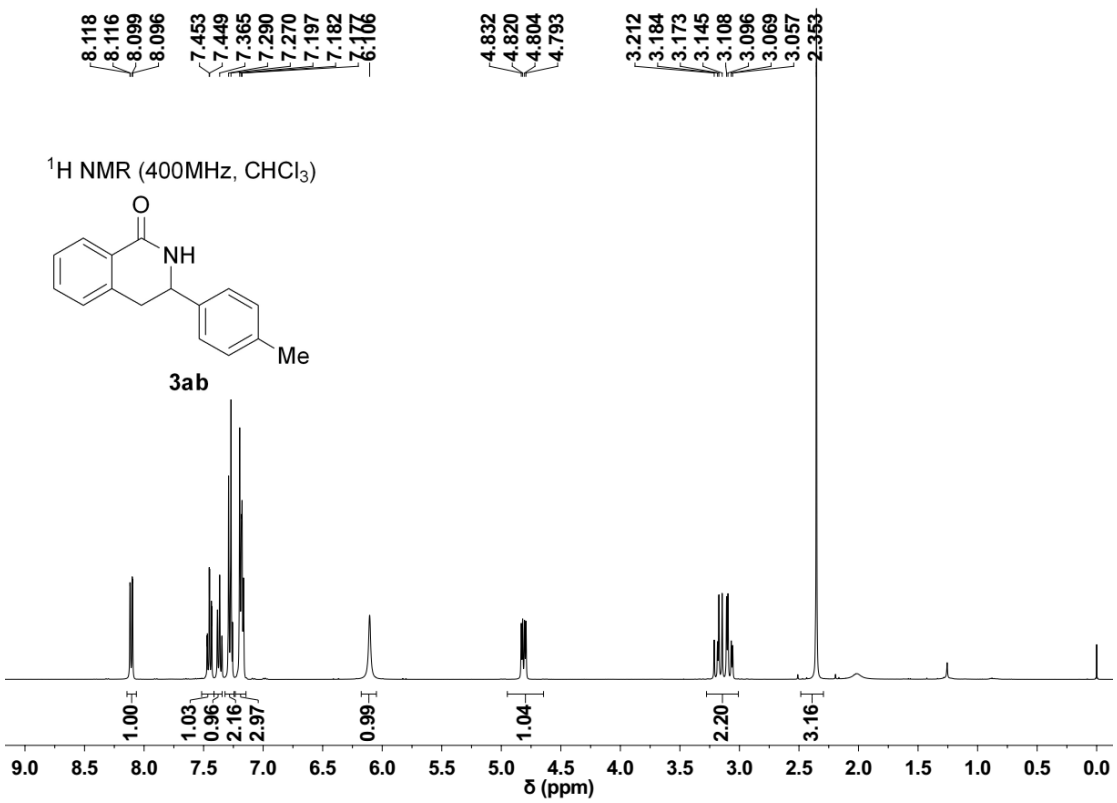

166.756
141.076
137.082
134.749
134.602
133.321
128.996
128.433
128.367
128.189
127.280
126.450
56.278
37.106
21.084
13C NMR (101MHz, CHCl3)
Me
NH
Ph
3ha
δ (ppm)

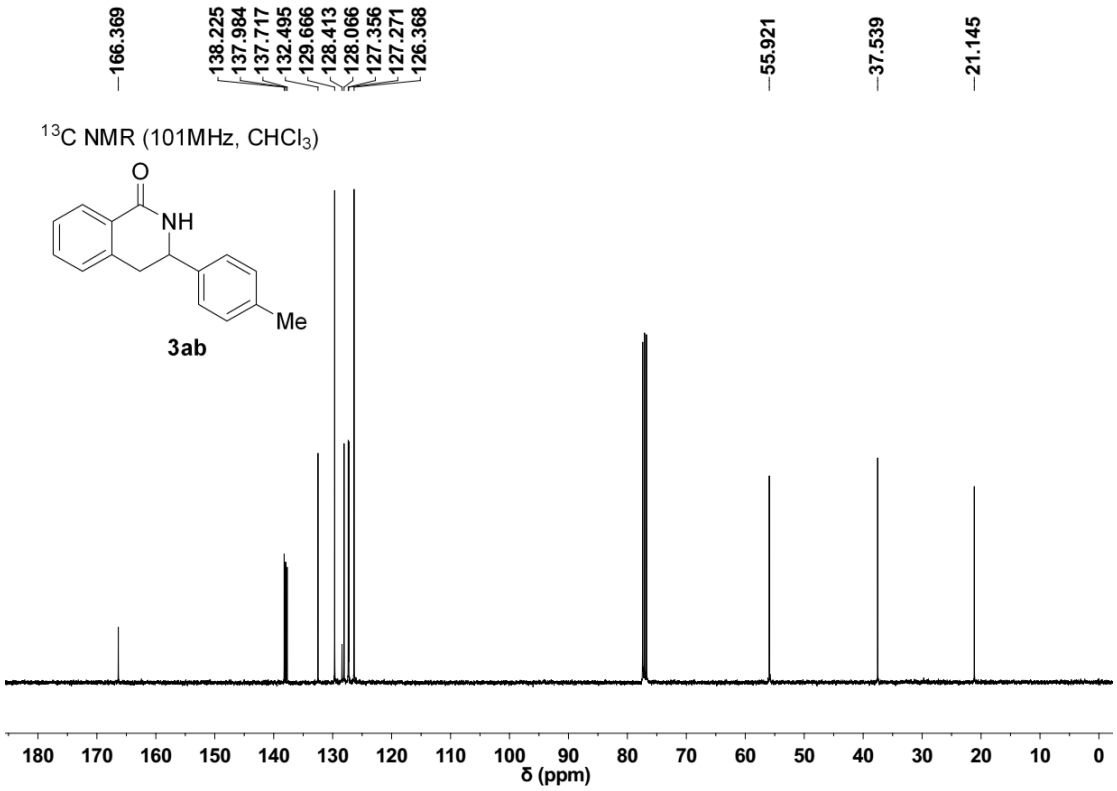

7.924
7.906
7.406
7.395
7.380
7.370
7.360
7.349
7.210
7.165
7.161
7.147
6.329
6.285
4.867
4.854
4.853
4.845
4.838
4.836
4.827
3.356
3.344
3.315
3.304
3.149
3.146
3.137
3.122
3.063
3.035
3.023
2.995
1H NMR (400MHz, CHCl3)
3ial
3iall
3ia (3ial:3iall = 1.4:1)
1.00
0.64
9.68
1.11
1.38
0.74
1.01
1.80
3.84
δ (ppm)

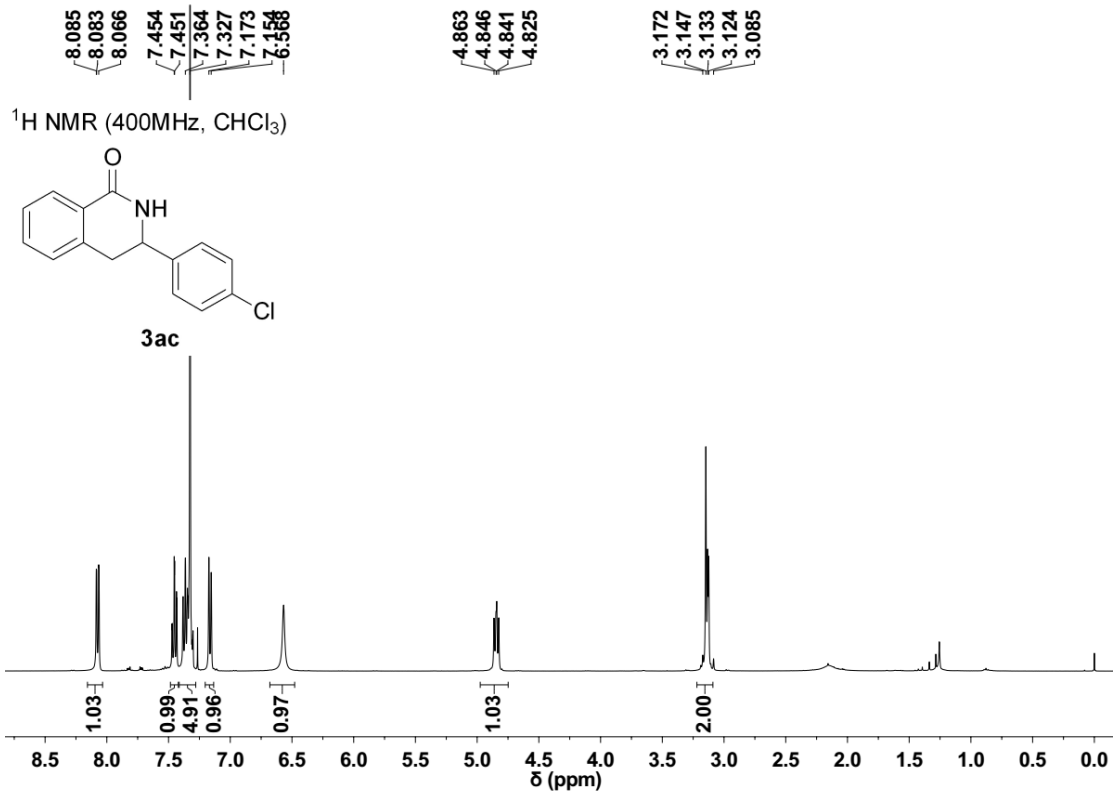

165.506
163.221
160.777
160.294
157.846
140.628
140.574
133.221
130.428
129.145
129.101
129.063
128.590
128.520
128.144
128.065
126.446
126.427
124.714
124.532
123.762
123.729
119.690
119.473
119.297
119.081
114.840
114.610
56.142
55.596
36.680
29.850
29.826
13C NMR (101MHz, CHCl3)
3ial
3iall
3ia (3ial:3iall = 1.4:1)
δ (ppm)

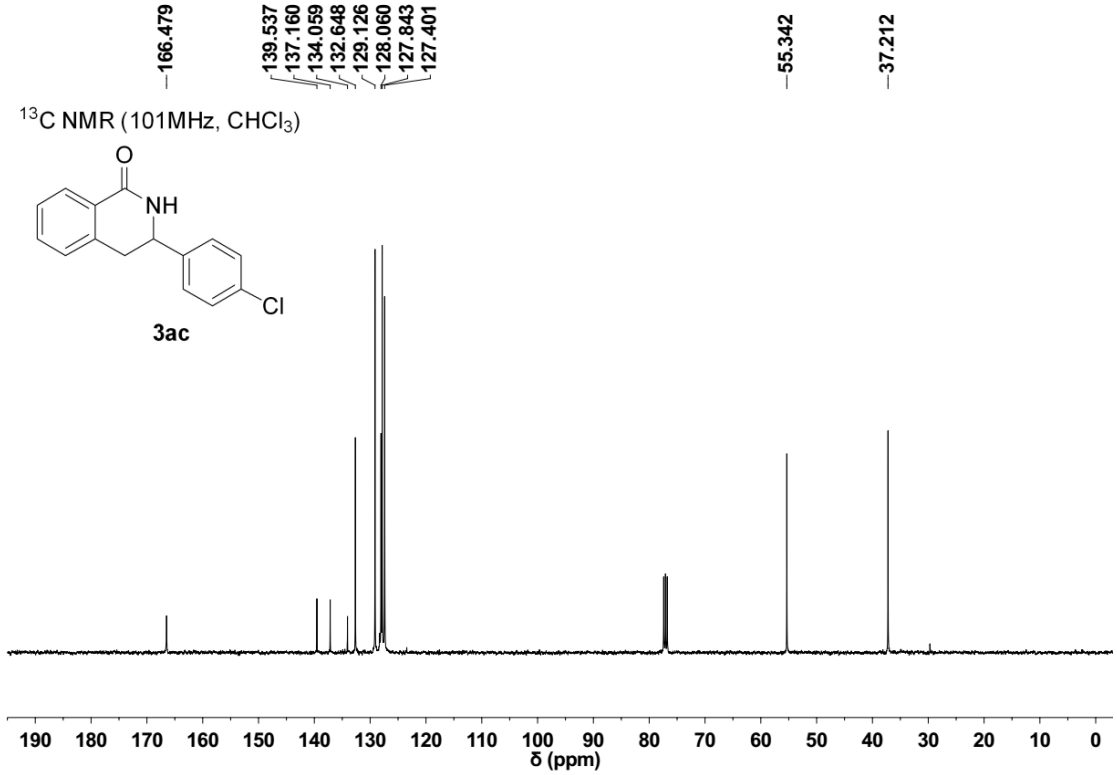

7.868
7.391
7.383
6.013
4.845
4.833
4.819
4.806
3.152
3.125
3.113
3.086
3.073
3.060
3.034
3.021
2.294
2.282
1H NMR (400MHz, CHCl3)
Me
Me
NH
Ph
O
3ja
1.08
5.21
1.01
1.00
1.07
2.17
6.32
δ (ppm)

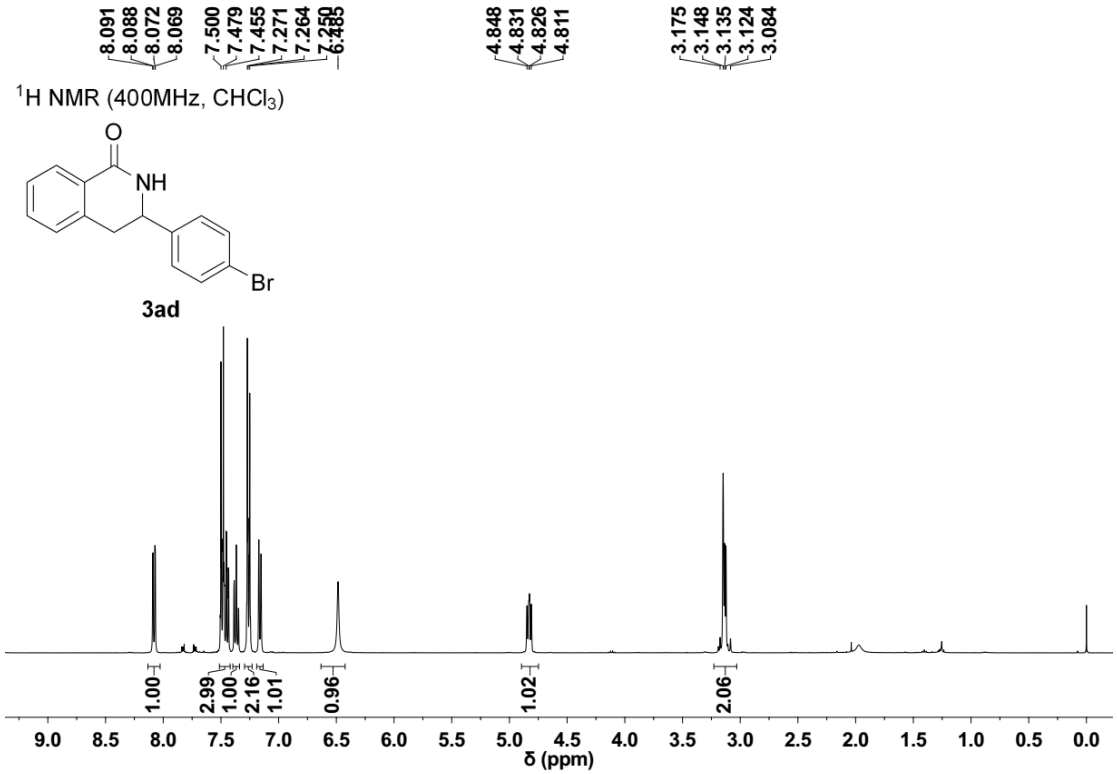

141.935
141.225
135.749
135.114
128.983
128.935
128.599
128.325
126.449
56.360
37.026
19.956
19.390
13C NMR (101MHz, CHCl3)
Me
Me
NH
Ph
O
3ja
δ (ppm)

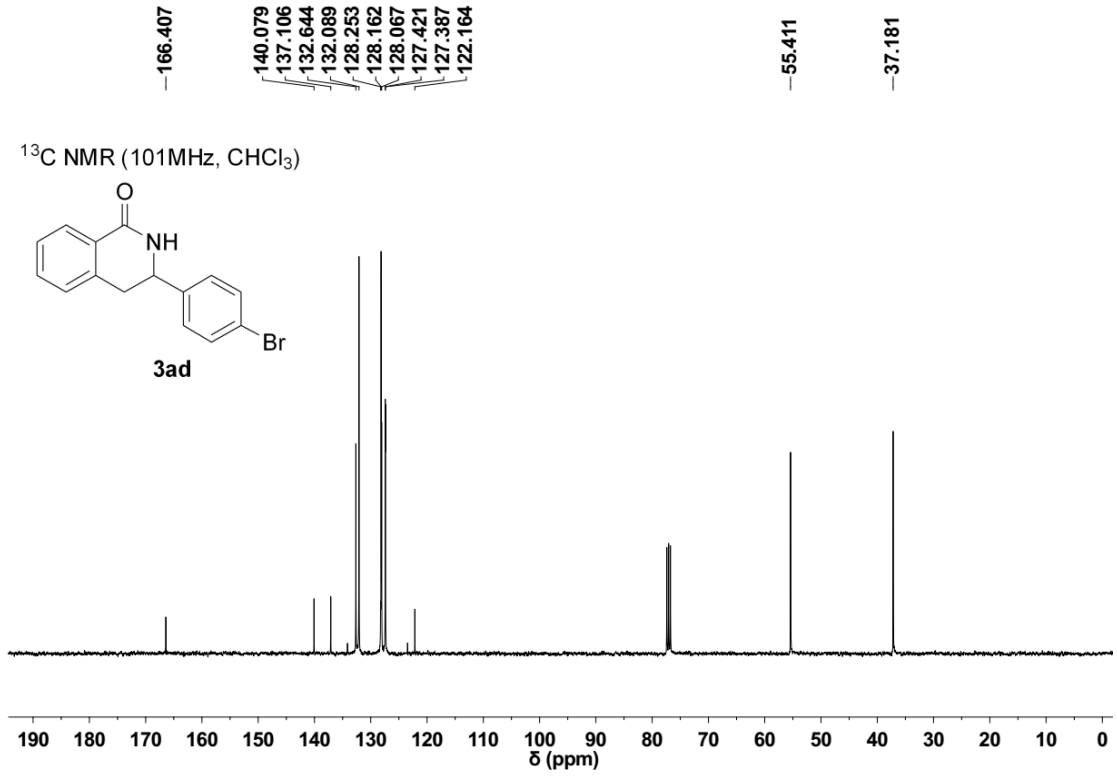

8.118
8.116
8.099
8.096
7.453
7.449
7.365
7.290
7.270
7.197
7.182
4.832
4.820
4.804
4.793
3.212
3.184
3.173
3.145
3.108
3.096
3.069
3.057
2.353
1H NMR (400MHz, CHCl3)
O
NH
Me
3ab
1.00
1.03
0.96
2.16
2.97
0.99
1.04
2.20
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

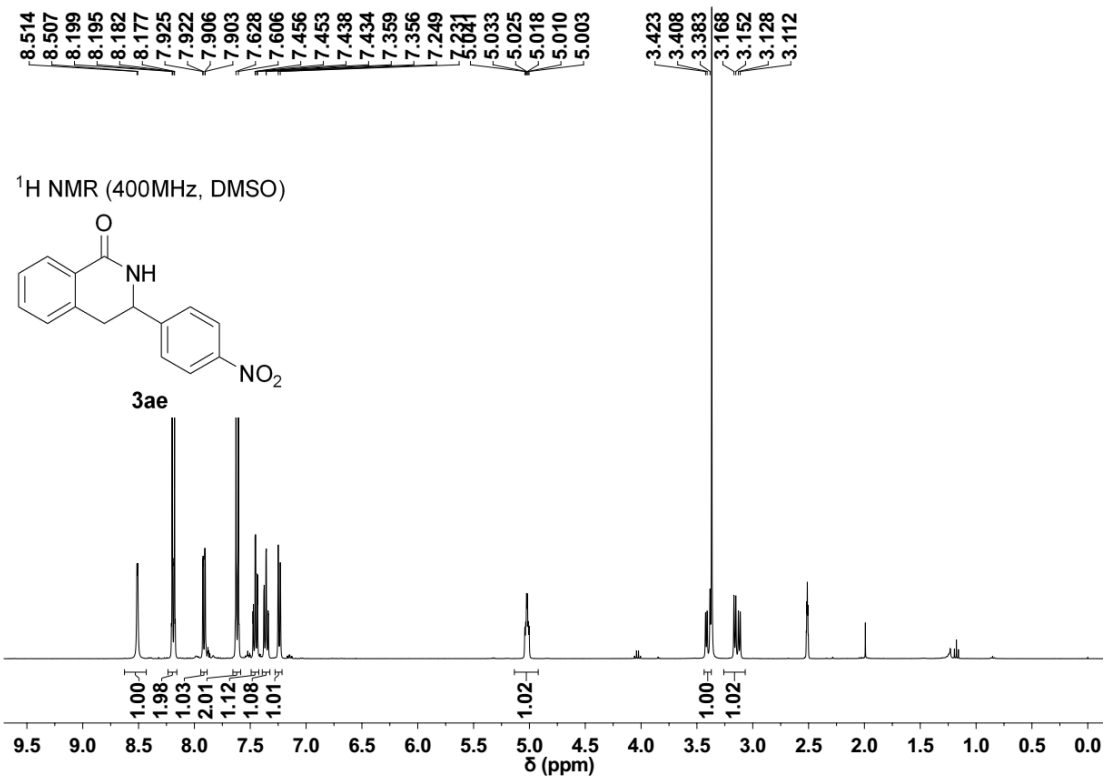

166.369
138.225
137.984
137.717
132.495
129.666
128.413
128.066
127.356
127.271
126.368
55.921
37.539
21.145
13C NMR (101MHz, CHCl3)
O
NH
Me
3ab
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

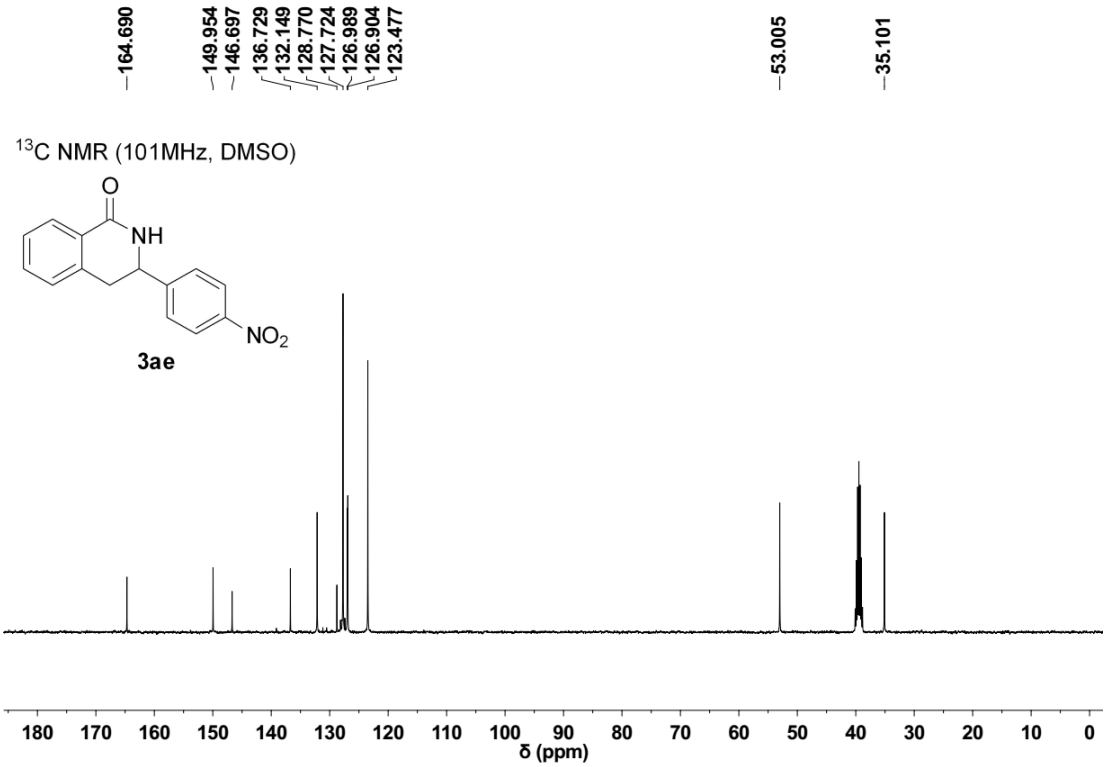

8.085
8.083
8.066
7.454
7.451
7.364
7.327
7.173
7.154
6.568
4.863
4.846
4.841
4.825
3.172
3.147
3.133
3.124
3.085
1H NMR (400MHz, CHCl3)
O
NH
Cl
3ac
1.03
0.99
4.91
0.96
0.97
1.03
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

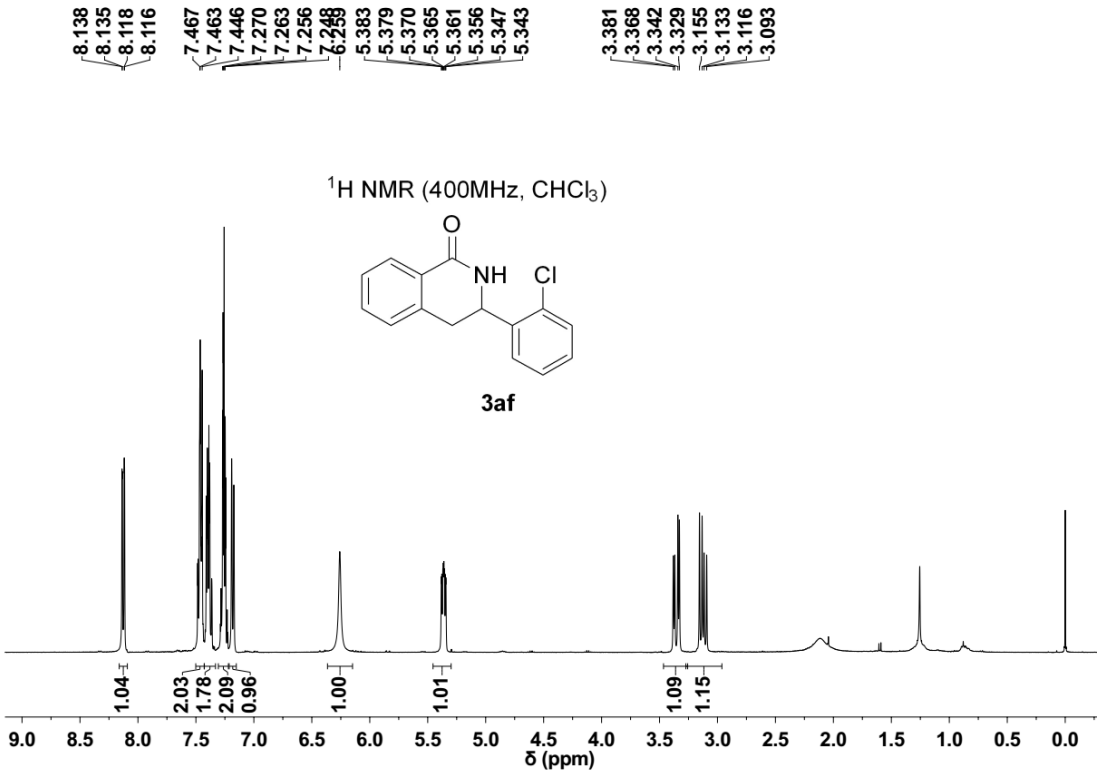

166.479
139.537
137.160
134.059
132.648
129.126
128.060
127.843
127.401
55.342
37.212
13C NMR (101MHz, CHCl3)
O
NH
Cl
3ac
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

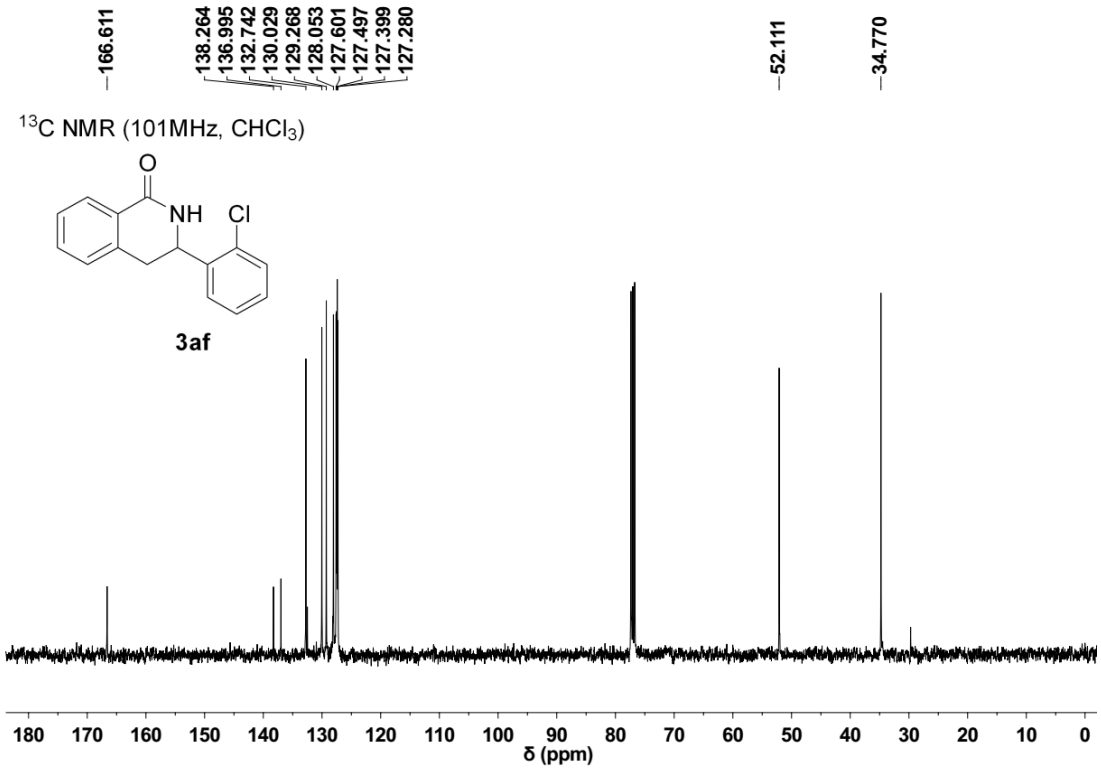

8.091
8.088
8.072
8.069
7.500
7.479
7.455
7.271
7.264
4.848
4.831
4.826
4.811
3.175
3.148
3.135
3.124
3.084
1H NMR (400MHz, CHCl3)
O
NH
Br
3ad
1.00
2.99
1.00
2.16
1.01
0.96
1.02
2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

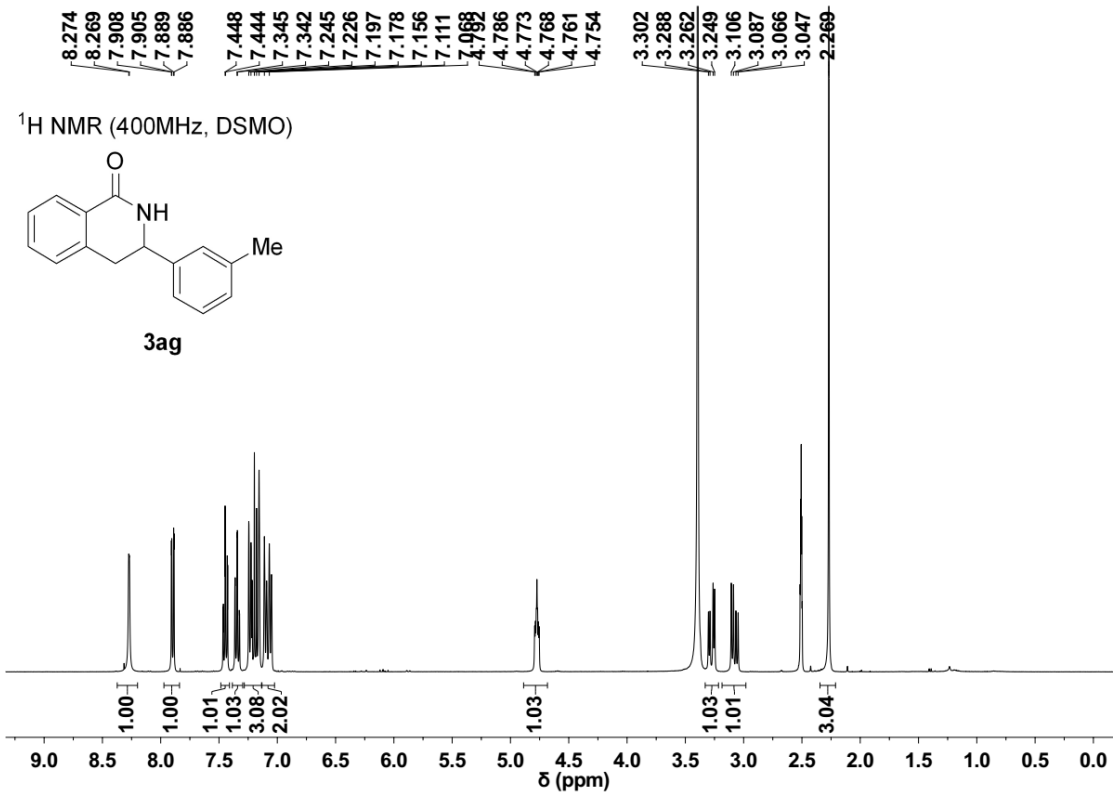

166.407
140.079
137.106
132.644
132.089
128.253
128.162
128.067
127.421
127.387
122.164
55.411
37.181
13C NMR (101MHz, CHCl3)
O
NH
Br
3ad
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

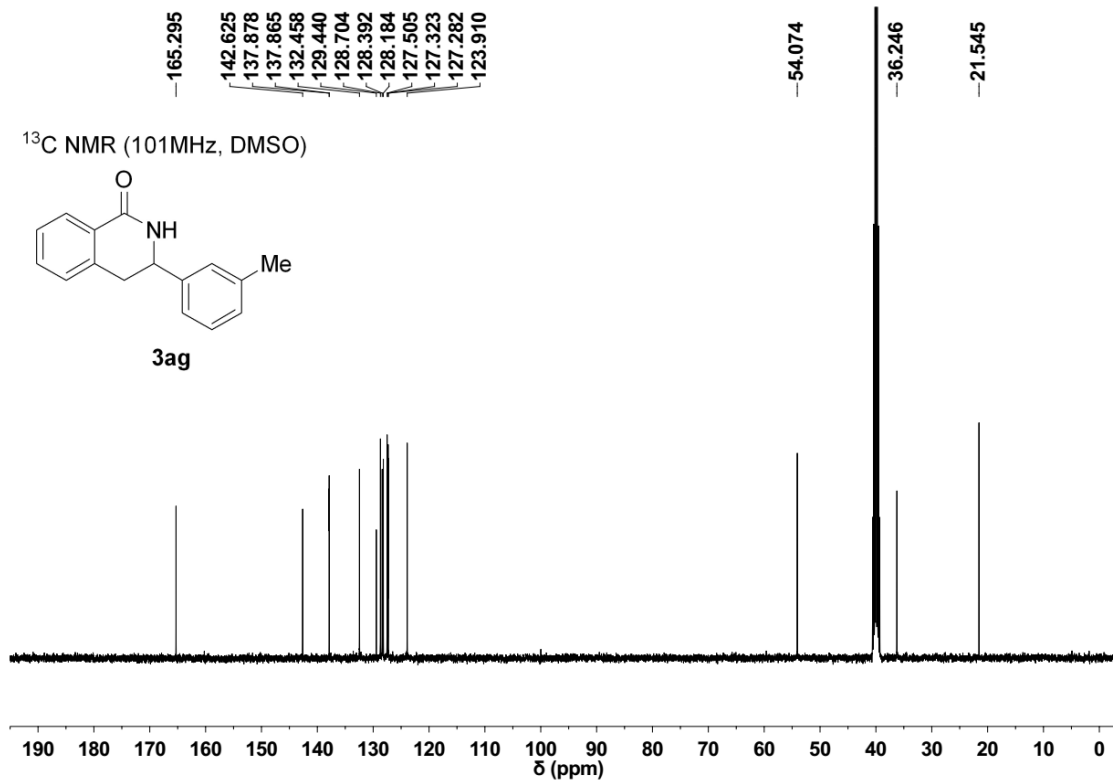

8.514
8.507
8.199
8.195
8.182
8.177
7.925
7.922
7.906
7.903
7.628
7.606
7.456
7.453
7.438
7.434
7.359
7.356
7.249
7.231
5.041
5.033
5.025
5.018
5.010
5.003
3.423
3.408
3.383
3.168
3.152
3.128
3.112
1H NMR (400MHz, DMSO)
O
NH
NO2
3ae
1.00
1.98
1.03
2.01
1.12
1.08
1.01
1.02
1.00
1.02
9.5 9.0 8.5 8.0 7.5 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
δ (ppm)

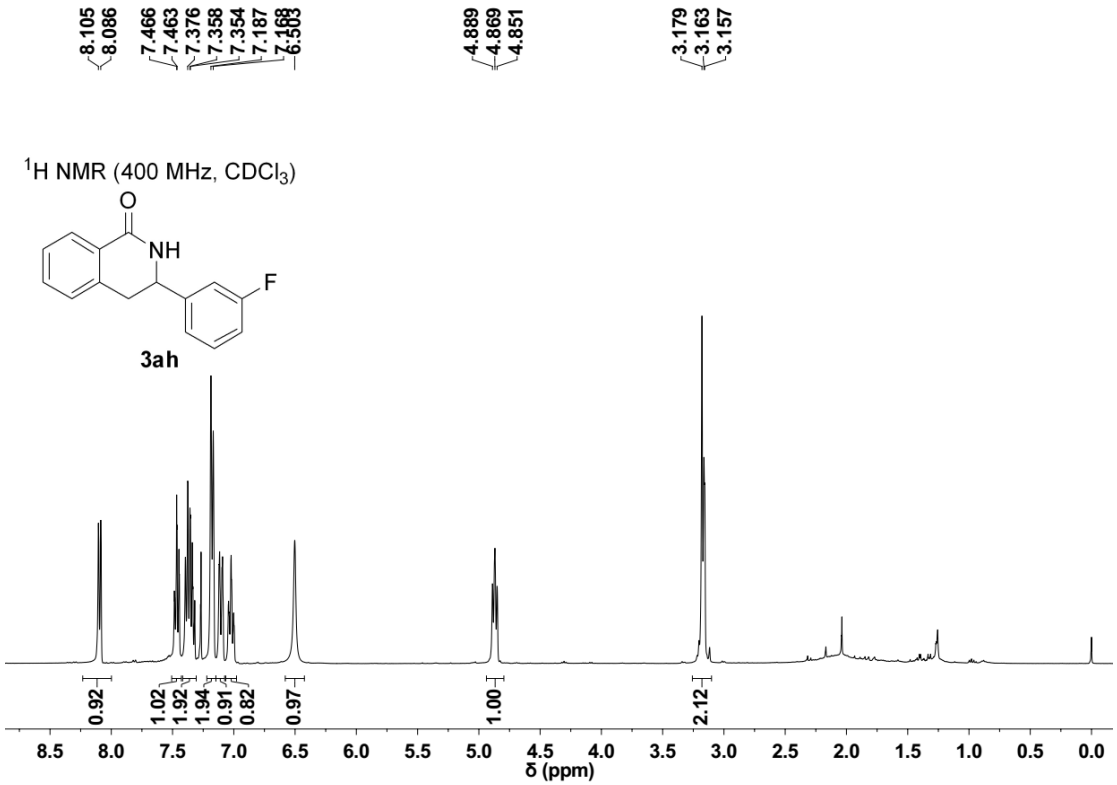

164.690
149.954
146.697
136.729
132.149
128.770
127.724
126.989
126.904
123.477
53.005
35.101
13C NMR (101MHz, DMSO)
O
NH
NO2
3ae
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

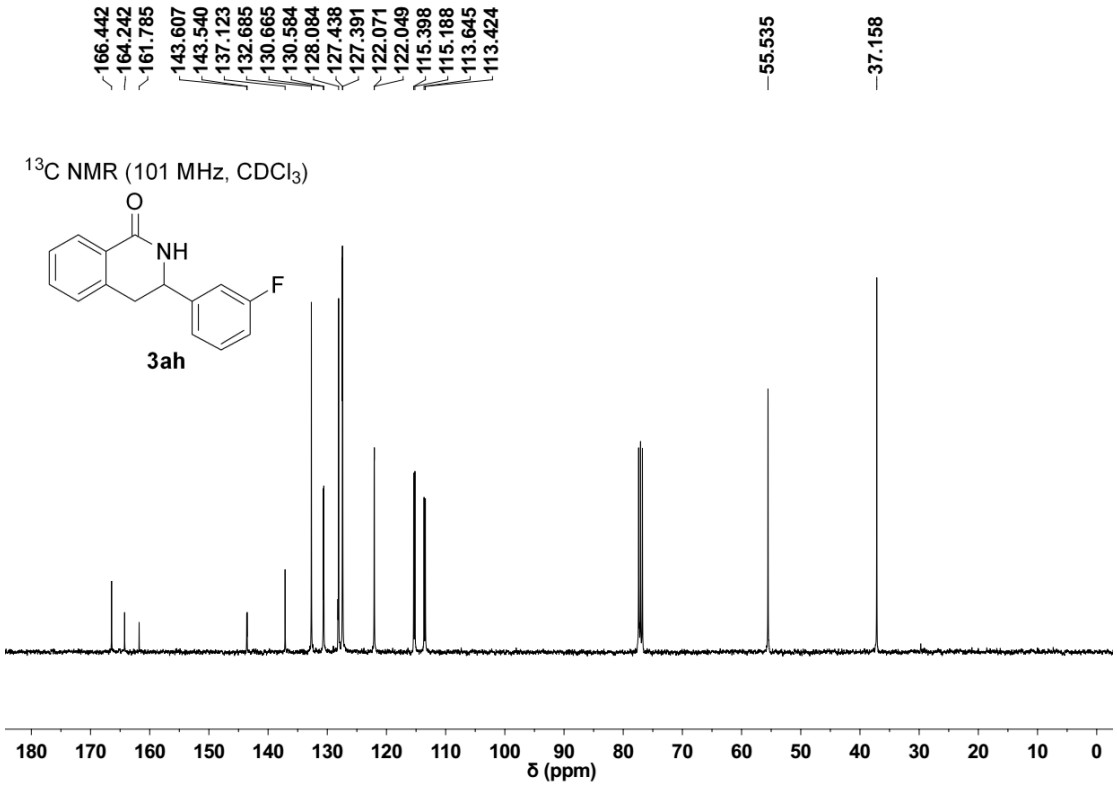

8.138
8.135
8.118
8.116
7.467
7.463
7.446
7.270
7.263
7.256
5.383
5.379
5.370
5.365
5.361
5.356
5.347
5.343
3.381
3.368
3.342
3.329
3.155
3.133
3.116
3.093
1H NMR (400MHz, CHCl3)
O
NH
Cl
3af
1.04
2.03
1.78
2.09
0.96
1.00
1.01
1.09
1.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

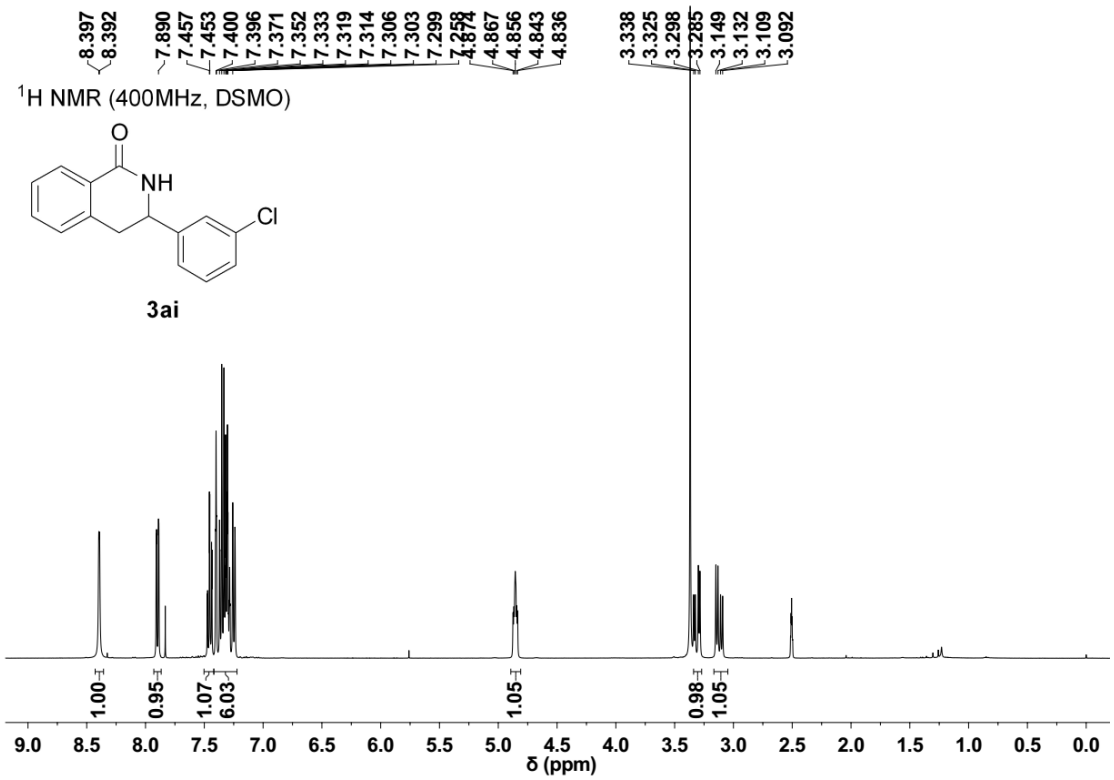

166.611
138.264
136.995
132.742
130.029
129.268
128.053
127.601
127.497
127.399
127.280
52.111
34.770
13C NMR (101MHz, CHCl3)
O
NH
Cl
3af
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

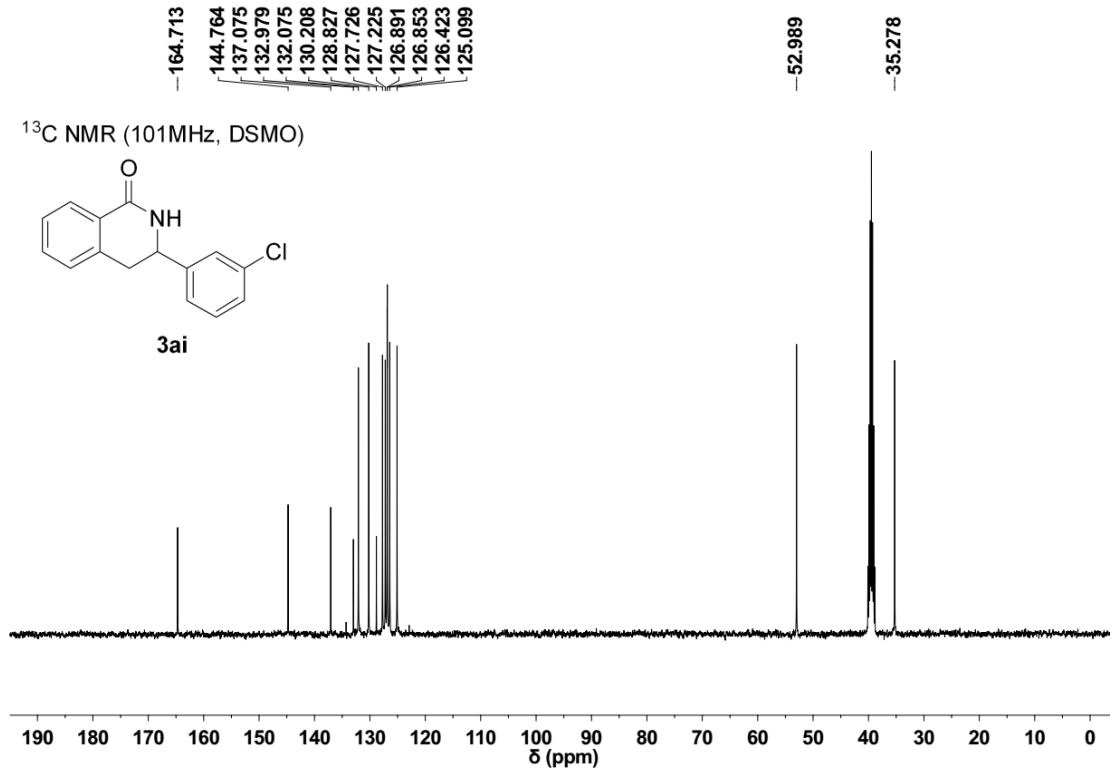

8.274
8.269
7.908
7.905
7.889
7.886
7.448
7.444
7.345
7.342
7.245
7.226
7.197
7.178
7.156
7.111
4.792
4.786
4.773
4.768
4.761
4.754
3.302
3.288
3.262
3.249
3.106
3.087
3.066
3.047
2.269
1H NMR (400MHz, DSMO)
O
NH
Me
3ag
1.00
1.00
1.01
1.03
3.08
2.02
1.03
1.03
1.01
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

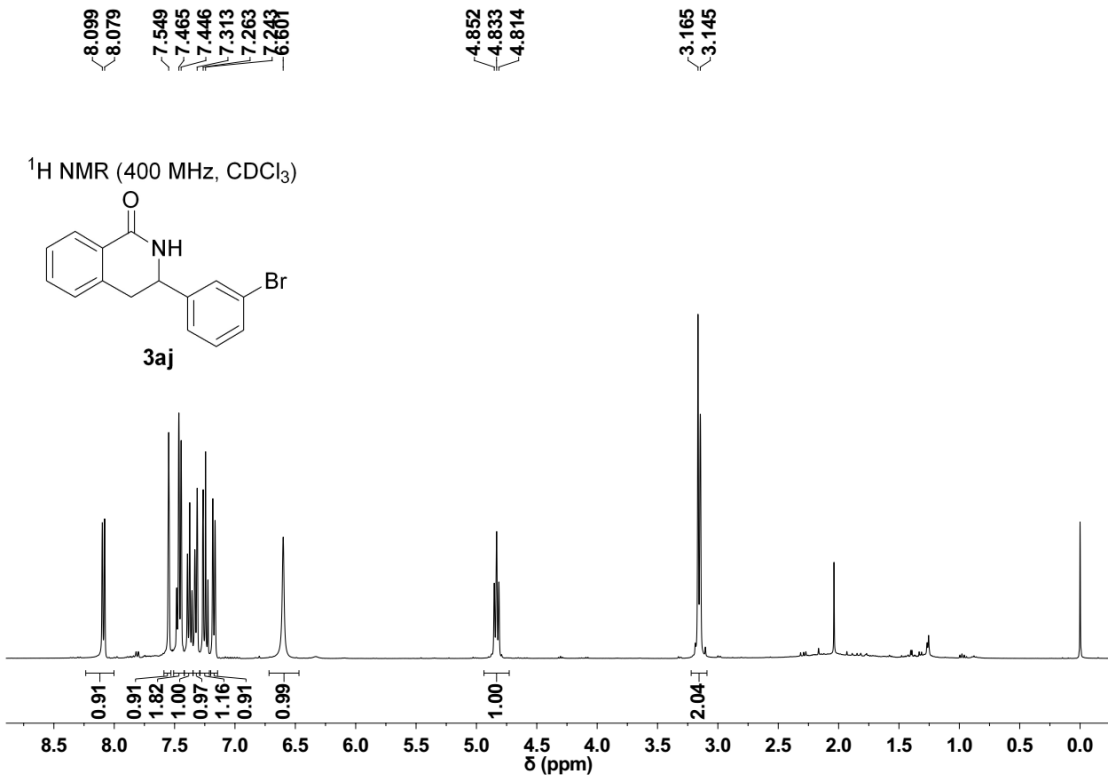

165.295
142.625
137.878
137.865
132.458
129.440
128.704
128.392
128.184
127.505
127.323
127.282
123.910
54.074
36.246
21.545
13C NMR (101MHz, DMSO)
O
NH
Me
3ag
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

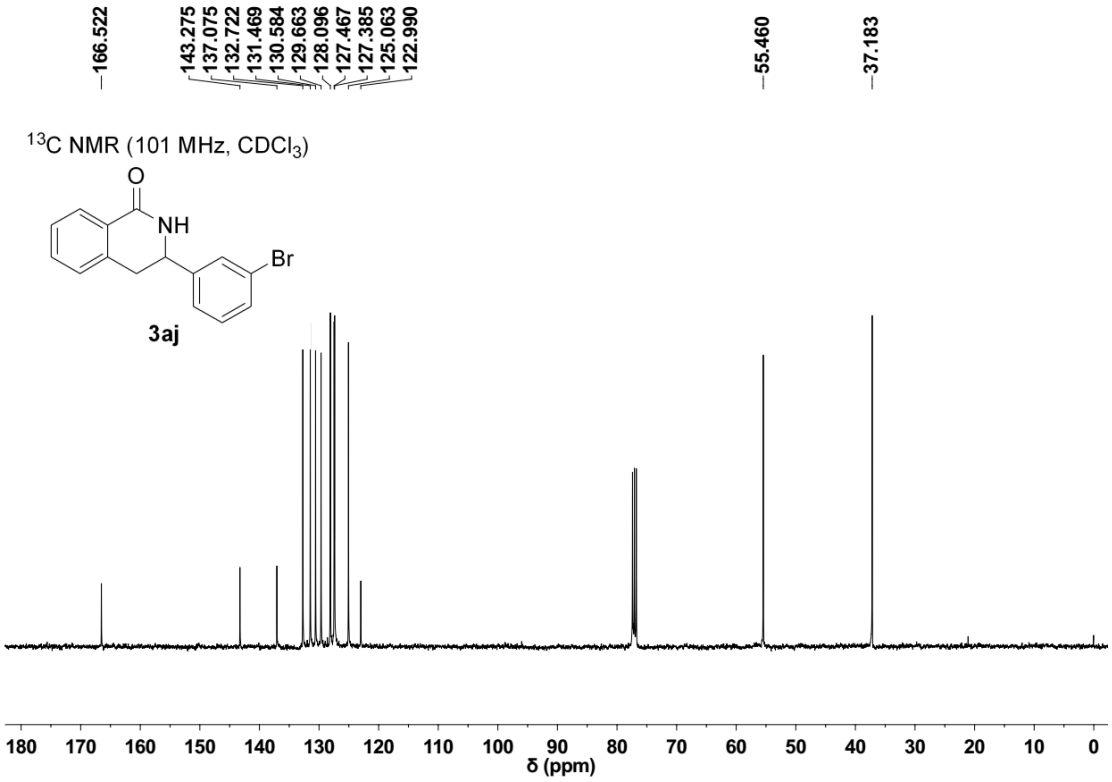

8.105
8.086
7.466
7.463
7.376
7.358
7.354
7.187
6.503
4.889
4.869
4.851
3.179
3.163
3.157
1H NMR (400 MHz, CDCl3)
O
NH
F
3ah
0.92
1.02
1.92
1.94
0.91
0.82
0.97
1.00
2.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

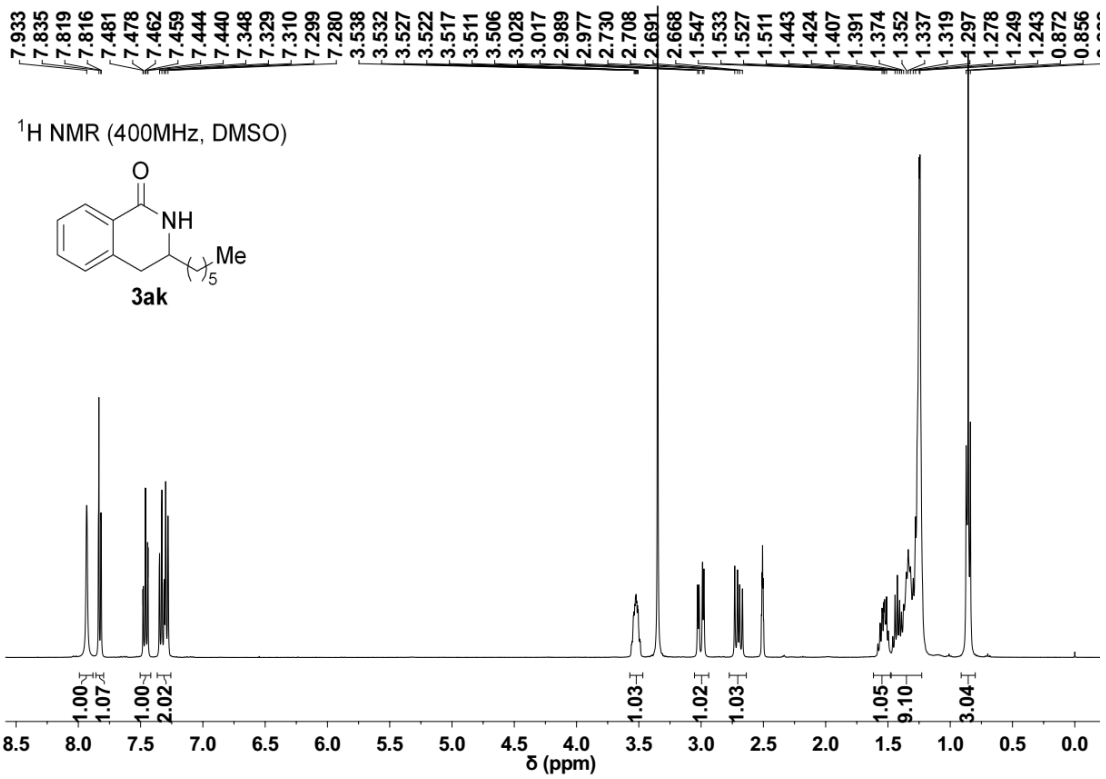

166.442
164.242
161.785
143.607
143.540
137.123
132.685
130.665
130.584
128.084
127.438
127.391
122.071
122.049
115.398
115.188
113.645
113.424
55.535
37.158
13C NMR (101 MHz, CDCl3)
O
NH
F
3ah
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

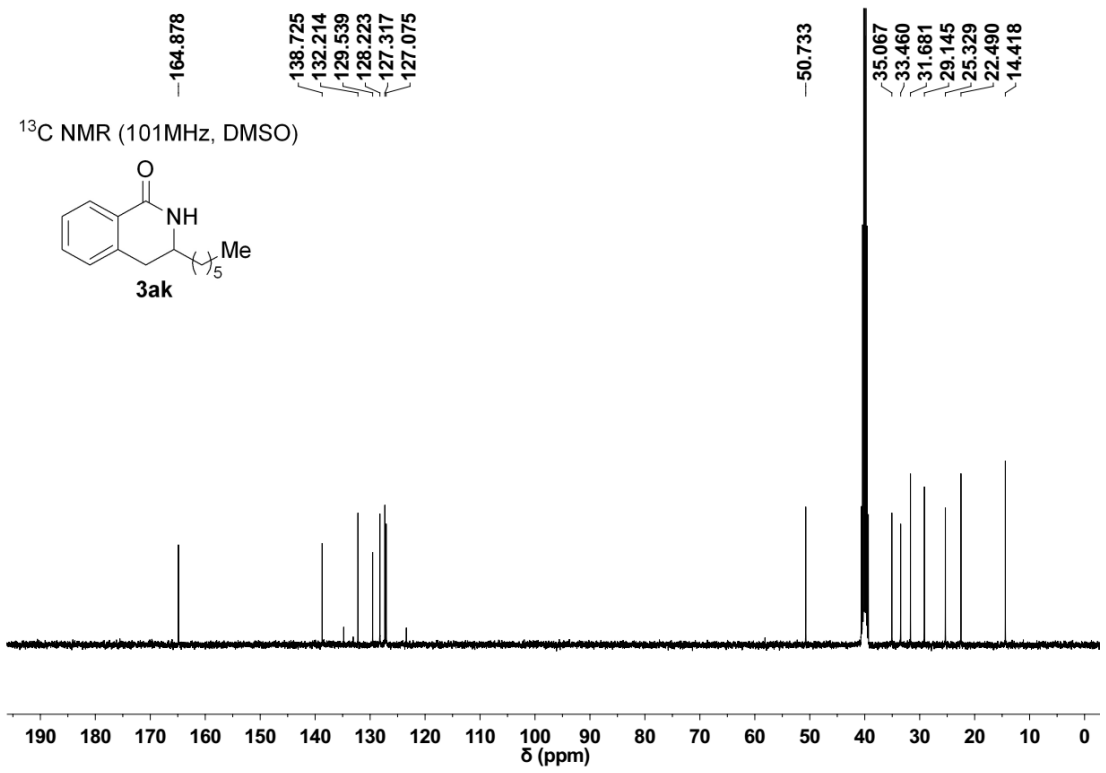

8.397
8.392
7.890
7.457
7.453
7.400
7.396
7.371
7.352
7.333
7.319
7.314
7.306
7.303
7.299
4.867
4.856
4.843
4.836
3.338
3.325
3.298
3.285
3.149
3.132
3.109
3.092
1H NMR (400MHz, DSMO)
O
NH
Cl
3ai
1.00
0.95
1.07
6.03
1.05
0.98
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

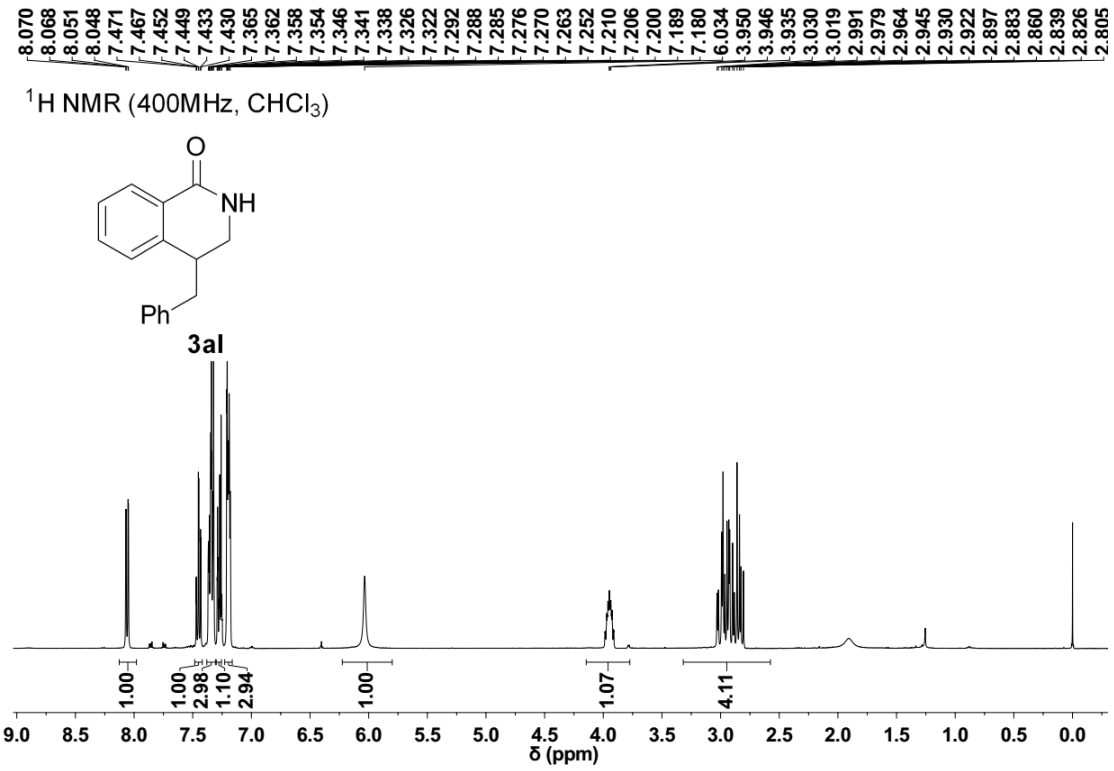

164.713
144.764
137.075
132.979
132.075
130.208
128.827
127.726
127.225
126.891
126.853
126.423
125.099
52.989
35.278
13C NMR (101MHz, DSMO)
O
NH
Cl
3ai
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

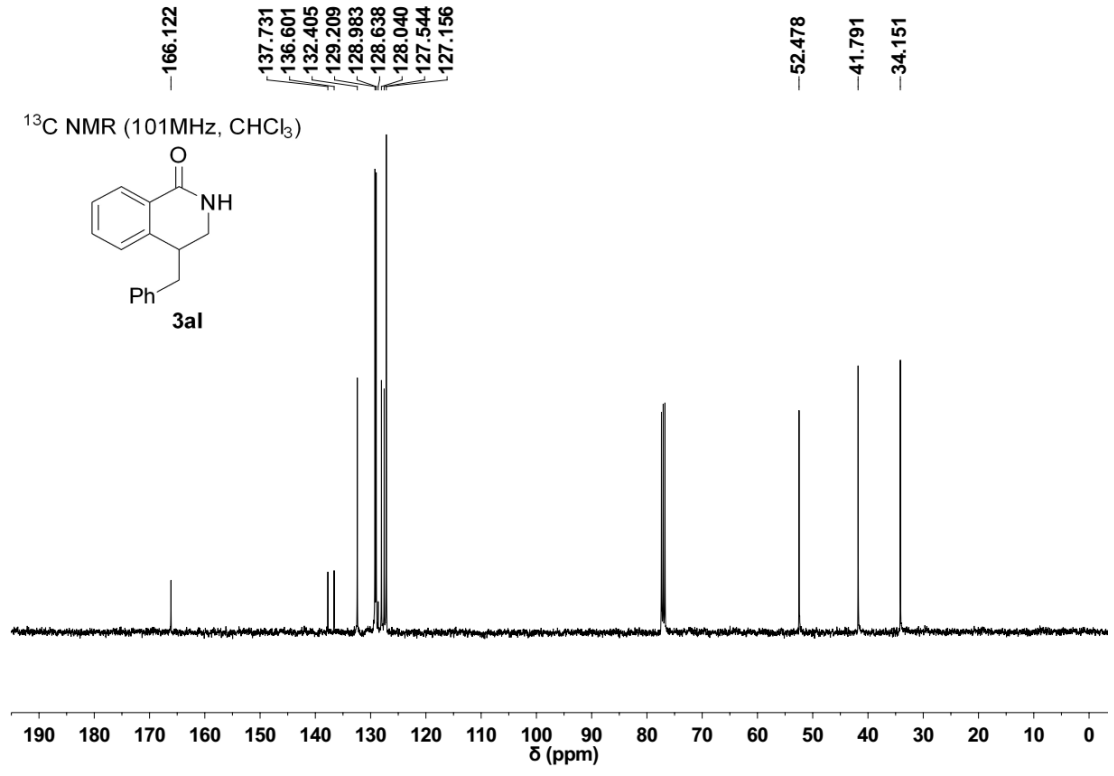

8.099
8.079
7.549
7.465
7.446
7.313
7.263
7.243
6.601
4.852
4.833
4.814
3.165
3.145
1H NMR (400 MHz, CDCl3)
O
NH
Br
3aj
0.91
0.91
1.82
1.00
0.97
1.16
0.91
0.99
1.00
2.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

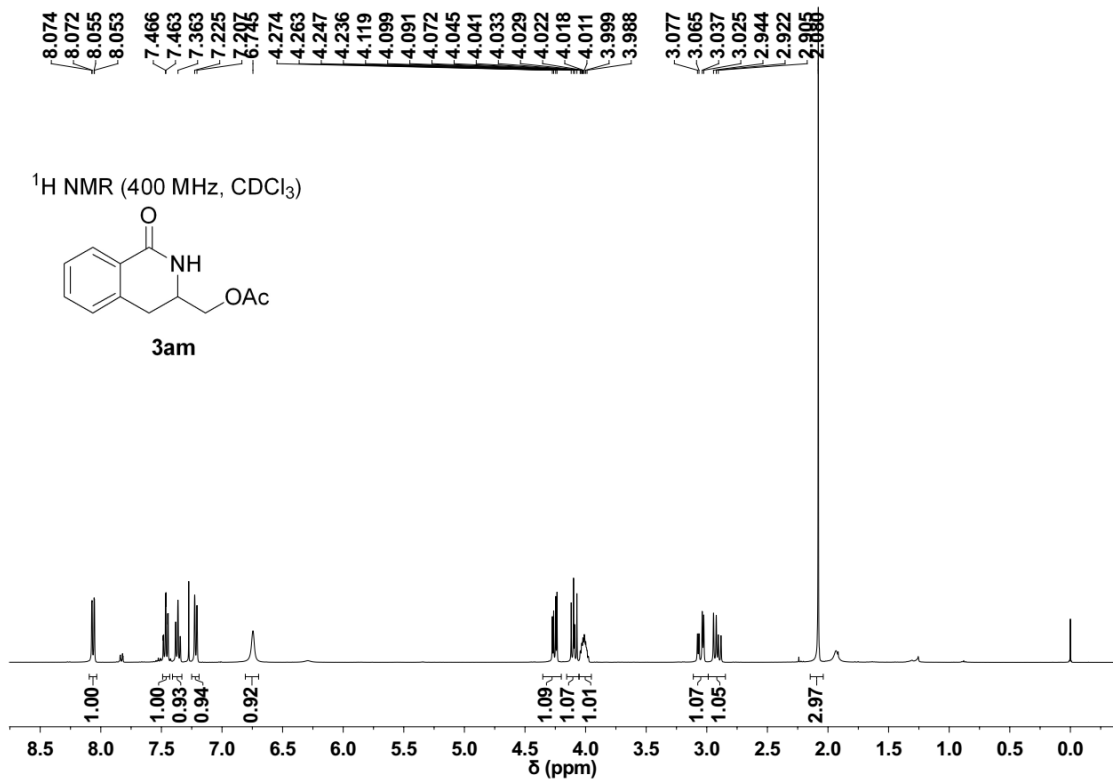

166.522
143.275
137.075
132.722
131.469
130.584
129.663
128.096
127.467
127.385
125.063
122.990
55.460
37.183
13C NMR (101 MHz, CDCl3)
O
NH
Br
3aj
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

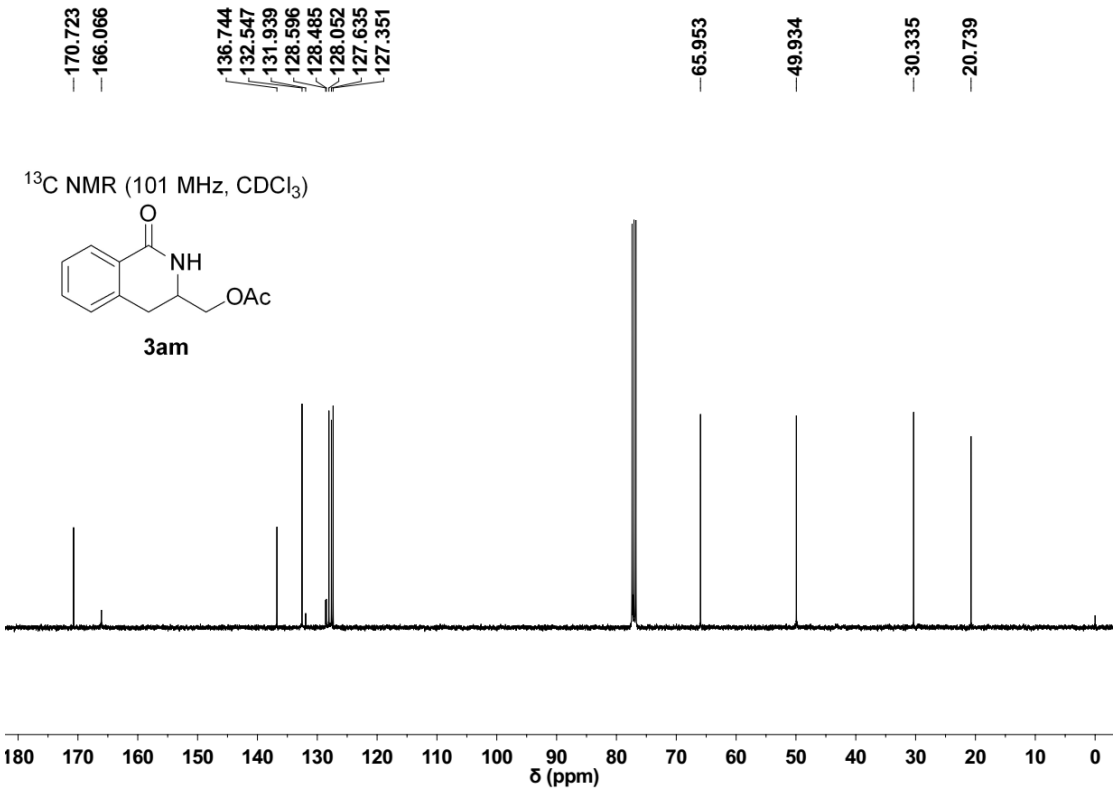

7.933
7.835
7.819
7.816
7.481
7.478
7.462
7.459
7.444
7.440
7.348
7.329
7.310
7.299
7.280
3.538
3.532
3.527
3.522
3.517
3.511
3.506
3.028
3.017
2.989
2.977
2.730
2.708
2.691
2.668
1.547
1.533
1.527
1.511
1.443
1.424
1.407
1.391
1.374
1.352
1.337
1.319
1.297
1.278
1.249
1.243
0.872
0.856
1H NMR (400MHz, DMSO)
O
NH
Me
5
3ak
1.00
1.07
1.00
2.02
1.03
1.02
1.03
1.05
9.10
3.04
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
δ (ppm)

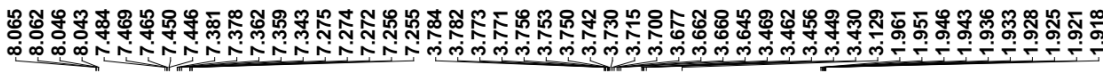

164.878
138.725
132.214
129.539
128.223
127.317
127.075
50.733
35.067
33.460
31.681
29.145
25.329
22.490
14.418
13C NMR (101MHz, DMSO)
O
NH
Me
5
3ak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

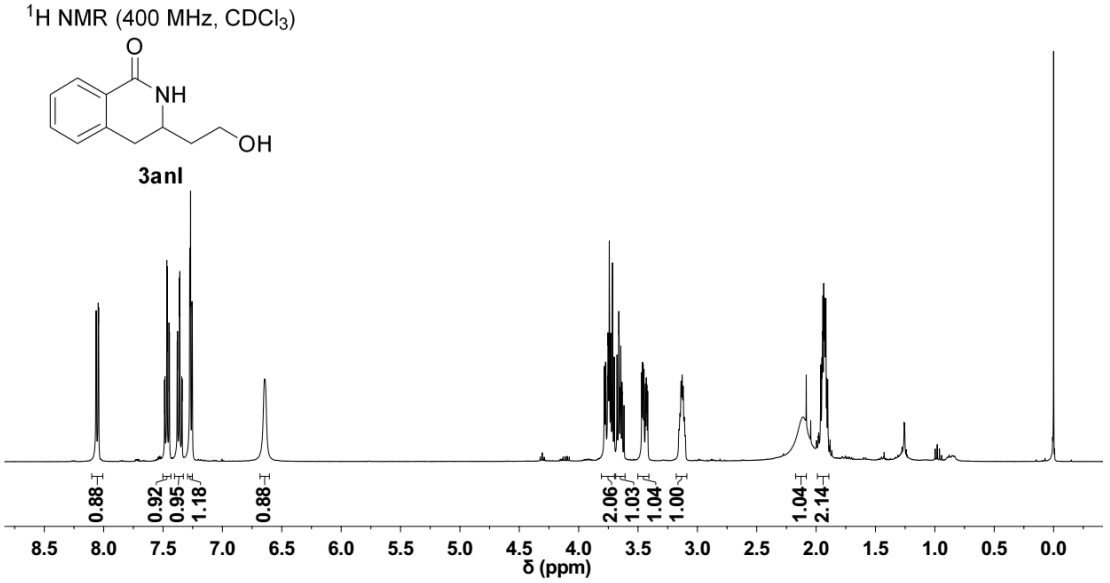

8.070
8.068
8.051
8.048
7.471
7.467
7.452
7.449
7.433
7.430
7.365
7.362
7.358
7.354
7.346
7.341
7.338
7.326
7.322
7.292
7.288
7.285
7.276
7.270
7.263
7.252
7.210
7.206
7.200
7.189
7.180
6.034
3.950
3.946
3.935
3.030
3.019
2.991
2.979
2.964
2.945
2.930
2.922
2.897
2.883
2.860
2.839
2.826
2.805
1H NMR (400MHz, CHCl3)
O
NH
Ph
3al
1.00
1.00
2.98
1.10
2.94
1.00
1.07
4.11
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
δ (ppm)

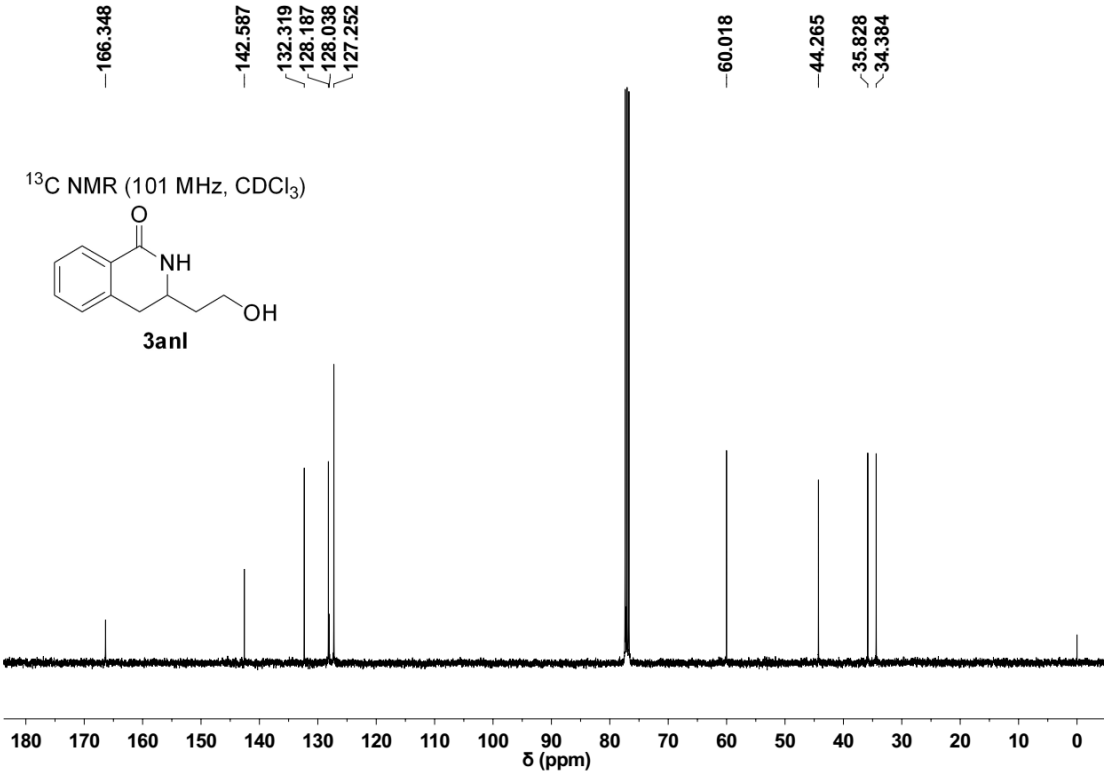

166.122
137.731
136.601
132.405
129.209
128.983
128.638
128.040
127.544
127.156
52.478
41.791
34.151
13C NMR (101MHz, CHCl3)
O
NH
Ph
3al
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

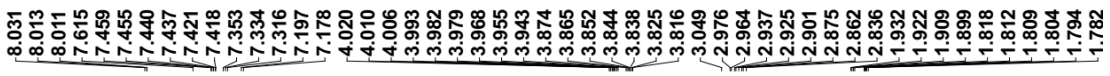

8.074
8.072
8.055
8.053
7.466
7.463
7.363
7.225
6.745
4.274
4.263
4.247
4.236
4.119
4.099
4.091
4.072
4.045
4.041
4.033
4.029
4.022
4.018
4.011
3.999
3.988
3.077
3.065
3.037
3.025
2.944
2.922
2.905
2.080
1H NMR (400 MHz, CDCl3)
O
NH
OAc
3am
1.00
1.00
0.93
0.94
0.92
1.09
1.07
1.01
1.07
1.05
2.97
8.5 8.0 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
δ (ppm)


170.723
166.066
136.744
132.547
131.939
128.596
128.485
128.052
127.635
127.351
65.953
49.934
30.335
20.739
13C NMR (101 MHz, CDCl3)
O
NH
OAc
3am
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

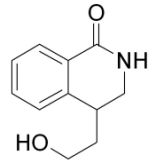

8.065
8.062
8.046
8.043
7.484
7.469
7.465
7.450
7.446
7.381
7.378
7.362
7.359
7.343
7.275
7.274
7.272
7.256
7.255
3.784
3.782
3.773
3.771
3.756
3.753
3.750
3.742
3.730
3.715
3.700
3.677
3.662
3.660
3.645
3.469
3.462
3.456
3.449
3.430
3.129
1.961
1.951
1.946
1.943
1.936
1.933
1.928
1.925
1.921
1.918


^{1}H NMR (400 MHz, CDCl$_3$)
O
NH
OH
3anl
0.88
0.92
0.95
1.18
0.88
2.06
1.03
1.04
1.00
1.04
2.14
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
δ (ppm)

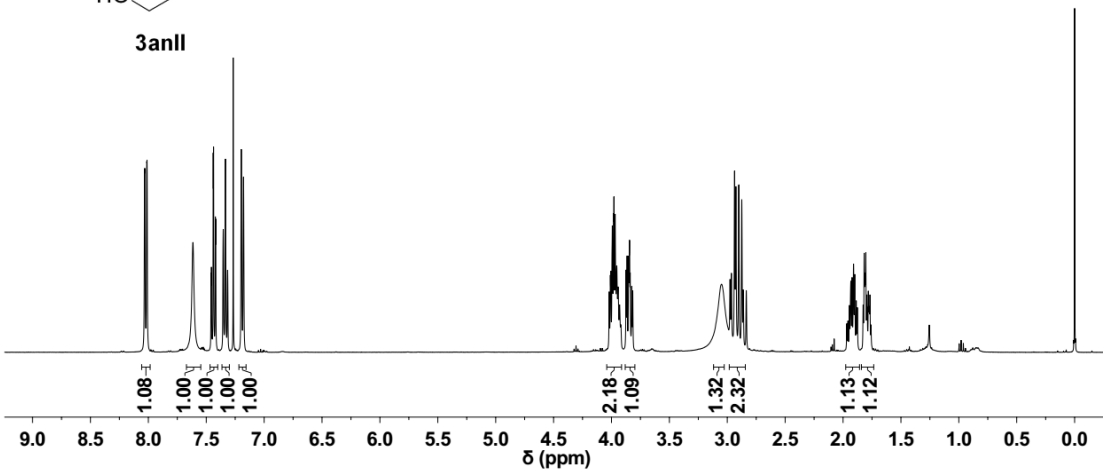

166.348
142.587
132.319
128.187
128.038
127.252
60.018
44.265
35.828
34.384
^{13}C NMR (101 MHz, CDCl$_3$)
O
NH
OH
3anl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

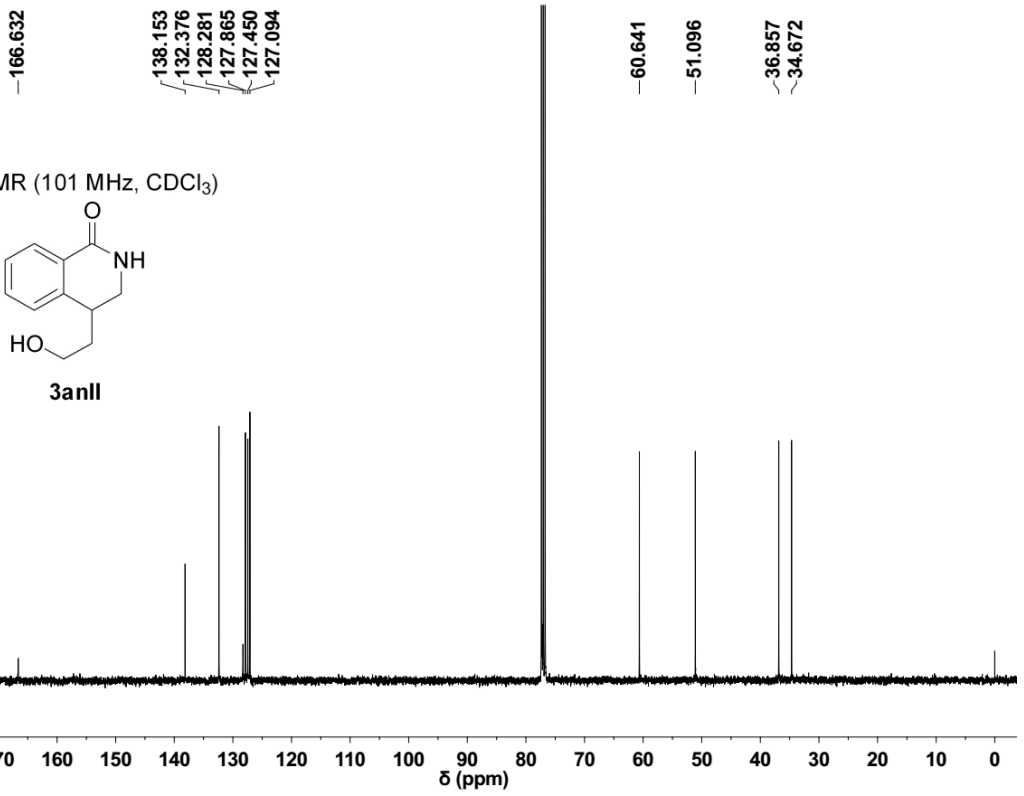


^{1}H NMR (400 MHz, $CDCl_3$)



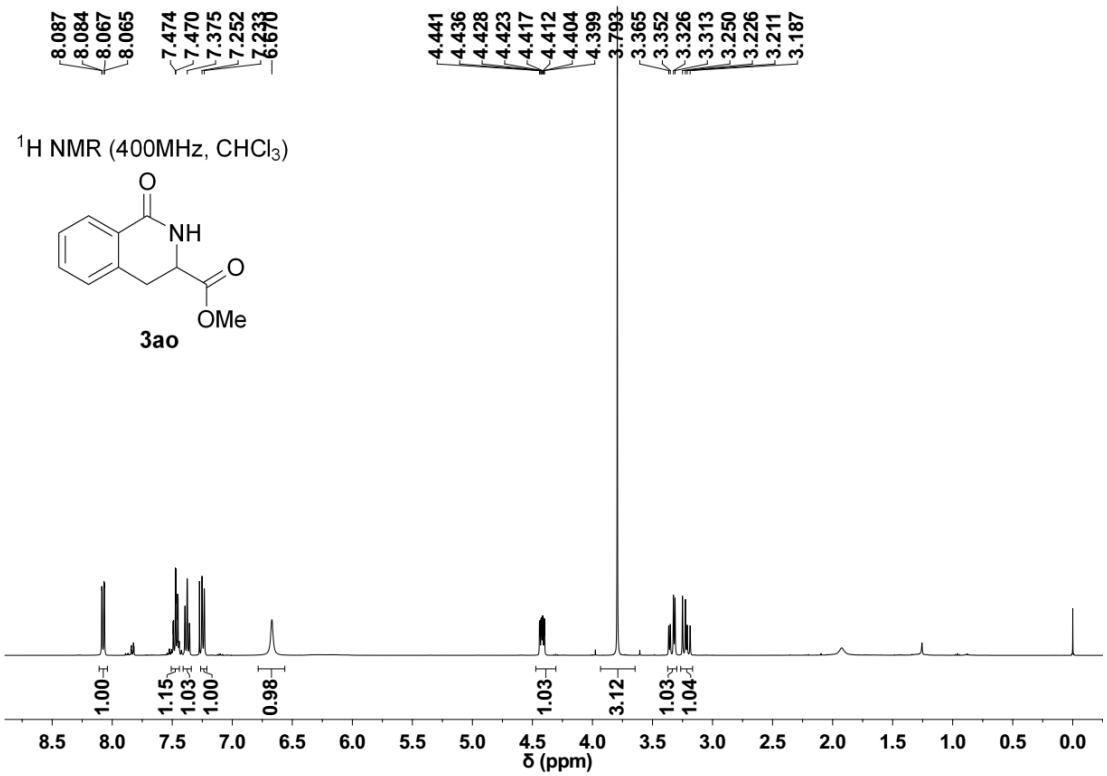
3anII

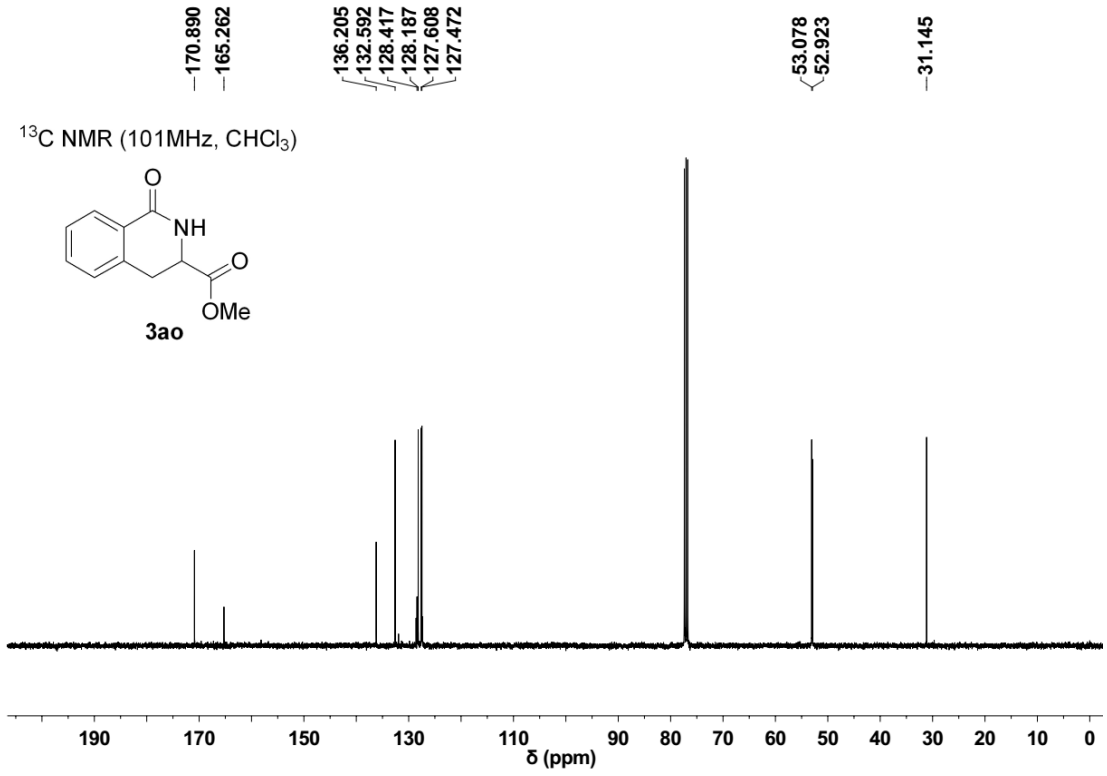


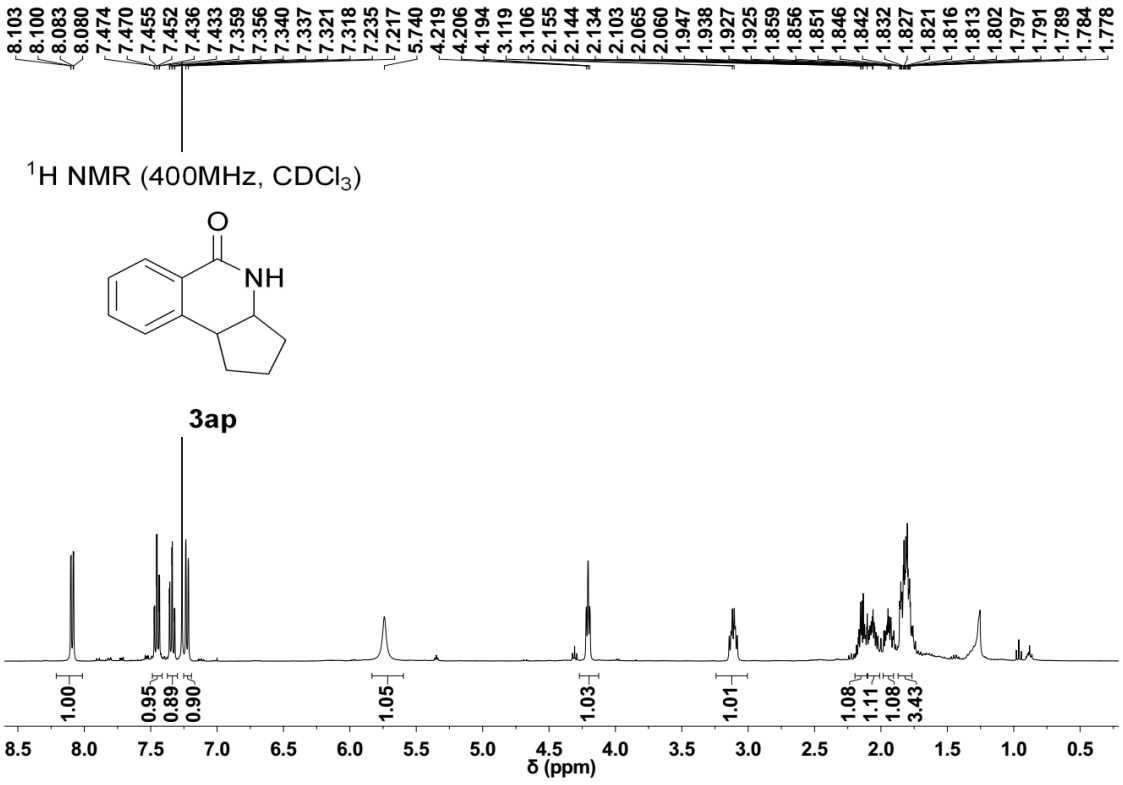


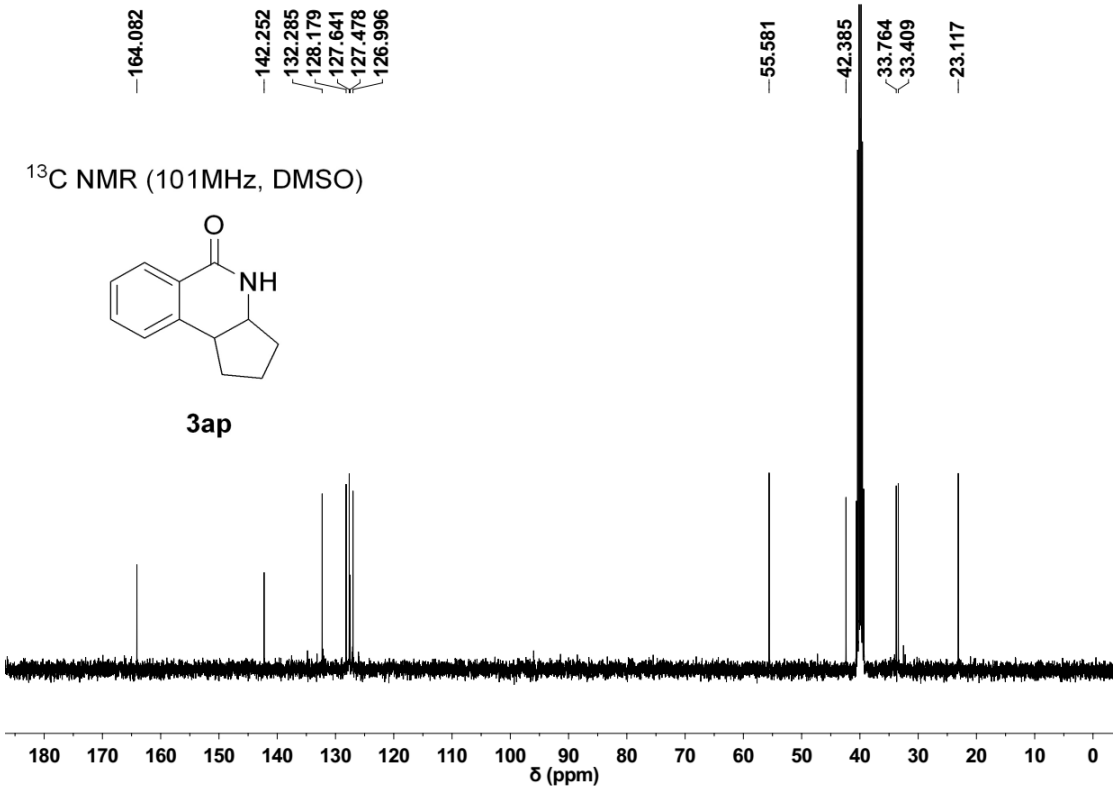
^{13}C NMR (101 MHz, $CDCl_3$)

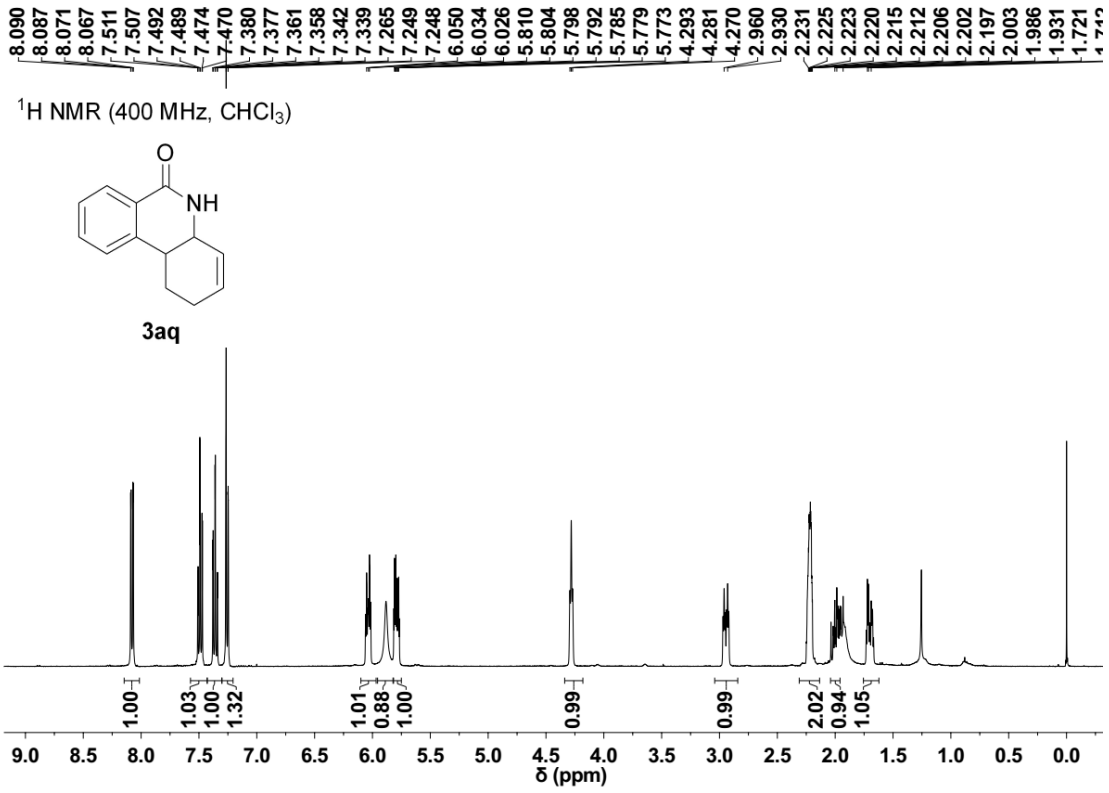
3anII

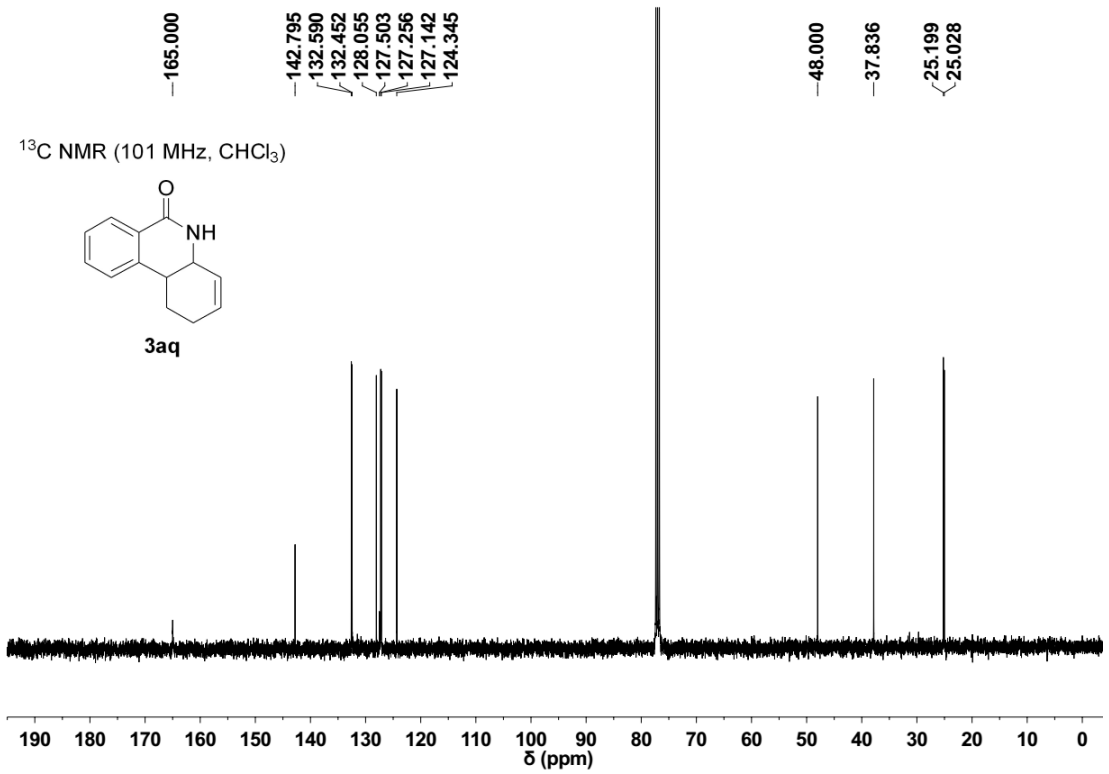

8.087
8.084
8.067
8.065
7.474
7.470
7.375
7.252
6.670
4.441
4.436
4.428
4.423
4.417
4.412
4.404
4.399
3.793
3.365
3.352
3.326
3.313
3.250
3.226
3.211
3.187
1H NMR (400MHz, CHCl3)
O
NH
O
OMe
3ao
1.00
1.15
1.03
1.00
0.98
1.03
3.12
1.03
1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

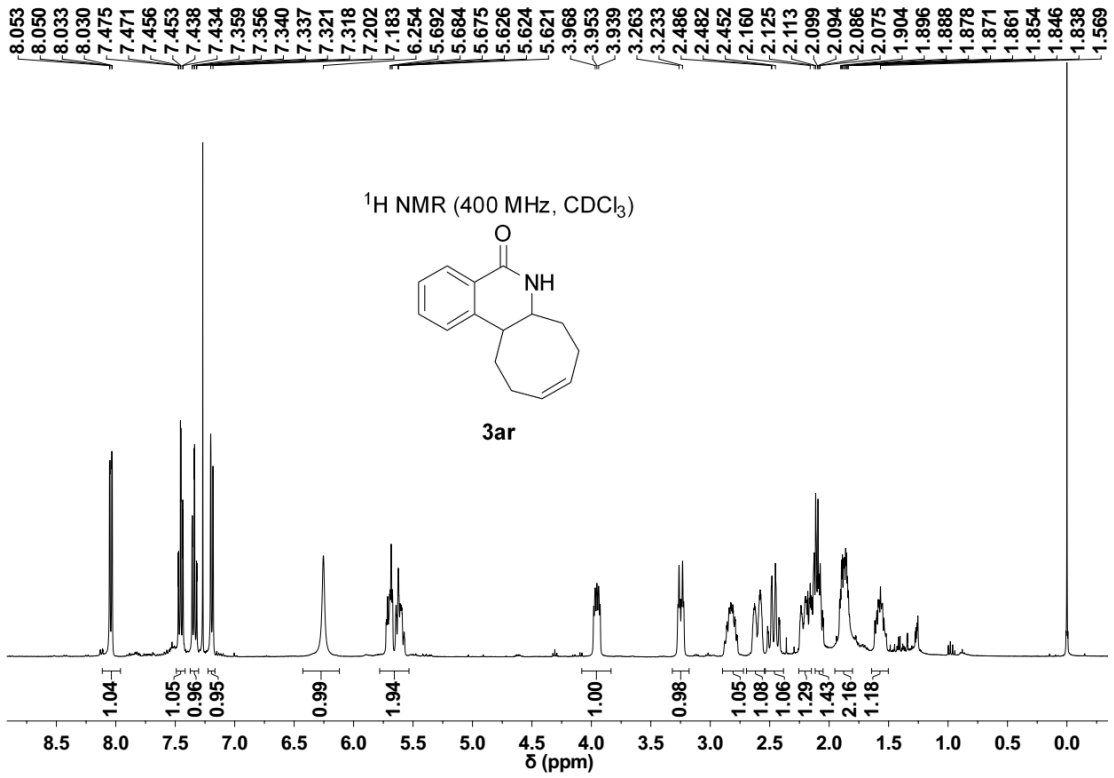

170.890
165.262
136.205
132.592
128.417
128.187
127.608
127.472
53.078
52.923
31.145
13C NMR (101MHz, CHCl3)
O
NH
O
OMe
3ao
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ (ppm)

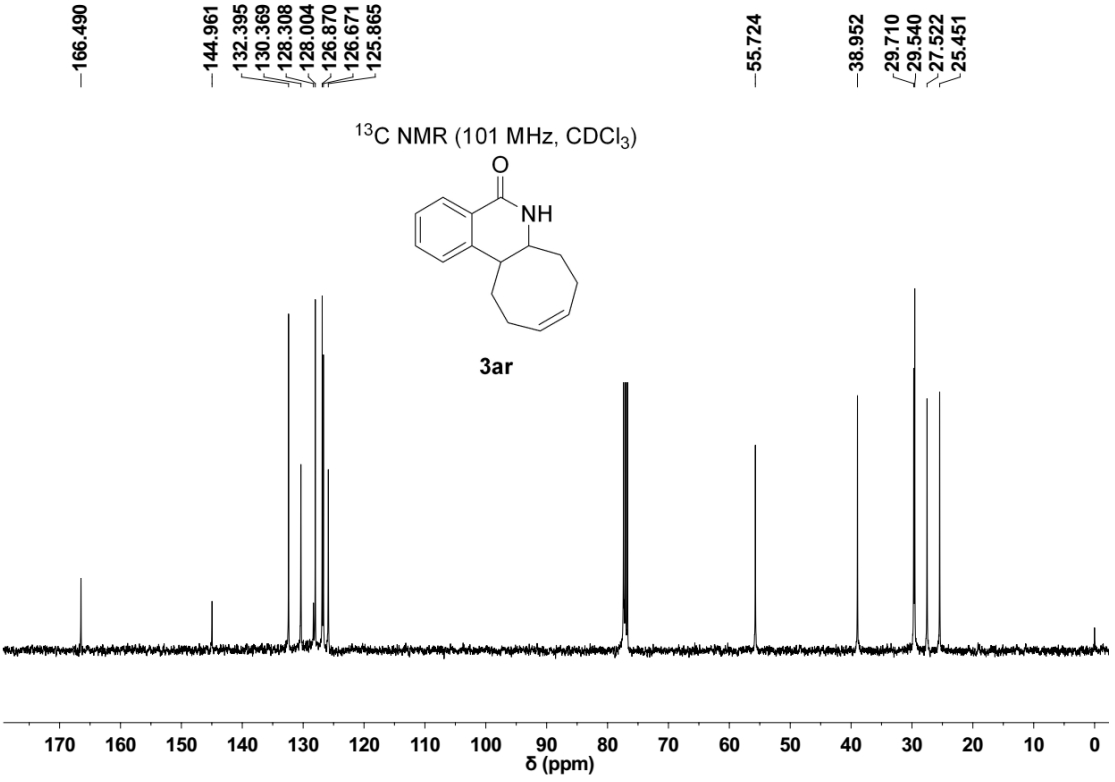

8.103
8.100
8.083
8.080
7.474
7.470
7.455
7.452
7.436
7.433
7.359
7.356
7.340
7.337
7.321
7.318
7.235
7.217
5.740
4.219
4.206
4.194
3.119
3.106
2.155
2.144
2.134
2.103
2.065
2.060
1.947
1.938
1.927
1.925
1.859
1.856
1.851
1.846
1.842
1.832
1.827
1.821
1.816
1.813
1.802
1.797
1.791
1.789
1.784
1.778
1H NMR (400MHz, CDCl3)
O
NH
3ap
1.00
0.95
0.89
0.90
1.05
1.03
1.01
1.08
1.11
1.08
3.43
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
δ (ppm)

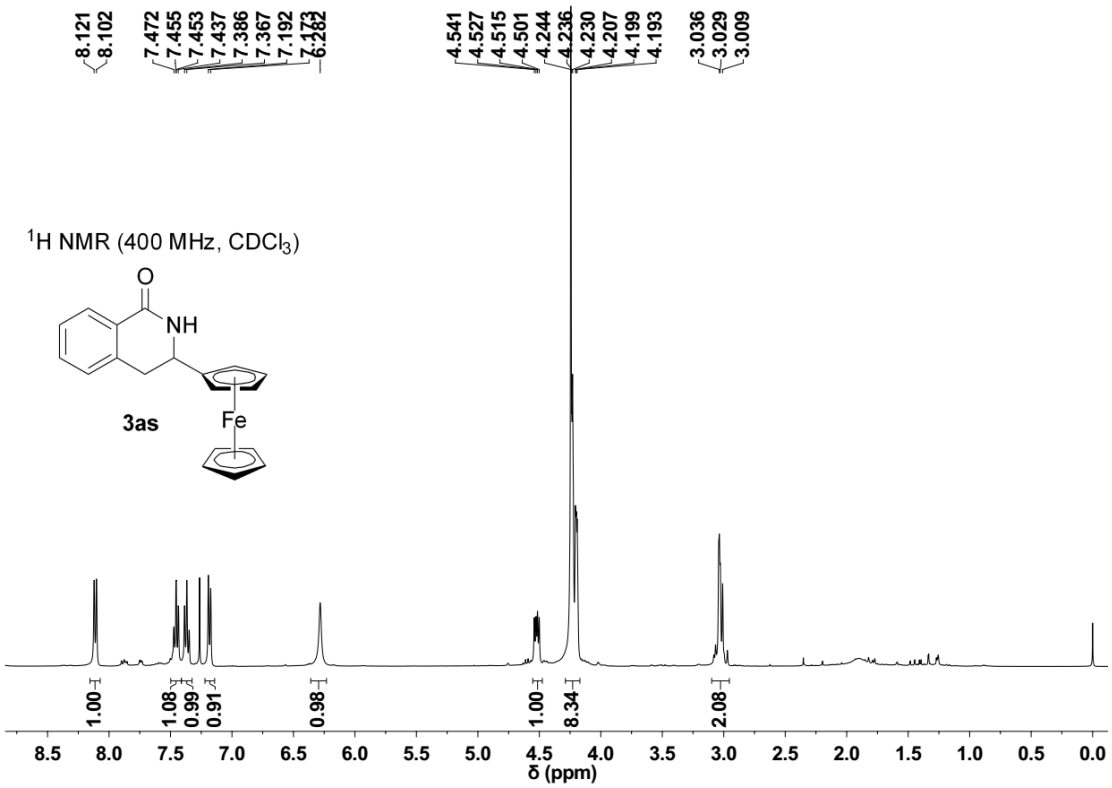

164.082
142.252
132.285
128.179
127.641
127.478
126.996
55.581
42.385
33.764
33.409
23.117
13C NMR (101MHz, DMSO)
O
NH
3ap
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

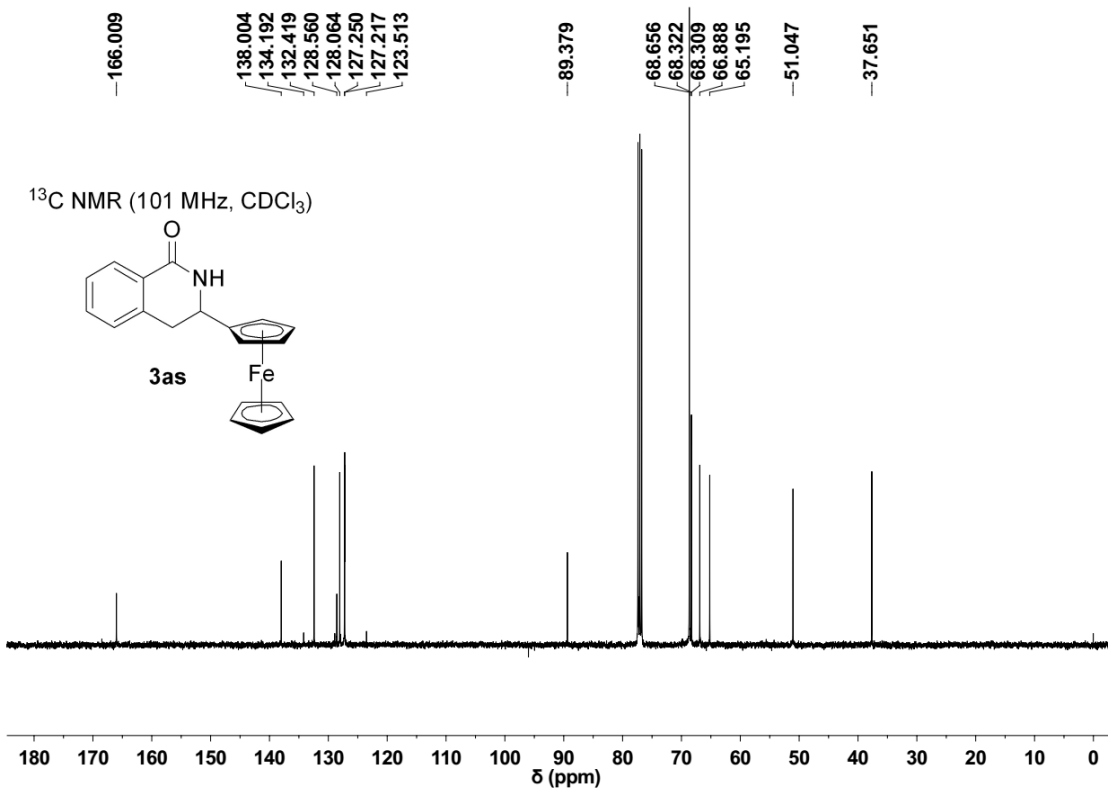

8.090
8.087
8.071
8.067
7.511
7.507
7.492
7.489
7.474
7.470
7.380
7.377
7.361
7.358
7.342
7.339
7.265
7.249
7.248
6.050
6.034
6.026
5.810
5.804
5.798
5.792
5.785
5.779
5.773
4.293
4.281
4.270
2.960
2.930
2.231
2.225
2.223
2.220
2.215
2.212
2.206
2.202
2.197
2.003
1.986
1.931
1.721
^{1}H NMR (400 MHz, $CHCl_3$)
O
NH
3aq
1.00
1.03
1.00
1.32
1.01
0.88
1.00
0.99
0.99
2.02
0.94
1.05
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
δ (ppm)

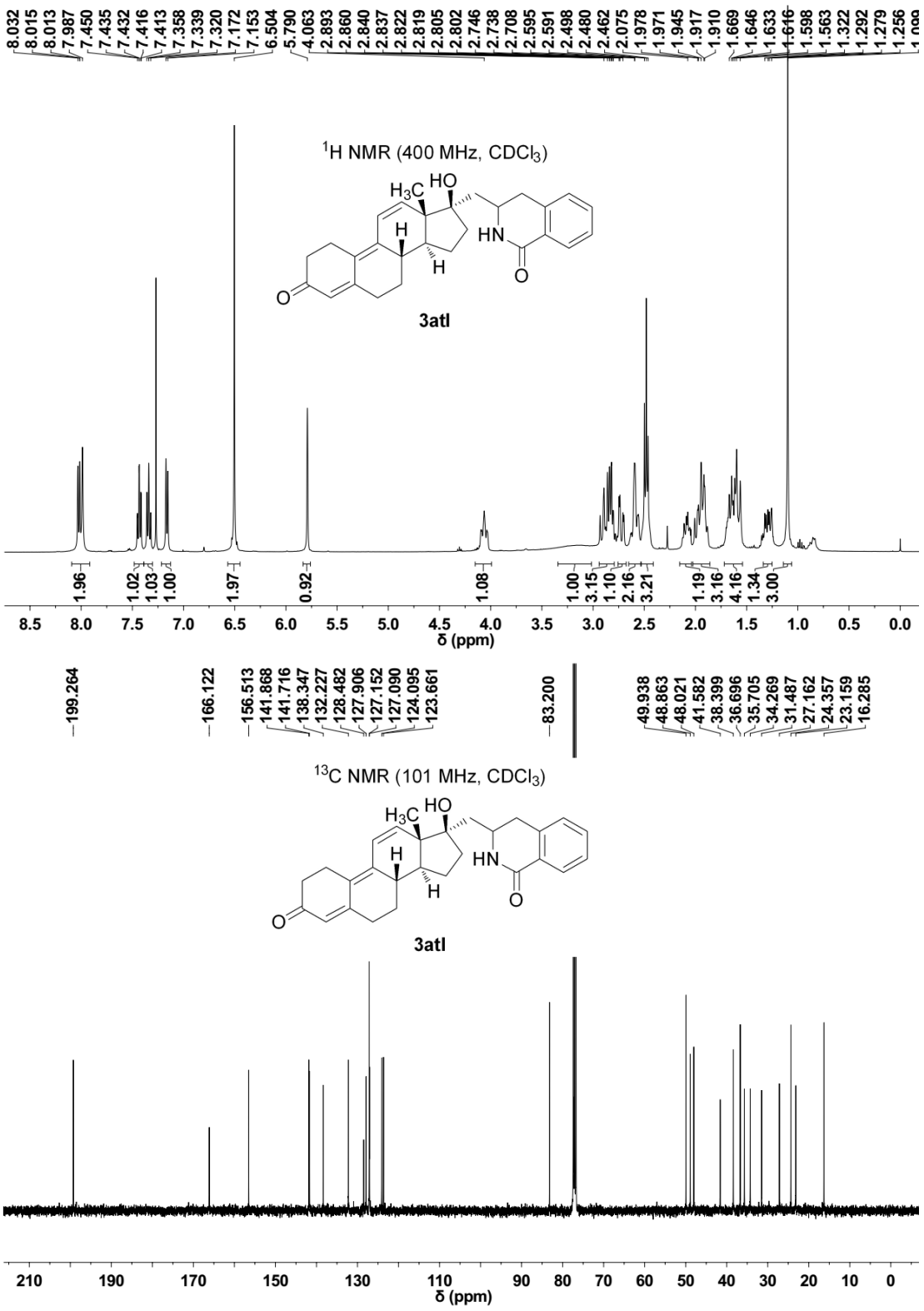

165.000
142.795
132.590
132.452
128.055
127.503
127.256
127.142
124.345
48.000
37.836
25.199
25.028
^{13}C NMR (101 MHz, $CHCl_3$)
O
NH
3aq
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

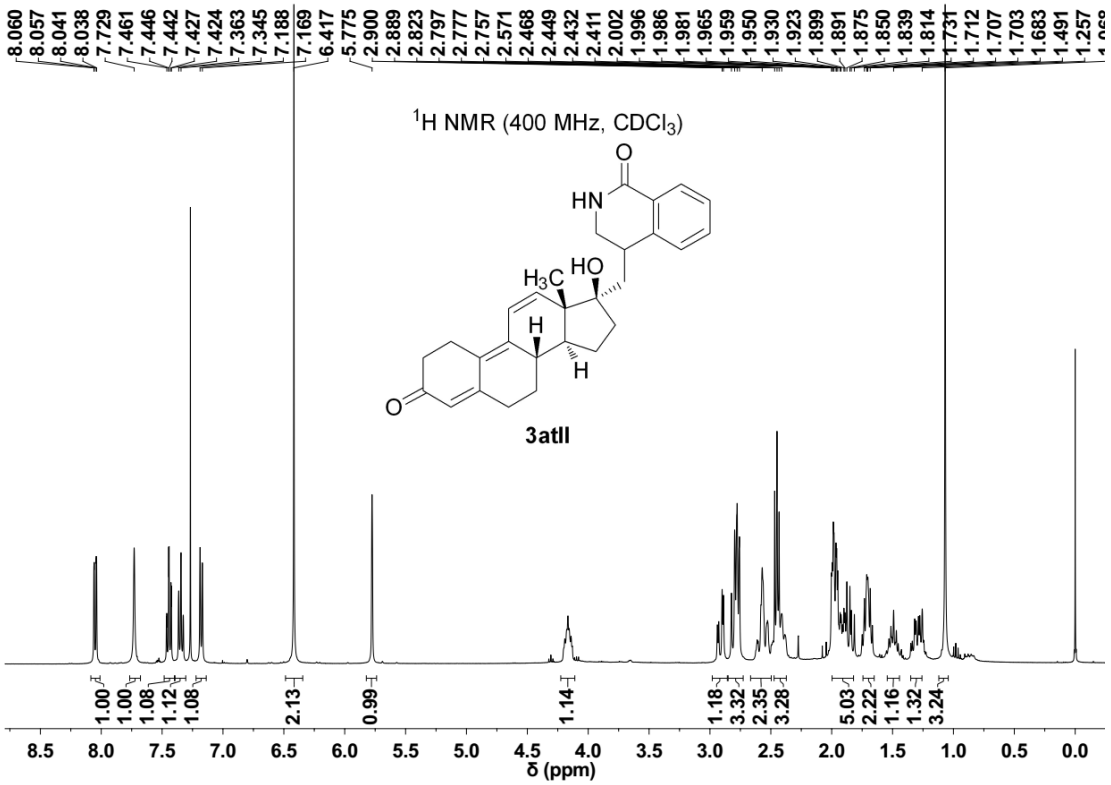

8.053
8.050
8.033
8.030
7.475
7.471
7.456
7.453
7.438
7.434
7.359
7.356
7.340
7.337
7.321
7.318
7.202
7.183
6.254
5.692
5.684
5.675
5.626
5.624
5.621
3.968
3.953
3.939
3.263
3.233
2.486
2.482
2.452
2.160
2.125
2.113
2.099
2.094
2.086
2.075
1.904
1.896
1.888
1.878
1.871
1.861
1.854
1.846
1.838
1.569
1H NMR (400 MHz, CDCl3)
O
NH
3ar
1.04
1.05
0.96
0.95
0.99
1.94
1.00
0.98
1.05
1.08
1.06
1.29
1.43
2.16
1.18
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
δ (ppm)

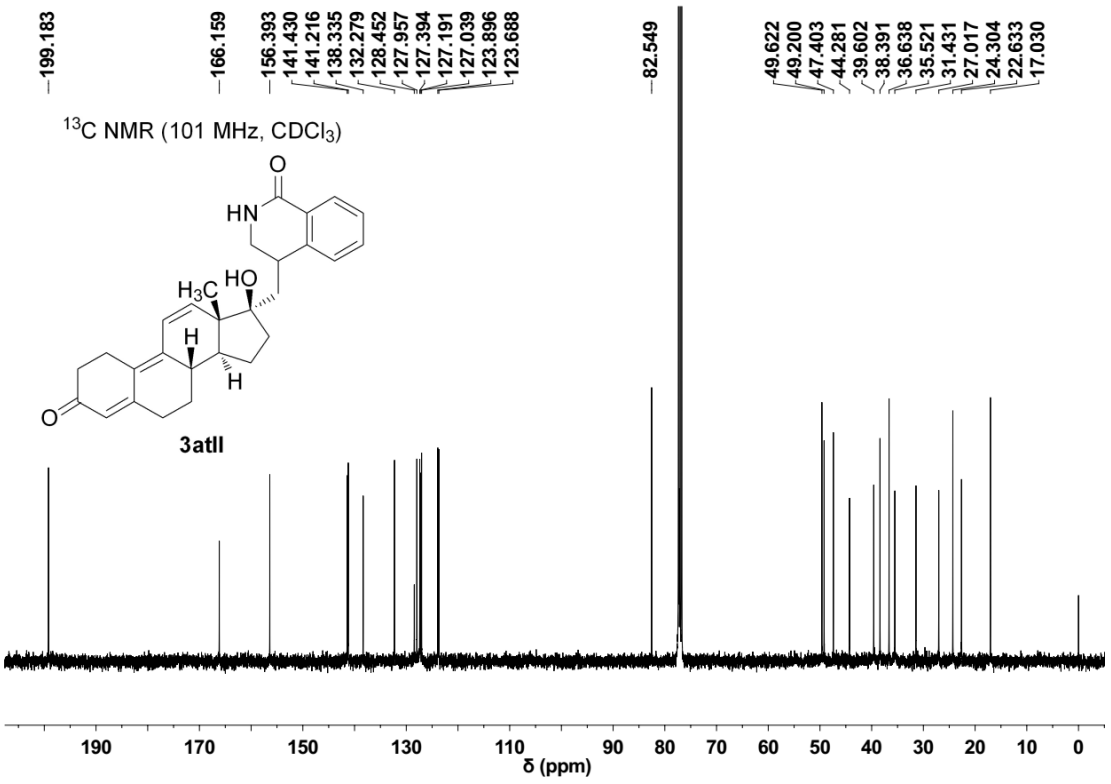

166.490
144.961
132.395
130.369
128.308
128.004
126.870
126.671
125.865
55.724
38.952
29.710
29.540
27.522
25.451
13C NMR (101 MHz, CDCl3)
O
NH
3ar
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)


8.121
8.102
7.472
7.455
7.453
7.437
7.386
7.367
7.192
7.173
6.282
4.541
4.527
4.515
4.501
4.244
4.236
4.230
4.207
4.199
4.193
3.036
3.029
3.009
1H NMR (400 MHz, CDCl3)
O
NH
3as
Fe
1.00
1.08
0.99
0.91
0.98
1.00
8.34
2.08
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
δ (ppm)


166.009
138.004
134.192
132.419
128.560
128.064
127.250
127.217
123.513
89.379
68.656
68.322
68.309
66.888
65.195
51.047
37.651
13C NMR (101 MHz, CDCl3)
O
NH
3as
Fe
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


8.032
8.015
8.013
7.987
7.450
7.435
7.432
7.416
7.413
7.358
7.339
7.320
7.172
7.153
6.504
5.790
4.063
2.893
2.860
2.840
2.837
2.822
2.819
2.805
2.802
2.746
2.738
2.708
2.595
2.591
2.498
2.480
2.462
2.075
1.978
1.971
1.945
1.917
1.910
1.669
1.646
1.633
1.616
1.598
1.563
1.322
1.292
1.279
1.256
^{1}H NMR (400 MHz, $CDCl_3$)
H_3C
HO
H
HN
H
O
O
3atl
1.96
1.02
1.03
1.00
1.97
0.92
1.08
1.00
3.15
1.10
2.16
3.21
1.19
3.16
4.16
1.34
3.00
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
δ (ppm)
199.264
166.122
156.513
141.868
141.716
138.347
132.227
128.482
127.906
127.152
127.090
124.095
123.661
83.200
49.938
48.863
48.021
41.582
38.399
36.696
35.705
34.269
31.487
27.162
24.357
23.159
16.285
^{13}C NMR (101 MHz, $CDCl_3$)
H_3C
HO
H
HN
H
O
O
3atl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


8.060
8.057
8.041
8.038
7.729
7.461
7.446
7.442
7.427
7.424
7.363
7.345
7.188
7.169
6.417
5.775
2.900
2.889
2.823
2.797
2.777
2.757
2.571
2.468
2.449
2.432
2.411
2.002
1.996
1.986
1.981
1.965
1.959
1.950
1.930
1.923
1.899
1.891
1.875
1.850
1.839
1.814
1.731
1.712
1.707
1.703
1.683
1.491
1.257
^{1}H NMR (400 MHz, $CDCl_3$)
HN
O
H_3C
HO
H
H
O
3atII
1.00
1.00
1.08
1.12
1.08
2.13
0.99
1.14
1.18
3.32
2.35
3.28
5.03
2.22
1.16
1.32
3.24
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
δ (ppm)


199.183
166.159
156.393
141.430
141.216
138.335
132.279
128.452
127.957
127.394
127.191
127.039
123.896
123.688
82.549
49.622
49.200
47.403
44.281
39.602
38.391
36.638
35.521
31.431
27.017
24.304
22.633
17.030
^{13}C NMR (101 MHz, $CDCl_3$)
HN
O
H_3C
HO
H
H
O
3atII
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)