Supporting Information

Pd/NBE-Catalyzed Sequential Carbamoylation/Olefination of Aryl Iodides

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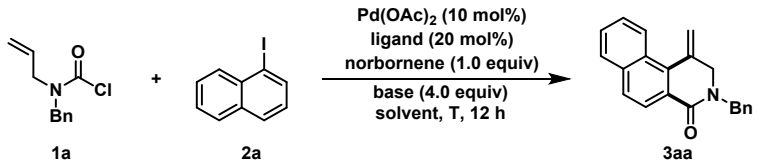
General information:

The ^{1}H NMR, ^{19}F NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Optimization of reaction conditions



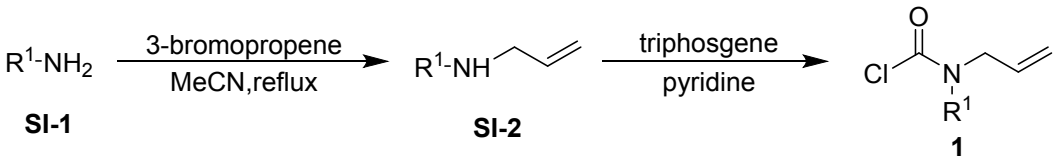
Entry	Ligand	Base	Solvent	Temperature	Yield[b](%)
1	P(4-F-C_6H_4)$_3$	Cs_2CO_3	DCE	100℃	36%
2	P(2-furyl)$_3$	Cs_2CO_3	DCE	100℃	77%
3	P(4-OMe-C_6H_4)$_3$	Cs_2CO_3	DCE	100℃	25%
4	DPPF	Cs_2CO_3	DCE	100℃	20%
5	DPPE	Cs_2CO_3	DCE	100℃	25%
6	P(2-furyl)$_3$	K_2CO_3	DCE	100℃	22%
7	P(2-furyl)$_3$	NaOAc	DCE	100℃	20%
8	P(2-furyl)$_3$	K_3PO_4	DCE	100℃	30%
9	P(2-furyl)$_3$	Na_2CO_3	DCE	100℃	22%
10	P(2-furyl)$_3$	$NaHCO_3$	DCE	100℃	20%
11	P(2-furyl)$_3$	Et_3N	DCE	100℃	25%
12	P(2-furyl)$_3$	Cs_2CO_3	MeCN	100℃	50%
13	P(2-furyl)$_3$	Cs_2CO_3	Toluene	100℃	55%
14	P(2-furyl)$_3$	Cs_2CO_3	Dioxane	100℃	63%
15	P(2-furyl)$_3$	Cs_2CO_3	DME	100℃	75%

16	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	100℃	80%
17	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	70℃	90%
18	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	50℃	93%
19	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	30℃	92%
20[d]	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	30℃	64%
21[e]	$P(2\text{-furyl})_3$	Cs_2CO_3	THF	30℃	80%

[a] The reactions were conducted with **1a** (0.4 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), ligand (0.04 mmol), norbornene (0.2 mmol), base (0.8 mmol), and indicated solvent (2.0 mL) under N_2 atmosphere at 100 °C for 12 h. [b] Isolated yield. [c] ligand (0.02 mmol). [d] norbornene (0.1 mmol), [e] Cs_2CO_3 (0.4 mmol).

Preparation of Starting Materials:

General Procedure 1:



SI-1 **SI-2** **1**

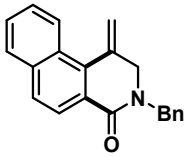
The mixture of **SI-1** (1.0 equiv), 3-bromopropene (1.5 equiv), K_2CO_3 (1.5 equiv) and an appropriate amount of KI in MeCN (1g/45mL) was stirred at 90 °C and stirred until the starting material disappeared. The solvent was evaporated under reduced pressure, the mixture was extracted with ethyl acetate, and washed twice with brine, the organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain **SI-2**.

SI-2 (1.0 equiv) was dissolved in dichloromethane (0.3 M) and cooled to 0 °C. Then pyridine (2.0 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until TLC indicated completion. The reaction was quenched with water and extracted twice with dichloromethane. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting material was purified by flash column chromatography in an ethyl acetate / petroleum ether mixture to give **1**.

General Procedure for the Synthesis of 4-methylene-3,4-dihydro-1(2H)-isoquinolin-1-one analogues

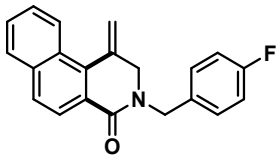
In a 38 mL sealed tube, the mixture of **2** (0.2 mmol), **1** (0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), tri(2-furyl)phosphine (9.3 mg, 0.04 mmol), NBE (18.8 mg, 0.2 mmol) and Cs_2CO_3 (260.8 mg, 0.8 mmol) was dissolved in anhydrous THF (2.0 mL). The tube was then purged 3 times with N_2 and sealed with a PTEF cap. The reaction mixture was allowed to react at 30 °C for 12 h. After the reaction was completed, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give product **3** and **3'**.

Characterization of Products:



3-Benzyl-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3aa**)

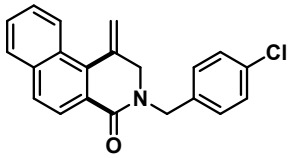
Yellow oil (55 mg, 92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.56 – 7.51 (m, 2H), 7.35 – 7.27 (m, 5H), 5.69 (s, 1H), 5.59 (s, 1H), 4.88 (s, 2H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 136.9, 135.7, 135.5, 135.0, 128.7, 128.6, 128.5, 128.4, 127.9, 127.4, 126.8, 126.3, 126.1, 124.3, 119.7, 53.6, 50.2. ESI-MS: Calcd for $C_{21}H_{17}NO$: [M+H$^+$] 300.1383, found 300.1385.



3-(4-Fluoro-benzyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ba**)

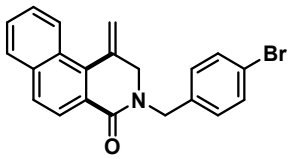
Yellow oil (53 mg, 83%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.57 – 7.53 (m, 2H), 7.36 – 7.32 (m, 2H),

7.05 – 7.01 (m, 2H), 5.70 (s, 1H), 5.61 (s, 1H), 4.84 (s, 2H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 163.4, 161.0, 135.7, 135.5, 135.0, 132.7 (d, *J* = 3.0 Hz), 129.6 (d, *J* = 8.0 Hz), 128.7, 128.5, 127.5, 126.9, 126.2 , 126.1, 124.2, 119.7, 115.5 (d, *J* = 21.0 Hz), 53.5, 49.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.93. ESI-MS: Calcd for $C_{21}H_{16}FNO$: [M+H$^+$] 318.1289, found 318.1290.



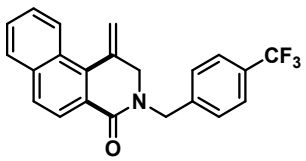
3-(4-Chloro-benzyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ca**)

Yellow oil (48 mg, 72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.58 – 7.53 (m, 2H), 7.34 – 7.30 (m, 4H), 5.71 (s, 1H), 5.61 (s, 1H), 4.84 (s, 2H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 135.7, 135.5, 135.4, 135.0, 133.3, 130.3, 129.3, 128.8, 128.7, 128.5, 127.5, 126.9, 126.1, 124.2, 119.8, 53.6, 49.6. ESI-MS: Calcd for $C_{21}H_{16}ClNO$: [M+H$^+$] 334.0993, found 334.0995.



3-(4-Bromo-benzyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3da**)

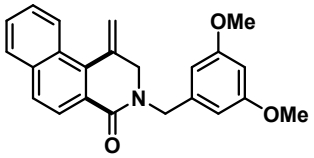
White solid (34 mg, 45%) M.P.:148-152 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 2H), 7.59 – 7.45 (m, 4H), 7.26 – 7.22 (m, 2H), 5.71 (s, 1H), 5.61 (s, 1H), 4.82 (s, 2H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 136.1, 135.7, 135.4, 135.0, 131.8, 129.7, 128.7, 128.5, 128.5, 127.6, 126.9, 126.2, 124.2, 121.4, 119.9, 53.7, 49.7. ESI-MS: Calcd for $C_{21}H_{16}BrNO$: [M+H$^+$] 378.0488, found 378.0486.



1-Methylene-3-(4-trifluoromethyl-benzyl)-2,3-dihydro-1H-benzo[f]isoquinolin-4-one(**3ea**)

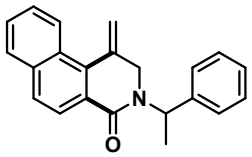
Yellow oil (44 mg, 60%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H),

8.26 (d, J = 8.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.62 – 7.54 (m, 4H), 7.48 (d, J = 8.0 Hz, 2H), 5.74 (s, 1H), 5.64 (s, 1H), 4.93 (s, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 141.2, 135.8, 135.3, 135.1, 129.8 (q, J = 32.0 Hz), 128.8, 128.6, 128.5, 128.1, 127.6, 127.0, 126.2, 126.1, 125.7 (q, J = 4.0 Hz), 124.2, 122.7, 120.0, 53.9, 50.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.45. ESI-MS: Calcd for $C_{22}H_{16}F_3NO$: [M+H$^+$] 368.1257, found 368.1255.



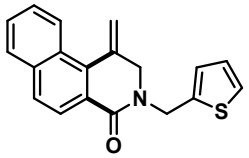
3-(3,5-Dimethoxy-benzyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3fa**)

Yellow oil (54 mg, 75%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.55 – 7.47 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 6.48 – 6.42 (m, 2H), 5.67 (s, 1H), 5.61 (s, 1H), 4.81 (s, 2H), 4.16 (s, 2H), 3.82 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 160.2, 158.5, 136.0, 135.5, 134.9, 130.4, 128.6, 128.4, 128.2, 127.3, 126.7, 126.6, 126.1, 124.2, 119.3, 117.4, 104.1, 98.3, 55.3, 55.2, 53.9, 44.8. ESI-MS: Calcd for $C_{23}H_{21}NO_3$: [M+H$^+$] 360.1594, found 360.1596.



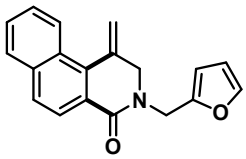
1-methylene-3-(1-phenylethyl)-2,3-dihydrobenzo[f]isoquinolin-4(1H)-one (**3ga**)

Yellow oil (44 mg, 70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.56 – 7.48 (m, 2H), 7.42 – 7.24 (m, 5H), 6.32 (q, J = 7.2 Hz, 1H), 5.63 (s, 1H), 5.48 (s, 1H), 4.01 (d, J = 12.8 Hz，1H)，3.71 (d, J = 12.8 Hz, 1H), 1.65 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 140.3, 136.0, 135.6, 134.8, 128.7, 128.5, 128.4, 128.4, 127.4, 127.4, 127.3, 126.8, 126.6, 126.1, 124.4, 119.2, 50.5, 48.5, 15.8. ESI-MS: Calcd for $C_{22}H_{19}NO$: [M+H$^+$] 314.1539, found 314.1539.



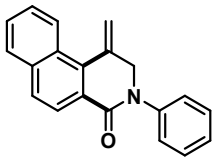
1-Methylene-3-thiophen-2-ylmethyl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ha**)

Yellow oil (26 mg, 43%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.50 – 7.43 (m, 2H), 7.16 (t, *J* = 5.6 Hz, 1H), 6.99 (d, *J* = 3.6 Hz, 1H), 6.90 – 6.86 (m, 1H), 5.63 (s, 1H), 5.58 (s, 1H), 4.93 (s, 2H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 139.4, 135.7, 135.5, 135.1, 128.7, 128.5, 128.4, 127.5, 126.8, 126.7, 126.2, 126.2, 125.5, 124.2, 119.9, 53.6, 45.1. ESI-MS: Calcd for $C_{19}H_{15}NOS$: [M+H$^+$] 306.0947, found 306.0946.



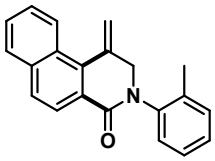
3-Furan-2-ylmethyl-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ia**)

Yellow oil (46 mg, 80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.56 – 7.51 (m, 2H), 7.38 – 7.37 (m, 1H), 6.36 – 6.32 (m, 2H), 5.71 (s, 1H), 5.68 (s, 1H), 4.85 (s, 2H), 4.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 150.6, 142.4, 135.7, 135.5, 135.1, 128.7, 128.5, 128.4, 127.5, 126.8, 126.3, 126.1, 124.2, 119.7, 110.4, 108.5, 53.8, 43.0. ESI-MS: Calcd for $C_{19}H_{15}NO_2$: [M+H$^+$] 290.1176, found 290.1175.



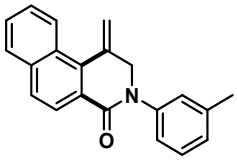
1-Methylene-3-phenyl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ja**)

Yellow oil (36 mg, 63%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.2 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.53 – 7.49 (m, 2H), 7.38 – 7.36 (m, 4H), 7.21 – 7.17 (m, 1H), 5.73 (s, 1H), 5.71 (s, 1H), 4.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 142.4, 135.9, 135.7, 135.4, 129.0, 128.8, 128.6, 128.5, 127.7, 127.0, 126.8, 126.4, 126.2, 125.3, 124.4, 119.8, 57.4. ESI-MS: Calcd for $C_{20}H_{15}NO$: [M+H$^+$] 286.1226, found 286.1226.



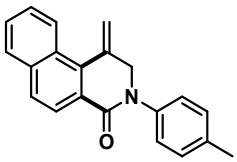
1-Methylene-3-o-tolyl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ka**)

Yellow oil (42 mg, 71%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.60 – 7.55 (m, 2H), 7.34 – 7.25 (m, 4H), 5.81 (s, 1H), 5.77 (s, 1H), 4.61 (d, *J* = 12.8 Hz, 1H), 4.30 (d, *J* = 12.8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 141.3, 135.9, 135.8, 135.7, 135.4, 131.1, 128.8, 128.5, 128.5, 127.9, 127.6, 127.1, 126.9, 126.7, 126.2, 124.4, 119.6, 57.3, 18.1. ESI-MS: Calcd for $C_{21}H_{17}NO$: [M+H$^+$] 300.1383, found 300.1385.



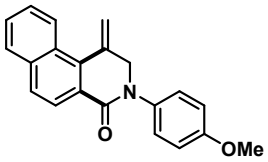
1-Methylene-3-m-tolyl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3la**)

White solid (37 mg, 63%) M.P.:143-146 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.60 – 7.53 (m, 2H), 7.35 – 7.21 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 5.78 (s, 1H), 5.76 (s, 1H), 4.57 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 142.3, 138.7, 135.8, 135.7, 135.3, 128.8, 128.7, 128.5, 128.4, 127.6, 127.3, 126.9, 126.8, 126.2, 126.1, 124.4, 122.2, 119.7, 57.4, 21.3. ESI-MS: Calcd for $C_{21}H_{17}NO$: [M+H$^+$] 300.1383, found 300.1385.



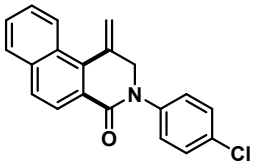
1-Methylene-3-p-tolyl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3ma**)

White solid (27 mg, 44%) M.P.:142-145 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.61 – 7.54 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.79 (s, 1H), 5.77 (s, 1H), 4.58 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 139.8, 136.2, 135.8, 135.3, 129.6, 128.8, 128.5, 128.5, 127.6, 126.9, 126.8, 126.2, 125.1, 124.4, 119.7, 57.5, 21.0. ESI-MS: Calcd for $C_{21}H_{17}NO$: [M+H$^+$] 300.1383, found 300.1386.



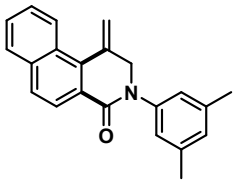
3-(4-Methoxy-phenyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3na**)

Yellow oil (59 mg, 95%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.60 – 7.56 (m, 2H), 7.38 – 7.35 (m, 2H), 7.00 – 6.95 (m, 2H), 5.79 (s, 1H), 5.78 (s, 1H), 4.56 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.9, 135.7, 135.7, 135.2, 135.2, 128.7, 128.5, 128.4, 127.6, 126.9, 126.7, 126.6, 126.2, 124.3, 119.7, 114.3, 57.6, 55.5. ESI-MS: Calcd for $C_{21}H_{17}NO_2$: [M+H$^+$] 316.1332, found 316.1332.



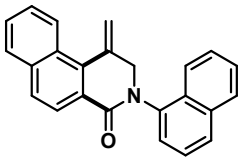
3-(4-Chloro-phenyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3oa**)

Yellow oil (20 mg, 32%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.6 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.62 – 7.58 (m, 2H), 7.41 (s, 4H), 5.82 (s, 1H), 5.81 (s, 1H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 140.8, 135.9, 135.4, 131.8, 129.1, 128.8, 128.7, 128.4, 127.8, 127.1, 126.4, 126.2, 124.3, 120.1, 57.3. ESI-MS: Calcd for $C_{20}H_{14}ClNO$: [M+H$^+$] 320.0837, found 320.0839.



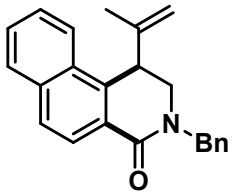
3-(3,5-Dimethyl-phenyl)-1-methylene-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3pa**)

White solid (46 mg, 74%) M.P.:149-152 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 9.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.90 – 7.84 (m, 2H), 7.59 – 7.52 (m, 2H), 7.05 (s, 2H), 6.92 (s, 1H), 5.77 (s, 1H), 5.75 (s, 1H), 4.55 (s, 2H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 142.2, 138.7, 135.8, 135.8, 135.2, 128.7, 128.5, 128.4, 128.3, 127.5, 126.9, 126.8, 126.2, 124.4, 123.1, 119.6, 57.5, 21.3, 21.2. ESI-MS: Calcd for $C_{22}H_{19}NO$: [M+H$^+$] 314.1539, found 314.1537.



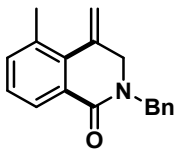
1-Methylene-3-naphthalen-1-yl-2,3-dihydro-1H-benzo[f]isoquinolin-4-one (**3qa**)

White solid (34 mg, 50%) M.P.:113-116 ºC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.8 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.90 (m, 5H), 7.66 – 7.51 (m, 6H), 5.91 (s, 1H), 5.84 (s, 1H), 4.75 (d, *J* = 12.8 Hz, 1H), 4.49 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 139.2, 135.9, 135.9, 135.6, 134.8, 129.9, 128.8, 128.6, 128.5, 128.4, 127.7, 127.0, 127.0, 126.7, 126.3, 126.3, 125.8, 124.9, 124.5, 122.9, 120.0, 58.0. ESI-MS: Calcd for $C_{24}H_{17}NO$: [M+H$^+$] 336.1383, found 336.1374.



(R) -3-benzyl-1-(prop-1-en-2-yl)-2,3-dihydrobenzo[f]isoquinolin-4(1H)-one (**3ra**)

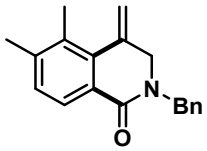
Yellow oil (46 mg, 70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 1H), 7.88 – 7.80 (m, 3H), 7.55 – 7.47 (m, 2H), 7.35 – 7.26 (m, 5H), 5.08 (d, *J* = 14.8 Hz, 1H), 4.80 (s, 1H), 4.49 (d, *J* = 14.4 Hz, 1H), 4.18 (s, 1H), 3.97 (d, *J* = 4.8 Hz, 1H), 3.80 (dd, J_1 = 4.8 Hz, J_2 = 12.8 Hz, 1H), 3.53 (dd, J_1 = 1.2 Hz, J_2 = 12.8 Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 143.1, 136.9, 136.9, 135.1, 130.0, 128.7, 128.6, 128.4, 127.6, 127.4, 127.3, 127.1, 126.6, 124.3, 124.3, 115.6, 115.5, 50.2, 47.9, 41.1, 21.3.ESI-MS: Calcd for $C_{23}H_{21}NO$: [M+H$^+$] 328.1696, found 328.1695.



2-Benzyl-5-methyl-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ab**)

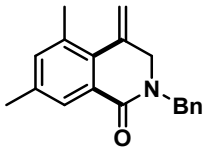
Yellow oil (38 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.38– 7.27(m, 7H), 5.42 (s, 1H), 5.32 (s, 1H), 3.95 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 136.9, 136.2, 135.1, 134.8, 133.9, 129.5, 128.6, 127.9, 127.7, 127.4, 126.7, 117.9, 53.7, 50.1, 21.2. ESI-MS: Calcd for $C_{18}H_{17}NO$: [M+H$^+$]

264.1383, found 264.1388.



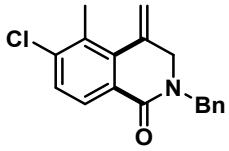
2-Benzyl-5,6-dimethyl-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ac**)

Yellow oil (43 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.23 (m, 6H), 5.77 (s, 1H), 5.43 (s, 1H), 5.24 (s, 2H), 3.94 (s, 2H), 2.36 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 142.0, 137.0, 136.6, 135.8, 132.3, 129.5, 128.5, 127.9, 127.4, 127.3, 126.1, 118.4, 53.8, 50.0, 21.3, 17.1. ESI-MS: Calcd for $C_{19}H_{19}NO$: [M+H$^+$] 278.1539, found 278.1535.



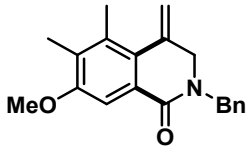
2-Benzyl-5,7-dimethyl-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ad**)

Yellow oil (17 mg, 31%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.32 – 7.20 (m, 6H), 5.37 (s, 1H), 5.28 (s, 1H), 4.82 (s, 2H), 3.93 (s, 2H), 2.44 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 137.6, 136.9, 136.1, 135.6, 135.6, 133.9, 132.4, 129.3, 128.6, 127.9, 127.4, 127.2, 117.1, 53.9, 50.2, 21.2, 21.0. ESI-MS: Calcd for $C_{19}H_{19}NO$: [M+H$^+$] 278.1539, found 278.1535.



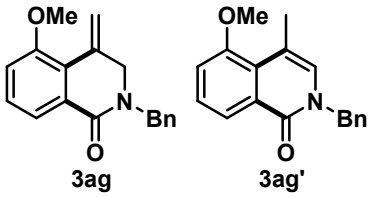
2-Benzyl-6-chloro-5-methyl-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ae**)

Yellow oil (52 mg, 88%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.25 (m, 5H), 5.48 (s, 1H), 5.30 (s, 1H), 4.81 (s, 2H), 3.95 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 139.7, 137.4, 136.7, 135.9, 131.9, 128.8, 128.6, 128.0, 127.9, 127.5, 127.4, 119.6, 53.5, 50.1, 18.1. ESI-MS: Calcd for $C_{18}H_{16}ClNO$: [M+H$^+$] 298.0993, found 298.0998.



2-Benzyl-7-methoxy-5,6-dimethyl-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3af**)

Yellow solid (43 mg, 70%) M.P.:101-104 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.33 – 7.27 (s, 5H), 5.35 (s, 1H), 5.15 (s, 1H), 4.83 (s, 2H), 3.94 (s, 2H), 3.91 (s, 3H), 2.38 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 157.1, 137.0, 136.5, 134.0, 130.6, 128.9, 128.6, 127.9, 127.7, 127.4, 117.1, 107.4, 55.6, 54.1, 50.3, 17.6, 12.7. ESI-MS: Calcd for $C_{20}H_{21}NO_2$: [M+H$^+$] 308.1645, found 308.1645.

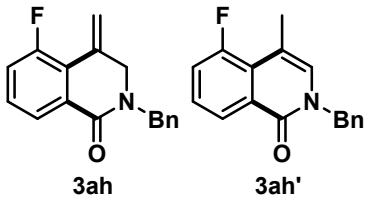


3ag 3ag' (1:1.24)

2-Benzyl-5-methoxy-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ag**)

2-Benzyl-5-methoxy-4-methyl-2H-isoquinolin-1-one (**3ag'**)

Yellow oil (18 mg, 33%,23 mg, 41%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 0.8H), 7.43 – 7.24 (m, 11H), 7.06 (d, *J* = 8.0 Hz, 1.6H), 6.73 (s, 1H), 5.98 (s, 0.8H), 5.37 (s, 0.8H), 5.17 (s, 2H), 4.80 (s, 1.6H), 3.99 (s, 1.6H), 3.87 (s, 2.4H), 3.85 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.3, 156.8, 156.0, 136.9, 136.7, 132.5, 130.0, 128.8, 128.8, 128.6, 128.5, 128.0, 127.9, 127.8, 127.8, 127.6, 127.3, 127.1, 124.2, 120.9, 120.5, 118.1, 114.2, 113.0, 112.6, 55.6, 53.5, 51.4, 50.1, 20.7, 20.7. ESI-MS: Calcd for $C_{18}H_{17}NO_2$: [M+H$^+$] 280.1332, found 280.1330.



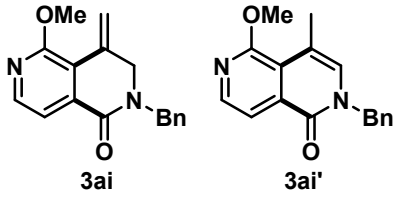
3ah 3ah' （1.37:1）

2-Benzyl-5-fluoro-4-methylene-3,4-dihydro-2H-isoquinolin-1-one (**3ah**)

2-Benzyl-5-fluoro-4-methyl-2H-isoquinolin-1-one (**3ah'**)

Yellow oil (20 mg, 37%, 14 mg, 27%), ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.21 (m, 16.58H), 6.81 (s, 1H), 5.82 (s,

1.36H), 5.41 (s, 1.36H), 5.18 (s, 2H), 4.81 (s, 2.71H), 4.06 (s, 2.70H), 2.37 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.7, 160.3 (d, J = 11.0 Hz), 157.7 (d, J = 11.0Hz), 136.7, 136.5, 131.0 (d, J = 2.0 Hz), 130.3 (d, J = 2.0 Hz), 129.8, 129.1 (d, J = 9.0 Hz), 128.8, 128.7, 128.3 (d, J = 5.0 Hz), 127.9, 127.9, 127.8, 127.6, 127.2 (d, J = 8.0 Hz), 126.4 (d, J = 12.0 Hz), 124.7 (d, J = 3.0 Hz), 124.4 (d, J = 3.0 Hz), 123.4 (d, J = 13.0 Hz), 119.4 (d, J = 22.0 Hz), 118.5 (d, J = 22.0 Hz), 110.2, 52.7, 51.5, 50.2, 18.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.78, -116.53. ESI-MS: Calcd for $C_{17}H_{14}FNO$: [M+H$^+$] 268.1132, found 268.1125.



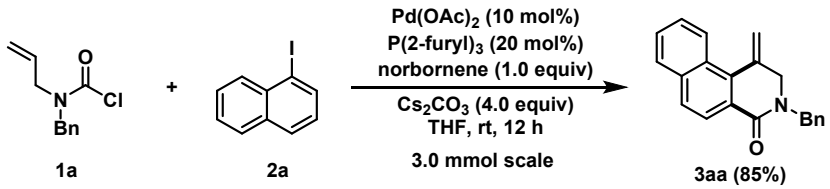
（1:1）

2-benzyl-5-methoxy-4-methylene-3,4-dihydro-2,6-naphthyridin-1(2H)-one (**3ai**)

2-benzyl-5-methoxy-4-methyl-2,6-naphthyridin-1(2H)-one (**3ai'**)

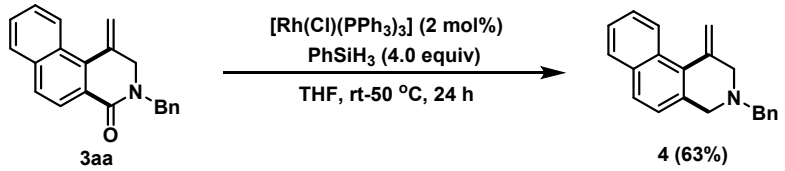
Yellow oil (20 mg, 35%, 20 mg, 35%), ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 5.2 Hz, 1H), 8.13 (d, J = 5.6 Hz, 1H), 7.83 (d, J = 5.6 Hz, 1H), 7.66 (d, J = 5.2 Hz, 1H), 7.35 – 7.27 (m, 10H), 6.86 (s, 1H), 6.11 (s, 1H), 6.5.39 (s, 1H), 5.17 (s, 2H), 4.78 (s, 2H), 4.05 (s, 2H), 4.03 (s, 3H), 4.01 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 161.1, 160.6, 160.1, 145.9, 142.8, 137.2, 136.4, 136.3, 133.8, 131.0, 130.4, 128.8, 128.7, 128.0, 127.9, 127.6, 122.4, 118.5, 118.5, 118.0, 115.2, 114.1, 112.1, 53.9, 53.4, 52.9, 51.7, 50.3, 19.9. ESI-MS: Calcd for $C_{17}H_{16}N_2O_2$: [M+H$^+$] 281.1285, found: 281.1288.

Application investigation:



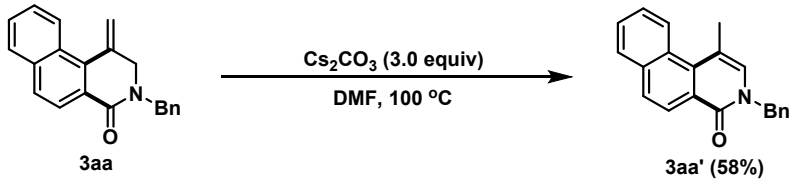
In a round bottom flask, the mixture of **1a** (6.0 mmol), **2a** (3.0 mmol), $Pd(OAc)_2$ (67.3 mg, 0.3 mmol), tri(2-furyl)phosphine (139.3 mg, 0.6 mmol), NBE (282.5 mg,

3.0 mmol) and Cs_2CO_3 (3.9 g, 12.0 mmol) was dissolved in anhydrous THF (30 mL). The flask was then purged 3 times with N_2 and protected with N_2. The reaction mixture was allowed to react at 30 °C for 12 h. After the reaction was completed, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to give product **3aa** (760 mg, 85% yield) as a yellow oil.



A 10-mL dried Schlenk tube containing a stirring bar was charged with tris(triphenylphosphine)rhodium(I) chloride (2 mol%) and **3aa** (0.5 mmol). After then, the schlenk tube kept under argon and vaccum for three times. Under Ar flow dry THF (2.0 mL) and $PhSiH_3$ (2.0 mmol) were added, and the mixture was stirred at rt-50°C for 24 h. Then, the reaction mixture was cooled to room temperature. Next, the solvent was removed from the mixture under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to give product **4** (90 mg, 63% yield) as a yellow oil.

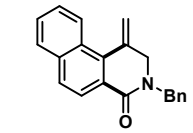
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.33 (m, 7H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 5.48 (s, 1H), 3.98 (s, 2H), 3.78 (s, 2H), 3.54 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.1, 133.2, 133.0, 130.2, 129.1, 128.5, 128.3, 127.7, 127.2, 126.1, 125.2, 125.1, 124.7, 116.0, 61.2, 59.3, 56.4. ESI-MS: Calcd for $C_{21}H_{19}N$: [M+H$^+$] 286.1590, found 286.1592.



In a 38 mL sealed tube, the mixture of **3aa** (0.20 mmol) and Cs_2CO_3 (195.6 mg, 0.6 mmol) was dissolved in anhydrous DMF (2.0 mL). The reaction mixture was allowed

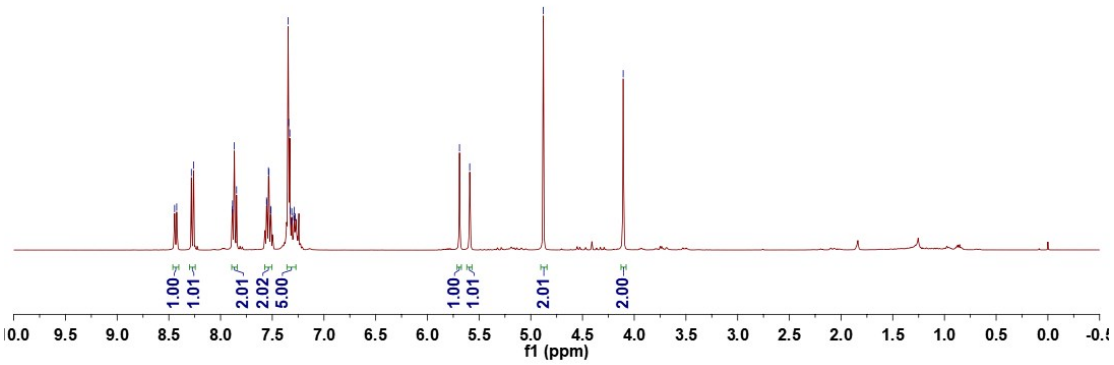
to react at 100 °C for 12 h. The resulting mixture was diluted with water and extracted with EtOAc. Combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel to give product **3aa'** (35 mg, 58% yield) as a white solid. M.P.:193-196 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.66 – 7.57(m, 2H), 7.37 – 7.29(m, 5H), 7.10 (s, 1H), 5.29 (s, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 136.7, 136.1, 136.1, 132.3, 132.2, 130.2, 129.0, 128.8, 127.9, 127.8, 127.5, 127.0, 125.9, 124.9, 124.6, 113.2, 51.6, 23.4. ESI-MS: Calcd for $C_{21}H_{17}NO$: [M+H$^+$] 300.1383, found 300.1380.

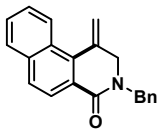
NMR Spectra:



3aa

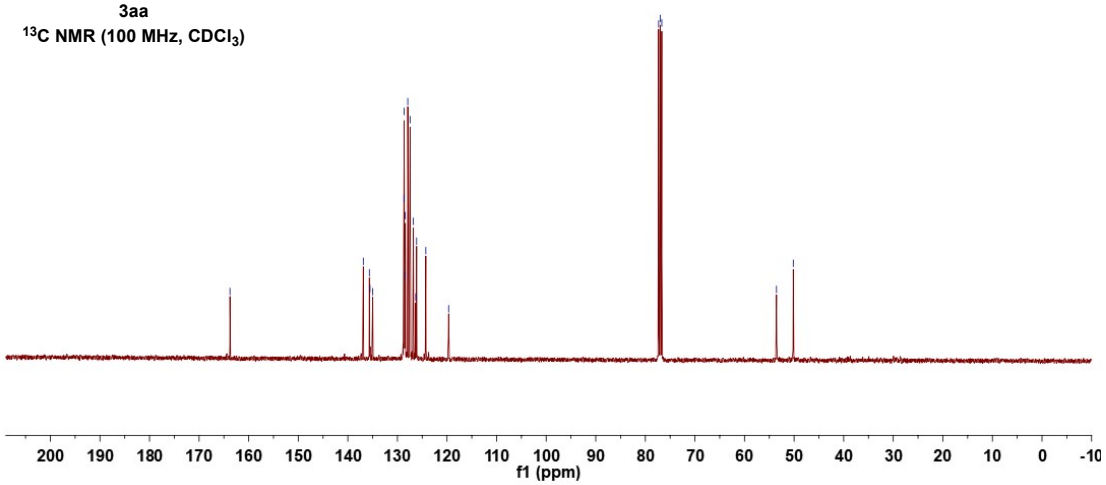
^{1}H NMR (400 MHz, $CDCl_3$)

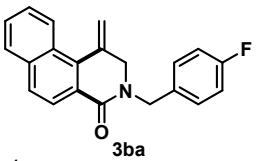




3aa

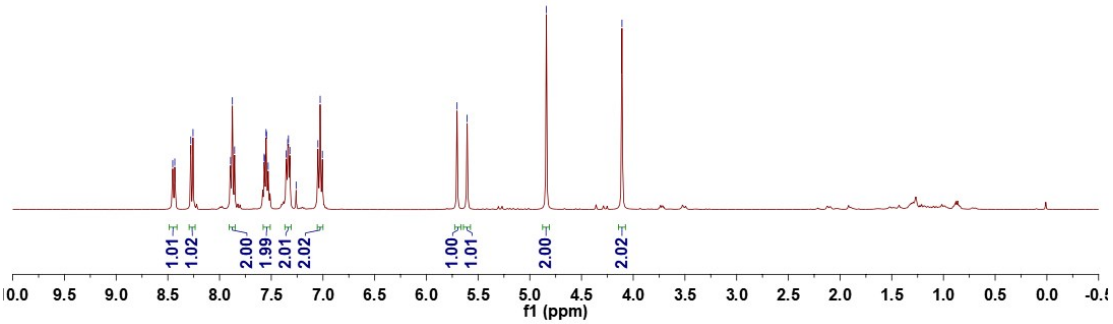
^{13}C NMR (100 MHz, $CDCl_3$)

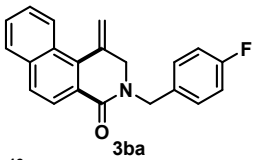




3ba

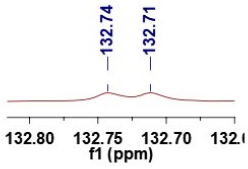
^{1}H NMR (400 MHz, $CDCl_3$)

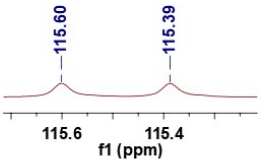


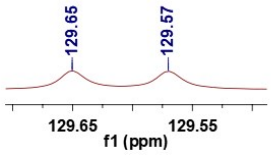


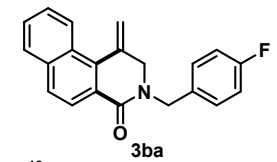
3ba

^{13}C NMR (100 MHz, $CDCl_3$)



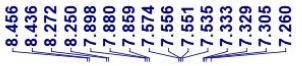


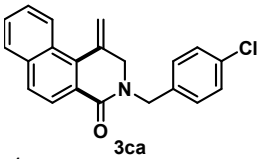




3ba

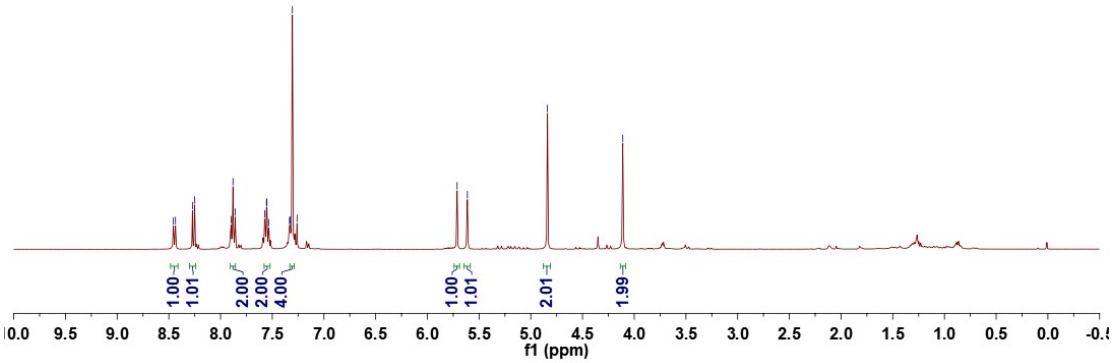
^{19}F NMR (376 MHz, $CDCl_3$)

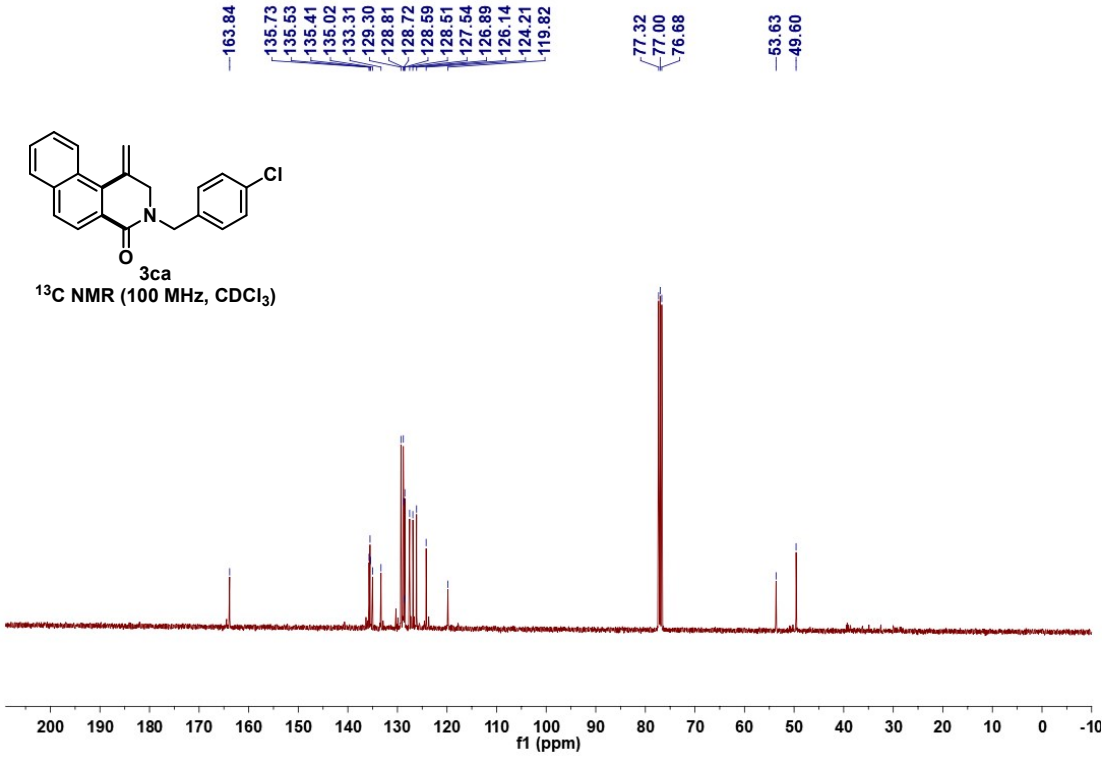




3ca

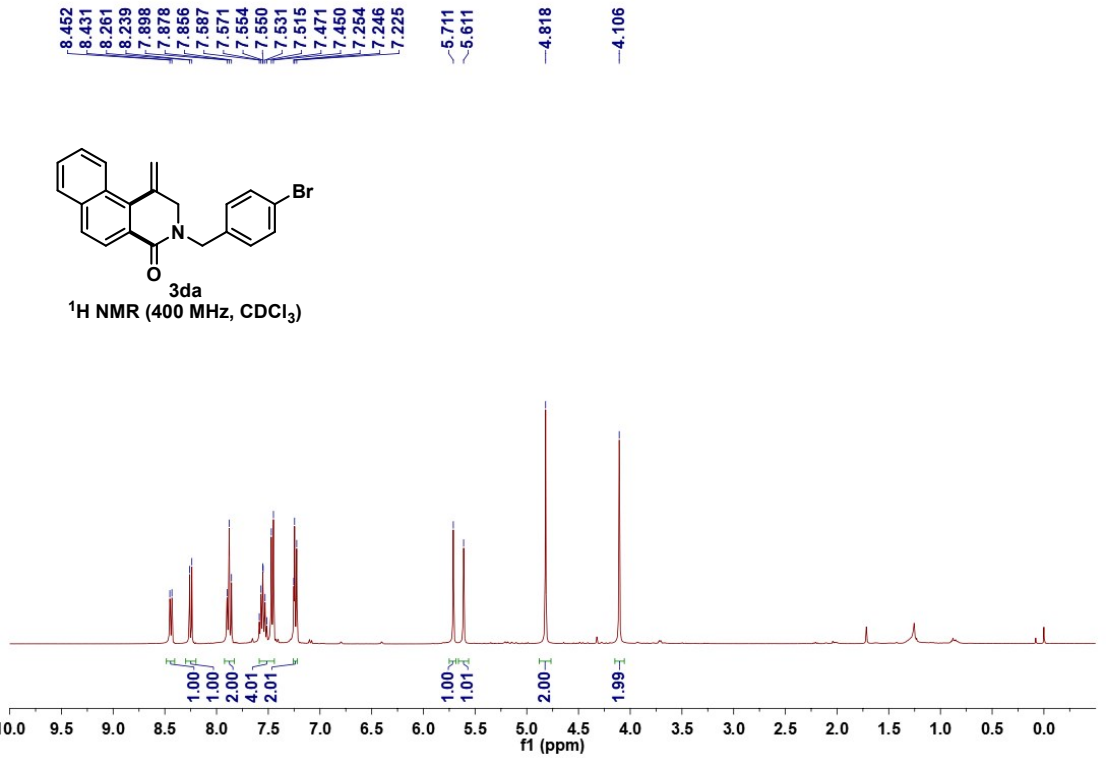
^{1}H NMR (400 MHz, $CDCl_3$)





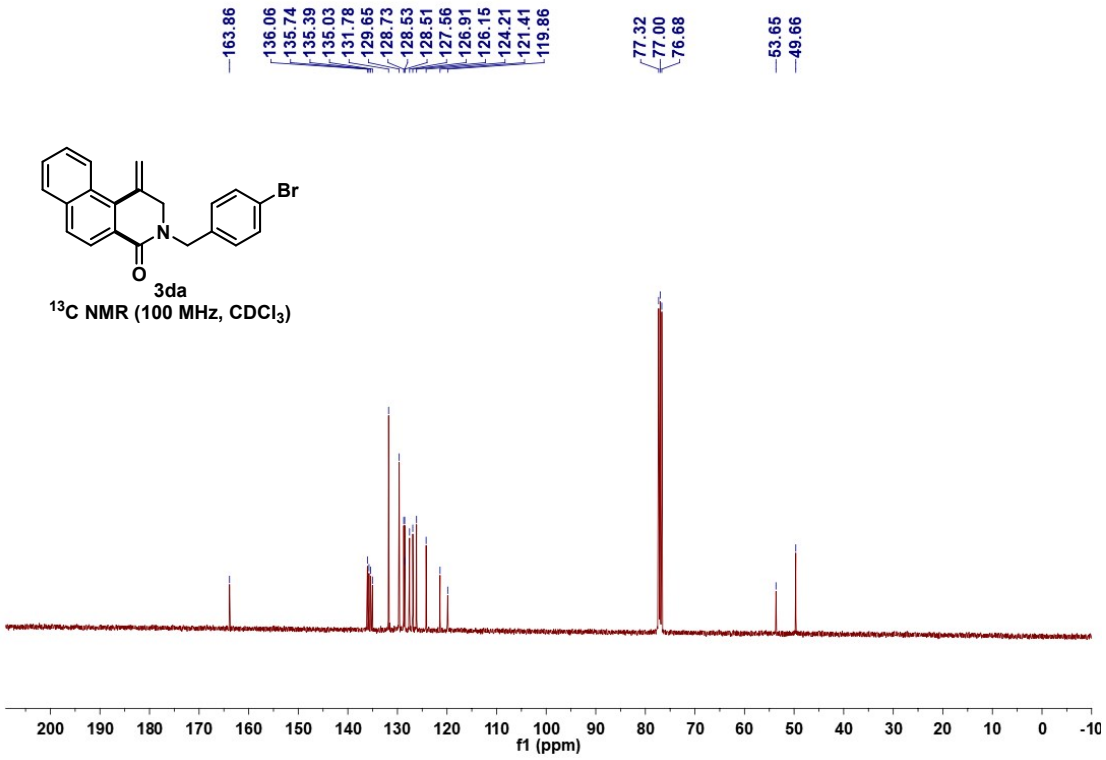
3ca

^{13}C NMR (100 MHz, $CDCl_3$)



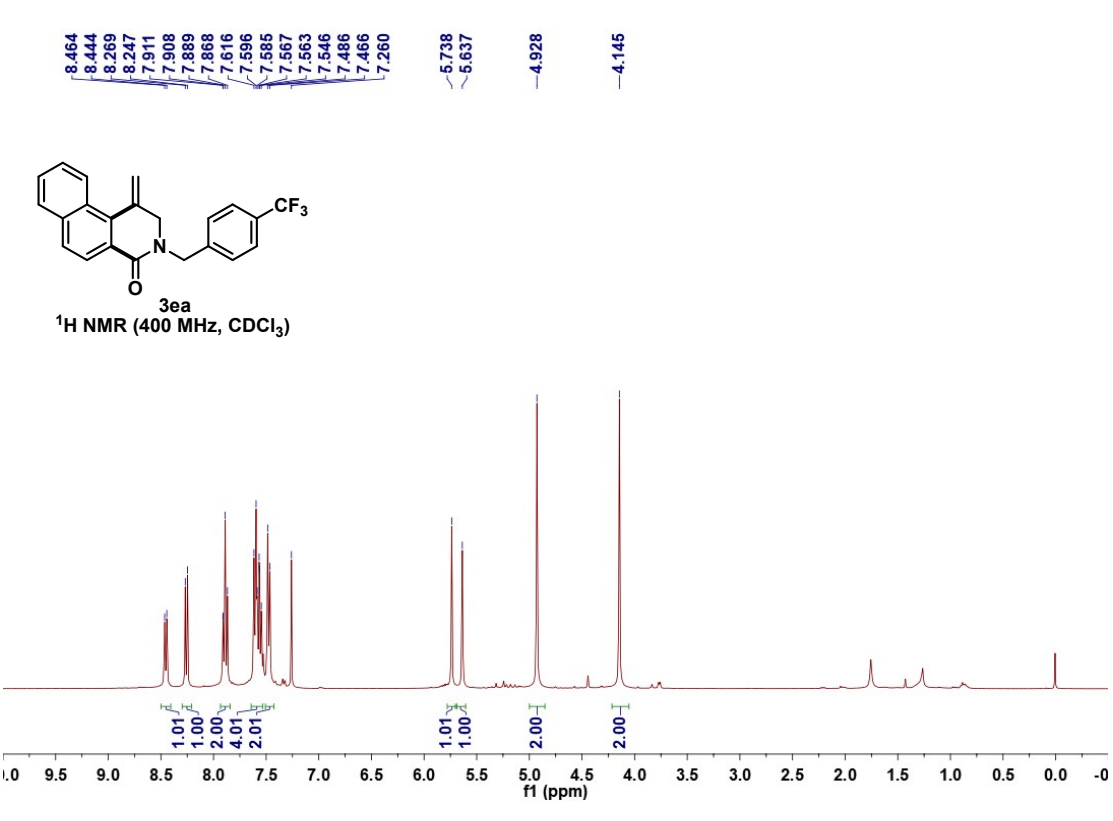
3da

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



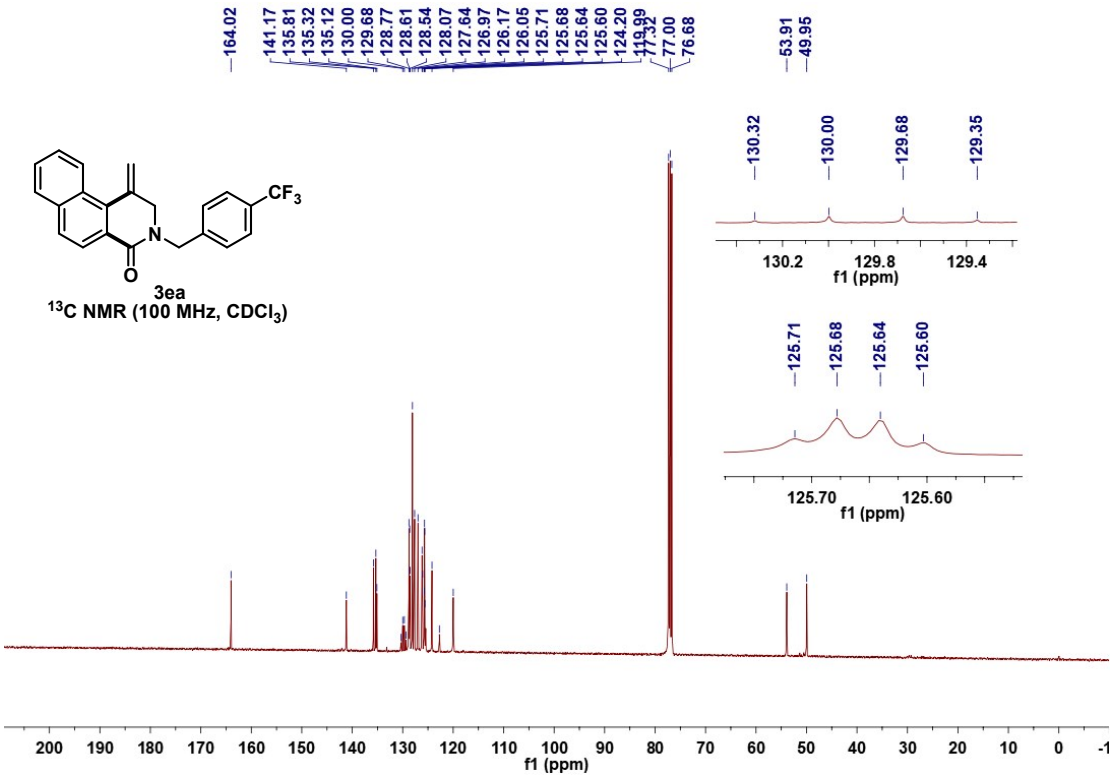
3da

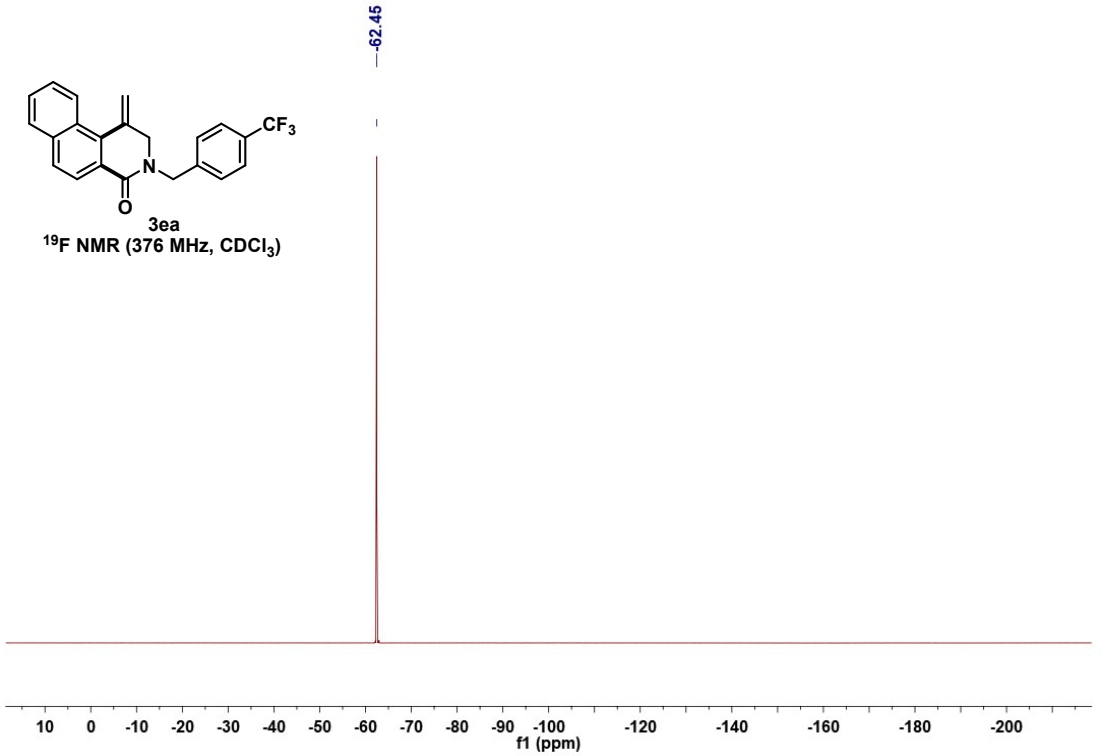
^{13}C NMR (100 MHz, $CDCl_3$)

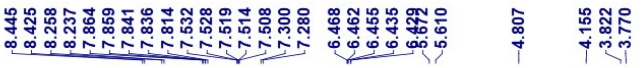


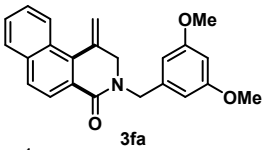
3ea

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


164.02
141.17
135.81
135.32
135.12
130.00
129.68
128.77
128.61
128.54
128.07
127.64
126.97
126.17
126.05
125.71
125.68
125.64
125.60
124.20
119.99
77.32
77.00
76.68
53.91
49.95
130.32
130.00
129.68
129.35
130.2
129.8
129.4
f1 (ppm)
125.71
125.68
125.64
125.60
125.70
125.60
f1 (ppm)
CF3
N
O
3ea
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

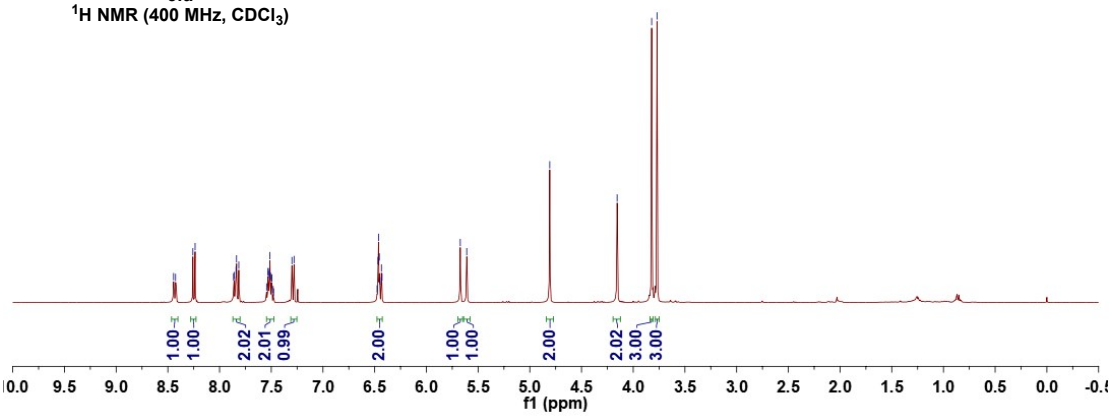

-62.45
CF3
N
O
3ea
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

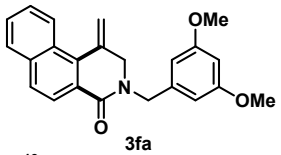




3fa

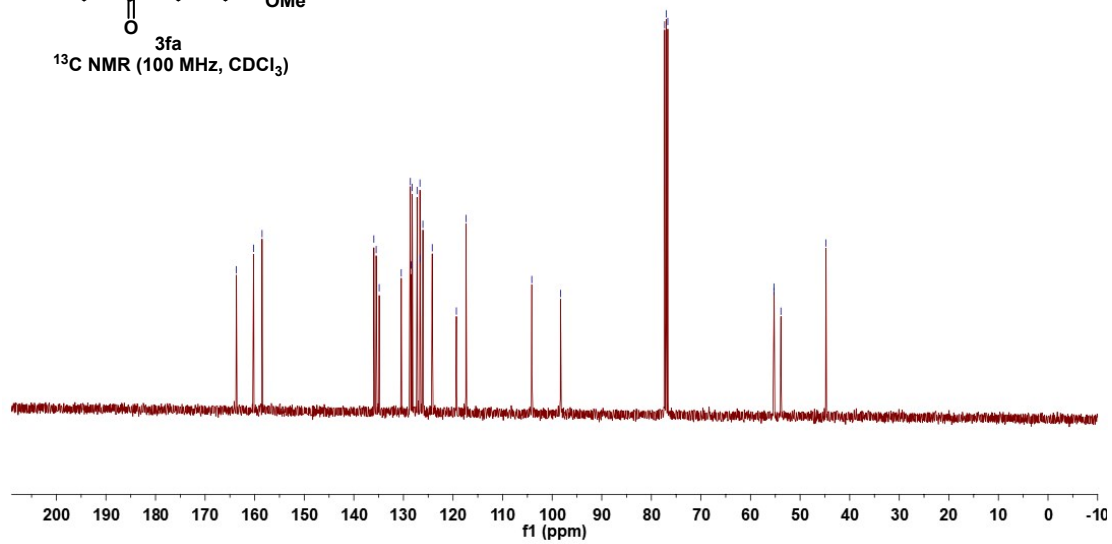
^{1}H NMR (400 MHz, $CDCl_3$)

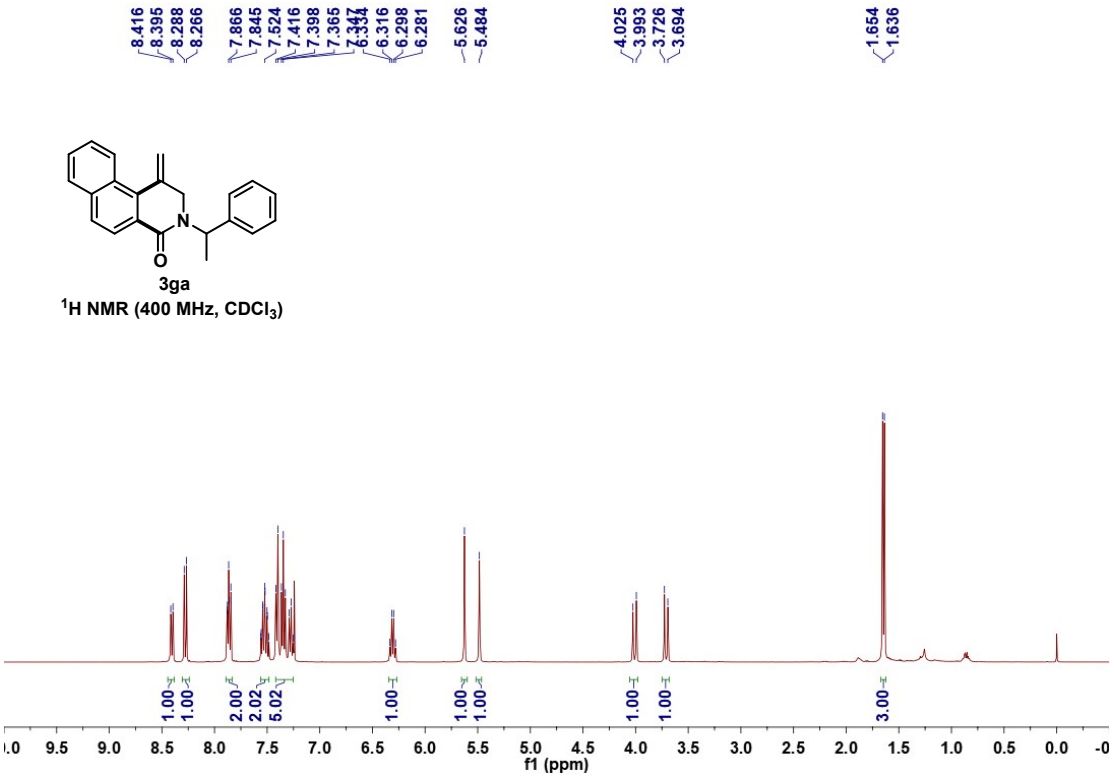




3fa

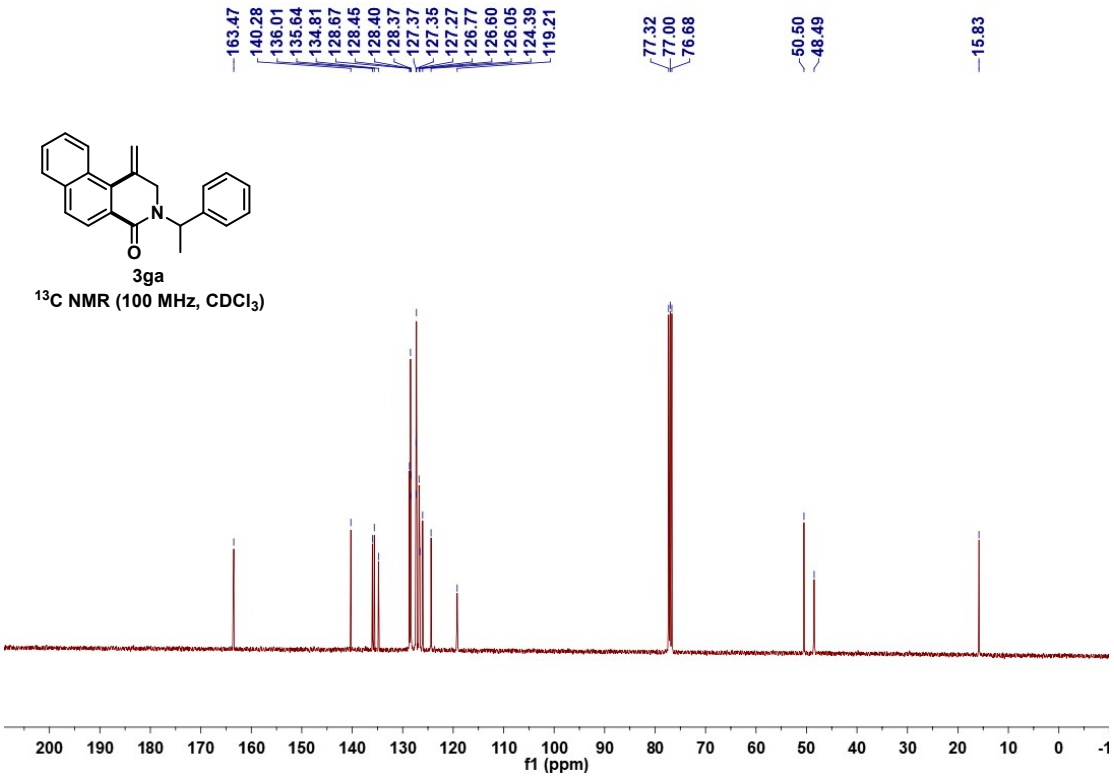
^{13}C NMR (100 MHz, $CDCl_3$)





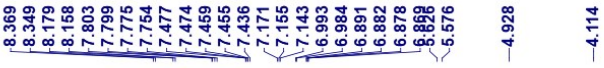
3ga

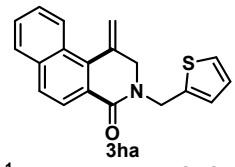
^{1}H NMR (400 MHz, $CDCl_3$)



3ga

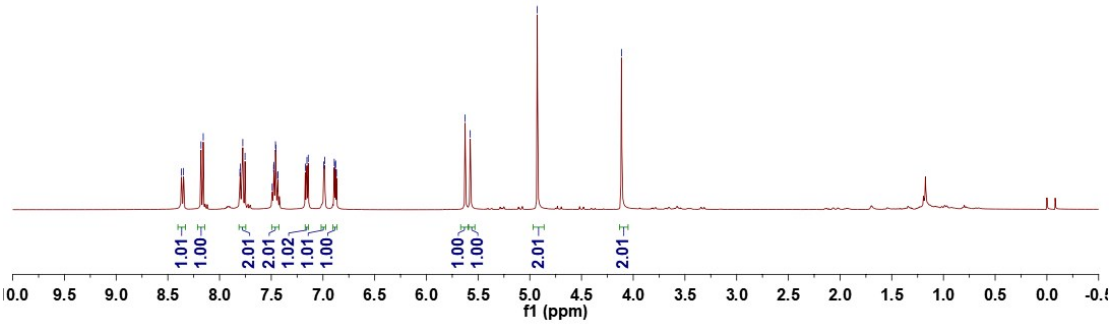
^{13}C NMR (100 MHz, $CDCl_3$)

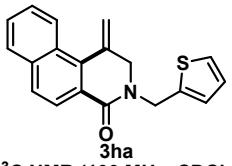




3ha

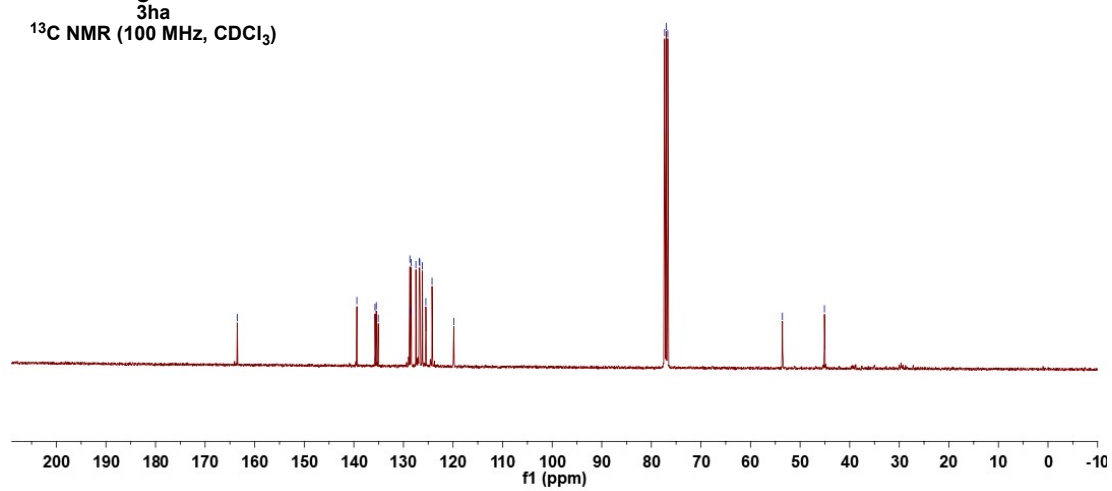
^{1}H NMR (400 MHz, $CDCl_3$)

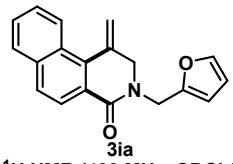




3ha

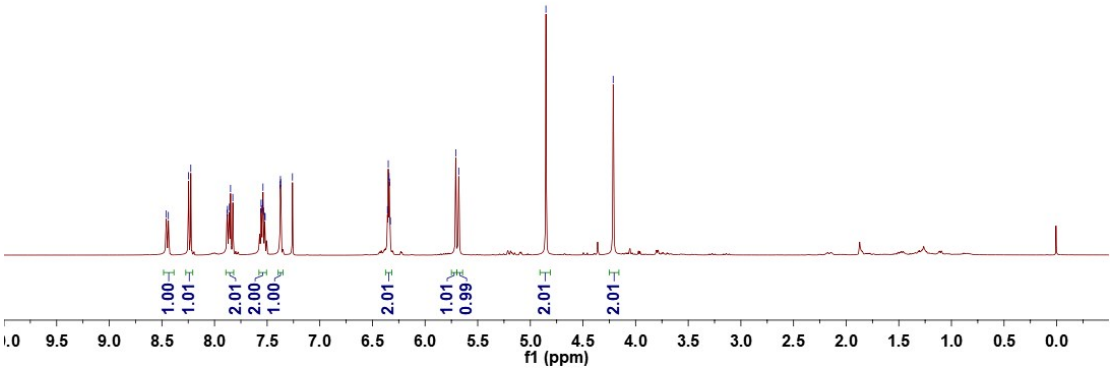
^{13}C NMR (100 MHz, $CDCl_3$)

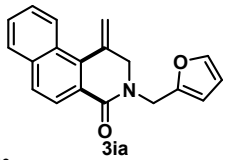




3ia

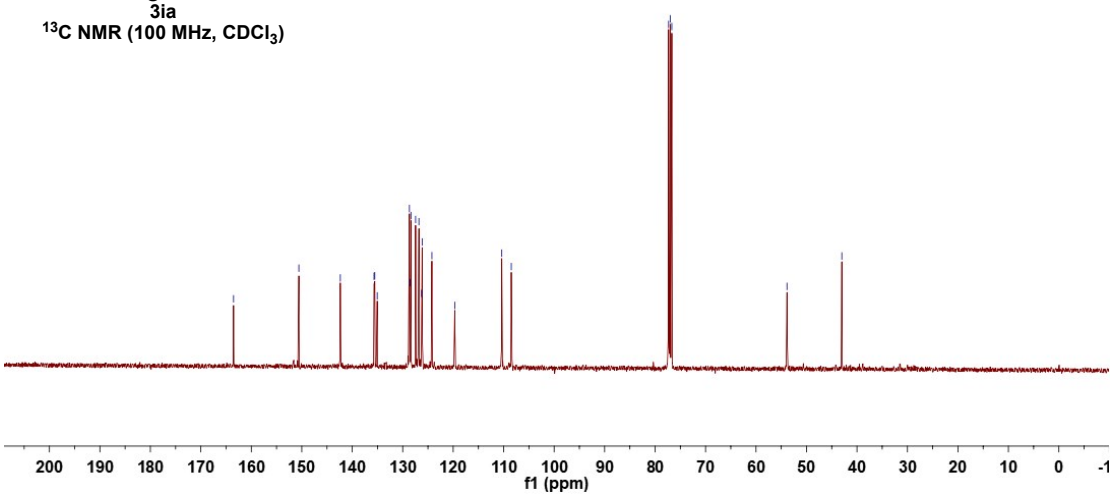
^{1}H NMR (400 MHz, $CDCl_3$)

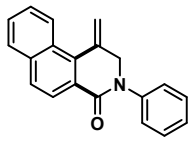




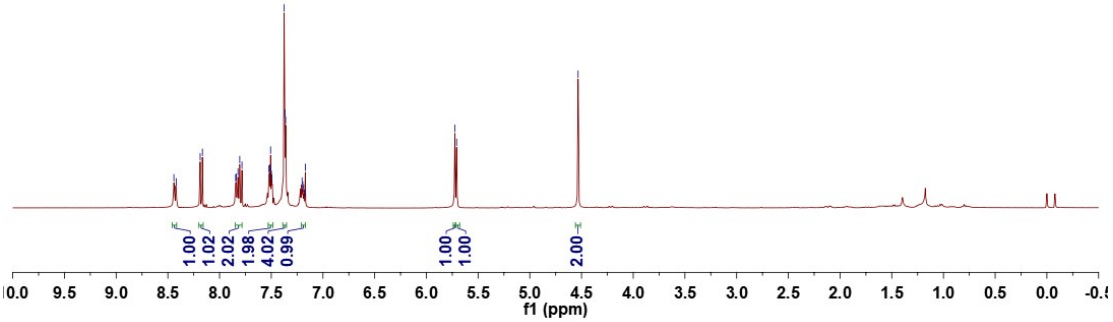
3ia

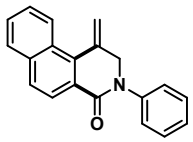
^{13}C NMR (100 MHz, $CDCl_3$)



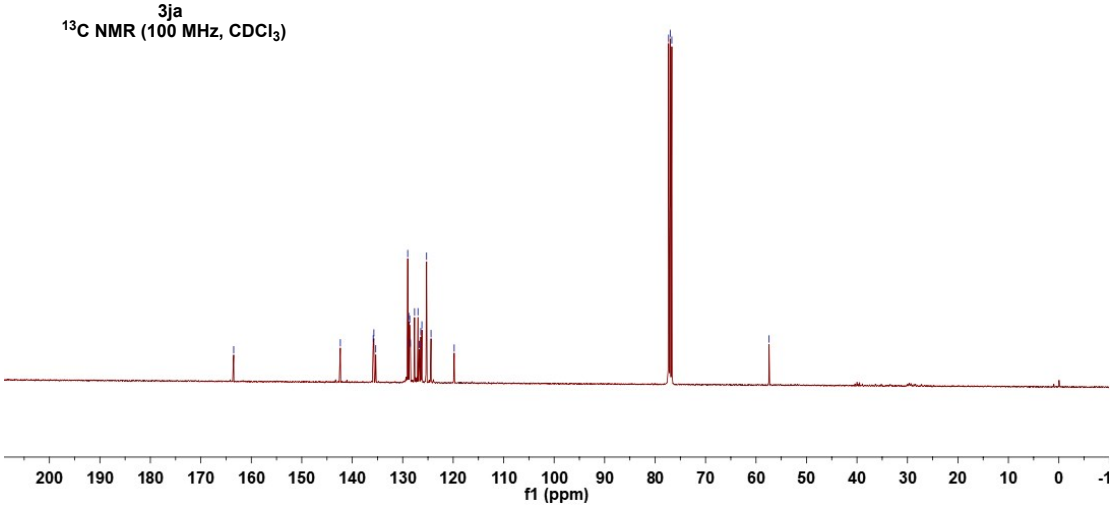


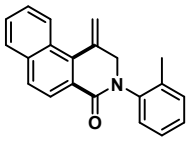
3ja
^{1}H NMR (400 MHz, $CDCl_3$)





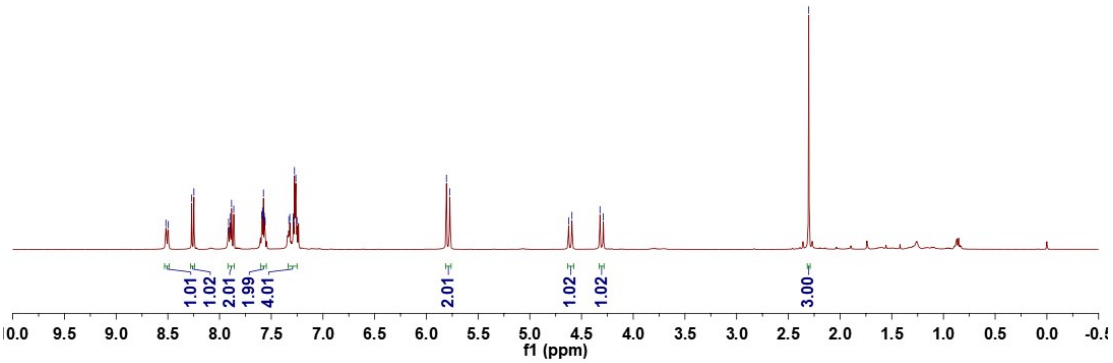
3ja
^{13}C NMR (100 MHz, $CDCl_3$)

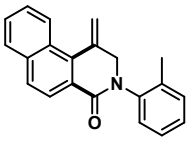




3ka

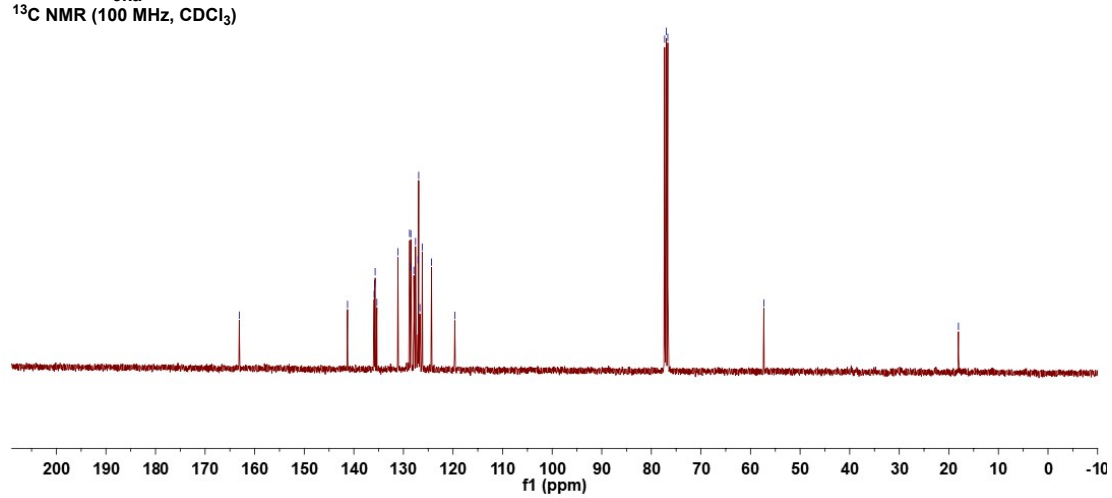
^{1}H NMR (400 MHz, $CDCl_3$)

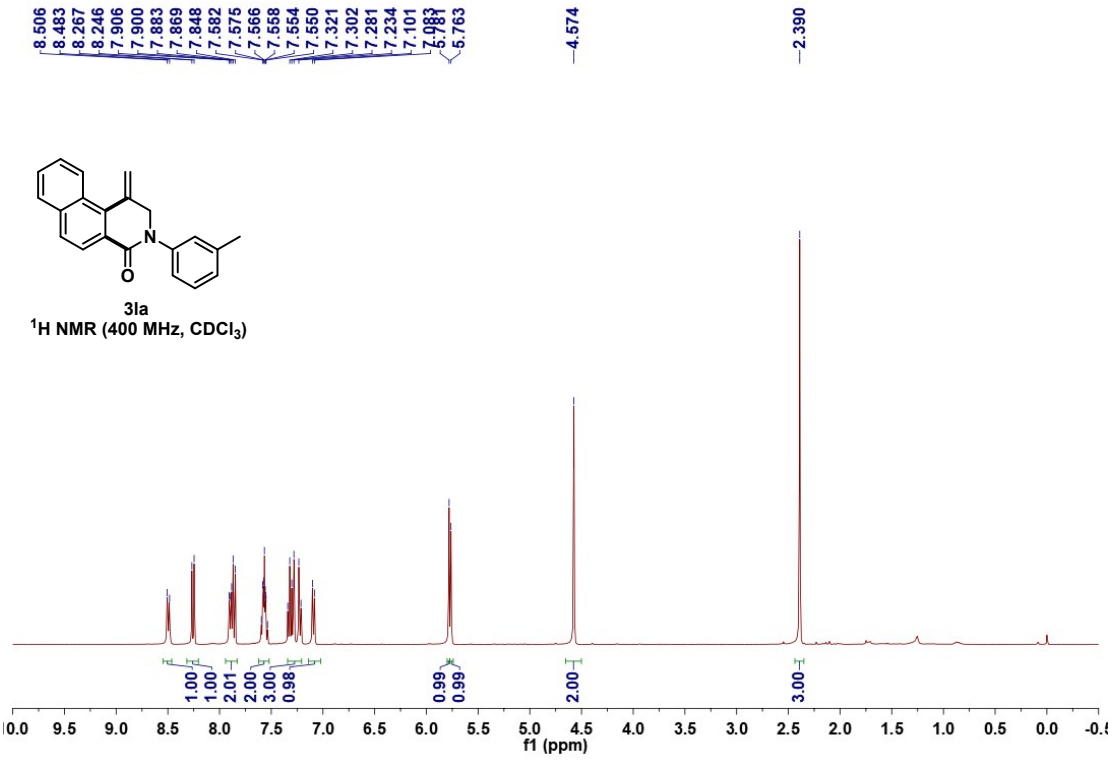




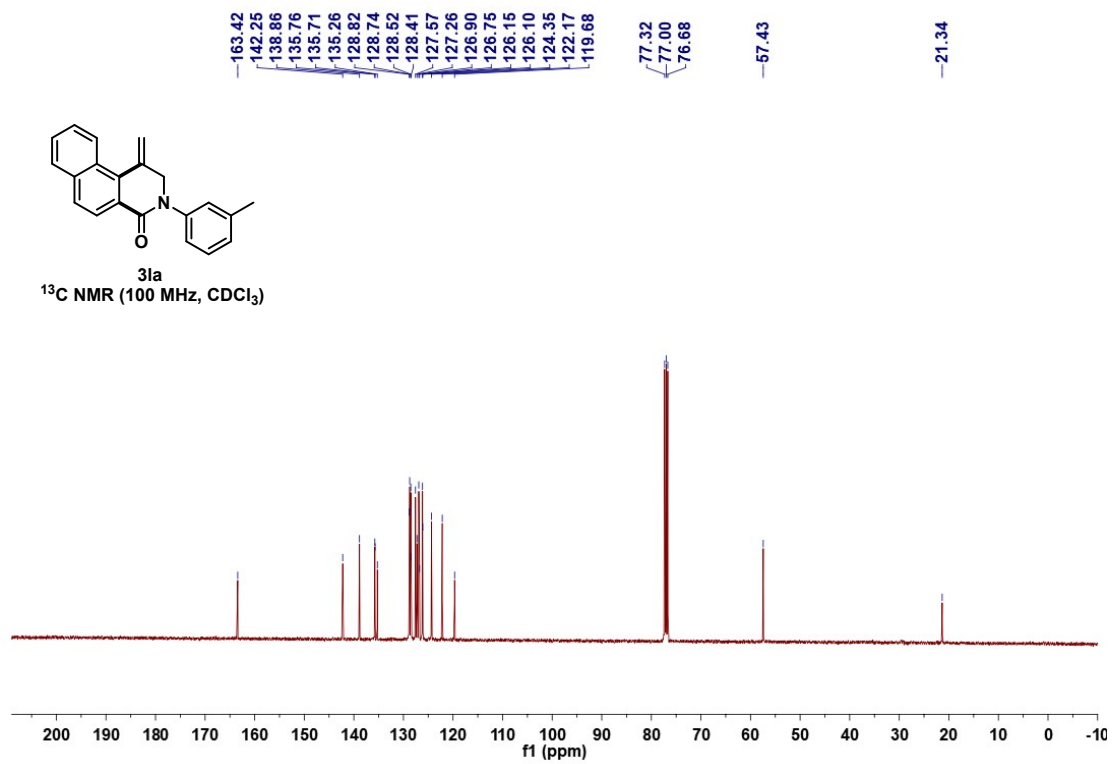
3ka

^{13}C NMR (100 MHz, $CDCl_3$)

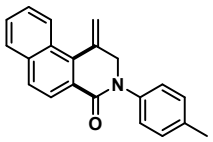




3la
^{1}H NMR (400 MHz, $CDCl_3$)

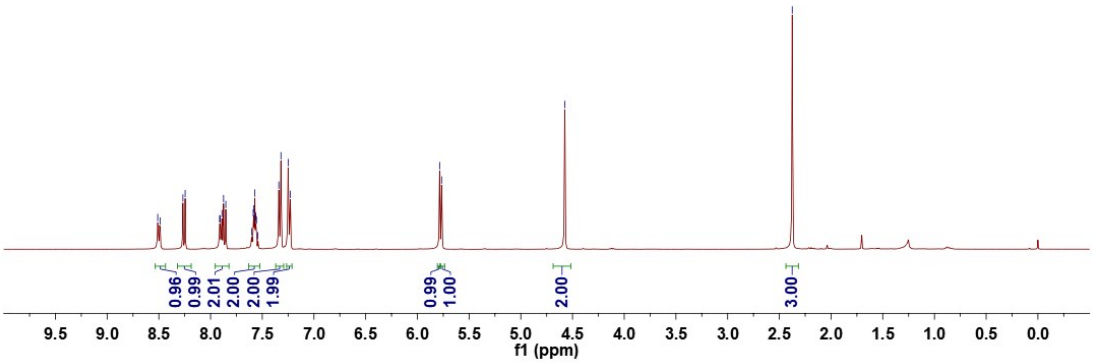


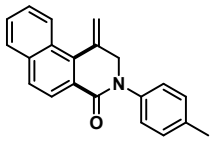
3la
^{13}C NMR (100 MHz, $CDCl_3$)



3ma

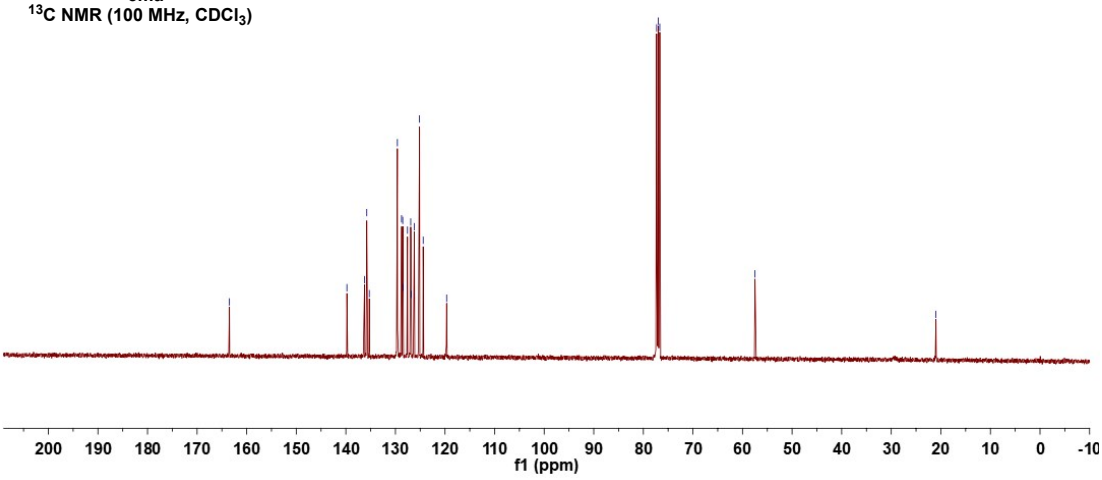
^{1}H NMR (400 MHz, $CDCl_3$)

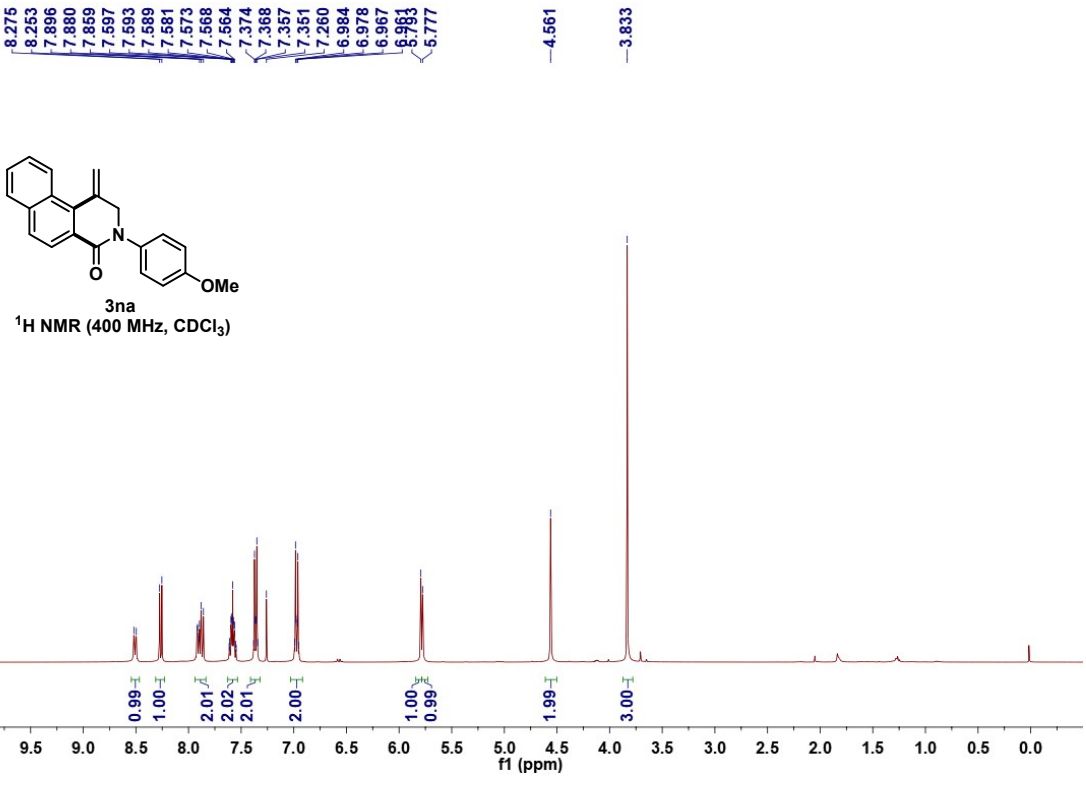




3ma

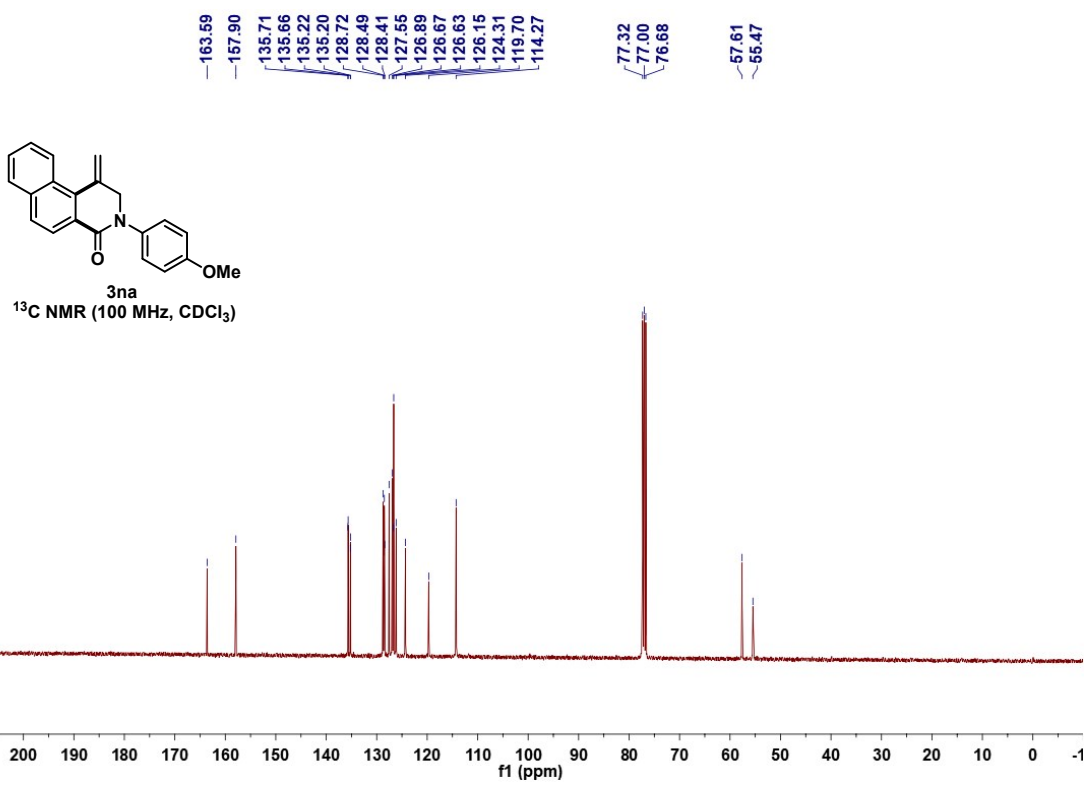
^{13}C NMR (100 MHz, $CDCl_3$)





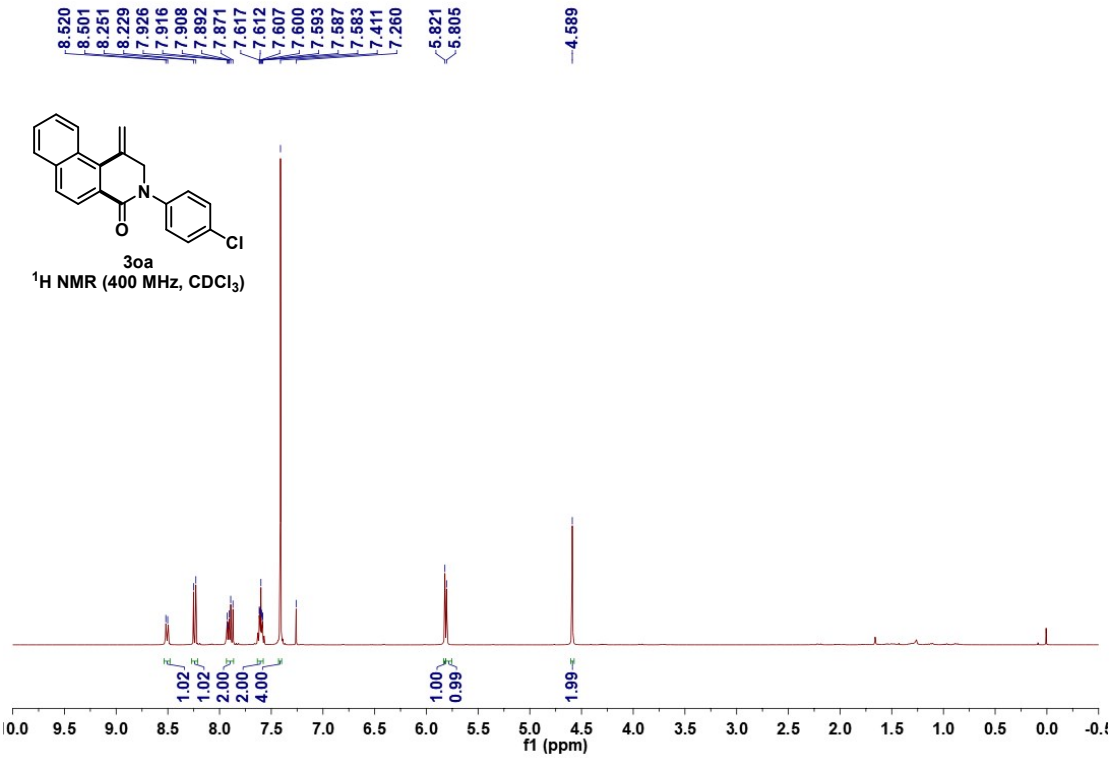
3na

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



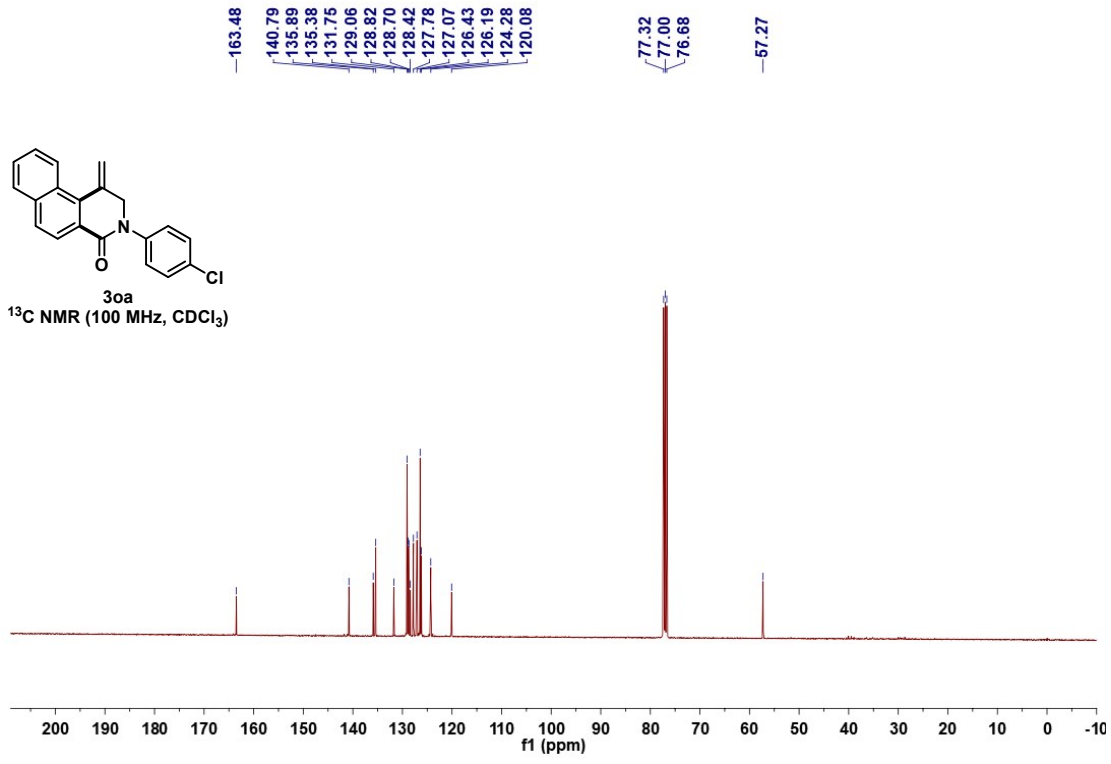
3na

^{13}C NMR (100 MHz, $CDCl_3$)



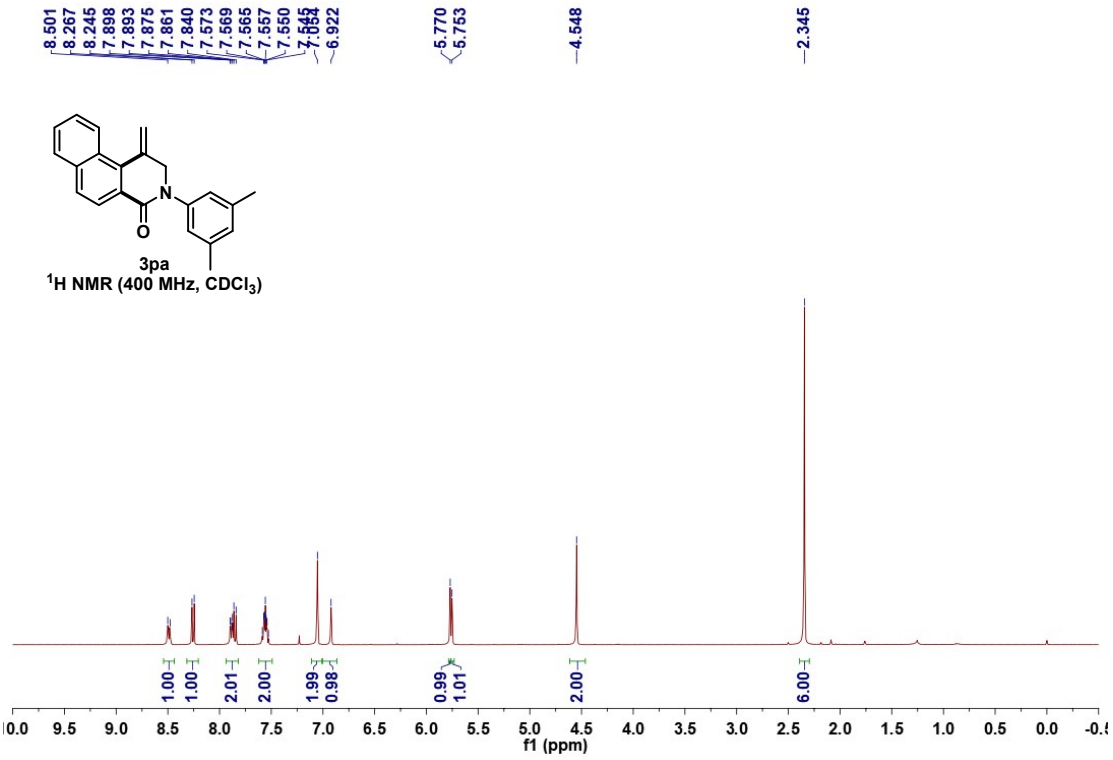
3oa

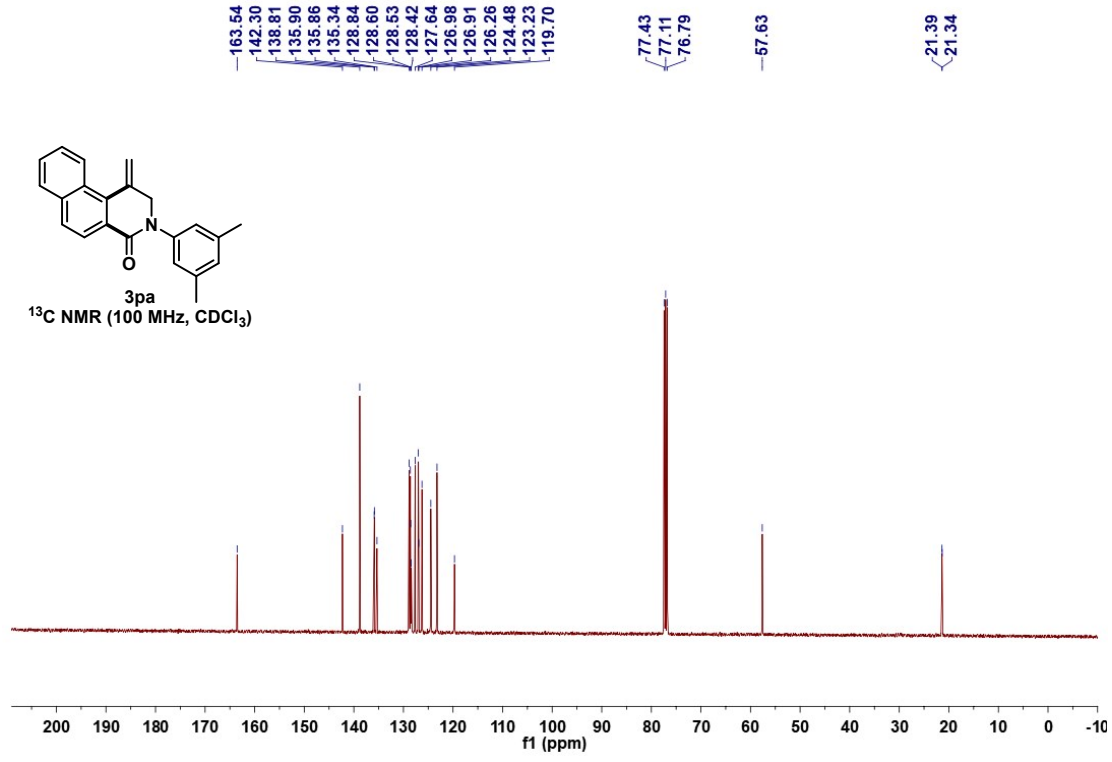
^{1}H NMR (400 MHz, $CDCl_3$)

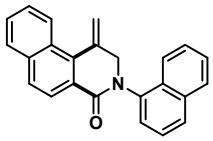


3oa

^{13}C NMR (100 MHz, $CDCl_3$)

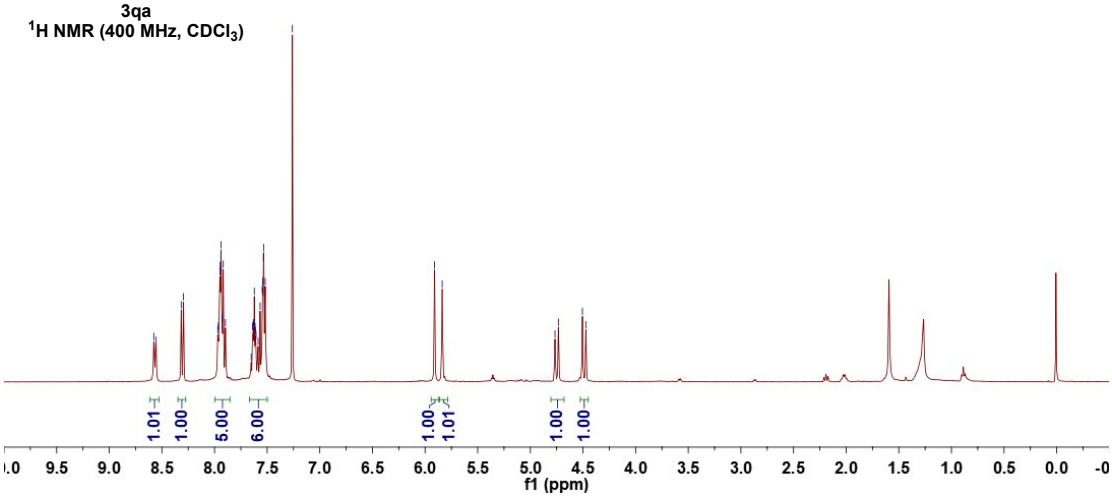

8.501
8.267
8.245
7.898
7.893
7.875
7.861
7.840
7.573
7.569
7.565
7.557
7.550
7.545
7.054
6.922
5.770
5.753
4.548
2.345
3pa
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.01
2.00
1.99
0.98
0.99
1.01
2.00
6.00
f1 (ppm)

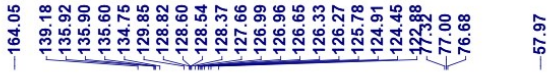

163.54
142.30
138.81
135.90
135.86
135.34
128.84
128.60
128.53
128.42
127.64
126.98
126.91
126.26
124.48
123.23
119.70
77.43
77.11
76.79
57.63
21.39
21.34
3pa
13C NMR (100 MHz, CDCl3)
f1 (ppm)

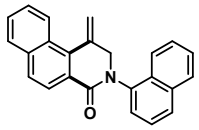


3qa

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

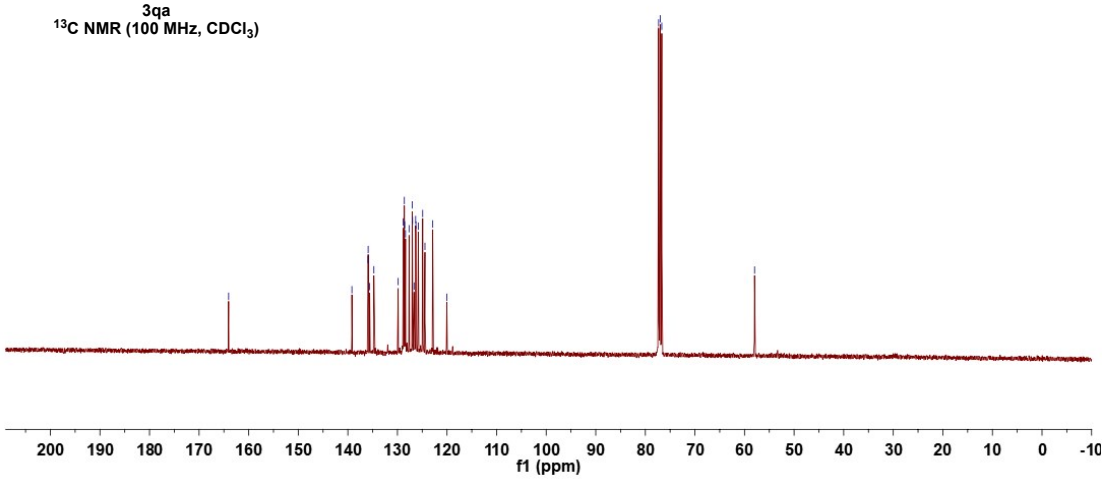


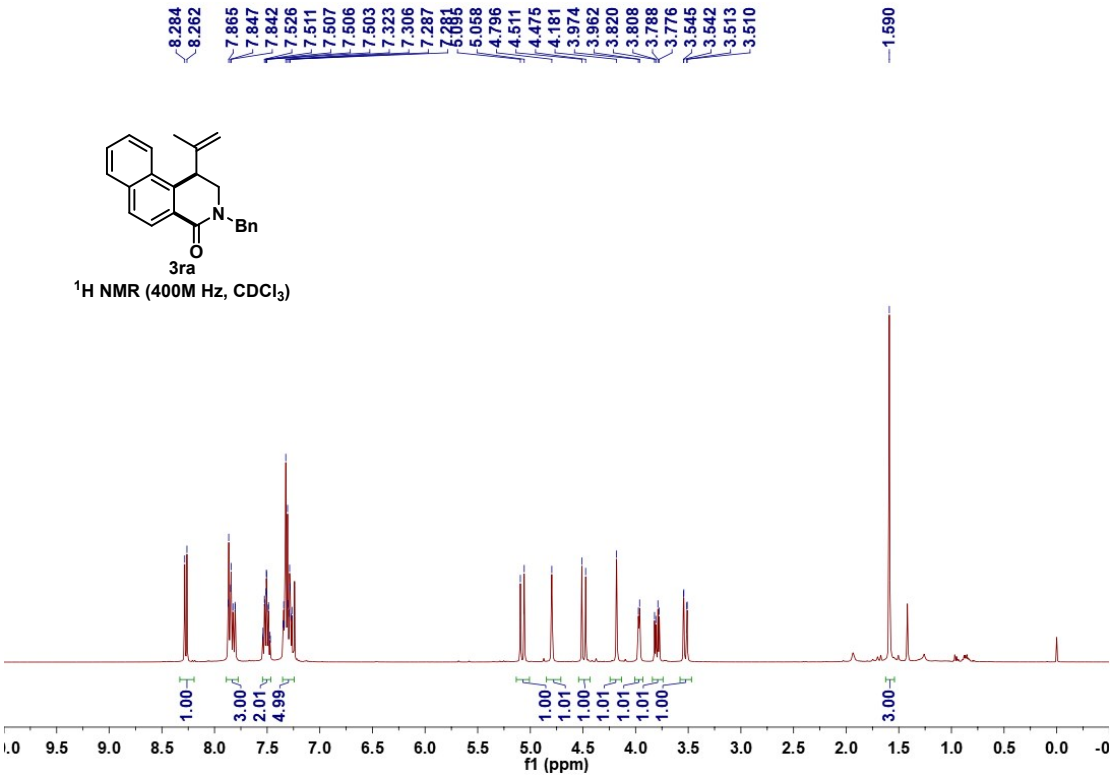




3qa

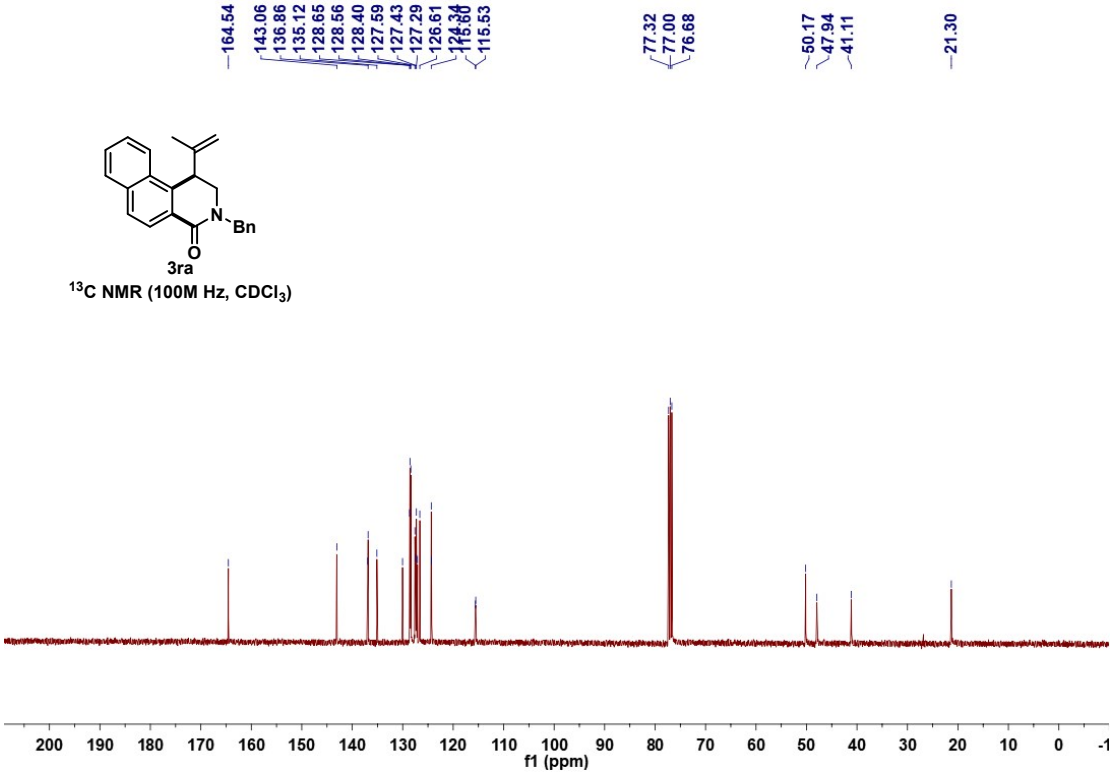
^{13}C NMR (100 MHz, $CDCl_3$)





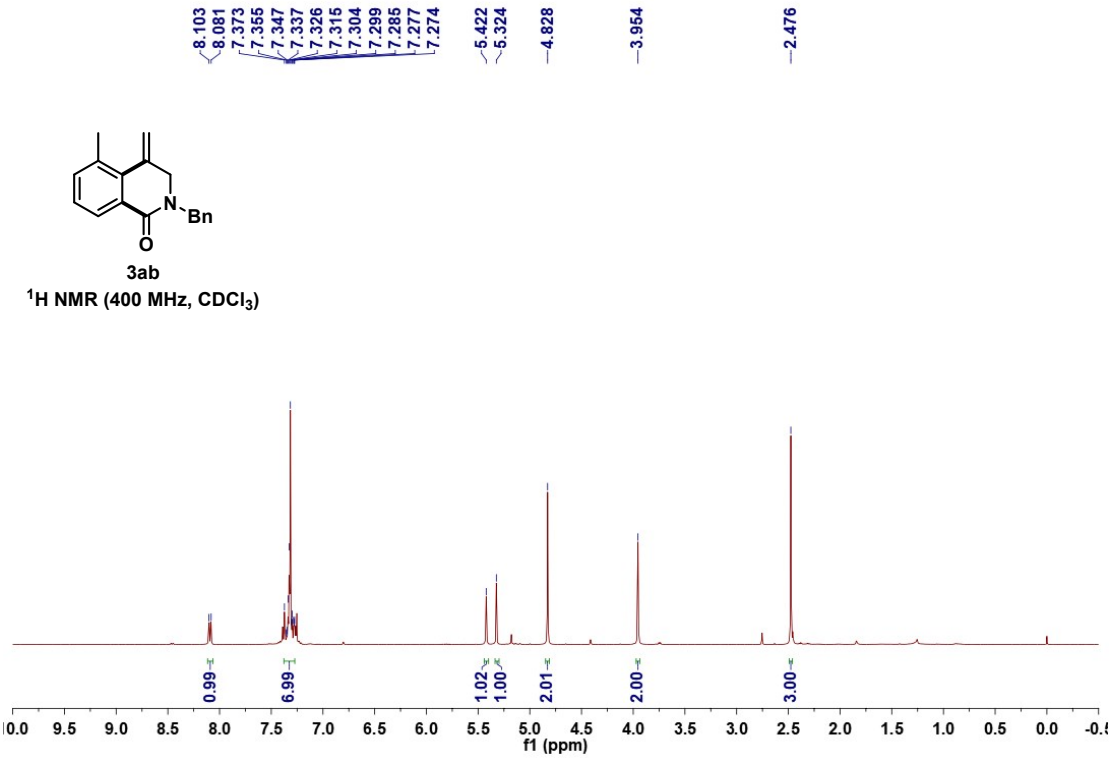
3ra

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



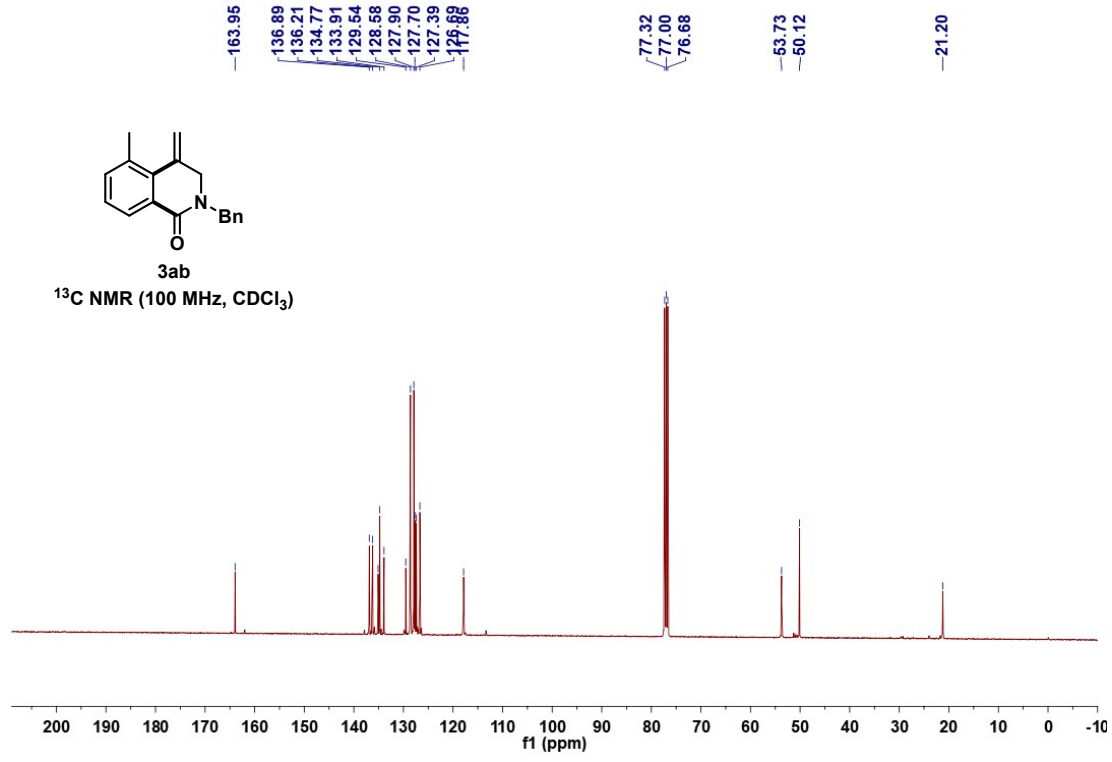
3ra

^{13}C NMR (100M Hz, $CDCl_3$)



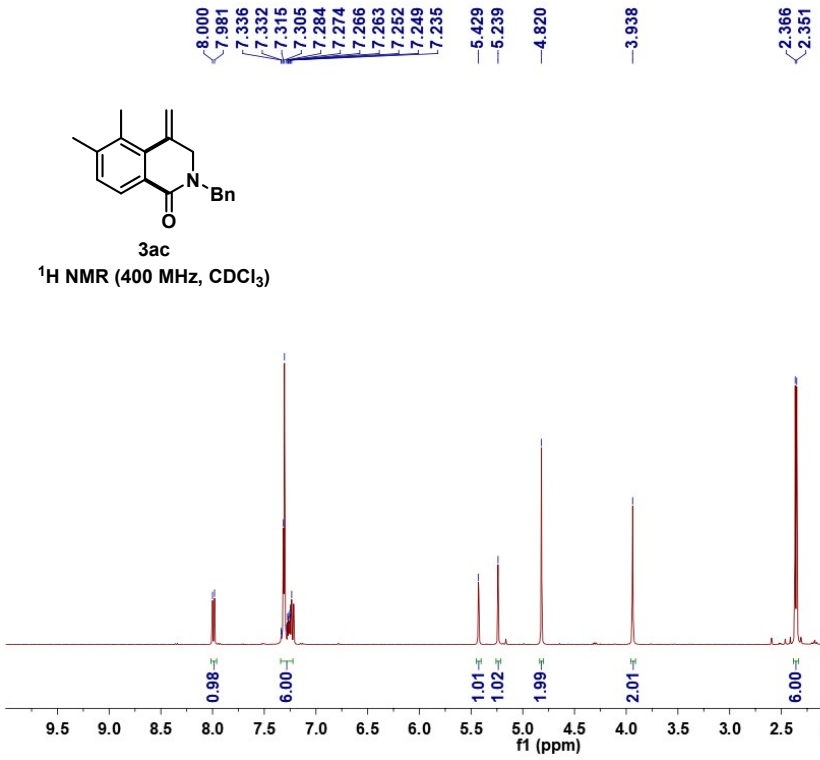
3ab

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



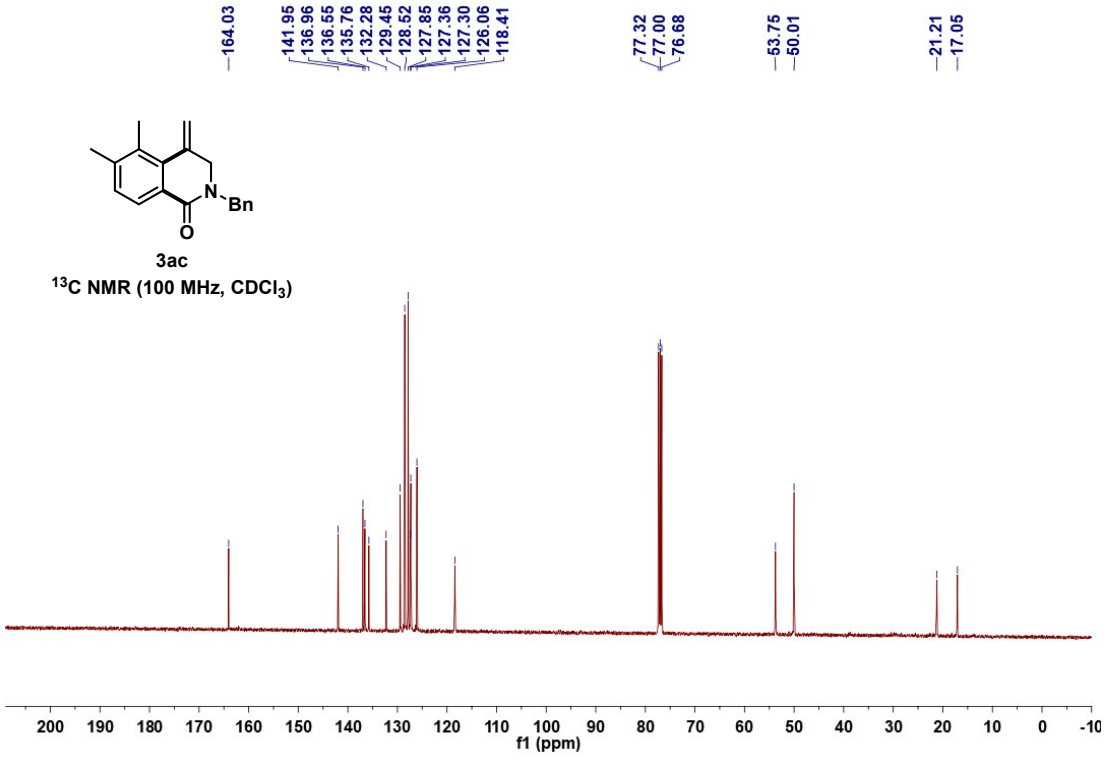
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



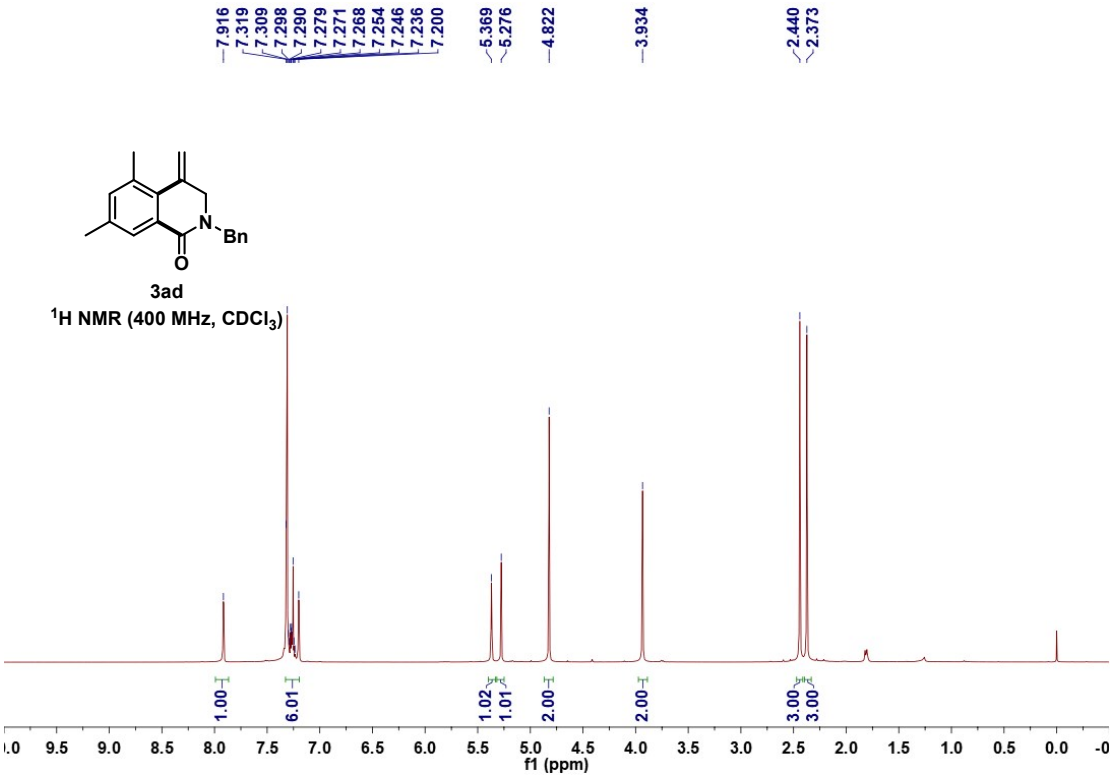
3ac

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



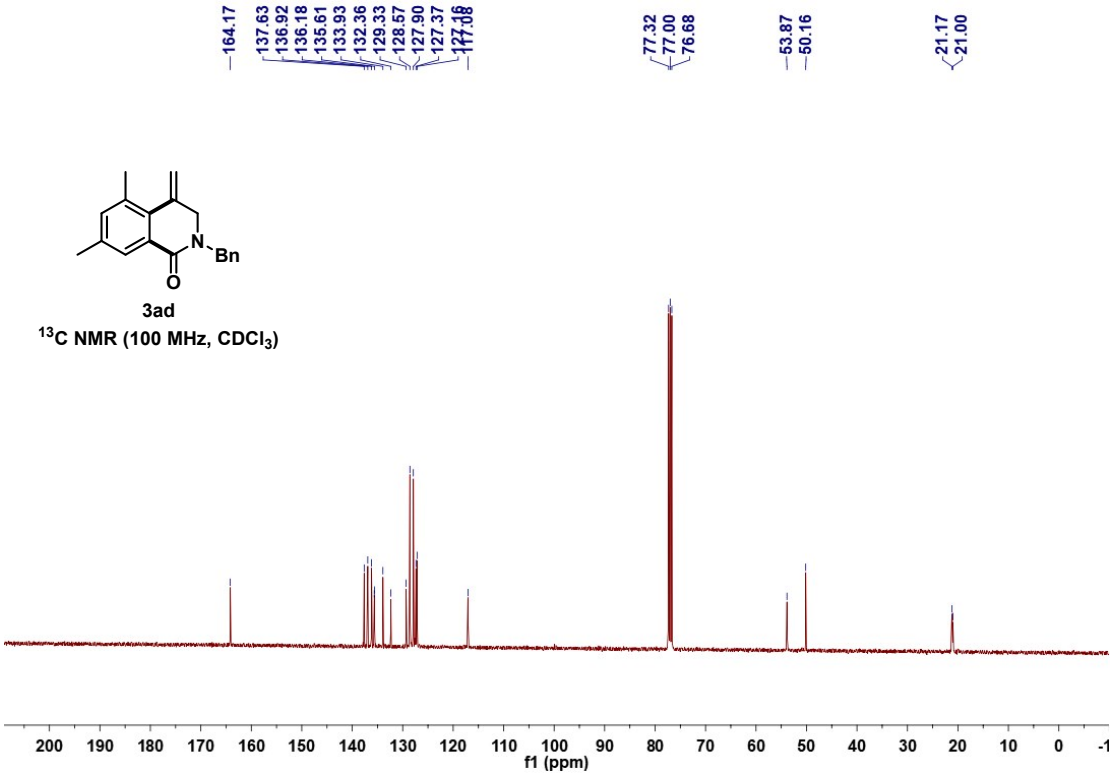
3ac

^{13}C NMR (100 MHz, $CDCl_3$)



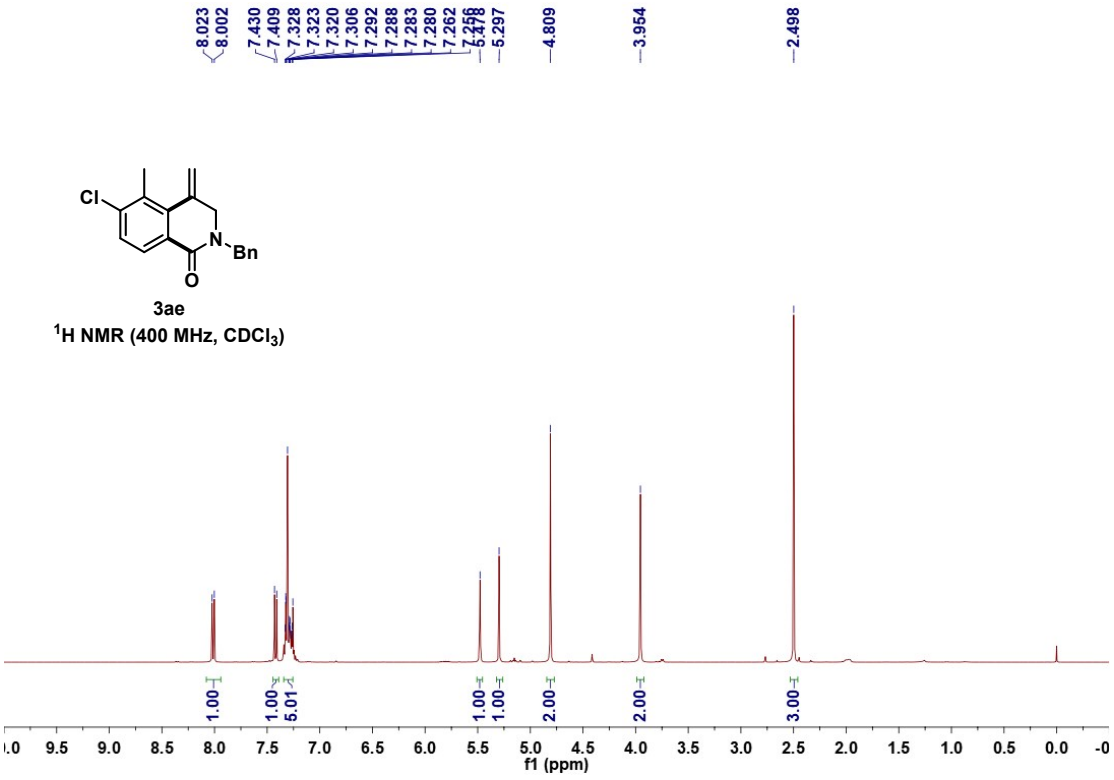
3ad

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



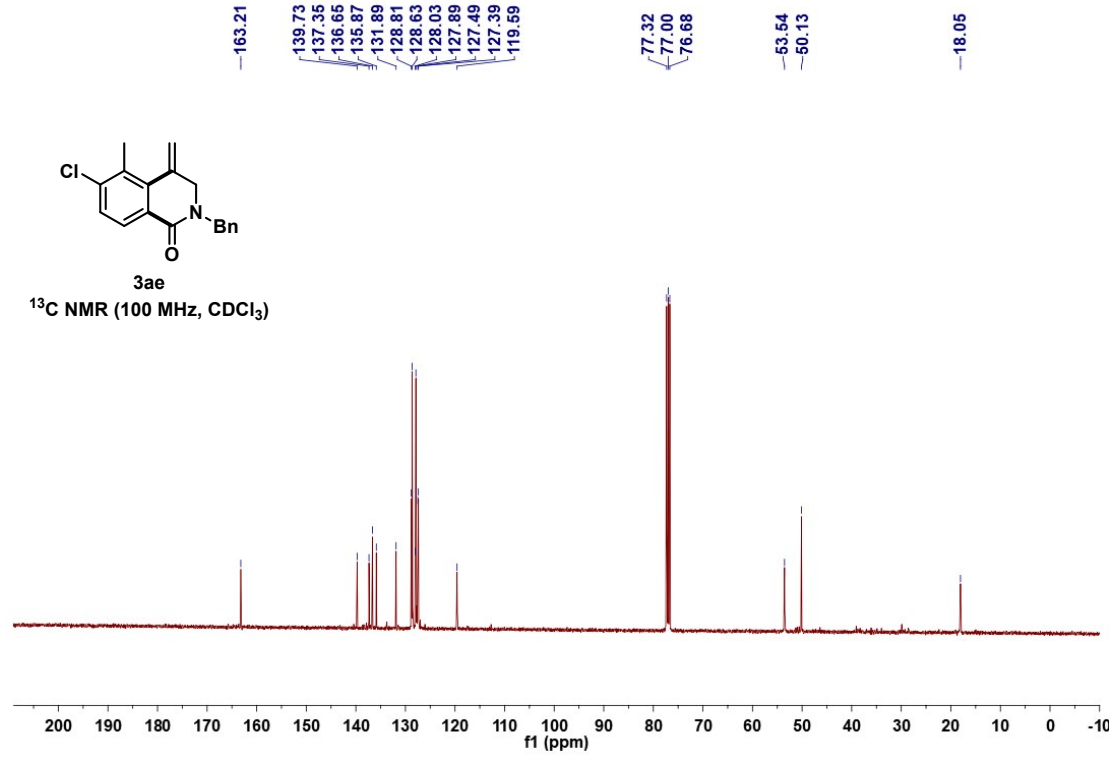
3ad

^{13}C NMR (100 MHz, $CDCl_3$)



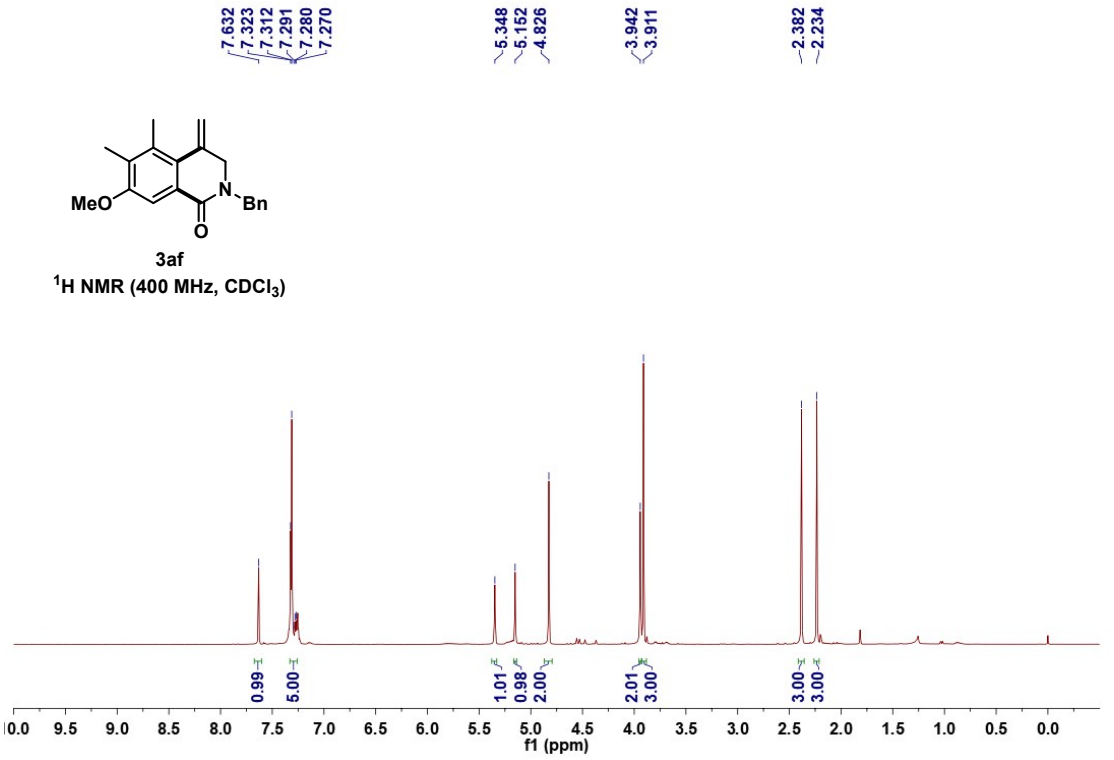
3ae

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



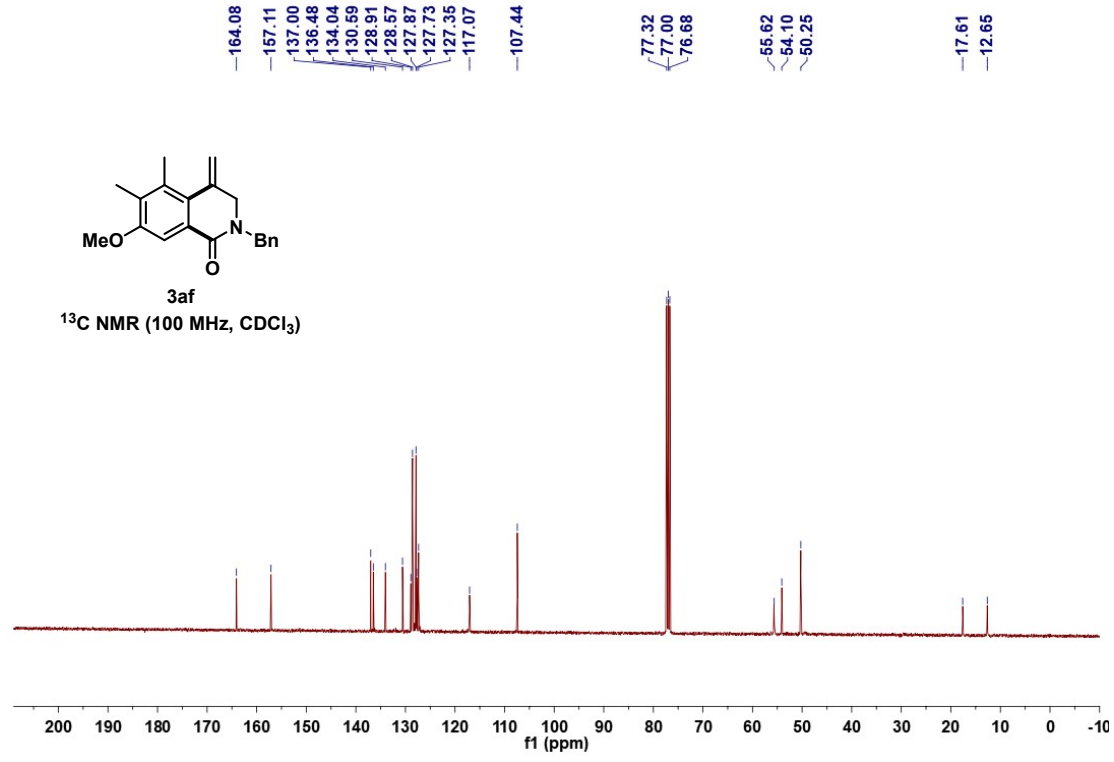
3ae

^{13}C NMR (100 MHz, $CDCl_3$)



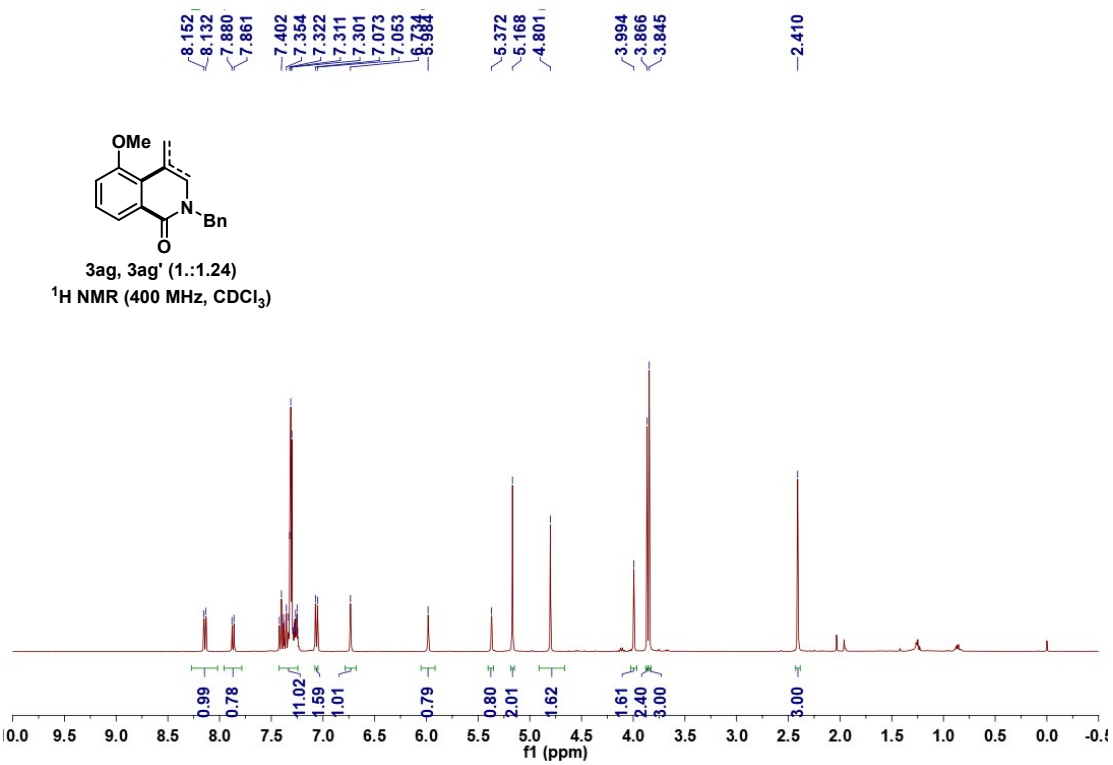
3af

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

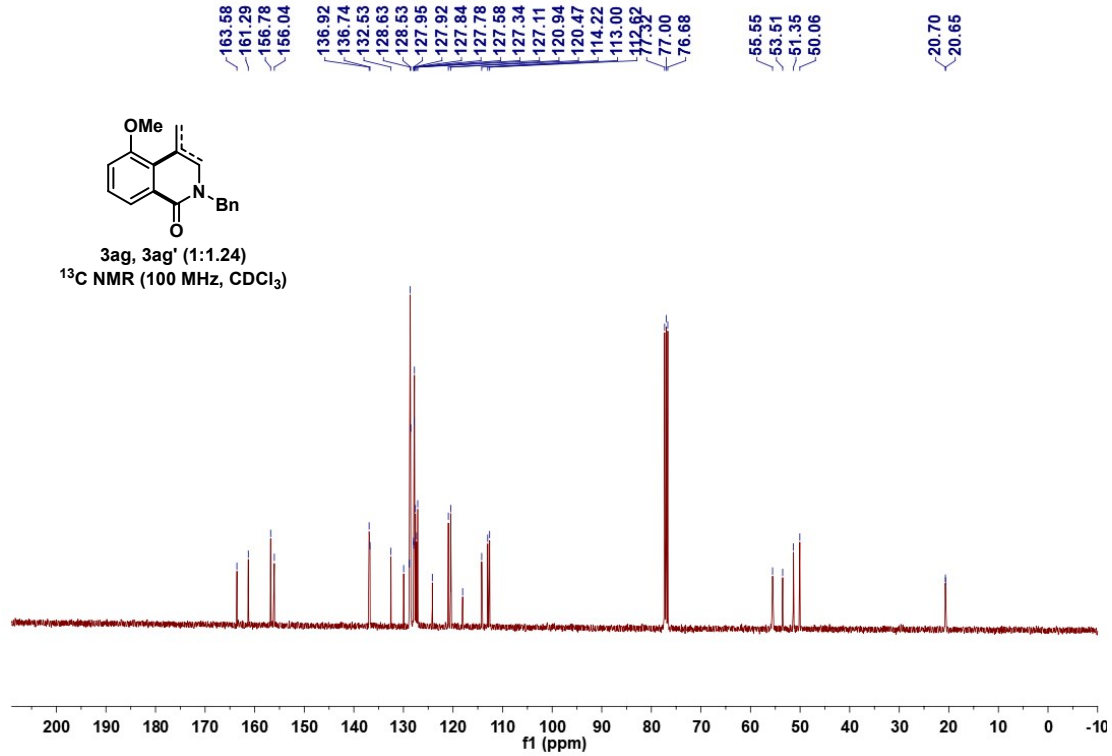


3af

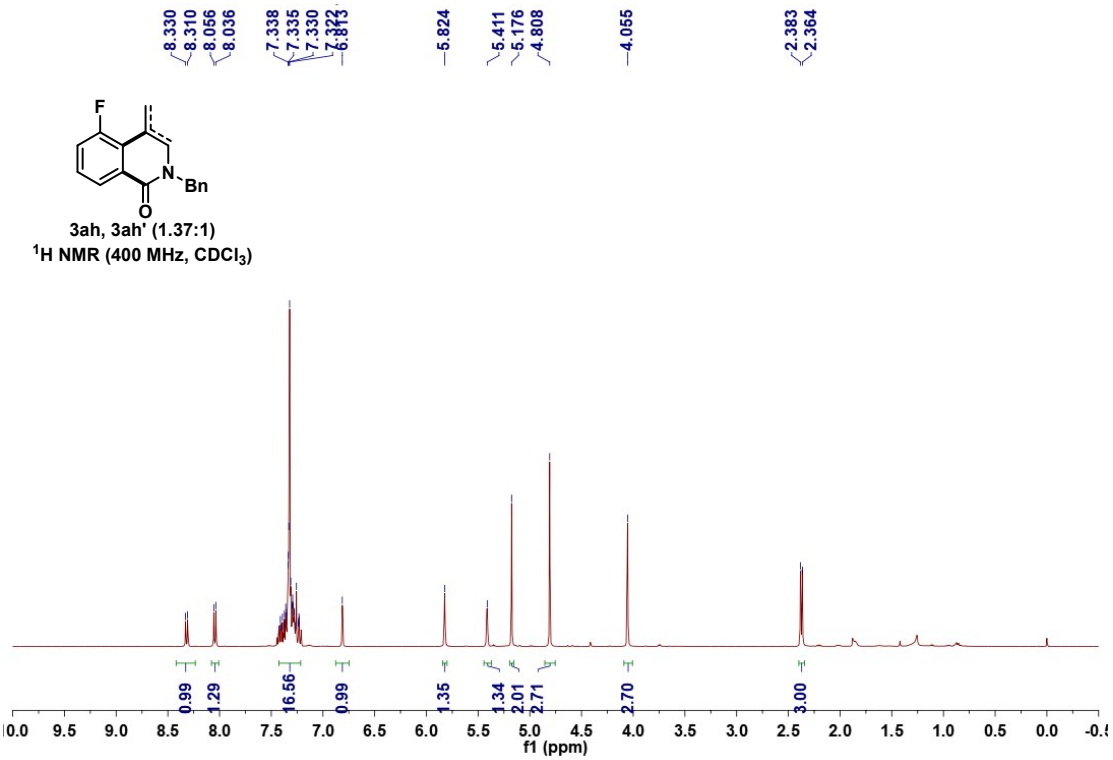
^{13}C NMR (100 MHz, $CDCl_3$)

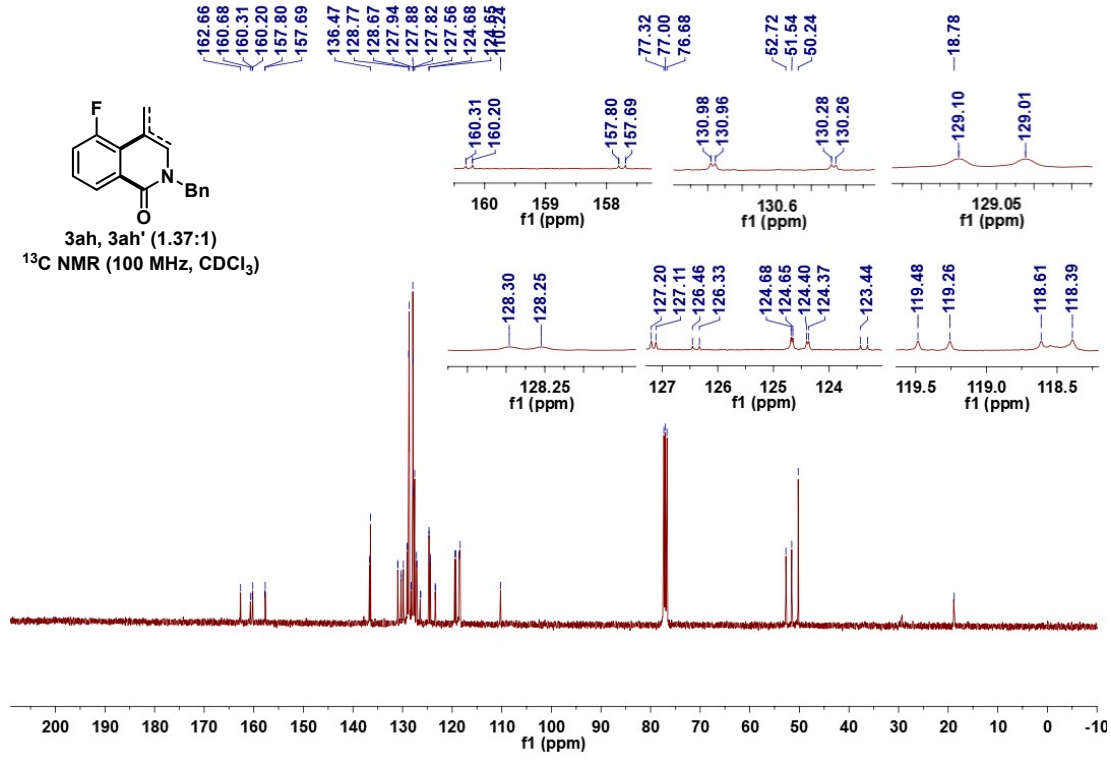


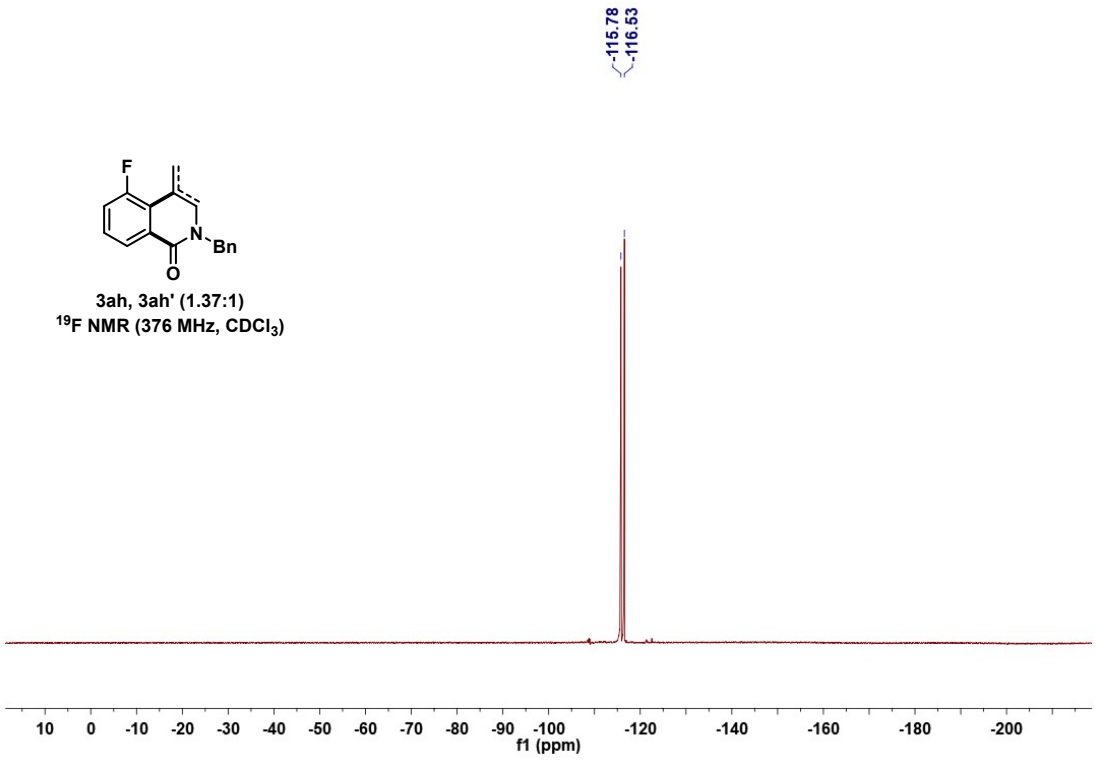
3ag, 3ag' (1.:1.24)
^{1}H NMR (400 MHz, $CDCl_3$)



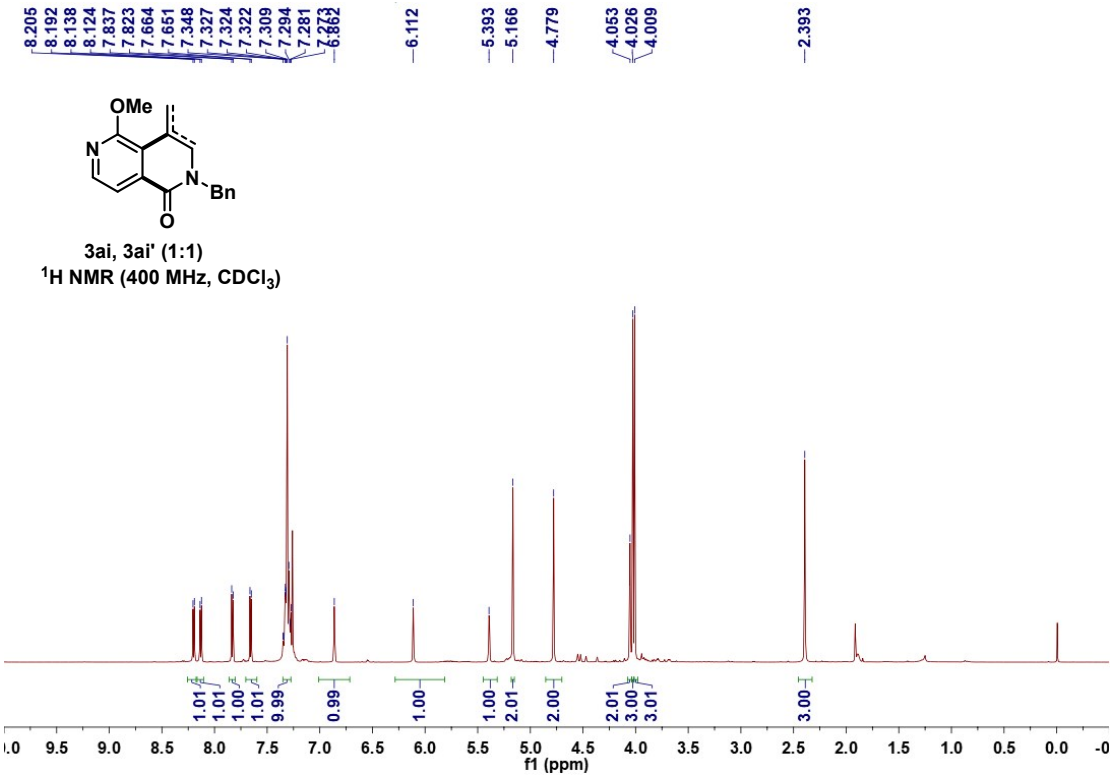
3ag, 3ag' (1:1.24)
^{13}C NMR (100 MHz, $CDCl_3$)


8.330
8.310
8.056
8.036
7.338
7.335
7.330
7.322
6.813
5.824
5.411
5.176
4.808
4.055
2.383
2.364
F
N
Bn
O
3ah, 3ah' (1.37:1)
1H NMR (400 MHz, CDCl3)
0.99
1.29
16.56
0.99
1.35
1.34
2.01
2.71
2.70
3.00
f1 (ppm)

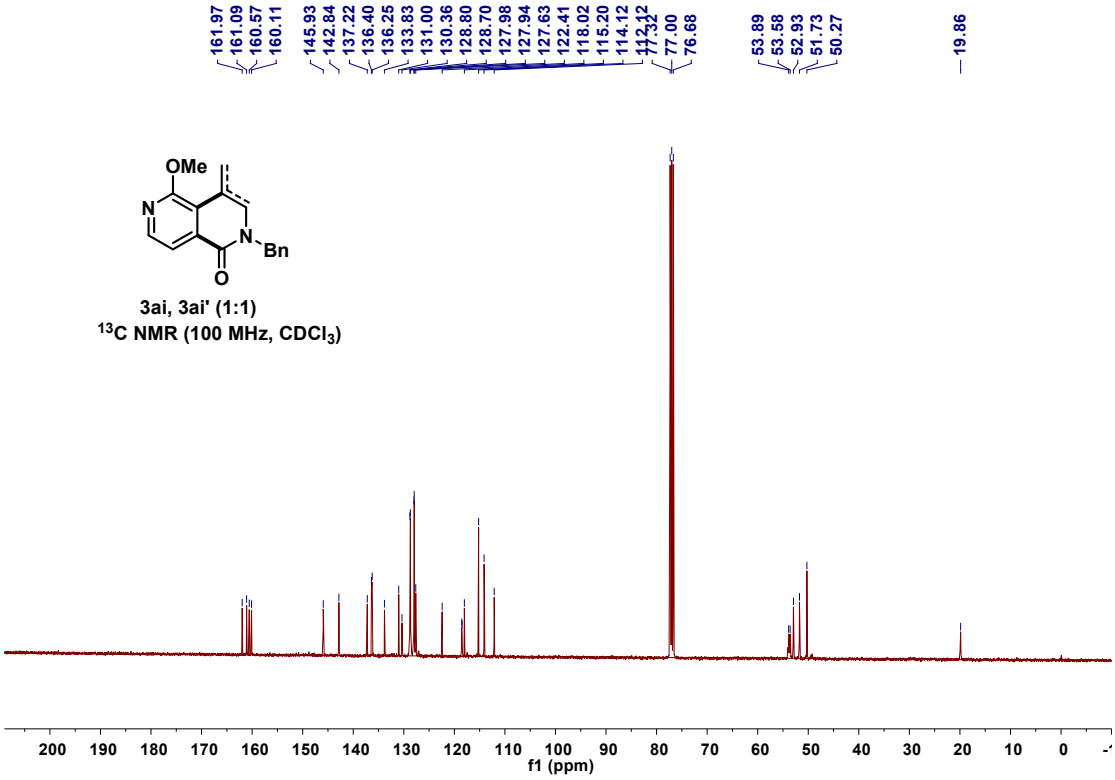

162.66
160.68
160.31
160.20
157.80
157.69
136.47
128.77
128.67
127.94
127.88
127.82
127.56
124.68
77.32
77.00
76.68
52.72
51.54
50.24
18.78
160.31
160.20
157.80
157.69
130.98
130.96
130.28
130.26
129.10
129.01
F
N
Bn
O
3ah, 3ah' (1.37:1)
13C NMR (100 MHz, CDCl3)
128.30
128.25
127.20
127.11
126.46
126.33
124.68
124.65
124.40
124.37
123.44
119.48
119.26
118.61
118.39
f1 (ppm)



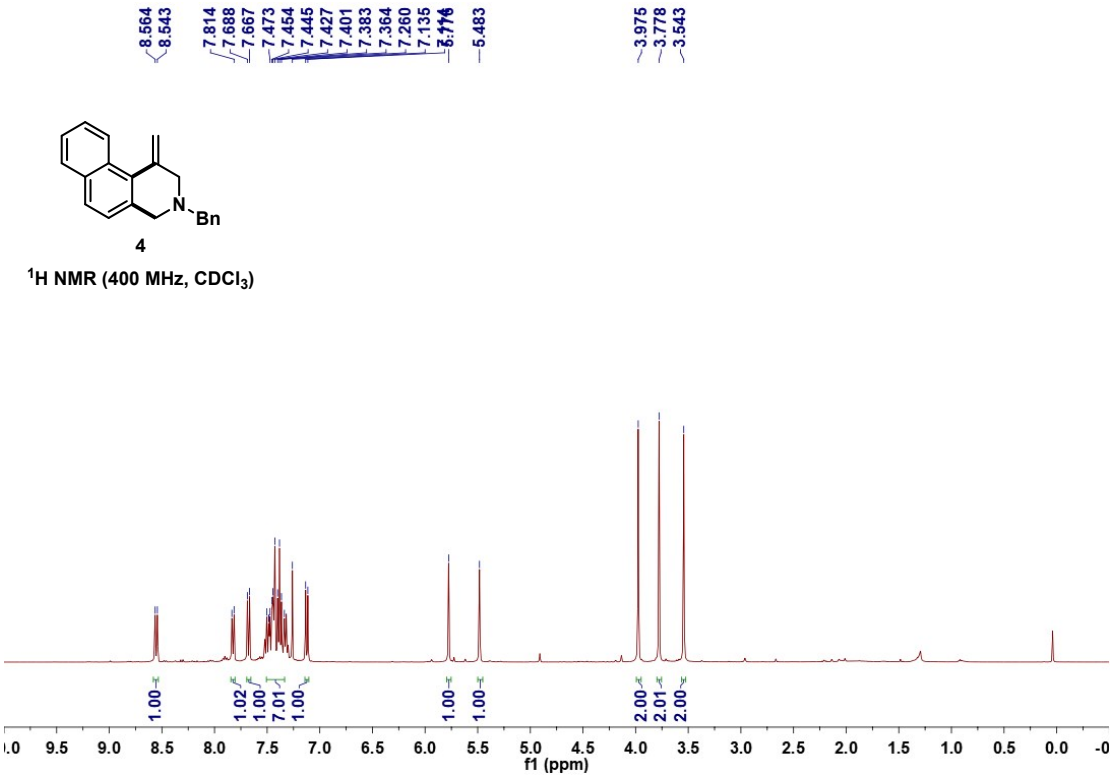
3ah, 3ah' (1.37:1)
^{19}F NMR (376 MHz, $CDCl_3$)



3ai, 3ai' (1:1)
^{1}H NMR (400 MHz, $CDCl_3$)

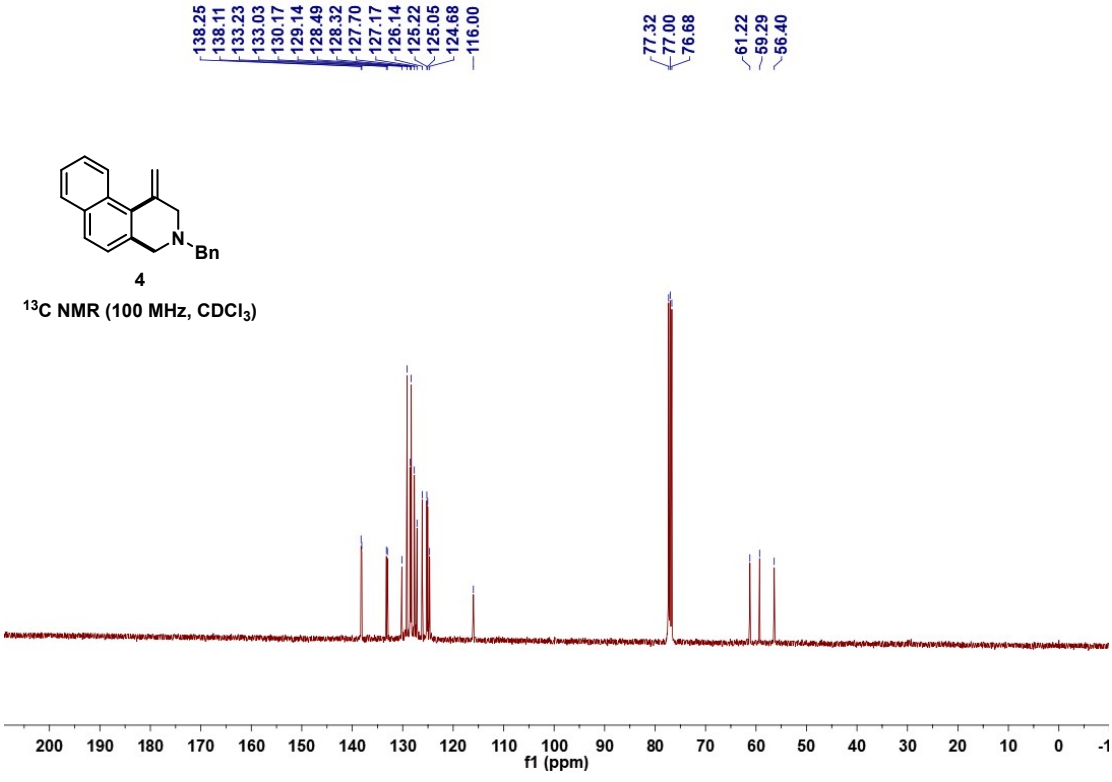


3ai, 3ai' (1:1)
^{13}C NMR (100 MHz, $CDCl_3$)



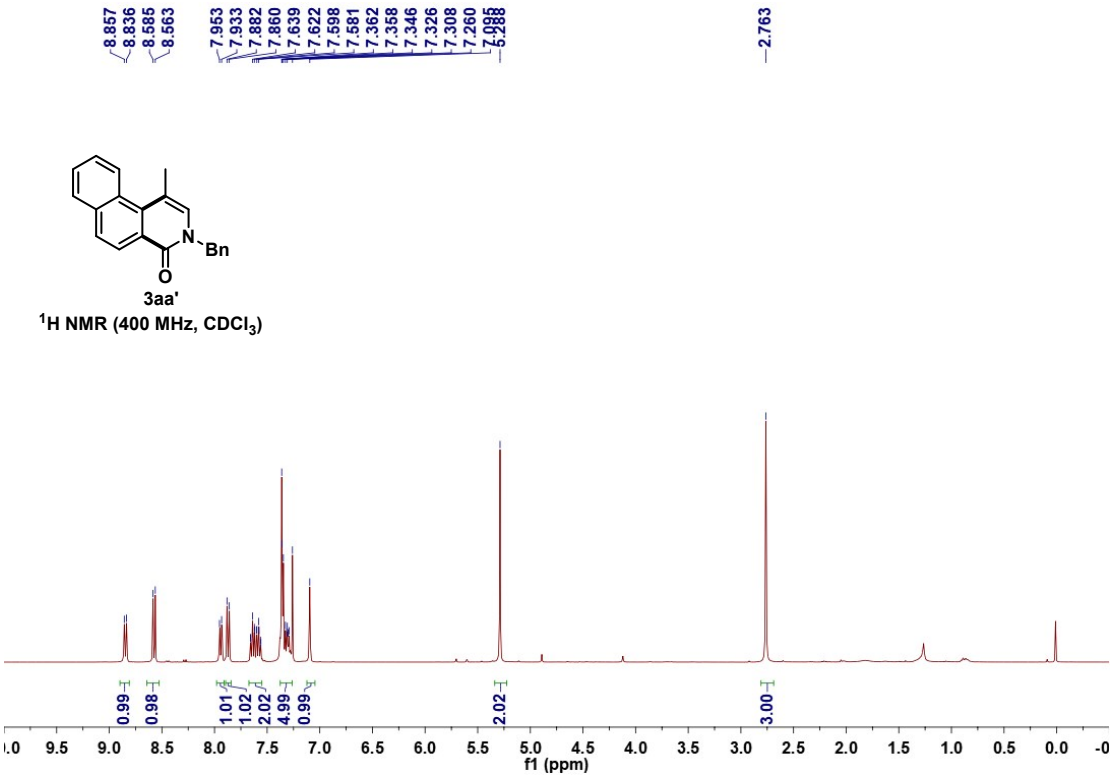
4

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



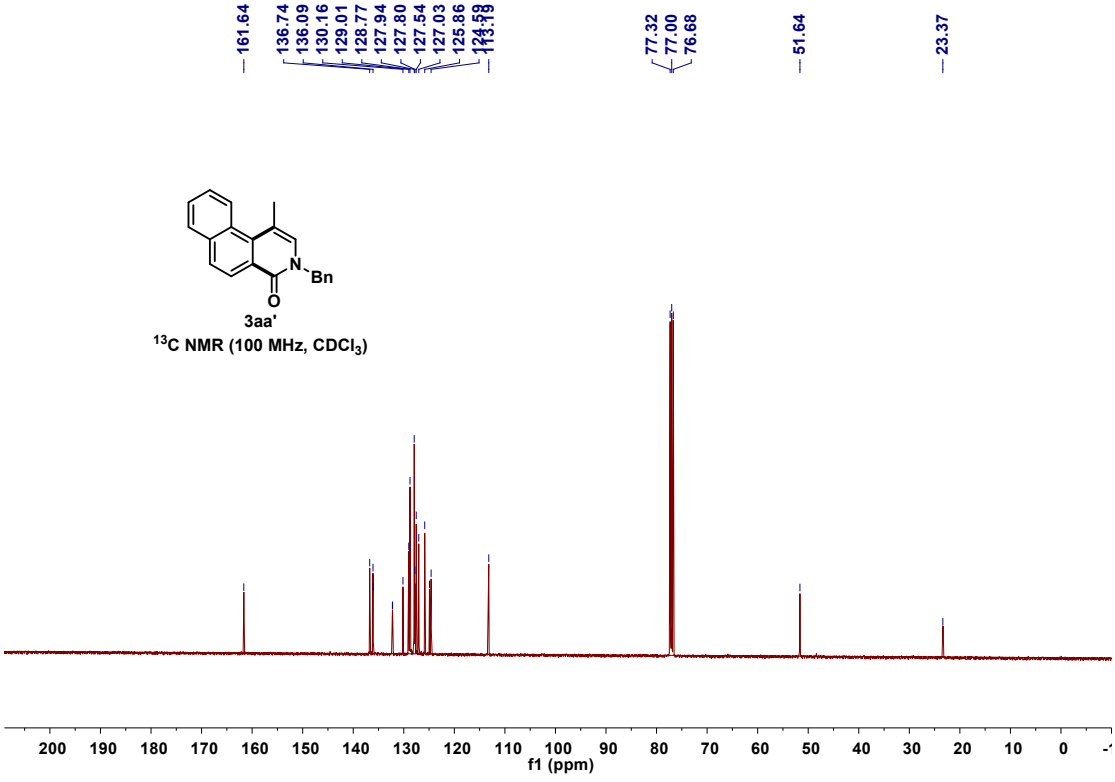
4

^{13}C NMR (100 MHz, $CDCl_3$)



3aa'

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



3aa'

^{13}C NMR (100 MHz, $CDCl_3$)