Co(III)-catalysed regioselective linear C(8)-H olefination of isoquinolone with terminal aromatic and aliphatic alkynes

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Supporting Information

Contents

1. General Information.

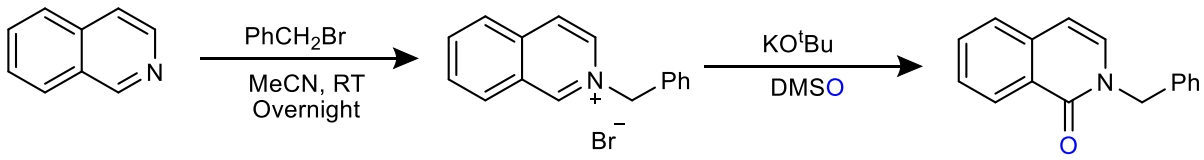
All experiments were performed under inert atmosphere in screw cap reaction tubes using Schlenk techniques and the workups were performed under air. All Chemicals were purchased from the Sigma- Aldrich, TCI and AVRA chemicals. TLC plates (Aluminium Sheet Silica gel 60 F_{254}) were purchased from Merck. Column chromatography was performed over silica gel (230−400 mesh) using *n*-hexane and ethyl acetate as eluents. All products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and high-resolution mass spectrometry (HRMS) and melting points. NMR spectra were recorded in on Bruker Advance at 600 MHz (^{1}H) and 150 MHz (^{13}C) respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δH = 7.26 and δC = 77.16) (H_2O, δH = 1.56) ppm, DMSO-d_6 (δH = 2.51, 3.33 and δC = 39.52) ppm, and coupling constants (J) are given in Hz. HRMS were recorded Mass spectra were recorded on Water Q-ToF Micromass, maXis Impact mass spectrometers, and a high-resolution 6560 Ion Mobility Q-TOF LC/MS (Agilent, Santa Clara, USA). IR was analyzed using a Shimadzu IR Prestige-21 with a ZnSe singlereflection ATR accessory.. The melting points were recorded on a Brønsted Electrothermal 9100 and Labindia visual melting range.

2. General procedure for the synthesis of Isoquinolone

Isoquinolone were prepared according to known literature method.[S1]

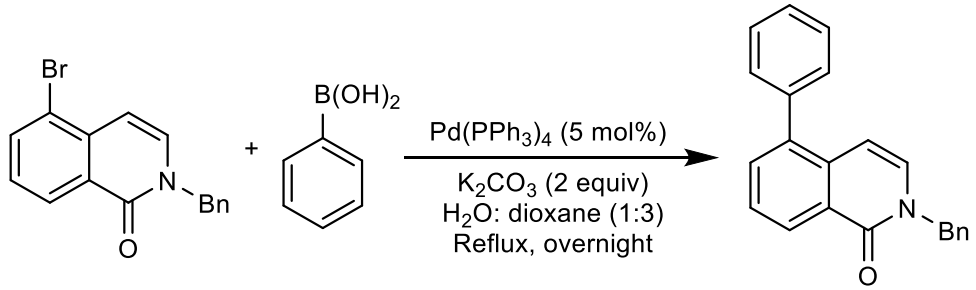
An oven-dried flask was charged with CH_3CN (10 mL), isoquinoline (10 mmol) and benzyl bromide (10 mmol). The reaction mixture was stirred at room temperature overnight. The residue was diluted with ethyl acetate, and the iminium salt precipitated quickly. The solid was separated by filtration to get *N*-benzylisoquinolin-2-ium bromide.

To the mixture of *N*-benzylisoquinolin-2-ium bromide (6.0 mmol) and potassium tert-butoxide (12.0 mmol) in a 100 mL flask was added DMSO (30 mL) with stirring. The reaction mixture was continually stirred in air at room temperature upto 72h. Then it was diluted with EtOAc(70 mL) and water (70 mL), and extracted with EtOAc (3 × 70 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=5:1) to provide *N*-benzylisoquinolin1(2H)-one as a yellow solid.



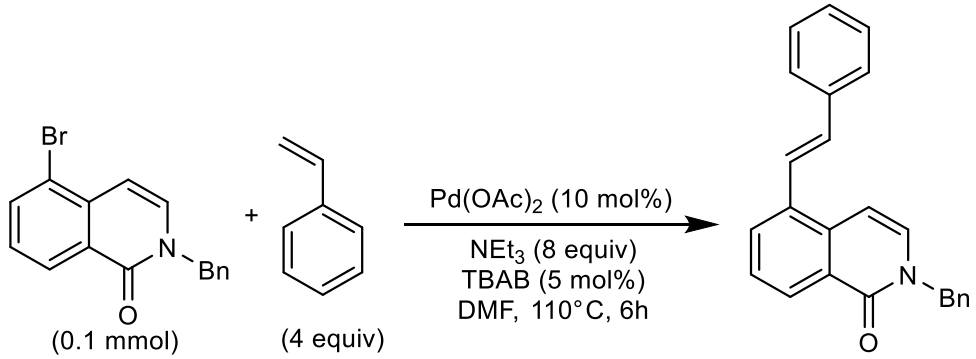
Procedure for synthesis of 5-(phenyl)-2-benzylisoquinolin-1(2H)-one[S2]

5-Bromo-2-benzylisoquinolin-1(2H)-one (1 mmol) was taken in a 25 mL round bottom flask and dissolved in 10 mL mixture of water and 1,4-dioxane (1:3). Then $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (2 eq.) and phenyl boronic acid (1.3 eq.) were added to the reaction mixture. The reaction mixture was allowed to reflux for overnight. After completion of the reaction, the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The organic layer was extracted, dried over anhydrous Na2SO4 and concentrated in vaccuo. product was purified by flash silica gel column chromatography.



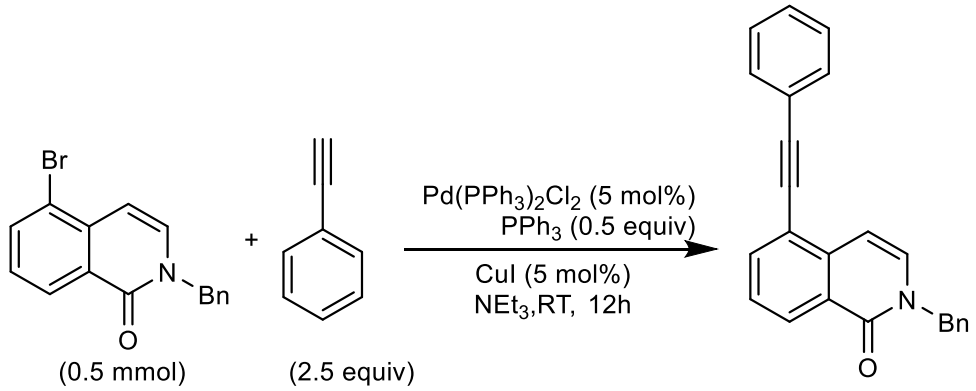
Procedure for synthesis of *(E)*- 2-benzyl-5-styrylisoquinolin-1(2H)-one:

5-Bromo-2-benzylisoquinolin-1(2H)-one (0.1 mmol) was taken in a reaction vial and dissolved in 0.5 mL DMF. Then $Pd(OAc)_2$ (10 mol%), Et_3N (8 eq.), TBAB (5 mol%) and styrene (4 eq.) were added to the reaction mixture. The reaction mixture was allowed to stir at 110 ºC for 6 h. After completion of the reaction, it was quenched with water and extracted with ethyl acetate. Organic layer was dried over anhydrous Na_2SO_4 and concentrated under vaccum. product was purified by flash silica gel column chromatography.



Procedure for synthesis of *N*-benzyl-5-(phenylethynyl)isoquinolin-1(2H)-one:

5-Bromo-2-methylisoquinolin-1(2H)-one (0.5 mmol) was taken in a 10 ml round bottom flask and dissolved in NEt_3 (5 mL). Then $Pd(PPh_3)_2Cl_2$ (5 mol%), PPh_3 (0.5 equiv), CuI (5 mol%) and phenyl acetylene (2.5 eq.) were added to it. The reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, solvent was removed in vaccuo and product was purified by flash silica gel column chromatography.



Procedure for synthesis of 5-methylphenanthridin-6(5H)-one: [S3]

Phenanthridin-6(5H)-one (0.5 mmol) was dissolved in DMF (1 mL) followed by Cs_2CO_3 (1.5 eq.) and MeI (3 eq.) were added to it. The reaction mixture was allowed to stir at room temperature for overnight. After completion of the reaction, it was quenched with water and extracted with ethyl acetate. Organic layer was dried over anhydrous Na_2SO_4 and concentrated under vaccuo to obtain product.

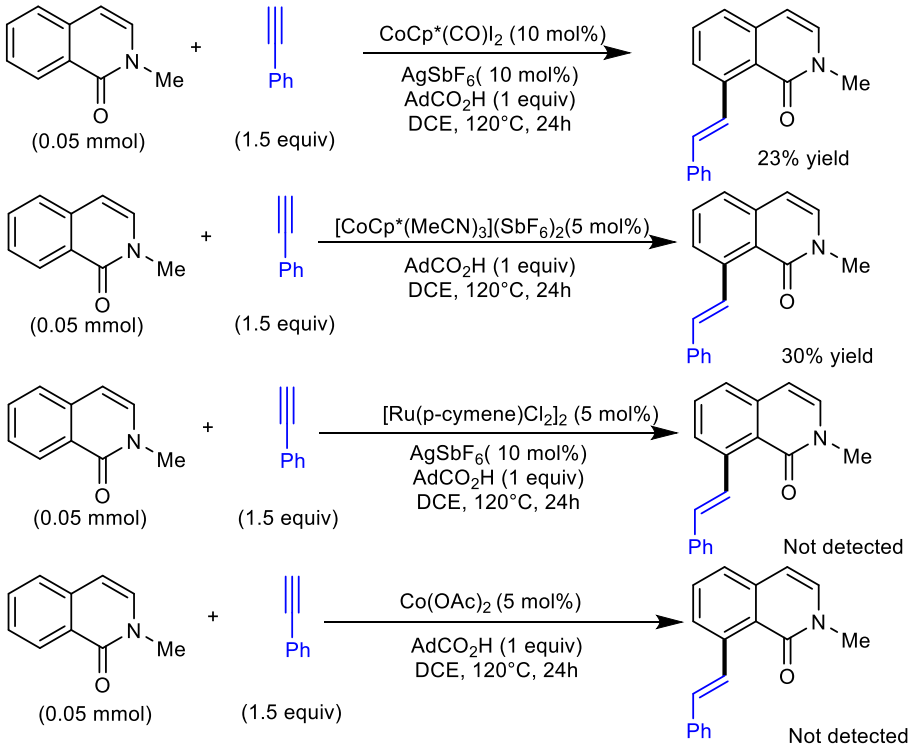
Procedure for synthesis of *N*-benzyl-3,4-dihydroisoquinolin-1(2H)-one: [S4-S5]

To the solution of 1,2,3,4-tetrahydroisoquinoline (500 mg, 3.75 mmol) in acetone (0.5 M) potassium carbonate (1.5 equiv.) was added. Benzyl bromide (1 equiv.) was added and the reaction was stirred at reflux for 5 hours. After the completion of the reaction, monitored by TLC, the mixture was diluted with EtOAc (10 mL) and washed with water (3 x 5 mL). The organic layer was dried over Na_2SO_4 and concentrated under vacuum. Purification by column chromatography to afford the *N*-benzyl-1,2,3,4-tetrahydroisoquinoline.

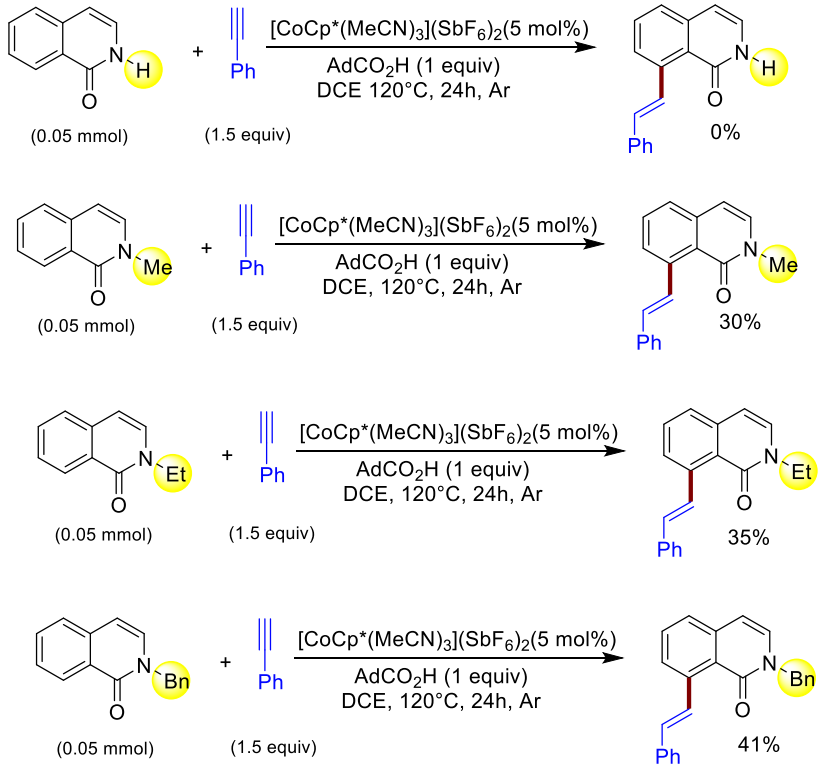
Iodine (1.68 mmol) was added to a mixture of *N*-benzyl-1,2,3,4-tetrahydroisoquinoline (0.22 mmol) and sodium bicarbonate (2.24 mmol) in THF/H2O (2.5:1, 0.025 M). The reaction mixture was stirred gently at room temperature for 4 h. The reaction mixture was then pipetted into a solution of saturated aqueous sodium thiosulfate (10 mL) and saturated aqueous sodium bicarbonate (10 mL). The crude material was extracted in DCM (2 x 10 mL), and the combined organic layers were washed with saturated aqueous sodium bicarbonate (10 mL), concentrated in vacuo and then purified by column chromatography to give product.

3. Optimization Data:

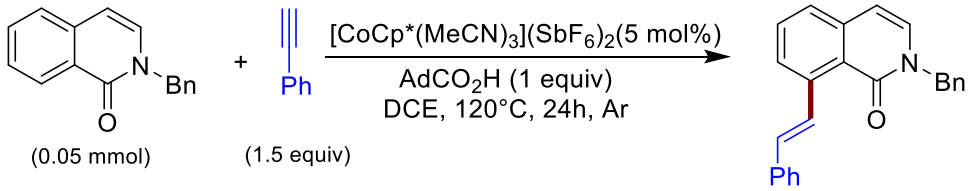
3.1 Screening of Catalyst



3.2 Screening of protecting group



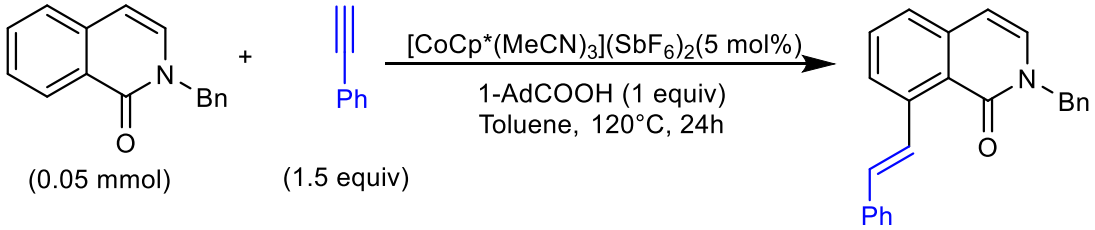
3.3 Screening of solvents



S.N.	Variation from above condition	Yield[a]
1	HFIP instead of DCE	ND
2	TFE instead of DCE	8%
3	THF instead of DCE	15%
4	1,4 Dioxane instead of DCE	18%
5	TCE instead of DCE	40%
6[b]	$CHCl_3$ instead of DCE	ND
7[b]	DCM instead of DCE	9%
8	O-DCB instead of DCE	48%
9	PhCl instead of DCE	52%
10	Benzene instead of DCE	58%
11	Toluene instead of DCE	**66%**
12	TFT instead of DCE	48%
13	Xylene instead of DCE	26%

[a] NMR yield are calculated using 1,1,2,2 tetrachloroethane as internal standard, [b] at 40°C

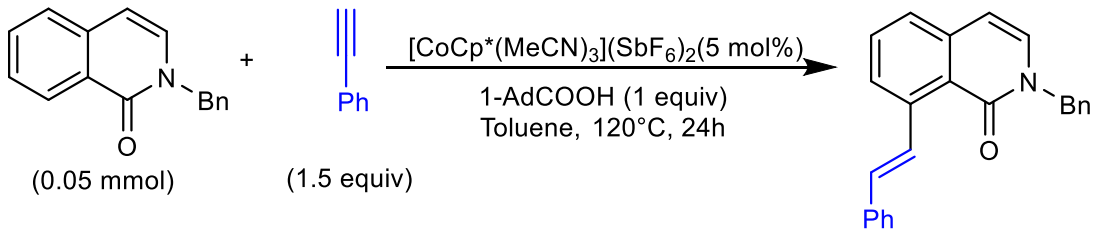
3.4 Screening of additives



S.N.	Variation from above condition	Yield[a]
1	AcOH (1) instead of AdCOOH (1)	ND
2	PivOH (1) instead of AdCOOH (1)	42%
3	MesCOOH (1) instead of AdCOOH (1)	52%
4	AdCOOH (2)instead of AdCOOH (1)	51%
5	AdCOOH (0.2) instead of AdCOOH (1)	3 %
6	TFA instead of AdCOOH (1)	12%
7	CSA instead of AdCOOH (1)	ND
8	Triflic acid instead of AdCOOH (1)	ND
9	Ag_2CO_3 (1) + AdCOOH (1)	ND
10	Na_2CO_3 (1) + AdCOOH (1)	ND
11	K_2CO_3 (1) + AdCOOH (1)	ND
12	Cs_2CO_3 (1) + AdCOOH (1)	ND
13	AgOAc(0.2) + AdCOOH (1)	52%
14	AgOAc(0.2) + AdCOOH (1) in DCE	55%
15	NaOPiv instead of AdCOOH (1)	ND

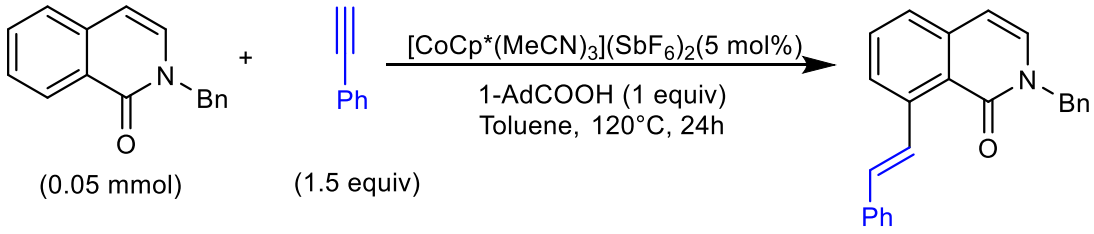
[a] NMR yield are calculated using 1,1,2,2 tetrachloroethane as internal standard

3.5 Variation of temperature



S.N.	Variation from above condition	Yield[a]
1	RT instead of 120°C	ND
2	40°C instead of 120°C	ND
3	50°C instead of 120°C	ND
4	60°C instead of 120°C	ND
5	80°C instead of 120°C	34%
6	100°C instead of 120°C	46%
7	140°C instead of 120°C	58%

3.6 Variation of Time



S.N.	Variation from above condition	Yield[a]
1	1h instead of 24 h	21%
2	3h instead of 24 h	32%
3	6h instead of 24 h	40%
4	12h instead of 24 h	54%
5	36h instead of 24 h	65%

3.7 Simultaneos screeining of Acids and solvents

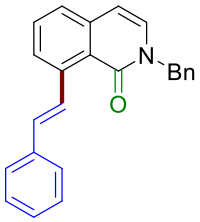
	[CoCp*(MeCN)3](SbF6)2 (5mol%)						
	HFIP	TFE	DCE	DCB	PhCl	Benzene	Toluene
1-AdCOOH (1 equiv)	0	8	41	48	52	58	66
PivOH (1 equiv)	5	0	36	36	38	36	42
AcOH (1 equiv)	3	0	0	0	26	0	0
MesCOOH (1 equiv)	4	0	34	35	44	48	52
1-AdCOOH (2 equiv)	0	0	32	48	51	21	51
1-AdCOOH (0.2 equiv)	0	0	8	25	20	24	3

4. General Procedure for the olefination of isoquinolone:

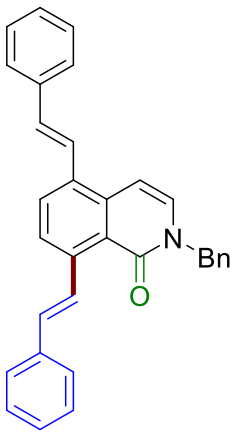
To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar isoquinolone **1** (0.1 mmol), alkyne **2** (1.5 equiuv), $[CoCp^*(MeCN)_3](SbF_6)_2$ (3.9 mg, 5 mol%), 1-$AdCO_2H$ (18 mg, 1.0 equiv.) were added under argon atmosphere, followed by the addition of toluene (0.5 mL) using schlenk technique. The subsequent reaction mixture was stirred at 120 °C for 24 h. Reaction mixture was cooled to room temperature and diluted with ethyl acetate, The mixture was washed with 2M aqueous NaOH solution. Organic layer was dried over Na_2SO_4. Solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using silica gel (230−400 mesh size) and *n*-hexane:EtOAc as the eluent.

5. Characterization Data

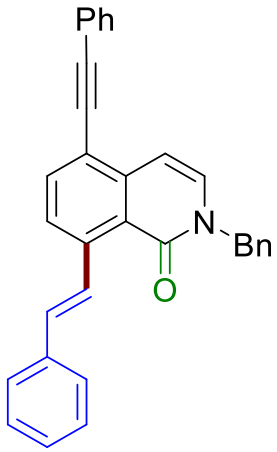
(E)-2-benzyl-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3aa): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 22 mg (65%); white solid*;* Mp: 125-128°C*;* ^{1}H NMR (600 MHz, DMSO-d_6 δ): 8.69 (d, J =16.2 Hz, 1H), 7.69 (dt, J =15.6, 7.8 Hz, 2H), 7.58 (dd, J =13.2, 7.2 Hz, 4H), 7.39 (t, J =7.8 Hz, 2H), 7.33 – 7.24 (m, 6H), 6.97 (d, J =16.2 Hz, 1H), 6.65 (d, J =7.2 Hz, 1H), 5.17 (s, 2H) ; ^{13}C NMR (150 MHz, DMSO-d_6 δ): 161.7, 139.9, 138.8, 137.8, 137.6, 133.1, 131.9, 130.3, 129.9, 128.7, 128.6, 127.6, 127.4, 127.3, 126.6, 126.3, 125.7, 122.2, 105.8, 51.2. IR (ZnSe): ν_{max}(cm^{-1}) 1645, 1608, 1492, 1365, 1165, 1072, 954, 813, 748, 690; HRMS (ESI-TOF): m/z calcd for $[C_{24}H_{20}NO]$ $[M+H]^+$: 338.1539, found: 338.1533.



(E)-2-benzyl-5-(phenylethynyl)-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3ba): Synthesized by following general procedure on a 0.05 mmol scale, Isolated yield = 19 mg (86%); Yellow solid; Mp: 131-134 °C*;* ^{1}H NMR (600 MHz, DMSO-d_6 δ): 8.69 (d, J =16.2 Hz, 1H), 8.06 (d, J =8.4 Hz, 1H), 7.81 (d, J =16.2 Hz, 1H), 7.76 – 7.73 (m, 3H), 7.67 (d, J =7.8 Hz, 1H), 7.58 (d, J =7.8 Hz, 2H), 7.42 – 7.38 (m, 4H), 7.35 – 7.25 (m, 8H), 7.15 (d, J =7.8 Hz, 1H), 7.00 (d, J =16.2 Hz, 1H), 5.21 (s, 2H) ; ^{13}C NMR (150 MHz, DMSO-d_6 δ): 161.8, 139.4, 137.73, 137.66, 137.1, 136.3, 133.1, 132.8, 131.7, 130.6, 129.6, 128.75, 128.71, 128.66, 128.57, 128.0, 127.6, 127.4, 127.3, 127.0, 126.6, 125.8, 124.1, 122.9, 101.9, 51.2 ; IR (ZnSe):ν_{max}(cm^{-1}) 2918, 2848, 1647, 1616, 1494, 1448, 1365, 1261, 1176, 1074, 962, 812, 734, 688.; HRMS (ESI-TOF):m/z calcd for $[C_{32}H_{26}NO]$ $[M+H]^+$: 440.2009, found: 440.2009.

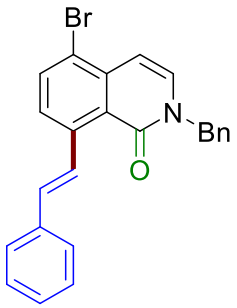


(E)-2-benzyl-5-(phenylethynyl)-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3ca):

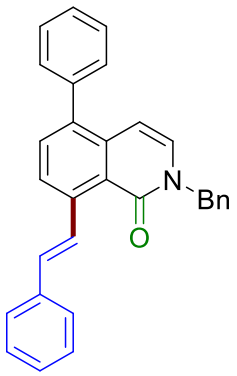


Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 25 mg (56%); white solid; Mp: 135-138°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.76 (d, J =16.2 Hz, 1H), 7.70 (d, J =7.2 Hz, 1H), 7.64 (d, J =7.2 Hz, 2H), 7.56 (d, J =7.8 Hz, 1H), 7.46 – 7.45 (m, 2H), 7.43 – 7.39 (m, 3H), 7.37 – 7.35 (m, 3H), 7.34 – 7.27 (m, 5H), 6.99 (d, J =7.8 Hz, 1H), 6.92 (d, J =16.2 Hz, 1H), 6.50 (d, J =7.8 Hz, 1H), 5.22 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 140.9, 139.9, 138.6, 138.1, 137.1, 136.6, 132.9, 131.24, 131.20, 130.6, 129.9, 128.9, 128.7, 128.6, 128.2, 128.0, 127.9, 127.7, 127.6, 127.1, 126.4, 123.9, 104.7, 51.5 ;IR (ZnSe):ν_{max}(cm^{-1}) 2918, 2848, 1647, 1616, 1494, 1448, 1365, 1261, 1176, 1074, 962, 812, 734, 688.; HRMS (ESI-TOF):m/z calcd for $[C_{32}H_{24}NO]$ $[M+Na]^+$: 460.1672, found: 460.1667.

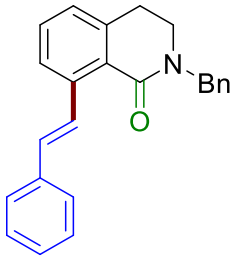
(E)-2-benzyl-5-bromo-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3da): Synthesized by following general procedure A on a 0.1 mmol scale, Isolated yield = 25 mg (60%); white solid; Mp: 110-112°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.61 (d, J =16.2 Hz, 1H), 7.85 (d, J =7.8 Hz, 1H), 7.60 (d, J =7.8 Hz, 2H), 7.48 (d, J =8.4 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.31 – 7.25 (m, 5H), 7.16 (d, J =7.8 Hz, 1H), 6.87 (dd, J =12.0, 4.2 Hz, 2H), 5.21 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, δ):162.3, 141.5, 137.8, 137.6, 136.7, 135.8, 132.7, 131.2, 130.4, 129.1, 128.8, 128.1, 128.0, 127.8, 127.1, 124.8, 120.0, 105.4, 51.8; IR (ZnSe):ν_{max}(cm^{-1}) 2924, 1764, 1651, 1620, 1494, 1454, 1359, 1269, 1197, 1105, 692.; HRMS (ESI-TOF):m/z calcd for $[C_{24}H_{19}BrNO]$ $[M+H]^+$: 416.0645, found: 416.0616.



(E)-2-benzyl-5-phenyl-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3ea): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 27 mg (66%); white solid; Mp: 96-99°C; ^{1}H NMR (600 MHz, DMSO-d_6 δ): 8.69 (d, J =16.2 Hz, 1H), 7.76 (d, J =7.8 Hz, 1H), 7.61 – 7.59 (m, 3H), 7.56 (d, J =7.2 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.46 (d, J =7.2 Hz, 1H), 7.44 – 7.38 (m, 4H), 7.35 – 7.26 (m, 6H), 7.00 (d, J =15.6 Hz, 1H), 6.43 (d, J =7.2 Hz, 1H), 5.18 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6 δ): 161.8, 139.6, 139.2, 138.0, 137.64, 137.60, 136.1, 129.6, 128.6, 127.7, 127.4, 126.6, 122.8, 103.0, 51.2 ; IR (ZnSe):ν_{max}(cm^{-1}) 1649, 1618, 1492, 1365, 1070, 954, 813, 725, 692; HRMS (ESI-TOF): m/z calcd for $[C_{24}H_{24}NO]$ $[M+H]^+$: 414.1852, found: 414.1830

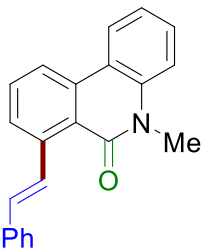


(E)-2-benzyl-8-styryl-3,4-dihydroisoquinolin-1(2H)-one (Scheme 3. entry 3fa): Synthesized

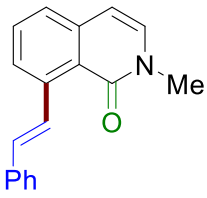


by following general procedure on a 0.1 mmol scale, Isolated yield = 17 mg (50%); Red viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.39 (d, J =16.2 Hz, 1H), 7.62 (d, J =7.8 Hz, 1H), 7.59 (d, J =7.8 Hz, 2H), 7.38 (t, J =7.8 Hz, 1H), 7.36 – 7.32 (m, 6H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H) 7.08 (d, J =7.2 Hz, 1H), 6.96 (d, J =16.2 Hz, 1H), 4.81 (s, 2H), 3.48 – 3.46 (m, 2H), 2.89 – 2.87 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 164.9, 140.3, 139.8, 138.0, 137.9, 131.2, 130.5, 129.6, 128.8, 128.7, 128.1, 127.60, 127.56, 127.1, 127.0, 126.7, 126.5, 50.5, 45.1, 29.8. δ IR (ZnSe):ν_{max}(cm^{-1}); 1635, 1587, 1477, 1444, 1340, 1244, 1028, 962, HRMS (ESI-TOF):m/z calcd for [$C_{24}H_{21}NO$] [M+Na] $^{+}$: 362.1515, found: 362.1498.

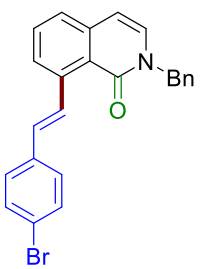
(E)-5-methyl-7-styrylphenanthridin-6(5H)-one (Scheme 3. entry 3ga): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 17 mg (56%); Yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.61 (d, J =15.6 Hz, 1H), 8.29 (dd, J =7.8, 1.2 Hz, 1H), 8.27 (t, J =4.8 Hz, 1H), 7.73 – 7.72 (m, 2H), 7.64 (d, J =6.6 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.40 – 7.36 (m, 3H), 7.33 – 7.30 (m, 1H), 7.28 – 7.25 (m, 1H), 6.86 (d, J =27.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.3, 142.3, 138.2, 138.1, 135.1, 132.0, 131.7, 130.3, 129.9, 128.7, 128.5, 127.6, 127.1, 123.8, 122.9, 122.5, 121.5, 119.4, 114.9, 30.2.; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1618, 1585, 1494, 1363, 1263, 1244, 1028, 1002, 962, 948, 815, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{22}H_{17}NO$] [M+Na] $^{+}$: 334.1202, found: 334.1184



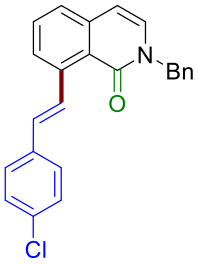
(E)-2-methyl-8-styrylisoquinolin-1(2H)-one (Scheme 3. entry 3ha): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 11 mg (42%); White solid; Mp: 112-115°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.75 (d, J =16.2 Hz, 1H), 7.64 – 7.62 (m, 3H), 7.59 – 7.57 (m, 1H), 7.43 (d, J =7.8 Hz, 1H), 7.35 (t, J =7.8 Hz, 2H), 7.26 – 7.23 (m, 1H), 7.08 (d, J =7.2 Hz, 1H), 6.88 (d, J =16.2 Hz, 1H), 6.46 (d, J =7.2 Hz, 1H), 3.58 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ):163.4, 141.3, 139.0, 138.0, 132.6, 131.7, 130.9, 130.7, 128.7, 127.6, 127.1, 126.4, 125.9, 123.2, 106.4, 37.7; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1618, 1585, 1494, 1363, 1263, 1244, 1028, 1002, 962, 948, 815, 790, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{18}H_{15}NO$] [M+Na] $^{+}$: 284.1046, found: 284.1030.



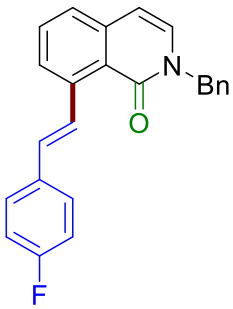
(E)-2-benzyl-8-(4-bromostyryl) isoquinolin-1(2H)-one (Scheme 3. entry 3ab): Synthesized by following general procedure A on a 0.1 mmol scale, Isolated yield = 32 mg (79%); Yellow solid; Mp: 96-99°C; ^{1}H NMR (600 MHz, DMSO-d_6 δ): 8.70 (d, J =16.2 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.60 – 7.56 (m, 4H), 7.51 (d, J =8.4 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.26 – 7.23 (m, 1H), 6.94 (d, J =10.8 Hz, 1H), 6.65 (d, J =7.2 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d_6 δ): 161.7, 139.7, 138.8, 137.8, 136.9, 133.2, 131.9, 131.6, 131.2, 128.58, 128.54, 127.4, 127.3, 126.5, 125.8, 122.2, 120.5, 105.8, 51.2; IR (ZnSe):ν_{max}(cm^{-1}) 2924, 2852, 1764, 1645, 1614, 1494, 1471, 1454, 1361, 1263, 1105, 956, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{21}H_{18}BrNO$] [M+Na] $^{+}$: 438.0464, found: 438.0442.



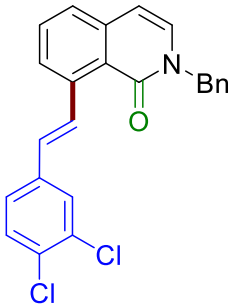
(E)-2-benzyl-8-(4-chlorostyryl) isoquinolin-1(2H)-one (Scheme 3. entry 3ac): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 26 mg (70%); White solid; Mp: 110-113°C; ^{1}H NMR (600 MHz, DMSO-d$_6$ δ): 8.67 (d, J =19.2 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.59 – 7.57 (m, 4H), 7.43 (d, J =8.4 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.25 (t, J =7.2, 1H), 6.95 (d, J =16.2 Hz, 1H), 6.65 (d, J =7.2 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$, δ): 162.9, 141.2, 138.9, 137.1, 136.6, 133.1, 131.9, 131.6, 131.5, 129.4, 128.8, 128.3, 127.9, 126.6, 126.2, 123.5, 106.8, 51.7; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1616, 1489, 1365, 1278, 815, 725, 690.; HRMS (ESI-TOF):m/z calcd for [$C_{24}H_{19}ClNO$] [M+H] $^{+}$: 372.1150, found: 372.1130.



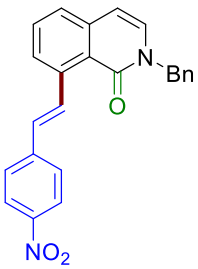
(E)-2-benzyl-8-(4-fluorostyryl) isoquinolin-1(2H)-one (Scheme 3. entry 3ad): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 22 mg (62%);Yellow viscous liquid; ^{1}H NMR (600 MHz, CDCl$_3$, δ): 8.75 (d, J =16.2 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.42 (d, J =7.2 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.31 – 7.28 (m, 3H), 7.25 – 7.23 (m, 1H), 7.05 (d, J =7.2 Hz, 1H), 6.90 (d, J =16.2 Hz, 1H), 6.45 (d, J =7.2 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (150 MHz, CDCl$_3$, δ): 162.9, 161.7 (d, J_{C-F} = 259.5 Hz), 141.7, 138.8, 138.0, 137.2, 131.9, 131.5, 130.9 (J_{C-F} = 16.5 Hz), 128.9, 128.7, 127.9 (J_{C-F} = 12Hz), 127.6, 127.1, 126.6, 126.0, 123.5, 106.8, 51.6; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1620, 1585, 1494, 1363, 1263, 1244, 962, 948, 815, 721, 692, 615.;HRMS (ESI-TOF):m/z calcd for [$C_{21}H_{18}FNO$] [M+Na] $^{+}$: 378.1265, found: 378.1250.



(E)-2-benzyl-8-(3,4-dichlorostyryl) isoquinolin-1(2H)-one (Scheme 3. entry 3ae): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 13.4 mg (33%); yellow solid; Mp: 96-99°C; ^{1}H NMR (600 MHz, DMSO-d$_6$ δ): 8.69 (d, J = 16.2 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.65 – 7.62 (m, 2H), 7.61 – 7.57 (m, 2H), 7.34 – 7.25 (m, 5H), 6.94 (d, J = 16.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 1H), 5.18 (s, 2H).; ^{13}C NMR (150 MHz, DMSO-d$_6$ δ): 161.8, 139.3, 138.8, 138.5, 137.7, 133.3, 132.7, 132.0, 131.4, 130.9, 128.6, 128.3, 127.4, 127.2, 126.7, 126.4, 126.0, 122.3, 105.8, 51.2; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1616, 1587, 1477, 1444, 1340, 1244, 1028, 962, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{24}H_{18}Cl_2NO$] [M+H]$^{+}$: 406.0760, found: 406.0758.

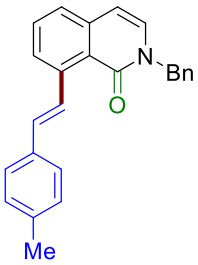


(E)-2-benzyl-8-(4-nitrostyryl) isoquinolin-1(2H)-one (Scheme 3. entry 3af): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 30 mg (78%); yellow solid; Mp: 149-152°C; ^{1}H NMR (600 MHz, DMSO-d$_6$ δ): 8.89 (d, J =16.2 Hz, 1H), 8.26 (d, J =8.4 Hz, 2H), 7.83 (d, J =8.4 Hz, 2H), 7.75 – 7.71 (m, 2H), 7.66 (d, J =7.2Hz, 1H), 7.62 (d, J =7.2 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.26 (t, J =7.2 Hz, 1H), 7.11 (d, J =16.2 Hz, 1H), 6.69 (d, J =7.2 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (150 MHz, DMSO-d$_6$ δ): 162.8, 146.8, 144.6, 140.4, 138.9, 136.9, 135.9, 132.0, 131.8, 129.0, 128.1, 128.0, 127.9, 127.5, 127.0, 126.8, 124.2, 123.7, 106.8, 51.8. IR (ZnSe): ν_{max}(cm^{-1}) 1651,



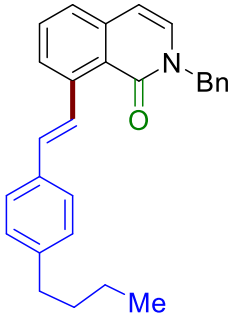
1622, 1589, 1506, 1332, 1249, 1105, 964, 719, 690.; HRMS (ESI-TOF):m/z calcd for $[C_{24}H_{19}N_2O]$ $[M+H]^+$: 383.1390, found: 383.1362.

(E)-2-benzyl-8-(4-methylstyryl)isoquinolin-1(2H)-one (Scheme 3. entry 3ag): Synthesized



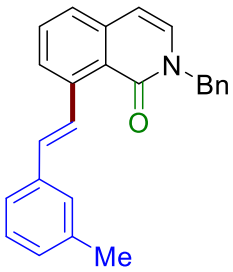
by following general procedure A on a 0.1 mmol scale, Isolated yield = 21 mg (61%); Yellow solid; Mp: 78-81°C*;* ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.72 (d, *J* =16.2 Hz, 1H), 7.66 (d, *J* =7.8 Hz, 1H), 7.58 (t, *J* =7.8 Hz, 1H), 7.51 (d, *J* =7.8 Hz, 2H), 7.40 (d, *J* =7.2 Hz, 1H), 7.33 – 7.28 (m, 5H), 7.15 (d, *J* =7.8 Hz, 2H), 7.05 (d, *J* =7.2 Hz, 1H), 6.88 (d, *J* =16.2 Hz, 1H), 6.45 (d, *J* =7.2 Hz, 1H), 5.22 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 141.8, 138.8, 137.2, 135.3, 131.9, 131.4, 130.9, 129.8, 129.4, 128.9, 127.95, 127.86, 127.1, 126.5, 125.8, 106.8, 51.6, 21.4.; IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1618, 1585, 1494, 1363, 1263,1244, 1028, 1002, 962, 815, 695.; HRMS (ESI-TOF):m/z calcd for $[C_{25}H_{21}NO]$ $[M+Na]^+$: 374.1515, found: 374.1497.

(E)-2-benzyl-8-(4-butylstyryl)isoquinolin-1(2H)-one (Scheme 3. entry 3ah): Synthesized by



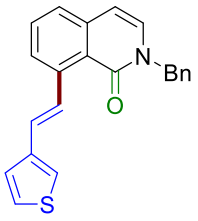
following general procedure on a 0.1 mmol scale, Isolated yield = 9 mg (24%); yellow viscous liquid*;* ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.73 (d, *J* =16.2 Hz, 1H), 7.66 (d, *J* =7.2 Hz, 1H), 7.58 (t, *J* =7.8 Hz, 1H), 7.54 (d, *J* =7.8 Hz, 2H), 7.40 (d, *J* =7.8 Hz, 1H), 7.35-7.28 (m, 5H), 7.17 (d, *J* =8.4 Hz, 2H), 7.05 (d, *J* =7.2 Hz, 1H), 6.89 (d, *J* =16.2 Hz, 1H), 6.44 (d, *J* =7.2 Hz, 1H), 5.22 (s, 2H), 2.62 (t, *J* =7.8 Hz, 2H), 1.62 – 1.60 (m, 2H), 1.39-1.34 (m, 2H), 0.95 – 0.93 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 142.5, 141.8, 138.8, 137.2, 135.5, 131.9, 131.4, 130.9, 129.9, 128.9, 128.8, 127.9, 127.8, 127.1, 126.5, 125.8, 123.4, 106.8, 51.6, 35.6, 33.8, 22.5, 14.1. IR (ZnSe):ν_{max}(cm^{-1}) 1649, 1618, 1587, 1365, 1244, 960, 825, 788, 727, 692.; HRMS (ESI-TOF):m/z calcd for $[C_{28}H_{28}NO]$ $[M+H]^+$: 394.2165, found: 394.2163.

(E)-2-benzyl-8-(3-methylstyryl)isoquinolin-1(2H)-one (Scheme 3. entry 3ai): Synthesized



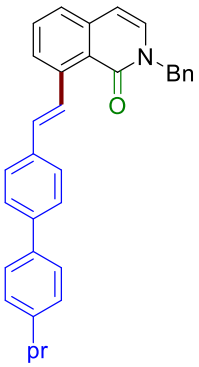
by following general procedure on a 0.1 mmol scale, Isolated yield = 22 mg (62%); white solid; Mp: 98-101°C*;* ^{1}H NMR (600 MHz, DMSO-d_6 δ): 8.67 (d, *J* =16.2 Hz, 1H), 7.68 (dd, *J* =7.8 Hz, 2H), 7.59 – 7.58 (m, 2H), 7.38 (s, 1H), 7.37 – 7.25 (m, 7H), 7.10 (d, *J* =7.2 Hz, 1H), 6.93 (d, *J* =16.2 Hz, 1H), 6.65 (d, *J* =7.8 Hz, 1H), 5.18 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 161.8, 140.1, 138.8, 137.8, 137.7, 137.5, 131.9, 130.1, 128.6, 127.4, 127.1, 126.2, 125.7, 124.0, 122.2, 105.8, 51.1, 21.1. IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1618, 1585, 1494, 1363, 1263, 1244, 1028, 1002, 962, 815, 790, 692.; HRMS (ESI-TOF):m/z calcd for $[C_{25}H_{22}NO]$ $[M+H]^+$: 352.1696, found: 352.1678.

(E)-2-benzyl-8-(2-(thiophen-3-yl)vinyl)isoquinolin-1(2H)-oneone (Scheme 3. entry 3aj):

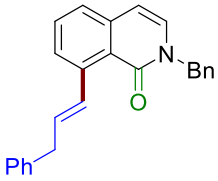


Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 13 mg (38%); brown viscous liquid*;* ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.60 (d, *J* =15.6 Hz, 1H), 7.62 (d, *J* =7.8 Hz, 1H), 7.57 (t, *J* =7.8 Hz, 1H), 7.49 (dd, *J* =4.8, 1.2 Hz, 1H), 7.40 (d, *J* =7.8 Hz, 1H), 7.36 - 7.32 (m, 3H), 7.30 - 7.27 (m, 5H), 7.05 (d, *J* =7.2 Hz, 1H), 6.92 (d, *J* =16.2 Hz, 1H), 6.45 (d, *J* =7.2 Hz, 1H), 5.21 (s, 2H) ; ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 141.6, 140.9, 138.8, 137.2, 131.9, 131.5, 130.9, 128.9, 127.94, 127.87, 126.4, 125.96, 125.88,

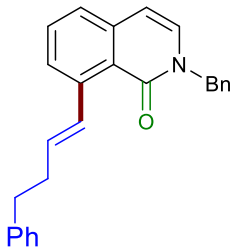
122.5, 106.8, 51.6. IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1616, 1365, 1261, 1070, 1028, 956, 725, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{22}H_{17}NOS$] [M+Na] $^{+}$: 366.0923, found: 366.0906.

(E)-2-benzyl-8-(2-(4'-propyl-[1,1'-biphenyl]-4-yl)vinyl)isoquinolin-1(2H)-one (Scheme 3. entry 3ak): 

Synthesized by following general procedure A on a 0.1 mmol scale, Isolated yield = 29 mg (64%); White solid; Mp: 145-148°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.80 (d, J =16.2 Hz, 1H), 7.68 (d, J =8.4 Hz, 3H), 7.61-7.58 (m, 3H), 7.55 (d, J =8.4 Hz, 2H), 7.42 (d, J =7.2 Hz, 1H), 7.35-7.28 (m, 5H), 7.26-7.25 (m, 2H), 7.07 (d, J =7.2 Hz, 1H), 6.94 (d, J =16.2 Hz, 1H), 6.46 (d, J =7.2 Hz, 1H), 5.23 (s, 2H), 2.65 – 2.62 (m, 2H), 1.72-1.65 (m, 2H), 0.98 (t, J =7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 141.9, 141.7, 140.3, 138.9, 138.4, 137.2, 136.9, 131.9, 131.5, 130.8, 130.5, 129.0, 128.9, 127.96, 127.88, 127.5, 127.2, 126.9, 126.6, 125.9, 123.5, 106.8, 51.6, 37.9, 24.7, 14.0. IR (ZnSe):ν_{max}(cm^{-1}) 1647, 1620, 1585, 1494, 1363, 1263, 1028, 1002, 962, 815, 790, 692.; HRMS (ESI-TOF):m/z calcd for [$C_{33}H_{30}NO$] [M+H] $^{+}$: 456.2322, found: 456.2294.

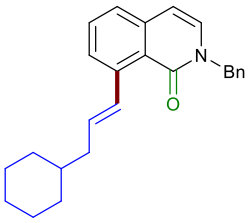
(E)-2-benzyl-8-(3-phenylprop-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3al): 

Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 20 mg (58%); yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.08 (d, J =15.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.38 – 7.34 (m, 4H), 7.32 – 7.28 (m, 6H), 7.23 – 7.20 (m, 1H), 7.05 (d, J =7.2 Hz, 1H), 6.43 (d, J =7.2 Hz, 1H), 6.15 – 6.09 (m, 1H), 5.22 (s, 2H), 3.68 (d, J =7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 141.7, 140.9, 138.6, 137.2, 133.0, 131.8, 131.3, 130.9, 129.3, 128.94, 128.90, 128.8, 128.6, 128.2, 128.1, 127.9, 127.8, 127.1, 126.1, 125.6, 123.2, 106.8, 51.7, 39.8.; IR (ZnSe):ν_{max}(cm^{-1}) 3026, 1649, 1614, 1589, 1492, 1363, 1273, 1161, 1072, 960, 823, 790.; HRMS (ESI-TOF):m/z calcd for [$C_{25}H_{21}NO$] [M+Na] $^{+}$: 374.1515, found: 374.1497.

(E)-2-benzyl-8-(4-phenylbut-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3am): 

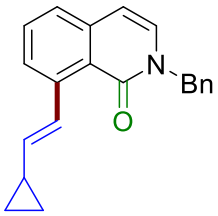
Synthesized by following general procedure A on a 0.1 mmol scale, Isolated yield = 19 mg (52%); yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.98 (d, J =15.6 Hz, 1H), 7.52 (t, J =7.8 Hz, 1H), 7.46 (d, J =7.2 Hz, 1H), 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 6H), 7.20 (t, J =7.2 Hz, 1H), 7.03 (d, J =7.2 Hz, 1H), 6.43 (d, J =7.2 Hz, 1H), 6.08 – 6.03 (m, 1H), 5.20 (s, 2H), 2.89 – 2.86 (m, 2H), 2.67 – 2.63 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 142.2, 142.0, 138.6, 137.2, 132.2, 131.9, 131.8, 131.3, 128.9, 128.7, 128.4, 127.9, 127.8, 127.0, 125.9, 125.5, 123.1, 106.8, 51.6, 36.0, 35.0. IR (ZnSe):ν_{max}(cm^{-1}) 2922, 2852, 1651, 1620, 1589, 1556, 1435, 1363, 1267, 1163, 958, 823, 788, 731.; HRMS (ESI-TOF):m/z calcd for [$C_{26}H_{23}NO$] [M+Na] $^{+}$: 388.1672, found: 388.1652

(E)-2-benzyl-8-(3-cyclohexylprop-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3an):



Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 24 mg (68%); yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.90 (d, J =15.6 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.35 – 7.27 (m, 6H), 7.02 (d, J =7.2 Hz, 1H), 6.41 (d, J =7.2 Hz, 1H), 6.03 (dt, J =15.6, 7.2 Hz, 1H), 5.19 (s, 2H), 2.22 (t, J =7.2 Hz, 2H), 1.81 (d, J =12.6 Hz, 2H), 1.73 – 1.71 (m, 2H), 1.65 (d, J =12.0 Hz, 1H), 1.49 – 1.42 (m, 1H), 1.29 – 1.15 (m, 4H), 1.03 – 0.96 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 142.3, 138.6, 137.3, 132.5, 131.80, 131.76, 131.2, 128.9, 127.9, 127.8, 126.9, 125.3, 123.1, 106.8, 51.6, 41.3, 38.5, 33.4, 26.8, 26.5. IR (ZnSe):ν_{max}(cm^{-1}) 2918, 2846, 1651, 1618, 1587, 1556, 1446, 1363, 1271, 1163, 1130, 1072, 962, 788, 731, 688.; HRMS (ESI-TOF):m/z calcd for $[C_{25}H_{27}NO]$ $[M+Na]^+$: 380.1985, found: 380.1963.

(E)-2-benzyl-8-(2-cyclopropylvinyl)isoquinolin-1(2H)-one (Scheme 3. entry 3ao):



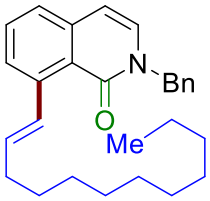
Synthesized by following general procedure A on a 0.1 mmol scale, Isolated yield = 17 mg (55%); yellow viscous liquid ^{1}H NMR (600 MHz, DMSO-d_6 δ): 7.94 (d, J =15.6 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.44 (dd, J =17.4, 7.8 Hz, 2H), 7.32 – 7.23 (m, 5H), 6.56 (d, J =7.2 Hz, 1H), 5.52 (dd, J =15.6, 9.0 Hz, 1H), 5.11 (s, 2H), 1.62 – 1.56 (m, 1H), 0.79 – 0.76 (m, 2H), 0.49 – 0.47 (m, 2H); ^{13}C NMR (150 MHz, DMSO-d_6 δ): 162.1, 140.9, 139.1, 138.3, 137.2, 133.3, 132.2, 129.0, 128.6, 127.9, 127.8, 125.8, 125.7, 121.9, 106.2, 51.7, 15.4, 7.7. IR (ZnSe):ν_{max}(cm^{-1}) 2924, 1764, 1647, 1620, 1494, 1473, 1454, 1361, 1271, 1147, 1076, 1024, 958, 650.; HRMS (ESI-TOF):m/z calcd for $[C_{21}H_{19}NO]$ $[M+Na]^+$: 324.1359, found: 324.1343.

(E)-2-benzyl-8-(oct-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3ap): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 14 mg (40%); yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.91 (d, J =15.6 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.35 – 7.27 (m, 6H), 7.02 (d, J =7.2 Hz, 1H), 6.41 (d, J =7.2 Hz, 1H), 6.05 – 6.00 (m, 1H), 5.22 (s, 2H), 2.33 – 2.29 (m, 2H), 1.55 – 150 (m, 2H), 1.41 – 1.29 (m, 6H), 0.91 – 0.89 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 138.6, 137.2, 133.3, 131.8, 131.5, 131.2, 128.9, 127.9, 127.8, 126.9, 125.3, 123.1, 106.8, 51.6, 33.4, 32.1, 29.82, 29.80, 29.71, 29.6, 29.5, 22.8, 14.3. IR (ZnSe):ν_{max}(cm^{-1}) 2922, 2852, 1651, 1622, 1454, 1365, 1267, 1161, 1070, 960, 835, 788. HRMS (ESI-TOF):m/z calcd for $[C_{24}H_{27}NO]$ $[M+Na]^+$: 368.1985, found: 368.1964.

(E)-2-benzyl-8-(non-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3aq): Synthesized by following general procedure on a 0.1 mmol scale, Isolated yield = 22 mg (62%); yellow viscous liquid ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.91 (d, J =15.6 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.35 – 7.25 (m, 6H), 7.02 (d, J =7.2 Hz, 1H), 6.41 (d, J =7.2 Hz, 1H), 6.05 - 6.00 (m, 1H), 5.19 (s, 2H), 2.33 – 2.29 (m, 2H), 1.55 – 1.50 (m, 2H), 1.38 – 1.29 (m, 8H), 0.90 – 0.88 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 142.3, 138.6, 137.2, 133.3, 131.8, 131.5, 131.2, 128.9, 127.9, 127.8, 126.9, 125.3, 123.1, 106.8, 51.6, 33.4, 32.0, 29.7,

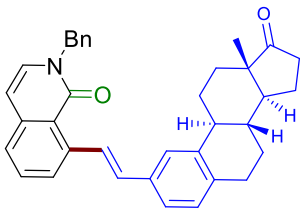
29.5, 29.4, 22.8, 14.3. IR (ZnSe):ν_{max}(cm^{-1}) 2922, 2852, 1651, 1620, 1589, 1454, 1363, 1269, 1163, 1029, 958, 839, 788.; HRMS (ESI-TOF):m/z calcd for [$C_{25}H_{30}NO$] [M+H] $^{+}$: 360.2322, found: 360.2318.

(E)-2-benzyl-8-(dodec-1-en-1-yl)isoquinolin-1(2H)-one (Scheme 3. entry 3ar): Synthesized



by following general procedure on a 0.1 mmol scale, Isolated yield = 18 mg (46%); yellow viscous liquid; ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.53 (d, *J* =15.6 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.35 – 7.27 (m, 7H), 7.02 (d, *J* =7.2 Hz, 1H), 6.42 (d, *J* =7.2 Hz, 1H), 6.05 – 5.99 (m, 1H), 5.22 (s, 2H), 2.32 – 2.29 (m, 2H), 1.54 – 1.49 (m, 2H), 1.30 – 1.25 (m, 13H), 0.89 – 0.86 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.9, 142.3, 138.6, 137.2, 133.3, 131.8, 131.5, 131.2, 128.9, 127.9, 127.8, 126.9, 125.3, 123.1, 106.8, 51.6, 33.4, 31.9, 29.6, 29.2, 22.8, 14.3. IR (ZnSe):ν_{max}(cm^{-1}) 2922, 2852, 1651, 1622, 1454, 1365, 1267, 1161, 1070, 960, 835, 788.; HRMS (ESI-TOF):m/z calcd for [$C_{28}H_{35}NO$] [M+Na] $^{+}$: 424.2611, found: 424.2581.

2-benzyl-8-((E)-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17 deca hydro-6H-cyclopenta[a]phenanthren-3-yl)vinyl)isoquinolin-1(2H)-one (Scheme 3. entry 3ia): Synthesized by following general procedure on a 0.1 mmol scale, a readily degradable product isolated in traces amount.^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.71 (d, *J* = 16.2 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.41 – 7.38 (m, 3H), 7.37 – 7.28 (m, 6H), 7.05 (d, J = 7.2 Hz, 1H), 6.85 (d, *J* = 16.2 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 5.22 (s, 2H), 2.96 – 2.94 (m, 2H), 2.54 – 2.43 (m, 3H), 2.36 – 1.96 (m, 9H), 1.44 – 1.43 (m, 1H), 0.92 (s, 3H). HRMS (ESI-TOF):m/z calcd for [$C_{36}H_{35}NO_2$] [M+Na] $^{+}$: 536.2560, found: 536.2523.

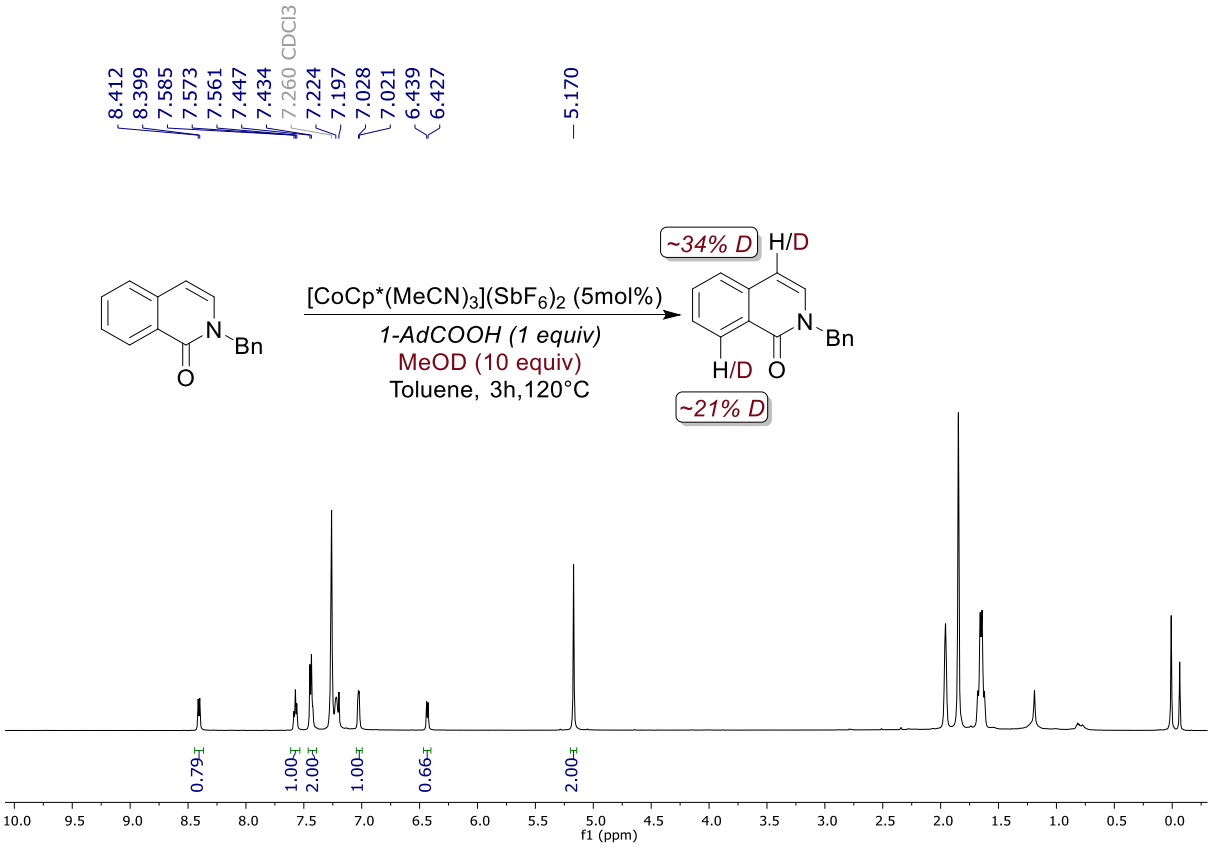


6. Mechanistic Study

6.1 Reversibility (Deuterium Scrambling) Experiments

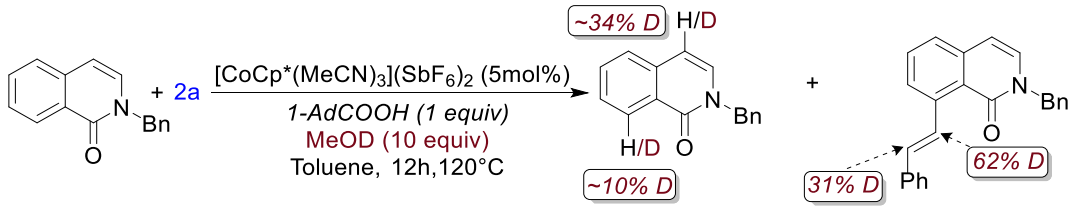
6.1.1 Without coupling partner

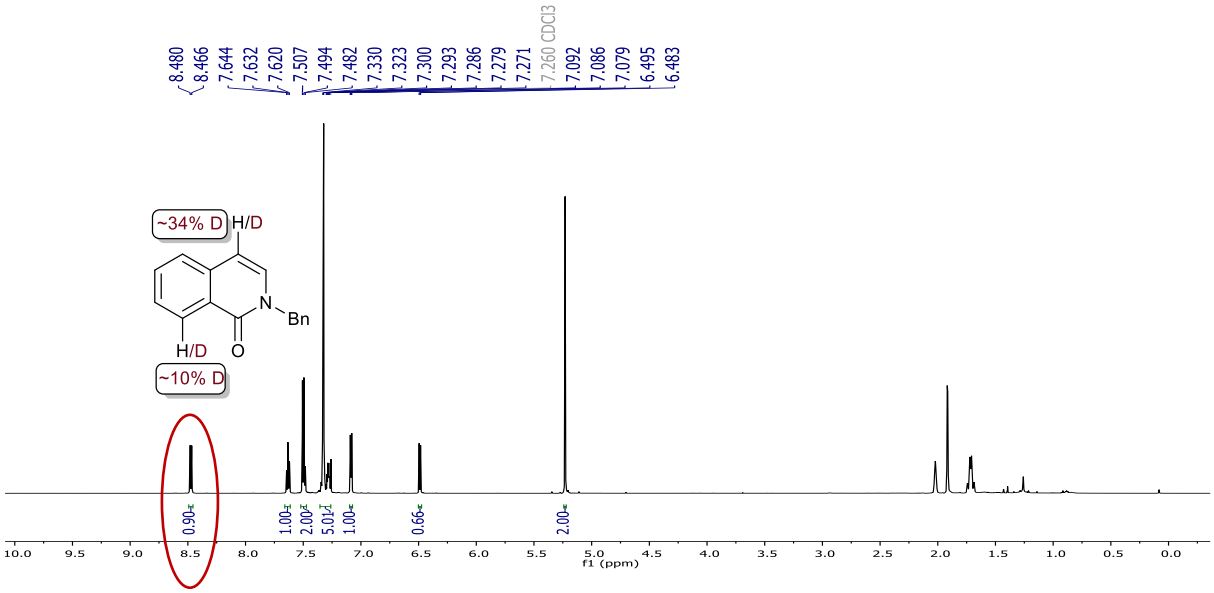
The substrate **1a** (0.05 mmol), $CoCp^*(MeCN)_3(SbF_6)_2$ (5 mol%) and 1-AdCOOH (1 equiv), MeOD (10 equiv) and Toluene (250 μL) were added to a screw-cap tube equipped with magnetic stirring bar under a argon atmosphere and the mixture was stirred at 120 °C for 3 h. The reaction mixture was then allowed to cool to room temperature. The deuterium incorporation was determined by ^{1}H NMR.

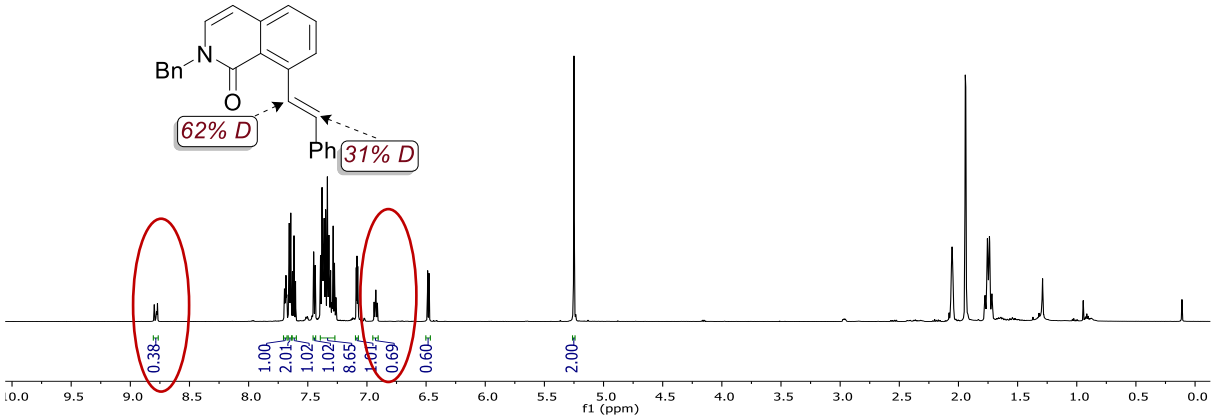


6.1.2. *Standard reaction*

The substrate **1a** (0.1 mmol), $CoCp^*(MeCN)_3(SbF_6)_2$ (5 mol%), **2a** 0.15 mmol), 1-AdCOOH (1 equiv) and MeOD (10 equiv) were added to a screw-cap tube equipped with magnetic stirring bar under argon atmosphere and the mixture was stirred at 120 °C for 12h. The reaction mixture was then allowed to cool to room temperature. The mixture was diluted with ethyl acetate (10 mL) and the organic layer was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give [D]-1a and [D]-3aa. The deuterium incorporation was determined by ^{1}H NMR.







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

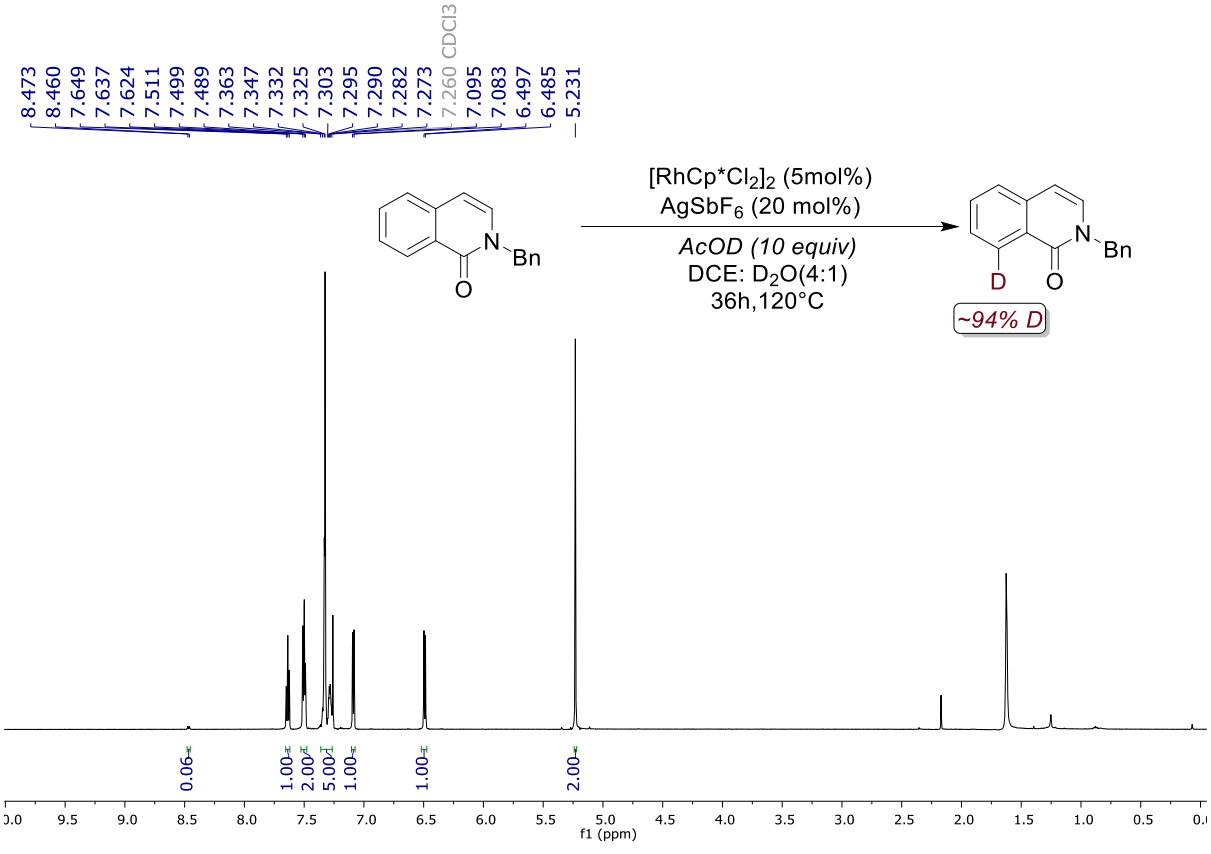
(i) The step accompanied C-H metalation is reversible in nature.

(ii) H/D exchange at the α-position of 3a is higher than *β*-position which suggest that the formation of linear product is favoured over the branched product.

6.2 Kinetic isotope effect experiments for alkenylation

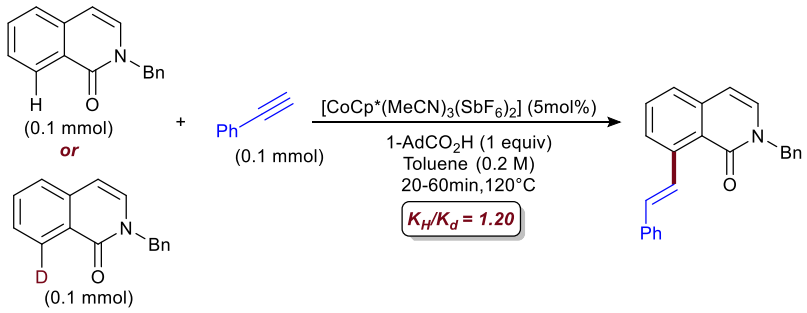
6.2.1 Synthesis of 1aa-d

1a (0.1 mmol × 3) was taken in 10 mL screw cap vial equipped with magnetic stirrer and dissolved in mixture of 0.5 ml of DCE: D_2O (4:1) and AcOD (10 equiv). $[Cp^*RhCl_2]_2$ (5 mol%), followed by $AgSbF_6$ (20 mol%) were added to the solution. The reaction mixture was stirred for 36 h at 120 °C. Next the reaction mixture was filtered through a short pad of silica gel, Deuterium incorporation was measured with help of ^1H NMR of isolated isoquinolone.



6.2.2 Determination of Kinetic Isotope Effect through parallel reactions:

In two different screwcapped vials with a stir bar separately placed **1a** and **8-d1- 1a'** (0.1 mmol), were reacted with alkyene **2a** (0.1 mmol) under standard reaction conditions. Yield of product in both reaction was analyzed at various interval by ^{1}H NMR.



Time	20 min	40 min	60 min
yield (1aa-d)	4	7	12
yield (1aa-H)	8	11	14

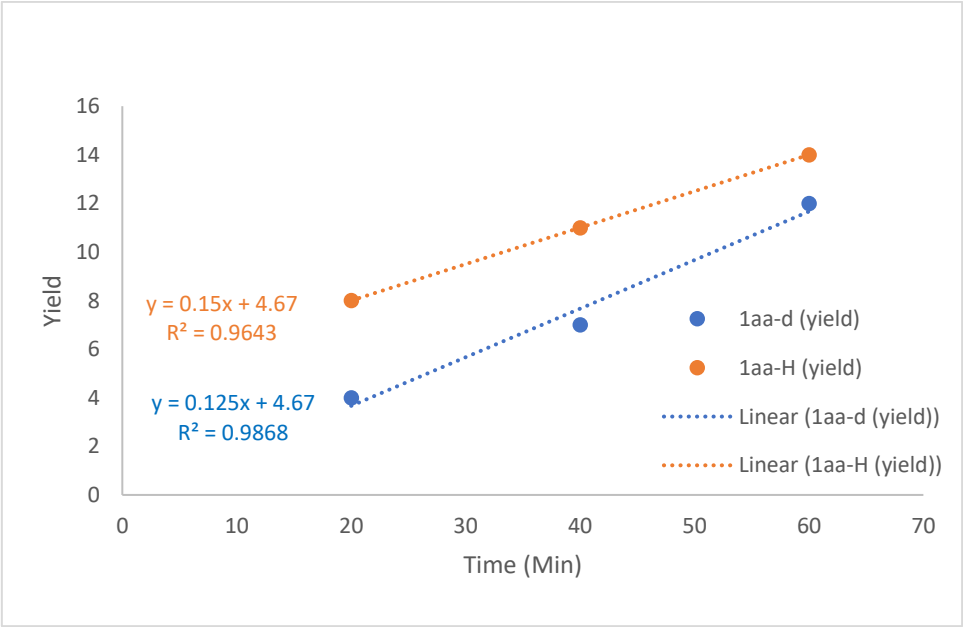
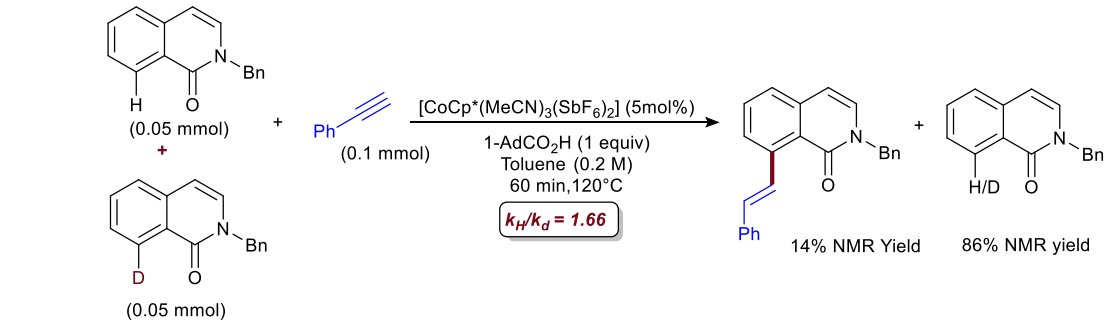


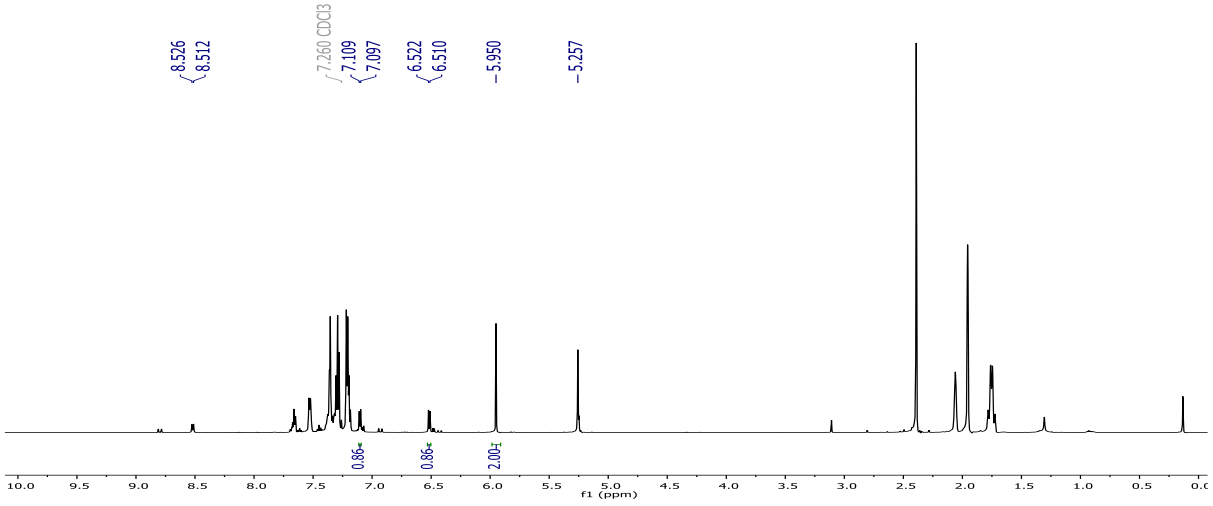
Fig S1: rate constant wrt to 1a and 8-d1-1a

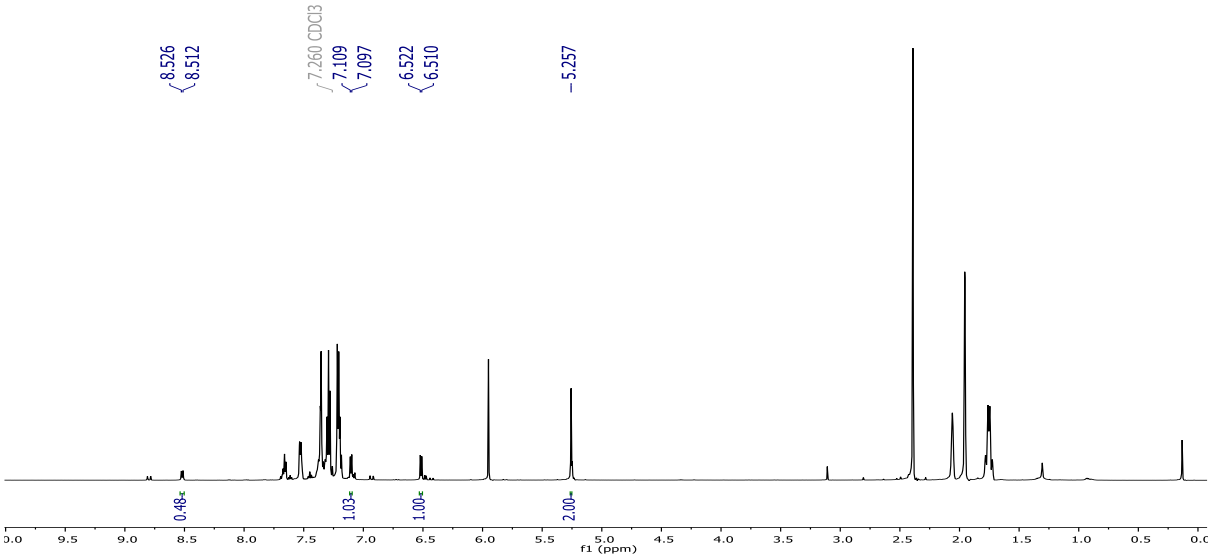
Conclusions: k_H/k_d =1.20 for parallel reactions

6.2.3 Determination of Kinetic Isotope Effect from an intermolecular competition experiment:

1a and **8-d1- 1a'** (1:1) (total 0.1 mmol), were reacted with alkyene **2a** (0.1 mmol) Consumption of starting material was estimated by NMR. After 60 minutes, residual starting material (mixture of **1a** and **8-d1- 1a'**) was 86%, which was analyzed by ^{1}H NMR spectrum. The k_H/k_d= 1.66 was calculated by ^{1}H NMR of the crude reaction mixture.







Conclusions: k_H/k_d =1.66 for competition experiment

6.3 Hammett Analysis of para-Substituted ethynylarene

All reactions were performed using the general procedure on 0.05 mmol scale. In five different reaction vials, under an argon atmosphere, five different substrates (-OMe, -Me, -Br, H and -F) (0.05 mmol), **2a** (0.075 mmol), $CoCp^*(MeCN)_3(SbF_6)_2$ (5 mol%), 1-AdCOOH (1 equiv) and toluene (250 μL) were added with the subsequent addition of *n*-decane (0.05 mmol) as an internal standard The reaction mixture was heated at 120 °C and the consumption of the substrate was monitored by GC at stipulated times. The initial slope method was used to calculate the rate constants.

Table: Datasheet for the Hammett analysis

	Ethynylbenzene	***p-Me-Ethynylbenzene***	***p-OMe-Ethynylbenzene***	***p-Br-Ethynylbenzene***	***p-F-Ethynylbenzene***
k_X	*0.003*	*0.0023*	*0.001*	*0.0063*	*0.0046*
k_X/k_H	*1*	*0.78*	*0.33*	*2.1*	*1.5*
$log(k_X/k_H)$	*0*	*-0.11*	*-0.47*	*0.32*	*0.18*
σ	*0*	*-0.14*	*-0.28*	*0.39*	*0.15*

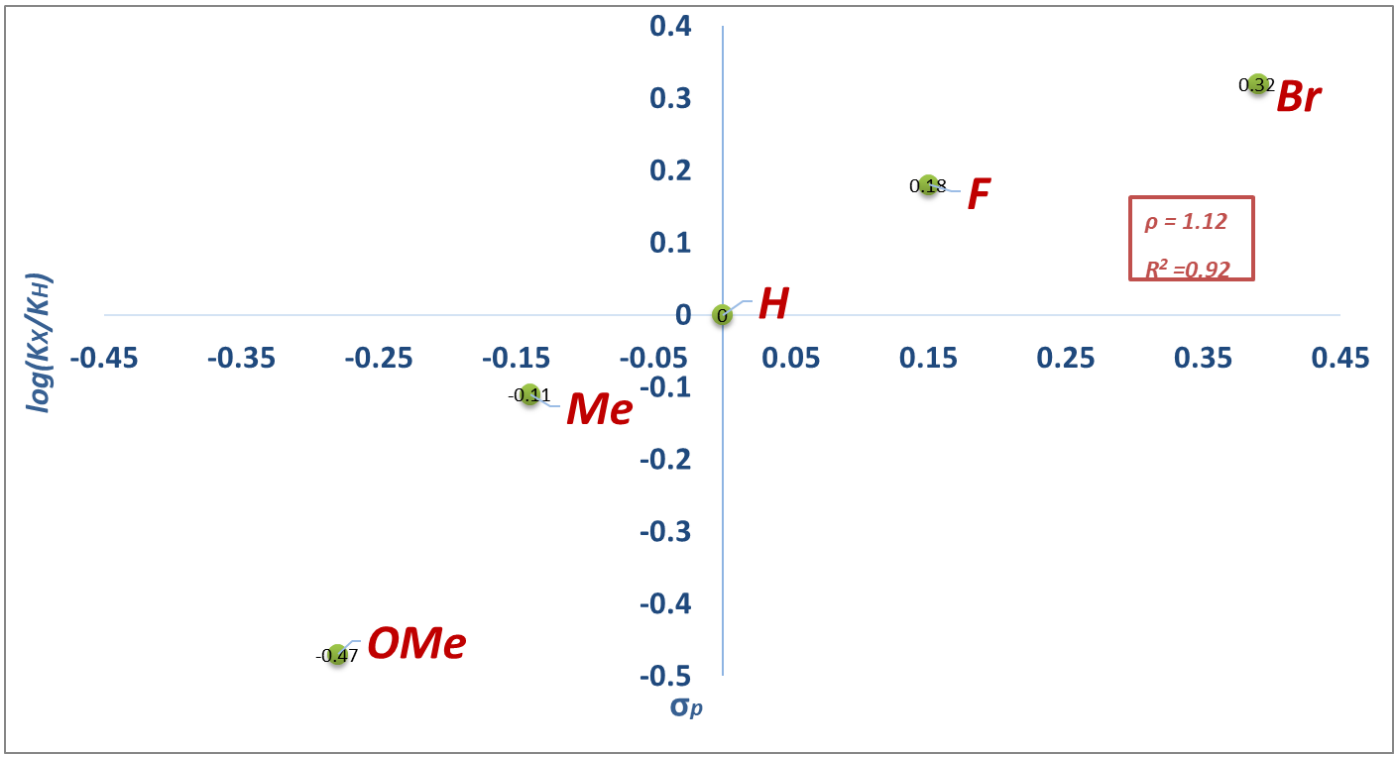
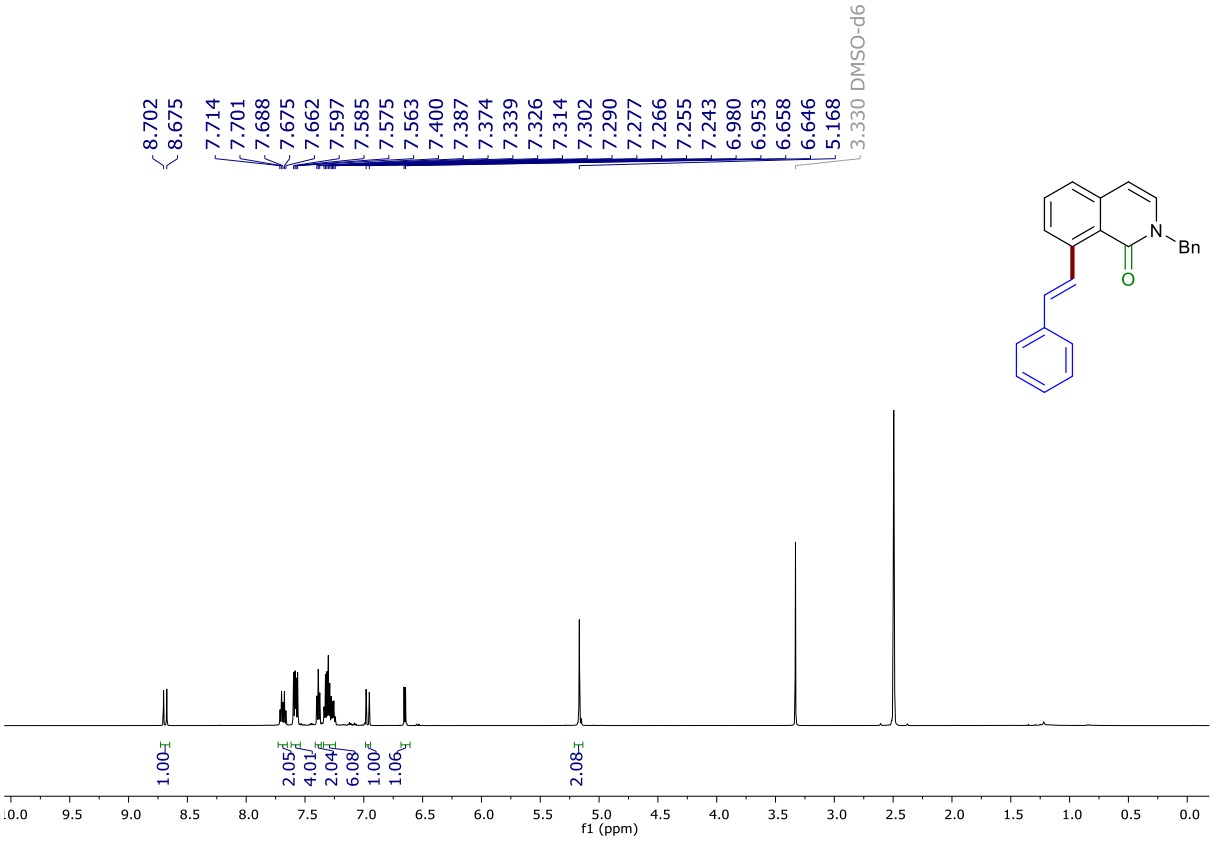


Fig S2: **Hammett plot of the reaction of different *p*-substituted ethynyl arene with 1a. observed rate constant are the calculated-on basis of disappearance of 1a**

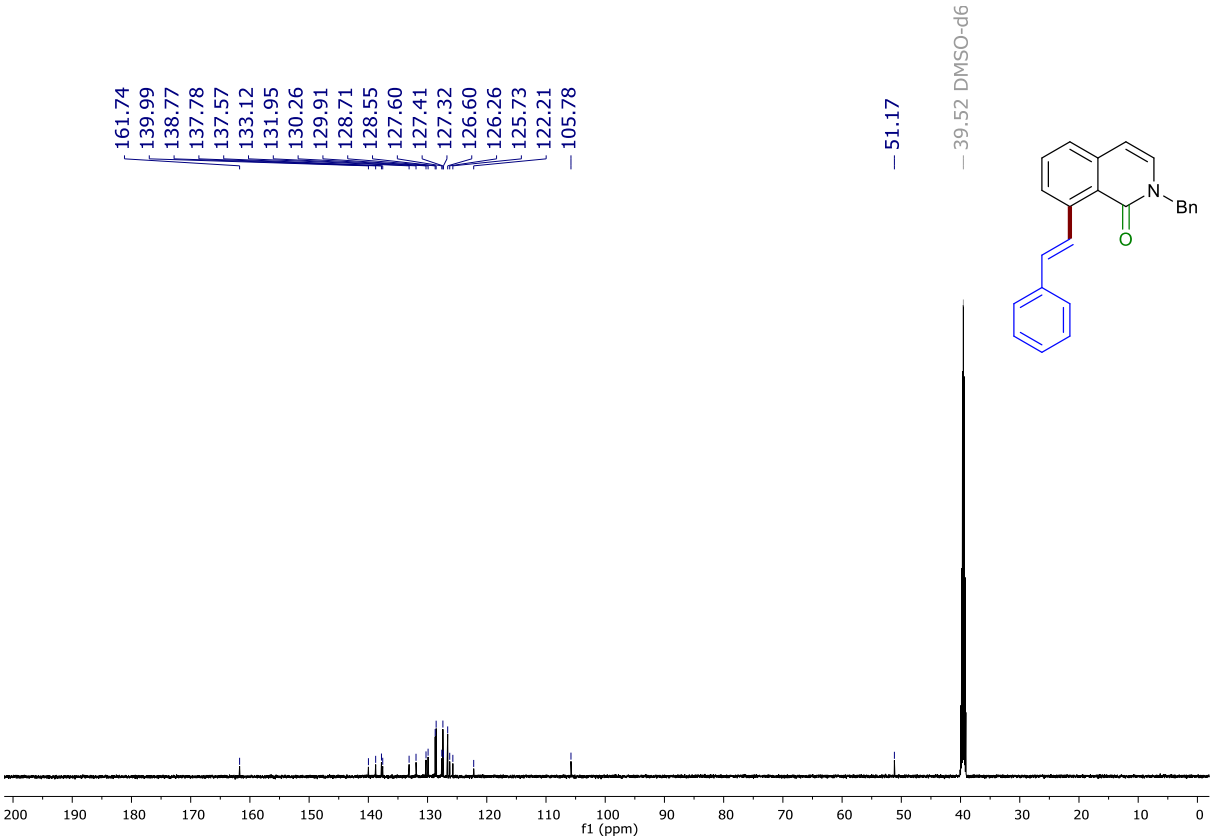
Conclusions: An electron-withdrawing group (EWG) in para-substituted ethynylarene facilitated the reaction.

7. Copy of ^{1}H and ^{13}C NMR

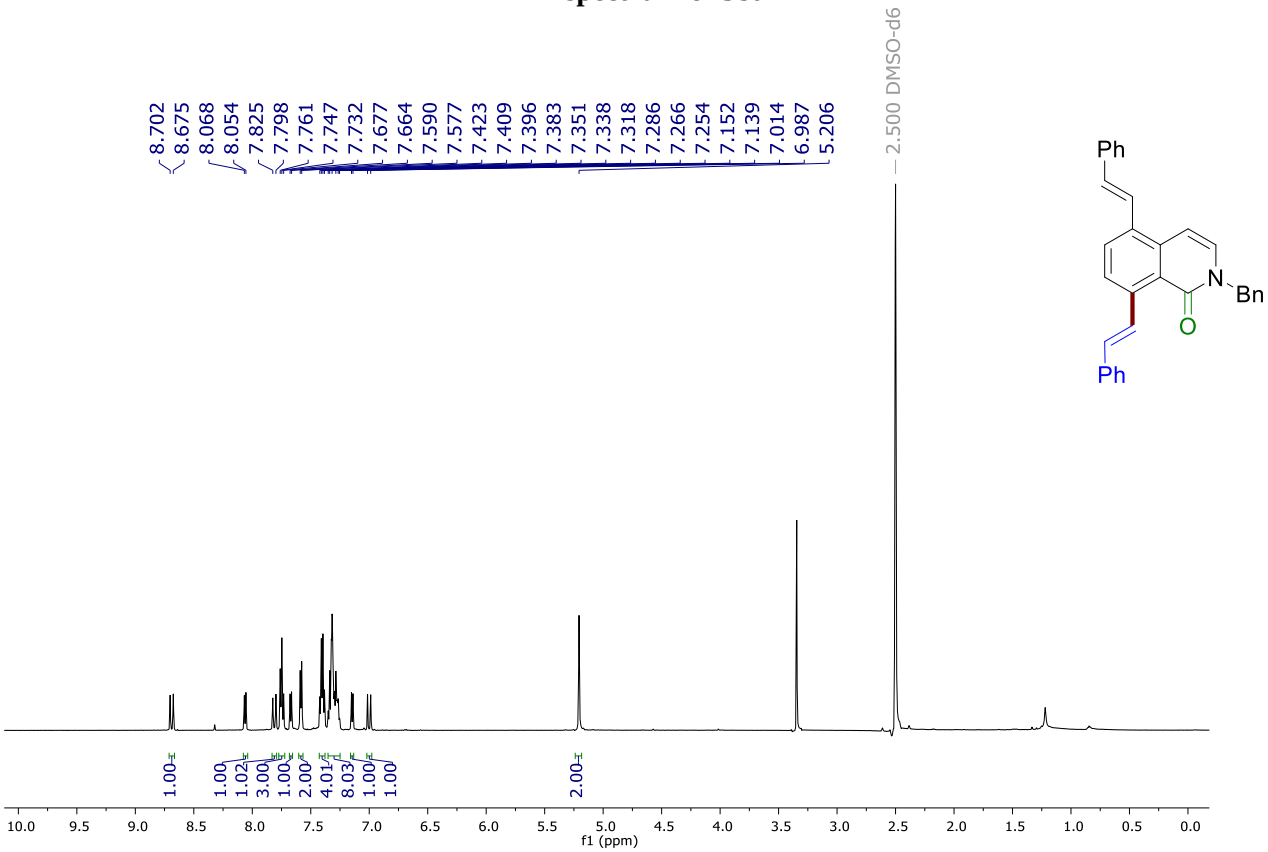
^{1}H-NMR spectrum of 3aa



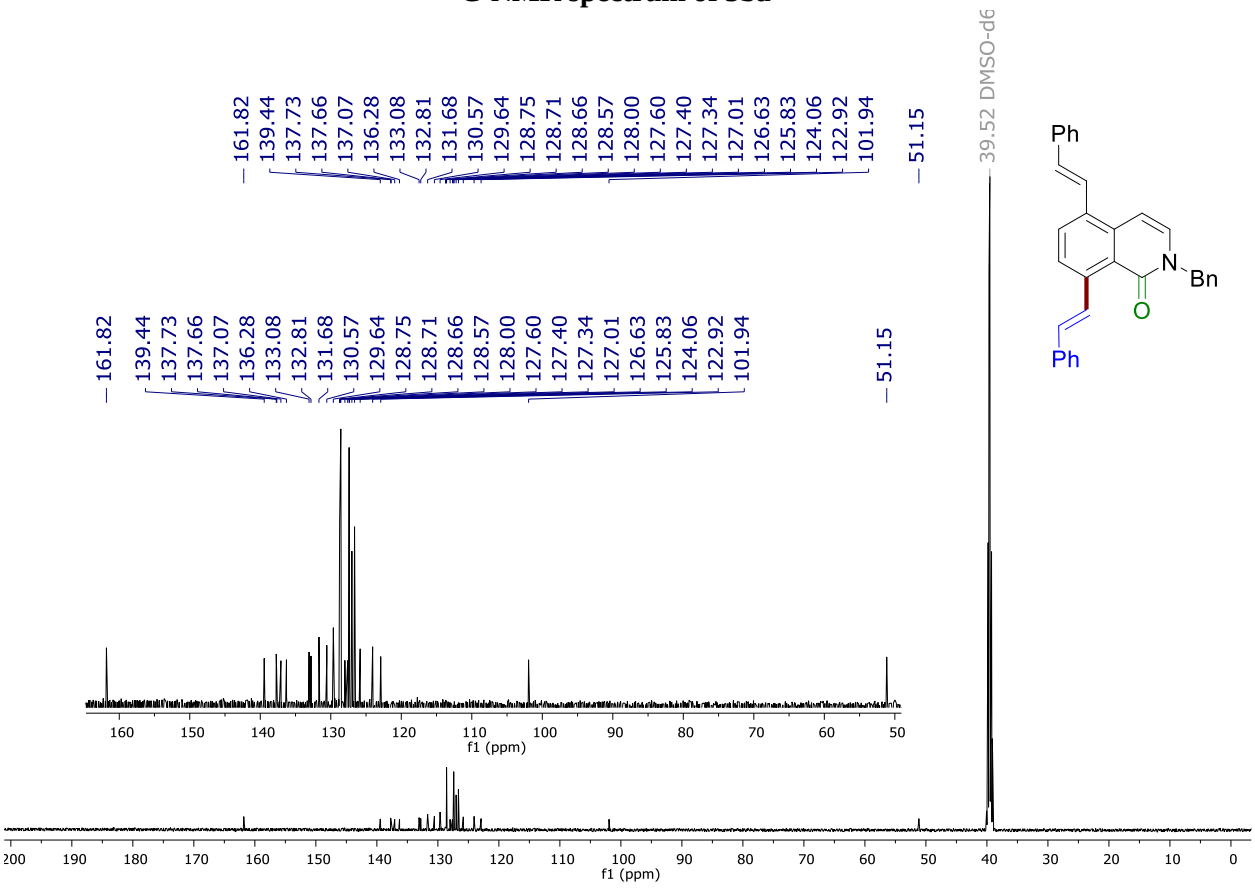
^{13}C-NMR spectrum of 3aa



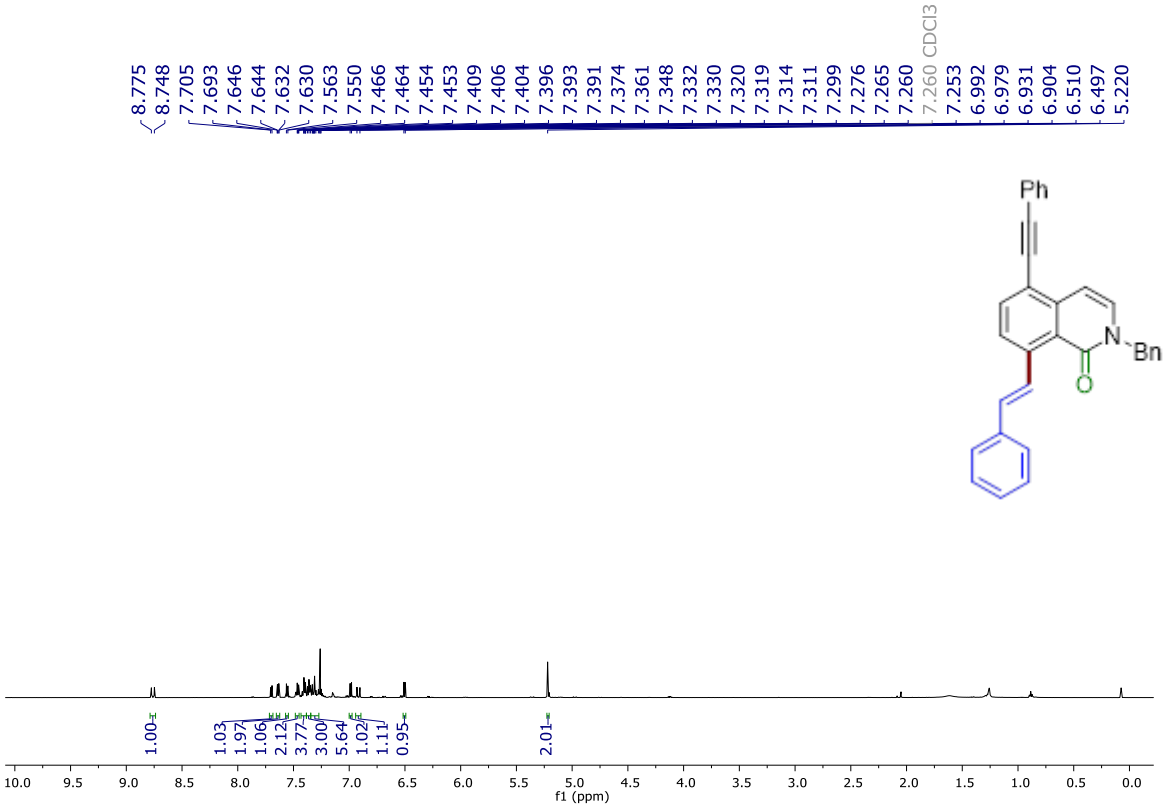
^{1}H-NMR spectrum of 3ba



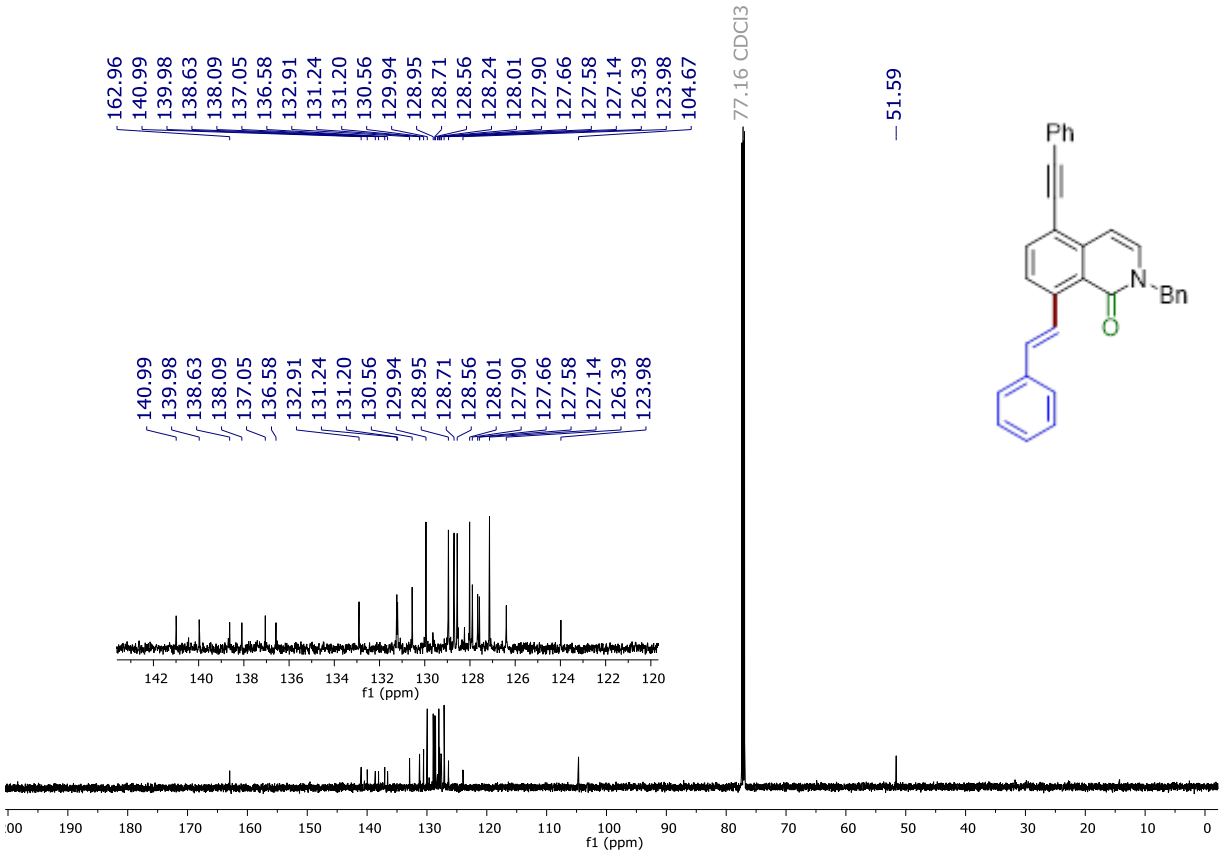
^{13}C-NMR spectrum of 3ba



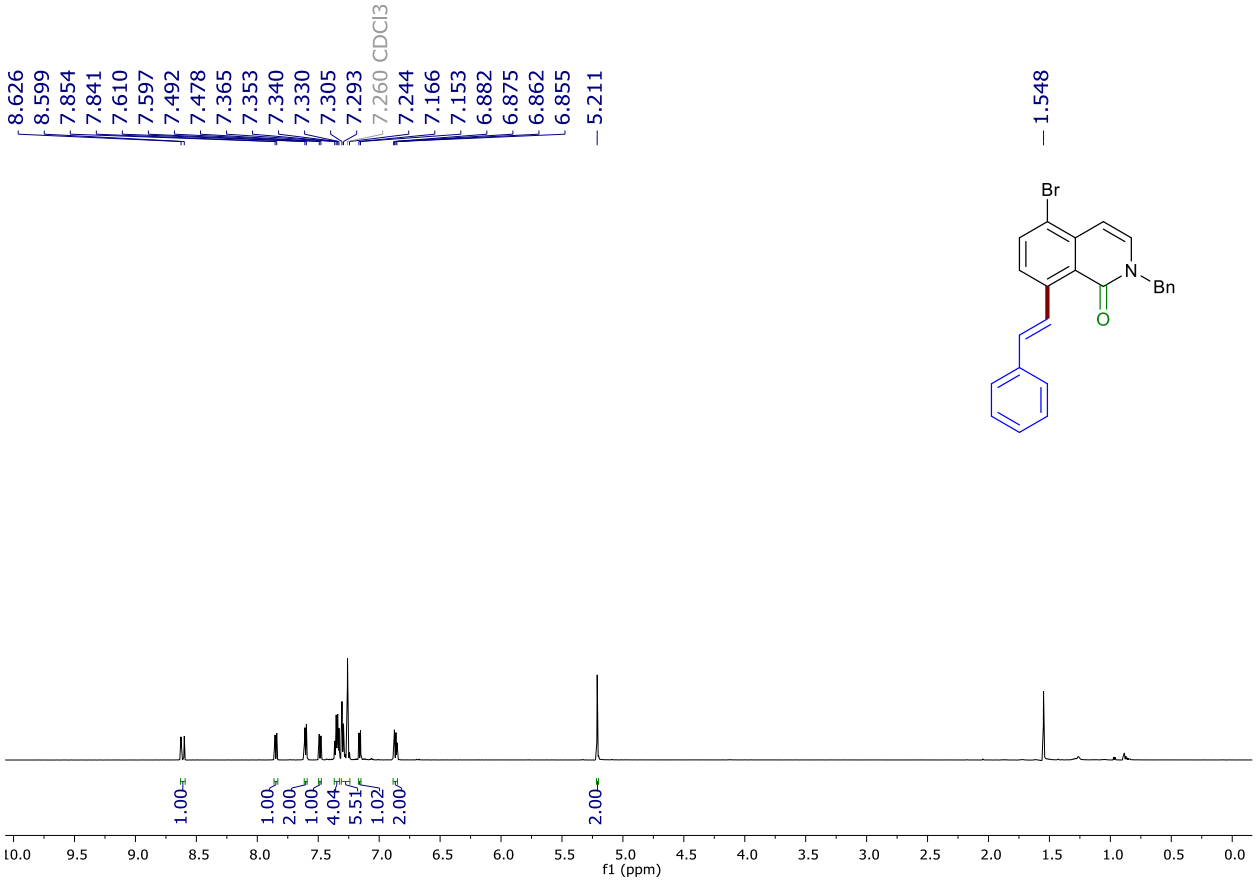
^{1}H-NMR spectrum of 3ca



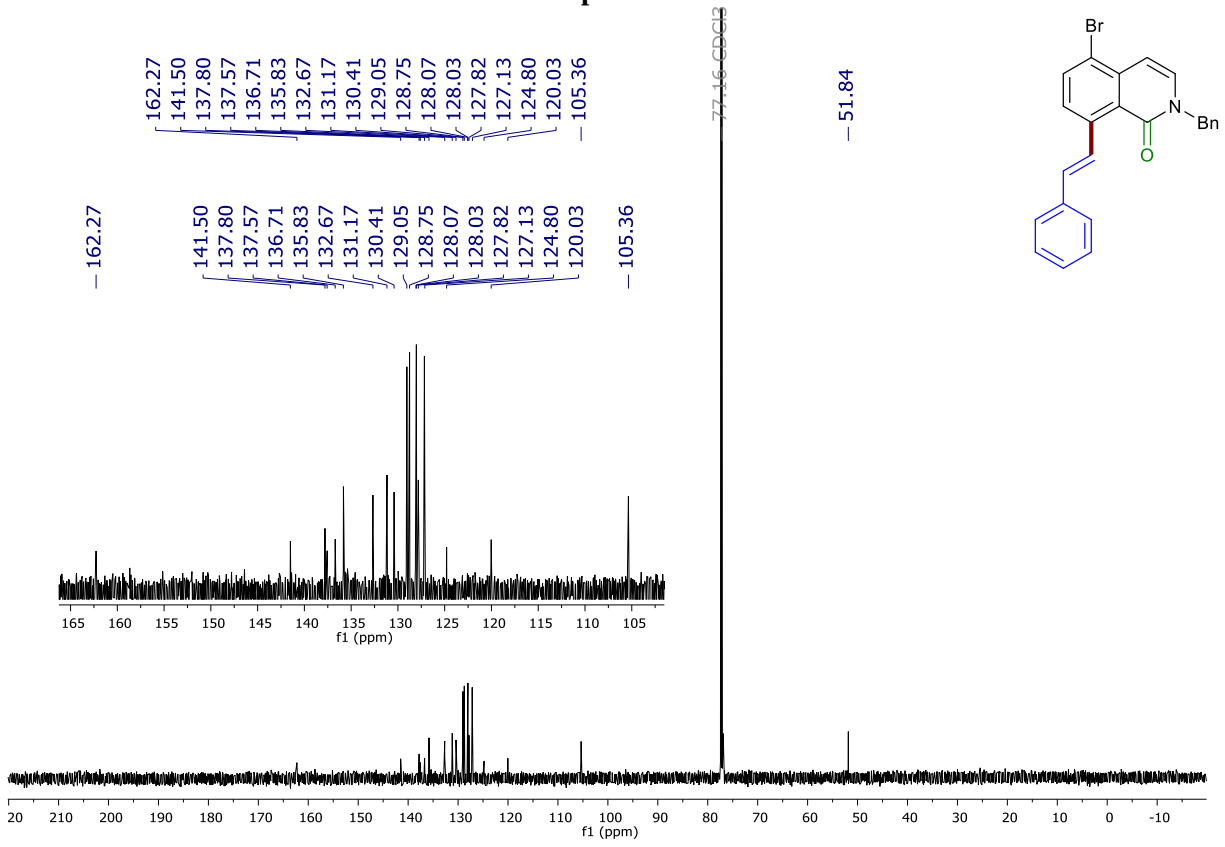
^{13}C-NMR spectrum of 3ca



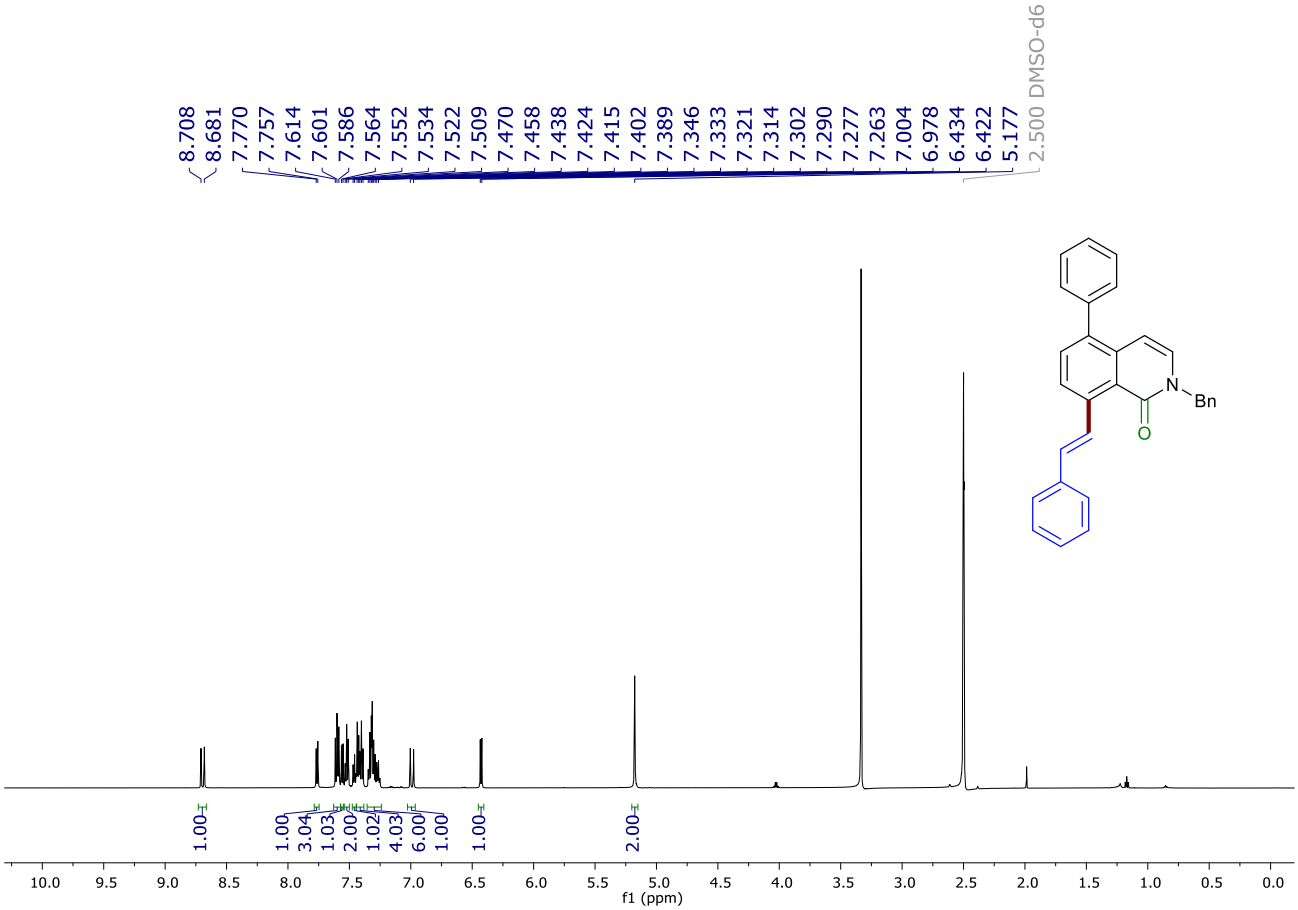
^{1}H-NMR spectrum of 3da



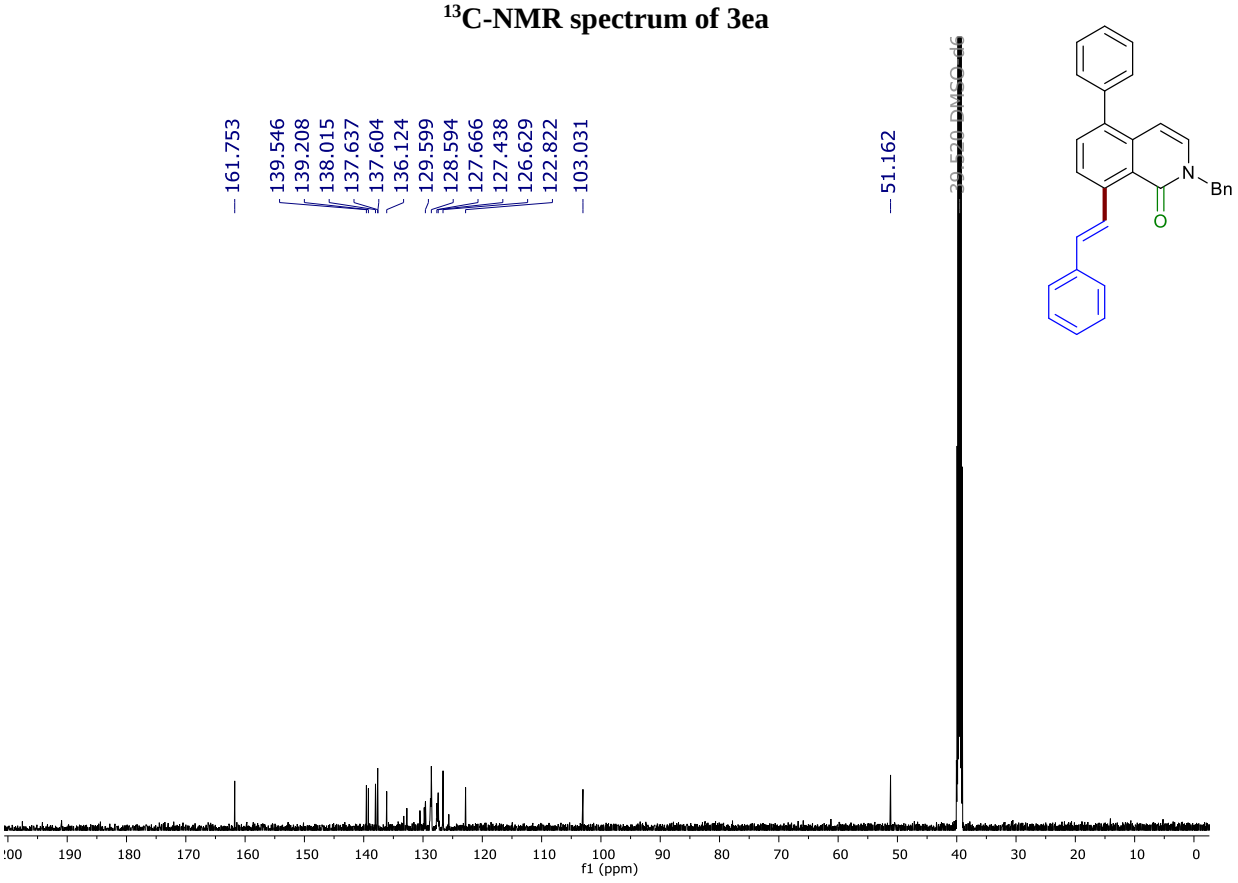
^{13}C-NMR spectrum of 3da



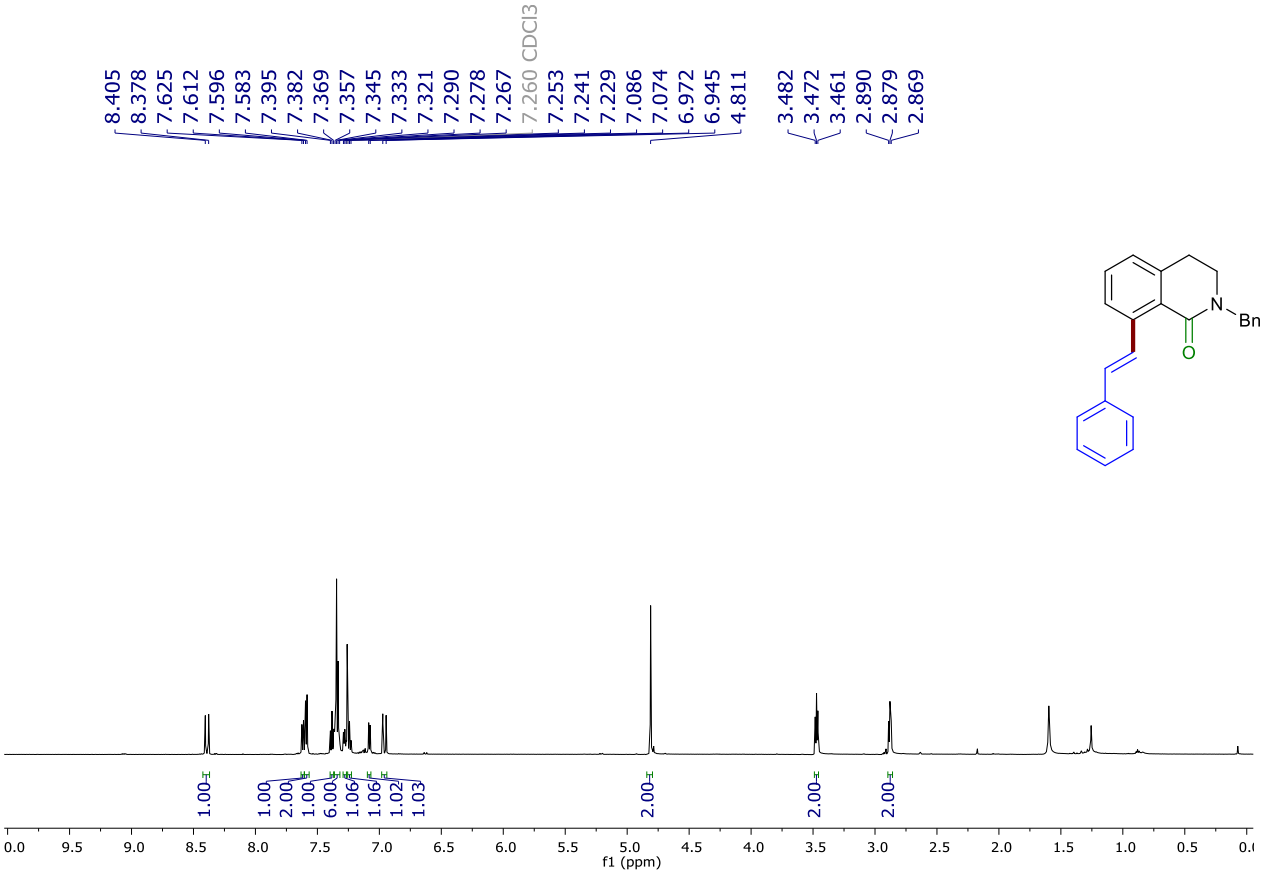
^{1}H-NMR spectrum of 3ea



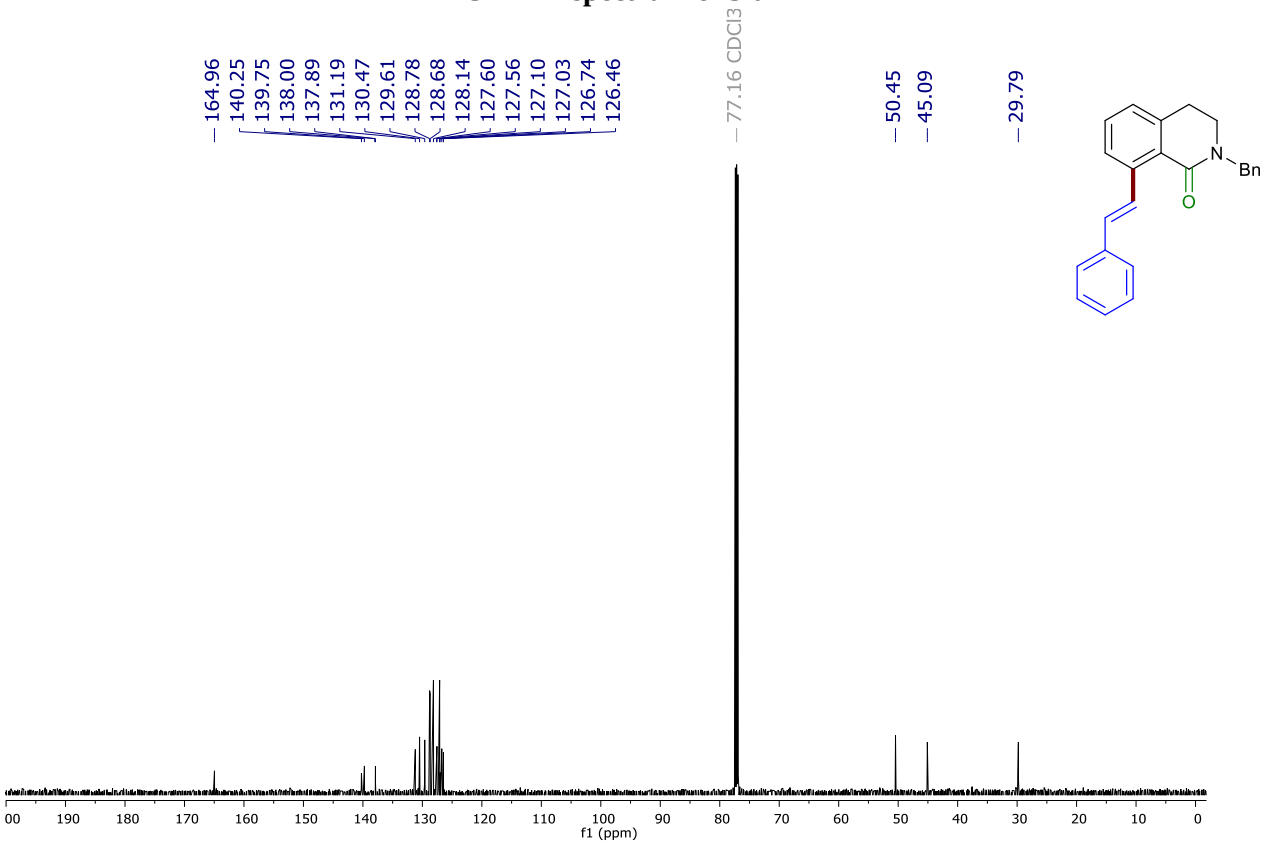
^{13}C-NMR spectrum of 3ea



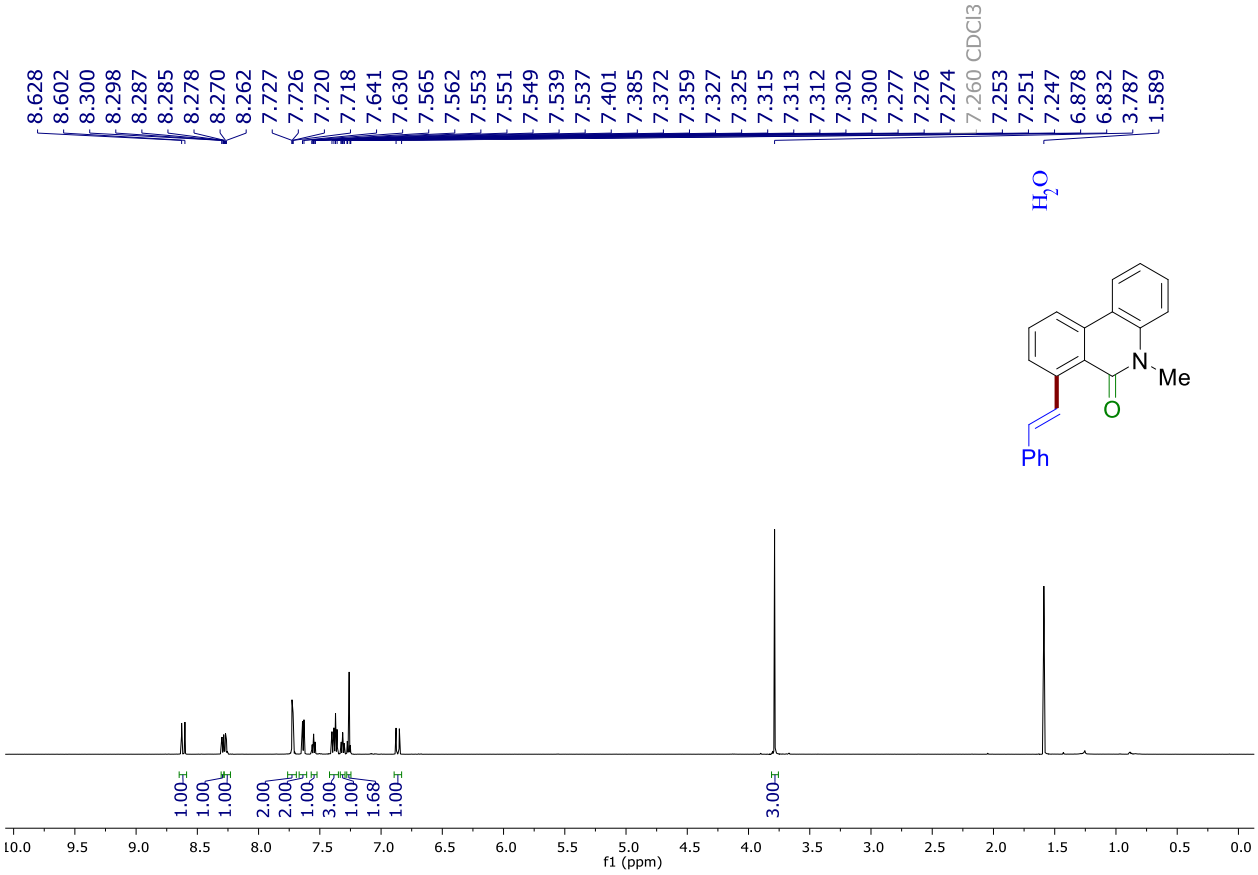
^{1}H-NMR spectrum of 3fa



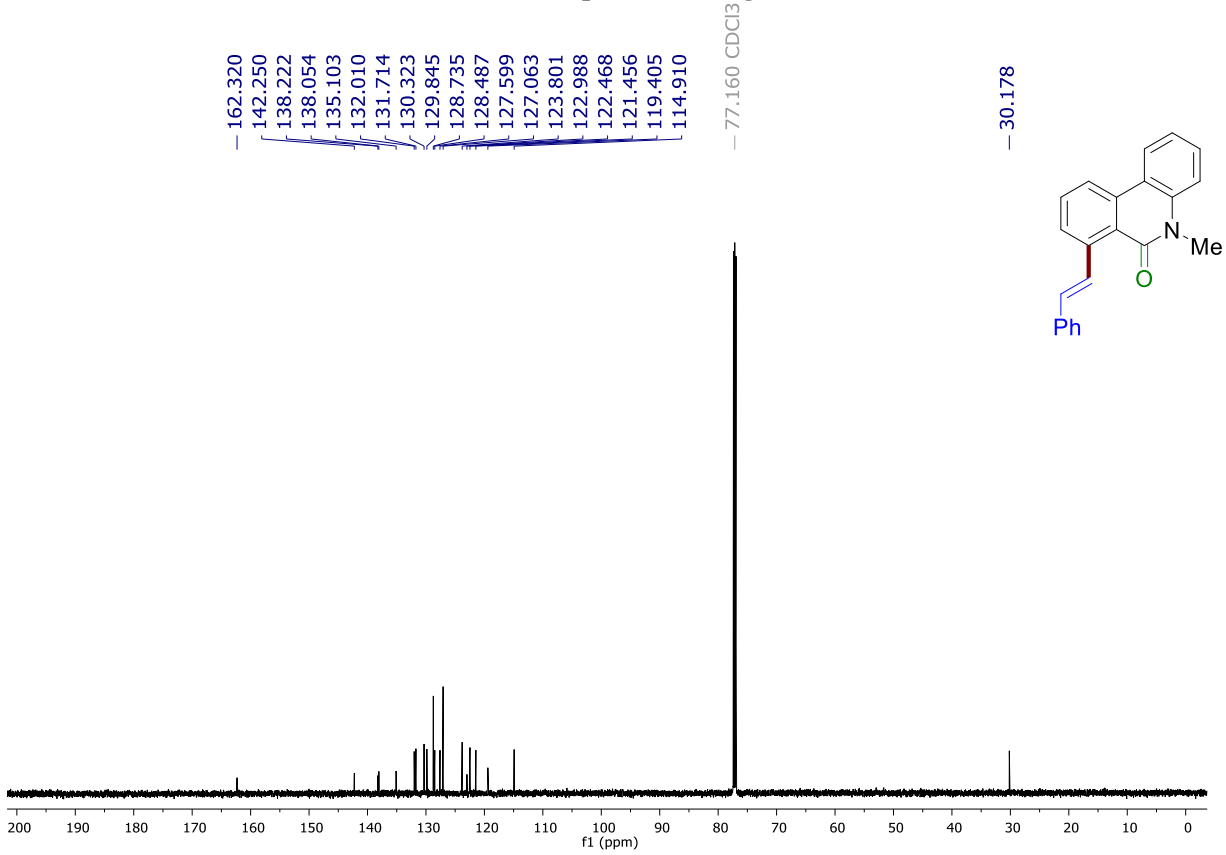
^{13}C-NMR spectrum of 3fa



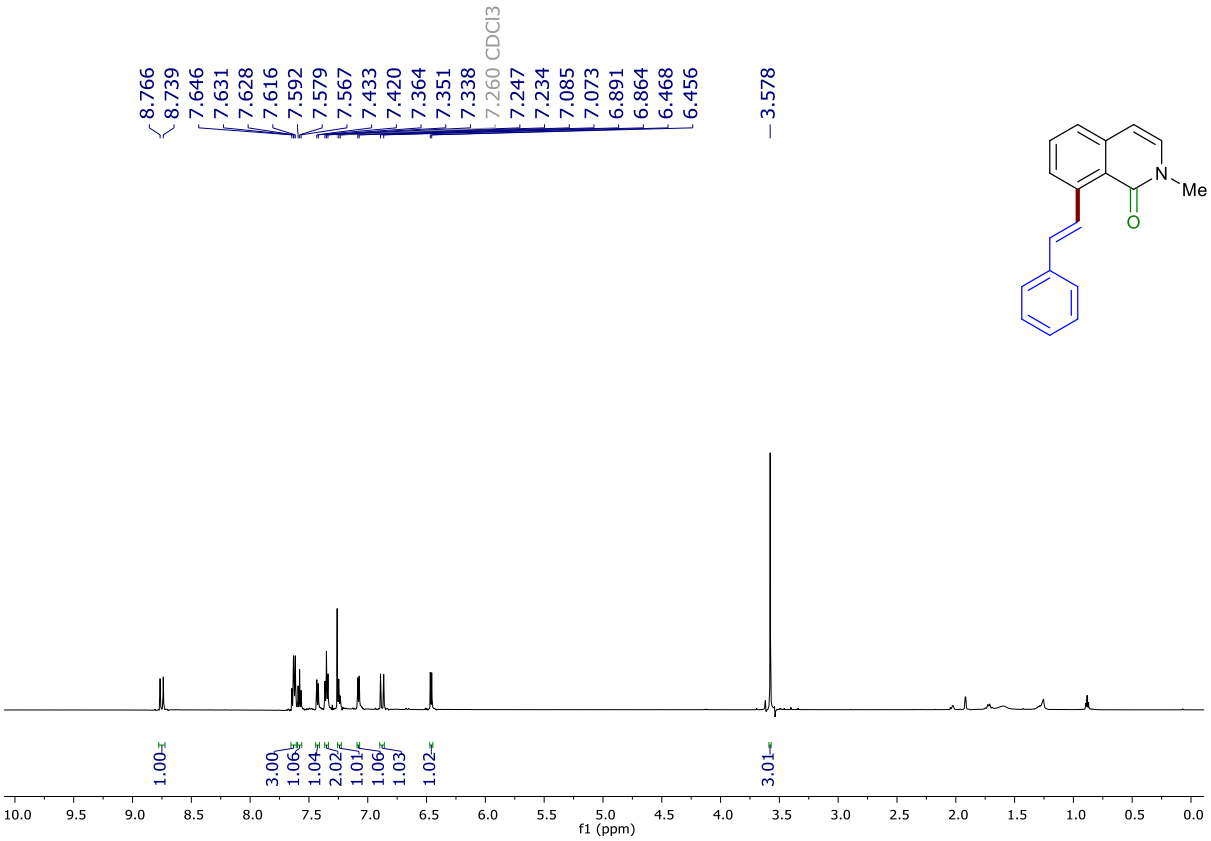
^{1}H-NMR spectrum of 3ga



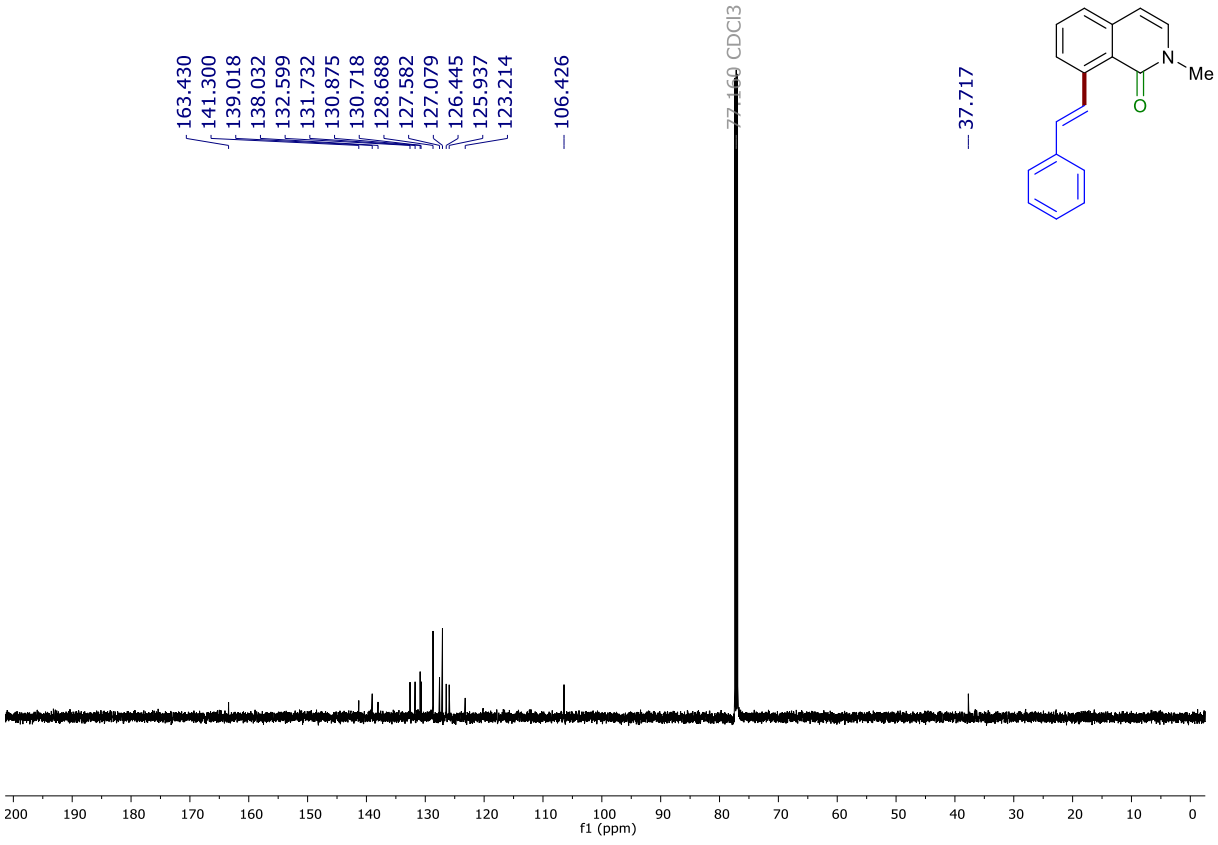
^{13}C-NMR spectrum of 3ga



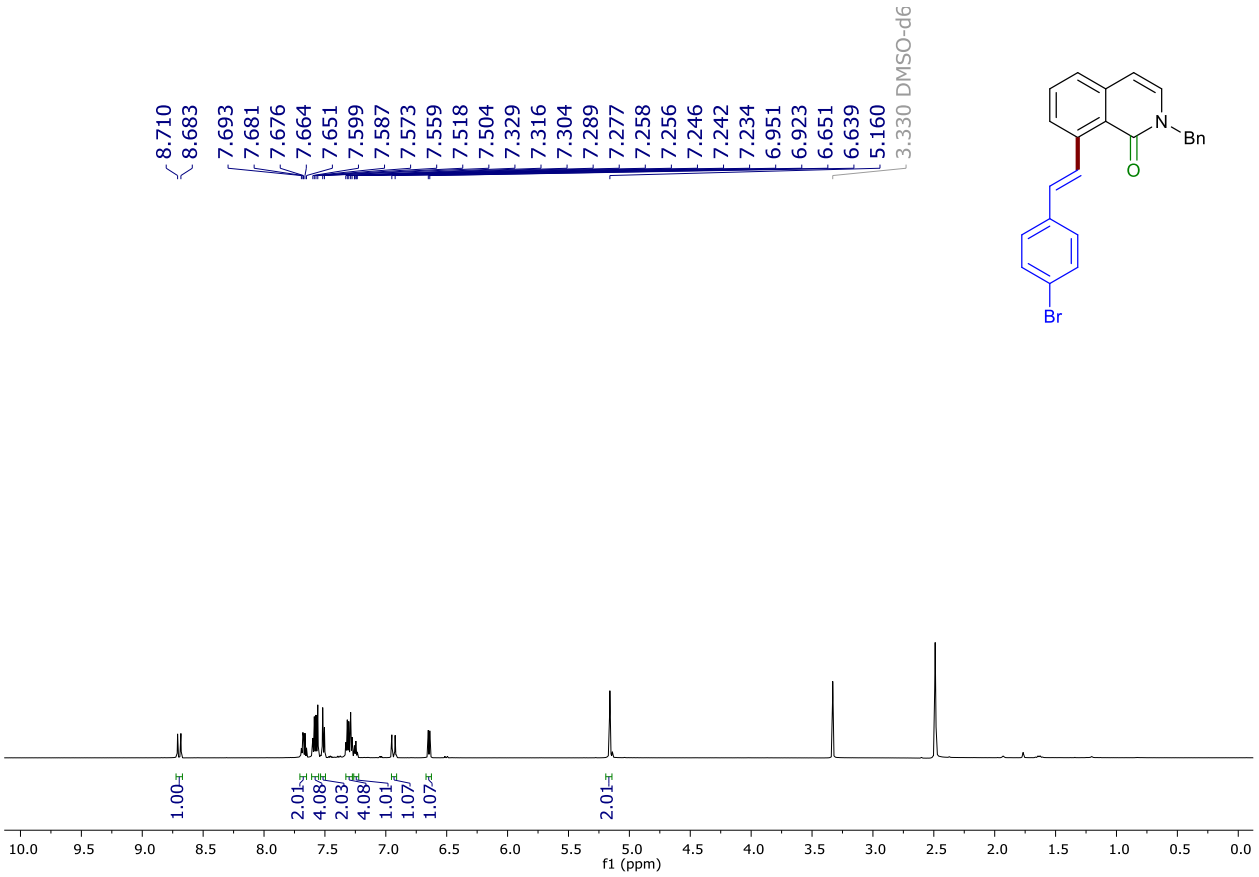
^{1}H-NMR spectrum of 3ha



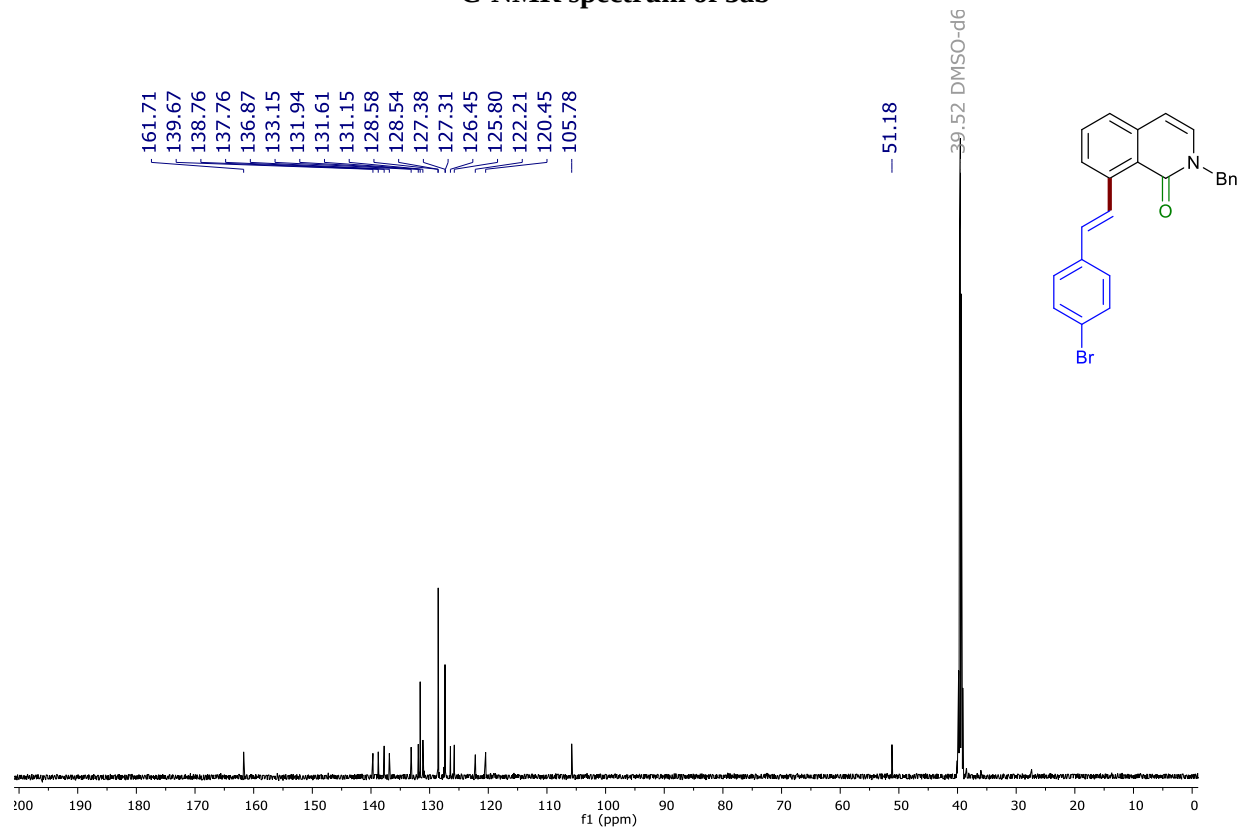
^{13}C-NMR spectrum of 3ha



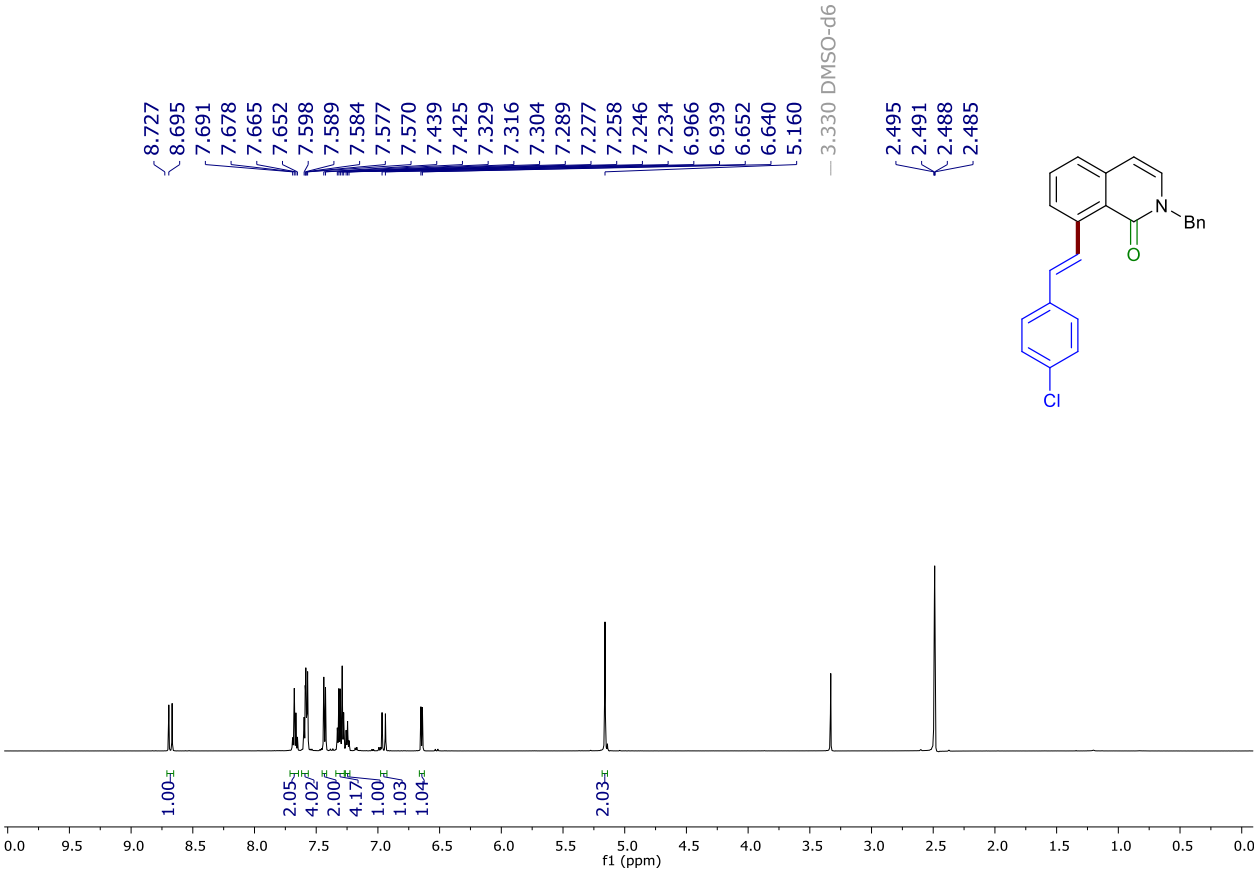
^{1}H-NMR spectrum of 3ab



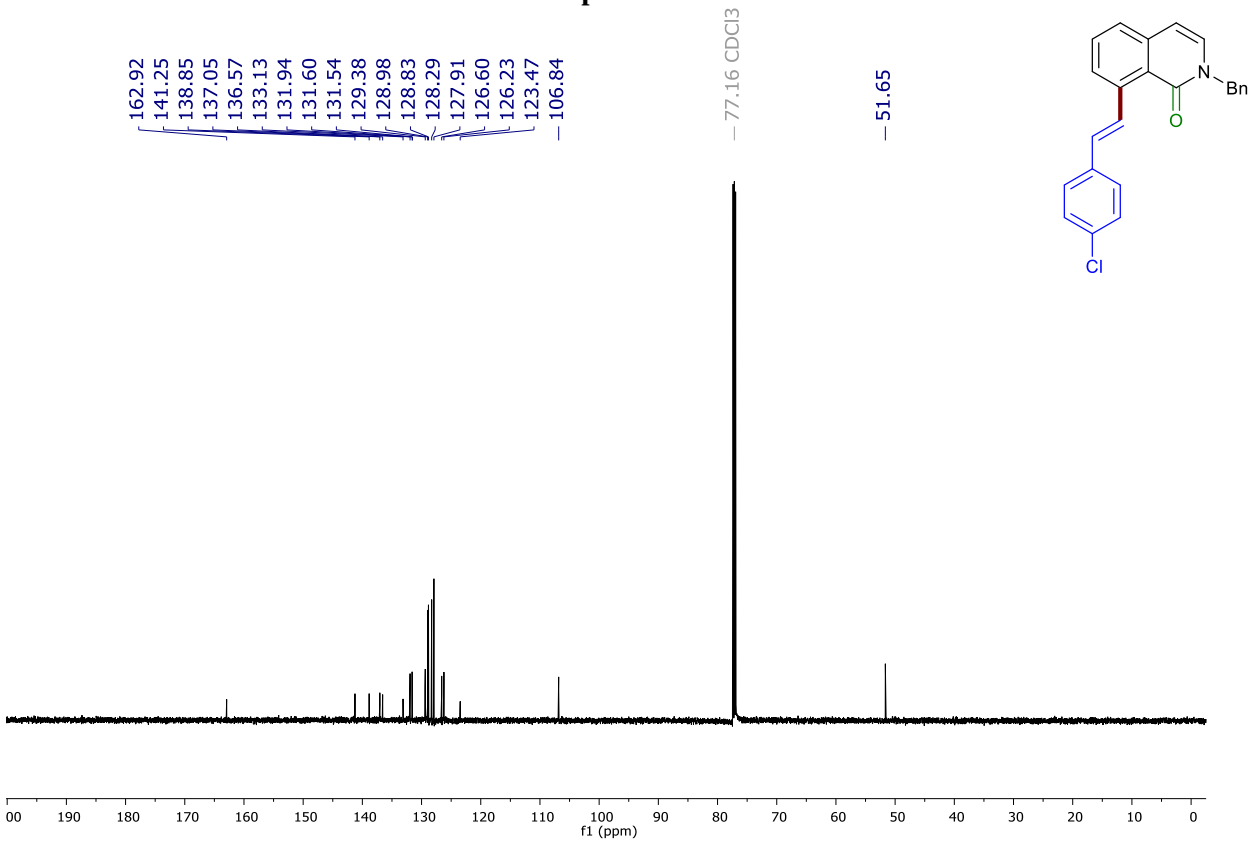
^{13}C-NMR spectrum of 3ab



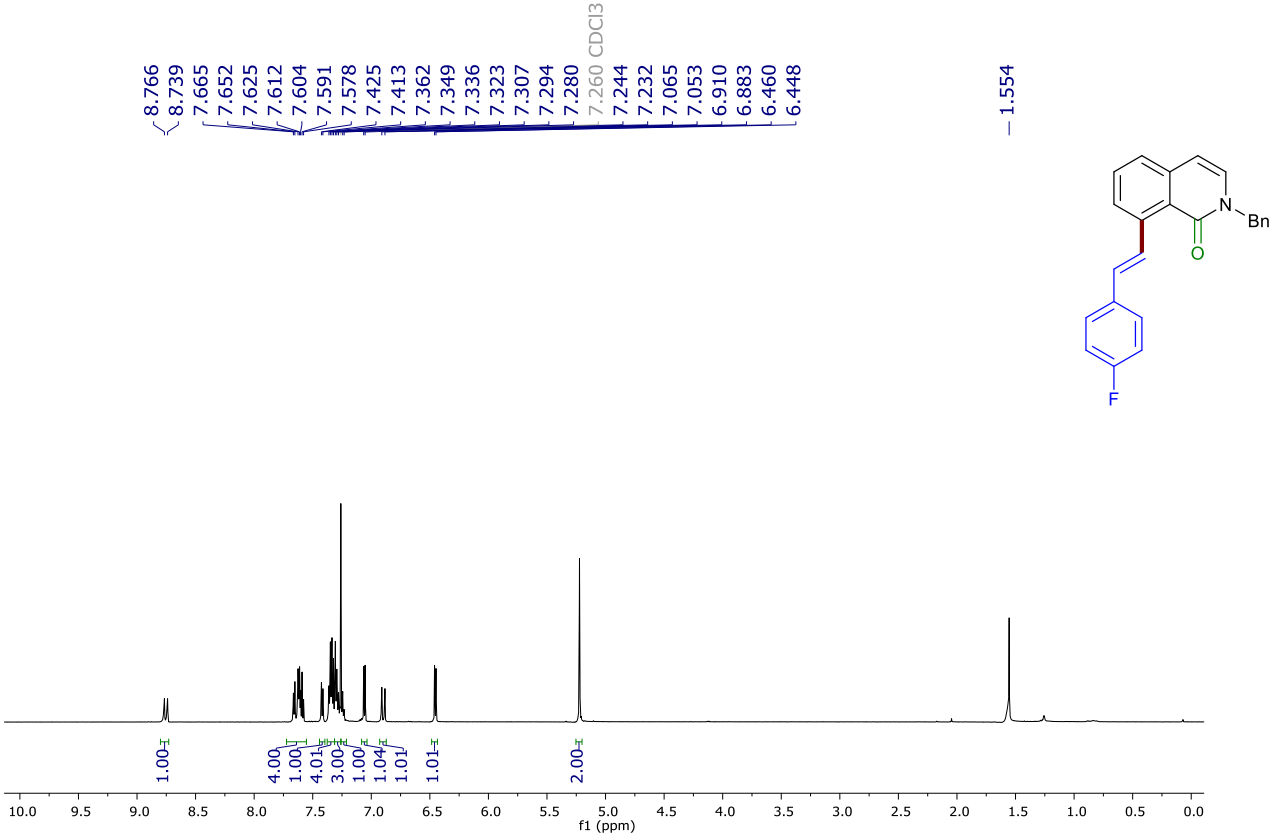
^{1}H-NMR spectrum of 3ac



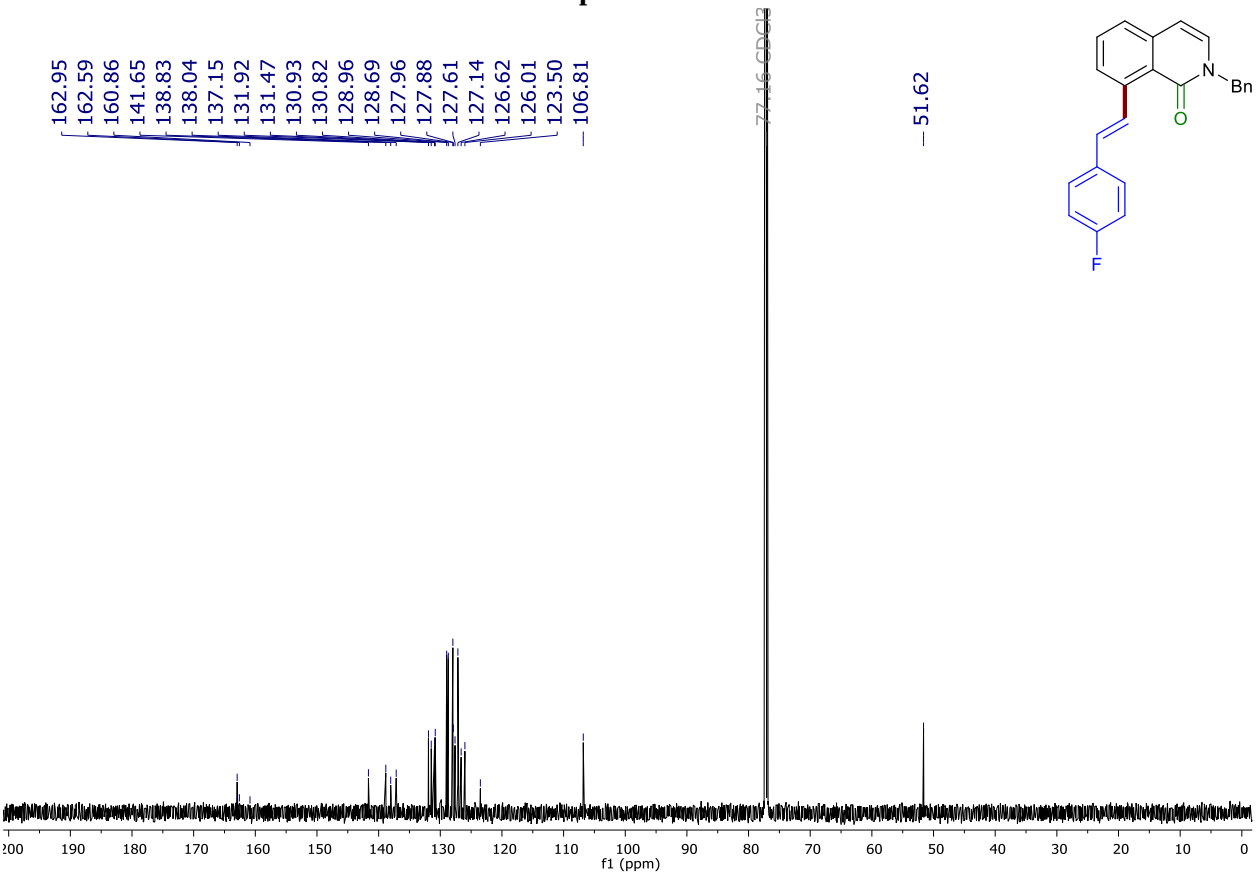
^{13}C-NMR spectrum of 3ac



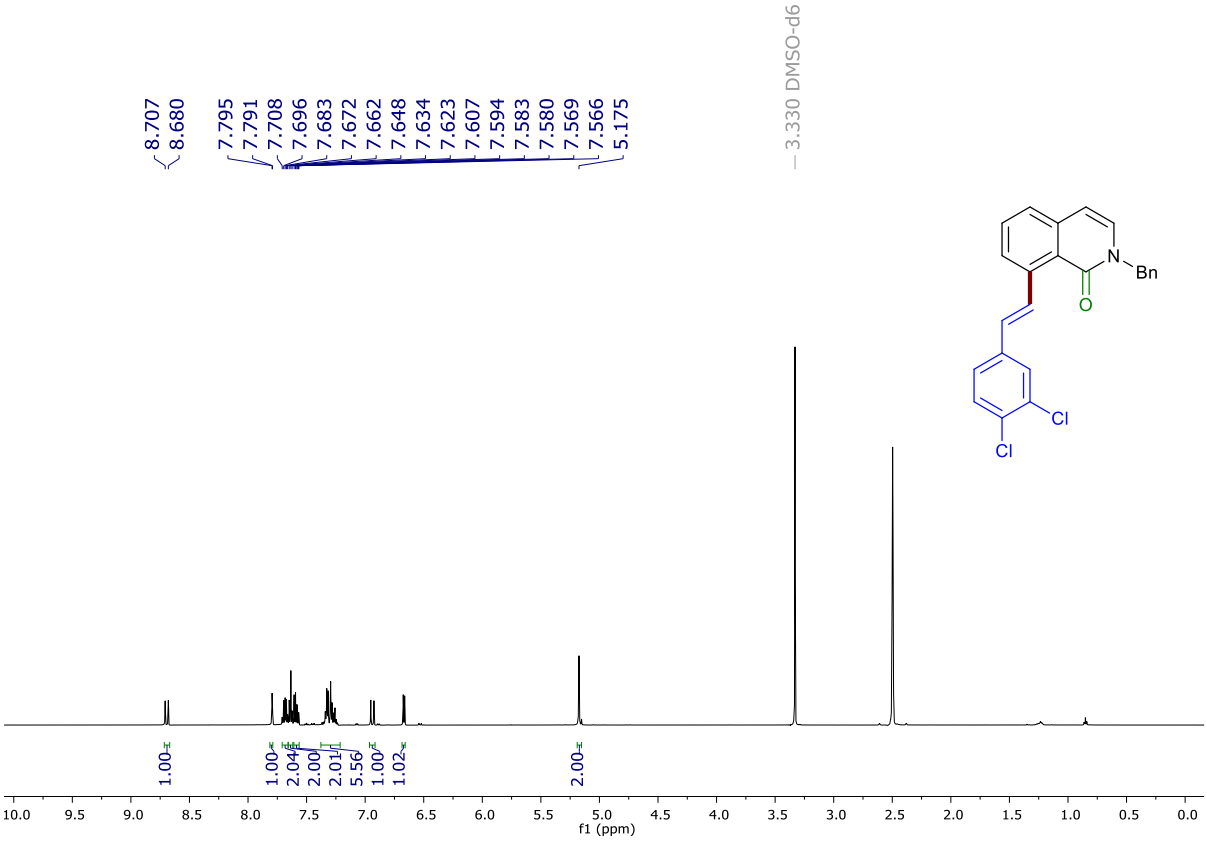
[1]H-NMR spectrum of 3ad



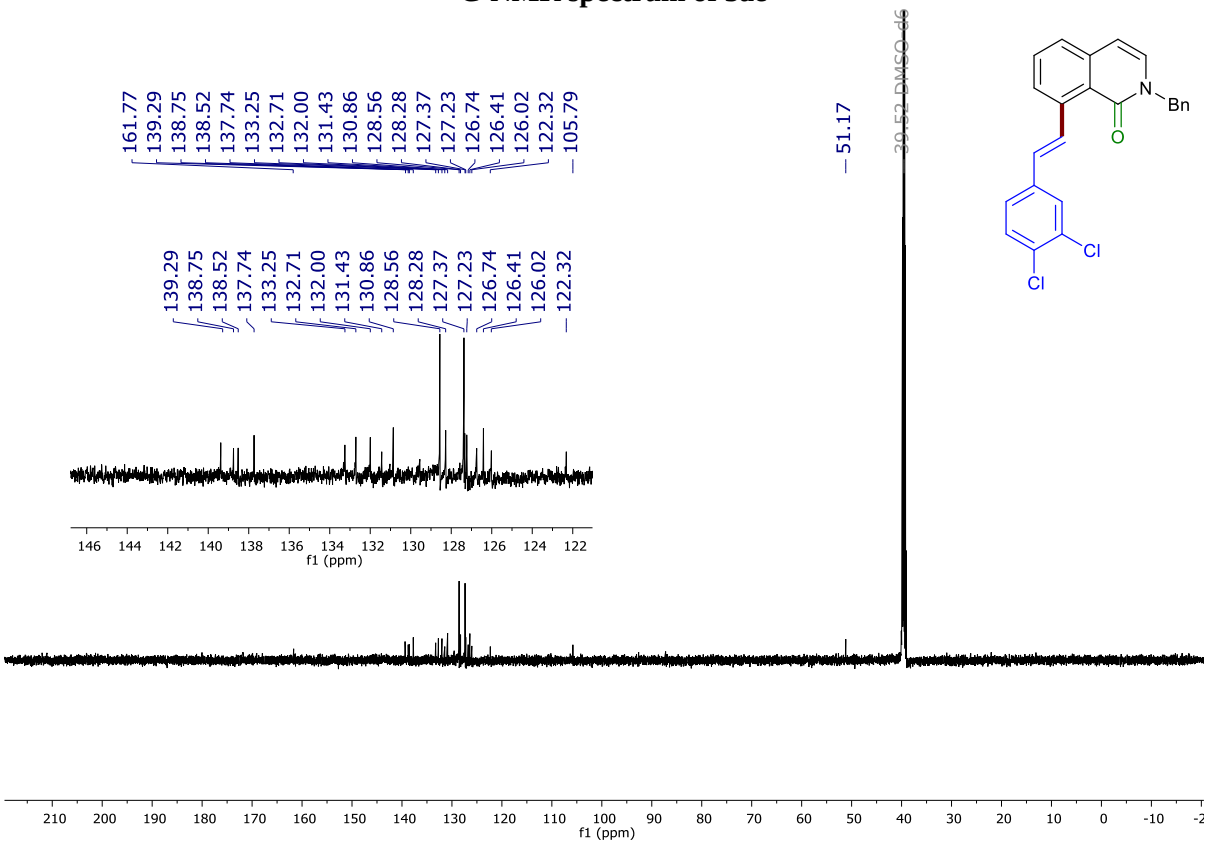
[13]C-NMR spectrum of 3ad



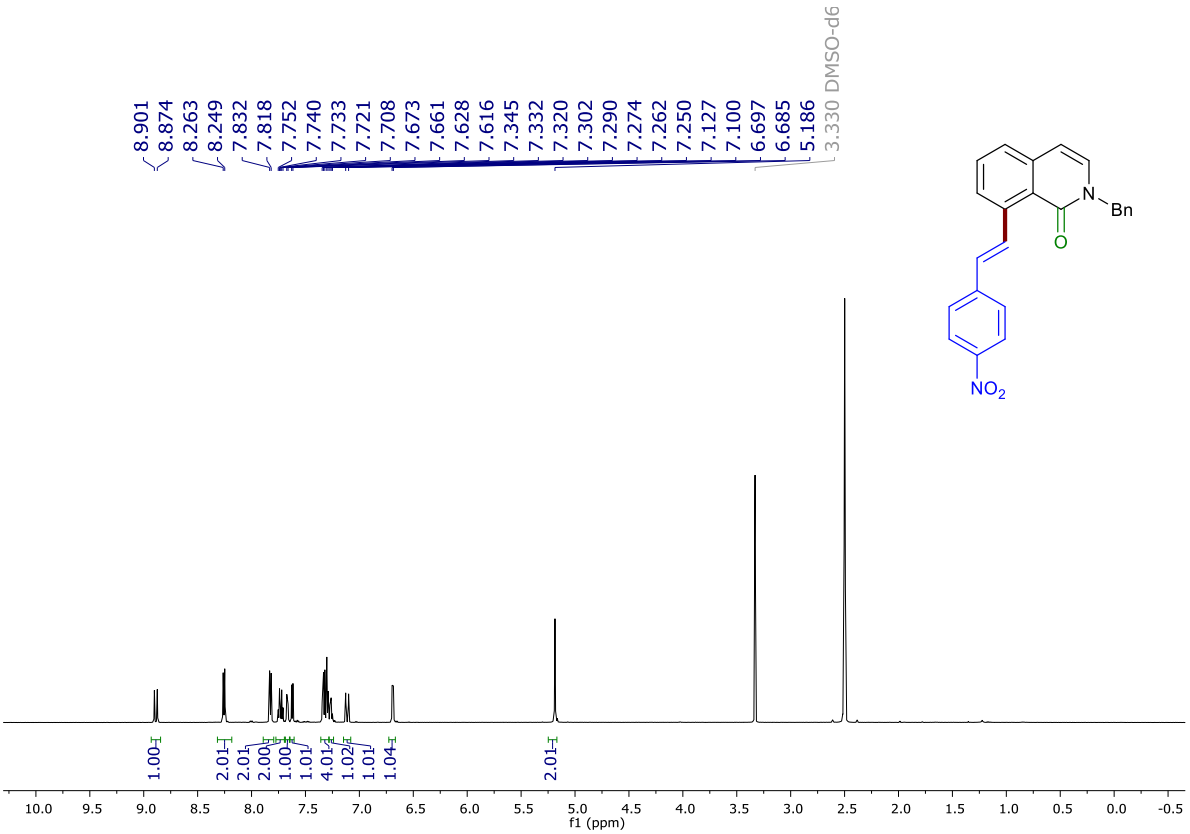
^{1}H-NMR spectrum of 3ae



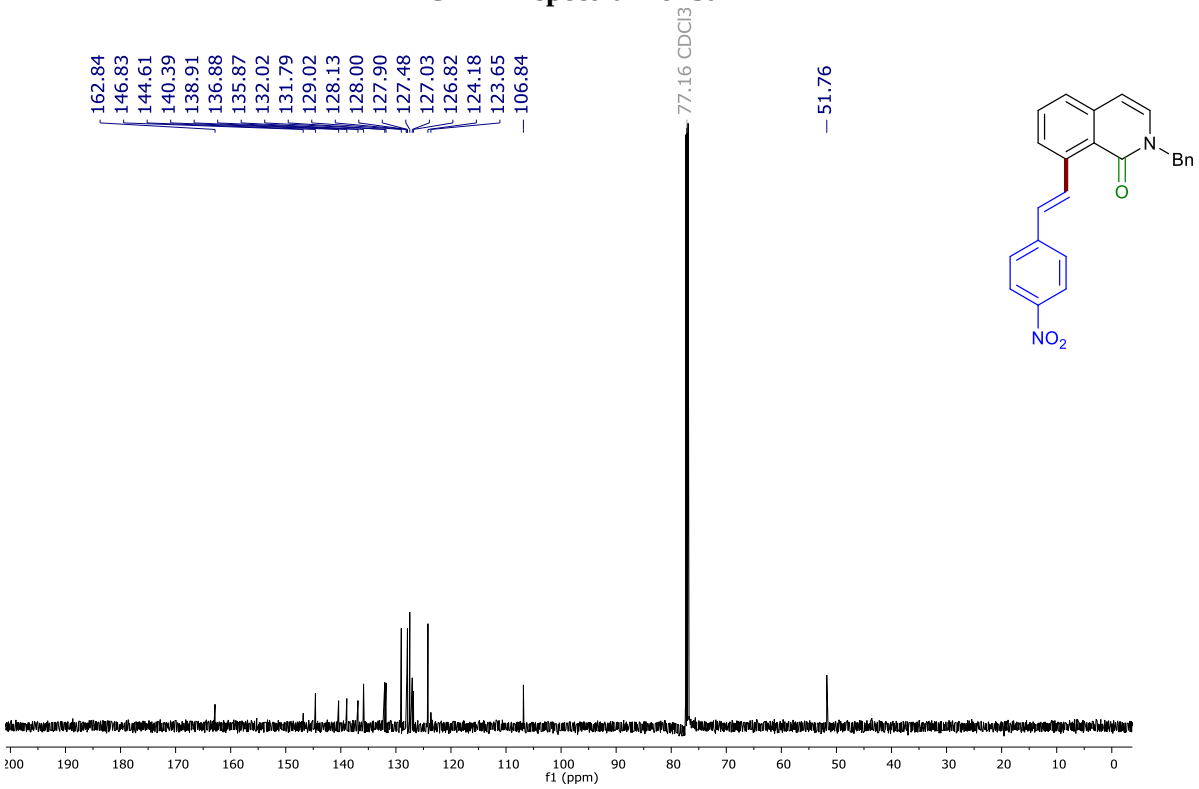
^{13}C-NMR spectrum of 3ae



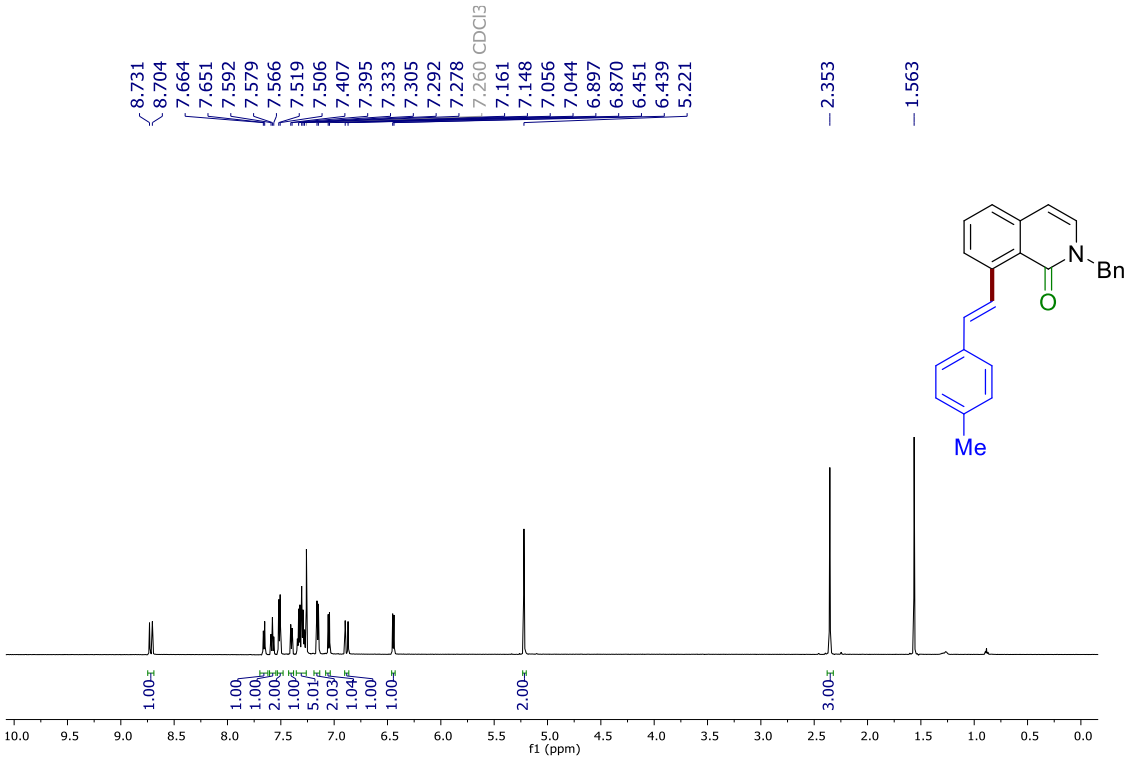
^{1}H-NMR spectrum of 3af



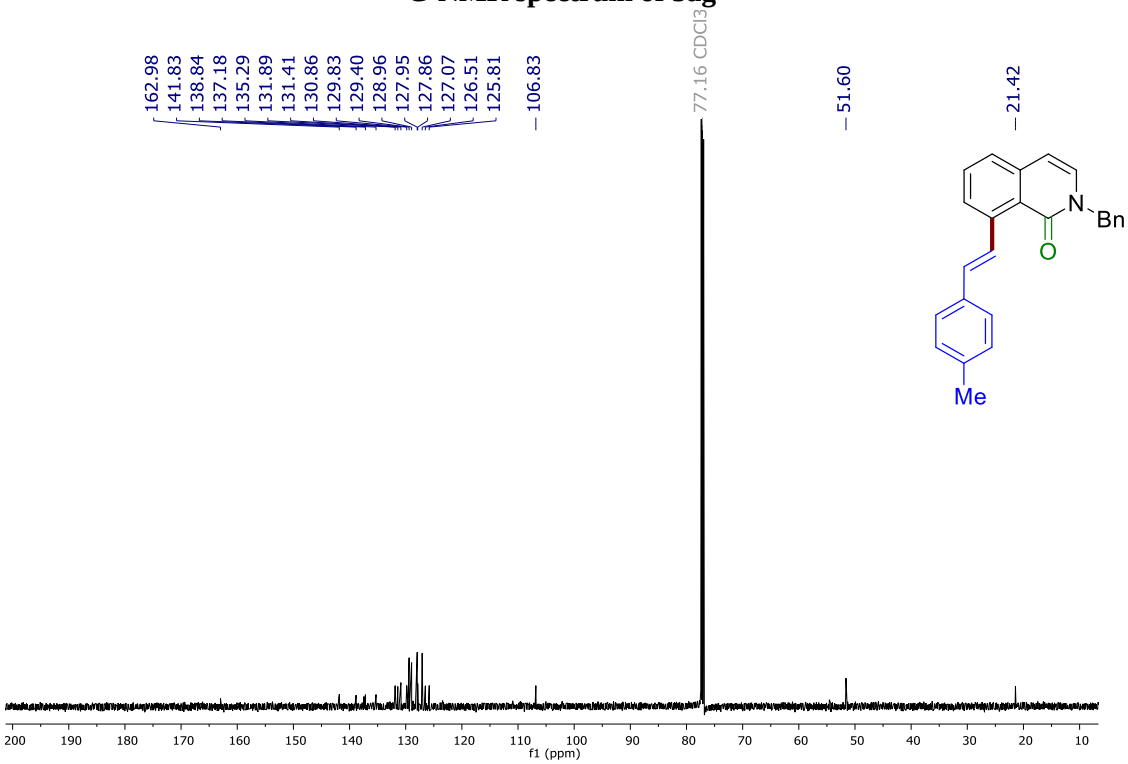
^{13}C-NMR spectrum of 3af



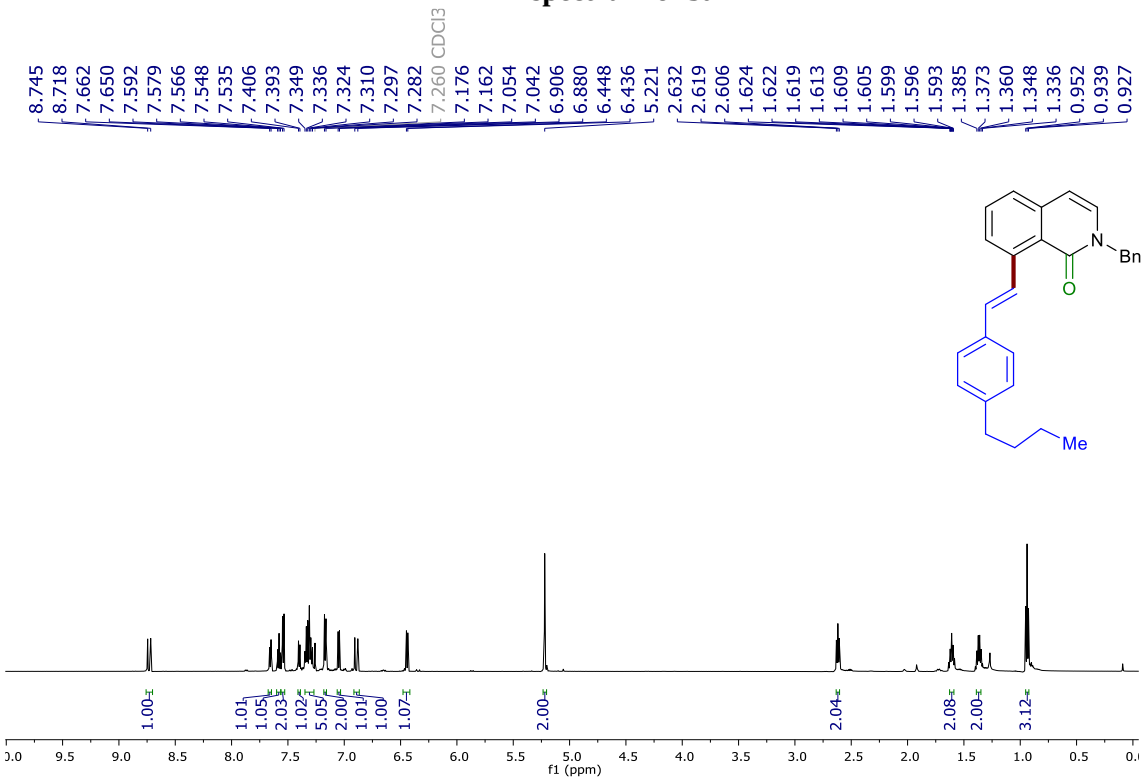
^{1}H-NMR spectrum of 3ag



^{13}C-NMR spectrum of 3ag



^{1}H-NMR spectrum of 3ah



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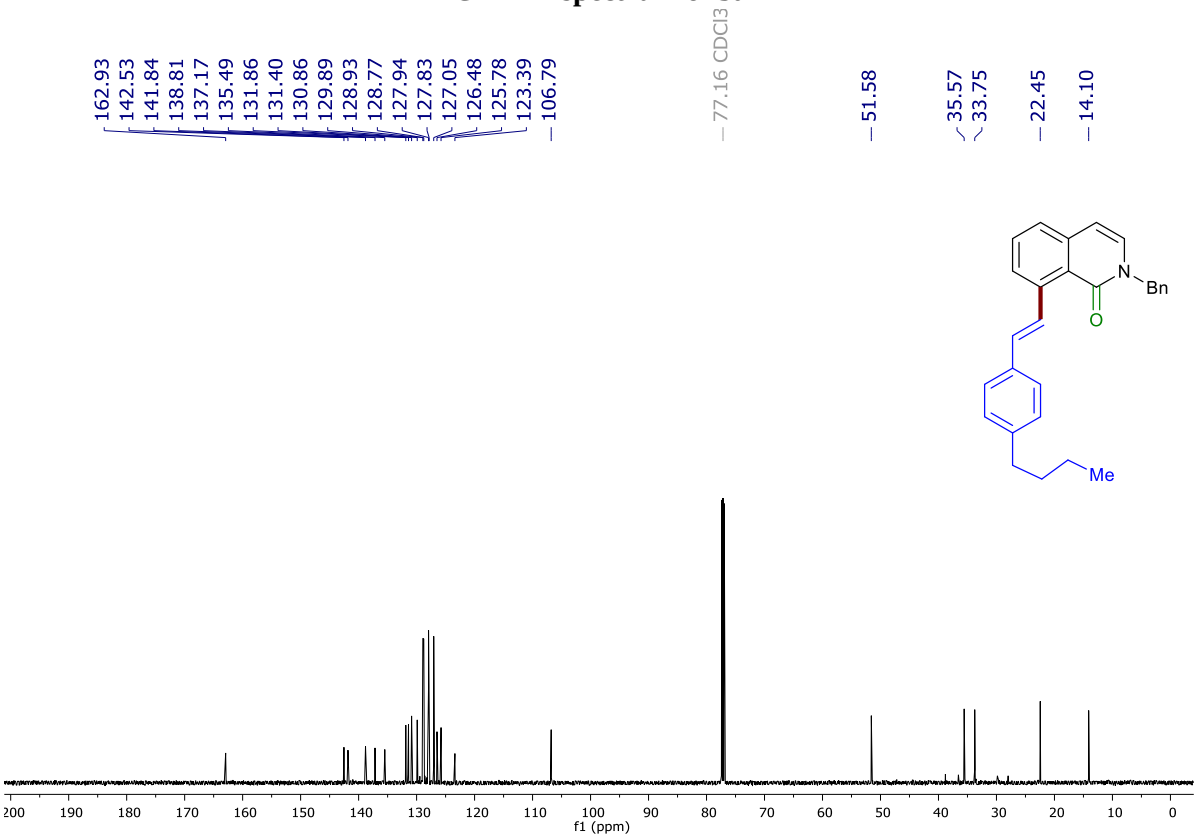
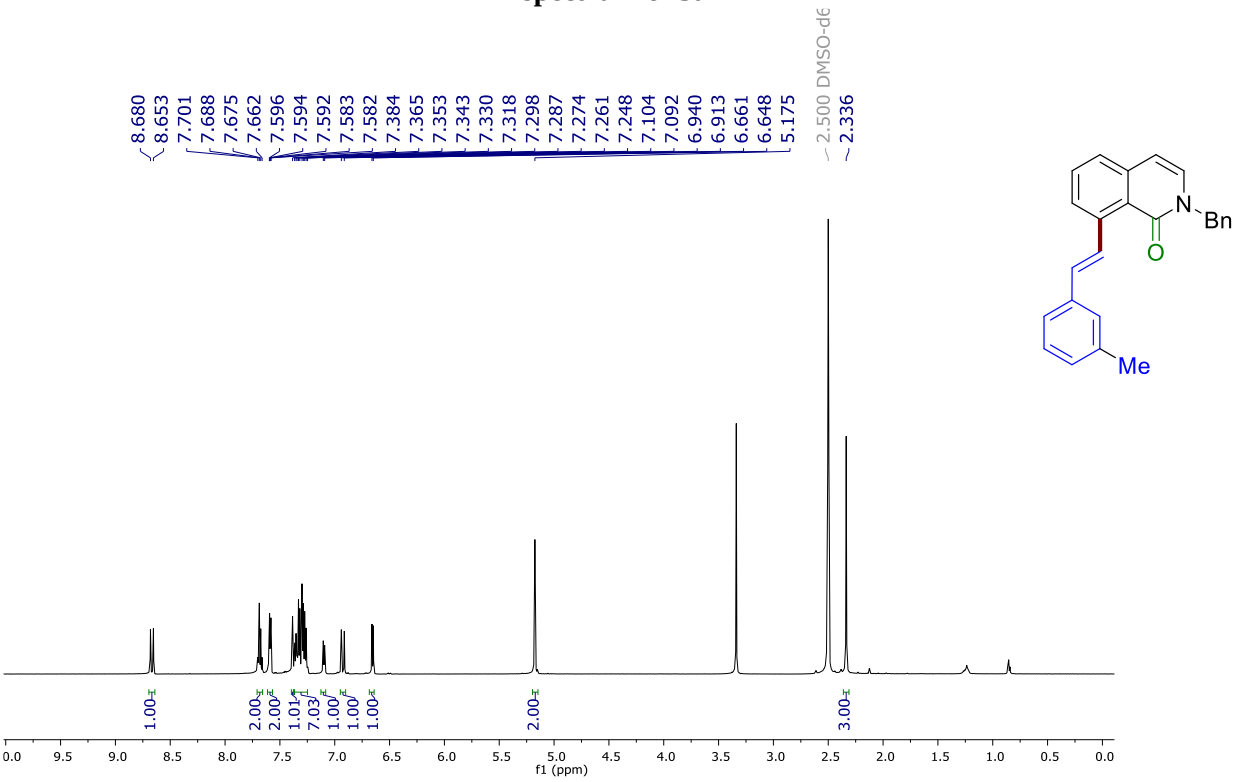
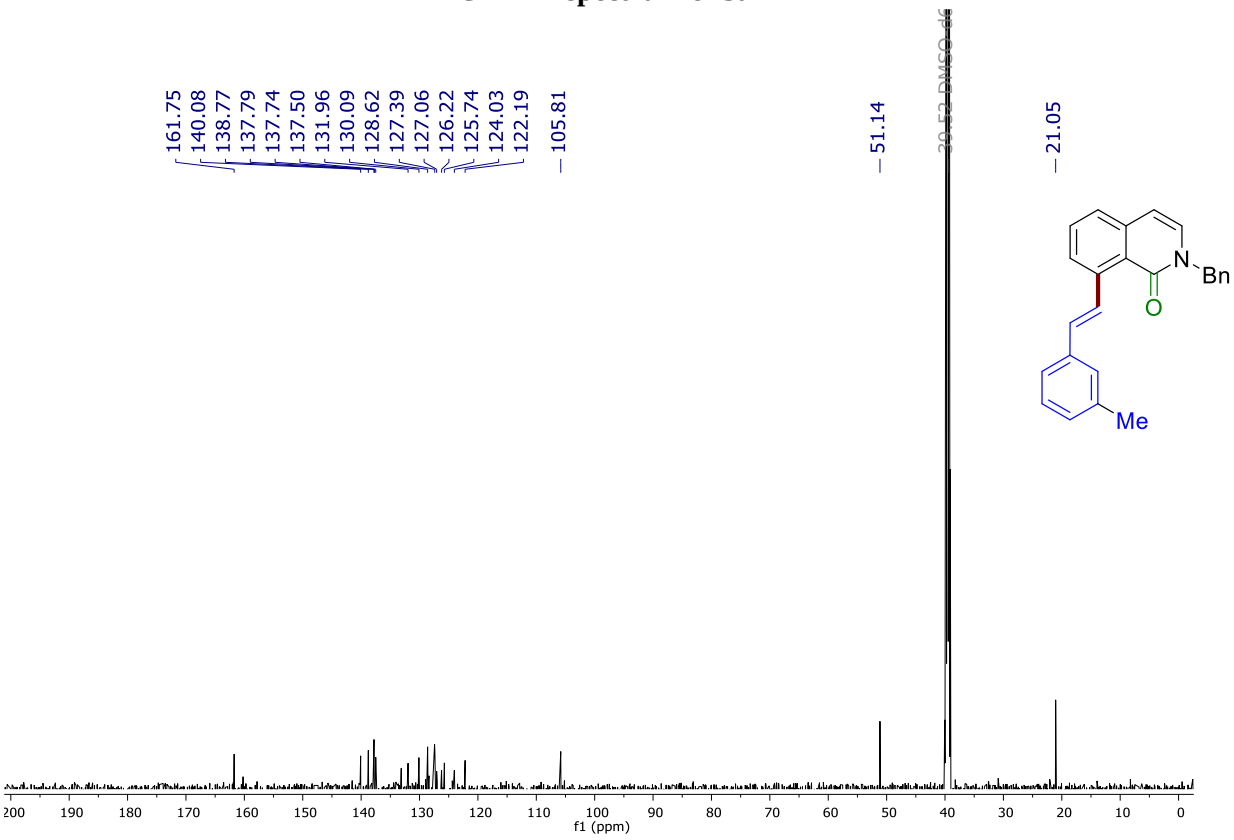


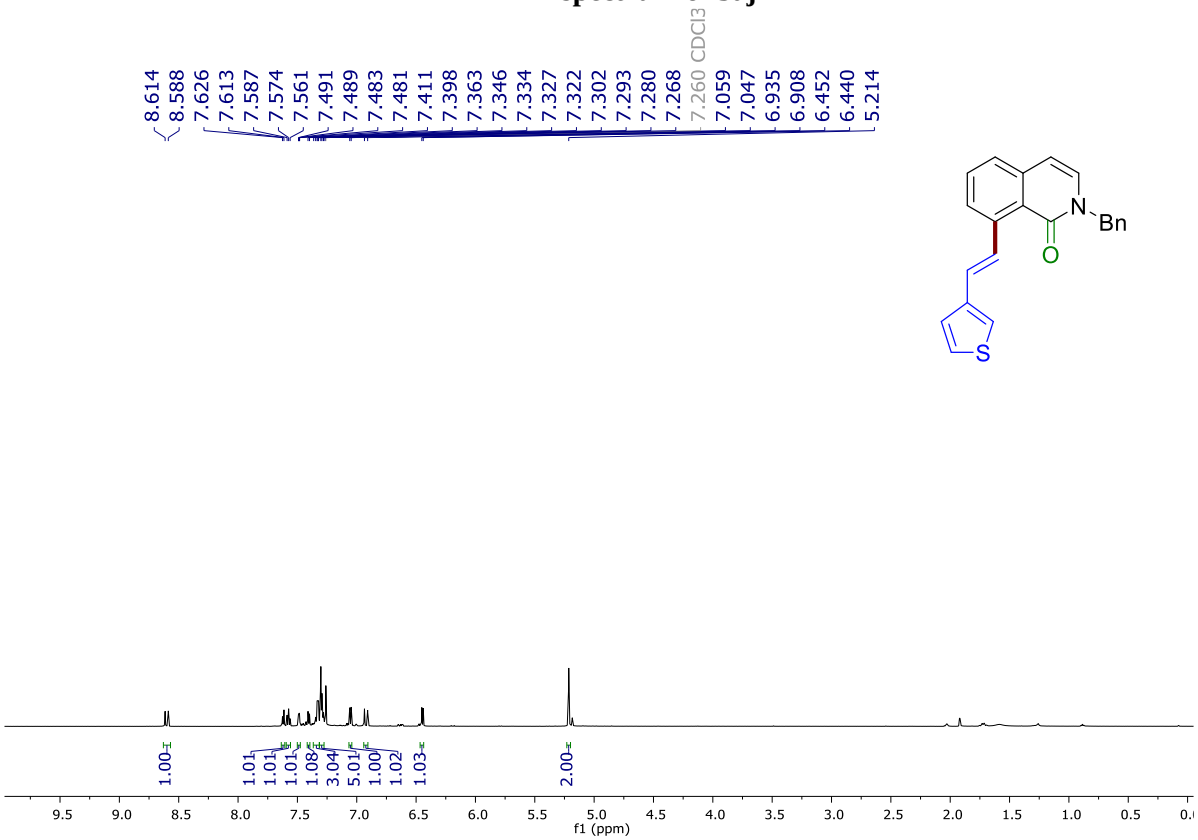
^{1}H-NMR spectrum of 3ai



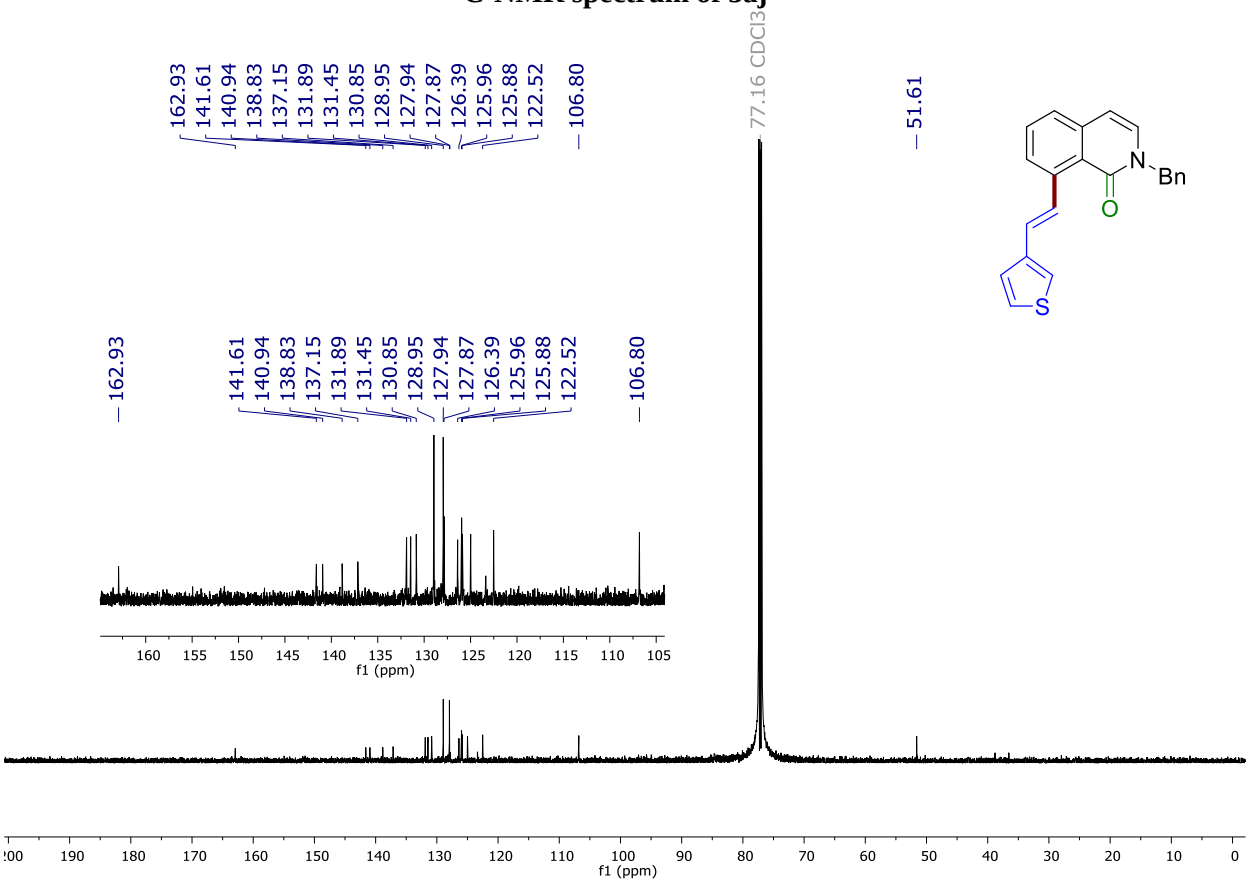
^{13}C-NMR spectrum of 3ai



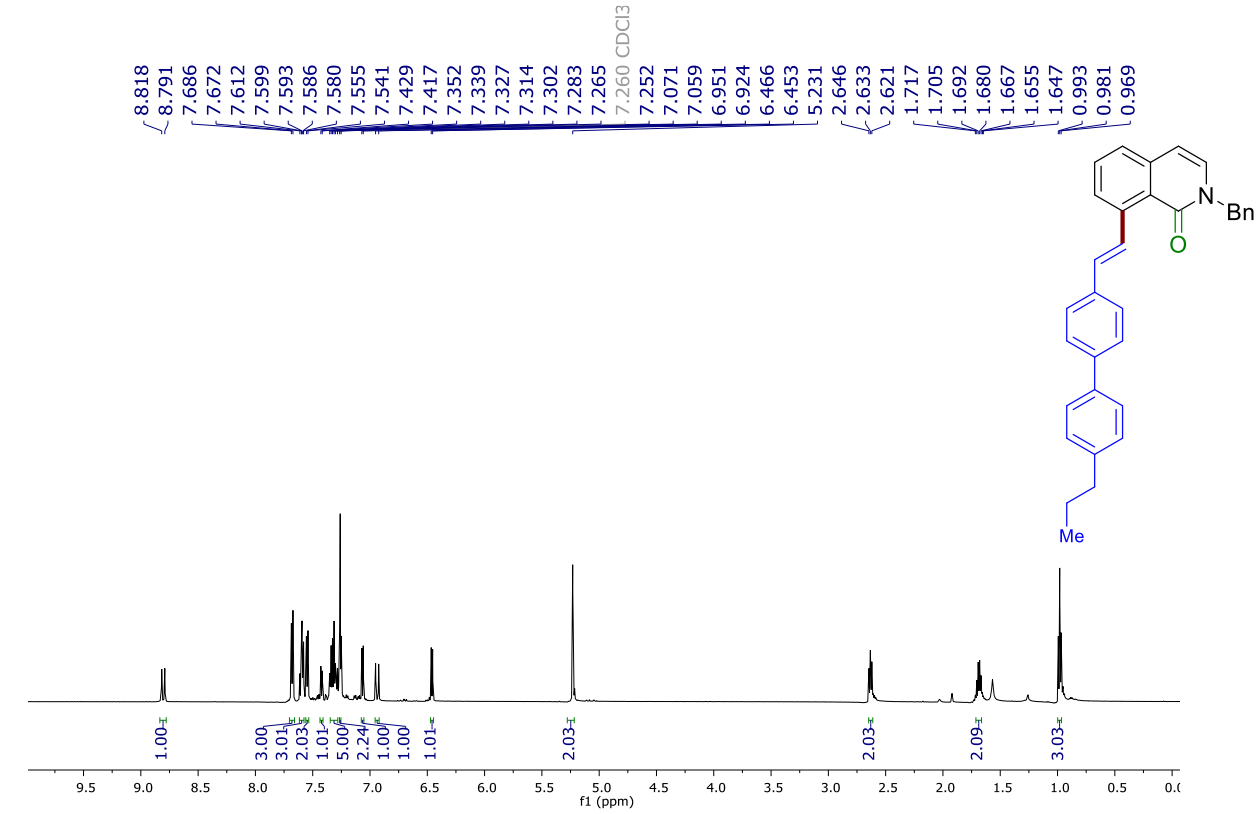
^{1}H-NMR spectrum of 3aj



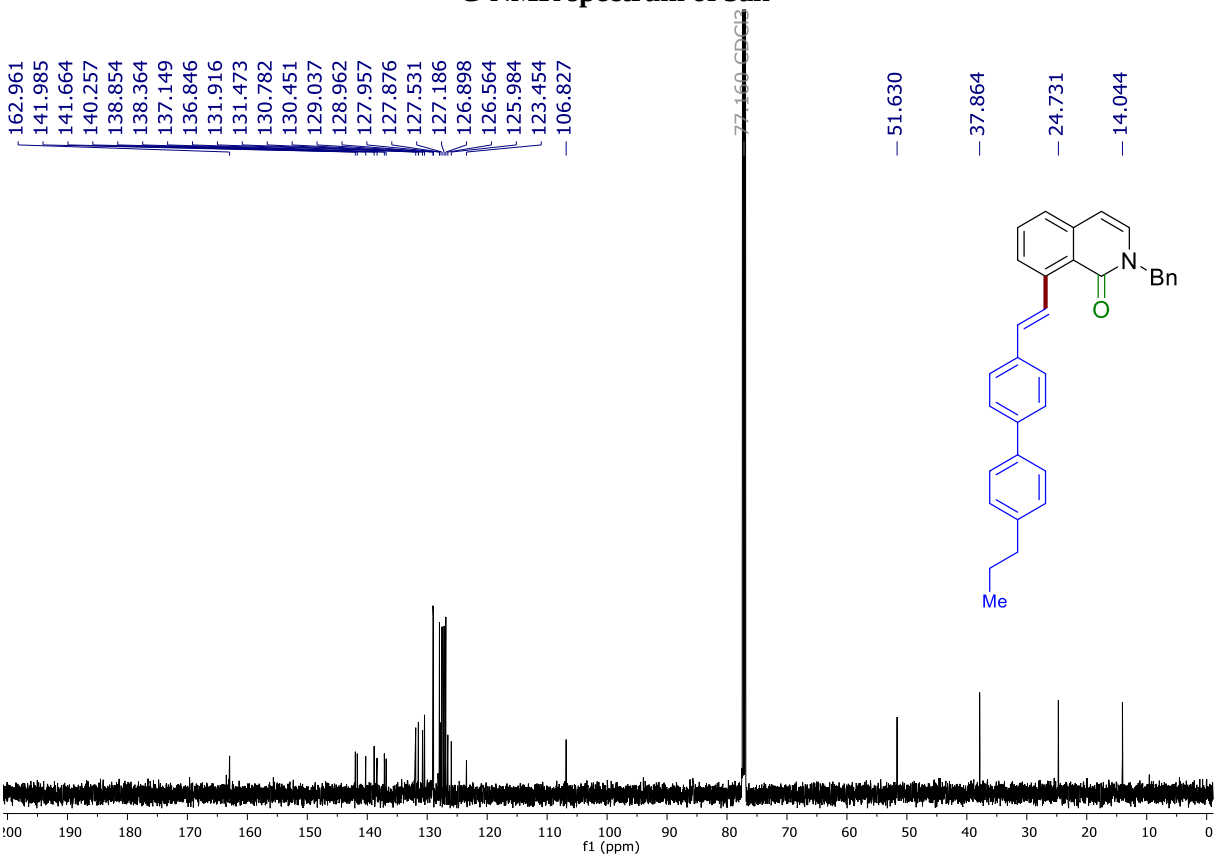
^{13}C-NMR spectrum of 3aj



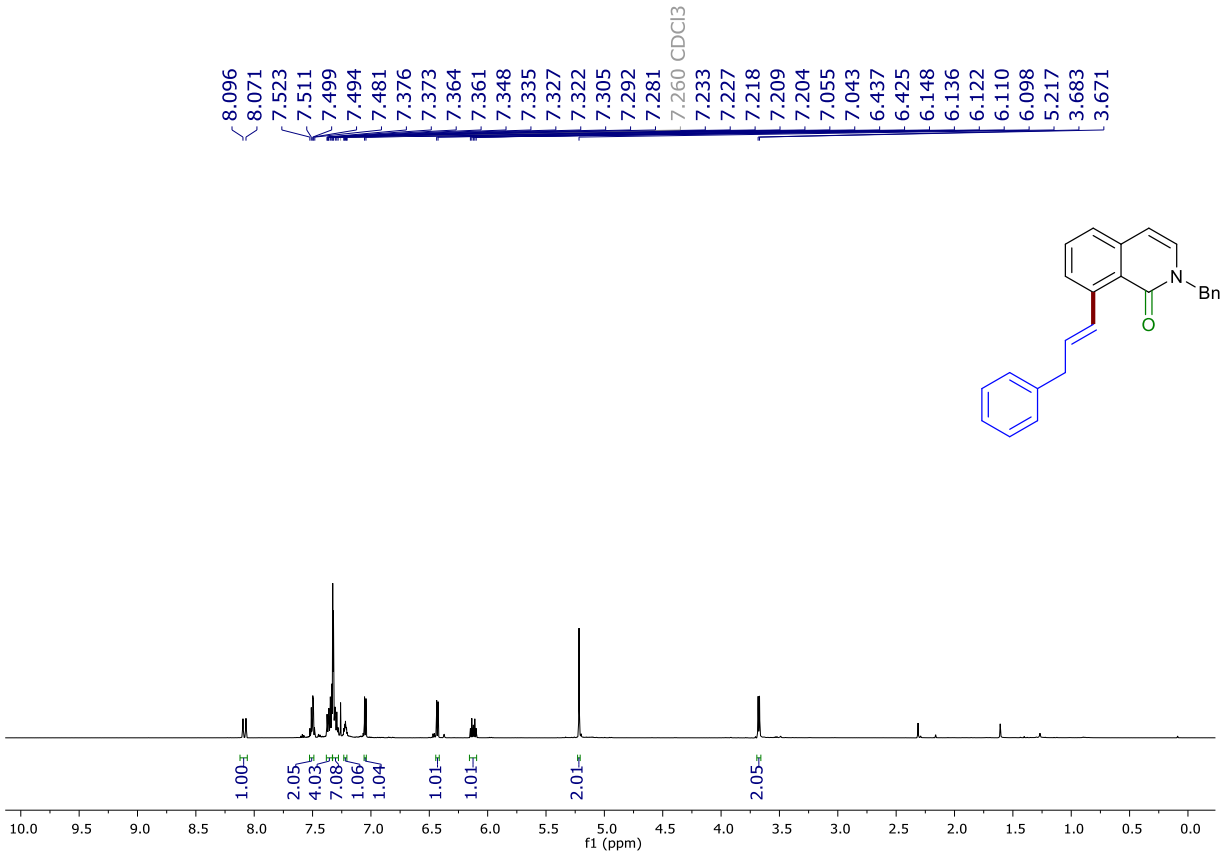
^{1}H-NMR spectrum of 3ak



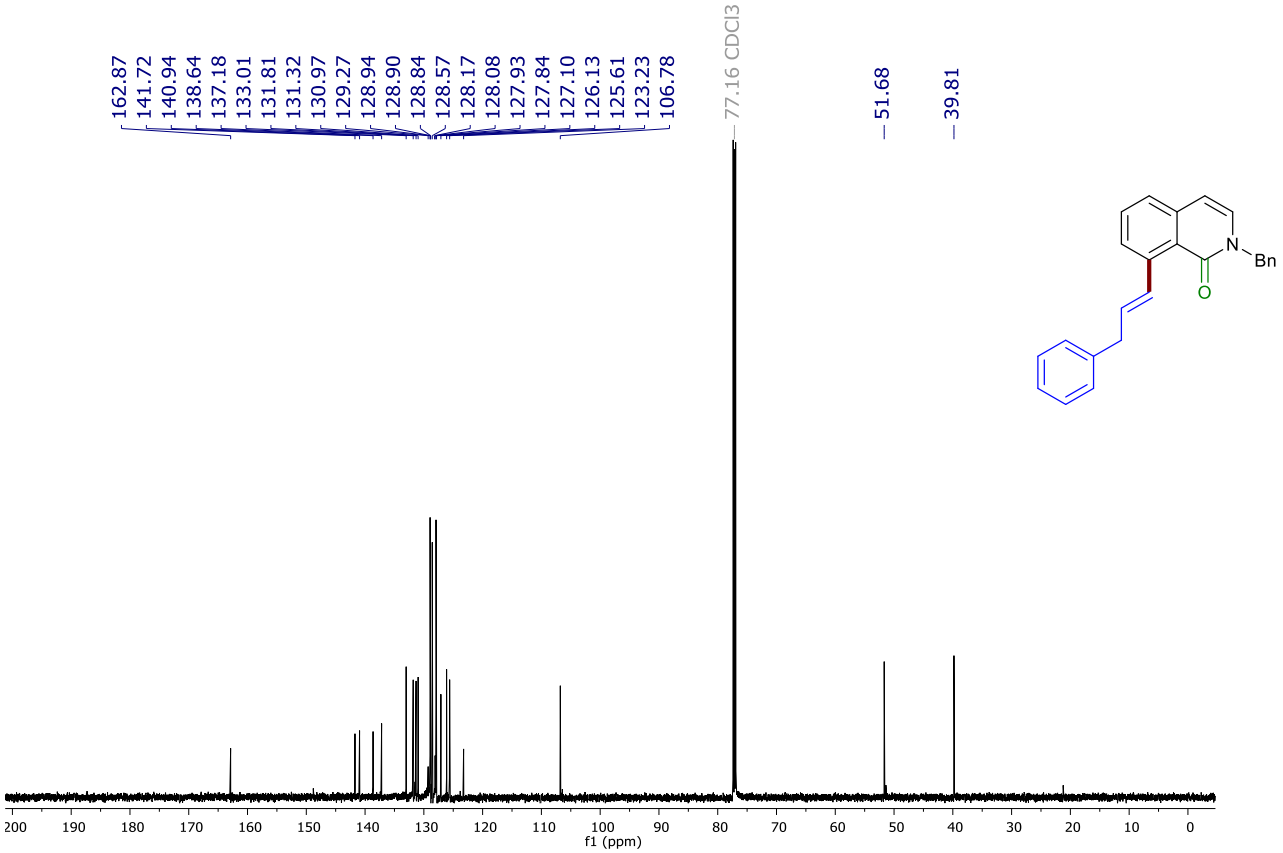
^{13}C-NMR spectrum of 3ak



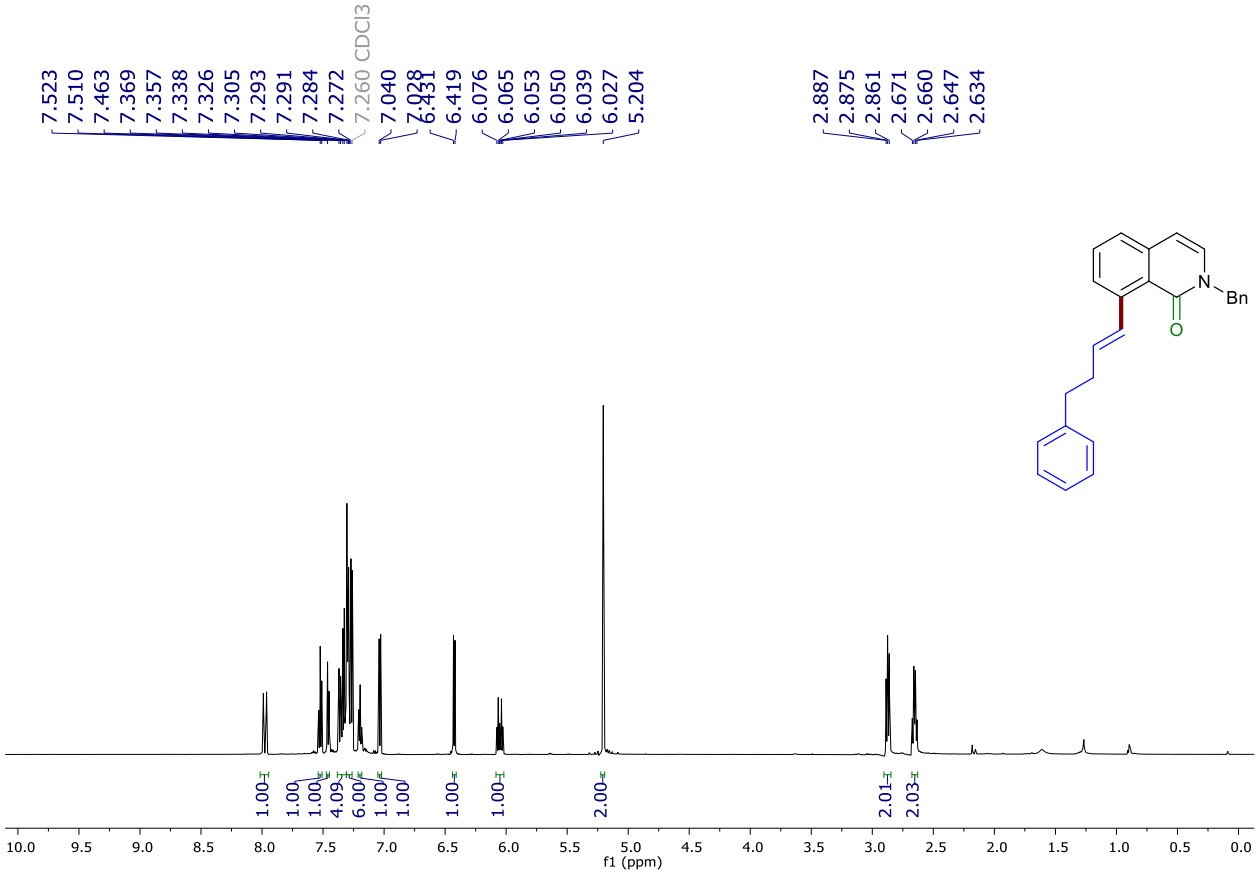
^{1}H-NMR spectrum of 3al



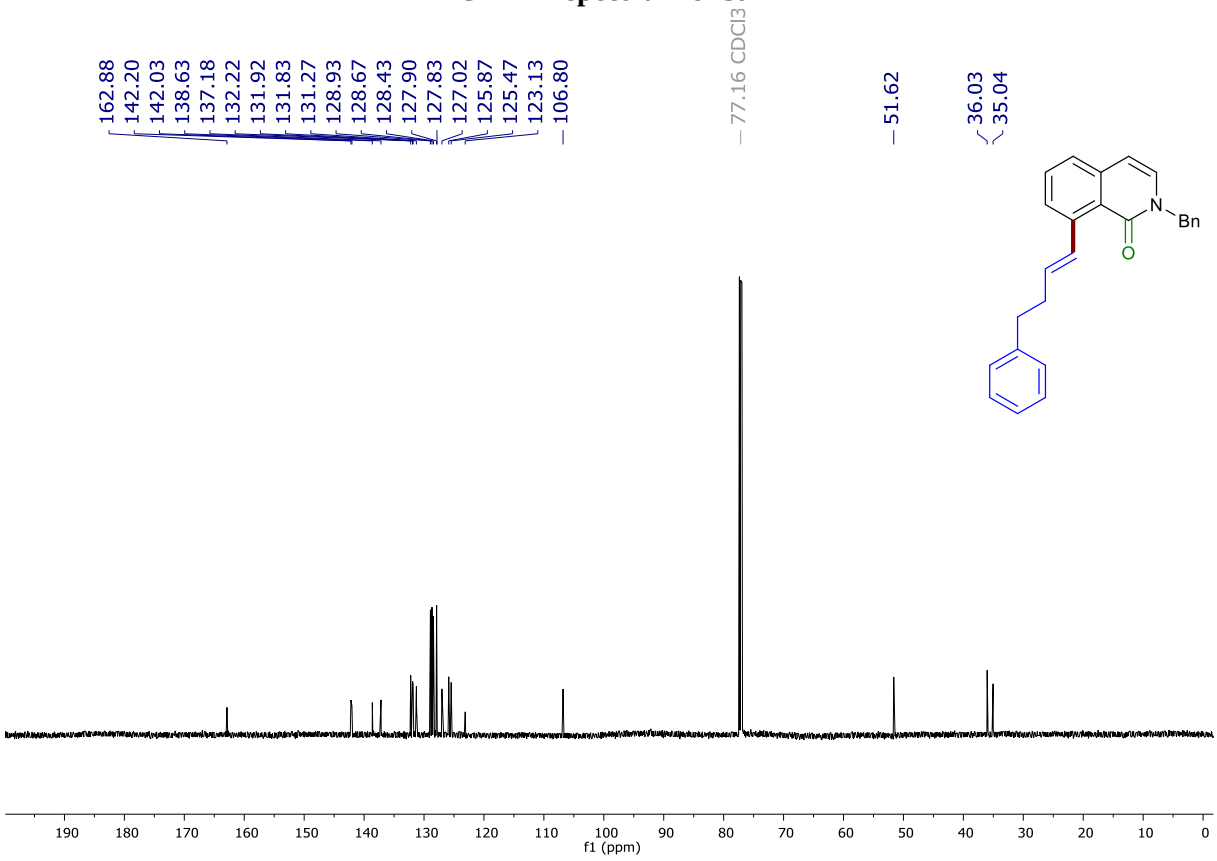
^{13}C-NMR spectrum of 3al



^{1}H-NMR spectrum of 3am



^{13}C-NMR spectrum of 3am



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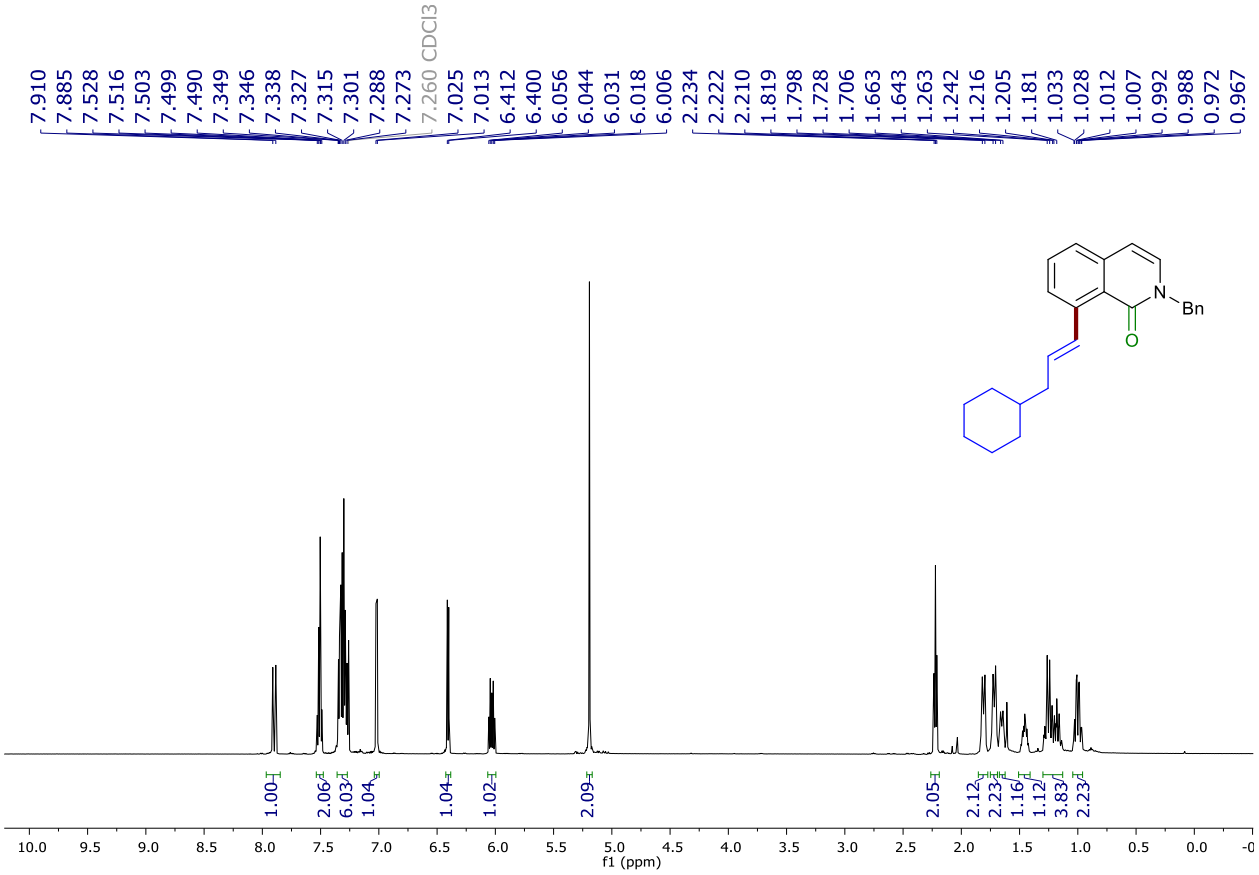

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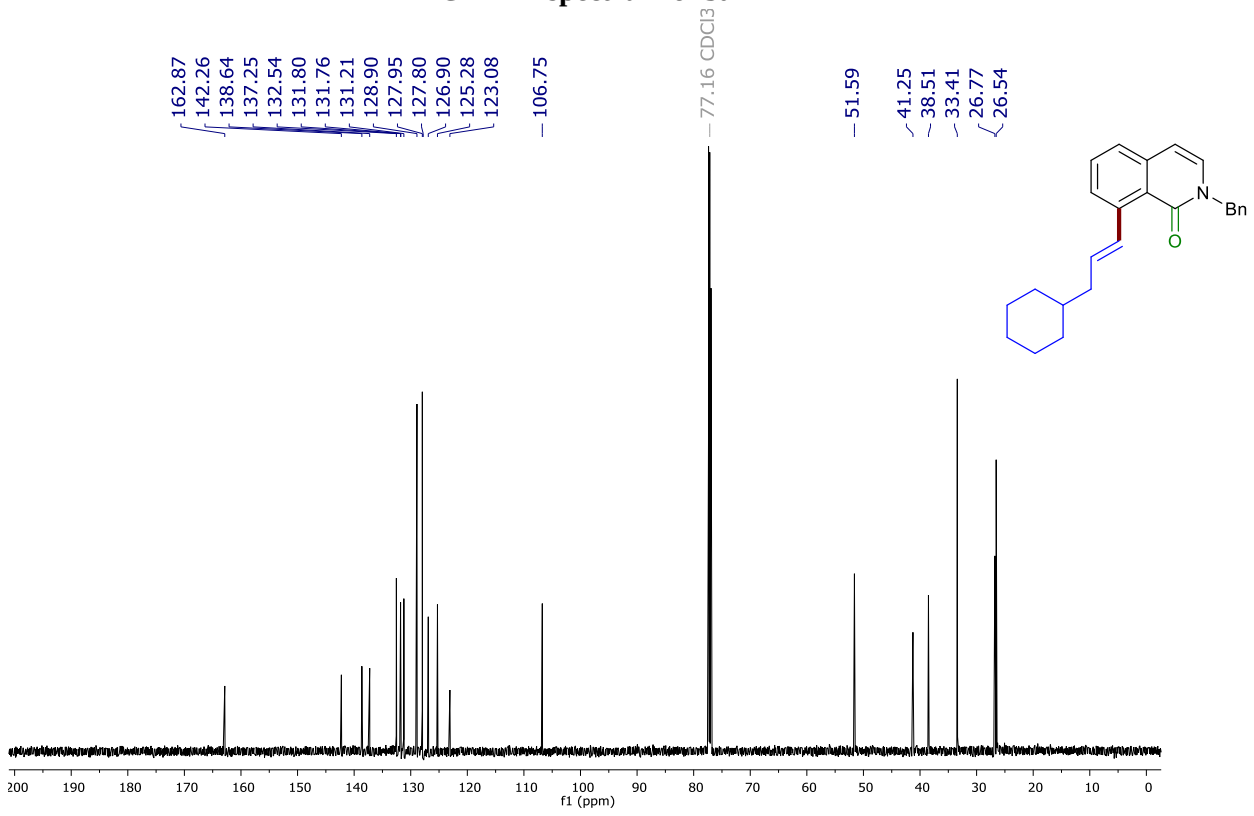

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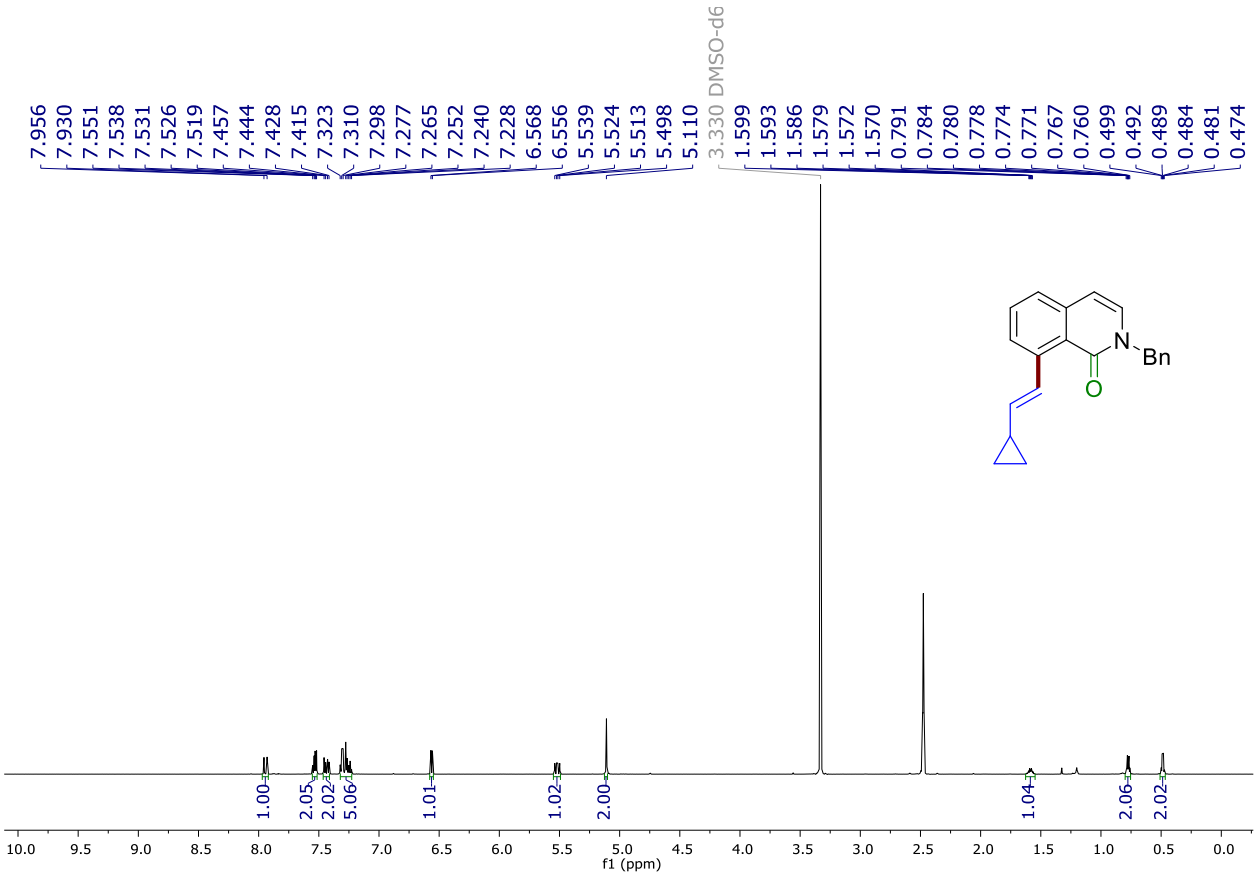
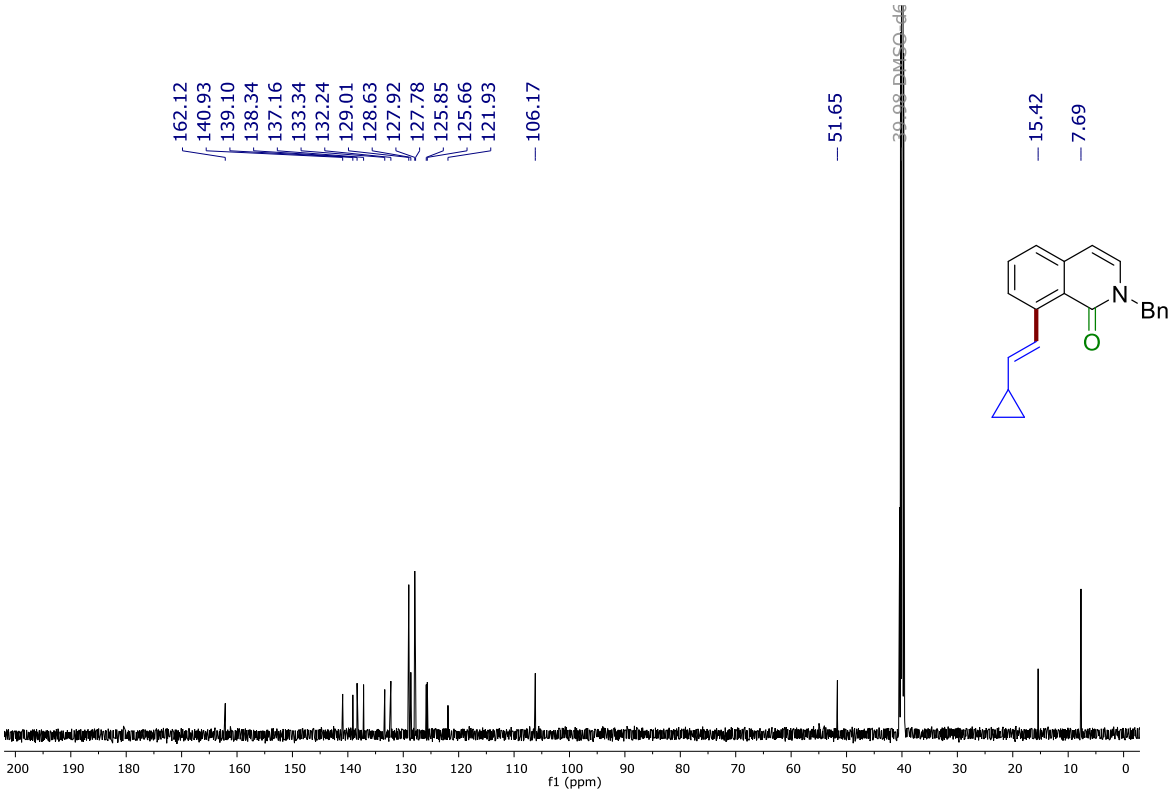
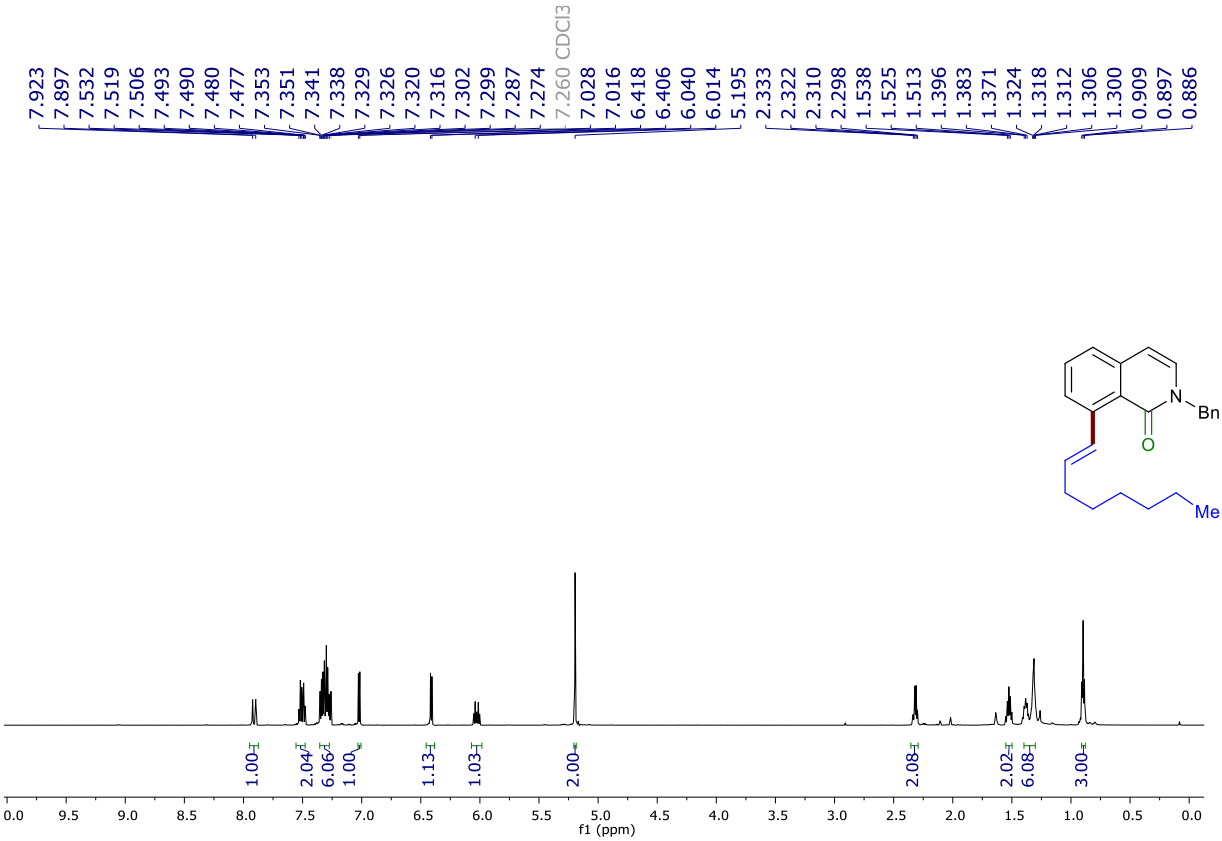


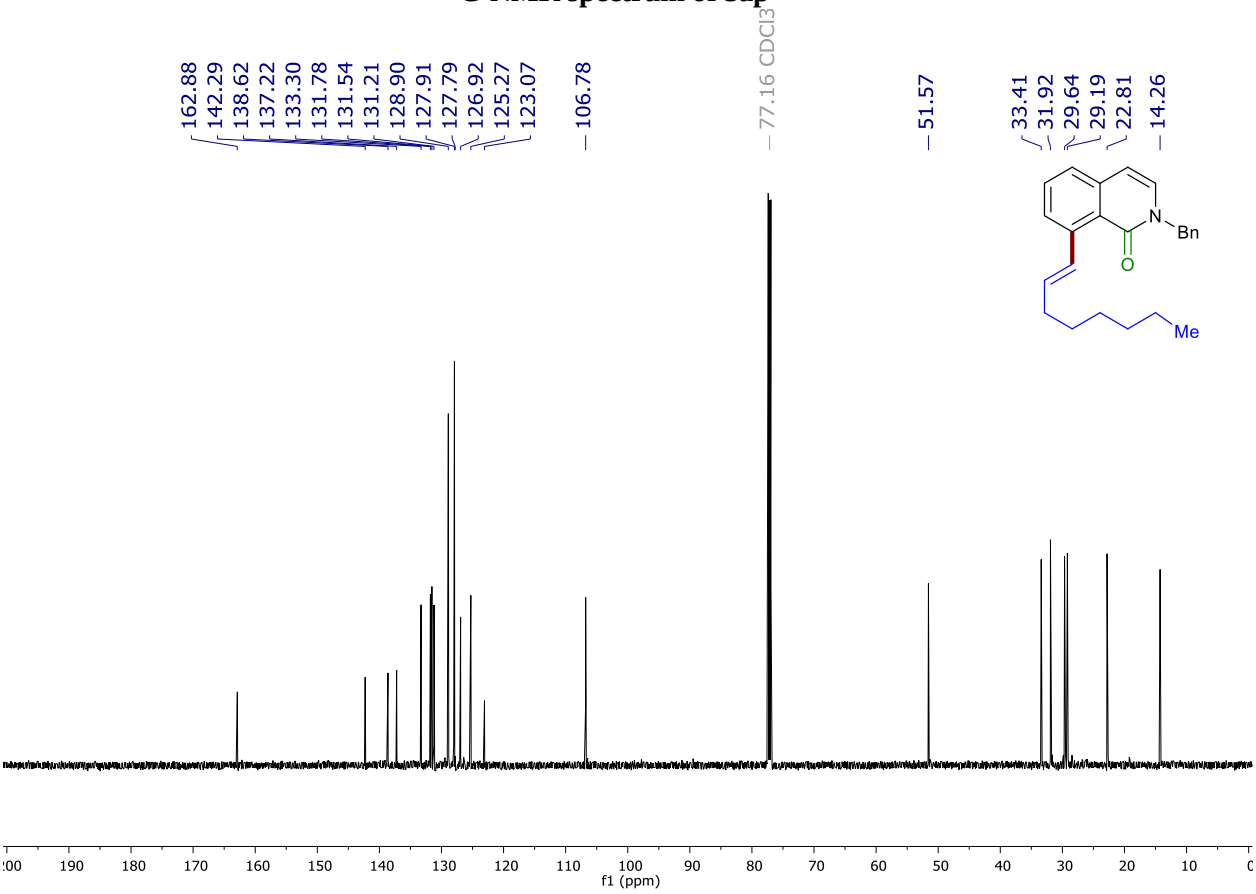
^{13}C-NMR spectrum of 3ao



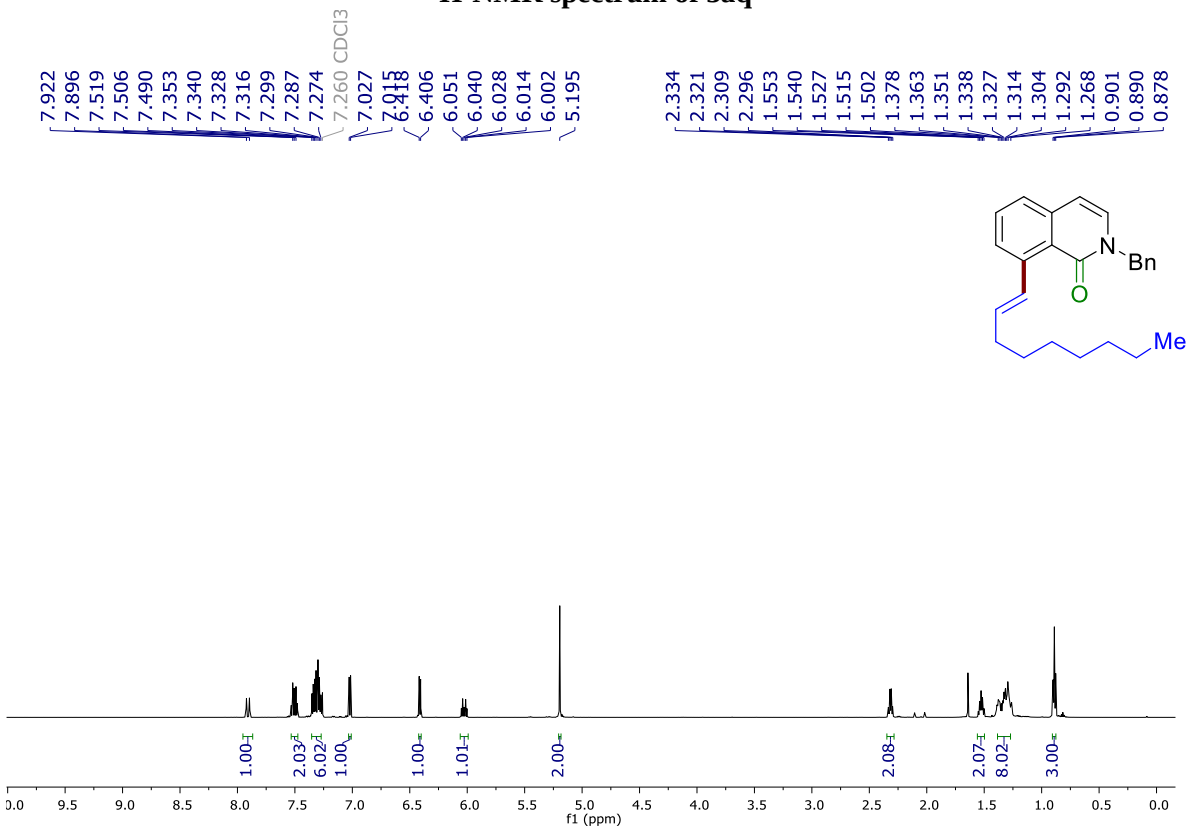
^{1}H-NMR spectrum of 3ap



^{13}C-NMR spectrum of 3ap



^{1}H-NMR spectrum of 3aq



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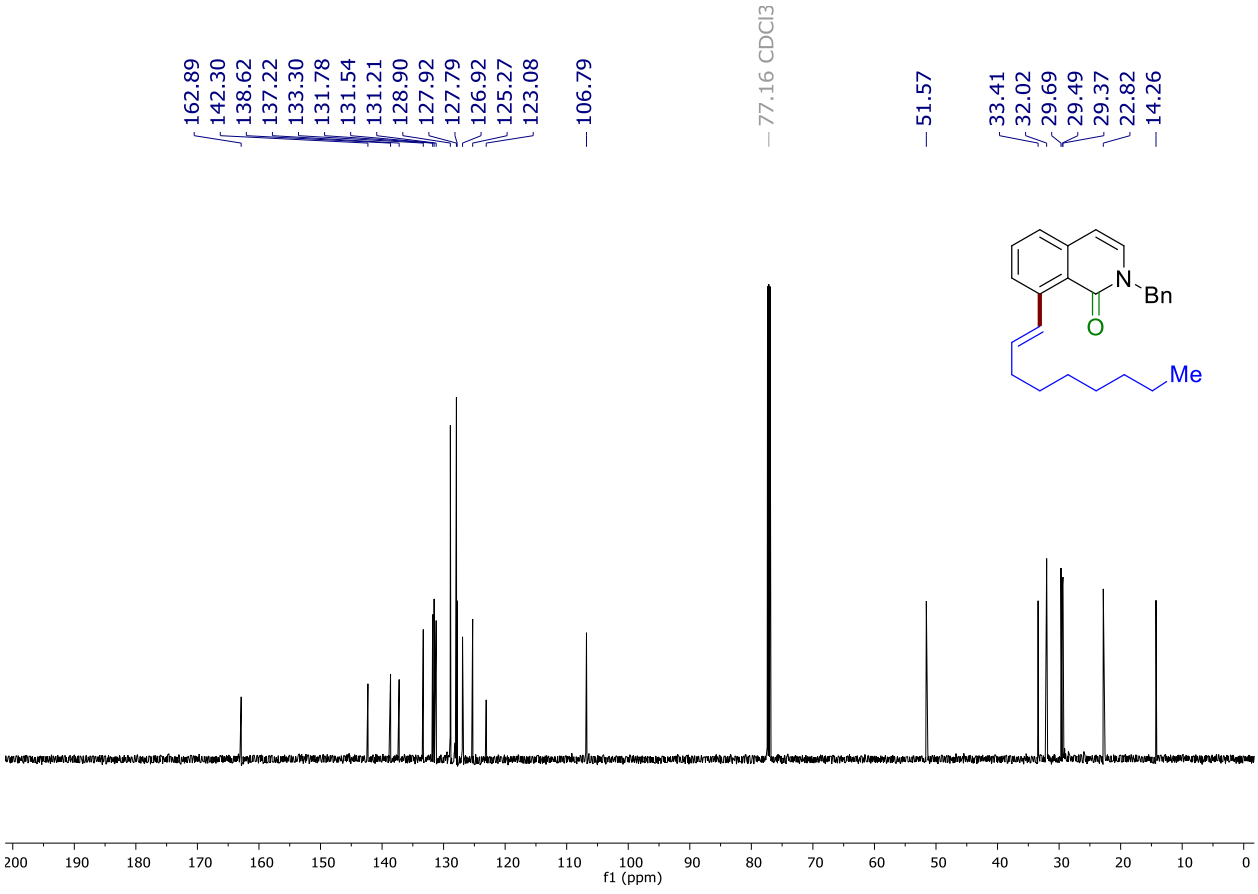
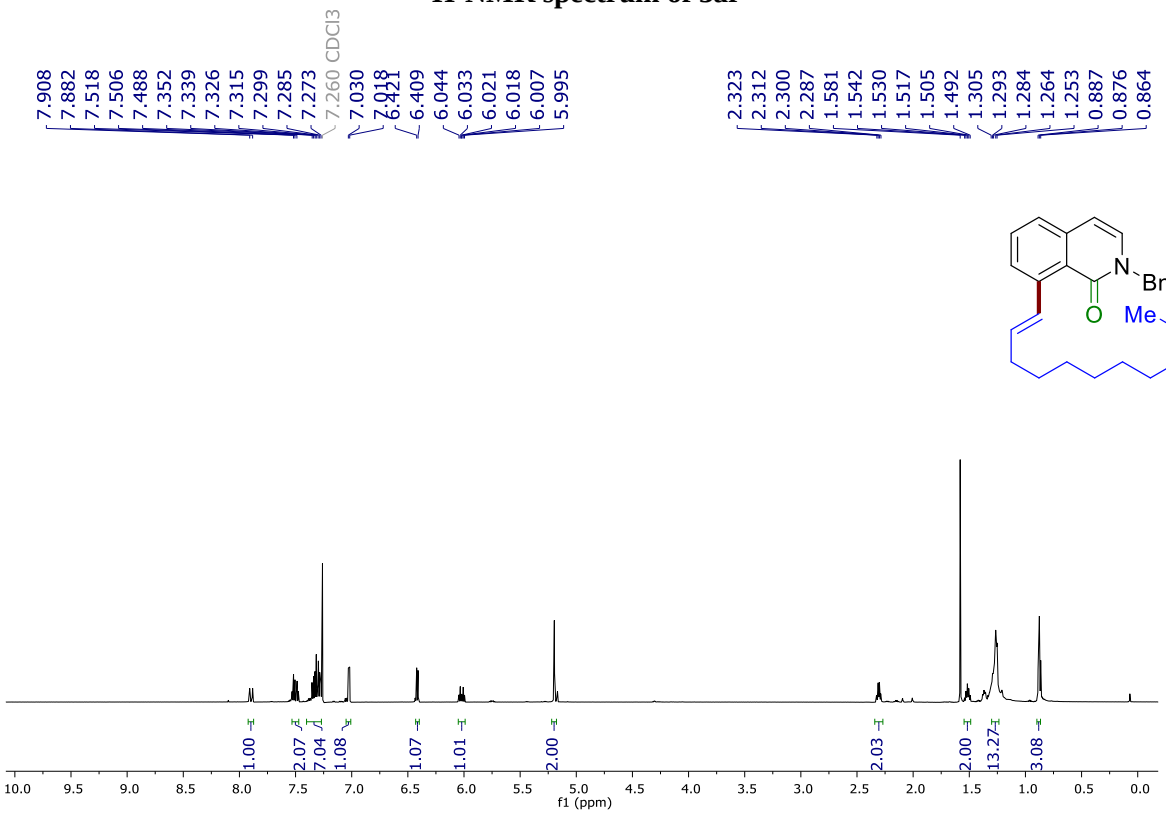
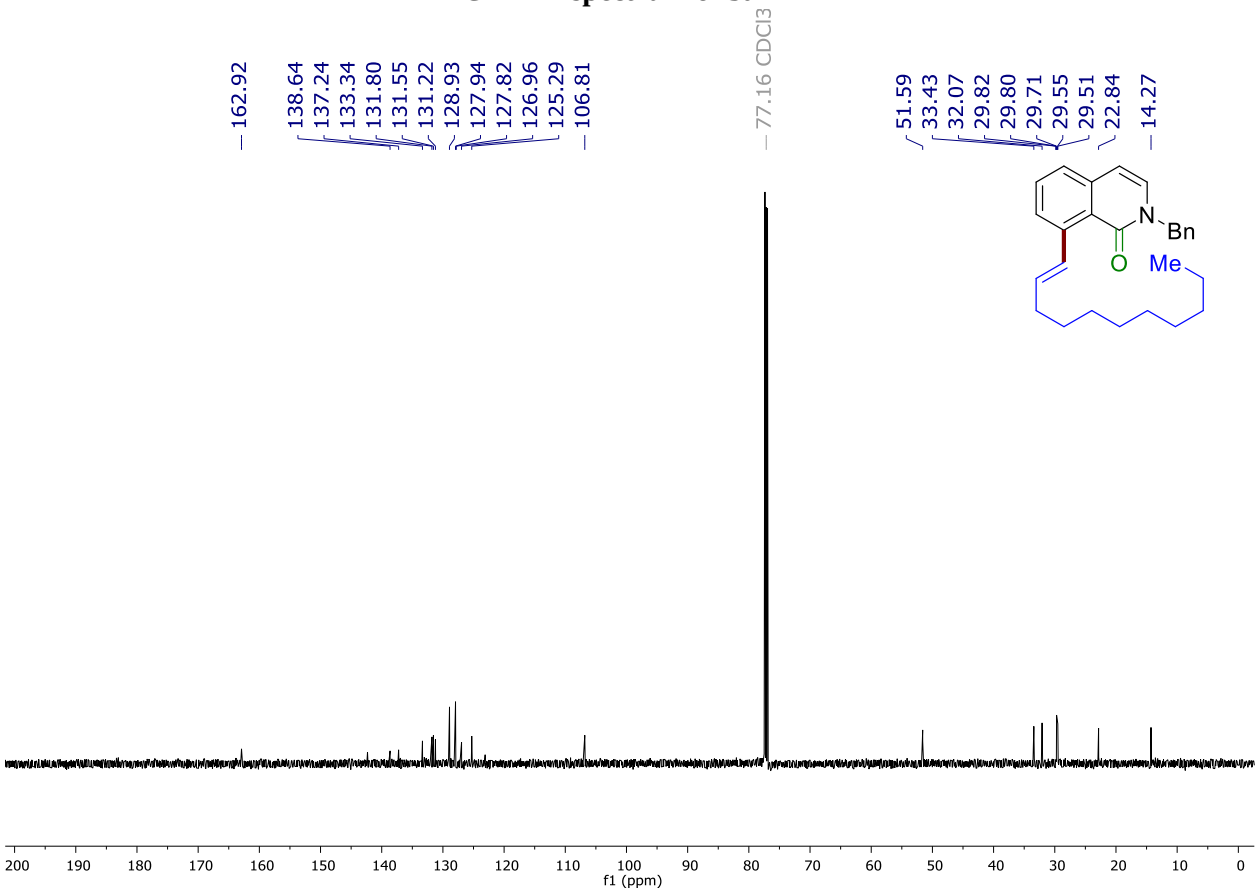


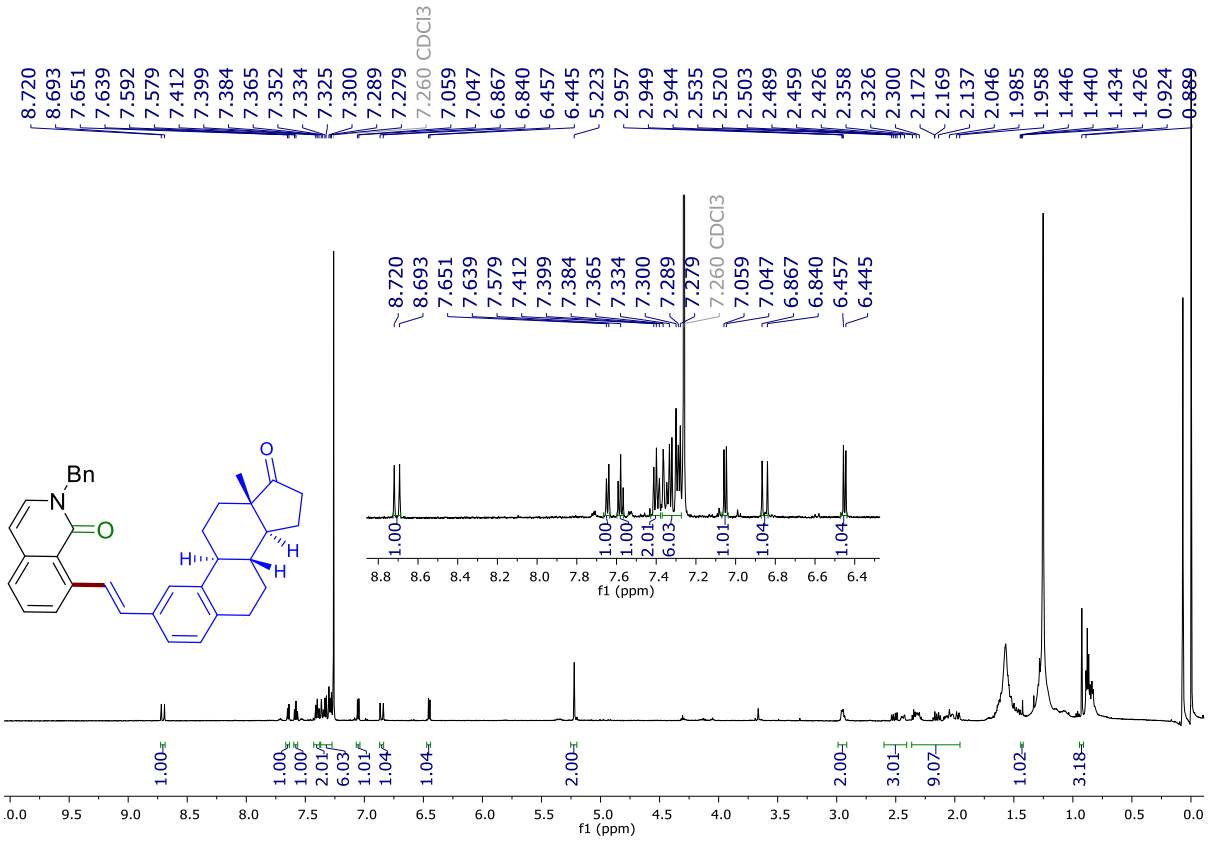
^{1}H-NMR spectrum of 3ar



^{13}C-NMR spectrum of 3ar



^{1}H-NMR spectrum of trace product form with estrone alkyne



8. Computational studies

8.1. DFT details

Density functional theory (DFT) calculations were performed to understand the detailed mechanism of the cobalt-catalyzed C8 linear olefination of isoquinoline-1H-2-one with terminal alkynes. All computations were performed with the ORCA quantum chemical package[S6] version 4.1.2. Geometries were optimized applying the BP86[S7,S8] generalized gradient approximation (GGA) functional in conjunction with the split valence basis set def2-SVP[S9]. The RI[S10-S12] (resolution-of-identity) approximation was used to accelerate the calculations. Dispersion corrections were included in all calculations via the Grimme D3 correction incorporating a Becke-Johnson (D3BJ) damping[S13] function. Harmonic vibrational frequency analysis was carried out to verify the nature of the stationary points. Corrections for solvation were considered in all calculations by invoking the implicit Conductor-like Polarizable Continuum Model (CPCM[S14]) with the selection of toluene as the solvent. The relative Gibbs free energies reported in mechanistic studies were obtained by performing solvation corrected single point energy calculations at RIJCOSX[S15]-M06[S16]/def2-TZVP[S9]/CPCM(toluene) //BP86-D3/def2-SVP.

Choice of DFT method: We chose BP86 functional in our calculations as recent studies are available on using BP86 functional for Cp*Co-catalyzed reactions.[S17,18] Moreover, studies are also available where BP86 was used for optimizing geometries, followed by the use of a second density functional for energy calculations. On the basis of the literature survey[S19,20], we have selected M06 for the energy calculation. Hence, the relative Gibbs free energies reported in mechanistic studies were obtained by performing solvation corrected single point energy calculations at M06/def2-TZVP/CPCM(toluene)//BP86-D3/def2-SVP.

Comparison of pathway determining parameters using different DFT functionals: Single point energy calculations were performed on BP86 optimized geometries using different types of DFT functionals available in the ORCA. GGA functional (BP86**)**, meta- and hybrid meta-GGA functionals (M06, M06-L[S21], TPPS[S22], TPSSH[S22], TPSS0[S22]), hybrid functionals (B3LYP[S23], PBE0[S24]), range-separated hybrid functionals (wB97X-D3[S25], wB97X-D3BJ[S26], CAM-B3LYP[S27]) were used for single-point solvation corrected energies computation. Using numerous functionals, we compared the pathway determining parameters (Fig. S3); $\Delta\Delta\mathbf{G}_{\mathbf{4B-4L}}$: the difference between the free energy of **4B** and **4L**, $\Delta\mathbf{G}_{\mathbf{L}}^{\#}$: reaction energy barrier in the linear pathway, $\Delta\mathbf{G}_{\mathbf{B}}^{\#}$: reaction energy barrier in the branch pathway. $\Delta\Delta\mathbf{G}_{\mathbf{4B-4L}}$ calculated from all the chosen density functionals do not differ significantly (in blue), and $\Delta\mathbf{G}_{\mathbf{B}}^{\#}$ (in gray) was found to be greater than $\Delta\mathbf{G}_{\mathbf{L}}^{\#}$ (in orange) in all the cases. Hence, these computational findings with different functionals support the outcome that the linear product is always preferred over the branch product.

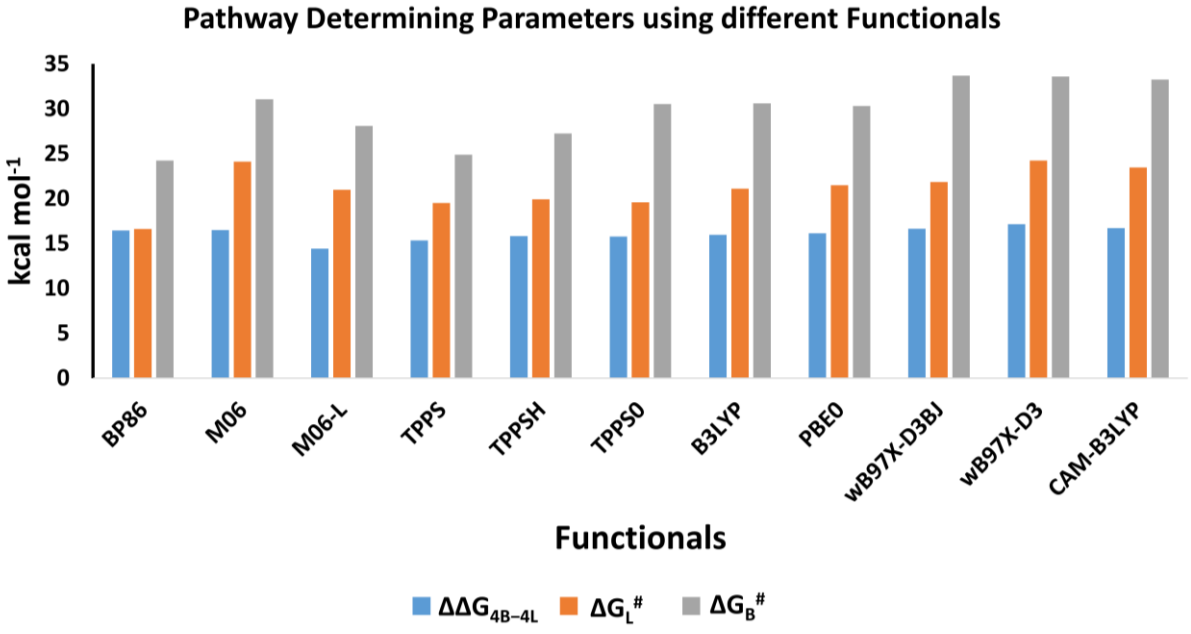


Fig. S3 Comparison of pathway determining parameters using different DFT functionals.

8.2. 3-D strucutures relevant to Fig. 2

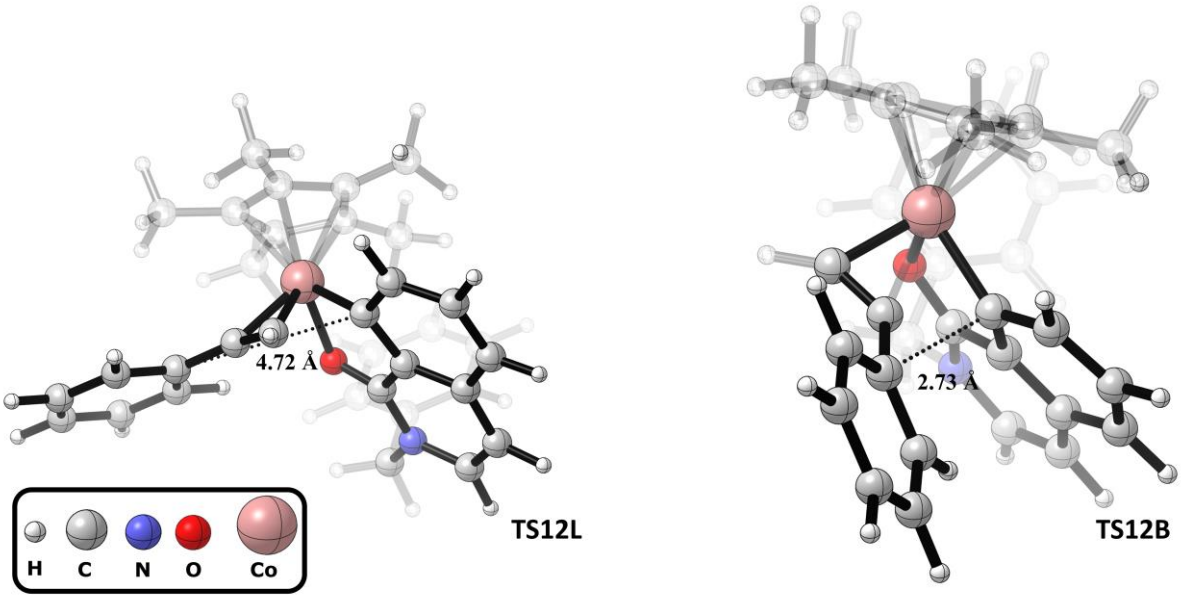


Fig. S4 3-D structures showing intermolecular distances between phenyl ring and isoquinolone in **TS12L** and **TS12B.**

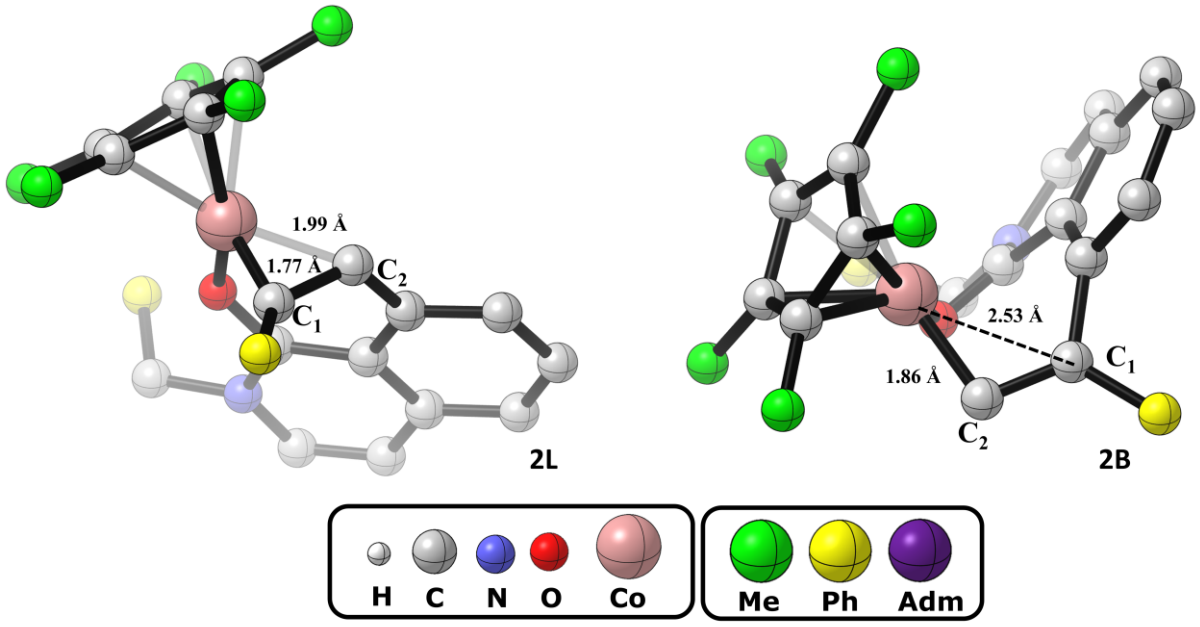


Fig. S5 3-D structures showing internuclelar distances between the cobalt and C's of phenylacetylene in **2L** and **2B**; H attached to the C atoms are omitted; methyl (Me), phenyl (Ph), and adamantane (Ad) group are replaced by green, yellow and purple balls, respectively to enhance the visual clarity.

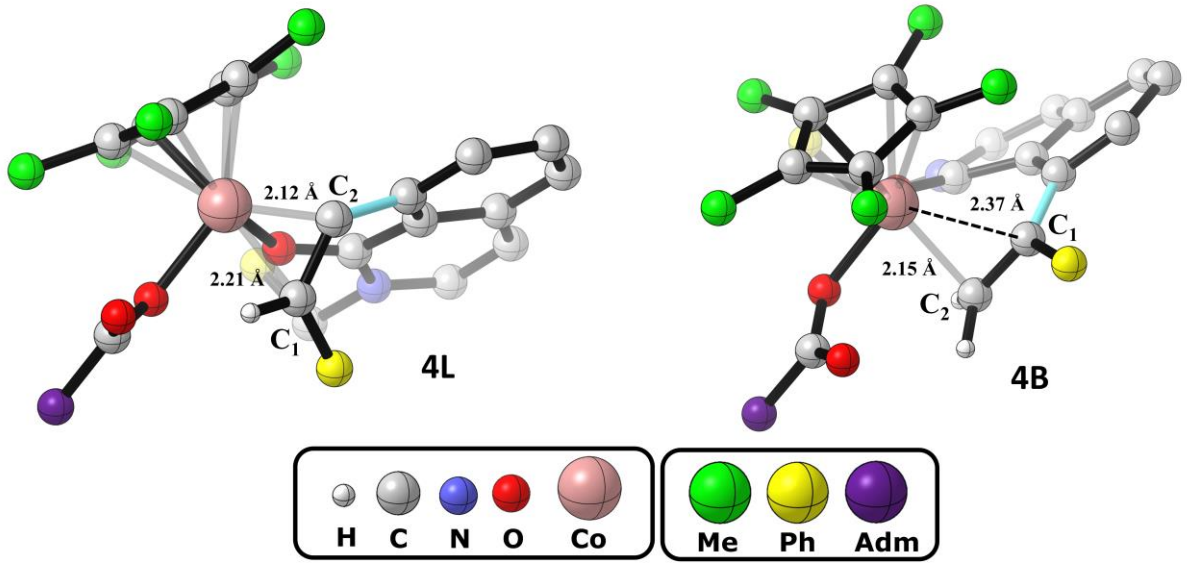


Fig. S6 3-D structures showing internuclelar distances between the cobalt and C's of phenylacetylene in **4L** and **4B**; H attached to the C atoms are omitted; methyl (Me), phenyl (Ph), and adamantane (Ad) group are replaced by green, yellow and purple balls, respectively to enhance the visual clarity.

8.3. Concerted metalation deprotonation mechanism for the formation of 1L and 1B

The reaction commences from the cationic Co(III) 1-adamantane carboxylate intermediate **A**, as shown in the calculated free energy profile (Fig. S7). The coordination of (isoquinolone) **1a** to **A** generates the relatively stable intermediate **B** with the release of 15.3 kcal mol^{-1}. The subsequent CMD process occurs via a transition state **TSBC** where the hydrogen attached to C8 of isoquinolone gets transferred to O of 1-adamantane carboxylate with the formation of Co−C bond at the C8 position of isoquinolone. This step requires a barrier of 23.8 kcal mol^{-1}, generating the intermediate **C**. In the connecting endoergic step, **C** eliminates 1-adamantane carboxylic acid to yield **D**. With phenylacetylene (**2a**) in the vicinity, it can coordinate to **D** to produce species **1L** and **1B** depending upon the orientation of the **2a**.

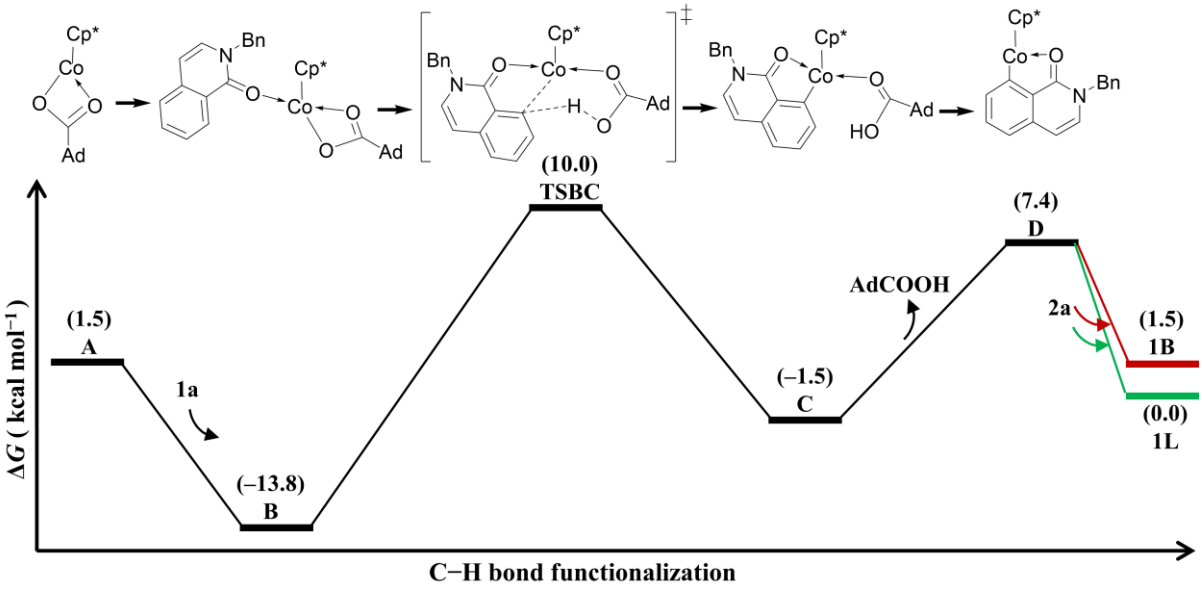


Fig. S7 Free energy profile for the initiation steps of the cobalt catalyzed C–H bond functionalization. Values in parenthesis are in kcal mol^{-1} are the free energies (relative to **1L**) calculated by M06/def2-TZVP/CPCM(toluene) //BP86-D3/def2-SVP**.**

8.4. Energy Table for C–H functionalization

Total electronic energies and Gibbs free energies (298 K) of the molecules involved in C–H functionalization. Employed DFT method: M06/def2-TZVP/CPCM(toluene)//BP86-D3/def2-SVP.

Molecule	E_{tot} [au]	G_{298} [au]	Imaginary Frequency
A	–2351.0305	–2350.6258	
B	–3098.3301	–3097.6908	
TSBC	–3098.2895	–3097.6528	*i254*
C	–3098.3122	–3097.6712	
D	–2519.1589	–2518.7634	
1a	–747.2443	–747.0406	
AdCOOH	–579.1093	–578.8936	

8.5 Energy Table for linear and branch coupling of isoquinoline-1*H*-2-one with phenylacetylene

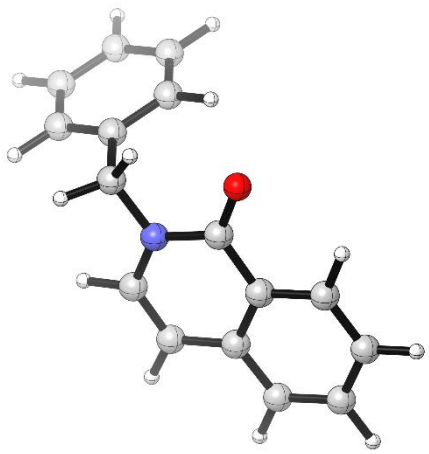
Total electronic energies and Gibbs free energies (298 K) of the molecules involved in linear and branch coupling of isoquinoline-1*H*-2-one with phenylacetylene. Employed DFT method: M06/def2-TZVP/CPCM(toluene)//BP86-D3/def2-SVP.

Molecule	E_{tot} [au]	G_{298} [au]	Imaginary Frequency
2a	–308.2552	–308.1792	
1L	–2827.4546	–2826.9544	
TS12L	–2827.4415	–2826.9403	*i336*
2L	–2827.4695	–2826.9663	
3L	–3406.5833	–3405.8381	
TS34L	–3406.5663	–3405.8215	*i115*
4L	–3406.6266	–3405.8776	
1B	–2827.4518	–2826.9519	
TS12B	–2827.4337	–2826.9337	*i380*
2B	–2827.4554	–2828.57993	
3B	–2827.4554	–2826.9545	
TS34B	–3406.5604	–3405.8189	*i1081*
4B	–3406.5997	–3405.8514	

8.6. Cartesian coordinates of the optimized structures

DFT optimization method: BP86-D3/def2-SVP

1a



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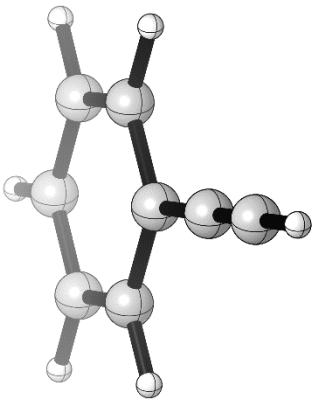
C	-0.395070000	0.567769000	-1.792018000
C	-0.886732000	0.902540000	-3.054075000

C	-1.843733000	0.069901000	-3.680453000
C	-2.248534000	-2.627868000	-1.063540000
C	-1.724509000	-2.912167000	0.167207000
N	-0.777167000	-2.111589000	0.772686000
H	-3.045901000	-1.731959000	-3.535816000
H	0.345437000	1.191292000	-1.270050000
H	-0.533982000	1.813065000	-3.561006000
H	-2.232295000	0.336319000	-4.675099000
H	-2.994523000	-3.299113000	-1.510038000
H	-2.031126000	-3.794533000	0.747751000
C	-0.280839000	-2.463328000	2.115930000
C	-0.302983000	-0.908681000	0.200255000
O	0.502715000	-0.195268000	0.809583000
H	-0.103808000	-3.556578000	2.141847000
H	0.687007000	-1.937841000	2.223742000
C	-1.238147000	-2.048016000	3.214040000
C	-1.976382000	-3.008590000	3.930830000
C	-1.420032000	-0.679156000	3.509518000
H	-1.834357000	-4.079602000	3.710492000
H	-0.837101000	0.066935000	2.947842000
C	-2.882764000	-2.614499000	4.930167000
C	-2.325742000	-0.286294000	4.505157000
H	-3.451084000	-3.375442000	5.486608000
H	-2.457963000	0.782979000	4.732238000
C	-3.059547000	-1.251804000	5.217635000
H	-3.767246000	-0.939529000	6.001355000

2a



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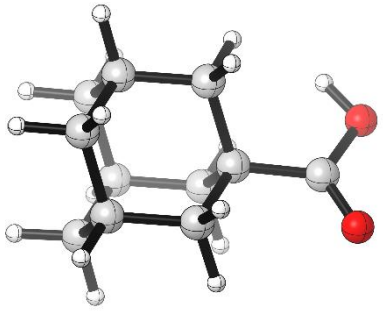
C	4.522710394	9.074819300	2.810889341
H	5.528457445	9.017004647	3.202323485
C	0.454102836	10.092723855	0.214865928
C	-0.580033846	9.359569532	0.822602813
C	1.759604374	10.025104638	0.718714729
H	-1.604067762	9.414345208	0.422835058
H	2.572614961	10.595882576	0.247242674
C	-0.301908051	8.555273568	1.941642664
C	2.050882956	9.215367277	1.846221792
H	-1.108923544	7.980985531	2.421455669
C	1.000357571	8.480041369	2.452706704
H	1.223446719	7.853509551	3.328584657
H	0.241147977	10.721984743	-0.662776793

AdCOOH



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H	-2.408793000	-1.447381000	5.205750000
C	-0.354335000	0.373711000	5.592070000
H	0.403366000	1.075599000	5.185134000
H	-1.207835000	-1.475612000	7.463367000
C	-0.525517000	0.573222000	7.109990000
C	-1.561032000	-0.437358000	7.645722000
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H	-1.678312000	-0.322966000	8.744670000
C	-1.014105000	2.009825000	7.388106000
H	-0.264804000	2.747773000	7.028311000
H	-1.126915000	2.172591000	8.481893000
C	-2.367254000	2.238150000	6.683953000
H	-2.720205000	3.274114000	6.875439000
H	-4.390186000	1.398845000	6.733111000
H	-1.479575000	2.777512000	4.748776000
C	-2.197538000	2.038480000	5.163892000
H	-3.177406000	2.233809000	4.667455000
H	-3.554425000	1.378338000	8.308813000
C	-3.404238000	1.227946000	7.218318000
H	-3.663065000	-0.939500000	7.323105000
C	-2.916214000	-0.209830000	6.943724000
H	0.012510000	-0.646845000	5.362944000
C	-1.518136000	0.354667000	3.360086000
O	-0.537365000	-0.150223000	2.858429000
O	-2.574506000	0.718940000	2.575371000
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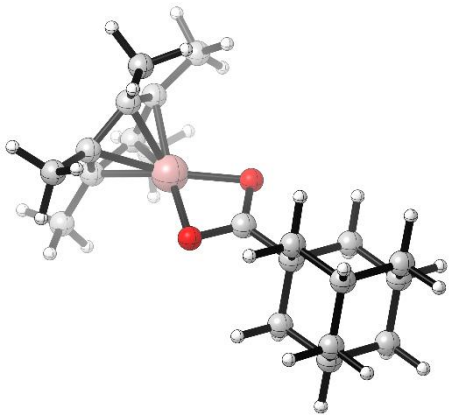
A



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H	-2.417993000	-1.105009000	6.018607000
C	-0.678654000	-0.510911000	3.915968000
H	-0.337798000	-0.657075000	2.870298000
H	-0.199732000	0.057105000	6.589012000
C	-0.053322000	0.764020000	4.519858000
C	-0.525999000	0.927611000	5.979847000

H	1.051851000	0.667111000	4.491532000
H	-0.059906000	1.827880000	6.432026000
C	-0.489416000	1.990414000	3.691131000
H	-0.142864000	1.886596000	2.640379000
H	-0.017868000	2.910454000	4.094835000
C	-2.024782000	2.121811000	3.732691000
H	-2.346427000	2.997467000	3.129609000
H	-3.602004000	2.403304000	5.227024000
H	-2.350557000	0.731389000	2.066361000
C	-2.667977000	0.859592000	3.123093000
H	-3.775445000	0.933501000	3.138592000
H	-2.062280000	3.210300000	5.627246000
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H	-2.407617000	1.170419000	7.064837000
C	-2.062363000	1.058024000	6.015707000
H	-0.358786000	-1.408190000	4.486271000
C	-2.882500000	-1.574680000	3.332125000
O	-2.256602000	-2.430883000	2.588082000
O	-4.156607000	-1.802250000	3.452679000
Co	-3.934214000	-3.356034000	2.340093000
C	-5.739431000	-3.802533000	1.528917000
C	-4.678970000	-3.708858000	0.525031000
C	-5.352312000	-4.806822000	2.472659000
C	-3.660733000	-4.700049000	0.831742000
C	-4.059392000	-5.357982000	2.043533000
C	-6.952344000	-2.936201000	1.587696000
H	-7.740614000	-3.343329000	0.918416000
H	-6.733725000	-1.904270000	1.252354000
C	-4.641713000	-2.746715000	-0.609074000
H	-5.098879000	-3.222801000	-1.505797000
H	-5.220945000	-1.828193000	-0.398326000
H	-3.607081000	-2.466295000	-0.880878000
C	-2.395535000	-4.914552000	0.069817000
H	-2.578769000	-5.590447000	-0.792620000
H	-1.995978000	-3.963782000	-0.330505000
H	-1.610657000	-5.374361000	0.698303000
C	-3.285137000	-6.388534000	2.789953000
H	-3.724640000	-7.392497000	2.596832000
H	-2.225618000	-6.420975000	2.478468000
H	-3.329627000	-6.225891000	3.885239000
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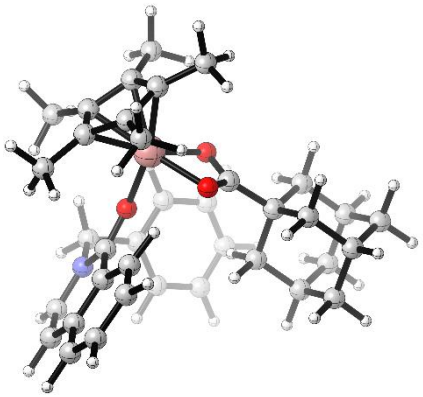
B



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Co	-3.903109000	-2.369147000	1.519096000
C	-5.465528000	-1.731706000	0.386300000
C	-4.447471000	-2.406923000	-0.406290000
C	-5.931215000	-2.647695000	1.392416000

C	-4.326511000	-3.763962000	0.095933000
C	-5.215731000	-3.909119000	1.218039000
C	-5.868250000	-0.305040000	0.213393000
H	-6.482352000	-0.191212000	-0.705313000
H	-4.976212000	0.342844000	0.102192000
C	-3.688378000	-1.819362000	-1.549561000
H	-4.238989000	-1.980548000	-2.501748000
H	-3.547721000	-0.729254000	-1.424324000
H	-2.691374000	-2.286162000	-1.657320000
C	-3.350091000	-4.771987000	-0.411734000
H	-3.624940000	-5.081976000	-1.441412000
H	-2.329595000	-4.340528000	-0.449984000
H	-3.317860000	-5.676751000	0.220987000
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H	-6.162408000	-5.795557000	1.631509000
H	-4.451788000	-5.707410000	2.146951000
H	-5.721990000	-4.859121000	3.086977000
C	-6.978134000	-2.386442000	2.425715000
H	-7.083366000	-1.309747000	2.652024000
H	-7.961402000	-2.757940000	2.064576000
H	-6.762477000	-2.912558000	3.375587000
H	-6.463285000	0.063799000	1.068488000
C	-6.023573000	0.556471000	6.355233000
C	-5.351754000	-0.674484000	6.126191000
C	-4.811963000	-0.936396000	4.822001000
C	-4.909080000	0.052300000	3.809962000
C	-5.560897000	1.255537000	4.067505000
C	-6.133016000	1.502368000	5.339894000
C	-5.174276000	-1.653238000	7.160111000
C	-4.492080000	-2.806426000	6.887625000
N	-4.001163000	-3.079808000	5.623395000
H	-6.446455000	0.754220000	7.351389000
H	-4.425816000	-0.124318000	2.842570000
H	-5.618153000	2.025429000	3.283264000
H	-6.650391000	2.454230000	5.531854000
H	-5.567606000	-1.477038000	8.169990000
H	-4.303799000	-3.583964000	7.639742000
C	-3.259812000	-4.333945000	5.373842000
C	-4.157615000	-2.209158000	4.554786000
O	-3.704921000	-2.612657000	3.442025000
H	-3.460262000	-4.993099000	6.240718000
H	-3.688233000	-4.810288000	4.473804000
C	-1.770121000	-4.129230000	5.187572000
C	-0.992242000	-3.549462000	6.210308000
C	-1.140723000	-4.565081000	4.007551000
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H	-1.348063000	-0.010201000	3.882758000
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C	-0.456112000	-0.563754000	3.520648000
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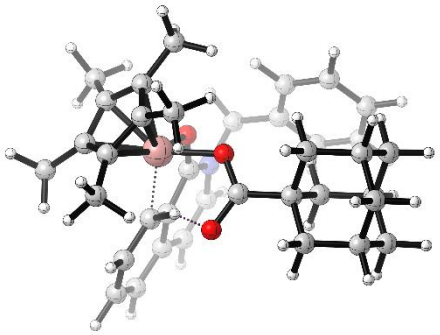
C	0.721392000	-1.454223000	1.465446000
H	0.684842000	-1.550406000	0.359225000
H	2.050832000	-1.667262000	3.885978000
C	2.016765000	-0.739806000	1.903527000
C	2.058577000	-0.651353000	3.442773000
H	2.889675000	-1.321219000	1.538366000
H	2.999288000	-0.159199000	3.769333000
C	2.051090000	0.682475000	1.306749000
H	2.036537000	0.632487000	0.196649000
H	2.995067000	1.194093000	1.593034000
C	0.837275000	1.487890000	1.816818000
H	0.858522000	2.511146000	1.386766000
H	0.010087000	2.161914000	3.728728000
H	-0.520258000	0.737459000	0.267730000
C	-0.462962000	0.787903000	1.376429000

H	-1.352811000	1.353229000	1.722562000
H	1.793990000	2.098811000	3.687826000
C	0.874724000	1.570690000	3.357241000
H	0.863245000	0.200524000	5.059818000
C	0.841626000	0.148428000	3.950809000
H	0.677656000	-2.479491000	1.883353000

TSBC



C	0.352370000	1.217538000	-0.803607000
O	0.059596000	-0.040874000	-0.860351000
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Co	-1.822034000	-0.503358000	-0.861568000
C	-2.860013000	0.085790000	-2.540406000
C	-1.692345000	-0.672021000	-2.910812000
C	-3.701312000	-0.768591000	-1.706576000
C	-1.762976000	-1.967241000	-2.266427000
C	-3.028714000	-2.028664000	-1.551096000
C	-3.153759000	1.479039000	-2.999321000
H	-3.246115000	1.508852000	-4.105238000
H	-2.338631000	2.174897000	-2.713158000
C	-0.577323000	-0.190516000	-3.774381000
H	-0.734130000	-0.547496000	-4.815174000
H	-0.524717000	0.913771000	-3.800519000
H	0.397738000	-0.577455000	-3.426541000
C	-0.719466000	-3.032697000	-2.339910000
H	-0.738604000	-3.538462000	-3.328977000
H	0.291345000	-2.601598000	-2.200779000
H	-0.872203000	-3.807187000	-1.565481000
C	-3.512768000	-3.187693000	-0.745696000
H	-3.966477000	-3.951644000	-1.413132000
H	-2.679913000	-3.667952000	-0.199039000
H	-4.280698000	-2.882645000	-0.011258000
C	-5.059969000	-0.435504000	-1.182702000
H	-5.204811000	0.653930000	-1.070278000
H	-5.834761000	-0.811290000	-1.884423000
H	-5.246295000	-0.901227000	-0.196729000
H	-4.100794000	1.861606000	-2.577973000
C	-3.774861000	1.849170000	2.955646000
C	-2.907827000	0.725353000	3.023413000
C	-2.353385000	0.233114000	1.806701000
C	-2.565394000	0.871458000	0.543019000
C	-3.435965000	1.974442000	0.533315000
C	-4.046682000	2.440481000	1.721795000
C	-2.551106000	0.044467000	4.239452000
C	-1.734475000	-1.055099000	4.193527000
N	-1.272727000	-1.580629000	2.995882000
H	-4.221470000	2.247477000	3.878405000
H	-1.650958000	1.219306000	-0.258973000
H	-3.582456000	2.544477000	-0.395526000
H	-4.715548000	3.313222000	1.673162000
H	-2.921804000	0.401918000	5.209331000
H	-1.418636000	-1.599983000	5.092684000
C	-0.422181000	-2.793837000	2.964926000
C	-1.611639000	-0.999248000	1.798609000
O	-1.316751000	-1.577372000	0.700376000

H	-0.502834000	-3.260976000	3.964654000
H	-0.859912000	-3.488599000	2.223251000
C	1.022080000	-2.492642000	2.618270000
C	1.853204000	-1.838591000	3.550895000
C	1.554966000	-2.879464000	1.373980000
H	1.448095000	-1.526139000	4.526424000
H	0.901870000	-3.364967000	0.634356000
C	3.203779000	-1.601534000	3.255028000
C	2.908364000	-2.649169000	1.080068000
H	3.847885000	-1.104402000	3.995615000
H	3.318957000	-2.966898000	0.110006000
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H	4.799343000	-1.846534000	1.797324000
H	1.797904000	1.562375000	1.447192000
C	1.837419000	1.555414000	-0.747171000
C	2.361599000	1.057474000	0.633155000
H	2.174839000	-0.031582000	0.724901000
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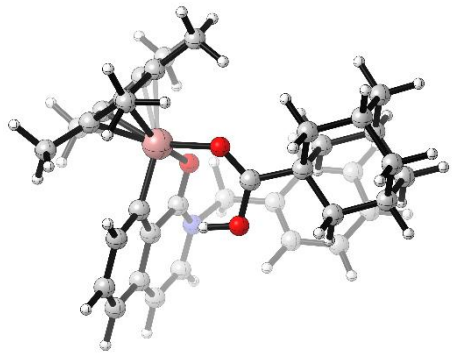

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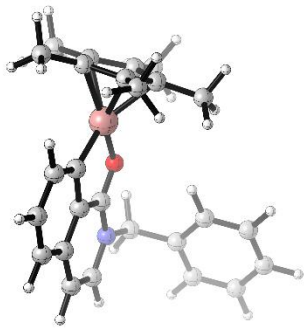

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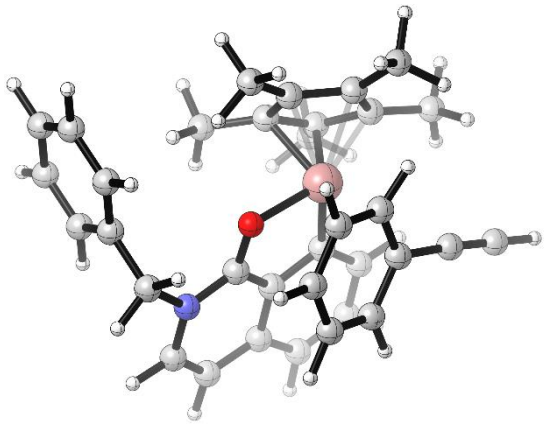

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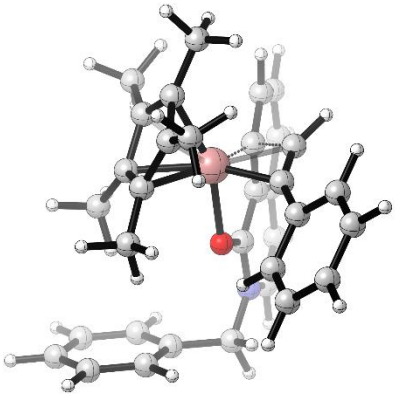

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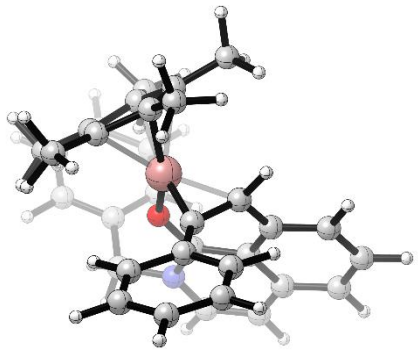

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C	3.453707000	8.160408000	8.161882000
C	2.353865000	7.421843000	7.830845000
N	2.203077000	6.883715000	6.566563000
H	5.796205000	9.465383000	8.545677000
H	7.209885000	9.077770000	4.467706000
H	7.583845000	9.808231000	6.817801000
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C	1.488431000	4.494437000	6.464767000
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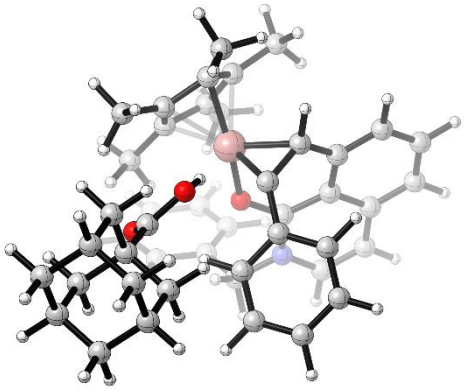

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C	2.137249000	8.080063000	1.224722000
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C	3.664420000	3.308345000	1.738475000
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H	2.028980000	2.628119000	-2.060214000
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Co	3.133708000	5.223673000	1.050986000
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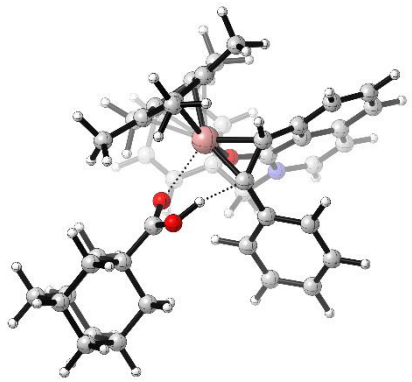
TS34L



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Co	3.054485000	5.489702000	0.789984000
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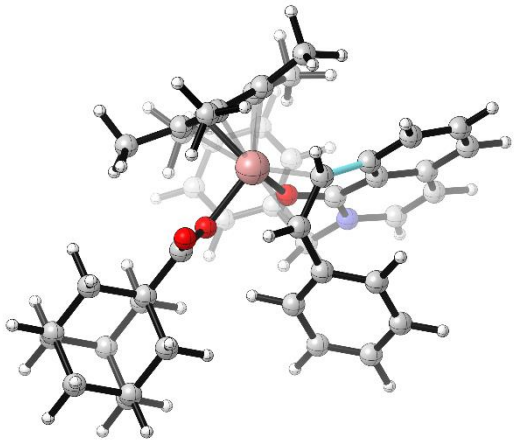

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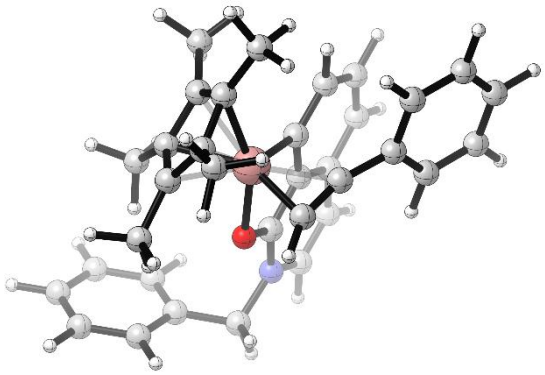
H	-0.168937000	8.881295000	-1.191514000

1B



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C	6.772505000	10.440731000	1.963639000
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H	6.700430000	12.220621000	5.449017000
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C	6.665059000	7.010426000	0.481367000
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Co	4.475568000	7.151764000	2.842151000
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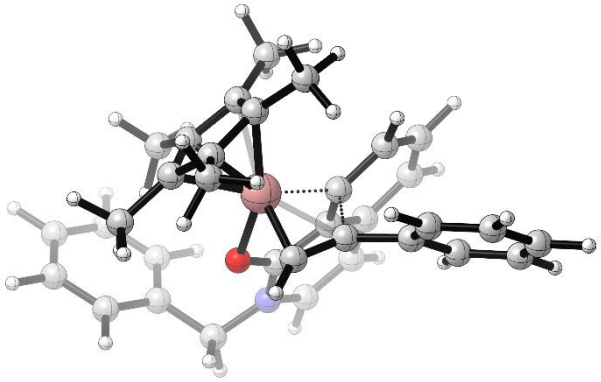
TS12B



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C	6.326126000	10.914957000	4.172188000
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C	4.311350000	4.995776000	2.849062000
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C	5.669056000	5.348836000	2.588659000
C	1.977994000	5.492191000	1.763270000
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H	1.526307000	5.545536000	2.772783000
H	1.520058000	6.278714000	1.134999000
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C	5.008243000	7.790517000	5.517288000
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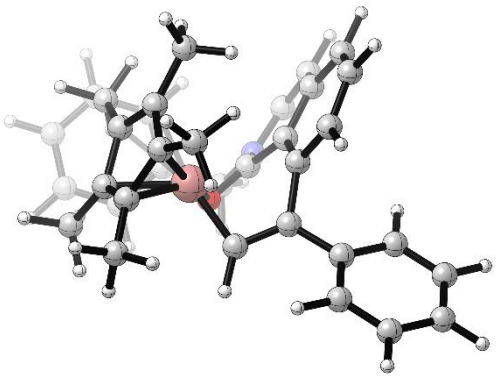
2B



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H	1.393181000	8.010786000	5.867734000
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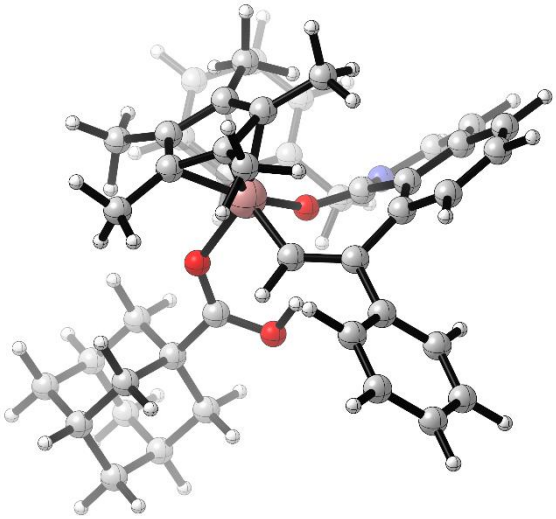
3B



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H	3.121290000	6.697320000	-1.263128000
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H	4.442890000	9.190483000	-2.254516000
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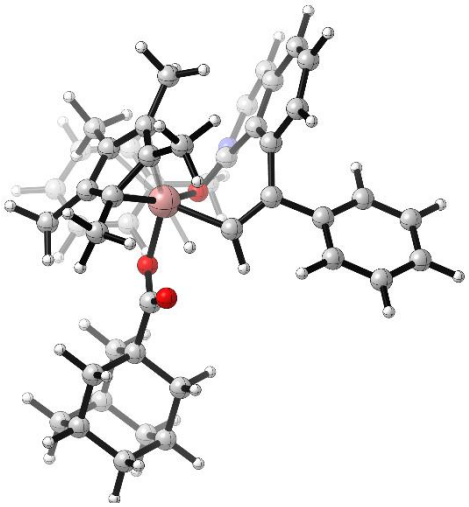
TS34B



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C	1.809013000	-2.260751000	-0.749959000
C	2.905540000	-0.327820000	-1.478949000
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H	-0.592939000	-1.761313000	-3.208978000
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H	0.460144000	-3.822082000	-0.103245000
H	2.181162000	-4.305159000	-0.230994000
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Co	1.060229000	-0.304416000	-0.484806000
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C	3.369498000	-0.442091000	3.615086000
C	2.505352000	0.041730000	2.573762000
C	2.905697000	1.173498000	1.787883000
C	4.205007000	1.674651000	1.960605000
C	5.112736000	1.088405000	2.868067000
C	2.849538000	-1.385035000	4.567160000
C	1.533600000	-1.754388000	4.508151000
N	0.721612000	-1.357412000	3.463775000
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H	3.482098000	-1.748462000	5.387862000
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C	-1.743280000	-2.710455000	1.289932000
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H	-2.577393000	2.991918000	-2.059856000
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H	-3.106017000	-1.304533000	-1.740546000
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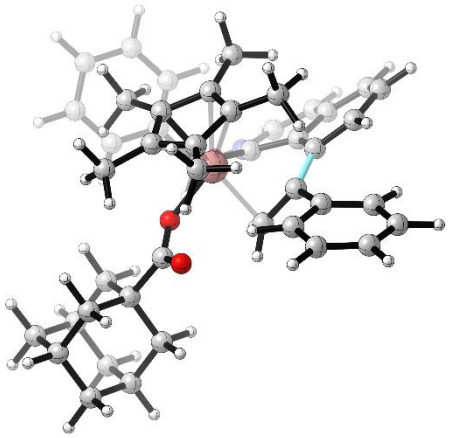
4B



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Co	3.160768000	10.146453000	2.150972000
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