Supporting Information

Enantioselective Synthesis of 3-Allylindolizines via Sequential Rh-Catalyzed Asymmetric Allylation and Tschitschibabin Reaction

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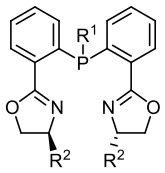
1. General information.

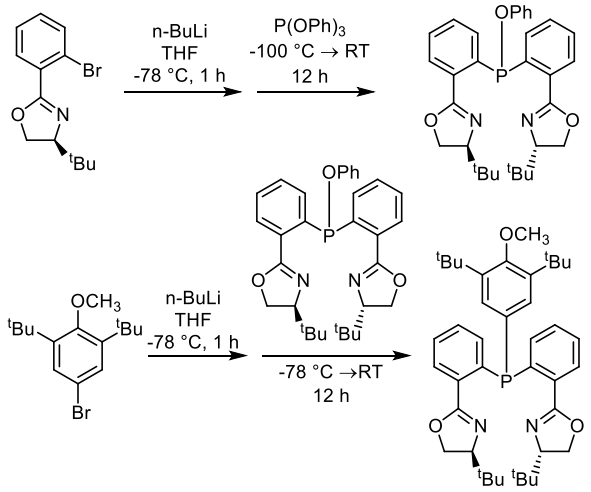
Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under dry argon atmosphere. All reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted by solvent purification system (Vigor YJC-7). Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 101 MHz, ^{13}C); Bruker-400 instrument (400 MHz, ^{1}H; 101 MHz, ^{13}C); Bruker-500 instrument (500 MHz, ^{1}H; 126 MHz, ^{13}C), spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent and the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; $(CD_3)_2SO$ at 2.05 ppm; ^{13}C NMR: $CDCl_3$ at 77.1 ppm; $(CD_3)_2SO$ at 39.5 ppm). ^{19}F NMR spectra were recorded on a Varian instrument (376 MHz, respectively) and referenced relative to $PhCF_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). XRD and High-resolution mass spectra (HRMS) were performed at Instrumental Analysis Center of Shanghai Jiao Tong University with electrospray spectrometer Waters Micro mass Q-TOF Premier Mass Spectrometer. Enantiomeric excess was determined by HPLC using a Daicel chiral column. Melting points were measured with Hanon MP100 melting point apparatus. Optical rotations were measured on an Anton Paar MCP100 automatic polarimeter using a 100 mm path-length cell at 589 nm.

2. Procedure for the ligand synthesis.



L1, R^1 = Ph, R^2 = Me
L2, R^1 = Ph, R^2 = Bn
L3, R^1 = Ph, R^2 = Ph
L4, R^1 = Ph, R^2 = i-Pr
L5, R^1 = Ph, R^2 = t-Bu
L6, R^1 = 3,5-t-Bu_2-4-$MeOC_6H_2$, R^2 = t-Bu
L7, R^1 = 4-$CF_3C_6H_4$, R^2 = t-Bu
L8, R^1 = 4-$OMeC_6H_4$, R^2 = i-Pr

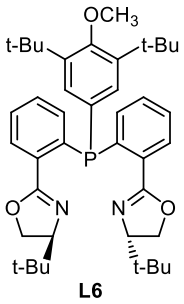
L1-L5 and **L8** were prepared according to the literature.[1]



L6 [R^1 =4-OMe-3,5-t-$Bu_2C_6H_2$, R^2 = t-Bu]

The reaction was performed according to the modified literature procedure.[1] In a flame dried schlenk tube, 2-(2-bromophenyl)-4-(tert-butyl)-4,5-dihydrooxazole (2.81 g, 10 mmol, 2.0 equiv) was dissolved in THF solvent (20 mL) under an argon atmosphere and the solution was cooled down to -78 °C. n-BuLi (7.5 mL, 1.6 M in hexane, 2.4 equiv, 12 mmol) was added dropwise and the mixture was stirred for 1 hour at -78 °C. The reaction mixture was further cooled to ~ -100 °C and was added triphenyl phosphite (1.55 g, 5.0 mmol, 1.0 equiv) in 2.0 mL of THF in one portion under vigorous stirring. The reaction was slowly warmed up to room temperature and stirred for 5 hours. The reaction mixture **A** was used in the next step directly.

In another flame dried schlenk tube, 5-bromo-1,3-di-tert-butyl-2-methoxybenzene (1.79 g, 6 mmol, 1.2 equiv) was dissolved in THF (20 mL) under an argon atmosphere and the mixture was cooled down to -78 °C. n-BuLi (4 mL, 1.3 equiv, 1.6 M in hexane, 6.5 mmol) was slowly added to the solution at -78 °C, and the reaction mixture **B** was stirred at this temperature for 1 hour. Then the reaction mixture **A** was added to the reaction mixture **B** dropwise via a syringe at -78 °C. The resulted solution was allowed to warm to room temperature slowly and stirred for 12 hours. The reaction was quenched with water, and the mixture was washed with sodium hydroxide. The aqueous phase was extracted with ethyl acetate, and the combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (PE : EA 50 : 1) as eluent to afforded the product **L6** 2.25 g (69% yield) as light yellow solid.



L6

L6 [R^1 =4-OMe-3,5-t-Bu$_2$C$_6$H$_2$, R^2 = t-Bu].

m. p. 175.1 °C ~ 176.8 °C, TLC R_f = 0.2 (PE : EA 50 : 1).

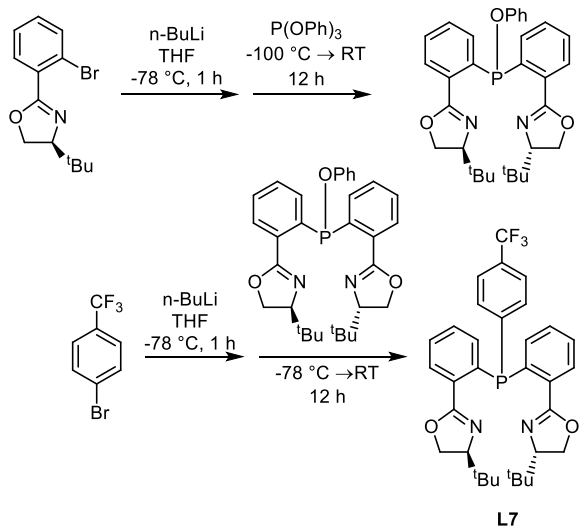
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.32-7.26 (m, 3H), 7.25-7.18 (m, 1H), 7.08 (d, J = 7.4 Hz, 2H), 6.92-6.84 (m, 2H), 4.13-3.84 (m, 6H), 3.65 (s, 3H), 1.27 (s, 18H), 0.65 (s, 9H), 0.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J = 2.9 Hz), 162.5 (d, J = 3.3 Hz), 143.0, 143.0, 142.3, 142.0, 141.0, 140.8, 134.6, 133.8, 133.0, 132.7, 132.2, 132.0, 131.9, 131.8, 131.7, 131.5, 130.2, 130.0, 129.7 (d, J = 2.2 Hz), 129.4 (d, J = 3.9 Hz), 127.5, 76.6 (d, J = 0.8 Hz), 68.1, 64.2, 35.8, 33.8, 33.6, 32.1, 26.0, 25.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ -5.69.

$[\alpha]_D^{25}$ = -44.5 (*c* 1.1, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{41}H_{56}N_2O_3P$ 655.4029; Found 655.4045.



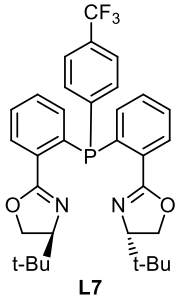
L7

L7 [R^1 =4-$CF_3C_6H_4$, R^2 = t-Bu]

The reaction was performed according to the modified literature procedure.[1] In a flame dried schlenk tube, 2-(2-bromophenyl)-4-(tert-butyl)-4,5-dihydrooxazole (2.81 g, 10 mmol, 2.0 equiv) was dissolved in THF solvent (20 mL) under an argon atmosphere and the solution was cooled down to -78 °C. n-BuLi (7.5 mL, 1.6 M in hexane, 2.4 equiv, 12 mmol) was added dropwise and the mixture was stirred for 1 hour at -78 °C. The reaction mixture was further cooled to ~ -100 °C and was added triphenyl phosphite (1.55 g, 5.0 mmol, 1.0 equiv) in 2.0 mL of THF in one portion under vigorous stirring. The reaction was slowly warmed up to room temperature and stirred for 5 hours. The reaction mixture **A** was used in the next step directly.

In another flame dried schlenk tube, 1-bromo-4-(trifluoromethyl)benzene (1.34 g, 6 mmol, 1.2 equiv) was dissolved in THF (20 mL) under an argon atmosphere and the solution was cooled down to -78 °C. n-BuLi (4 mL, 1.3 equiv, 1.6 M in hexane, 6.5 mmol) was slowly added to the solution at -78 °C, and the reaction mixture **B** was stirred at this temperature for 1 hour. Then the reaction mixture **A** was added to the reaction mixture **B** dropwise via a syringe at -78 °C. The resulted solution was allowed to warm to room temperature slowly and stirred for 12 hours. The reaction was quenched with water, and the mixture was washed with sodium hydroxide. The aqueous phase was extracted with ethyl acetate, and the

combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (PE : EA 10 : 1) as eluent to afforded the product **L7** 1.65 g (57% yield) as white solid.



L7

L7 [R^1 = 4-$CF_3C_6H_4$, R^2 = t-Bu].

m. p. 75.0 ºC ~ 76.0 ºC, TLC R_f = 0.4 (PE : EA 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.40-7.31 (m, 4H), 7.28-7.22 (m, 2H), 6.91-6.83 (m, 2H), 4.16-3.96 (m, 4H), 3.93-3.85 (m, 2H), 0.63 (d, *J* = 2.1 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 2.2 Hz), 162.1 (d, *J* = 3.1 Hz), 145.6, 145.6, 145.5, 140.1, 139.9, 139.4, 139.1, 135.0, 134.3, 134.2, 134.1, 132.2, 132.2, 132.0, 131.9, 130.5, 130.4, 129.8 (q, *J* = 32.5 Hz), 129.7 (d, *J* = 3.1 Hz), 128.2 (d, *J* = 3.5 Hz), 125.0-124.5 (m), 124.4 (q, *J* = 273.0 Hz), 76.8 (d, *J* = 28.6 Hz), 68.3, 68.2, 33.7, 33.5, 25.7, 25.7.

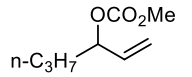
^{31}P NMR (162 MHz, $CDCl_3$) δ -7.68.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63.

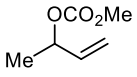
$[\alpha]_D^{25}$ = -23.1 (*c* 1.1, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{33}H_{37}F_3N_2O_2P$ 581.2545; Found 581.2554.

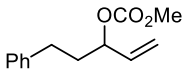
3. Syntheses of allylic carbonates, pyridinium salts.



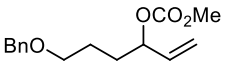
1a



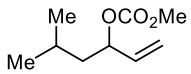
1b



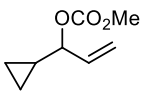
1c



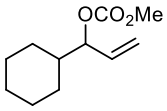
1d



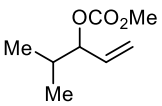
1e



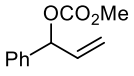
1f



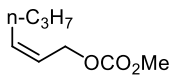
1g



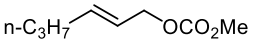
1h



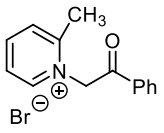
1i



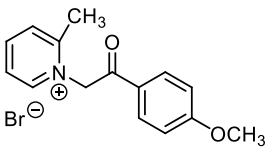
Z-1j



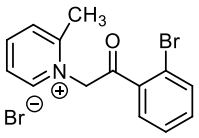
E-1k



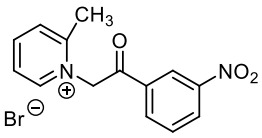
2a



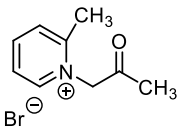
2b



2c



2d



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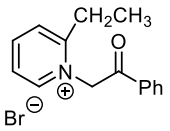
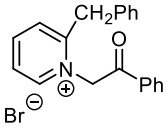
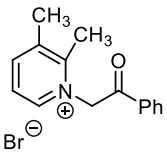


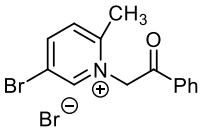
2f



2g

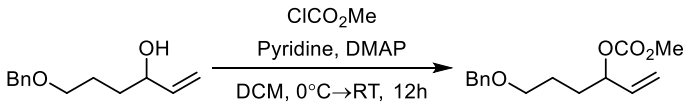


2h



2i

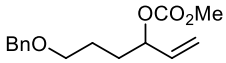
The allylic carbonate **1a – 1c**[2], **1g – 1i**[2], **Z – 1j**[2], **E – 1k**[2], **1e**[2], **1f**[1] were prepared according to the literature. The pyridinium salts **2a – 2c**[3-4], **2e – 2f**[3-4]were prepared according to the literature.



1d' 1d

Allylic carbonate **1d** was synthesized in similar way to the other allylic carbonate reported in the literature.[1-2]

In a flame dried schlenk tube, a solution of allyl alcohol substrate **1d'** (1.65 g, 8 mmol, 1.0 equiv) and 4-dimethylaminopyridine (195.2 mg, 1.6 mmol, 0.2 equiv) in DCM (15 mL) was added pyridine (1.89 g, 24 mmol, 3.0 equiv) under an argon atmosphere and cooled down to 0 ºC. Methyl chloroformate (1.13 g, 12 mmol, 1.5 equiv) was slowly added to the mixed solution at 0 ºC. After being stirred at 0 ºC for 30 minutes, the reaction solution was allowed to warm to room temperature and continues to stir overnight. The reaction was quenched with saturated sodium bicarbonate, and the aqueous phase was extracted with ether. The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE : EA 20 : 1) to give **1d** (1.58 g, 75%) as a colorless oil.



1d

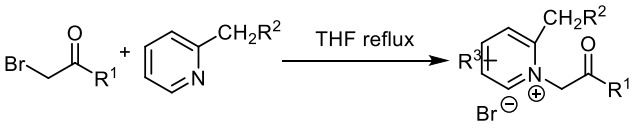
6-(benzyloxy)hex-1-en-3-yl methyl carbonate (1d).

Colorless oil, 1.58 g, 75%. TLC R_f = 0.2 (PE : EA 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.30-7.26 (m, 1H), 5.86-5.74 (m, 1H), 5.30 (dt, J = 17.2, 1.2 Hz, 1H), 5.21 (dt, J = 10.5, 1.1 Hz, 1H), 5.09 (q, J = 6.7 Hz, 1H), 4.50 (s, 2H), 3.77 (s, 3H), 3.52-3.46 (m, 2H), 1.82-1.74 (m, 2H), 1.72-1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 138.5, 135.9, 128.4, 127.6, 127.6, 117.6, 78.9, 72.9, 69.8, 54.7, 31.0, 25.3.

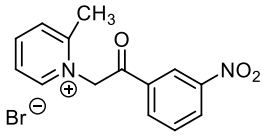
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{20}O_4Na$ 287.1254; Found 287.1260.



2

All the pyridinium salts (**2a** to **2c, 2e** to **2f**) were prepared according to the reported literature procedure.[4]

General Method for the Preparation of the Pyridinium Salts (2d, 2g, 2h, 2i) : The reaction was performed according to the modified literature procedure.[3-4] In a flame dried schlenk tube, the pyridine (5 mmol, 1.0 equiv) was dissolved in THF (10 ml) and the alpha-bromo ketone (5 mmol, 1.0 equiv) was added dropwise. After stirring in refluxing THF (oil bath as heat source), the formed precipitate is filtered out, washed with Et_2O (20 mL) and recrystallized from methanol/toluene (1 : 1).



2d

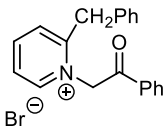
2-methyl-1-(2-(3-nitrophenyl)-2-oxoethyl)pyridin-1-ium bromide (2d).

According to the general procedure, the reaction of 2-bromo-1-(3-nitrophenyl)ethan-1-one (1.22 g, 5 mmol), 2-methylpyridine (0.465 g, 5 mmol) reflux in THF (10 mL) for 6 hours afforded the product **2d** 1.42 g (84% yield) as yellow solid, the products were purified through by crystallization (methanol/toluene 1:1). m. p. 224.1 ºC ~ 224.5 ºC, TLC R_f = 0.3 (DCM : MeOH 10 : 1).

^{1}H NMR (400 MHz, DMSO) δ 9.11-9.09 (m, 1H), 8.80 (t, *J* = 1.9 Hz, 1H), 8.66 (td, *J* = 7.9, 1.3 Hz, 1H), 8.62-8.58 (m, 1H), 8.57-8.53 (m, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.17-8.09 (m, 1H), 7.98 (t, *J* = 8.0 Hz, 1H), 6.85 (s, 2H), 2.78 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 189.7, 156.6, 147.9, 146.6, 146.5, 134.8, 134.7, 130.9, 129.7, 128.7, 125.6, 123.0, 64.0, 19.9.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{14}H_{13}N_2O_3$ 257.0921; Found 257.0925.



2g

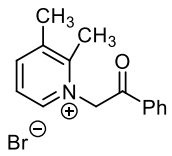
2-benzyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (2g).

According to the general procedure, the reaction of 2-bromo-1-phenylethan-1-one (0.99 g, 5 mmol), 2-benzylpyridine (0.845 g, 5 mmol) reflux in THF (10 mL) for 12 hours afforded the product **2g** 1.59 g (87% yield) as white solid, the products were purified through by crystallization (methanol/toluene 1:1). m. p. 190.5 °C ~ 191.0 °C, TLC R_f = 0.3 (DCM : MeOH 10 : 1).

^{1}H NMR (400 MHz, DMSO) δ 9.11 (dd, *J* = 6.2, 0.9 Hz, 1H), 8.68 (td, *J* = 7.9, 1.3 Hz, 1H), 8.23-8.11 (m, 1H), 8.08-7.96 (m, 3H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.26-7.11 (m, 5H), 6.81 (s, 2H), 4.65 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 190.1, 157.4, 147.7, 146.6, 134.6, 134.3, 133.2, 129.5, 129.3, 128.8, 128.4, 127.3, 125.8, 63.5, 37.4.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{20}H_{18}NO$ 288.1383; Found 288.1383.



2h

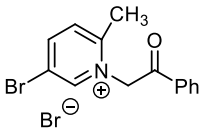
2,3-dimethyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (2h).

According to the general procedure, the reaction of 2-bromo-1-phenylethan-1-one (0.99 g, 5 mmol), 2,3-dimethylpyridine (0.535 g, 5 mmol) reflux in THF (10 mL) for 12 hours afforded the product **2h** 1.19 g (78% yield) as white solid, the products were purified through by crystallization (methanol/toluene 1:1). m. p. 182.5 °C ~ 183.0 °C, TLC R_f = 0.3 (DCM : MeOH 10 : 1).

^{1}H NMR (400 MHz, DMSO) δ 8.89 (d, *J* = 5.9 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 1H), 8.16-8.08 (m, 2H), 7.99 (dd, *J* = 7.6, 6.5 Hz, 1H), 7.84-7.77 (m, 1H), 7.71-7.63 (m, 2H), 6.71 (s, 2H), 2.61 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 190.8, 155.6, 146.4, 144.4, 138.4, 134.9, 133.4, 129.1, 128.6, 124.6, 64.6, 19.3, 16.9.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{15}H_{16}NO$ 226.1226; Found 226.1230.



2i

5-bromo-2-methyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (2i).

According to the general procedure, the reaction of 2-bromo-1-phenylethan-1-one (0.99 g, 5 mmol), 5-bromo-2-methylpyridine (0.855 g, 5 mmol) reflux in THF (10 mL) for 24 hours afforded the product **2i** 1.49 g (81% yield) as white solid, the products were purified through by crystallization (methanol/toluene 1:1). m. p. 205.8 °C ~ 206.2 °C, TLC R_f = 0.3 (DCM : MeOH 10 : 1).

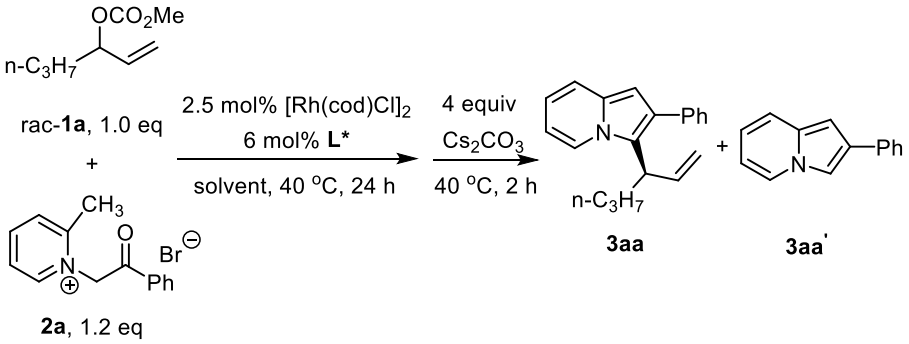
^{1}H NMR (400 MHz, DMSO) δ 9.42 (d, *J* = 2.1 Hz, 1H), 8.91 (dd, *J* = 8.6, 2.1 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.13-8.05 (m, 2H), 7.85-7.76 (m, 1H), 7.72-7.62 (m, 2H), 6.58 (s, 2H), 2.70 (s, 3H).

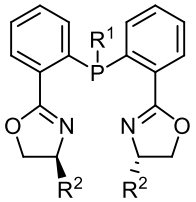
^{13}C NMR (101 MHz, DMSO) δ 190.2, 156.0, 148.5, 147.4, 134.9, 133.4, 130.5, 129.1, 128.5, 118.8, 63.9, 19.4.

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{14}H_{13}BrNO$ 290.0175; Found 290.018

4. Optimization of reaction conditions.

Table S1: Optimization of reaction conditions.



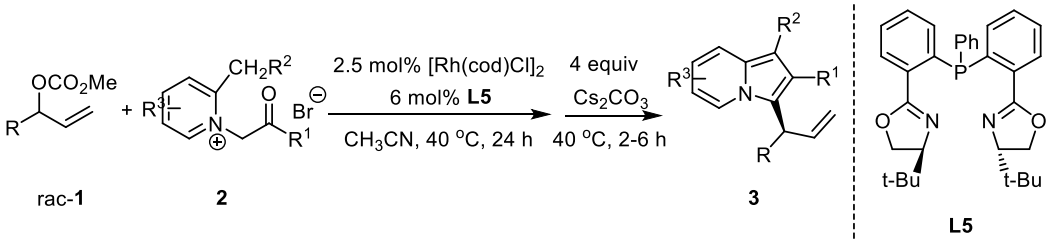


L1, R^1 = Ph, R^2 = Me
L2, R^1 = Ph, R^2 = Bn
L3, R^1 = Ph, R^2 = Ph
L4, R^1 = Ph, R^2 = i-Pr
L5, R^1 = Ph, R^2 = t-Bu
L6, R^1 = 3,5-t-Bu_2-4-$MeOC_6H_2$, R^2 = t-Bu
L7, R^1 = 4-$CF_3C_6H_4$, R^2 = t-Bu
L8, R^1 = 4-$OMeC_6H_4$, R^2 = i-Pr

entry[a]	Ligand	solvent	**3aa/3aa'**[b]	yield(**3aa**)(%)[c]	*ee*(**3aa**)(%)[d]	B/L[e]
1	**L1**	CH_3CN	0.25 : 1	23	33	3 : 1
2	**L2**	CH_3CN	0.24 : 1	21	23	2 : 1
3	**L3**	CH_3CN	1.38 : 1	65	98	> 20 : 1
4	**L4**	CH_3CN	1.05 : 1	61	98	> 20 : 1
5	**L5**	CH_3CN	3.85 : 1	95	99	> 20 : 1
6	**L6**	CH_3CN	2.99 : 1	88	>99	13 : 1
7	**L7**	CH_3CN	2.64 : 1	85	99	> 20 : 1
8	**L8**	CH_3CN	0.88 : 1	51	98	12 : 1
9	**L5**	DCE	2.02 : 1	78	99	> 20 : 1
10	**L5**	DMF	2.14 : 1	79	99	> 20 : 1
11	**L5**	MeOH	-	< 5	-	-
12	**L5**	Et_2O	0.14 : 1	12	91	6 : 1
13[f]	**L5**	CH_3CN	2.15 : 1	82	99	> 20 : 1
14[g]	**L5**	CH_3CN	1.75 : 1	76	99	> 20 : 1

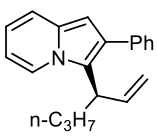
[a] Conditions: All reactions were run with 2.5 mol% catalyst precursor and 6 mol% ligand on a 0.3 mmol scale at 40 °C for 24 hours unless otherwise noted, and the reactions with 4 equivalent Cs_2CO_3 were conducted in the presence of air. [b] The ratio were determined by ^{1}H-NMR. [c] Yield of isolated product. [d] The enantiomeric excess values were determined by HPLC analysis with a chiral column. [e] The ratio of branch products to linear products were determined by ^{1}H-NMR. [f] The reaction was carried out at room temperature. [g] The reaction was carried out at 60 °C.

5. General procedure for the enantioselective 3-allyl indolizines.



General Method: To an oven-dried 10 mL Schlenk flask were added $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%) and 2 mL CH_3CN. Then the mixture was added rac-**1** (0.3 mmol, 1.0 equiv) and **2** (0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere unless otherwise noted. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the reaction mixture was treated with 4 equiv of Cs_2CO_3 under the air. After being stirred at 40 °C (oil bath as heat source) for 2-6 hours, the reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give desired product **3**.

6. Spectral data of 3-allyl indolizines products and 3aa'.



3aa

(R)-3-(hex-1-en-3-yl)-2-phenylindolizine (3aa).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3aa** (78.6 mg, 95%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.5 (100% PE), 99% *ee*.

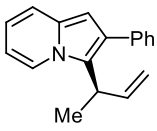
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.50-7.38 (m, 5H), 7.37-7.31 (m, 1H), 6.67 (ddd, *J* = 8.9, 6.4, 0.9 Hz, 1H), 6.55 (s, 1H), 6.50-6.43 (m, 1H), 6.23-6.11 (m, 1H), 5.21 (ddd, *J* = 10.4, 2.2, 1.5 Hz, 1H), 5.05 (ddd, *J* = 17.4, 2.1, 1.5 Hz, 1H), 4.14-4.05 (m, 1H), 2.03-1.91 (m, 1H), 1.87-1.75 (m, 1H), 1.15-0.96 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.4, 132.4, 129.8, 129.6, 128.3, 126.4, 124.0, 120.8, 119.3, 116.1, 115.1, 109.6, 99.5, 39.5, 32.6, 21.0, 13.8.

$[\alpha]_D^{25}$ = +59.0 (*c* 0.1, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{22}N$ 276.1747; Found 276.1747.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 15.365 min (major) and 16.749 min (minor), 99% *ee*.



3ba

(R)-3-(but-3-en-2-yl)-2-phenylindolizine (3ba).

Following the general method, the reaction of rac-**1b** (39.0 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ba** (69.8 mg, 94%) as white solid [eluent: petroleum ether = 250 mL], TLC R_f = 0.5 (100% PE), 99% *ee*, m. p. 47.3 °C ~ 47.9 °C.

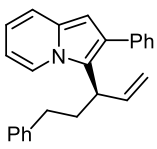
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.50-7.37 (m, 5H), 7.36-7.29 (m, 1H), 6.66 (dd, *J* = 8.9, 6.5 Hz, 1H), 6.53 (s, 1H), 6.50-6.42 (m, 1H), 6.17-6.05 (m, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 5.10 (d, *J* = 17.4 Hz, 1H), 4.32- 4.20 (m, 1H), 1.52 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.2, 132.4, 129.5, 128.4, 128.4, 126.5, 124.0, 122.1, 119.3, 116.2, 114.7, 109.6, 99.4, 33.5, 15.8.

$[\alpha]_D^{25}$ = +15.8 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{18}N$ 248.1434; Found 248.1444.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0.9 : 99.1, 0.9 ml/min), 40 °C, 254 nm, R*t* = 76.730 min (major) and 82.711 min (minor), 99% *ee* (The *ee* value was determined after the hydroboration/oxidation sequence **9**).



3ca

(R)-2-phenyl-3-(5-phenylpent-1-en-3-yl)indolizine (3ca).

Following the general method, the reaction of rac-**1c** (66.0 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ca** (97.3 mg, 96%) as brown oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.45 (PE : EA 100 : 1), 99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.1 Hz, 1H), 7.48-7.37 (m, 5H), 7.36-7.31 (m, 1H), 7.19-7.10 (m, 3H), 6.90 (d, *J* = 6.7 Hz, 2H), 6.68 (dd, *J* = 8.7, 6.6 Hz, 1H), 6.55 (s, 1H), 6.50-6.42 (m, 1H), 6.14 (ddd, *J* = 17.3, 10.4, 4.5 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 17.4 Hz, 1H), 4.18-4.02 (m, 1H), 2.37-2.24 (m, 3H), 2.18-2.12 (m, 1H).

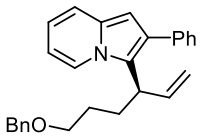
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.2, 137.3, 132.6, 129.9, 129.6, 128.4, 128.4, 128.3, 126.5,

125.7, 123.8, 120.2, 119.3, 116.3, 115.5, 109.8, 99.7, 39.3, 34.0, 32.5.

$[\alpha]_D^{25}$ = +16.6 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{24}N$ 338.1903; Found 338.1918.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 10 : 90, 2 ml/min), 40 °C, 254 nm, R*t* = 8.042 min (major) and 11.189 min (minor), 99% *ee* (The *ee* value was determined after the hydroboration/oxidation sequence).



3da

(R)-3-(6-(benzyloxy)hex-1-en-3-yl)-2-phenylindolizine (3da).

Following the general method, the reaction of rac-**1d** (79.2 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3da** (104.1 mg, 91%) as brown oil [eluent: petroleum ether/ethyl acetate 50 : 1 = 250 mL], TLC R_f = 0.5 (PE : EA 20 : 1), 99% *ee*.

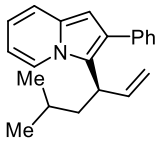
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.43-7.33 (m, 5H), 7.30-7.17 (m, 6H), 6.61 (dd, *J* = 8.6, 6.7 Hz, 1H), 6.49 (s, 1H), 6.44-6.36 (m, 1H), 6.18-6.05 (m, 1H), 5.21-5.12 (m, 1H), 5.07-4.96 (m, 1H), 4.30-4.22 (m, 2H), 4.11-3.98 (m, 1H), 3.22-3.10 (m, 2H), 2.05-1.90 (m, 2H), 1.33-1.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3, 137.2, 132.5, 129.9, 129.5, 128.3, 128.3, 127.6, 127.5, 126.5, 123.9, 120.3, 119.3, 116.2, 115.3, 109.6, 99.5, 72.7, 69.7, 39.4, 27.8, 26.7.

$[\alpha]_D^{25}$ = +18.6 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{28}NO$ 382.2165; Found 382,2166.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0.5 : 95.5, 1 ml/min), 40 °C, 254 nm, R*t* = 47.152 min (major) and 30.775 min (minor), 99% *ee*.



3ea

(R)-3-(5-methylhex-1-en-3-yl)-2-phenylindolizine (3ea).

Following the general method, the reaction of rac-**1e** (51.6 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ea** (74.7 mg, 86%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.6 (100% PE), >99% *ee*.

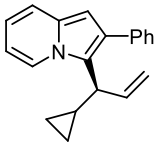
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.52-7.39 (m, 5H), 7.38-7.31 (m, 1H), 6.68 (ddd, *J* = 8.9, 6.4, 0.9 Hz, 1H), 6.56 (s, 1H), 6.51-6.44 (m, 1H), 6.25-6.13 (m, 1H), 5.22 (ddd, *J* = 10.4, 2.2, 1.5 Hz, 1H), 5.06 (ddd, *J* = 17.3, 2.1, 1.5 Hz, 1H), 4.24-4.15 (m, 1H), 2.03-1.92 (m, 1H), 1.68-1.57 (m, 1H), 1.23-1.09 (m, 1H), 0.70 (d, *J* = 6.6 Hz, 3H), 0.60 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.3, 132.5, 129.8, 129.5, 128.3, 126.5, 124.0, 120.8, 119.3, 116.1, 115.0, 109.6, 99.5, 39.5, 37.7, 26.1, 23.0, 21.9.

$[\alpha]_D^{25}$ = +32.3 (*c* 0.48, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}N$ 290.1903; Found 290.1916.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 12.716 min (major) and 18.106 min (minor), 99% *ee*.



3fa

(S)-3-(1-cyclopropylallyl)-2-phenylindolizine (3fa).

Following the general method, the reaction of rac-**1f** (46.8 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3fa** (76.2 mg, 93%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.5 (100% PE), 90% *ee*.

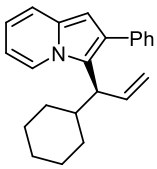
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.45-7.36 (m, 5H), 7.33-7.28 (m, 1H), 6.67 (ddd, *J* = 8.9, 6.5, 0.9 Hz, 1H), 6.53 (s, 1H), 6.50-6.42 (m, 1H), 6.26-6.14 (m, 1H), 5.28-5.22 (m, 1H), 5.22-5.15 (m, 1H), 3.35-3.23 (m, 1H), 1.44-1.32 (m, 1H), 0.70-0.58 (m, 1H), 0.33-0.20 (m, 2H), -0.05--0.14 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 137.2, 132.3, 129.6, 129.1, 128.2, 126.4, 124.1, 121.5, 119.2, 116.3, 115.7, 109.6, 99.6, 44.8, 12.1, 5.9, 4.3.

$[\alpha]_D^{25}$ = +66.0 (*c* 0.25, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590; Found 274.1602.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0.3 : 99.7, 0.7 ml/min), 40 °C, 254 nm, R_t = 15.745 min (major) and 16.669 min (minor), 90% *ee*.



3ga

(S)-3-(1-cyclohexylallyl)-2-phenylindolizine (3ga).

Following the general method, the reaction of rac-**1g** (89.1 mg, 0.45 mmol), **2a** (87.3 mg, 0.3 mmol), BSA (N, O-Bis(trimethylsilyl)acetamide)(183 mg, 0.9 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol), 2 mL CH_3CN and the reaction was run for 72 hours afforded product **3ga** (77.1 mg, 81%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.6 (100% PE), 99% *ee*.

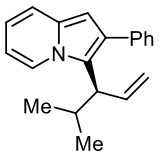
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.49-7.36 (m, 5H), 7.35-7.29 (m, 1H), 6.69-6.61 (m, 1H), 6.51 (s, 1H), 6.49-6.44 (m, 1H), 6.30-6.18 (m, 1H), 5.16 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.99 (dt, *J* = 17.1, 1.7 Hz, 1H), 3.76-3.64 (m, 1H), 2.12-1.91 (m, 2H), 1.78-1.67 (m, 1H), 1.60-1.53 (m, 1H), 1.51-1.43 (m, 1H), 1.28-1.17 (m, 1H), 1.08-0.87 (m, 4H), 0.66-0.52 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 136.2, 132.1, 130.0, 129. 7, 128.2, 126.4, 123.8, 121.1, 119.3, 116.2, 115.9, 109.7, 99.7, 46.9, 38.2, 32.5, 31.4, 26.3, 26.3, 26.3.

$[\alpha]_D^{25}$ = -16.3 (*c* 0.56, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{26}N$ 316.2060; Found 316.2073.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 17.307 min (major) and 18.700 min (minor), 99% *ee*.



3ha

(R)-3-(4-methylpent-1-en-3-yl)-2-phenylindolizine (3ha).

Following the general method, the reaction of rac-**1h** (71.1 mg, 0.45 mmol), **2a** (87.3 mg, 0.3 mmol), BSA (N, O-Bis(trimethylsilyl)acetamide)(183 mg, 0.9 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol), 2 mL CH_3CN and the reaction was run for 48 hours afforded product **3ha** (79.0 mg, 96%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.5 (100% PE), 99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.2, 0.7 Hz, 1H), 7.48-7.37 (m, 5H), 7.36-7.30 (m, 1H), 6.65 (ddd, *J* = 8.9, 6.4, 0.9 Hz, 1H), 6.52 (s, 1H), 6.49-6.43 (m, 1H), 6.32-6.19 (m, 1H), 5.18 (dt, *J* = 10.3, 1.7 Hz, 1H), 5.01 (dt, *J* = 17.2, 1.7 Hz, 1H), 3.66-3.55 (m, 1H), 2.45-2.27 (m, 1H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.51 (d, *J* = 6.6 Hz, 3H).

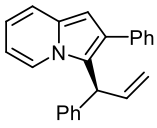
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 136.5, 132.2, 130.0, 129.7, 128.2, 126.4, 123.8, 121.5, 119.3, 116.3, 115.9, 109.7, 99.8, 48.3, 28.8, 22.0, 21.3.

$[\alpha]_D^{25}$ = -20.0 (*c* 0.06, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{22}N$ 276.1747; Found 276.1759.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH : Hexane = 0.1 : 99.9 0.5 ml/min),

40 °C, 254 nm, R*t* = 12.948 min (major) and 11.721 min (minor), 99% *ee*.



3ia

(S)-2-phenyl-3-(1-phenylallyl)indolizine (3ia).
Following the general method, the reaction of rac-**1i** (115.2 mg, 0.6 mmol), **2a** (87.3 mg, 0.3 mmol), BSA (N, O-Bis(trimethylsilyl)acetamide)(183 mg, 0.9 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3 (391 mg, 1.2 mmol), 2 mL CH_3CN and the reaction was run for 72 hours afforded product **3ia** (76.6 mg, 83%) as brown oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.45 (PE : EA 100 : 1), 99% *ee*.

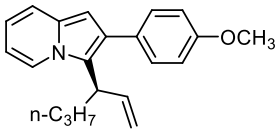
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 3H), 7.44-7.37 (m, 3H), 7.34-7.26 (m, 3H), 7.23-7.18 (m, 1H), 7.17-7.11 (m, 2H), 6.68-6.61 (m, 1H), 6.61 (s, 1H), 6.47 (ddd, *J* = 16.9, 10.2, 6.4 Hz, 1H), 6.31-6.25 (m, 1H), 5.49 (d, *J* = 6.3 Hz, 1H), 5.33 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.07 (dt, *J* = 17.1, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.9, 135.4, 132.7, 130.1, 129.4, 128.7, 128.4, 127.6, 126.6, 126.6, 123.9, 119.9, 119.1, 118.1, 116.6, 109.7, 99.5, 44.8.

$[\alpha]_D^{25}$ = -120.0 (*c* 0.18, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{20}N$ 310.1590; Found 310.1591.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0.3 : 99.7, 0.7 ml/min), 40 °C, 254 nm, R*t* = 15.310 min (major) and 14.349 min (minor), 99% *ee*.



3ab

(R)-3-(hex-1-en-3-yl)-2-(4-methoxyphenyl)indolizine (3ab).
Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2b** (115.6 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ab** (83.5 mg, 91%) as brown oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.7 (100% PE), 99% *ee*.

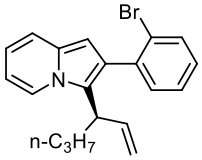
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.42-7.31 (m, 3H), 7.00-6.92 (m, 2H), 6.63 (dd, *J* = 8.5, 6.8 Hz, 1H), 6.52-6.38 (m, 2H), 6.19-6.06 (m, 1H), 5.22-5.10 (m, 1H), 5.07-4.93 (m, 1H), 4.07-3.99 (m, 1H), 3.85 (s, 3H), 1.98-1.87 (m, 1H), 1.81-1.74 (m, 1H), 1.10-0.93 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 138.6, 132.3, 130.6, 129.8, 129.4, 123.9, 120.7, 119.1, 116.0, 115.0, 113.8, 109.4, 99.4, 55.4, 39.6, 32.6, 21.0, 13.9.

$[\alpha]_D^{25}$ = +30.9 (*c* 0.55, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}NO$ 306.1852; Found 306.1857.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH : Hexane = 0.2 : 99.8, 0.5 ml/min), 40 °C, 254 nm, R*t* = 14.473 min (major) and 13.261 min (minor), 99% *ee*.



3ac

(R)-2-(2-bromophenyl)-3-(hex-1-en-3-yl)indolizine (3ac).
Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2c** (132.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ac** (94.8 mg, 89%) as green oil [eluent: petroleum ether = 250 mL], TLC R_f = 0.7 (100% PE), 99% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.33 (dd, *J* = 10.4, 2.7 Hz, 2H), 7.24-7.14 (m, 1H), 6.66 (ddd, *J* = 8.9, 6.5, 0.6 Hz, 1H), 6.56-6.39 (m, 2H), 6.15-6.00 (m, 1H), 5.20-5.12 (m, 1H), 5.04 (d, *J* = 17.3 Hz, 1H), 3.76-3.61 (m, 1H), 1.96-1.80

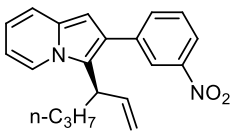
(m, 1H), 1.77-1.65 (m, 1H), 1.18-1.02 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 138.2, 132.8, 132.7, 132.0, 128.5, 128.2, 126.7, 125.0, 123.7, 121.7, 119.5, 116.1, 115.1, 109.7, 100.5, 39.9, 32.6, 21.0, 13.9.

$[\alpha]_D^{25}$ = +20.7 (*c* 0.27, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}BrN$ 354.0852; Found 354.0853.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0.3 : 99.7, 0.7 ml/min), 40 °C, 254 nm, R*t* = 11.723 min (major) and 12.802 min (minor), 99% *ee*.



3ad

(R)-3-(hex-1-en-3-yl)-2-(3-nitrophenyl)indolizine (3ad).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2d** (121 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ad** (91.5 mg, 95%) as green oil [eluent: petroleum ether/ethyl acetate 50 : 1 = 250 mL], TLC R_f = 0.4 (PE : EA 50 : 1), 99% *ee*.

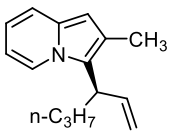
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (t, *J* = 1.9 Hz, 1H), 8.16 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.92 (dd, *J* = 7.2, 0.7 Hz, 1H), 7.78-7.72 (m, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 6.74-6.67 (m, 1H), 6.54 (s, 1H), 6.52-6.47 (m, 1H), 6.20-6.08 (m, 1H), 5.22 (ddd, *J* = 10.4, 2.0, 1.3 Hz, 1H), 5.03 (ddd, *J* = 17.3, 2.0, 1.4 Hz, 1H), 4.04-3.94 (m, 1H), 2.00-1.89 (m, 1H), 1.88-1.76 (m, 1H), 1.14-0.94 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 139.2, 137.9, 135.4, 132.7, 129.2, 127.2, 124.2, 124.1, 121.3, 121.2, 119.5, 116.8, 115.6, 110.2, 99.4, 39.7, 32.8, 21.1, 13.8.

$[\alpha]_D^{25}$ = +16.8 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}N_2O_2$ 321.1598; Found 321.1600.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 5 : 95, 1 ml/min), 40 °C, 254 nm, R*t* = 60.440 min (major) and 29.567 min (minor), 99% *ee* (The *ee* value was determined after the hydroboration/oxidation sequence).



3ae

(R)-3-(hex-1-en-3-yl)-2-methylindolizine (3ae).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2e** (82.4 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ae** (57.3 mg, 89%) as brown oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.5 (PE : EA 100 : 1), 99% *ee*.

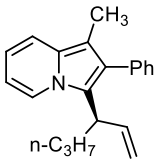
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.1 Hz, 1H), 7.29-7.23 (m, 1H), 6.62-6.49 (m, 1H), 6.36 (t, *J* = 6.7 Hz, 1H), 6.26 (s, 1H), 6.10-5.97 (m, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.98 (d, *J* = 17.3 Hz, 1H), 3.84 (dt, *J* = 8.6, 6.5 Hz, 1H), 2.30 (s, 3H), 1.95-1.83 (m, 2H), 1.32-1.23 (m, 1H), 1.19-1.09 (m, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 131.8, 122.8, 122.6, 121.3, 118.5, 115.2, 114.6, 108.9, 100.3, 39.5, 33.3, 21.1, 14.1, 12.8.

$[\alpha]_D^{25}$ = +0.6 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{20}N$ 214.1590; Found 214.1589.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 0.3 ml/min), 40 °C, 254 nm, R*t* = 39.709 min (major) and 38.074 min (minor), 99% *ee*.



3af

(R)-3-(hex-1-en-3-yl)-1-methyl-2-phenylindolizine (3af).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2f** (137.3 mg, 0.45 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L7** (10.4 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol), N, O-Bis(trimethylsilyl)acetamide(121.8 mg, 0.6 mmol), 2 mL CH_3CN and the reaction was run for 48 hours afforded product **3af** (79.0 mg, 91%) as colorless oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.5 (PE : EA 100 : 1), 99% *ee*.

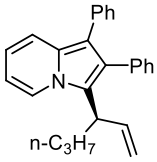
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38-7.29 (m, 4H), 6.64-6.56 (m, 1H), 6.40 (t, *J* = 6.8 Hz, 1H), 6.13-6.01 (m, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 17.3 Hz, 1H), 3.91-3.80 (m, 1H), 2.26 (s, 3H), 1.93-1.81 (m, 1H), 1.77-1.65 (m, 1H), 1.11-0.96 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 136.4, 130.7, 129.7, 129.2, 128.0, 126.5, 123.5, 120.7, 117.6, 114.8, 114.5, 109.2, 106.2, 39.7, 32.7, 21.0, 13.9, 9.3.

$[\alpha]_D^{25}$ = +24.0 (*c* 0.35, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}N$ 290.1903; Found 290.1906.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 49.114 min (major) and 44.506 min (minor), 99% *ee*.



3ag

(R)-3-(hex-1-en-3-yl)-1,2-diphenylindolizine (3ag).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2g** (132.1 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L7** (10.4 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol), N, O-Bis(trimethylsilyl)acetamide(121.8 mg, 0.6 mmol) and 2 mL CH_3CN afforded product **3ag** (78.0 mg, 74%) as brown oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.3 (100% PE), 99% *ee*.

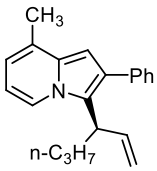
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.35-7.26 (m, 4H), 7.25-7.20 (m, 5H), 7.18-7.13 (m, 1H), 6.75-6.64 (m, 1H), 6.55-6.47 (m, 1H), 6.22-6.09 (m, 1H), 5.25-5.16 (m, 1H), 5.14-5.04 (m, 1H), 4.03-3.88 (m, 1H), 2.01-1.90 (m, 1H), 1.83-1.74 (m, 1H), 1.17-0.99 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 136.0, 135.4, 131.1, 130.0, 128.3, 128.1, 127.9, 126.4, 125.1, 123.9, 122.0, 118.3, 116.9, 115.1, 113.2, 110.2, 39.5, 32.6, 21.0, 13.9.

$[\alpha]_D^{25}$ = +4.2 (*c* 0.38, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{26}N$ 352.2060; Found 352.2064.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 9.799 min (major) and 11.326 min (minor), 99% *ee*.



3ah

(R)-3-(hex-1-en-3-yl)-8-methyl-2-phenylindolizine (3ah).

Following the general method, the reaction of rac-**1a** (47.4 mg, 0.3 mmol), **2h** (109.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol) and 2 mL CH_3CN afforded product **3ah** (79.6 mg, 92%) as brown oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.7 (PE : EA 100 : 1), 99% *ee*.

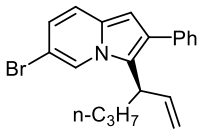
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.1 Hz, 1H), 7.49-7.38 (m, 4H), 7.35-7.28 (m, 1H), 6.50 (s, 1H), 6.50-6.47 (m, 1H), 6.41 (t, *J* = 6.8 Hz, 1H), 6.23-6.09 (m, 1H), 5.18 (ddd, *J* = 10.4, 2.2, 1.5 Hz, 1H), 5.03 (ddd, *J* = 17.4, 2.1, 1.5 Hz, 1H), 4.11-4.01 (m, 1H), 2.43 (s, 3H), 2.02-1.88 (m, 1H), 1.85-1.73 (m, 1H), 1.14-0.94 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.5, 133.3, 129.6, 129.3, 128.3, 128.2, 126.4, 122.1, 121.3, 115.6, 115.1, 109.7, 98.0, 39.6, 32.8, 21.0, 18.3, 13.9.

$[\alpha]_D^{25}$ = +17.1 (*c* 0.45, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}N$ 290.1903; Found 290.1907.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak ID Column, ^{i}PrOH : Hexane = 0 : 100, 0.3 ml/min), 40 °C, 254 nm, R*t* = 20.019 min (major) and 19.262 min (minor), 99% *ee*.



3ai

(R)-6-bromo-3-(hex-1-en-3-yl)-2-phenylindolizine (3ai).

Following the general method, the reaction of rac-**1a** (56.9 mg, 0.36 mmol), **2i** (100.7 mg, 0.3 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L5** (9.2 mg, 6 mol%), Cs_2CO_3(391 mg, 1.2 mmol), 2 mL CH_3CN and the reaction was run for 48 hours afforded product **3ai** (95.3 mg, 90%) as green oil [eluent: petroleum ether = 350 mL], TLC R_f = 0.7 (PE : EA 100 : 1), 99% *ee*.

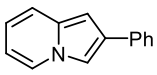
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.01 (m, 1H), 7.42 (d, *J* = 4.4 Hz, 4H), 7.37-7.31 (m, 1H), 7.31-7.27 (m, 1H), 6.72 (dd, *J* = 9.4, 1.6 Hz, 1H), 6.55 (s, 1H), 6.18-6.07 (m, 1H), 5.23 (ddd, *J* = 10.4, 2.3, 1.3 Hz, 1H), 5.03 (ddd, *J* = 17.4, 2.2, 1.3 Hz, 1H), 4.09-4.00 (m, 1H), 1.97-1.85 (m, 1H), 1.84-1.73 (m, 1H), 1.12-0.96 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.7, 130.7, 130.5, 129.5, 128.4, 126.7, 123.7, 121.7, 119.9, 119.4, 115.6, 104.7, 101.0, 39.5, 32.5, 21.0, 13.8.

$[\alpha]_D^{25}$ = +31.7 (*c* 0.6, $CHCl_3$).

HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}BrN$ 354.0852; Found 354.0864.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 7.379 min (major) and 8.318 min (minor), 99% *ee*.



3aa'

2-phenylindolizine(3aa').

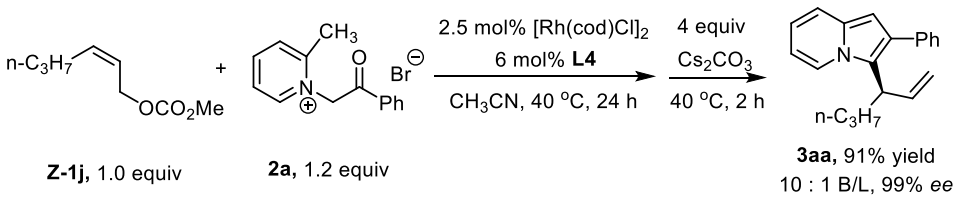
Following the general method, the reaction was carried out with rac-**1a** (47.4 mg, 0.3 mmol), **2a** (104.8 mg, 0.36 mmol), $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%), **L1** (7.7 mg, 6 mol%) and 2 mL CH_3CN (Table 1, entry 1) afforded product **3aa** (19 mg, 23%) and **3aa'** (55.6 mg) as silvery white flake solid [eluent: petroleum ether/ethyl acetate 50 : 1 = 250 mL], TLC R_f = 0.35 (PE : EA 100 : 1), m. p. 211 °C ~ 214 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 6.8 Hz, 1H), 7.71-7.62 (m, 2H), 7.58 (s, 1H), 7.49-7.32 (m, 3H), 7.31-7.22 (m, 2H), 6.70 (s, 1H), 6.68-6.61 (m, 1H), 6.51-6.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 133.8, 129.6, 128.9, 126.7, 126.3, 125.2, 119.2, 117.5, 110.6, 109.4, 96.8.

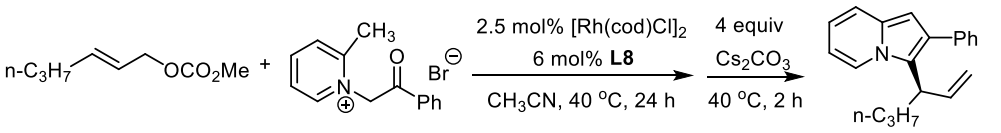
HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{12}N$ 194.0964; Found 194.0966.

7. The Reactions of Linear Allylic Carbonates.



Z-1j, 1.0 equiv　　**2a,** 1.2 equiv　　**3aa,** 91% yield
10 : 1 B/L, 99% *ee*

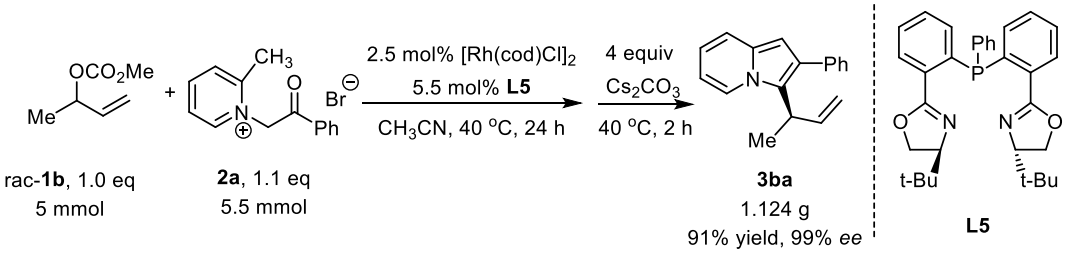
To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L4** (8.7 mg, 6 mol%) in CH_3CN (2 mL) was added **Z-1j** (47.4 mg, 0.3 mmol, 1.0 equiv) and **2a** (104.8 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the reaction mixture was treated with 4 equiv of Cs_2CO_3 under the air. After being stirred at 40 °C (oil bath as heat source) for 2 hours, the reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (100% PE) to give **3aa** (75.1 mg, 91%) as a brown oil.



E-1k, 1.0 equiv　　**2a,** 1.2 equiv　　**3aa,** 84% yield
> 20 :1 B/L, 99% *ee*

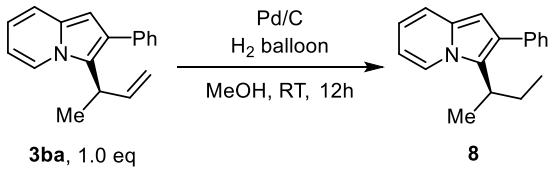
To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L8** (9.0 mg, 6 mol%) in CH_3CN (2 mL) was added **E-1j** (47.4 mg, 0.3 mmol, 1.0 equiv) and **2a** (104.8 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the reaction mixture was treated with 4 equiv of Cs_2CO_3 under the air. After being stirred at 40 °C (oil bath as heat source) for 2 hours, the reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (100% PE) to give **3aa** (69.3 mg, 84%) as a brown oil.

8. Large scale synthesis of 3ba.



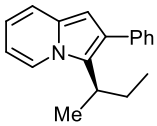
To a solution of $[Rh(cod)Cl]_2$ (61 mg, 2.5 mol%) and **L5** (140 mg, 5.5 mol%) in CH_3CN (30 mL) was added rac-**1b** (650 mg, 5 mmol, 1.0 equiv) and **2a** (1.6 g, 5.5 mmol, 1.1 euqiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the reaction mixture was treated with 4 equiv of Cs_2CO_3 under the air. After being stirred at 40 °C (oil bath as heat source) for 2 hours, the reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (100% PE) to give **3ba** (1.124 g, 91%) as a colorless oil, freeze-dried to obtain a white solid.

9. Procedures of derivatization and spectral data of the products.



3ba, 1.0 eq **8**

A 10 mL tube equipped with a magnetic stirring bar was charged with **3ba** (24.7 mg, 0.1 mmol), Pd/C (1.3 mg, 5% wt), and MeOH (1.0 ml). The reaction mixture was flushed with H_2 (3x), and stirred at room temperature with a H_2 balloon for 12 hours. The reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and concentrated. The residue was purified by silica gel column chromatography (100% PE) to give **8** (23.9 mg, 96%) as a yellow oil.



8

(R)-3-(sec-butyl)-2-phenylindolizine (8).

Yellow oil, 23.9 mg, 96%. TLC R_f = 0.7 (100% PE), 99% *ee*.

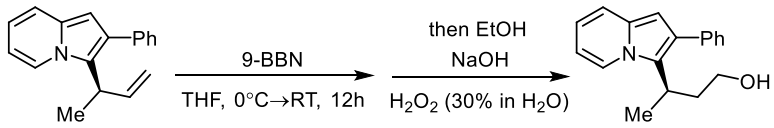
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.45-7.35 (m, 5H), 7.35-7.30 (m, 1H), 6.63 (ddd, *J* = 8.9, 6.4, 0.8 Hz, 1H), 6.51-6.47 (m, 1H), 6.47 (s, 1H), 3.38-3.26 (m, 1H), 1.96-1.86 (m, 1H), 1.81- 1.68 (m, 1H), 1.42 (d, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8 (s), 132.0 (s), 129.9 (s), 128.5 (s), 128.1 (s), 126.3 (s), 124.7 (s), 123.4 (d, *J* = 4.1 Hz), 119.5 (d, *J* = 3.8 Hz), 115.7 (d, *J* = 7.0 Hz), 109.8 (d, *J* = 5.5 Hz), 99.9 (d, *J* = 7.3 Hz), 32.7 (s), 27.0 (s), 18.0 (d, *J* = 6.1 Hz), 12.8 (d, *J* = 5.0 Hz).

$[\alpha]_D^{25}$ = -42.0 (*c* 0.05, $CHCl_3$).

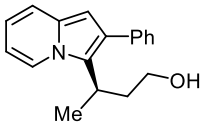
HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{20}N$ 250.1590; Found 250.1592.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OD-H Column, ^{i}PrOH : Hexane = 0 : 100, 1 ml/min), 40 °C, 254 nm, R*t* = 19.809 min (major) and 19.070 min (minor), 99% *ee*.



3ba, 1.0 eq **9**

The reaction was performed according to the modified literature procedure.[5] 3-Allyl indolizines **3ba** (74.1 mg, 0.3 mmol, 1.0 euqiv) was dissolved in THF (1.5 ml) and cooled to 0 °C, then 9-BBN (1.5 ml, 90.8 mg, 0.75 mmol, 0.5 M in THF, 2.5 equiv) was slowly added. The reaction was stirred for 15 min at 0 °C, and then slowly warmed up to room temperature and stir for 12 hours. The reaction mixture was cooled to 0 °C, then EtOH (0.5 ml), NaOH (0.5 ml, 2 M in H_2O) and H_2O_2 (0.5 ml, 30% wt in H_2O) were added slowly in the given order. The reaction was warmed up to room temperature and stirred for 3 hours. The reaction mixture was diluted with dichloromethane and transferred into a separation funnel. The aqueous phase was extracted with dichloromethane (3x). The combined organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE : EA 10 : 1) to give 9 (72.6 mg, 91%) as a yellow oil.



9

(R)-3-(2-phenylindolizin-3-yl)butan-1-ol (9).

Yellow oil, 72.6 mg, 91%. TLC R_f = 0.15 (PE : EA 10 : 1), 99% *ee*.

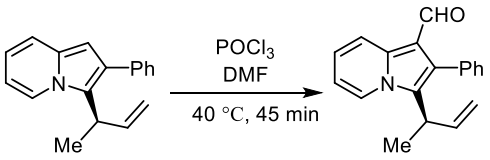
^{1}H NMR (400 MHz, DMSO) δ 8.19 (d, *J* = 6.7 Hz, 1H), 7.45-7.37 (m, 5H), 7.34-7.27 (m, 1H), 6.72-6.62 (m, 1H), 6.60-6.52 (m, 1H), 6.41 (s, 1H), 4.42 (t, *J* = 4.3 Hz, 1H), 3.64-3.49 (m, 1H), 3.32-3.19 (m, 2H), 2.03-1.81 (m, 2H), 1.32 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 132.2, 129.8, 128.6, 128.3, 126.6, 123.6, 123.3, 119.5, 116.0, 110.2, 100.03 61.31 36.52 27.4, 18.5.

$[\alpha]_D^{25}$ = -34.4 (*c* 0.55, $CHCl_3$).

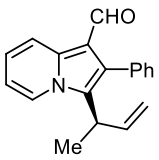
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{19}NONa$ 288.1359; Found 288.1373.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH : Hexane = 0.9 : 99.1, 0.9 ml/min), 40 °C, 254 nm, R*t* = 76.730 min (major) and 82.711 min (minor), 99% *ee*.



3ba, 1.0 eq **10**

The reaction was performed according to the modified literature procedure.[6, 4c] (R)-3-(but-3-en-2-yl)-2-phenylindolizine **3ba** (74.1 mg, 0.3 mmol, 1.0 equiv) was dissolved in DMF (0.5 mL). A solution of freshly distilled $POCl_3$ (55.2 mg, 0.36 mmol, 35 uL, 1.2 equiv) in DMF (110 uL) was added to the indolizines solution. After being stirred at 40 °C (oil bath as heat source) for 45 minutes, the mixture was allowed to cool and carefully quenched with water (0.5 ml). The reaction mixture was diluted with dichloromethane and transferred into a separation funnel. The aqueous phase was extracted with dichloromethane (3x). The combined organic layers were dried over anhydrous sodium sulfate, filtered and concentrated in vacuum. The residue was purified by silica gel column chromatography (PE : EA 50 : 1) to give **10** (81.0 mg, 98%) as a white solid.



10

(R)-3-(but-3-en-2-yl)-2-phenylindolizine-1-carbaldehyde (10).

White solid, m. p. 121.3 °C ~ 121.9 °C, 81.0 mg, 98%. TLC R_f = 0.15 (PE : EA 10 : 1), 99% *ee*.

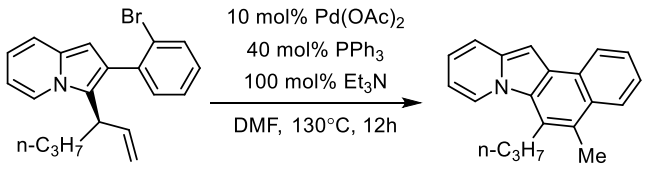
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.10 (d, *J* = 7.0 Hz, 1H), 7.57-7.33 (m, 5H), 7.31-7.07 (m, 1H), 6.85 (t, *J* = 6.8 Hz, 1H), 6.16-5.93 (m, 1H), 5.34-5.13 (m, 1H), 5.17-4.99 (m, 1H), 4.12-3.88 (m, 1H), 1.44 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.7, 138.9, 135.7, 133.1, 131.7, 130.9, 128.3, 127.8, 125.1, 125.0, 124.4, 120.5, 115.4, 113.7, 112.0, 33.2, 16.1.

$[\alpha]_D^{25}$ = 38.2 (*c* 0.5, $CHCl_3$).

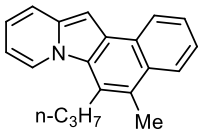
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{17}NONa$ 298.1202; Found 298.1216.

HPLC (Shimadzu LC-2030) (Daicel Chiralpak OJ-H Column, ^{i}PrOH : Hexane = 0.4 : 99.6, 0.4 ml/min), 40 °C, 254 nm, R*t* = 70.948 min (major) and 66.125 min (minor), 99% *ee*.



3ac, 1.0 eq **11**

To a solution of $Pd(OAc)_2$ (6.7 mg, 10 mol%, 0.03 mmol) and PPh_3 (31.4 mg, 40 mol%, 0.12 mmol) in DMF (1 mL) was added **3ac** (105.9 mg, 0.3 mmol, 1.0 equiv) and Et_3N (30.4 mg, 100 mol%, 0.3 mmol) at room temperature under an argon atmosphere. After being stirred at 130 °C (oil bath as heat source) for 12 hours, the reaction mixture was filtered through a short pad of silica gel eluting with ethyl acetate and concentrated. The residue was purified by silica gel column chromatography (100% PE) to give **11** (59.3 mg, 72%) as a green oil.



11

5-methyl-6-propylbenzo[e]pyrido[1,2-a]indole (11).

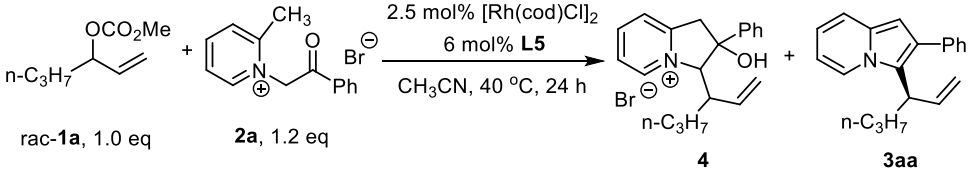
Green oil, 59.3 mg, 72%. TLC R_f = 0.6 (100% PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (t, *J* = 174.4 Hz, 1H), 8.48-8.39 (m, 1H), 8.18-8.10 (m, 1H), 7.62-7.54 (m, 3H), 7.31 (s, 1H), 6.86 (dd, *J* = 9.0, 6.3 Hz, 1H), 6.61-6.53 (m, 1H), 3.38-3.26 (m, 2H), 2.78 (s, 3H), 1.95-1.77 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 130.3, 126.7, 126.4, 126.3, 125.7, 125.5, 125.0, 124.8, 124.7, 124.2, 124.1, 119.9, 119.2, 109.3, 92.0, 31.7, 23.2, 14.7, 14.3.

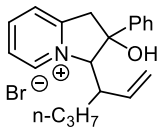
HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{20}N$ 274.1590; Found 274.1591.

10. Procedures of control experiments and spectral data of the products.



rac-**1a**, 1.0 eq **2a**, 1.2 eq **4** **3aa**

To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L5** (9.2 mg, 6 mol%) in CH_3CN (2 mL) was added rac-**1a** (47.4 mg, 0.3 mmol, 1.0 equiv) and **2a** (104.8 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the crude reaction mixture was directly subjected to flash column chromatography (100% PE) to give **3aa** (7.4 mg, 9%) as a brown oil and (DCM : MeOH 10 : 1) to give **4** (97.4 mg, 87%, 1 : 1.3 dr) as a white solid.



4

3-(hex-1-en-3-yl)-2-hydroxy-2-phenyl-2,3-dihydro-1H-indolizin-4-ium bromide (4).

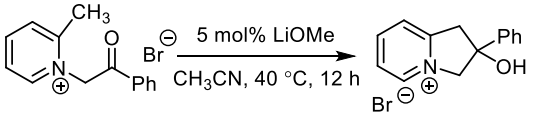
White solid, m. p. 190.5 °C ~ 191.3 °C, 97.4 mg, 87%. TLC R_f = 0.4 (DCM : MeOH 10 : 1), 1 : 1.3 dr.

Minor diastereomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 6.2 Hz, 1H), 8.22 (dd, *J* = 17.3, 8.3 Hz, 2H), 7.87-7.79 (m, 2H), 7.78-7.73 (m, 2H), 7.26-7.18 (m, 3H), 6.08 (dt, *J* = 17.4, 9.9 Hz, 1H), 5.74 (s, 1H), 5.47 (d, *J* = 4.4 Hz, 1H), 5.05-4.95 (m, 2H), 4.36-4.23 (m, 2H), 3.86 (d, *J* = 6.9 Hz, 1H), 3.17-3.04 (m, 2H), 1.21-1.04 (m, 4H), 0.62 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 144.9, 142.4, 140.9, 137.9, 128.5, 127.8, 125.9, 125.4, 125.2, 119.4, 81.3, 81.2, 49.5, 45.7, 32.3, 20.8, 13.7.

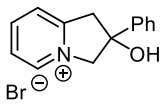
$[\alpha]_D^{25}$ = +22.7 (*c* 0.3, $CHCl_3$).

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{20}H_{24}NO$ 294.1852; Found 294.1854.



2a **5**

To a solution of **2a** (87.3 mg, 1.0 equiv) in CH_3CN (2 mL) was added LiOMe (0.6 mg, 5 mol%) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 12 hours, the formed precipitate was filtered out and then washed with dichloromethane (2 mL). The crude product was sonicated and centrifuged sequentially (3x) to obtain target compound **5** (71.5 mg, 82%) as a white solid.



5

2-hydroxy-2-phenyl-2,3-dihydro-1H-indolizin-4-ium bromide (5).

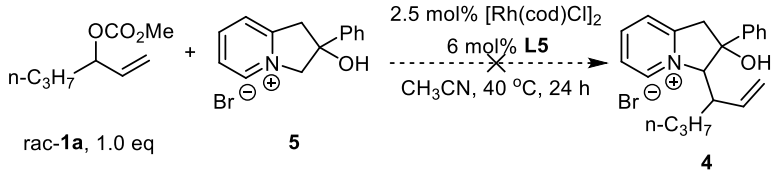
White solid, m. p. 221.3 °C ~ 222.5 °C, 71.5 mg, 82%. TLC R_f = 0.2 (DCM : MeOH 5 : 1).

^{1}H NMR (400 MHz, DMSO) δ 9.16 (d, *J* = 6.0 Hz, 1H), 8.60 (t, *J* = 7.7 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.08 (t, *J* = 6.8 Hz, 1H), 7.69 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.51-7.43 (m, 2H), 7.42-7.35 (m, 1H), 6.39 (s, 1H), 5.18 (d, *J* = 13.4 Hz, 1H), 5.03 (d, *J* = 13.4 Hz, 1H), 4.00 (d, *J* = 17.7 Hz, 1H),

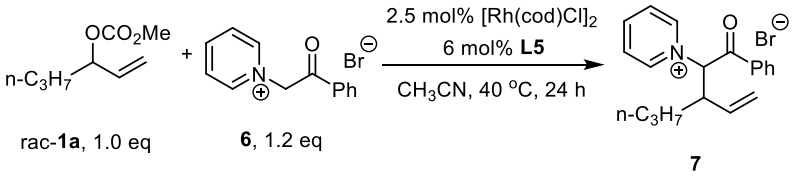
3.78 (d, J = 17.7 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 157.1, 145.7, 141.7, 140.8, 128.4, 128.0, 125.9, 125.8, 125.1, 78.6, 70.3, 47.4.

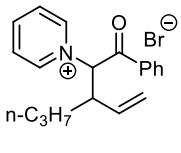
HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{14}H_{14}NO$ 212.1070; Found 212.1077.



To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L5** (9.2 mg, 6 mol%) in CH_3CN (2 mL) was added rac-**1a** (47.4 mg, 0.3 mmol, 1.0 equiv) and **5** (104.8 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the crude reaction mixture was analyzed by TLC and NMR, and the target compound **4** was not observed.



To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L5** (9.2 mg, 6 mol%) in CH_3CN (2 mL) was added rac-**1a** (47.4 mg, 0.3 mmol, 1.0 equiv) and **6** (99.7 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at 40 °C (oil bath as heat source) for 24 hours, the crude reaction mixture was directly subjected to flash column chromatography (DCM : MeOH 10 : 1) to give **7** (100.1 mg, 93%, 2.7 : 1 dr) as a light yellow solid.



7

1-(1-oxo-1-phenyl-3-vinylhexan-2-yl)pyridin-1-ium bromide (7).

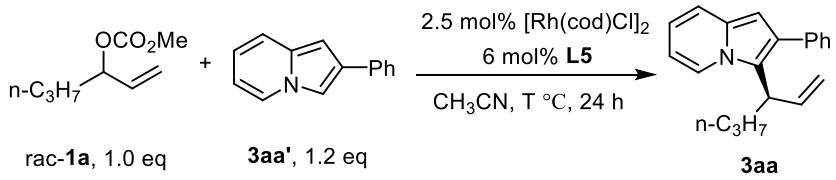
Light yellow solid, m. p. 111.0 °C ~ 112.3 °C, 100.1 mg, 93%. TLC R_f = 0.5 (DCM : MeOH 10 : 1), 2.7 : 1 dr.

Major diastereomer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.78 (d, J = 5.9 Hz, 2H), 8.58 (t, J = 7.8 Hz, 1H), 8.54-8.45 (m, 2H), 8.08 (t, J = 7.3 Hz, 2H), 7.83 (d, J = 9.6 Hz, 1H), 7.53-7.39 (m, 3H), 5.91-5.76 (m, 1H), 4.88-4.72 (m, 2H), 3.10-2.88 (m, 1H), 1.56-1.40 (m, 1H), 1.35-1.24 (m, 2H), 1.15-1.05 (m, 1H), 0.66 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 146.2, 145.0, 135.3, 135.1, 134.4, 130.2, 129.4, 127.9, 120.4, 72.1, 49.8, 32.4, 20.2, 13.3.

$[\alpha]_D^{25}$ = -58.0 (*c* 0.5, $CHCl_3$).

HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{19}H_{22}NO$ 280.1696; Found 280.1696.



rac-**1a**, 1.0 eq **3aa'**, 1.2 eq **3aa**

To a solution of $[Rh(cod)Cl]_2$ (3.7 mg, 2.5 mol%) and **L5** (9.2 mg, 6 mol%) in CH_3CN (2 mL) was added rac-**1a** (47.4 mg, 0.3 mmol, 1.0 equiv) and **3aa'** (69.5 mg, 0.36 mmol, 1.2 equiv) at room temperature under an argon atmosphere. After being stirred at **40 ºC** (oil bath as heat source) for 24 hours, the crude reaction mixture was directly subjected to flash column chromatography (100% PE) to give **3aa** (8.5 mg, 10%, 98% *ee*) as a brown oil. When the reaction of **3aa'** was conducted at **80 ºC** (oil bath as heat source) under otherwise the identical condition, **3aa** (8.2 mg, 10%, 98% ee) was obtained.

11. Single crystal X-ray diffraction data.

11.1 Crystal data of 3ba.

Single crystals of **3ba** were obtained by recrystallization from pentane at 0 °C (very fast evaporation in air). Absolute configuration of compound **3ba** was tested by Single-crystal X-ray diffractometer (D8 Venture) analysis.

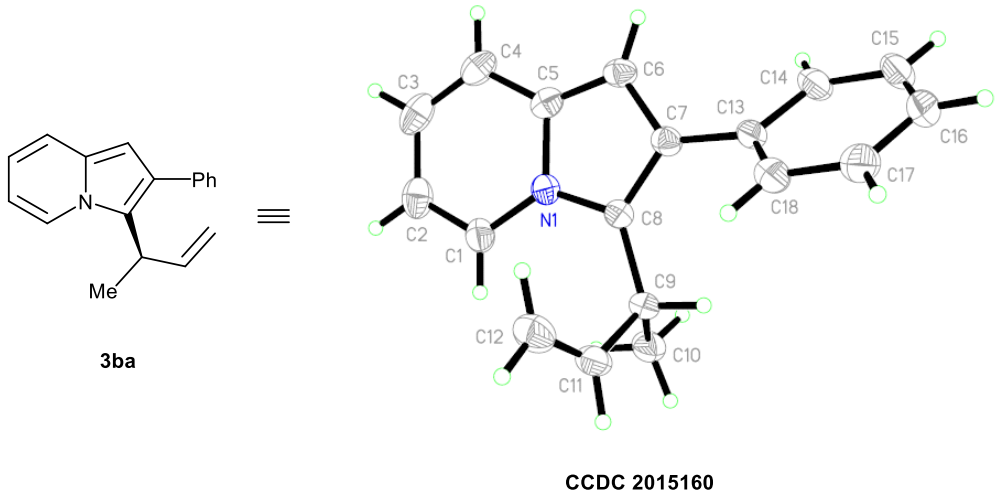


Figure S1. Compound structure with atom labeling scheme of **3ba**. H atoms and counter anions are omitted for structural clarity. ORTEP diagram are drawn at the 30% probability level.

Table S2: Crystal data.

Bond precision:	C-C = 0.0047 A		Wavelength = 1.54178
Cell:	a = 8.8552 (11) alpha = 90	b = 9.7214 (11) beta = 90	c = 16.4722 (18) gamma = 90
Temperature: 297 K			
	Calculated		Reported
Volume	1418.0 (3)		1418.0 (3)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C18 H17 N		C18 H17 N
Sum formula	C18 H17 N		C18 H17 N
Mr	247.33		247.32
Dx, g cm^{-3}	1.158		1.159
Z	4		4

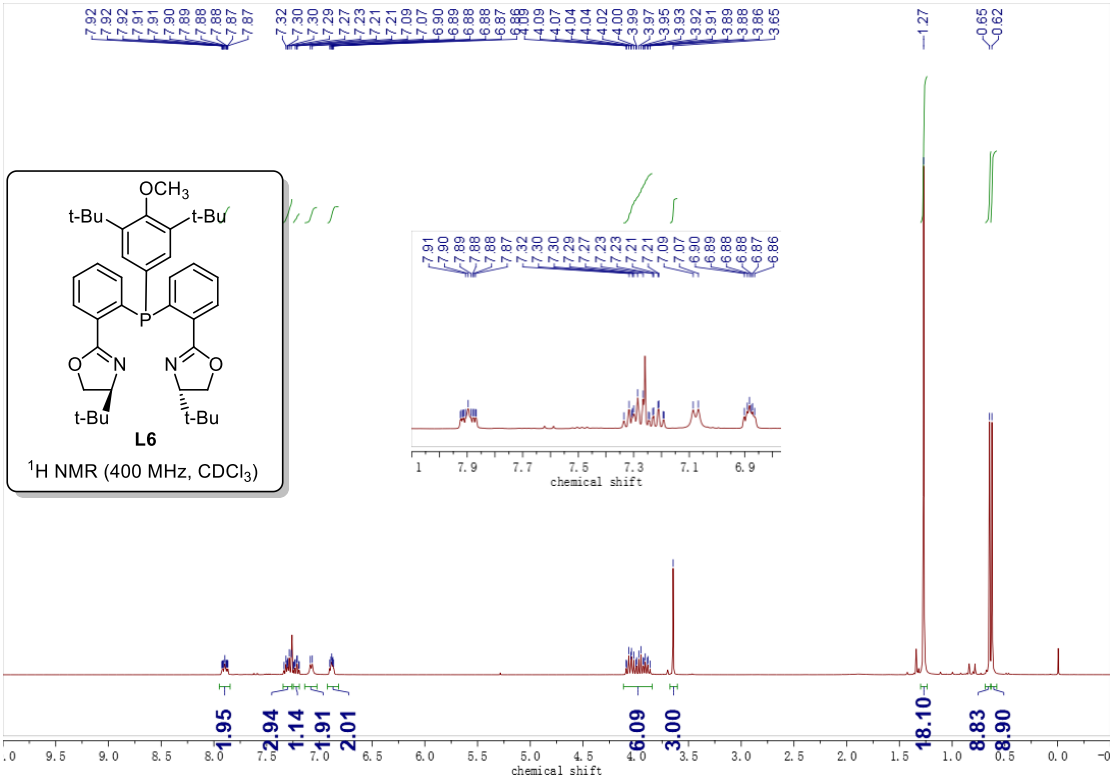
Mu (mm^{-1})	0.508	0.508
F000	528.0	528.0
F000’	529.35	
h, k, lmax	10, 11, 19	10, 11, 19
Nref	2595 [1509]	2525
Tmin, Tmax	0.903, 0.927	0.665, 0.753
Tmin’	0.903	

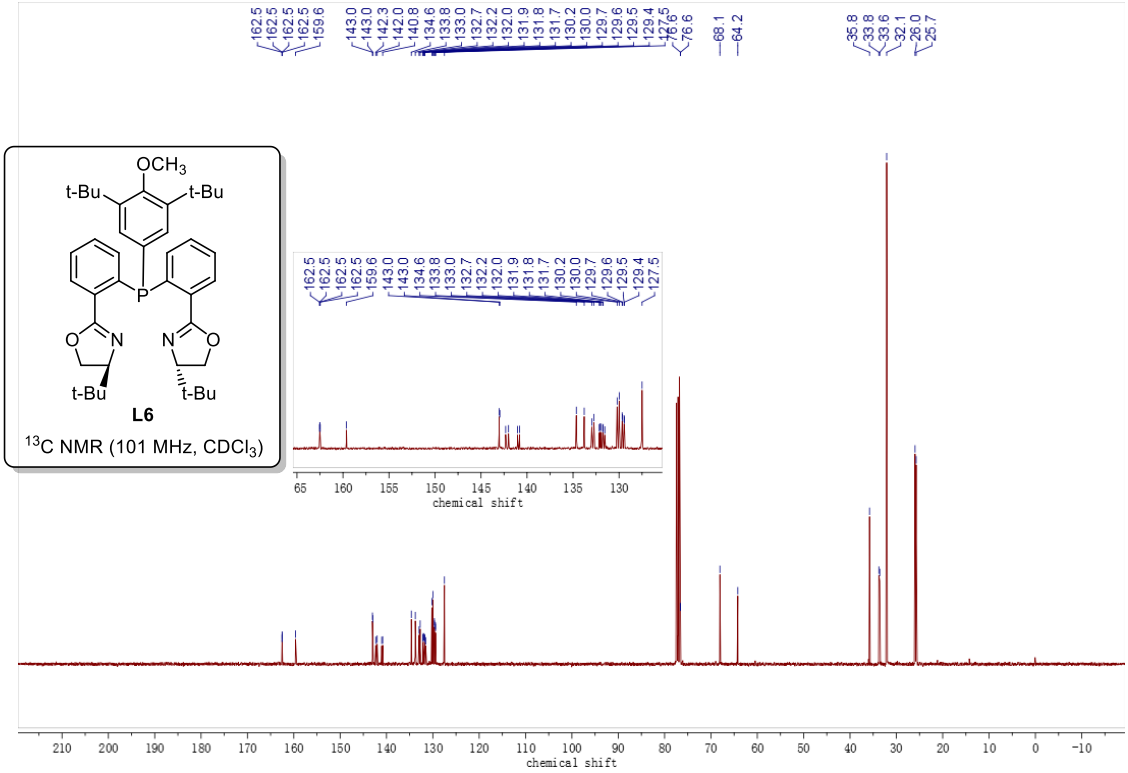
Correction method = # Reported T Limits: Tmin = 0.665 Tmax = 0.753
AbsCorr = ?		

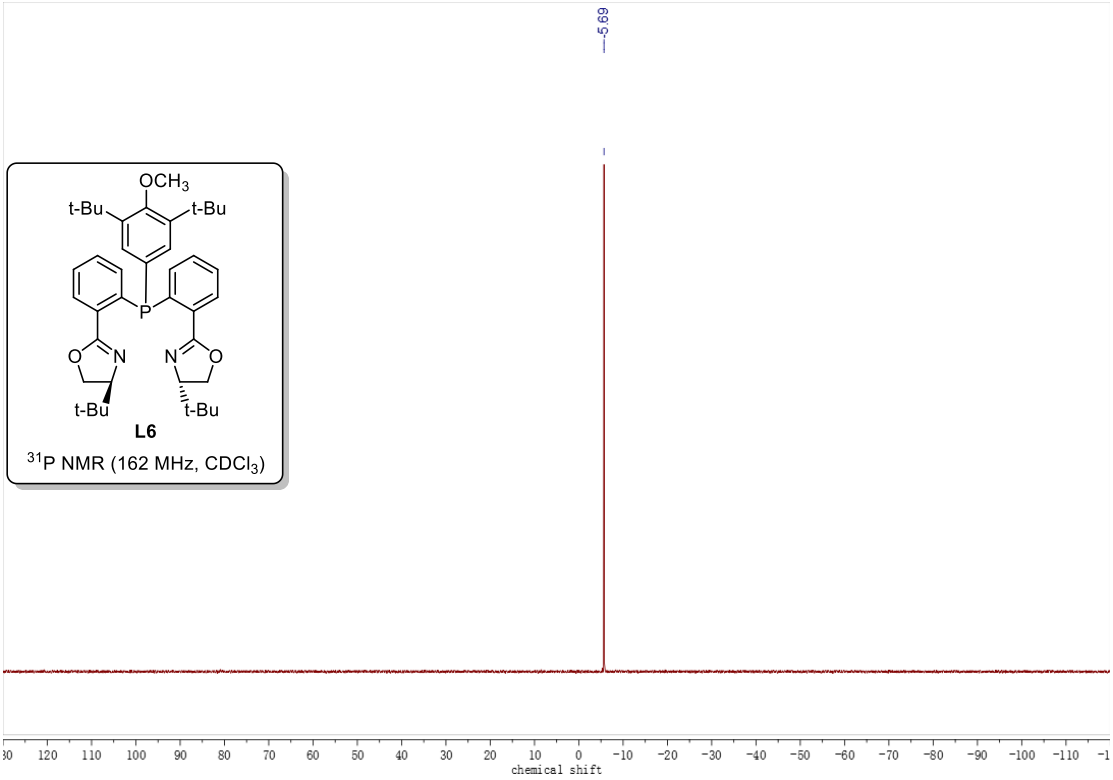
Data completeness = 1.67/0.97	Theta (max) = 68.023	
R (reflections) = 0.0355 (1873)	wR2 (reflections) = 0.1272 (2525)	
S = 1.093	Npar = 174	

12. NMR spectra and HPLC data.

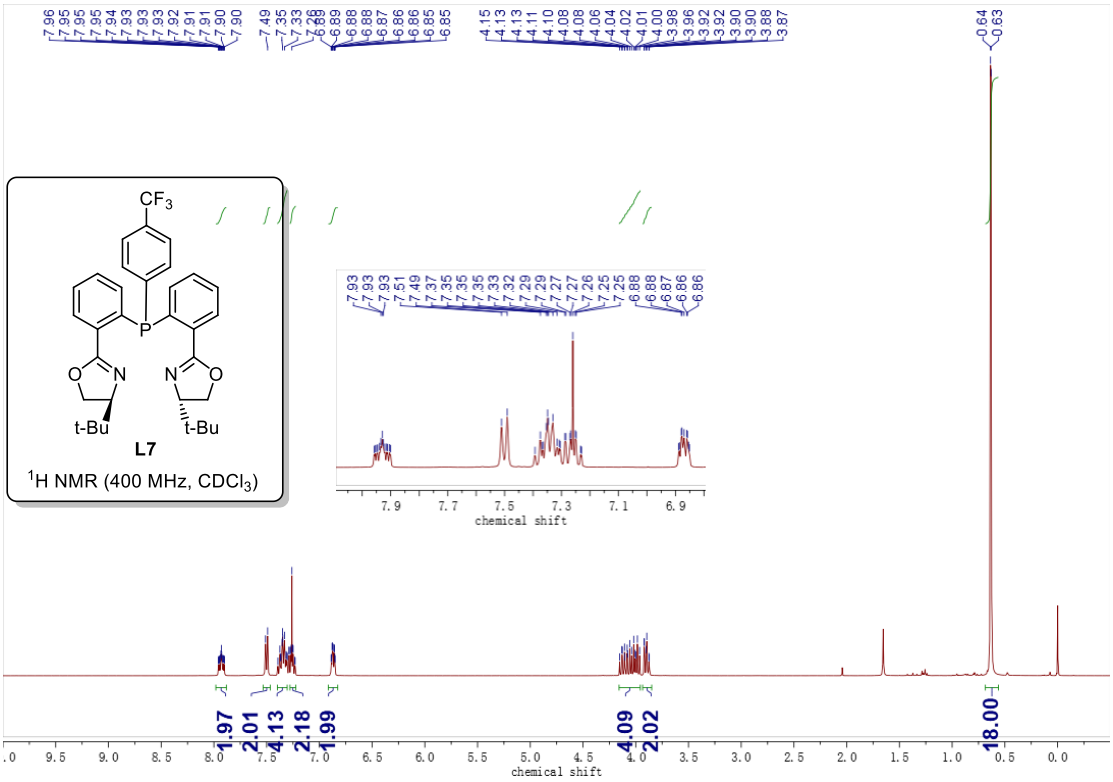
(4S,4'S)-2,2'-(((3,5-di-tert-butyl-4-methoxyphenyl)phosphanediyl)bis(2,1-phenylene))bis(4-(tert-butyl)-4,5-dihydrooxazole) (**L6**).

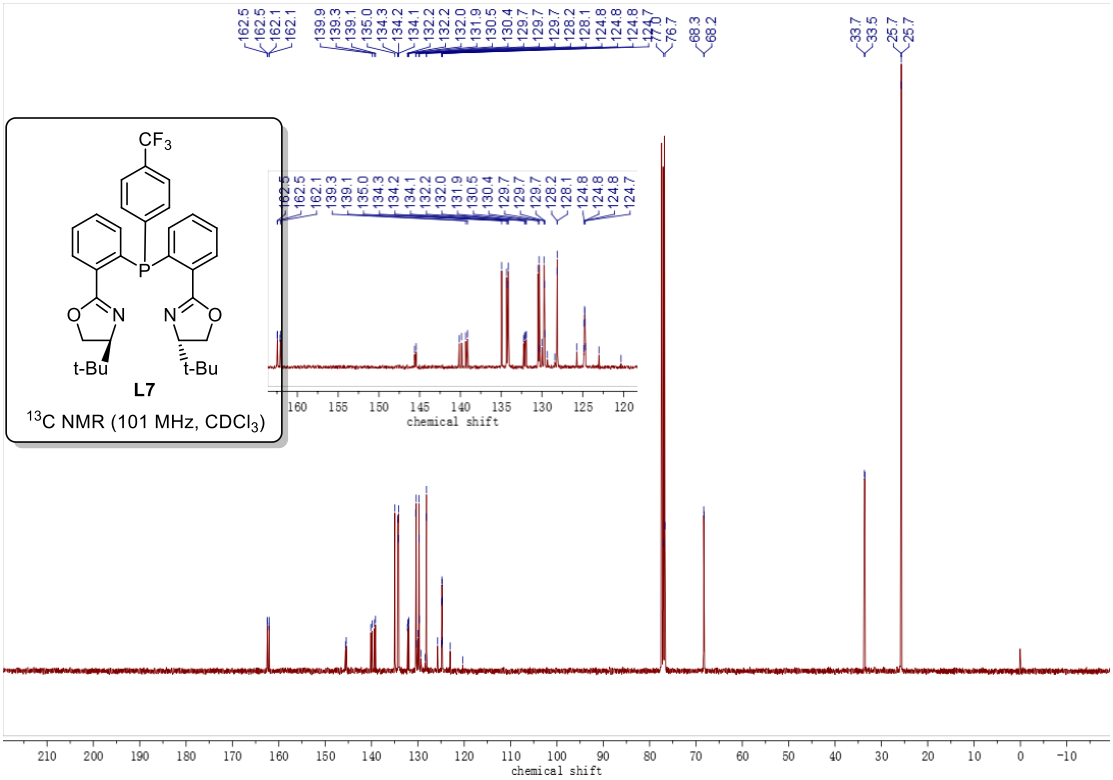


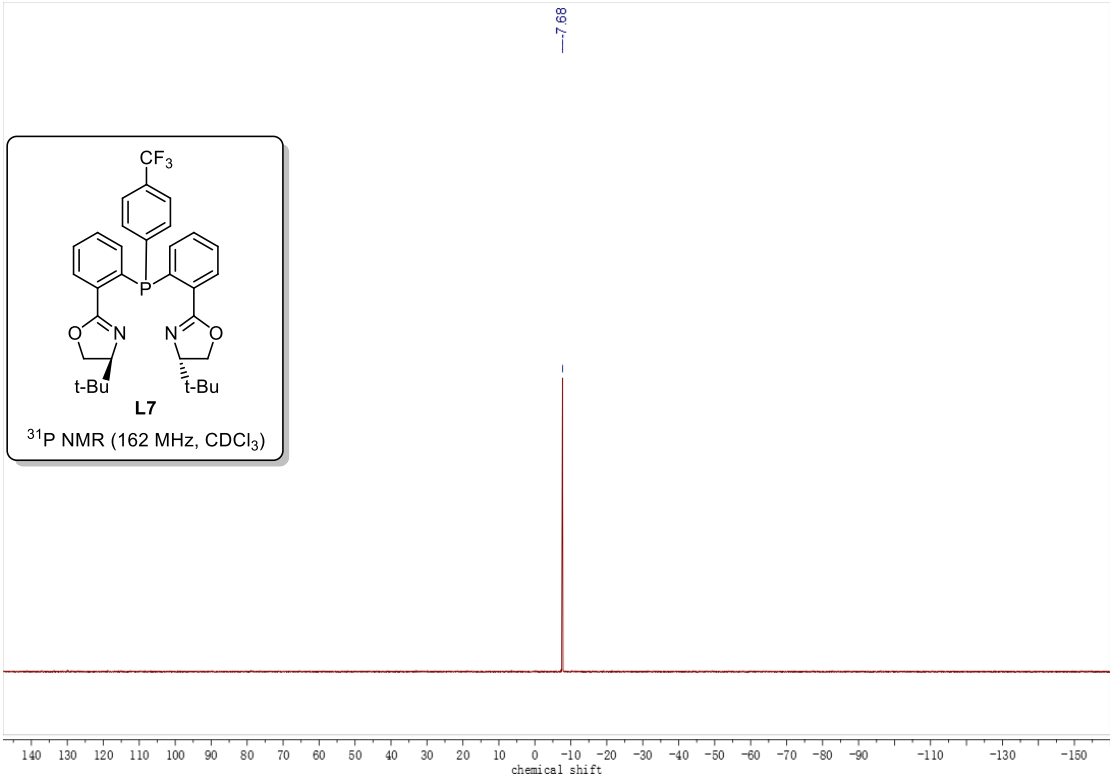


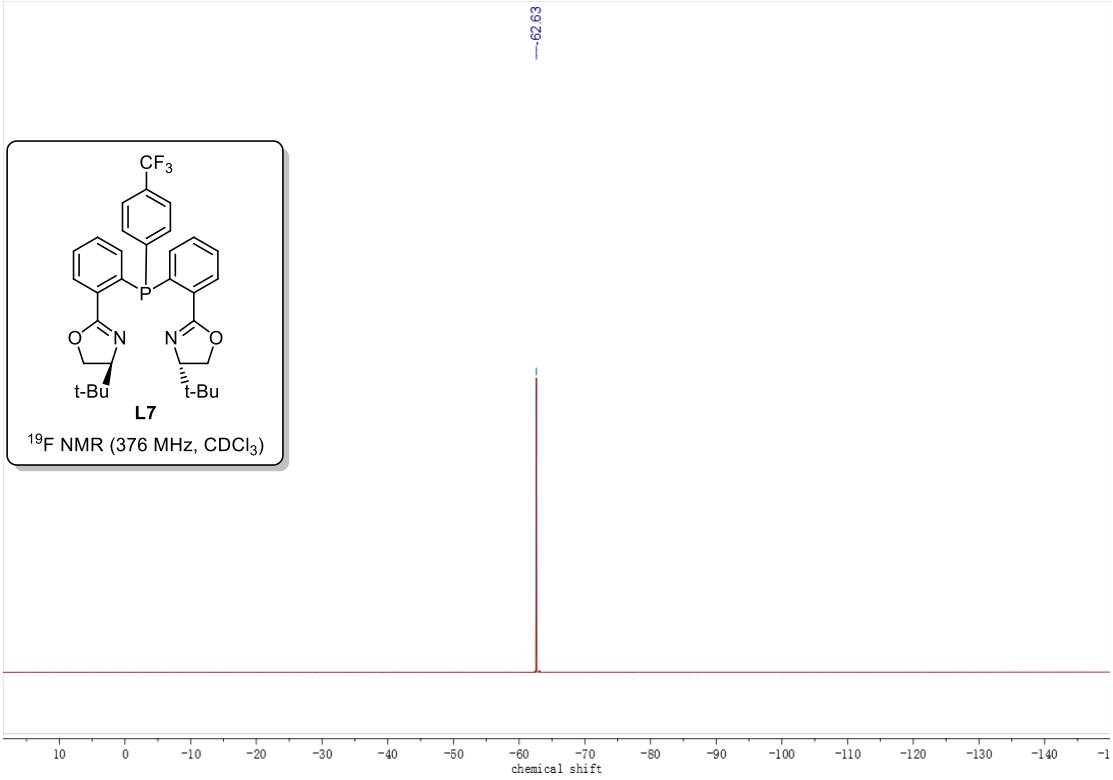

-5.69
OCH3
t-Bu
t-Bu
P
O
N
N
O
t-Bu
t-Bu
L6
31P NMR (162 MHz, CDCl3)
chemical shift

(4S,4'S)-2,2'-(((4-(trifluoromethyl)phenyl)phosphanediyl)bis(2,1-phenylene))bis(4-(tert-butyl)-4,5-dihydrooxazole) (**L7**).

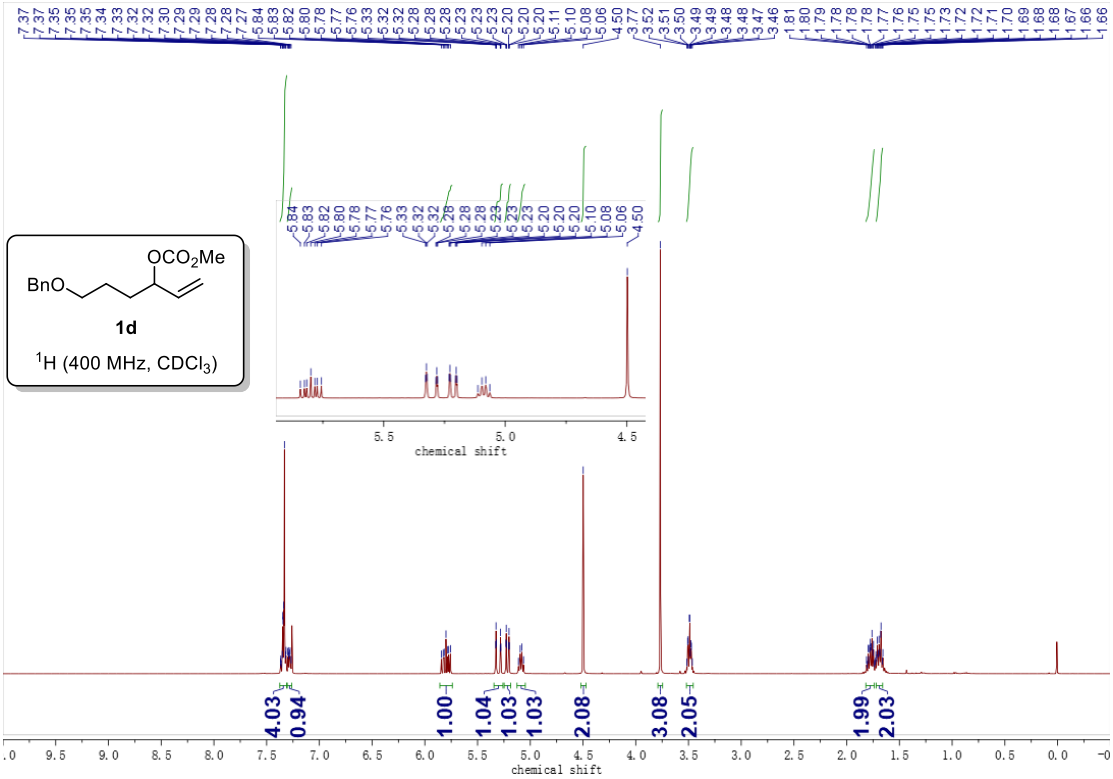


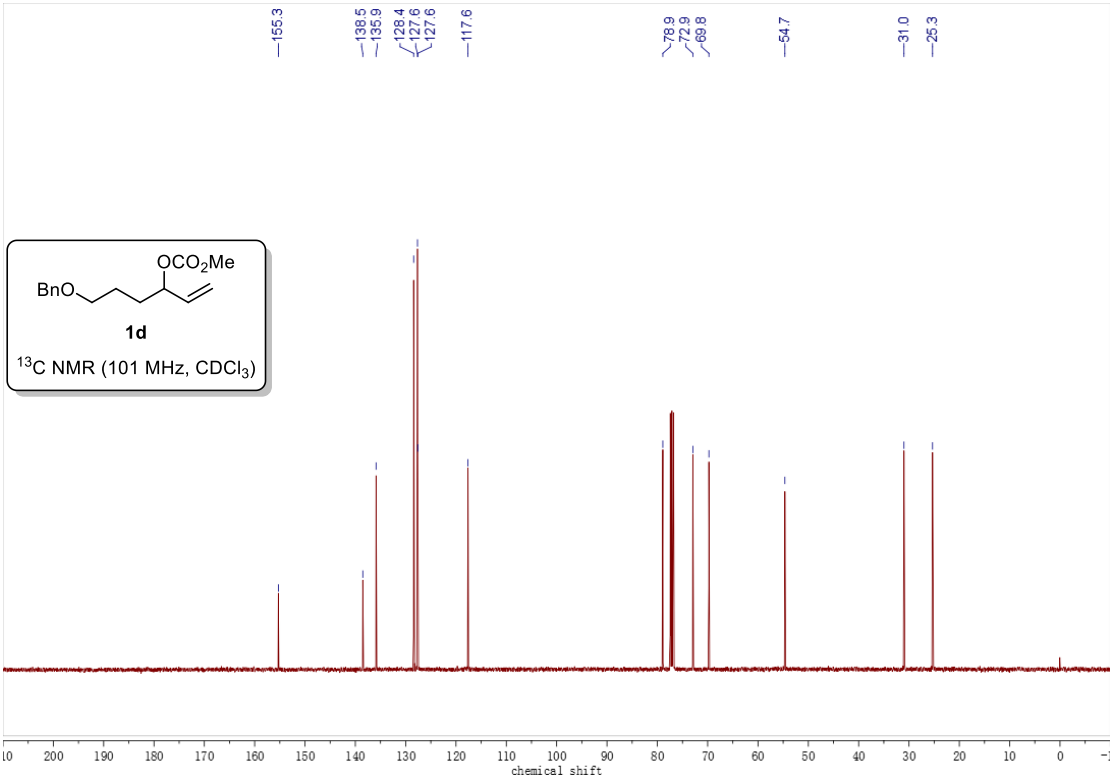



-7.68
CF3
P
O
N
N
O
t-Bu
t-Bu
L7
31P NMR (162 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150
chemical shift

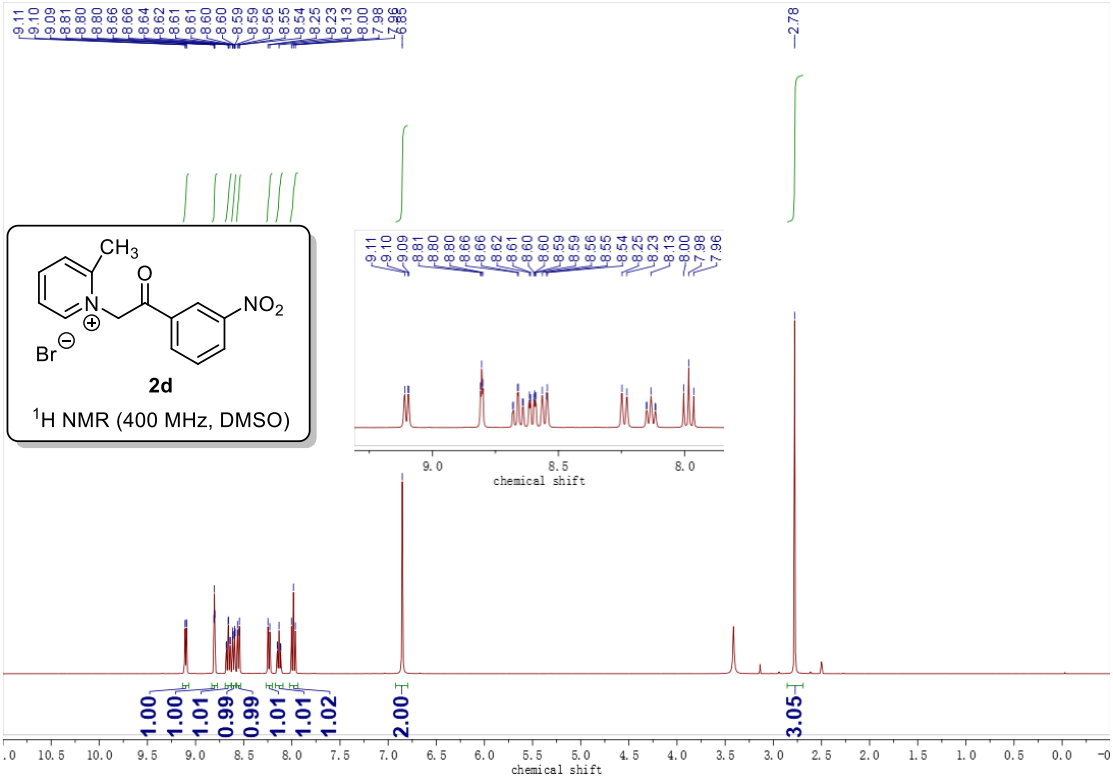

-62.63
CF3
P
O
N
N
O
t-Bu
t-Bu
L7
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
chemical shift

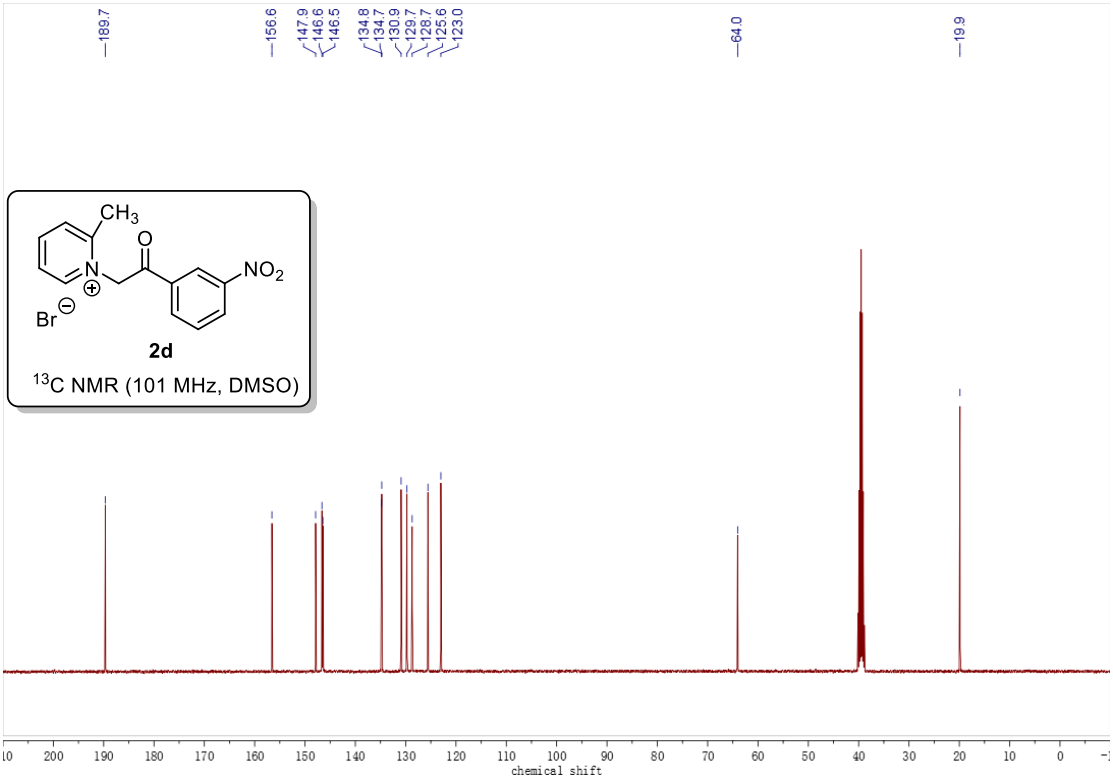
6-(benzyloxy)hex-1-en-3-yl methyl carbonate (**1d**).



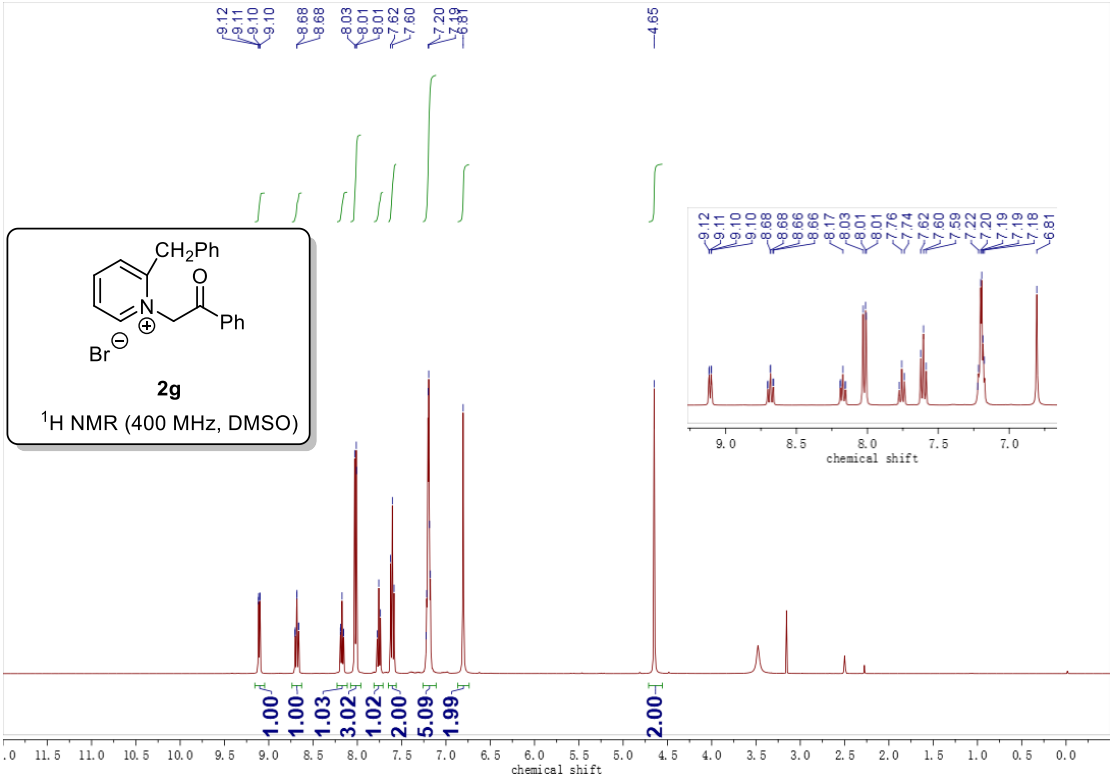


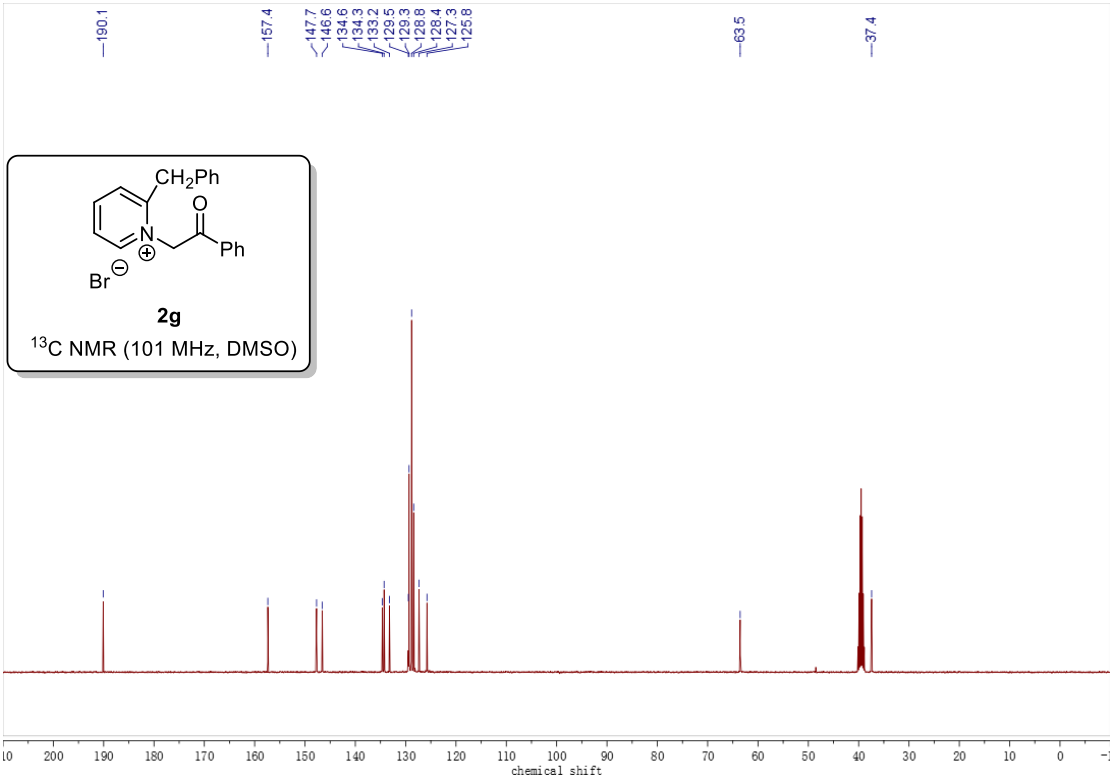
2-methyl-1-(2-(3-nitrophenyl)-2-oxoethyl)pyridin-1-ium bromide (**2d**).



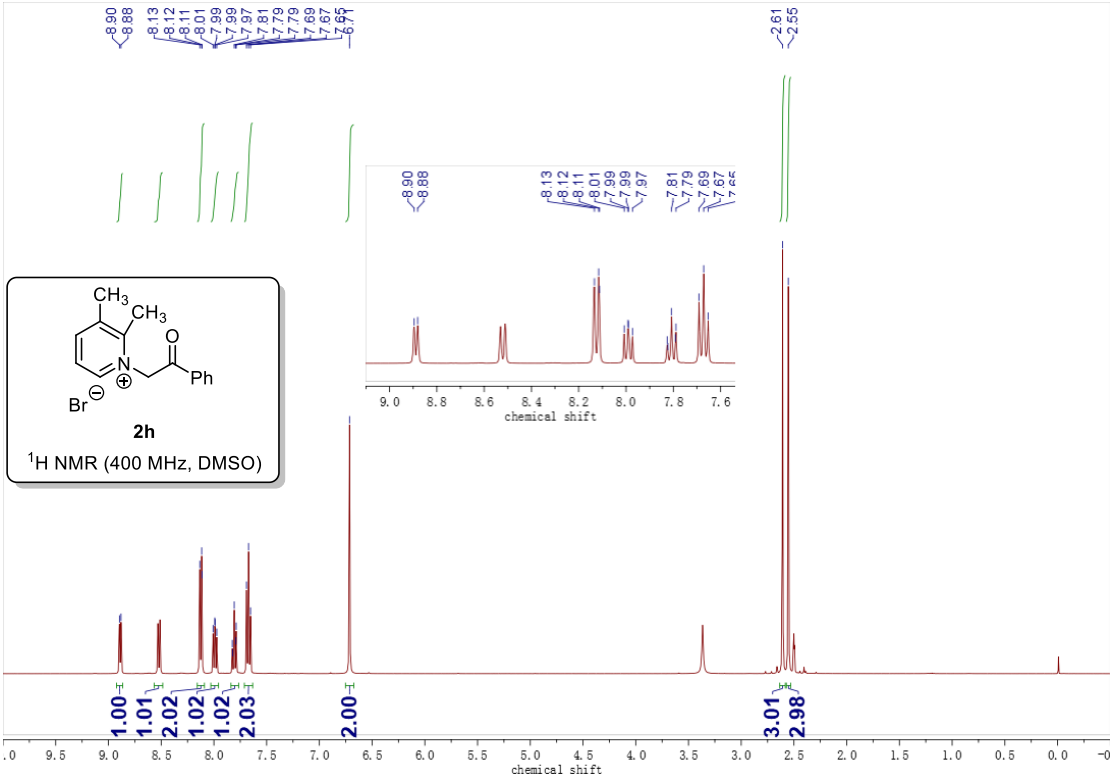


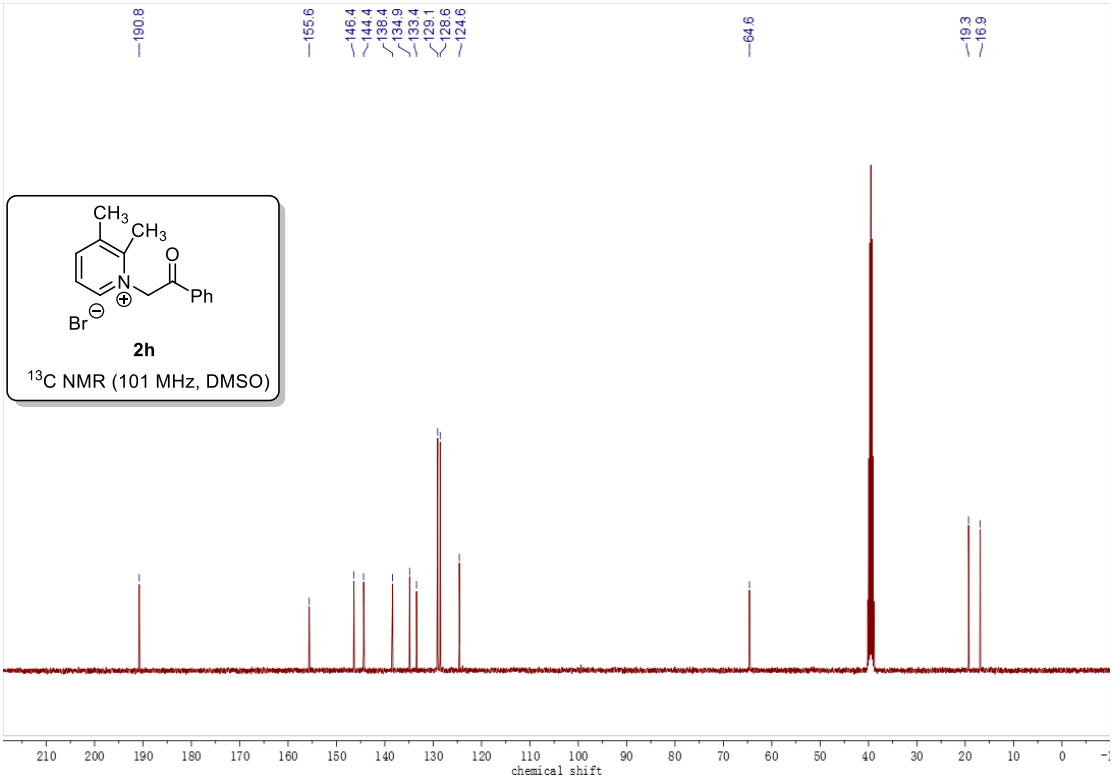
2-benzyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (**2g**).



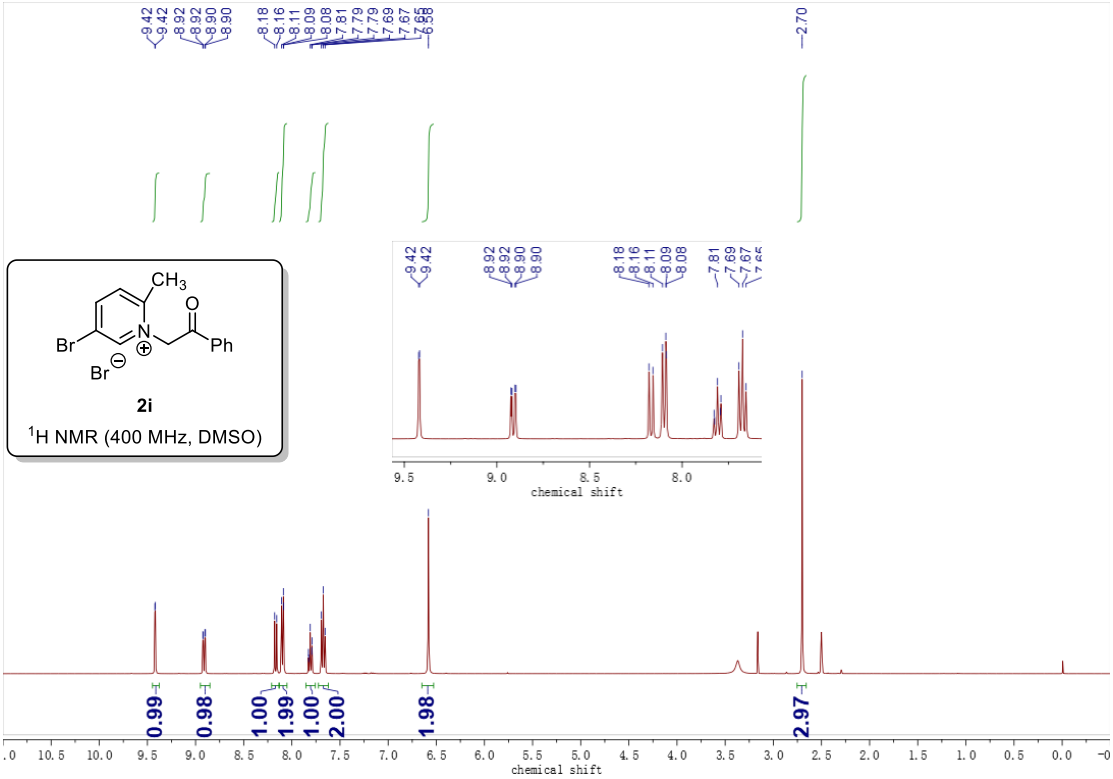


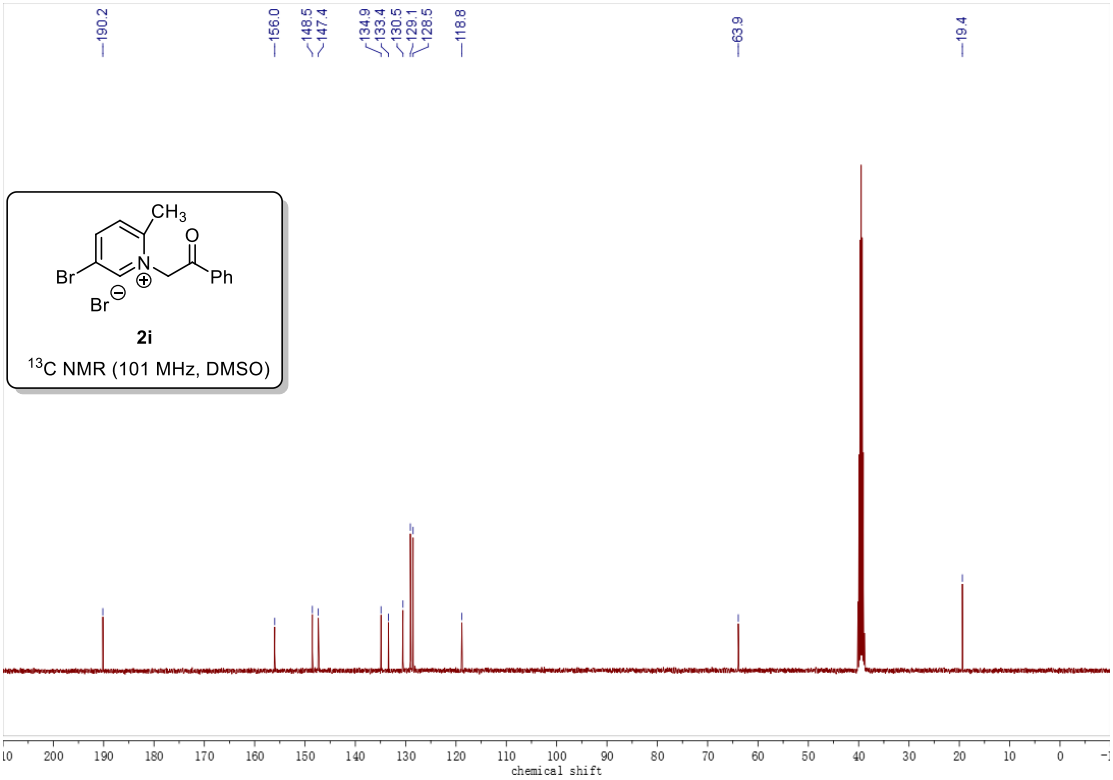
2,3-dimethyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (**2h**).



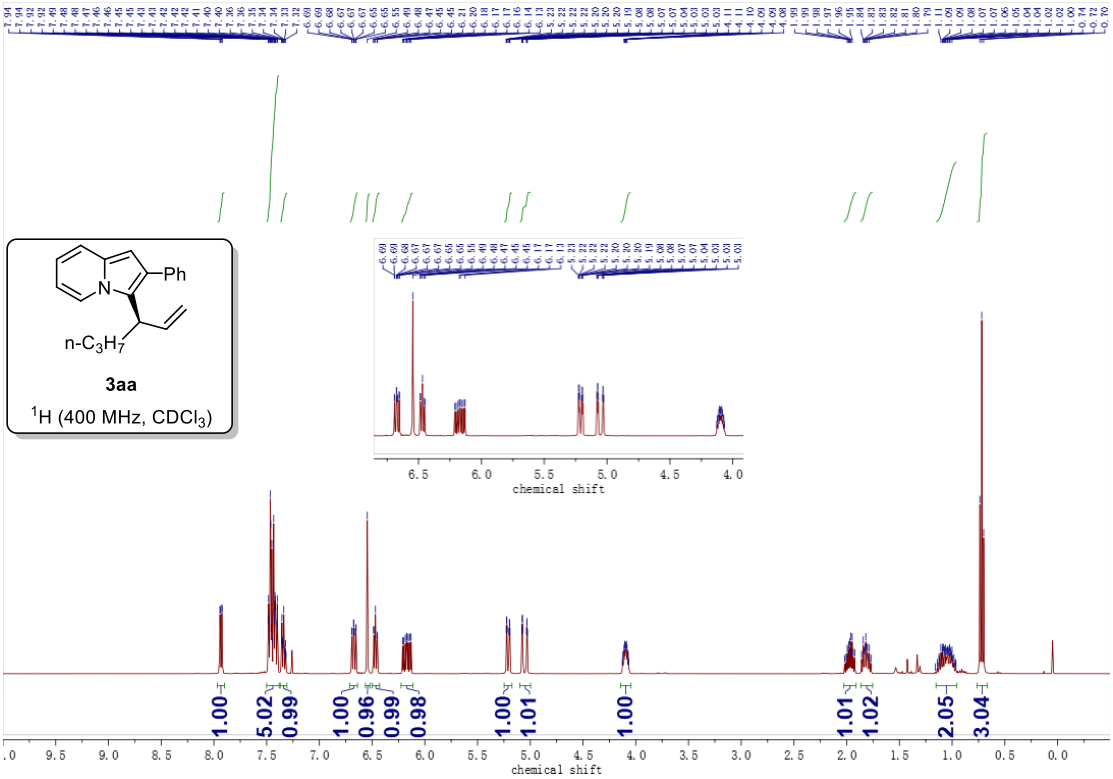


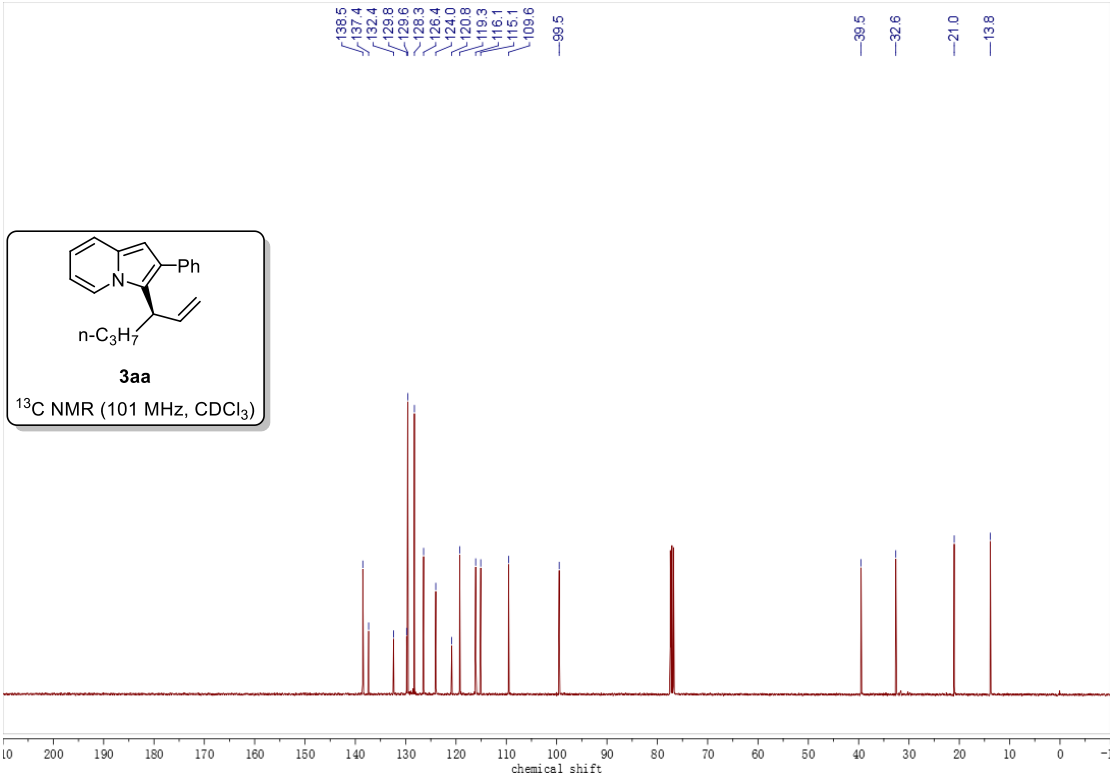
5-bromo-2-methyl-1-(2-oxo-2-phenylethyl)pyridin-1-ium bromide (**2i**).



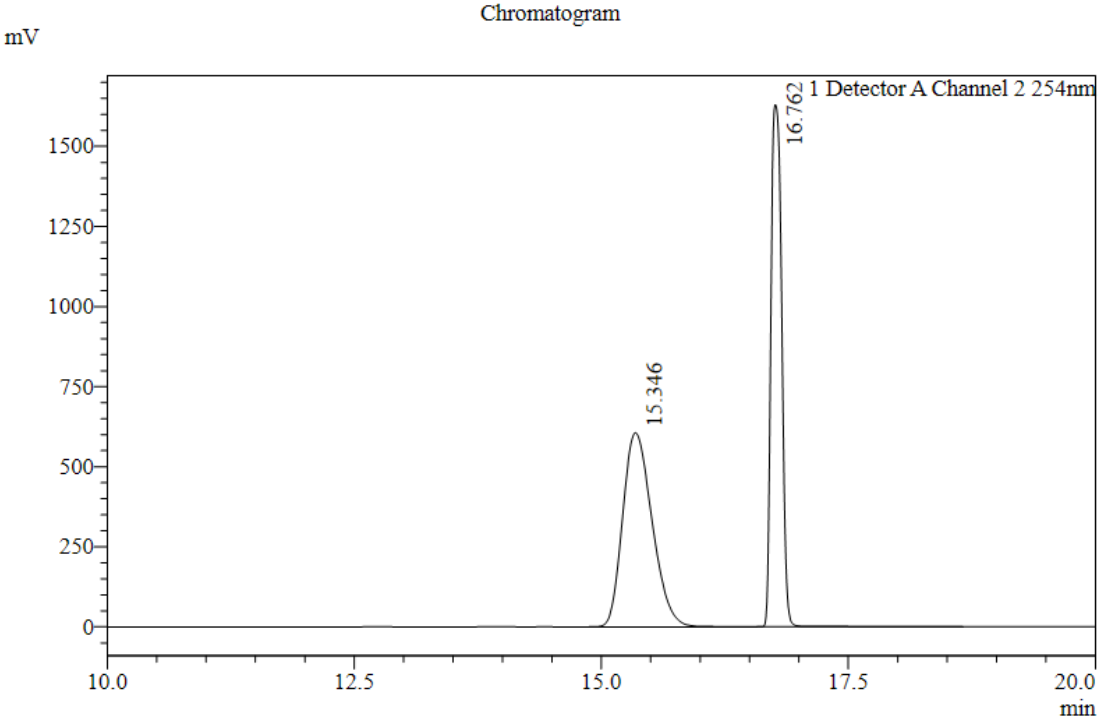


(R)-3-(hex-1-en-3-yl)-2-phenylindolizine (**3aa**).





Chromatogram

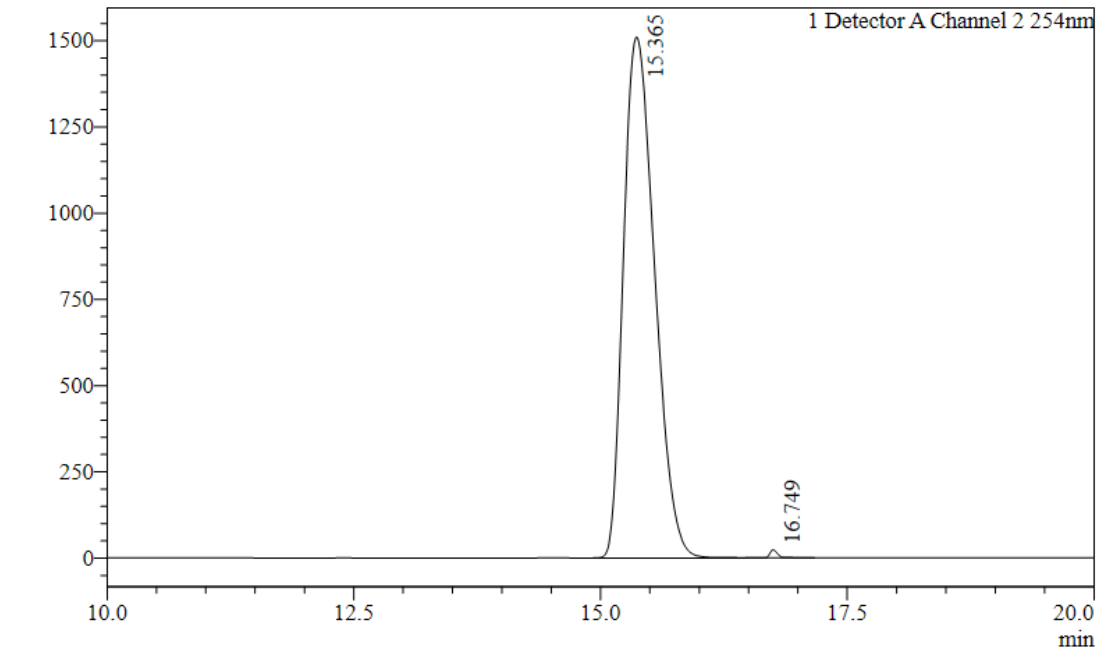


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.346	12589395	605792	50.453	50.453
2	16.762	12363444	1629567	49.547	49.547
Total		24952839	2235359		100.000

Chromatogram

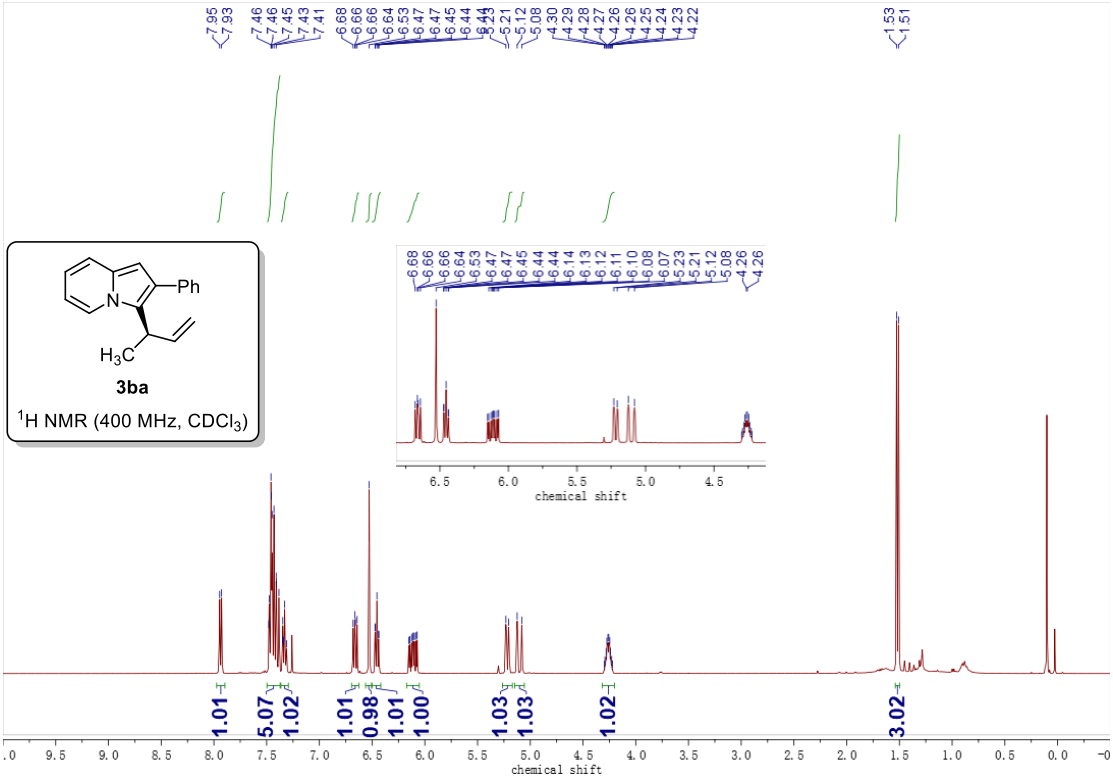


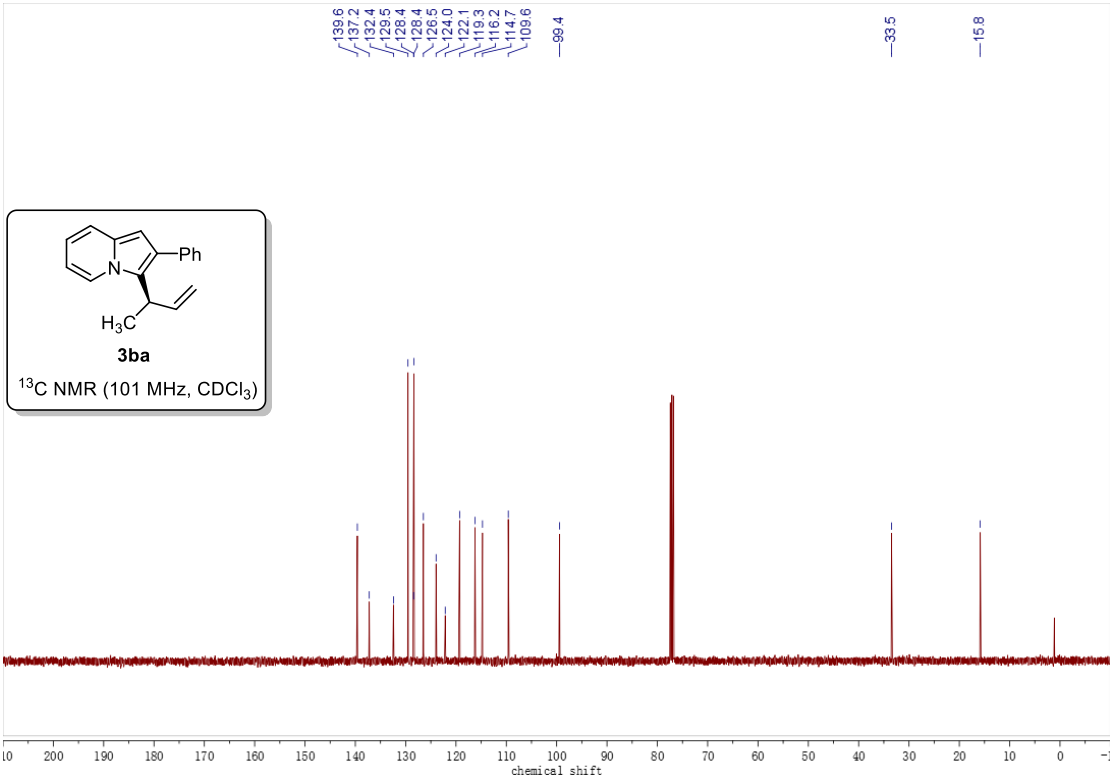
Peak Table

Detector A Channel 2 254nm

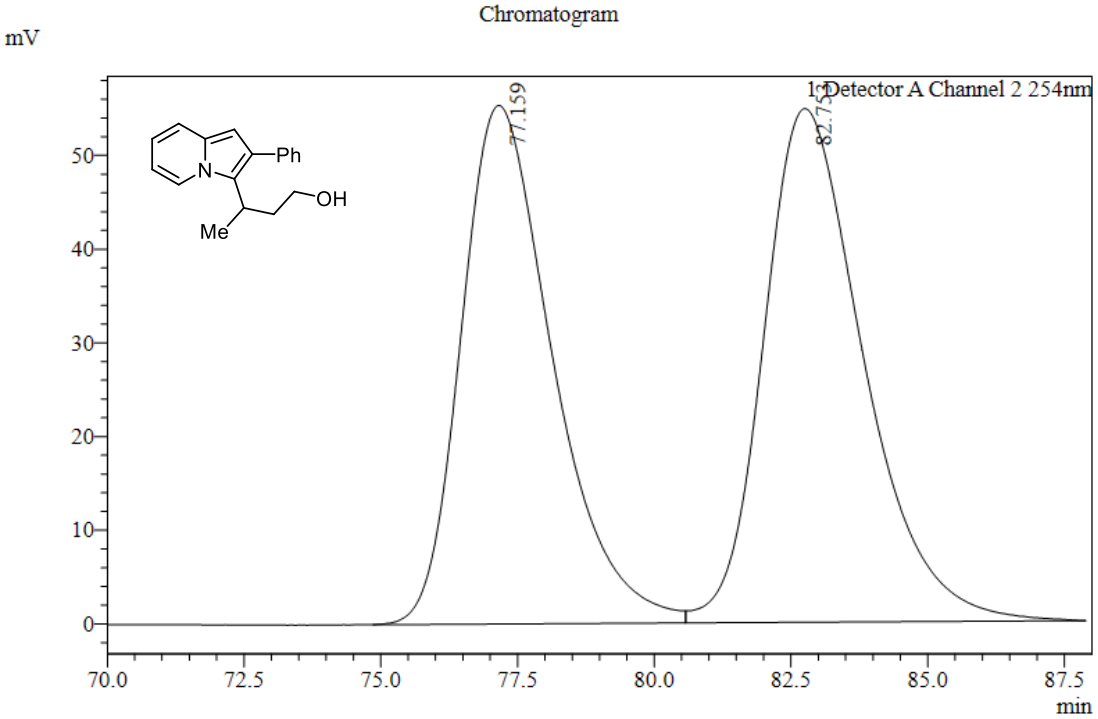
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.365	33165704	1510315	99.638	99.638
2	16.749	120662	22807	0.362	0.362
Total		33286366	1533121		100.000

(R)-3-(but-3-en-2-yl)-2-phenylindolizine (**3ba**).





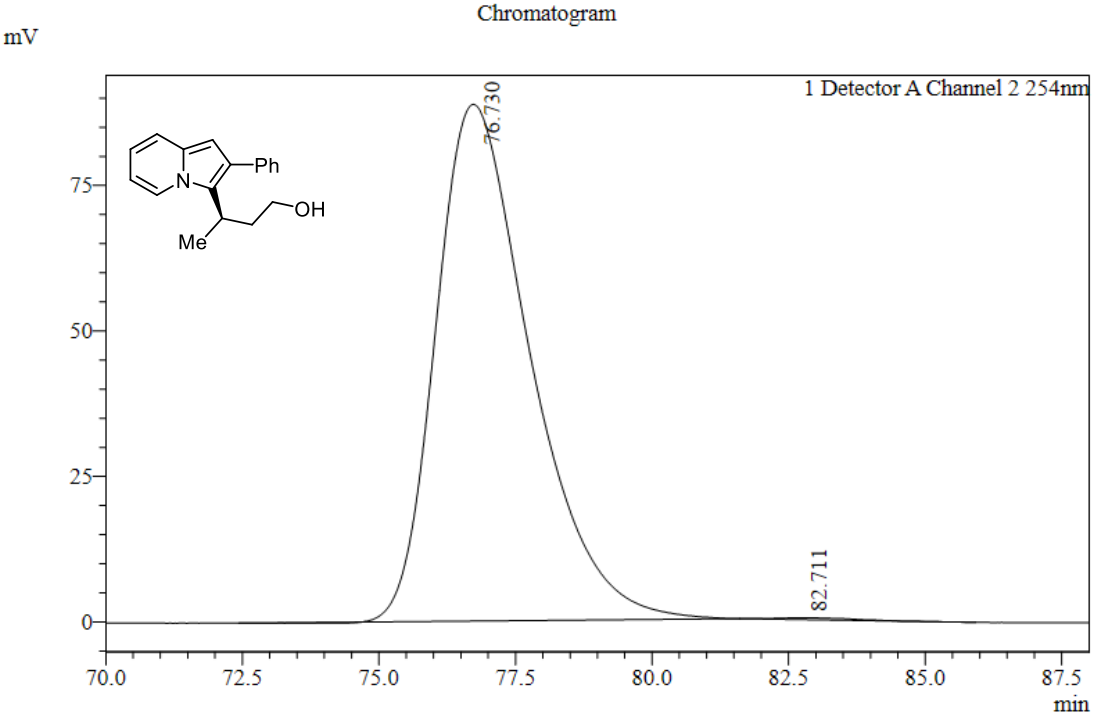
The *ee* value was determined after the hydroboration/oxidation sequence (**9**).



Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	77.159	6431756	55351	48.049	48.049
2	82.753	6954116	54824	51.951	51.951
Total		13385872	110175		100.000

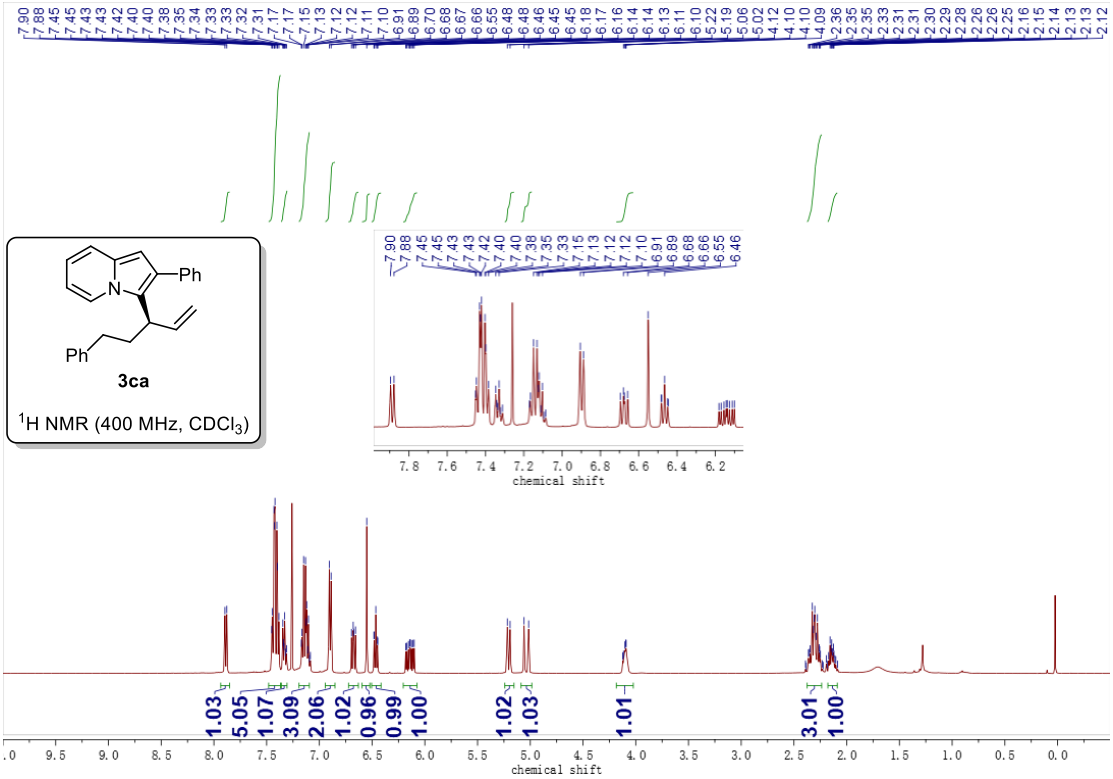


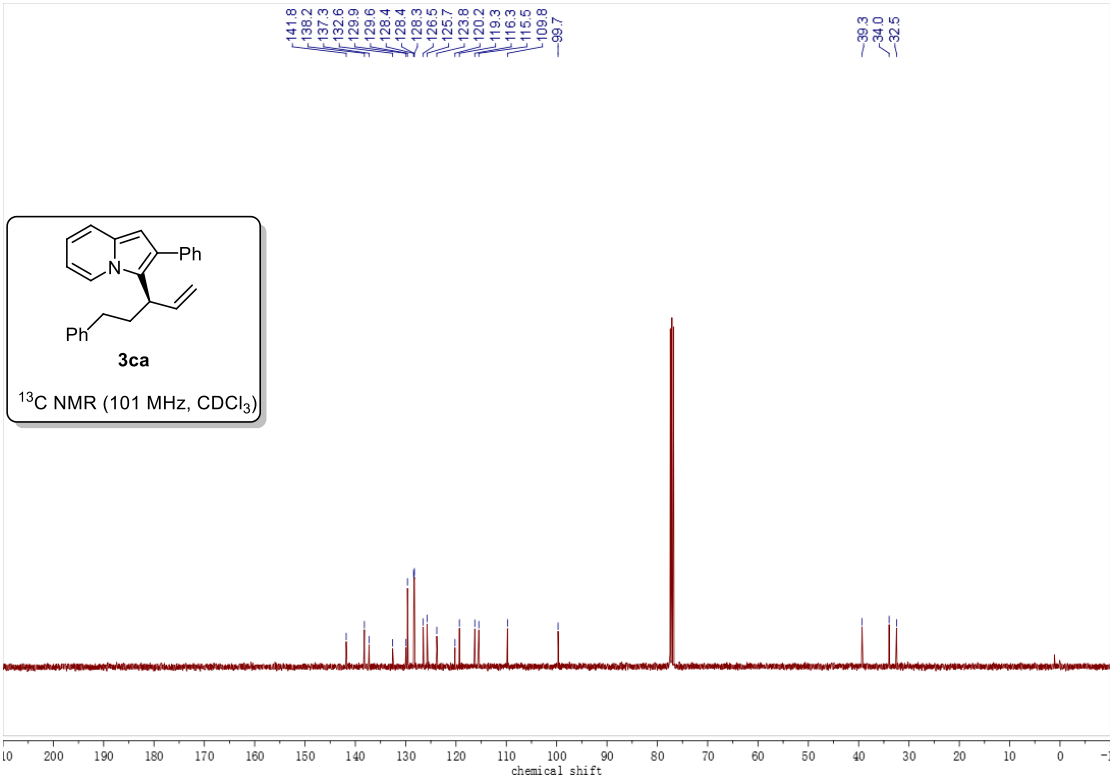
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	76.730	10663560	88753	99.745	99.745
2	82.711	27298	294	0.255	0.255
Total		10690857	89047		100.000

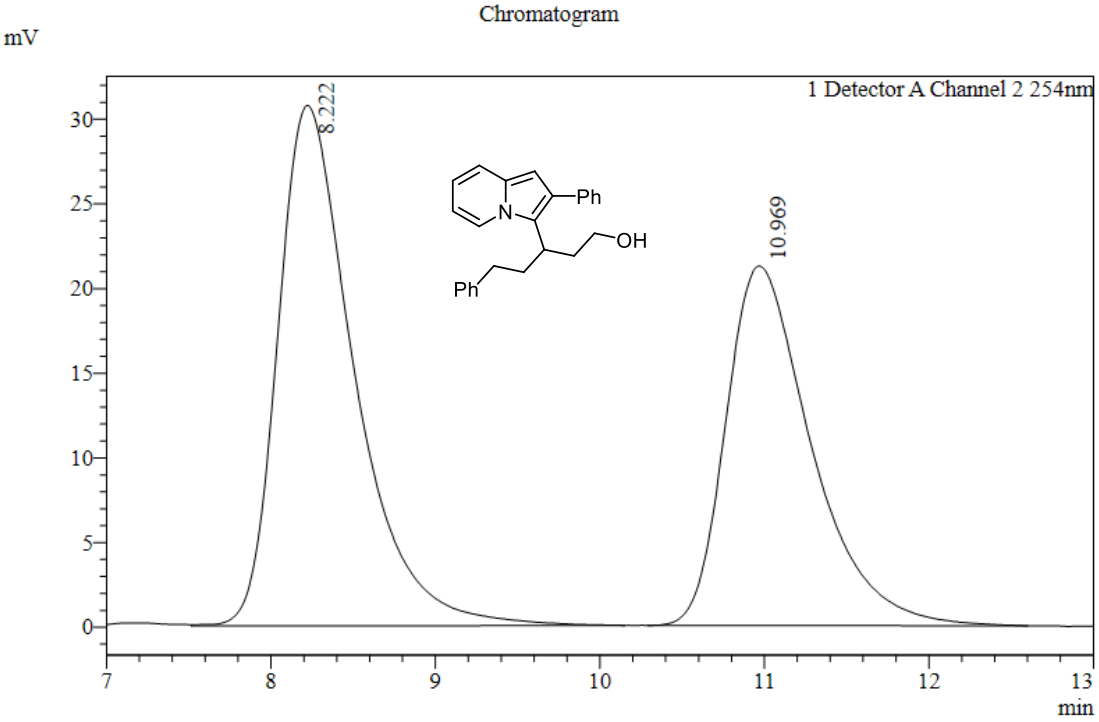
(R)-2-phenyl-3-(5-phenylpent-1-en-3-yl)indolizine (**3ca**).





The *ee* value was determined after the hydroboration/oxidation sequence.

Chromatogram

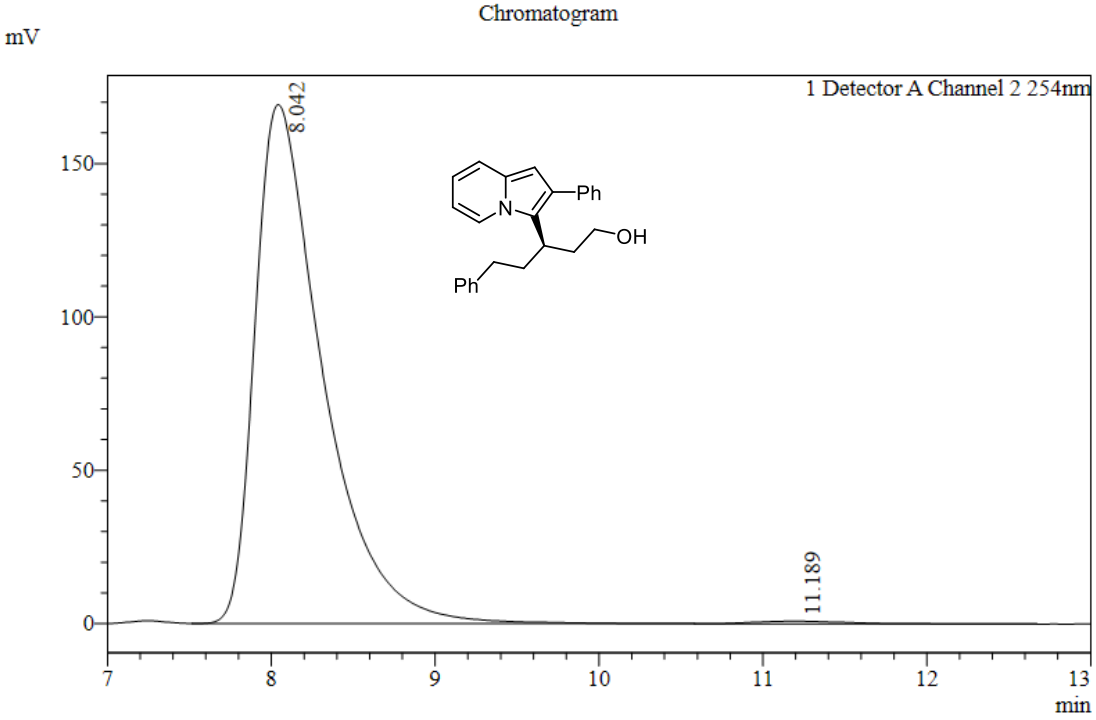


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.222	996906	30737	56.461	56.461
2	10.969	768749	21232	43.539	43.539
Total		1765655	51970		100.000

Chromatogram

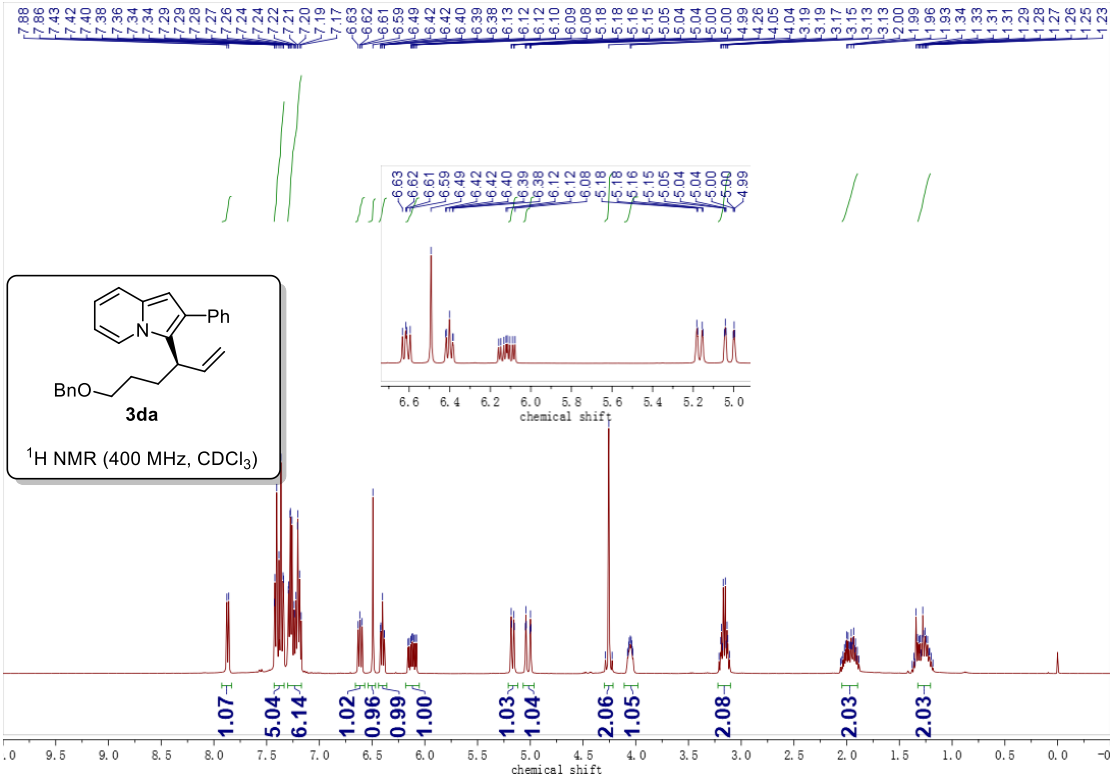


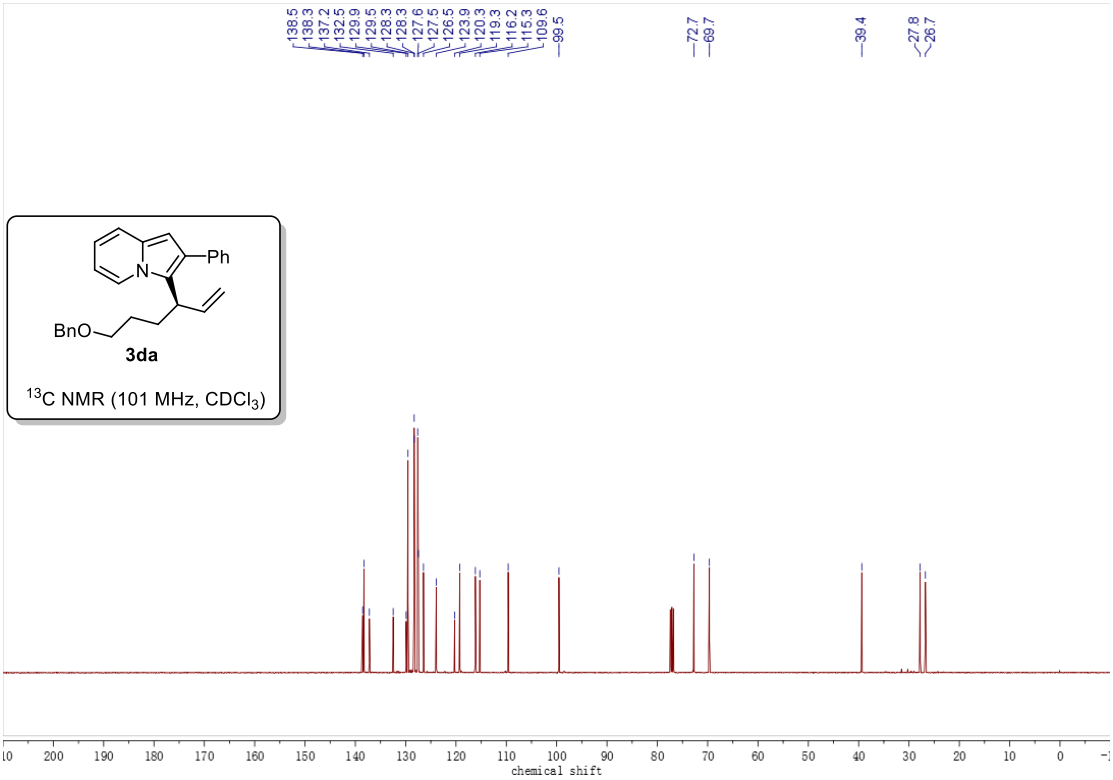
Peak Table

Detector A Channel 2 254nm

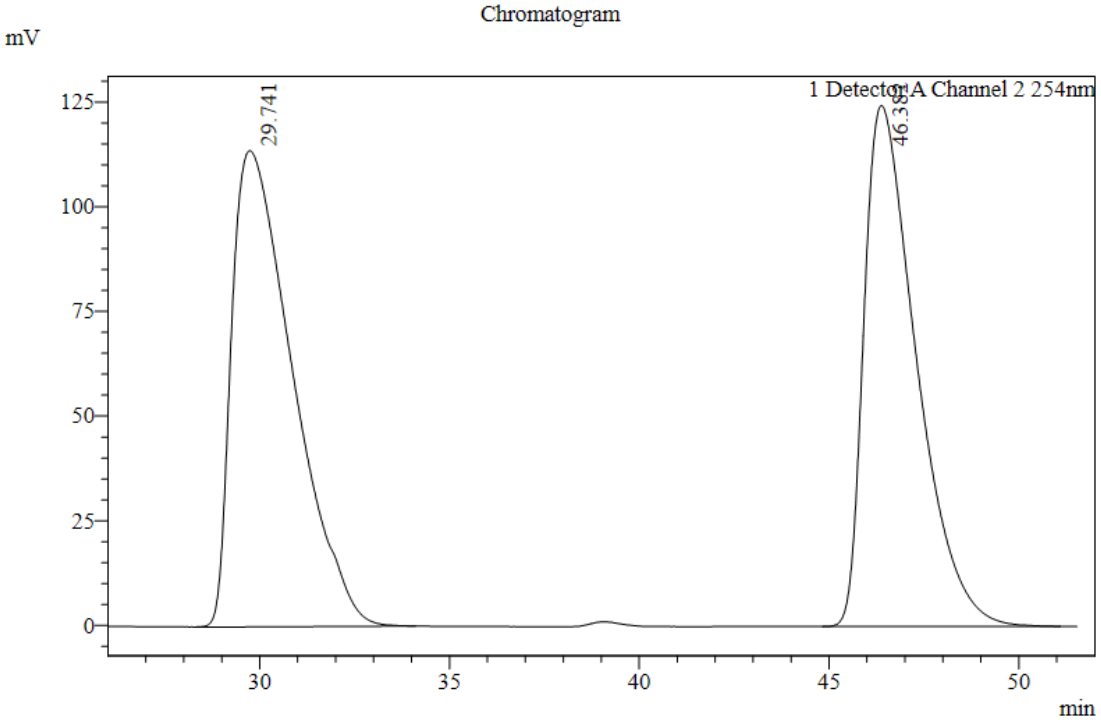
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	8.042	4873916	169220	99.326	99.326
2	11.189	33075	843	0.674	0.674
Total		4906991	170063		100.000

(R)-3-(6-(benzyloxy)hex-1-en-3-yl)-2-phenylindolizine (**3da**).





Chromatogram

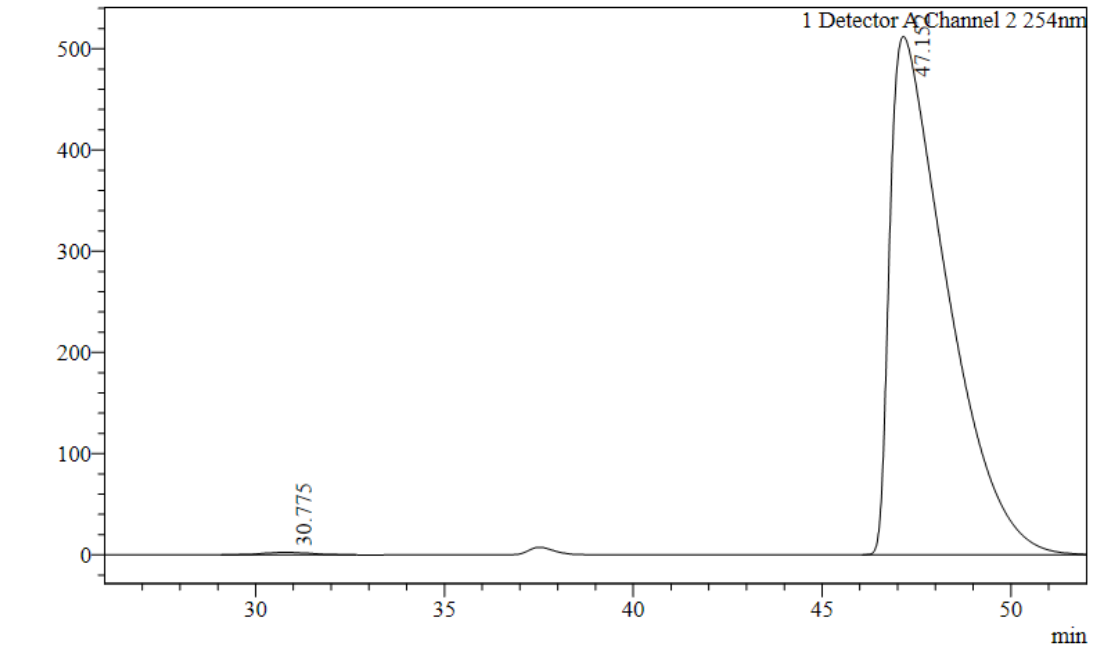


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	29.741	12680139	113683	51.545	51.545
2	46.382	11920020	124423	48.455	48.455
Total		24600160	238106		100.000

Chromatogram

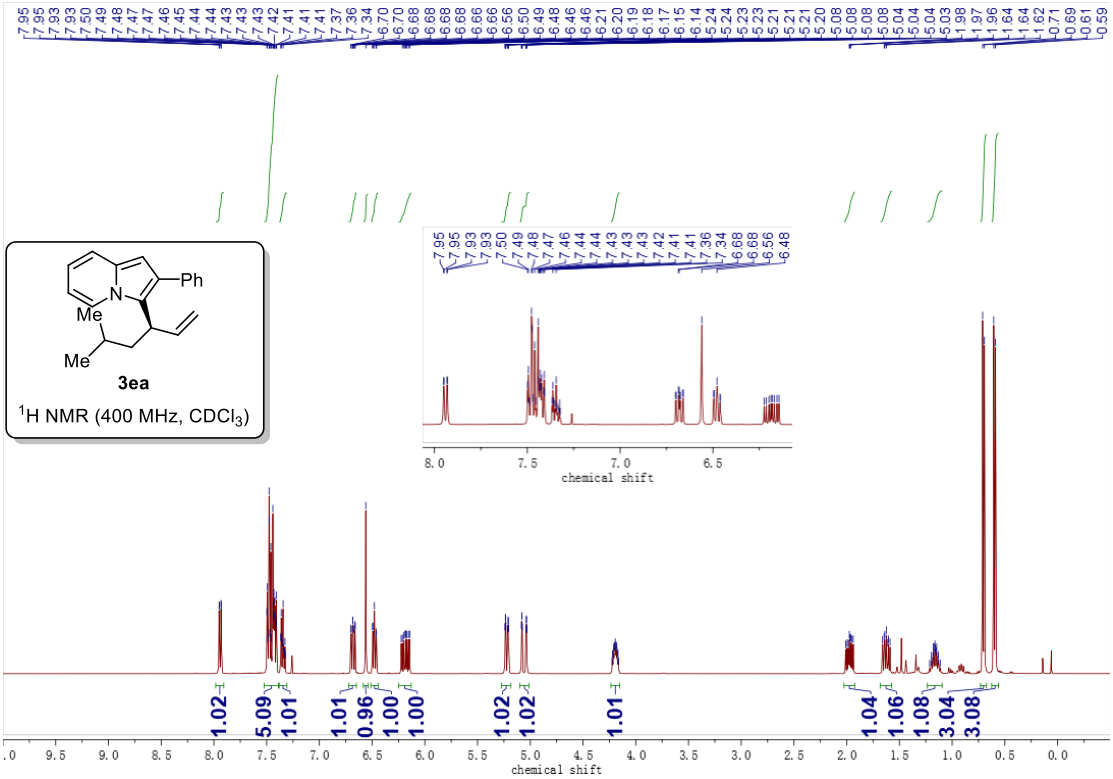


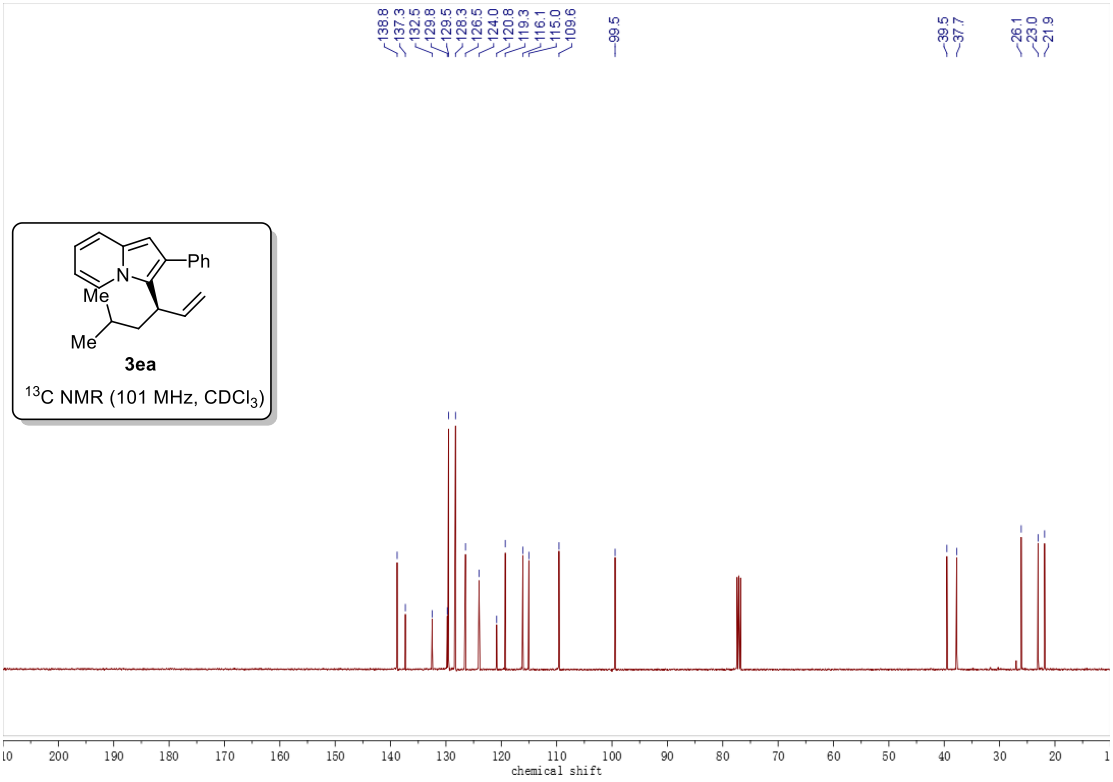
Peak Table

Detector A Channel 2 254nm

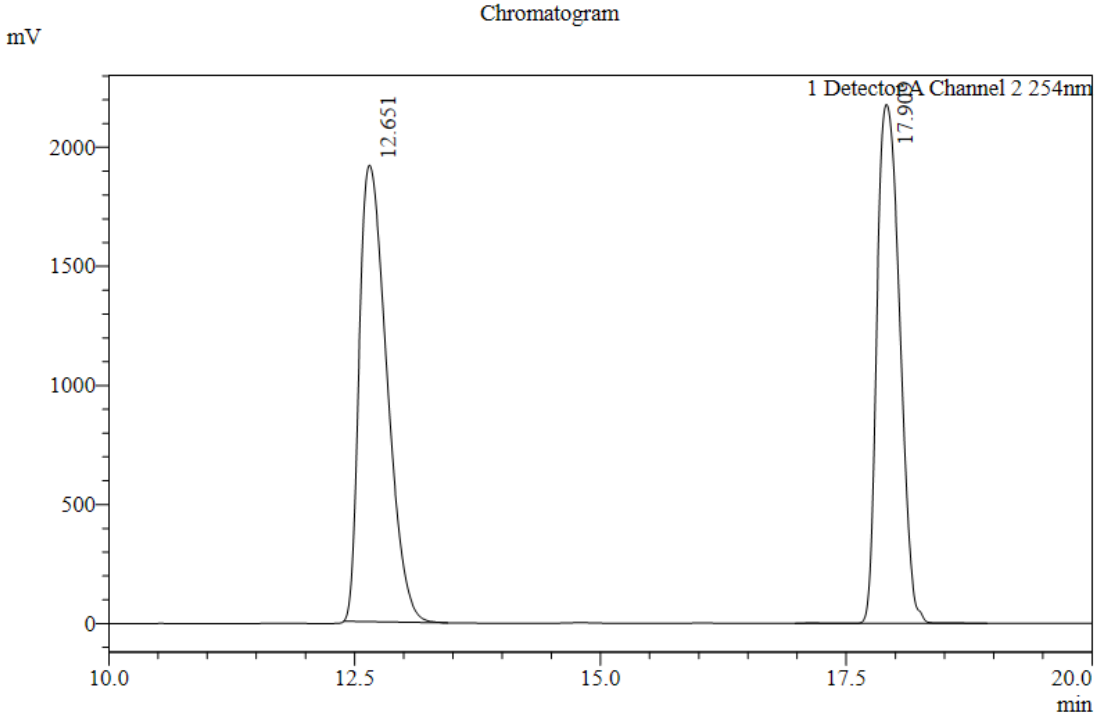
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	30.775	234014	2580	0.431	0.431
2	47.152	54044899	512159	99.569	99.569
Total		54278913	514739		100.000

(R)-3-(5-methylhex-1-en-3-yl)-2-phenylindolizine (**3ea**).





Chromatogram

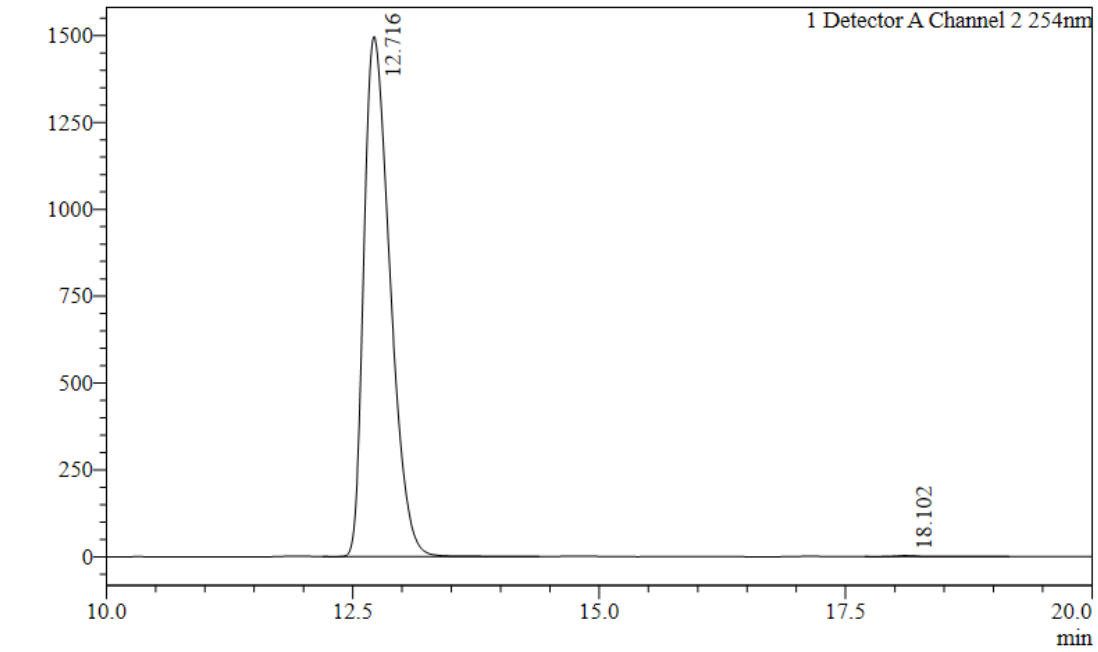


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.651	37330928	1916956	51.493	51.493
2	17.909	35165654	2179889	48.507	48.507
Total		72496581	4096845		100.000

Chromatogram

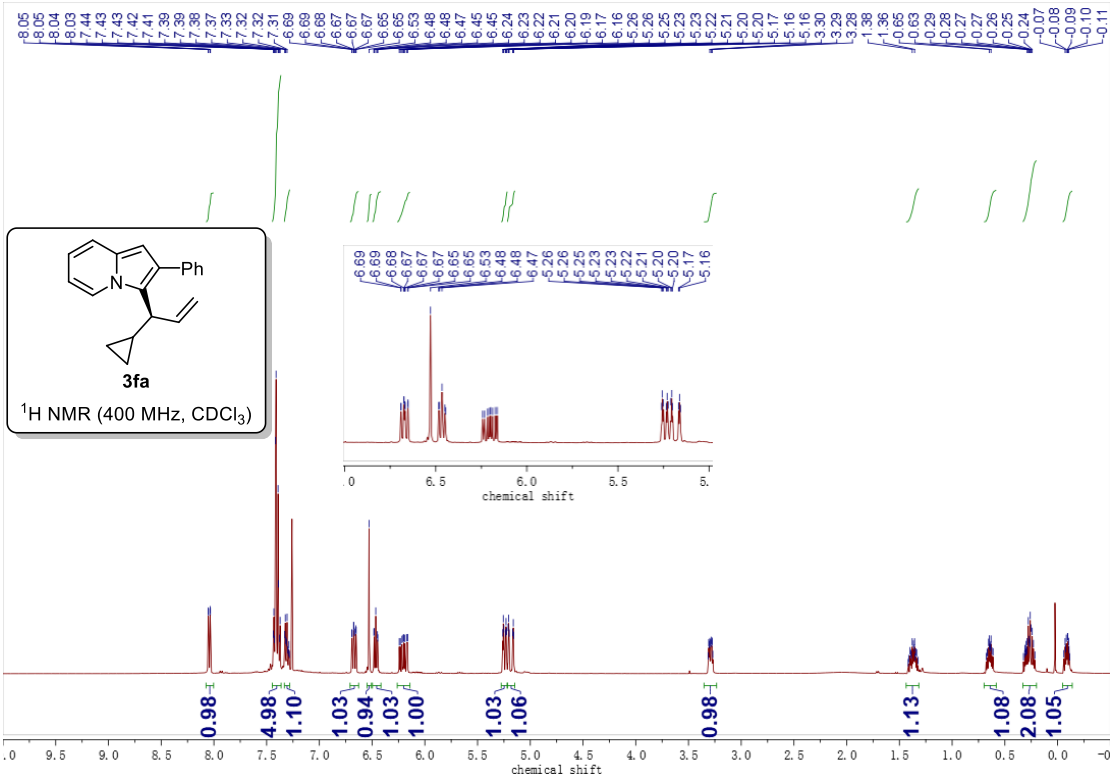


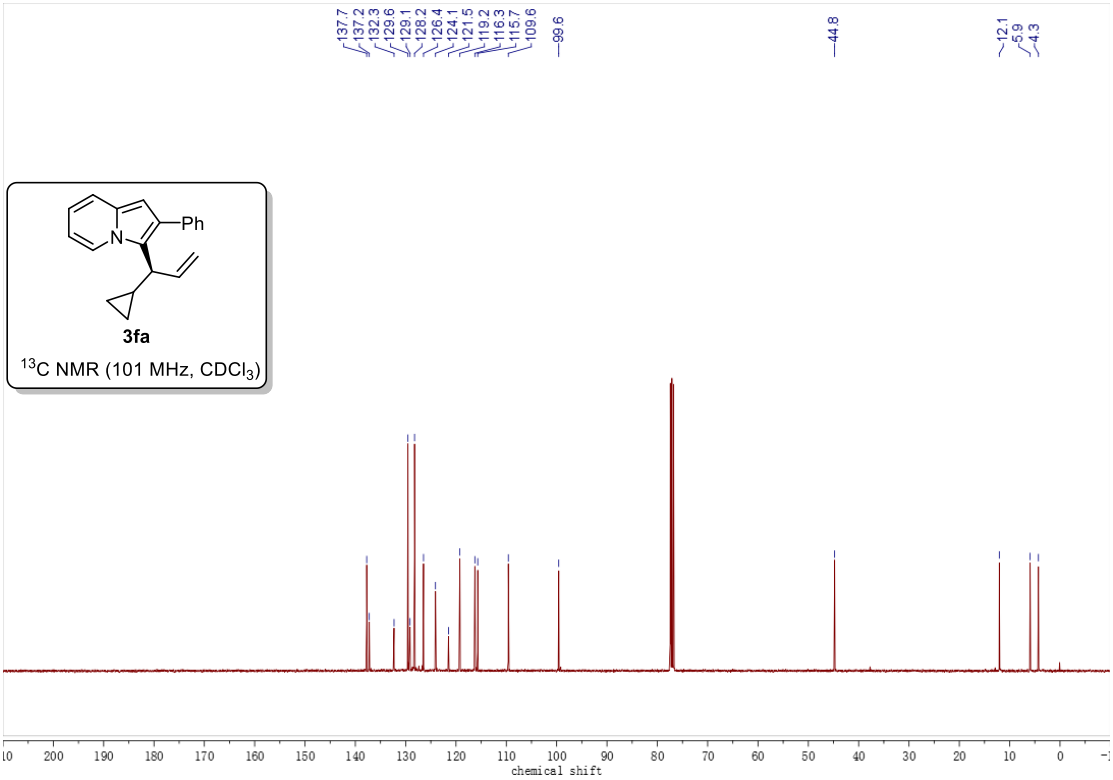
Peak Table

Detector A Channel 2 254nm

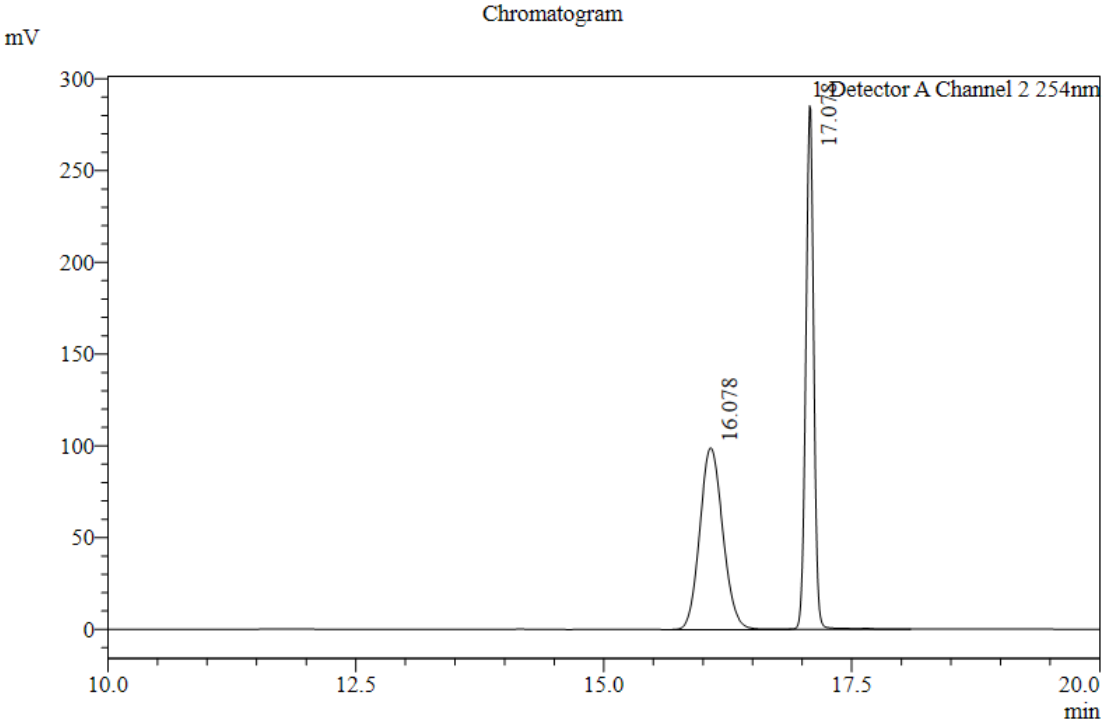
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	12.716	27646053	1497287	99.828	99.828
2	18.102	47520	3313	0.172	0.172
Total		27693574	1500600		100.000

(S)-3-(1-cyclopropylallyl)-2-phenylindolizine (**3fa**).





Chromatogram

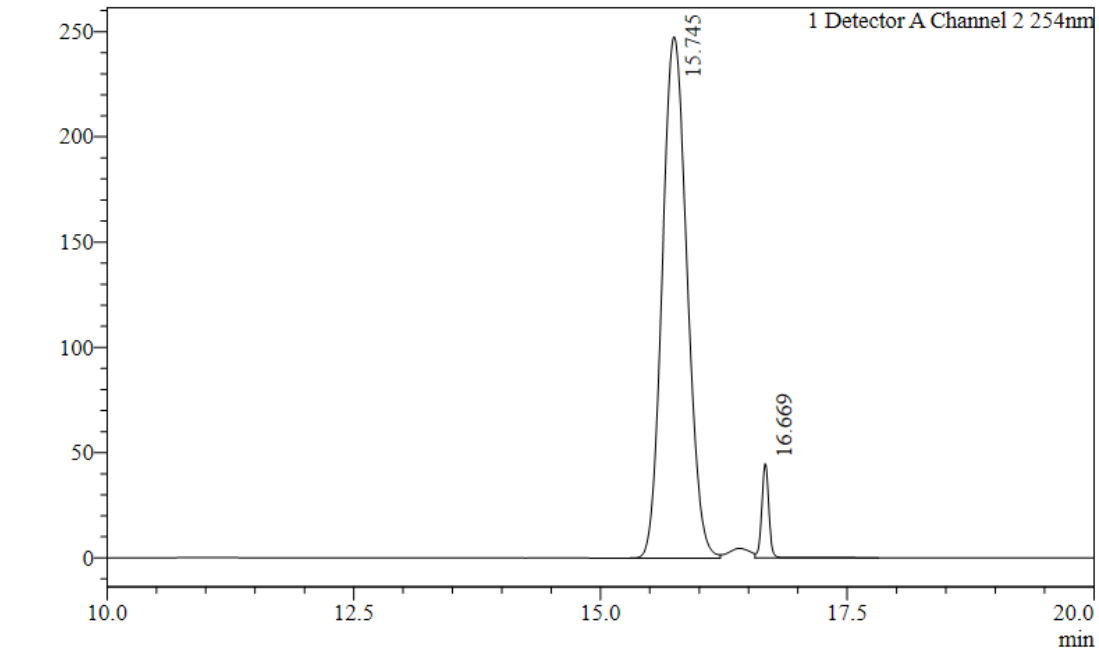


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	16.078	1605560	98970	49.947	49.947
2	17.078	1608973	285426	50.053	50.053
Total		3214533	384396		100.000

Chromatogram

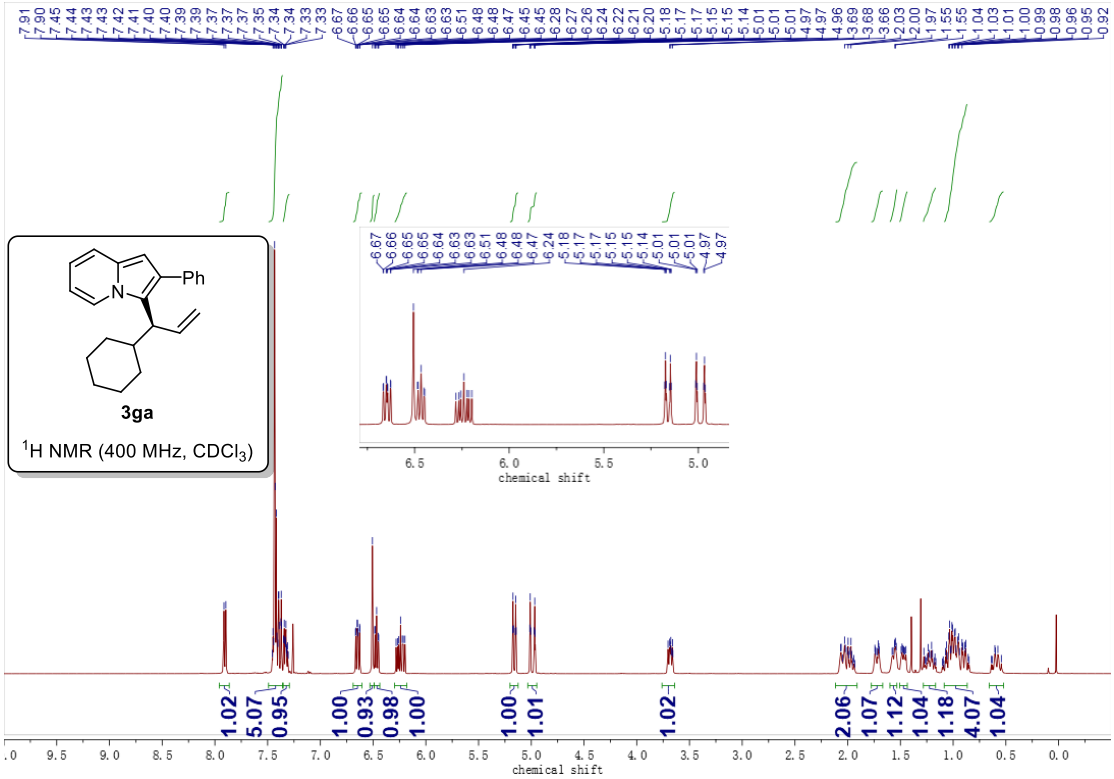


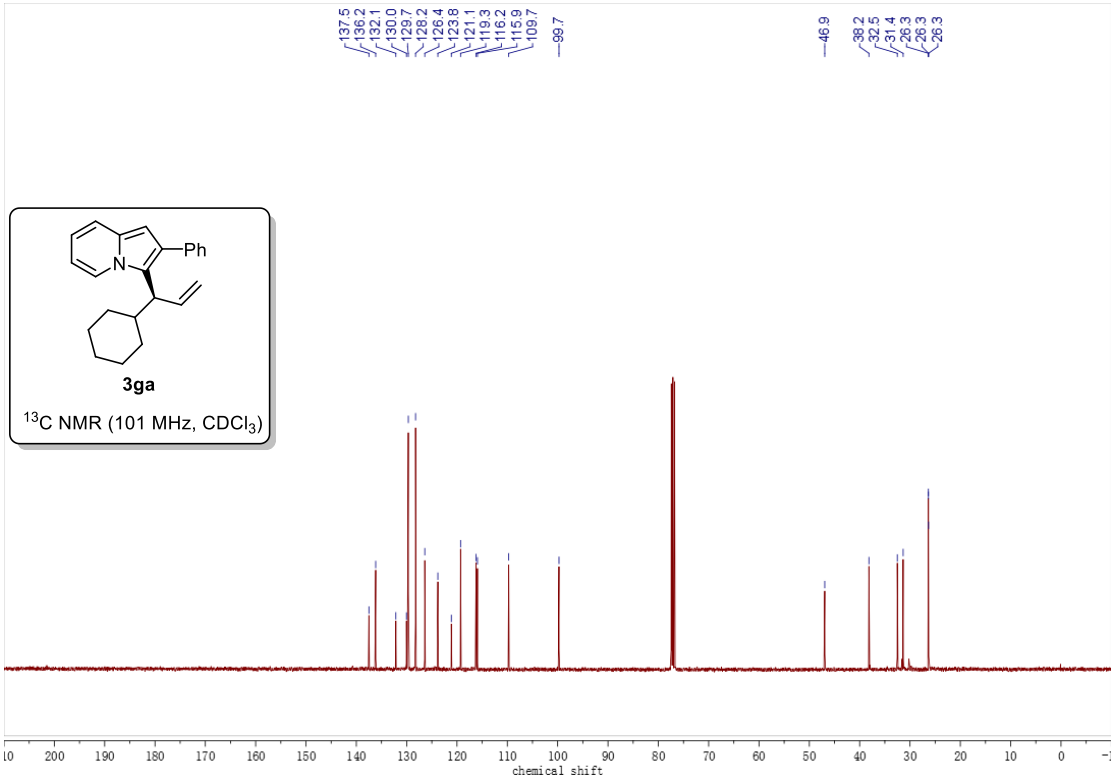
Peak Table

Detector A Channel 2 254nm

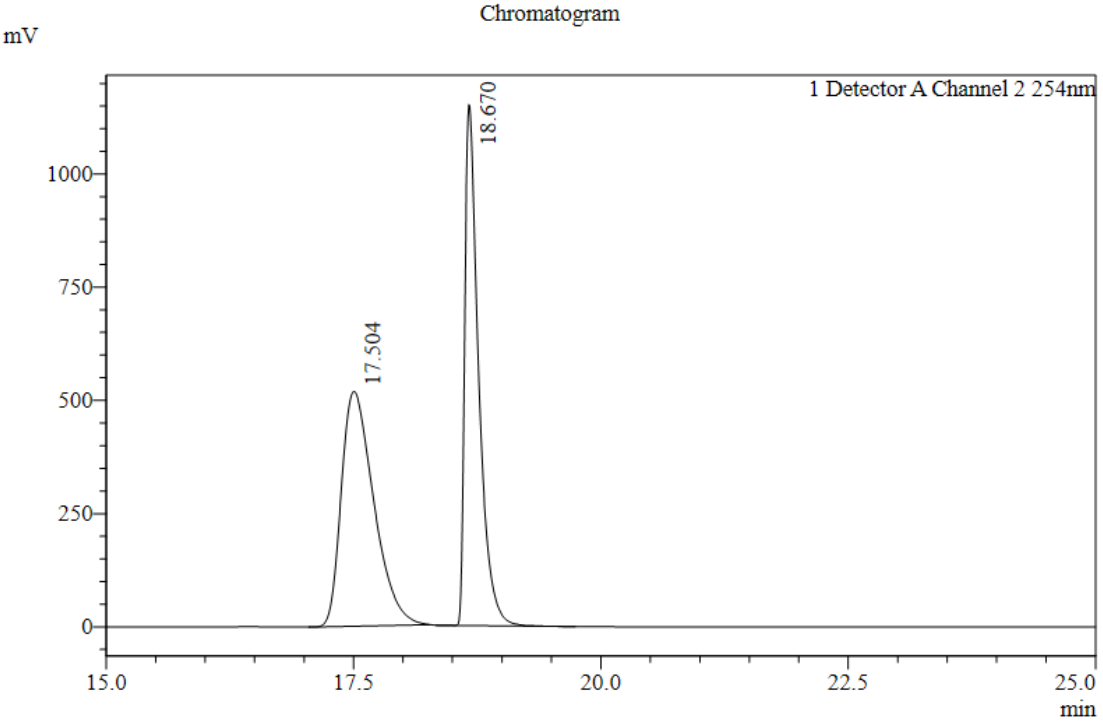
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	15.745	4317079	247591	95.016	95.016
2	16.669	226448	44941	4.984	4.984
Total		4543526	292531		100.000

(S)-3-(1-cyclohexylallyl)-2-phenylindolizine (**3ga**).





Chromatogram

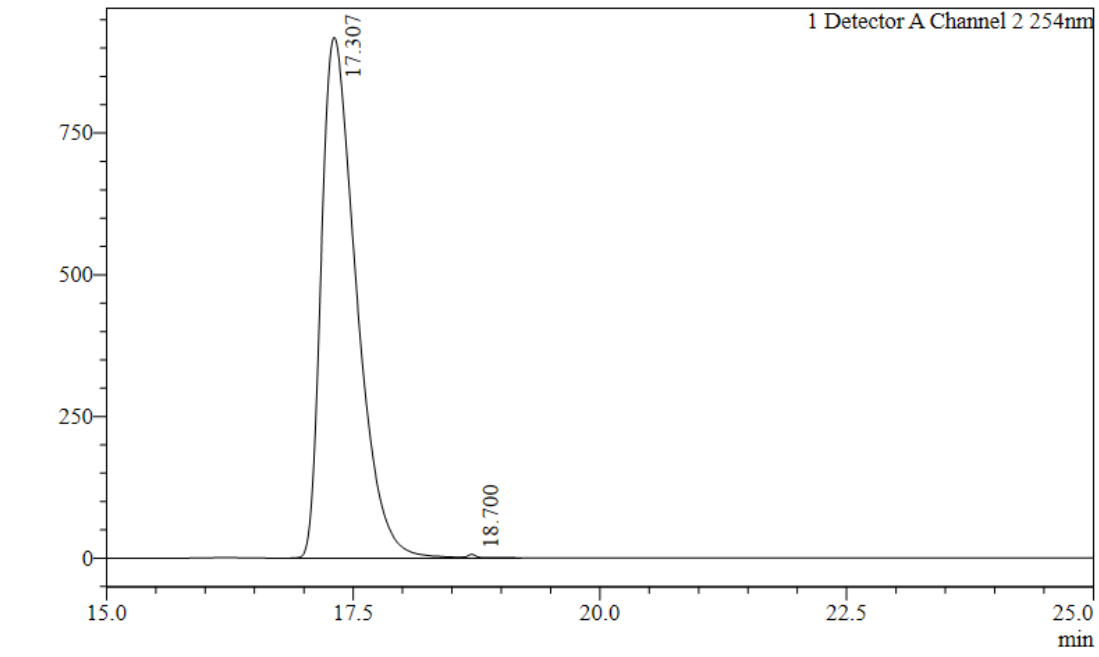


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.504	11833903	518072	51.298	51.298
2	18.670	11235135	1150511	48.702	48.702
Total		23069038	1668583		100.000

Chromatogram

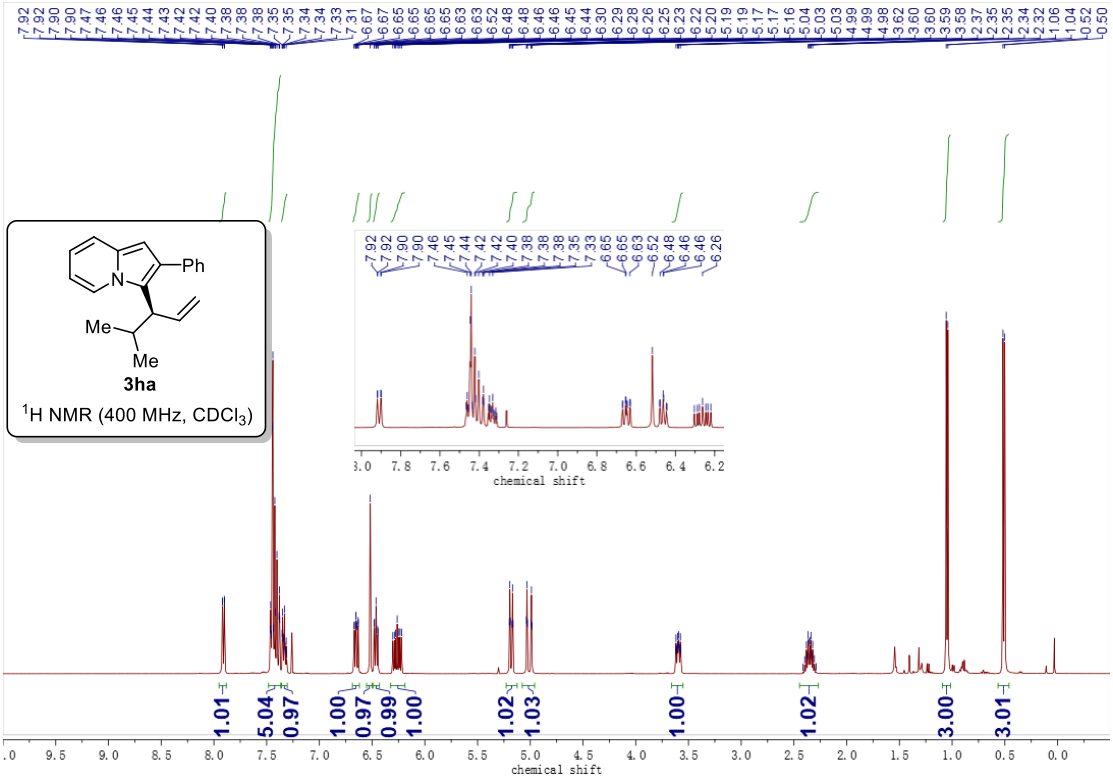


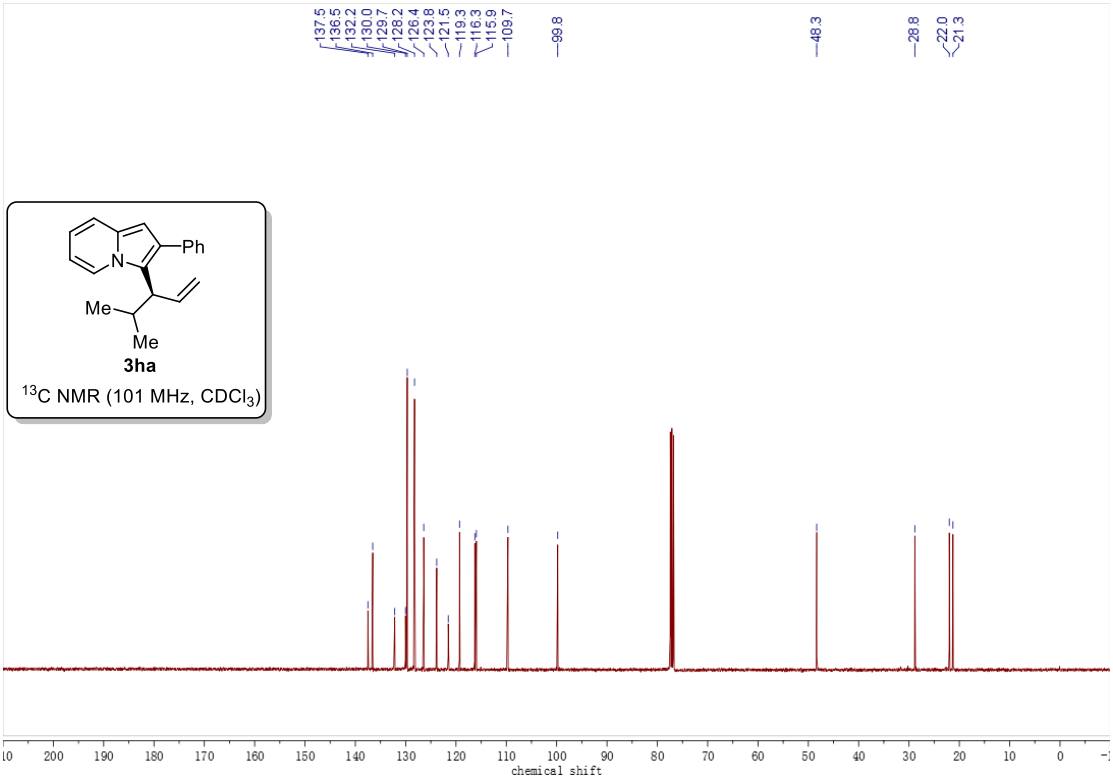
Peak Table

Detector A Channel 2 254nm

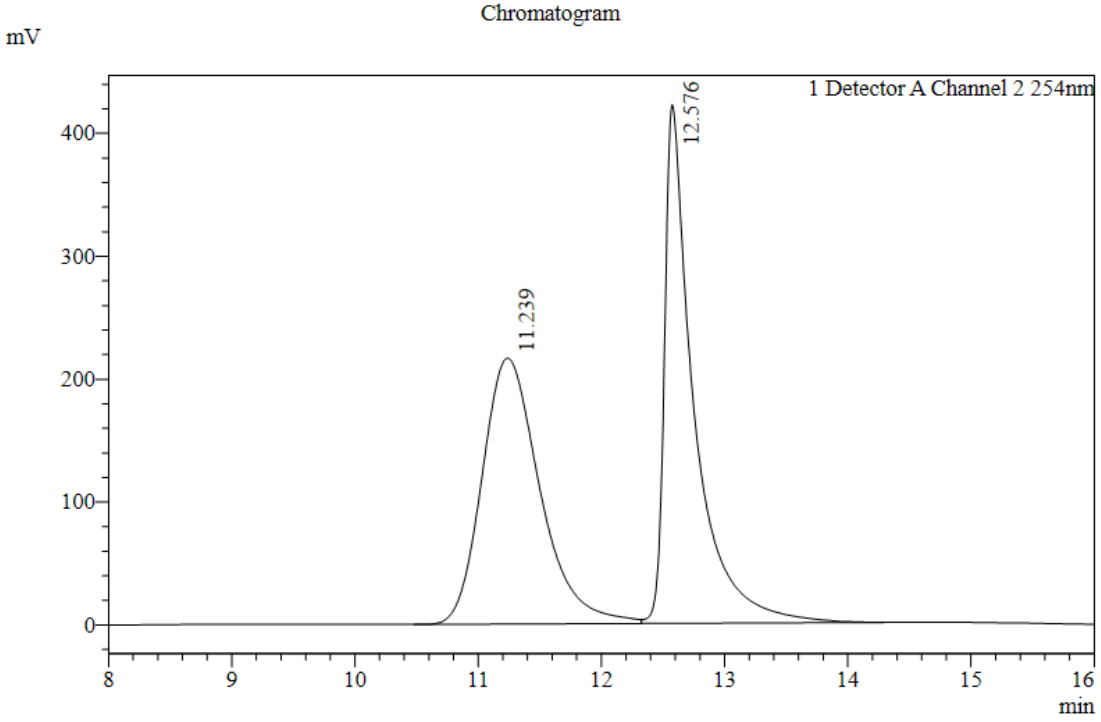
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	17.307	22658649	918919	99.777	99.777
2	18.700	50543	6920	0.223	0.223
Total		22709192	925839		100.000

(R)-3-(4-methylpent-1-en-3-yl)-2-phenylindolizine (**3ha**).





Chromatogram

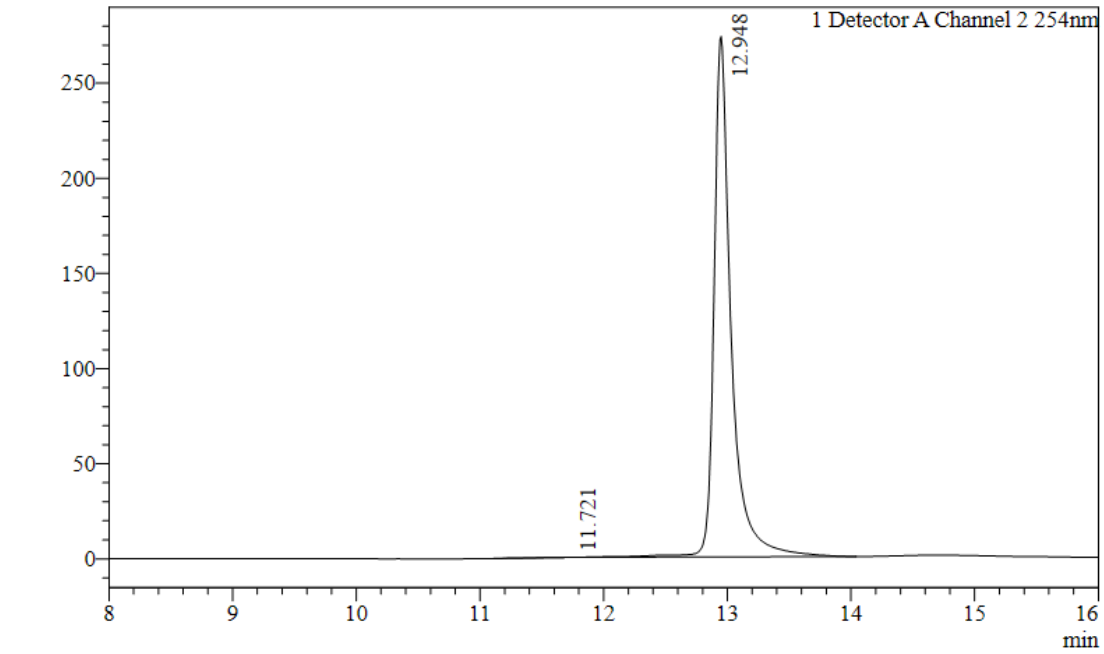


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.239	7080925	216513	50.274	50.274
2	12.576	7003703	422285	49.726	49.726
Total		14084628	638798		100.000

Chromatogram

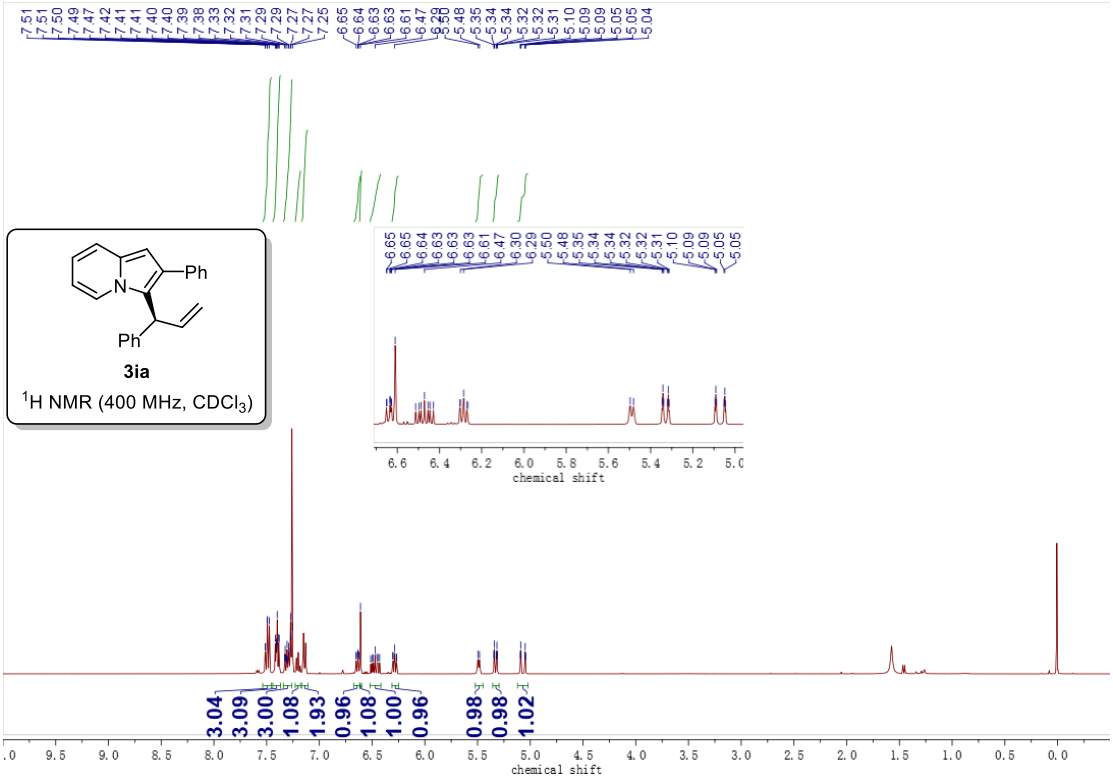


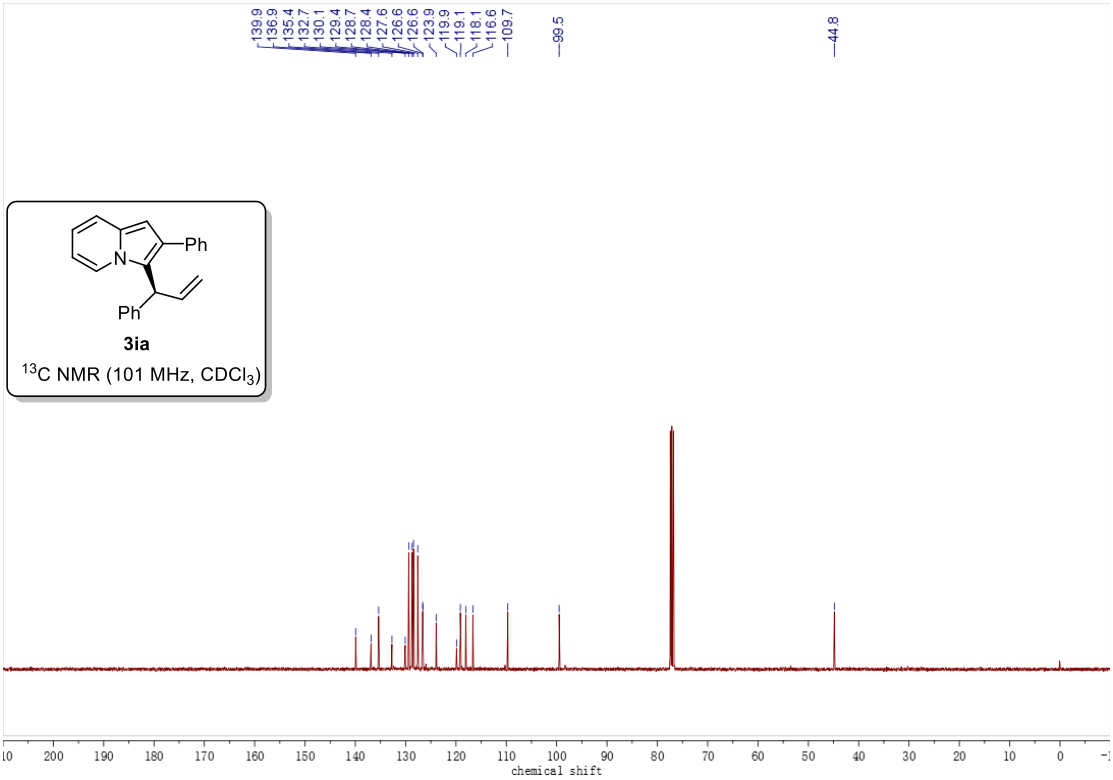
Peak Table

Detector A Channel 2 254nm

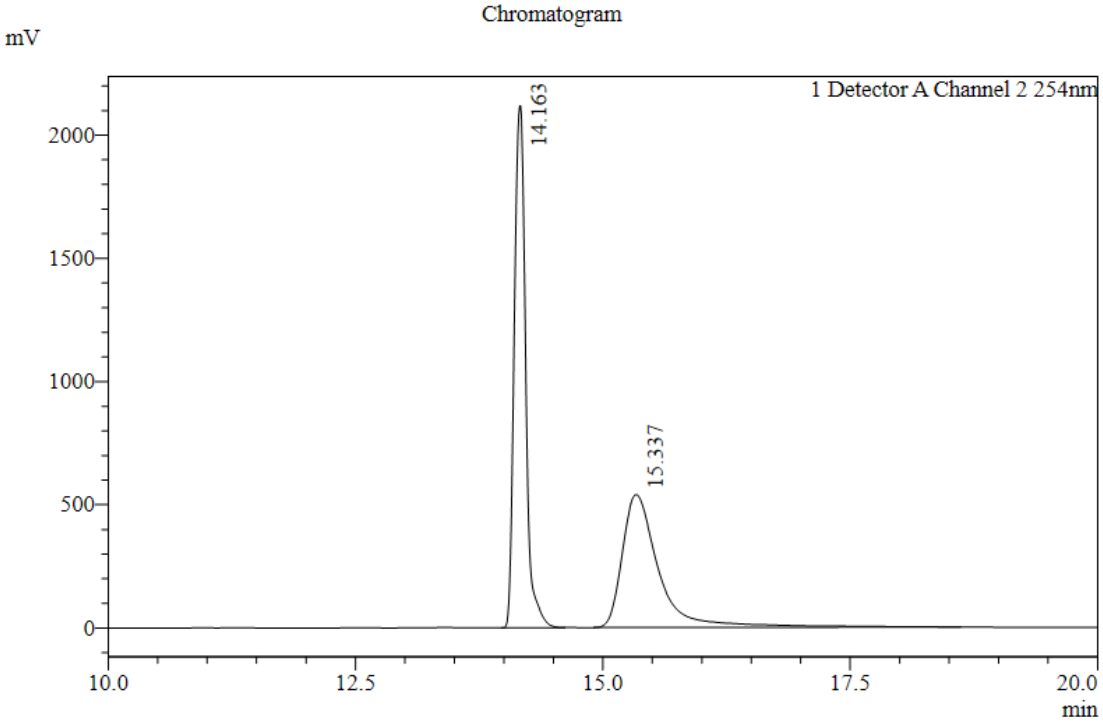
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.721	2347	-2	0.088	0.088
2	12.948	2656411	273626	99.912	99.912
Total		2658758	273624		100.000

(S)-2-phenyl-3-(1-phenylallyl)indolizine (**3ia**).





Chromatogram

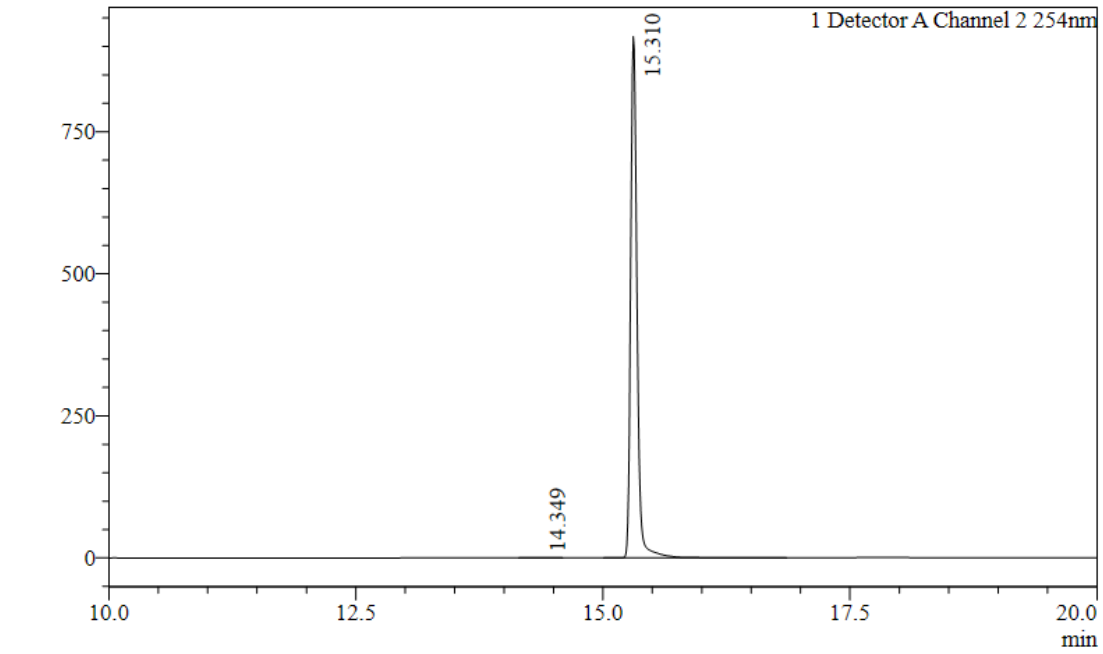


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	14.163	17014715	2117425	54.891	54.891
2	15.337	13982322	539804	45.109	45.109
Total		30997037	2657230		100.000

Chromatogram

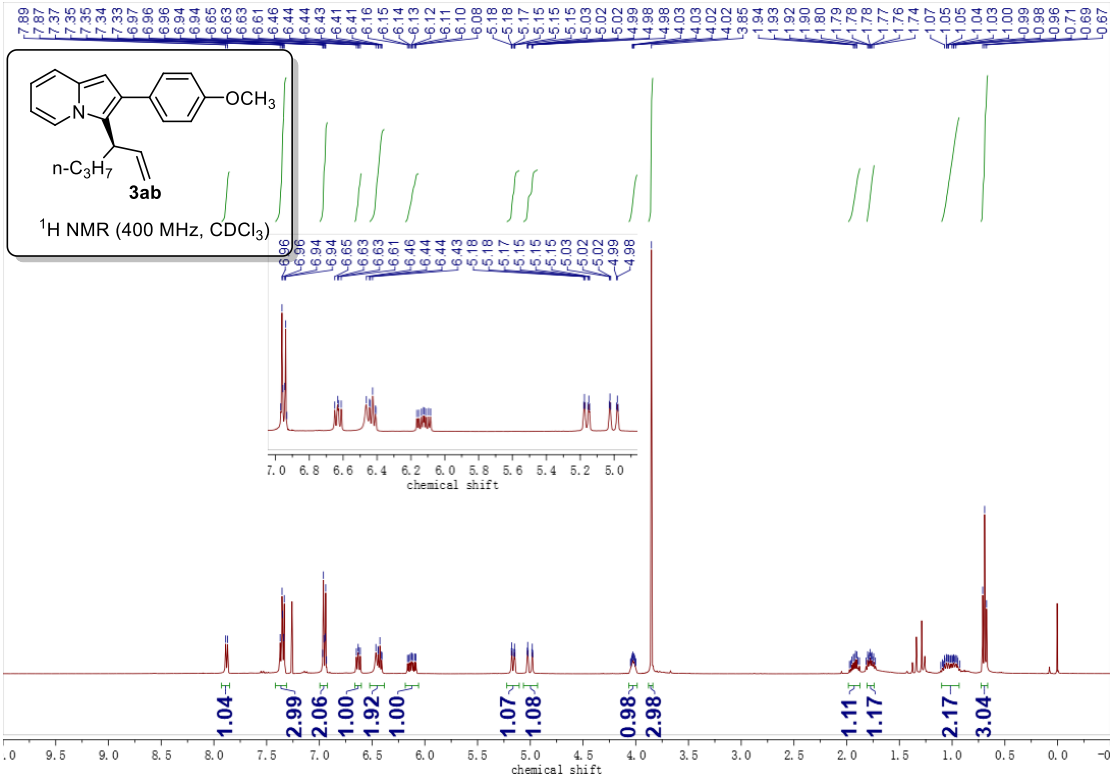


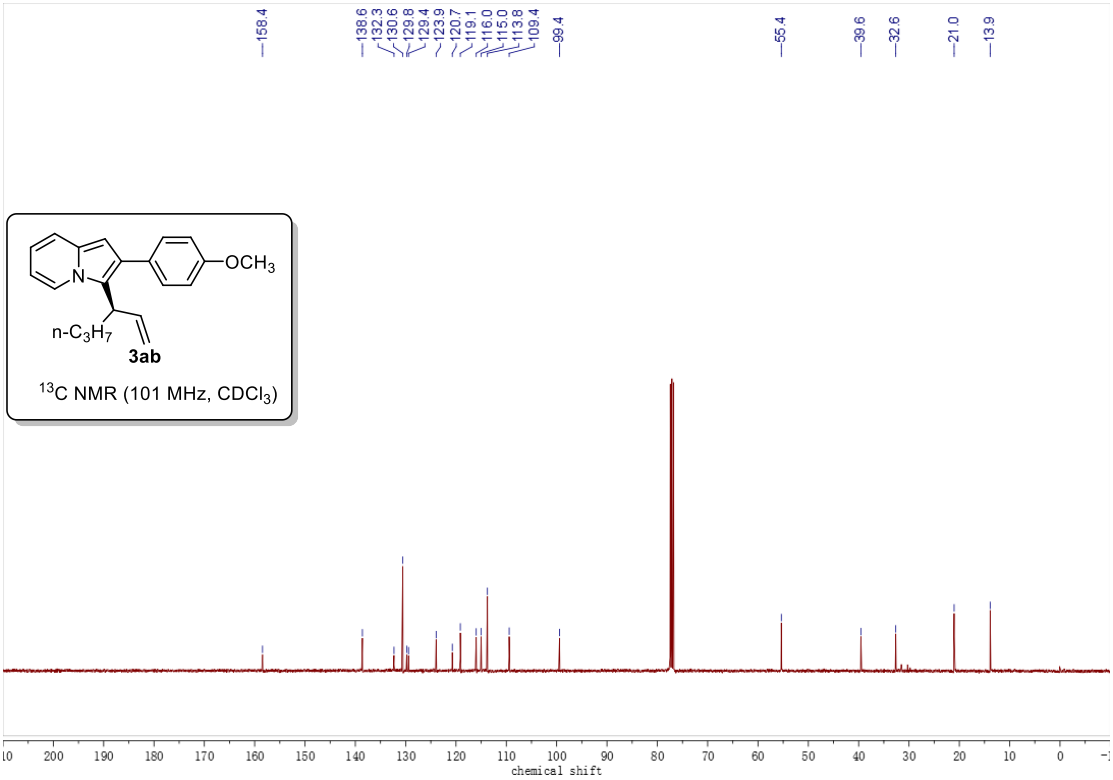
Peak Table

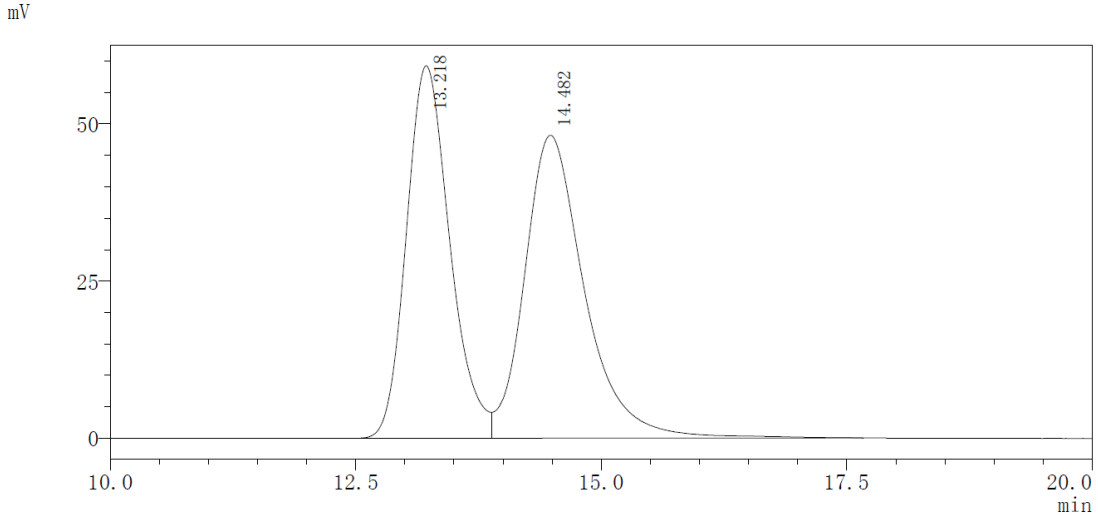
Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	14.349	1515	102	0.036	0.036
2	15.310	4150046	917487	99.964	99.964
Total		4151561	917589		100.000

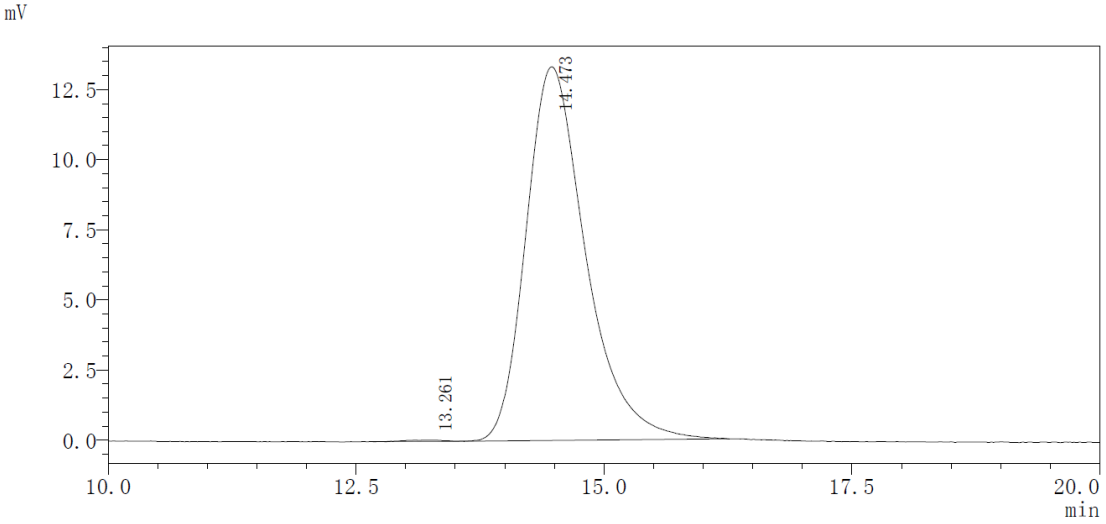
(R)-3-(hex-1-en-3-yl)-2-(4-methoxyphenyl)indolizine (**3ab**).





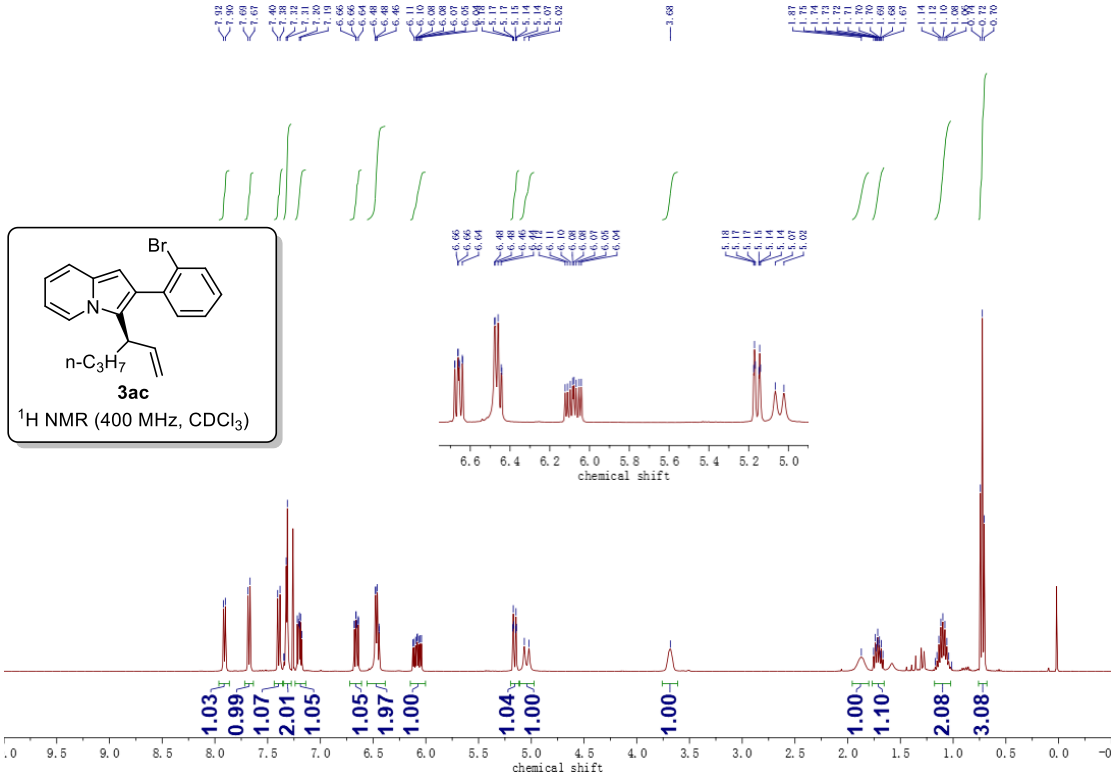


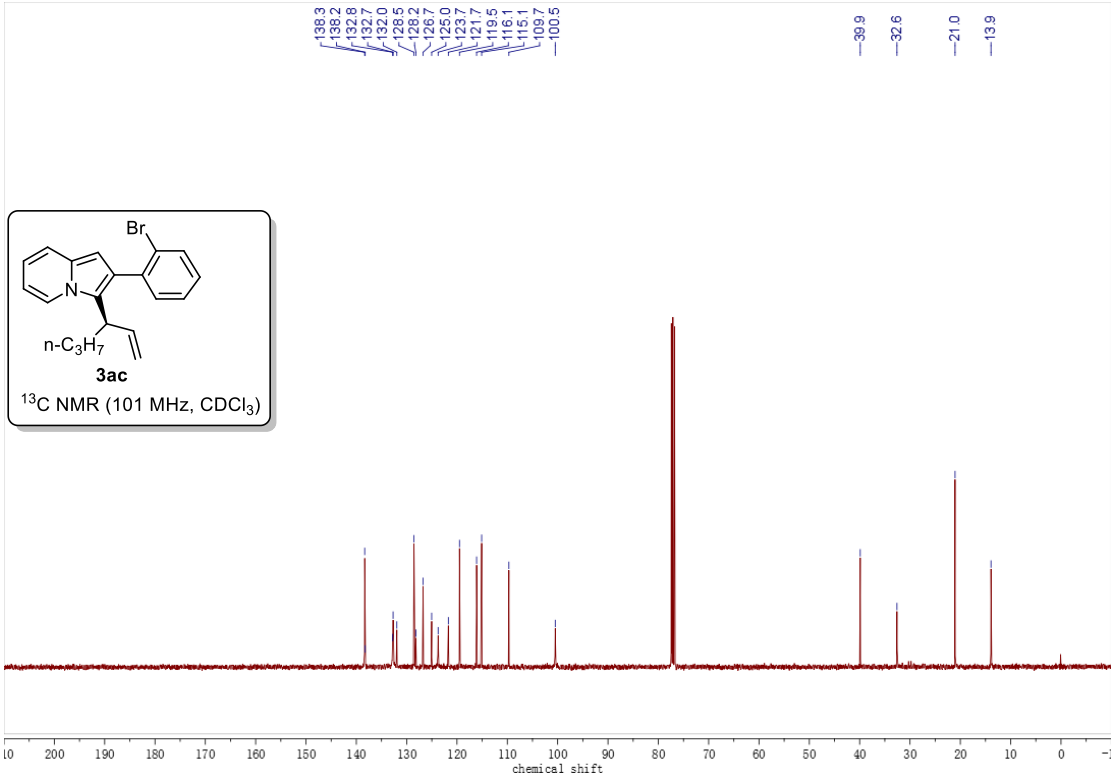
Peak NO.	Retention Time	Height	Height%	Area	Area%
1	13.218	59282	55.145	1829570	47.157
2	14.482	48220	44.855	2050213	52.843
总计		107502	100.000	3879783	100.000



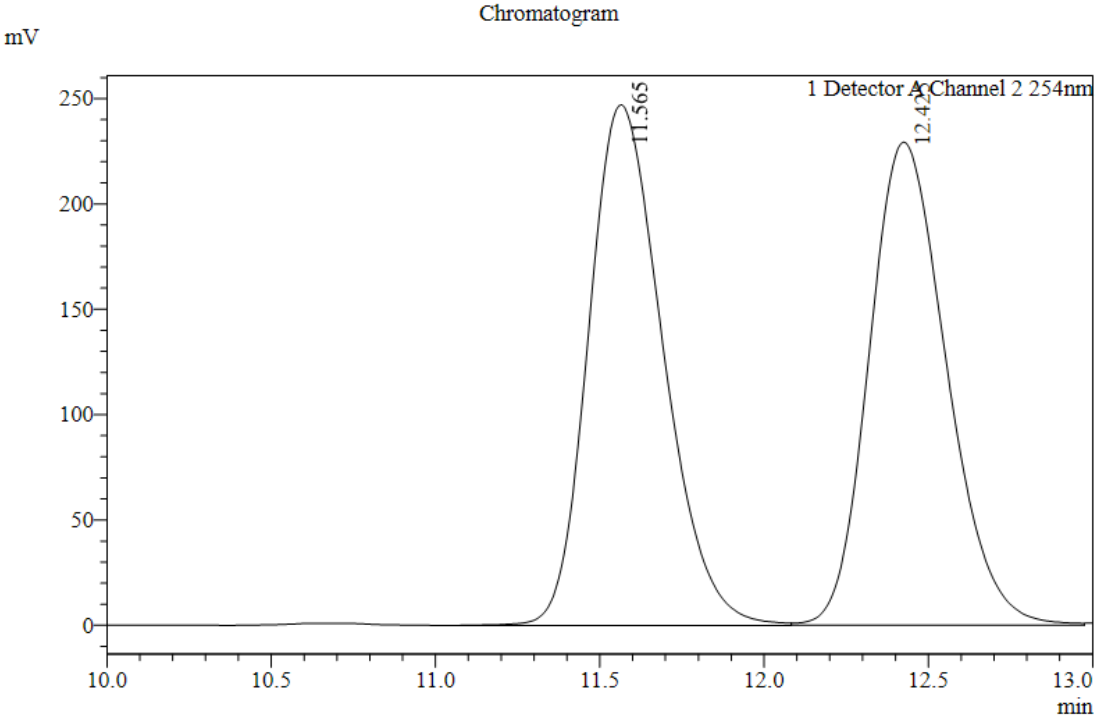
Peak NO.	Retention Time	Height	Height%	Area	Area%
1	13.261	51	0.385	1320	0.235
2	14.473	13329	99.615	559088	99.765
总计		13380	100.000	560408	100.000

(R)-2-(2-bromophenyl)-3-(hex-1-en-3-yl)indolizine (**3ac**).





Chromatogram

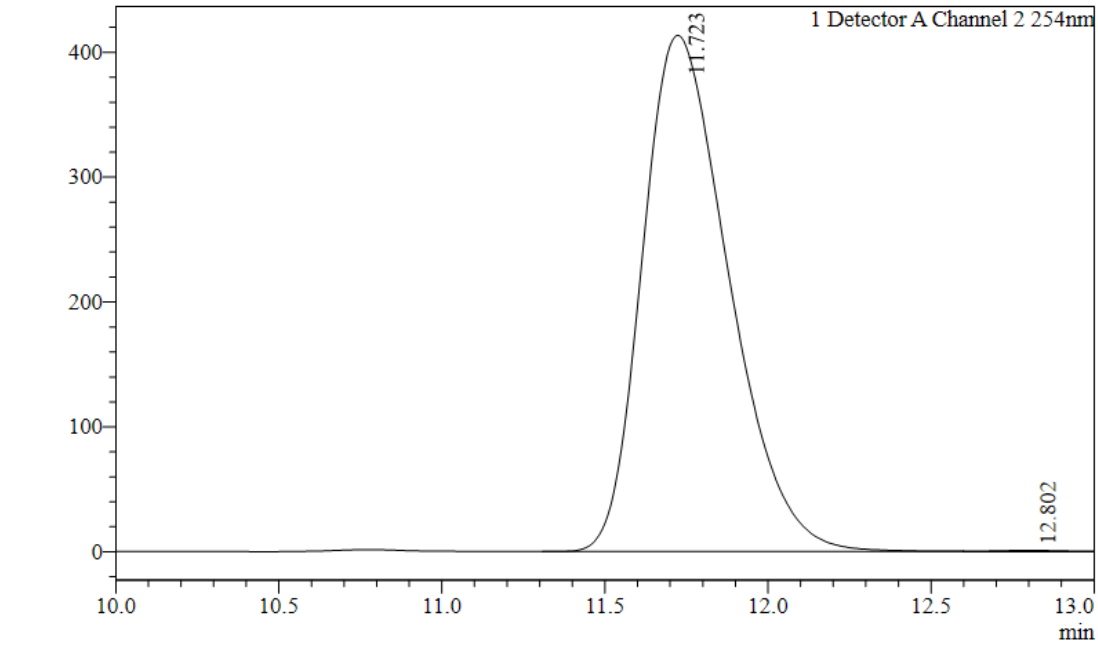


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.565	3892965	247093	50.882	50.882
2	12.425	3758077	229354	49.118	49.118
Total		7651041	476447		100.000

Chromatogram

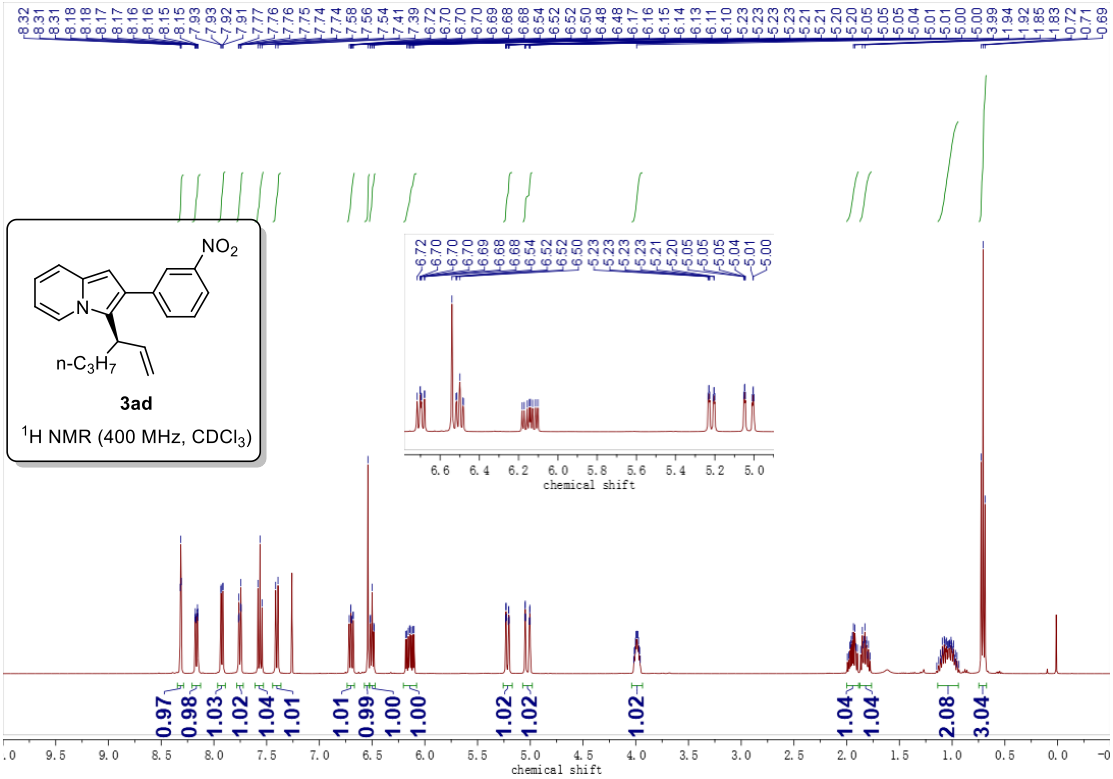


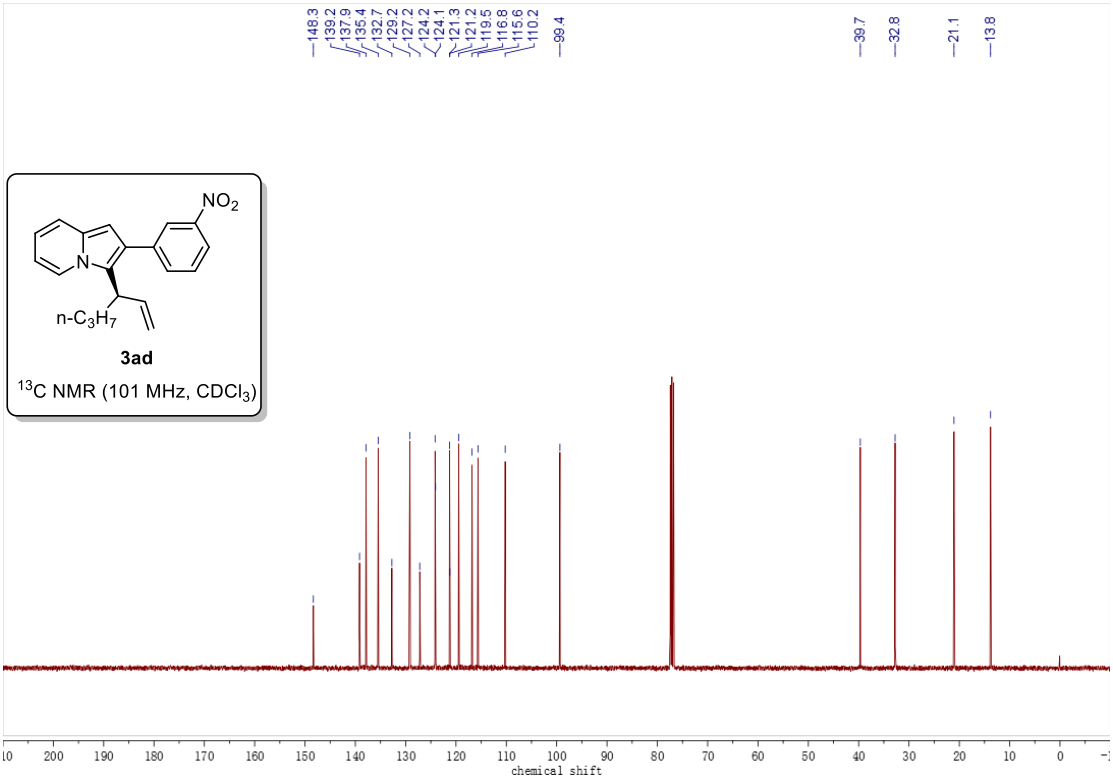
Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	11.723	7632555	413466	99.751	99.751
2	12.802	19072	1001	0.249	0.249
Total		7651627	414467		100.000

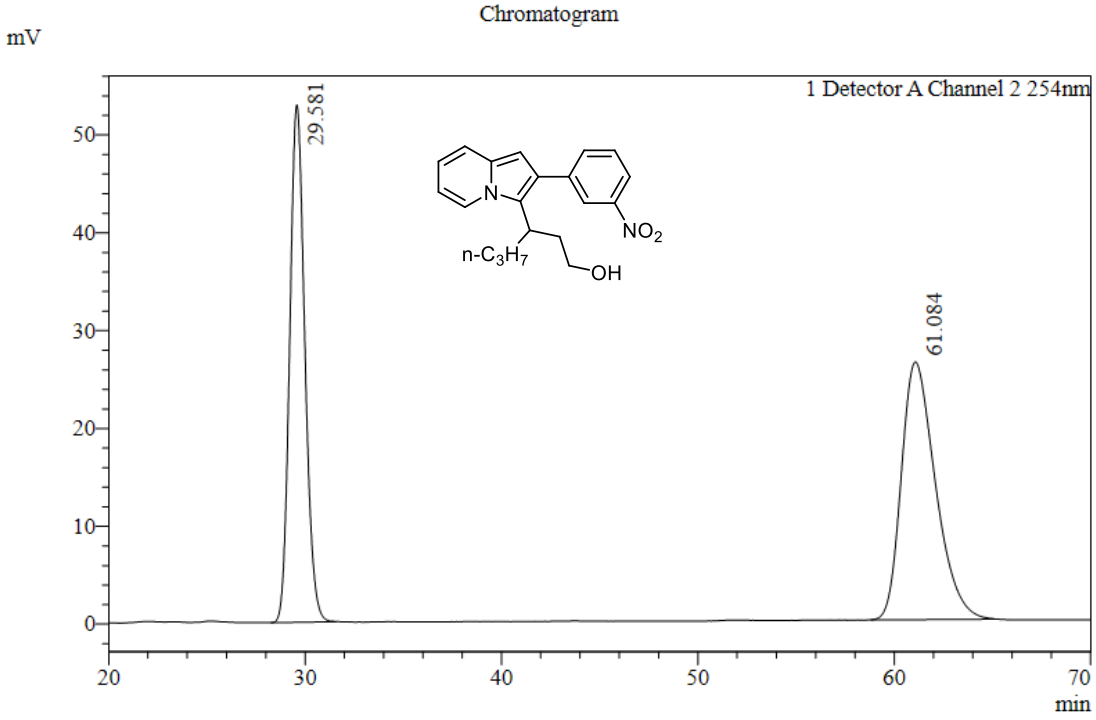
(R)-3-(hex-1-en-3-yl)-2-(3-nitrophenyl)indolizine (**3ad**).





The *ee* value was determined after the hydroboration/oxidation sequence.

Chromatogram

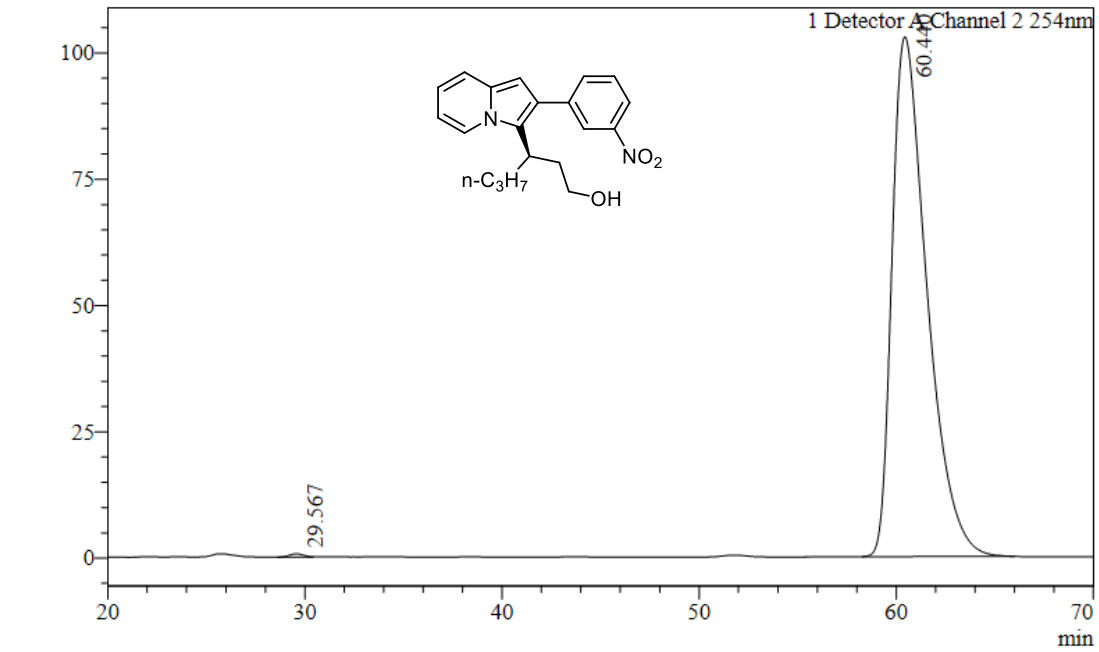


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	29.581	2830059	52884	47.100	47.100
2	61.084	3178514	26322	52.900	52.900
Total		6008574	79206		100.000

Chromatogram

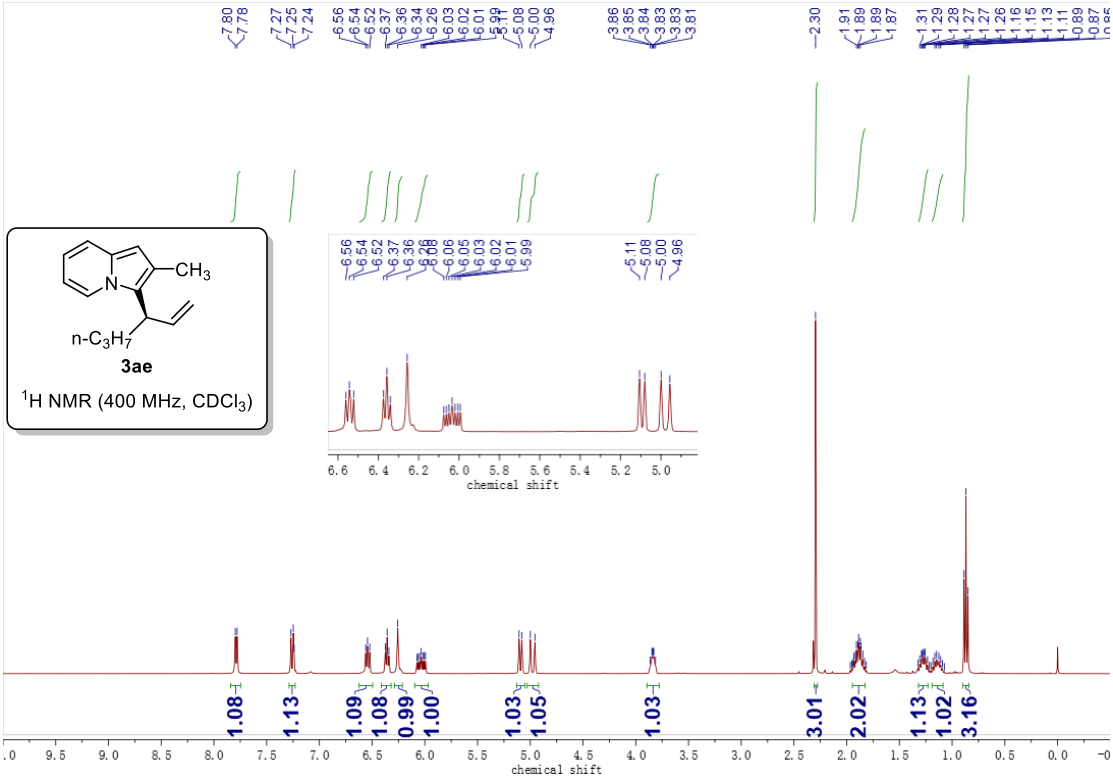


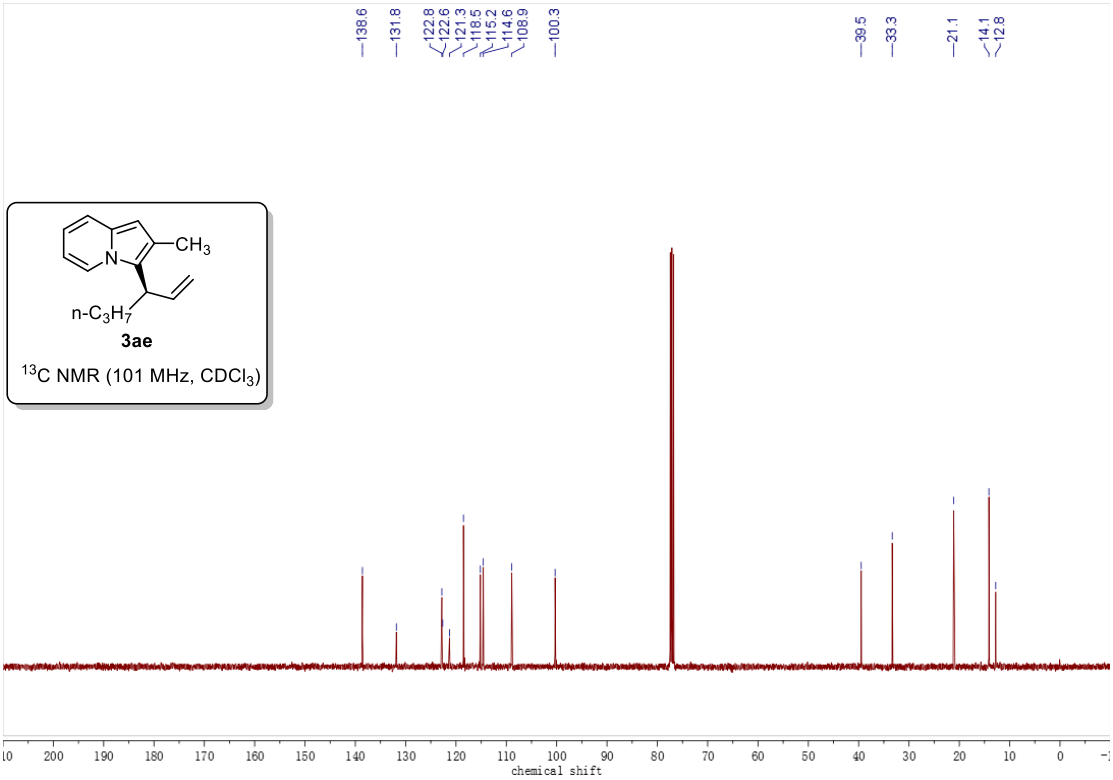
Peak Table

Detector A Channel 2 254nm

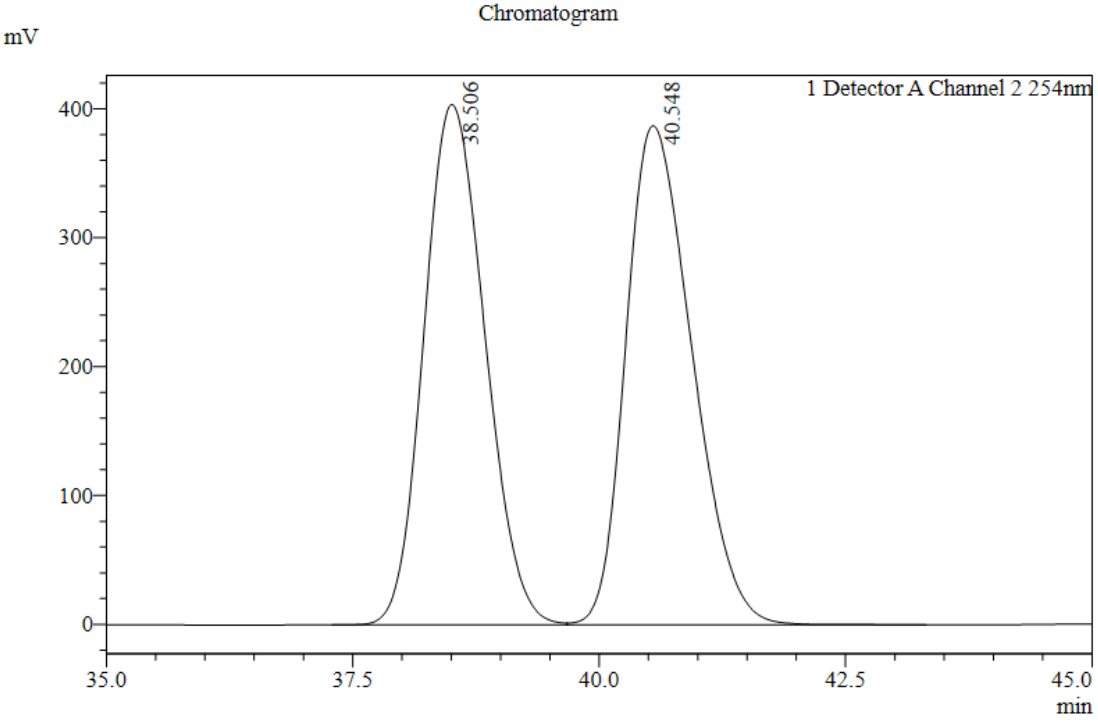
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	29.567	32678	648	0.257	0.257
2	60.440	12675949	102855	99.743	99.743
Total		12708627	103503		100.000

(R)-3-(hex-1-en-3-yl)-2-methylindolizine (**3ae**).





Chromatogram

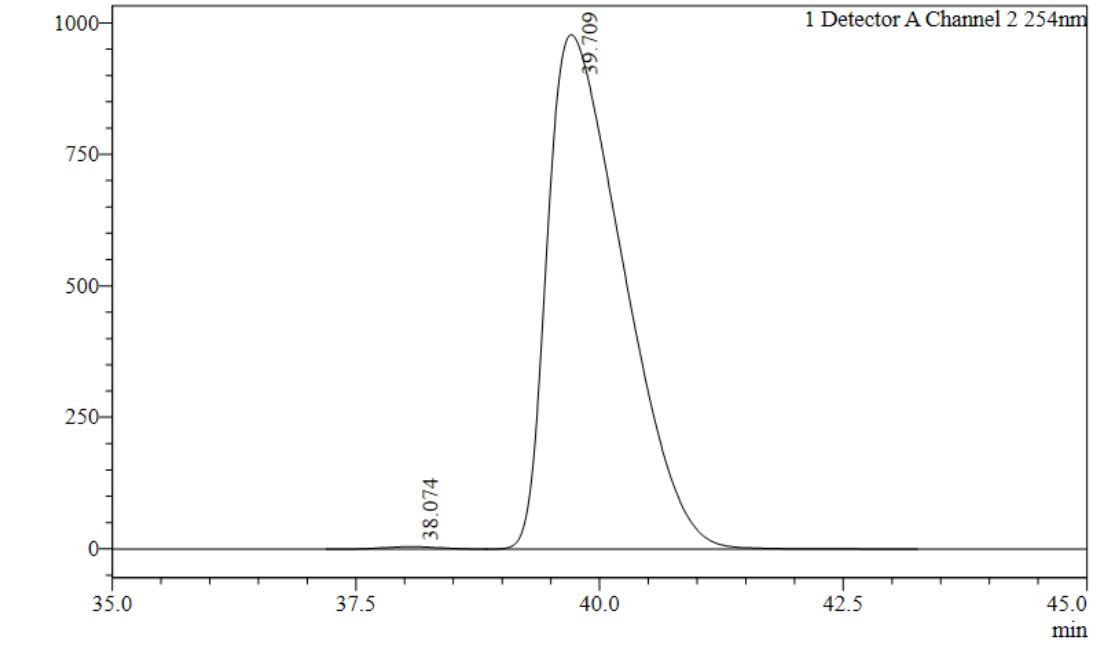


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	38.506	17394612	403843	49.049	49.049
2	40.548	18069283	387251	50.951	50.951
Total		35463895	791094		100.000

Chromatogram

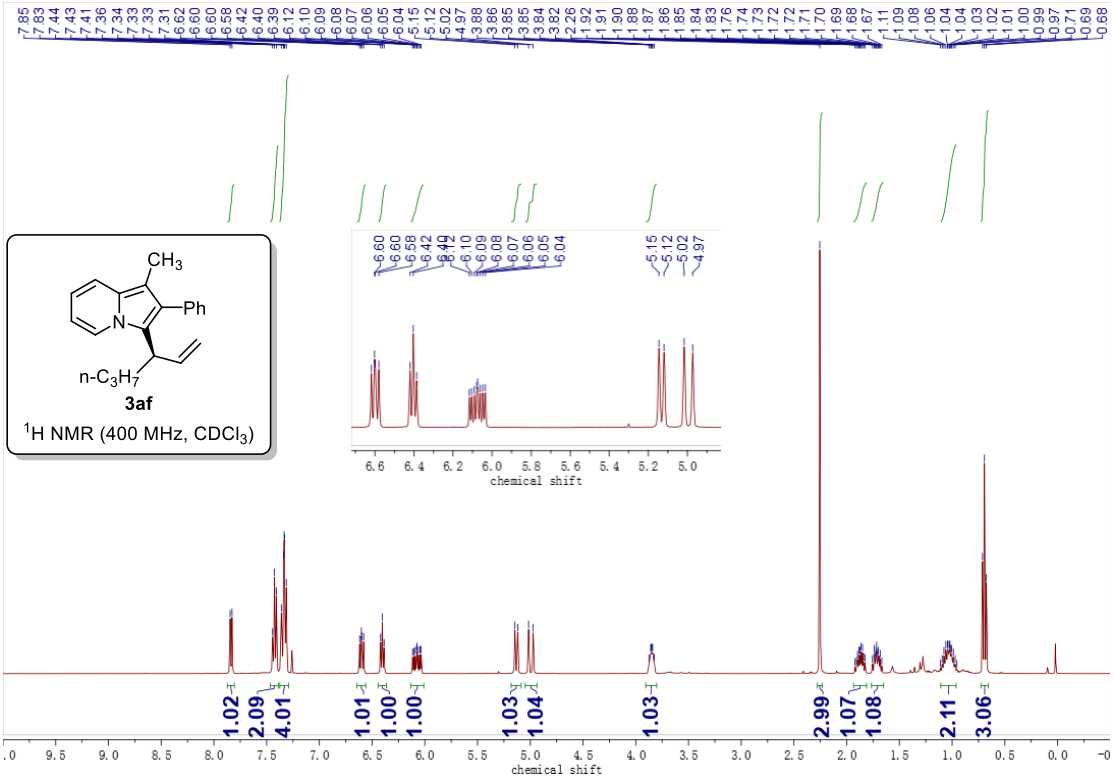


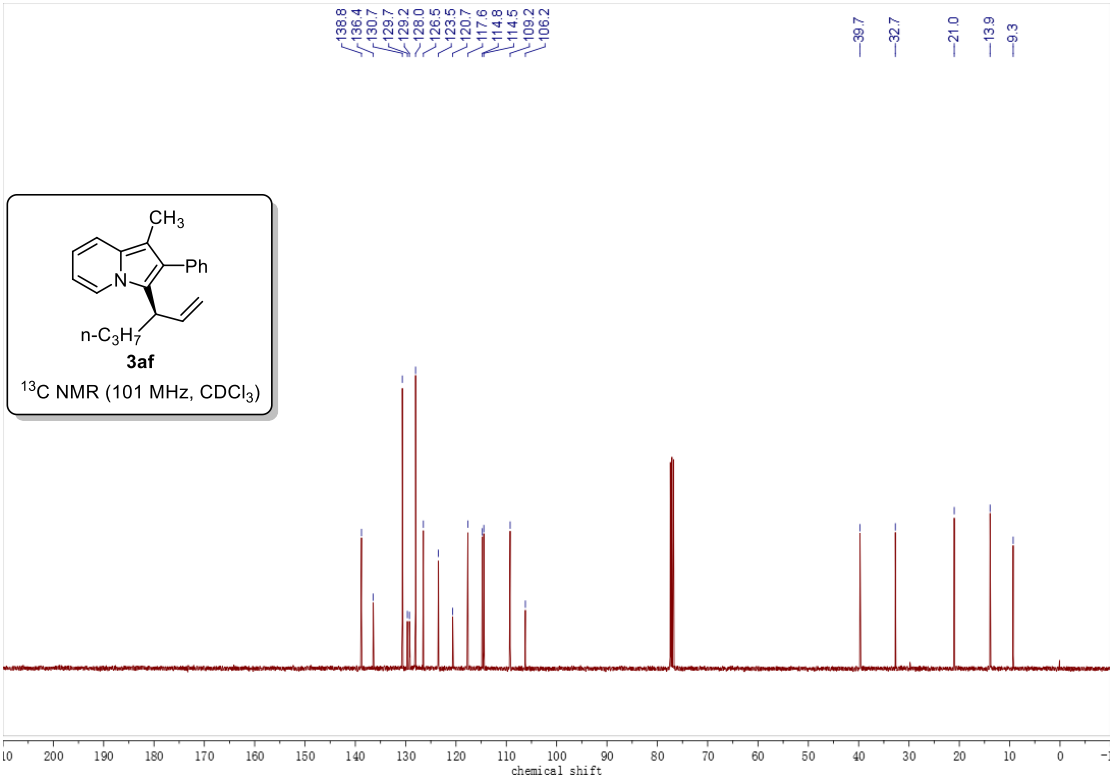
Peak Table

Detector A Channel 2 254nm

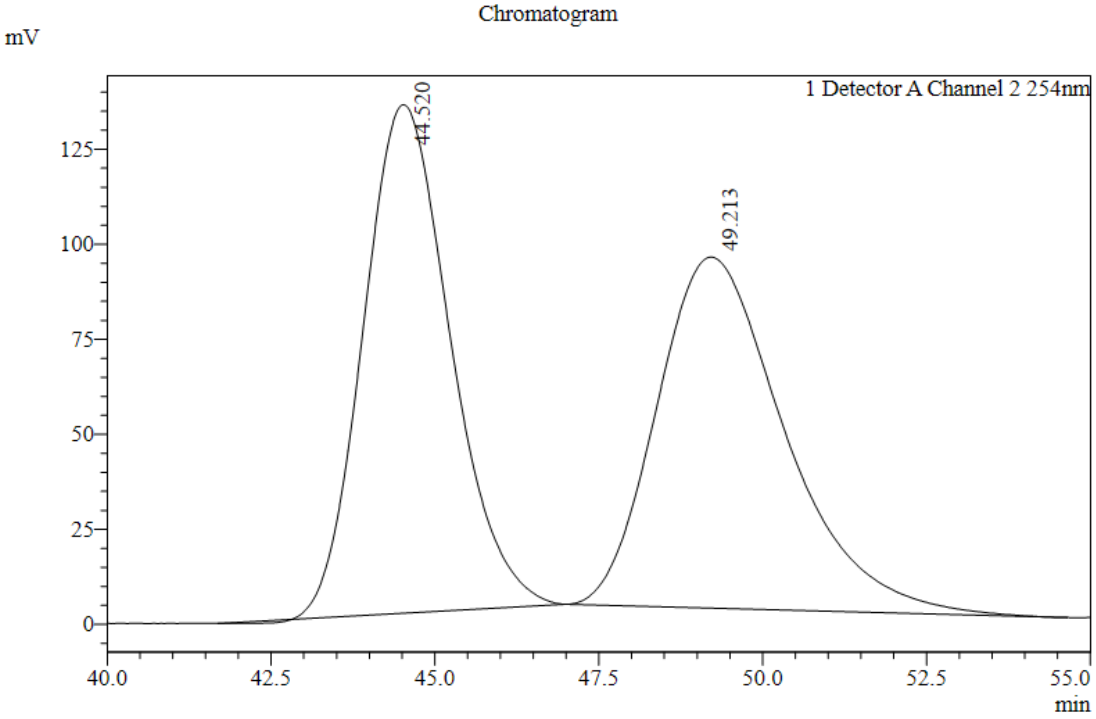
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	38.074	183792	4559	0.346	0.346
2	39.709	52897015	977984	99.654	99.654
Total		53080807	982542		100.000

(R)-3-(hex-1-en-3-yl)-1-methyl-2-phenylindolizine (**3af**).





Chromatogram

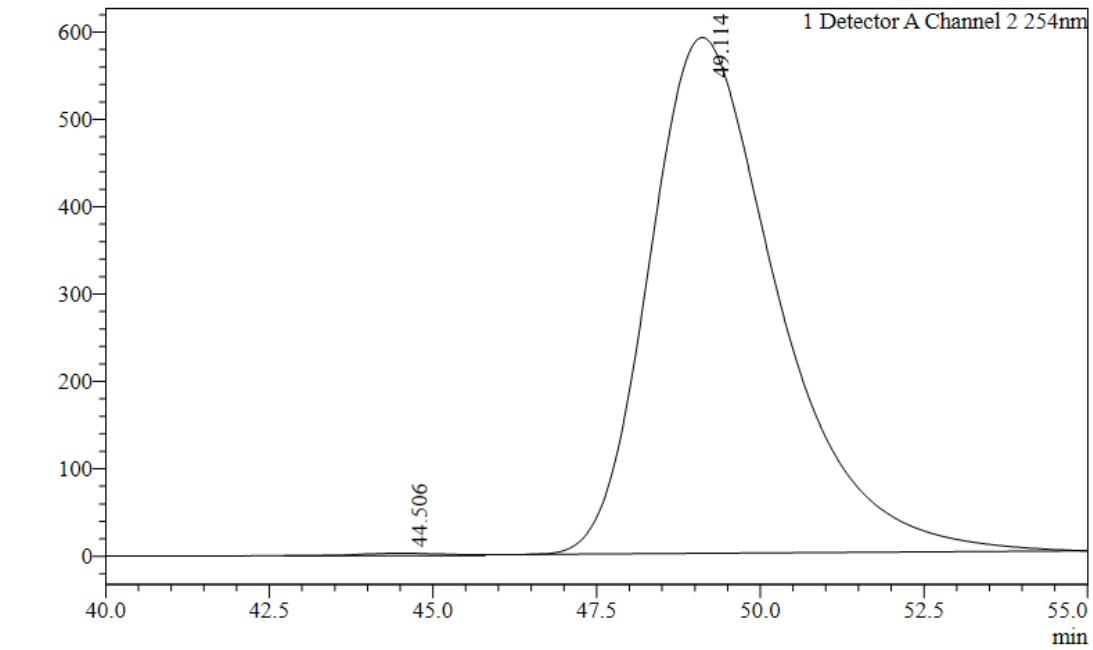


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	44.520	12346386	133761	49.650	49.650
2	49.213	12520352	92361	50.350	50.350
Total		24866738	226122		100.000

Chromatogram

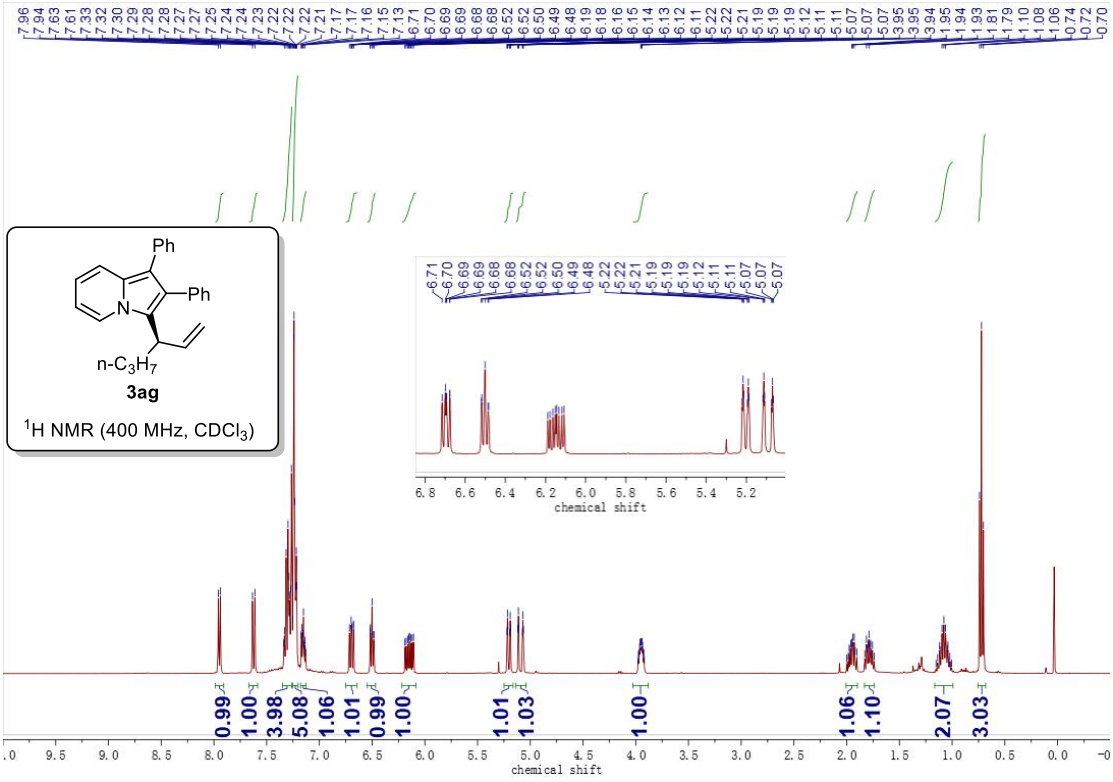


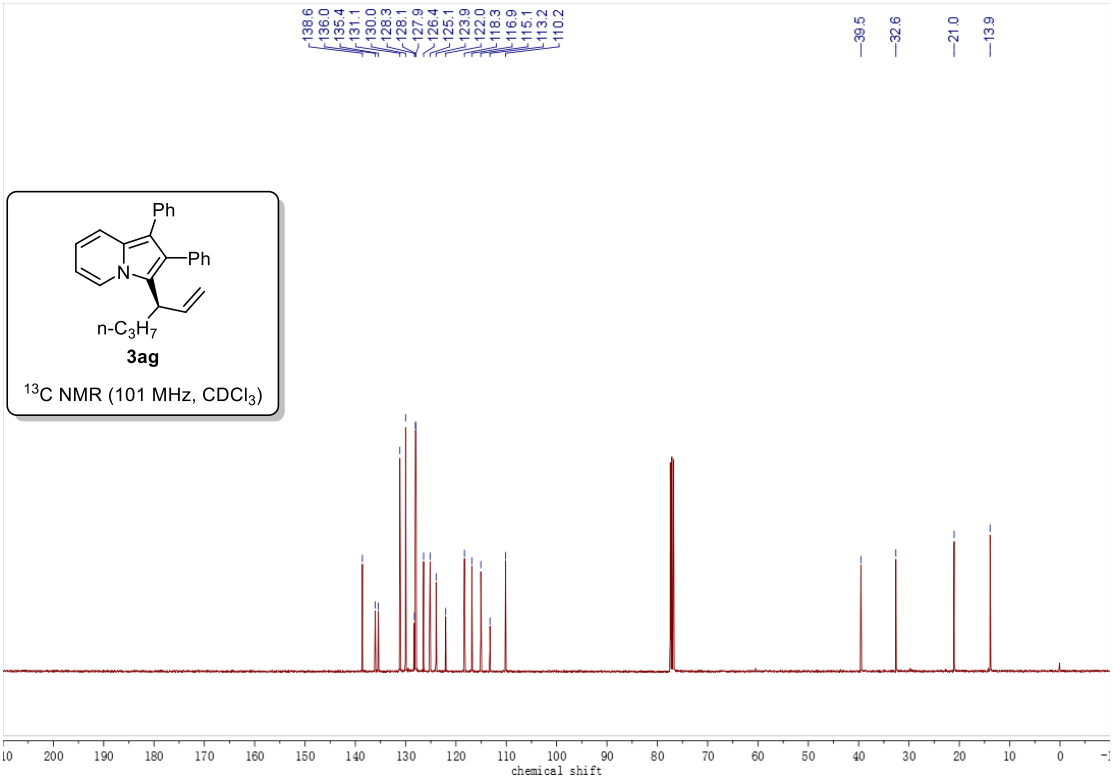
Peak Table

Detector A Channel 2 254nm

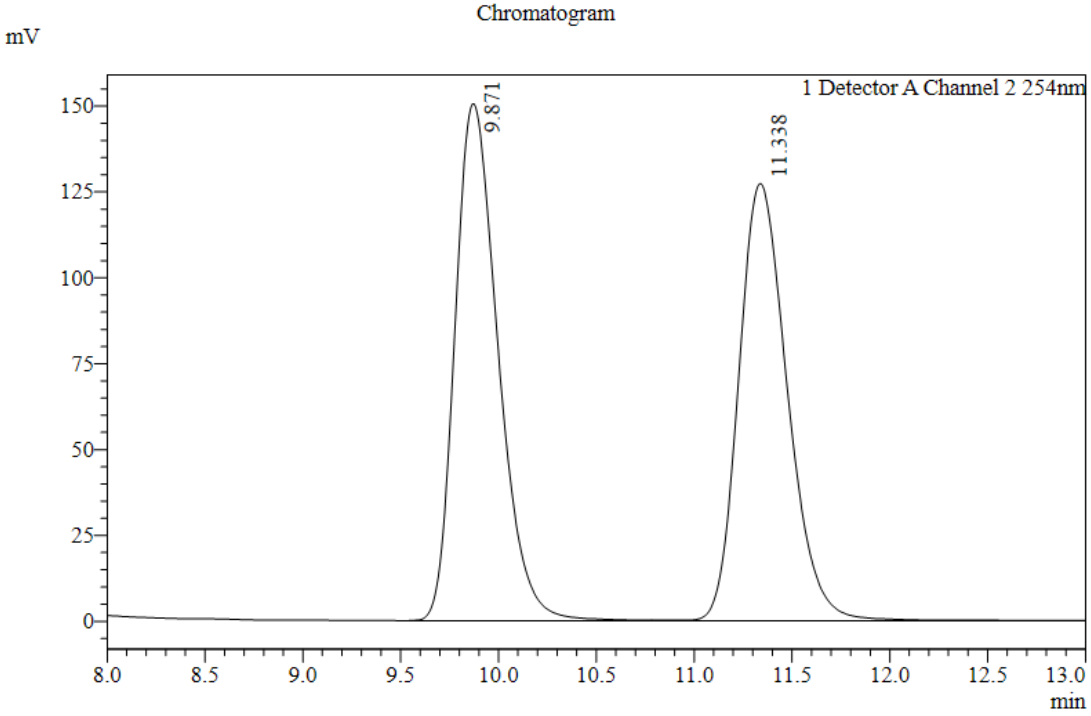
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	44.506	281408	3022	0.346	0.346
2	49.114	81030640	590752	99.654	99.654
Total		81312048	593774		100.000

(R)-3-(hex-1-en-3-yl)-1,2-diphenylindolizine (**3ag**).





Chromatogram

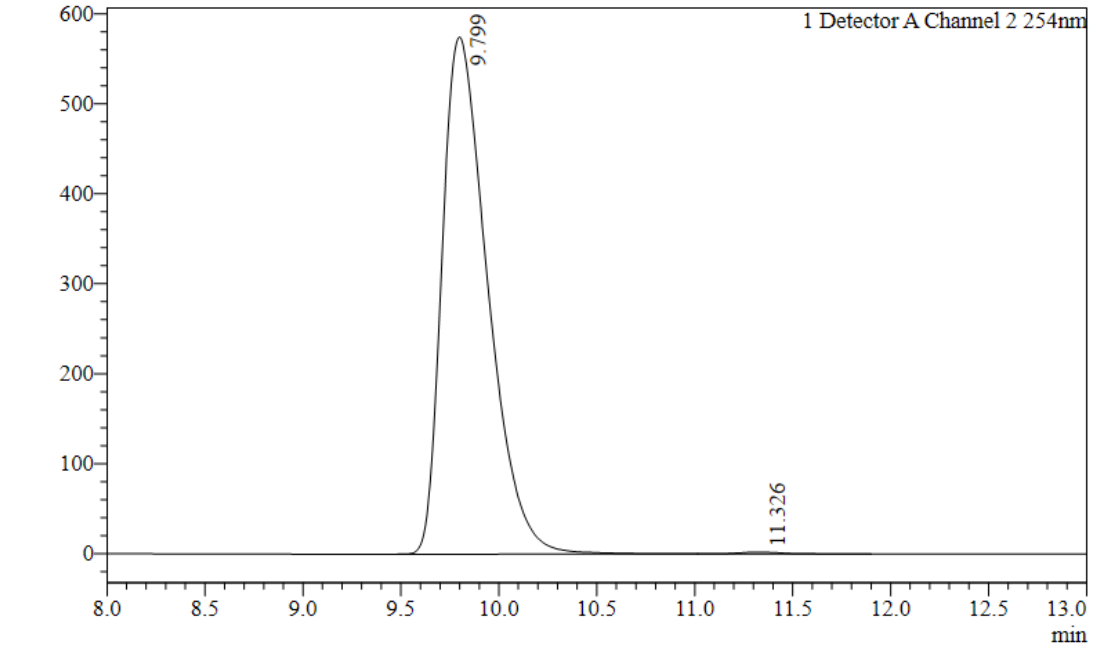


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.871	2306686	150483	51.190	51.190
2	11.338	2199427	127206	48.810	48.810
Total		4506113	277689		100.000

Chromatogram

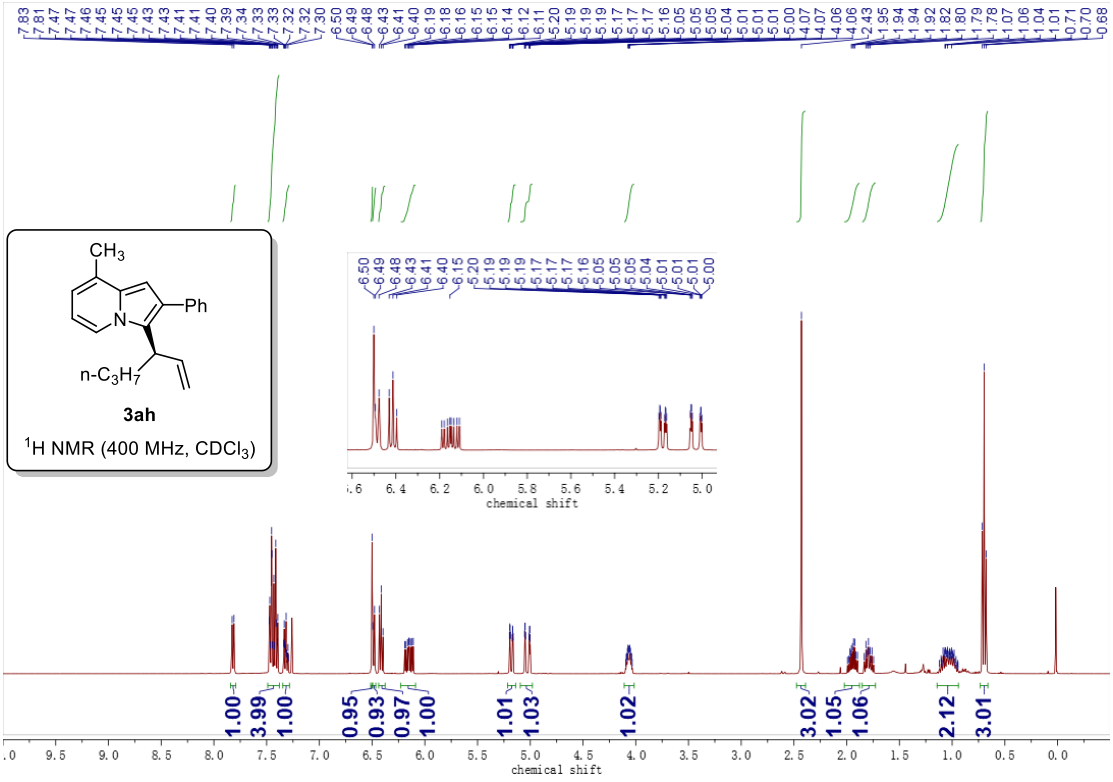


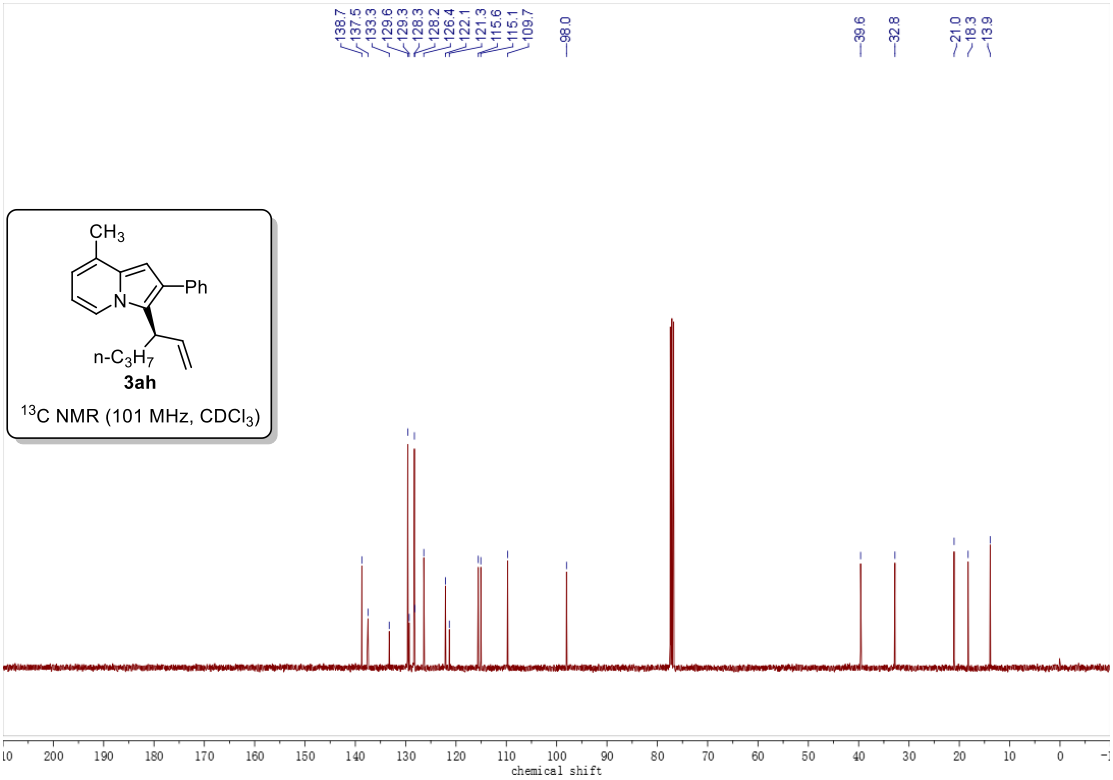
Peak Table

Detector A Channel 2 254nm

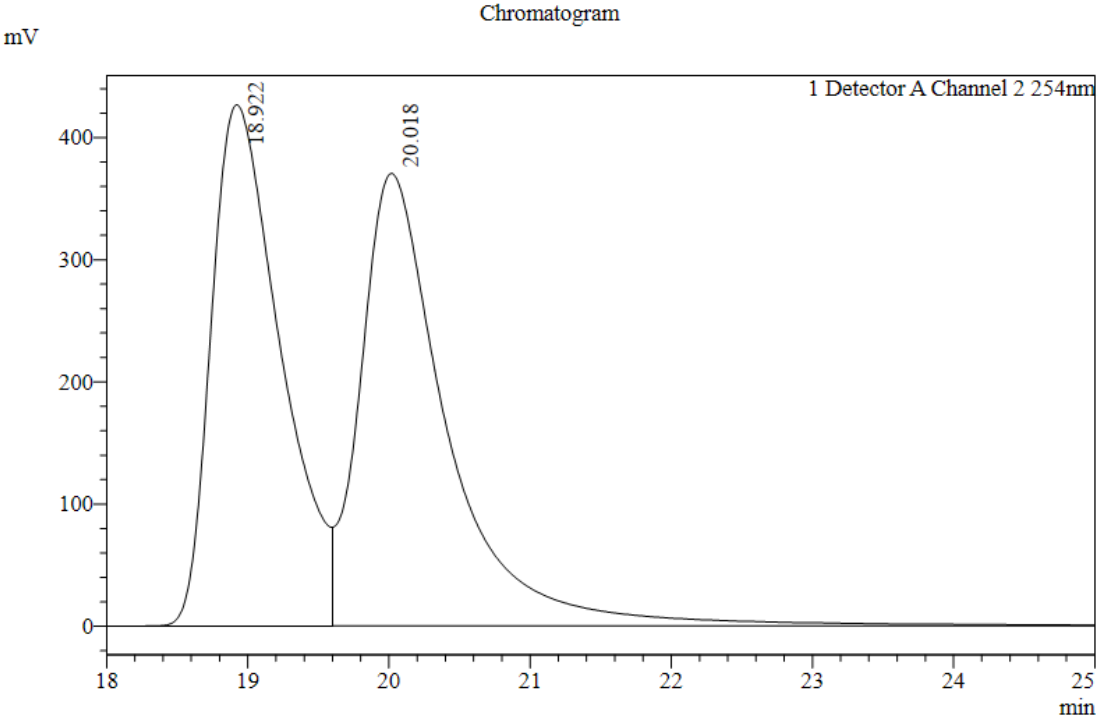
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	9.799	9294982	574968	99.689	99.689
2	11.326	28972	1810	0.311	0.311
Total		9323954	576778		100.000

(R)-3-(hex-1-en-3-yl)-8-methyl-2-phenylindolizine (**3ah**).





Chromatogram

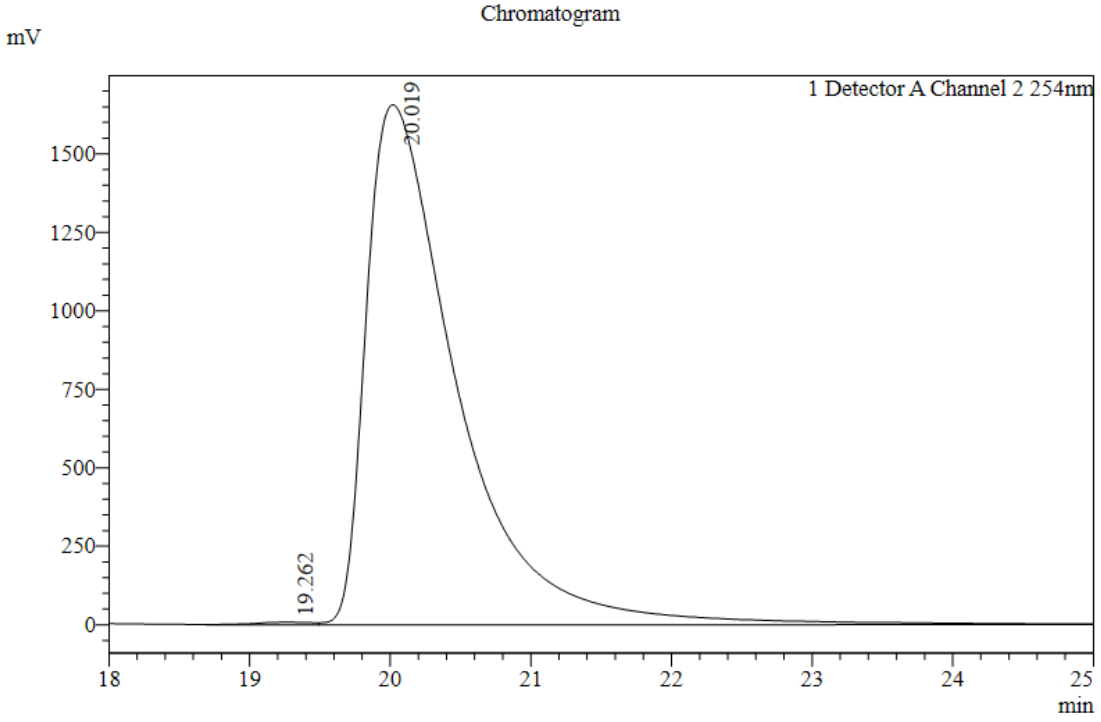


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	18.922	14598161	426704	47.670	47.670
2	20.018	16025148	370478	52.330	52.330
Total		30623309	797182		100.000

Chromatogram

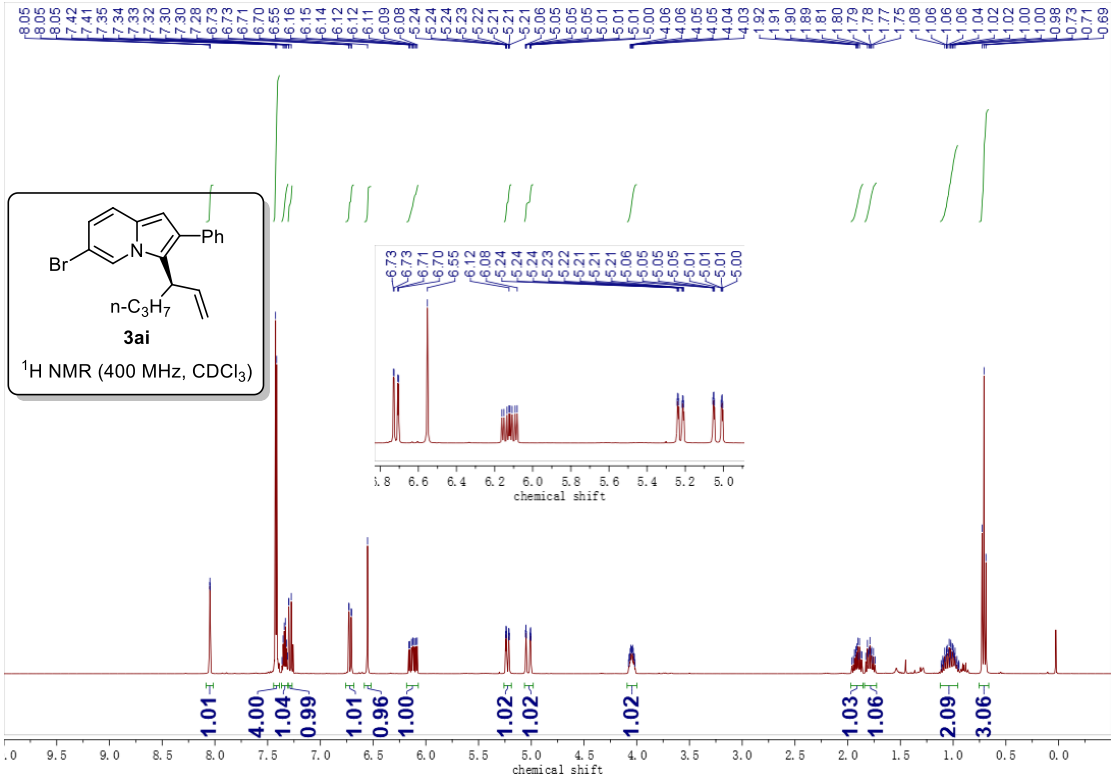


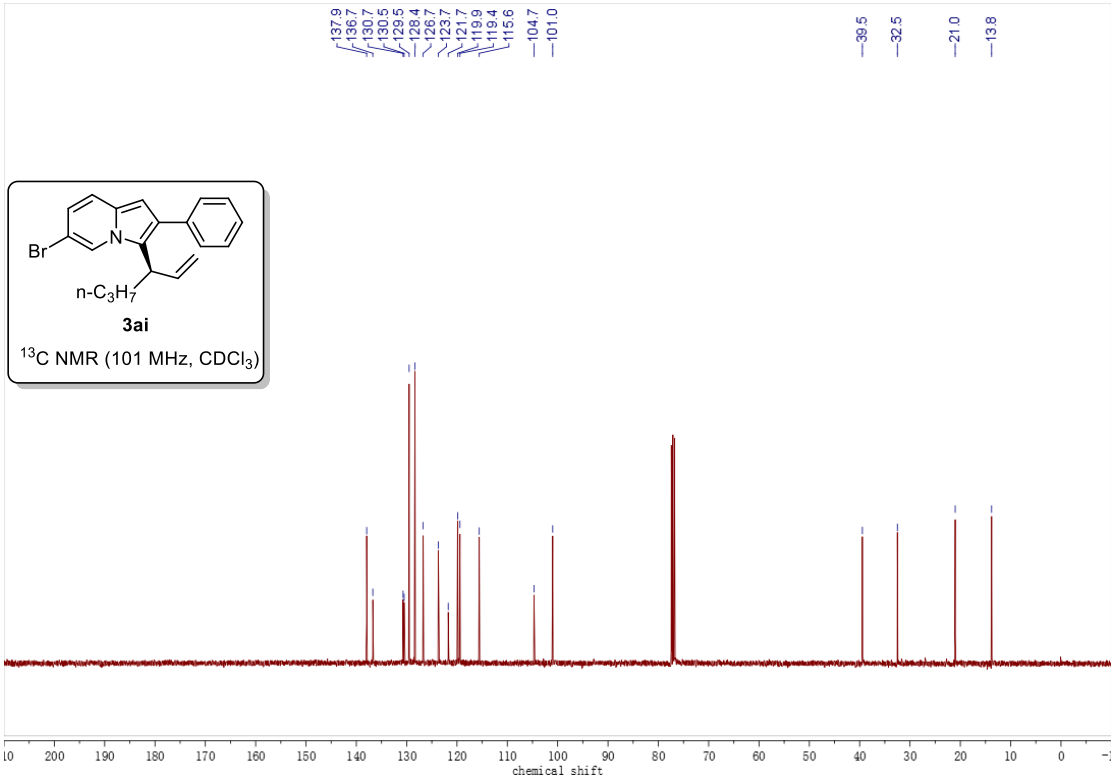
Peak Table

Detector A Channel 2 254nm

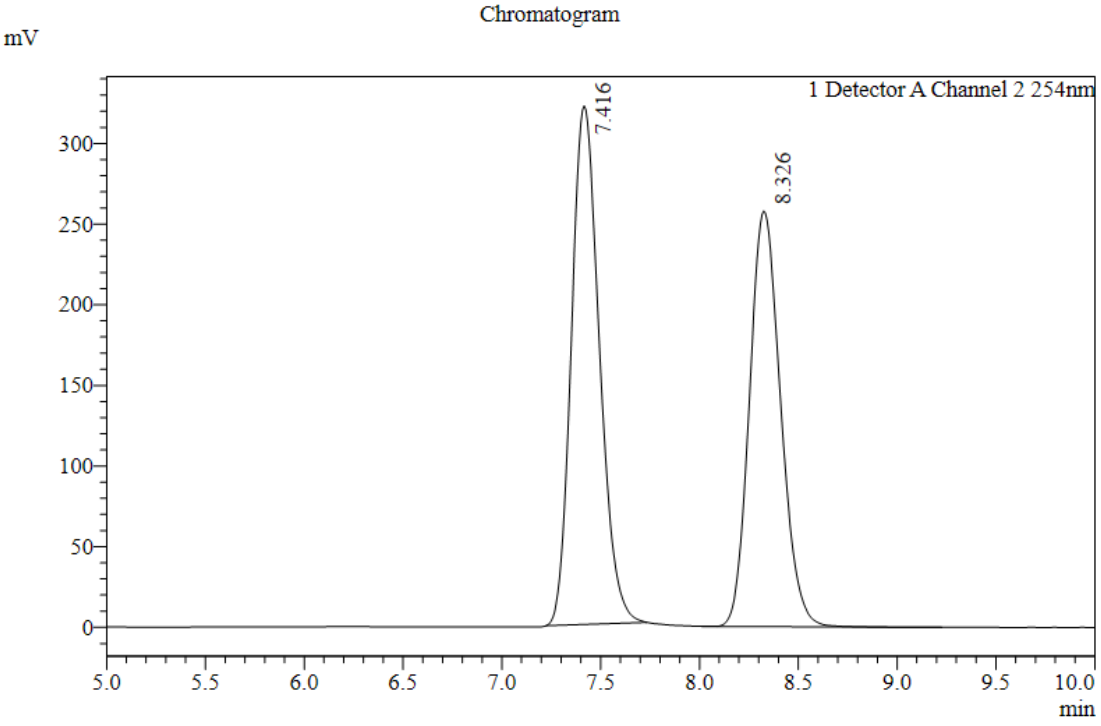
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	19.262	229582	8257	0.305	0.305
2	20.019	75051013	1656558	99.695	99.695
Total		75280596	1664815		100.000

(R)-6-bromo-3-(hex-1-en-3-yl)-2-phenylindolizine (**3ai**).





Chromatogram

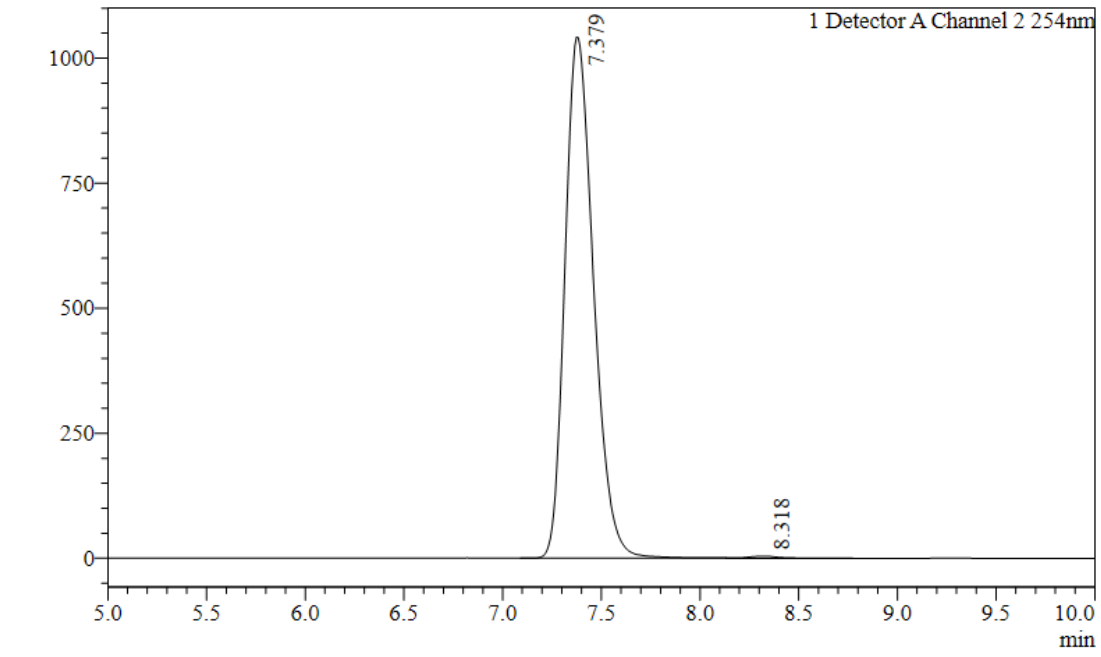


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.416	3162900	321544	52.907	52.907
2	8.326	2815272	257775	47.093	47.093
Total		5978172	579319		100.000

Chromatogram

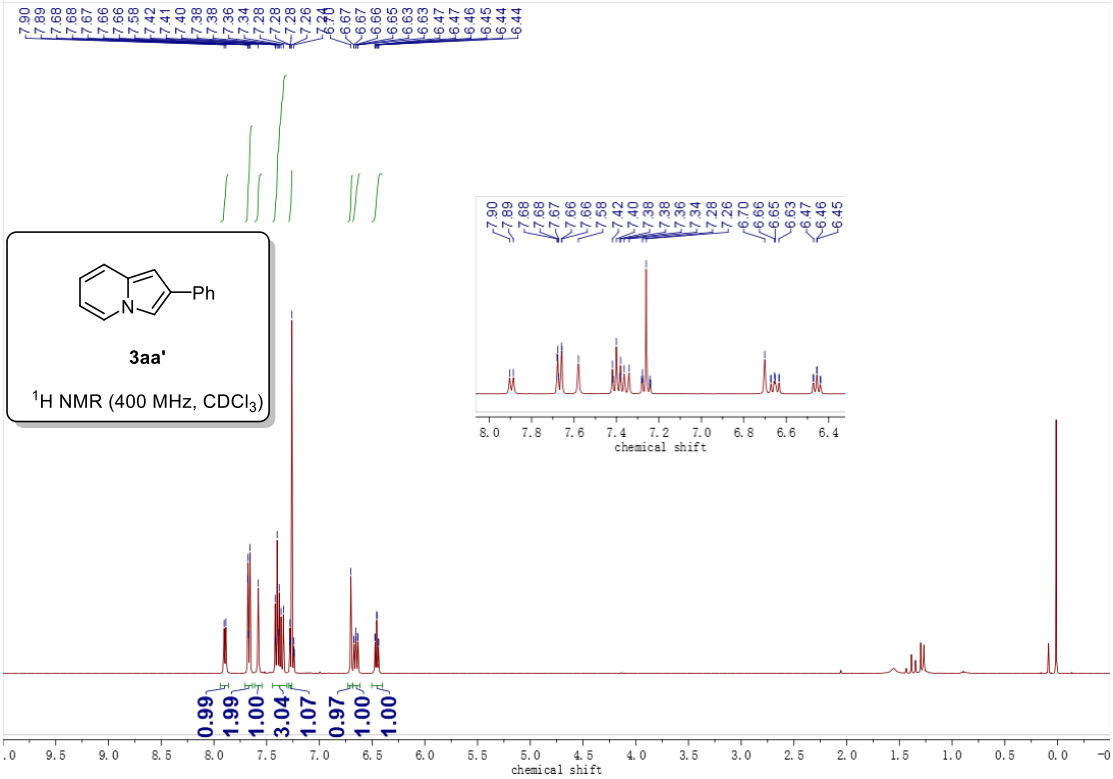


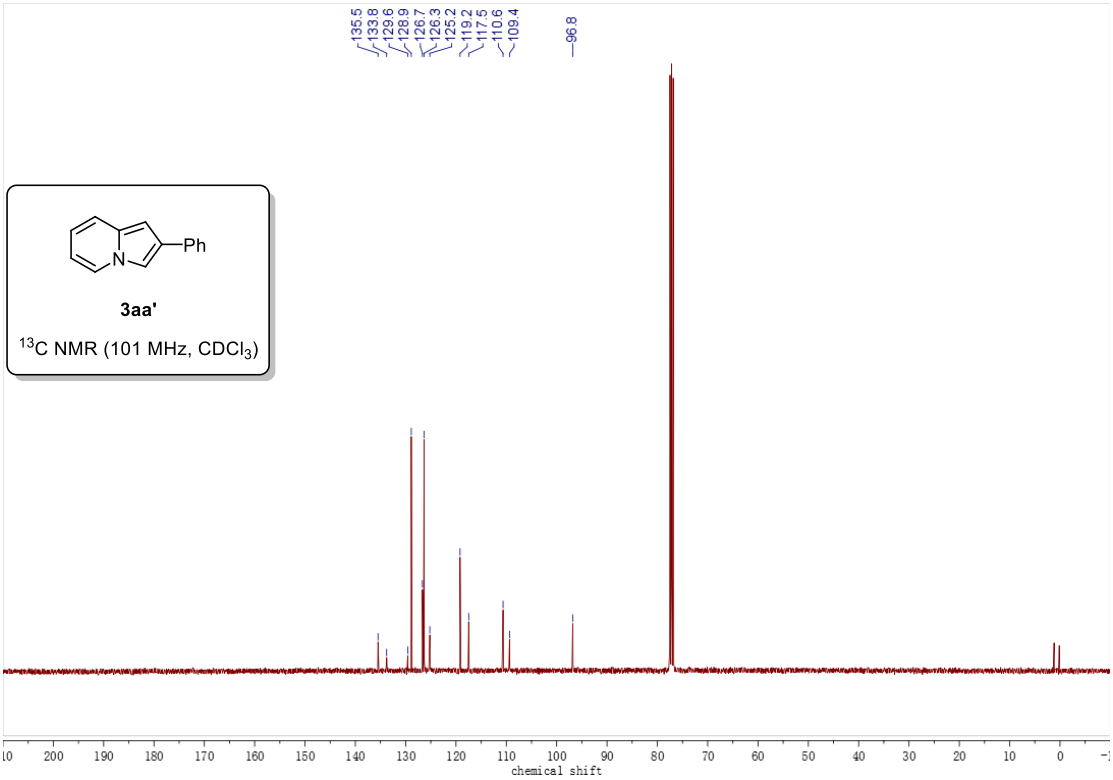
Peak Table

Detector A Channel 2 254nm

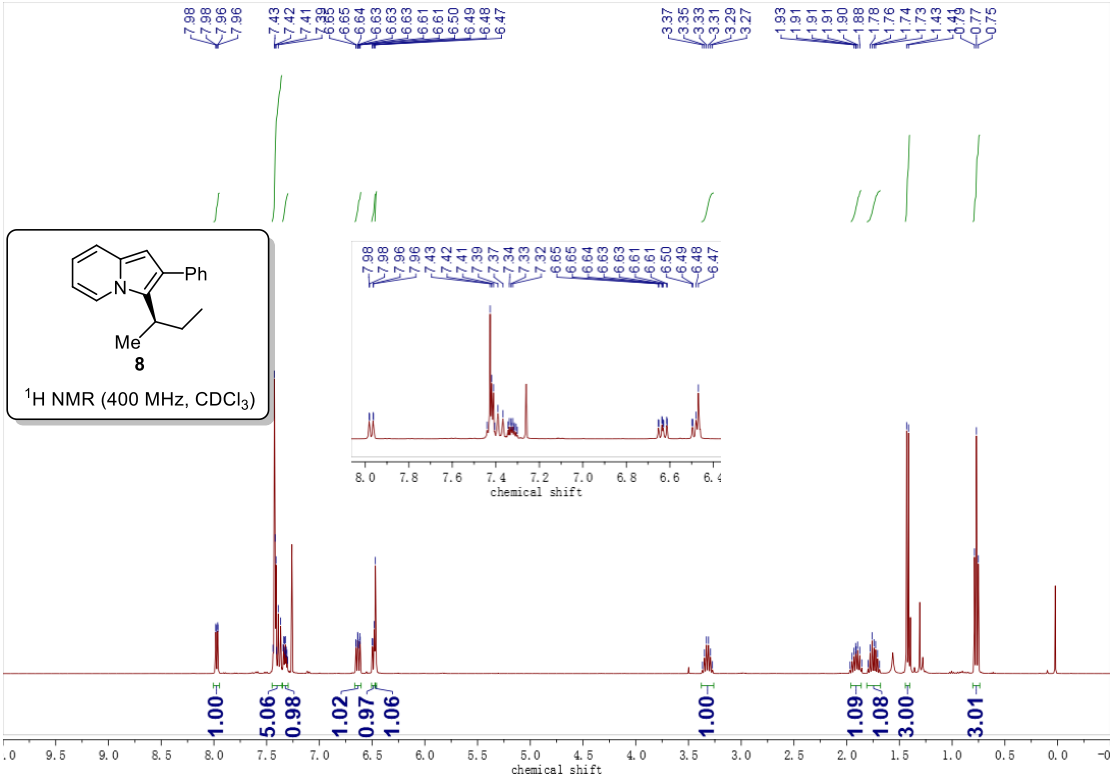
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	7.379	10516020	1042000	99.558	99.558
2	8.318	46679	3883	0.442	0.442
Total		10562698	1045883		100.000

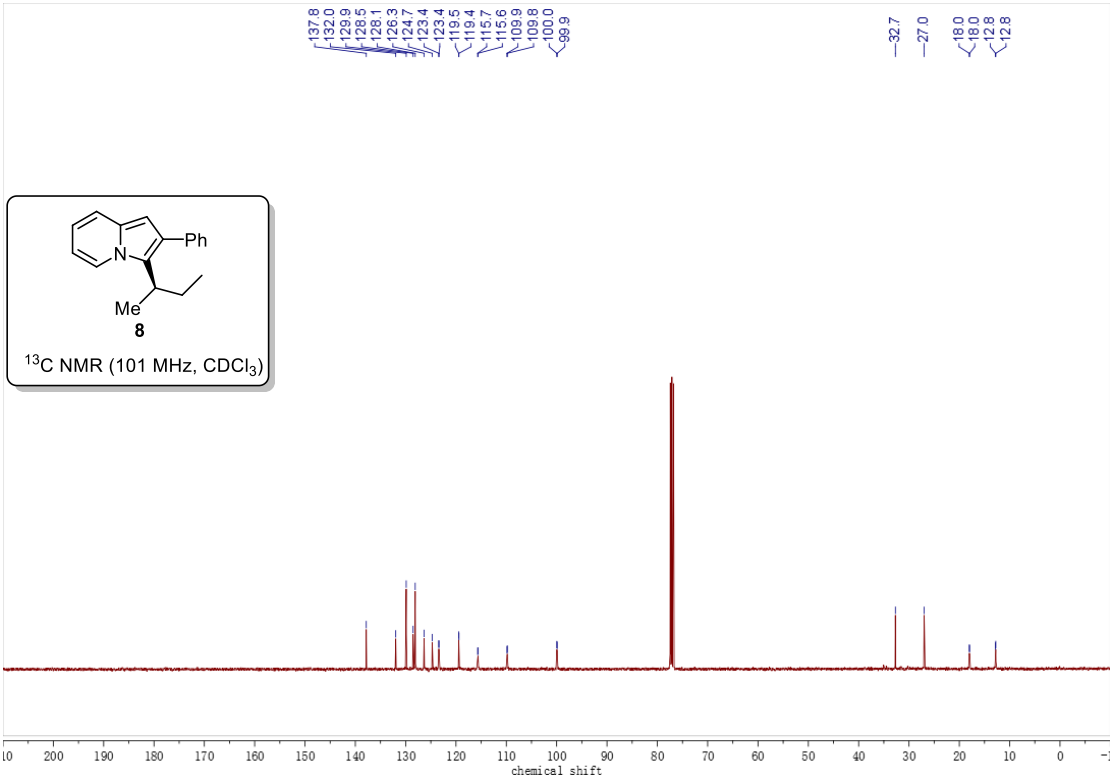
2-phenylindolizine(**3aa'**).



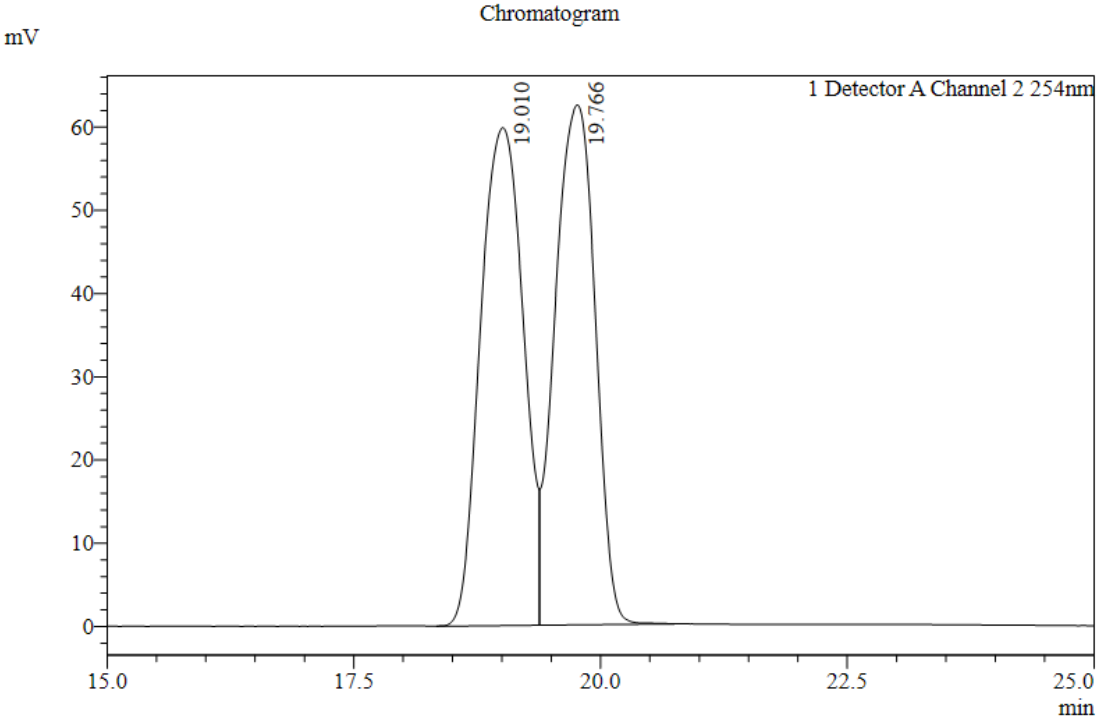


(R)-3-(sec-butyl)-2-phenylindolizine (**8**).





Chromatogram

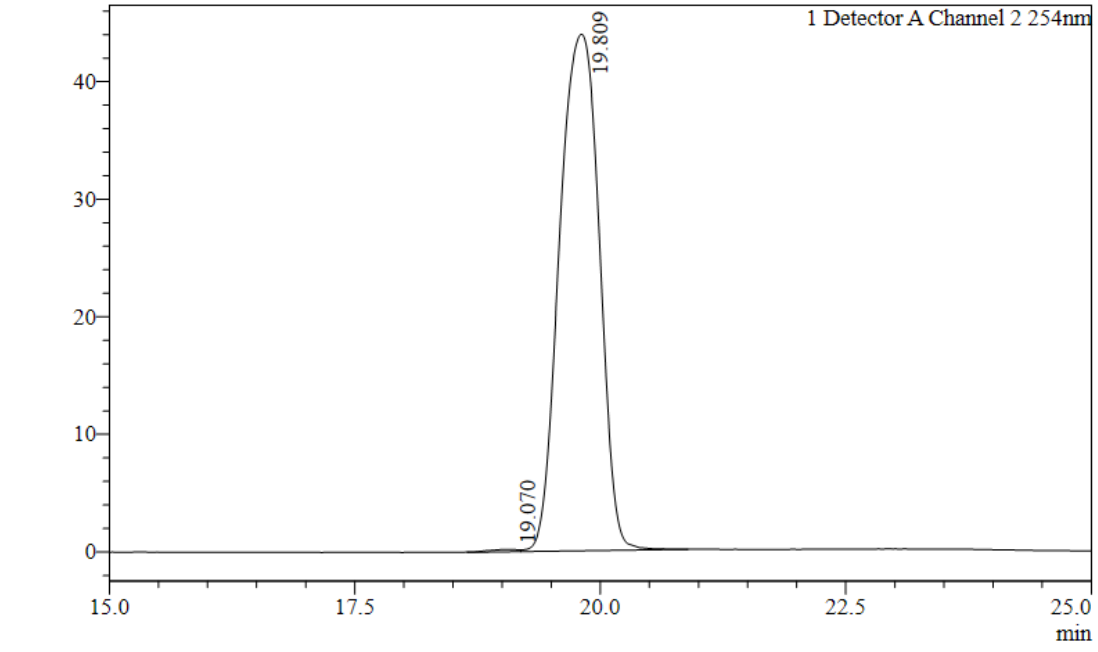


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	19.010	1811859	59846	50.559	50.559
2	19.766	1771817	62481	49.441	49.441
Total		3583676	122327		100.000

Chromatogram

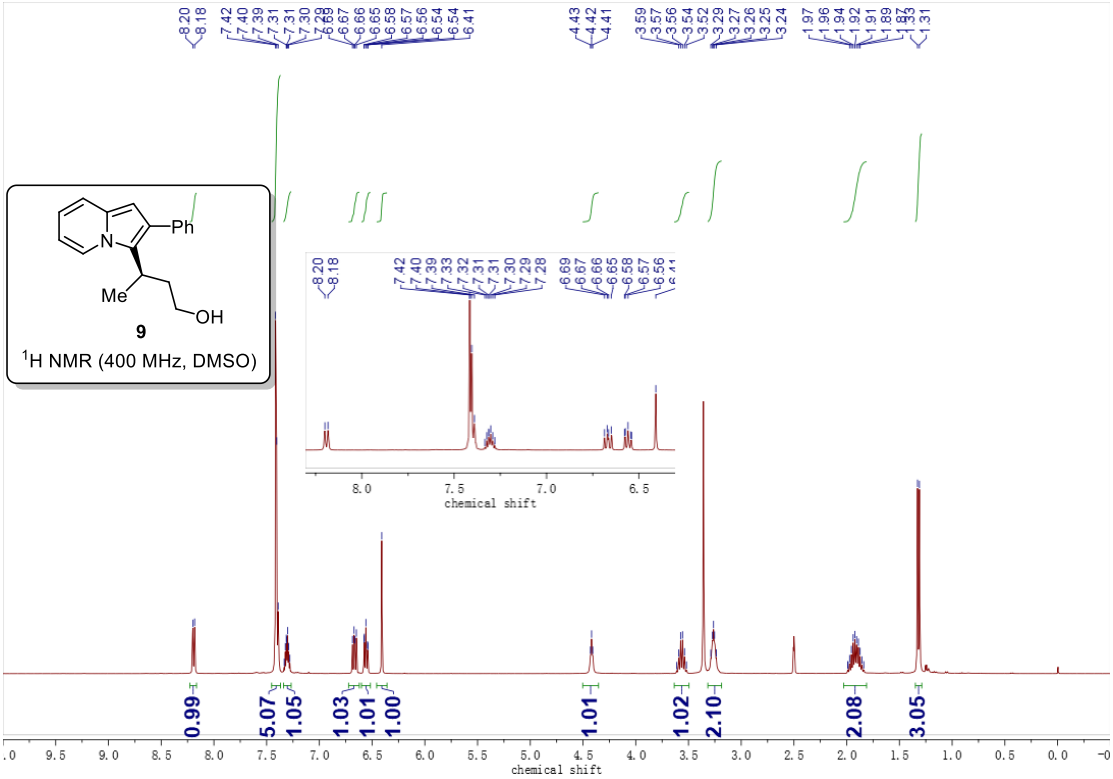


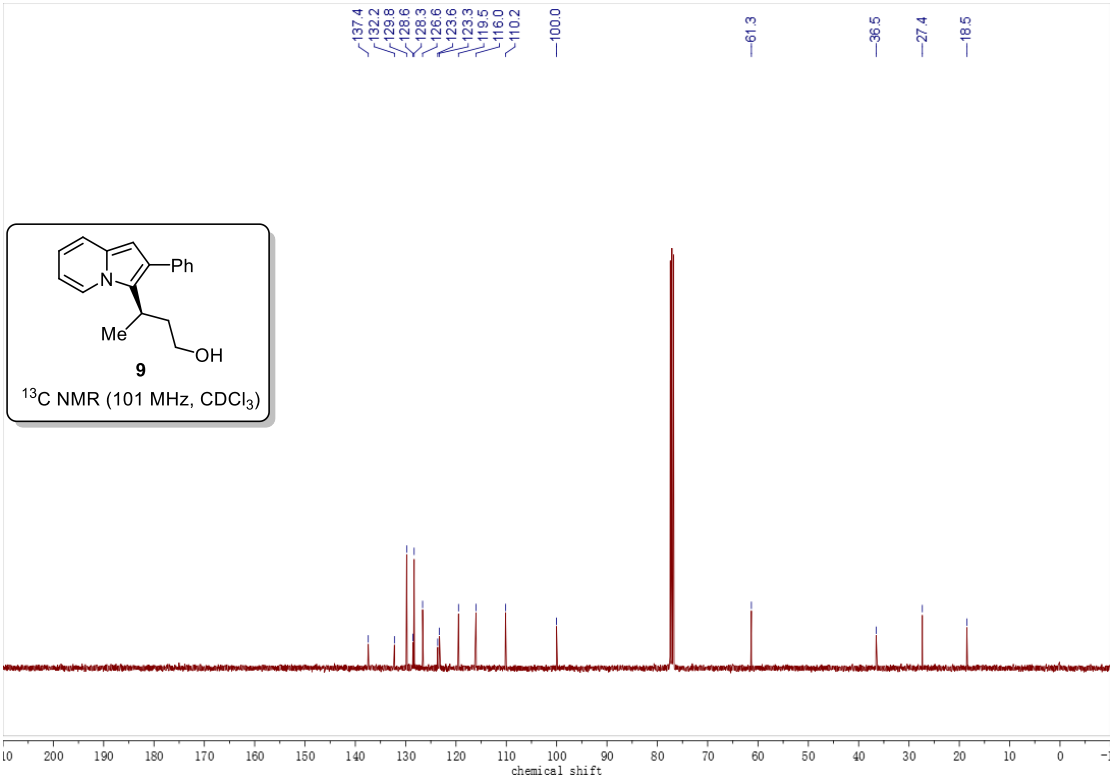
Peak Table

Detector A Channel 2 254nm

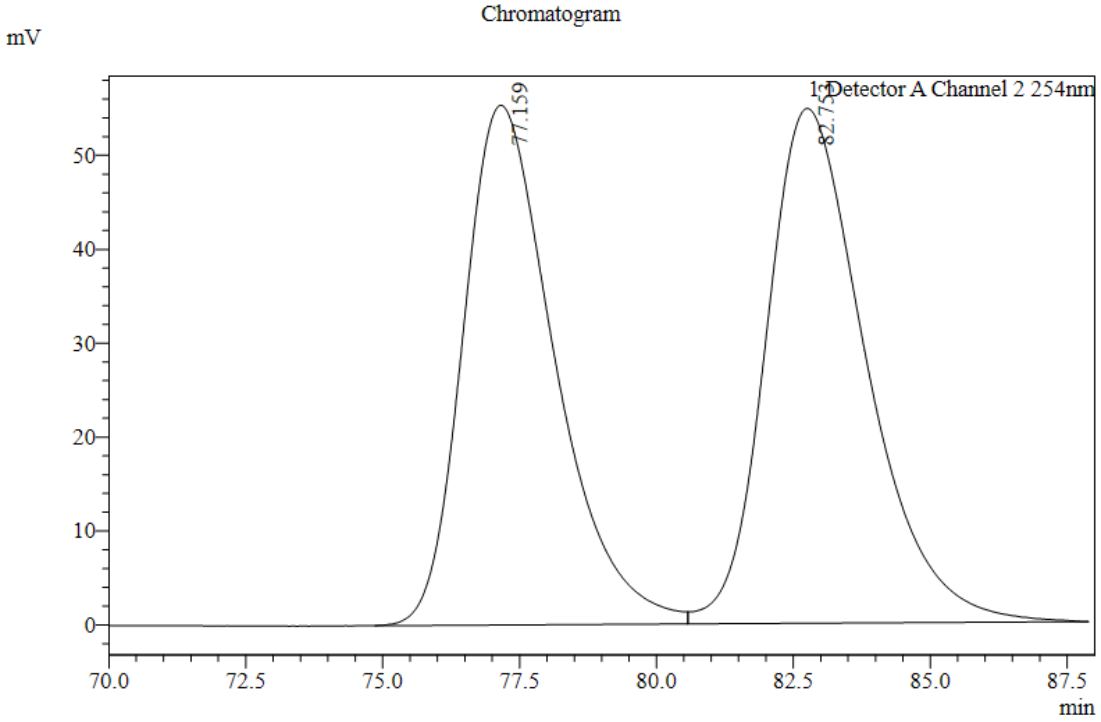
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	19.070	4181	188	0.337	0.337
2	19.809	1235814	43918	99.663	99.663
Total		1239995	44106		100.000

(R)-3-(2-phenylindolizin-3-yl)butan-1-ol (**9**).





Chromatogram

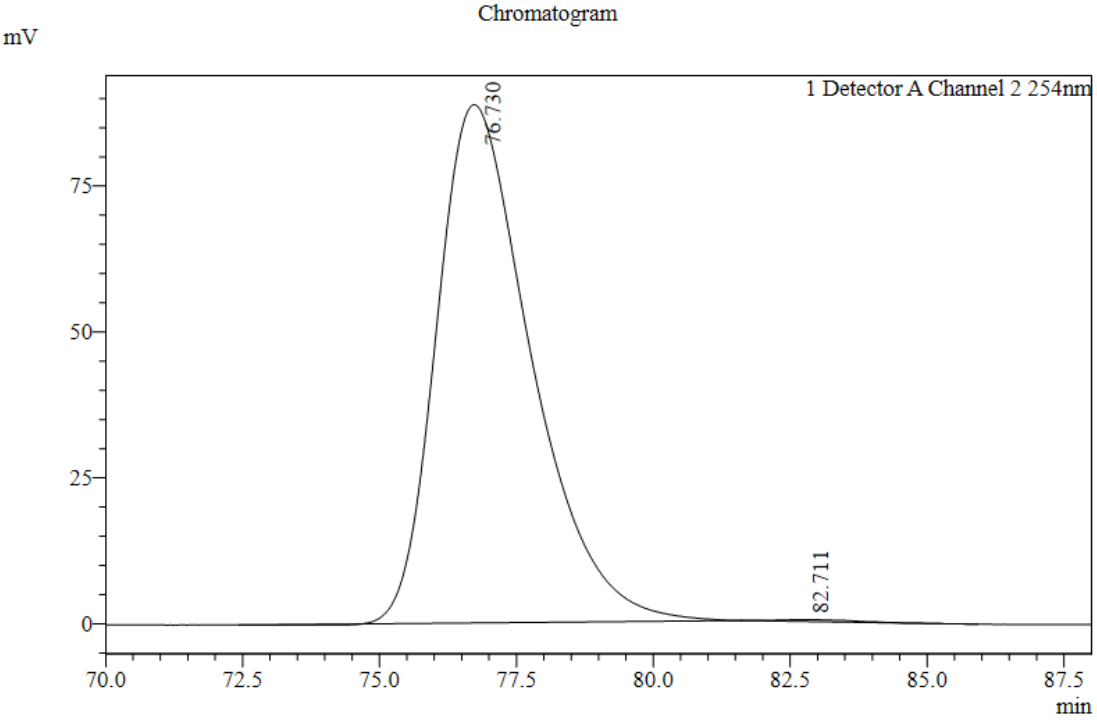


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	77.159	6431756	55351	48.049	48.049
2	82.753	6954116	54824	51.951	51.951
Total		13385872	110175		100.000

Chromatogram

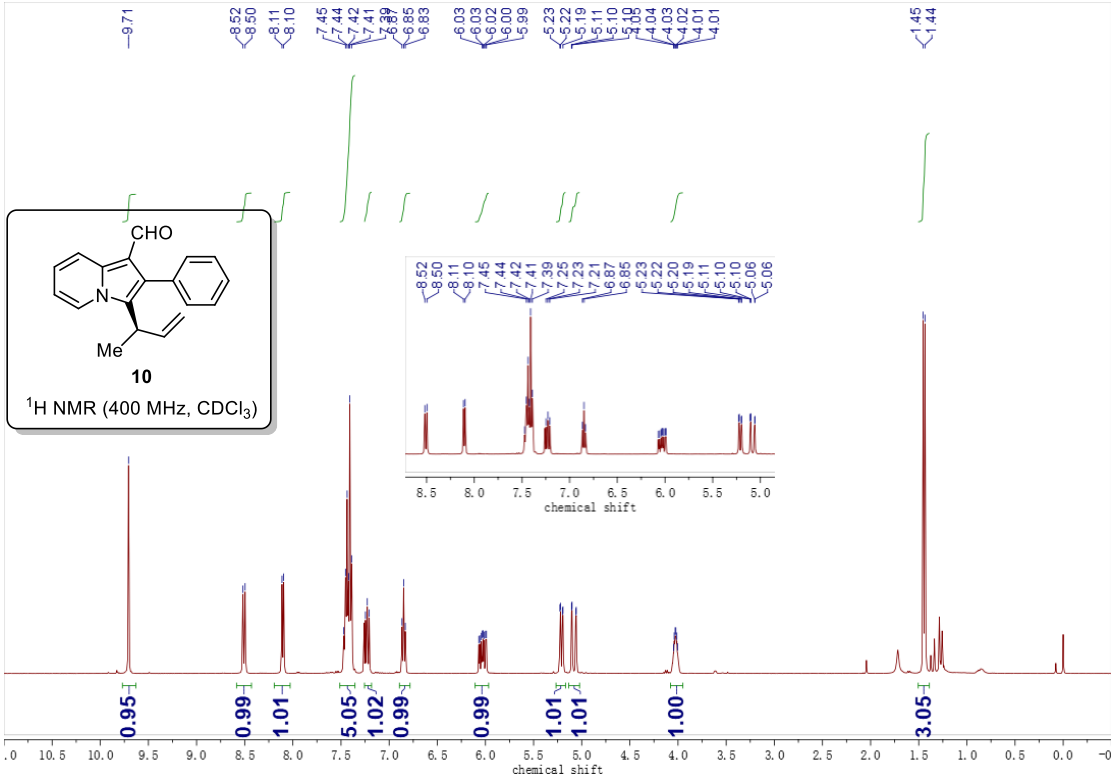


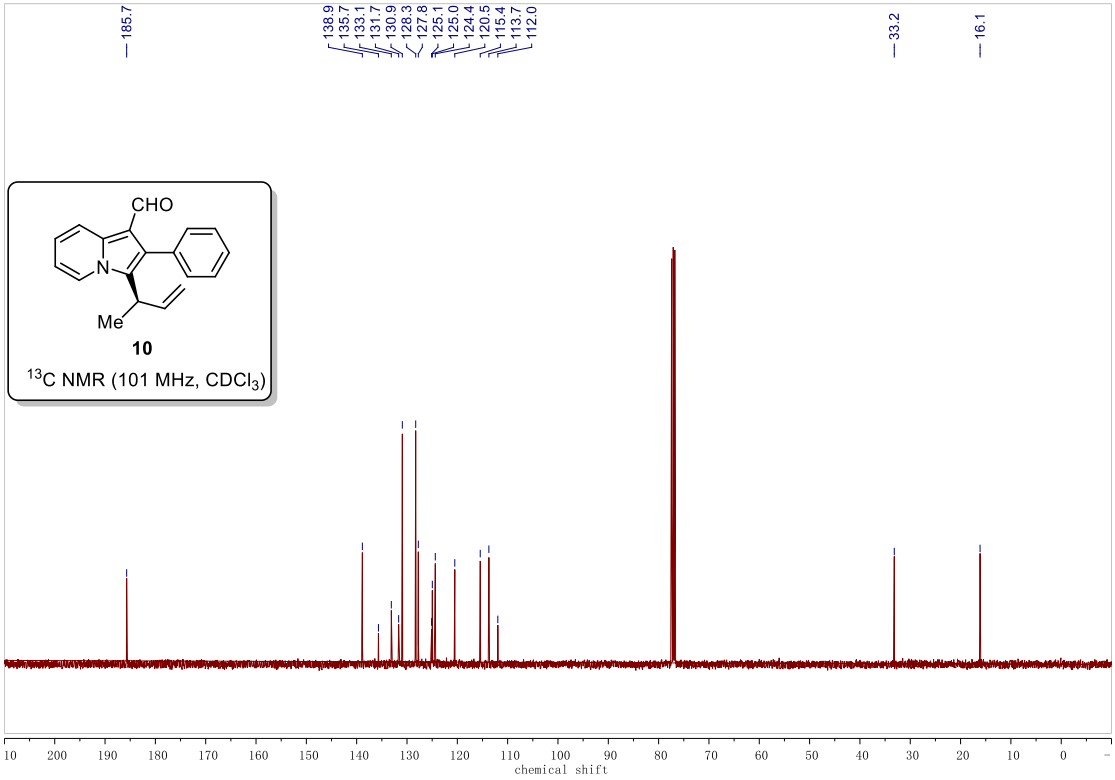
Peak Table

Detector A Channel 2 254nm

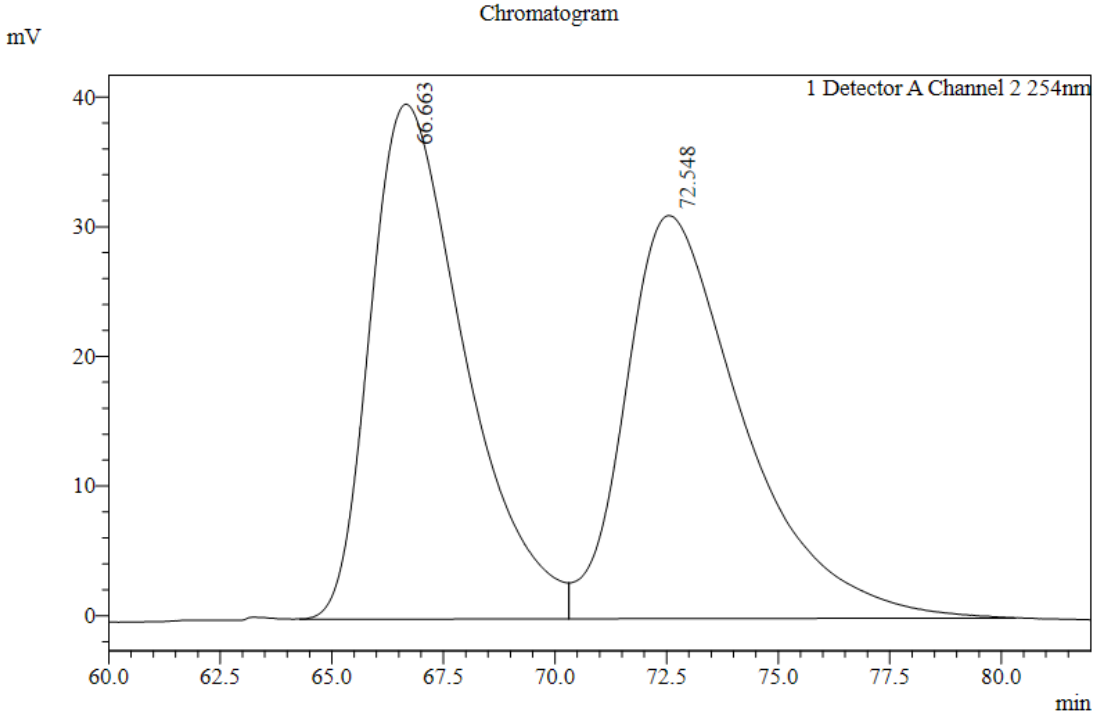
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	76.730	10663560	88753	99.745	99.745
2	82.711	27298	294	0.255	0.255
Total		10690857	89047		100.000

(R)-3-(but-3-en-2-yl)-2-phenylindolizine-1-carbaldehyde (**10**).





Chromatogram

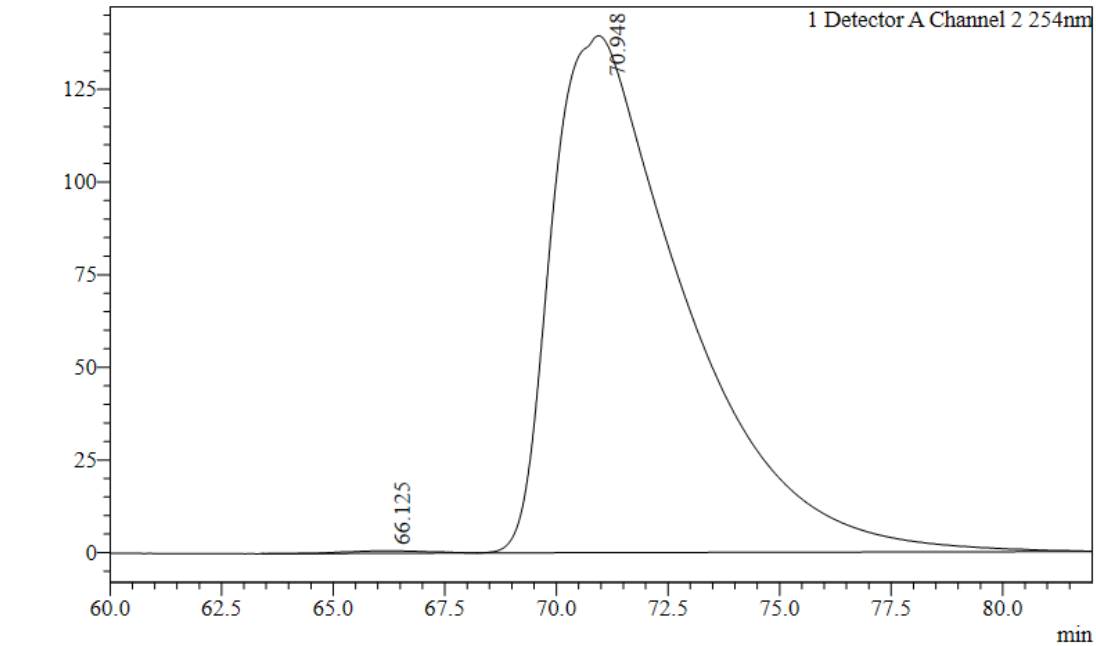


Peak Table

Detector A Channel 2 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%
1	66.663	5860494	39709	50.533	50.533
2	72.548	5736890	31079	49.467	49.467
Total		11597384	70788		100.000

Chromatogram

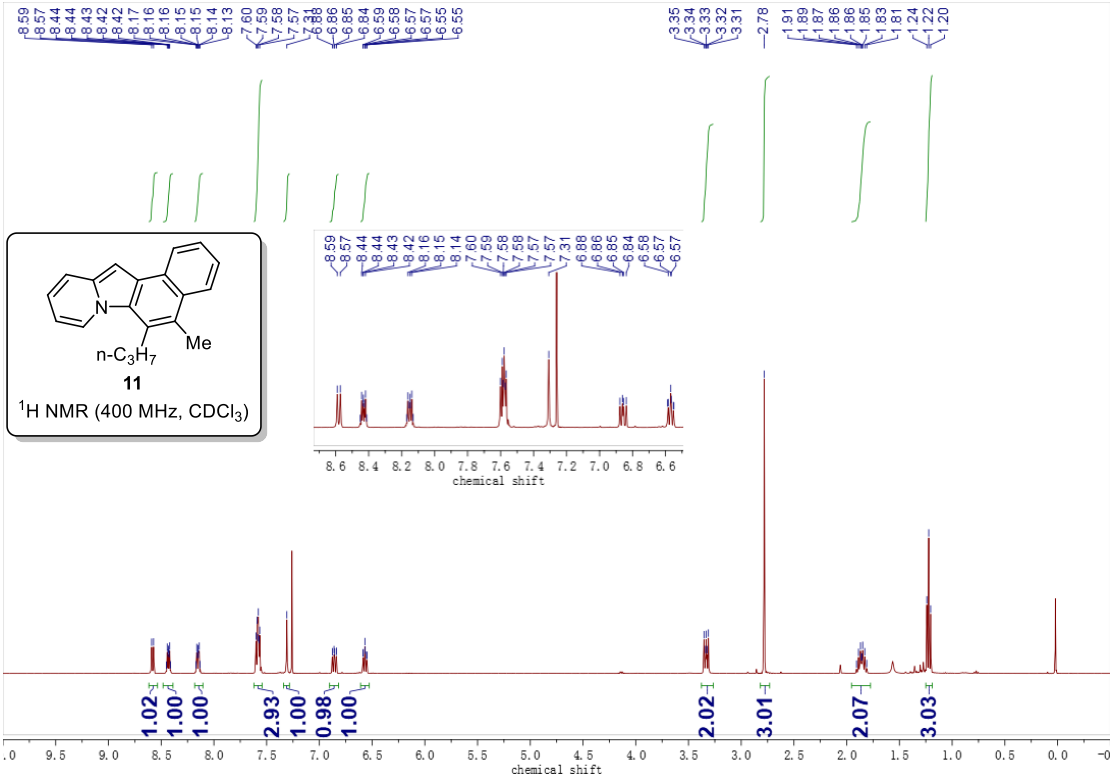


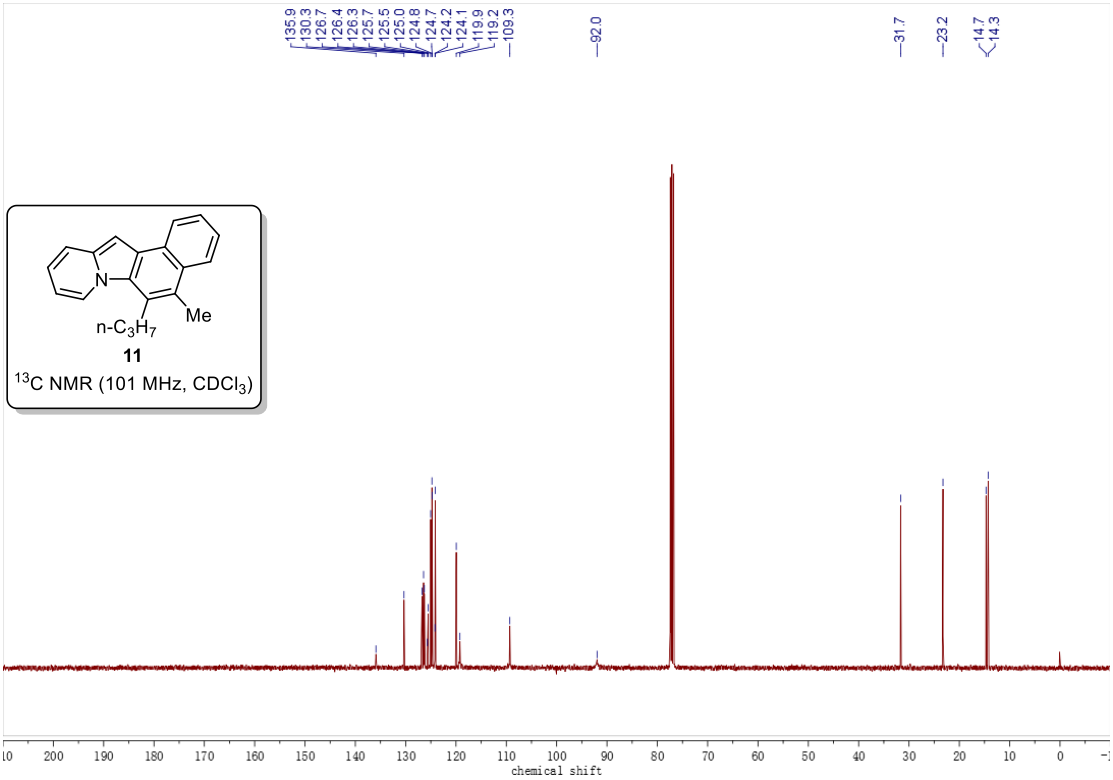
Peak Table

Detector A Channel 2 254nm

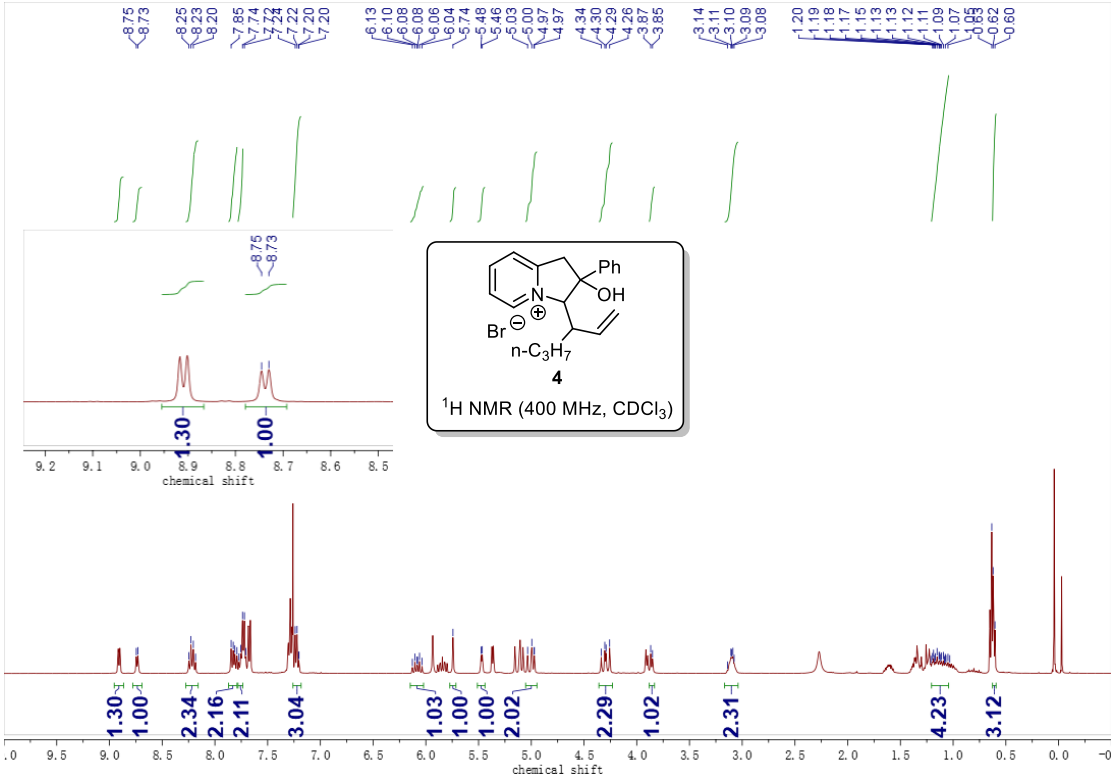
Peak#	Ret. Time	Area	Height	Conc.	Area%
1	66.125	84364	653	0.288	0.288
2	70.948	29173479	139457	99.712	99.712
Total		29257843	140110		100.000

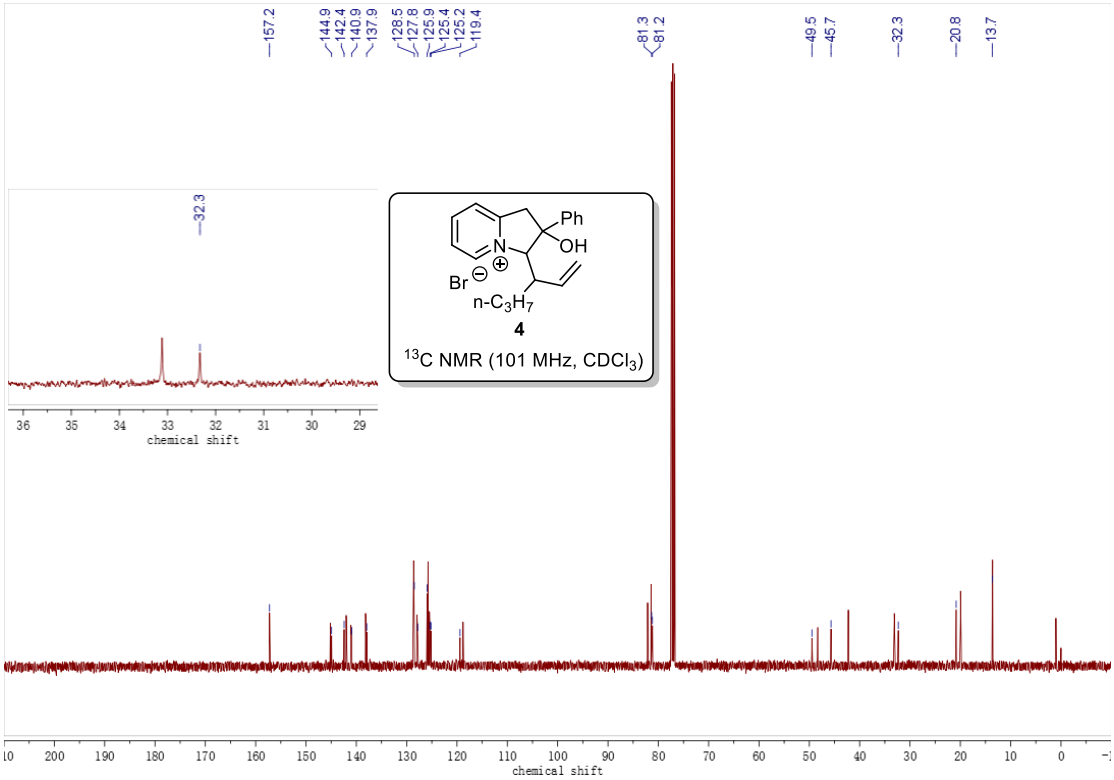
5-methyl-6-propylbenzo[e]pyrido[1,2-a]indole (**11**).



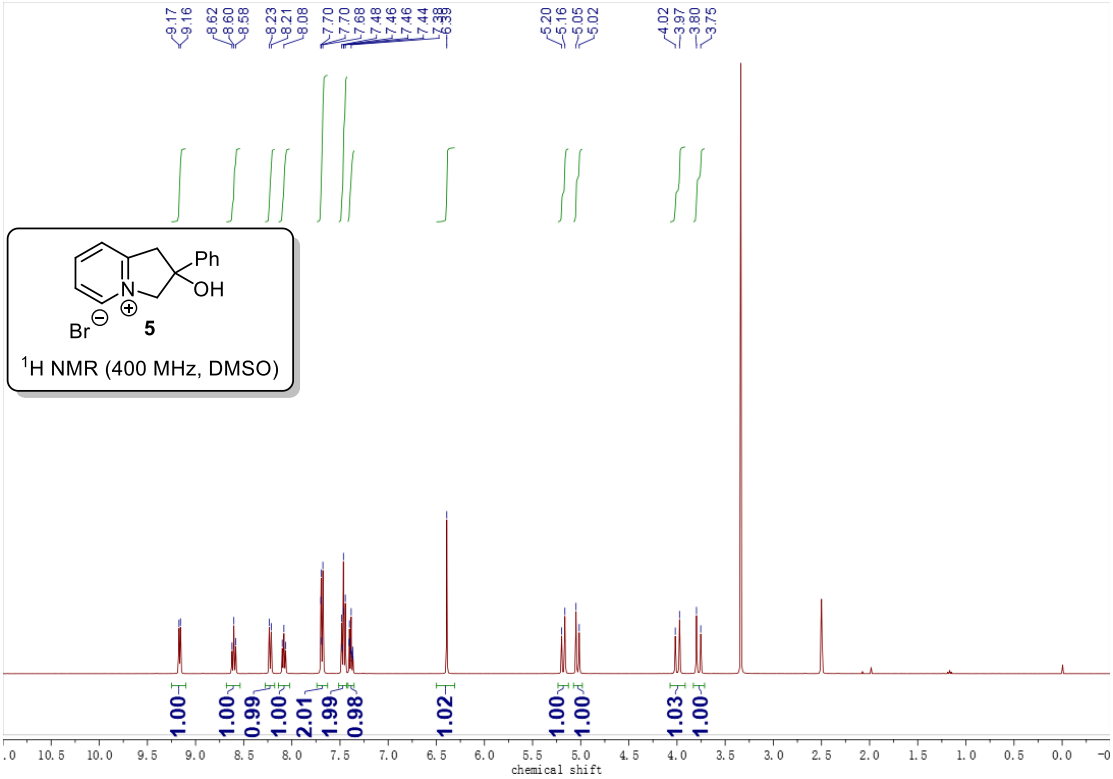


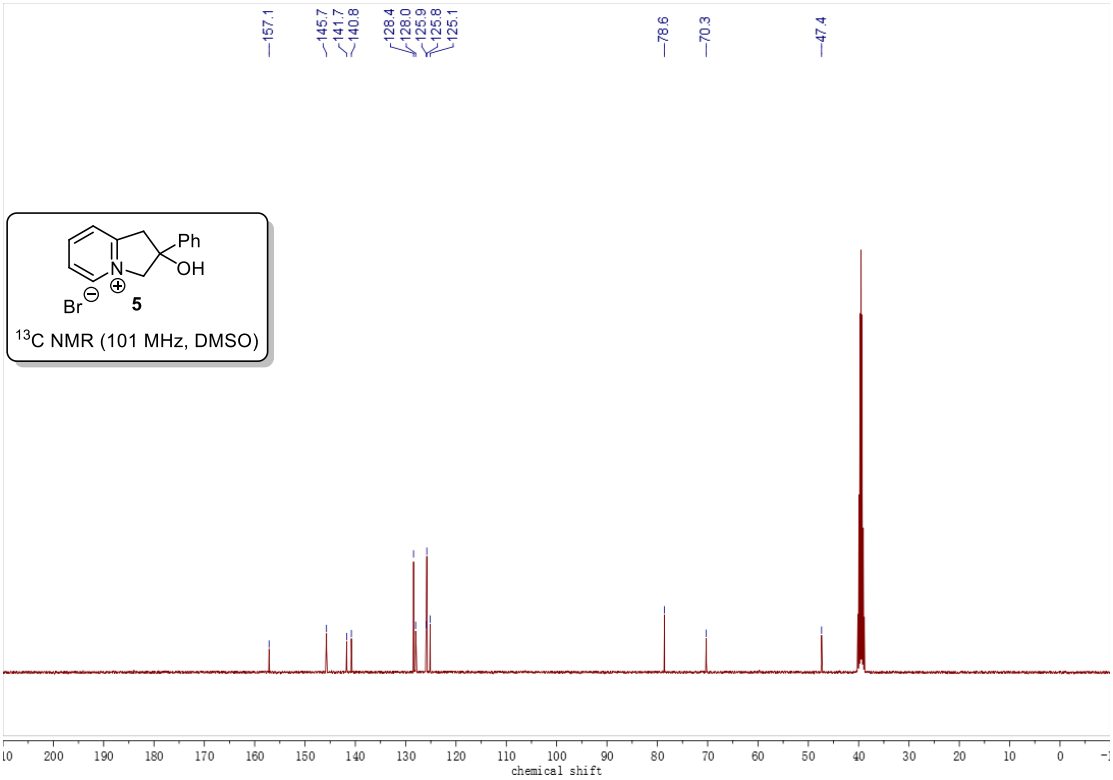
3-(hex-1-en-3-yl)-2-hydroxy-2-phenyl-2,3-dihydro-1H-indolizin-4-ium bromide (**4**).



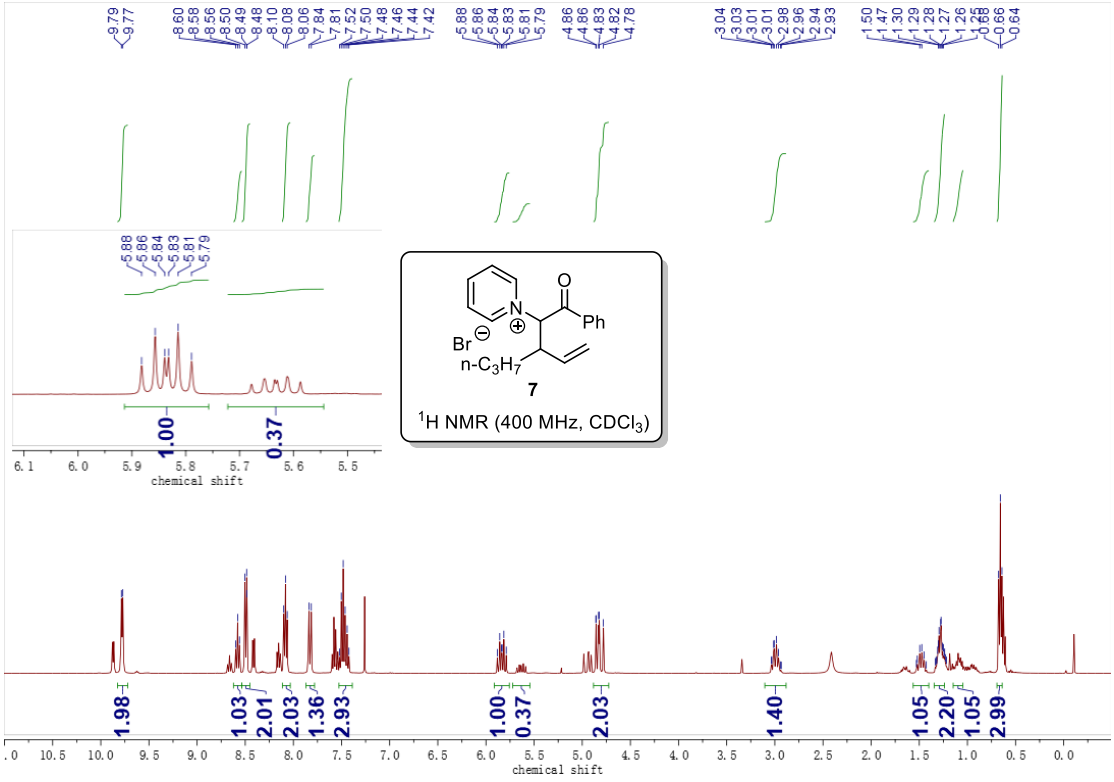


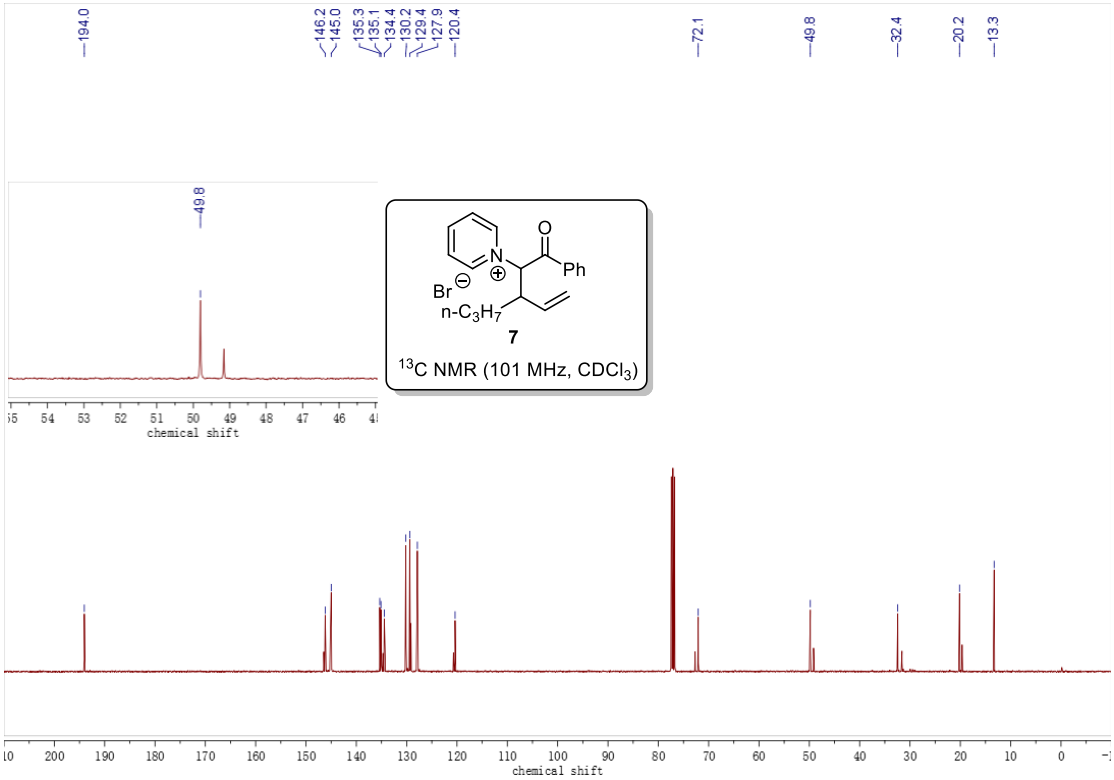
2-hydroxy-2-phenyl-2,3-dihydro-1H-indolizin-4-ium bromide (**5**).





1-(1-oxo-1-phenyl-3-vinylhexan-2-yl)pyridin-1-ium bromide (**7**).





13. References.

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