Supplementary Information

Enantiodivergent Intermolecular Hydroamination of Acyclic 1,3-Dienes Using Aniline Nucleophiles

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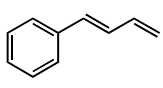
I. General Information

^{1}H NMR spectra were recorded with a Bruker Avance 400 at 25 °C and internally referenced to tetramethylsilane signal. ^{13}C NMR spectra were recorded with a Bruker Avance 400 at 25 °C and internally referenced to residual solvent signals ($CDCl_3$: δ 77.0). Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant (Hz) when applicable. ^{13}C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV spectrometer. Chiral HPLC analyses were carried out on a Shimadzu LC-20AD system. Infrared spectra were recorded on a Varian 3100 FT-IR. Specific rotations were measured on a Jasco P-2000 Polarimeter.

All reactions were carried out using flame-dried glassware under a nitrogen atmosphere unless otherwise noted. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel. HPLC-grade tetrahydrofuran, methylene chloride, diethyl ether and toluene were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). **L1** and **L2** ligands were prepared according to the reported procedure.[S1] Chemical reagents were purchased from Adamas, Energy Chemicals, J&K, Innochem or Macklin and used without purification.

II. Preparation of Diene Substrates



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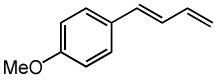

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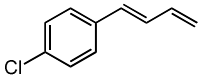

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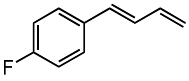

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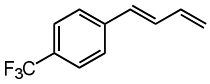

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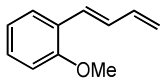

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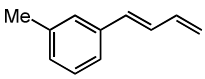

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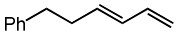

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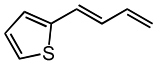

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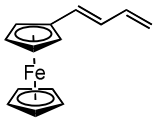

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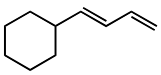

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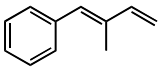
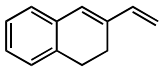


1l



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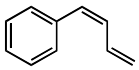
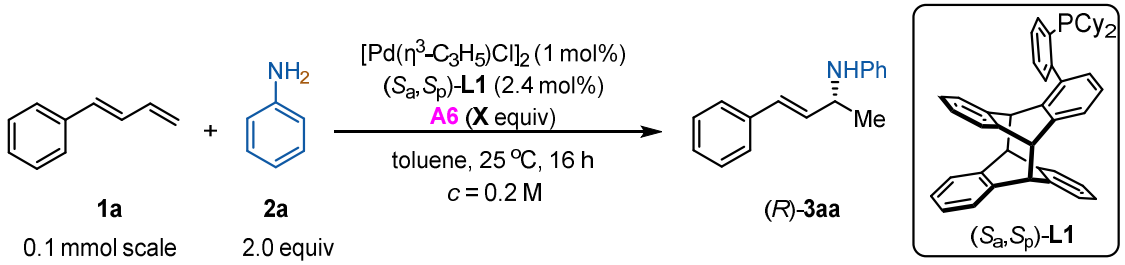


(*Z*)-**1a**

Diene substrates **1a**, **1b**, **1c**, **1d**, **1f**, **1l**, and **1m** were prepared according to the procedure reported by Yin et al.[S2] Diene substrates **1e**, **1g**, **1h**, **1i**, **1j**, and **1k** were prepared according to the procedure reported by Fernandes et al.[S3] Diene substrate (*Z*)-**1a** was prepared according to the procedure reported by Malcolmson et al.[S4]

III. Optimization of the Reaction Conditions for *R*-Products

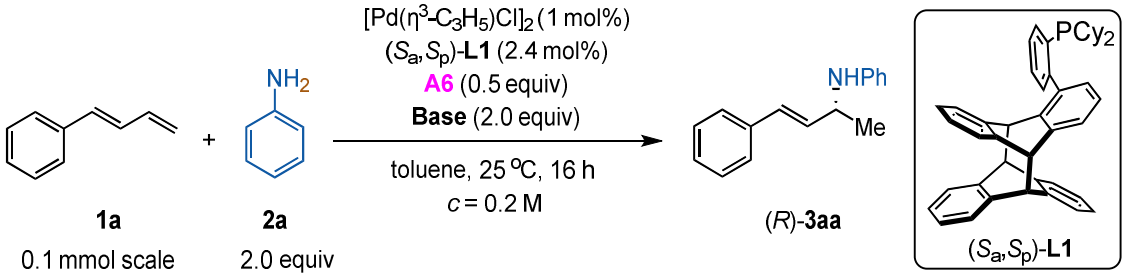
Table S1. Optimization of additive loadings.



Entry	**A6**	Yield (%)[a]	*ee* (%)[b]
1	0.1 equiv	32	94
2	0.5 equiv	51	93
3	1.0 equiv	61	92
4	2.0 equiv	54	86

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

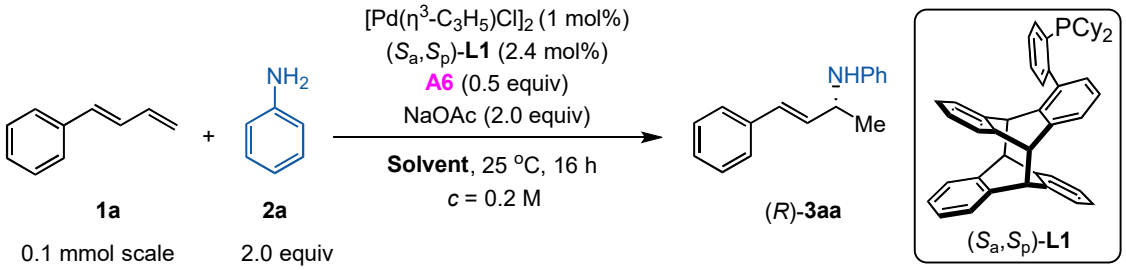
Table S2. Screening of bases.



Entry	Base	Yield (%)[a]	*ee* (%)[b]
1	none	51	93
2	LiOAc	44	94
3	NaOAc	86	93
4	KOAc	62	92
5	CsOAc	14	84
6	Na_2CO_3	63	80
7	Na_3PO_4	93	86
8	Et_3N	5	87
9	DBU	<2	-

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

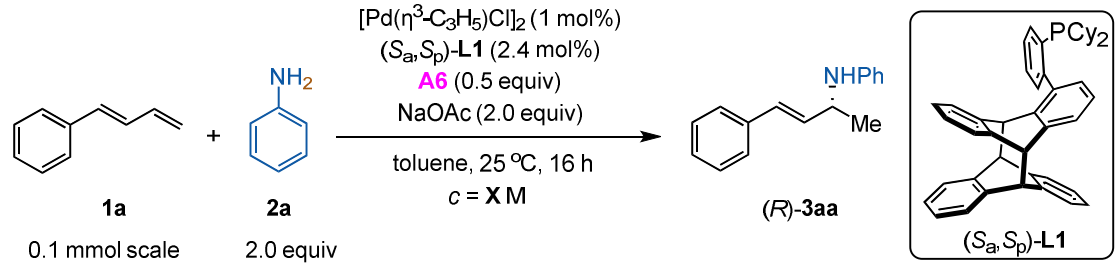
Table S3. Screening of solvents.



Entry	Solvent	Yield (%)[a]	*ee* (%)[b]
1	toluene	86	93
2	fluorobenzene	79	85
3	benzotrifluoride	37	87
4	chlorobenzene	46	89
5	THF	<2	-
6	1,4-dioxane	<2	-
7	DCE	87	72
8	DMF	<2	-
9	CH_3CN	86	58

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

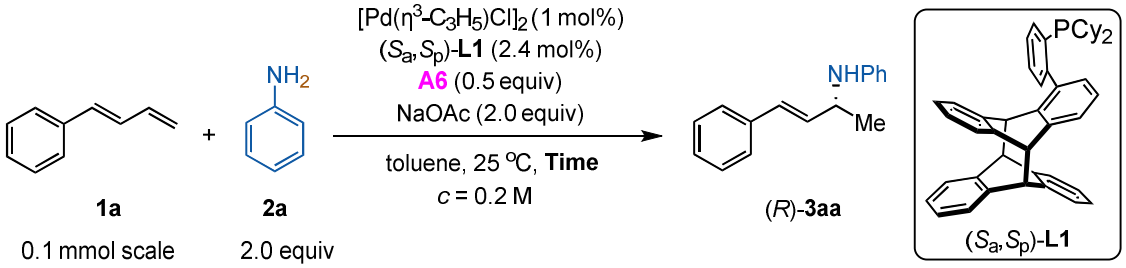
Table S4. Optimization of concentrations.



Entry	Conc.	Yield (%)[a]	*ee* (%)[b]
1	0.1 M	52	93
2	0.2 M	86	93
3	0.4 M	91	92

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

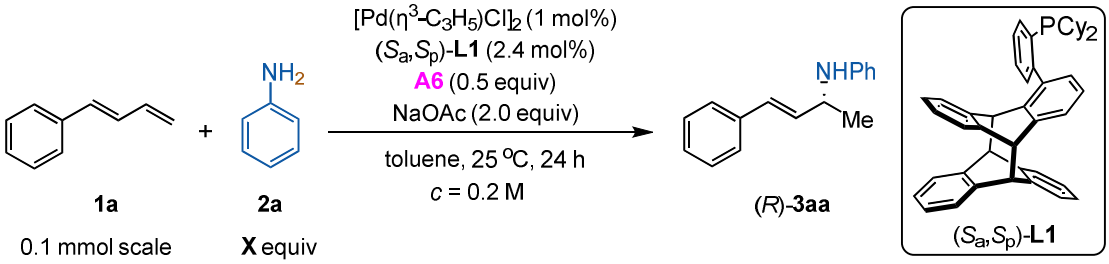
Table S5. Optimization of reaction time.



Entry	Time	Yield (%)[a]	*ee* (%)[b]
1	8 h	80	92
2	16 h	86	93
3	24 h	92	92
4	36 h	98	87

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

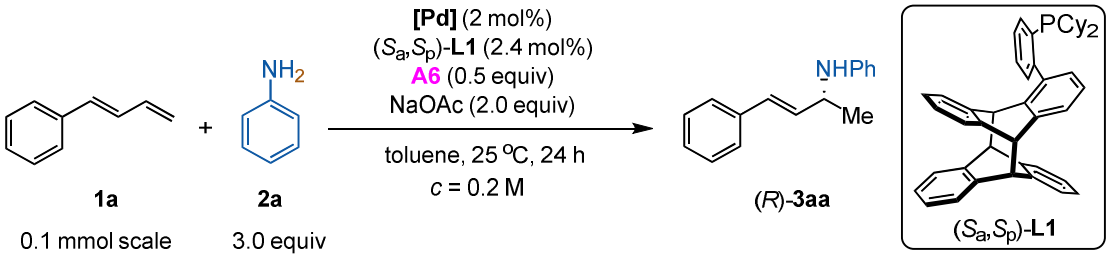
Table S6. Optimization of nucleophile loadings.



Entry	**2a**	Yield (%)[a]	*ee* (%)[b]
1	2.0 equiv	92	92
2	3.0 equiv	99	92

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

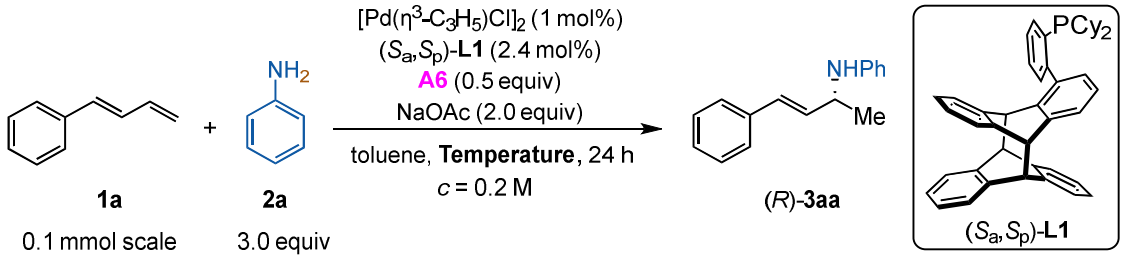
Table S7. Screening of Pd sources.



Entry	[Pd]	Yield (%)[a]	*ee* (%)[b]
1	$Pd(OAc)_2$	<2	-
2	Pd_2dba_3	18	92
3	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	99	92
4	Pd G4 dimer	<2	-

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

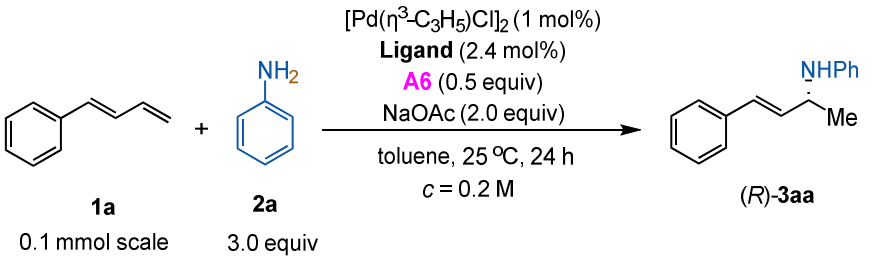
Table S8. Optimization of temperature.

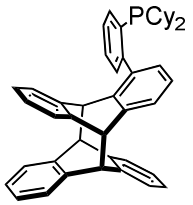


Entry	Temperature	Yield (%)[a]	*ee* (%)[b]
1	25 °C	99	92
2	0 °C	13	94

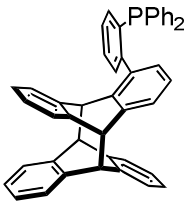
[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

Table S9. Screening of ligands.

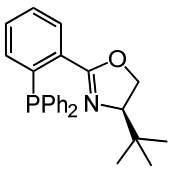




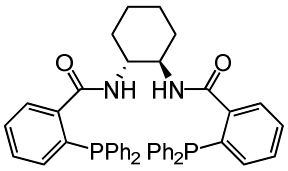
(S_a,S_p)-**L1**



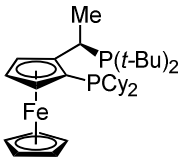
(S_a,S_p)-**L2**



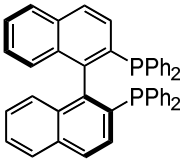
(*R*)-**L3**



(*R*,*R*)-**L4**



(*R*,S_p)-**L5**



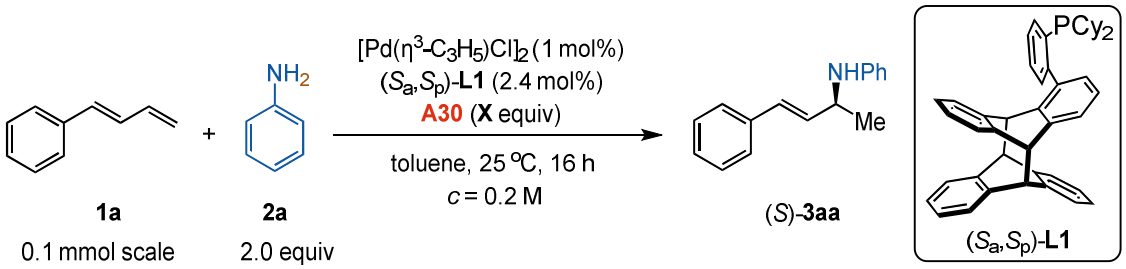
(*S*)-**L6**

Entry	Ligand	Yield (%)[a]	*ee* (%)[b]
1	**L1**	99	92
2	**L2**	47	65
3	**L3**	43	68
4	**L4**	6	14
5	**L5**	59	33
6	**L6**	84	5

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*R*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

IV. Optimization of the Reaction Conditions for *S*-Products

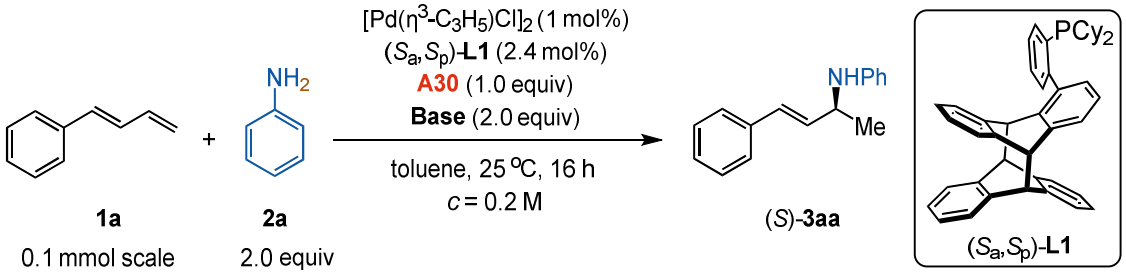
Table S10. Optimization of additive loadings.



Entry	**A30**	Yield (%)[a]	*ee* (%)[b]
1	0.1 equiv	20	56
2	0.5 equiv	40	59
3	1.0 equiv	59	60
4	2.0 equiv	47	60

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

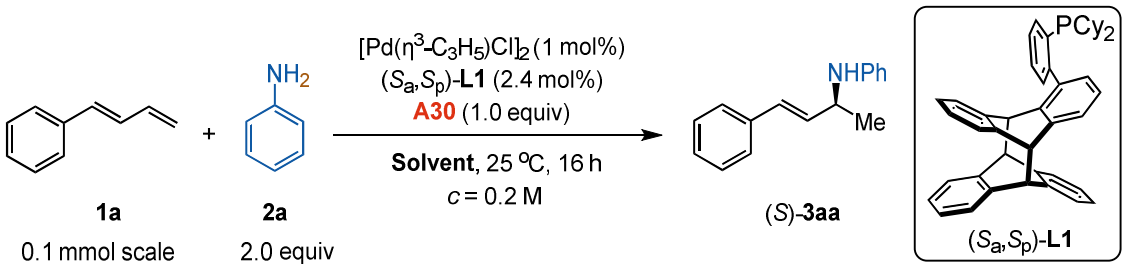
Table S11. Screening of bases.



Entry	Base	Yield (%)[a]	*ee* (%)[b]
1	none	59	60
2	LiOAc	58	57
3	NaOAc	88	51
4	KOAc	73	37
5	CsOAc	94	45
6	Na_2CO_3	56	51
7	Na_3PO_4	43	48
8	Et_3N	14	51
9	DBU	<2	-

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

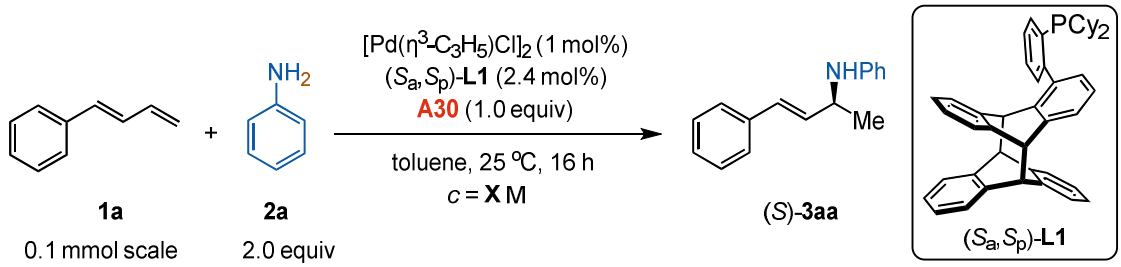
Table S12. Screening of solvents.



Entry	Solvent	Yield (%)[a]	*ee* (%)[b]
1	toluene	59	60
2	fluorobenzene	40	58
3	benzotrifluoride	21	54
4	chlorobenzene	27	59
5	THF	3	55
6	1,4-dioxane	3	52
7	DCE	6	59
8	DMF	<2	-
9	CH_3CN	4	44

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

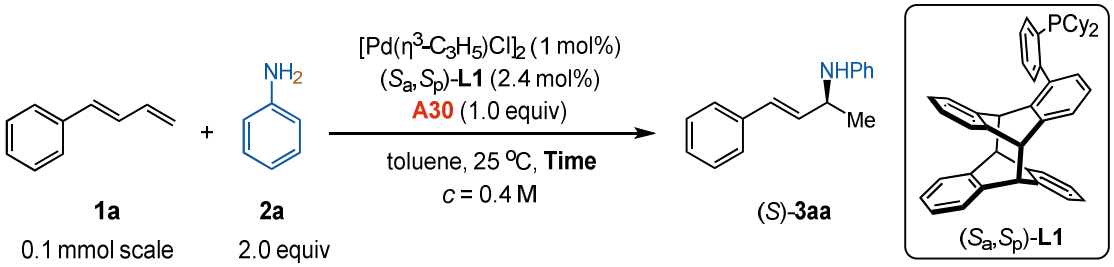
Table S13. Optimization of concentrations.



Entry	Conc.	Yield (%)[a]	*ee* (%)[b]
1	0.1 M	30	60
2	0.2 M	59	60
3	0.4 M	73	60

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

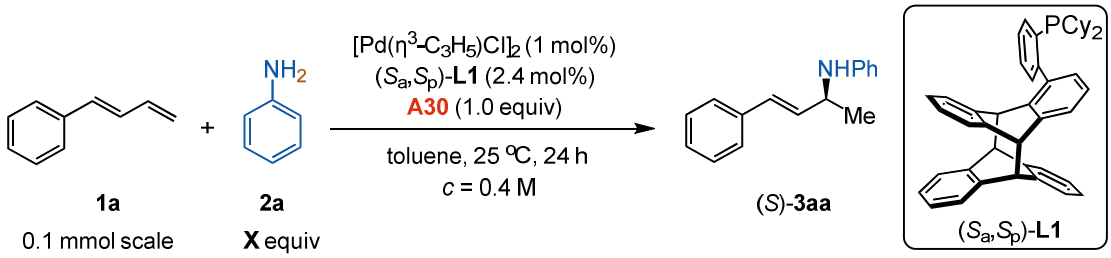
Table S14. Optimization of reaction time.



Entry	Time	Yield (%)[a]	*ee* (%)[b]
1	8 h	64	60
2	16 h	73	60
3	24 h	82	60
4	36 h	84	59

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

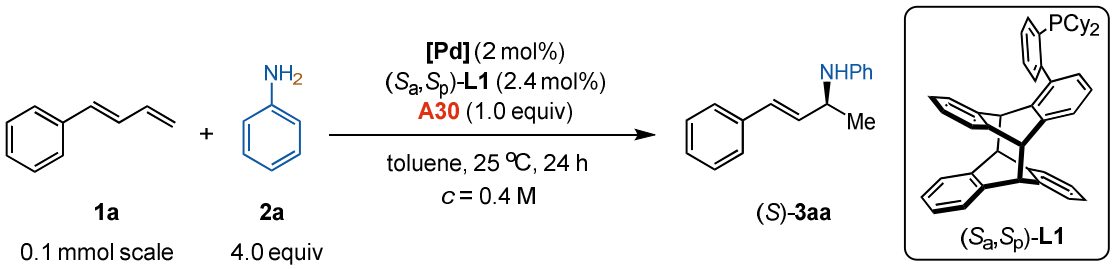
Table S15. Optimization of nucleophile loadings.



Entry	**2a**	Yield (%)[a]	*ee* (%)[b]
1	2.0 equiv	82	60
2	3.0 equiv	86	59
3	4.0 equiv	94	59
4	5.0 equiv	94	59

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

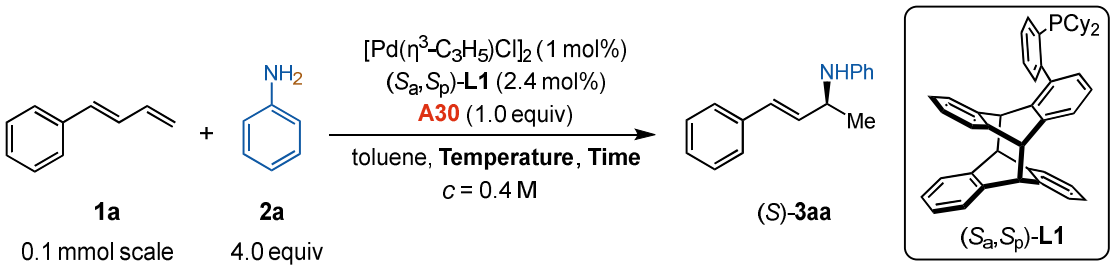
Table S16. Screening of Pd sources.



Entry	[Pd]	Yield (%)[a]	*ee* (%)[b]
1	$Pd(OAc)_2$	94	53
2	Pd_2dba_3	8	60
3	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	94	59
4	Pd G4 dimer	<2	-

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

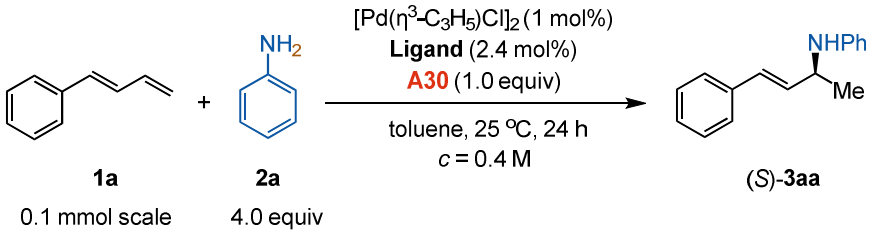
Table S17. Optimization of temperatures.

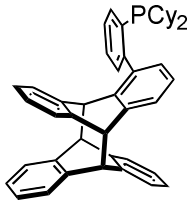


Entry	Temperature	Time	Yield (%)[a]	*ee* (%)[b]
1	25 °C	24 h	94	59
2	0 °C	40 h	72	65
3	0 °C	48 h	80	65

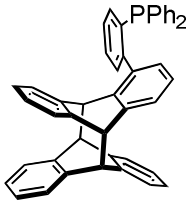
[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

Table S18. Screening of ligands.

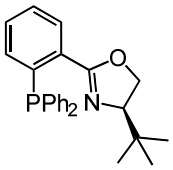




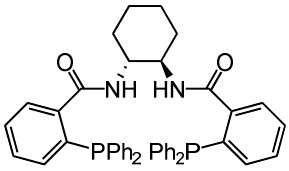
(S_a,S_p)-**L1**



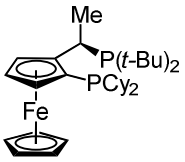
(S_a,S_p)-**L2**



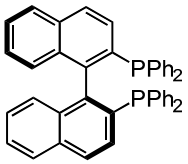
(*R*)-**L3**



(*R*,*R*)-**L4**



(R,S_p)-**L5**

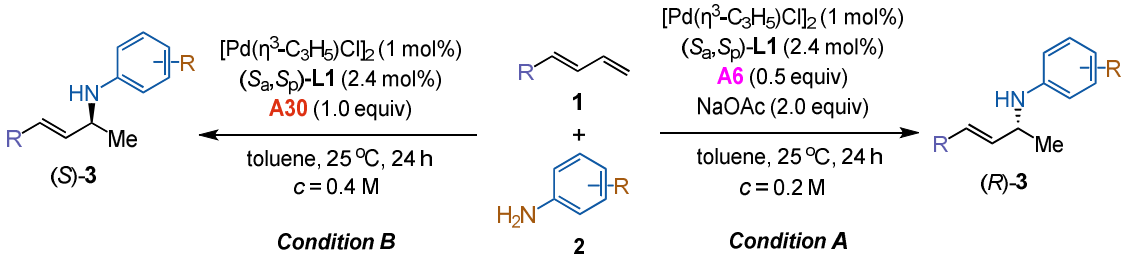


(*S*)-**L6**

Entry	Ligand	Yield (%)[a]	*ee* (%)[b]
1	**L1**	94	59
2	**L2**	21	39
3	**L3**	<2	-
4	**L4**	2	10
5	**L5**	<2	-
6	**L6**	<2	-

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. [b] The *ee* values of (*S*)-**3aa** were determined by HPLC analysis on a chiral stationary phase.

V. Substrate Scope



General Procedure A (Condition A):

In a nitrogen-filled glove box, an 8-mL glass vial was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.4 mg, 0.0092 mmol) and (S_a,S_p)-**L1** (13.9 mg, 0.022 mmol), and the mixture was dissolved in dry toluene (2.3 mL). The solution was stirred at 25 °C for 10 min, providing a 0.008 M stock solution of Pd-(S_a,S_p)-**L1** catalyst.

In a nitrogen-filled glove box, an 8-mL glass vial was charged with stock solution of Pd-(S_a,S_p)-**L1** (0.50 mL, 0.008 M). **1** (0.20 mmol, 1.0 equiv) in 0.50 mL toluene was subsequently added, followed by 1-adamantanecarboxylic acid (**A6**, 18.0 mg, 0.10 mmol, 0.5 equiv), **2** (0.60 mmol, 3.0 equiv), NaOAc (32.8 mg, 0.40 mmol, 2.0 equiv). The vial was sealed with a Teflon-lined cap, transferred out of the glove box, and stirred at 25 °C for 24 h. The crude reaction mixture was analyzed by ^{1}H NMR to determine regioisomer ratio, and was then concentrated and purified by flash silica gel chromatography to afford the desired product.

General Procedure B (Condition B):

In a nitrogen-filled glove box, an 8-mL glass vial was charged with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.4 mg, 0.0092 mmol) and (S_a,S_p)-**L1** (13.9 mg, 0.022 mmol), and the mixture was dissolved in dry toluene (0.92 mL). The solution was stirred at 25 °C for 10 min, providing a 0.02 M stock solution of Pd-(S_a,S_p)-**L1** catalyst.

In a nitrogen-filled glove box, an 8-mL glass vial was charged with stock solution of Pd-(S_a,S_p)-**L1** (0.20 mL, 0.02 M). **1** (0.20 mmol, 1.0 equiv) in 0.30 mL toluene was subsequently added, followed by 2-trifluoromethylphenylboronic acid (**A30**, 38.0 mg, 0.20 mmol, 1.0 equiv), **2** (0.80 mmol, 4.0 equiv). The vial was sealed with a Teflon-lined cap, transferred out of the glove box, and stirred at 25 °C for 24 h. The crude reaction mixture was analyzed by ^{1}H NMR to determine regioisomer ratio, and was then concentrated and purified by flash silica gel chromatography to afford the desired product.

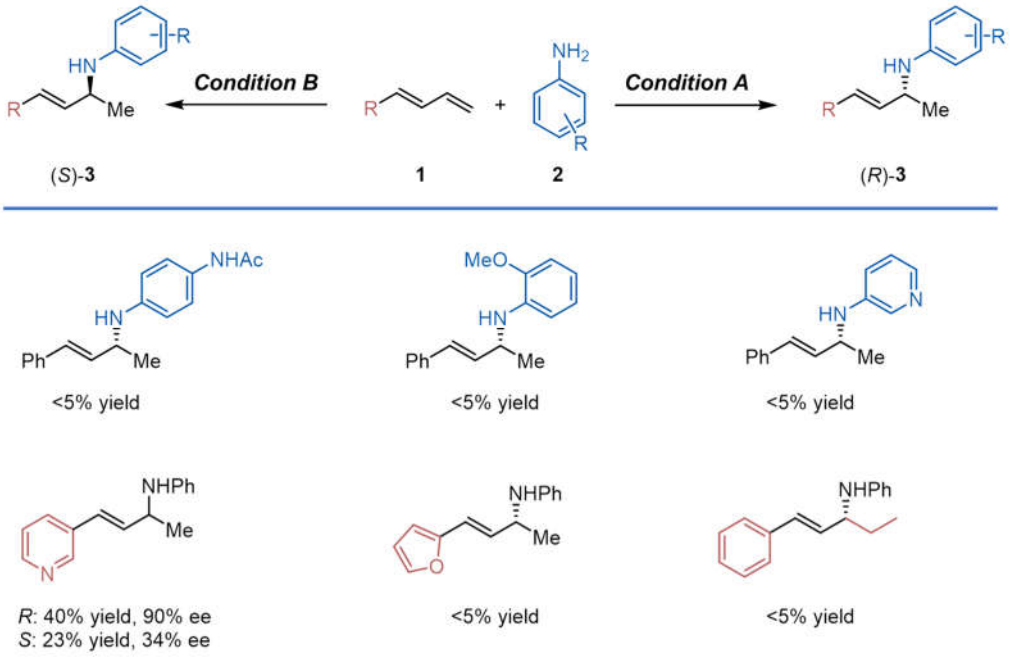
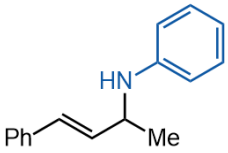


Figure S1. Summary of unsuccessful substrates.



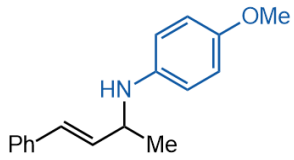
(*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline (**3aa**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 43.2 mg, 97% yield, 92% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 10.57 min, t (major) = 12.28 min]. $[\alpha]_D^{20}$ = +57.2 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 38.9 mg, 87% yield, 59% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.55 min, t (major) = 10.52 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.32–7.25 (m, 2H), 7.24–7.11 (m, 3H), 6.72–6.61 (m, 3H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 5.8 Hz, 1H), 4.20–4.07 (m, 1H), 3.73 (br, s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H);

Spectral data match those previously reported.[S5]



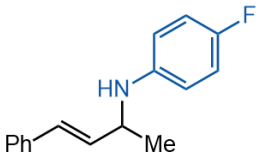
(*E*)-4-methoxy-*N*-(4-phenylbut-3-en-2-yl)aniline (**3ab**)

(*R*,*E*)-4-methoxy-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 44.9 mg, 89% yield, 93% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 13.28 min, t (major) = 16.06 min]. $[\alpha]_D^{20}$ = +62.5 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-4-methoxy-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 47.9 mg, 95% yield, 57% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 15.54 min, t (major) = 12.88 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.31–7.26 (m, 2H), 7.23–7.17 (m, 1H), 6.79–6.72 (m, 2H), 6.65–6.60 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.12–4.02 (m, 1H), 3.73 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H);

Spectral data match those previously reported.[S6]



(*E*)-4-fluoro-*N*-(4-phenylbut-3-en-2-yl)aniline (**3ac**)

(*R*,*E*)-4-fluoro-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 46.1 mg, 96% yield, 91% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 99/1, v = 1.0 mL/min, λ = 254 nm, t (minor) = 13.05 min, t (major) = 14.12 min]. $[\alpha]_D^{20}$ = +51.7 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-4-fluoro-N-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 44.9 mg, 93% yield, 58% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 99/1, v = 1.0 mL/min, λ = 254 nm, t (minor) = 13.81 min, t (major) = 12.75 min].

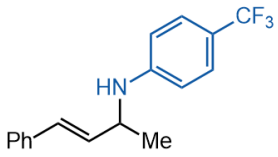
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 7.32–7.26 (m, 2H), 7.24–7.18 (m, 1H), 6.92–6.81 (m, 2H), 6.63–6.50 (m, 3H), 6.18 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.13–4.01 (m, 1H), 3.60 (br, s, 1H), 1.39 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (d, *J* = 235.0 Hz), 143.7 (d, *J* = 1.9 Hz), 136.9, 133.0, 129.5, 128.5, 127.4, 126.3, 115.6 (d, *J* = 22.2 Hz), 114.3 (d, *J* = 7.4 Hz), 51.6, 22.1;

^{19}F NMR (377 MHz, $CDCl_3$) δ -128.1;

IR (neat): ν_{max} (cm^{-1}) = 3412, 3028, 2967, 2923, 2859, 1608, 1501, 1306, 1205;

HRMS (ESI) calcd for $C_{16}H_{17}NF$ $[M+H]^+$: 242.1340. Found: 242.1346.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline (**3ad**)

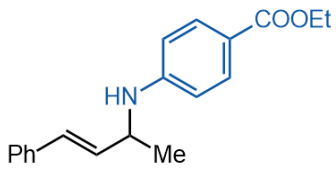
(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline was prepared following the General Procedure A as yellow oil: 56.2 mg, 96% yield, 79% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.91 min, t (major) = 10.71 min]. $[\alpha]_D^{20}$ = +53.6 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)aniline was prepared following the General Procedure B as yellow oil: 5.2 mg, 9% yield, 45% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 9.99 min, t (major) = 13.73 min].

Note: The low yield of (*S*)-**3ad** was due to incomplete conversion.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 4H), 7.32–7.27 (m, 2H), 7.25–7.19 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 15.9, 5.8 Hz, 1H), 4.23–4.12 (m, 1H), 4.07 (br, s, 1H), 1.42 (d, *J* = 6.5 Hz, 3H);

Spectral data match those previously reported.[S5]



ethyl (*E*)-4-((4-phenylbut-3-en-2-yl)amino)benzoate (**3ae**)

ethyl (*R*,*E*)-4-((4-phenylbut-3-en-2-yl)amino)benzoate was prepared following the General Procedure A as colorless oil: 56.5 mg, 96% yield, 81% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 15.74 min, t (major) = 28.01 min]. $[\alpha]_D^{20}$ = +98.1 (*c* = 1.0, CH_2Cl_2).

ethyl (*S*,*E*)-4-((4-phenylbut-3-en-2-yl)amino)benzoate was prepared following the General Procedure B as colorless oil: 14.6 mg, 25% yield, 57% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 27.54 min, t (major) = 15.44 min].

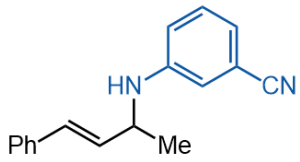
Note: The low yield of (*S*)-**3ae** was due to incomplete conversion.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 2H), 7.36–7.31 (m, 2H), 7.31–7.26 (m, 2H), 7.24–7.19 (m, 1H), 6.63–6.51 (m, 3H), 6.17 (dd, *J* = 15.9, 5.7 Hz, 1H), 4.36–4.10 (m, 4H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 151.0, 136.6, 131.9, 131.4, 129.8, 128.5, 127.5, 126.3, 118.8, 112.1, 60.1, 50.4, 21.8, 14.4;

IR (neat): ν_{max} (cm^{-1}) = 3366, 3028, 2975, 2927, 1689, 1600, 1520, 1264, 1165, 1104;

HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ $[M+H]^+$: 296.1645. Found: 296.1652.



(*E*)-3-((4-phenylbut-3-en-2-yl)amino)benzonitrile (**3af**)

(*R*,*E*)-3-((4-phenylbut-3-en-2-yl)amino)benzonitrile was prepared following the General Procedure A as bright yellow oil: 42.9 mg, 86% yield, 84% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.45 min, t (major) = 16.99 min]. $[\alpha]_D^{20}$ = +59.6 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-3-((4-phenylbut-3-en-2-yl)amino)benzonitrile was prepared following the General Procedure B as bright yellow oil: 3.5 mg, 7% yield, 58% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 16.48 min, t (major) = 14.13 min].

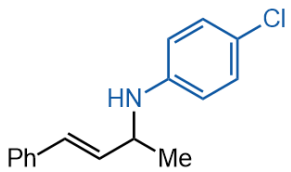
Note: The low yield of (*S*)-**3af** was due to incomplete conversion.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 4H), 7.25–7.16 (m, 2H), 6.95–6.90 (m, 1H), 6.87–6.76 (m, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.17–4.06 (m, 1H), 3.98 (s, 1H), 1.42 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 136.5, 131.7, 129.9, 129.8, 128.6, 127.6, 126.3, 120.7, 119.5, 117.6, 115.6, 112.8, 50.7, 21.9;

IR (neat): ν_{max} (cm^{-1}) = 3381, 3028, 2971, 2927, 2870, 1598, 1484, 1332, 964;

HRMS (ESI) calcd for $C_{17}H_{16}N_2Na$ $[M+Na]^+$: 271.1206. Found: 271.1211.



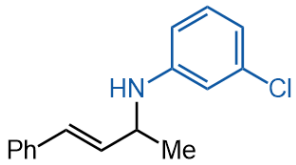
(*E*)-4-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline (**3ag**)

(*R*,*E*)-4-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 50.7 mg, 98% yield, 83% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 10.61 min, t (major) = 8.67 min]. $[\alpha]_D^{20}$ = +66.2 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-4-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 49.9 mg, 97% yield, 57% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 8.56 min, t (major) = 10.25 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 7.32–7.26 (m, 2H), 7.24–7.19 (m, 1H), 7.13–7.05 (m, 2H), 6.62–6.48 (m, 3H), 6.17 (dd, *J* = 15.9, 5.8 Hz, 1H), 4.15–4.03 (m, 1H), 3.74 (br, s, 1H), 1.39 (d, *J* = 6.6 Hz, 3H);

Spectral data match those previously reported.[S7]



(*E*)-3-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline (**3ah**)

(*R*,*E*)-3-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 48.2 mg, 93% yield, 83% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 8.96 min, t (major) = 10.95 min]. $[\alpha]_D^{20}$ = +56.9 (*c* = 1.0, CH_2Cl_2).

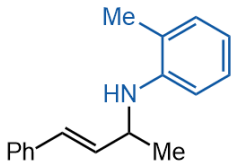
(*S*,*E*)-3-chloro-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 48.9 mg, 95% yield, 60% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 10.75 min, t (major) = 8.85 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.32–7.27 (m, 2H), 7.24–7.19 (m, 1H), 7.05 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.67–6.60 (m, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.50 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.17 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.18–4.06 (m, 1H), 3.82 (br, s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 136.8, 134.9, 132.4, 130.1, 129.6, 128.5, 127.5, 126.3, 117.2, 113.0, 111.6, 50.7, 22.0;

IR (neat): ν_{max} (cm^{-1}) = 3415, 3028, 2969, 2923, 2863, 1596, 1492, 1321, 1165, 1078;

HRMS (ESI) calcd for $C_{16}H_{17}NCl$ $[M+H]^+$: 258.1044. Found: 258.1054.



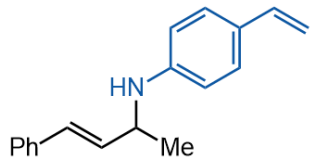
(*E*)-2-methyl-*N*-(4-phenylbut-3-en-2-yl)aniline (**3ai**)

(*R*,*E*)-2-methyl-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 42.6 mg, 90% yield, 85% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 7.79 min, t (major) = 14.76 min]. $[\alpha]_D^{20}$ = +23.0 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-2-methyl-*N*-(4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 45.7 mg, 96% yield, 57% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.87 min, t (major) = 7.68 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.31–7.26 (m, 2H), 7.22–7.17 (m, 1H), 7.12–7.02 (m, 2H), 6.70–6.61 (m, 2H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.24–4.14 (m, 1H), 3.55 (br, s, 1H), 2.18 (s, 3H), 1.44 (d, *J* = 6.6 Hz, 3H);

Spectral data match those previously reported.[S5]



(*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-vinylaniline (**3aj**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-vinylaniline was prepared following the General Procedure A as yellow oil: 49.0 mg, 98% yield, 91% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 10.24 min, t (major) = 11.84 min]. $[\alpha]_D^{20}$ = +77.9 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)-4-vinylaniline was prepared following the General Procedure B as yellow oil: 8.3 mg, 17% yield, 56% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.04 min, t (major) = 10.36 min].

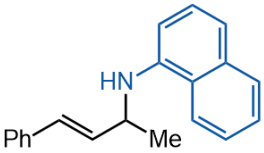
Note: The low yield of (*S*)-**3aj** was due to incomplete conversion.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 2H), 7.31–7.25 (m, 2H), 7.25–7.17 (m, 3H), 6.64–6.52 (m, 4H), 6.19 (dd, *J* = 16.0, 5.8 Hz, 1H), 5.50 (d, *J* = 17.6 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.20–4.10 (m, 1H), 3.77 (br, s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 136.9, 136.6, 132.9, 129.4, 128.5, 127.4, 127.3, 127.2, 126.3, 113.3, 109.4, 50.8, 22.0;

IR (neat): ν_{max} (cm^{-1}) = 3404, 3026, 2965, 2923, 2865, 1611, 1513, 1317, 1175;

HRMS (ESI) calcd for $C_{18}H_{20}N$ $[M+H]^+$: 250.1590. Found: 250.1596.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-1-amine (**3ak**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-1-amine was prepared following the General Procedure A as red oil: 52.9 mg, 97% yield, 80% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 18.94 min, t (major) = 27.20 min]. $[\alpha]_D^{20}$ = -85.6 (*c* = 1.0, CH_2Cl_2).

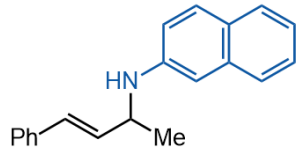
(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-1-amine was prepared following the General Procedure B as red oil: 46.7 mg, 85% yield, 66% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 27.60 min, t (major) = 18.28 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 1H), 7.82–7.76 (m, 1H), 7.49–7.40 (m, 2H), 7.38–7.33 (m, 2H), 7.33–7.25 (m, 3H), 7.24–7.17 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.40 (br, s, 1H), 4.37–4.28 (m, 1H), 1.54 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 136.9, 134.4, 132.9, 129.5, 128.7, 128.5, 127.4, 126.6, 126.3, 125.6, 124.6, 123.3, 119.8, 117.3, 105.7, 50.9, 22.2;

IR (neat): ν_{max} (cm^{-1}) = 3430, 3058, 3026, 2969, 2925, 2863, 1581, 1520, 1399;

HRMS (ESI) calcd for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590. Found: 274.1596.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-2-amine (**3al**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-2-amine was prepared following the General Procedure A as a red solid: 54.0 mg, 99% yield, 88% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 10.18 min, t (major) = 11.31 min]. $[\alpha]_D^{20}$ = +159.9 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)naphthalen-2-amine was prepared following the General Procedure B as a red solid: 49.8 mg, 91% yield, 58% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v =

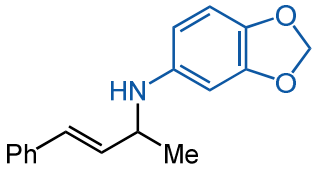
1.0 mL/min, λ = 254 nm, t (minor) = 11.41 min, t (major) = 10.24 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 11.7, 8.4 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.38–7.25 (m, 5H), 7.22–7.14 (m, 2H), 6.91 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 16.0, 5.6 Hz, 1H), 4.34–4.22 (m, 1H), 3.90 (br, s, 1H), 1.46 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 136.9, 135.1, 132.8, 129.4, 128.9, 128.5, 127.6, 127.5, 127.4, 126.3, 126.2, 126.0, 121.9, 118.1, 105.6, 50.8, 21.9;

IR (thin film): ν_{max} (cm^{-1}) = 3427, 3056, 3015, 2963, 2920, 2859, 1627, 1515, 1357;

HRMS (ESI) calcd for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590. Found: 274.1598.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d][1,3]dioxol-5-amine (**3am**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d][1,3]dioxol-5-amine was prepared following the General Procedure A as a yellow solid: 46.2 mg, 86% yield, 93% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 11.68 min, t (major) = 15.61 min]. $[\alpha]_D^{20}$ = +70.2 (*c* = 1.0, CH_2Cl_2).

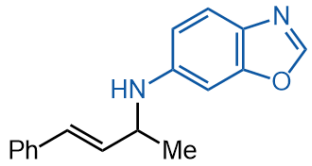
(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d][1,3]dioxol-5-amine was prepared following the General Procedure B as a yellow solid: 36.7 mg, 69% yield, 58% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.32 min, t (major) = 11.06 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 7.31–7.25 (m, 2H), 7.23–7.17 (m, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 2.3 Hz, 1H), 6.18 (dd, *J* = 16.0, 5.9 Hz, 1H), 6.08 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.82 (s, 2H), 4.08–3.98 (m, 1H), 3.45 (br, s, 1H), 1.37 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 143.1, 139.6, 136.9, 133.3, 129.3, 128.5, 127.3, 126.3, 108.6, 105.4, 100.5, 96.6, 51.9, 22.1;

IR (thin film): ν_{max} (cm^{-1}) = 3419, 2975, 2958, 2920, 2857, 1636, 1488, 1209, 1032;

HRMS (ESI) calcd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332. Found: 268.1337.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d]oxazol-6-amine (**3an**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d]oxazol-6-amine was prepared following the General Procedure A as a yellow solid: 44.9 mg, 85% yield, 91% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 80/20, v = 1.0 mL/min, λ = 254 nm, t (minor) = 9.71 min, t (major) = 21.00 min]. $[\alpha]_D^{20}$ = +82.1 (*c* = 1.0, CH_2Cl_2).

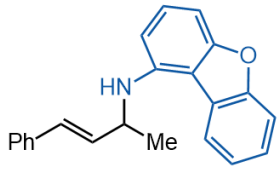
(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)benzo[d]oxazol-6-amine was prepared following the General Procedure B as a yellow solid: 18.9 mg, 36% yield, 48% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 80/20, v = 1.0 mL/min, λ = 254 nm, t (minor) = 21.44 min, t (major) = 9.70 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.32–7.26 (m, 2H), 7.24–7.18 (m, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.20–4.09 (m, 1H), 3.99 (br, s, 1H), 1.44 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 150.2, 146.4, 136.7, 132.5, 131.4, 129.7, 128.5, 127.5, 126.3, 120.4, 112.6, 94.1, 51.4, 22.0;

IR (thin film): ν_{max} (cm^{-1}) = 3341, 3113, 3024, 2963, 2923, 2842, 1625, 1488, 1201, 1070;

HRMS (ESI) calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335. Found: 265.1340.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]furan-1-amine (**3ao**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]furan-1-amine was prepared following the General Procedure A as a yellow solid: 62.0 mg, 99% yield, 78% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.17 min, t (major) = 13.99 min]. $[\alpha]_D^{20}$ = -153.9 (*c* = 1.0, CH_2Cl_2).

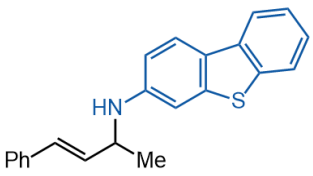
(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]furan-1-amine was prepared following the General Procedure B as a yellow solid: 23.2 mg, 37% yield, 58% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.34 min, t (major) = 12.20 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.43–7.32 (m, 4H), 7.31–7.25 (m, 3H), 7.23–7.18 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.32 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.48–4.33 (m, 2H), 1.57 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 155.3, 143.7, 136.8, 132.6, 129.7, 128.5, 128.4, 127.5, 126.4, 125.4, 124.0, 122.5, 120.1, 111.3, 110.3, 105.1, 100.8, 50.9, 22.3;

IR (thin film): ν_{max} (cm^{-1}) = 3436, 3026, 2963, 2925, 2861, 1596, 1501, 1237, 1175, 1061;

HRMS (ESI) calcd for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1539. Found: 314.1544.



(*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]thiophen-3-amine (**3ap**)

(*R*,*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]thiophen-3-amine was prepared following the General Procedure A as yellow oil: 61.4 mg, 93% yield, 82% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 15.71 min, t (major) = 18.10 min]. $[\alpha]_D^{20}$ = +119.9 (*c* = 1.0, CH_2Cl_2).

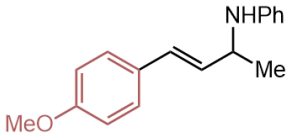
(*S*,*E*)-*N*-(4-phenylbut-3-en-2-yl)dibenzo[b,d]thiophen-3-amine was prepared following the General Procedure B as yellow oil: 64.6 mg, 98% yield, 18% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 18.36 min, t (major) = 15.90 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.38–7.31 (m, 3H), 7.31–7.24 (m, 3H), 7.21–7.16 (m, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.59 (dd, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 5.6 Hz, 1H), 4.27–4.14 (m, 1H), 3.93 (br, s, 1H), 1.42 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 141.5, 137.9, 136.8, 136.1, 132.6, 129.5, 128.5, 127.4, 126.4, 126.3, 124.7, 124.2, 122.5, 122.1, 120.0, 112.6, 104.9, 51.0, 22.0;

IR (neat): ν_{max} (cm^{-1}) = 3411, 3062, 3024, 2969, 2920, 1602, 1494, 1452;

HRMS (ESI) calcd for $C_{22}H_{20}NS$ $[M+H]^+$: 330.1311. Found: 330.1315.



(*E*)-*N*-(4-(4-methoxyphenyl)but-3-en-2-yl)aniline (**3ba**)

(*R*,*E*)-*N*-(4-(4-methoxyphenyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as a white solid: 49.1 mg, 97% yield, 84% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 9.45 min, t (major) = 12.39 min]. $[\alpha]_D^{20}$ = +60.0 (*c* = 1.0, CH_2Cl_2).

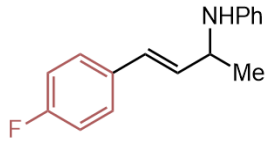
(*S*,*E*)-*N*-(4-(4-methoxyphenyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as a white solid: 47.3 mg, 93% yield, 40% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 90/10, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.51 min, t (major) = 9.24 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 7.19–7.09 (m, 2H), 6.87–6.79 (m, 2H), 6.73–6.59 (m, 3H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.06 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.16–4.06 (m, 1H), 3.78 (s, 3H), 3.68 (br, s, 1H), 1.38 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 147.5, 131.0, 129.8, 129.1, 128.7, 127.4, 117.2, 113.9, 113.4, 55.3, 50.8, 22.1;

IR (thin film): ν_{max} (cm^{-1}) = 3366, 3051, 3022, 2963, 2920, 1600, 1507, 1494, 1251, 1019;

HRMS (ESI) calcd for $C_{17}H_{19}NONa$ $[M+Na]^+$: 276.1359. Found: 276.1365.



(*E*)-*N*-(4-(4-fluorophenyl)but-3-en-2-yl)aniline (**3ca**)

(*R*,*E*)-*N*-(4-(4-fluorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as colorless oil: 44.3 mg, 92% yield, 92% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 9.93 min, t (major) = 12.59 min]. $[\alpha]_D^{20}$ = +55.5 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-(4-fluorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as colorless oil: 46.3 mg, 96% yield, 64% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.75 min, t (major) = 9.52 min].

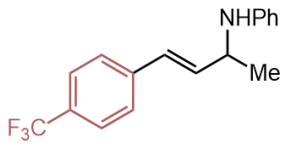
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 2H), 7.16 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.97 (dd, *J* = 8.7, 8.7 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.18–4.07 (m, 1H), 3.70 (br, s, 1H), 1.39 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.4 Hz), 147.3, 133.1 (d, *J* = 3.3 Hz), 132.9 (d, *J* = 2.2 Hz), 129.2, 128.1, 127.8 (d, *J* = 8.0 Hz), 117.4, 115.4 (d, *J* = 21.5 Hz), 113.4, 50.8, 22.1;

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.9;

IR (neat): ν_{max} (cm^{-1}) = 3411, 3049, 2969, 2920, 1600, 1503, 1315, 1224, 1156;

HRMS (ESI) calcd for $C_{16}H_{17}NF$ $[M+H]^+$: 242.1340. Found: 242.1346.



(*E*)-*N*-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)aniline (**3da**)

(*R*,*E*)-*N*-(4-(4-fluorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 28.3 mg, 49% yield, 92% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.00 min, t (major) = 14.29 min]. $[\alpha]_D^{20}$ = +47.4 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(4-(4-fluorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 12.6 mg, 22% yield, 62% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.35 min, t (major) = 11.46 min].

Note: The low yield of (*S*)-**3da** was due to incomplete conversion.

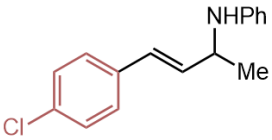
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.20-7.13 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.67–6.57 (m, 3H), 6.32 (dd, *J* = 16.0, 5.6 Hz, 1H), 4.21–4.09 (m, 1H), 3.72 (br, s, 1H), 1.42 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 140.5, 135.9, 129.2, 129.1 (q, *J* = 32.4 Hz), 128.0, 126.5, 125.4 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.7 Hz), 117.5, 113.4, 50.8, 22.0;

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.5;

IR (neat): ν_{max} (cm^{-1}) = 3427, 3054, 3028, 2977, 2929, 1604, 1501, 1323, 1158, 1118;

HRMS (ESI) calcd for $C_{17}H_{17}NF_3$ $[M+H]^+$: 292.1308. Found: 292.1313.



(*E*)-*N*-(4-(4-chlorophenyl)but-3-en-2-yl)aniline (**3ea**)

(*R*,*E*)-*N*-(4-(4-chlorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as a yellow solid: 38.6 mg, 75% yield, 93% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 11.08 min, t (major) = 13.71 min]. $[\alpha]_D^{20}$ = +67.9 (*c* = 1.0, CH_2Cl_2).

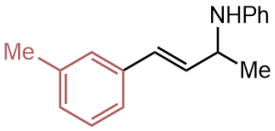
(*S*,*E*)-*N*-(4-(4-chlorophenyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as a yellow solid: 48.2 mg, 93% yield, 68% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 13.97 min, t (major) = 10.75 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 4H), 7.19–7.12 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.17–4.07 (m, 1H), 3.70 (br, s, 1H), 1.39 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 135.5, 133.9, 132.9, 129.2, 128.6, 128.1, 127.5, 117.4, 113.4, 50.8, 22.0;

IR (thin film): ν_{max} (cm^{-1}) = 3408, 3049, 3022, 2967, 2925, 2865, 1600, 1501, 1488, 1315;

HRMS (ESI) calcd for $C_{16}H_{16}NClNa$ $[M+Na]^+$: 280.0863. Found: 280.0871.



(*E*)-*N*-(4-(m-tolyl)but-3-en-2-yl)aniline (**3fa**)

(*R*,*E*)-*N*-(4-(m-tolyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as colorless oil: 44.8 mg, 94% yield, 92% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 9.59 min, t (major) = 11.20 min]. $[\alpha]_D^{20}$ = +61.9 (*c* = 1.0, CH_2Cl_2).

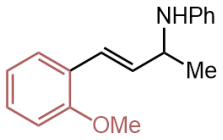
(*S*,*E*)-*N*-(4-(m-tolyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as colorless oil: 46.3 mg, 98% yield, 58% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 11.57 min, t (major) = 9.16 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.12 (m, 5H), 7.04–7.00 (m, 1H), 6.71–6.61 (m, 3H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 16.0, 5.8 Hz, 1H), 4.18–4.08 (m, 1H), 3.70 (br, s, 1H), 2.32 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 138.0, 136.9, 133.0, 129.3, 129.2, 128.4, 128.1, 127.0, 123.5, 117.3, 113.4, 50.8, 22.1, 21.3;

IR (neat): ν_{max} (cm^{-1}) = 3406, 3054, 3020, 2967, 2920, 2865, 1598, 1501, 1313, 960;

HRMS (ESI) calcd for $C_{17}H_{20}N$ $[M+H]^+$: 238.1590. Found: 238.1595.



(*E*)-*N*-(4-(2-methoxyphenyl)but-3-en-2-yl)aniline (**3ga**)

(*R*,*E*)-*N*-(4-(2-methoxyphenyl)but-3-en-2-yl)aniline was prepared following the General Procedure A as colorless oil: 42.0 mg, 83% yield, 92% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 16.35 min, t (major) = 12.32 min]. $[\alpha]_D^{20}$ = +45.3 (*c* = 1.0, CH_2Cl_2).

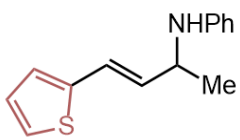
(*S*,*E*)-*N*-(4-(2-methoxyphenyl)but-3-en-2-yl)aniline was prepared following the General Procedure B as colorless oil: 48.1 mg, 95% yield, 27% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 12.48 min, t (major) = 15.62 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.22-7.11 (m, 3H), 6.94–6.82 (m, 3H), 6.71–6.61 (m, 3H), 6.21 (dd, *J* = 16.1, 6.1 Hz, 1H), 4.21–4.11 (m, 1H), 3.82 (s, 3H), 3.78–3.61 (br, s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.5, 133.9, 129.1, 128.4, 126.7, 126.0, 124.2, 120.6, 117.2, 113.5, 110.9, 55.5, 51.2, 22.1;

IR (neat): ν_{max} (cm^{-1}) = 3400, 2984, 2956, 2920, 2844, 1608, 1505, 1319, 1239, 1027;

HRMS (ESI) calcd for $C_{17}H_{20}NO$ $[M+H]^+$: 254.1539. Found: 254.1545.



(*E*)-*N*-(4-(thiophen-2-yl)but-3-en-2-yl)aniline (**3ha**)

(*R*,*E*)-*N*-(4-(thiophen-2-yl)but-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 28.8 mg, 63% yield, 91% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 11.47 min, t (major) = 14.90 min]. $[\alpha]_D^{20}$ = +69.4 (*c* = 1.0, CH_2Cl_2).

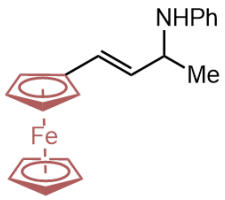
(*S*,*E*)-*N*-(4-(thiophen-2-yl)but-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 43.4 mg, 95% yield, 34% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 14.60 min, t (major) = 10.65 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.13 (m, 2H), 7.11 (d, *J* = 5.0 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.91–6.88 (m, 1H), 6.74–6.66 (m, 2H), 6.65–6.60 (m, 2H), 6.07 (dd, *J* = 15.8, 5.6 Hz, 1H), 4.13–4.04 (m, 1H), 3.68 (br, s, 1H), 1.38 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 142.2, 132.8, 129.2, 127.3, 125.3, 123.8, 122.5, 117.4, 113.3, 50.6, 22.0;

IR (neat): ν_{max} (cm^{-1}) = 3406, 3051, 3018, 2967, 2925, 2865, 1600, 1503, 1317, 956;

HRMS (ESI) calcd for $C_{14}H_{16}NS$ $[M+H]^+$: 230.0998. Found: 230.1005.



(*E*)-*N*-[4-(ferrocenyl)but-3-en-2-yl]aniline (**3ia**)

(*R*,*E*)-*N*-[4-(ferrocenyl)but-3-en-2-yl]aniline was prepared following the General Procedure A as an orange-yellow solid: 52.8 mg, 80% yield, 68% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 15.46 min, t (major) = 16.85 min]. $[\alpha]_D^{20}$ = +21.2 (*c* = 1.0, CH_2Cl_2).

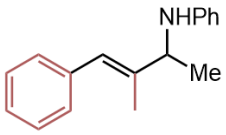
(*S*,*E*)-*N*-[4-(ferrocenyl)but-3-en-2-yl]aniline was prepared following the General Procedure B as an orange-yellow solid: 60.8 mg, 92% yield, 13% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 15.68 min, t (major) = 13.45 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.14 (m, 2H), 6.71–6.65 (m, 3H), 6.28 (d, *J* = 15.8 Hz, 1H), 5.76 (dd, *J* = 15.8, 6.1 Hz, 1H), 4.31–4.25 (m, 2H), 4.18–4.14 (m, 2H), 4.08–3.95 (m, 6H), 3.67 (br, s, 1H), 1.34 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 130.3, 129.1, 126.8, 117.4, 113.6, 82.9, 69.0, 68.53, 68.47, 66.7, 66.5, 51.1, 22.3;

IR (thin film): ν_{max} (cm^{-1}) = 3394, 3089, 2963, 2920, 2851, 1604, 1503, 1101, 956;

HRMS (ESI) calcd for $C_{20}H_{21}NFe$ $[M]^+$: 331.1018. Found: 331.1023.



(*E*)-*N*-(3-methyl-4-phenylbut-3-en-2-yl)aniline (**3ja**)

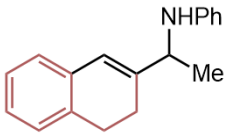
(*R*,*E*)-*N*-(3-methyl-4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure A as colorless oil: 39.1 mg, 82% yield, 92% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 5.58 min, t (major) = 6.10 min]. $[\alpha]_D^{20}$ = +27.5 (*c* = 1.0, CH_2Cl_2). (*S*,*E*)-*N*-(3-methyl-4-phenylbut-3-en-2-yl)aniline was prepared following the General Procedure B as colorless oil: 44.9 mg, 95% yield, 67% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 5.89 min, t (major) = 5.46 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.26–7.21 (m, 2H), 7.21–7.10 (m, 3H), 6.70–6.65 (m, 1H), 6.64–6.59 (m, 2H), 6.56 (s, 1H), 3.97 (q, *J* = 6.7 Hz, 1H), 3.80 (br, s, 1H), 1.84 (d, *J* = 1.4 Hz, 3H), 1.40 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 140.5, 138.0, 129.1, 128.9, 128.0, 126.2, 125.0, 117.1, 113.2, 56.8, 21.5, 13.8;

IR (neat): ν_{max} (cm^{-1}) = 3411, 3054, 3020, 2971, 2923, 1600, 1503, 1317, 1254;

HRMS (ESI) calcd for $C_{17}H_{20}N$ $[M+H]^+$: 238.1590. Found: 238.1597.



N-(1-(3,4-dihydronaphthalen-2-yl)ethyl)aniline (**3ka**)

(*R*)-*N*-(1-(3,4-dihydronaphthalen-2-yl)ethyl)aniline was prepared following the General Procedure A as yellow oil: 22.5 mg, 45% yield, 70% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 6.33 min, t (major) = 7.14 min]. $[\alpha]_D^{20}$ = +32.8 (*c* = 0.5, CH_2Cl_2).

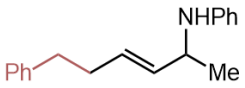
(*S*)-*N*-(1-(3,4-dihydronaphthalen-2-yl)ethyl)aniline was prepared following the General Procedure B as yellow oil: 18.9 mg, 38% yield, 85% ee. [Daicel Chiralcel AD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 97/3, v = 1.0 mL/min, λ = 254 nm, t (minor) = 6.92 min, t (major) = 6.18 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.06 (m, 5H), 7.02–6.98 (m, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.63–6.59 (m, 2H), 6.46 (s, 1H), 4.03 (q, *J* = 6.7 Hz, 1H), 3.78 (br, s, 1H), 2.87–2.70 (m, 2H), 2.28 (t, *J* = 8.1 Hz, 2H), 1.39 (d, *J* = 6.7 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 143.6, 135.0, 134.4, 129.1, 127.2, 126.5, 126.4, 125.9, 122.3, 117.2, 113.3, 54.3, 28.2, 23.6, 21.2;

IR (neat): ν_{max} (cm^{-1}) = 3413, 3018, 2965, 2927, 2878, 2825, 1602, 1503, 1315;

HRMS (ESI) calcd for $C_{18}H_{19}NNa$ $[M+Na]^+$: 272.1410. Found: 272.1416.



(*E*)-*N*-(6-phenylhex-3-en-2-yl)aniline (**3la**)

(*R*,*E*)-*N*-(6-phenylhex-3-en-2-yl)aniline was prepared following the General Procedure A as colorless oil: 24.6 mg, 49% yield, 81% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 7.76 min, t (major) = 8.55 min]. $[\alpha]_D^{20}$ = +15.0 (*c* = 1.0, CH_2Cl_2).

(*S*,*E*)-*N*-(6-phenylhex-3-en-2-yl)aniline was prepared following the General Procedure B as colorless oil: 42.7 mg, 85% yield, 44% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 95/5, v = 1.0 mL/min, λ = 254 nm, t (minor) = 8.55 min, t (major) = 7.33 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (m, 2H), 7.20–7.10 (m, 5H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.60–6.55 (m, 2H), 5.71–5.60 (m, 1H), 5.41 (dd, *J* = 15.4, 6.0 Hz, 1H), 3.98–3.86 (m, 1H), 3.57 (br, s, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.39–2.27 (m, 2H), 1.25 (d, *J* = 6.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 141.8, 133.8, 129.4, 129.1, 128.5, 128.2, 125.7, 117.1, 113.4, 50.4, 35.8, 34.0, 22.0;

IR (neat): ν_{max} (cm^{-1}) = 3406, 3024, 2971, 2920, 2853, 1600, 1501, 1317;

HRMS (ESI) calcd for $C_{18}H_{22}N$ $[M+H]^+$: 252.1747. Found: 252.1752.

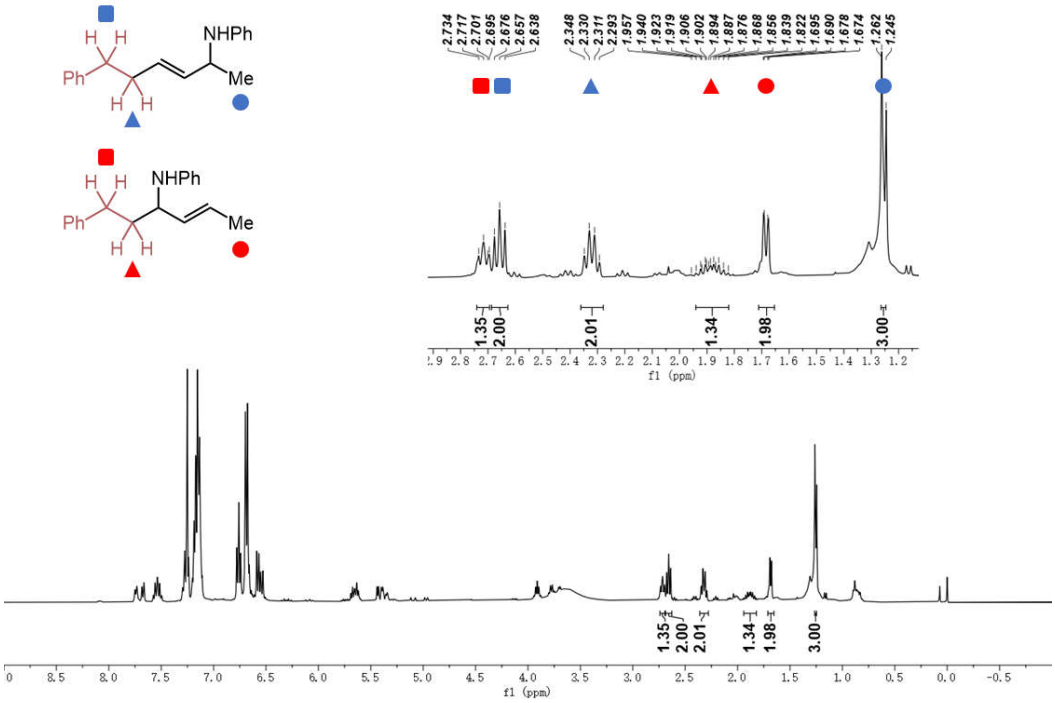
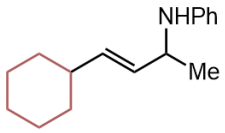


Figure S2. ^{1}H NMR analysis for determining the ratio of regioisomers in the crude product (*S*)-**3la**.



(*E*)-*N*-(4-cyclohexylbut-3-en-2-yl)aniline (**3ma**)

(*R*,*E*)-*N*-(4-cyclohexylbut-3-en-2-yl)aniline was prepared following the General Procedure A as yellow oil: 20.0 mg, 44% yield, 87% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 100/0, v = 1.0 mL/min, λ = 254 nm, t (minor) = 17.07 min, t (major) = 19.36 min]. $[\alpha]_D^{20}$ = +18.2 (*c* = 0.5, CH_2Cl_2).

(*S*,*E*)-*N*-(4-cyclohexylbut-3-en-2-yl)aniline was prepared following the General Procedure B as yellow oil: 35.4 mg, 77% yield, 30% ee. [Daicel Chiralcel OD-H (0.46 cm × 25 cm), *n*-hexane/*i*-PrOH = 100/0, v = 1.0 mL/min, λ = 254 nm, t (minor) = 19.99 min, t (major) = 16.72 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.10 (m, 2H), 6.69–6.63 (m, 1H), 6.63–6.56 (m, 2H), 5.57 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.35 (dd, *J* = 15.6, 6.1 Hz, 1H), 4.00–3.83 (m, 1H), 3.58 (br, s, 1H), 1.97–1.83 (m, 1H), 1.73–1.58 (m, 5H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.26–1.18 (m, 2H), 1.18–1.10 (m, 1H), 1.10–0.98 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 136.5, 130.4, 129.0, 117.0, 113.5, 50.7, 40.3, 33.0, 32.9, 26.2, 26.0, 22.1;

IR (neat): ν_{max} (cm^{-1}) = 3411, 2969, 2920, 2849, 1600, 1499, 1315, 966;

HRMS (ESI) calcd for $C_{16}H_{24}N$ $[M+H]^+$: 230.1903. Found: 230.1912.

VI. Crystallographic Data

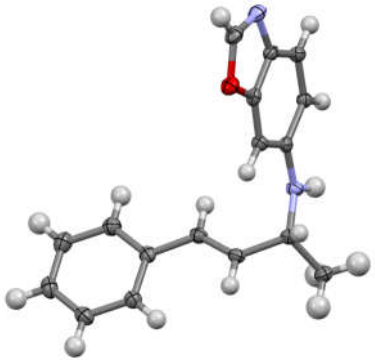


Figure S3. X-ray crystallographic structure of (*R*)-**3an** (CCDC #2491238)

Table S19. Crystal data and structure refinement for (*R*)-**3an**

Identification code	(*R*)-**3an**
Empirical formula	$C_{17}H_{16}N_2O$
Formula weight	264.32
Temperature/K	130.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.6491(13)
b/Å	12.775(3)
c/Å	22.835(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1356.3(6)
Z	4
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.411
F(000)	560.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.736 to 115.864
Index ranges	$-3 \leqslant h \leqslant 5, -16 \leqslant k \leqslant 16, -28 \leqslant l \leqslant 28$
Reflections collected	22137
Independent reflections	2797 [R_{int} = 0.0453, R_{sigma} = 0.0232]
Data/restraints/parameters	2797/0/186
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0693
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0705
Largest diff. peak/hole / e Å^{-3}	0.13/-0.14
Flack parameter	-0.06(14)

VII. References

[S1] Ren, T.; Wang, X.; Cong H. *Chin. J. Org. Chem.* **2025**, *45*, 2208-2221.

[S2] Long, J.; Wang, P.; Wang, W.; Li, Y.-Q.; Yin, G.-Y. *iScience* **2019**, *22*, 369-379.

[S3] Bhowmik, A.; Fernandes, R. A. *Org. Lett.* **2019**, *21*, 9203-9207.

[S4] Adamson, N. J.; Hull, E.; Malcolmson, S. J. *J. Am. Chem. Soc.* **2017**, *139*, 7180-7183.

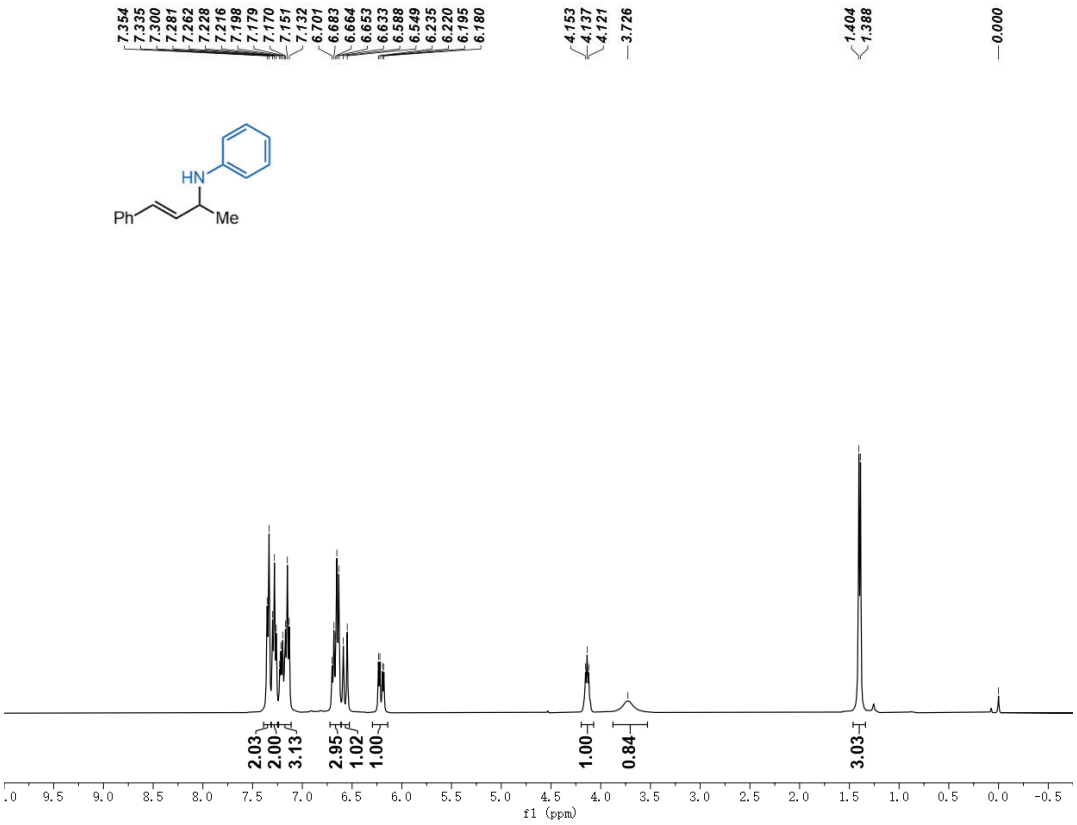
[S5] Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. *J. Am. Chem. Soc.* **2014**, *136*, 6227-6230.

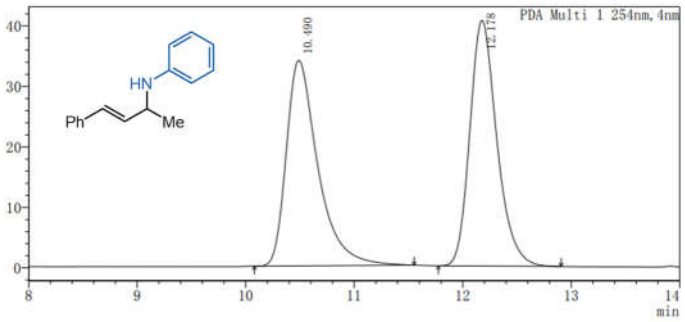
[S6] Denmark, S. E.; Nakajima, N.; Stiff, C. M.; Nicaise, O. J. C.; Kranz, M. *Adv. Synth. Catal.* **2008**, *350*, 1023-1045.

[S7] Hood, T. S.; Huehls, C. B.; Yang, J. *Tetrahedron Lett.* **2012**, *53*, 4679-4682.

VIII. Copies of NMR and HPLC Spectra

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



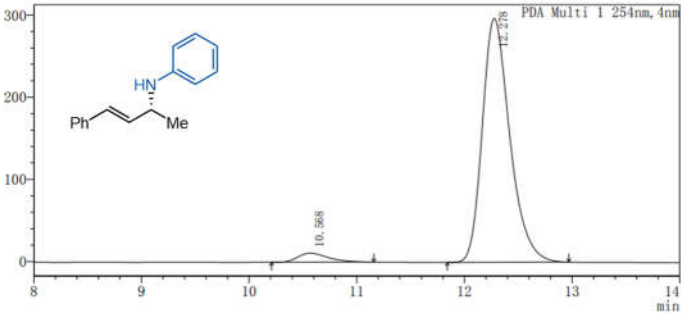


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.490	688249	33974	49.466
2	12.178	703106	40580	50.534
总计		1391355	74553	100.000

Total

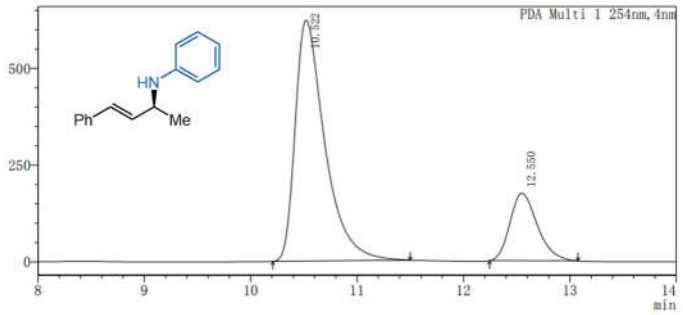


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.568	216391	11075	3.938
2	12.278	5278145	296861	96.062
总计		5494535	307936	100.000

Total



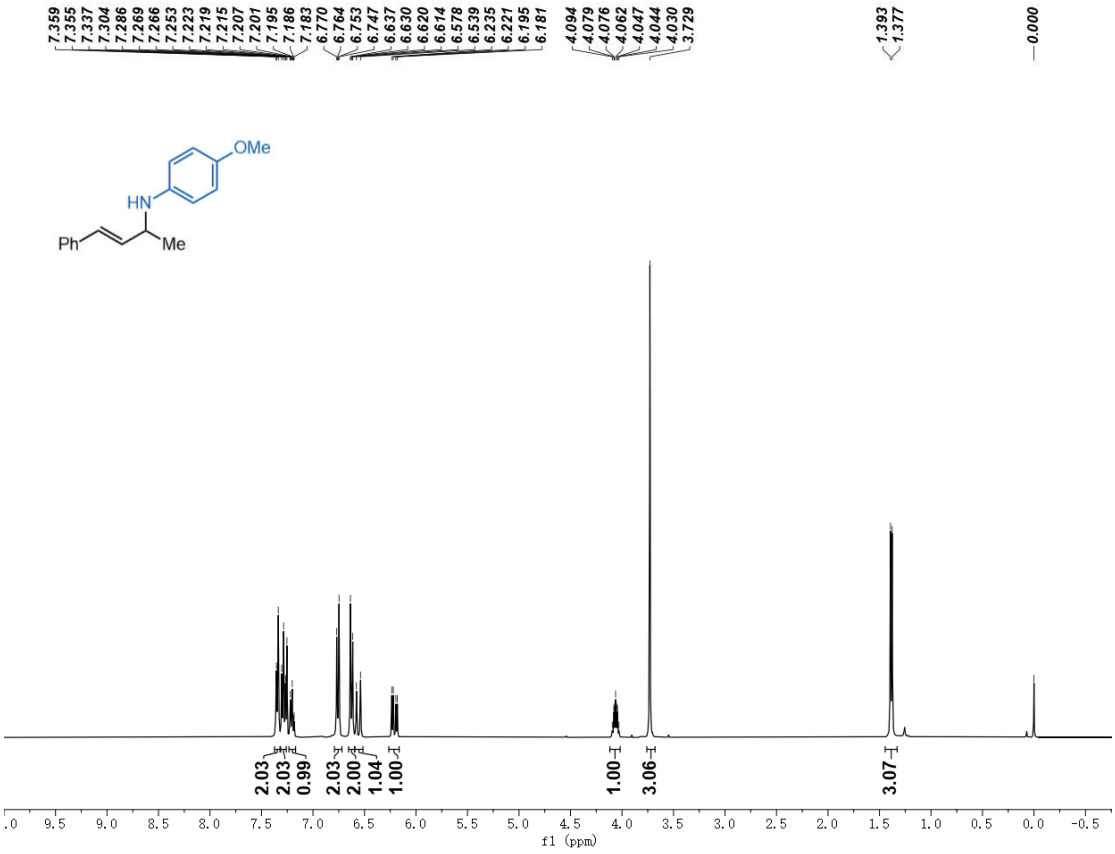
Entry Retention time Area Height Area%

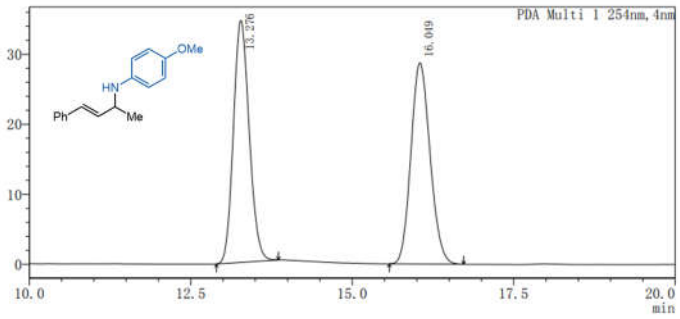
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.522	12081775	623211	79.384
2	12.550	3137696	174324	20.616
总计		15219471	797535	100.000

Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



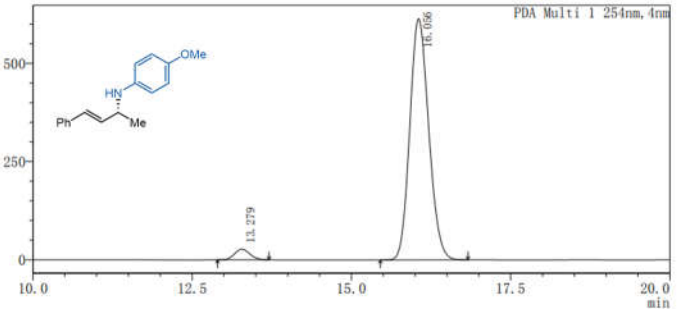


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	13.276	587921	34516	49.760
2	16.049	593581	28721	50.240
总计		1181502	63237	100.000

Total

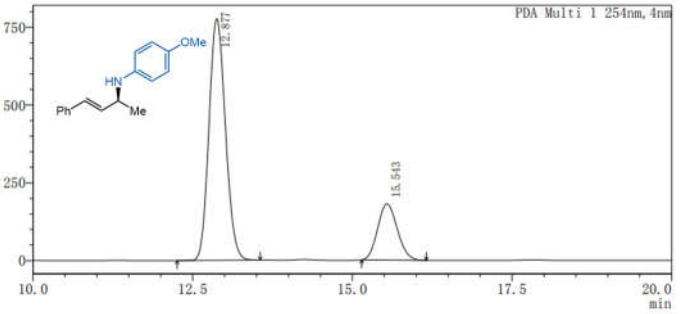


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	13.279	457401	27187	3.476
2	16.056	12700005	614189	96.524
总计		13157406	641376	100.000

Total



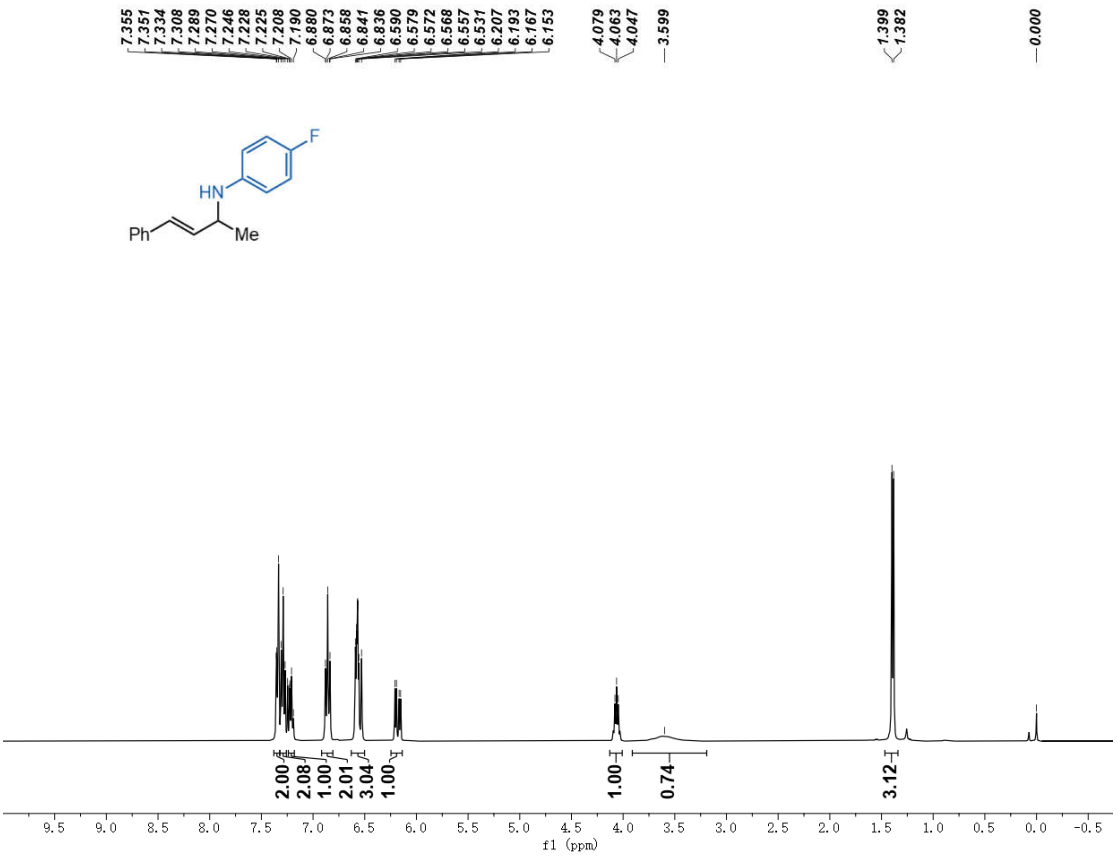
Entry Retention time Area Height Area%

PDA Ch1 254nm

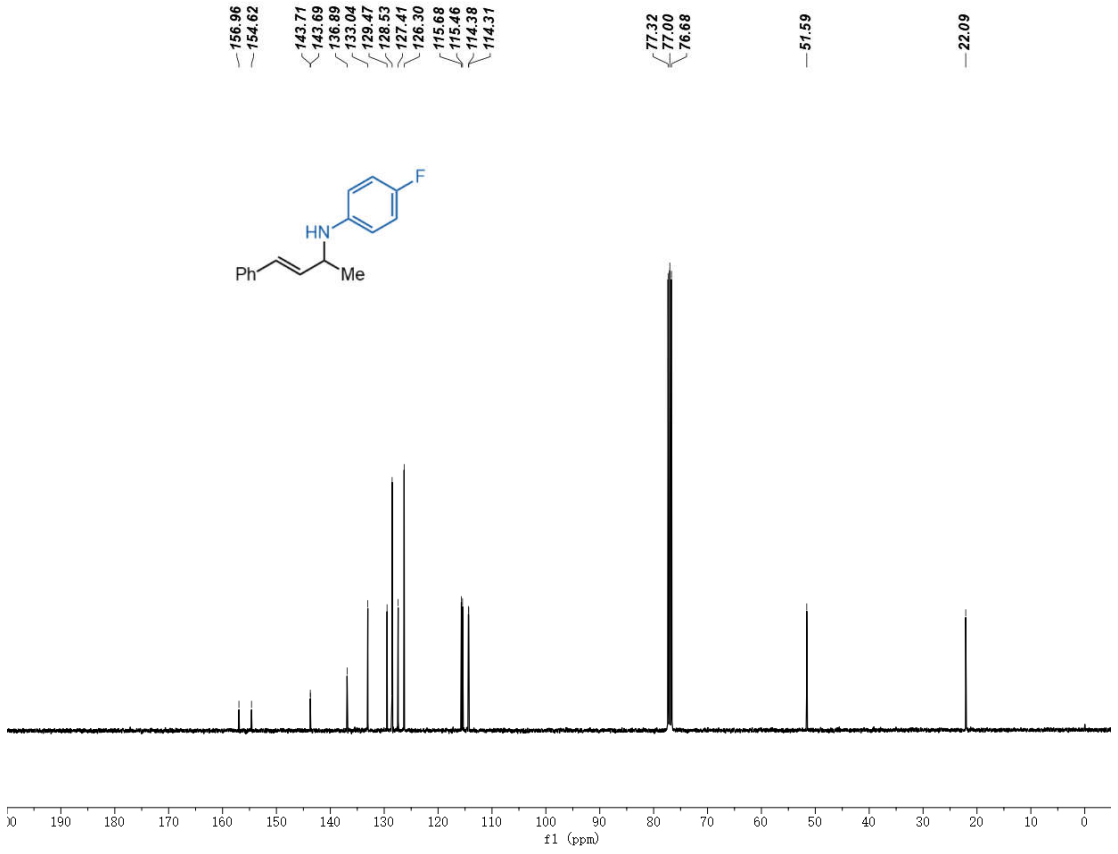
峰号	保留时间	面积	高度	面积%
1	12.877	13915712	776330	78.276
2	15.543	3862126	180956	21.724
总计		17777838	957287	100.000

Total

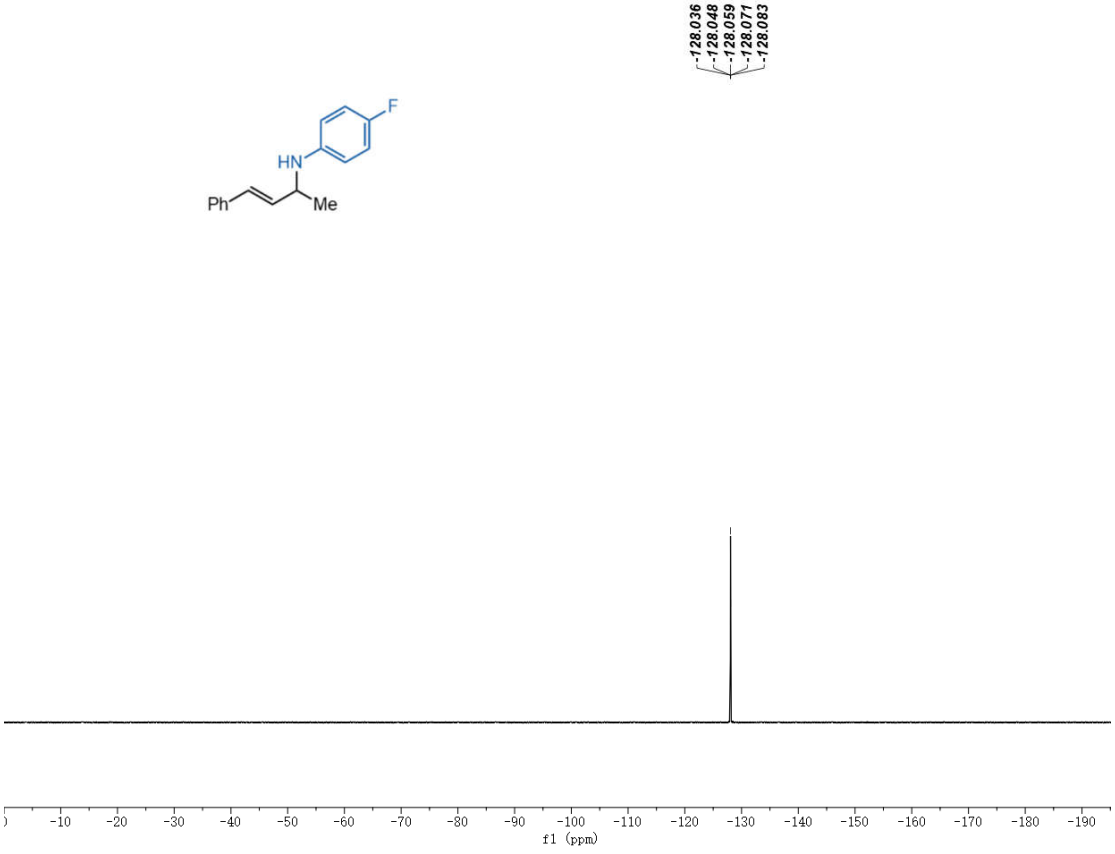
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**

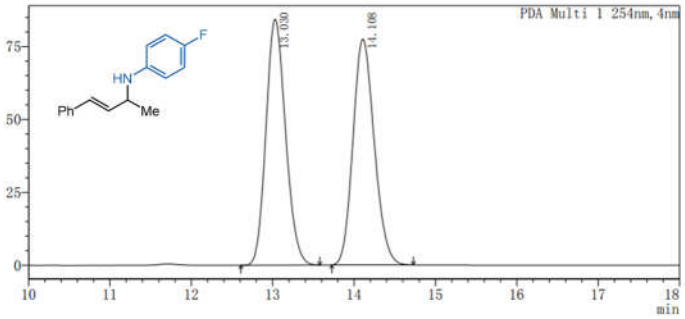


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3ac**





Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	13.030	1414947	84274	50.048
2	14.108	1412257	77454	49.952
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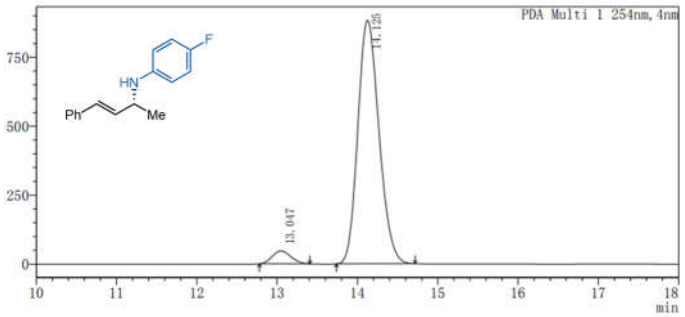
Total

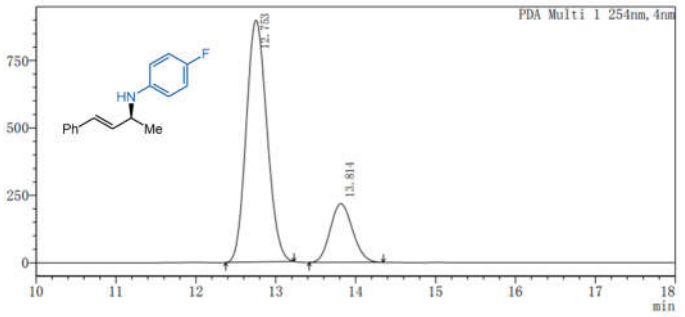


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	13.047	755218	46885	4.457
2	14.125	16187865	882696	95.543
总计		16943083	929581	100.000

Total



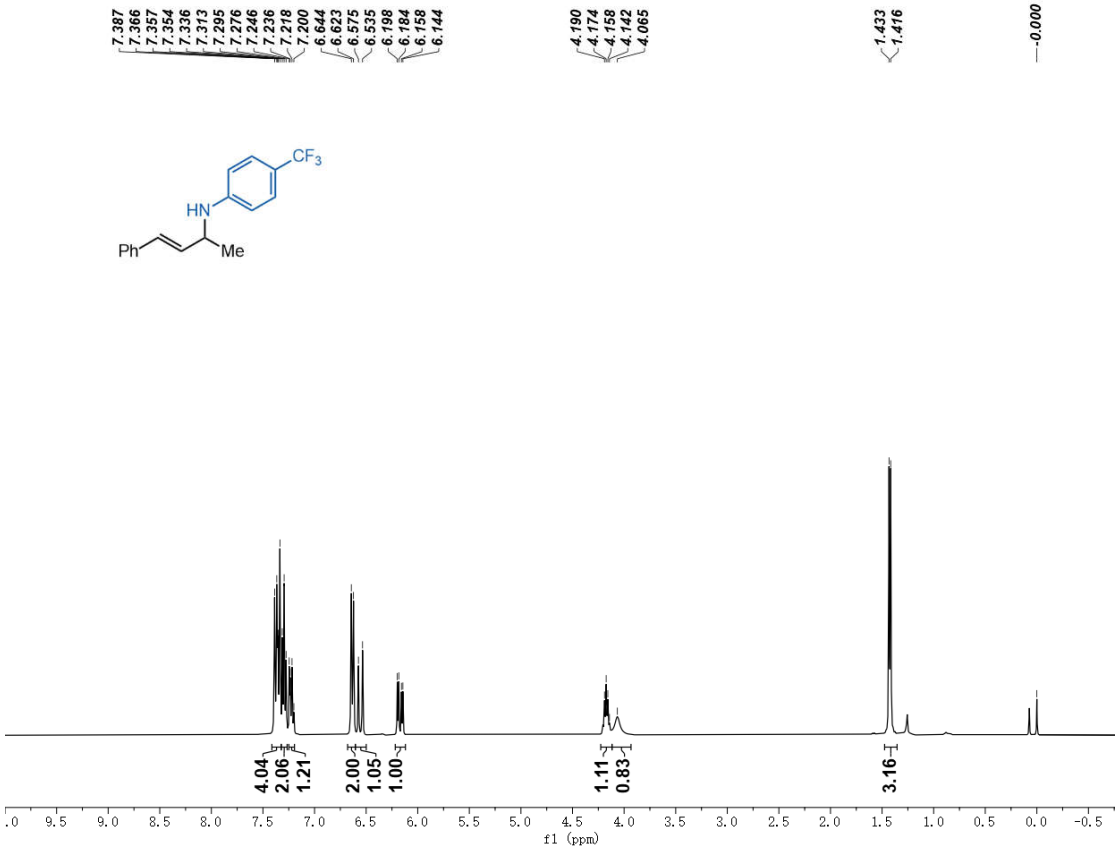
Entry Retention time Area Height Area%

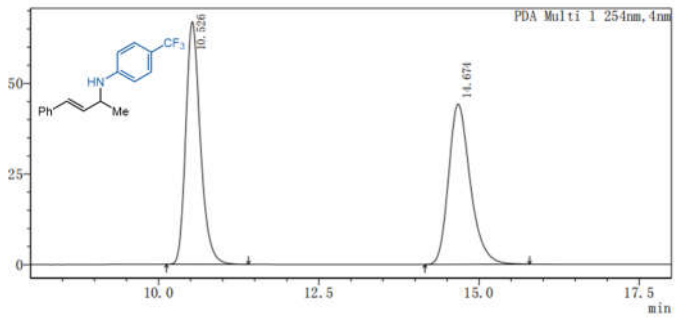
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	12.753	16200250	896290	79.245
2	13.814	4242957	217971	20.755
总计		20443207	1114260	100.000

Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



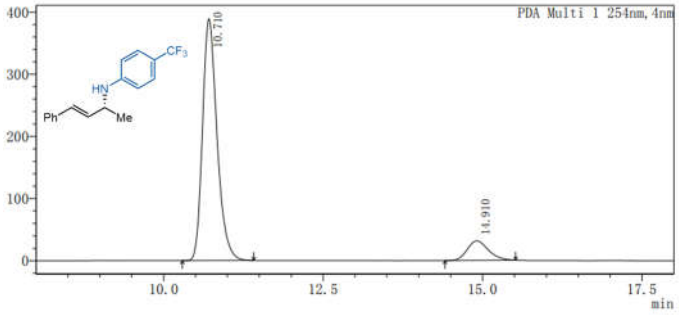


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.526	1061071	66802	50.443
2	14.674	1042446	44182	49.557
总计		2103517	110984	100.000

Total

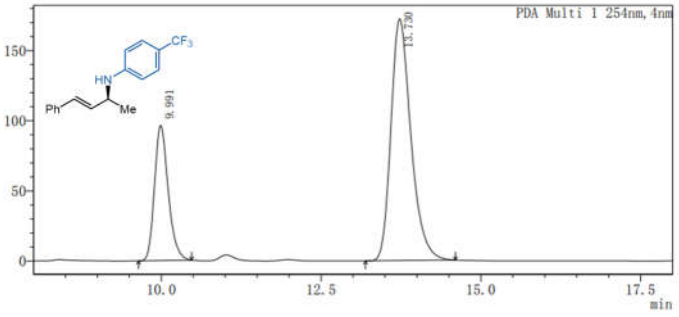


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.710	6159533	389037	89.439
2	14.910	727286	31541	10.561
总计		6886819	420578	100.000

Total



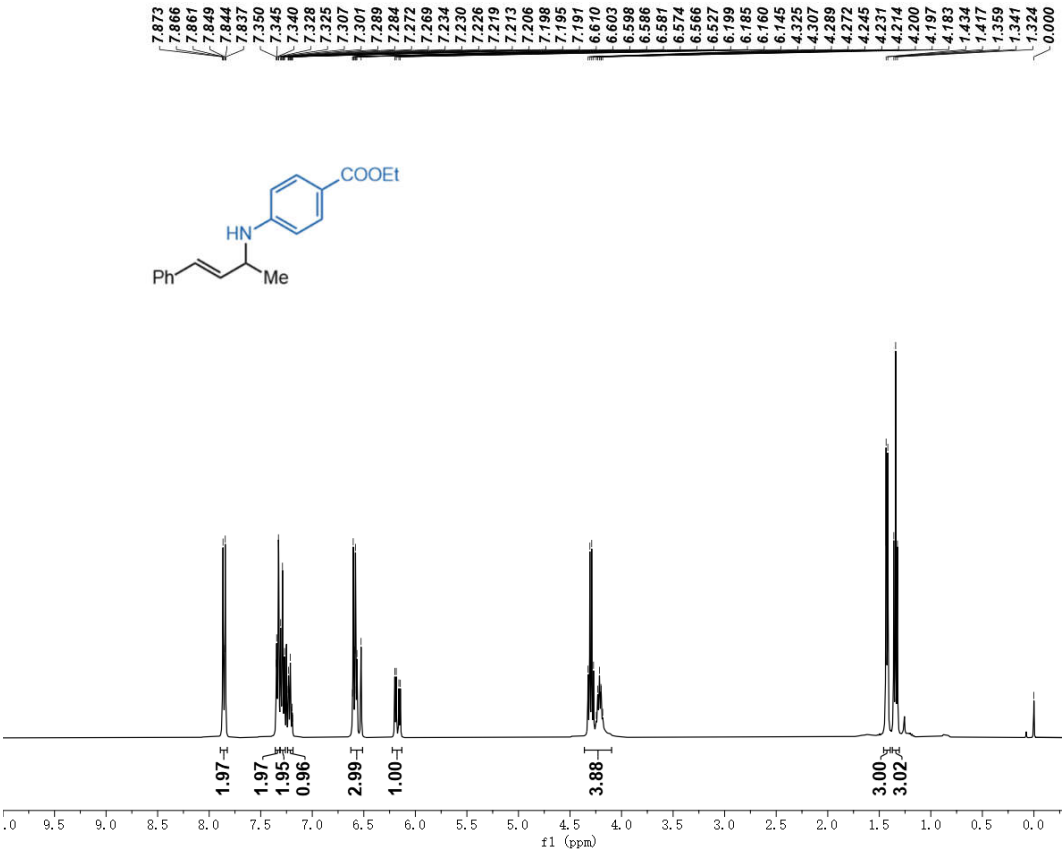
Entry Retention time Area Height Area%

PDA Ch1 254nm

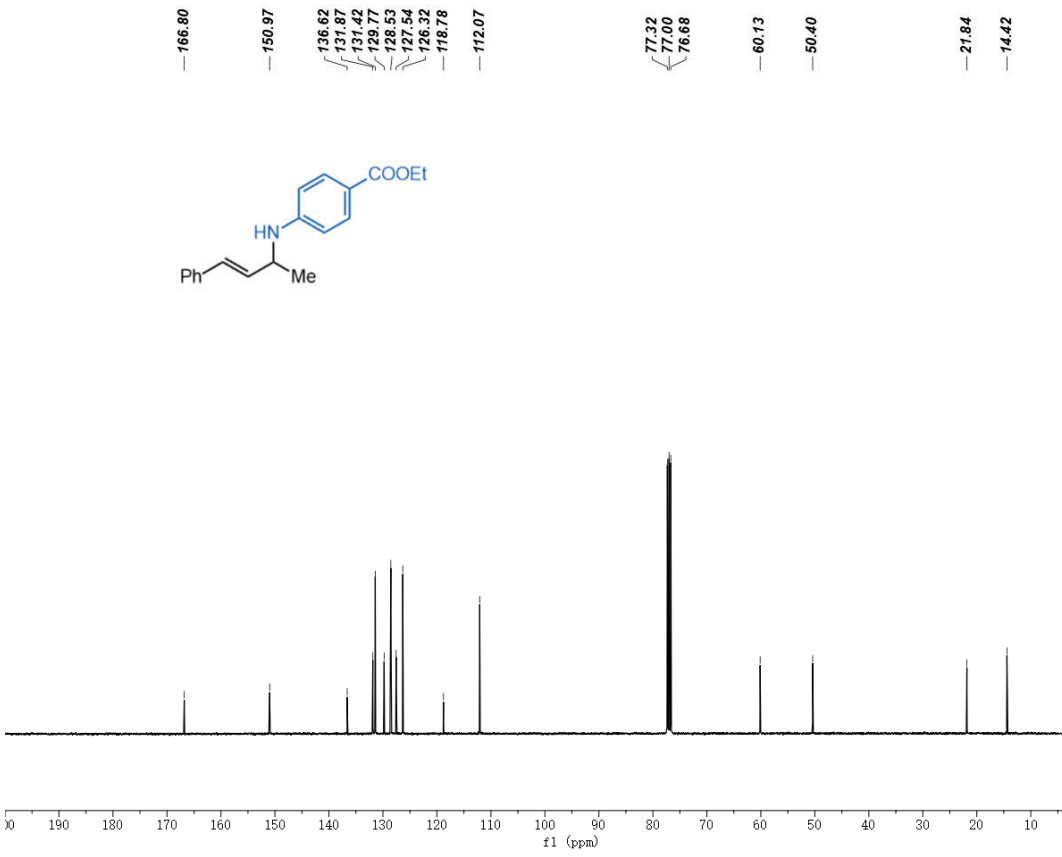
峰号	保留时间	面积	高度	面积%
1	9.991	1441594	96434	27.748
2	13.730	3753787	172171	72.252
总计		5195381	268604	100.000

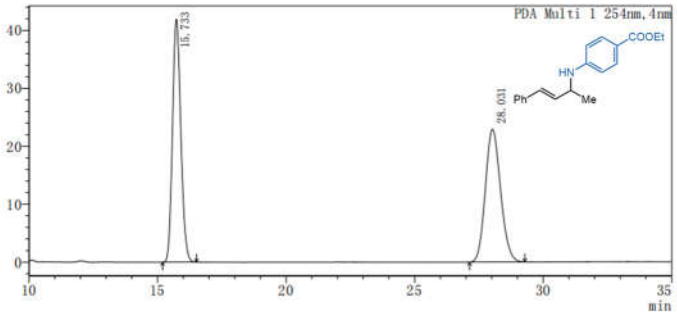
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ae**



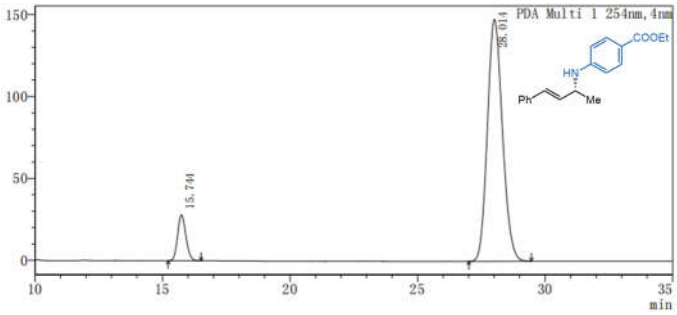


Entry	Retention time	Area	Height	Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.733	944295	41871	50.040
2	28.031	942791	22919	49.960
总计		1887086	64790	100.000

Total

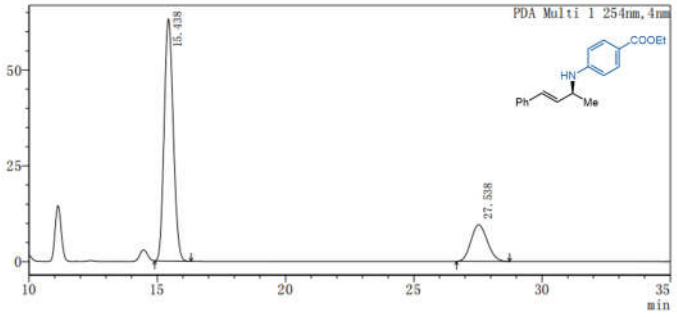


Entry	Retention time	Area	Height	Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.744	628663	27968	9.404
2	28.014	6056549	147529	90.596
总计		6685212	175497	100.000

Total

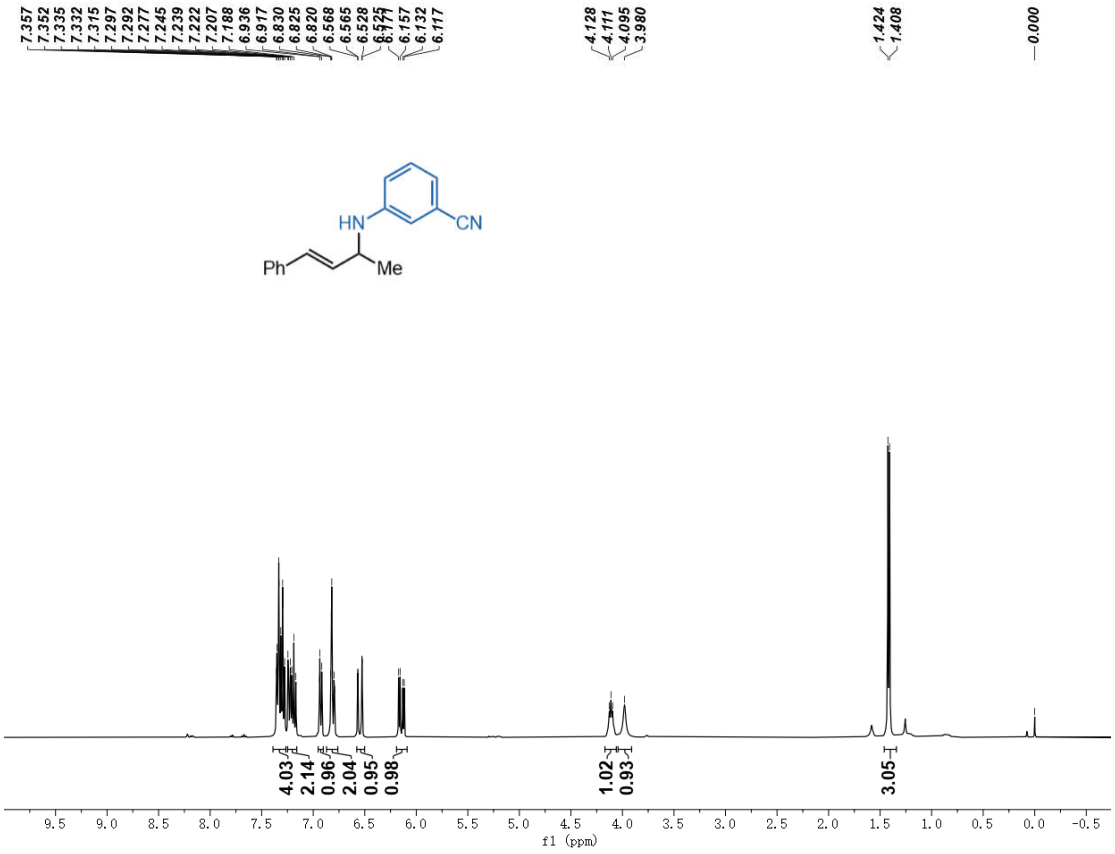


Entry	Retention time	Area	Height	Area%

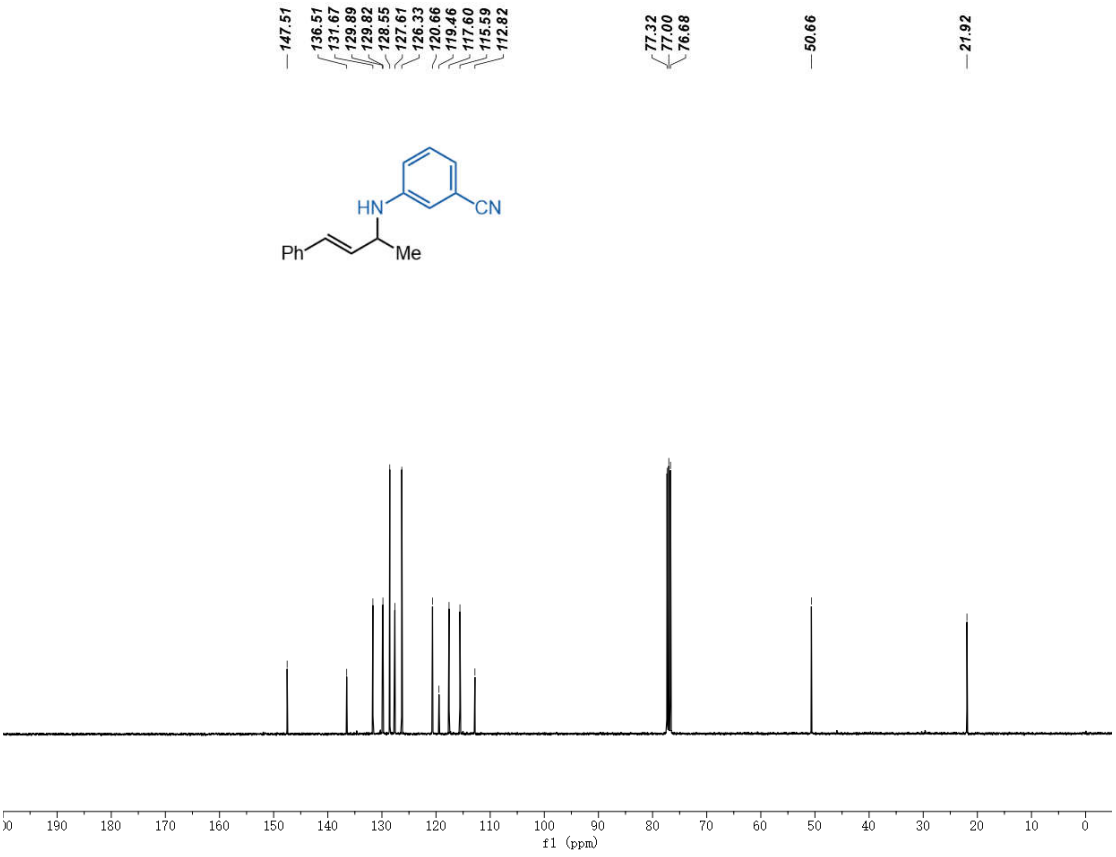
PDA Ch1 254nm

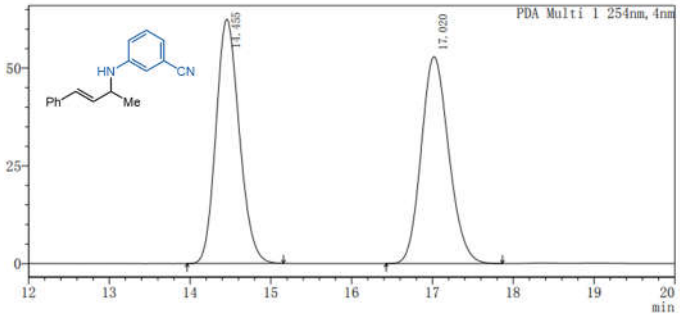
峰号	保留时间	面积	高度	面积%
1	15.438	1557654	63160	78.627
2	27.538	423408	9549	21.373
总计		1981062	72709	100.000

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3af**



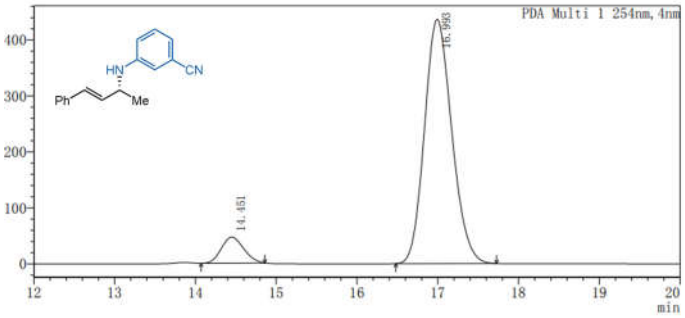


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	14.455	1258812	62479	50.042
2	17.020	1256685	52922	49.958
总计		2515498	115401	100.000

Total

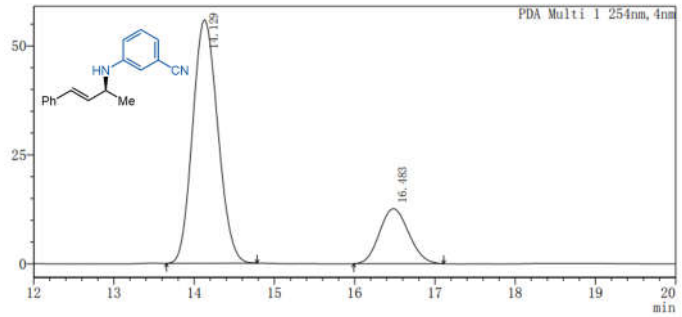


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	14.451	892521	46478	8.006
2	16.993	10255448	436326	91.994
总计		11147969	482804	100.000

Total



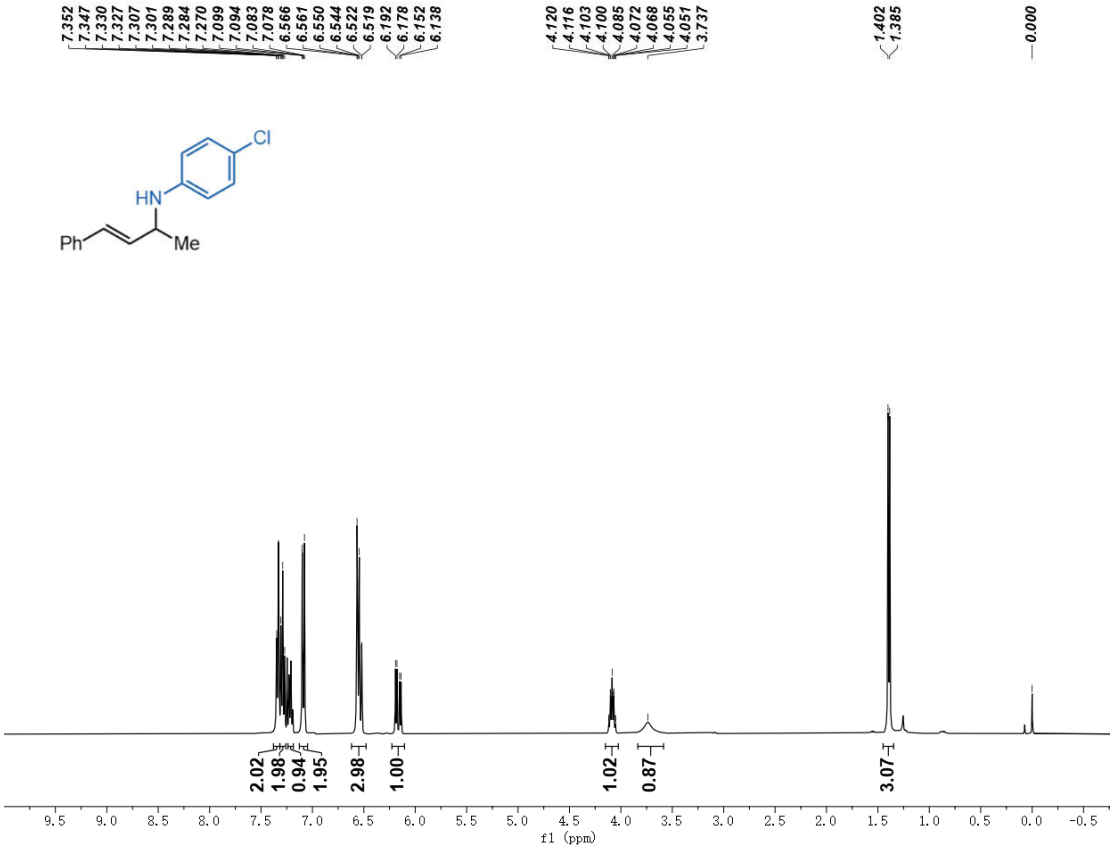
Entry Retention time Area Height Area%

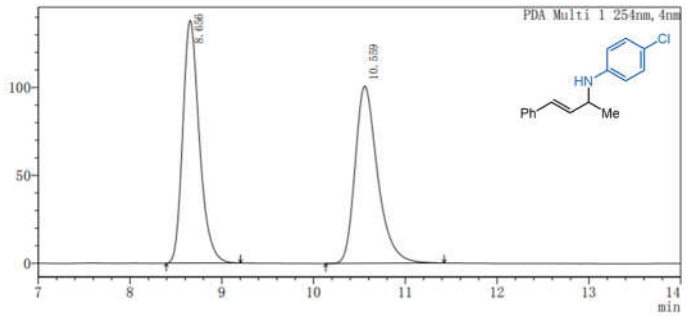
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	14.129	1221222	55831	79.236
2	16.483	320034	12621	20.764
总计		1541256	68452	100.000

Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**



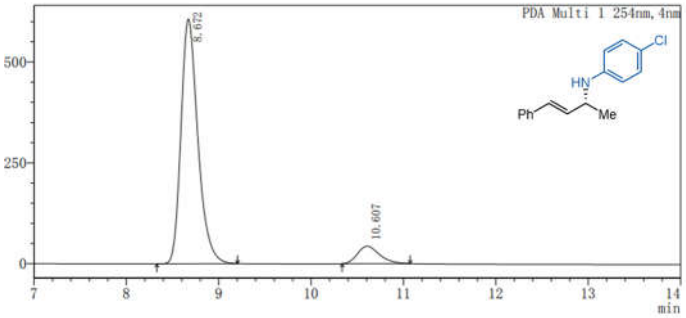


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	8.656	1737141	137810	50.168
2	10.559	1725537	100897	49.832
总计		3462678	238706	100.000

Total

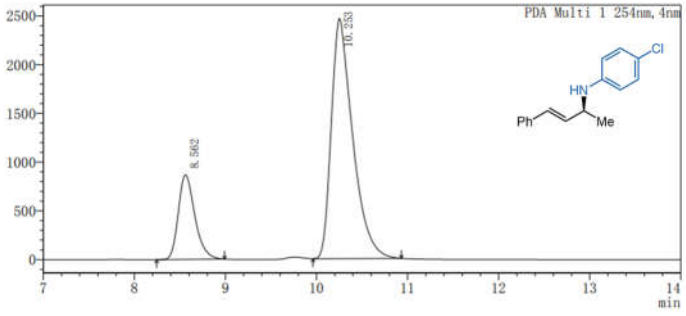


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	8.672	7714555	607201	91.450
2	10.607	721301	43492	8.550
总计		8435855	650693	100.000

Total



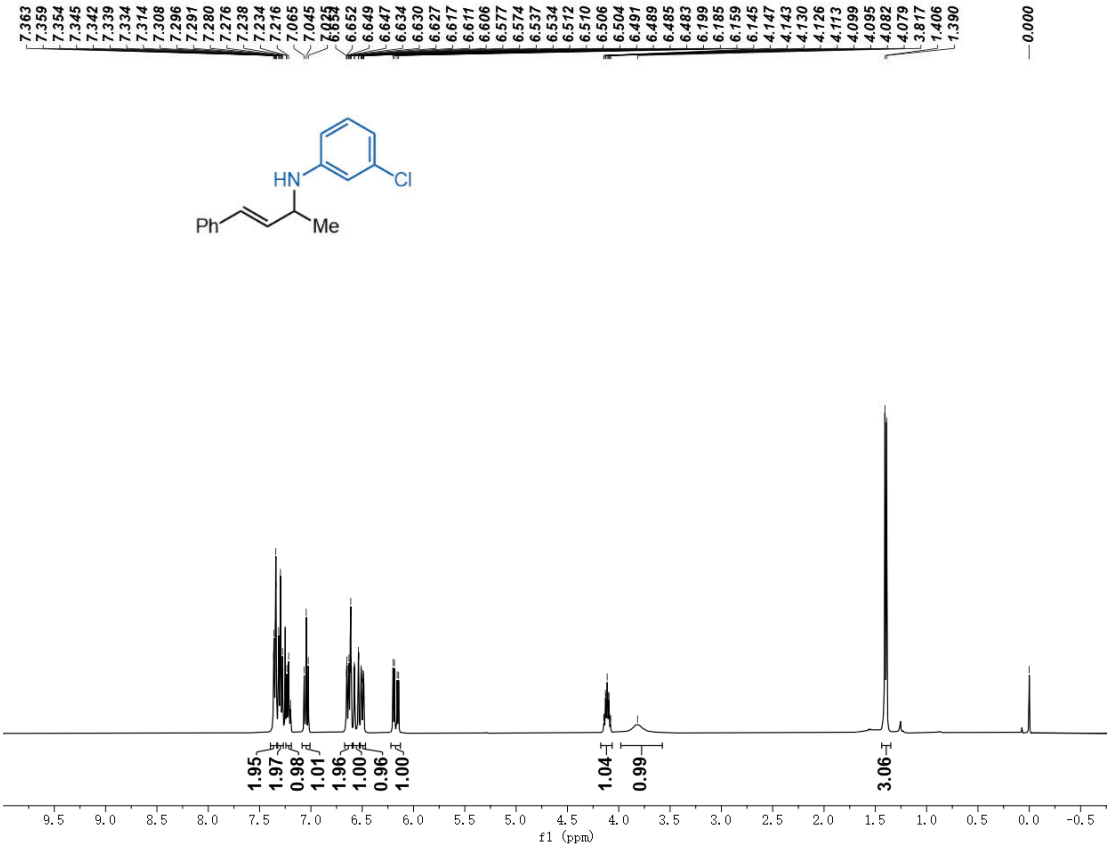
Entry Retention time Area Height Area%

PDA Ch1 254nm

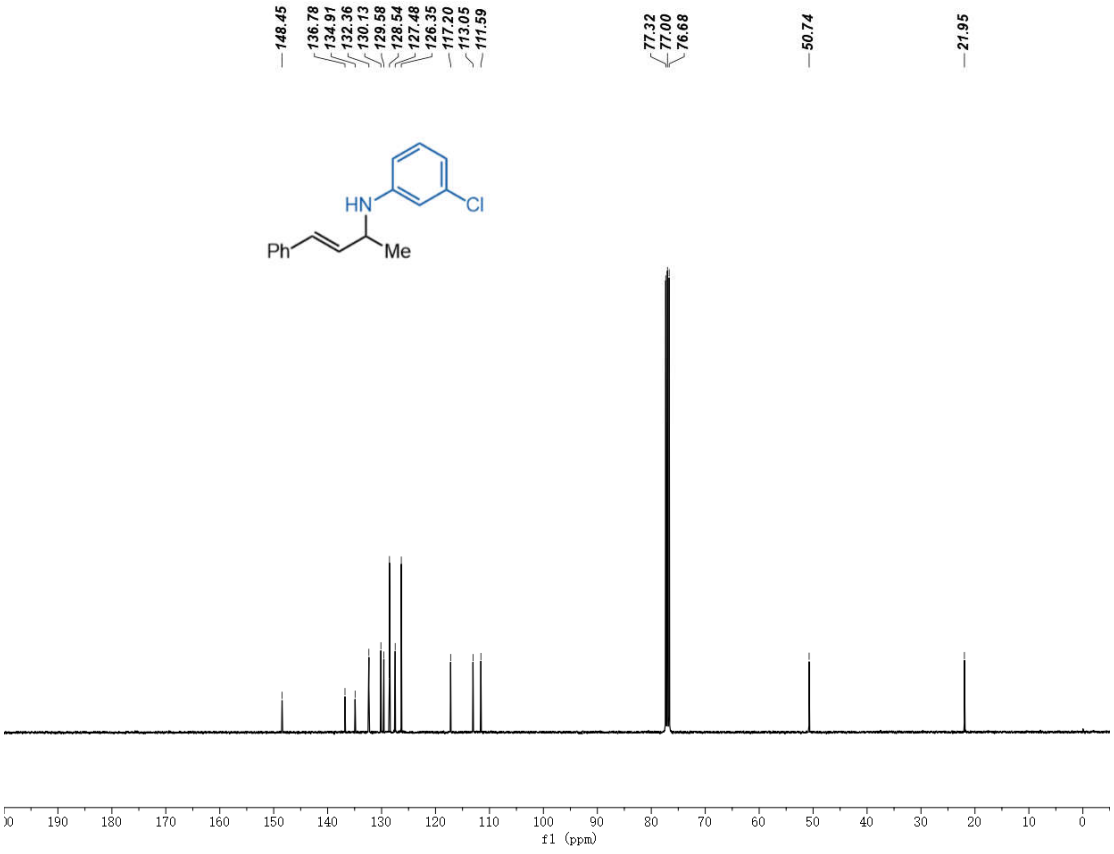
峰号	保留时间	面积	高度	面积%
1	8.562	10945270	867740	21.423
2	10.253	40146965	2463907	78.577
总计		51092235	3331647	100.000

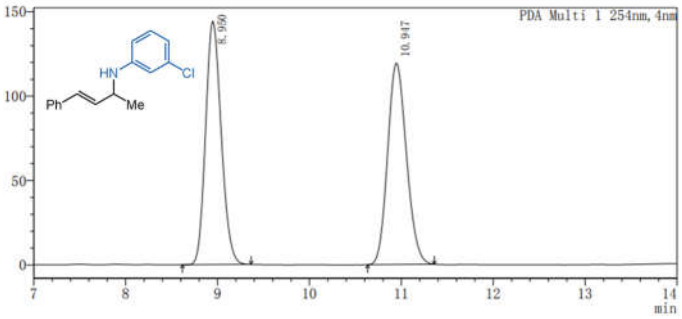
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ah**



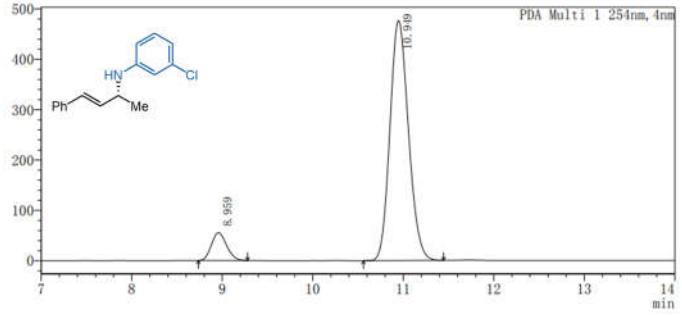


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	8.950	1704776	144113	50.071
2	10.947	1699929	119344	49.929
总计		3404705	263457	100.000

Total

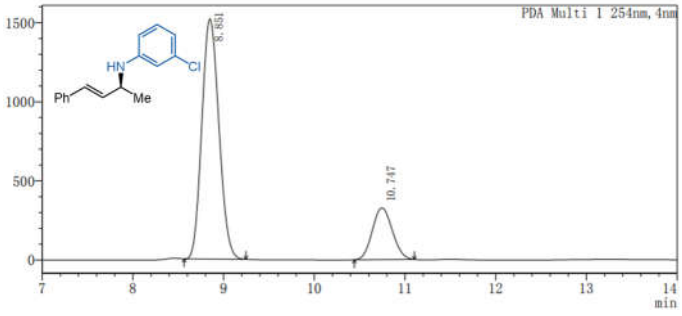


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	8.959	644329	55412	8.691
2	10.949	6769293	476401	91.309
总计		7413622	531814	100.000

Total



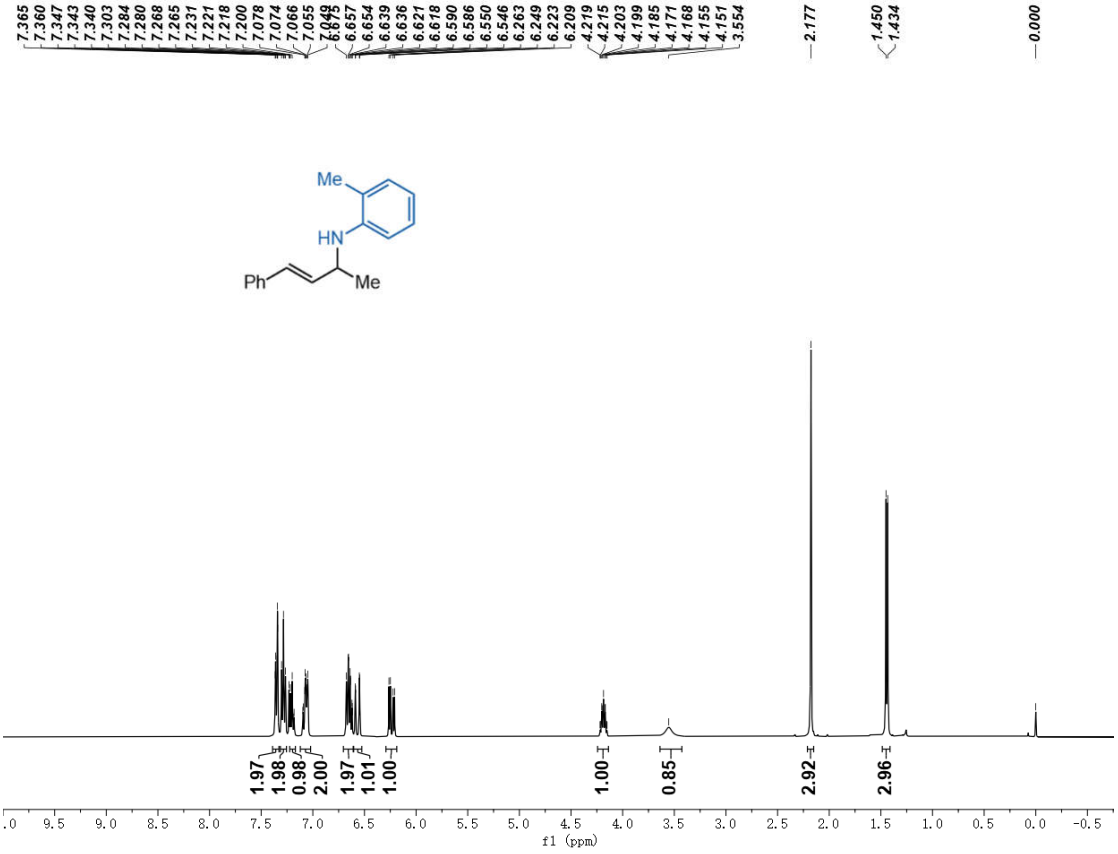
Entry Retention time Area Height Area%

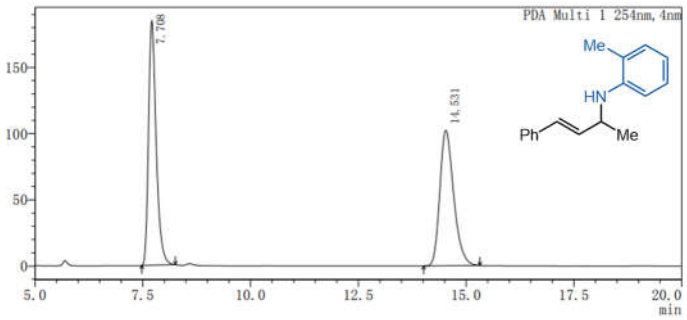
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	8.851	19979766	1519033	79.939
2	10.747	5014054	327476	20.061
总计		24993820	1846509	100.000

Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



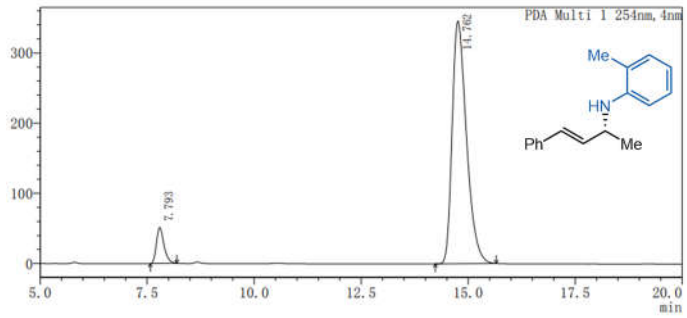


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	7.708	2279171	184404	49.826
2	14.531	2295059	102356	50.174
总计		4574230	286759	100.000

Total

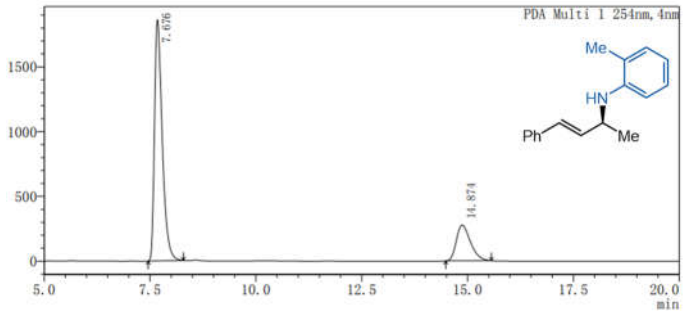


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	7.793	649691	51566	7.446
2	14.762	8075834	345968	92.554
总计		8725525	397534	100.000

Total



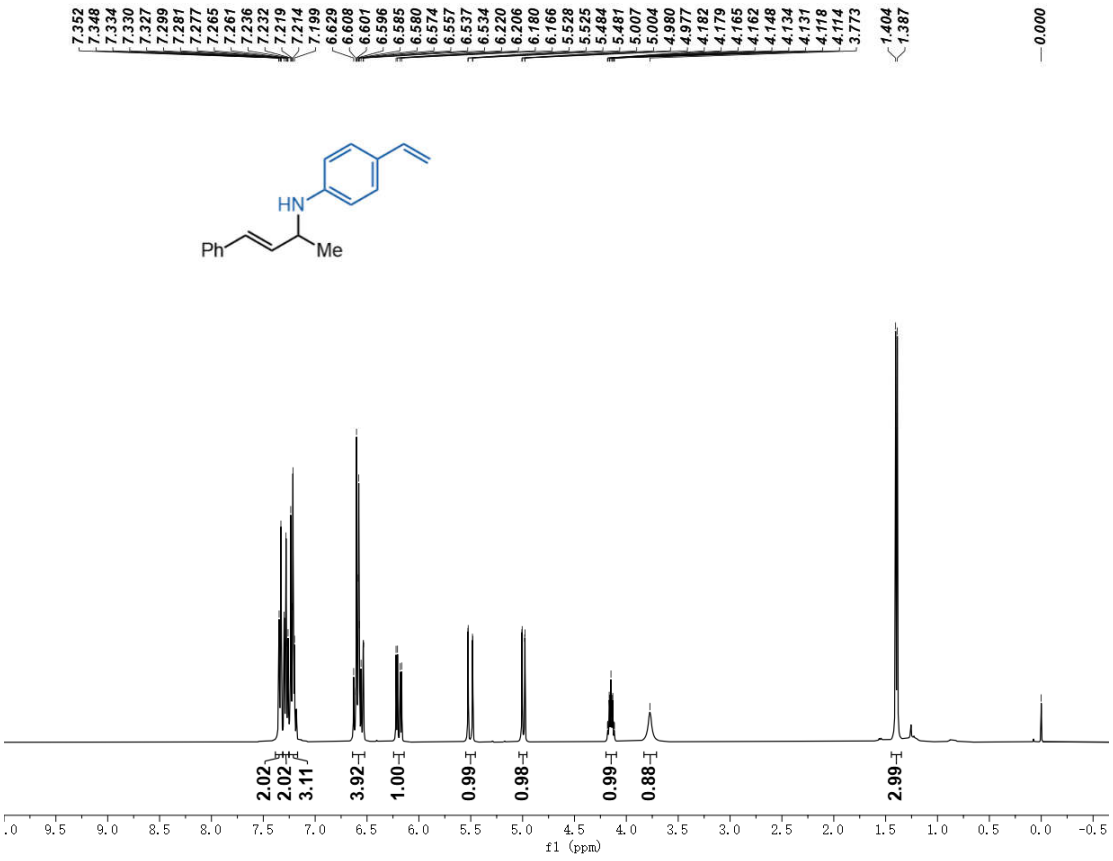
Entry Retention time Area Height Area%

PDA Ch1 254nm

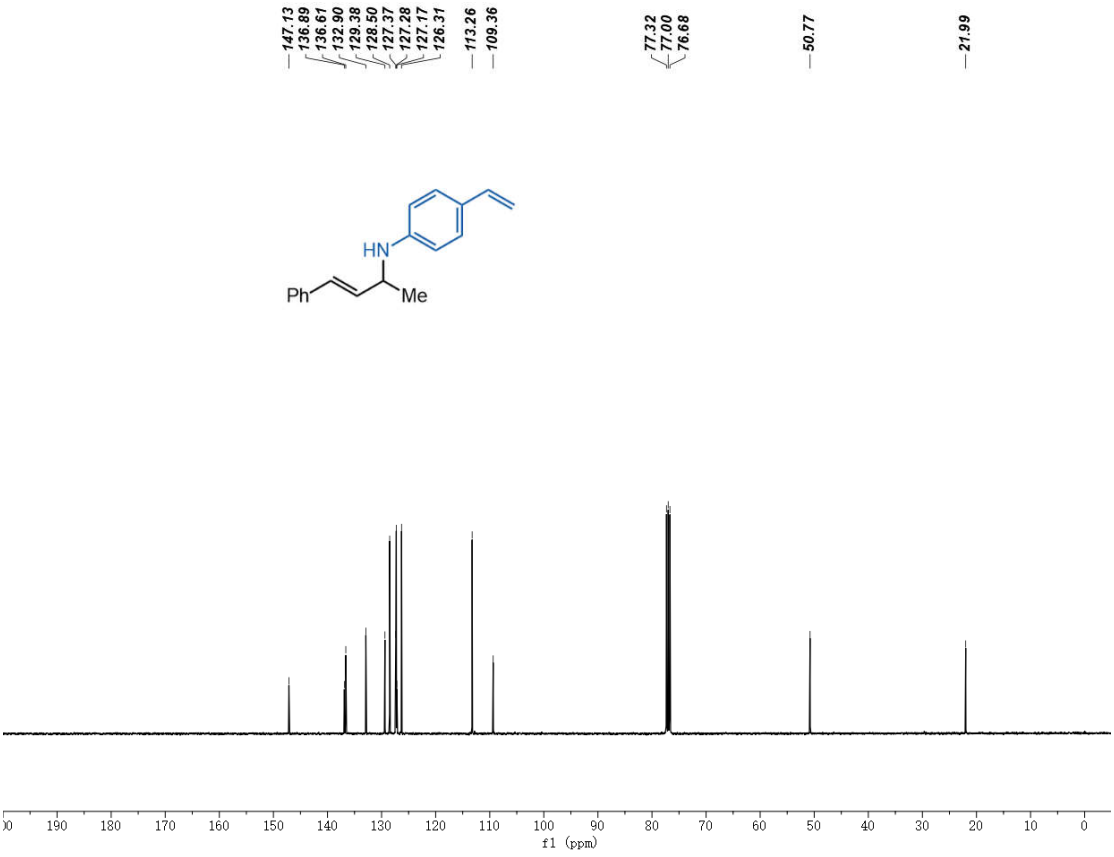
峰号	保留时间	面积	高度	面积%
1	7.676	23658911	1859884	78.654
2	14.874	6420768	276659	21.346
总计		30079680	2136543	100.000

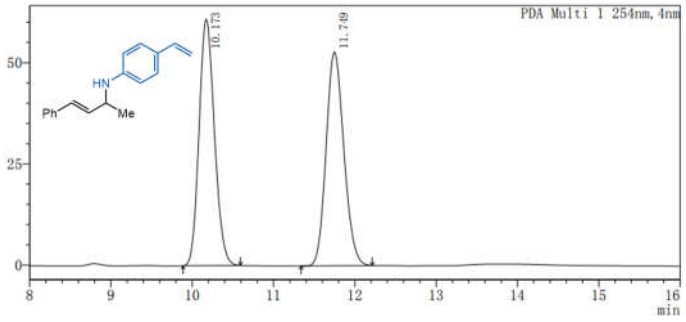
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aj**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3aj**



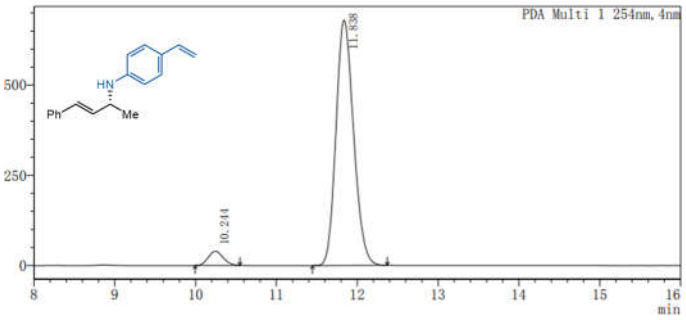


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.173	803265	60930	49.977
2	11.749	804014	52835	50.023
总计		1607279	113765	100.000

Total

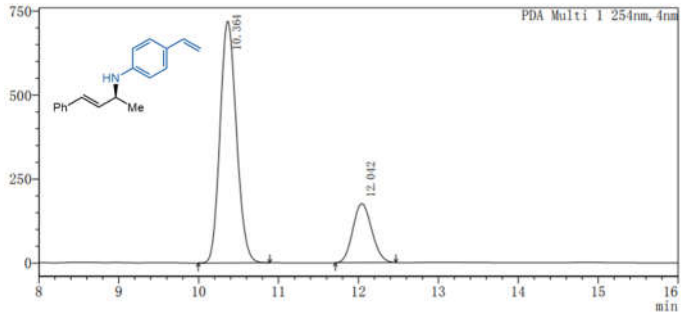


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.244	505448	39179	4.676
2	11.838	10303432	680014	95.324
总计		10808879	719193	100.000

Total



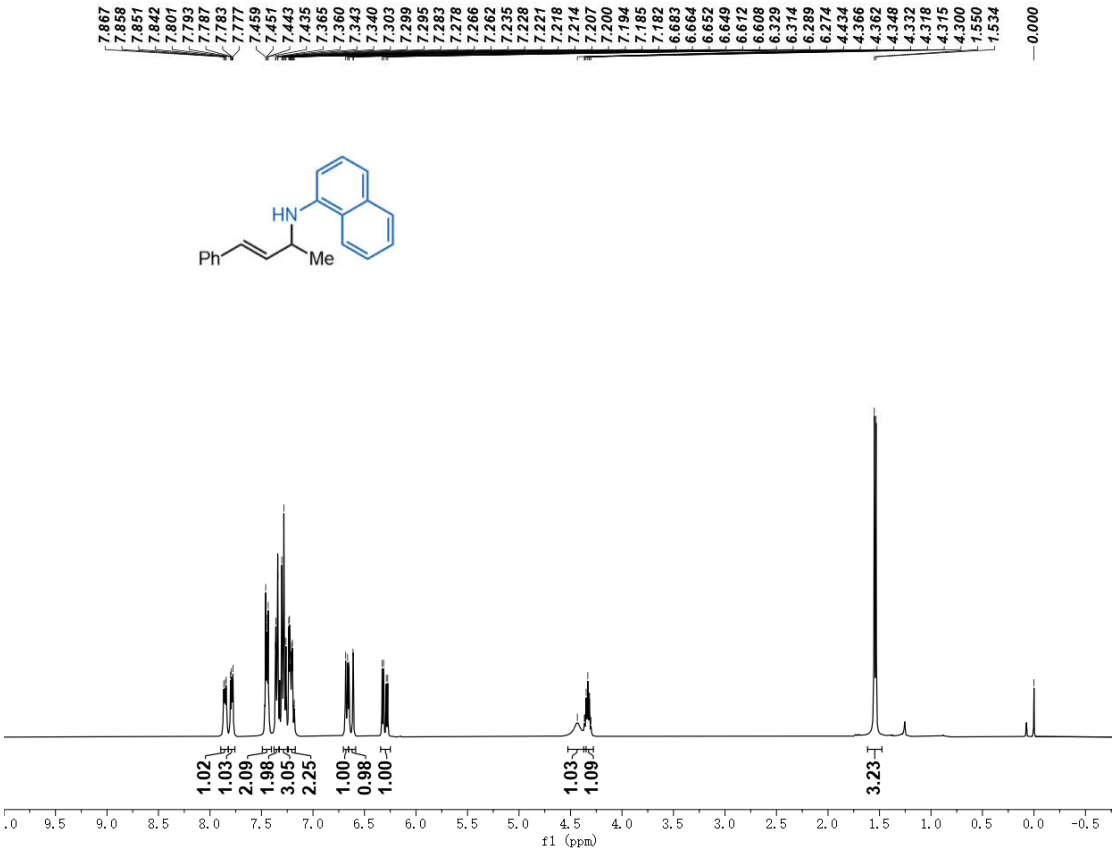
Entry Retention time Area Height Area%

PDA Ch1 254nm

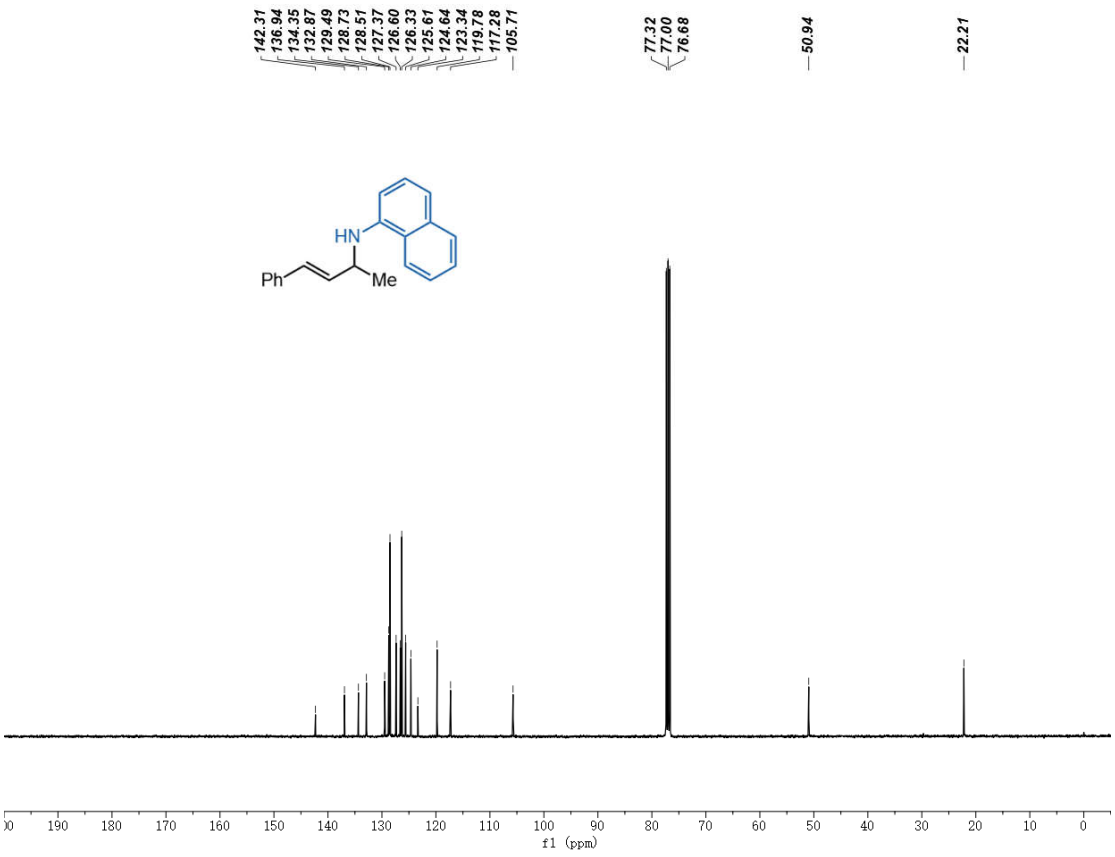
峰号	保留时间	面积	高度	面积%
1	10.364	10297639	719175	77.988
2	12.042	2906501	176129	22.012
总计		13204140	895305	100.000

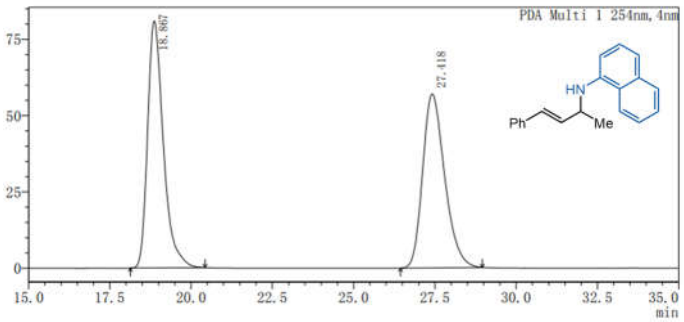
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ak**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ak**



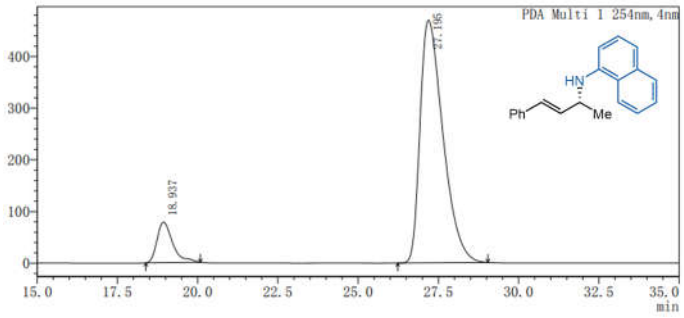


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	18.867	2732894	80897	50.424
2	27.418	2686943	56960	49.576
总计		5419838	137857	100.000

Total

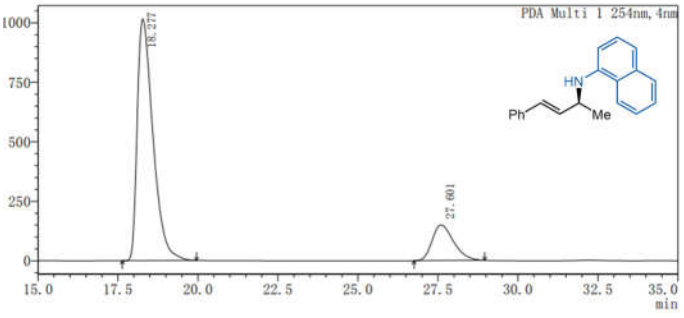


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	18.937	2657623	78365	10.224
2	27.195	23335447	469553	89.776
总计		25993070	547917	100.000

Total



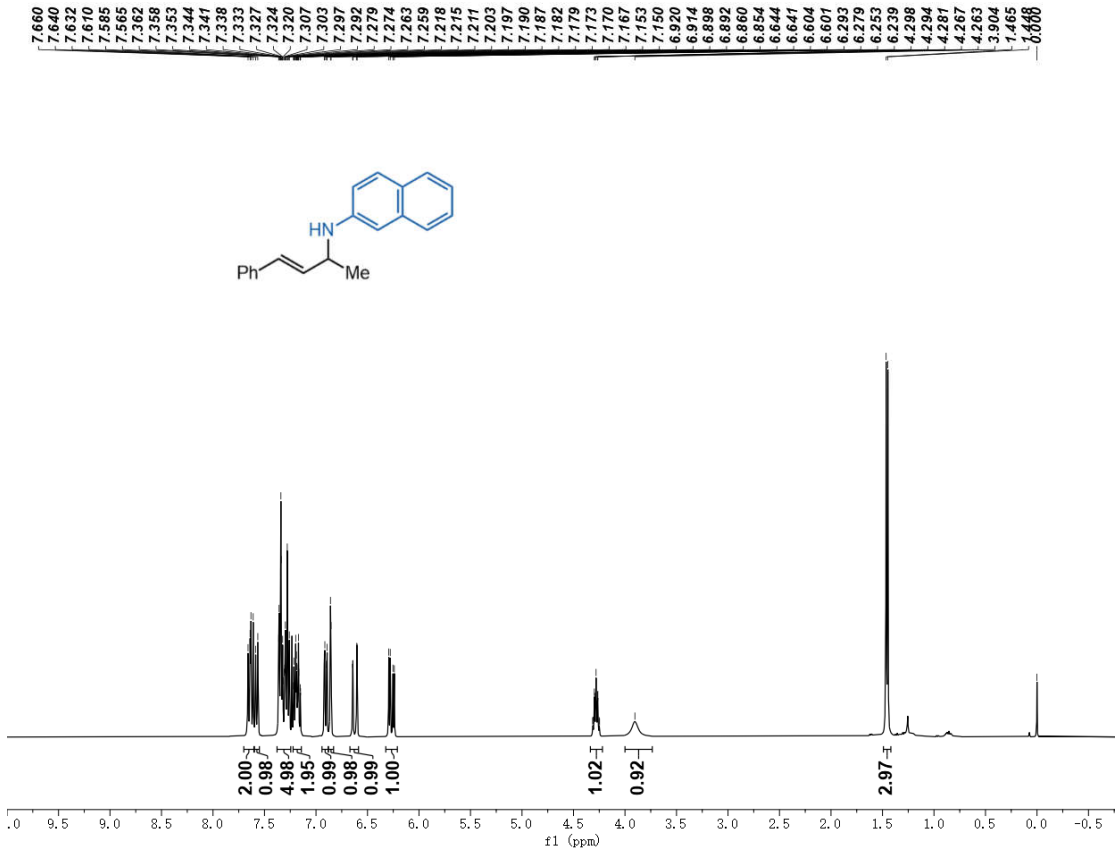
Entry Retention time Area Height Area%

PDA Ch1 254nm

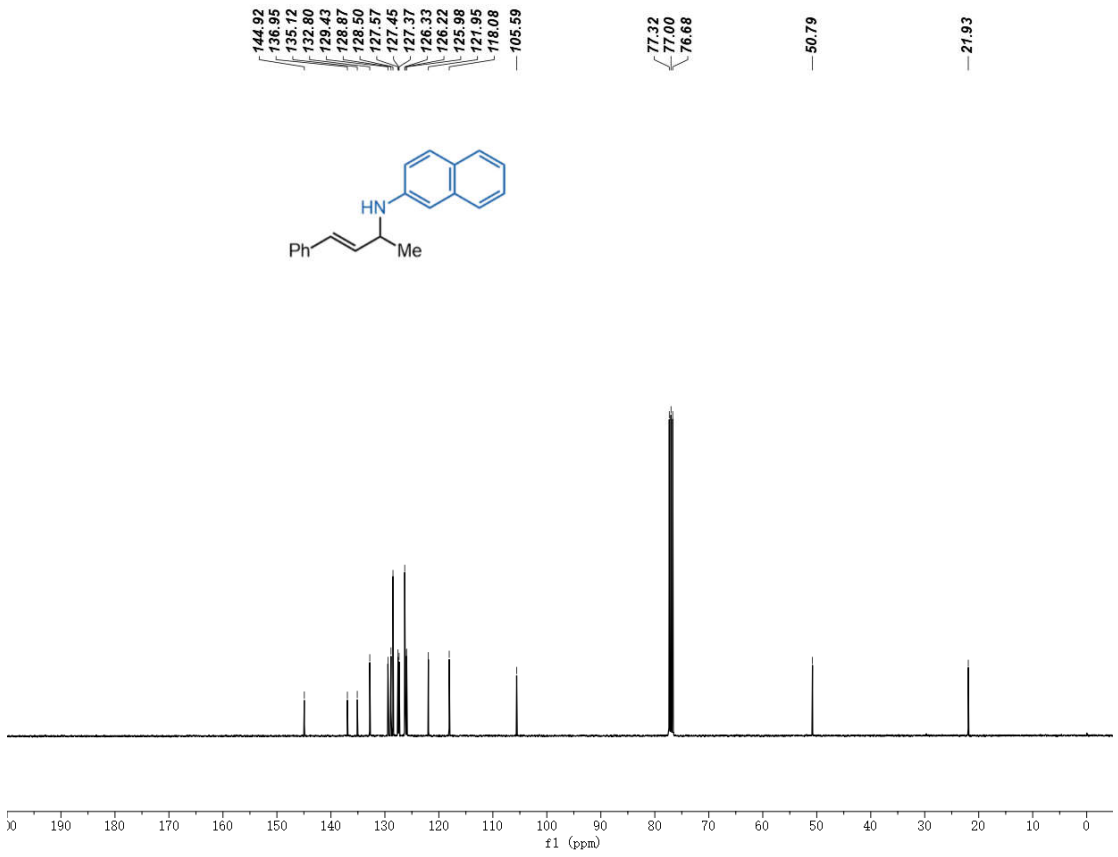
峰号	保留时间	面积	高度	面积%
1	18.277	34719368	1014984	83.201
2	27.601	7009930	149639	16.799
总计		41729299	1164623	100.000

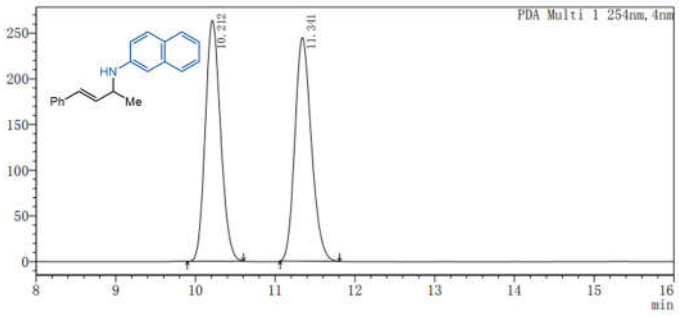
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3al**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3al**



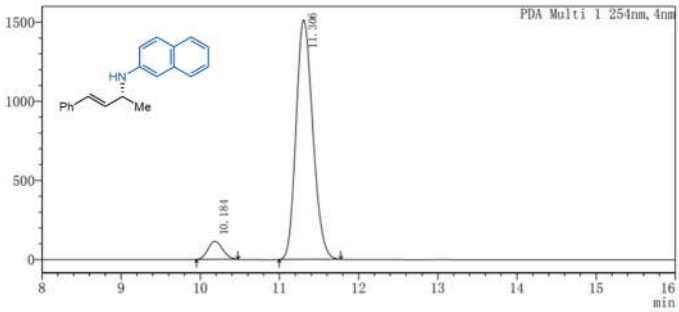


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.212	3511912	263338	49.970
2	11.341	3516147	244729	50.030
总计		7028059	508067	100.000

Total

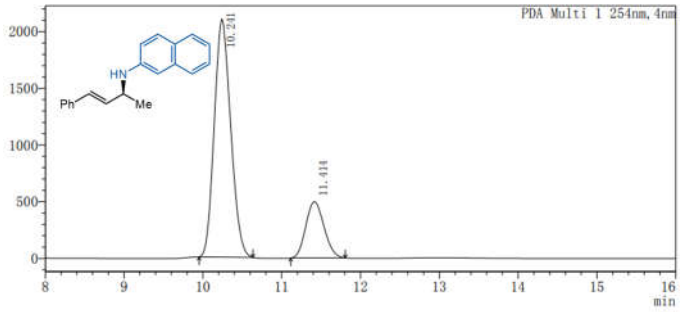


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	10.184	1470287	114609	6.187
2	11.306	22292540	1514055	93.813
总计		23762827	1628664	100.000

Total



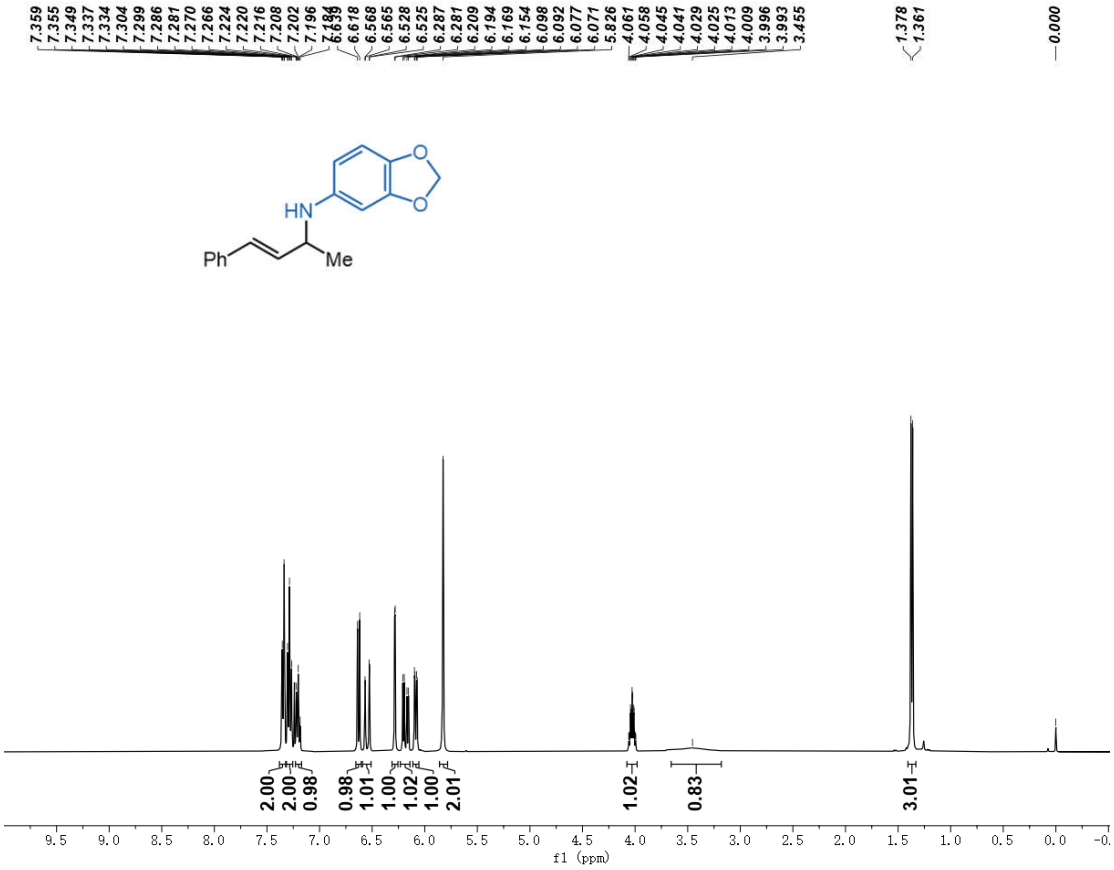
Entry Retention time Area Height Area%

PDA Ch1 254nm

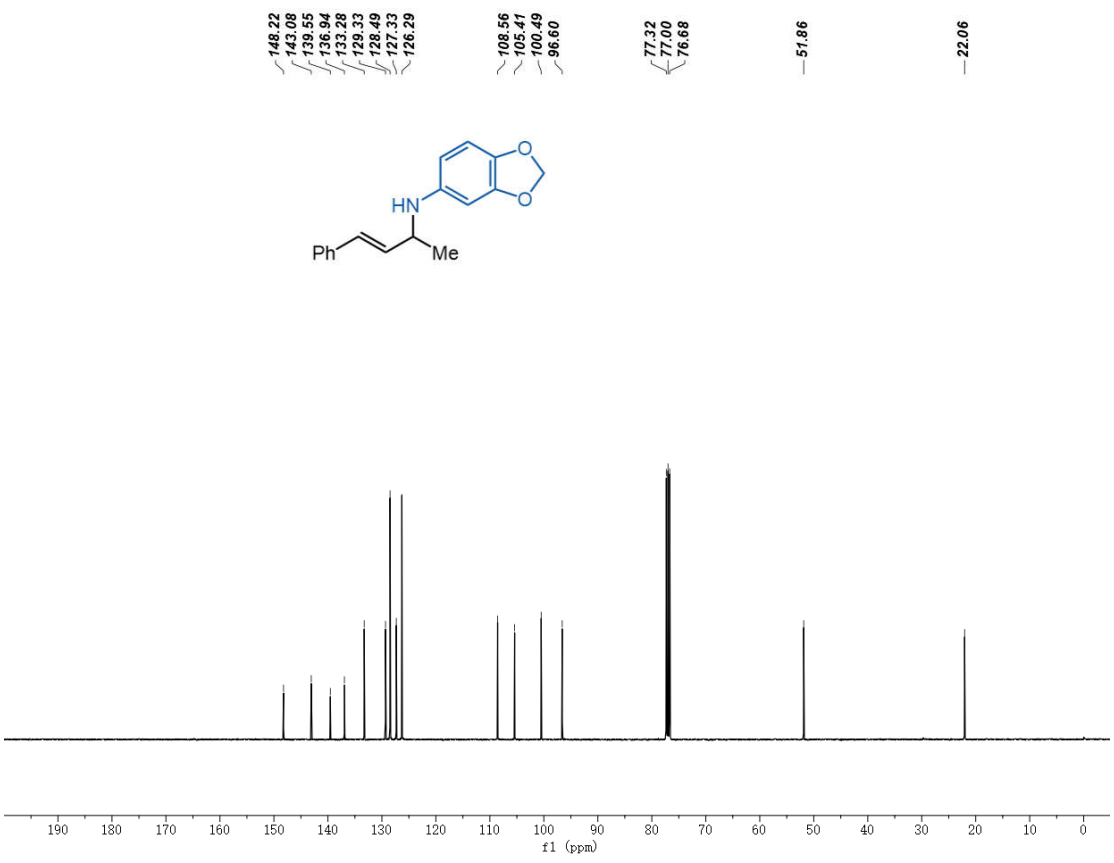
峰号	保留时间	面积	高度	面积%
1	10.241	30421833	2098326	79.196
2	11.414	7991439	496651	20.804
总计		38413272	2594977	100.000

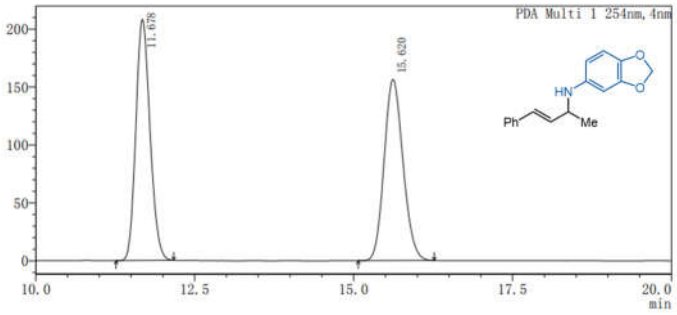
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3am**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3am**



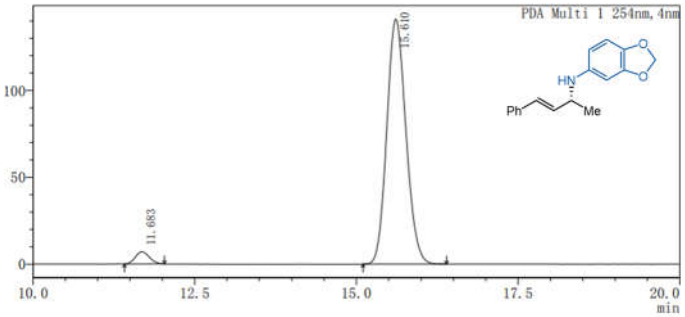


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.678	3229408	207923	49.986
2	15.620	3231261	156204	50.014
总计		6460668	364127	100.000

Total

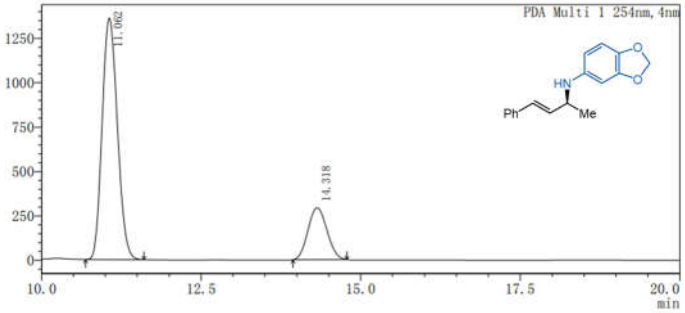


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.683	107275	7084	3.569
2	15.610	2898864	140870	96.431
总计		3006139	147954	100.000

Total



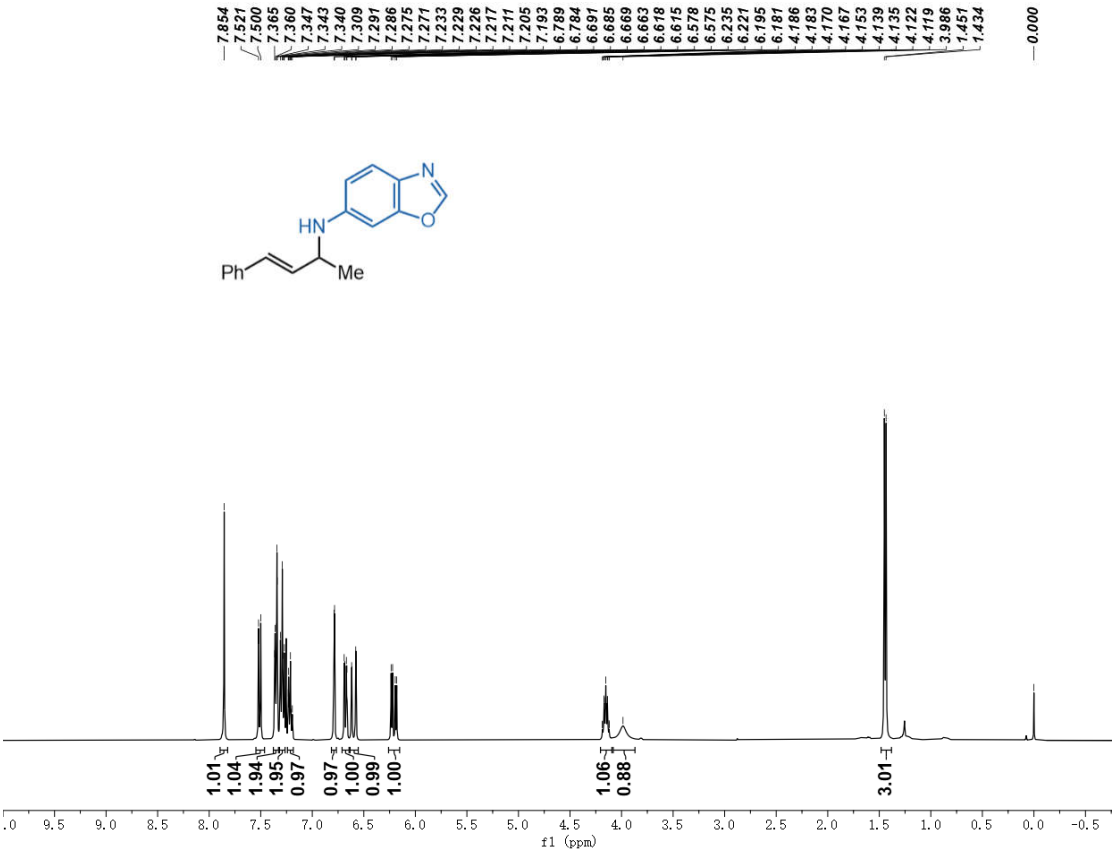
Entry Retention time Area Height Area%

PDA Ch1 254nm

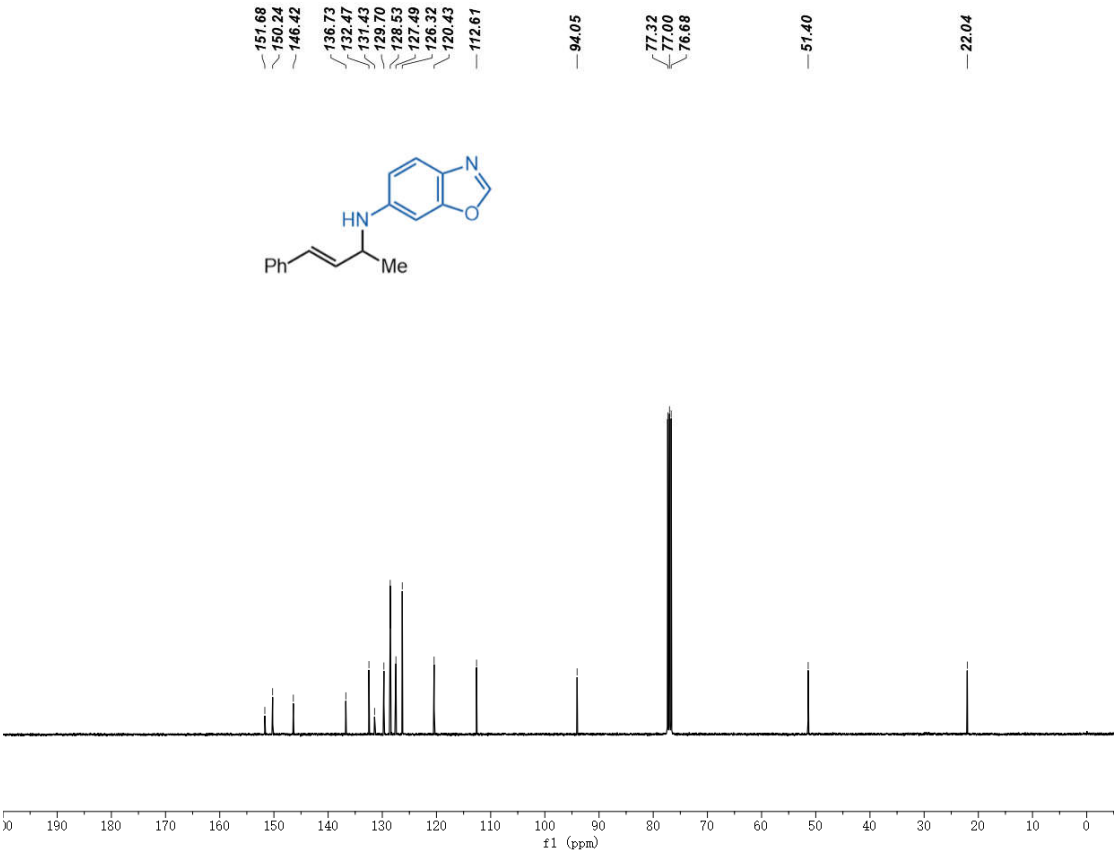
峰号	保留时间	面积	高度	面积%
1	11.062	22604830	1360330	78.902
2	14.318	6044444	292812	21.098
总计		28649274	1653142	100.000

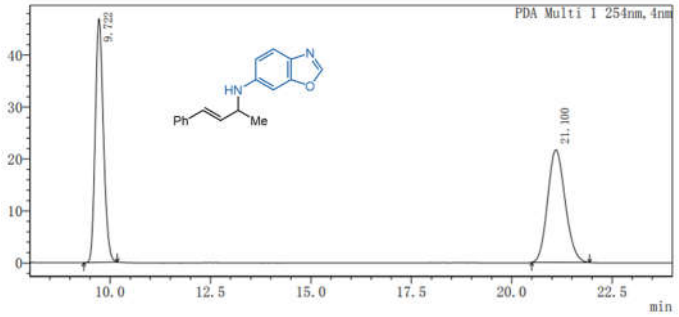
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3an**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3an**



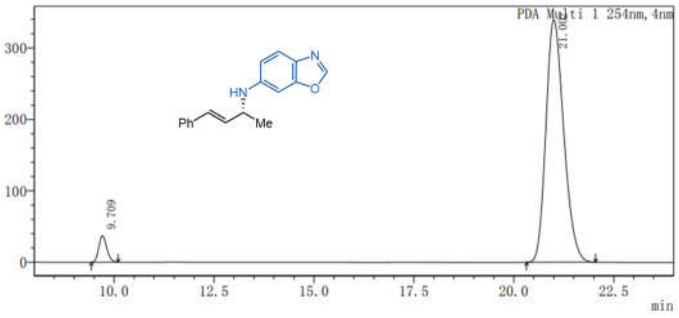


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.722	662286	46823	50.105
2	21.100	659500	21655	49.895
总计		1321786	68479	100.000

Total

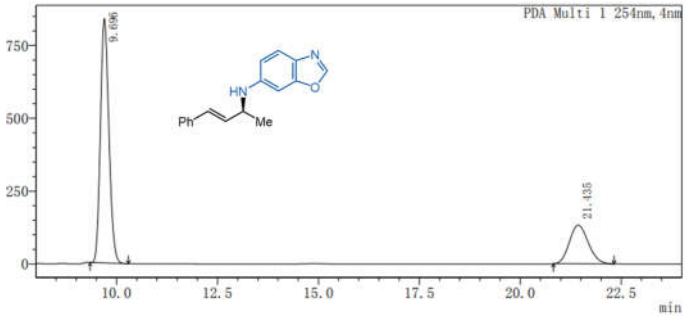


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.709	518941	37277	4.682
2	21.002	10565866	339522	95.318
总计		11084806	376799	100.000

Total



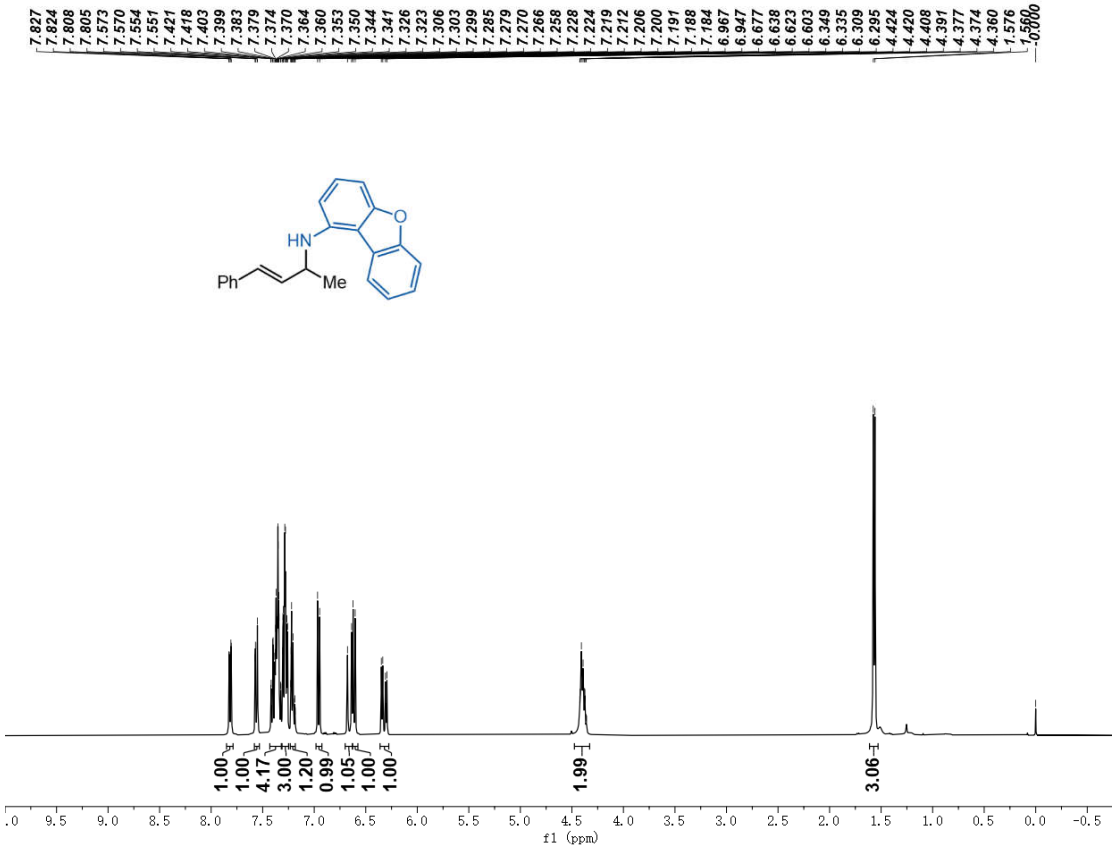
Entry Retention time Area Height Area%

PDA Ch1 254nm

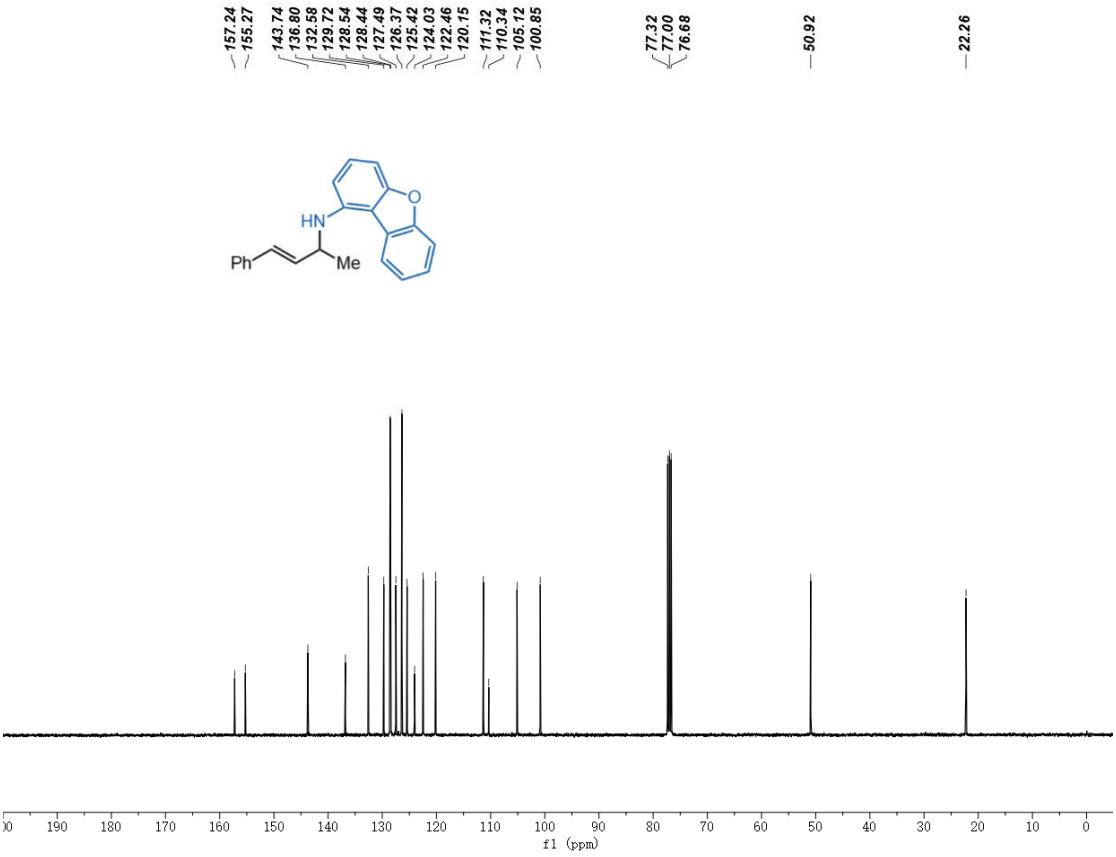
峰号	保留时间	面积	高度	面积%
1	9.696	12264470	836761	73.953
2	21.435	4319613	132600	26.047
总计		16584083	969361	100.000

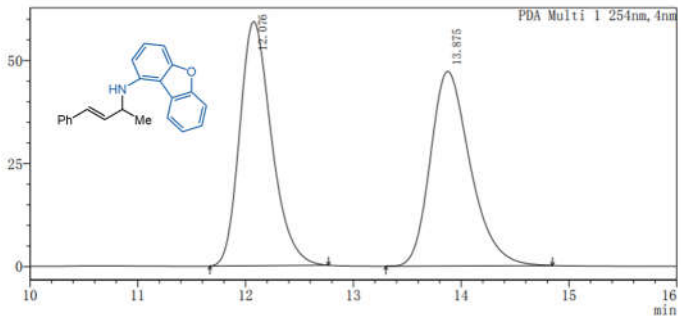
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ao**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ao**



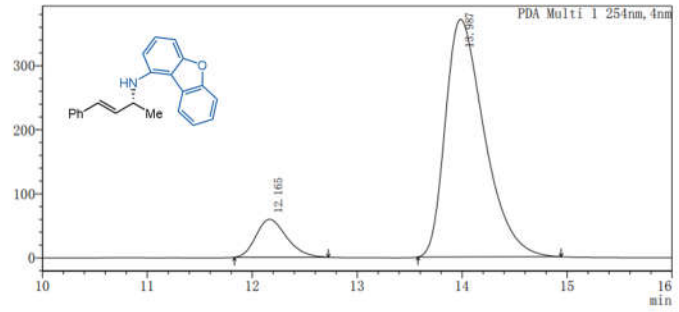


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	12.076	1217249	59262	50.002
2	13.875	1217158	47205	49.998
总计		2434407	106468	100.000

Total

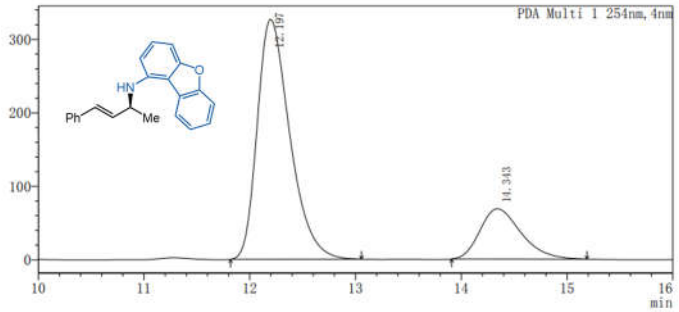


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	12.165	1201276	59282	11.123
2	13.987	9598312	370898	88.877
总计		10799588	430180	100.000

Total



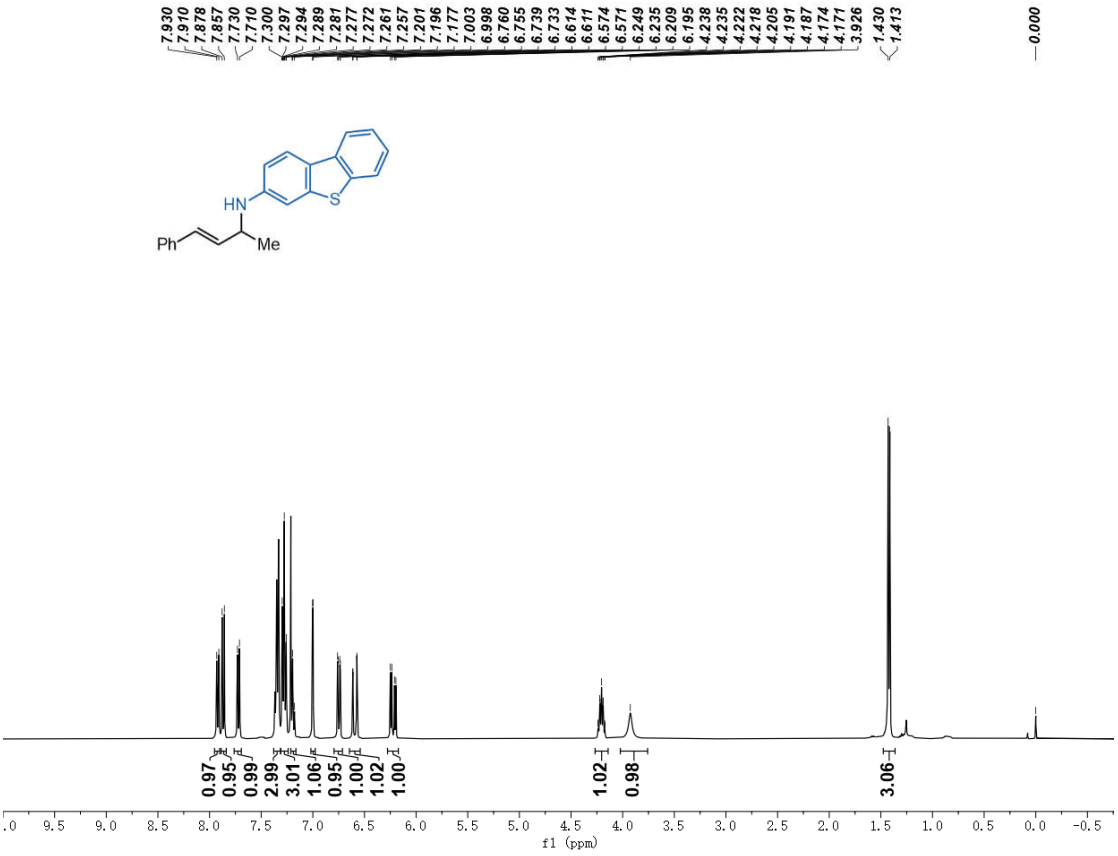
Entry Retention time Area Height Area%

PDA Ch1 254nm

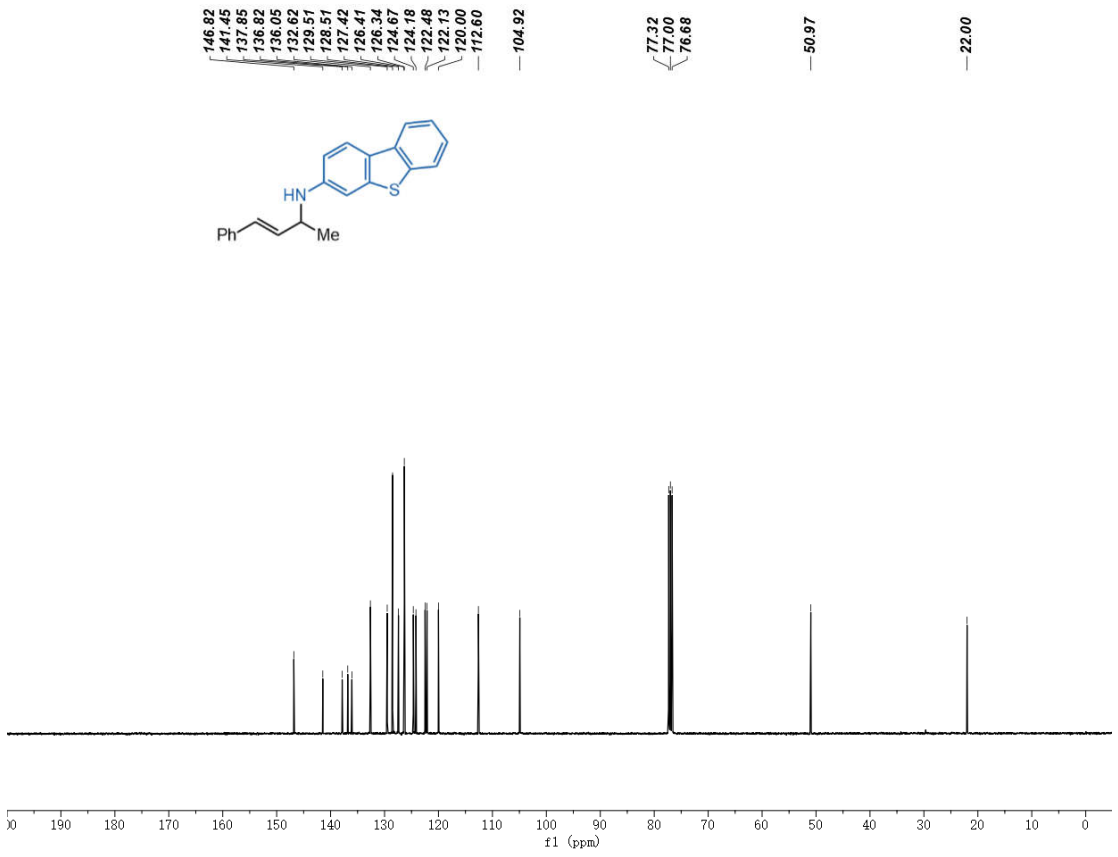
峰号	保留时间	面积	高度	面积%
1	12.197	6990913	326574	79.032
2	14.343	1854721	68500	20.968
总计		8845634	395074	100.000

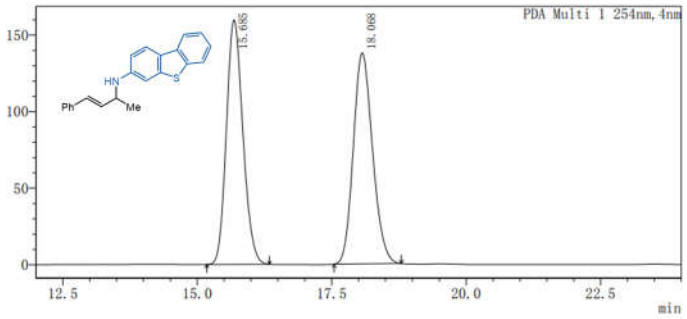
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ap**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ap**



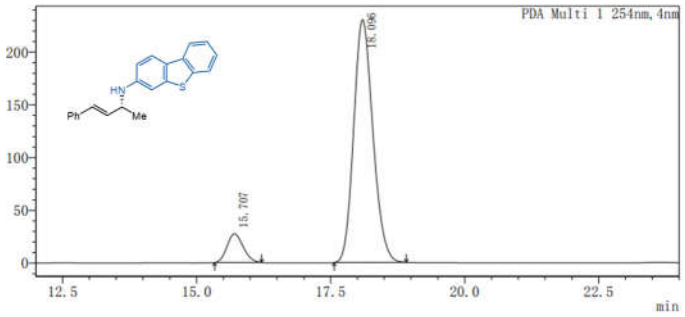


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.685	3409024	159597	49.847
2	18.068	3430009	137912	50.153
总计		6839033	297510	100.000

Total

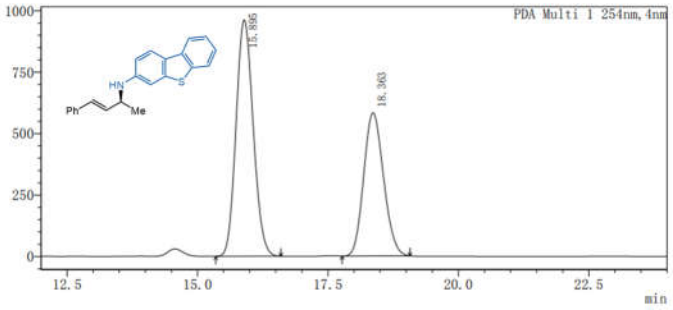


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.707	571930	27309	9.063
2	18.096	5738516	230166	90.937
总计		6310446	257474	100.000

Total



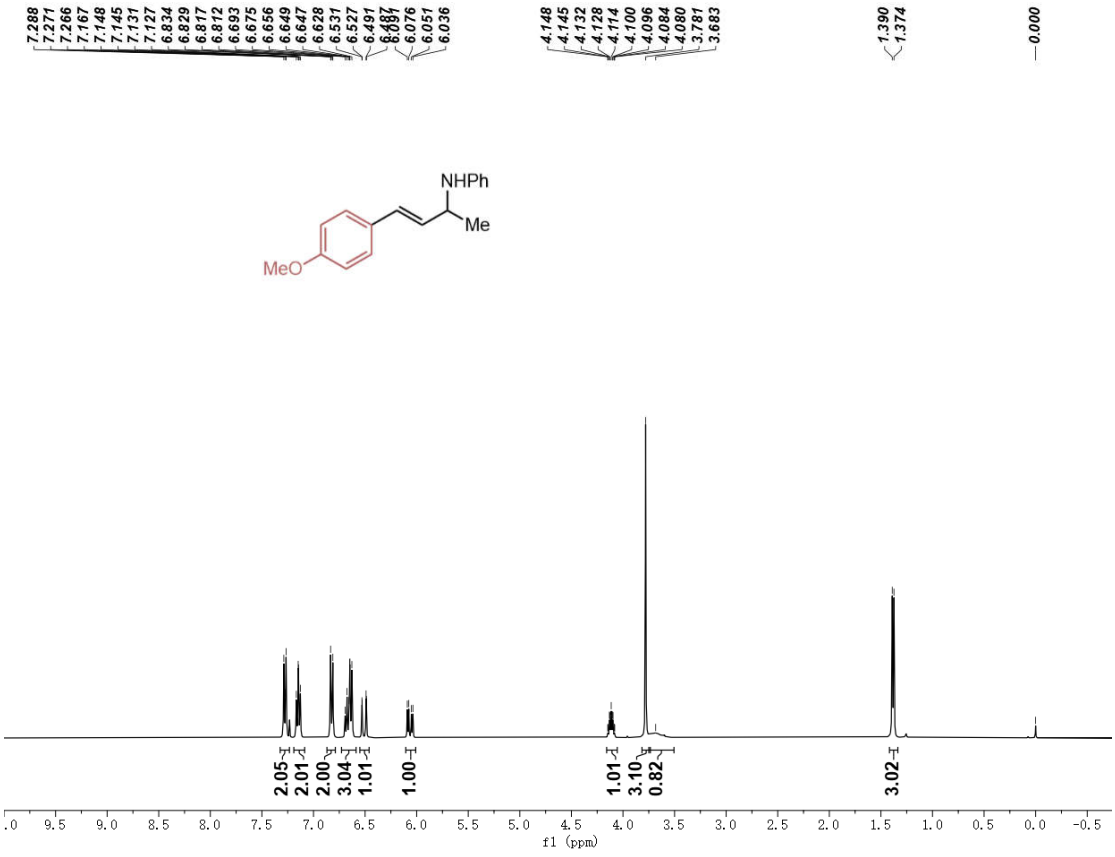
Entry Retention time Area Height Area%

PDA Ch1 254nm

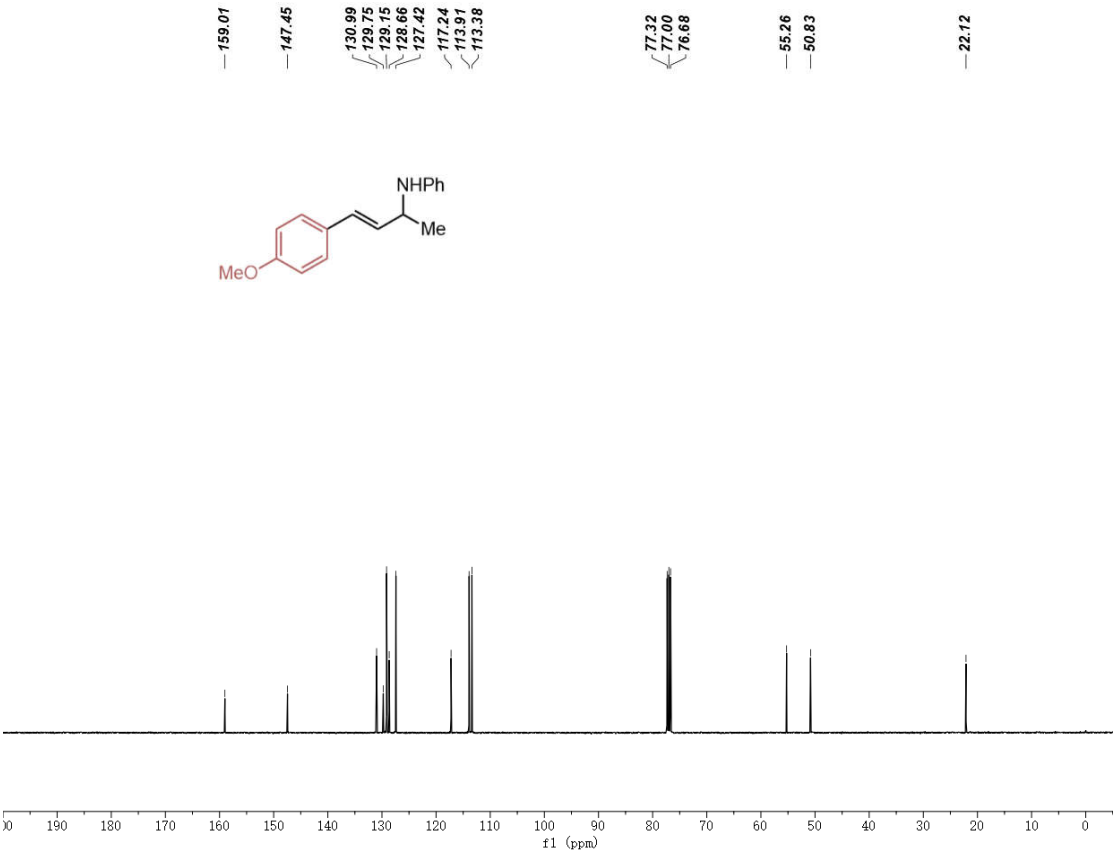
峰号	保留时间	面积	高度	面积%
1	15.895	22013862	961914	58.768
2	18.363	15445058	583125	41.232
总计		37458920	1545039	100.000

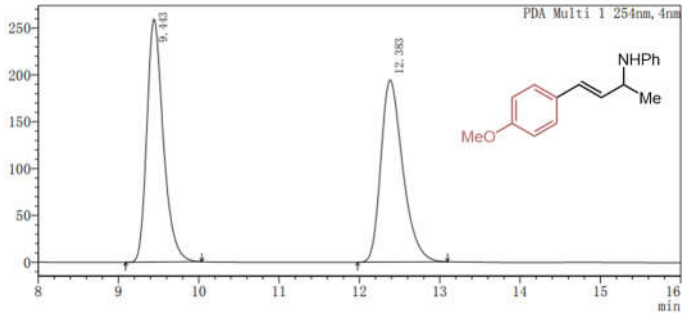
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



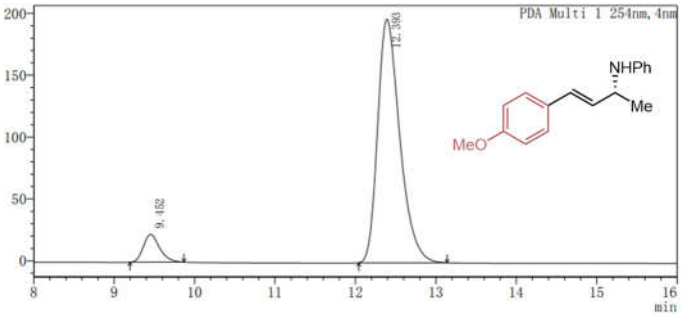


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.443	3697815	259265	50.035
2	12.383	3692645	194379	49.965
总计		7390461	453644	100.000

Total

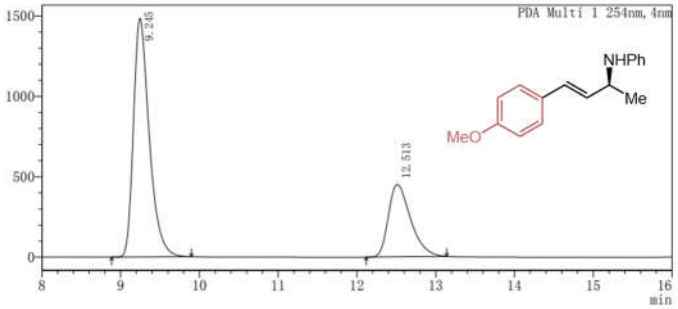


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.452	317051	22465	7.757
2	12.393	3770246	196857	92.243
总计		4087296	219322	100.000

Total



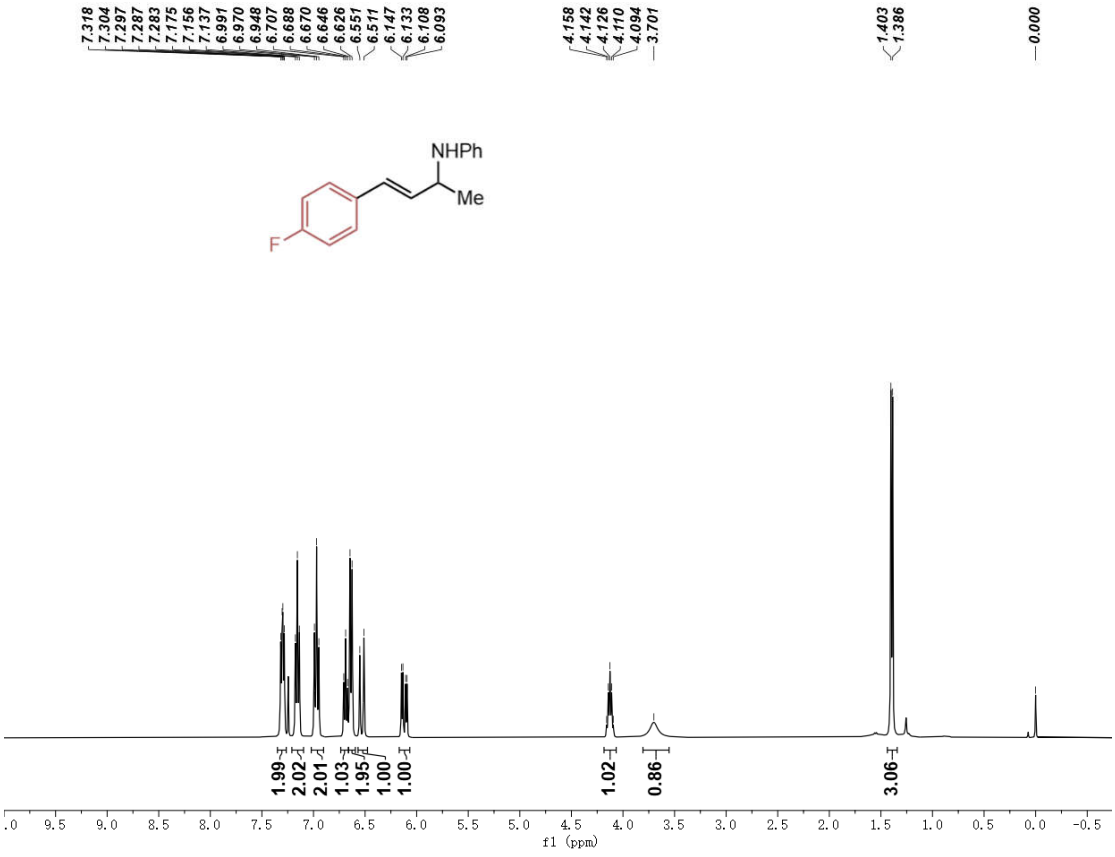
Entry Retention time Area Height Area%

PDA Ch1 254nm

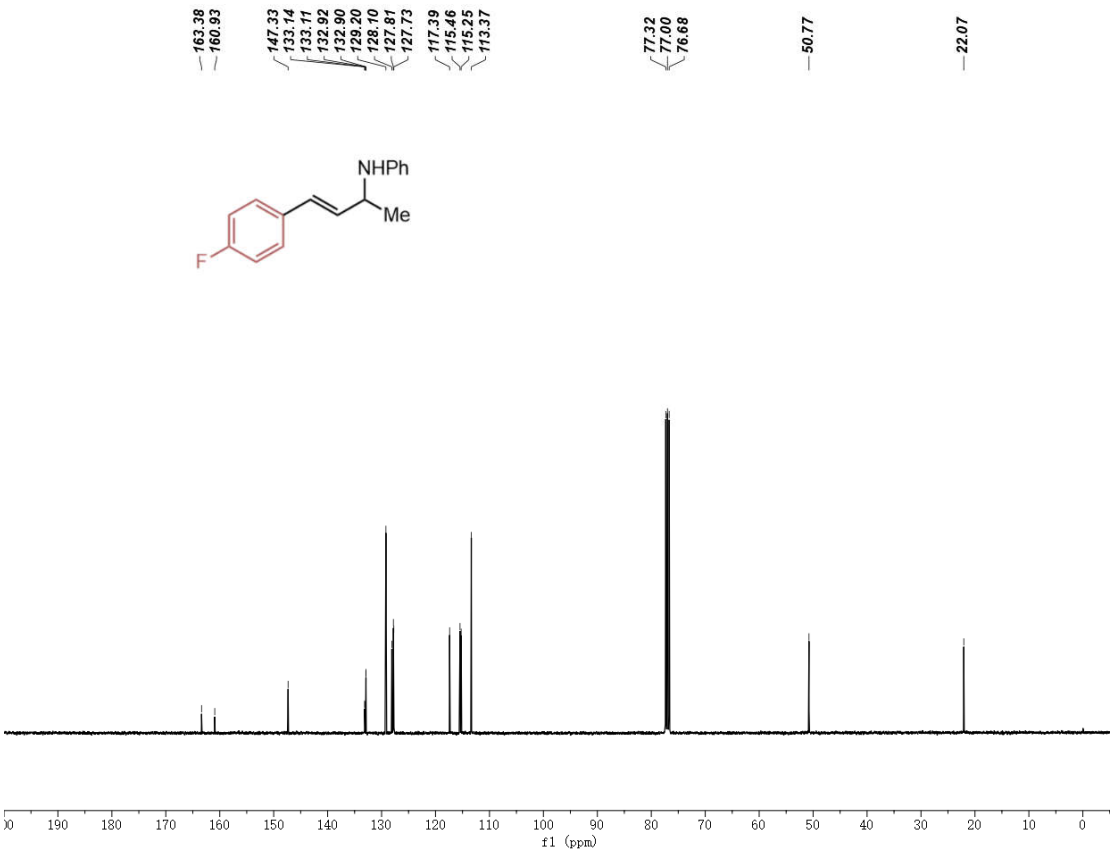
峰号	保留时间	面积	高度	面积%
1	9.245	20697262	1483775	70.099
2	12.513	8828332	450940	29.901
总计		29525593	1934716	100.000

Total

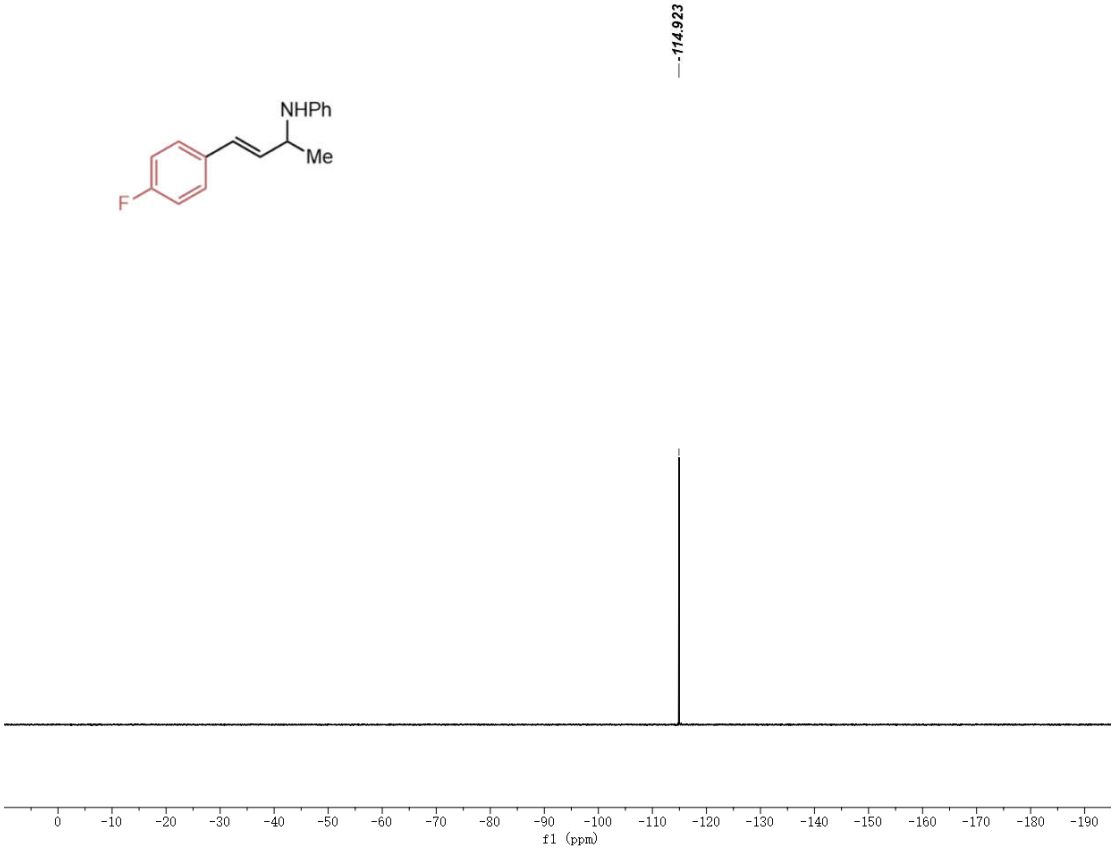
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca**

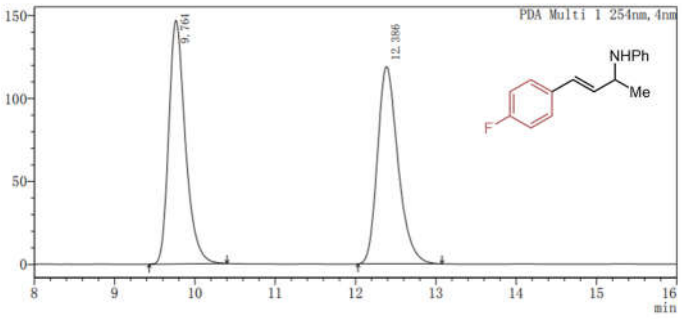


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ca**



^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3ca**



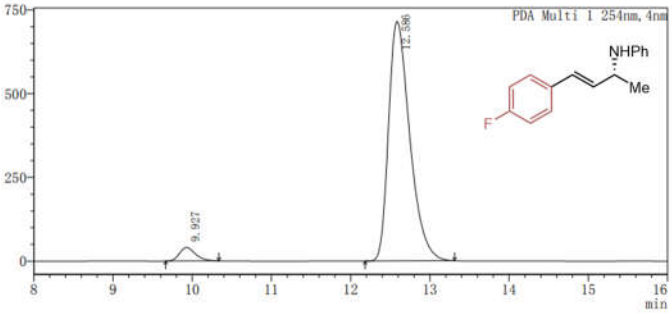


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.764	2110586	146764	49.895
2	12.386	2119449	118848	50.105
总计		4230035	265611	100.000

Total

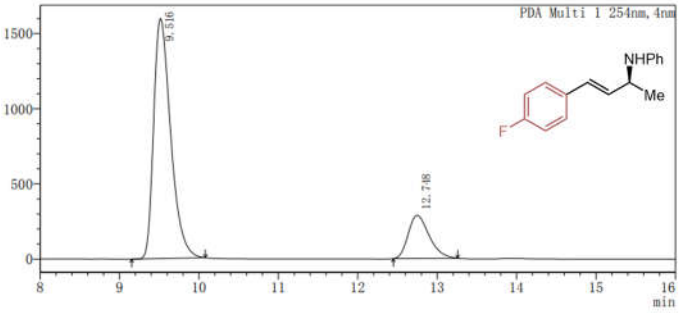


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.927	571047	40629	4.105
2	12.586	13341298	715325	95.895
总计		13912345	755954	100.000

Total



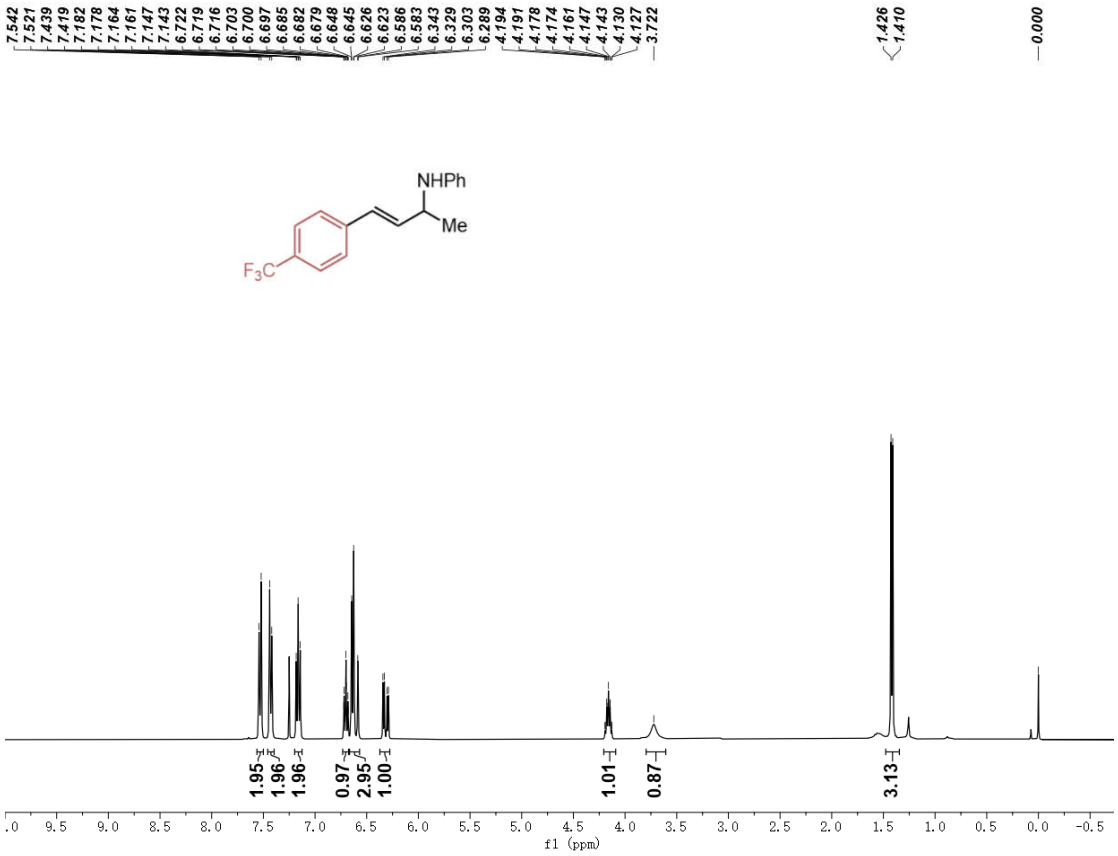
Entry Retention time Area Height Area%

PDA Ch1 254nm

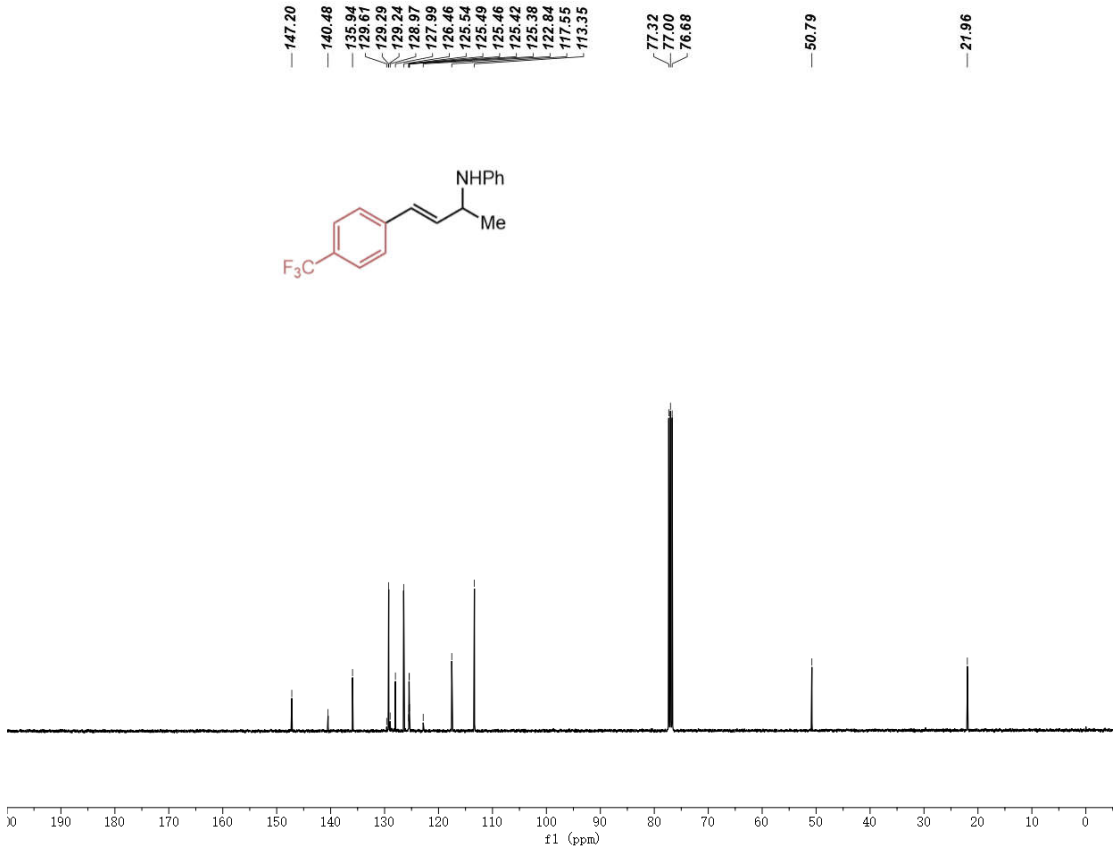
峰号	保留时间	面积	高度	面积%
1	9.516	23776274	1595986	81.890
2	12.748	5258252	286962	18.110
总计		29034526	1882947	100.000

Total

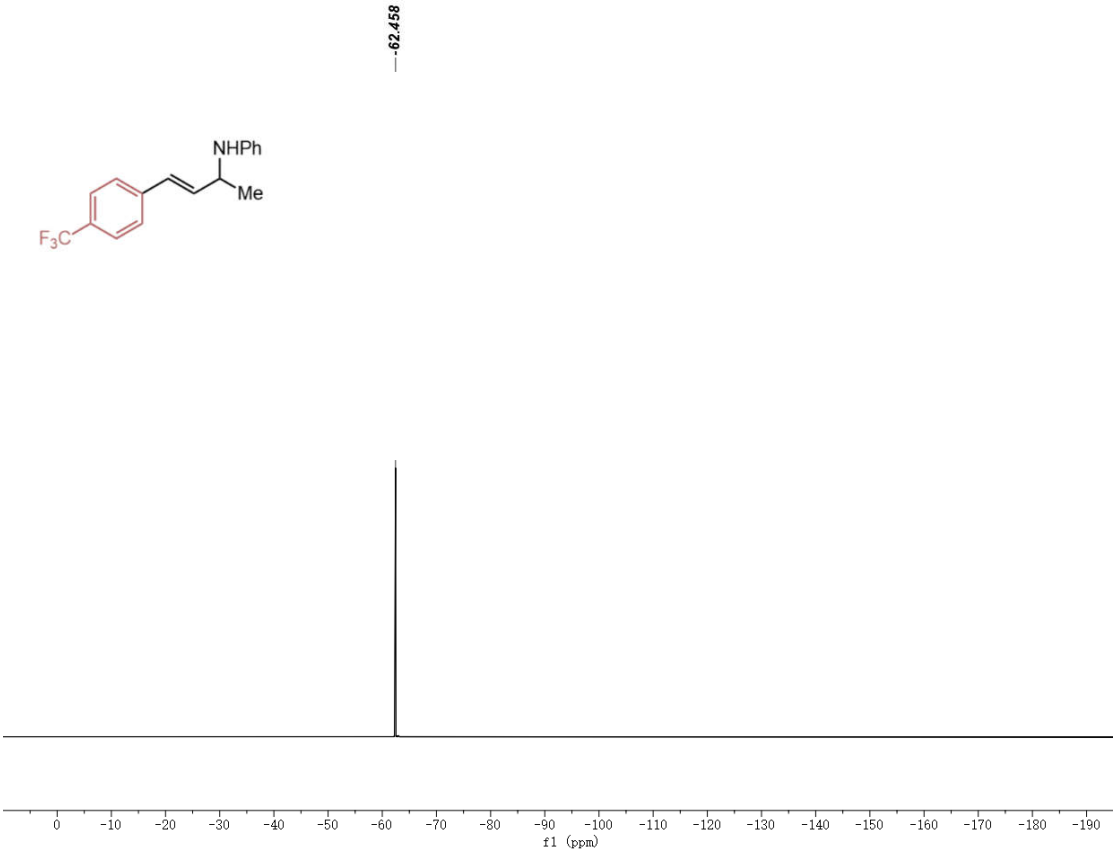
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**

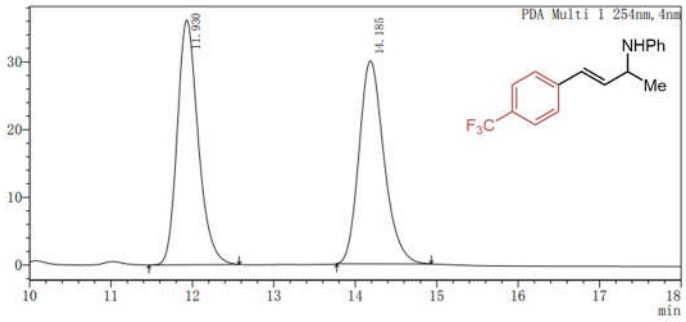


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3da**



^{19}F NMR (377 MHz, $CDCl_3$) spectrum of **3da**



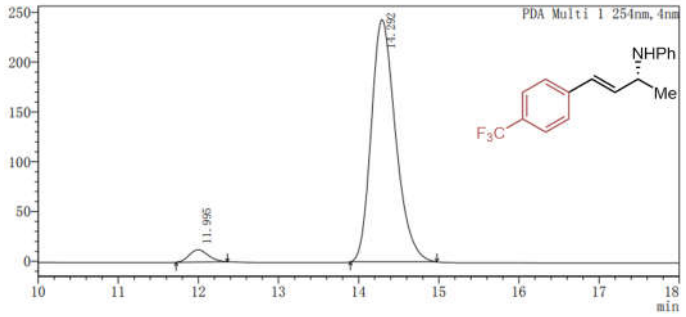


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.930	644693	36119	50.169
2	14.185	640351	29988	49.831
总计		1285044	66107	100.000

Total

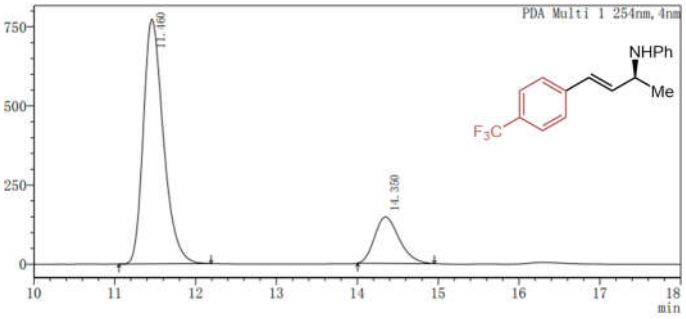


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.995	203089	12351	3.793
2	14.292	5151080	243060	96.207
总计		5354169	255411	100.000

Total



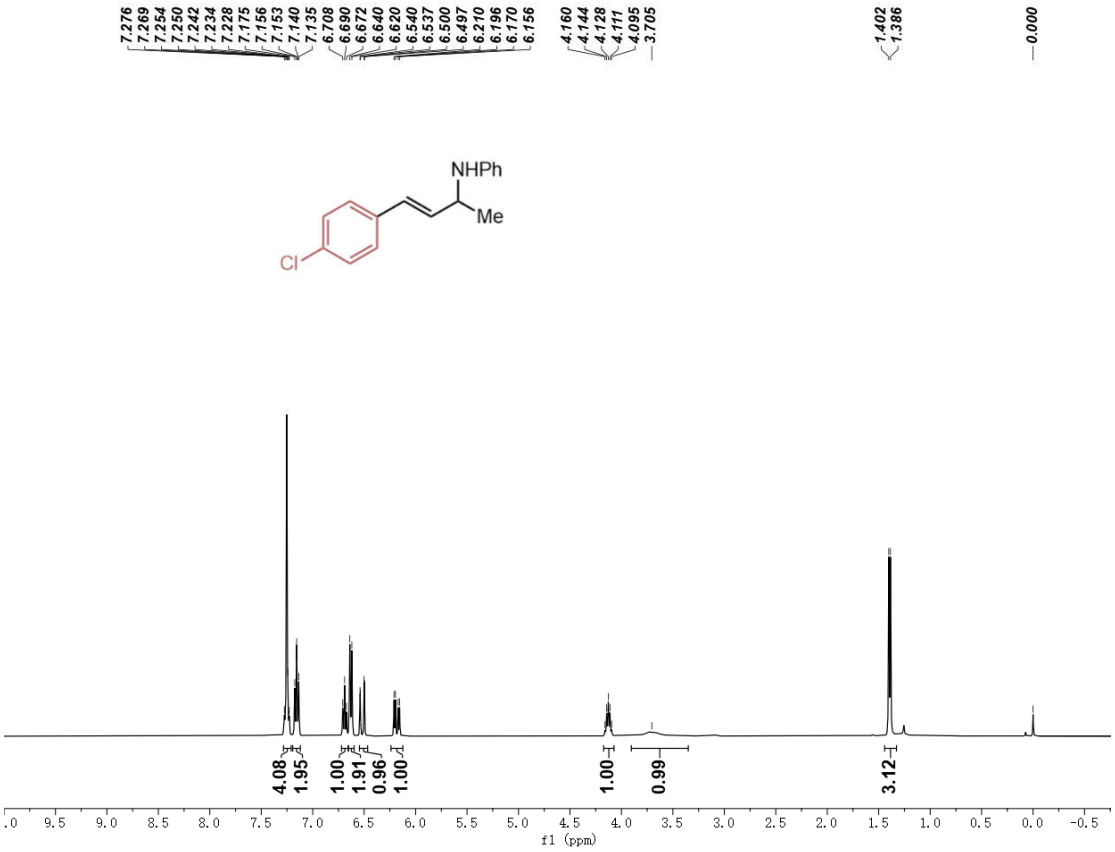
Entry Retention time Area Height Area%

PDA Ch1 254nm

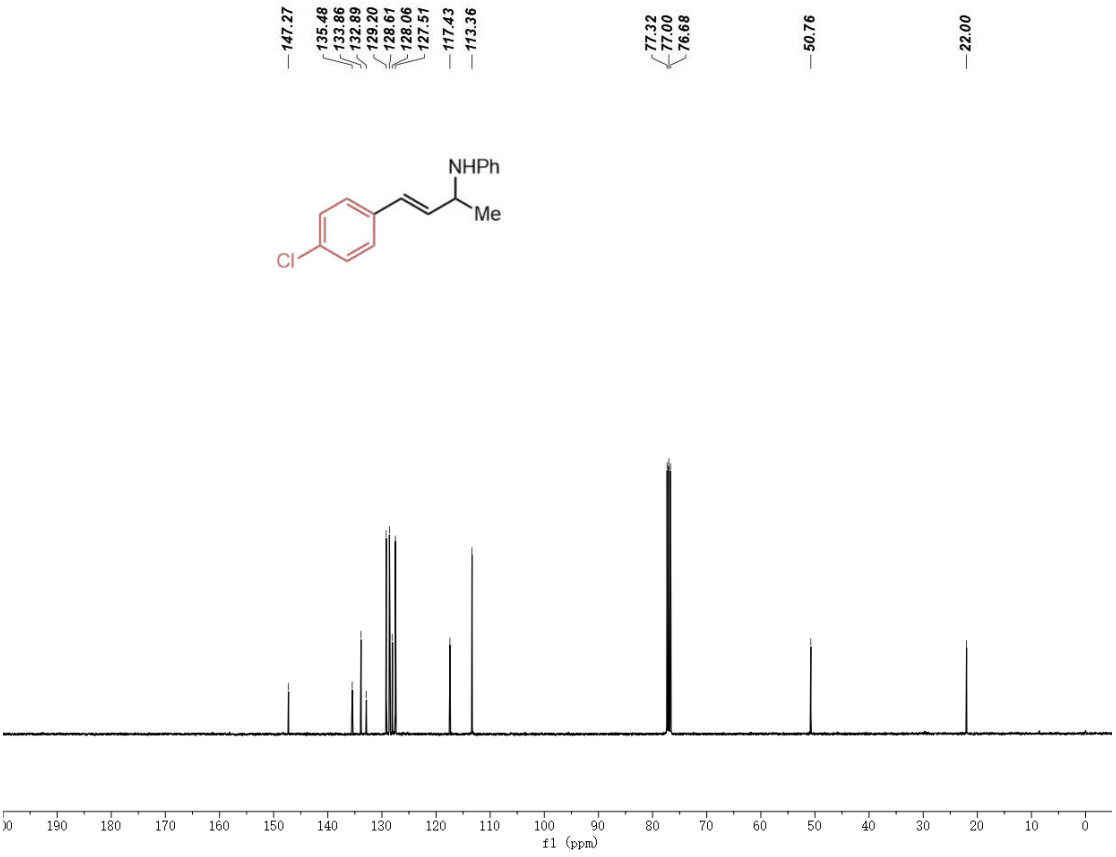
峰号	保留时间	面积	高度	面积%
1	11.460	13388127	772849	81.133
2	14.350	3113398	146457	18.867
总计		16501524	919305	100.000

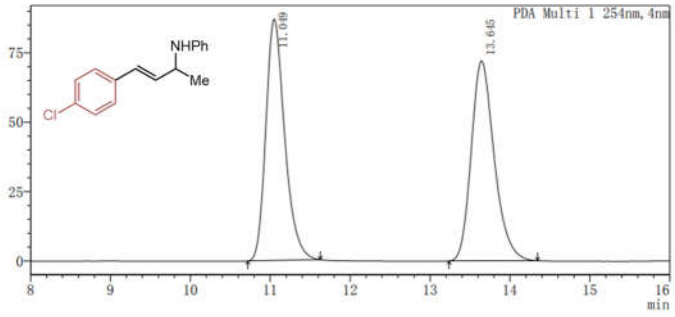
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



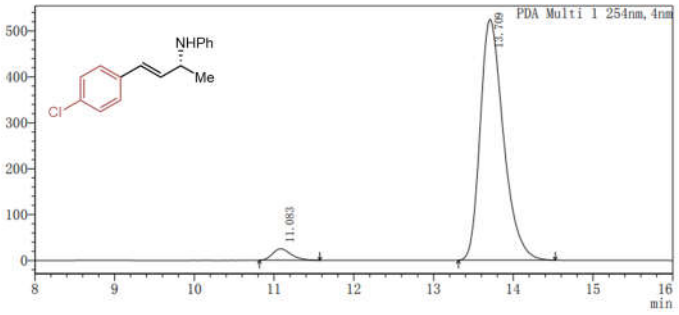


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.049	1429500	86965	49.750
2	13.645	1443842	72011	50.250
总计		2873342	158976	100.000

Total

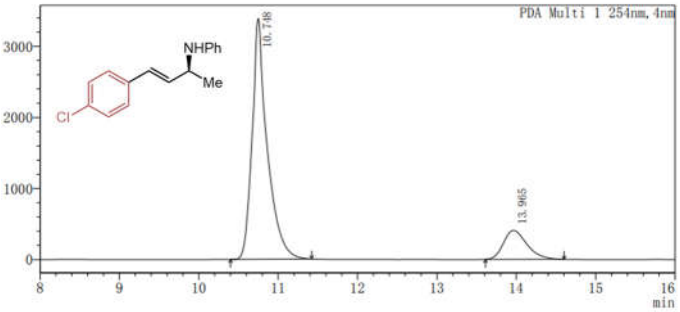


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.083	404620	25143	3.662
2	13.709	10644026	524702	96.338
总计		11048646	549845	100.000

Total



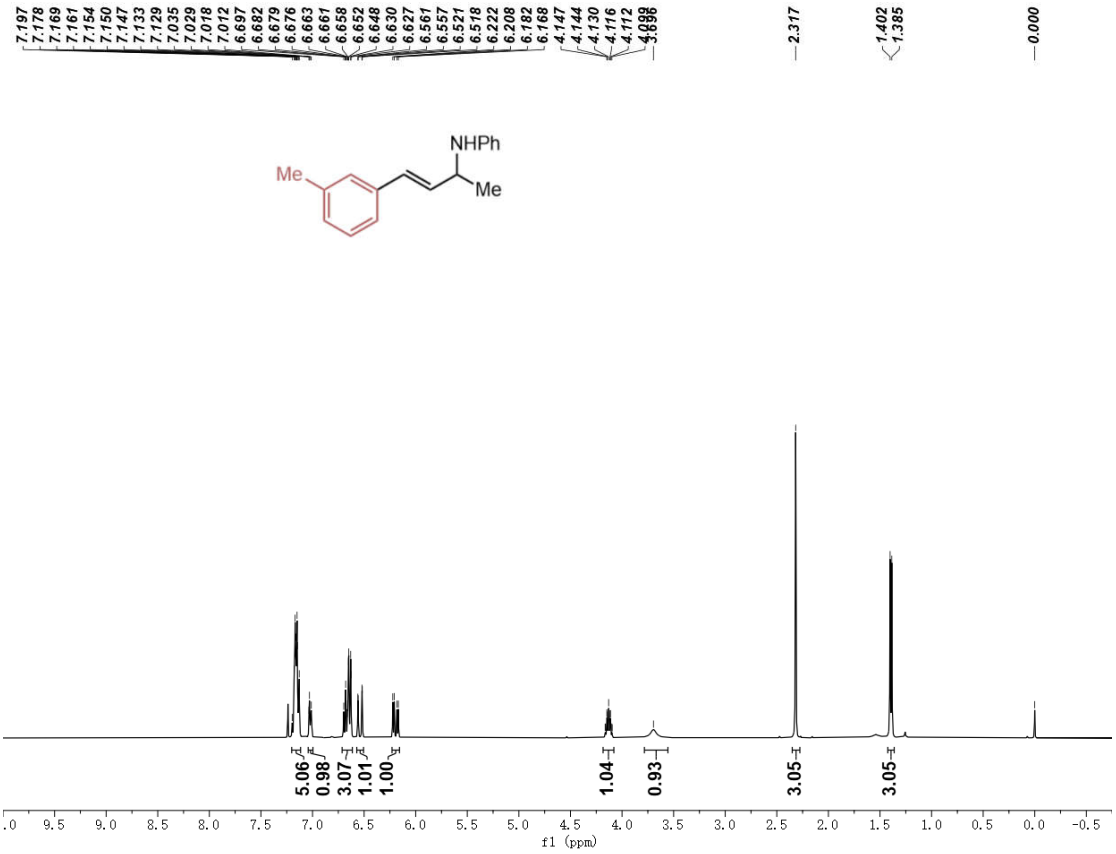
Entry Retention time Area Height Area%

PDA Ch1 254nm

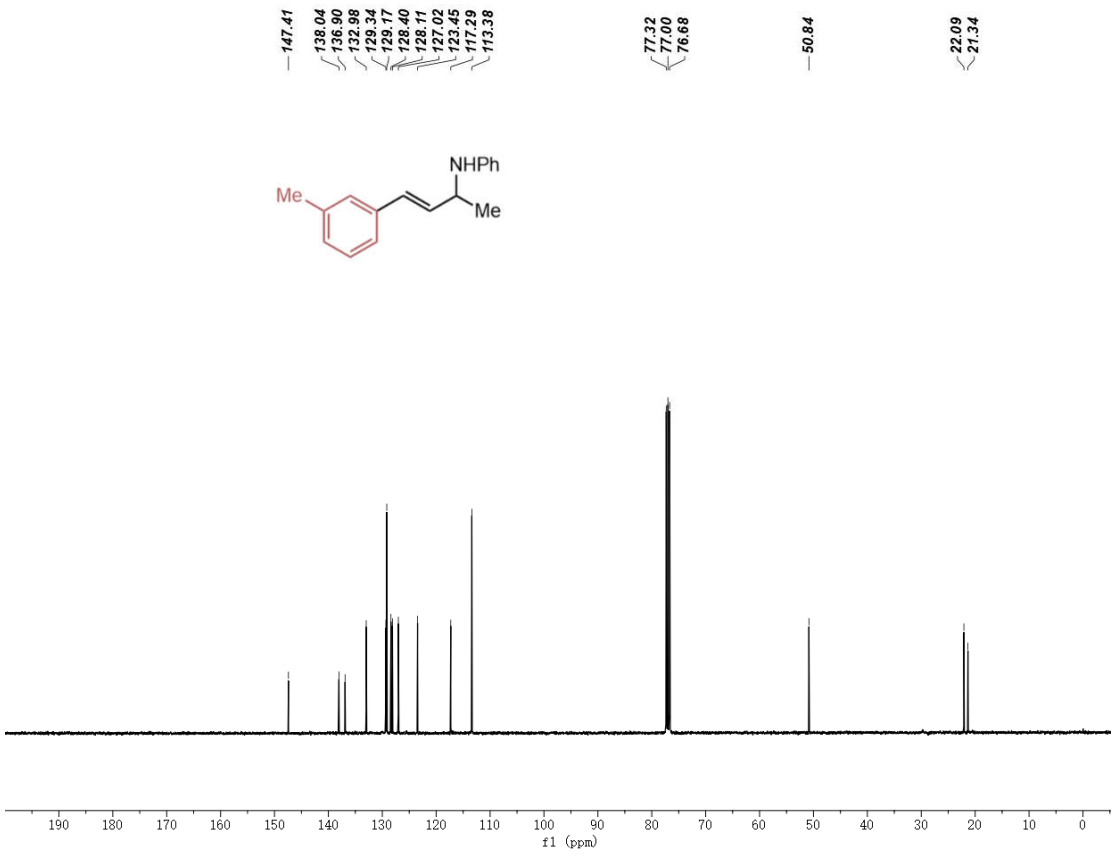
峰号	保留时间	面积	高度	面积%
1	10.748	44759509	3385102	84.233
2	13.965	8378410	407853	15.767
总计		53137919	3792955	100.000

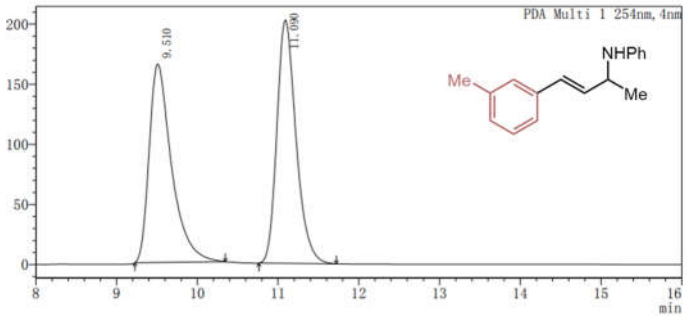
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



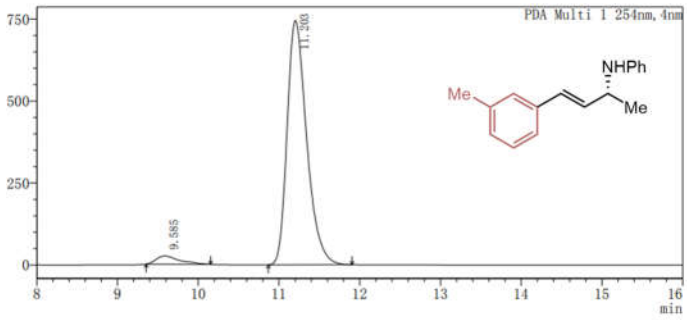


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.510	3341748	166518	49.681
2	11.090	3384602	203197	50.319
总计		6726350	369715	100.000

Total

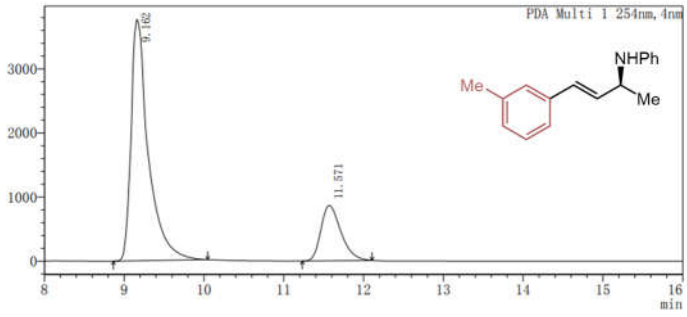


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	9.585	504909	25217	3.875
2	11.203	12525999	744666	96.125
总计		13030908	769882	100.000

Total



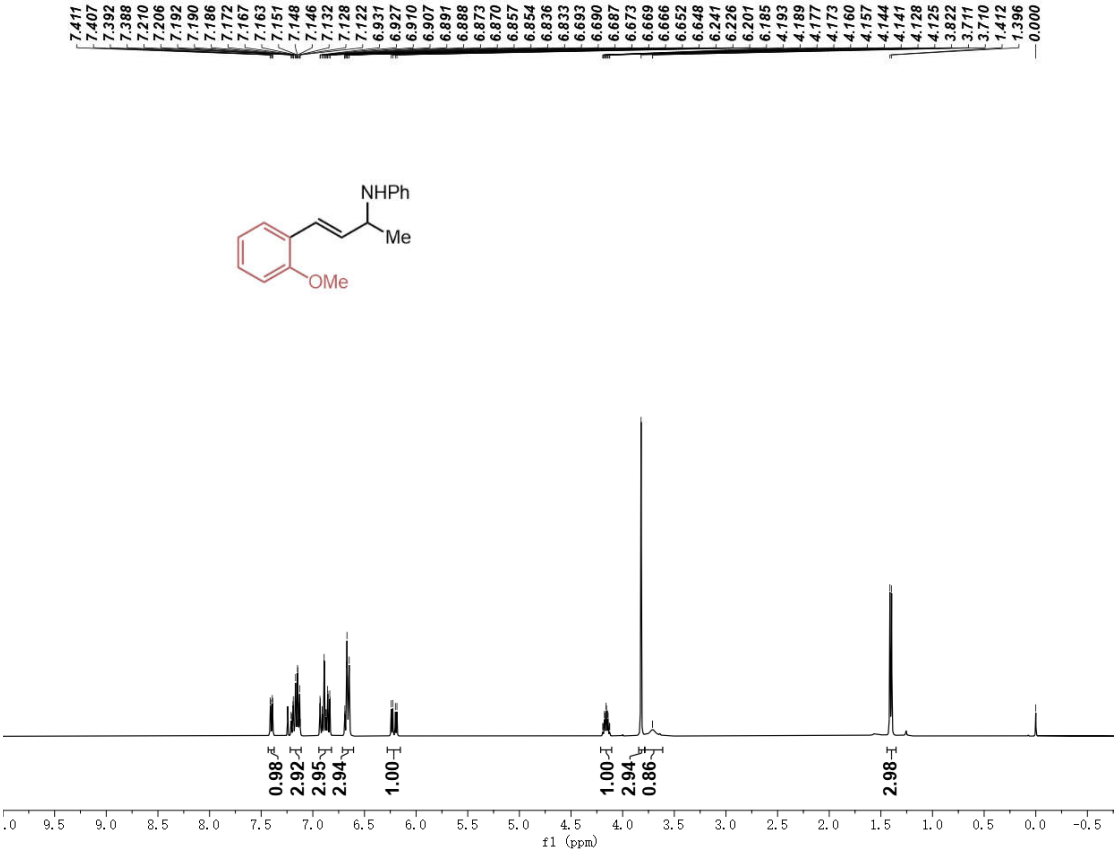
Entry Retention time Area Height Area%

PDA Ch1 254nm

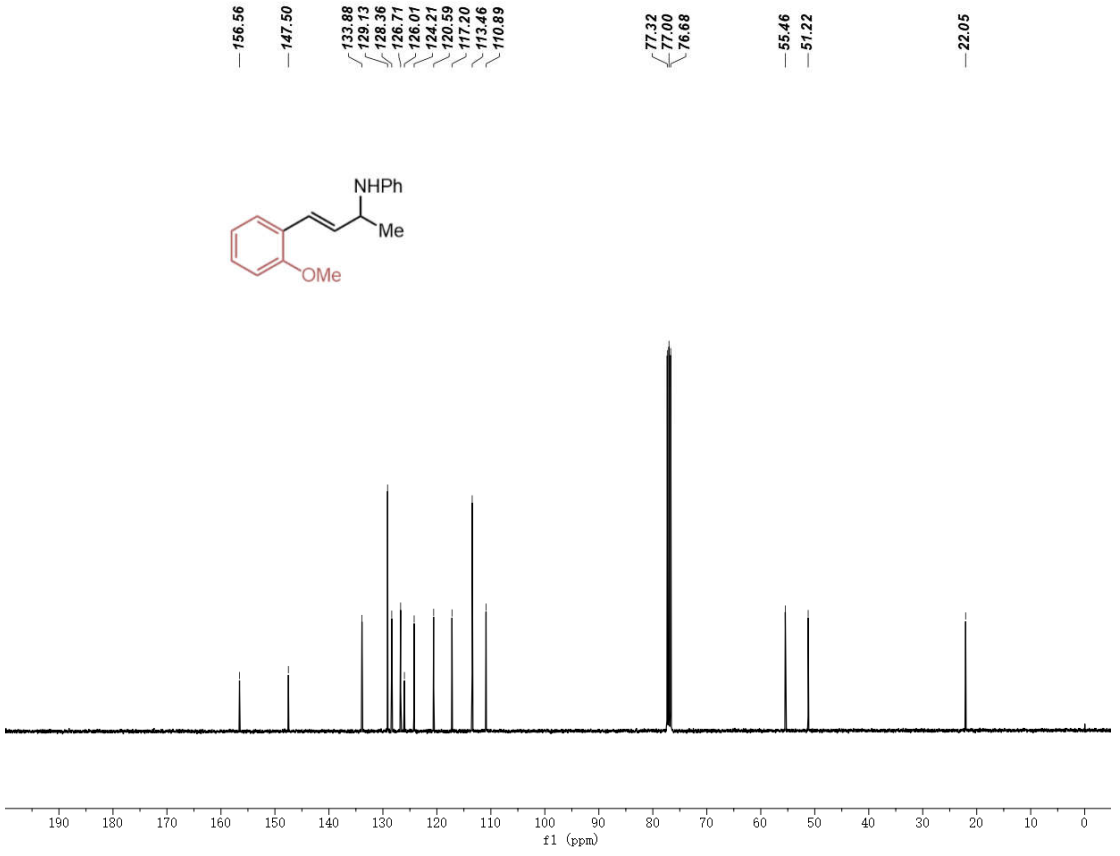
峰号	保留时间	面积	高度	面积%
1	9.162	56642281	3762742	78.997
2	11.571	15059593	863343	21.003
总计		71701874	4626085	100.000

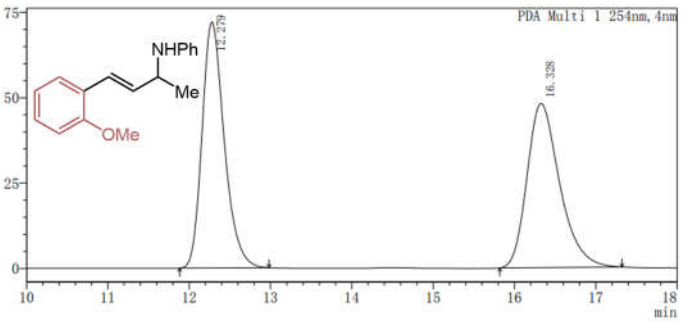
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ga**



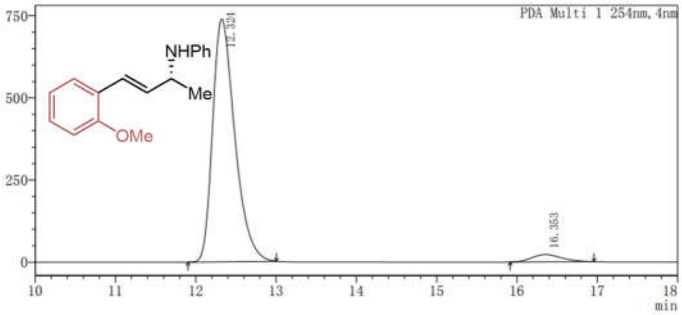


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	12.279	1369002	72070	50.498
2	16.328	1341975	48104	49.502
总计		2710977	120173	100.000

Total

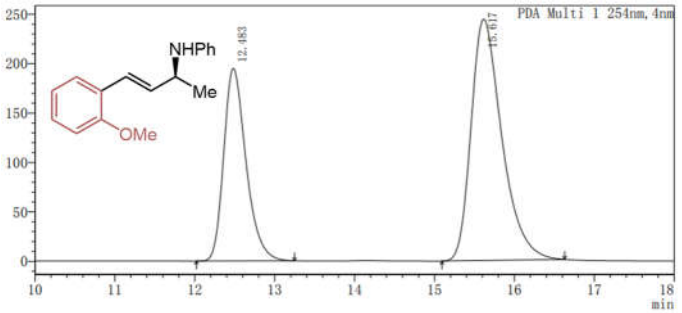


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	12.324	14213763	739050	96.047
2	16.353	585042	22306	3.953
总计		14798806	761356	100.000

Total



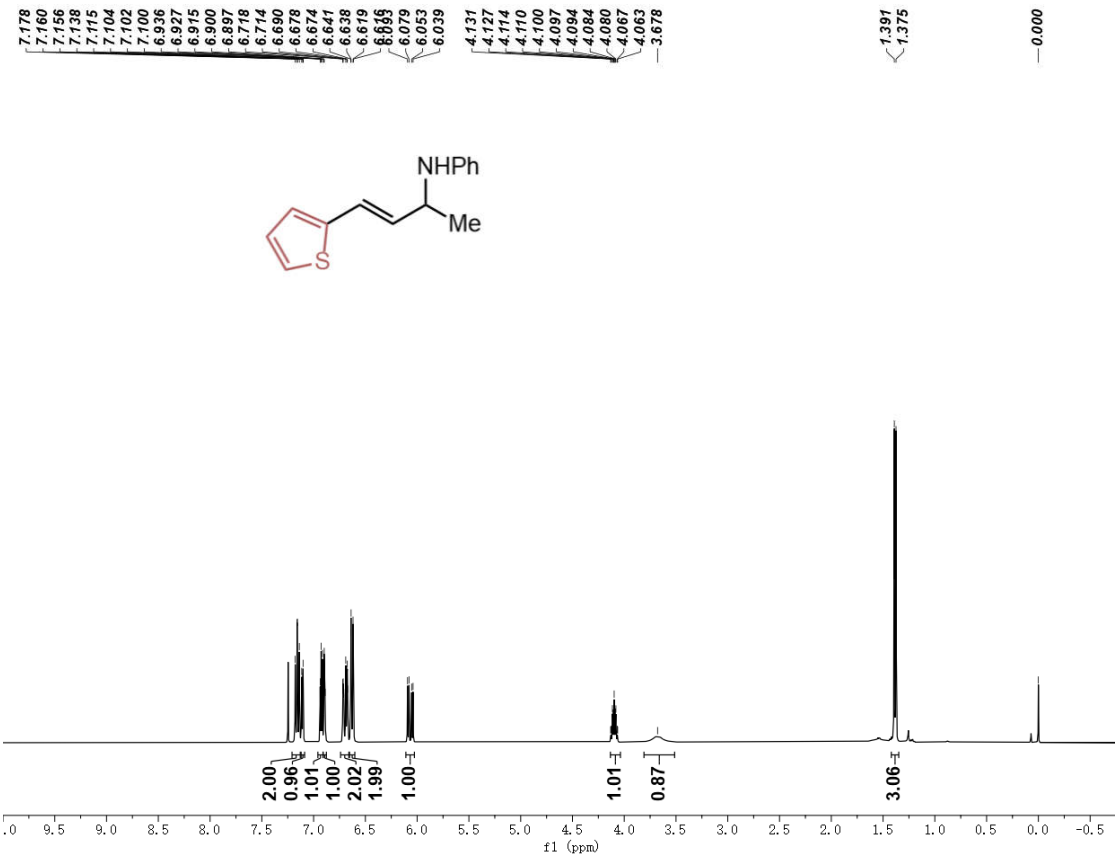
Entry Retention time Area Height Area%

PDA Ch1 254nm

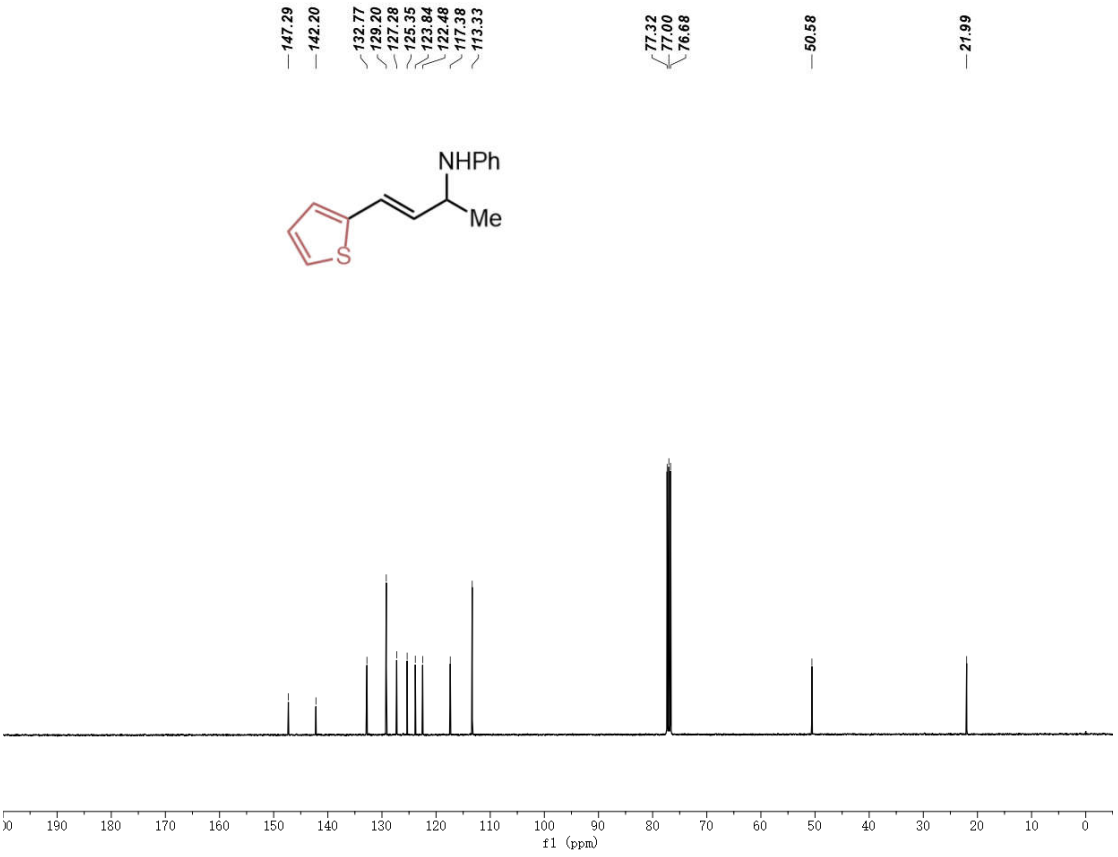
峰号	保留时间	面积	高度	面积%
1	12.483	3788295	194971	36.657
2	15.617	6546246	244263	63.343
总计		10334541	439234	100.000

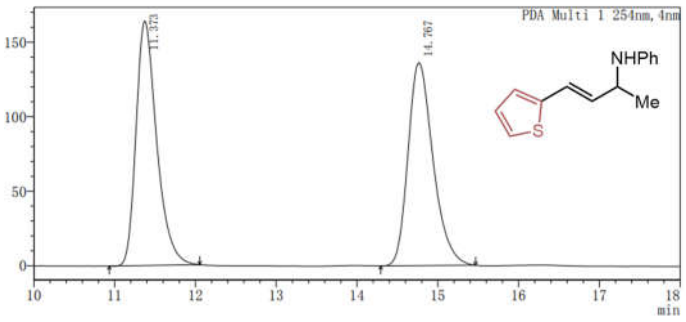
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



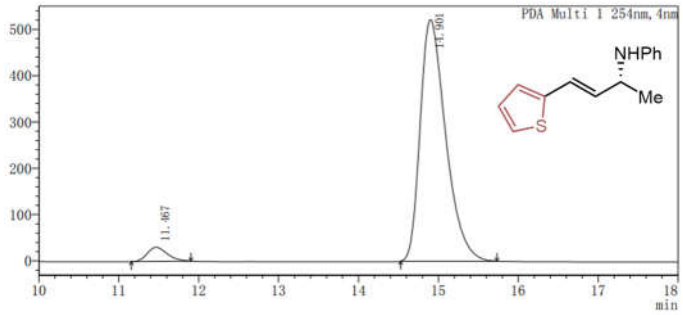


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.373	2924081	164131	49.837
2	14.767	2943266	136245	50.163
总计		5867347	300376	100.000

Total

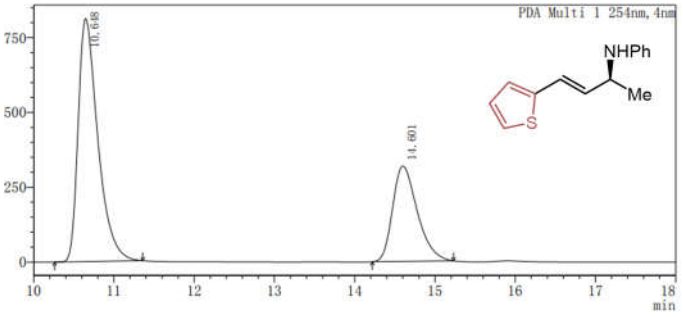


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	11.467	532209	30598	4.387
2	14.901	11598826	521444	95.613
总计		12131036	552042	100.000

Total



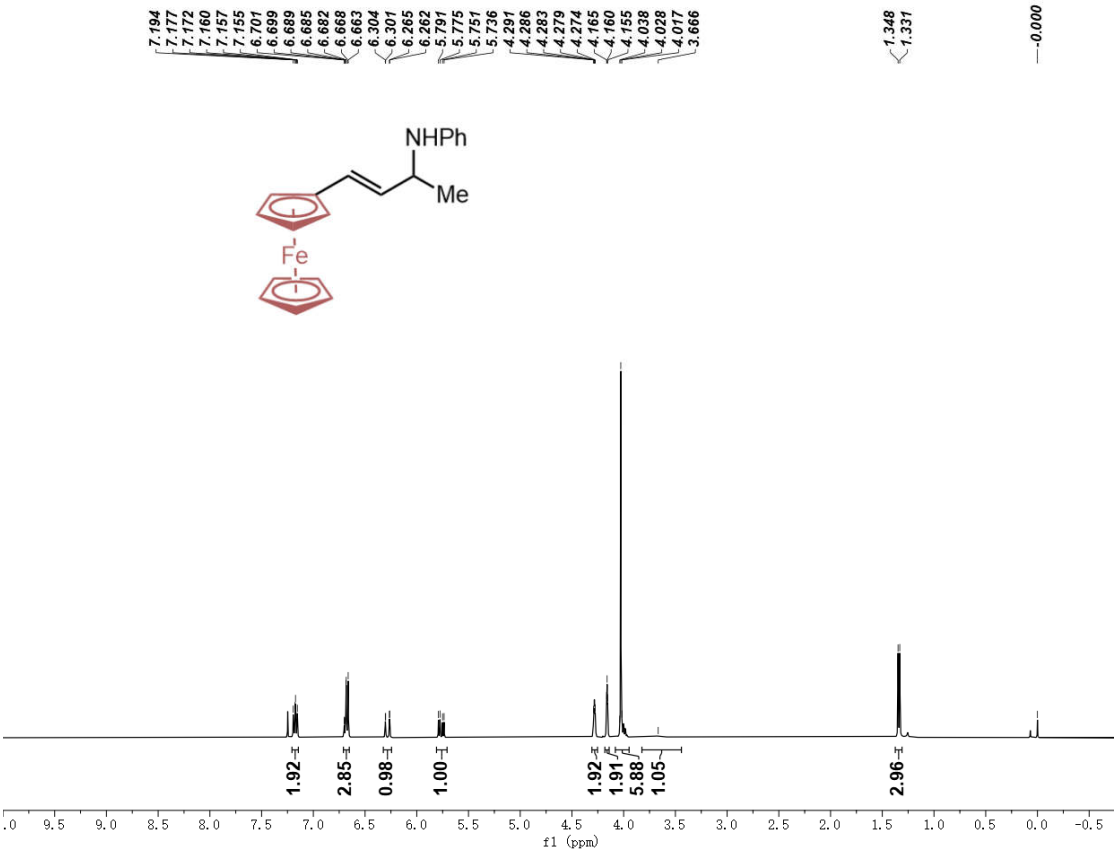
Entry Retention time Area Height Area%

PDA Ch1 254nm

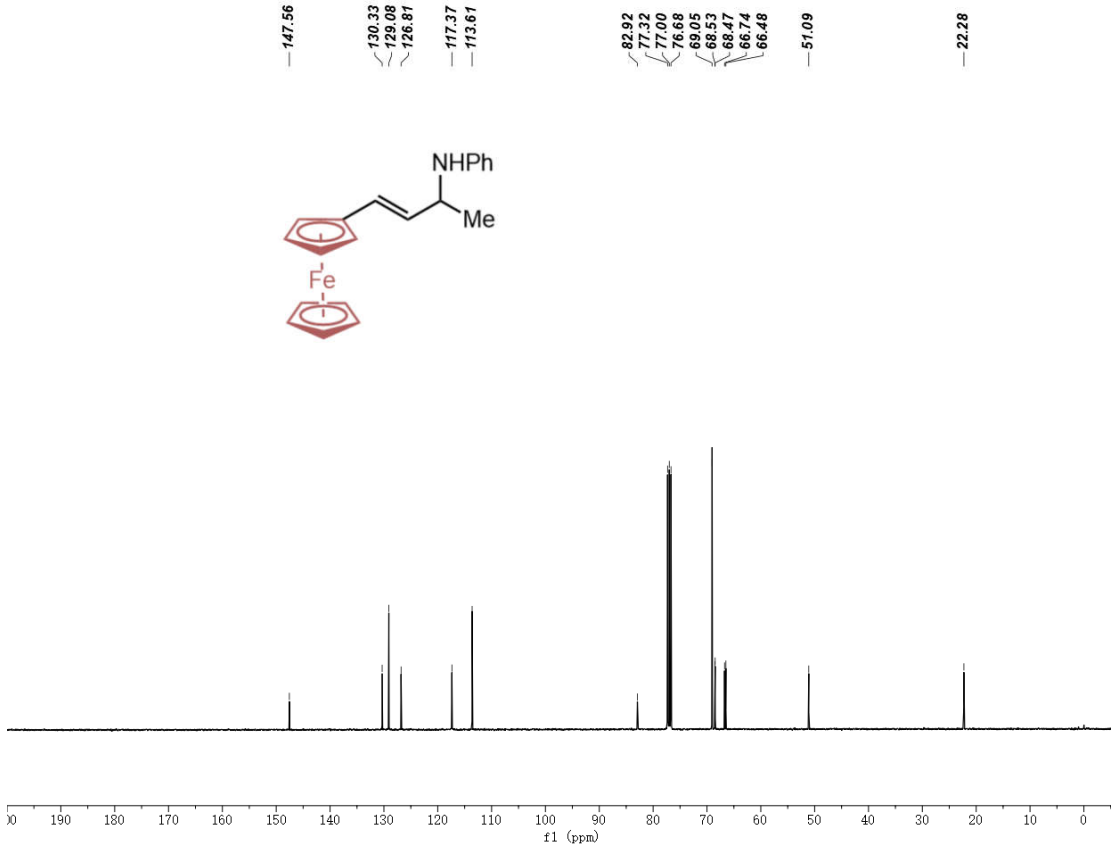
峰号	保留时间	面积	高度	面积%
1	10.648	13849175	811952	67.032
2	14.601	6811493	318872	32.968
总计		20660668	1130824	100.000

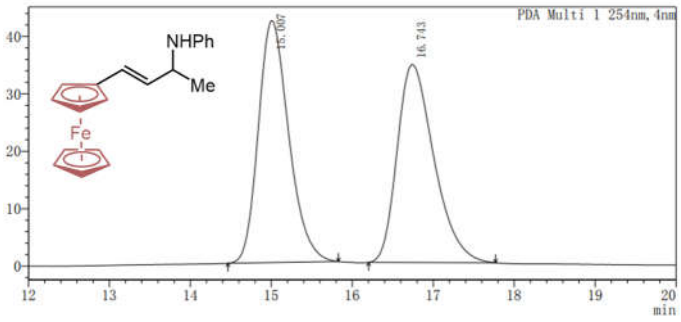
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ia**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ia**



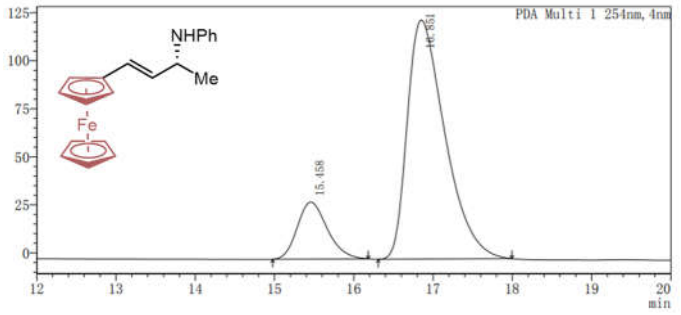


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.007	1102121	42135	50.203
2	16.743	1093224	34479	49.797
总计		2195345	76614	100.000

Total

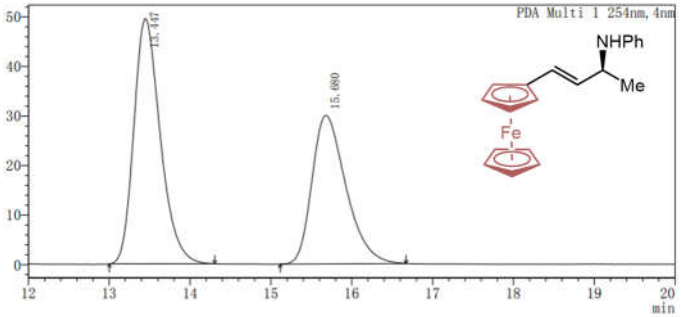


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	15.458	781830	29687	15.966
2	16.851	4115051	124398	84.034
总计		4896881	154085	100.000

Total



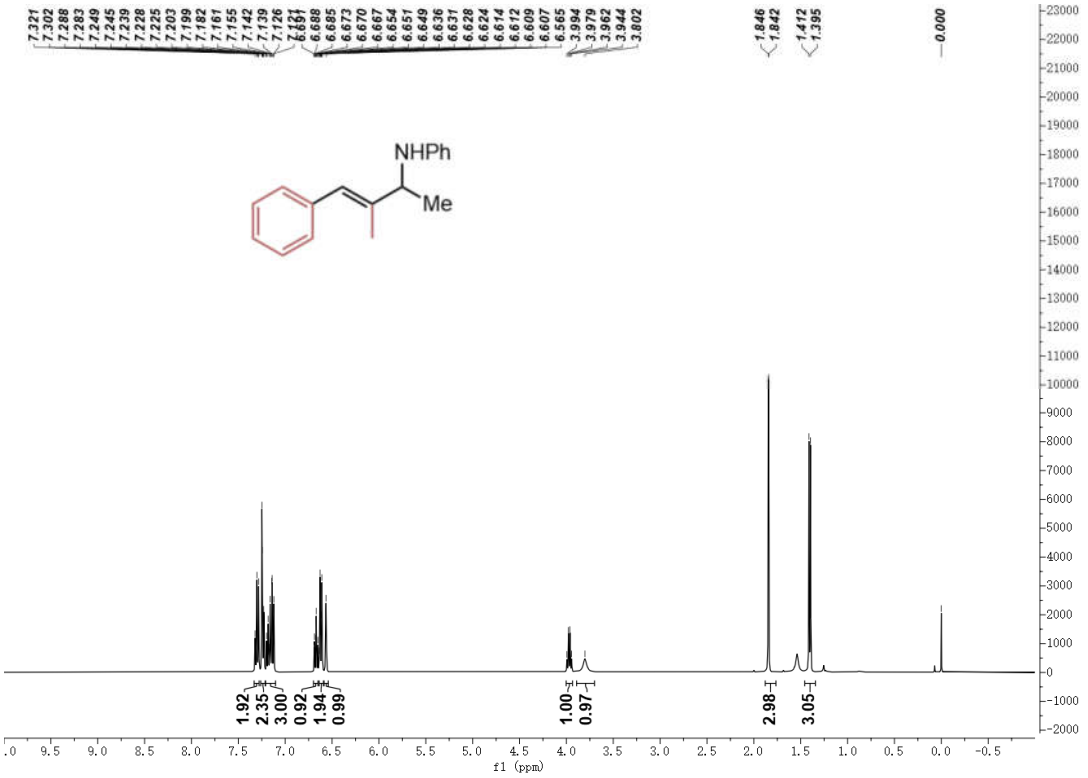
Entry Retention time Area Height Area%

PDA Ch1 254nm

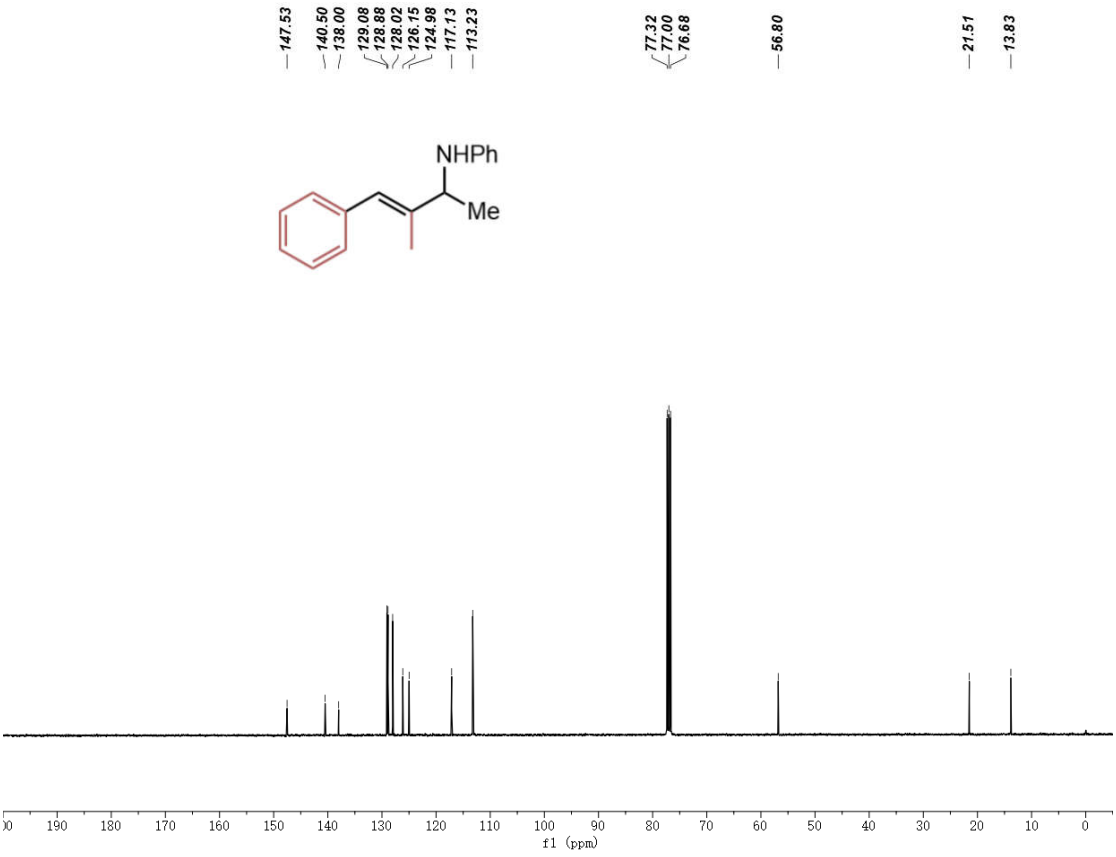
峰号	保留时间	面积	高度	面积%
1	13.447	1126103	49456	56.281
2	15.680	874766	29967	43.719
总计		2000869	79423	100.000

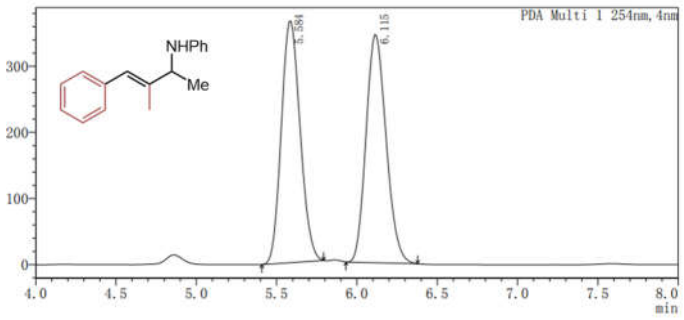
Total

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



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ja**



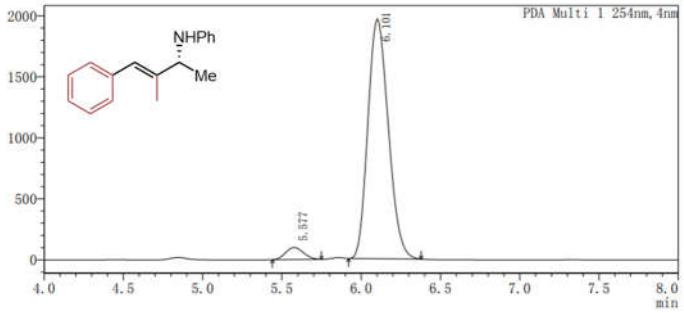


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	5.584	2982304	365077	49.816
2	6.115	3004338	345233	50.184
总计		5986642	710310	100.000

Total

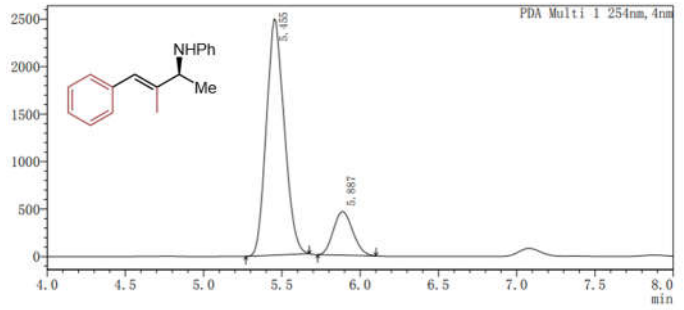


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	5.577	778143	99072	4.233
2	6.101	17603521	1964925	95.767
总计		18381665	2063997	100.000

Total



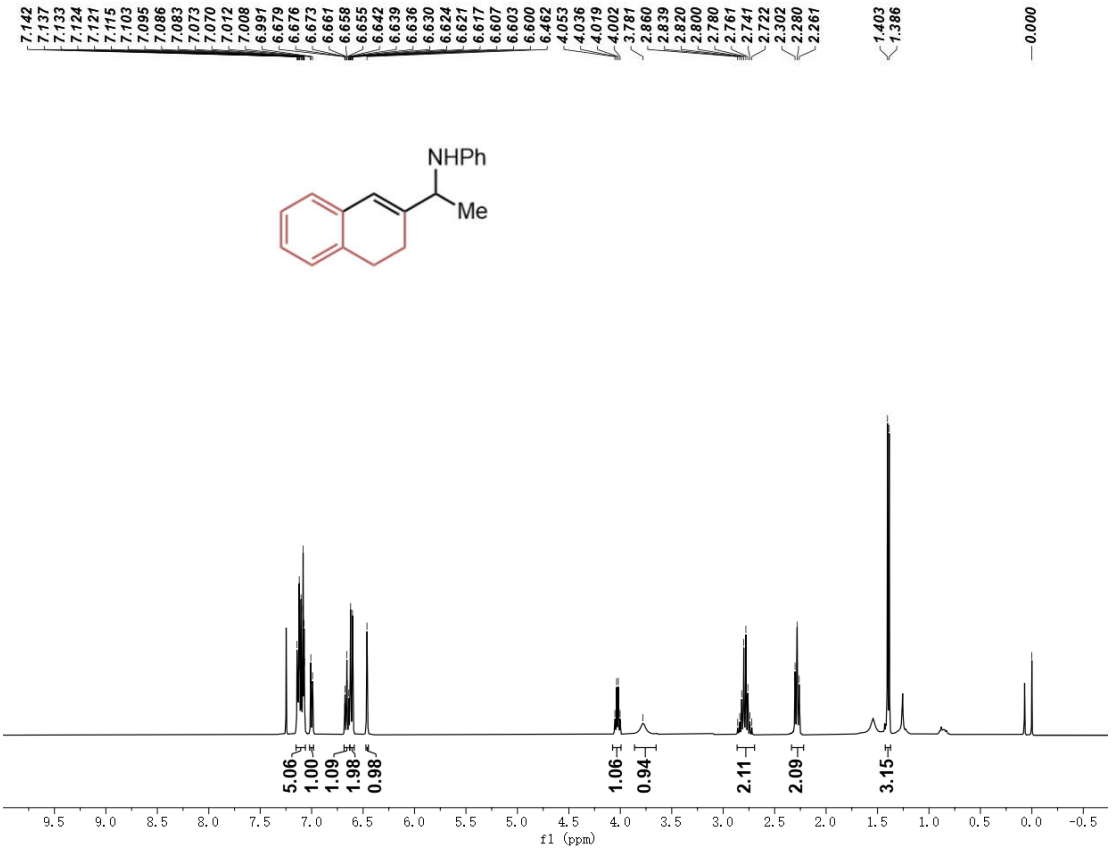
Entry Retention time Area Height Area%

PDA Ch1 254nm

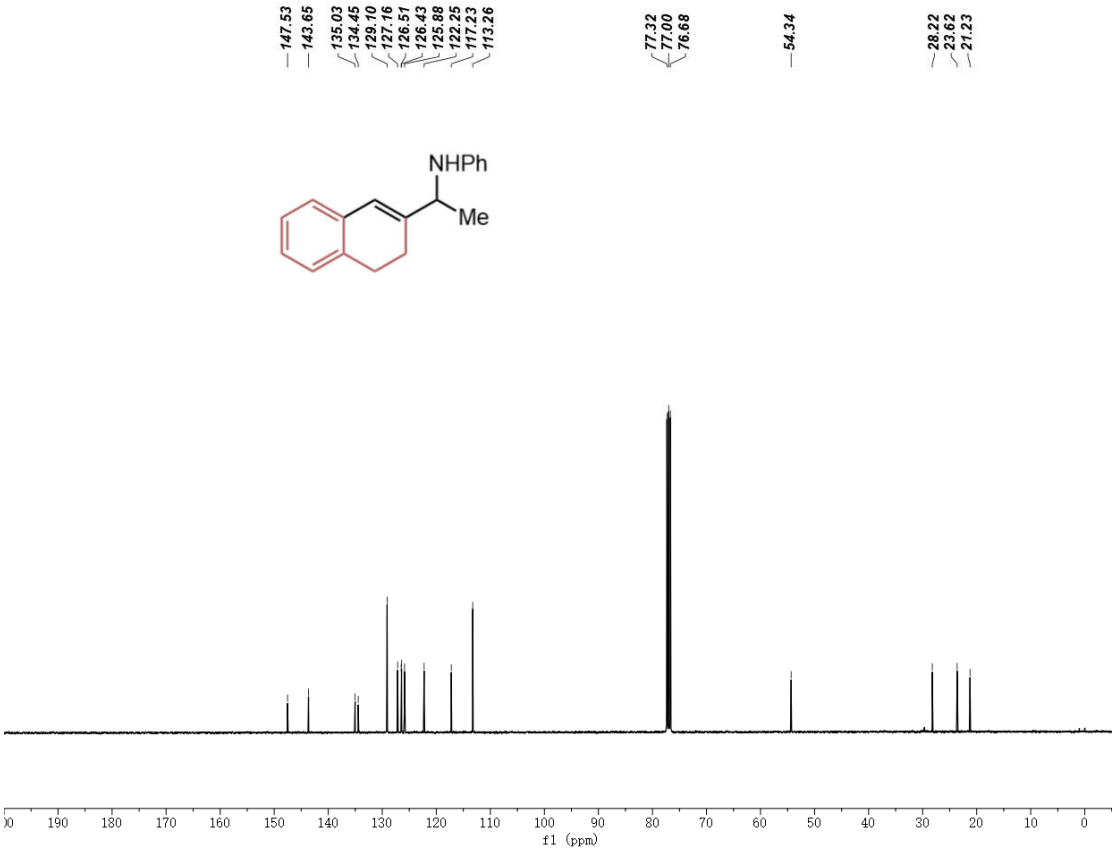
峰号	保留时间	面积	高度	面积%
1	5.455	19865136	2487865	83.313
2	5.887	3978775	460365	16.687
总计		23843911	2948230	100.000

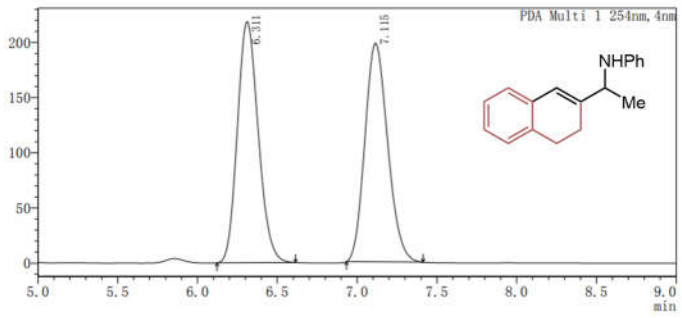
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ka**



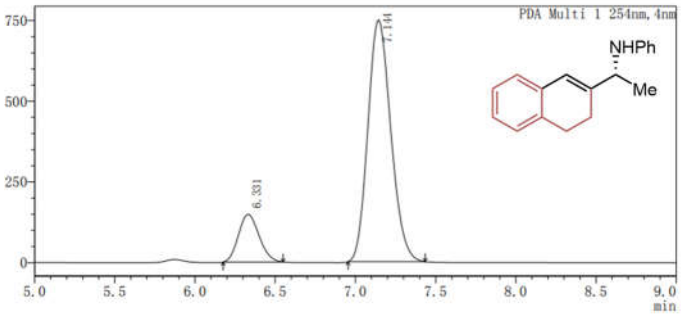


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	6.311	1990648	218452	50.226
2	7.115	1972709	198270	49.774
总计		3963357	416722	100.000

Total

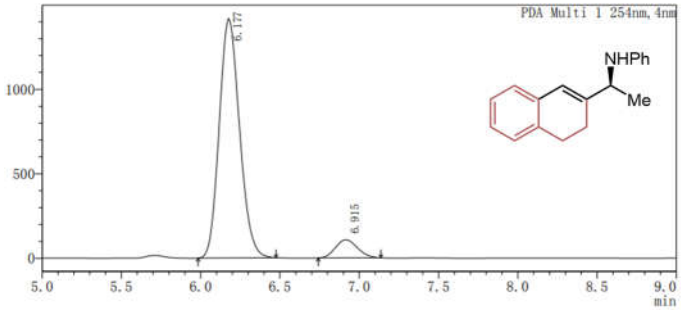


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	6.331	1319423	147369	15.052
2	7.144	7446240	749117	84.948
总计		8765663	896486	100.000

Total



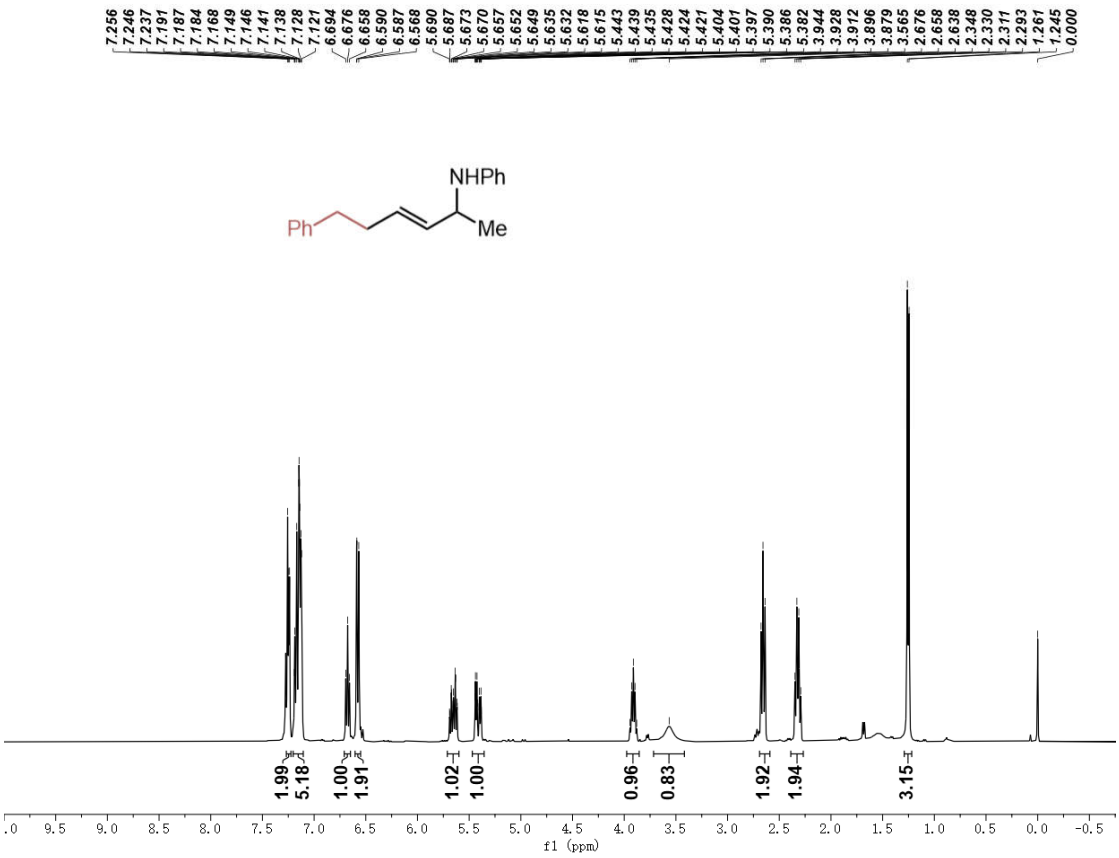
Entry Retention time Area Height Area%

PDA Ch1 254nm

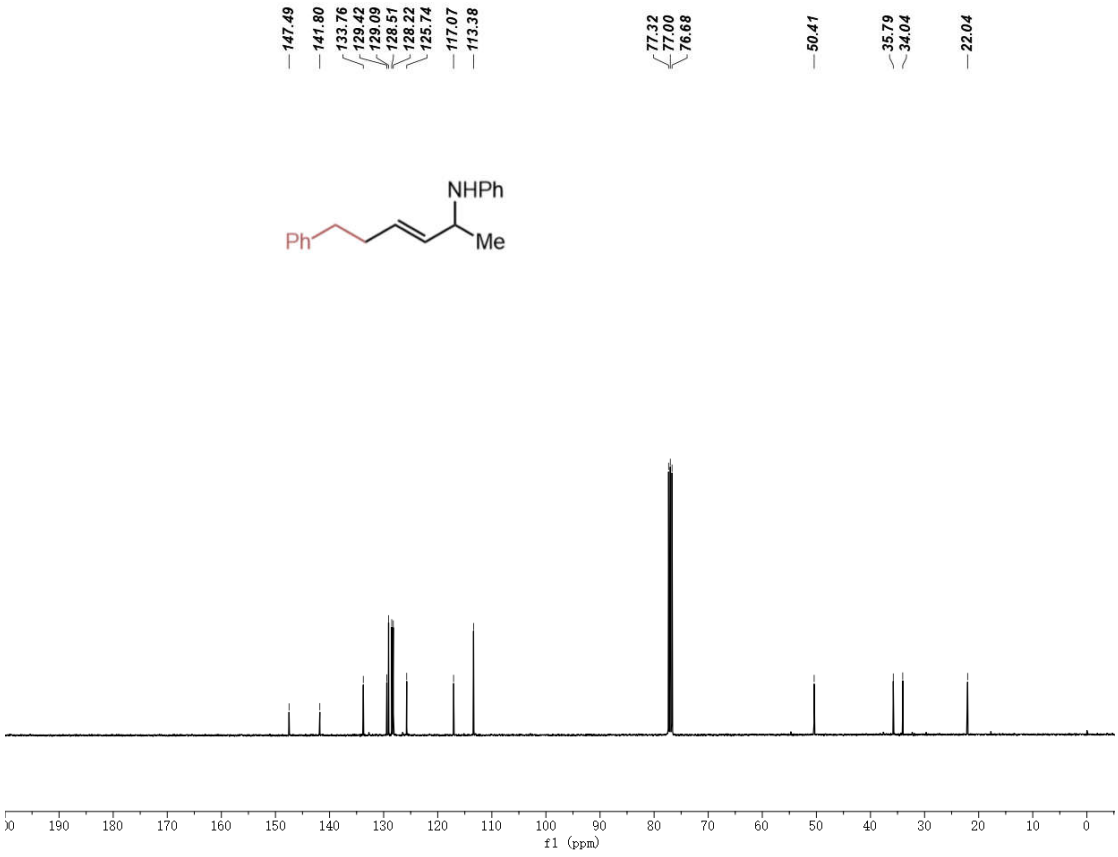
峰号	保留时间	面积	高度	面积%
1	6.177	12630016	1417203	92.389
2	6.915	1040527	107466	7.611
总计		13670544	1524669	100.000

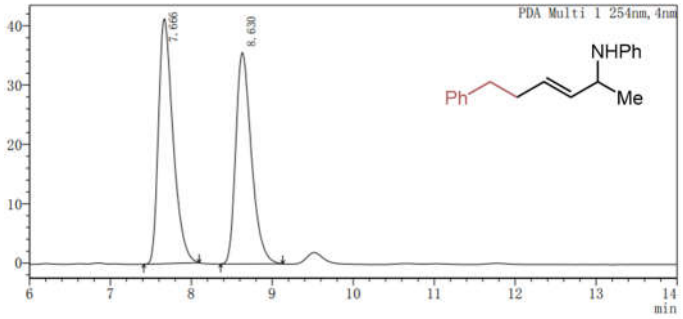
Total

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



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3la**



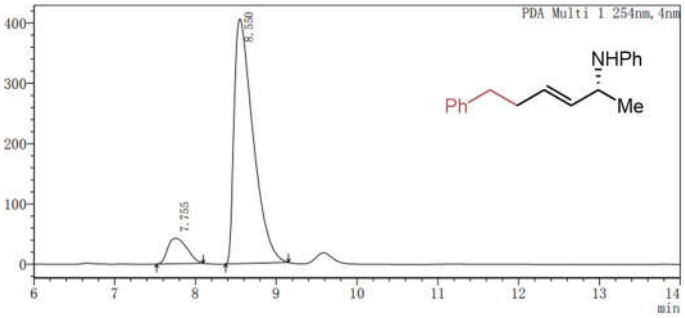


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	7.666	519527	41245	51.957
2	8.630	480382	35627	48.043
总计		999909	76872	100.000

Total

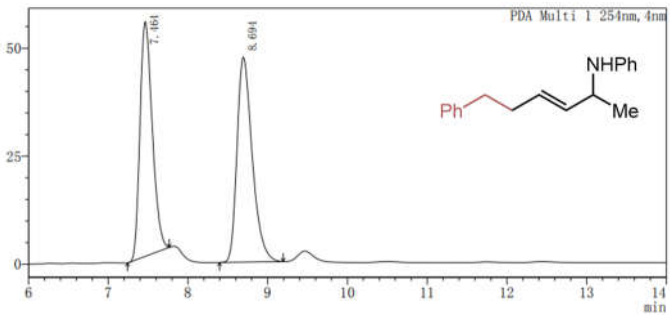


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	7.755	698904	42267	9.542
2	8.550	6625230	405174	90.458
总计		7324134	447441	100.000

Total

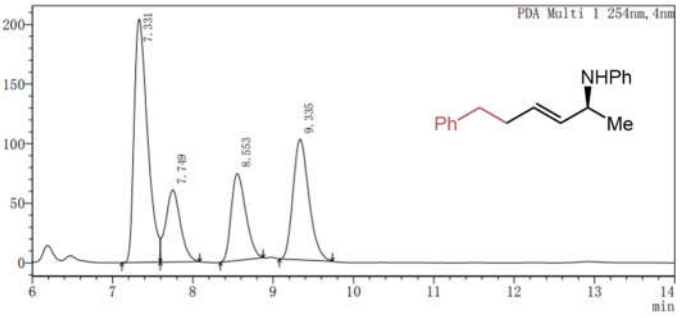


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	7.464	583317	54302	48.035
2	8.694	631029	47461	51.965
总计		1214346	101762	100.000

Total



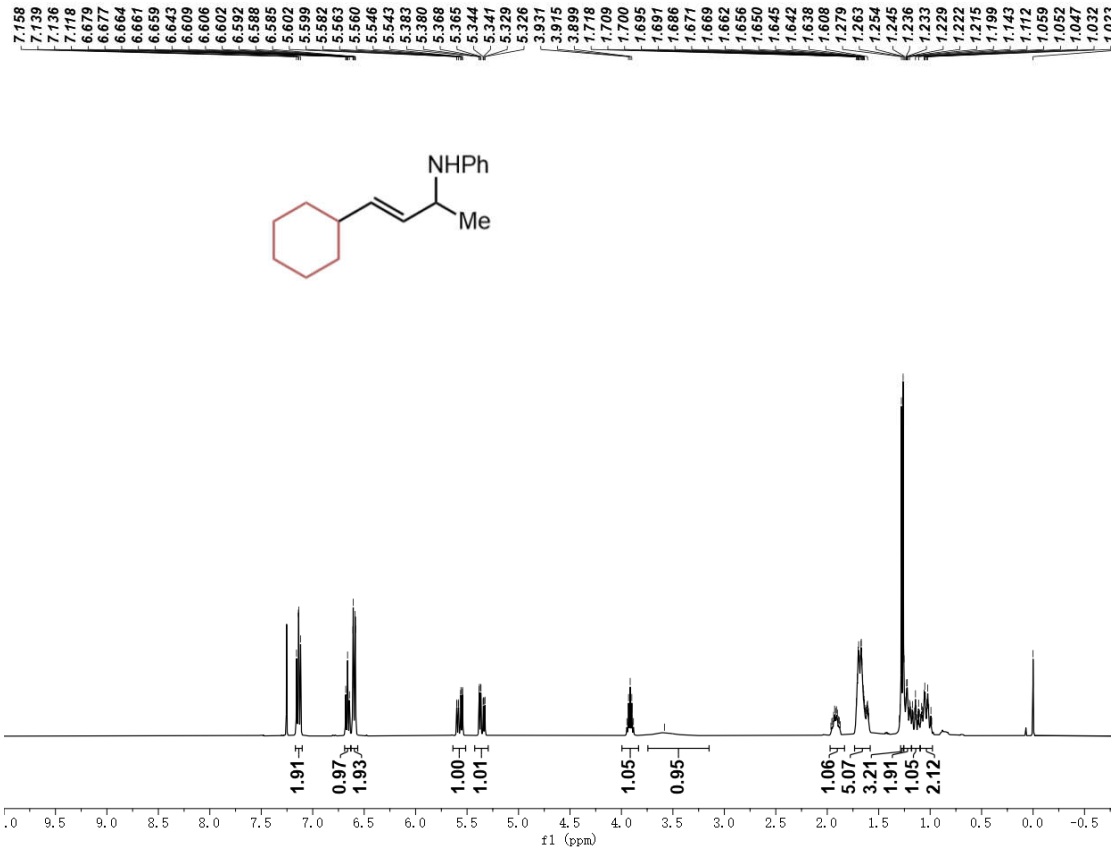
Entry Retention time Area Height Area%

PDA Ch1 254nm

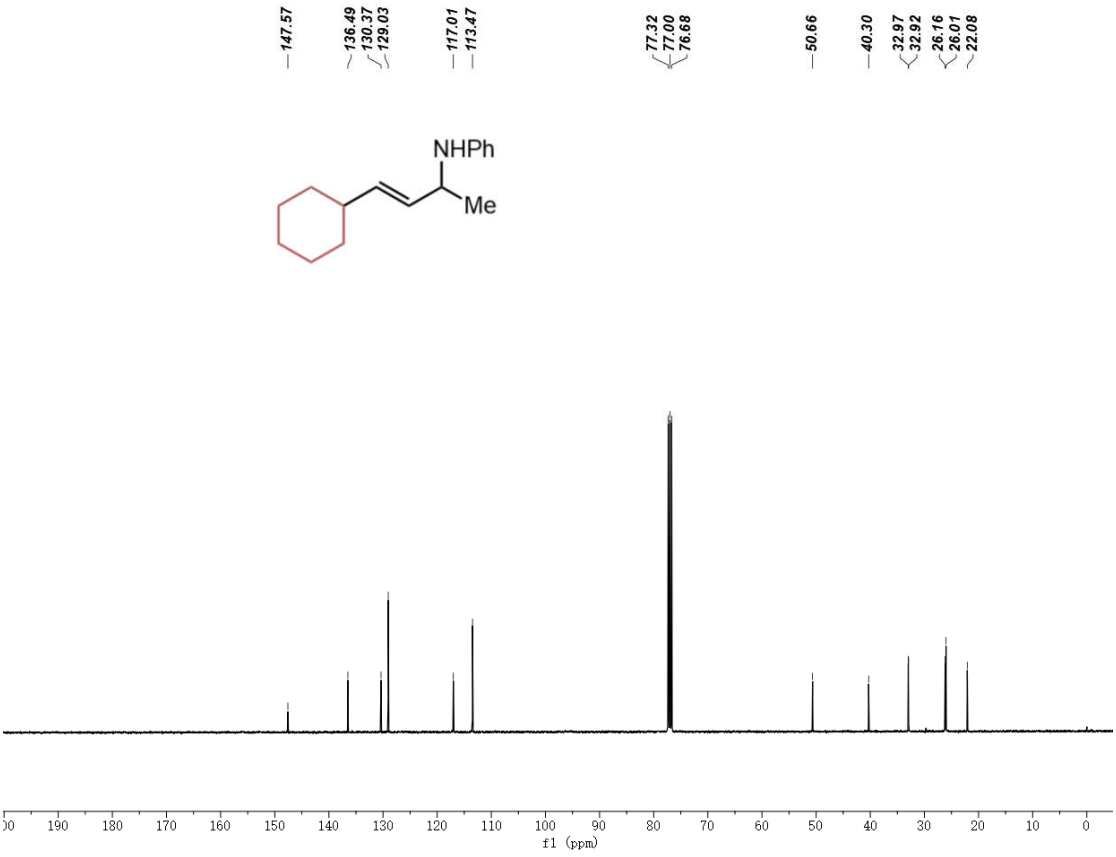
峰号	保留时间	面积	高度	面积%
1	7.331	2370102	204061	43.474
2	7.749	766516	60367	14.060
3	8.553	922586	72963	16.923
4	9.335	1392537	101283	25.543
总计		5451741	438674	100.000

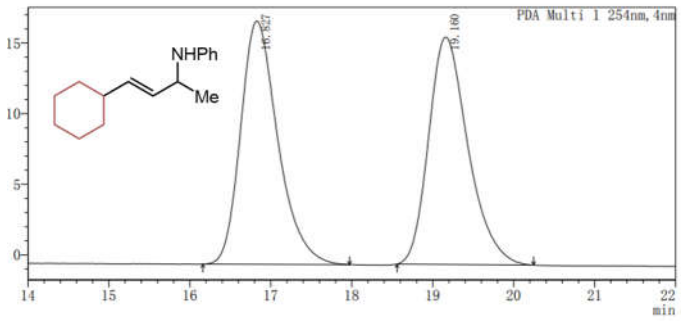
Total

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ma**



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3ma**



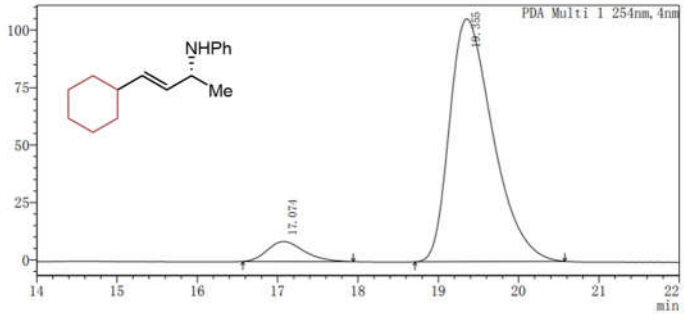


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	16.827	551601	17224	50.324
2	19.160	544490	16100	49.676
总计		1096091	33324	100.000

Total

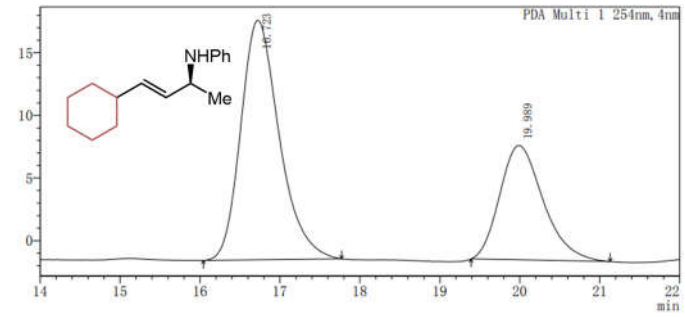


Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	17.074	276717	8726	6.519
2	19.355	3968037	105622	93.481
总计		4244754	114349	100.000

Total



Entry Retention time Area Height Area%

PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%
1	16.723	640641	19105	64.998
2	19.989	344997	9124	35.002
总计		985638	28228	100.000

Total