Supplementary Information

Regio- and Diastereoselective Annulation of α,β-Unsaturated Aldimines with 1,3-Dienes by Rare-Earth-Catalyzed Allylic C(sp^3)−H Activation

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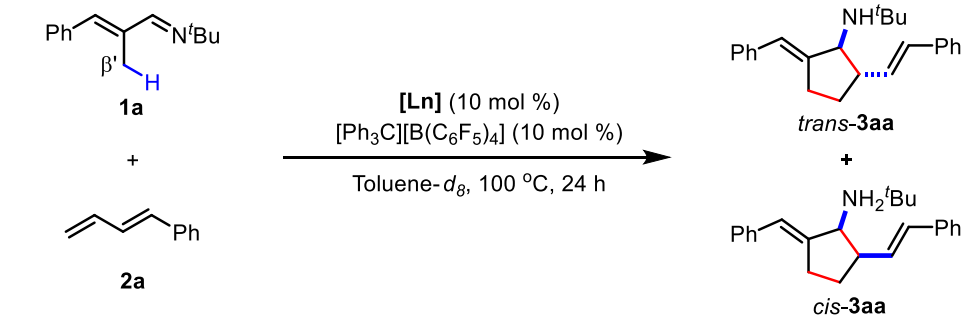
1. General and Materials

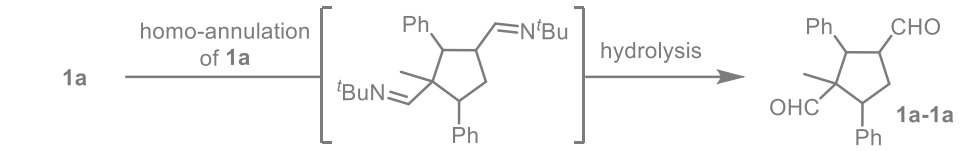
General. All manipulations of air- and moisture-sensitive compounds were performed under dry nitrogen atmosphere in a glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O CombiAnalyzer to ensure both were always below 0.1 ppm. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. All ^{1}H and ^{13}C NMR spectra of organic products were recorded on Bruker AVANCE III HD 400 NMR, JEOL JNM-ECS400 or JEOL JNM-ECS600 instrument. ^{1}H NMR spectra were recorded at 400 or 600 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 or 126 MHz and referenced to the solvent resonance. The data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, brs = broad singlet, coupling constant(s) in Hz, integration). High Resolution Mass Spectra were obtained on a Bruker microTOF-Q III (Ion source: EI, APCI, or FD).

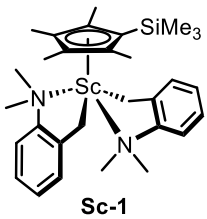
Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas and other commercial suppliers and used as received. Solvents (THF, toluene and benzene) (dehydrated, stabilizer-free) were obtained from J&K Scientific, dried over sodium (for ANHYDROUS THF) by refluxing for overnight and freshly distilled, and dried over fresh Na chips in a glovebox. Butadiene is commercial and used as received. Isoprene, myrcene and 1,3-cyclohexadiene are commercial and were distilled from CaH_2 before use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Strem and used without purification. All rare earth catalysts were synthesized according to literature.[1]

2. Optimizing Reaction Parameters

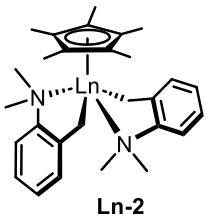
Table S1. Evaluation of effect of *catalysts* for *trans*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimine 1a with (*E*)-1-phenyl-1,3-butadiene 2a *via β′*-allylic C–H activation[a]





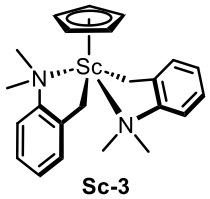


Sc-1



Ln-2

Ln = Sc, Sc-2
Ln = Y, Y-2
Ln = La, La-2
Ln = Ce, Ce-2
Ln = Sm, Sm-2
Ln = Gd, Gd-2
Ln = Ho, Ho-2
Ln = Lu, Lu-2

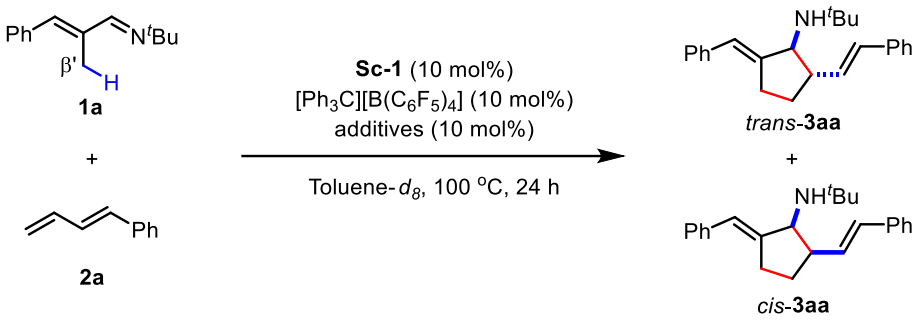


Sc-3

Entry	[Ln]	Yield of **3aa**[b]	d.r. (*trans*-**3aa**/*cis*-**3aa**)[c]	Yield of **1a-1a**[d]
1	**Sc-1**	**76%**	**>19:1**	**trace**
2	**Sc-2**	74%	>19:1	trace
3	**Sc-3**	10%	>19:1	60%
4	**Y-2**	44%	>19:1	42%
5	**La-2**	n.d.	-	85%
6	**Ce-2**	n.d.	-	85%
7	**Sm-2**	n.d.	-	85%
8	**Gd-2**	n.d.	-	78%
9	**Ho-2**	n.d.	-	80%
10	**Lu-2**	n.d.	-	52%

[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), **2a** (0.30 mmol), [**Ln**] (10 mol%), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 mol%), toluene-d_8 (1 mL), 100 °C, 24 h. [b]Combined NMR yield of both diastereomers. [c]Determined by ^{1}H NMR analysis. [d]Combined NMR yield of all diastereomers of **1a-1a**.

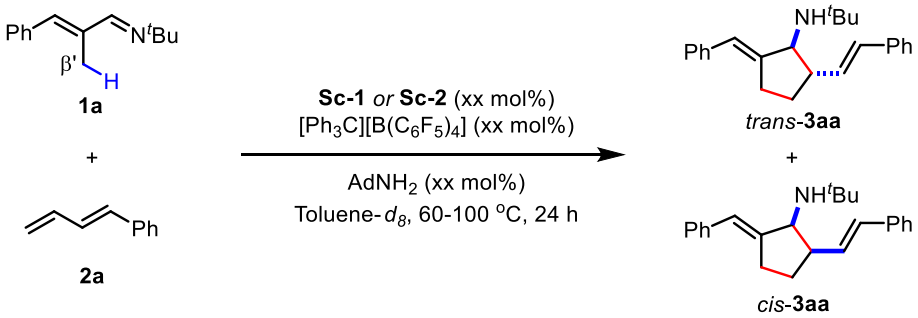
Table S2. Investigation of the effect of *additives* for *trans*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimine 1a with 2a *via β′*-allylic C–H activation by Sc-1[a]



Entry	Additives	Yield of *trans*-3aa[b]	d.r. (*trans*-3aa/*cis*-3aa)
1	**AdNH$_2$**	**98%**	**> 19:1**
1	CyNH$_2$	85%	> 19:1
2	Bn$_2$NH	85%	> 19:1
3	Cy$_2$NH	90%	> 19:1
4	(Me$_3$Si)$_2$NH	78%	> 19:1
5	^{n}Bu$_2$NH	80%	> 19:1
6	-	76%	> 19:1

[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), **2a** (0.30 mmol), **Sc-1** (10 mol%), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 mol%), additives (10 mol%), toluene-d_8 (1 mL), 100 °C, 24 h. [b]Combined NMR yield of both diastereomers.

Table S3. Investigation of the effect of *loading of catalyst* and *reaction temperature* for *trans*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimine 1a with 2a *via* β′-allylic C–H activation[a]

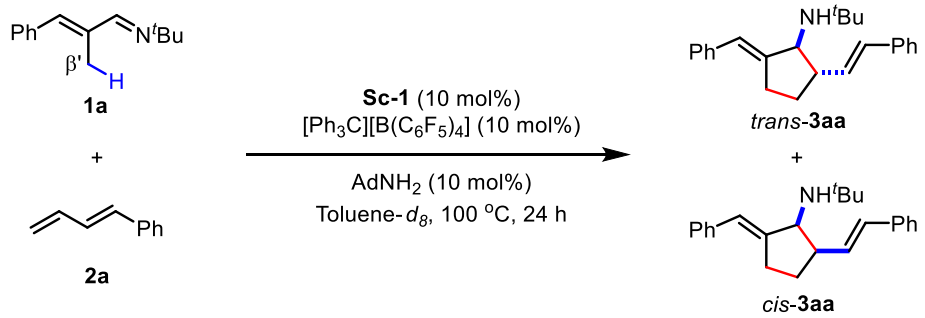


Entry	[Ln]	Temp (°C)	Yield of **3aa**[b]	*trans* : *cis*[c]
1	**Sc-1 (10 mol%)**	**100**	**98%**	**> 19 : 1**

2	**Sc-1** (10 mol%)	80	45%	> 19 : 1
3	**Sc-1** (10 mol%)	60	*trace*	-
4	**Sc-1** (8 mol%)	100	90%	> 19 : 1
5	**Sc-1** (5 mol%)	100	50%	> 19 : 1
6	**Sc-2** (10 mol%)	100	94%	> 19 : 1
7	**Sc-2** (8 mol%)	100	90%	> 19 : 1

[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), **2a** (0.30 mmol), [**Ln**] (xx mol%), $[Ph_3C][B(C_6F_5)_4]$ (xx mol%), $AdNH_2$ (xx mol %), toluene-d_8 (1 mL), 60-100 °C, 24 h. [b]Combined NMR yield of both diastereomers. [c]Determined by ^1H NMR analysis.

Table S4. Investigation of the effect of *loading of 2a* for *trans*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimine 1a with 2a *via* β′-allylic C–H activation by Sc-1[a]

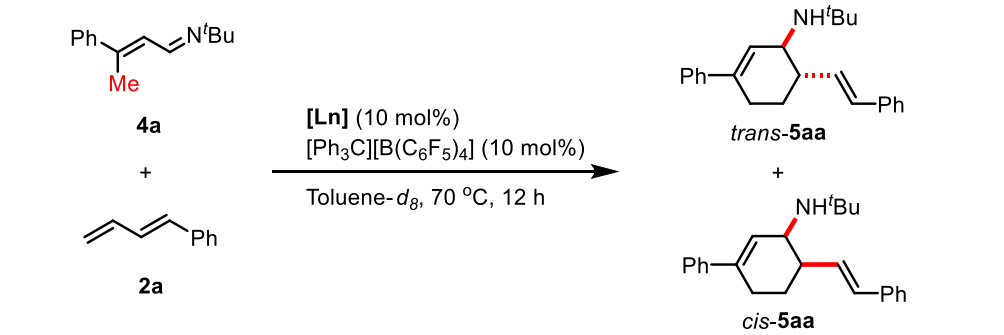


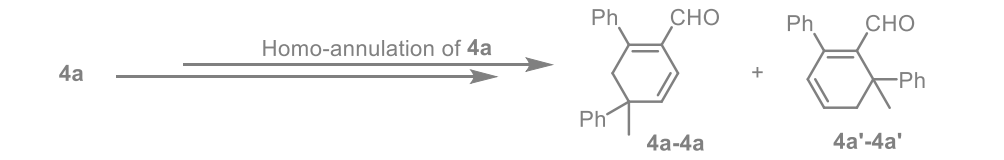
Entry	**Sc-1**	**2a** (equiv.)	Yield of **3aa**[b]	*trans* : *cis*[c]
1	**Sc-1** (10 mol%)	4.0	98%	> 19 : 1
2	**Sc-1** (10 mol%)	3.0	98%	> 19 : 1
3	**Sc-1** (10 mol%)	2.0	75%	> 19 : 1
4	**Sc-1** (10 mol%)	1.5	60%	> 19 : 1
5	**Sc-1** (10 mol%)	1.0	50%	> 19 : 1

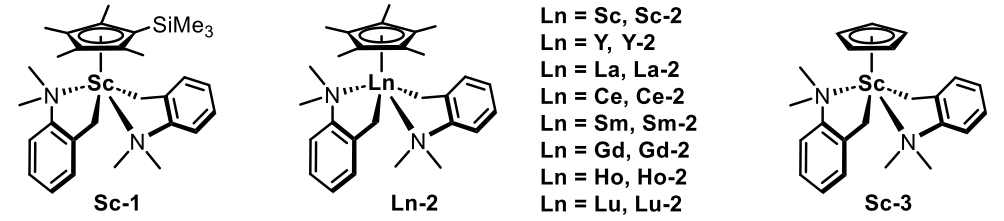
[a]Reaction conditions unless otherwise noted: **1a** (0.1 mmol), **2a** (0.10-0.40 mmol), **Sc-1** (10 mol%), $[Ph_3C][B(C_6F_5)_4]$ (10 mol%), $AdNH_2$ (10 mol%), toluene-d_8 (1 mL),

100 °C, 24 h. [b]Combined NMR yield of both diastereomers. [c]Determined by ^{1}H NMR analysis.

Table S5. Evaluation of effect of *catalysts* for *cis*-diastereoselective [4 + 2] annulation of α,β-unsaturated aldimine 4a with 2a *via* γ-allylic C–H activation[a]



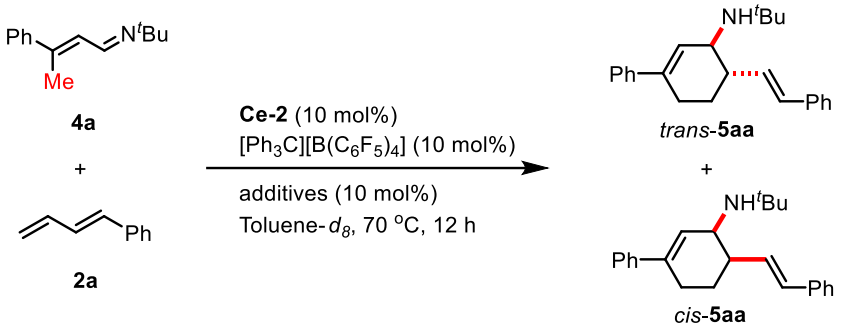




Entry	[Ln]	Yield of **5aa**[b]	d.r. (*trans*-**5aa**/*cis*-**5aa**)[c]	Yield of (**4a-4a+4a'-4a'**)[d]
1	**Sc-1**	n.d.	-	50%
2	**Sc-2**	n.d.	-	60%
3	**Sc-3**	n.d.	-	80%
4	**Y-2**	n.d.	-	74%
5	**La-2**	n.d.	-	50%
6	**Ce-2**	≈ 5%	< 1:19	66%
7	**Sm-2**	trace	-	80%
8	**Gd-2**	n.d.	-	75%
9	**Ho-2**	n.d.	-	79%
10	**Lu-2**	n.d.	-	60%

[a]Reaction conditions unless otherwise noted: **4a** (0.1 mmol), **2a** (0.30 mmol), [**Ln**] (10 mol%), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 mol%), toluene-d_8 (1 mL), 70 °C, 12 h. [b]Combined NMR yield of both diastereomers. [c]Determined by ^{1}H NMR analysis. [d]Combined NMR yield of **4a-4a** and **4a'-4a'**.

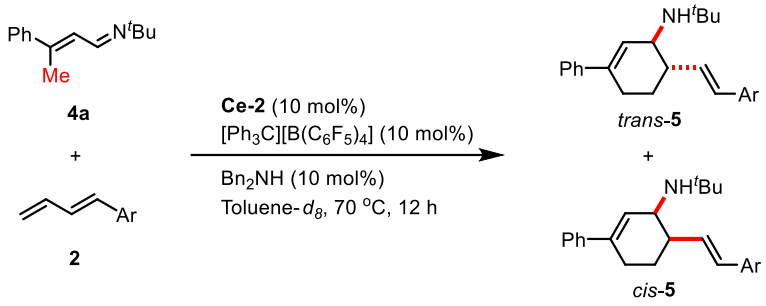
Table S6. Investigation of the effect of *additives* for *cis*-diastereoselective [4 + 2] annulation of α,β-unsaturated aldimine 4a with 2a *via* γ-allylic C–H activation by Ce-2[a]

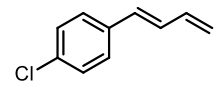


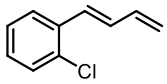
Entry	Additives	Yield of *cis*-5aa[b]	*trans* : *cis*[c]
1	$AdNH_2$	n.d.	-
2	**Bn_2NH**	**≈ 15%**	< 1 : 19
3	Cy_2NH	trace	-
4	$(Me_3Si)_2NH$	trace	-
5	$^nBu_2NH$	trace	-
6	$CyNH_2$	n.d.	-

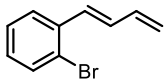
[a]Reaction conditions unless otherwise noted: **4a** (0.1 mmol), **2a** (0.30 mmol), **Ce-2** (10 mol%), $[Ph_3C][B(C_6F_5)_4]$ (10 mol%), additives (10 mol%), toluene-d_8 (1 mL), 70 °C, 12 h. [b]Combined NMR yield of both diastereomers.

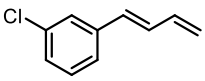
Table S7. Investigation of the effect of substituents on 1,3-dienes for *cis*-diastereoselective [4 + 2] annulation of α,β-unsaturated aldimine 4a via γ-allylic C–H activation by Ce-2

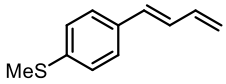


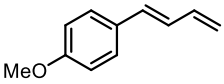

n.d.
(homo-annulation of **4a**)

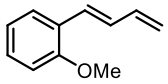

n.d.
(homo-annulation of **4a**)

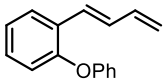

n.d.
(homo-annulation of **4a**)

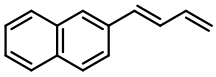

n.d.
(homo-annulation of **4a**)

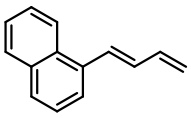

n.d.
(homo-annulation of **4a**)

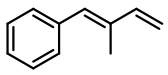

n.d.
(homo-annulation of **4a**)


cis-**5ba**, 63% (d.r. > 19:1)
(homo-annulation of **4a**: 30%)


trace
(homo-annulation of **4a**)

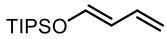

n.d.
(homo-annulation of **4a**)


n.d.
(homo-annulation of **4a**)


n.d.
(homo-annulation of **4a**)


n.d.
(homo-annulation of **4a**)


n.d.
(homo-annulation of **4a**)

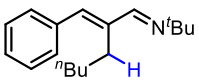

n.d.
(homo-annulation of **4a**)

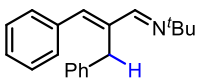

n.d.
(homo-annulation of **4a**)

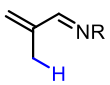

n.d.
(homo-annulation of **4a**)

Table S8. Ineffective aldimine substrates for *trans*-diastereoselective [3 + 2] annulation with 2a *via* β′-allylic C–H activation by Sc-1

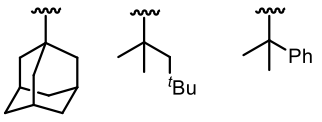
Secondary sp^3 C–H activation:


n.d.

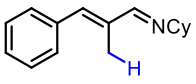

n.d.

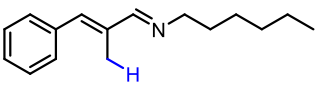

n.d.

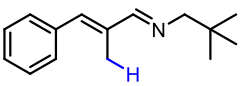
R =



***N*-substituents:**


n.d.


n.d.

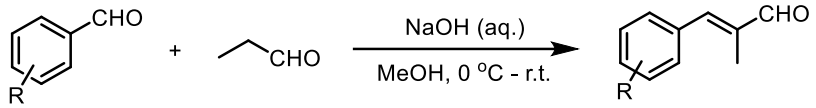

n.d.

3. The Preparation of Substrates

Synthesis of the corresponding 1,3-dienes

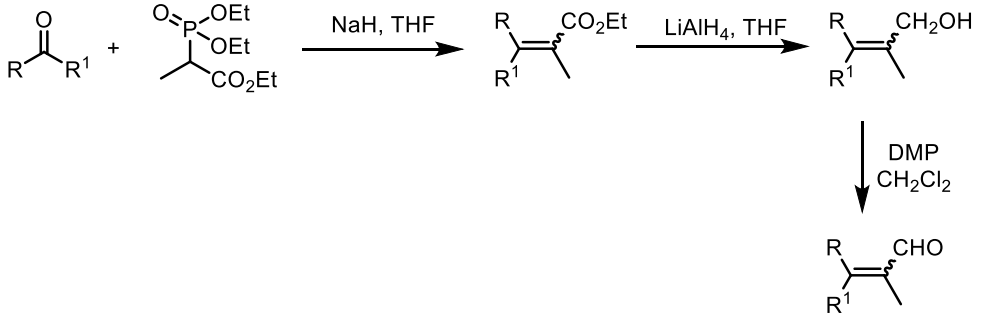
1-Aryl- and -alkyl-substituted 1,3-dienes[2] buta-1,3-dien-2-ylcyclopentane[3] and α,β-unsaturated aldimines[4] were prepared following literature method.

General procedure for the synthesis of the α-methyl α,β-unsaturated aldehydes



According to a reported procedure,[5] an aqueous sodium hydroxide solution (10 wt%, 6 mL) is added dropwise to a solution of the aromatic aldehyde (10 mmol, 1.0 equiv) in MeOH (20 mL) at 0 °C. A solution of the aliphatic aldehyde (15 mmol, 1.5 equiv) in MeOH (5 mL) is slowly added dropwise. The resulting reaction mixture is stirred for the 3 h at room temperature. Aqueous hydrochloric acid (1 M, 8 mL) is added to the reaction mixture and the phases are separated. The aqueous phase is extracted with EtOAc (3 × 25 mL), and the combined organic phases are washed with brine (1 × 25 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel affords the α,β-unsaturated aldehydes.

General procedure for synthesis of the tetra-substituted α-methyl α,β-unsaturated aldehydes



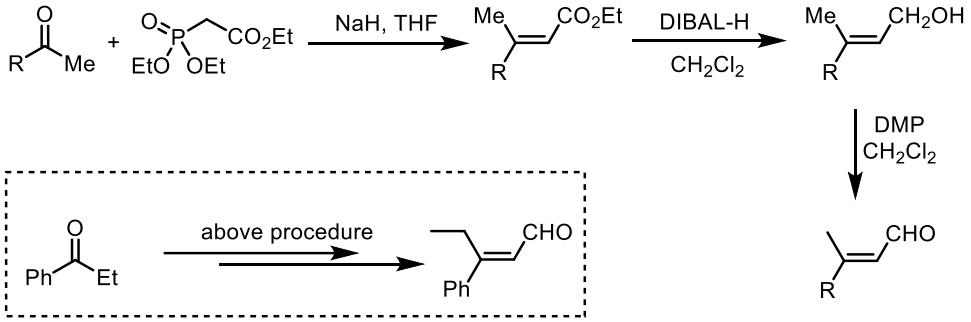
According to a reported procedure,[6] to a stirred suspension of NaH (1.96g, 50 mmol, 60 % mineral dispersion) in anhydrous THF (30 mL) at 0 °C was added triethyl 2-phosphonopropionate (1.20 g, 50 mmol) dropwise. The reaction mixture was then heated to 40 °C and stirred for 1 h. After cooling to 0 °C, the corresponding ketone (50 mmol) was added dropwise and the resulting mixture was stirred at 40 °C for further 12 h. After then, the reaction was quenched with water. The organic layer was collected, and the aqueous layer was extracted with EtOAc (2 × 25 mL). The

combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography (Hexane/EtOAc = 95/5) to afford the corresponding α,β-unsaturated ester ((*E*)-isomers, (*Z*)-isomers or the mixture of (*E*)-isomers and (*Z*)-isomers).

To a solution of unsaturated ester (20 mmol) obtained above and anhydrous THF (30 mL) was carefully added $LiAlH_4$ (1.52 g, 40 mmol) in a few portions at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. The reaction mixture was then cooled to 0 °C and quenched with 1 M aqueous HCl. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography (Hexane/EtOAc = 1/1) to afford the corresponding allylic alcohol.

To a 100 mL round bottom flask containing the allylic alcohol (10 mmol) obtained above, was added activated Dess-Martin Periodinane (11 mmol) and anhydrous CH_2Cl_2 (40 mL) at 0 °C. The solution was stirred at this temperature for 2 h and judged to be complete by TLC. The reaction mixture washed sequentially with saturated $NaHCO_3$ (aq.) solution, H_2O, and brine. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (Hexane/EA = 95/5).

General procedure for the synthesis of the β-alkyl α,β-unsaturated aldehydes



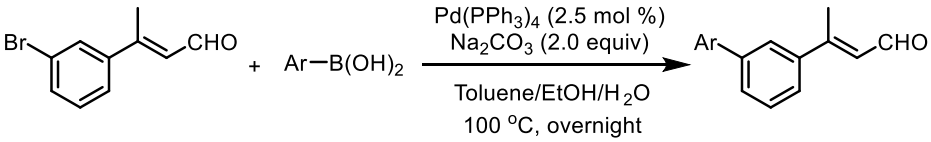
According to a reported procedure,[7] to a 200 mL round bottom flask containing NaH (20 mmol, 60% mineral dispersion) and anhydrous THF (80 mL) at 0 °C, was added triethyl phosphonoacetate (43 mmol) dropwise via an addition funnel. The reaction mixture was naturally warmed to rt, followed by a dropwise addition of an acetophenone solution (26 mmol, in 20 mL anhydrous THF). The reaction mixture was stirred for 12 h, and then poured into a separating funnel containing water. The organic layer was collected, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated

under reduced pressure. The crude residue was subjected to flash chromatography (Hexane/EA = 95/5) (75-90% yield).

A solution of unsaturated ester (10 mmol) in CH_2Cl_2 (50 mL) was cooled to -78 °C then DIBAL-H (25 mmol, 1 M in toluene) was added via syringe. The solution was stirred at this temperature for 1 h and judged to be complete by TLC. After this time the reaction mixture was quenched at -78 °C by the dropwise addition of water (10 mL), then NaOH (aq.) was added (10 mL, 2 M), the mixture was allowed to reach 0 °C and then an additional 10 mL of water was added. The mixture was diluted with ether and $MgSO_4$ was added and the mixture was stirred for 15 min. The mixture was filtered and concentrated under reduced pressure. The product was purified by column chromatography (Hexane/EA = 15/1) (80-95% yield).

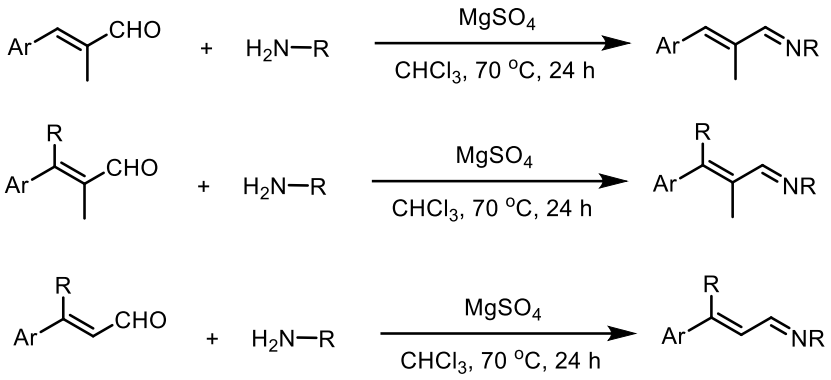
To a 100 mL round bottom flask containing the allylic alcohol (8 mmol) obtained above, was added activated Dess-Martin Periodinane (9 mmol) and anhydrous CH_2Cl_2 (30 mL) at 0 °C. The solution was stirred at this temperature for 2 h and judged to be complete by TLC. The reaction mixture washed sequentially with saturated $NaHCO_3$ (aq.) solution, H_2O, and brine. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (Hexane/EA = 95/5) (85-95% yield).

General procedure for the synthesis of the β-alkyl α,β-unsaturated aldehydes



A mixture of Br-substituted α,β-unsaturated aldehyde (5.0 mmol), arylboronic acid (7.5 mmol), $Pd(PPh_3)_4$ (2.5 mol %), Na_2CO_3 (10 mmol) and Toluene/EtOH/H_2O (7.5/2.5/2.5 mL) was stirred at 100 °C for 12 hours. The mixture was added to brine and extracted with ethyl acetate (3 × 15 mL). The solvent was concentrated in vacuo and the product was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent (80-90% yield).

General procedure for the synthesis of *N*-alkyl-substituted α,β-unsaturated aldimines



A 30 mL Schlenk tube with a stirring bar was charged with the α,β-unsaturated aldehydes (5 or 10 mmol), *tert*-butyl amine (20 or 40 mmol) or primary alkyl amines (5 or 10 mmol), and anhydrous magnesium sulfate (2.0 g or 4.0 g) in $CHCl_3$ (5 mL). The mixture was stirred at 70 ℃ for 24 h. After cooling to room temperature, the $MgSO_4$ was then removed *via* filtration and the filtrate was evaporated under a reduced pressure. The corresponding imine product was generally obtained in very high purity and employed without further purification after checking by ^{1}H NMR and ^{13}C NMR or purified by distillation if necessary.

4. General Procedure for the Diastereoselective [3 + 2] Annulation of α,β-Unsaturated Aldimines with 1,3-Dienes *via β′*-Allylic C–H Activation

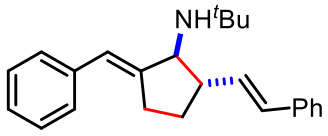
General procedure for the *trans*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimines with 1-substituted 1,3-dienes *via β′*-allylic C–H activation by Sc-1 in the presence of $AdNH_2$

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 0.01 mmol) was added to a toluene-d_8 solution (1.0 mL) of **Sc-1** (5.1 mg, 0.01 mmol) in a J. Young NMR tube. After 5 min, 1-adamantylamine (1.5 mg, 0.010 mmol) was added to this tube. After 5 min, α,β-unsaturated aldimines **1** (0.1 mmol) and 1-substituted 1,3-dienes **2** (0.3 mmol) were added. The tube was sealed, taken outside of glovebox, and stirred at indicated temperatures for indicated times. Then, the tube was cooled to room temperature and the reaction mixture was monitored by NMR. The crude NMR yields were calculated on the basis of formation of the corresponding product **3**. The solution was concentrated and purified directly by column chromatography on silica gel (hexane/EtOAc = 3/1, v/v) to give the pure product *trans*-**3**. The d.r. ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Identical results were obtained when the reactions were conducted in toluene using a Schlenk tube.

General procedure for the *cis*-diastereoselective [3 + 2] annulation of α,β-unsaturated aldimines with 1,3-butadiene, 2-alkyl-substituted 1,3-butadienes

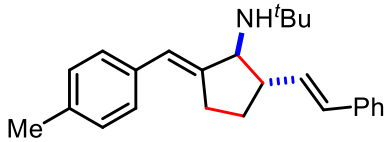
and 1,3-cyclohexadiene *via β′*-allylic C–H activation by Sc-2 in the presence of $AdNH_2$

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 0.01 mmol) was added to a toluene-d_8 solution (1.0 mL) of **Sc-2** (4.6 mg, 0.01 mmol) in a J. Young NMR tube. After 5 min, 1-adamantylamine (1.5 mg, 0.010 mmol) was added to this tube. After 5 min, α,β-unsaturated aldimines **1** (0.1 mmol) and 1,3-dienes (1.0 mmol), isoprene (1.0 mmol), 2-alkyl-substituted 1,3-butadienes (0.5 mmol) or 1,3-cyclohexadiene (0.5 mmol) were added. The tube was sealed, taken outside of glovebox, and stirred at indicated temperatures for indicated times. Then, the tube was cooled to room temperature and the reaction mixture was monitored by NMR. The crude NMR yields were calculated on the basis of formation of the corresponding product **3**. The solution was concentrated and purified directly by column chromatography on silica gel (hexane/EtOAc = 10/1, v/v) to give the pure product *cis*-**3** as major products and *trans*-**3** as minor products. The d.r. ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Identical results were obtained when the reactions were conducted in toluene using a Schlenk tube.



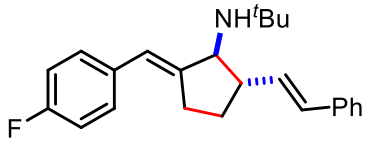
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3aa)

The title compound was prepared according to the general procedure as a yellow solid (32.2 mg, 97% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 8H), 7.21-7.18 (m, 2H), 6.54 (s, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.17 (dd, J = 15.6, 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 2.77-2.66 (m, 2H), 2.33-2.27 (m, 1H), 2.08-2.05 (m, 1H), 1.75-1.69 (m, 1H), 1.29 (brs, 1H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.2, 138.4, 137.7, 133.5, 130.4, 128.6, 128.5, 128.3, 127.1, 126.1, 122.0, 64.4, 51.5, 51.1, 30.7, 29.3, 28.4. HRMS (ESI$^+$): calcd for $C_{24}H_{30}N$ $[M+H]^+$ 332.2373, found 332.2389.



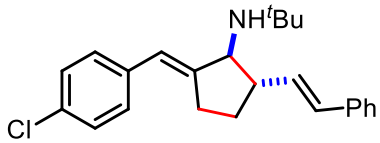
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-methylbenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ba)

The title compound was prepared according to the general procedure as a yellow solid (33.9 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.26 (m, 2H), 7.20 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 2.4 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.16 (dd, J = 15.6, 9.0 Hz, 1H), 3.37 (d, J = 9.0 Hz, 1H), 2.75-2.64 (m, 2H), 2.34 (s, 3H), 2.30-2.28 (m, 1H), 2.07-2.02 (m, 1H), 1.72-1.67 (m, 1H), 1.33 (brs, 1H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.4, 137.7, 135.8, 135.5, 133.6, 130.3, 129.0, 128.6, 128.4, 127.1, 126.1, 121.8, 64.3, 51.6, 51.1, 30.7, 29.3, 28.5, 21.3. HRMS (ESI$^+$): calcd for $C_{25}H_{31}N$ $[M+H]^+$ 346.2530, found 346.2545.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-fluorobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ca)

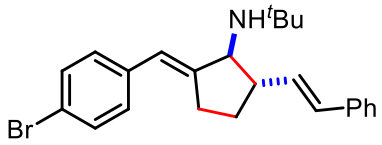
The title compound was prepared according to the general procedure as a yellow solid (21.7 mg, 62% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.2 Hz, 2H), 7.32-7.29 (m, 4H), 7.21 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 6.6 Hz, 1H), 6.50 (s, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.16 (dd, J = 15.6, 8.4 Hz, 1H), 3.39 (d, J = 9.0 Hz, 1H), 2.72-2.61 (m, 2H), 2.30-2.28 (m, 1H), 2.06-2.05 (m, 1H), 1.75-1.70 (m, 1H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.5 (d, J = 246.4 Hz), 148.9, 137.6, 134.5 (d, J = 3.0 Hz), 130.6, 130.0 (d, J = 7.1 Hz), 128.6, 127.2, 126.1, 121.0, 115.2 (d, J = 21.2 Hz), 64.2, 51.4, 51.2, 30.6, 29.2, 28.3. HRMS (ESI$^+$): calcd for $C_{24}H_{29}FN$ $[M+H]^+$ 350.2279, found 350.2294.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-chlorobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3da)

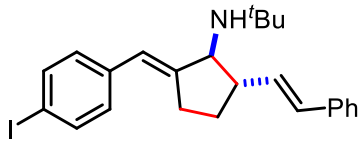
The title compound was prepared according to the general procedure as a yellow solid (35.9 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.2 Hz, 2H), 7.31-7.26 (m, 6H), 7.20 (t, J = 7.2 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.14 (dd, J = 15.6, 9.0 Hz, 1H), 3.37 (d, J = 9.0 Hz, 1H), 2.76-2.57 (m, 2H), 2.32-2.24 (m, 1H), 2.09-2.01 (m, 1H), 1.76-1.67 (m, 1H), 1.41 (brs, 1H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1, 137.5, 136.8, 133.2, 131.7, 130.7, 129.7,

128.6, 128.4, 127.2, 126.1, 120.9, 64.3, 51.4, 51.2, 30.6, 29.2, 28.4. HRMS (ESI^+): calcd for $C_{24}H_{29}CIN$ $[M+H]^+$366.1984, found 366.2001.



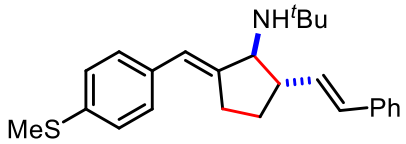
(*Trans*)-2-((*E*)-4-bromobenzylidene)-*N*-(*tert*-butyl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ea)

The title compound was prepared according to the general procedure as a yellow solid (40.2 mg, 98% yield). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.23-7.19 (m, 3H), 6.47 (s, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.14 (dd, J = 15.6, 9.0 Hz, 1H), 3.36 (d, J = 9.0 Hz, 1H), 2.73-2.56 (m, 2H), 2.29-2.22 (m, 1H), 2.09-2.01 (m, 1H), 1.76-1.67 (m, 1H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.3, 137.5, 137.2, 133.2, 131.3, 130.7, 130.1, 128.6, 127.2, 126.1, 121.0, 119.8, 64.3, 51.3, 51.2, 30.6, 29.2, 28.4. HRMS (ESI^+): calcd for $C_{24}H_{29}BrN$ $[M+H]^+$ 410.1478, found 410.1487.



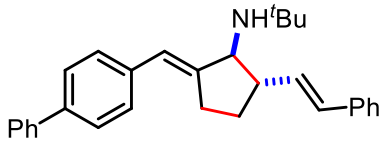
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-iodobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3fa)

The title compound was prepared according to the general procedure as a yellow solid (45.3 mg, 99% yield). ^1H NMR (600 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.48-6.41 (m, 2H), 6.14 (dd, J = 15.6, 9.0 Hz, 1H), 3.35 (d, J = 9.0 Hz, 1H), 2.74-2.56 (m, 2H), 2.30-2.22 (m, 1H), 2.08-1.99 (m, 1H), 1.77-1.68 (m, 1H), 1.25 (brs, 1H), 1.11 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.6, 137.8, 137.5, 137.3, 130.7, 130.4, 128.7, 127.2, 126.1, 121.0, 91.2, 64.3, 51.4, 51.1, 30.7, 29.2, 28.4. HRMS (ESI^+): calcd for $C_{24}H_{29}IN$ $[M+H]^+$ 458.1340, found 458.1358.



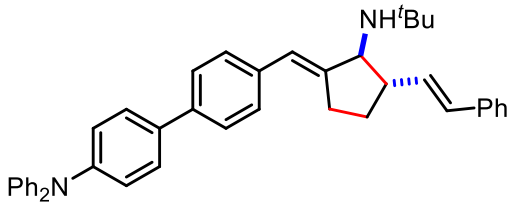
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-(methylthio)benzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ga)

The title compound was prepared according to the general procedure as a yellow solid (34.4 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.2 Hz, 2H), 7.32-7.26 (m, 4H), 7.24-7.18 (m, 3H), 6.49-6.41 (m, 2H), 6.15 (dd, J = 15.6, 9.0 Hz, 1H), 3.39 (d, J = 9.0 Hz, 1H), 2.79-2.59 (m, 2H), 2.48 (s, 3H), 2.37-2.22 (m, 1H), 2.11-2.00 (m, 1H), 1.78-1.65 (m, 1H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.9, 137.6, 135.9, 135.4, 133.4, 130.5, 128.9, 128.6, 127.1, 126.7, 126.1, 121.5, 64.3, 51.4, 51.3, 30.6, 29.3, 28.5, 16.1. HRMS (ESI$^+$): calcd for $C_{25}H_{32}NS$ $[M+H]^+$ 378.2250, found 378.2255.



(*Trans,E*)-2-([1,1'-biphenyl]-4-ylmethylene)-*N*-(*tert*-butyl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ha)

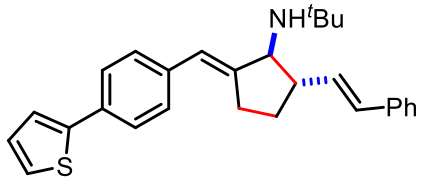
The title compound was prepared according to the general procedure as a yellow solid (28.9 mg, 71% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.47-7.41 (m, 4H), 7.39-7.28 (m, 5H), 7.21 (t, J = 7.2 Hz, 1H), 6.57 (s, 1H), 6.46 (d, J = 15.6 Hz, 1H), 6.17 (dd, J = 15.6, 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 2.84-2.67 (m, 2H), 2.35-2.26 (m, 1H), 2.13-2.03 (m, 1H), 1.78-1.70 (m, 1H), 1.37 (brs, 1H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.7, 141.0, 138.8, 137.6, 137.4, 133.5, 130.5, 128.9, 128.8, 128.6, 127.2, 127.1, 127.02, 126.96, 126.1, 121.5, 64.4, 51.5, 51.2, 30.7, 29.3, 28.6. HRMS (ESI$^+$): calcd for $C_{30}H_{34}N$ $[M+H]^+$ 408.2686, found 408.2703.



(*Trans*)-4'-((*E*)-(2-(*tert*-butylamino)-3-((*E*)-styryl)cyclopentylidene)methyl)-*N*,*N*-diphenyl-[1,1'-biphenyl]-4-amine (*trans*-3ia)

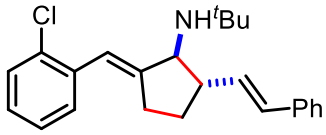
The title compound was prepared according to the general procedure as a yellow solid (43.1 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.2 Hz, 2H), 7.28-7.26 (m, 4H), 7.21 (t, J = 7.2 Hz, 1H), 7.15-7.11 (m, 6H), 7.03 (t, J = 7.2 Hz, 2H), 6.56 (s, 1H), 6.46 (d, J = 15.6 Hz, 1H), 6.18 (dd, J = 15.6, 9.0 Hz, 1H), 3.42 (d, J = 9.0 Hz, 1H), 2.84-2.68 (m, 2H), 2.37-2.26 (m, 1H), 2.11-2.04 (m, 1H),

1.78-1.69 (m, 1H), 1.41 (brs, 1H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.4, 147.8, 147.1, 138.2, 137.6, 136.9, 134.9, 133.5, 130.5, 129.4, 128.9, 128.7, 127.6, 127.1, 126.4, 126.1, 124.5, 124.1, 123.0, 121.6, 64.4, 51.5, 51.2, 30.7, 29.3, 28.6. HRMS (ESI$^+$): calcd for $C_{42}H_{43}N_2$ $[M+H]^+$ 575.3421, found 575.3431.



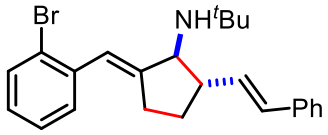
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-styryl)-5-((*E*)-4-(thiophen-2-yl)benzylidene)cyclopentan-1-amine (*trans*-3ja)

The title compound was prepared according to the general procedure as a yellow oil (35.2 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.4 Hz, 2H), 7.37-7.35 (m, 4H), 7.32-7.29 (m, 3H), 7.26 (m, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.07 (dd, J = 5.4, 4.2 Hz, 1H), 6.53 (d, J = 1.8 Hz, 1H), 6.46 (d, J = 16.2 Hz, 1H), 6.17 (dd, J = 16.2, 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 2.79-2.68 (m, 2H), 2.31-2.28 (m, 1H), 2.09-2.05 (m, 1H), 1.75-1.71 (m, 1H), 1.38 (brs, 1H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.8, 144.5, 137.6, 133.4, 132.1, 130.5, 129.0, 128.7, 128.1, 127.1, 126.1, 125.8, 124.6, 122.9, 121.5, 64.4, 51.5, 51.2, 30.7, 29.3, 28.6. HRMS (ESI$^+$): calcd for $C_{28}H_{32}NS$ $[M+H]^+$ 414.2250, found 414.2269.



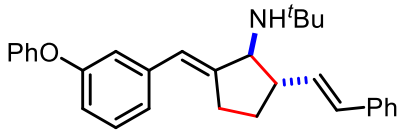
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-2-chlorobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ka)

The title compound was prepared according to the general procedure as a yellow solid (34.8 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.8 Hz, 1H), 7.38-7.35 (m, 3H), 7.30 (t, J = 7.2 Hz, 2H), 7.23-7.19 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H), 6.80 (d, J = 2.4 Hz, 1H), 6.47 (d, J = 16.2 Hz, 1H), 6.18 (dd, J = 16.2, 9.0 Hz, 1H), 3.41 (d, J = 9.0 Hz, 1H), 2.66-2.59 (m, 2H), 2.35-2.33 (m, 1H), 2.04-1.99 (m, 1H), 1.71-1.65 (m, 1H), 1.36 (brs, 1H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.7, 137.7, 136.3, 133.7, 133.4, 130.4, 129.5, 129.4, 128.6, 127.4, 127.1, 126.4, 126.1, 118.7, 64.3, 51.8, 51.2, 30.7, 29.1, 28.1. HRMS (ESI$^+$): calcd for $C_{24}H_{29}ClN$ $[M+H]^+$ 366.1984, found 366.1981.



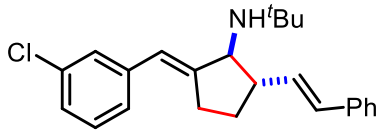
(*Trans*)--2-((*E*)-2-bromobenzylidene)-*N*-(*tert*-butyl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3la)

The title compound was prepared according to the general procedure as a yellow solid (40.6 mg, 99% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.27-7.26 (m, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.04 (t, J = 8.4 Hz, 1H), 6.74 (d, J = 1.8 Hz, 1H), 6.47 (d, J = 16.2 Hz, 1H), 6.18 (dd, J = 16.2, 8.4 Hz, 1H), 3.43 (d, J = 9.0 Hz, 1H), 2.61-2.55 (m, 2H), 2.38-2.34 (m, 1H), 2.03-1.98 (m, 1H), 1.70-1.63 (m, 1H), 1.43 (brs, 1H), 1.15 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.6, 138.0, 137.7, 133.4, 132.8, 130.3, 129.5, 128.6, 127.7, 127.1, 127.0, 126.1, 124.5, 121.4, 64.2, 51.8, 51.2, 30.8, 29.1, 28.0. HRMS (ESI$^+$): calcd for $C_{24}H_{29}BrN$ $[M+H]^+$ 410.1478, found 410.1471.



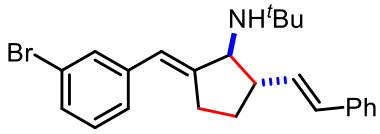
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-3-phenoxybenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ma)

The title compound was prepared according to the general procedure as a yellow solid (39.8 mg, 94% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.27 (m, 7H), 7.20 (t, J = 7.8 Hz, 1H), 7.11-7.08 (m, 2H), 7.03-7.01 (m, 3H), 6.85-6.84 (m, 1H), 6.50 (d, J = 1.8 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.14 (dd, J = 15.6, 9.0 Hz, 1H), 3.39 (d, J = 9.0 Hz, 1H), 2.70-2.60 (m, 2H), 2.35-2.26 (m, 1H), 2.09-2.01 (m, 1H), 1.73-1.66 (m, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 157.5, 157.1, 150.2, 150.1, 140.2, 137.6, 133.3, 130.6, 129.8, 129.5, 128.6, 127.2, 126.1, 123.8, 123.1, 121.7, 119.0, 118.8, 116.8, 64.3, 51.3, 30.6, 29.3, 28.4. HRMS (ESI$^+$): calcd for $C_{30}H_{34}NO$ $[M+H]^+$ 424.2635, found 424.2640.



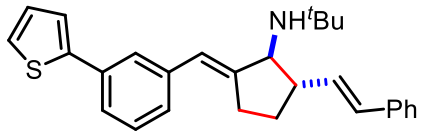
(*Trans*)-*N*-(*tert*-butyl)--2-((*E*)-3-chlorobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3na)

The title compound was prepared according to the general procedure as a yellow solid (35.9 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (t, *J* = 7.2 Hz, 3H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26-7.19 (m, 3H), 7.16-7.14 (m, 1H), 6.48 (d, *J* = 1.8 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.15 (dd, *J* = 15.7, 9.0 Hz, 1H), 3.38 (d, *J* = 9.6 Hz, 1H), 2.75-2.63 (m, 2H), 2.28-2.23 (m, 1H), 2.07-2.03 (m, 1H), 1.76-1.71 (m, 1H), 1.30 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.1, 140.2, 137.5, 134.1, 133.2, 130.7, 129.5, 128.7, 128.4, 127.2, 126.7, 126.13, 126.05, 120.8, 64.3, 51.4, 51.2, 30.7, 29.1, 28.4. HRMS (ESI^{+}): calcd for $C_{24}H_{29}ClN$ $[M+H]^{+}$ 366.1984, found 366.1975.



(*Trans*)-2-((*E*)-3-bromobenzylidene)-*N*-(*tert*-butyl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3oa)

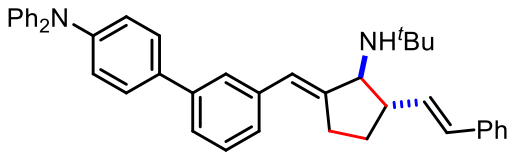
The title compound was prepared according to the general procedure as a yellow solid (40.2 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.31-7.26 (m, 4H), 7.22-7.17 (m, 2H), 6.48 (d, *J* = 1.8 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.14 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.75-2.61 (m, 2H), 2.33-2.24 (m, 1H), 2.11-2.02 (m, 1H), 1.75-1.69 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.0, 140.5, 137.5, 133.1, 131.3, 130.7, 129.8, 129.0, 128.6, 127.2, 127.1, 126.1, 122.5, 120.9, 64.3, 51.3, 51.2, 30.6, 29.2, 28.3. HRMS (ESI^{+}): calcd for $C_{24}H_{29}BrN$ $[M+H]^{+}$ 410.1478, found 410.1487.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-styryl)-5-((*E*)-3-(thiophen-2-yl)benzylidene)cyclopentan-1-amine (*trans*-3pa)

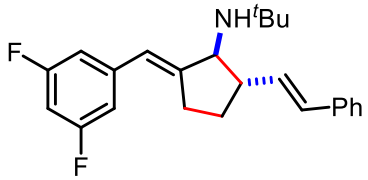
The title compound was prepared according to the general procedure as a yellow solid (29.0 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.37-7.27 (m, 8H), 7.22-7.09 (m, 1H), 7.08-7.07 (m, 1H), 6.57 (d, *J* = 3.0 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.17 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.41 (d, *J* = 9.0 Hz, 1H), 2.81-2.69 (m, 2H), 2.30-2.28 (m, 1H), 2.09-2.04 (m, 1H), 1.77-1.70 (m, 1H),

1.33 (brs, 1H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.1, 144.7, 138.9, 137.6, 134.4, 133.4, 130.6, 128.8, 128.7, 128.1, 127.6, 127.2, 126.2, 126.1, 124.8, 123.8, 123.2, 121.6, 64.3, 51.4, 51.2, 30.7, 29.2, 28.4. HRMS (ESI^+): calcd for $C_{28}H_{32}NS$ $[M+H]^+$ 414.2250, found 414.2238.



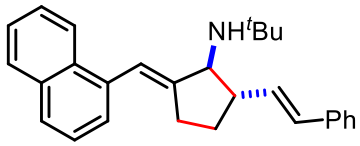
(*Trans*)-3'-((*E*)-(2-(*tert*-butylamino)-3-((*E*)-styryl)cyclopentylidene)methyl)-*N*,*N*-diphenyl-[1,1'-biphenyl]-4-amine (*trans*-3qa)

The title compound was prepared according to the general procedure as a yellow solid (43.1 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.40-7.27 (m, 11H), 7.23-7.13 (m, 8H), 7.03 (t, J = 7.2 Hz, 2H), 6.60 (s, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.18 (dd, J = 15.6, 8.8 Hz, 1H), 3.43 (d, J = 8.8 Hz, 1H), 2.80-2.70 (m, 2H), 2.33-2.26 (m, 1H), 2.10-2.03 (m, 1H), 1.79-1.71 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.7, 147.8, 147.2, 140.7, 138.7, 137.6, 135.4, 133.4, 130.5, 129.4, 128.70, 128.65, 128.6, 127.9, 127.2, 127.1, 127.0, 126.1, 124.6, 124.5, 124.0, 123.0, 122.0, 64.3, 51.5, 51.2, 30.7, 29.3, 28.6. HRMS (ESI^+): calcd for $C_{42}H_{43}N_2$ $[M+H]^+$ 575.3421, found 575.3435.



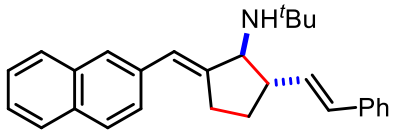
(*Trans*)-*N*-(*tert*-butyl)--2-((*E*)-3,5-difluorobenzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3ra)

The title compound was prepared according to the general procedure as a yellow oil (33.4 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.2 Hz, 2H), 6.62 (t, J = 8.4 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.13 (dd, J = 15.6, 9.0 Hz, 1H), 3.37 (d, J = 10.2 Hz, 1H), 2.74-2.62 (m, 2H), 2.26-2.24 (m, 1H), 2.08-2.04 (m, 1H), 1.76-1.71 (m, 1H), 1.36 (brs, 1H), 1.11 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 163.0 (dd, J = 247.5, 13.1 Hz), 152.5, 141.6 (t, J = 10.1 Hz), 137.4, 133.0, 130.9, 128.7, 127.2, 126.1, 120.4, 110.0 (dd, J = 19.2, 7.1 Hz), 101.3 (t, J = 25.3 Hz), 64.2, 51.3, 51.1, 30.6, 29.1, 28.4. HRMS (ESI^+): calcd for $C_{24}H_{28}F_2N$ $[M+H]^+$ 368.2185, found 368.2185.



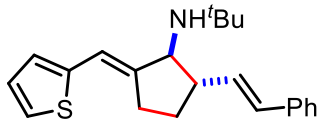
(*Trans*)-(*E*)-*N*-*(tert*-butyl)-2-(naphthalen-1-ylmethylene)-5-((*E*)-styryl)cyclopenta n-1-amine (*trans*-3sa)

The title compound was prepared according to the general procedure as a yellow solid (31.7 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.04 (m, 1H), 7.87-7.84 (m, 1H), 7.5-7.72 (m, 1H), 7.51-7.44 (m, 4H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24-7.22 (m, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.49 (d, *J* = 9.1 Hz, 1H), 2.57-2.52 (m, 2H), 2.41-2.37 (m, 1H), 2.02-1.95 (m, 1H), 1.72-1.64 (m, 1H), 1.43 (brs, 1H), 1.21 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.3, 137.7, 135.6, 133.7, 133.6, 131.9, 130.4, 128.7, 128.6, 127.1, 126.8, 126.1, 126.0, 125.8, 125.7, 125.4, 124.7, 119.1, 63.9, 52.0, 51.2, 30.8, 29.0, 27.8. HRMS (ESI$^+$): calcd for $C_{28}H_{32}N$ $[M+H]^+$ 382.2530, found 382.2544.



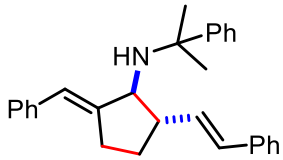
(*Trans*)-(*E*)-*N*-(*tert*-butyl)-2-(naphthalen-2-ylmethylene)-5-((*E*)-styryl)cyclopenta n-1-amine (*trans*-3ta)

The title compound was prepared according to the general procedure as a yellow solid (27.4 mg, 72% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81-7.79 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.46-7.42 (m, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.19 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.44 (d, *J* = 9.6 Hz, 1H), 2.89-2.75 (m, 2H), 2.35-2.31 (m, 1H), 2.30-2.06 (m, 1H), 1.79-1.74 (m, 1H), 1.33 (brs, 1H), 1.16 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.1, 137.6, 135.9, 133.6, 133.5, 132.0, 130.5, 128.6, 128.0, 127.7, 127.6, 127.2, 127.1, 127.0, 126.13, 126.07, 125.5, 122.0, 64.4, 51.6, 51.2, 30.7, 29.3, 28.6. HRMS (ESI$^+$): calcd for $C_{28}H_{32}N$ $[M+H]^+$ 382.2530, found 382.2543.



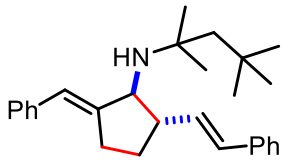
(*Trans*)-(*E*)-*N*-(*tert*-butyl)-2-((*E*)-styryl)-5-(thiophen-2-ylmethylene)cyclopentan-1-amine (*trans*-3ua)

The title compound was prepared according to the general procedure as a brown solid (24.3 mg, 72% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.24-7.19 (m, 2H), 7.03 (d, J = 3.6 Hz, 1H), 6.98 (d, J = 3.6 Hz, 1H), 6.73 (d, J = 2.5 Hz, 1H), 6.46 (d, J = 15.6 Hz, 1H), 6.16 (dd, J = 15.6, 9.0 Hz, 1H), 3.41 (d, J = 10.8 Hz, 1H), 2.67-2.64 (m, 2H), 2.32-2.28 (m, 1H), 2.11-2.08 (m, 1H), 1.76-1.72 (m, 1H), 1.28 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.0, 142.4, 137.6, 133.2, 130.5, 128.6, 127.1, 127.0, 126.1, 125.6, 124.5, 115.5, 64.1, 52.2, 51.1, 30.7, 29.2, 29.0. HRMS (ESI$^+$): calcd for $C_{27}H_{28}NS$ $[M+H]^+$ 338.1937, found 338.1940.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(2-phenylpropan-2-yl)-5-((*E*)-styryl)cyclopentan-1-amine (*trans*-3va)

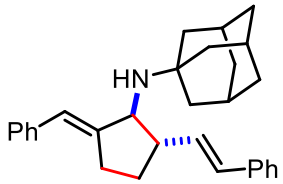
The title compound was prepared according to the general procedure as a yellow solid (38.6 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.8 Hz, 2H), 7.34-7.18 (m, 13H), 6.38 (s, 1H), 6.33 (d, J = 16.2 Hz, 1H), 5.76 (dd, J = 15.6, 9.0 Hz, 1H), 3.30 (d, J = 7.8 Hz, 1H), 2.65-2.63 (m, 2H), 2.33-2.31 (m, 1H), 2.05-2.00 (m, 1H), 1.64-1.59 (m, 1H), 1.53 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.1, 148.6, 138.3, 137.5, 133.2, 130.2, 128.5, 128.3, 128.1, 127.1, 126.5, 126.4, 126.3, 126.2, 122.5, 64.8, 56.1, 50.9, 30.5, 29.7, 29.6, 28.2. HRMS (ESI$^+$): calcd for $C_{29}H_{32}N$ $[M+H]^+$ 394.2530, found 394.2540.



(*Trans*)-2-((*E*)-benzylidene)-5-((*E*)-styryl)-*N*-(2,4,4-trimethylpentan-2-yl)cyclopentan-1-amine (*trans*-3wa)

The title compound was prepared according to the general procedure as a yellow solid (36.8 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 8H), 7.22-7.17 (m, 2H), 6.56 (d, J = 2.0 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 6.16 (dd, J = 15.6, 8.8 Hz, 1H), 3.42 (d, J = 8.8 Hz, 1H), 2.73-2.66 (m, 2H), 2.32-2.28 (m, 1H), 2.09-2.01 (m, 1H), 1.76-1.67 (m, 1H), 1.48 (d, J = 6.0 Hz, 2H), 1.47 (brs, 1H), 1.18 (s, 3H), 1.14 (s,

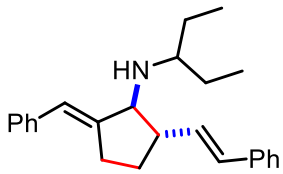
3H), 1.00 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.8, 138.4, 137.7, 133.7, 130.3, 128.6, 128.5, 128.3, 127.1, 126.1, 122.1, 64.1, 57.2, 55.1, 51.7, 32.1, 31.8, 29.7, 29.4, 29.3, 28.4. HRMS (ESI^+): calcd for $C_{28}H_{38}N$ $[M+H]^+$ 388.2999, found 388.2980.



(*Trans*)-*N*-(-2-((*E*)-benzylidene)-5-((*E*)-styryl)cyclopentyl)adamantan-1-amine

(*trans*-3xa)

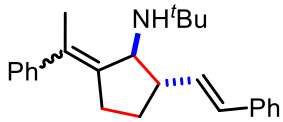
The title compound was prepared according to the general procedure as a yellow solid (40.1 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.29 (m, 8H), 7.22-7.16 (m, 2H), 6.56 (d, J = 2.0 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 8.8 Hz, 1H), 3.53 (d, J = 8.8 Hz, 1H), 2.78-2.64 (m, 2H), 2.31-2.27 (m, 1H), 2.09-2.04 (m, 4H), 1.71-1.57 (m, 13H), 1.35 (brs, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.8, 138.4, 137.8, 133.5, 130.4, 128.6, 128.5, 128.3, 127.1, 126.2, 126.1, 122.0, 62.1, 51.6, 51.1, 44.5, 36.8, 29.9, 29.3, 28.5. HRMS (ESI^+): calcd for $C_{30}H_{36}N$ $[M+H]^+$ 410.2843, found 410.2850.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(pentan-3-yl)-5-((*E*)-styryl)cyclopentan-1-amine

(*trans*-3ya)

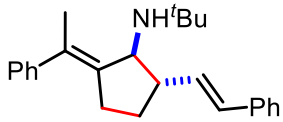
The title compound was prepared according to the general procedure as a yellow oil (15.5 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.26 (m, 8H), 7.22-7.16 (m, 2H), 6.53 (d, J = 2.4 Hz, 1H), 6.45 (d, J = 15.6 Hz, 1H), 6.19 (dd, J = 15.6, 8.8 Hz, 1H), 3.42 (d, J = 8.4 Hz, 1H), 2.73-2.62 (m, 3H), 2.45-2.41 (m, 1H), 2.10-2.05 (m, 1H), 1.69-1.64 (m, 1H), 1.48-1.38 (m, 4H), 0.92 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 148.1, 138.3, 137.7, 133.3, 130.2, 128.6, 128.5, 128.3, 127.1, 126.2, 126.1, 122.1, 67.6, 58.7, 51.0, 30.4, 28.8, 26.7, 26.5, 10.1. HRMS (ESI^+): calcd for $C_{25}H_{32}N$ $[M+H]^+$ 346.2530, found 346.2531.



(*Trans,E*)-*N*-(*tert*-butyl)-2-(1-phenylethylidene)-5-((*E*)-styryl)cyclopentan-1-amin e (*trans,E*-3za)

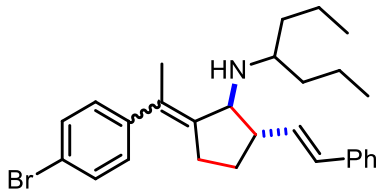
(*Trans,Z*)-*N*-(*tert*-butyl)-2-(1-phenylethylidene)-5-((*E*)-styryl)cyclopentan-1-amin e (*trans,Z*-3za)

The title compound was prepared according to the general procedure as a yellow oil (**Sc-1**: total: 19.3 mg, 56% yield, *E*/*Z* = 1:1). (***E***): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.17 (m, 10H), 6.43-6.37 (m, 1H), 6.20-6.16 (m, 1H), 3.80 (s, 1H), 2.84 (m, 1H), 2.61-2.19 (m, 3H), 2.09 (s, 3H), 1.51-1.44 (m, 1H), 1.24 (brs, 1H), 1.24 (s, 9H); (***Z***): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.17 (m, 10H), 6.43-6.37 (m, 1H), 6.20-6.16 (m, 1H), 3.66 (s, 1H), 2.84 (m, 1H), 2.61-2.22 (m, 3H), 1.97 (s, 3H), 1.74-1.69 (m, 1H), 0.69 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.6, 144.1, 144.0, 143.4, 143.3, 142.4, 142.3, 137.9, 137.7, 133.8, 133.1, 128.9, 128.64, 128.61, 128.1, 127.9, 127.1, 127.0, 126.3, 126.14, 126.10, 61.4, 60.5, 51.2, 39.3, 35.1, 30.6, 30.5, 29.7, 29.5, 29.4, 28.7, 22.9, 21.2. HRMS (ESI^{+}): calcd for $C_{25}H_{32}N$ $[M+H]^{+}$ 346.2530, found 346.2540.



(*Trans,E*)-*N*-(*tert*-butyl)-2-(1-phenylethylidene)-5-((*E*)-styryl)cyclopentan-1-amin e (*trans*-3za)

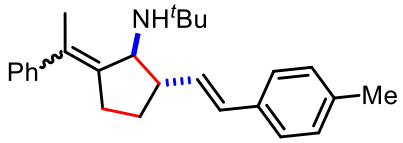
The title compound was prepared according to the general procedure as a yellow oil (**Y-2**: 28.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 7H), 7.22-7.20 (m, 3H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.79 (s, 1H), 2.83-2.81 (m, 1H), 2.43-2.38 (m, 1H), 2.24-2.13 (m, 1H), 2.09 (s, 3H), 1.52-1.48 (m, 1H), 1.22 (brs, 1H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.7, 143.6, 137.9, 133.9, 130.1, 128.9, 128.6, 128.1, 127.9, 127.0, 126.3, 126.1, 61.4, 51.5, 51.3, 30.6, 29.7, 21.1. HRMS (ESI^{+}): calcd for $C_{25}H_{32}N$ $[M+H]^{+}$ 346.2530, found 346.2540.



(*Trans,E*)-2-(1-(4-bromophenyl)ethylidene)-*N*-(heptan-4-yl)-5-((*E*)-styryl)cyclope ntan-1-amine (*trans,E*-3aaa)

(*Trans,Z*)-2-(1-(4-bromophenyl)ethylidene)-*N*-(heptan-4-yl)-5-((*E*)-styryl)cyclope ntan-1-amine (*trans,Z*-3aaa)

(*trans,E*-3aaa): The title compound was prepared according to the general procedure as a yellow oil (20.5 mg, 44% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.34-7.28 (m, 4H), 7.21-7.18 (m, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.42 (d, J = 15.6 Hz, 1H), 6.16 (dd, J = 15.6, 8.4 Hz, 1H), 3.73 (s, 1H), 2.77-2.70 (m, 2H), 2.36 (m, 1H), 2.22 (m, 1H), 2.06 (s, 3H), 1.60-1.56 (m, 5H), 1.50-1.35 (m, 6H), 0.92-0.89 (m, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.3, 137.8, 137.7, 133.8, 131.2, 129.6, 129.2, 128.6, 127.1, 126.1, 124.5, 120.1, 63.8, 54.9, 49.7, 37.4, 36.0, 30.8, 30.2, 20.7, 19.3, 18.9, 14.51, 14.49. HRMS (ESI$^+$): calcd for $C_{28}H_{37}BrN$ [M+H]$^+$ 466.2104, found 466.2106. **(*trans,Z*-3aaa):** The title compound was prepared according to the general procedure as a yellow oil (13.5 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.4 Hz, 2H), 7.36-7.28 (m, 4H), 7.22-7.18 (m, 1H), 7.10 (d, J = 8.4 Hz, 2H), 6.37 (d, J = 15.6 Hz, 1H), 6.13 (dd, J = 16.0, 8.0 Hz, 1H), 3.52 (s, 1H), 2.71-2.67 (m, 1H), 2.55-2.41 (m, 2H), 2.25-2.16 (m, 2H), 1,93 (s, 3H), 1.45-1.42 (m, 3H), 1.17-1.10 (m, 2H), 1.04-0.96 (m, 1H), 0.83-0.80 (m, 6H), 0.72-0.70 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 142.9, 137.7, 133.2, 131.7, 129.8, 129.2, 128.6, 127.1, 126.1, 120.5, 63.1, 54.8, 48.4, 37.5, 35.5, 29.8, 28.8, 22.3, 19.3, 18.3, 14.5, 14.4. HRMS (ESI$^+$): calcd for $C_{28}H_{37}BrN$ [M+H]$^+$ 466.2104, found 466.2101.

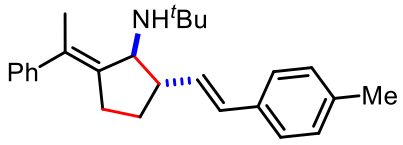


(*Trans,E*)-*N*-(*tert*-butyl)-2-((*E*)-4-methylstyryl)-5-(1-phenylethylidene)cyclopenta n-1-amine (*trans,E*-3aba)

(*Trans,Z*)-*N*-(*tert*-butyl)-2-((*E*)-4-methylstyryl)-5-(1-phenylethylidene)cyclopenta n-1-amine (*trans,Z*-3aba)

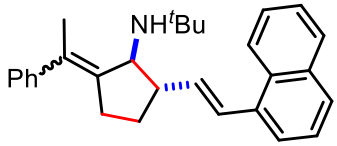
The title compound was prepared according to the general procedure as a yellow oil (**Sc-1**: total: 15.8 mg, 44% yield, E/Z = 2:1). (***E***): ^{1}H NMR (400 MHz, $CDCl_3$): δ =

7.33-7.10 (m, 9H), 6.38-6.33 (m, 1H), 6.15-6.06 (m, 1H), 3.78 (s, 1H), 2.80-2.75 (m, 1H), 2.43-2.36 (m, 1H), 2.32 (s, 3H), 2.24-2.16 (m, 2H), 2.08 (s, 3H), 1.50-1.45 (m, 1H), 1.21 (brs, 1H), 1.21 (s, 9H); (***Z***): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.10 (m, 4.5H), 6.38-6.33 (m, 0.5H), 6.15-6.06 (m, 0.5H), 3.61 (s, 0.5H), 2.80-2.75 (m, 0.5H), 2.56-2.50 (m, 0.5H), 2.33 (s, 1.5H), 2.24-2.16 (m, 1H), 1.96 (s, 1.5H), 1.73-1.67 (m, 0.5H), 0.65 (s, 4.5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.7, 144.2, 143.7, 143.6, 136.8, 136.7, 135.1, 132.9, 132.4, 130.0, 129.3, 128.7, 128.6, 128.1, 127.9, 126.5, 126.3, 126.00, 125.98, 61.4, 60.5, 51.5, 51.3, 50.6, 30.7, 29.8, 29.5, 28.7, 22.8, 21.3, 21.1. HRMS (ESI$^+$): calcd for $C_{26}H_{34}N$ $[M+H]^+$ 360.2686, found 360.2680.



(*Trans,E*)-*N*-(*tert*-butyl)-2-((*E*)-4-methylstyryl)-5-(1-phenylethylidene)cyclopenta n-1-amine (*trans*-3aba)

The title compound was prepared according to the general procedure as a yellow oil (**Y-2**: 20.1 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (m, 2H), 7.26-7.24 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.79 (s, 1H), 2.82 (m, 1H), 2.42-2.29 (m, 4H), 2.23-2.08 (m, 5H), 1.50-1.46 (m, 1H), 1.23 (brs, 1H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.7, 136.7, 135.1, 132.8, 129.3, 128.7, 128.1, 127.9, 126.3, 126.0, 61.4, 51.6, 51.1, 30.7, 30.6, 29.8, 21.3, 21.2. HRMS (ESI$^+$): calcd for $C_{26}H_{34}N$ $[M+H]^+$ 360.2686, found 360.2688.

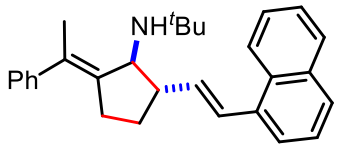


(*Trans,E*)-*N*-(*tert*-butyl)-2-((*E*)-2-(naphthalen-1-yl)vinyl)-5-(1-phenylethylidene)c yclopentan-1-amine (*trans,E*-3aca)

(*Trans,Z*)-*N*-(*tert*-butyl)-2-((*E*)-2-(naphthalen-1-yl)vinyl)-5-(1-phenylethylidene)c yclopentan-1-amine (*trans,Z*-3aca)

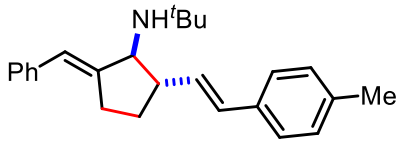
The title compound was prepared according to the general procedure as a yellow solid (**Sc-1**: total: 18.6 mg, 47% yield, *E*/*Z* = 1.4:1). (***E***): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.06 (m, 1H), 7.86-7.82 (m, 1H), 7.77-7.73 (m, 1H), 7.59-7.41 (m, 4H), 7.33-7.29 (m, 2H), 7.23-7.09 (m, 4H), 3.89 (s, 1H), 2.94-2.90 (m, 1H), 2.57-2.43 (m, 1H), 2.35-2.20 (m, 2H), 2.10 (s, 3H), 1.61-1.57 (m, 1H), 1.26 (brs, 1H), 1.26 (s, 9H); (***Z***): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.06 (m, 0.6H), 7.86-7.82 (m, 0.8H),

7.77-7.73 (m, 0.8H), 7.59-7.41 (m, 3.2H), 7.33-7.29 (m, 1.6H), 7.23-7.09 (m, 3.2H), 3.89 (s, 0.8H), 2.94-2.90 (m, 0.8H), 2.57-2.43 (m, 1.6H), 2.35-2.20 (m, 0.8H), 1.98 (s, 2.4H), 1.83-1.78 (m, 0.8H), 0.71 (s, 7.2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 144.7, 144.2, 143.7, 143.6, 136.8, 136.7, 135.1, 132.9, 132.4, 130.0, 129.3, 128.7, 128.6, 128.1, 127.9, 126.5, 126.3, 126.00, 125.98, 61.4, 60.5, 51.5, 51.3, 50.6, 30.7, 29.8, 29.5, 28.7, 22.8, 21.3, 21.1. HRMS (ESI^+): calcd for $C_{29}H_{34}N$ $[M+H]^+$ 396.2686, found 396.2695.



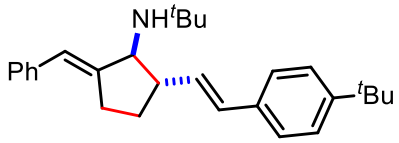
(*Trans,E*)-*N*-(*tert*-butyl)-2-((*E*)-2-(naphthalen-1-yl)vinyl)-5-(1-phenylethylidene)cyclopentan-1-amine (*trans*-3aca)

The title compound was prepared according to the general procedure as a yellow solid (**Y-2**: 31.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 9.2 Hz, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.56-7.42 (m, 4H), 7.32 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 9.4 Hz, 3H), 7.13 (d, J = 15.6 Hz, 1H), 6.18 (dd, J = 15.6, 8.4 Hz, 1H), 3.89 (s, 1H), 2.97-2.95 (m, 1H), 2.49-2.41 (m, 1H), 2.30-2.20 (m, 2H), 2.11 (s, 3H), 1.62-1.56 (m, 1H), 1.27 (brs, 1H), 1.27 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 144.7, 143.6, 137.3, 135.8, 133.7, 131.2, 130.1, 128.6, 128.1, 127.9, 127.4, 126.3, 126.1, 125.9, 125.8, 124.0, 123.6, 61.4, 51.5, 30.7, 30.6, 29.8, 21.3. HRMS (ESI^+): calcd for $C_{29}H_{34}N$ $[M+H]^+$ 396.2686, found 396.2690.



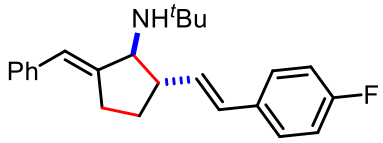
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-methylstyryl)cyclopentan-1-amine (*trans*-3ab)

The title compound was prepared according to the general procedure as a yellow solid (33.9 mg, 98% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.32 (m, 4H), 7.26 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 2H), 6.53 (s, 1H), 6.41 (d, J = 16.2 Hz, 1H), 6.11 (dd, J = 16.2, 9.0 Hz, 1H), 3.38 (d, J = 9.0 Hz, 1H), 2.77-2.64 (m, 2H), 2.33 (s, 3H), 2.28-2.26 (m, 1H), 2.07-2.03 (m, 1H), 1.74-1.69 (m, 1H), 1.26 (brs, 1H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.5, 138.4, 136.9, 134.9, 132.4, 130.3, 129.3 , 128.5, 128.3, 126.1, 126.0, 121.9, 64.3, 51.5, 51.1, 30.7, 29.3, 28.4, 21.3. HRMS (ESI^+): calcd for $C_{25}H_{32}N$ $[M+H]^+$ 346.2530, found 346.2537.



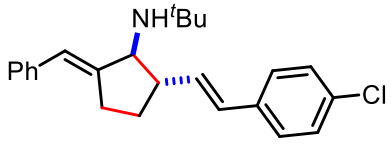
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-(*tert*-butyl)styryl)cyclopentan-1-amine (*trans*-3ac)

The title compound was prepared according to the general procedure as a yellow solid (23.6 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.28 (m, 8H), 7.21-7.18 (m, 1H), 6.53 (d, J = 2.0 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 6.12 (dd, J = 15.6, 8.8 Hz, 1H), 3.39 (d, J = 8.8 Hz, 1H), 2.75-2.66 (m, 2H), 2.29-2.23 (m, 1H), 2.09-1.99 (m, 1H), 1.75-1.67 (m, 1H), 1.31 (s, 9H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.2, 149.4, 138.4, 134.9, 132.7, 130.2, 128.5, 128.3, 126.1, 125.8, 125.6, 121.9, 64.3, 51.5, 51.2, 34.6, 31.4, 30.7, 29.3, 28.4. HRMS (ESI$^+$): calcd for $C_{28}H_{38}N$ $[M+H]^+$ 388.2999, found 388.3011.



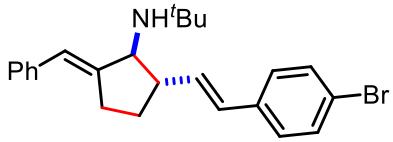
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-fluorostyryl)cyclopentan-1-amine (*trans*-3ad)

The title compound was prepared according to the general procedure as a yellow solid (28.0 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 6H), 7.21-7.17 (m, 1H), 6.98 (t, J = 8.8 Hz, 2H), 6.52 (d, J = 2.0 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.07 (dd, J = 15.6, 8.6 Hz, 1H), 3.39 (d, J = 8.6 Hz, 1H), 2.77-2.67 (m, 2H), 2.29-2.25 (m, 1H), 2.08-2.01 (m, 1H), 1.72-1.67 (m, 1H), 1.31 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.3 (d, J = 246.4 Hz), 149.3, 138.3, 133.8 (d, J = 3.0 Hz), 133.3, 129.2, 128.5, 128.3, 127.6 (d, J = 8.1 Hz), 126.2, 122.0, 115.6 (d, J = 21.8 Hz), 64.3, 51.5, 51.1, 30.7, 29.2, 28.5. HRMS (ESI$^+$): calcd for $C_{24}H_{29}FN$ $[M+H]^+$ 350.2279, found 350.2281.



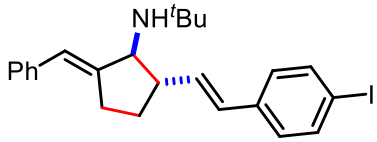
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-chlorostyryl)cyclopentan-1-amine (*trans*-3ae)

The title compound was prepared according to the general procedure as a yellow solid (36.2 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 4H), 7.28-7.26 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.14 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.77-2.64 (m, 2H), 2.31-2.25 (m, 1H), 2.07-2.02 (m, 1H), 1.73-1.66 (m, 1H), 1.30 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.3, 138.3, 136.2, 134.3, 132.6, 129.2, 128.8, 128.5, 128.3, 127.3, 126.2, 122.0, 64.4, 51.6, 51.1, 30.7, 29.2, 28.5. HRMS (ESI^{+}): calcd for $C_{24}H_{29}ClN$ $[M+H]^{+}$ 366.1984, found 366.1999.



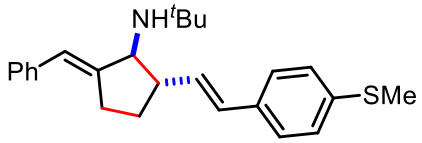
(*Trans*)-2-((*E*)-benzylidene)-5-((*E*)-4-bromostyryl)-*N*-(*tert*-butyl)cyclopentan-1-amine (*trans*-3af)

The title compound was prepared according to the general procedure as a yellow solid (40.6 mg, 99% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.36-7.31 (m, 4H), 7.22-7.17 (m, 3H), 6.51 (d, *J* = 1.2 Hz, 1H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.16 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.37 (d, *J* = 9.0 Hz, 1H), 2.77-2.65 (m, 2H), 2.29-2.26 (m, 1H), 2.06-2.03 (m, 1H), 1.71-1.68 (m, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.3, 138.3, 136.6, 134.4, 131.7, 129.2, 128.5, 128.3, 127.6, 126.2, 122.0, 120.7, 64.4, 51.6, 51.1, 30.7, 29.2, 28.5. HRMS (ESI^{+}): calcd for $C_{24}H_{29}BrN$ $[M+H]^{+}$ 410.1478, found 410.1486.



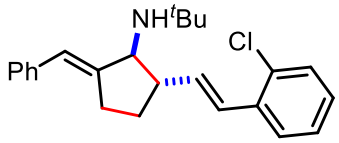
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-iodostyryl)cyclopentan-1-amine (*trans*-3ag)

The title compound was prepared according to the general procedure as a yellow solid (39.8 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 2H), 7.36-7.29 (m, 4H), 7.21-7.16 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.51 (d, *J* = 1.6 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.39 (d, *J* = 9.2 Hz, 1H), 2.78-2.64 (m, 2H), 2.29-2.25 (m, 1H), 2.08-2.01 (m, 1H), 1.74-1.66 (m, 1H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.3, 138.2, 137.7, 137.2, 134.6, 129.3, 128.5, 128.3, 127.9, 126.2, 122.0, 92.1, 64.3, 51.6, 51.1, 30.7, 29.2, 28.5. HRMS (ESI^{+}): calcd for $C_{24}H_{29}IN$ $[M+H]^{+}$ 458.1340, found 458.1360.



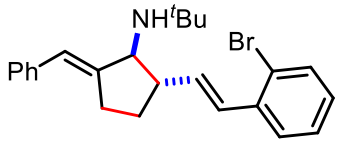
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-(methylthio)styryl)cyclopenta n-1-amine (*trans*-3ah)

The title compound was prepared according to the general procedure as a yellow solid (26.4 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 4H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20-7.17 (m, 3H), 6.52 (d, *J* = 1.8 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.12 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.39 (d, *J* = 9.0 Hz, 1H), 2.75-2.65 (m, 2H), 2.47 (s, 3H), 2.31-2.28 (m, 1H), 2.06-2.03 (m, 1H), 1.73-1.66 (m, 1H), 1.47 (brs, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.2, 138.3, 137.0, 134.7, 133.0, 129.8, 128.5, 128.3, 127.0, 126.5, 126.2, 122.1, 64.4, 51.5, 51.3, 30.6, 29.3, 28.5, 16.1. HRMS (ESI$^+$): calcd for $C_{25}H_{32}NS$ $[M+H]^+$ 378.2250, found 378.2253.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-2-chlorostyryl)cyclopentan-1-a mine (*trans*-3ai)

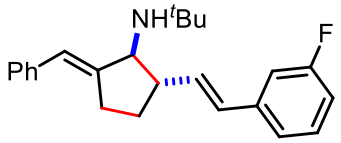
The title compound was prepared according to the general procedure as a yellow solid (23.4 mg, 64% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.2 Hz, 1H), 7.36-7.32 (m, 5H), 7.21-7.13 (m, 3H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.54 (s, 1H), 6.15 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.39 (d, *J* = 9.0 Hz, 1H), 2.77-2.65 (m, 2H), 2.38-2.32 (m, 1H), 2.09-2.08 (m, 1H), 1.76-1.70 (m, 1H), 1.37 (brs, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.2, 138.3, 136.4, 135.7, 132.7, 129.7, 128.5, 128.3, 128.1, 126.9, 126.8, 126.7, 126.2, 122.1, 64.3, 51.6, 51.1, 30.7, 29.2, 28.4. HRMS (ESI$^+$): calcd for $C_{24}H_{29}ClN$ $[M+H]^+$ 366.1984, found 366.1991.



(*Trans*)-2-((*E*)-benzylidene)-5-((*E*)-2-bromostyryl)-*N*-(*tert*-butyl)cyclopentan-1-a mine (*trans*-3aj)

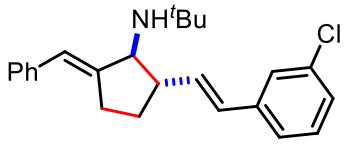
The title compound was prepared according to the general procedure as a yellow solid (31.6 mg, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.4 Hz, 1H), 7.48

(d, *J* = 7.8 Hz, 1H), 7.36-7.31 (m, 4H), 7.25-7.23 (m, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.54 (s, 1H), 6.10 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.40 (d, *J* = 9.0 Hz, 1H), 2.77-2.66 (m, 2H), 2.38-2.35 (m, 1H), 2.10-2.08 (m, 1H), 1.77-1.70 (m, 1H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.0, 138.3, 137.5, 136.5, 133.0, 129.5, 128.5, 128.4, 128.3, 127.5, 127.0, 126.2, 123.3, 122.2, 64.2, 51.4, 51.3, 30.6, 29.2, 28.4. HRMS (ESI^+): calcd for $C_{24}H_{29}BrN$ $[M+H]^+$ 410.1478, found 410.1486.



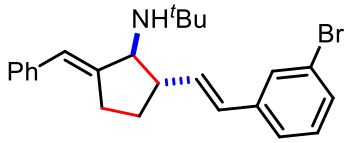
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-3-fluorostyryl)cyclopentan-1-amine (*trans*-3ak)

The title compound was prepared according to the general procedure as a yellow solid (24.8 mg, 71% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.32 (m, 4H), 7.24-7.23 (m, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 10.2 Hz, 1H), 6.89 (t, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.40 (d, *J* = 9.0 Hz, 1H), 2.77-2.67 (m, 2H), 2.32-2.26 (m, 1H), 2.07-2.02 (m, 1H), 1.74-1.67 (m, 1H), 1.28 (brs, 1H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 164.5 (d, *J* = 245.4 Hz), 149.3, 140.1 (d, *J* = 8.1 Hz), 138.3, 130.5, 130.1 (d, *J* = 8.1Hz), 129.3 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 20.2 Hz), 128.3, 126.2, 122.0, 114.0 (d, *J* = 22.2Hz), 112.6 (d, *J* = 21.2 Hz), 64.4, 51.5, 51.1, 30.7, 29.2, 28.5. HRMS (ESI^+): calcd for $C_{24}H_{29}FN$ $[M+H]^+$ 350.2279, found 350.2280.



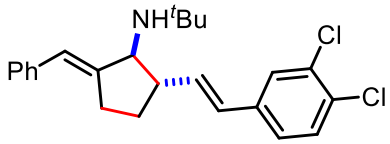
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-3-chlorostyryl)cyclopentan-1-amine (*trans*-3al)

The title compound was prepared according to the general procedure as a yellow solid (29.3 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 5H), 7.22-7.16 (m, 4H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.40 (d, *J* = 9.0 Hz, 1H), 2.77-2.66 (m, 2H), 2.32-2.30 (m, 1H), 2.08-2.03 (m, 1H), 1.73-1.66 (m, 1H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.2, 139.5, 138.2, 135.1, 134.6, 129.8, 129.1, 128.5, 128.3, 127.0, 126.2, 126.0, 124.3, 122.2, 64.4, 51.5, 51.2, 30.7, 29.2, 28.5. HRMS (ESI^+): calcd for $C_{24}H_{29}ClN$ $[M+H]^+$ 366.1984, found 366.1987.



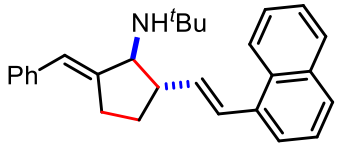
(*Trans*)-2-((*E*)-benzylidene)-5-((*E*)-3-bromostyryl)-*N*-(*tert*-butyl)cyclopentan-1-amine (*trans*-3am)

The title compound was prepared according to the general procedure as a yellow solid (37.3 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49 (s, 1H), 7.36-7.31 (m, 5H), 7.26-7.25 (m, 1H), 7.19-7.14 (m, 2H), 6.52 (d, J = 2.4 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.17 (dd, J = 15.6, 9.0 Hz, 1H), 3.40 (d, J = 8.4 Hz, 1H), 2.76-2.66 (m, 2H), 2.33-2.30 (m, 1H), 2.08-2.03 (m, 1H), 1.71-1.68 (m, 1H), 1.29 (brs, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.1, 139.8, 138.2, 135.1, 130.1, 130.0, 129.0, 128.5, 128.3, 126.2, 124.7, 122.9, 122.3, 64.4, 51.5, 51.2, 30.6, 29.3, 28.5. HRMS (ESI$^+$): calcd for $C_{24}H_{29}BrN$ $[M+H]^+$ 410.1478, found 410.1493.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-3,4-dichlorostyryl)cyclopentan-1-amine (*trans*-3an)

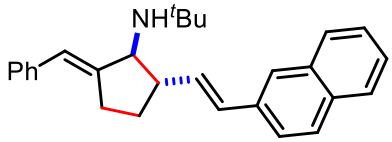
The title compound was prepared according to the general procedure as a yellow solid (24.0 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 2.4 Hz, 1H), 7.36-7.31 (m, 5H), 7.21-7.15 (m, 2H), 6.50 (d, J = 2.4 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 8.8 Hz, 1H), 3.38 (d, J = 9.2 Hz, 1H), 2.75-2.65 (m, 2H), 2.31-2.27 (m, 1H), 2.08-2.00 (m, 1H), 1.35 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.1, 138.2, 137.8, 135.8, 132.7, 130.6, 130.5, 128.5, 128.3, 128.1, 127.8, 126.2, 125.3, 122.1, 64.4, 51.7, 51.1, 30.7, 29.1, 28.5. HRMS (ESI$^+$): calcd for $C_{24}H_{28}Cl_2N$ $[M+H]^+$ 400.1594, found 400.1605.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-2-(naphthalen-1-yl)vinyl)cyclopentan-1-amine (*trans*-3ao)

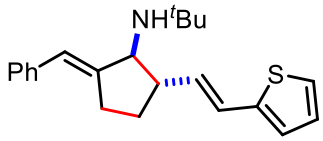
The title compound was prepared according to the general procedure as a yellow solid (30.5 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.8 Hz, 1H), 7.85

(d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51-7.48 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.21-7.19 (m, 2H), 6.57 (s, 1H), 6.20 (dd, *J* = 15.0, 9.0 Hz, 1H), 3.47 (d, *J* = 9.0 Hz, 1H), 2.81-2.69 (m, 2H), 2.47-2.44 (m, 1H), 2.17-2.13 (m, 1H), 1.83-1.78 (m, 1H), 1.49 (brs, 1H), 1.17 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.4, 138.3, 136.6, 135.3, 131.2, 128.59, 128.56, 128.3, 127.63, 127.55, 126.2, 126.0, 125.79, 125.76, 123.9, 123.5, 122.1, 64.3, 51.9, 51.3, 30.7, 29.5, 28.5. HRMS (ESI^+): calcd for $C_{28}H_{32}N$ $[M+H]^+$ 382.2530, found 382.2538.



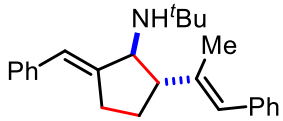
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-2-(naphthalen-2-yl)vinyl)cyclopentan-1-amine (*trans*-3ap)

The title compound was prepared according to the general procedure as a yellow solid (29.4 mg, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79-7.76 (m, 3H), 7.70 (s, 1H), 7.58 (d, *J* = 9.6 Hz, 1H), 7.45-7.25 (m, 6H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 6.30 (dd, *J* = 15.6, 9.0 Hz, 1H), 3.46 (d, *J* = 8.4 Hz, 1H), 2.80-2.69 (m, 2H), 2.40-2.37 (m, 1H), 2.13-2.09 (m, 1H), 1.79-1.73 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.2, 138.3, 135.1, 133.9, 133.8, 132.8, 130.6, 128.5, 128.3, 128.2, 128.0, 127.7, 126.3, 126.2, 125.69, 125.67, 123.6, 122.2, 64.5, 51.6, 51.3, 30.6, 29.4, 28.5. $C_{28}H_{32}N$ $[M+H]^+$ 382.2530, found 382.2538.



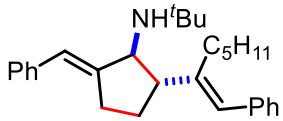
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-2-(thiophen-2-yl)vinyl)cyclopentan-1-amine (*trans*-3aq)

The title compound was prepared according to the general procedure as a brown solid (27.0 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10-7.09 (m, 1H), 6.95-6.93 (m, 1H), 6.89 (s, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.51 (s, 1H), 6.00 (dd, *J* = 15.6, 7.2 Hz, 1H), 3.37 (d, *J* = 8.4 Hz, 1H), 2.75-2.64 (m, 2H), 2.27-2.25 (m, 1H), 2.06-2.02 (m, 1H), 1.72-1.67 (m, 1H), 1.47 (brs, 1H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.1, 142.9, 138.2, 133.4, 128.5, 128.3, 127.4, 126.2, 124.7, 123.7, 123.5, 122.1, 64.4, 51.3, 30.6, 29.1, 28.5. HRMS (ESI^+): calcd for $C_{22}H_{28}NS$ $[M+H]^+$ 338.1937, found 338.1958.



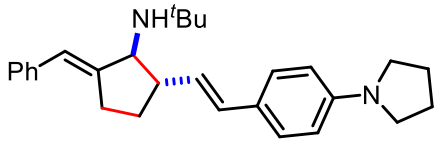
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-1-phenylprop-1-en-2-yl)cyclope ntan-1-amine (*trans*-3ar)

The title compound was prepared according to the general procedure as a colorless solid (33.5 mg, 97% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 6H), 7.26-7.25 (m, 2H), 7.20-7.17 (m, 2H), 6.59 (s, 1H), 6.37 (s, 1H), 3.48 (d, J = 9.6 Hz, 1H), 2.76-2.64 (m, 2H), 2.30-2.26 (m, 1H), 1.94-1.87 (m, 5H), 1.32 (brs, 1H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.7, 138.8, 138.5, 138.3, 129.0, 128.6, 128.22, 128.16, 127.8, 126.2, 126.0, 122.2, 61.5, 57.4, 50.9, 30.6, 28.3, 26.8, 14.8. HRMS (ESI$^+$): calcd for $C_{25}H_{32}N$ $[M+H]^+$ 346.2530, found 346.2538.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-1-phenylhept-1-en-2-yl)cyclopen tan-1-amine (*trans*-3as)

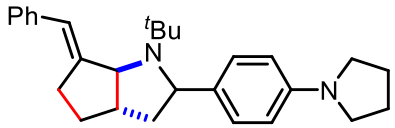
The title compound was prepared according to the general procedure as a yellow solid (20.5 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 6H), 7.24-7.17 (m, 4H), 6.57 (d, J = 2.0 Hz, 1H), 6.30 (s, 1H), 3.51 (d, J = 8.4 Hz, 1H), 2.72-2.65 (m, 2H), 2.35-2.28 (m, 2H), 2.13-2.05 (m, 2H), 1.84-1.81 (m, 1H), 1.49-1.45 (m, 2H), 1.30-1.28 (m, 4H), 1.13 (s, 9H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.0, 144.7, 138.5, 128.6, 128.3, 126.4, 126.12, 126.08, 122.4, 63.4, 55.2, 51.0, 32.4, 30.9, 30.6, 29.1, 28.6, 28.5, 22.5, 14.2. HRMS (ESI$^+$): calcd for $C_{29}H_{40}N$ $[M+H]^+$ 402.3156, found 402.3166.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-(pyrrolidin-1-yl)styryl)cyclope ntan-1-amine (*trans*-3av)

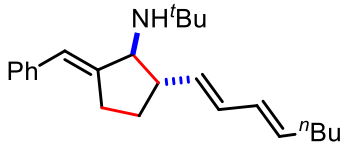
The title compound was prepared according to the general procedure as a yellow solid (12.4 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.29 (m, 5H), 7.23 (s, 1H), 7.18 (t, J = 7.2 Hz, 1H), 6.55 (s, 1H), 6.52 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 15.6

Hz, 1H), 5.89 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.38 (d, *J* = 8.0 Hz, 1H), 3.30-3.27 (m, 4H), 2.72-2.66 (m, 2H), 2.33-2.26 (m, 1H), 2.01 (m, 1H), 2.00-1.98 (m, 4H), 1.73-1.67 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 147.3, 138.4, 130.7, 128.6, 128.2, 128.0, 127.2, 125.1, 111.7, 64.4, 51.1, 47.7, 30.4, 29.6, 28.4, 25.6. HRMS (ESI^+): calcd for $C_{28}H_{37}N_2$ $[M+H]^+$ 401.2952, found 401.2955.



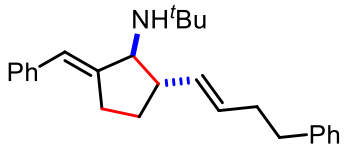
(*Trans*)-6-((*E*)-benzylidene)-1-(*tert*-butyl)-2-(4-(pyrrolidin-1-yl)phenyl)octahydro cyclopenta[*b*]pyrrole (*trans*-3av')

The title compound was prepared according to the general procedure as a yellow solid (16.4 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27-7.25 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.47 (d, *J* = 8.4 Hz, 2H), 4.16 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.96 (d, *J* = 7.6 Hz, 1H), 3.26-3.22 (m, 4H), 2.74-2.65 (m, 2H), 2.48-2.43 (m, 1H), 2.11-2.05 (m, 1H), 1.97-1.91 (m, 6H), 1.63-1.58 (m, 1H), 1.06 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.7, 146.4, 139.2, 136.4, 128.6, 128.3, 127.5, 125.7, 124.3, 111.3, 70.0, 66.2, 54.9, 47.7, 44.4, 41.8, 28.3, 27.7, 25.6, 25.5. HRMS (ESI^+): calcd for $C_{28}H_{37}N_2$ $[M+H]^+$ 401.2952, found 401.2958.



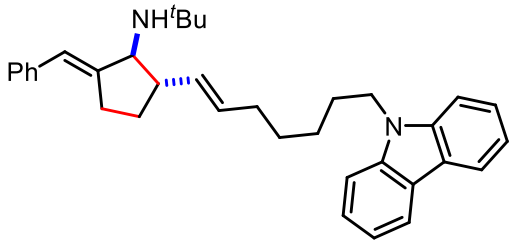
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((1*E*,3*E*)-octa-1,3-dien-1-yl)cyclopent an-1-amine (*trans*-3aw)

The title compound was prepared according to the general procedure as a yellow solid (29.7 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 4H), 7.17 (d, *J* = 6.8 Hz, 1H), 6.51 (t, *J* = 2.0 Hz, 1H), 6.09-5.97 (m, 2H), 5.61 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.49 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.31 (d, *J* = 8.4 Hz, 1H), 2.68-2.62 (m, 2H), 2.19-2.17 (m, 1H), 2.08-1.99 (m, 3H), 1.63-1.58 (m, 1H), 1.40-1.36 (m, 2H), 1.31-1.25 (m, 5H), 1.14 (s, 9H), 0.88 (t, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 138.3, 134.3, 133.6, 131.2, 130.1, 128.5, 128.2, 126.1, 122.1, 64.4, 50.7, 32.7, 31.5, 30.5, 29.4, 29.1, 28.4, 22.6, 14.2. HRMS (ESI^+): calcd for $C_{24}H_{36}N$ $[M+H]^+$ 338.2843, found 338.2845.



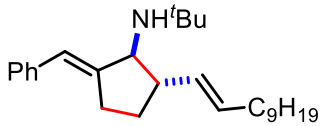
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-4-phenylbut-1-en-1-yl)cyclopentan-1-amine (*trans*-3ax)

The title compound was prepared according to the general procedure as a yellow solid (30.9 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.27 (m, 7H), 7.18-7.16 (m, 3H), 6.50 (t, *J* = 2.4 Hz, 1H), 5.56-5.49 (m, 1H), 5.37 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.24 (d, *J* = 8.8 Hz, 1H), 2.71-2.61 (m, 4H), 2.37-2.32 (m, 2H), 2.13-2.06 (m, 1H), 2.00-1.92 (m, 1H), 1.62-1.54 (m, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.5, 142.1, 138.4, 133.6, 130.6, 128.5, 128.4, 128.2, 126.1, 125.9, 121.9, 64.1, 53.2, 50.4, 36.1, 34.6, 30.5, 19.3, 28.3. HRMS (ESI$^+$): calcd for $C_{26}H_{34}N$ $[M+H]^+$ 360.2686, found 360.2680.



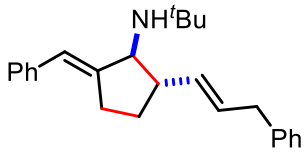
(*Trans*)-2-((*E*)-7-(9*H*-carbazol-9-yl)hept-1-en-1-yl)-5-((*E*)-benzylidene)-*N*-(*tert*-butyl)cyclopentan-1-amine (*trans*-3ay)

The title compound was prepared according to the general procedure as a yellow solid (44.2 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.0 Hz, 2H), 7.49-7.46 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 4H), 7.26-7.22 (m, 2H), 7.19 (t, *J* = 6.8 Hz, 1H), 6.52 (s, 1H), 5.49-5.42 (m, 1H), 5.32 (dd, *J* = 15.2, 8.4 Hz, 1H), 4.30 (t, *J* = 7.2 Hz, 2H), 3.23 (d, *J* = 9.2 Hz, 1H), 2.68-2.61 (m, 2H), 2.07-1.87 (m, 6H), 1.57-1.52 (m, 1H), 1.43-1.42 (m, 4H), 1.14 (brs, 1H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.6, 140.5, 138.5, 133.3, 131.1, 128.5, 128.3, 126.0, 125.7, 122.9, 121.7, 120.5, 118.8, 108.7, 64.0, 51.1, 50.7, 43.1, 32.5, 30.7, 29.4, 29.3, 29.0, 28.3, 27.0. HRMS (ESI$^+$): calcd for $C_{35}H_{43}N_2$ $[M+H]^+$ 491.3421, found 491.3431.



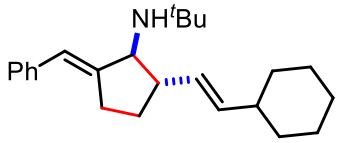
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-undec-1-en-1-yl)cyclopentan-1-amine (*trans*-3az)

The title compound was prepared according to the general procedure as a yellow oil (34.7 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.29 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.50 (s, 1H), 5.50-5.45 (m, 1H), 5.35-5.31 (m, 1H), 3.20 (d, *J* = 9.6 Hz, 1H), 2.66-2.58 (m, 2H), 2.05-1.99 (m, 3H), 1.96-1.92 (m, 1H), 1.60-1.56 (m, 1H), 1.38-1.27 (m, 14H), 1.23 (s, 9H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.7, 138.5, 132.8, 131.9, 128.5, 128.2, 126.0, 121.6, 63.9, 51.1, 50.7, 32.7, 32.0, 30.6, 29.6, 29.34, 29.29, 28.2, 22.8, 14.2. HRMS (ESI^{+}): calcd for $C_{27}H_{44}N$ $[M+H]^{+}$ 382.3469, found 382.3475.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-3-phenylprop-1-en-1-yl)cyclopentan-1-amine (*trans*-3aaa)

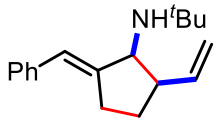
The title compound was prepared according to the general procedure as a yellow solid (32.1 mg, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.26 (m, 6H), 7.21-7.17 (m, 4H), 6.50 (d, *J* = 2.0 Hz, 1H), 5.69-5.62 (m, 1H), 5.44 (dd, *J* = 15.2, 8.6 Hz, 1H), 3.37 (d, *J* = 6.4 Hz, 2H), 3.24 (d, *J* = 9.2 Hz, 1H), 2.67-2.60 (m, 2H), 2.13-2.09 (m, 1H), 2.00-1.93 (m, 1H), 1.67-1.58 (m, 1H), 1.38 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.6, 140.8, 138.4, 134.5, 130.0, 128.6, 128.50, 128.45, 128.2, 126.0, 121.7, 64.0, 51.1, 50.6, 39.1, 30.7, 29.1, 28.3. HRMS (ESI^{+}): calcd for $C_{25}H_{32}N$ $[M+H]^{+}$ 346.2530, found 346.2513.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-2-cyclohexylvinyl)cyclopentan-1-amine (*trans*-3aab)

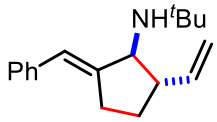
The title compound was prepared according to the general procedure as a yellow oil (26.3 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.28 (m, 4H), 7.16 (t, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 5.43 (dd, *J* = 15.4, 6.4 Hz, 1H), 5.28 (dd, *J* = 15.4, 8.5 Hz, 1H), 3.19 (d, *J* = 9.2 Hz, 1H), 2.66-2.59 (m, 2H), 2.03-2.01 (m, 3H), 1.96-1.72 (m, 4H), 1.69-1.58 (m, 2H), 1.28-1.18 (m, 3H), 1.13 (s, 9H), 1.08-1.05 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.6, 138.5, 137.8, 130.2, 128.5, 128.2,

126.0, 121.6, 63.9, 51.1, 50.1, 40.8, 33.2, 30.7, 29.3, 28.2, 26.3, 26.2. HRMS (ESI^+): calcd for $C_{24}H_{36}N$ $[M+H]^+$ 338.2843, found 338.2827.



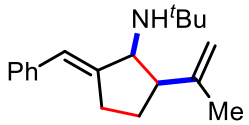
(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine (*cis*-3aac)

The title compound was prepared according to the general procedure as a yellow solid (12.0 mg, 47% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 2.4 Hz, 1H), 5.60-5.50 (m, 1H), 5.10-5.04 (m, 2H), 3.61 (d, J = 8.0 Hz, 1H), 2.69-2.64 (m, 3H), 1.95-1.92 (m, 1H), 1.91-1.77 (m, 1H), 1.14 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 147.6, 138.6, 138.1, 128.4, 128.2, 125.8, 122.1, 117.1, 61.5, 50.8, 48.3, 30.5, 28.0, 27.1. HRMS (ESI^+): calcd for $C_{18}H_{26}N$ $[M+H]^+$ 256.2060, found 256.2070.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine (*trans*-3aac)

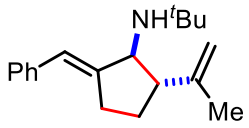
The title compound was prepared according to the general procedure as a yellow solid (4.1 mg, 16% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.29 (m, 4H), 7.19-7.17 (m, 1H), 6.51 (d, J = 2.4 Hz, 1H), 5.82-5.73 (m, 1H), 5.10-5.03 (m, 2H), 3.28 (d, J = 9.2 Hz, 1H), 2.68-2.62 (m, 2H), 2.14-2.10 (m, 1H), 2.01-1.94 (m, 1H), 1.66-1.61 (m, 1H), 1.14 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.5, 141.5, 138.4, 128.5, 128.3, 126.1, 121.9, 115.3, 63.9, 51.9, 51.0, 30.7, 28.9, 28.3. HRMS (ESI^+): calcd for $C_{18}H_{26}N$ $[M+H]^+$ 256.2060, found 256.2070.



(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(prop-1-en-2-yl)cyclopentan-1-amine (*cis*-3aad)

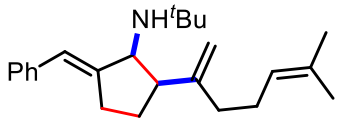
The title compound was prepared according to the general procedure as a yellow solid (9.6 mg, 36% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.29 (m, 4H), 7.15 (t, J = 7.2 Hz, 1H), 6.58 (s, 1H), 4.86 (s, 1H), 4.68 (s, 1H), 3.63 (d, J = 6.0 Hz, 1H), 2.73-2.63 (m, 3H), 1.93-1.91 (m, 2H), 1.62 (s, 3H), 1.42 (brs, 1H), 1.12 (s, 9H);

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.6, 145.6, 138.8, 125.8, 128.2, 125.8, 121.4, 113.2, 60.8, 50.7, 50.3, 30.3, 27.7, 26.8, 22.4. HRMS (ESI^+): calcd for $C_{19}H_{28}N$ $[M+H]^+$ 270.2217, found 270.2219.



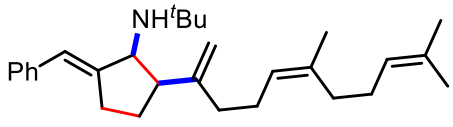
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(prop-1-en-2-yl)cyclopentan-1-amine (*trans*-3aad)

The title compound was prepared according to the general procedure as a yellow solid (3.2 mg, 12% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.29 (m, 4H), 7.17-7.15 (m, 1H), 6.54 (s, 1H), 4.81-4.77 (m, 2H), 3.40 (d, J = 8.4 Hz, 1H), 2.69-2.61 (m, 2H), 2.20-2.18 (m, 1H), 1.91-1.88 (m, 1H), 1.79-1.74 (m, 4H), 1.39 (brs, 1H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.9, 146.1, 138.5, 128.5, 128.2, 126.0, 122.3, 112.7, 61.9, 54.8, 50.8, 30.5, 28.2, 27.0, 19.5. HRMS (ESI^+): calcd for $C_{19}H_{28}N$ $[M+H]^+$ 270.2217, found 270.2219.



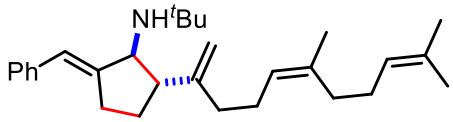
(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(6-methylhepta-1,5-dien-2-yl)cyclopentan-1-amine (*cis*-3aae)

The title compound was prepared according to the general procedure as a yellow solid (total: 10.8 mg, 32% yield, d.r. = 2:1). **(*Cis*):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.29 (m, 4H), 7.16 (t, J = 7.2 Hz, 1H), 6.55 (d, J = 2.0 Hz, 1H), 5.12-5.08 (m, 1H), 4.91 (s, 1H), 4.75 (s, 1H), 3.64 (d, J = 6.0 Hz, 1H), 2.76-2.69 (m, 1H), 2.62-2.60 (m, 2H), 2.14-2.10 (m, 2H), 2.01-1.97 (m, 3H), 1.86-1.81 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.11 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.0, 148.6, 138.7, 131.8, 128.4, 128.2, 125.8, 124.2, 121.8, 111.3, 61.0, 50.7, 49.2, 36.7, 30.4, 27.6, 27.3, 26.4, 25.8, 17.9. HRMS (ESI^+): calcd for $C_{24}H_{36}N$ $[M+H]^+$ 338.2843, found 338.2845.



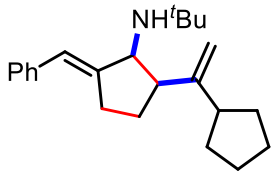
(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*Z*)-6,10-dimethylundeca-1,5,9-trien-2-yl)cyclopentan-1-amine (*cis*-3aaf)

The title compound was prepared according to the general procedure as a yellow solid (7.3 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.29 (m, 4H), 7.16 (t, J = 6.8 Hz, 1H), 6.56 (s, 1H), 5.12-5.06 (m, 2H), 4.91 (s, 1H), 4.75 (s, 1H), 3.66 (d, J = 6.0 Hz, 1H), 2.79-2.59 (m, 3H), 2.16-2.11 (m, 2H), 2.06-1.95 (m, 7H), 1.89-1.81 (m, 1H), 1.67 (s, 3H), 1.59 (s, 6H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.5, 143.2, 138.7, 135.4, 131.4, 128.4, 128.2, 125.8, 124.4, 124.0, 121.8, 111.3, 61.0, 50.7, 49.2, 39.8, 36.7, 30.4, 27.6, 27.3, 26.8, 26.3, 25.8, 17.8, 16.2. HRMS (ESI$^+$): calcd for $C_{29}H_{44}N$ $[M+H]^+$ 406.3469, found 406.3478.



(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*Z*)-6,10-dimethylundeca-1,5,9-trien-2-yl)cyclopentan-1-amine (*trans*-3aaf)

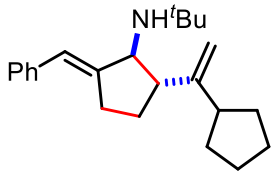
The title compound was prepared according to the general procedure as a yellow solid (7.3 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.29 (m, 4H), 7.18-7.15 (m, 1H), 6.53 (d, J = 2.0 Hz, 1H), 5.16 (t, J = 8.0 Hz, 1H), 5.12-5.08 (m, 1H), 4.84 (d, J = 9.6 Hz, 2H), 3.46 (d, J = 8.0 Hz, 1H), 2.67-2.61 (m, 2H), 2.23-2.14 (m, 2H), 2.08-2.05 (m, 5H), 2.00-1.97 (m, 4H), 1.68 (s, 3H), 1.60 (s, 6H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.4, 150.2, 138.4, 135.4, 131.5, 128.5, 128.2, 126.1, 124.4, 124.1, 122.4, 110.5, 62.9, 54.1, 51.0, 39.8, 33.9, 30.5, 28.4, 27.9, 26.9, 26.8, 25.8, 17.8, 16.1. HRMS (ESI$^+$): calcd for $C_{29}H_{44}N$ $[M+H]^+$ 406.3469, found 406.3480.



(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(1-cyclopentylvinyl)cyclopentan-1-amine (*cis*-3aag)

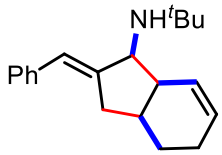
The title compound was prepared according to the general procedure as a yellow solid (6.7 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.29 (m, 4H), 7.17-7.14 (m, 1H), 6.56 (s, 1H), 4.94 (s, 1H), 4.69 (s, 1H), 3.66 (s, 1H), 2.76-2.53 (m, 3H), 2.36-2.29 (m, 1H), 2.00-1.93 (m, 1H), 1.85-1.77 (m, 3H), 1.71-1.66 (m, 2H), 1.59-1.55 (m, 3H), 1.42-1.35 (m, 2H), 1.13 (brs, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR

(101 MHz, $CDCl_3$): δ = 152.0, 138.7, 129.9, 128.4, 128.2, 127.8, 125.8, 108.9, 65.2, 61.1, 48.5, 47.3, 32.4, 31.7, 30.5, 30.4, 28.1, 27.5, 24.9. HRMS (ESI^+): calcd for $C_{23}H_{34}N$ $[M+H]^+$ 324.2686, found 324.2680.



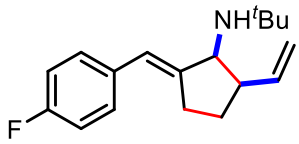
(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(1-cyclopentylvinyl)cyclopentan-1-amine (*trans*-3aag)

The title compound was prepared according to the general procedure as a yellow solid (6.7 mg, 19% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.29 (m, 4H), 7.19-7.15 (m, 1H), 6.52 (d, J = 2.0 Hz, 1H), 6.87 (s, 1H), 6.74 (s, 1H), 3.54 (d, J = 6.4 Hz, 1H), 2.66-2.60 (m, 3H), 2.45-2.41 (m, 1H), 2.30-2.24 (m, 1H), 2.06-2.01 (m, 1H), 1.88-1.65 (m, 7H), 1.59-1.55 (m, 3H), 1.13 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 155.5, 150.8, 138.4, 128.5, 128.3, 126.1, 122.7, 107.4, 63.9, 52.9, 51.0, 45.7, 33.3, 32.0, 30.6, 30.0, 28.6, 25.2. HRMS (ESI^+): calcd for $C_{23}H_{34}N$ $[M+H]^+$ 324.2686, found 324.2692.



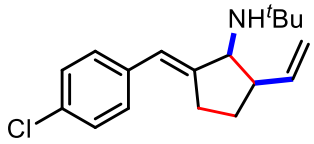
(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-2,3,3a,4,5,7a-hexahydro-1*H*-inden-1-amine (*cis*-3aah)

The title compound was prepared according to the general procedure as a yellow solid (11.3 mg, 40% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.31 (m, 4H), 7.20-7.15 (m, 1H), 6.42-6.41 (m, 1H), 5.74 (s, 2H), 3.42 (d, J = 6.4 Hz, 1H), 2.86-2.80 (m, 1H), 2.42-2.36 (m, 2H), 2.20-2.17 (m, 1H), 2.07-2.01 (m, 2H), 1.72-1.67 (m, 1H), 1.58-1.51 (m, 1H), 1.17 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.7, 138.3, 128.9, 128.5, 128.3, 127.5, 126.2, 122.6, 64.2, 51.0, 47.1, 34.6, 34.2, 30.6, 25.6, 23.3. HRMS (ESI^+): calcd for $C_{20}H_{28}N$ $[M+H]^+$ 282.2217, found 282.2219.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-4-fluorobenzylidene)-5-vinylcyclopentan-1-amine (*cis*-3cac)

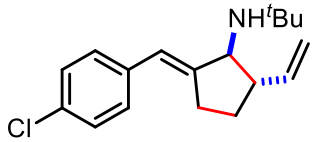
The title compound was prepared according to the general procedure as a yellow oil (total: 17.0 mg, 62% yield, d.r. = 9:1). **(*Cis*):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.30 (m, 2H), 7.00 (t, J = 8.8 Hz, 2H), 6.53 (d, J = 2.4 Hz, 1H), 5.58-5.49 (m, 1H), 5.11-5.05 (m, 2H), 3.62 (d, J = 4.8 Hz, 1H), 2.71-2.60 (m, 3H), 1.97-1.90 (m, 1H), 1.83-1.77 (m, 2H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 162.3 (d, J = 246.4 Hz), 147.1 (d, J = 1.0 Hz), 137.9, 134.8 (d, J = 3.0 Hz), 129.9 (d, J = 8.1 Hz), 121.1, 117.2, 115.1 (d, J = 21.2 Hz), 61.4, 50.8, 48.3, 30.5, 28.0, 26.9. HRMS (ESI^{+}): calcd for $C_{18}H_{25}FN$ $[M+H]^{+}$ 274.1966, found 274.1960.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-4-chlorobenzylidene)-5-vinylcyclopentan-1-amine

(*cis*-3dac)

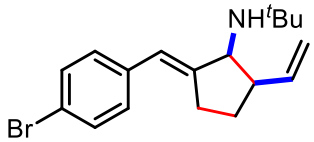
The title compound was prepared according to the general procedure as a yellow solid (20.3mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.23 (m, 4H), 6.53 (d, J = 2.4 Hz, 1H), 5.57-5.05 (m, 2H), 3.59 (d, J = 8.0 Hz, 1H), 2.71-2.61 (m, 3H), 1.97-1.87 (m, 1H), 1.82-1.76 (m, 1H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.5, 137.8, 137.1, 131.3, 129.6, 128.3, 121.1, 117.4, 61.5, 50.8, 48.3, 30.5, 27.9, 27.0. HRMS (ESI^{+}): calcd for $C_{18}H_{25}ClN$ $[M+H]^{+}$ 290.1671, found 290.1665.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-chlorobenzylidene)-5-vinylcyclopentan-1-amine

(*trans*-3dac)

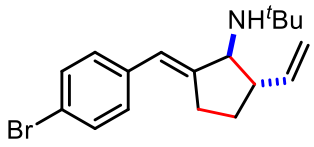
The title compound was prepared according to the general procedure as a yellow solid (2.3mg, 8% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.23 (m, 4H), 6.46 (d, J = 2.4 Hz, 1H), 5.80-5.71 (m, 1H), 5.09-5.03 (m, 2H), 3.28 (d, J = 9.2 Hz, 1H), 2.63-2.56 (m, 2H), 1.99-1.93 (m, 1H), 1.66-1.61 (m, 1H), 1.12 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.3, 141.3, 136.8, 131.6, 129.7, 128.4, 120.8, 115.6, 63.8, 51.8, 51.0, 30.7, 28.8, 28.2. HRMS (ESI^{+}): calcd for $C_{18}H_{25}ClN$ $[M+H]^{+}$ 290.1671, found 290.1673.



(*Cis*)-2-((*E*)-4-bromobenzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine

(*cis*-3eac)

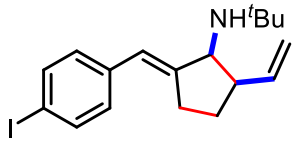
The title compound was prepared according to the general procedure as a yellow solid (23.4 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 2.4 Hz, 1H), 5.56-5.47 (m, 1H), 5.11-5.04 (m, 2H), 3.60 (d, J = 6.0 Hz, 1H), 2.71-2.59 (m, 3H), 1.95-1.90 (m, 1H), 1.82-1.76 (m, 1H), 1.13 (brs, 3H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.7, 137.8, 137.5, 131.3, 130.0, 121.2, 119.5, 117.4, 61.6, 50.8, 48.3, 30.5, 27.9, 27.0. HRMS (ESI$^+$): calcd for $C_{18}H_{25}BrN$ $[M+H]^+$ 334.1165, found 334.1155.



(*Trans*)-2-((*E*)-4-bromobenzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine

(*trans*-3eac)

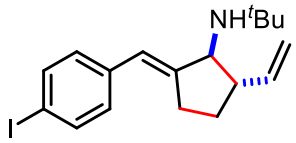
The title compound was prepared according to the general procedure as a yellow solid (4.3 mg, 13% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H), 6.45 (d, J = 2.4 Hz, 1H), 5.80-5.71 (m, 1H), 5.09-5.03 (m, 2H), 3.27 (d, J = 9.2 Hz, 1H), 2.62-2.56 (m, 2H), 2.12-2.06 (m, 1H), 2.01-1.94 (m, 1H), 1.66-1.61 (m, 1H), 1.38 (brs, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.5, 141.3, 137.3, 131.3, 130.1, 120.8, 119.7, 115.6, 63.8, 51.8, 51.0, 30.7, 28.8, 28.2. HRMS (ESI$^+$): calcd for $C_{18}H_{25}BrN$ $[M+H]^+$ 334.1165, found 334.1168.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-4-iodobenzylidene)-5-vinylcyclopentan-1-amine

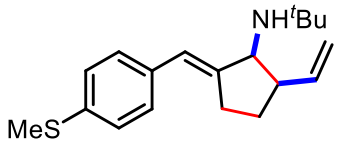
(*cis*-3fac)

The title compound was prepared according to the general procedure as a yellow solid (22.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 2.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 2.4 Hz, 1H), 5.56-5.46 (m, 1H), 5.11-5.04 (m, 2H), 3.60 (d, J = 7.6 Hz, 1H), 2.71-2.58 (m, 3H), 1.94-1.87 (m, 1H), 1.82-1.76 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.0, 138.1, 137.8, 137.3, 130.3, 121.3, 117.4, 90.9, 61.6, 50.8, 48.2, 30.5, 27.9, 27.1. HRMS (ESI$^+$): calcd for $C_{18}H_{25}IN$ $[M+H]^+$ 382.1027, found 382.1017.



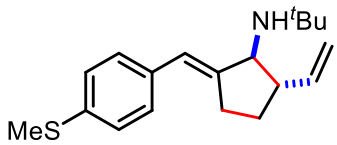
(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-iodobenzylidene)-5-vinylcyclopentan-1-amine (*trans*-3fac)

The title compound was prepared according to the general procedure as a yellow solid (3.8 mg, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.43 (d, J = 2.0 Hz, 1H), 5.80-5.71 (m, 1H), 5.09-5.03 (m, 2H), 3.27 (d, J = 8.8 Hz, 1H), 2.62-2.53 (m, 2H), 2.12-2.08 (m, 1H), 2.01-1.93 (m, 1H), 1.66-1.62 (m, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 150.7, 141.3, 137.9, 137.3, 130.4, 120.9, 115.6, 91.1, 63.9, 51.8, 51.0, 30.7, 28.8, 28.2. HRMS (ESI$^+$): calcd for $C_{18}H_{25}IN$ $[M+H]^+$ 382.1027, found 382.1027.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-4-(methylthio)benzylidene)-5-vinylcyclopentan-1-amine (*cis*-3gac)

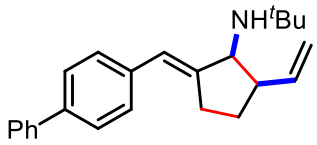
The title compound was prepared according to the general procedure as a yellow solid (14.1 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 2.8 Hz, 1H), 5.58-5.49 (m, 1H), 5.10-5.04 (m, 2H), 3.61 (d, J = 4.0 Hz, 1H), 2.71-2.61 (m, 3H), 2.47 (s, 3H), 1.96-1.86 (m, 1H), 1.82-1.77 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.4, 138.0, 135.8, 135.4, 128.9, 126.7, 121.6, 117.2, 61.5, 50.8, 48.3, 30.5, 28.0, 27.1, 16.2. HRMS (ESI$^+$): calcd for $C_{19}H_{28}NS$ $[M+H]^+$ 302.1937, found 302.1945.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-4-(methylthio)benzylidene)-5-vinylcyclopentan-1-amine (*trans*-3gac)

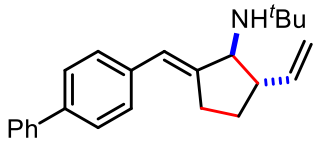
The title compound was prepared according to the general procedure as a yellow solid (4.8 mg, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.27 (m, 1H), 7.25 (m, 1H), 7.21-7.19 (m, 2H), 6.45 (d, J = 2.4 Hz, 1H), 5.81-5.72 (m, 1H), 5.09-5.02 (m, 2H), 3.26 (d, J = 8.4 Hz, 1H), 2.68-2.58 (m, 2H), 2.47 (s, 3H), 2.13-2.09 (m, 1H), 2.01-1.93 (m, 1H), 1.67-1.62 (m, 1H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):

δ = 149.2, 141.4, 135.8, 135.5, 128.9, 126.6, 121.3, 115.4, 63.9, 51.9, 51.0, 30.7, 28.7, 28.3, 16.1. HRMS (ESI$^+$): calcd for $C_{19}H_{28}NS$ $[M+H]^+$ 302.1937, found 302.1950.



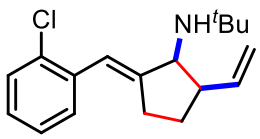
(*Cis*,*E*)-2-([1,1'-biphenyl]-4-ylmethylene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine (*cis*-3hac)

The title compound was prepared according to the general procedure as a yellow solid (12.9 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.57 (m, 4H), 7.47-7.42 (m, 4H), 7.33 (t, J = 7.6 Hz, 1H), 6.63 (d, J = 2.4 Hz, 1H), 5.62-5.53 (m, 1H), 5.13-5.07 (m, 1H), 3.66 (d, J = 4.4 Hz, 1H), 2.74-2.70 (m, 3H), 1.99-1.93 (m, 1H), 1.86-1.81 (m, 1H), 1.17 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.0, 141.1, 138.4, 138.1, 137.7, 128.9, 127.2, 127.0, 126.9, 121.8, 117.2, 61.7, 50.8, 48.4, 30.5, 28.0, 27.2. HRMS (ESI$^+$): calcd for $C_{24}H_{30}N$ $[M+H]^+$ 332.2373, found 332.2379.



(*Trans*,*E*)-2-([1,1'-biphenyl]-4-ylmethylene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine (*trans*-3hac)

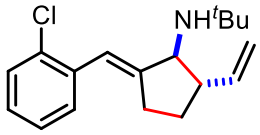
The title compound was prepared according to the general procedure as a yellow solid (4.3 mg, 13% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.56 (m, 4H), 7.43-7.25 (m, 5H), 6.55 (s, 1H), 5.83-5.74 (m, 1H), 5.11-5.04 (m, 1H), 3.33 (d, J = 7.2 Hz, 1H), 2.70-2.69 (m, 2H), 2.17-2.13 (m, 1H), 2.02-2.00 (m, 1H), 1.69-1.64 (m, 1H), 1.15 (brs, 1H), 1.15 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.8, 141.4, 141.0, 138.7, 137.4, 128.93, 128.85, 127.2, 127.0, 126.9, 121.5, 111.4, 64.0, 51.9, 51.0, 30.7, 28.9, 28.4. HRMS (ESI$^+$): calcd for $C_{24}H_{30}N$ $[M+H]^+$ 332.2373, found 332.2365.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-2-chlorobenzylidene)-5-vinylcyclopentan-1-amine (*cis*-3kac)

The title compound was prepared according to the general procedure as a yellow solid (10.7 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 9.2 Hz, 1H), 7.34

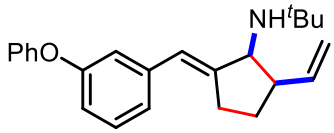
(d, *J* = 6.8 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 5.67-5.58 (m, 1H), 5.13-5.06 (m, 2H), 3.65 (d, *J* = 6.0 Hz, 1H), 2.71-2.53 (m, 3H), 1.91-1.89 (m, 1H), 1.88-1.74 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.1, 138.1, 126.8, 133.5, 129.5, 129.3, 127.1, 126.3, 119.1, 117.1, 61.5, 50.8, 48.4, 30.5, 27.9, 26.6. HRMS (ESI^+): calcd for $C_{18}H_{15}ClN$ $[M+H]^+$ 290.1671, found 290.1689.\



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-2-chlorobenzylidene)-5-vinylcyclopentan-1-amine

(*trans*-3kac)

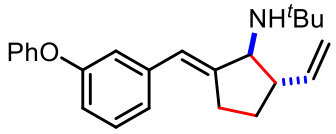
The title compound was prepared according to the general procedure as a yellow solid (2.5 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.35 (m, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 5.84-5.75 (m, 1H), 5.11-5.03 (m, 2H), 3.34 (d, *J* = 9.2 Hz, 1H), 2.58-2.54 (m, 2H), 2.20-2.13 (m, 1H), 1.98-1.90 (m, 1H), 1.62-1.57 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 151.9, 141.4, 136.3, 133.6, 129.5, 129.4, 127.3, 126.3, 118.6, 115.2, 63.8, 52.3, 50.9, 30.8, 28.7, 28.0. HRMS (ESI^+): calcd for $C_{18}H_{15}ClN$ $[M+H]^+$ 290.1671, found 290.1674.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-3-phenoxybenzylidene)-5-vinylcyclopentan-1-amine

(*cis*-3mac)

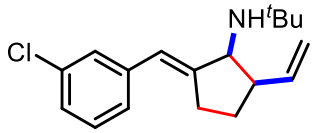
The title compound was prepared according to the general procedure as a yellow solid (11.5 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 3H), 7.13-7.00 (m, 5H), 6.82 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.53 (d, *J* = 2.8 Hz, 1H), 5.57-5.48 (m, 1H), 5.10-5.04 (m, 2H), 3.59 (d, *J* = 6.0 Hz, 1H), 2.69-2.59 (m, 3H), 1.92-1.87 (m, 1H), 1.80-1.74 (m, 1H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 157.6, 157.0, 148.7, 140.5, 137.9, 129.8, 129.4, 123.7, 123.0, 121.7, 118.9, 118.7, 117.2, 116.6, 61.6, 50.8, 48.3, 30.5, 28.0, 27.1. HRMS (ESI^+): calcd for $C_{24}H_{30}NO$ $[M+H]^+$ 348.2322, found 348.2322.



(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-3-phenoxybenzylidene)-5-vinylcyclopentan-1-amine

(*trans*-3mac)

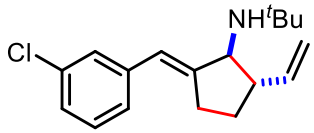
The title compound was prepared according to the general procedure as a yellow solid (5.9 mg, 17% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.29 (m, 3H), 7.27-6.99 (m, 5H), 6.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 5.80-5.71 (m, 1H), 5.09-5.02 (m, 2H), 3.27 (d, *J* = 8.0 Hz, 1H), 2.60-2.56 (m, 2H), 2.12-2.08 (m, 1H), 1.98-1.91 (m, 1H), 1.64-1.56 (m, 1H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 157.5, 157.1, 150.5, 141.4, 140.2, 129.8, 129.4, 123.7, 123.1, 121.4, 119.0, 118.8, 116.7, 115.5, 63.9, 51.8, 51.0, 30.7, 28.8, 28.3. HRMS (ESI$^+$): calcd for $C_{24}H_{30}NO$ $[M+H]^+$ 348.2322, found 348.2329.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-3-chlorobenzylidene)-5-vinylcyclopentan-1-amine

(*cis*-3nac)

The title compound was prepared according to the general procedure as a yellow solid (18.6 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 7.25-7.22 (m, 2H), 7.13-7.11 (m, 1H), 6.52 (d, *J* = 2.8 Hz, 1H), 5.56-5.47 (m, 1H), 5.11-5.04 (m, 2H), 3.62 (d, *J* = 4.0 Hz, 1H), 2.72-2.62 (m, 3H), 1.97-1.90 (m, 1H), 1.88-1.77 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.5, 140.5, 137.8, 134.1, 129.4, 128.2, 126.6, 125,8m 121,1, 117.4, 61.6, 50.8, 48.2, 30.5, 38.0, 27.0. HRMS (ESI$^+$): calcd for $C_{18}H_{25}ClN$ $[M+H]^+$ 290.1671, found 290.1685.

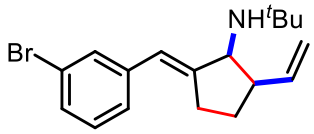


(*Trans*)-*N*-(*tert*-butyl)-2-((*E*)-3-chlorobenzylidene)-5-vinylcyclopentan-1-amine

(*trans*-3nac)

The title compound was prepared according to the general procedure as a yellow solid (2.6 mg, 9% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 1H), 7.23-7.13 (m, 3H), 6.46 (d, *J* = 2.0 Hz, 1H), 5.80-5.71 (m, 1H), 5.10-5.03 (m, 2H), 3.26 (d, *J* = 9.2 Hz, 1H), 2.71-2.60 (m, 2H), 2.12-2.08 (m, 1H), 2.02-1.94 (m, 1H), 1.67-1.61 (m, 1H),

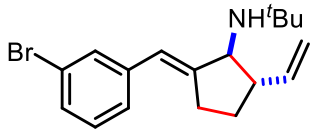
1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 151.2, 141.2, 140.2, 134.1, 129.4, 128.3, 126.7, 126.0, 120.7, 115.6, 63.8, 51.8, 51.0, 30.7, 28.7, 28.2. HRMS (ESI^+): calcd for $C_{18}H_{25}ClN$ $[M+H]^+$ 290.1671, found 290.1673.



(*Cis*)-2-((*E*)-3-bromobenzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine

(*cis*-3oac)

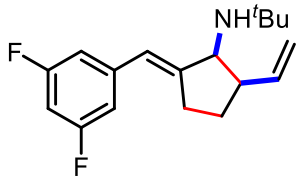
The title compound was prepared according to the general procedure as a yellow solid (21.7 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.29-7.25 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.56-5.47 (m, 1H), 5.11-5.05 (m, 2H), 3.60 (d, J = 7.6 Hz, 1H), 2.72-2.62 (m, 3H), 1.98-1.90 (m, 1H), 1.83-1.77 (m, 1H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.5, 140.8, 137.7, 131.2, 129.7, 128.7, 127.0, 122.5, 121.0, 117.4, 61.6, 50.8, 48.2, 30.5, 27.9, 27.0. HRMS (ESI^+): calcd for $C_{18}H_{25}BrN$ $[M+H]^+$ 334.1165, found 334.1150.



(*Trans*)-2-((*E*)-3-bromobenzylidene)-*N*-(*tert*-butyl)-5-vinylcyclopentan-1-amine

(*trans*-3oac)

The title compound was prepared according to the general procedure as a yellow solid (3.0 mg, 9% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 1H), 7.30-7.28 (m, 1H), 7.25-7.24 (m, 1H), 6.19 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 5.80-5.71 (m, 1H), 5.10-5.04 (m, 2H), 3.28 (d, J = 9.2 Hz, 1H), 2.66-2.57 (m, 2H), 2.66-2.57 (m, 2H), 2.00-1.94 (m, 1H), 1.65-1.61 (m, 1H), 1.42 (brs, 1H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 151.3, 141.2, 140.5, 131.3, 129.7, 128.9, 127.1, 122.4, 120.6, 115.6, 63.8, 51.8, 51.0, 30.7, 28.7, 28.2. HRMS (ESI^+): calcd for $C_{18}H_{25}BrN$ $[M+H]^+$ 334.1165, found 334.1177.



(*Cis*)-*N*-(*tert*-butyl)-2-((*E*)-3,5-difluorobenzylidene)-5-vinylcyclopentan-1-amine

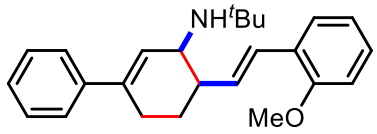
(*cis*-3rac)

The title compound was prepared according to the general procedure as a yellow solid (total: 24.8 mg, 85% yield, d.r. = 16:1). **(*Cis*):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (d, J = 7.2 Hz, 2H), 6.63-6.57 (m, 1H), 6.52 (d, J = 2.4 Hz, 1H), 5.54-5.44 (m, 1H), 5.13-5.05 (m, 2H), 3.61 (d, J = 6.0 Hz, 1H), 2.73-2.61 (m, 3H), 1.98-1.88 (m, 1H), 1.84-1.78 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 164.3 (dd, J = 247.5, 13.1 Hz), 150.9, 141.8 (t, J = 10.1 Hz), 137.5, 120.8, 117.6, 111.0 (dd, J = 18.1, 6.1 Hz), 101.0 (t, J = 26.3 Hz), 61.6, 50.8, 48.2, 30.5, 27.8, 27.1. HRMS (ESI$^+$): calcd for $C_{18}H_{24}F_2N$ $[M+H]^+$ 292.1872, found 292.1876.

5. General Procedure for the *cis*-Diastereoselective [4 + 2] Annulation of α,β-Unsaturated Aldimines with 1,3-Dienes *via* γ-Allylic C–H Activation

General procedure for *cis*-diastereoselective [4 + 2] annulation of α,β-unsaturated aldimines 4 with *o*-OMe-substituted 1-aryl-1,3-butadienes 2 *via* γ-allylic C–H activation by Ce-2 in the presence of Bn_2NH

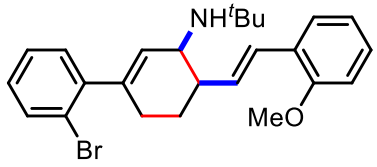
In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 0.010 mmol) was added to a toluene-d_8 solution (1.0 mL) of **Ce-2** (5.4 mg, 0.010 mmol) in a J. Young NMR tube. After 5 min, *N*,*N*-dibenzylamine (1.9 mg, 0.010 mmol) was added to this tube. After 5 min, α,β-unsaturated aldimines **4** (0.1 mmol) and *o*-OMe-substituted 1-aryl-1,3-butadienes **2** (0.4 mmol) were added. The tube was sealed, taken outside of glovebox, and stirred at indicated temperatures for indicated times. Then, the tube was cooled to room temperature and the reaction mixture was monitored by NMR. The crude NMR yields were calculated on the basis of formation of the corresponding product **5**. The reaction mixture was filtered through a short silica gel column (EtOAc). The filtrate was evaporated under a reduced pressure. The d.r. ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. The solution was concentrated and purified directly by column chromatography on silica gel (hexane/EtOAc = 15/1, v/v) to give the pure product *cis*-**5**. Identical results were obtained when the reactions were conducted in toluene using a Schlenk tube.



(*Cis*)-*N*-(*tert*-butyl)-4-((*E*)-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5ba)

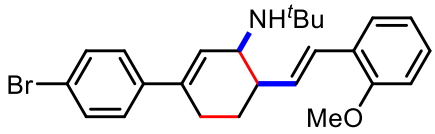
The title compound was prepared according to the general procedure as a yellow oil (22.8 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, J = 7.6, 2.4 Hz, 1H), 7.44-7.42 (m, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.23-7.16 (m, 2H), 6.90 (t, J = 7.6 Hz,

1H), 6.86-6.80 (m, 2H), 6.46 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.17 (d, *J* = 4.4 Hz, 1H), 3.84 (s, 3H), 3.43 (s, 1H), 2.58-2.38 (m, 3H), 1.93-1.88 (m, 2H), 1.12 (brs, 1H), 1.12 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 156.3, 141.9, 135.9, 133.5, 130.3, 128.3, 128.0, 127.0, 126.4, 125.3, 124.7, 120.7, 110.9, 55.6, 51.1, 50.6, 43.9, 30.3, 26.3, 26.0. HRMS (ESI^+): calcd for $C_{25}H_{32}NO$ $[M+H]^+$ 362.2479, found 362.2463.



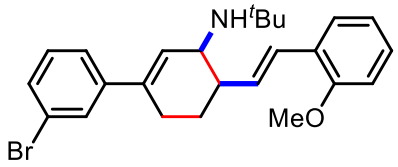
(*Cis*)-2'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5ea)

The title compound was prepared according to the general procedure as a yellow oil (25.5 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.50 (m, 2H), 7.28-7.24 (m, 1H), 7.21-7.17 (m, 2H), 7.12-7.08 (m, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.87-6.82 (m, 2H), 6.56 (dd, *J* = 16.0, 8.8 Hz, 1H), 5.71-5.70 (m, 1H), 3.85 (s, 3H), 3.41-3.39 (m, 1H), 2.61-2.56 (m, 1H), 2.39-2.26 (m, 2H), 1.93-1.86 (m, 2H), 1.09 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 156.4, 144.6, 138.4, 133.9, 132.84, 132.75, 130.0, 128.3, 127.9, 127.3, 127.1, 126.4, 124.6, 122.7, 120.8, 110.9, 55.6, 51.1, 50.2, 43.9, 30.3, 28.1, 26.3. HRMS (ESI^+): calcd for $C_{25}H_{31}BrNO$ $[M+H]^+$ 440.1584, found 440.1594.



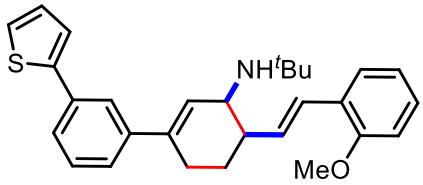
(*Cis*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5fa)

The title compound was prepared according to the general procedure as a yellow oil (28.6 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.41 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.86-6.80 (m, 2H), 6.42 (dd, *J* = 16.1, 4.8 Hz, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 3.83 (s, 3H), 3.42 (s, 1H), 2.58-2.33 (m, 3H), 1.93-1.88 (m, 2H), 1.11 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 156.3, 140.7, 134.9, 133.0, 131.3, 130.9, 128.1, 126.94, 126.86, 126.4, 125.1, 120.8, 120.7, 110.9, 55.6, 51.2, 50.6, 43.7, 30.2, 26.3, 25.7. HRMS (ESI^+): calcd for $C_{25}H_{31}BrNO$ $[M+H]^+$ 440.1584, found 440.1580.



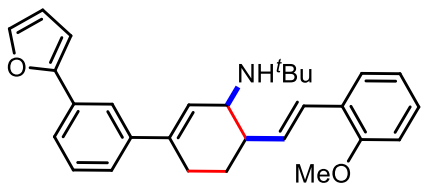
(*Cis*)-3'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-bi phenyl]-3-amine (*cis*-5ga)

The title compound was prepared according to the general procedure as a yellow oil (23.8 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (t, *J* = 2.0 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37-7.33 (m, 2H), 7.20-7.16 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.87-6.81 (m, 2H), 6.42 (dd, *J* = 16.0, 8.8 Hz, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 3.84 (s, 3H), 3.431 (m, 1H), 2.59-2.38 (m, 3H), 1.93-1.88 (m, 2H), 1.12 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 156.4, 144.1, 134.8, 133.0, 131.6, 129.9, 129.8, 128.5, 128.1, 126.9, 126.4, 125.1, 123.9, 122.6, 120.7, 110.9, 55.6, 51.2, 50.6, 43.8, 30.3, 26.3, 25.8. HRMS (ESI$^+$): calcd for $C_{25}H_{31}BrNO$ $[M+H]^+$ 440.1584, found 440.1585.



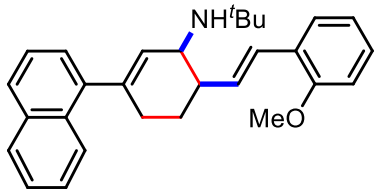
(*Cis*)-*N*-(*tert*-butyl)-4-((*E*)-2-methoxystyryl)-3'-(thiophen-2-yl)-3,4,5,6-tetrahydro -[1,1'-biphenyl]-3-amine (*cis*-5ha)

The title compound was prepared according to the general procedure as a yellow oil (17.7 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.56-7.54 (m, 1H), 7.48-7.46 (m, 2H), 7.33 (d, *J* = 4.4 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 1H), 6.92-6.82 (m, 3H), 6.67 (d, *J* = 5.6 Hz, 1H), 6.48-6.42 (m, 2H), 6.20 (d, *J* = 5.6 Hz, 1H), 3.84 (s, 3H), 3.49 (s, 1H), 2.64-2.41 (m, 3H), 1.94-1.91 (m, 2H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 154.6, 154.1, 142.2, 142.1, 132.9, 130.9, 129.9, 128.7, 128.1, 126.8, 126.7, 126.4, 125.3, 124.5, 122.7, 120.9, 120.7, 111.7, 110.9, 105.1, 55.6, 50.8, 43.7, 30.1, 29.8, 26.3, 26.0. HRMS (ESI$^+$): calcd for $C_{29}H_{34}NOS$ $[M+H]^+$ 444.2356, found 444.2350.



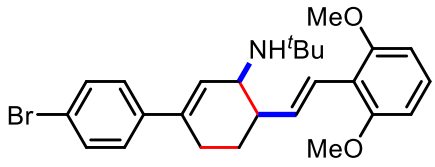
(*Cis*)-*N*-(*tert*-butyl)-3'-(furan-2-yl)-4-((*E*)-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5ia)

The title compound was prepared according to the general procedure as a yellow oil (15.0 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 1H), 7.50-7.46 (m, 2H), 7.36-7.32 (m, 3H), 7.28 (d, *J* = 4.4 Hz, 1H), 7.21-7.17 (m, 1H), 7.08 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.87-6.82 (m, 2H), 6.44 (dd, *J* = 16.8, 8.4 Hz, 1H), 6.20 (t, *J* = 4.0 Hz, 1H), 3.84 (s, 3H), 3.50 (s, 1H), 2.65-2.53 (m, 2H), 2.48-2.31 (m, 1H), 1.96-1.91 (m, 2H), 1.15 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 158.1, 156.4, 144.5, 142.4, 134.5, 128.9, 128.2, 128.1, 126.7, 126.5, 124.9, 124.7, 123.3, 123.3, 120.8, 118.5, 110.9, 104.5, 103.1, 55.6, 51.2, 50.8, 43.6, 30.0, 26.2, 26.0. HRMS (ESI$^+$): calcd for $C_{29}H_{34}NO_2$ $[M+H]^+$ 428.2585, found 428.2598.



(*Cis*)-*N*-(*tert*-butyl)-6-((*E*)-2-methoxystyryl)-3-(naphthalen-1-yl)cyclohex-2-en-1-amine (*cis*-5ja)

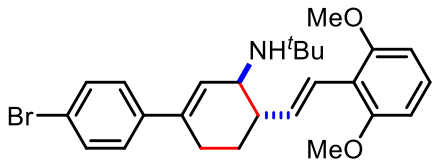
The title compound was prepared according to the general procedure as a yellow oil (15.6 mg, 38% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01-8.00 (m, 1H), 7.85-7.83 (m, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.47-7.42 (m, 3H), 7.31 (d, *J* = 6.6 Hz, 1H), 7.21 (d, *J* = 6.6 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.90-6.87 (m, 2H), 6.42 (dd, *J* = 16.2, 8.4 Hz, 1H), 5.56 (s, 1H), 3.86 (s, 3H), 3.52 (s, 1H), 2.71-2.68 (m, 1H), 2.50-2.38 (m, 2H), 2.05-1.93 (m, 2H), 1.10 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 156.5, 142.2, 137.6, 133.8, 132.9, 131.4, 128.4, 128.0, 127.9, 127.09, 127.05, 126.5, 125.7, 125.1, 125.0, 124.8, 120.7, 111.0, 55.6, 51.3, 50.5, 44.0, 30.2, 30.0, 26.4. HRMS (ESI$^+$): calcd for $C_{29}H_{34}NO$ $[M+H]^+$ 412.2635, found 412.2644.



(*Cis*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2,6-dimethoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5ka)

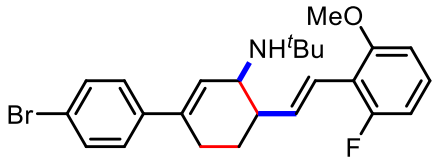
The title compound was prepared according to the general procedure as a yellow oil (17.4 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 8.4 Hz, 1H), 6.73-6.72 (m, 2H), 6.55 (d, *J* = 8.0 Hz,

2H), 6.13 (d, *J* = 3.6 Hz, 1H), 3.81 (s, 6H), 3.47 (s, 1H), 2.62-2.47 (m, 2H), 2.39-2.31 (m, 1H), 1.98-1.93 (m, 2H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 158.3, 140.9, 136.2, 135.0, 131.3, 128.5, 128.3, 127.5, 127.1, 127.0, 121.7, 120.7, 115.2, 104,1, 55.8, 52.3, 51.3, 50.8, 44.7, 30.2, 26.8, 25.6. HRMS (ESI^+): calcd for $C_{26}H_{33}BrNO_2$ $[M+H]^+$ 470.1690, found 470.1692.



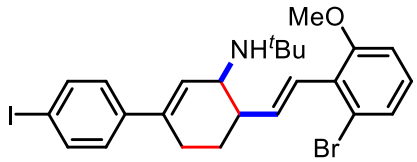
(*Trans*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2,6-dimethoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*trans*-5ka)

The title compound was prepared according to the general procedure as a yellow oil (8.5 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 6.49 (dd, *J* = 16.2, 9.0 Hz, 1H), 6.09 (s, 1H), 3.81 (s, 6H), 3.29 (d, *J* = 8.4 Hz, 1H), 2.48-2.42 (m, 2H), 2.21-2.20 (m, 1H), 2.07-2.04 (m, 1H), 1.83-1.77 (m, 1H), 1.15 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 158.4, 140.9, 137.4, 135.5, 131.3, 130.0, 128.5, 127.7, 127.1, 127.0, 121.9, 120.8, 114.7, 104.0, 55.7, 53.2, 51.8, 46.7, 30.0, 29.8, 28.7, 26.5. HRMS (ESI^+): calcd for $C_{26}H_{33}BrNO_2$ $[M+H]^+$ 470.1690, found 470.1700.



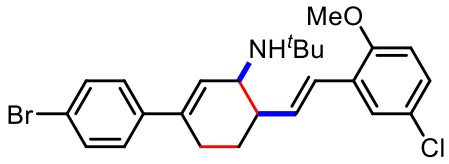
(*Cis*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-2-fluoro-6-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5la)

The title compound was prepared according to the general procedure as a yellow oil (total: 29.3 mg, 64% yield, d.r. = 4:1). **(*Cis*):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.10-7.06 (m, 1H), 6.72-6.59 (m, 4H), 6.14 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 1H), 2.57-2.47 (m, 2H), 2.38-2.35 (m, 1H), 1.94-1.89 (m, 2H), 1.13 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 249.5 Hz), 158.3 (d, *J* = 12.1 Hz), 140.8, 138.2 (d, *J* = 9.1 Hz), 135.3, 131.3, 130.5, 127.5 (d, *J* = 11.1 Hz), 127.0, 120.8, 119.5, 115.0 (d, *J* = 14.1 Hz), 108.5 (d, *J* = 23.2 Hz), 106.4, 56.0, 51.4, 50.6, 44.6, 30.1, 26.2, 25.8. HRMS (ESI^+): calcd for $C_{25}H_{30}BrFNO$ $[M+H]^+$ 458.1490, found 458.1487.



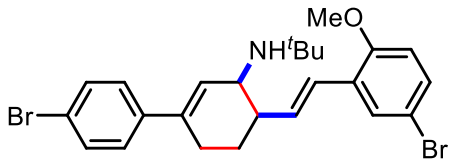
(*Cis*)-4-((*E*)-2-bromo-6-methoxystyryl)-*N*-(*tert*-butyl)-4'-iodo-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5ma)

The title compound was prepared according to the general procedure as a yellow oil (total: 36.8 mg, 65% yield, d.r. = 9:1). **(*Cis*):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.8 Hz, 2H), 7.17 (t, J = 8.4 Hz, 3H), 7.00 (t, J = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.57-6.44 (m, 2H), 6.11 (d, J = 3.2 Hz, 1H), 3.78 (s, 3H), 3.52 (s, 1H), 2.71-2.65 (m, 1H), 2.54-2.46 (m, 1H), 2.40-2.34 (m, 1H), 2.03-1.94 (m, 2H), 1.15 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 158.3, 141.3, 138.3, 137.3, 135.4, 130.8, 128.1, 127.2, 126.9, 126.8, 125.3, 124.8, 110.0, 92.3, 51.9, 51.6, 50.9, 44.0, 30.0, 26.8, 25.0. HRMS (ESI$^+$): calcd for $C_{25}H_{30}BrINO$ $[M+H]^+$ 566.0550, found 566.0554.



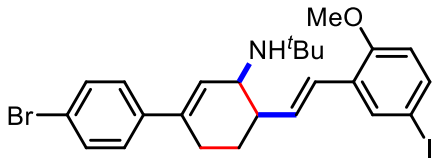
(*Cis*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-5-chloro-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5na)

The title compound was prepared according to the general procedure as a yellow oil (total: 19.5 mg, 41% yield, d.r. = 8:1). **(*Cis*):** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 3.0 Hz, 1H), 7.29 (d, J = 9.0 Hz, 2H), 7.11 (dd, J = 8.4 3.0, Hz, 1H), 6.76-6.72 (m, 2H), 6.42 (dd, J = 16.2, 8.4 Hz, 1H), 6.15 (d, J = 4.2 Hz, 1H), 3.81 (s, 3H), 3.42 (s, 1H), 2.57-2.53 (m, 2H), 2.48-2.33 (m, 1H), 1.92-1.88 (m, 2H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 154.9, 140.6, 135.2, 134.6, 131.4, 130.4, 128.5, 127.5, 127.0, 126.1, 125.8, 124.0, 120.9, 112.1, 55.9, 51.3, 50.6, 43.7, 30.2, 26.0, 25.8. HRMS (ESI$^+$): calcd for $C_{25}H_{30}BrClNO$ $[M+H]^+$ 474.1194, found 474.1180.



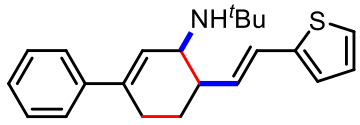
(*Cis*)-4'-bromo-4-((*E*)-5-bromo-2-methoxystyryl)-*N*-(*tert*-butyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5oa)

The title compound was prepared according to the general procedure as a yellow oil (total: 20.8 mg, 40% yield, d.r. = 7:1). **(*Cis*):** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 2.4 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 1H), 6.73-6.70 (m, 2H), 6.41 (dd, *J* = 16.2, 9.0 Hz, 1H), 6.14 (d, *J* = 4.2 Hz, 1H), 3.81 (s, 3H), 3.42 (s, 1H), 2.56-2.44 (m, 2H), 2.39-2.33 (m, 1H), 1.93-1.85 (m, 2H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 155.4, 144.1, 140.6, 135.2, 134.6, 131.4, 130.4, 129.0, 127.0, 124.0, 120.9, 113.3, 112.6, 55.8, 51.4, 50.6, 43.7, 30.1, 26.1, 25.8. HRMS (ESI^{+}): calcd for $C_{25}H_{30}Br_2NO$ $[M+H]^{+}$ 520.0669, found 520.0678.



(*Cis*)-4'-bromo-*N*-(*tert*-butyl)-4-((*E*)-5-iodo-2-methoxystyryl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5pa)

The title compound was prepared according to the general procedure as a yellow oil (total: 20.8 mg, 38% yield, d.r. = 7:1). **(*Cis*):** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 1.8 Hz, 1H), 7.47-7.42 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 16.2 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.39 (dd, *J* = 16.2, 8.4 Hz, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 3.80 (s, 3H), 3.42 (s, 1H), 2.55-2.44 (m, 2H), 2.37-2.33 (m, 1H), 1.91-1.87 (m, 2H), 1.11 (brs, 1H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 156.2, 140.6, 138.4, 136.5, 135.0, 134.5, 131.4, 130.4, 129.5, 127.0, 123.9, 120.9, 113.1, 83.4, 55.7, 51.3, 50.6, 43.7, 30.2, 26.1, 25.8. HRMS (ESI^{+}): calcd for $C_{25}H_{30}BrINO$ $[M+H]^{+}$ 566.0550, found 566.0557.



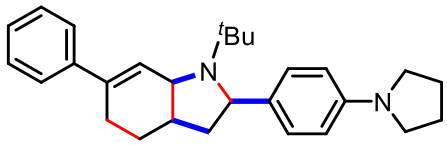
(*Cis*)-*N*-(*tert*-butyl)-4-((*E*)-2-(thiophen-2-yl)vinyl)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (*cis*-5qa)

The title compound was prepared according to the general procedure as a yellow oil (11.5 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25-7.22 (m, 1H), 7.09 (d, *J* = 5.2 Hz, 1H), 6.94-6.92 (m, 1H), 6.89-6.88 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.17 (d, *J* = 4.4 Hz, 1H), 3.38 (s, 1H), 2.53-2.36 (m, 3H), 1.88-1.82 (m, 2H), 1.11 (brs, 1H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.5, 141.8, 136.1, 133.9, 129.7,

128.4, 127.3, 127.1, 125.3, 124.3, 123.3, 123.1, 51.1, 50.3, 43.6, 30.3, 26.3, 25.6. HRMS (ESI$^+$): calcd for $C_{22}H_{28}NS$ $[M+H]^+$ 338.1937, found 338.1945.

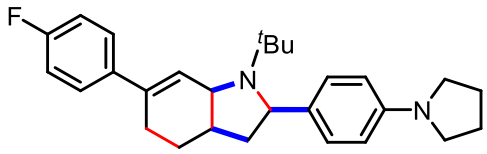
General procedure for cascade *cis*-diastereoselective [4 + 2] annulation and hydroamination of α,β-unsaturated aldimines 4 with amino-substituted 1-aryl-1,3-butadienes 2 *via* γ-allylic C–H activation by Ce-2 in the presence of Bn_2NH

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 0.010 mmol) was added to a toluene-d_8 solution (1.0 mL) of **Ce-2** (5.4 mg, 0.010 mmol) in a J. Young NMR tube. After 5 min, *N*,*N*-dibenzylamine (1.9 mg, 0.010 mmol) was added to this tube. After 5 min, α,β-unsaturated aldimines **4** (0.1 mmol) and amino-substituted 1-aryl-1,3-butadienes **2** (0.4 mmol) were added. The tube was sealed, taken outside of glovebox, and stirred at indicated temperatures for indicated times. Then, the tube was cooled to room temperature and the reaction mixture was monitored by NMR. The crude NMR yields were calculated on the basis of formation of the corresponding product *cis*-**6**. The reaction mixture was filtered through a short silica gel column (EtOAc). The filtrate was evaporated under a reduced pressure. The d.r. ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. The solution was concentrated and purified directly by column chromatography on silica gel (hexane/EtOAc = 5/1, v/v) to give the pure product *cis*-**6**. Identical results were obtained when the reactions were conducted in toluene using a Schlenk tube.



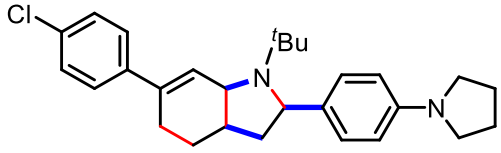
(*Cis*)-1-(*tert*-butyl)-6-phenyl-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6aa)

The title compound was prepared according to the general procedure as a yellow solid (25.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.25-7.21 (m, 3H), 6.46 (d, J = 8.4 Hz, 2H), 6.02 (s, 1H), 4.06 (dd, J = 10.4, 6.8 Hz, 1H), 3.77 (d, J = 8.8 Hz, 1H), 3.23 (t, J = 6.4 Hz, 4H), 2.32-2.25 (m, 3H), 1.98-1.87 (m, 7H), 1.71-1.62 (m, 1H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.4, 142.9, 137.1, 133.0, 131.1, 128.2, 127.2, 126.6, 125.5, 111.3, 62.7, 57.9, 55.1, 47.7, 40.7, 36.2, 27.8, 25.6, 23.7, 22.3. HRMS (ESI$^+$): calcd for $C_{28}H_{37}N_2$ $[M+H]^+$ 401.2952, found 401.2941.



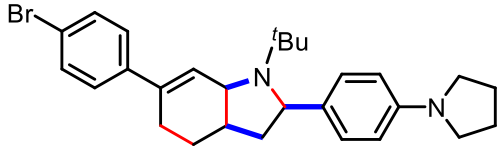
(*Cis*)-1-(*tert*-butyl)-6-(4-fluorophenyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ba)

The title compound was prepared according to the general procedure as a red oil (31.0 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.36 (m, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.44 (d, J = 8.8 Hz, 2H), 5.95 (s, 1H), 4.06 (dd, J = 10.4, 6.8 Hz, 1H), 3.74 (d, J = 7.2 Hz, 1H), 3.23 (t, J = 6.4 Hz, 4H), 2.31-2.23 (m, 3H), 1.98-1.87 (m, 7H), 1.68-1.59 (m, 1H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 163.1 (d, J = 246.4 Hz), 146.4, 138.9 (d, J = 3.0 Hz), 137.1, 132.0, 131.0, 127.2, 127.0 (d, J = 8.1 Hz), 115.1 (d, J = 27.3 Hz), 111.3, 62.6, 57.9, 55.1, 47.7, 40.7, 36.1, 27.8, 25.6, 23.6, 22.5. HRMS (ESI^{+}): calcd for $C_{28}H_{36}FN_2$ $[M+H]^{+}$ 419.2858, found 419.2841.



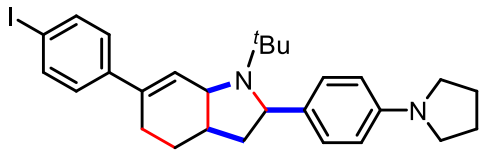
(*Cis*)-1-(*tert*-butyl)-6-(4-chlorophenyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ca)

The title compound was prepared according to the general procedure as a brown oil (27.4 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.44 (d, J = 8.4 Hz, 2H), 5.99 (s, 1H), 4.05 (dd, J = 10.4, 6.8 Hz, 1H), 3.74 (d, J = 7.2 Hz, 1H), 3.22 (t, J = 6.4 Hz, 4H), 2.32-2.18 (m, 3H), 1.99-1.83 (m, 7H), 1.68-1.54 (m, 1H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.4, 141.2, 137.0, 132.3, 131.9, 131.6, 128.3, 127.1, 126.7, 111.3, 62.6, 57.9, 55.1, 47.7, 40.6, 36.1, 27.8, 25.6, 23.5, 22.2. HRMS (ESI^{+}): calcd for $C_{28}H_{36}ClN_2$ $[M+H]^{+}$ 435.2562, found 435.2545.



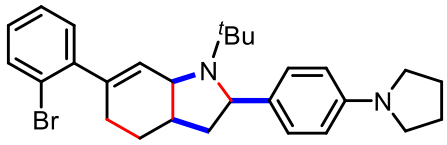
(*Cis*)-6-(4-bromophenyl)-1-(*tert*-butyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6da)

The title compound was prepared according to the general procedure as a brown oil (32.6 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 8.8 Hz, 2H), 6.00 (s, 1H), 4.05 (dd, J = 10.4, 6.4 Hz, 1H), 3.73 (d, J = 8.4 Hz, 1H), 3.22 (t, J = 6.4 Hz, 4H), 2.34-2.16 (m, 3H), 2.00-1.84 (m, 7H), 1.68-1.58 (m, 1H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.5, 146.4, 141.7, 137.0, 131.9, 131.7, 131.3, 127.1, 120.4, 111.3, 62.6, 58.0, 55.1, 47.7, 40.6, 36.0, 27.7, 25.6, 23.5, 22.2. HRMS (ESI$^+$): calcd for $C_{28}H_{36}BrN_2$ $[M+H]^+$ 479.2057, found 479.2038.



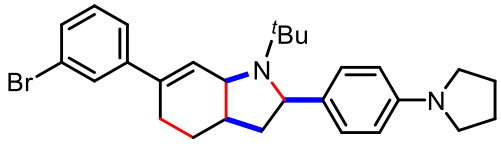
(*Cis*)-1-(*tert*-butyl)-6-(4-iodophenyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ea)

The title compound was prepared according to the general procedure as a brown solid (30.5 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 8.8 Hz, 3H), 6.44 (d, J = 8.4 Hz, 2H), 6.01 (s, 1H), 4.05 (dd, J = 10.4, 6.4 Hz, 1H), 3.73 (d, J = 5.6 Hz, 1H), 3.23 (t, J = 6.4 Hz, 4H), 2.34-2.14 (m, 3H), 2.01-1.81 (m, 7H), 1.68-1.56 (m, 1H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.4, 142.3, 137.3, 137.0, 132.0, 131.7, 127.4, 127.1, 111.3, 91.8, 62.6, 57.9, 55.1, 47.7, 40.6, 36.0, 27.8, 25.6, 23.5, 22.0. HRMS (ESI$^+$): calcd for $C_{28}H_{36}IN_2$ $[M+H]^+$ 527.1918, found 527.1901.



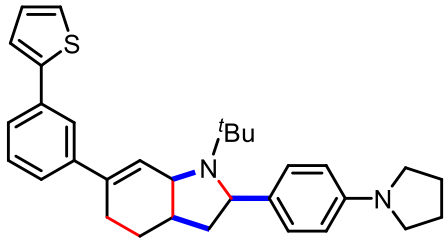
(*Cis*)-6-(2-bromophenyl)-1-(*tert*-butyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6fa)

The title compound was prepared according to the general procedure as a yellow solid (19.2 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.27-7.25 (m, 1H), 7.20-7.18 (m, 1H), 7.11-7.08 (m, 1H), 6.52 (d, J = 8.4 Hz, 2H), 5.57 (s, 1H), 4.07 (dd, J = 10.4, 6.4 Hz, 1H), 3.74 (d, J = 6.8 Hz, 1H), 3.29-3.25 (m, 4H), 2.32-2.12 (m, 3H), 2.01-1.95 (m, 7H), 1.83-1.77 (m, 1H), 0.97 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.4, 145.4, 137.2, 135.8, 133.0, 132.6, 130.4, 128.1, 127.4, 127.3, 122.8, 111.2, 62.7, 57.3, 55.1, 47.8, 40.9, 36.1, 27.7, 25.6, 24.1, 23.6. HRMS (ESI$^+$): calcd for $C_{28}H_{36}BrN_2$ $[M+H]^+$ 479.2057, found 479.2069.



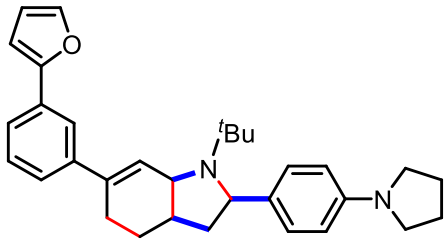
(*Cis*)-6-(3-bromophenyl)-1-(*tert*-butyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a -hexahydro-1*H*-indole (*cis*-6ga)

The title compound was prepared according to the general procedure as a yellow solid (21.6 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.53 (m, 1H), 7.37-7.31 (m, 2H), 7.23-7.15 (m, 3H), 6.45 (d, *J* = 8.8 Hz, 2H), 6.01 (s, 1H), 4.06 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.75 (d, *J* = 5.6 Hz, 1H), 3.23 (t, *J* = 6.8 Hz, 4H), 2.36-2.15 (m, 3H), 2.02-1.82 (m, 7H), 1.67-1.55 (m, 1H), 1.01 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.5, 145.0, 136.9, 132.3, 131.8, 129.8, 129.5, 128.6, 127.1, 124.1, 122.6, 111.3, 62.6, 57.9, 55.1, 47.7, 40.6, 36.1, 27.8, 25.6, 23.5, 22.2. HRMS (ESI^{+}): calcd for $C_{28}H_{36}BrN_2$ $[M+H]^{+}$ 479.2057, found 479.2074.



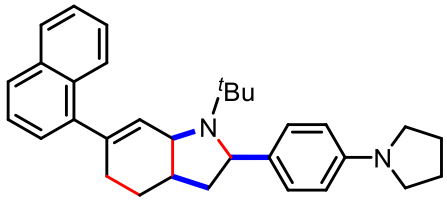
(*Cis*)-*N*-(*tert*-butyl)-3'-methyl-1',2',5',6'-tetrahydro-[1,1':4',1''-terphenyl]-2'-amin e (*cis*-6ha)

The title compound was prepared according to the general procedure as a brown oil (21.6 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.57-7.52 (m, 1H), 7.49-7.46 (m, 1H), 7.37-7.32 (m, 2H), 7.26-7.21 (m, 2H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.50-6.42 (m, 3H), 6.06 (s, 1H), 4.08 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.78 (d, *J* = 6.0 Hz, 1H), 3.22 (t, *J* = 6.4 Hz, 4H), 2.36-2.27 (m, 3H), 2.03-1.82 (m, 7H), 1.74-1.62 (m, 1H), 1.02 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 154.3, 146.4, 143.4, 142.0, 137.1, 132.9, 131.4, 130.8, 128.6, 127.2, 124.7, 122.2, 121.0, 111.7, 111.3, 105.0, 62.6, 58.0, 55.1, 47.7, 40.7, 36.2, 17.8, 25.6, 23.6, 22.5. HRMS (ESI^{+}): calcd for $C_{32}H_{39}N_2S$ $[M+H]^{+}$ 483.2829, found 483.2839.



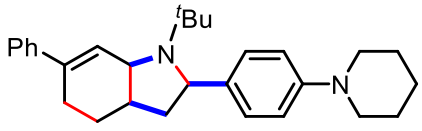
(*Cis*)-1-(*tert*-butyl)-6-(3-(furan-2-yl)phenyl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ia)

The title compound was prepared according to the general procedure as a brown oil (17.7 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.63 (m, 1H), 7.51-7.46 (m, 1H), 7.37-7.32 (m, 3H), 7.28 (dd, *J* = 5,2, 1.2 Hz, 1H), 7.25-7.22 (m, 2H), 7.09 (dd, *J* = 5.2, 4.0 Hz, 1H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 4.08 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.78 (d, *J* = 5.6 Hz, 1H), 3.23 (t, *J* = 6.4 Hz, 4H), 2.38-2.24 (m, 3H), 2.03-1.86 (m, 7H), 1.73-1.62 (m, 1H), 1.02 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.4, 144.9, 143.7, 137.1, 134.3, 132.8, 131.6, 128.8, 128.0, 127.2, 124.9, 124.8, 124.4, 123.4, 123.2, 111.3, 62.6, 58.0, 55.1, 47.7, 40.7, 36.2, 27.8, 25.6, 23.6, 22.5. HRMS (ESI$^+$): calcd for $C_{32}H_{39}N_2O$ $[M+H]^+$ 467.3057, found 467.3077.



(*Cis*)-1-(*tert*-butyl)-6-(naphthalen-1-yl)-2-(4-(pyrrolidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ja)

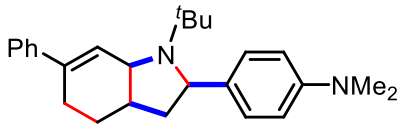
The title compound was prepared according to the general procedure as a yellow solid (16.2 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-8.04 (m, 1H), 7.85-7.83 (m, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.47-7.39 (m, 5H), 7.30-7.28 (m, 1H), 6.54 (d, *J* = 8.8 Hz, 2H), 5.73 (s, 1H), 4.15 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.83 (d, *J* = 7.2 Hz, 1H), 3.32-3.29 (m, 4H), 2.40-2.15 (m, 3H), 2.11-1.86 (m, 8H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.5, 143.0, 137.4, 134.1, 133.7, 133.5, 131.7, 128.3, 127.2, 126.8, 126.3, 125.7, 125.63, 125.60, 125.1, 111.4, 62.7, 57.5, 55.1, 47.8, 41.2, 36.2, 27.7, 26.0, 25.6, 24.0. HRMS (ESI$^+$): calcd for $C_{32}H_{39}N_2$ $[M+H]^+$ 451.3108, found 451.3110.



(*Cis*)-1-(*tert*-butyl)-6-phenyl-2-(4-(piperidin-1-yl)phenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole (*cis*-6ab)

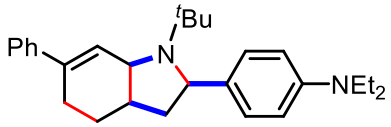
The title compound was prepared according to the general procedure as a yellow solid (24.9 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.27-7.20 (m, 3H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 1H), 4.06 (dd,

J = 10.0, 6.4 Hz, 1H), 3.77 (d, *J* = 7.2 Hz, 1H), 3.11-3.02 (m, 4H), 2.33-2.23 (m, 3H), 2.02-1.83 (m, 3H), 1.73-1.62 (m, 5H), 1.56-1.49 (m, 2H), 0.99 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 150.6, 142.8, 141.2, 133.0, 131.0, 128.3, 127.0, 126.7, 125.5, 116.3, 62.6, 58.0, 55.1, 51.1, 40.6, 36.2, 27.7, 26.2, 24.4, 23.6, 22.3. HRMS (ESI^+): calcd for $C_{29}H_{39}N_2$ $[M+H]^+$ 415.3108, found 415.3091.



(*Cis*)-4-(1-(*tert*-butyl)-6-phenyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-2-yl)-*N*,*N*-dime thylaniline (*cis*-6ac)

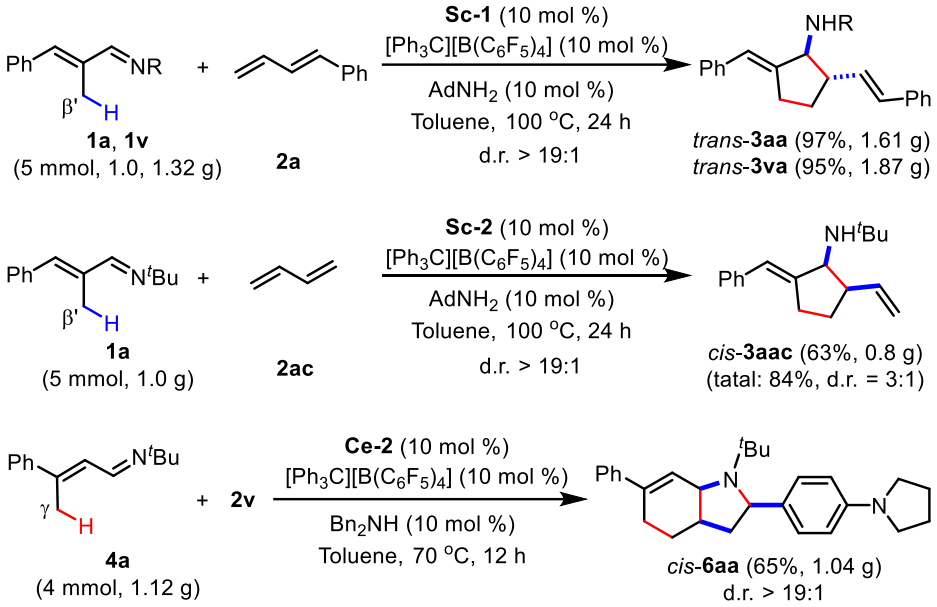
The title compound was prepared according to the general procedure as a yellow solid (23.6 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27-7.21 (m, 3H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 4.07 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.77 (d, *J* = 9.2 Hz, 1H), 2.88 (s, 6H), 2.35-2.24 (m, 3H), 2.03-1.82 (m, 3H), 1.74-1.61 (m, 1H), 1.01 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 149.1, 142.8, 138.6, 133.0, 131.0, 128.3, 127.1, 126.7, 125.5, 112.6, 62.6, 58.0, 55.1, 41.0, 40.7, 36.2, 27.8, 23.7, 22.3. HRMS (ESI^+): calcd for $C_{26}H_{35}N_2$ $[M+H]^+$ 375.2795, found 375.2779.



(*Cis*)-4-(1-(*tert*-butyl)-6-phenyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-2-yl)-*N*,*N*-dieth ylaniline (*cis*-6ad)

The title compound was prepared according to the general procedure as a yellow solid (28.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$)``: δ = 7.45 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 4.05 (dd, *J* = 10.0, 6.4 Hz, 1H), 3.76 (d, *J* = 7.4 Hz, 1H), 3.33-3.23 (m, 4H), 2.35-2.23 (m, 3H), 2.01-1.86 (m, 3H), 1.73-1.63 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 6H), 1.01 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 146.3, 142.8, 137.3, 132.9, 131.1, 128.3, 127.3, 126.6, 125.5, 62.6, 58.0, 55.1, 44.5, 40.7, 36.2, 27.8, 23.7, 22.3, 12.8. HRMS (ESI^+): calcd for $C_{28}H_{38}N_2$ $[M+H]^+$ 403.3108, found 403.3090.

6. Gram-Scale Reactions



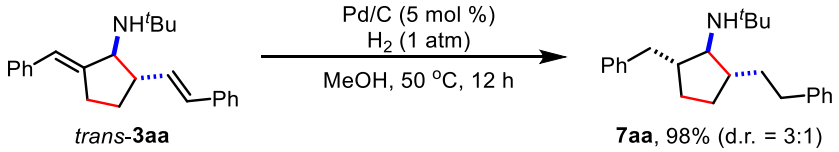
In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (0.50 mmol) was added to a stirred toluene solution (40.0 mL) of **Sc-1** (0.50 mmol) in a Schlenk tube. After 5 min, 1-admantyl amine (0.50 mmol) was added to the Schlenk tube. After 5 min, to this tube was added α,β-unsaturated aldimine **1a** or **1v** (5 mmol) and **2a** (15 mmol). After that, the tube was sealed, taken outside, and stirred at 100 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 3:1) to give the desired product *trans*-**3aa** (97%, 1.61 g) or *trans*-**3av** (95%, 1.87 g).

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (0.50 mmol) was added to a stirred toluene solution (30.0 mL) of **Sc-2** (0.50 mmol) in a Schlenk tube. After 5 min, 1-admantyl amine (0.50 mmol) was added to the Schlenk tube. After 5 min, to this tube was added α,β-unsaturated aldimine **1a** (5 mmol) and **2ac** (50 mmol). After that, the tube was sealed, taken outside, and stirred at 100 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give the desired product *cis*-**3aac** (63%, 0.8 g) and *trans*-**3aac** (20%, 0.25 g).

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (0.4 mmol) was added to a stirred toluene solution (30.0 mL) of **Ce-2** (0.4 mmol) in a Schlenk tube. After 5 min, *N*,*N*-dibenzylamine (0.40 mmol) was added to the Schlenk tube. After 5 min, to this tube was added α,β-unsaturated aldimine **4a** (4 mmol) and **2v** (16 mmol). After that, the tube was sealed, taken outside, and stirred at 70 °C for 12 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 15:1) to give the desired product *cis*-**6aa** (65%, 1.04 g).

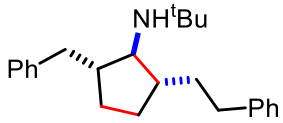
7. Transformations of *trans*-3aa, *trans*-3va and *cis*-3aac

Transformation of *trans*-3aa



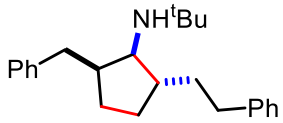
trans-**3aa** **7aa**, 98% (d.r. = 3:1)

Compound *trans*-**3aa** (0.2 mmol) and Pd/C (10 wt%, 0.01 mmol) in methanol (2.0 mL, 0.1 M) were stirred at 50 ºC under hydrogen atmosphere (balloon) for 12 h. The resulting mixture was passed through a plug of silica, and then concentrated in vacuo to give the mixture of diastereomers (98%). The diastereomeric ratio was determined based on crude ^{1}H NMR (d.r. = 3:1), and each diastereoisomer was separated by flash column chromatography. Both isomers were isolated as a colorless oil.



(*Trans,trans*)-2-benzyl-*N*-(*tert*-butyl)-5-phenethylcyclopentan-1-amine (7aa)

The title compound was prepared according to the general procedure as a colorless soild (49.7 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.25 (m, 4H), 7.20-7.16 (m, 6H), 2.88 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.74-2.67 (m, 1H), 2.58-2.55 (m, 2H), 2.46-2.40 (m, 1H), 1.96-1.82 (m, 4H), 1.68-1.55 (m, 3H), 1.43-1.29 (m, 2H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 142.8, 141.7, 129.0, 128.5, 128.43, 128.37, 125.9, 125.8, 65.7, 51.2, 50.8, 49.1, 40.7, 37.1, 35.2, 30.3, 29.4, 29.2. HRMS (ESI$^+$): calcd for $C_{24}H_{34}N$ $[M+H]^+$ 336.2686, found 336.2692.

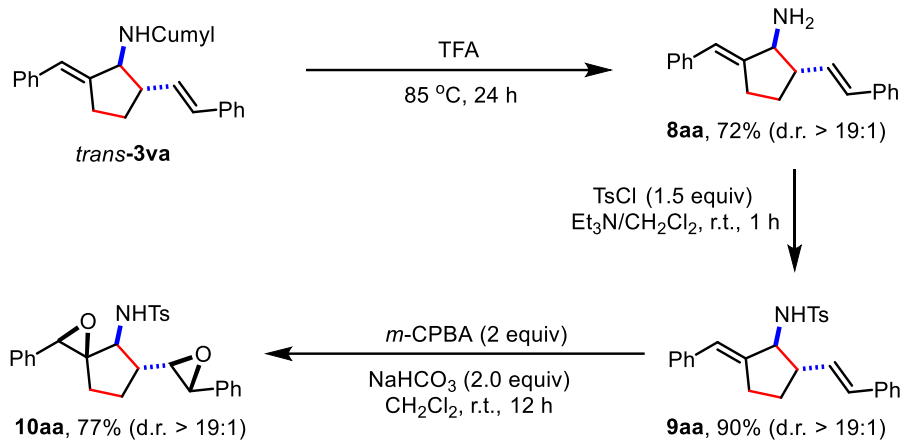


(*Trans,cis*) -2-benzyl-*N*-(*tert*-butyl)-5-phenethylcyclopentan-1-amine (7aa')

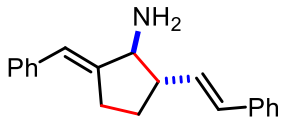
The title compound was prepared according to the general procedure as a colorless soild (16.1 mg, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.26 (m, 4H), 7.20-7.15 (m, 6H), 3.02 (d, *J* = 12.8 Hz 1H), 2.77-2.68 (m, 2H), 2.59-2.51 (m, 1H), 2.21-2.12 (m, 2H), 1.99-1.91 (m, 2H), 1.64-1.51 (m, 2H), 1.45-1.33 (m, 3H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.0, 142.8, 129.2, 128.44, 128.41,

128.3, 125.7, 125.5, 62.4, 50.8, 45.1, 44.3, 36.9, 35.0, 30.3, 29.8, 27.3, 27.1. HRMS (ESI$^+$): calcd for $C_{24}H_{34}N$ $[M+H]^+$ 336.2686, found 336.2693.

Transformations of *trans*-3va



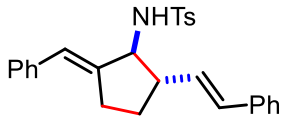
The *trans*-**3va** (0.5 mmol) was placed in a Schlenk tube, and TFA was subsequently added to the tube. The mixture was stirred at 85 ºC for 24 h. After cooling to room temperature, the reaction was diluted with 10% NaOH aq. and extracted with DCM (5 mL x 3). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by PLC (DCM/MeOH = 15:1) to afford the desired product **8aa** (72% yield).



(*Trans*)-2-((*E*)-benzylidene)-5-((*E*)-styryl)cyclopentan-1-amine (8aa)

The title compound was prepared according to the general procedure as a yellow soild (99.1 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.29 (m, 8H), 7.24-7.18 (m, 2H), 6.54-6.50 (m, 2H), 6.19 (dd, J = 15.6, 8.4 Hz, 1H), 3.46 (d, J = 10.0 Hz, 1H), 2.85-2.67 (m, 2H), 2.23-2.04 (m, 2H), 1.71-1.60 (m, 1H), 1.54 (brs, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.6, 138.1, 137.3, 132.3, 131.4, 128.7, 128.4, 127.4, 126.3, 126.2, 121.5, 63.3, 53.9, 29.6, 29.2. HRMS (ESI$^+$): calcd for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1757.

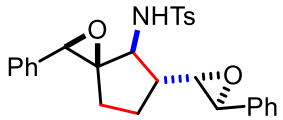
Compound **8aa** (0.3 mmol) and TsCl (0.3 mmol) were dissolved in DCM (2 mL, 0.1 M). To this solution was added Et_3N (0.8 mmol), and the resulting solution was stirred at room temperature for 1 h. Then the reaction was diluted with ethyl acetate (5.0 mL). The organic phase was concentrated in vacuo. The crude residue was purified by flash column chromatography (PE/EA = 2:1) to afford **9aa** (90% yield).



(*Trans*)-*N*-(2-((*E*)-benzylidene)-5-((*E*)-styryl)cyclopentyl)-4-methylbenzenesulfonamide (9aa)

The title compound was prepared according to the general procedure as a yellow soild (116.0 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 8.4 Hz, 2H), 7.34-7.27 (m, 6H), 7.12-7.10 (m, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 5.70 (dd, J = 16.0, 8.4 Hz, 1H), 4.61 (d, J = 8.8 Hz, 1H), 4.04 (t, J = 9.6 Hz, 1H), 2.79-2.60 (m, 2H), 2.41-2.32 (m, 1H), 2.20 (s, 3H), 2.04-1.96 (m, 1H), 1.66-1.58 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.4, 142.9, 137.3, 137.0, 132.5, 131.7, 129.9, 129.6, 128.54, 128.45, 128.4, 127.4, 127.2, 126.8, 126.3, 124.3, 64.4, 50.5, 29.8, 28.7, 21.5. HRMS (ESI^+): calcd for $C_{27}H_{28}NO_2S$ $[M+H]^+$ 430.1836, found 430.1830.

Compound **9aa** (0.2 mmol) was dissolved in CH_2Cl_2 (3 mL), and $NaHCO_3$ (0.4 mmol) was added to the resulting solution. The reaction mixture was stirred at room temperature for 5 min and then *m*-CPBA (75 wt %, 0.4 mmol) was added. The resultant solution was stirred at room temperature for 12 h and then solid Na_2SO_3 was added until starch-iodide paper indicated that no *m*-CPBA was present. The resultant mixture was diluted with 2.0 M aq. NaOH (3 mL) and extracted with $CHCl_3$ (2× 10 mL). The combined organics were dried and concentrated in vacuo. The crude residue was purified by flash column chromatography (DCM/MeOH = 50:1-20:1) to afford the compound **10aa** (77% yield).

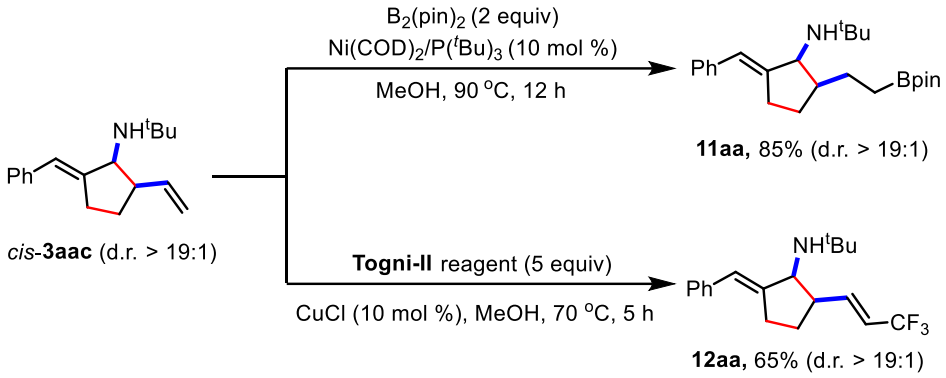


(*Trans*)-4-methyl-*N*-(2-phenyl-5-(-3-phenyloxiran-2-yl)-1-oxaspiro[2.4]heptan-4-yl)benzenesulfonamide (10aa)

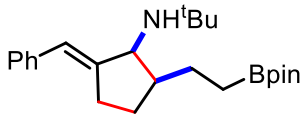
The title compound was prepared according to the general procedure as a yellow soild (71.1 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.0 Hz, 2H), 7.33-7.27 (m, 8H), 7.21-7.19 (m, 2H), 6.97 (dd, J = 8.0, 1.6 Hz, 2H), 4.94 (d, J = 8.0 Hz, 1H), 3.75 (dd, J = 10.8, 8.0 Hz, 1H), 3.70 (m, 1H), 3.12 (s, 1H), 2.98-2.97 (m, 1H), 2.45 (s, 3H), 2.21-2.14 (m, 1H), 1.87-1.79 (m, 1H), 1.75-1.69 (m, 2H), 1.41-1.35 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.9, 137.8, 137.2, 130.0, 128.41, 128.36, 128.2, 128.1, 127.3, 126.1, 125.9, 134.9, 69.1, 62.1, 59.3, 57.6, 57.0, 47.4,

25.3, 21.7, 21.0. HRMS (ESI$^+$): calcd for $C_{27}H_{28}NO_4S$ $[M+H]^+$ 462.1734, found 462.1738.

Transformations of *cis*-3aac



Compound *cis*-**3aac** (0.2 mmol) and B_2Pin_2 (47.0 mg, 0.4 mmol, 2.0 eq.) were added to the MeOH solution of $Ni(COD)_2$ (10 mol%) and $P(^tBu)_3$ (10 mol%). The resulting solution was stirred at 90 °C for 12 h. The reaction mixture was concentrated in vacuo. The crude residue was purified by flash column chromatography (PE/EA = 2:1) to afford the compound **11aa** (85% yield).

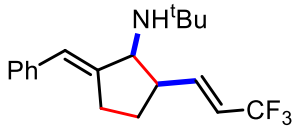


(*Cis*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclopentan-1-amine (11aa)

The title compound was prepared according to the general procedure as a yellow soild (65.2 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.27 (m, 4H), 7.14 (t, J = 7.2 Hz, 1H), 6.44 (d, J = 2.4 Hz, 1H), 3.64 (d, J = 5.6 Hz, 1H), 2.56-2.54 (m, 2H), 1.87-1.74 (m, 2H), 1.68-1.63 (m, 1H), 1.57-1.48 (m, 1H), 1.22 (s, 12H), 1.15 (s, 9H), 0.90-0.79 (m, 2H), 0.71-0.63 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 149.0, 138.7, 128.3, 128.2, 125.7, 120.8, 83.0, 62.0, 50.6, 45.0, 30.5, 26.9, 25.6, 25.0, 24.9, 20.3; ^{11}B NMR (193 MHz, $CDCl_3$): δ = 30.1. HRMS (ESI$^+$): calcd for $C_{24}H_{39}BNO_2$ $[M+H]^+$ 384.3069, found 384.3071.

Compound *cis*-**3aac** (0.2 mmol), Togni-II reagent (1.0 mmol) and CuCl (10 mol%) were placed in a Schlenk tube, and MeOH (1 mL) was subsequently added to the tube. The resulting solution was stirred at 70 °C for 5 h. Then the reaction mixture was

concentrated in vacuo. The crude residue was purified by flash column chromatography (PE/EA = 20:1) to afford the compound **12aa** (65% yield).

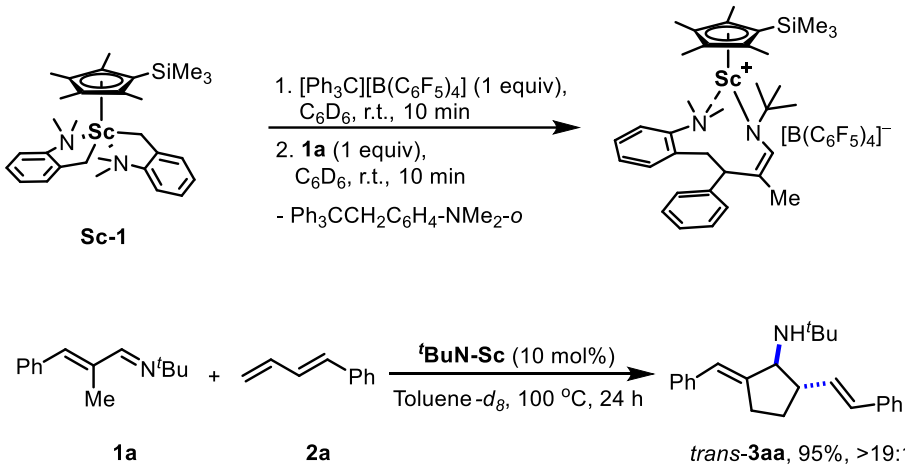


(*Trans*)-2-((*E*)-benzylidene)-*N*-(*tert*-butyl)-5-((*E*)-3,3,3-trifluoroprop-1-en-1-yl)cyclopentan-1-amine (12aa)

The title compound was prepared according to the general procedure as a yellow soild (67.9 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.31 (m, 4H), 7.19 (t, J = 6.6 Hz, 1H), 6.52 (t, J = 2.4 Hz, 1H), 6.24 (dd, J = 15.6, 9.6 Hz, 1H), 5.66-5.62 (m, 1H), 3.76 (d, J = 6.6 Hz, 1H), 2.75-2.66 (m, 3H), 1.98-1.91 (m, 1H), 1.84-1.80 (m, 1H), 1.13 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.6, 140.9(q, J = 4.0 Hz), 138.1, 128.5, 128.4, 126.3, 122.8, 119.9, 119.7, 61.9, 50.8, 46.5, 30.5, 27.9, 27.2. ^{19}F NMR (565 MHz, $CDCl_3$): δ = 63.56; HRMS (ESI^{+}): calcd for $C_{29}H_{39}N_2$ $[M+H]^{+}$ 324.1934, found 324.1935.

8. Mechanistic Investigation

8.1 Mechanistic investigation for the *trans*-diastereoselective [3 + 2] annulation of 1a with 2a



In a 2-mL flask, **Sc-1** (101 mg, 0.2 mmol) was mixed with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (184.0 mg, 0.2 mmol) in C_6D_6 (3 mL), and the mixture was stirred at room temperature for 10 min. 1.0 equiv of **1a** (40.0 mg, 0.21 mmol) was then added to the mixture. In 10 minutes, a red oily product deposited to the bottom of the flask. The upper clear solution was measured by ^{1}H NMR, which showed the disappearance

of the starting chemicals and formation of $Ph_3CCH_2C_6H_4NMe_2$-*o*.[8] The oily red product was washed with a small amount of C_6D_6 and hexane, yielding orange powder after drying in vacuum. The orange powder was determined to be the cationic amido-Sc complex **ᵗBuN-Sc** (85% yield) by NMR spectroscopy. The complex **ᵗBuN-Sc:** ^{1}H NMR (500 MHz, C_6D_5Cl, 25 °C): δ = 7.20-7.14 (m, 2H), 7.12-7.07 (m, 4H), 7.00-6.94 (m, 3H), 6.59 (s, 1H), 4.29 (d, J = 13.5 Hz, 1H), 3.69-3.62 (m, 1H), 2.98 (s, 3H), 2.65 (s, 3H), 1.93 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_5Cl, 25 °C): δ = 150.9, 149.9 (m), 148.0 (m), 140.8, 139.7 (m), 137.8 (m), 136.1, 136.0, 135.9 (m), 134.9, 133.2, 132.6, 132.1, 131.0, 126.6, 120.8, 108.8, 58.5, 47.0, 42.0, 30.2, 25.4, 15.7, 15.5, 15.1, 12.8, 12.4, 1.3; ^{19}F NMR (377.5 MHz, C_6D_5Cl): δ = -132.30 (8F), -162.94 (4F), -166.77 (8F); ^{11}B NMR (128 MHz, C_6D_5Cl): δ = -17.68. The cationic enamido scandium complex **ᵗBuN-Sc** showed catalytic activity towards the annulation of **1a** with **2a**.

8.2 Proposed reaction mechanism for *cis*-diastereoselective [3 + 2] annulation of 1a with 2ac by Sc-2

In the reaction of **2ac** by **Sc-2**, the β'-allylic C(sp^3)−H activation (deprotonation) of the coordinated **1a** by the Sc−N bond in **M** would form a π-allyl scandium species **N** bearing an $AdNH_2$ ligand. The 1,2-insertion of **2ac** into the less sterically hindered Sc−alkyl bond in **N** could afford a major σ-allyl species **O** and a minor σ-allyl species **O′** via a major transition state **TSIII** and a minor transition state **TSIII′**. An interaction between the Sc atom and the two C=C units of **2ac** could be possible in the major transition state **TSIII** because of much smaller steric hindrance of **2ac** than that of **2a**. This interaction would promote the *cis*-selective annulation reaction. The intramolecular addition (cyclization) of the Sc−allyl bond to the C=N unit in **O** and **O′** would give **P** and **P′**. The subsequent intramolecular amido exchange reaction between the Sc−N bond and an N−H bond of $AdNH_2$ in **P** and **P′**, followed by the coordination of **1a** to the Sc atom would regenerate **M** with the release of the final annulation products *cis*-**3aac** as a major product and *trans*-**3aac** as a minor product.

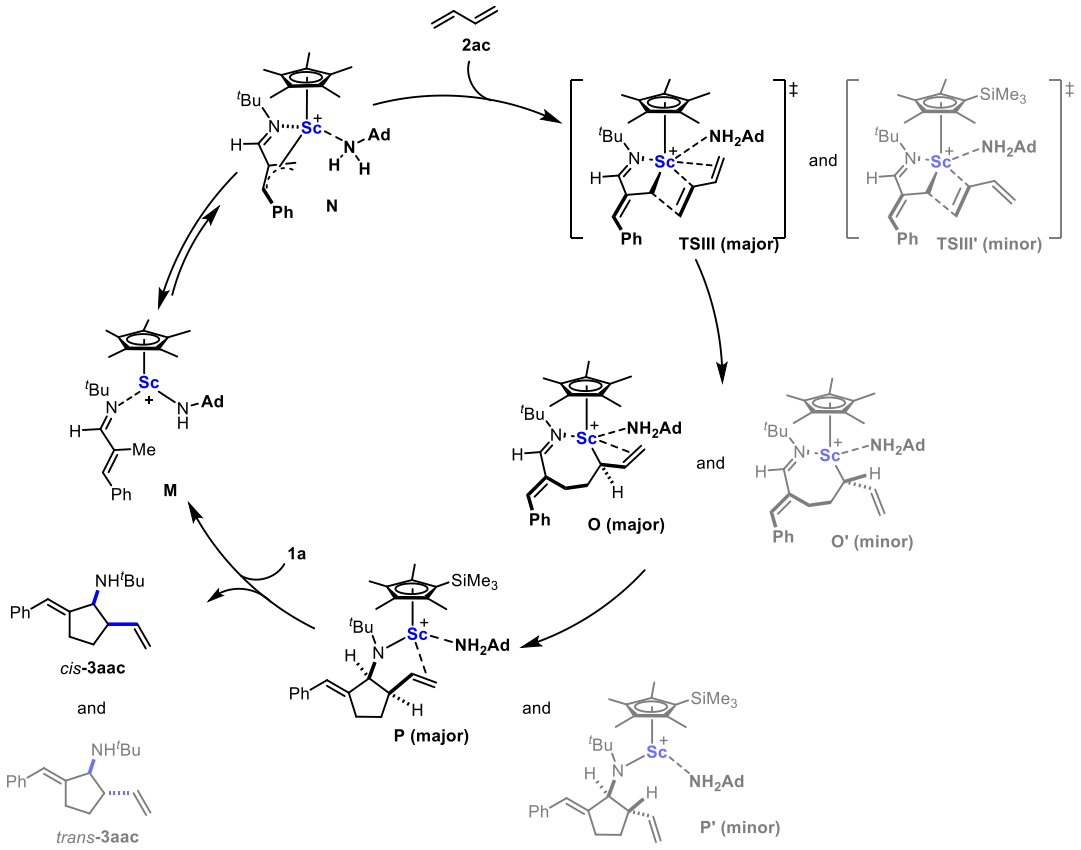


Fig. S1 Proposed reaction mechanism for *cis*-diastereoselective [3+2] annulation of **1a** with **2ac** by **Sc-2**.

9. X-ray Crystallographic Studies

Suitable crystals for an X-ray diffraction study were obtained as described below. These were manipulated under a microscope in a glovebox filled with nitrogen. Data collections were performed at –100 ˚C on a Bruker D8 QUEST diffractometer equipped with a CMOS area detector, using a IμS (Incoatec Microfocus Source) microfocus sealed tube with Mo Kα radiation (λ = 0.71073 Å) at 173 K. The Bravais lattice and the unit cell parameters were determined by the Bruker APEX3 software package.[9] The raw frame data were processed, and absorption corrections were done using SAINT and SADABS embedded in Bruker APEX3 to yield the reflection data (hkl) file. All of the structures were solved using SIR-2014[10] and SHELXL-2017.[11] Structural refinement was performed using the WINGX-Version 2014.1 system,[12] on F^2 anisotropically for all of the non-hydrogen atoms by the fullmatrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. CCDC numbers 2492573 (for *trans*-**3aa**), 2492574 (for *trans*-**3ha**), 2492575 (for *cis*-**3dac**), 2492576 (for

cis-**6ac**) and 2492577 (for *cis*-**6ad**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

X-ray structure of *trans*-3aa (CCDC: 2492573)

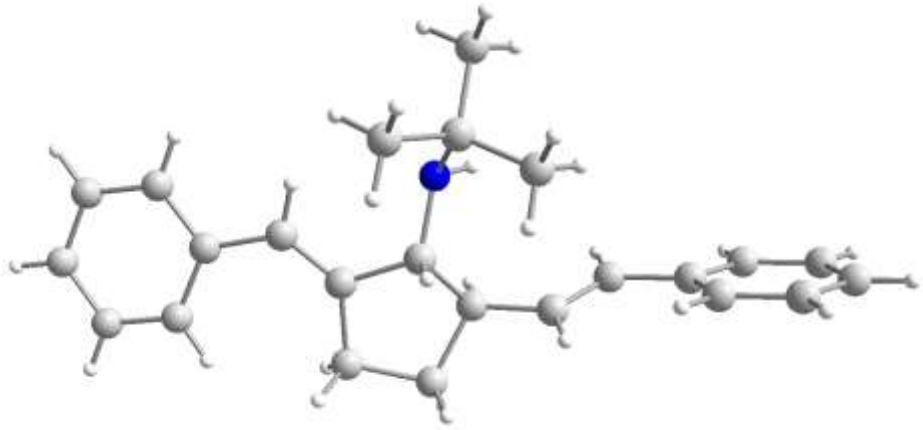


Fig. S2 X-ray structure of *trans*-**3aa**

Table 1 Crystal data and structure refinement for *trans*-3aa.

Identification code	exp_271_auto
Empirical formula	$C_{24}H_{29}N$
Formula weight	331.48
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0735(2)
b/Å	8.6334(2)
c/Å	22.3530(6)
α/°	90
β/°	95.243(2)
γ/°	90
Volume/Å^3	1935.87(8)
Z	4
ρ_{calc}g/cm^3	1.137
μ/mm^{-1}	0.065
F(000)	720.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	3.66 to 64.736
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 12, -33 ≤ l ≤ 27

Reflections collected	25838
Independent reflections	6199 [R_{int} = 0.0299, R_{sigma} = 0.0266]
Data/restraints/parameters	6199/0/233
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1196
Final R indexes [all data]	R_1 = 0.0561, wR_2 = 0.1299
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.30

X-ray structure of *trans*-3ha (CCDC: 2492574)

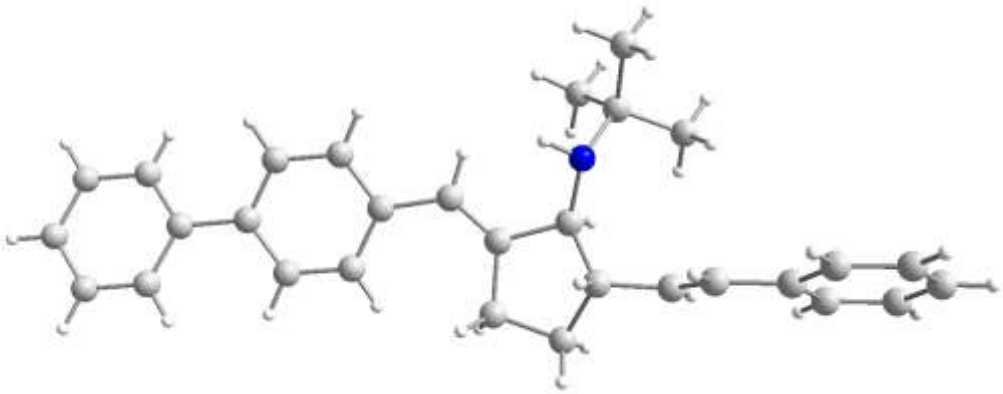


Fig. S3 X-ray structure of *trans*-**3ha**

Table 2 Crystal data and structure refinement for *trans*-3ha.

Identification code	exp_274_auto
Empirical formula	$C_{30}H_{33}N$
Formula weight	407.57
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.0380(3)
b/Å	7.9426(2)
c/Å	20.6714(4)
α/°	90
β/°	109.062(2)
γ/°	90
Volume/$Å^3$	2333.62(9)
Z	4
$\rho_{calc}g/cm^3$	1.160

μ/mm^{-1}	0.066
F(000)	880.0
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	5.536 to 64.738
Index ranges	-21 ≤ h ≤ 22, -11 ≤ k ≤ 10, -31 ≤ l ≤ 30
Reflections collected	43354
Independent reflections	7571 [R_{int} = 0.0322, R_{sigma} = 0.0227]
Data/restraints/parameters	7571/0/287
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0461, wR_2 = 0.1283
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.1360
Largest diff. peak/hole / e Å^{-3}	0.38/-0.21

X-ray structure of *cis*-3dac (CCDC: 2492575)

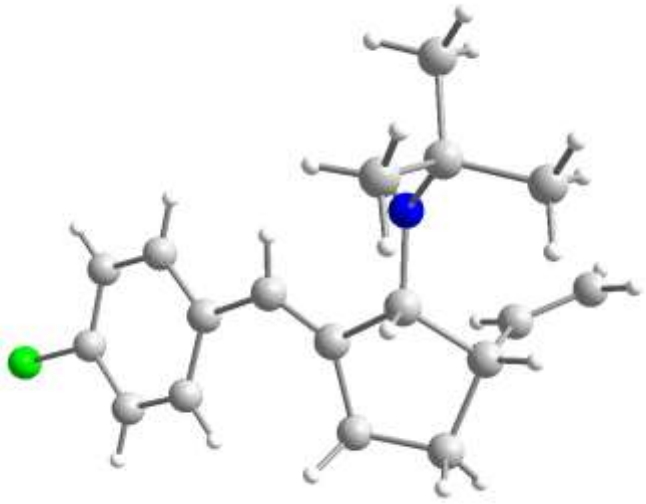


Fig. S4 X-ray structure of *cis*-**3dac**

Table 3 Crystal data and structure refinement for *cis*-3dac.

Identification code	exp_273_auto
Empirical formula	$C_{18}H_{24}ClN$
Formula weight	289.83
Temperature/K	99.95(18)
Crystal system	monoclinic
Space group	$P2_1/c$

a/Å	5.44060(10)
b/Å	22.7821(4)
c/Å	13.0809(3)
α/°	90
β/°	99.810(2)
γ/°	90
Volume/$Å^3$	1597.65(6)
Z	4
$\rho_{calc}g/cm^3$	1.205
μ/mm^{-1}	0.230
F(000)	624.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	4.772 to 64.374
Index ranges	-5 ≤ h ≤ 7, -33 ≤ k ≤ 32, -19 ≤ l ≤ 18
Reflections collected	23632
Independent reflections	5153 [R_{int} = 0.0339, R_{sigma} = 0.0289]
Data/restraints/parameters	5153/0/184
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0507, wR_2 = 0.1162
Largest diff. peak/hole / e $Å^{-3}$	0.84/-0.81

X-ray structure of *cis*-6ac (CCDC: 2492576)

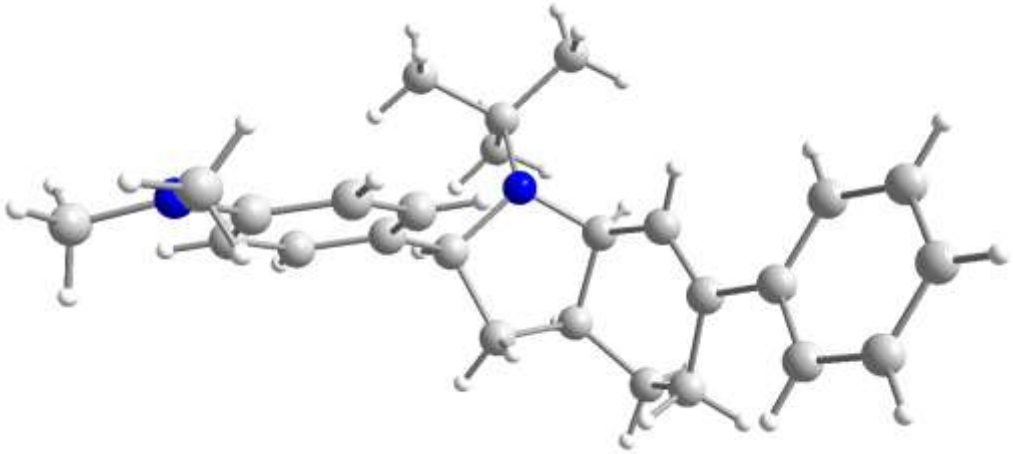


Fig. S5 X-ray structure of *cis*-**6ac**

Table 4 Crystal data and structure refinement for *cis*-6ac.

Identification code	exp_272_auto
Empirical formula	C26H34N2
Formula weight	374.55
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.3215(3)
b/Å	11.3772(4)
c/Å	11.9103(5)
α/°	66.962(3)
β/°	71.581(3)
γ/°	77.689(3)
Volume/Å3	1097.01(8)
Z	2
ρcalcg/cm3	1.134
μ/mm-1	0.066
F(000)	408.0
Crystal size/mm3	0.3 × 0.25 × 0.25
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	4.424 to 64.472
Index ranges	-10 ≤ h ≤ 13, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	27704
Independent reflections	6963 [Rint = 0.0333, Rsigma = 0.0305]
Data/restraints/parameters	6963/0/258
Goodness-of-fit on F2	1.074
Final R indexes [I>=2σ (I)]	R1 = 0.0483, wR2 = 0.1286
Final R indexes [all data]	R1 = 0.0601, wR2 = 0.1373
Largest diff. peak/hole / e Å-3	0.61/-0.35

X-ray structure of *cis*-6ad (CCDC: 2492577)

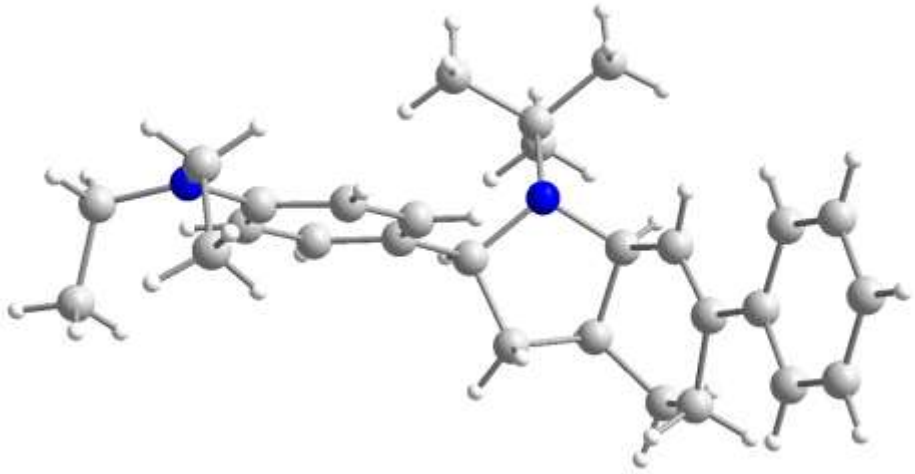


Fig. S6 X-ray structure of *cis*-**6ad**

Table 5 Crystal data and structure refinement for *cis*-6ad.

Identification code	exp_275_auto
Empirical formula	C28H38N2
Formula weight	402.60
Temperature/K	100.03(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.1167(2)
b/Å	12.0749(3)
c/Å	13.3460(3)
α/°	65.930(2)
β/°	82.836(2)
γ/°	81.205(2)
Volume/Å3	1177.42(5)
Z	2
ρcalcg/cm3	1.136
μ/mm-1	0.065
F(000)	440.0
Crystal size/mm3	0.3 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/	5.09 to 64.656
Index ranges	-9 ≤ h ≤ 12, -17 ≤ k ≤ 18, -18 ≤ l ≤ 19
Reflections collected	30627
Independent reflections	7499 [Rint = 0.0327, Rsigma =

	0.0292]
Data/restraints/parameters	7499/0/276
Goodness-of-fit on F2	1.074
Final R indexes [I>=2σ (I)]	R1 = 0.0483, wR2 = 0.1286
Final R indexes [all data]	R1 = 0.0601, wR2 = 0.1373
Largest diff. peak/hole / e Å-3	0.61/-0.35

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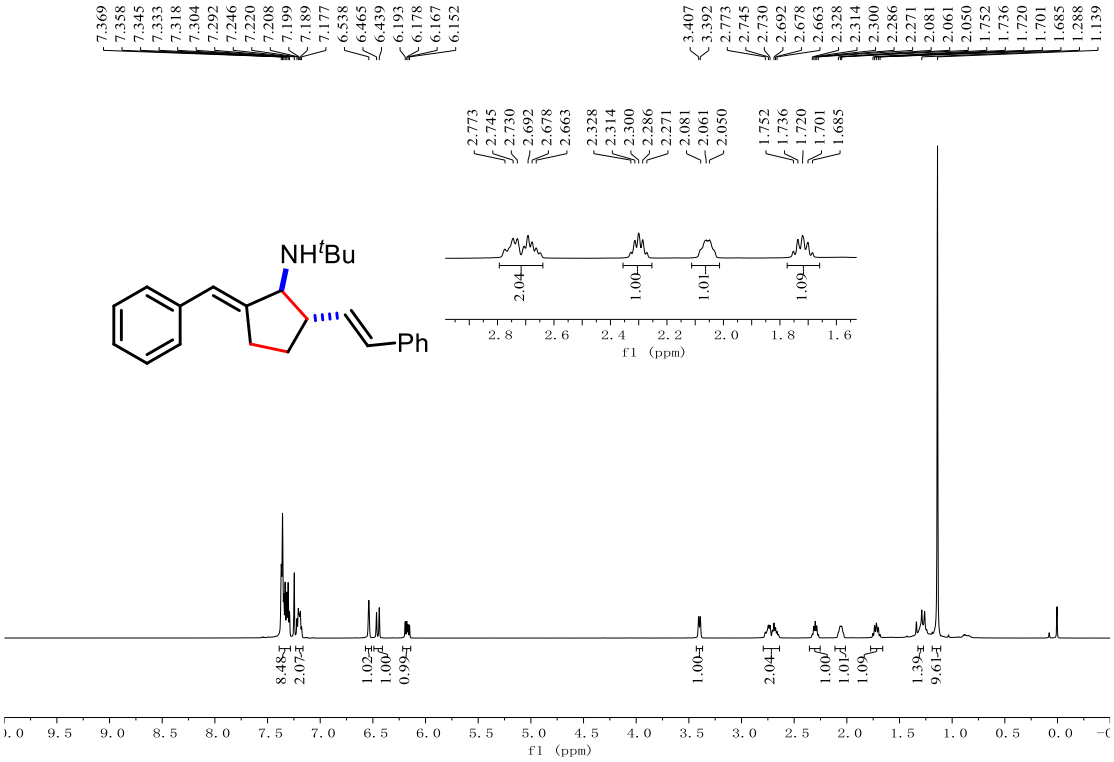
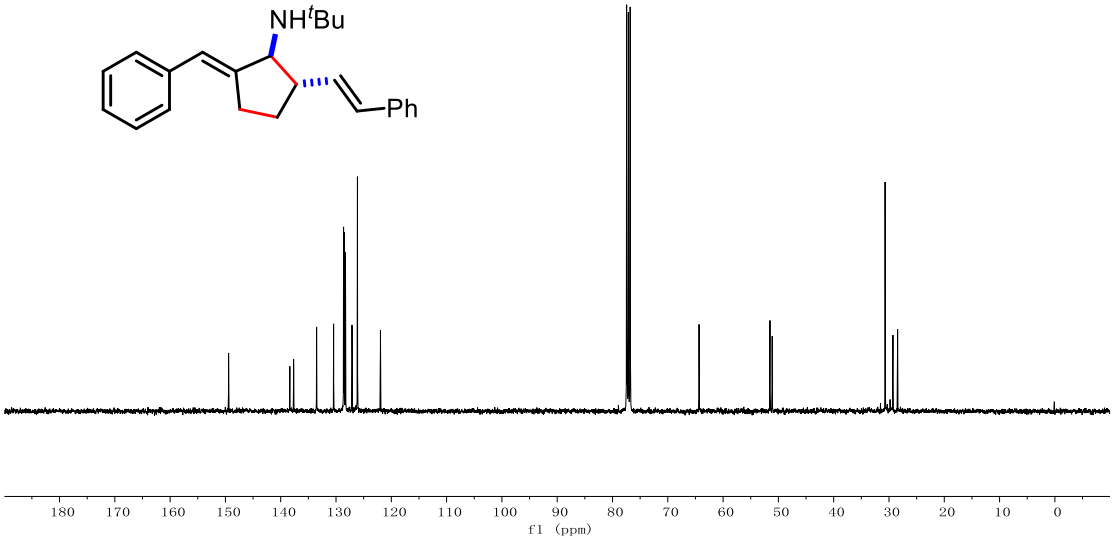
10. Copies of ^{1}H, and ^{13}C NMR Spectra

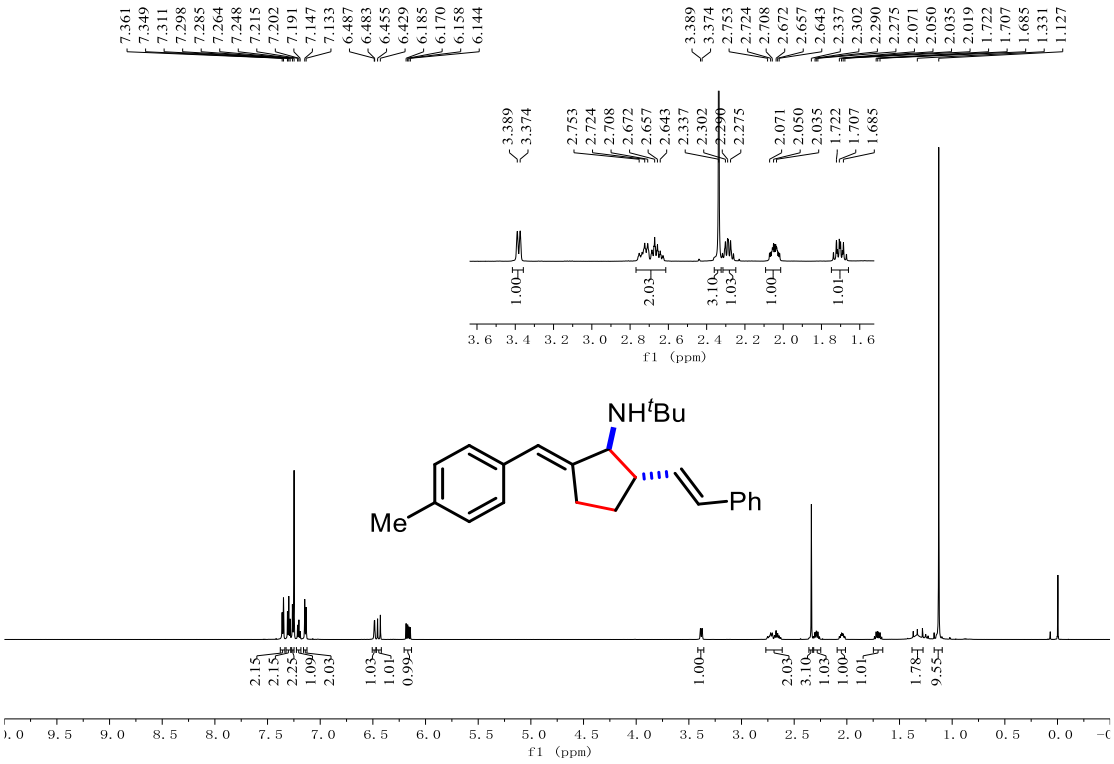
^{1}H NMR spectrum of *trans*-3aa (600 MHz, $CDCl_3$)



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



^{1}H NMR spectrum of *trans*-3ba (600 MHz, $CDCl_3$)



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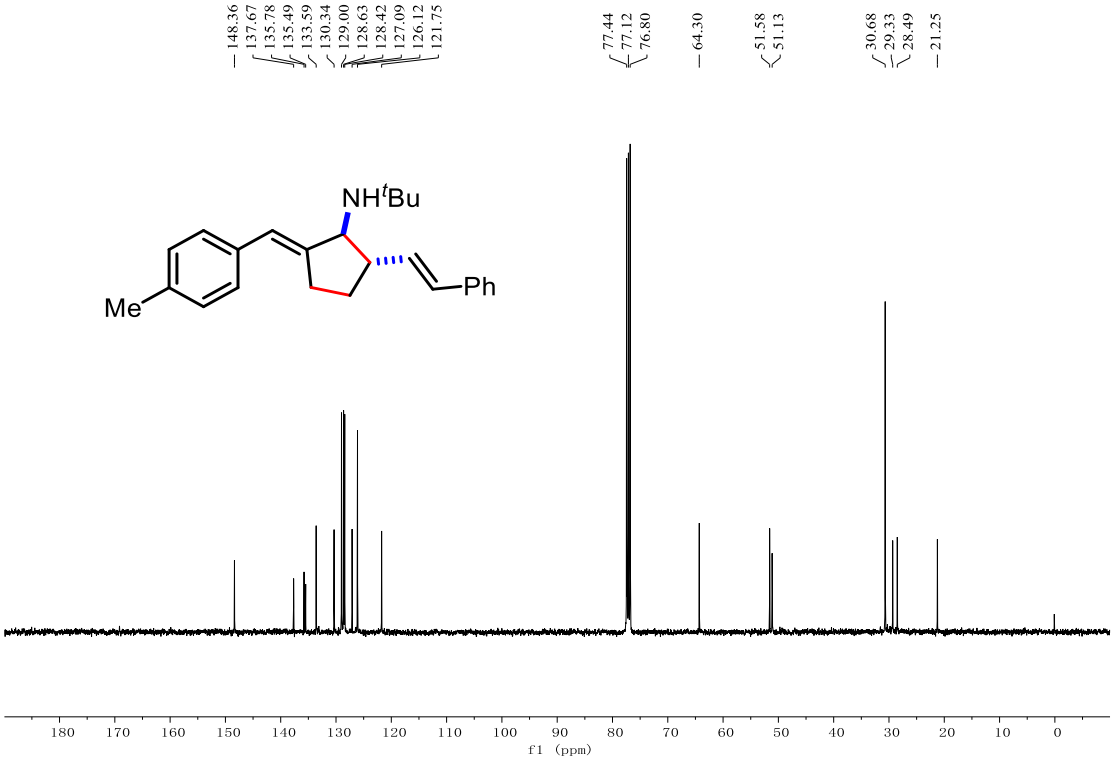
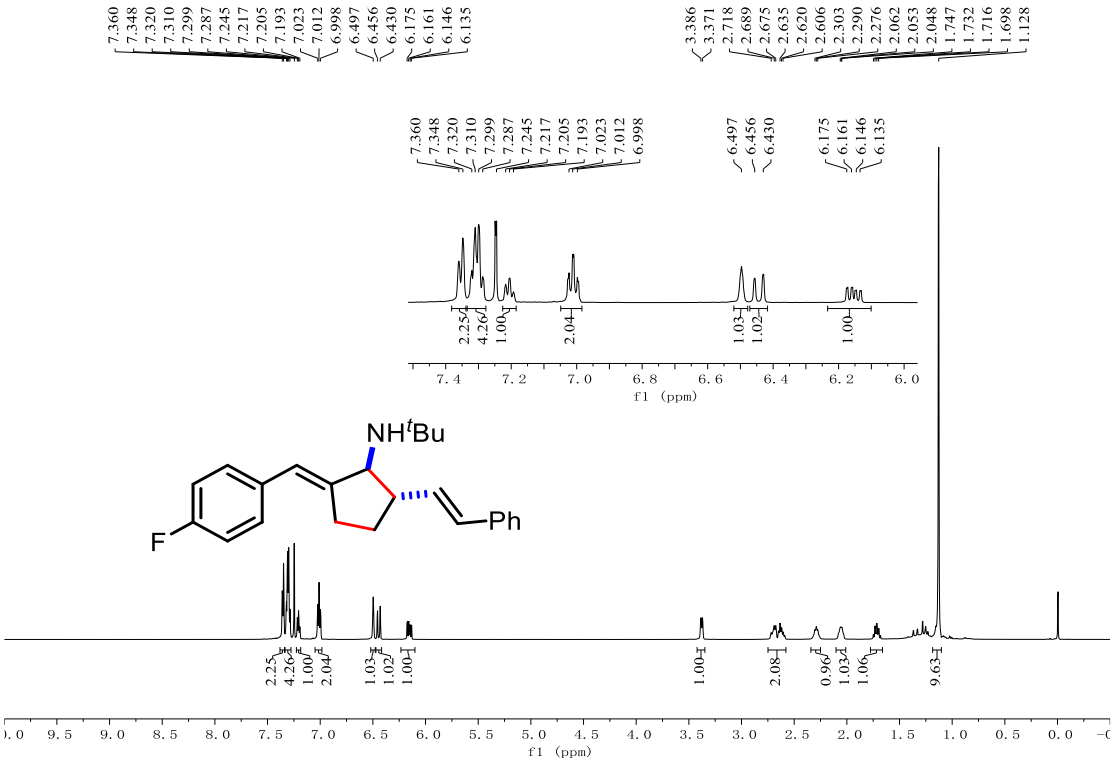


^{1}H NMR spectrum of *trans*-3ca (600 MHz, $CDCl_3$)



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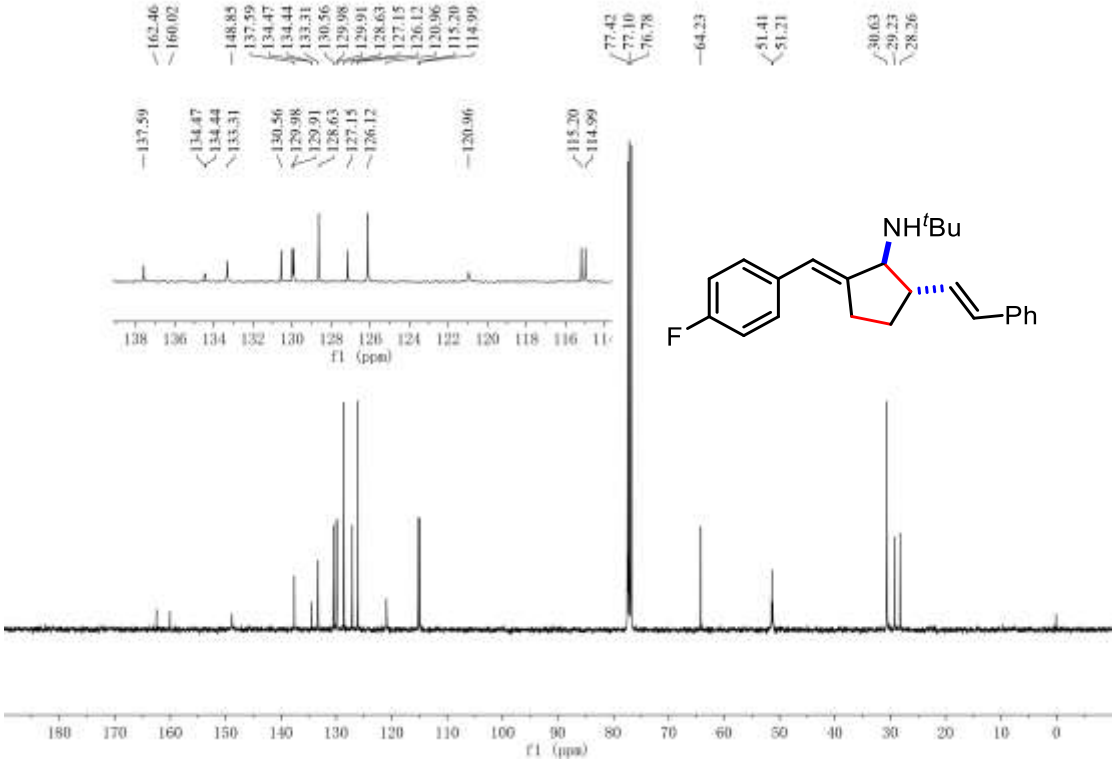

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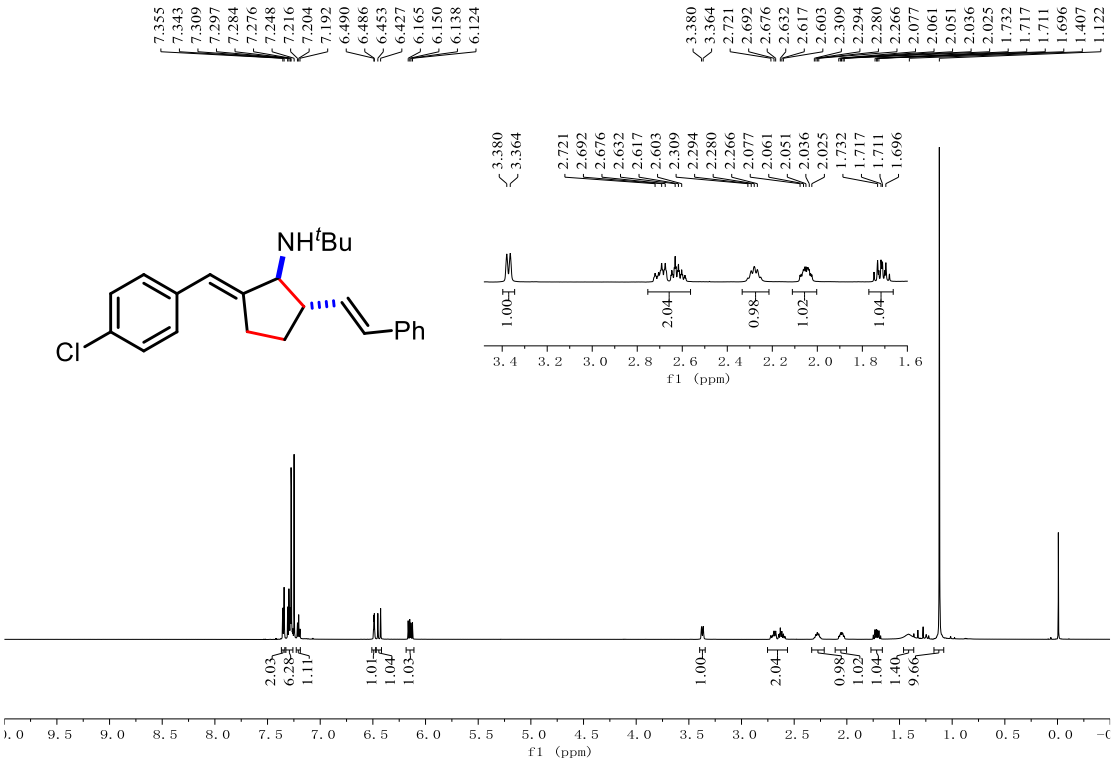

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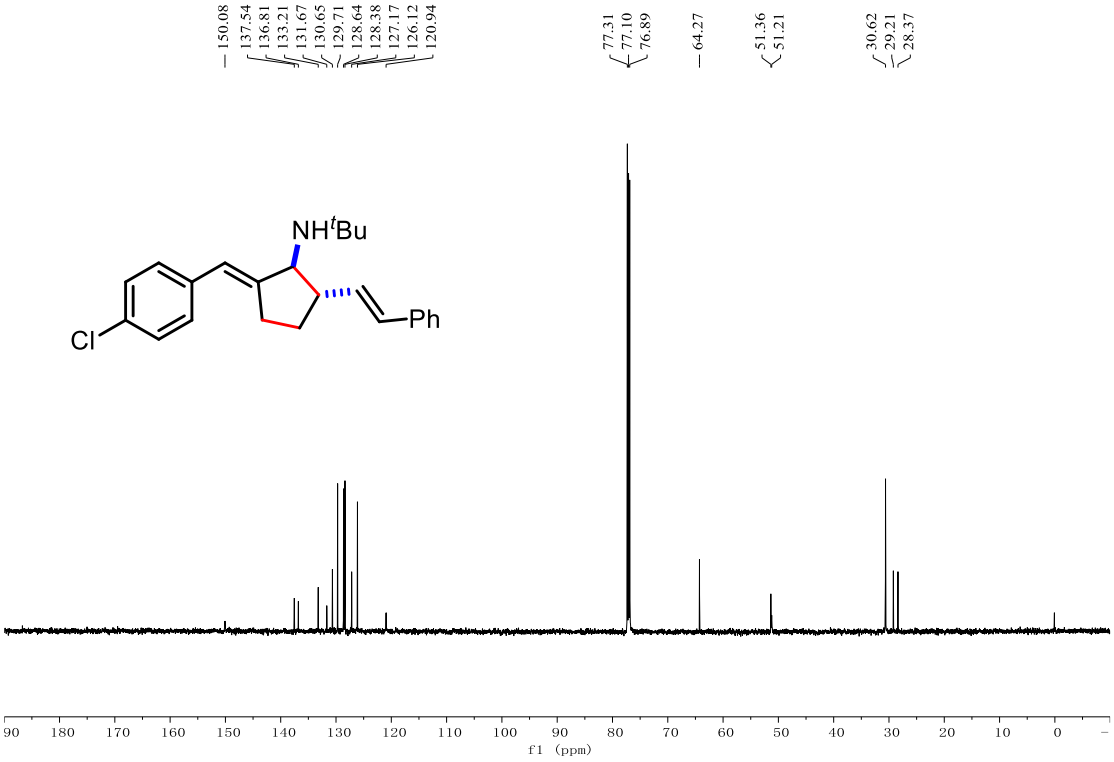

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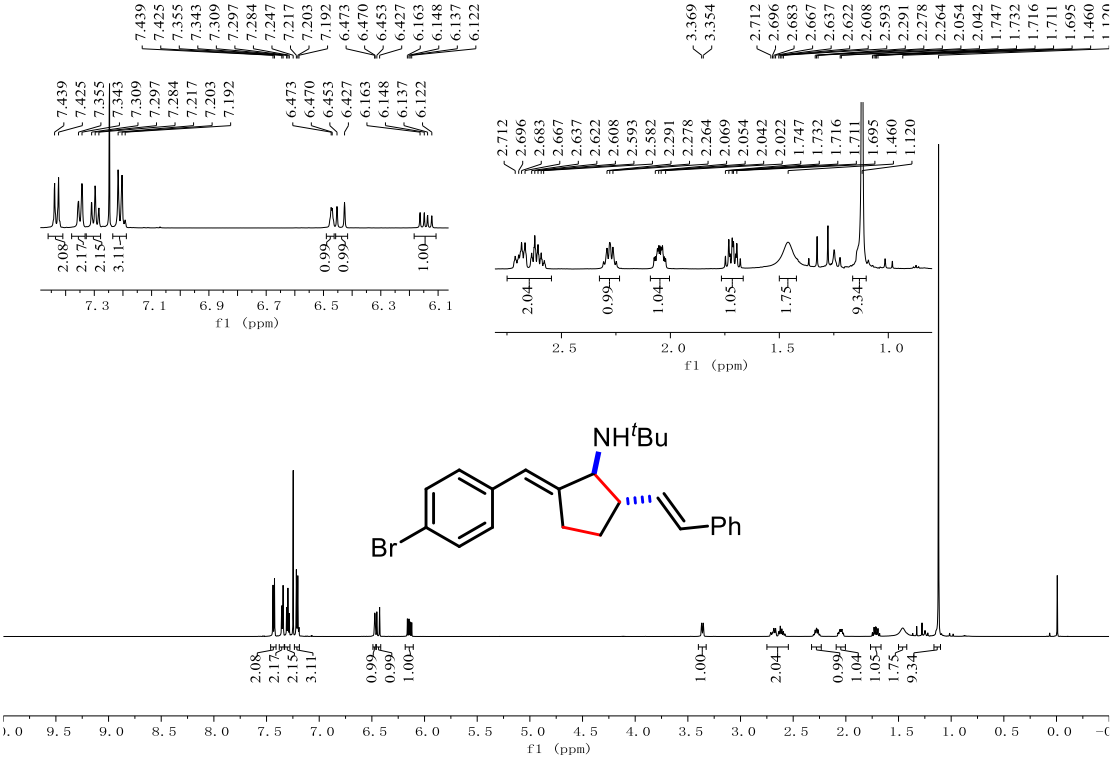

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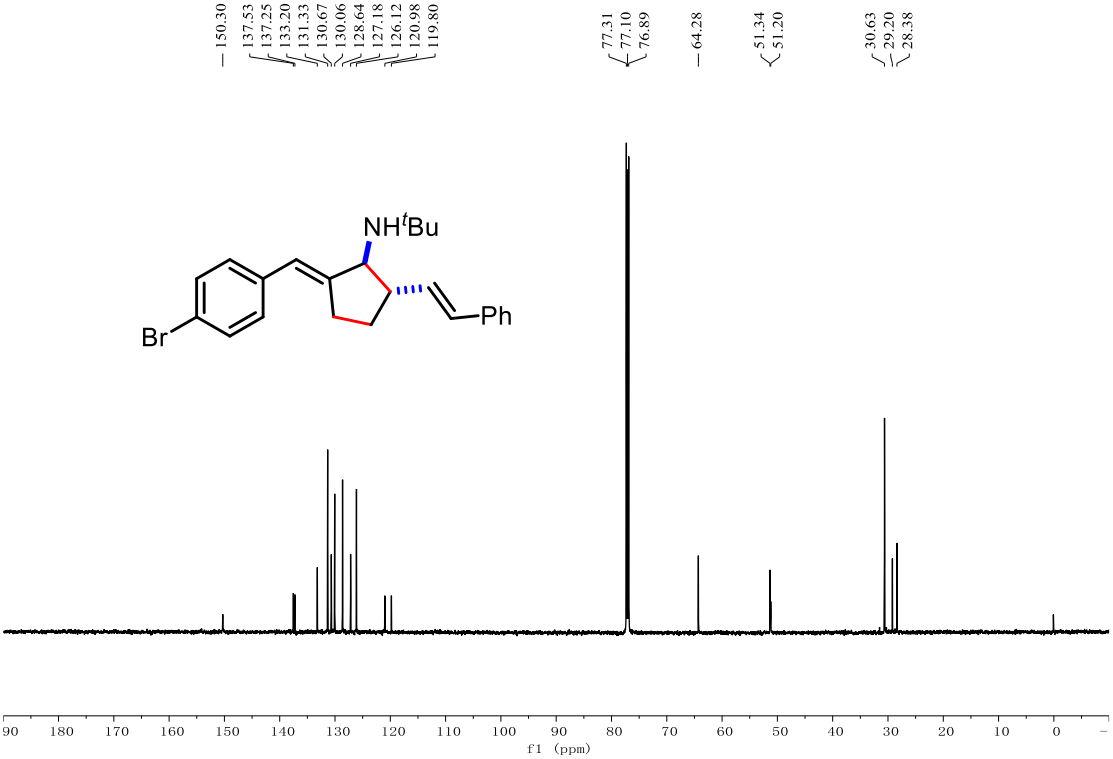

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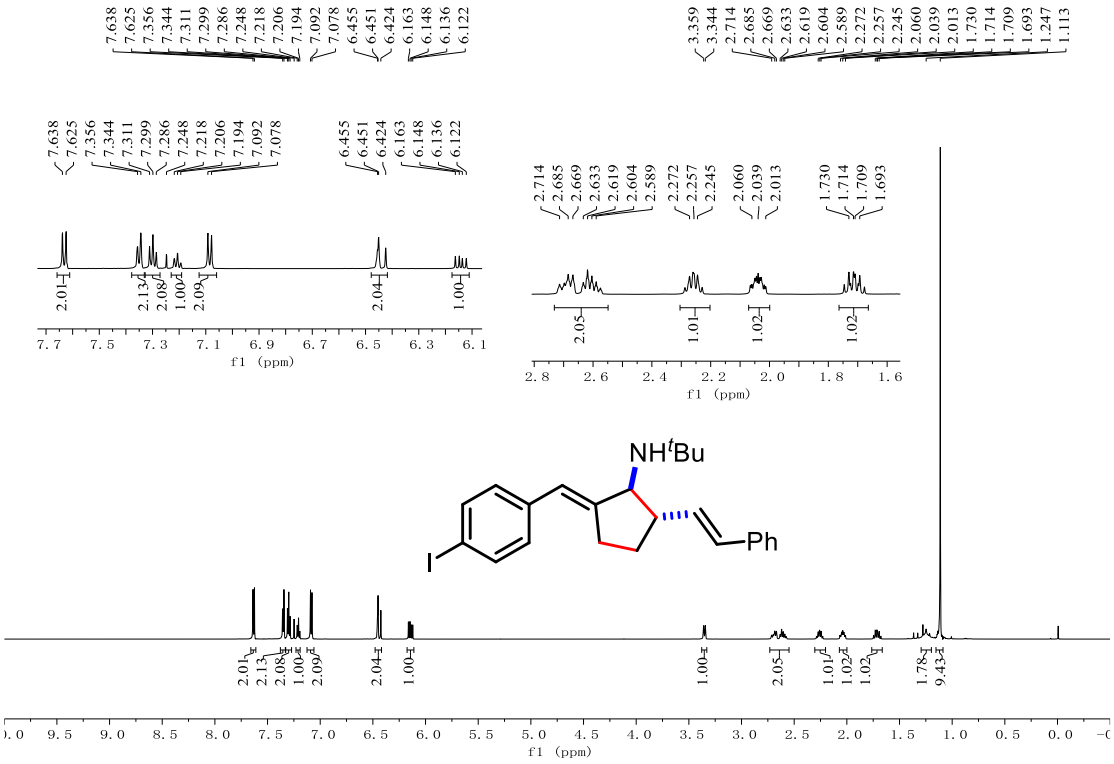

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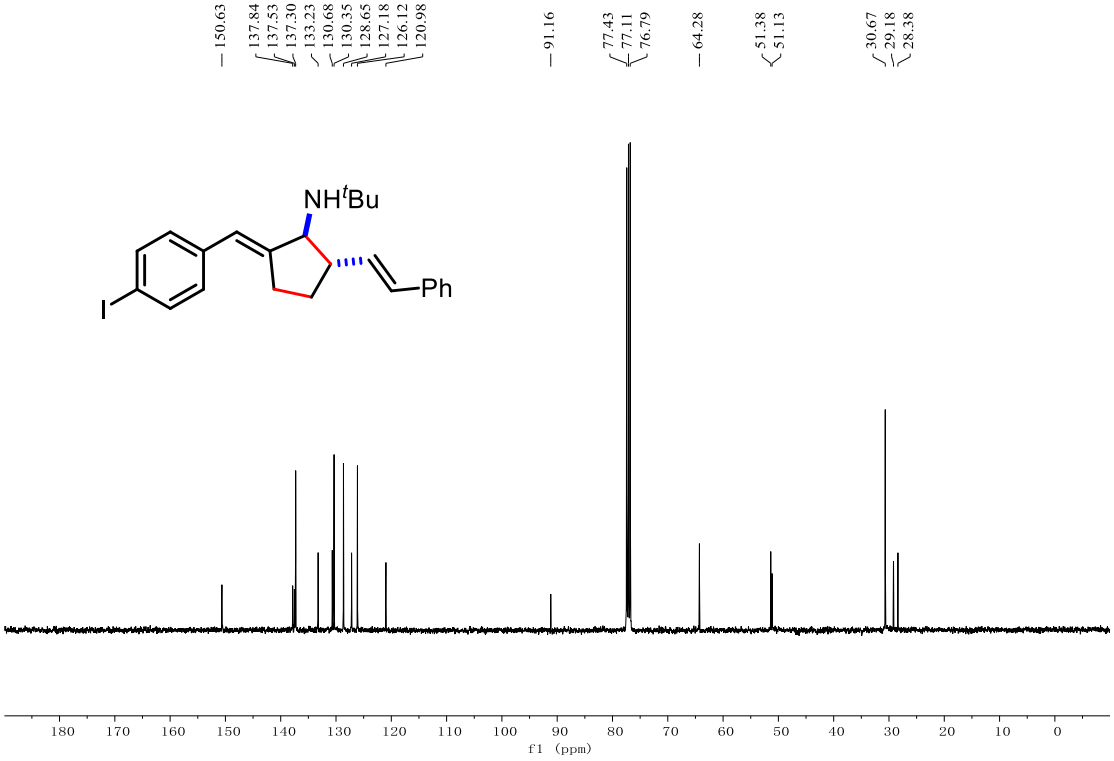
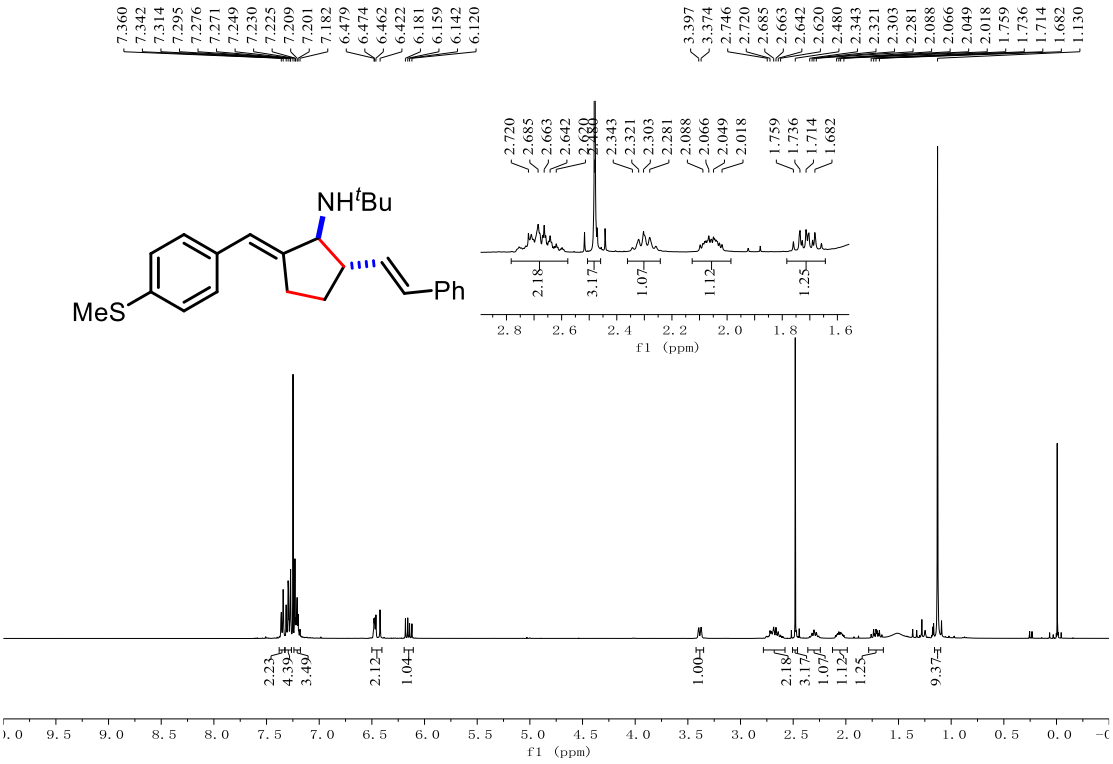
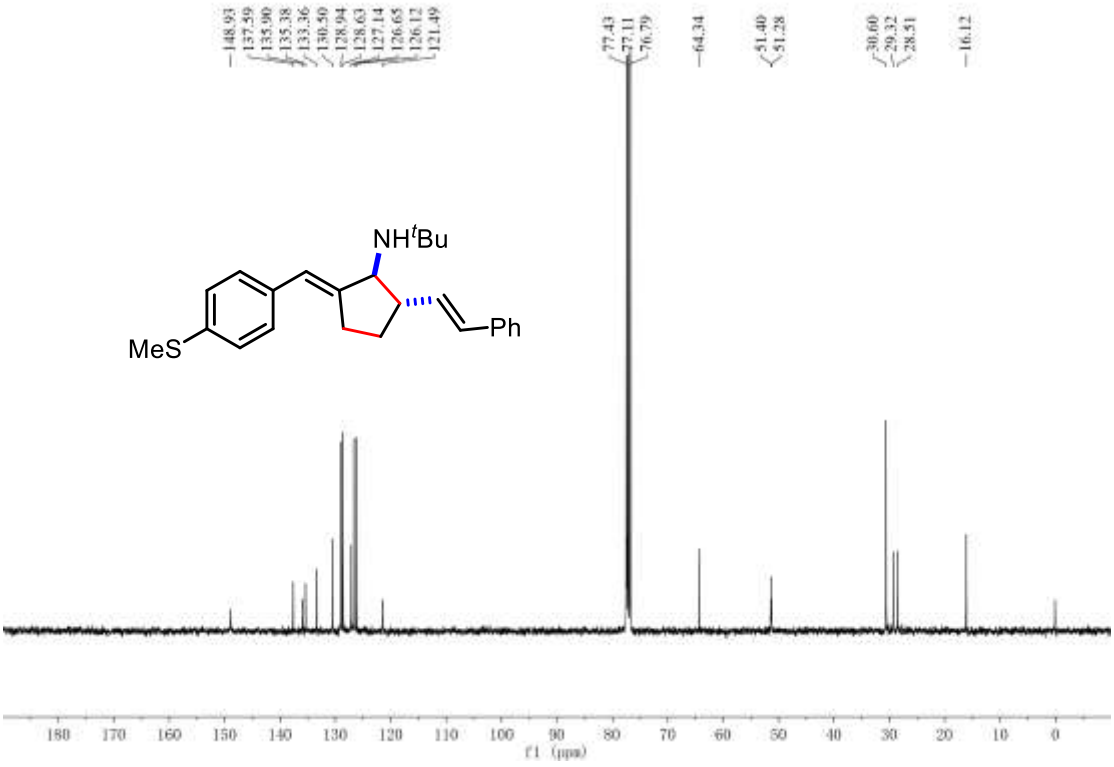


^{1}H NMR spectrum of *trans*-3ga (600 MHz, $CDCl_3$)



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



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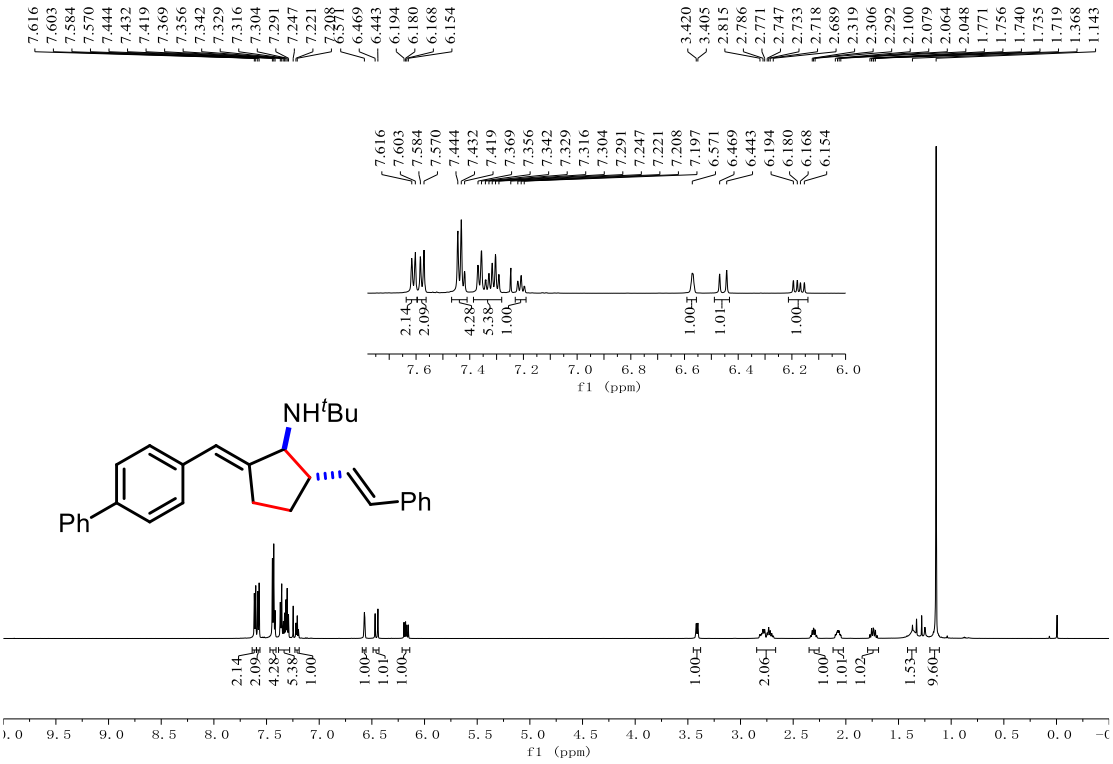
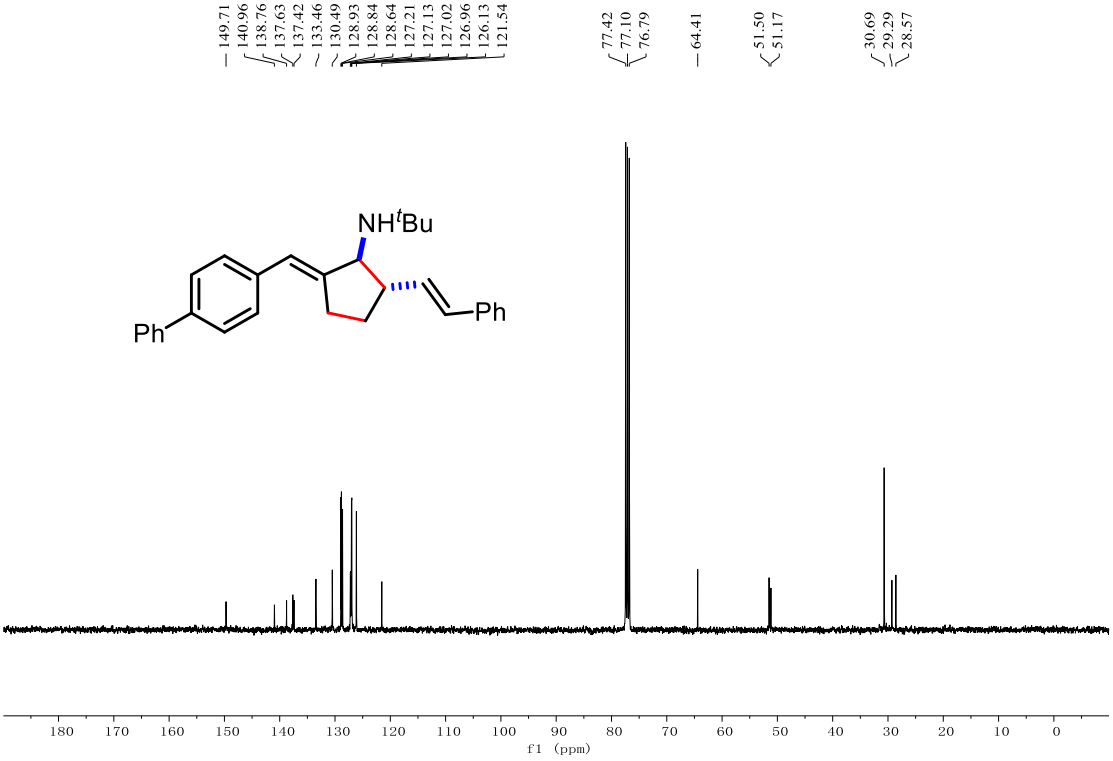
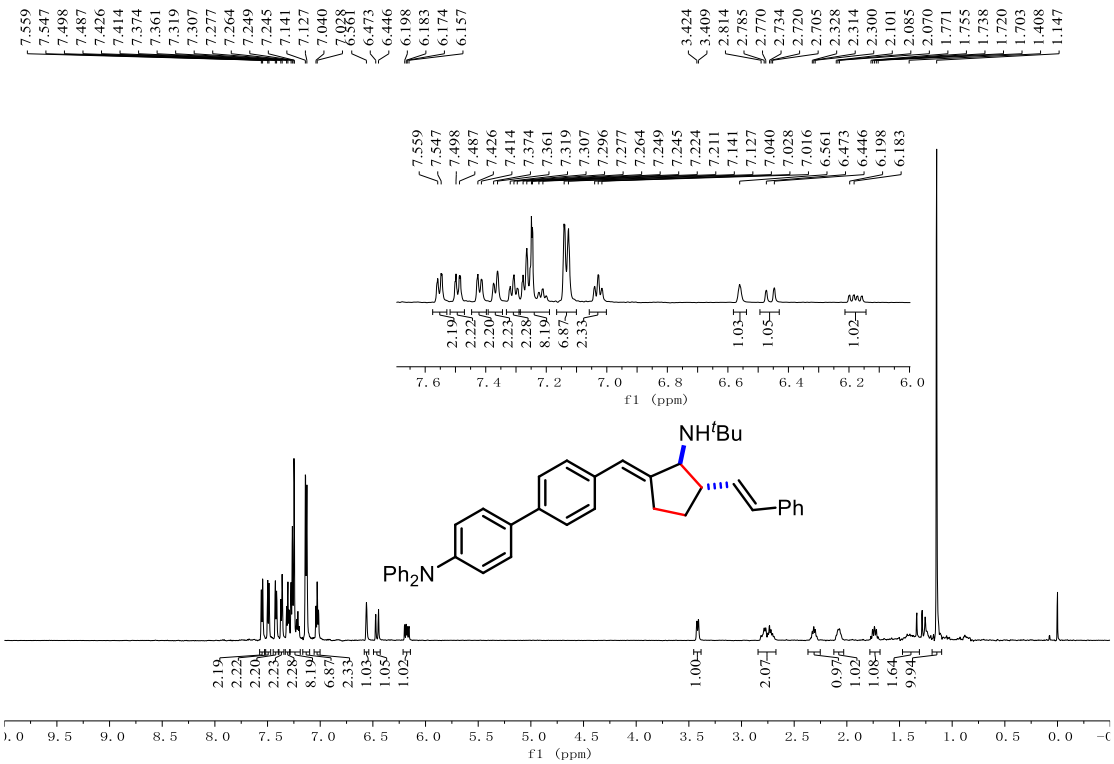


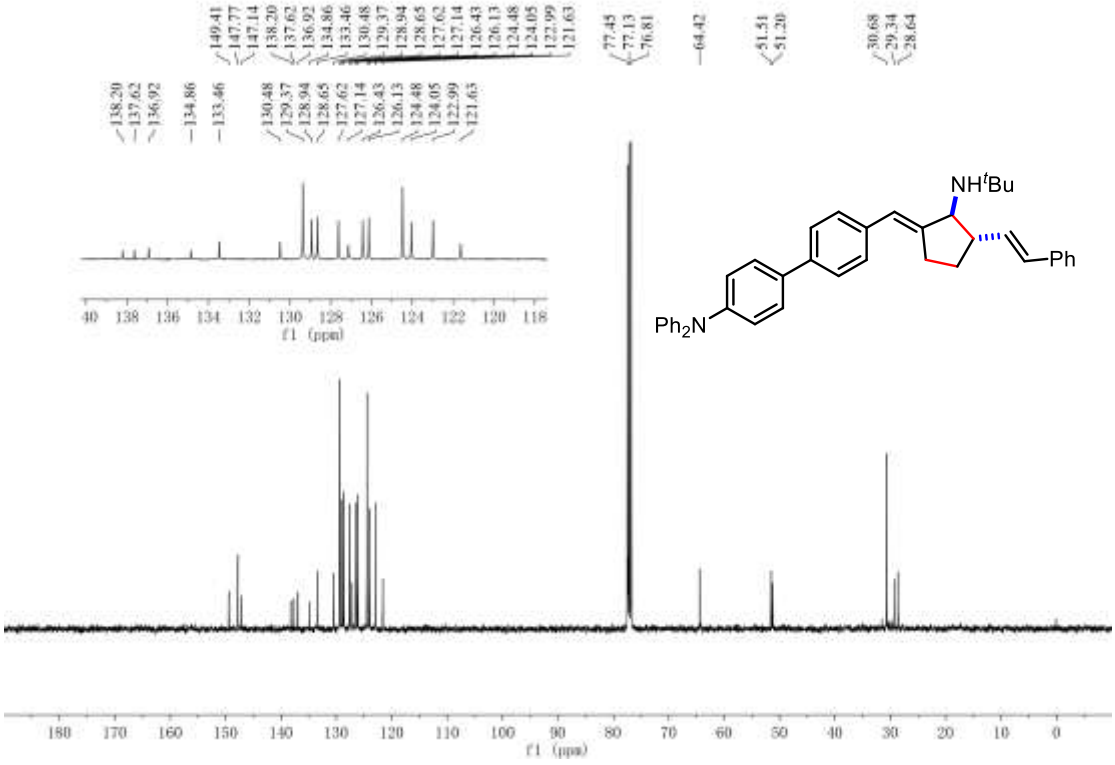
^{13}C NMR spectrum of *trans*-3ha (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of *trans*-3ia (600 MHz, $CDCl_3$)



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



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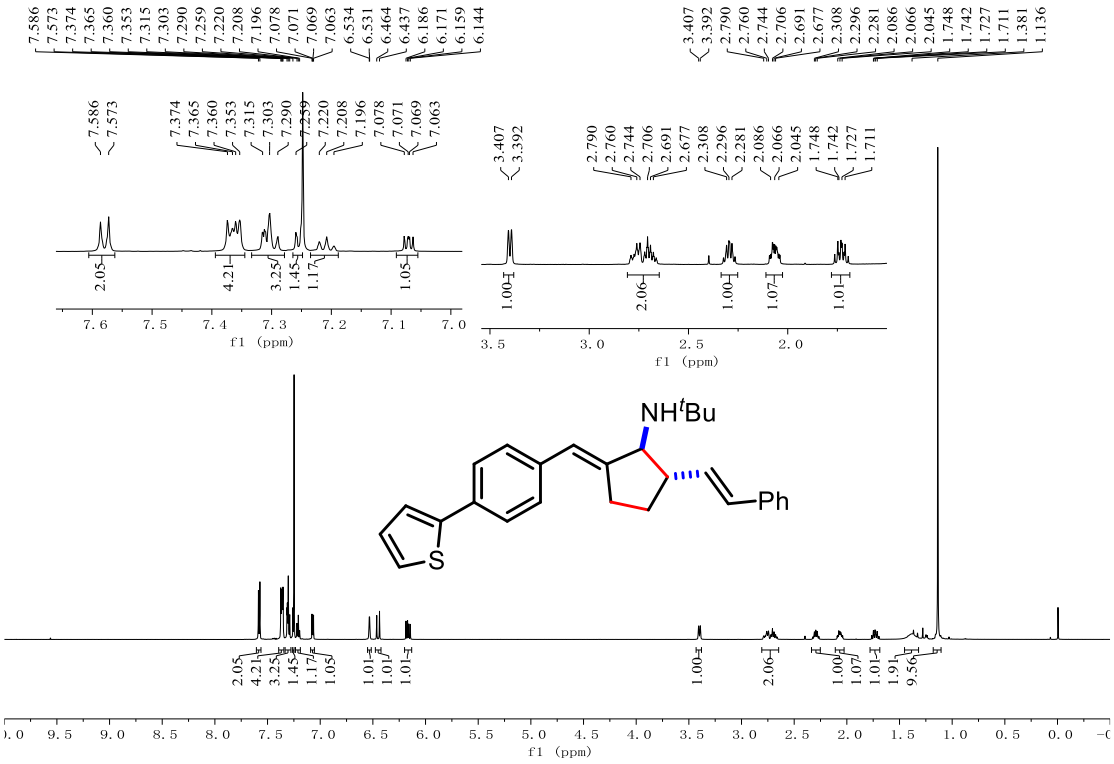

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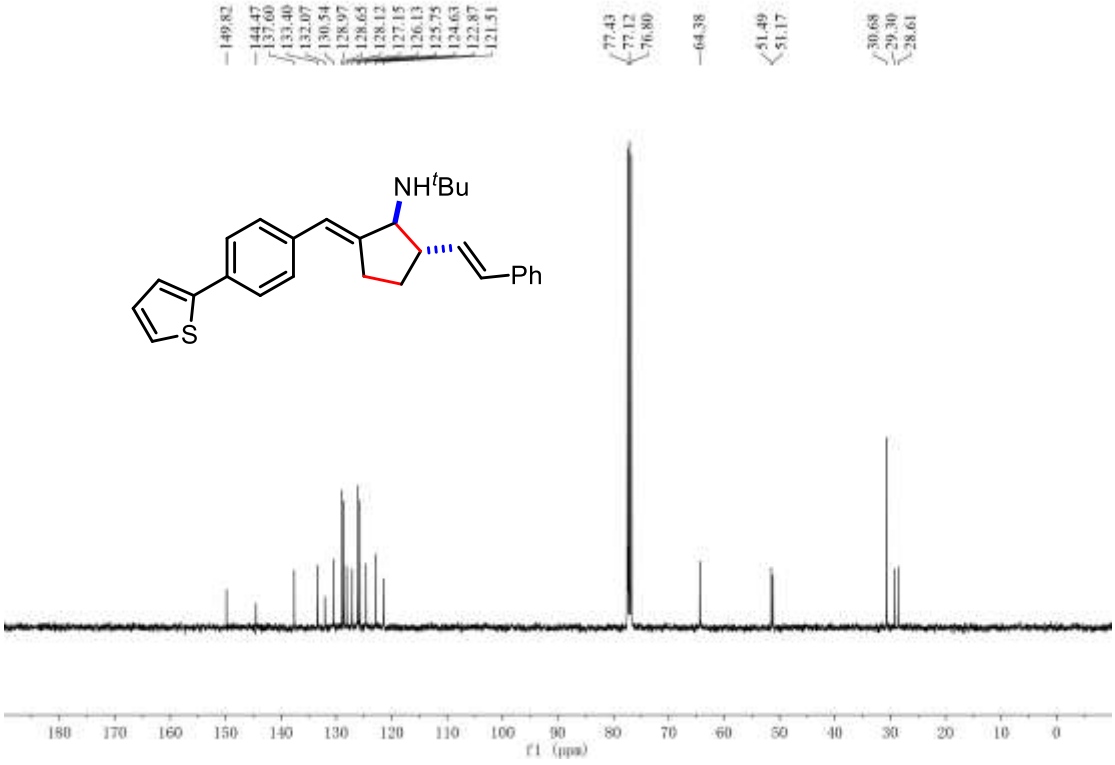
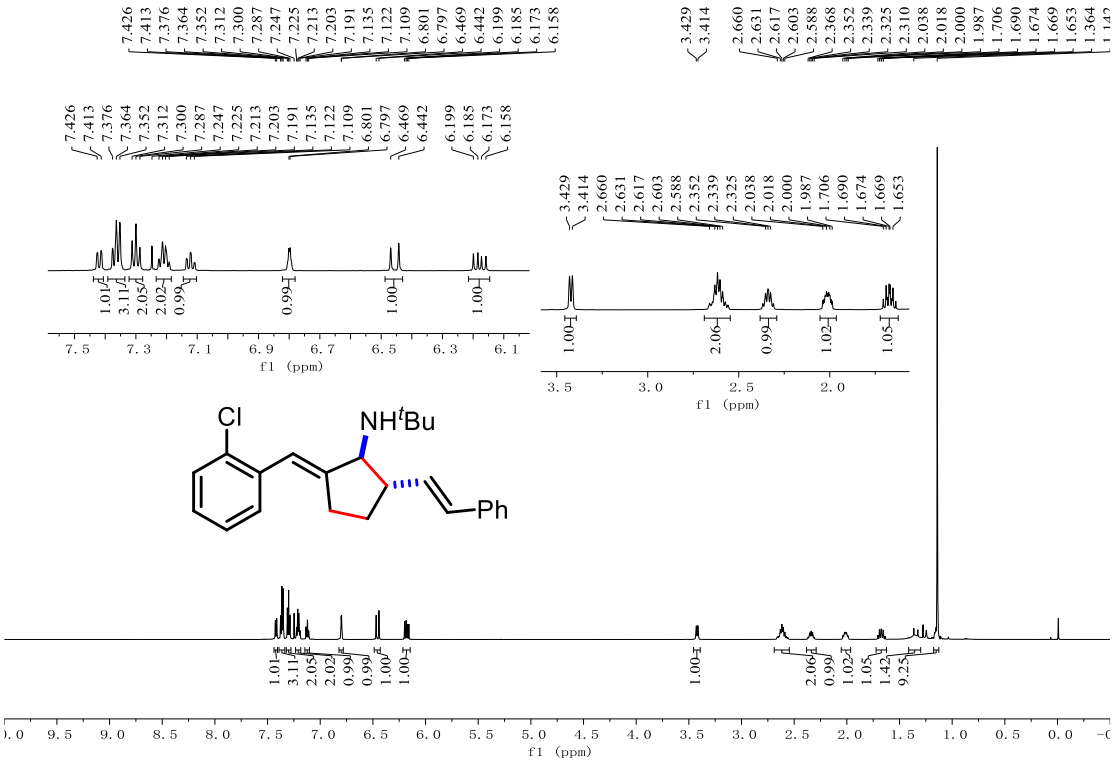
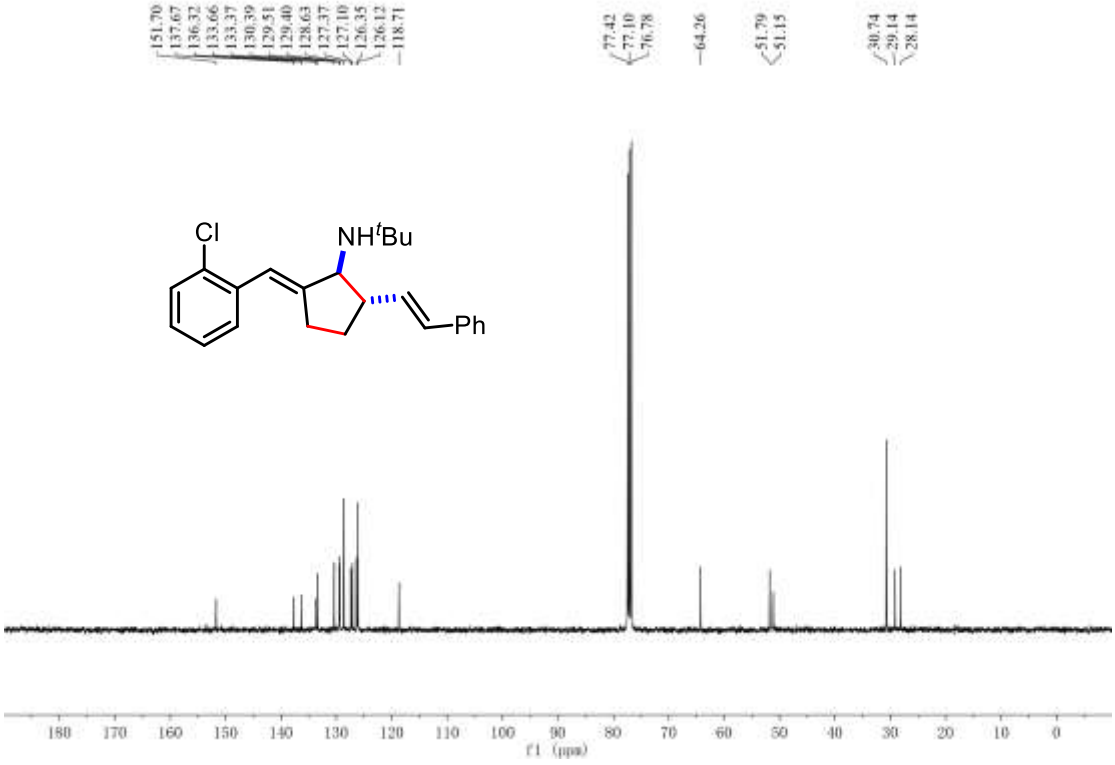


^{1}H NMR spectrum of *trans*-3ka (600 MHz, $CDCl_3$)



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



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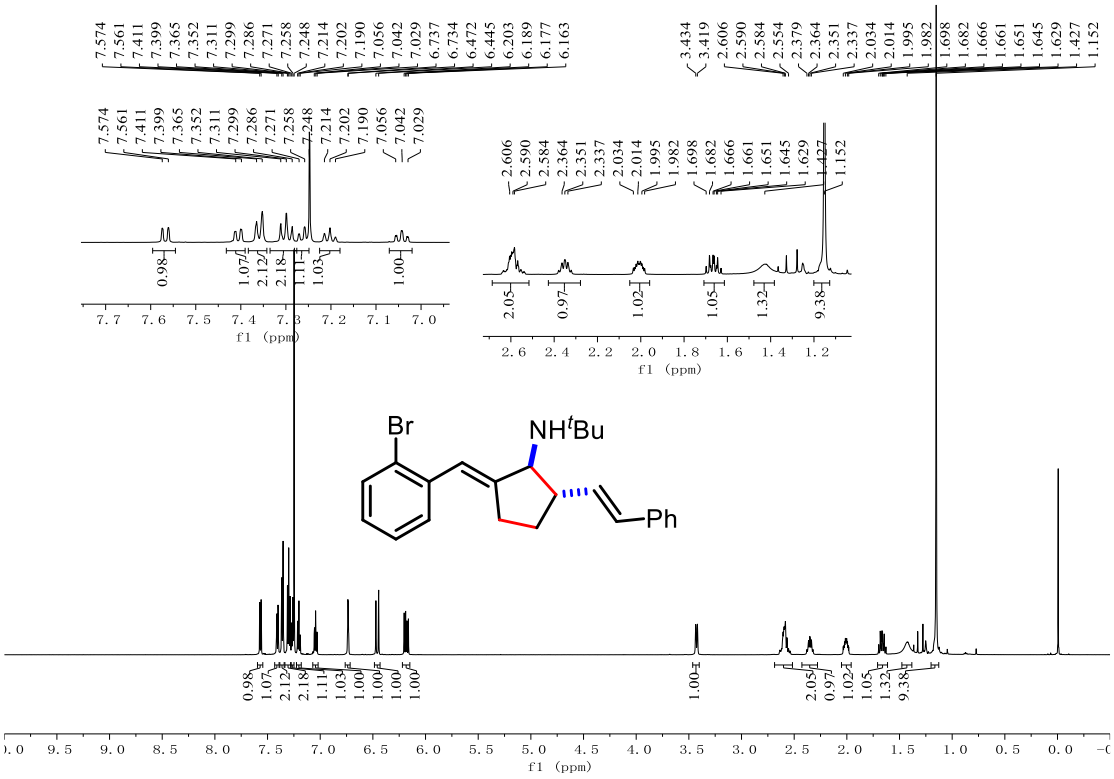

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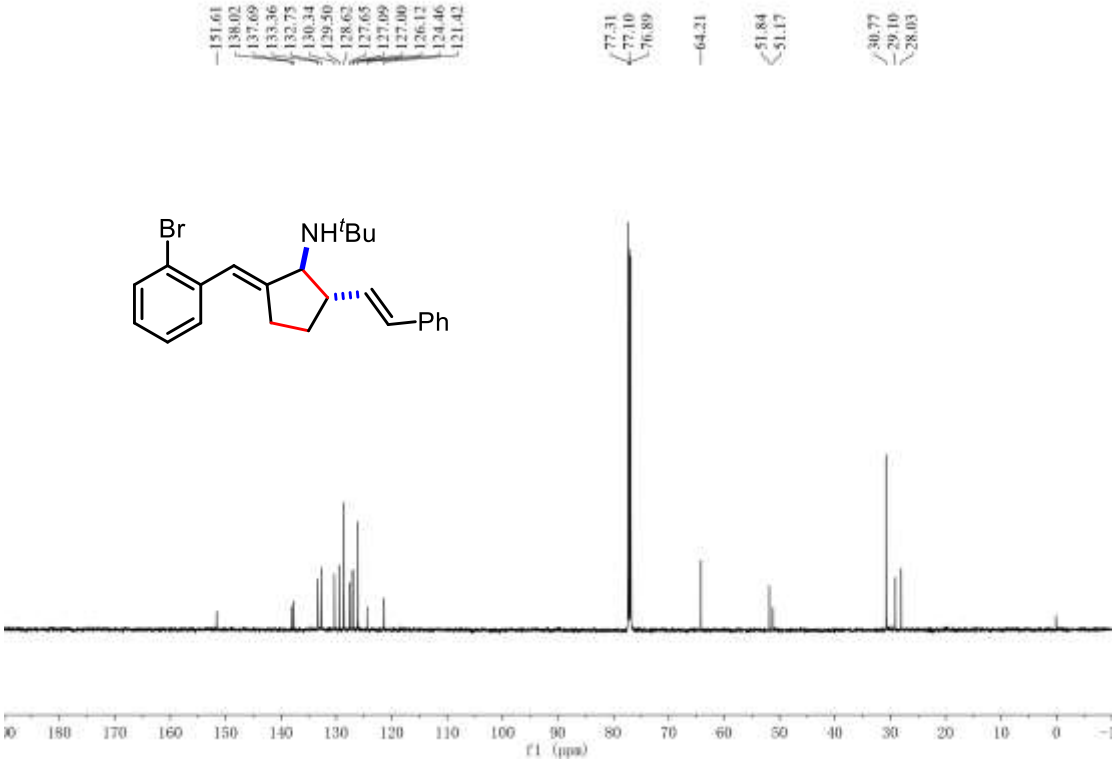

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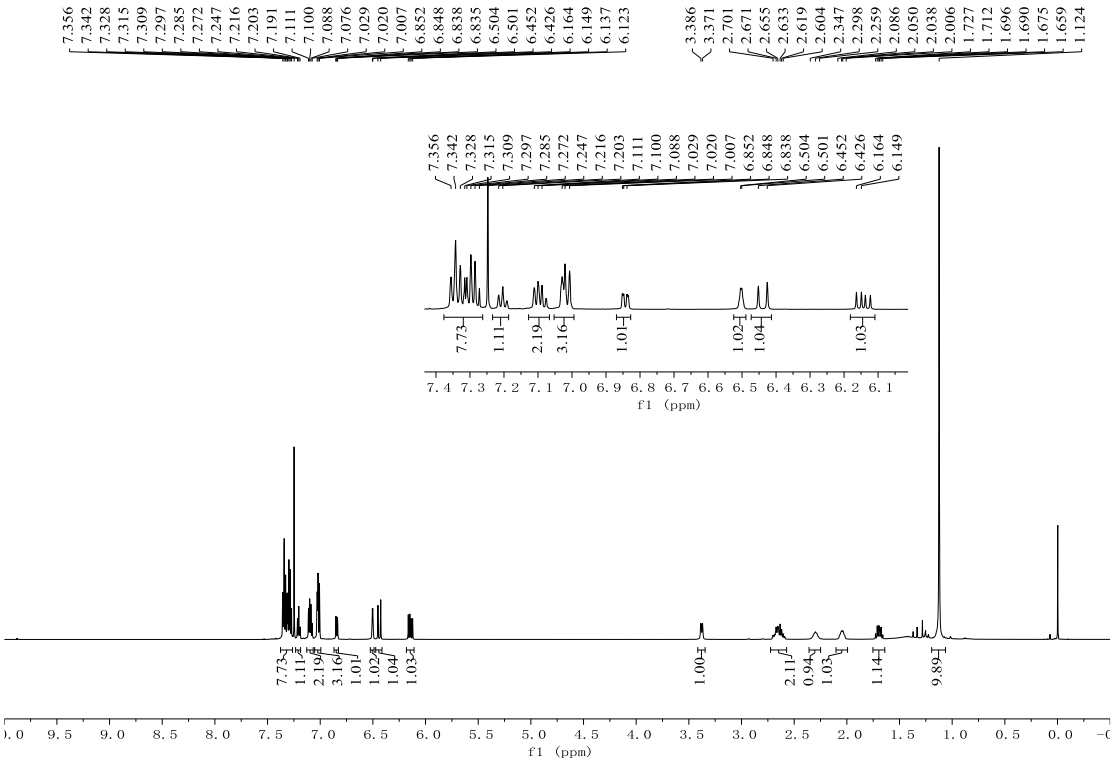
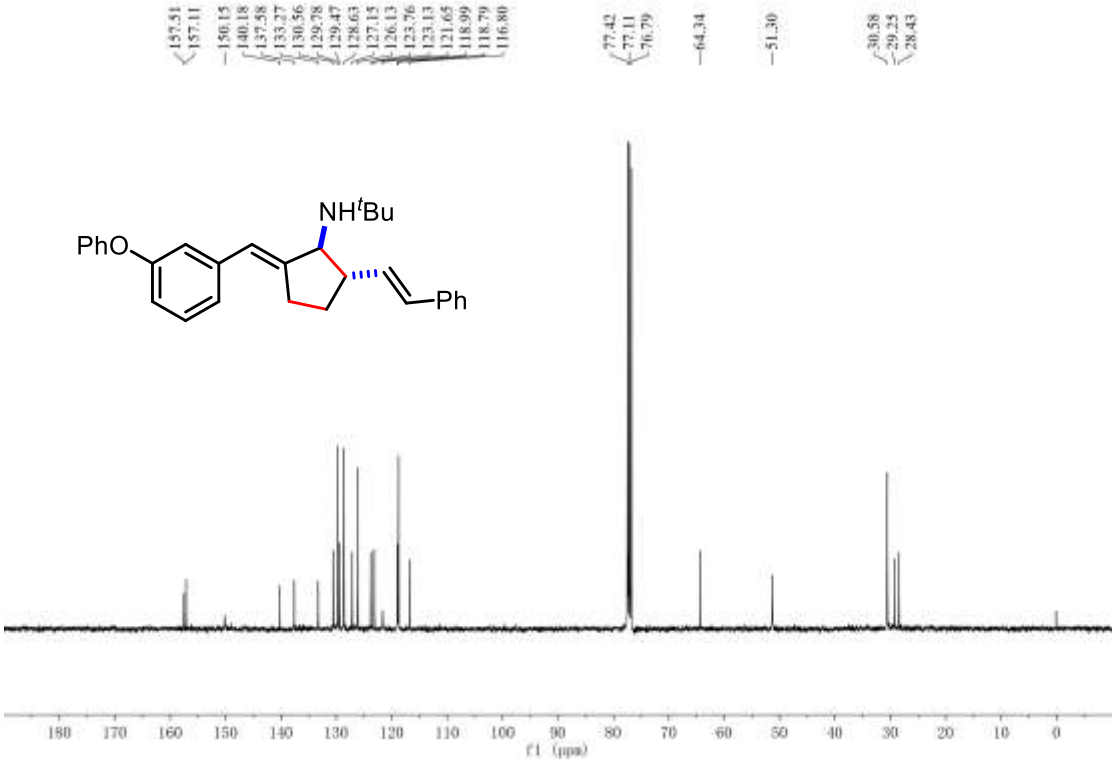


^{13}C NMR spectrum of *trans*-3ma (101 MHz, $CDCl_3$)



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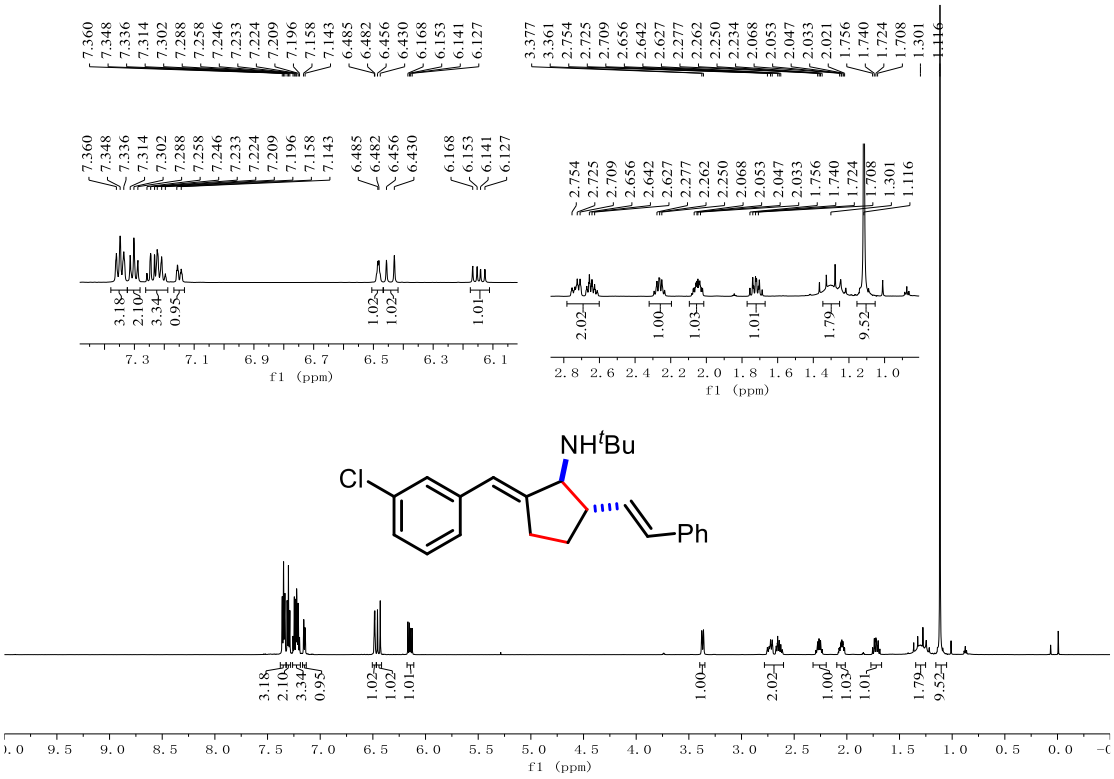
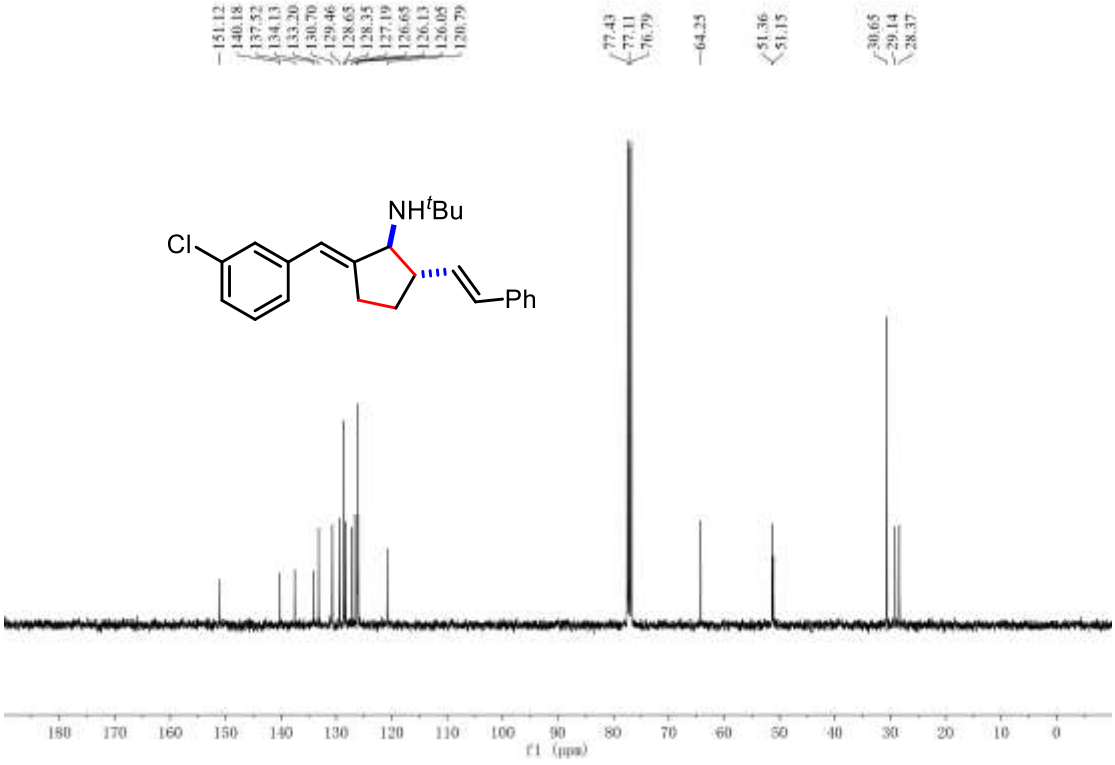
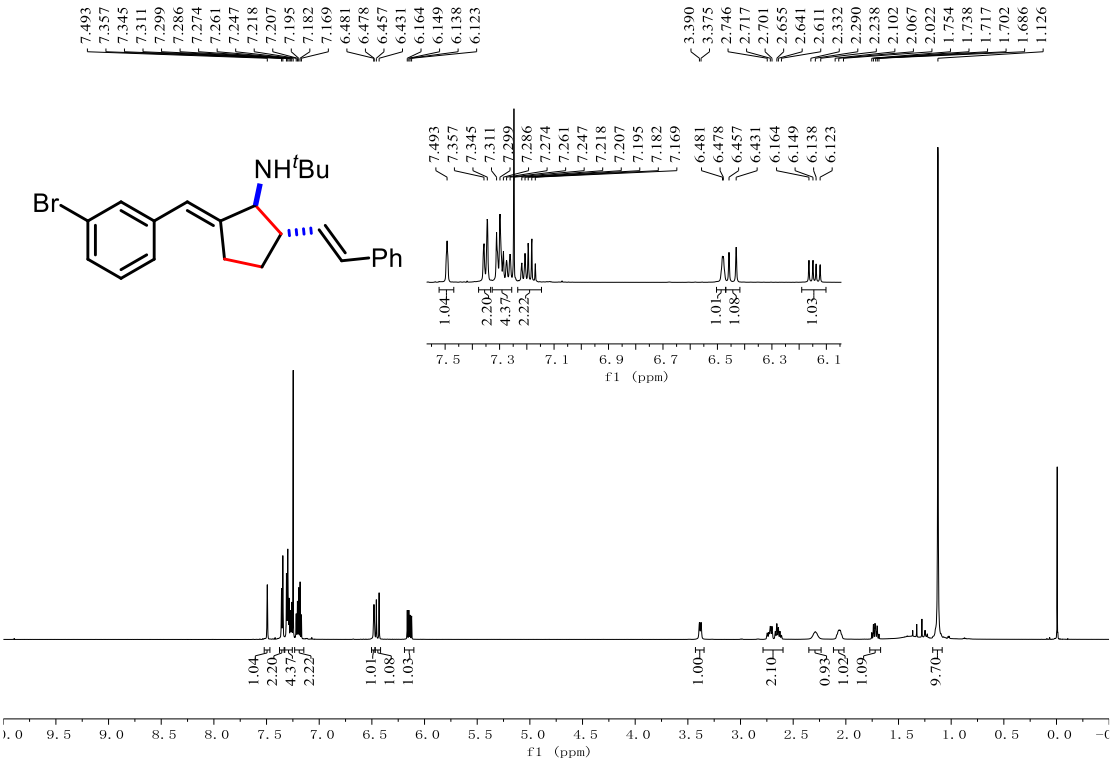


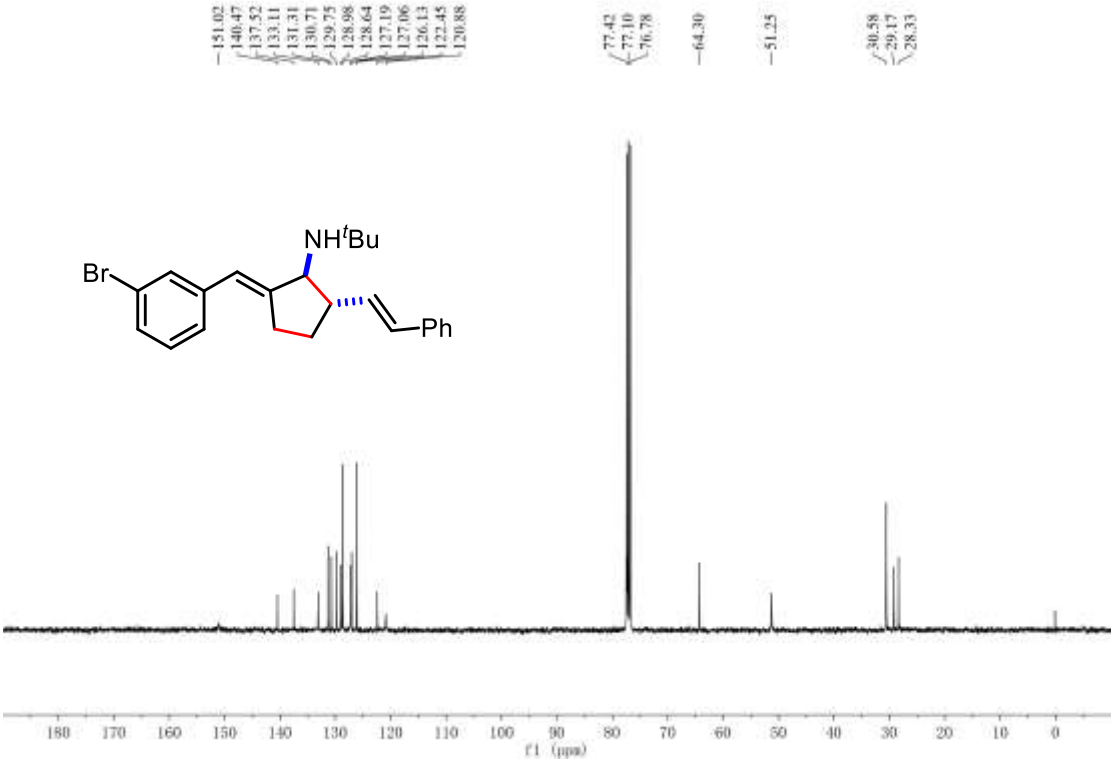
^{13}C NMR spectrum of *trans*-3na (101 MHz, $CDCl_3$)



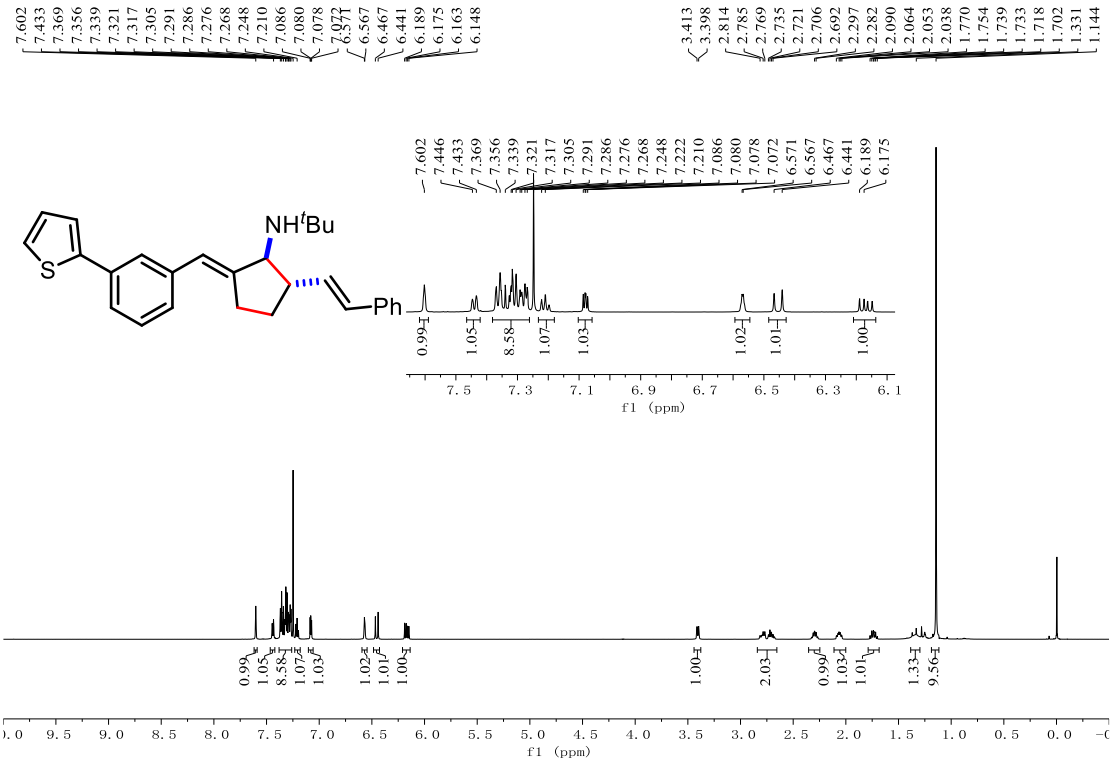
^{1}H NMR spectrum of *trans*-3oa (600 MHz, $CDCl_3$)



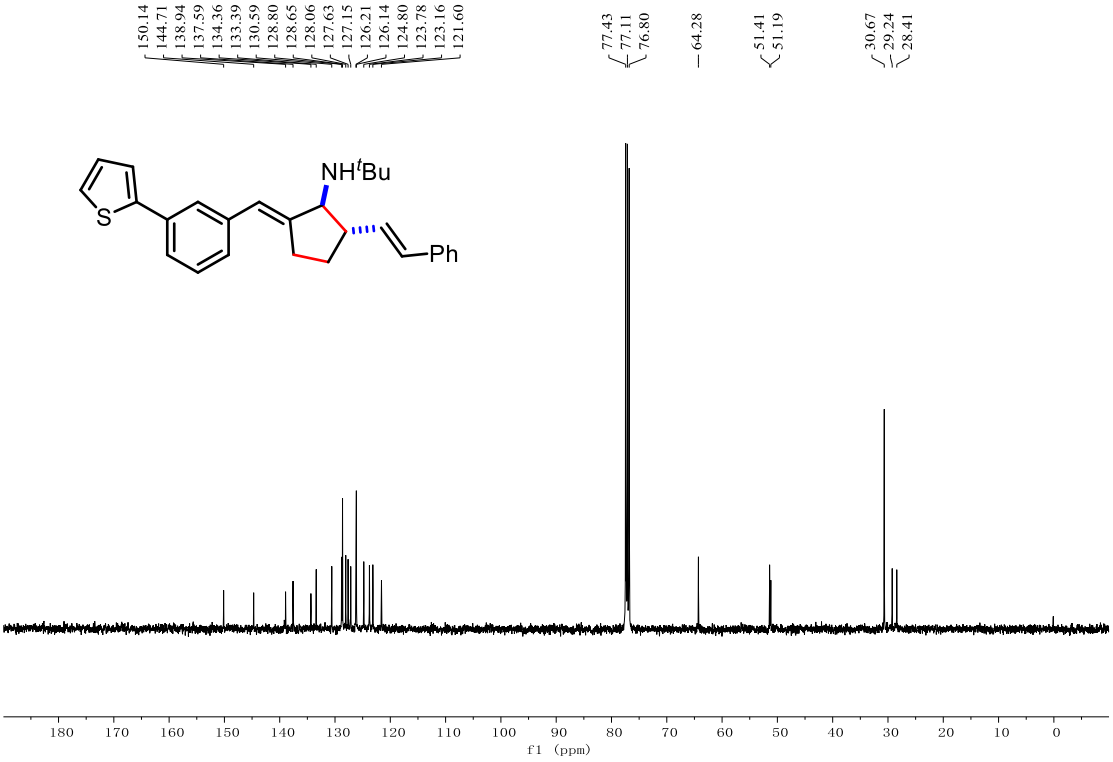
^{13}C NMR spectrum of *trans*-3oa (101 MHz, $CDCl_3$)



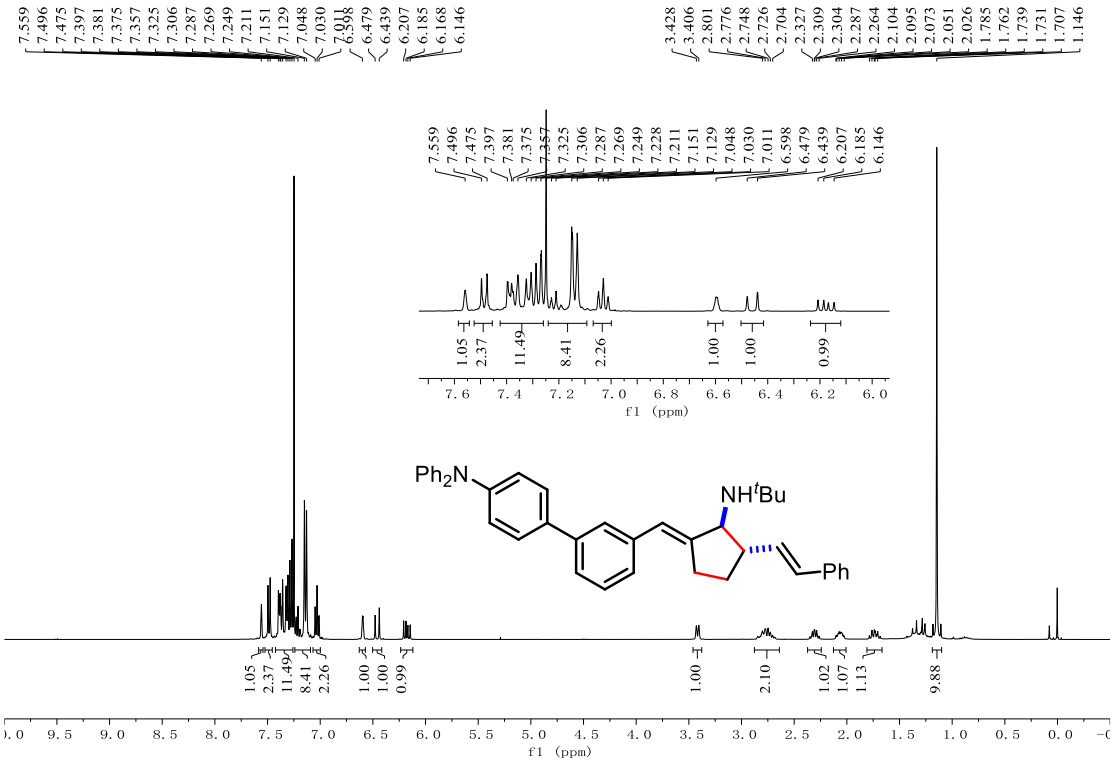
^{1}H NMR spectrum of *trans*-3pa (600 MHz, $CDCl_3$)



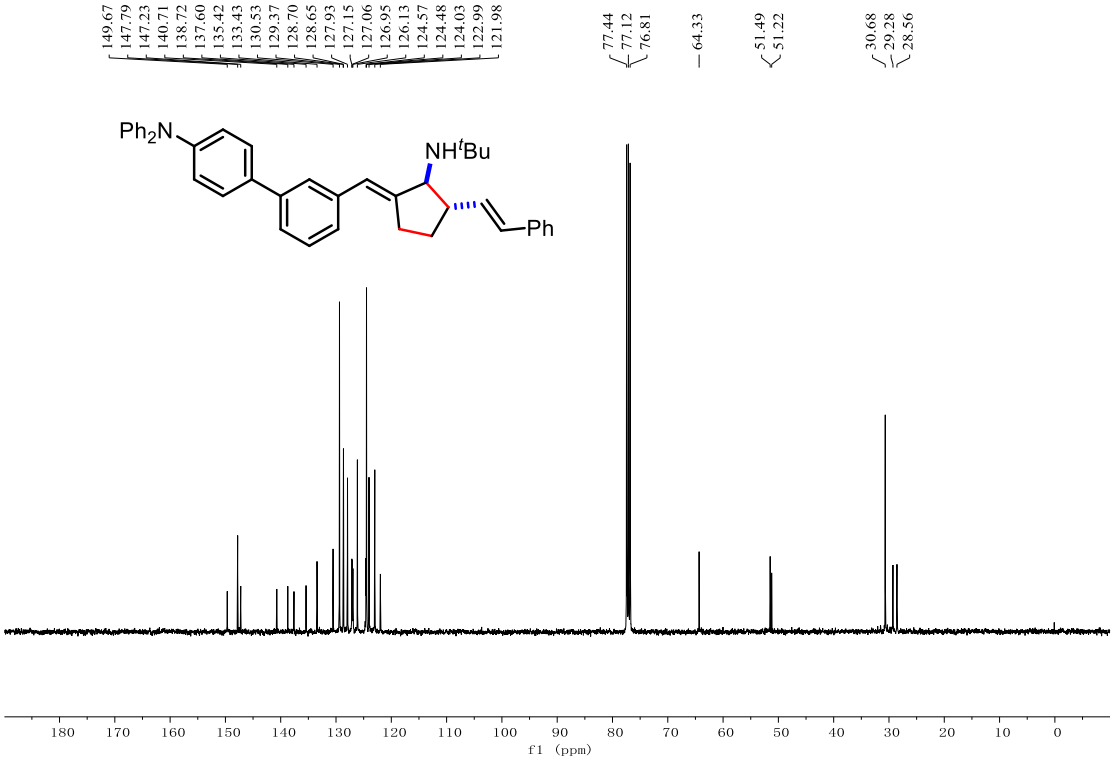
^{13}C NMR spectrum of *trans*-3pa (101 MHz, $CDCl_3$)



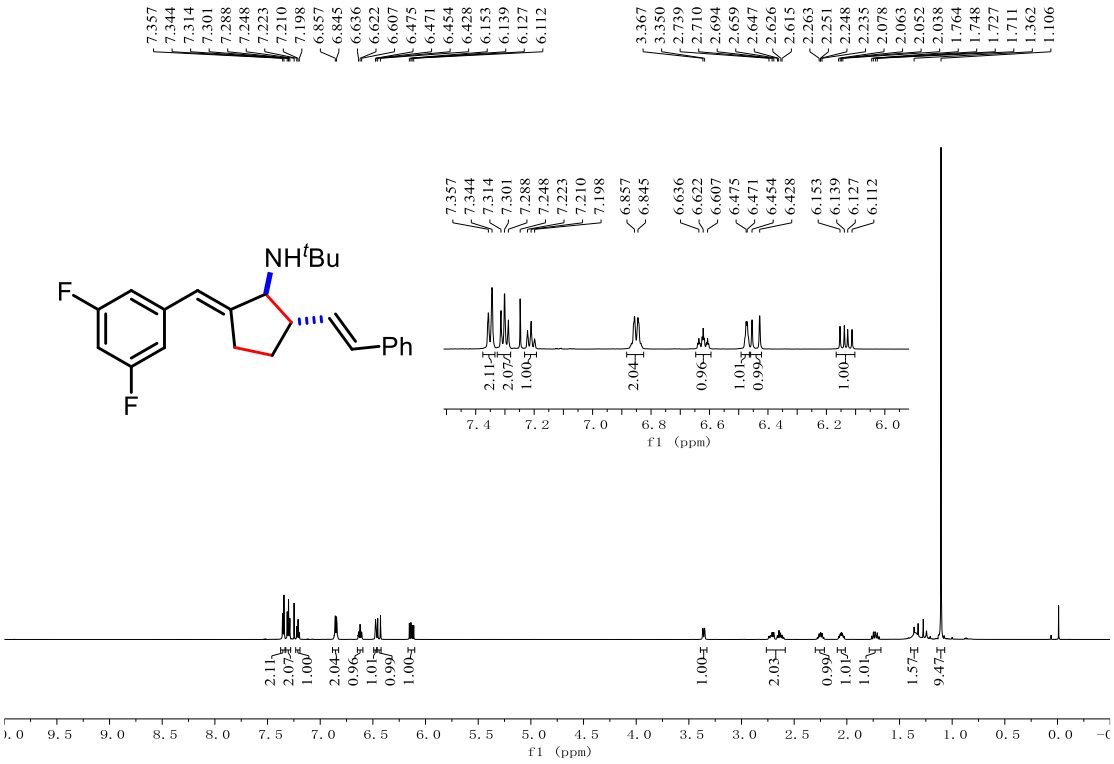
^{1}H NMR spectrum of *trans*-3qa (400 MHz, $CDCl_3$)



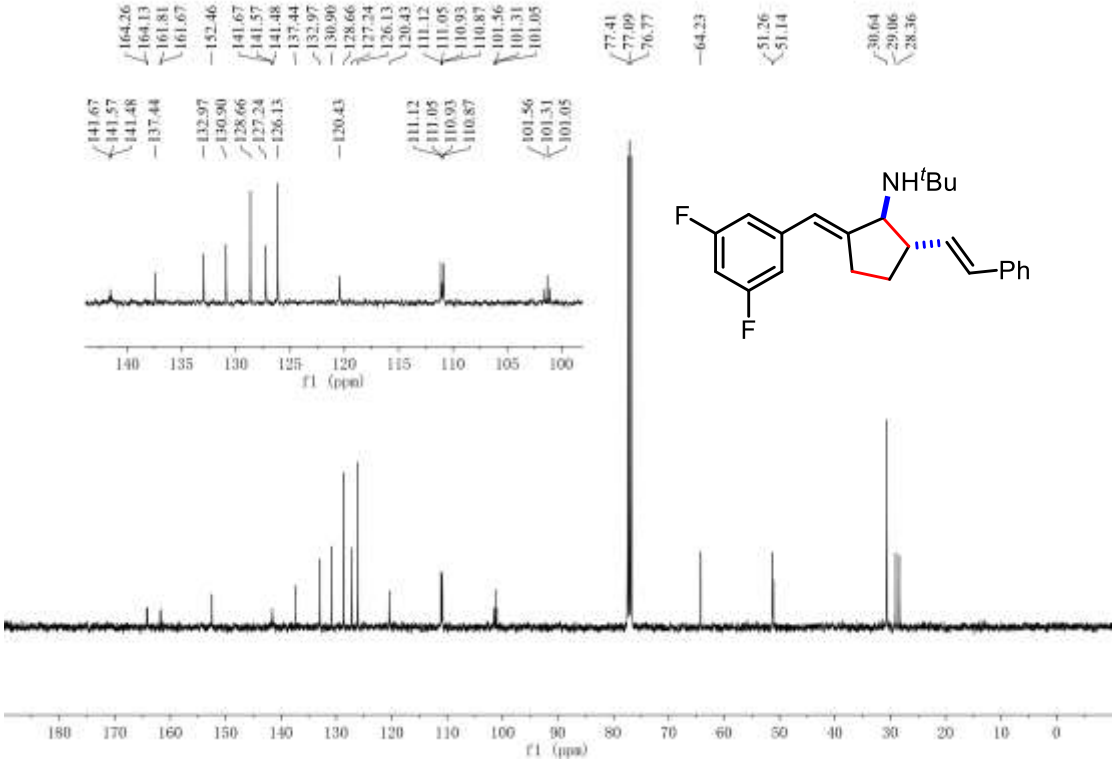
^{13}C NMR spectrum of *trans*-3qa (101 MHz, $CDCl_3$)



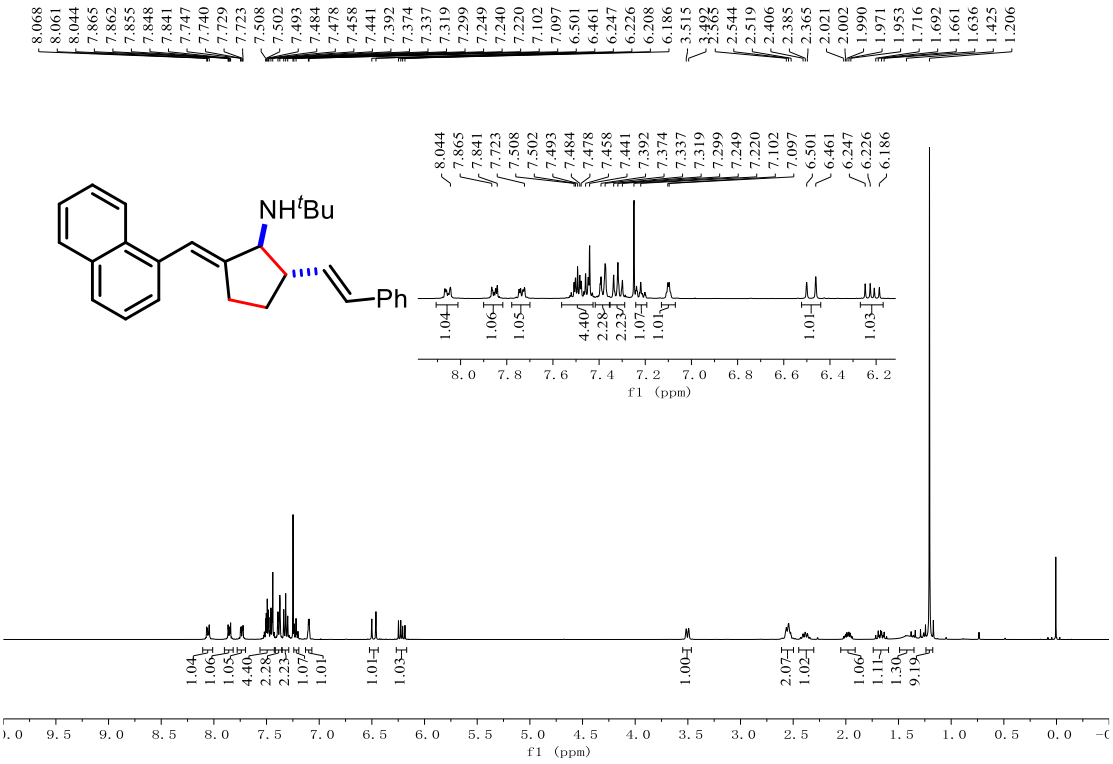
^{1}H NMR spectrum of *trans*-3ra (600 MHz, $CDCl_3$)



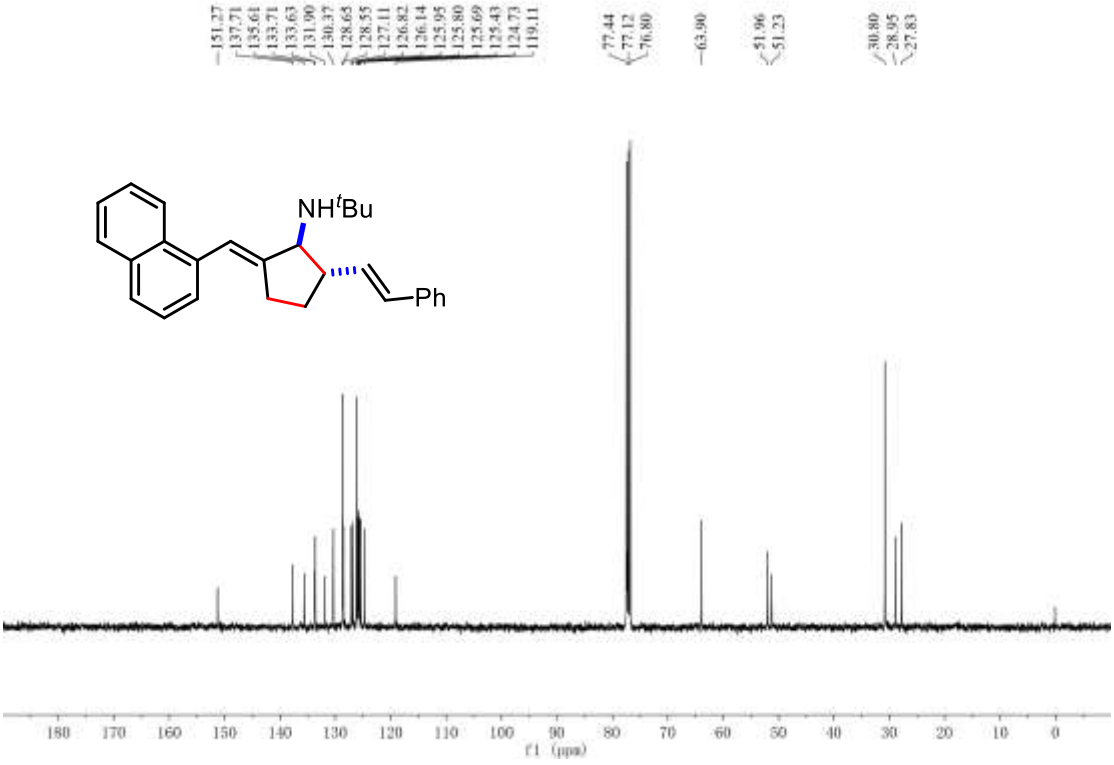
^{13}C NMR spectrum of *trans*-3ra (101 MHz, $CDCl_3$)



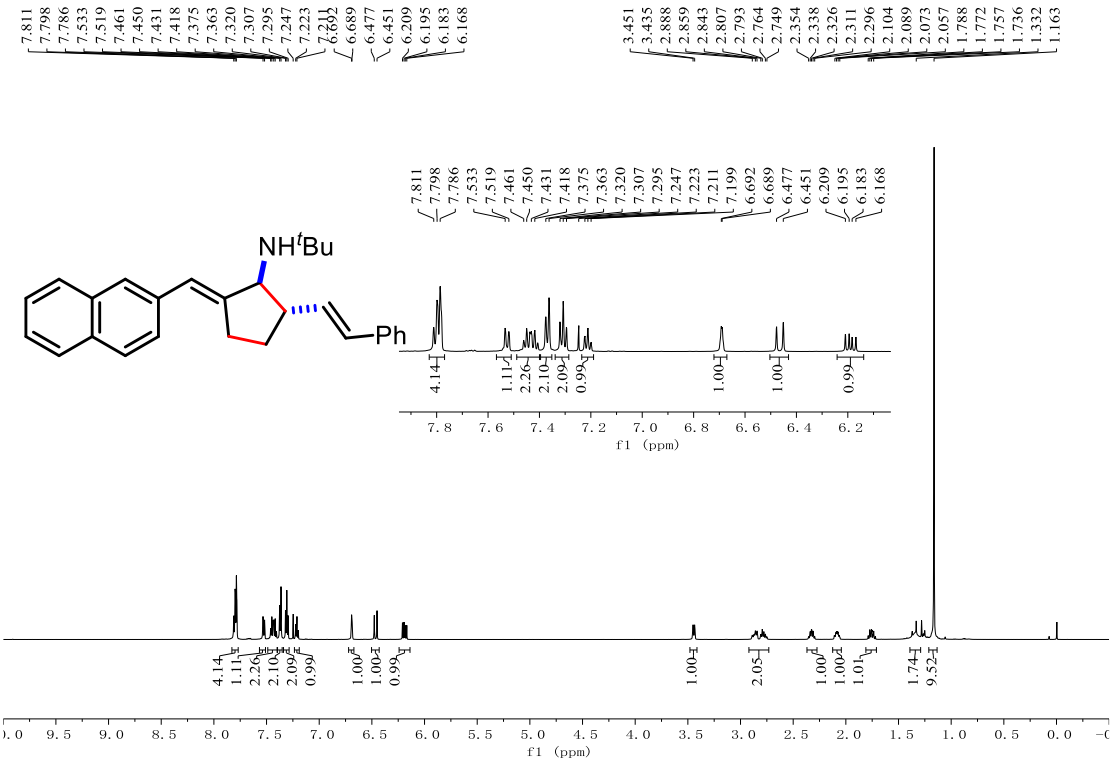
^{1}H NMR spectrum of *trans*-3sa (400 MHz, $CDCl_3$)



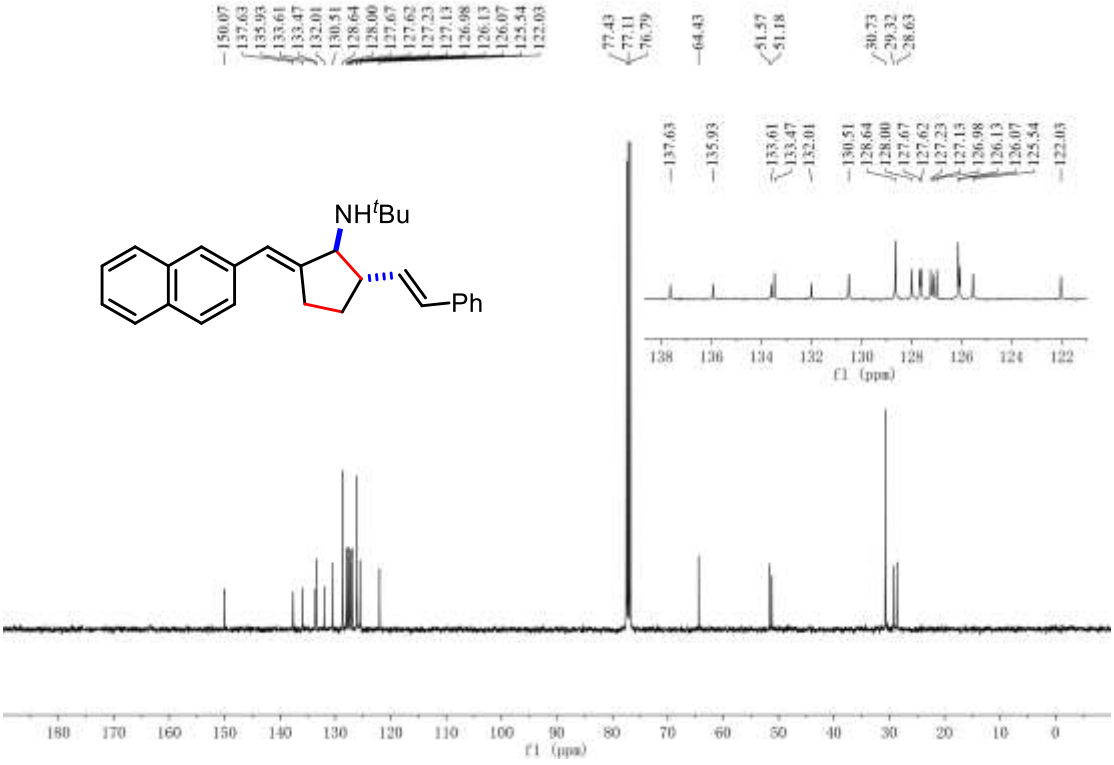
^{13}C NMR spectrum of *trans*-3sa (101 MHz, $CDCl_3$)



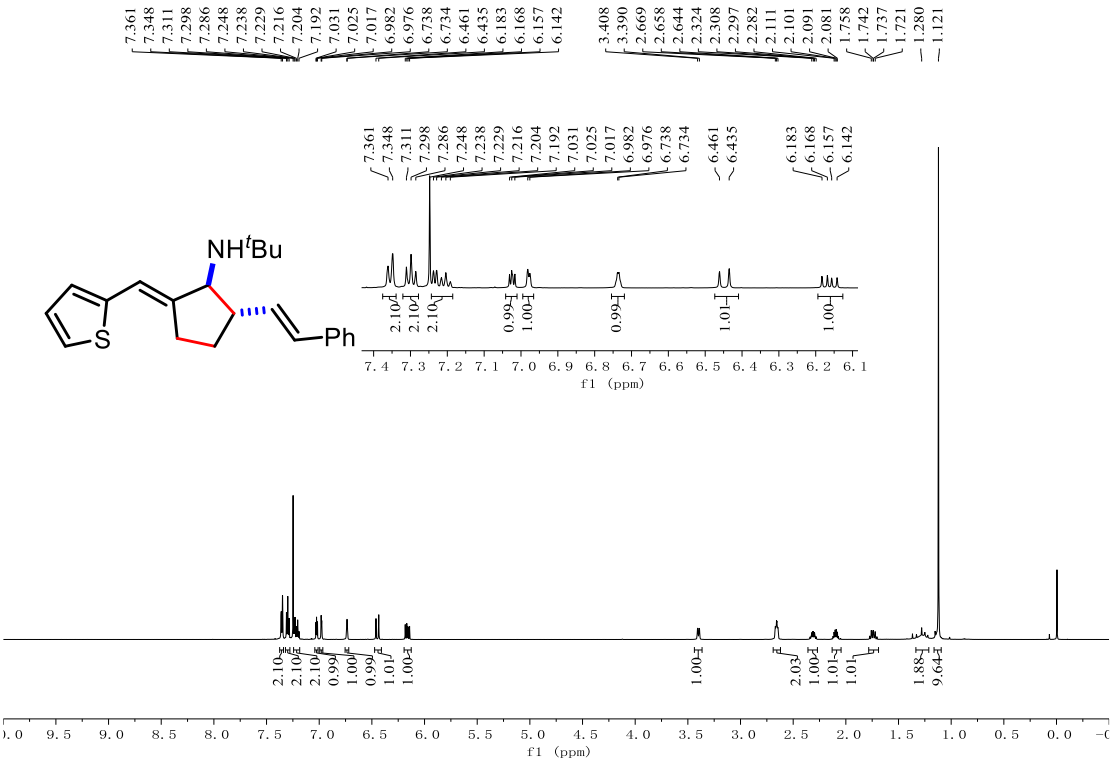
^{1}H NMR spectrum of *trans*-3ta (600 MHz, $CDCl_3$)



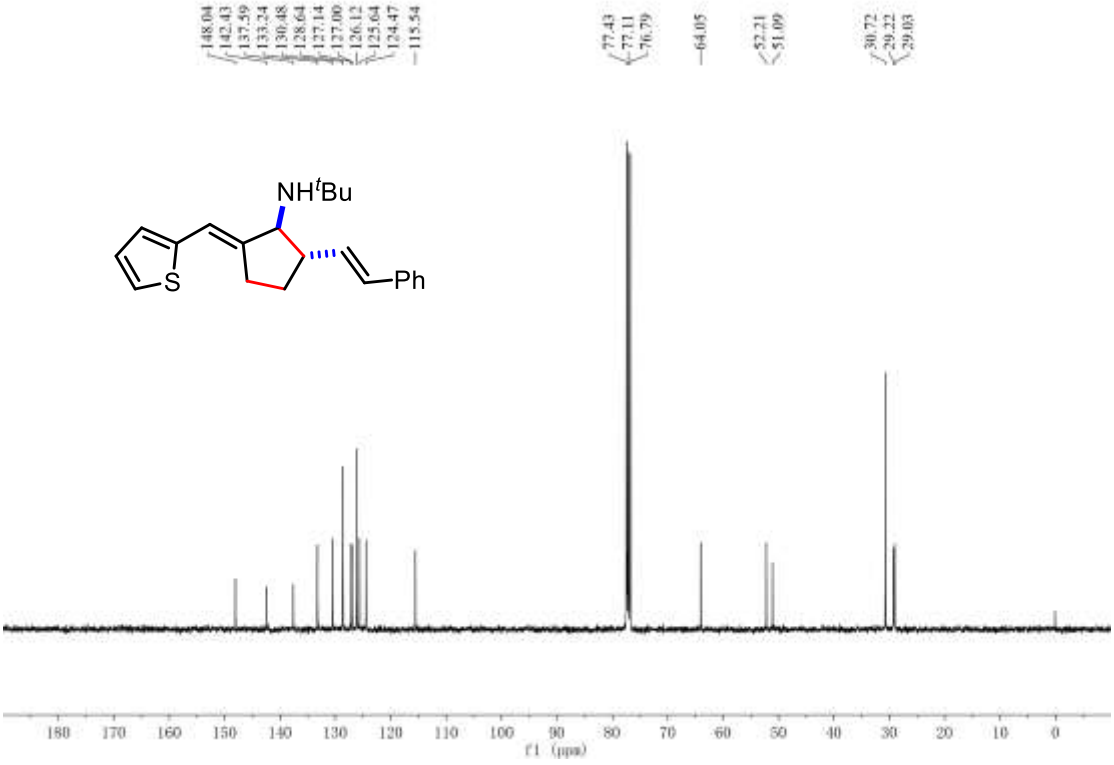
^{13}C NMR spectrum of *trans*-3ta (101 MHz, $CDCl_3$)



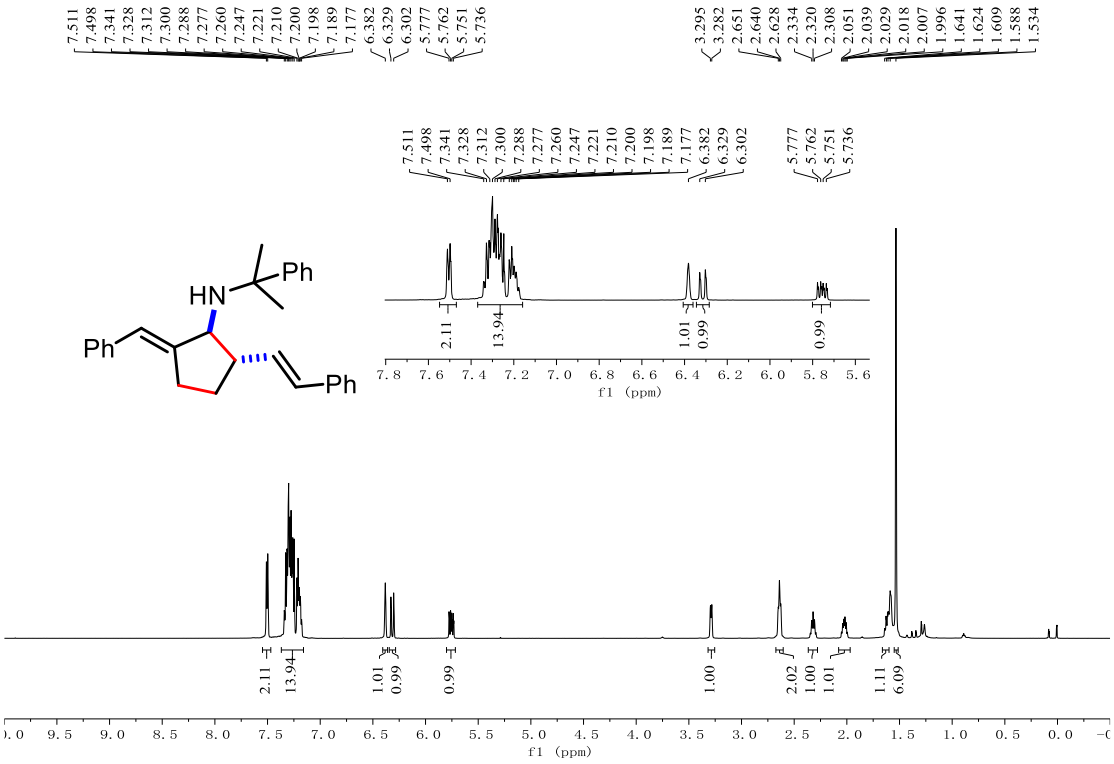
^{1}H NMR spectrum of *trans*-3ua (600 MHz, $CDCl_3$)



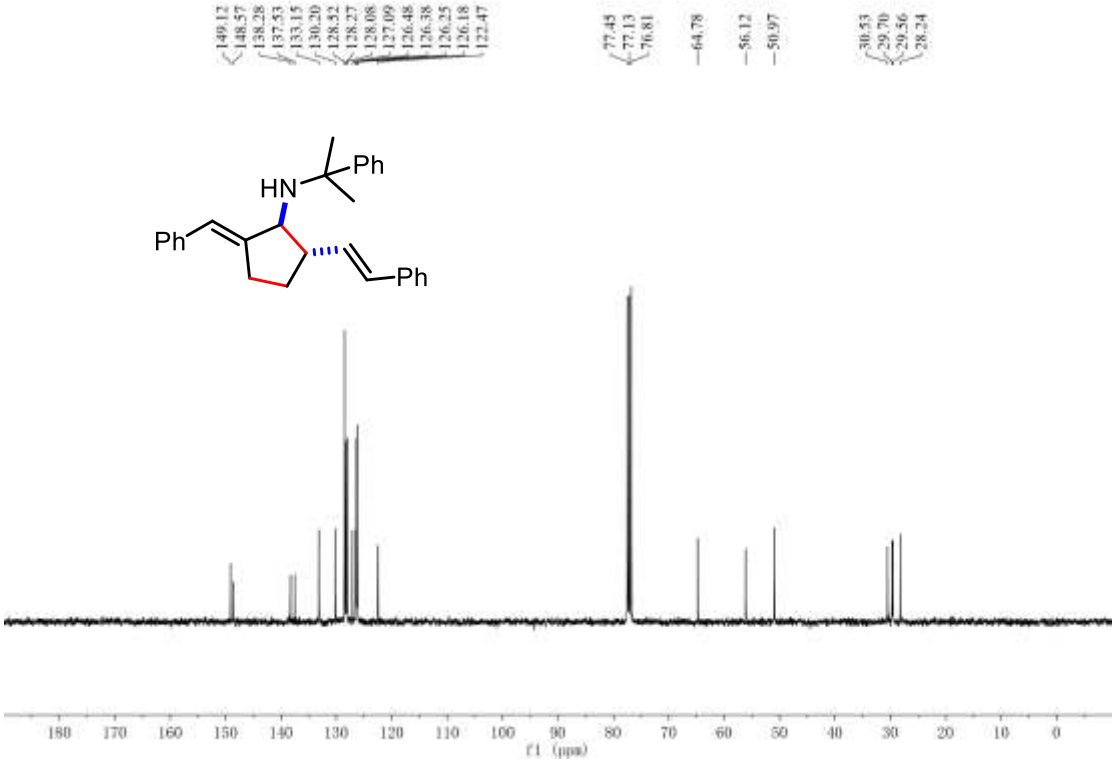
^{13}C NMR spectrum of *trans*-3ua (101 MHz, $CDCl_3$)



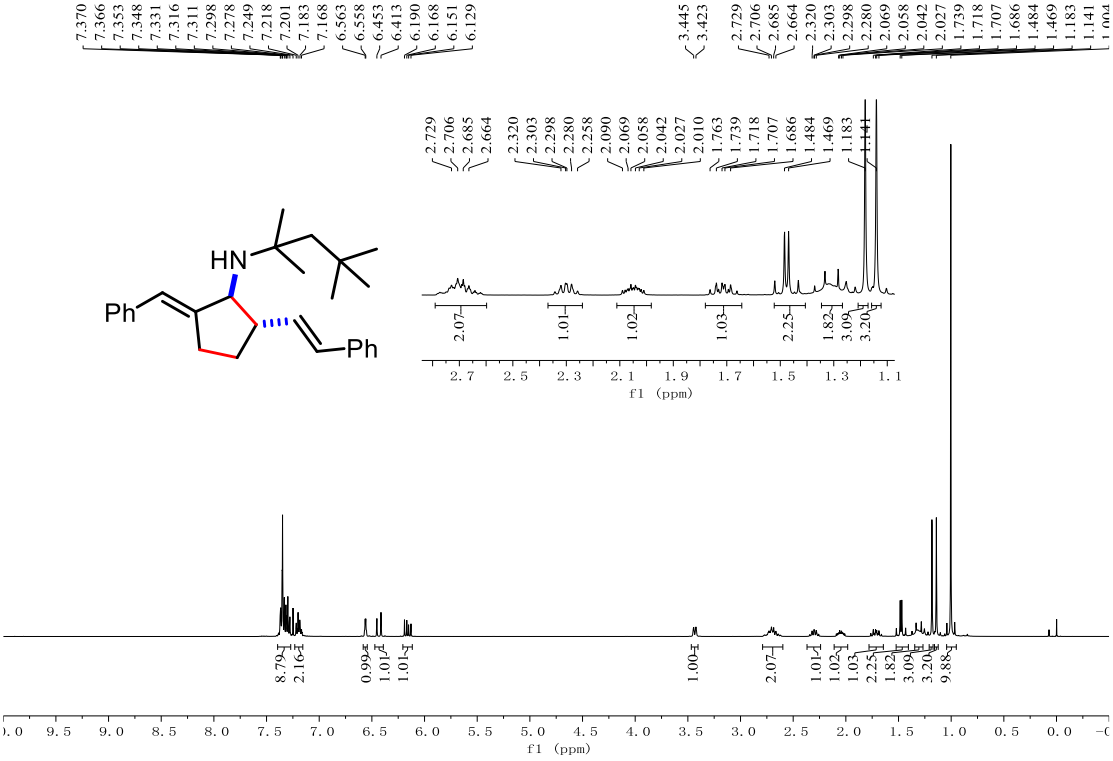
^{1}H NMR spectrum of *trans*-3va (600 MHz, $CDCl_3$)



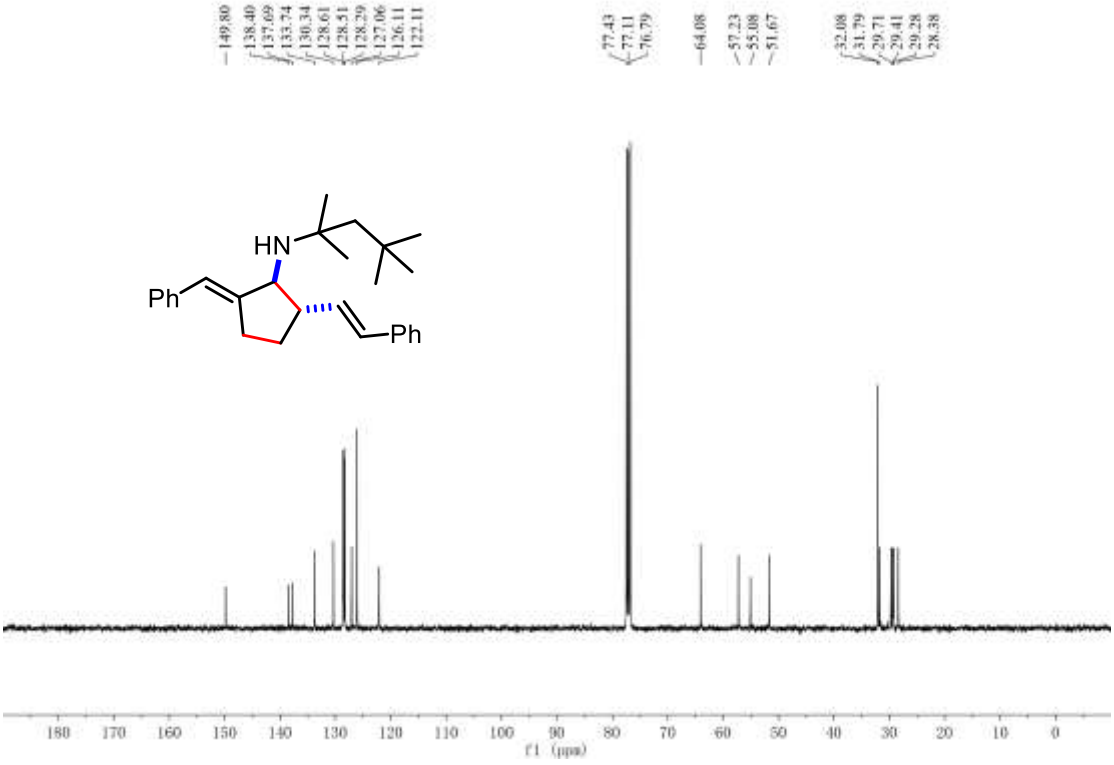
^{13}C NMR spectrum of *trans*-3va (101 MHz, $CDCl_3$)



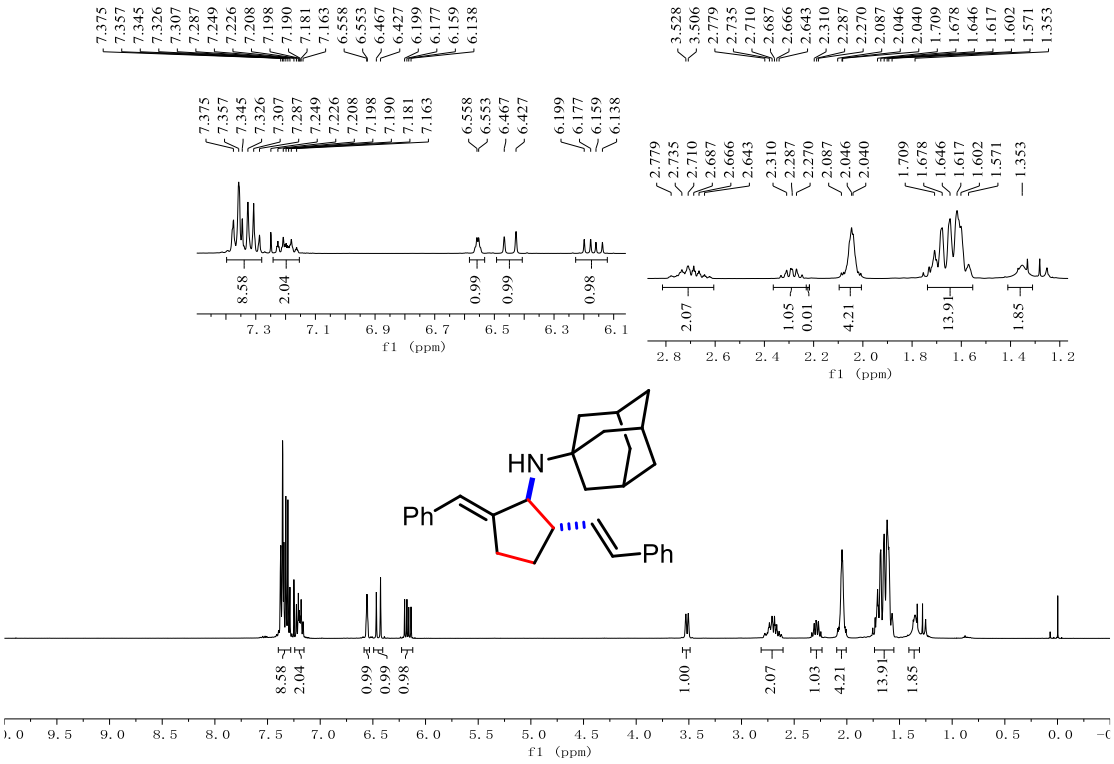
^{1}H NMR spectrum of *trans*-3wa (400 MHz, $CDCl_3$)



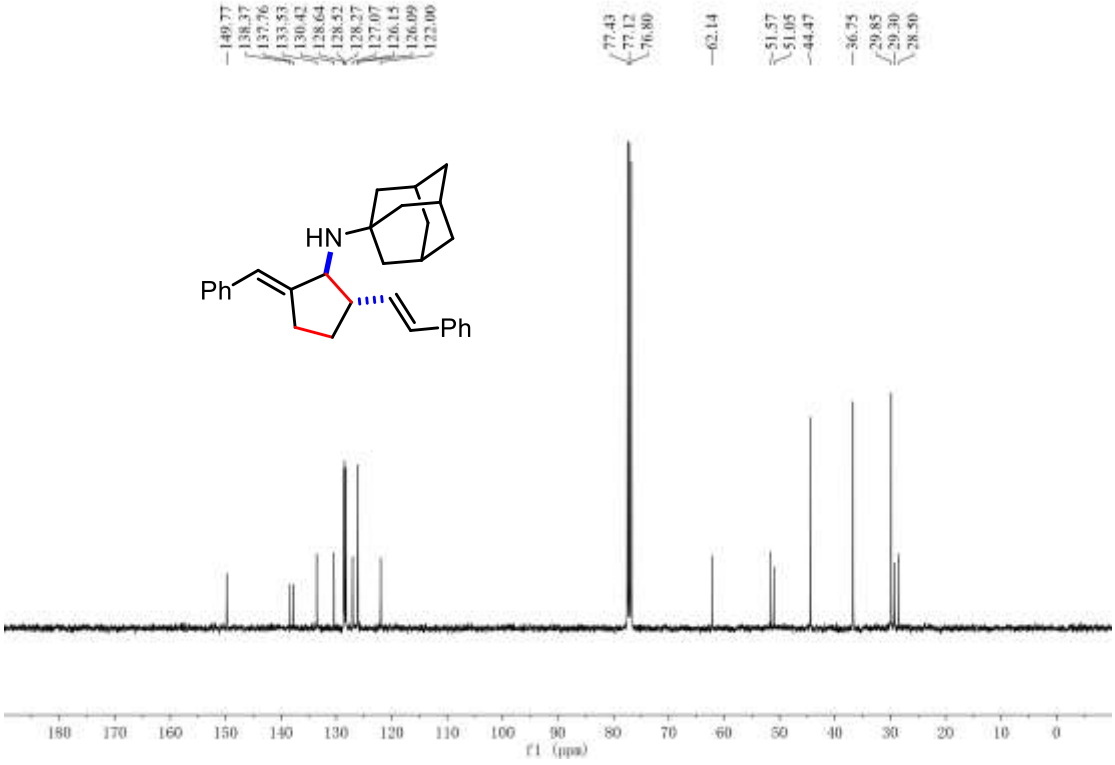
^{13}C NMR spectrum of *trans*-3wa (101 MHz, $CDCl_3$)



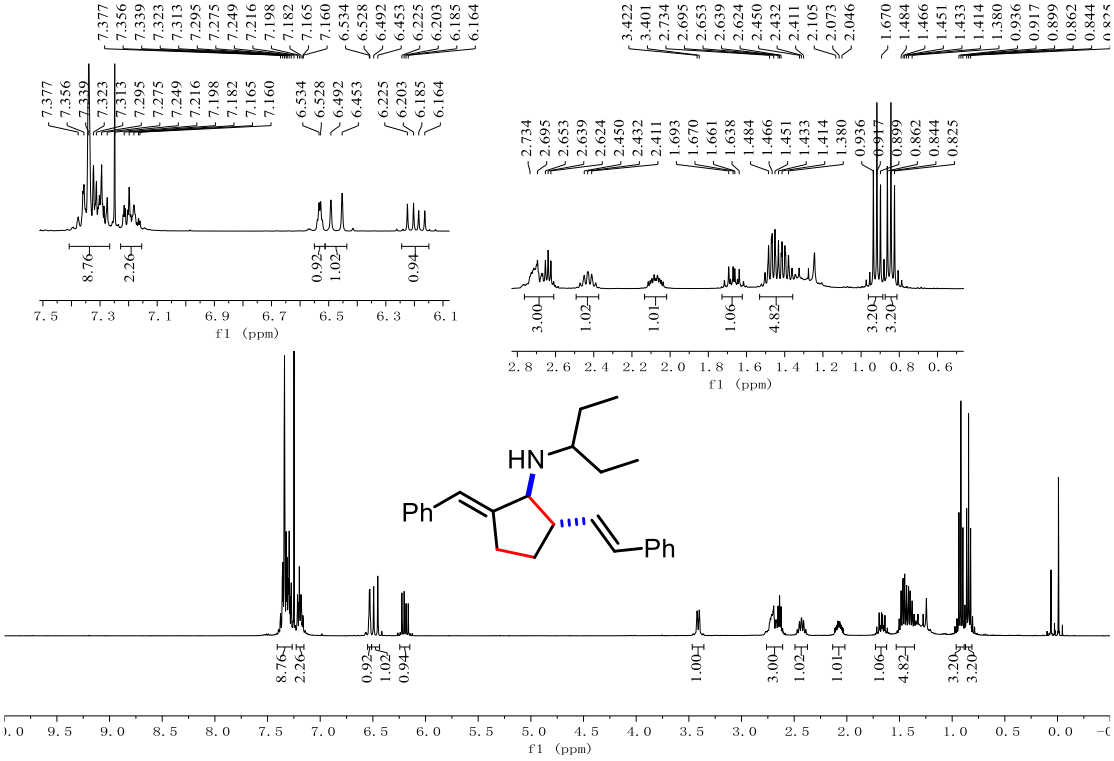
^{1}H NMR spectrum of *trans*-3xa (400 MHz, $CDCl_3$)



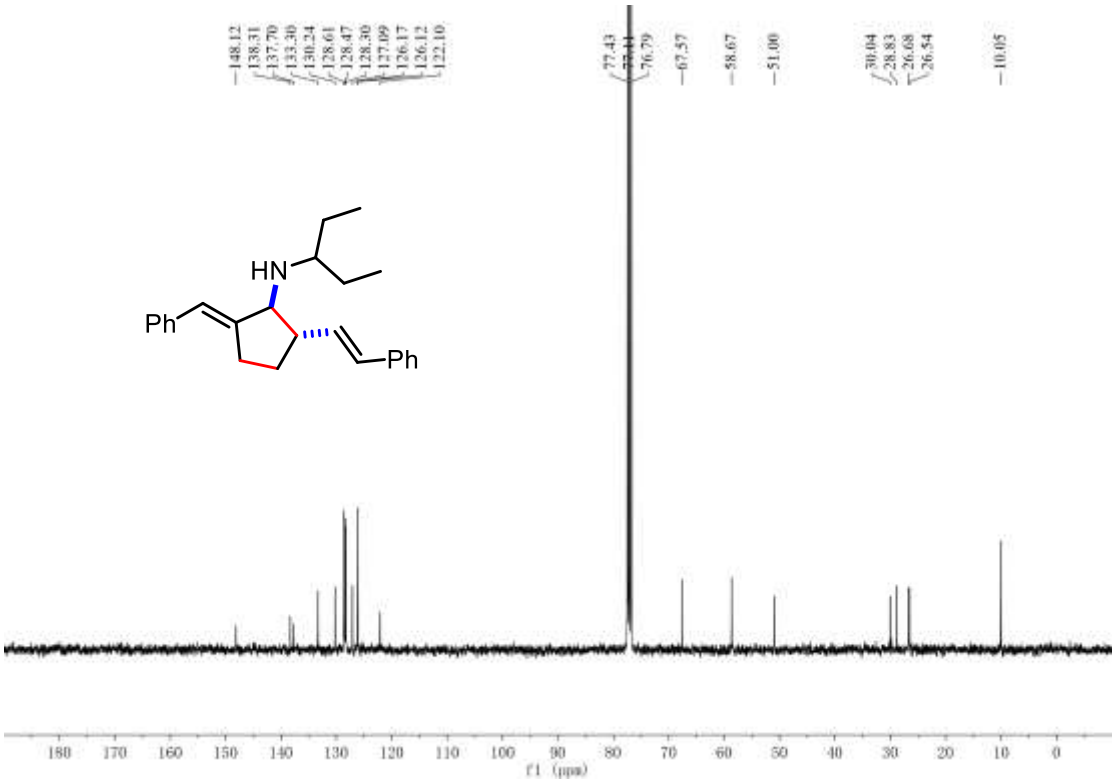
^{13}C NMR spectrum of *trans*-3xa (101 MHz, $CDCl_3$)



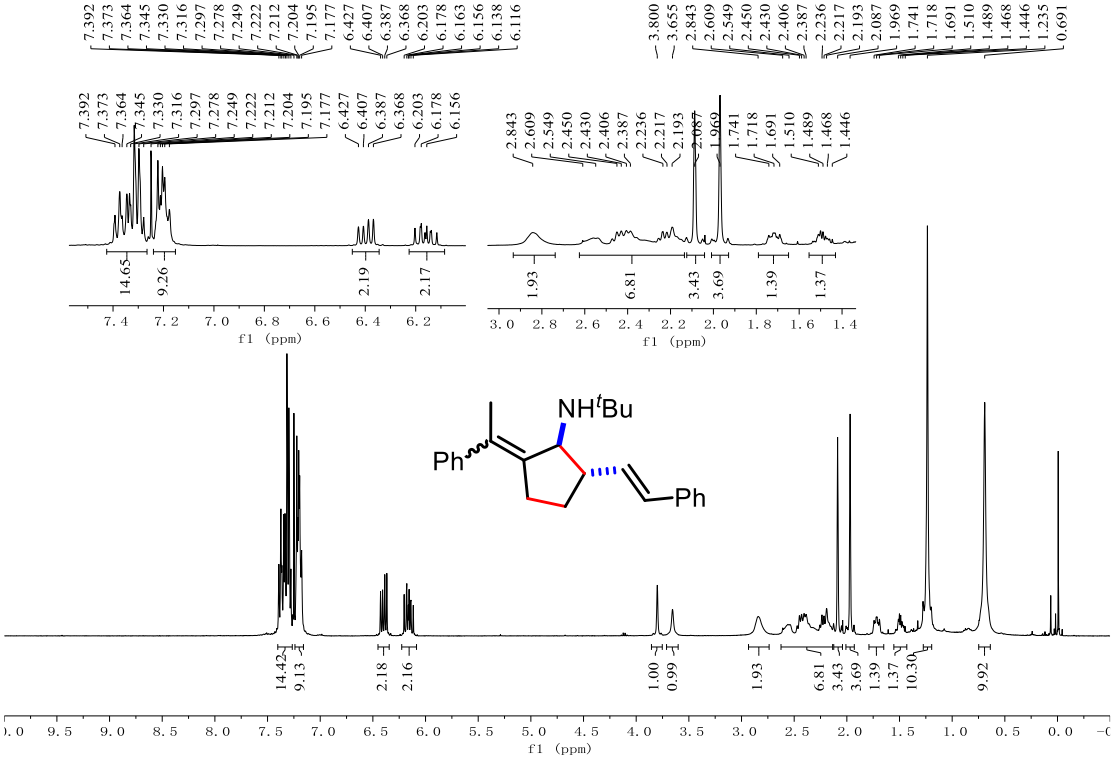
^{1}H NMR spectrum of *trans*-3ya (400 MHz, $CDCl_3$)



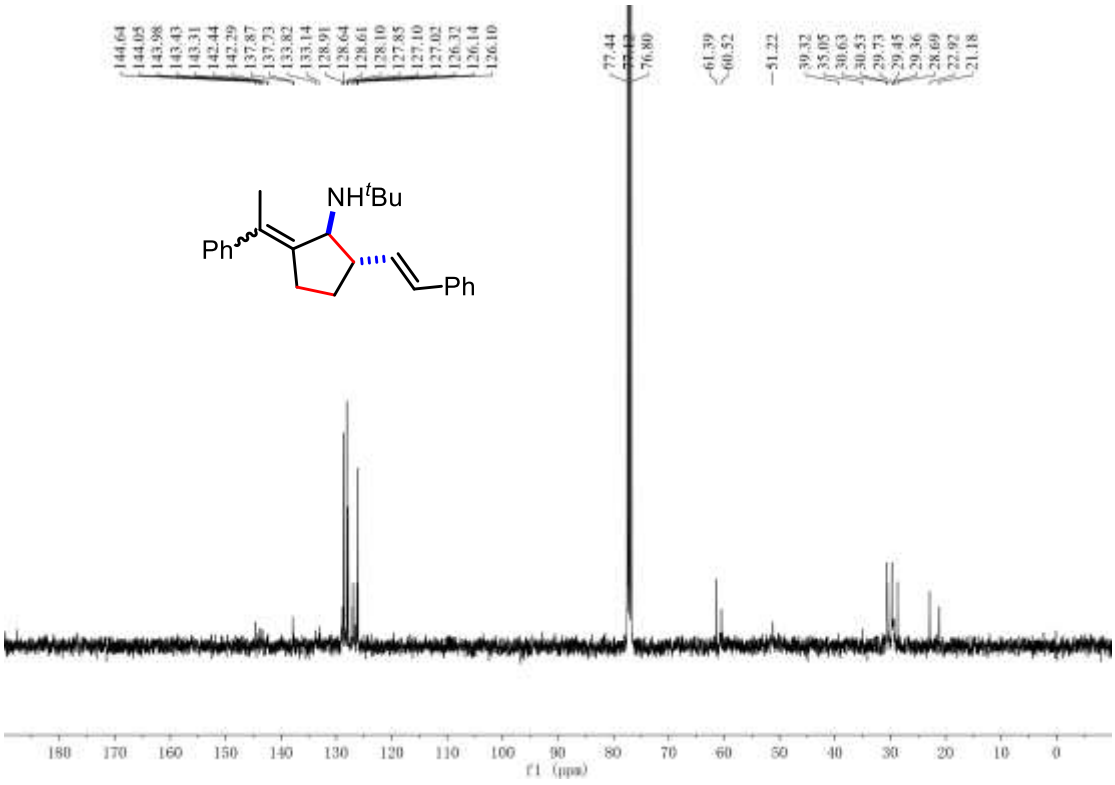
^{13}C NMR spectrum of *trans*-3ya (101 MHz, $CDCl_3$)



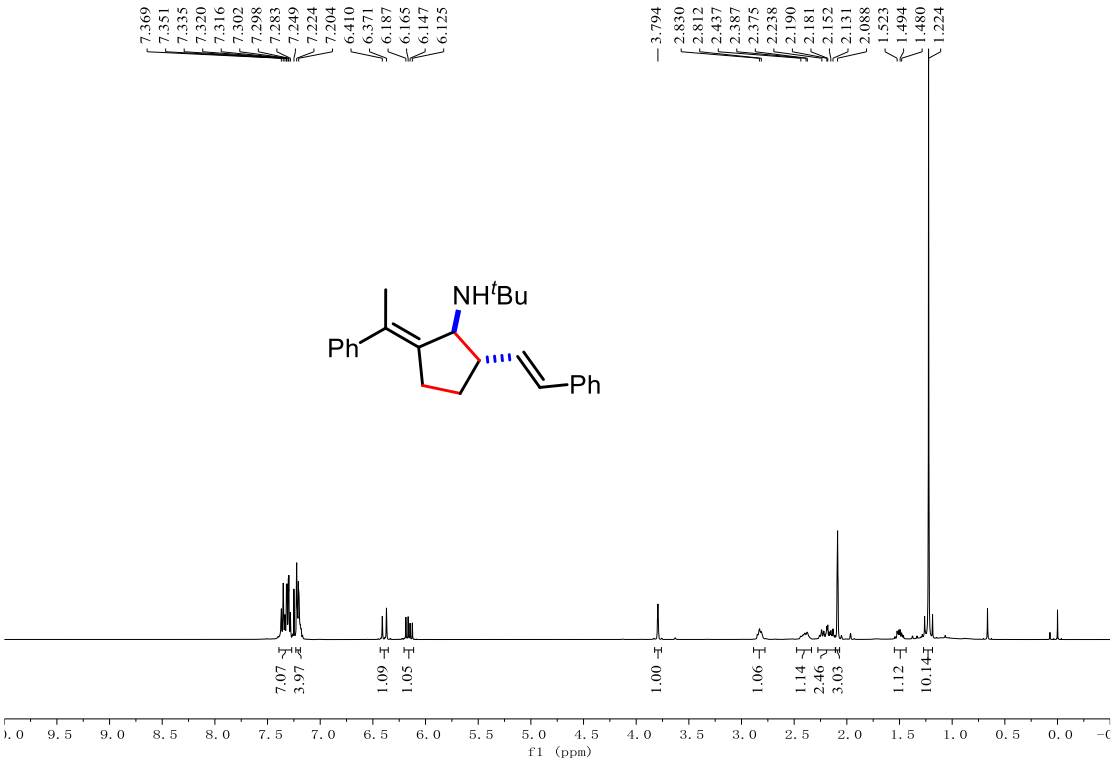
^{1}H NMR spectrum of *trans*-3za (Sc-1) (400 MHz, $CDCl_3$)



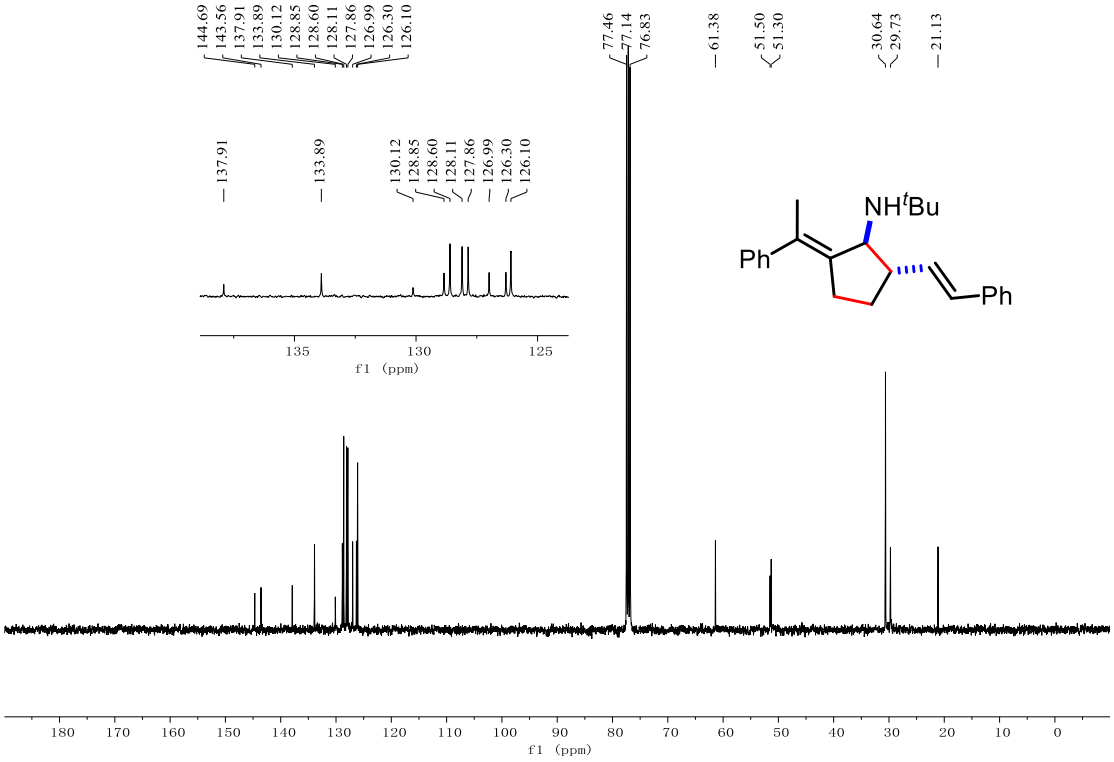
^{13}C NMR spectrum of *trans*-3za (Sc-1) (101 MHz, $CDCl_3$)



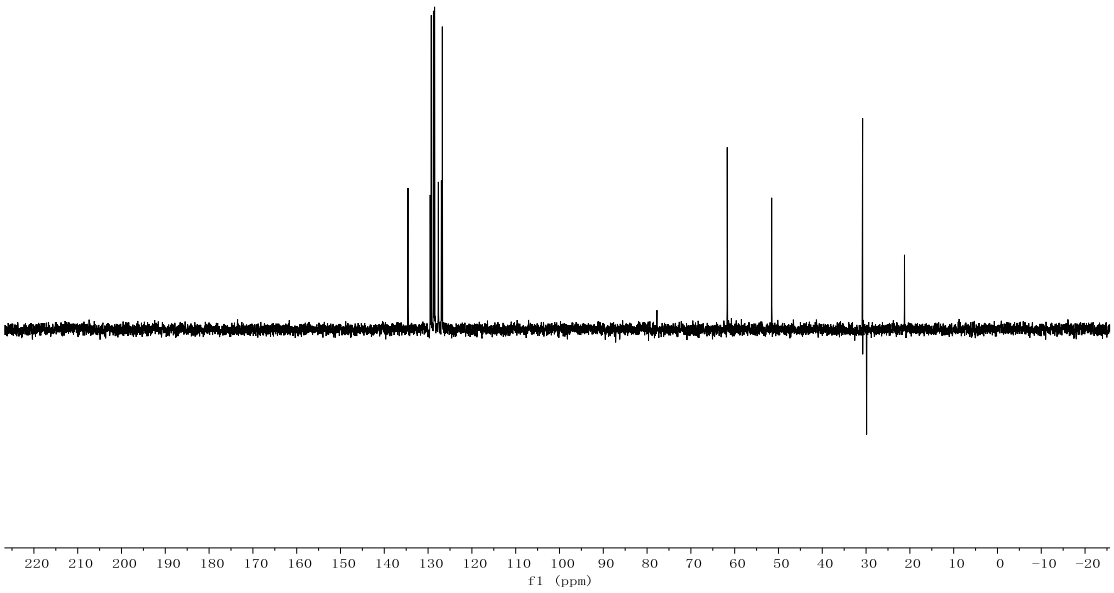
^{1}H NMR spectrum of *trans*-3za (Y-2) (400 MHz, $CDCl_3$)



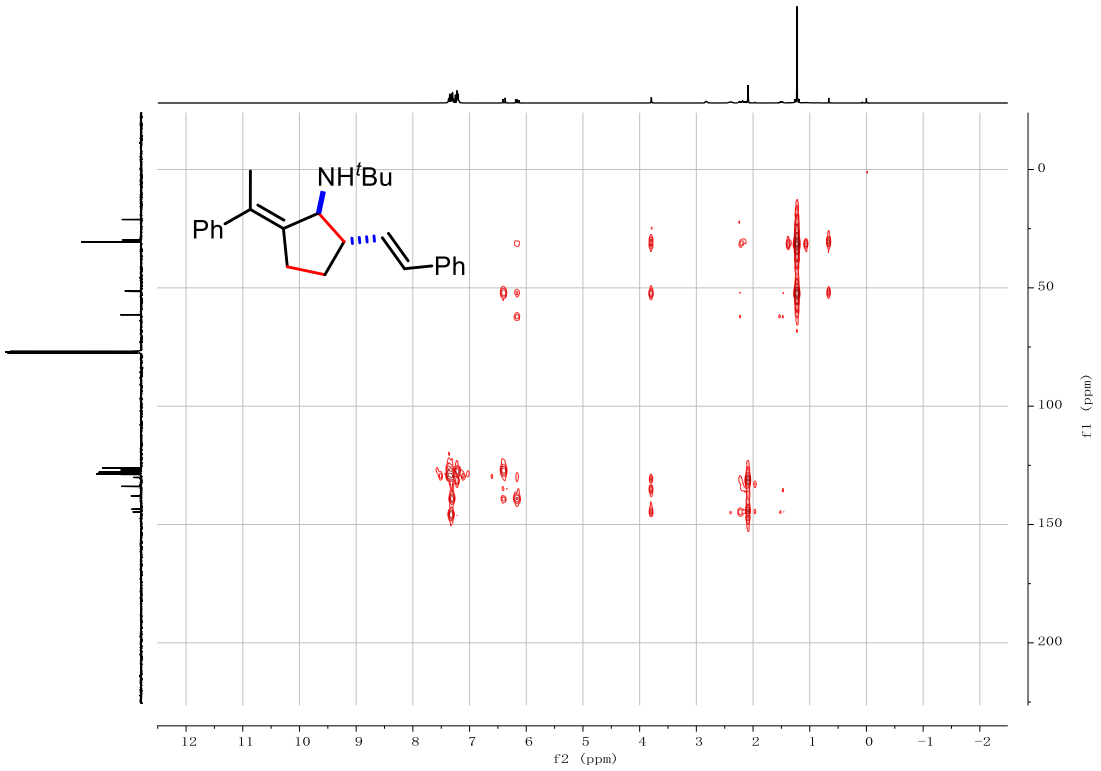
^{13}C NMR spectrum of *trans*-3za (Y-2) (101 MHz, $CDCl_3$)



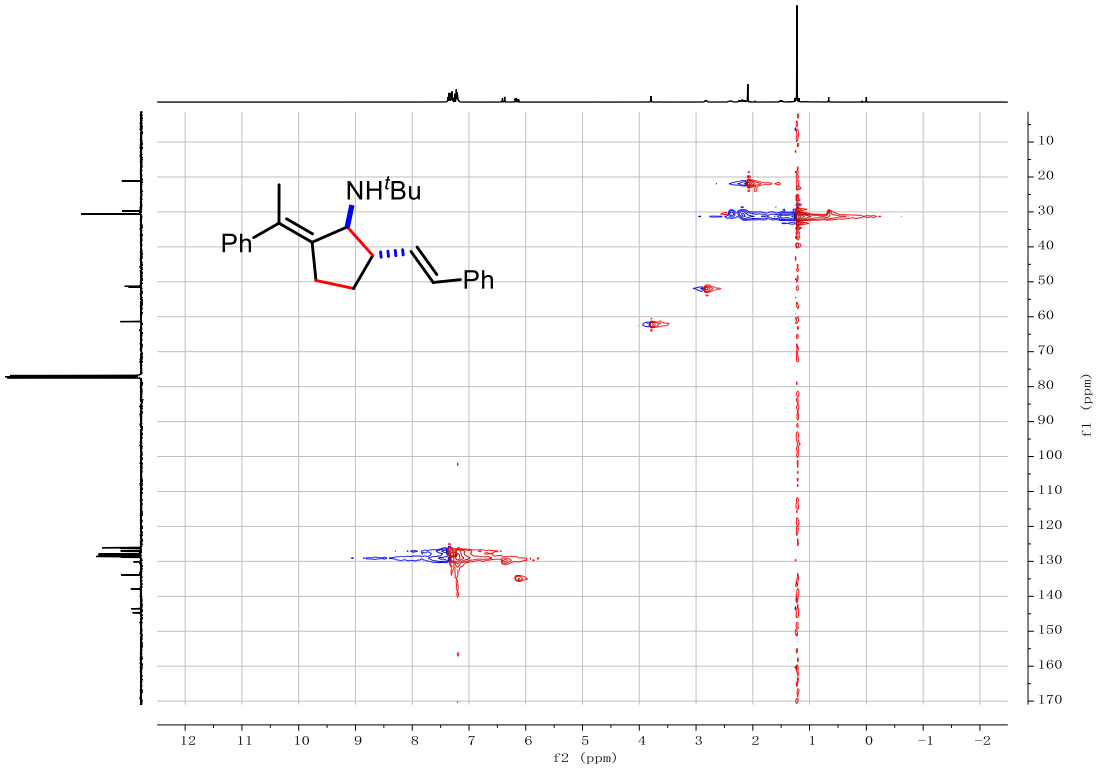
^{135}DEPT NMR spectrum of *trans*-3za (Y-2)



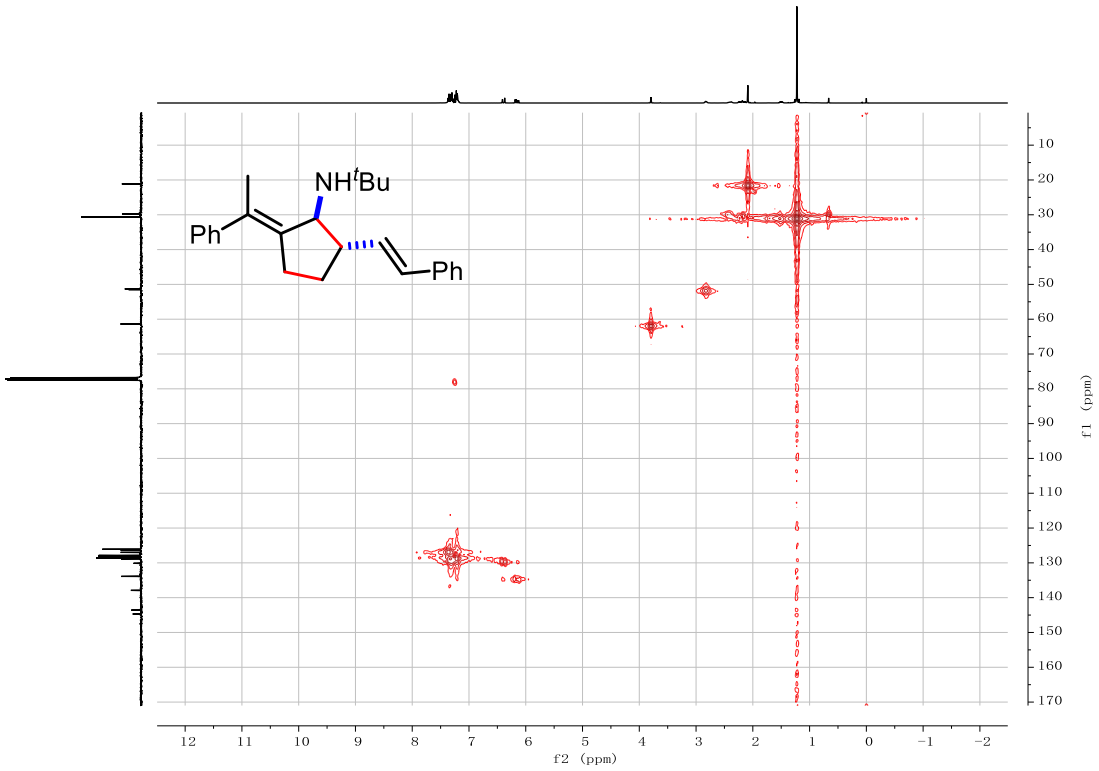
HMBC spectrum of *trans*-3za (Y-2)



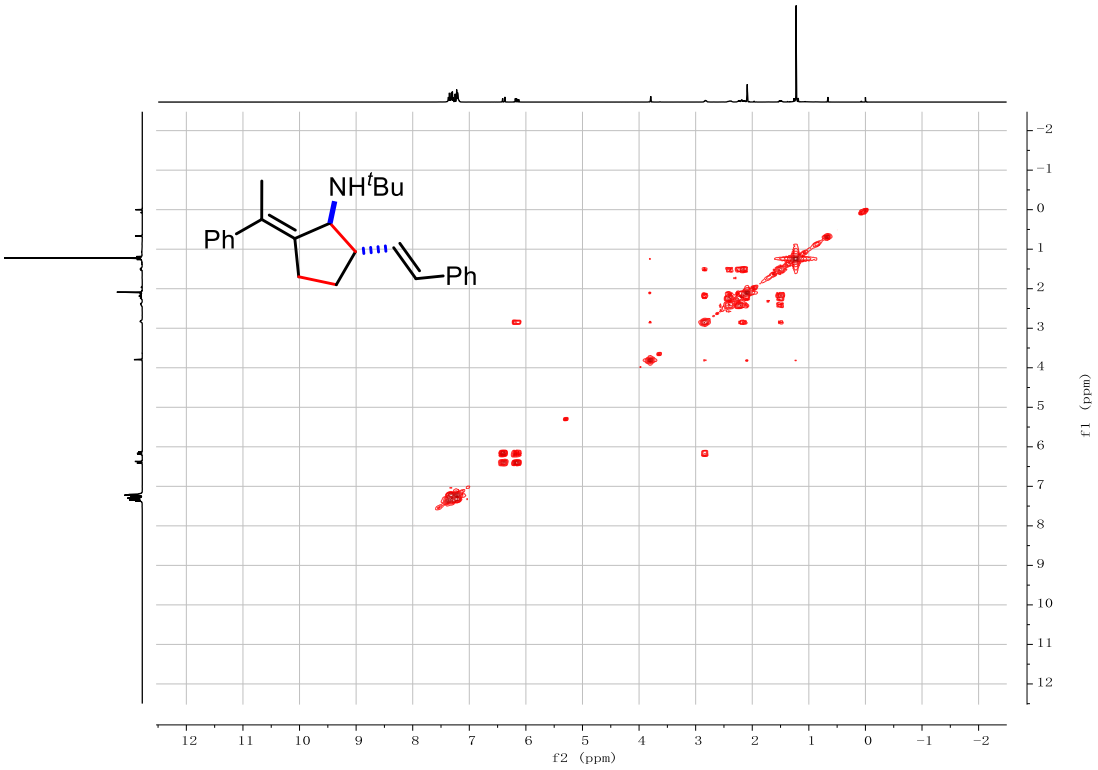
HSQC spectrum of *trans*-3za (Y-2)



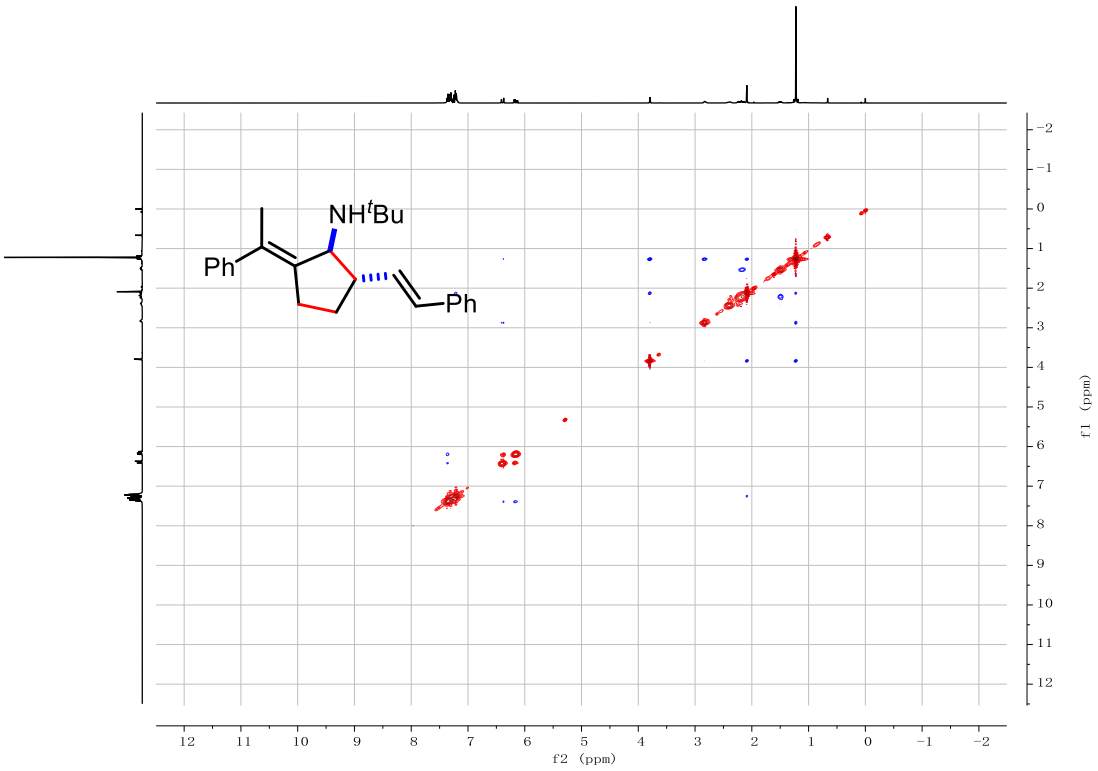
HMQC spectrum of *trans*-3za (Y-2)



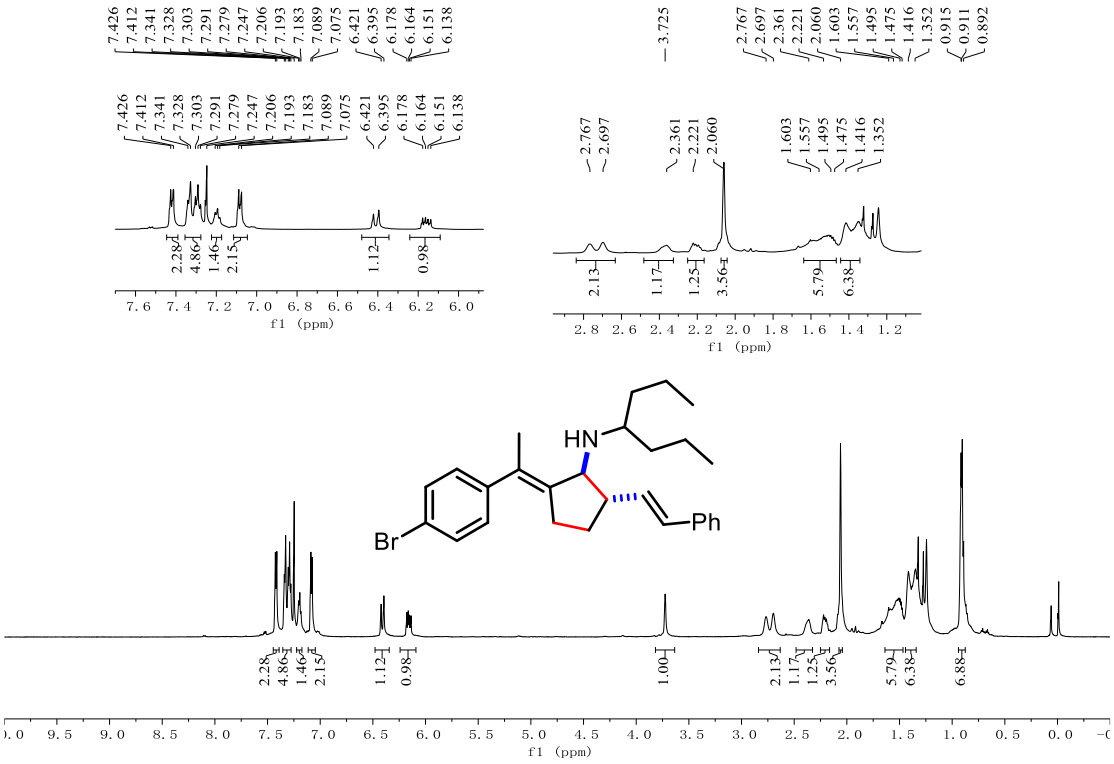
COSY spectrum of *trans*-3za (Y-2)



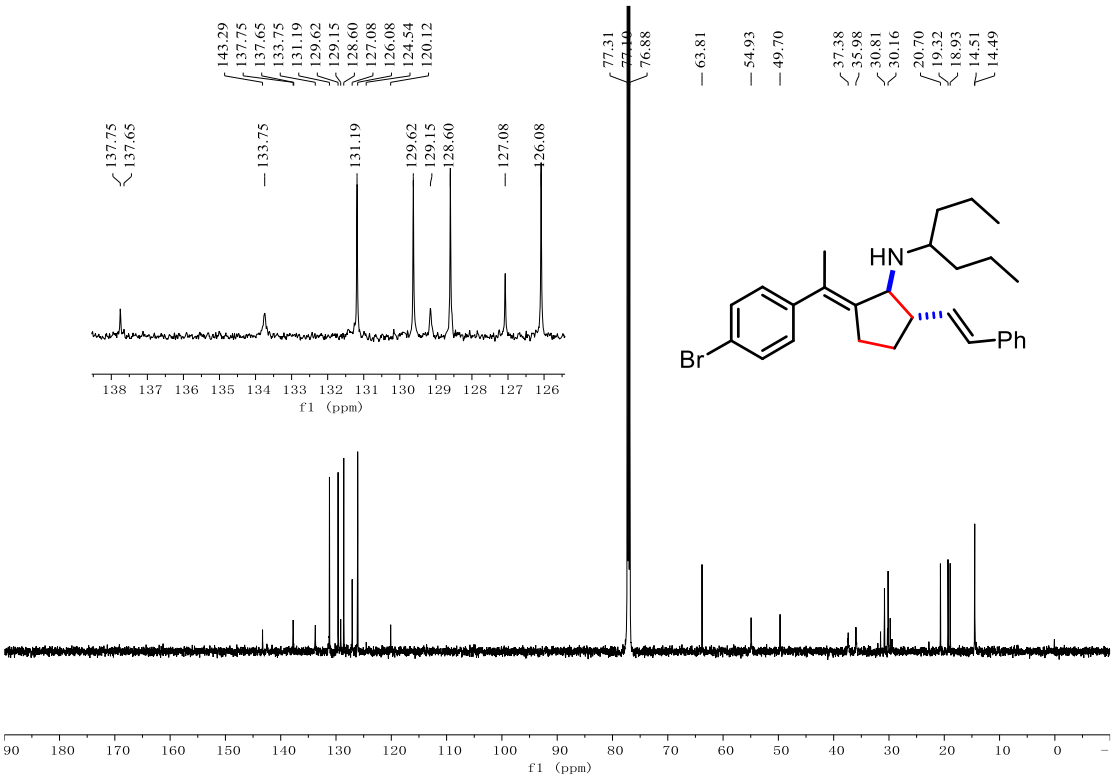
NOE spectrum of *trans*-3za (Y-2)



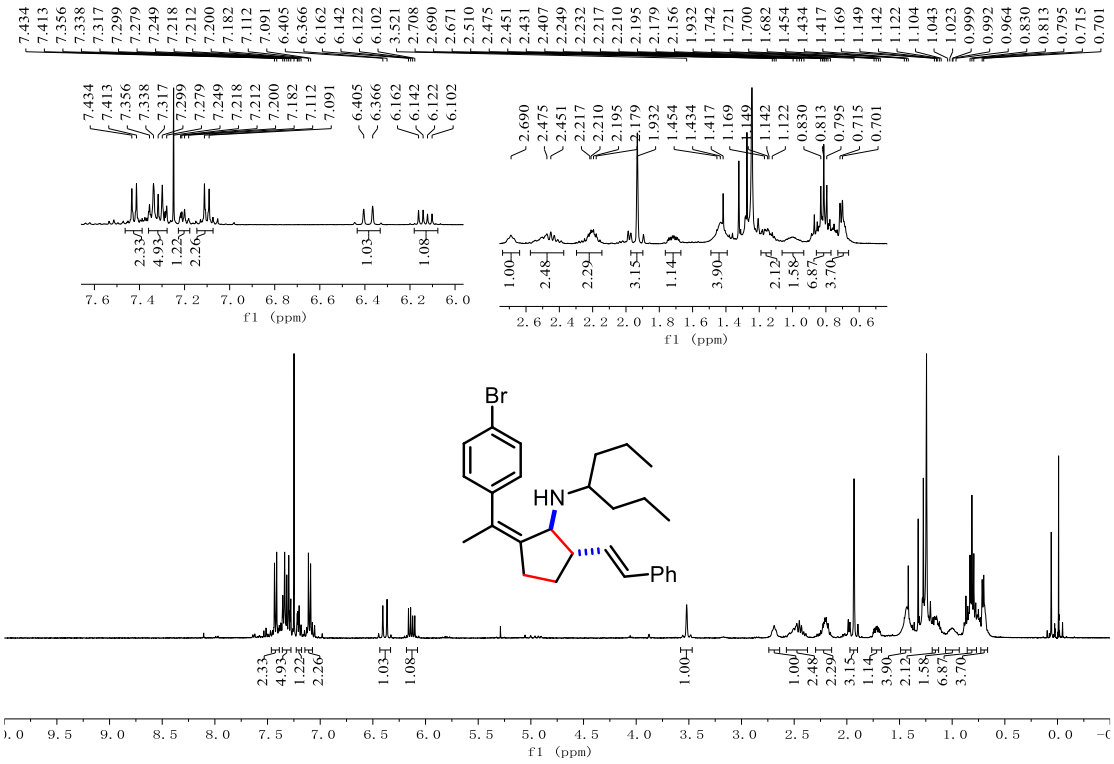
^{1}H NMR spectrum of *trans,E*-3aaa (Y-2) (400 MHz, $CDCl_3$)



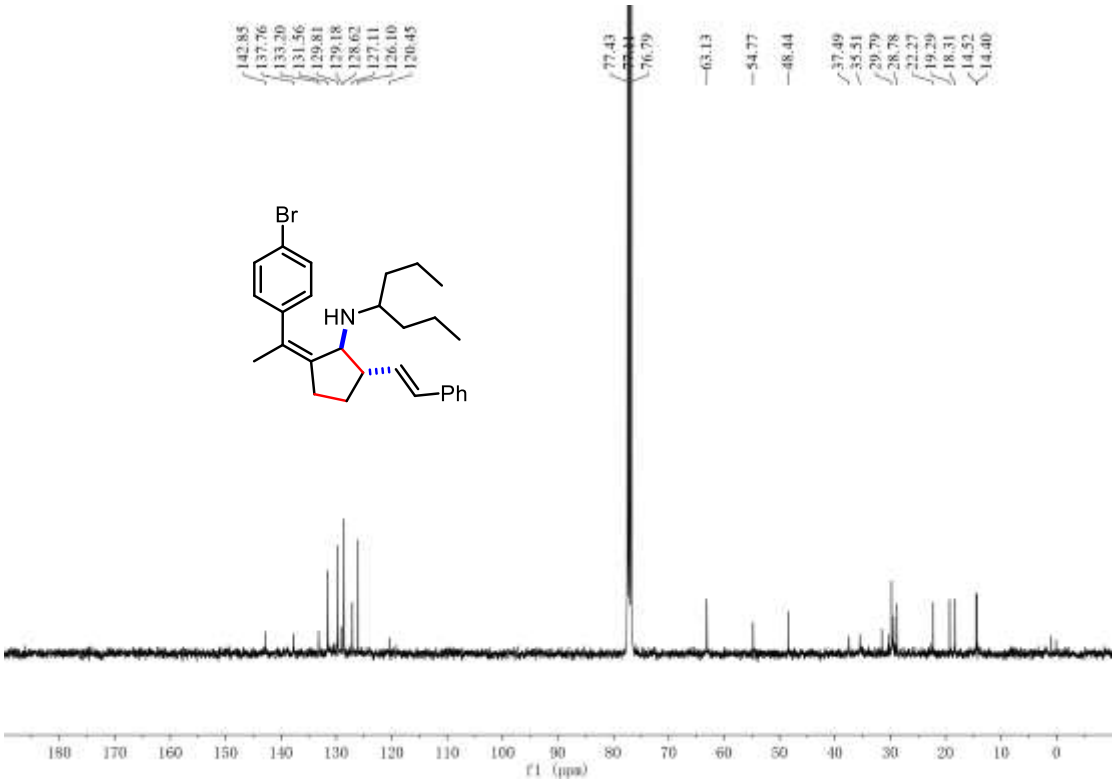
^{13}C NMR spectrum of *trans,E*-3aaa (Y-2) (101 MHz, $CDCl_3$)



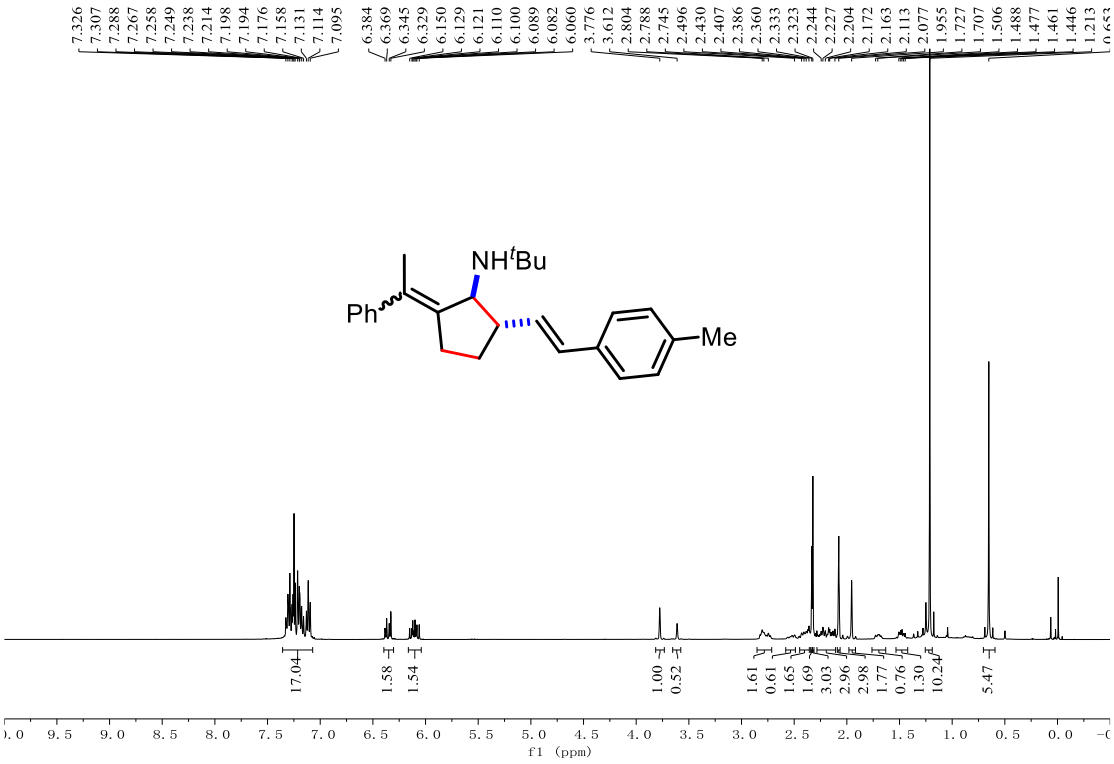
^{1}H NMR spectrum of *trans,Z*-3aaa (Y-2) (400 MHz, $CDCl_3$)



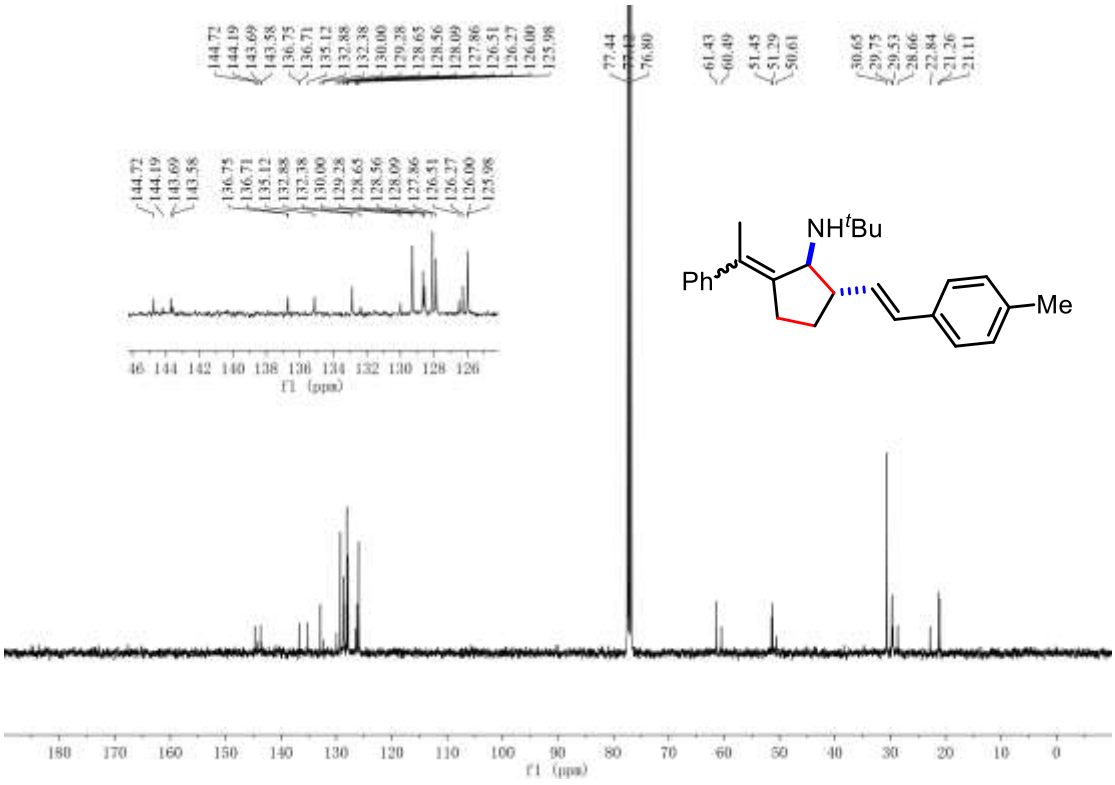
^{13}C NMR spectrum of *trans,Z*-3aaa (Y-2) (101 MHz, $CDCl_3$)



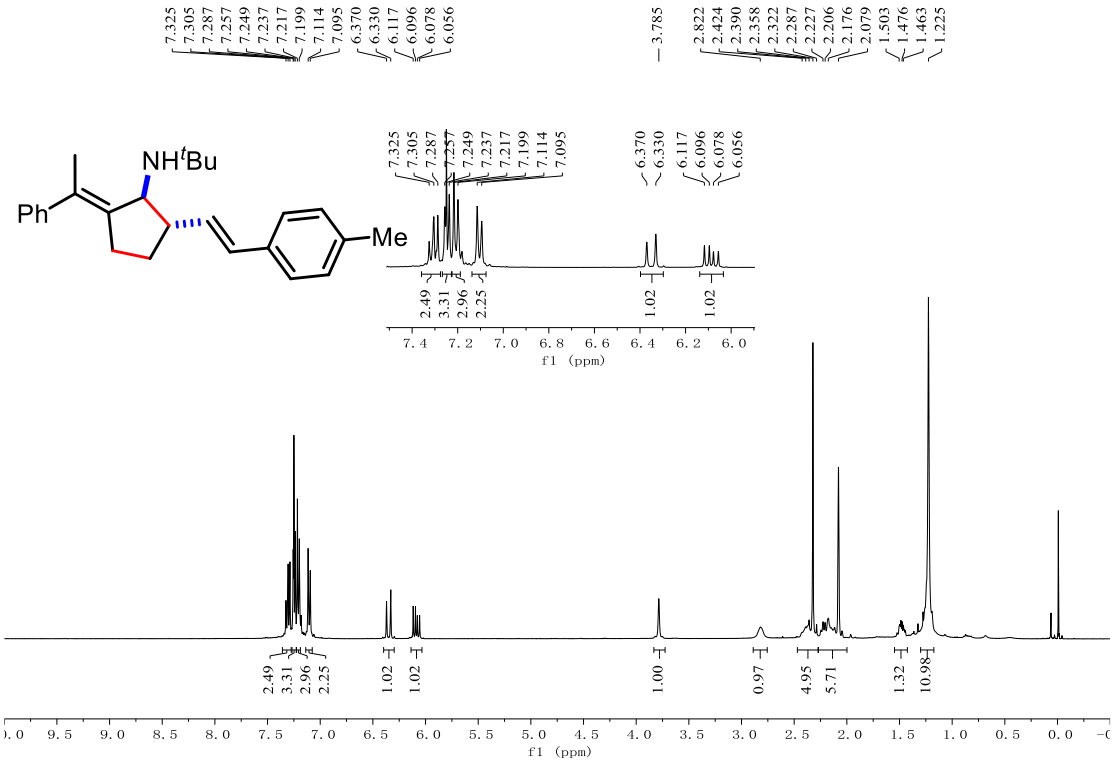
^{1}H NMR spectrum of *trans*-3aba (Sc-1) (400 MHz, $CDCl_3$)



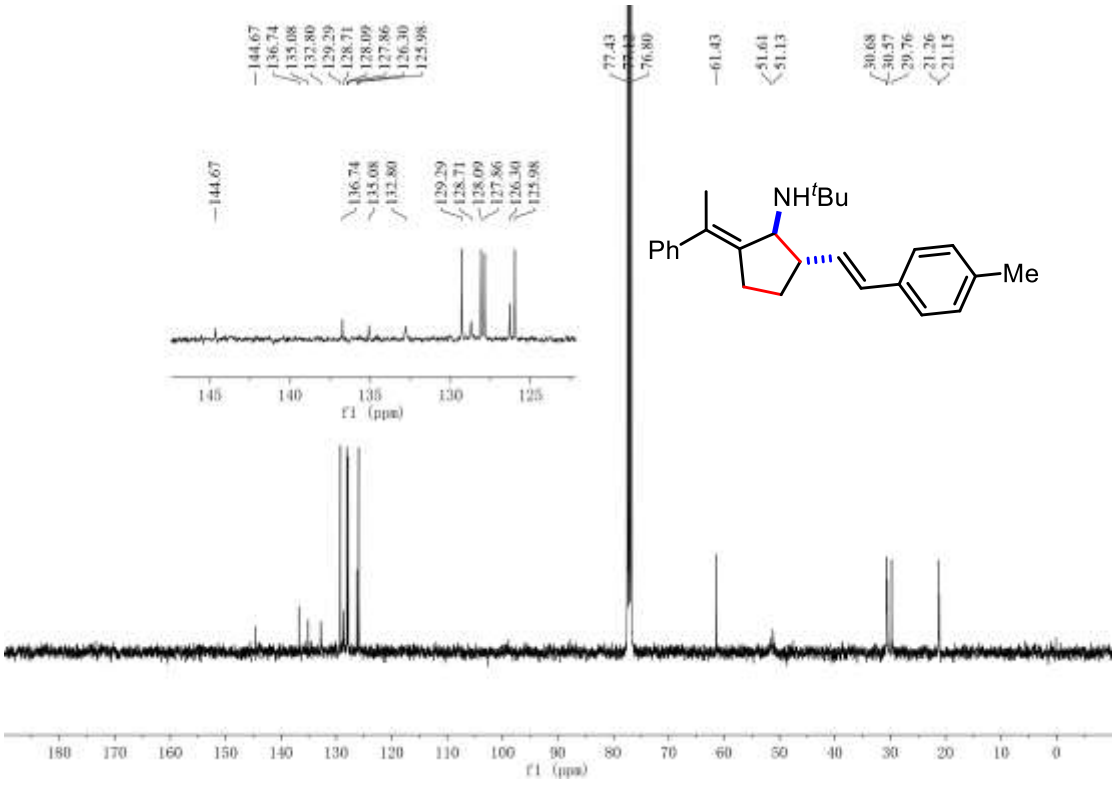
^{13}C NMR spectrum of *trans*-3aba (Sc-1) (101 MHz, $CDCl_3$)



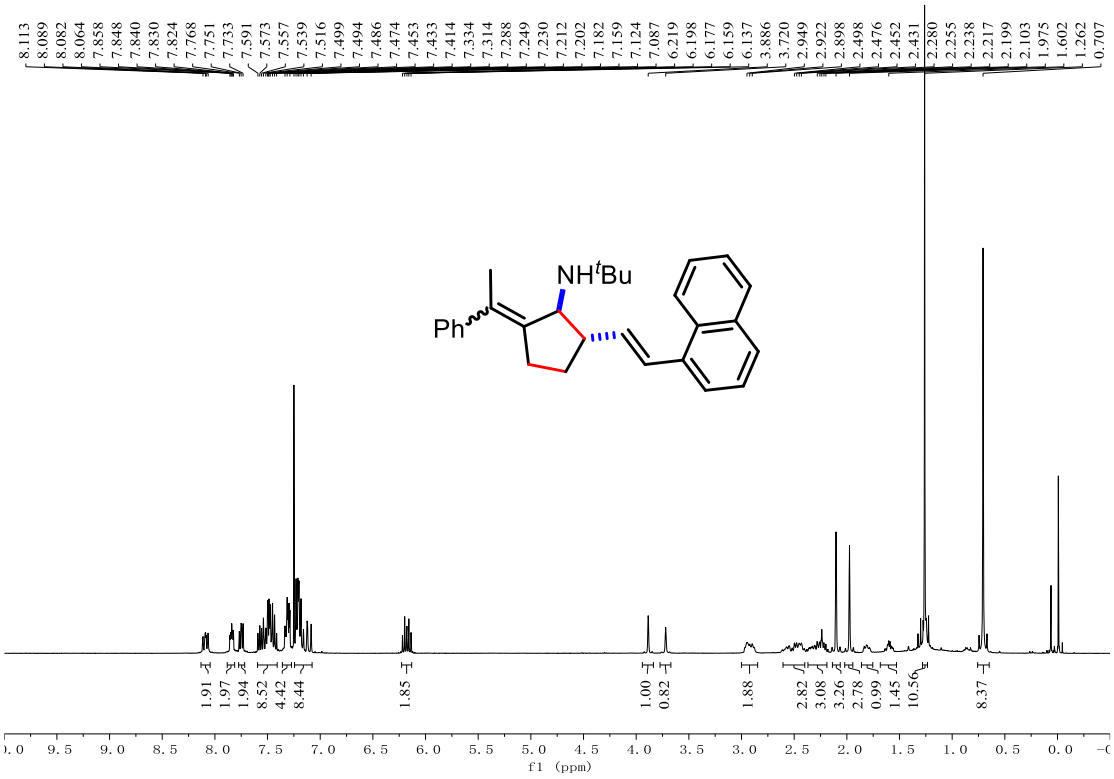
^{1}H NMR spectrum of *trans*-3aba (Y-2) (400 MHz, $CDCl_3$)



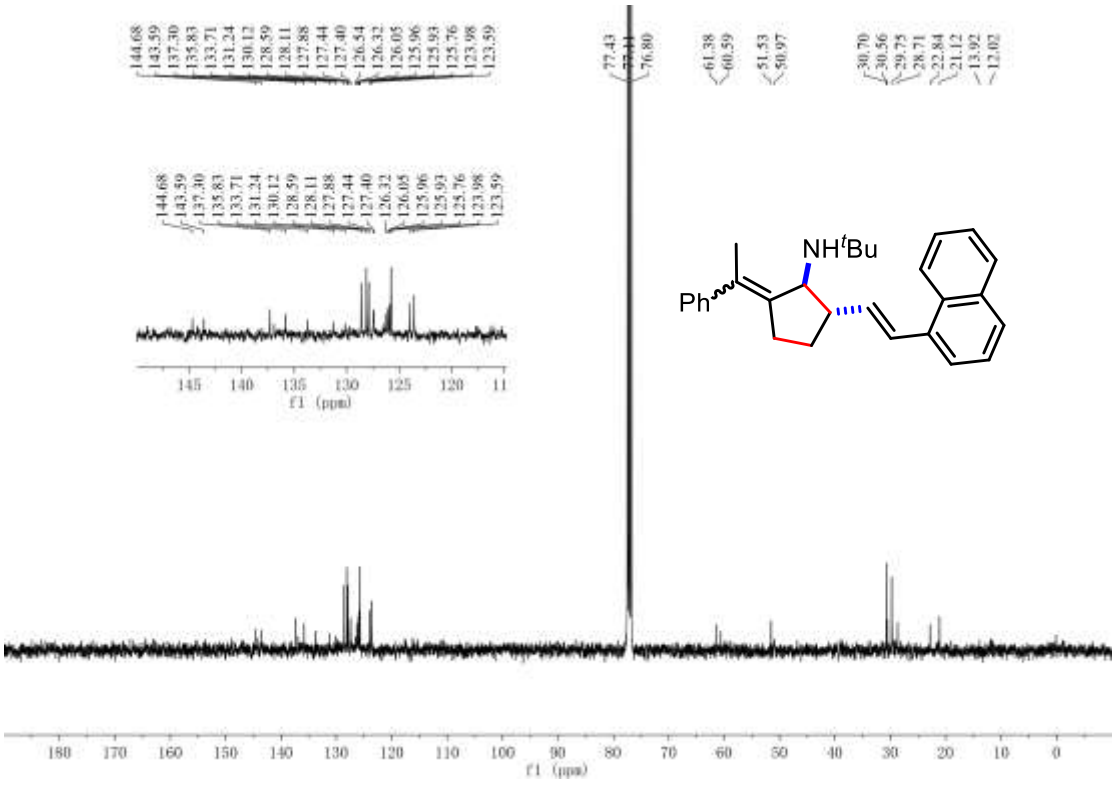
^{13}C NMR spectrum of *trans*-3aba (Y-2) (101 MHz, $CDCl_3$)



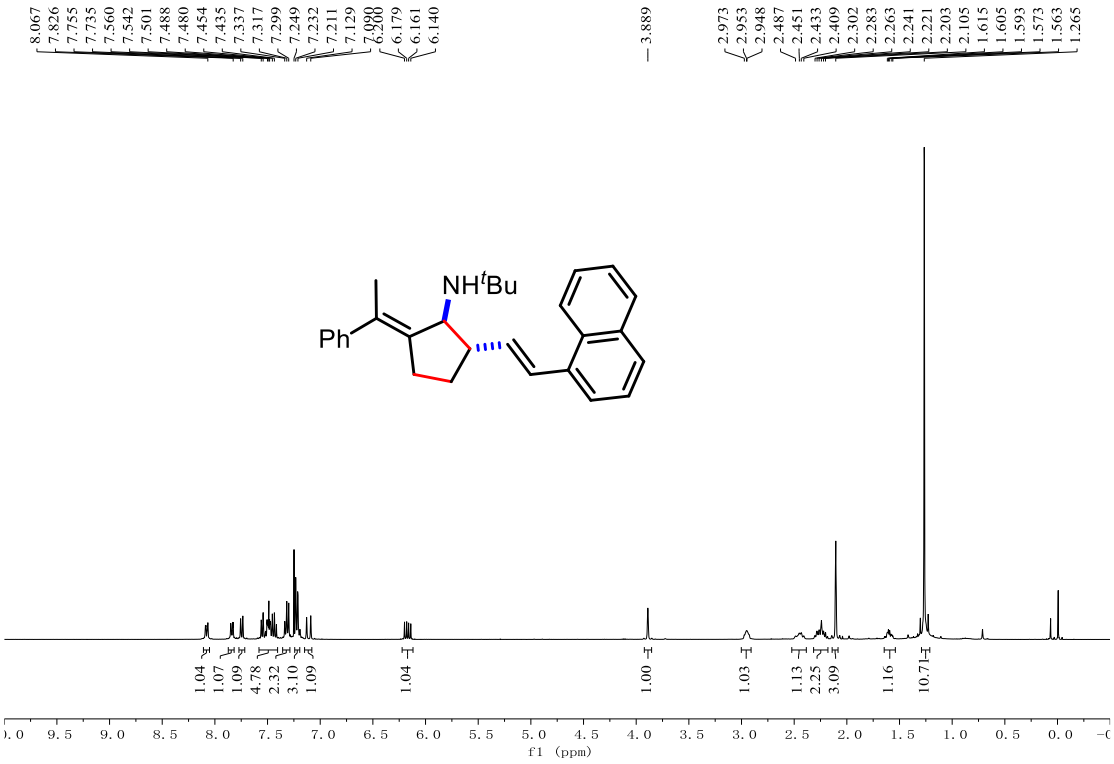
^{1}H NMR spectrum of *trans*-3aca (Sc-1) (400 MHz, $CDCl_3$)



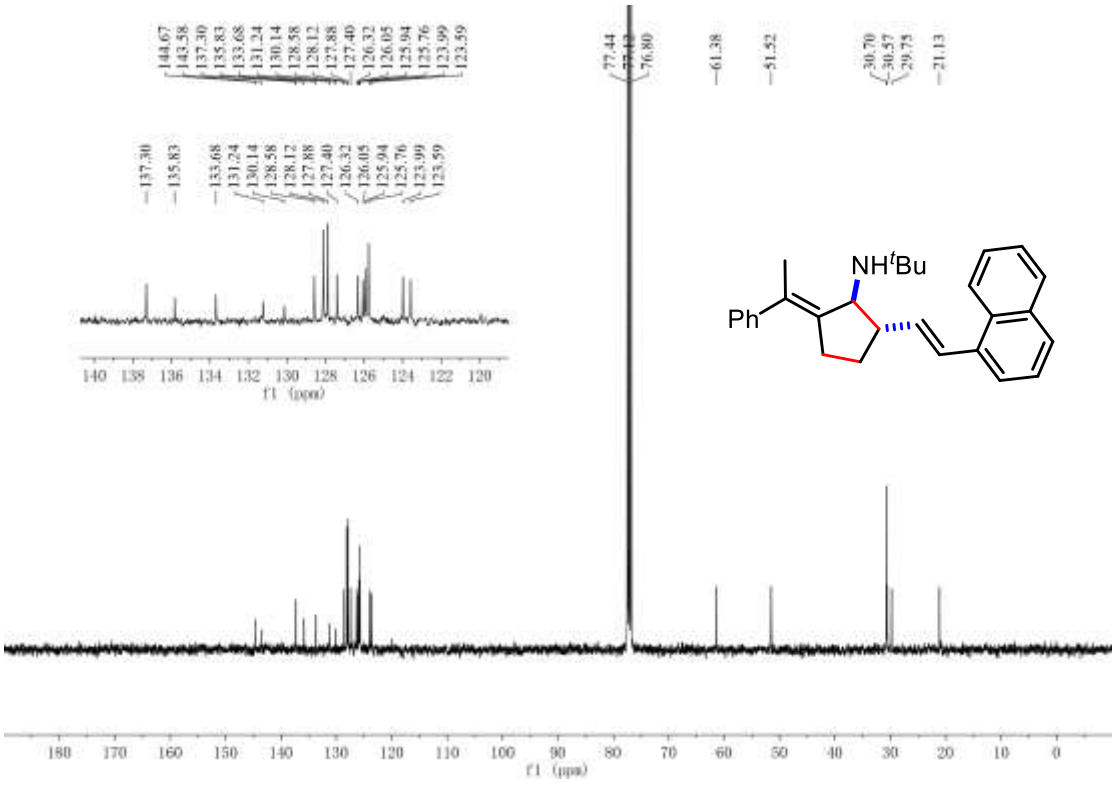
^{13}C NMR spectrum of *trans*-3aca (Sc-1) (101 MHz, $CDCl_3$)



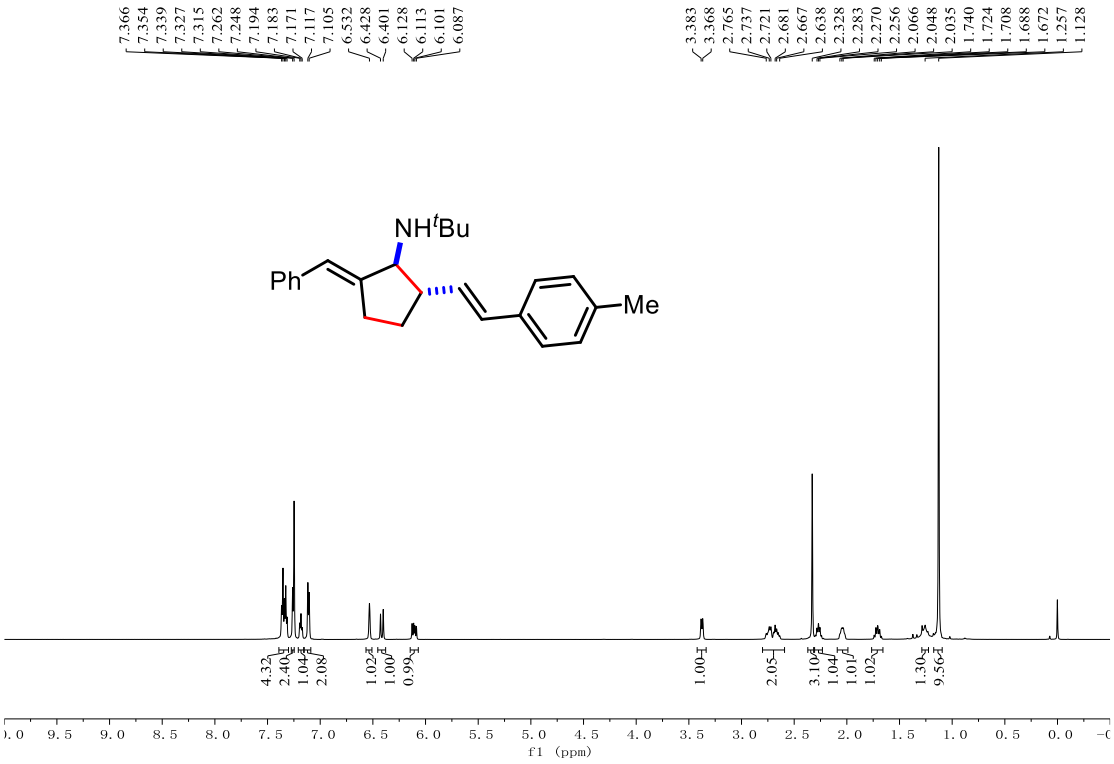
^{1}H NMR spectrum of *trans*-3aca (Y-2) (400 MHz, $CDCl_3$)



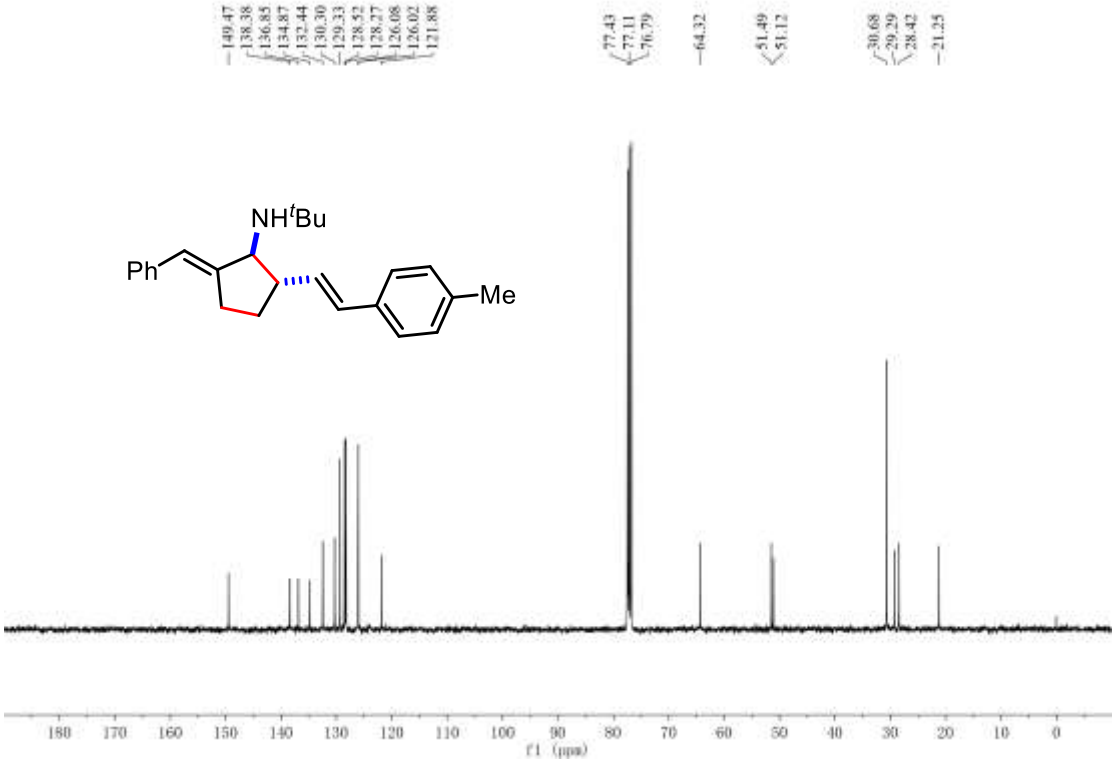
^{13}C NMR spectrum of *trans*-3aca (Y-2) (101 MHz, $CDCl_3$)



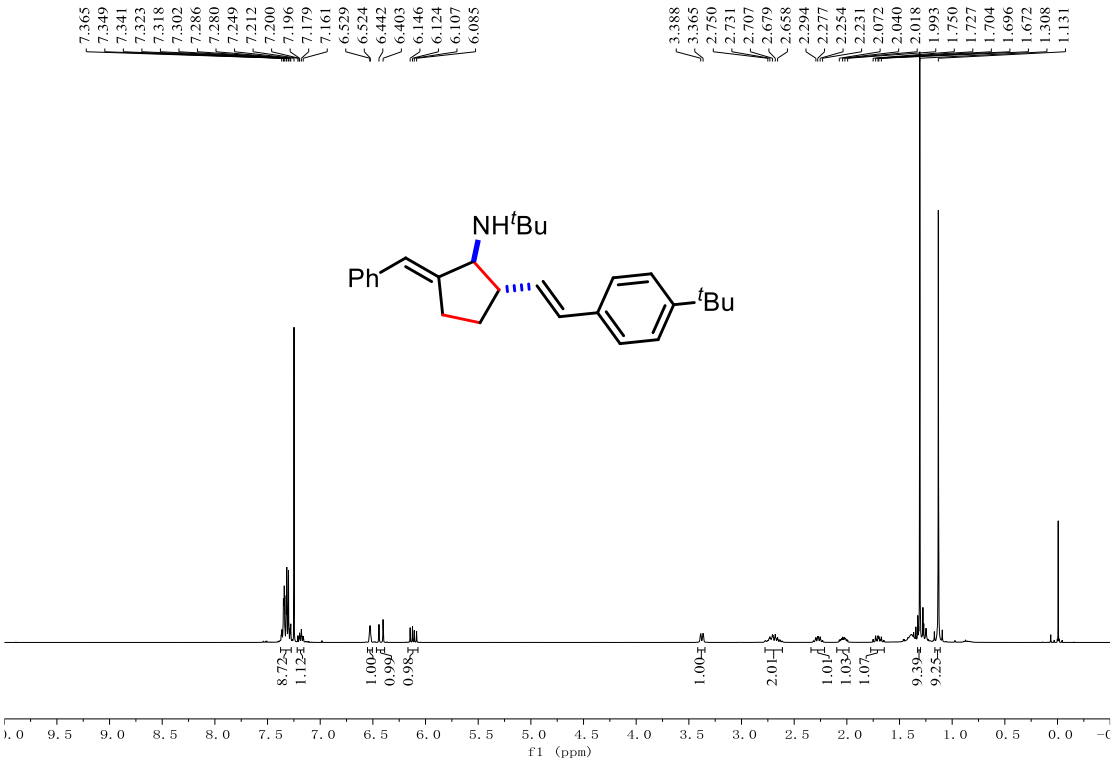
^{1}H NMR spectrum of *trans*-3ab (600 MHz, $CDCl_3$)



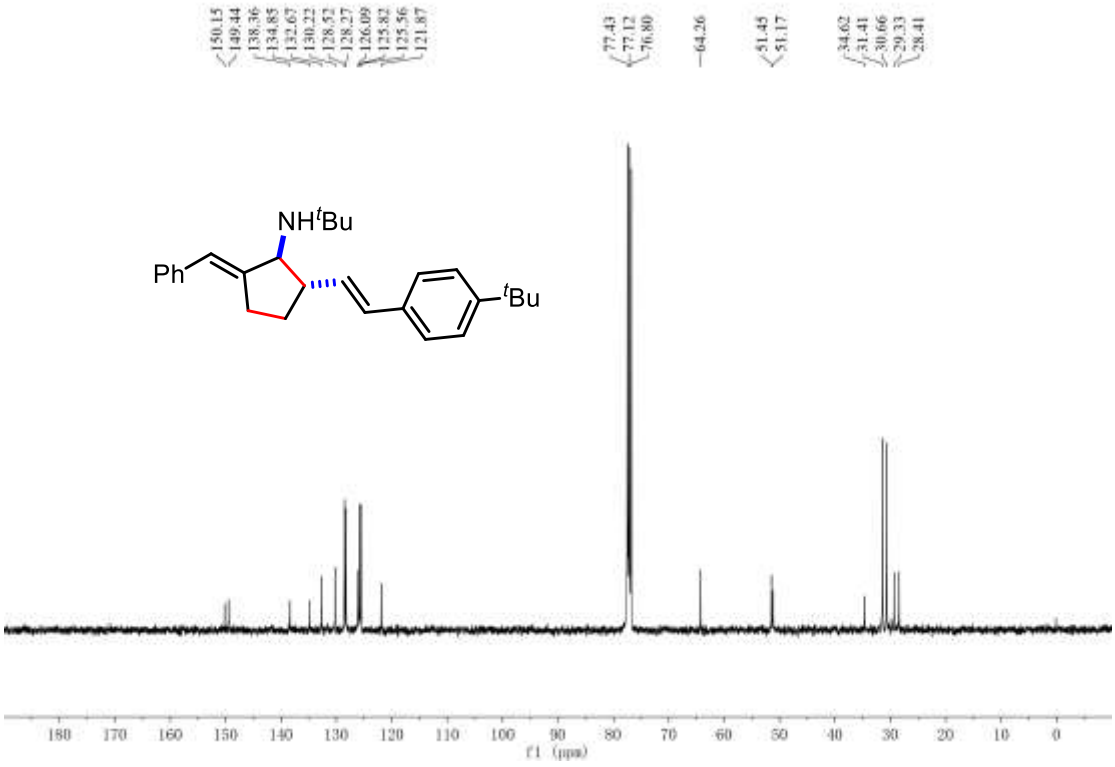
^{13}C NMR spectrum of *trans*-3ab (101 MHz, $CDCl_3$)



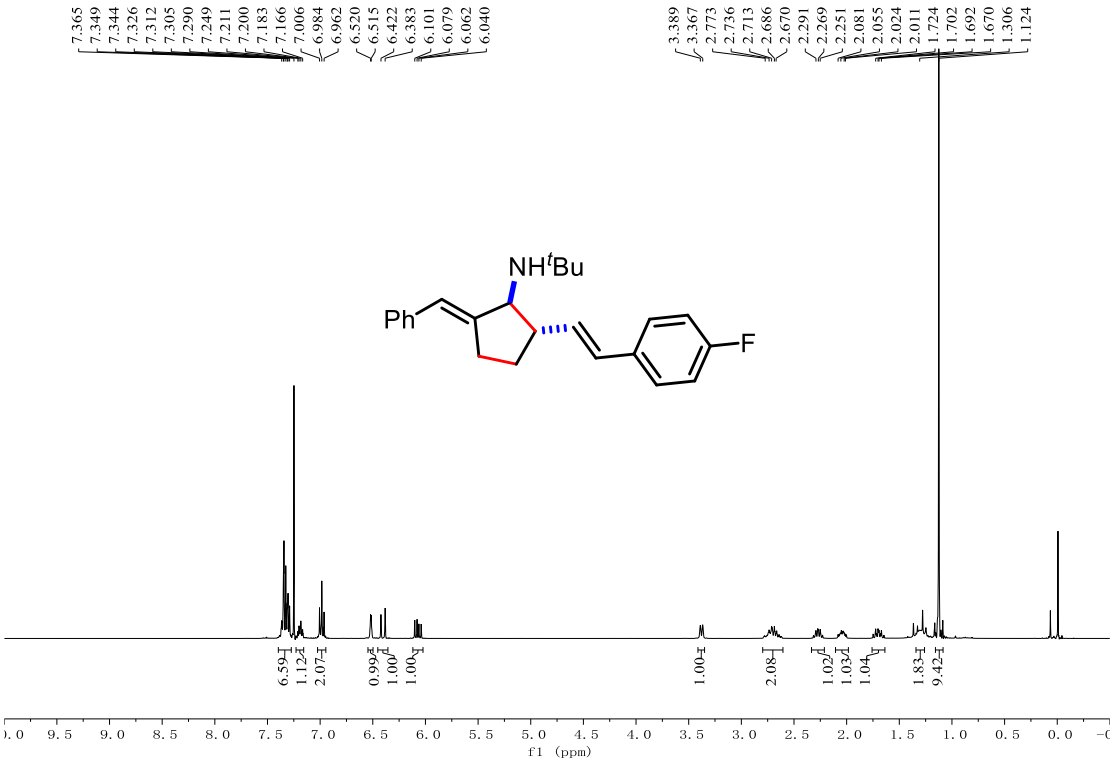
^{1}H NMR spectrum of *trans*-3ac (400 MHz, $CDCl_3$)



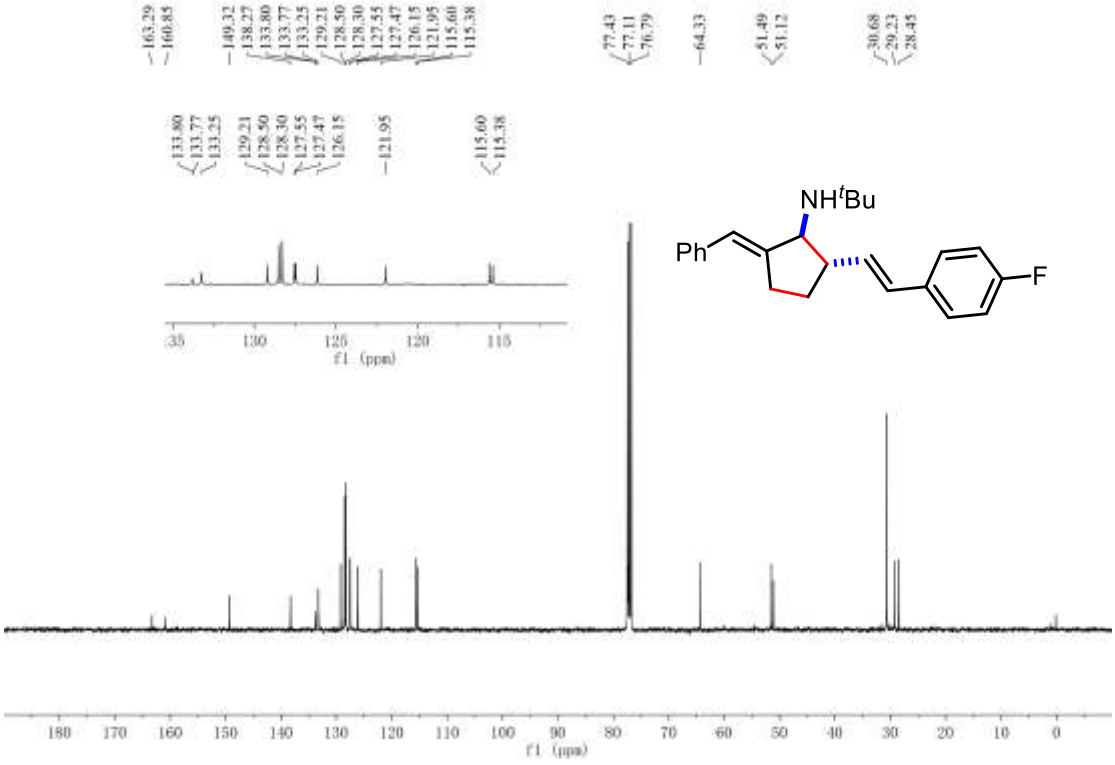
^{13}C NMR spectrum of *trans*-3ac (101 MHz, $CDCl_3$)



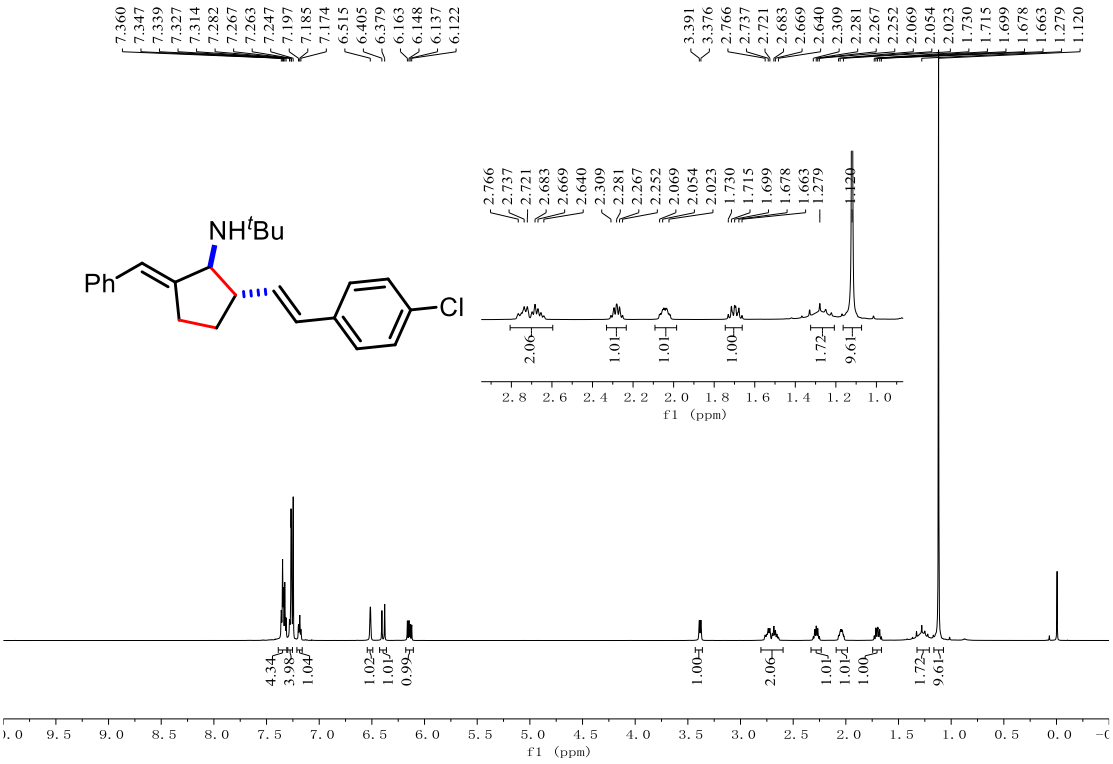
^{1}H NMR spectrum of *trans*-3ad (400 MHz, $CDCl_3$)



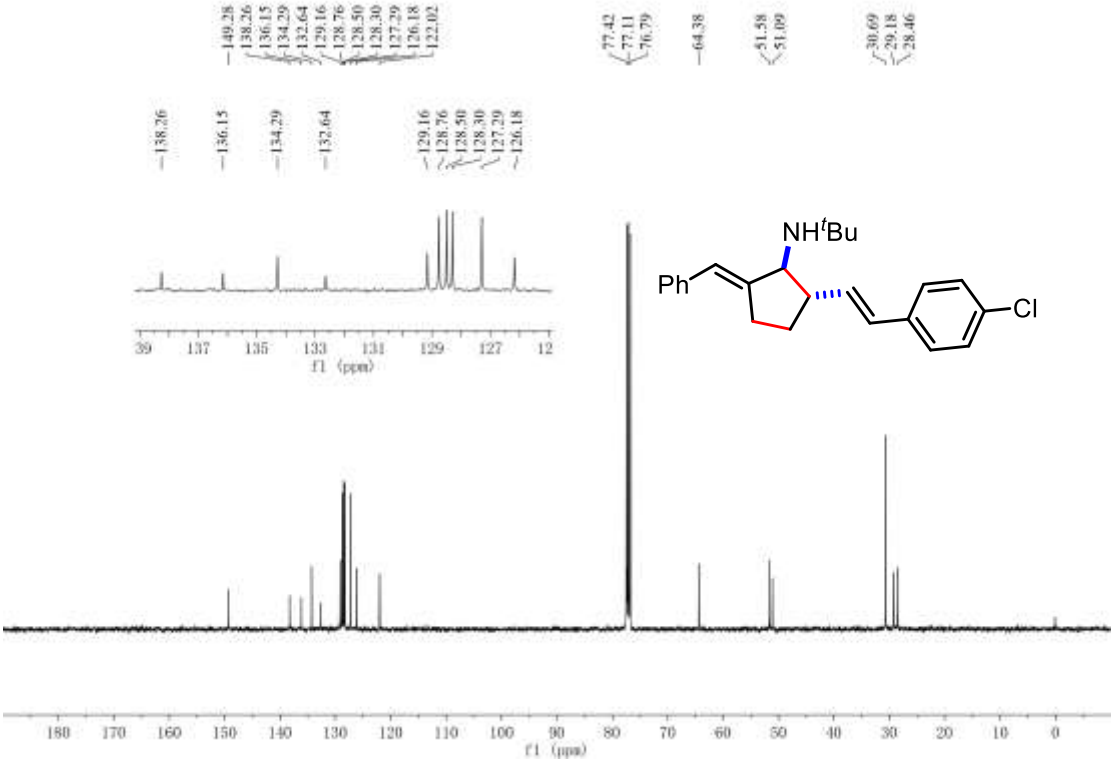
^{13}C NMR spectrum of *trans*-3ad (101 MHz, $CDCl_3$)



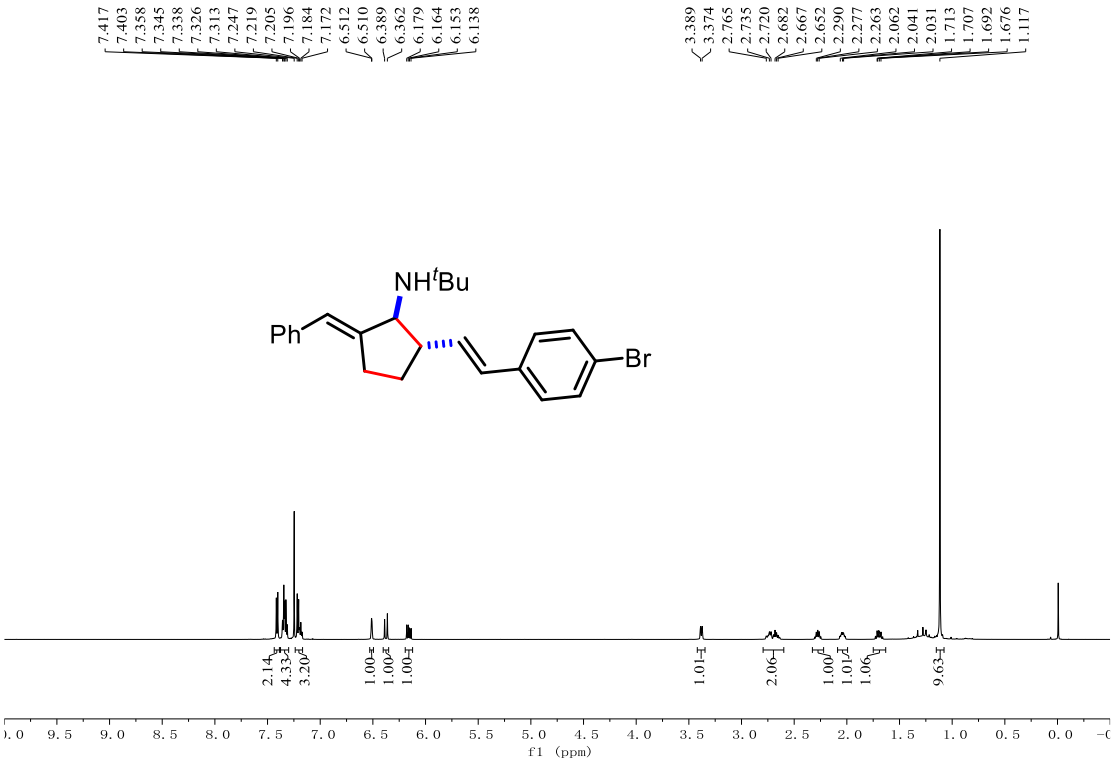
^{1}H NMR spectrum of *trans*-3ae (400 MHz, $CDCl_3$)



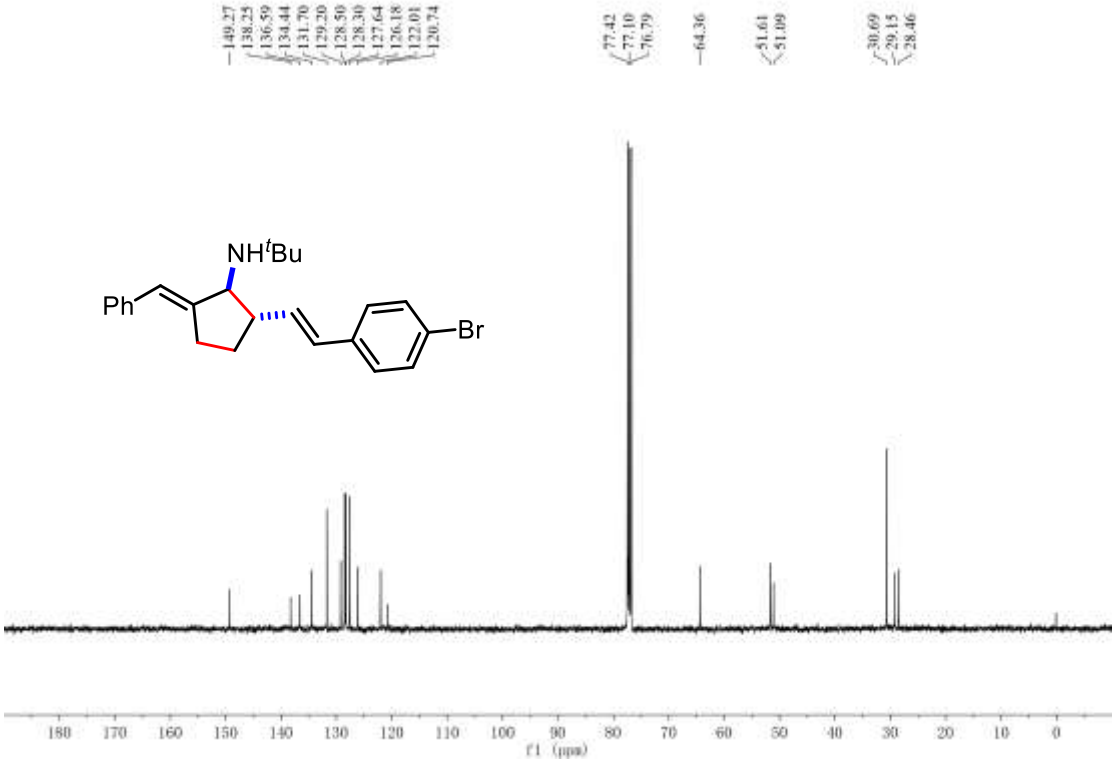
^{13}C NMR spectrum of *trans*-3ae (101 MHz, $CDCl_3$)



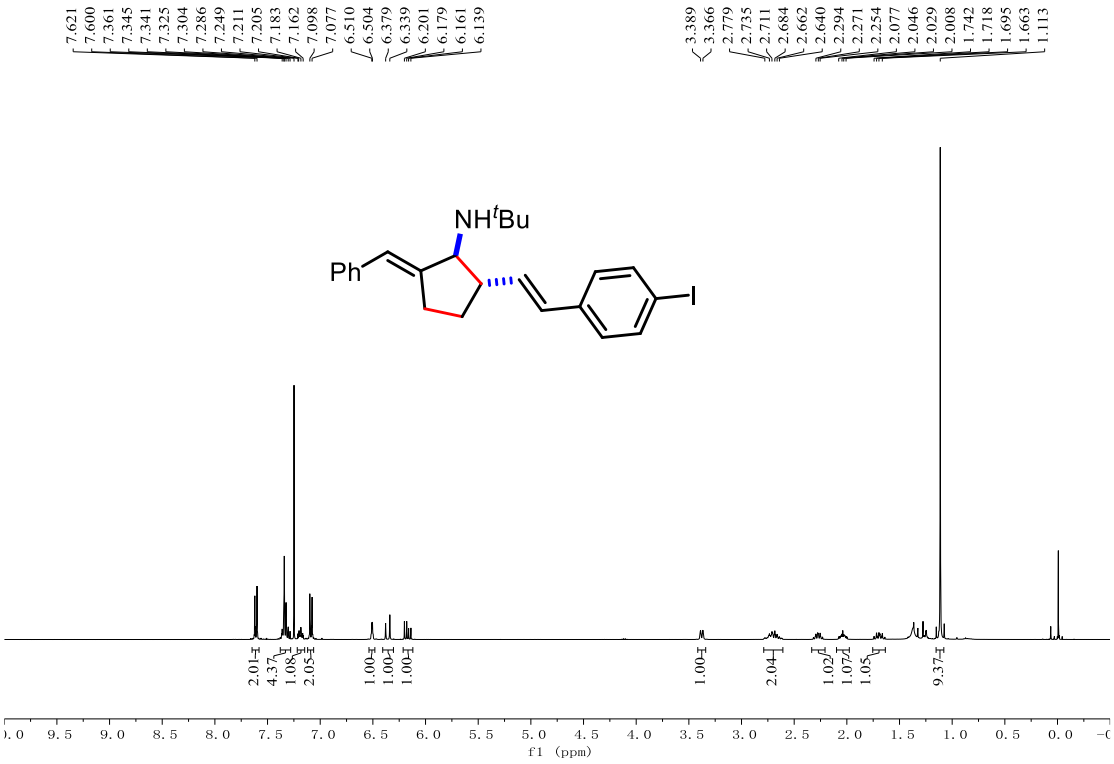
^{1}H NMR spectrum of *trans*-3af (600 MHz, $CDCl_3$)



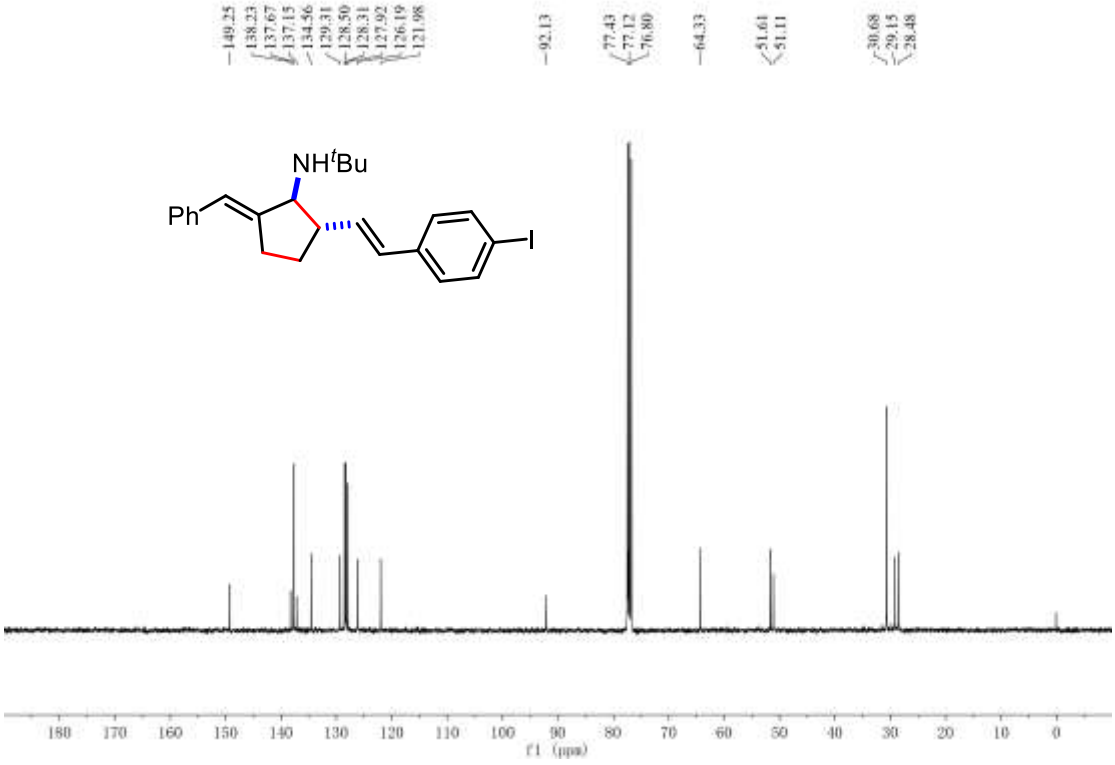
^{13}C NMR spectrum of *trans*-3af (101 MHz, $CDCl_3$)



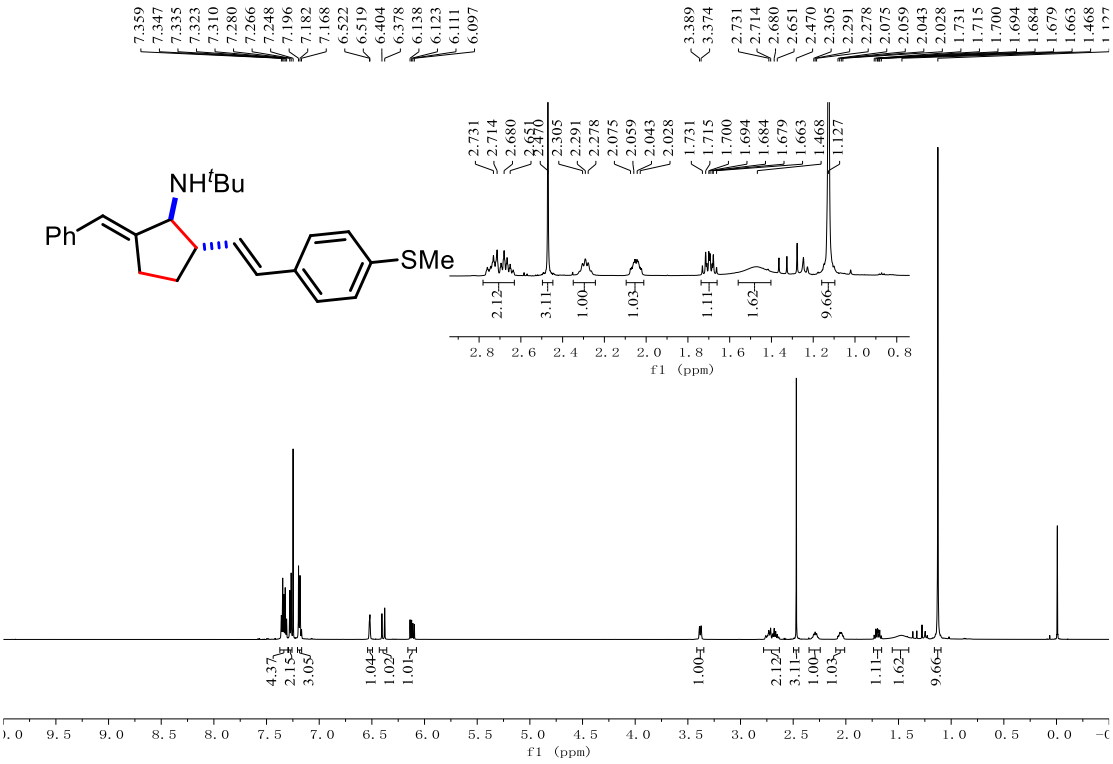
^{1}H NMR spectrum of *trans*-3ag (400 MHz, $CDCl_3$)



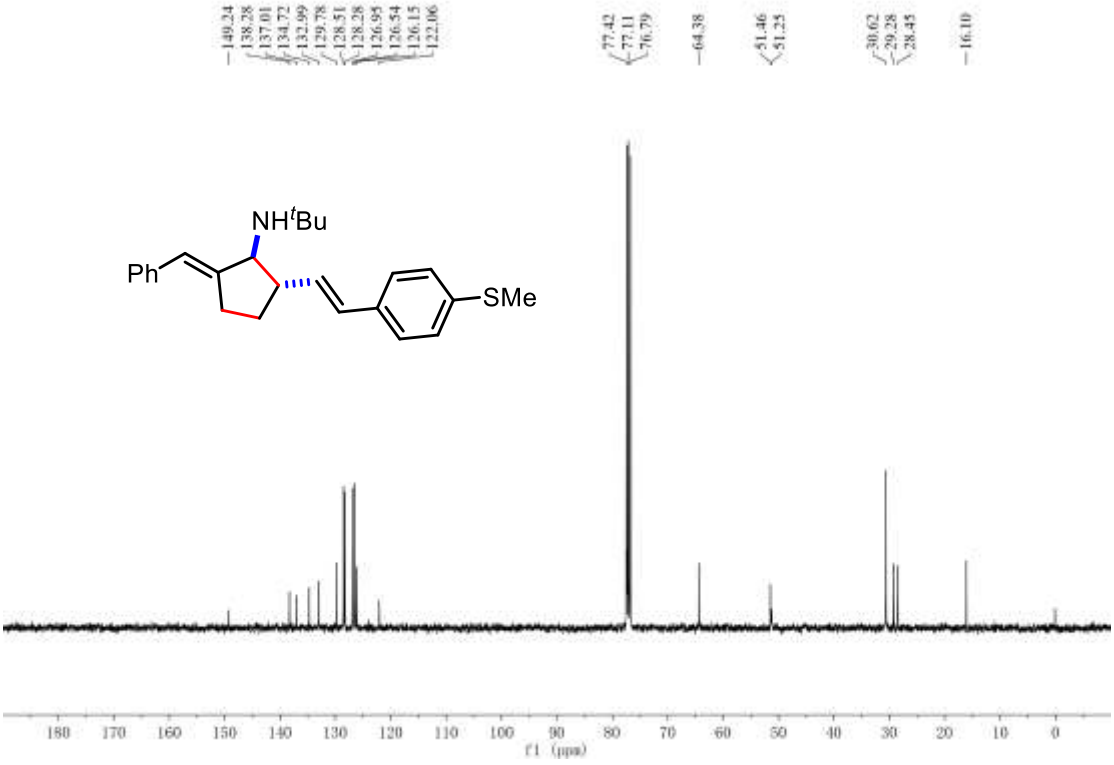
^{13}C NMR spectrum of *trans*-3ag (101 MHz, $CDCl_3$)



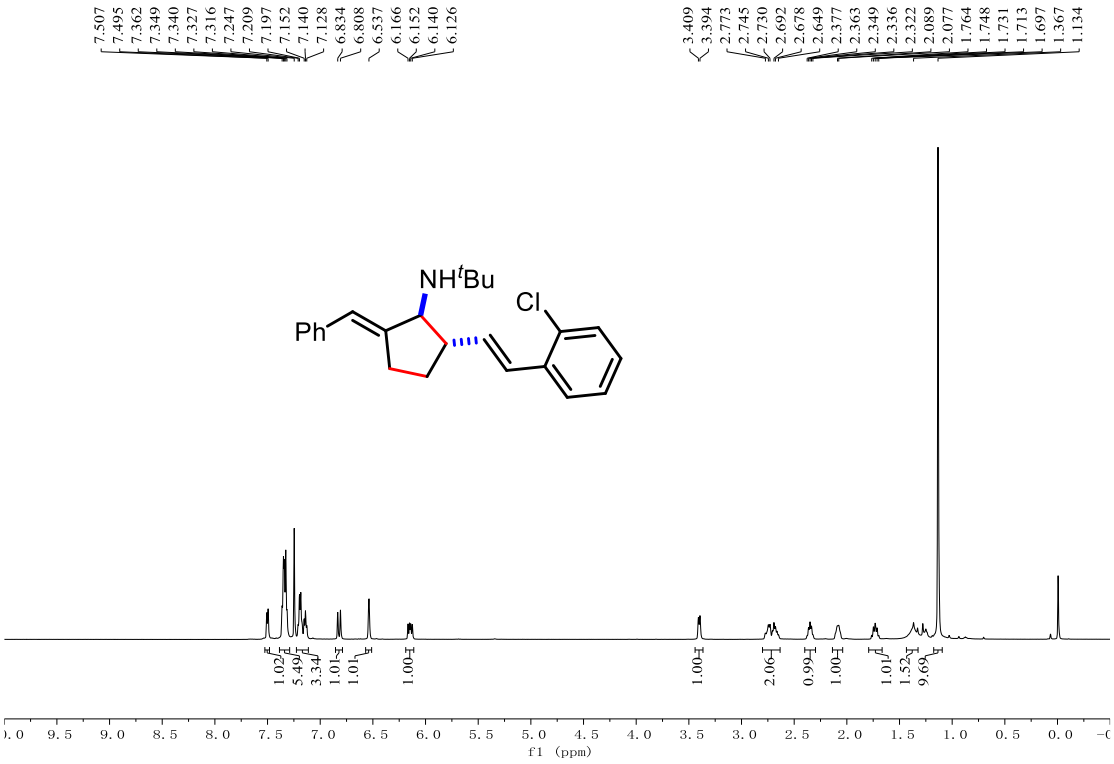
^{1}H NMR spectrum of *trans*-3ah (600 MHz, $CDCl_3$)



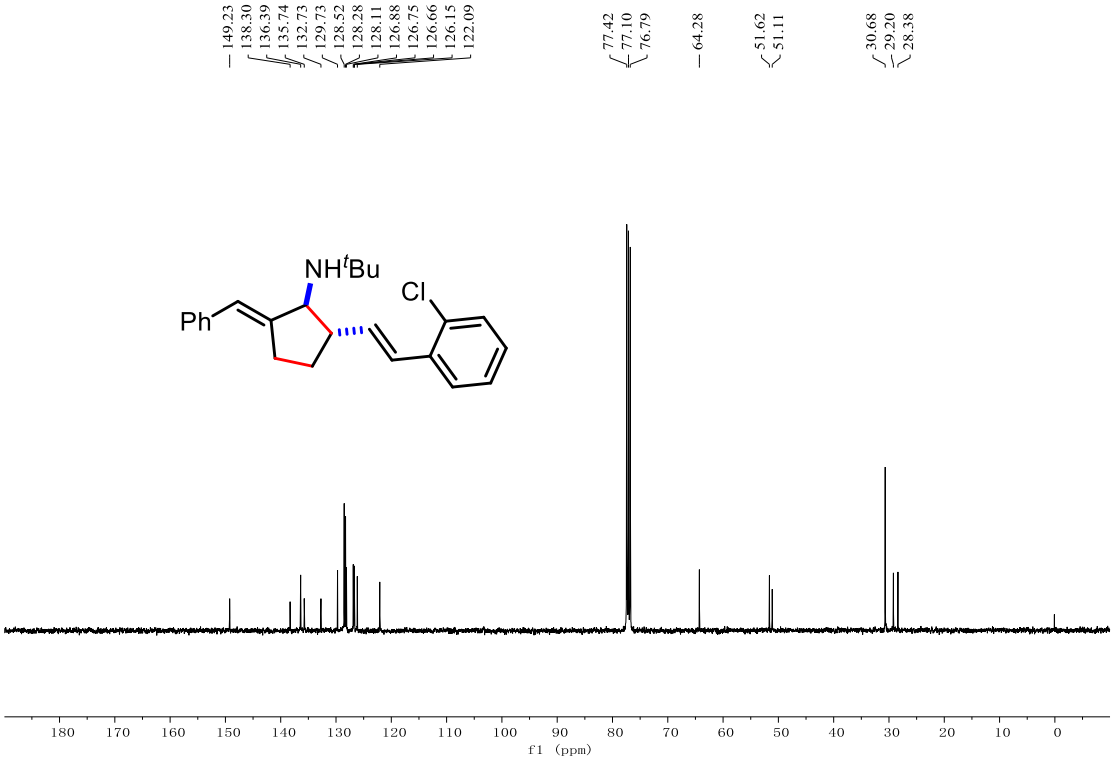
^{13}C NMR spectrum of *trans*-3ah (101 MHz, $CDCl_3$)



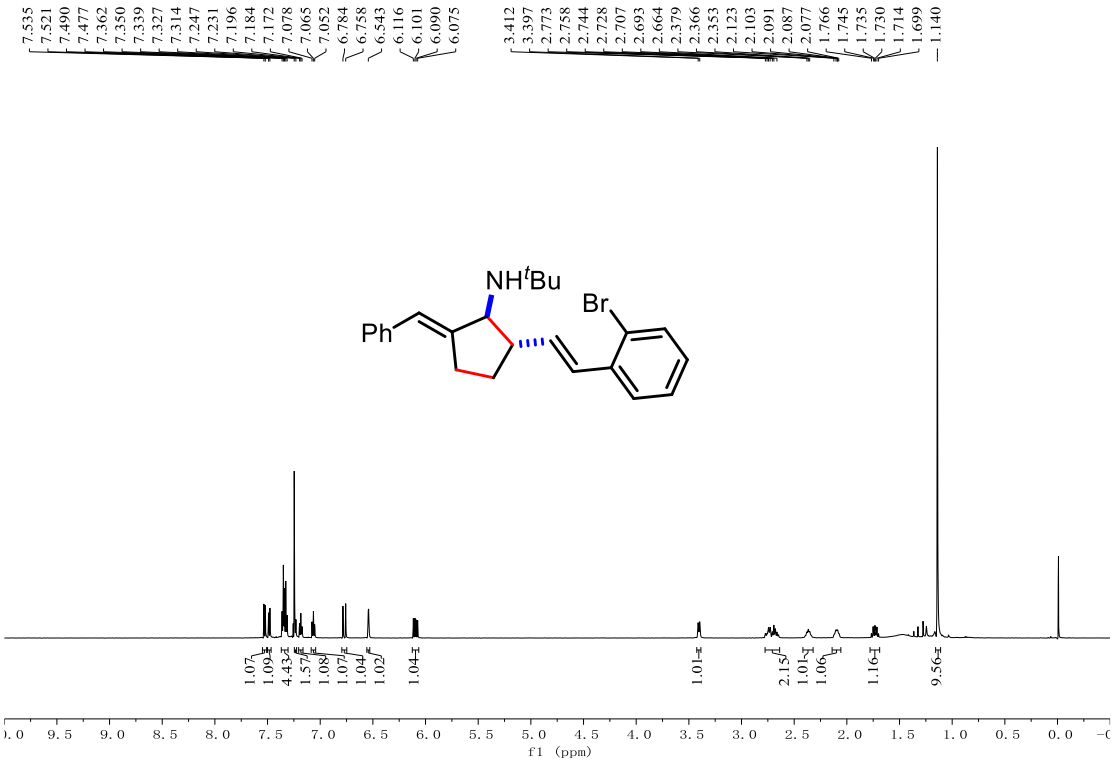
^{1}H NMR spectrum of *trans*-3ai (600 MHz, $CDCl_3$)



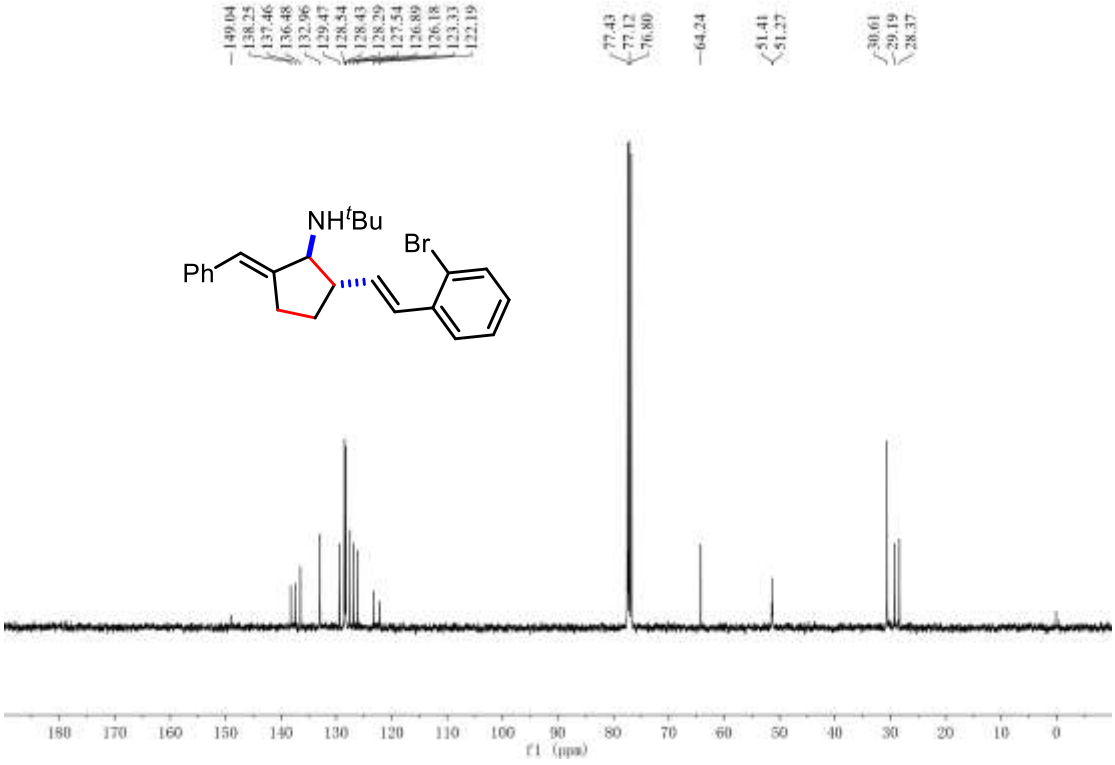
^{13}C NMR spectrum of *trans*-3ai (101 MHz, $CDCl_3$)



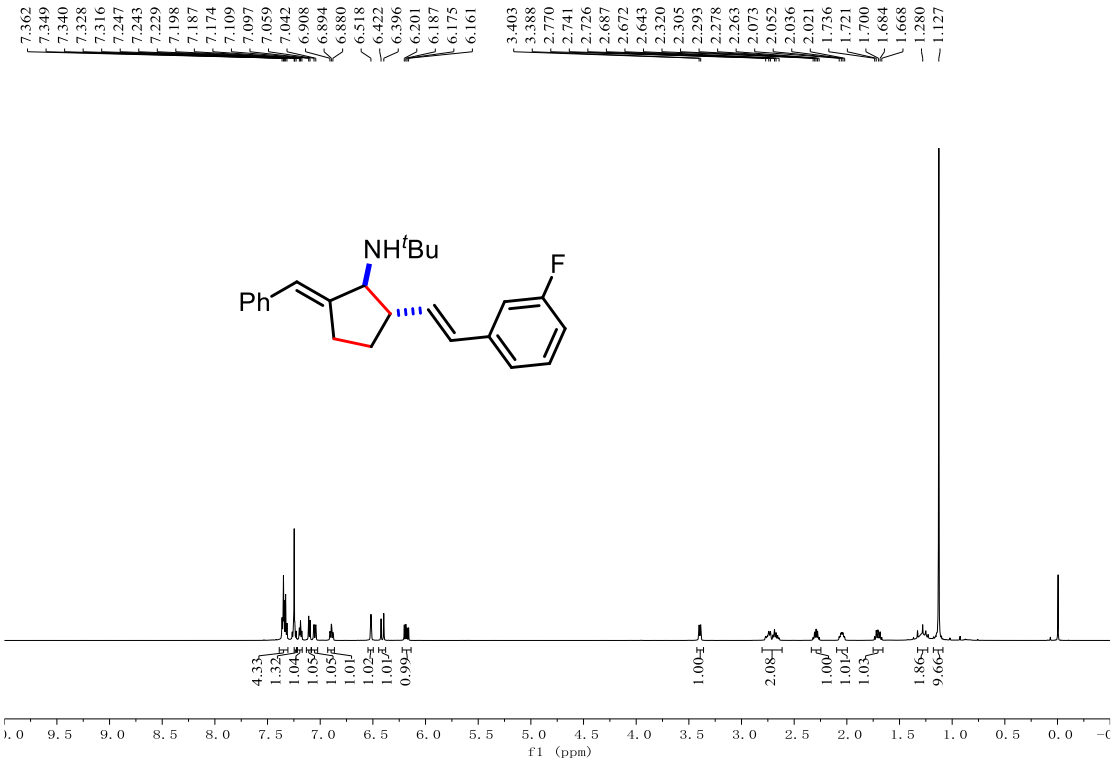
^{1}H NMR spectrum of *trans*-3aj (600 MHz, $CDCl_3$)



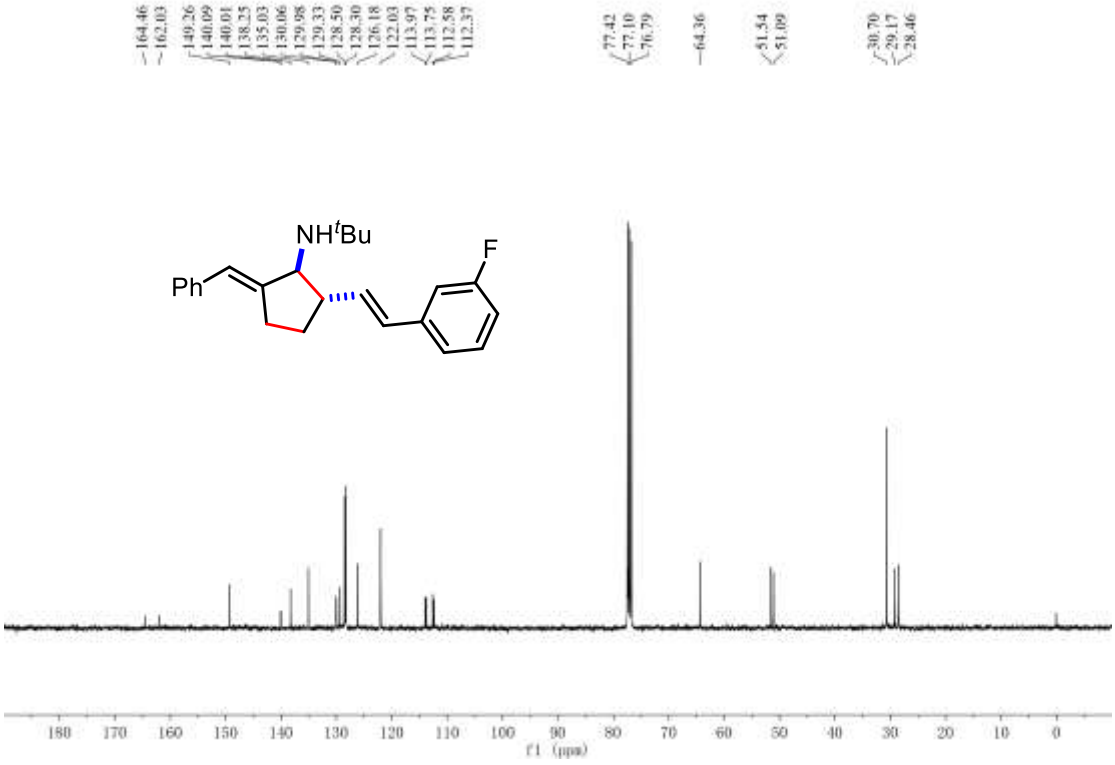
^{13}C NMR spectrum of *trans*-3aj (101 MHz, $CDCl_3$)



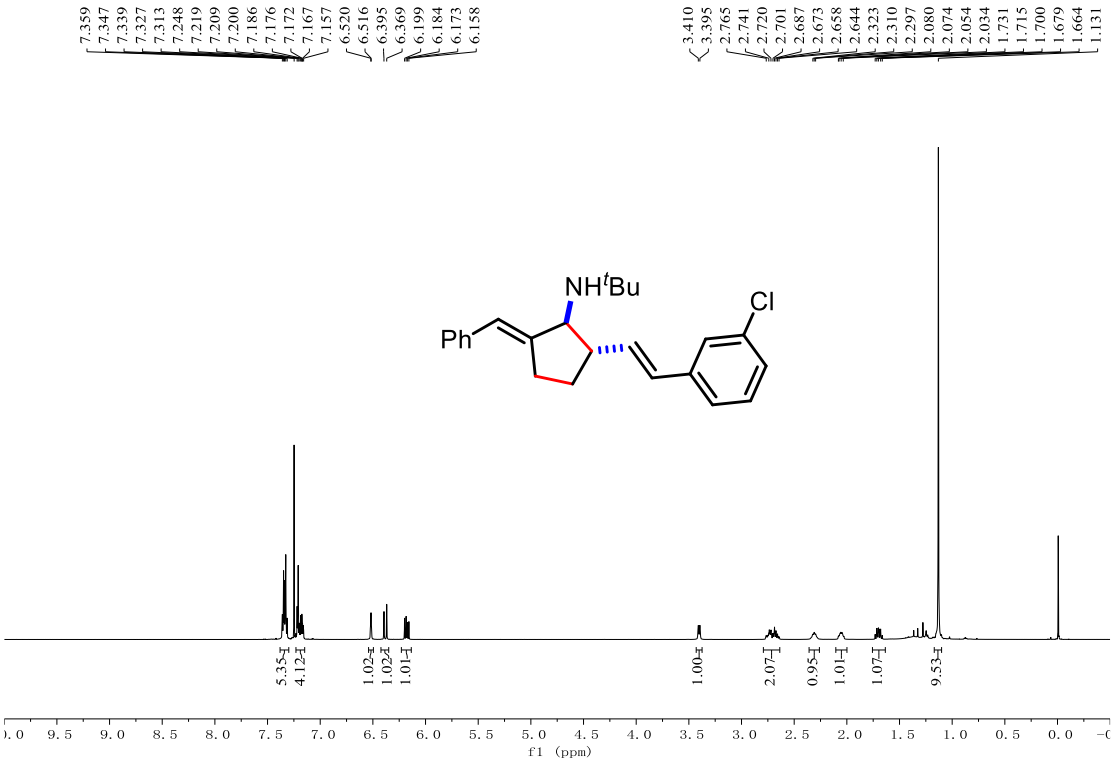
^{1}H NMR spectrum of *trans*-3ak (600 MHz, $CDCl_3$)



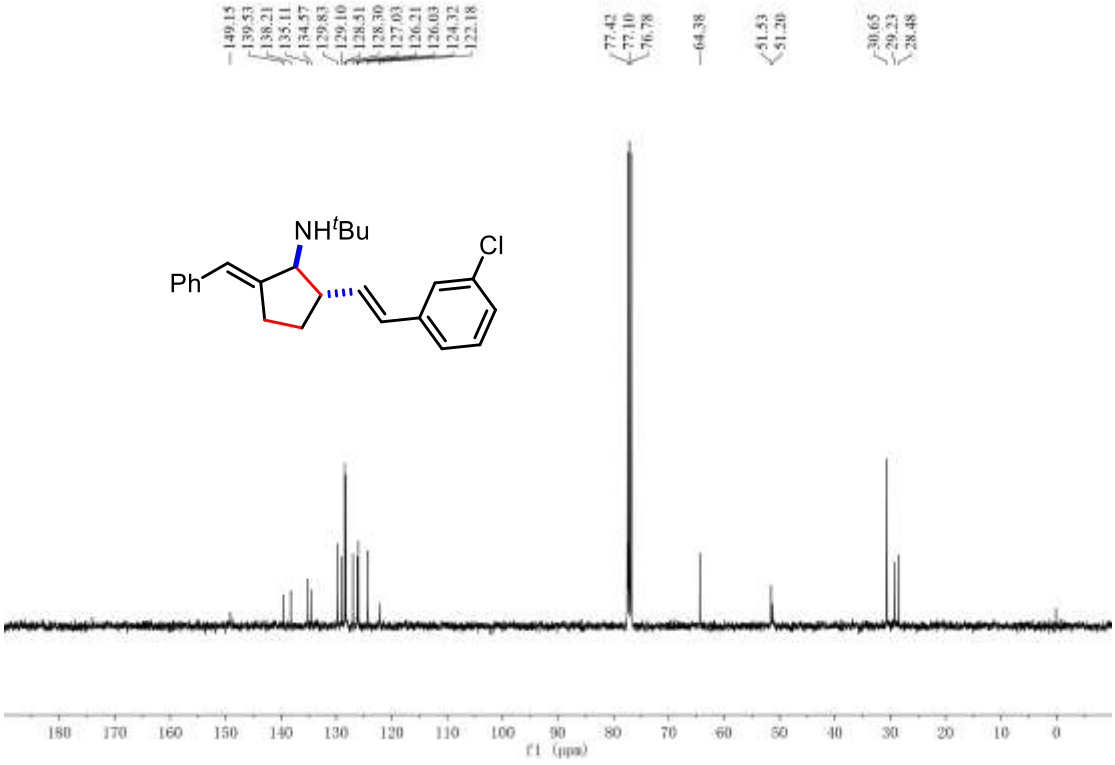
^{13}C NMR spectrum of *trans*-3ak (101 MHz, $CDCl_3$)



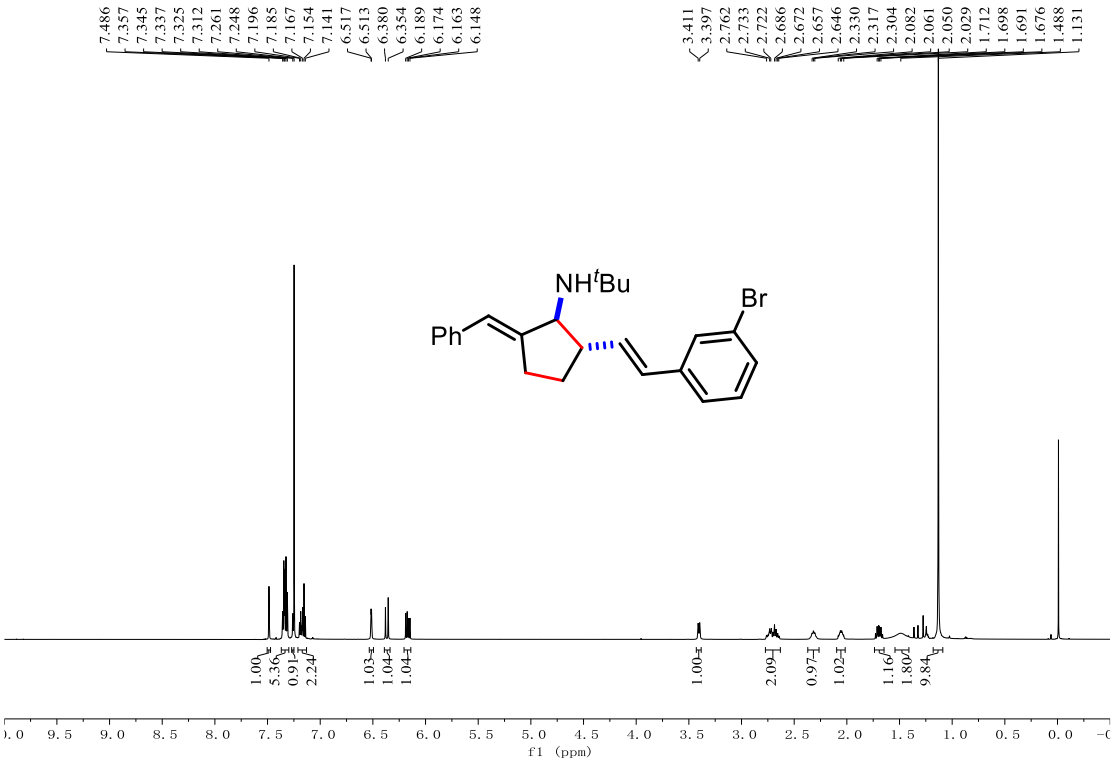
^{1}H NMR spectrum of *trans*-3al (600 MHz, $CDCl_3$)



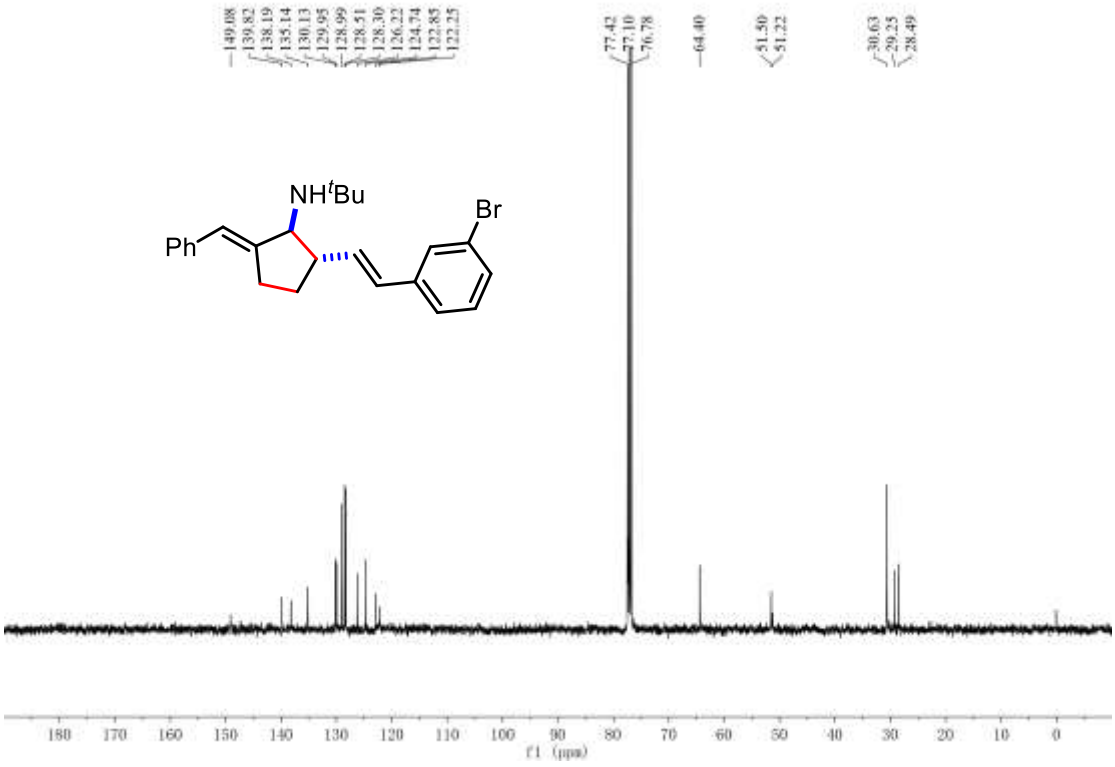
^{13}C NMR spectrum of *trans*-3al (101 MHz, $CDCl_3$)



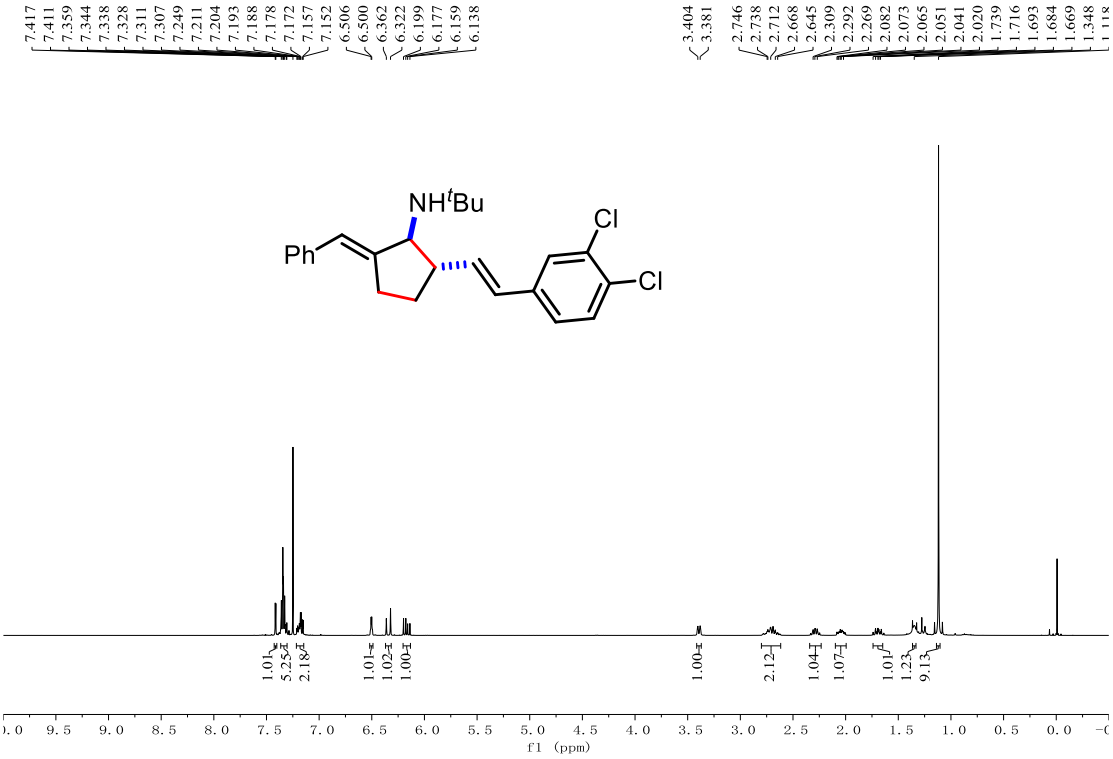
^{1}H NMR spectrum of *trans*-3am (600 MHz, $CDCl_3$)



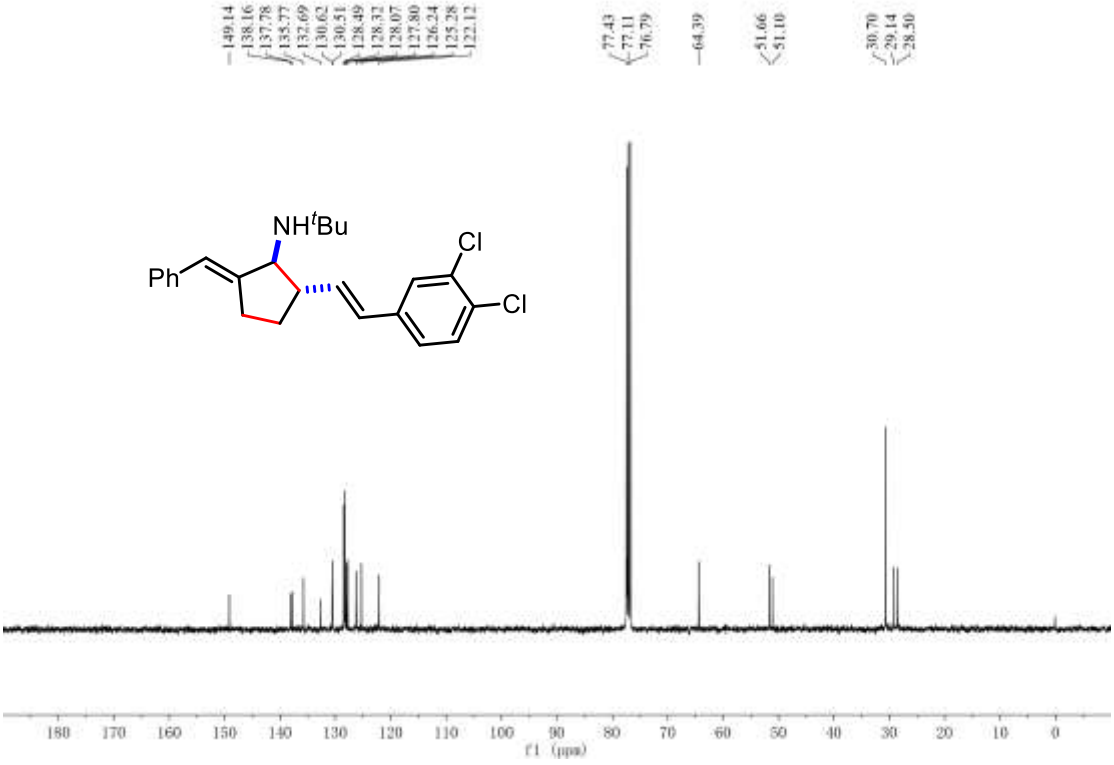
^{13}C NMR spectrum of *trans*-3am (101 MHz, $CDCl_3$)



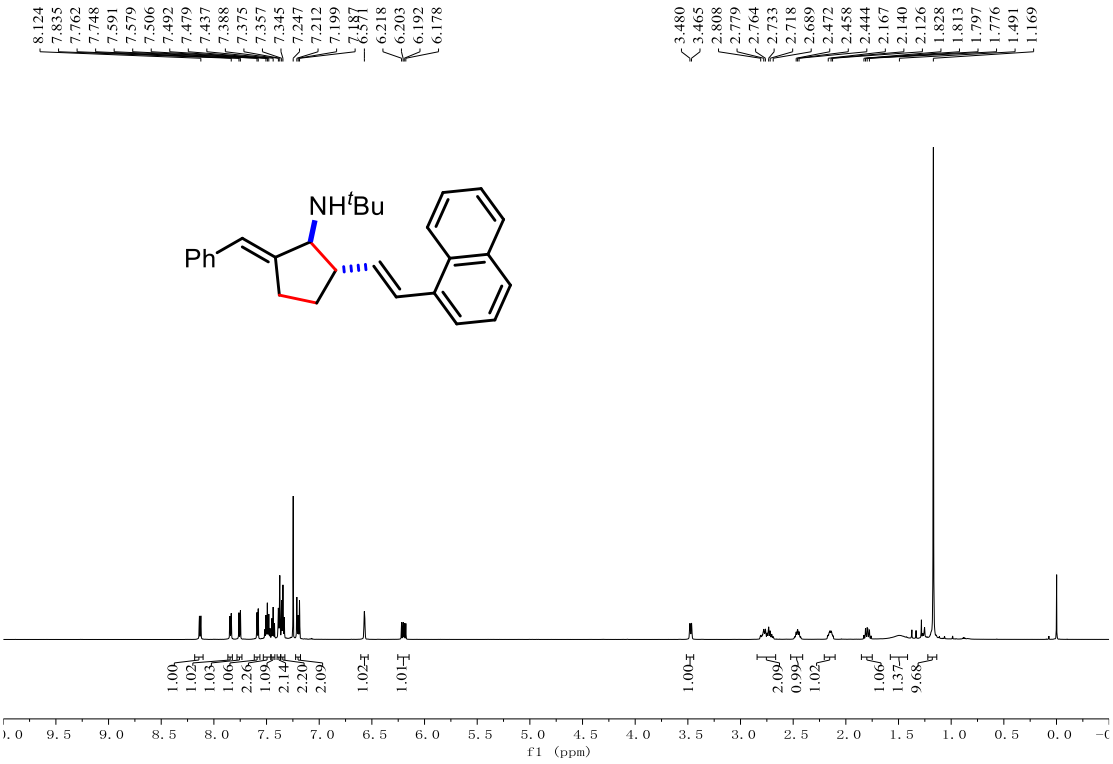
^{1}H NMR spectrum of *trans*-3an (400 MHz, $CDCl_3$)



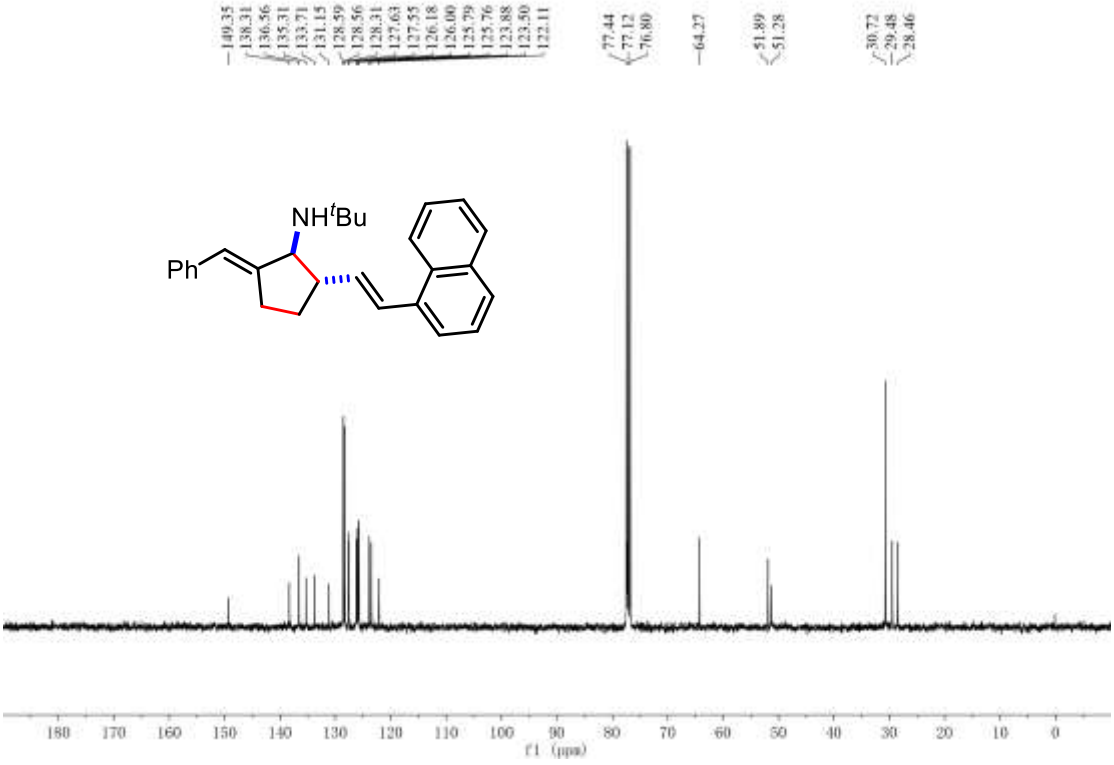
^{13}C NMR spectrum of *trans*-3an (101 MHz, $CDCl_3$)



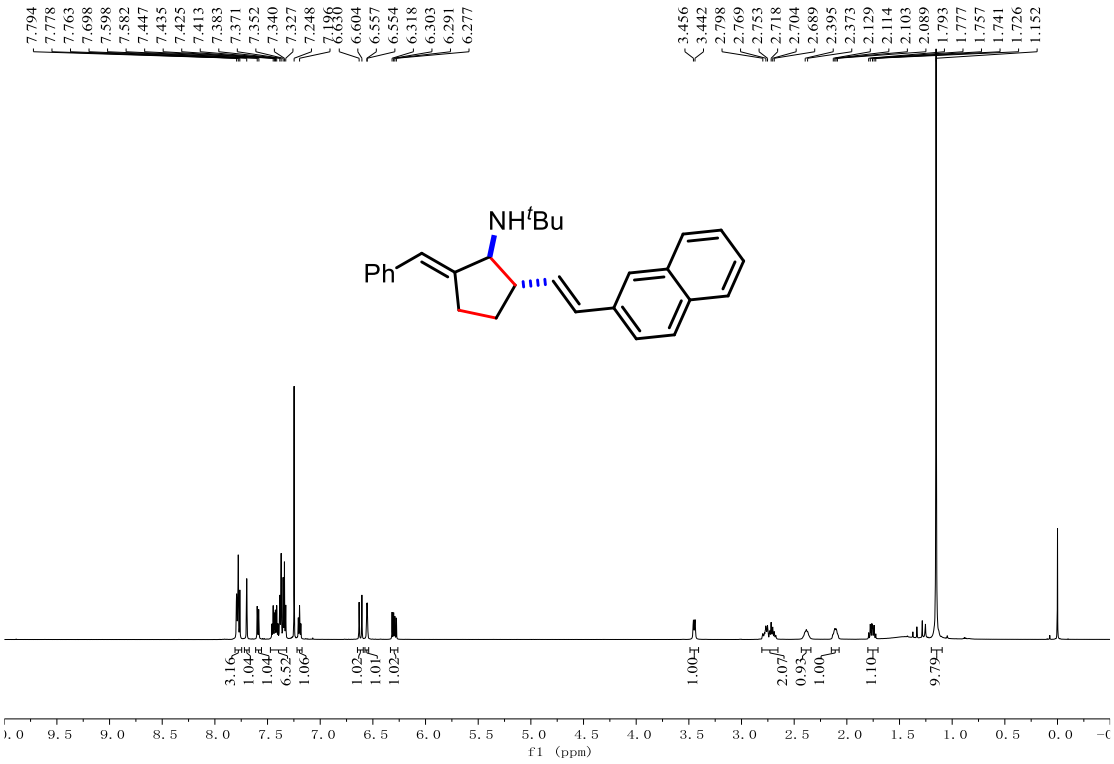
^{1}H NMR spectrum of *trans*-3ao (600 MHz, $CDCl_3$)



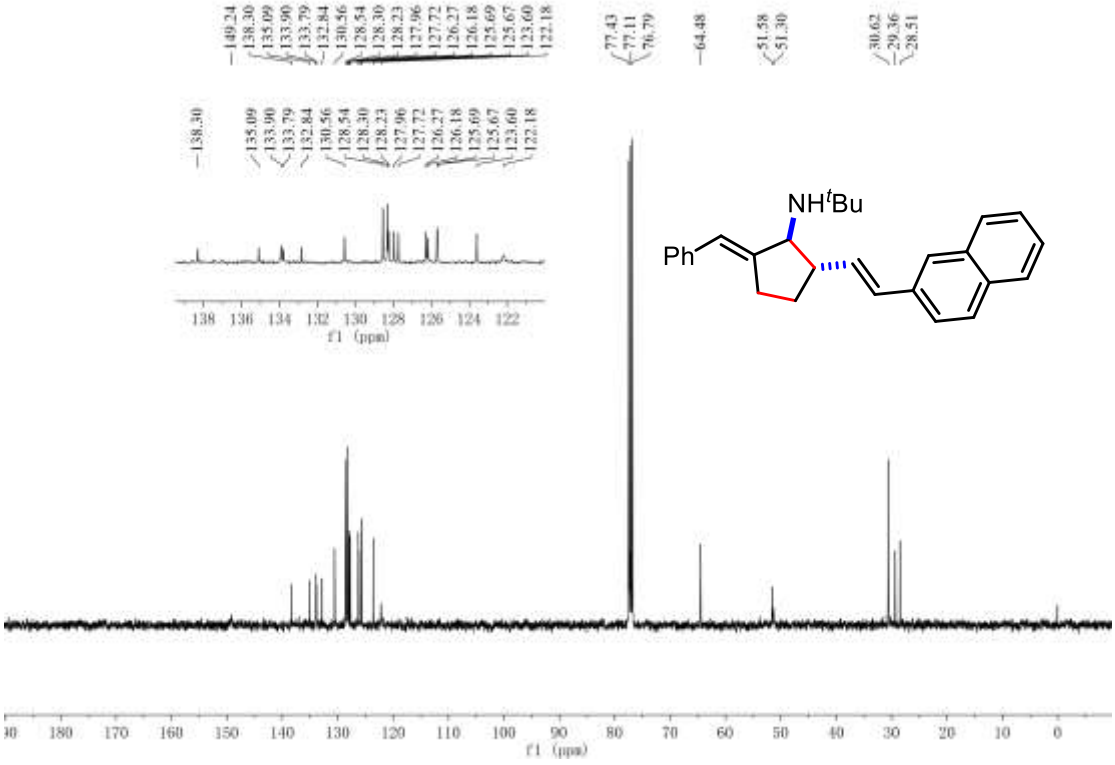
^{13}C NMR spectrum of *trans*-3ao (101 MHz, $CDCl_3$)



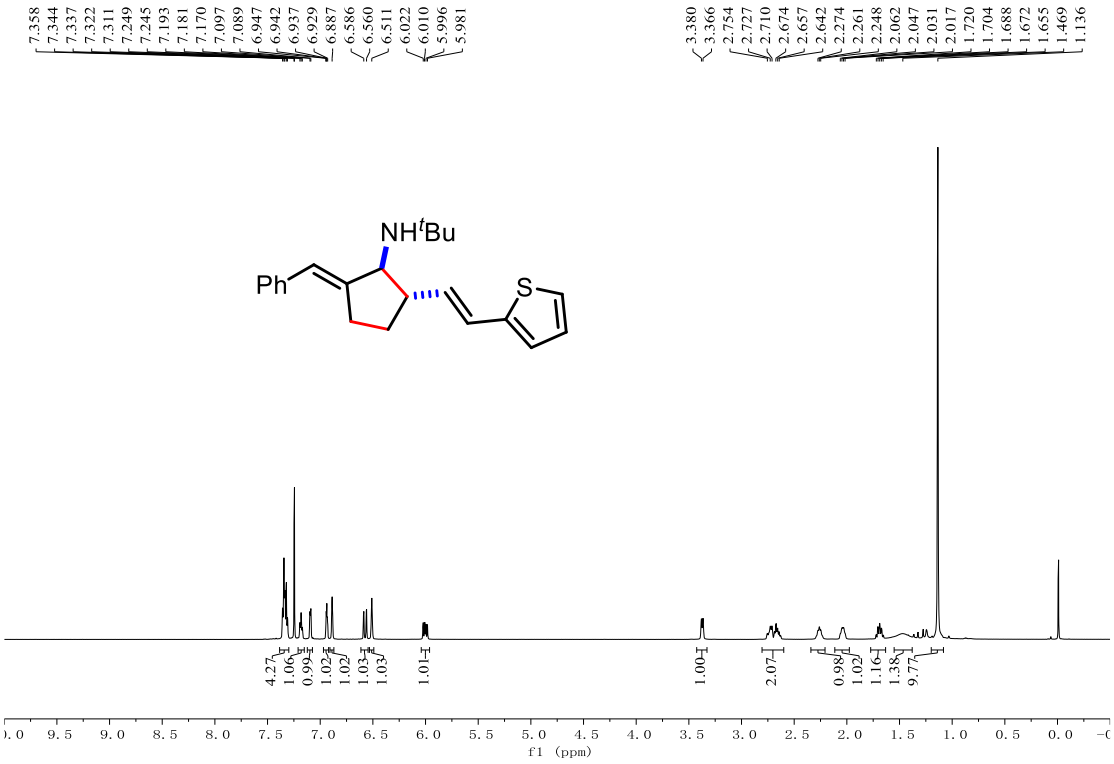
^{1}H NMR spectrum of *trans*-3ap (600 MHz, $CDCl_3$)



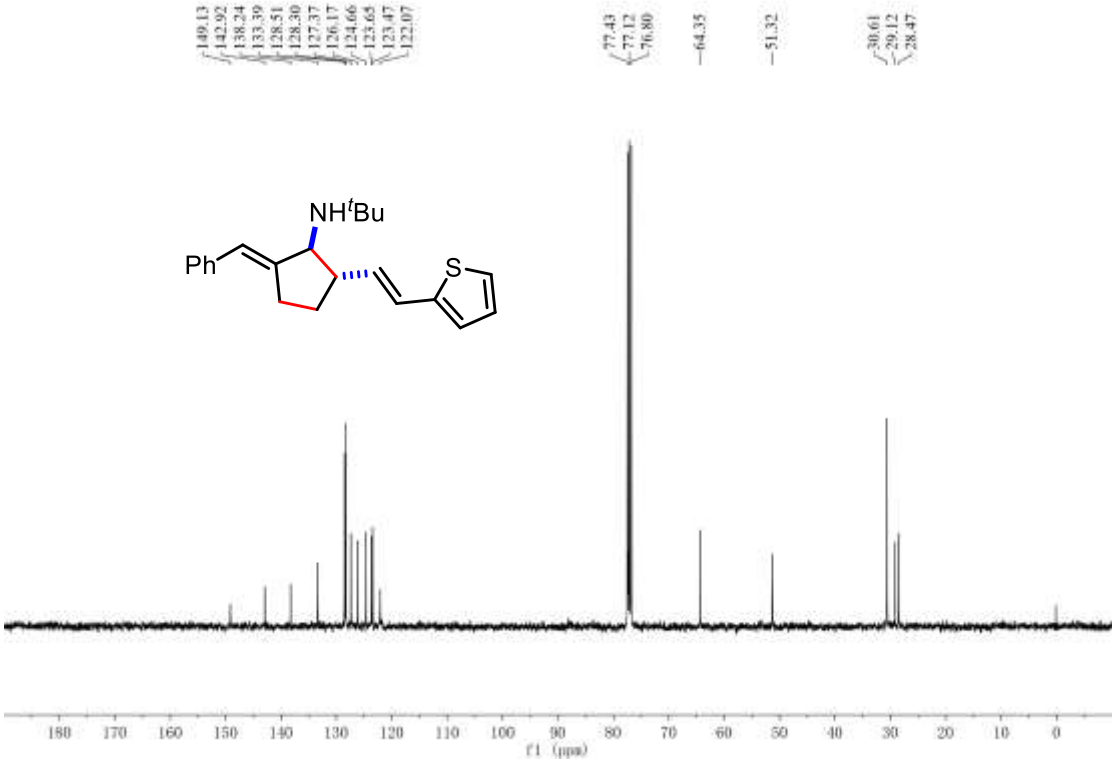
^{13}C NMR spectrum of *trans*-3ap (101 MHz, $CDCl_3$)



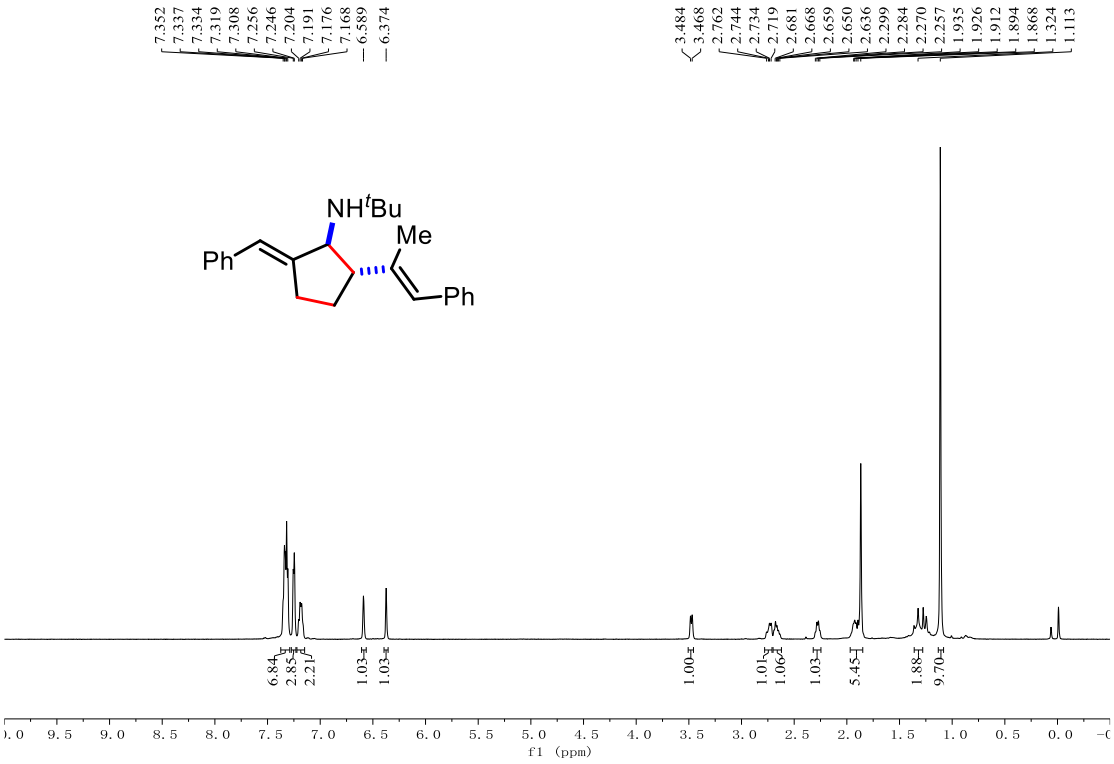
^{1}H NMR spectrum of *trans*-3aq (600 MHz, $CDCl_3$)



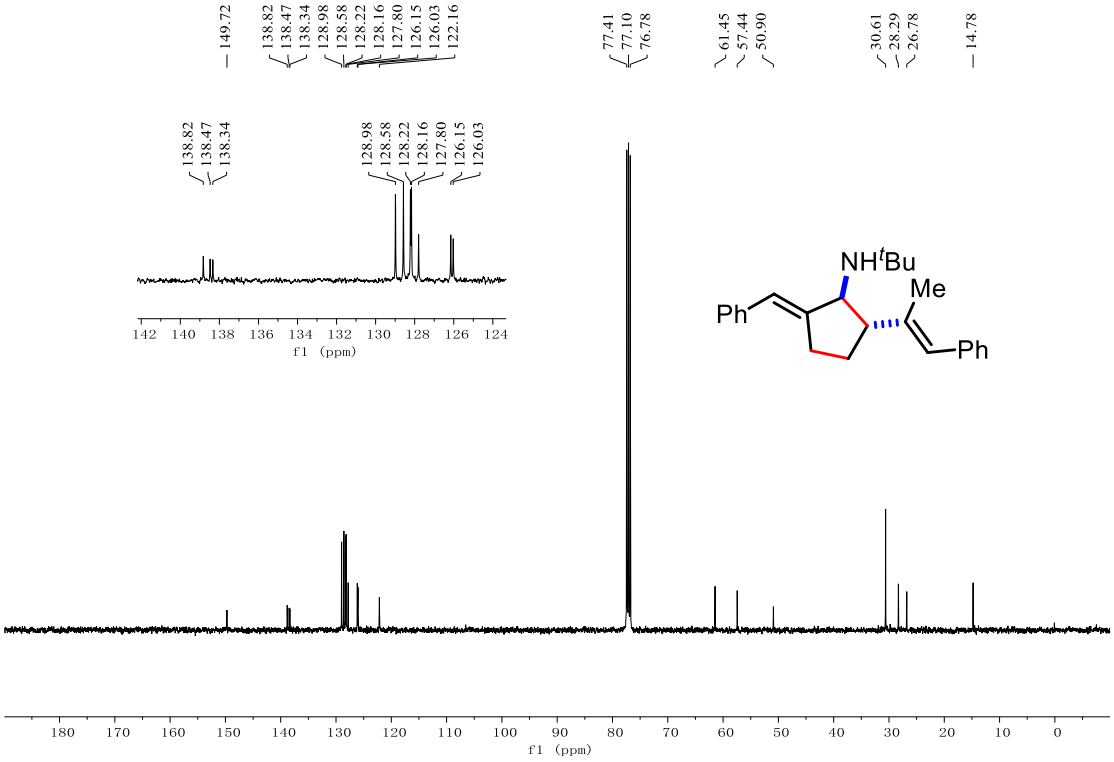
^{13}C NMR spectrum of *trans*-3aq (101 MHz, $CDCl_3$)



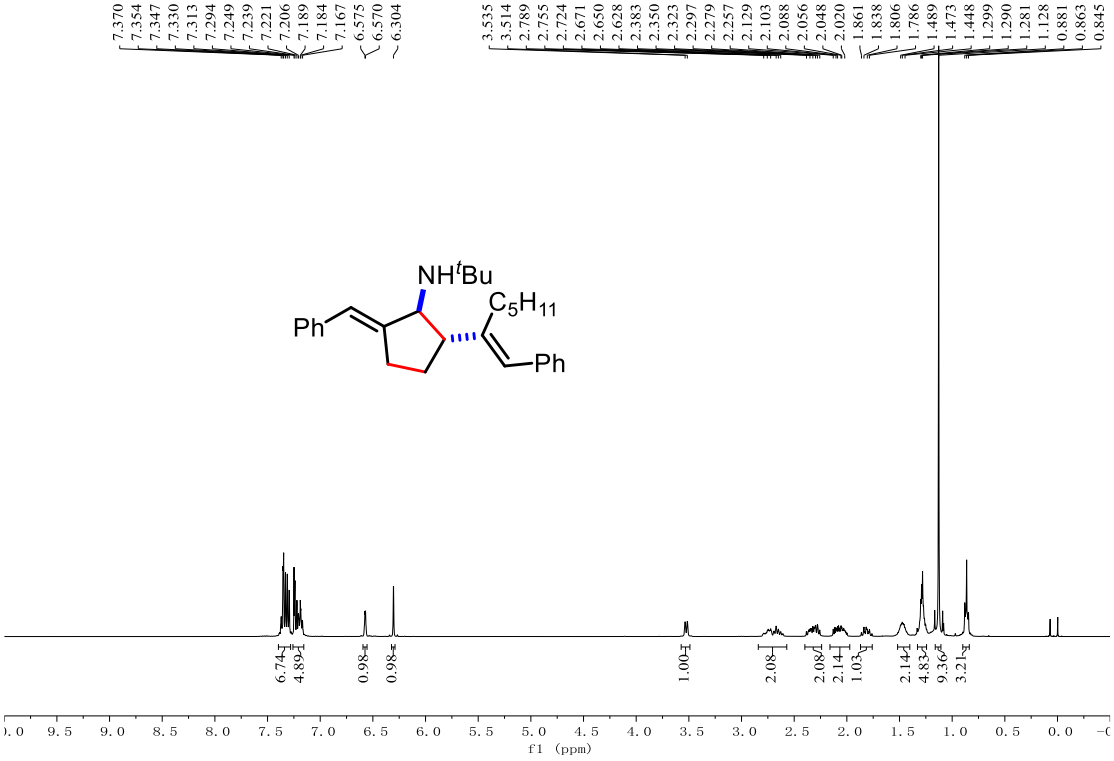
^{1}H NMR spectrum of *trans*-3ar (600 MHz, $CDCl_3$)



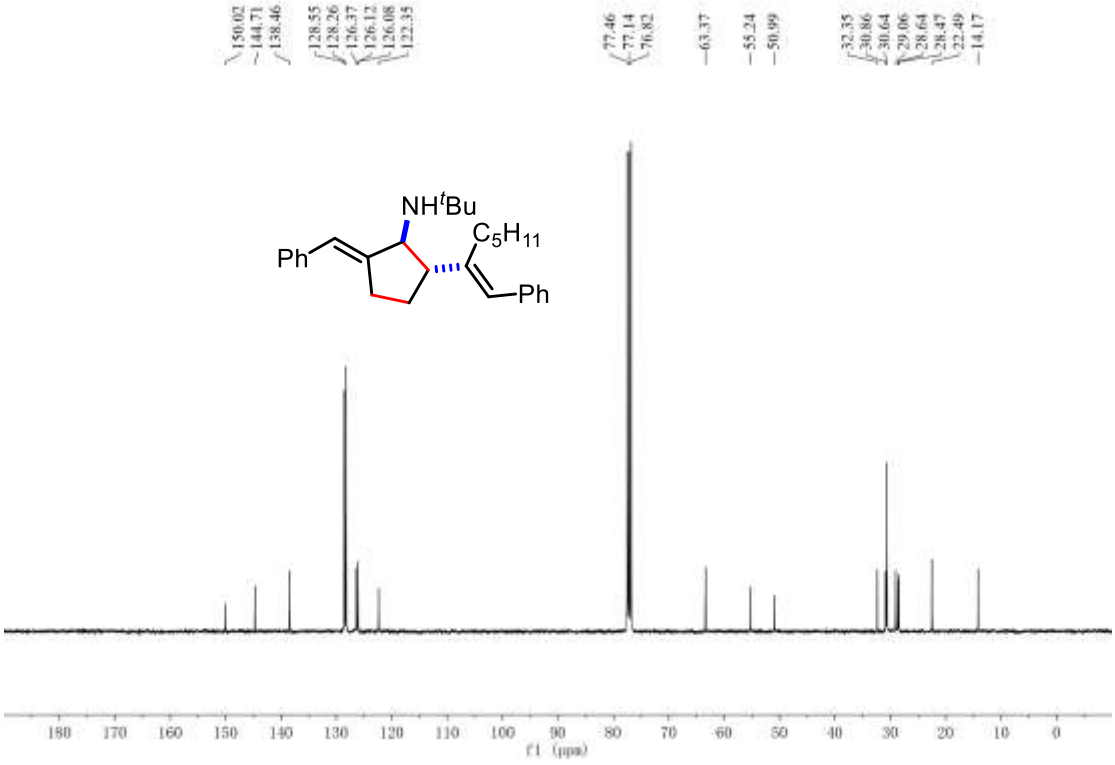
^{13}C NMR spectrum of *trans*-3ar (101 MHz, $CDCl_3$)



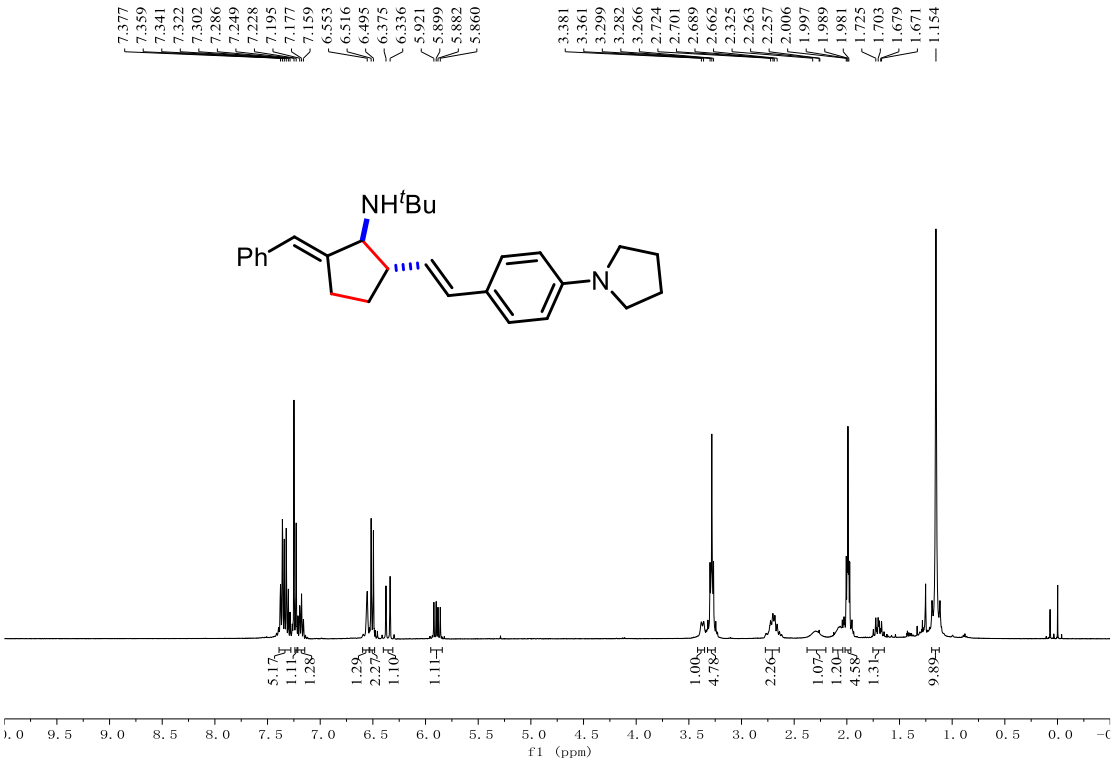
^{1}H NMR spectrum of *trans*-3as (400 MHz, $CDCl_3$)



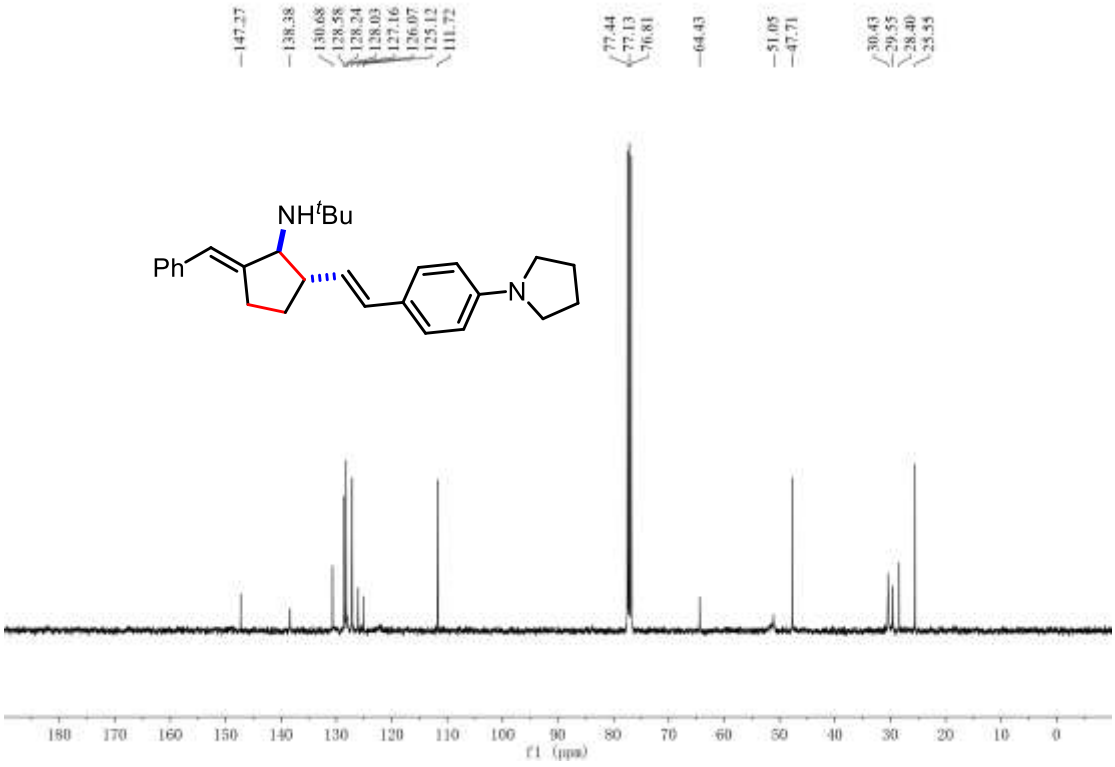
^{13}C NMR spectrum of *trans*-3as (101 MHz, $CDCl_3$)



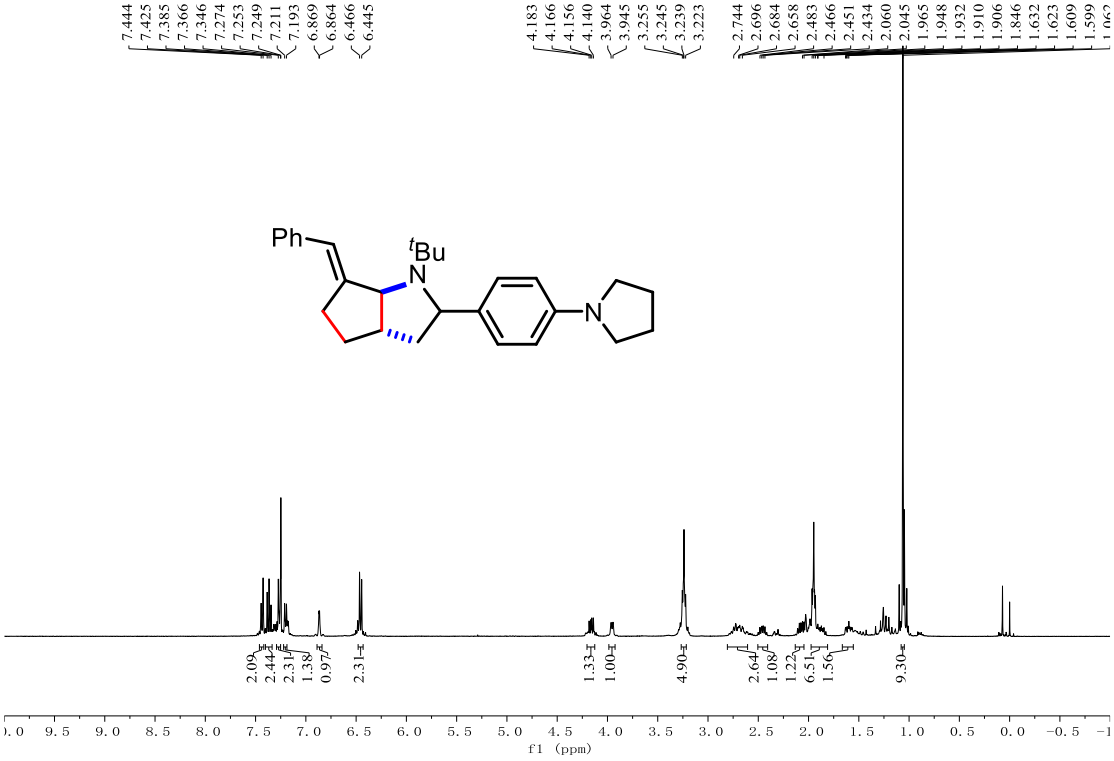
^{1}H NMR spectrum of *trans*-3av (400 MHz, $CDCl_3$)



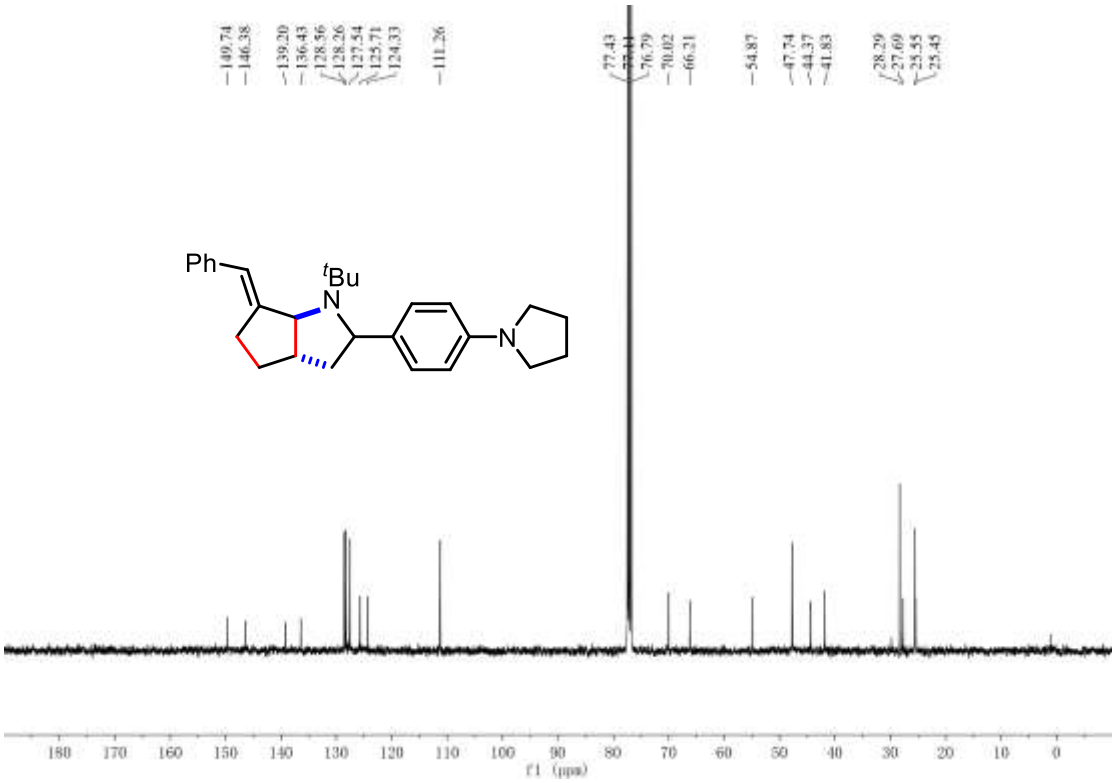
^{13}C NMR spectrum of *trans*-3av (101 MHz, $CDCl_3$)



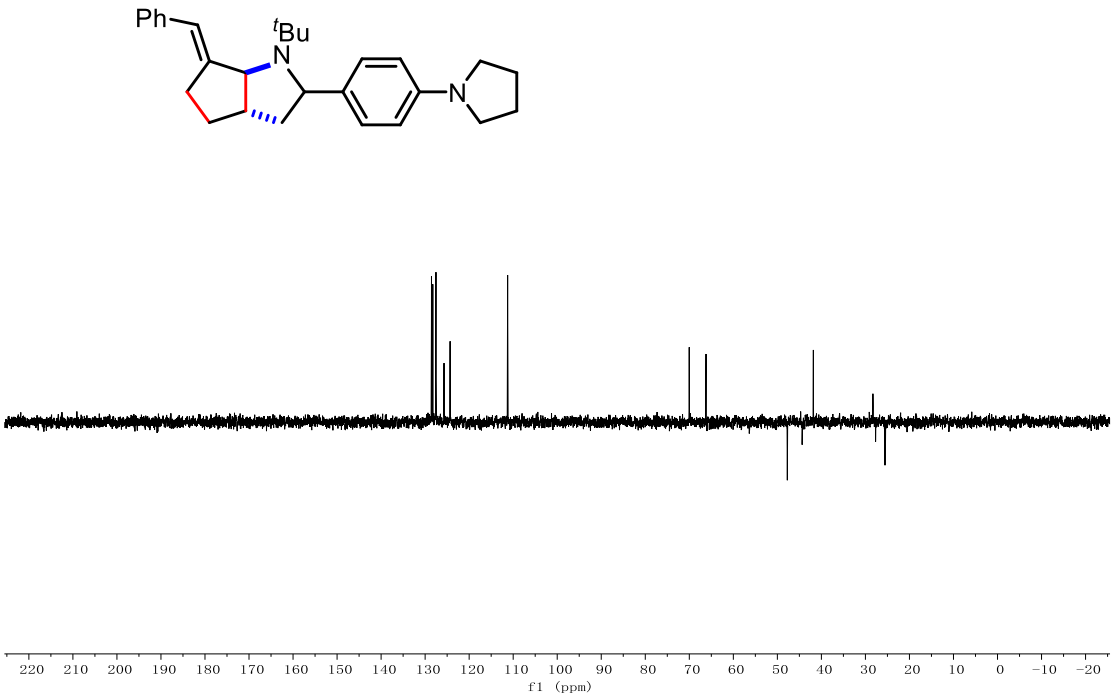
^{1}H NMR spectrum of *trans*-3av' (600 MHz, $CDCl_3$)



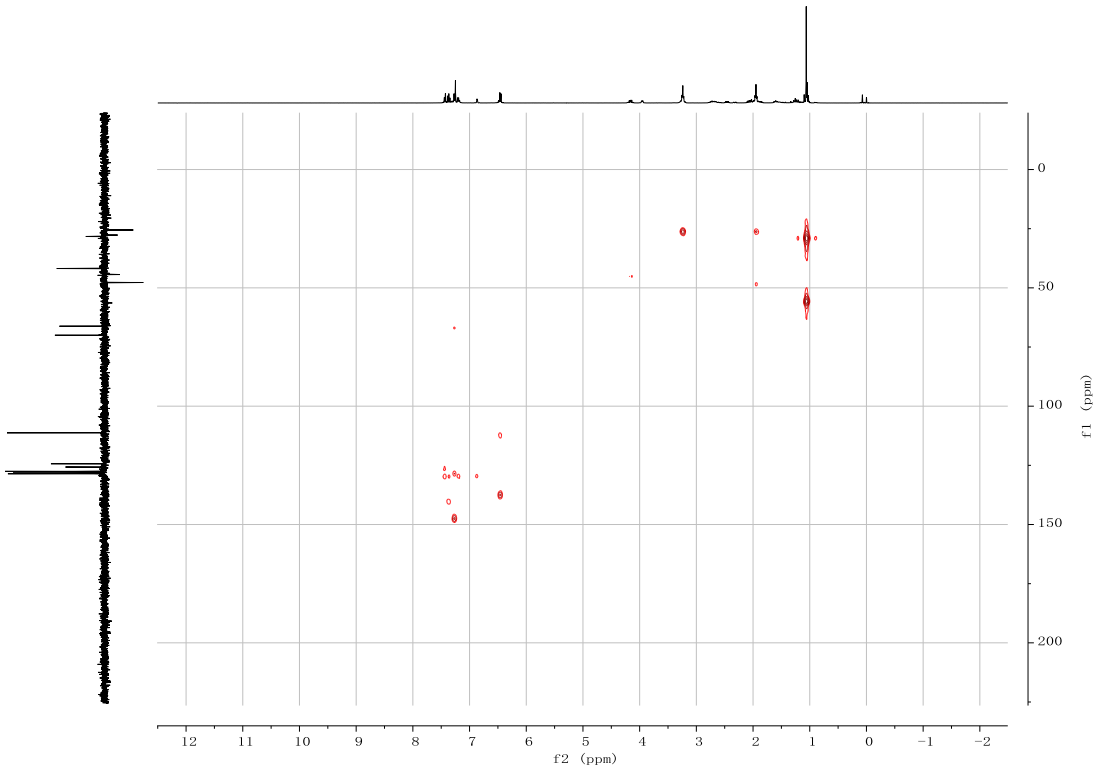
^{13}C NMR spectrum of *trans*-3av' (101 MHz, $CDCl_3$)



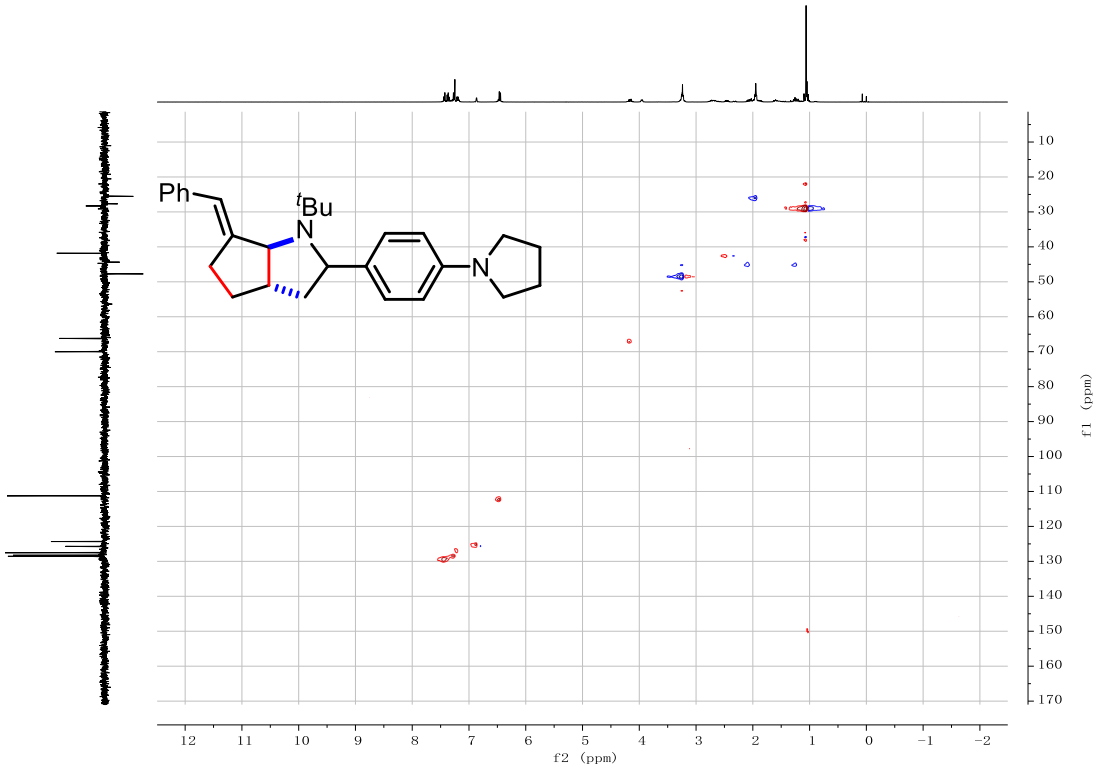
^{135}DEPT spectrum of *trans*-3av'



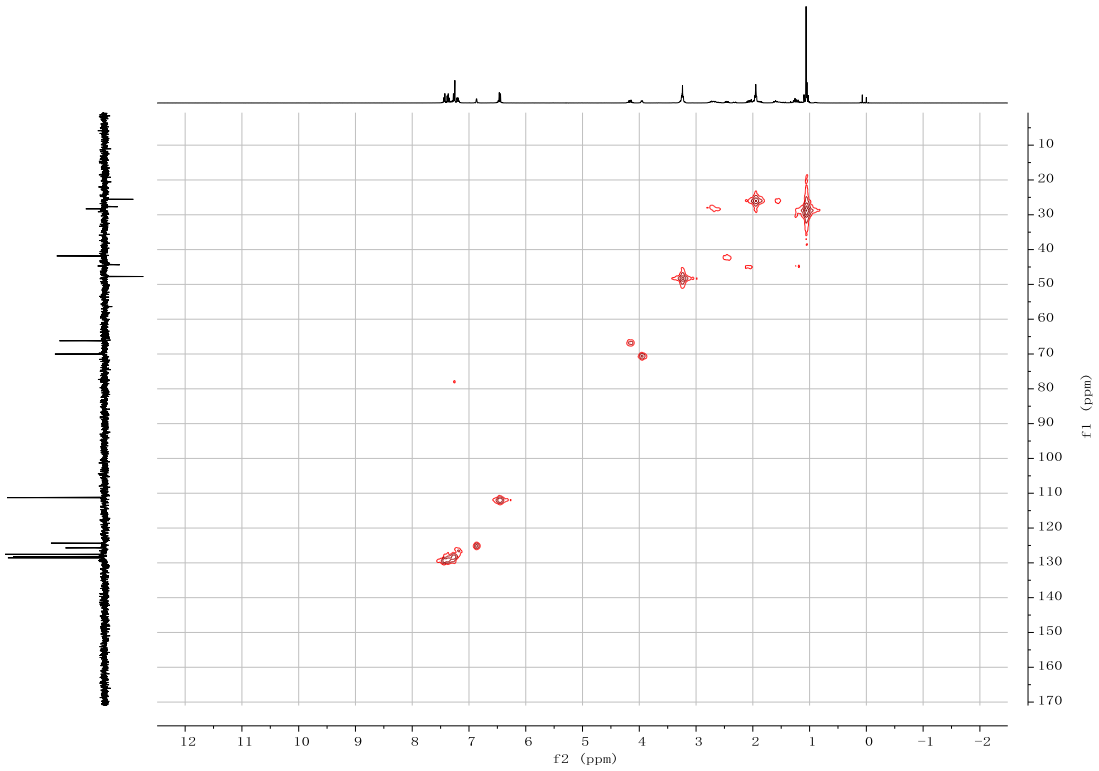
HMBC spectrum of *trans*-3av'



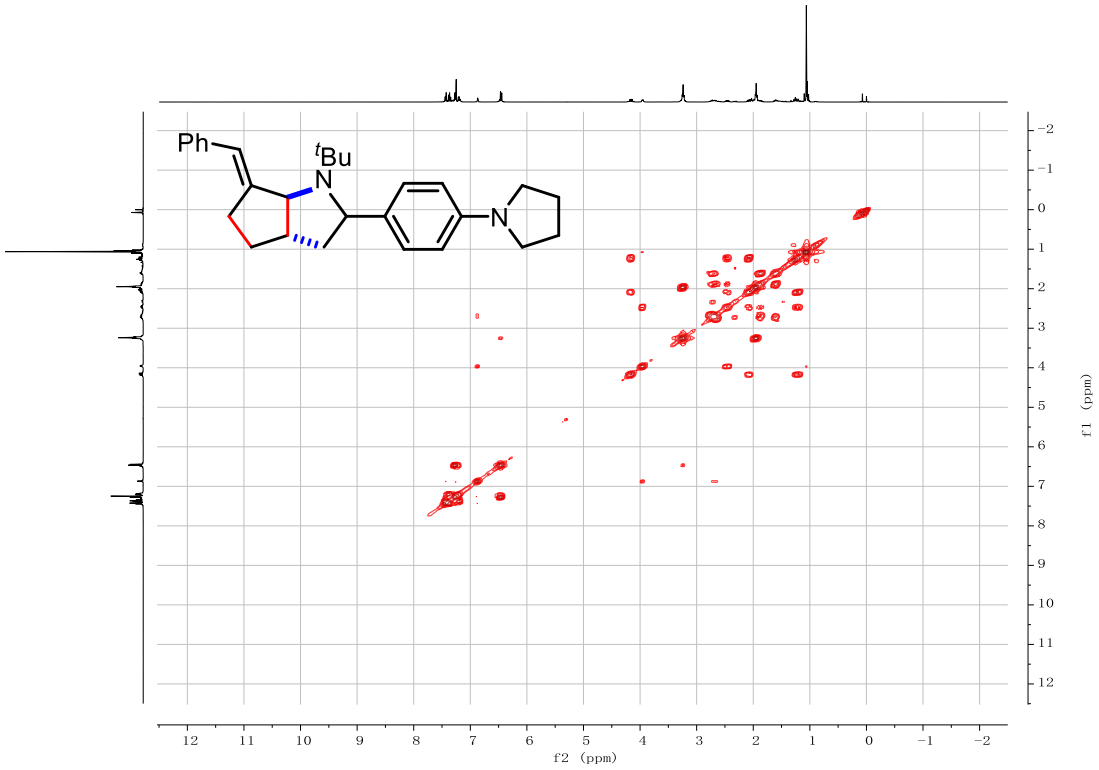
HSQC spectrum of *trans*-3av'



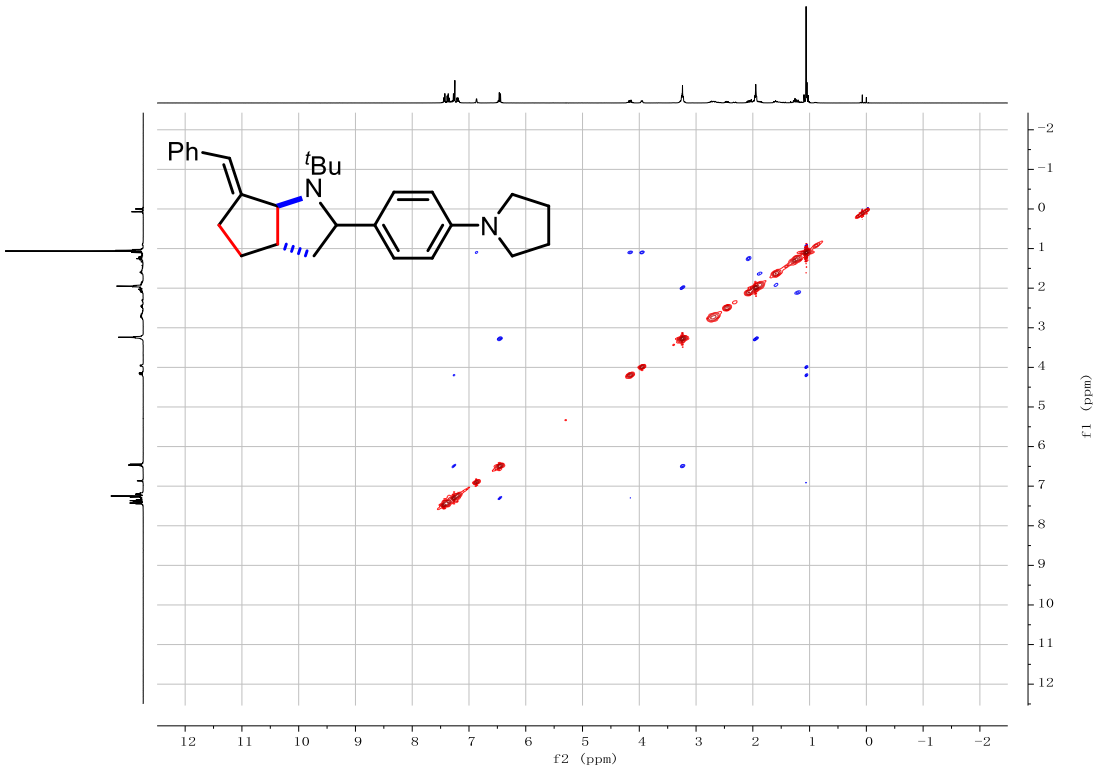
HMQC spectrum of *trans*-3av'



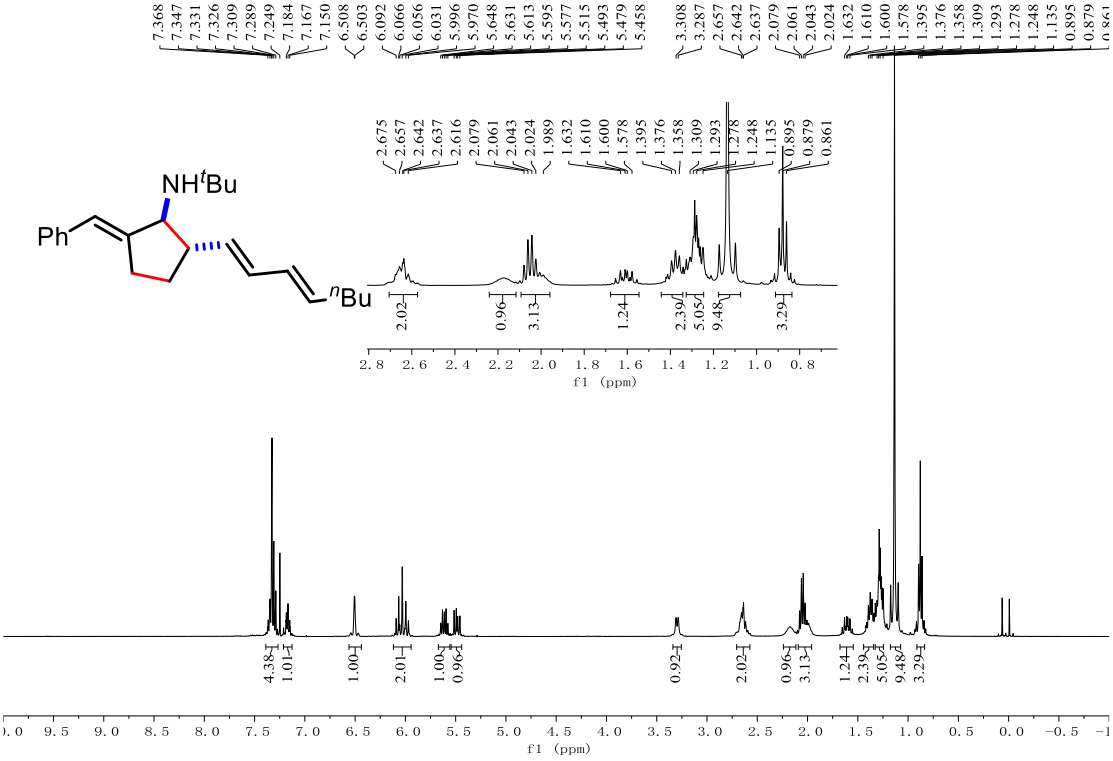
COSY spectrum of *trans*-3av'



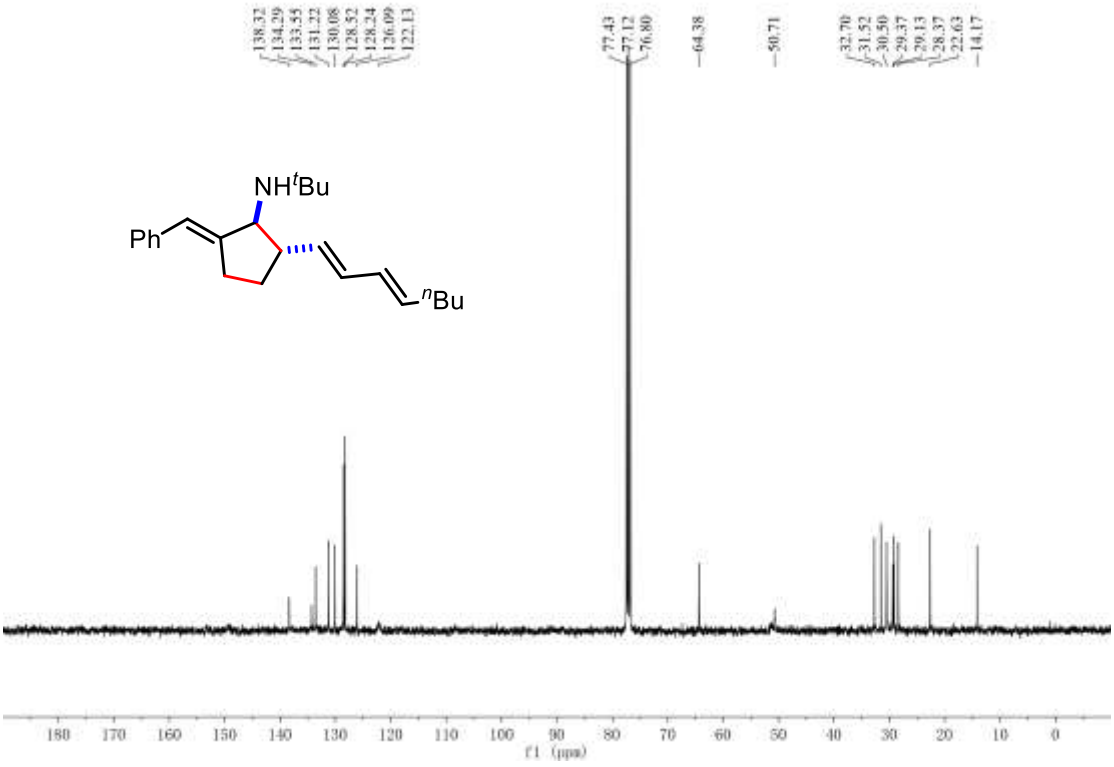
NOE spectrum of *trans*-3av'



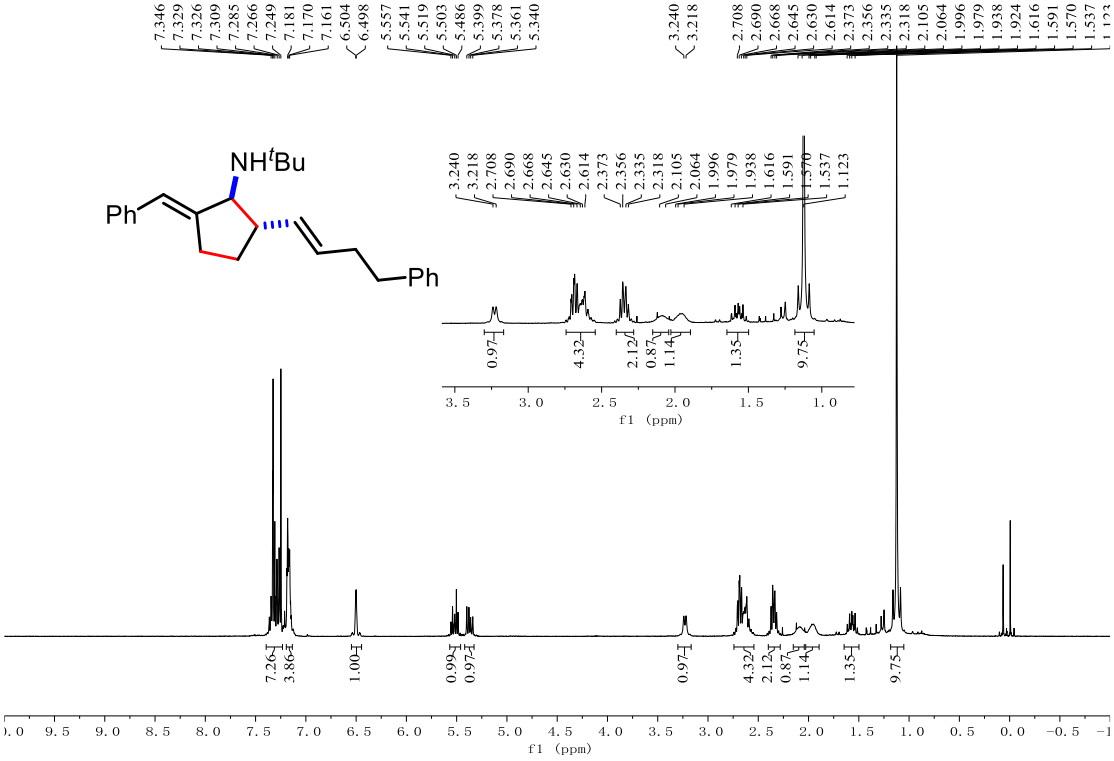
^{1}H NMR spectrum of *trans*-3aw (400 MHz, $CDCl_3$)



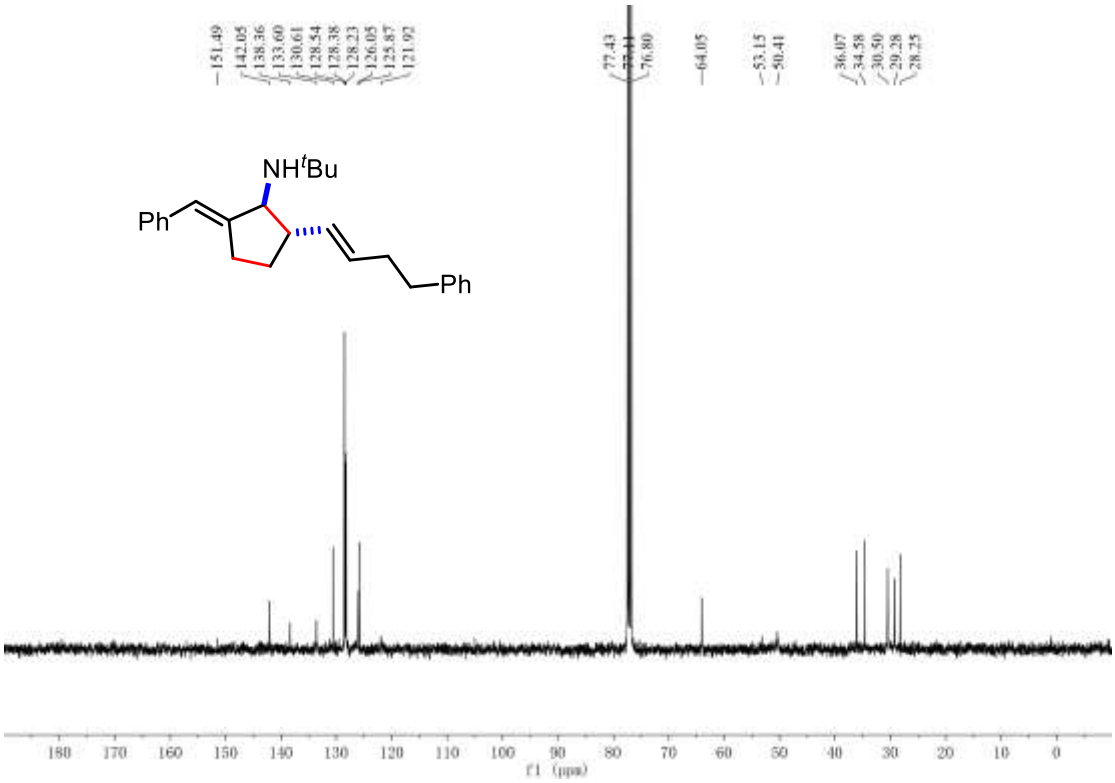
^{13}C NMR spectrum of *trans*-3aw (101 MHz, $CDCl_3$)



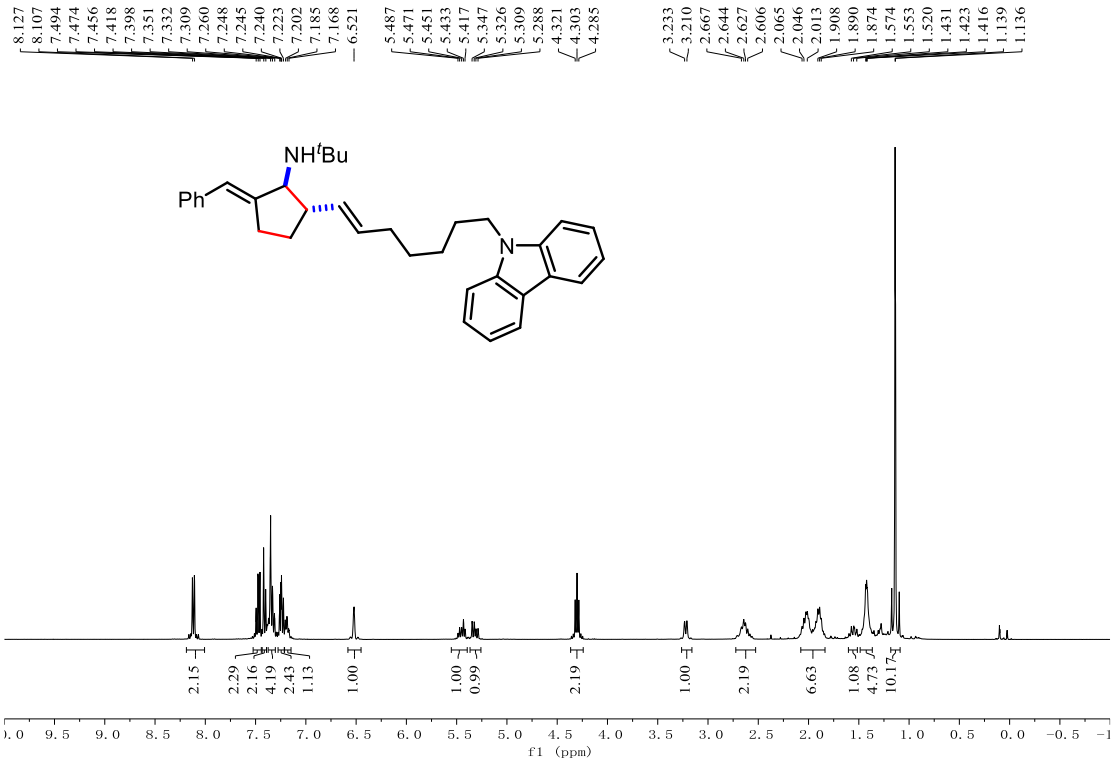
^{1}H NMR spectrum of *trans*-3ax (400 MHz, $CDCl_3$)



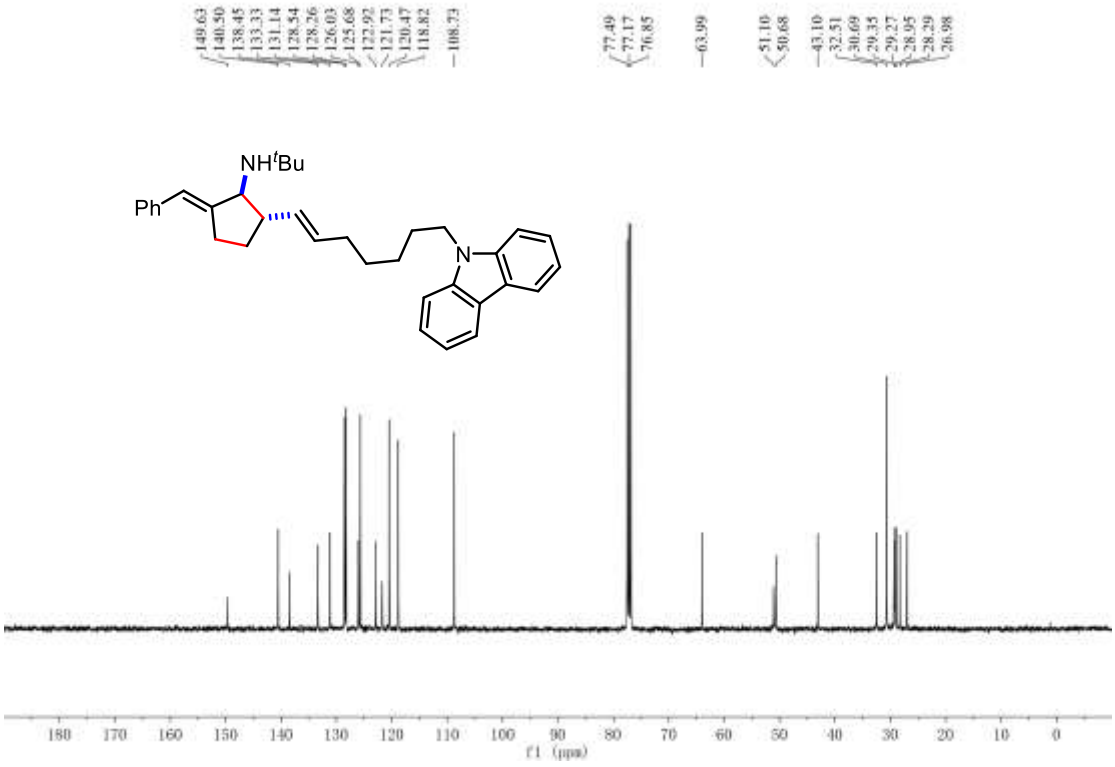
^{13}C NMR spectrum of *trans*-3ax (101 MHz, $CDCl_3$)



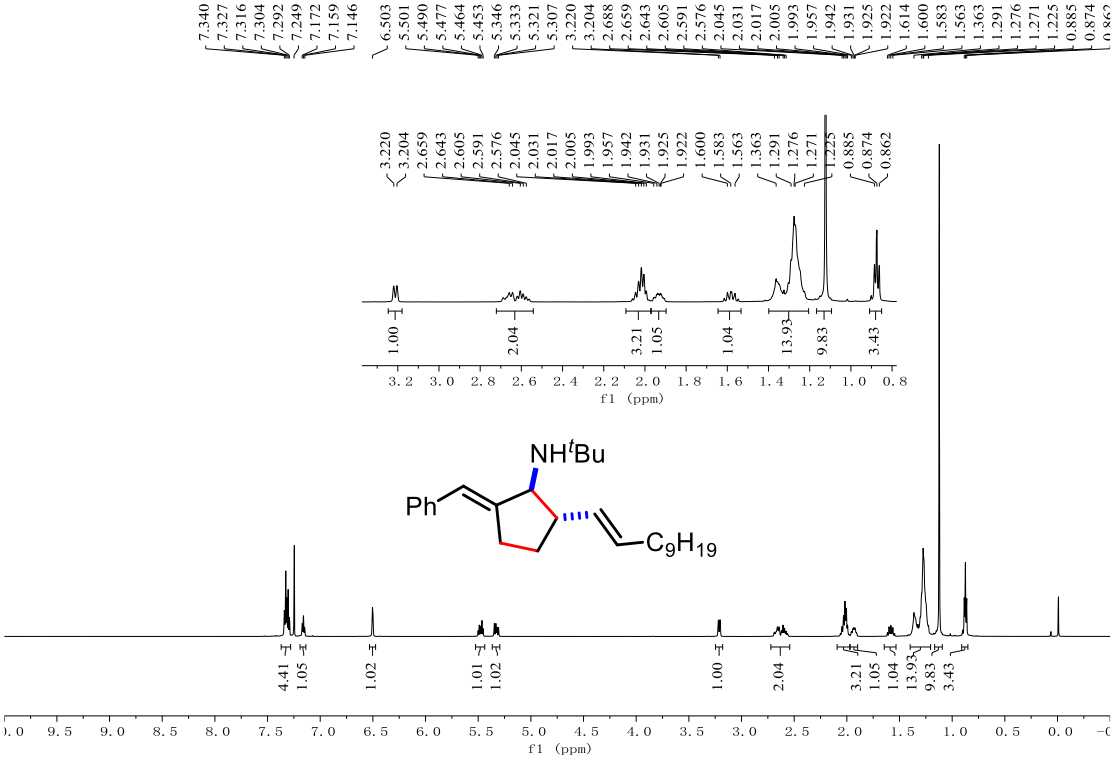
^{1}H NMR spectrum of *trans*-3ay (400 MHz, $CDCl_3$)



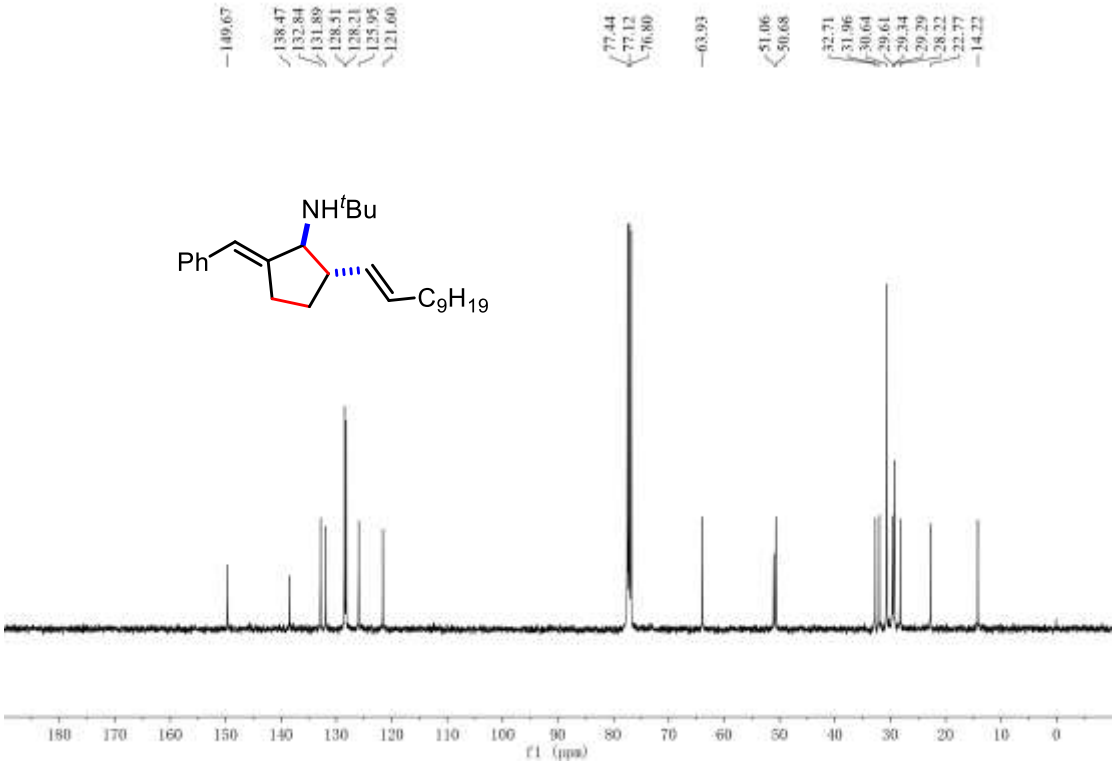
^{13}C NMR spectrum of *trans*-3ay (101 MHz, $CDCl_3$)



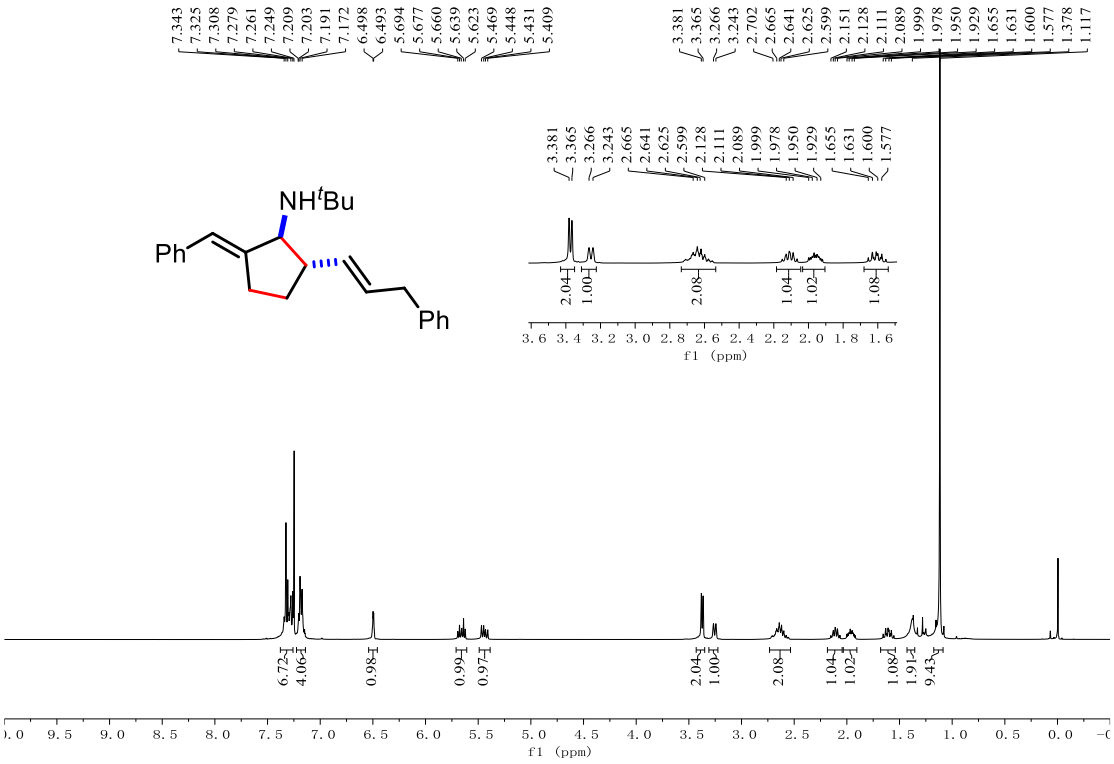
^{1}H NMR spectrum of *trans*-3az (600 MHz, $CDCl_3$)



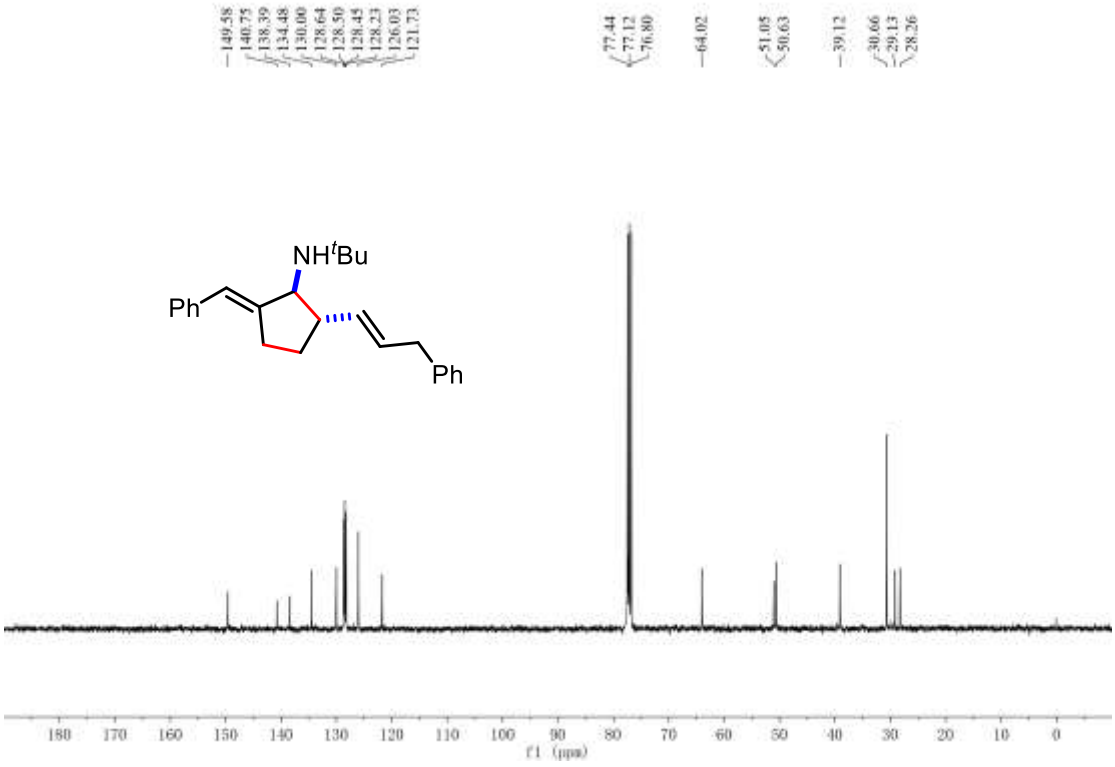
^{13}C NMR spectrum of *trans*-3az (101 MHz, $CDCl_3$)



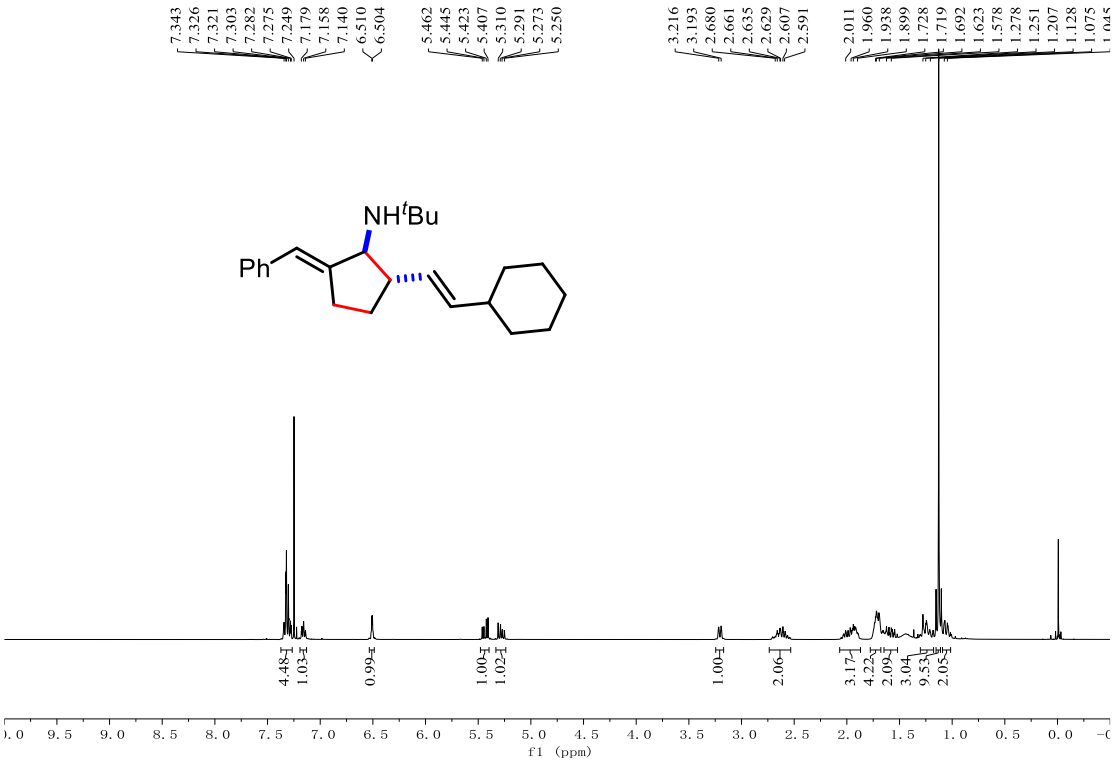
^{1}H NMR spectrum of *trans*-3aaa (600 MHz, $CDCl_3$)



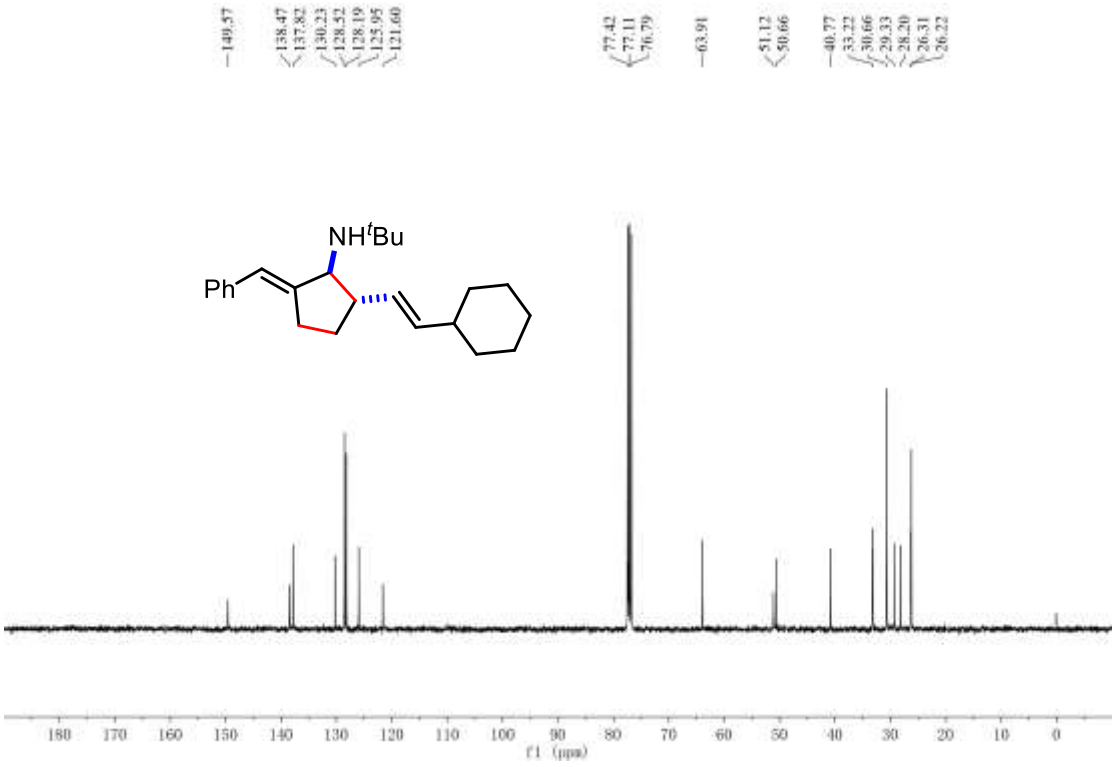
^{13}C NMR spectrum of *trans*-3aaa (101 MHz, $CDCl_3$)



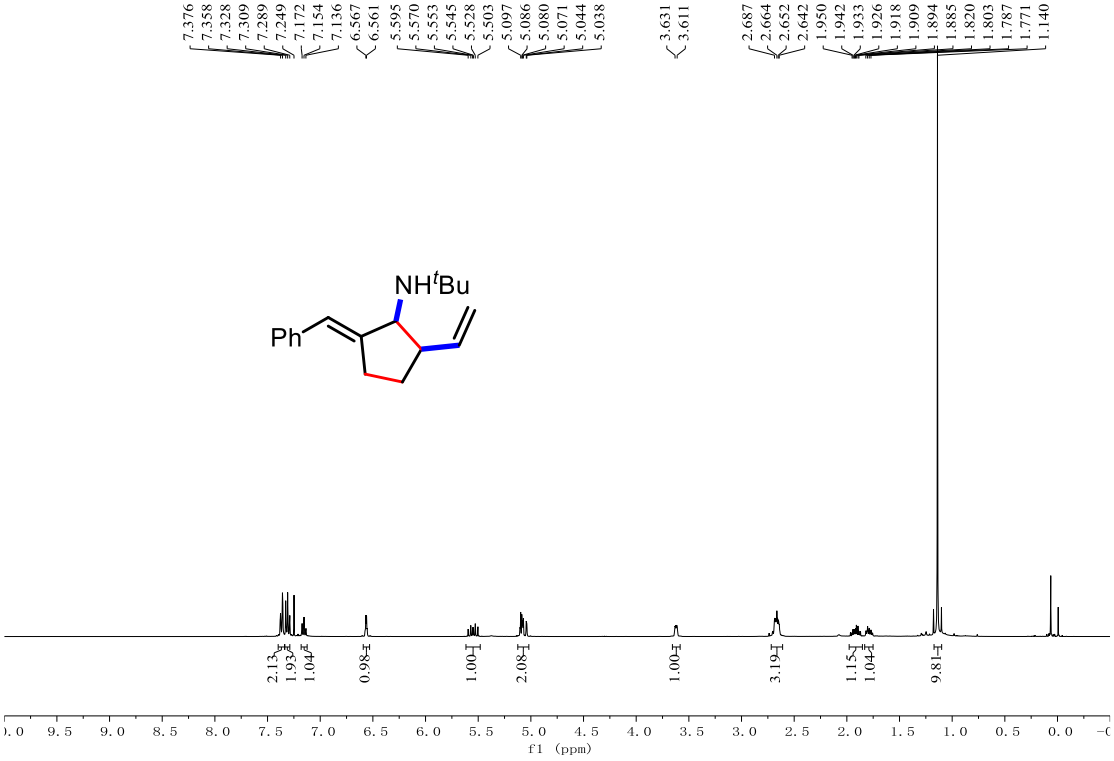
^{1}H NMR spectrum of *trans*-3aab (600 MHz, $CDCl_3$)



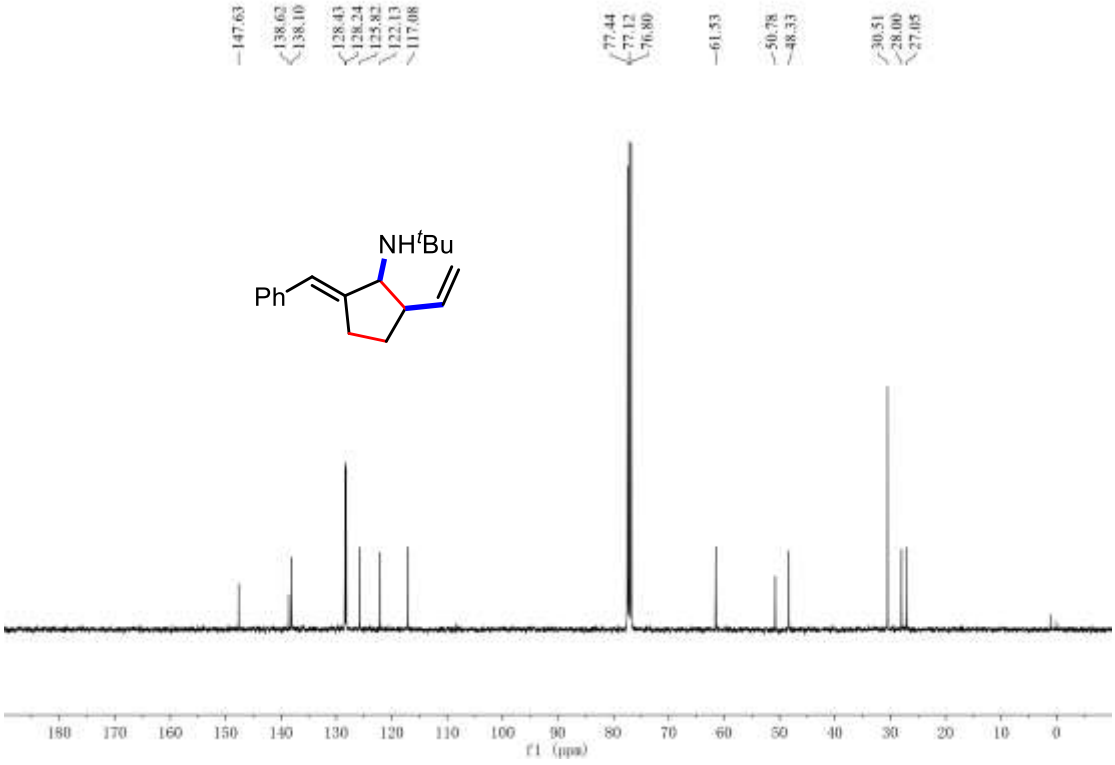
^{13}C NMR spectrum of *trans*-3aab (101 MHz, $CDCl_3$)



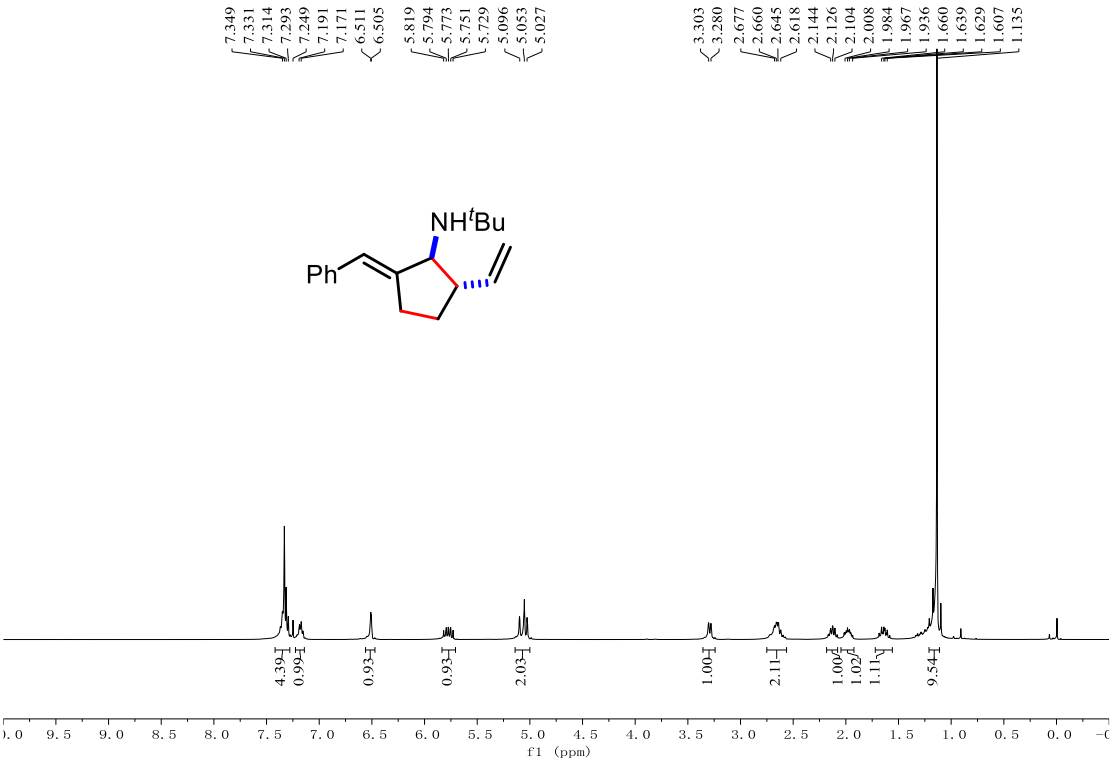
^{1}H NMR spectrum of *cis*-3aac (400 MHz, $CDCl_3$)



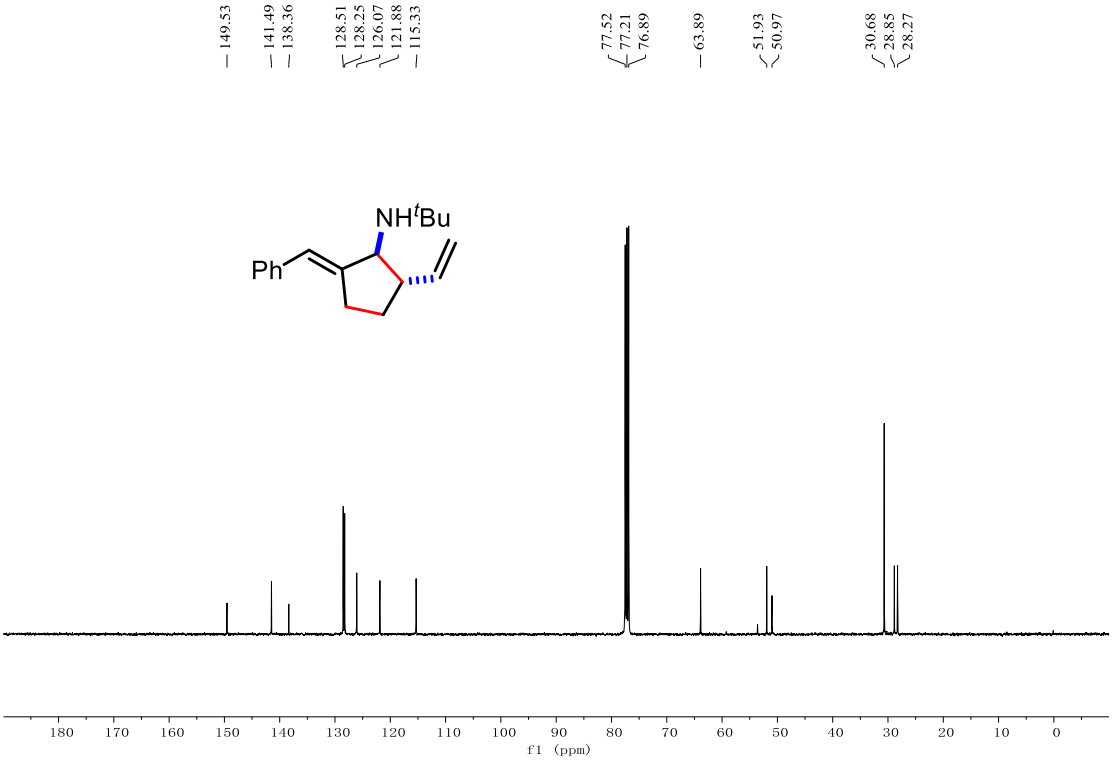
^{13}C NMR spectrum of *cis*-3aac (101 MHz, $CDCl_3$)



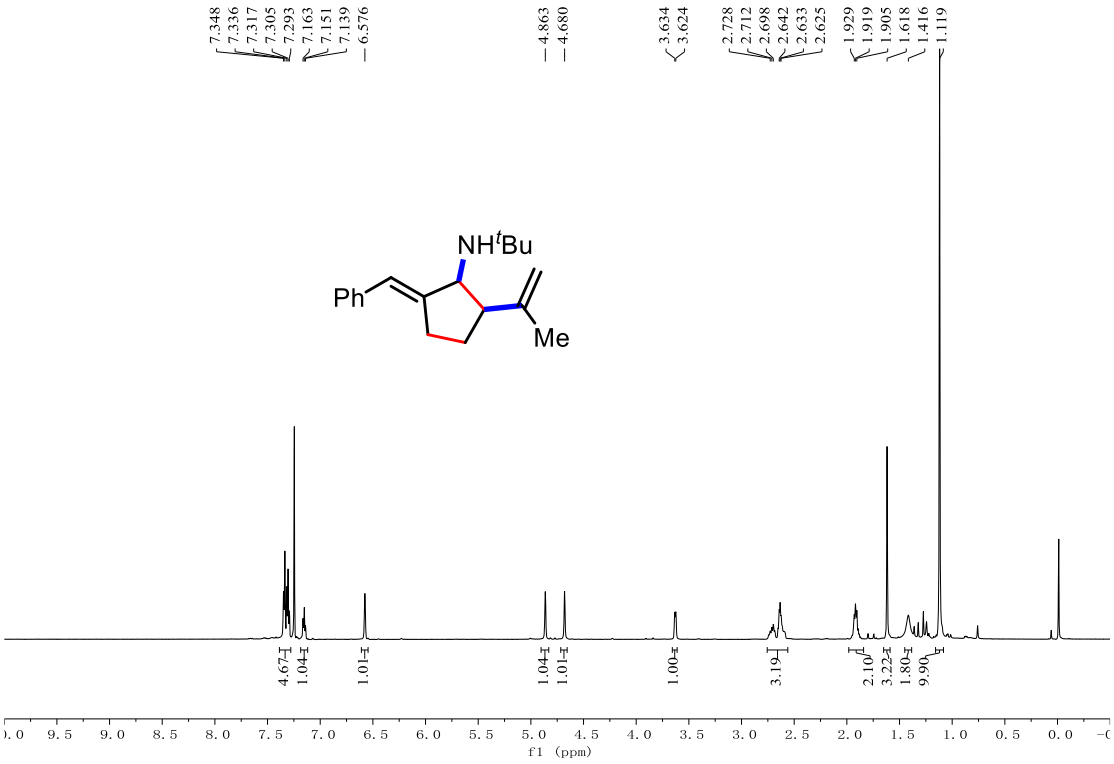
^{1}H NMR spectrum of *trans*-3aac (400 MHz, $CDCl_3$)



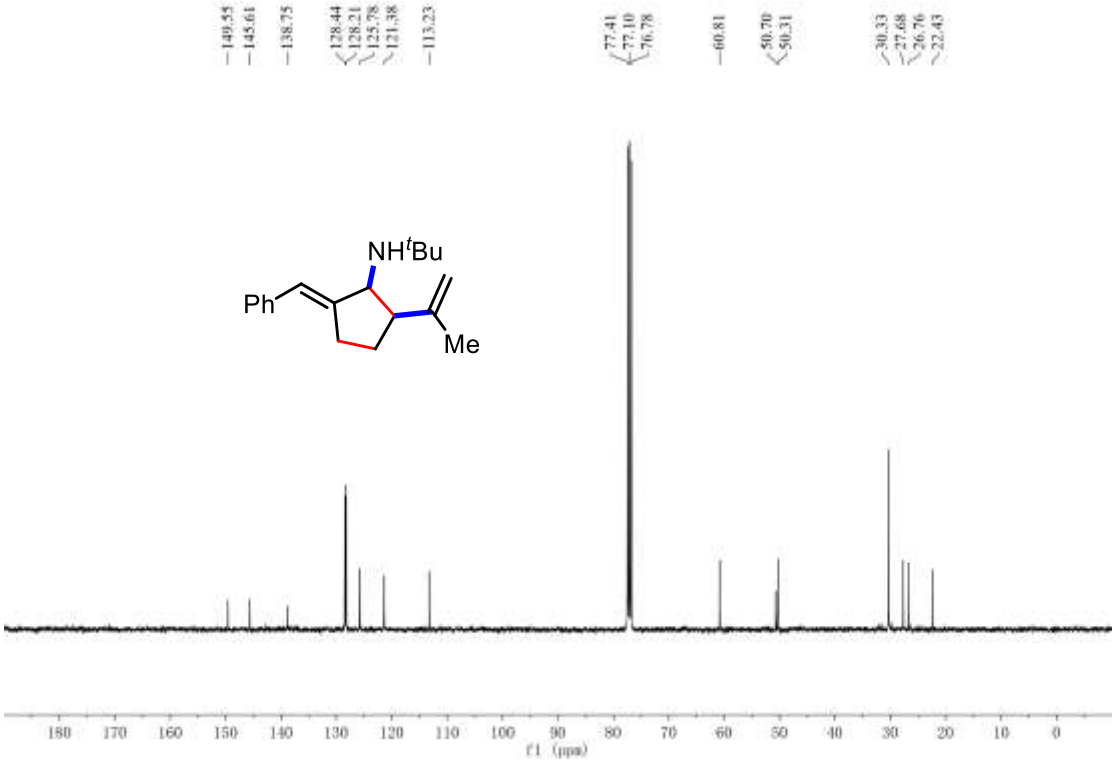
^{13}C NMR spectrum of *trans*-3aac (101 MHz, $CDCl_3$)



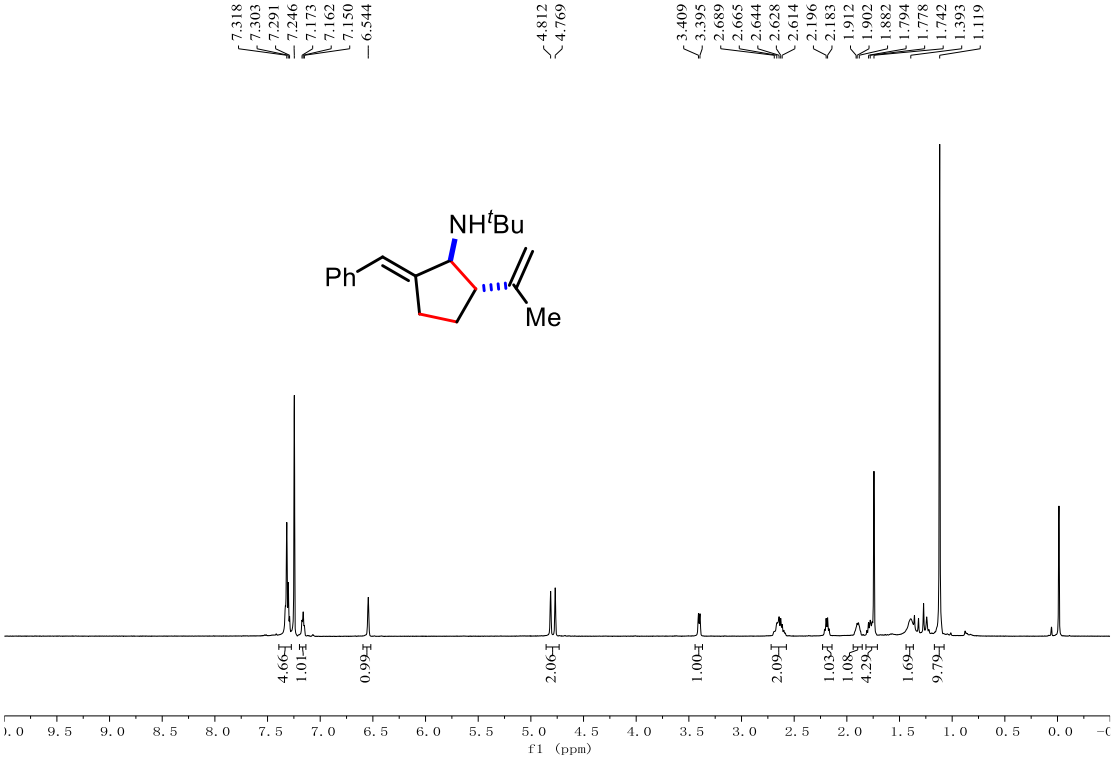
^{1}H NMR spectrum of *cis*-3aad (400 MHz, $CDCl_3$)



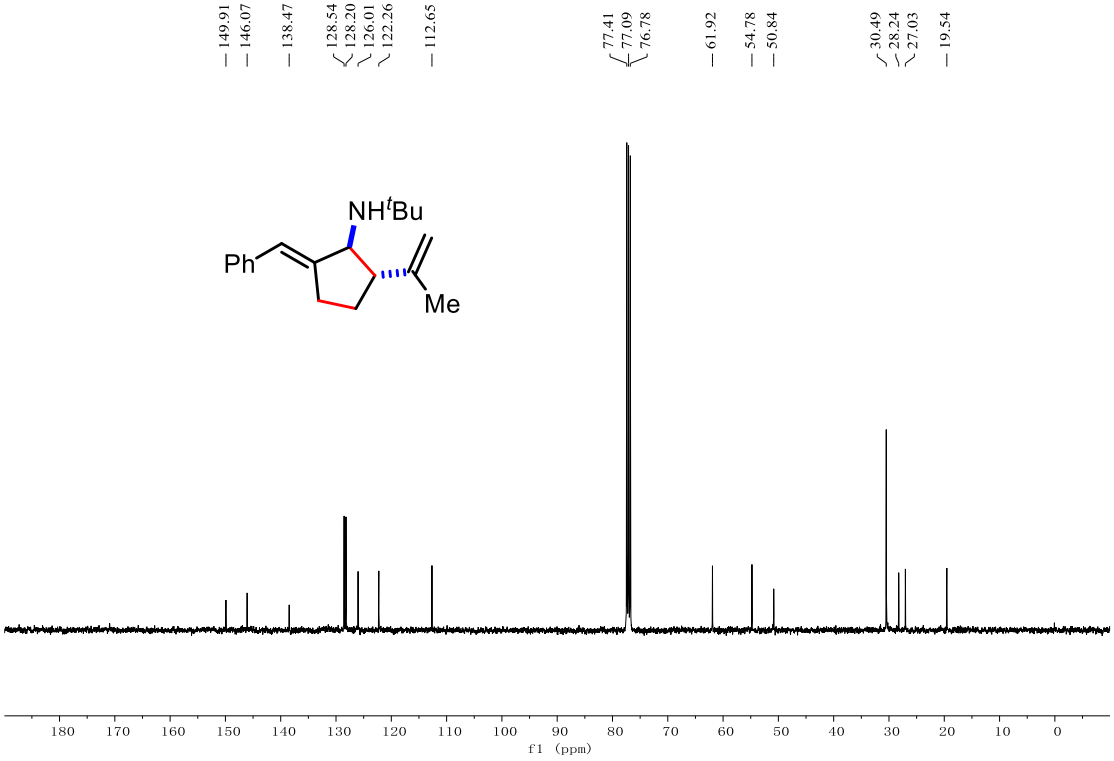
^{13}C NMR spectrum of *cis*-3aad (101 MHz, $CDCl_3$)



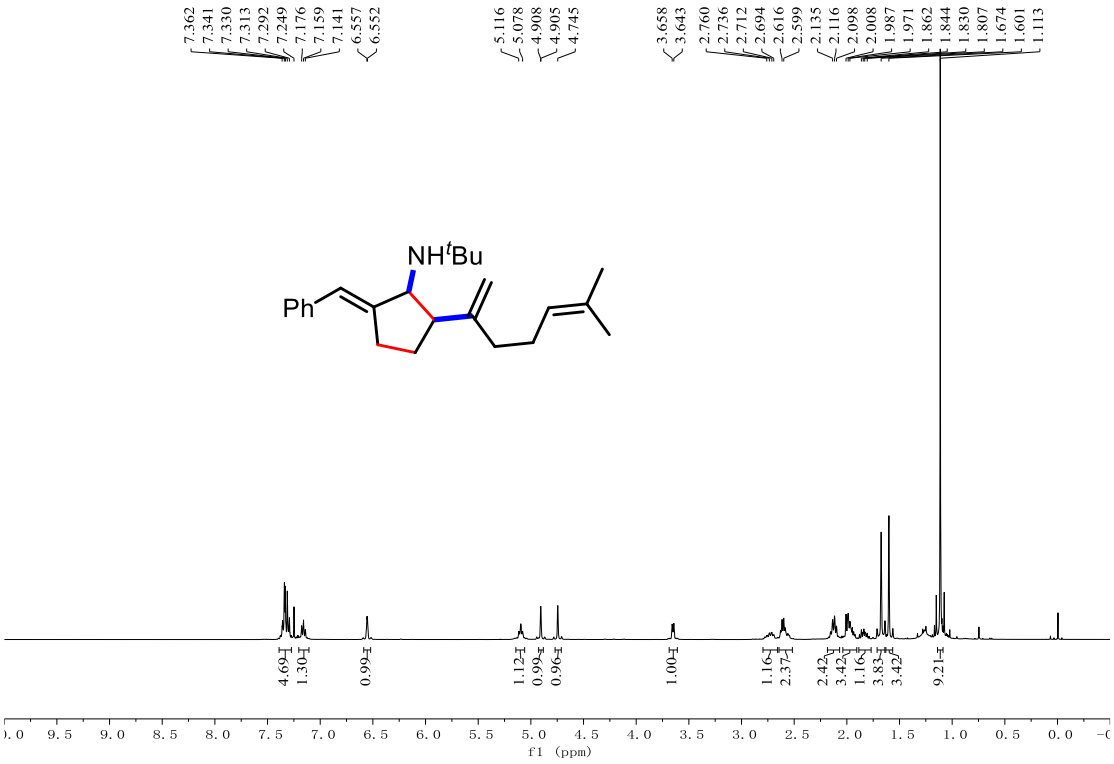
^{1}H NMR spectrum of *trans*-3aad (400 MHz, $CDCl_3$)



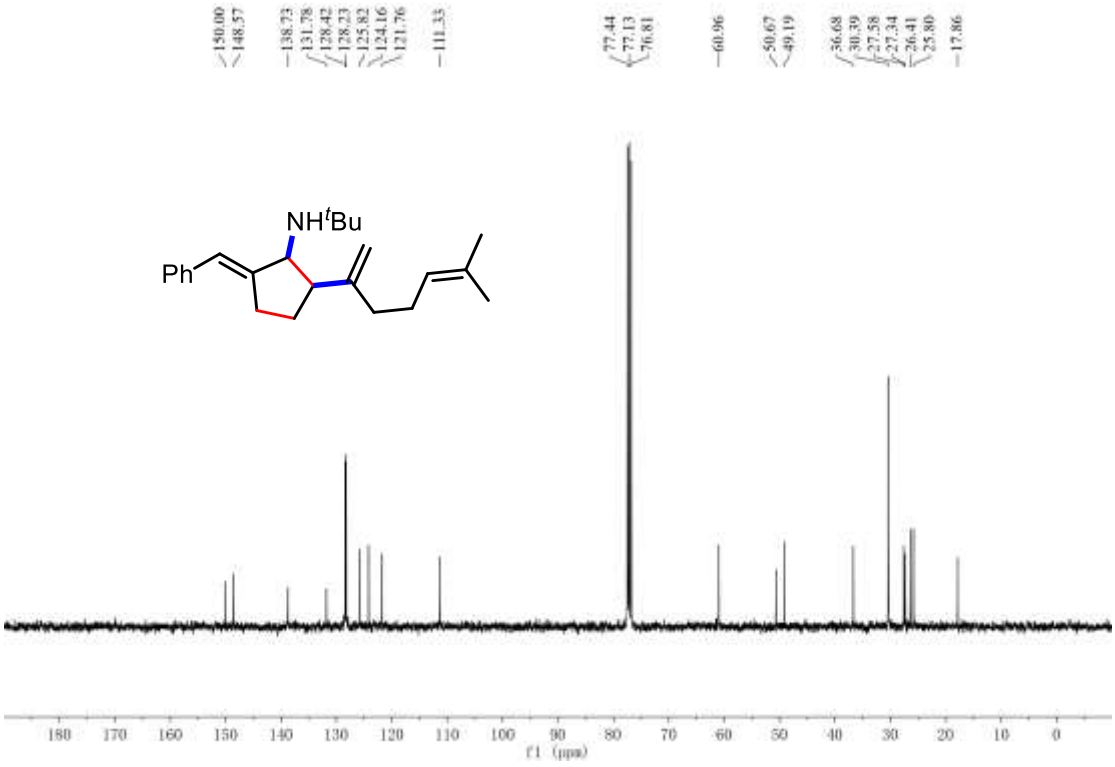
^{13}C NMR spectrum of *trans*-3aad (101 MHz, $CDCl_3$)



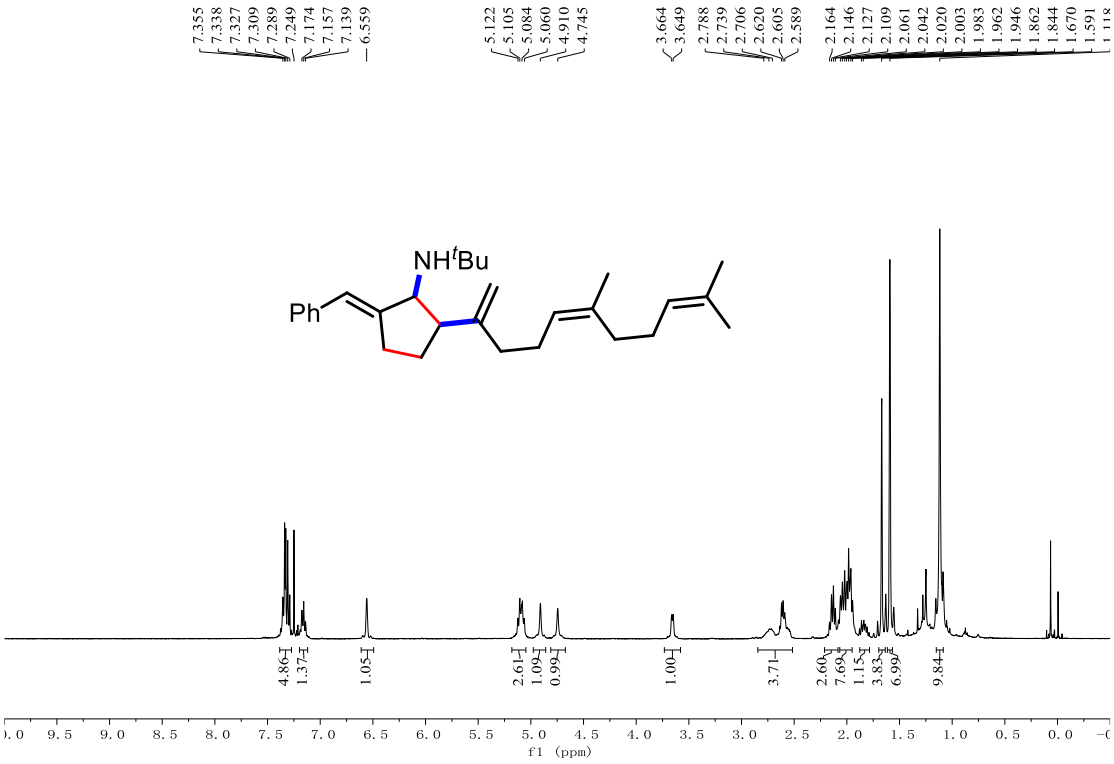
^{1}H NMR spectrum of *cis*-3aae (400 MHz, $CDCl_3$)



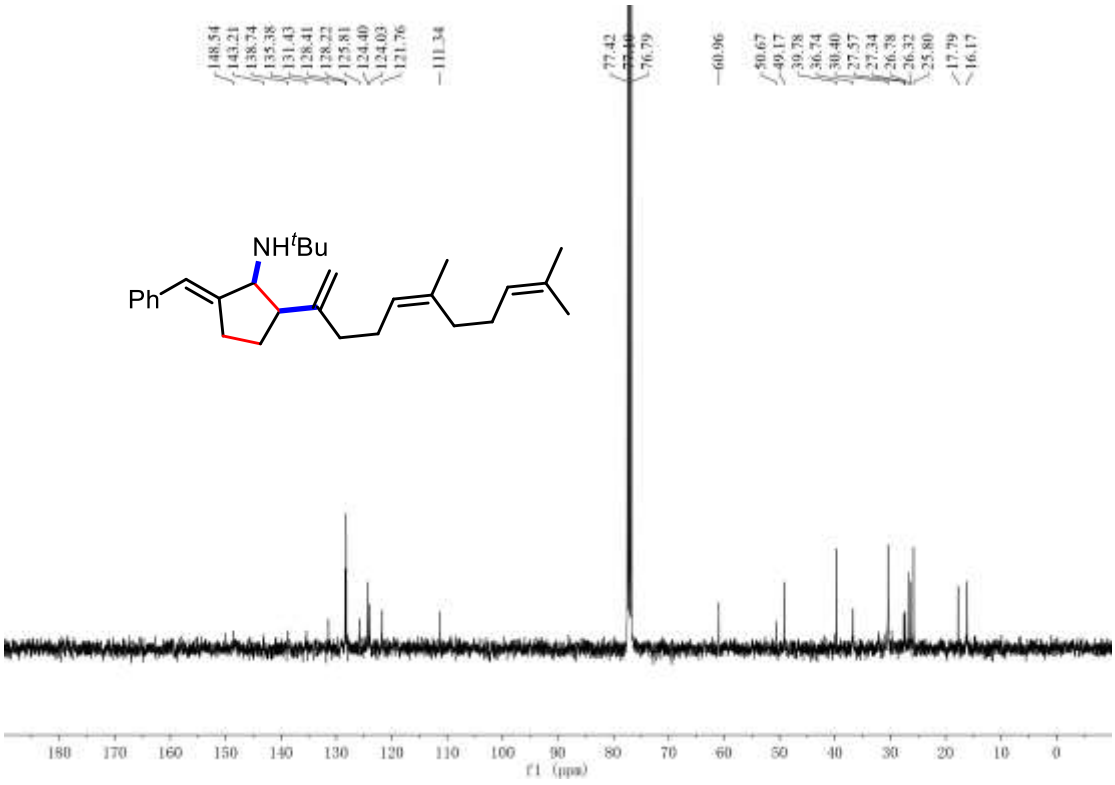
^{13}C NMR spectrum of *cis*-3aae (101 MHz, $CDCl_3$)



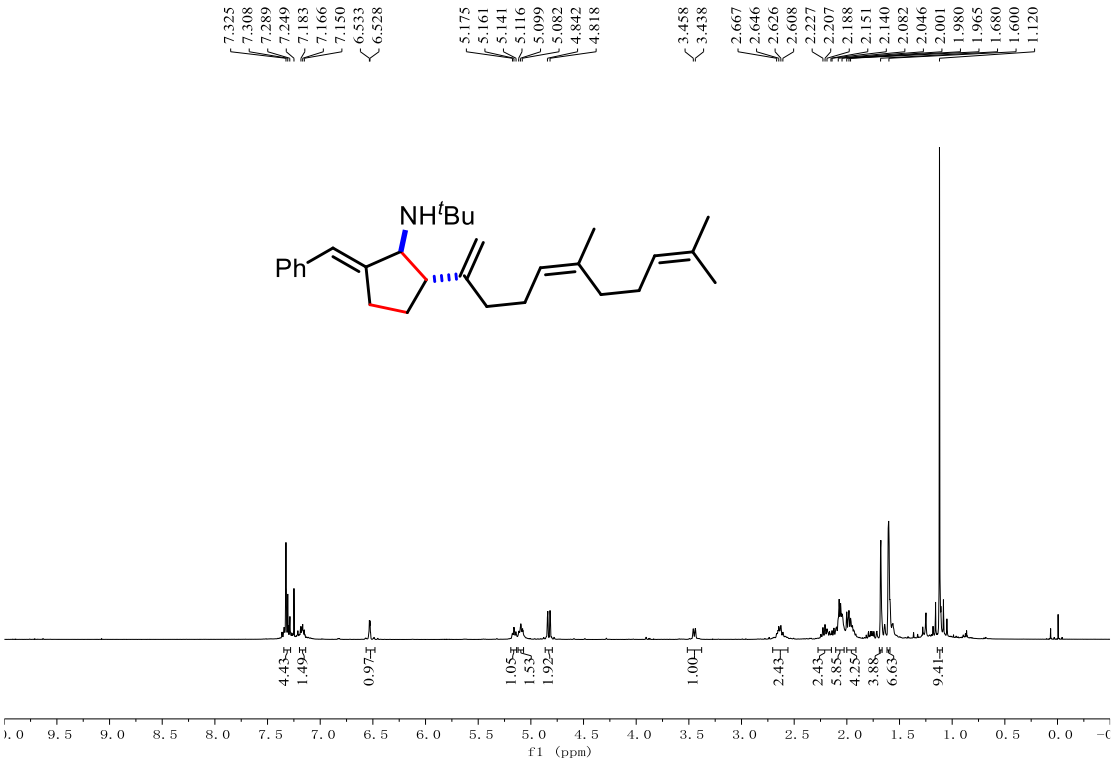
^{1}H NMR spectrum of *cis*-3aaf (400 MHz, $CDCl_3$)



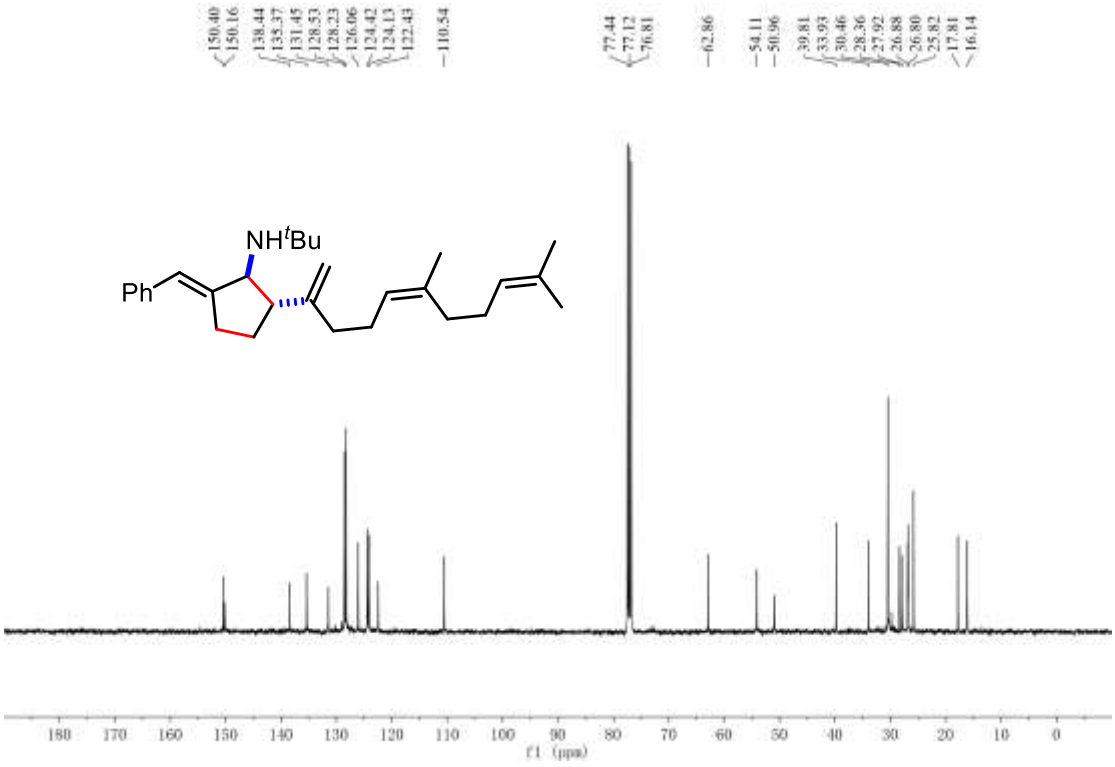
^{13}C NMR spectrum of *cis*-3aaf (101 MHz, $CDCl_3$)



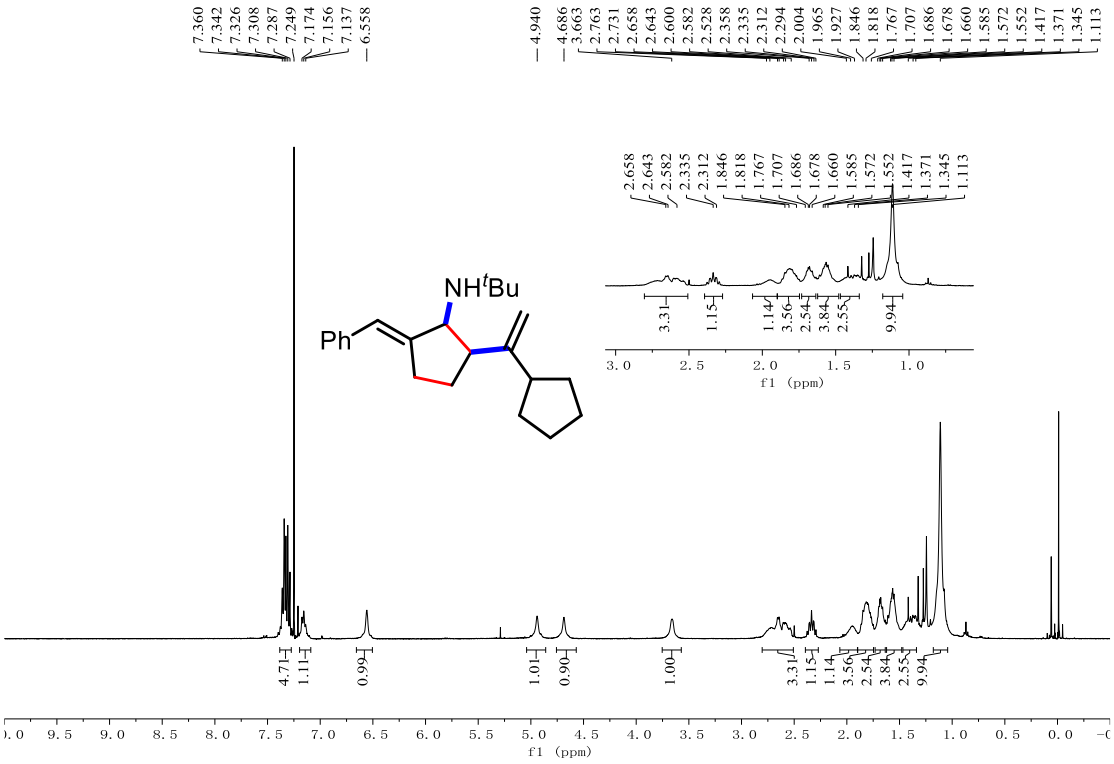
^{1}H NMR spectrum of *trans*-3aaf (400 MHz, $CDCl_3$)



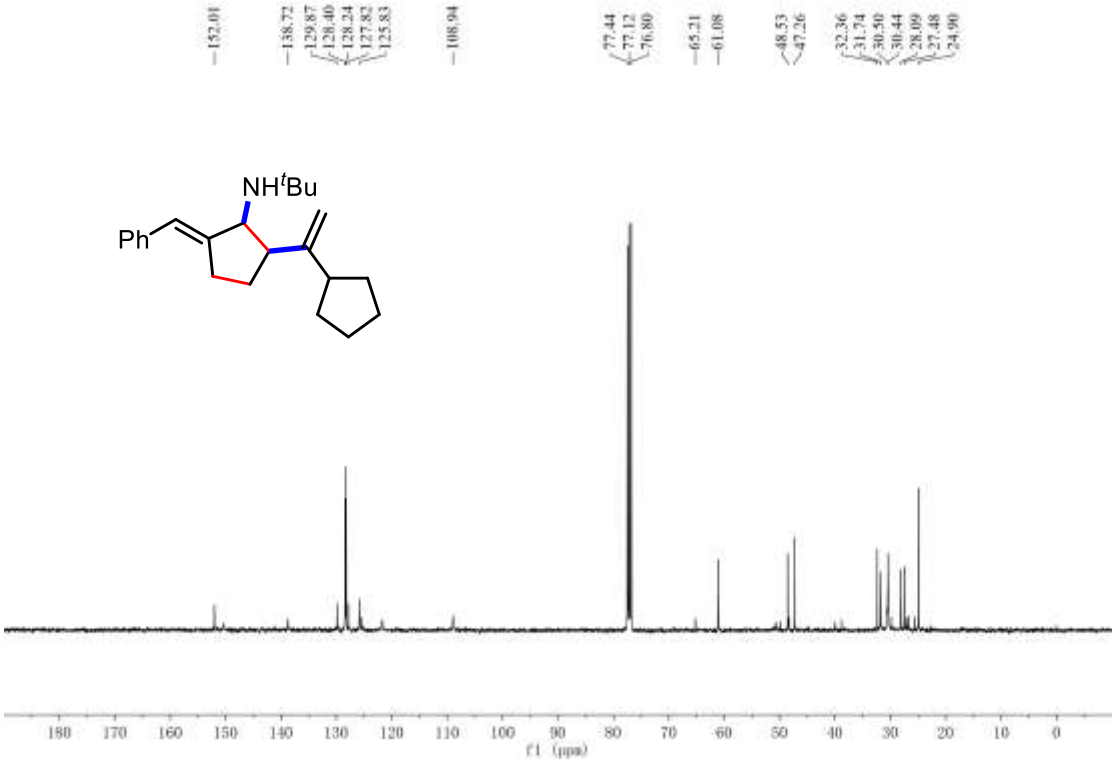
^{13}C NMR spectrum of *trans*-3aaf (101 MHz, $CDCl_3$)



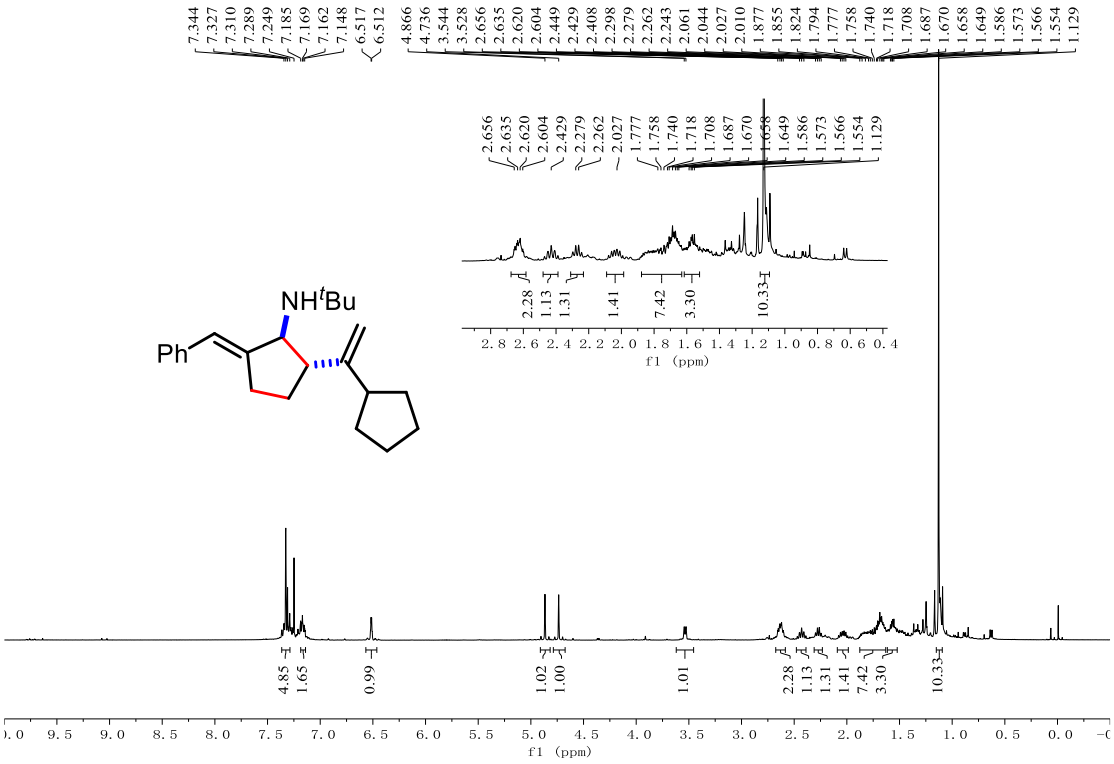
^{1}H NMR spectrum of *cis*-3aag (400 MHz, $CDCl_3$)



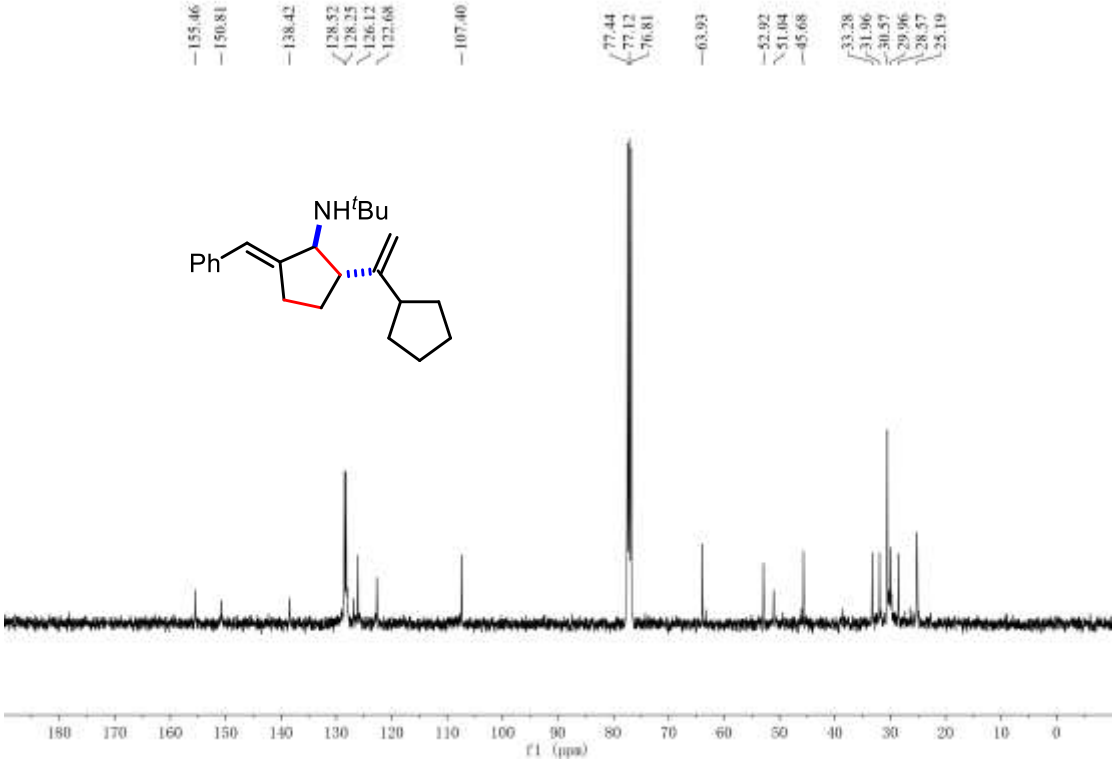
^{13}C NMR spectrum of *cis*-3aag (101 MHz, $CDCl_3$)



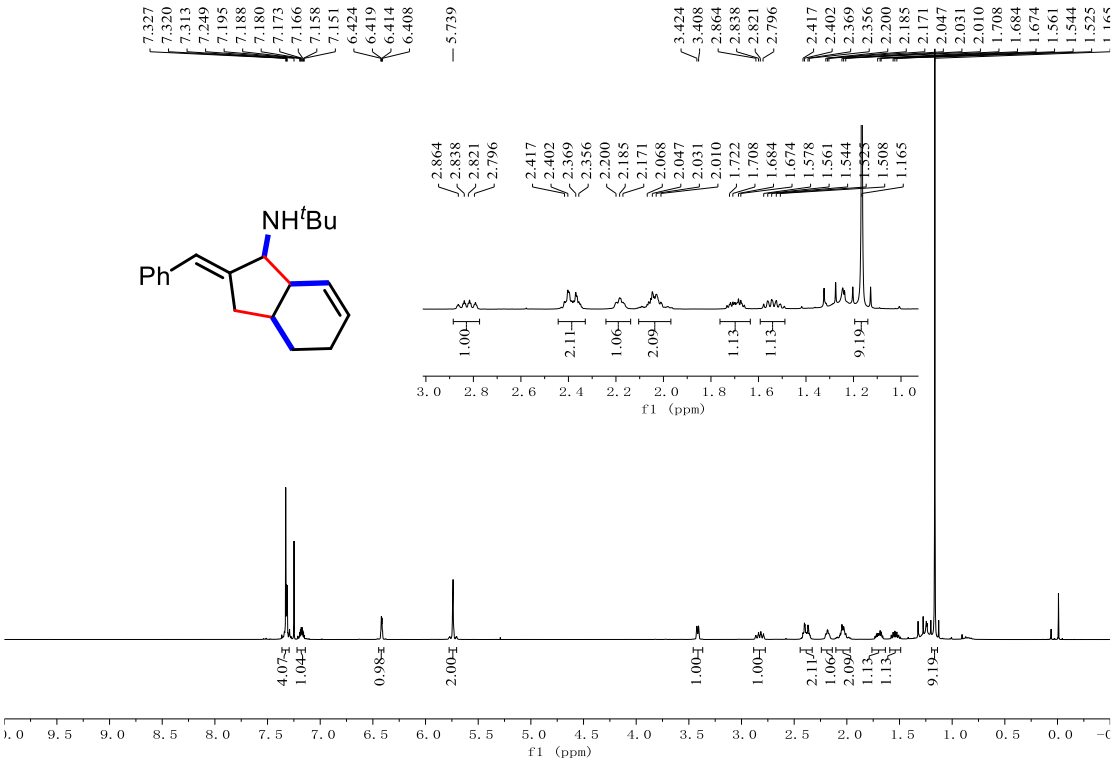
^{1}H NMR spectrum of *trans*-3aag (400 MHz, $CDCl_3$)



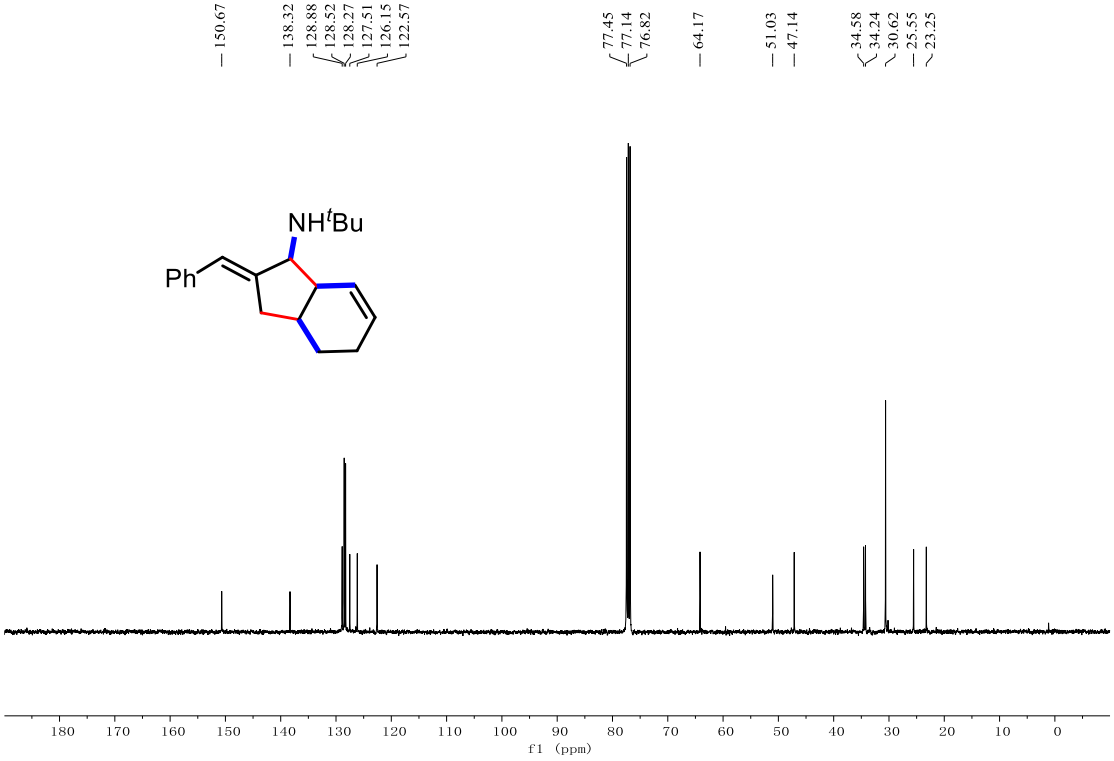
^{13}C NMR spectrum of *trans*-3aag (101 MHz, $CDCl_3$)



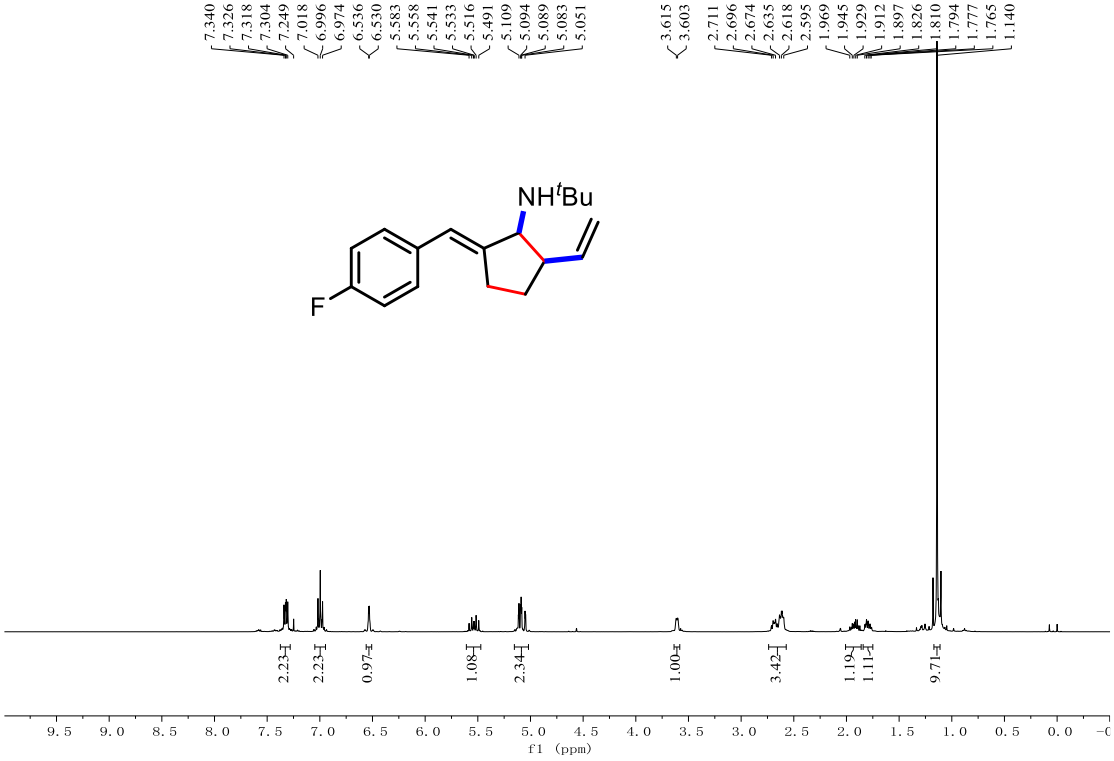
^{1}H NMR spectrum of *cis*-3aah (400 MHz, $CDCl_3$)



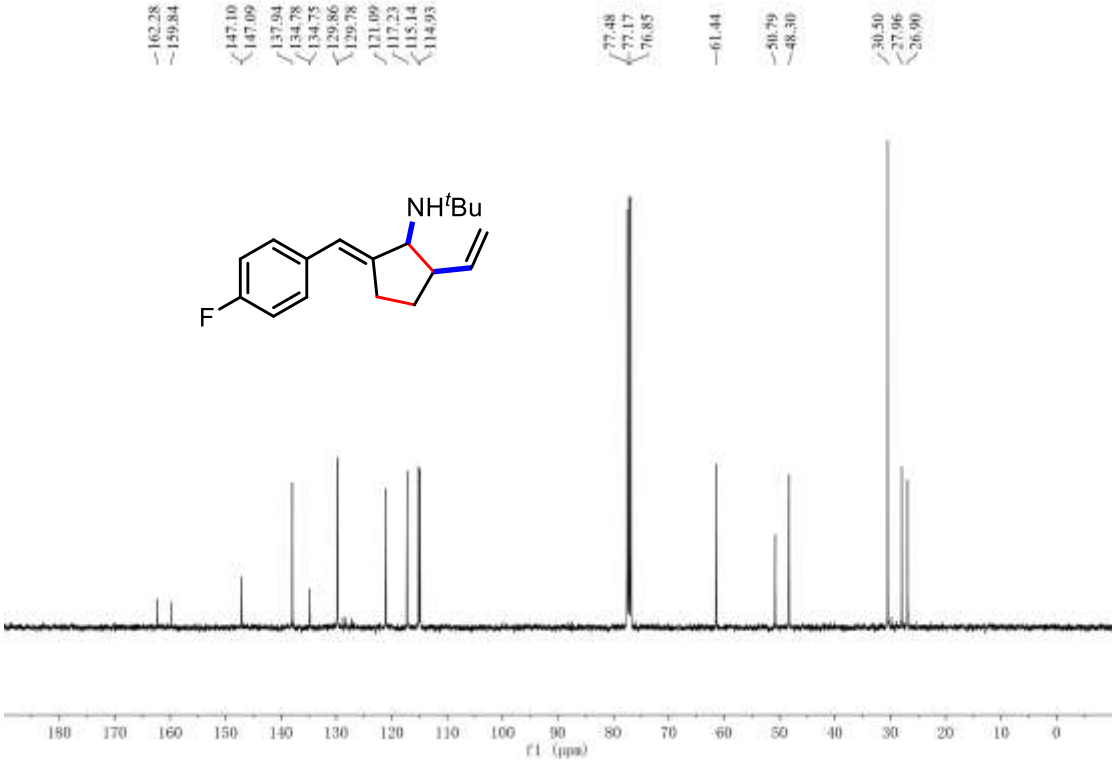
^{13}C NMR spectrum of *cis*-3aah (101 MHz, $CDCl_3$)



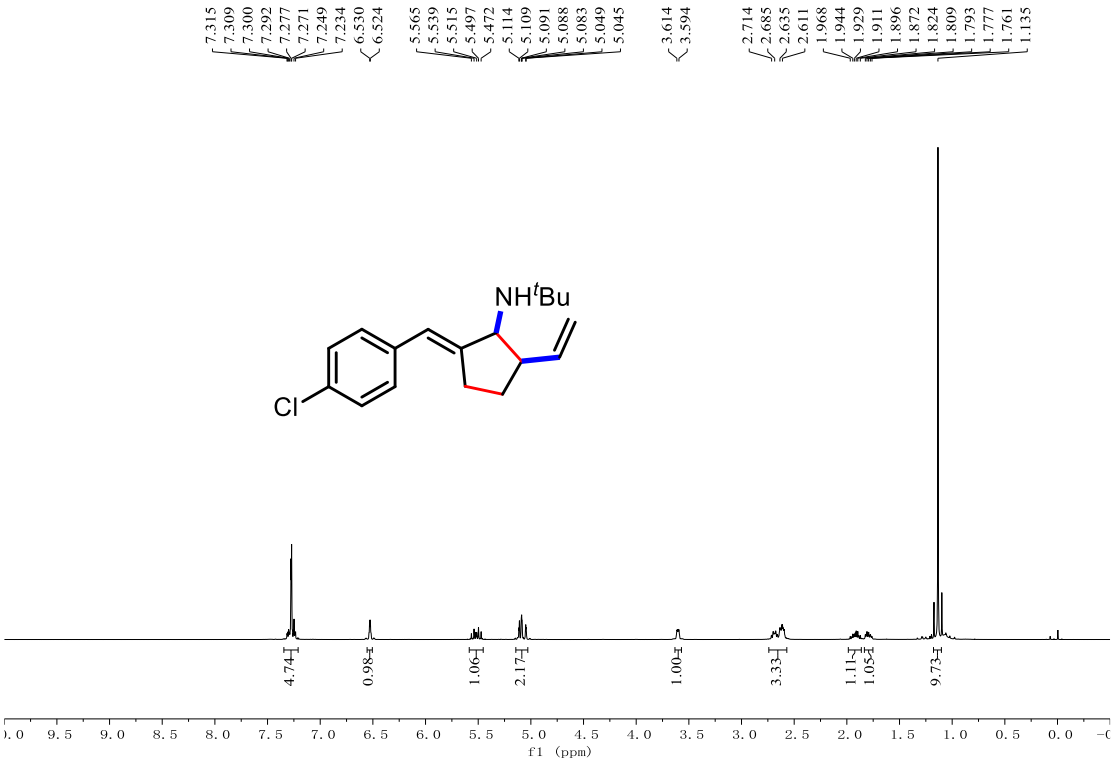
^{1}H NMR spectrum of *cis*-3cac (400 MHz, $CDCl_3$)



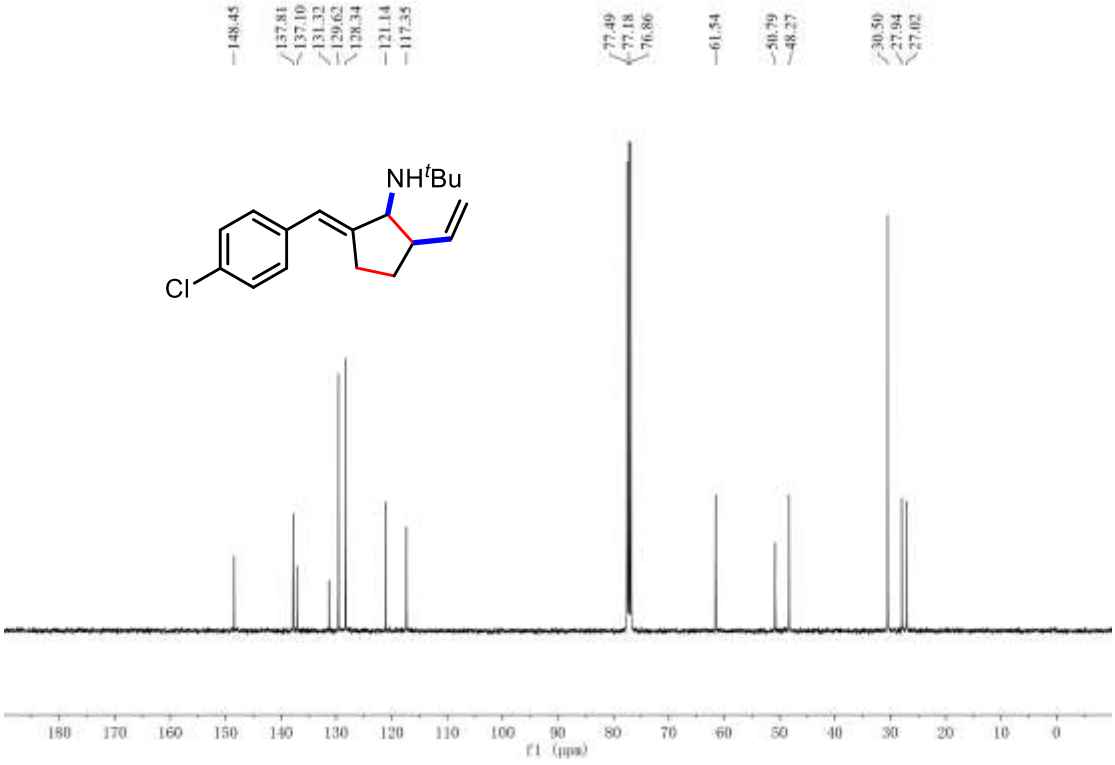
^{13}C NMR spectrum of *cis*-3cac (101 MHz, $CDCl_3$)



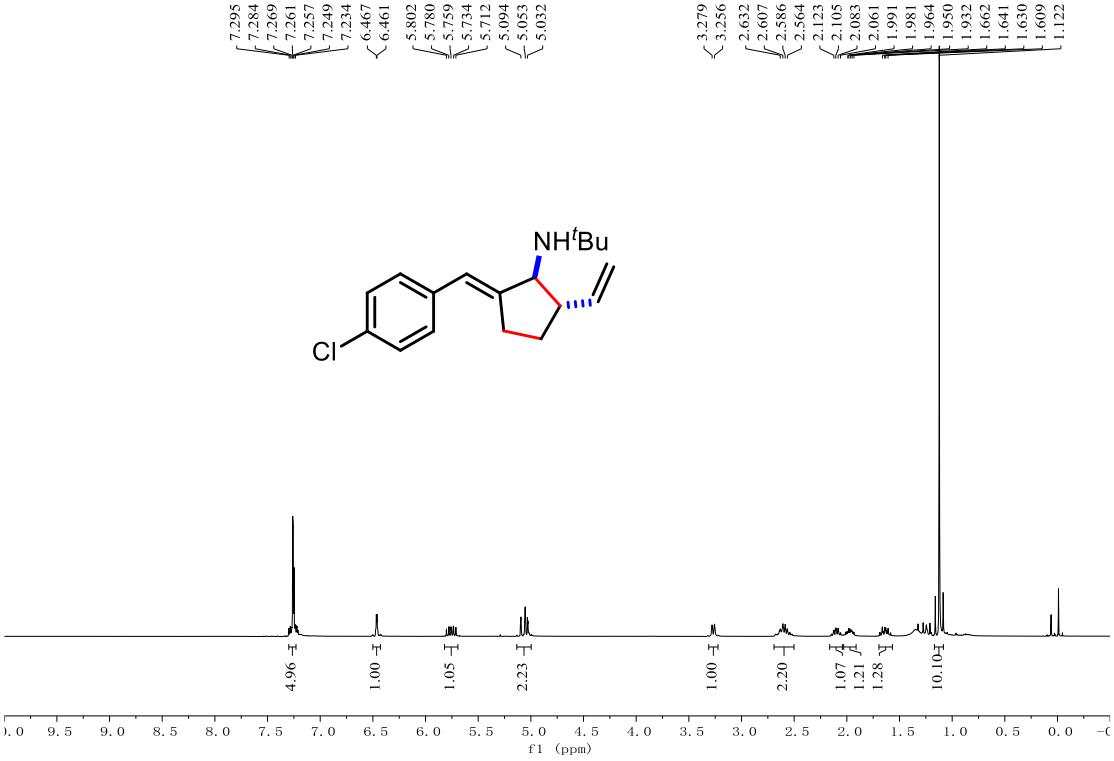
^{1}H NMR spectrum of *cis*-3dac (400 MHz, $CDCl_3$)



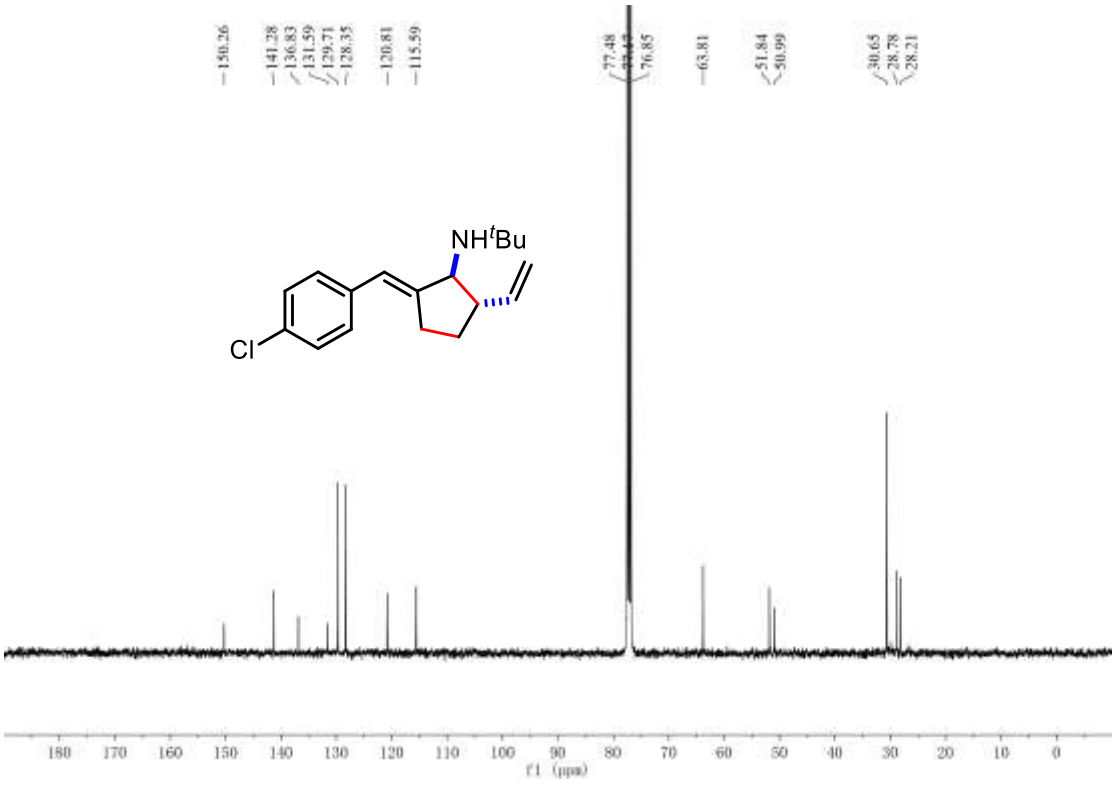
^{13}C NMR spectrum of *cis*-3dac (101 MHz, $CDCl_3$)



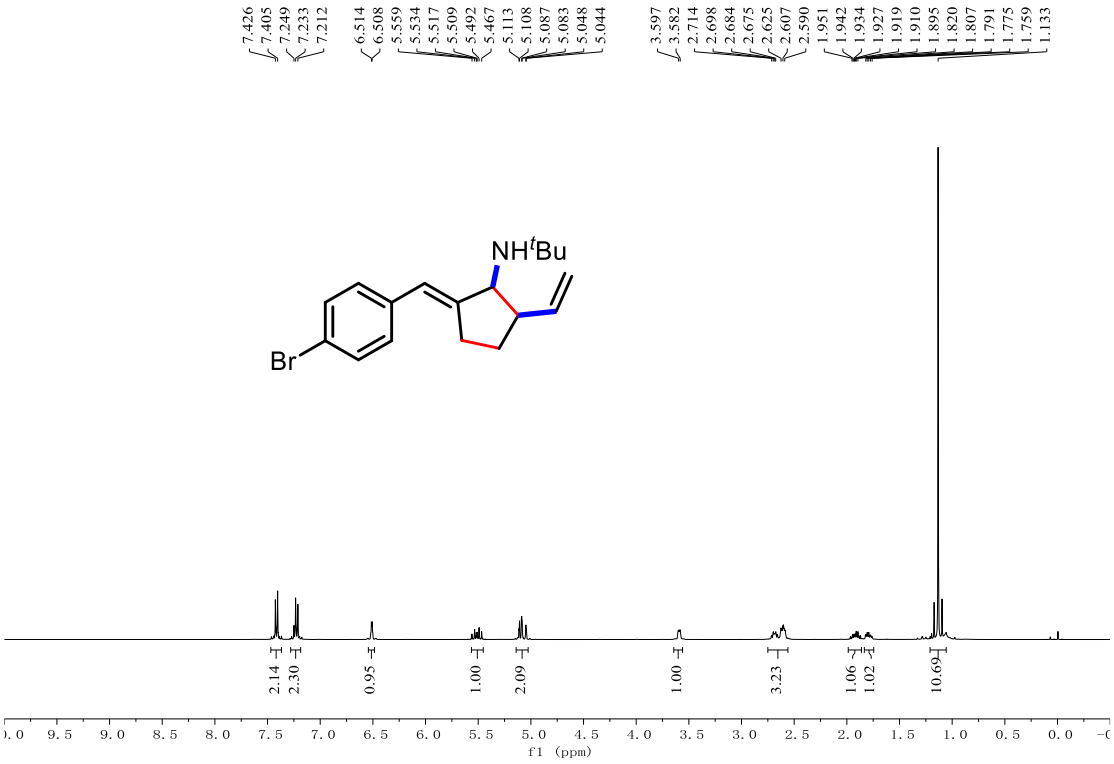
^{1}H NMR spectrum of *trans*-3dac (400 MHz, $CDCl_3$)



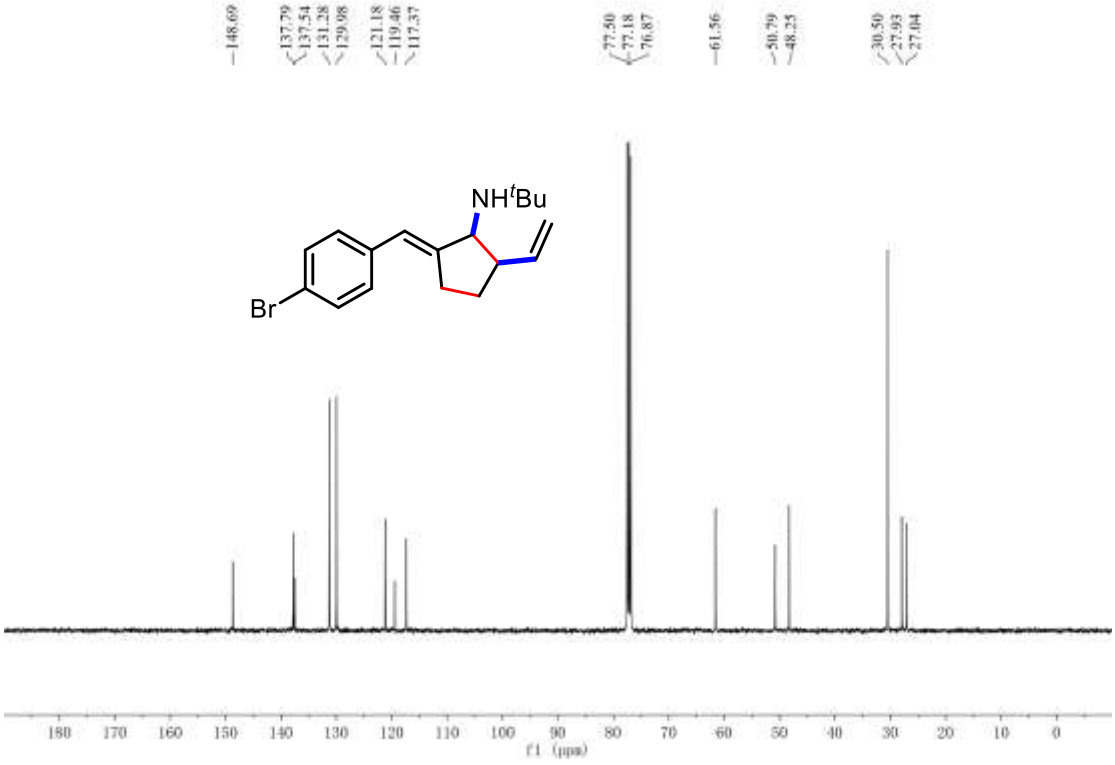
^{13}C NMR spectrum of *trans*-3dac (101 MHz, $CDCl_3$)



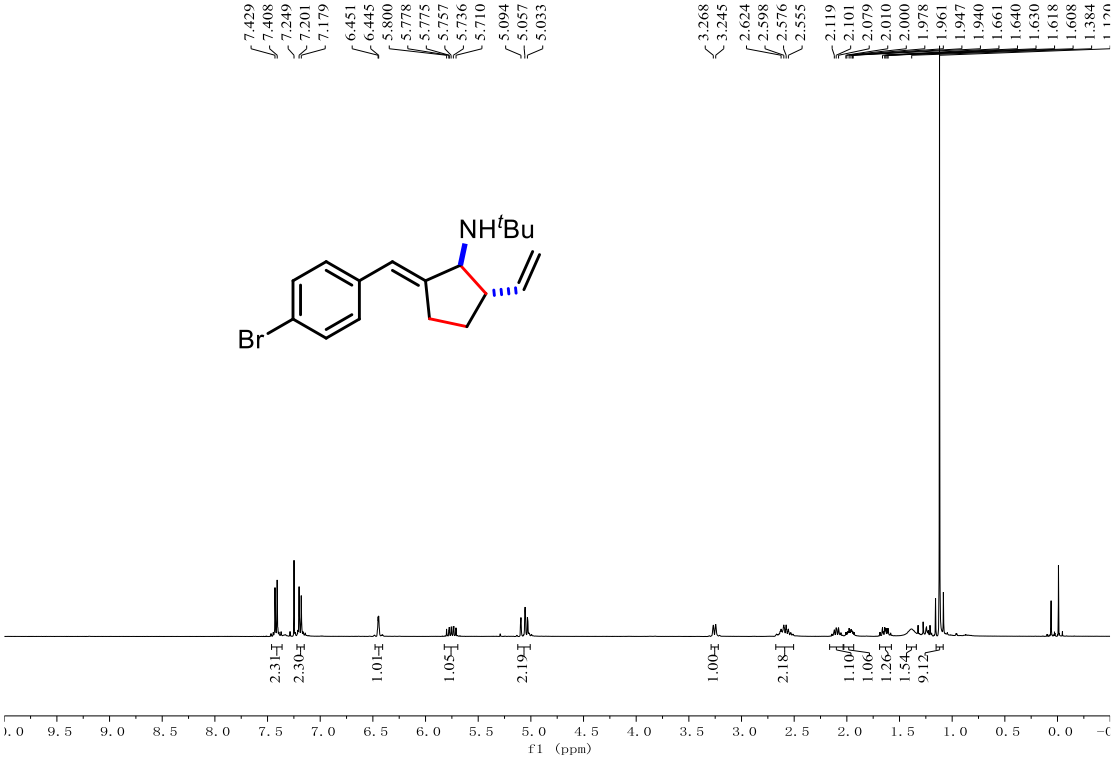
^{1}H NMR spectrum of *cis*-3eac (400 MHz, $CDCl_3$)



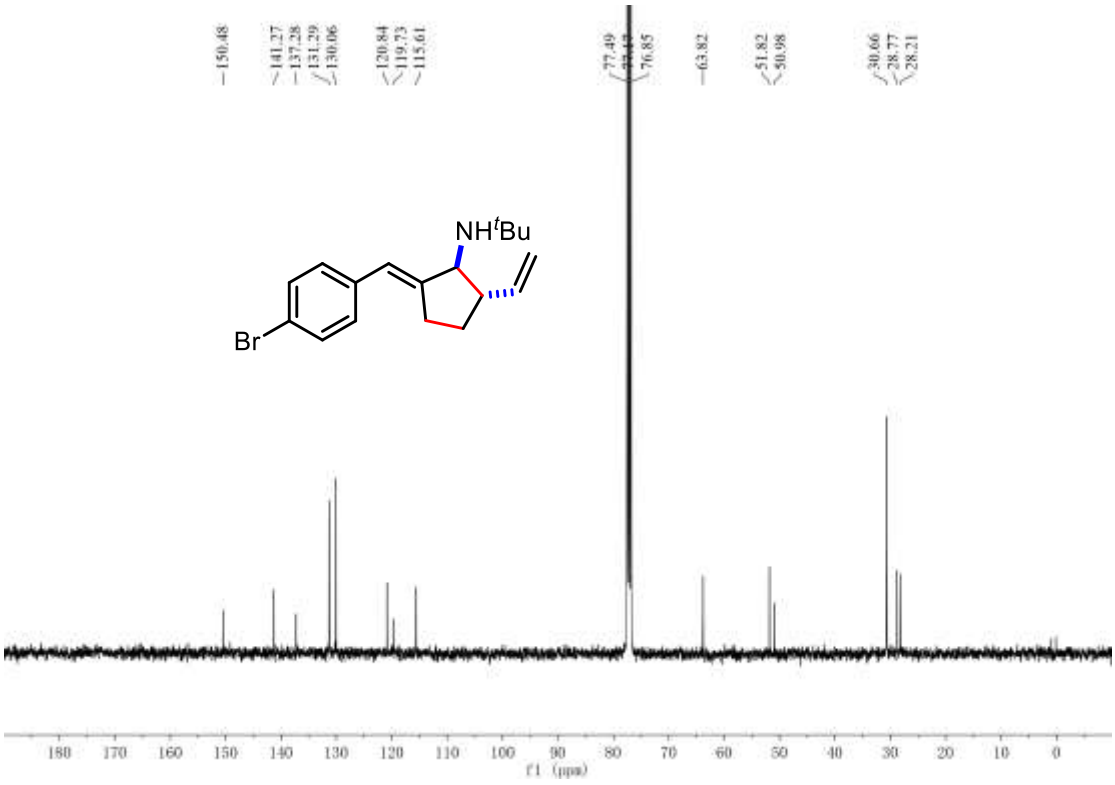
^{13}C NMR spectrum of *cis*-3eac (101 MHz, $CDCl_3$)



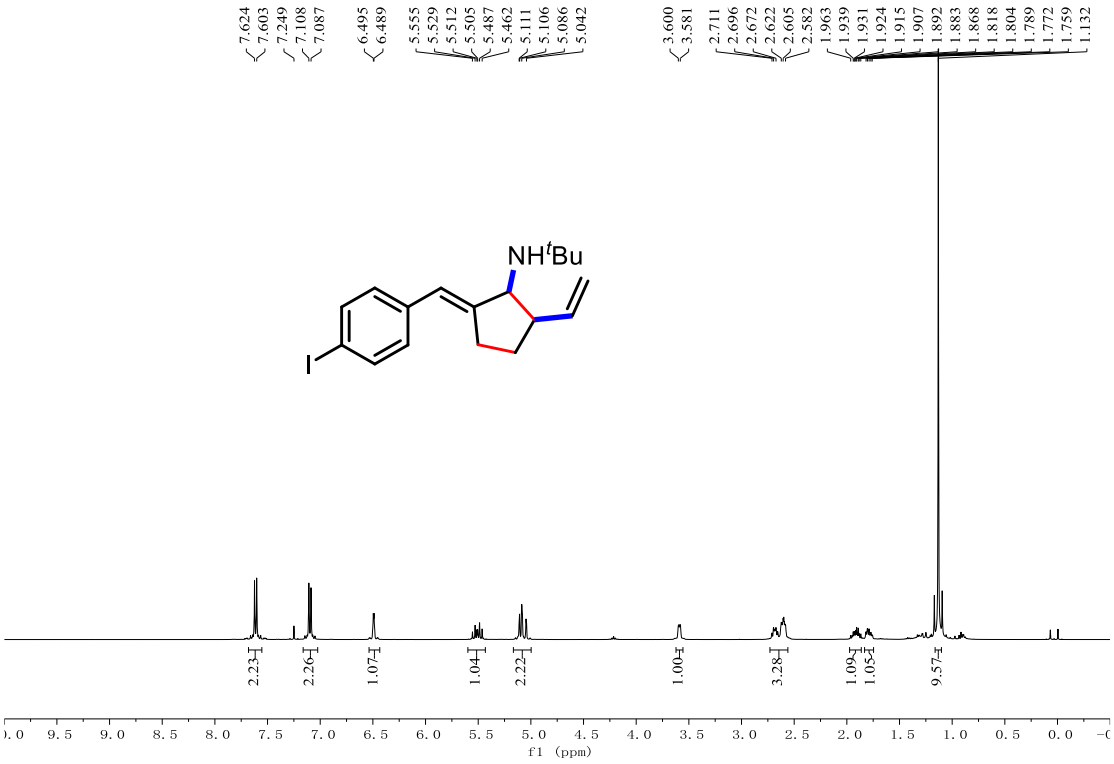
^{1}H NMR spectrum of *trans*-3eac (400 MHz, $CDCl_3$)



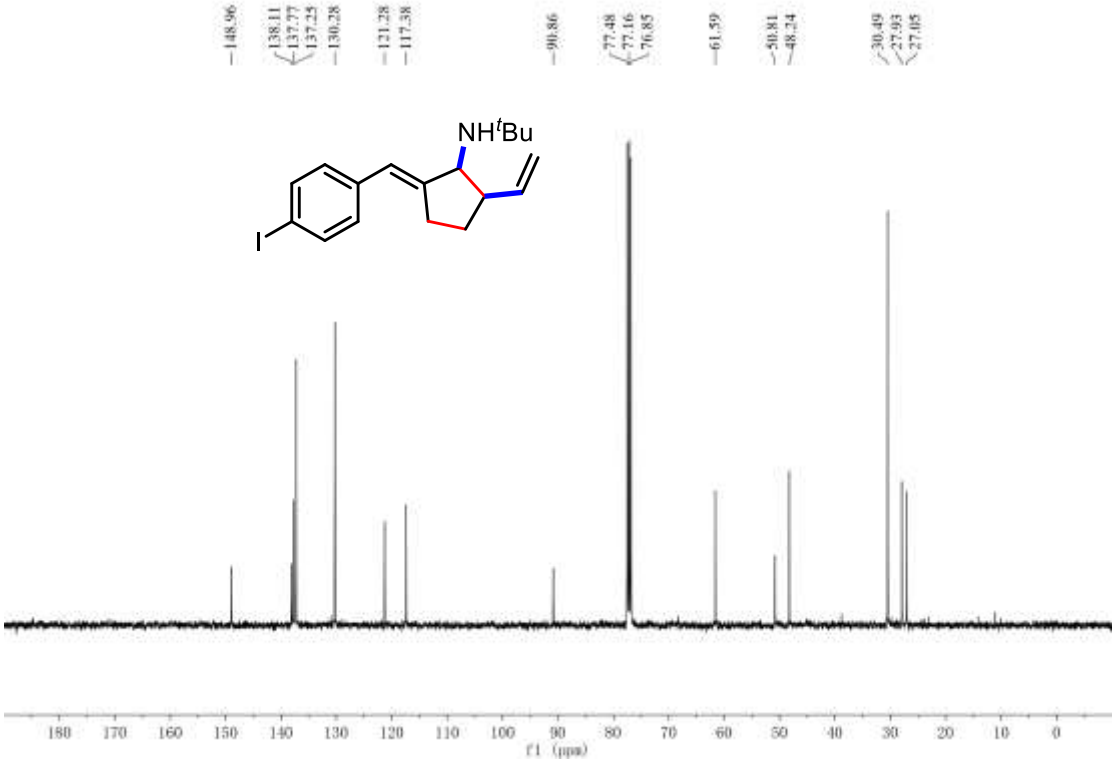
^{13}C NMR spectrum of *trans*-3eac (101 MHz, $CDCl_3$)



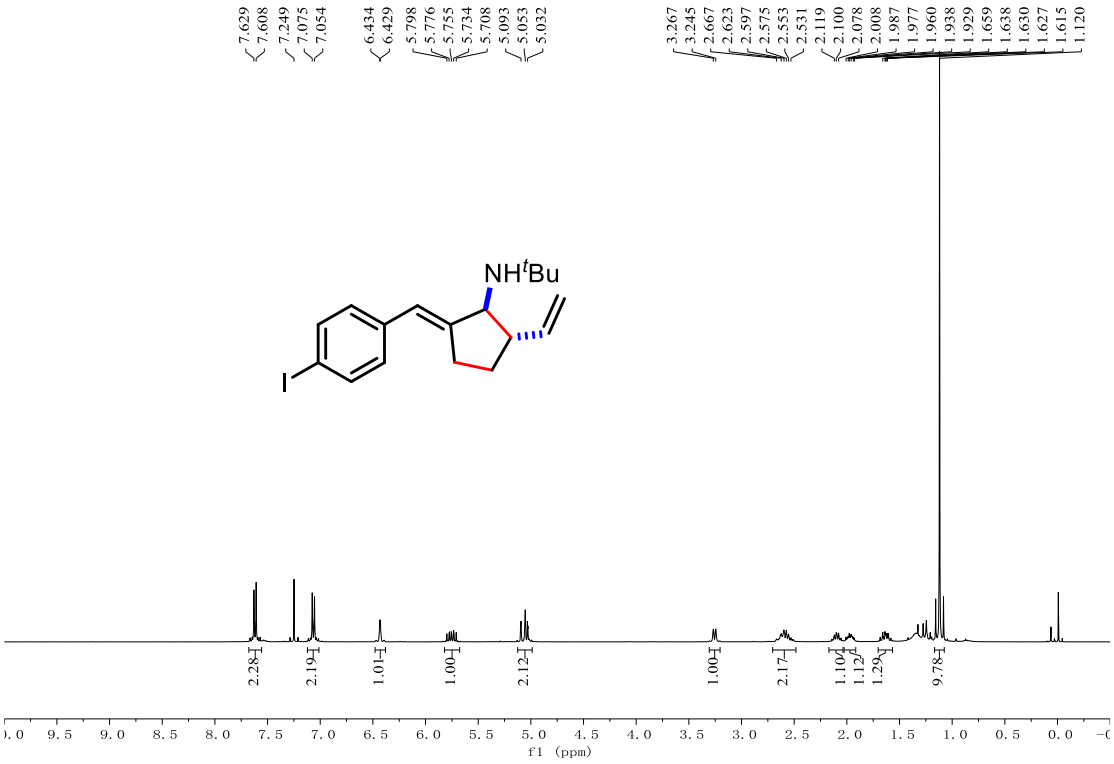
^{1}H NMR spectrum of *cis*-3fac (400 MHz, $CDCl_3$)



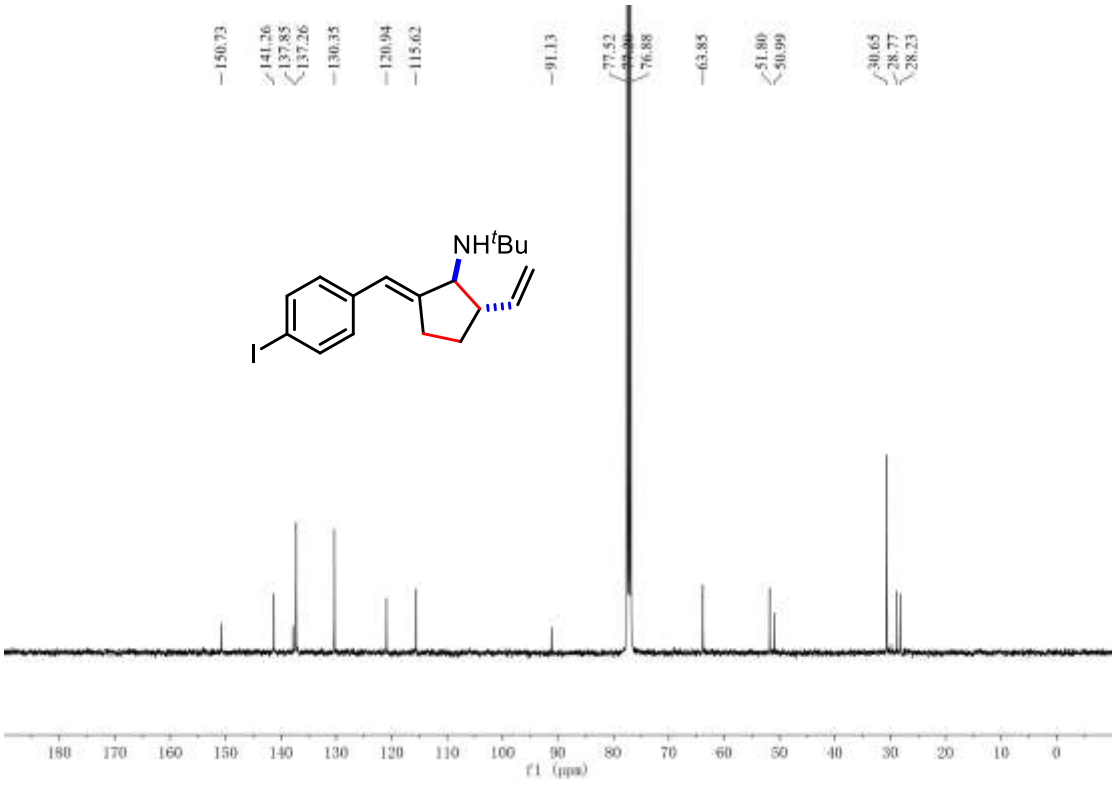
^{13}C NMR spectrum of *cis*-3fac (101 MHz, $CDCl_3$)



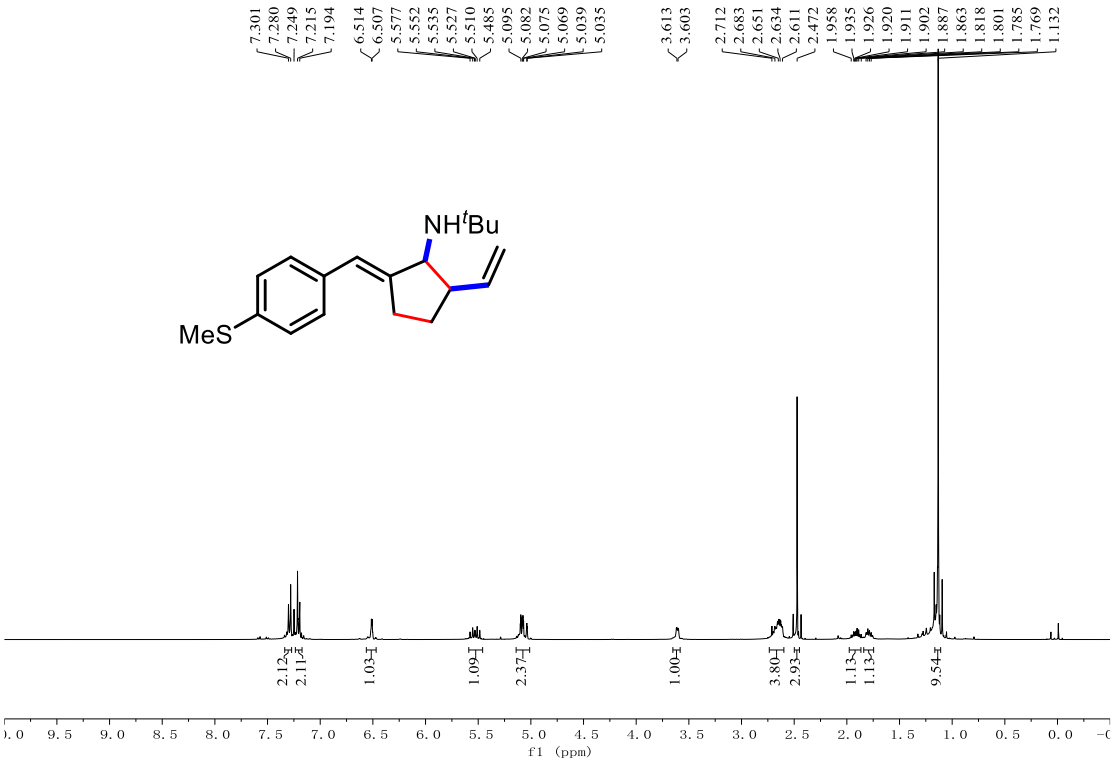
^{1}H NMR spectrum of *trans*-3fac (400 MHz, $CDCl_3$)



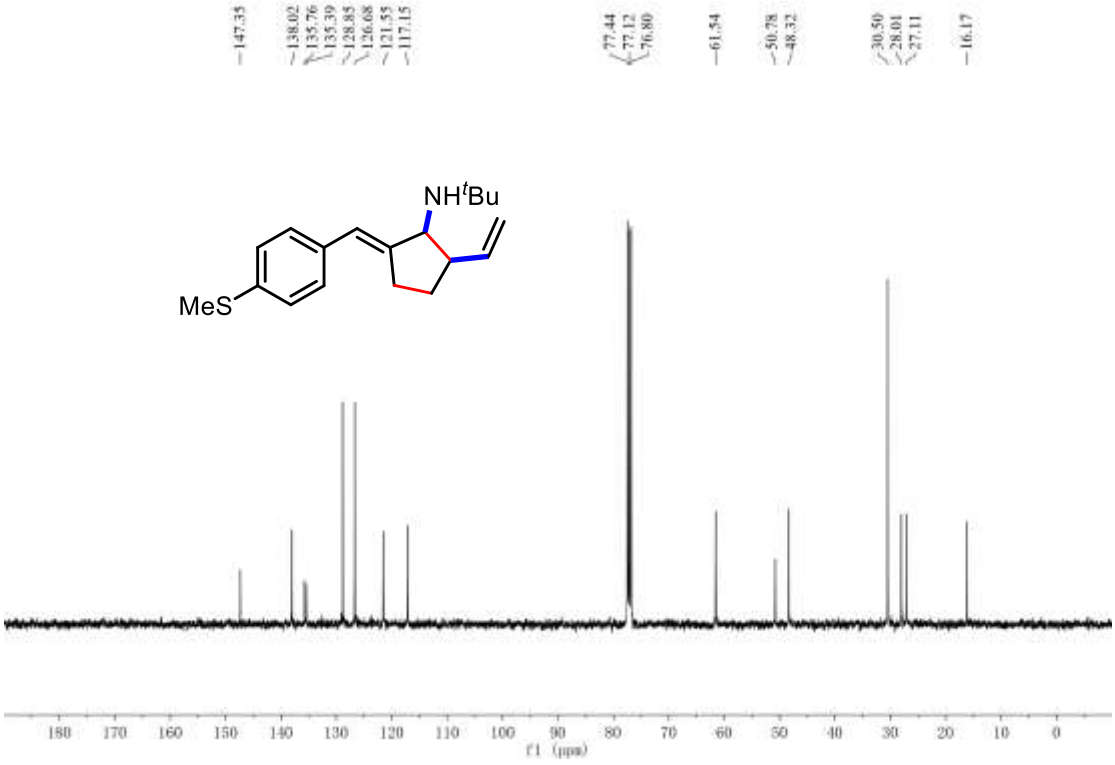
^{13}C NMR spectrum of *trans*-3fac (101 MHz, $CDCl_3$)



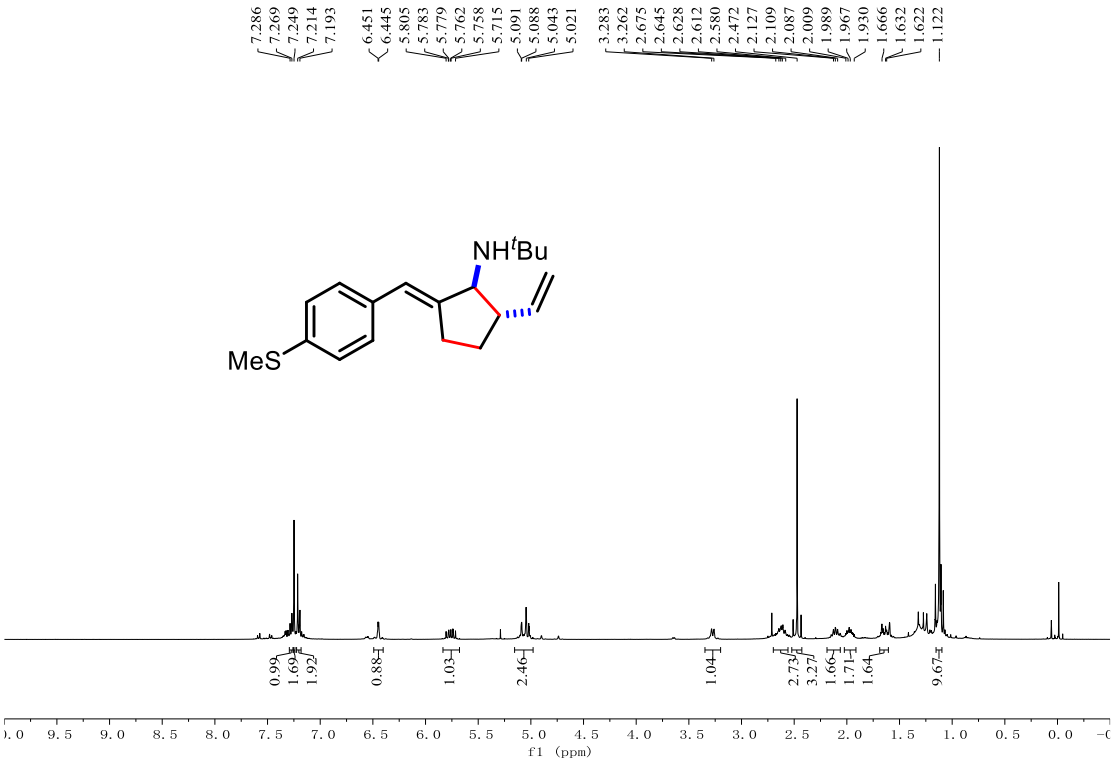
^{1}H NMR spectrum of *cis*-3gac (400 MHz, $CDCl_3$)



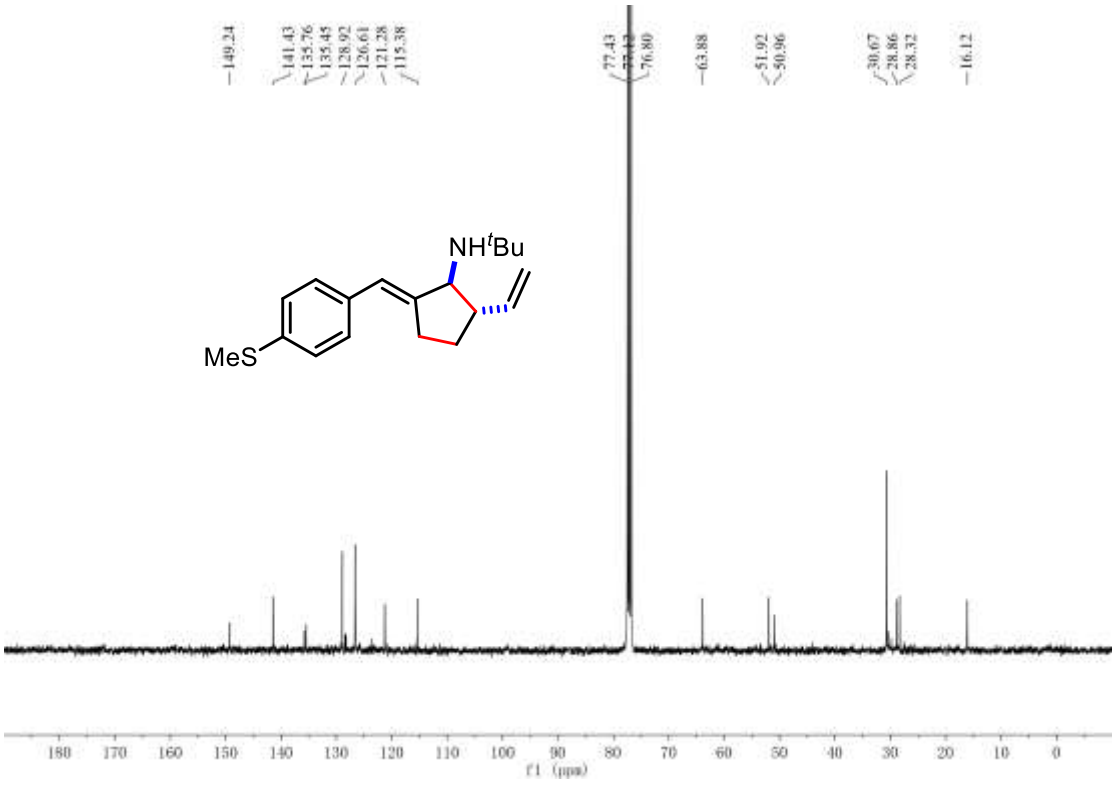
^{13}C NMR spectrum of *cis*-3gac (101 MHz, $CDCl_3$)



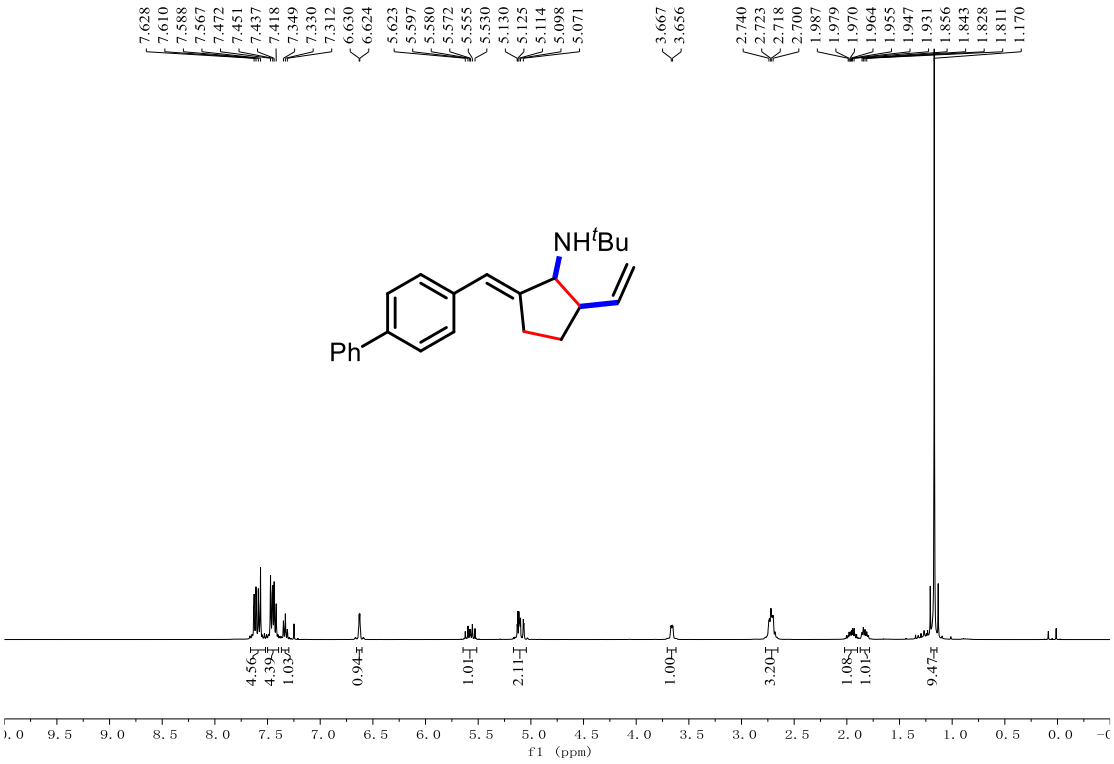
^{1}H NMR spectrum of *trans*-3gac (400 MHz, $CDCl_3$)



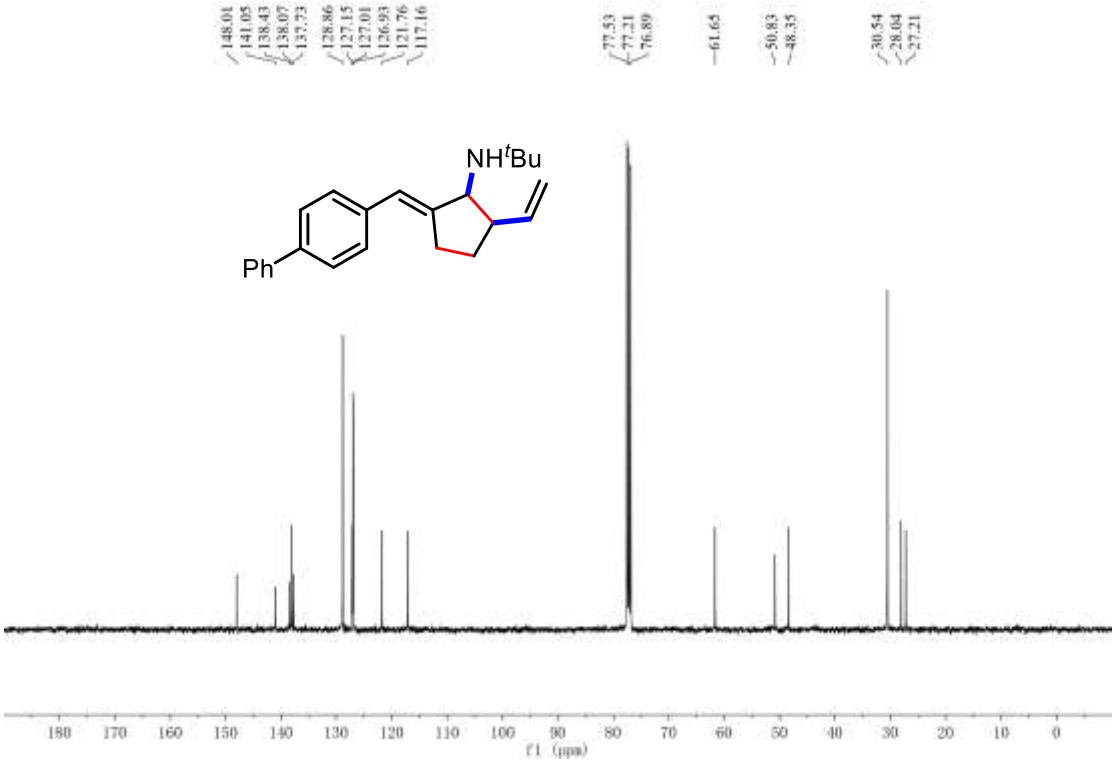
^{13}C NMR spectrum of *trans*-3gac (101 MHz, $CDCl_3$)



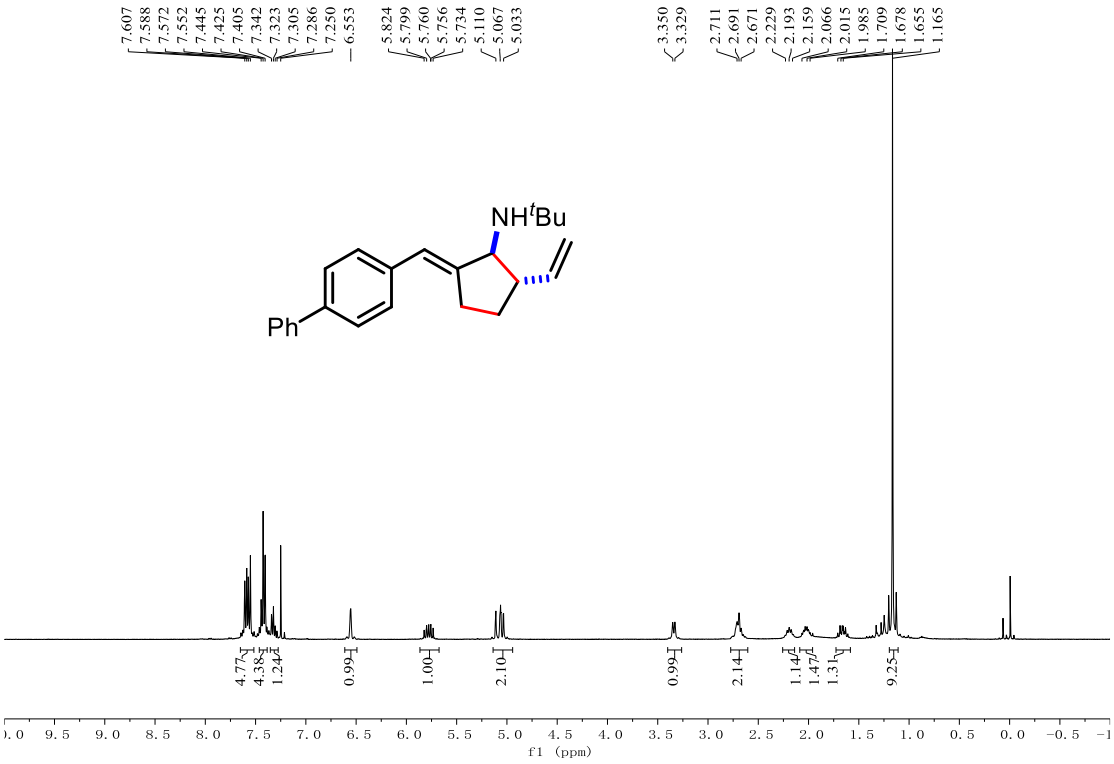
^{1}H NMR spectrum of *cis*-3hac (400 MHz, $CDCl_3$)



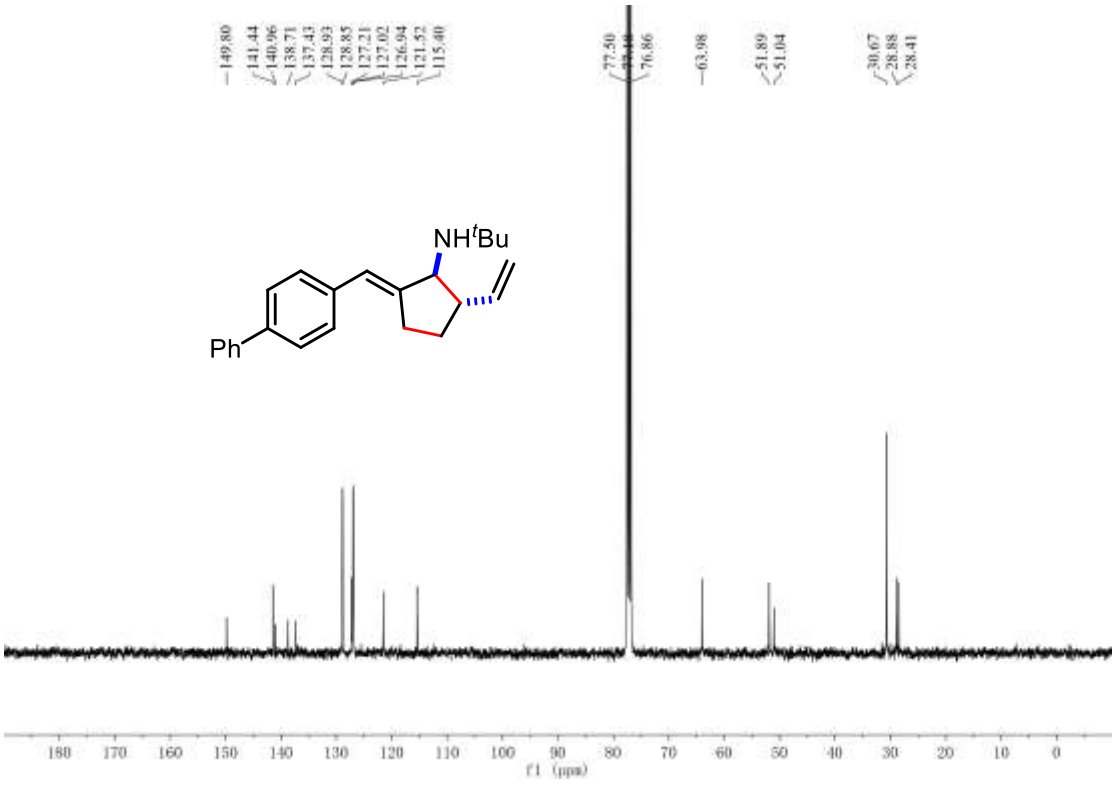
^{13}C NMR spectrum of *cis*-3hac (101 MHz, $CDCl_3$)



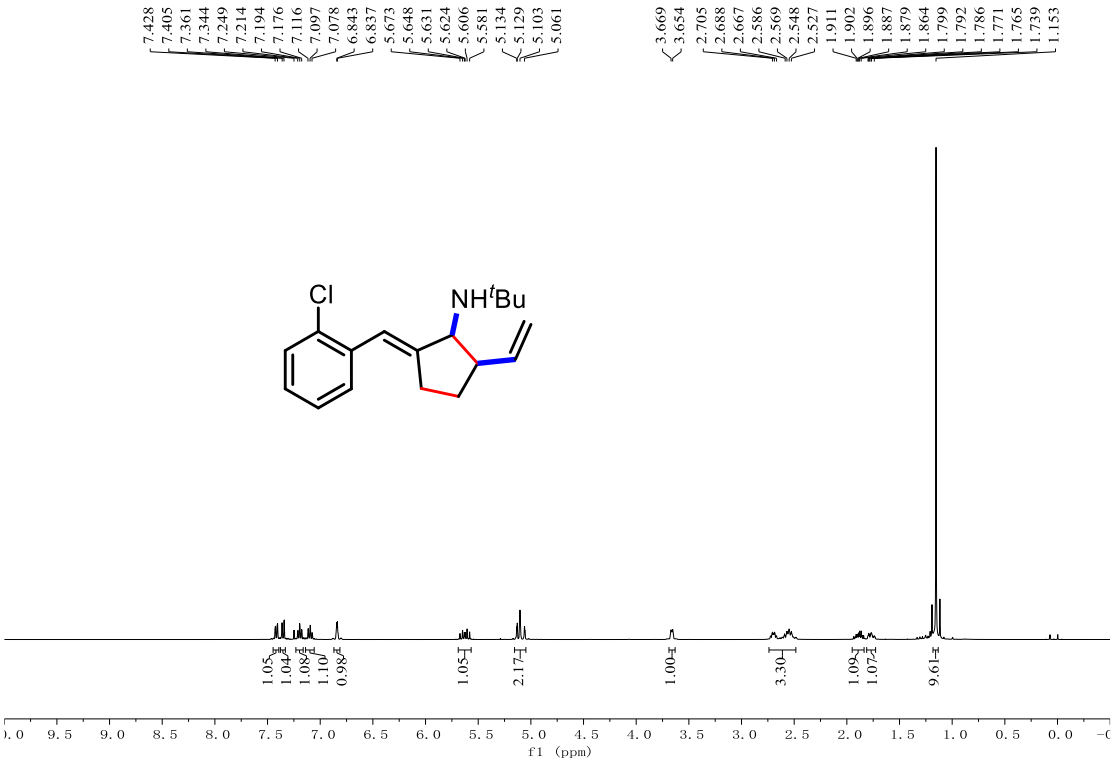
^{1}H NMR spectrum of *trans*-3hac (400 MHz, $CDCl_3$)



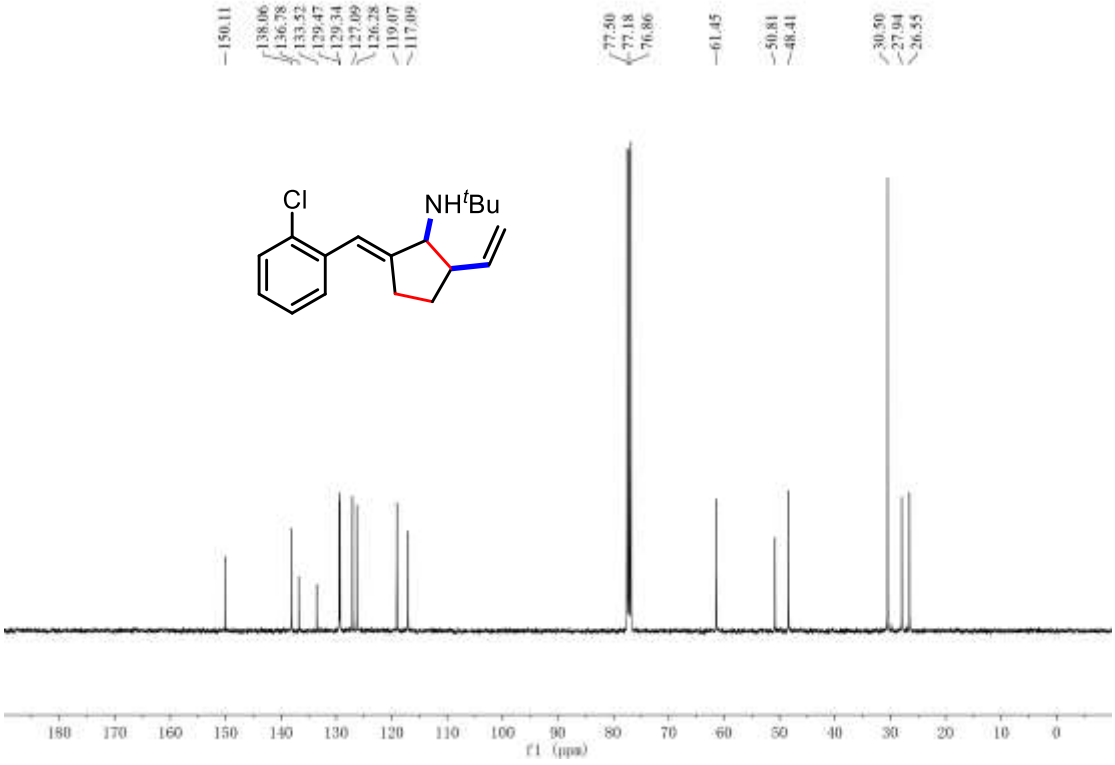
^{13}C NMR spectrum of *trans*-3hac (101 MHz, $CDCl_3$)



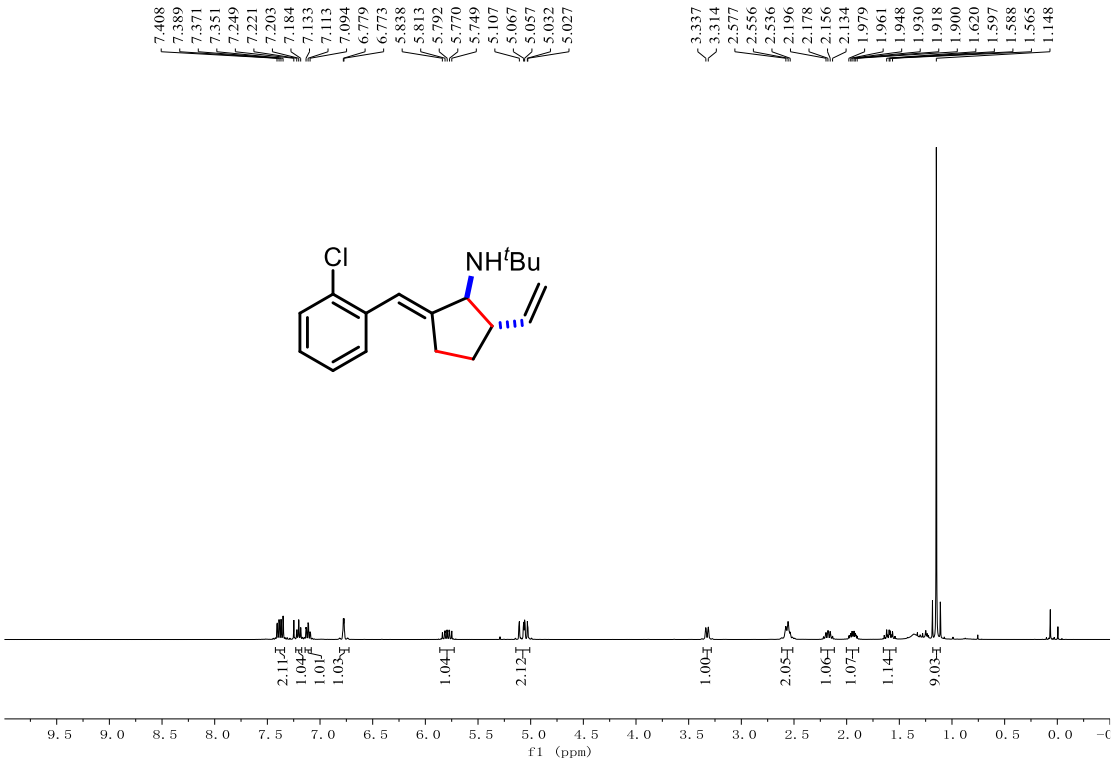
^{1}H NMR spectrum of *cis*-3kac (400 MHz, $CDCl_3$)



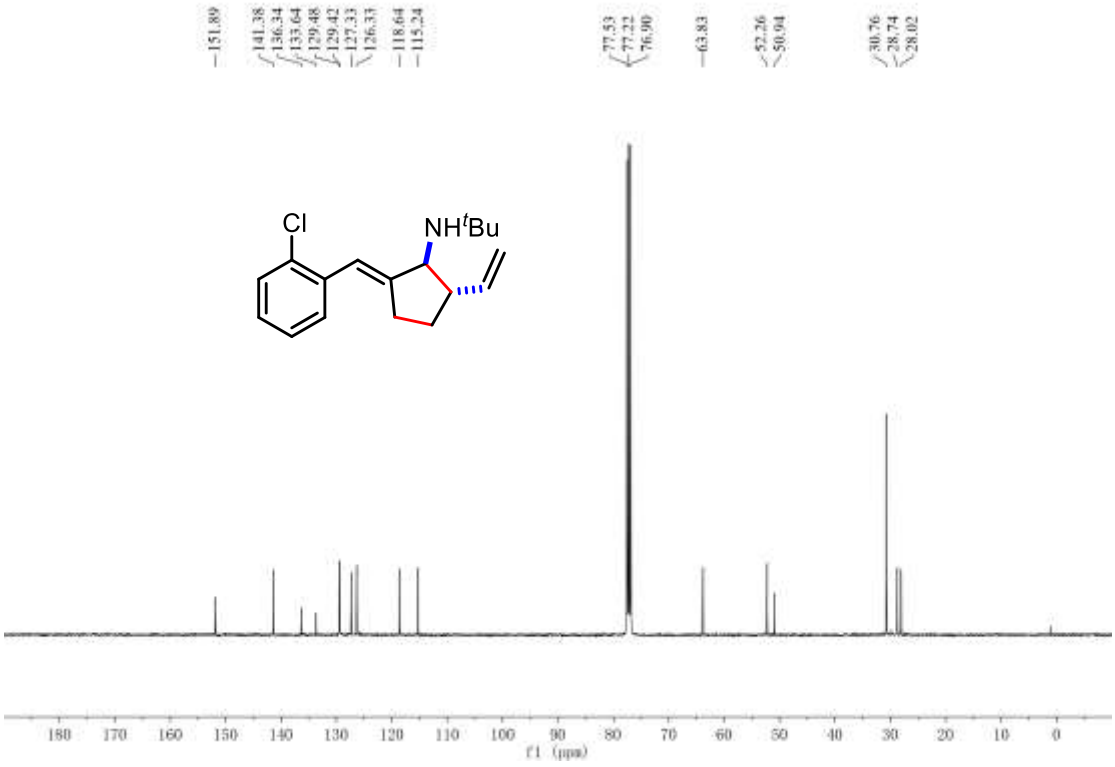
^{13}C NMR spectrum of *cis*-3kac (101 MHz, $CDCl_3$)



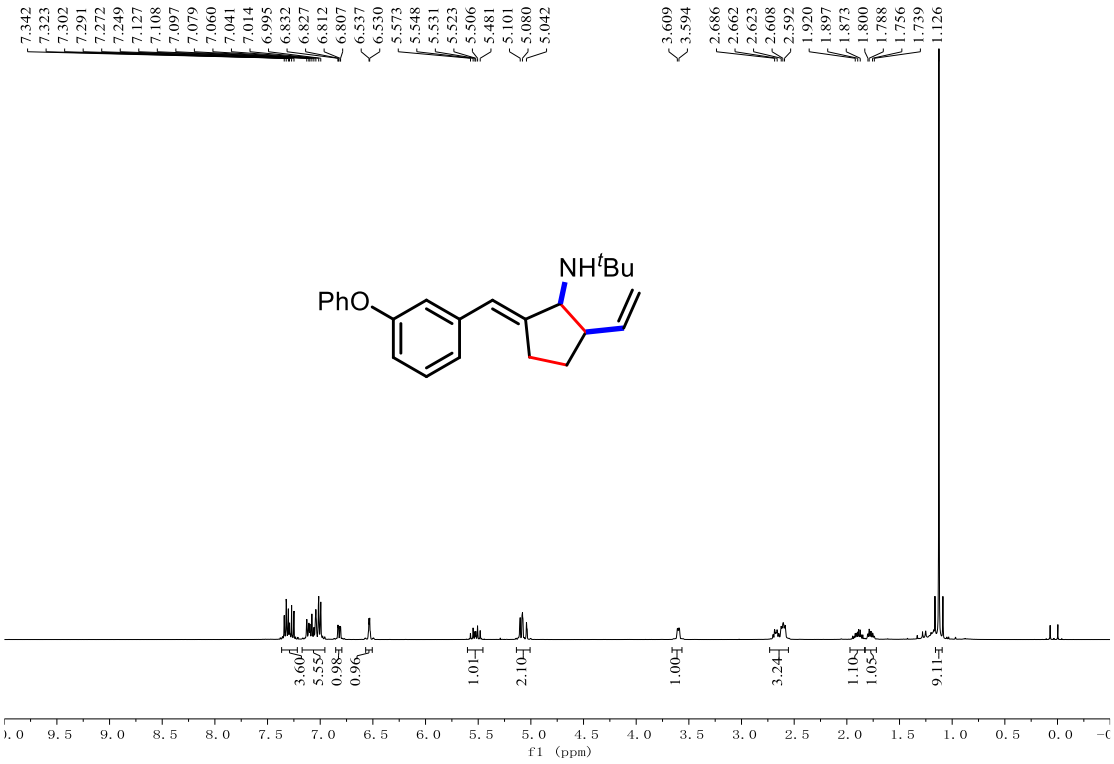
^{1}H NMR spectrum of *trans*-3kac (400 MHz, $CDCl_3$)



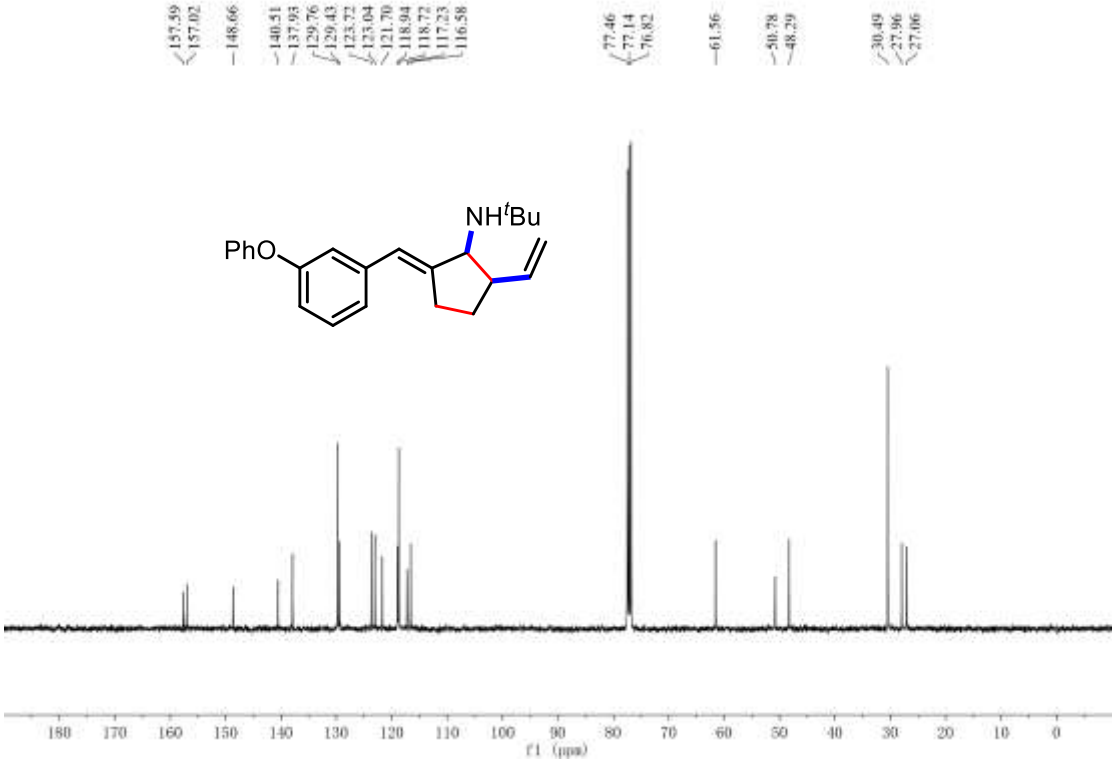
^{13}C NMR spectrum of *trans*-3kac (101 MHz, $CDCl_3$)



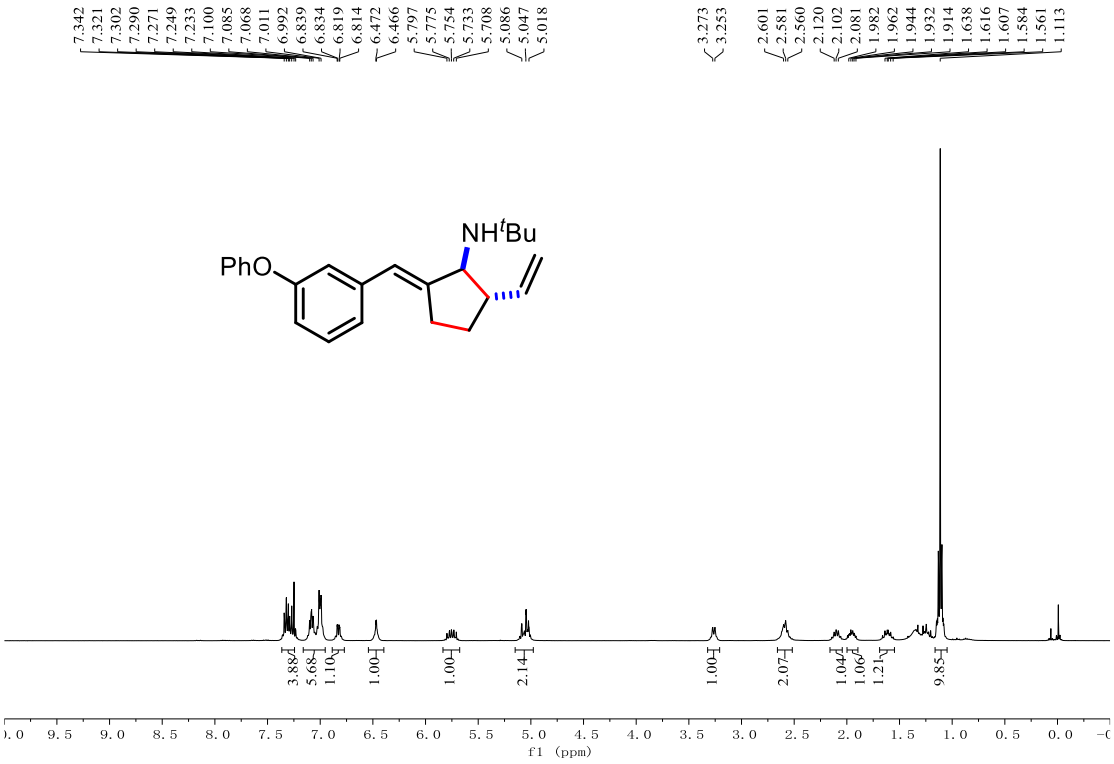
^{1}H NMR spectrum of *cis*-3mac (400 MHz, $CDCl_3$)



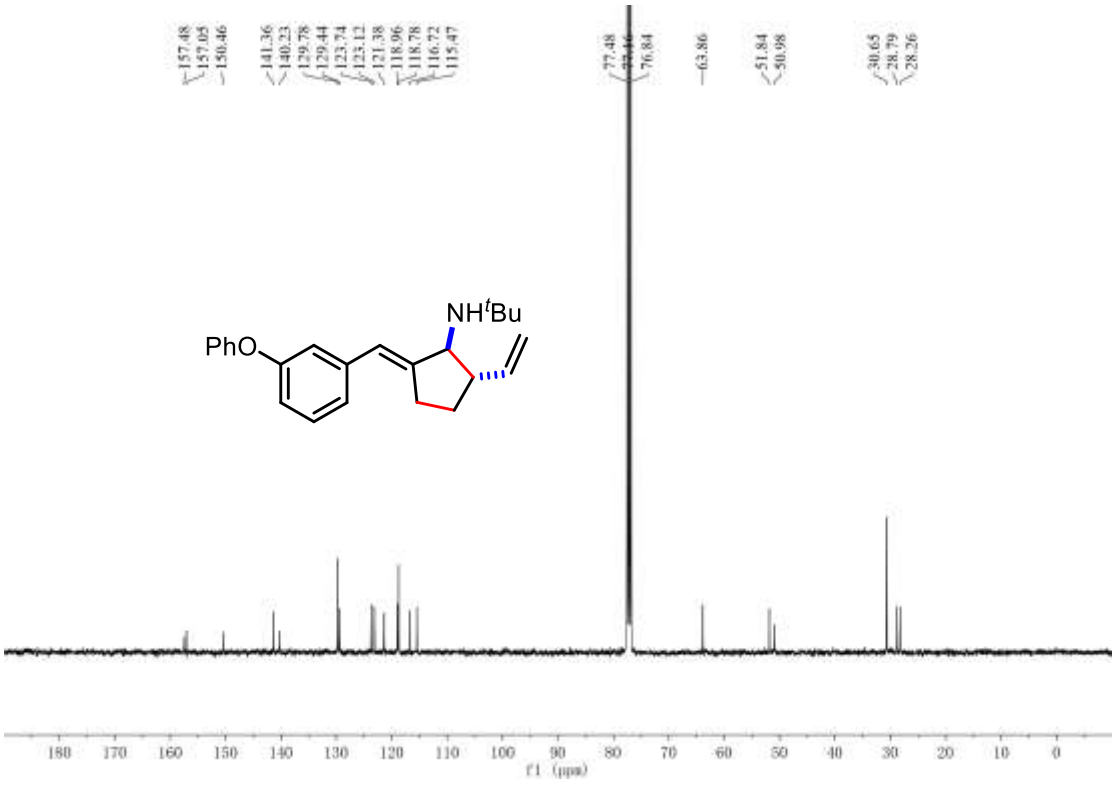
^{13}C NMR spectrum of *cis*-3mac (101 MHz, $CDCl_3$)



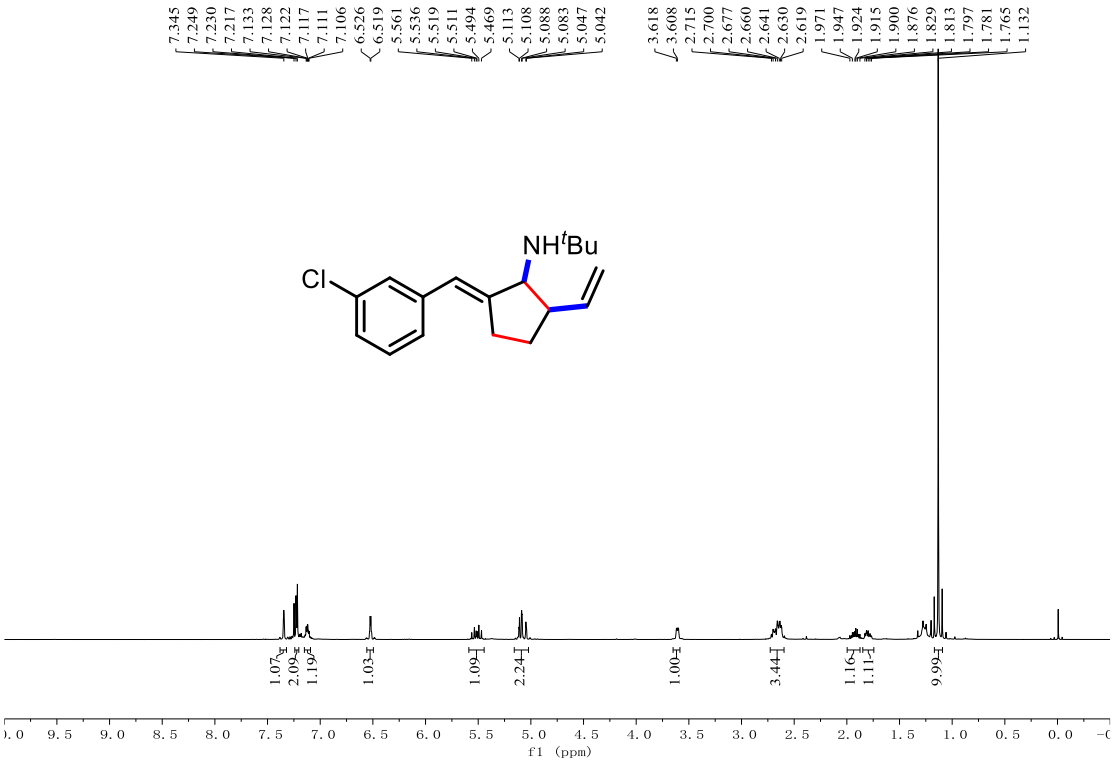
^{1}H NMR spectrum of *trans*-3mac (400 MHz, $CDCl_3$)



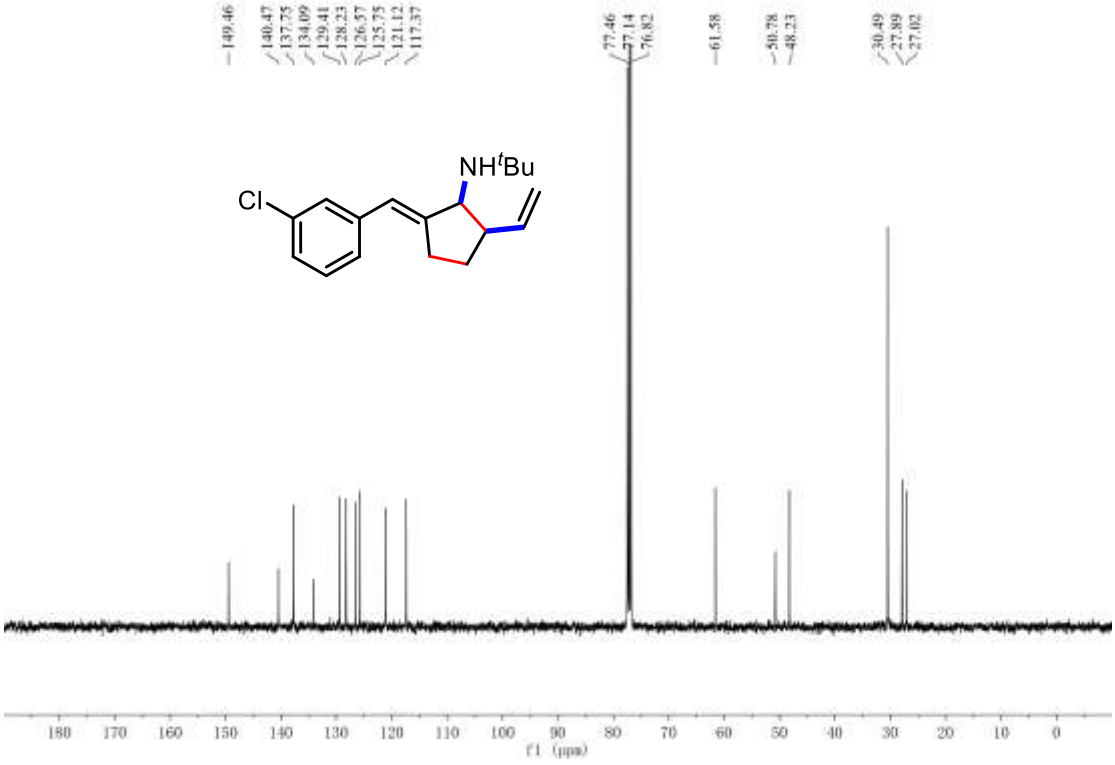
^{13}C NMR spectrum of *trans*-3mac (101 MHz, $CDCl_3$)



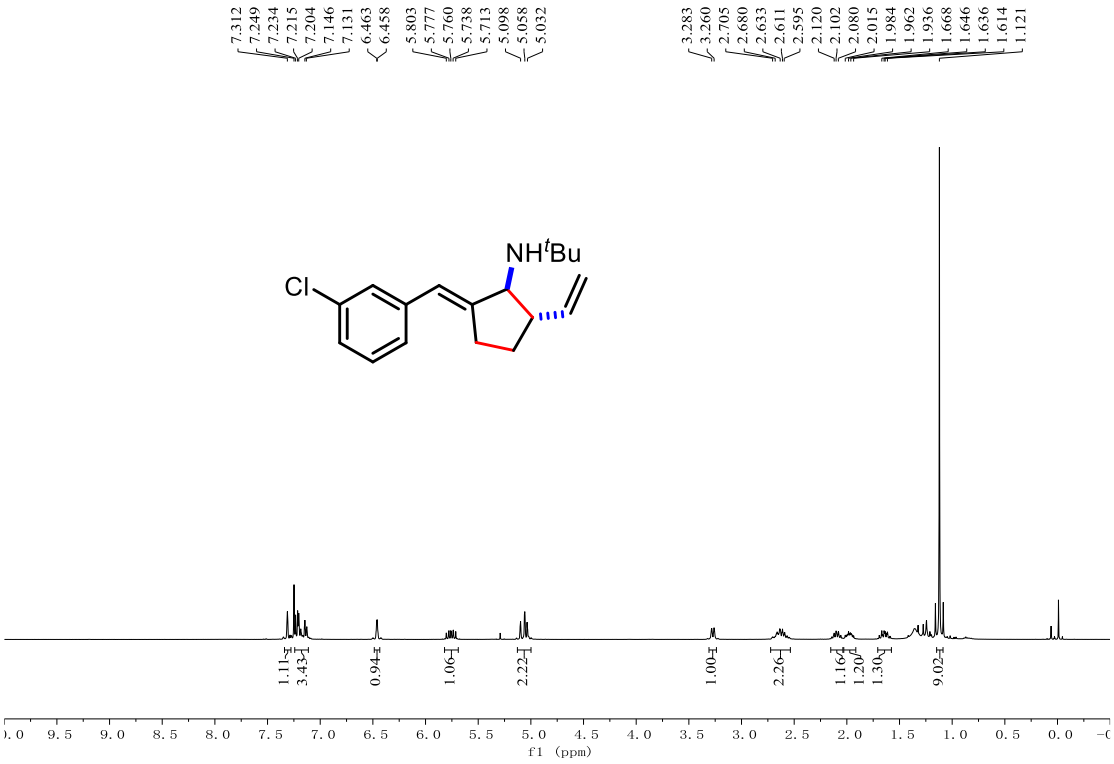
^{1}H NMR spectrum of *cis*-3nac (400 MHz, $CDCl_3$)



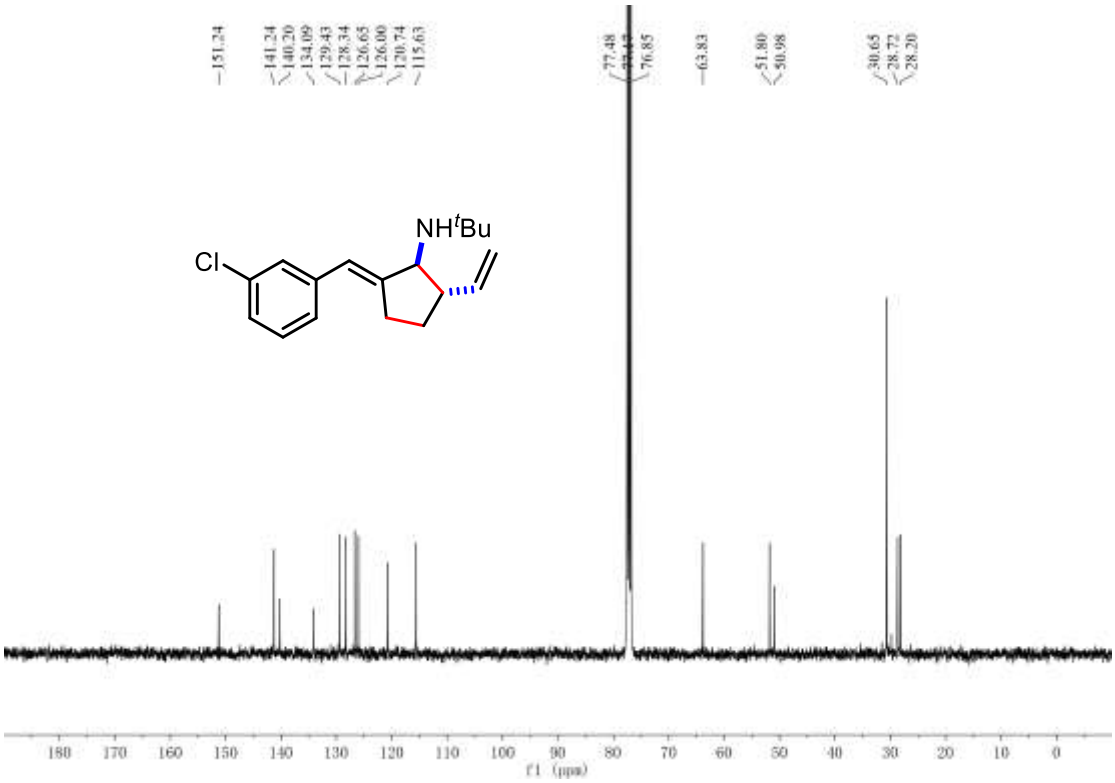
^{13}C NMR spectrum of *cis*-3nac (101 MHz, $CDCl_3$)



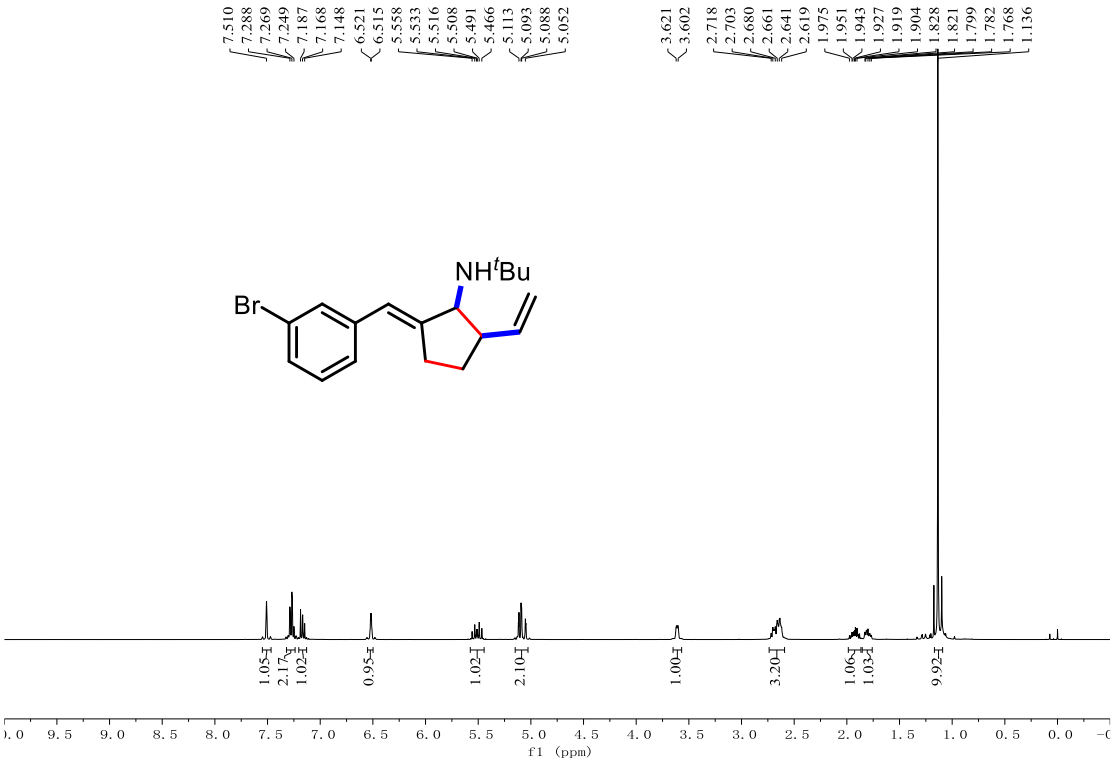
^{1}H NMR spectrum of *trans*-3nac (400 MHz, $CDCl_3$)



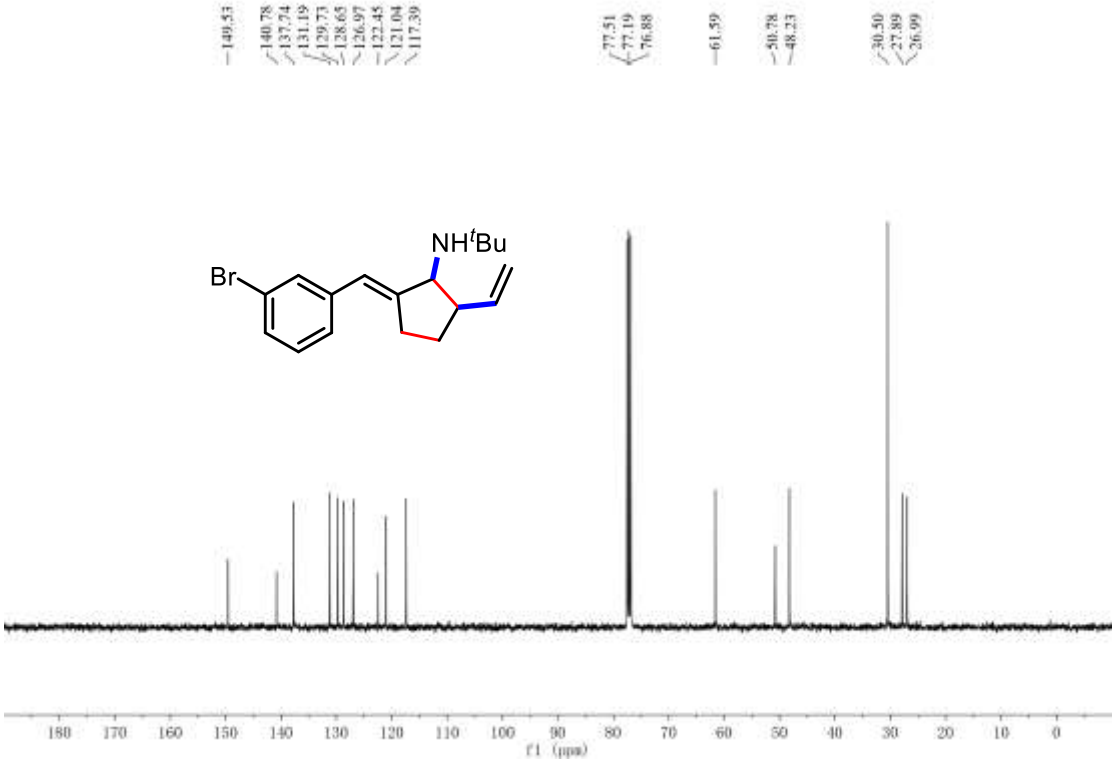
^{13}C NMR spectrum of *trans*-3nac (101 MHz, $CDCl_3$)



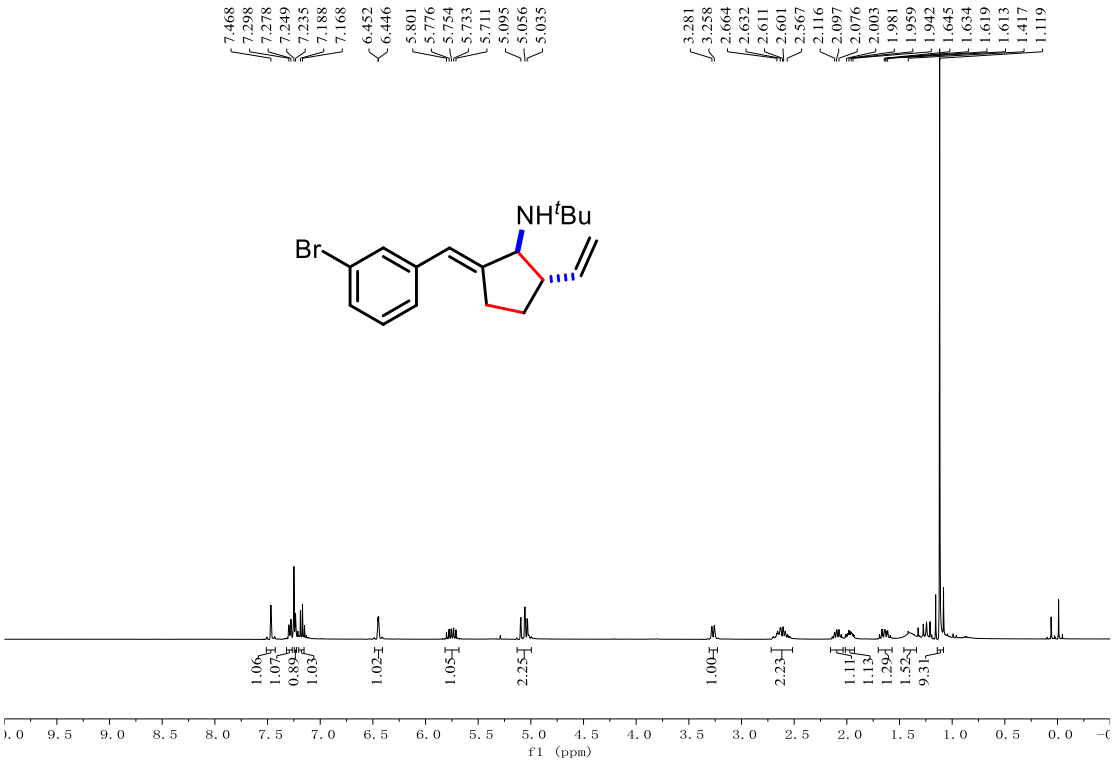
^{1}H NMR spectrum of *cis*-3oac (400 MHz, $CDCl_3$)



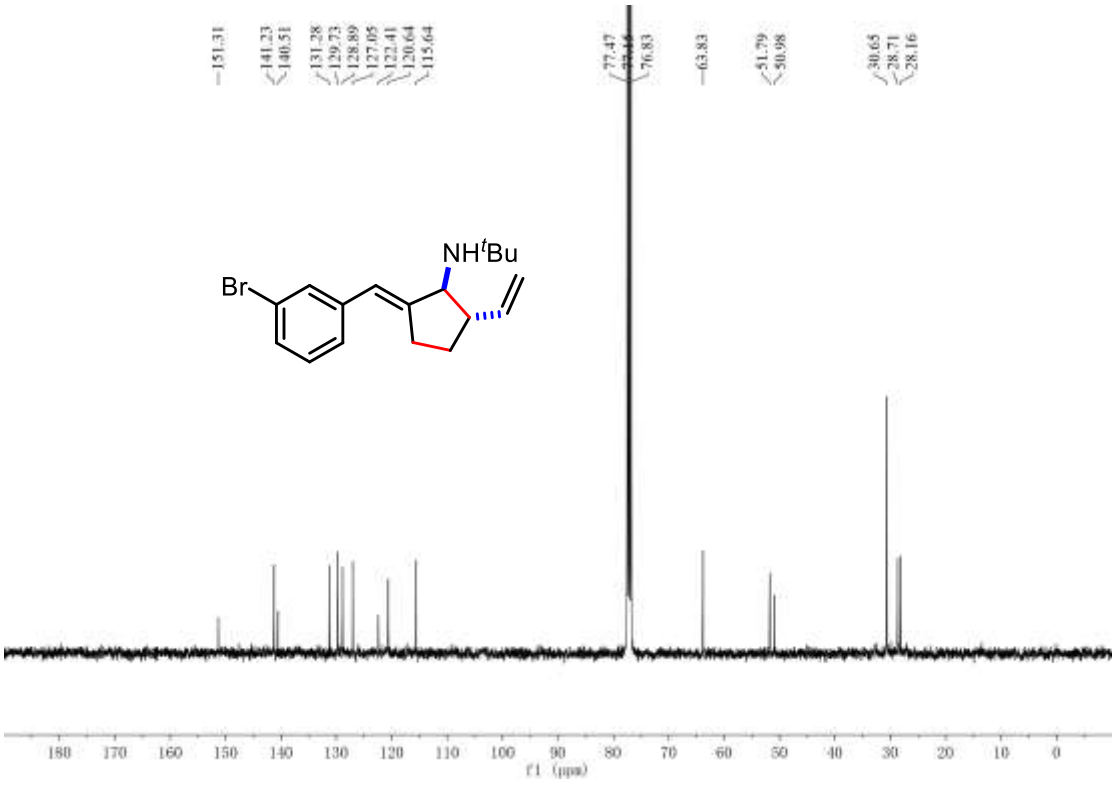
^{13}C NMR spectrum of *cis*-3oac (101 MHz, $CDCl_3$)



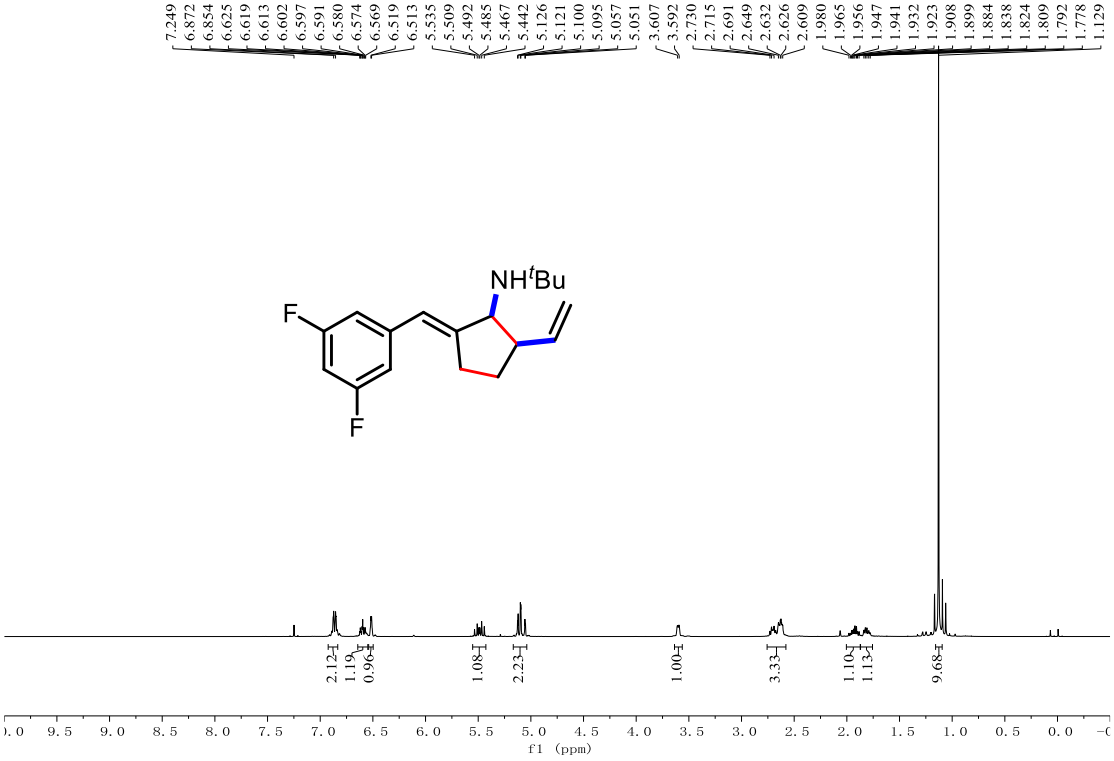
^{1}H NMR spectrum of *trans*-3oac (400 MHz, $CDCl_3$)



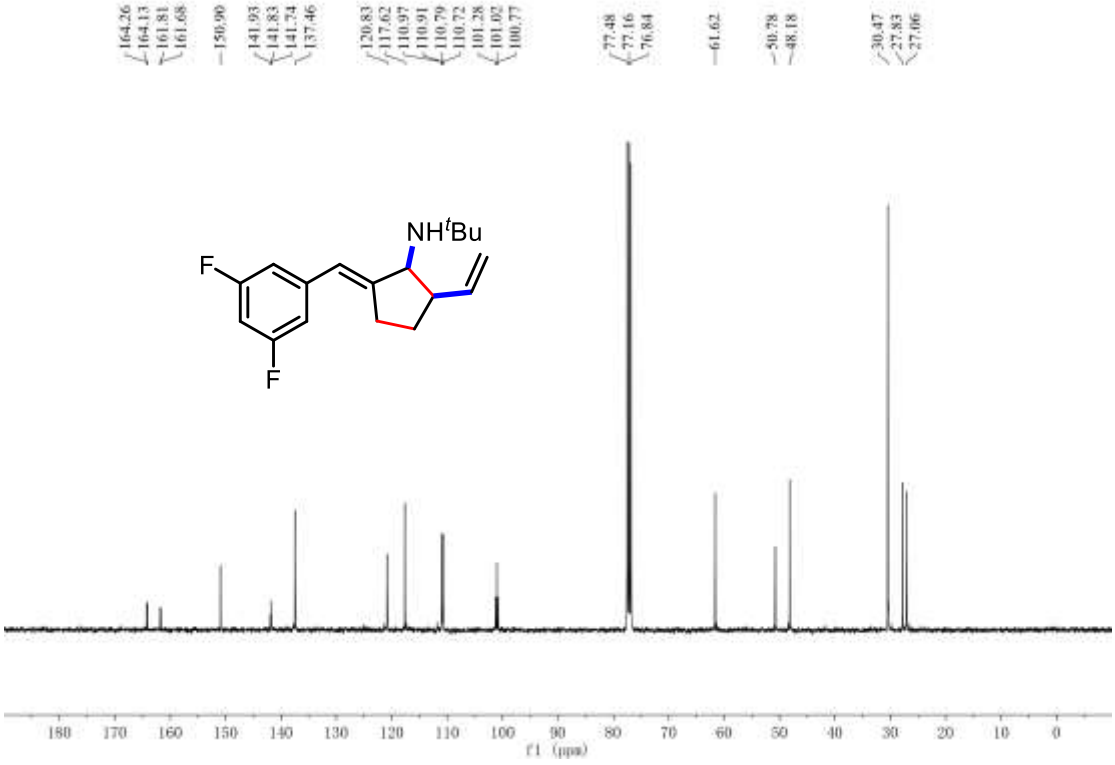
^{13}C NMR spectrum of *trans*-3oac (101 MHz, $CDCl_3$)



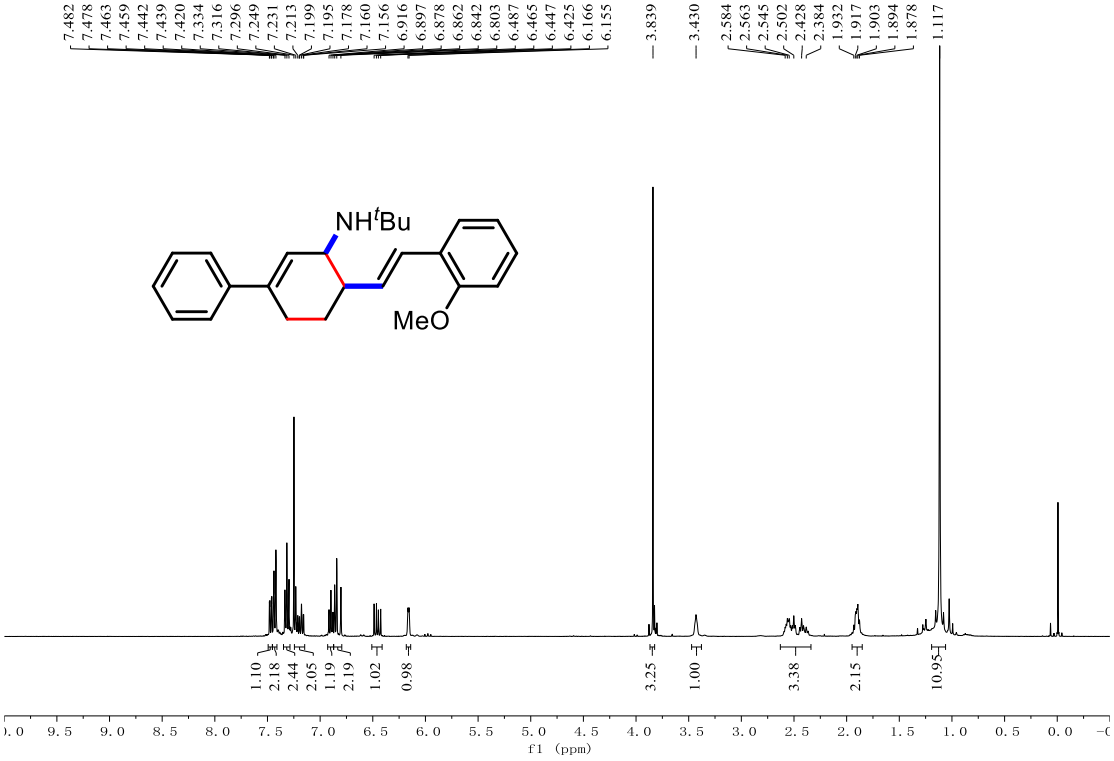
^{1}H NMR spectrum of *cis*-3rac (400 MHz, $CDCl_3$)



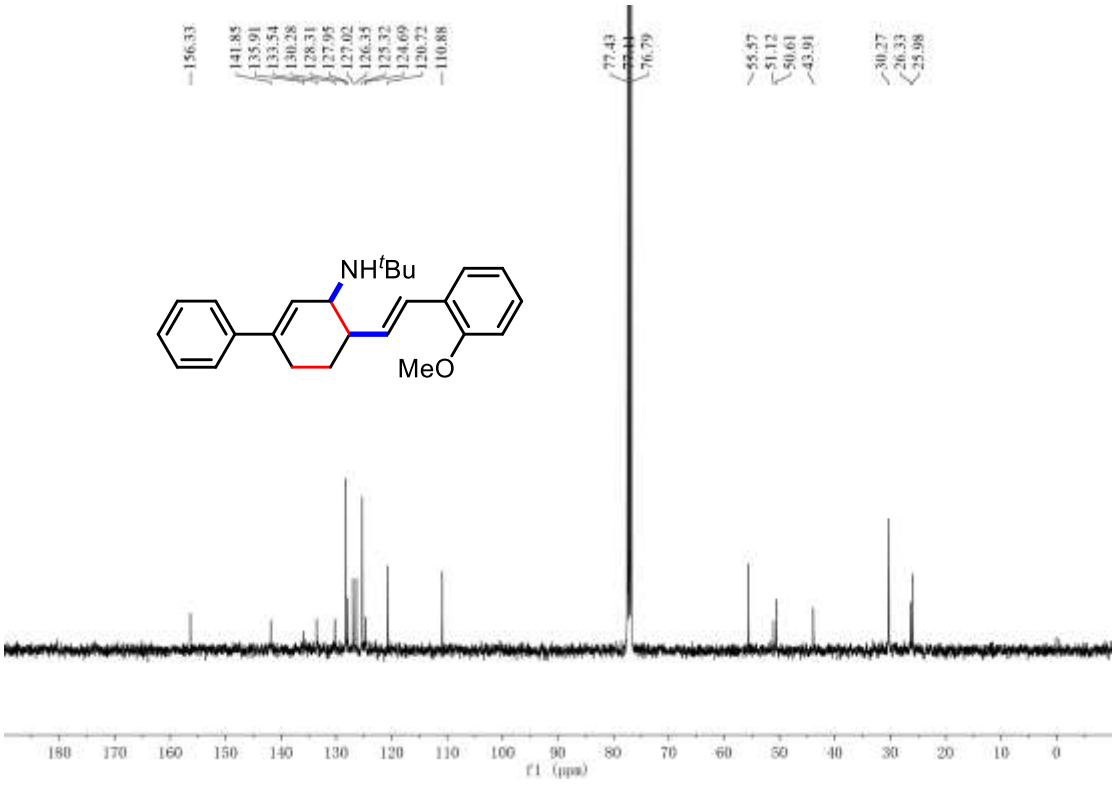
^{13}C NMR spectrum of *cis*-3rac (101 MHz, $CDCl_3$)



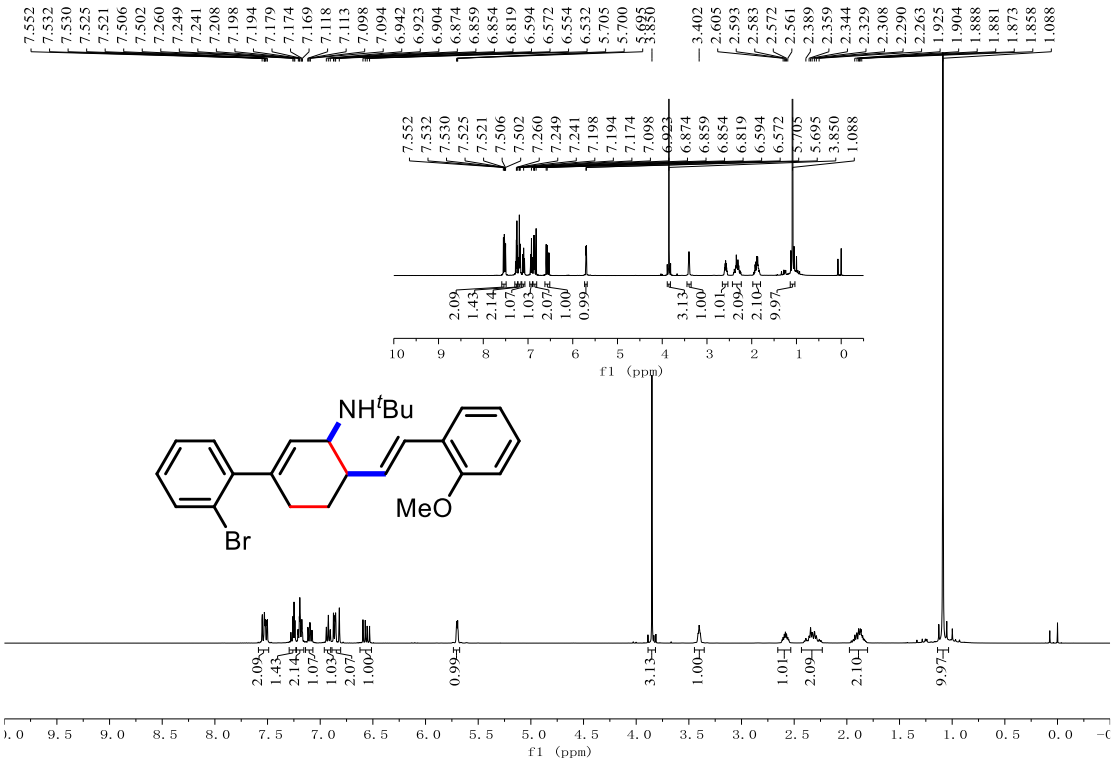
^{1}H NMR spectrum of *cis*-5ba (400 MHz, $CDCl_3$)



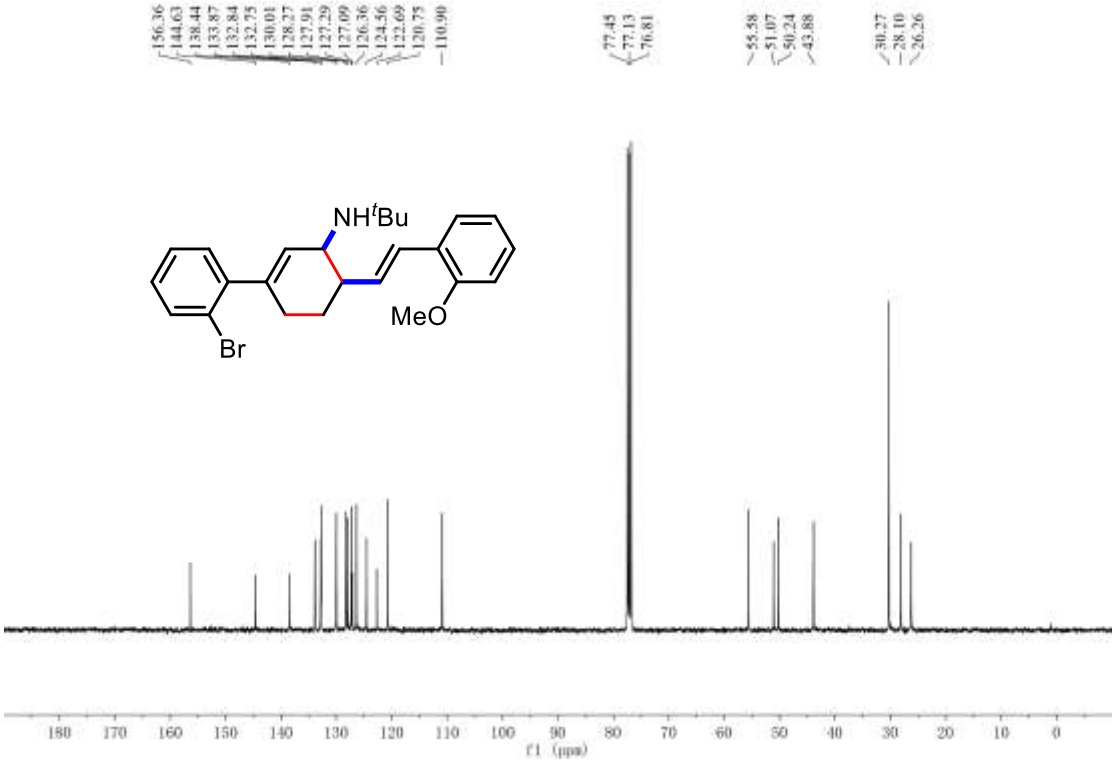
^{13}C NMR spectrum of *cis*-5ba (101 MHz, $CDCl_3$)



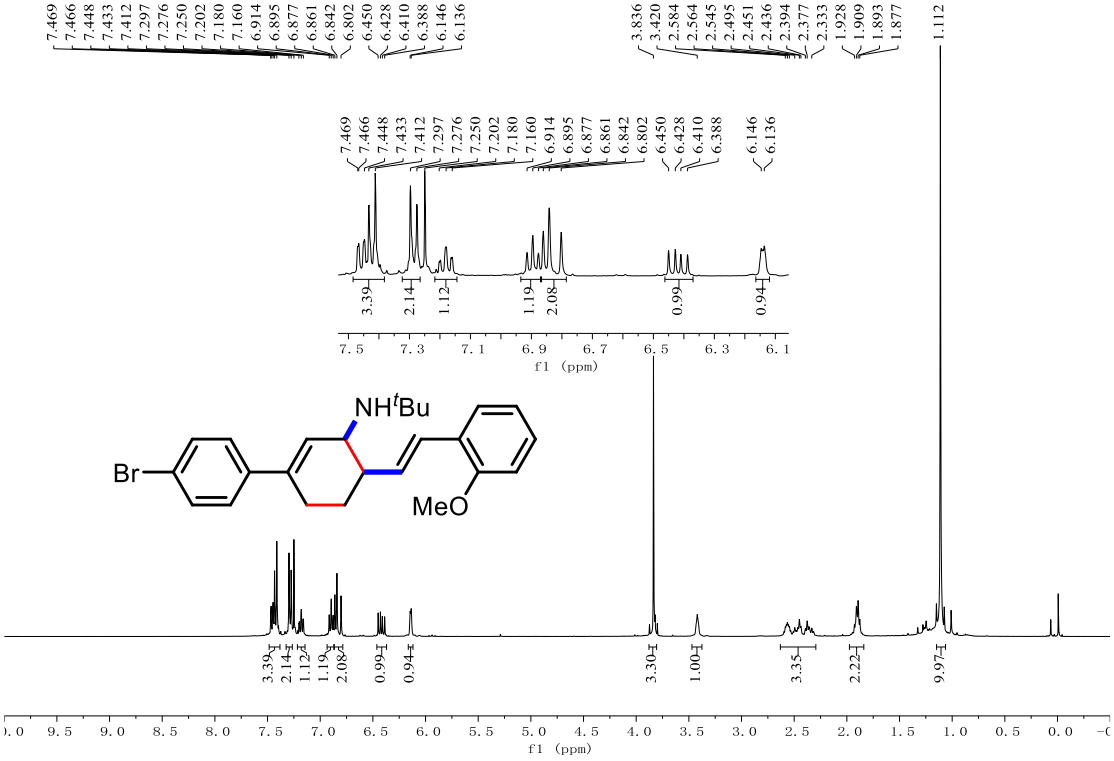
^{1}H NMR spectrum of *cis*-5ea (400 MHz, $CDCl_3$)



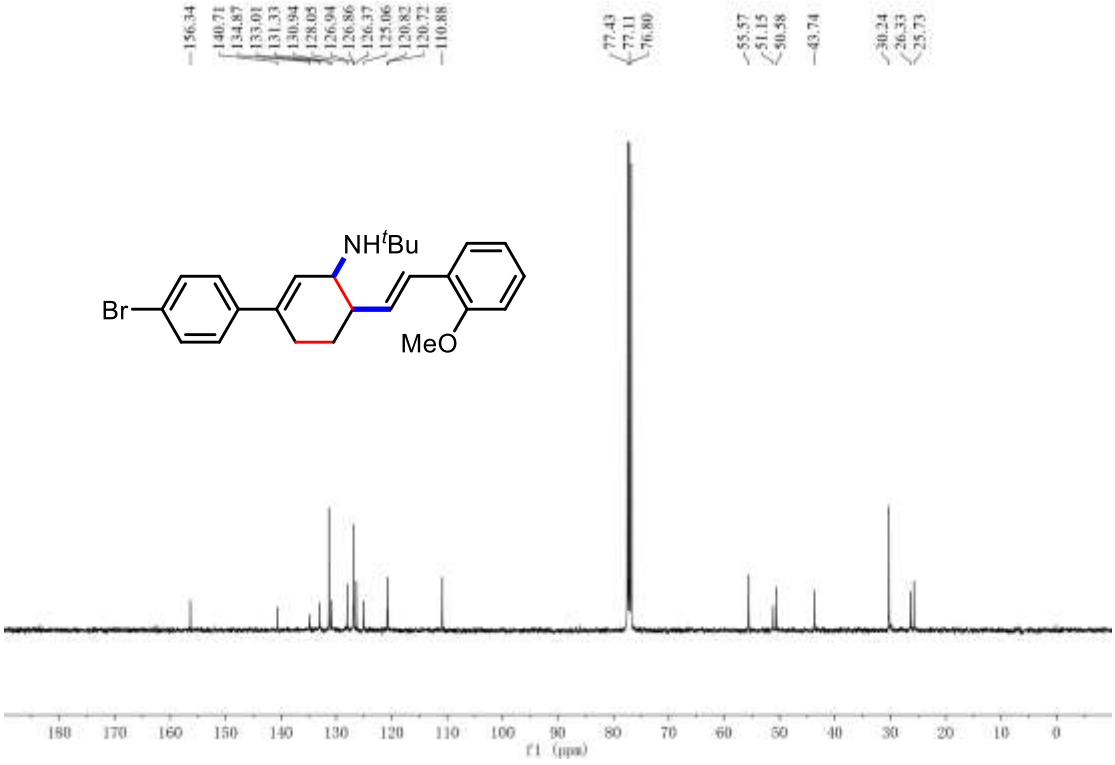
^{13}C NMR spectrum of *cis*-5ea (101 MHz, $CDCl_3$)



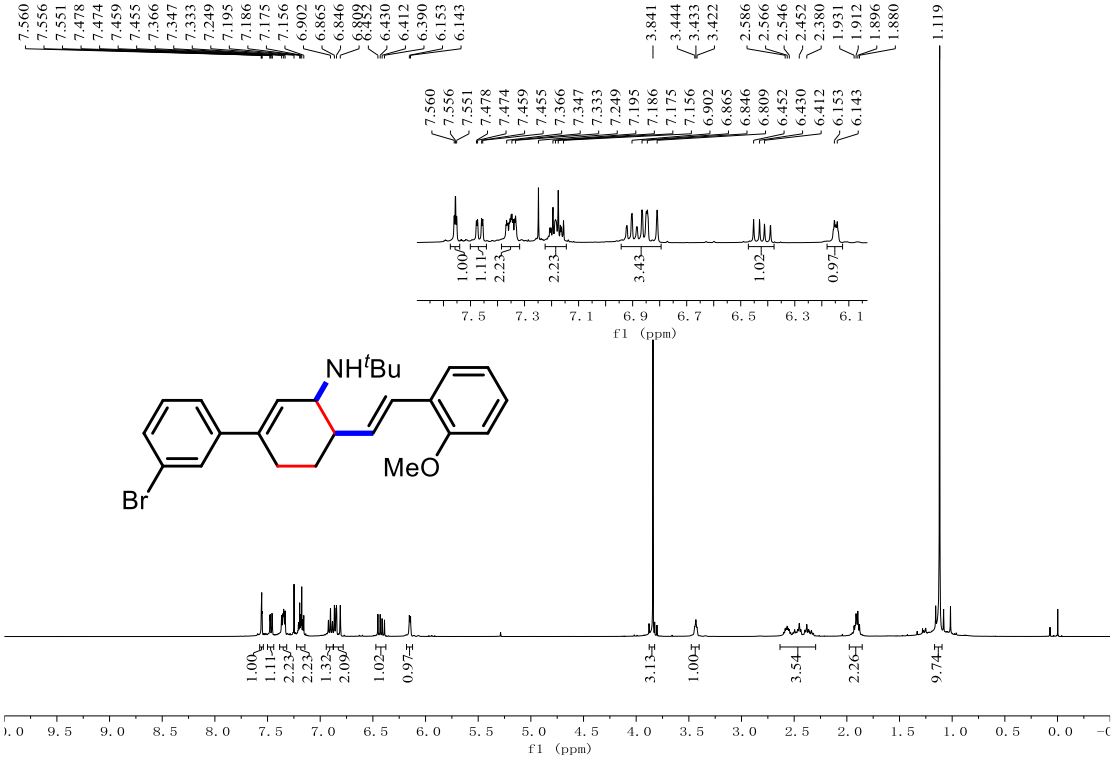
^{1}H NMR spectrum of *cis*-5fa (400 MHz, $CDCl_3$)



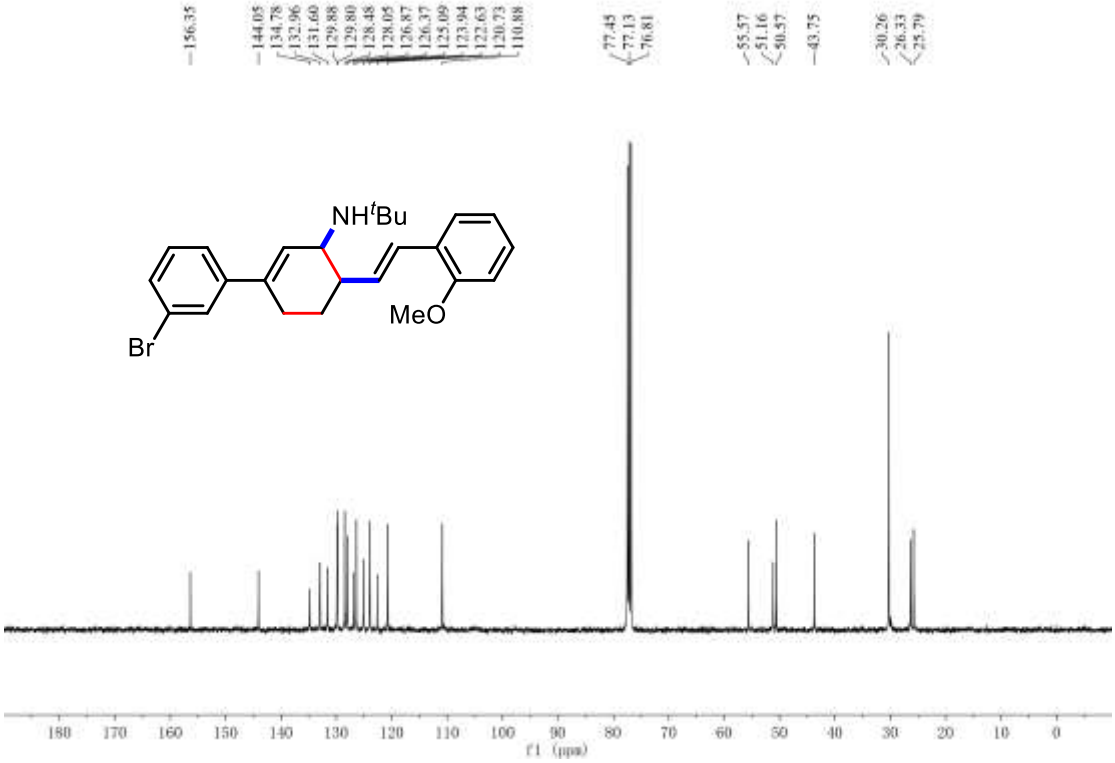
^{13}C NMR spectrum of *cis*-5fa (101 MHz, $CDCl_3$)



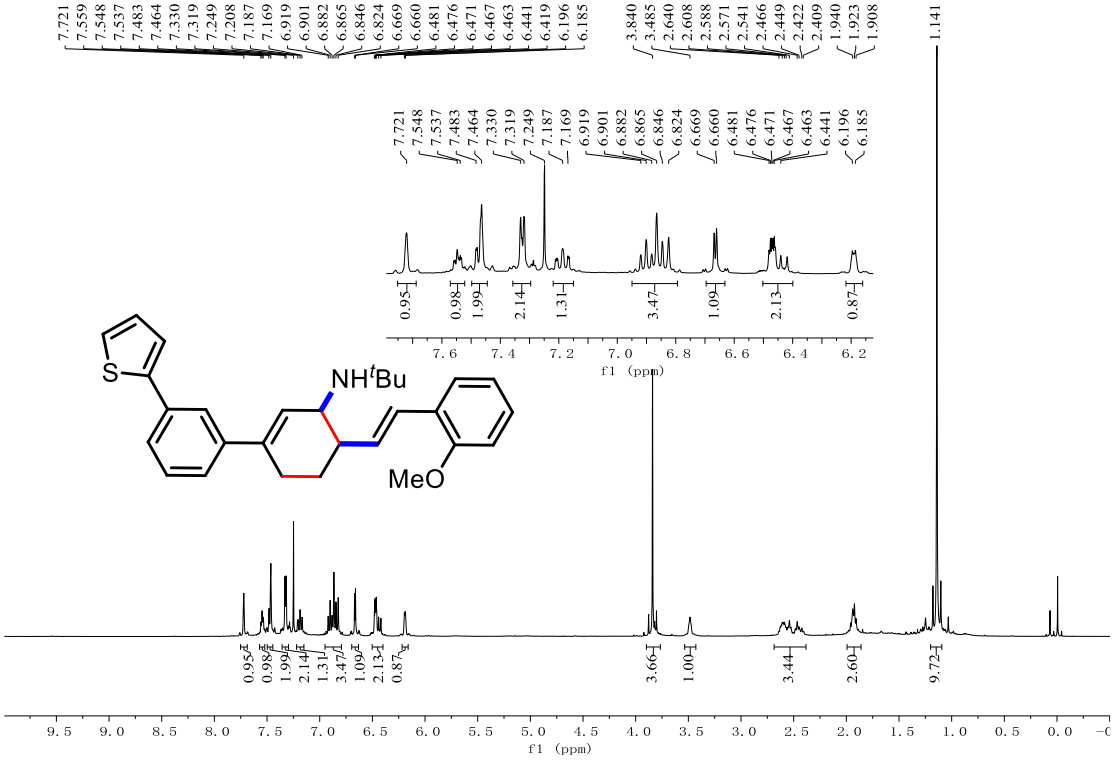
^{1}H NMR spectrum of *cis*-5ga (400 MHz, $CDCl_3$)



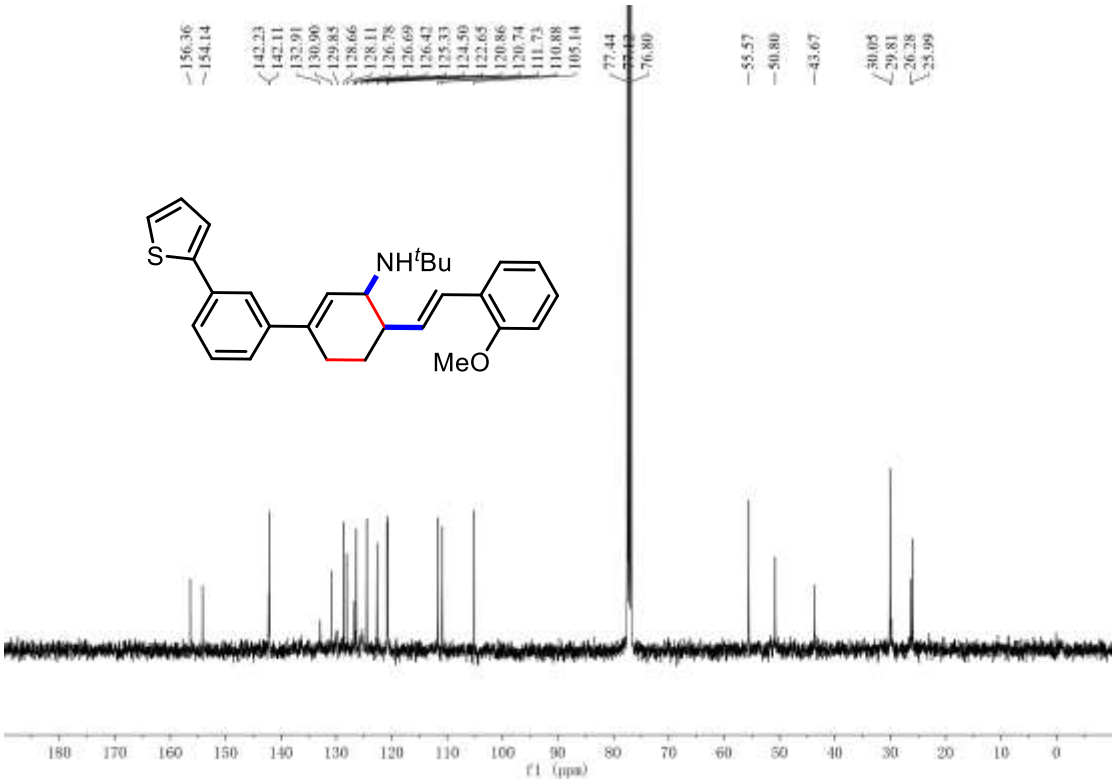
^{13}C NMR spectrum of *cis*-5ga (101 MHz, $CDCl_3$)



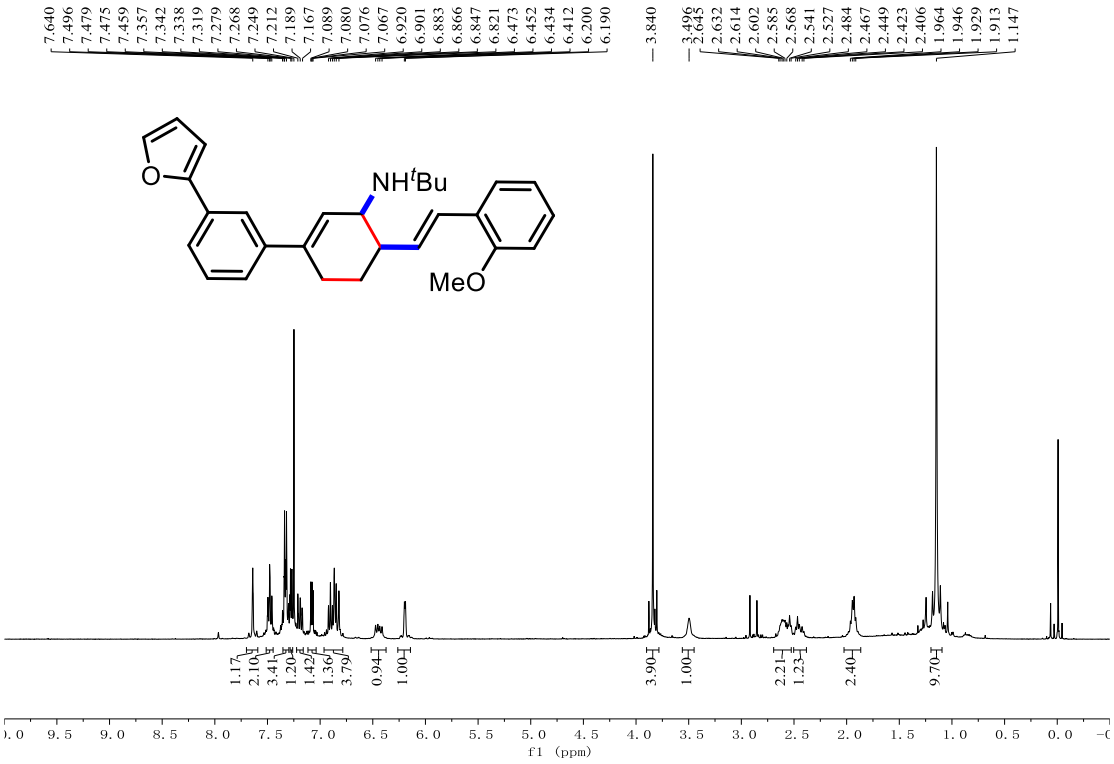
^{1}H NMR spectrum of *cis*-5ha (400 MHz, $CDCl_3$)



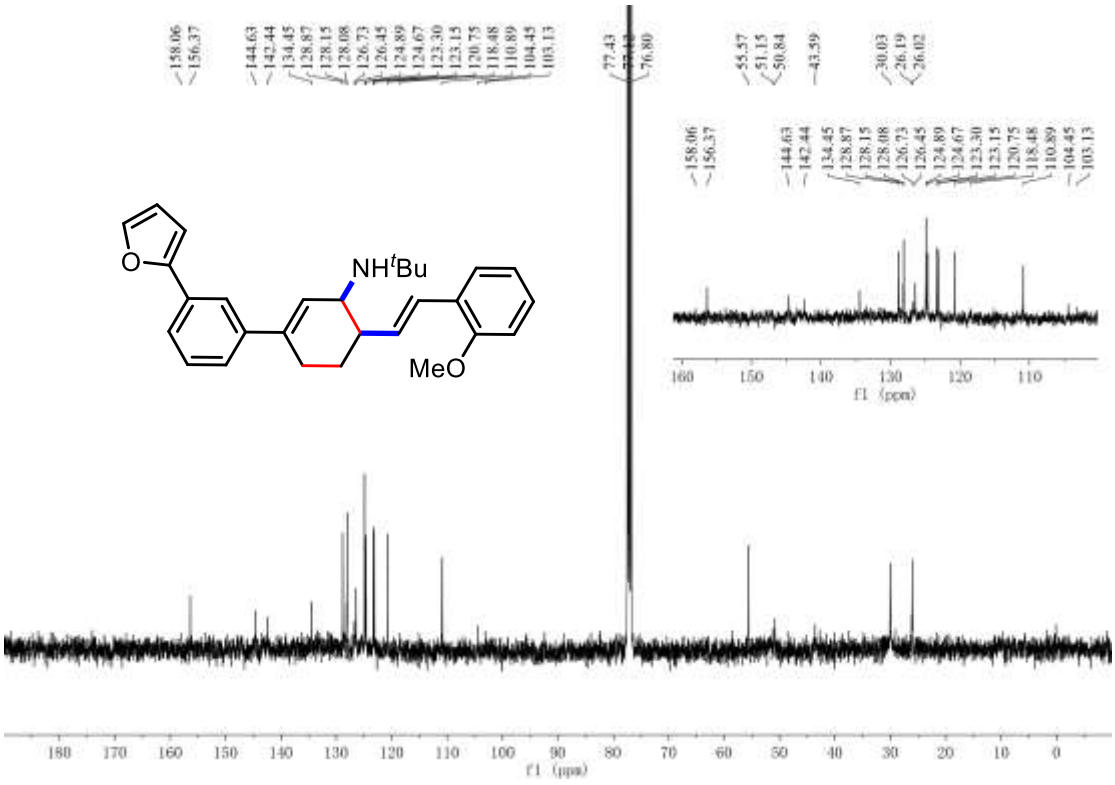
^{13}C NMR spectrum of *cis*-5ha (101 MHz, $CDCl_3$)



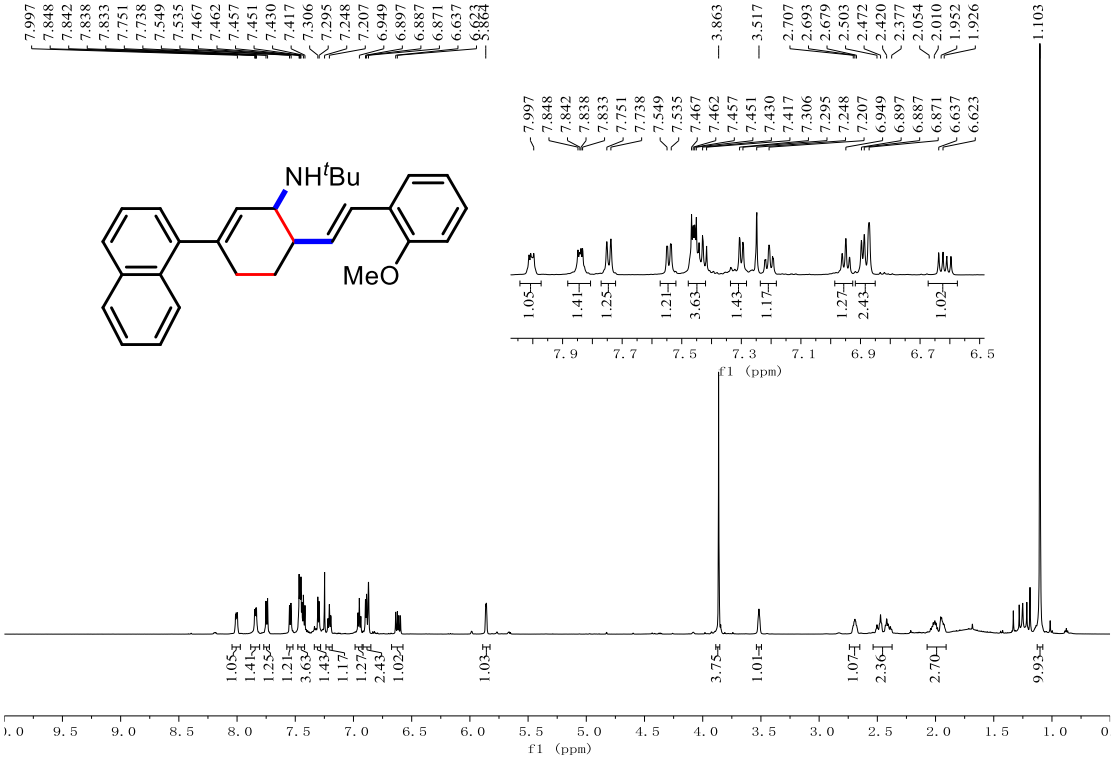
^{1}H NMR spectrum of *cis*-5ia (400 MHz, $CDCl_3$)



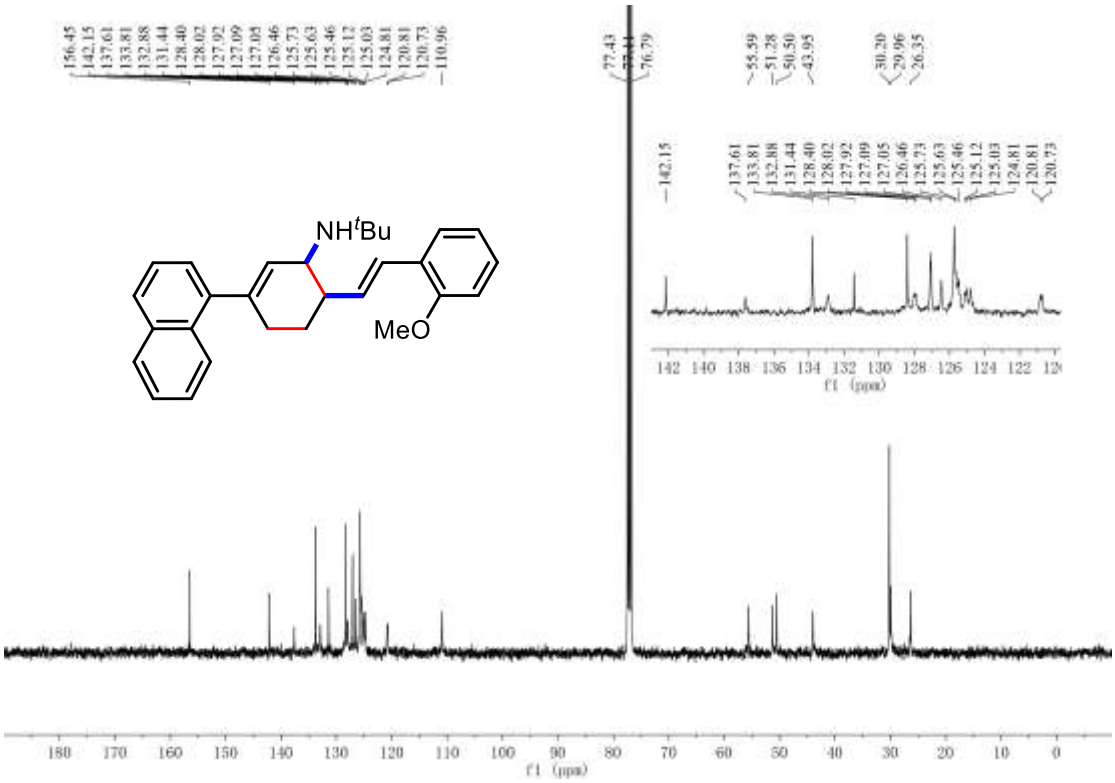
^{13}C NMR spectrum of *cis*-5ia (101 MHz, $CDCl_3$)



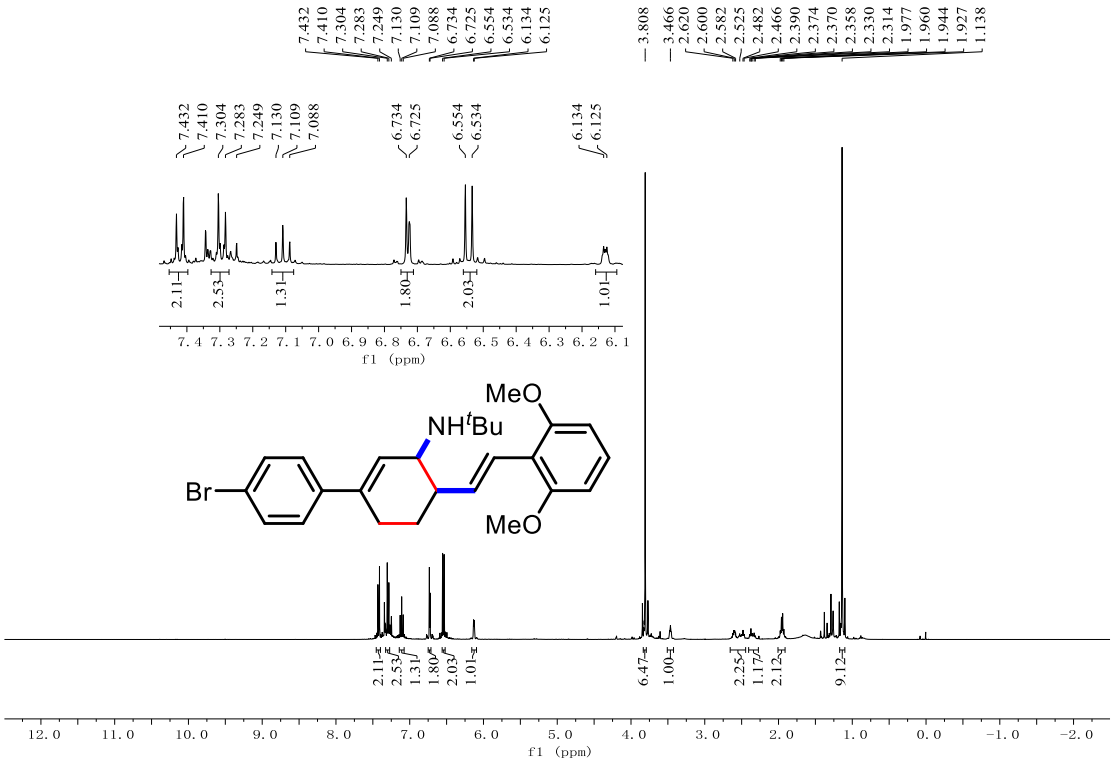
^{1}H NMR spectrum of *cis*-5ja (400 MHz, $CDCl_3$)



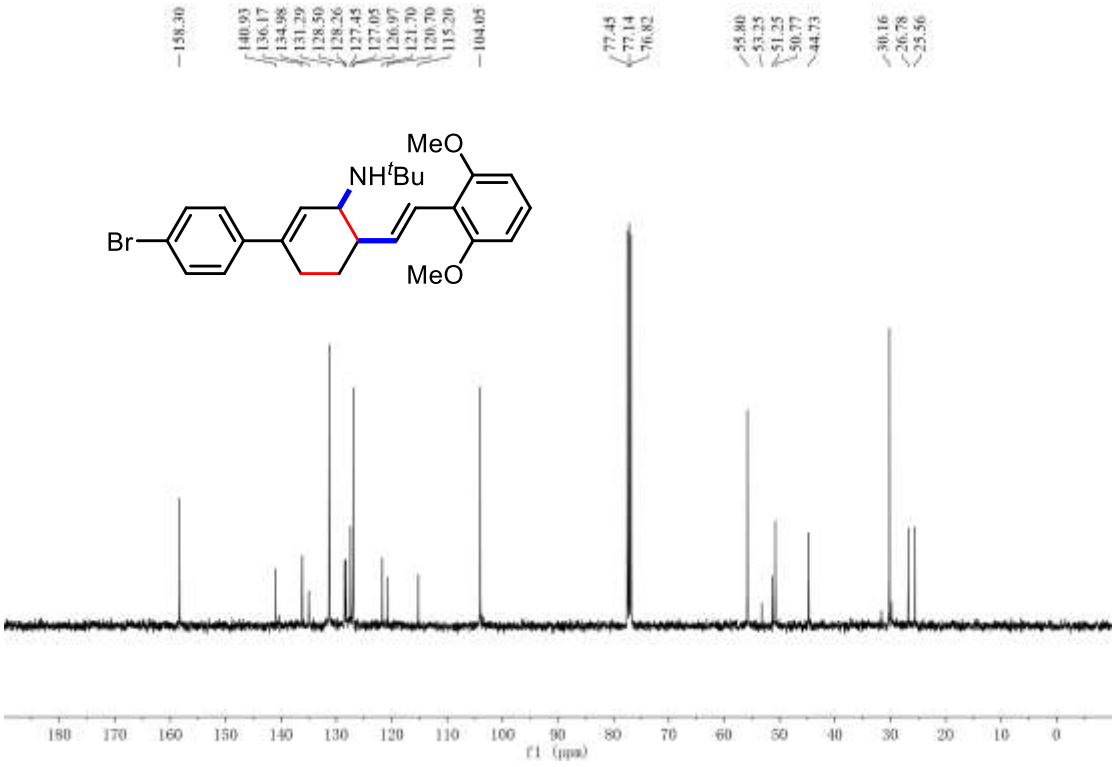
^{13}C NMR spectrum of *cis*-5ja (101 MHz, $CDCl_3$)



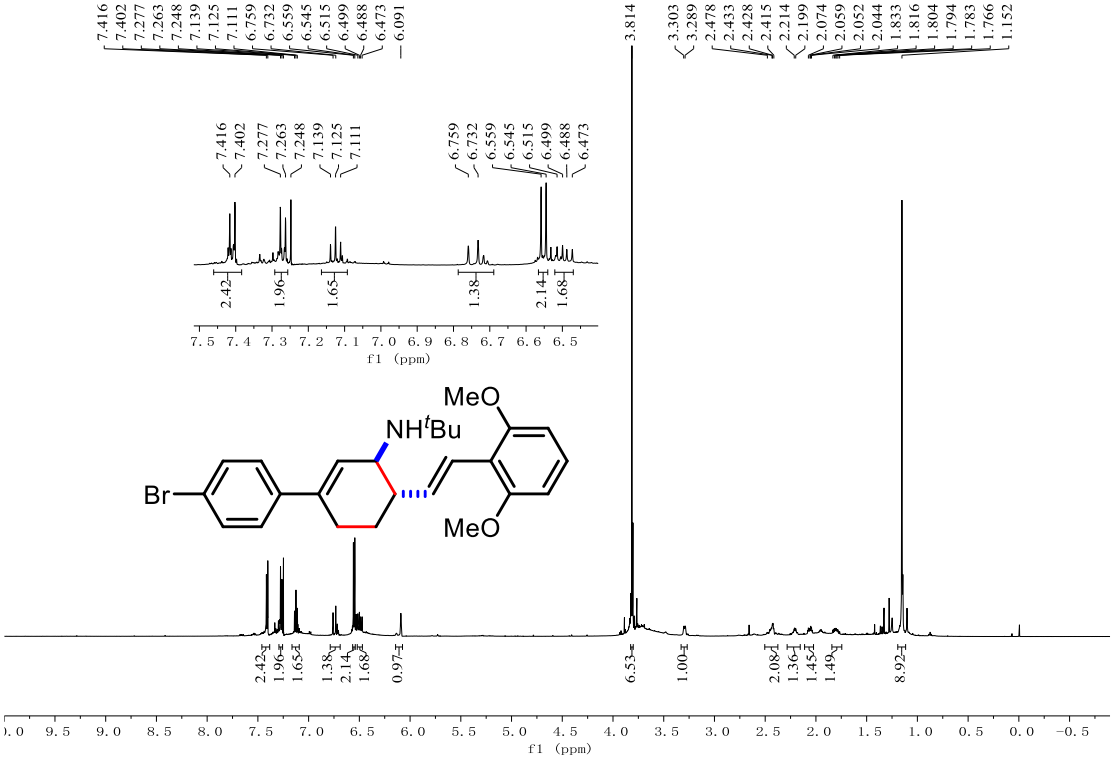
^{1}H NMR spectrum of *cis*-5ka (400 MHz, $CDCl_3$)



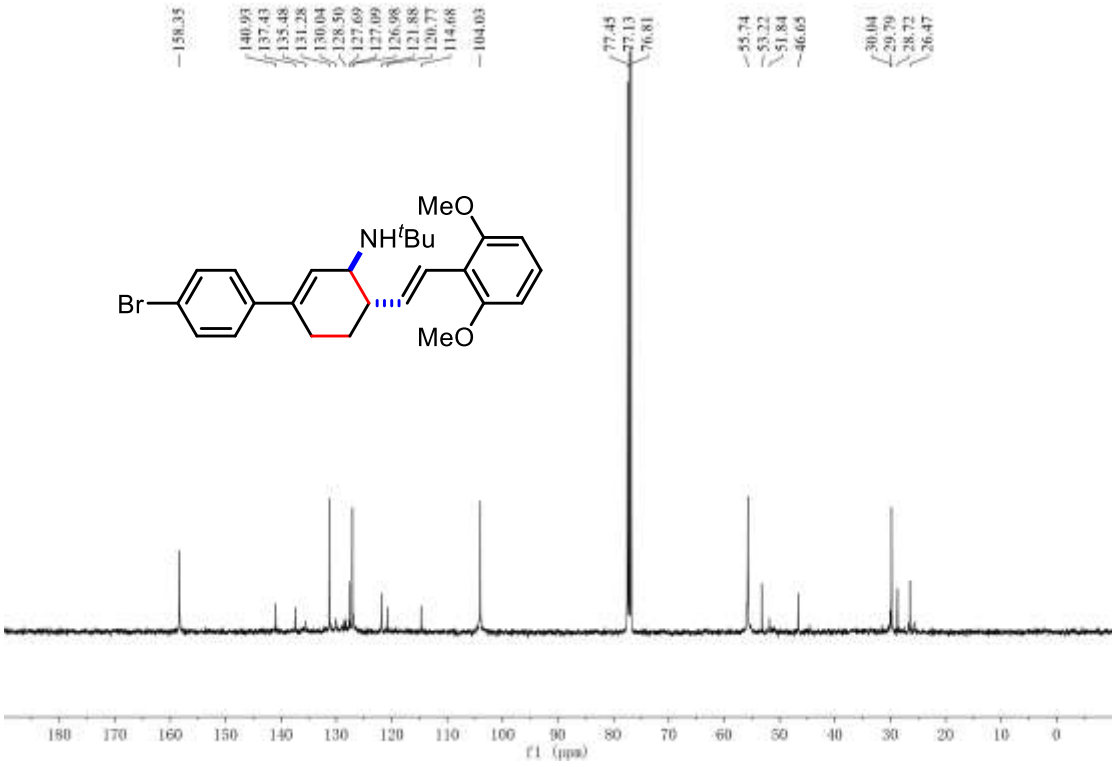
^{13}C NMR spectrum of *cis*-5ka (101 MHz, $CDCl_3$)



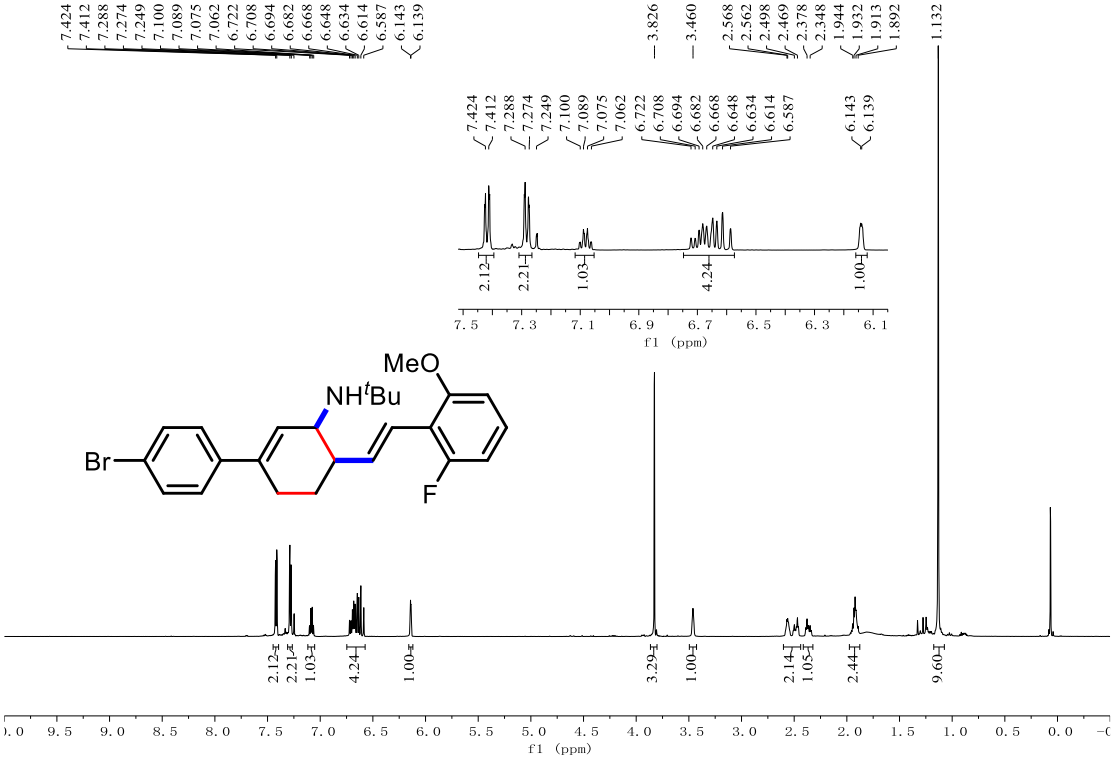
^{1}H NMR spectrum of *trans*-5ka (400 MHz, $CDCl_3$)



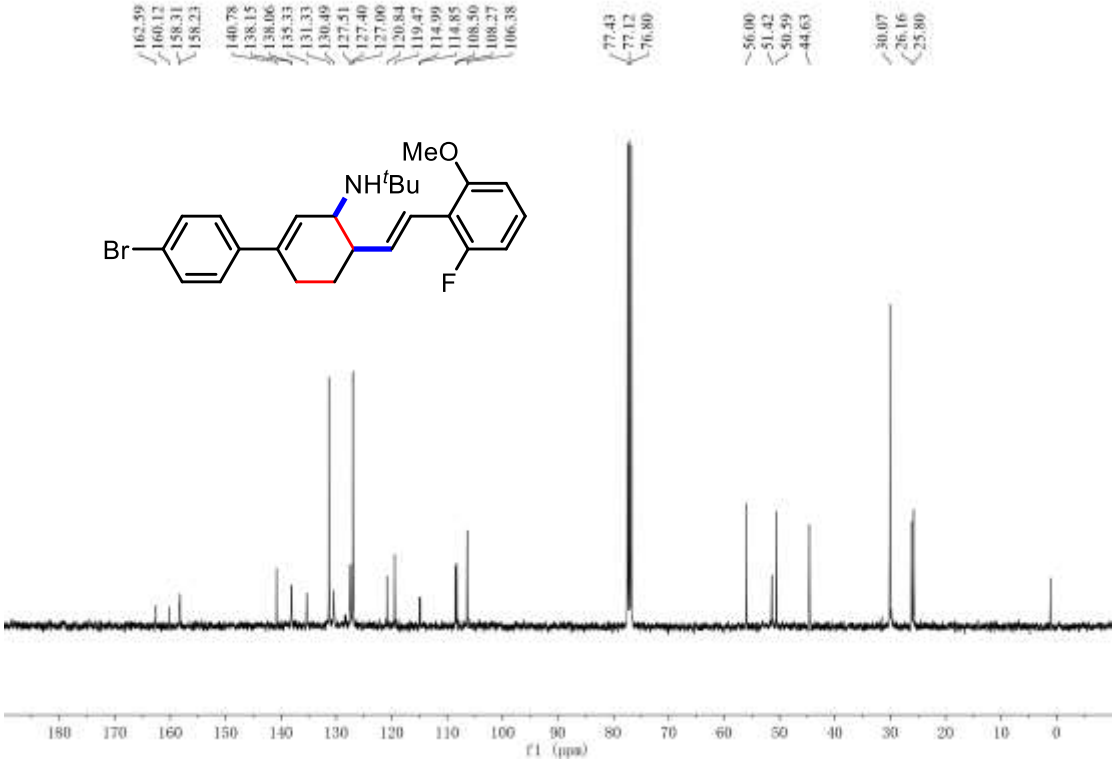
^{13}C NMR spectrum of *trans*-5ka (101 MHz, $CDCl_3$)



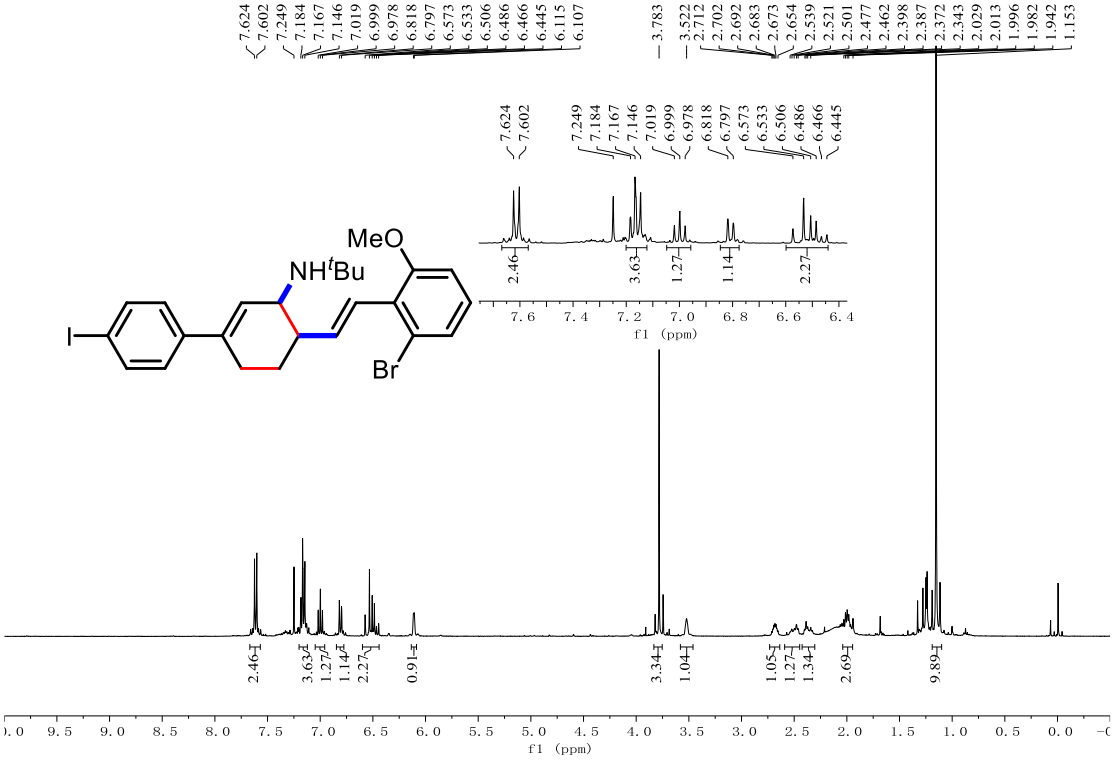
^{1}H NMR spectrum of *cis*-5la (400 MHz, $CDCl_3$)



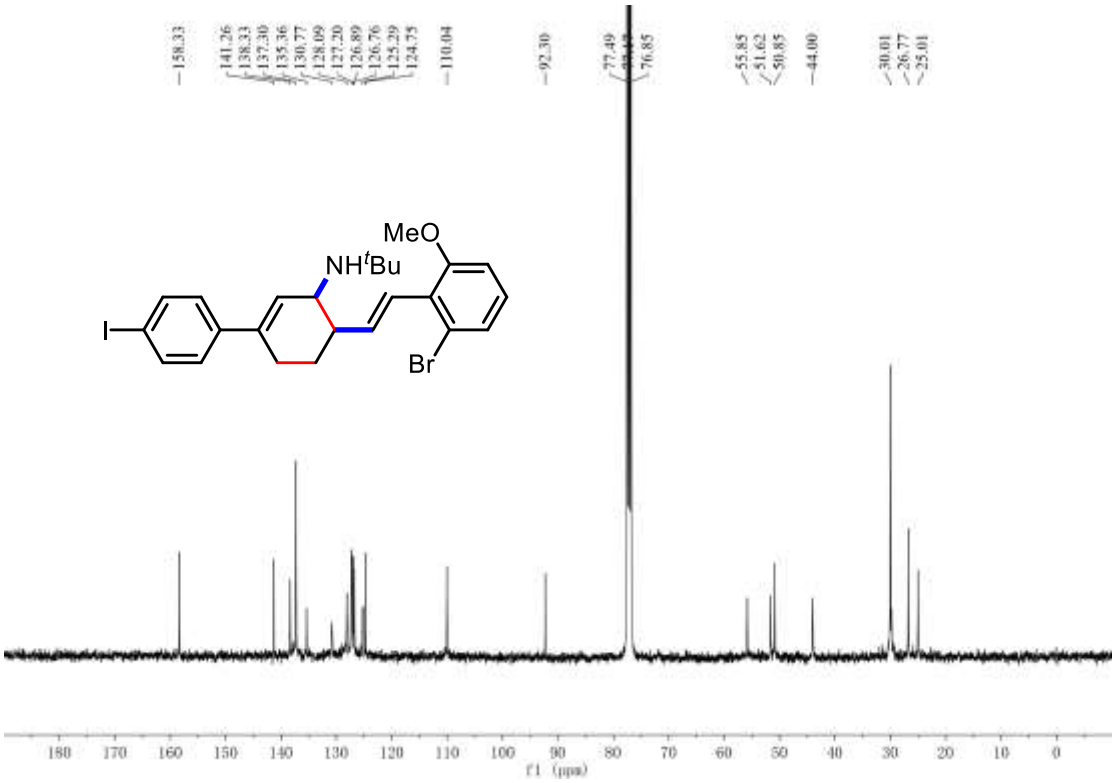
^{13}C NMR spectrum of *cis*-5la (101 MHz, $CDCl_3$)



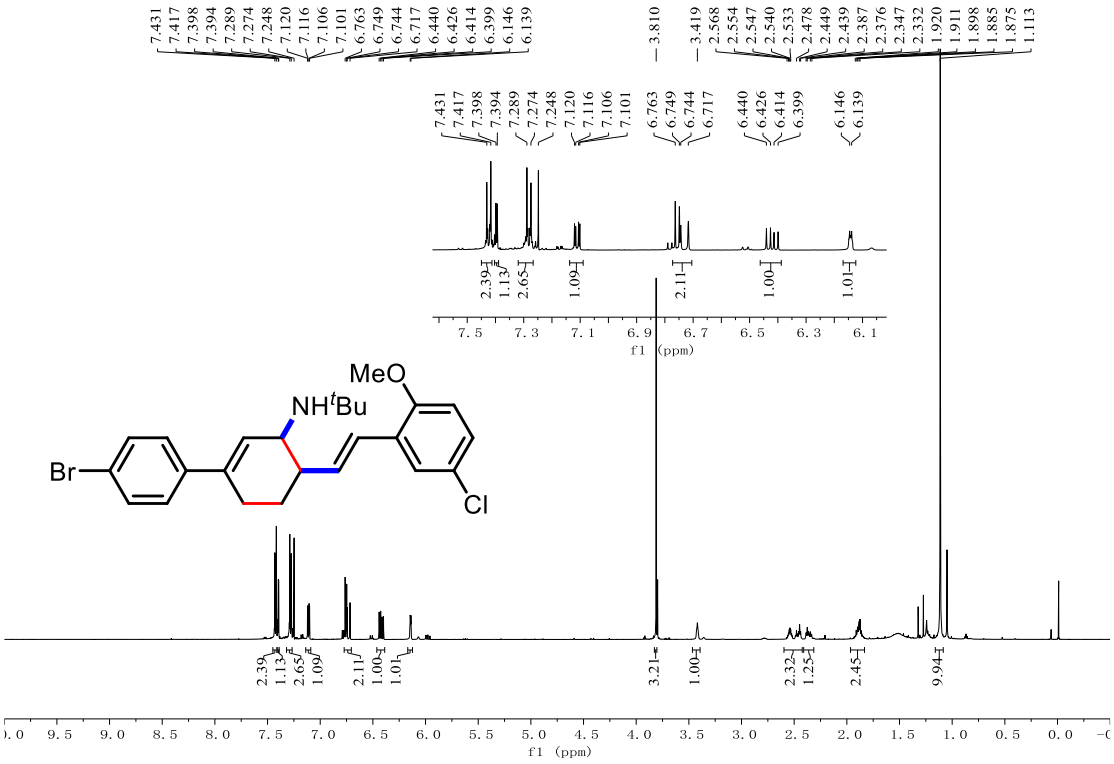
^{1}H NMR spectrum of *cis*-5ma (400 MHz, $CDCl_3$)



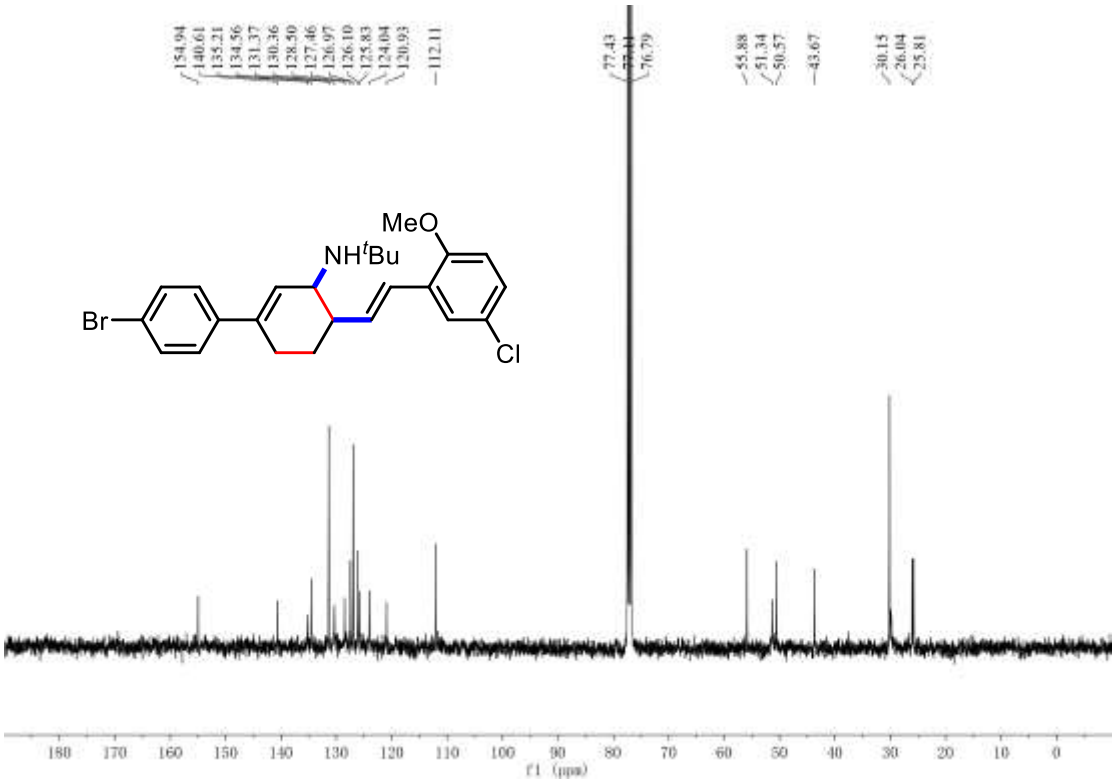
^{13}C NMR spectrum of *cis*-5ma (101 MHz, $CDCl_3$)



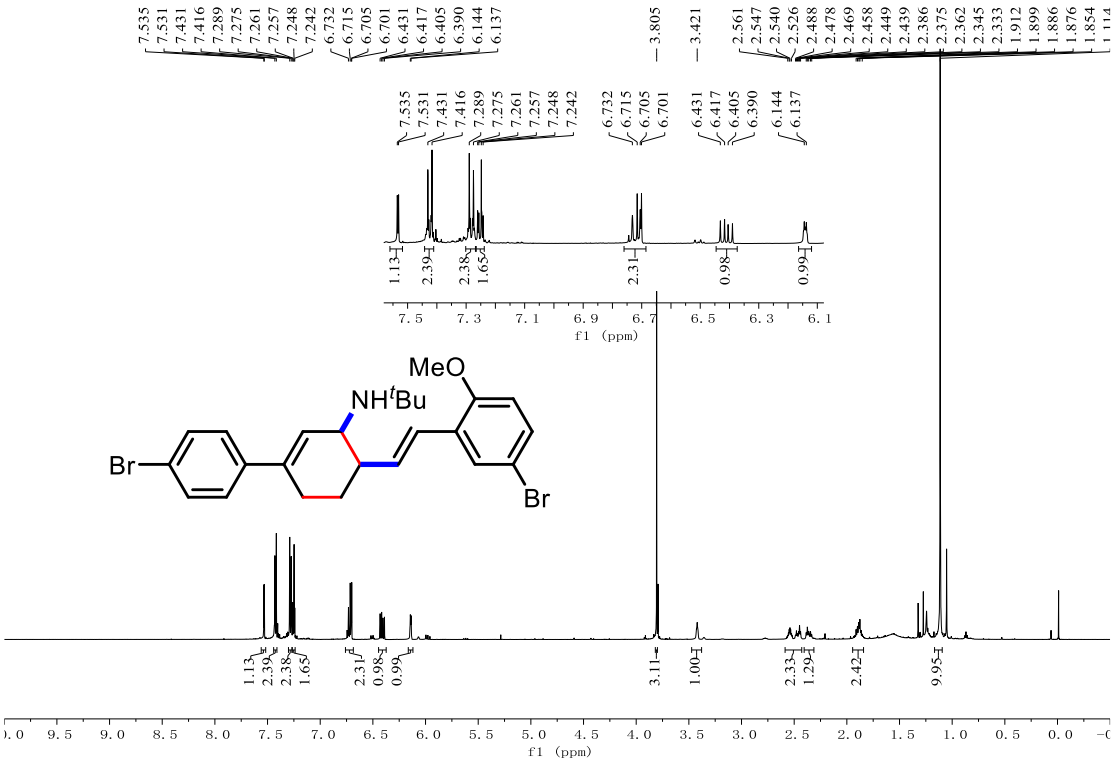
^{1}H NMR spectrum of *cis*-5na (600 MHz, $CDCl_3$)



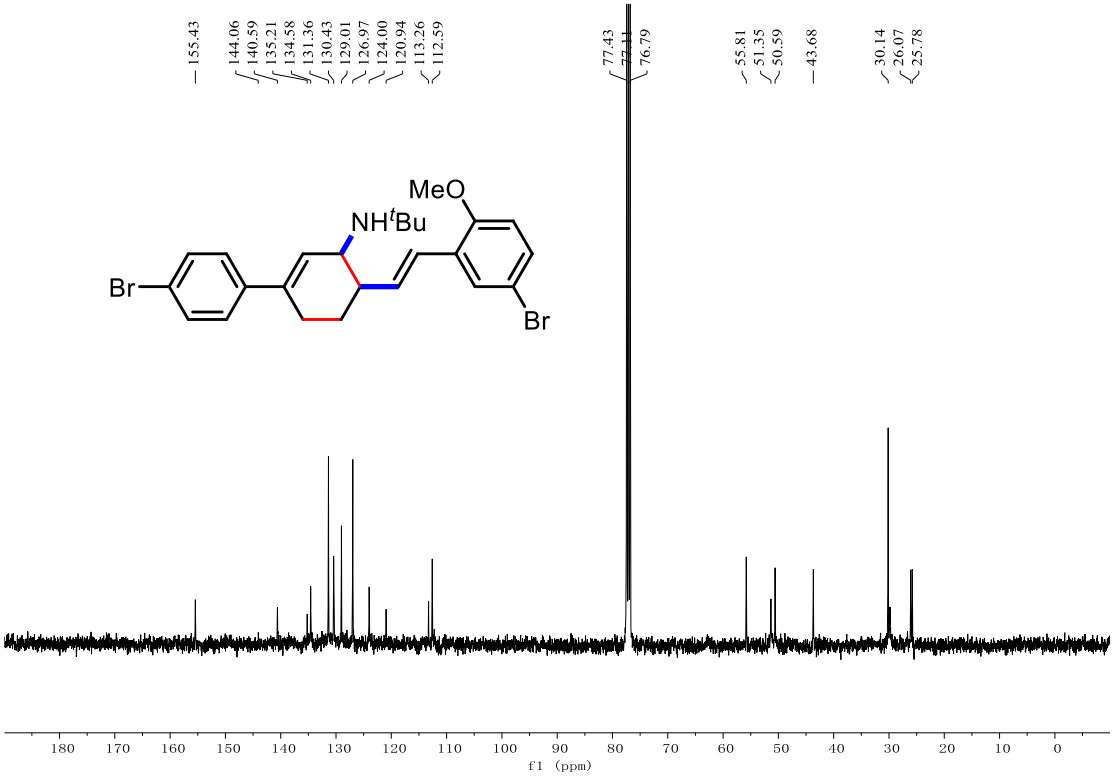
^{13}C NMR spectrum of *cis*-5na (101 MHz, $CDCl_3$)



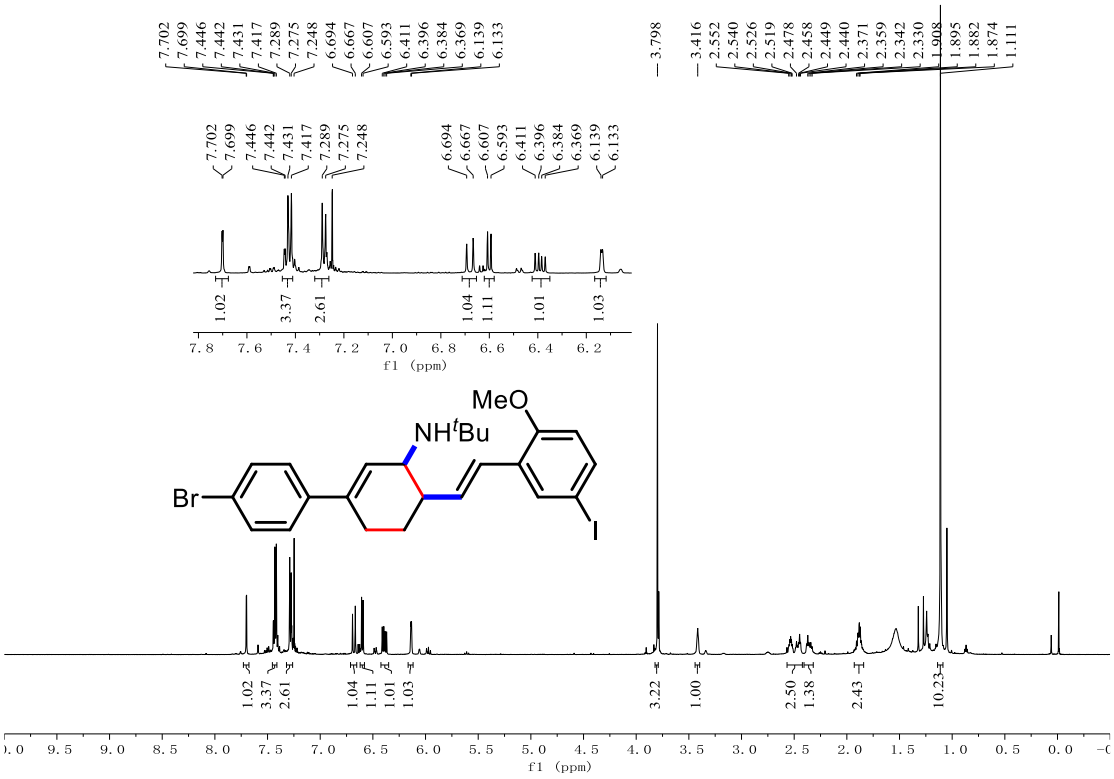
^{1}H NMR spectrum of *cis*-5oa (600 MHz, $CDCl_3$)



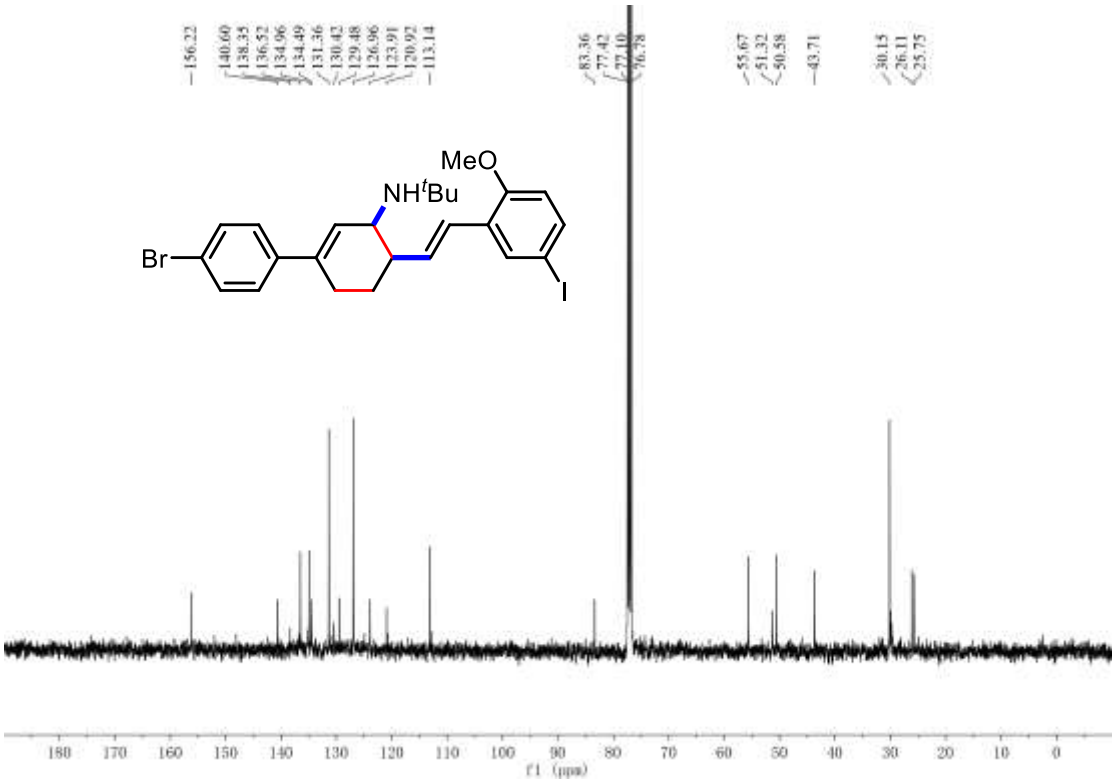
^{13}C NMR spectrum of *cis*-5oa (101 MHz, $CDCl_3$)



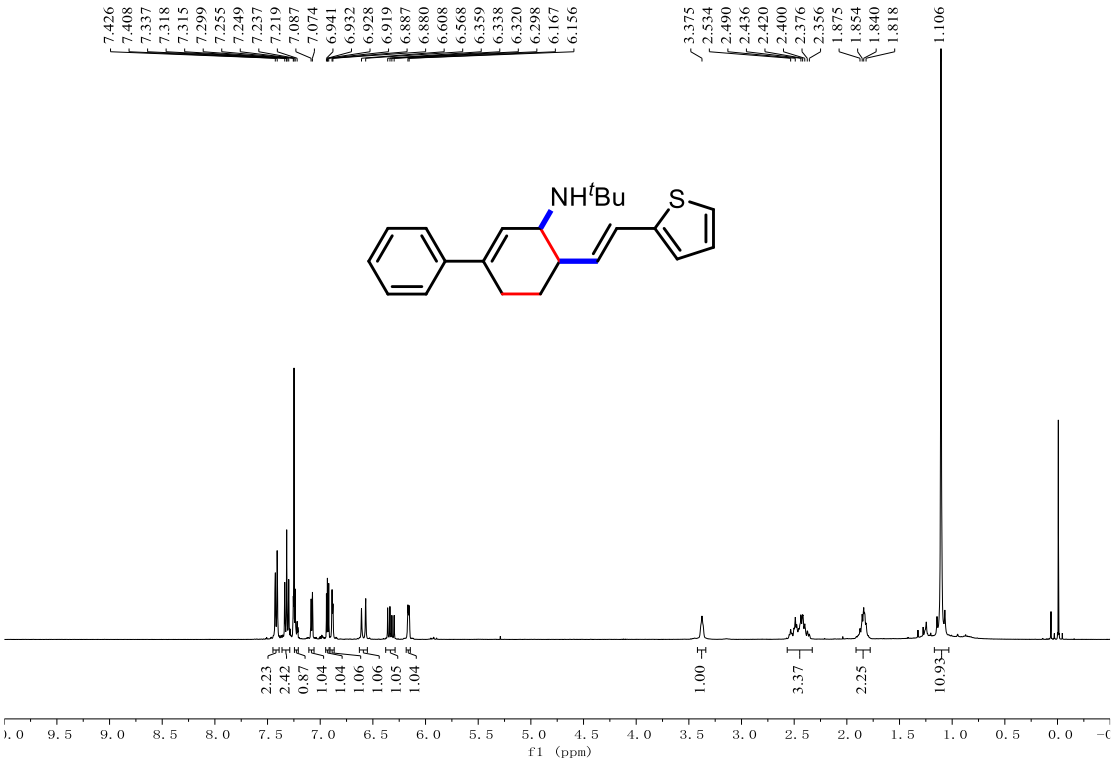
^{1}H NMR spectrum of *cis*-5pa (600 MHz, $CDCl_3$)



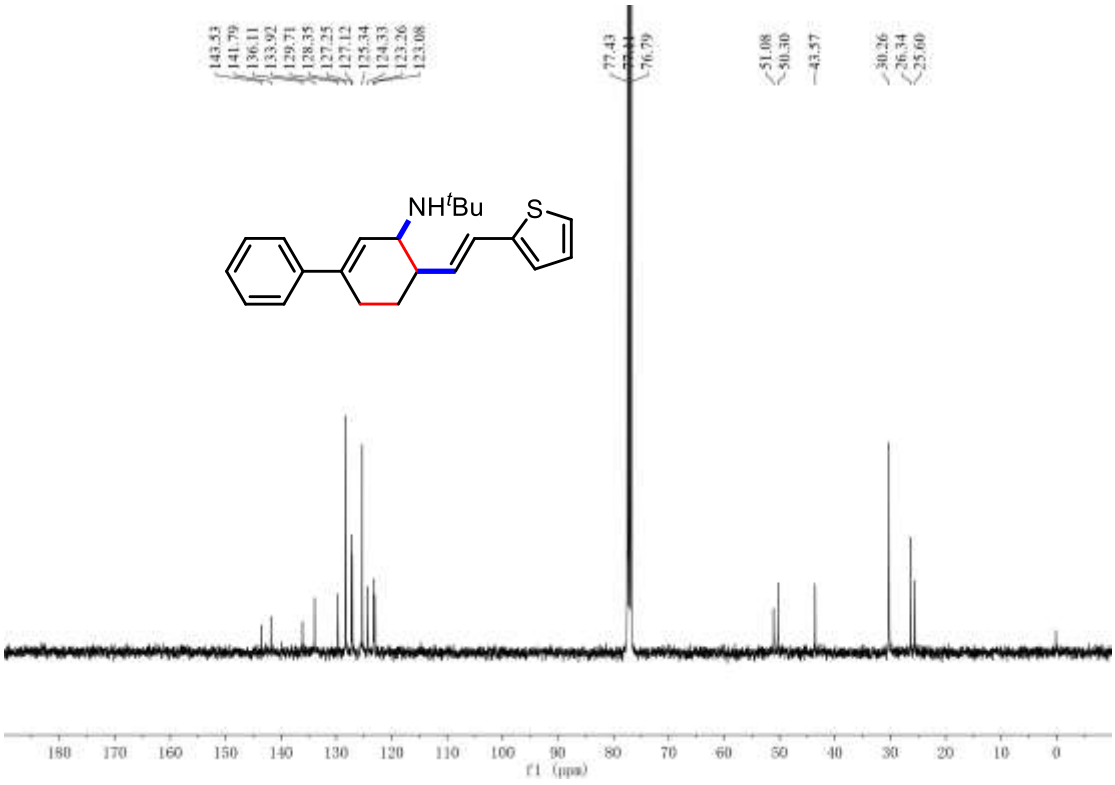
^{13}C NMR spectrum of *cis*-5pa (101 MHz, $CDCl_3$)



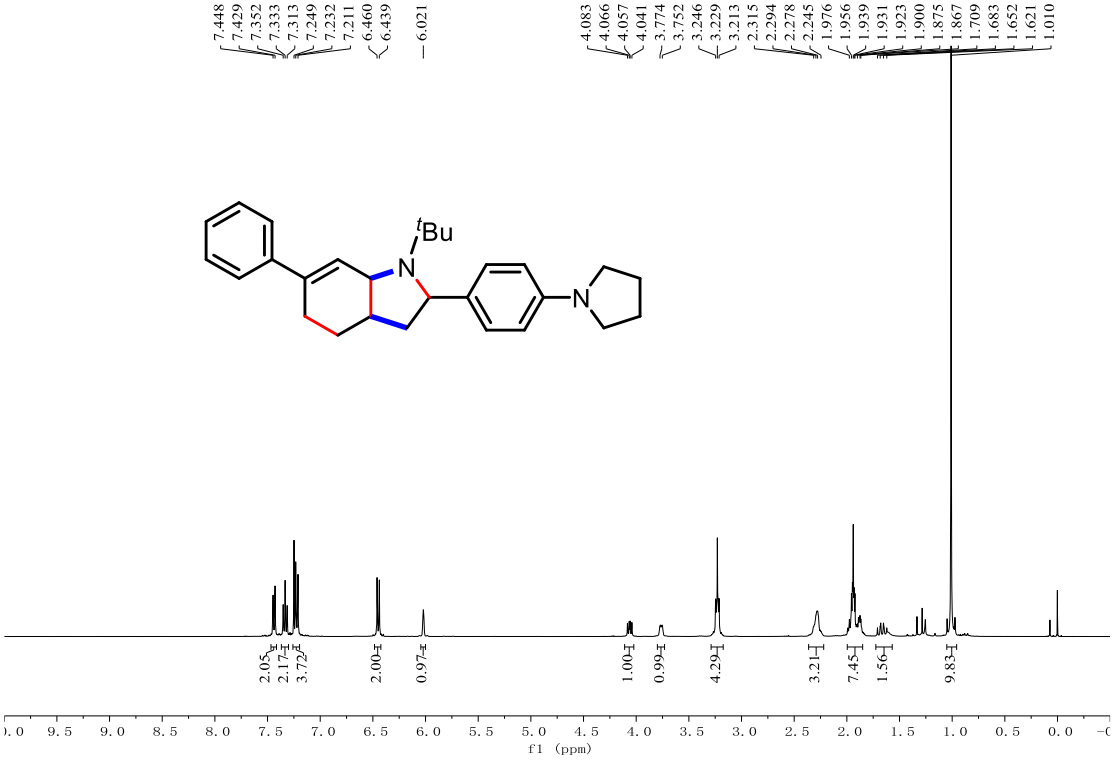
^{1}H NMR spectrum of *cis*-5qa (400 MHz, $CDCl_3$)



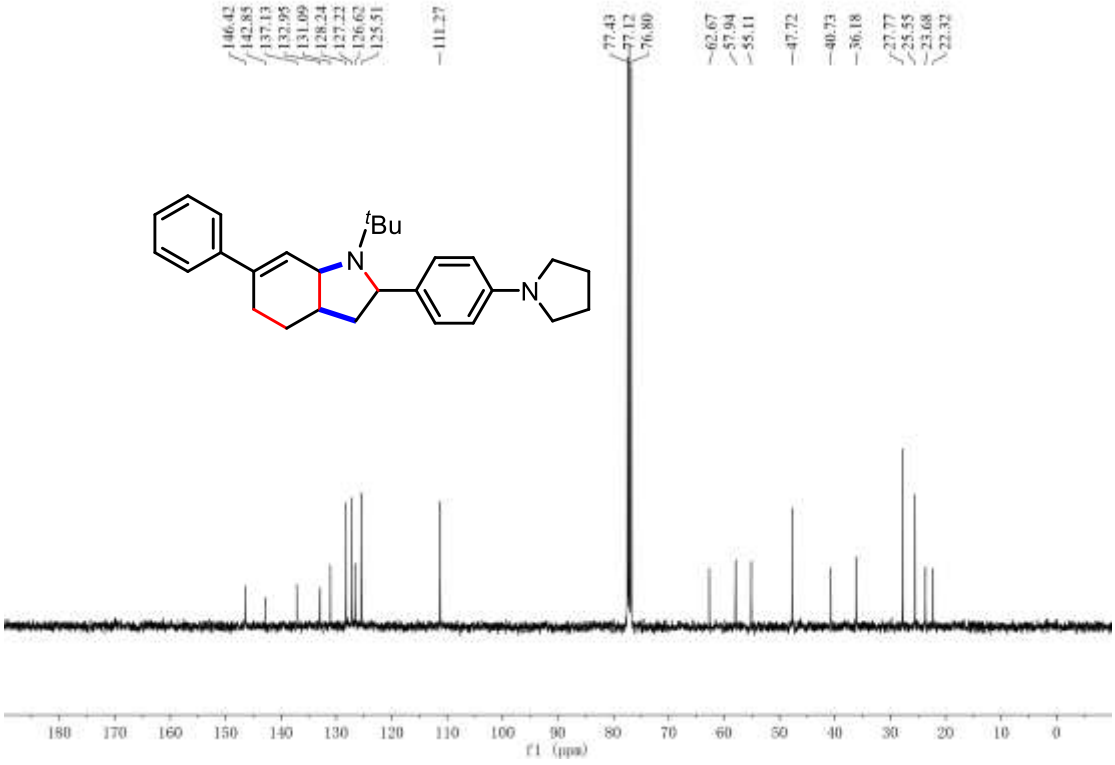
^{13}C NMR spectrum of *cis*-5qa (101 MHz, $CDCl_3$)



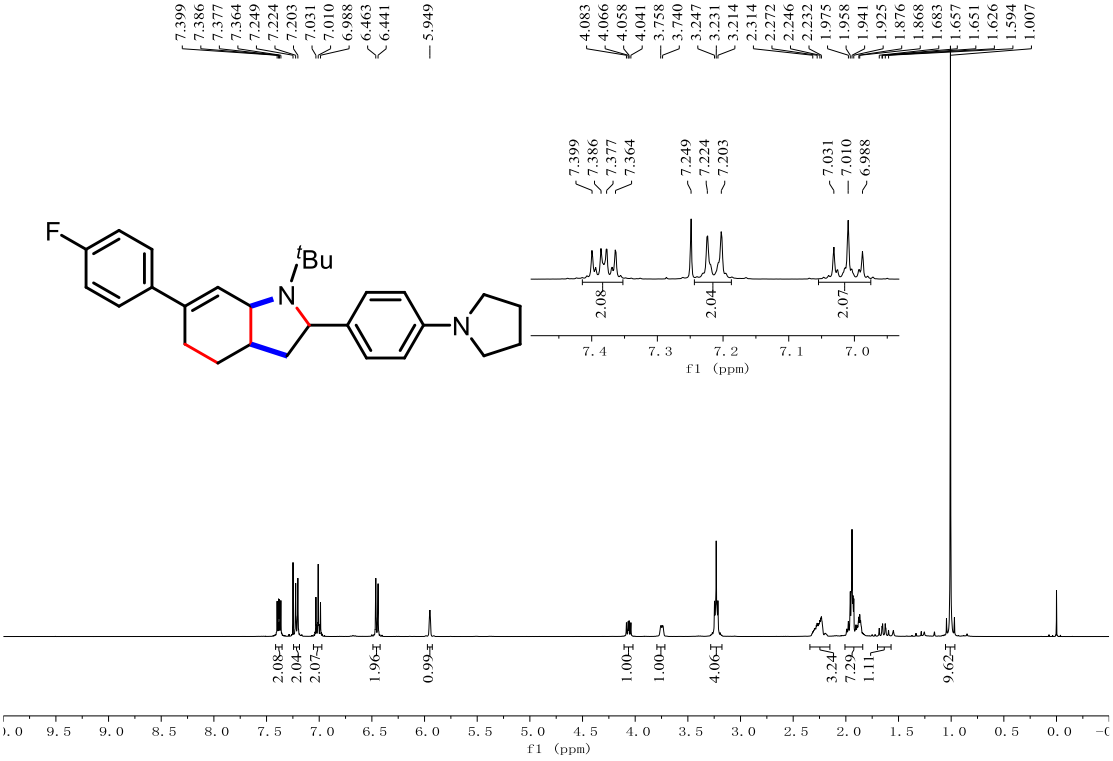
^{1}H NMR spectrum of *cis*-6aa (400 MHz, $CDCl_3$)



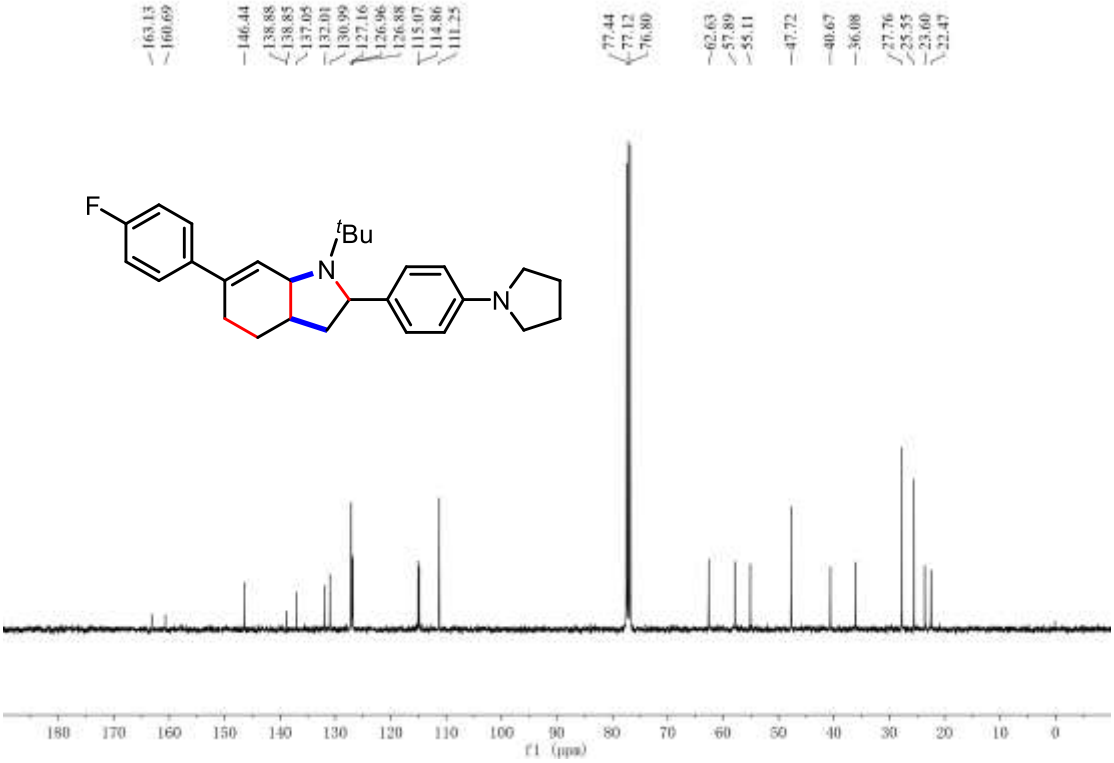
^{13}C NMR spectrum of *cis*-6aa (101 MHz, $CDCl_3$)



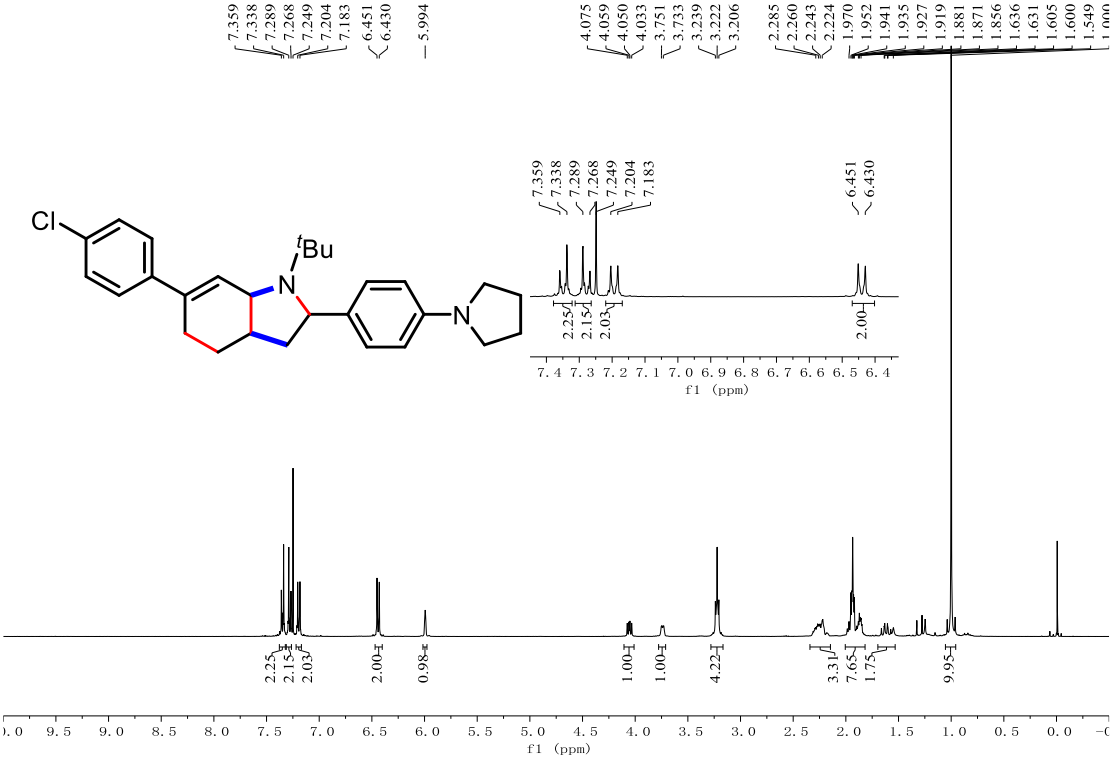
^{1}H NMR spectrum of *cis*-6ba (400 MHz, $CDCl_3$)



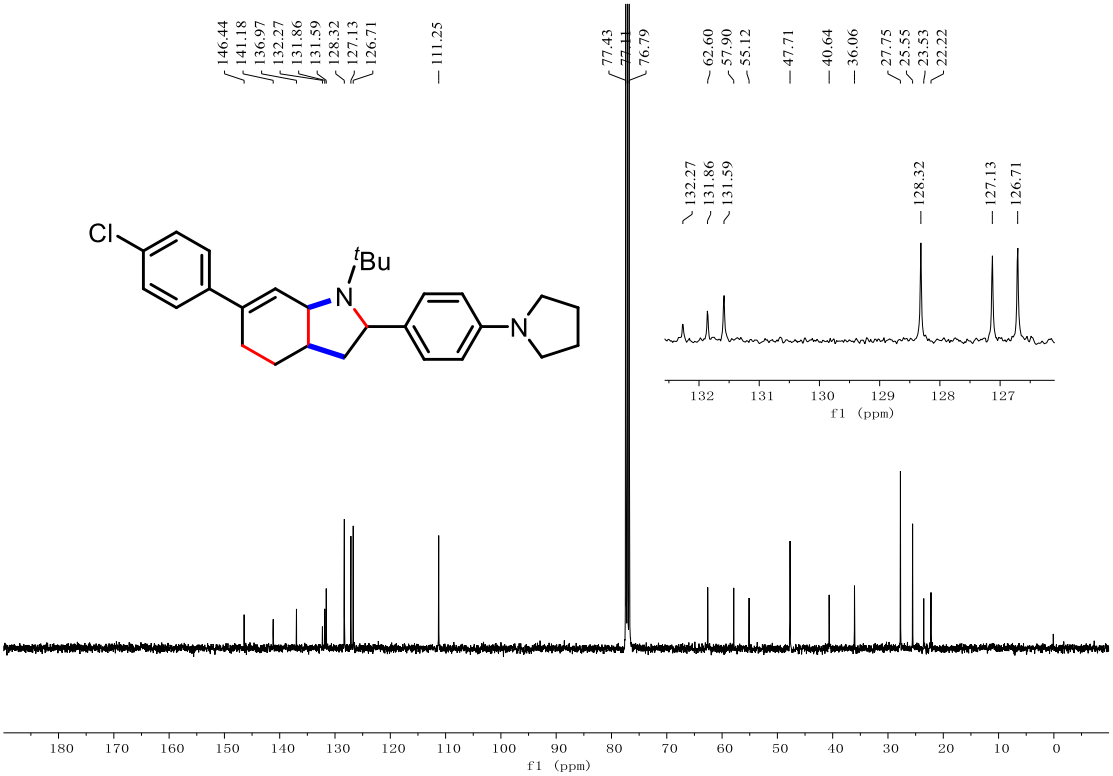
^{13}C NMR spectrum of *cis*-6ba (101 MHz, $CDCl_3$)



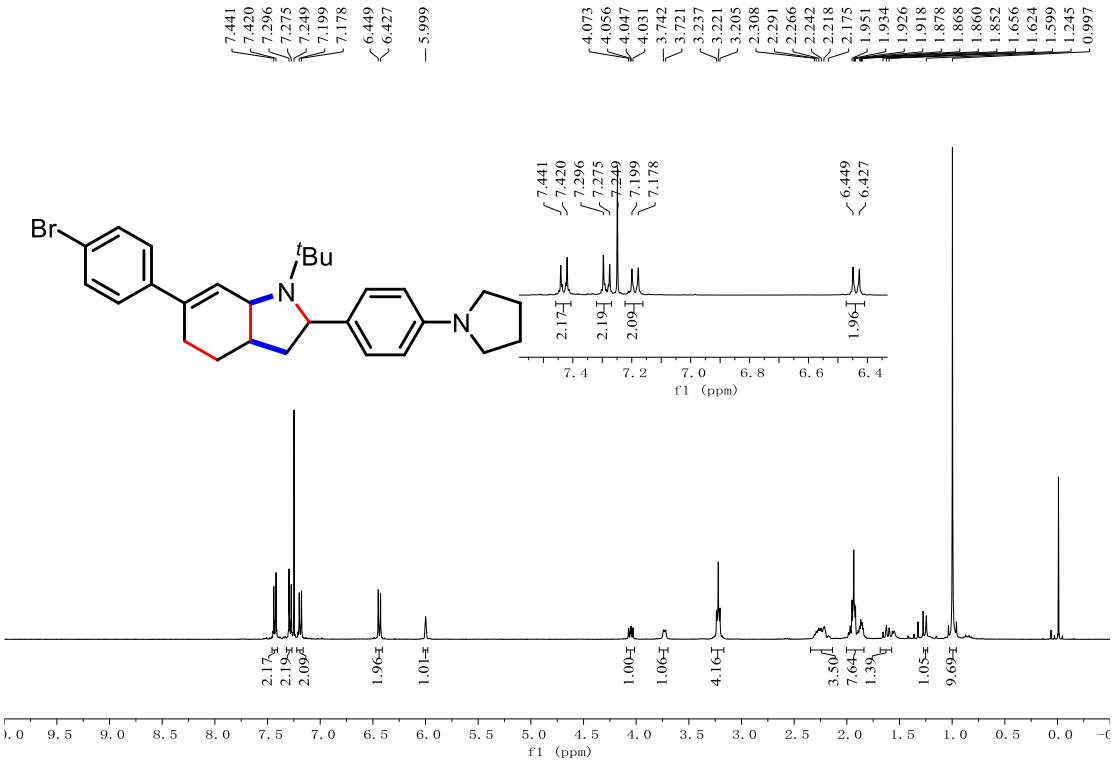
^{1}H NMR spectrum of *cis*-6ca (400 MHz, $CDCl_3$)



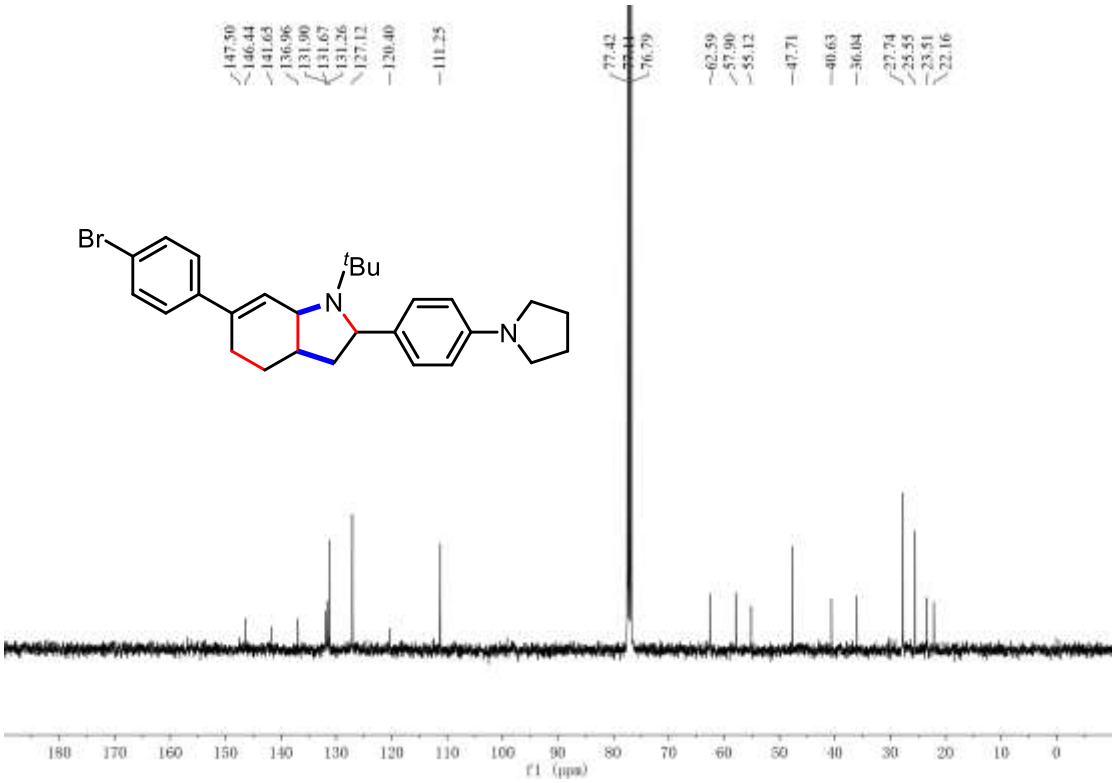
^{13}C NMR spectrum of *cis*-6ca (101 MHz, $CDCl_3$)



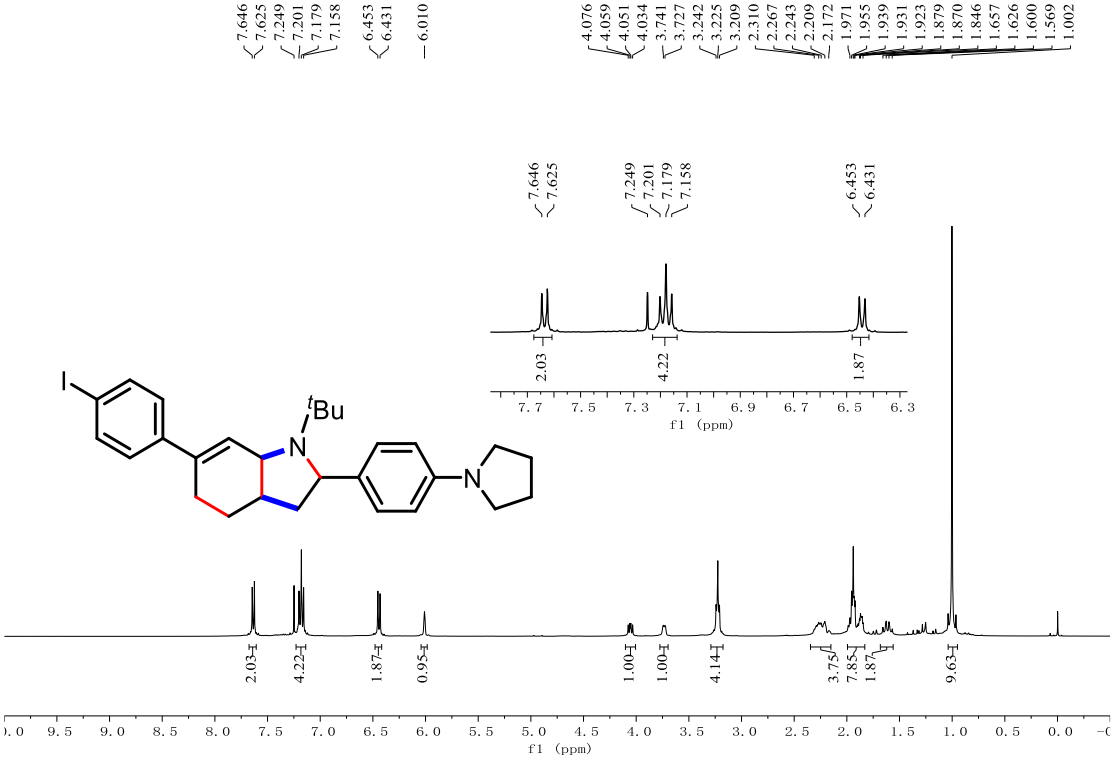
^{1}H NMR spectrum of *cis*-6da (400 MHz, $CDCl_3$)



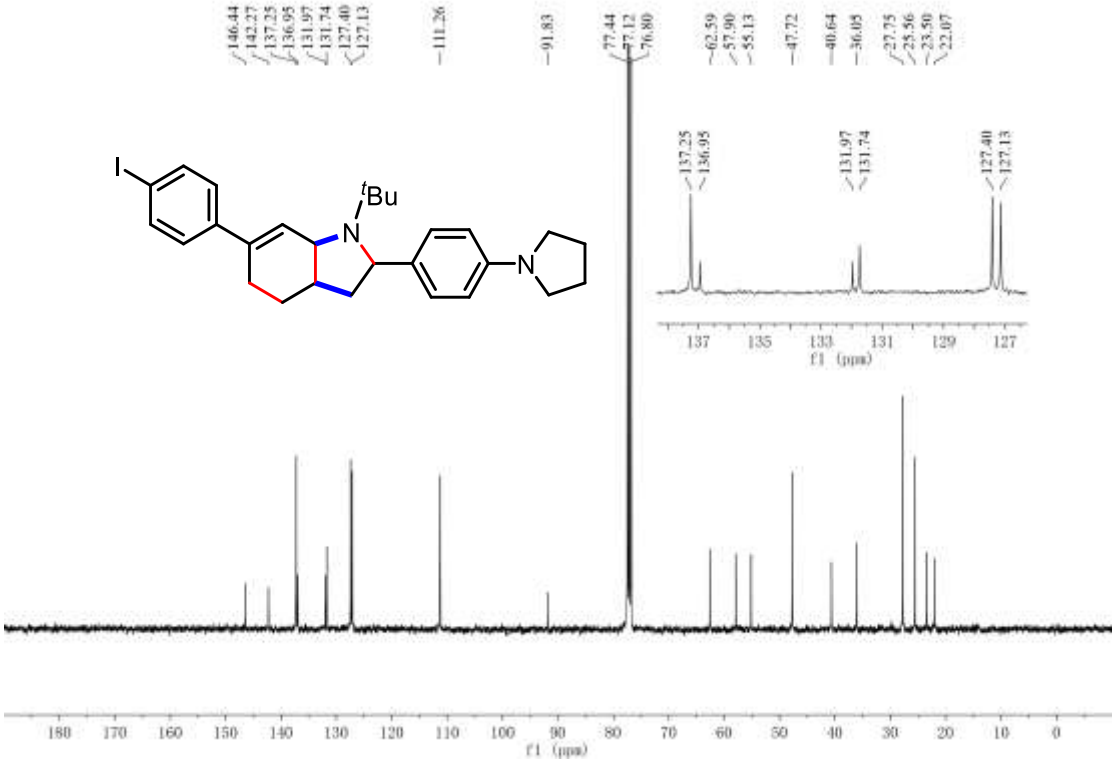
^{13}C NMR spectrum of *cis*-6da (101 MHz, $CDCl_3$)



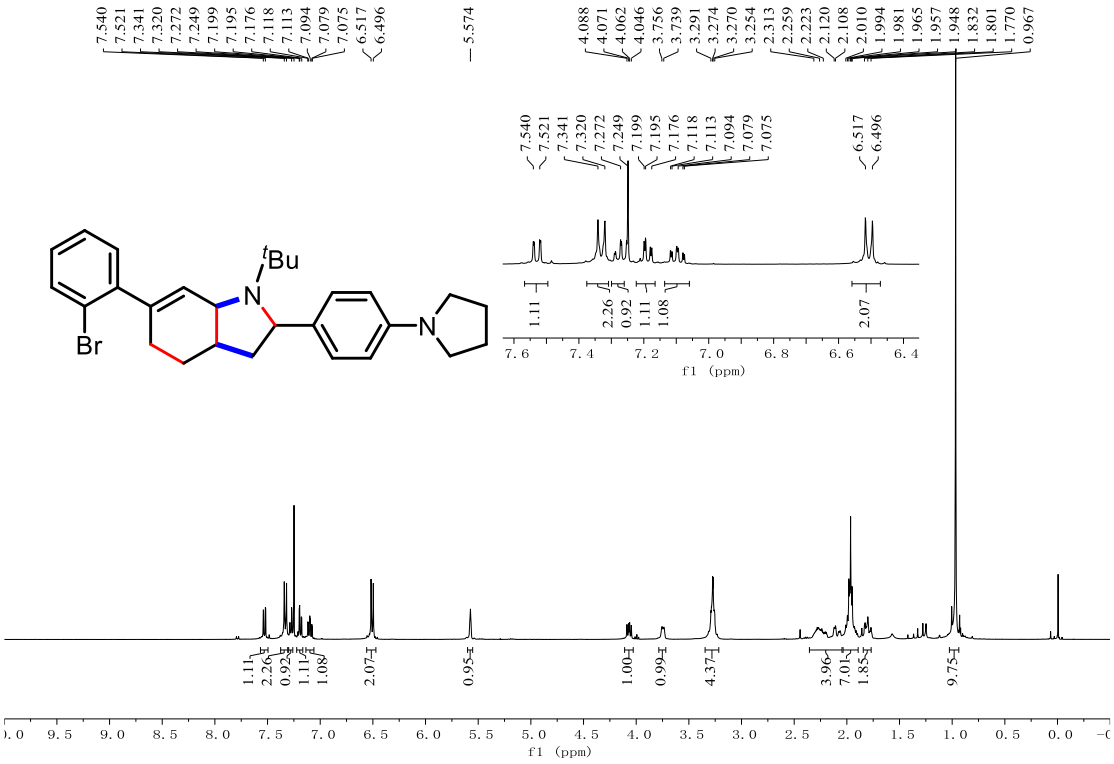
^{1}H NMR spectrum of *cis*-6ea (400 MHz, $CDCl_3$)



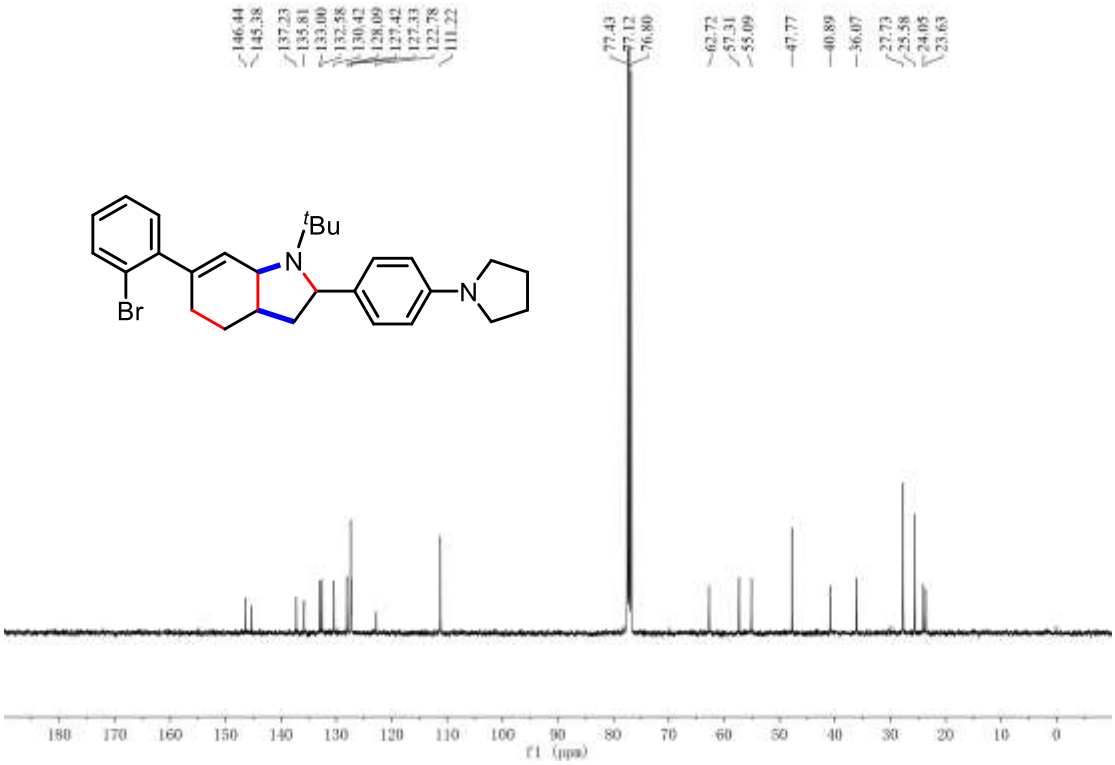
^{13}C NMR spectrum of *cis*-6ea (101 MHz, $CDCl_3$)



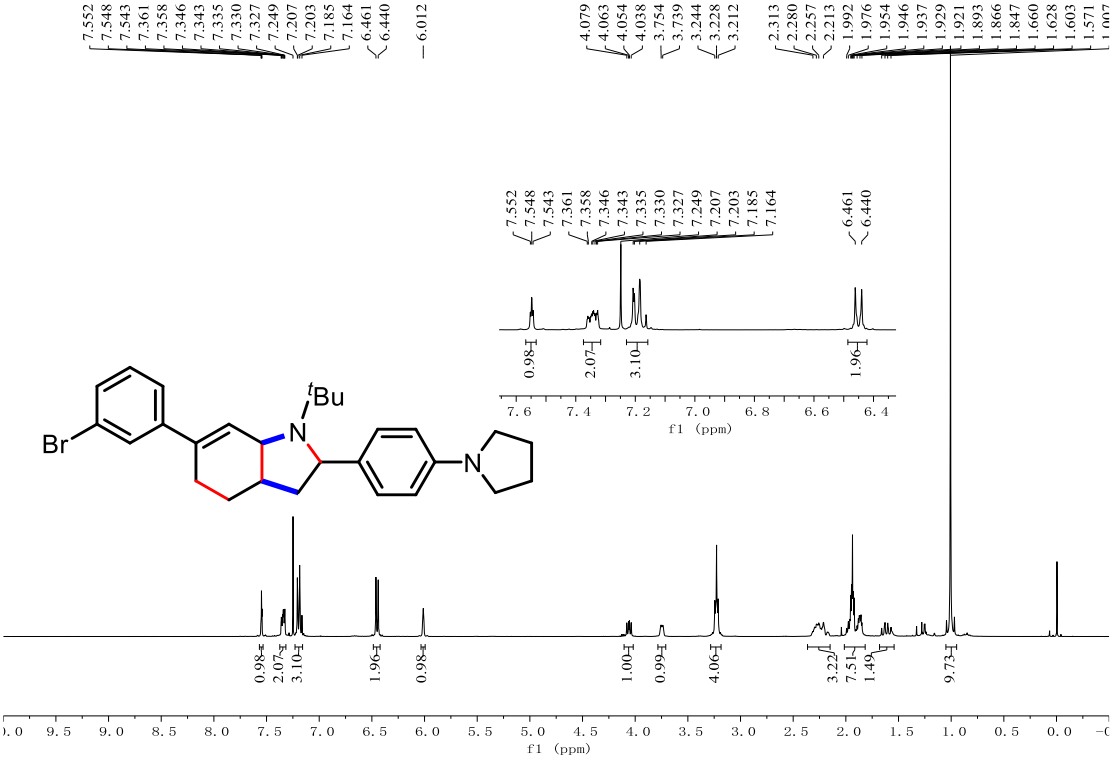
^{1}H NMR spectrum of *cis*-6fa (400 MHz, $CDCl_3$)



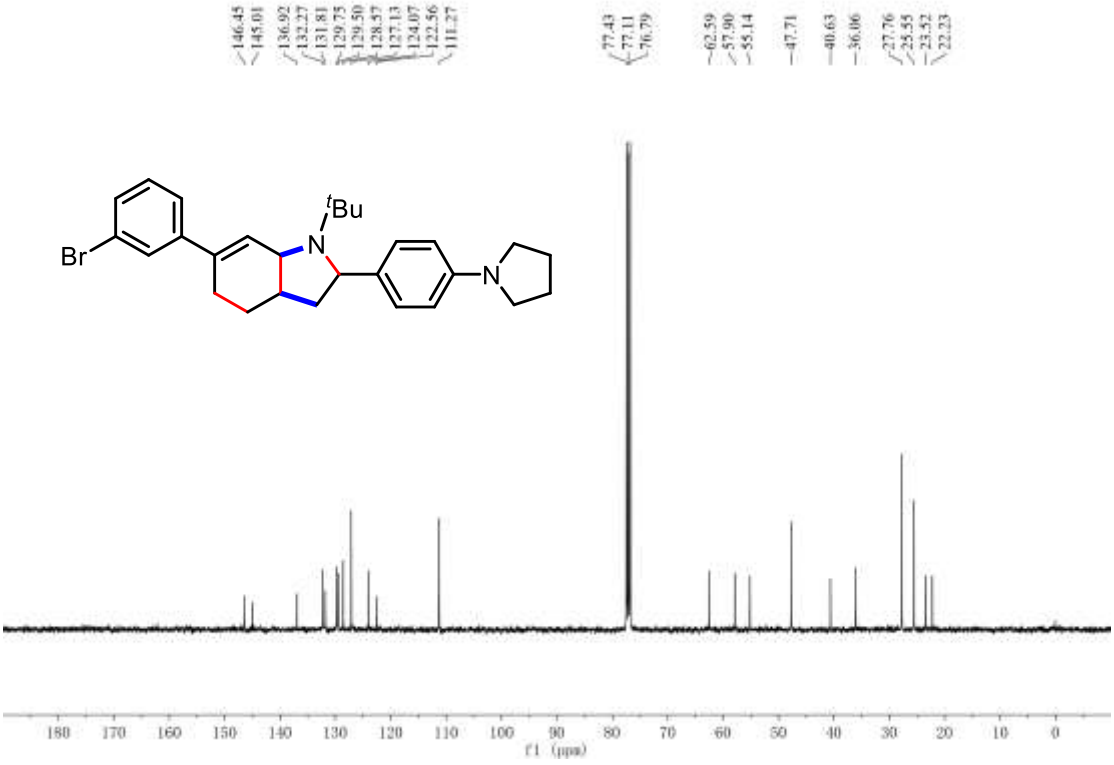
^{13}C NMR spectrum of *cis*-6fa (101 MHz, $CDCl_3$)



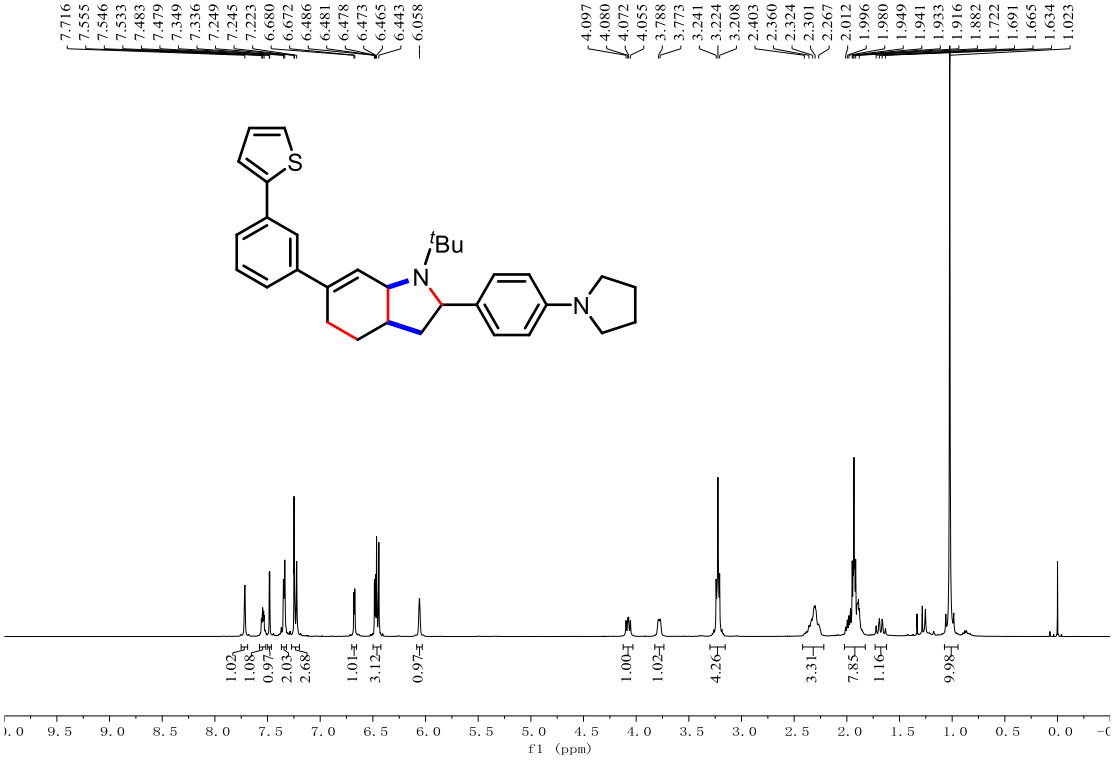
^{1}H NMR spectrum of *cis*-6ga (400 MHz, $CDCl_3$)



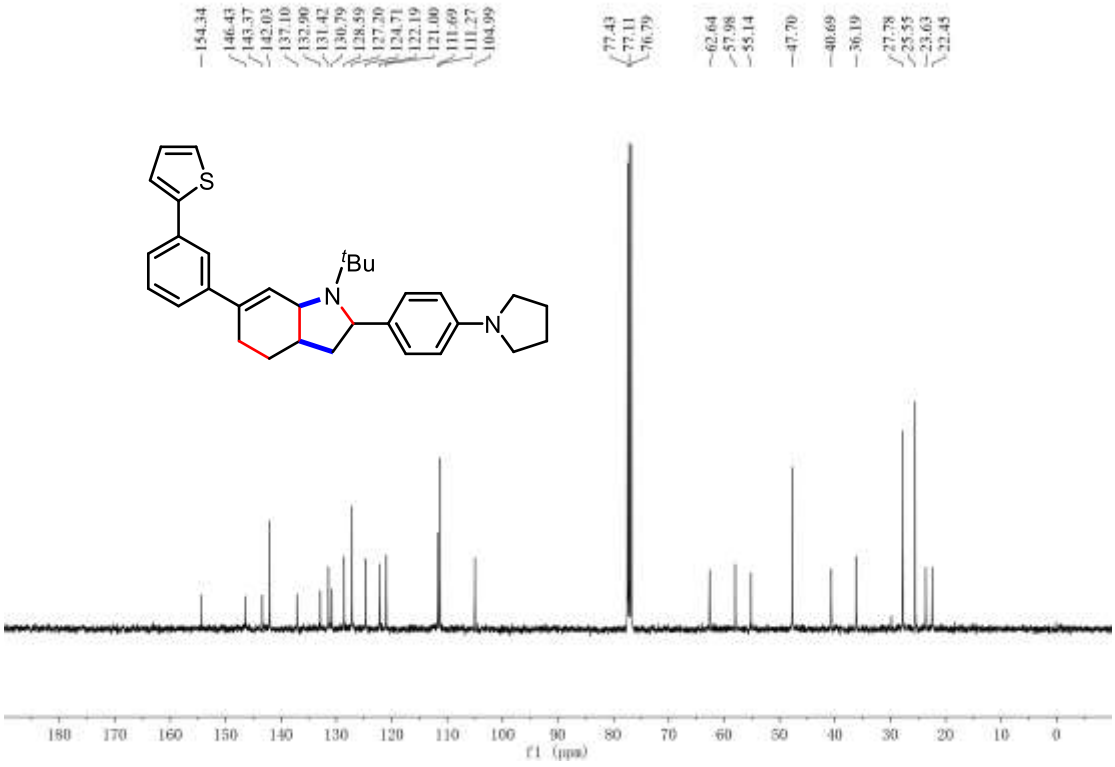
^{13}C NMR spectrum of *cis*-6ga (101 MHz, $CDCl_3$)



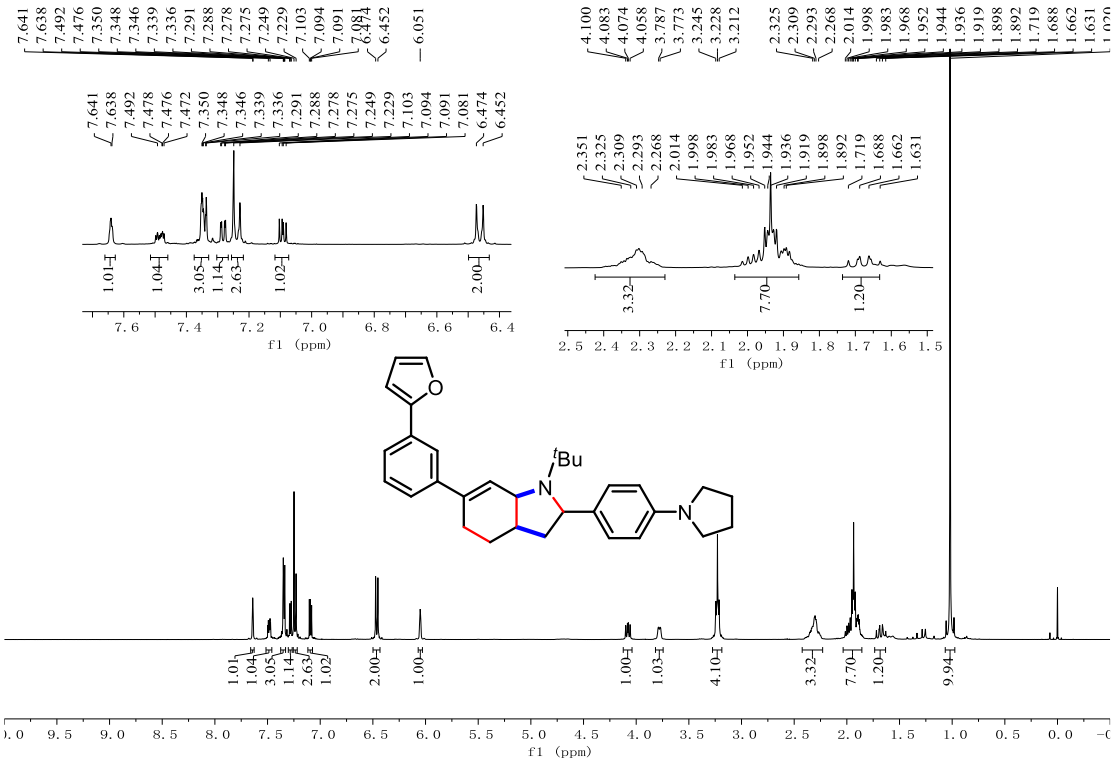
^{1}H NMR spectrum of *cis*-6ha (400 MHz, $CDCl_3$)



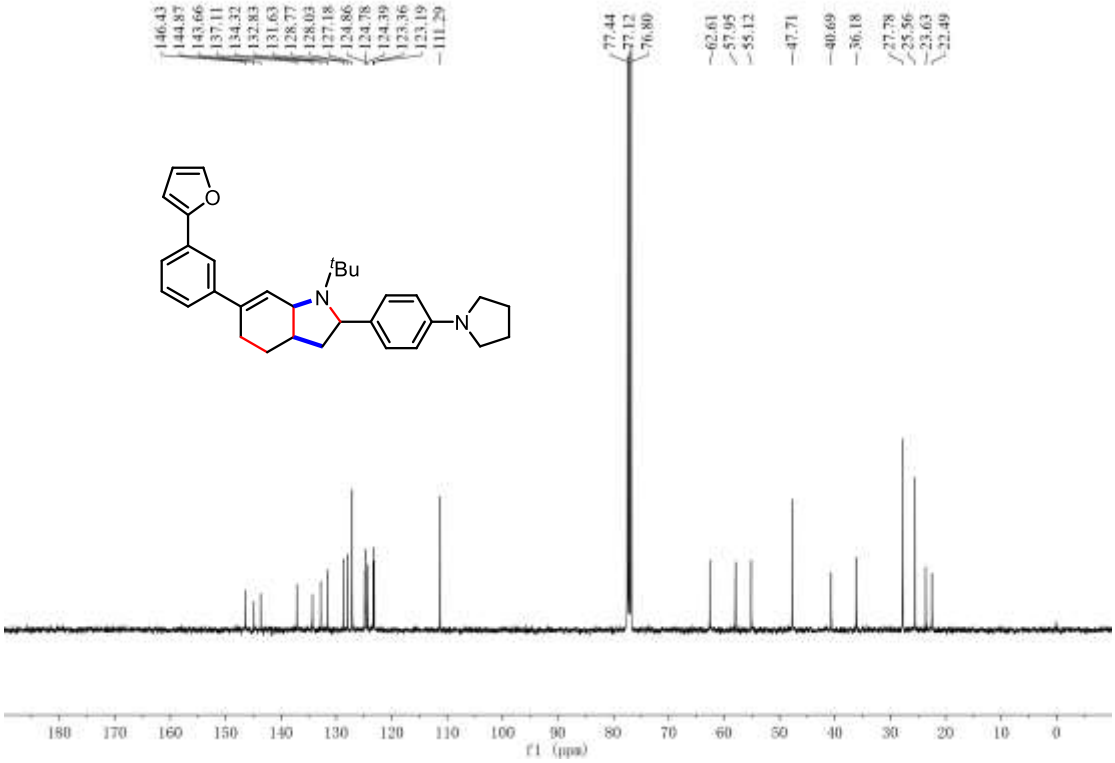
^{13}C NMR spectrum of *cis*-6ha (101 MHz, $CDCl_3$)



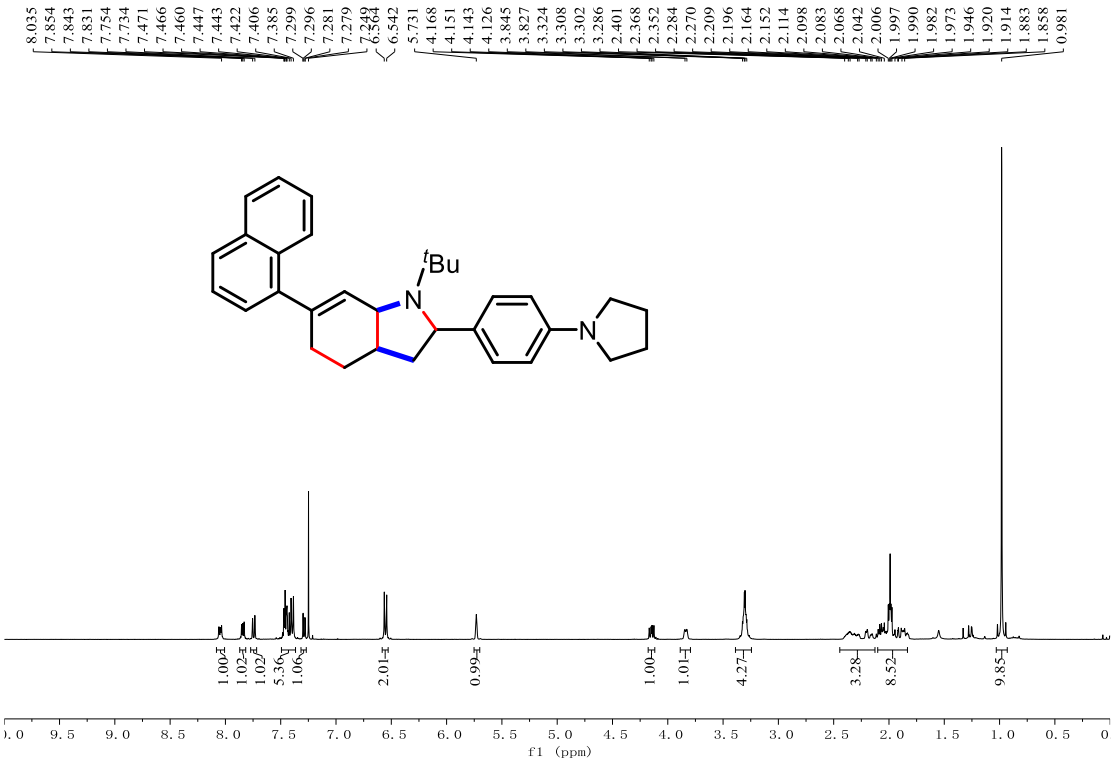
^{1}H NMR spectrum of *cis*-6ia (400 MHz, $CDCl_3$)



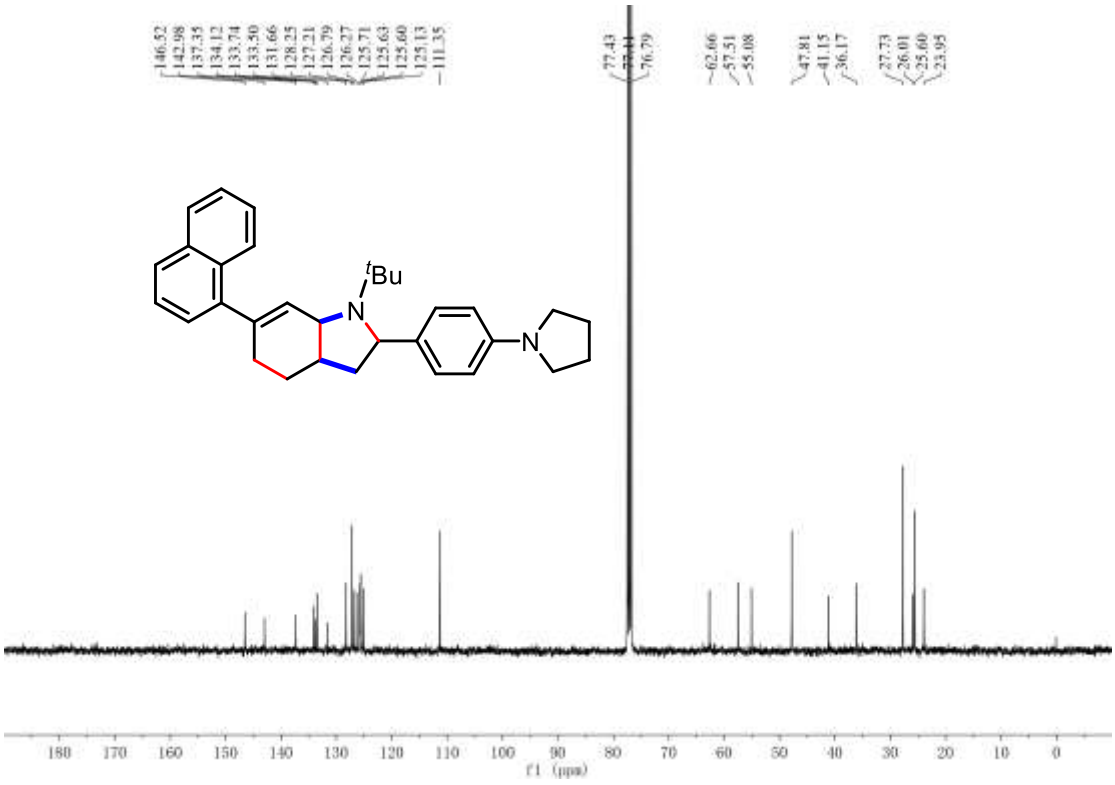
^{13}C NMR spectrum of *cis*-6ia (101 MHz, $CDCl_3$)



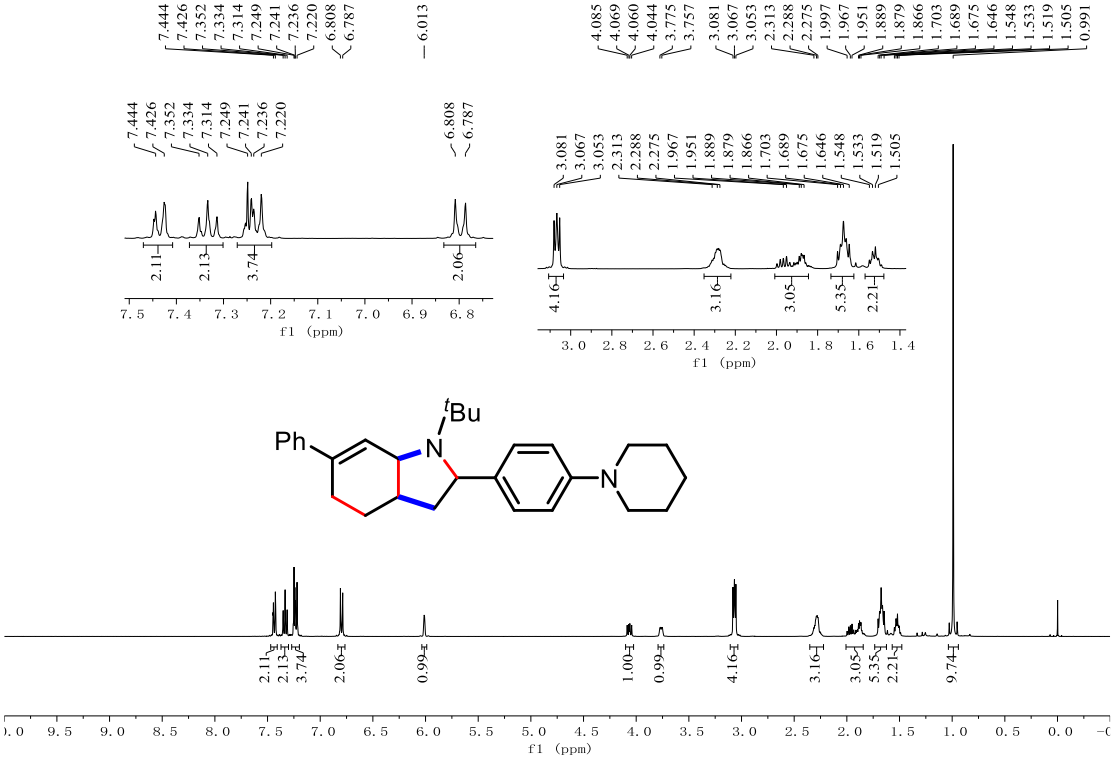
^{1}H NMR spectrum of *cis*-6ja (400 MHz, $CDCl_3$)



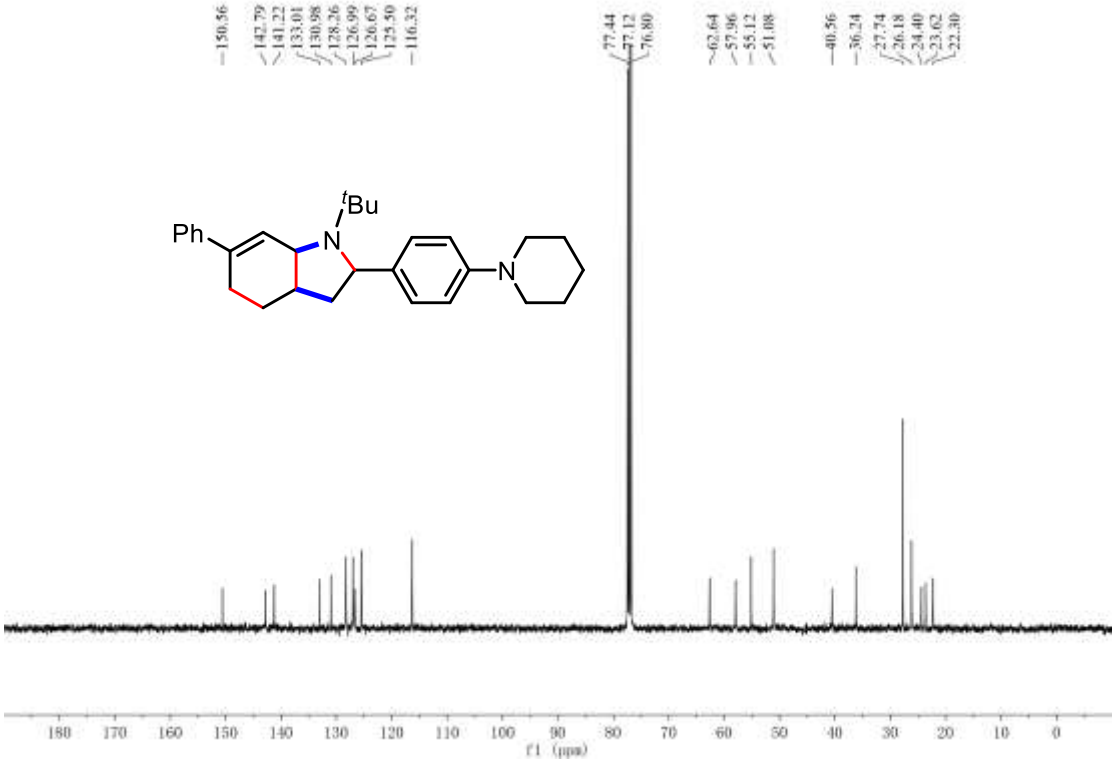
^{13}C NMR spectrum of *cis*-6ja (101 MHz, $CDCl_3$)



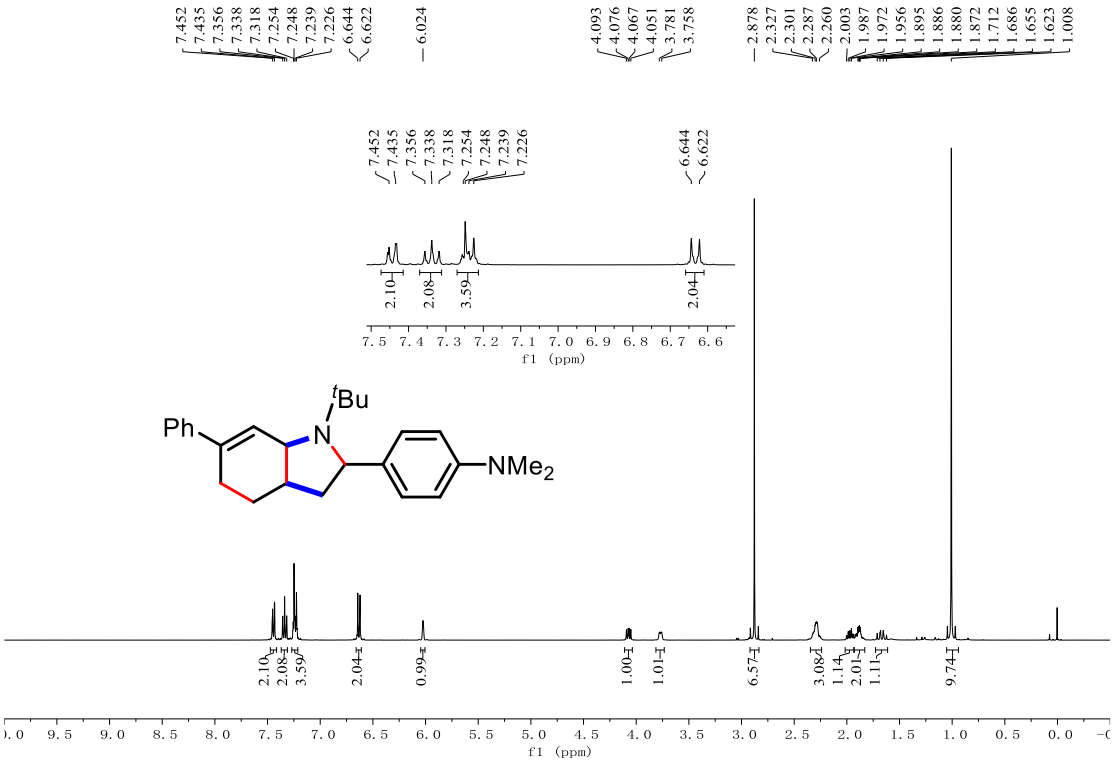
^{1}H NMR spectrum of *cis*-6ab (400 MHz, $CDCl_3$)



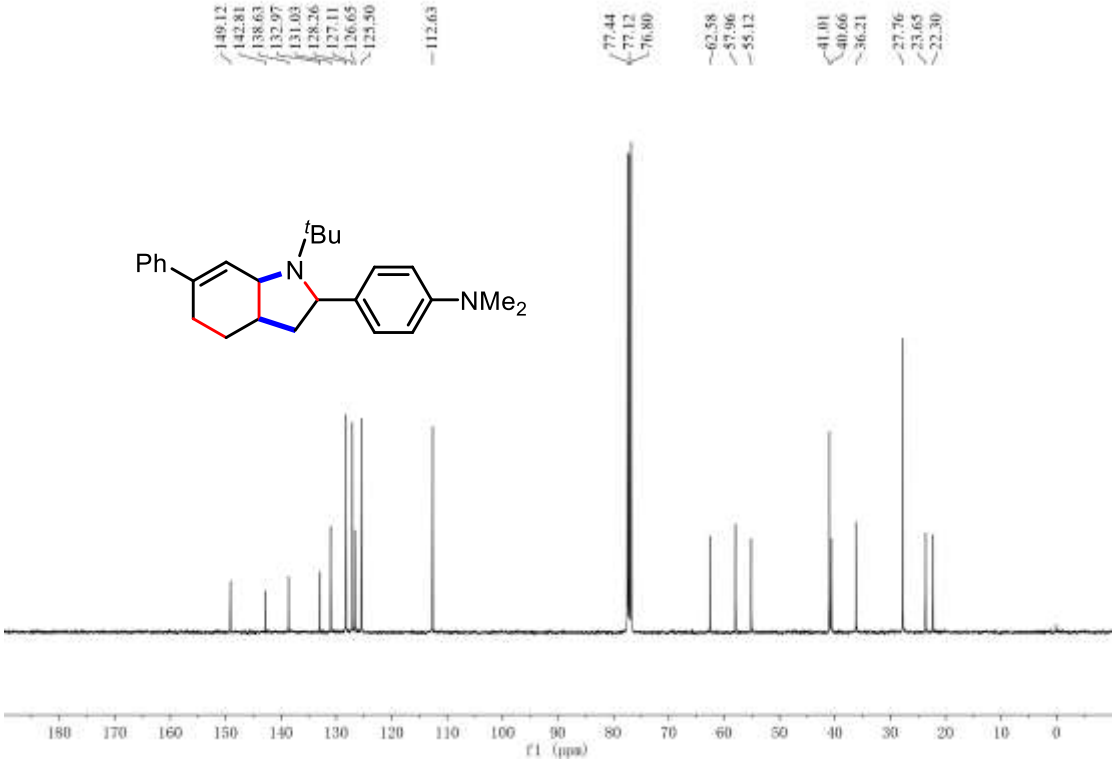
^{13}C NMR spectrum of *cis*-6ab (101 MHz, $CDCl_3$)



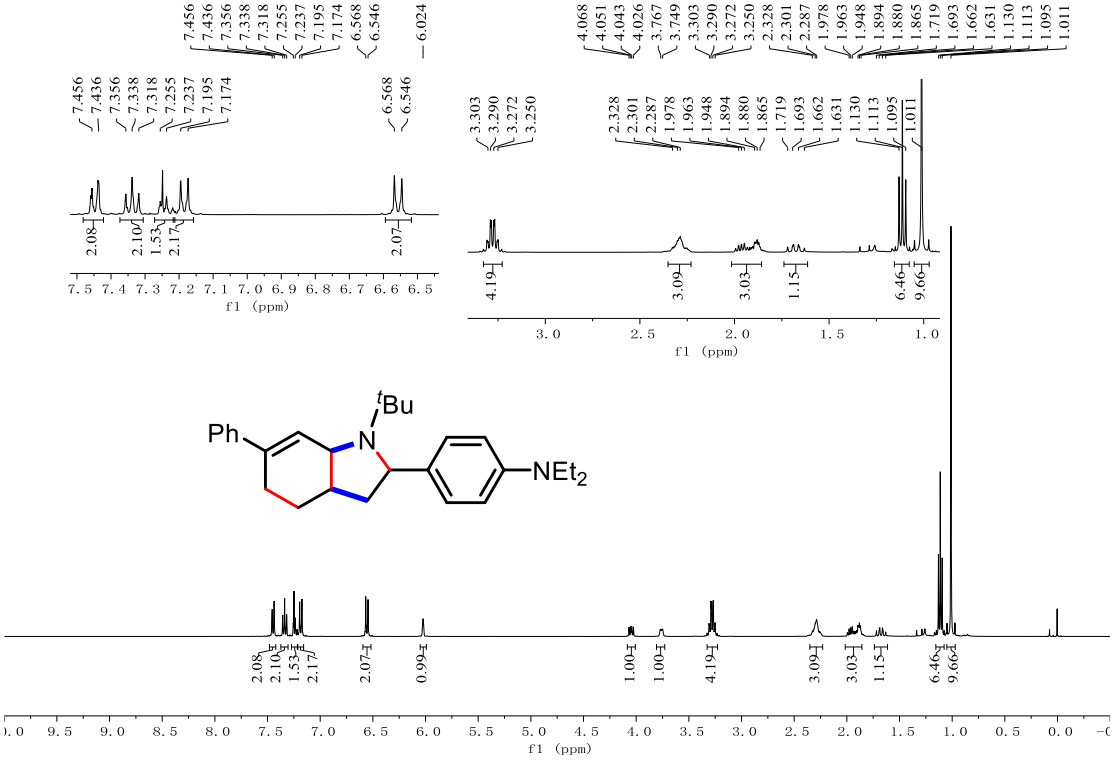
^{1}H NMR spectrum of *cis*-6ac (400 MHz, $CDCl_3$)



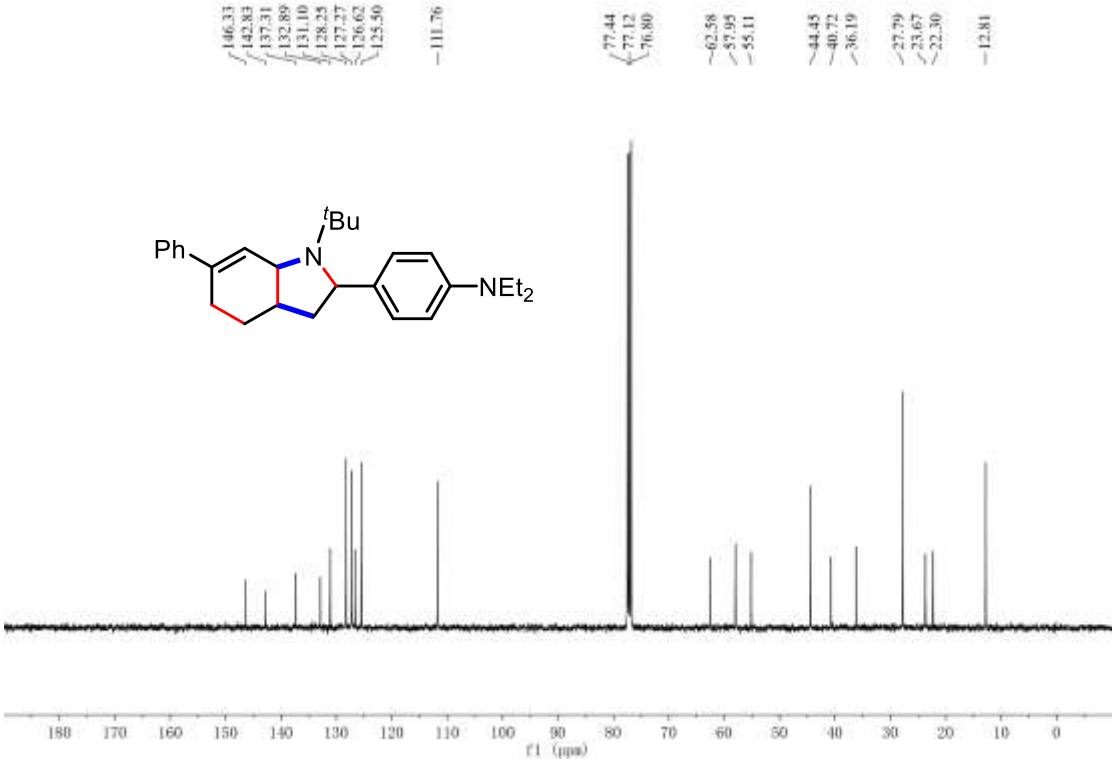
^{13}C NMR spectrum of *cis*-6ac (101 MHz, $CDCl_3$)



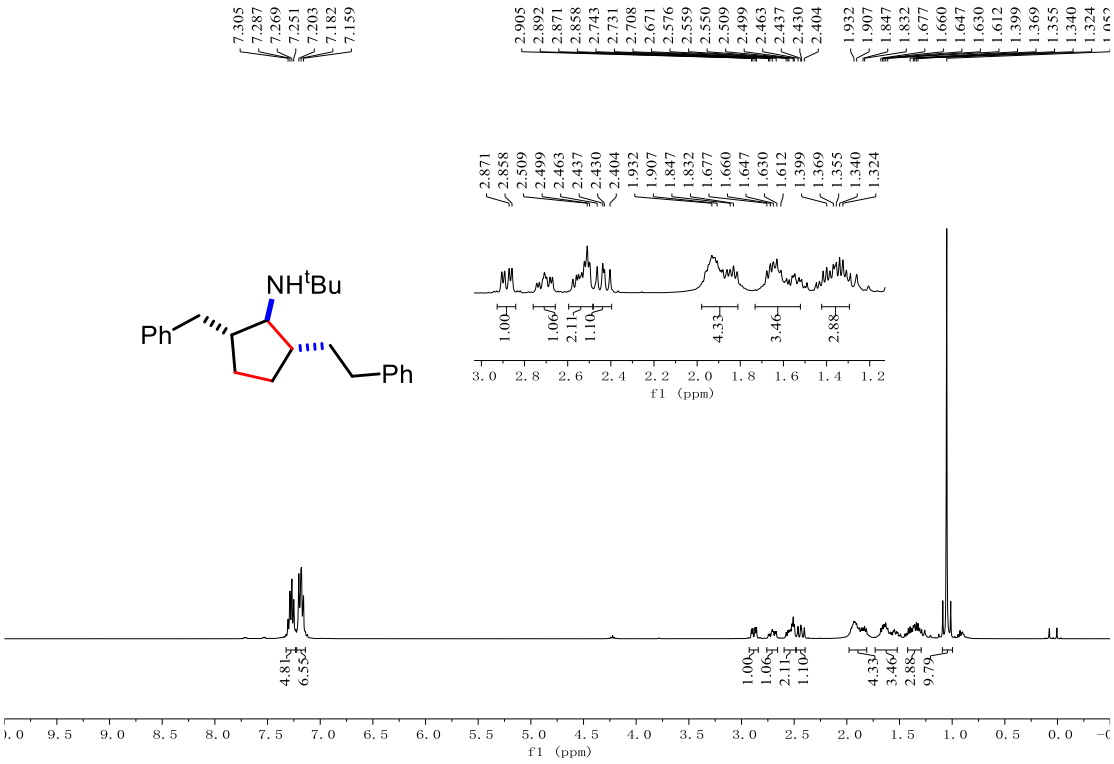
^{1}H NMR spectrum of *cis*-6ad (400 MHz, $CDCl_3$)



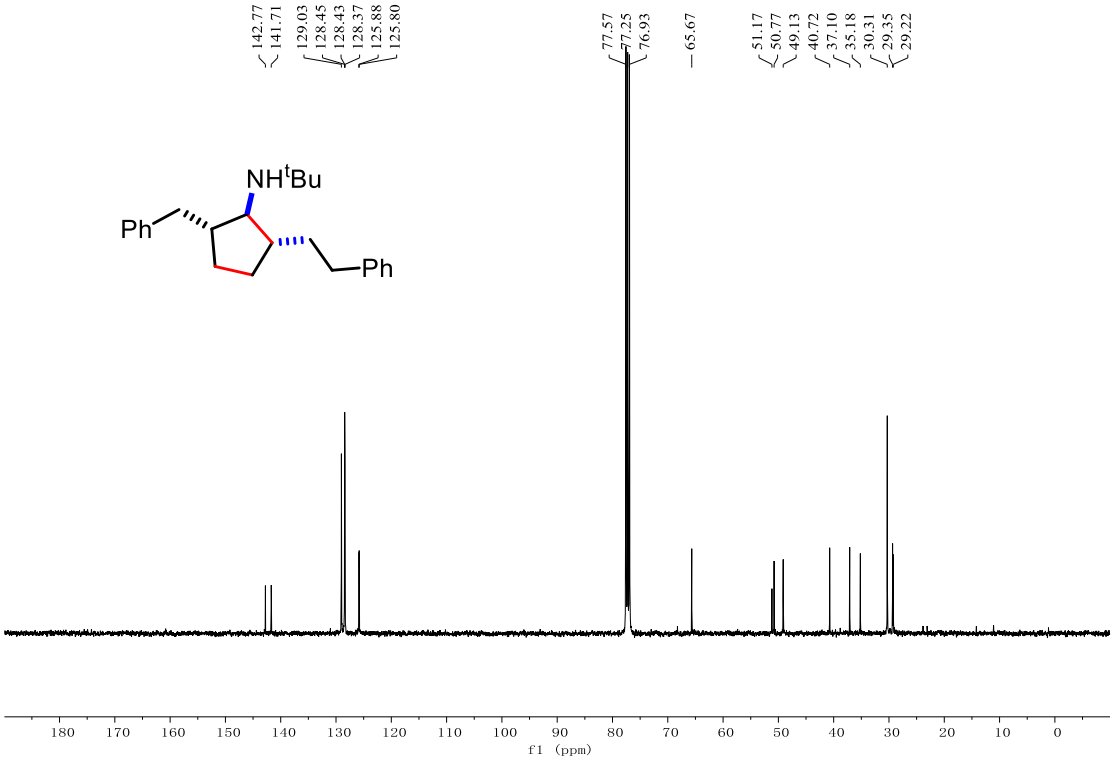
^{13}C NMR spectrum of *cis*-6ad (101 MHz, $CDCl_3$)



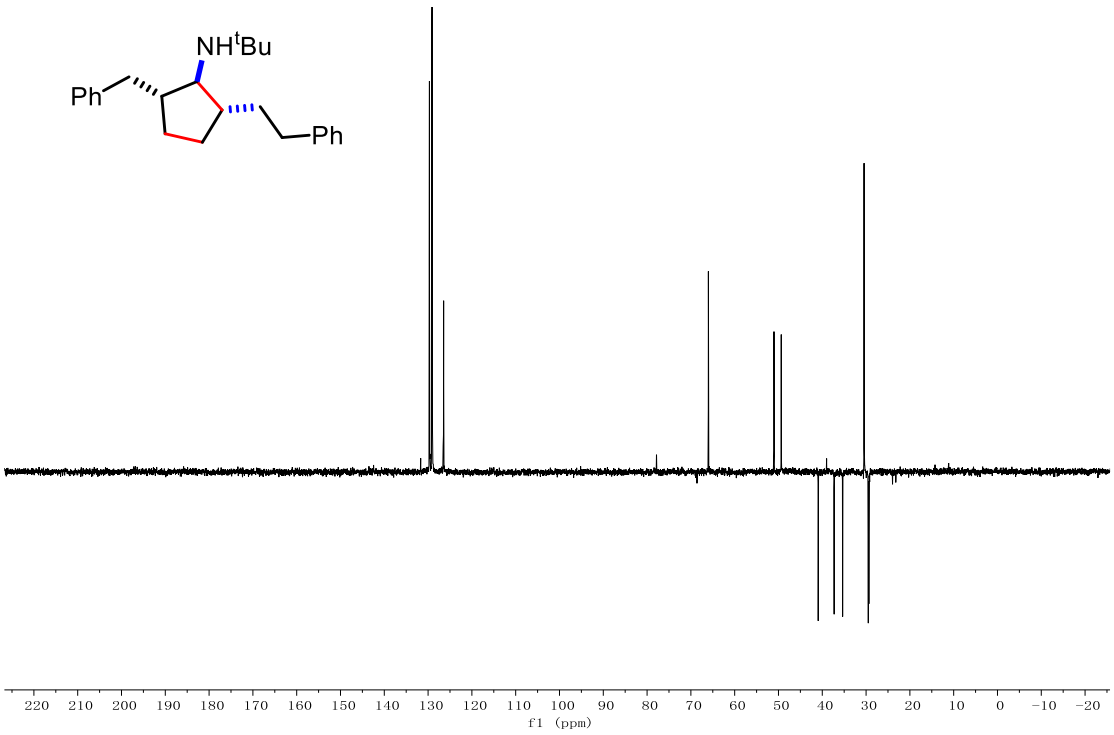
^{1}H NMR spectrum of 7aa (400 MHz, $CDCl_3$)



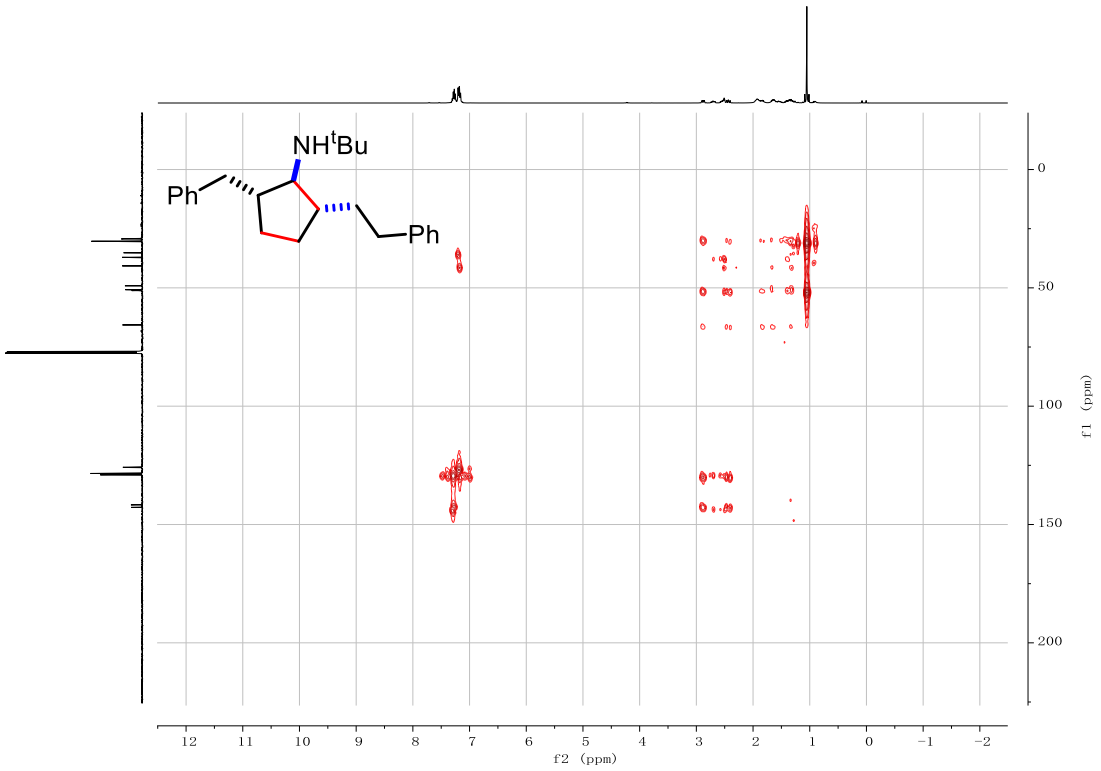
^{13}C NMR spectrum of 7aa (101 MHz, $CDCl_3$)



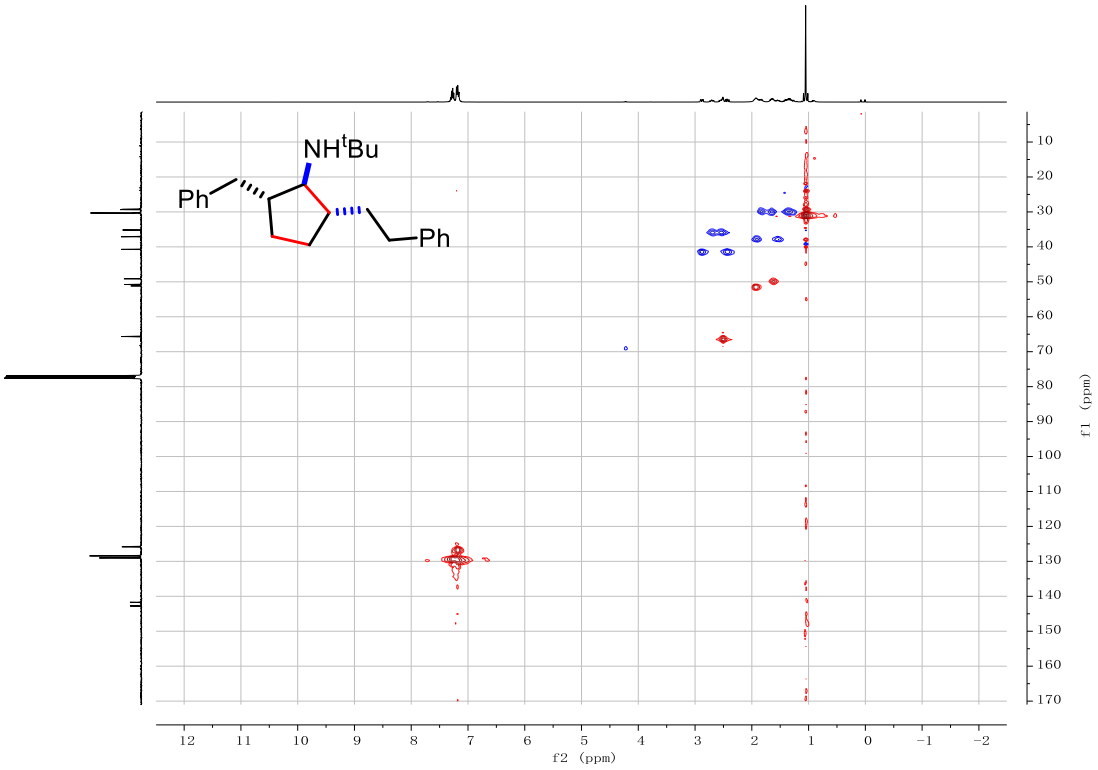
^{135}DEPT spectrum of 7aa



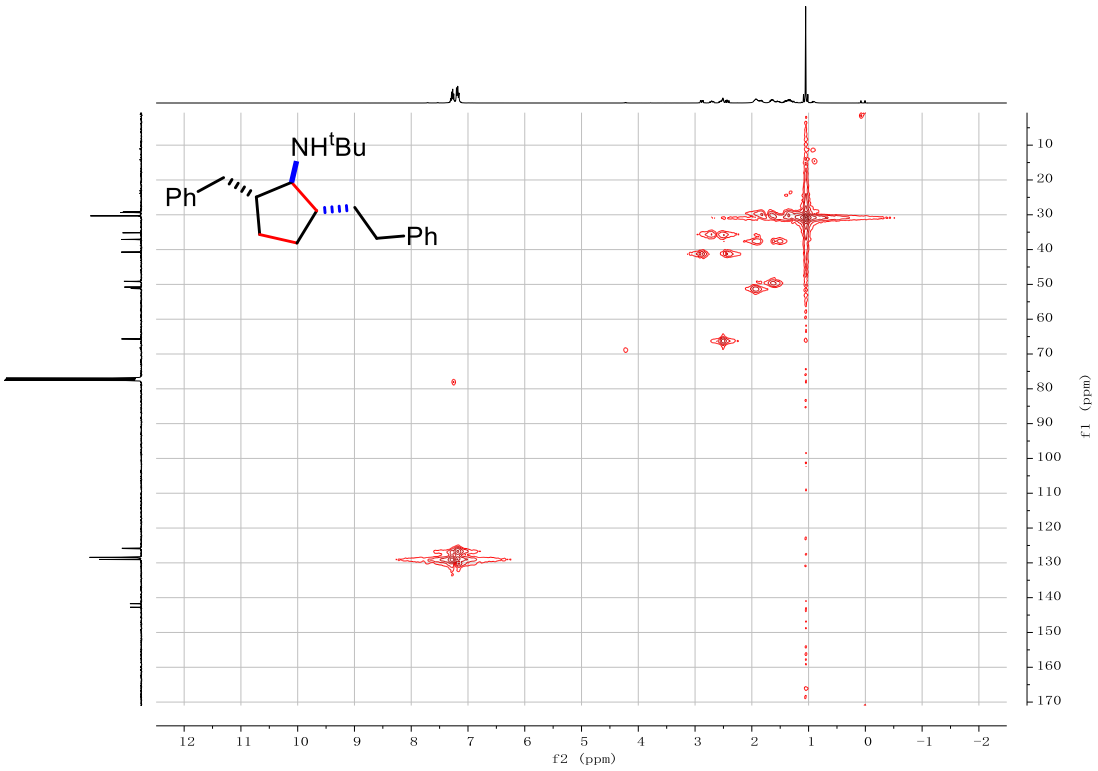
HMBC spectrum of 7aa



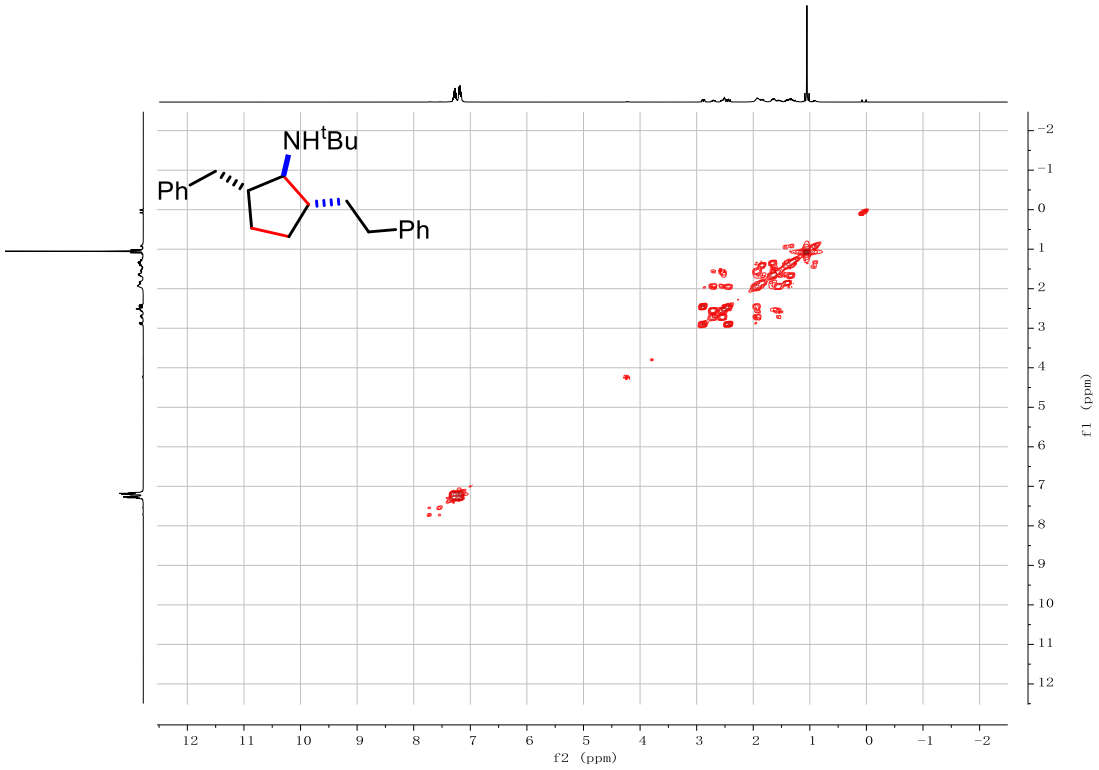
HSQC spectrum of 7aa



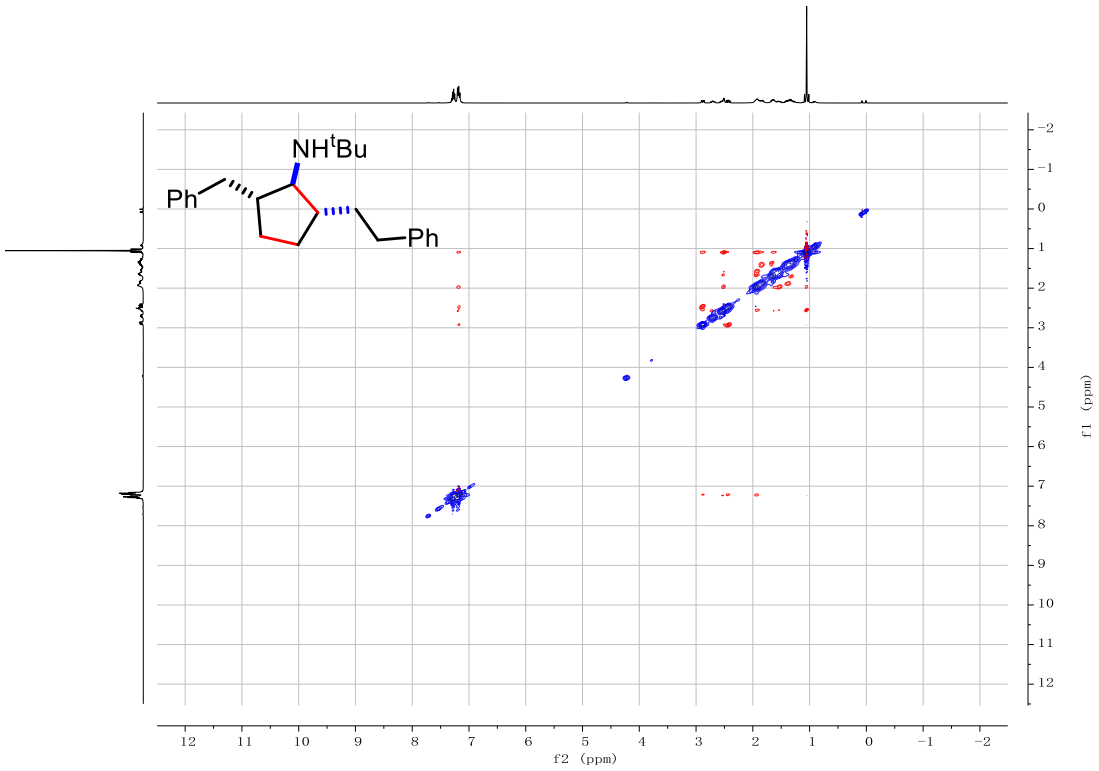
HMQC spectrum of 7aa



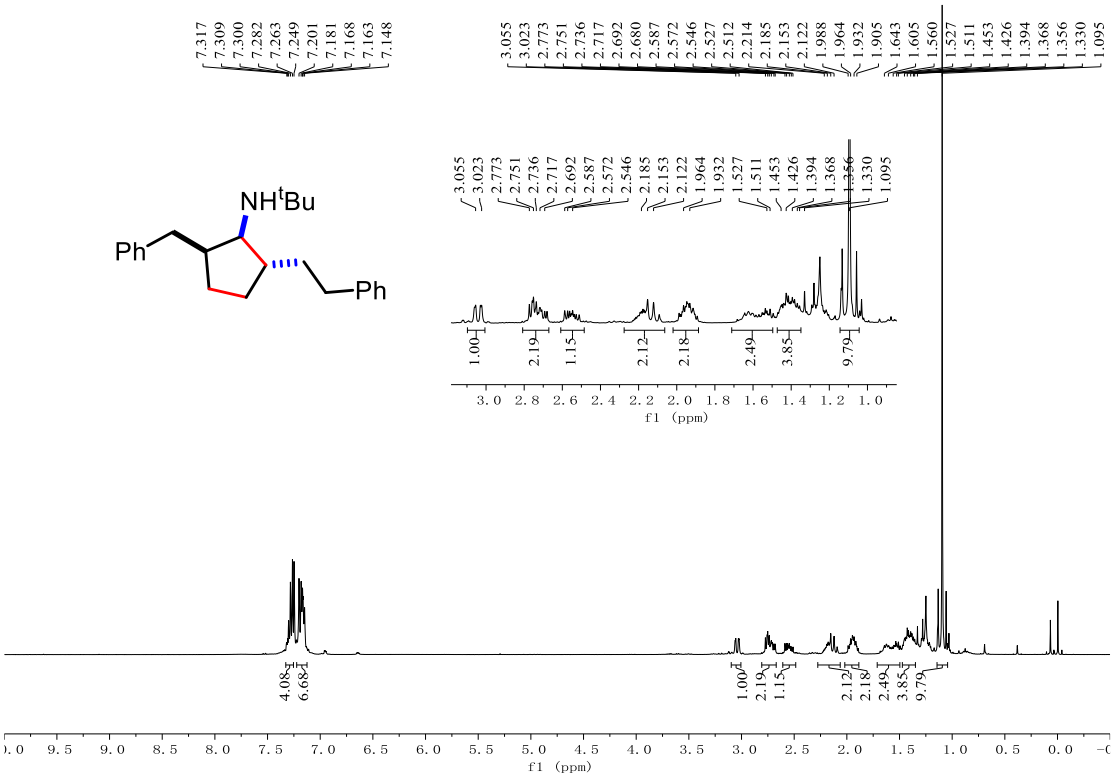
COSY NMR spectrum of 7aa



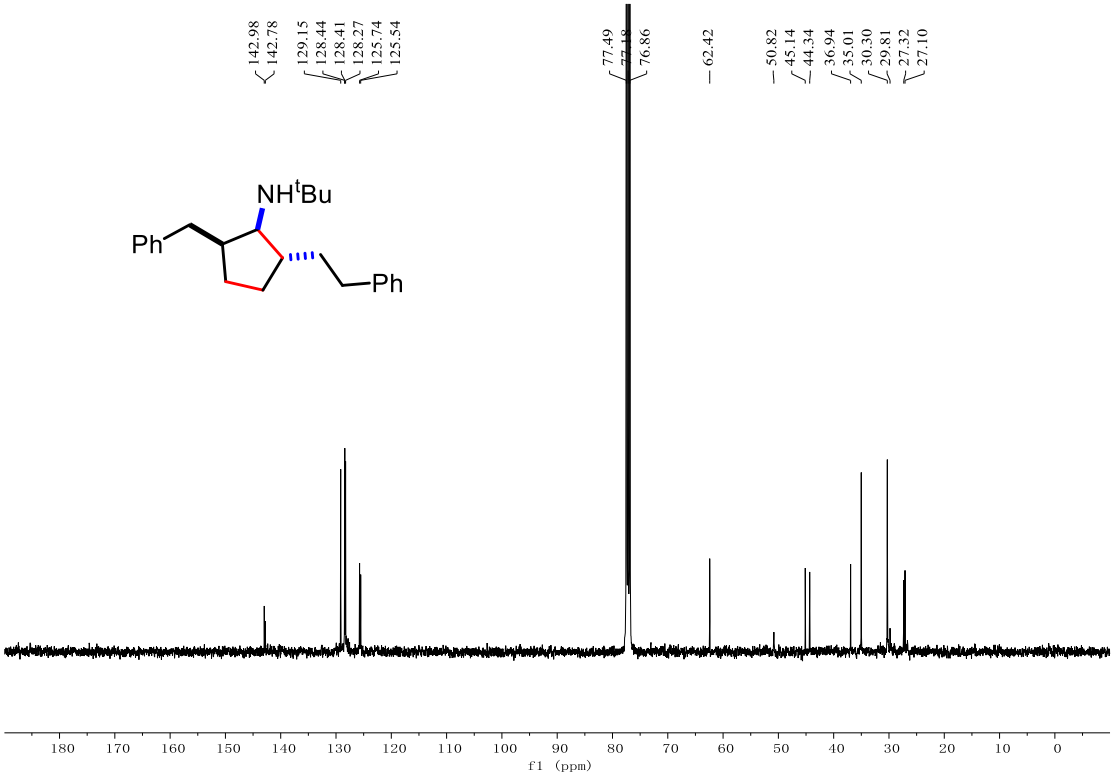
NOE spectrum of 7aa



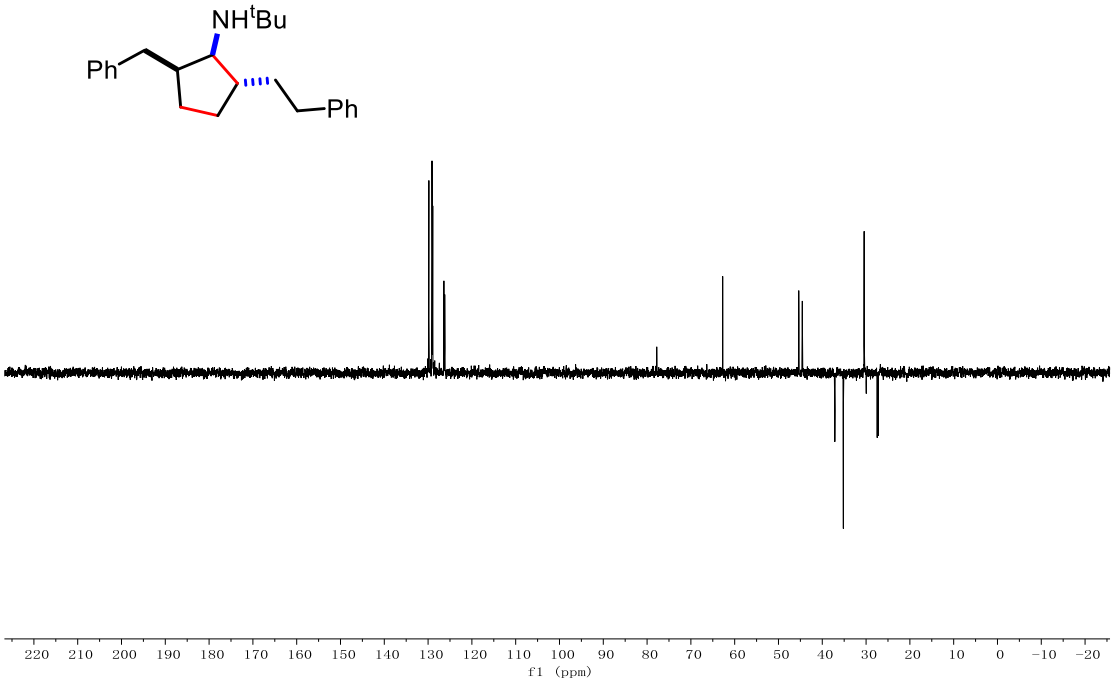
^{1}H NMR spectrum of 7aa' (400 MHz, $CDCl_3$)



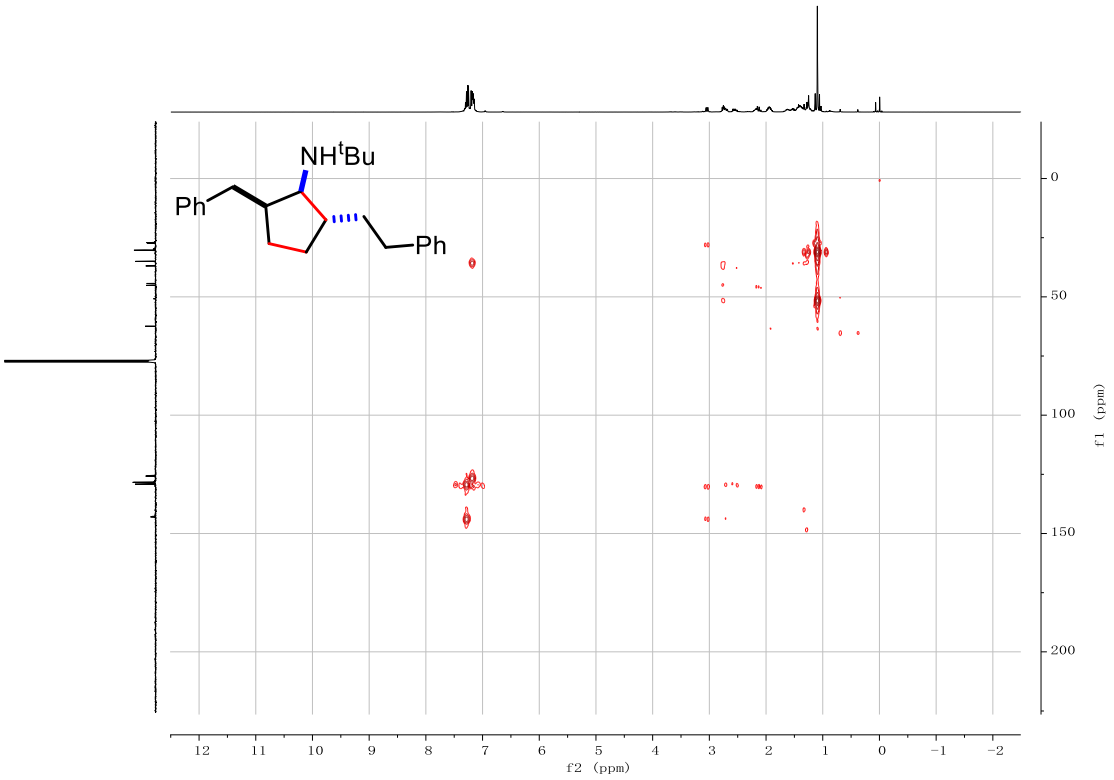
^{13}C NMR spectrum of 7aa' (101 MHz, $CDCl_3$)



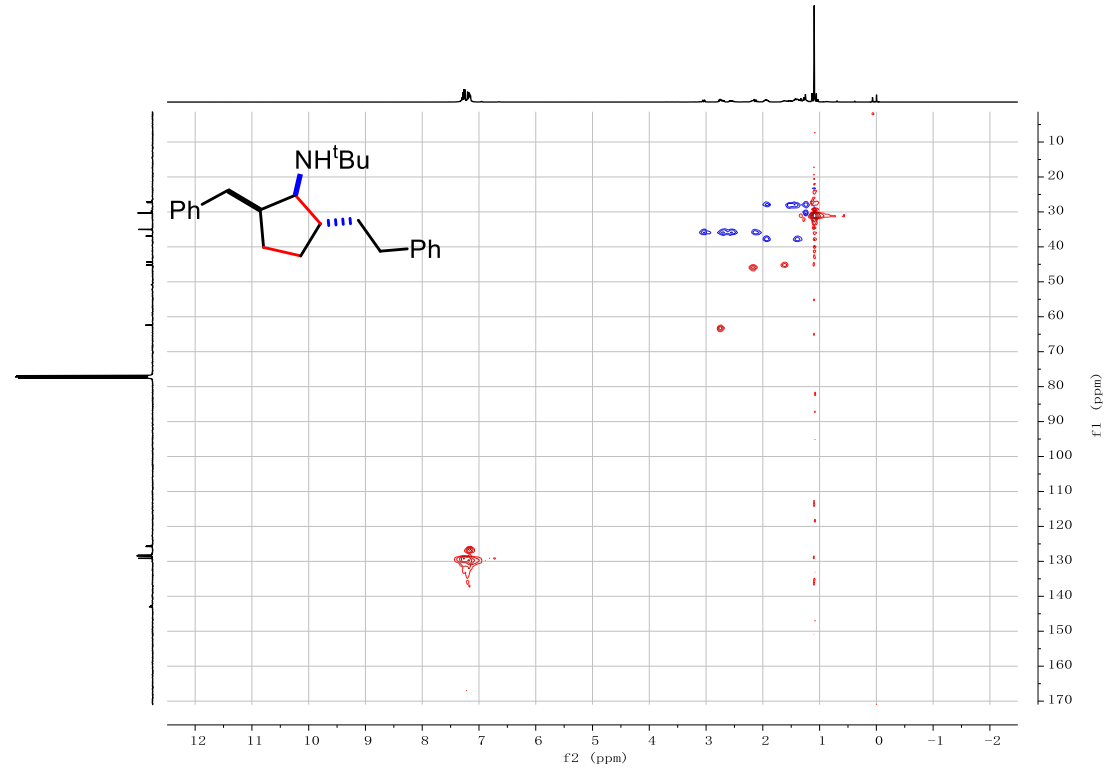
^{135}DEPT spectrum of 7aa'



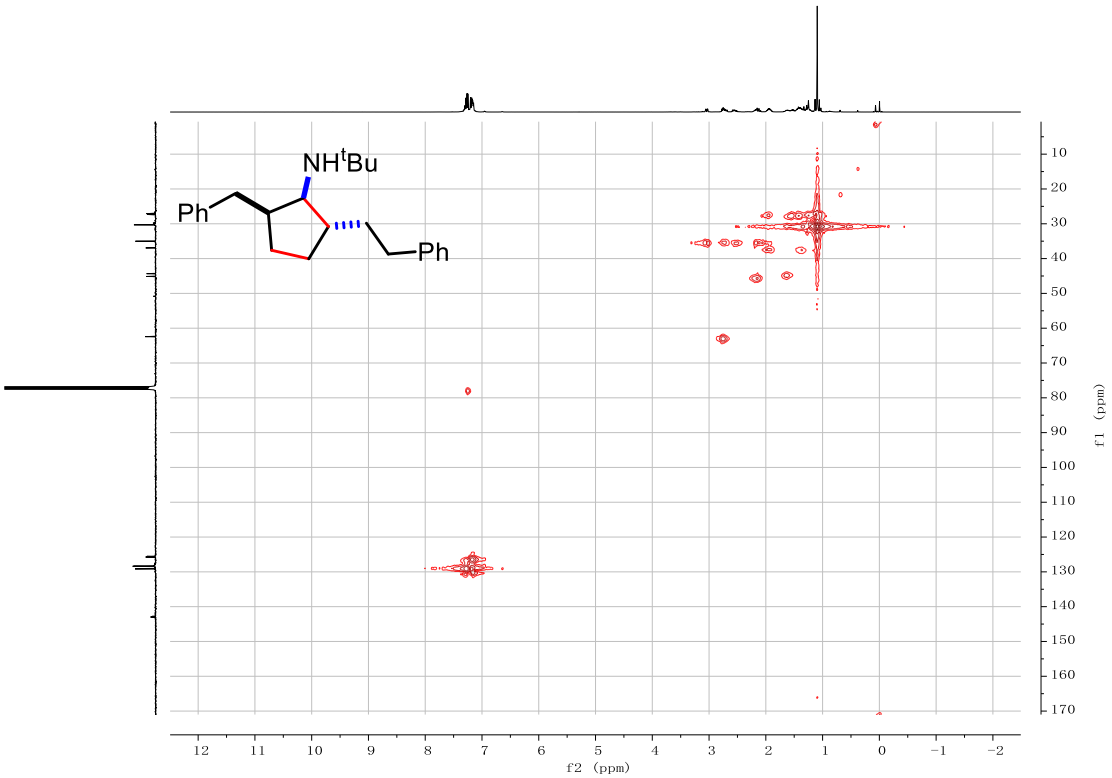
HMBC spectrum of 7aa'



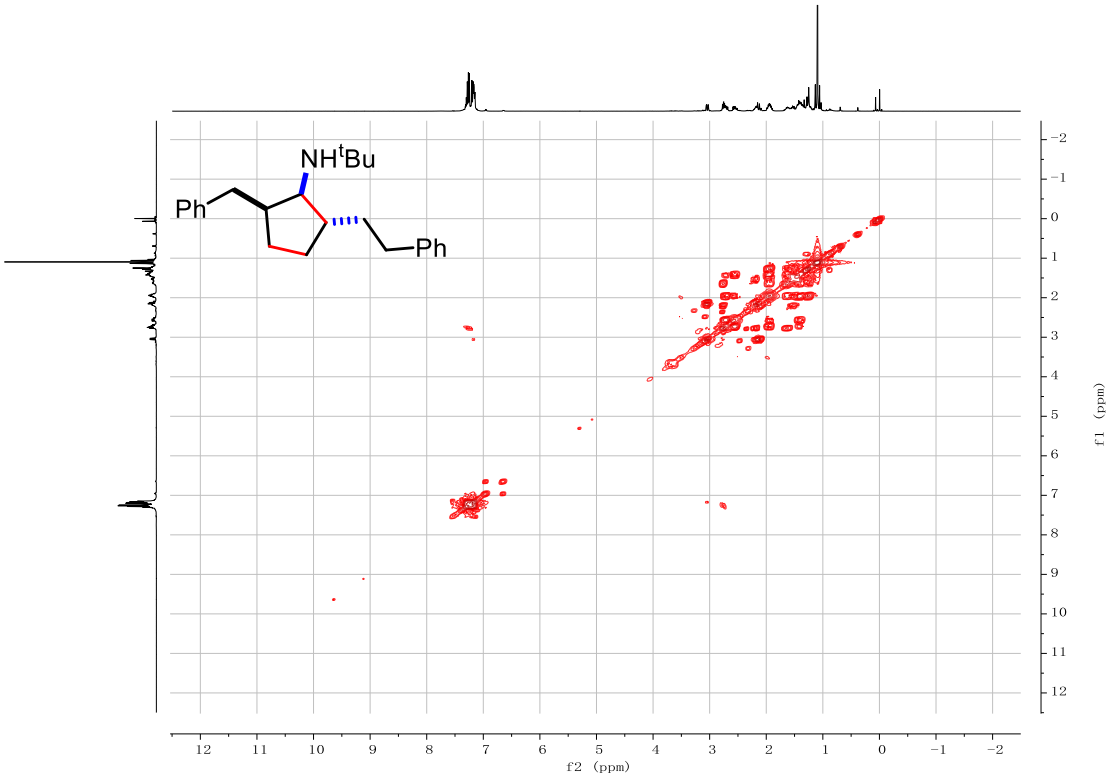
HSQC spectrum of 7aa'



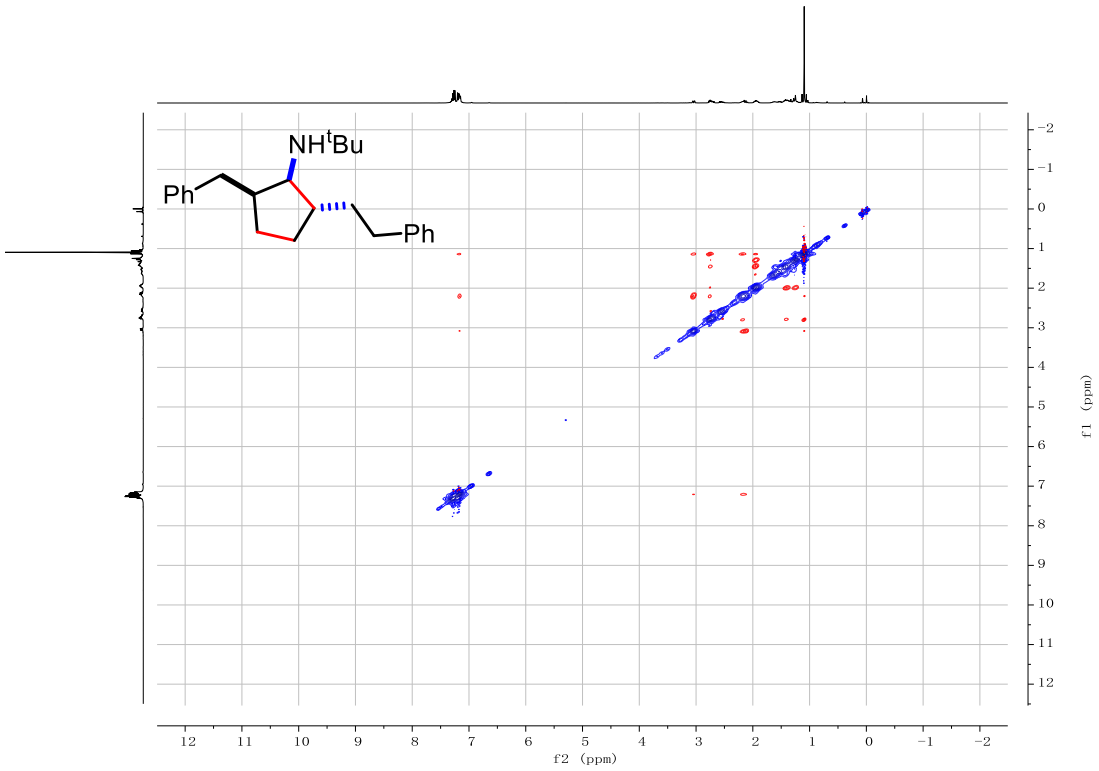
HMQC spectrum of 7aa'



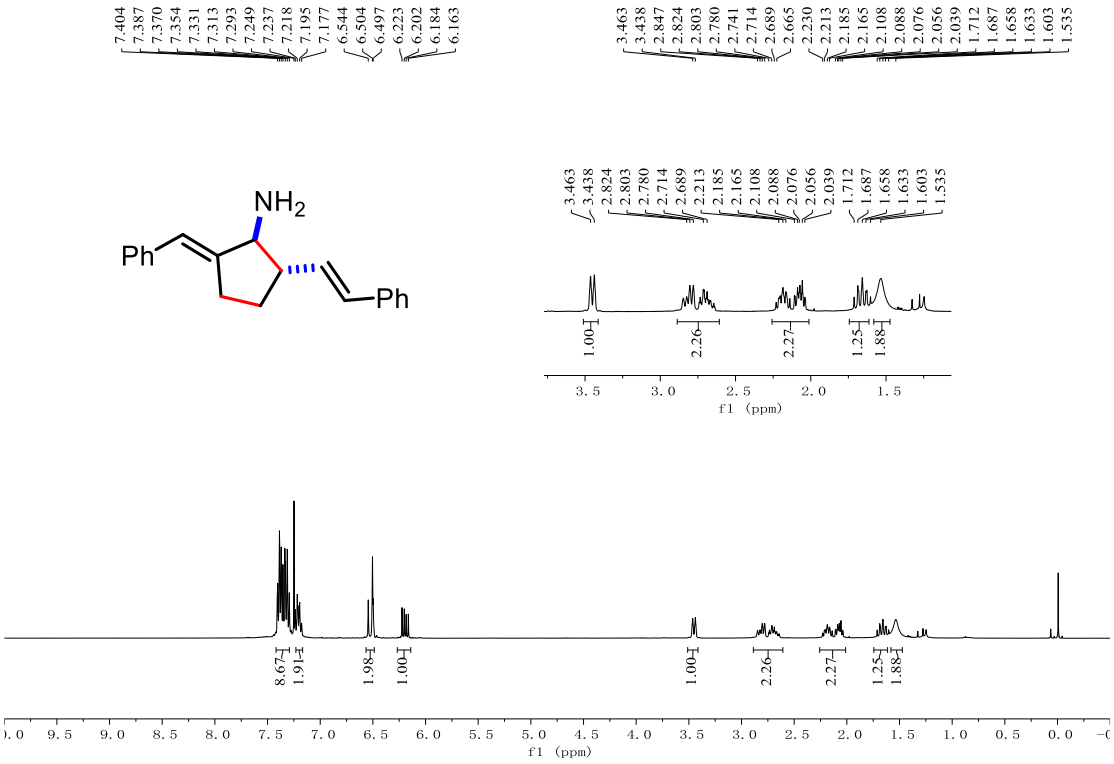
COSY spectrum of 7aa'



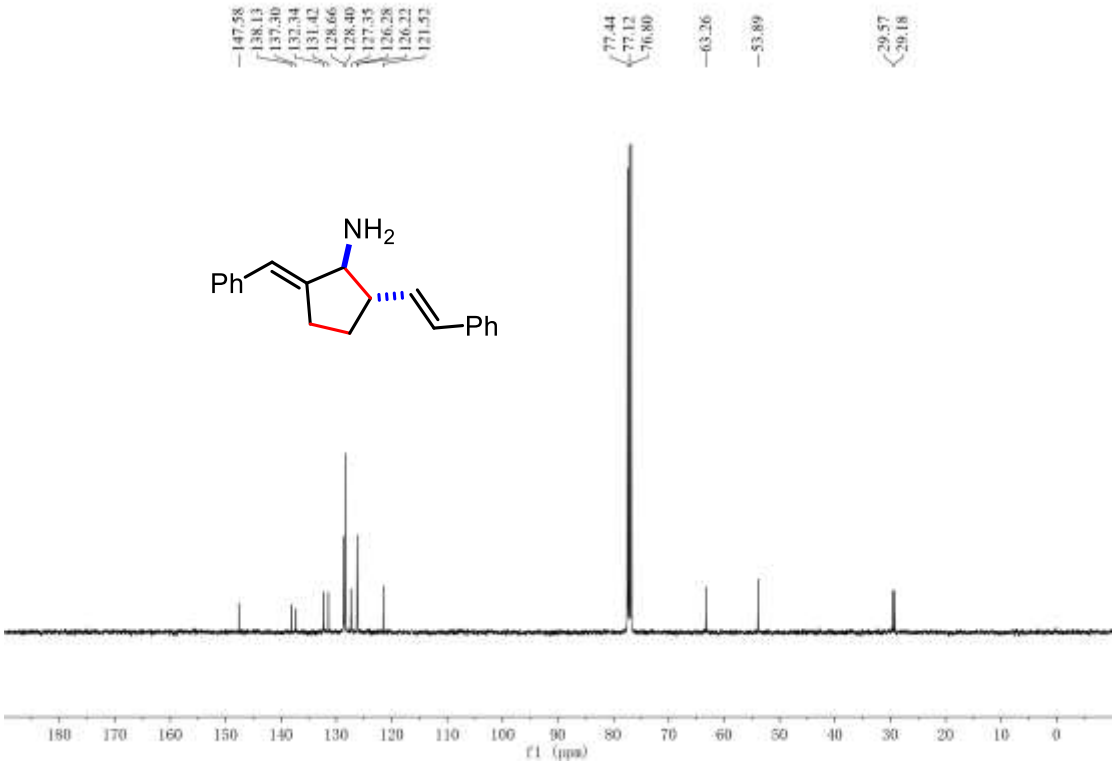
NOE spectrum of 7aa'



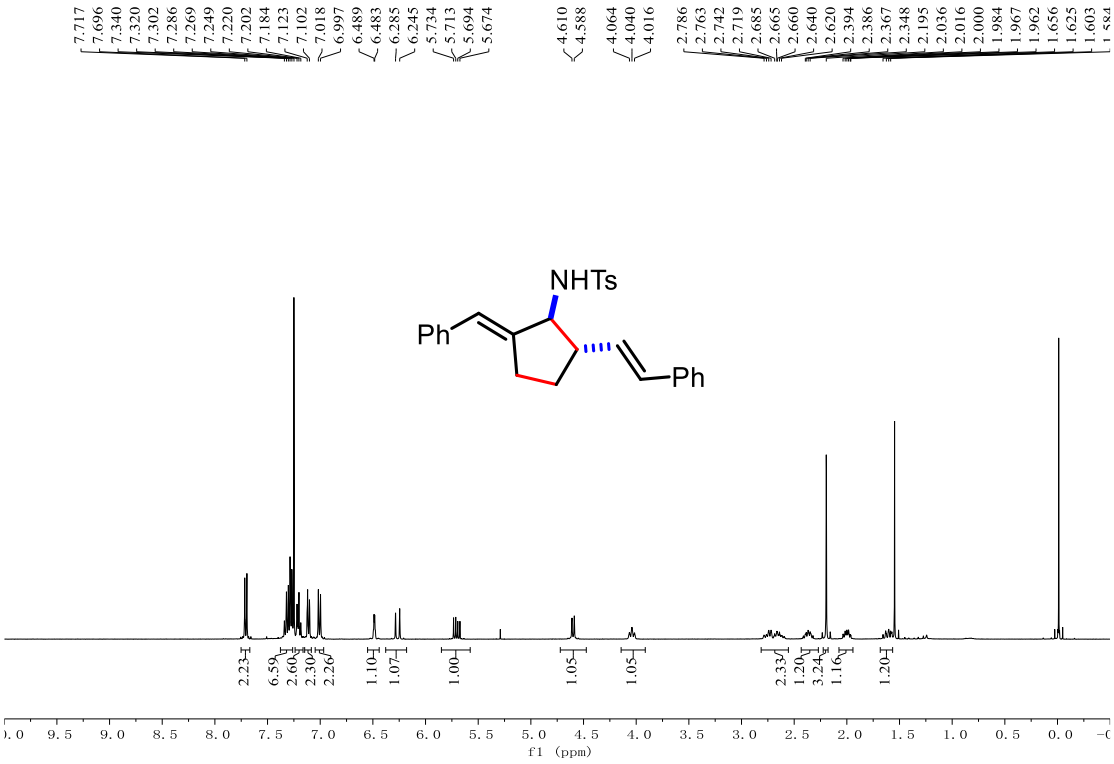
^{1}H NMR spectrum of 8aa (400 MHz, $CDCl_3$)



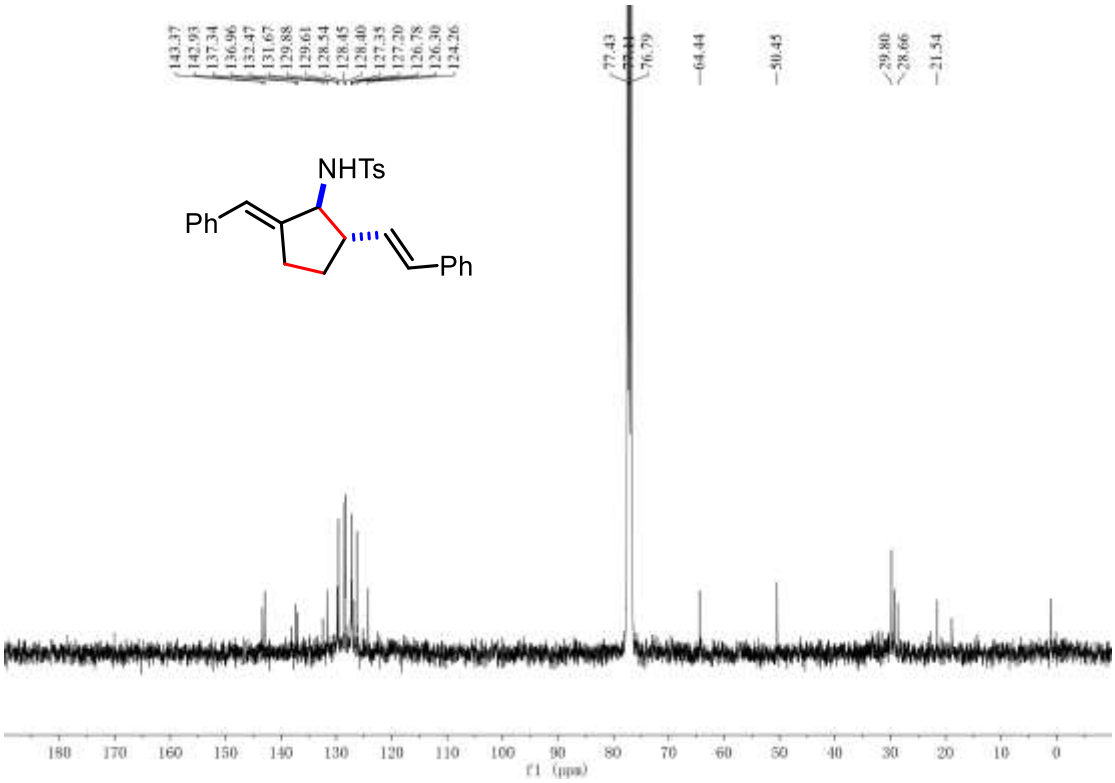
^{13}C NMR spectrum of 8aa (101 MHz, $CDCl_3$)



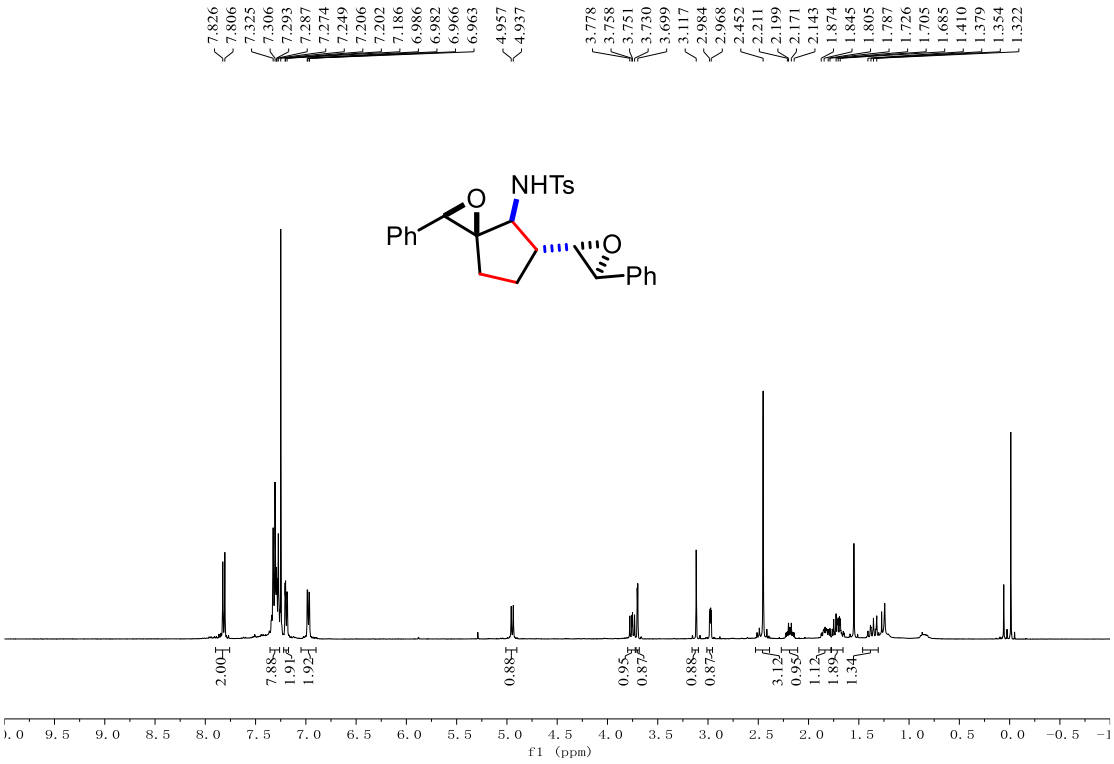
^{1}H NMR spectrum of 9aa (400 MHz, $CDCl_3$)



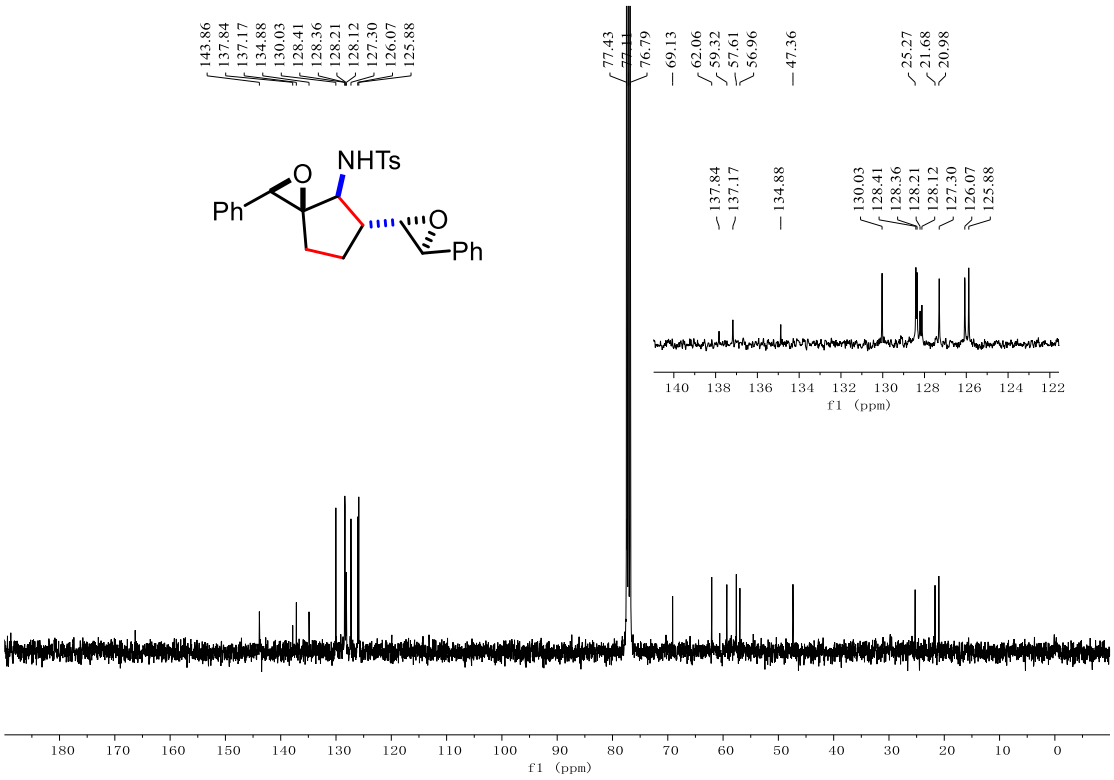
^{13}C NMR spectrum of 9aa (101 MHz, $CDCl_3$)



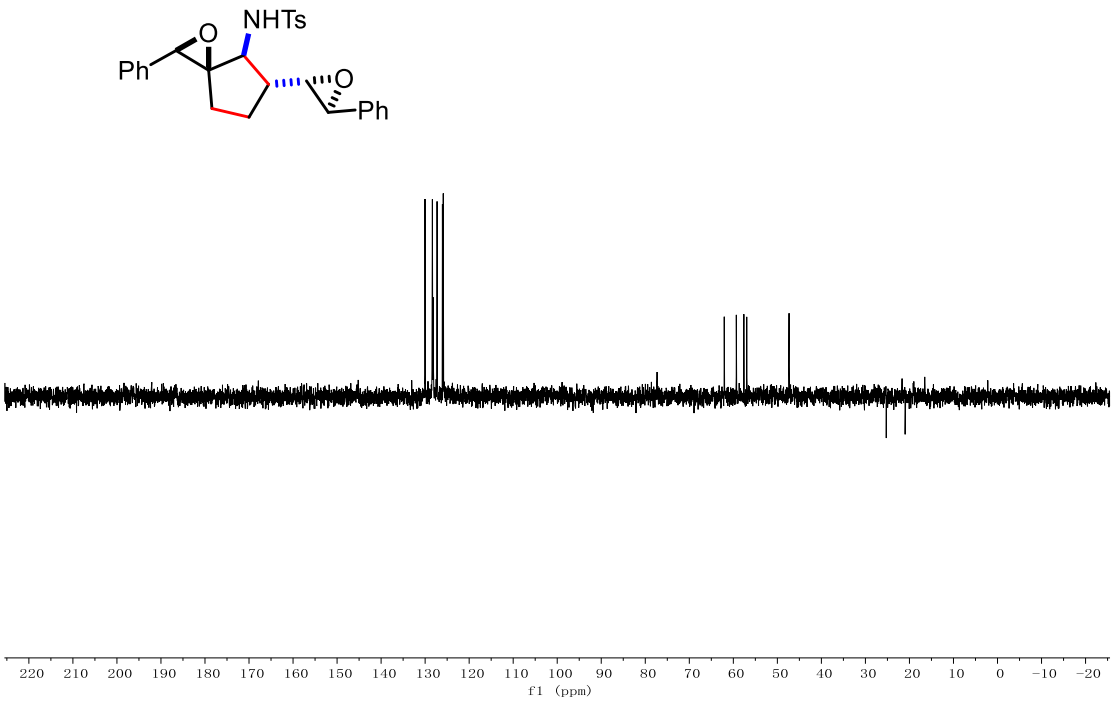
^{1}H NMR spectrum of 10aa (400 MHz, $CDCl_3$)



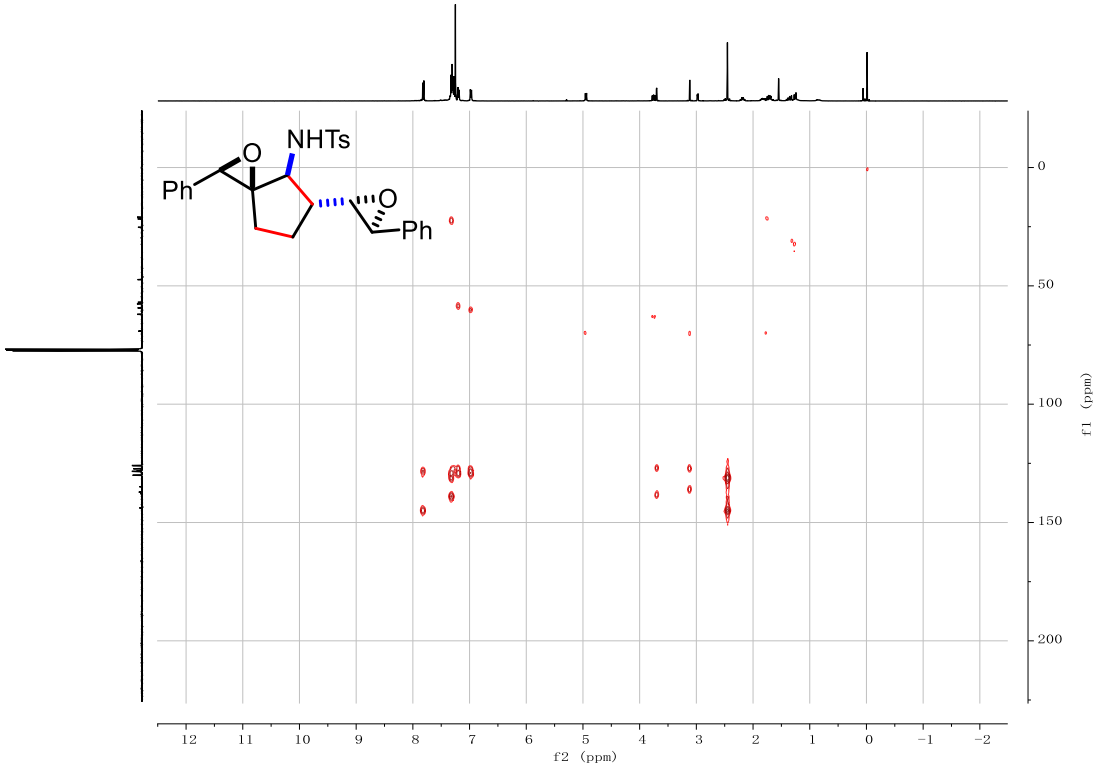
^{13}C NMR spectrum of 10aa (101 MHz, $CDCl_3$)



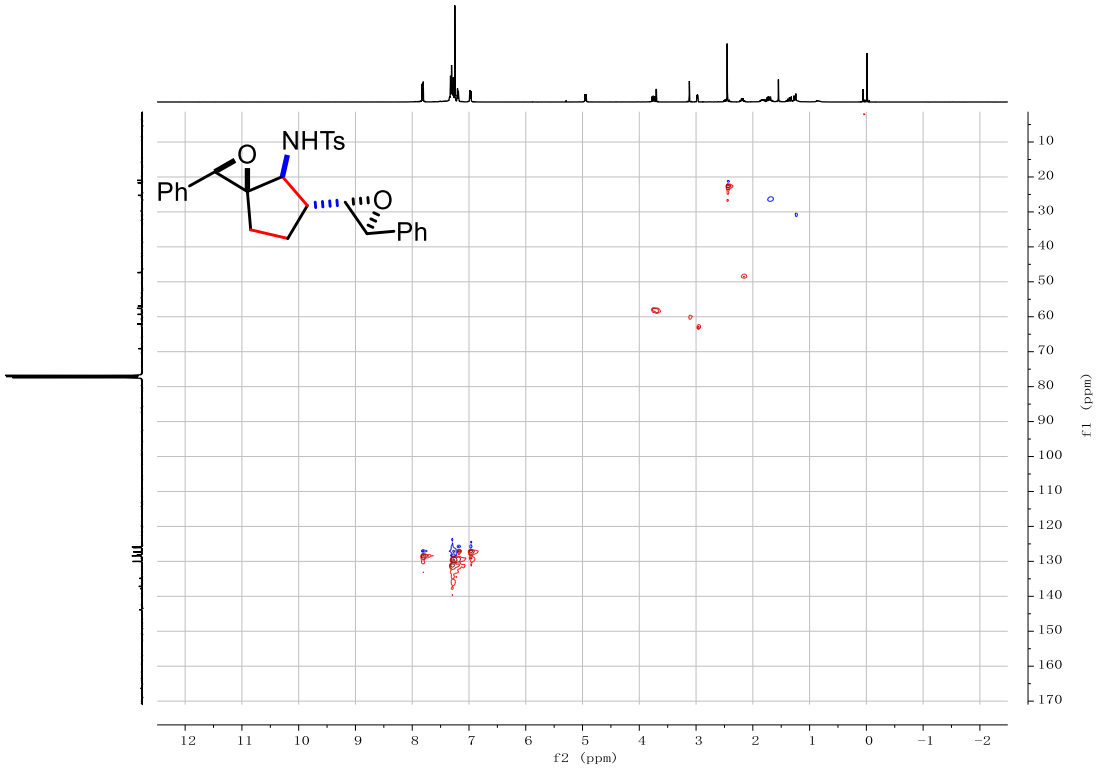
^{135}DEPT spectrum of 10aa



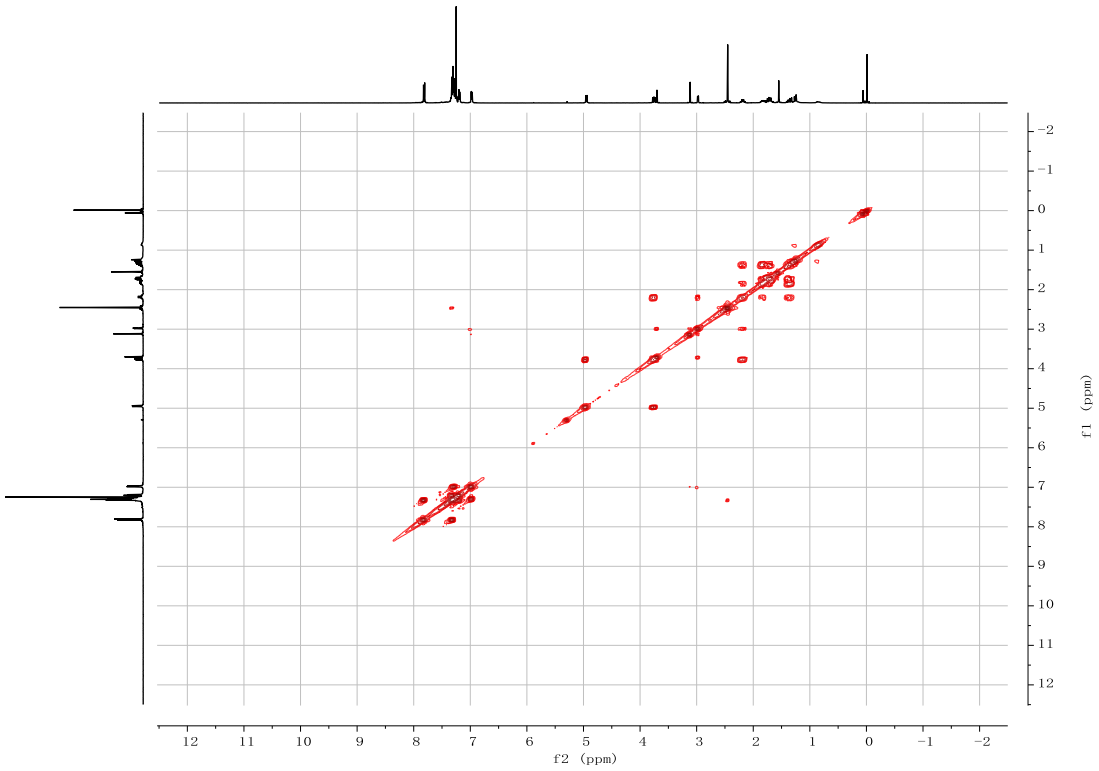
HMBC spectrum of 10aa



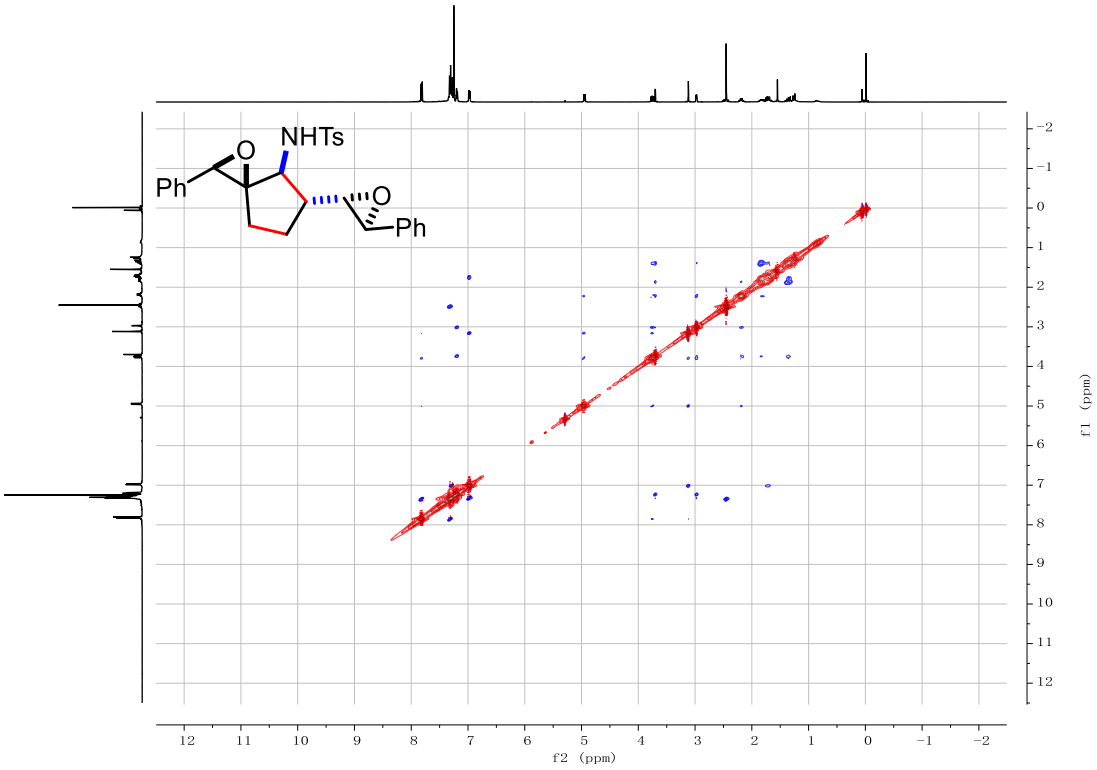
HSQC spectrum of 10aa



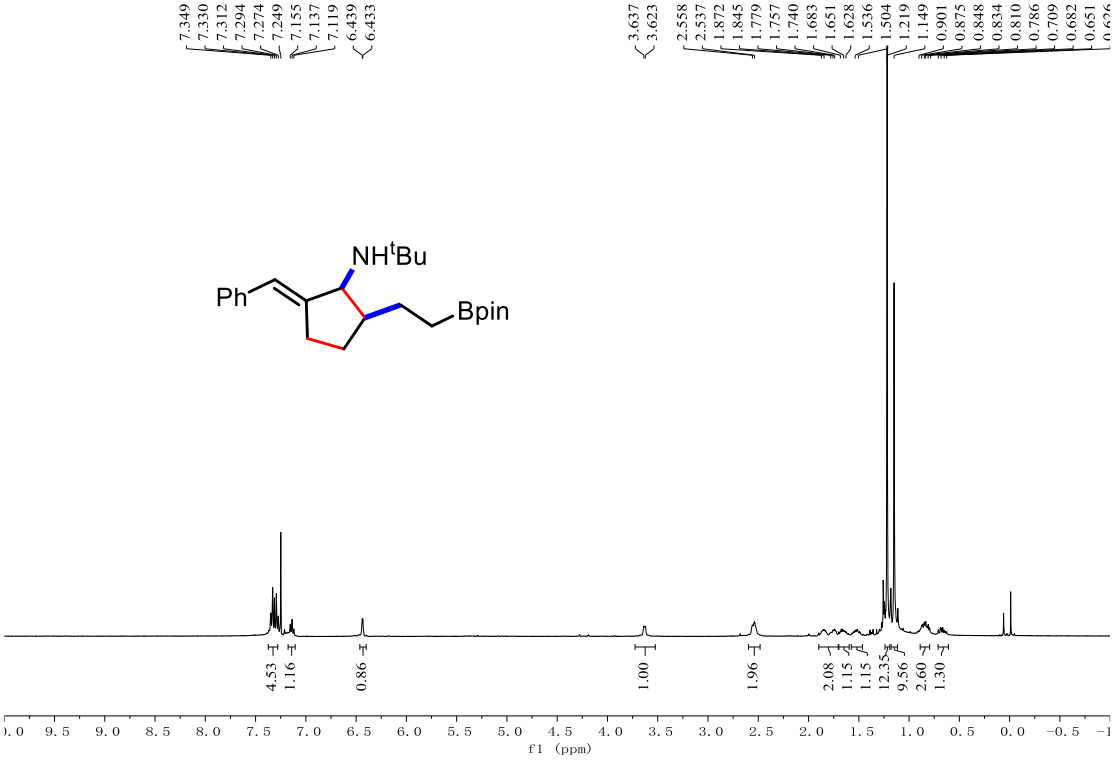
COSY spectrum of 10aa



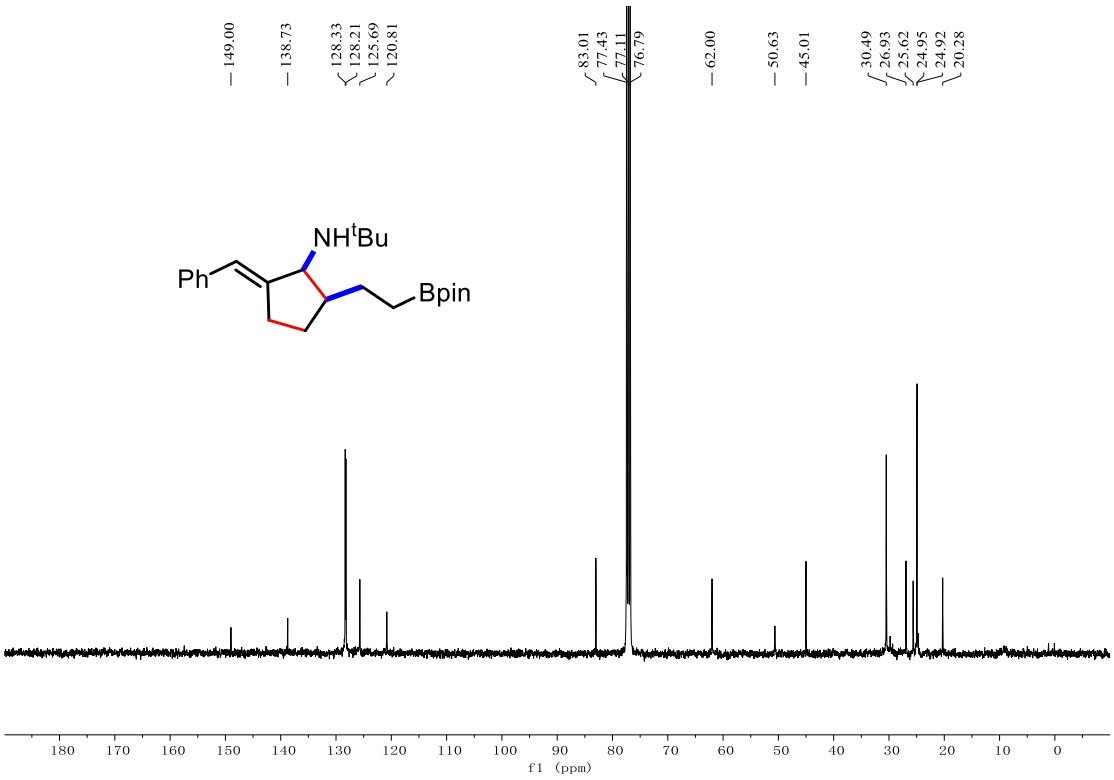
NOE spectrum of 10aa



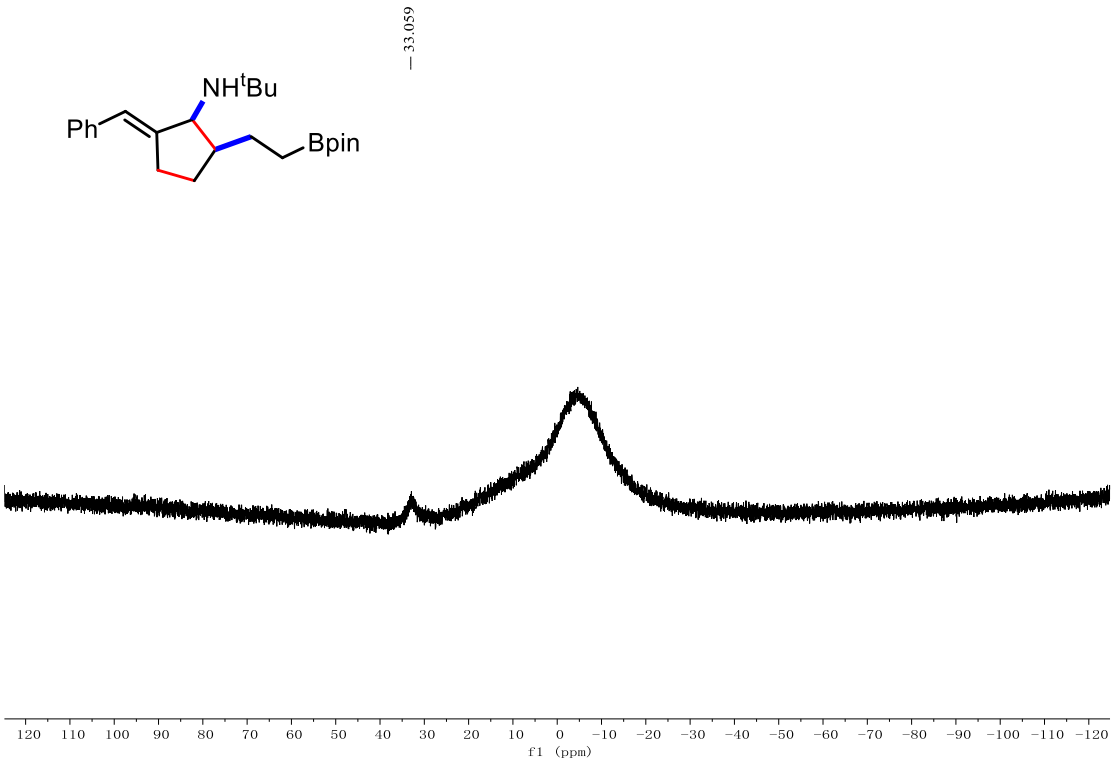
^{1}H NMR spectrum of 11aa (400 MHz, $CDCl_3$)



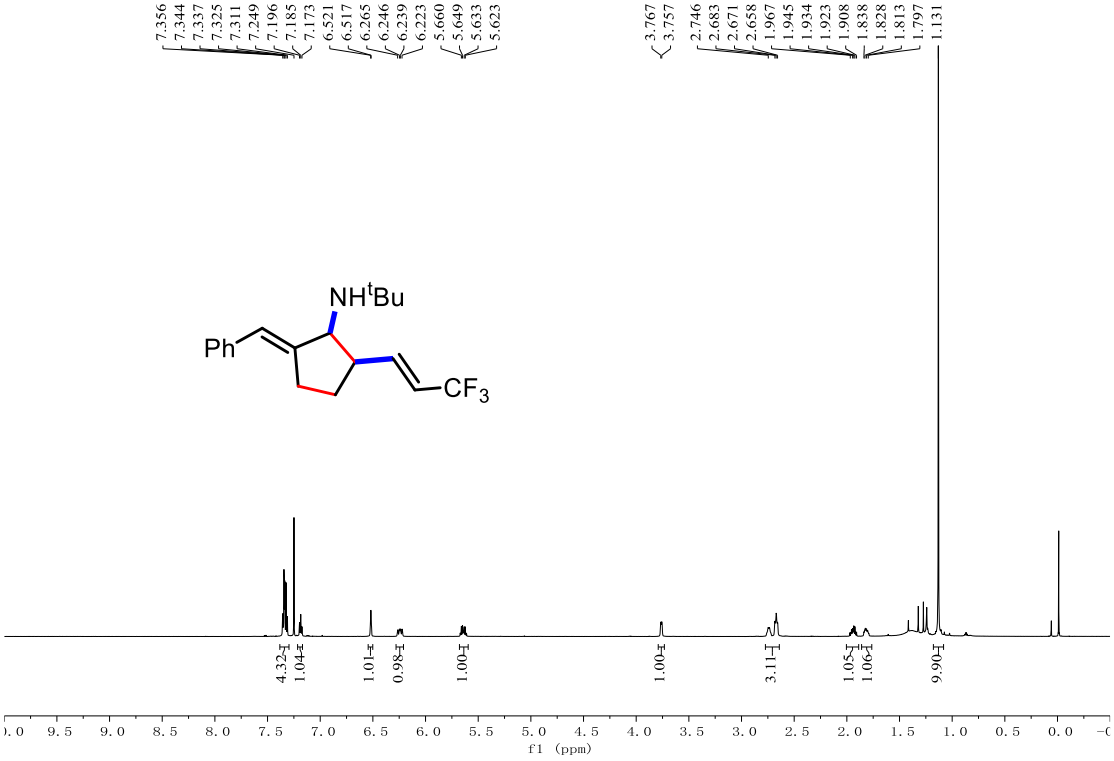
^{13}C NMR spectrum of 11aa (101 MHz, $CDCl_3$)



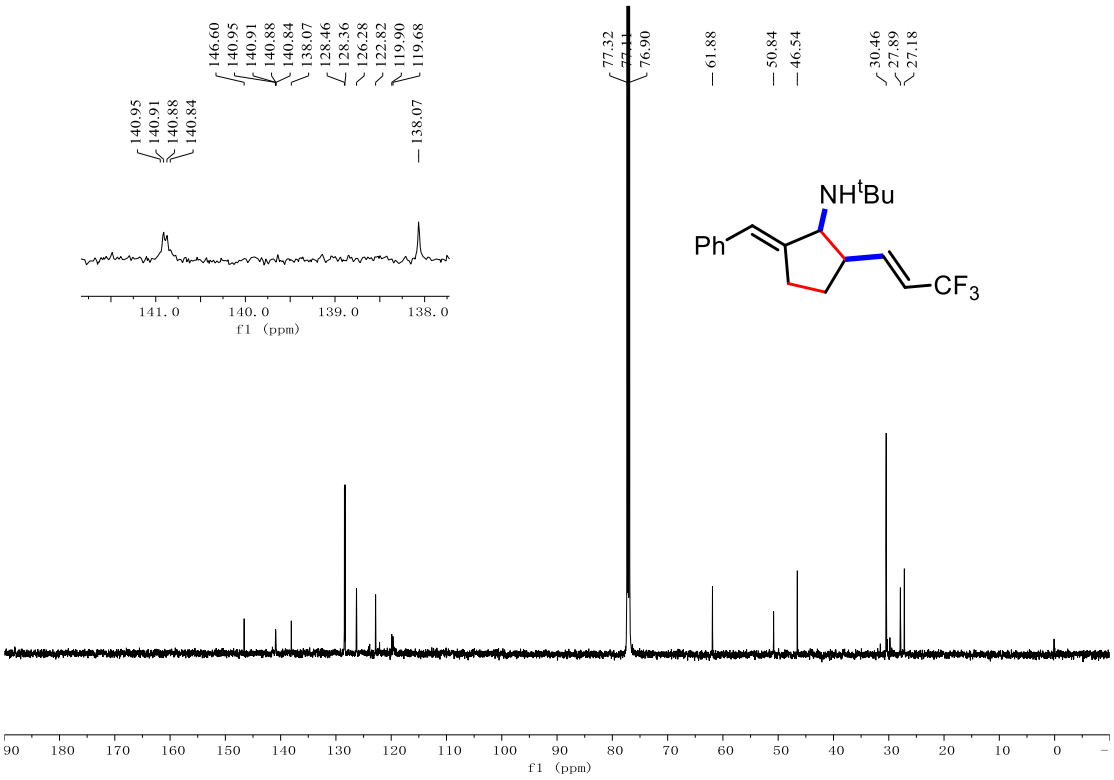
^{11}B spectrum of 11aa



^{1}H NMR spectrum of 12aa (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 12aa (101 MHz, $CDCl_3$)



^{19}F spectrum of 12aa