Supplementary Information

Diastereodivergent [3+2] Annulation of Aromatic Aldimines with Alkenes via C−H Activation by Half-Sandwich Rare-Earth Catalysts

Xuefeng Cong[†], Gu Zhan[‡], Zhenbo Mo[‡], Masayoshi Nishiura[†,‡], and Zhaomin Hou[†,‡,*]

[†]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

[‡]*Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

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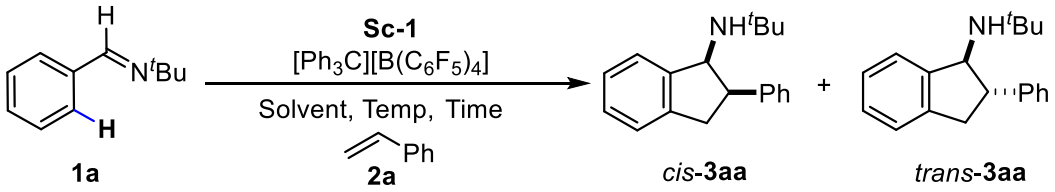
1. General and Materials

General. All manipulations of air- and moisture-sensitive compounds were performed under dry nitrogen atmosphere in an mBRAUN Labmaster glovebox. Nitrogen was purified by being passed through a dry column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). 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 (Mbraun) 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). Silica gel column chromatography was performed with Silica Gel 60 N (spherical, neutral, 40-50 μm) obtained from Kanto Chemical Co.. All ^{1}H NMR and ^{13}C NMR spectra of organic products were recorded on Bruker AVANCE III HD 500 NMR (500 MHz) instrument and ^{19}F NMR spectra of organic products were recorded on a JEOL ECS-400 (377 MHz for ^{19}F). ^{1}H NMR spectra were recorded at 500 MHz in $CDCl_3$ and were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 125 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: ESI, APCI, or FD).

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., and other commercial suppliers and used as received. Solvents (THF, toluene and benzene) (dehydrated, stabilizer-free) were obtained from Kanto Kagaku Co., purified by an mBRAUN SPS-800 solvent purification system, and dried over fresh Na chips in a glovebox. Alkenes obtained commercially were distilled from CaH_2 before use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Strem and used without purification. *N*-Benzylidene-*tert*-butylamine (**1a**) is widely available from suppliers and was purified by redistilled before use. All rare earth catalysts were synthesized according to literature.[1]

2. Optimizing Reaction Parameters

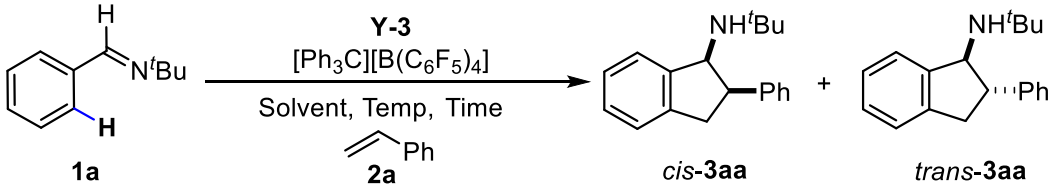
Table S1. Investigation of the effect of *the loading of Sc-1, solvent, reaction temperature* and *reaction time* for the Sc-catalyzed *trans* selective [3+2] annulation of aldimine 1a with styrene 2a[a]



Entry	**Sc-1**	Solvent	Temp	Time (h)	Yield of *trans*-**3aa**	*trans* : *cis*[b]
1	7.5 mol %	Toluene	120 ^{o}C	24	99%	> 19 : 1
2	7.5 mol %	Toluene	120 ^{o}C	12	67%	> 19 : 1
3	7.5 mol %	Toluene	110 ^{o}C	24	65%	> 19 : 1
4	5 mol %	Toluene	120 ^{o}C	24	76%	> 19 : 1
5	7.5 mol %	Benzene	120 ^{o}C	24	99%	> 19 : 1
6	7.5 mol %	THF	120 ^{o}C	24	n.d.	-

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), **Sc-1** (5.0-7.5 mol %), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (5.0-7.5 mol %), solvent (2 mL). NMR yields are given. [b] The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture.

Table S2. Investigation of the effect of *the loading of Y-3, solvent, reaction temperature* and *reaction time* for the Y-catalyzed *cis* selective [3+2] annulation of aldimine 1a with styrene 2a[a]

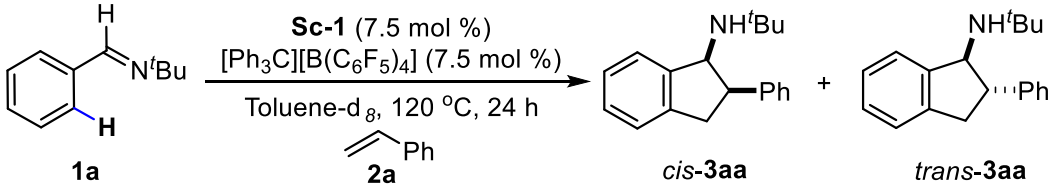


Entry	**Y-3**	Solvent	Temp	Time (h)	Yield of ***cis*-3aa**	*trans* : *cis*[b]
1	10 mol %	Toluene	120 ^{o}C	24	95%	< 1 : 19
2	7.5 mol %	Toluene	120 ^{o}C	24	90%	< 1 : 19
3	5 mol %	Toluene	120 ^{o}C	24	67%	< 1 : 19

4	10 mol %	Toluene	110 °C	24	88%	< 1 : 19
5	10 mol %	Benzene	120 °C	24	95%	< 1 : 19
6	10 mol %	THF	120 °C	24	n.d.	-

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **Y-3** (5.0-10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (5.0-10 mol %), solvent (2 mL). NMR yields are given. [b] The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture.

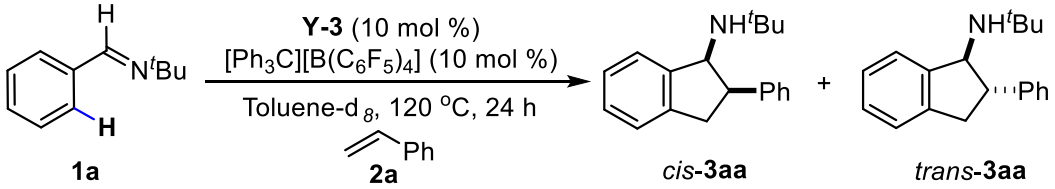
Table S3. Investigation of the effect of *the amount of styrene 2a* for the Sc-catalyzed *trans* selective [3+2] annulation of aldimine 1a with styrene 2a[a]



Entry	**1a**	**2a**	Yield of *trans*-**3aa**	*trans* : *cis*[b]	Recovery (**1a**)	Recovery (**2a**)
1	0.2 mmol	0.4 mmol	70%	> 19 : 1	29%	0.25 mmol
2	0.2 mmol	0.6 mmol	85%	> 19 : 1	14%	0.420 mmol
3	0.2 mmol	0.8 mmol	99%	> 19 : 1	-	0.590 mmol
4	0.2 mmol	1.0 mmol	99%	> 19 : 1	-	0.780 mmol

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4-1.0 mmol), **Sc-1** (7.5 mol %), $[Ph_3C][B(C_6F_5)_4]$ (7.5 mol %), toluene (2 mL), at 120 °C, 24 h. NMR yields are given. [b] The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture.

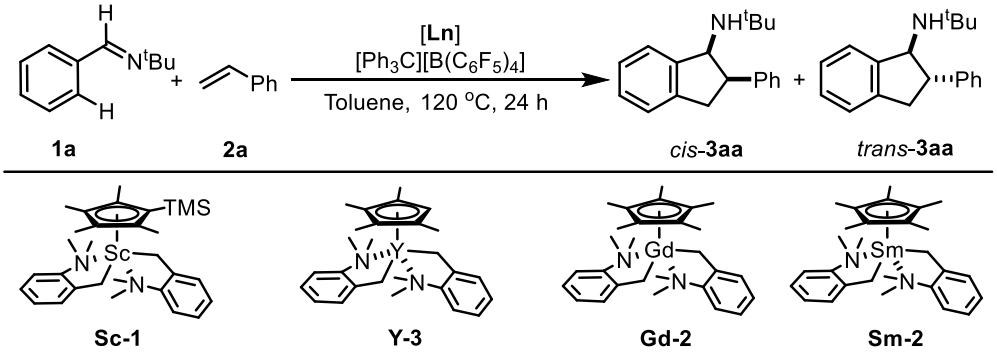
Table S4. Investigation of the effect of *the amount of styrene 2a* for the Y-catalyzed *cis* selective [3+2] annulation of aldimine 1a with styrene 2a[a]



Entry	**1a**	**2a**	Yield of *cis*-**3aa**	*trans* : *cis*[b]	Recovery (**1a**)	Recovery (**2a**)
1	0.2 mmol	0.3 mmol	82%	< 1 : 19	19%	0.13 mmol
2	0.2 mmol	0.4 mmol	90%	< 1 : 19	10%	0.21 mmol
3	0.2 mmol	0.6 mmol	95%	< 1 : 19	-	0.39 mmol
4	0.2 mmol	0.8 mmol	95%	< 1 : 19	-	0.059 mmol

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3-0.8 mmol), **Y-3** (10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (10 mol %), toluene (2 mL), at 120 °C, 24 h. NMR yields are given. [b] The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture.

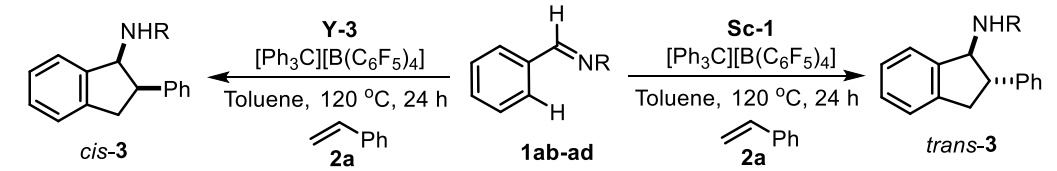
Table S5. Investigation of the effect of *different rare-earth catalysts* for the diastereoselective [3+2] annulation of aldimine 1a with styrene 2a[a]

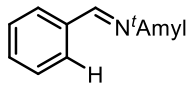


Entry	[**Ln**]	Yield of **3aa**	*trans* : *cis*[b]
1[c]	**Sc-1**	99%	> 19 : 1
2	**Y-3**	95%	< 1 : 19
3	**Gd-2**	81%	1 : 11
4	**Sm-2**	40%	1 : 5

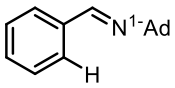
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), [**Ln**] (10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (10 mol %), toluene (2 mL), at 120 °C, 24 h. Combined NMR yields of both diastereomers are given. [b] The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture. [c] **Sc-1** (7.5 mol %), $[Ph_3C][B(C_6F_5)_4]$ (7.5 mol %) and **2a** (0.8 mmol).

Table S6. Investigation of *the auxiliary effect* on diastereoselective [3+2] annulation of aldimines 1 with styrene 2a[a]

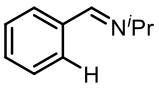




Sc-1: *trans*-**3aba**, 90%, d.r. > 20:1
Y-3: *cis*-**3aba**, 80%, d.r. = 1:10



Sc-1: *trans*-**3aca**, 97%, d.r. > 20:1
Y-3: *cis*-**3aca**, 35%, d.r. = 1.5:1



Sc-1: *trans*-**3ada,** trace
Y-3: *cis*-**3ada,** trace

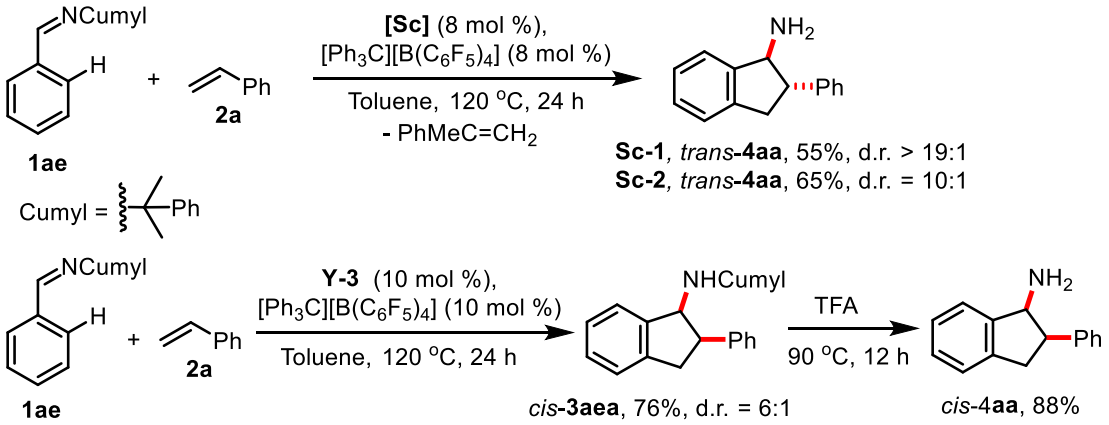
[a]Reaction conditions: **Sc-1**: **1** (0.2 mmol), **2a** (0.8 mmol), **Sc-1** (7.5 mol %), $[Ph_3C][B(C_6F_5)_4]$ (7.5 mol %), toluene (2 mL), at 120 °C, 24 h; **Y-3**: **1** (0.2 mmol), **2a** (0.6 mmol), **Y-3** (10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (10 mol %), toluene (2 mL), at 120 °C, 24 h. Isolated yields of major isomers. The d.r. values were determined by ^{1}H NMR analysis of the crude reaction mixture.

In addition to the *N*-^{t}Bu-substituted benzaldimine **1a**, the *N*-*tert*-amyl-substituted analog **1ab** was also suitable for the present diastereodivergent annulations by **Sc-1** and **Y-3** (Table S6). In the case of the more sterically demanding *N*-adamantyl-substituted benzaldimine **1ac**, **Sc-1** remained highly selective for the formation of *trans*-**3ca** (> 19:1 d.r.), but **Y-3** showed a rather poor selectivity (1.5:1 d.r.) possibly because of a poor matching between the sterically hindered adamantyl group and the large yttrium ion. The smaller *N*-isopropyl-substituted benzaldimine **1ad** did not work well with either **Sc-1** or **Y-3** for the annulation reaction, probably because the ^{i}Pr group was too small to prevent the imine group from receiving a possible direct attack of the highly nucleophilic rare-earth alkyl species, thus deactivating the catalysts.

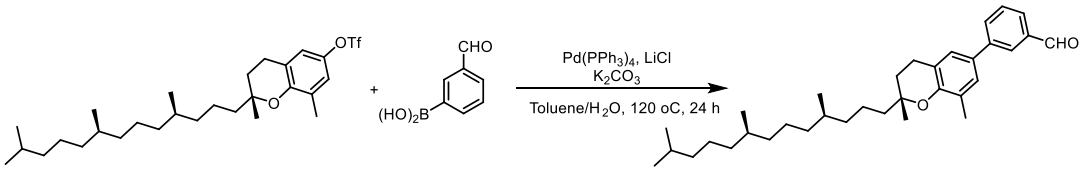
Attempts to remove the *tert*-butyl group from the annulation product **3aa** were unsuccessful. However, the reaction of *N*-cumyl-substituted benzaldimine **1ae** with styrene in the presence of **Sc-1** or **Sc-2** yielded the corresponding unsubstituted primary 1-aminoindane product *trans*-**4aa** in a highly *trans*-selective fashion with release of α-methylstyrene (Scheme S1, top). The decumylation was probably caused by the strongly Lewis acidic scandium species and the facile formation of α -methylstyrene.[2] The reaction of **1ae** with styrene by **Y-3** gave the *cis*-selective *N*-cumyl-containing annulation product *cis*-**3aea**, which on treatment with TFA at 90

°C afforded the unsubstituted primary 1-aminoindane *cis*-**4aa** in 88% yield (Scheme S1, bottom).[3]

Scheme S1. Diastereoselectivive Synthesis of *trans* and *cis* Unsubstituted Primary 1-Aminoindanes



3. The Preparation of Substrates



A solution of 3-formylphenylboronic acid (900 mg, 6 mmol), $Pd(PPh_3)_4$ (462 mg, 0.4 mmol), LiCl (507 mg, 12 mmol), (+)-δ-tocopherol-triflate (2.08 g, 4 mmol) and K_2CO_3 (1.66 g, 12 mmol) in Toluene/H_2O (6 mL/1.5 mL) was heated at 120 °C for 24 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature and diluted with water (30 mL) followed by extraction with ether (30 mL x 3). The ethereal solution was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluting with hexane/ethyl acetate 40:1) to yield (+)-*δ*-tocopherol-aldehyde (1.1 g, 58%).

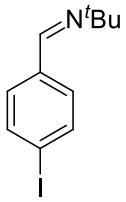
^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 8.05 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.25 (s, 1H), 7.19 (s, 1H), 2.86–2.81 (m, 2H), 2.24 (s, 3H), 1.88-1.78 (m, 2H), 1.64-1.49 (m, 3H), 1.48-1.19 (m, 15H), 0.87-0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 192.7, 152.6, 142.4, 137.0, 132.7, 130.0, 129.4, 127.8, 127.7, 127.2, 127.1, 125.7, 121.1, 40.4, 39.5, 37.60, 37.59, 37.57, 37.44, 33.4, 32.9, 31.3, 28.1, 25.0, 24.6, 24.5, 22.9, 22.8, 22.6, 21.2,

19.9, 19.8, 16.4. HRMS (ESI^+): calcd for $C_{34}H_{51}O_2$ $[M+H]^+$ 491.3884, found 491.3870.

General procedure for the synthesis of *N*-*tert*-butyl-substituted aromatic imines

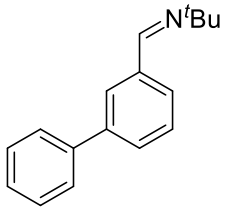
In a 30 mL Schlenk tube with a stirring bar, the aromatic aldehyde (5 mmol) was treated with *tert*-butylamine (25 mmol). The mixture was stirred at 100 °C for overnight. After cooling to room temperature, the reaction mixture was dried over anhydrous $MgSO_4$. The $MgSO_4$ were then removed via filtration 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 ^1H NMR and ^{13}C NMR or purified by distillation if necessary.

Spectral data for aldimines **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1i**, **1u**, **1y**, **1ab, 1ac** and **1ad** showed good agreement with the literature data.[4] **1ae** was prepared according the known procedure.[4d]



(*E*)-*N*-*tert*-butyl-1-(4-iodophenyl)methanimine (1h)

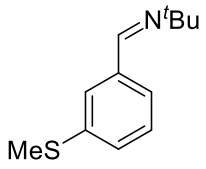
The title compound was prepared according to the general procedure as a pale yellow solid (94% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 137.8, 136.8, 129.6, 96.7, 57.6, 29.8. HRMS (ESI^+): calcd for $C_{11}H_{15}IN$ $[M+H]^+$ 288.0244, found 288.0240.



(*E*)-1-([1,1'-Biphenyl]-3-yl)-*N*-(*tert*-butyl)methanimine (1j)

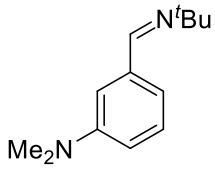
The title compound was prepared according to the general procedure as a colorless oil (96% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.97(s, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.64-7.61 (m, 3H), 7.48-7.43 (m, 3H), 7.34 (t, J = 7.5 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.2, 141.7, 141.0, 137.8, 129.09, 129.05,

128.9, 127.6, 127.4, 126.93, 126.87, 57.5, 29.9. HRMS (ESI^+): calcd for $C_{17}H_{29}N$ $[M+H]^+$ 238.1590, found 238.1587.



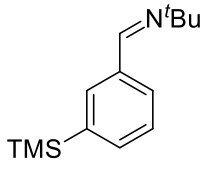
(*E*)-*N*-*tert*-butyl-1-(3-(methylthio)phenyl)methanimine (1k)

The title compound was prepared according to the general procedure as a colorless oil (92% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.66 (s, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.33-7.27 (m, 2H), 2.52 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.8, 139.2, 137.9, 129.0, 128.4, 125.8, 125.0, 57.5, 29.8, 16.0. HRMS (ESI^+): calcd for $C_{12}H_{18}NS$ $[M+H]^+$ 208.1154, found 208.1147.



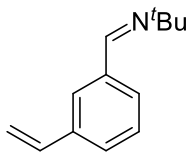
(*E*)-3-((*Tert*-butylimino)methyl)-*N*,*N*-dimethylaniline (1l)

The title compound was prepared according to the general procedure as yellow oil (93% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.28-7.24 (m, 1H), 7.13(s, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.77 (dd, J = 8.0, 2.5 Hz, 1H), 2.98 (s, 6H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.2, 151.0, 138.1, 129.3, 116.9, 114.8, 111.7, 57.2, 40.8, 29.9. HRMS (ESI^+): calcd for $C_{13}H_{21}N_2$ $[M+H]^+$ 205.1699, found 205.1693.



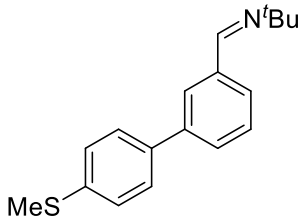
(*E*)-*N*-*tert*-butyl-1-(3-(trimethylsilyl)phenyl)methanimine (1m)

The title compound was prepared according to the general procedure as a colorless oil (95% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.80-7.79 (m, 2H), 7.54 (dd, J = 7.0, 1.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 1.30 (s, 9H), 0.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.7, 140.8, 136.5, 135.3, 133.6, 128.1, 128.0, 57.4, 29.9, -0.95. HRMS (ESI^+): calcd for $C_{14}H_{24}NSi$ $[M+H]^+$ 234.1673, found 234.1680.



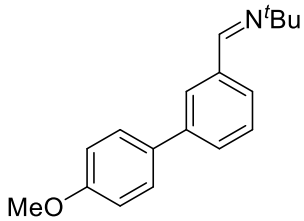
(*E*)-*N*-tert-butyl-1-(3-vinylphenyl)methanimine (1n)

The title compound was prepared according to the general procedure as a yellow oil (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.28 (s, 1H), 7.78(s, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 6.73 (dd, J = 22.25, 11.0 Hz, 1H), 5.79 (d, J = 17.5 Hz, 1H), 5.27 (d, J = 15.5 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.3, 138.0, 137.6, 136.6, 128.8, 127.6, 125.8, 114.5, 57.5, 29.9. HRMS (ESI^+): calcd for $C_{13}H_{18}N$ $[M+H]^+$ 188.1434, found 188.1433.



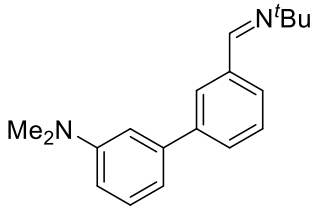
(*E*)-*N*-*tert*-butyl-1-(4'-(methylthio)-[1,1'-biphenyl]-3-yl)methanimine (1o)

The title compound was prepared according to the general procedure as a white solid (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.95 (s, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.60-7.56 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 2.53 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.2, 141.0, 137.94, 137.88, 137.7, 129.1, 128.7, 127.7, 127.1, 126.9, 126.5, 57.5, 29.9, 16.1. HRMS (ESI^+): calcd for $C_{18}H_{22}NS$ $[M+H]^+$ 284.1467, found 284.1465.



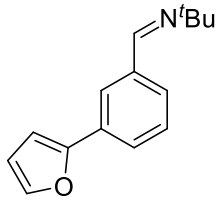
(*E*)-*N*-tert-butyl-1-(4'-methoxy-[1,1'-biphenyl]-3-yl)methanimine (1p)

The title compound was prepared according to the general procedure as a white solid (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.93 (s, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.58-7.56 (m, 3H), 7.42 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.4, 155.3, 141.3, 137.8, 133.5, 129.0, 128.6, 128.4, 126.39, 126.38, 114.3, 57.5, 55.5, 29.9. HRMS (ESI^+): calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1692.



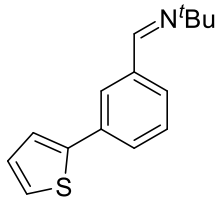
(*E*)-3'-((*Tert*-butylimino)methyl)-*N*,*N*-dimethyl-[1,1'-biphenyl]-3-amine (1q)

The title compound was prepared according to the general procedure as a pale yellow solid (98% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.92 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 1H), 6.98-6.95 (m, 2H), 6.74 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.01 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.3, 151.1, 142.7, 142.0, 137.7, 129.5, 128.9, 127.3, 126.5, 116.1, 112.0, 111.8, 57.5, 40.9, 29.9. HRMS (ESI$^+$): calcd for $C_{19}H_{25}N_2$ $[M+H]^+$ 281.2012, found 281.2010.



(*E*)-*N*-*tert*-butyl-1-(3-(furan-2-yl)phenyl)methanimine (1r)

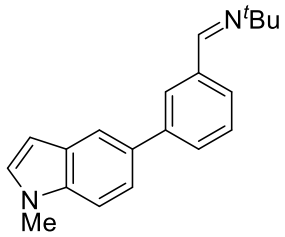
The title compound was prepared according to the general procedure as a yellowish oil (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 8.03 (s, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 1.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 3.5 Hz, 1H), 6.48 (dd, *J* = 3.0, 1.5 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.1, 153.8, 142.3, 137.8, 131.3, 129.0, 126.9, 125.6, 123.5, 111.8, 105.6, 57.5, 29.9. HRMS (ESI$^+$): calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383, found 228.1384.



(*E*)-*N*-*tert*-butyl-1-(3-(thiophen-2-yl)phenyl)methanimine (1s)

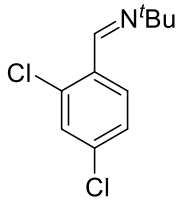
The title compound was prepared according to the general procedure as a yellow oil (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.97 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 3.5 Hz, 1H), 7.29 (d, *J* = 5.0 Hz, 1H), 7.10-7.08 (m, 1H), 1.31 (s, 9H); ^{13}C NMR (126 MHz,

$CDCl_3$): δ = 155.0, 144.1, 138.0, 134.9, 129.2, 128.2, 127.8, 127.0, 125.6, 125.1, 123.6, 57.6, 29.9. HRMS (ESI^+): calcd for $C_{15}H_{18}NS$ $[M+H]^+$ 244.1154, found 244.1147.



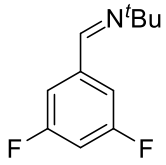
(*E*)-*N*-*tert*-butyl-1-(3-(1-methyl-1H-indol-5-yl)phenyl)methanimine (1t)

The title compound was prepared according to the general procedure as a colorless oil (95% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.36 (s, 1H), 8.01 (s, 1H), 7.89 (s, 1H), 7.72-7.67 (m, 2H), 7.53-7.51 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.53 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.6, 143.0, 137.7, 136.5, 132.5, 129.6, 129.3, 129.1, 129.0, 127.2, 125.8, 121.5, 119.6, 109.5, 101.5, 57.4, 33.1, 29.9. HRMS (ESI^+): calcd for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856, found 291.1850.



(*E*)-*N*-*tert*-butyl-1-(2,4-dichlorophenyl)methanimine (1v)

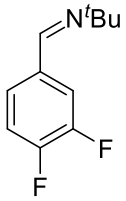
The title compound was prepared according to the general procedure as a colorless oil (95% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.27-7.25 (m, 1H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.3, 136.5, 135.7, 132.9, 129.5, 129.3, 127.6, 58.3, 29.8. HRMS (ESI^+): calcd for $C_{11}H_{14}Cl_2N$ $[M+H]^+$ 230.0498, found 230.0496.



(*E*)-*N*-*tert*-butyl-1-(3,5-difluorophenyl)methanimine (1w)

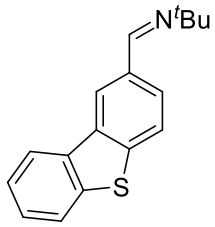
The title compound was prepared according to the general procedure as a colorless oil (90% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.30-7.26 (m, 2H), 6.84-6.80 (m, 1H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.1 (dd, J =

246.9, 11.9 Hz), 152.7 (t, *J* = 3.78 Hz), 140.6 (t, *J* = 8.82 Hz), 110.5 (dd, *J* = 31.3, 6.3 Hz), 105.1 (t, *J* = 25.2 Hz), 57.7, 29.5. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −109.71. HRMS (ESI^+): calcd for $C_{11}H_{14}F_2N$ $[M+H]^+$ 198.1089, found 198.1082.



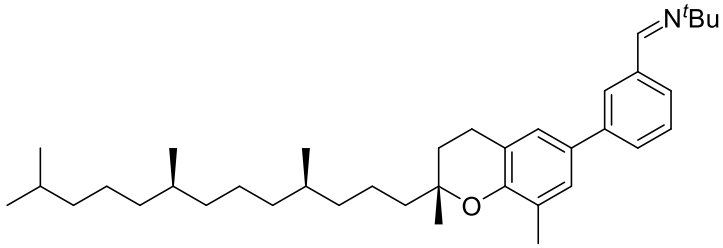
(*E*)-*N*-*tert*-butyl-1-(3,4-difluorophenyl)methanimine (1x)

The title compound was prepared according to the general procedure as a yellowish oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.67-7.63 (m, 1H), 7.42-7.40 (m, 1H), 7.20-7.15 (m, 1H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.80 (t, *J* = 1.3 Hz), 151.79 (dd, *J* = 250.0, 12.5 Hz), 150.85 (dd, *J* = 246.3, 12.5 Hz), 134.64 (dd, *J* = 5.0, 3.8 Hz), 124.6 (dd, *J* = 6.3, 3.8 Hz), 117.3 (d, *J* = 17.6 Hz), 116.0 (d, *J* = 17.6 Hz), 57.8, 29.8. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −135.16 (m, 1F), −137.41 (m, 1F). HRMS (ESI^+): calcd for $C_{11}H_{14}F_2N$ $[M+H]^+$ 198.1089, found 198.1083.



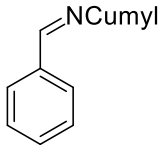
(*E*)-*N*-*tert*-butyl-1-(dibenzo[b,d]thiophen-2-yl)methanimine (1z)

The title compound was prepared according to the general procedure as a pale yellow solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 8.44 (s, 1H), 8.24-8.22 (m, 1H), 7.89-7.83 (m, 3H), 7.48-7.44 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.2, 141.5, 139.9, 135.9, 135.6, 134.0, 127.1, 126.4, 124.7, 123.0, 122.9, 122.1, 121.3, 57.5, 30.0. HRMS (ESI^+): calcd for $C_{17}H_{18}NS$ $[M+H]^+$ 268.1154, found 268.1156.



(*E*)-*N*-*tert*-butyl-1-(3-((*R*)-2,8-dimethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yl)phenyl)methanimine (1aa)

The title compound was prepared according to the general procedure as a colorless oil (96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.88 (s, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.25 (s, 1H), 7.18 (s, 1H), 2.87-2.77 (m, 2H), 2.23 (s, 3H), 1.89-1.76 (m, 2H), 1.65-1.03 (m, 33H), 0.87-0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.5, 152.2, 141.8, 137.6, 131.5, 128.9, 128.6, 127.3, 126.7, 126.5, 125.8, 125.75, 120.8, 76.5, 57.4, 40.3, 39.5, 37.61, 37.59, 37.4, 33.0, 32.9, 31.4, 29.9, 28.1, 25.0, 24.6, 24.5, 22.9, 22.8, 22.6, 21.2, 19.9, 19.8, 16.4. HRMS (ESI$^+$): calcd for $C_{38}H_{60}NO$ $[M+H]^+$ 546.4669, found 546.4698.



(*E*)-1-phenyl-*N*-(2-phenylpropan-2-yl)methanimine (1ae)

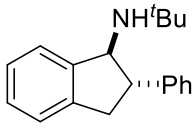
The title compound was prepared according to the general procedure as a colorless oil (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 7.79-7.77 (m, 2H), 7.44-7.40 (m, 5H), 7.33 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 1.66 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.4, 148.3, 137.1, 130.6, 128.7, 128.29, 128.25, 126.5, 126.3, 62.8, 29.9. HRMS (ESI$^+$): calcd for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434, found 224.1430.

4. General Procedure for the Diastereodivergent [3+2] Annulation of Aldimines with Alkenes

General procedure for the scandium-catalyzed *trans* diastereoselective [3+2] annulation of aldimines with alkenes

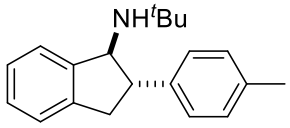
In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (13.8 mg, 0.015 mmol) was added to a stirred toluene solution (2.0 mL) of **Sc-1** (7.6 mg, 0.015 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimines **1** (0.2 mmol) and olefins **2** (0.8 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the

mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 4:1) to afford the desired products *trans*-**3**.



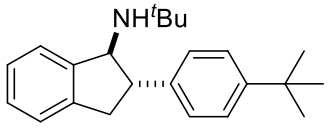
(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3aa)

The title compound was prepared according to the general procedure as a pale yellow solid (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.23 (m, 9H), 4.29 (d, J = 7.0 Hz, 1H), 3.44 (dd, J = 16.0, 8.0 Hz, 1H), 3.24 (q, J = 7.5 Hz, 1H), 3.07 (dd, J = 16.0, 8.0 Hz, 1H), 1.43 (brs, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 144.5, 142.3, 128.5, 127.9, 127.5, 127.1, 126.5, 124.5, 124.3, 66.3, 57.6, 50.9, 39.4, 30.5. HRMS (ESI$^+$): calcd for $C_{19}H_{24}N$ $[M+H]^+$ 266.1903, found 266.1902.



(*Trans*)-*N*-(*tert*-butyl)-2-(*p*-tolyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ab)

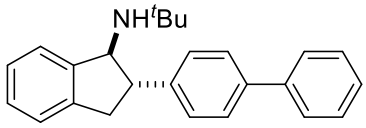
The title compound was prepared according to the general procedure as a yellowish oil (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, J = 7.0 Hz, 1H), 7.25-7.20 (m, 3H), 7.21 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 4.23 (d, J = 7.0 Hz, 1H), 3.38 (dd, J = 16.0, 8.0 Hz, 1H), 3.18 (q, J = 7.5 Hz, 1H), 2.99 (dd, J = 15.5, 7.5 Hz, 1H), 2.32 (s, 2H), 1.64 (brs, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.0, 142.4, 141.4, 136.0, 129.2, 127.7, 127.5, 127.0, 124.5, 124.3, 66.2, 56.9, 51.0, 39.5, 30.4, 21.2. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



(*Trans*)-*N*-(*tert*-butyl)-2-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ac)

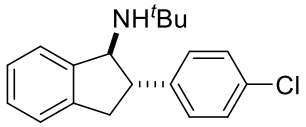
The title compound was prepared according to the general procedure as a yellowish oil (98% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 3H), 7.25-7.21 (m, 3H), 7.15 (d, J = 8.5 Hz, 2H), 4.21 (d, J = 6.5 Hz, 1H), 3.39 (dd, J = 16.0, 8.0 Hz, 1H), 3.19 (q, J = 7.0 Hz, 1H), 3.02 (dd, J = 16.0, 7.5 Hz, 1H), 1.51 (brs, 1H), 1.30 (s, 9H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.4, 147.1, 142.5, 141.4, 127.4,

127.0, 125.3, 124.5, 124.3, 66.2, 56.8, 51.0, 39.2, 34.5, 31.5, 30.4. HRMS (ESI^+): calcd for $C_{23}H_{32}N$ $[M+H]^+$ 322.2529, found 322.2529.



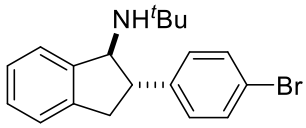
(*Trans*)-2-([1,1'-biphenyl]-4-yl)-*N*-(tert-butyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ad)

The title compound was prepared according to the general procedure as a pale yellow solid (89% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.34-7.30 (m, 4H), 7.28-7.22 (m, 3H), 4.29 (d, J = 6.5 Hz, 1H), 3.44 (dd, J = 16.0, 7.5 Hz, 1H), 3.27 (q, J = 7.5 Hz, 1H), 3.05 (dd, J = 16.0, 7.5 Hz, 1H), 1.61 (brs, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.9, 143.8, 142.3, 141.1, 139.3, 128.8, 128.3, 127.6, 127.18, 127.15, 127.12, 127.06, 124.5, 124.3, 66.3, 57.1, 51.0, 39.4, 30.5. HRMS (ESI^+): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2216.



(*Trans*)-*N*-(*tert*-butyl)-2-(4-chlorophenyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ae)

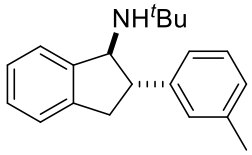
The title compound was prepared according to the general procedure as a colorless oil (67% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30 (d, J = 7.0 Hz, 1H), 7.27-7.20 (m, 5H), 7.16 (d, J = 8.5 Hz, 1H), 4.20 (d, J = 6.5 Hz, 1H), 3.40 (dd, J = 16.0, 8.0 Hz, 1H), 3.20 (q, J = 7.5 Hz, 1H), 2.96 (dd, J = 16.0, 8.0 Hz, 1H), 1.55 (brs, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.7, 143.2, 142.0, 132.1, 129.2, 128.6, 127.7, 127.2, 124.6, 124.3, 66.3, 56.9, 50.9, 39.4, 30.5. HRMS (ESI^+): calcd for $C_{19}H_{23}ClN$ $[M+H]^+$ 300.1514, found 300.1514.



(*Trans*)-2-(4-bromophenyl)-*N*-(*tert*-butyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3af)

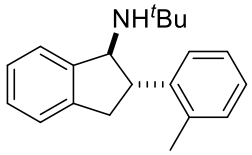
The title compound was prepared according to the general procedure as a yellowish oil (67% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.0 Hz, 2H), 7.29 (d, J

= 6.5 Hz, 1H), 7.27-7.20 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.20 (d, *J* = 6.5 Hz, 1H), 3.40 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.18 (q, *J* = 7.5 Hz, 1H), 2.95 (dd, *J* = 15.5, 7.5 Hz, 1H), 1.53 (brs, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.7, 143.8, 142.0, 131.5, 129.6, 127.7, 124.6, 124.3, 120.1, 66.3, 56.9, 50.9, 39.3, 30.5. HRMS (ESI^+): calcd for $C_{19}H_{23}BrN$ $[M+H]^+$ 344.1008 and 346.0988, found 344.1007 and 346.0987.



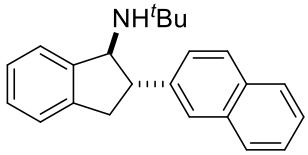
(*Trans*)-*N*-(*tert*-butyl)-2-(*m*-tolyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ag)

The title compound was prepared according to the general procedure as a yellowish oil (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.0 Hz, 1H), 7.30-7.19 (m, 4H), 7.10-7.15 (m, 3H), 4.28 (d, *J* = 6.5 Hz, 1H), 3.41 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.20 (q, *J* = 7.5 Hz, 1H), 3.05 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.36 (s, 3H), 1.37 (brs, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 144.3, 142.3, 138.0, 128.8, 128.4, 127.4, 127.2, 127.1, 124.9, 124.5, 124.3, 66.2, 57.6, 50.9, 39.5, 30.5, 21.6. HRMS (ESI^+): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



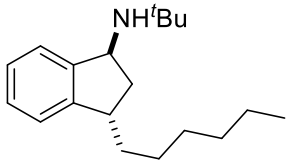
(*Trans*)-*N*-(*tert*-butyl)-2-(*o*-tolyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ah)

The title compound was prepared according to the general procedure as a yellowish oil (46% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 7.5 Hz, 1H), 7.27-7.07 (m, 7H), 4.38 (d, *J* = 6.5 Hz, 1H), 3.62 (q, *J* = 7.5 Hz, 1H), 3.40 (dd, *J* = 16.0, 8.5 Hz, 1H), 2.90 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.36 (s, 3H), 1.37 (brs, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 143.3, 142.2, 136.4, 130.3, 127.5, 127.1, 126.4, 126.2, 126.0, 124.7, 124.1, 66.1, 52.3, 50.8, 39.4, 30.4, 20.5. HRMS (ESI^+): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



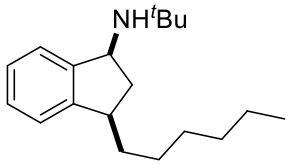
(*Trans*)-*N*-(*tert*-butyl)-2-(naphthalen-2-yl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ai)

The title compound was prepared according to the general procedure as a yellowish oil (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (t, J = 8.5 Hz, 1H), 7.68 (s, 1H), 7.46-7.40 (m, 3H), 7.34 (d, J = 7.0 Hz, 1H), 7.29-7.23 (m, 3H), 4.38 (d, J = 6.5 Hz, 1H), 3.49-3.38 (m, 2H), 3.11 (dd, J = 15.5, 7.5 Hz, 1H), 1.61 (brs, 1H), 0.95 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.0, 142.2, 142., 133.6, 132.5, 128.2, 127.74, 127.73, 127.6, 127.2, 126.6, 126.1, 126.0, 125.4, 124.5, 124.3, 66.1, 57.7, 51.0, 39.6, 30.5. HRMS (ESI$^+$): calcd for $C_{23}H_{26}N$ $[M+H]^+$ 316.2060, found 316.2059.



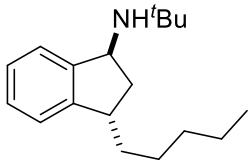
(*Trans*)-*N*-(*tert*-butyl)-3-hexyl-2,3-dihydro-1H-inden-1-amine (*trans*-3aj)

The title compound was prepared according to the general procedure as a yellowish oil (62% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 1H), 7.21-7.16 (m, 3H), 4.32 (t, J = 6.5 Hz, 1H), 3.23-3.19 (m, 1H), 2.13-2.08 (m, 1H), 2.01-1.95 (m, 1H), 1.70-1.65 (m, 1H), 1.43-1.26 (m, 9H), 1.20 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 147.1, 127.2, 126.8, 124.19, 124.15, 56.5, 51.1, 44.8, 43.0, 36.1, 32.0, 30.5, 29.7, 28.1, 22.8, 14.3. HRMS (ESI$^+$): calcd for $C_{19}H_{32}N$ $[M+H]^+$ 274.2529, found 274.2530.



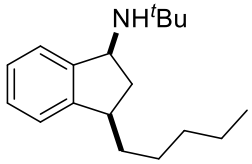
(*Cis*)-*N*-(*tert*-butyl)-3-hexyl-2,3-dihydro-1H-inden-1-amine (*cis*-3aj)

The title compound was prepared according to the general procedure as a yellowish oil (12% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.29 (m, 1H), 7.22-7.18 (m, 3H), 4.15 (t, J = 8.5 Hz, 1H), 2.96-2.91 (m, 1H), 2.72-2.67 (m, 1H), 2.03-1.99 (m, 1H), 1.40-1.24 (m, 10H), 1.21 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 146.4, 127.0, 126.6, 123.6, 123.1, 56.7, 51.0, 46.6, 42.4, 34.9, 32.0, 30.6, 29.7, 27.7, 22.8, 14.3. HRMS (ESI$^+$): calcd for $C_{19}H_{32}N$ $[M+H]^+$ 274.2529, found 274.2530.



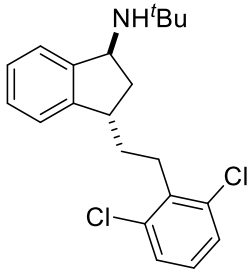
(*Trans*)-*N*-(*tert*-butyl)-3-pentyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ak)

The title compound was prepared according to the general procedure as a yellowish oil (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 1H), 7.20-7.17 (m, 3H), 4.33 (t, J = 6.0 Hz, 1H), 3.25-3.21 (m, 1H), 2.13-2.08 (m, 1H), 2.03-1.98 (m, 1H), 1.39-1.31 (m, 8H), 1.21 (s, 9H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 146.9, 127.3, 126.8, 124.2, 56.5, 51.3, 44.6, 43.0, 36.0, 32.2, 30.4, 27.7, 22.8, 14.3. HRMS (ESI$^+$): calcd for $C_{18}H_{30}N$ $[M+H]^+$ 260.2373, found 260.2373.



(*Cis*)-*N*-(*tert*-butyl)-3-pentyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ak)

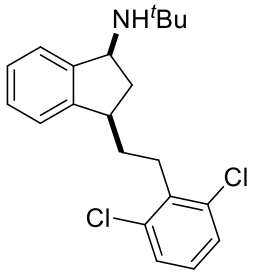
The title compound was prepared according to the general procedure as a yellowish oil (12% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30-7.29 (m, 1H), 7.21-7.19 (m, 3H), 4.16 (t, J = 8.5 Hz, 1H), 2.96-2.93 (m, 1H), 2.72-2.67 (m, 1H), 2.03-1.99 (m, 1H), 1.44-1.28 (m, 8H), 1.22 (s, 9H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.5, 146.3, 126.8, 126.5, 123.4, 123.0, 56.6, 50.9, 46.3, 42.3, 34.7, 32.1, 30.5, 27.2, 22.7, 14.1. HRMS (ESI$^+$): calcd for $C_{18}H_{30}N$ $[M+H]^+$ 260.2373, found 260.2373.



(*Trans*)-*N*-(*tert*-butyl)-3-(2,6-dichlorophenethyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3al)

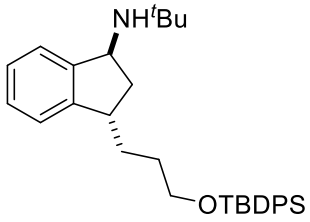
The title compound was prepared according to the general procedure as a yellowish oil (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.27 (m, 1H), 7.26-7.25 (m, 1H), 7.24-7.19 (m, 4H), 7.02 (t, J = 8.0 Hz, 1H), 4.38 (t, J = 6.5 Hz, 1H), 3.43-3.37 (m, 1H), 3.05-2.95 (m, 2H), 2.35-2.30 (m, 1H), 2.12-2.06 (m, 1H), 1.69-1.64 (m, 1H),

1.29 (brs, 1H), 1.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 146.5, 138.5, 135.3, 128.3, 127.6, 127.4, 127.1, 124.2, 124.1, 56.6, 51.2, 44.1, 43.2, 33.8, 30.5, 30.0. HRMS (ESI$^+$): calcd for $C_{21}H_{26}Cl_2N$ $[M+H]^+$ 362.1437, found 362.1437.



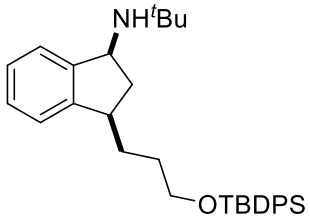
(*Cis*)-*N*-(*tert*-butyl)-3-(2,6-dichlorophenethyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3al)

The title compound was prepared according to the general procedure as a colorless oil (12% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, J = 7.0 Hz, 1H), 7.28-7.26 (m, 2H), 7.23-7.18 (m, 3H), 7.05 (t, J = 8.0 Hz, 1H), 4.21 (t, J = 8.0 Hz, 1H), 3.11-3.06 (m, 1H), 3.04-2.99 (m, 2H), 2.84-2.79 (m, 1H), 2.27-2.20 (m, 1H), 1.76-1.71 (m, 1H), 1.70-1.48 (m, 3H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.5, 138.6, 135.4, 128.3, 127.6, 127.1, 126.8, 123.7, 123.3, 56.7, 51.0, 45.9, 42.6, 32.8, 30.7, 29.6. HRMS (ESI$^+$): calcd for $C_{21}H_{26}Cl_2N$ $[M+H]^+$ 362.1437, found 362.1437.



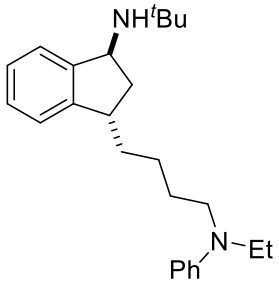
(*Trans*)-*N*-(*tert*-butyl)-3-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3am)

The title compound was prepared according to the general procedure as a yellowish oil (50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.0 Hz, 4H), 7.43-7.35 (m, 6H), 7.27-7.25 (m, 1H), 7.21-7.13 (m, 3H), 4.31 (t, J = 6.5 Hz, 1H), 3.70-3.67 (m, 2H), 3.25-3.20 (m, 1H), 2.11-2.06 (m, 1H), 2.00-1.94 (m, 1H), 1.78-1.71 (m, 1H), 1.70-1.60 (m, 2H), 1.51-1.44 (m, 2H), 1.96 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.11, 147.06, 135.7, 134.2, 129.7, 127.7, 127.3, 126.9, 124.2, 64.2, 56.5, 51.2, 44.7, 42.7, 32.0, 31.0, 30.4, 27.0, 19.4. HRMS (ESI$^+$): calcd for $C_{32}H_{44}NOSi$ $[M+H]^+$ 486.3187, found 486.3187.



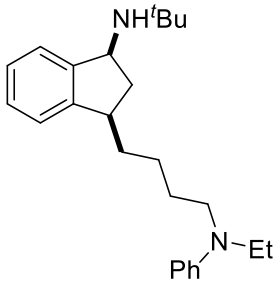
(*Cis*)-*N*-(*tert*-butyl)-3-(3-((tert-butyldiphenylsilyl)oxy)propyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3am)

The title compound was prepared according to the general procedure as a yellowish oil (6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.0 Hz, 4H), 7.43-7.36 (m, 6H), 7.29 (d, J = 6.0 Hz, 4H), 7.22-7.15 (m, 3H), 4.14 (t, J = 8.0 Hz, 1H), 3.73 (t, J = 6.5 Hz, 2H), 2.96-2.90 (m, 1H), 2.69-2.64 (m, 1H), 2.13-2.07 (m, 1H), 1.76-1.55 (m, 3H), 1.49-1.41 (m, 1H), 1.21 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 146.1, 135.7, 134.2, 129.7, 127.8, 127.0, 126.7, 123.6, 123.1, 64.2, 56.7, 51.0, 46.4, 42.1, 30.9, 30.62, 30.60, 27.1, 19.4. HRMS (ESI$^+$): calcd for $C_{32}H_{44}NOSi$ $[M+H]^+$ 486.3187, found 486.3187.



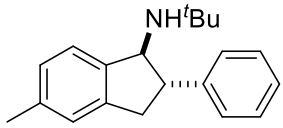
(*Trans*)-*N*-(*tert*-butyl)-3-(4-(ethyl(phenyl)amino)butyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3an)

The title compound was prepared according to the general procedure as a yellow oil (50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.27 (m, 1H), 7.22-7.15 (m, 5H), 6.67-6.61 (m, 3H), 4.33 (t, J = 6.5 Hz, 1H), 3.35 (q, J = 7.0 Hz, 2H), 3.27-3.21 (m, 3H), 2.14-2.10 (m, 1H), 2.02-1.97 (m, 1H), 1.74-1.70 (m, 1H), 1.64-1.59 (m, 1H), 1.47-1.41 (m, 3H), 1.31 (brs, 1H), 1.20 (s, 9H), 1.13 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.1, 147.1, 147.0, 129.4, 127.2, 127.0, 124.24, 124.18, 115.4, 112.0, 56.5, 51.1, 50.5, 45.1, 44.9, 43.0, 36.0, 30.5, 27.9, 25.7, 12.5. HRMS (ESI$^+$): calcd for $C_{25}H_{37}N_2$ $[M+H]^+$ 365.2951, found 365.2962.



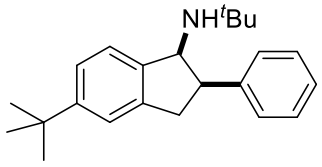
(*Cis*)-*N*-(*tert*-butyl)-3-(4-(ethyl(phenyl)amino)butyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3an)

The title compound was prepared according to the general procedure as a yellow oil (7% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.30 (m, 1H), 7.22-7.17 (m, 5H), 6.67 (d, J = 8.5 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 4.16 (t, J = 7.5 Hz, 1H), 3.37 (q, J = 7.0 Hz, 2H), 3.28 (t, J = 7.5 Hz, 2H), 2.98-2.92 (m, 2H), 2.72-2.63 (m, 1H), 2.08-1.99 (m, 1H), 1.73-1.59 (m, 2H), 1.52-1.43 (m, 4H), 1.33-1.30 (m, 3H), 1.22 (s, 9H), 1.14 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.1, 146.1, 129.4, 127.0, 126.7, 123.7, 123.1, 115.5, 112.2, 56.7, 51.0, 50.6, 45.1, 42.4, 34.8, 30.7, 29.9, 27.9, 25.3, 12.5. HRMS (ESI$^+$): calcd for $C_{25}H_{37}N_2$ $[M+H]^+$ 365.2951, found 365.2950.



(*Trans*)-*N*-(*tert*-butyl)-5-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ba)

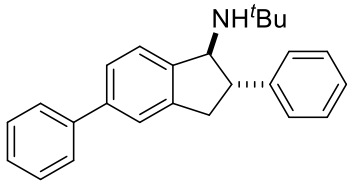
The title compound was prepared according to the general procedure as a yellowish oil (68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.18 (m, 6H), 7.05 (d, J = 7.5 Hz, 1H), 7.03 (s, 1H), 4.20 (d, J = 6.5 Hz, 1H), 3.38 (dd, J = 16.0, 8.5 Hz, 1H), 3.21 (q, J = 7.5 Hz, 1H), 2.97 (dd, J = 16.0, 7.5 Hz, 1H), 2.35 (s, 3H), 1.60 (brs, 1H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.8, 144.0, 142.6, 137.3, 128.5, 127.9, 127.8, 126.4, 125.2, 124.0, 66.1, 57.5, 50.9, 39.4, 30.4, 21.4. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2059.



(*Trans*)-*N*,5-di-tert-butyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ca)

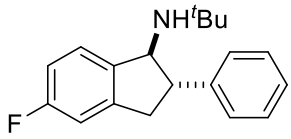
The title compound was prepared according to the general procedure as a pale yellow solid (58% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.22 (m, 8H), 4.26 (d, J =

7.0 Hz, 1H), 3.39 (dd, *J* = 15.5, 8.0 Hz, 1H), 3.23 (q, *J* = 7.5 Hz, 1H), 3.05 (dd, *J* = 16.0, 8.5 Hz, 1H), 1.57 (brs, 1H), 1.36 (s, 9H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.7, 144.6, 144.1, 142.0, 128.5, 128.0, 126.5, 124.2, 123.7, 121.4, 66.0, 58.0, 50.8, 39.6, 34.8, 31.7, 30.5. HRMS (ESI^+): calcd for $C_{23}H_{32}N$ $[M+H]^+$ 322.2529, found 322.2530.



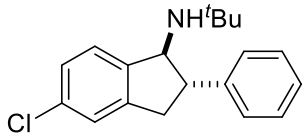
(*Trans*)-*N*-(*tert*-butyl)-2,5-diphenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3da)

The title compound was prepared according to the general procedure as a pale yellow solid (64% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.5 Hz, 2H), 7.49-7.42 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.35-7.27 (m, 5H), 7.24-7.20 (m, 1H), 4.29 (d, *J* = 6.5 Hz, 1H), 3.45 (dd, *J* = 15.5, 8.0 Hz, 1H), 3.26 (q, *J* = 7.5 Hz, 1H), 3.08 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.70 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.2, 144.4, 143.0, 141.6, 140.9, 128.8, 128.5, 127.9, 127.3, 127.2, 126.6, 126.3, 124.6, 123.3, 66.1, 57.7, 51.0, 39.4, 30.4. HRMS (ESI^+): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2217.



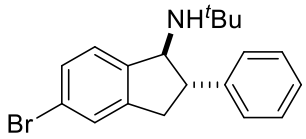
(*Trans*)-*N*-(*tert*-butyl)-5-fluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ea)

The title compound was prepared according to the general procedure as a yellowish oil (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (t, *J* = 7.5 Hz, 2H), 7.25-7.20 (m, 4H), 6.94-6.88 (m, 2H), 4.19 (d, *J* = 6.5 Hz, 1H), 3.37 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.21 (q, *J* = 7.5 Hz, 1H), 2.99 (dd, *J* = 16.0, 7.5 Hz, 1H), 1.40 (brs, 1H), 0.96 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 161.8 (d, *J* = 245.7 Hz), 144.3 (d, *J* = 8.72 Hz), 144.1, 142.5 (d, *J* = 2.6 Hz), 128.5, 127.8, 126.7, 125.44, 125.4 (d, *J* = 8.72 Hz), 113.9 (d, *J* = 21.42 Hz), 111.3 (d, *J* = 21.42 Hz), 65.5, 57.8, 50.9, 39.3, 39.2, 30.4. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −116.06. HRMS (ESI^+): calcd for $C_{19}H_{23}FN$ $[M+H]^+$ 284.1809, found 28401808.



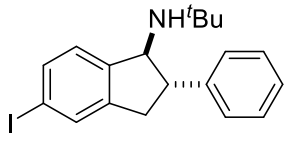
(*Trans*)-*N*-(*tert*-butyl)-5-chloro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3fa)

The title compound was prepared according to the general procedure as a yellowish oil (87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.5 Hz, 2H), 7.25-7.19 (m, 6H), 4.18 (d, J = 6.5 Hz, 1H), 3.36 (dd, J = 16.0, 8.0 Hz, 1H), 3.20 (q, J = 7.5 Hz, 1H), 2.99 (dd, J = 16.5, 8.0 Hz, 1H), 1.47 (brs, 1H), 0.95 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.6, 144.1, 143.9, 133.1, 128.6, 127.8, 127.2, 126.7, 125.5, 124.6, 65.6, 57.5, 50.9, 39.1, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{23}ClN$ $[M+H]^+$ 300.1514, found 300.1513.



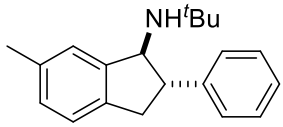
(*Trans*)-*5*-bromo-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ga)

The title compound was prepared according to the general procedure as a pale yellow solid (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.35 (m, 2H), 7.28 (t, J = 7.0 Hz, 2H), 7.23-7.20 (m, 3H), 7.16 (d, J = 8.0 Hz, 1H), 4.17 (d, J = 6.5 Hz, 1H), 3.36 (dd, J = 16.5, 8.5 Hz, 1H), 3.19 (q, J = 7.5 Hz, 1H), 3.00 (dd, J = 16.0, 8.0 Hz, 1H), 1.48 (brs, 1H), 0.95 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.1, 144.5, 143.8, 130.1, 128.6, 127.8, 127.6, 126.7, 126.0, 121.2, 65.7, 57.5, 50.9, 39.0, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{23}BrN$ $[M+H]^+$ 344.1008 and 346.0988, found 344.1009 and 346.0989.



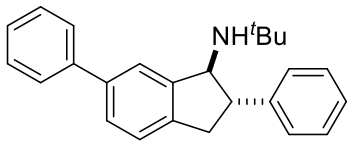
(*Trans*)-*N*-(*tert*-butyl)-5-iodo-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ha)

The title compound was prepared according to the general procedure as a pale yellow solid (91% yield). Recrystallization from chloroform solution gave single crystals suitable for X-ray analysis. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.23-7.20 (m, 3H), 7.05 (d, J = 8.0 Hz, 1H), 4.17 (d, J = 7.0 Hz, 1H), 3.35 (dd, J = 16.0, 8.0 Hz, 1H), 3.17 (q, J = 7.0 Hz, 1H), 2.99 (dd, J = 16.0, 8.0 Hz, 1H), 1.45 (brs, 1H), 0.94 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.9, 144.8, 143.8, 136.1, 133.6, 128.6, 127.8, 126.7, 126.4, 90.8, 65.8, 57.4, 50.9, 38.9, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{23}IN$ $[M+H]^+$ 392.0870, found 392.0870.



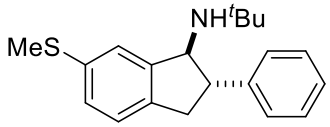
(*Trans*)-*N*-(*tert*-butyl)-6-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ia)

The title compound was prepared according to the general procedure as a pale yellow solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.5 Hz, 1H), 4.24 (d, J = 6.5 Hz, 1H), 3.40 (dd, J = 15.5, 8.0 Hz, 1H), 3.23 (q, J = 7.5 Hz, 1H), 3.00 (dd, J = 16.0, 7.5 Hz, 1H), 2.4 (s, 3H), 1.56 (brs, 1H), 1.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.0, 144.7, 139.3, 136.7, 128.5, 128.4, 127.9, 126.5, 124.9, 124.2, 66.2, 57.6, 51.0, 39.1, 30.4, 21.6. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



(*Trans*)-*N*-(*tert*-butyl)-2,6-diphenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ja)

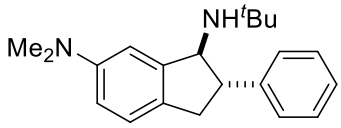
The title compound was prepared according to the general procedure as a pale yellow solid (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.0 Hz, 2H), 7.52 (s, 1H), 7.47-7.42 (m, 2H), 7.35-7.27 (m, 6H), 7.23-7.20 (m, 1H), 4.30 (d, J = 6.5 Hz, 1H), 3.43 (dd, J = 16.0, 8.0 Hz, 1H), 3.26 (q, J = 7.5 Hz, 1H), 3.06 (dd, J = 16.0, 7.5 Hz, 1H), 1.54 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 144.4, 141.8, 141.5, 140.5, 128.9, 128.5, 127.9, 127.3, 127.1, 126.7, 126.6, 124.8, 123.1, 66.3, 57.8, 51.0, 39.1, 30.5. HRMS (ESI$^+$): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2215.



(*Trans*)-*N*-(*tert*-butyl)-6-(methylthio)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ka)

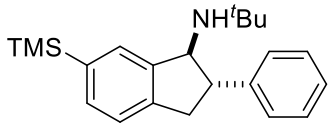
The title compound was prepared according to the general procedure as a colorless oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.5 Hz, 2H), 7.25-7.19 (m, 4H), 7.17-7.12 (m, 2H), 4.20 (d, J = 7.0 Hz, 1H), 3.34 (dd, J = 16.0, 8.0 Hz, 1H), 3.19 (q, J = 7.5 Hz, 1H), 2.98 (dd, J = 15.5, 8.0 Hz, 1H), 2.50 (s, 3H), 1.46 (brs, 1H), 0.96 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.0, 144.2, 139.7, 136.6, 128.5, 127.9,

126.64, 126.62, 124.9, 123.4, 66.2, 57.7, 50.9, 38.9, 30.5, 16.9. HRMS (ESI^+): calcd for $C_{20}H_{26}NS$ $[M+H]^+$ 312.1780, found 312.1780.



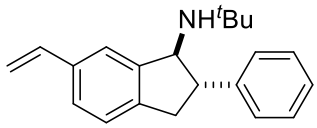
(*Trans*)-*N*^{1}-(*tert*-butyl)-*N*^{6},*N*^{6}-dimethyl-2-phenyl-2,3-dihydro-1H-indene-1,6-diamine (*trans*-3la)

The title compound was prepared according to the general procedure as a yellow oil (70% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29-7.24 (m, 4H), 7.19 (t, J = 6.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 1.5 Hz, 1H), 6.67 (dd, J = 8.5, 2.5 Hz, 1H), 4.19 (d, J = 6.5 Hz, 1H), 3.32 (dd, J = 15.5, 8.0 Hz, 1H), 3.20 (q, J = 7.5 Hz, 1H), 2.94-2.90 (m, 7H), 1.60 (brs, 1H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.8, 147.9, 145.0, 130.7, 128.4, 127.9, 126.4, 124.8, 112.9, 109.0, 66.6, 57.8, 50.9, 41.4, 38.6, 30.5. HRMS (ESI^+): calcd for $C_{21}H_{29}N_2$ $[M+H]^+$ 309.2325, found 309.2325.



(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-6-(trimethylsilyl)-2,3-dihydro-1H-inden-1-amine (*trans*-3ma)

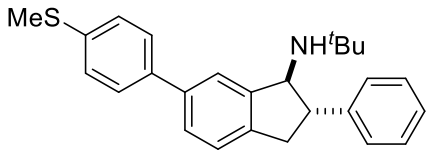
The title compound was prepared according to the general procedure as a colorless oil (88% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (s, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.30-7.19 (m, 6H), 4.24 (d, J = 7.0 Hz, 1H), 3.37 (dd, J = 16.0, 8.0 Hz, 1H), 3.19 (q, J = 8.0 Hz, 1H), 3.03 (dd, J = 16.0, 8.0 Hz, 1H), 1.42 (brs, 1H), 0.97 (s, 9H), 0.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.4, 144.3, 143.1, 139.0, 132.6, 129.1, 128.5, 127.9, 126.5, 124.0, 66.2, 57.6, 50.8, 39.3, 30.5, -0.8. HRMS (ESI^+): calcd for $C_{22}H_{32}NSi$ $[M+H]^+$ 338.2299, found 338.2300.



(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-6-vinyl-2,3-dihydro-1H-inden-1-amine (*trans*-3na)

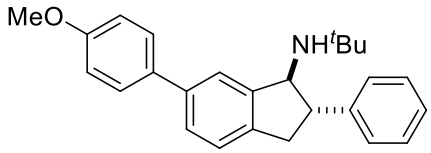
The title compound was prepared according to the general procedure as a colorless oil (80% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 7.30-7.27 (m, 3H),

7.23-7.19 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.75 (dd, *J* = 18.0, 11.0 Hz, 1H), 5.71 (d, *J* = 17.5 Hz, 1H), 5.20 (d, *J* = 10.5 Hz, 1H), 4.23 (d, *J* = 6.5 Hz, 1H), 3.39 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.22 (q, *J* = 7.5 Hz, 1H), 3.00 (dd, *J* = 16.0, 7.5 Hz, 1H), 1.56 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 144.5, 142.3, 137.2, 136.8, 128.5, 127.8, 126.6, 125.9, 124.6, 122.0, 113.0, 66.1, 57.5, 51.0, 39.2, 30.4. HRMS (ESI^+): calcd for $C_{21}H_{26}N$ $[M+H]^+$ 292.2060, found 292.2060.



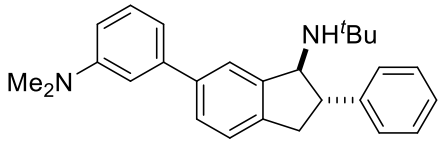
(*Trans*)-*N*-(*tert*-butyl)-6-(4-(methylthio)phenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3oa)

The title compound was prepared according to the general procedure as a white solid (89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.34-7.20 (m, 8H), 4.28 (d, *J* = 7.0 Hz, 1H), 3.42 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.24 (q, *J* = 7.5 Hz, 1H), 3.06 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.52 (s, 3H), 1.44 (brs, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 144.3, 141.4, 139.8, 138.7, 137.3, 128.5, 127.9, 127.6, 127.2, 126.6, 126.4, 124.8, 122.8, 66.2, 57.8, 50.9, 39.1, 30.5, 16.2. HRMS (ESI^+): calcd for $C_{26}H_{30}NS$ $[M+H]^+$ 388.2093, found 388.2090.



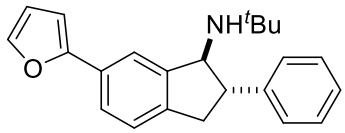
(*Trans*)-*N*-(*tert*-butyl)-6-(4-methoxyphenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3pa)

The title compound was prepared according to the general procedure as a colorless oil (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.5 Hz, 2H), 7.47 (s, 1H), 7.41 (d, *J* = 6.0 Hz, 1H), 7.31-7.20 (m, 7H), 6.97 (d, *J* = 9.0 Hz, 1H), 4.29 (d, *J* = 6.5 Hz, 1H), 3.85 (s, 3H), 3.42 (dd, *J* = 15.5, 8.0 Hz, 1H), 3.26 (q, *J* = 8.0 Hz, 1H), 3.05 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.63 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.1, 147.7, 144.5, 140.9, 140.1, 134.4, 128.5, 128.3, 127.9, 126.6, 126.3, 124.7, 122.7, 114.3, 66.3, 57.7, 55.5, 51.0, 39.1, 30.5. HRMS (ESI^+): calcd for $C_{26}H_{30}NO$ $[M+H]^+$ 372.2322, found 372.2321.



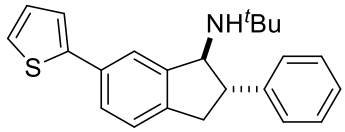
(*Trans*)-*N*-(*tert*-butyl)-6-(3-(dimethylamino)phenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3qa)

The title compound was prepared according to the general procedure as a yellow oil (93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.32-7.20 (m, 7H), 6.96-6.94 (m, 2H), 6.73 (dd, J = 8.0, 2.5 Hz, 1H), 4.29 (d, J = 7.0 Hz, 1H), 3.43 (dd, J = 16.0, 8.0 Hz, 1H), 3.26 (q, J = 7.5 Hz, 1H), 3.04 (dd, J = 16.0, 7.5 Hz, 1H), 3.00 (s, 6H), 1.53 (brs, 1H), 0.98 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.1, 147.5, 144.5, 142.9, 141.5, 141.3, 129.5, 128.5, 127.9, 126.9, 126.5, 124.6, 123.3, 116.1, 111.8, 111.6, 66.3, 57.8, 50.9, 40.9, 39.1, 30.5. HRMS (ESI$^+$): calcd for $C_{27}H_{33}N_2$ $[M+H]^+$ 385.2638, found 385.2640.



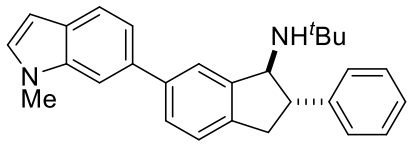
(*Trans*)-*N*-(*tert*-butyl)-6-(furan-2-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ra)

The title compound was prepared according to the general procedure as a yellowish oil (82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 1.0 Hz, 1H), 7.30-7.19 (m, 6H), 6.61 (d, J = 3.5 Hz, 1H), 6.46 (dd, J = 4.0, 2.0 Hz, 1H), 4.26 (d, J = 6.5 Hz, 1H), 3.41 (dd, J = 16.0, 8.0 Hz, 1H), 3.23 (q, J = 7.5 Hz, 1H), 3.01 (dd, J = 16.5, 7.5 Hz, 1H), 1.42 (brs, 1H), 1.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.6, 147.6, 144.5, 141.8, 141.7, 130.2, 128.5, 127.9, 126.6, 124.8, 123.5, 119.8, 111.7, 104.5, 66.2, 57.5, 51.0, 39.2, 30.5. HRMS (ESI$^+$): calcd for $C_{23}H_{26}NO$ $[M+H]^+$ 332.2009, found 332.2010.



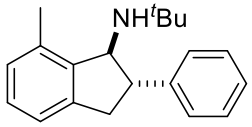
(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-6-(thiophen-2-yl)-2,3-dihydro-1H-inden-1-amine (*trans*-3sa)

The title compound was prepared according to the general procedure as a white solid (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.31-7.20 (m, 8H), 7.06 (t, J = 4.5 Hz, 1H), 4.26 (d, J = 6.5 Hz, 1H), 3.40 (dd, J = 16.0, 8.0 Hz, 1H), 3.23 (q, J = 7.5 Hz, 1H), 3.03 (dd, J = 16.0, 8.0 Hz, 1H), 1.46 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 145.1, 144.3, 141.8, 133.6, 128.5, 128.0, 127.9, 126.6, 125.6, 124.9, 124.4, 122.9, 122.1, 66.1, 57.6, 51.0, 39.1, 30.5. HRMS (ESI$^+$): calcd for $C_{23}H_{26}NS$ $[M+H]^+$ 348.1780, found 348.1781.



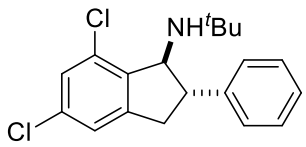
(*Trans*)-*N*-(*tert*-butyl)-6-(1-methyl-1H-indol-6-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ta)

The title compound was prepared according to the general procedure as a colorless oil (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (s, 1H), 7.57 (s, 1H), 7.53-7.48 (m, 2H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.31-7.26 (m, 5H), 7.23-7.20 (m, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 6.5 Hz, 1H), 3.44 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.27 (q, *J* = 7.5 Hz, 1H), 3.06 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.60 (brs, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.5, 144.7, 141.9, 140.4, 136.3, 133.4, 129.6, 129.1, 128.5, 127.9, 127.0, 126.5, 124.6, 123.3, 121.6, 119.4, 109.5, 101.4, 66.4, 57.8, 50.9, 39.1, 33.1, 30.5. HRMS (ESI$^+$): calcd for $C_{28}H_{31}N_2$ $[M+H]^+$ 395.2482, found 395.2484.



(*Trans*)-*N*-(*tert*-butyl)-7-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3ua)

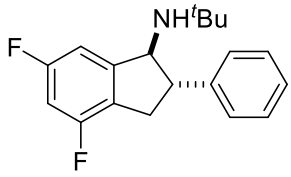
The title compound was prepared according to the general procedure as a yellowish oil (60% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22-7.15 (m, 4H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 4.35 (s, 1H), 3.77 (dd, *J* = 16.5, 8.5 Hz, 1H), 3.46 (d, *J* = 8.0 Hz, 1H), 2.83 (d, *J* = 16.5 Hz, 1H), 2.38 (s, 3H), 1.39 (brs, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.3, 144.3, 144.1, 134.4, 128.5, 128.4, 128.3, 126.8 , 126.1, 122.3, 65.4, 53.2, 51.8, 39.7, 30.5, 19.1. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



(*Trans*)-*N*-(*tert*-butyl)-5,7-dichloro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3va)

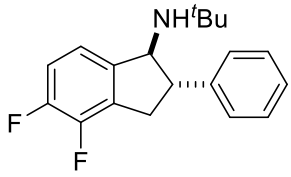
The title compound was prepared according to the general procedure as a colorless oil (55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22-7.16 (m, 4H), 7.14 (s, 1H), 6.93 (d, *J* = 7.0 Hz, 2H), 4.39 (s, 1H), 3.78 (dd, *J* = 16.5, 8.0 Hz, 1H), 3.46 (d, *J* = 8.5 Hz, 1H), 2.83 (d, *J* = 16.5 Hz, 1H), 1.43 (brs, 1H), 1.22 (s, 9H); ^{13}C NMR (126 MHz,

$CDCl_3$): δ = 148.2, 145.9, 142.2, 134.7, 131.4, 128.8, 127.5, 126.8, 126.5, 123.8, 65.5, 53.1, 52.1, 40.3, 30.3. HRMS (ESI^+): calcd for $C_{19}H_{22}Cl_2N$ $[M+H]^+$ 334.1124, found 334.1125.



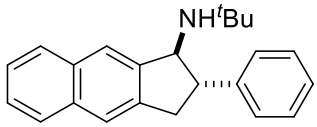
(*Trans*)-*N*-(*tert*-butyl)-4,6-difluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3wa)

The title compound was prepared according to the general procedure as a colorless oil (60% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30 (t, J = 7.5 Hz, 2H), 7.27-7.22 (m, 3H), 6.84 (d, J = 8.0 Hz, 1H), 6.65 (t, J = 9.0 Hz, 1H), 4.21 (d, J = 7.5 Hz, 1H), 3.37 (dd, J = 16.0, 8.5 Hz, 1H), 3.19 (q, J = 8.0 Hz, 1H), 2.95 (dd, J = 16.0, 8.5 Hz, 1H), 1.45 (brs, 1H), 0.92 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.8 (dd, J = 247.0, 10.1 Hz), 158.4 (dd, J = 249.5, 12.6 Hz), 151.9 (t, J = 7.6 Hz), 143.0, 128.7, 127.9, 127.0, 123.2 (dd, J = 17.64, 2.52 Hz), 107.3 (dd, J = 22.68, 2.52 Hz), 102.40 (dd, J = 26.3, 23.8 Hz), , 66.2 (d, J = 2.52 Hz), 57.8, 50.9, 34.3, 30.4. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −112.08 (s, 1F), −115.11 (s, 1F). HRMS (ESI^+): calcd for $C_{19}H_{22}F_2N$ $[M+H]^+$ 302.1715, found 302.1715.



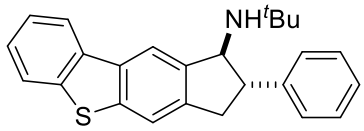
(*Trans*)-*N*-(*tert*-butyl)-4,5-difluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3xa)

The title compound was prepared according to the general procedure as a colorless oil (92% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.32 (m, 2H), 7.28-7.25 (m, 3H), 7.09-7.02 (m, 2H), 4.23 (d, J = 6.5 Hz, 1H), 3.49 (dd, J = 16.0, 8.0 Hz, 1H), 3.26 (q, J = 8.0 Hz, 1H), 3.03 (dd, J = 16.5, 8.0 Hz, 1H), 1.50 (brs, 1H), 0.97 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.0 (dd, J = 247.0, 12.6 Hz), 146.5 (dd, J = 249.5, 13.9 Hz), 144.8, 143.3, 130.4 (d, J = 15.1 Hz), 128.7, 127.8, 126.9, 119.6 (m), 116.2 (d, J = 18.9 Hz), 65.9 (d, J = 2.52 Hz), 57.8, 50.9, 34.8 (d, J = 2.52 Hz), 30.4. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −141.31 (m, 1F), −143.22 (m, 1F). HRMS (ESI^+): calcd for calcd for $C_{19}H_{22}F_2N$ $[M+H]^+$ 302.1715, found 302.1715.



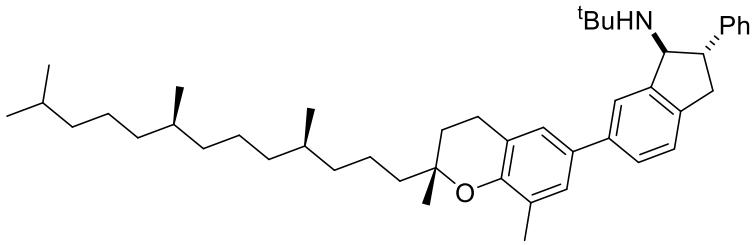
(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-amine (*trans*-3ya)

The title compound was prepared according to the general procedure as a pale yellow solid (63% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84-7.78 (m, 2H), 7.72 (s, 1H), 7.65 (s, 1H), 7.43-7.40 (m, 2H), 7.31-7.29 (m, 4H), 7.24-7.21 (m, 1H), 4.34 (d, *J* = 7.0 Hz, 1H), 3.52 (dd, *J* = 15.5, 7.0 Hz, 1H), 3.29-3.08 (m, 2H), 1.56 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.7, 143.8, 141.1, 133.7, 133.4, 128.5, 128.1, 128.0, 127.6, 126.7, 125.5, 125.1, 122.6, 122.4, 65.7, 57.7, 51.0, 38.6, 30.5. HRMS (ESI$^+$): calcd for $C_{23}H_{26}N$ $[M+H]^+$ 316.2060, found 316.2057.



(*Trans*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-benzo[b]indeno[5,6-d]thiophen-1-amine (*trans*-3za)

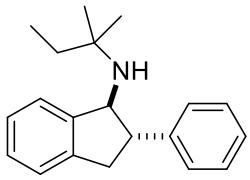
The title compound was prepared according to the general procedure as a pale yellow solid (31% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16-8.14 (m, 1H), 8.06 (s, 1H), 7.84-7.82 (m, 1H), 7.67 (s, 1H), 7.45-7.41 (m, 2H), 7.31-7.26 (m, 4H), 7.24-7.21 (m, 1H), 4.36 (d, *J* = 6.5 Hz, 1H), 3.53 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.31 (q, *J* = 7.5 Hz, 1H), 3.16 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.53 (brs, 1H), 1.06 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.6, 144.2, 142.1, 139.6, 139.1, 135.7, 128.6, 127.9, 126.7, 126.4, 124.3, 123.0, 121.4, 118.3, 117.2, 65.8, 57.8, 51.1, 39.1, 30.6. HRMS (ESI$^+$): calcd for $C_{25}H_{26}NS$ $[M+H]^+$ 372.1780, found 372.1780.



(*Trans*)-*N*-(*tert*-butyl)-6-((*R*)-2,8-dimethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3aaa)

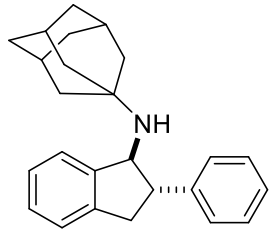
The title compound was prepared according to the general procedure as a yellowish oil (68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (s, 1H), 7.39 (d, *J* = 7.5, 1H),

7.30-7.20 (m, 7H), 7.13 (s, 1H), 4.28 (d, *J* = 6.0 Hz, 1H), 3.42 (dd, *J* = 16.0, 8.5 Hz, 1H), 3.25 (q, *J* = 7.5 Hz, 1H), 3.02 (dd, *J* = 16.0, 7.5 Hz, 1H), 2.87-2.78 (m, 2H), 2.23 (s, 3H), 1.89-1.76 (m, 2H), 1.61-1.07 (m, 25H), 0.99 (s, 9H), 0.87-0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.8, 147.5, 144.8, 140.8, 140.5, 132.5, 128.5, 127.9, 127.3, 126.7, 126.5, 126.4, 125.7, 124.6, 122.6, 120.8, 76.4, 66.4, 57.7, 50.9, 40.5, 40.4, 39.5, 39.1, 37.60, 37.58, 37.4, 33.0, 32.9, 31.4, 30.5, 28.1, 25.0, 24.6, 24.50, 24.48, 22.9, 22.8, 22.7, 21.2, 19.9, 19.8, 16.4. HRMS (ESI$^+$): calcd for $C_{46}H_{68}NO$ $[M+H]^+$ 650.5295, found 650.5336.



(*Trans*)-*N*-(*tert*-pentyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-3aba)

The title compound was prepared according to the general procedure as a colorless oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 6.5 Hz, 1H), 7.29-7.18 (m, 8H), 4.27 (d, *J* = 6.0 Hz, 1H), 3.42 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.22 (q, *J* = 7.5 Hz, 1H), 3.00 (dd, *J* = 16.0, 7.5 Hz, 1H), 1.42 (brs, 1H), 1.35-1.25 (m, 2H), 0.97 (s, 9H), 0.80-0.77 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 144.8, 142.4, 128.5, 127.8, 127.5, 127.0, 126.5, 124.5, 124.4, 65.8, 57.4, 53.2, 39.6, 35.5, 27.5, 27.4, 8.8. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.

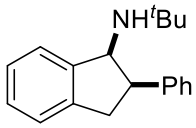


(*Trans*)-*N*-2-phenyl-2,3-dihydro-1H-inden-1-yl)adamantan-1-amine (*trans*-3aca)

The title compound was prepared according to the general procedure as a colorless oil (97% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.0 Hz, 1H), 7.34-7.24 (m, 8H), 4.39 (d, *J* = 7.0 Hz, 1H), 3.43 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.21 (q, *J* = 7.5 Hz, 1H), 3.04 (dd, *J* = 15.5, 7.5 Hz, 1H), 2.00 (s, 2H), 1.63-1.45 (m, 12H), 1.40 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.3, 144.4, 142.3, 128.5, 127.9, 127.4, 126.5, 124.4, 64.0, 57.7, 50.7, 44.3, 39.4, 36.7, 29.8. HRMS (ESI$^+$): calcd for $C_{25}H_{30}N$ $[M+H]^+$ 344.2373, found 344.2373.

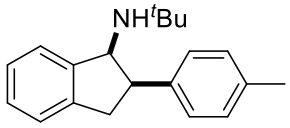
General procedure for the Yttrium-catalyzed *cis* diastereoselective [3+2] annulation of aldimines with alkenes

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 0.02 mmol) was added to a stirred toluene solution (2.0 mL) of **Y-3** (9.6 mg, 0.02 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimines **1** (0.2 mmol) and olefins **2** (0.6 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 20:1) to afford the desired products *cis*-**3**.



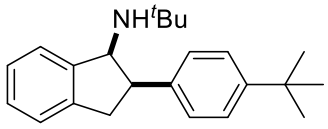
(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3aa)

The title compound was prepared according to the general procedure as a yellowish oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.0 Hz, 1H), 7.28-7.21 (m, 6H), 7.00 (d, J = 6.5 Hz, 2H), 4.54 (d, J = 7.0 Hz, 1H), 3.74 (td, J = 7.0, 2.5 Hz, 1H), 3.35 (dd, J = 15.5, 7.5 Hz, 1H), 3.13 (d, J = 15.5 Hz, 1H), 1.16 (brs, 1H), 1.07 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 142.5, 141.8, 129.0, 128.4, 127.0, 126.9, 126.7, 124.8, 124.3, 61.1, 52.0, 50.8, 38.6, 30.3. HRMS (ESI$^+$): calcd for $C_{19}H_{24}N$ $[M+H]^+$ 266.1903, found 266.1902.



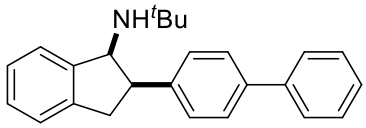
(*Cis*)-*N*-(*tert*-butyl)-2-(*p*-tolyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ab)

The title compound was prepared according to the general procedure as a yellowish oil (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, J = 7.0 Hz, 1H), 7.24-7.18 (m, 3H), 6.98 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 7.5 Hz, 2H), 4.48 (d, J = 7.5 Hz, 1H), 3.67 (td, J = 7.5, 3.0 Hz, 1H), 3.30 (dd, J = 16.0, 8.0 Hz, 1H), 3.07 (dd, J = 15.5, 2.5 Hz, 1H), 2.27 (s, 3H), 1.33 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.0, 141.8, 139.3, 136.2, 129.1, 128.8, 126.9, 126.8, 124.8, 124.3, 61.1, 51.6, 50.8, 38.7, 30.4, 21.1. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



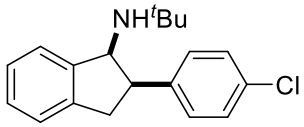
(*Cis*)-*N*-(*tert*-butyl)-2-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ac)

The title compound was prepared according to the general procedure as a yellowish oil (65% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.5 Hz, 1H), 7.28-7.21 (m, 6H), 6.90 (d, J = 8.0 Hz, 1H), 4.51 (d, J = 7.5 Hz, 1H), 3.71 (td, J = 7.5, 2.5 Hz, 1H), 3.33 (dd, J = 16.0, 7.5 Hz, 1H), 3.13 (dd, J = 16.0, 2.5 Hz, 1H), 1.50 (brs, 1H), 1.28 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.5, 148.0, 141.9, 139.1, 128.5, 126.9, 126.8, 125.3, 124.8, 124.2, 61.2, 51.4, 50.8, 38.5, 34.5, 31.5, 30.3. HRMS (ESI$^+$): calcd for $C_{23}H_{24}N$ $[M+H]^+$ 322.2529, found 322.2529.



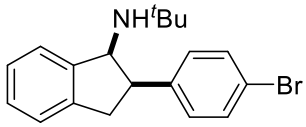
(*Cis*)-2-([1,1'-biphenyl]-4-yl)-*N*-(tert-butyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ad)

The title compound was prepared according to the general procedure as a pale yellow solid (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.0 Hz, 2H), 7.43-7.36 (m, 5H), 7.32-7.21 (m, 4H), 7.03 (d, J = 8.0 Hz, 1H), 4.54 (d, J = 7.0 Hz, 1H), 3.73 (td, J = 7.0, 2.5 Hz, 1H), 3.32 (dd, J = 16.0, 7.5 Hz, 1H), 3.12 (dd, J = 16.0, 2.5 Hz, 1H), 1.15 (brs, 1H), 1.06 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 141.7, 141.6, 141.0, 139.5, 129.4, 128.8, 127.2, 127.1, 127.03, 127.01, 126.9, 124.8, 124.3, 61.2, 51.7, 50.8, 38.6, 30.4. HRMS (ESI$^+$): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2216.



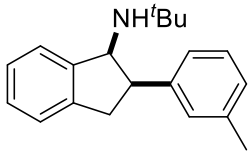
(*Cis*)-*N*-(*tert*-butyl)-2-(4-chlorophenyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ae)

The title compound was prepared according to the general procedure as a yellowish oil (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, J = 7.0 Hz, 2H), 7.26-7.19 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 4.49 (d, J = 7.0 Hz, 1H), 3.63 (td, J = 7.0, 3.0 Hz, 1H), 3.26 (dd, J = 16.0, 7.5 Hz, 1H), 3.03 (dd, J = 16.0, 3.5 Hz, 1H), 1.20 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.5, 141.5, 141.1, 132.3, 130.4, 128.3, 127.2, 127.0, 124.8, 124.4, 61.1, 51.6, 50.8, 38.5, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{23}ClN$ $[M+H]^+$ 300.1514, found 300.1515.



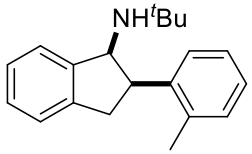
(*Cis*)-2-(4-bromophenyl)-*N*-(*tert*-butyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3af)

The title compound was prepared according to the general procedure as a yellowish oil (55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, J = 7.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.26-7.19 (m, 3H), 6.86 (d, J = 8.0 Hz, 2H), 4.49 (d, J = 7.0 Hz, 1H), 3.62 (td, J = 7.5, 3.5 Hz, 1H), 3.26 (dd, J = 15.5, 7.5 Hz, 1H), 3.02 (dd, J = 16.0, 3.5 Hz, 1H), 1.20 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.5, 141.6, 141.5, 131.2, 130.8, 127.2, 127.0, 124.8, 124.4, 120.4, 61.0, 51.6, 50.8, 38.5, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{23}BrN$ $[M+H]^+$ 344.1008 and 346.0988, found 344.1008 and 346.0988.



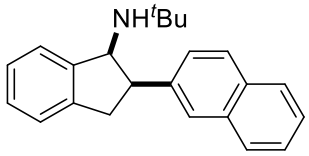
(*Cis*)-*N*-(*tert*-butyl)-2-(*m*-tolyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ag)

The title compound was prepared according to the general procedure as a colorless oil (73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.5 Hz, 1H), 7.28-7.24 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.52 (d, J = 7.0 Hz, 1H), 3.69 (td, J = 7.5, 2.5 Hz, 1H), 3.32 (dd, J = 15.5, 7.5 Hz, 1H), 3.12 (dd, J = 16.0, 2.5 Hz, 1H), 2.28 (s, 3H), 1.20 (brs, 1H), 1.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.0, 142.3, 141.8, 137.9, 129.8, 128.3, 127.5, 127.0, 126.8, 125.9, 124.8, 124.3, 61.1, 51.8, 50.8, 38.6, 30.4, 21.7. HRMS (ESI$^+$): calcd for 280.2060, found 280.2060.



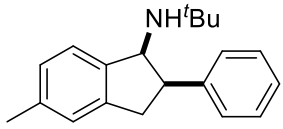
(*Cis*)-*N*-(*tert*-butyl)-2-(*o*-tolyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ah)

The title compound was prepared according to the general procedure as a colorless oil (92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38 (d, J = 7.0 Hz, 1H), 7.25-7.18 (m, 3H), 7.14 (d, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 4.44 (d, J = 6.5 Hz, 1H), 3.97 (q, J = 7.0 Hz, 1H), 3.16 (dd, J = 15.5, 7.5 Hz, 1H), 3.10 (dd, J = 15.5, 6.0 Hz, 1H), 2.39 (s, 3H), 1.23 (brs, 1H), 0.92 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.4, 142.1, 140.2, 136.5, 130.4, 127.9, 127.0, 126.8, 126.4, 125.8, 124.8, 124.5, 59.4, 50.6, 46.7, 38.0, 30.1, 20.4. HRMS (ESI$^+$): calcd for 280.2060, found 280.2060.



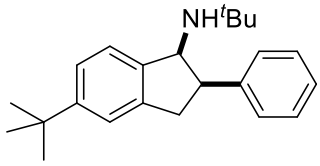
(*Cis*)-*N*-(*tert*-butyl)-2-(naphthalen-2-yl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ai)

The title compound was prepared according to the general procedure as a yellowish oil (75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.5 Hz, 2H), 7.57 (s, 1H), 7.46-7.41 (m, 3H), 7.33-7.28 (m, 2H), 7.23-7.15 (m, 3H), 7.00 (d, J = 7.0 Hz, 2H), 4.55 (d, J = 7.5 Hz, 1H), 3.73 (td, J = 7.5, 3.0 Hz, 1H), 3.33 (dd, J = 16.0, 7.5 Hz, 1H), 3.11 (dd, J = 16.0, 2.5 Hz, 1H), 1.12 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.7, 142.4, 141.9, 141.0, 140.2, 129.0, 128.8, 128.4, 127.3, 127.0, 126.8, 126.2, 124.6, 123.6, 61.2, 52.2, 50.8, 38.3, 30.4. HRMS (ESI$^+$): calcd for $C_{23}H_{26}N$ $[M+H]^+$ 316.2060, found 316.2061.



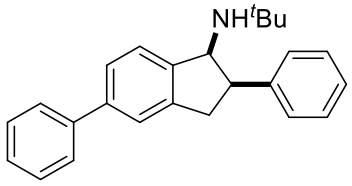
(*Cis*)-*N*-(*tert*-butyl)-5-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ba)

The title compound was prepared according to the general procedure as a pale yellow solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.14 (m, 4H), 7.05 (m, 2H), 6.99 (d, J = 7.0 Hz, 2H), 4.46 (d, J = 7.0 Hz, 1H), 3.66 (td, J = 7.5, 3.5 Hz, 1H), 3.24 (dd, J = 15.5, 7.5 Hz, 1H), 3.05 (dd, J = 16.0, 3.0 Hz, 1H), 2.36 (s, 3H), 1.17 (brs, 1H), 1.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.0, 142.6, 142.0, 136.7, 129.1, 128.3, 127.6, 126.6, 125.1, 124.6, 60.8, 52.1, 50.7, 38.4, 30.3, 21.5. HRMS (ESI$^+$): calcd for 280.2060, found 280.2060.



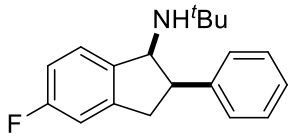
(*Cis*)-*N*,*5*-di-tert-butyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ca)

The title compound was prepared according to the general procedure as a yellowish oil (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.26 (m, 3H), 7.22-7.15 (m, 3H), 7.01 (d, J = 7.0 Hz, 2H), 4.46 (d, J = 7.0 Hz, 1H), 3.68 (td, J = 7.5, 3.5 Hz, 1H), 3.26 (dd, J = 15.5, 7.5 Hz, 1H), 3.09 (dd, J = 16.0, 3.5 Hz, 1H), 1.34 (s, 9H), 1.11 (brs, 1H), 0.99 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.3, 145.0, 142.7, 141.7, 129.1, 128.3, 126.6, 124.3, 124.0, 121.3, 60.7, 52.1, 50.7, 38.7, 34.8, 31.8, 30.3. HRMS (ESI$^+$): calcd for $C_{23}H_{24}N$ $[M+H]^+$ 322.2529, found 322.2527.



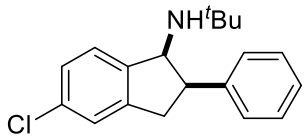
(*Cis*)-*N*-(*tert*-butyl)-2,5-diphenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3da)

The title compound was prepared according to the general procedure as a yellowish oil (91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.5 Hz, 2H), 7.49-7.40 (m, 5H), 7.31 (t, J = 7.0 Hz, 1H), 7.22-7.16 (m, 3H), 7.01 (d, J = 7.0 Hz, 2H), 4.54 (d, J = 7.5 Hz, 1H), 3.73 (td, J = 7.5, 3.0 Hz, 1H), 3.35 (dd, J = 16.0, 8.0 Hz, 1H), 3.14 (dd, J = 16.0, 3.0 Hz, 1H), 1.11 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 142.5, 142.4, 141.8, 140.4, 129.0, 128.8, 128.4, 127.3, 127.1, 126.8, 126.1, 125.1, 123.2, 60.9, 52.2, 50.8, 38.6, 30.4. HRMS (ESI$^+$): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2215.



(*Cis*)-*N*-(*tert*-butyl)-5-fluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ea)

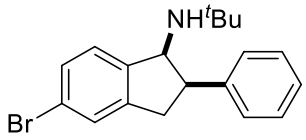
The title compound was prepared according to the general procedure as a yellowish oil (94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 1H), 7.22-7.16 (m, 3H), 6.96-6.91 (m, 4H), 4.46 (d, J = 7.5 Hz, 1H), 3.70 (td, J = 7.5, 2.5 Hz, 1H), 3.27 (dd, J = 16.0, 7.5 Hz, 1H), 3.05 (dd, J = 16.5, 2.5 Hz, 1H), 1.11 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.6 (d, J = 244.44 Hz), 143.7 (d, J = 7.56 Hz), 143.4 (d, J = 2.52 Hz), 142.1, 128.9, 128.5, 126.9, 125.8 (d, J = 8.82 Hz), 113.5 (d, J = 22.68 Hz), 111.2 (d, J = 22.68 Hz), 60.4, 52.3, 50.7, 38.5 (d, J = 2.52 Hz), 30.3. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −116.89. HRMS (ESI$^+$): calcd for $C_{19}H_{23}FN$ $[M+H]^+$ 284.1809, found 284.1809.



(*Cis*)-*N*-(*tert*-butyl)-5-chloro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3fa)

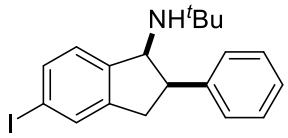
The title compound was prepared according to the general procedure as a pale yellow solid (90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.27-7.25 (m, 1H), 7.21-7.16 (m, 5H), 6.95-6.94 (m, 2H), 4.45 (d, J = 7.5 Hz, 1H), 3.70 (td, J = 7.5, 2.5 Hz, 1H), 3.27 (dd, J = 16.0, 7.5 Hz, 1H), 3.04 (dd, J = 16.0, 2.5 Hz, 1H), 1.15 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.6, 143.6, 141.9, 132.6, 128.8, 128.5, 127.0,

126.9, 126.0, 124.5, 60.7, 52.1, 50.8, 38.4, 30.3. HRMS (ESI^+): calcd for $C_{19}H_{23}ClN$ $[M+H]^+$ 300.1514, found 300.1514.



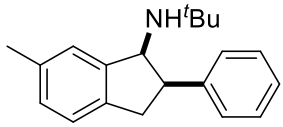
(*Cis*)-*5*-bromo-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ga)

The title compound was prepared according to the general procedure as a pale yellow solid (91% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.35 (m, 2H), 7.22-7.16 (m, 4H), 6.95-6.93 (m, 2H), 4.43 (d, J = 7.0 Hz, 1H), 3.68 (td, J = 7.5, 3.0 Hz, 1H), 3.28 (dd, J = 16.0, 7.5 Hz, 1H), 3.05 (dd, J = 16.0, 2.5 Hz, 1H), 1.15 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 144.0, 141.9, 129.9, 128.8, 128.5, 127.4, 127.0, 126.5, 120.7, 60.7, 52.0, 50.8, 38.3, 30.3. HRMS (ESI^+): calcd for $C_{19}H_{23}BrN$ $[M+H]^+$ 344.1007 and 346.0987, found 344.1008 and 346.0987.



(*Cis*)-*N*-(*tert*-butyl)-5-iodo-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ha)

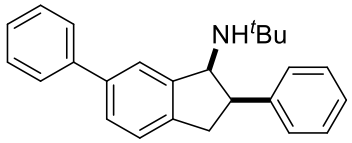
The title compound was prepared according to the general procedure as a pale yellow solid (91% yield). Recrystallization from hexane solution gave single crystals suitable for X-ray analysis. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57-7.55 (m, 2H), 7.21-7.16 (m, 3H), 7.09 (d, J = 7.5 Hz, 1H), 6.95-6.93 (m, 2H), 4.44 (d, J = 7.0 Hz, 1H), 3.66 (td, J = 7.5, 2.5 Hz, 1H), 3.27 (dd, J = 16.0, 7.5 Hz, 1H), 3.03 (dd, J = 16.0, 2.5 Hz, 1H), 1.14 (brs, 1H), 1.02 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 144.4, 141.9, 135.9, 133.3, 128.8, 128.5, 126.94, 126.92, 92.2, 60.9, 51.9, 50.8, 38.2, 30.3. HRMS (ESI^+): calcd for $C_{19}H_{23}IN$ $[M+H]^+$ 392.0870, found 392.0870.



(*Cis*)-*N*-(*tert*-butyl)-6-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ia)

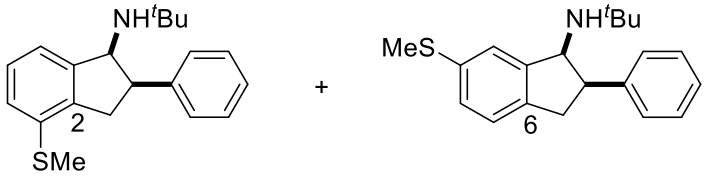
The title compound was prepared according to the general procedure as a yellowish oil (86% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.15 (m, 4H), 7.10 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 6.0 Hz, 2H), 4.48 (d, J = 7.5 Hz, 1H), 3.68 (td, J = 7.5, 2.5 Hz, 1H), 3.26 (dd, J = 15.5, 7.5 Hz, 1H), 3.03 (dd, J = 15.5, 2.0 Hz, 1H), 2.37 (s, 3H), 1.19 (brs, 1H), 1.04 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ =

148.0, 142.7, 138.7, 136.5, 129.0, 128.4, 127.8, 126.7, 125.4, 124.0, 61.1, 52.2, 50.8, 38.3, 30.4, 21.6. HRMS (ESI^+): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2059.



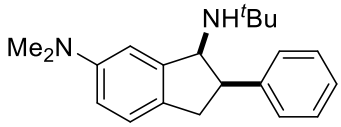
(*Cis*)-*N*-(*tert*-butyl)-2,6-diphenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ja)

The title compound was prepared according to the general procedure as a yellowish oil (91% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.5 Hz, 2H), 7.57 (s, 1H), 7.46-7.41 (m, 3H), 7.33-7.28 (m, 2H), 7.23-7.15 (m, 3H), 7.00 (d, J = 7.0 Hz, 2H), 4.55 (d, J = 7.5 Hz, 1H), 3.73 (td, J = 7.5, 3.0 Hz, 1H), 3.33 (dd, J = 16.0, 7.5 Hz, 1H), 3.11 (dd, J = 16.0, 2.5 Hz, 1H), 1.12 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.7, 142.4, 141.9, 141.0, 140.2, 129.0, 128.8, 128.4, 127.3, 127.0, 126.8, 126.2, 124.6, 123.6, 61.2, 52.2, 50.8, 38.3, 30.4. HRMS (ESI^+): calcd for $C_{25}H_{28}N$ $[M+H]^+$ 342.2216, found 342.2215.



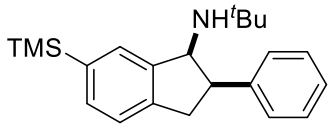
(*Cis*)-*N*-(*tert*-butyl)-4-(methylthio)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ka) and (*Cis*)-*N*-(*tert*-butyl)-6-(methylthio)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ka′)

The title compound was prepared according to the general procedure as a white solid (total: 90% yield, C2:C6 = 4:1). ^1H NMR (500 MHz, C_6D_6): ***cis*-3ka:** δ = 7.33 (d, J = 7.5 Hz, 0.82H), 7.19 (t, J = 7.5 Hz, 0.82H), 6.99-6.96 (m, 4.92H), 4.32 (d, J = 7.5 Hz, 0.82H), 3.42 (td, J = 7.5, 3.0 Hz, 0.82H), 3.24 (dd, J = 16.5, 3.0 Hz, 0.82H), 3.13 (dd, J = 16.0, 7.5 Hz, 0.82H), 2.05 (s, 2.46 H), 0.93 (brs, 0.82H), 0.93 (s, 7.38H); ***cis*-3ka′:** δ = 7.61 (s, 0.18H), 6.99-6.96 (m, 1.28H), 4.32 (d, J = 7.5 Hz, 0.18H), 3.42 (td, J = 7.5, 3.0 Hz, 0.18H), 3.02 (dd, J = 16.5, 7.5 Hz, 0.18H), 2.89 (dd, J = 15.5, 2.5 Hz, 0.18H), 2.13 (s, 0.54 H), 0.92 (brs, 0.18H), 0.92 (s, 1.62H); ^{13}C NMR (126 MHz, Benzene-d_6): δ = 149.8, 149.1, 143.32, 143.27, 140.3, 139.5, 137.8, 135.1, 129.63, 129.58, 128.93, 128.87, 128.8, 128.6, 128.4, 127.4, 127.3, 126.8, 125.4, 124.7, 123.9, 122.3, 62.2, 61.9, 53.2, 52.4, 50.9, 39.0, 38.3, 30.8, 30.7, 16.7, 15.2. HRMS (ESI^+): calcd for $C_{20}H_{26}NS$ $[M+H]^+$ 312.1780, found 312.1781.



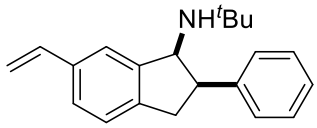
(*Cis*)-*N*^{1}-(*tert*-butyl)-*N*^{6},*N*^{6}-dimethyl-2-phenyl-2,3-dihydro-1H-indene-1,6-diamin e (*cis*-3la)

The title compound was prepared according to the general procedure as a yellow oil (60% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19-7.13 (m, 3H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 2H), 6.80 (d, *J* = 1.5 Hz, 2H), 6.63 (dd, *J* = 8.0, 2.5 Hz, 1H), 4.45 (d, *J* = 7.0 Hz, 1H), 3.65 (td, *J* = 7.5, 2.5 Hz, 1H), 3.21 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.97 (dd, *J* = 15.5, 3.0 Hz, 1H), 2.94 (s, 6H), 1.16 (brs, 1H), 1.04 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 150.7, 148.9, 143.0, 130.0, 129.0, 128.3, 126.6, 124.6, 112.2, 109.7, 61.4, 52.3, 50.7, 41.4, 37.7, 30.4. HRMS (ESI$^+$): calcd for $C_{21}H_{29}N_2$ $[M+H]^+$ 309.2325, found 309.2326.



(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-6-(trimethylsilyl)-2,3-dihydro-1H-inden-1-amine (*cis*-3ma)

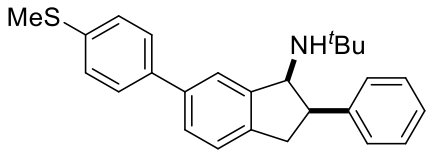
The title compound was prepared according to the general procedure as a yellowish oil (62% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (s, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.28-7.20 (m, 4H), 7.04 (d, *J* = 6.5 Hz, 2H), 4.52 (d, *J* = 7.5 Hz, 1H), 3.71 (td, *J* = 8.0, 3.5 Hz, 1H), 3.30 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.14 (dd, *J* = 16.0, 3.0 Hz, 1H), 1.13 (brs, 1H), 1.07 (s, 9H), 0.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 142.8, 142.4, 138.6, 132.2, 129.6, 129.1, 128.4, 126.7, 123.9, 61.1, 51.7, 50.8, 38.5, 30.3, -0.7. HRMS (ESI$^+$): calcd for $C_{22}H_{32}NSi$ $[M+H]^+$ 338.2299, found 338.2299.



(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-6-vinyl-2,3-dihydro-1H-inden-1-amine (*cis*-3na)

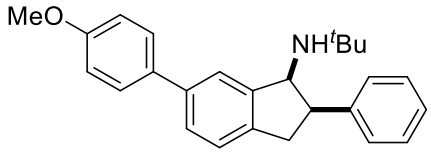
The title compound was prepared according to the general procedure as a yellowish oil (46% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.73 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.73 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 11.0 Hz, 1H), 4.49 (d, *J* = 7.5 Hz, 1H), 3.70 (td, *J* = 7.5, 2.5 Hz, 1H), 3.29 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.05 (dd, *J* = 16.0, 2.5 Hz, 1H), 1.20 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.4, 142.4, 141.6,

137.4, 136.6, 128.9, 128.4, 126.8, 125.4, 124.4, 122.5, 112.9, 61.0, 52.2, 50.8, 38.5, 30.4. HRMS (ESI^+): calcd for $C_{21}H_{26}N$ $[M+H]^+$ 292.2060, found 292.2060.



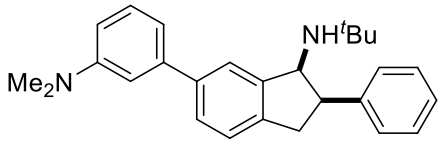
(*Cis*)-*N*-(*tert*-butyl)-6-(4-(methylthio)phenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3oa)

The title compound was prepared according to the general procedure as a white solid (90% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57-7.54 (m, 3H), 7.41 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.5 Hz, 1H), 7.21-7.15 (m, 3H), 7.00 (d, J = 6.5 Hz, 2H), 4.54 (d, J = 7.5 Hz, 1H), 3.73 (td, J = 7.5, 3.0 Hz, 1H), 3.32 (dd, J = 16.0, 8.0 Hz, 1H), 3.11 (dd, J = 16.0, 2.5 Hz, 1H), 1.13 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.7, 142.4, 141.0, 139.4, 138.8, 137.1, 129.0, 128.4, 127.7, 127.2, 126.8, 125.8, 124.6, 123.3, 61.1, 52.2, 50.8, 38.3, 30.4, 16.2. HRMS (ESI^+): calcd for $C_{26}H_{30}NS$ $[M+H]^+$ 388.2093, found 388.2094.



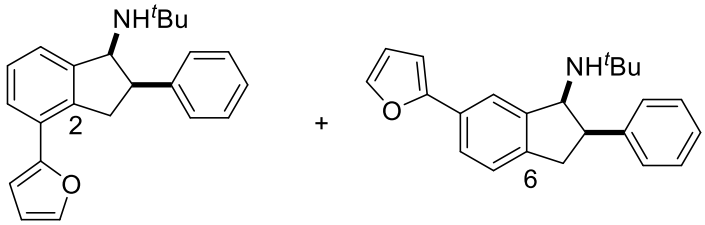
(*Cis*)-*N*-(*tert*-butyl)-6-(4-methoxyphenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3pa)

The title compound was prepared according to the general procedure as a pale yellow solid (89% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.5 Hz, 2H), 7.52 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.21-7.15 (m, 3H), 7.00 (d, J = 7.0 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 4.54 (d, J = 7.0 Hz, 1H), 3.84 (s, 3H), 3.72 (td, J = 7.5, 3.0 Hz, 1H), 3.31 (dd, J = 16.0, 7.5 Hz, 1H), 3.10 (dd, J = 16.0, 3.0 Hz, 1H), 1.13 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.0, 148.6, 142.5, 140.4, 139.8, 134.5, 129.0, 128.4, 128.3, 126.7, 125.7, 124.5, 123.2, 114.2, 61.2, 55.5, 52.2, 50.8, 38.3, 30.4. HRMS (ESI^+): calcd for $C_{26}H_{30}NO$ $[M+H]^+$ 372.2322, found 372.2321.



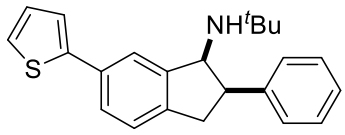
(*Cis*)-*N*-(*tert*-butyl)-6-(3-(dimethylamino)phenyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3qa)

The title compound was prepared according to the general procedure as a yellow oil (82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.31-7.27 (m, 2H), 7.22-7.15 (m, 3H), 7.02 (d, J = 7.0 Hz, 2H), 6.99-6.97 (m, 2H), 6.72 (d, J = 8.0 Hz, 1H), 4.54 (d, J = 7.0 Hz, 1H), 3.72 (td, J = 7.5, 3.0 Hz, 1H), 3.31 (dd, J = 16.0, 8.0 Hz, 1H), 3.12 (dd, J = 16.0, 3.0 Hz, 1H), 2.99 (s, 6H), 1.11 (brs, 1H), 1.03 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.1, 148.4, 143.0, 142.5, 141.2, 140.8, 129.4, 129.1, 128.3, 126.7, 126.4, 124.4, 123.8, 116.3, 111.9, 111.6, 61.2, 52.2, 50.8, 41.0, 38.3, 30.4. HRMS (ESI$^+$): calcd for $C_{27}H_{33}N_2$ $[M+H]^+$ 385.2638, found 385.2638.



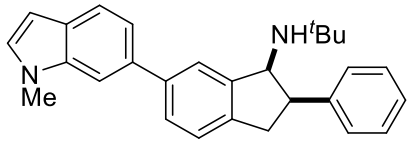
(*Cis*)-*N*-(*tert*-butyl)-4-(furan-2-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ra) and(*Cis*)-*N*-(*tert*-butyl)-6-(furan-2-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ra′)

The title compound was prepared according to the general procedure as a pale yellow solid (total: 85% yield; C2:C6 = 4:1). ^{1}H NMR (500 MHz, C_6D_6): ***cis*-3ra:** δ = 7.83 (d, J = 7.5 Hz, 0.8H), 7.44 (d, J = 7.5 Hz, 0.8H), 7.27 (t, J = 7.5 Hz, 0.8H), 7.09-6.95 (m, 4.8H), 6.40 (d, J = 3.0 Hz, 0.8H), 6.20 (dd, J = 3.5, 2.0 Hz, 0.8H), 4.34 (d, J = 7.5 Hz, 0.8H), 3.47 (td, J = 7.5, 3.0 Hz, 0.8H), 3.34 (dd, J = 16.5, 3.0 Hz, 0.8H), 3.24 (dd, J = 16.5, 7.5 Hz, 0.8H), 1.00 (s, 7.2 H); ***cis*-3ra′:** δ = 8.04 (s, 0.2H), 7.64 (d, J = 7.5 Hz, 0.2H), 7.27 (t, J = 7.5 Hz, 0.2H), 7.09-6.95 (m, 1.2H), 6.50 (d, J = 3.0 Hz, 0.2H), 6.17 (dd, J = 3.0, 1.5 Hz, 0.2H), 4.37 (d, J = 7.0 Hz, 0.2H), 3.47 (td, J = 7.5, 3.0 Hz, 0.2H), 3.05 (dd, J = 16.0, 7.5 Hz, 0.2H), 2.92 (dd, J = 16.0, 2.5 Hz, 0.2H), 1.00 (s, 1.8H); ^{13}C NMR (126 MHz, Benzene-d_6): δ = 155.8, 154.6, 150.0, 149.5, 143.41, 143.37, 142.38, 142.31, 141.8, 138.0, 130.9, 129.7, 129.6, 128.92, 128.90, 128.1, 127.9, 127.33, 127.27, 125.3, 124.9, 124.6, 123.9, 121.4, 112.32, 112.25, 108.4, 105.2, 61.9, 61.72, 61.69, 53.2, 52.4, 51.0, 40.2, 39.2, 30.9, 30.8. HRMS (ESI$^+$): calcd for $C_{23}H_{26}NO$ $[M+H]^+$ 332.2009, found 332.2010.



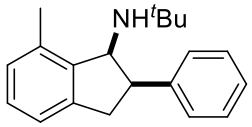
(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-6-(thiophen-2-yl)-2,3-dihydro-1H-inden-1-amine (*cis*-3sa)

The title compound was prepared according to the general procedure as a pale yellow solid (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 3.0 Hz, 1H), 7.23-7.16 (m, 5H), 7.05 (t, J = 4.5 Hz, 1H), 6.98 (d, J = 6.5 Hz, 2H), 4.52 (d, J = 7.0 Hz, 1H), 3.72 (td, J = 8.0, 2.5 Hz, 1H), 3.30 (dd, J = 16.0, 7.5 Hz, 1H), 3.07 (dd, J = 16.0, 2.5 Hz, 1H), 1.06 (s, 10H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.9, 145.3, 142.3, 141.3, 133.3, 128.9, 128.0, 126.8, 125.1, 124.7, 124.3, 122.8, 122.5, 61.1, 52.2, 50.8, 38.4, 30.4. HRMS (ESI^+): calcd for $C_{23}H_{26}NS$ $[M+H]^+$ 348.1780, found 348.1781.



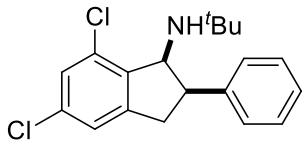
(*Cis*)-*N*-(*tert*-butyl)-6-(1-methyl-1H-indol-6-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ta)

The title compound was prepared according to the general procedure as a colorless oil (82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (s, 1H), 7.62 (s, 1H), 7.50 (t, J = 6.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.22-7.15 (m, 3H), 7.06-7.04 (m, 3H), 4.55 (d, J = 7.5 Hz, 1H), 3.80 (s, 3H), 3.73 (td, J = 7.5, 3.5 Hz, 1H), 3.32 (dd, J = 15.5, 7.5 Hz, 1H), 3.12 (dd, J = 16.0, 3.0 Hz, 1H), 1.13 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.5, 142.6, 141.6, 139.9, 136.3, 133.6, 129.4, 129.1, 128.3, 126.7, 126.4, 124.5, 123.8, 121.7, 119.5, 109.4, 101.4, 61.2, 52.3, 50.8, 38.2, 33.1, 30.4. HRMS (ESI^+): calcd for $C_{28}H_{31}N_2$ $[M+H]^+$ 395.2482, found 395.2483.



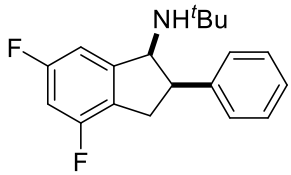
(*Cis*)-*N*-(*tert*-butyl)-7-methyl-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3ua)

The title compound was prepared according to the general procedure as a yellowish oil (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24-7.17 (m, 3H), 7.11-7.09 (m, 3H), 7.04 (d, J = 7.0 Hz, 1H), 6.97 (d, J = 7.0 Hz, 1H), 4.62 (d, J = 6.0 Hz, 1H), 3.60 (q, J = 6.5 Hz, 1H), 3.19-3.10 (m, 2H), 2.51 (s, 3H), 1.19 (brs, 1H), 0.90 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.6, 143.1, 142.7, 135.6, 129.5, 129.2, 128.2, 127.2, 126.6, 122.1, 61.5, 52.7, 50.8, 38.5, 30.5, 19.7. HRMS (ESI^+): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2062.



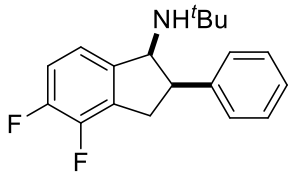
(*Cis*)-*N*-(*tert*-butyl)-5,7-dichloro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3va)

The title compound was prepared according to the general procedure as a colorless oil (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28 (t, J = 7.0 Hz, 2H), 7.25-7.22 (m, 3H), 7.19 (s, 1H), 7.13 (s, 1H), 4.50 (d, J = 6.0 Hz, 1H), 3.59-3.55 (m, 1H), 3.34 (dd, J = 16.0, 8.5 Hz, 1H), 2.99 (dd, J = 15.5, 7.5 Hz, 1H), 1.06 (brs, 1H), 0.81 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.3, 143.3, 140.9, 133.6, 131.3, 129.8, 128.2, 127.9, 127.0, 123.6, 60.3, 52.8, 50.8, 37.6, 30.4. HRMS (ESI$^+$): calcd for $C_{19}H_{22}Cl_2N$ $[M+H]^+$ 334.1124, found 334.1124.



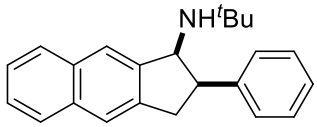
(*Cis*)-*N*-(*tert*-butyl)-4,6-difluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3wa)

The title compound was prepared according to the general procedure as a yellowish oil (70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24-7.18 (m, 3H), 6.94-6.93 (m, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.63 (td, J = 9.0, 1.5 Hz, 1H), 4.48 (d, J = 7.5 Hz, 1H), 3.74 (td, J = 7.5, 2.5 Hz, 1H), 3.21 (dd, J = 16.0, 7.5 Hz, 1H), 3.11 (d, J = 16.0 Hz, 1H), 1.13 (brs, 1H), 1.03 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.0 (dd, J = 247.0, 10.1 Hz), 158.5 (dd, J = 249.5, 12.6 Hz), 153.2 (dd, J = 7.56, 6.30 Hz), 141.5, 128.7, 127.2, 122.4 (dd, J = 18.9, 2.5 Hz), 107.8 (dd, J = 22.7, 3. 8 Hz), 102.1 (d, J = 25.2 Hz), 101.9 (d, J = 23.9 Hz), 61.3 (t, J = 2.5 Hz), 51.8, 50.8, 33.8, 30.3. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −112.61 (s, 1F), −116.00 (s, 1F). HRMS (ESI$^+$): calcd for $C_{19}H_{22}F_2N$ $[M+H]^+$ 302.1715, found 302.1715.



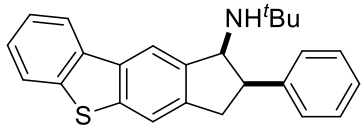
(*Cis*)-*N*-(*tert*-butyl)-4,5-difluoro-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3xa)

The title compound was prepared according to the general procedure as a yellowish oil (80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.18 (m, 3H), 7.04-7.00 (m, 2H), 6.94 (d, *J* = 6.5 Hz, 2H), 4.47 (d, *J* = 7.5 Hz, 1H), 3.74 (td, *J* = 7.5, 2.5 Hz, 1H), 3.26 (dd, *J* = 16.5, 7.5 Hz, 1H), 3.18 (dd, *J* = 16.5, 2.0 Hz, 1H), 1.05 (brs, 1H), 1.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.8 (dd, *J* = 245.7, 12.6 Hz), 146.7 (dd, *J* = 247.0, 11.3 Hz), 145.7 (t, *J* = 2.5 Hz), 141.4, 129.5 (d, *J* = 15.12 Hz), 128.7, 128.6, 127.1, 120.0 (dd, *J* = 3.8 Hz), 115.8 (d, *J* = 17.6 Hz), 60.8 (d, *J* = 1.26 Hz), 52.0, 50.7, 34.1 (d, *J* = 2.52 Hz), 30.3. ^{19}H NMR (377 MHz, $CDCl_3$): δ = −142.01 (m, 1F), −144.00 (m, 1F). HRMS (ESI^+): calcd for $C_{19}H_{22}F_2N$ $[M+H]^+$ 302.1715, found 302.1715.



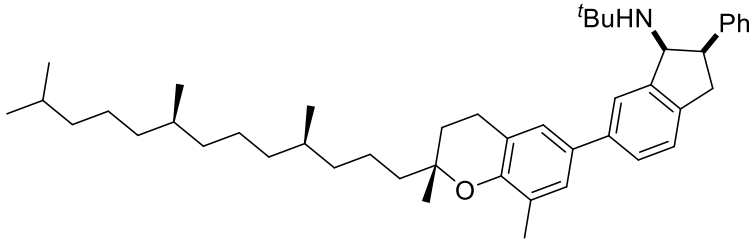
(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-amine (*cis*-3ya)

The title compound was prepared according to the general procedure as a pale yellow solid (84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84-7.78 (m, 2H), 7.76 (s, 1H), 7.66 (s, 1H), 7.42-7.40 (m, 2H), 7.14-7.12 (m, 3H), 6.90-6.89 (m, 2H), 4.65 (d, *J* = 7.0 Hz, 1H), 3.75 (t, *J* = 7.0 Hz, 1H), 3.45 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.21 (d, *J* = 16.0 Hz, 1H), 1.15 (brs, 1H), 1.13 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 142.3, 140.7, 133.6, 133.5, 128.8, 128.4, 128.1, 127.6, 126.8, 125.3, 125.1, 123.0, 122.4, 61.1, 52.4, 50.9, 38.2, 30.5. HRMS (ESI^+): calcd for $C_{23}H_{26}N$ $[M+H]^+$ 316.2060, found 316.2061.



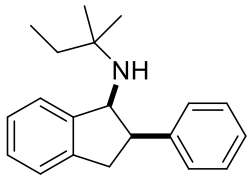
(*Cis*)-*N*-(*tert*-butyl)-2-phenyl-2,3-dihydro-1H-benzo[b]indeno[5,6-d]thiophen-1-amine (*cis*-3za)

The title compound was prepared according to the general procedure as a yellow oil (88% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23-8.21 (m, 1H), 8.14 (s, 1H), 7.87-7.85 (m, 1H), 7.72 (s, 1H), 7.48-7.43 (m, 2H), 7.20-7.19 (m, 3H), 7.00-6.98 (m, 2H), 4.69 (d, *J* = 7.0 Hz, 1H), 3.83 (t, *J* = 6.5 Hz, 1H), 3.49 (dd, *J* = 16.0, 7.5 Hz, 1H), 3.22 (d, *J* = 16.0 Hz, 1H), 1.26 (brs, 1H), 1.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.5, 142.2, 141.5, 139.5, 138.5, 135.9, 134.9, 128.8, 128.5, 126.9, 126.2, 124.3, 122.9, 121.7, 118.2, 117.7, 60.9, 52.6, 50.9, 38.5, 30.5. HRMS (ESI^+): calcd for $C_{25}H_{26}NS$ $[M+H]^+$ 372.1780, found 372.1780.



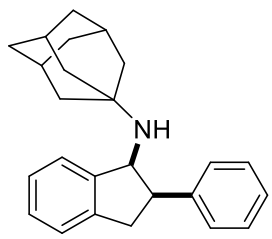
(*Cis*)-*N*-(*tert*-butyl)-6-((*R*)-2,8-dimethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3aaa)

The title compound was prepared according to the general procedure as a yellowish oil (83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (s, 1H), 7.37 (d, J = 7.0, 1H), 7.24-7.17 (m, 6H), 7.01 (d, J = 6.0, 2H), 4.53 (d, J = 7.0 Hz, 1H), 3.71 (t, J = 7.5 Hz, 1H), 3.30 (dd, J = 16.0, 7.5 Hz, 1H), 3.09 (d, J = 15.5 Hz, 1H), 2.83-2.79 (m, 2H), 2.23 (s, 3H), 1.88-1.75 (m, 2H), 1.41-1.05 (m, 34H), 0.86-0.84 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.7, 148.4, 142.6, 140.4, 139.9, 132.6, 129.0, 128.4, 127.4, 126.7, 126.6, 125.8, 125.7, 124.4, 123.1, 120.7, 76.3, 61.2, 52.3, 50.8, 40.4, 39.5, 30.3, 37.61, 37.59, 37.4, 33.0, 32.9, 31.5, 30.4, 28.1, 25.0, 24.6, 24.5, 22.9, 22.8, 22.6, 21.2, 19.9, 19.8, 16.4. HRMS (ESI$^+$): calcd for $C_{46}H_{68}NO$ $[M+H]^+$ 650.5295, found 650.5342.



(*Cis*)-*N*-(*tert*-pentyl)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-3aba)

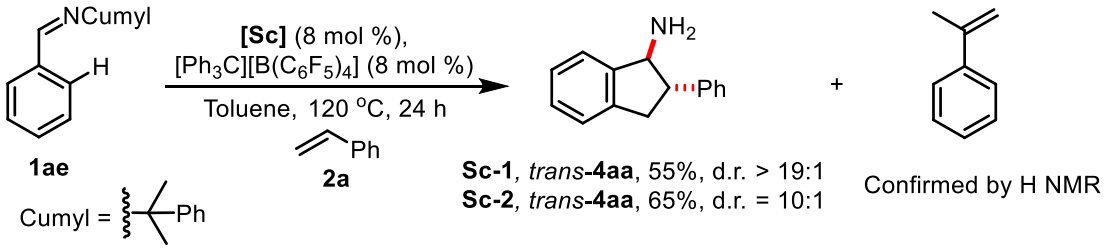
The title compound was prepared according to the general procedure as a yellowish oil (80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (d, J = 7.0 Hz, 1H), 7.25-7.15 (m, 6H), 6.97-6.95 (m, 2H), 4.52 (d, J = 7.5 Hz, 1H), 3.68 (td, J = 7.5, 2.5 Hz, 1H), 3.30 (dd, J = 15.5, 7.5 Hz, 1H), 3.06 (dd, J = 15.5, 2.5 Hz, 1H), 1.40-1.27 (m, 2H), 1.26 (brs, 1H), 1.02 (s, 3H), 0.93 (s, 3H), 0.73 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.1, 142.7, 141.8, 129.0, 128.4, 127.0, 126.8, 126.7, 124.9, 124.3, 60.8, 53.1, 52.3, 38.7, 35.5, 28.0, 27.1, 8.7. HRMS (ESI$^+$): calcd for $C_{20}H_{26}N$ $[M+H]^+$ 280.2060, found 280.2060.



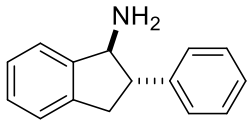
(*Cis*)-*N*-2-phenyl-2,3-dihydro-1H-inden-1-yl)adamantan-1-amine (*cis*-3aca)

The title compound was prepared according to the general procedure as a yellowish oil (35% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, J = 7.0 Hz, 1H), 7.24-7.14 (m, 6H), 6.97 (d, J = 6.5 Hz, 2H), 4.62 (d, J = 7.0 Hz, 1H), 3.64 (td, J = 7.5, 3.0 Hz, 1H), 3.29 (dd, J = 16.0, 7.5 Hz, 1H), 3.08 (dd, J = 15.5, 2.5 Hz, 1H), 2.02 (s, 3H), 1.64-1.62 (m, 3H), 1.57-1.52 (m, 9H), 1.19 (brs, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.1, 142.6, 141.8, 129.0, 128.4, 126.9, 126.8, 126.7, 124.9, 124.2, 59.0, 52.3, 50.7, 44.2, 38.6, 36.9, 29.9. HRMS (ESI$^+$): calcd for $C_{25}H_{30}N$ $[M+H]^+$ 344.2373, found 344.2372.

Diastereoselective synthesis of *trans* and *cis* unsubstituted primary 1-aminoindanes

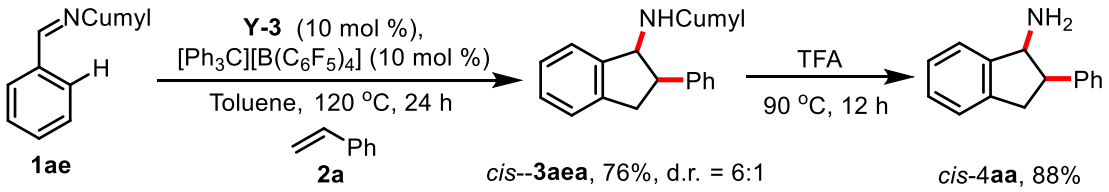


In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (14.7 mg, 0.016 mmol) was added to a stirred toluene solution (2.0 mL) of **Sc-1** (8.1 mg, 0.016 mmol) or of **Sc-2** (7.2 mg, 0.016 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1a** (0.2 mmol) and styrene **2a** (0.8 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the mixture was concentrated and purified by PLC (ethyl acetate) to afford the desired product *trans*-**4aa** (**Sc-1**: 55% yield; **Sc-2**: 65% yield). When the reaction was performed in benzene-d_6, the reaction mixture was analyzed by ^{1}H NMR to confirm that α-methylstyrene was formed.



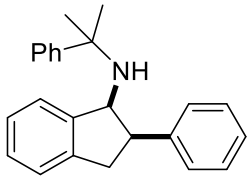
(*Trans*)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*trans*-4aa)

The title compound was obtained as a slight yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.35 (m, 5H), 7.30-7.27 (m, 2H), 7.27-7.23 (m, 2H), 4.40 (d, J = 9.0 Hz, 1H), 3.30-3.26 (m, 1H), 3.15-3.06 (m, 2H), 1.57 (brs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.1, 142.6, 141.4, 128.8, 127.9, 127.7, 127.1, 126.9, 124.5, 123.5, 64.7, 59.4, 38.9. HRMS (ESI$^+$): calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1277, found 210.1271.



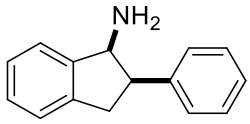
In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (18.4 mg, 0.02 mmol) was added to a stirred toluene solution (2.0 mL) of **Y-3** (9.6 mg, 0.02 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1a** (0.2 mmol) and styrene **2a** (0.6 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 20:1) to obtain the desired product *cis*-**3aea** (76% yield). The d.r. was determined by NMR analysis of the crude product.

The *cis*-**3aea** (0.1 mmol) was placed in a Schlenk tube, and TFA was subsequently added to the tube. The mixture was stirred at 90 ºC for 12 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 (hexane/EtOAc = 1:1) to afford the desired product *cis*-**4aa** (88% yield).



(*Cis*)-2-phenyl-*N*-(2-phenylpropan-2-yl)-2,3-dihydro-1*H*-inden-1-amine (*cis*-3aea)

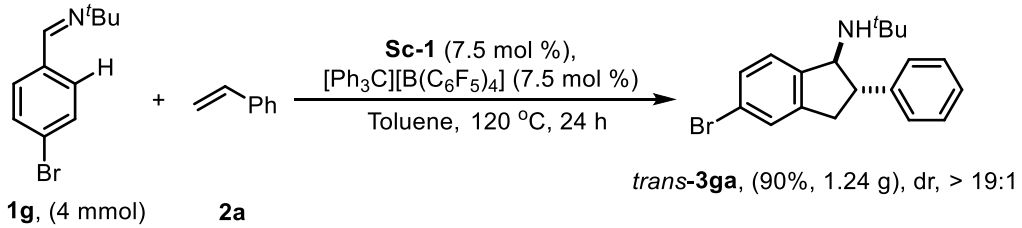
The title compound was obtained as a colorless oil (76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.5 Hz, 2H), 7.35-7.29 (m, 3H), 7.24-7.14 (m, 7H), 6.93-6.91 (m, 2H), 4.27 (d, J = 7.0 Hz, 1H), 3.48 (td, J = 7.5, 2.0 Hz, 1H), 3.18 (dd, J = 16.0, 7.5 Hz, 1H), 2.95 (dd, J = 16.0, 8.0 Hz, 1H), 1.54 (brs, 1H)1.43 (s, 3H), 1.36 (s, 3H),; ^{13}C NMR (126 MHz, $CDCl_3$): δ =148.9, 147.7, 142.9, 141.5, 128.8, 128.5, 128.1, 127.0, 126.8, 126.7, 126.5, 126.4, 124.6, 124.4, 62.1, 56.3, 52.1, 39.0, 31.3, 29.7. HRMS (ESI$^+$): calcd for $C_{24}H_{26}N$ $[M+H]^+$ 328.2060, found 328.2061.



(*Cis*)-2-phenyl-2,3-dihydro-1H-inden-1-amine (*cis*-4aa)

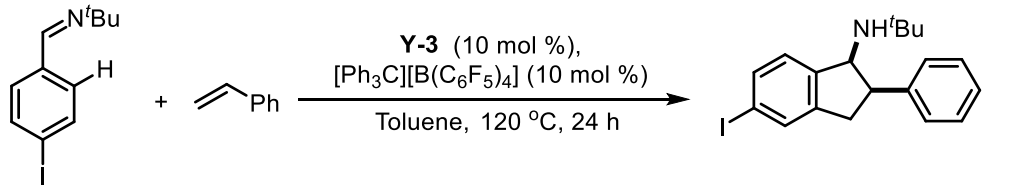
The title compound was obtained as a slight yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.38 (m, 1H), 7.32-7.28 (m, 3H), 7.27-7.22 (m, 3H), 7.18 (d, J = 7.0 Hz, 2H), 4.58 (d, J = 7.0 Hz, 1H), 3.74 (q, J = 7.0 Hz, 1H), 3.32 (dd, J = 15.5, 7.0 Hz, 1H), 3.23 (dd, J = 15.5, 7.5 Hz, 1H), 1.44 (brs, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.1, 142.8, 141.0, 128.7, 128.6, 127.8, 127.0, 126.8, 124.74, 124.71, 60.3, 51.4, 35.8. HRMS (ESI$^+$): calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1277, found 210.1275.

5. Gram-Scale Reactions



1g, (4 mmol) **2a** *trans*-**3ga**, (90%, 1.24 g), dr, > 19:1

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (276 mg, 0.3 mmol) was added to a stirred toluene solution (40.0 mL) of **Sc-1** (152 mg, 0.3 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1g** (0.96 g, 4 mmol) and styrene **2a** (1.67 g, 16 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 4:1) to obtain the desired product *trans*-**3ga** (90%, 1.24 g).



1h, (4 mmol) **2a** *cis*-**3ha**, (91%, 1.42 g), dr, >19:1

In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (368 mg, 0.4 mmol) was added to a stirred toluene solution (40 mL) of **Y-3** (192 mg, 0.4 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1h** (1.15 g, 4 mmol) and styrene **2a** (1.67 g, 16 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 24 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 20:1) to obtain the desired product *cis*-**3ha** (91%, 1.42 g).

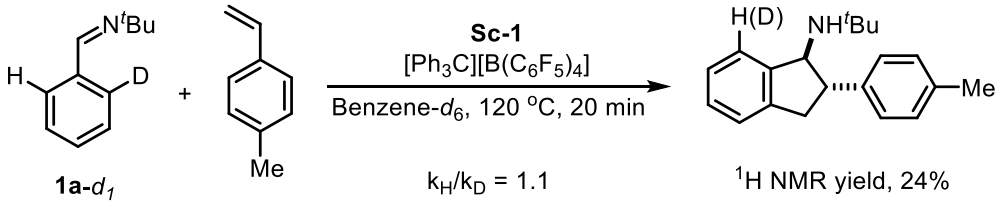
6. Kinetic Isotope Effect Experiments

To gain information on the reaction mechanism, kinetic isotope effect (KIE) studies were conducted. To enable better analyze the ^{1}H NMR spectrum of a crude reaction mixture, 4-methylstyrene was employed in the intramolecular KIE studies on the

reaction with an *ortho*-deuterated benzaldimine **1a-*d*$_1$**, which gave the KIE values of k_H/k_D = 1.1 for **Sc-1** and k_H/k_D = 3.0 for **Y-3**, respectively. The intermolecular KIE studies on the side-by-side reactions of **1a** and **1a-*d*$_5$** with styrene showed k_H/k_D = 1.5 for **Sc-1** and k_H/k_D = 6.7 for **Y-3**. These results suggest that the *ortho*-C−H cleavage of the benzaldimine may be involved in the rate-determining step of the annulation reaction catalyzed by **Y-3**, but not in that by **Sc-1**.

6.1 Intramolecular kinetic isotope effect experiment

Scandium-catalyzed trans diastereoselective [3+2] annulation



In a glovebox, [Ph_3C][$B(C_6F_5)_4$] (13.8 mg, 0.015 mmol) was added to a stirred benzene-d_6 solution (2.0 mL) of **Sc-1** (7.6 mg, 0.015 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1a-*d*$_1$** (0.2 mmol) and 4-methylstyrene (0.8 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 20 min. After cooling to room temperature, the reaction mixture was analyzed by ^{1}H NMR using dibromomethane as an internal standard. In order to analyze the ^{1}H NMR of the desired product more clearly, the reaction mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 4:1) to obtain the desired product *trans*-**3ab-*d*$_n$**.

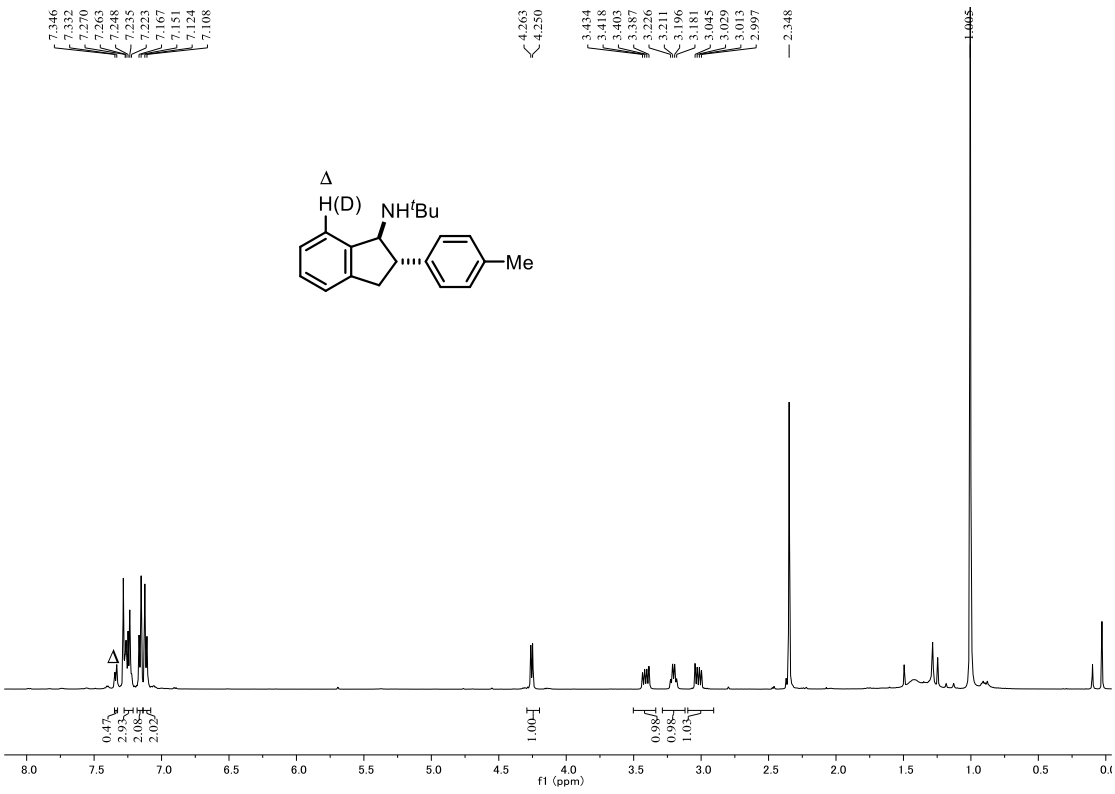
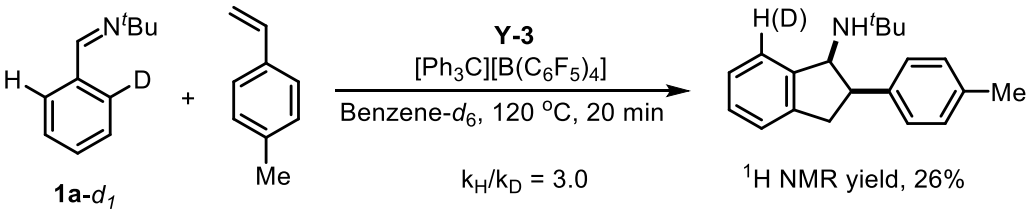


Fig. S1. ^{1}H NMR spectrum of *trans*-**3ab**-**D**

Yttrium-catalyzed cis diastereoselective [3+2] annulation



In a glovebox, [Ph$_3$C][B(C$_6$F$_5$)$_4$] (18.4 mg, 0.02 mmol) was added to a stirred benzene-d_6 solution (2.0 mL) of **Y-3** (9.6 mg, 0.02 mmol) in a Schlenk tube. After 5 min, to this tube was added aldimine **1a**-$\boldsymbol{d_1}$ (0.2 mmol) and 4-methylstyrene (0.6 mmol). After that, the tube was sealed, taken outside, and stirred at 120 °C for 20 min. After cooling to room temperature, the reaction mixture was analyzed by ^{1}H NMR using dibromomethane as an internal standard. In order to analyze the ^{1}H NMR of the desired product more clearly, the reaction mixture was concentrated and purified by silica gel column chromatography (hexane/EtOAc = 20:1) to obtain the desired product *cis*-**3ab**-$\boldsymbol{d}_n$.

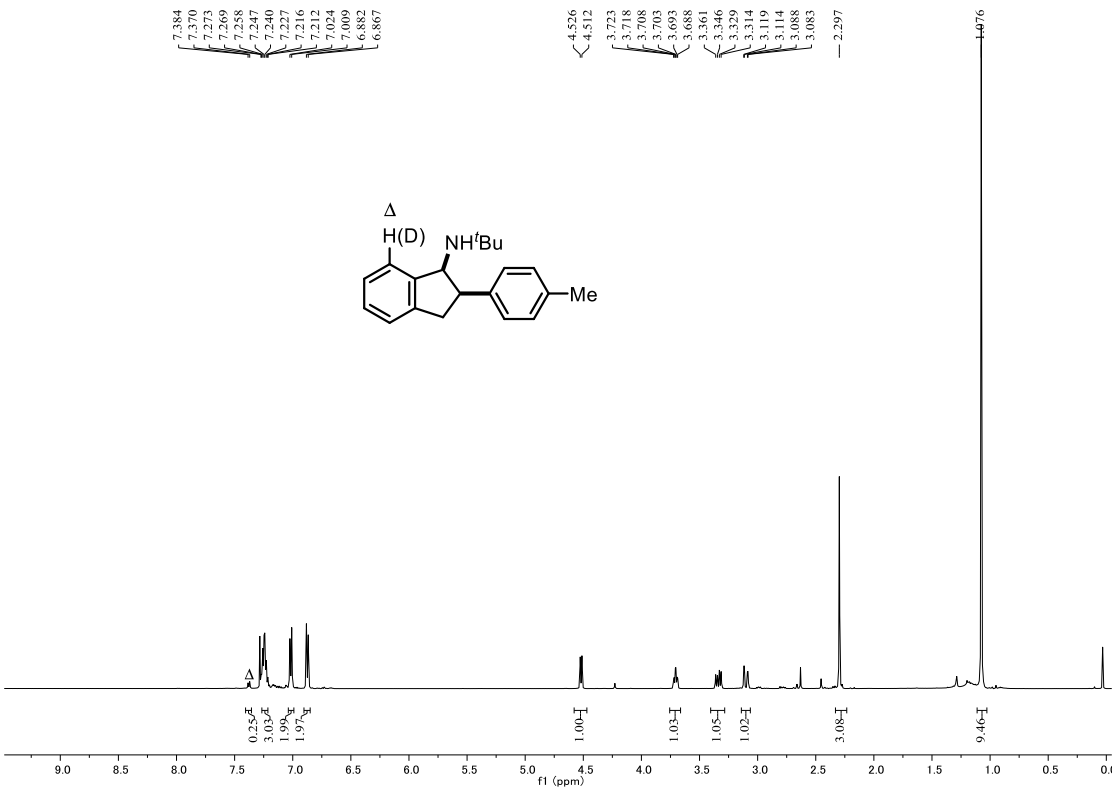
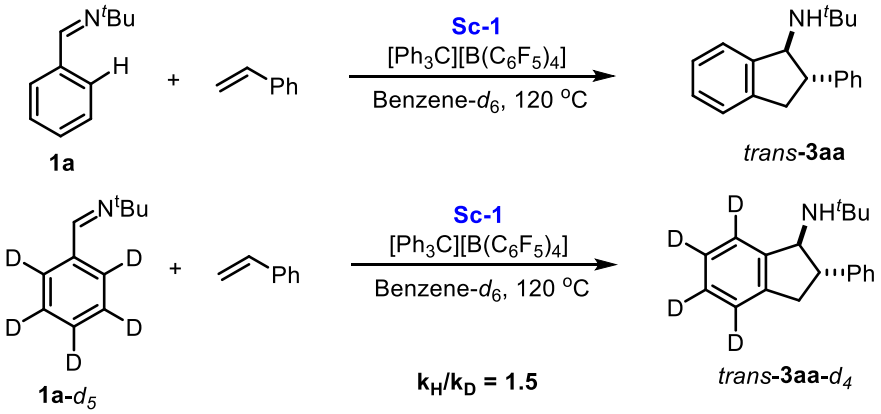


Fig. S2. ^{1}H NMR spectrum of *cis*-**3ab**-***d*$_n$**

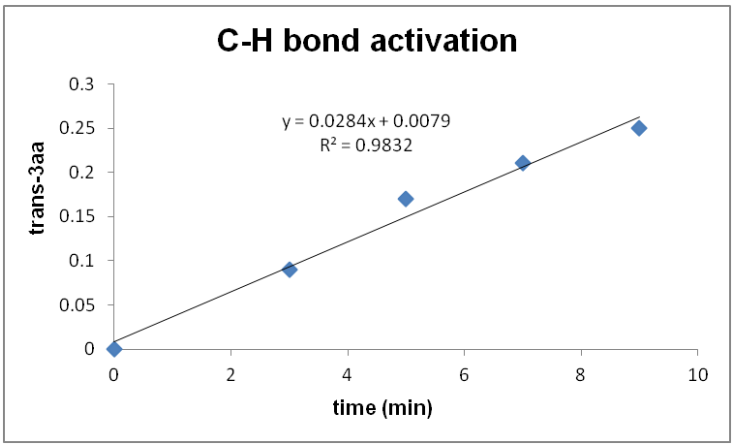
6.2 Intermolecular kinetic isotope effect experiment (Initial rates of two side-by-side reactions)

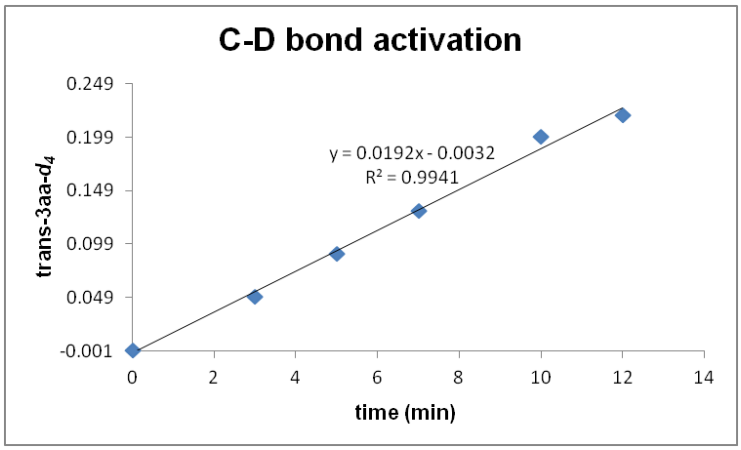
Scandium-catalyzed trans diastereoselective [3+2] annulation



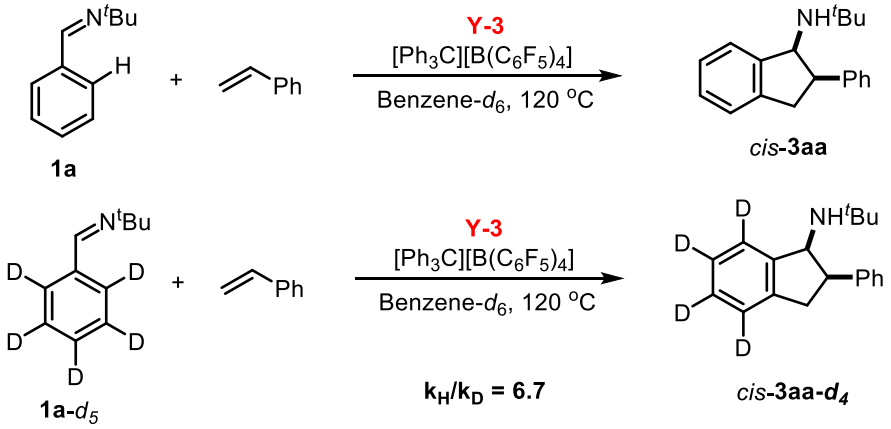
In a glovebox, a solution of ferrocene (internal standard, 4.7mg, 0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (4.6 mg, 0.005 mmol), and **Sc-1** (2.6 mg, 0.005 mmol) in benzene-d_6 (0.6 mL) was divided equally into two J-Young NMR tubes. To one tube was added the mixture of aldimine **1a** (0.1 mmol) and styrene (0.4 mmol) in benzene-d_6 (0.4 mL). And to the other tube was added the mixture of deuterated aldimine **1a-*d*$_5$** (0.1 mmol) and styrene (0.4 mmol) in benzene-d_6 (0.4 mL). These

tubes were sealed, taken out of the glovebox, and monitored by an NMR spectrometer at 120 °C. A KIE value of 1.5 was found in these side-by-side reactions.



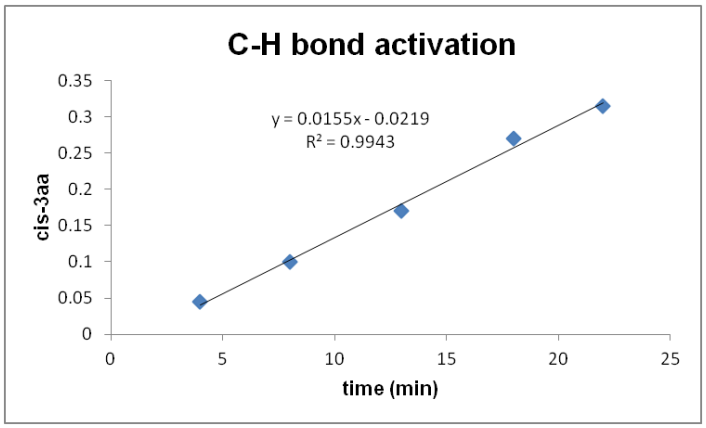


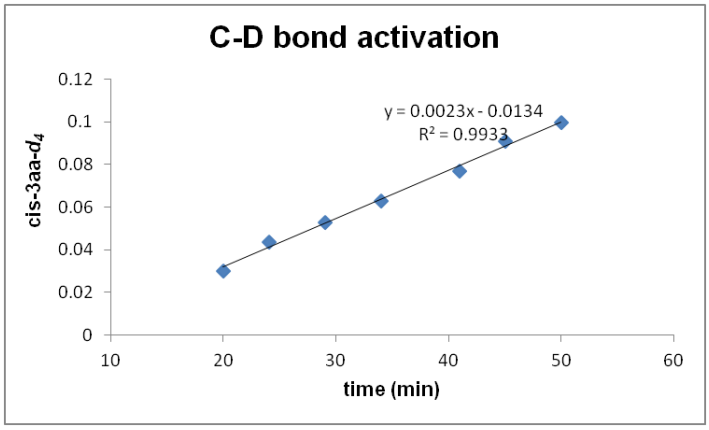
Yttrium-catalyzed cis diastereoselective [3+2] annulation



In a glovebox, a solution of ferrocene (internal standard, 4.7mg, 0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (4.6 mg, 0.005 mmol), and **Y-3** (2.4 mg, 0.005 mmol) in benzene-d_6 (0.6 mL) was divided equally into two J-Young NMR tubes. To one tube was added the mixture of aldimine **1a** (0.1 mmol) and styrene (0.4 mmol) in benzene-d_6 (0.4 mL). And to the other tube was added the mixture of deuterated aldimine **1a-*d*$_5$** (0.1 mmol)

and styrene (0.4 mmol) in benzene-d_6 (0.4 mL). These tubes were sealed, taken out of the glovebox, and monitored by an NMR spectrometer at 120 °C. A KIE value of 6.7 was found in these side-by-side reactions.





7. Proposed Reaction Mechanism of Sc-catalyzed [3+2] Annulation of Aldimines with Aliphatic Alkenes

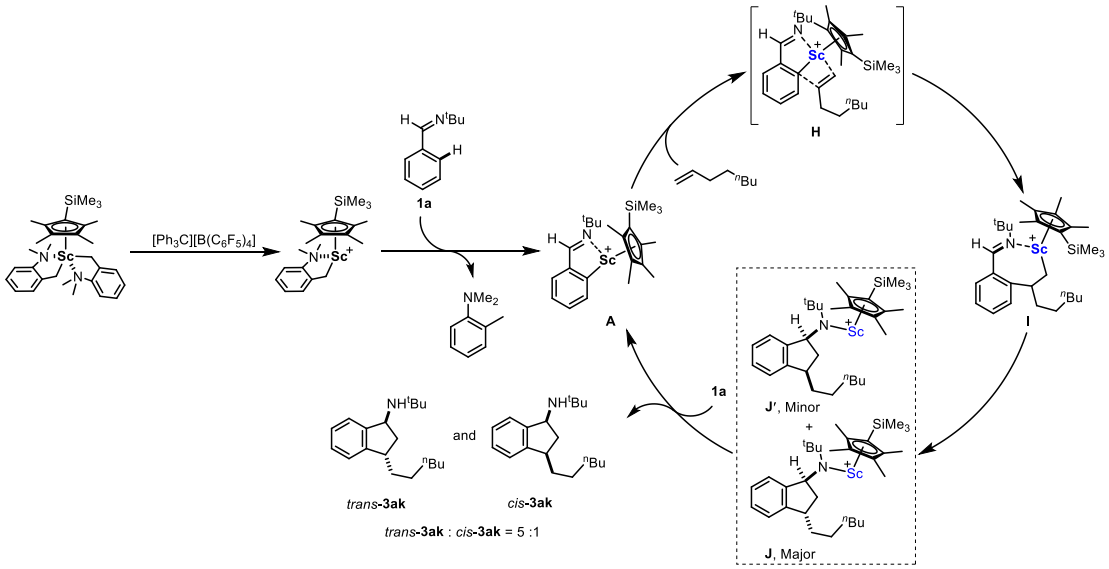


Fig. S3. Proposed reaction mechanism of aliphatic alkenes

8. 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.[5] 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[6] and SHELXL-2017.[7] Structural refinement was performed using the WINGX-Version 2014.1 system,[8] 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 1978404 (*trans*-**3ha**), and 1978405 (*cis*-**3ha**), 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*-3ha

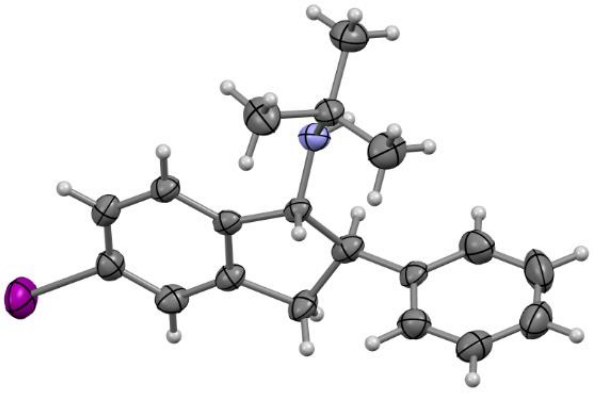


Fig. S4. X-ray structure of *trans*-**3ha**

Crystal data and structure refinement for *trans*-3ka

Bond precision: C-C = 0.0051 Å

Wavelength = 0.71073

Cell:	a = 8.8516(12)	b = 9.0513(12)	c = 13.0251(18)
	α =92.455(4)	β = 108.753(4)	γ = 115.373(4)
Temperature:	296 K		
	Calculated		Reported
Volume	872.7(2)		872.7(2)
Space group	P -1		P -1
Hall group :	-P 1		-P 1
Moiety formula	C19 H22 I N		C19 H22 I N
Sum formula	C19 H22 I N		C19 H22 I N
Mr	391.28		391.27
Dx,g cm^{-3}	1.489		1.489
Z	2		2
Mu (mm-1)	1.829		1.829
F000	392.0		392.0
F000′	391.16		
h,k,lmax	10,10,15		10,10,15
Nref	3092		3084
Tmin,Tmax			0.549,0.745
Tmin′			

Correction method= # Reported T Limits: Tmin=0.549 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness = 0.997 Theta(max) = 25.025

R(reflections) = 0.0340(2846) wR2(reflections) = 0.0931(3084)

S = 1.047 Npar= 200

X-ray structure of *cis*-3ha

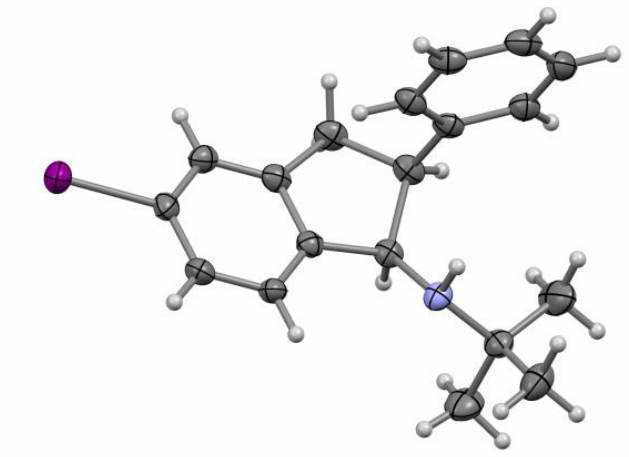


Fig. S5. X-ray structure of *cis*-**3ha**

Crystal data and structure refinement for *cis*-3ka

Bond precision:	C-C = 0.0023 Å		
Wavelength =	0.71073		
Cell:	a = 13.6969(3)	b = 5.6945(1)	c = 22.0831(6)
	α = 90	β = 93.300(1)	γ = 90
Temperature:	163 K		
	Calculated		Reported
Volume	1719.56 (7)		1719.56 (7)
Space group	P 21/n		P 1 21/n 1
Hall group	-P 2yn		-P 2yn
Moiety formula	$C_{19}H_{22}IN$		$C_{19}H_{22}IN$
Sum formula	$C_{19}H_{22}IN$		$C_{19}H_{22}IN$
Mr	391.28		392.28
Dx,g cm^{-3}	1.511		1.515
Z	4		4
Mu (mm-1)	1.857		1.857
F000	784.0		788.0
F000′	782.33		
h,k,lmax	16,6,26		16,6,26
Nref	3056		2962
Tmin,Tmax			0.669,0.745
Tmin′			

Correction method= # Reported T Limits: Tmin=0.669 Tmax=0.745
AbsCorr = MULTI-SCAN
Data completeness= 0.969 Theta(max)= 25.065
R(reflections)= 0.0173(2877) wR2(reflections)= 0.0426(2962)
S = 1.109 Npar = 196

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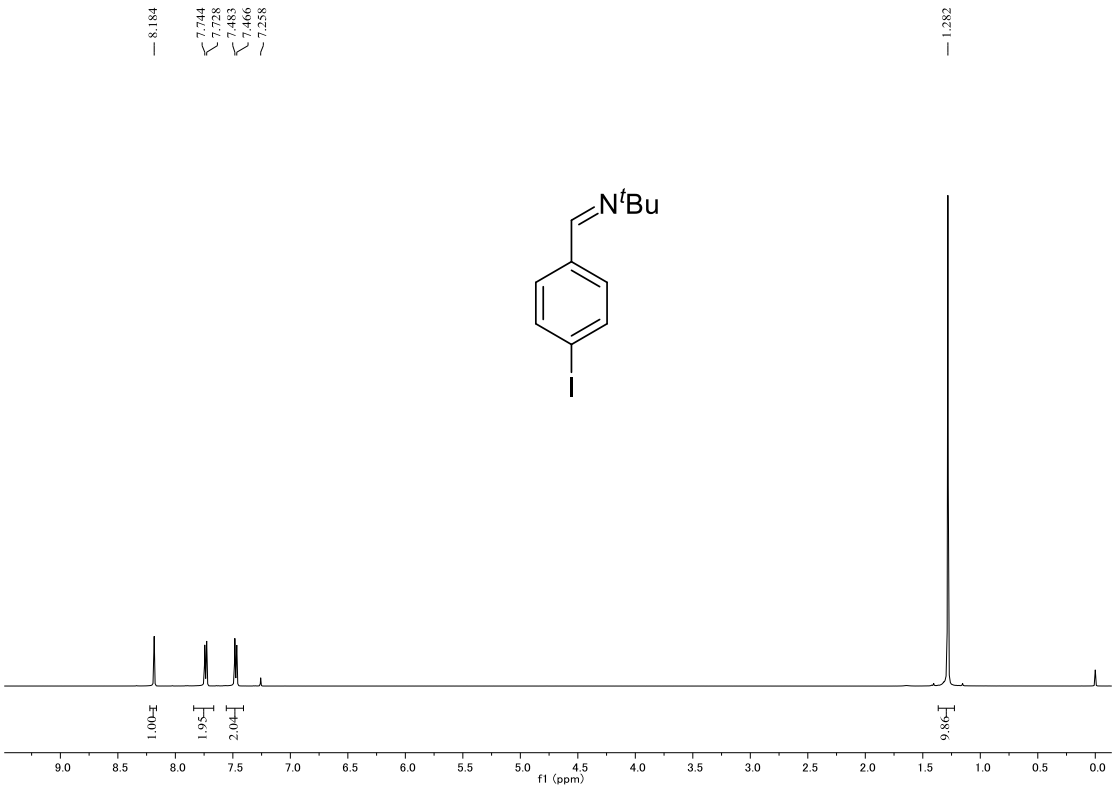
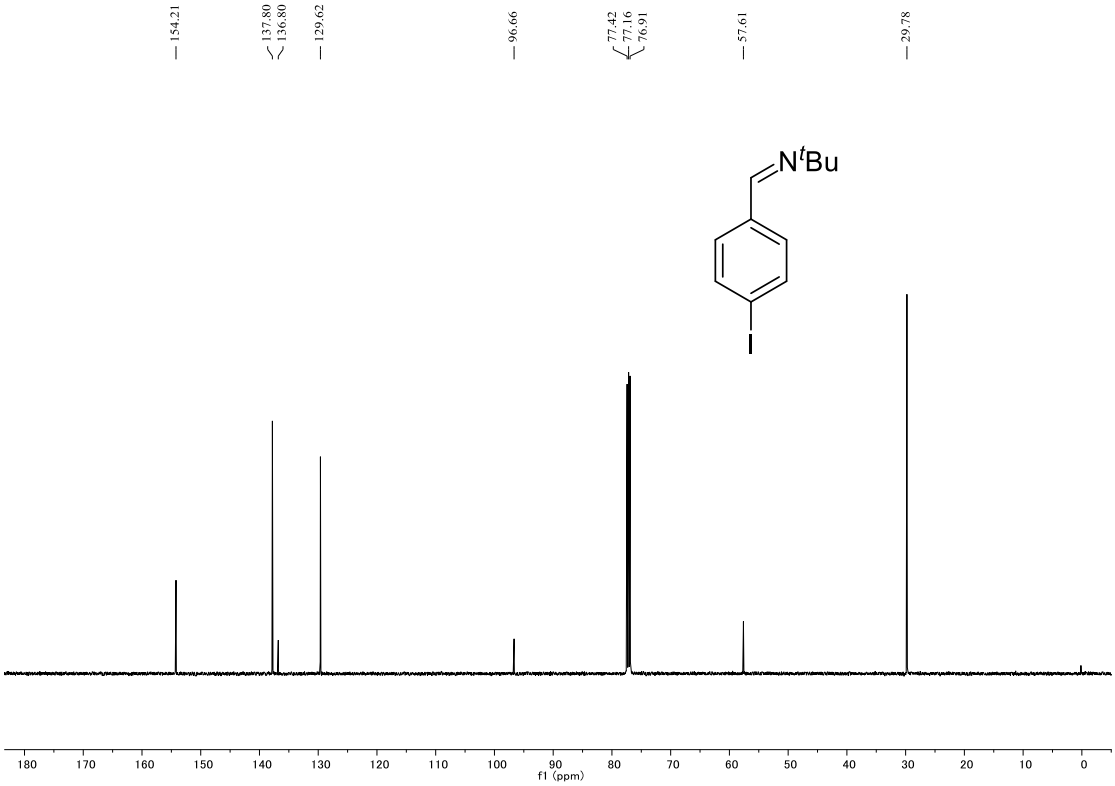
9. Copies of ^{1}H, and ^{13}C NMR Spectra

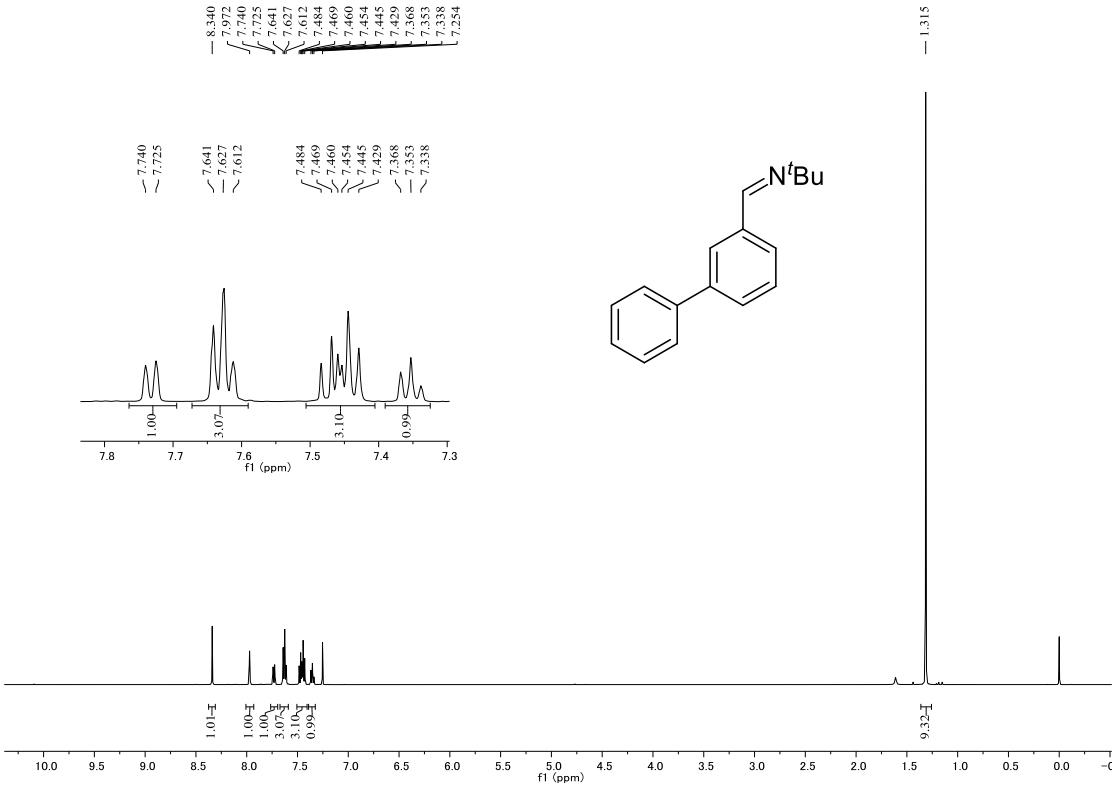
^{1}H NMR spectra of **1h** (500 MHz, $CDCl_3$)



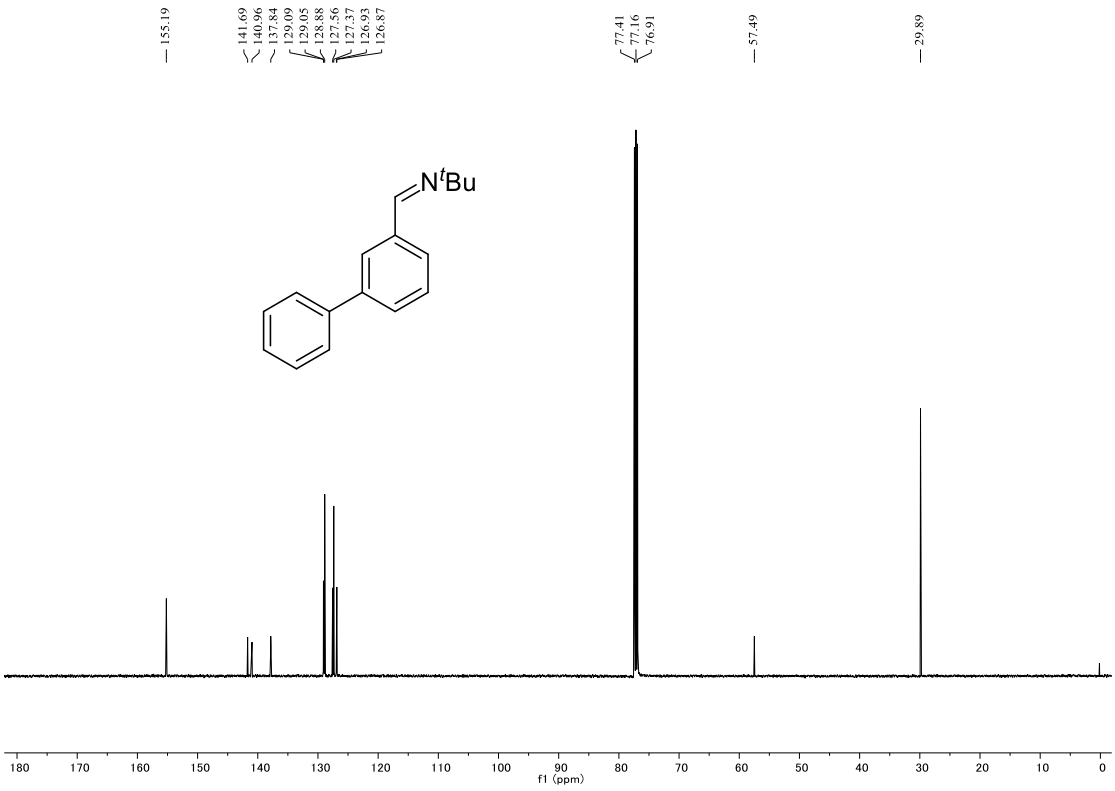
^{13}C NMR spectra of **1h** (126 MHz, $CDCl_3$)



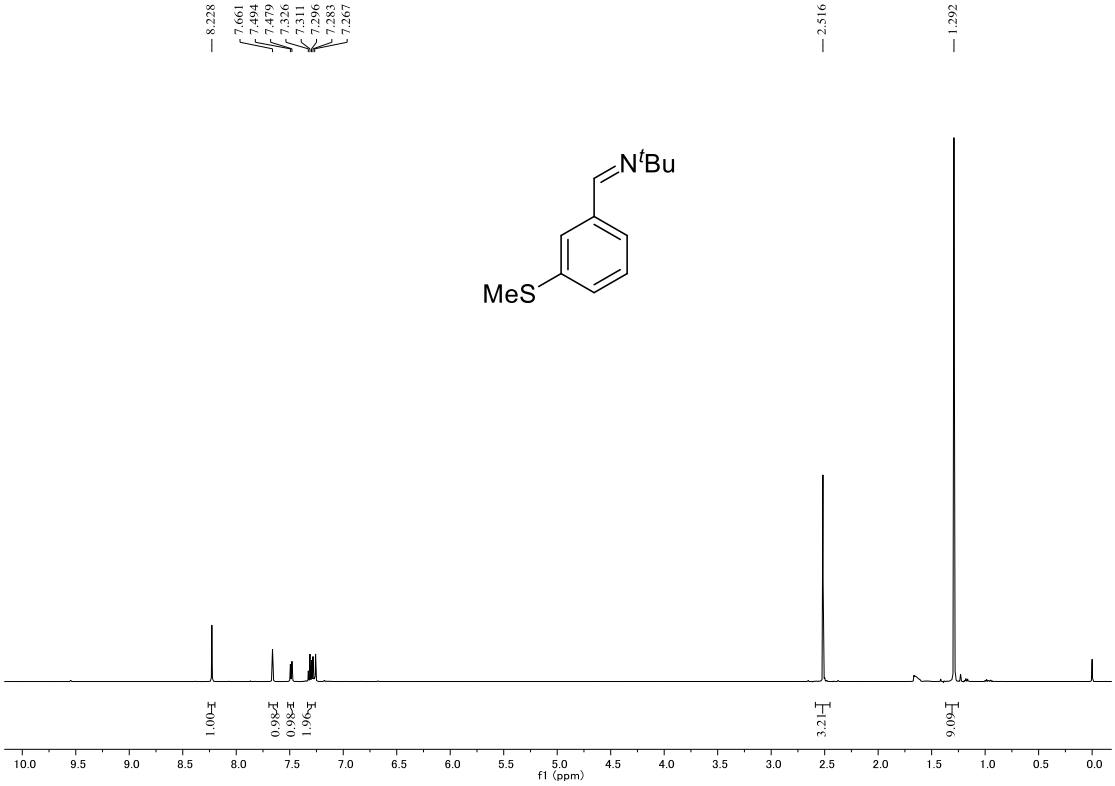
^{1}H NMR spectra of **1j** (500 MHz, $CDCl_3$)



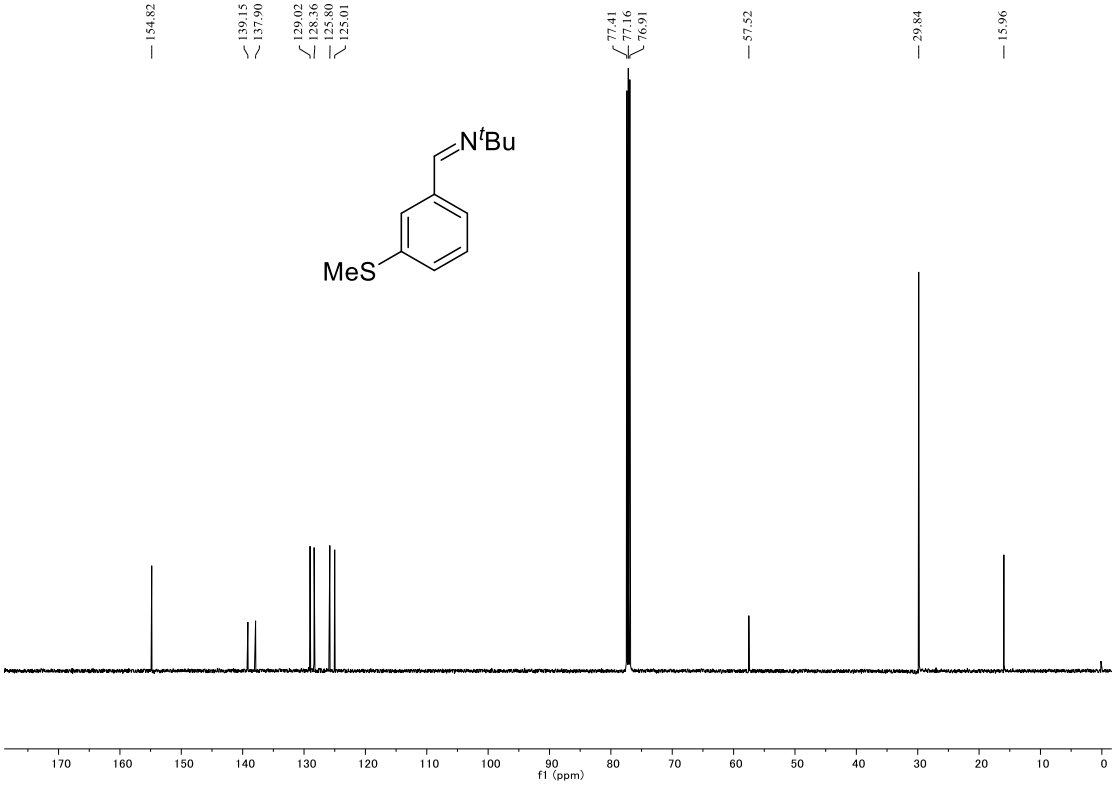
^{13}C NMR spectra of **1j** (126 MHz, $CDCl_3$)



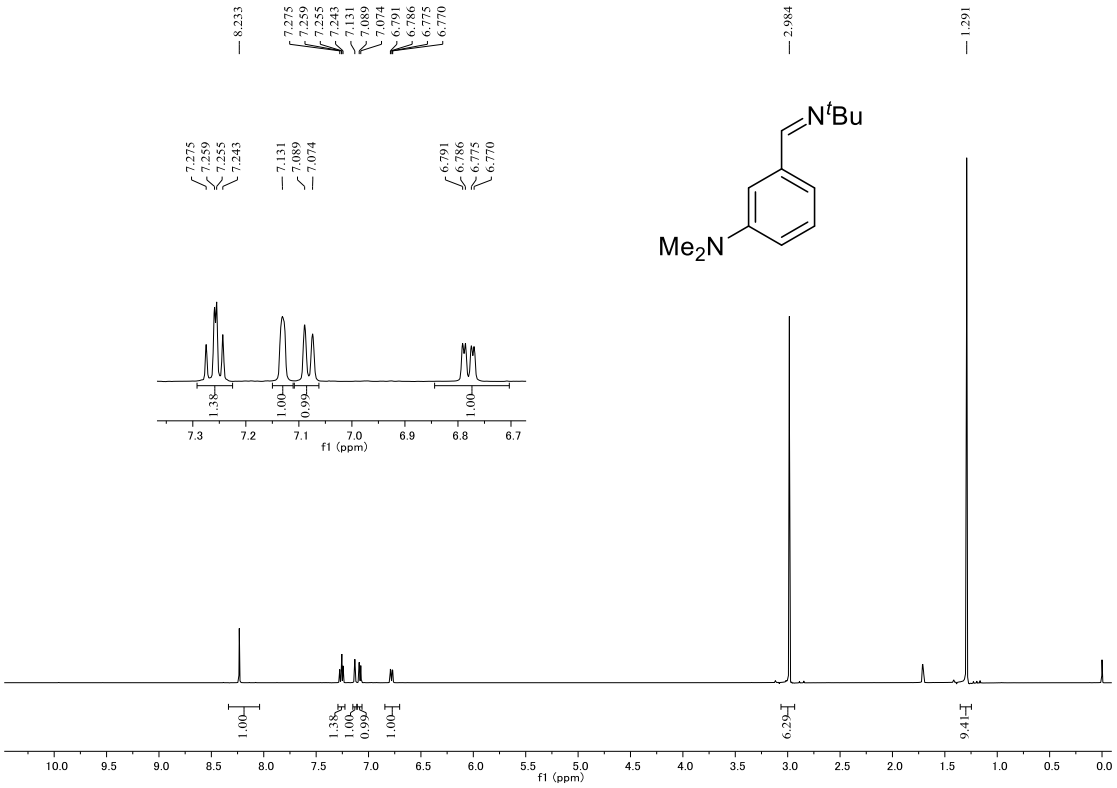
^{1}H NMR spectra of **1k** (500 MHz, $CDCl_3$)



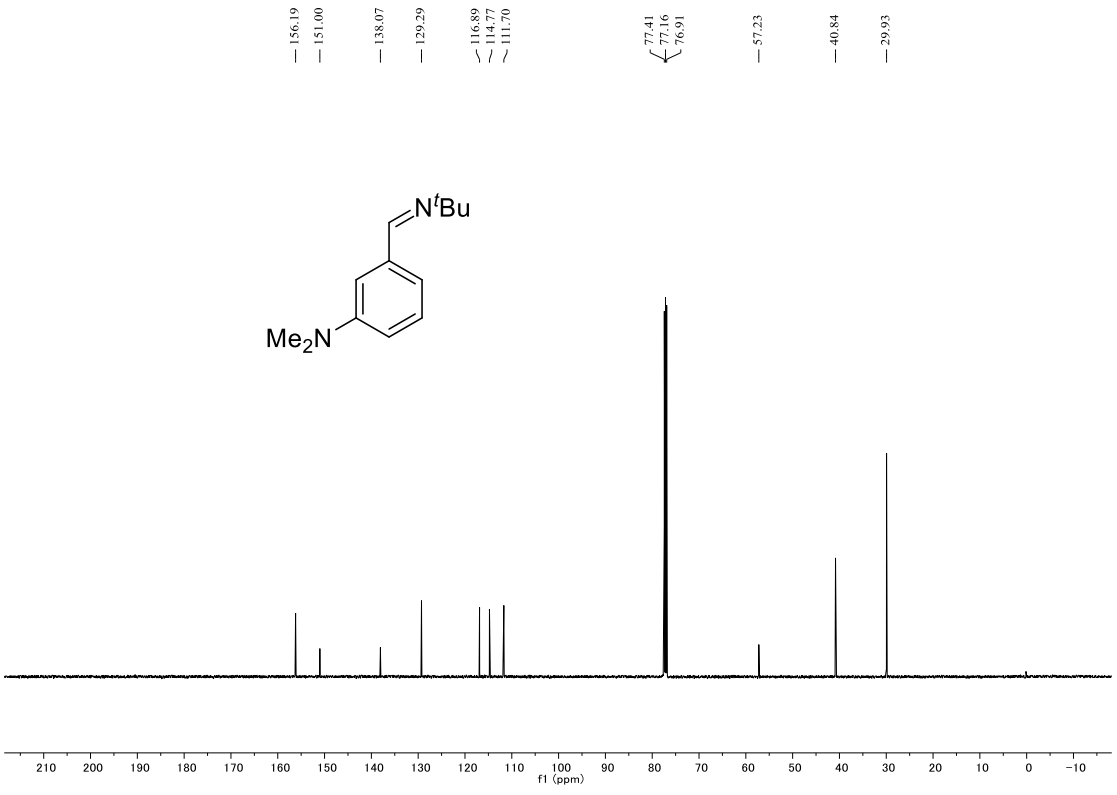
^{13}C NMR spectra of **1k** (126 MHz, $CDCl_3$)



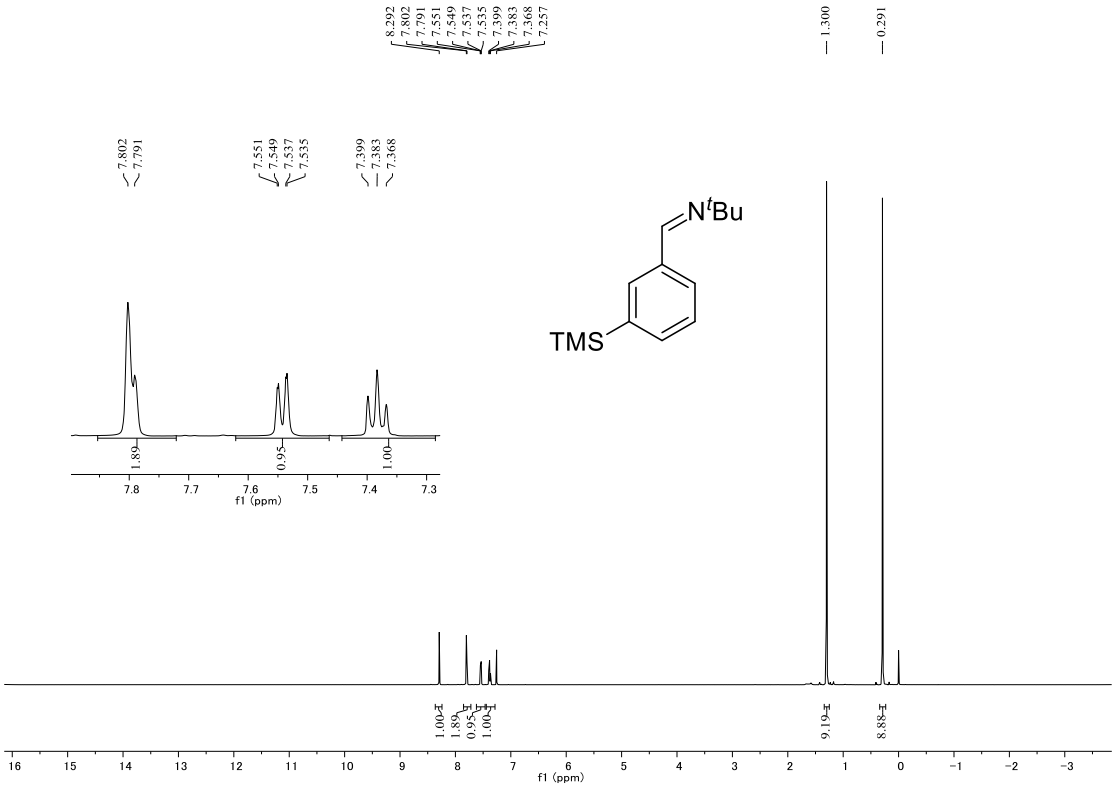
^{1}H NMR spectra of **1l** (500 MHz, $CDCl_3$)



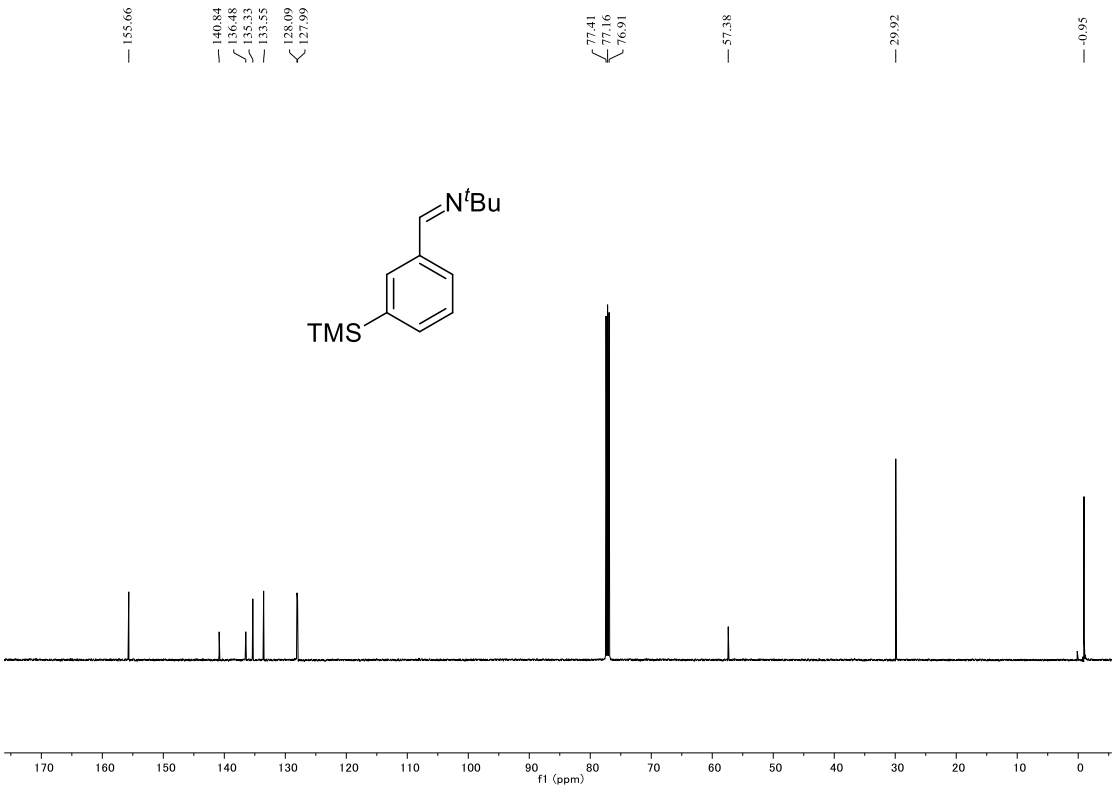
^{13}C NMR spectra of **1l** (126 MHz, $CDCl_3$)



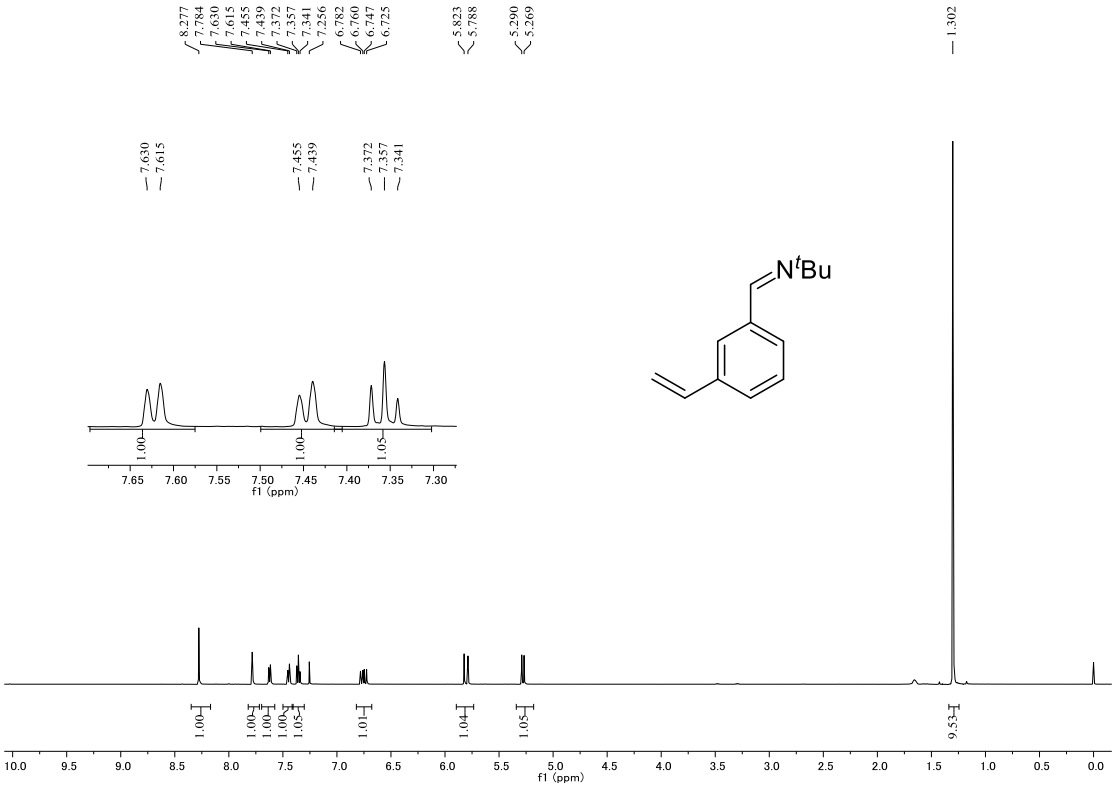
^{1}H NMR spectra of **1m** (500 MHz, $CDCl_3$)



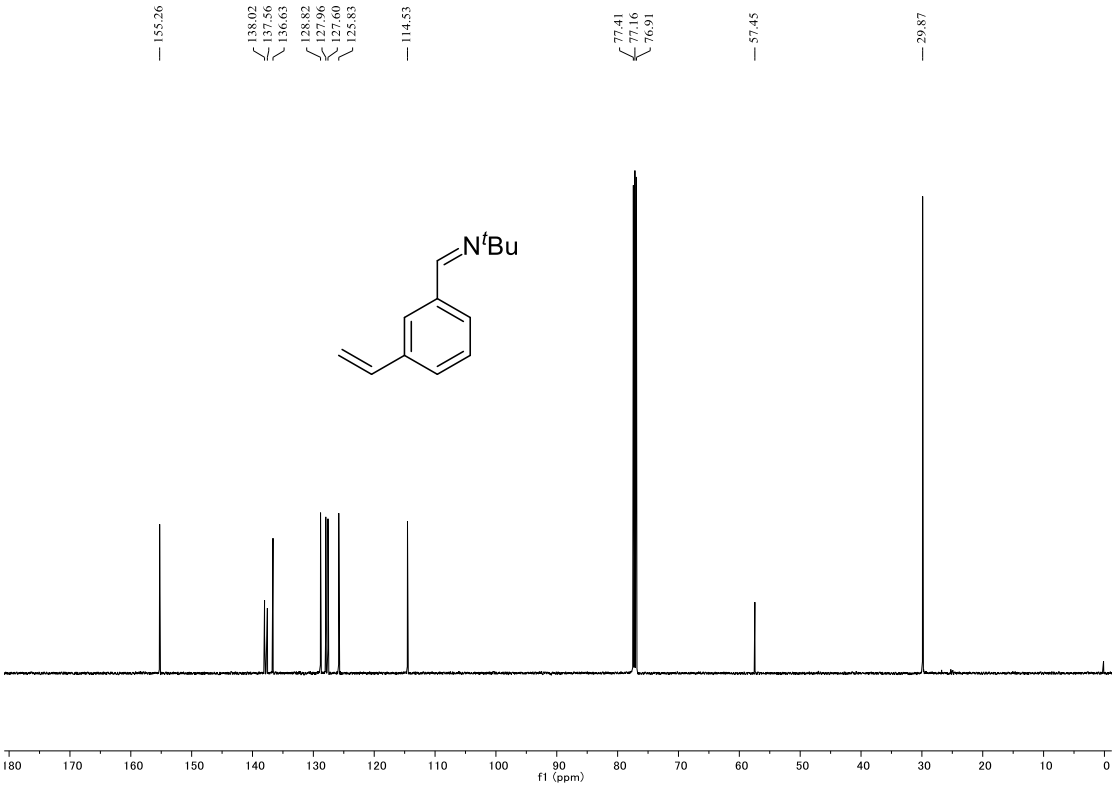
^{13}C NMR spectra of **1m** (126 MHz, $CDCl_3$)



^{1}H NMR spectra of **1n** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **1n** (126 MHz, $CDCl_3$)



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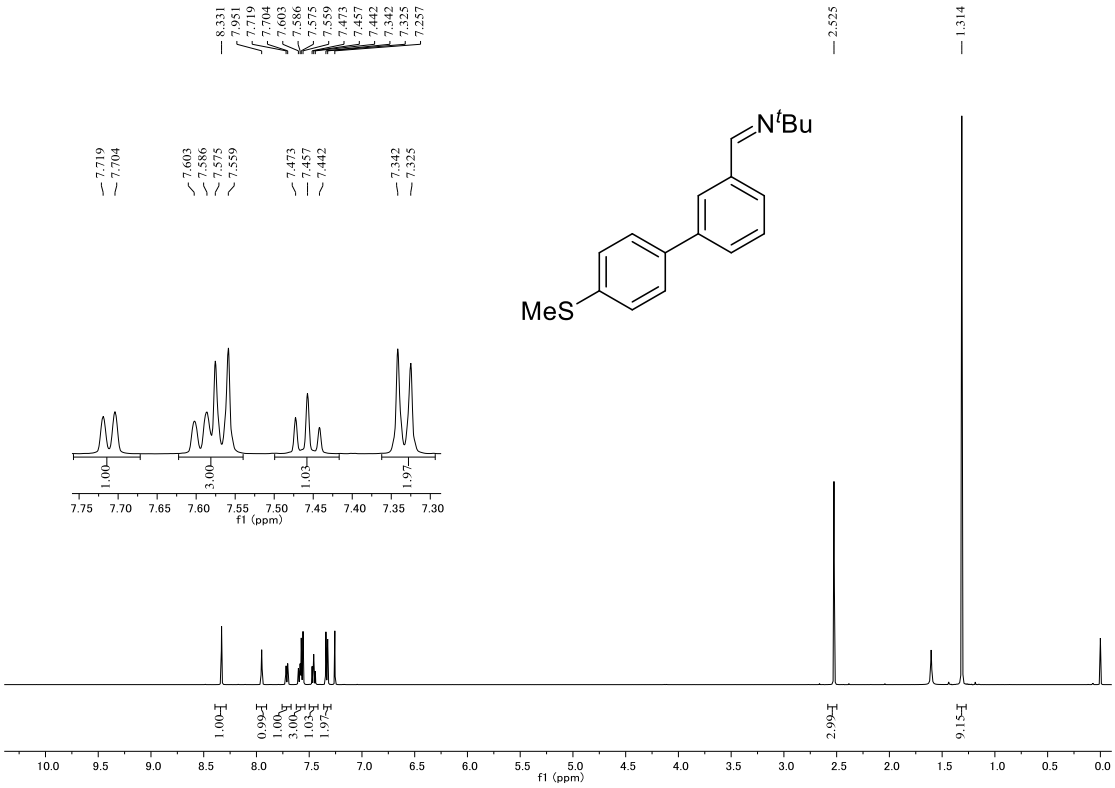

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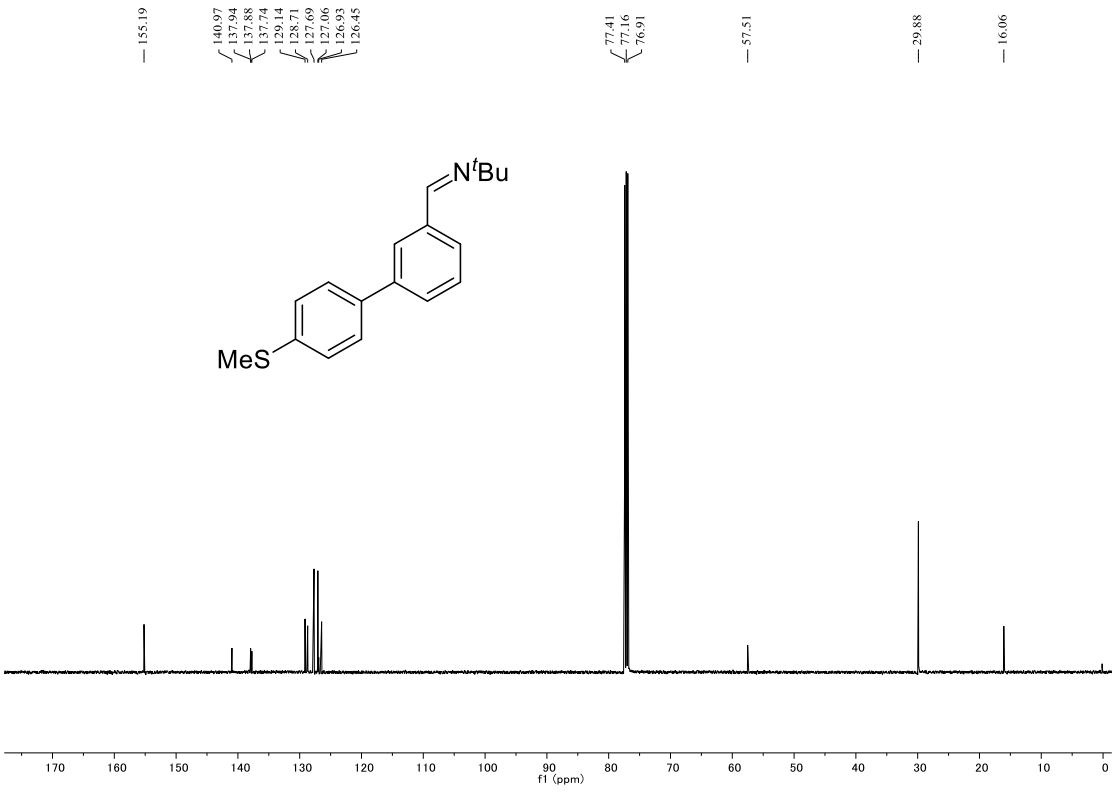
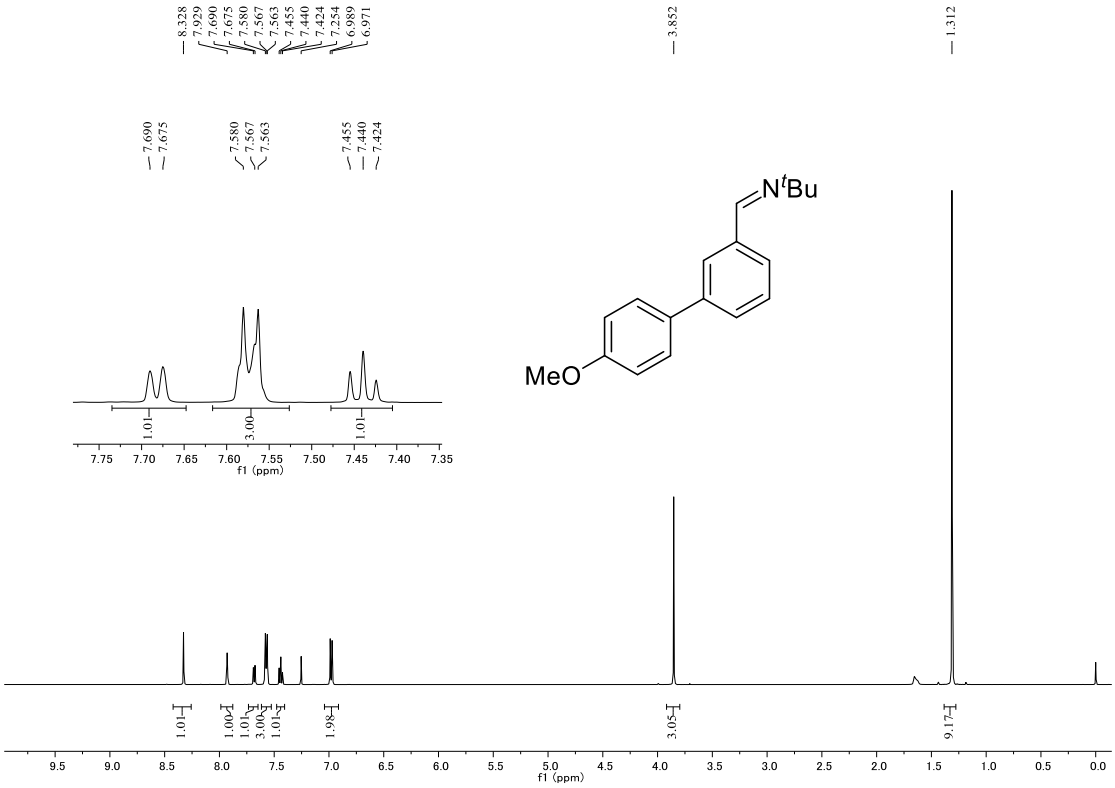
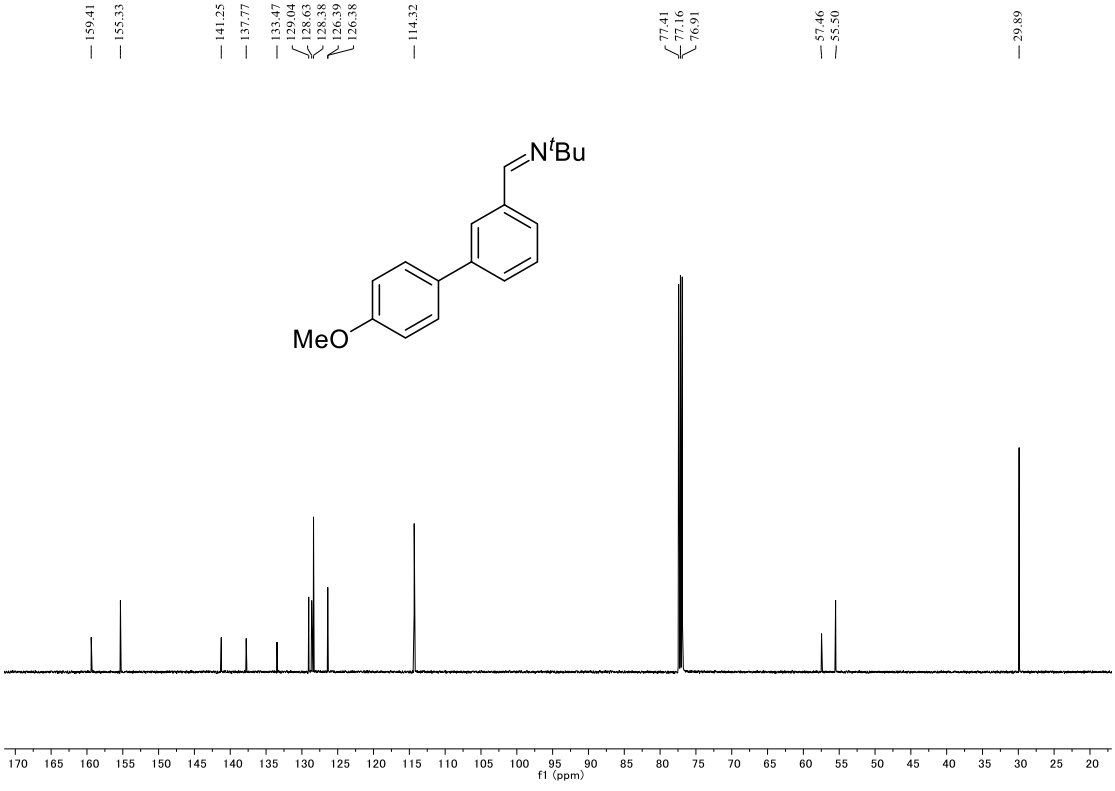


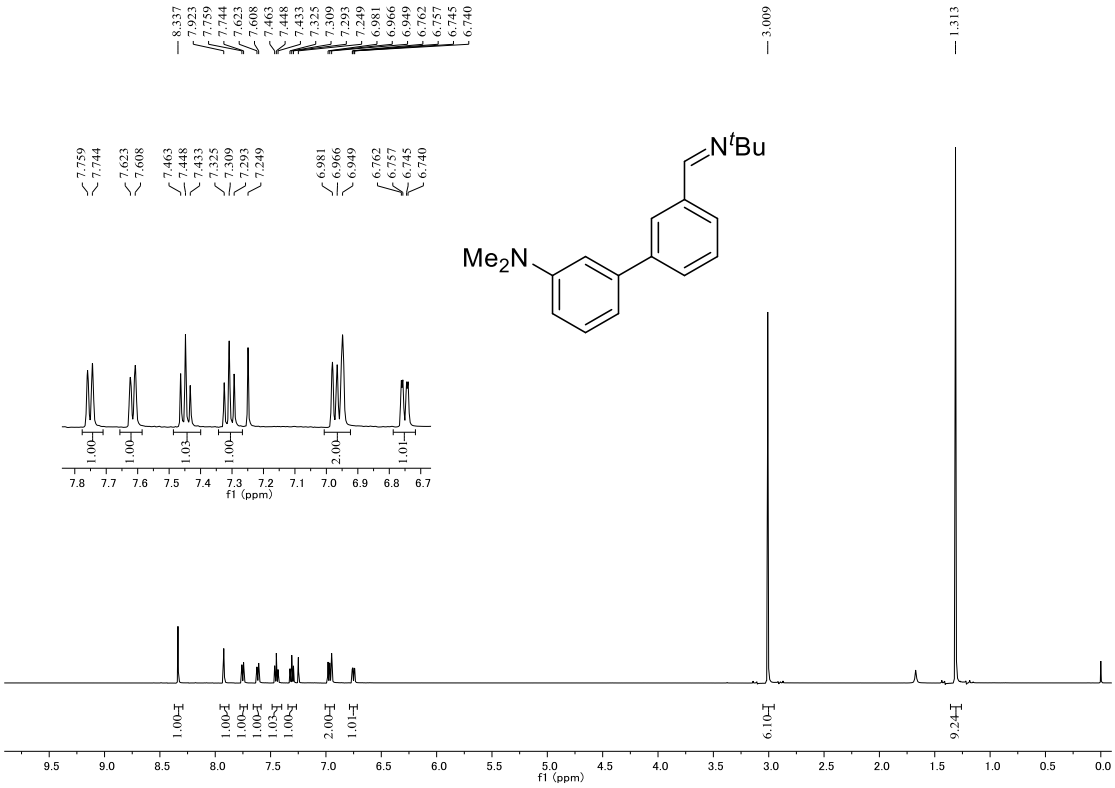
^{1}H NMR spectra of **1p** (500 MHz, $CDCl_3$)



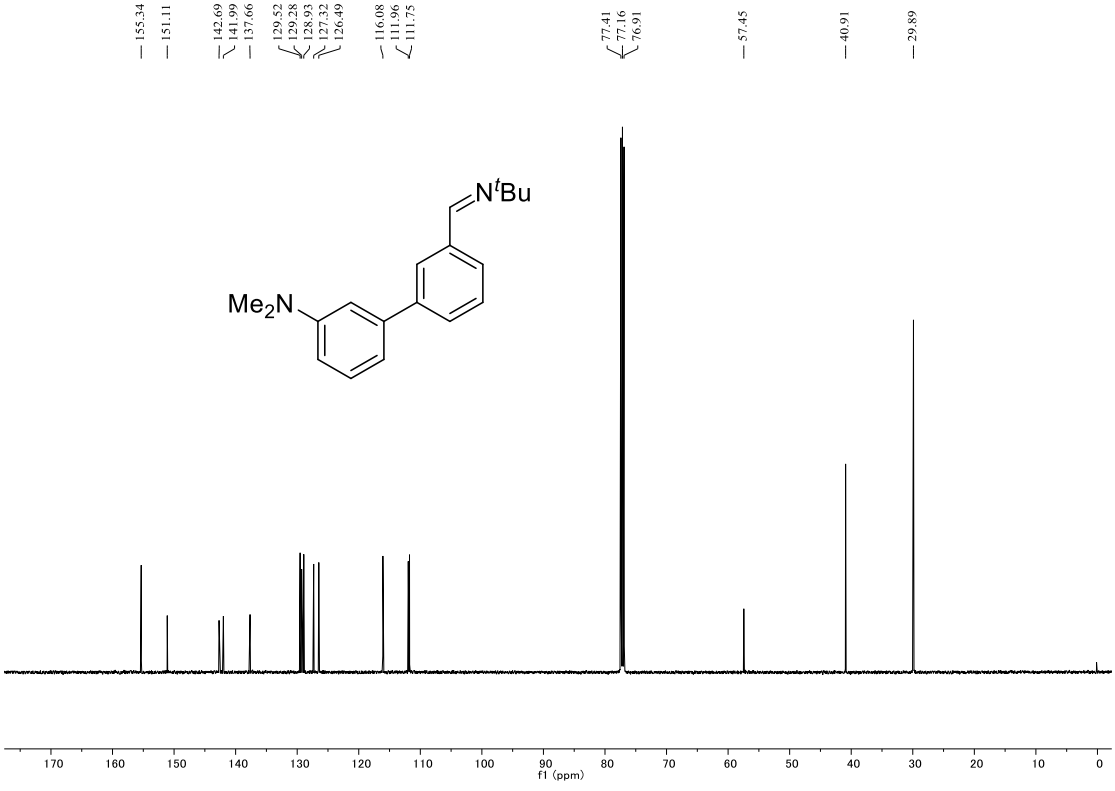
^{13}C NMR spectra of **1p** (126 MHz, $CDCl_3$)



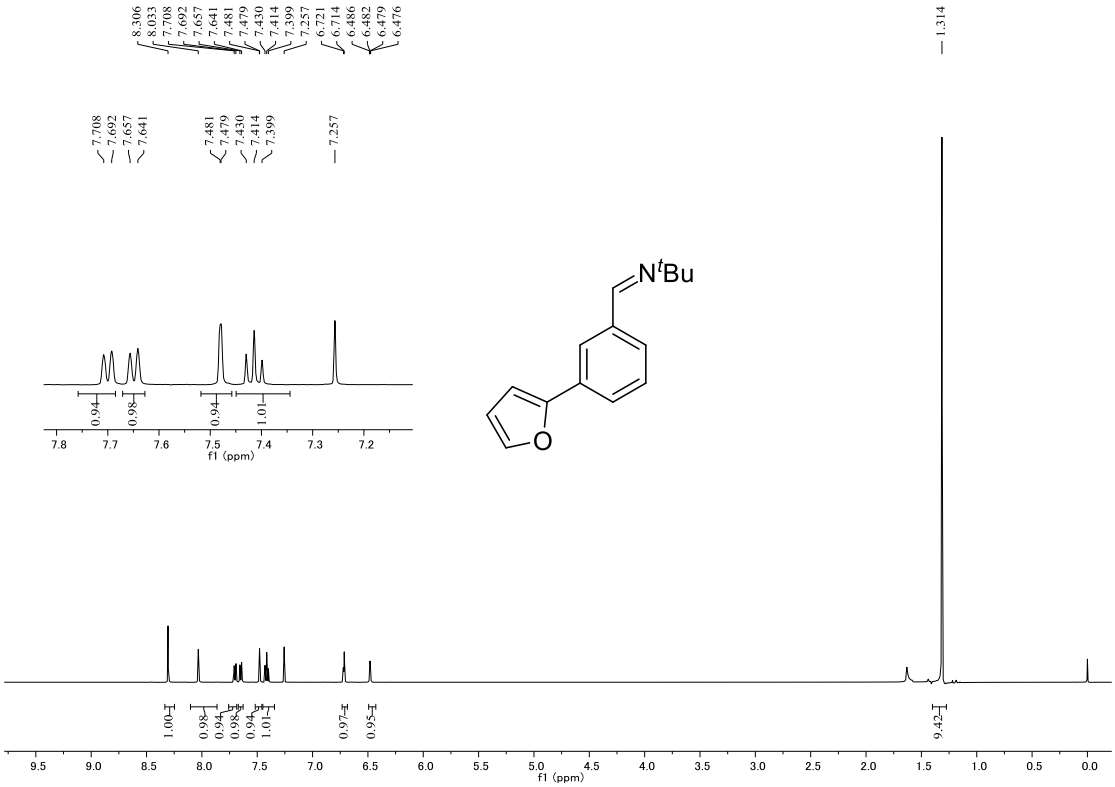
^{1}H NMR spectra of **1q** (500 MHz, $CDCl_3$)



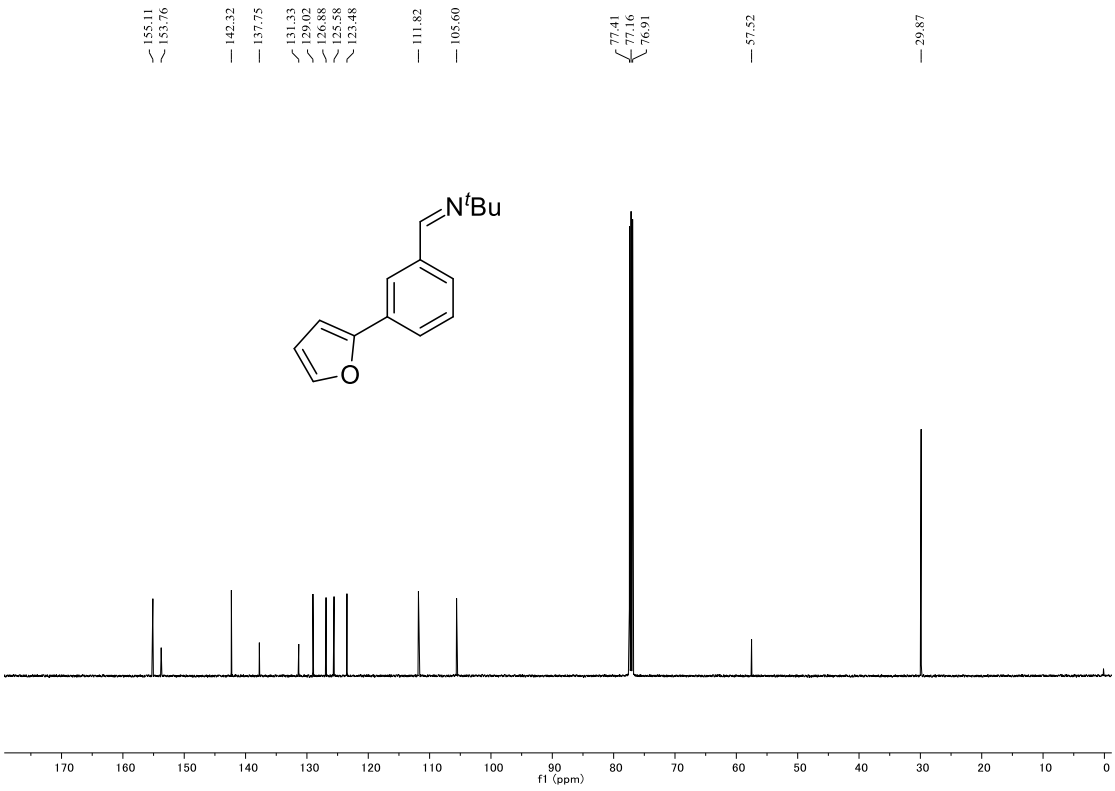
^{13}C NMR spectra of **1q** (126 MHz, $CDCl_3$)



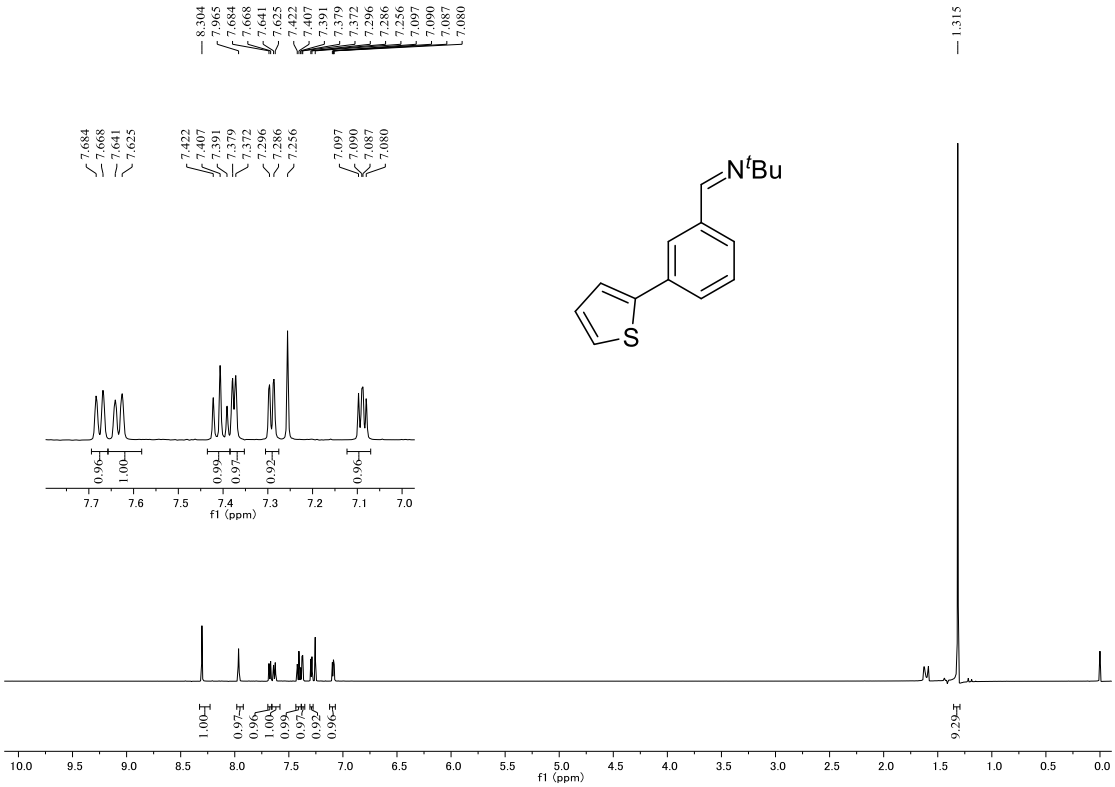
^{1}H NMR spectra of **1r** (500 MHz, $CDCl_3$)



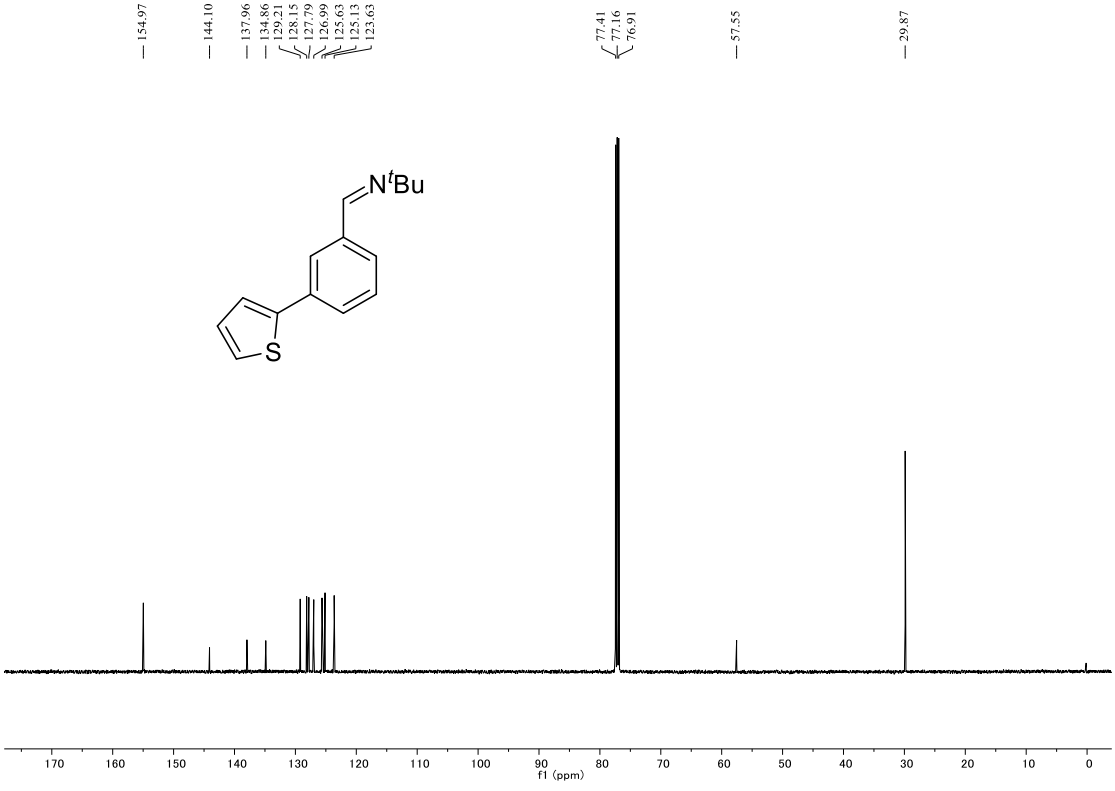
^{13}C NMR spectra of **1r** (126 MHz, $CDCl_3$)



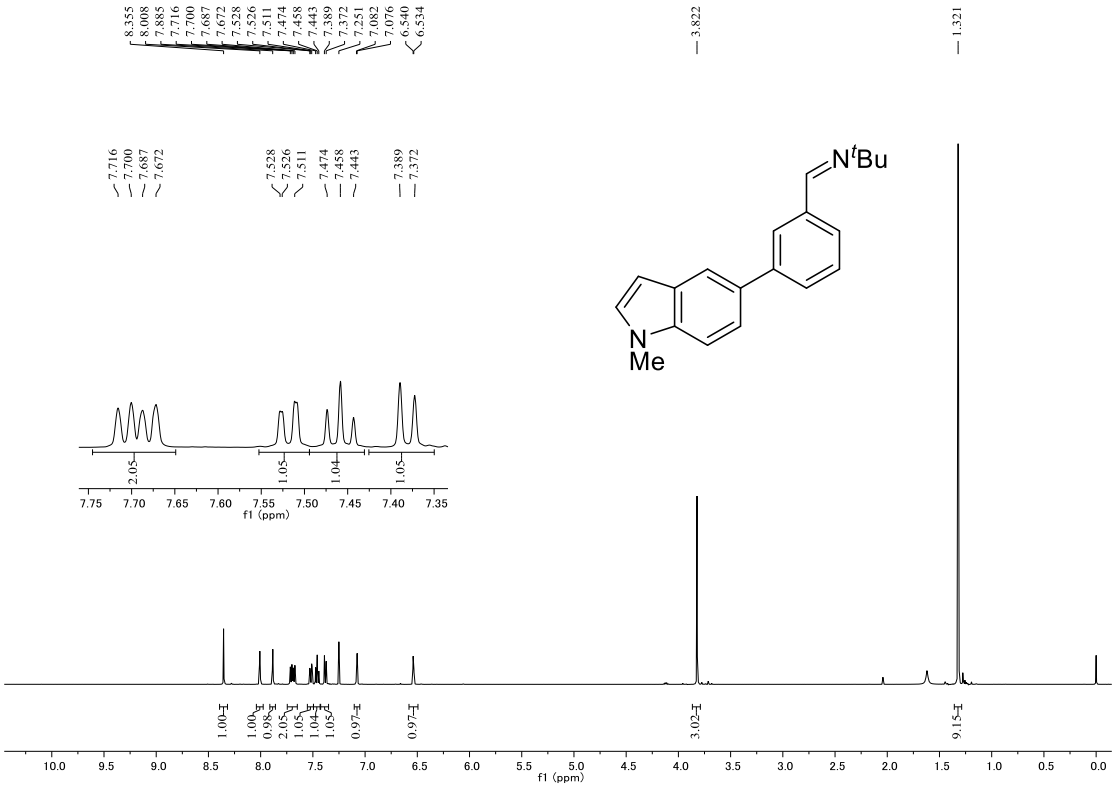
^{1}H NMR spectra of **1s** (500 MHz, $CDCl_3$)



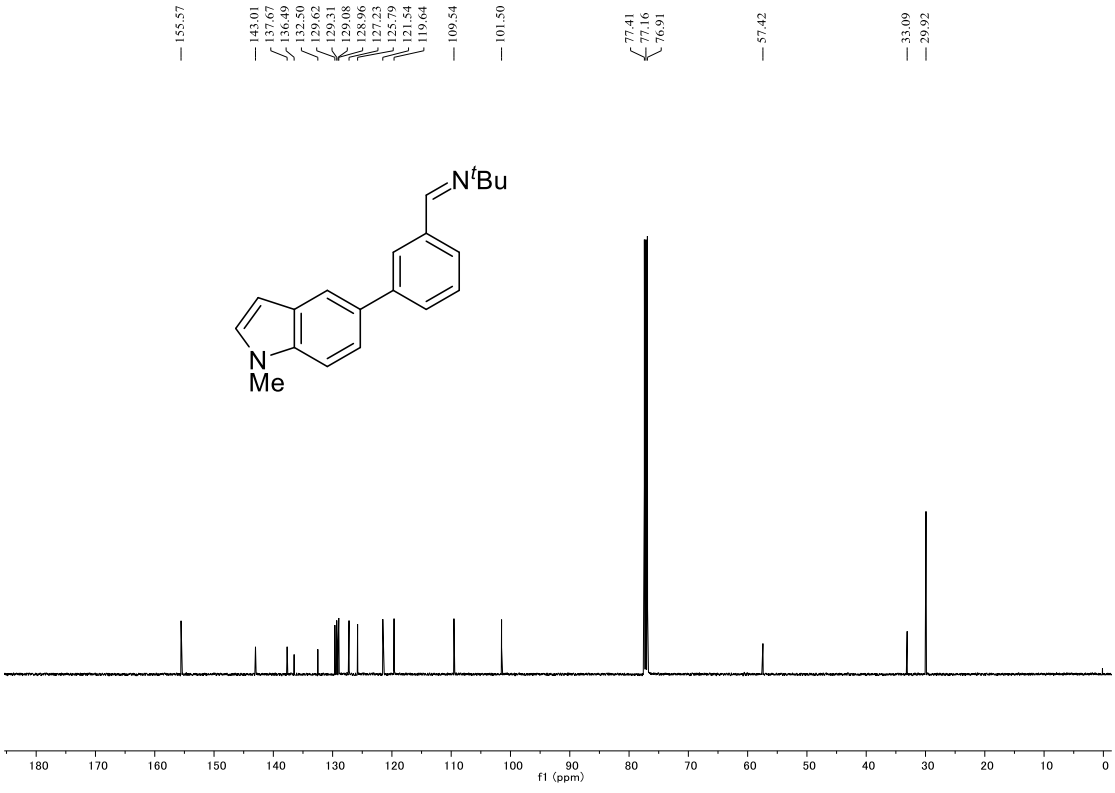
^{13}C NMR spectra of **1s** (126 MHz, $CDCl_3$)



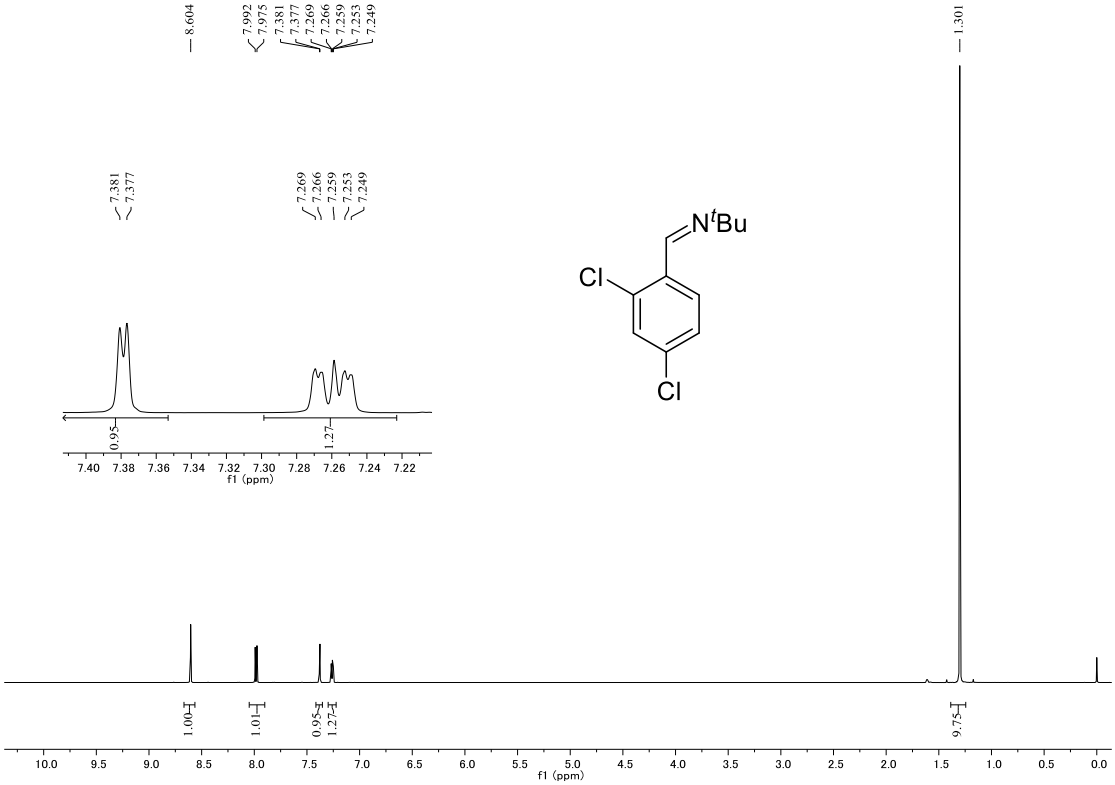
^{1}H NMR spectra of **1t** (500 MHz, $CDCl_3$)



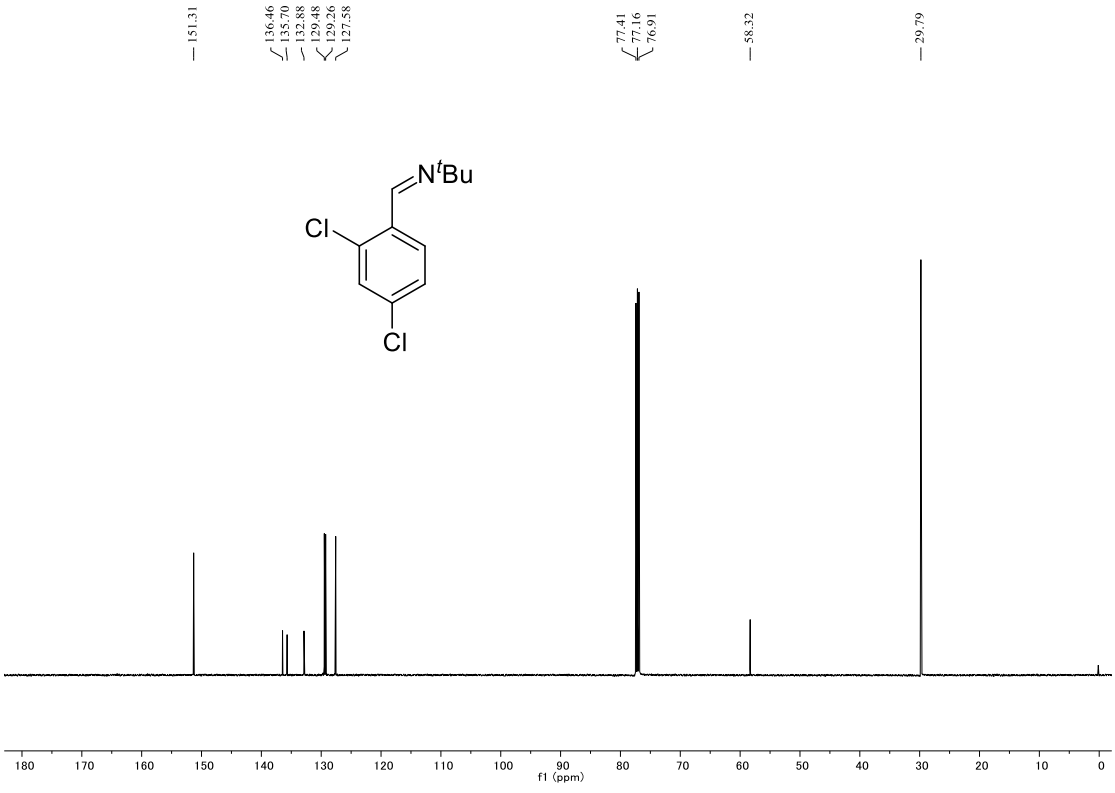
^{13}C NMR spectra of **1t** (126 MHz, $CDCl_3$)



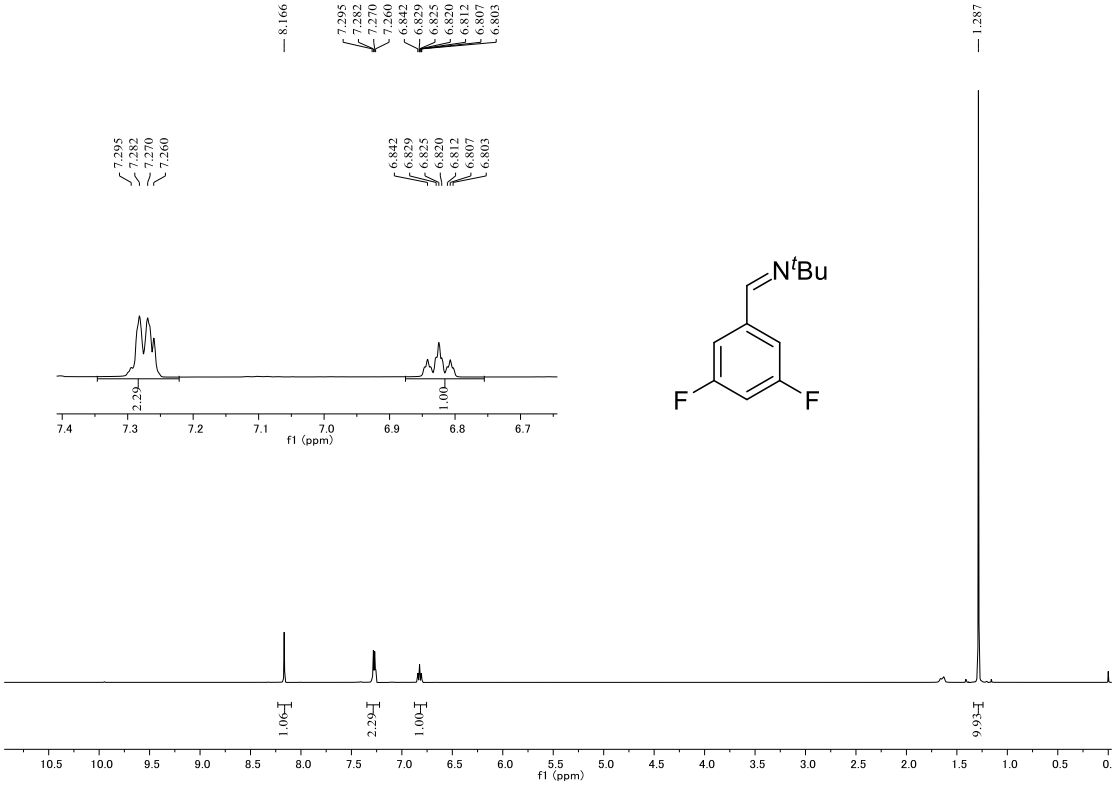
^{1}H NMR spectra of **1v** (500 MHz, $CDCl_3$)



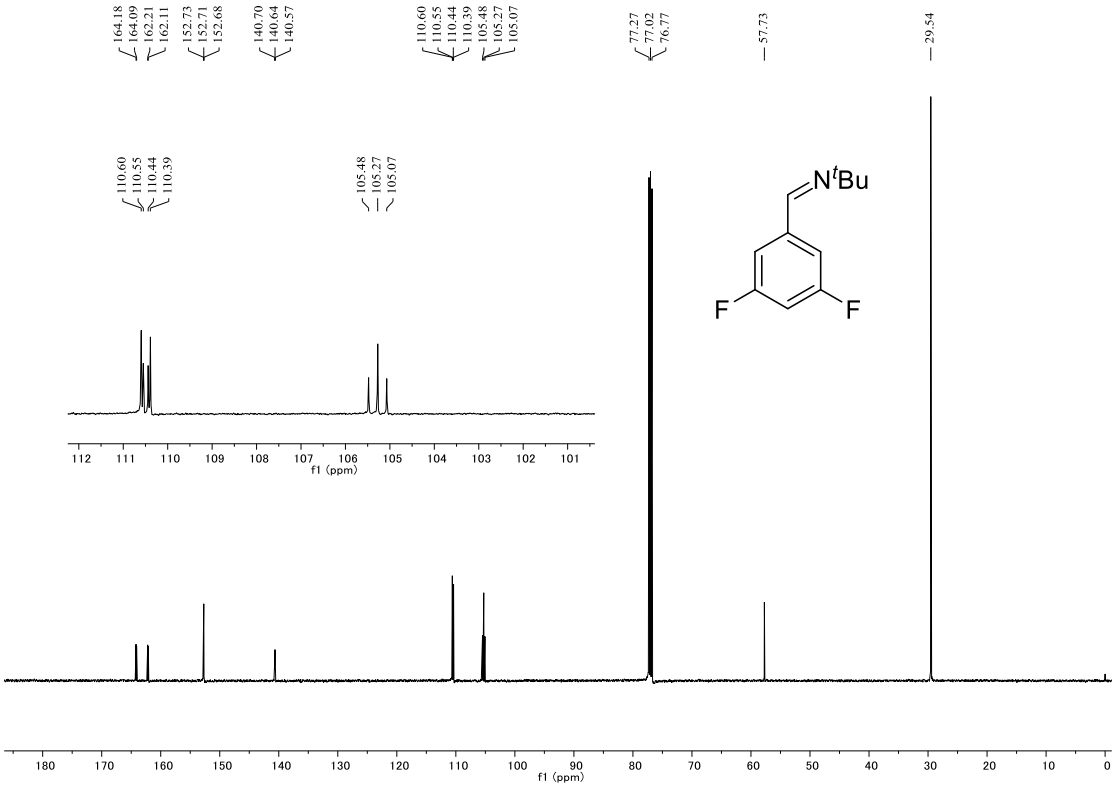
^{13}C NMR spectra of **1v** (126 MHz, $CDCl_3$)



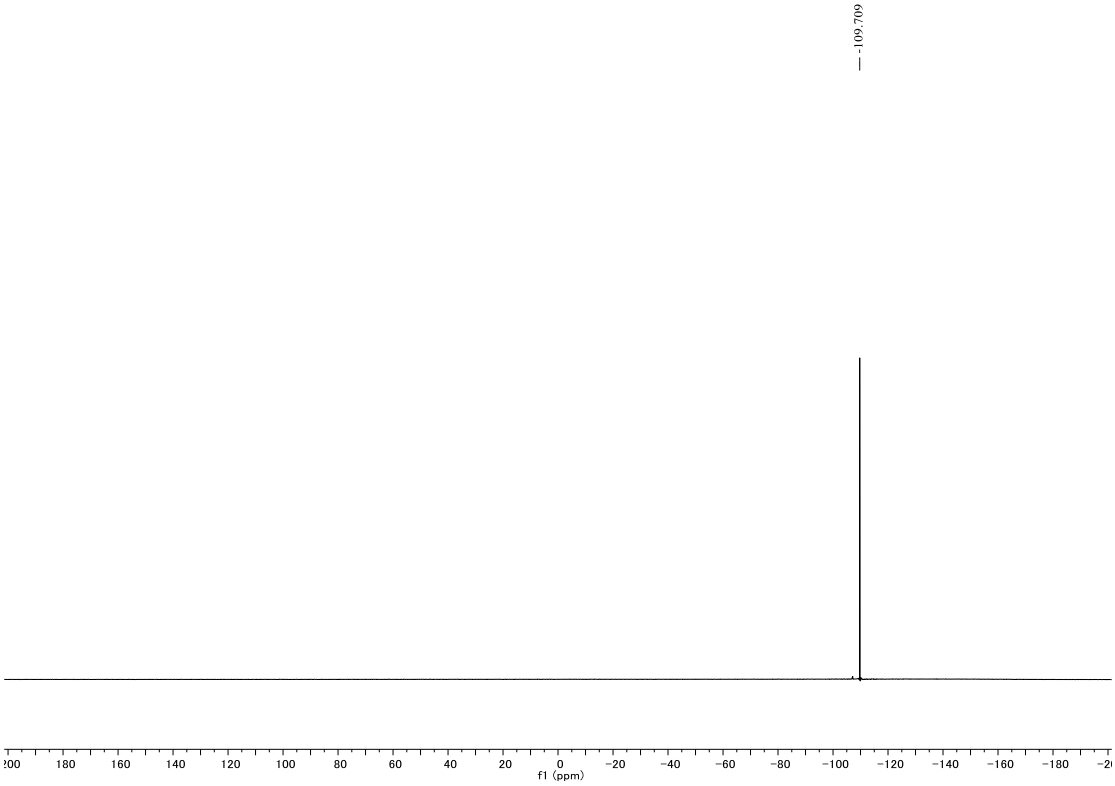
^{1}H NMR spectra of **1w** (500 MHz, $CDCl_3$)



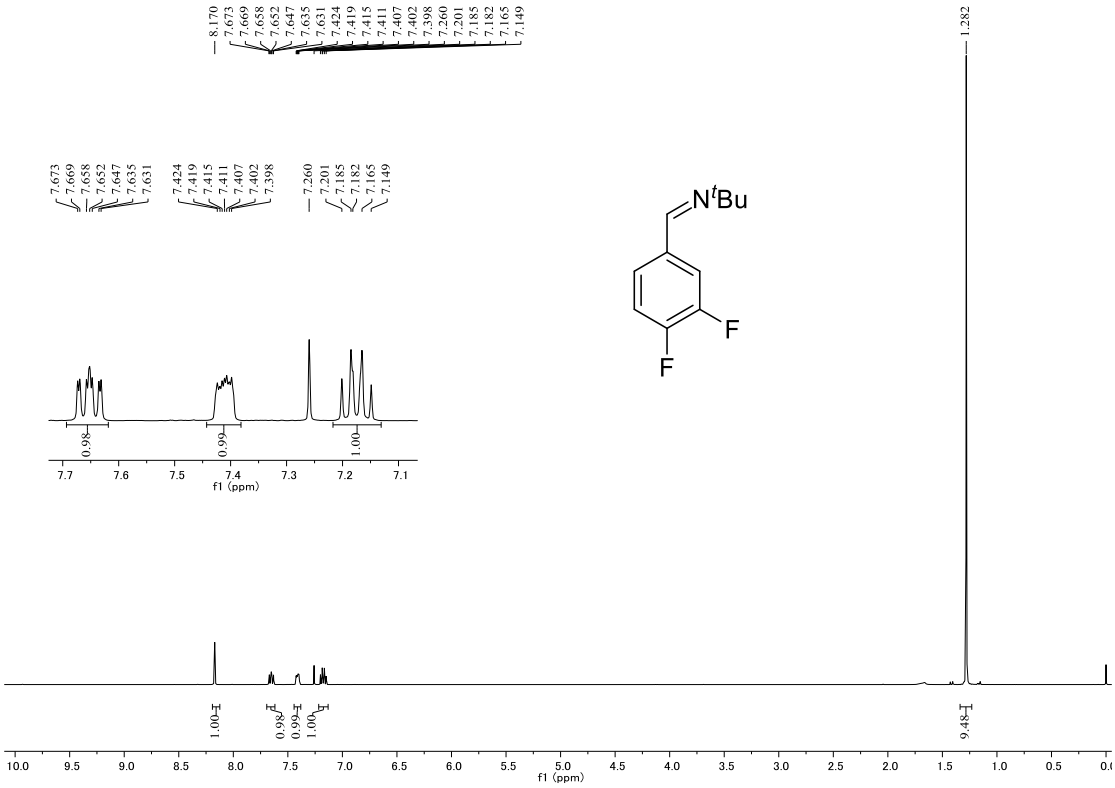
^{13}C NMR spectra of **1w** (126 MHz, $CDCl_3$)



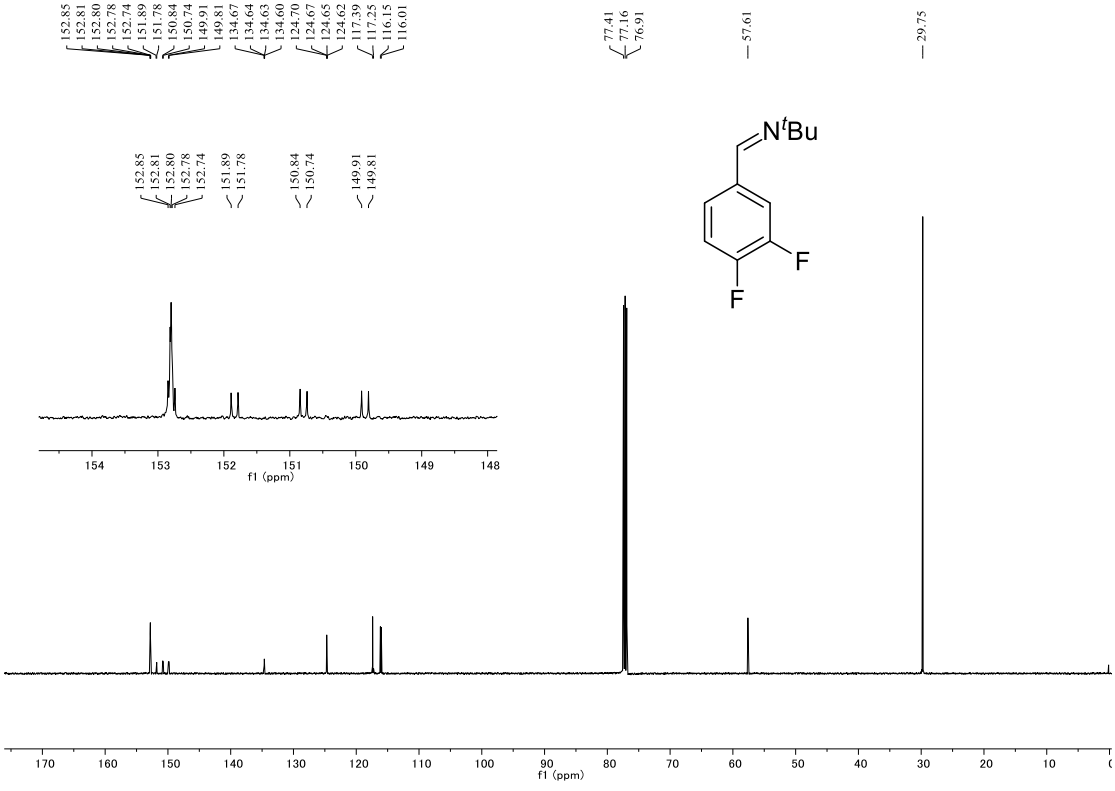
^{19}F NMR spectra of **1w** (377 MHz, $CDCl_3$)



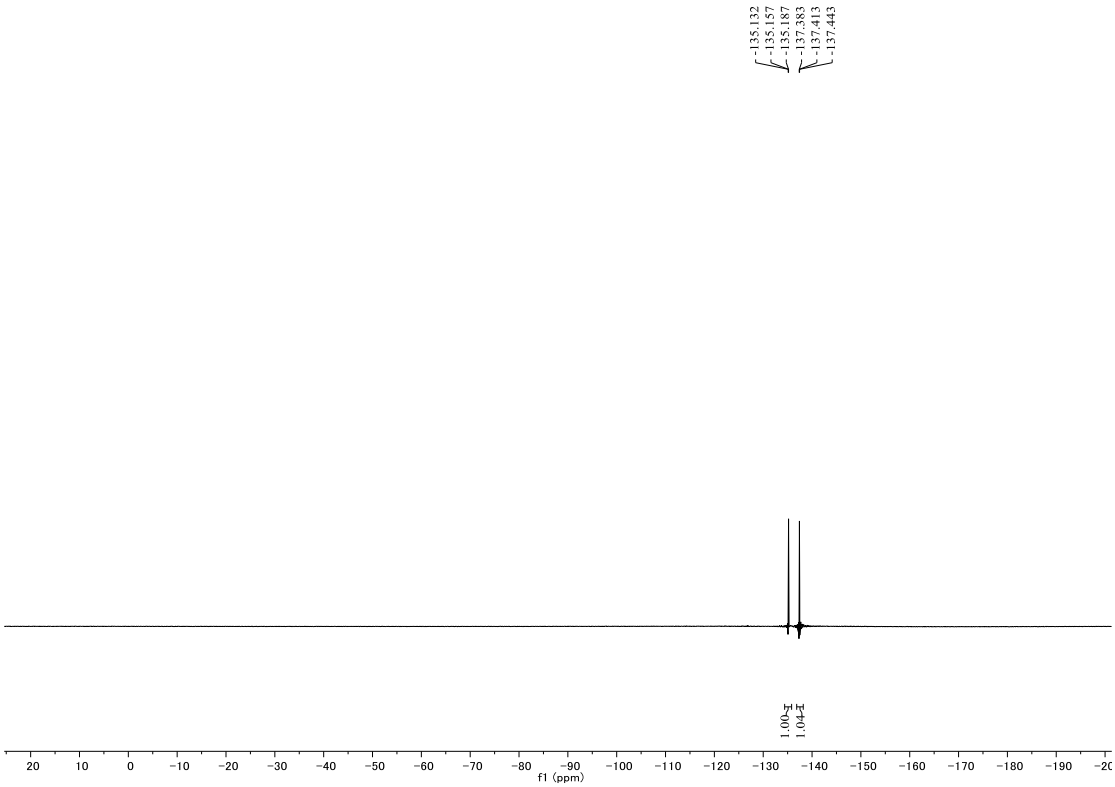
^{1}H NMR spectra of **1x** (500 MHz, $CDCl_3$)



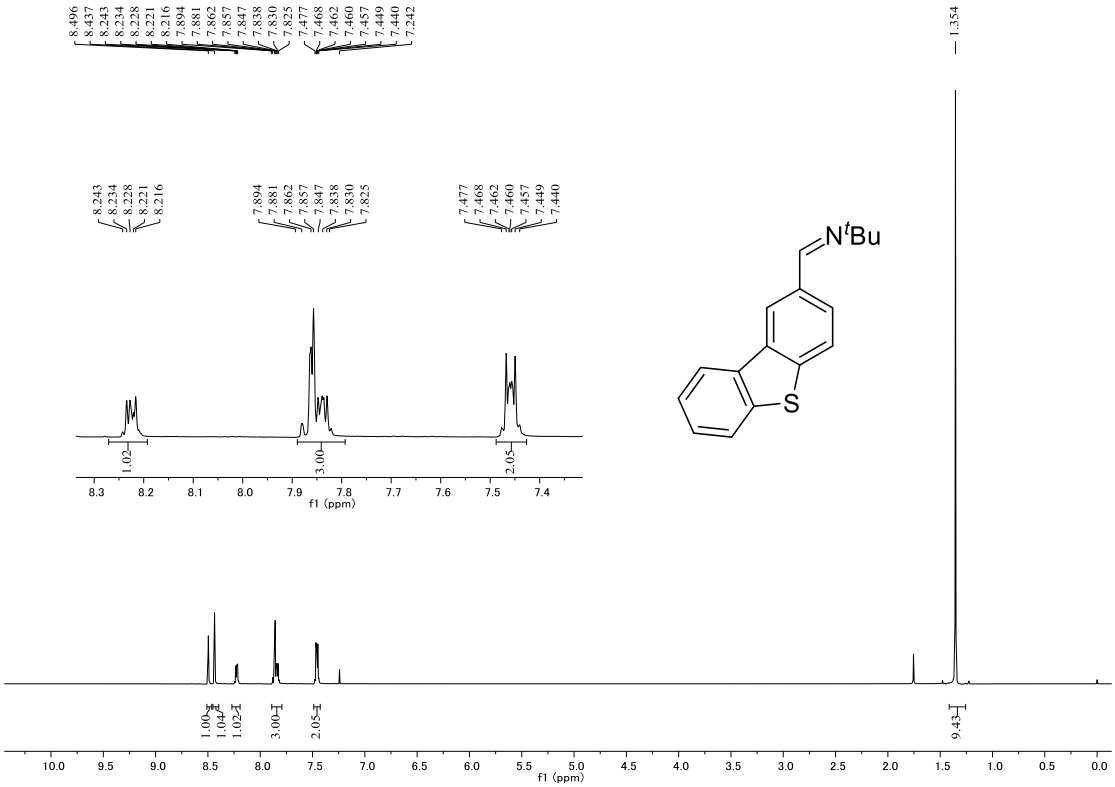
^{13}C NMR spectra of **1x** (126 MHz, $CDCl_3$)



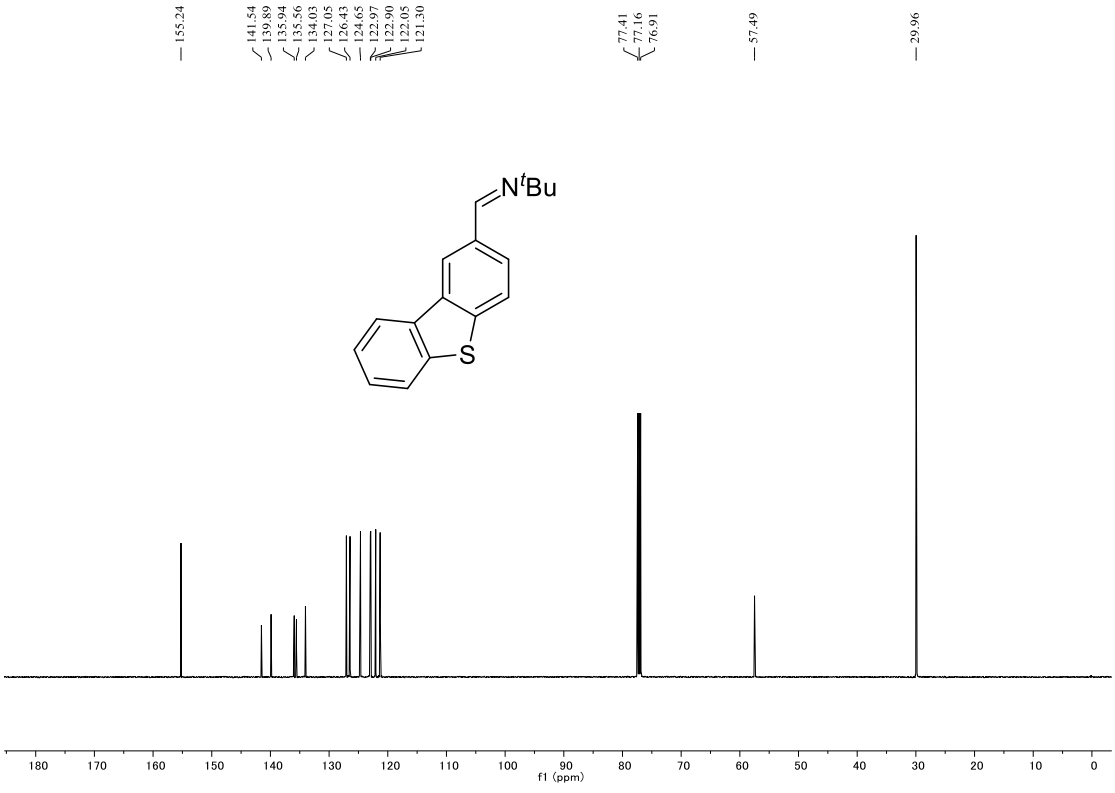
^{19}F NMR spectra of **1x** (377 MHz, $CDCl_3$)



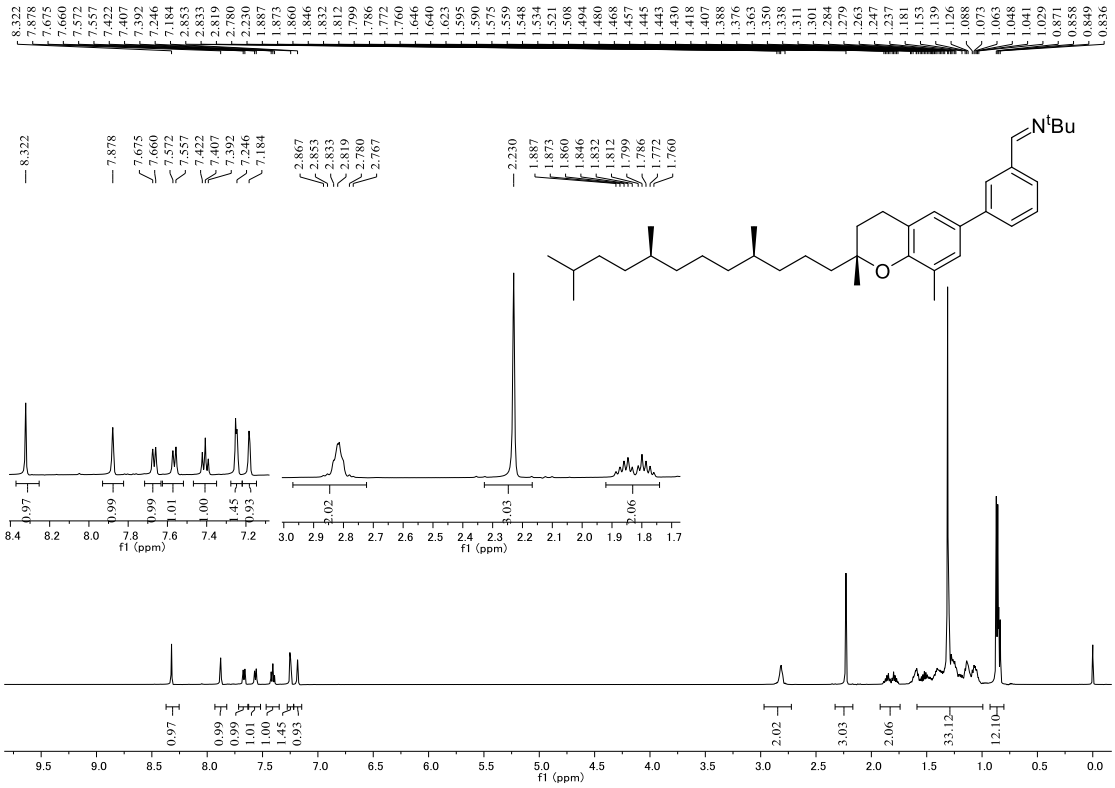
^{1}H NMR spectra of **1z** (500 MHz, $CDCl_3$)



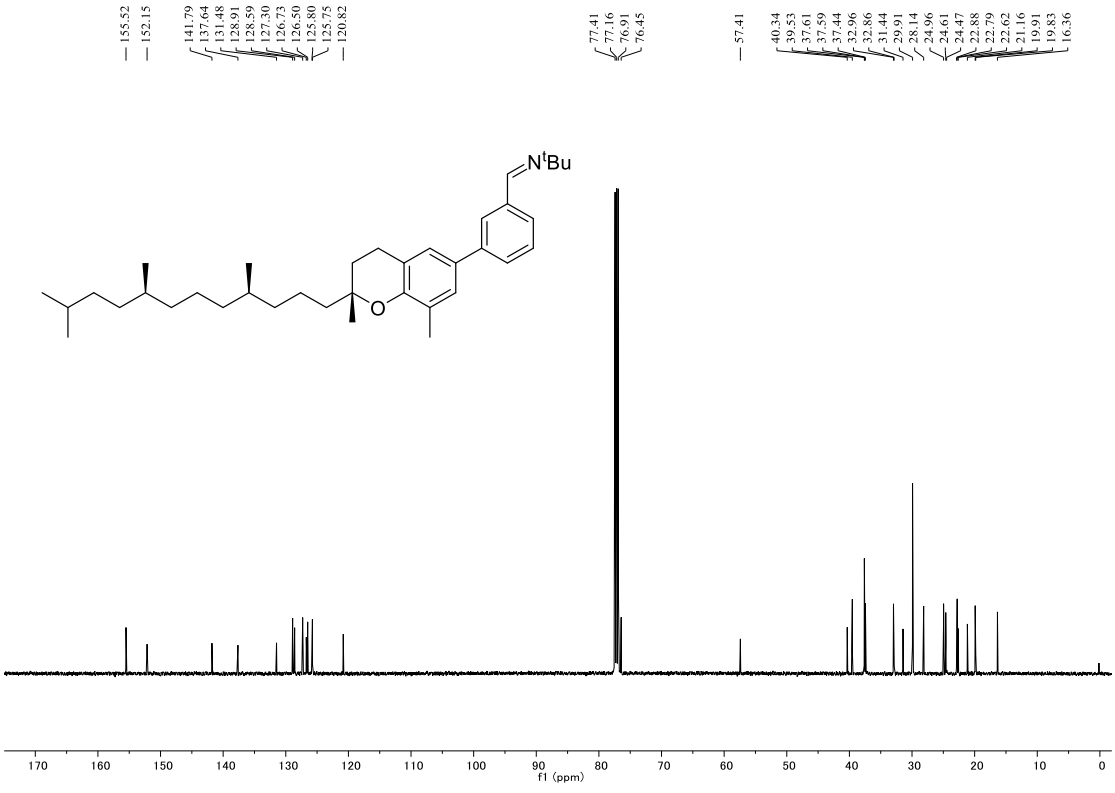
^{13}C NMR spectra of **1z** (126 MHz, $CDCl_3$)



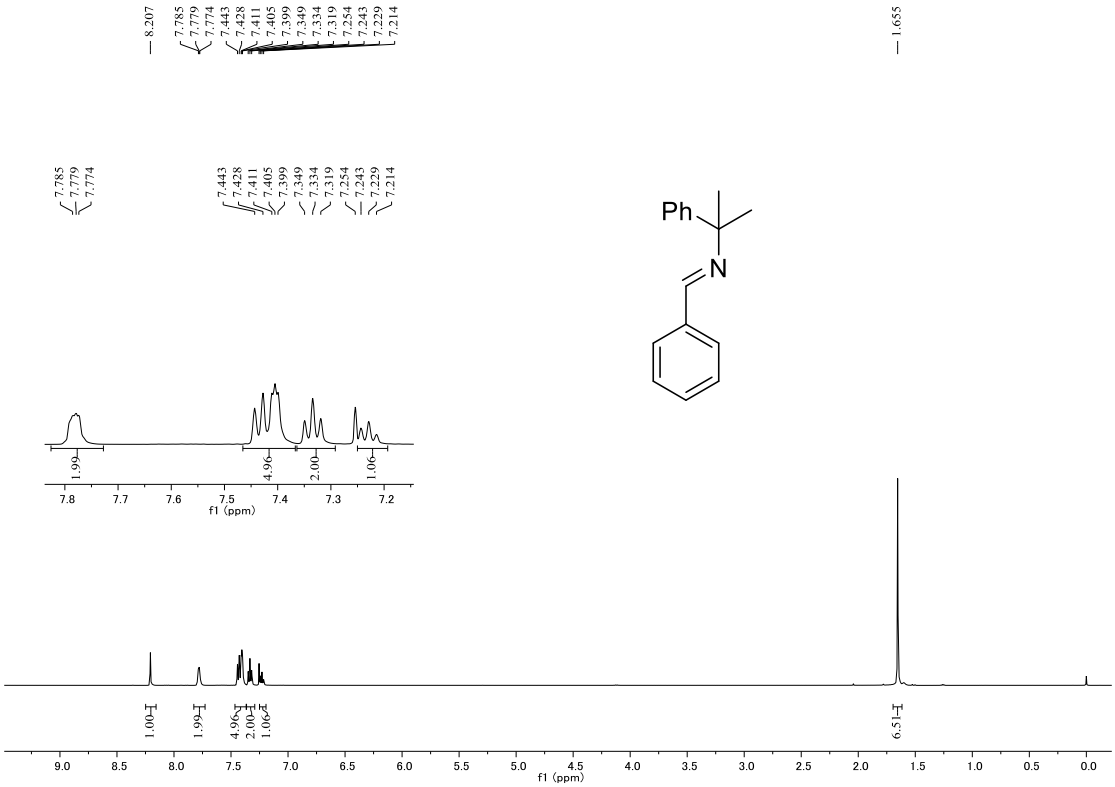
^{1}H NMR spectra of **1aa** (500 MHz, $CDCl_3$)



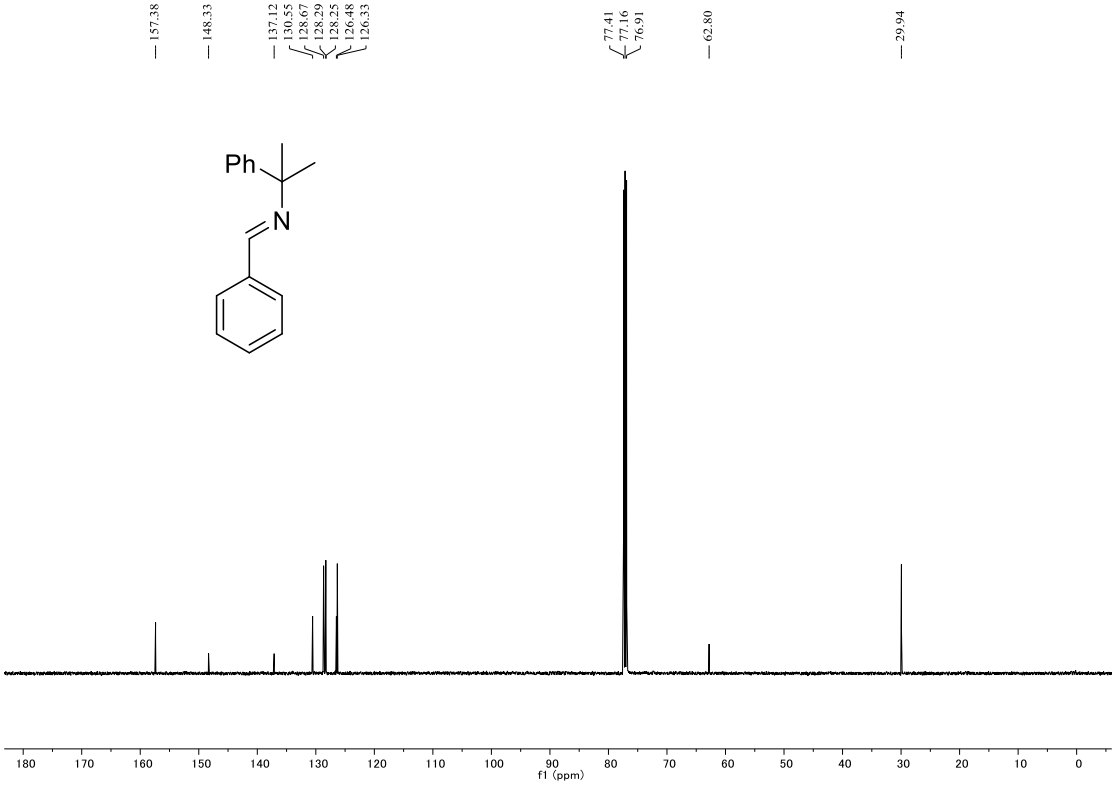
^{13}C NMR spectra of **1aa** (126 MHz, $CDCl_3$)



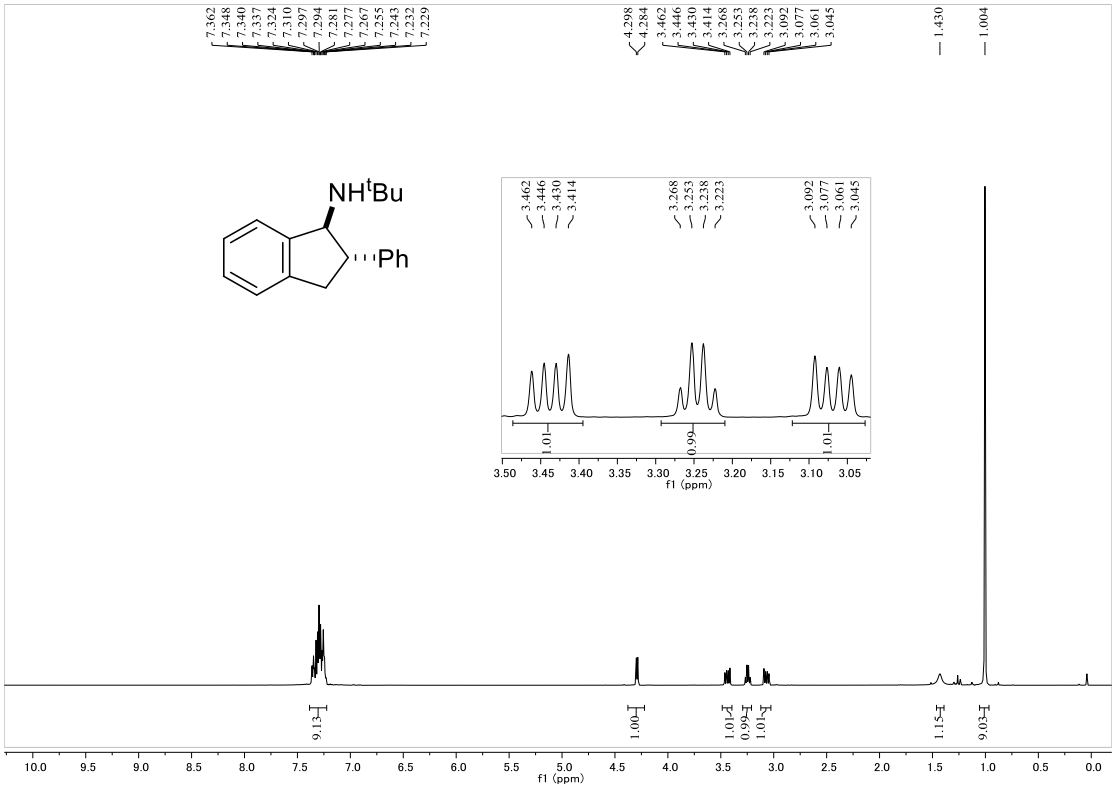
^{1}H NMR spectra of **1ae** (500 MHz, $CDCl_3$)



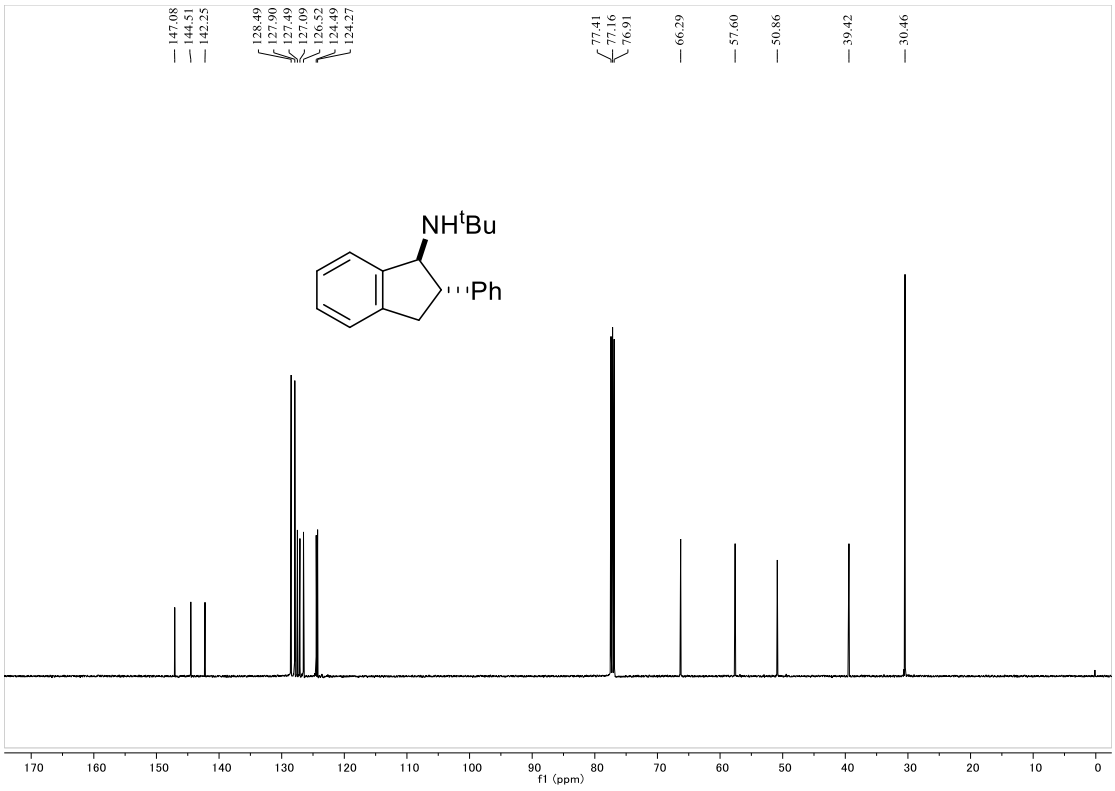
^{13}C NMR spectra of **1ae** (126 MHz, $CDCl_3$)



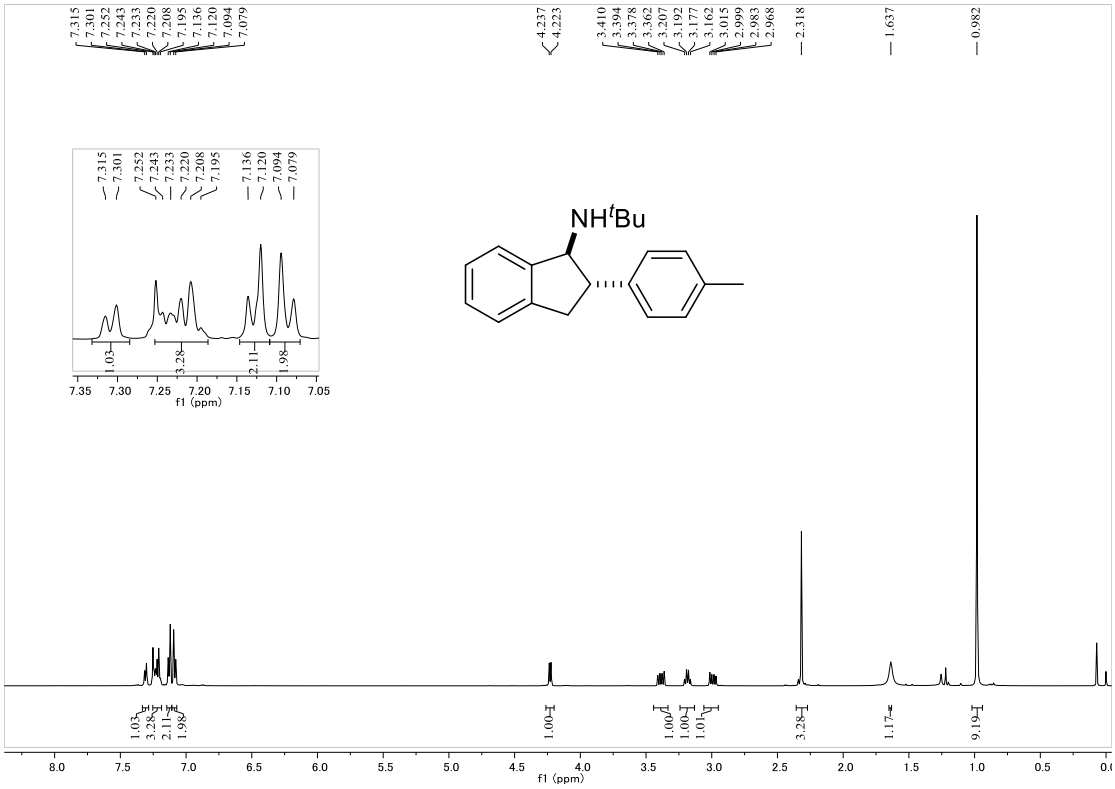
^{1}H NMR spectra of ***trans*-3aa** (500 MHz, $CDCl_3$)



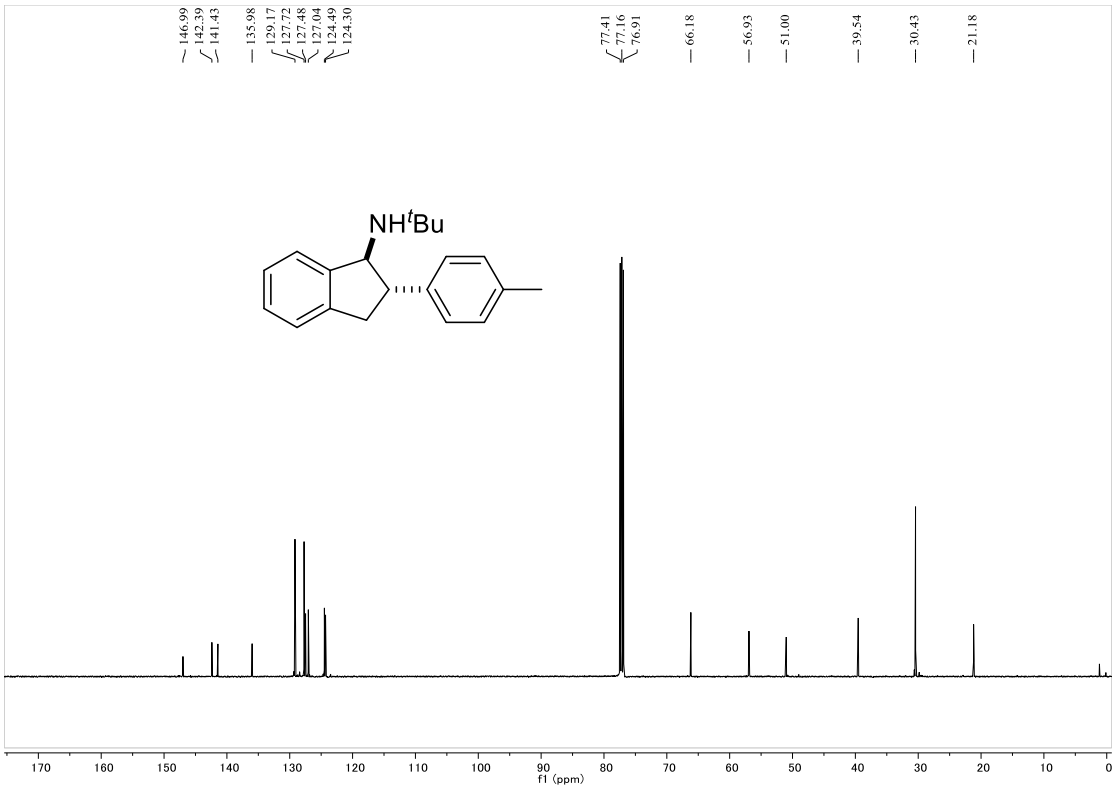
^{13}C NMR spectra of ***trans*-3aa** (126 MHz, $CDCl_3$)



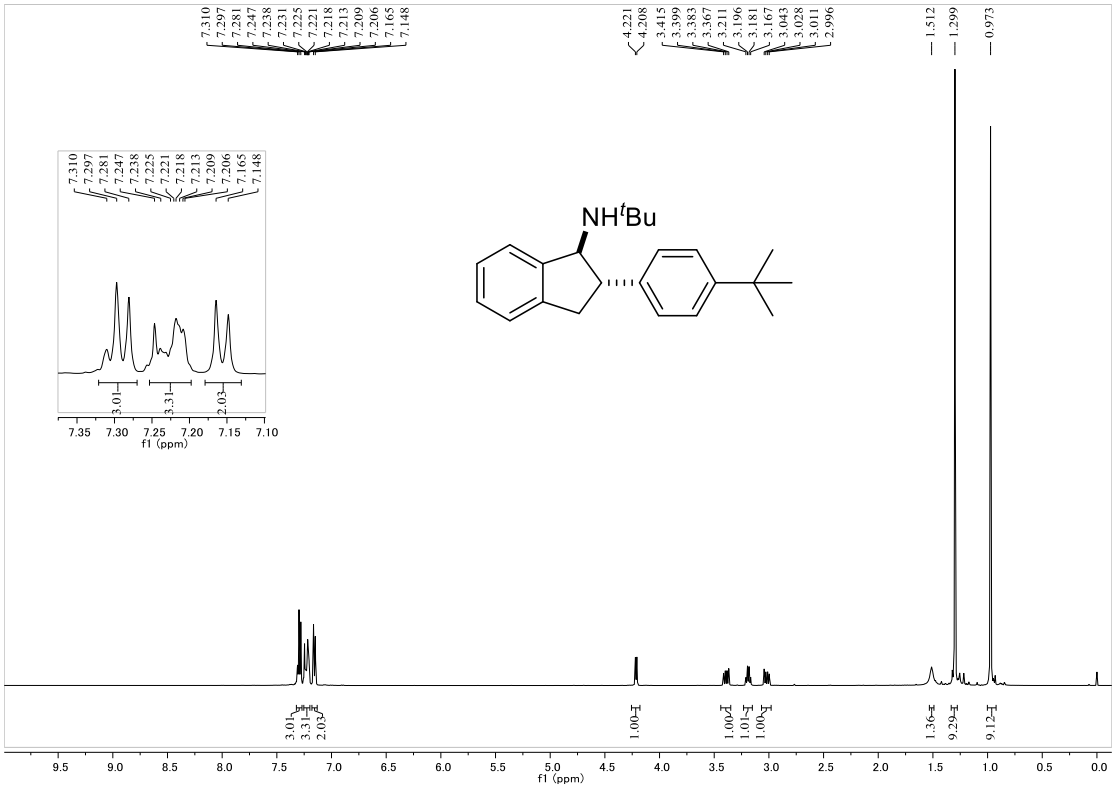
^{1}H NMR spectra of ***trans*-3ab** (500 MHz, $CDCl_3$)



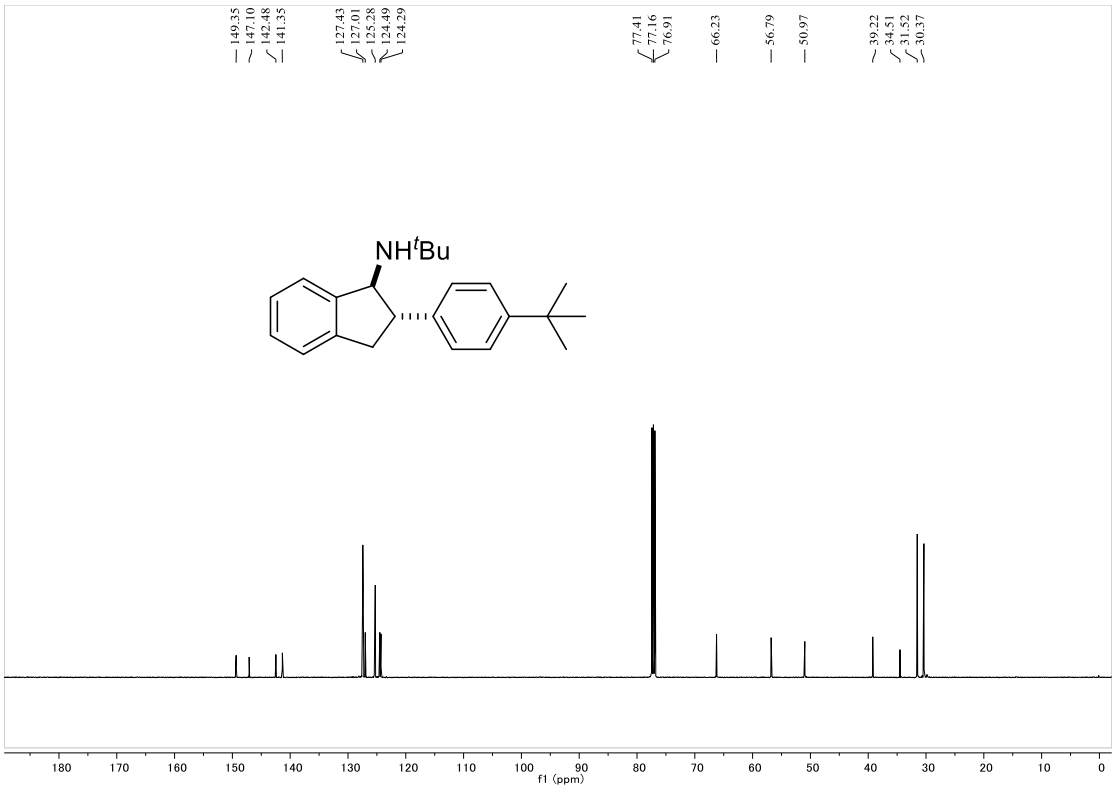
^{13}C NMR spectra of ***trans*-3ab** (126 MHz, $CDCl_3$)



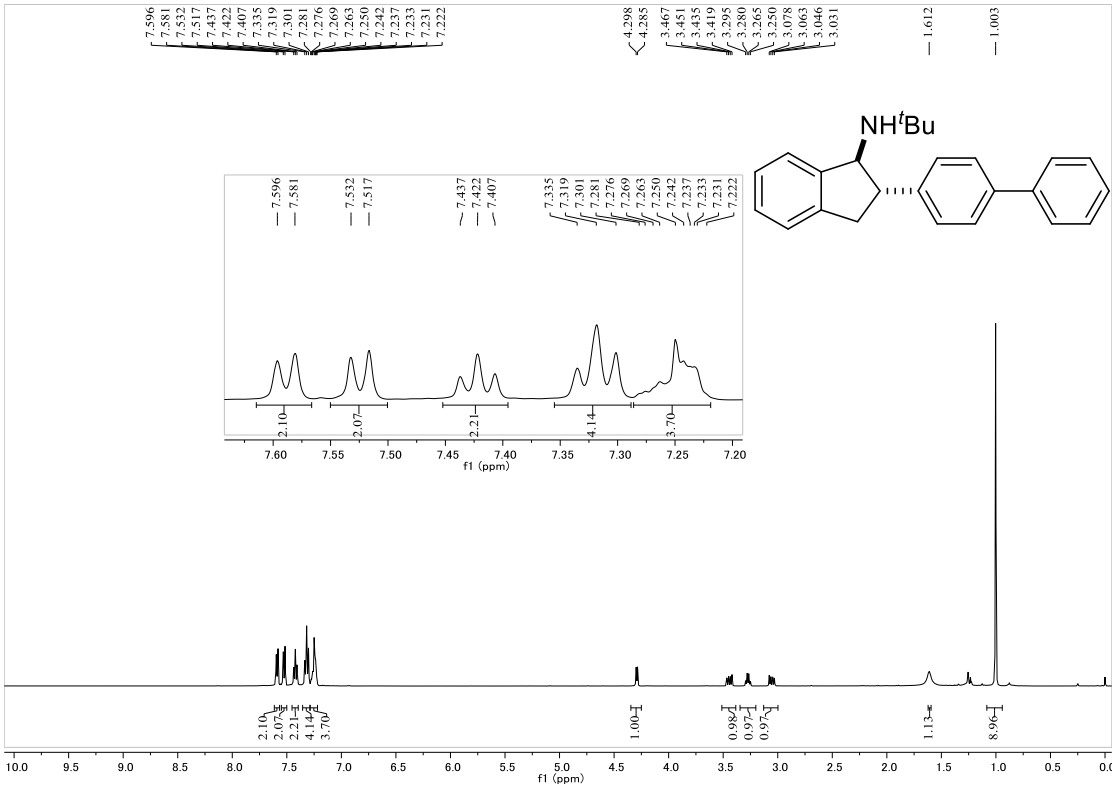
^{1}H NMR spectra of ***trans*-3ac** (500 MHz, $CDCl_3$)



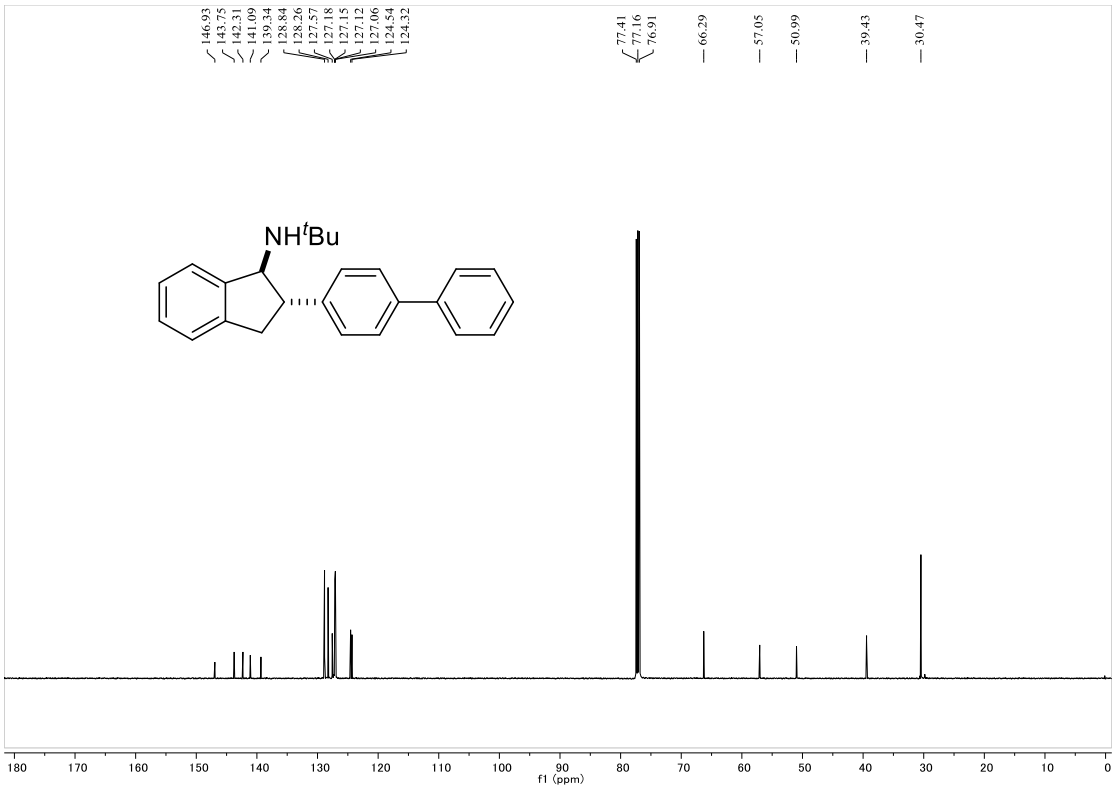
^{13}C NMR spectra of ***trans*-3ac** (126 MHz, $CDCl_3$)



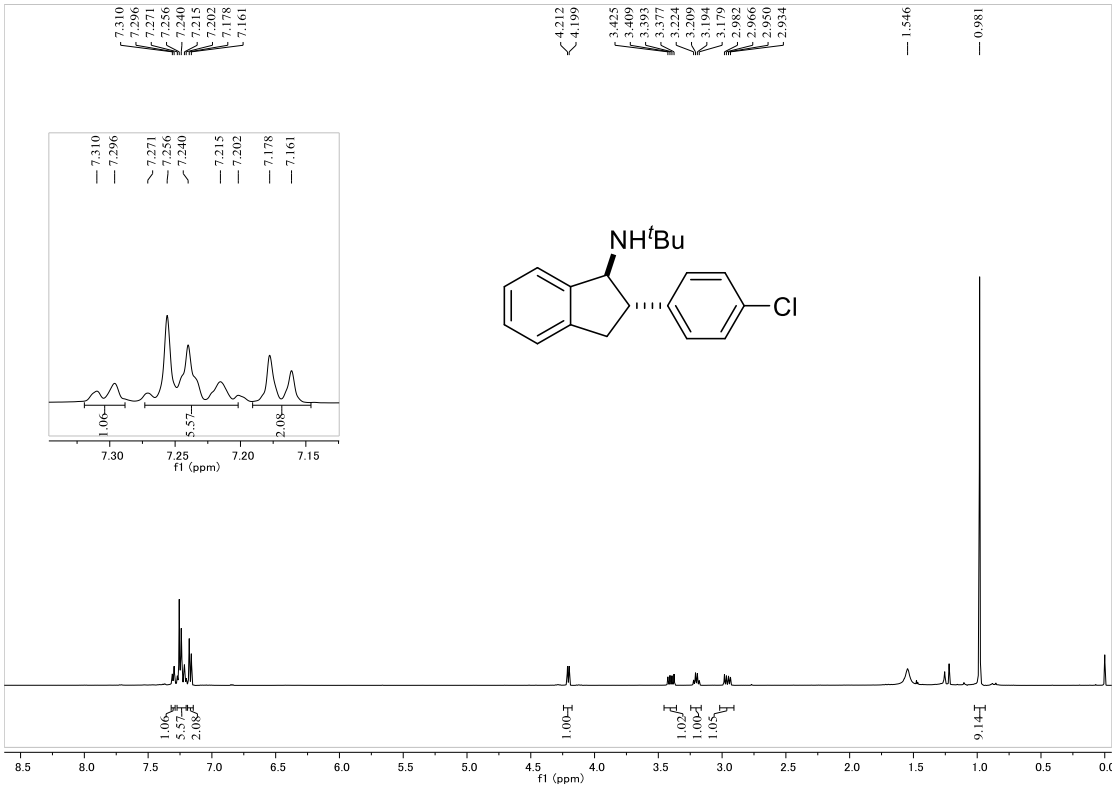
^{1}H NMR spectra of ***trans*-3ad** (500 MHz, $CDCl_3$)



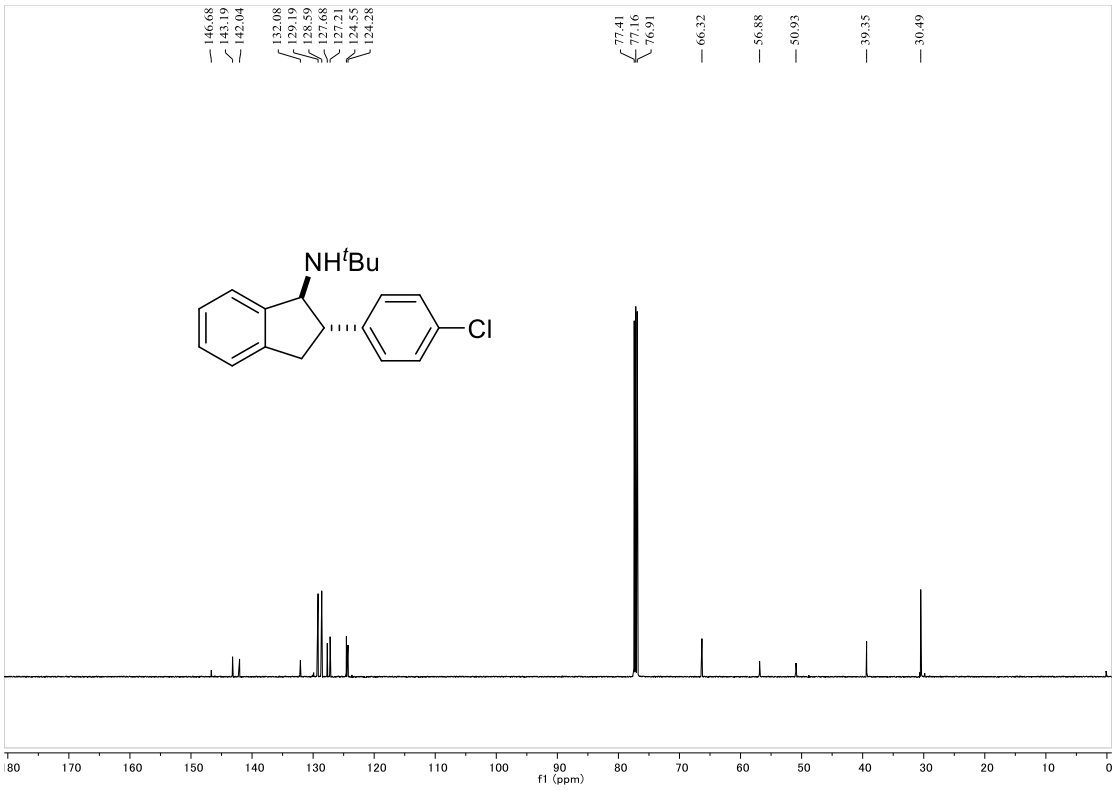
^{13}C NMR spectra of ***trans*-3ad** (126 MHz, $CDCl_3$)



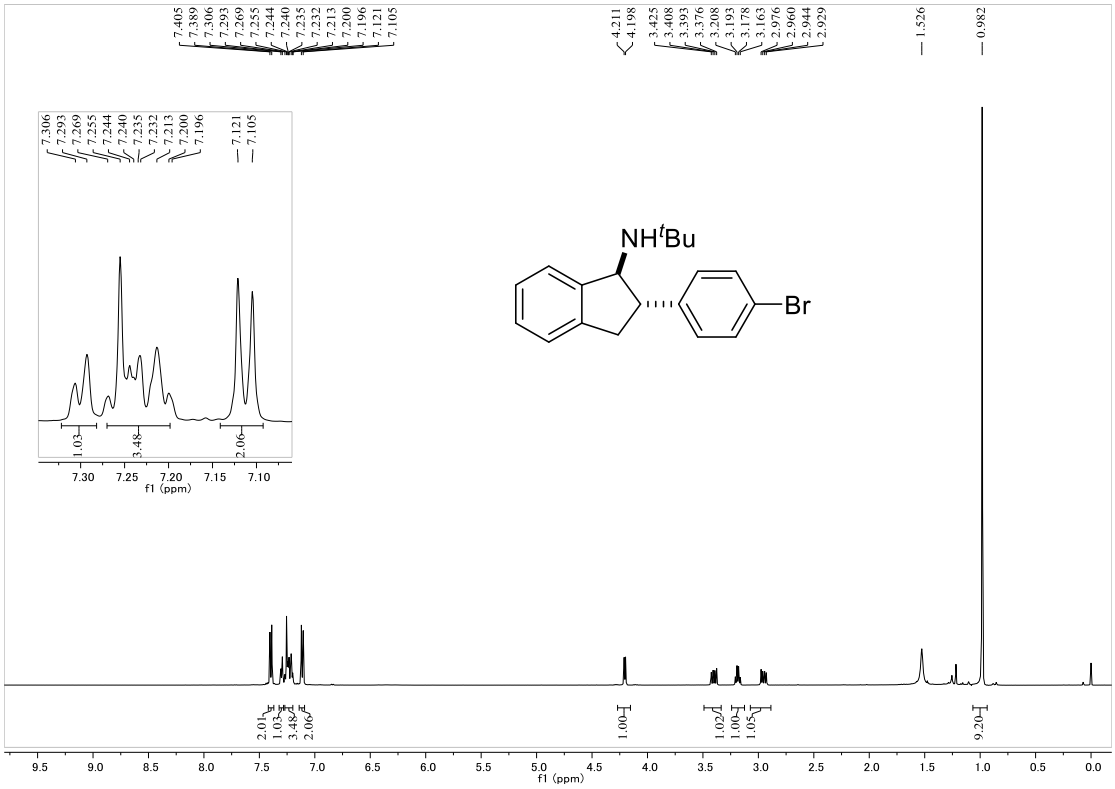
^{1}H NMR spectra of ***trans*-3ae** (500 MHz, $CDCl_3$)



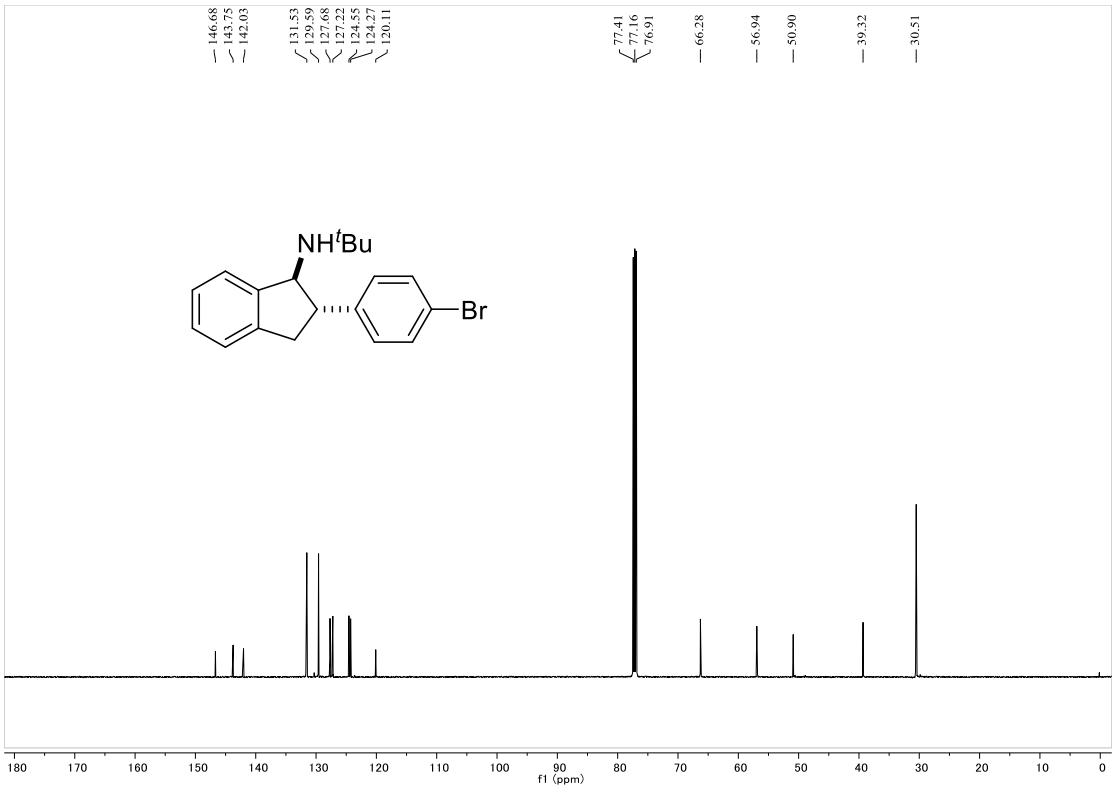
^{13}C NMR spectra of ***trans*-3ae** (126 MHz, $CDCl_3$)



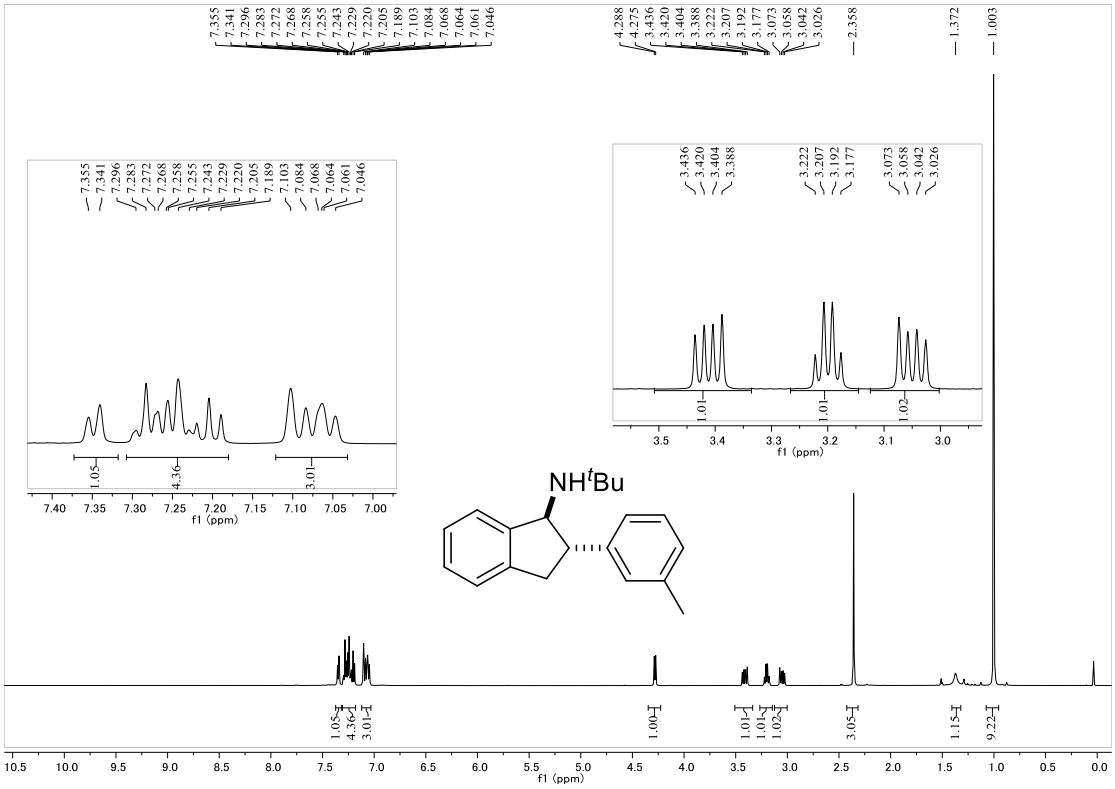
^{1}H NMR spectra of ***trans*-3af** (500 MHz, $CDCl_3$)



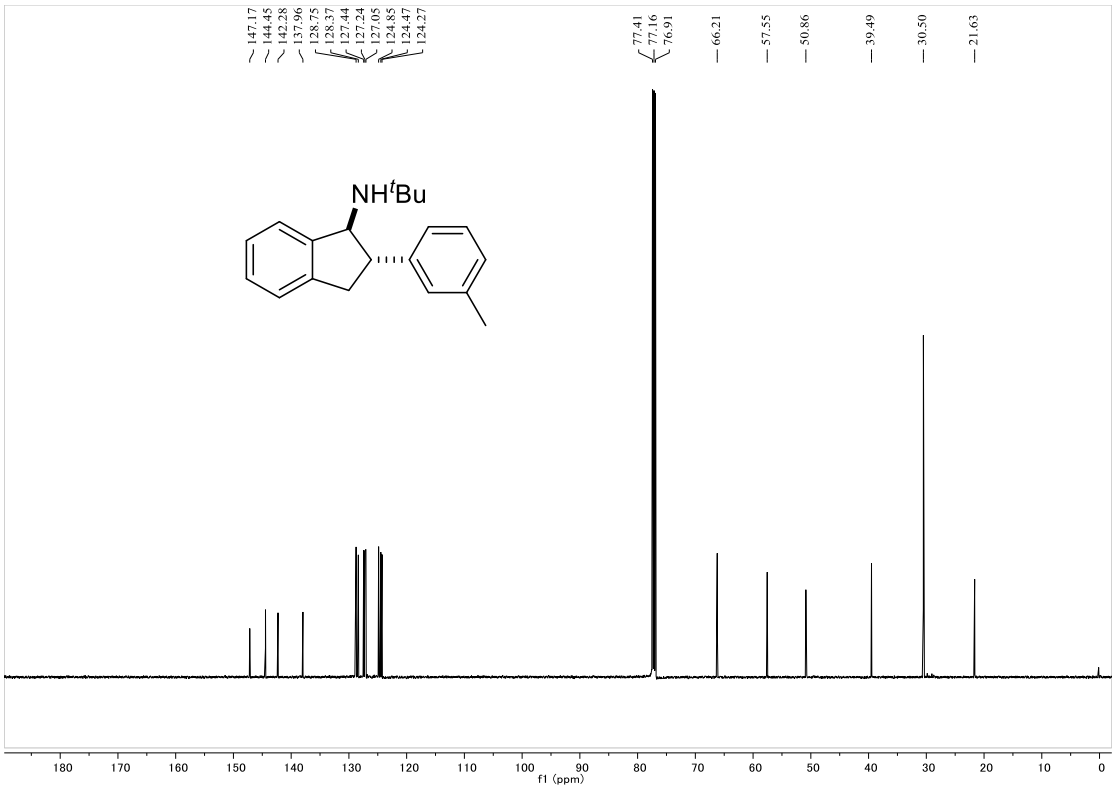
^{13}C NMR spectra of ***trans*-3af** (126 MHz, $CDCl_3$)



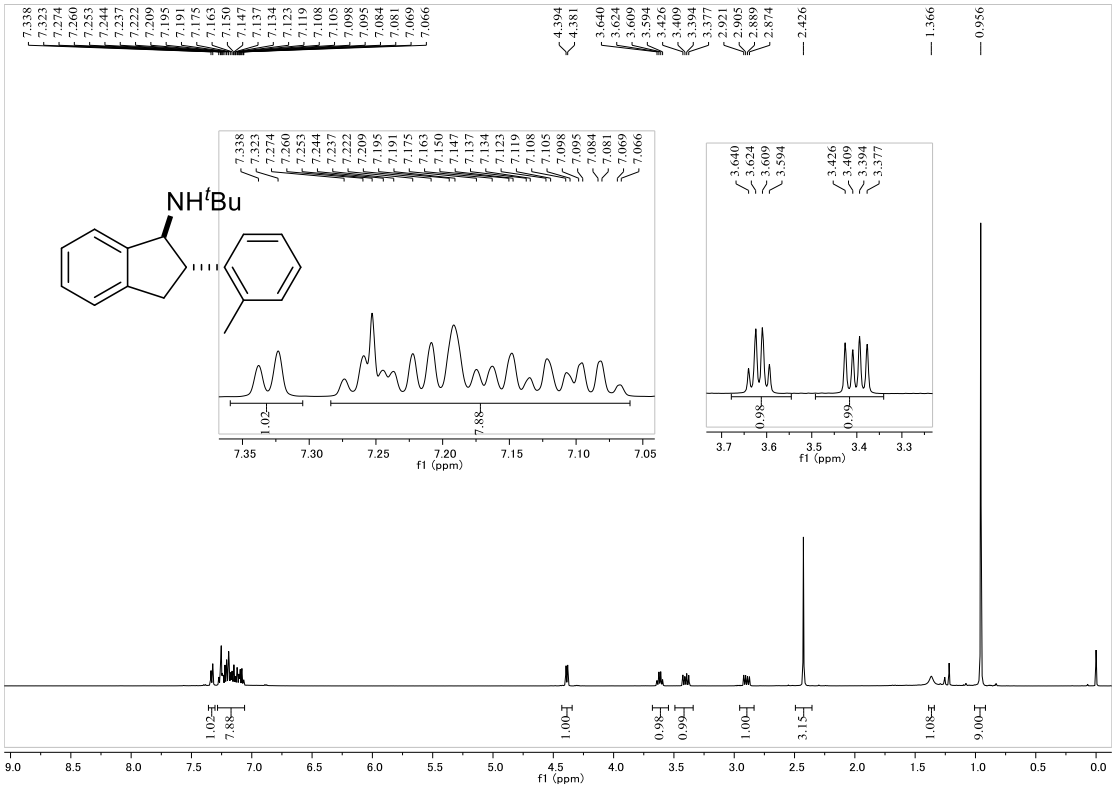
^{1}H NMR spectra of ***trans*-3ag** (500 MHz, $CDCl_3$)



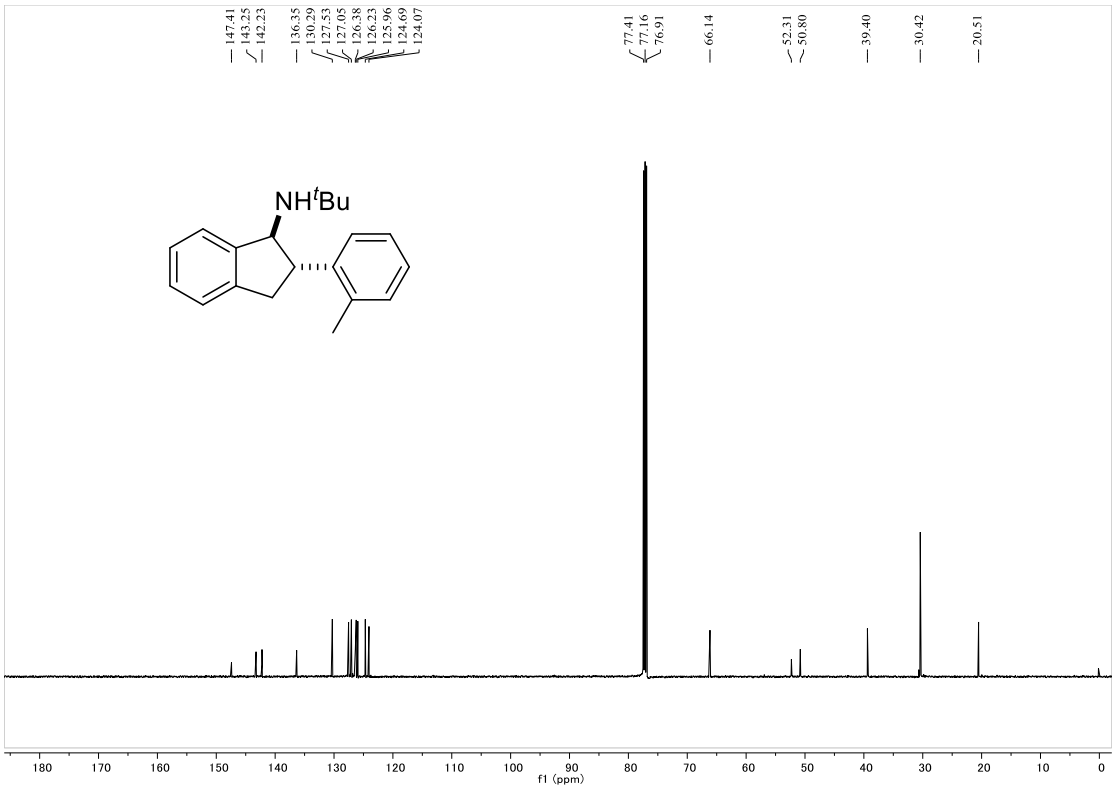
^{13}C NMR spectra of ***trans*-3ag** (126 MHz, $CDCl_3$)



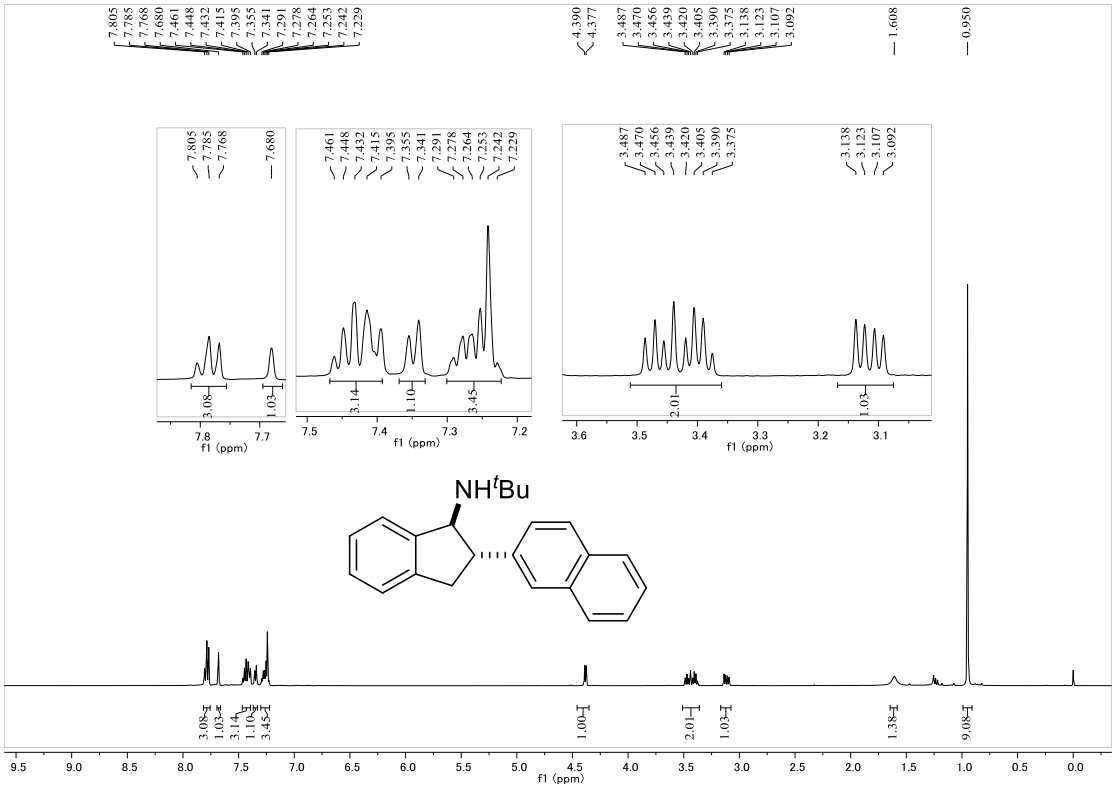
^{1}H NMR spectra of ***trans*-3ah** (500 MHz, $CDCl_3$)



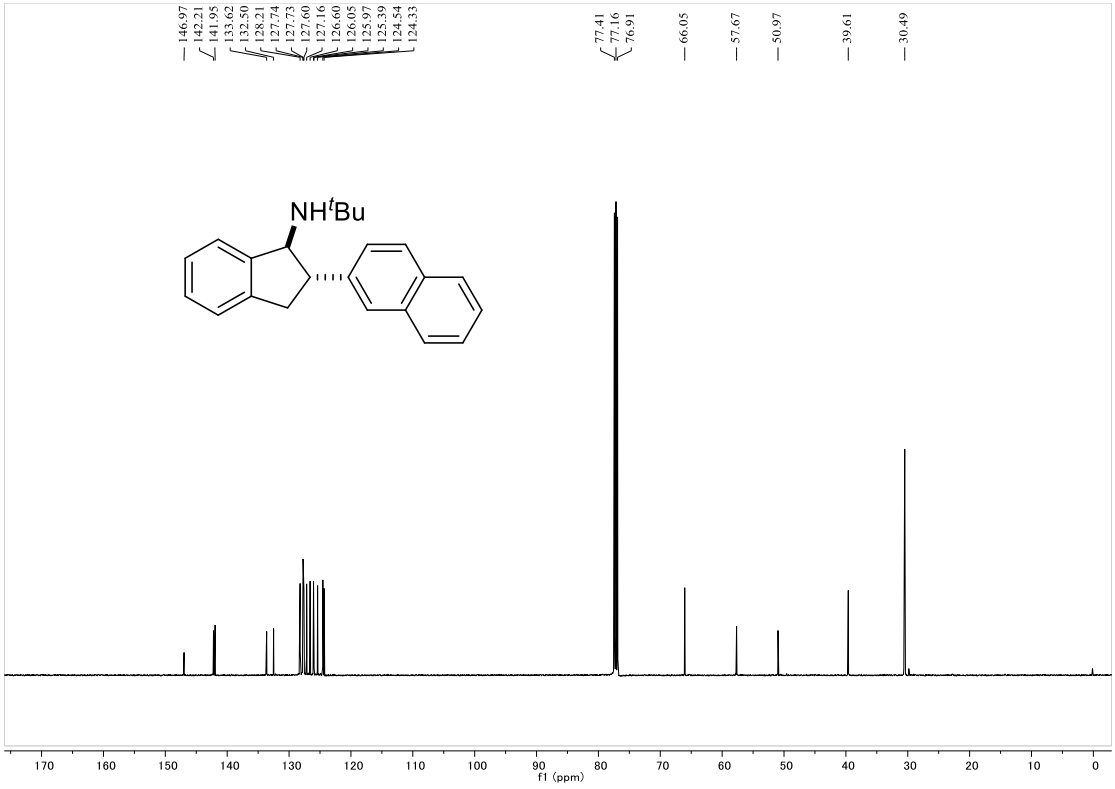
^{13}C NMR spectra of ***trans*-3ah** (126 MHz, $CDCl_3$)



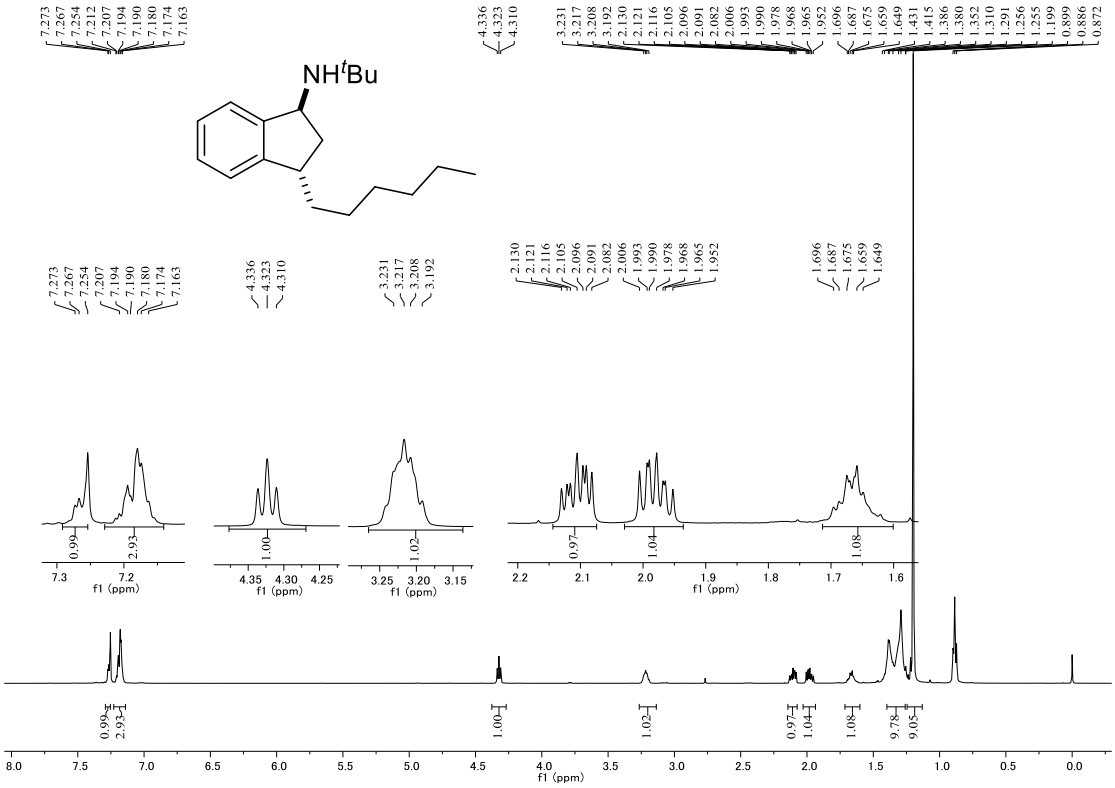
^{1}H NMR spectra of ***trans*-3ai** (500 MHz, $CDCl_3$)



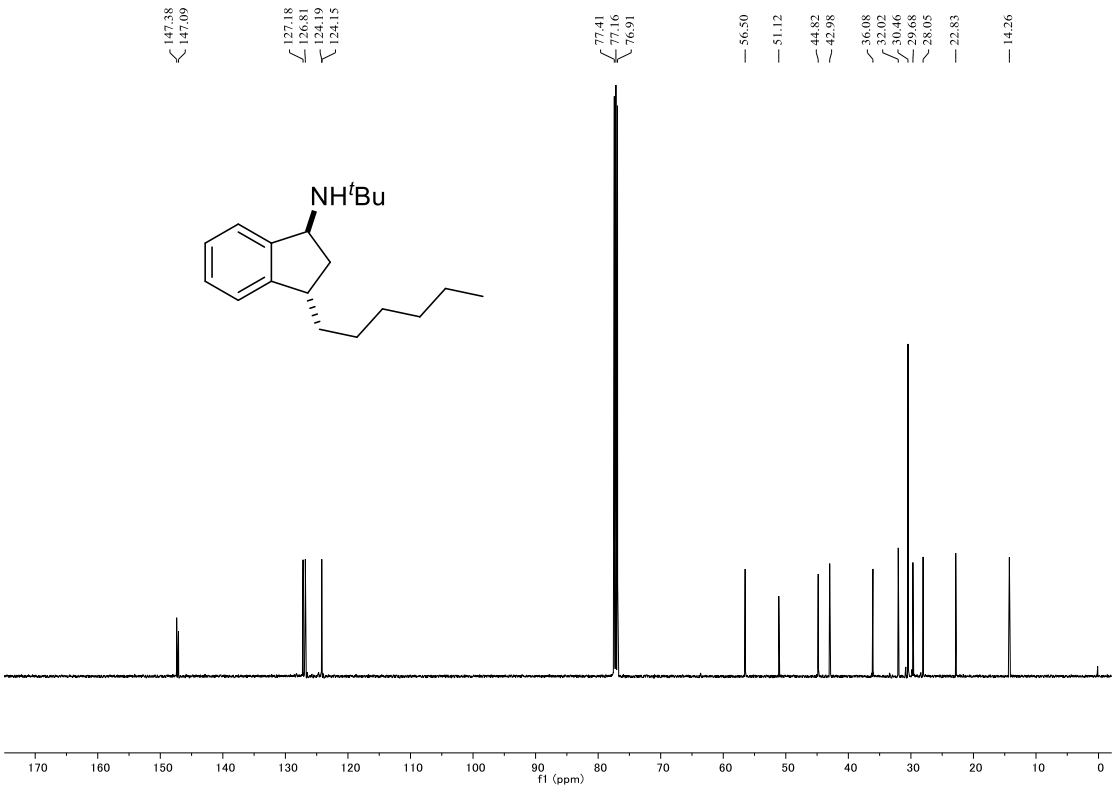
^{13}C NMR spectra of ***trans*-3ai** (126 MHz, $CDCl_3$)



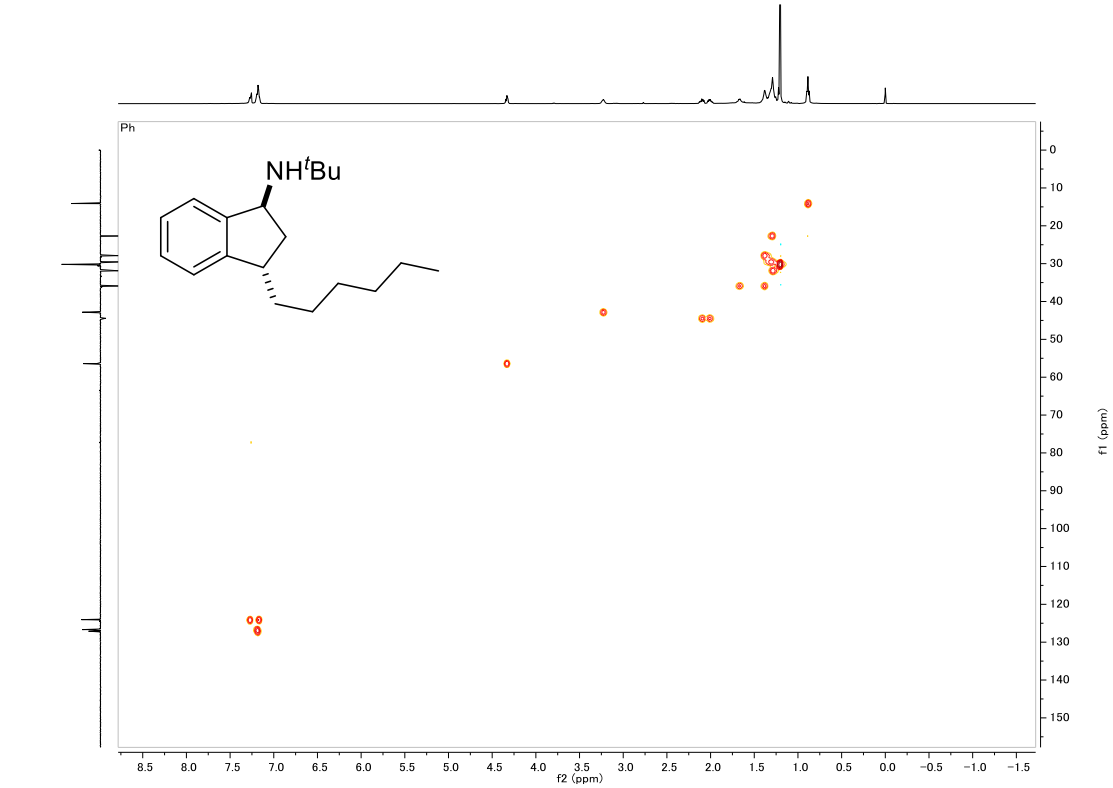
^{1}H NMR spectra of ***trans*-3aj** (500 MHz, $CDCl_3$)



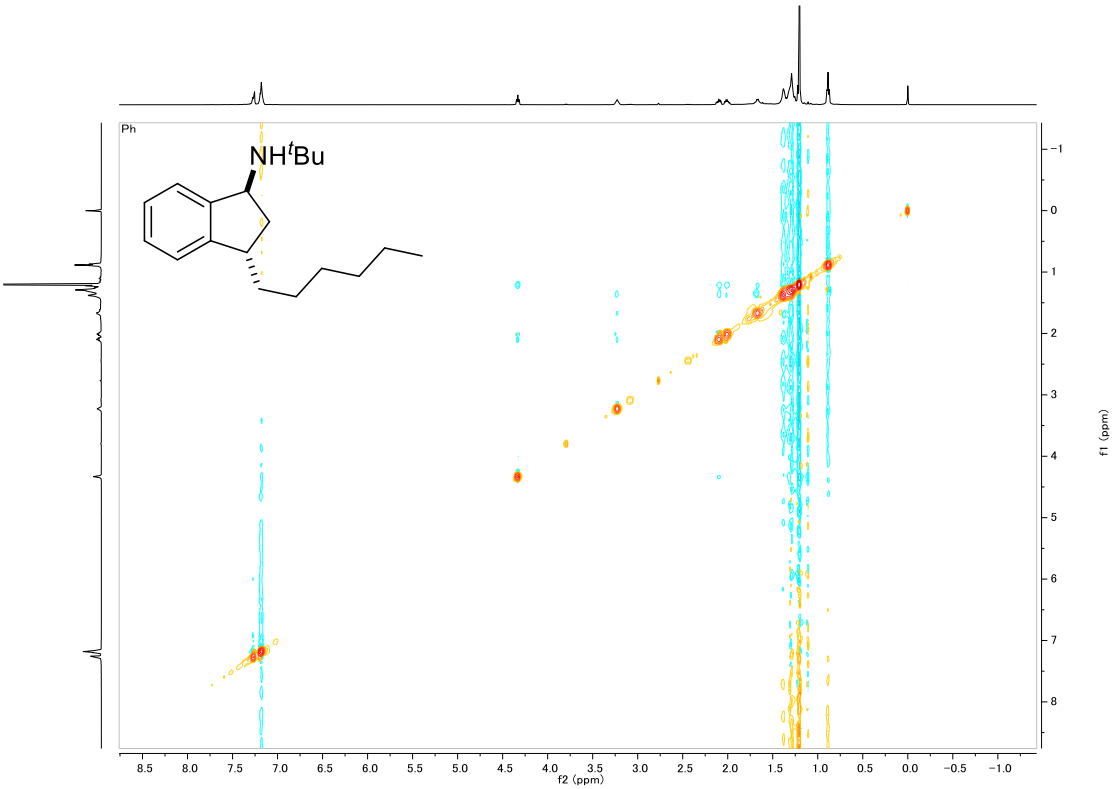
^{13}C NMR spectra of ***trans*-3aj** (126 MHz, $CDCl_3$)



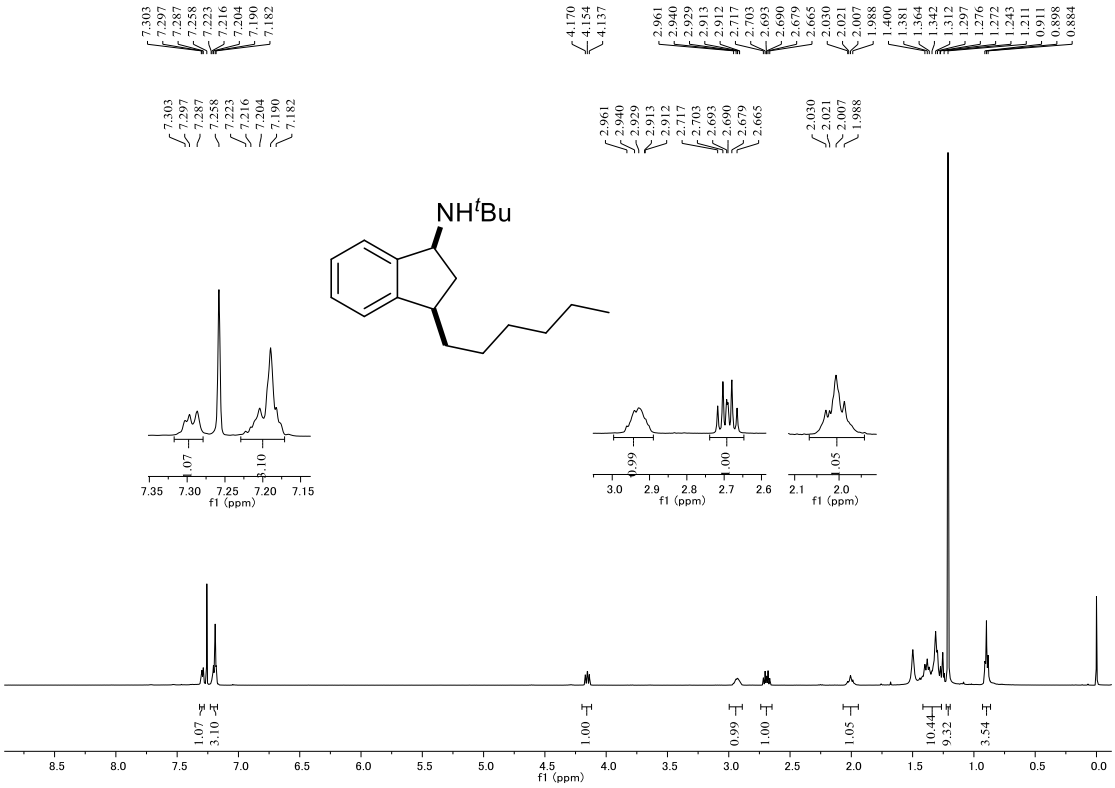
HSQC spectra of ***trans*-3aj** ($CDCl_3$)



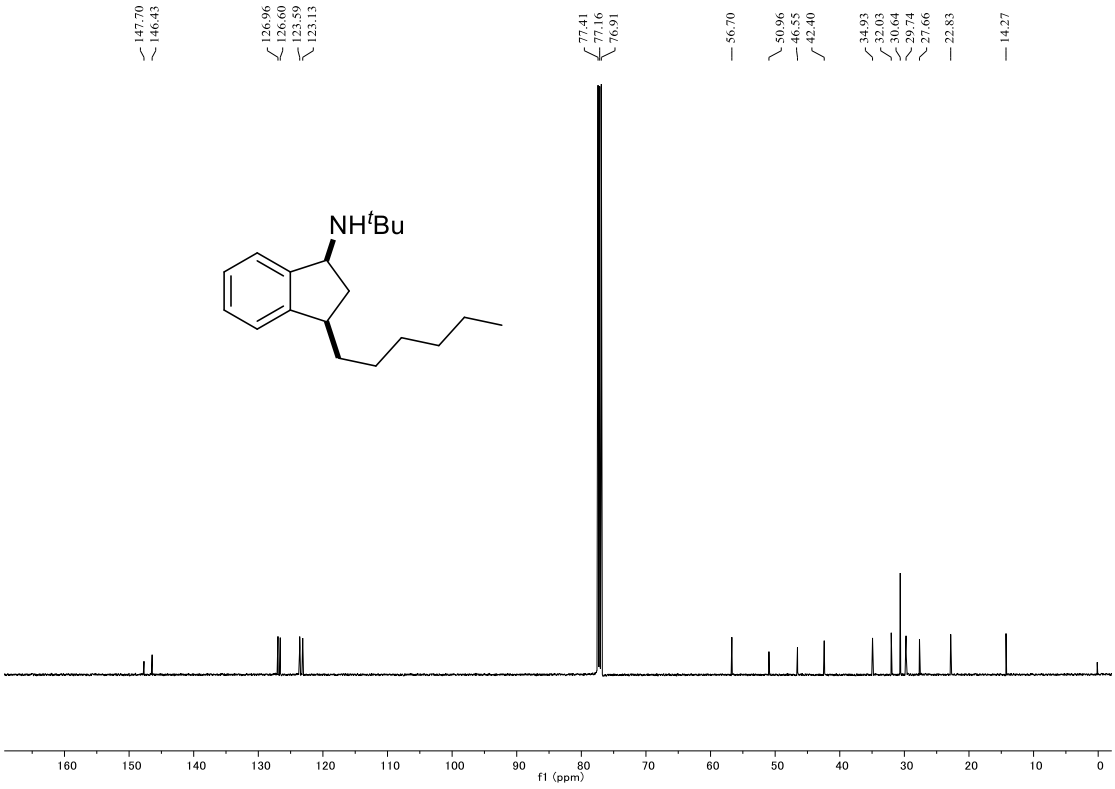
NOE spectra of ***trans*-3aj** (500 MHz, $CDCl_3$)



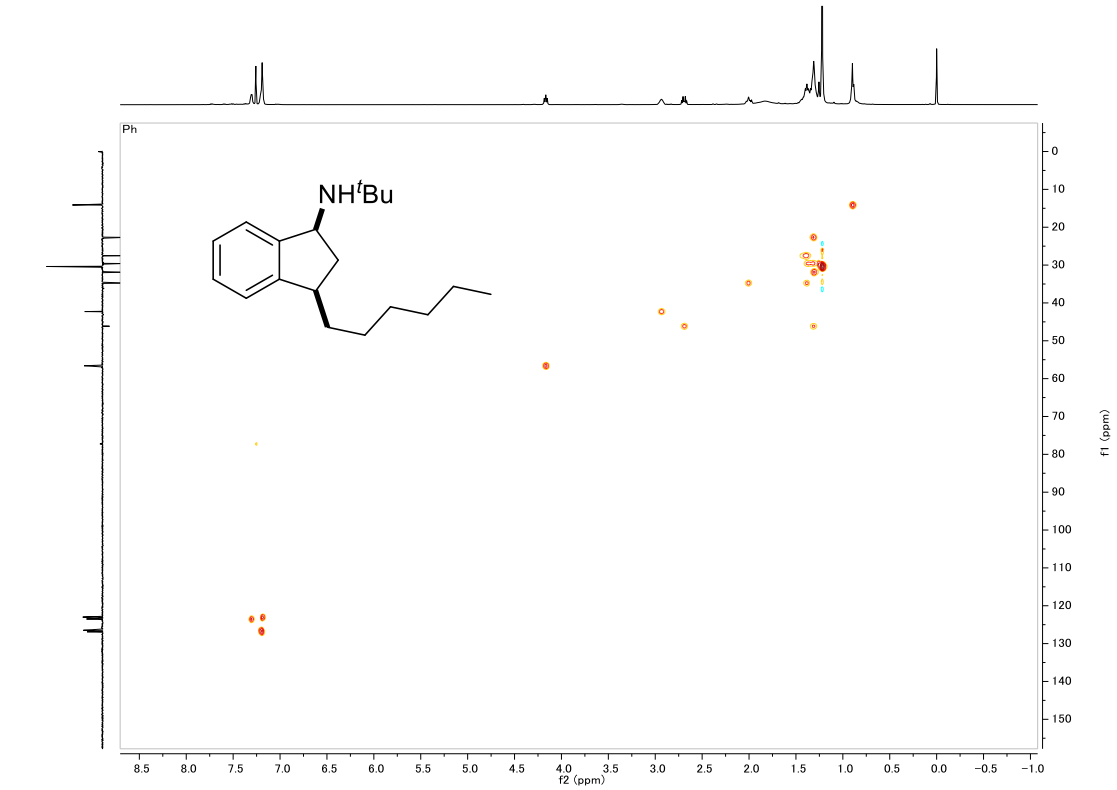
^{1}H NMR spectra of ***cis*-3aj** (500 MHz, $CDCl_3$)



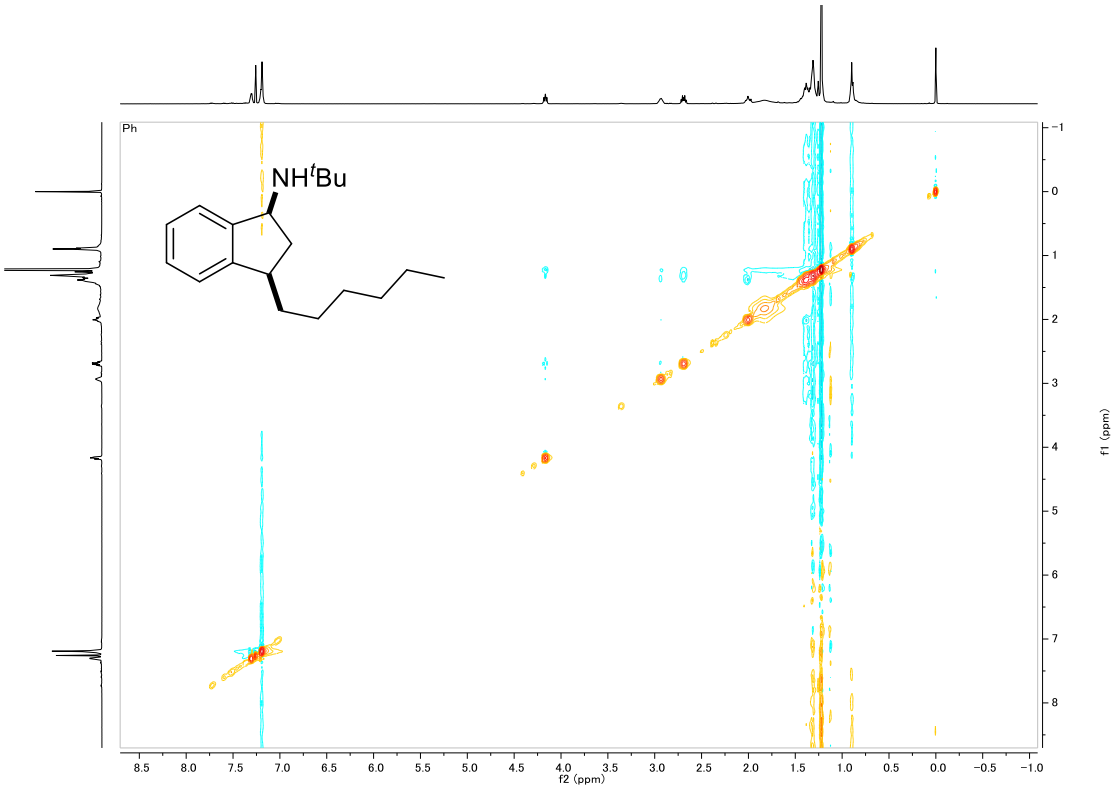
^{13}C NMR spectra of ***cis*-3aj** (126 MHz, $CDCl_3$)



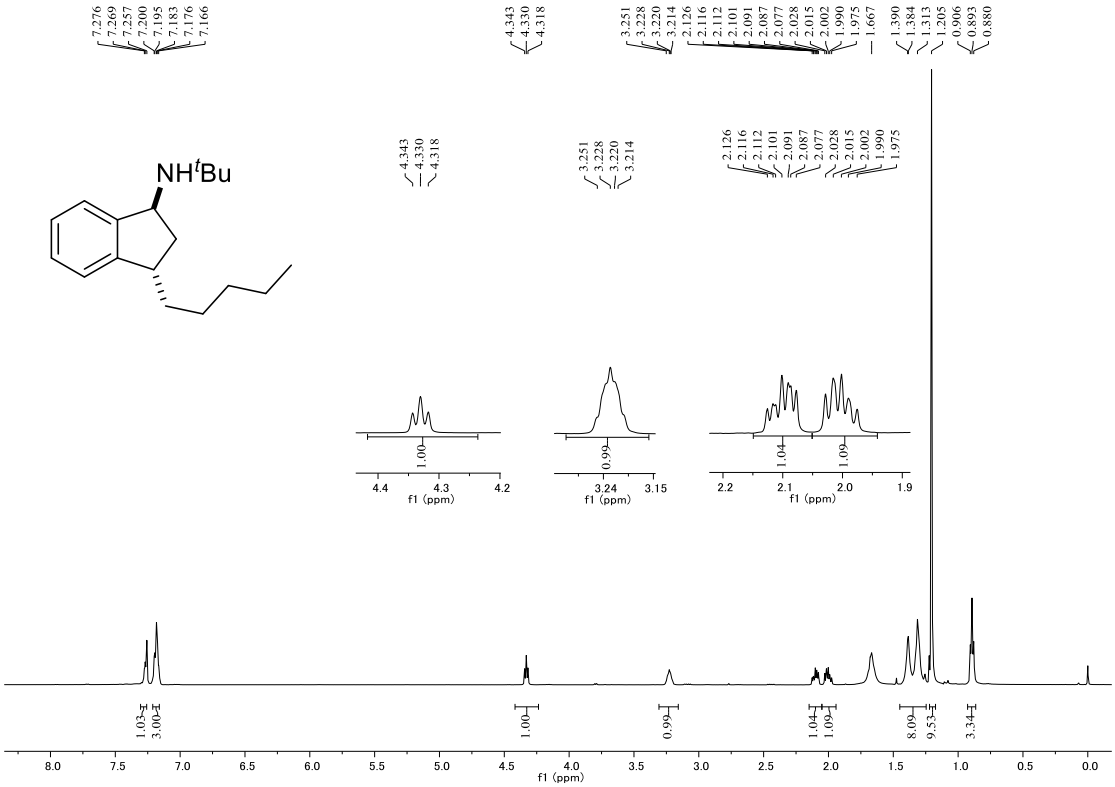
HSQC spectra of ***cis*-3aj** ($CDCl_3$)



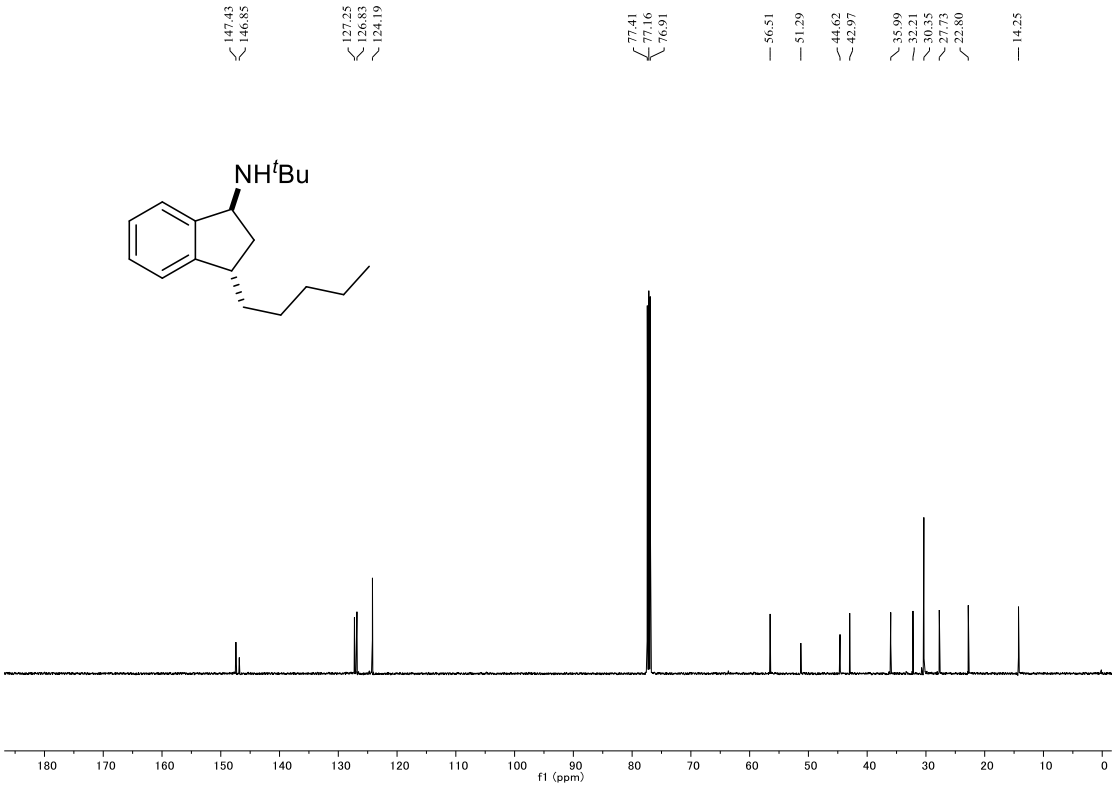
NOE spectra of ***cis*-3aj** (500 MHz, $CDCl_3$)



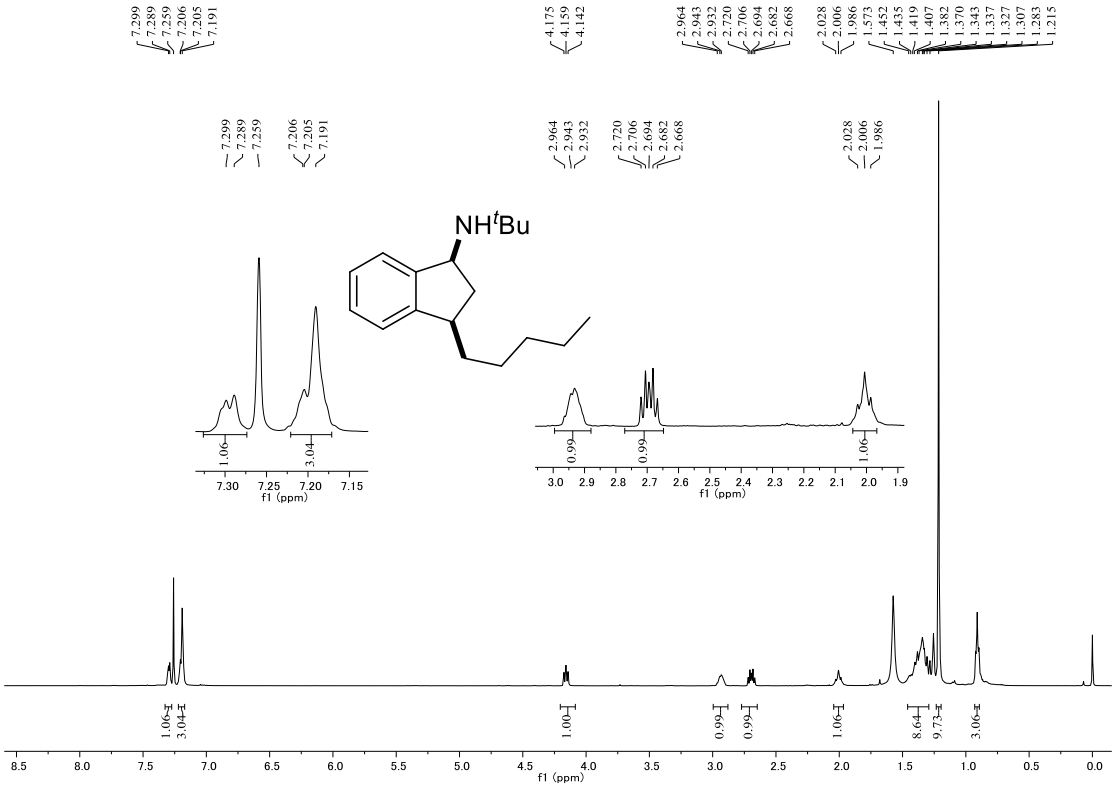
^{1}H NMR spectra of ***trans*-3ak** (500 MHz, $CDCl_3$)



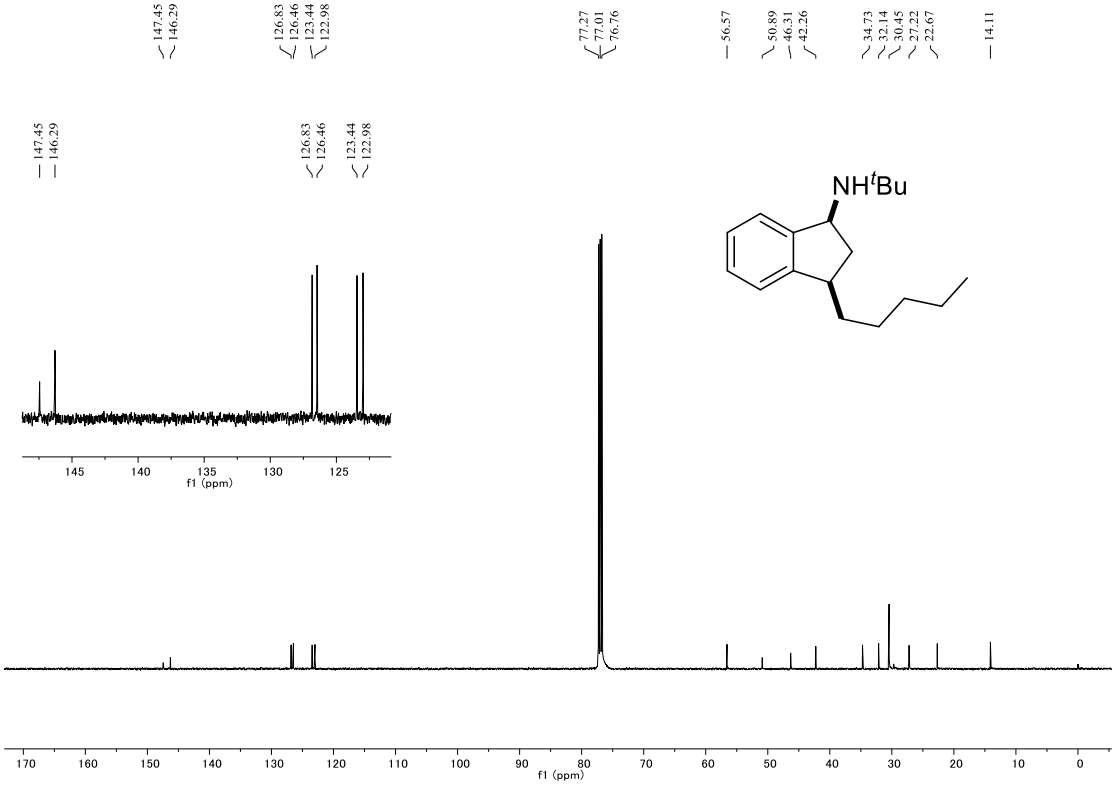
^{13}C NMR spectra of ***trans*-3ak** (126 MHz, $CDCl_3$)



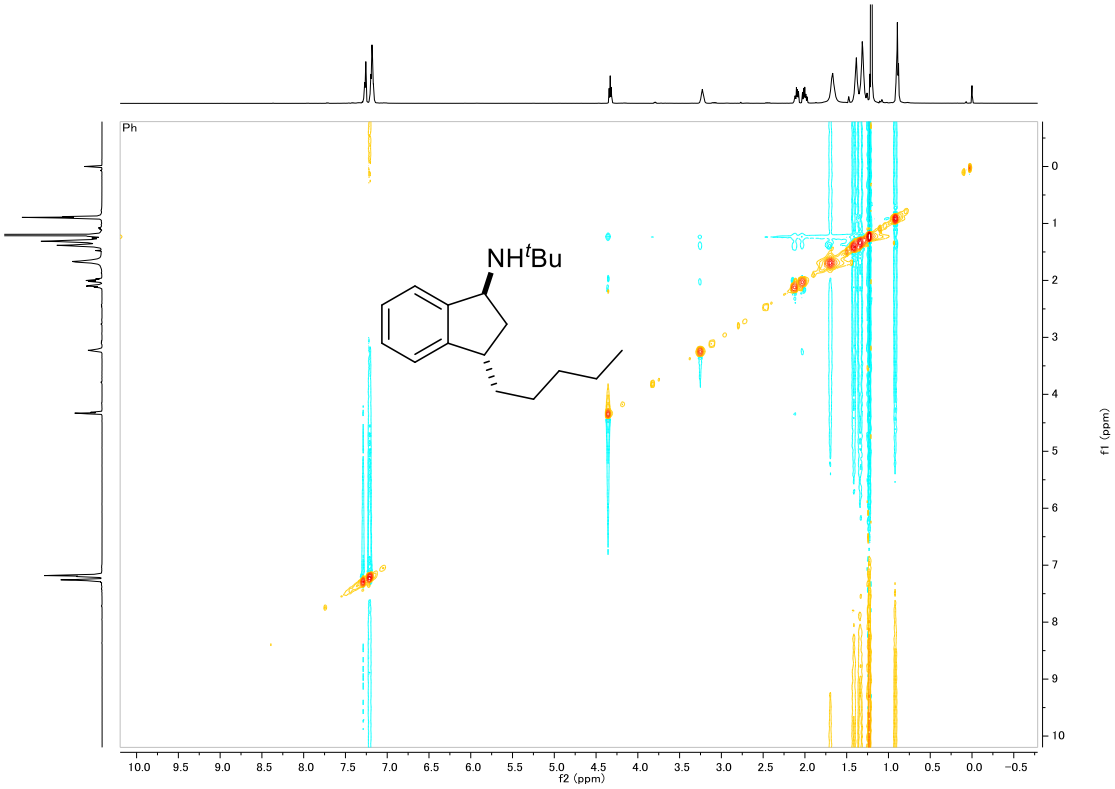
^{1}H NMR spectra of ***cis*-3ak** (500 MHz, $CDCl_3$)

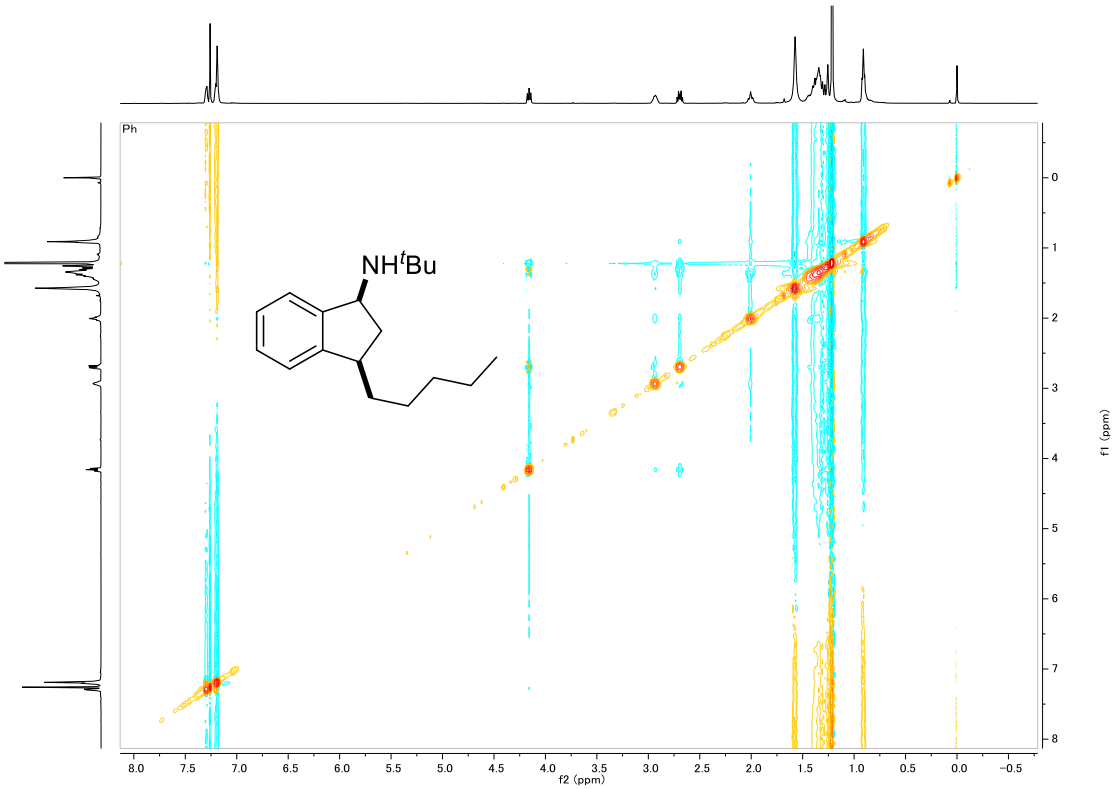


^{13}C NMR spectra of ***cis*-3ak** (126 MHz, $CDCl_3$)

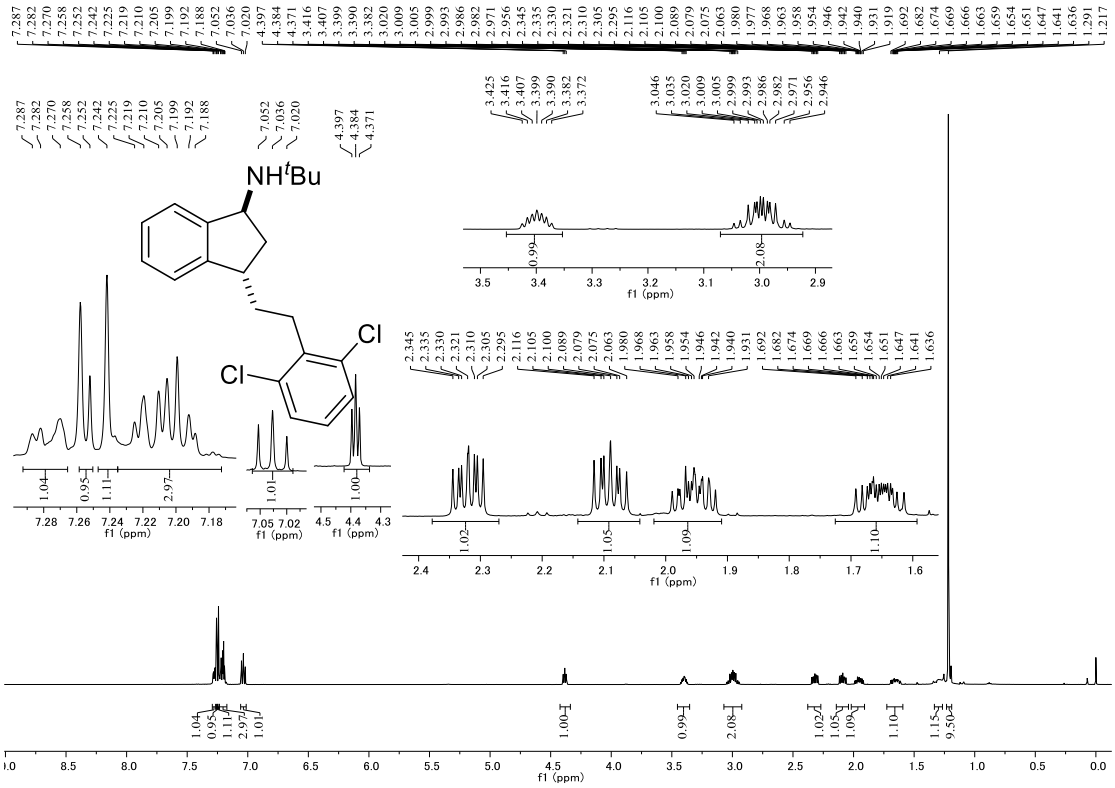


NOE spectra of ***trans*-3ak and *cis*-3ak** (500 MHz, $CDCl_3$)

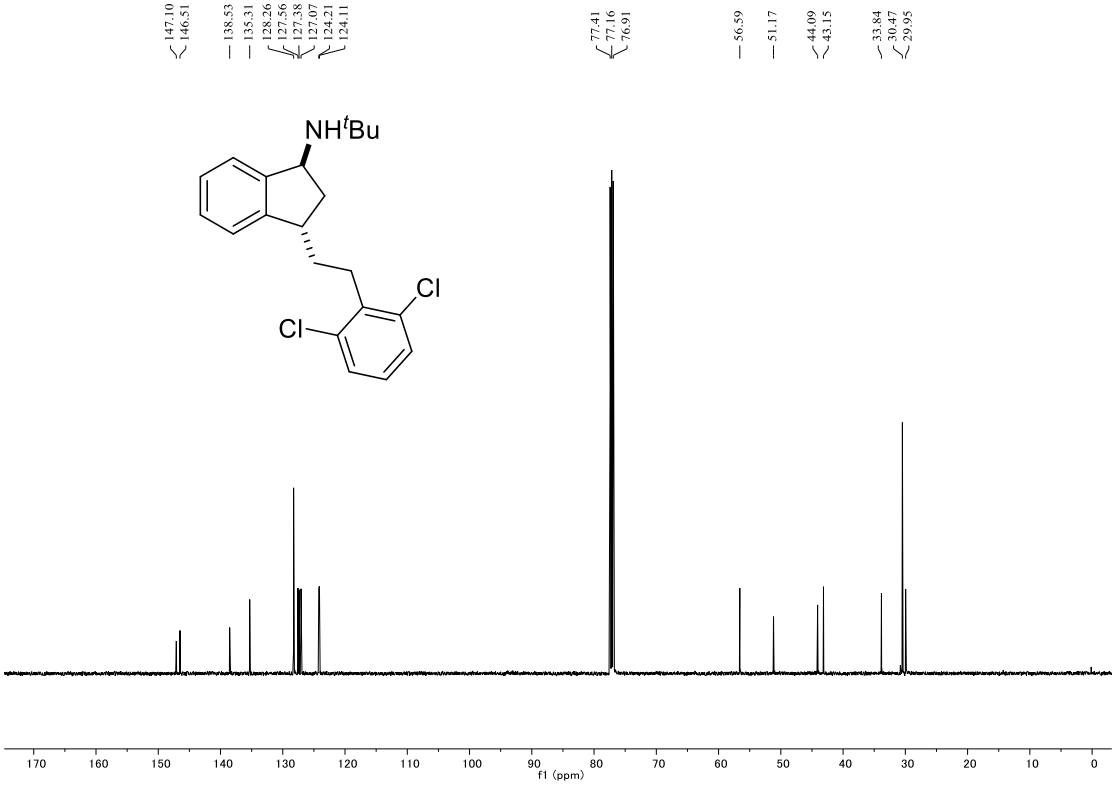




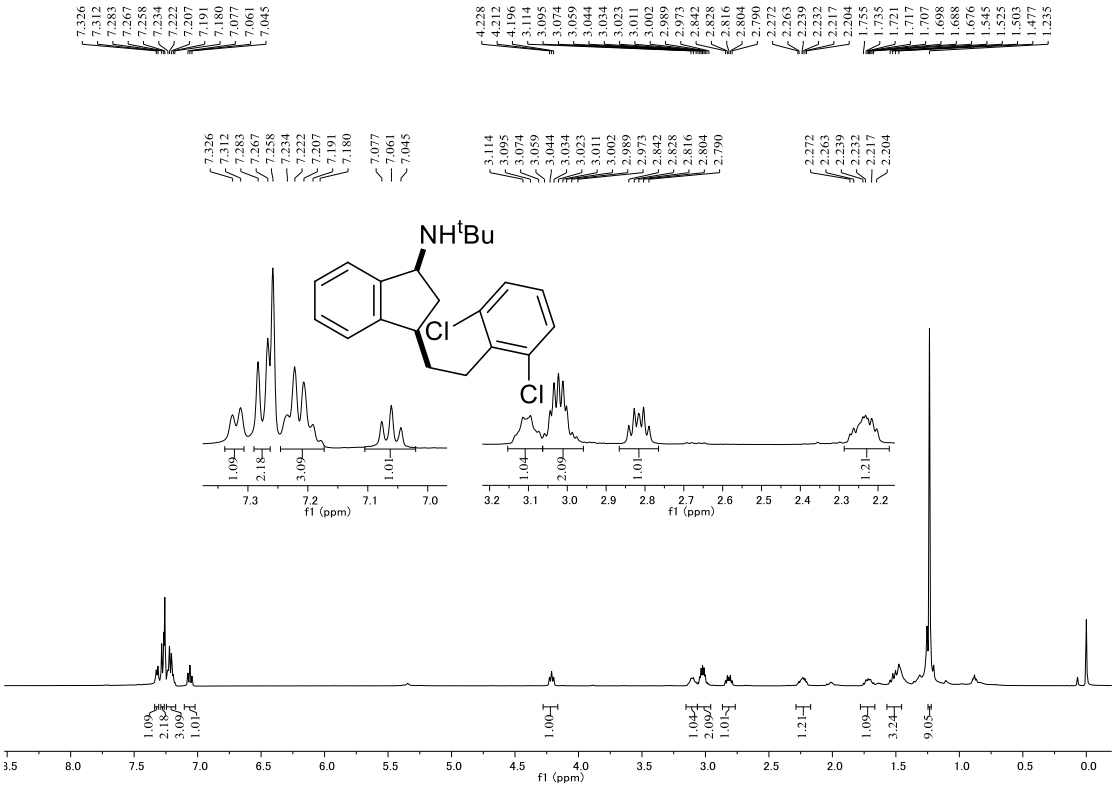
^{1}H NMR spectra of ***trans*-3al** (500 MHz, $CDCl_3$)



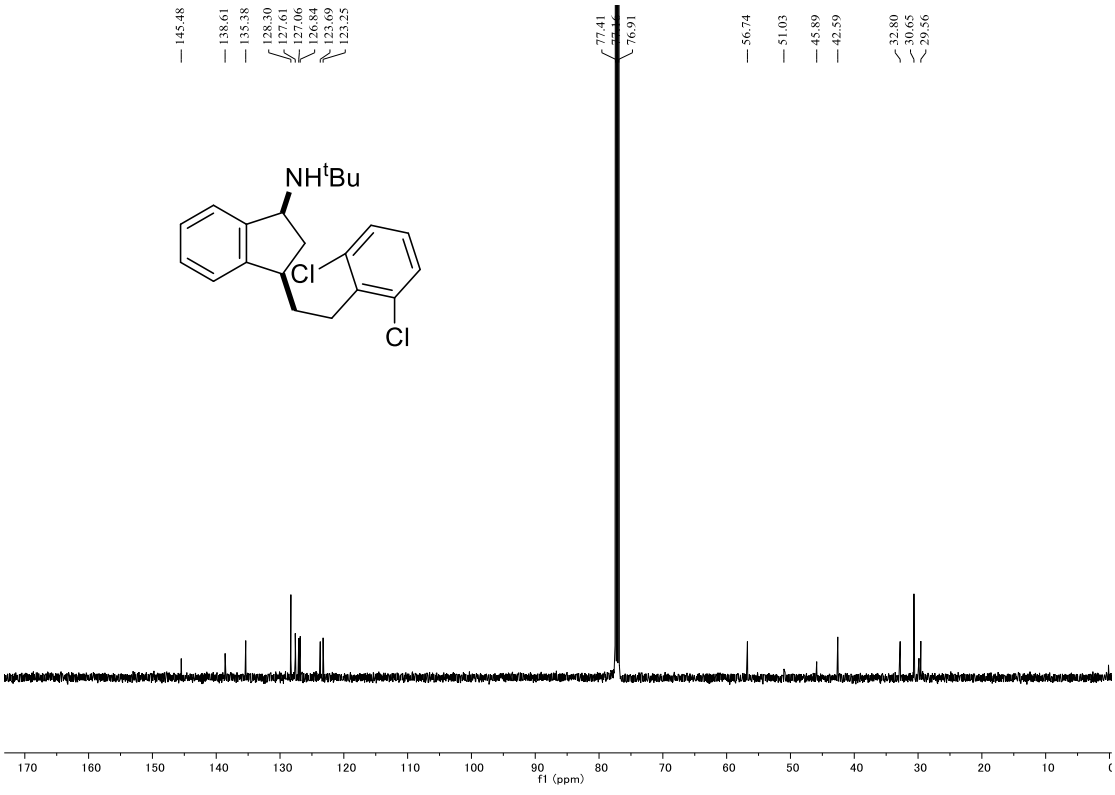
^{13}C NMR spectra of ***trans*-3al** (126 MHz, $CDCl_3$)



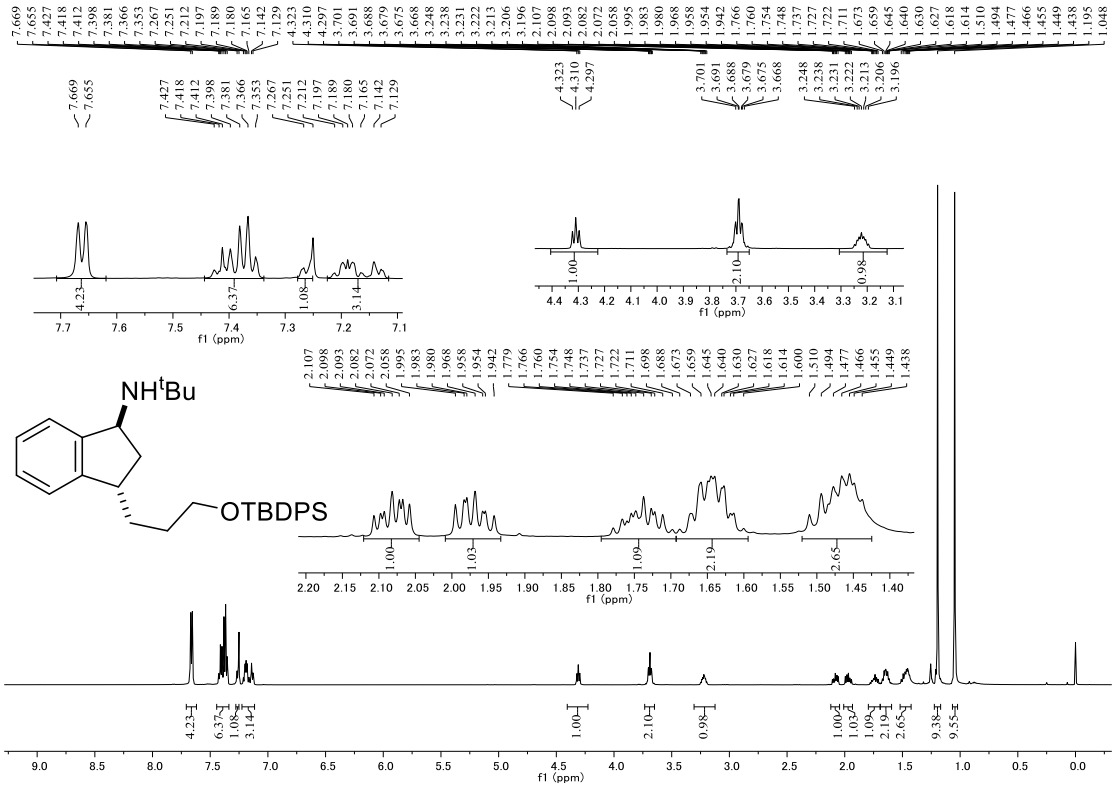
^{1}H NMR spectra of ***cis*-3al** (500 MHz, $CDCl_3$)



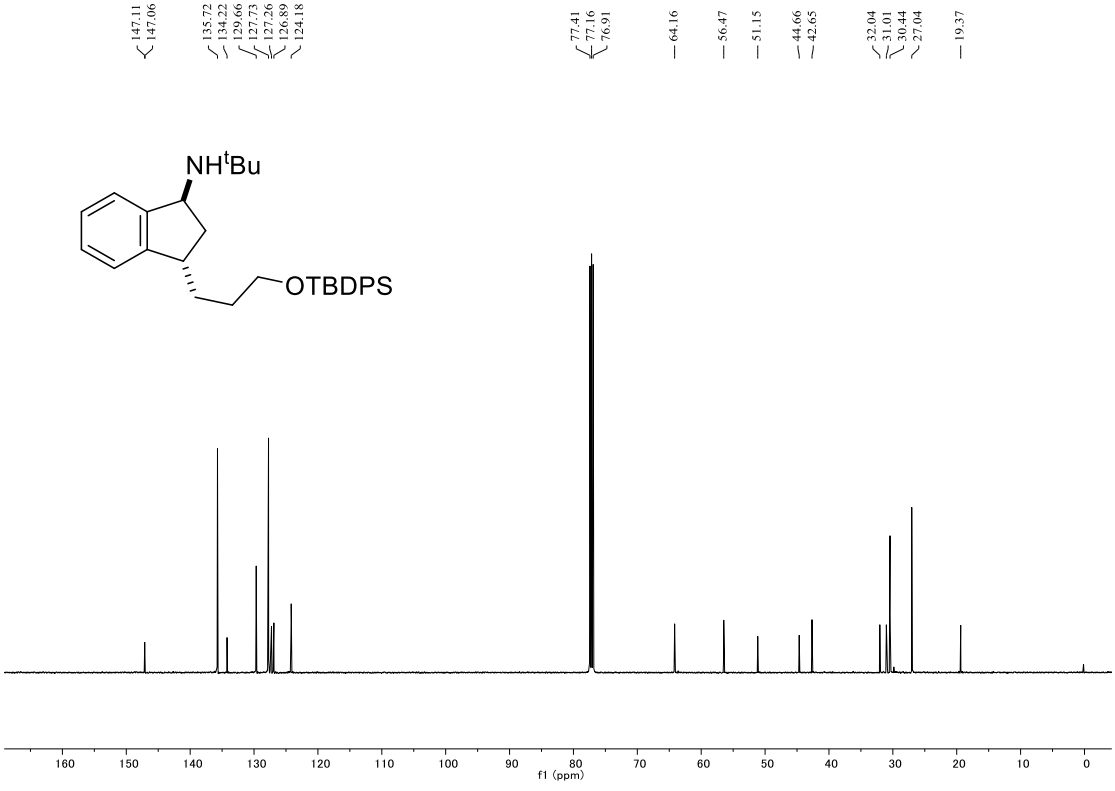
^{13}C NMR spectra of ***cis*-3al** (126 MHz, $CDCl_3$)



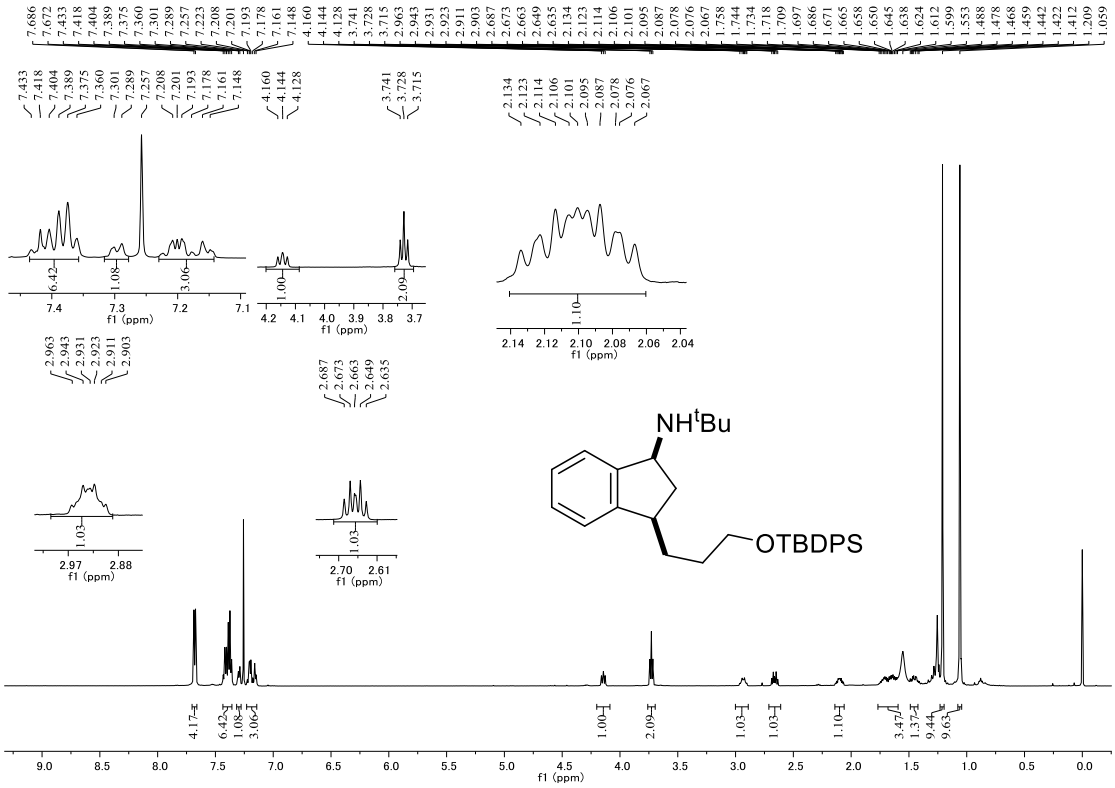
^{1}H NMR spectra of ***trans*-3am** (500 MHz, $CDCl_3$)



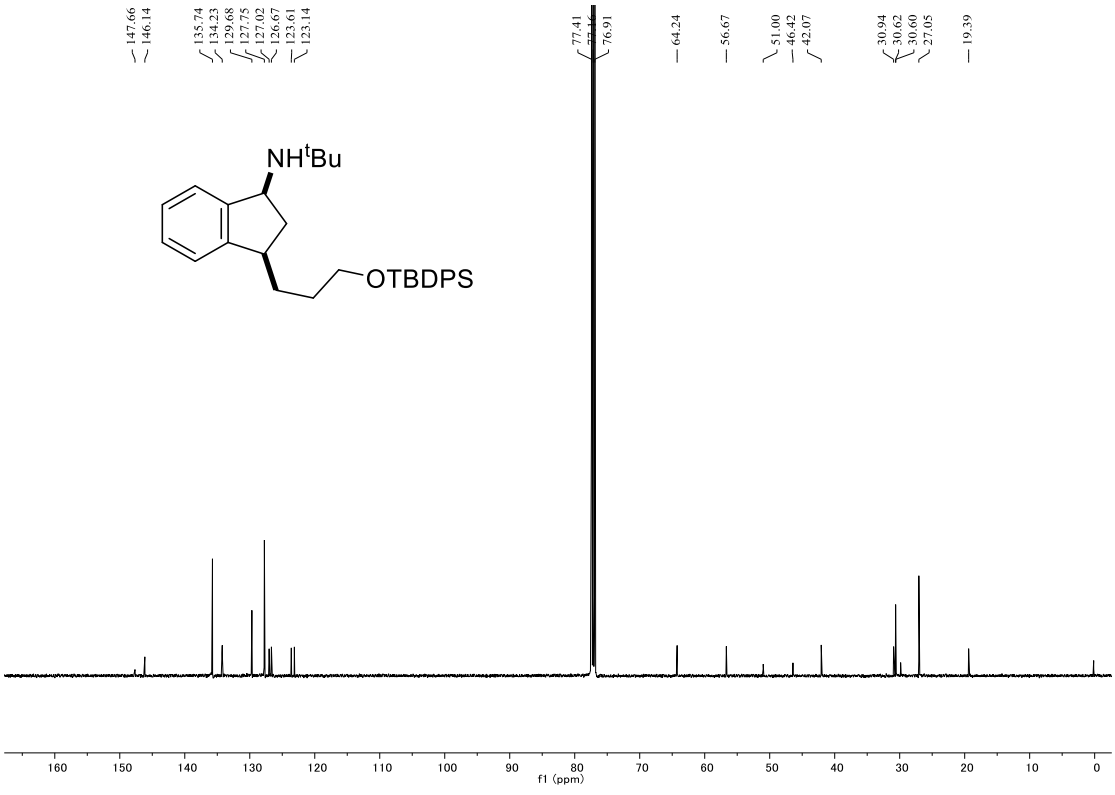
^{13}C NMR spectra of ***trans*-3am** (126 MHz, $CDCl_3$)



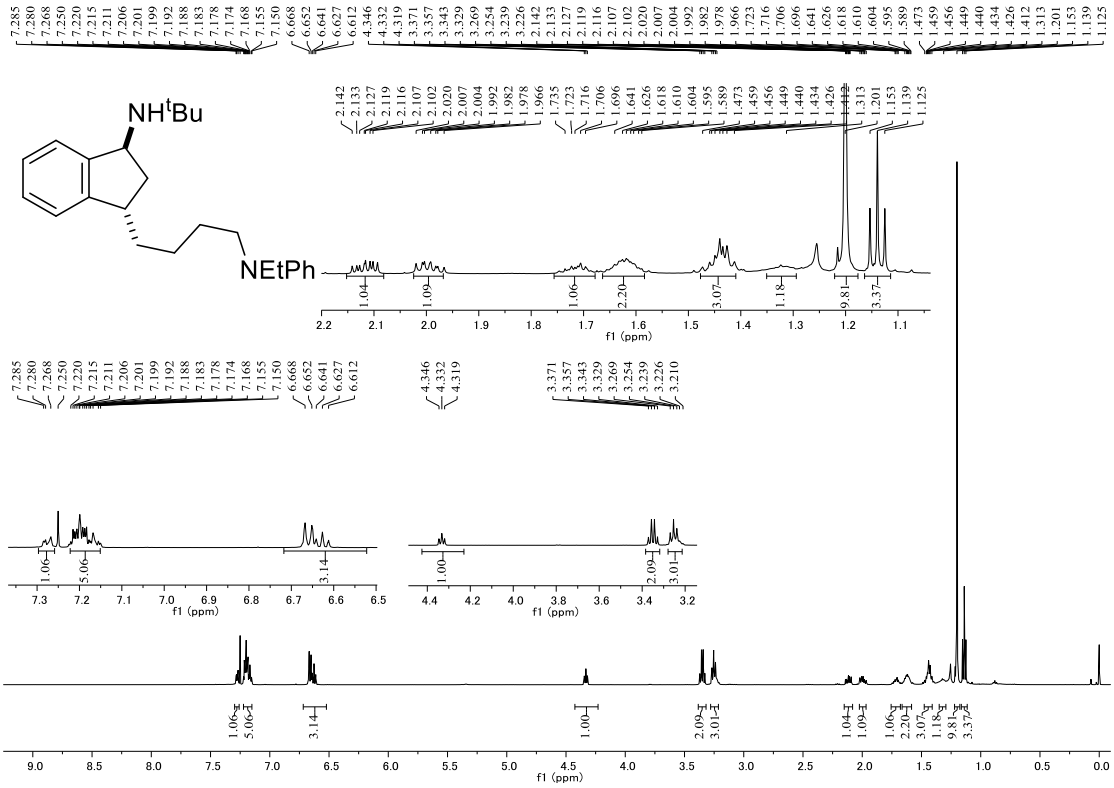
^{1}H NMR spectra of ***cis*-3am** (500 MHz, $CDCl_3$)



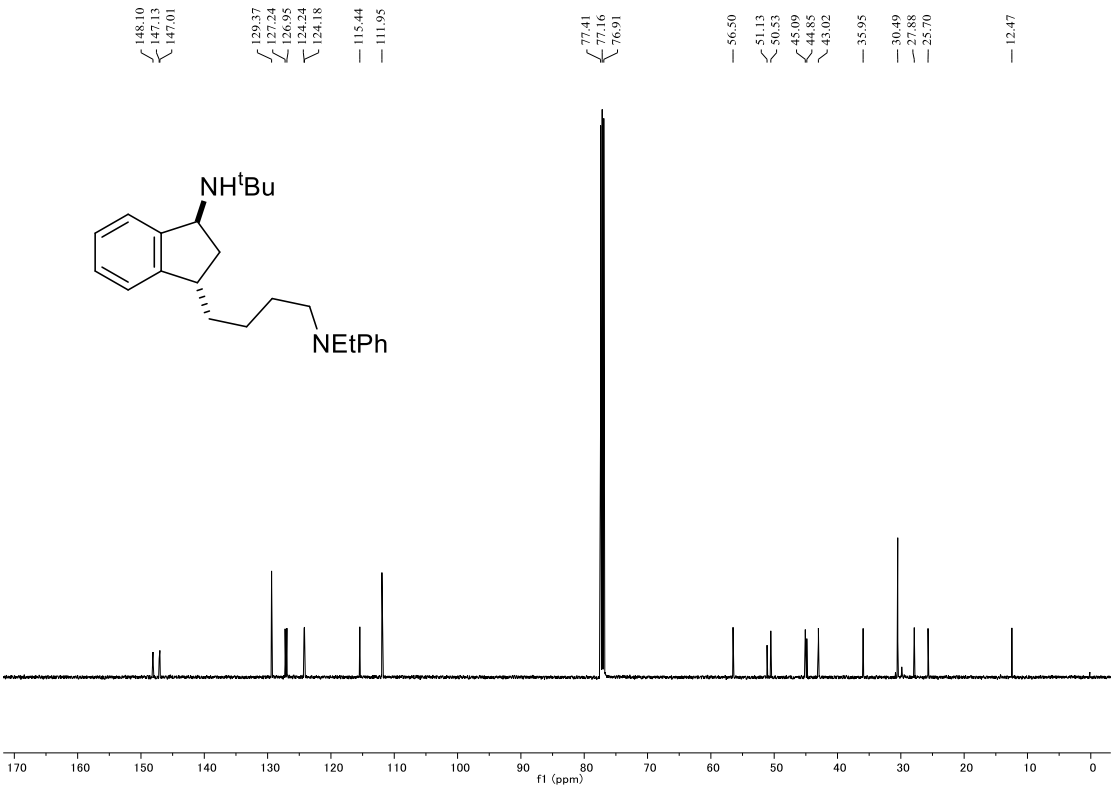
^{13}C NMR spectra of ***cis*-3am** (126 MHz, $CDCl_3$)



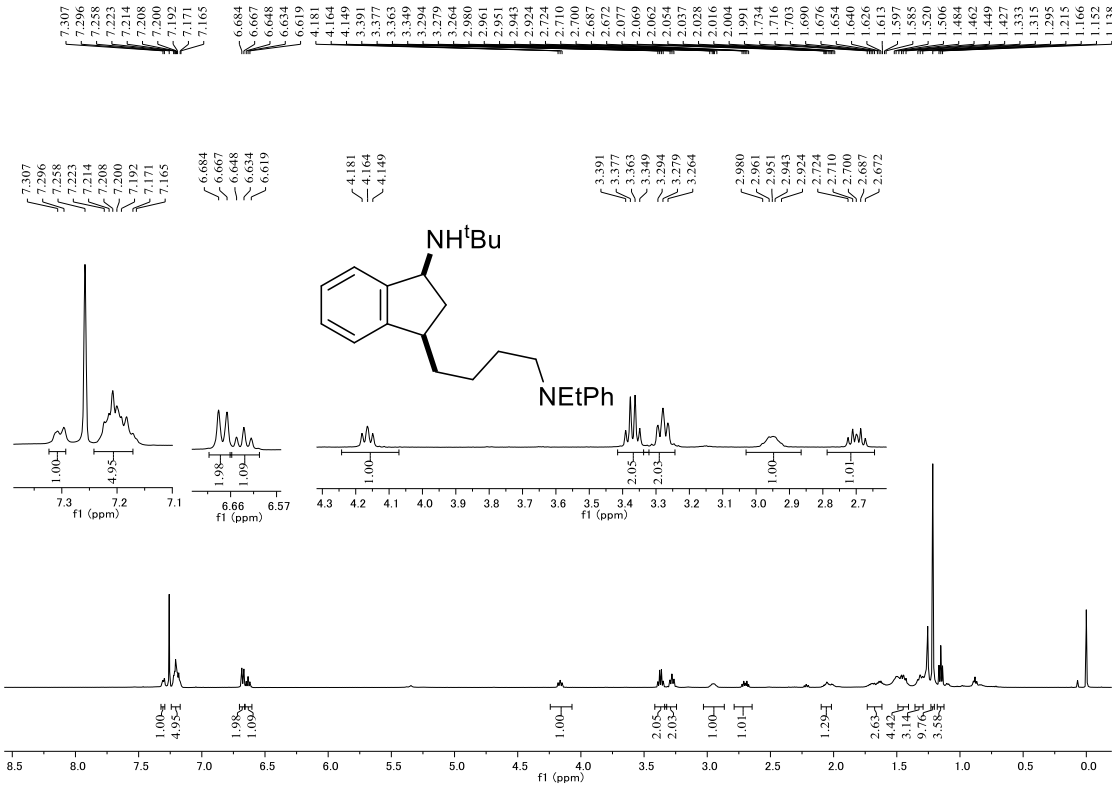
^{1}H NMR spectra of ***trans*-3an** (500 MHz, $CDCl_3$)



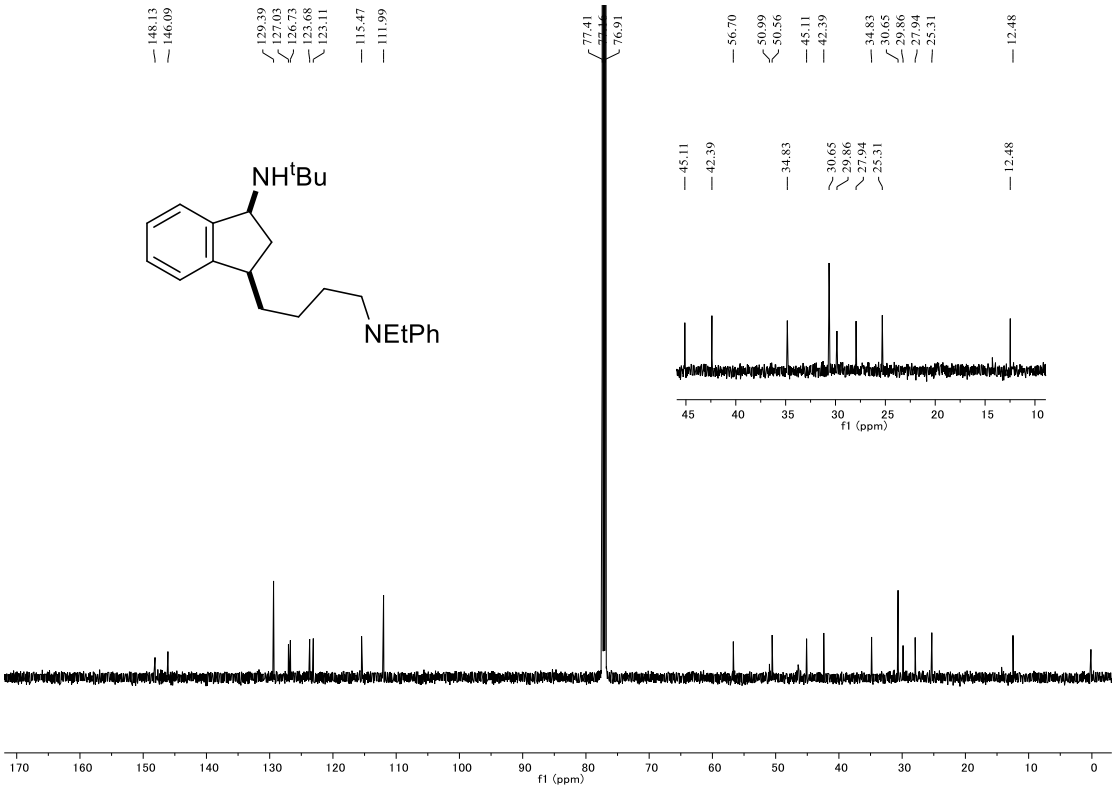
^{13}C NMR spectra of ***trans*-3an** (126 MHz, $CDCl_3$)



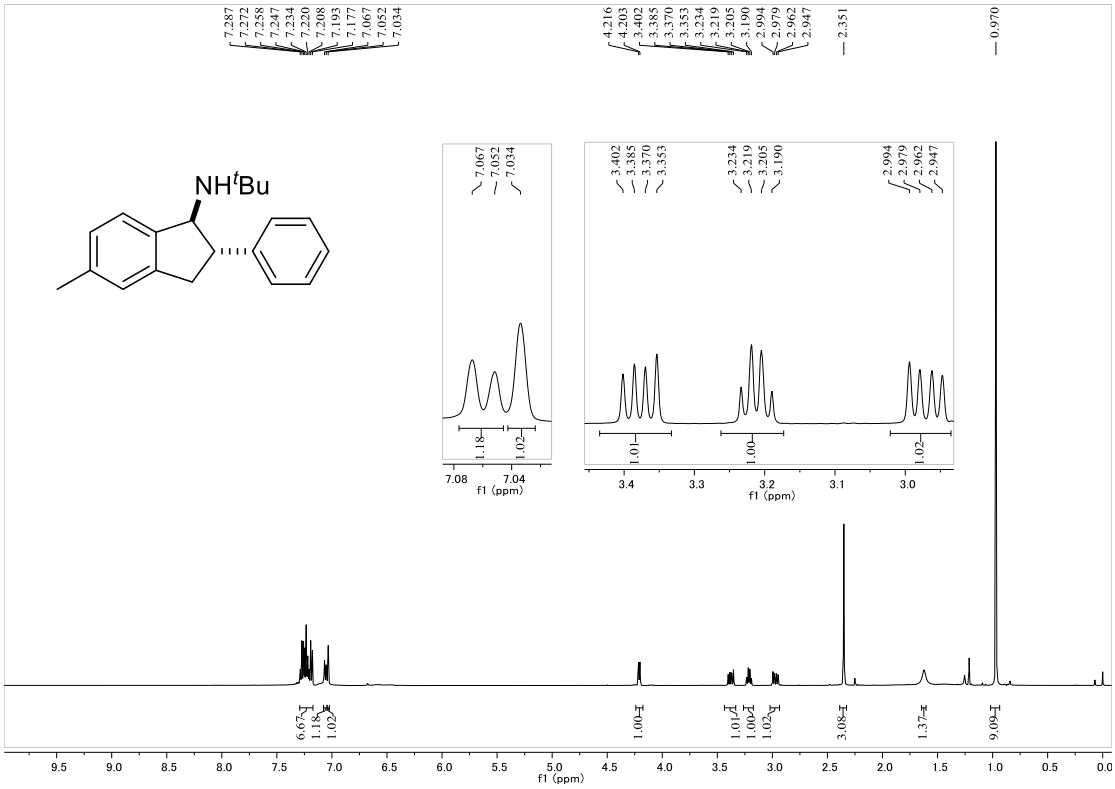
^{1}H NMR spectra of ***cis*-3an** (500 MHz, $CDCl_3$)



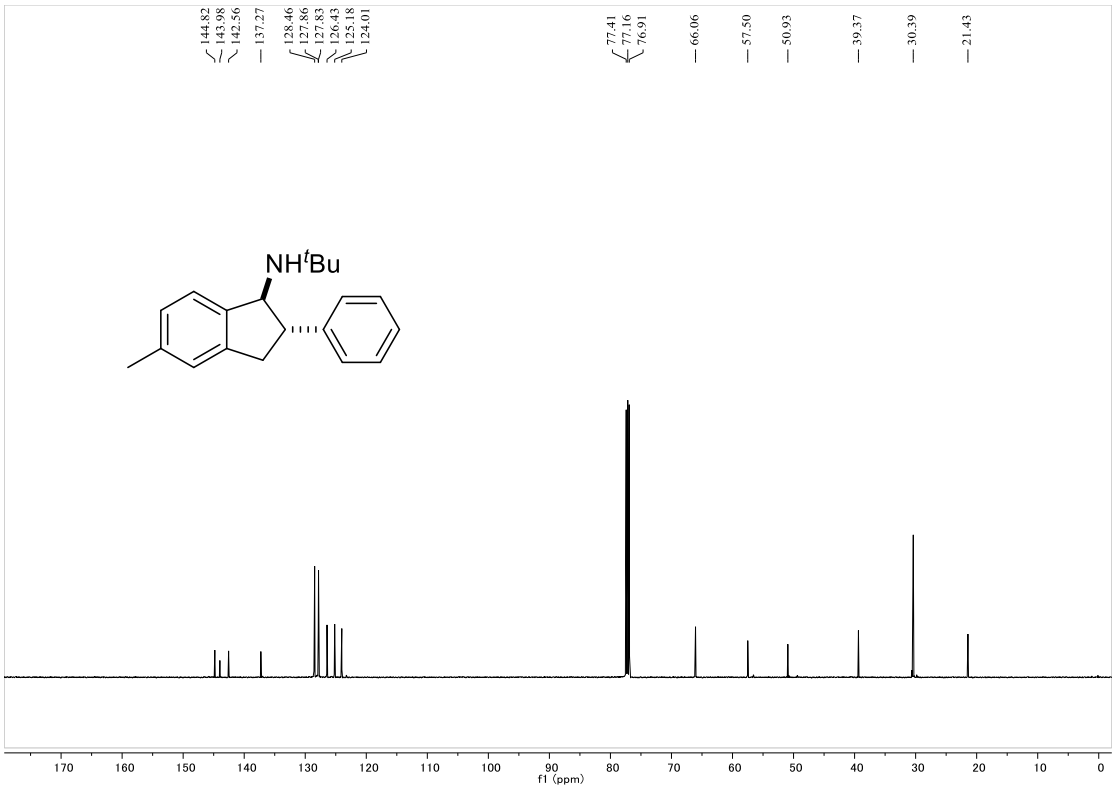
^{13}C NMR spectra of ***cis*-3an** (126 MHz, $CDCl_3$)



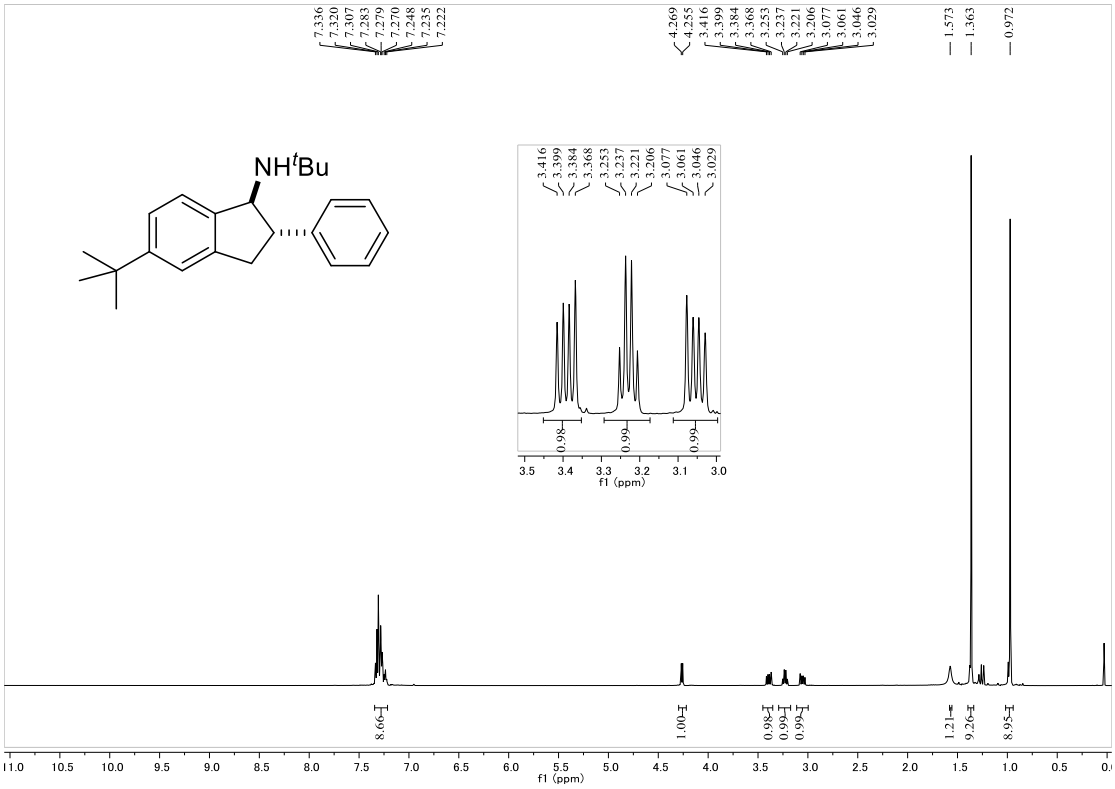
^{1}H NMR spectra of ***trans*-3ba** (500 MHz, $CDCl_3$)



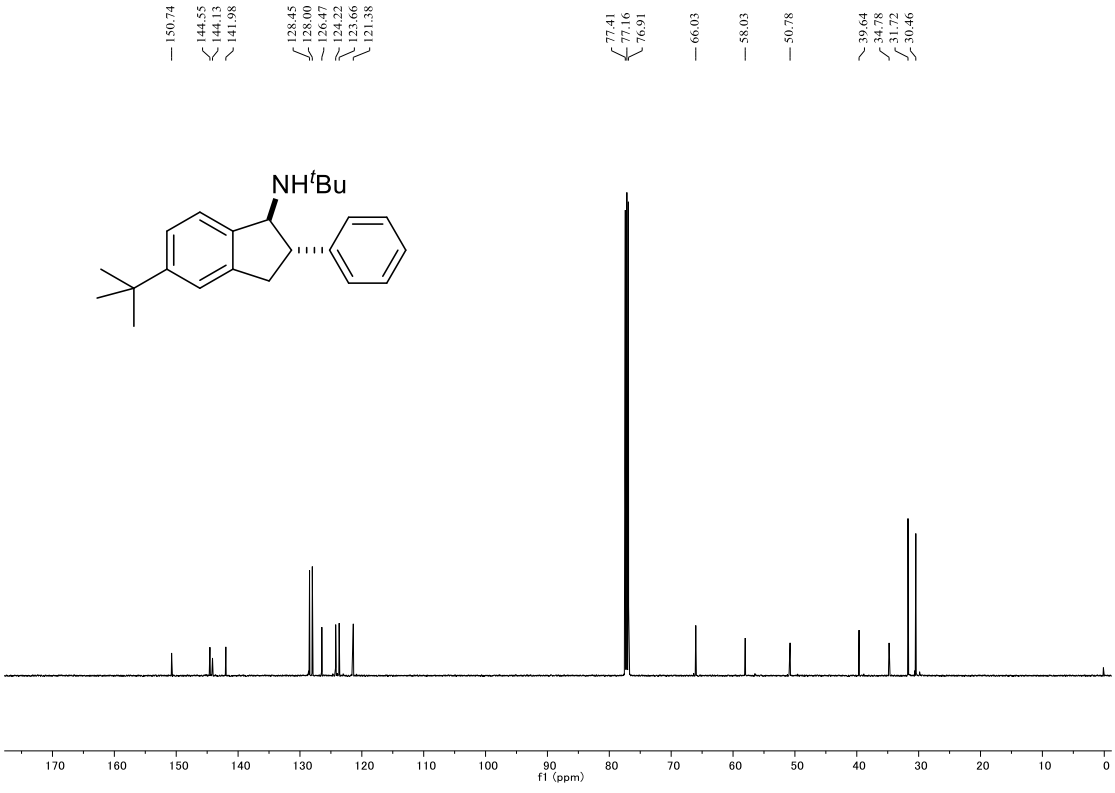
^{13}C NMR spectra of ***trans*-3ba** (126 MHz, $CDCl_3$)



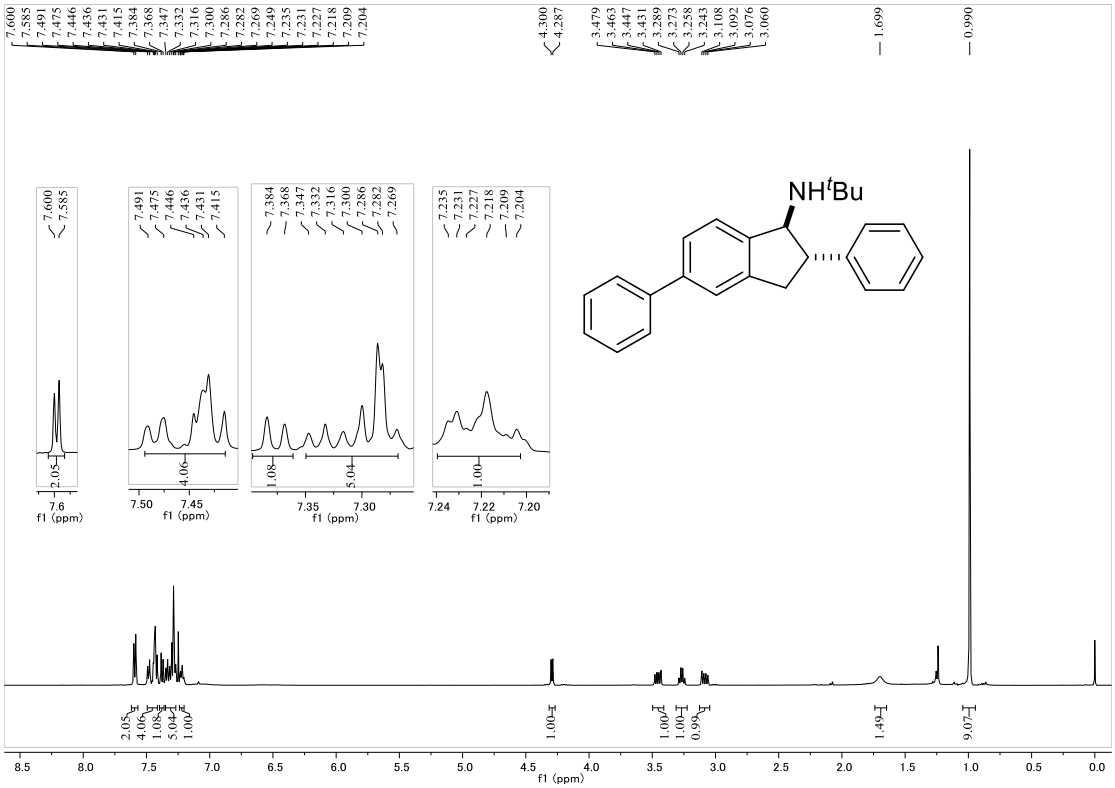
^{1}H NMR spectra of ***trans*-3ca** (500 MHz, $CDCl_3$)



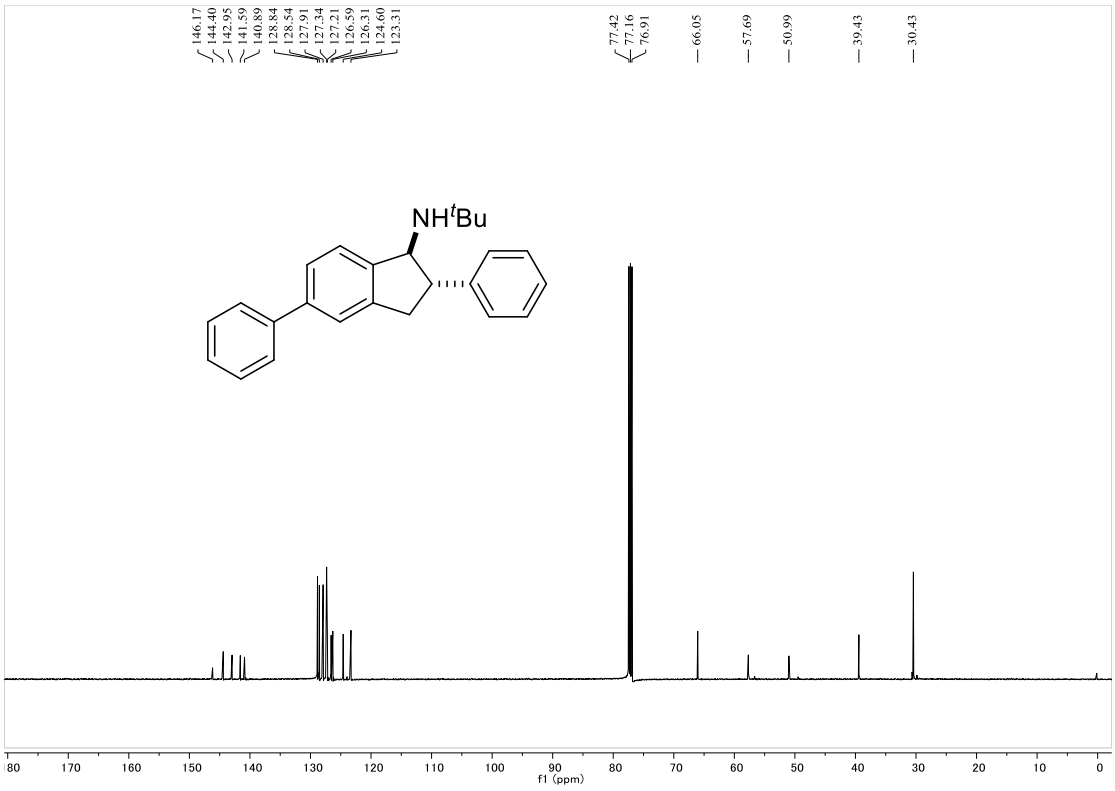
^{13}C NMR spectra of ***trans*-3ca** (126 MHz, $CDCl_3$)



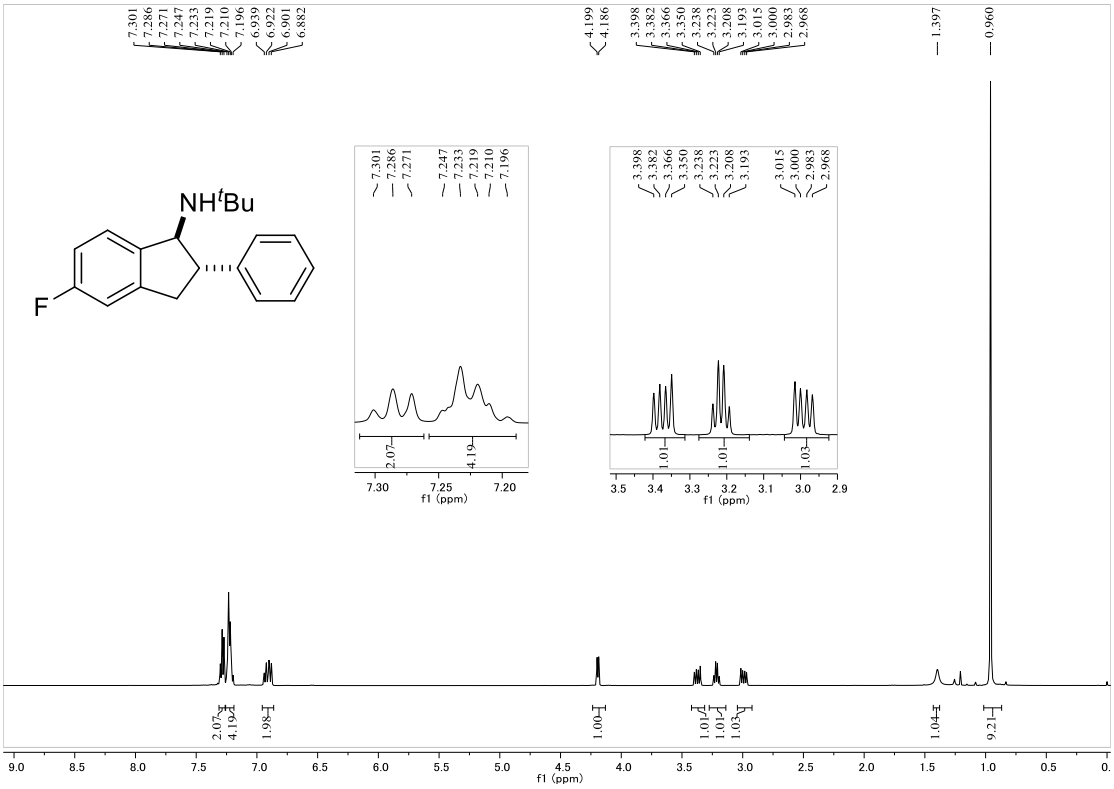
^{1}H NMR spectra of ***trans*-3da** (500 MHz, $CDCl_3$)



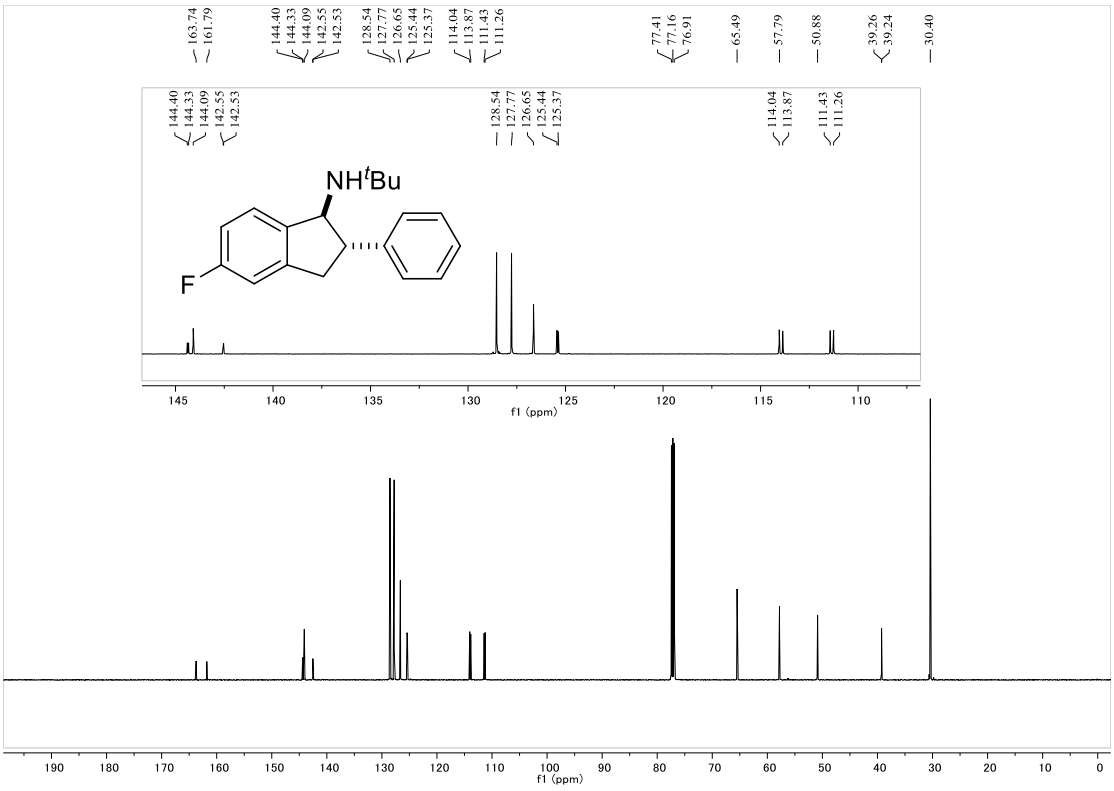
^{13}C NMR spectra of ***trans*-3da** (126 MHz, $CDCl_3$)



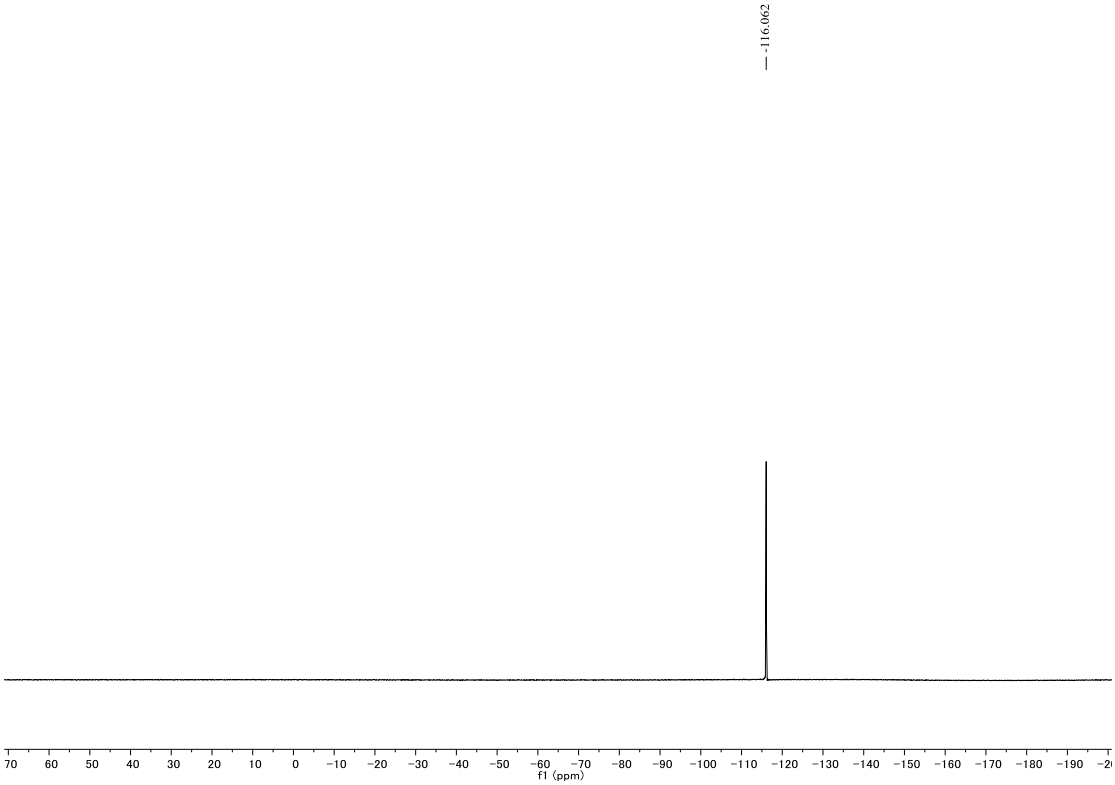
^{1}H NMR spectra of ***trans*-3ea** (500 MHz, $CDCl_3$)



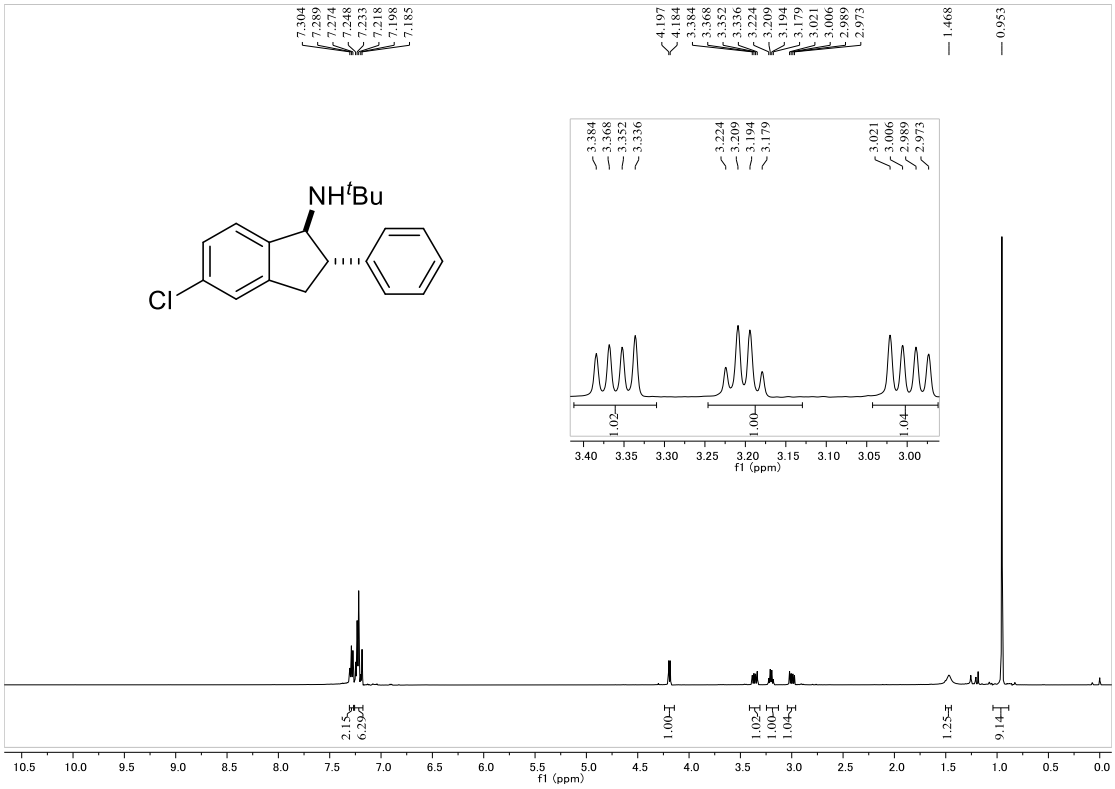
^{13}C NMR spectra of ***trans*-3ea** (126 MHz, $CDCl_3$)



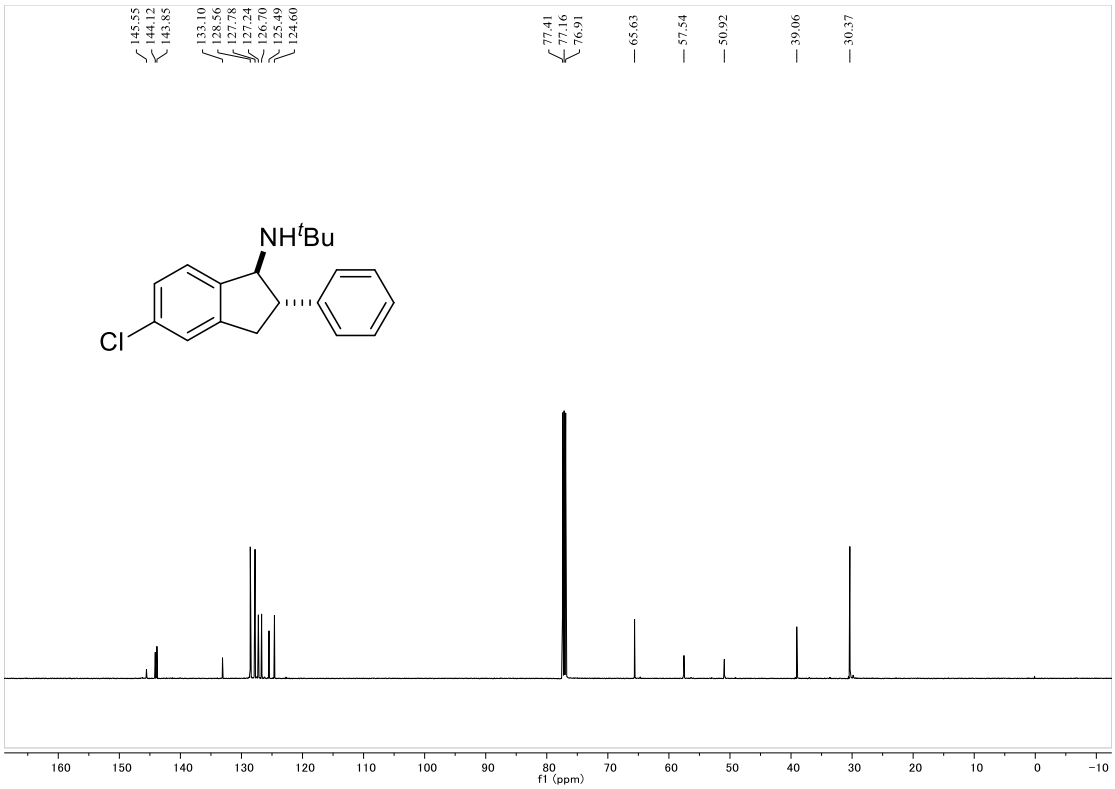
^{19}F NMR spectra of ***trans*-3ea** (377 MHz, $CDCl_3$)



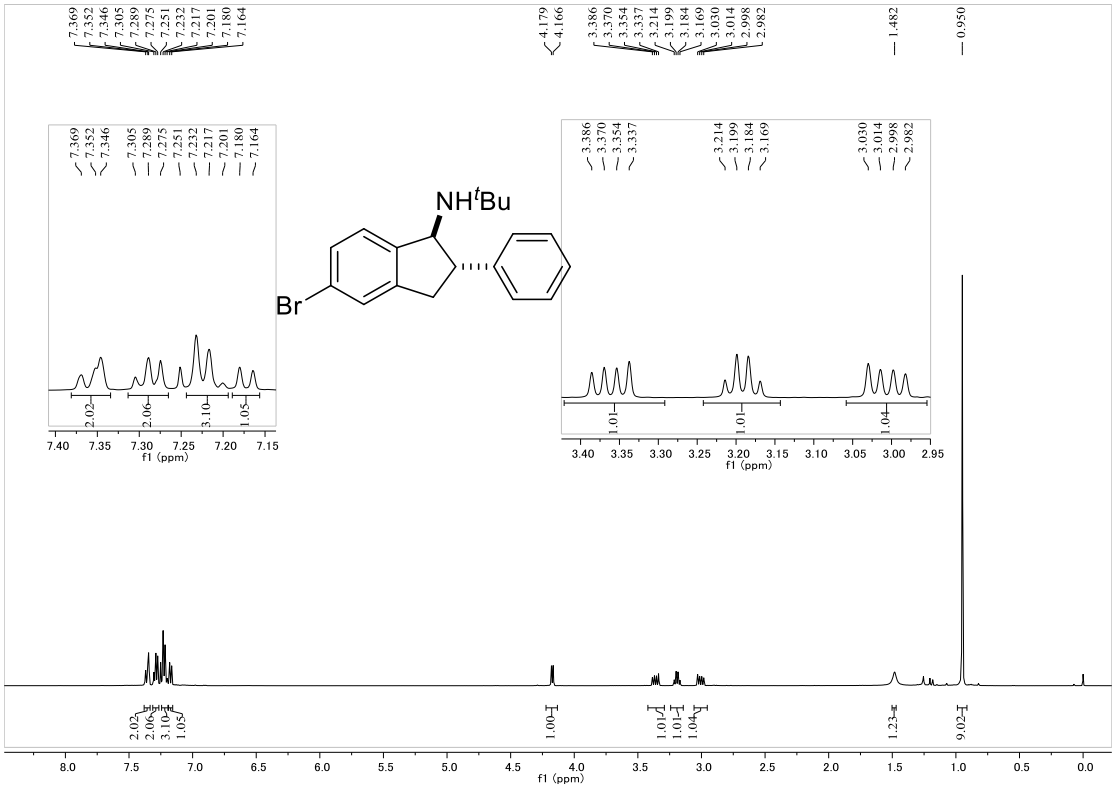
^{1}H NMR spectra of ***trans*-3fa** (500 MHz, $CDCl_3$)



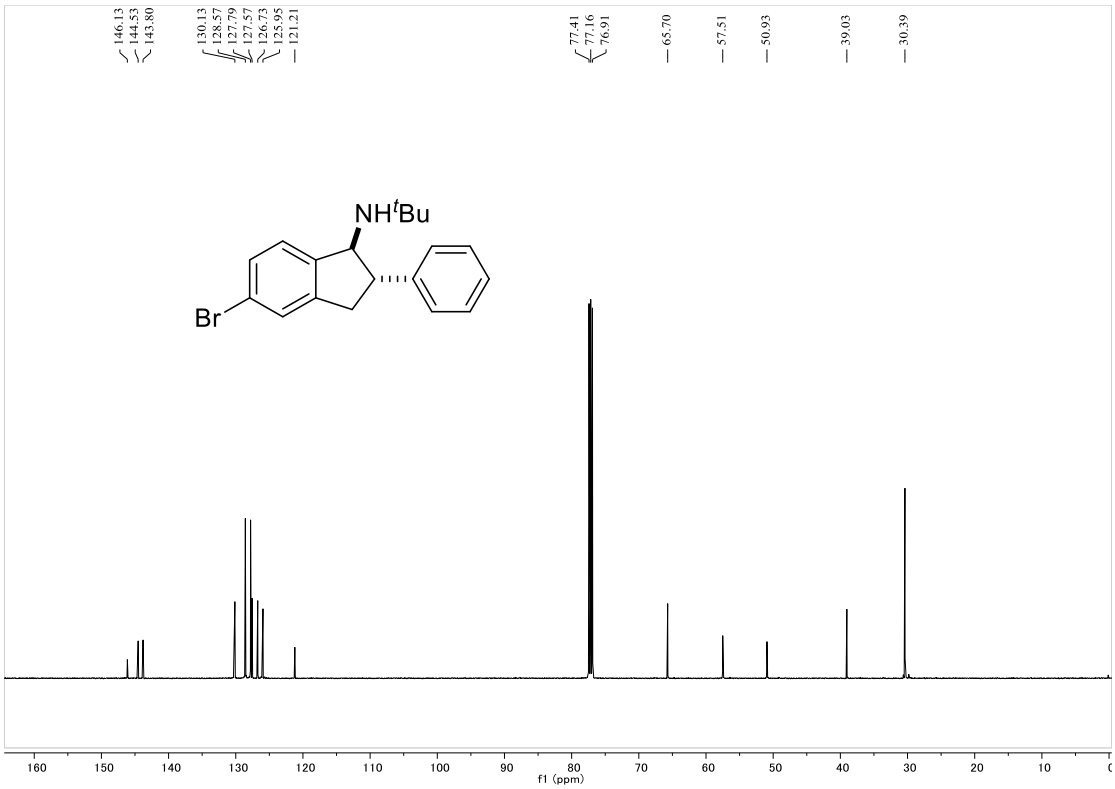
^{13}C NMR spectra of ***trans*-3fa** (126 MHz, $CDCl_3$)



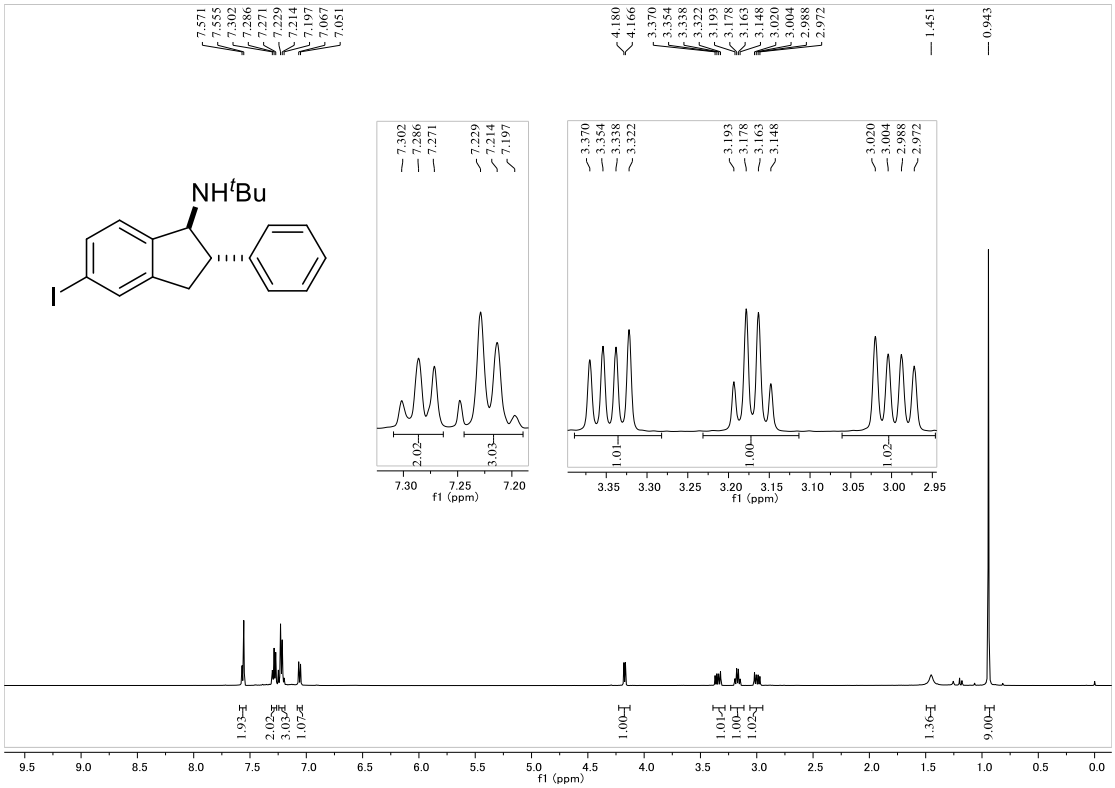
^{1}H NMR spectra of ***trans*-3ga** (500 MHz, $CDCl_3$)



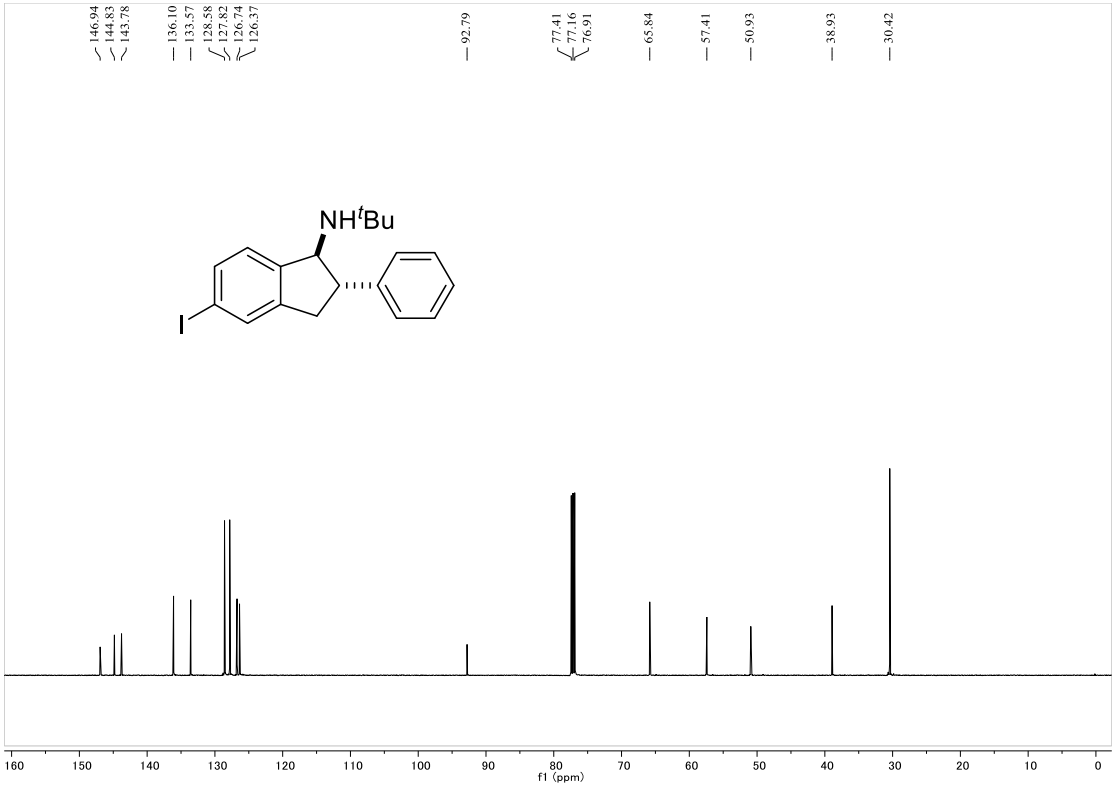
^{13}C NMR spectra of ***trans*-3ga** (126 MHz, $CDCl_3$)



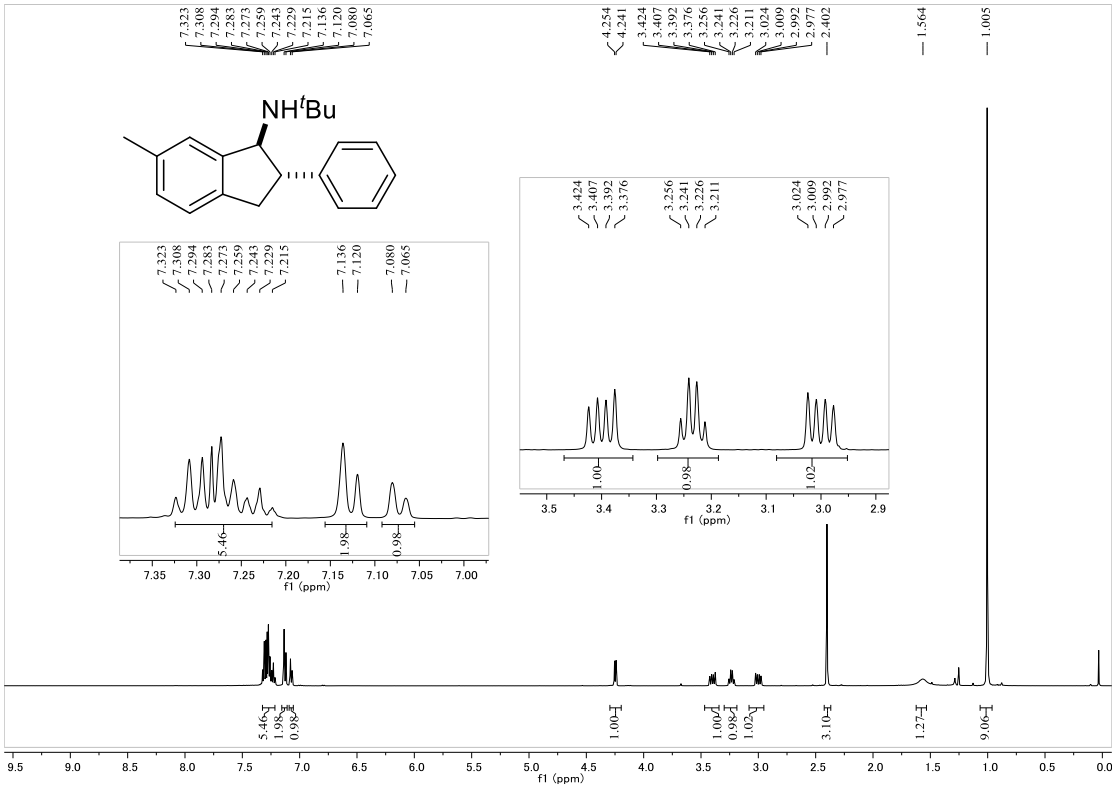
^{1}H NMR spectra of ***trans*-3ha** (500 MHz, $CDCl_3$)



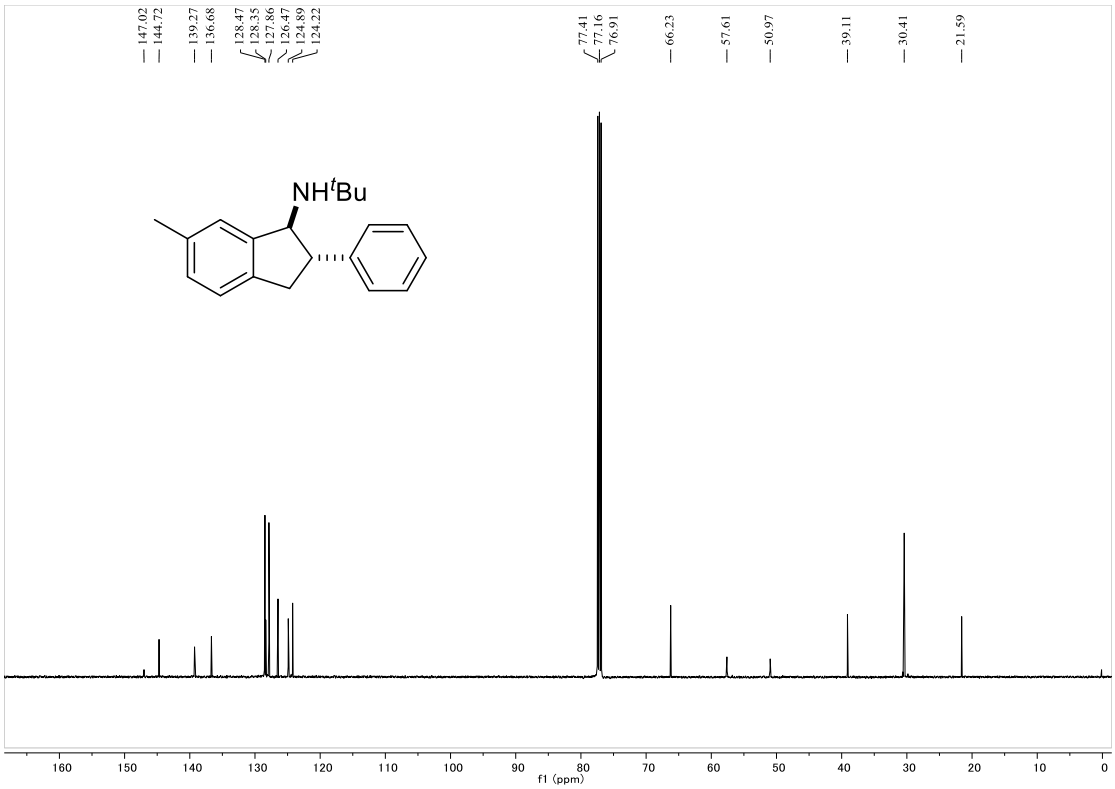
^{13}C NMR spectra of ***trans*-3ha** (126 MHz, $CDCl_3$)



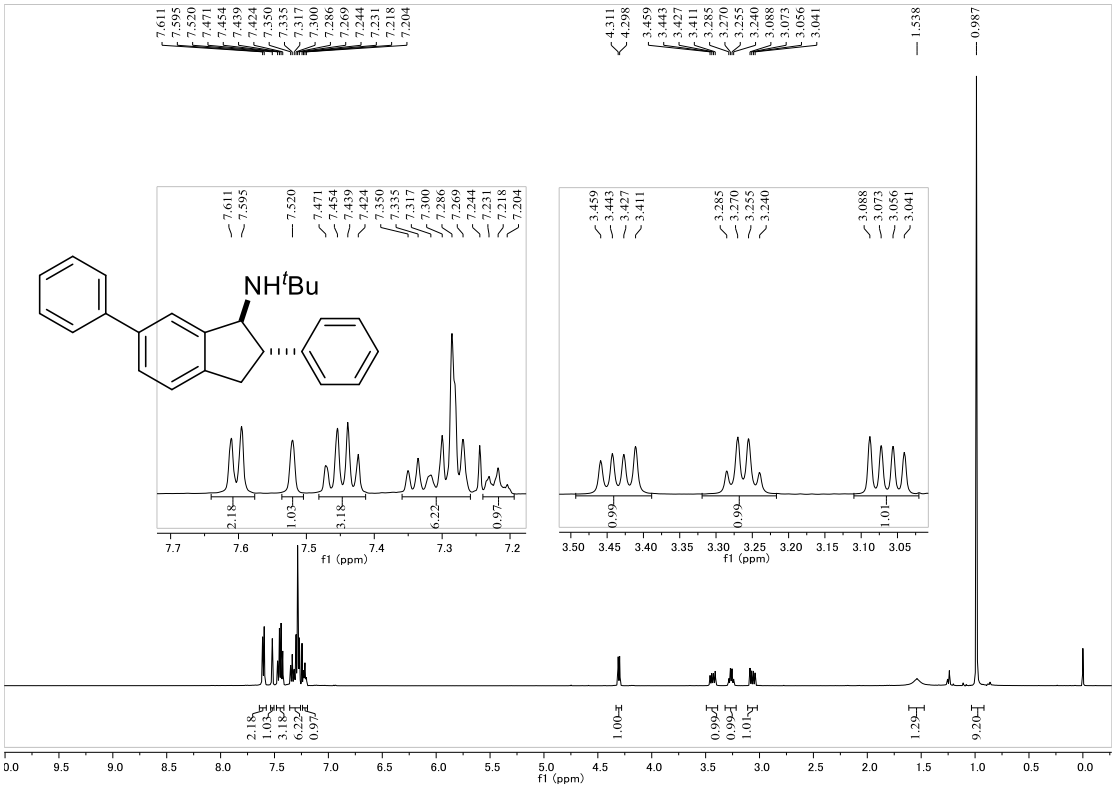
^{1}H NMR spectra of ***trans*-3ia** (500 MHz, $CDCl_3$)



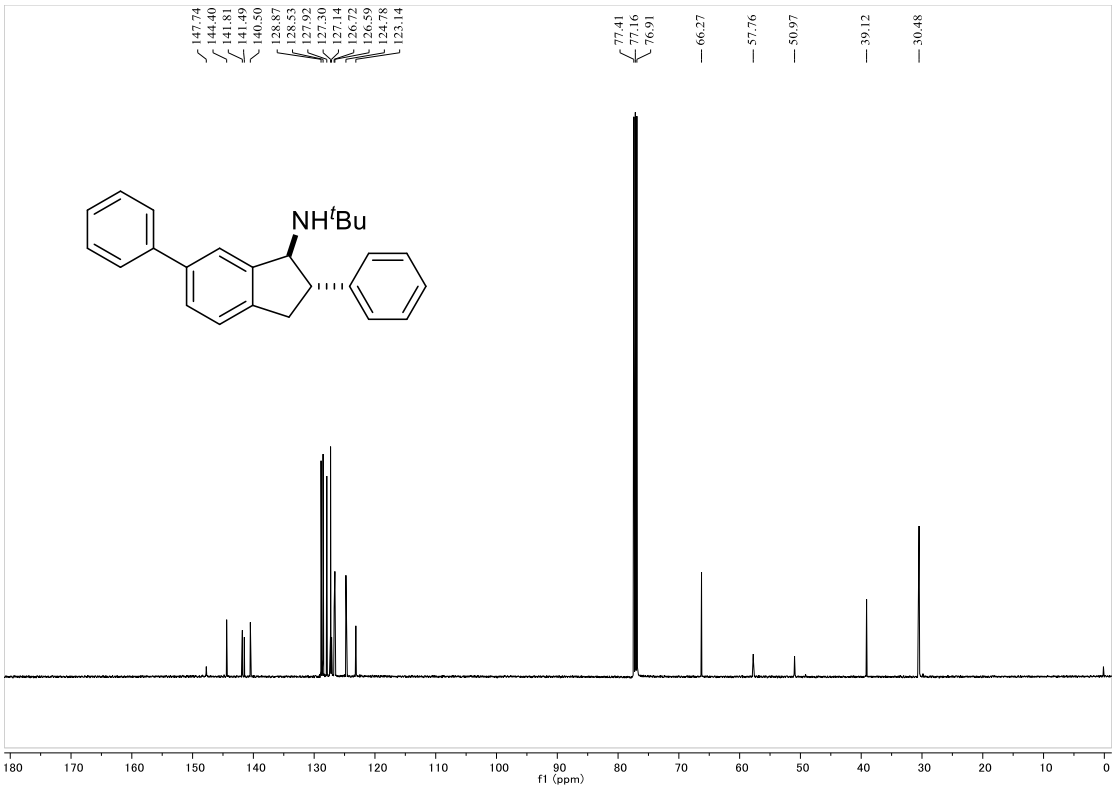
^{13}C NMR spectra of ***trans*-3ia** (126 MHz, $CDCl_3$)



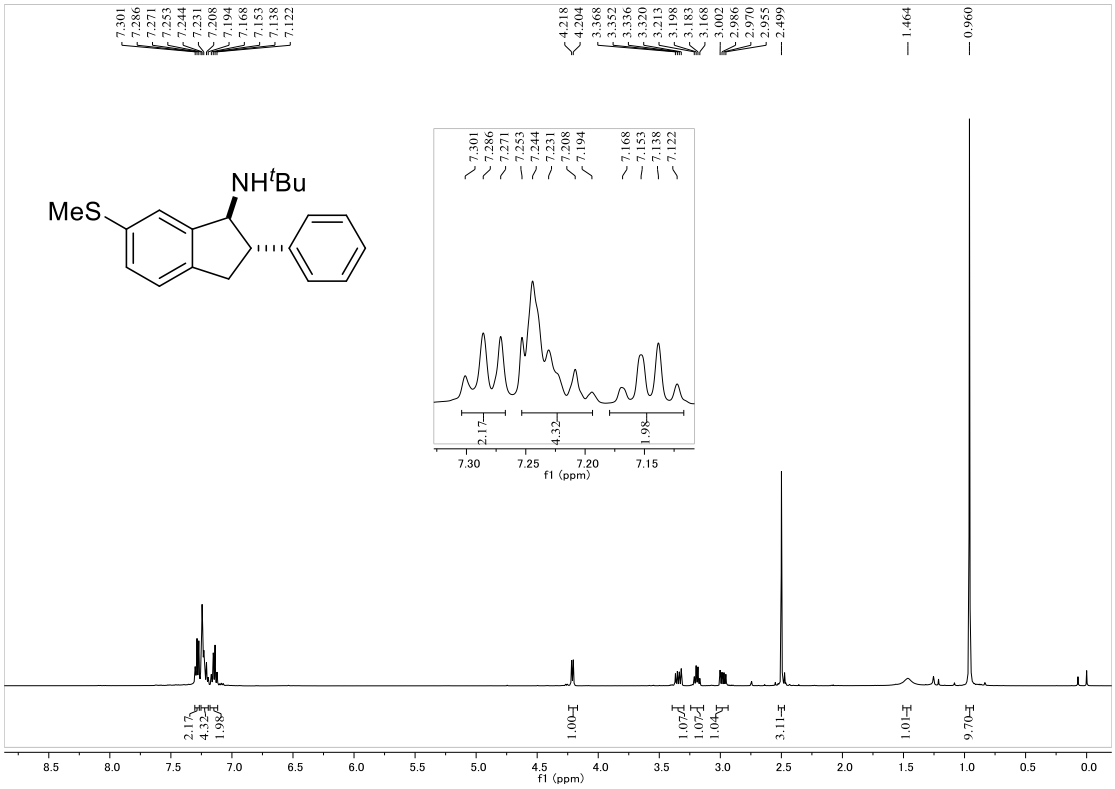
^{1}H NMR spectra of ***trans*-3ja** (500 MHz, $CDCl_3$)



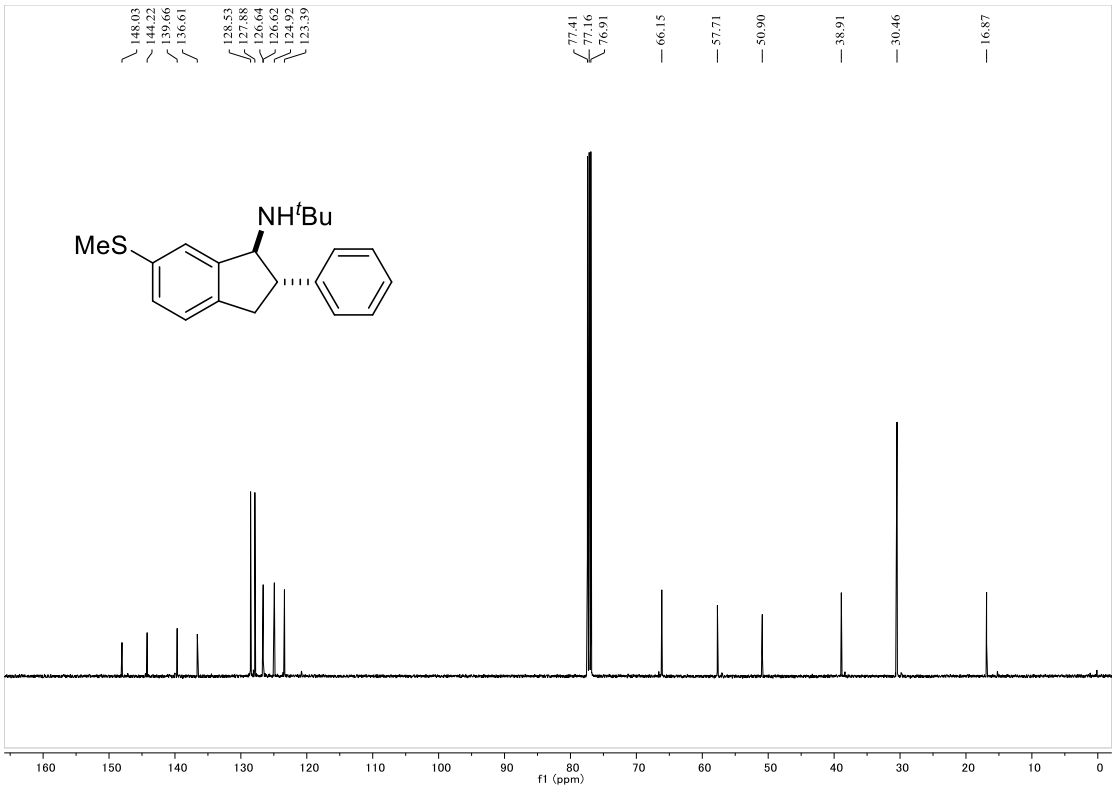
^{13}C NMR spectra of ***trans*-3ja** (126 MHz, $CDCl_3$)



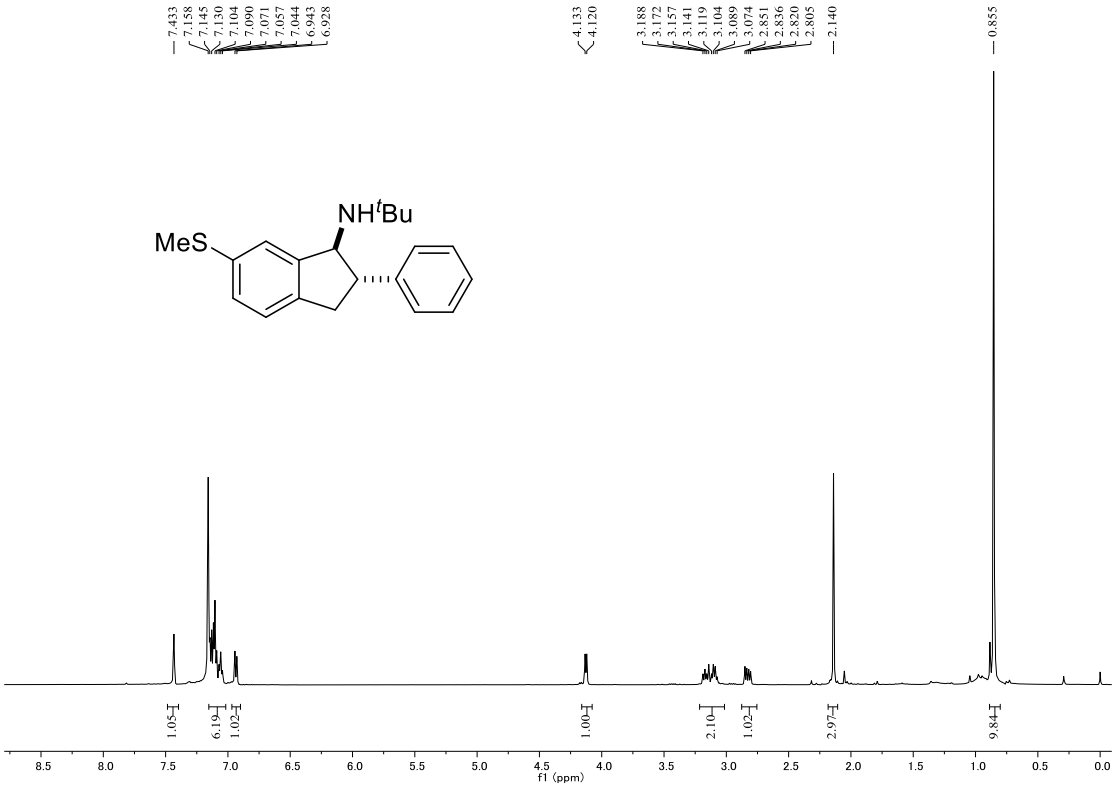
^{1}H NMR spectra of ***trans*-3ka** (500 MHz, $CDCl_3$)



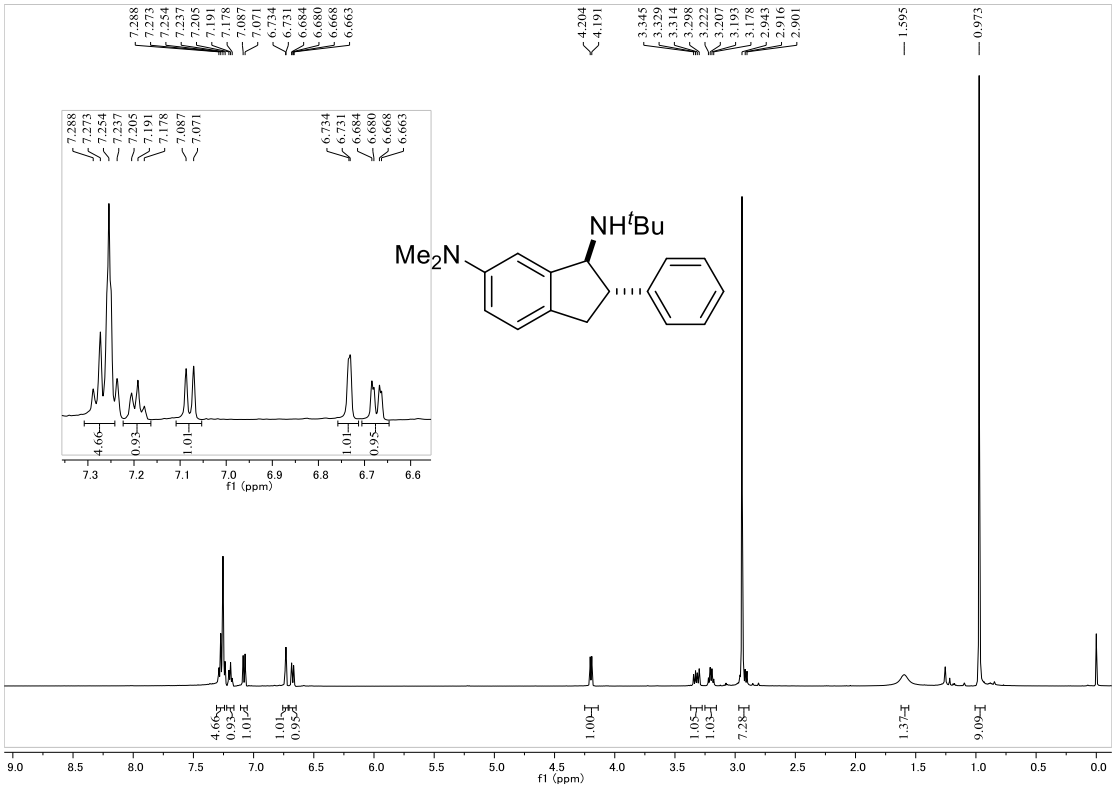
^{13}C NMR spectra of ***trans*-3ka** (126 MHz, $CDCl_3$)



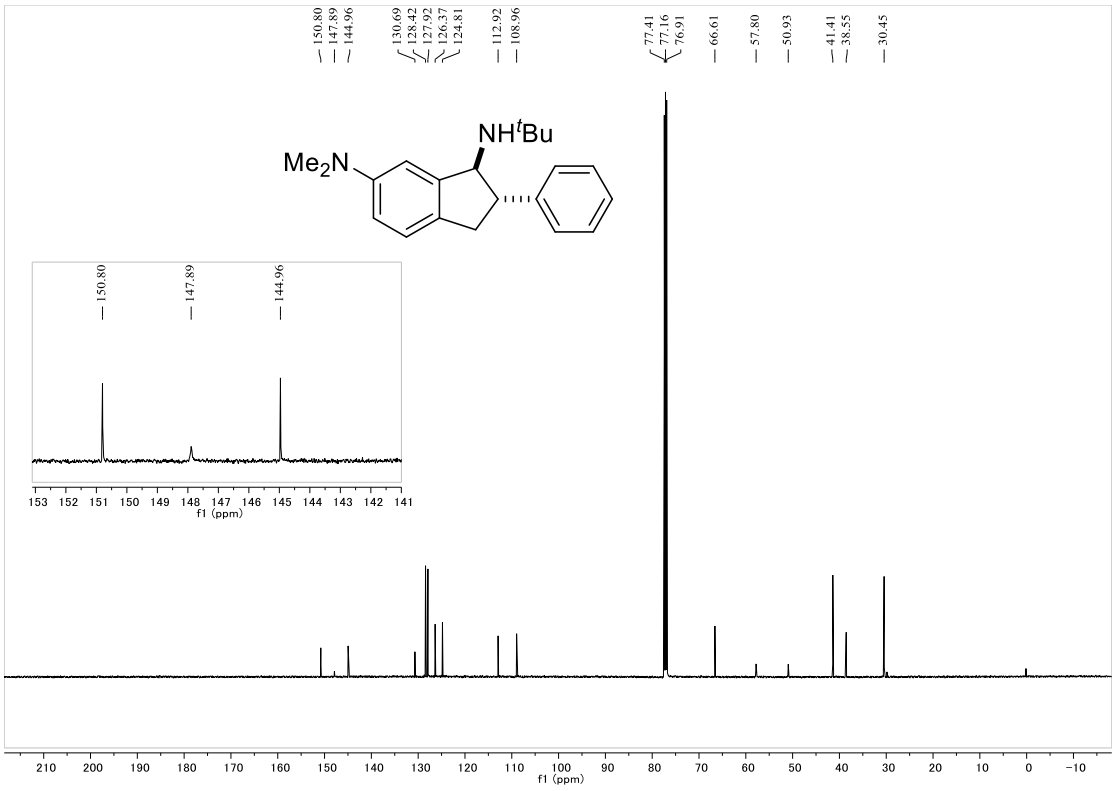
^{1}H NMR spectra of ***trans*-3ka** (500 MHz, C_6D_6)



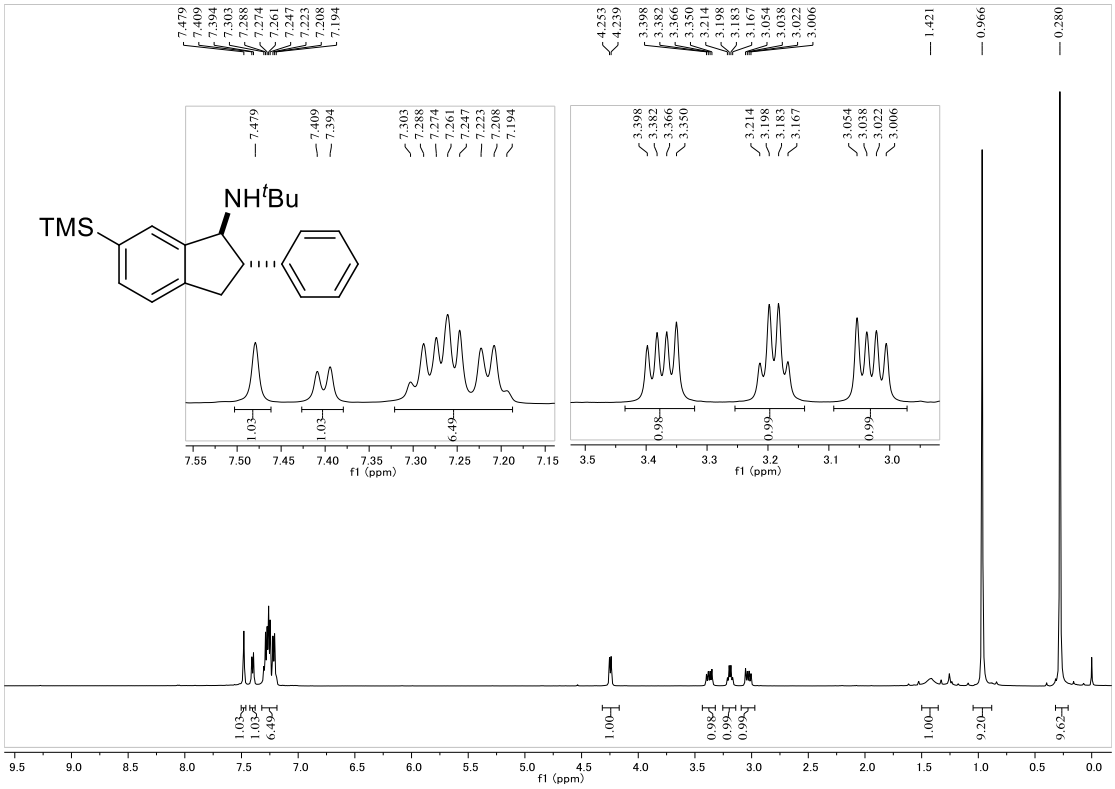
^{1}H NMR spectra of ***trans*-3la** (500 MHz, $CDCl_3$)



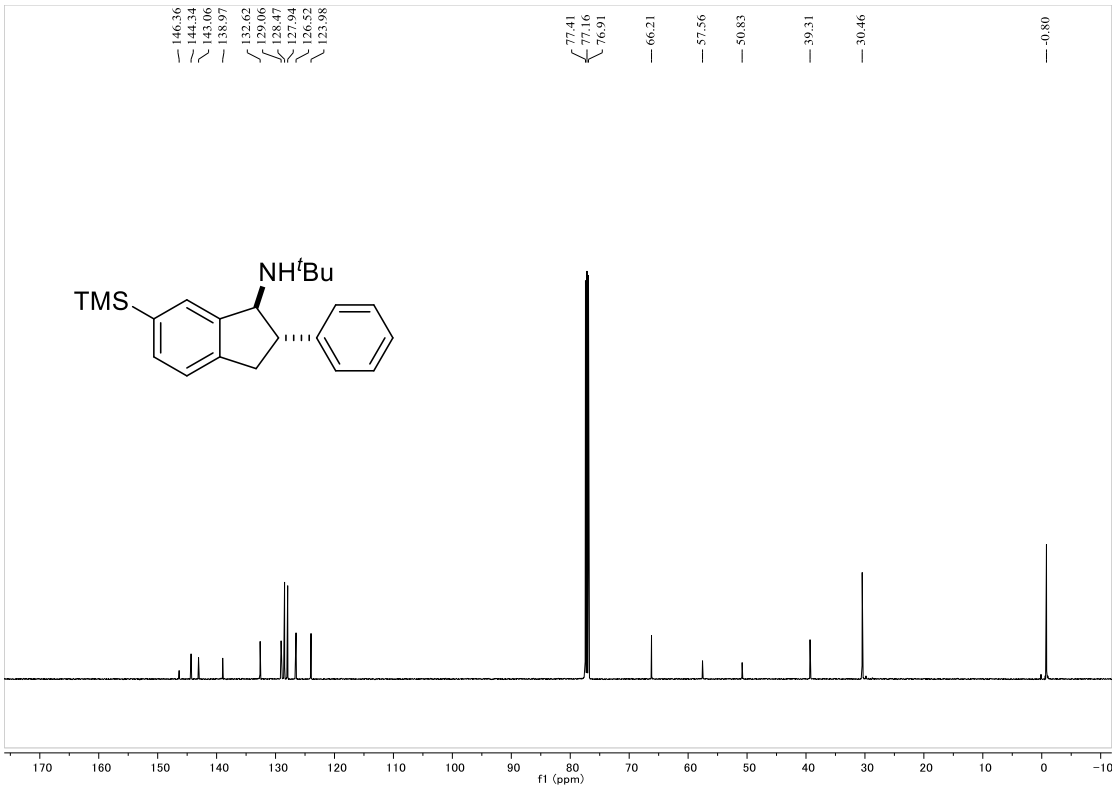
^{13}C NMR spectra of ***trans*-3la** (126 MHz, $CDCl_3$)



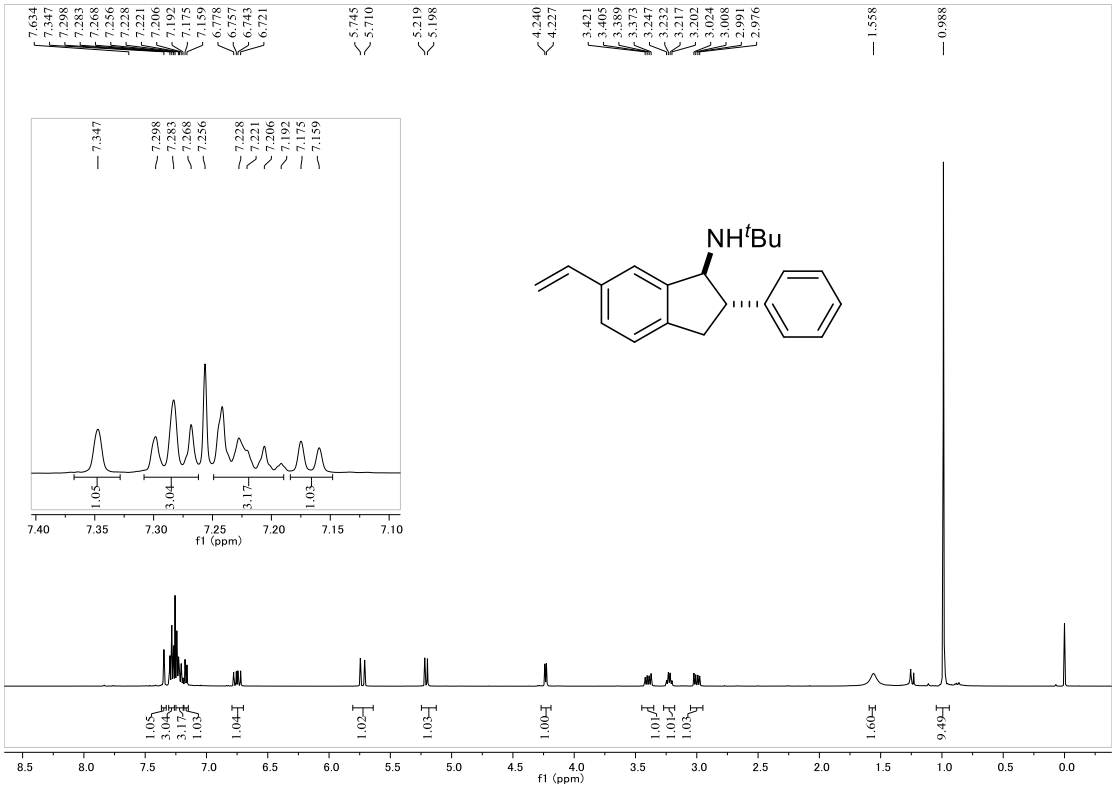
^{1}H NMR spectra of ***trans*-3ma** (500 MHz, $CDCl_3$)



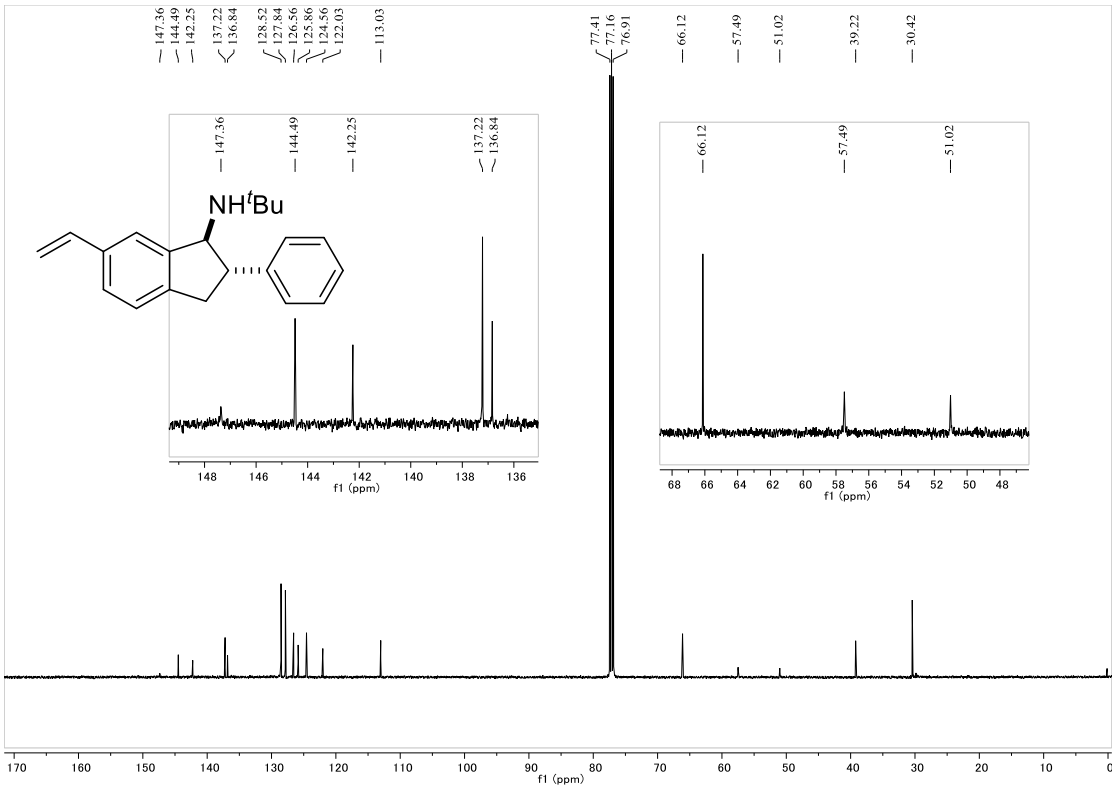
^{13}C NMR spectra of ***trans*-3ma** (126 MHz, $CDCl_3$)



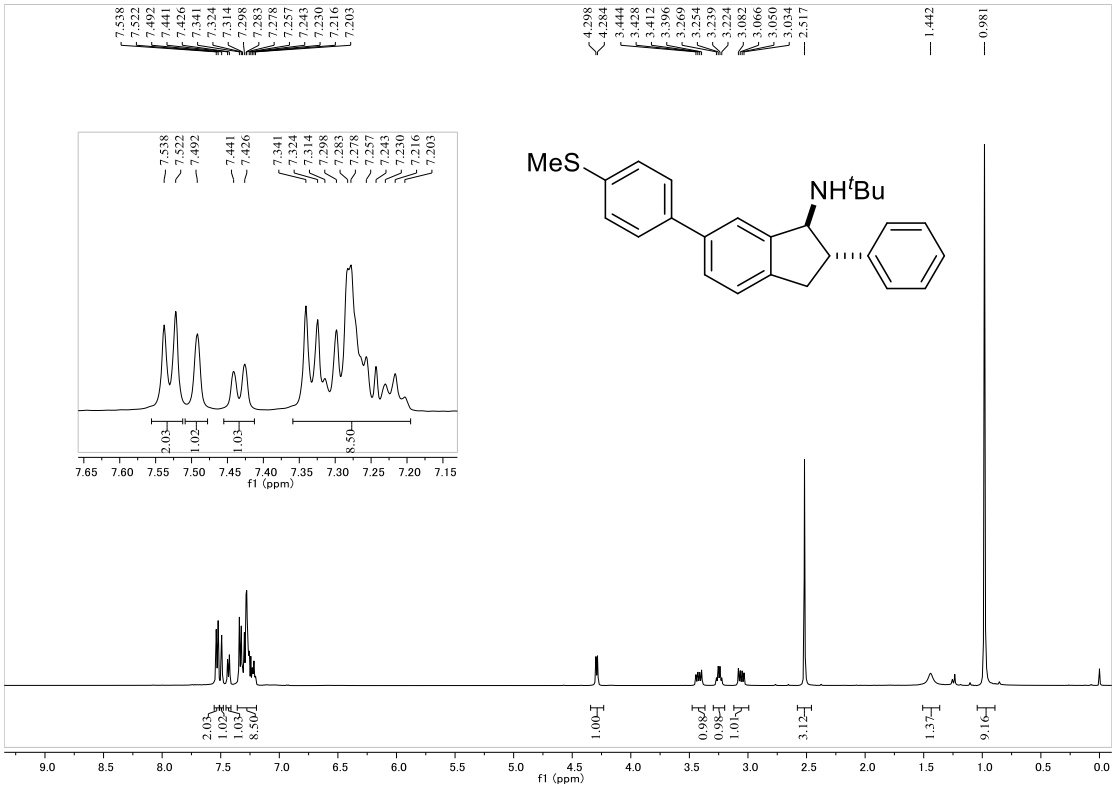
^{1}H NMR spectra of ***trans*-3na** (500 MHz, $CDCl_3$)



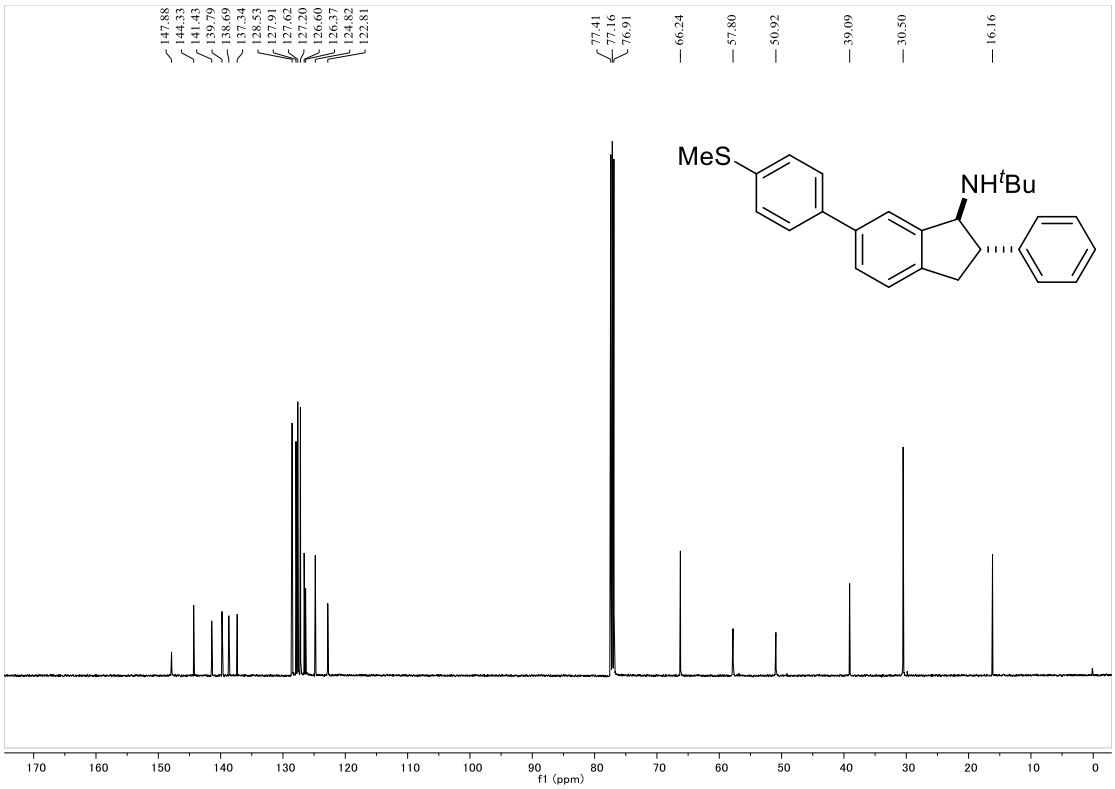
^{13}C NMR spectra of ***trans*-3na** (126 MHz, $CDCl_3$)



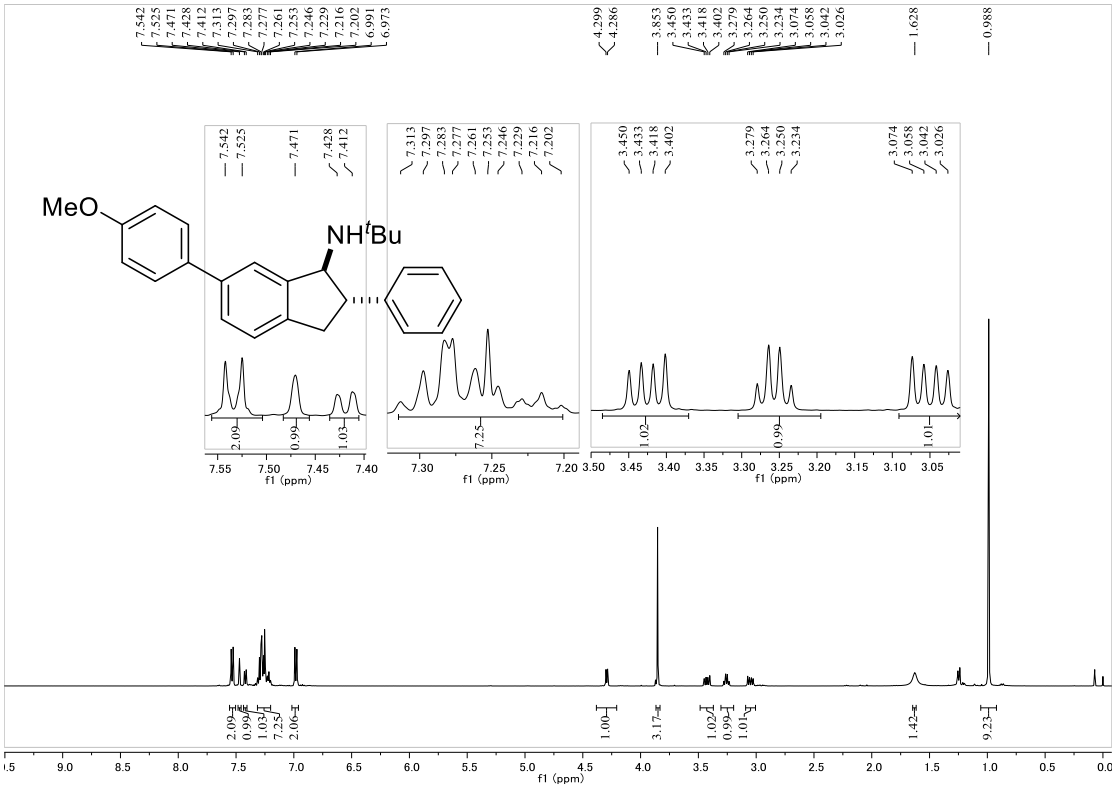
^{1}H NMR spectra of ***trans*-3oa** (500 MHz, $CDCl_3$)



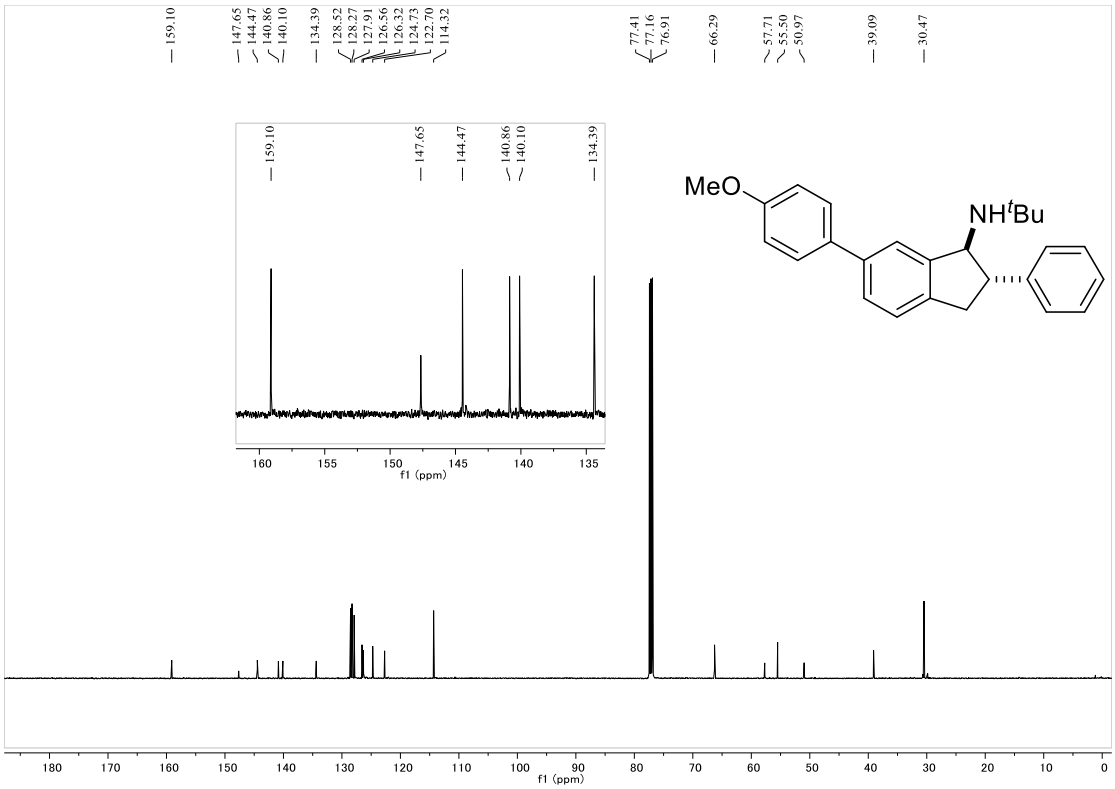
^{13}C NMR spectra of ***trans*-3oa** (126 MHz, $CDCl_3$)



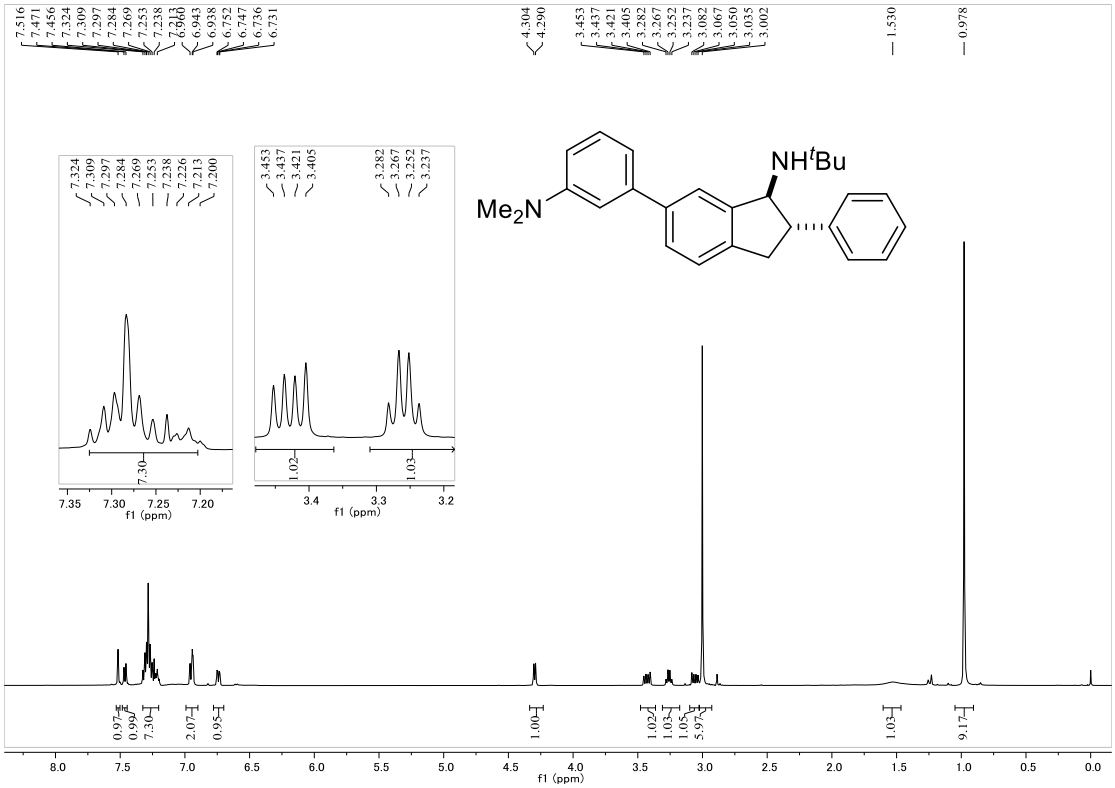
^{1}H NMR spectra of ***trans*-3pa** (500 MHz, $CDCl_3$)



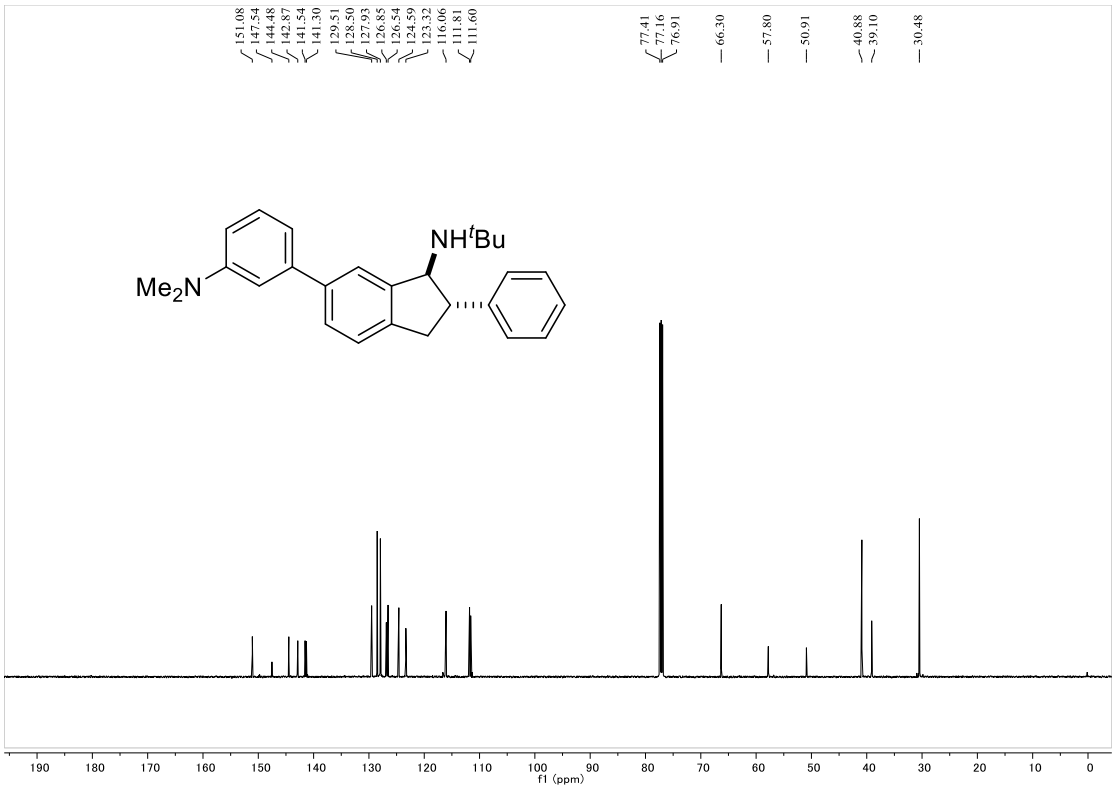
^{13}C NMR spectra of ***trans*-3pa** (126 MHz, $CDCl_3$)



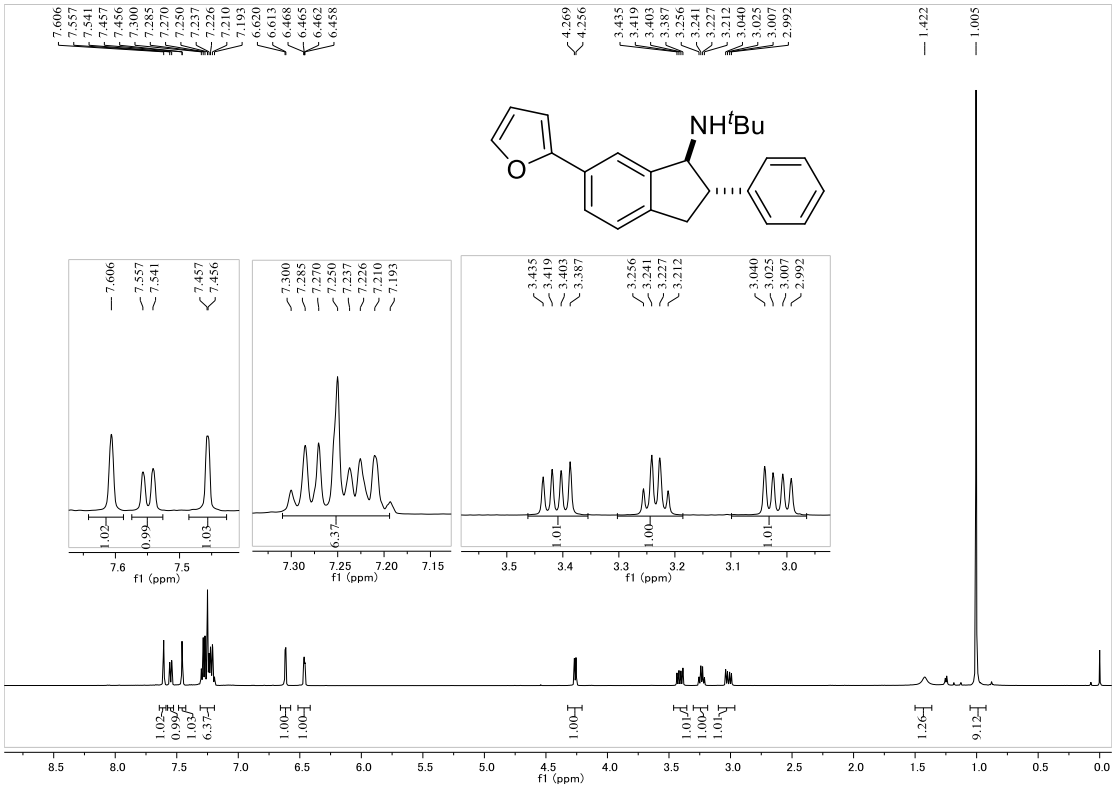
^{1}H NMR spectra of ***trans*-3qa** (500 MHz, $CDCl_3$)



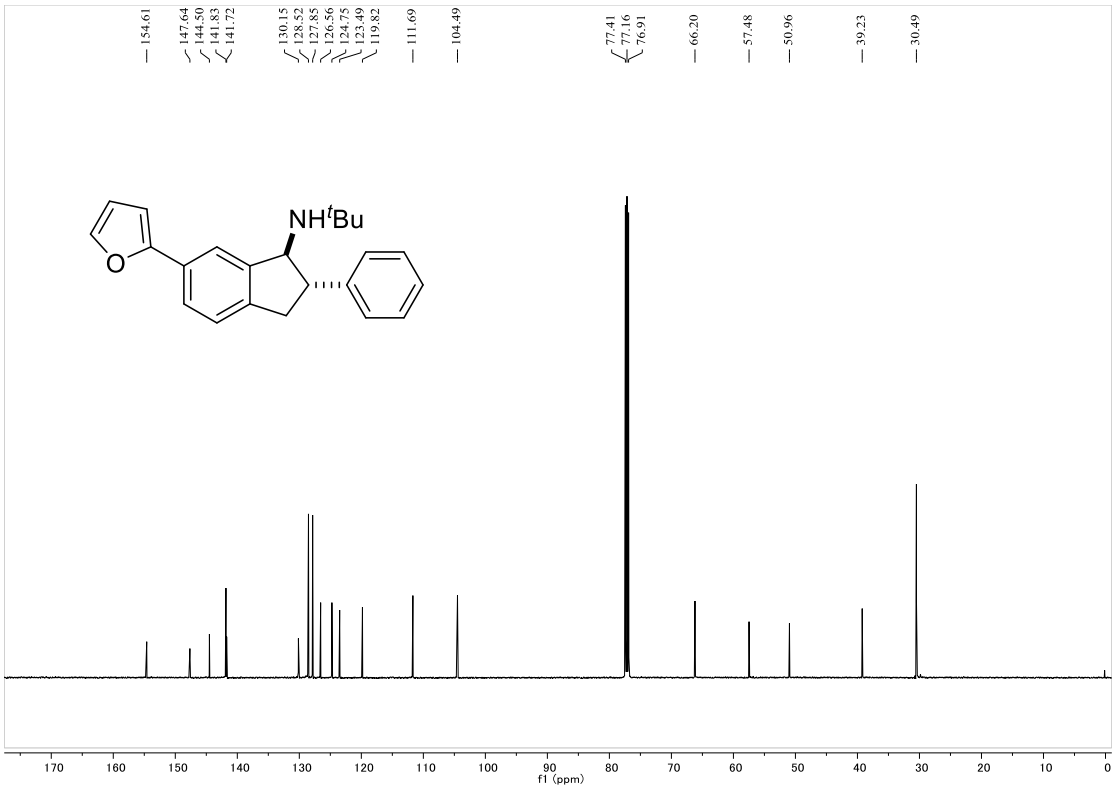
^{13}C NMR spectra of ***trans*-3qa** (126 MHz, $CDCl_3$)



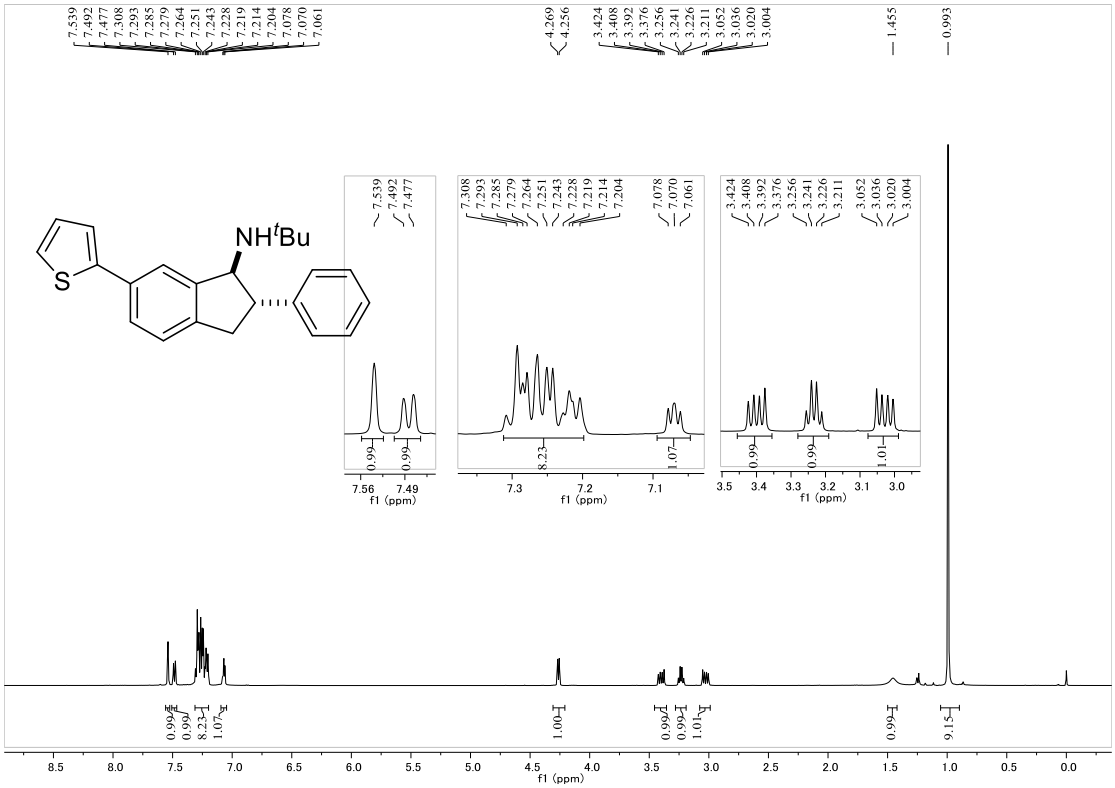
^{1}H NMR spectra of ***trans*-3ra** (500 MHz, $CDCl_3$)



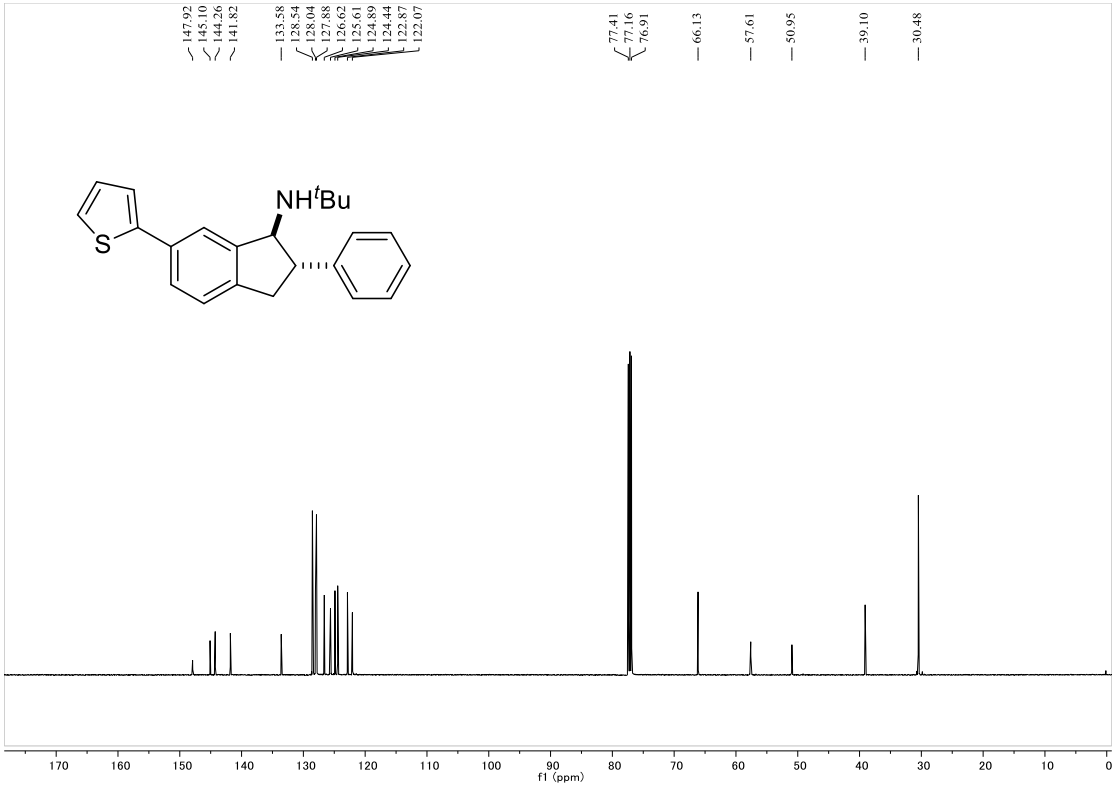
^{13}C NMR spectra of ***trans*-3ra** (126 MHz, $CDCl_3$)



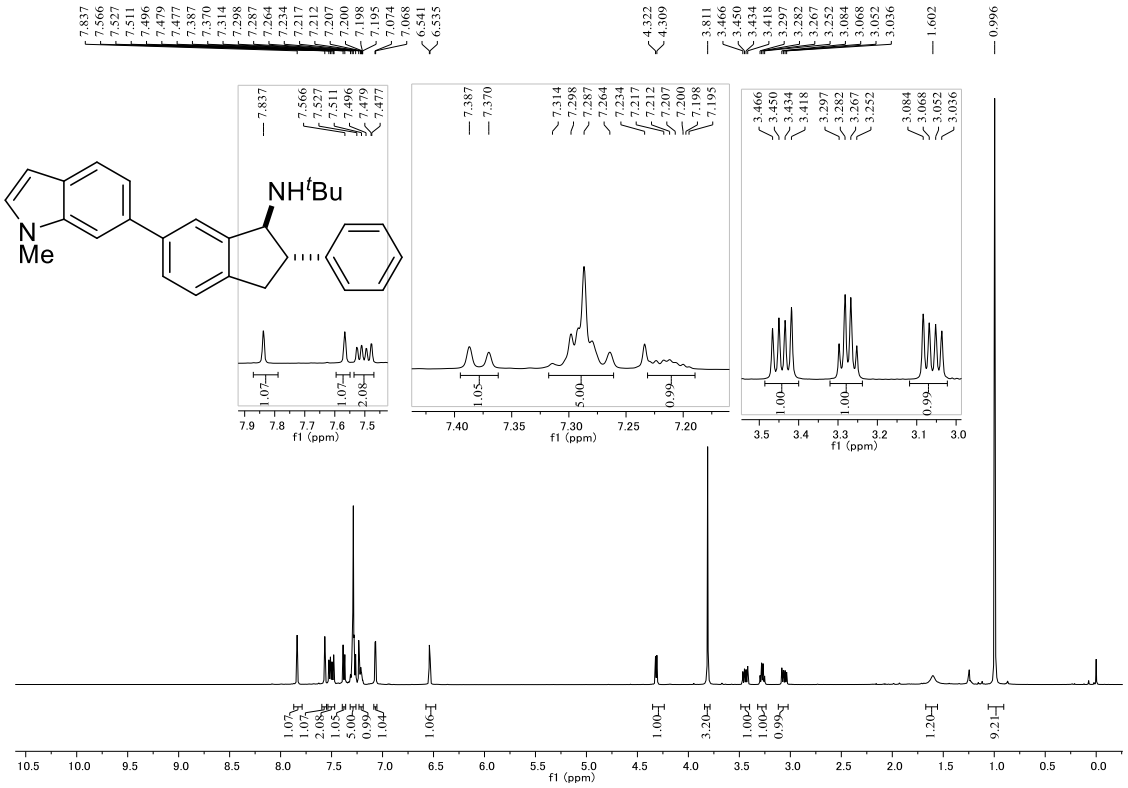
^{1}H NMR spectra of ***trans*-3sa** (500 MHz, $CDCl_3$)



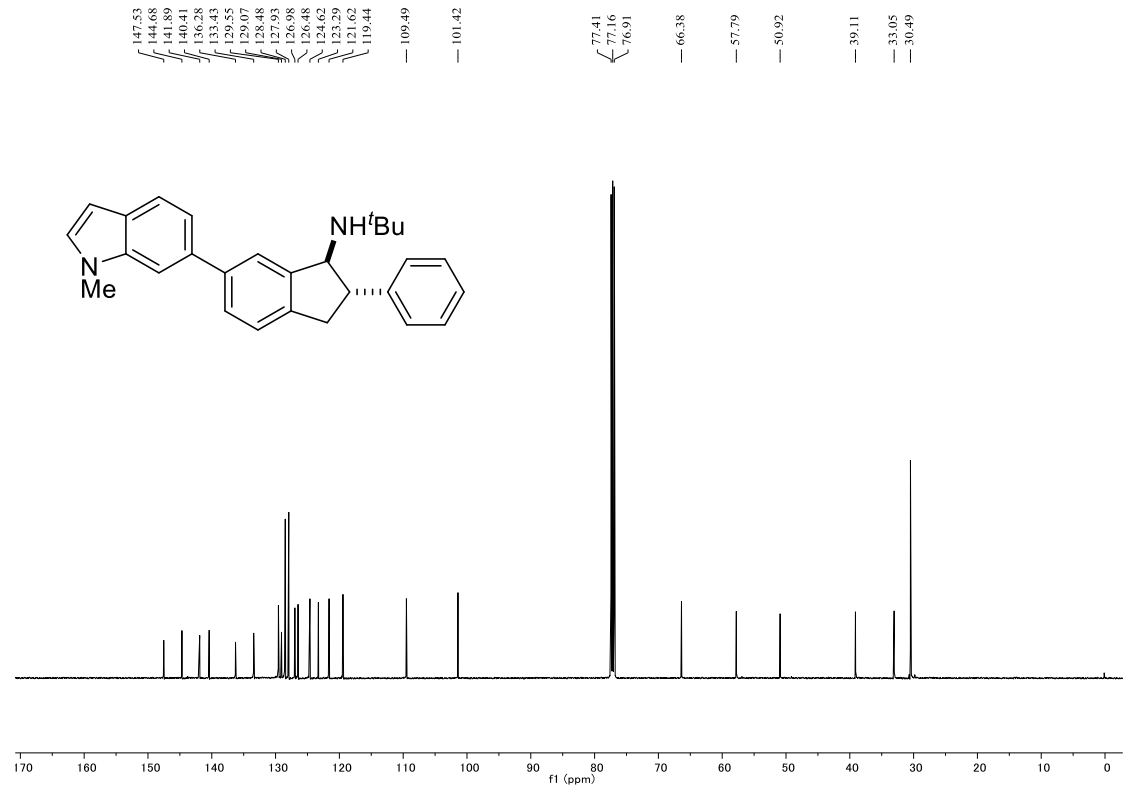
^{13}C NMR spectra of ***trans*-3sa** (126 MHz, $CDCl_3$)



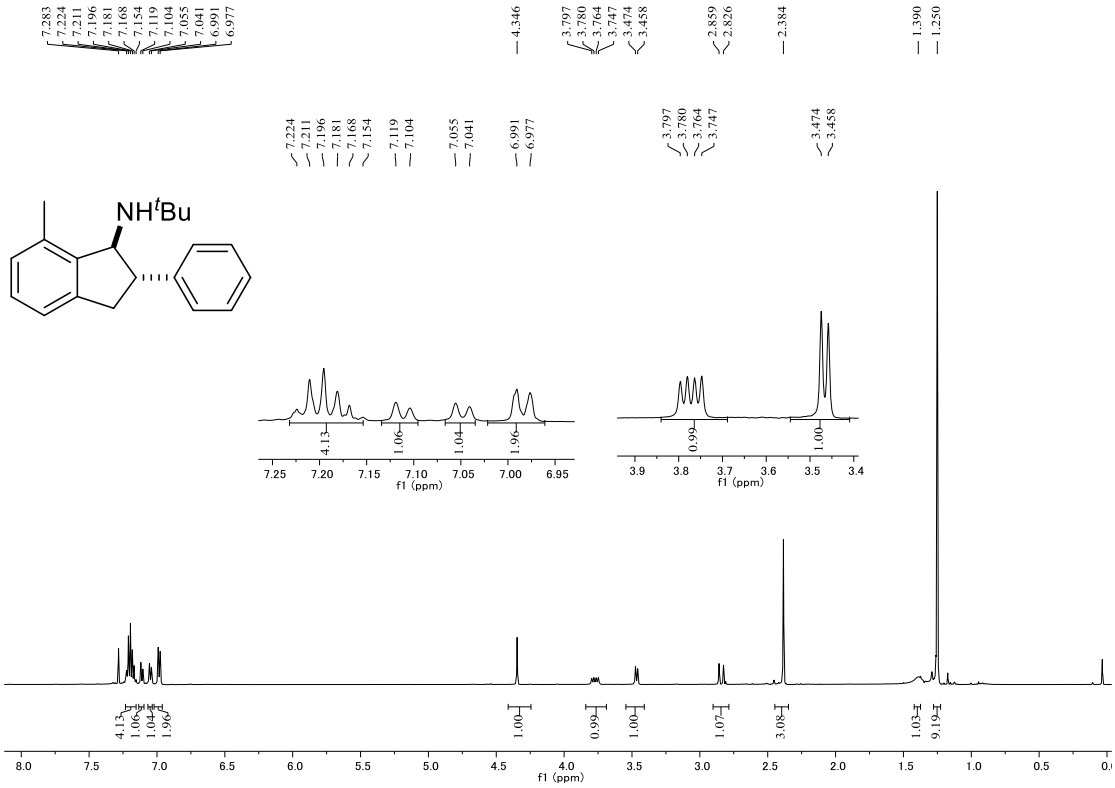
^{1}H NMR spectra of ***trans*-3ta** (500 MHz, $CDCl_3$)



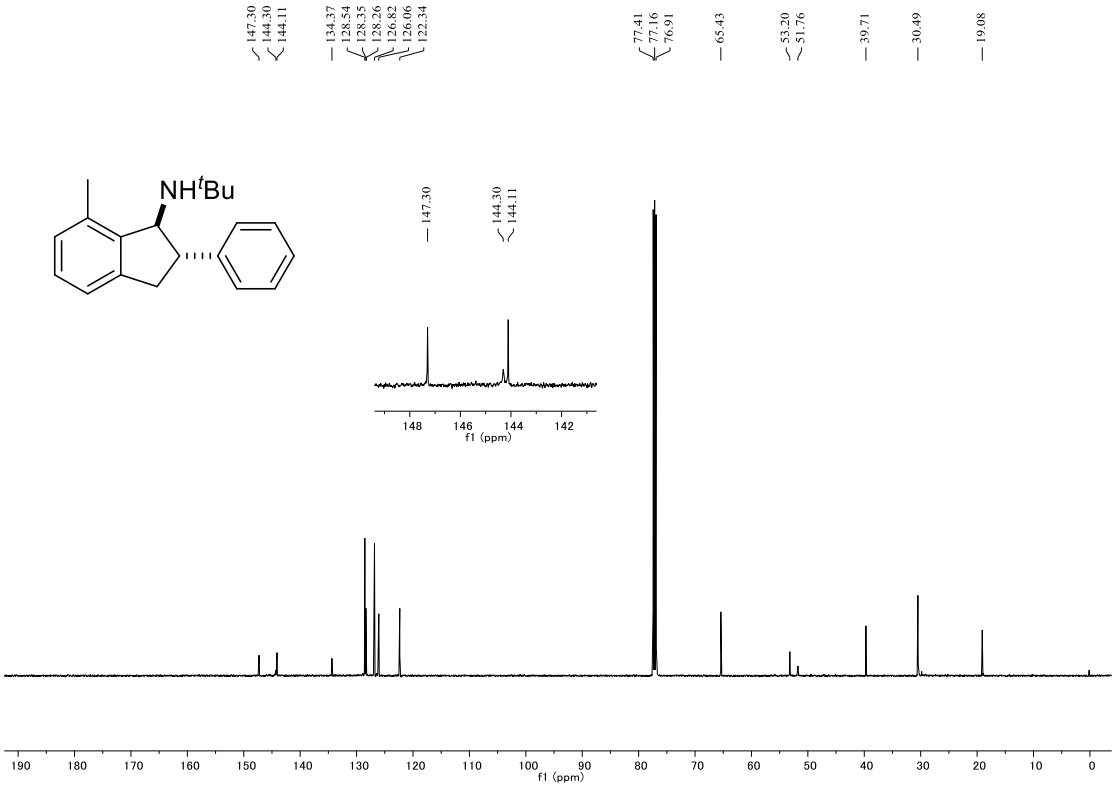
^{13}C NMR spectra of ***trans*-3ta** (126 MHz, $CDCl_3$)



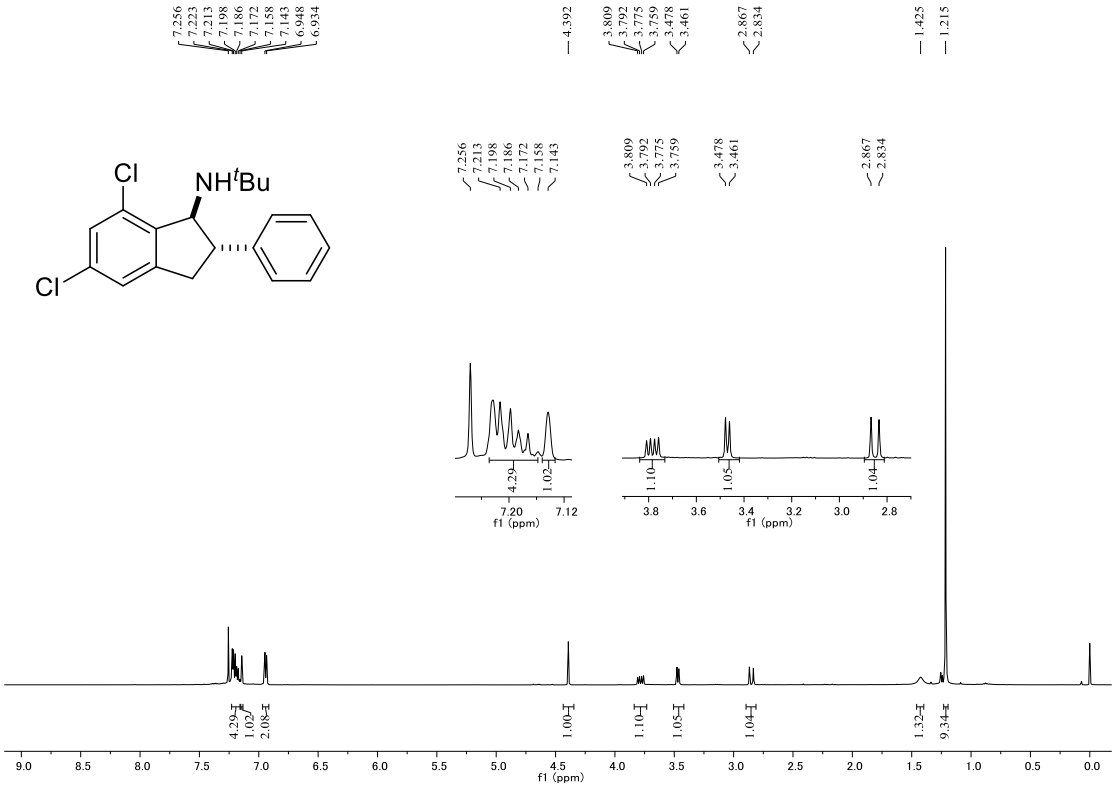
^{1}H NMR spectra of ***trans*-3ua** (500 MHz, $CDCl_3$)



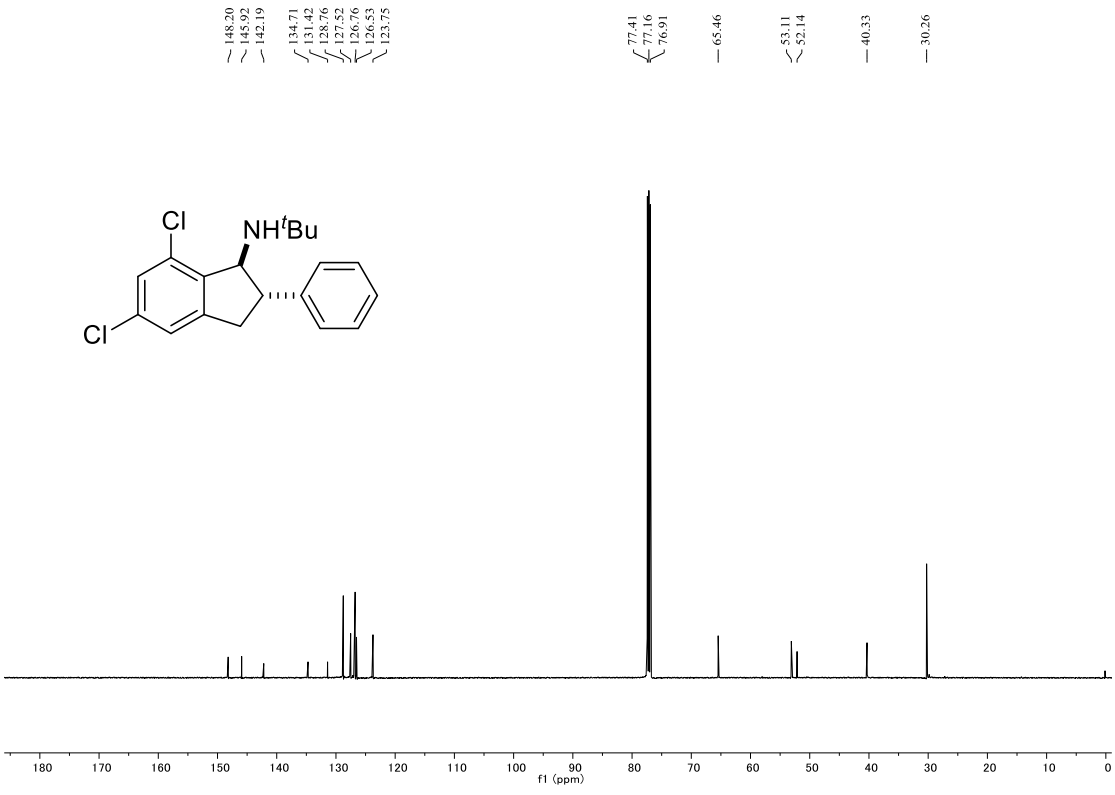
^{13}C NMR spectra of ***trans*-3ua** (126 MHz, $CDCl_3$)



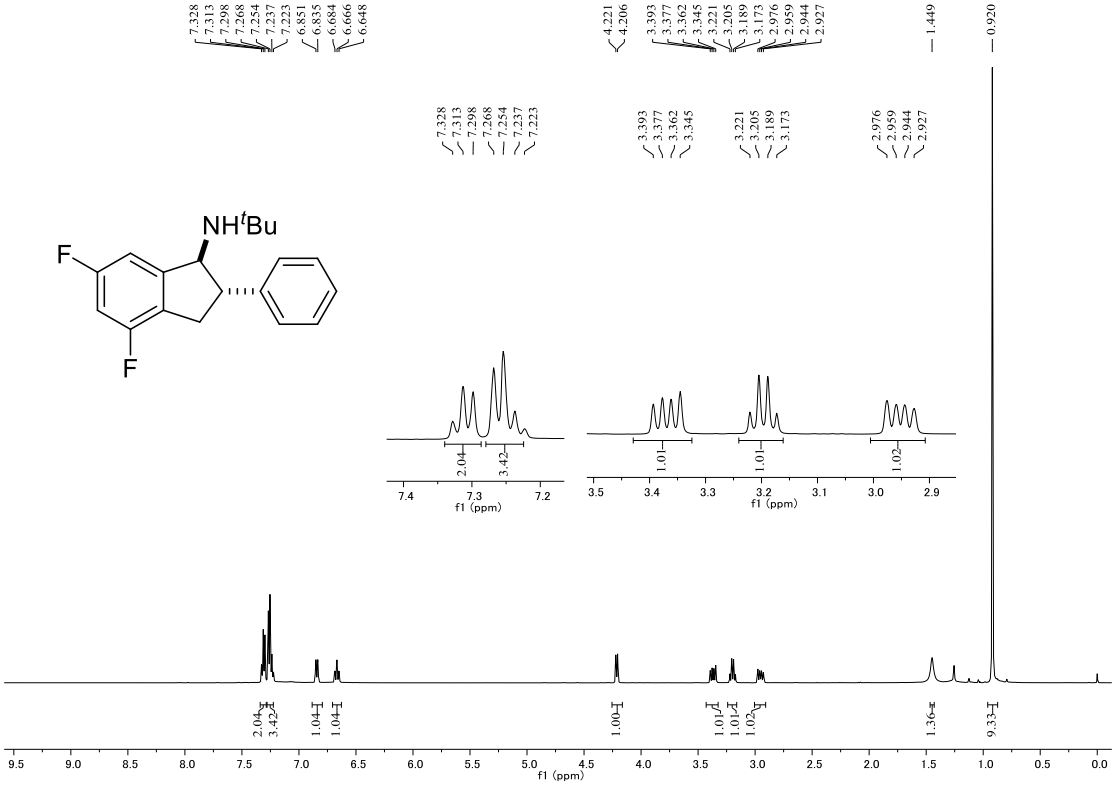
^{1}H NMR spectra of ***trans*-3va** (500 MHz, $CDCl_3$)



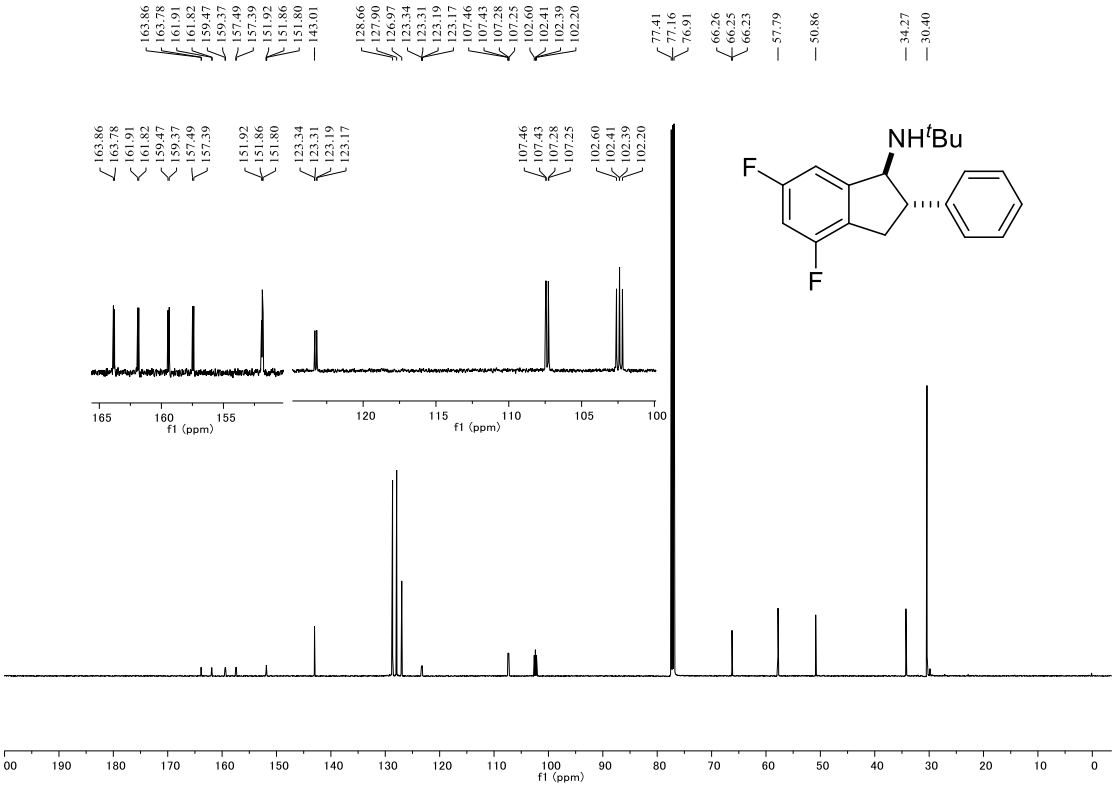
^{13}C NMR spectra of ***trans*-3va** (126 MHz, $CDCl_3$)



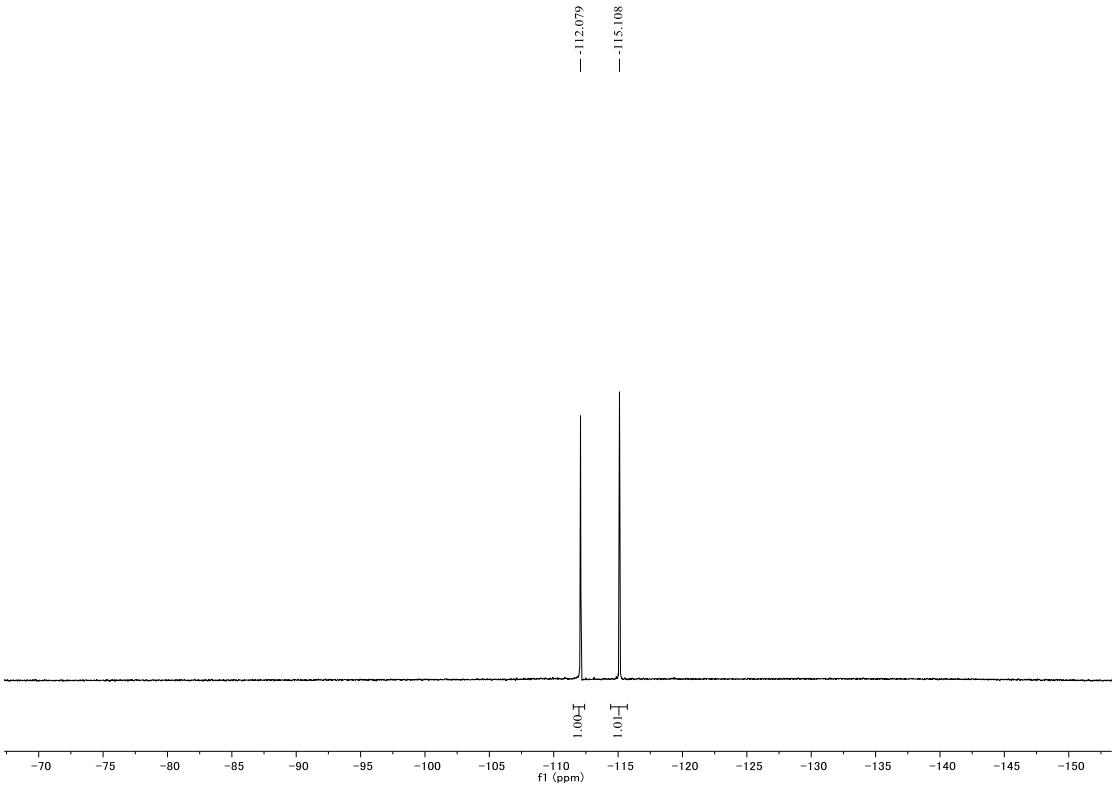
^{1}H NMR spectra of ***trans*-3wa** (500 MHz, $CDCl_3$)



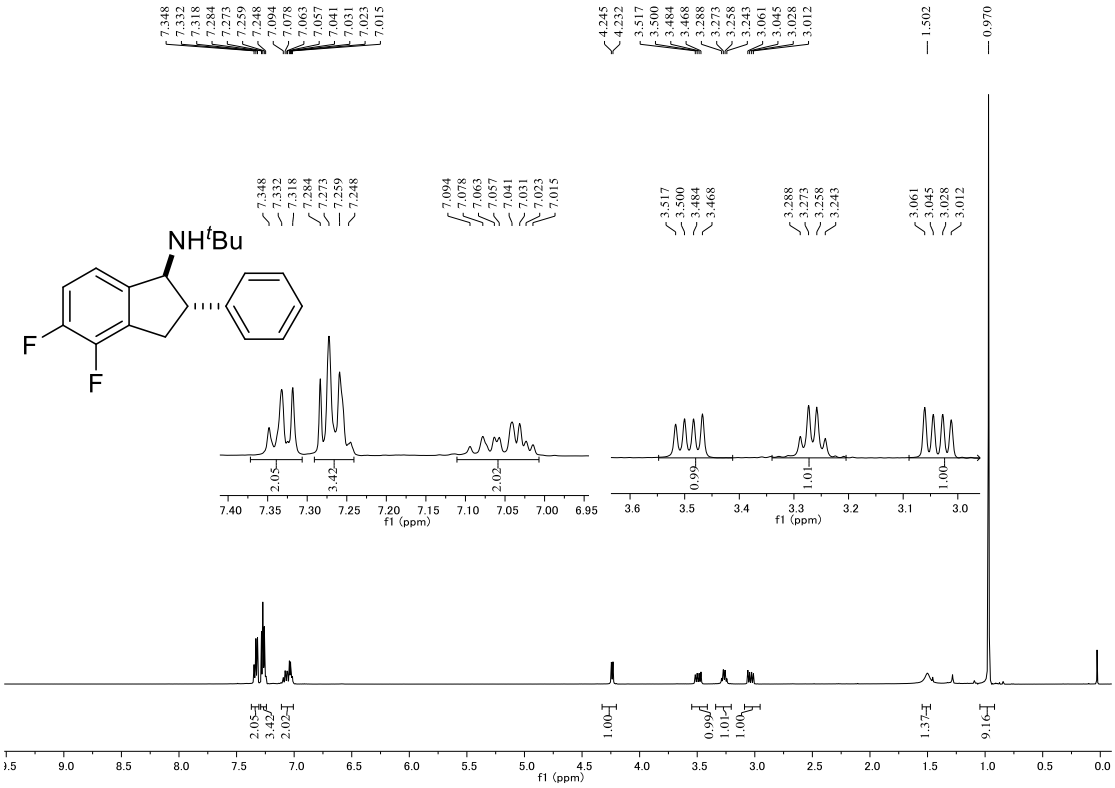
^{13}C NMR spectra of ***trans*-3wa** (126 MHz, $CDCl_3$)



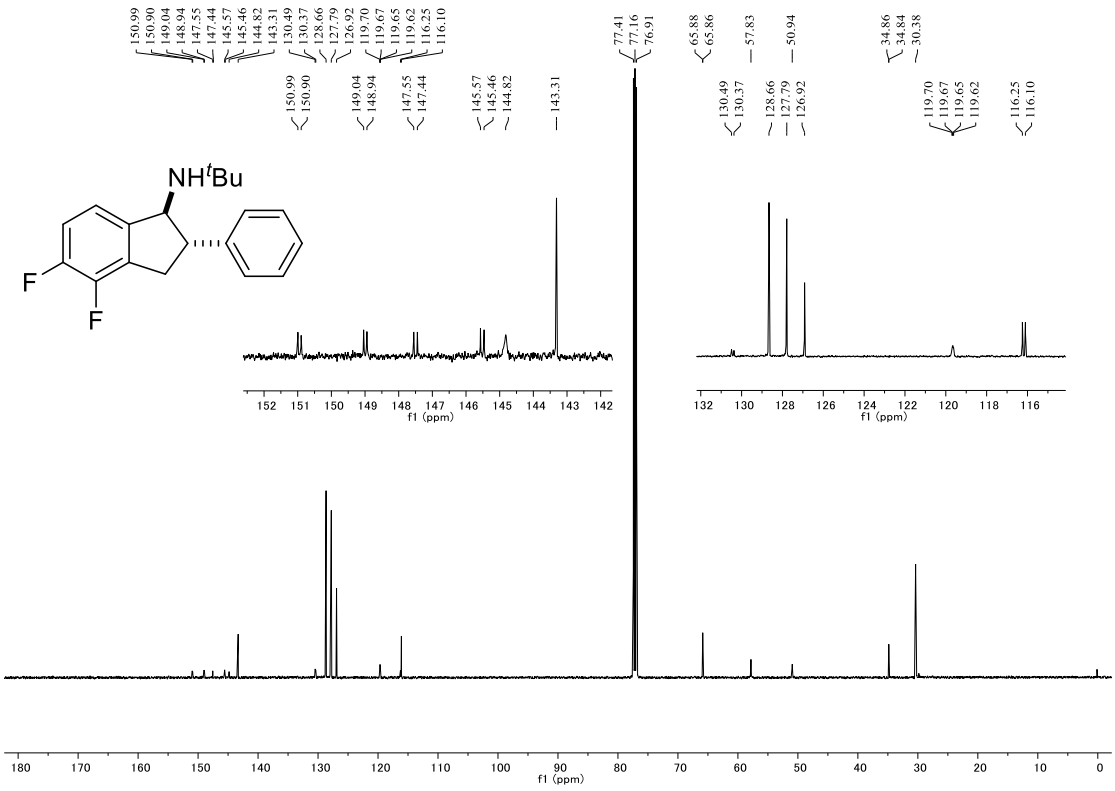
^{19}F NMR spectra of ***trans*-3wa** (377 MHz, $CDCl_3$)



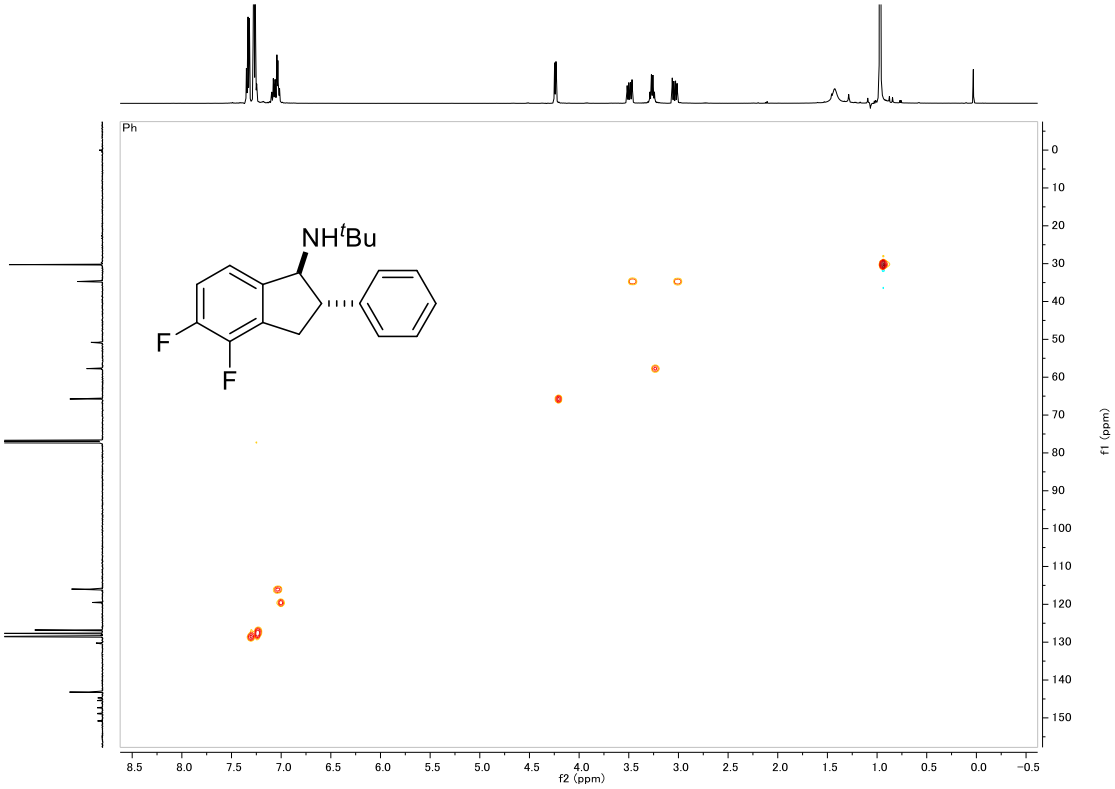
^{1}H NMR spectra of ***trans*-3xa** (500 MHz, $CDCl_3$)



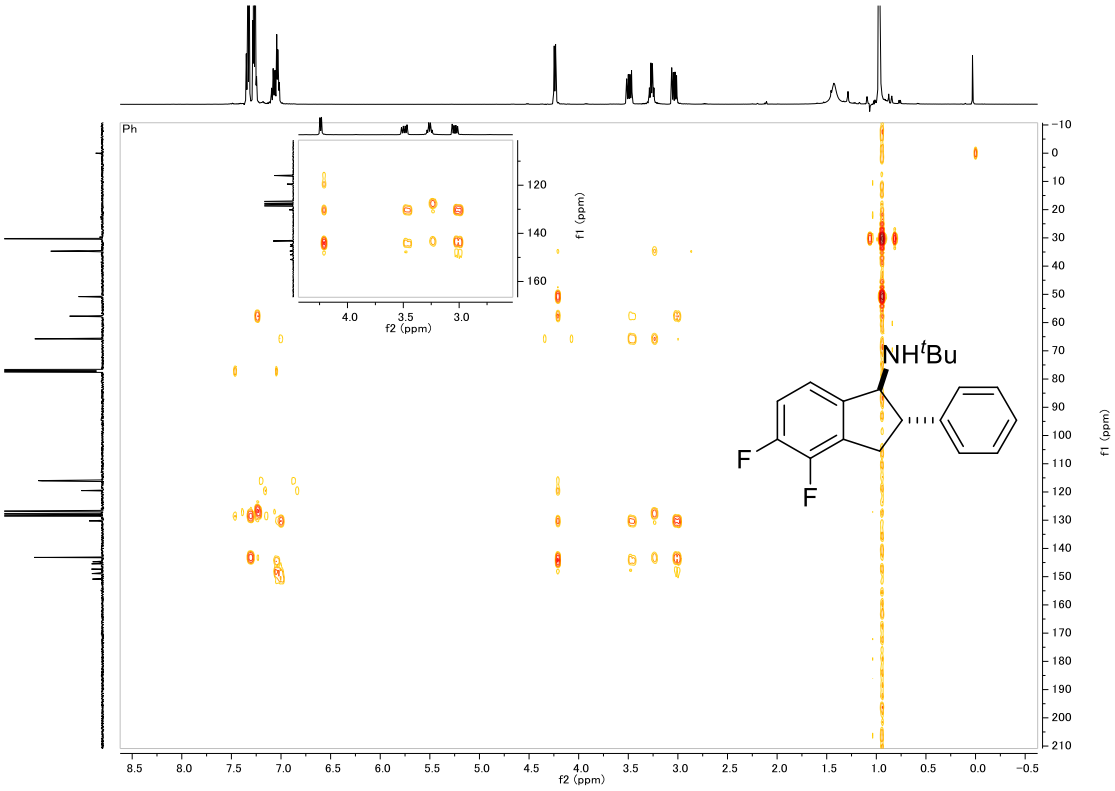
^{13}C NMR spectra of ***trans*-3xa** (126 MHz, $CDCl_3$)



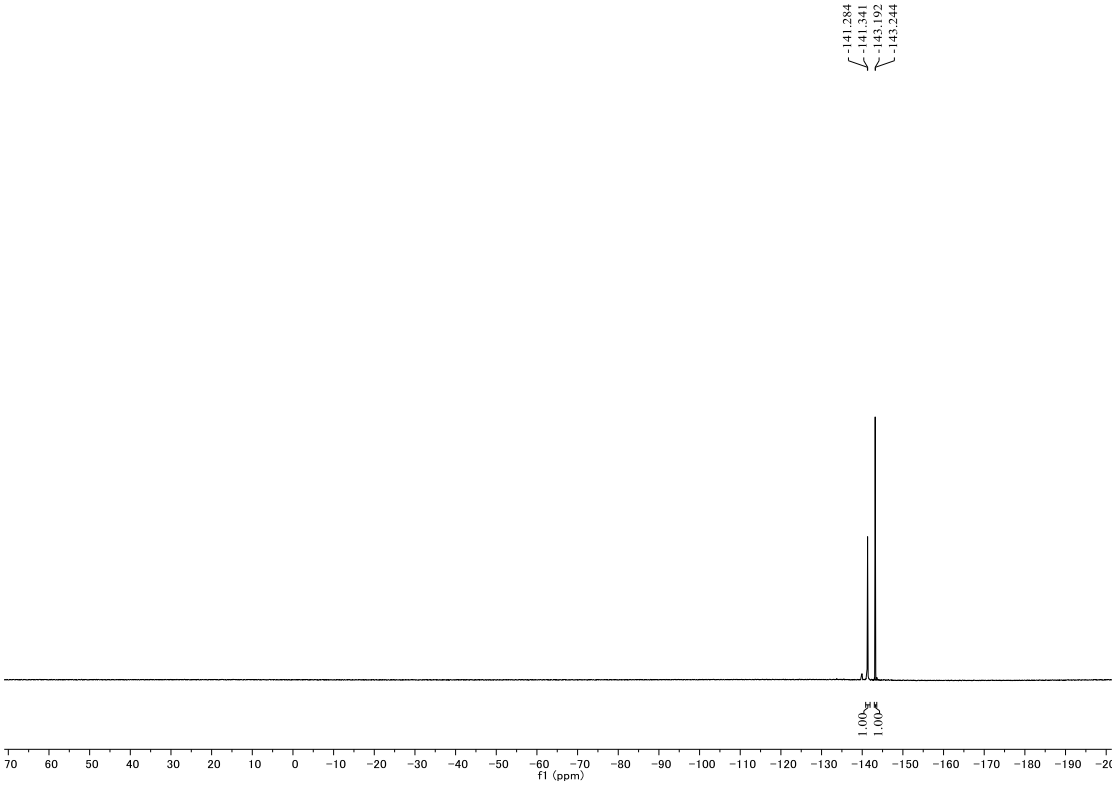
HSQC spectra of ***trans*-3xa** ($CDCl_3$)



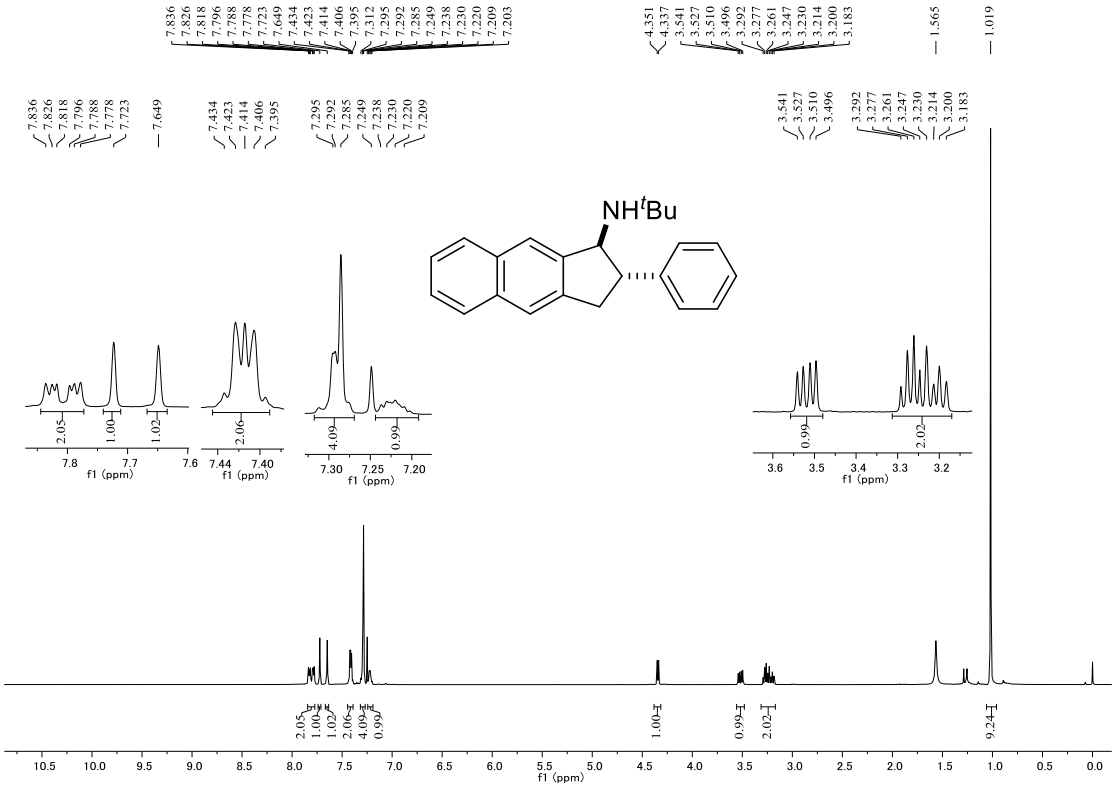
HMBC spectra of ***trans*-3xa** ($CDCl_3$)



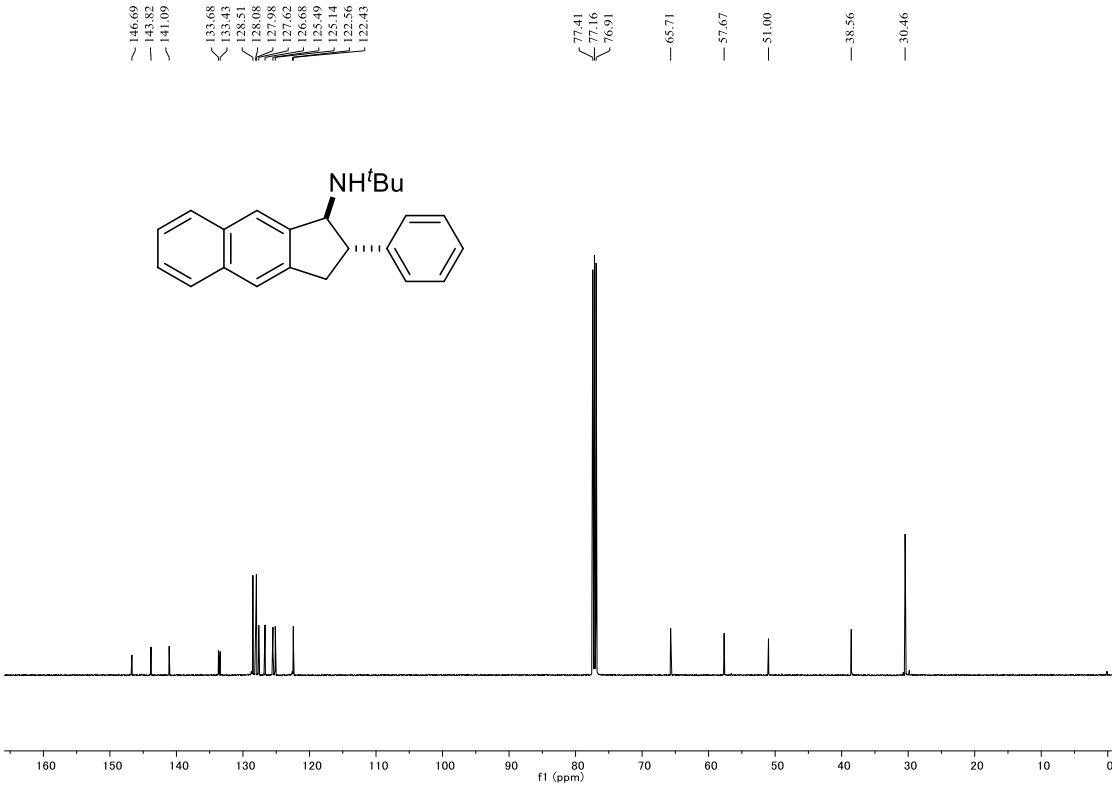
^{19}F NMR spectra of ***trans*-3xa** (377 MHz, $CDCl_3$)



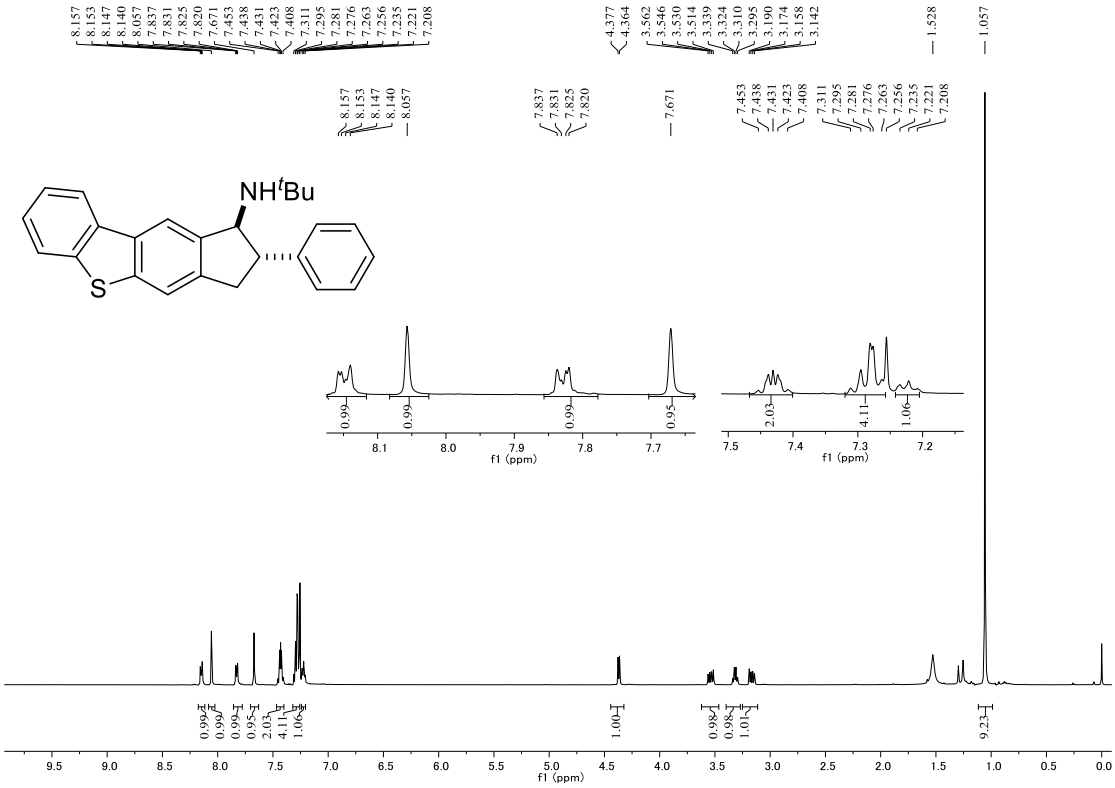
^{1}H NMR spectra of ***trans*-3ya** (500 MHz, $CDCl_3$)



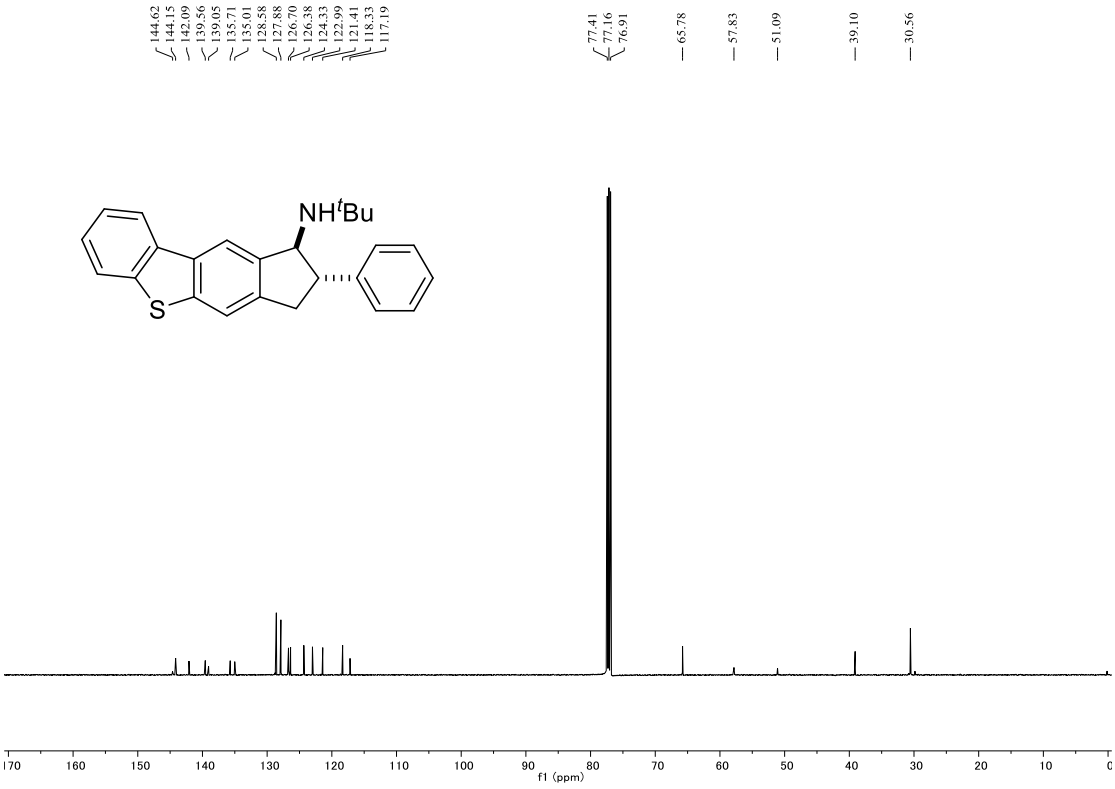
^{13}C NMR spectra of ***trans*-3ya** (126 MHz, $CDCl_3$)



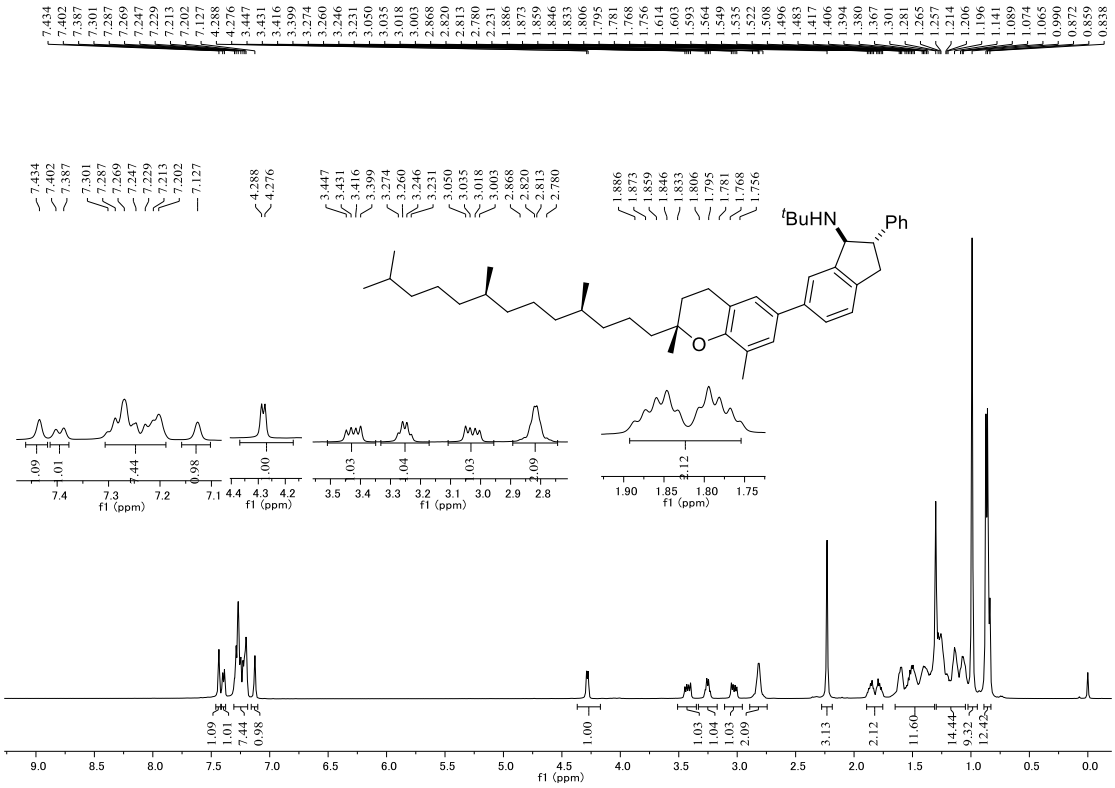
^{1}H NMR spectra of ***trans*-3za** (500 MHz, $CDCl_3$)



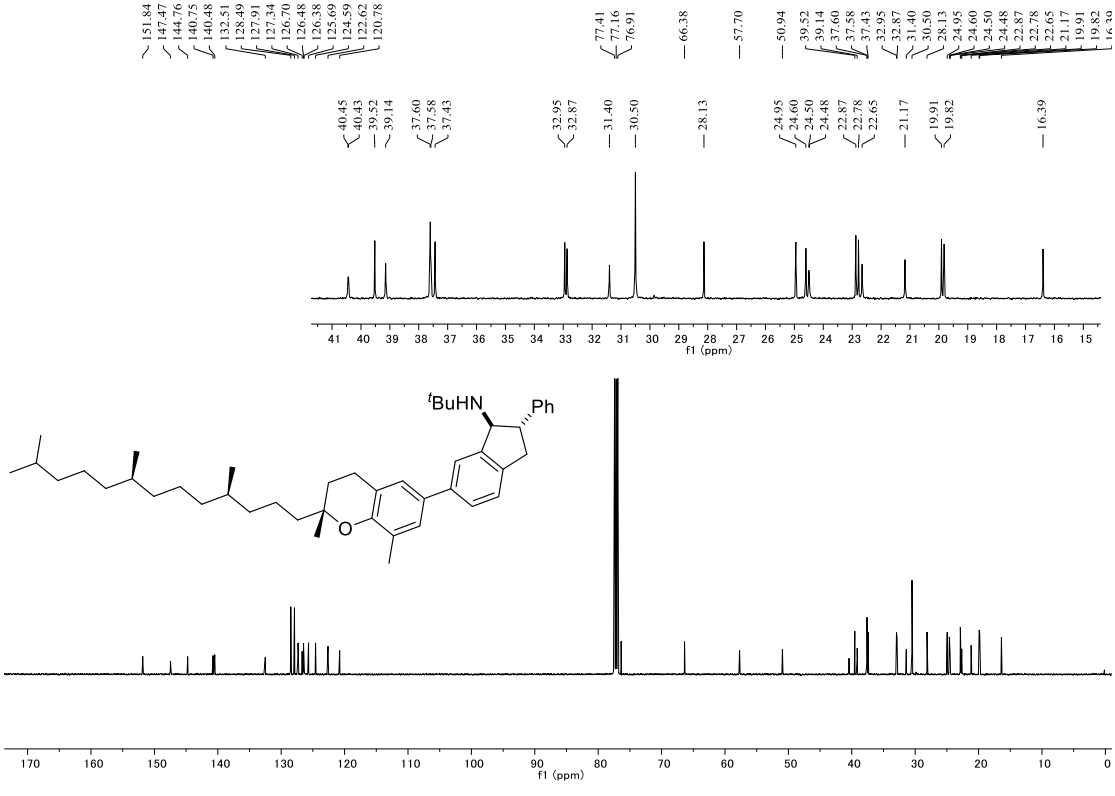
^{13}C NMR spectra of ***trans*-3za** (126 MHz, $CDCl_3$)



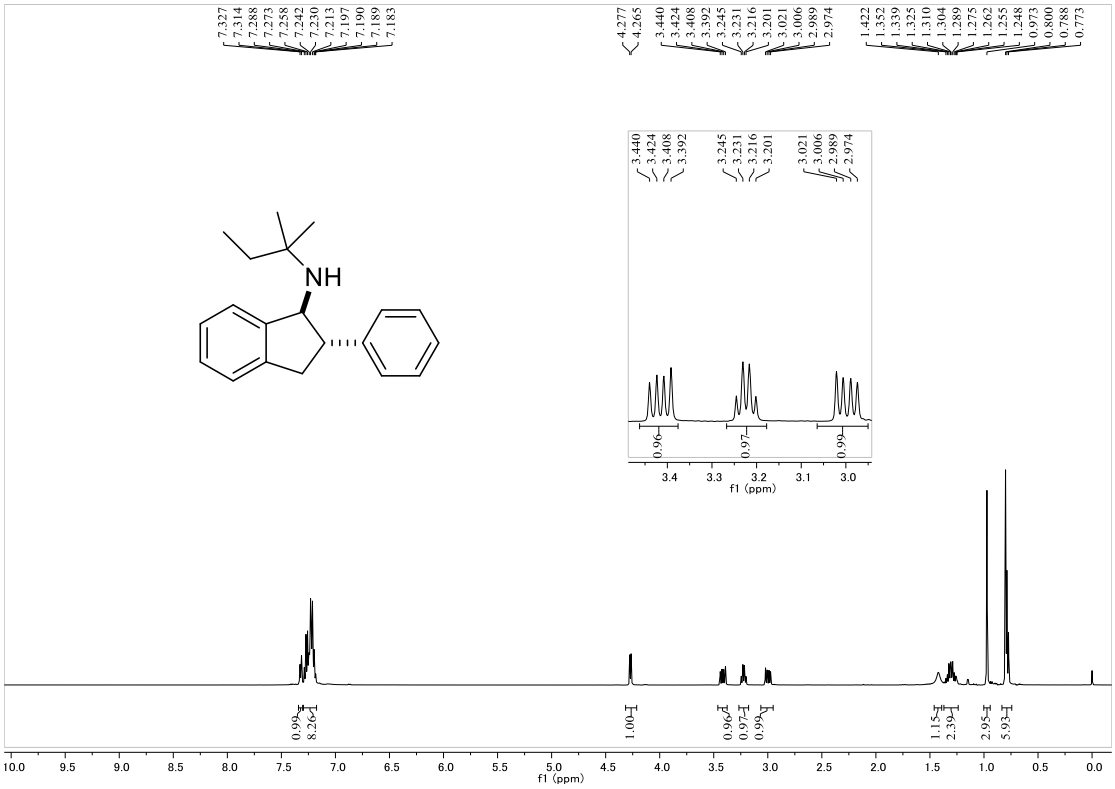
^{1}H NMR spectra of ***trans*-3aaa** (500 MHz, $CDCl_3$)



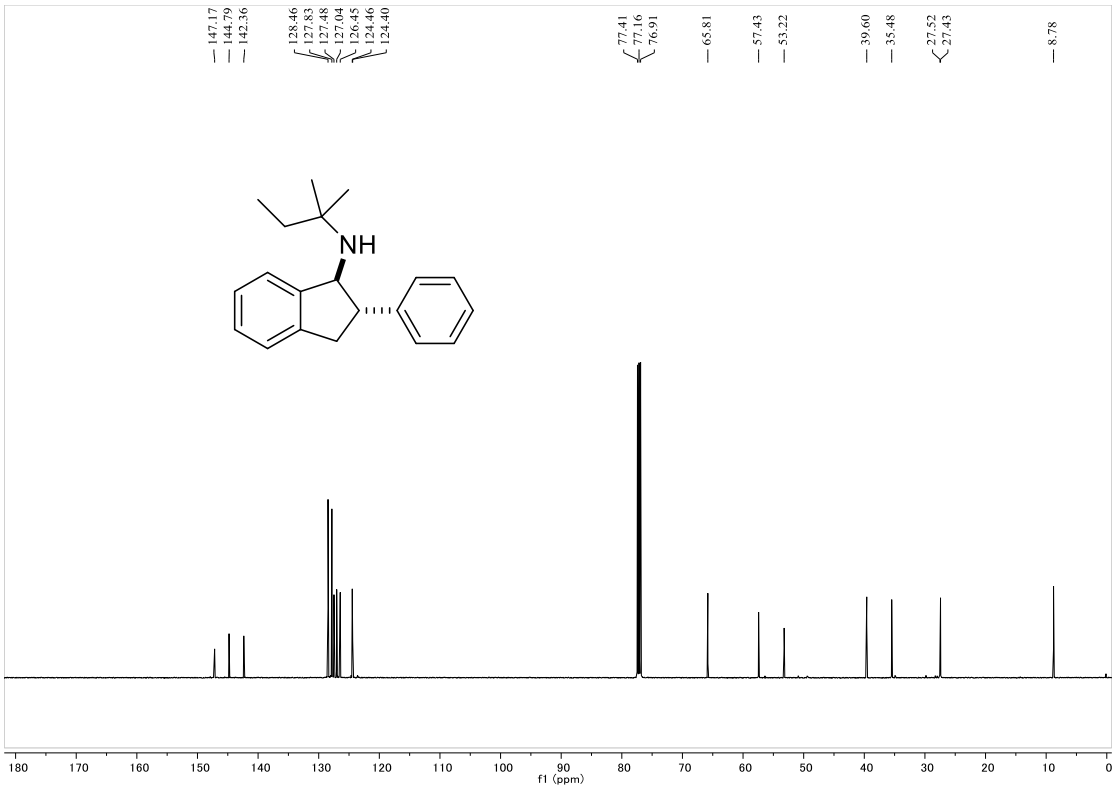
^{13}C NMR spectra of ***trans*-3aaa** (126 MHz, $CDCl_3$)



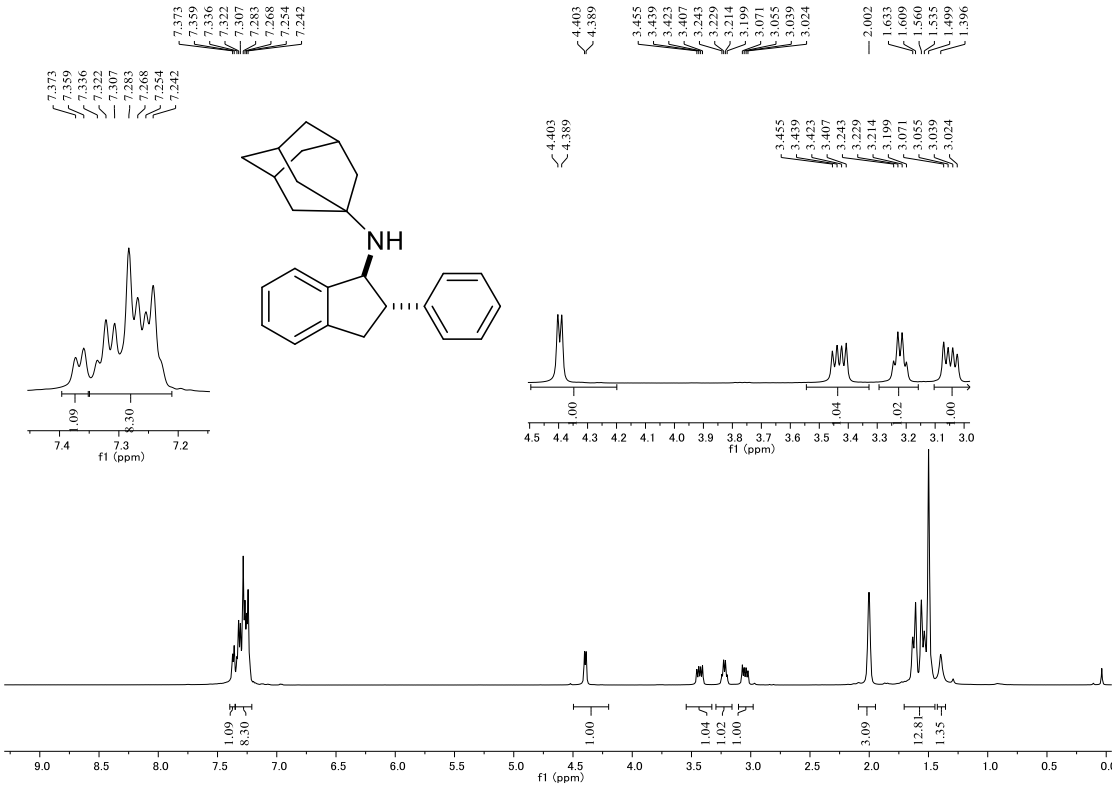
^{1}H NMR spectra of ***trans*-3aba** (500 MHz, $CDCl_3$)



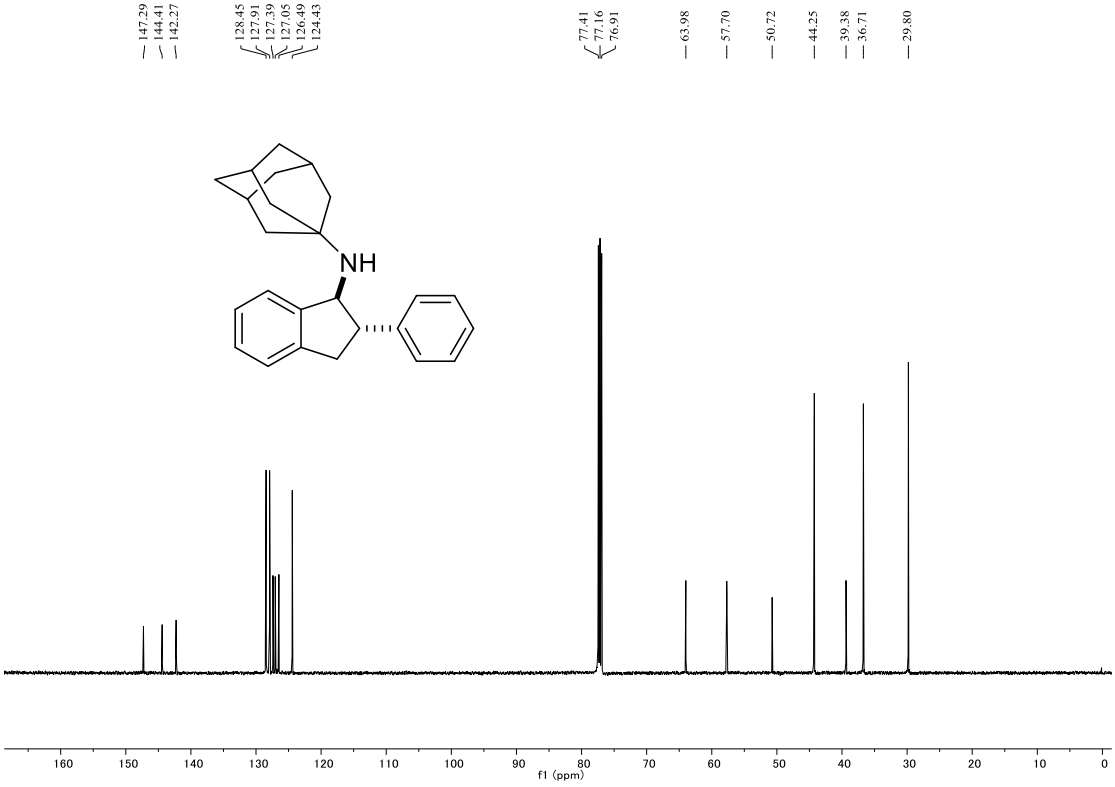
^{13}C NMR spectra of ***trans*-3aba** (126 MHz, $CDCl_3$)



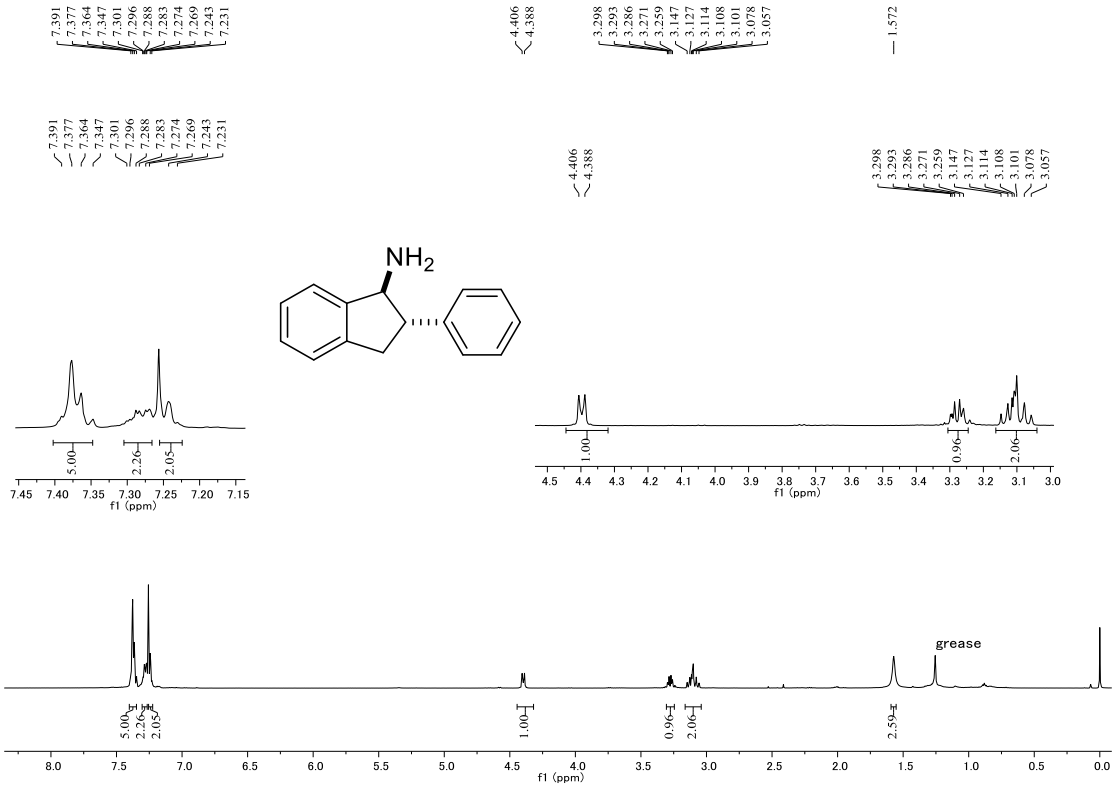
^{1}H NMR spectra of ***trans*-3aca** (500 MHz, $CDCl_3$)



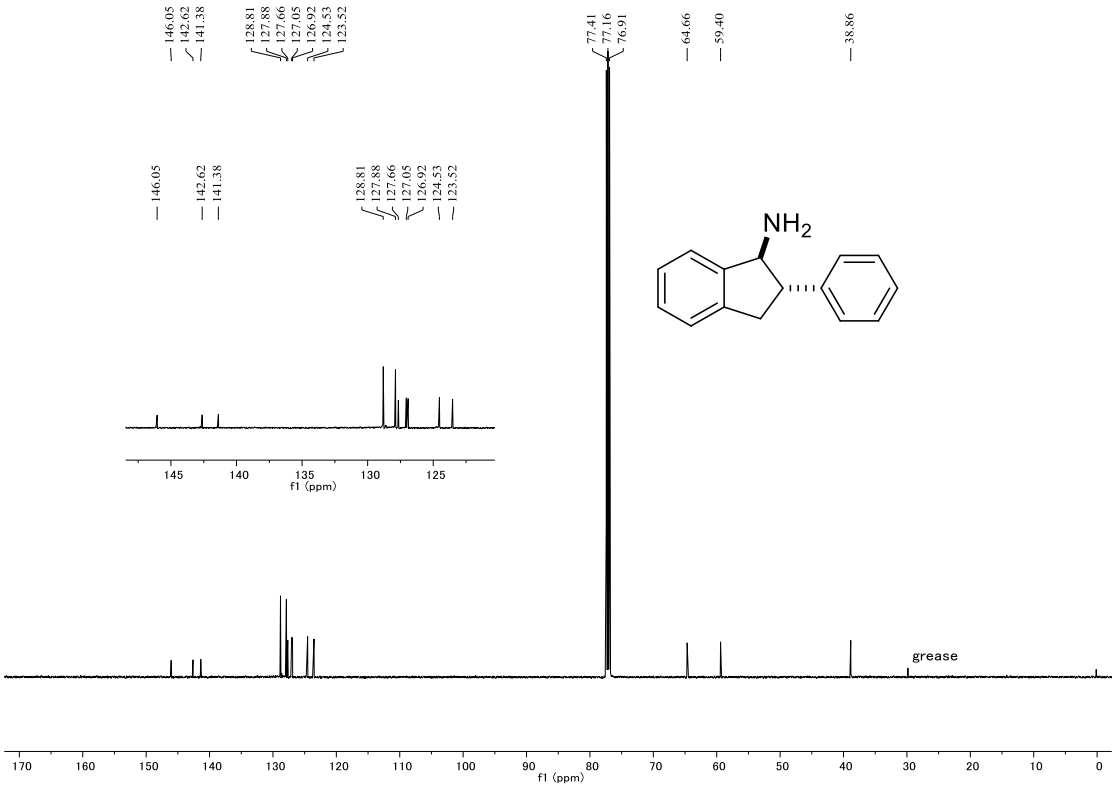
^{13}C NMR spectra of ***trans*-3aca** (126 MHz, $CDCl_3$)



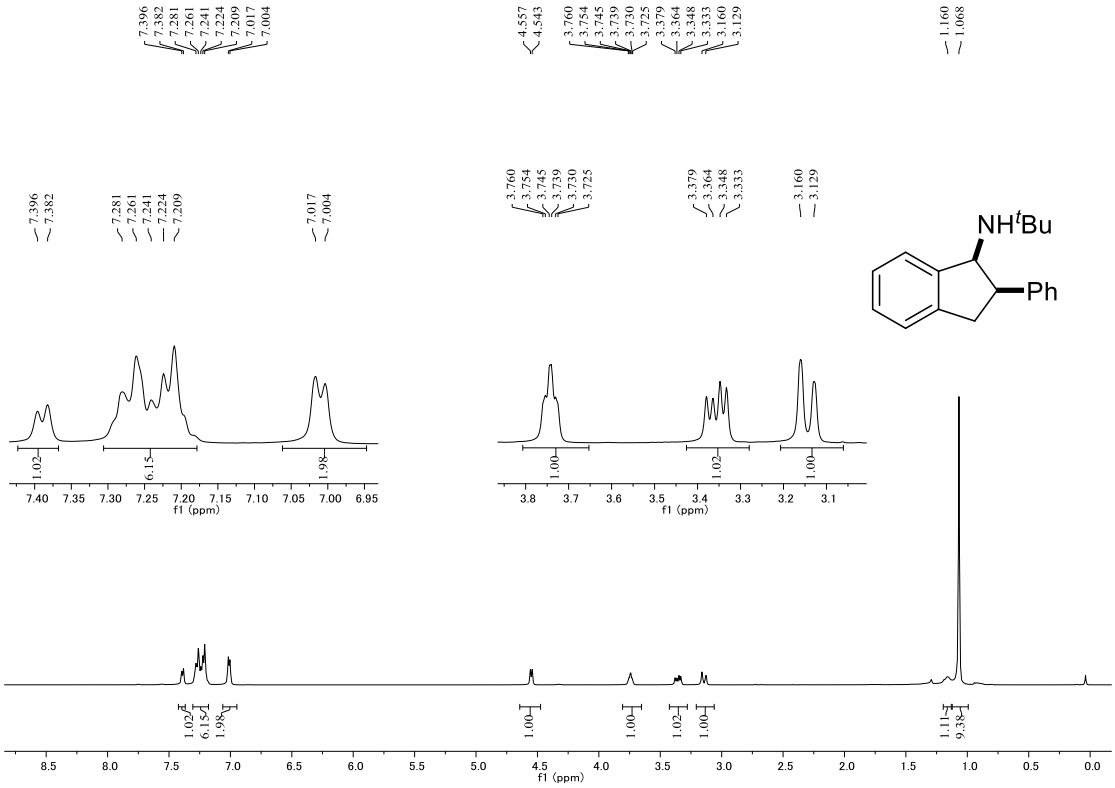
^{1}H NMR spectra of ***trans*-4aa** (500 MHz, $CDCl_3$)



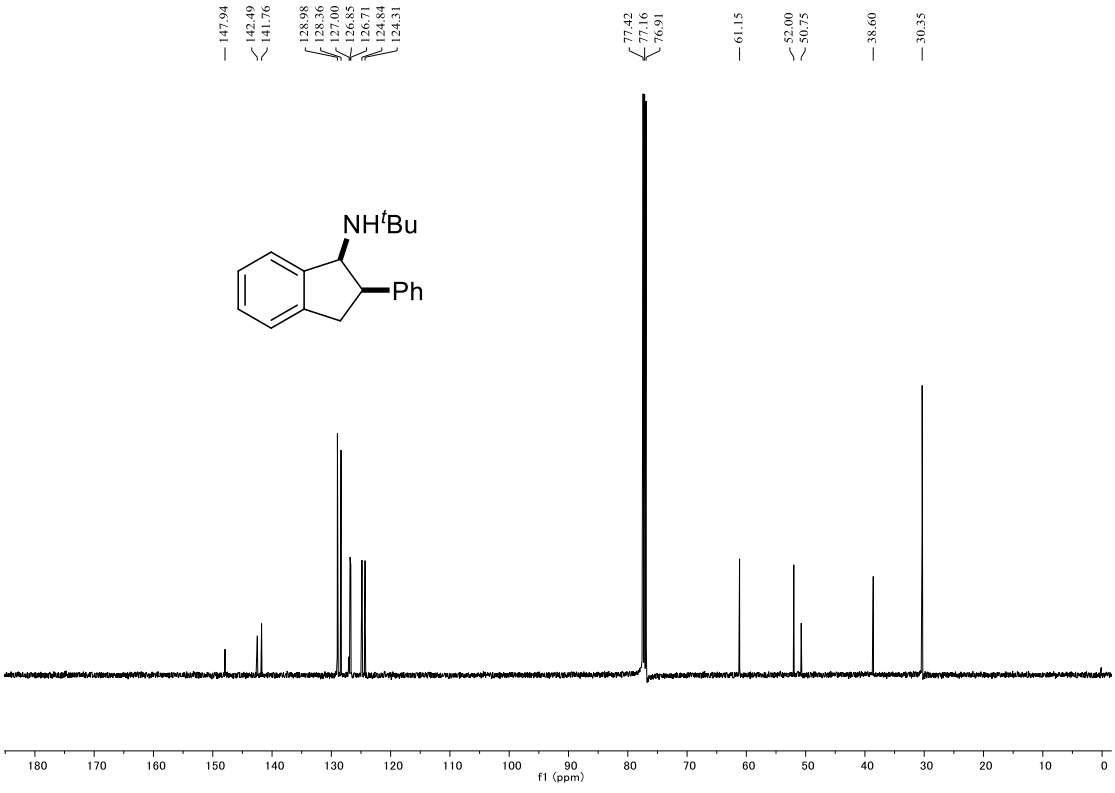
^{13}C NMR spectra of ***trans*-4aa** (126 MHz, $CDCl_3$)



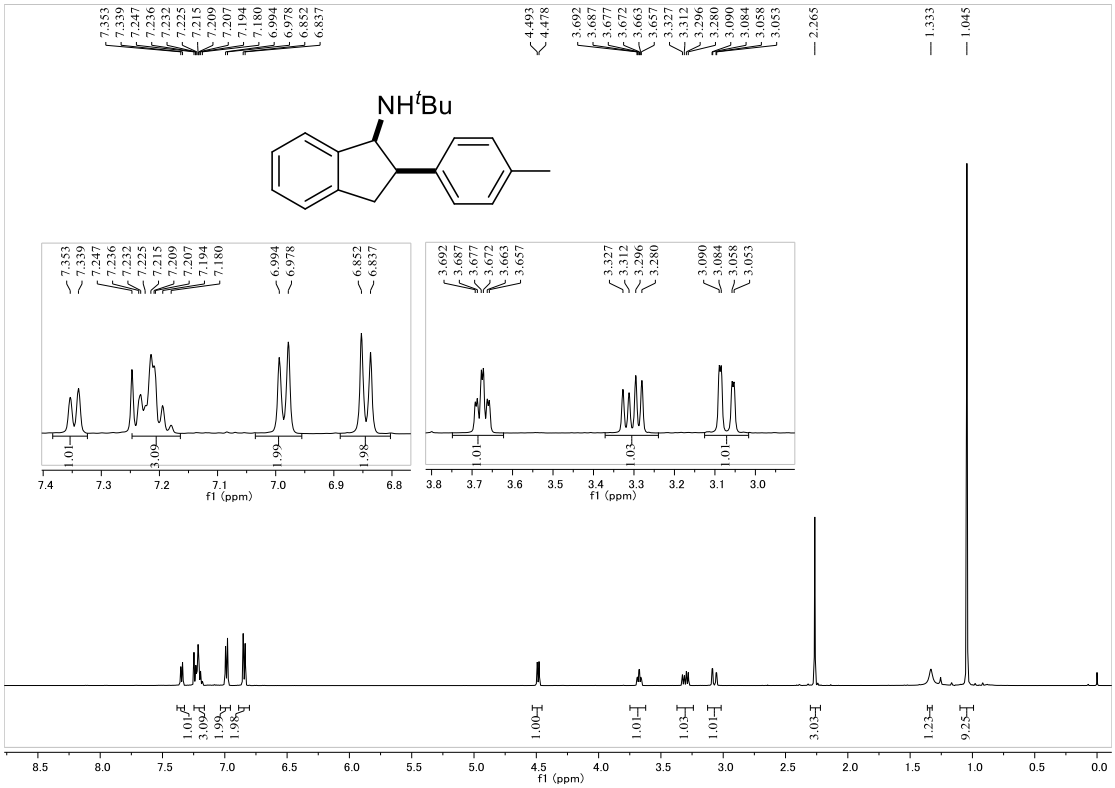
^{1}H NMR spectra of ***cis*-3aa** (500 MHz, $CDCl_3$)



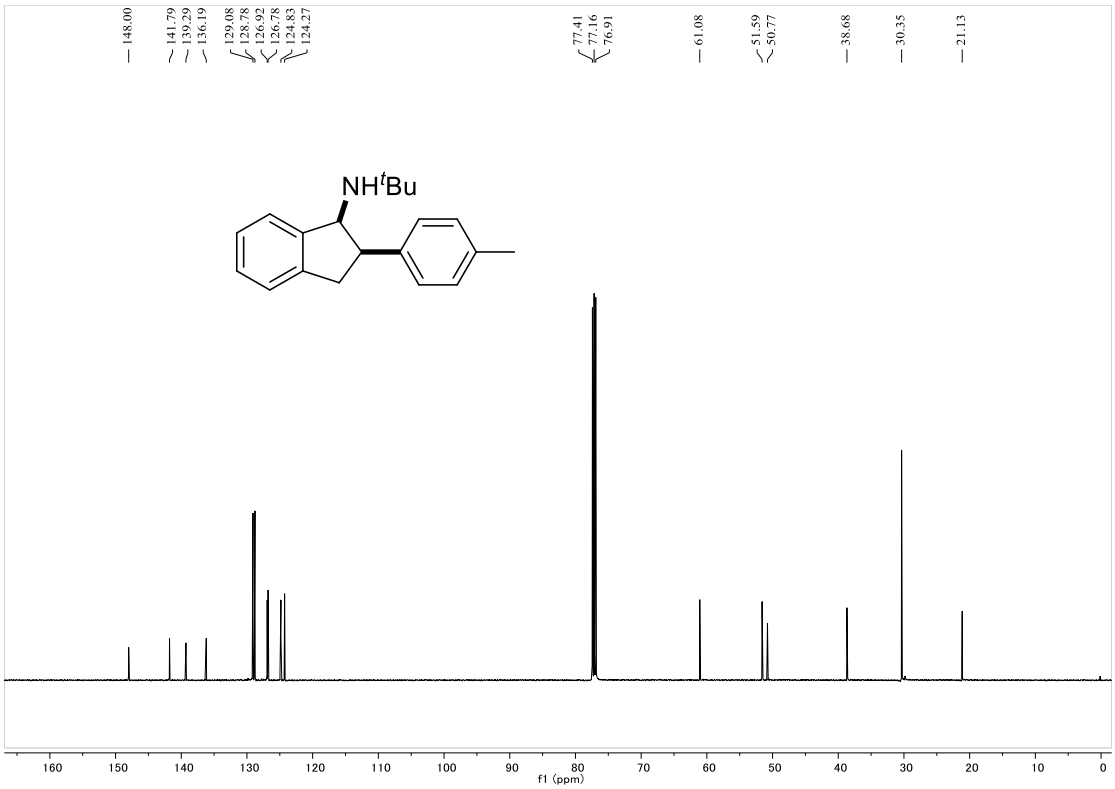
^{13}C NMR spectra of ***cis*-3aa** (126 MHz, $CDCl_3$)



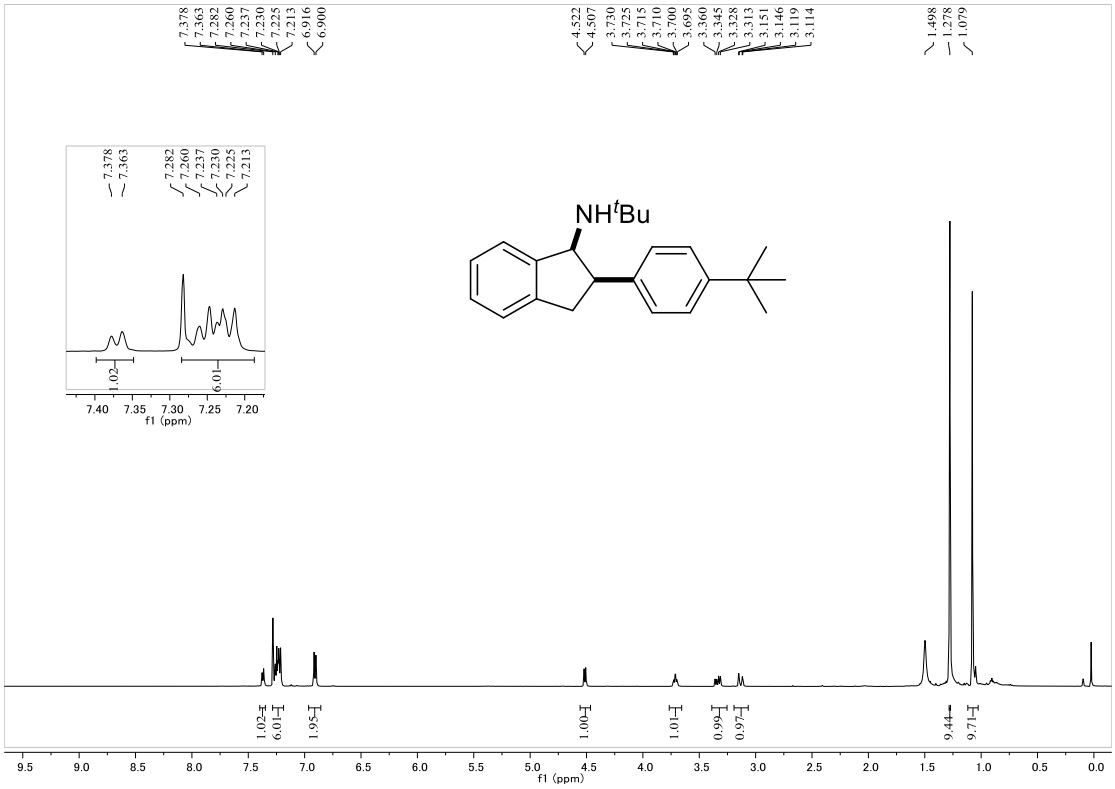
^{1}H NMR spectra of ***cis*-3ab** (500 MHz, $CDCl_3$)



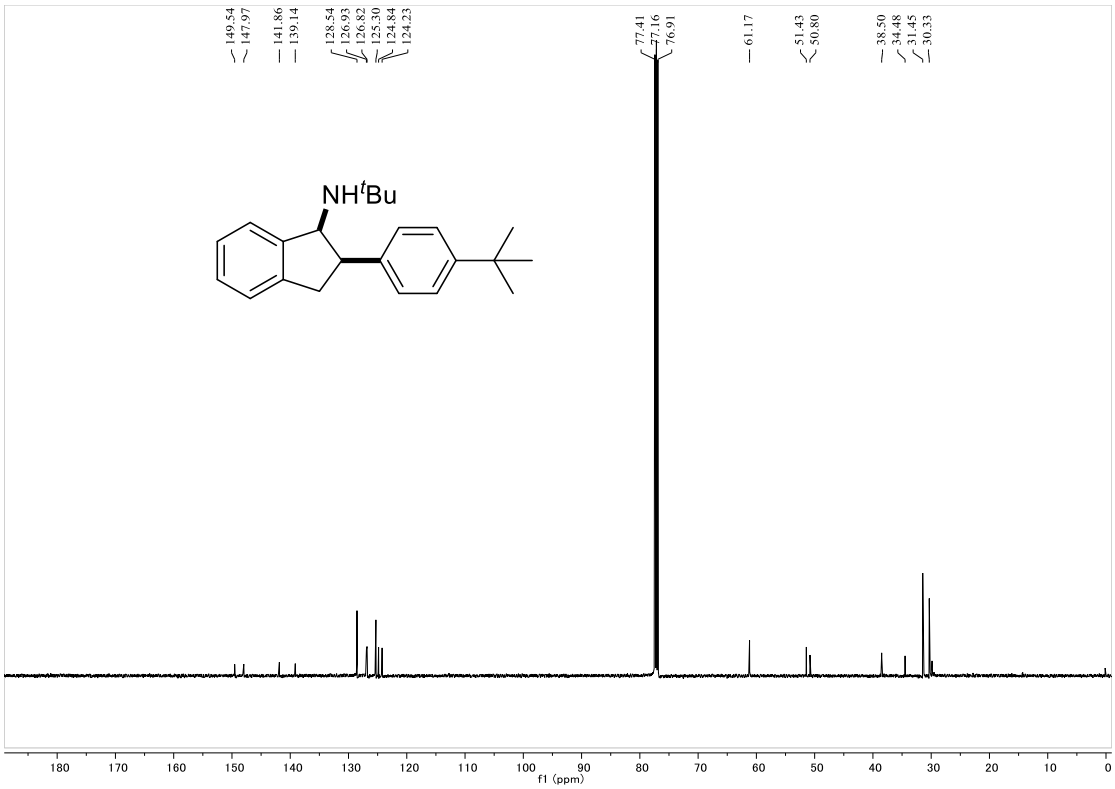
^{13}C NMR spectra of ***cis*-3ab** (126 MHz, $CDCl_3$)



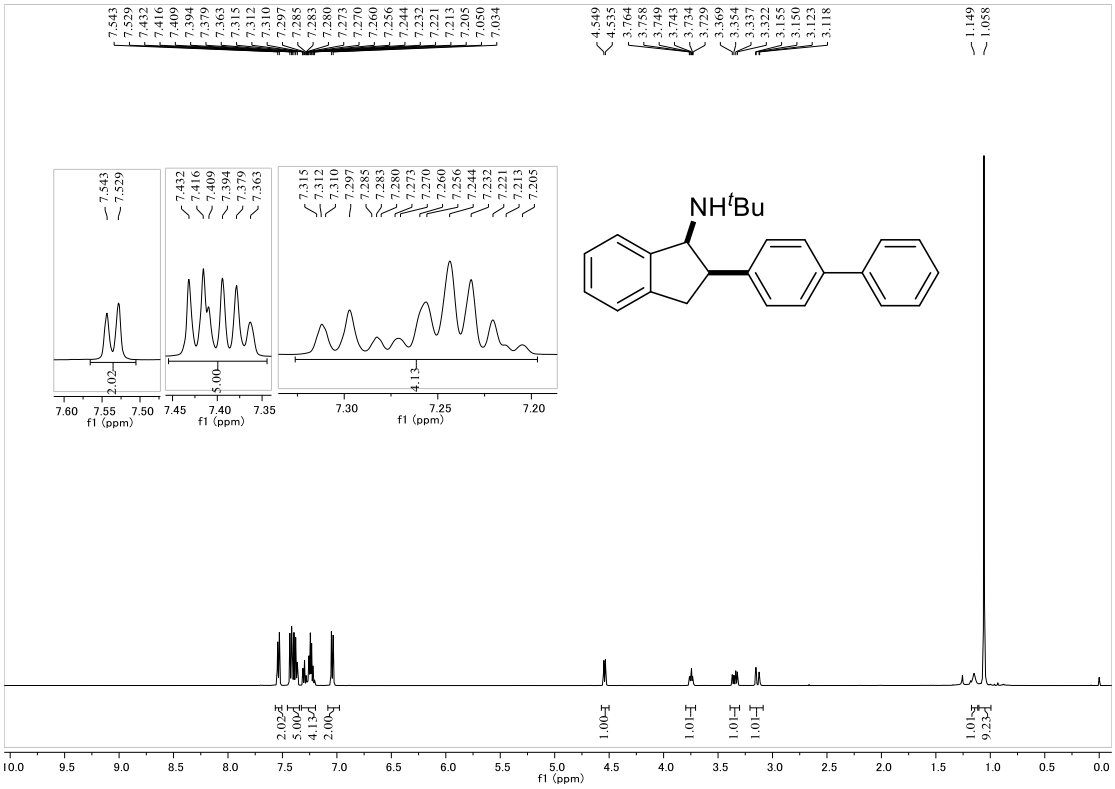
^{1}H NMR spectra of ***cis*-3ac** (500 MHz, $CDCl_3$)



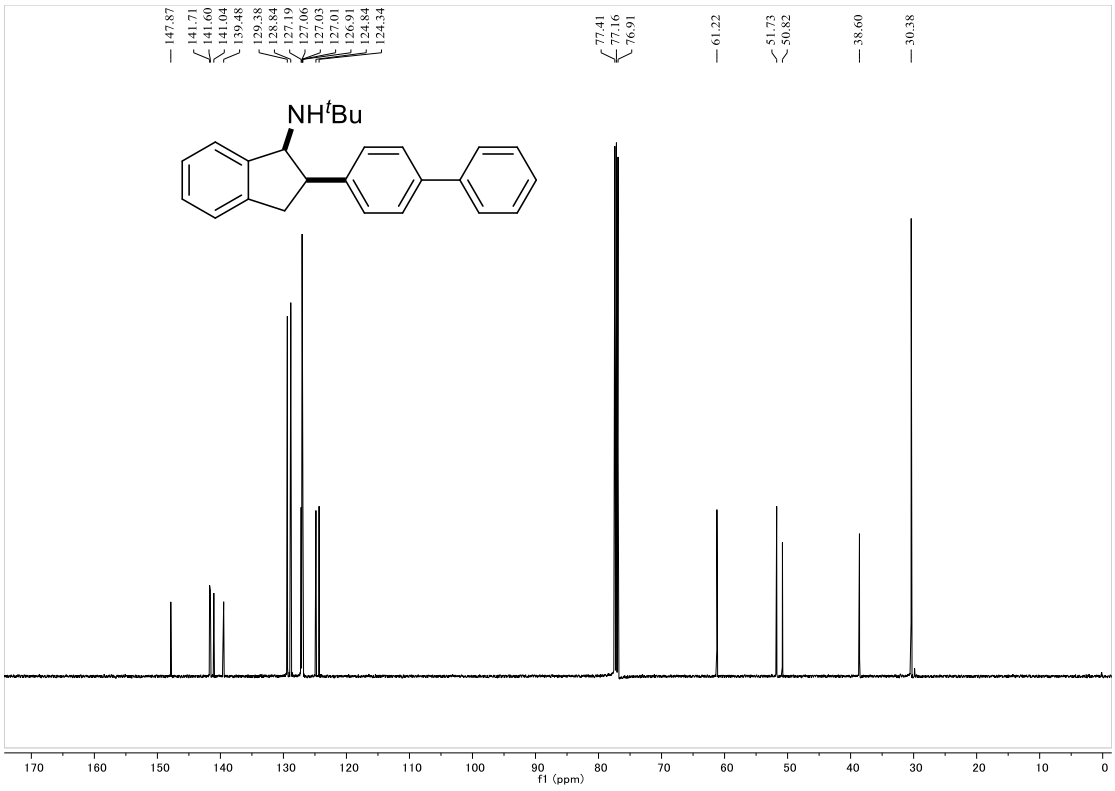
^{13}C NMR spectra of ***cis*-3ac** (126 MHz, $CDCl_3$)



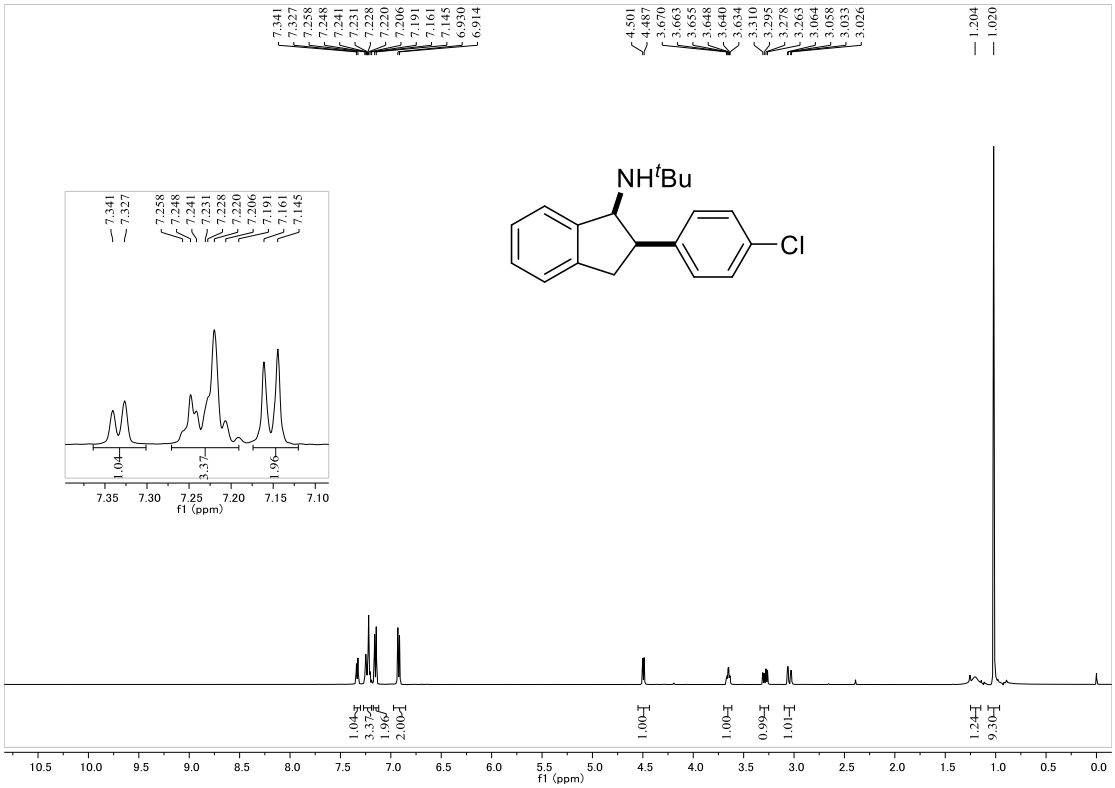
^{1}H NMR spectra of ***cis*-3ad** (500 MHz, $CDCl_3$)



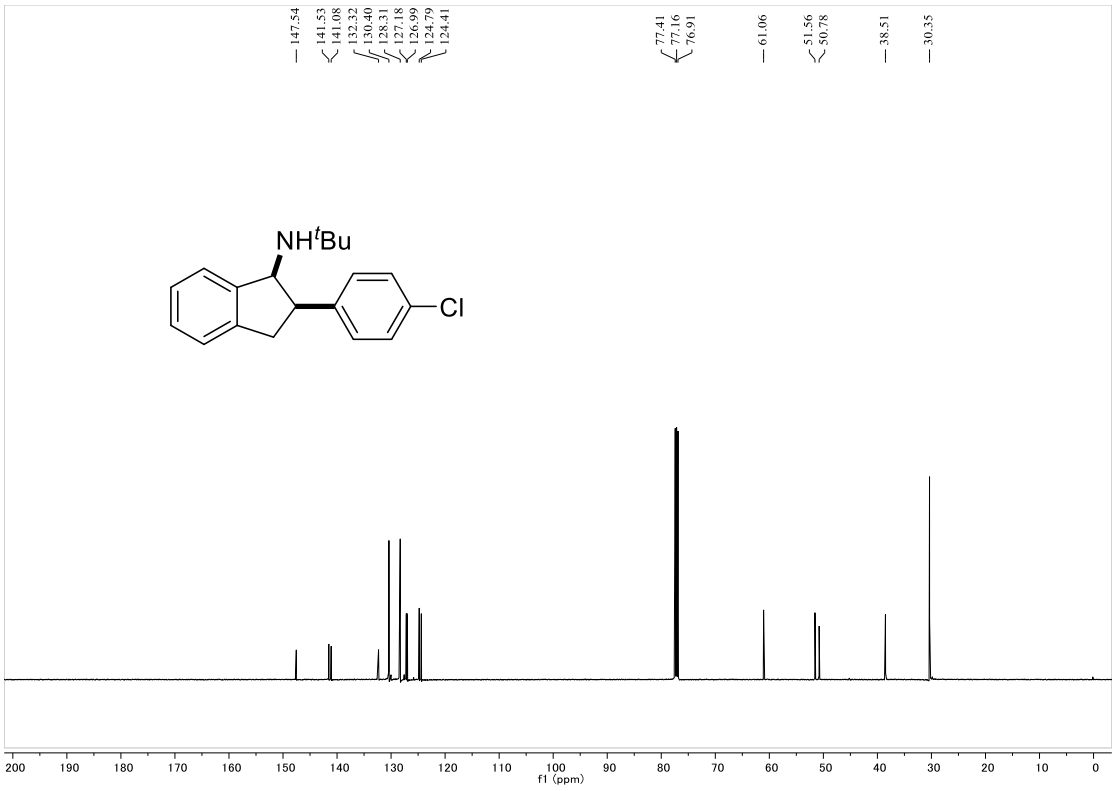
^{13}C NMR spectra of ***cis*-3ad** (126 MHz, $CDCl_3$)



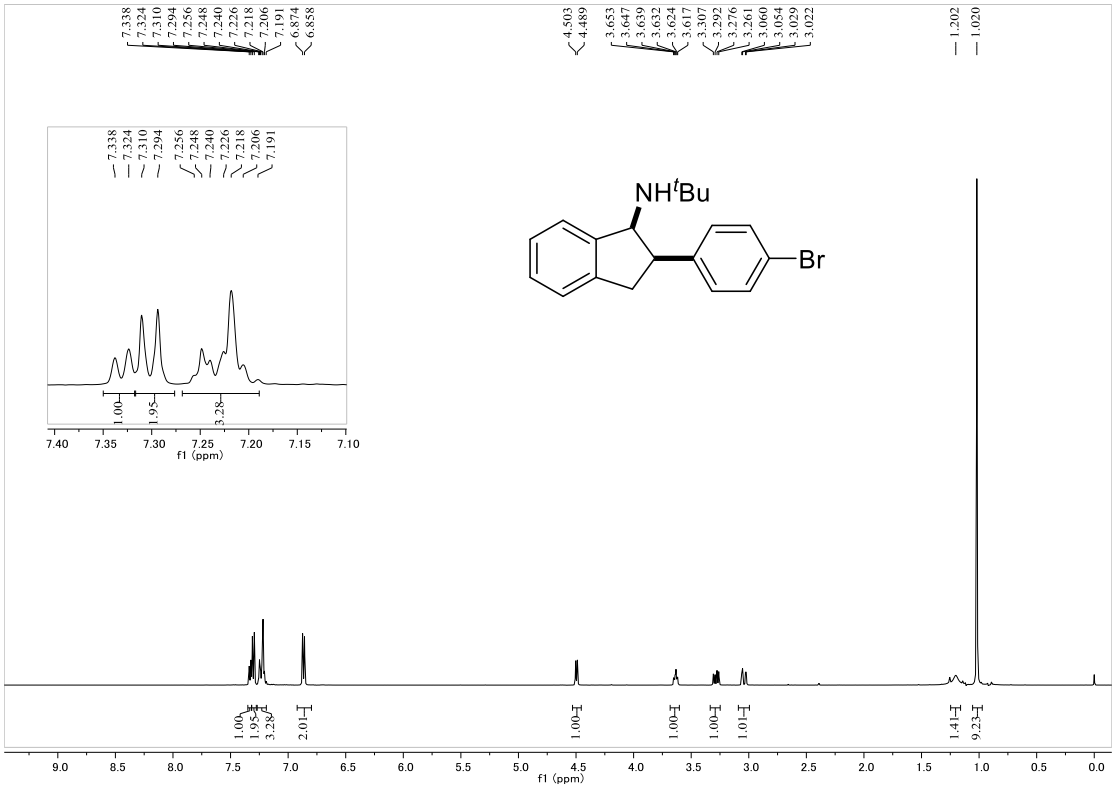
^{1}H NMR spectra of ***cis*-3ae** (500 MHz, $CDCl_3$)



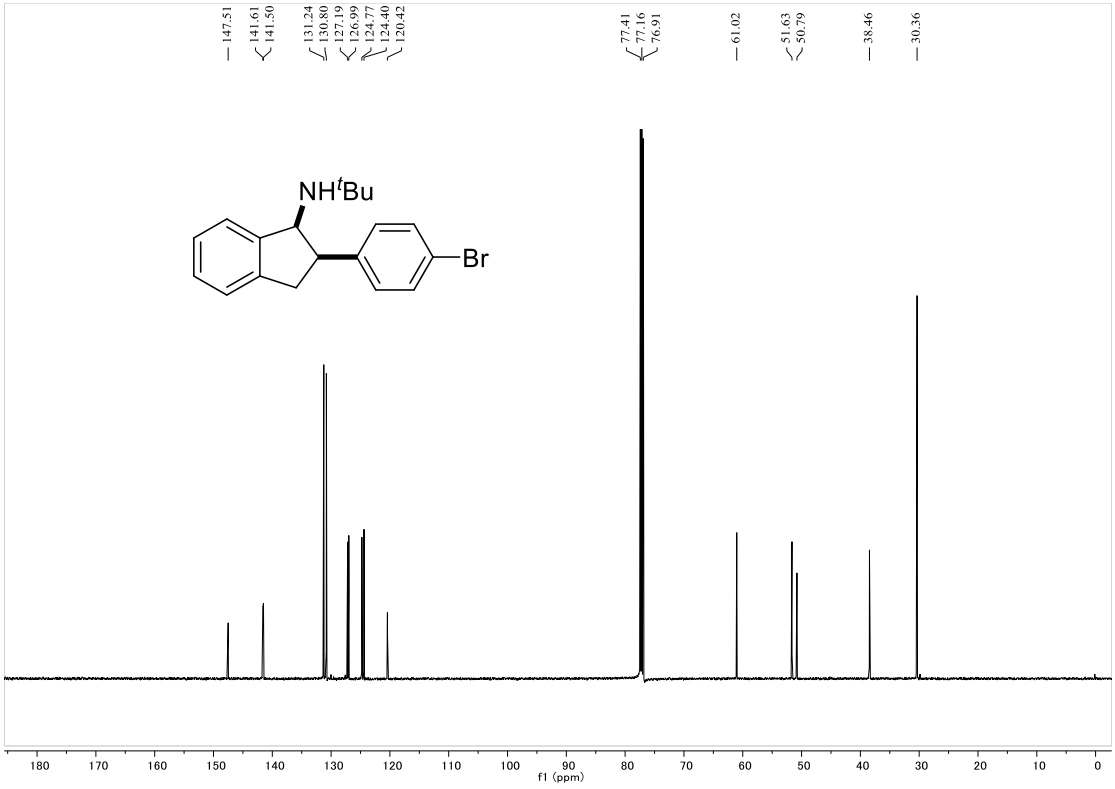
^{13}C NMR spectra of ***cis*-3ae** (126 MHz, $CDCl_3$)



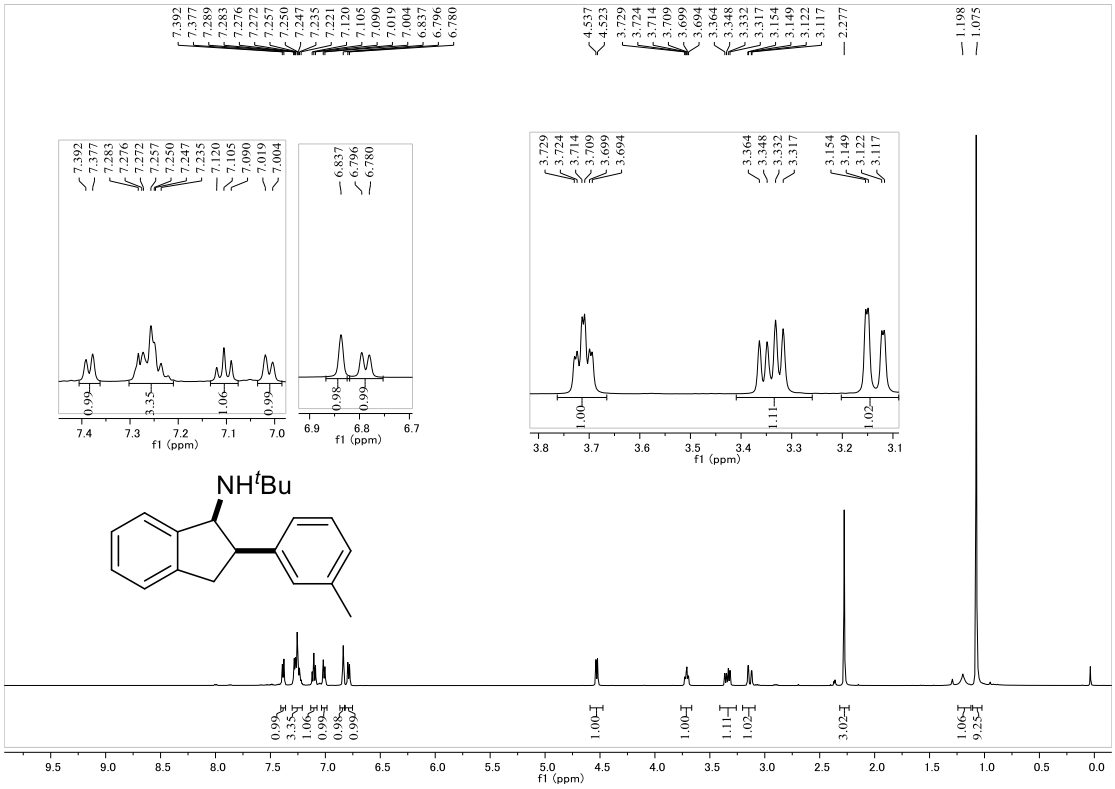
^{1}H NMR spectra of ***cis*-3af** (500 MHz, $CDCl_3$)



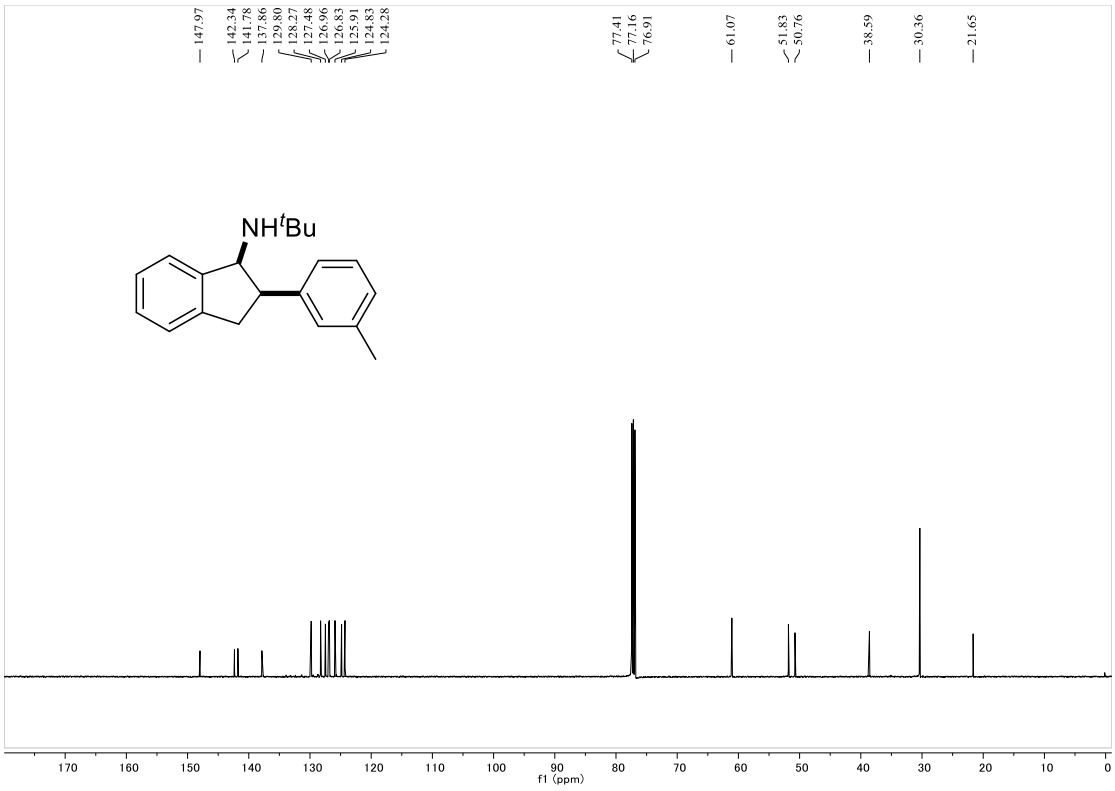
^{13}C NMR spectra of ***cis*-3af** (126 MHz, $CDCl_3$)



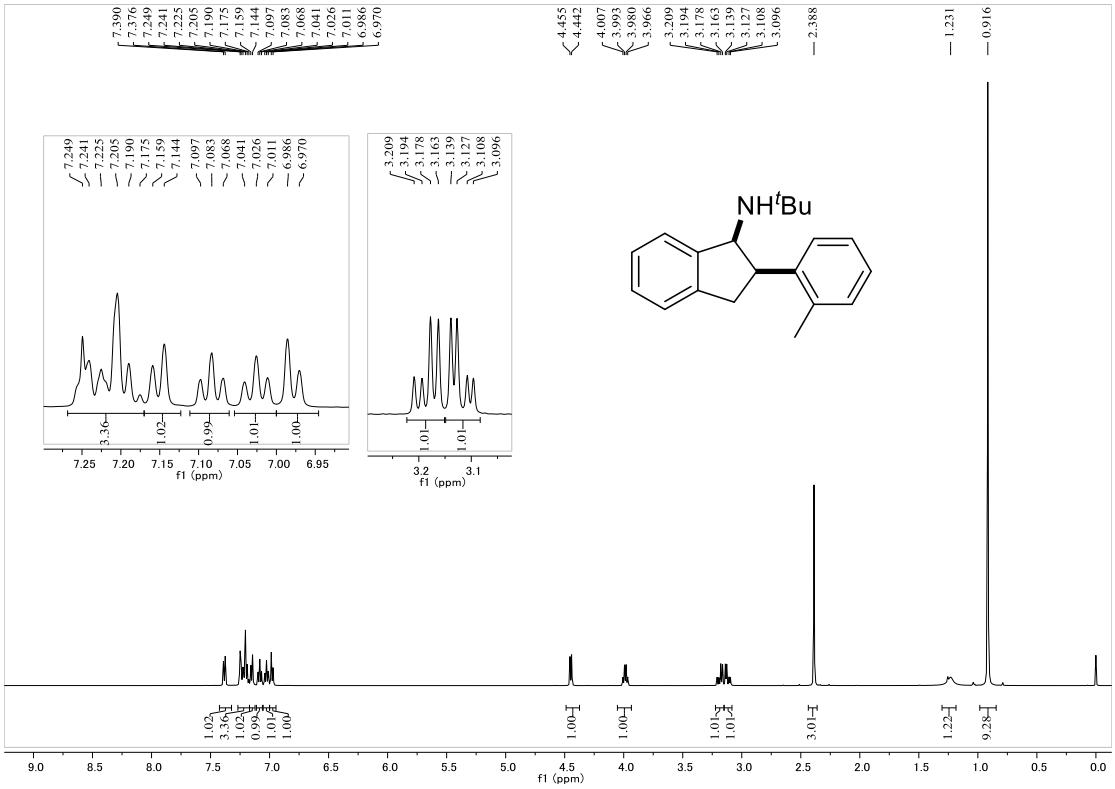
^{1}H NMR spectra of ***cis*-3ag** (500 MHz, $CDCl_3$)



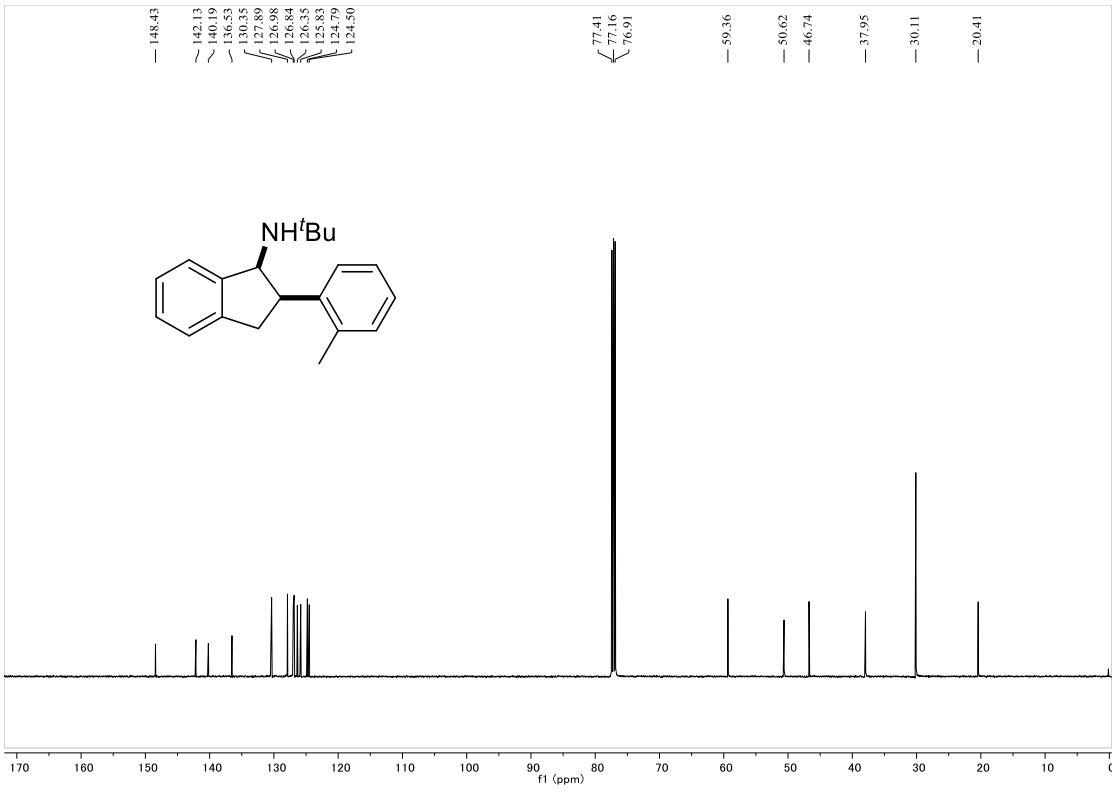
^{13}C NMR spectra of ***cis*-3ag** (126 MHz, $CDCl_3$)



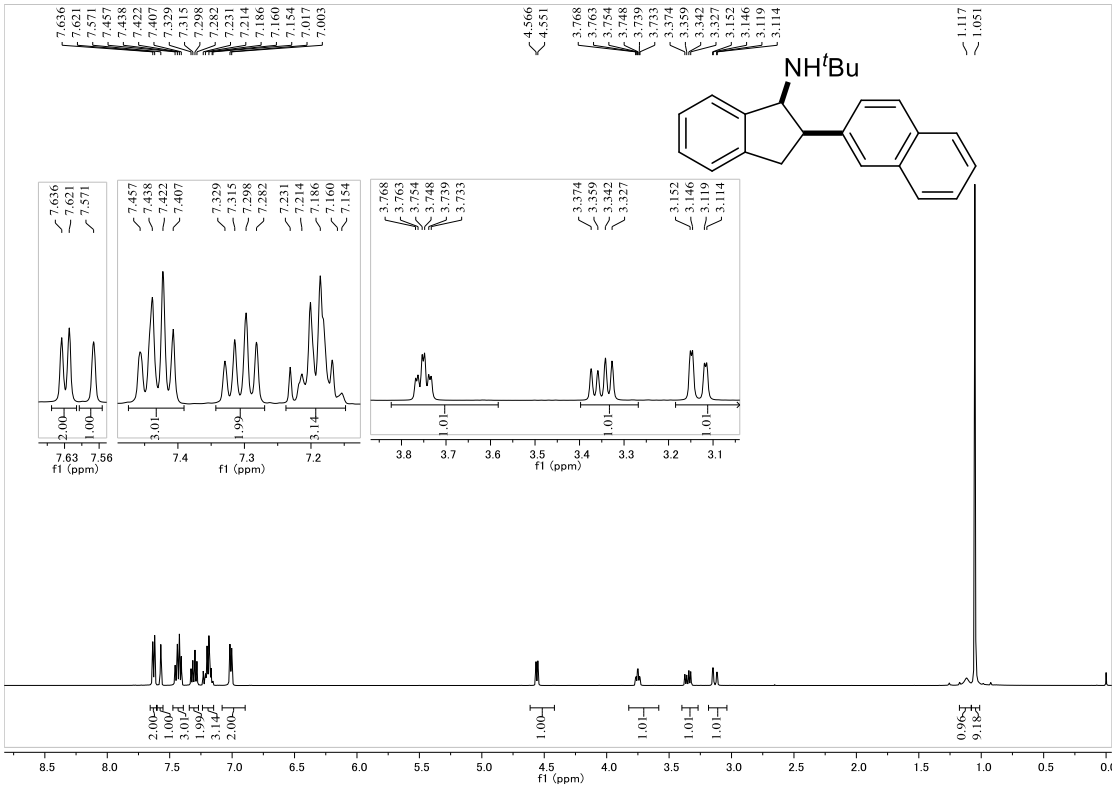
^{1}H NMR spectra of ***cis*-3ah** (500 MHz, $CDCl_3$)



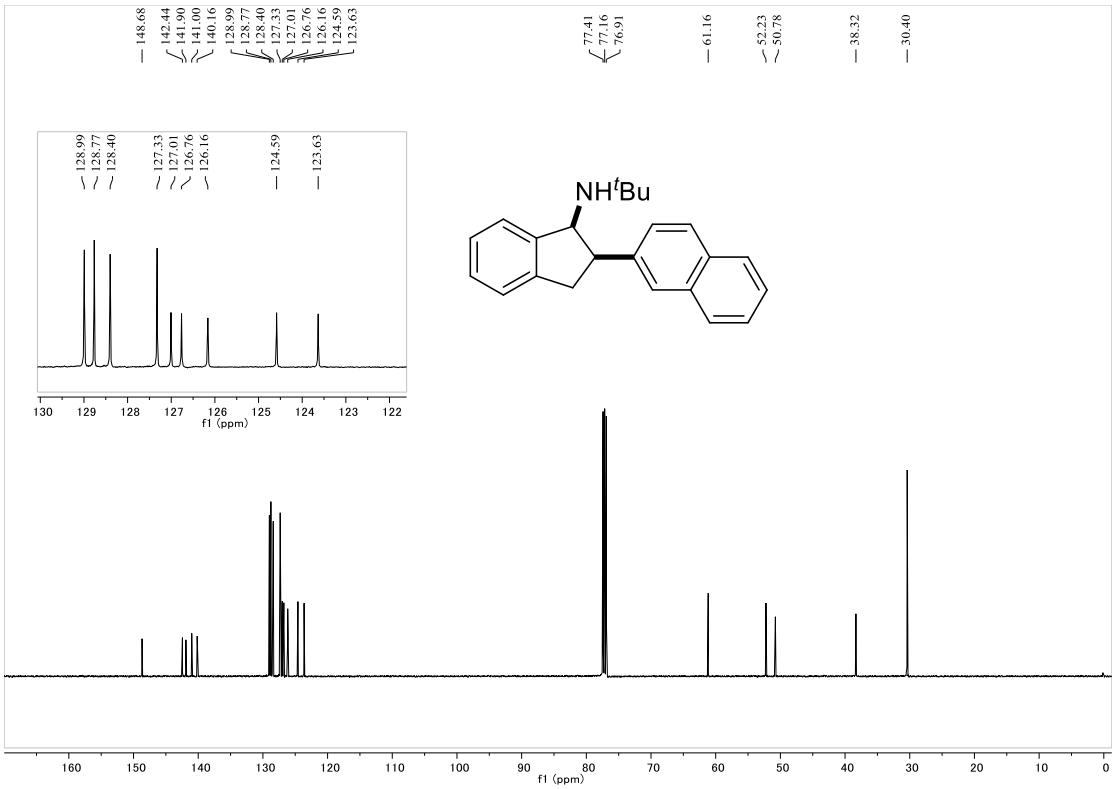
^{13}C NMR spectra of ***cis*-3ah** (126 MHz, $CDCl_3$)



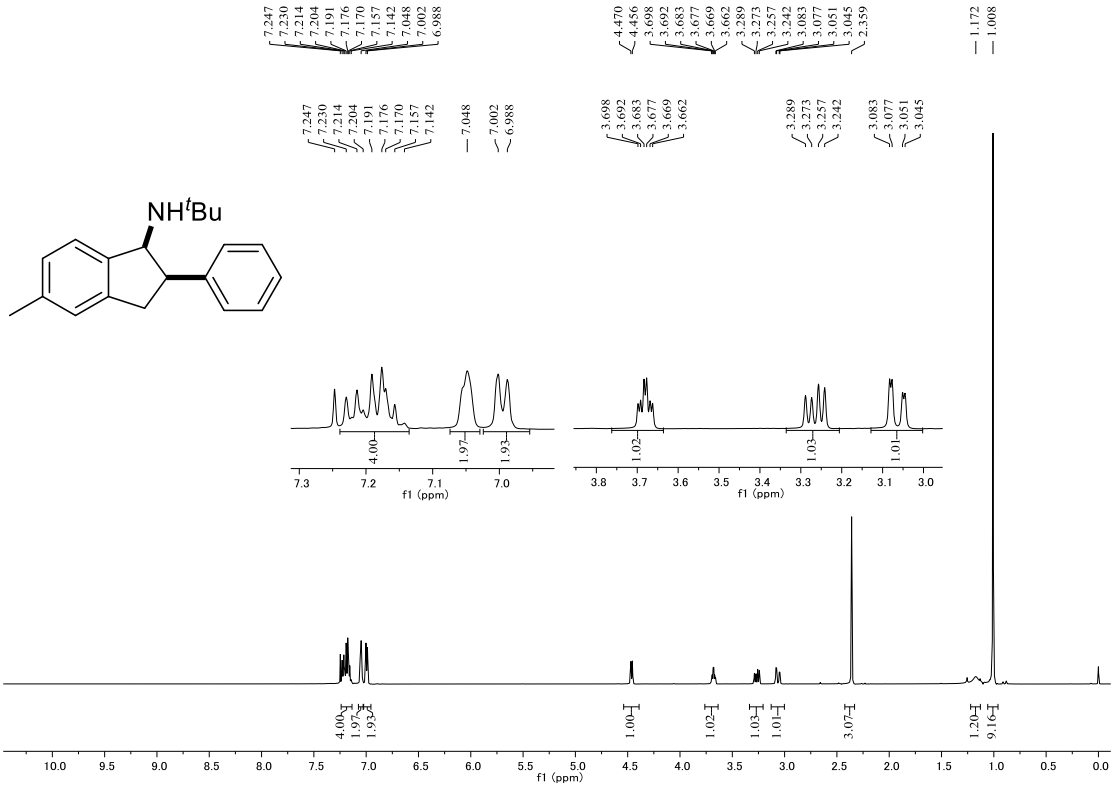
^{1}H NMR spectra of ***cis*-3ai** (500 MHz, $CDCl_3$)



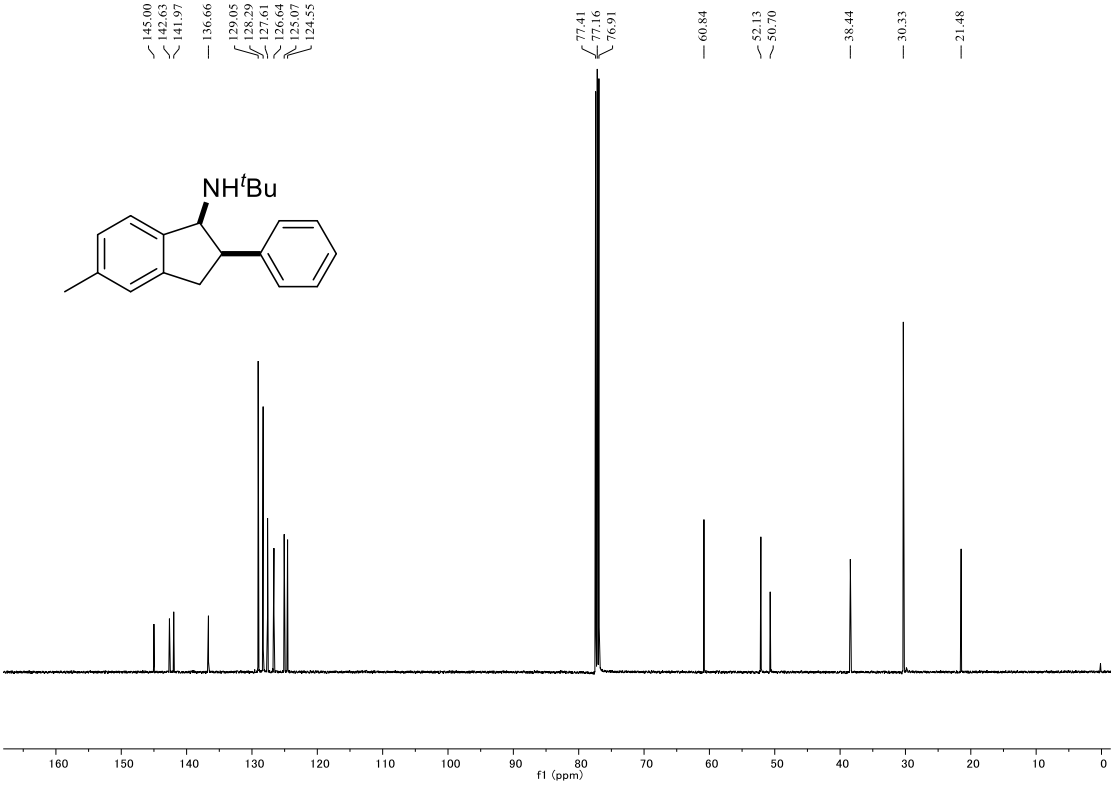
^{13}C NMR spectra of ***cis*-3ai** (126 MHz, $CDCl_3$)



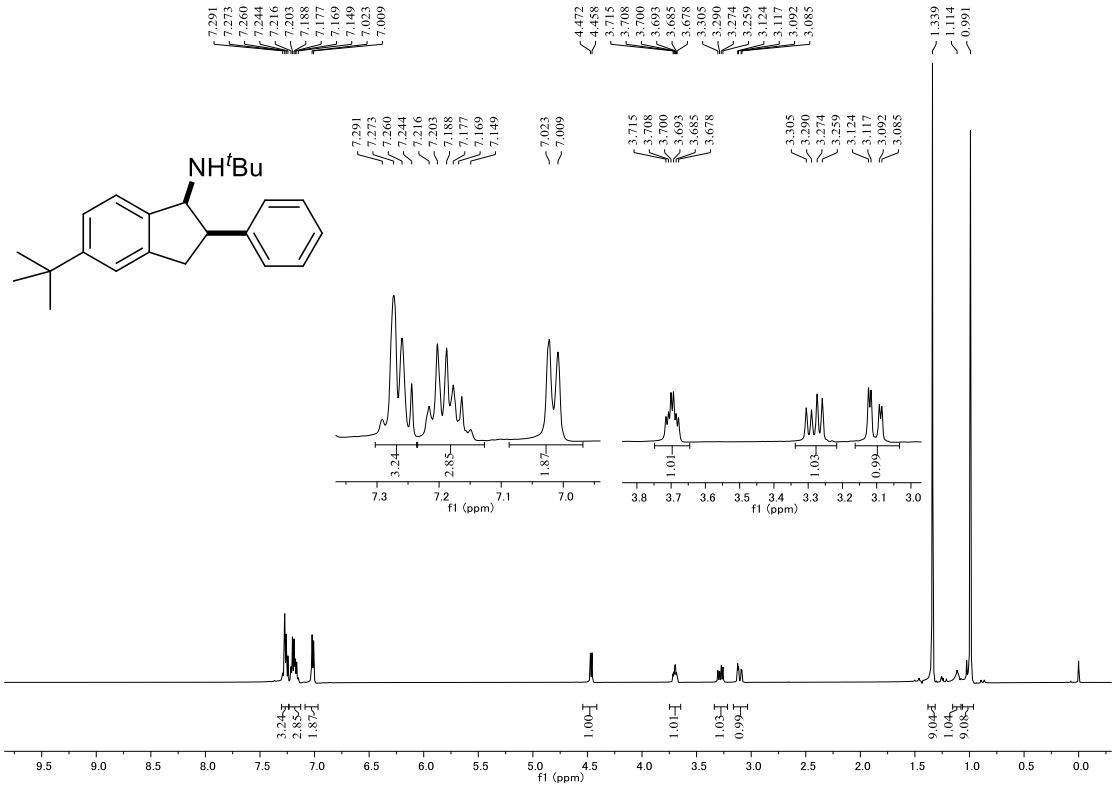
^{1}H NMR spectra of ***cis*-3ba** (500 MHz, $CDCl_3$)



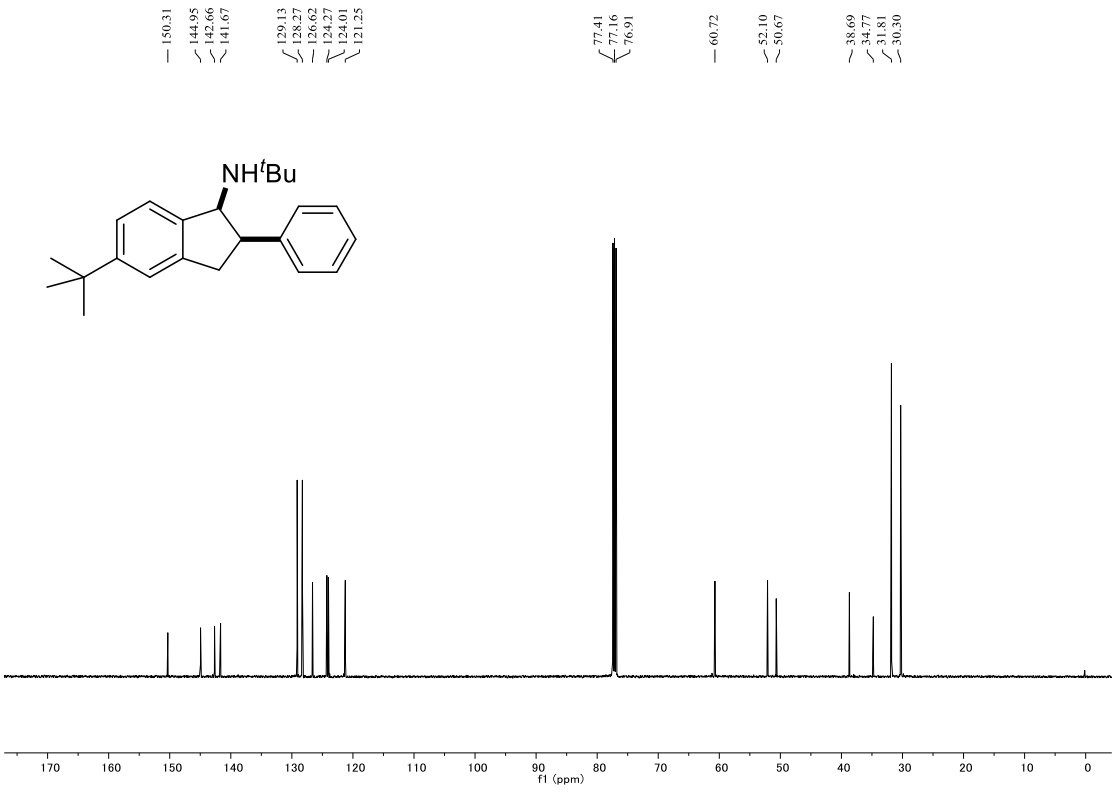
^{13}C NMR spectra of ***cis*-3ba** (126 MHz, $CDCl_3$)



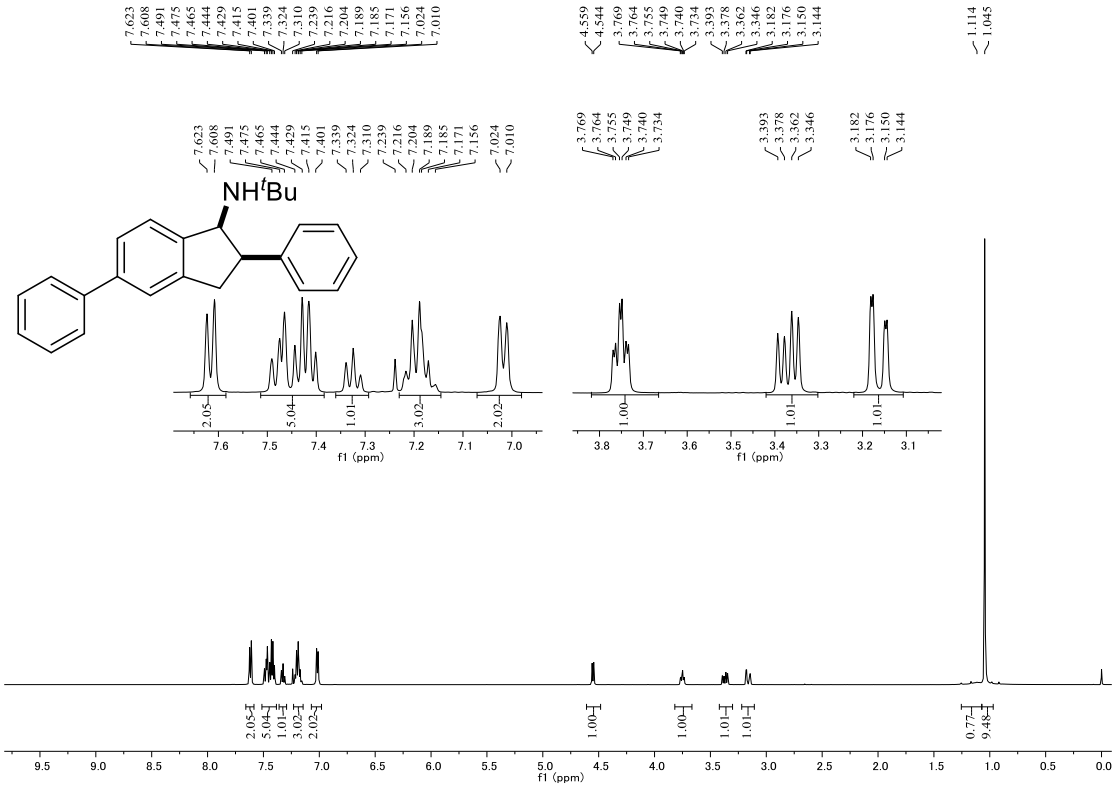
^{1}H NMR spectra of ***cis*-3ca** (500 MHz, $CDCl_3$)



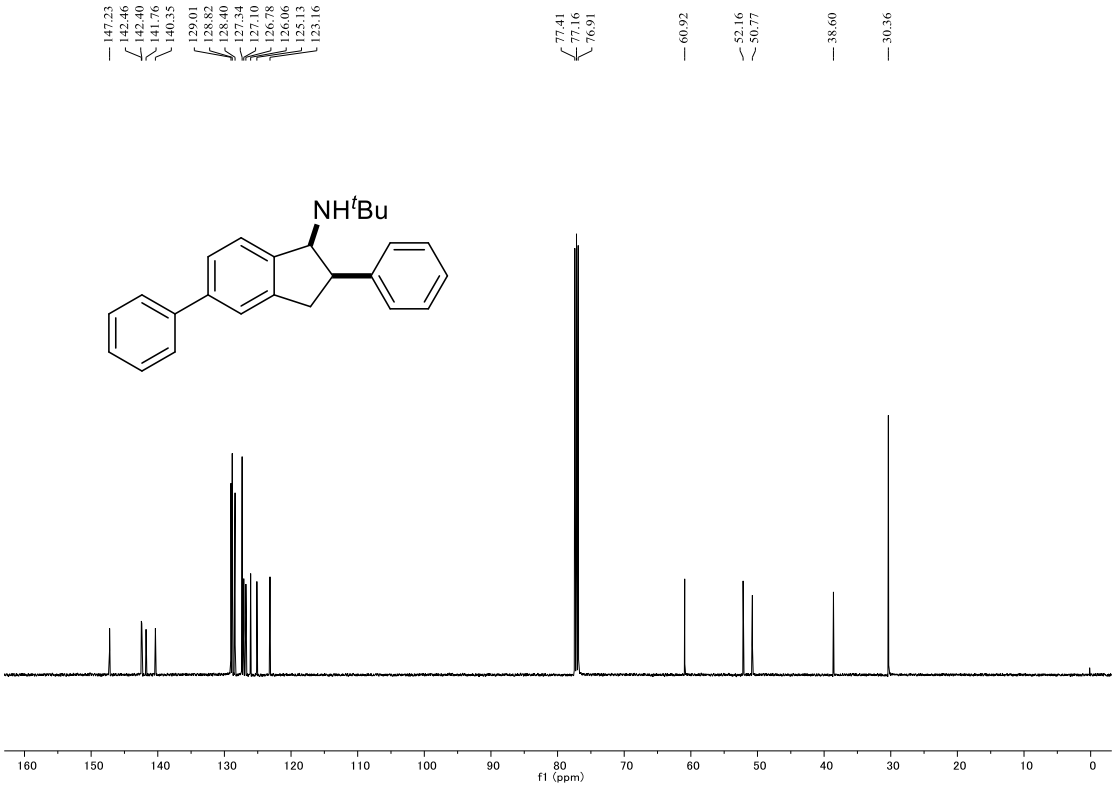
^{13}C NMR spectra of ***cis*-3ca** (126 MHz, $CDCl_3$)



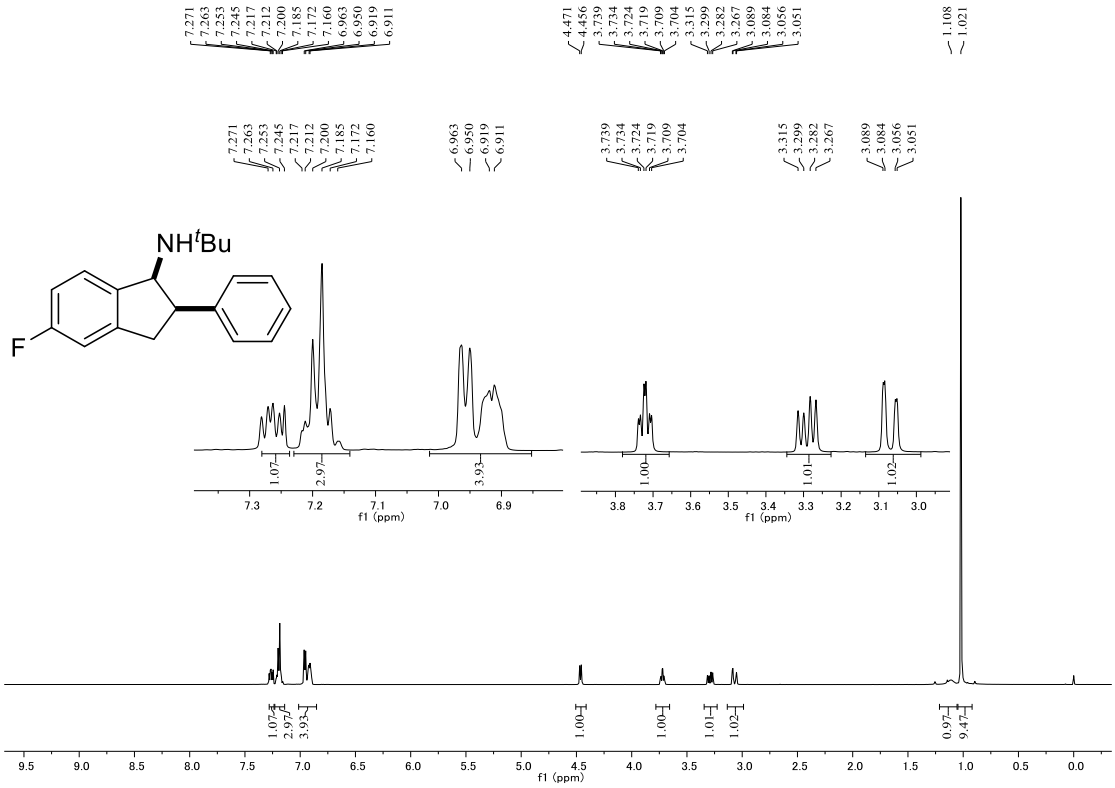
^{1}H NMR spectra of ***cis*-3da** (500 MHz, $CDCl_3$)



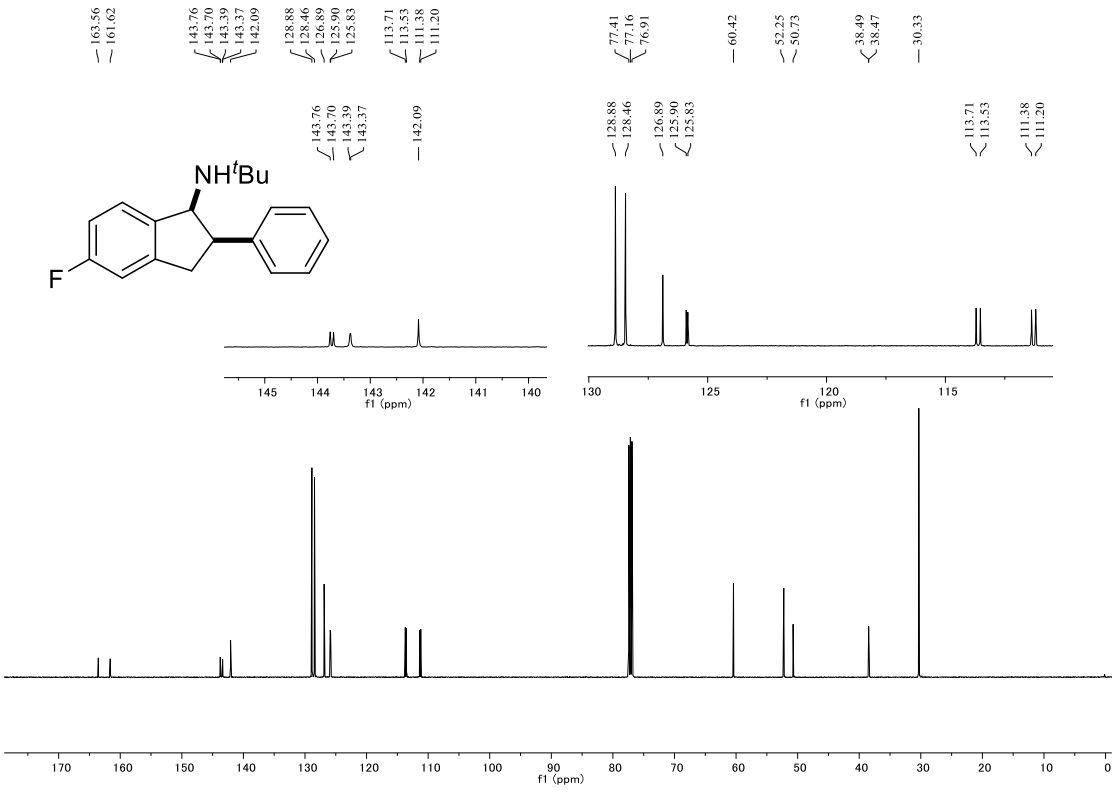
^{13}C NMR spectra of ***cis*-3da** (126 MHz, $CDCl_3$)



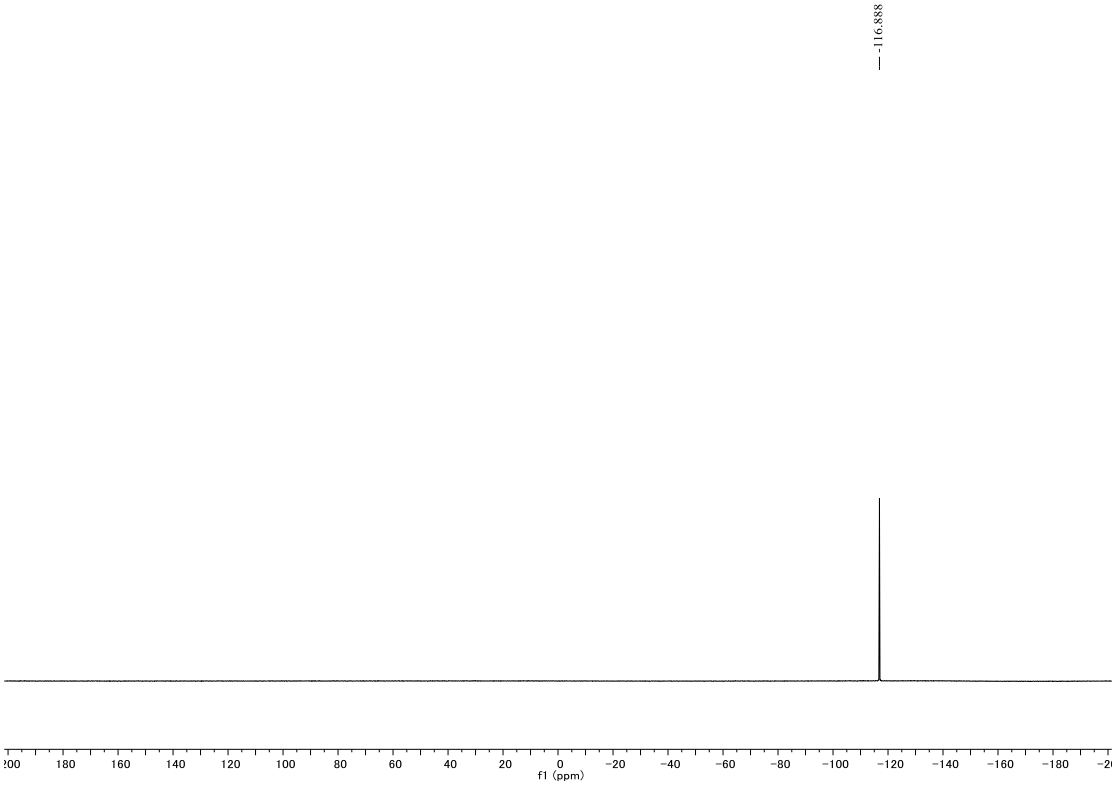
^{1}H NMR spectra of ***cis*-3ea** (500 MHz, $CDCl_3$)



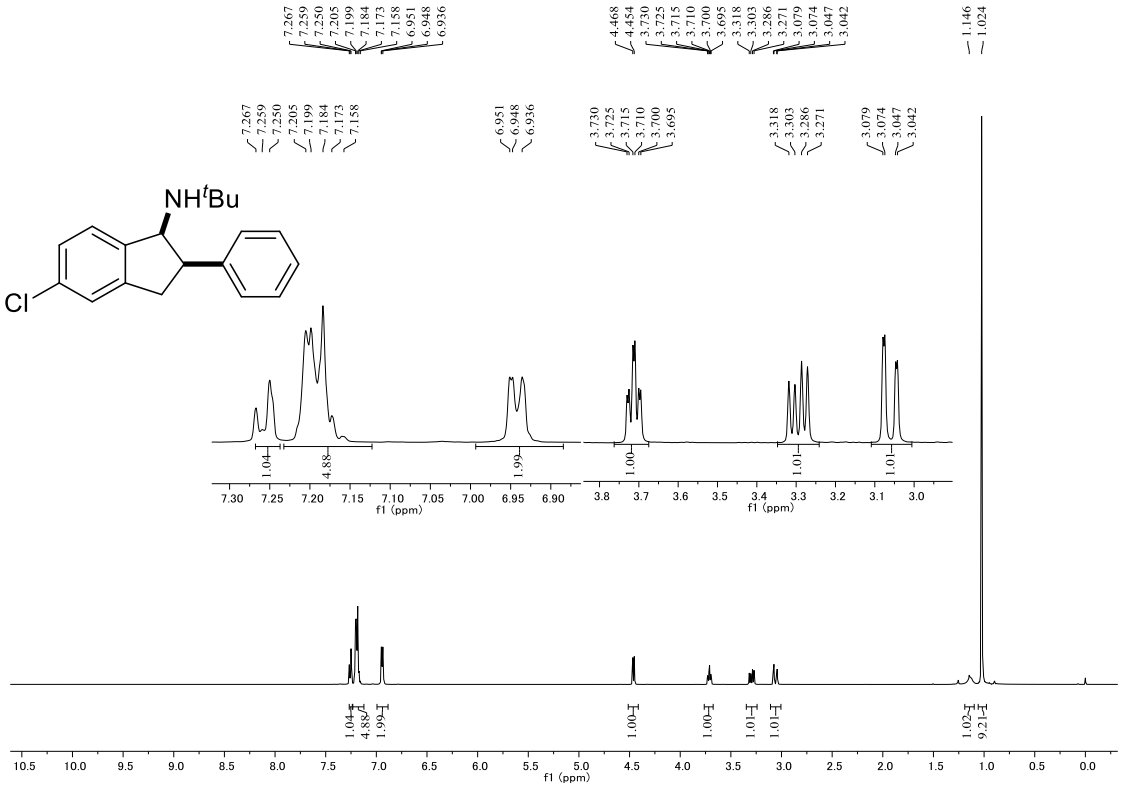
^{13}C NMR spectra of ***cis*-3ea** (126 MHz, $CDCl_3$)



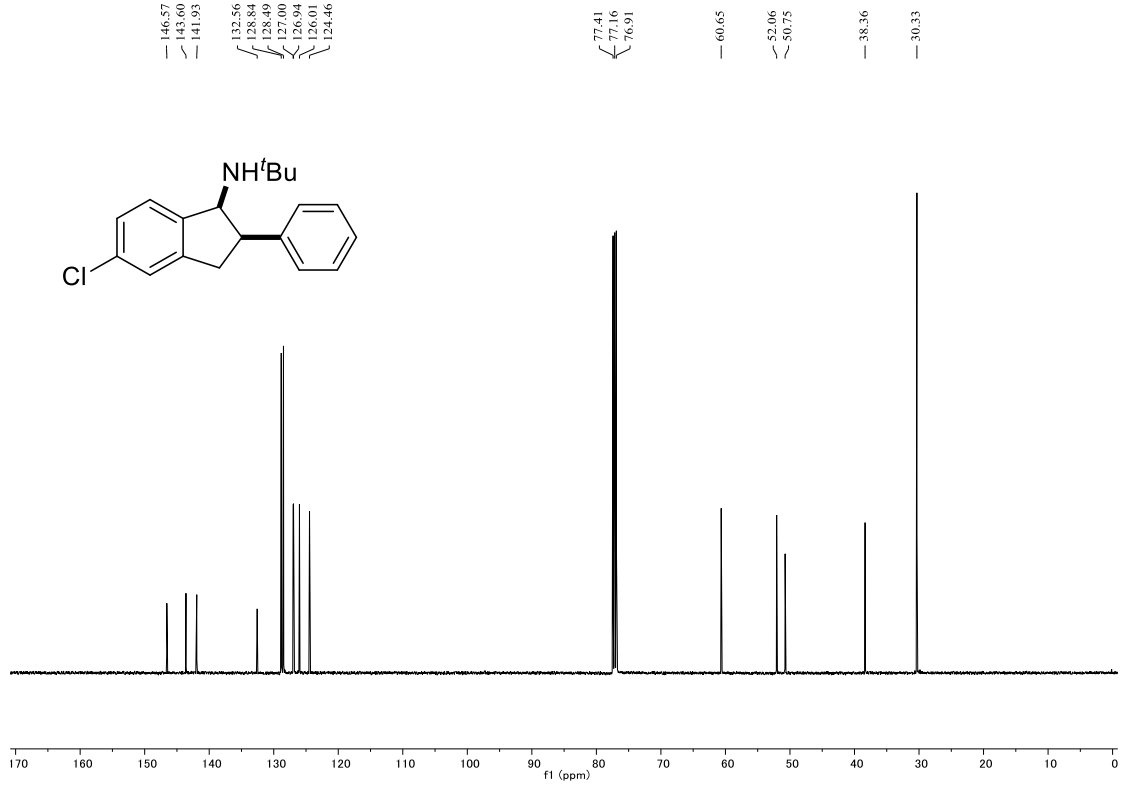
^{19}F NMR spectra of ***cis*-3ea** (377 MHz, $CDCl_3$)



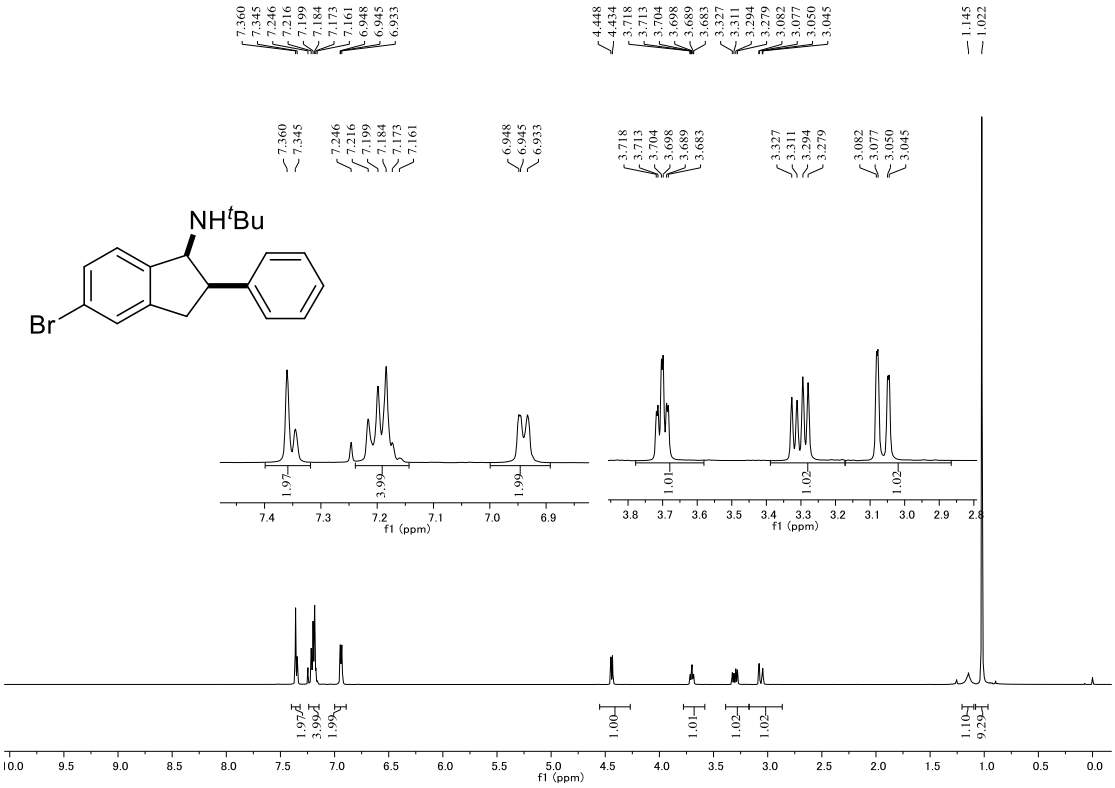
^{1}H NMR spectra of ***cis*-3fa** (500 MHz, $CDCl_3$)



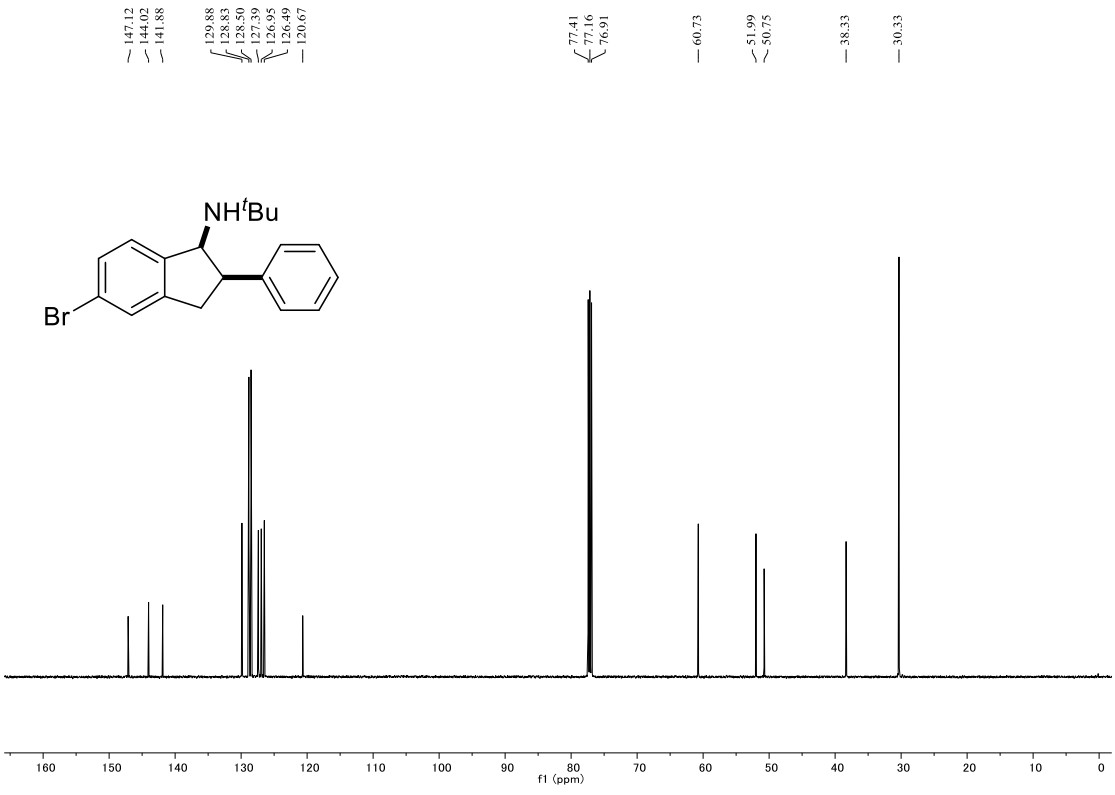
^{13}C NMR spectra of ***cis*-3fa** (126 MHz, $CDCl_3$)



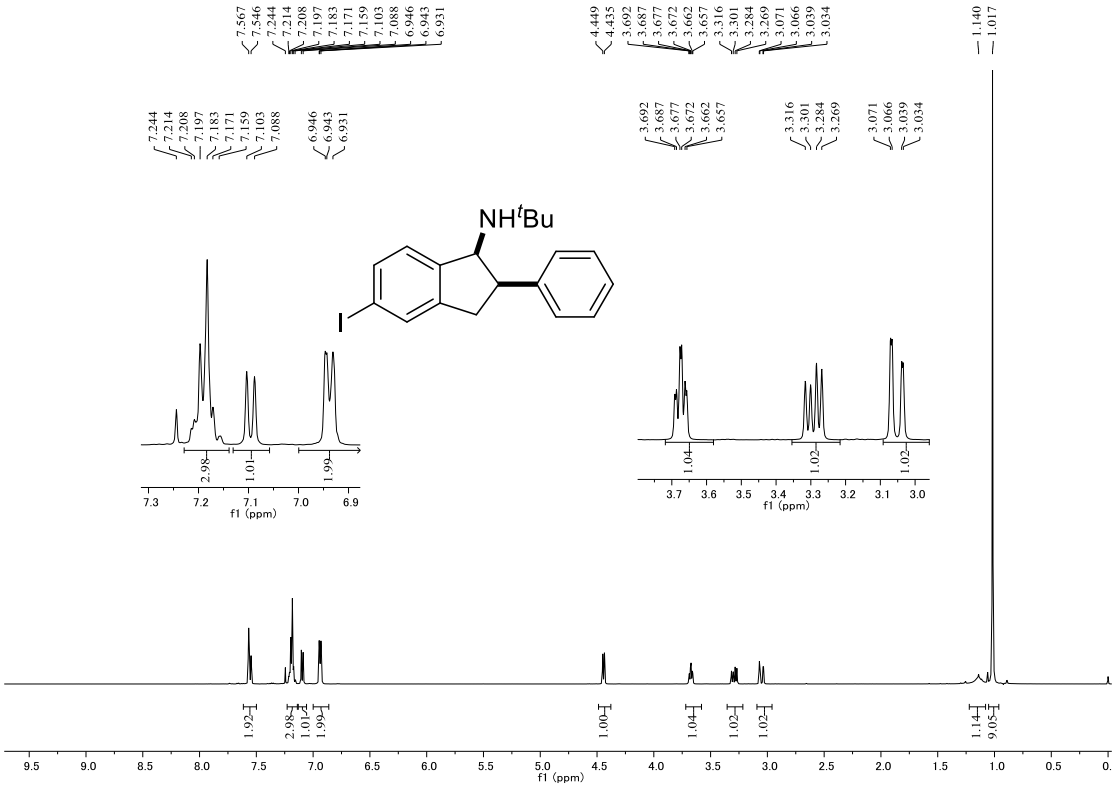
^{1}H NMR spectra of ***cis*-3ga** (500 MHz, $CDCl_3$)



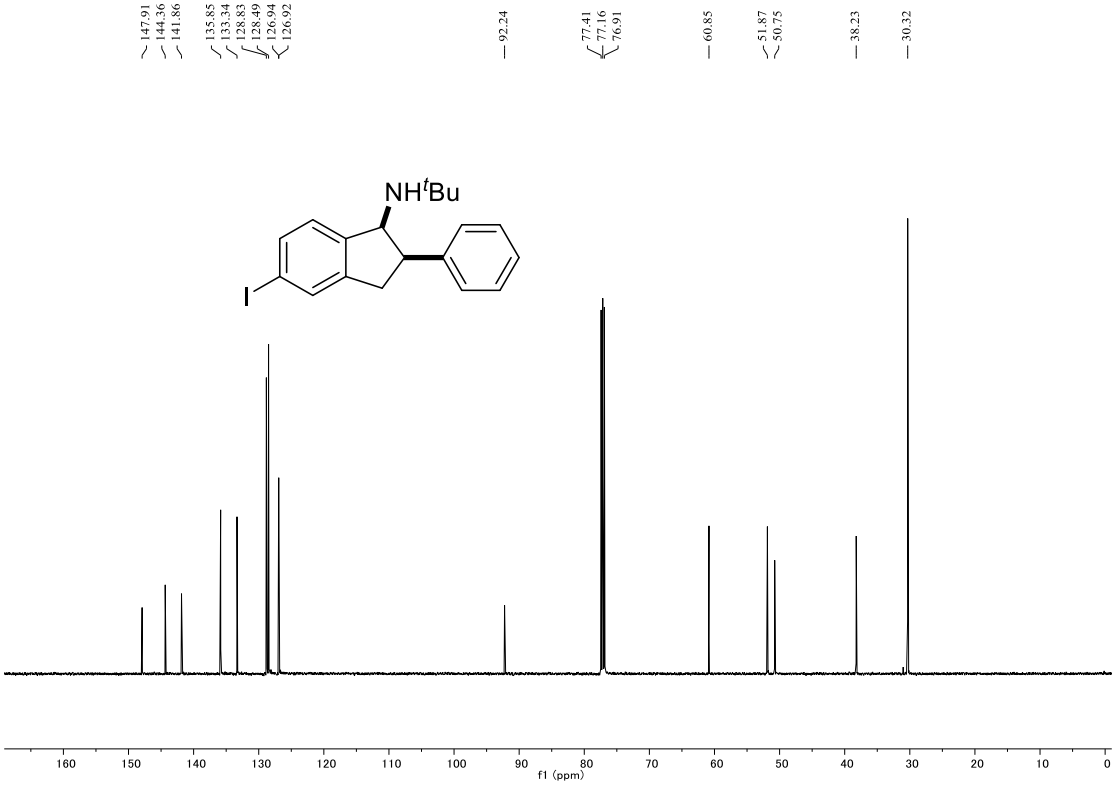
^{13}C NMR spectra of ***cis*-3ga** (126 MHz, $CDCl_3$)



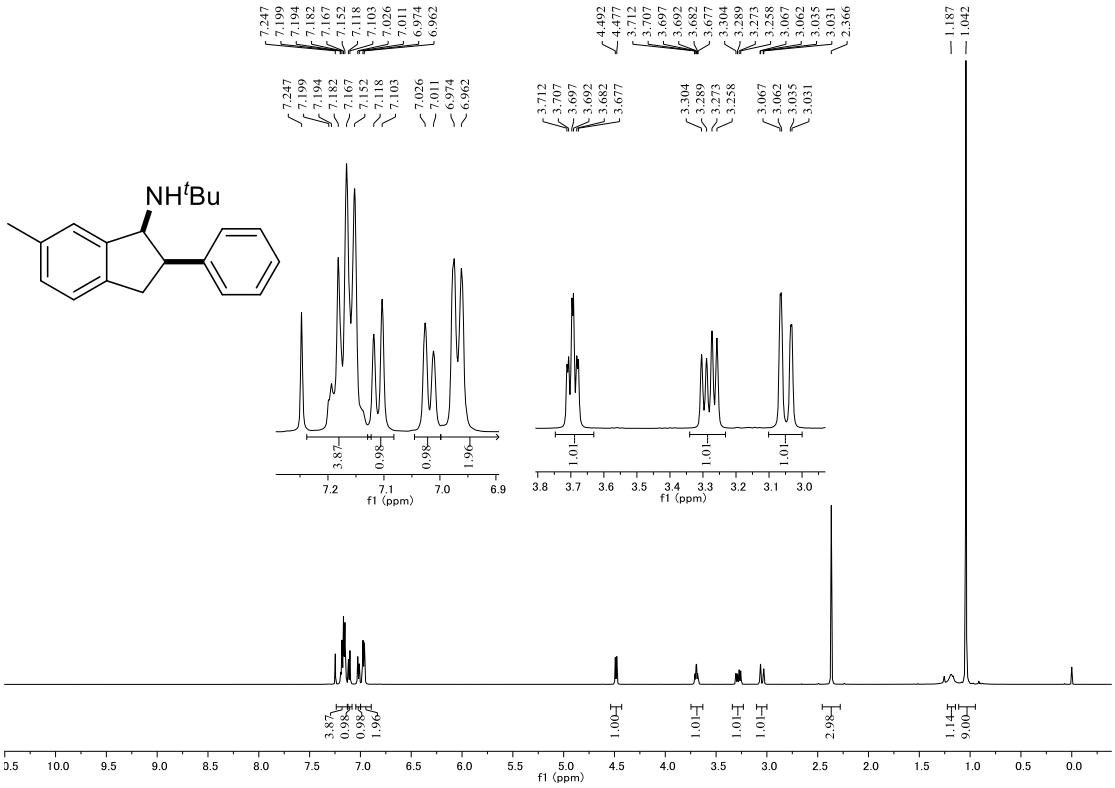
^{1}H NMR spectra of ***cis*-3ha** (500 MHz, $CDCl_3$)



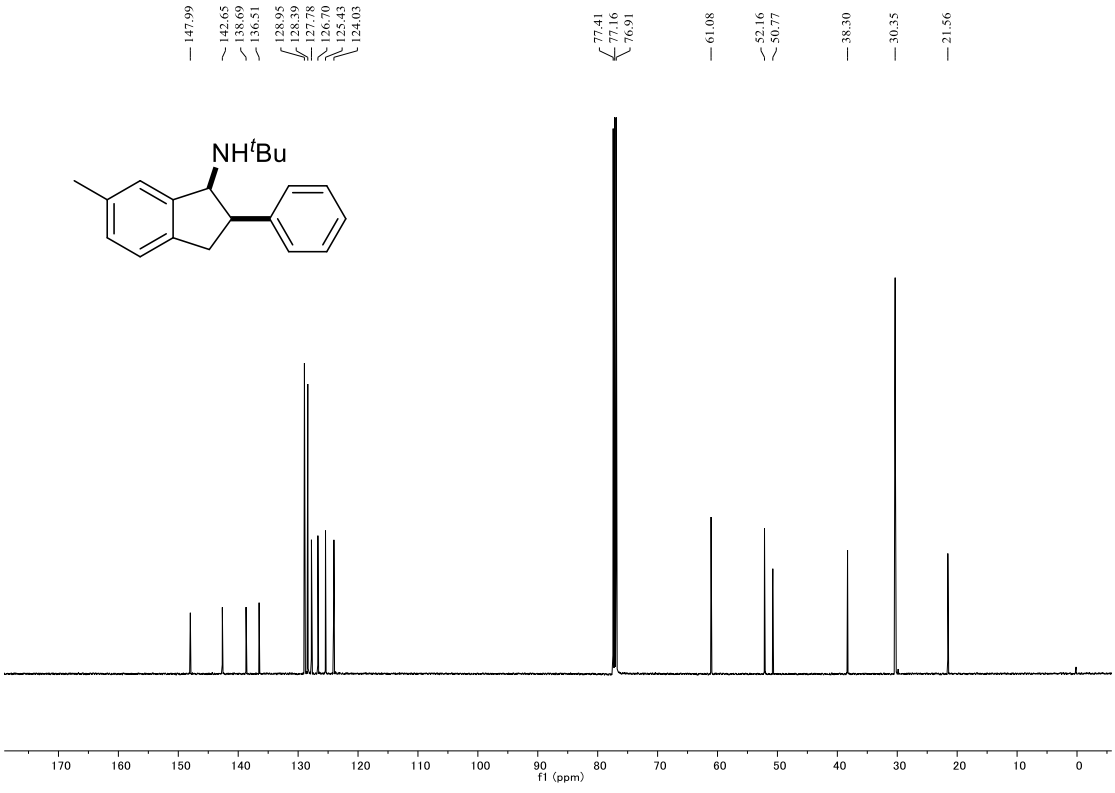
^{13}C NMR spectra of ***cis*-3ha** (126 MHz, $CDCl_3$)



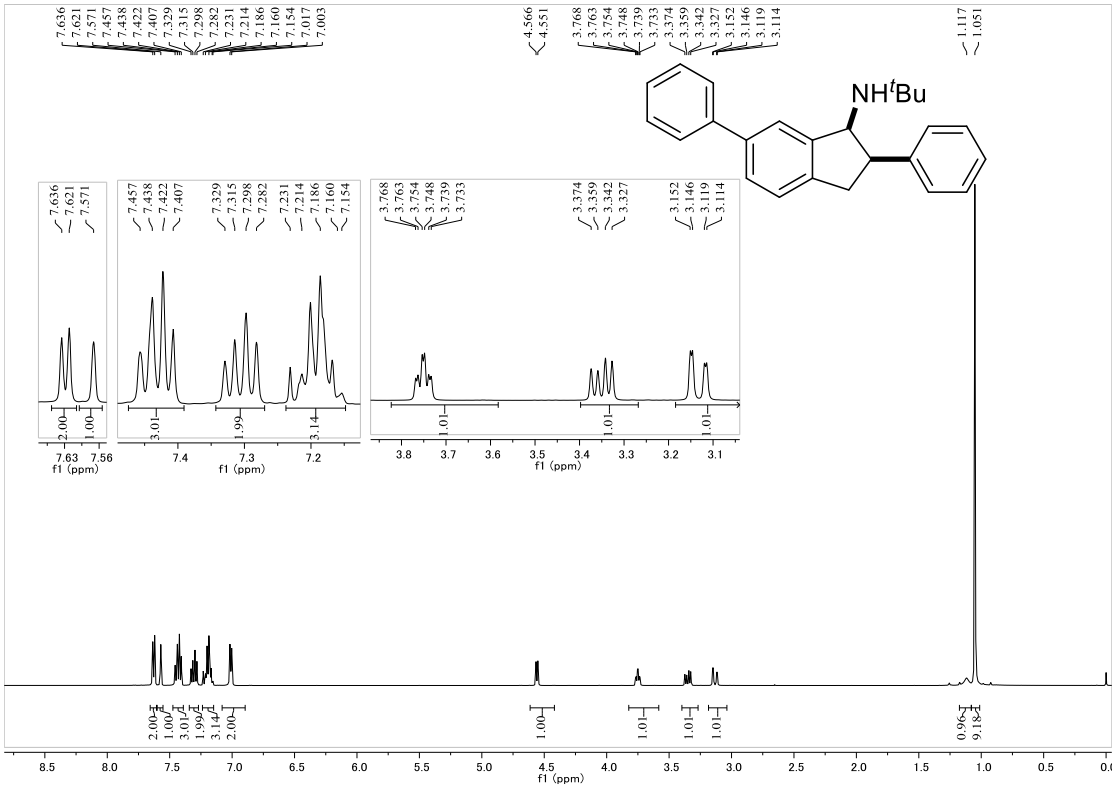
^{1}H NMR spectra of ***cis*-3ia** (500 MHz, $CDCl_3$)



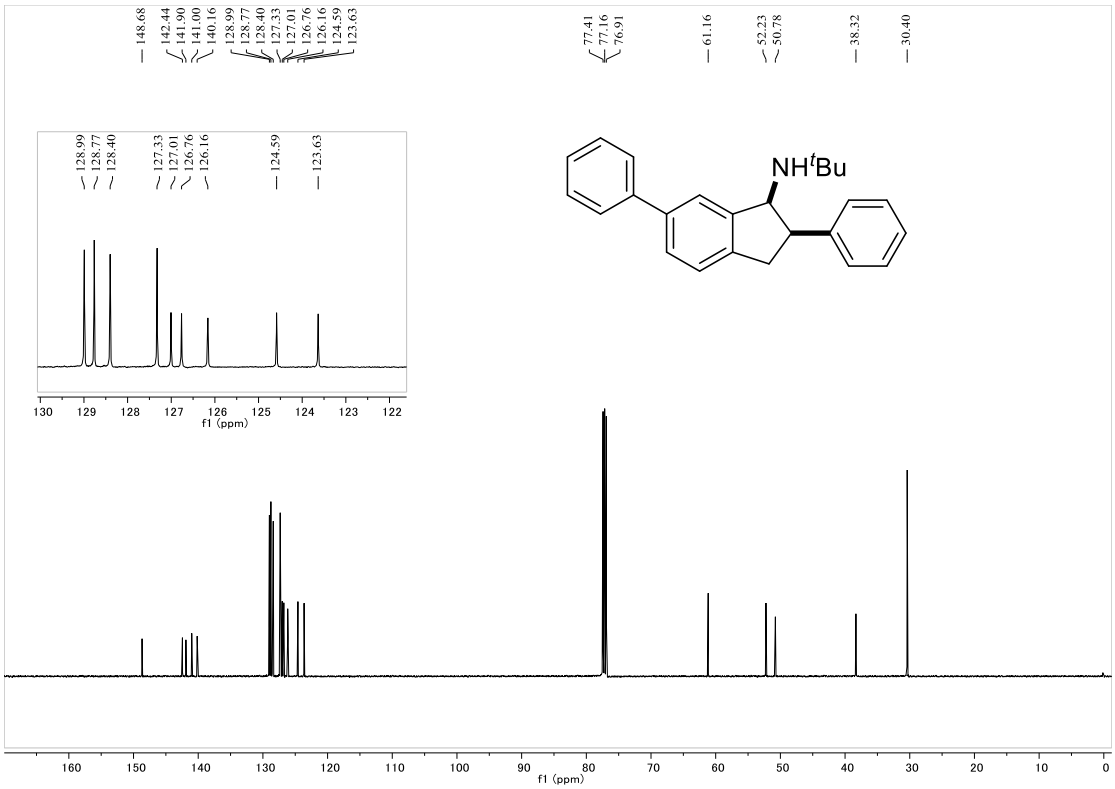
^{13}C NMR spectra of ***cis*-3ia** (126 MHz, $CDCl_3$)



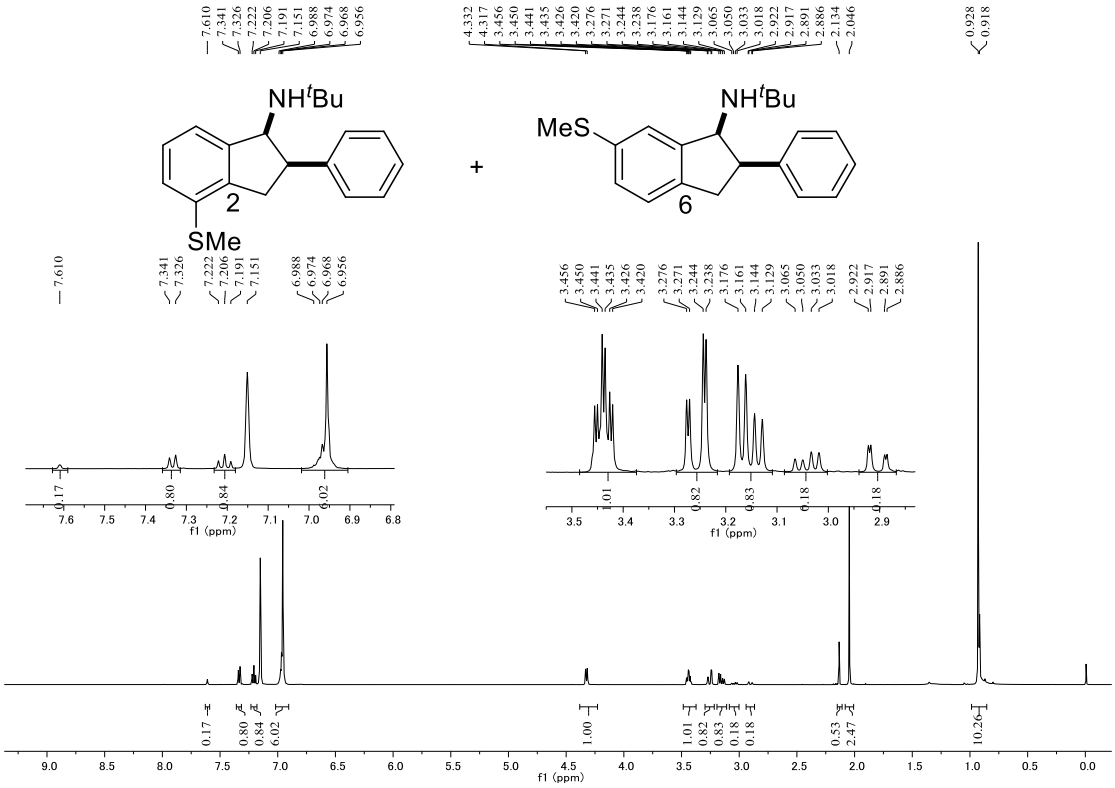
^{1}H NMR spectra of ***cis*-3ja** (500 MHz, $CDCl_3$)



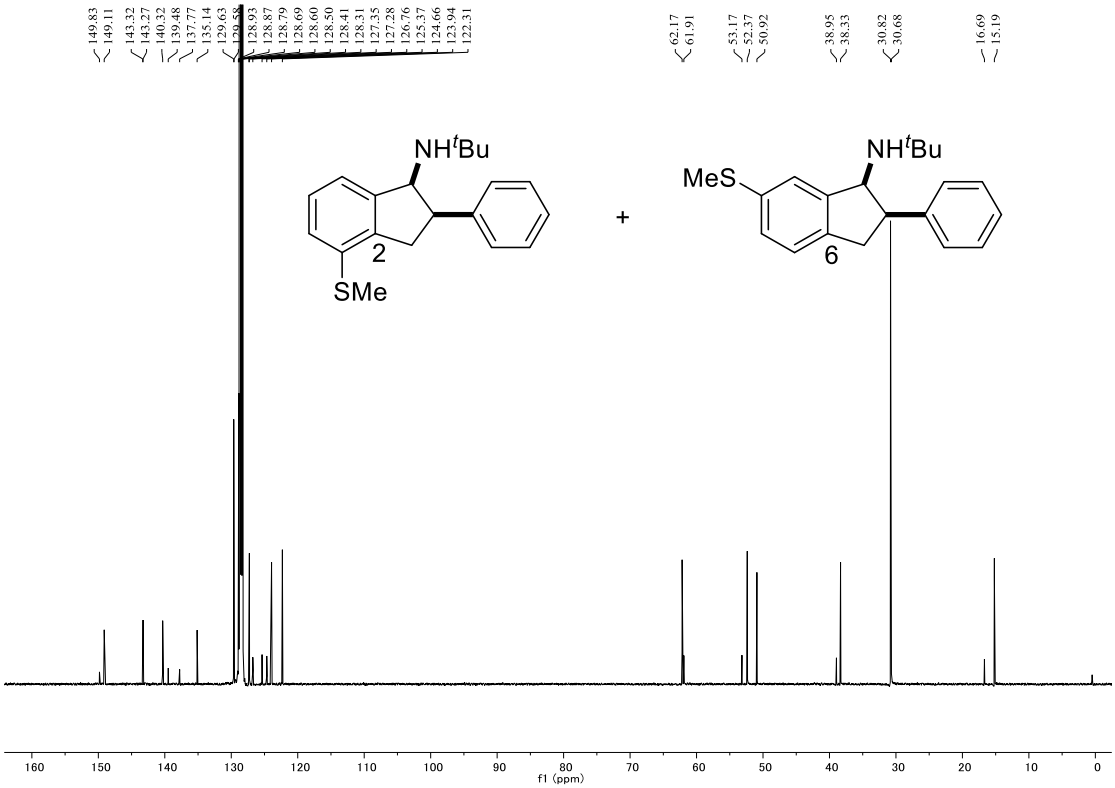
^{13}C NMR spectra of ***cis*-3ja** (126 MHz, $CDCl_3$)



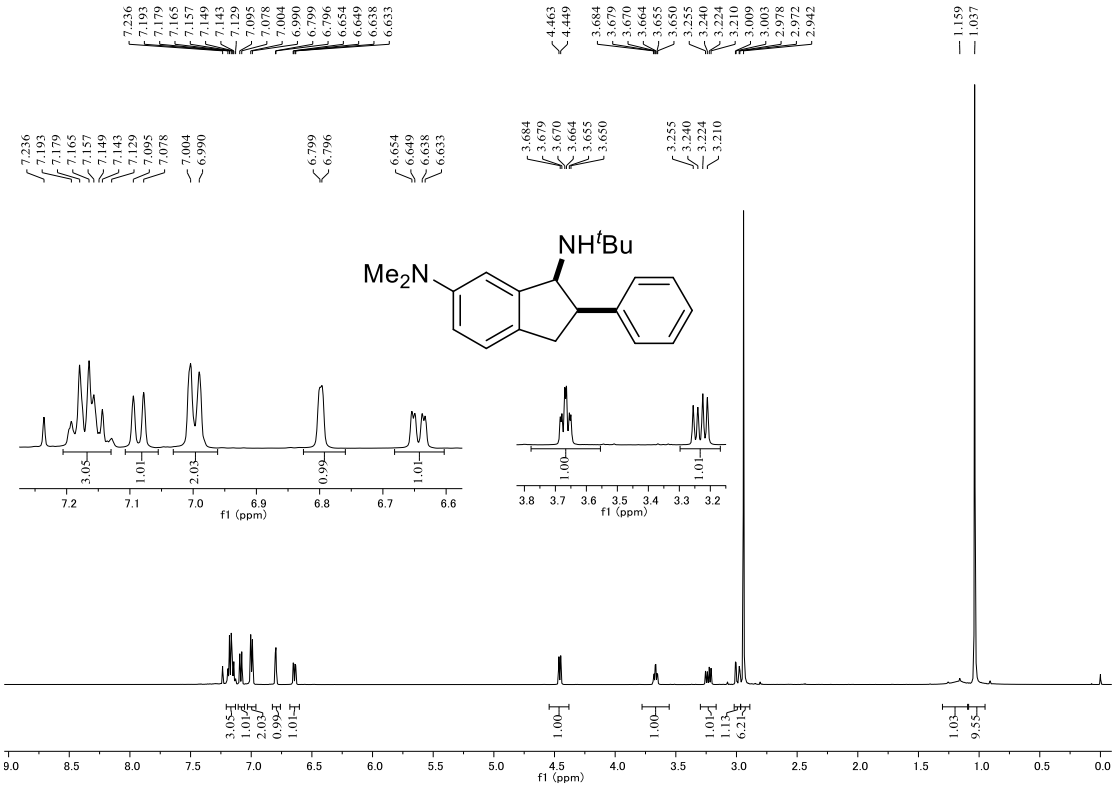
^{1}H NMR spectra of the mixture of ***cis*-3ka and *cis*-3ka** (500 MHz, C_6D_6)



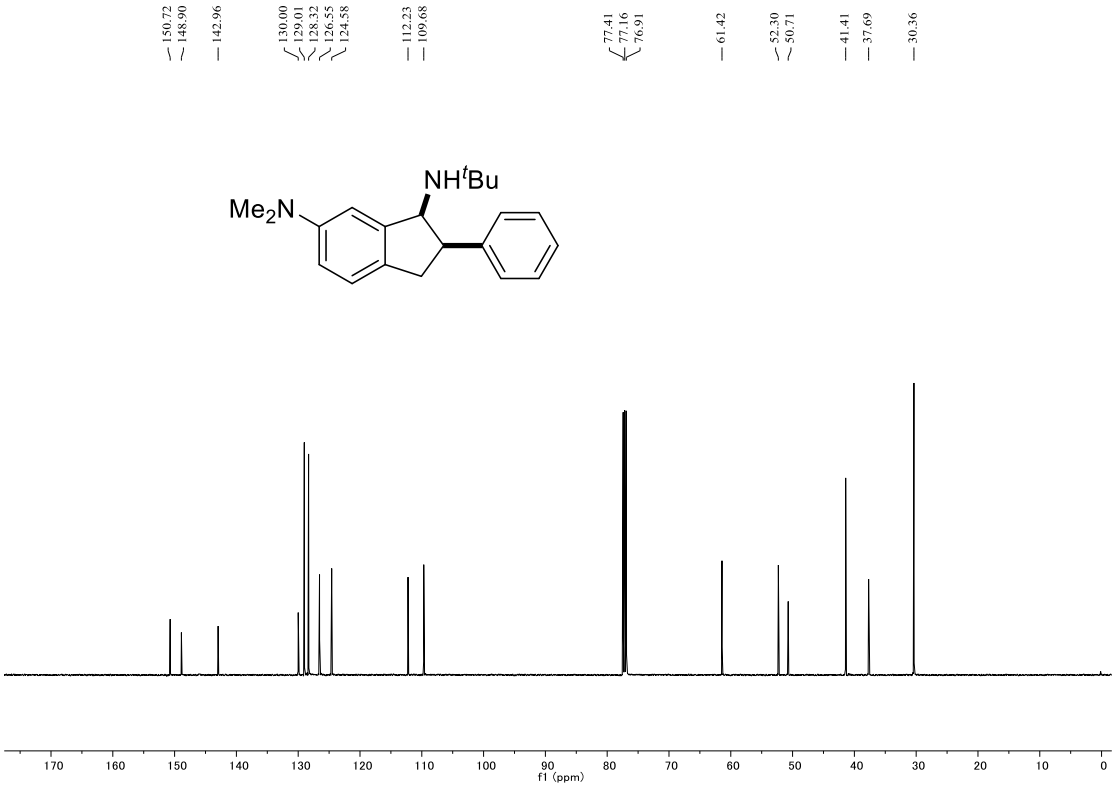
^{13}C NMR spectra of the mixture of ***cis*-3ka and *cis*-3ka** (126 MHz, C_6D_6)



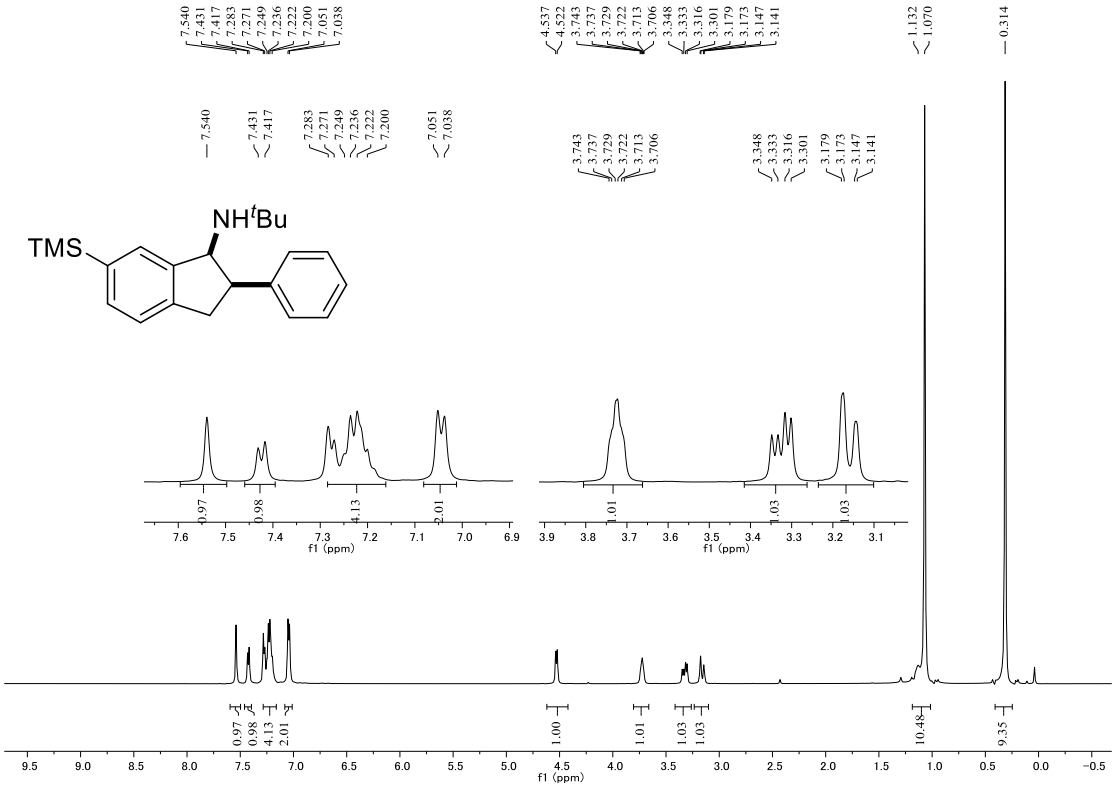
^{1}H NMR spectra of ***cis*-3la** (500 MHz, $CDCl_3$)



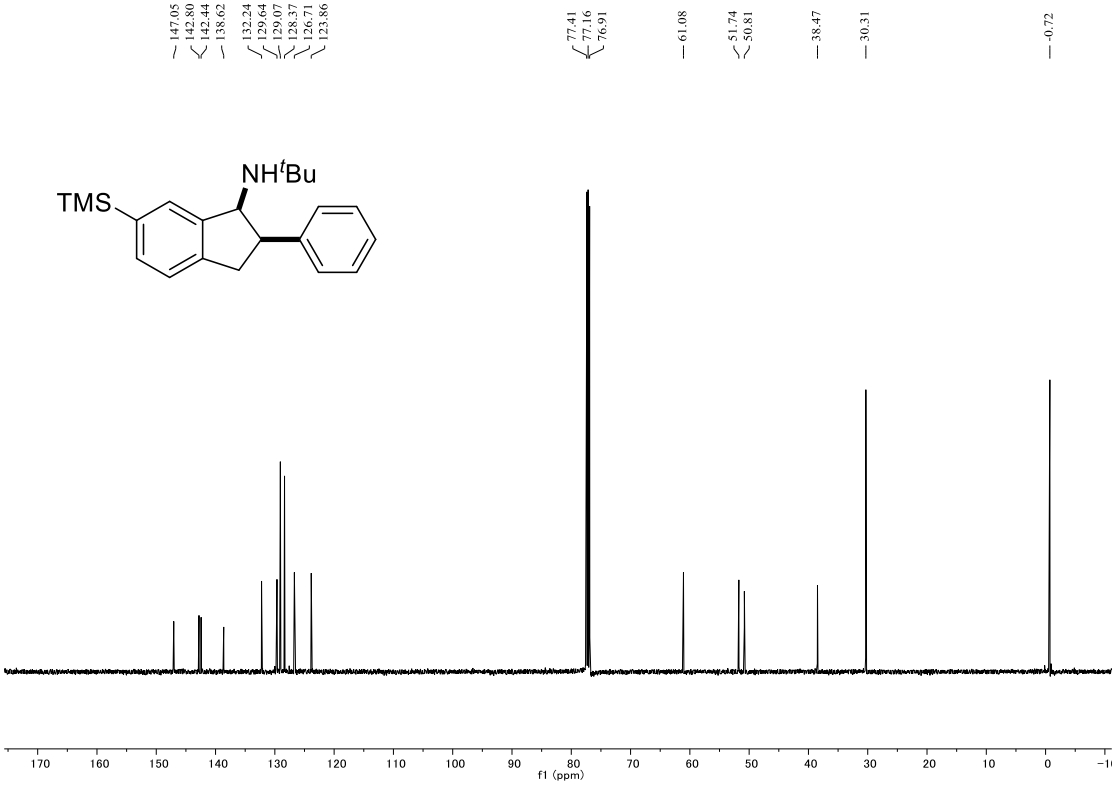
^{13}C NMR spectra of ***cis*-3la** (126 MHz, $CDCl_3$)



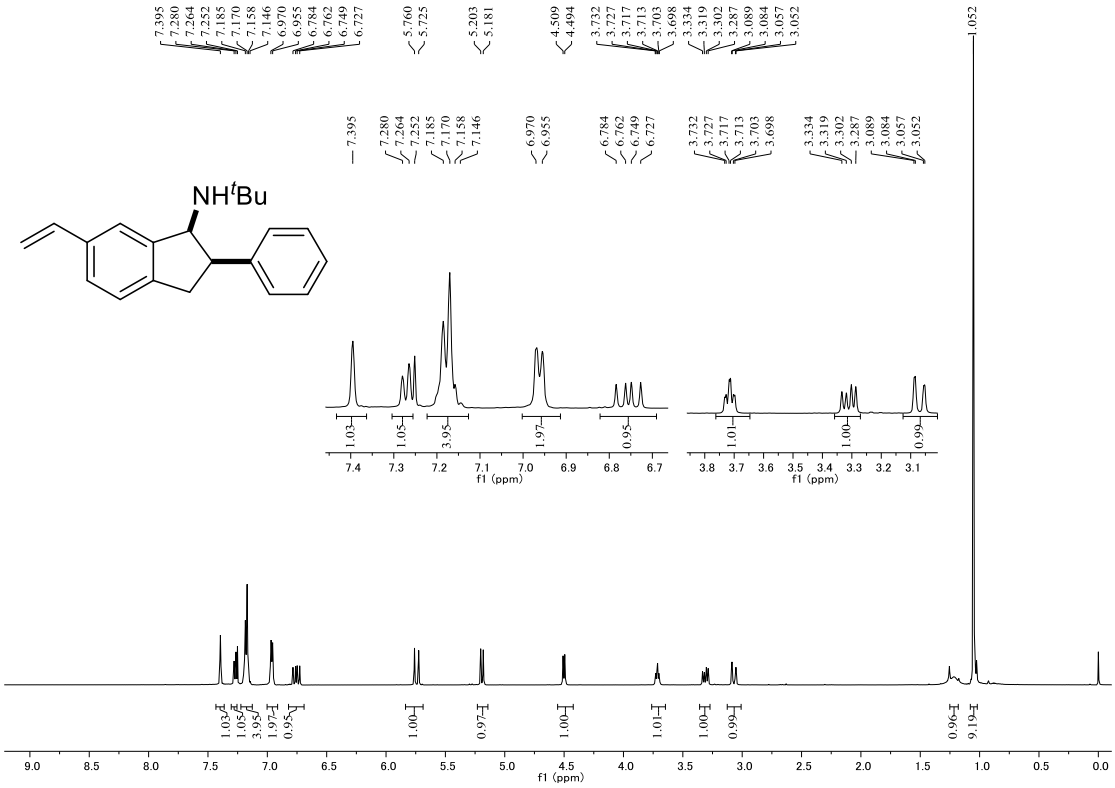
^{1}H NMR spectra of ***cis*-3ma** (500 MHz, $CDCl_3$)



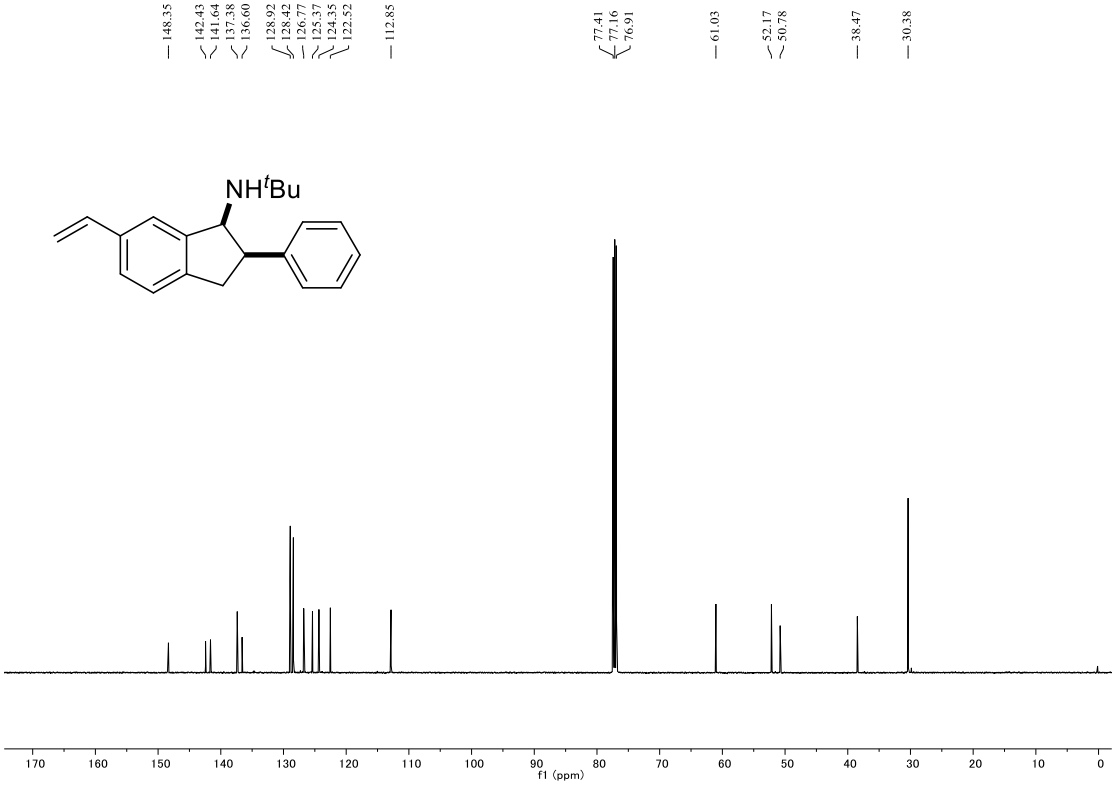
^{13}C NMR spectra of ***cis*-3ma** (126 MHz, $CDCl_3$)



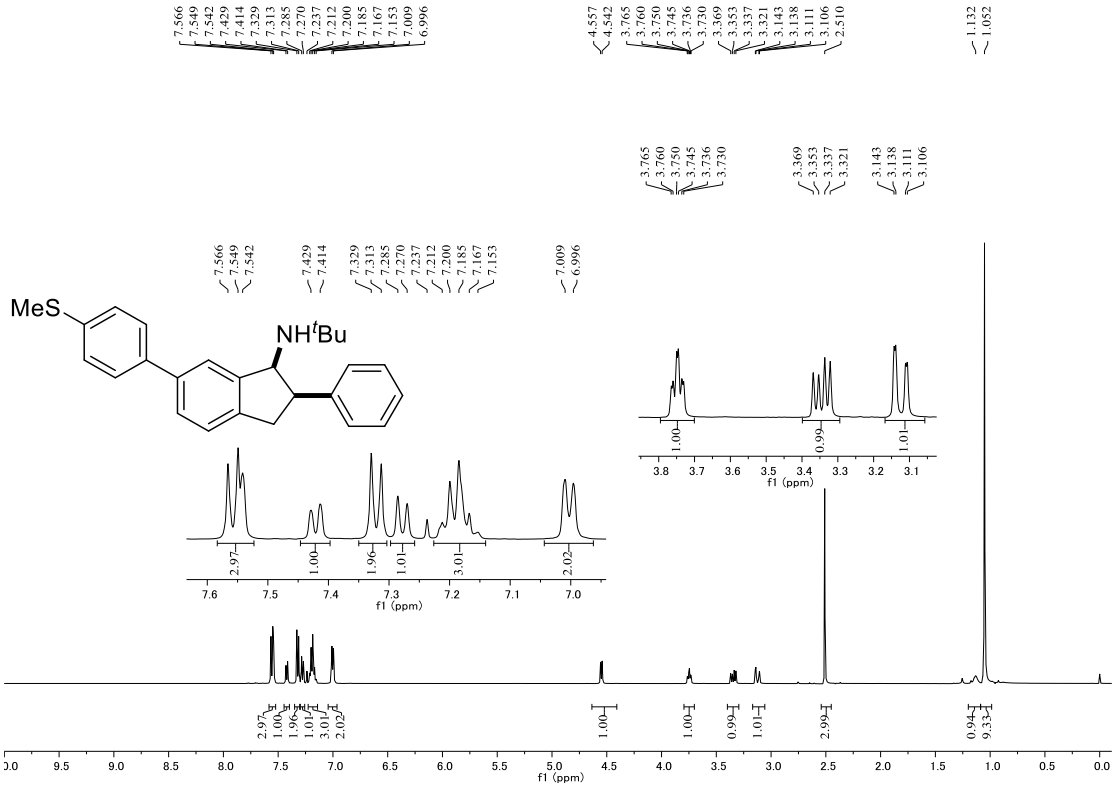
^{1}H NMR spectra of ***cis*-3na** (500 MHz, $CDCl_3$)



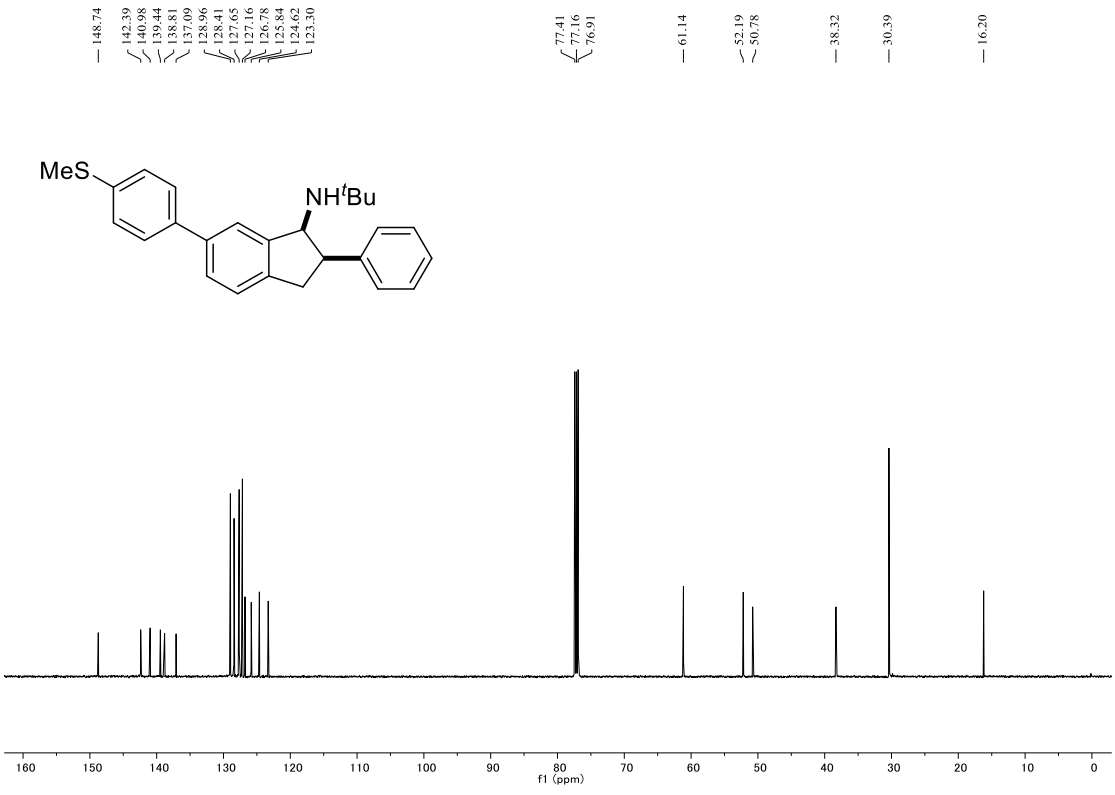
^{13}C NMR spectra of ***cis*-3na** (126 MHz, $CDCl_3$)



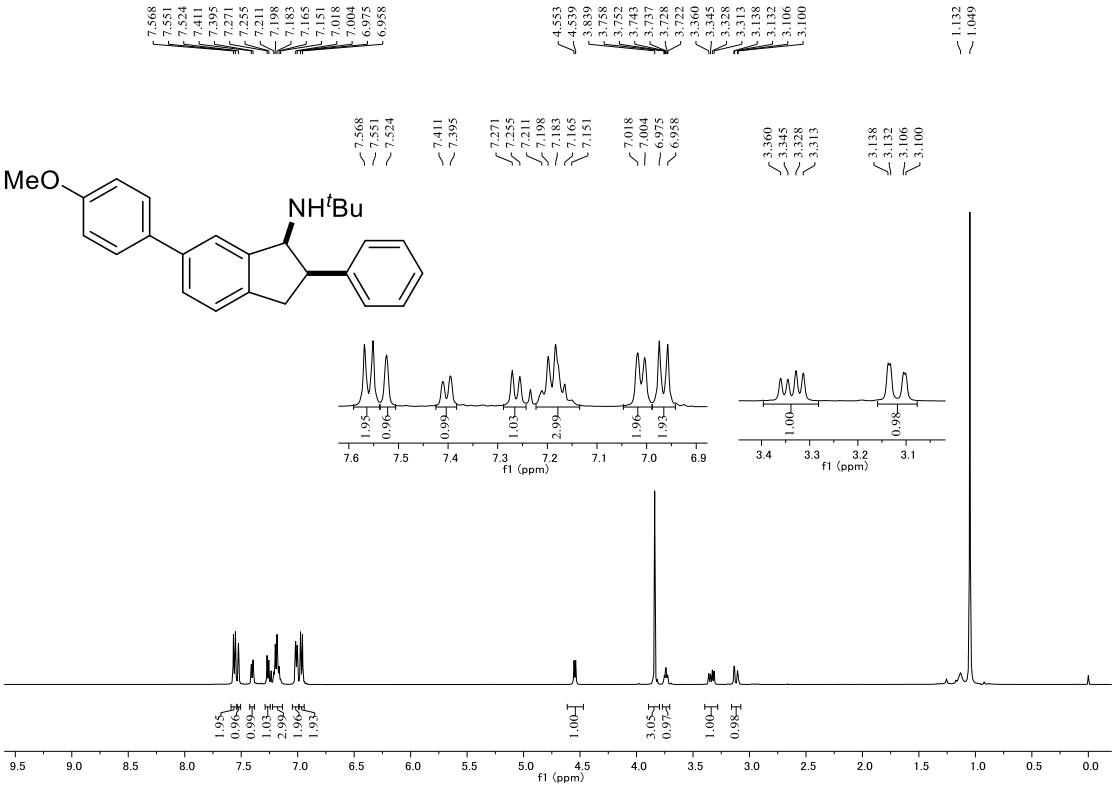
^{1}H NMR spectra of ***cis*-3oa** (500 MHz, $CDCl_3$)



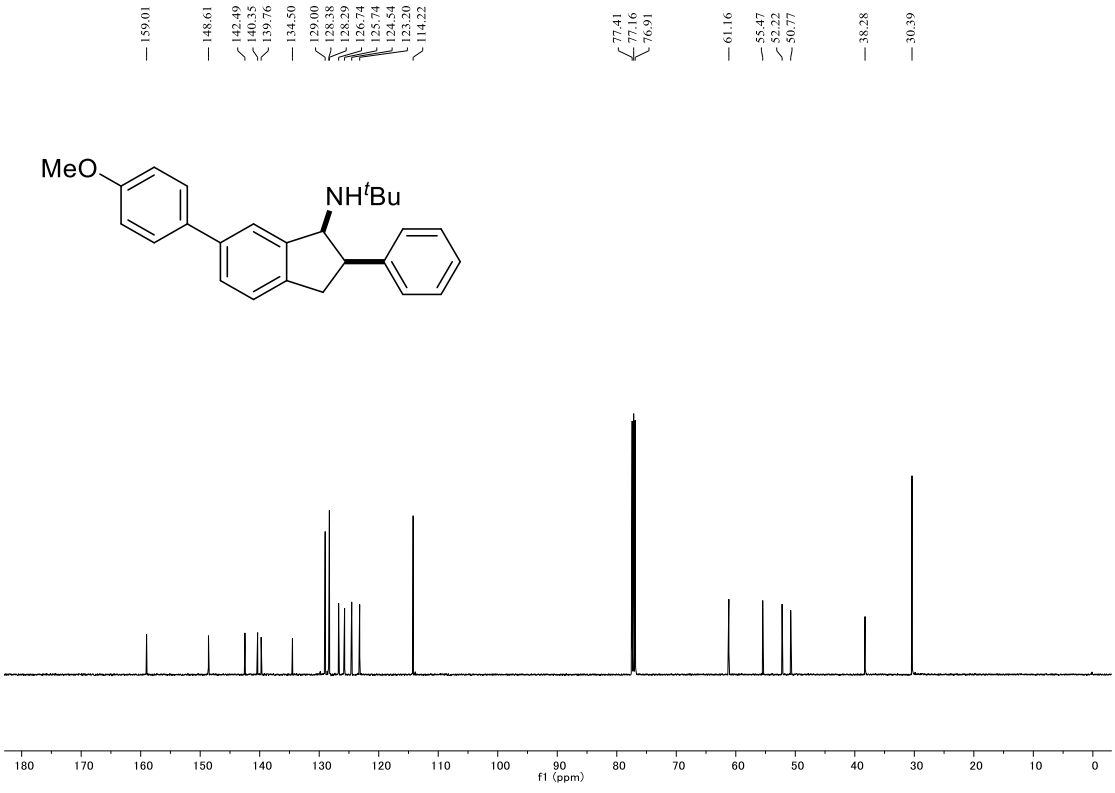
^{13}C NMR spectra of ***cis*-3oa** (126 MHz, $CDCl_3$)



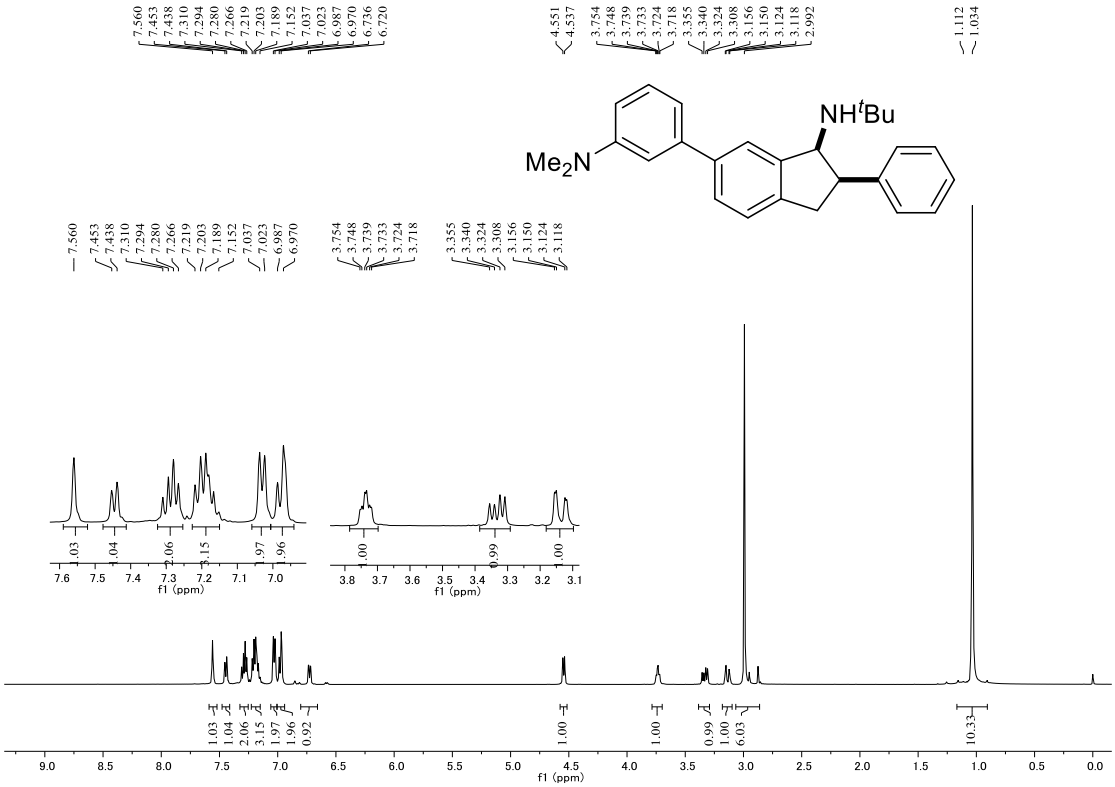
^{1}H NMR spectra of ***cis*-3pa** (500 MHz, $CDCl_3$)



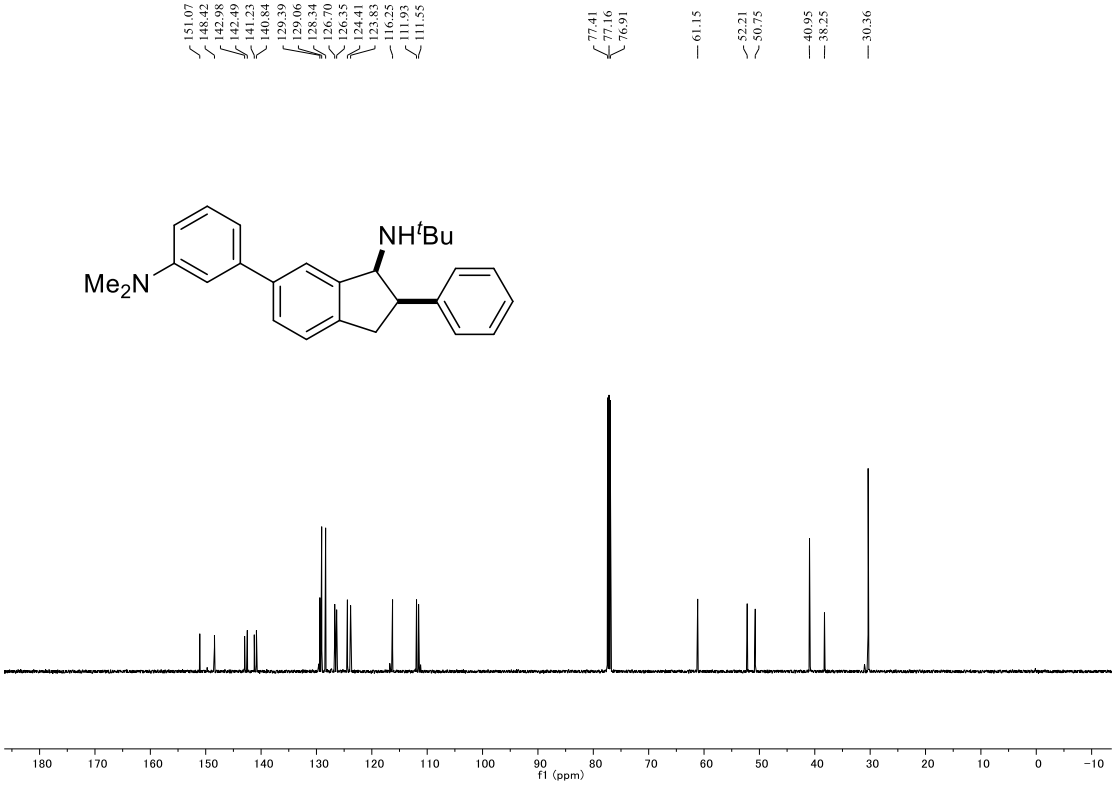
^{13}C NMR spectra of ***cis*-3pa** (126 MHz, $CDCl_3$)



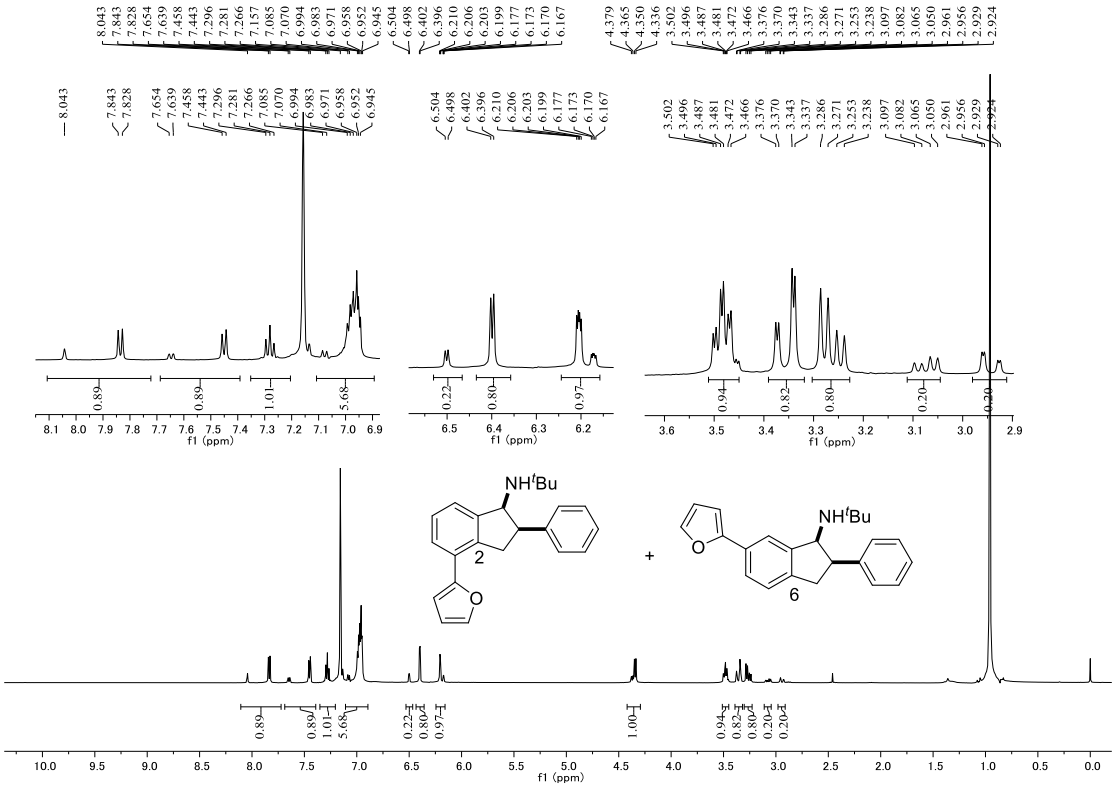
^{1}H NMR spectra of ***cis*-3qa** (500 MHz, $CDCl_3$)



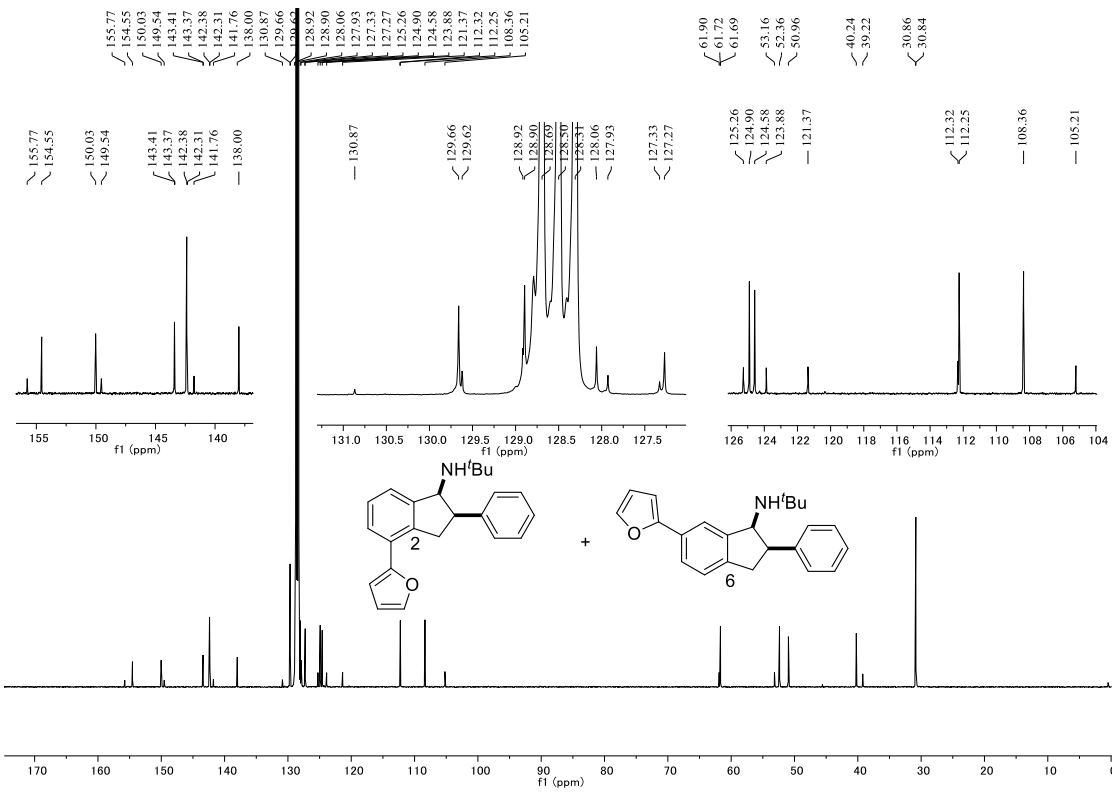
^{13}C NMR spectra of ***cis*-3qa** (126 MHz, $CDCl_3$)



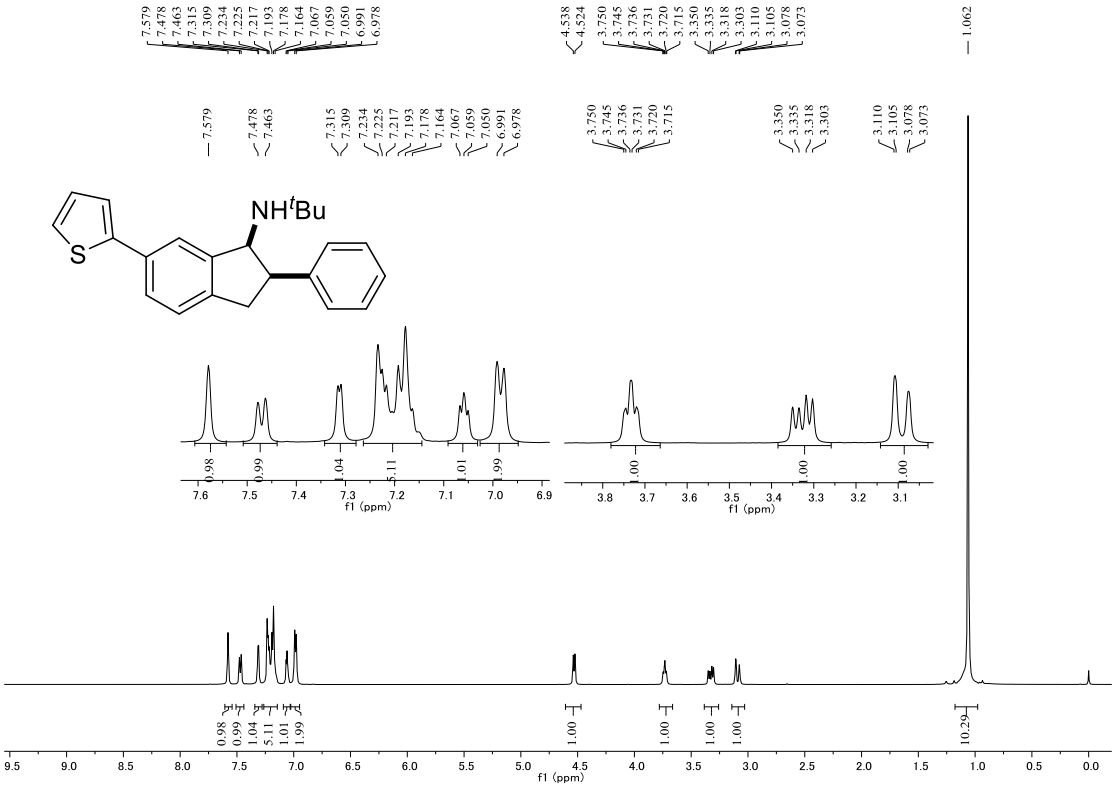
^{1}H NMR spectra of the mixture of ***cis*-3ra and *cis*-3ra′** (500 MHz, C_6D_6)



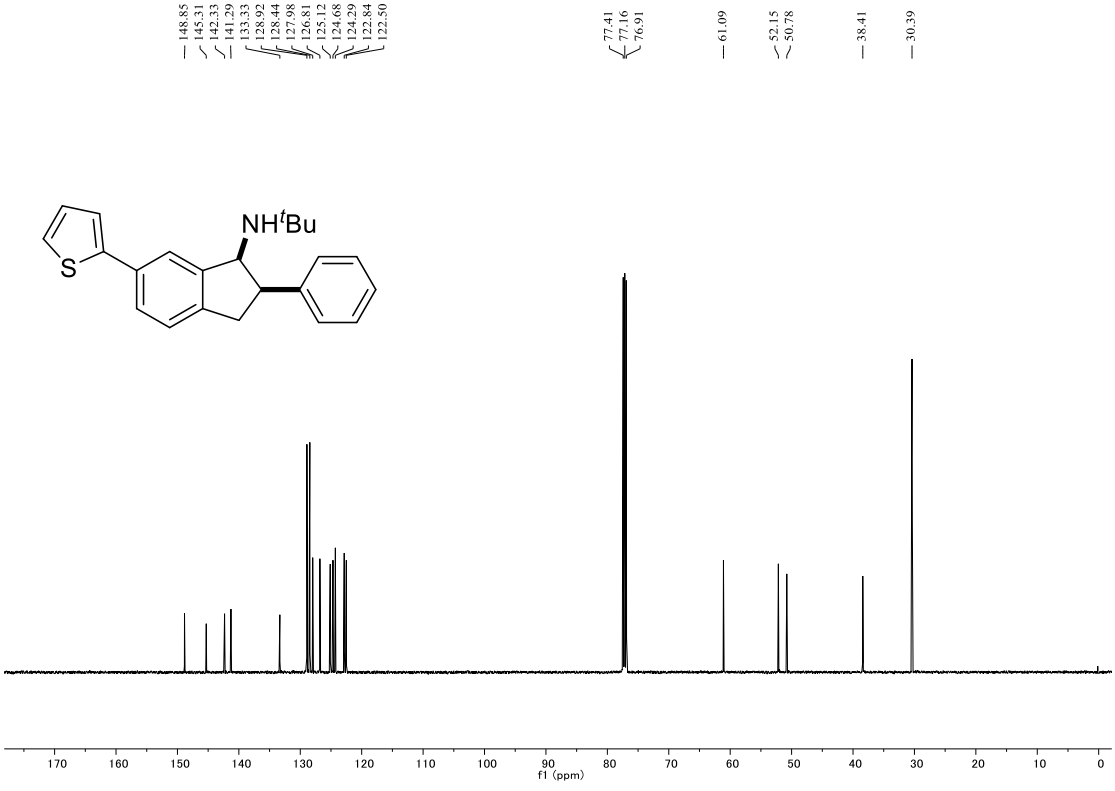
^{13}C NMR spectra of the mixture of ***cis*-3ra and *cis*-3ra′** (126 MHz, C_6D_6)



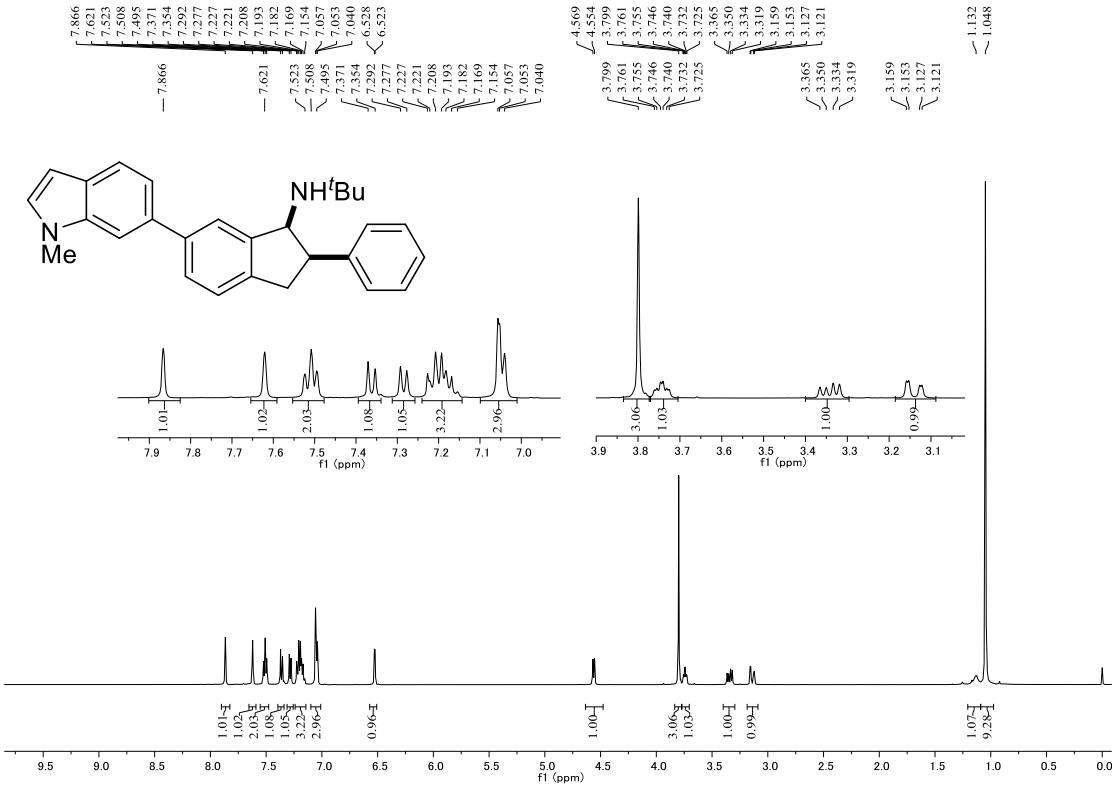
^{1}H NMR spectra of ***cis*-3sa** (500 MHz, $CDCl_3$)



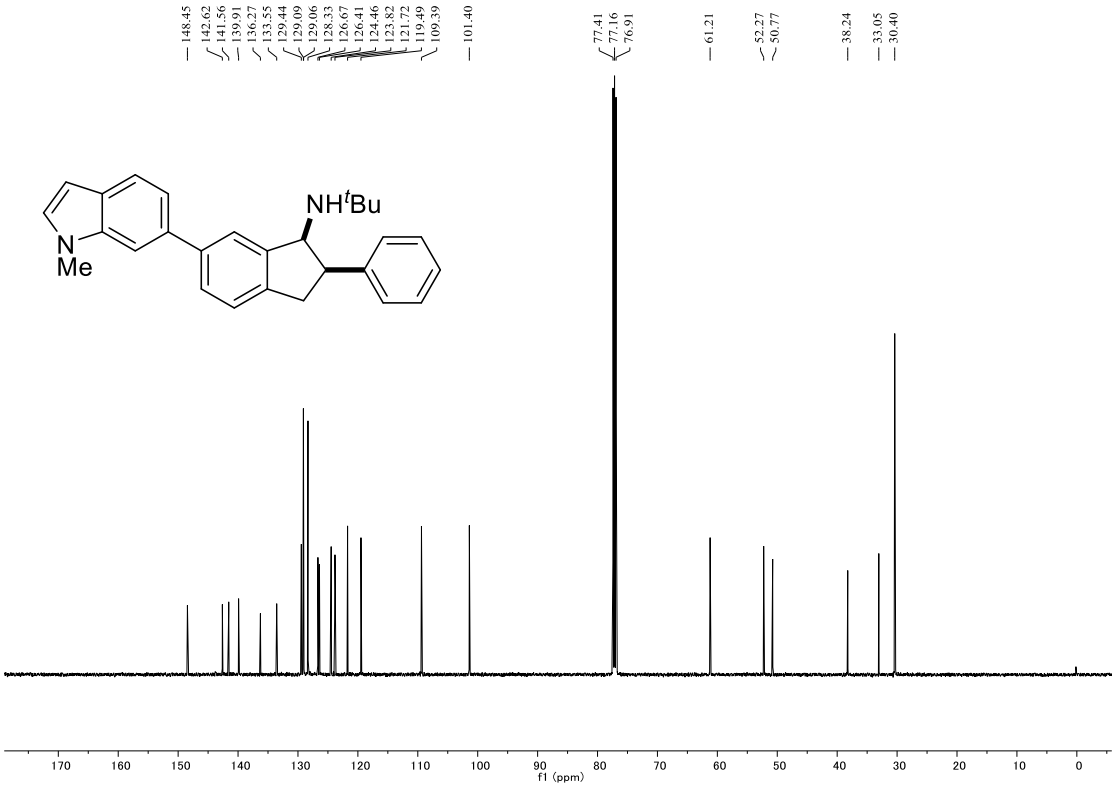
^{13}C NMR spectra of ***cis*-3sa** (126 MHz, $CDCl_3$)



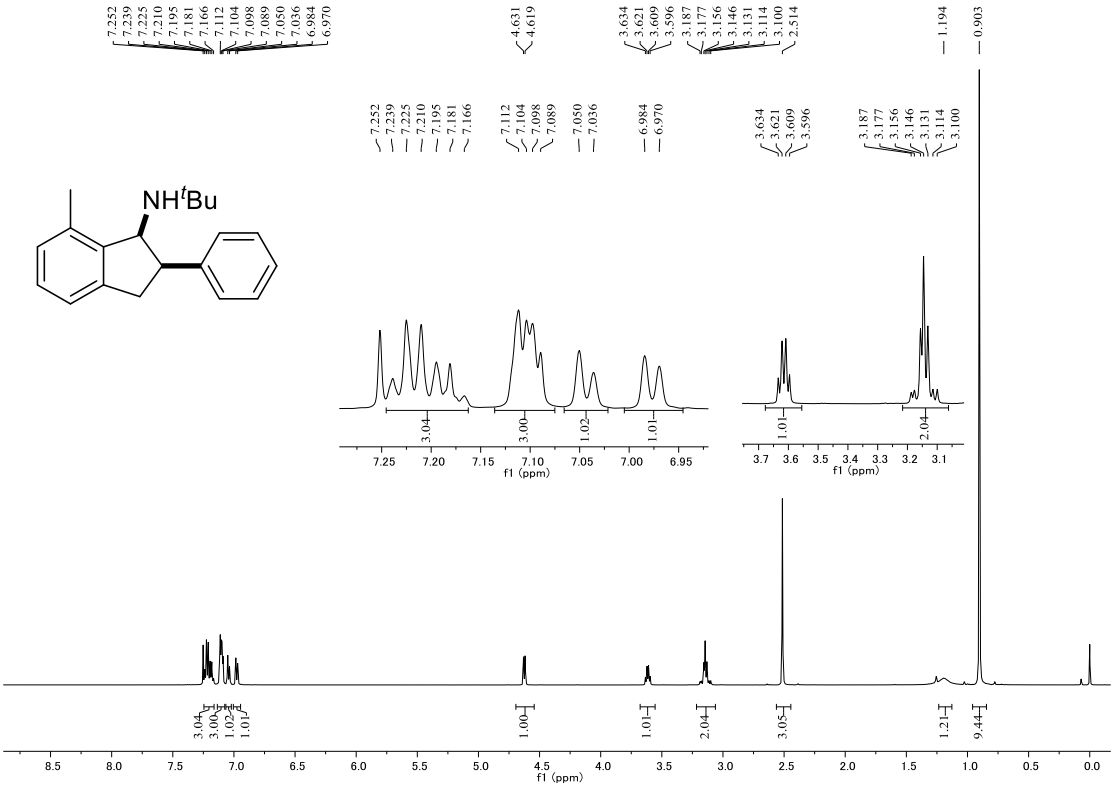
^{1}H NMR spectra of ***cis*-3ta** (500 MHz, $CDCl_3$)



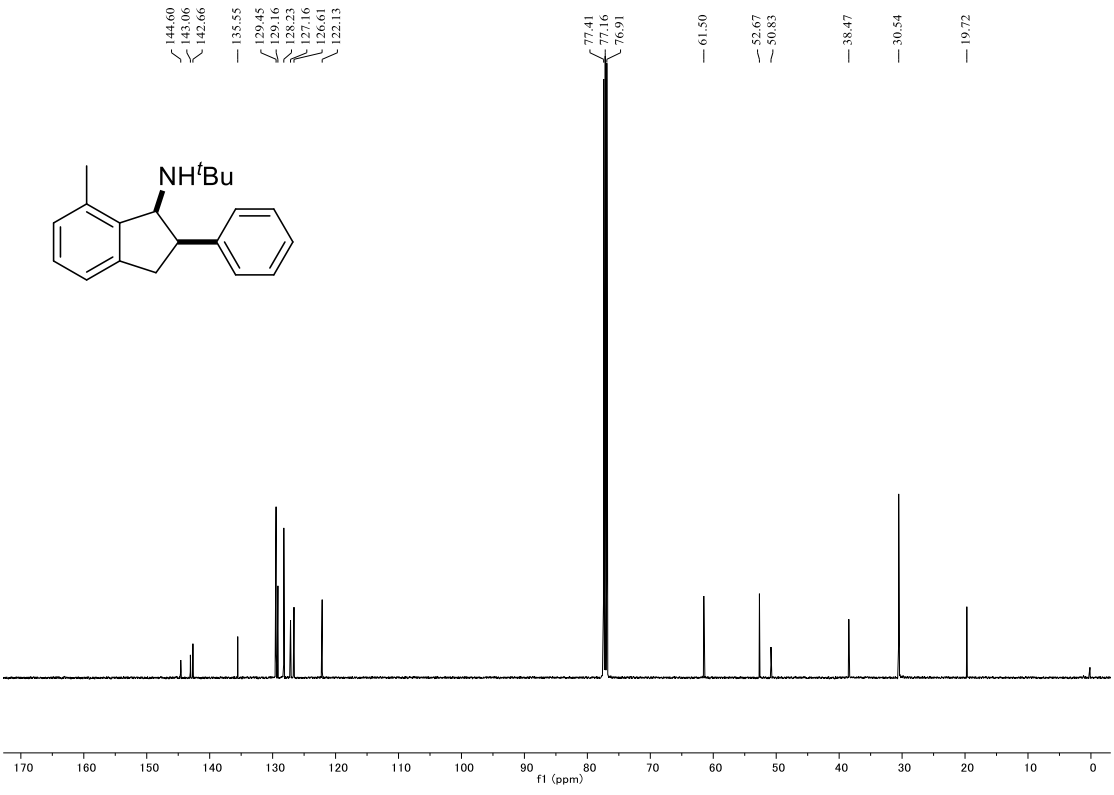
^{13}C NMR spectra of ***cis*-3ta** (126 MHz, $CDCl_3$)



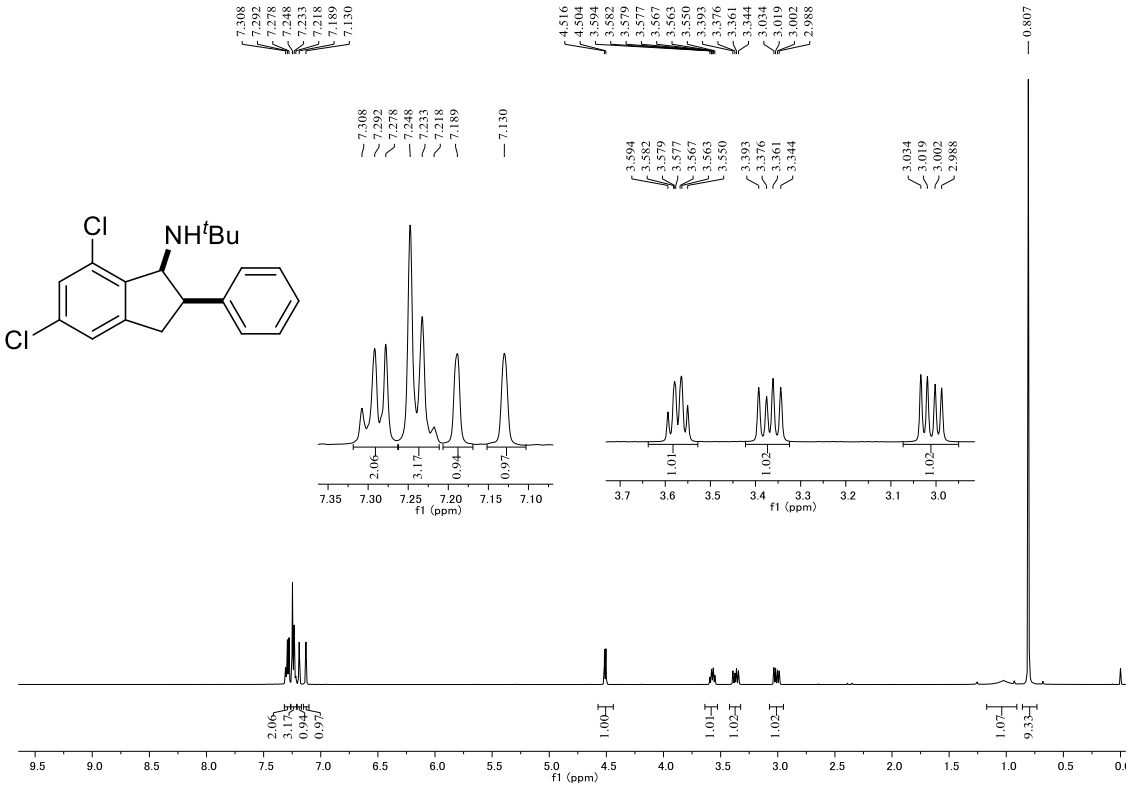
^{1}H NMR spectra of ***cis*-3ua** (500 MHz, $CDCl_3$)



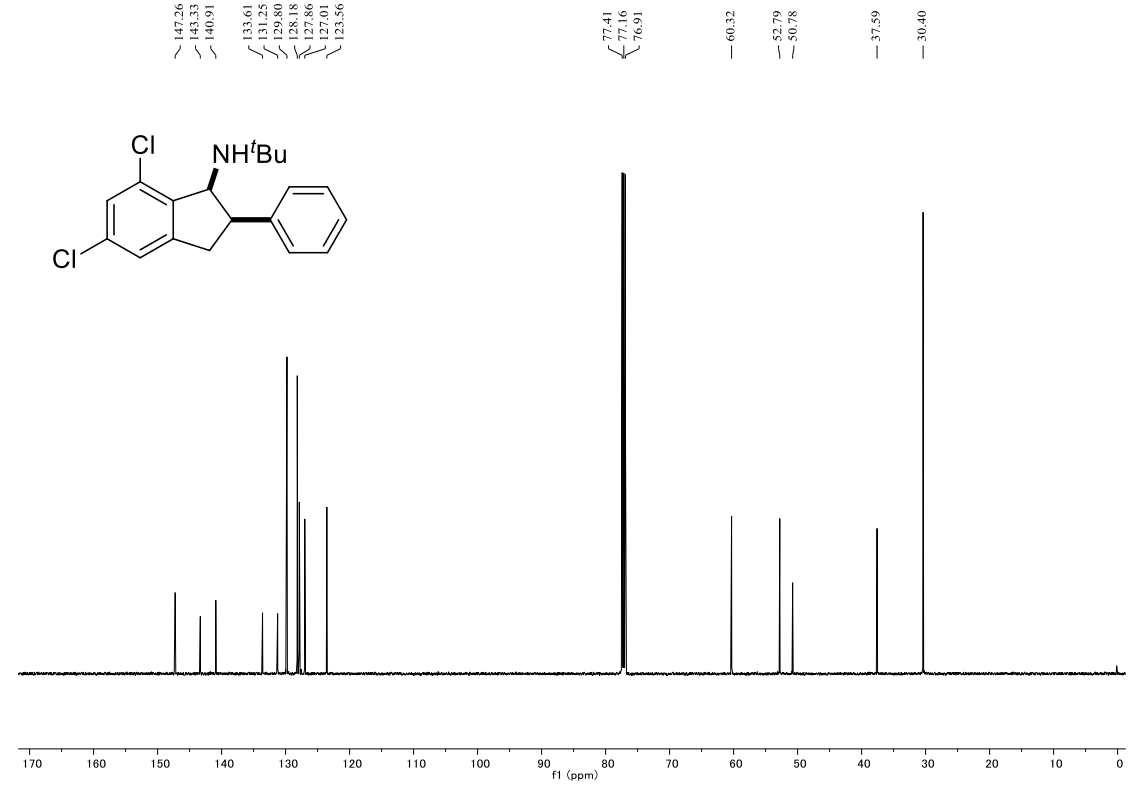
^{13}C NMR spectra of ***cis*-3ua** (126 MHz, $CDCl_3$)



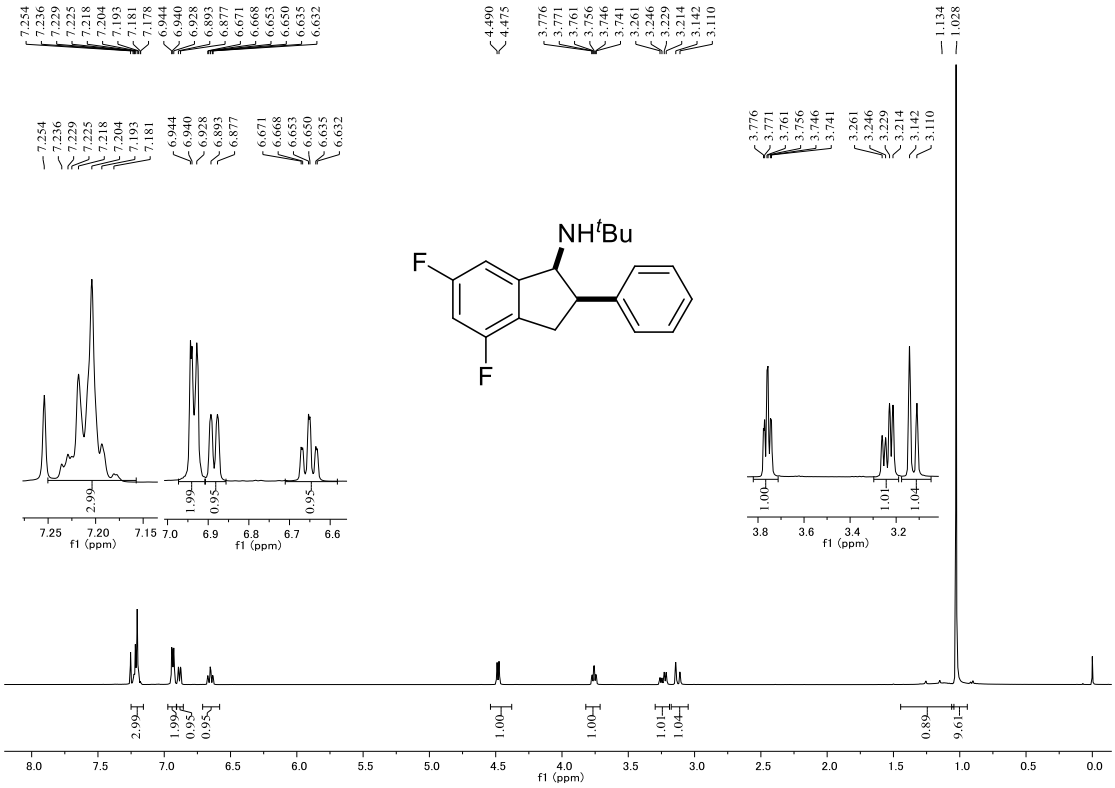
^{1}H NMR spectra of ***cis*-3va** (500 MHz, $CDCl_3$)



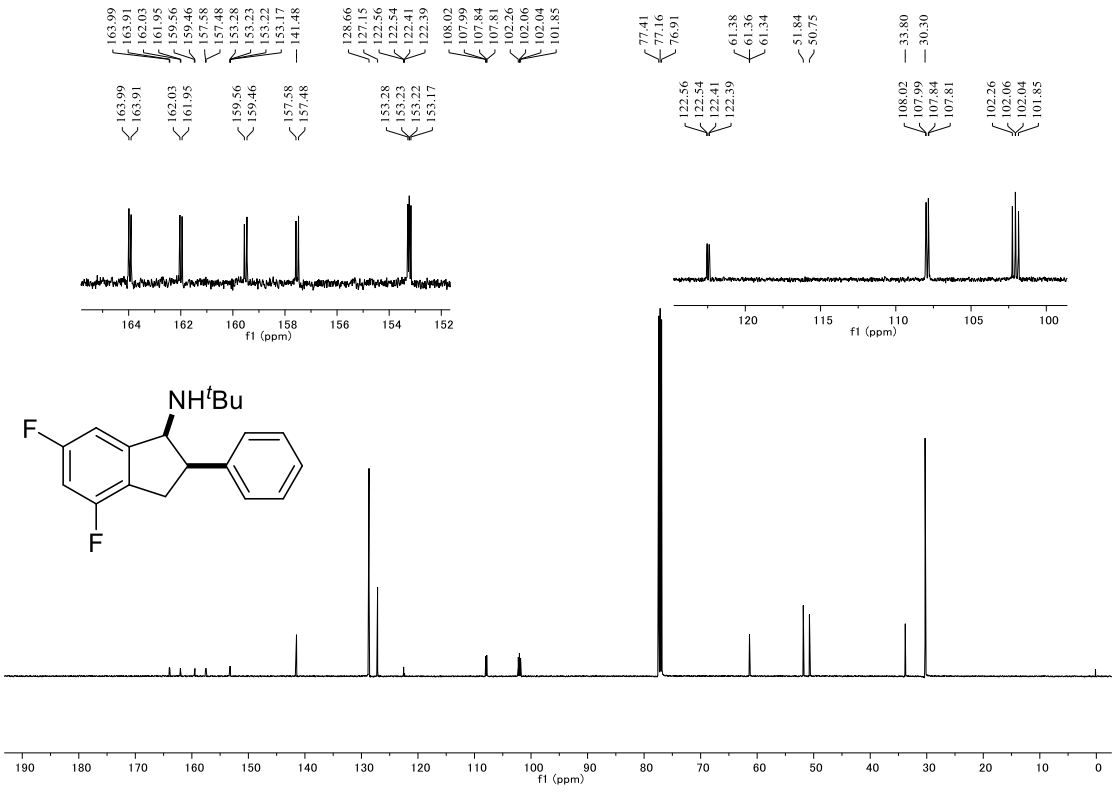
^{13}C NMR spectra of ***cis*-3va** (126 MHz, $CDCl_3$)



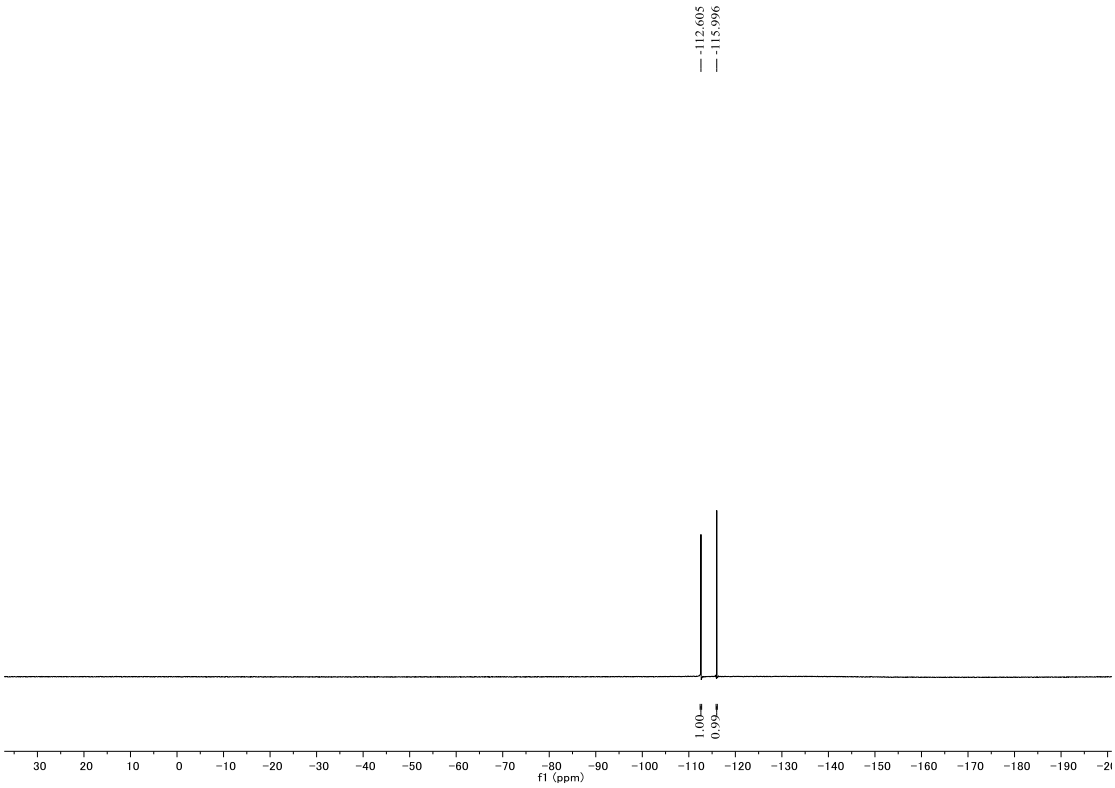
^{1}H NMR spectra of ***cis*-3wa** (500 MHz, $CDCl_3$)



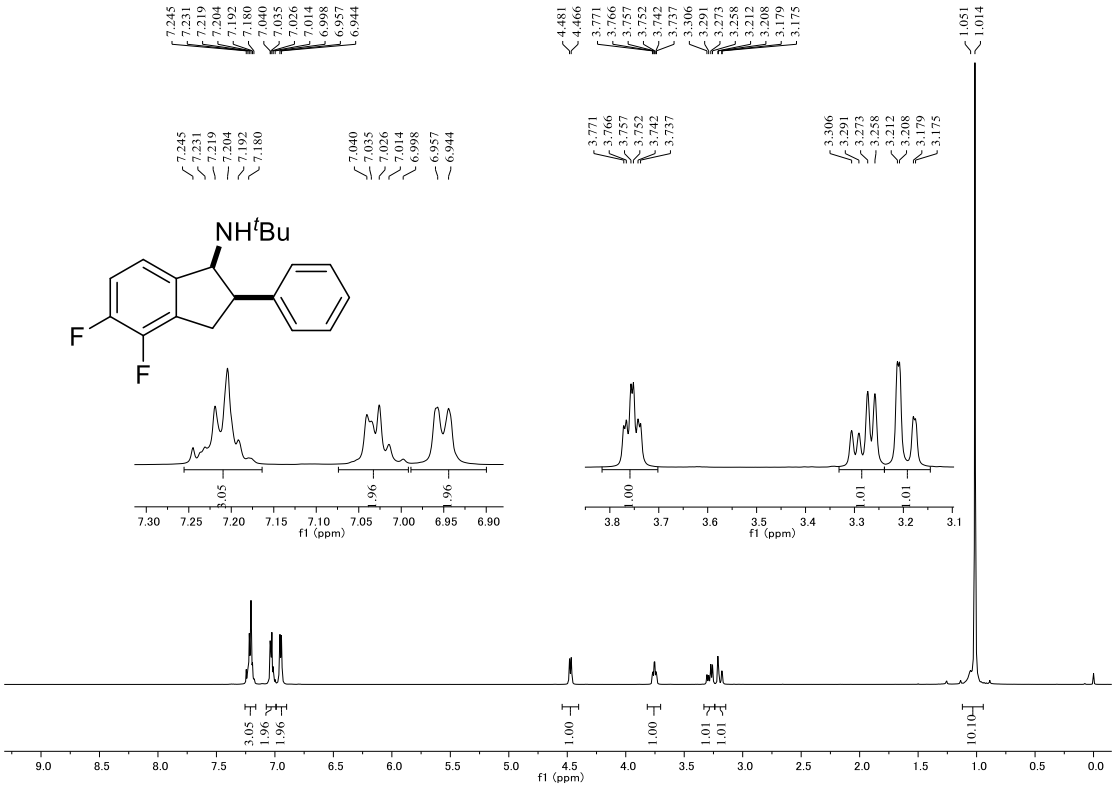
^{13}C NMR spectra of ***cis*-3wa** (126 MHz, $CDCl_3$)



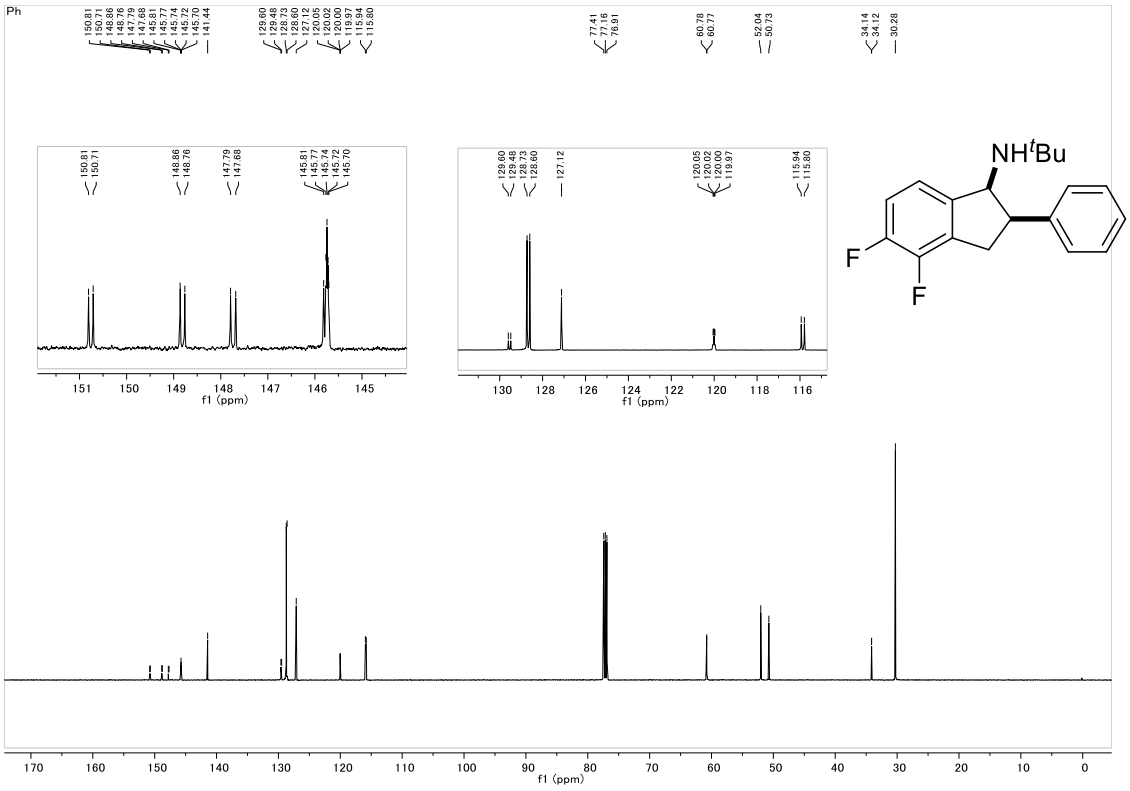
^{19}F NMR spectra of ***cis*-3wa** (377 MHz, $CDCl_3$)



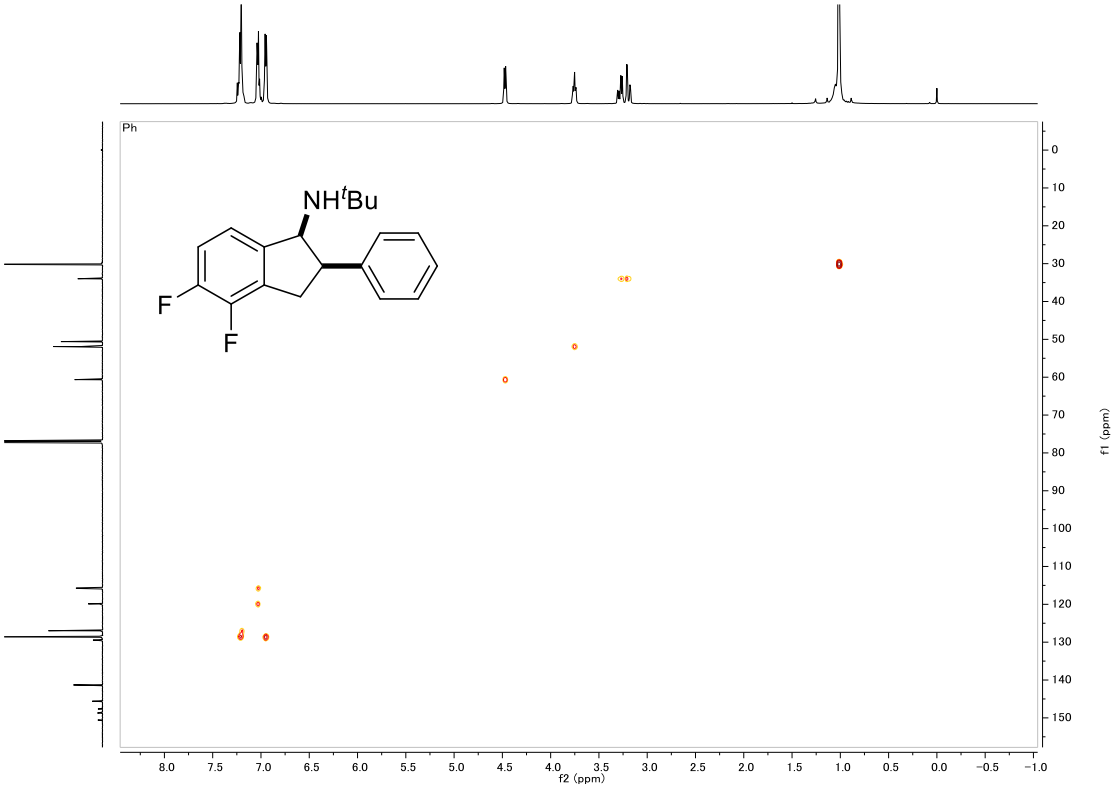
^{1}H NMR spectra of ***cis*-3xa** (500 MHz, $CDCl_3$)



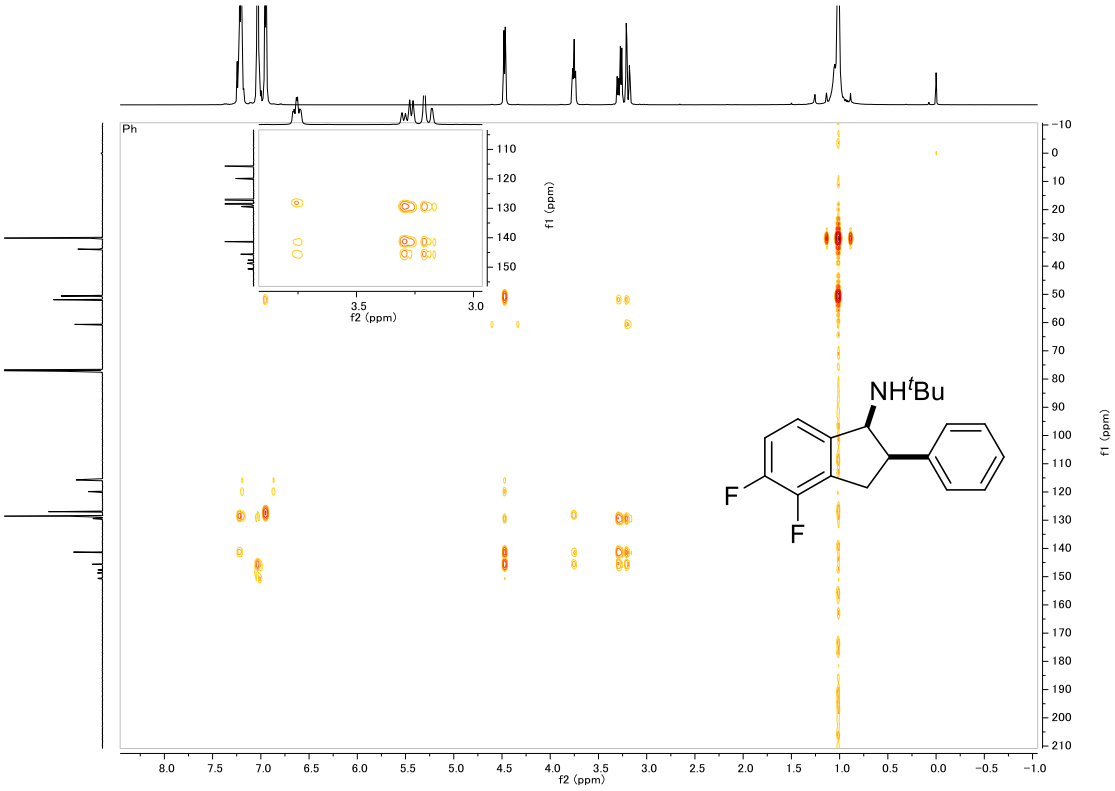
^{13}C NMR spectra of ***cis*-3xa** (126 MHz, $CDCl_3$)



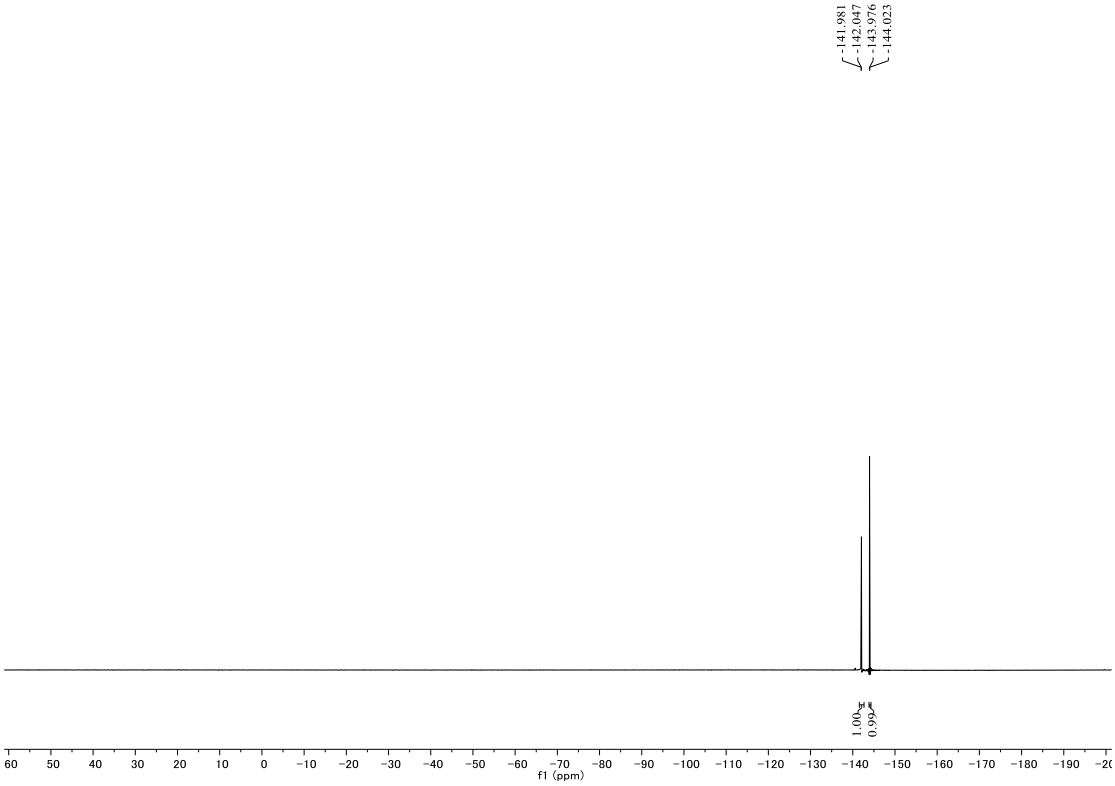
HSQC spectra of ***cis*-3xa** ($CDCl_3$)



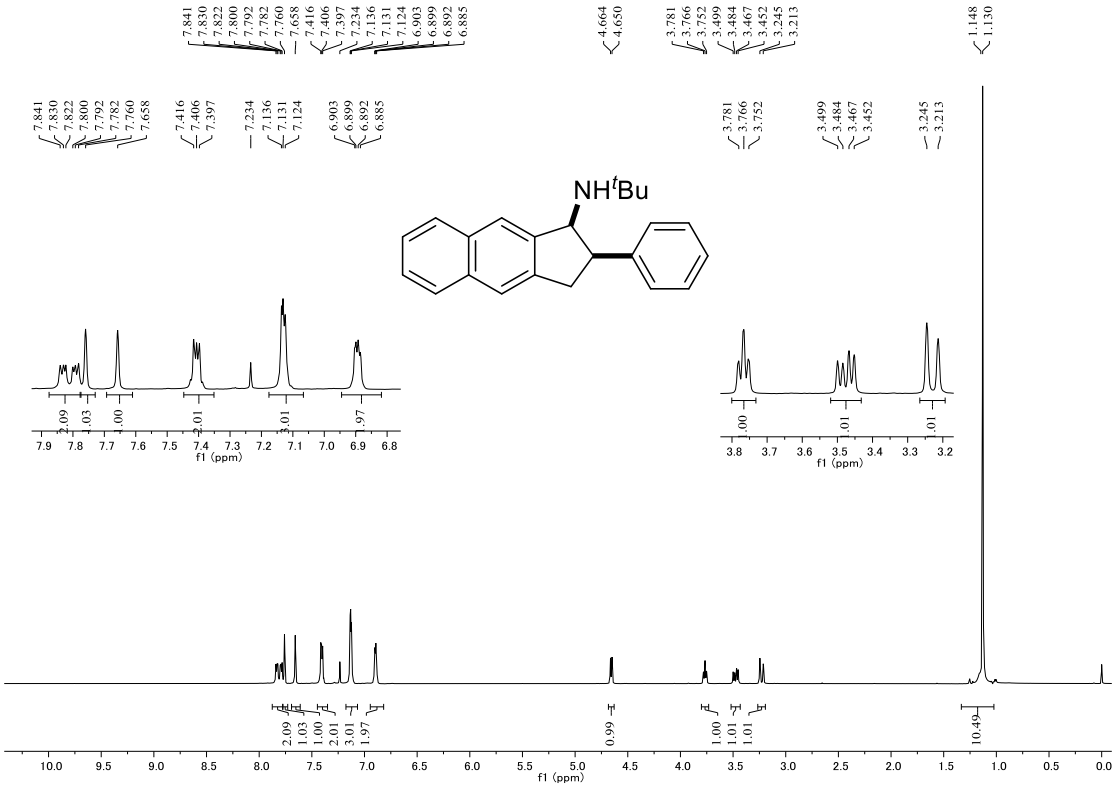
HMBC spectra of ***cis*-3xa** ($CDCl_3$)



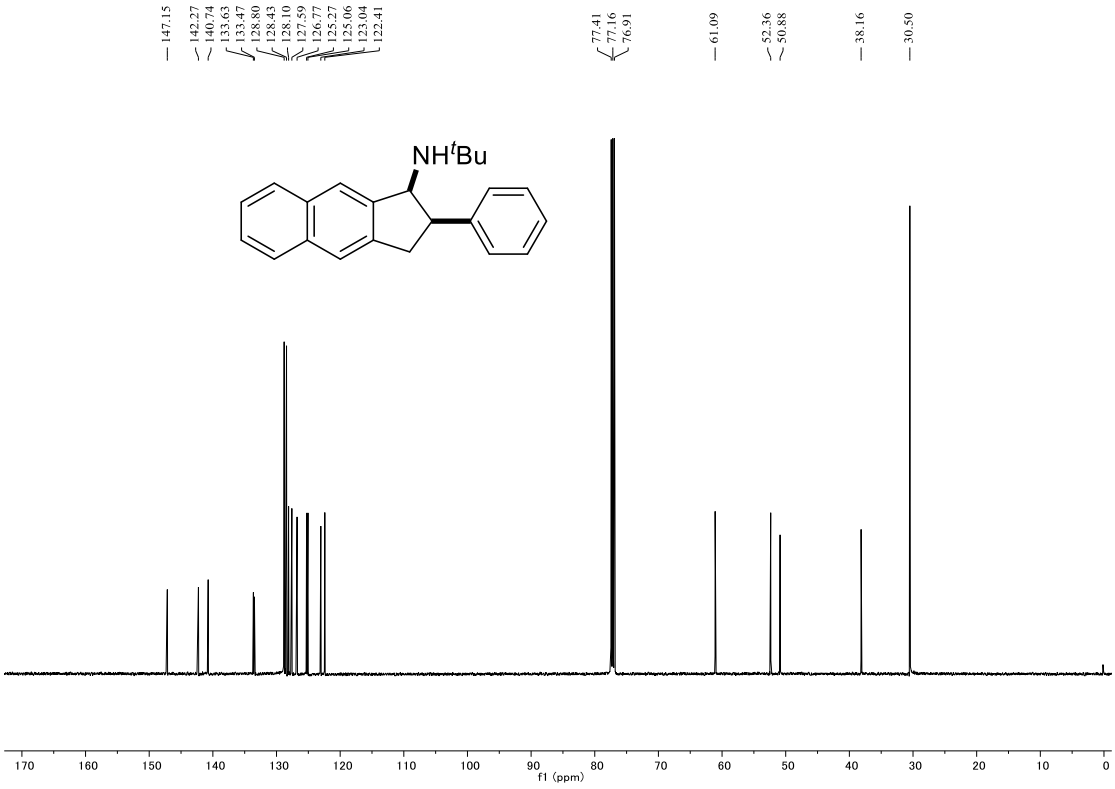
^{19}F NMR spectra of ***cis*-3xa** (377 MHz, $CDCl_3$)



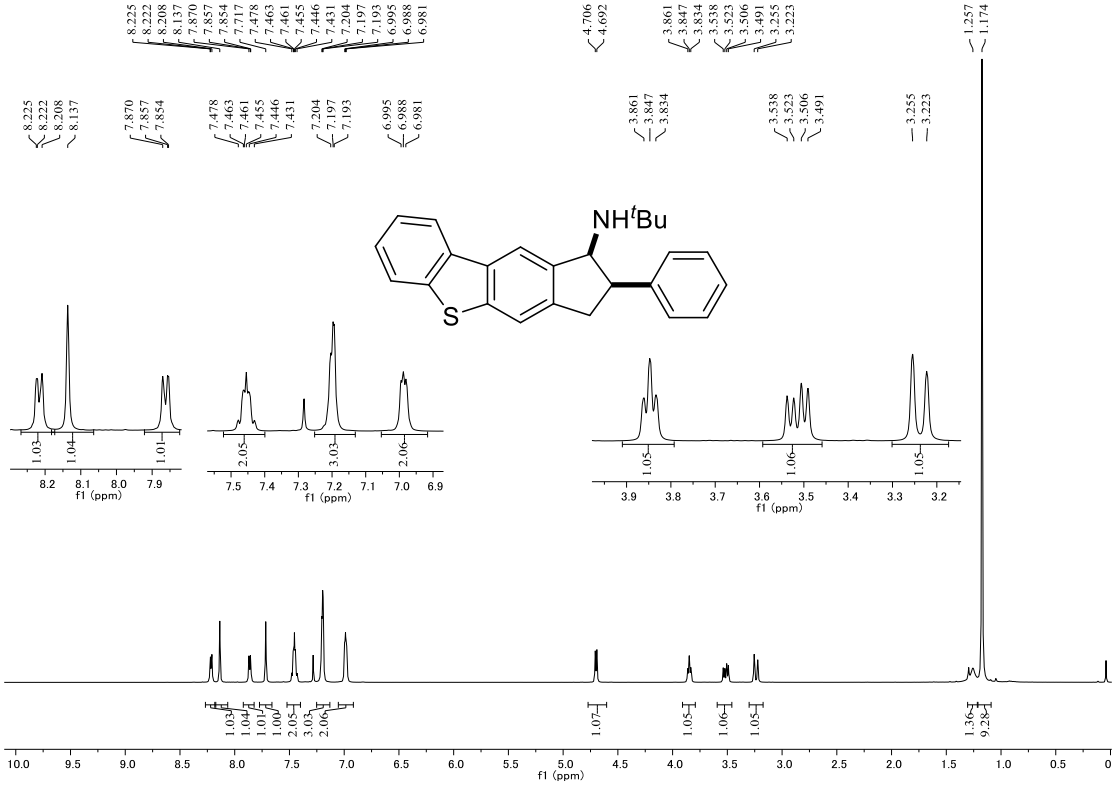
^{1}H NMR spectra of ***cis*-3ya** (500 MHz, $CDCl_3$)



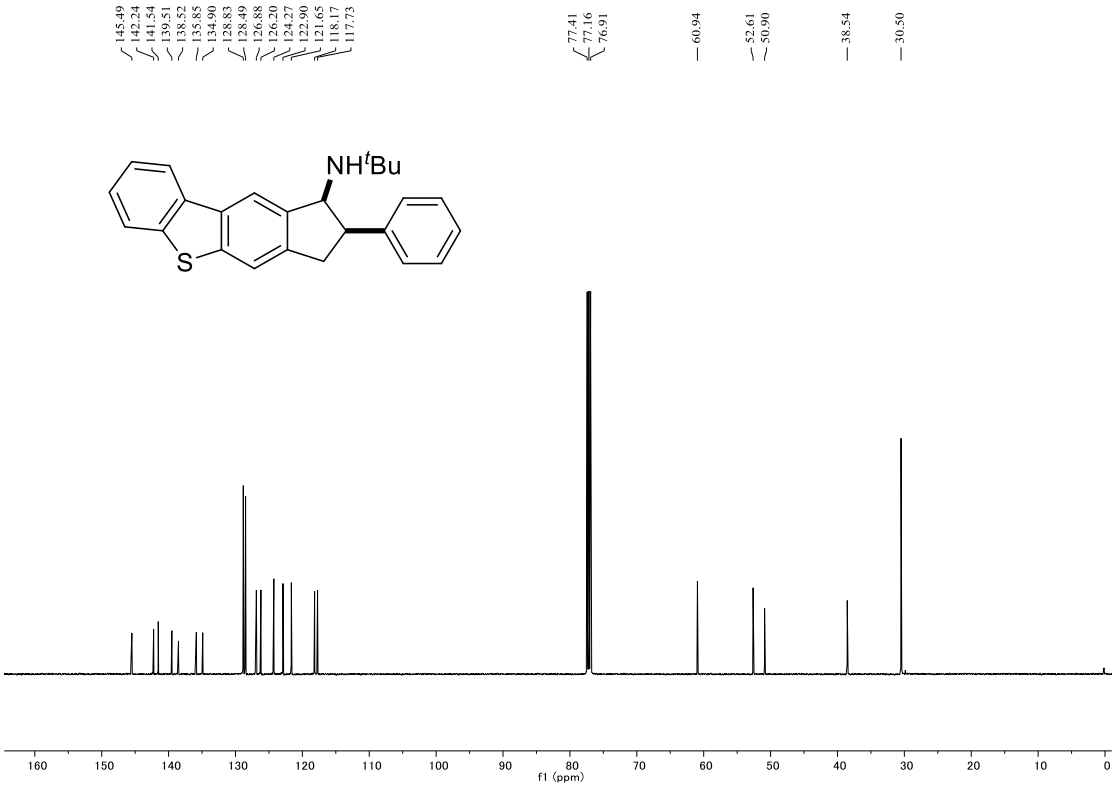
^{13}C NMR spectra of ***cis*-3ya** (126 MHz, $CDCl_3$)



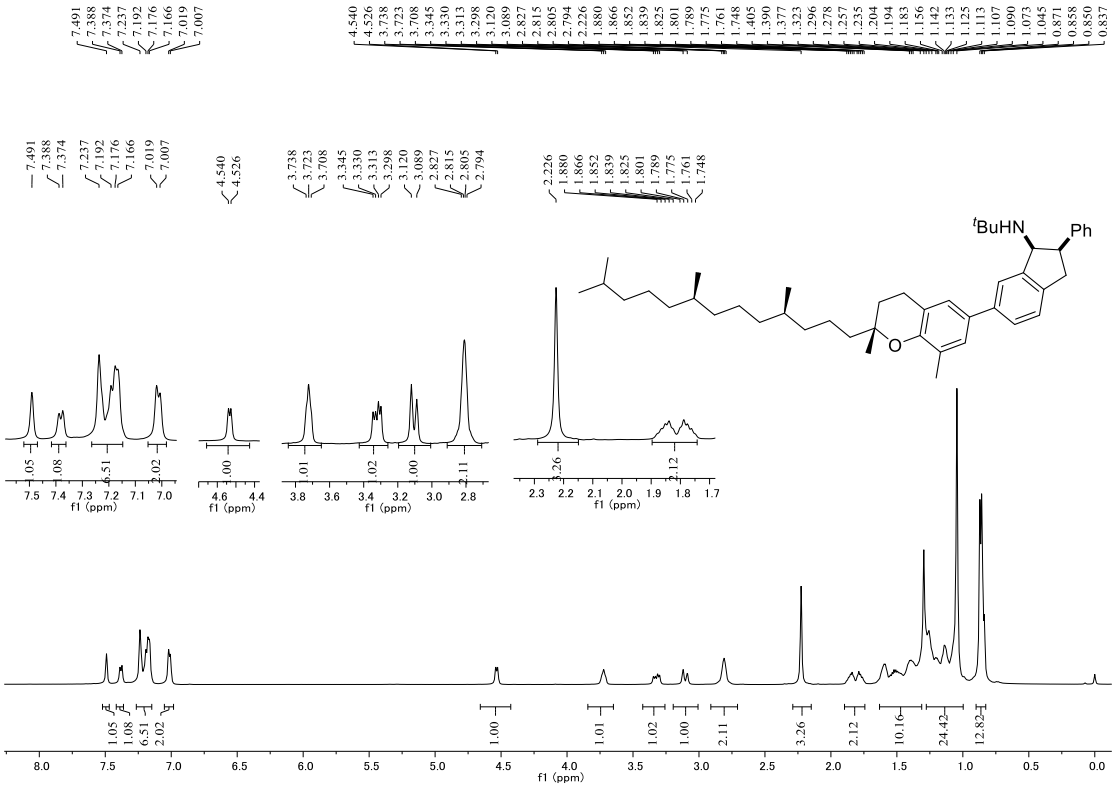
^{1}H NMR spectra of ***cis*-3za** (500 MHz, $CDCl_3$)



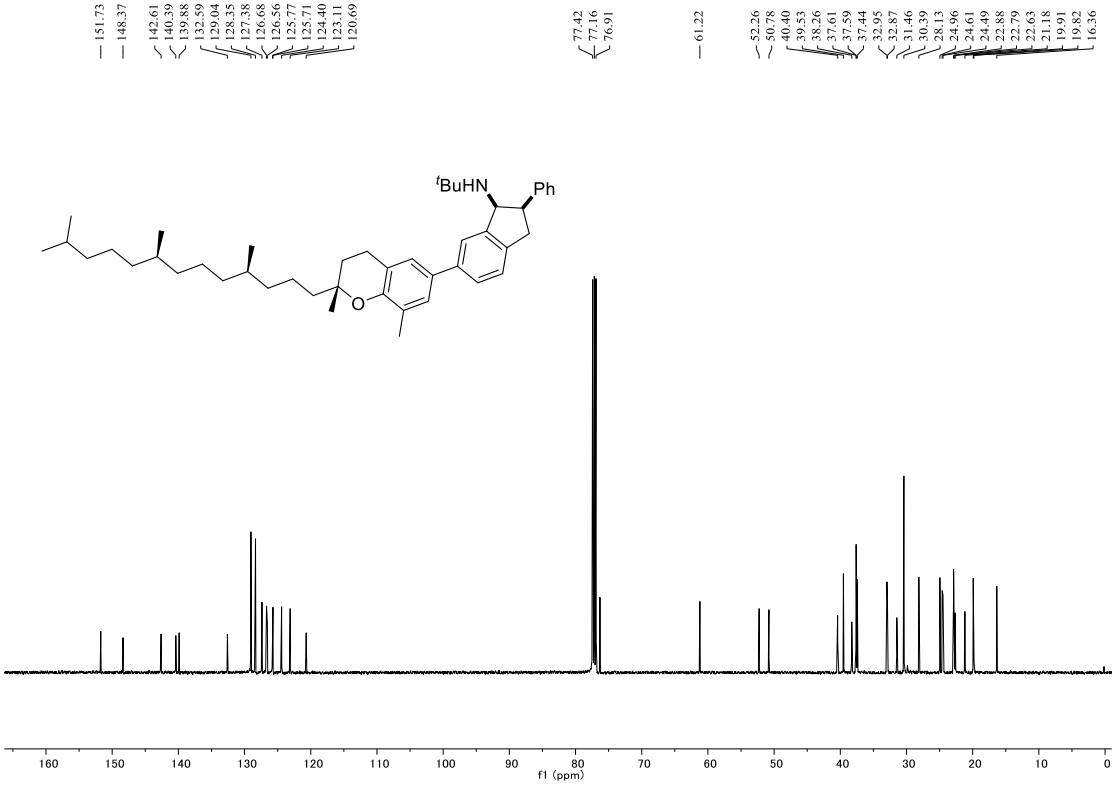
^{13}C NMR spectra of ***cis*-3za** (126 MHz, $CDCl_3$)



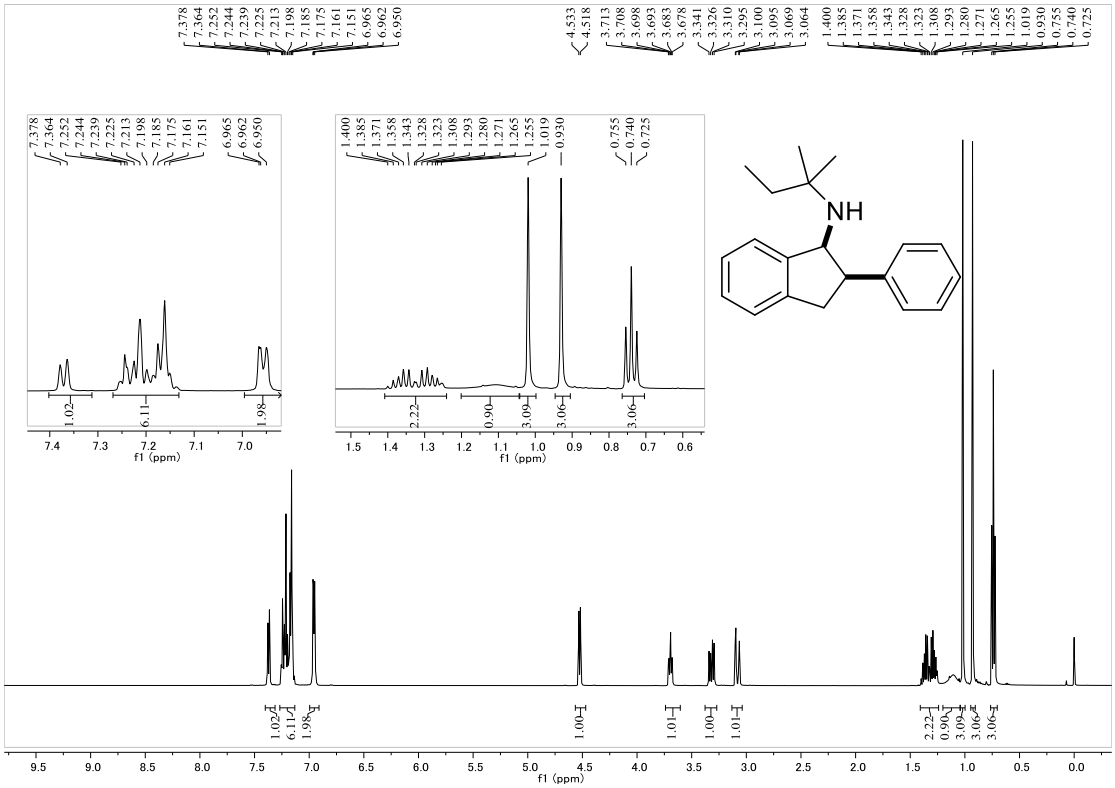
^{1}H NMR spectra of ***cis*-3aaa** (500 MHz, $CDCl_3$)



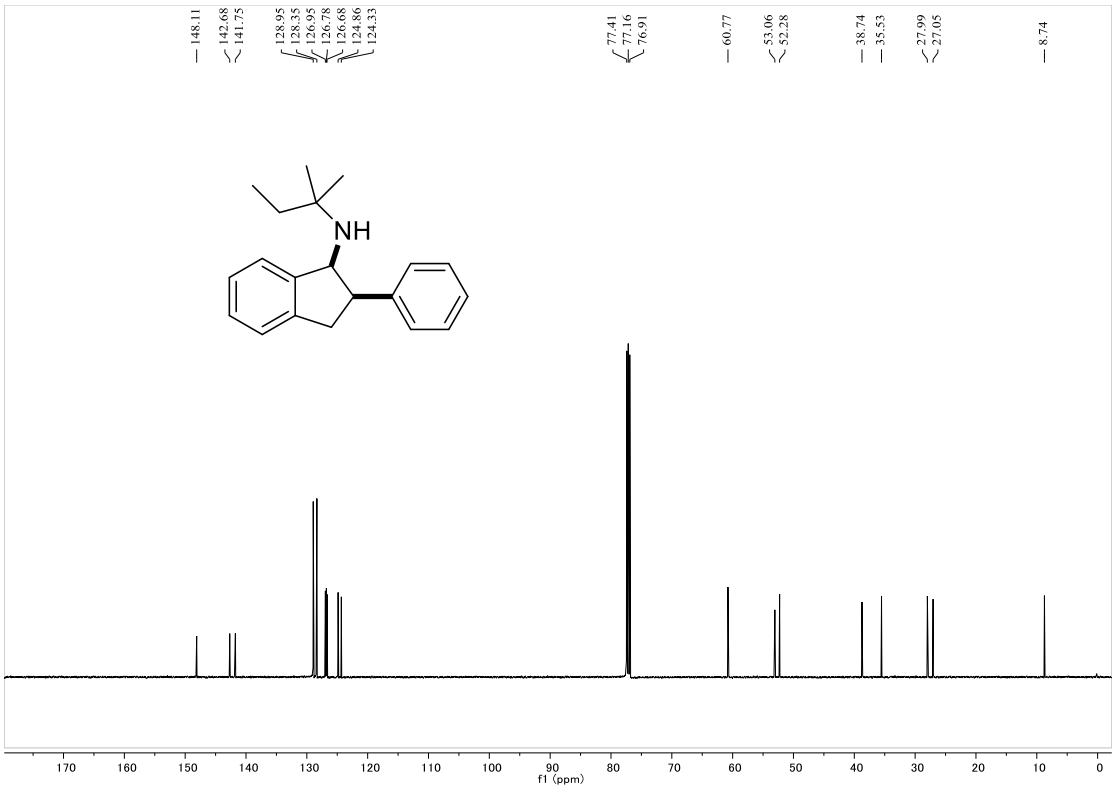
^{13}C NMR spectra of ***cis*-3aaa** (126 MHz, $CDCl_3$)



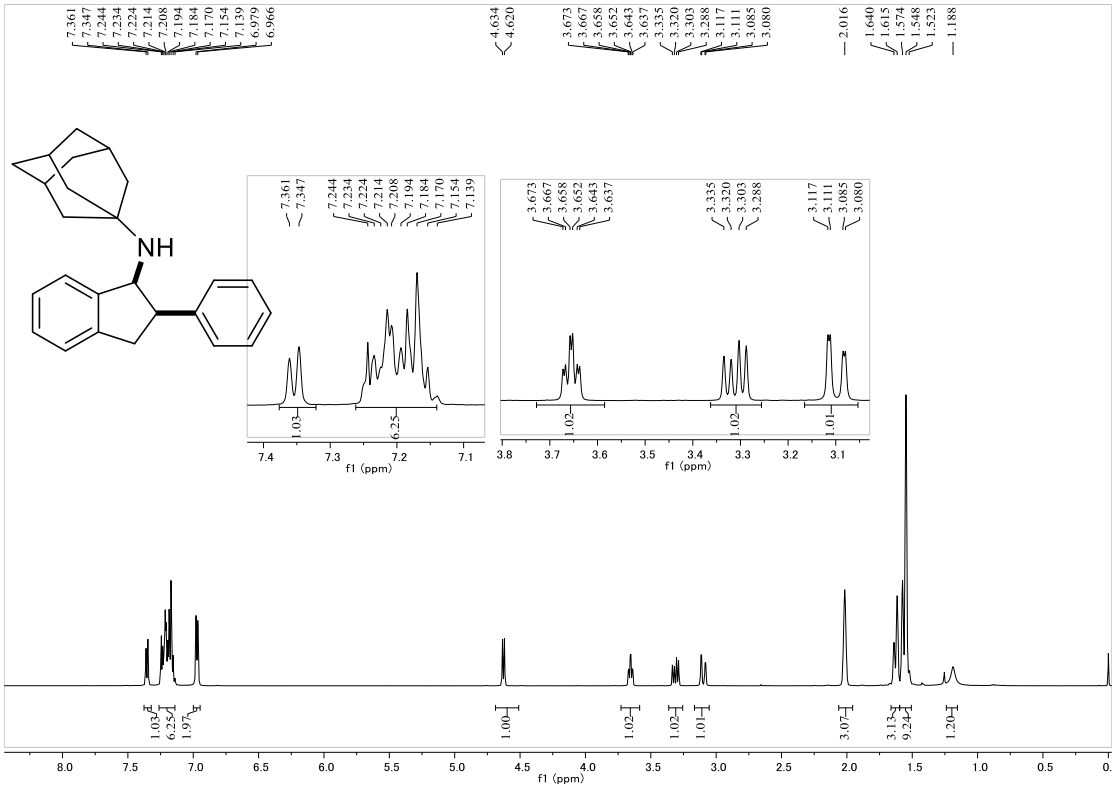
^{1}H NMR spectra of ***cis*-3aba** (500 MHz, $CDCl_3$)



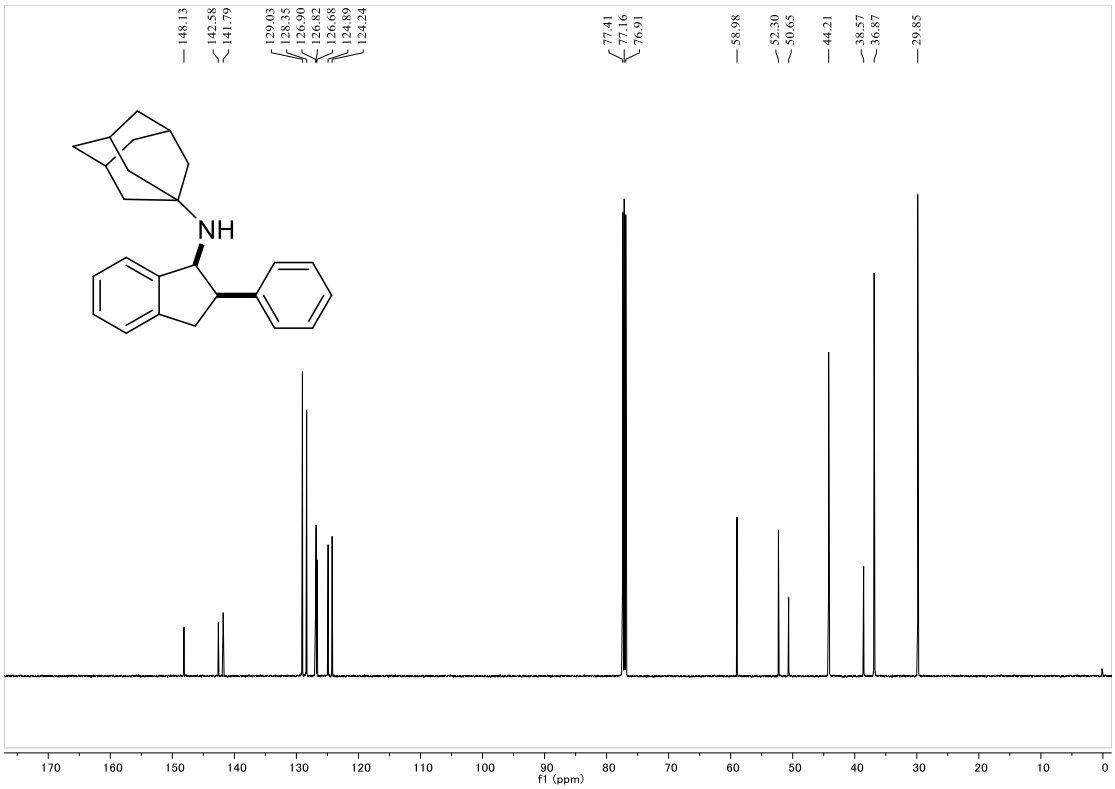
^{13}C NMR spectra of ***cis*-3aba** (126 MHz, $CDCl_3$)



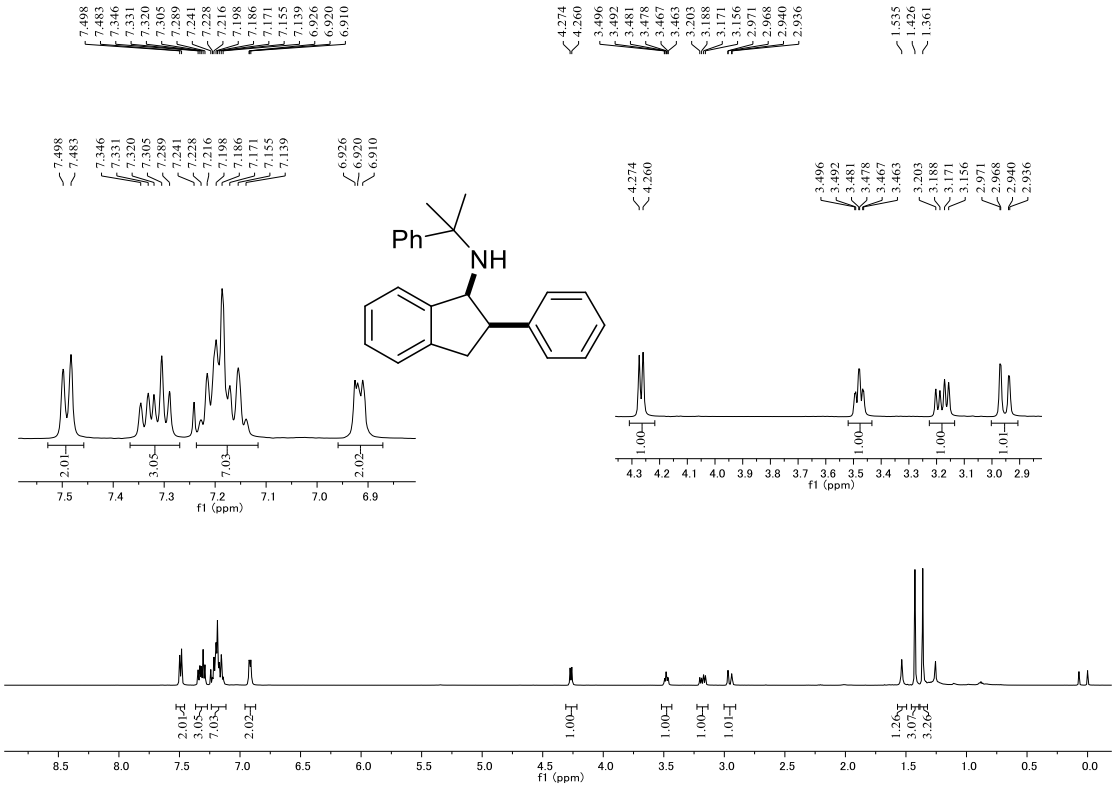
^{1}H NMR spectra of ***cis*-3aca** (500 MHz, $CDCl_3$)



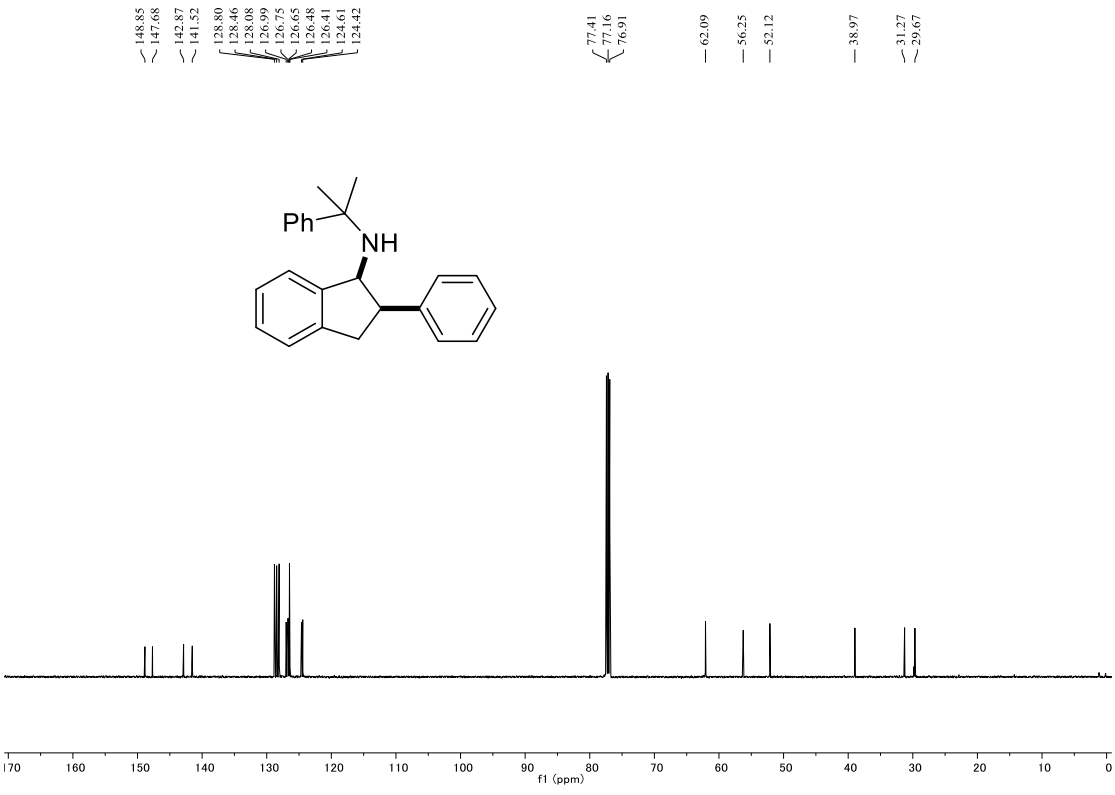
^{13}C NMR spectra of ***cis*-3aca** (126 MHz, $CDCl_3$)



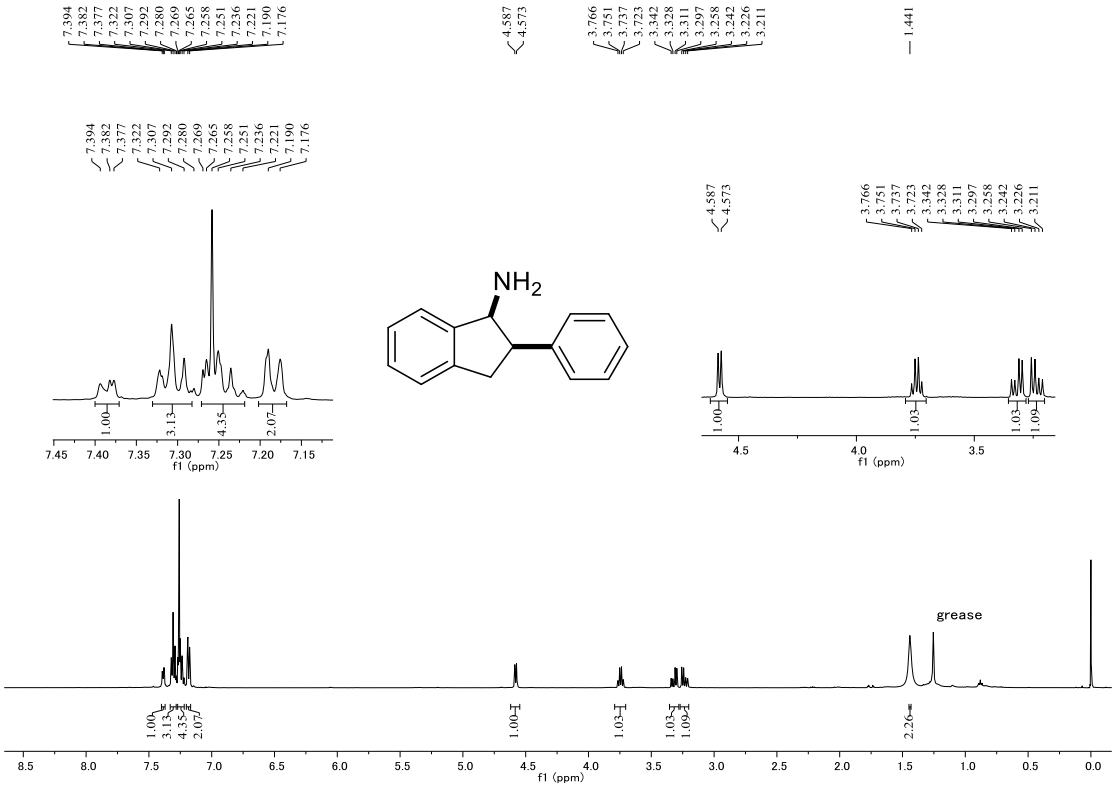
^{1}H NMR spectra of ***cis*-3aea** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of ***cis*-3aea** (126 MHz, $CDCl_3$)



^{1}H NMR spectra of ***cis*-4aa** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of ***cis*-4aa** (126 MHz, $CDCl_3$)