Supporting Information for:

Nickel(I)-catalyzed (de)hydrogenative coupling of amines and alkyl heteroarenes with alcohols

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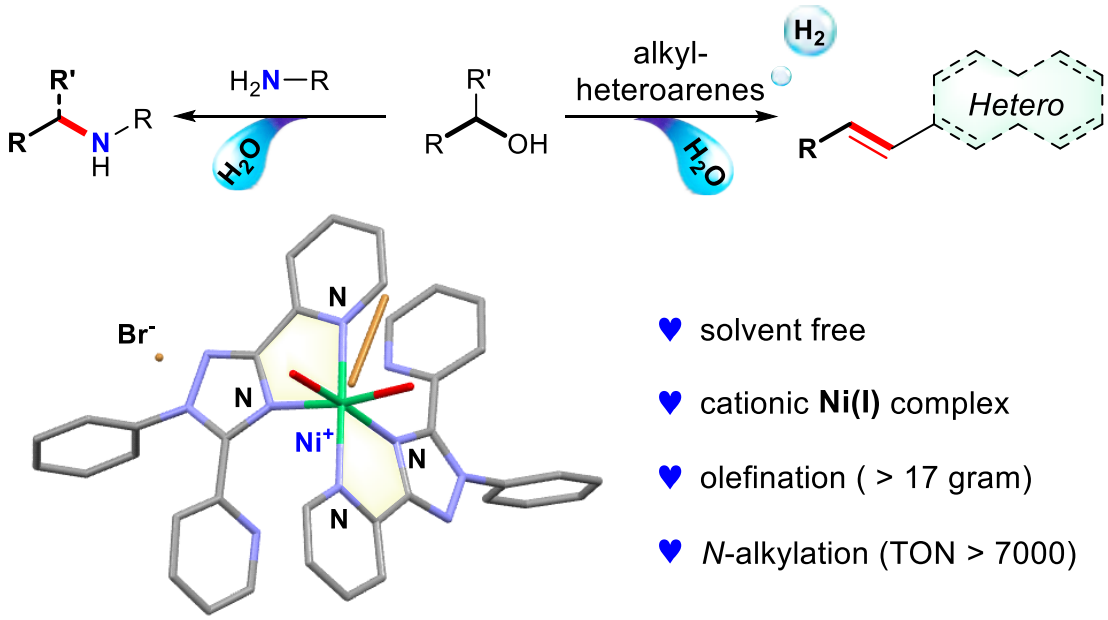


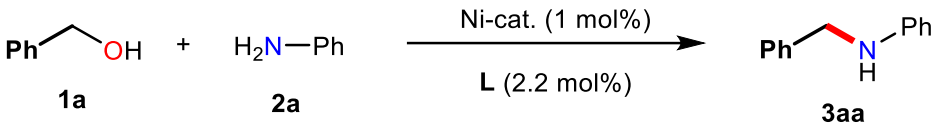
CONTENTS

1. General experiment details and materials

Experimental: All reactions and manipulations with air sensitive compounds being present were performed under dry argon (Ar) or nitrogen (N_2), using Schlenk and glove box techniques. Deuterated solvents were bought from Cambridge Isotope Laboratories, distilled accordingly, and stored over molecular sieves (3 Å). Other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were collected on a Varian INOVA 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signal. Coupling constants (J) are given in Hz (coupling patterns: s: singlet, br: broad singlet, d: doublet, t: triplet, q: quartet, m: multiplet). GC analyses were carried out using an Agilent Technologies 6890N system equipped with a Machinery-Nagel (MN) Optima 5 HT column (30 m, 320 µm, 0.25 µm) or an Agilent Technologies 6850 system equipped with a MN Optima 17 column (30 m, 320 µm, 0.25 µm). GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m, 320 µm, 0.25 µm). Gas mixtures were analyzed using an Agilent Technologies 6890N equipped with a TCD and an Agilent special plot and molsieve capillary column (30 m, 320 µm, 0.25 µm). Elemental analyses were performed using the Elementar Vario EL *III*. MN silica gel 60 (0.040 – 0.063 mm particle size) was used for flash column chromatography. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI).

2. Optimization of the reaction conditions

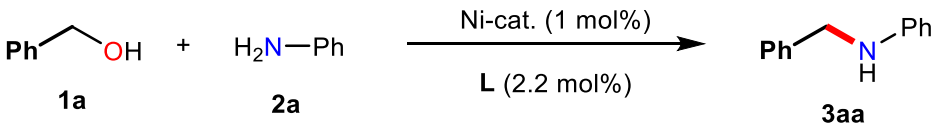
2.1 Optimization of the Ni-catalyzed *N*-alkylation of amines by alcohols



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (38 mL volume) was charged with a magnetic stirring bar, [Ni] (0.02 mmol), base, **1a** and **2a**. Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (design temperature). After design time the reaction was cooled and quenched with ethyl acetate, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. The **3aa** yield was determined by GC analysis relative to the **2a** with *n*-hexadecane as internal standard. After evaporation of the solvents under reduced pressure, the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 20/1) to afford the corresponding product **3aa** in the reported yield.

Entry	Parameter
Table S1	The difference of Ni-catalyst screening
Table S2	The difference of ligand screening
Table S3	The difference of base screening
Table S4	The loading of base screening
Table S5	The ratio of substrate screening
Table S6	Reaction temperature screening
Table S7	Reaction time screening
Table S8	The loading of Ni-catalyst screening
Table S9	Reaction system screening

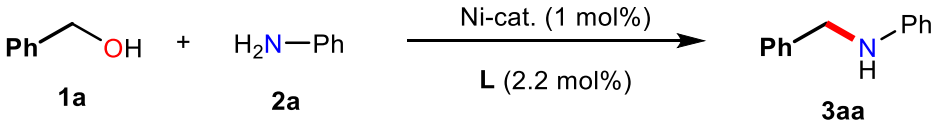
Table S1: The difference of Ni-catalyst screening[a]



Entry	Ni-catalyst	**3aa** (%)
1	-	0
2	$NiCl_2$	10
3	$NiBr_2$	12
4	NiI_2	8
5	$NiCl_2$(DME)	31
6	**$NiBr_2$(DME)**	**95**
7	Ni_2O_3	0
8	[NiCl(allyl)] $_2$	31
9	Li_2NiBr_4	20
10	$Ni(acac)_2$	28
11	$Ni(cod)_2$	21
12	$Ni(PPh_3)_4$	22
13	$Ni(PPh_3)_2Cl_2$	23
14	Ni(DPPM)Cl_2	32
15	Ni(DPPB)Cl_2	10
16	Ni(DPPP)Cl_2	24
17	Ni(DPPB)Cl_2	36
18	Ni(DPPH)Cl_2	21
19	$Ni(PCy_3)_2Cl_2$	12
20	**[Ni-N_4]Br**	**96**

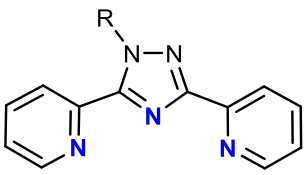
[a] Reaction conditions: **[Ni]** (0.02 mmol), **L3** (0.04 mmol), *t*-BuOK (2.0 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 ^oC, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.

Table S2: The difference of ligand screening[a]



Entry	Ligand	**3aa** (%)
1	**L1**	83
2	**L2**	78
3	**L3**	95
4	**L4**	82
5	**L5**	74
6	**L6**	<5
7	**L7**	<5
8	**L8**	<5
9	**L9**	<5
10	**L10**	<5
11	**L11**	26
12	1,10-phenanthroline	34
13	-	0
14	**[Ni-N$_4$]Br**	**96**

[a] Reaction conditions: $NiBr_2$(DME) (0.02 mmol), Ligand (0.04 mmol), *t*-BuOK (x mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 °C, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.



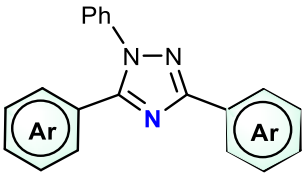
L1, R = H

L2, R = Bn

L3, R = Ph

L4, R = (4-$CH_3C_6H_4$)

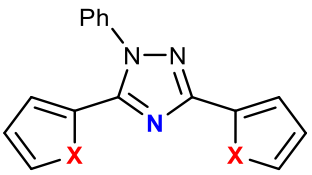
L5, R = (4-$CF_3C_6H_4$)



L6, Ar = Ph

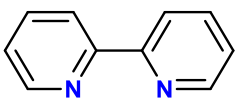
L7, Ar = 3-Py

L8, Ar = 4-Py



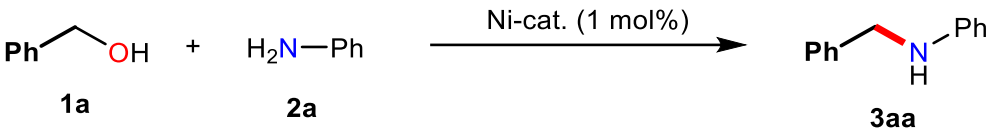
L9, X = O

L10, X = S



L11

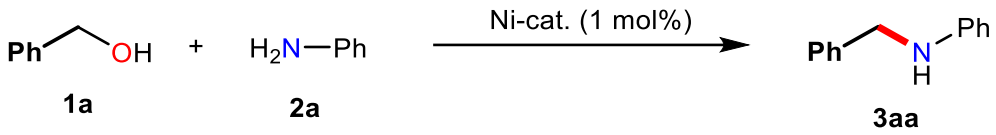
Table S3: The difference of base screening[a]



Entry	Base (1.0 equiv)	**3aa** (%)
1	LiOH	0
2	NaOH	<5
3	KOH	<5
4	CsOH	<5
5	Li_2CO_3	0
6	Na_2CO_3	0
7	K_2CO_3	0
8	Cs_2CO_3	0
9	*t*-BuOLi	<5
10	*t*-BuONa	68
11	***t*-BuOK**	**96**
12	*t*-BuOCs	<5
13	pyridine	<5
14	TEA	0
15	TBD	0
16	DBU	0
17	*t*-BuLi	0
18	NaH	41
19	$NaNH_2$	36
20	KH	71

[a] Reaction conditions: **[Ni-N_4]Br** (0.02 mmol), base (2.0 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 °C, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.

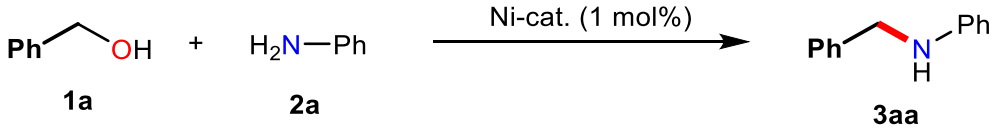
Table S4: The loading of base screening[a]



Entry	*t*-BuOK (mmol)	**3aa** (%)
1	0	0
2	0.5	23
3	1.0	51
4	1.75	86
5	**2.0**	**96**
6	2.25	95
7	2.5	93
8	3.0	90

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (x mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 °C, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.

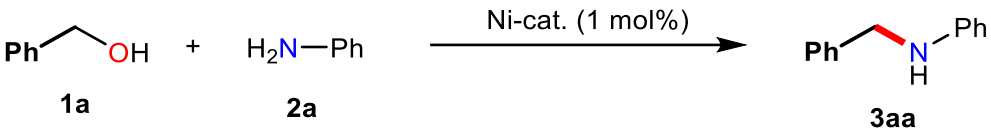
Table S5: The ratio of substrate screening[a]



Entry	**1a**	**2a**	**3aa** (%)
1	2	2	72
2	3	2	89
3	**4**	**2**	**96**
4	2	3	71
5	2	4	73

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (x mmol), **2a** (x mmol), N_2, 130 °C, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.

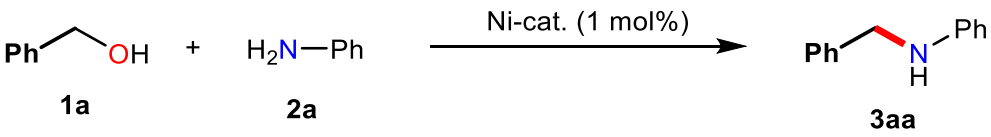
Table S6: Reaction temperature screening[a]



Entry	T [°C]	**3aa** (%)
1	RT	0
2	50	18
3	100	56
4	120	87
5	**130**	**96**
6	140	91
7	150	82

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, T °C, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

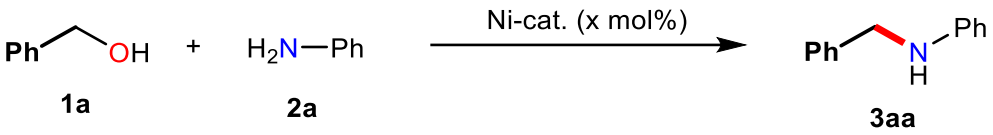
Table S7: Reaction time screening[a]



Entry	t [h]	**3aa** (%)
1	3	22
2	6	49
3	12	80
4	**15**	**96**
5	24	95

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 °C, x h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

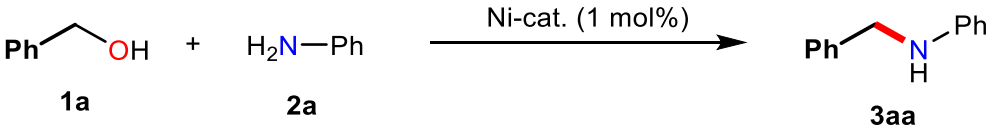
Table S8: The loading of Ni-catalyst screening[a]



Entry	**[Ni-N$_4$]Br** (mol%)	**3aa** (%)
1	0	0
2	0.05	86
3	**0.1**	**96**
4	0.5	95
5	1.0	96
6	2	95

[a] Reaction conditions: **[Ni-N$_4$]Br** (x mmol), *t*-BuOK (2.0 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 ^oC, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

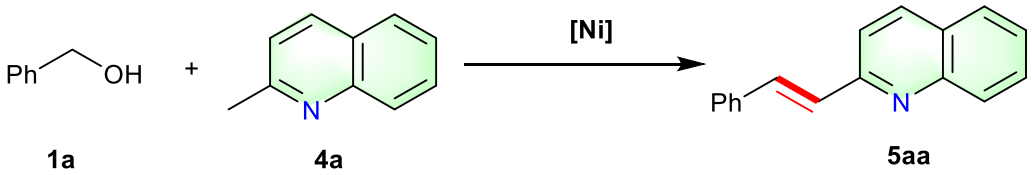
Table S9: Reaction system screening



Entry	system		**3aa** (%)
1	open	N_2	93
2	open	air	48
3	open	O_2	0
4	**closed**	**N_2**	**96**
5	closed	air	56
6	closed	O_2	0

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2.0 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol), N_2, 130 ^oC, 15 h. Yield of **3aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

2.2 Optimization of the Ni-catalyzed olefination of *N*-heteroarenes by alcohols

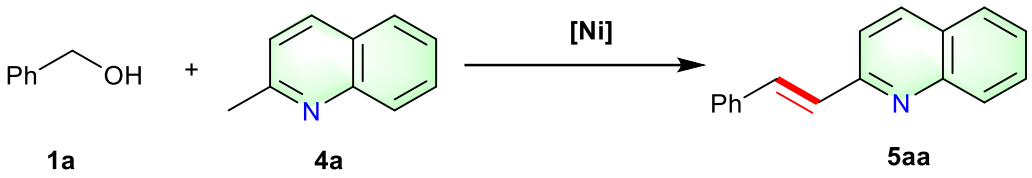


1a **4a** **5aa**

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (100 mL volume) was charged with a magnetic stirring bar, [Ni] (0.02 mmol), base, **1a** and **4a**. Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. A reflux condenser was evacuated and refilled with dry N_2 and then attached to the Schlenk tube maintaining dry air stream. A bubble counter was attached to the top of the condenser and the whole system was purged with dry N_2 for 30 seconds. The Schlenk tube was immersed into a pre-heated metal bath (design temperature). After design time the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 2/1) gave the corresponding products **5aa** in the reported yield.

Entry	Parameter
Table S10	The difference of ligand screening
Table S11	The difference of base screening
Table S12	The loading of base screening
Table S13	The ratio of substrate screening
Table S14	Reaction temperature screening
Table S15	Reaction time screening
Table S16	The loading of Ni-catalyst screening
Table S17	Reaction system screening

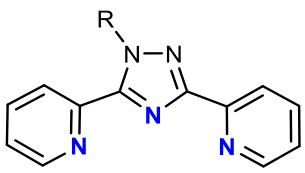
Table S10: The difference of ligand screening[a]



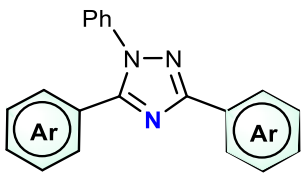
1a **4a** **5aa**

Entry	Ligand	**5aa** (%)
1	**L1**	78
2	**L2**	81
3	**L3**	**92**
4	**L4**	71
5	**L5**	70
6	**L6**	<5
7	**L7**	<5
8	**L8**	<5
9	**L9**	<5
10	**L10**	<5
11	**L11**	32
12	-	0
13	**[Ni-N_4]Br**	**93 (83)[b]**

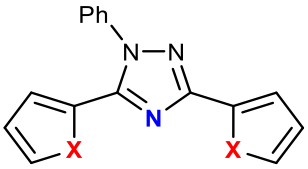
[a] Reaction conditions: $NiBr_2$(DME) (0.05 mmol), Ligand (0.1 mmol), KOH (2.0 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard. [b] Isolated product.



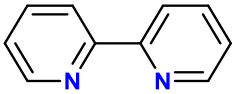
L1, R = H
L2, R = Bn
L3, R = Ph
L4, R = (4-$CH_3C_6H_4$)
L5, R = (4-$CF_3C_6H_4$)



L6, Ar = Ph
L7, Ar = 3-Py
L8, Ar = 4-Py

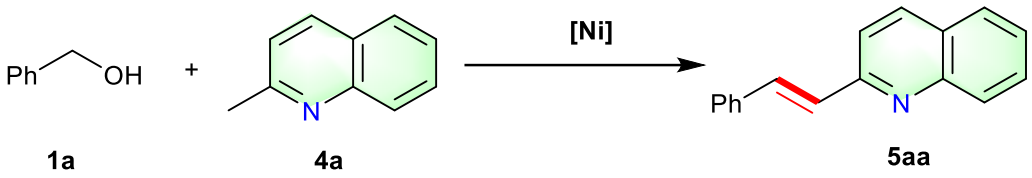


L9, X = O
L10, X = S



L11

Table S11: The difference of base screening[a]

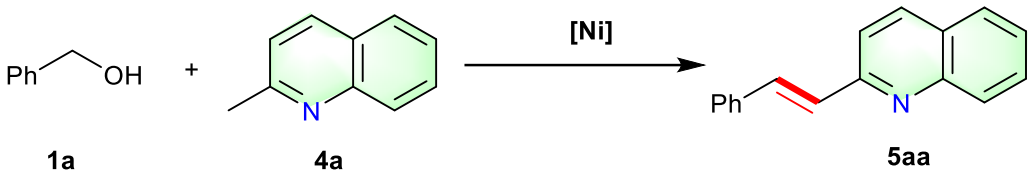


1a **4a** **5aa**

Entry	Base (1.0 equiv)	**5aa** (%)
1	LiOH	<5
2	NaOH	25
3	**KOH**	**93**
4	CsOH	32
5	Li_2CO_3	0
6	Na_2CO_3	0
7	K_2CO_3	0
8	Cs_2CO_3	0
9	*t*-BuOLi	<5
10	*t*-BuONa	49
11	*t*-BuOK	81
12	*t*-BuOCs	21
13	pyridine	0
14	TEA	0
15	TBD	0
16	DBU	0
17	*t*-BuLi	0
18	NaH	39
19	$NaNH_2$	52
20	KH	82

[a] Reaction conditions: **[Ni-N_4]Br** (0.05 mmol), base (2.0 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 μL) as internal standard.

Table S12: The loading of base screening[a]

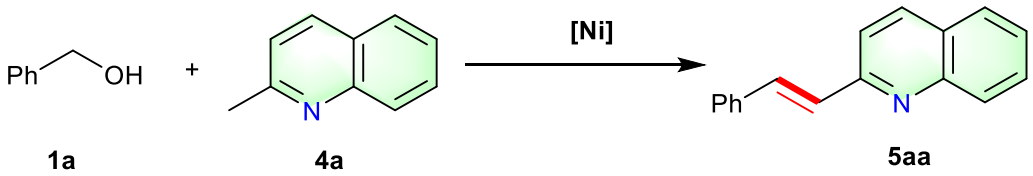


1a **4a** **5aa**

Entry	KOH (mmol)	**5aa** (%)
1	0	0
2	0.5	26
3	1.0	46
4	1.75	82
5	**2.0**	**93**
6	2.5	92
7	3.0	91

[a] Reaction conditions: **[Ni-N_4]Br** (0.05 mmol), KOH (x mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

Table S13: The ratio of substrate screening[a]

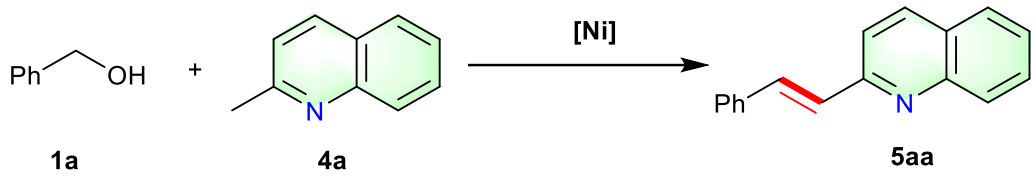


1a **4a** **5aa**

Entry	**1a**	**2a**	**5aa** (%)
1	2	2	74
2	3	2	87
3	**4**	**2**	**93**
4	2	3	75
5	2	4	79

[a] Reaction conditions: **[Ni-N_4]Br** (0.05 mmol), KOH (2 mmol), **1a** (x mmol), **4a** (x mmol), N_2, 130 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

Table S14: Reaction temperature screening[a]

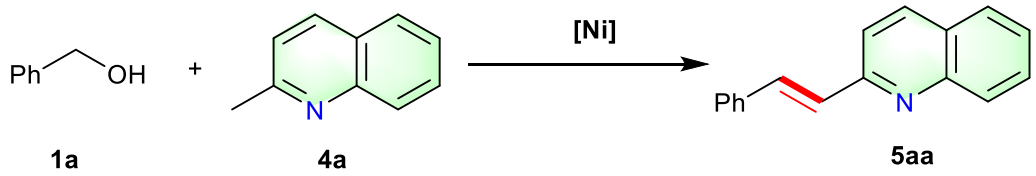


1a **4a** **5aa**

Entry	T [^{o} C]	**5aa** (%)
1	RT	0
2	50	26
3	100	43
4	120	83
5	130	90
6	**140**	**93**
7	150	82

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.05 mmol), KOH (2 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, T ^{o}C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

Table S15: Reaction time screening[a]

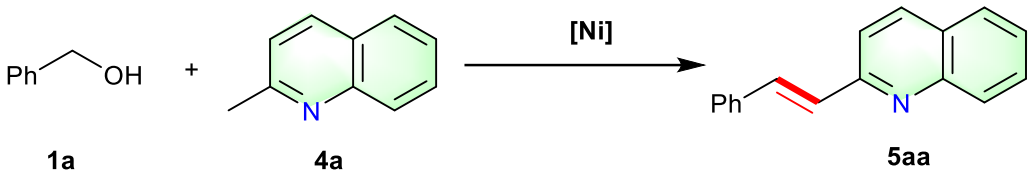


1a **4a** **5aa**

Entry	t [h]	**5aa** (%)
1	3	20
2	6	47
3	12	79
4	**15**	**93**
5	24	93

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.05 mmol), KOH (2 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 ^{o}C, x h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

Table S16: The loading of Ni-catalyst screening[a]

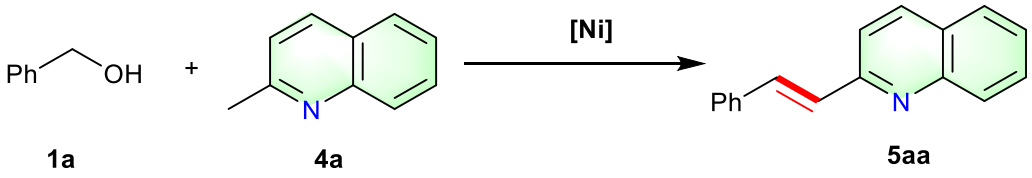


1a **4a** **5aa**

Entry	**[Ni-N$_4$]Br** (mol%)	**5aa** (%)
1	0	0
2	0.1	73
3	**2.5**	**93**
4	5	92
5	10	93
6	20	93

[a] Reaction conditions: **[Ni-N$_4$]Br** (x mmol), KOH (2.0 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

Table S17: Reaction system screening



1a **4a** **5aa**

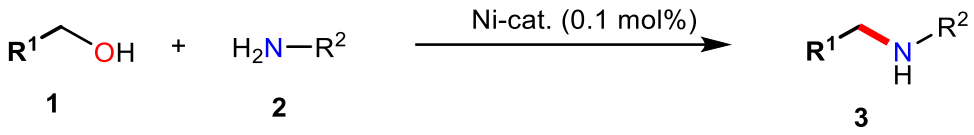
Entry	system		**5aa** (%)
1	**open**	**N_2**	**93**
2	open	air	52
3	open	O_2	0
4	closed	N_2	74
5	closed	air	44
6	closed	O_2	0

[a] Reaction conditions: **[Ni-N$_4$]Br** (0.05 mmol), KOH (2 mmol), **1a** (4.0 mmol), **4a** (2.0 mmol), N_2, 140 °C, 15 h. Yield of **5aa** determined by GC-analysis using *n*-hexadecane (100 µL) as internal standard.

3. General procedure for Ni-catalyzed *N*-alkylation

3.1 General procedure for Ni-catalyzed *N*-alkylation of amines by alcohols

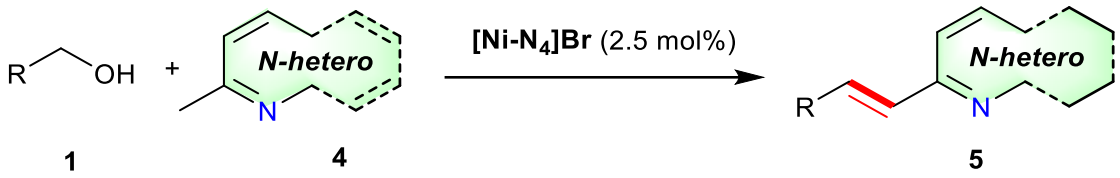
Closed system:



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (38 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.002 mmol, 0.1 mol%), *t*-BuOK (2.0 mmol), **1** (4.0 mmol) and **2** (2.0 mmol). Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (design temperature). After design time the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 5/1, Et$_3$N 1%) gave the corresponding products **3** in the reported yields.

3.2 General procedure for Ni-catalyzed olefination of *N*-heteroarenes by alcohols

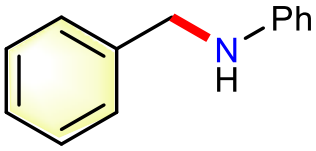
Opened system:



1 **4** **5**

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (100 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.05 mmol, 2.5 mol%), KOH (2.0 mmol), **1** (4.0 mmol) and **4** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. A reflux condenser was evacuated and refilled with dry N_2 and then attached to the Schlenk tube maintaining dry air stream. A bubble counter was attached to the top of the condenser and the whole system was purged with dry N_2 for 30 seconds. The Schlenk tube was immersed into a pre-heated metal bath (design temperature). After design time the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 2/1, DCM 2%) gave the corresponding products **5** in the reported yields.

4. Characterization data



N-benzylaniline (3aa)[1]

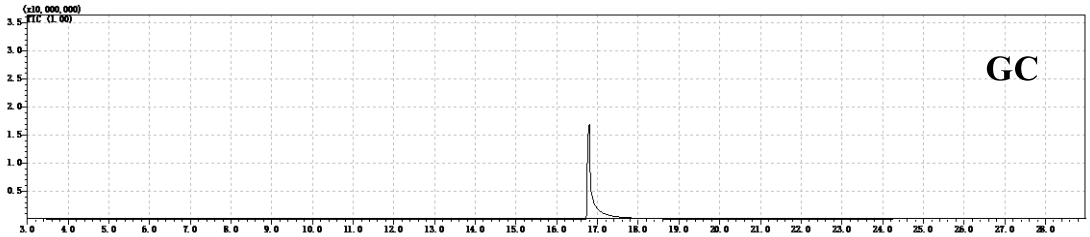
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 329.6 mg, 90% yield.

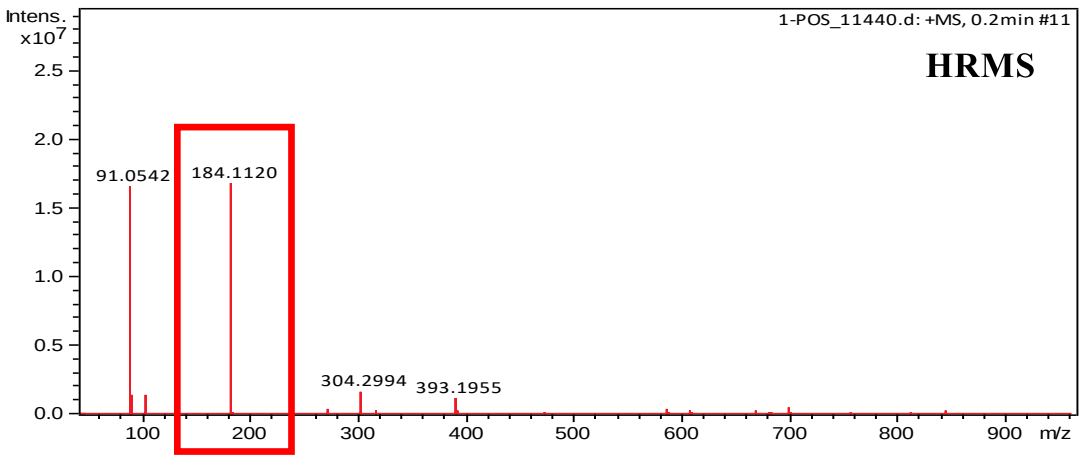
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.13 (m, 5H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.22 (s, 2H), 3.92 (s, 1H).

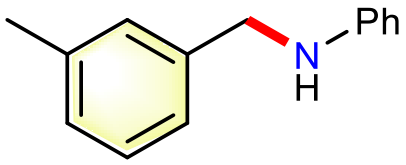
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.08, 139.37, 129.22, 128.59, 127.47, 127.18, 117.52, 112.80, 48.28.

MS (70 eV): m/z (%) = 183.

HRMS (ESI) calcd. for $C_{13}H_{14}N$ [M+H]: 184.1126, found: 184.1120.







N-(3-methylbenzyl)aniline (3ab) [1]

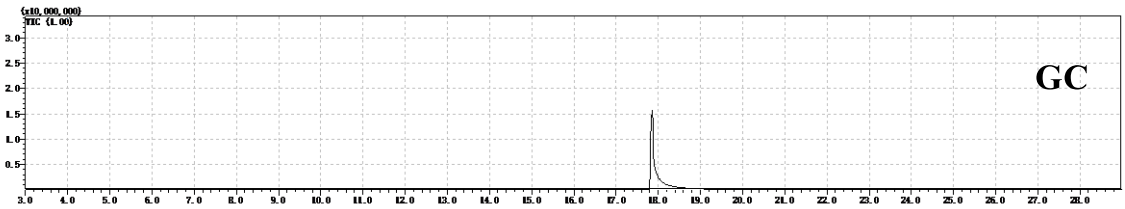
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 339.1 mg, 86% yield.

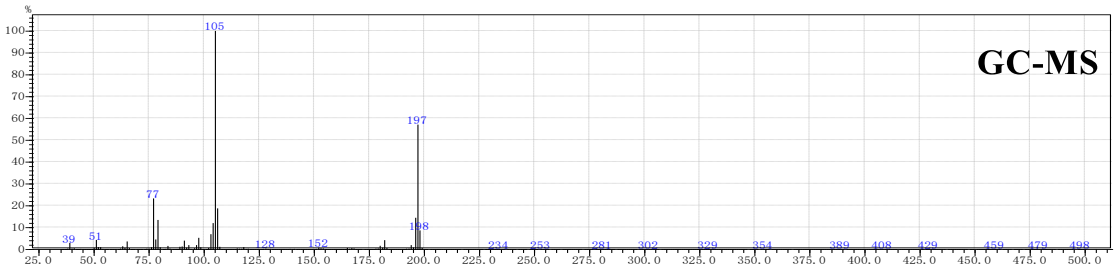
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 7.25 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 2H), 4.41 (s, 2H), 4.09 (s, 1H), 2.51 (s, 3H).

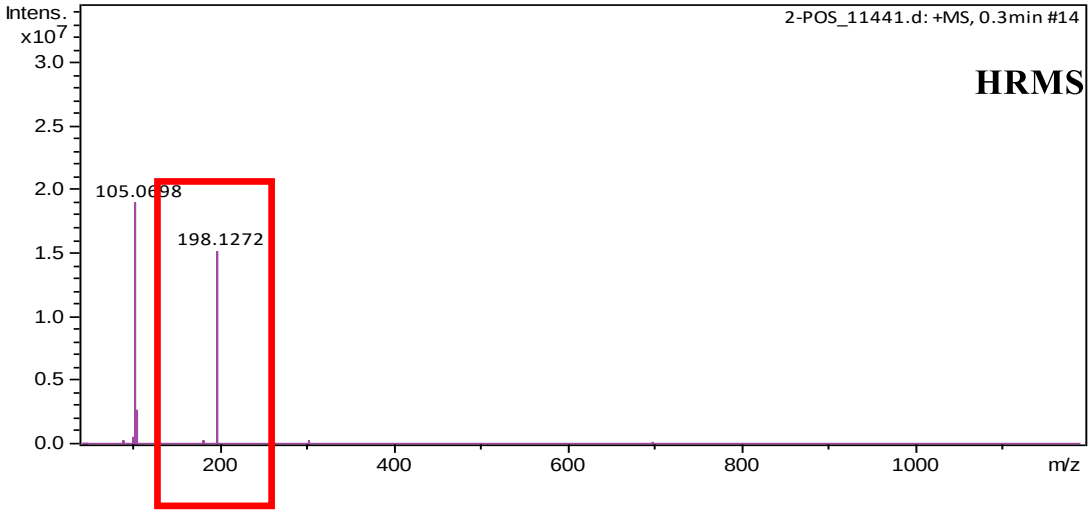
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.20, 139.36, 138.23, 129.23, 128.51, 128.25, 127.96, 124.56, 117.45, 112.79, 48.28, 21.43.

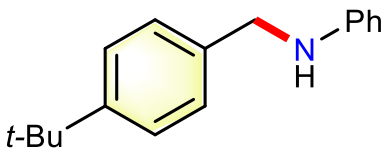
MS (70 eV): m/z (%) = 197.

HRMS (ESI) calcd. for $C_{14}H_{16}N$ [M+H]: 198.1283, found: 198.1272.









N-(4-(tert-butyl)benzyl)aniline (3ac) [1]

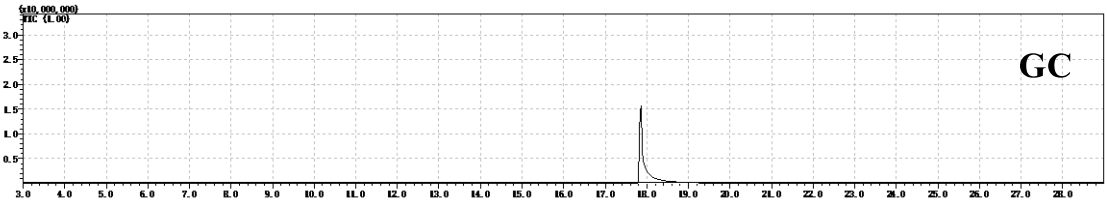
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 38.2 – 39.4 °C, 440.1 mg, 92% yield.

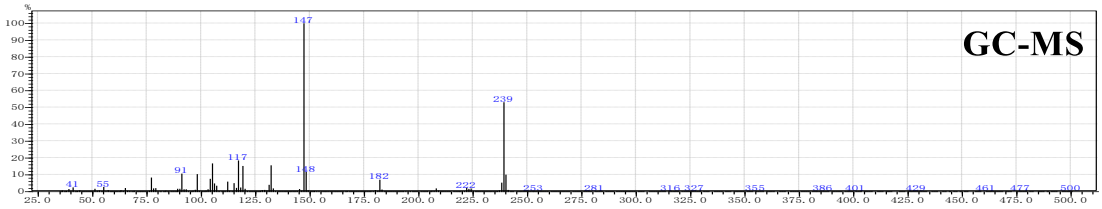
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 19.9, 8.3 Hz, 4H), 7.19 (t, *J* = 6.2 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 4.30 (s, 2H), 4.00 (s, 1H), 1.33 (s, 9H).

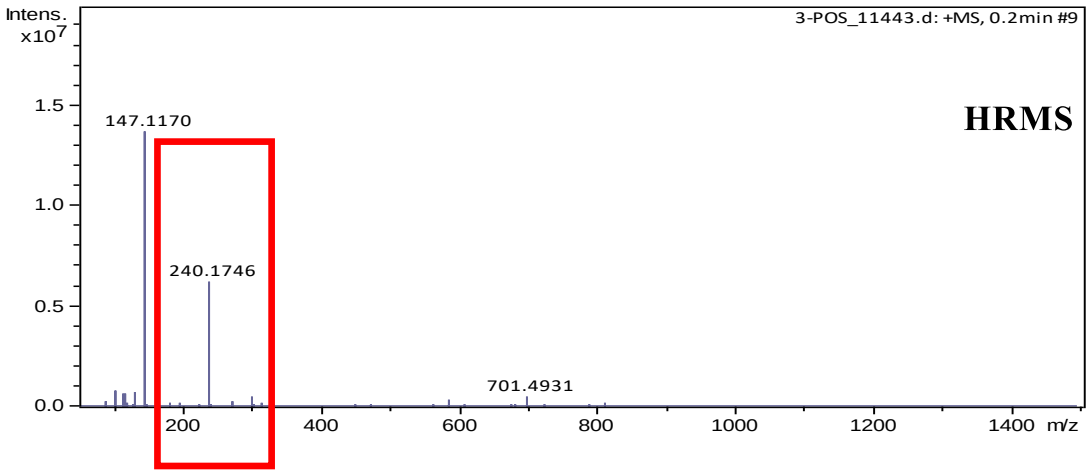
^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.75, 147.95, 136.21, 128.70, 126.77, 125.03, 116.80, 112.30, 47.28, 33.95, 30.70.

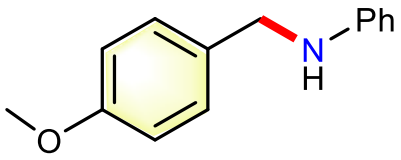
MS (70 eV): m/z (%) = 239.

HRMS (ESI) calcd. for $C_{17}H_{22}N$ [M+H]: 240.1752, found: 240.1746.









N-(4-methoxybenzyl)aniline (3ad) [1]

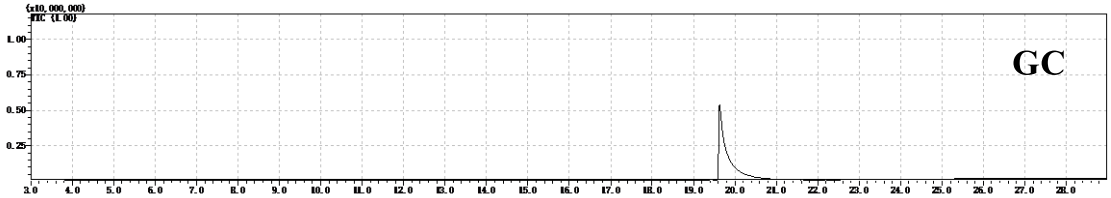
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 63.5 – 64.2 °C, 387.9 mg, 91% yield.

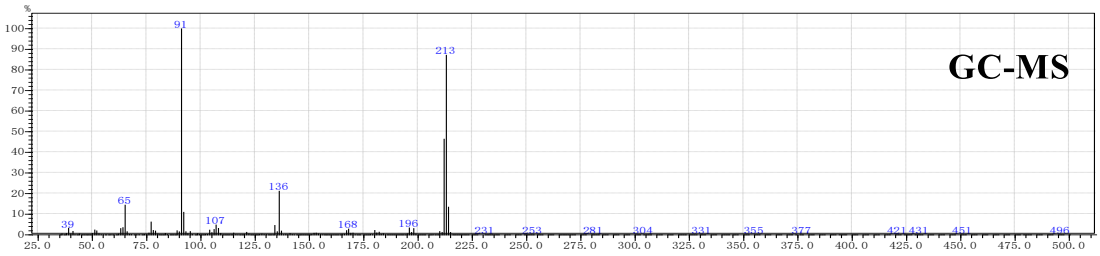
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.23 (s, 2H), 3.92 (s, 1H), 3.78 (s, 3H).

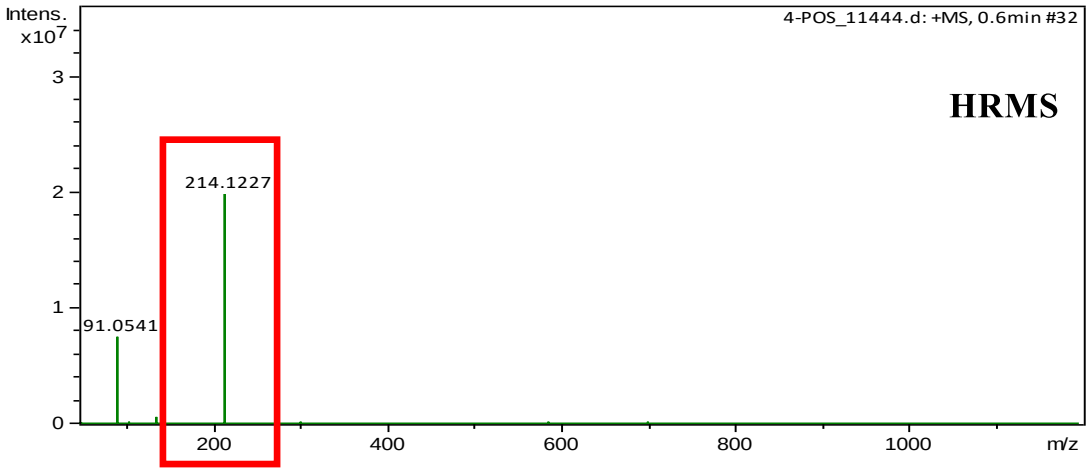
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.85, 148.20, 131.40, 129.26, 128.82, 117.50, 114.02, 112.83, 55.31, 47.80.

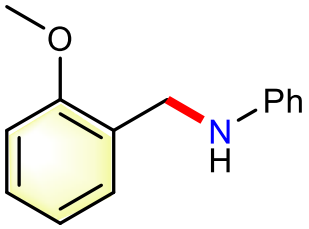
MS (70 eV): m/z (%) = 213.

HRMS (ESI) calcd. For $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1227.









N-(2-methoxybenzyl)aniline (3ae) [1]

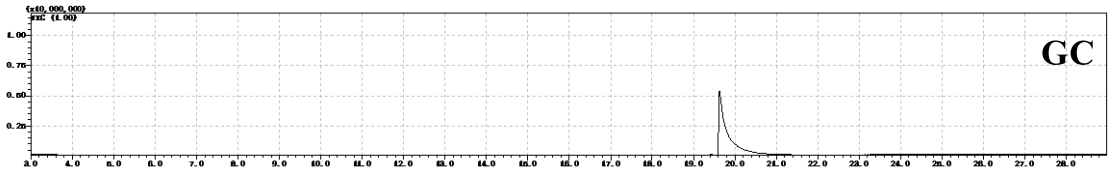
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 93.1 – 94.3 °C, 285.6 mg, 67% yield.

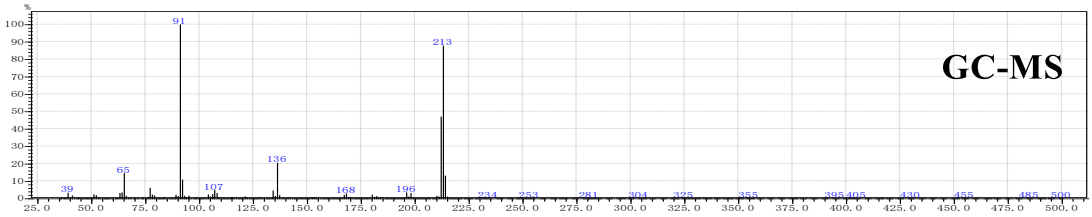
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.11 (dd, *J* = 11.3, 4.3 Hz, 2H), 6.85 (dd, *J* = 16.1, 7.9 Hz, 2H), 6.72 – 6.49 (m, 3H), 4.28 (s, 2H), 4.06 (s, 1H), 3.80 (s, 3H).

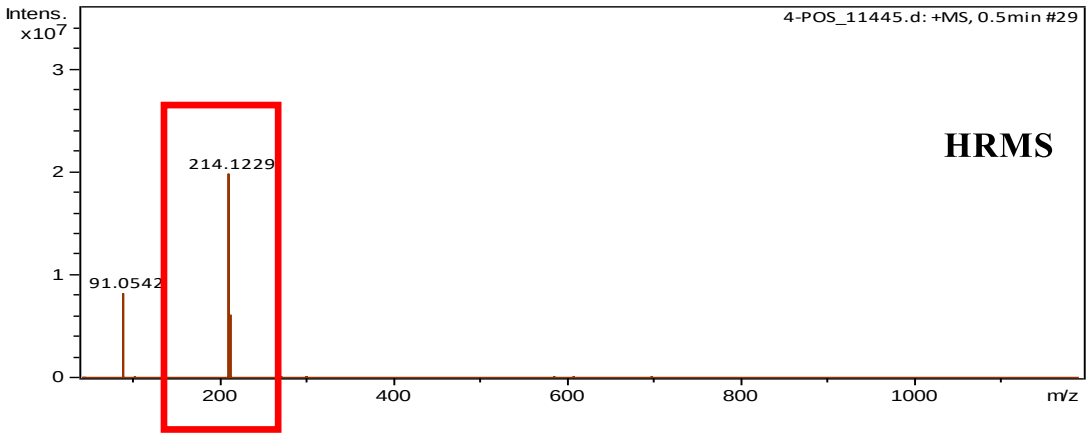
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58, 148.62, 129.38, 129.09, 128.50, 127.52, 120.72, 117.52, 113.25, 110.42, 55.50, 43.65.

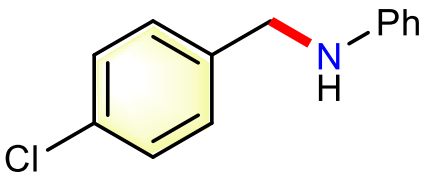
MS (70 eV): m/z (%) = 213.

HRMS (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1229.









N-(4-chlorobenzyl)aniline (3af) [1]

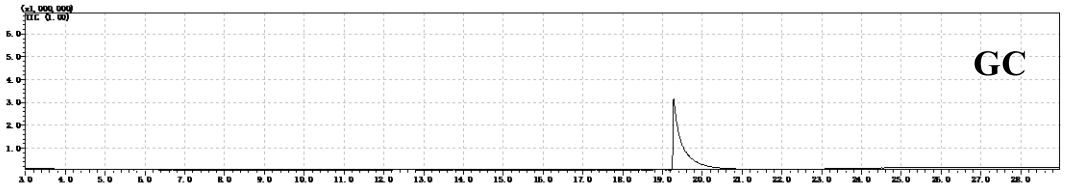
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 47.1 – 48.2 °C, 356.0 mg, 82% yield.

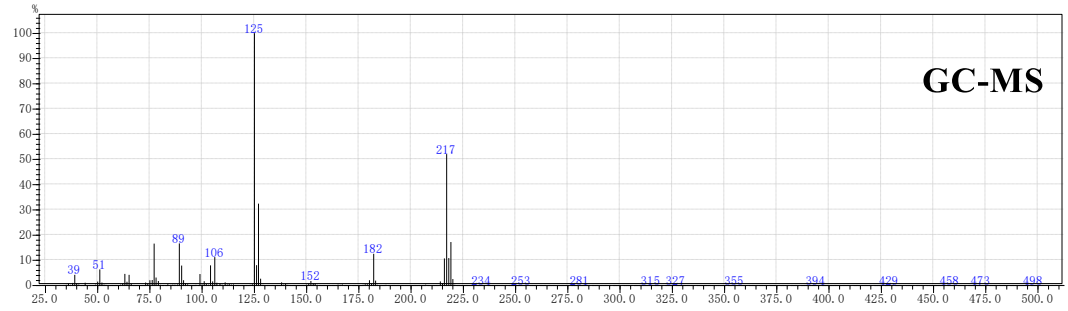
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.8 Hz, 4H), 7.32 – 7.21 (m, 2H), 6.89 – 6.74 (m, 1H), 6.74 – 6.59 (m, 2H), 4.37 (s, 2H), 4.11 (s, 1H).

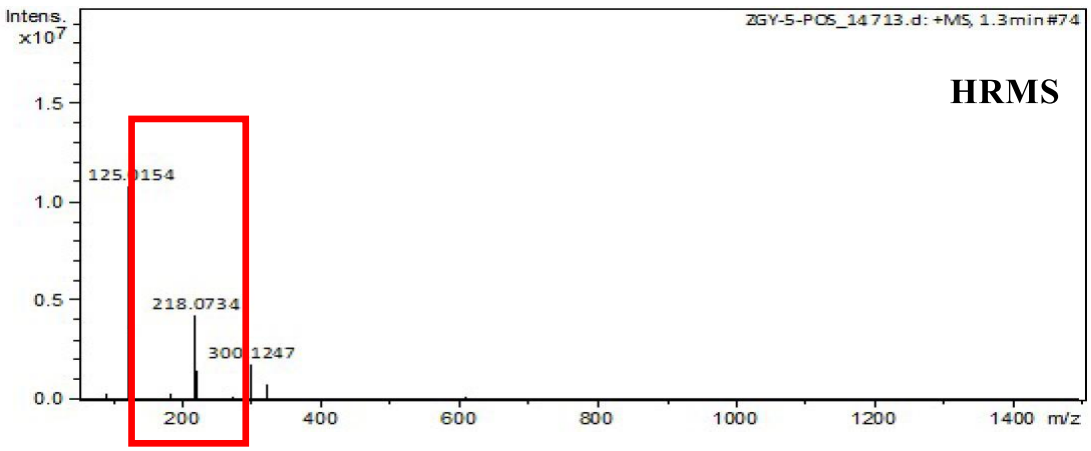
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.86, 138.05, 132.86, 129.35, 128.78, 128.73, 117.82, 112.91, 47.61.

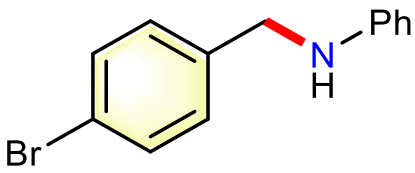
MS (70 eV): m/z (%) = 217.

HRMS (ESI) calcd. for $C_{13}H_{13}ClN$ [M+H]: 218.0737, found: 218.0734.









N-(4-bromobenzyl)aniline (3ag) [1]

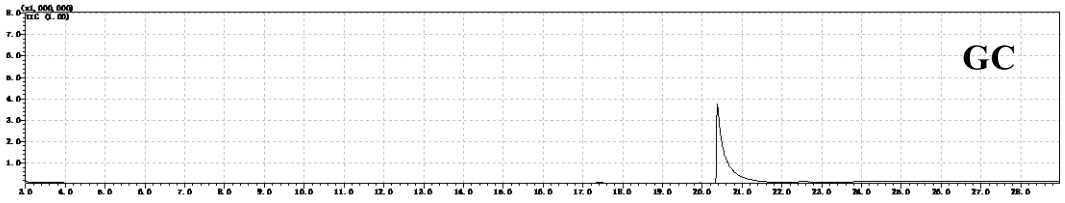
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 51.3 – 52.1 °C, 396.8 mg, 76% yield.

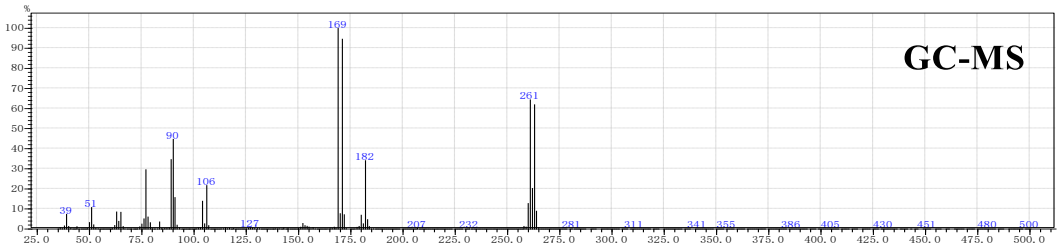
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.38 – 7.18 (m, 4H), 6.79 (dd, *J* = 10.4, 4.2 Hz, 1H), 6.66 (d, *J* = 7.1 Hz, 2H), 4.34 (s, 2H), 4.10 (s, 1H).

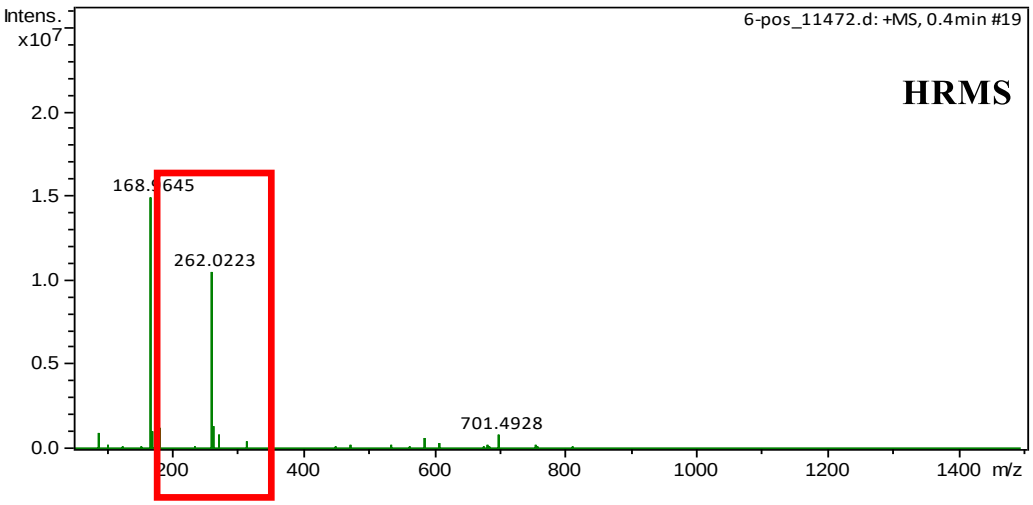
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.68, 138.44, 131.58, 129.19, 128.93, 120.80, 117.70, 112.78, 47.53.

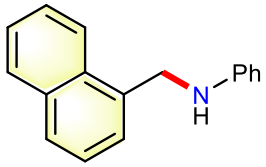
MS (70 eV): m/z (%) = 261.

HRMS (ESI) calcd. for $C_{13}H_{13}BrN$ [M+H]: 262.0231, found: 262.0223.









N-(naphthalen-1-ylmethyl)aniline (3ah) [1]

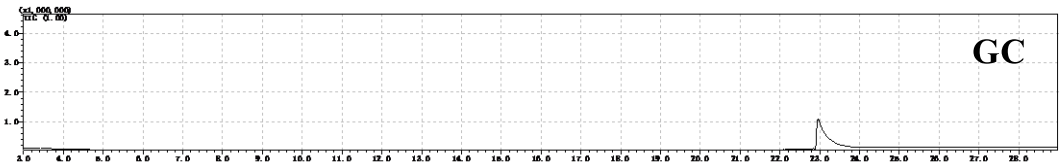
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 68.1 – 69.0 ºC, 289.1 mg, 62% yield.

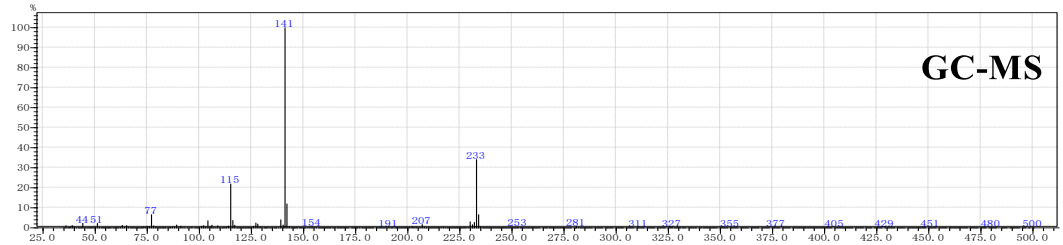
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 6.1, 3.4 Hz, 1H), 8.06 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.63 – 7.53 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 2H), 4.83 (s, 2H), 4.06 (s, 1H).

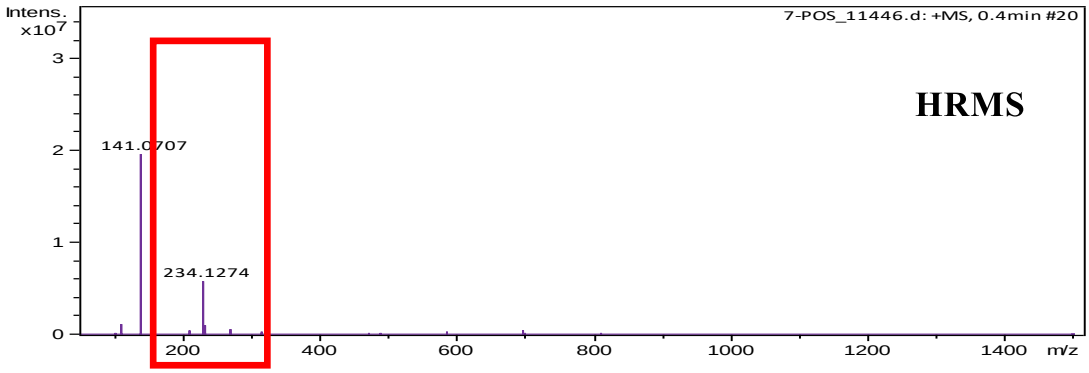
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.35, 134.46, 134.00, 131.66, 129.46, 128.90, 128.31, 126.46, 126.18, 125.97, 125.68, 123.72, 117.70, 112.86, 46.56.

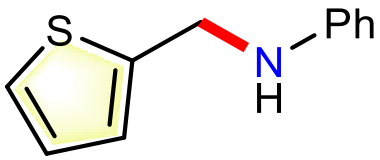
MS (70 eV): m/z (%) = 233.

HRMS (ESI) calcd. for $C_{17}H_{16}N$ [M+H]: 234.1283, found: 234.1274.









N-(thiophen-2-ylmethyl)aniline (3ai) [1]

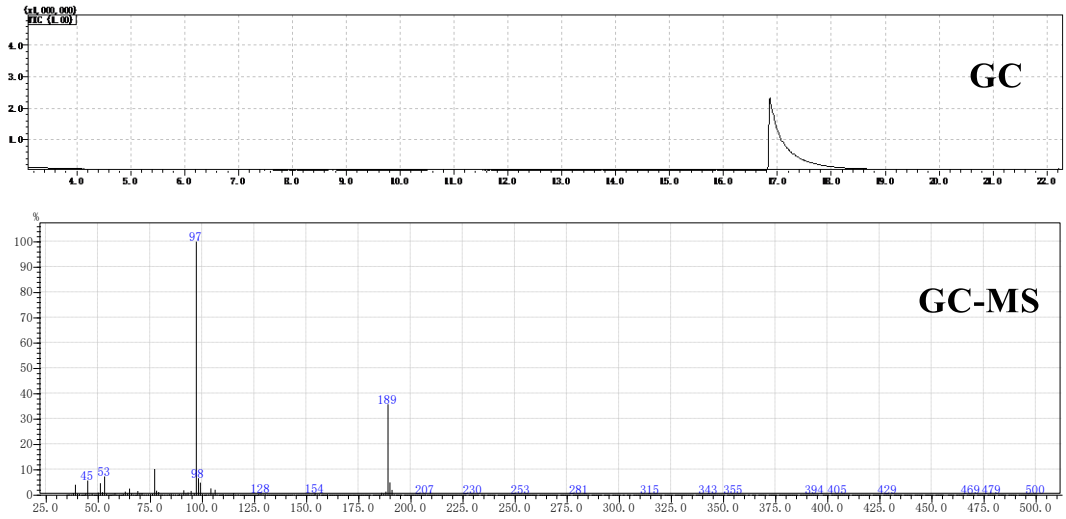
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 294.9 mg, 78% yield.

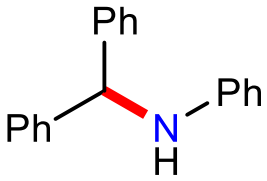
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30 – 7.12 (m, 3H), 7.09 – 6.88 (m, 2H), 6.80 – 6.56 (m, 3H), 4.51 (s, 2H), 4.16 (s, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.29, 142.95, 128.70, 126.36, 124.47, 123.98, 117.39, 112.59, 42.83.

MS (70 eV): m/z (%) = 189.

HRMS (ESI) calcd. for $C_{11}H_{12}NS$ [M+H]: 190.0690, found: 190.0684.





N-benzhydrylaniline (3aj) [1]

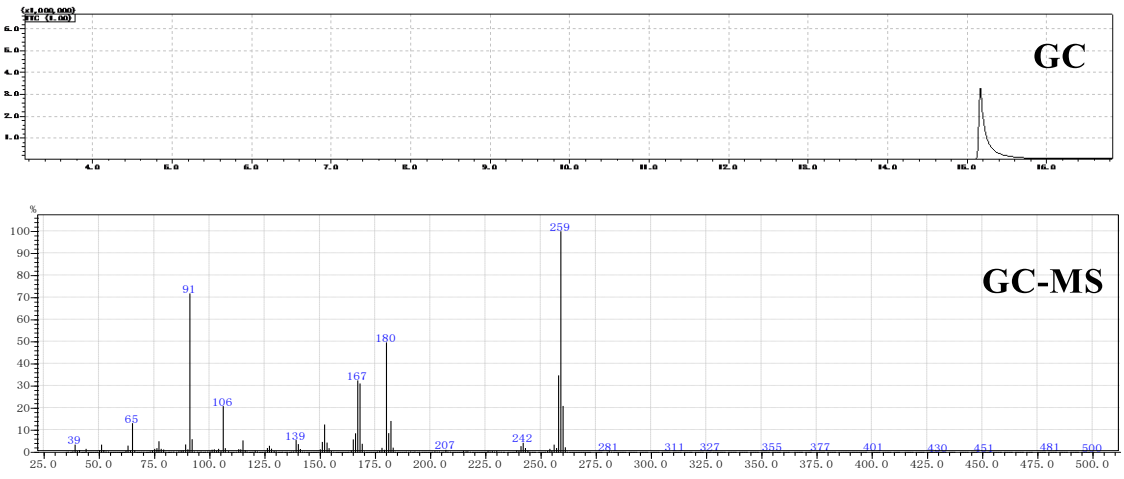
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 58.5 – 59.1 °C, 217.7 mg, 42% yield.

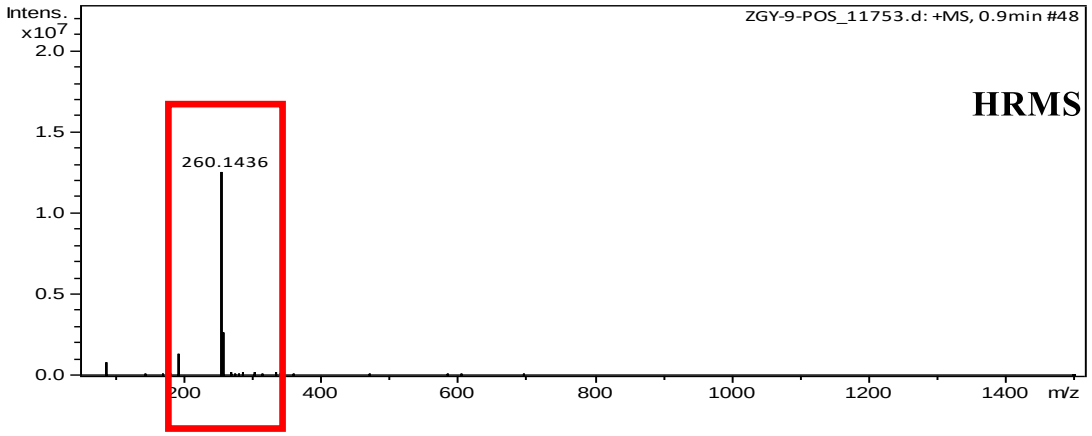
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 7H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.09 (m, 2H), 6.76 (dd, *J* = 10.5, 4.1 Hz, 1H), 6.66 – 6.44 (m, 2H), 5.56 (s, 1H), 4.28 (s, 1H).

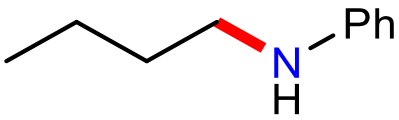
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.60, 143.19, 129.38, 129.01, 127.72, 127.62, 117.92, 113.74, 63.30.

MS (70 eV): m/z (%) = 259.

HRMS (ESI) calcd. for $C_{19}H_{18}N$ [M+H]: 260.1439, found: 260.1436.







N-butylaniline (3ak) [1]

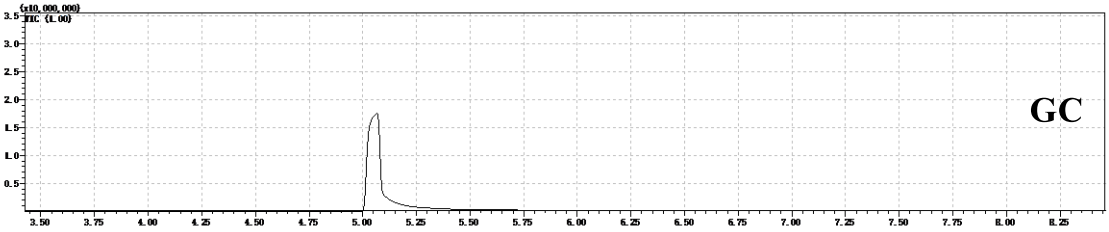
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 152.1 mg, 51% yield.

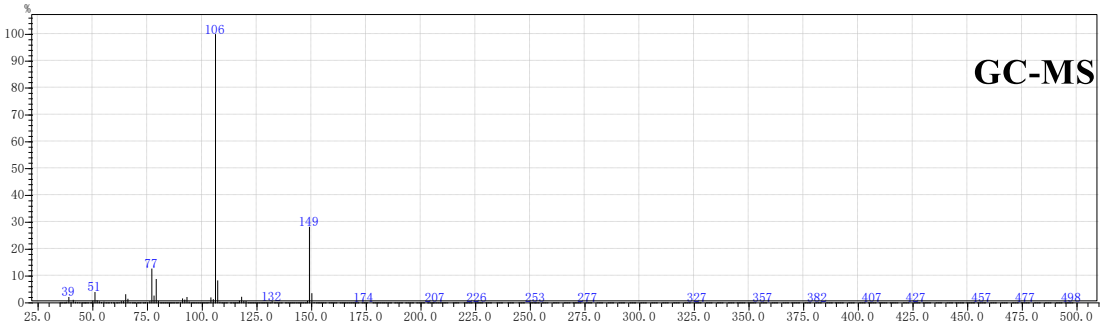
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.23 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 3.74 (s, 1H), 3.19 (t, *J* = 7.0 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.59 – 1.48 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

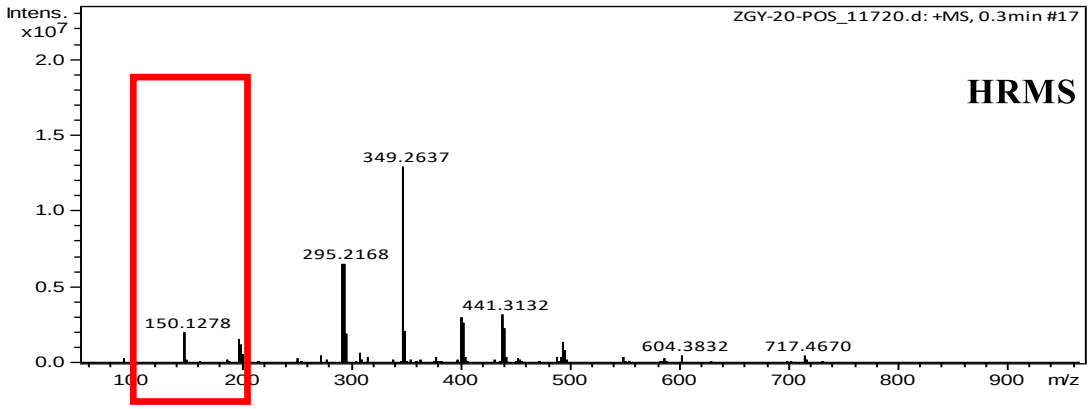
^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.37, 128.67, 116.33, 112.07, 43.18, 31.25, 19.90, 13.29.

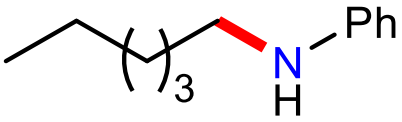
MS (70 eV): m/z (%) = 149.

HRMS (ESI) calcd. for $C_{10}H_{16}N$ [M+H]: 150.1283, found: 150.1278.









N-hexylaniline (3al) [1]

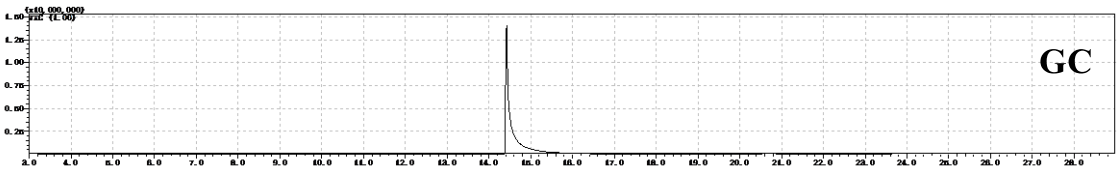
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 248.0 mg, 70% yield.

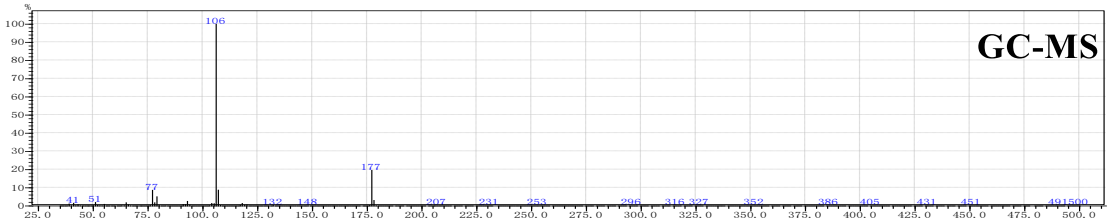
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.28 – 7.14 (m, 2H), 6.79 – 6.56 (m, 3H), 3.70 (s, 1H), 3.17 – 3.12 (m, 2H), 1.66 (dd, *J* = 14.6, 7.7 Hz, 2H), 1.49 – 1.35 (m, 6H), 0.98 (t, *J* = 6.8 Hz, 3H).

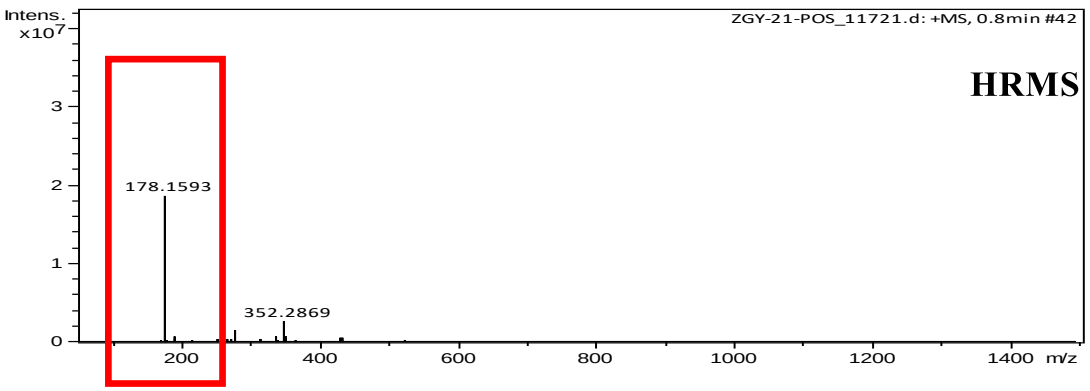
^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.79, 129.10, 116.75, 112.50, 43.94, 31.71, 29.55, 26.88, 22.69, 13.86.

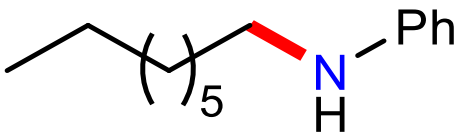
MS (70 eV): m/z (%) = 177.

HRMS (ESI) calcd. for $C_{12}H_{20}N$ [M+H]: 178.1596, found: 178.1593.









N-octylaniline (3am) [1]

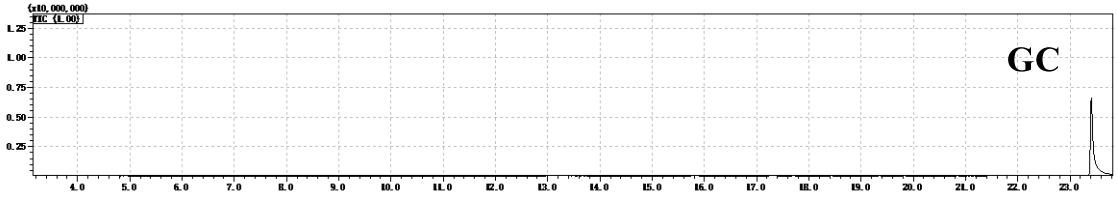
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 291.4 mg, 71% yield.

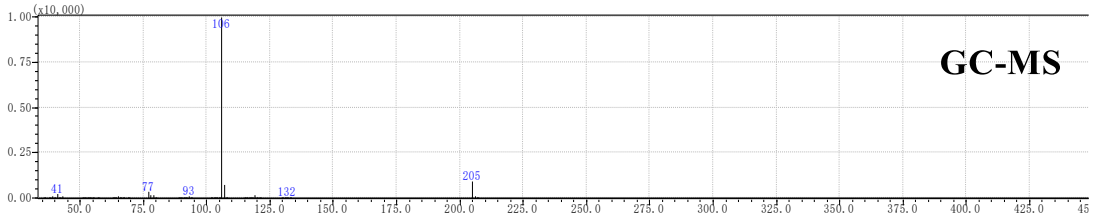
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 1H), 6.84 – 6.54 (m, 3H), 3.60 (s, 1H), 3.34 – 3.04 (m, 2H), 1.70 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.54 – 1.31 (m, 11H), 1.08 – 0.94 (m, 3H).

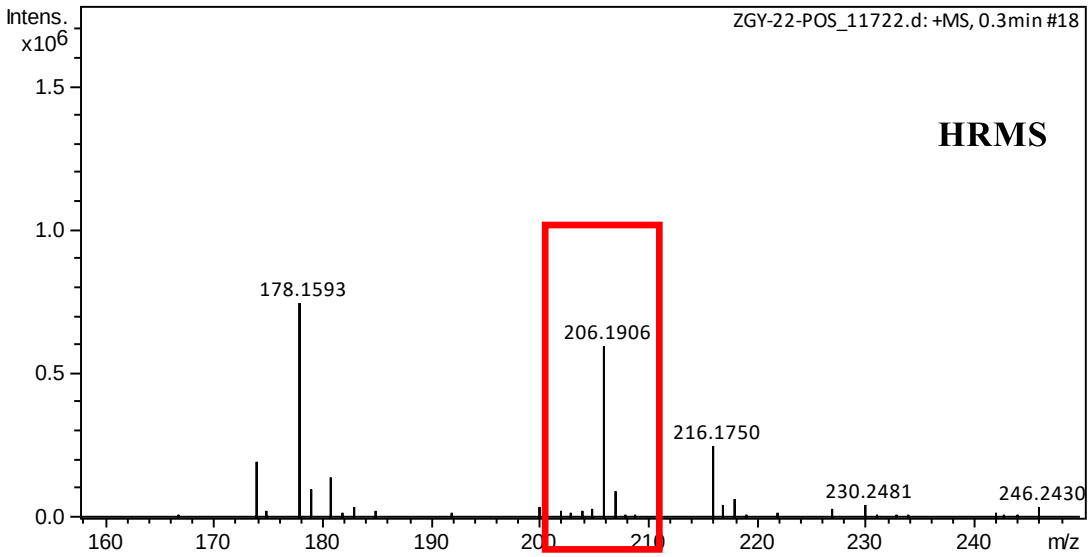
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.40, 129.06, 116.89, 112.53, 43.86, 31.74, 29.46, 29.33, 29.19, 27.09, 22.58, 14.01.

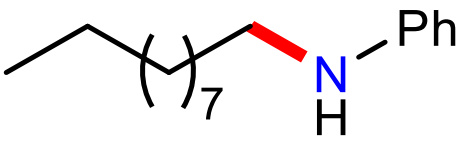
MS (70 eV): m/z (%) = 197.

HRMS (ESI) calcd. for $C_{14}H_{24}N$ [M+H]: 206.1909, found: 206.1906.









N-icosylaniline (3an) [1]

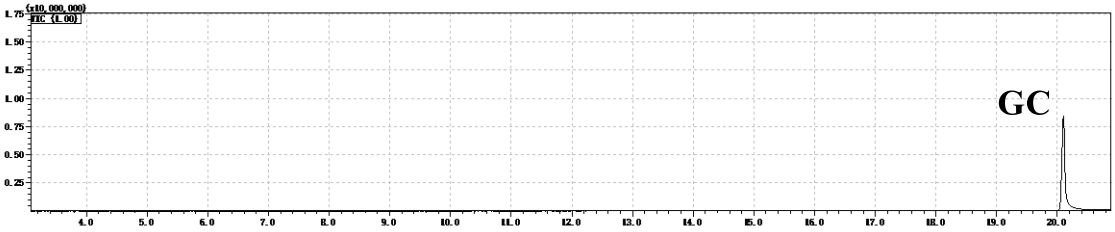
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 307.6 mg, 66% yield.

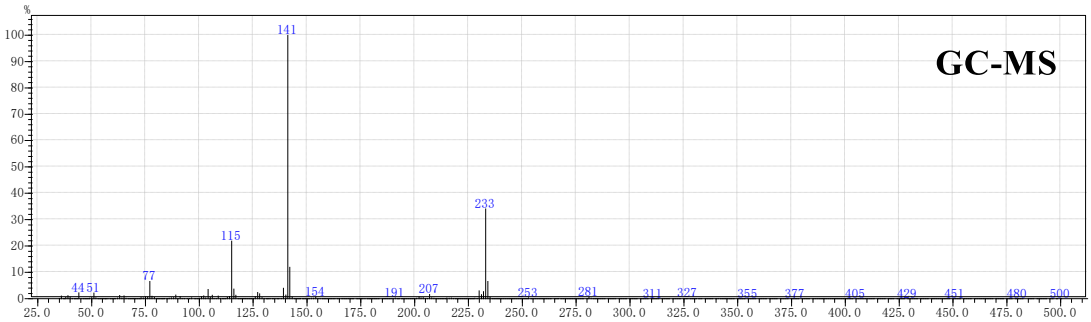
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 2H), 3.54 (s, 1H), 3.08 (t, *J* = 7.1 Hz, 2H), 1.65 – 1.52 (m, 2H), 1.46 – 1.15 (m, 16H), 0.88 (dd, *J* = 7.7, 5.9 Hz, 3H).

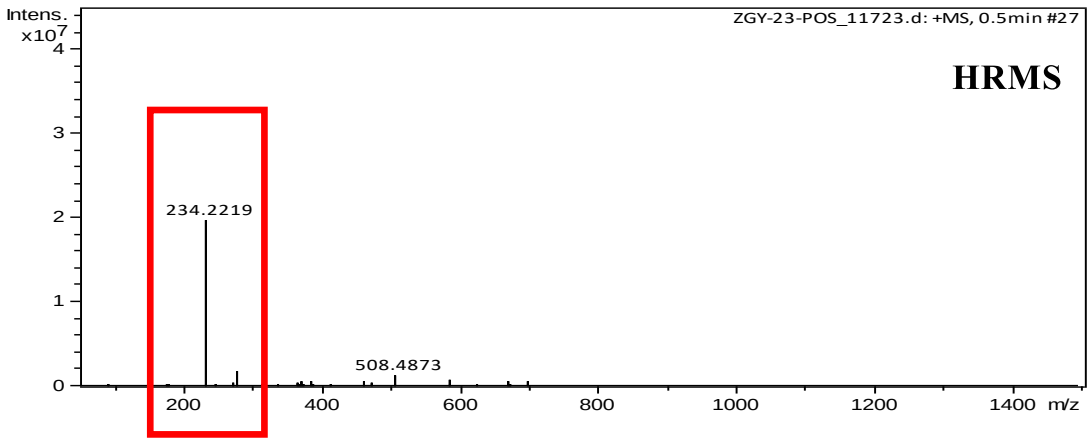
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59, 129.24, 117.09, 112.72, 44.05, 31.98, 29.69, 29.65, 29.54, 29.41, 27.26, 22.76, 14.19.

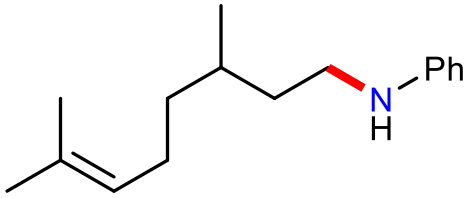
MS (70 eV): m/z (%) = 233.

HRMS (ESI) calcd. for $C_{16}H_{28}N$ [M+H]: 234.2222, found: 234.2219.









N-(3,7-dimethyloct-6-en-1-yl)aniline (3ao) [1]

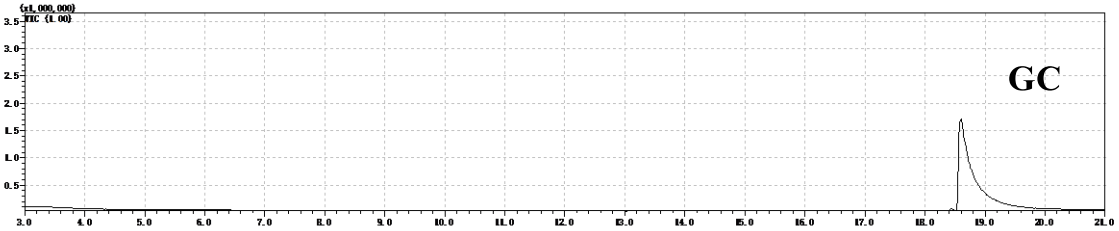
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 222.0 mg, 48% yield.

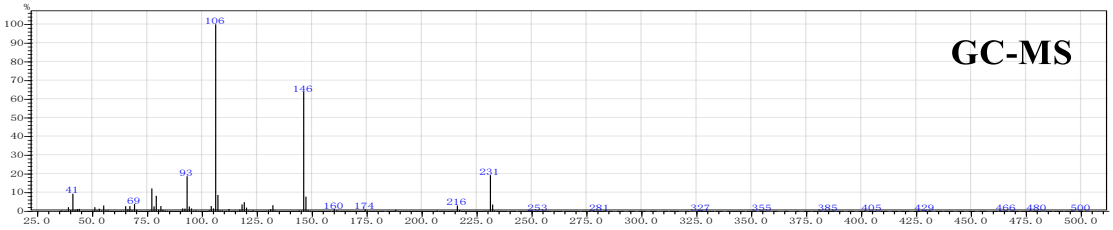
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.2, 7.6 Hz, 2H), 6.74 (td, *J* = 7.3, 0.8 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 2H), 5.16 (t, *J* = 7.1 Hz, 1H), 3.58 (s, 1H), 3.32 – 3.05 (m, 2H), 2.06 (dt, *J* = 15.5, 7.8 Hz, 2H), 1.75 (s, 3H), 1.72 – 1.56 (m, 5H), 1.46 (tdd, *J* = 11.9, 11.0, 7.0 Hz, 2H), 1.34 – 1.23 (m, 1H), 1.03 – 0.92 (m, 3H).

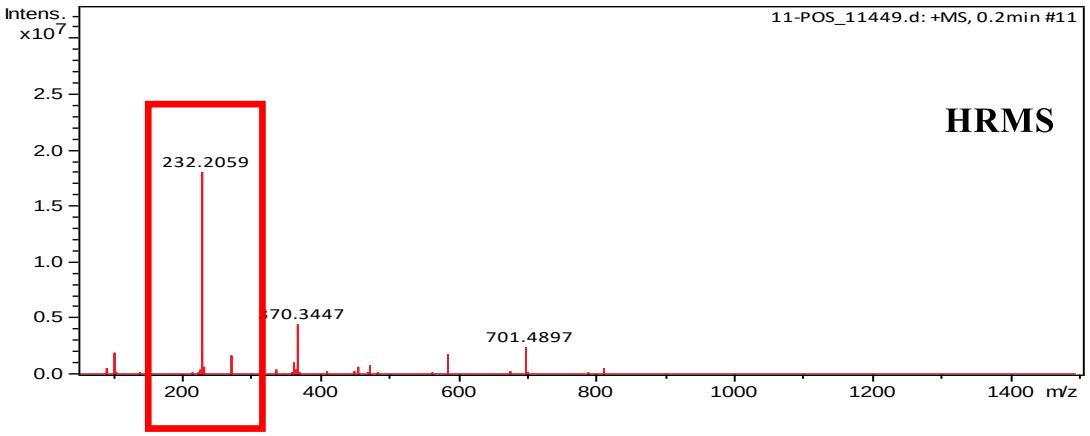
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.41, 131.17, 129.07, 124.54, 116.94, 112.54, 41.79, 36.97, 36.57, 30.30, 25.62, 25.36, 19.48, 17.56.

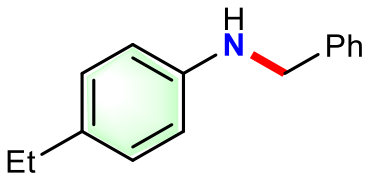
MS (70 eV): m/z (%) = 231.

HRMS (ESI) calcd. for $C_{16}H_{26}N$ [M+H]: 232.2065, found: 232.2059.









N-benzyl-4-ethylaniline (3ba) [1]

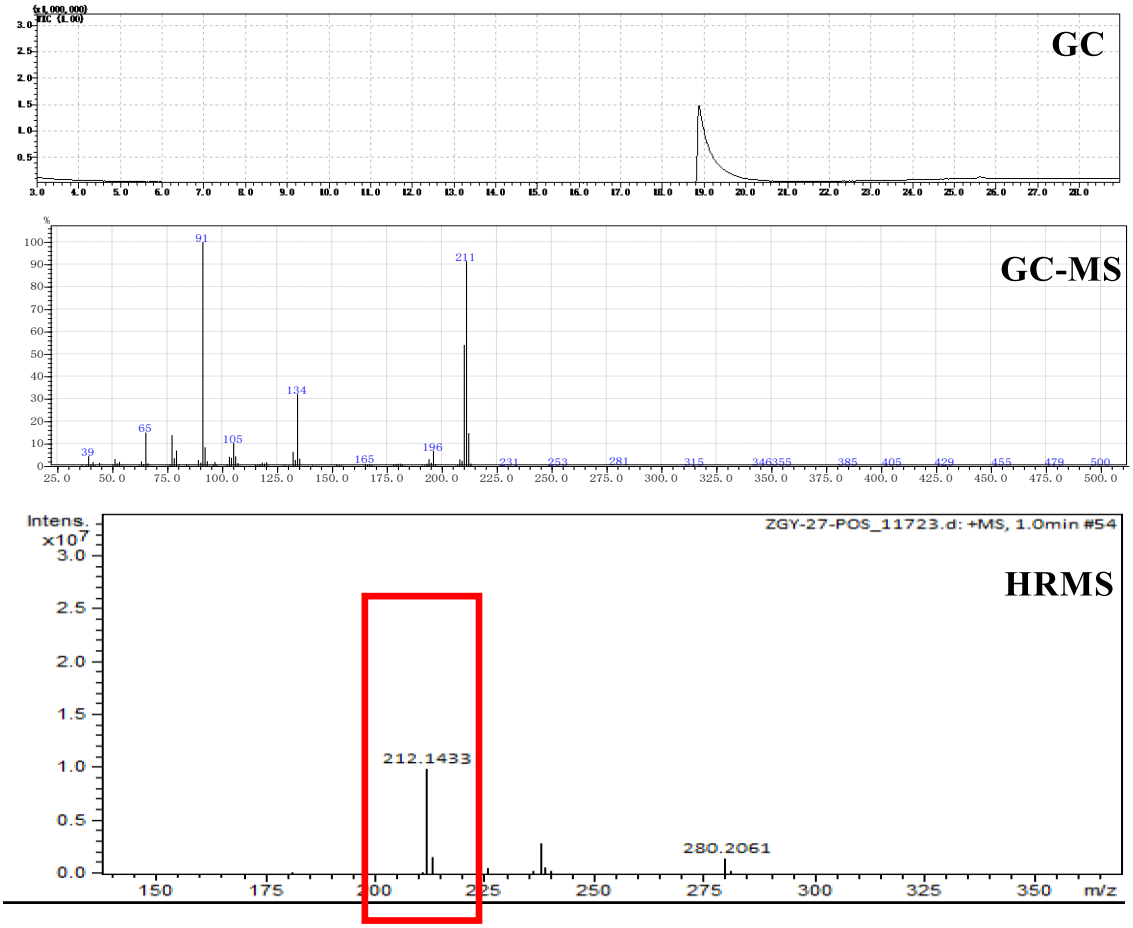
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 384.3 mg, 91% yield.

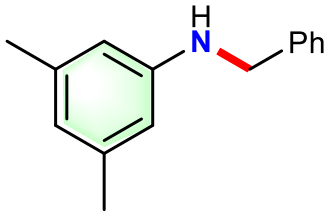
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.18 (m, 5H), 7.07 (dd, *J* = 8.2, 1.5 Hz, 2H), 6.64 (dd, *J* = 8.4, 1.8 Hz, 2H), 4.35 (d, *J* = 1.3 Hz, 2H), 3.95 (s, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.86, 139.39, 133.14, 128.33, 128.31, 127.26, 126.89, 112.70, 48.38, 27.69, 15.74.

MS (70 eV): m/z (%) = 211.

HRMS (ESI) calcd. for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1433.





N-benzyl-3,5-dimethylaniline (3ca) [1]

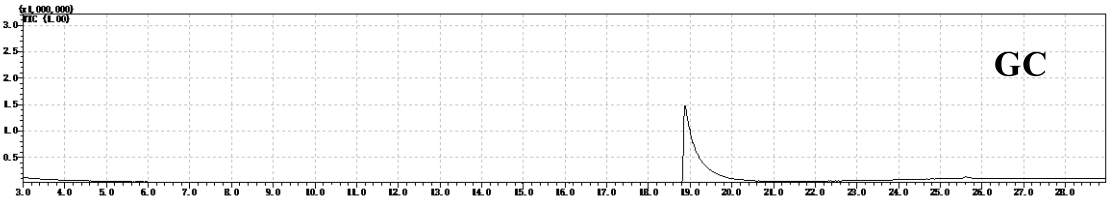
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 342.1 mg, 81% yield.

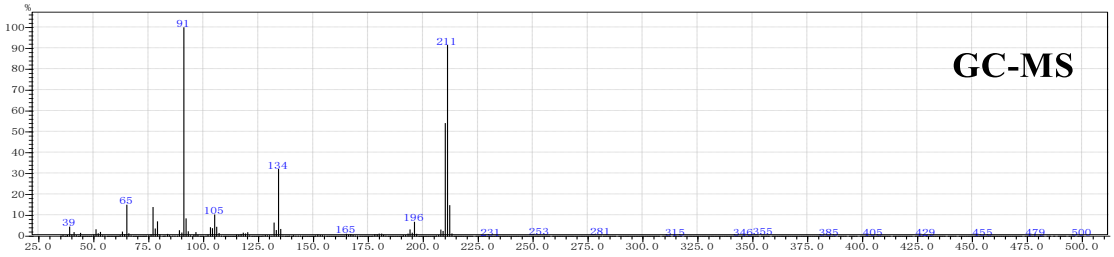
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.23 (m, 5H), 6.38 (d, *J* = 3.7 Hz, 1H), 6.26 (d, *J* = 4.2 Hz, 2H), 4.27 (d, *J* = 4.2 Hz, 2H), 3.84 (s, 1H), 2.23 (d, *J* = 4.0 Hz, 6H).

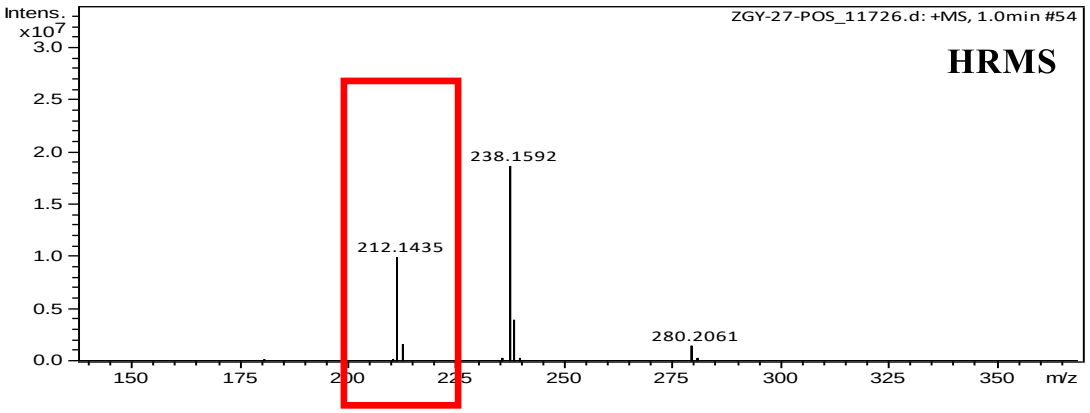
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.15, 139.51, 138.72, 128.42, 127.37, 126.98, 119.43, 110.60, 48.18, 21.36.

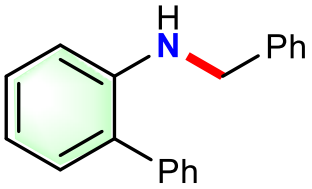
MS (70 eV): m/z (%) = 211.

HRMS (ESI) calcd. for $C_{15}H_{18}N$ [M+H]: 212.1439, found: 212.1435.









N-benzyl-[1,1'-biphenyl]-2-amine (3da) [1]

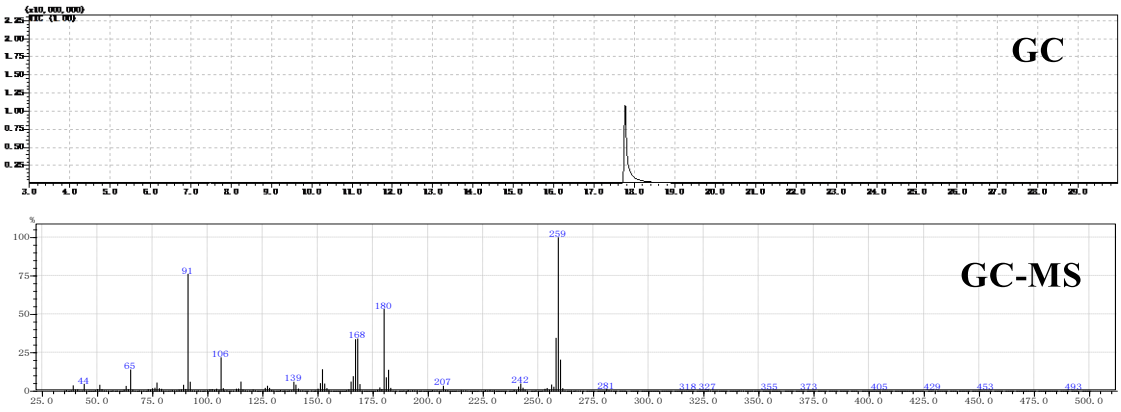
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 89.1 – 90.1 °C, 368.0 mg, 71% yield.

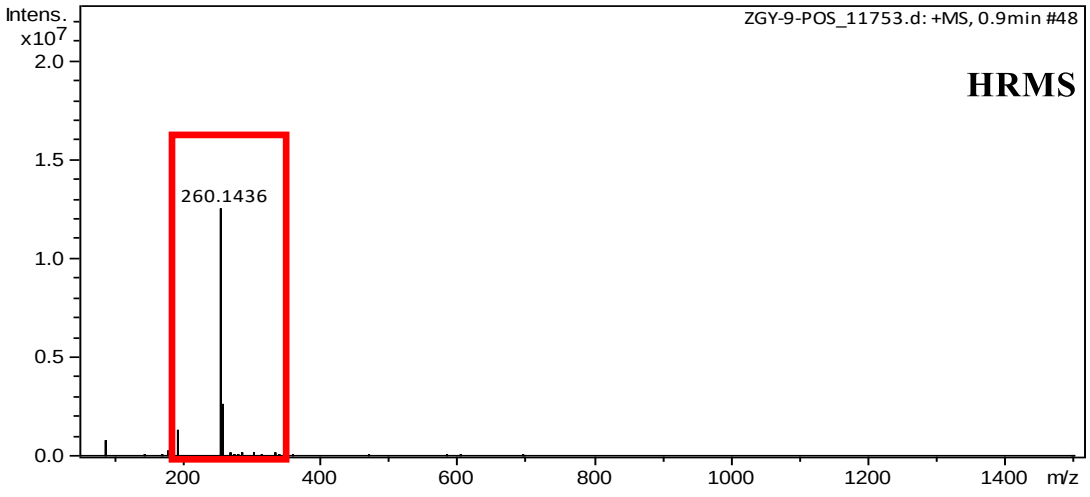
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.22 (m, 4H), 7.22 – 6.92 (m, 8H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 4.28 (s, 1H), 4.14 (s, 2H).

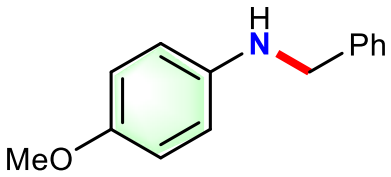
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.73, 139.35, 130.11, 129.25, 128.81, 128.61, 128.43, 127.49, 127.12, 126.86, 117.08, 110.65.

MS (70 eV): m/z (%) = 259.

HRMS (ESI) calcd. for $C_{19}H_{18}N$ [M+H]: 260.1439, found: 260.1436.







N-benzyl-4-methoxyaniline (3ea) [1]

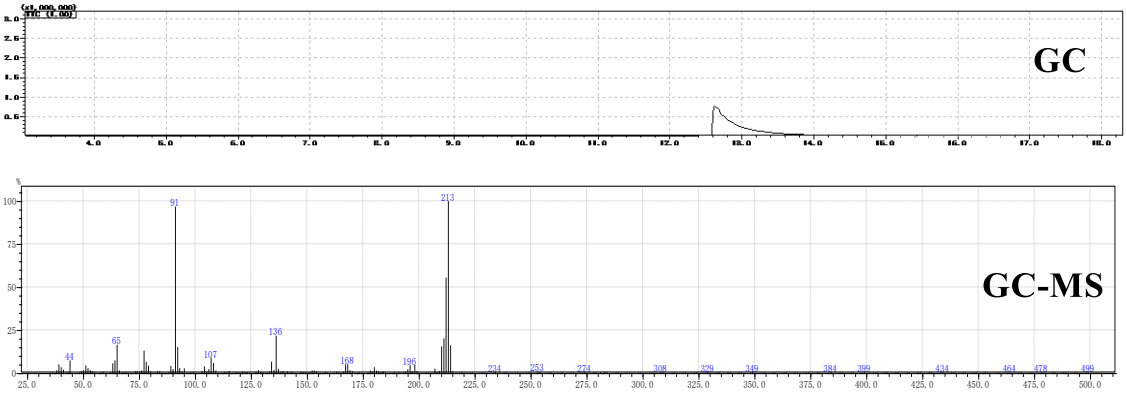
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 49.4 – 50.2 °C, 392.1 mg, 92% yield.

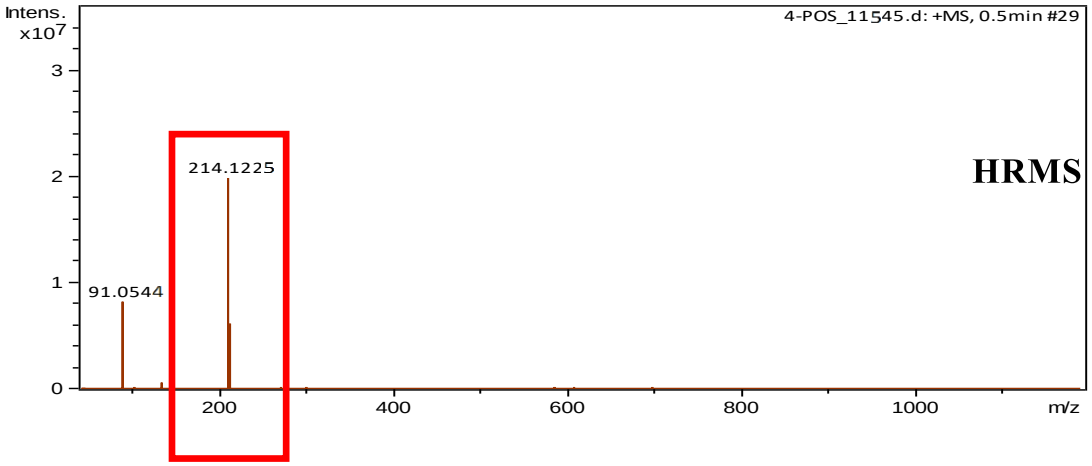
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 3H), 7.30 (d, *J* = 6.9 Hz, 1H), 6.87 – 6.73 (m, 2H), 6.70 – 6.57 (m, 2H), 4.30 (s, 2H), 4.27 (s, 1H), 3.76 (s, 3H).

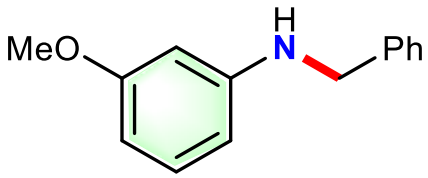
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.18, 142.22, 139.52, 128.54, 127.53, 127.14, 114.83, 114.15, 55.73, 49.23.

MS (70 eV): m/z (%) = 213.

HRMS (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1225.







N-benzyl-3-methoxyaniline (3fa) [1]

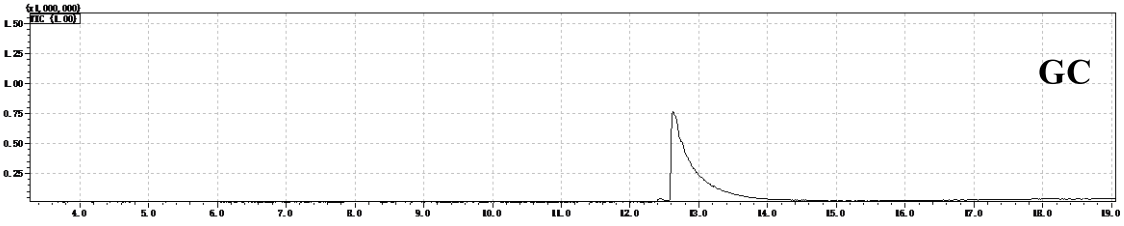
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 341.0 mg, 80% yield.

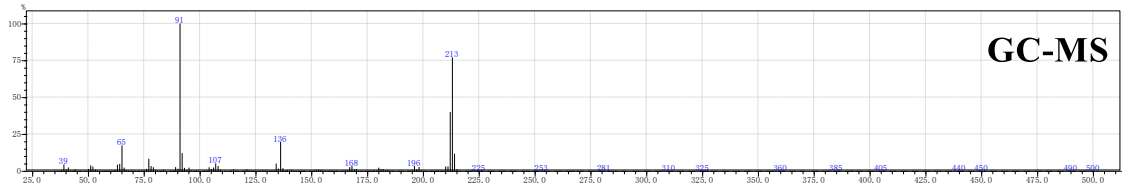
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 5H), 7.14 (t, *J* = 8.1 Hz, 1H), 6.41 – 6.28 (m, 2H), 6.25 (t, *J* = 2.3 Hz, 1H), 4.35 (s, 2H), 3.79 (s, 3H).

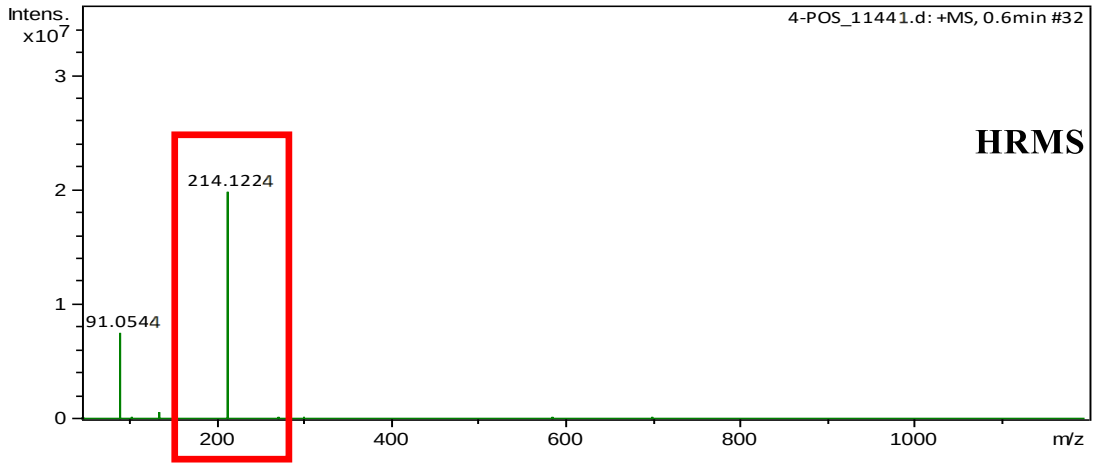
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.71, 149.40, 139.21, 129.91, 128.54, 127.43, 127.15, 105.91, 102.59, 98.79, 54.94, 48.20.

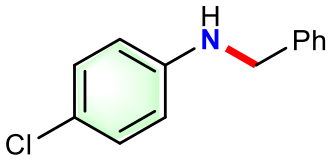
MS (70 eV): m/z (%) = 213.

HRMS (ESI) calcd. for $C_{14}H_{16}NO$ [M+H]: 214.1232, found: 214.1224.









N-benzyl-4-chloroaniline (3ga) [1]

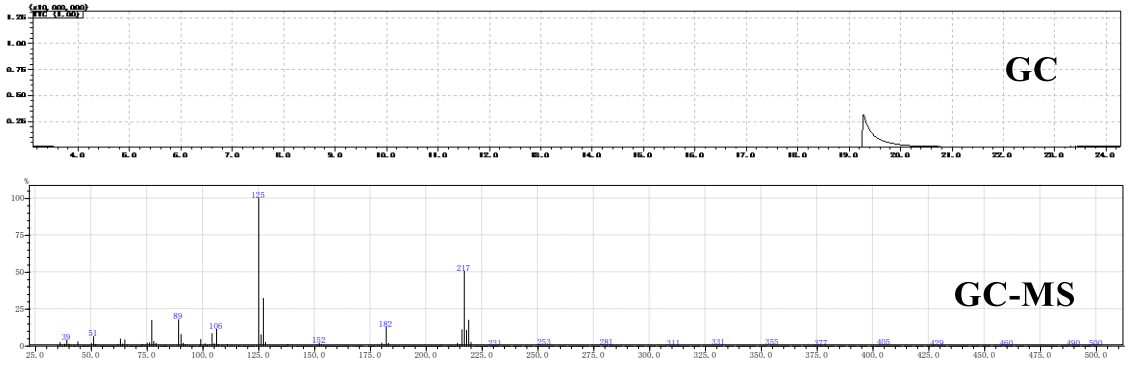
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 45.2 – 46.0 °C, 373.4 mg, 86% yield.

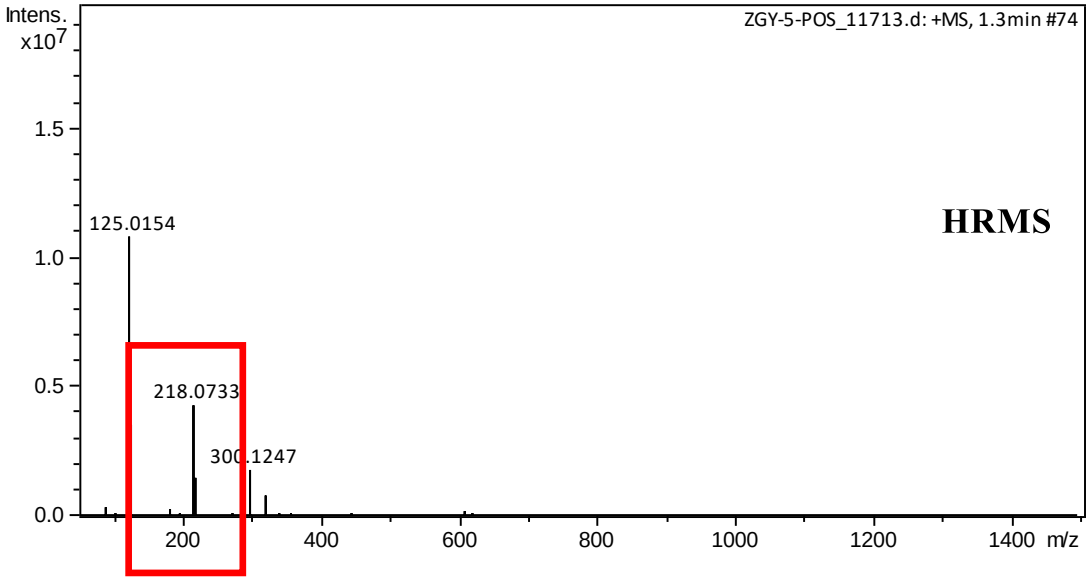
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.26 (m, 5H), 7.22 – 7.05 (m, 2H), 6.68 – 6.46 (m, 2H), 4.34 (s, 2H), 4.09 (s, 1H).

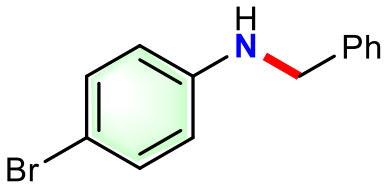
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.63, 138.93, 129.04, 128.68, 127.39, 127.35, 122.00, 113.90, 48.27.

MS (70 eV): m/z (%) = 217.

HRMS (ESI) calcd. for $C_{13}H_{13}ClN$ [M+H]: 218.0737, found: 218.0733.







N-benzyl-4-bromoaniline (3ha) [1]

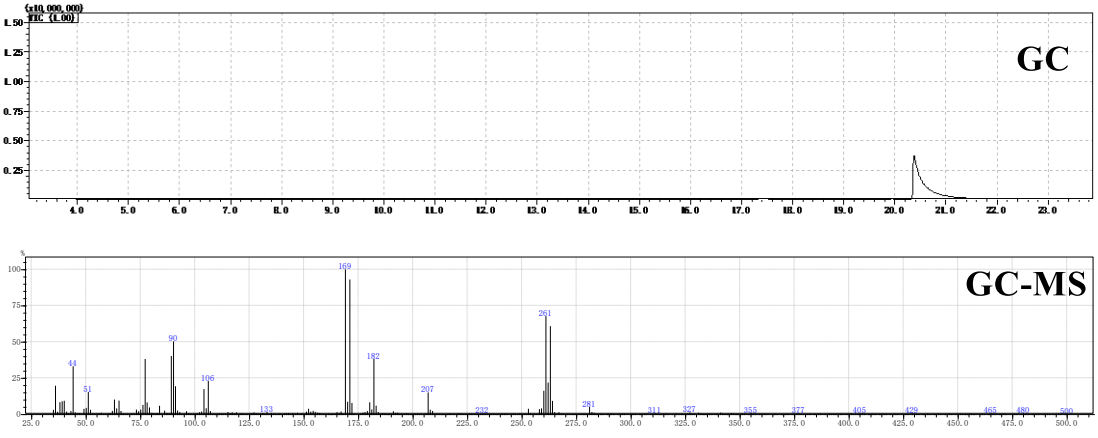
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 51.3 – 52.2 °C, 396.8 mg, 76% yield.

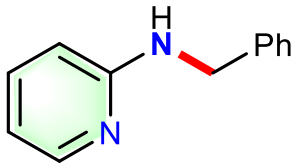
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.14 (m, 7H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.32 (s, 2H), 4.10 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.81, 138.63, 131.69, 128.48, 127.16, 114.19, 108.84, 47.96.

MS (70 eV): m/z (%) = 261.

HRMS (ESI) calcd. for $C_{13}H_{13}BrN$ [M+H]: 262.0231, found: 262.0225.





N-benzylpyridin-2-amine (3ia) [1]

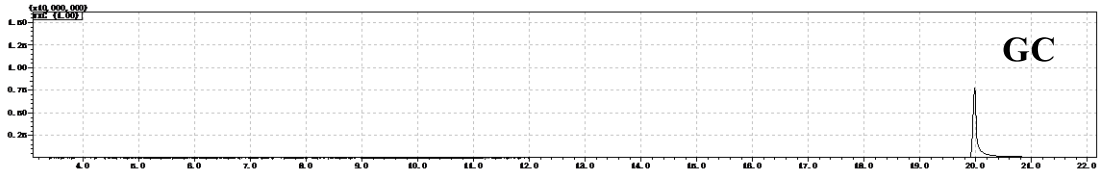
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 268.8 mg, 73% yield.

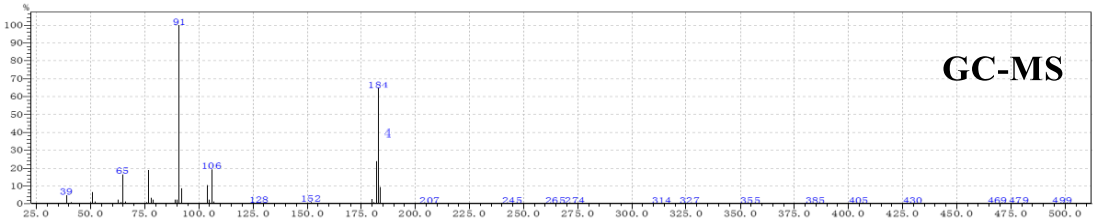
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 4.4 Hz, 1H), 7.42 – 7.24 (m, 5H), 7.24 – 7.18 (m, 1H), 6.61 – 6.45 (m, 1H), 6.31 (d, *J* = 8.4 Hz, 1H), 4.88 (s, 1H), 4.45 (d, *J* = 5.7 Hz, 2H).

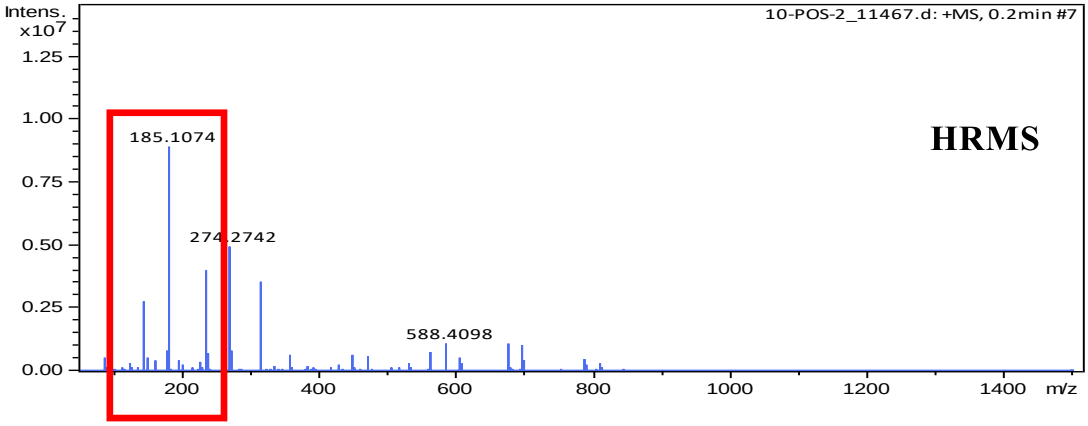
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.63, 155.79, 148.09, 138.85, 137.34, 131.65, 128.50, 127.27, 113.02, 106.66, 46.18.

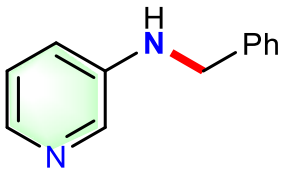
MS (70 eV): m/z (%) = 184

HRMS (ESI) calcd. for $C_{12}H_{13}N_2$ [M+H]: 185.1079, found: 185.1074.









N-benzylpyridin-3-amine (3ja) [1]

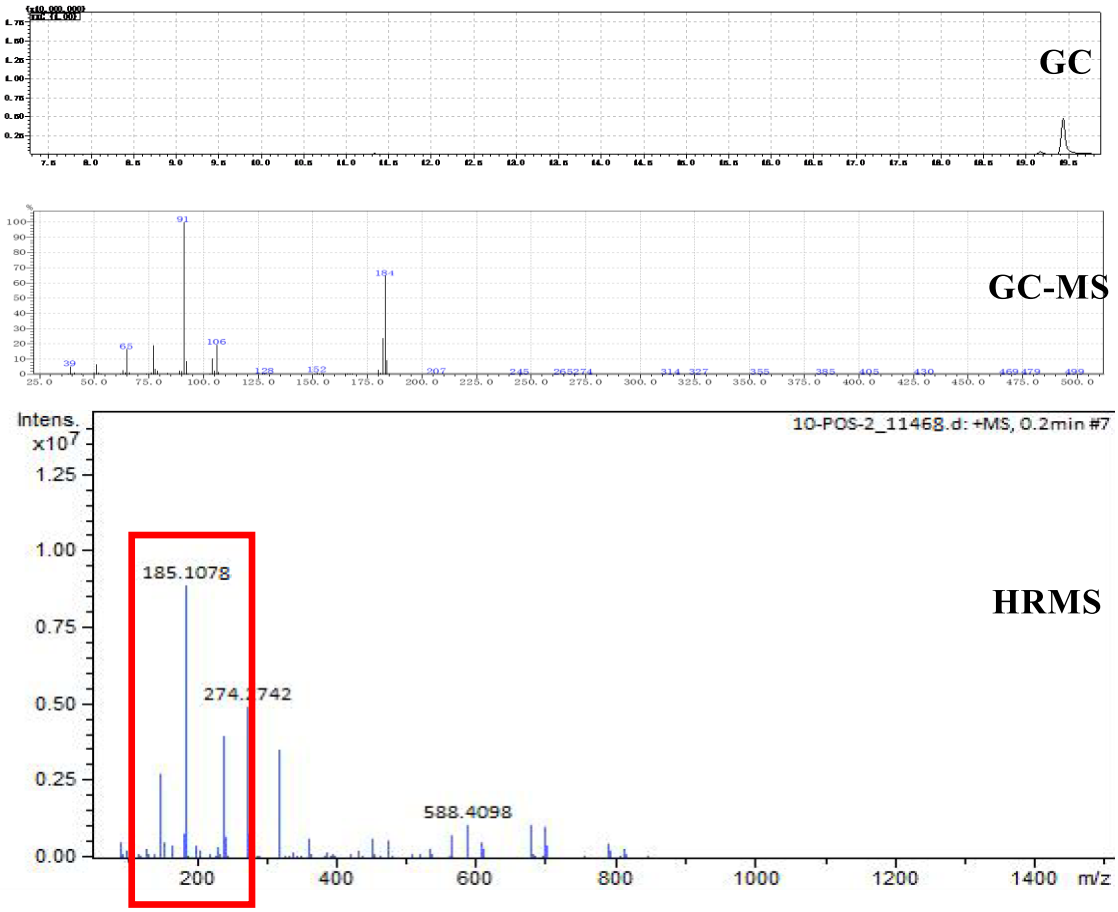
The title compound was prepared according to the general procedure and purified by column chromatography to give the yellow oil, 272.5 mg, 74% yield.

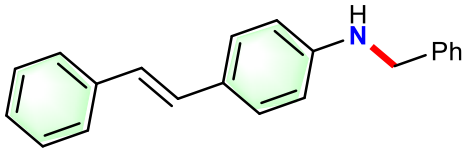
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (d, *J* = 2.9 Hz, 1H), 7.90 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.41 – 7.21 (m, 5H), 7.04 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.87 (ddd, *J* = 8.3, 2.9, 1.3 Hz, 1H), 4.34 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.09, 138.83, 138.51, 136.00, 128.55, 127.26, 127.22, 123.48, 118.26, 47.55.

MS (70 eV): m/z (%) = 184

HRMS (ESI) calcd. for $C_{12}H_{13}N_2$ [M+H]: 185.1079, found: 185.1078.





(*E*)-*N*-benzyl-4-styrylaniline (3ka) [1]

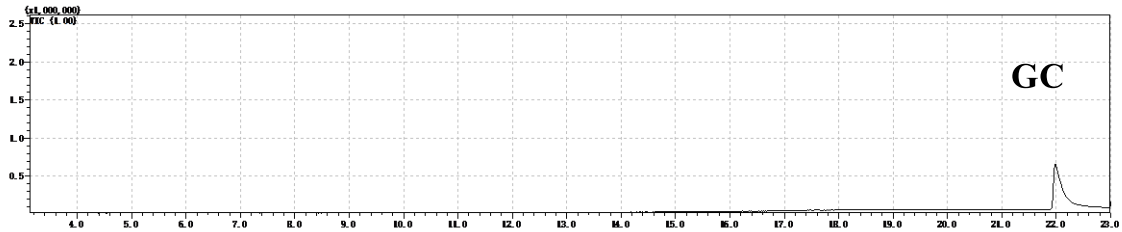
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 89.2 – 91.1 °C, 399.2 mg, 70% yield.

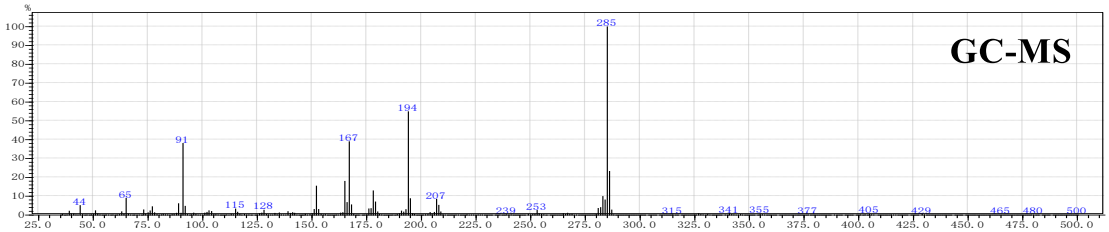
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.23 (m, 10H), 7.02 (dd, *J* = 39.8, 16.2 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 2H), 4.42 (s, 2H), 4.26 (s, 1H).

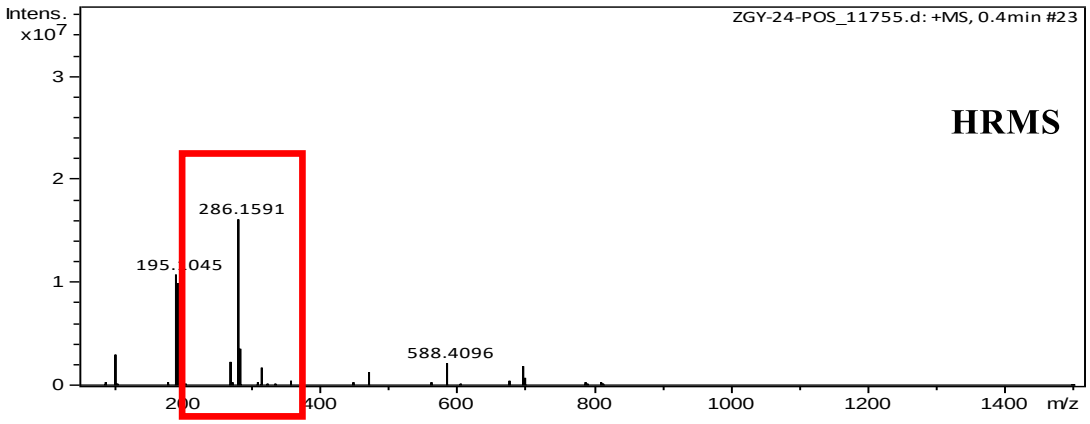
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 139.20, 138.15, 128.85, 128.76, 128.66, 127.85, 127.55, 127.40, 127.11, 126.84, 126.12, 124.68, 113.03, 48.29.

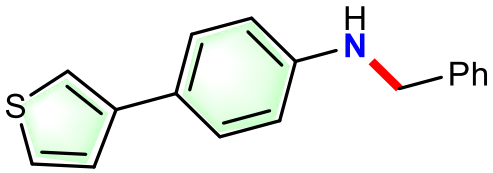
MS (70 eV): m/z (%) = 285.

HRMS (ESI) calcd. for $C_{12}H_{13}N_2$ [M+H]: 286.1596, found: 286.1591.









N-benzyl-4-(thiophen-3-yl)aniline (3la) [1]

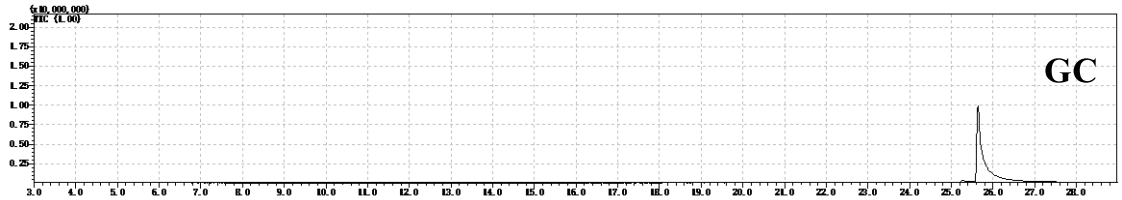
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 424.2 mg, 80% yield.

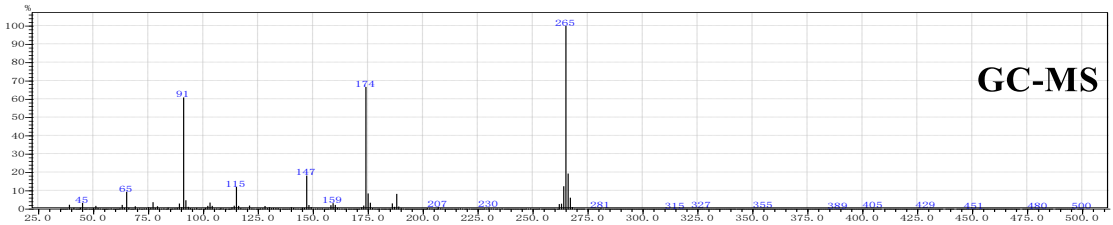
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02 (d, *J* = 2.9 Hz, 1H), 7.89 (dd, *J* = 4.6, 1.3 Hz, 1H), 7.40 – 7.20 (m, 5H), 7.03 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.86 (ddd, *J* = 8.3, 2.9, 1.3 Hz, 1H), 4.33 (s, 3H).

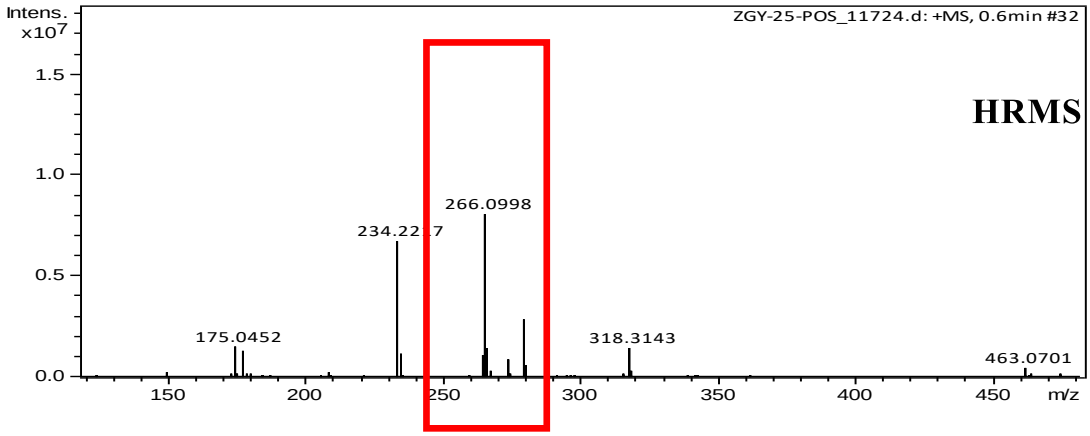
^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.17, 138.91, 138.59, 136.08, 128.62, 127.34, 127.30, 123.56, 118.34, 47.63.

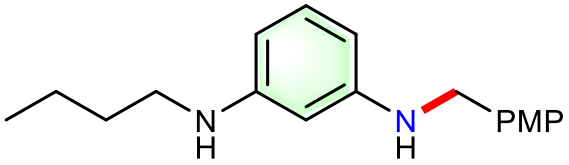
MS (70 eV): m/z (%) = 265.

HRMS (ESI) calcd. for $C_{21}H_{20}N$ [M+H]: 266.1003, found: 266.0998.









N^1-butyl-N^3-(4-methoxybenzyl)benzene-1,3-diamine (3ma) [1]

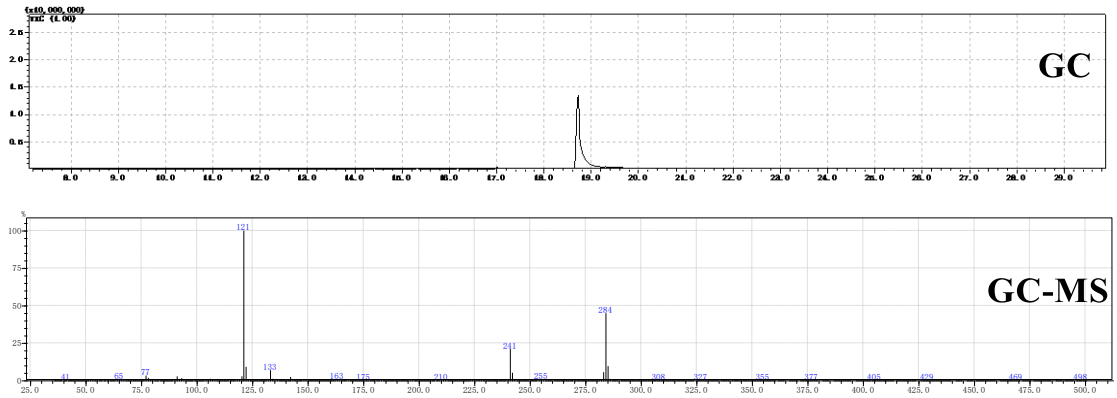
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 454.7 mg, 80% yield.

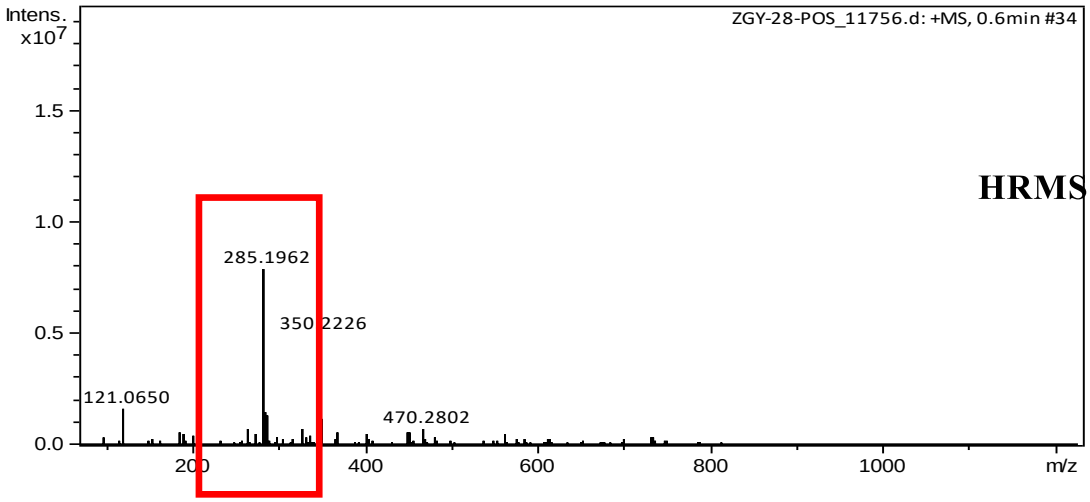
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 – 7.26 (m, 2H), 6.97 – 6.84 (m, 3H), 6.01 (dt, *J* = 7.9, 2.1 Hz, 2H), 5.90 (t, *J* = 2.2 Hz, 1H), 4.25 (s, 2H), 3.82 (s, 3H), 3.08 (t, *J* = 7.0 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.44 (dd, *J* = 15.2, 7.1 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

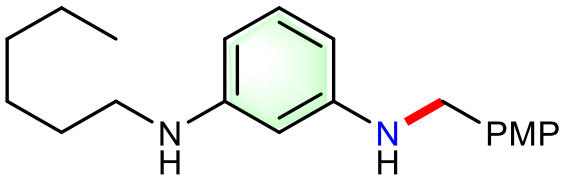
^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.73, 149.79, 149.39, 131.88, 129.64, 128.57, 113.74, 102.61, 102.35, 96.85, 55.12, 47.51, 43.54, 31.66, 20.25, 13.64.

MS (70 eV): m/z (%) = 284.

HRMS (ESI) calcd. for $C_{17}H_{16}NS$ [M+H]: 285.1967, found: 285.1962.







N^1-hexyl-N^3-(4-methoxybenzyl)benzene-1,3-diamine (3na) [1]

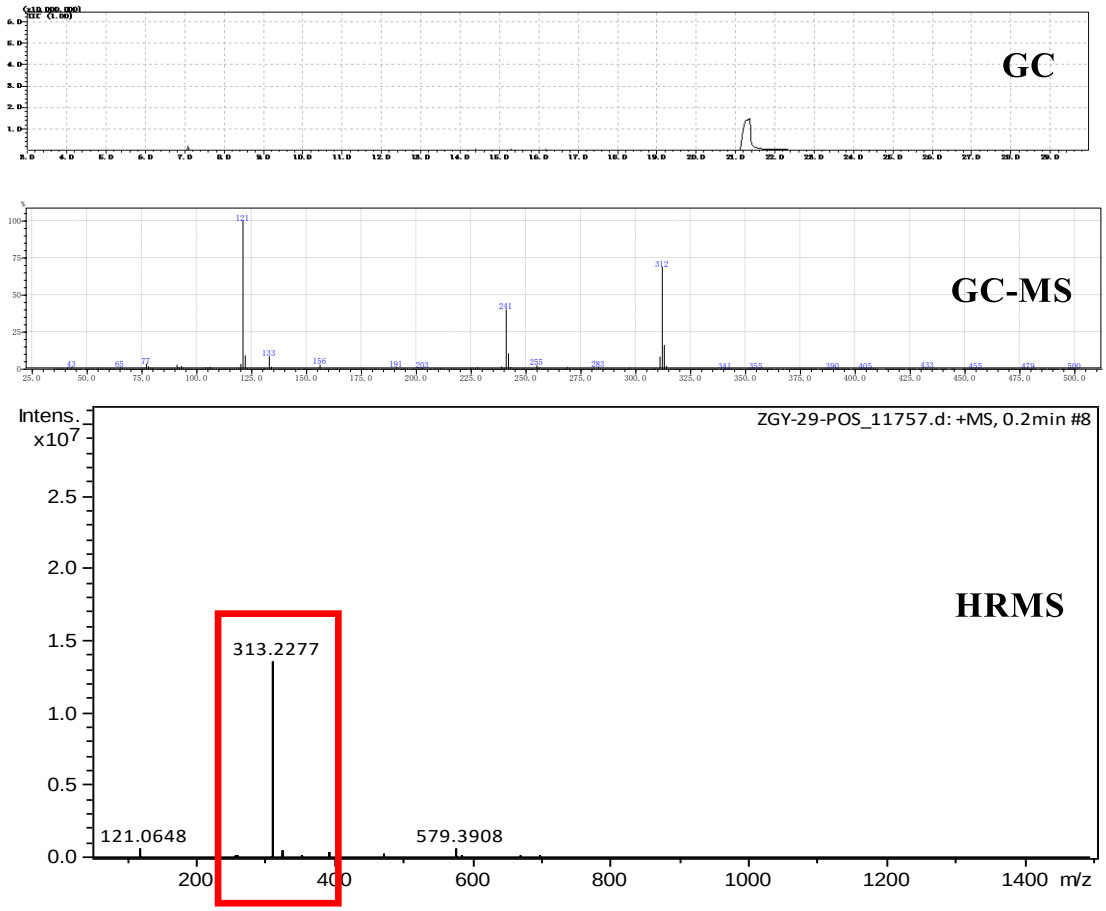
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 505.8 mg, 81% yield.

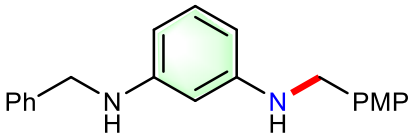
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.96 – 6.85 (m, 3H), 6.02 (d, *J* = 8.0 Hz, 2H), 5.90 (s, 1H), 4.26 (s, 2H), 3.82 (s, 3H), 3.08 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.54 (m, 2H), 1.41 (dd, *J* = 16.8, 5.9 Hz, 6H), 0.96 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.81, 149.87, 149.47, 131.96, 129.72, 128.65, 113.82, 102.68, 102.42, 96.93, 55.19, 47.58, 43.95, 31.70, 29.60, 26.88, 22.68, 13.86.

MS (70 eV): m/z (%) = 312.

HRMS (ESI) calcd. for $C_{18}H_{25}N_2O$ [M+H]: 313.2280, found: 313.2277.





N^1-benzyl-N^3-(4-methoxybenzyl)benzene-1,3-diamine (3oa) [1]

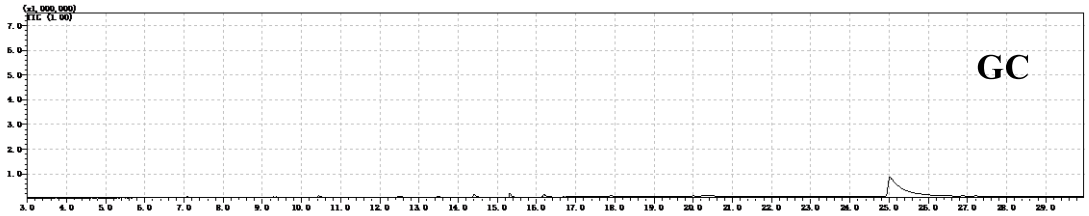
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, 445.5 mg, 70% yield.

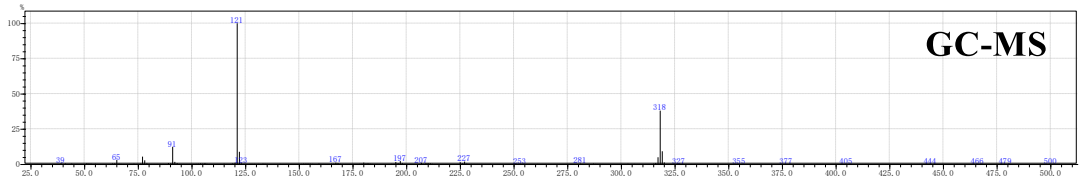
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.34 (m, 7H), 7.36 – 7.28 (m, 3H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.05 (dd, *J* = 8.0, 2.1 Hz, 2H), 5.94 (d, *J* = 2.1 Hz, 1H), 4.30 (d, *J* = 3.5 Hz, 4H), 4.07 (s, 2H).

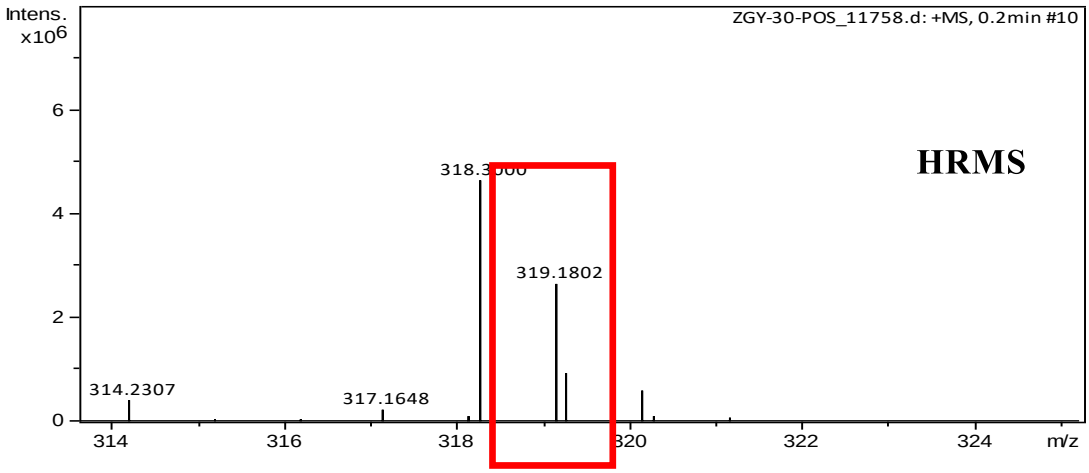
^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.41, 140.01, 129.82, 128.49, 127.41, 127.01, 102.89, 97.21, 48.08.

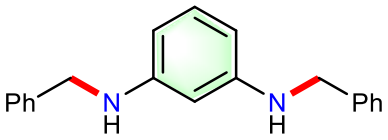
MS (70 eV): m/z (%) = 318.

HRMS (ESI) calcd. for $C_{20}H_{29}N_2O$ [M+H]: 319.1810, found: 319.1802.









N^1,N^3-dibenzylbenzene-1,3-diamine (3pa) [1]

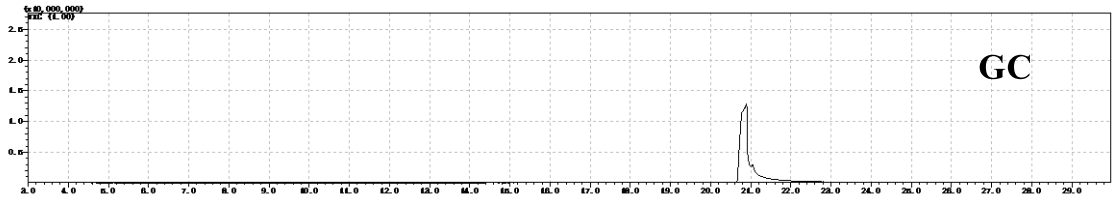
The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow solid, mp: 120.1 – 121.0 °C, 363.1 mg, 63% yield.

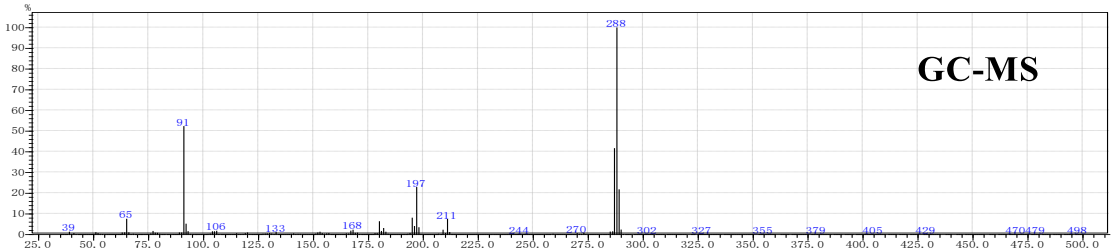
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.39 (dd, *J* = 7.2, 4.1 Hz, 4H), 7.36 – 7.23 (m, 3H), 7.03 – 6.82 (m, 3H), 6.05 (dd, *J* = 8.0, 2.2 Hz, 2H), 5.94 (t, *J* = 1.8 Hz, 1H), 4.31 (s, 2H), 4.23 (s, 2H), 4.05 (d, *J* = 7.4 Hz, 2H), 3.82 (s, 3H).

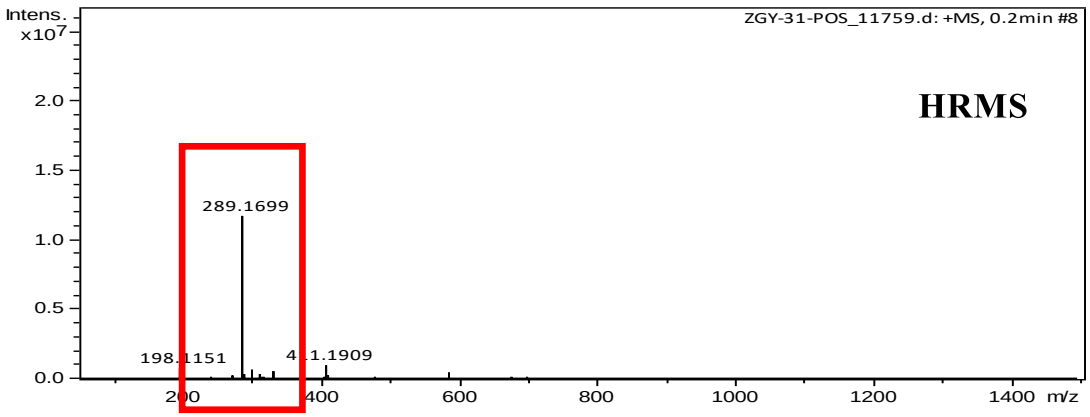
^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.81, 149.47, 149.40, 140.03, 131.86, 129.78, 128.66, 128.48, 128.42, 127.39, 126.99, 126.85, 113.84, 102.92, 102.84, 97.21, 65.03, 55.20, 48.08, 47.55.

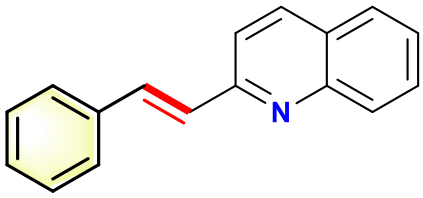
MS (70 eV): m/z (%) = 288.

HRMS (ESI) calcd. for $C_{21}H_{23}N_2O$ [M+H]: 289.1705, found: 289.1699.









(*E*)-2-styrylquinoline (5aa)[2]

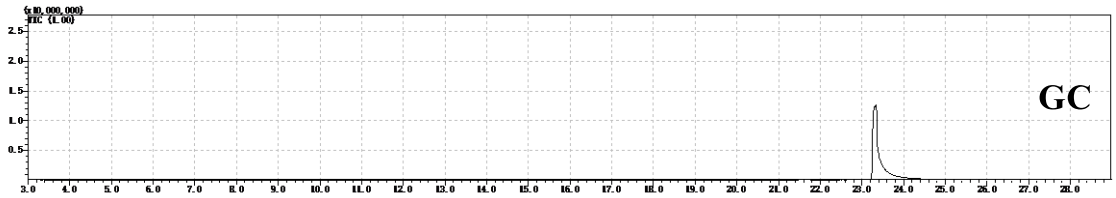
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 98.1 – 99.0 °C, 383.6 mg, 83% yield.

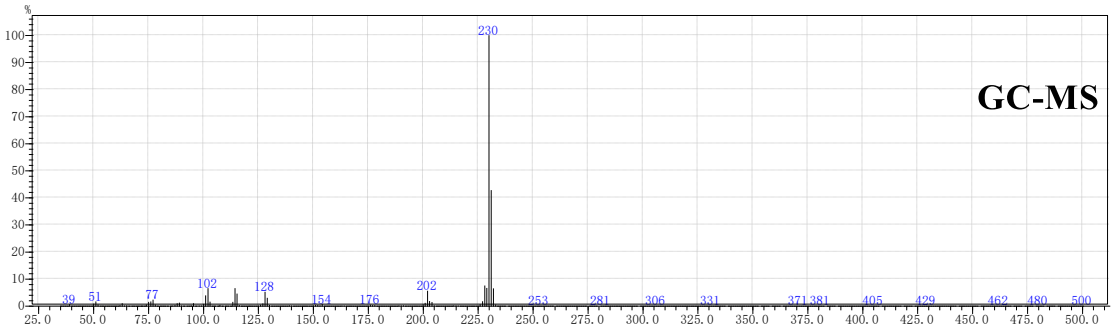
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.64 (m, 4H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.36 – 7.29 (m, 1H).

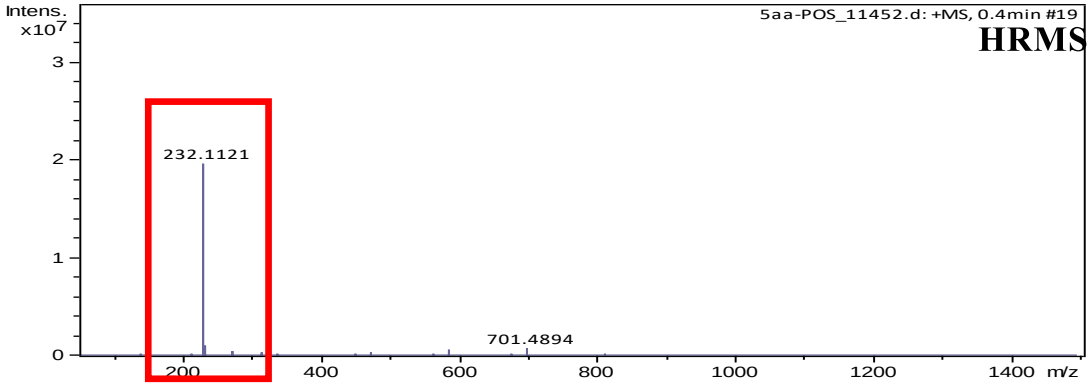
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.88, 148.14, 136.42, 136.27, 134.36, 129.67, 129.10, 128.90, 128.72, 128.56, 127.43, 127.19, 126.09, 119.17.

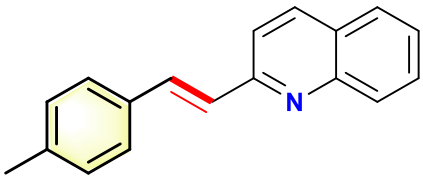
MS (70 eV): m/z (%) = 230.

HRMS (ESI) calcd. for $C_{17}H_{14}N$ [M+H]: 232.1126, found: 232.1121.









(*E*)-2-(4-methylstyryl)quinoline (5ab) [2]

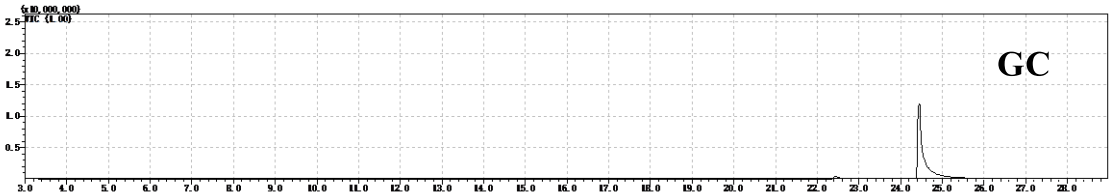
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 133.2 – 134.1 °C, 402.0 mg, 82% yield.

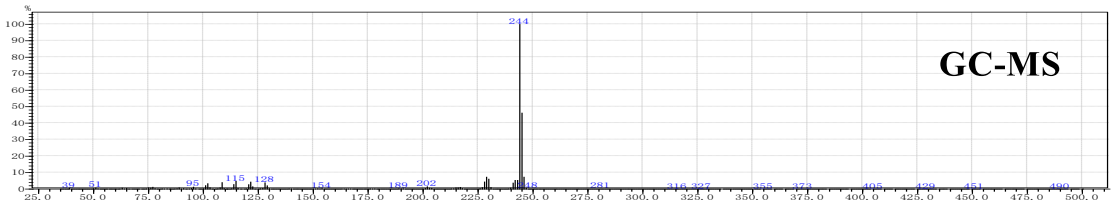
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.73 (dt, *J* = 5.3, 4.7 Hz, 2H), 7.68 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.40 (d, *J* = 16.3 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).

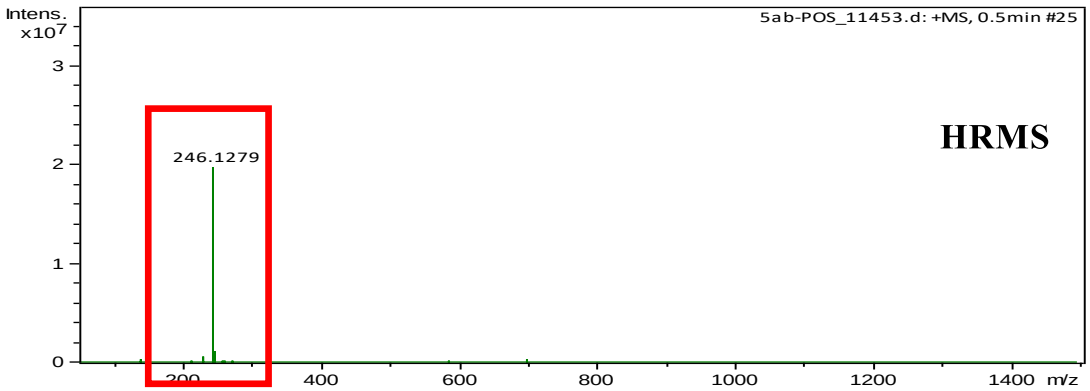
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.03, 148.11, 138.56, 136.09, 134.23, 133.58, 129.52, 129.37, 128.99, 127.89, 127.32, 127.11, 127.05, 125.87, 119.04, 21.22.

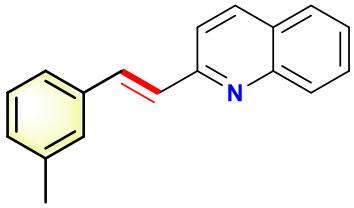
MS (70 eV): m/z (%) = 244.

HRMS (ESI) calcd. for $C_{18}H_{16}N$ [M+H]: 246.1283, found: 246.1279.









(*E*)-2-(3-methylstyryl)quinoline (5ac) [2]

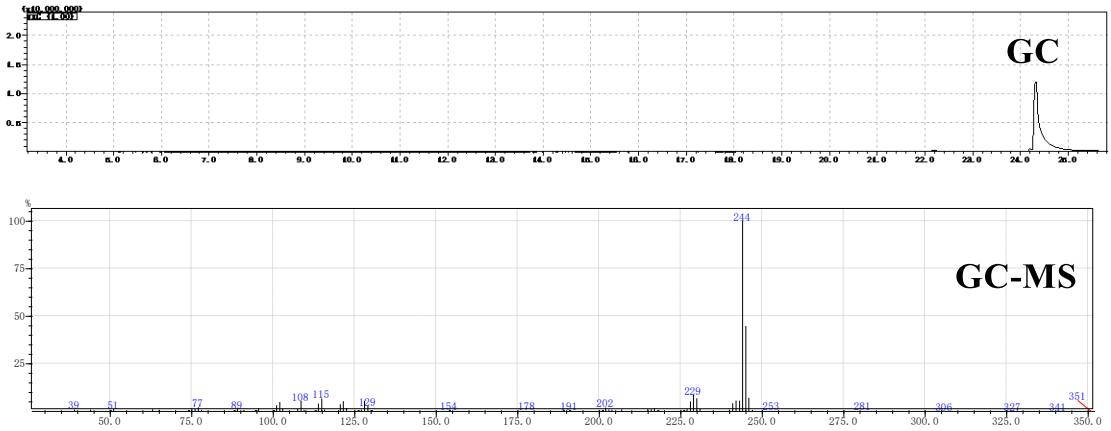
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 68.0 – 69.2 °C, 348.1 mg, 71% yield.

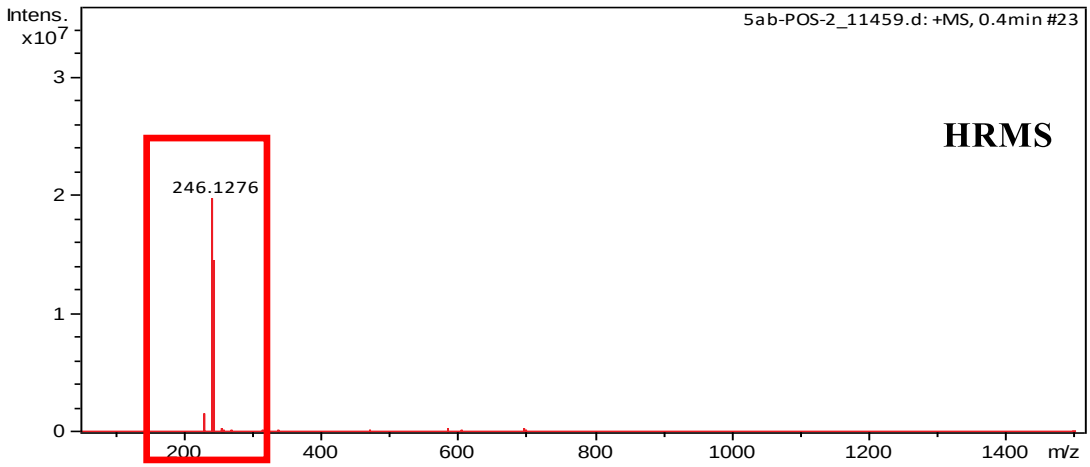
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.51 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 2.53 (s, 3H).

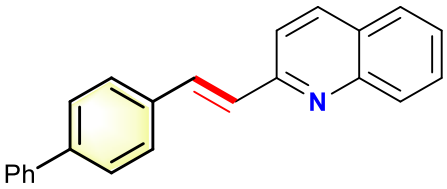
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.56, 148.73, 138.82, 136.94, 136.78, 135.00, 130.19, 129.95, 129.69, 129.36, 129.17, 128.43, 127.97, 126.60, 124.96, 119.70, 21.94.

MS (70 eV): m/z (%) = 244.

HRMS (ESI) calcd. for $C_{18}H_{16}N$ [M+H]: 246.1283, found: 246.1276.







(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)quinoline (5ad) [2]

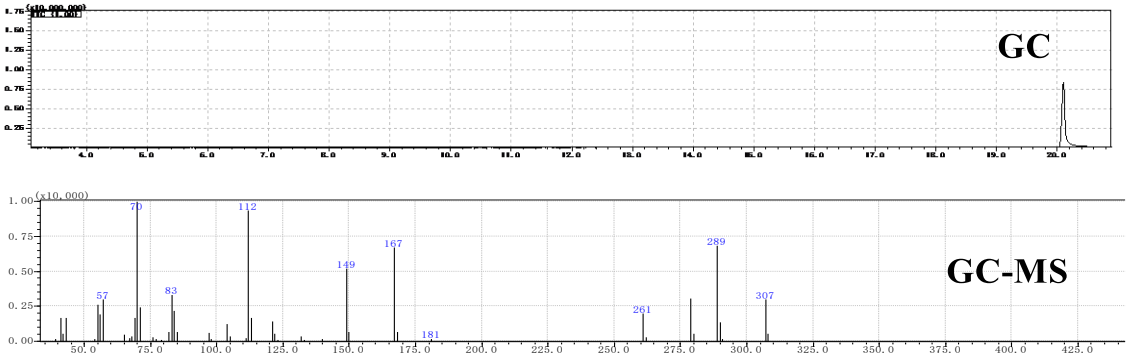
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 123.5 – 124.6 °C, 454.6 mg, 74% yield.

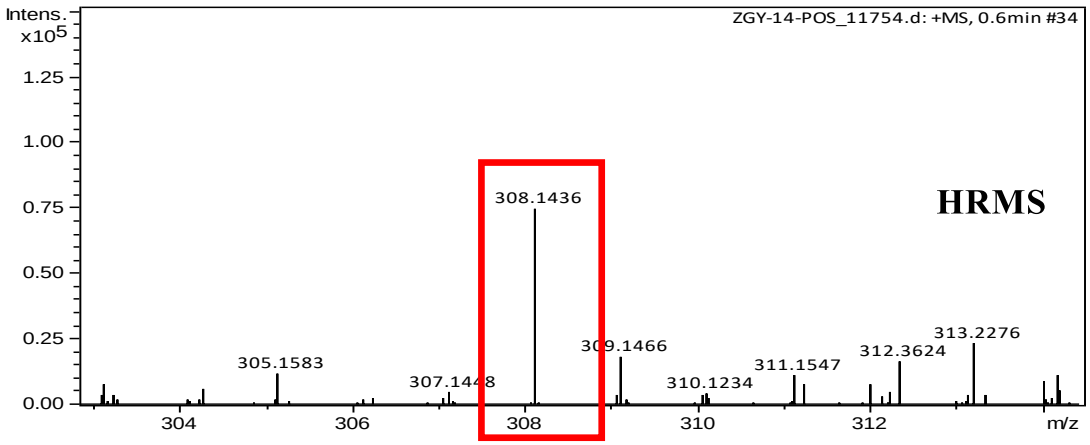
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.65 – 7.53 (m, 5H), 7.48 – 7.42 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.31 (dd, *J* = 11.2, 4.6 Hz, 1H).

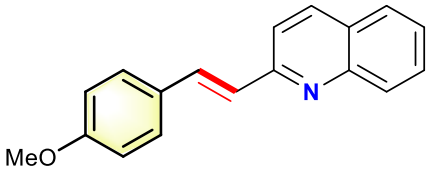
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 148.33, 141.40, 140.56, 136.45, 135.61, 134.04, 129.86, 129.26, 129.03, 128.92, 127.81, 127.60, 127.53, 127.43, 127.05, 126.27, 119.39.

MS (70 eV): m/z (%) = 307.

HRMS (ESI) calcd. for $C_{23}H_{18}N$ [M+H]: 308.1439, found: 308.1436.







(*E*)-2-(4-methoxystyryl)quinoline (5ae) [2]

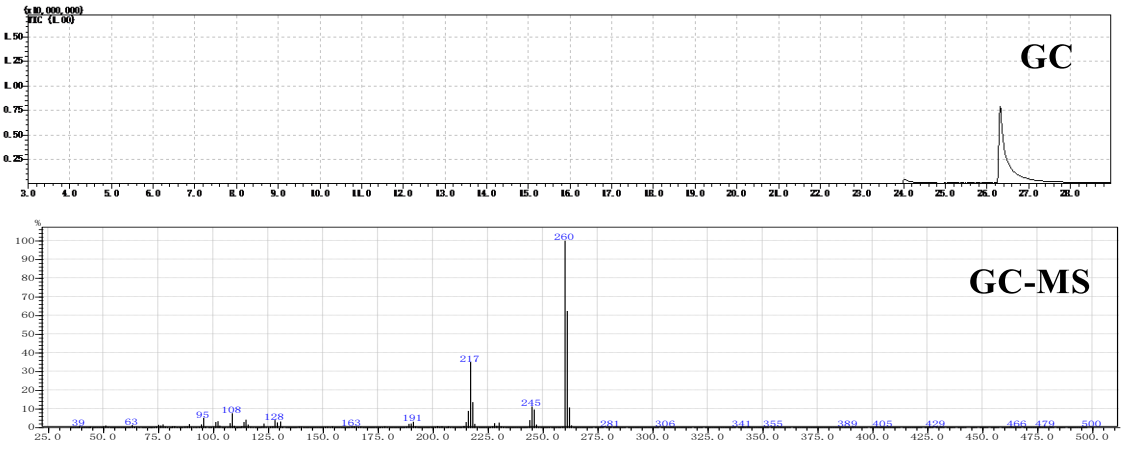
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 127.1 – 128.3 °C, 423.0 mg, 81% yield.

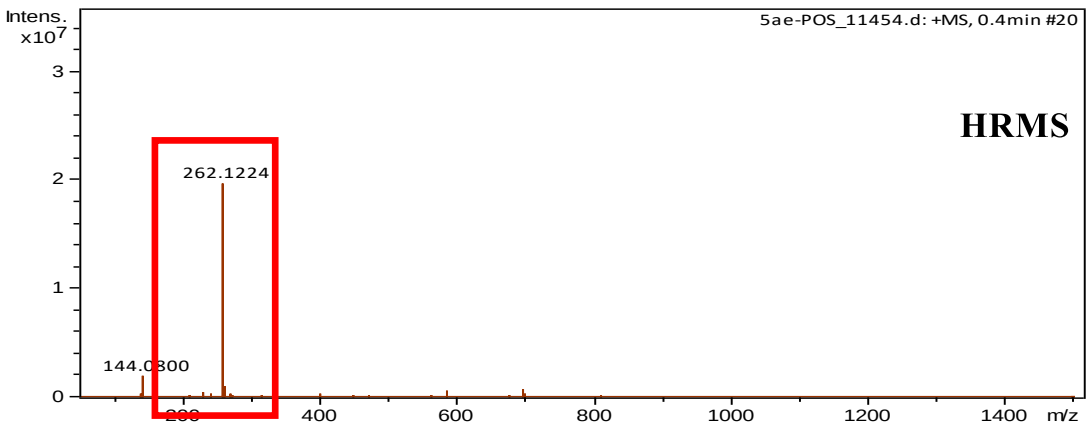
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.56 (dd, *J* = 11.4, 6.7 Hz, 3H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.20 (m, 2H), 6.89 (d, *J* = 7.3 Hz, 2H), 3.80 (s, 3H).

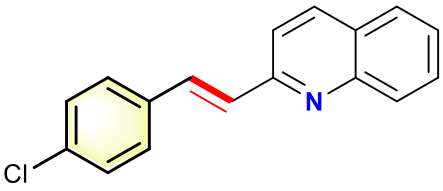
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.96, 156.19, 148.13, 136.07, 133.89, 129.52, 129.15, 128.94, 128.49, 127.34, 127.06, 126.72, 125.78, 119.00, 114.11, 55.20.

MS (70 eV): m/z (%) = 260.

HRMS (ESI) calcd. for $C_{18}H_{16}NO$ [M+H]: 262.1232, found: 262.1244.







(*E*)-2-(4-chlorostyryl)quinoline (5af) [2]

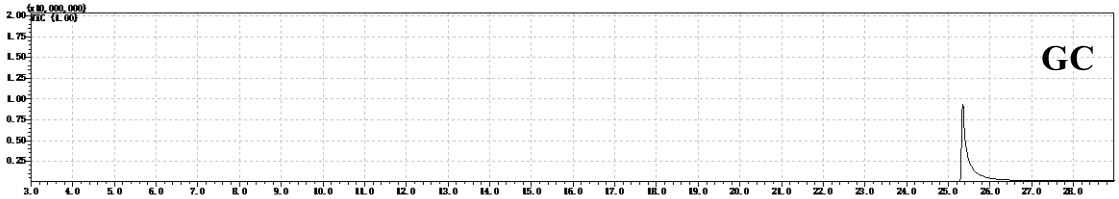
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 142.0 – 143.1 °C, 371.1 mg, 70% yield.

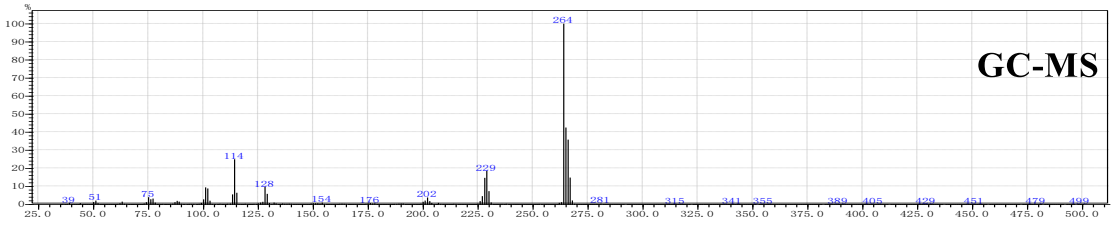
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.61 (m, 3H), 7.60 – 7.48 (m, 3H), 7.37 (dd, *J* = 12.1, 3.7 Hz, 3H).

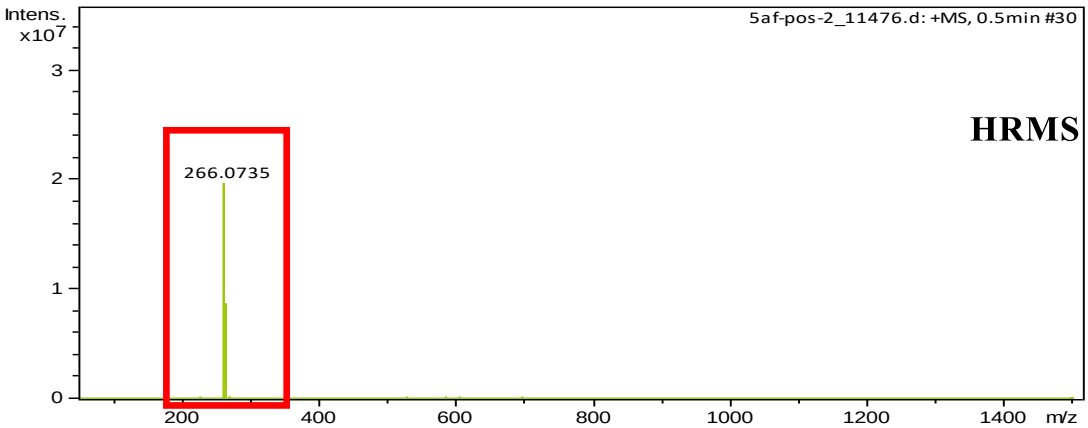
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.56, 148.25, 136.40, 135.02, 134.26, 132.96, 129.81, 129.50, 129.22, 128.99, 128.37, 127.51, 127.38, 126.28, 119.35.

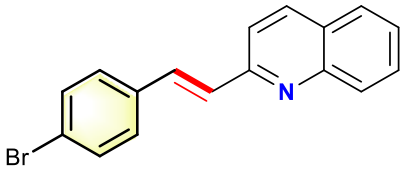
MS (70 eV): m/z (%) = 264.

HRMS (ESI) calcd. for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0735.









(*E*)-2-(4-bromostyryl)quinoline (5ag) [2]

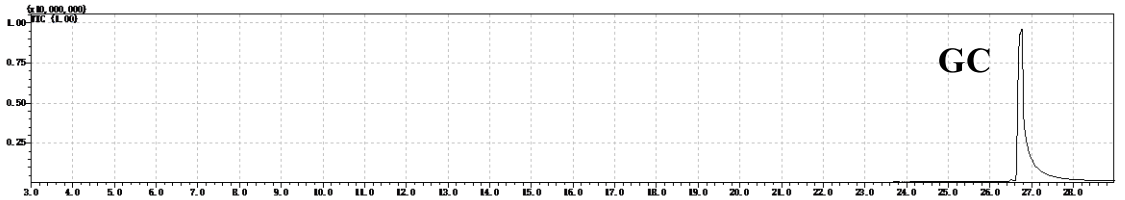
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 140.3 – 141.4 °C, 377.0 mg, 61% yield.

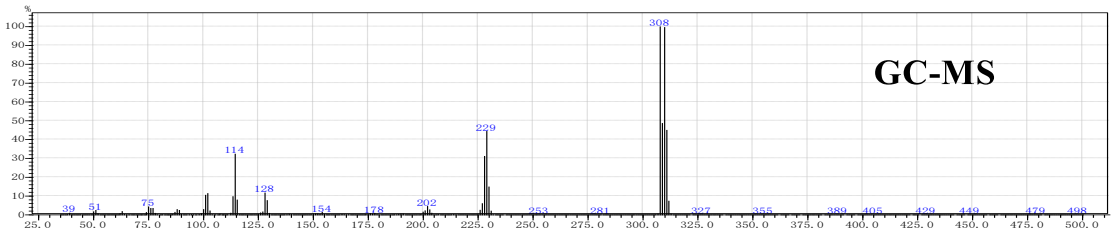
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.66 (d, *J* = 1.3 Hz, 1H), 7.62 (d, *J* = 5.8 Hz, 1H), 7.55 – 7.48 (m, 5H), 7.39 (d, *J* = 16.3 Hz, 1H).

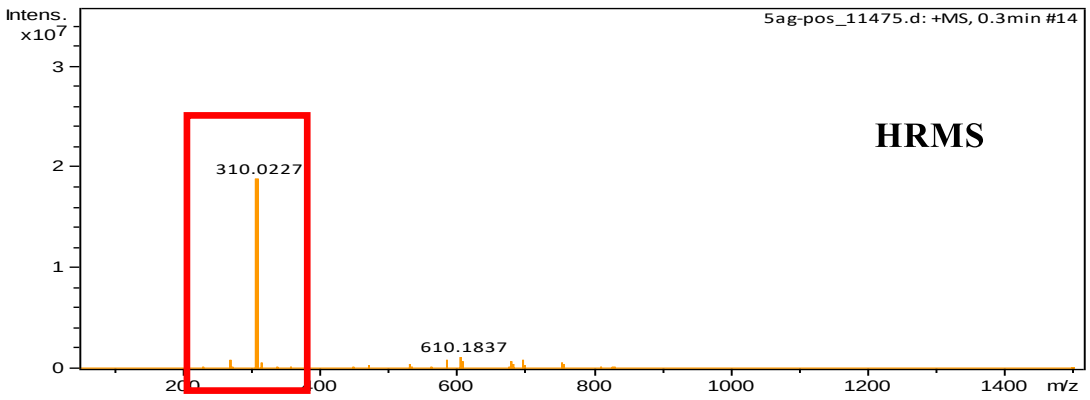
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.66, 148.31, 136.64, 135.59, 133.26, 132.09, 130.02, 129.67, 129.31, 128.82, 127.67, 127.54, 126.49, 122.70, 119.50.

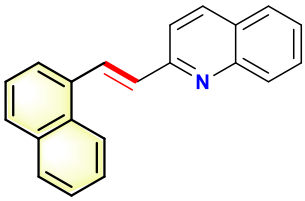
MS (70 eV): m/z (%) = 308.

HRMS (ESI) calcd. for $C_{17}H_{13}BrN$ [M+H]: 310.0231, found: 310.0227.









(*E*)-2-(2-(naphthalen-1-yl)vinyl)quinoline (5ah) [2]

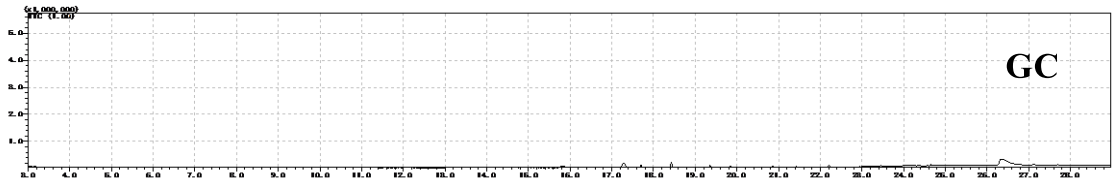
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 104.2 – 105.3 °C, 348.6 mg, 62% yield.

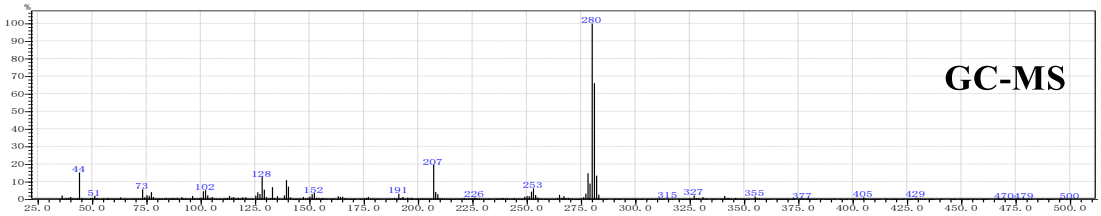
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 16.0 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 8.16 (t, *J* = 8.8 Hz, 2H), 7.97 – 7.84 (m, 3H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.65 – 7.53 (m, 3H), 7.53 – 7.45 (m, 2H).

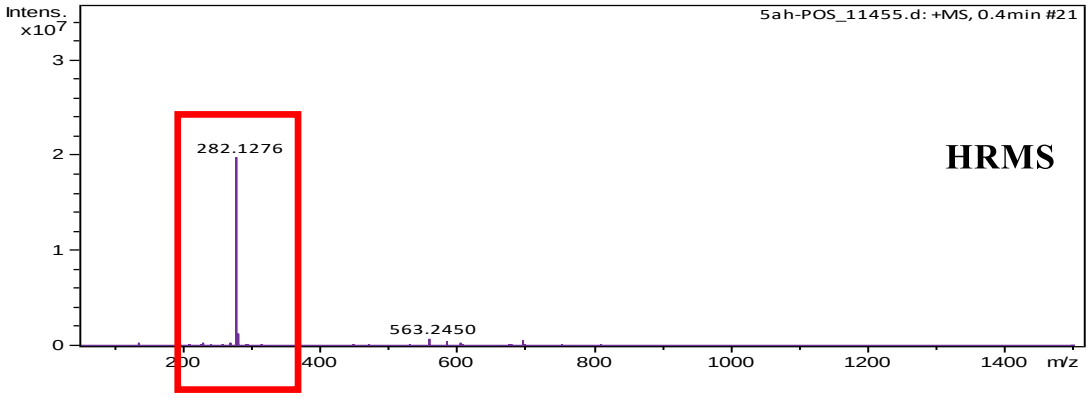
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 148.35, 136.43, 134.08, 133.78, 131.79, 131.51, 131.37, 129.79, 129.37, 128.97, 128.70, 127.54, 127.44, 126.35, 126.25, 125.97, 125.73, 124.22, 123.78, 119.60.

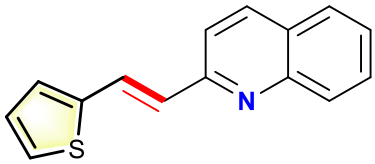
MS (70 eV): m/z (%) = 280.

HRMS (ESI) calcd. for $C_{21}H_{16}N$ [M+H]: 282.1283, found: 282.1276.









(*E*)-2-(2-(thiophen-2-yl)vinyl)quinoline (5ai) [2]

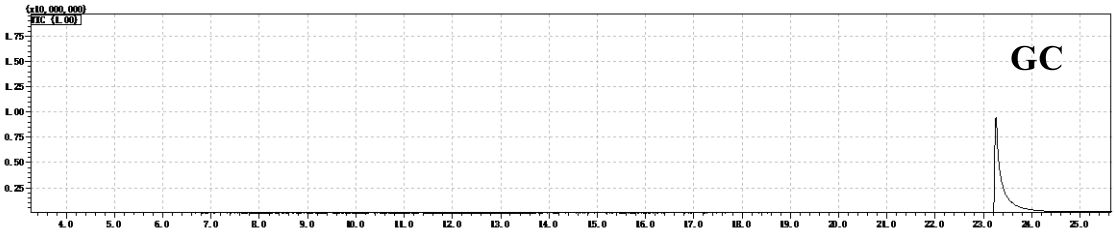
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 91.4 – 92.6 ºC, 331.9 mg, 70% yield.

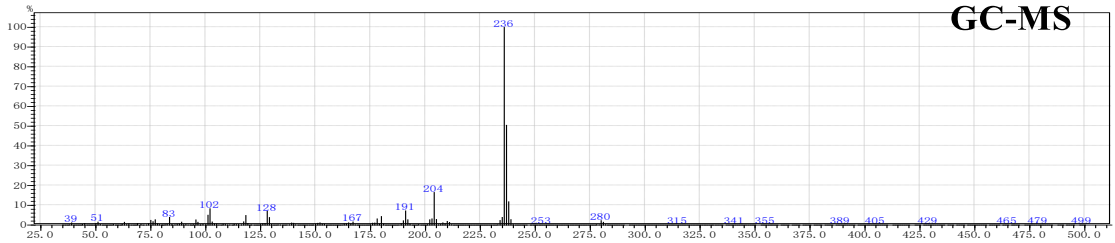
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 14.8, 8.5 Hz, 2H), 7.86 (d, *J* = 16.1 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.50 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.13 – 6.98 (m, 1H).

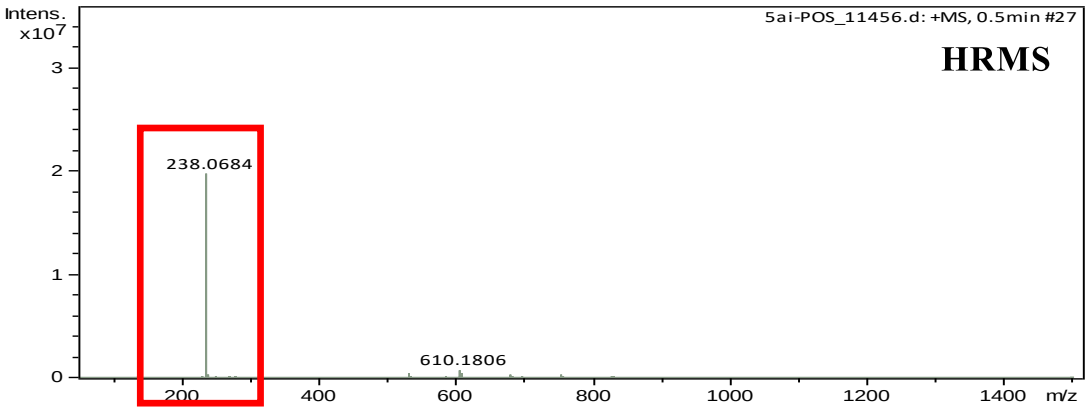
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.42, 148.17, 142.00, 136.18, 129.65, 129.01, 128.13, 128.01, 127.74, 127.42, 127.16, 125.98, 125.92, 119.24.

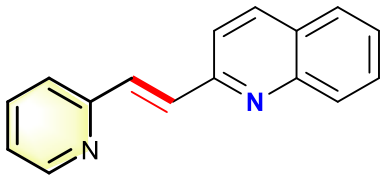
MS (70 eV): m/z (%) = 236.

HRMS (ESI) calcd. for $C_{15}H_{12}NS$ [M+H]: 238.0690, found: 238.0684.









(*E*)-2-(2-(pyridin-2-yl)vinyl)quinoline (5aj) [2]

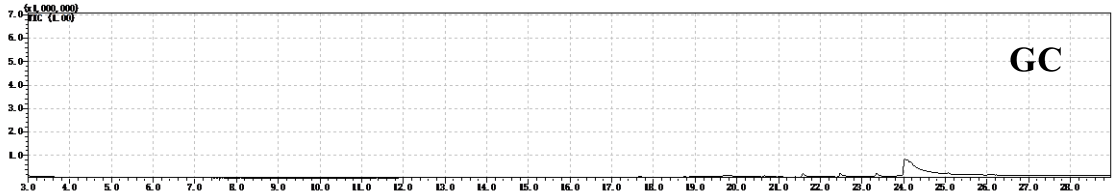
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 95.1 – 96.0 ºC, 190.3 mg, 41% yield.

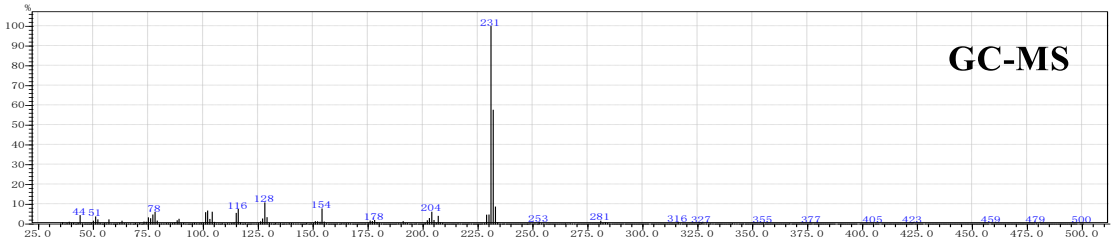
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.60 (m, 1H), 8.20 (t, *J* = 8.5 Hz, 2H), 7.90 (dd, *J* = 4.0, 2.3 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.75 (ddd, *J* = 13.0, 8.1, 5.0 Hz, 3H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 7.0, 3.8 Hz, 1H).

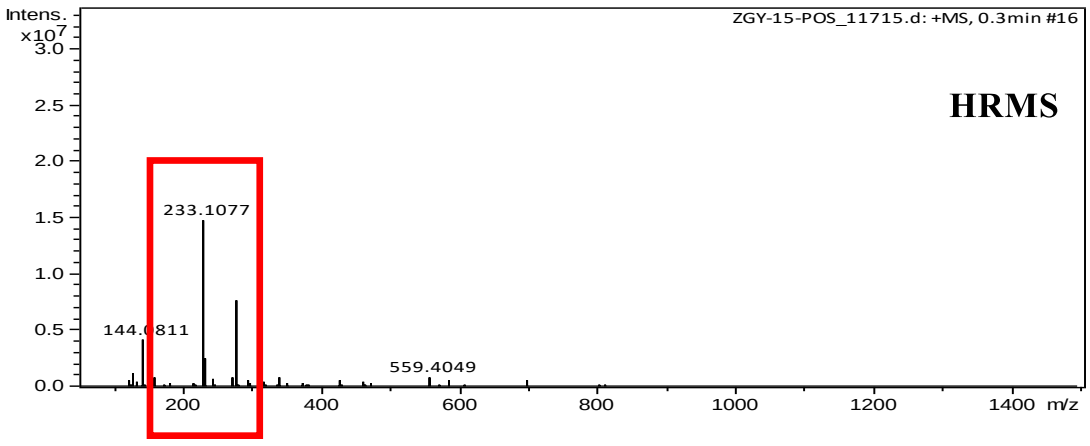
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.15, 154.93, 149.76, 136.89, 136.77, 134.07, 132.19, 130.02, 129.10, 127.57, 126.61, 122.95, 122.88, 120.32, 109.99.

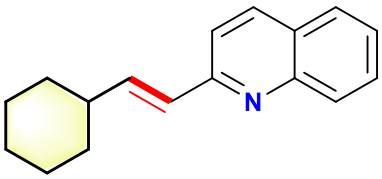
MS (70 eV): m/z (%) = 231.

HRMS (ESI) calcd. for $C_{16}H_{13}N_2$ [M+H]: 233.1079, found: 233.1077.









(*E*)-2-(2-cyclohexylvinyl)quinoline (5ak) [2]

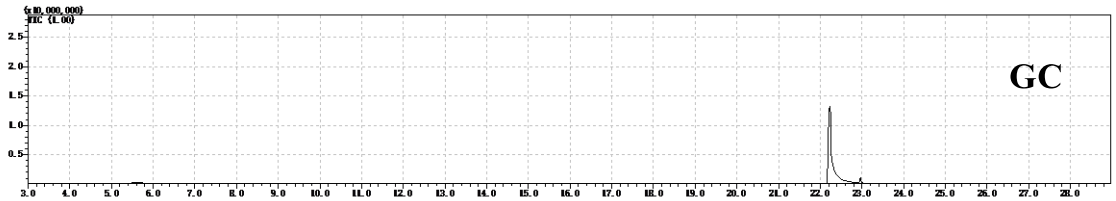
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 49.1 – 49.2 ºC, 237.2 mg, 50% yield.

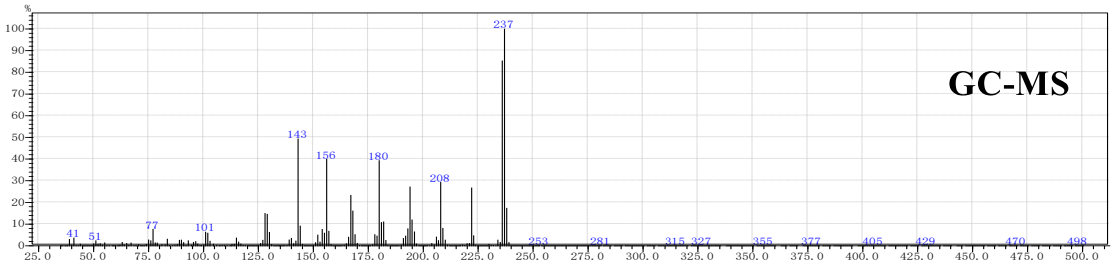
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.6, 2.7 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.52 – 7.32 (m, 2H), 6.76 (d, *J* = 15.7 Hz, 1H), 6.37 (dd, *J* = 15.7, 9.3 Hz, 1H), 1.83 – 1.56 (m, 1H), 0.95 – 0.87 (m, 2H), 0.69 – 0.56 (m, 2H).

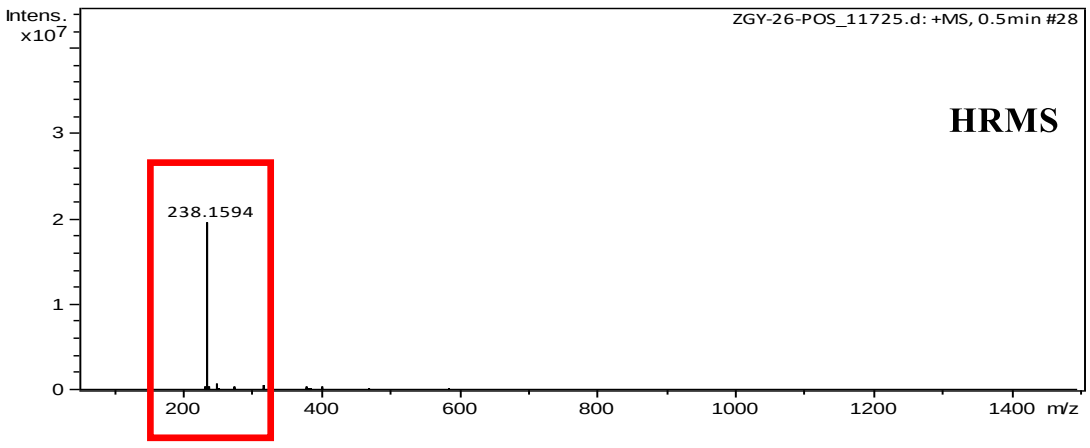
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 148.06, 141.96, 136.05, 129.41, 128.95, 128.19, 127.34, 126.96, 125.56, 118.78, 14.86, 8.00.

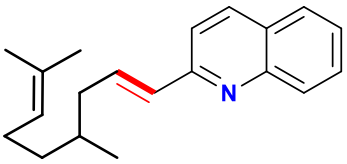
MS (70 eV): m/z (%) = 237.

HRMS (ESI) calcd. for $C_{17}H_{20}N$ [M+H]: 238.1596, found: 238.1594.









(*E*)-2-(4,8-dimethylnona-1,7-dien-1-yl)quinoline (5al) [2]

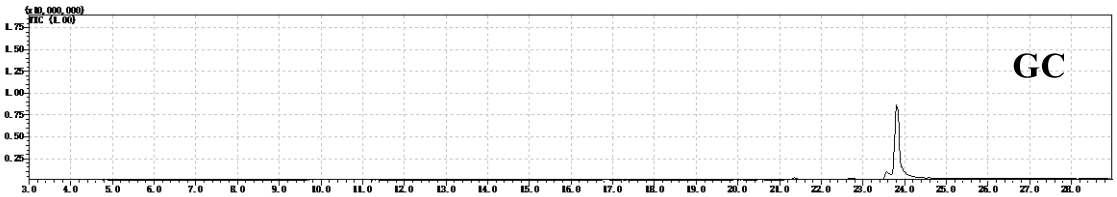
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 290.4 mg, 52% yield.

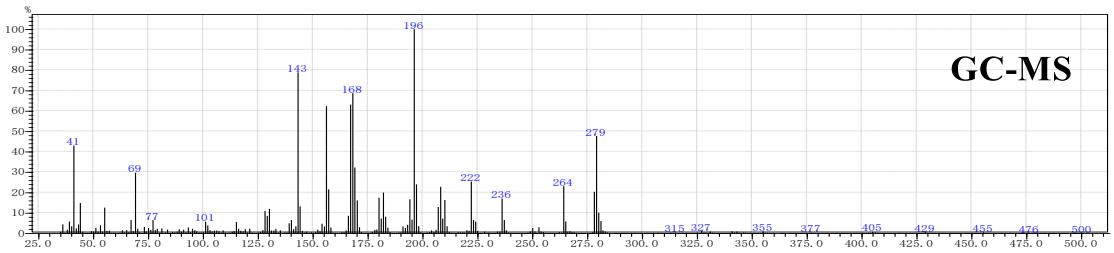
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.76 (dt, *J* = 30.0, 11.4 Hz, 2H), 5.10 (t, *J* = 6.3 Hz, 1H), 2.45 – 2.25 (m, 1H), 2.15 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.02 (dt, *J* = 15.6, 7.6 Hz, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.47 – 1.41 (m, 1H), 1.29 – 1.19 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H).

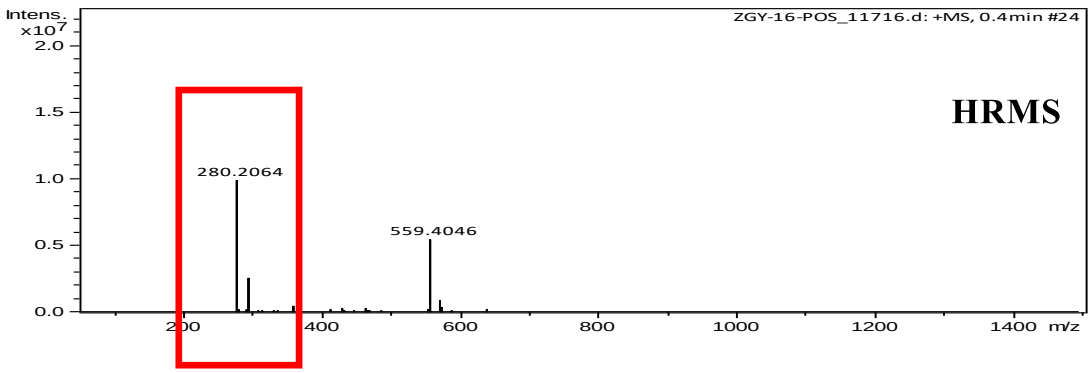
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.43, 136.31, 132.25, 131.37, 129.65, 129.10, 127.49, 127.21, 125.96, 124.75, 118.74, 40.72, 36.92, 32.79, 25.83, 25.71, 19.72, 17.78.

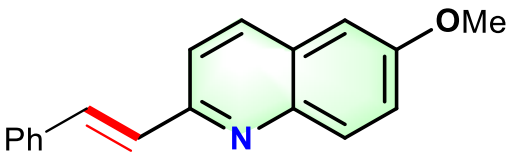
MS (70 eV): m/z (%) = 279.

HRMS (ESI) calcd. for $C_{20}H_{26}N$ [M+H]: 280.2065, found: 280.2064.









(*E*)-6-methoxy-2-styrylquinoline (5ba) [2]

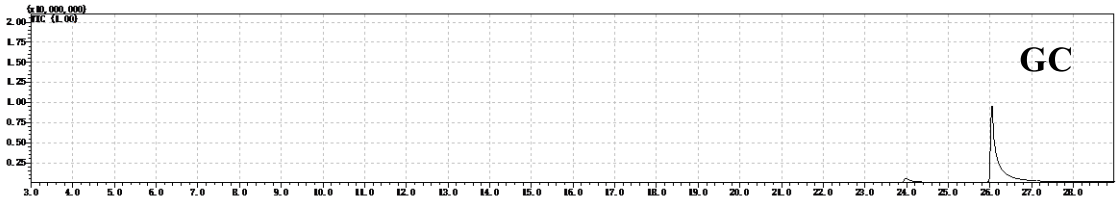
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 149.2 – 150.0 °C, 417.8 mg, 80% yield.

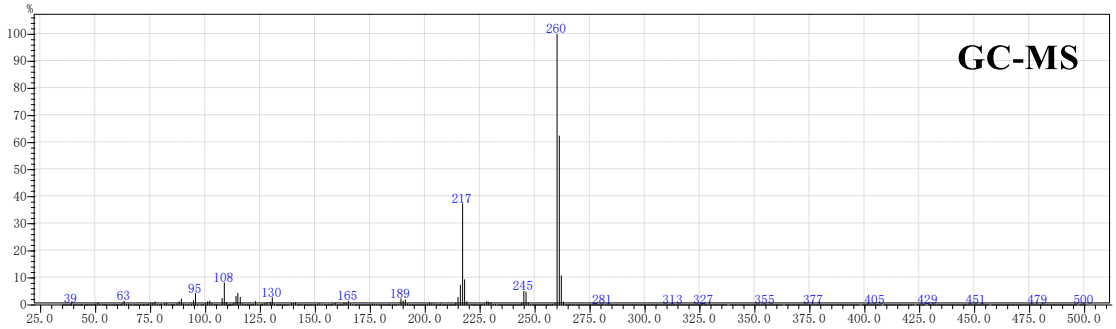
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.95 (s, 1H), 7.61 (d, *J* = 5.9 Hz, 2H), 7.59 – 7.56 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.24 (m, 2H), 7.01 (d, *J* = 2.8 Hz, 1H), 3.89 (s, 3H).

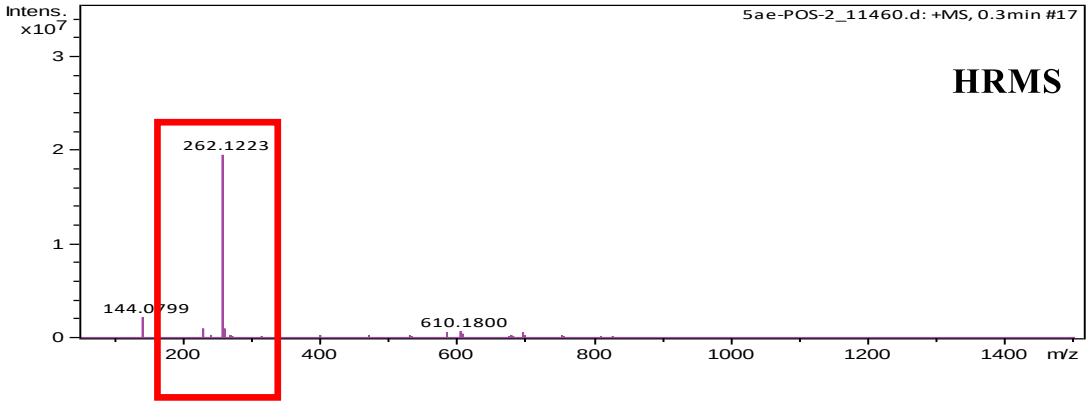
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 153.42, 143.91, 136.46, 134.97, 133.12, 130.33, 128.70, 128.57, 128.22, 128.09, 126.95, 122.17, 119.33, 105.05, 55.34.

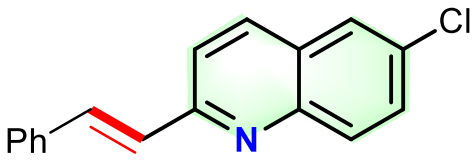
MS (70 eV): m/z (%) = 260.

HRMS (ESI) calcd. for $C_{18}H_{16}NO$ [M+H]: 262.1232, found: 262.1223.









(*E*)-6-chloro-2-styrylquinoline (5ca) [2]

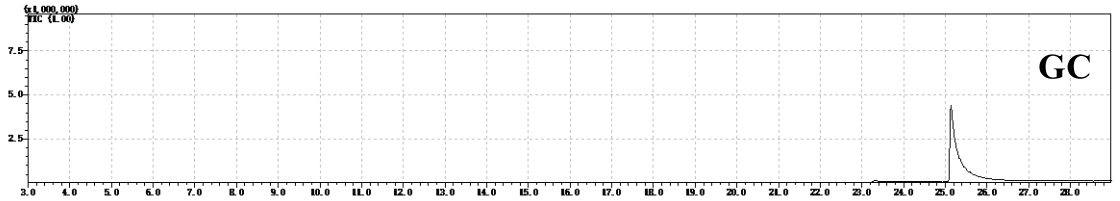
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 149.1 – 150.3 °C, 371.1 mg, 70% yield.

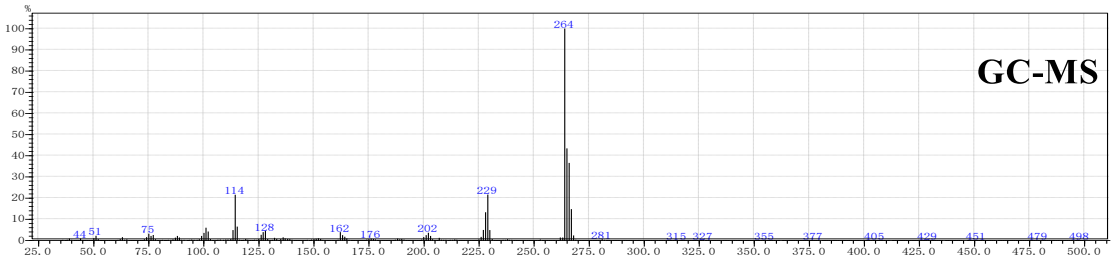
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.94 (m, 2H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.71 (d, *J* = 11.8 Hz, 1H), 7.68 – 7.58 (m, 4H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.30 (m, 2H).

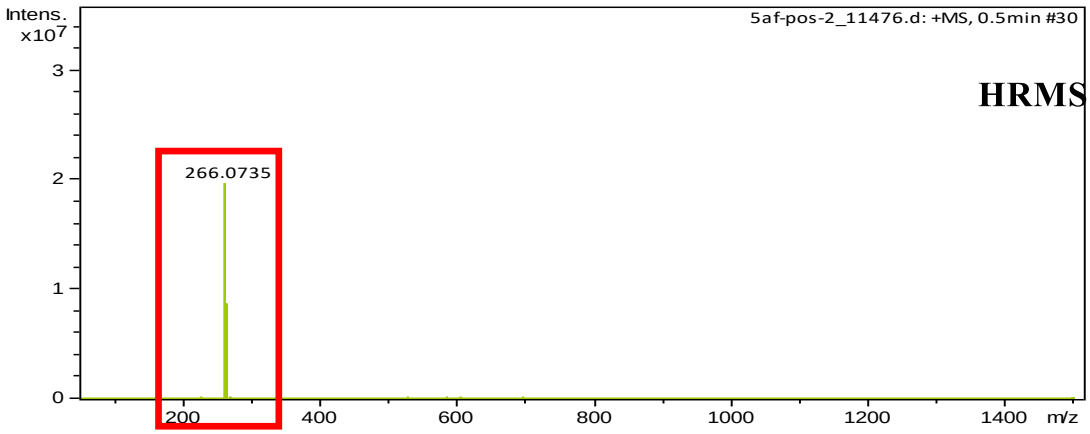
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.14, 146.50, 136.27, 135.40, 134.94, 131.76, 130.62, 128.80, 128.39, 127.80, 127.29, 126.17, 120.17.

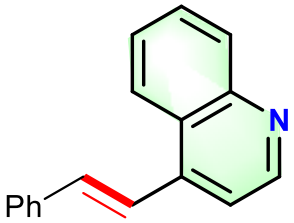
MS (70 eV): m/z (%) = 264.

HRMS (ESI) calcd. for $C_{17}H_{13}ClN$ [M+H]: 266.0736, found: 266.0735.









(*E*)-4-styrylquinoline (5da) [2]

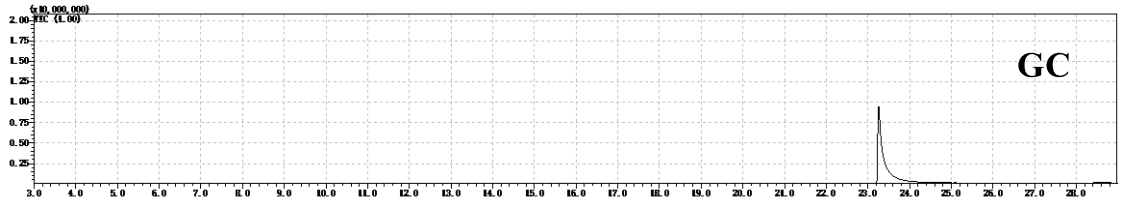
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 99.4 – 100.5 °C, 189.5 mg, 41% yield.

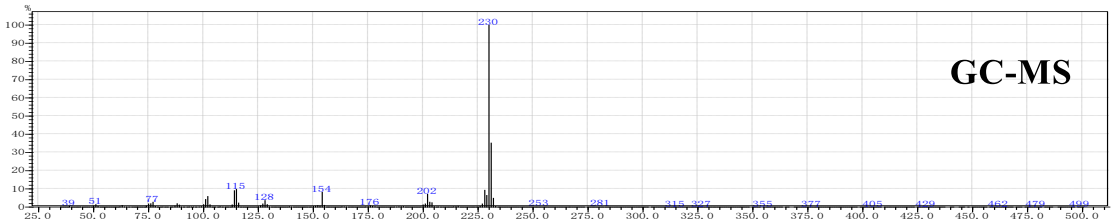
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.24 (t, *J* = 8.2 Hz, 2H), 7.88 – 7.74 (m, 2H), 7.71 – 7.57 (m, 4H), 7.47 (dd, *J* = 14.8, 7.1 Hz, 2H), 7.38 (d, *J* = 16.1 Hz, 2H).

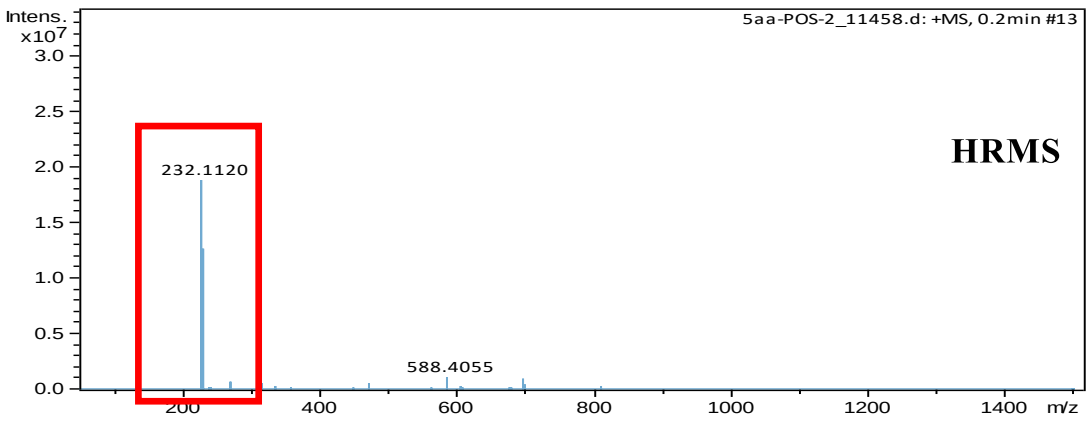
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.96, 148.41, 143.06, 136.46, 135.19, 129.88, 129.36, 128.86, 128.79, 127.10, 126.52, 126.36, 123.42, 122.73, 116.99.

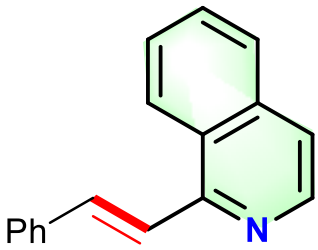
MS (70 eV): m/z (%) = 230.

HRMS (ESI) calcd. for $C_{17}H_{14}N$ [M+H]: 232.1126, found: 232.1120.









(*E*)-1-styrylisoquinoline (5ea) [2]

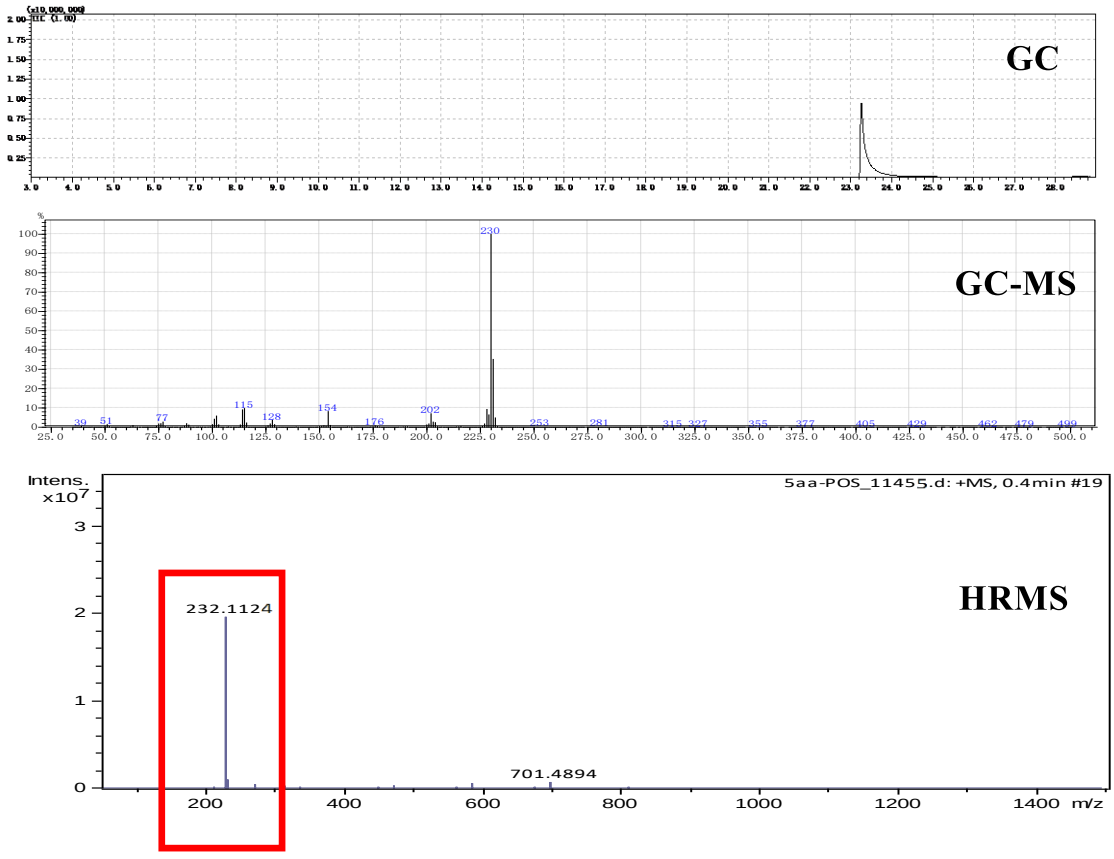
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 100.1 – 101.0 °C, 328.2 mg, 71% yield.

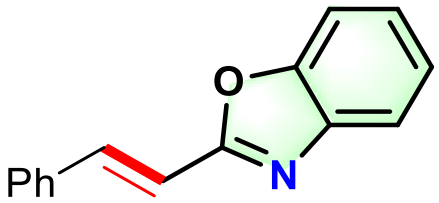
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.6 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.01 (s, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 15.3, 14.8, 7.1 Hz, 4H), 7.58 (d, *J* = 5.6 Hz, 1H), 7.43 (dd, *J* = 10.9, 4.4 Hz, 2H), 7.38 – 7.29 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 142.47, 136.91, 136.72, 135.81, 129.88, 128.75, 128.58, 127.42, 127.30, 127.17, 124.44, 122.82, 119.94.

MS (70 eV): m/z (%) = 230.

HRMS (ESI) calcd. for $C_{17}H_{14}N$ [M+H]: 232.1126, found: 232.1124.





(*E*)-2-styrylbenzo[d]oxazole (5fa) [2]

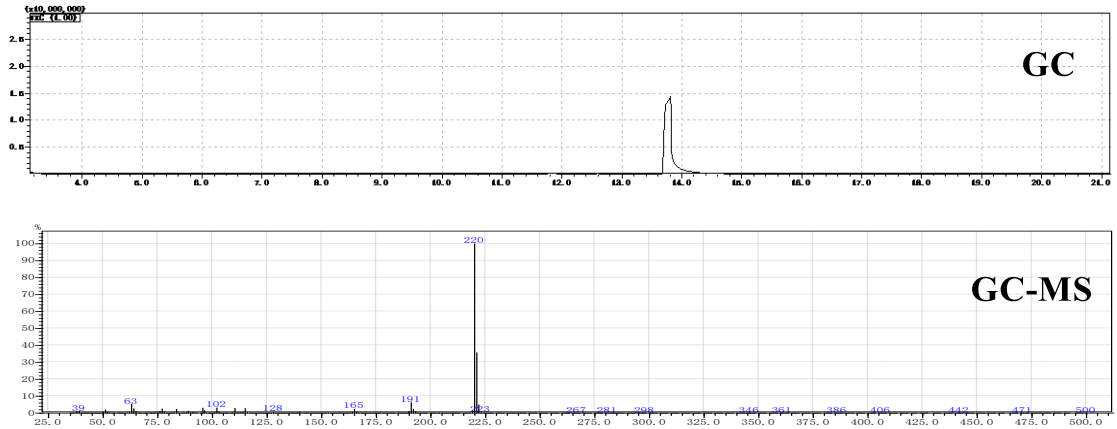
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 84.6 – 85.7 ºC, 287.4 mg, 65% yield.

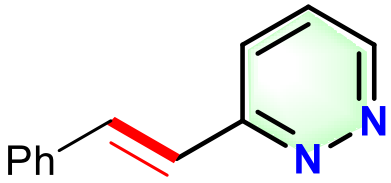
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.57 – 7.48 (m, 2H), 7.44 (dt, *J* = 8.0, 4.0 Hz, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.51 (d, *J* = 2.8 Hz, 1H), 6.43 (dd, *J* = 3.3, 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.84, 150.47, 142.25, 139.51, 135.20, 129.83, 129.03, 127.61, 125.27, 124.56, 119.94, 114.01, 110.38.

MS (70 eV): m/z (%) = 220.

HRMS (ESI) calcd. for $C_{15}H_{12}NO$ [M+H]: 222.0919, found: 222.0916.





(*E*)-3-styrylpyridazine (5ga) [2]

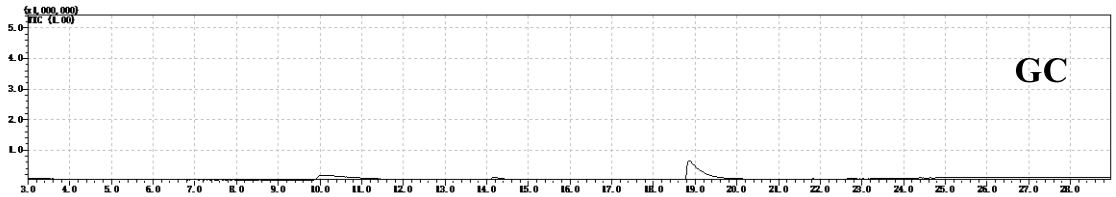
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 85.1 – 86.2 °C, 265.9 mg, 73% yield.

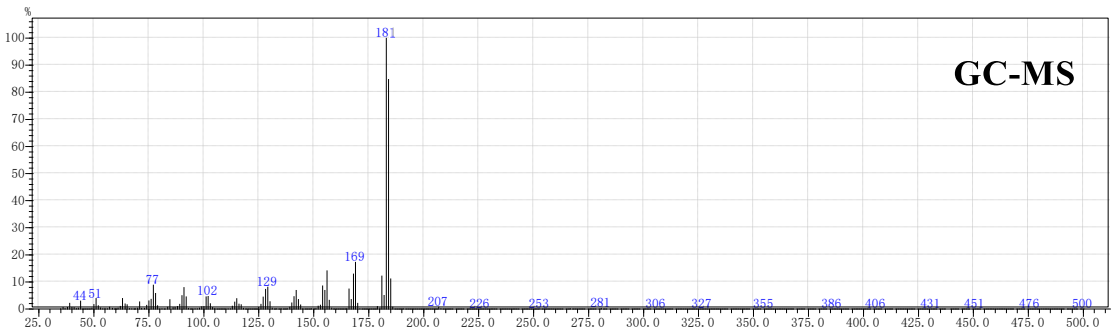
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 4.8 Hz, 1H), 7.69 (d, *J* = 16.4 Hz, 1H), 7.62 (t, *J* = 4.9 Hz, 2H), 7.59 (s, 1H), 7.46 – 7.43 (m, 1H), 7.38 (dd, *J* = 8.7, 4.6 Hz, 3H), 7.33 (d, *J* = 5.2 Hz, 1H).

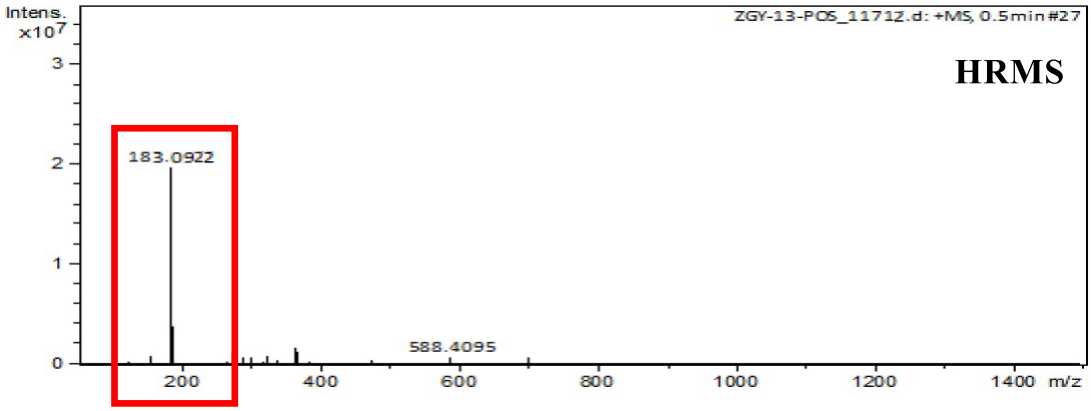
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.20, 149.60, 135.85, 135.12, 129.03, 128.83, 127.29, 126.36, 125.09, 123.88.

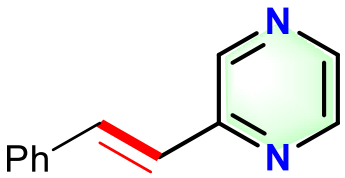
MS (70 eV): m/z (%) = 181.

HRMS (ESI) calcd. for $C_{12}H_{11}N_2$ [M+H]: 183.0922, found: 183.0922.









(*E*)-2-styrylpyrazine (5ha) [2]

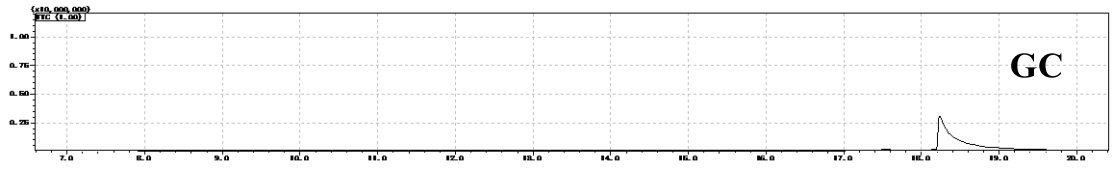
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 95.7 – 96.6 °C, 298.6 mg, 82% yield.

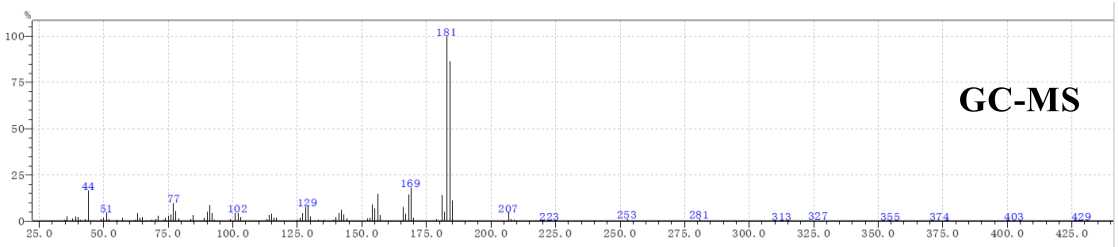
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.50 (s, 1H), 8.37 (d, *J* = 2.3 Hz, 1H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.40 – 7.28 (m, 3H), 7.12 (d, *J* = 16.1 Hz, 1H).

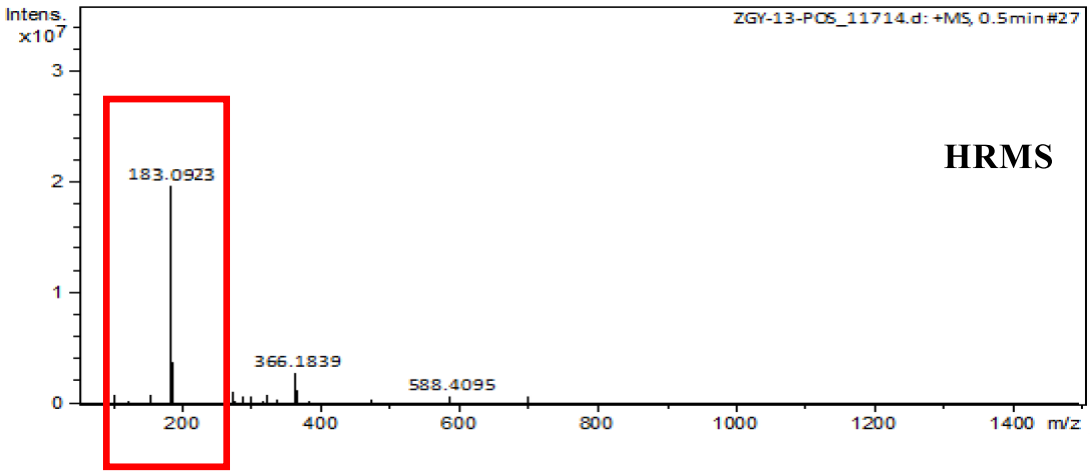
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.23, 144.31, 143.76, 142.74, 136.01, 135.15, 128.96, 128.82, 127.30, 124.00.

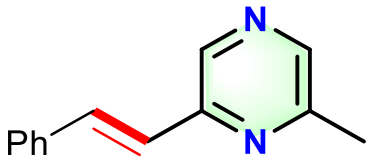
MS (70 eV): m/z (%) = 181.

HRMS (ESI) calcd. for $C_{12}H_{11}N_2$ [M+H]: 183.0922, found: 183.0923.









(*E*)-2-methyl-6-styrylpyrazine (5ia) [2]

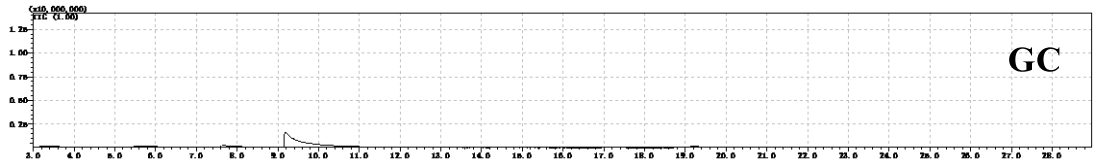
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 204.0 mg, 52% yield.

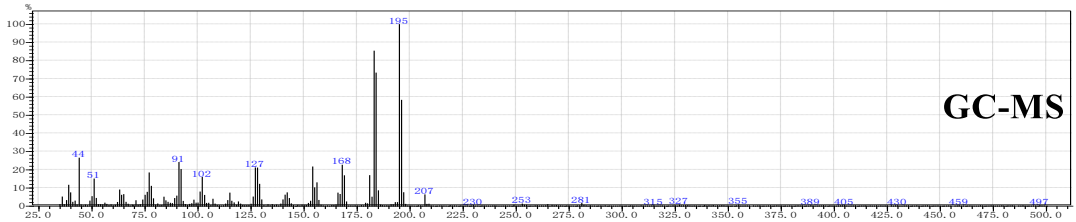
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.28 (s, 1H), 7.72 (d, *J* = 16.1 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.36 (dt, *J* = 13.9, 6.9 Hz, 3H), 7.13 (d, *J* = 16.1 Hz, 1H), 2.58 (s, 3H).

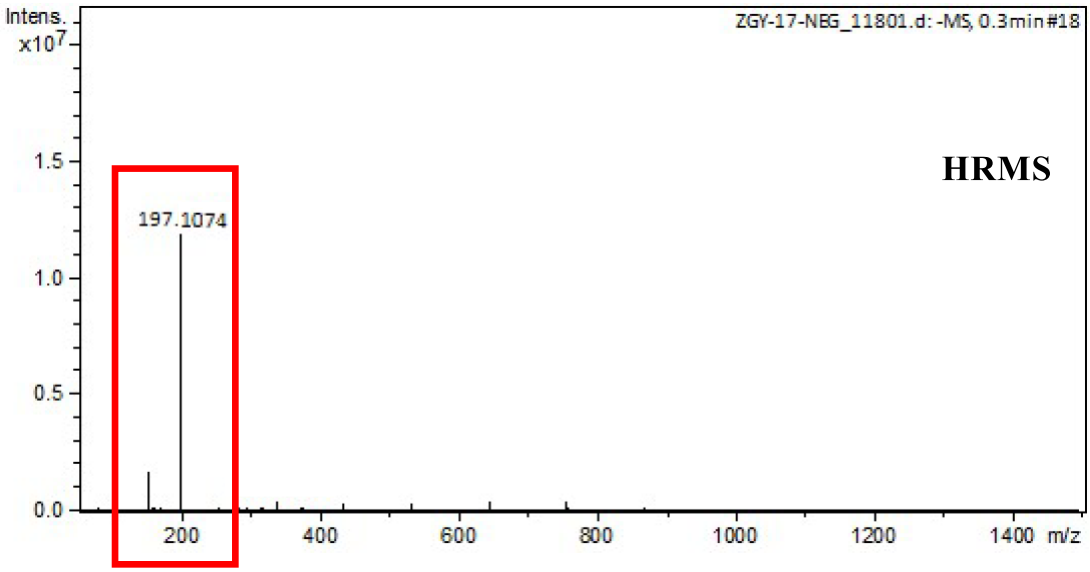
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.03, 149.80, 142.29, 140.22, 135.95, 134.36, 128.52, 126.98, 124.17, 21.46.

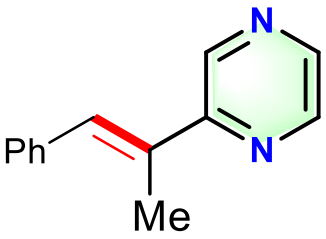
MS (70 eV): m/z (%) = 195 [M]+ (100).

HRMS (ESI) calcd. for $C_{13}H_{13}N_2$ [M+H]: 197.1079, found: 197.1074.









(*E*)- 2-(1-phenylprop-1-en-2-yl)pyrazine (5ja) [2]

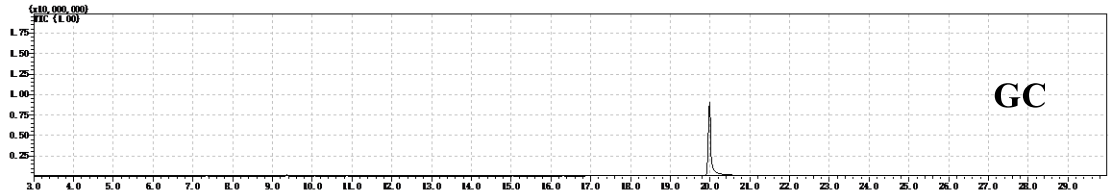
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 90.1 mg, 23% yield.

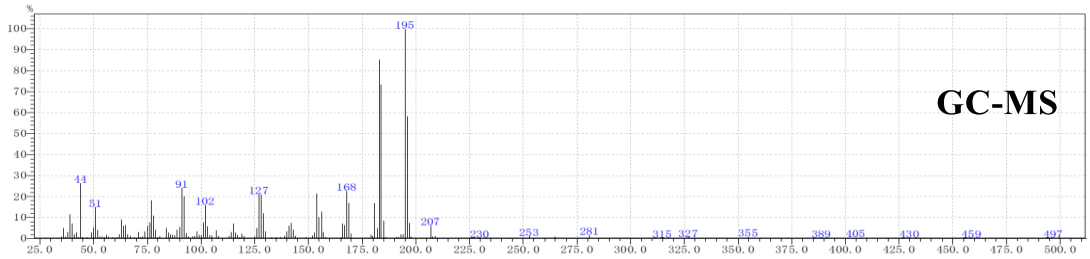
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.56 (s, 1H), 8.45 (d, J = 2.1 Hz, 1H), 7.50 (s, 1H), 7.45 – 7.38 (m, 4H), 7.33 – 7.28 (m, 1H), 2.38 (s, 3H).

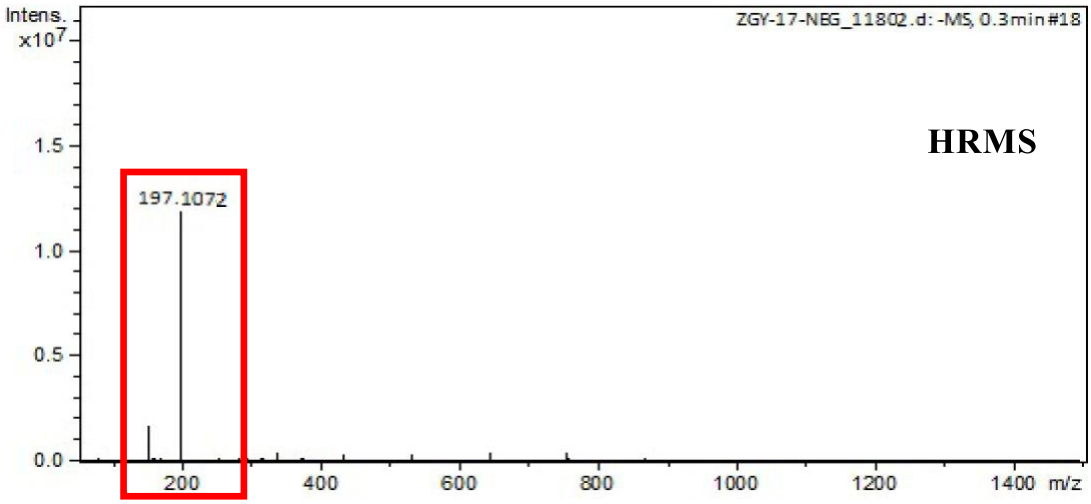
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.39, 142.53, 141.94, 137.12, 132.05, 129.39, 128.30, 127.39, 15.38.

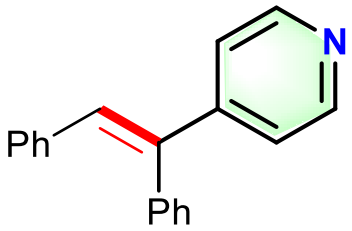
MS (70 eV): m/z (%) = 195.

HRMS (ESI) calcd. for $C_{13}H_{13}N_2$ [M+H]: 197.1079, found: 197.1072.









(*E*)-4-(1,2-diphenylvinyl)pyridine (5ka) [2]

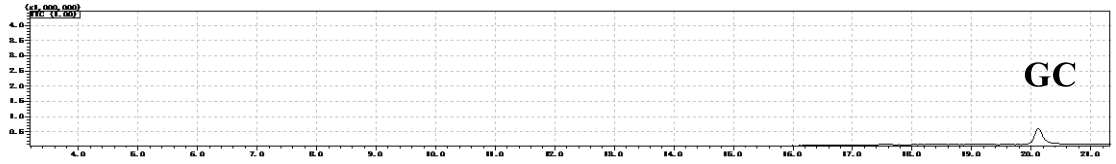
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 85.1 – 86.1 ºC, 164.2 mg, 32% yield.

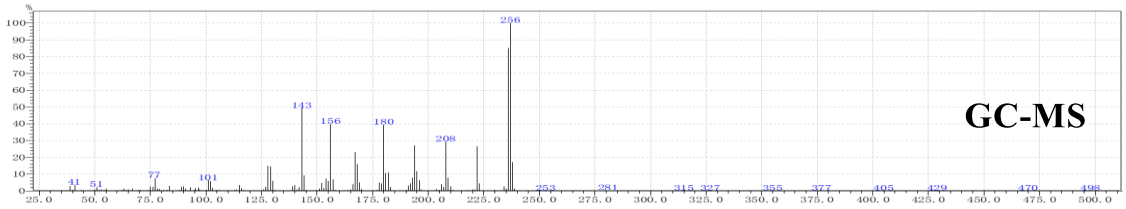
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (s, 2H), 7.73 (dd, J = 23.0, 11.7 Hz, 6H), 7.48 – 7.25 (m, 7H).

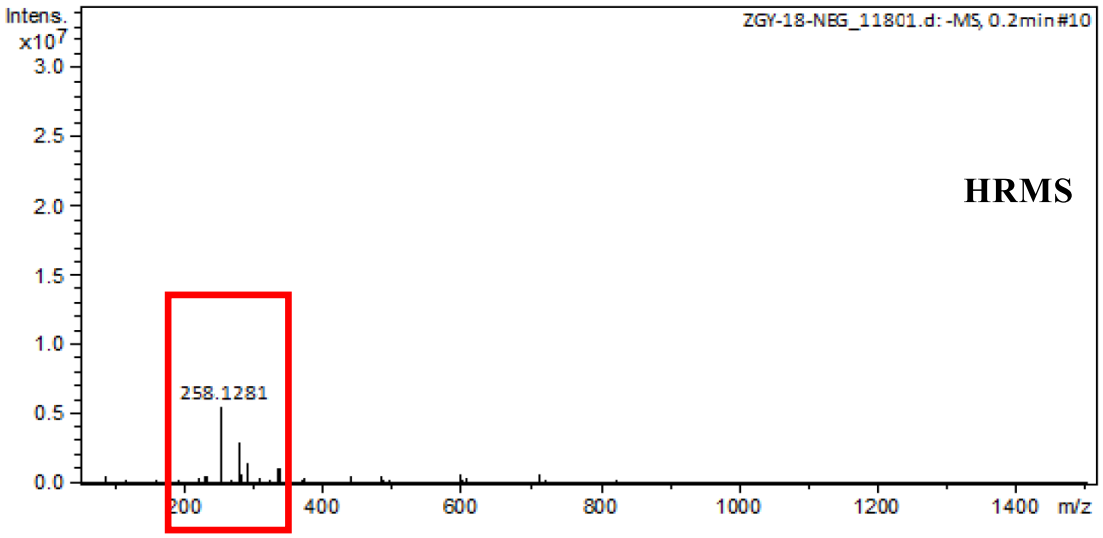
^{13}C NMR (101 MHz, DMSO-d_6) δ 148.36, 142.54, 135.80, 133.26, 128.20, 128.05, 126.61, 124.30.

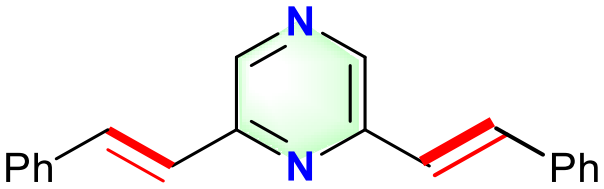
MS (70 eV): m/z (%) = 256.

HRMS (ESI) calcd. for $C_{19}H_{16}N$ [M+H]: 258.1283, found: 258.1281.









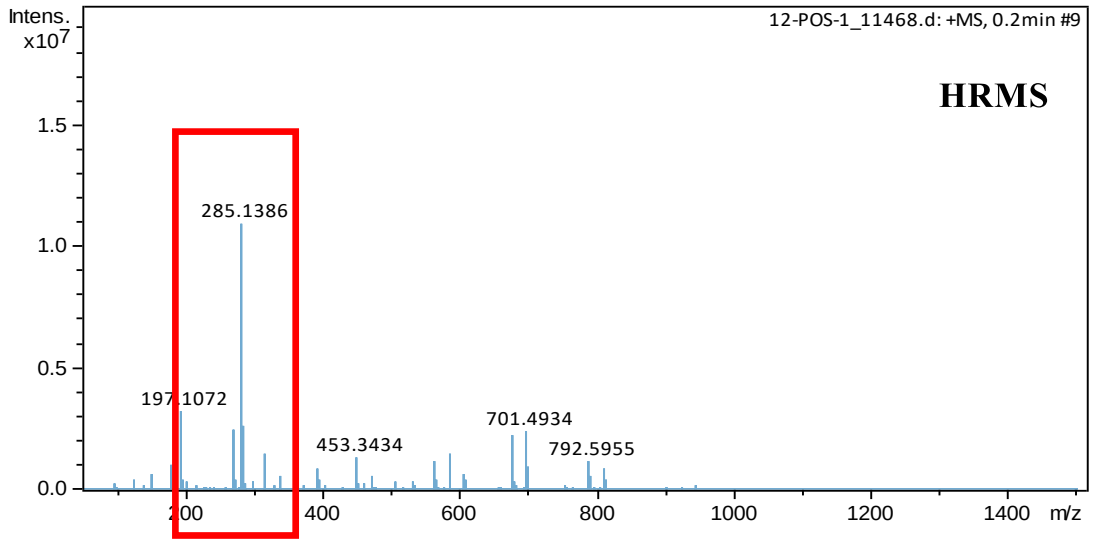
2,6-di((*E*)-styryl)pyrazine (5ma) [2]

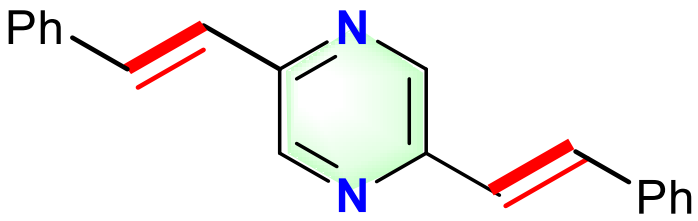
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 218.4 – 219.6 °C, 363.7 mg, 64% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.76 (s, 2H), 7.79 (s, 1H), 7.74 (s, 1H), 7.70 (d, J = 7.4 Hz, 4H), 7.43 (d, J = 6.4 Hz, 4H), 7.40 (s, 2H), 7.35 (d, J = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 149.31, 141.49, 135.52, 133.97, 128.41, 126.85, 124.17, 109.02.

HRMS (ESI) calcd. for $C_{20}H_{17}N_2$ [M+H]: 285.1392, found: 285.1386.





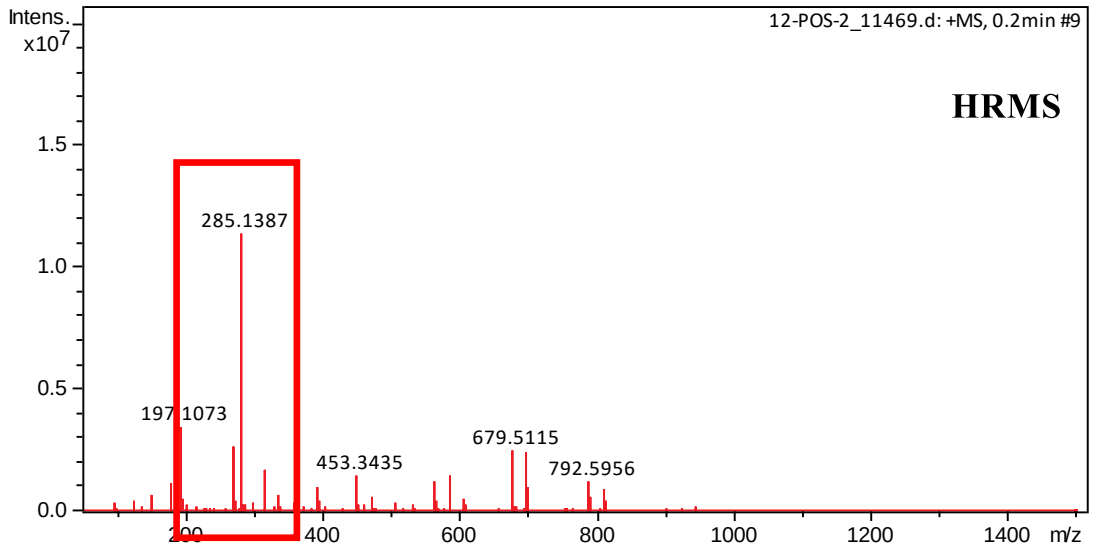
2,5-di((*E*)-styryl)pyrazine (5na) [2]

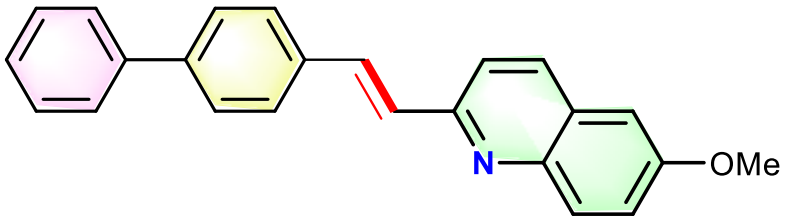
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 301.2 mg, 53% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 2H), 7.89 (d, J = 16.2 Hz, 2H), 7.74 (d, J = 7.8 Hz, 4H), 7.45 (t, J = 7.5 Hz, 5H), 7.40 – 7.30 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 147.62, 142.06, 135.10, 132.70, 127.58, 125.98, 123.57.

HRMS (ESI) calcd. for $C_{20}H_{17}N_2$ [M+H]: 285.1392, found: 285.1387.





(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-6-methoxyquinoline (STB-8) [2]

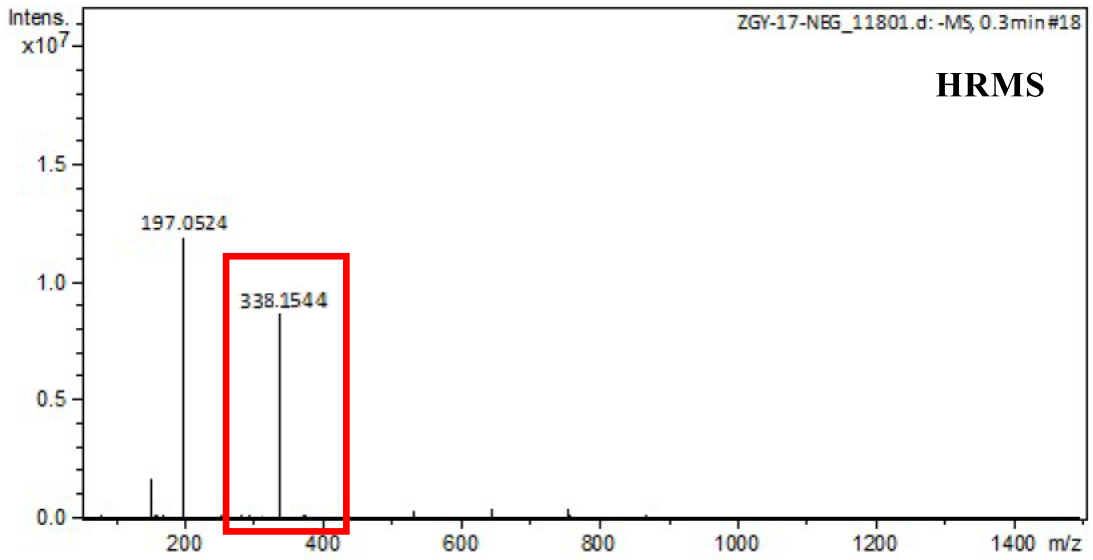
The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, mp: 151.6 – 152.3 °C, 492.0 mg, 73% yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (t, J = 8.2 Hz, 2H), 7.84 – 7.55 (m, 8H), 7.41 (dd, J = 22.4, 7.8 Hz, 5H), 7.07 (s, 1H), 3.94 (s, 3H).

^{13}C NMR: *Not in deuterium solvent* ($CDCl_3$, CD_2Cl_2, DMSO-d_6, THF-d_8, PhMe-d_9 and CD_3OD).

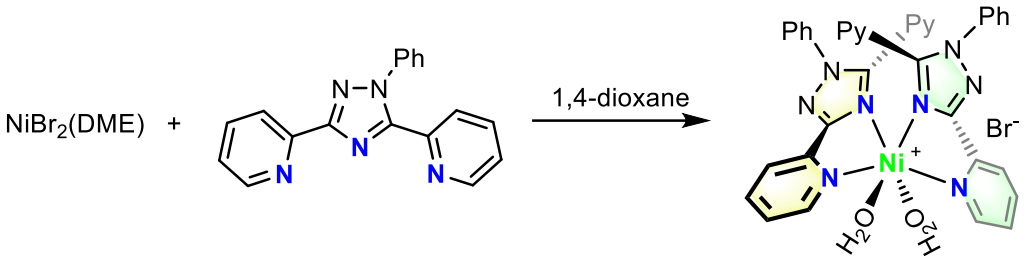
HRMS (ESI) calcd. for $C_{24}H_{20}NO$ [M+H]: 338.1545, found: 338.1544.

Elemental Analysis calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15; found: C, 85.45; H, 5.65; N, 4.16.

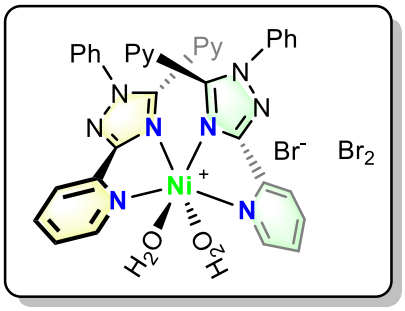


5. Synthesis of [Ni-N$_4$]Br

The ligand (**L1-L10**) was known compounds and synthesis according to the literature.[3]



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (50 mL volume) was charged with a magnetic stirring bar, $NiBr_2$(DME) (0.2 mmol), 2,2'-(1-phenyl-1H-1,2,4-triazole-3,5-diyl)dipyridine **L3** (0.4 mmol), and 1,4-dioxane (2.0 mL). Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (120 ^oC). After 10 hours the reaction was cooled, recrystallized in the MeOH under air gave the lumpy translucent bright green crystals **[Ni-N$_4$]Br** (**M**) in 47% yield (87.1 mg).



(di(2,2'-(1-phenyl-1H-1,2,4-triazole-3,5-diyl)dipyridine))(dibromine) nickel(I)bromide ([Ni-N$_4$]Br)

Elemental Analysis calcd for $C_{36}H_{30}Br_3N_{10}NiO_2$: C, 46.34; H, 3.24; Br, 25.69; N, 15.01; Ni, 6.29; O, 3.43; found: C, 46.30; H, 3.26; N, 15.03.

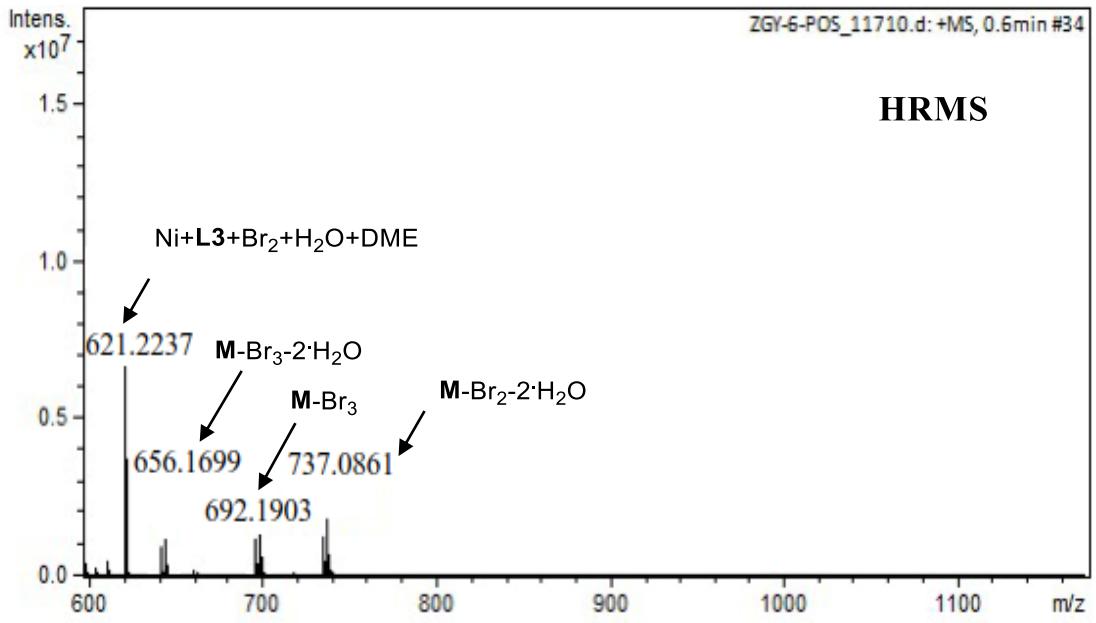
^{13}C Solid NMR (600 MHz) δ 168.1, 158.5, 144.2, 139.7, 137.0, 121.2

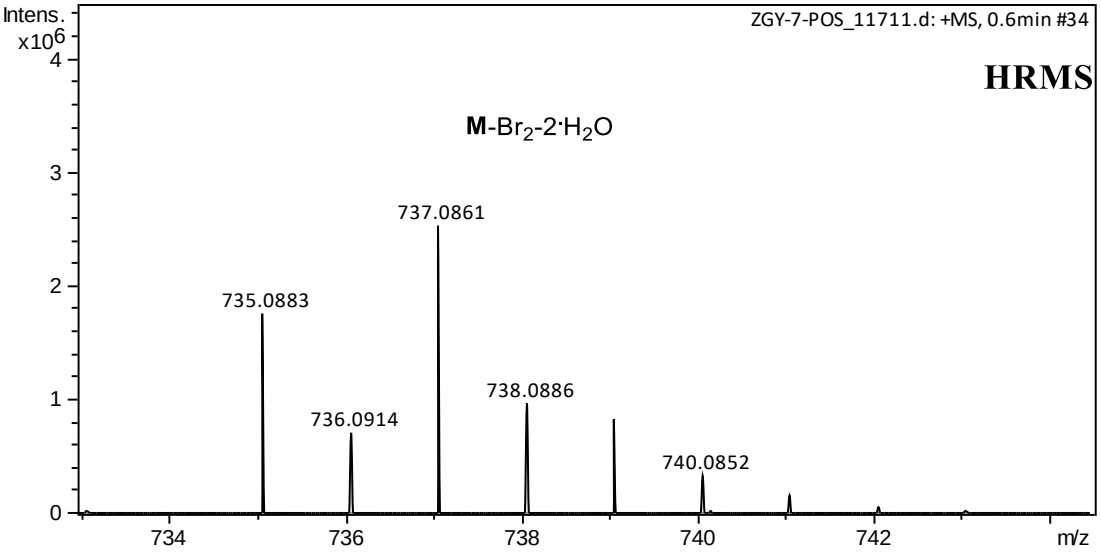
HRMS (ESI):

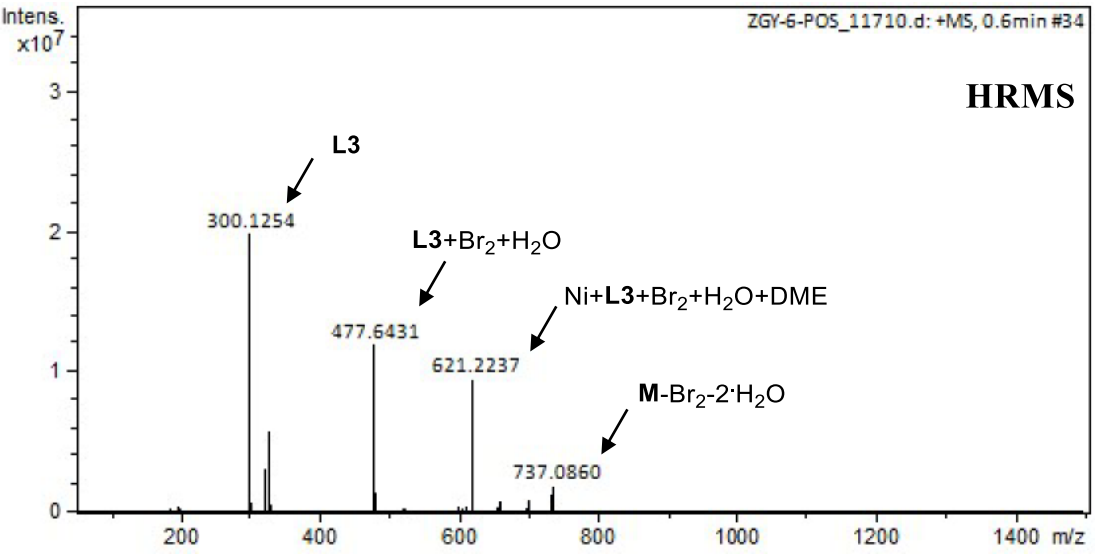
calcd. for $C_{36}H_{26}BrN_{10}Ni$ [M-Br_2-2·H_2O]: 735.0879, found: 735.0883.

calcd. for $C_{36}H_{30}N_{10}NiO_2$ [M-Br_3]$^+$: 692.1907, found: 692.1903.

calcd. for $C_{36}H_{26}N_{10}Ni$ [M-Br_3-2·H_2O]$^+$: 656.1695, found: 656.1699.


Intens.
x10^7
1.5
1.0
0.5
0.0
ZGY-6-POS_11710.d: +MS, 0.6min #34
HRMS
Ni+L3+Br2+H2O+DME
621.2237
M-Br3-2·H2O
656.1699
M-Br3
692.1903
M-Br2-2·H2O
737.0861
600
700
800
900
1000
1100
m/z


Intens.
x10^6
4
3
2
1
0
ZGY-7-POS_11711.d: +MS, 0.6min #34
HRMS
M-Br2-2·H2O
737.0861
735.0883
736.0914
738.0886
740.0852
734
736
738
740
742
m/z


Intens.
x10^7
3
2
1
0
ZGY-6-POS_11710.d: +MS, 0.6min #34
HRMS
L3
300.1254
L3+Br2+H2O
477.6431
Ni+L3+Br2+H2O+DME
621.2237
M-Br2-2·H2O
737.0860
200
400
600
800
1000
1200
1400
m/z

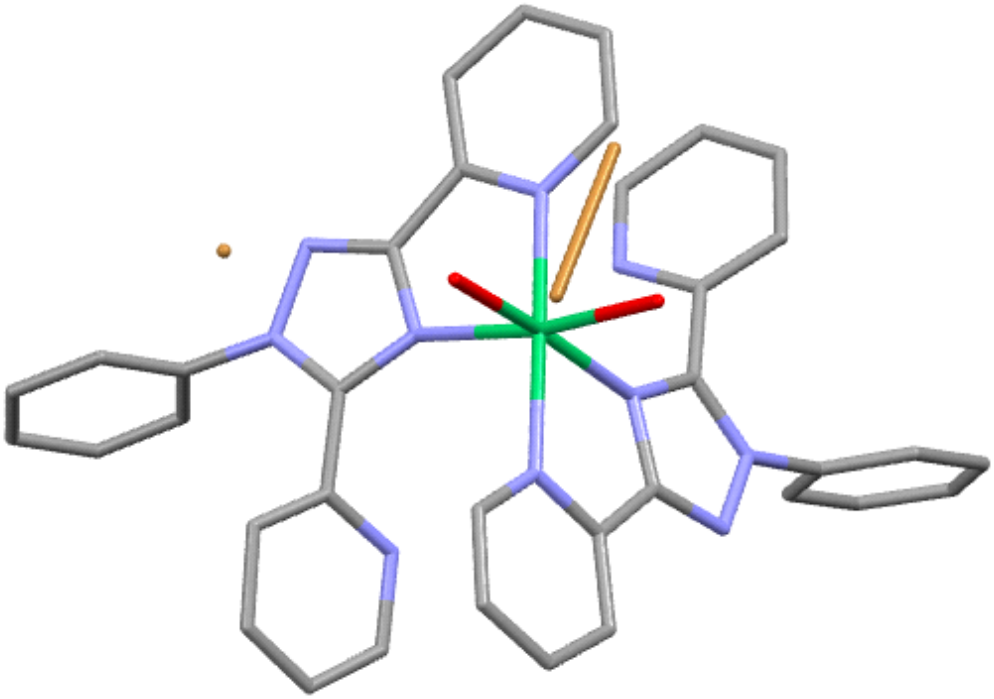


Figure S1 X-ray of [Ni-N$_4$]Br

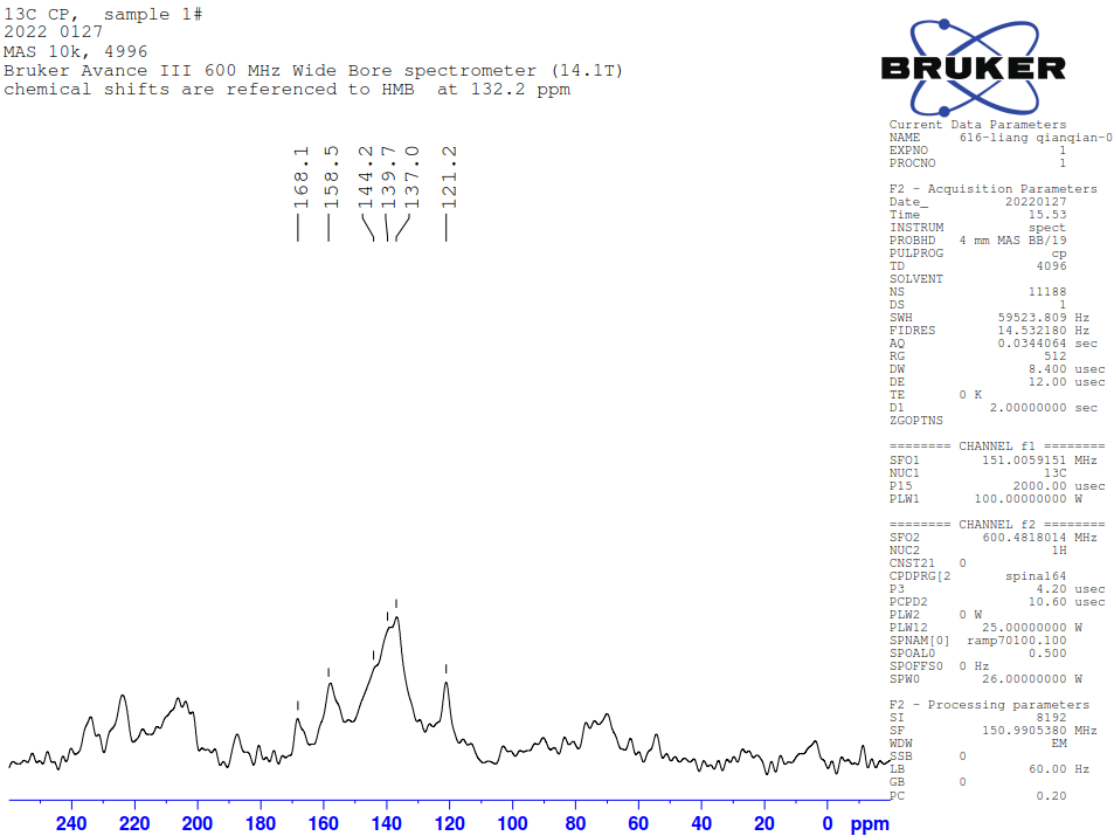
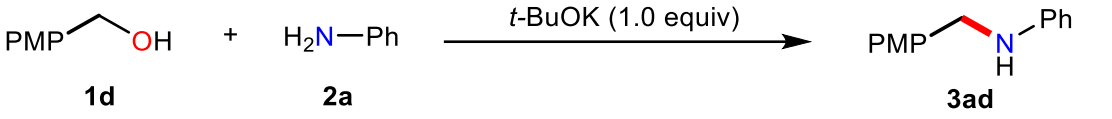


Figure S2 Solid-NMR of [Ni-N$_4$]Br

6. Gram scale experiments and tandem experiment

6.1 Gram scale experiment with 0.1 mol% catalyst



1d 20 mmol | **2a** 10 mmol | **3ad**

with **[Ni-N$_4$]Br** (0.1 mol%): 87% (1.85 g, TON: 868)

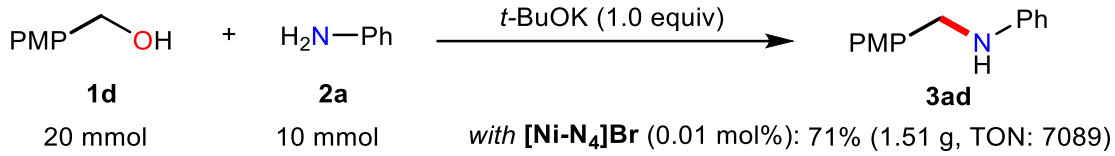
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (100 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.01 mmol, 0.1 mol%), *t*-BuOK (20.0 mmol), **1d** (20.0 mmol) and **2a** (10.0 mmol). Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 24 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 5/1, Et$_3$N 1%) gave the corresponding product **3ad** in 87% yield (1.85 g, TON = 868).

$$\mathrm{TON} = \frac{N_s}{Nc} = \frac{\frac{1850\ mg}{213\ mg/mmol}}{0.01\ mmol} = 868$$

Ns: The number of molecules of the substrate transformed in the reaction

Nc: The number of active catalyst centers involved in the reaction

6.2 Gram scale experiment with 0.01 mol% catalyst



1d 20 mmol | **2a** 10 mmol | **3ad**

with **[Ni-N$_4$]Br** (0.01 mol%): 71% (1.51 g, TON: 7089)

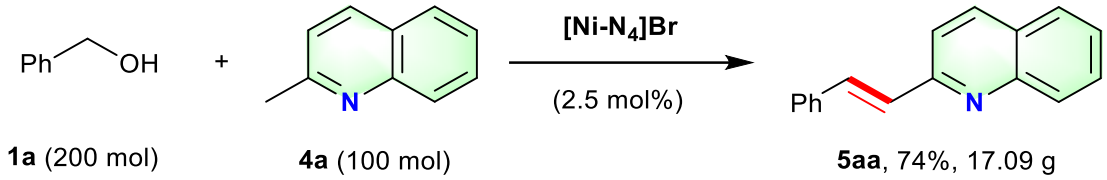
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (100 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.001 mmol, 0.01 mol%), *t*-BuOK (20.0 mmol), **1d** (20.0 mmol) and **2a** (10.0 mmol). Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 72 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 5/1, Et$_3$N 1%) gave the corresponding product **3ad** in 71% yield (1.51g, TON = 7089).

$$\mathrm{TON} = \frac{\mathrm{N_s}}{\mathrm{Nc}} = \frac{\frac{1510\ mg}{213\ mg/mmol}}{0.001\ mmol} = 7089$$

Ns: The number of molecules of the substrate transformed in the reaction

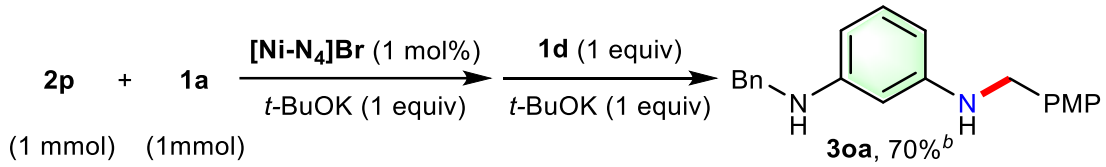
Nc: The number of active catalyst centers involved in the reaction

6.3 Gram scale experiment with 2.5 mol% catalyst



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (500 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (2.5 mmol, 2.5 mol%), KOH (100 mmol), **1a** (200 mmol) and **4a** (100 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. A reflux condenser was evacuated and refilled with dry N_2 and then attached to the Schlenk tube maintaining dry air stream. A bubble counter was attached to the top of the condenser and the whole system was purged with dry N_2 for 60 seconds. The Schlenk tube was immersed into a pre-heated metal bath (140 ^oC). After 72 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 10/1, DCM 1%) gave the **5aa** in 74% yield (17.09 g).

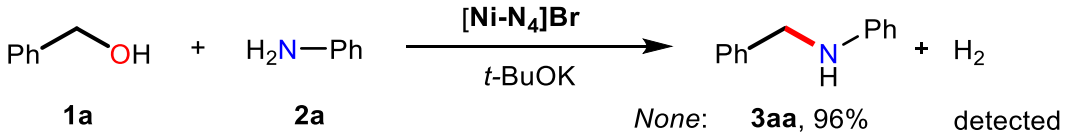
6.4 Tandem experiment



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (20 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.01 mmol, 1 mol%), *t*-BuOK (1.0 mmol), **1a** (1.0 mmol) and **2p** (1.0 mmol). Then the Schlenk tube was closed tightly with a teflon cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^oC). After 15 hours, *t*-BuOK (1.0 mmol) and **1d** (1.0 mmol) were added under the nitrogen. After another 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC or GC-MS to monitor product formation. Purification of the remainder by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 – 5/1, Et_3N 1%, DCM 5%) gave the corresponding product **3oa** in 70% yield.

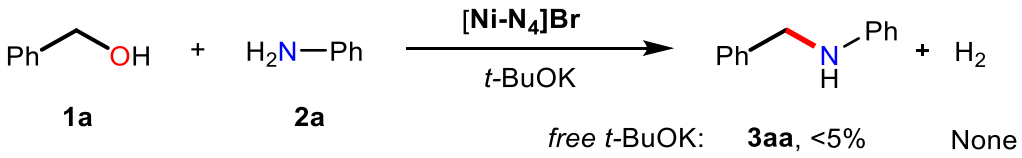
7. Control experiments

7.1



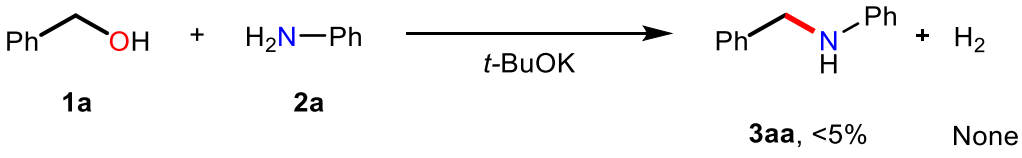
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol) and **2a** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small gas and aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

7.2



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), **1a** (4.0 mmol) and **2a** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small gas and aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

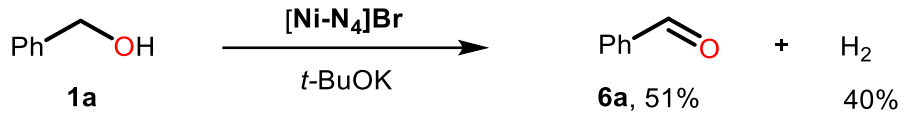
7.3



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, *t*-BuOK (2.0 mmol), **1a** (4.0 mmol) and **2a** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from

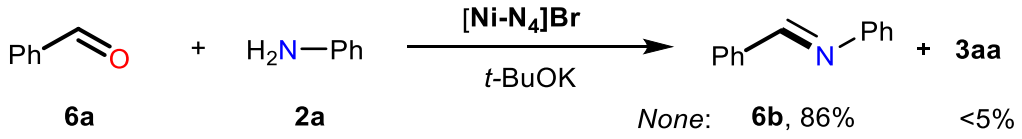
the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 °C). After 15 hours the reaction was cooled, a small gas and aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

7.4



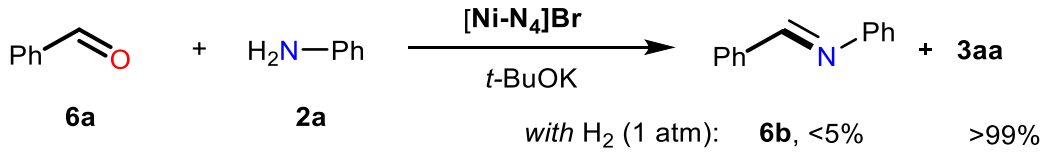
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2.0 mmol), **1a** (4.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 °C). After 15 hours the reaction was cooled, a small gas and aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

7.5



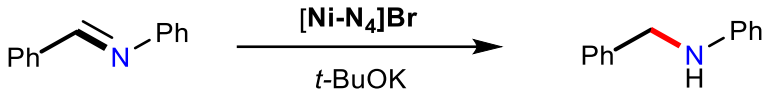
Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2.0 mmol), **6a** (4.0 mmol) and **2a** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 °C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

7.6



Using a nitrogen-filled glove box, an oven-dried pressure tube (25 mL) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **6a** (4.0 mmol) and **2a** (2.0 mmol). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with H_2 (1 atm) and immersed into a pre-heated metal bath (130 ℃) for 15 hours. After the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

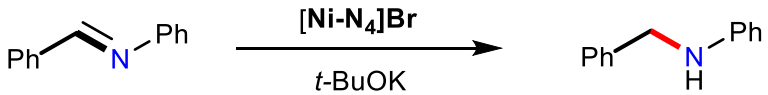
7.7



6b *None*: **3aa**, <5%

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **6b** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

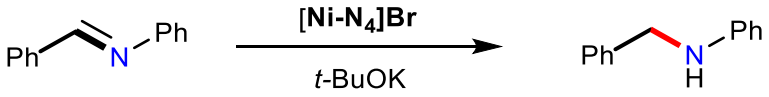
7.8



6b *with* H_2 (1 atm): **3aa**, >99%

Using a nitrogen-filled glove box, an oven-dried pressure tube (25 mL) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2.0 mmol), **6b** (1.0 mmol). Then the glass tube was placed in an autoclave which was closed tightly and removed from the glove box. Then the autoclave was purged and charged with H_2 (1 atm) and immersed into a pre-heated metal bath (130 ℃) for 15 hours. After the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

7.9



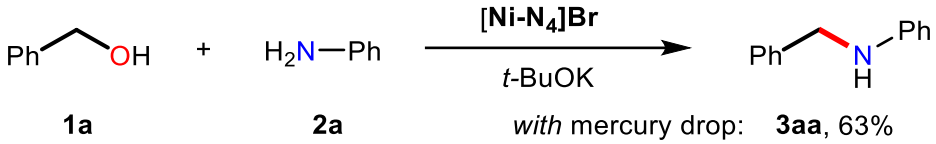
6b

with **1a** (1 equiv): **3aa**, 73%; **6a,** 62%

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N4]Br** (0.02 mmol), *t*-BuOK (2.0 mmol), **6b** (2.0 mmol) and **2a** (2.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor products formation.

8. Mechanism study experiments

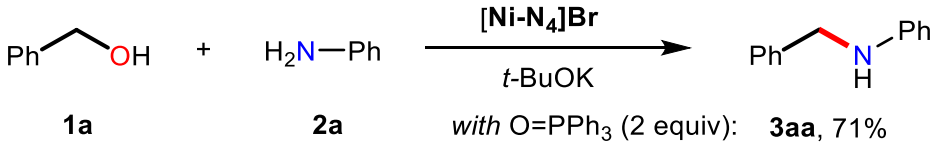
8.1



1a **2a** *with* mercury drop: **3aa**, 63%

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol) and mercury (2 drops). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

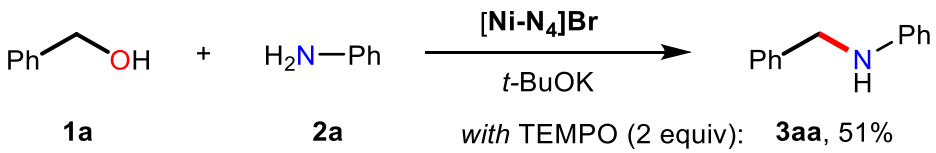
8.2



1a **2a** *with* O=PPh$_3$ (2 equiv): **3aa**, 71%

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol) and (O)PPh$_3$ (4.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

8.3

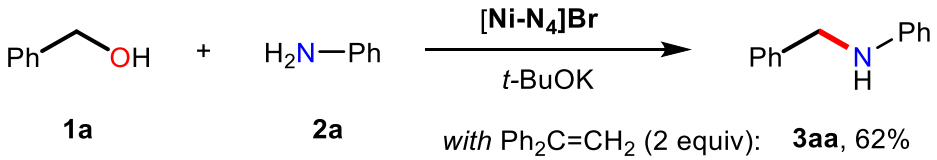


1a **2a** *with* TEMPO (2 equiv): **3aa**, 51%

Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol),

1a (4.0 mmol) , **2a** (2.0 mmol) and TEMPO (4.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

8.4



Using a nitrogen-filled glove box, an oven-dried Schlenk tube (25 mL volume) was charged with a magnetic stirring bar, **[Ni-N$_4$]Br** (0.02 mmol), *t*-BuOK (2 mmol), **1a** (4.0 mmol), **2a** (2.0 mmol) and PhCHCH$_2$ (4.0 mmol). Then the Schlenk tube was closed tightly with a rubber cap, removed from the glove box. The Schlenk tube was immersed into a pre-heated metal bath (130 ^{o}C). After 15 hours the reaction was cooled, a small aliquot of the organic phase was analyzed by GC and GC-MS to monitor product formation.

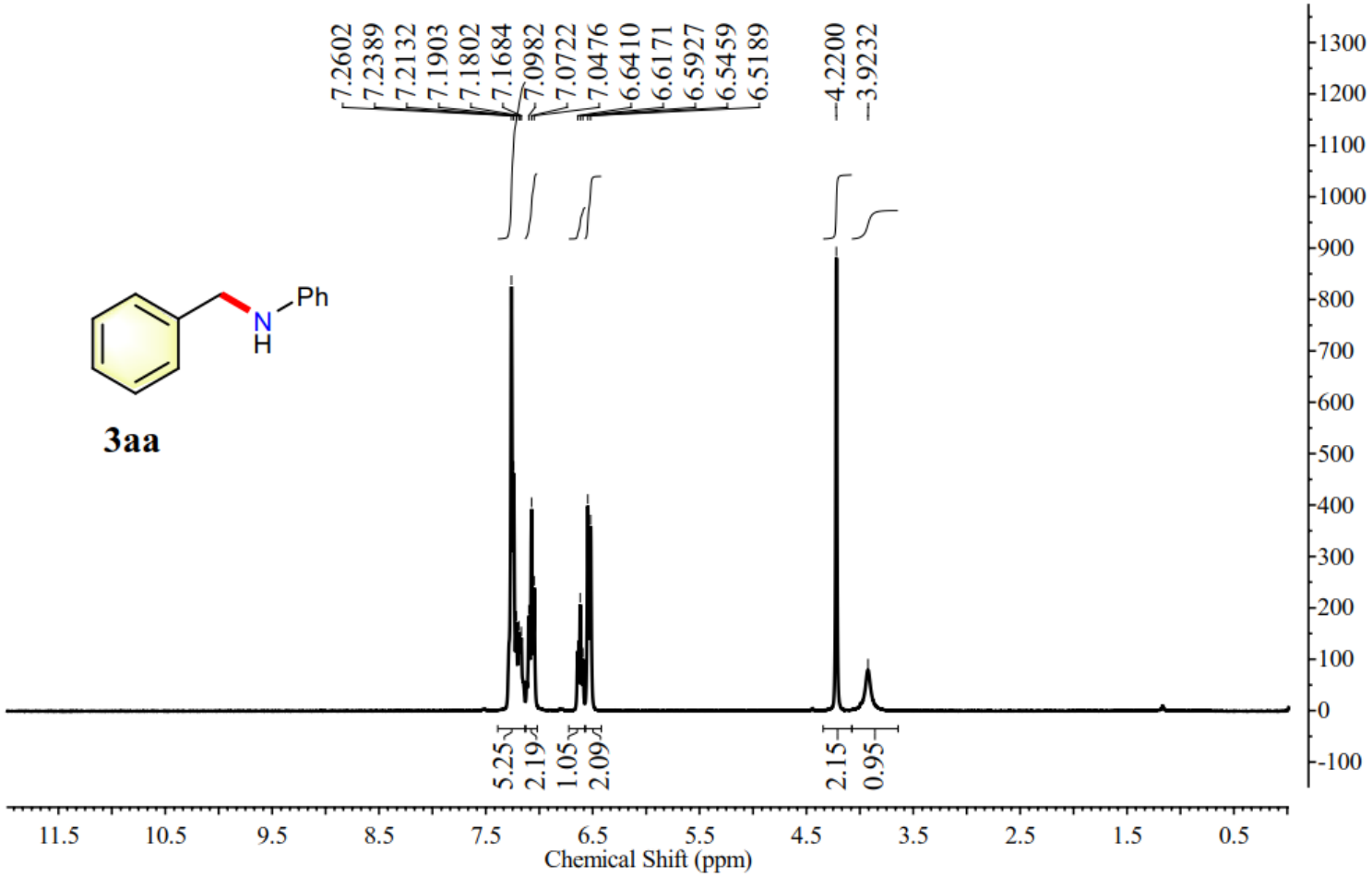
9. References：

1 (*a*) C. Zhang, Z. Li, J. Chen, S. Qi, Y. Fang, S. Zhang, C. Ren, F. Lu, Z. Liang, S. Jiang, X. Jia, S. Yu and G. Zhang, *J. Org. Chem*. 2020, **85**, 7728; (*b*) C. Zhang, Z. Li, Y. Fang, S. Jiang, M. Wang and G. Zhang, *Tetrahedron* 2020, **76**, 130968.

2 (*a*) G. Zhang, T. Irrgang, T. Dietel, F. Kallmeier, R. Kempe, *Angew. Chem. Int. Ed.* 2018, **57**, 9131; (*b*) M. K. Barman, S. Waiba, B. Maji, *Angew. Chem. Int. Ed.* 2018, **57**, 9126.

3 (*a*) C. Zhang, Z. Liang, X. Jia, M. Wang, G. Zhang and M.-L. Hu, *Chem. Commun*. **2020**, *56*, 14215; (*b*) Q. Wei, C. Qiao, Z. Xia, S. Chen, *Synthetic Commun*, **2013**, **43**, 3181.

10. Copies for NMR of the products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7.2132
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7.1802
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7.0982
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7.0476
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6.6171
6.5927
6.5459
6.5189
4.2200
3.9232
Ph
N
H
3aa
5.25
2.19
1.05
2.09
2.15
0.95
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)
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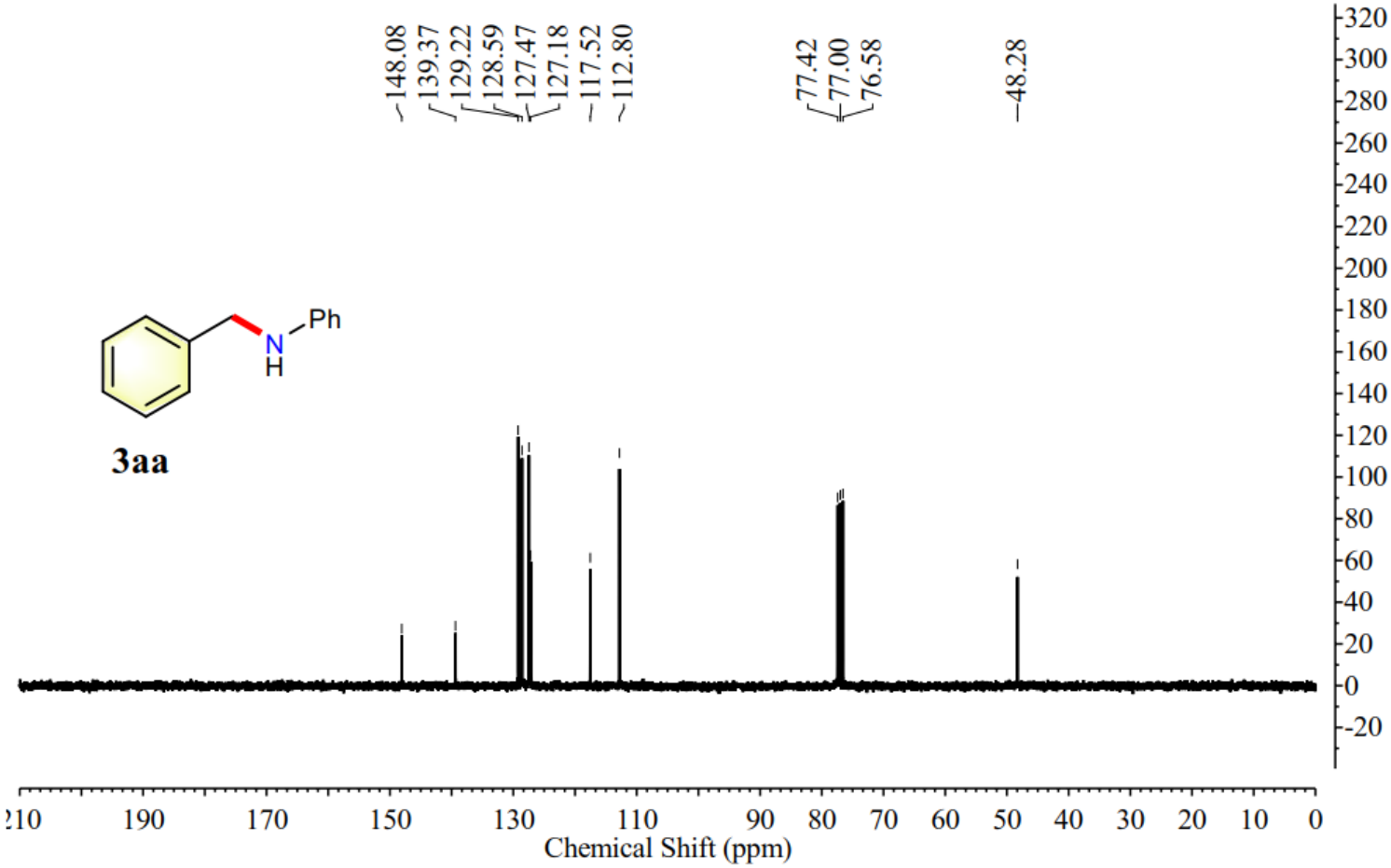
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100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129.22
128.59
127.47
127.18
117.52
112.80
77.42
77.00
76.58
48.28
N
H
Ph
3aa
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
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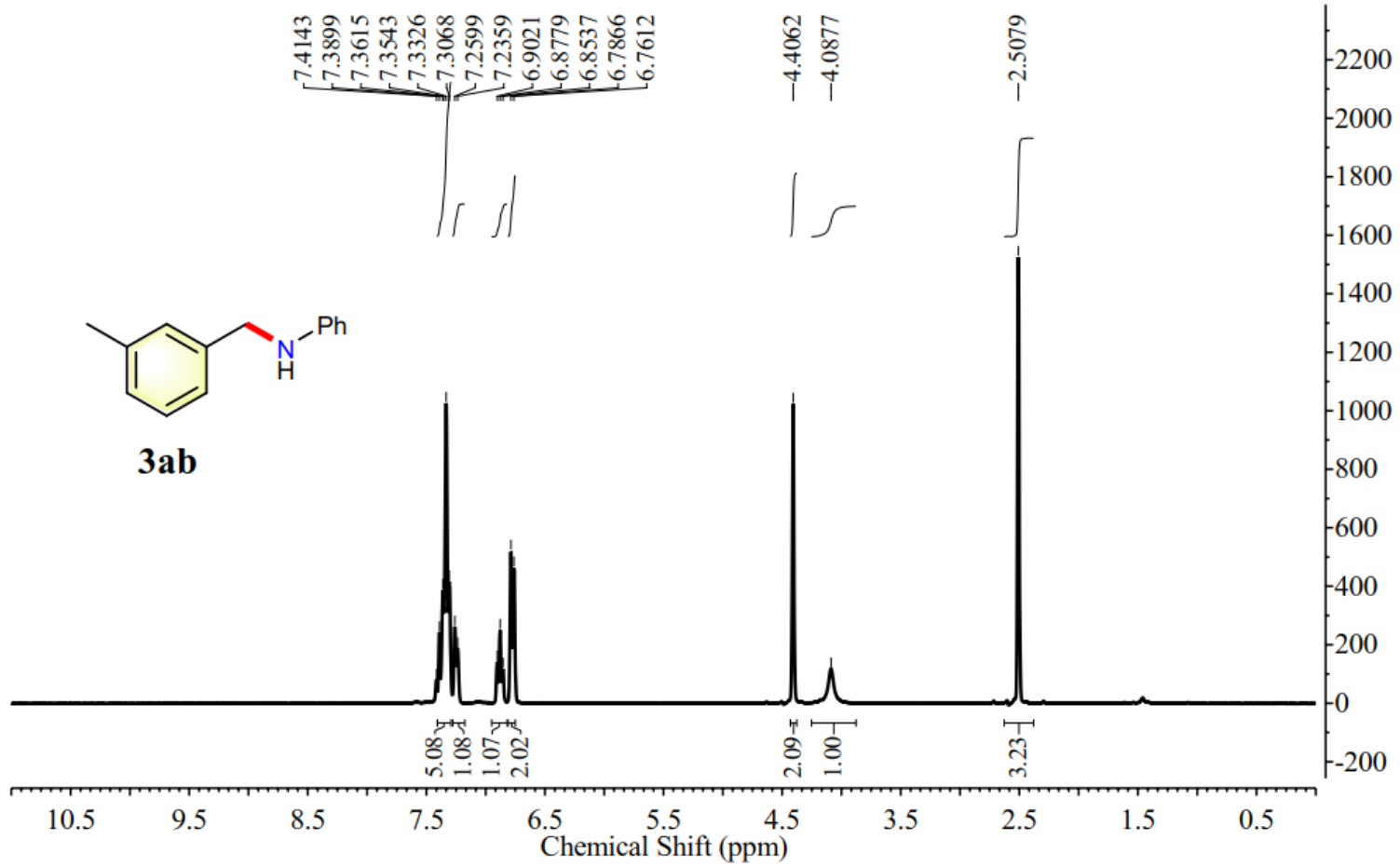
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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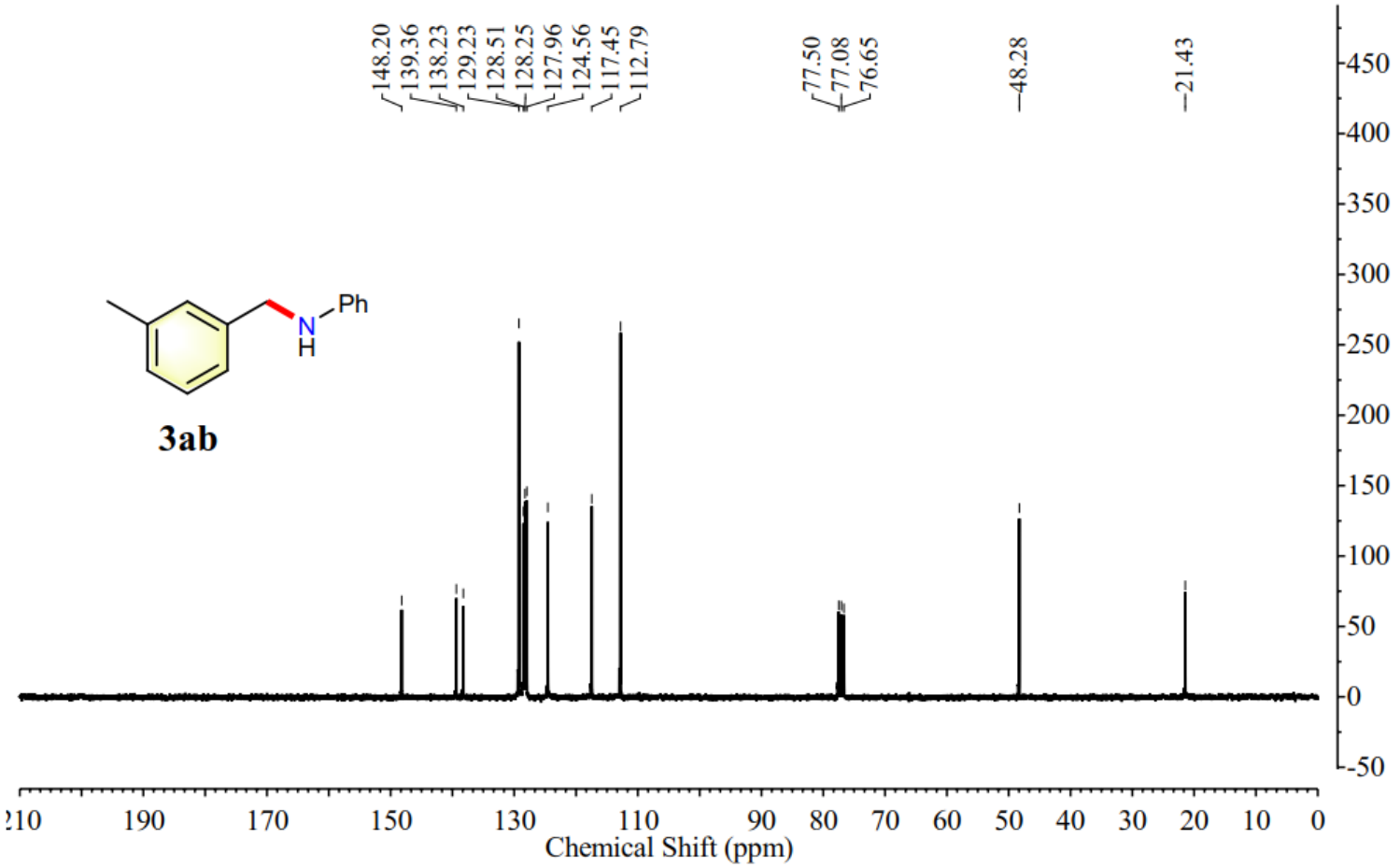
7.3326
7.3068
7.2599
7.2359
6.9021
6.8779
6.8537
6.7866
6.7612
4.4062
4.0877
2.5079
Ph
N
H
3ab
5.08
1.08
1.07
2.02
2.09
1.00
3.23
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)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129.23
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128.25
127.96
124.56
117.45
112.79
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77.08
76.65
48.28
21.43
N
H
Ph
3ab
450
400
350
300
250
200
150
100
50
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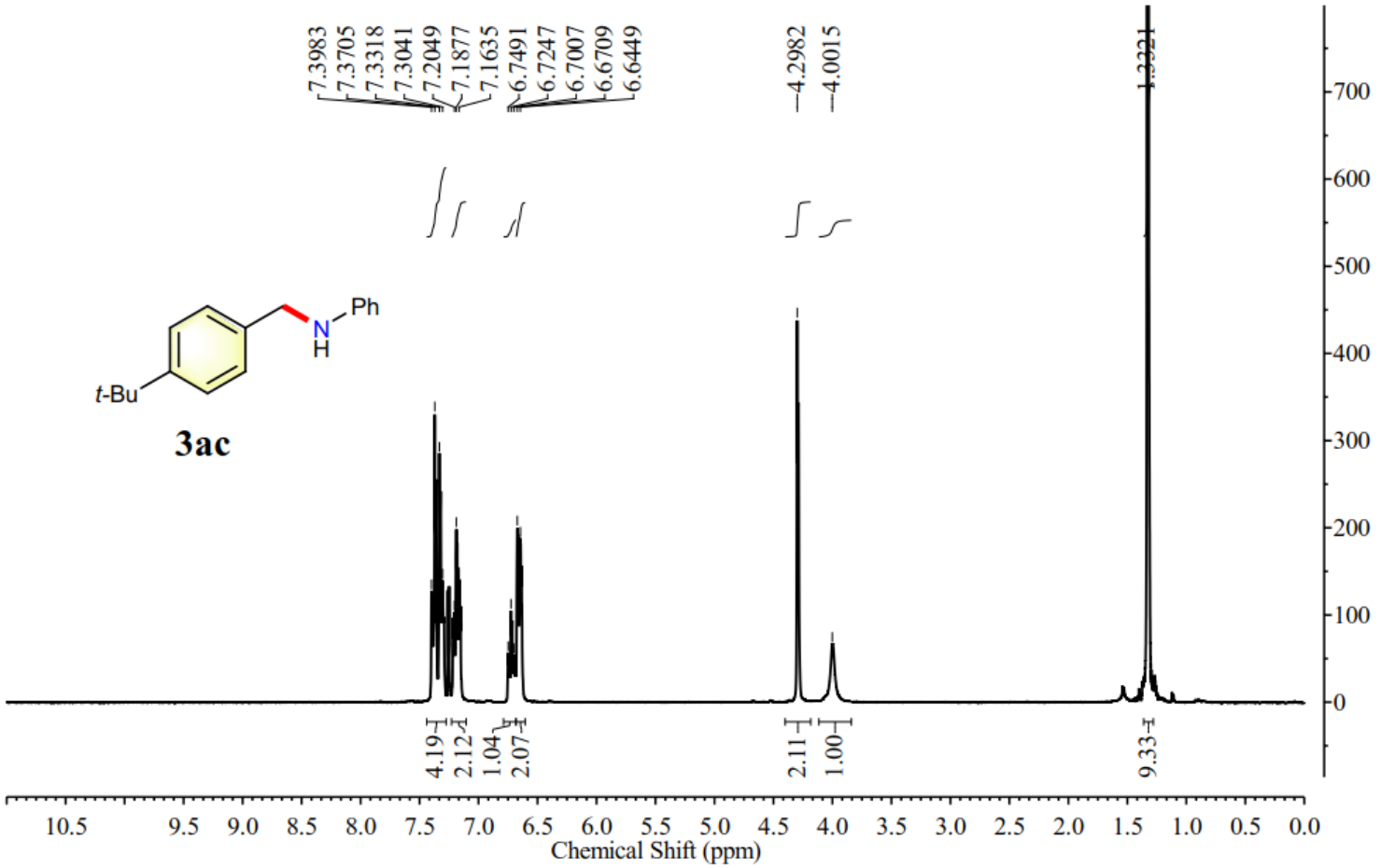
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.3318
7.3041
7.2049
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7.1635
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6.7247
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6.6709
6.6449
4.2982
4.0015
1.3321
t-Bu
N
H
Ph
3ac
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2.12
1.04
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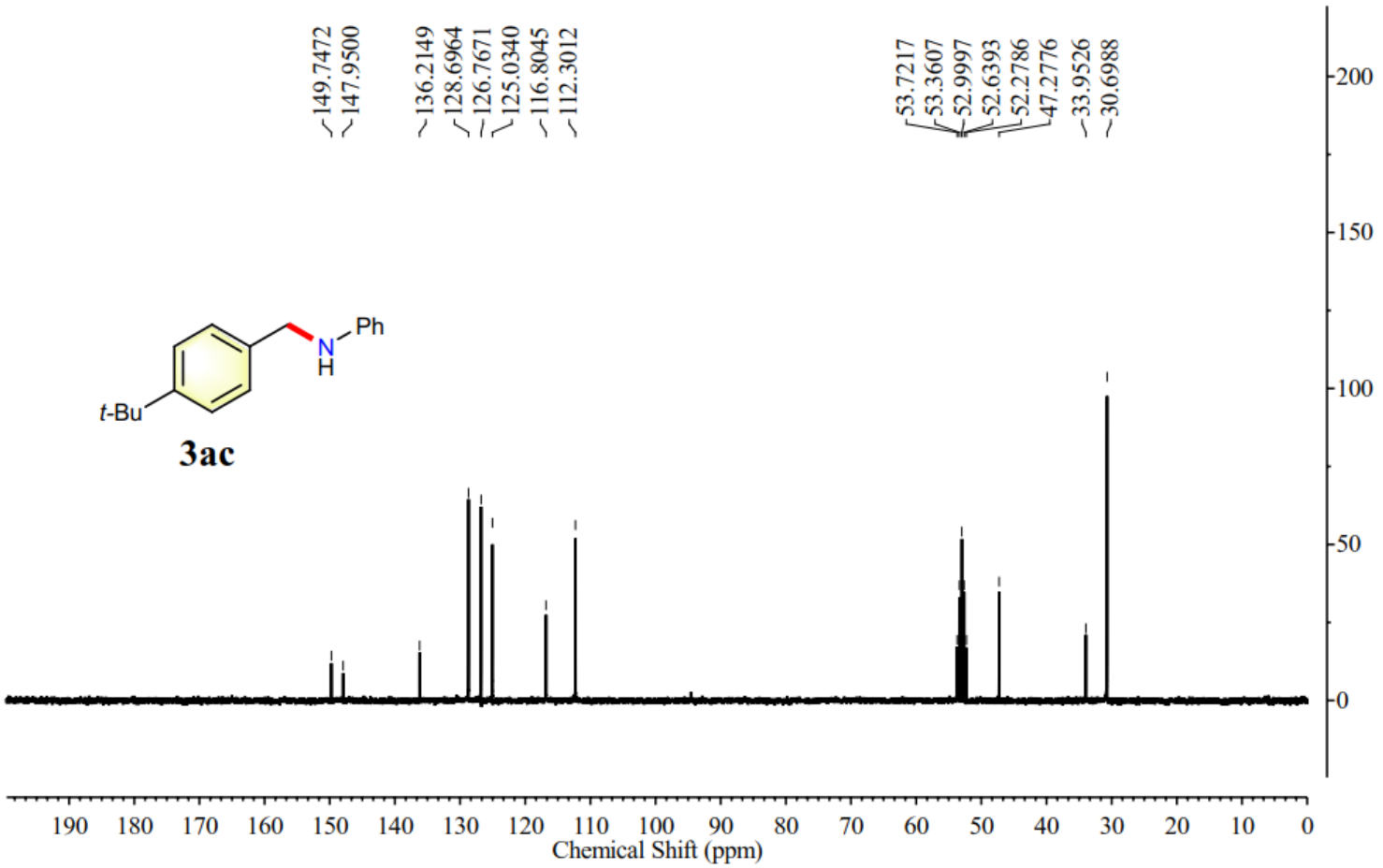
2.11
1.00
9.33
Chemical Shift (ppm)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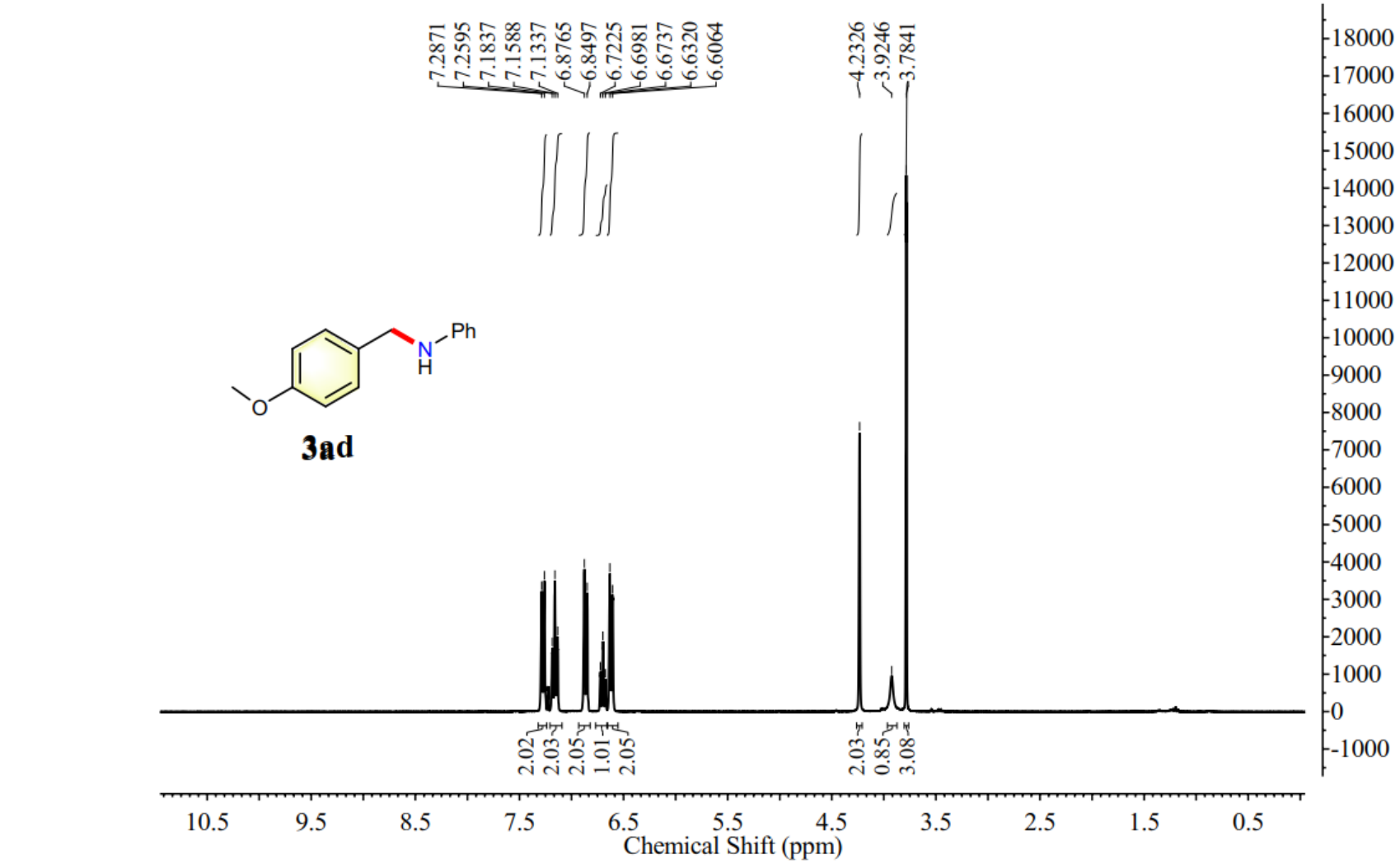
52.9997
52.6393
52.2786
47.2776
33.9526
30.6988
Ph
N
H
t-Bu
3ac
200
150
100
50
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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6.8497
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6.6320
6.6064
4.2326
3.9246
3.7841
N
H
Ph
O
3ad
2.02
2.03
2.05
1.01
2.05
2.03
0.85
3.08
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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2.5
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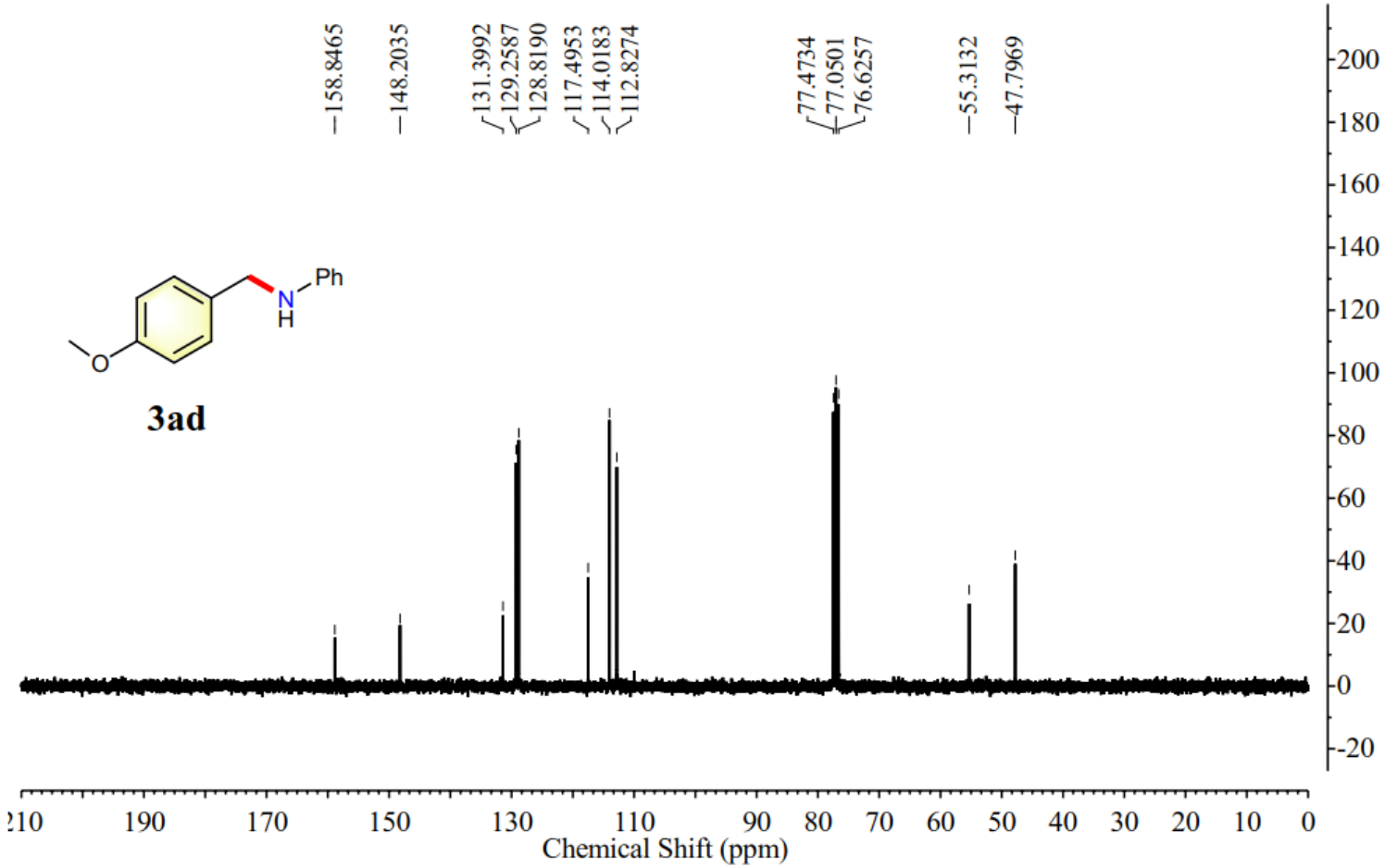
Chemical Shift (ppm)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55.3132
47.7969
Ph
N
H
O
3ad
200
180
160
140
120
100
80
60
40
20
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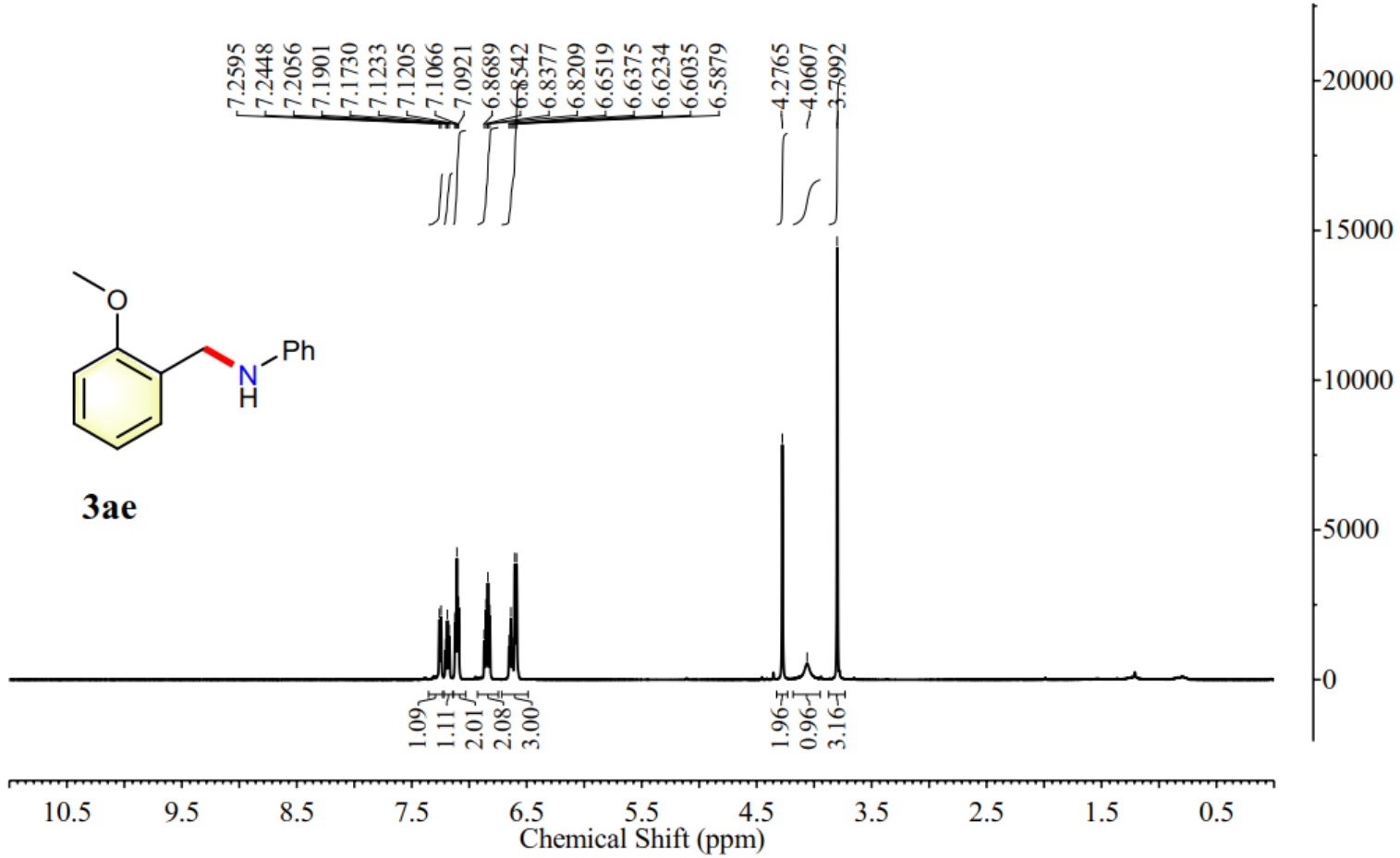
Chemical Shift (ppm)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4.0607
3.7992
O
N
H
Ph
3ae
1.09
1.11
2.01
2.08
3.00
1.96
0.96
3.16
20000
15000
10000
5000
0
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7.5
6.5
5.5
4.5
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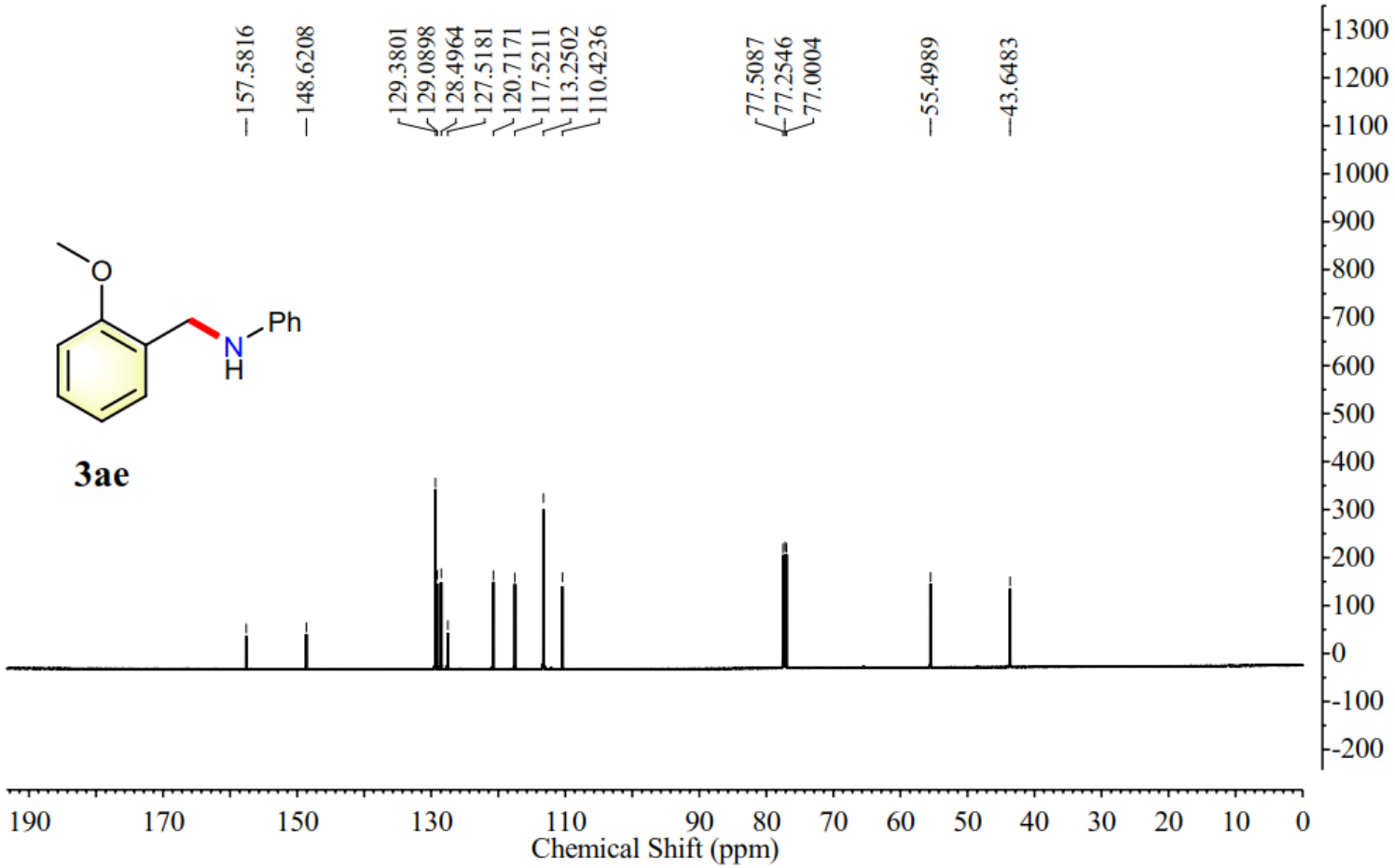
2.5
1.5
0.5
Chemical Shift (ppm)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300
200
100
0
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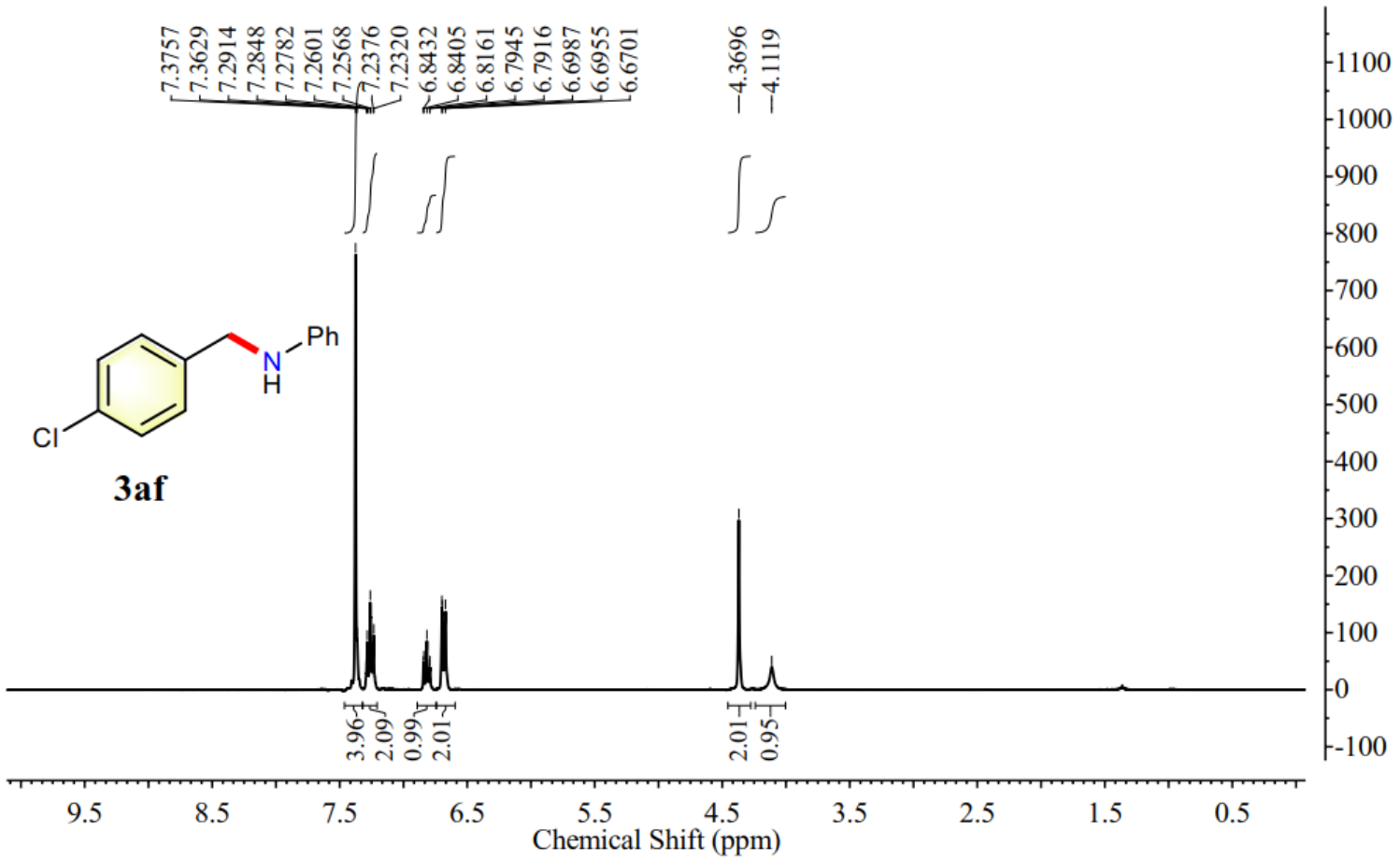
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6.8161
6.7945
6.7916
6.6987
6.6955
6.6701
4.3696
4.1119
Ph
N
H
Cl
3af
3.96
2.09
0.99
2.01
2.01
0.95
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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6.5
5.5
4.5
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2.5
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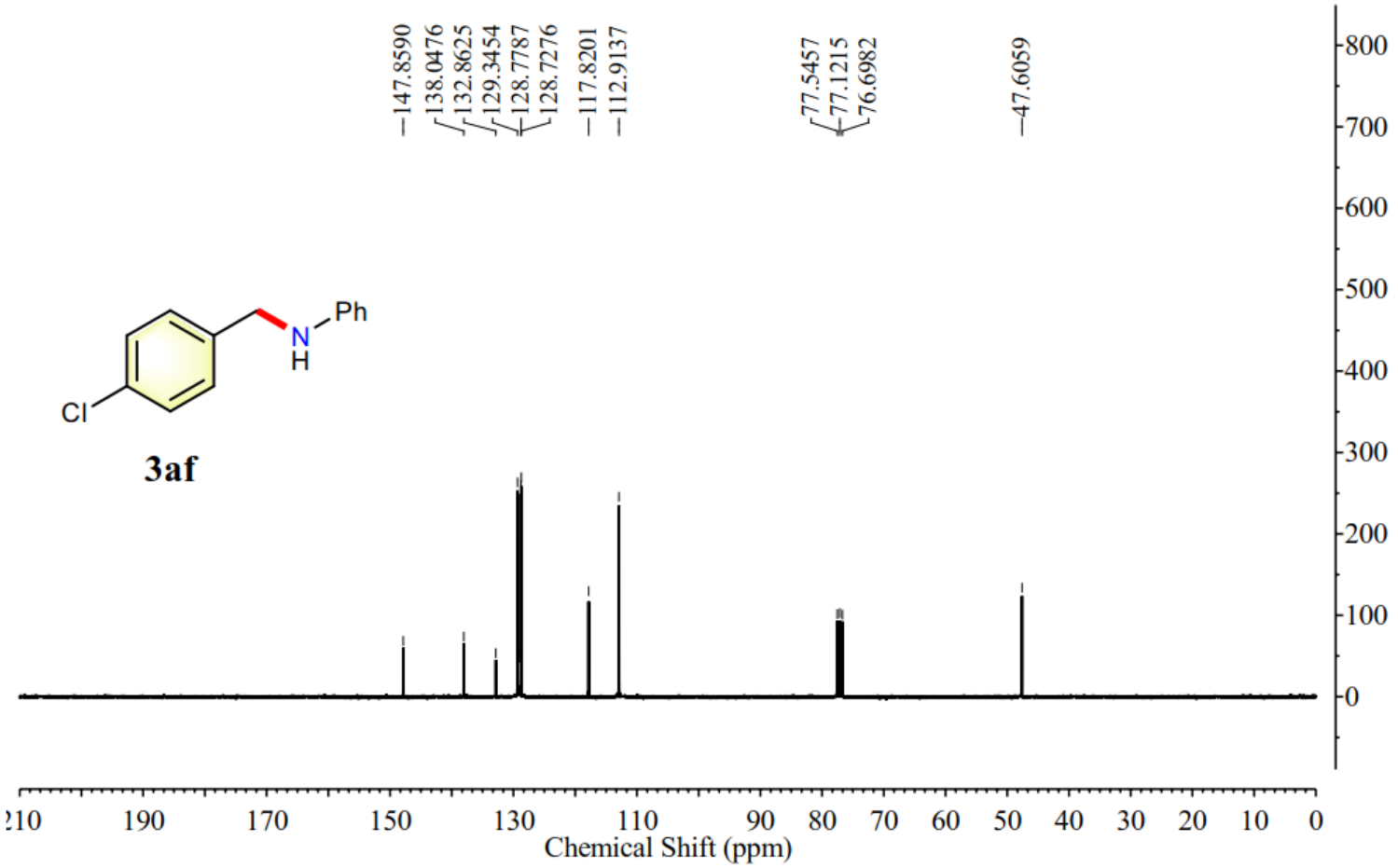
Chemical Shift (ppm)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76.6982
47.6059
Ph
N
H
Cl
3af
800
700
600
500
400
300
200
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130
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50
40
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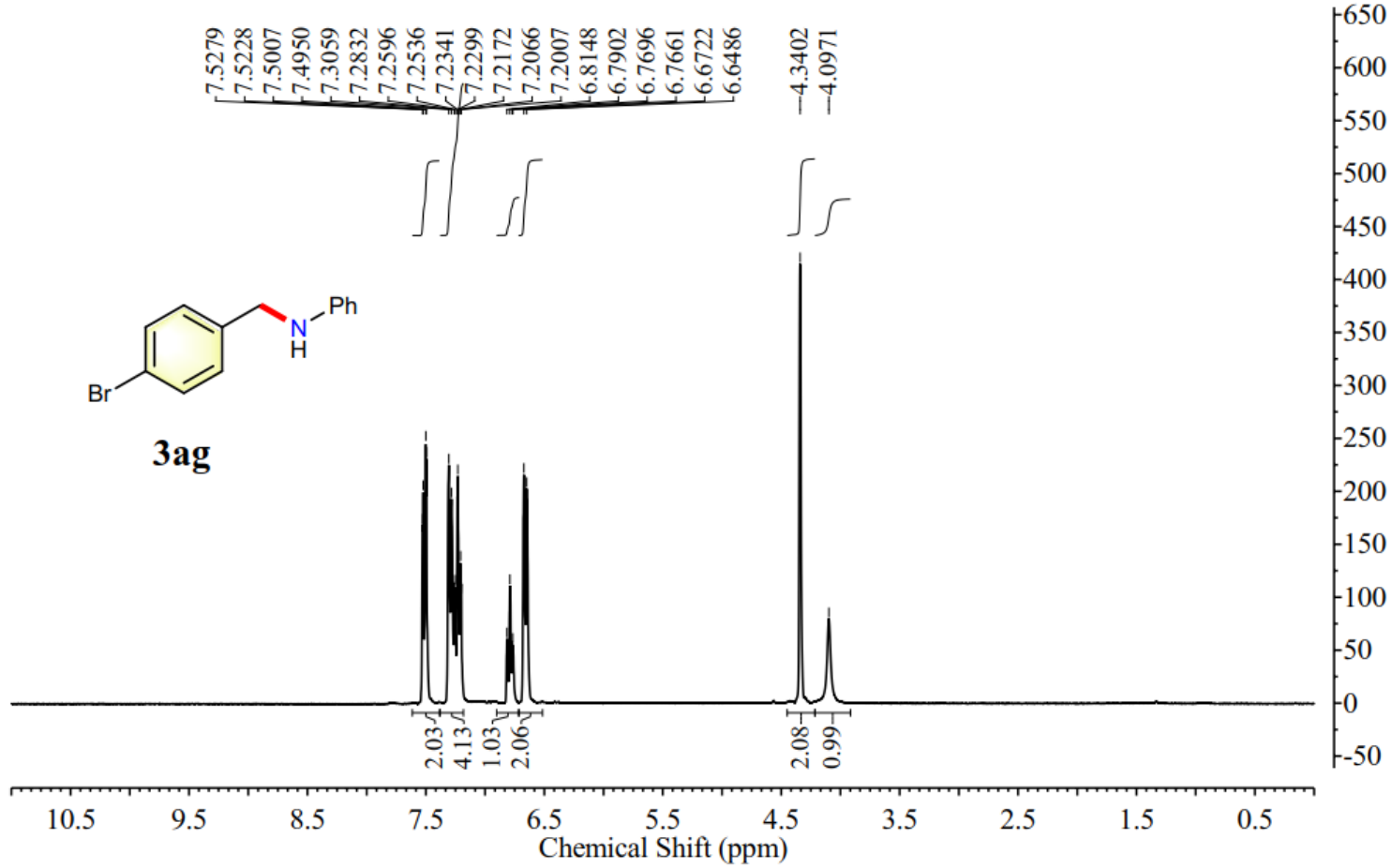
Chemical Shift (ppm)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7.2172
7.2066
7.2007
6.8148
6.7902
6.7696
6.7661
6.6722
6.6486
4.3402
4.0971
Ph
N
H
Br
3ag
2.03
4.13
1.03
2.06
2.08
0.99
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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7.5
6.5
5.5
4.5
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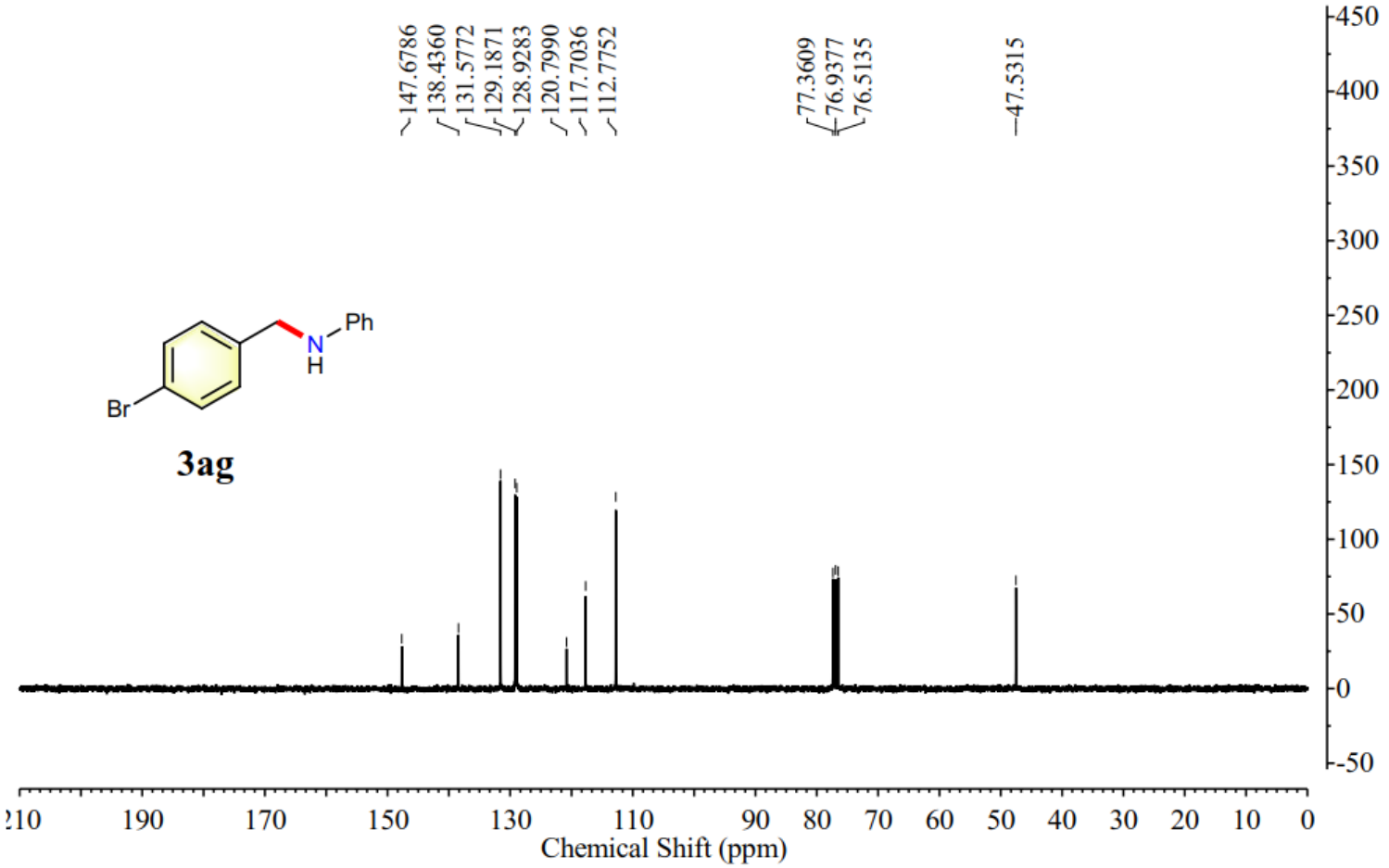
2.5
1.5
0.5
Chemical Shift (ppm)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47.5315
Ph
N
H
Br
3ag
450
400
350
300
250
200
150
100
50
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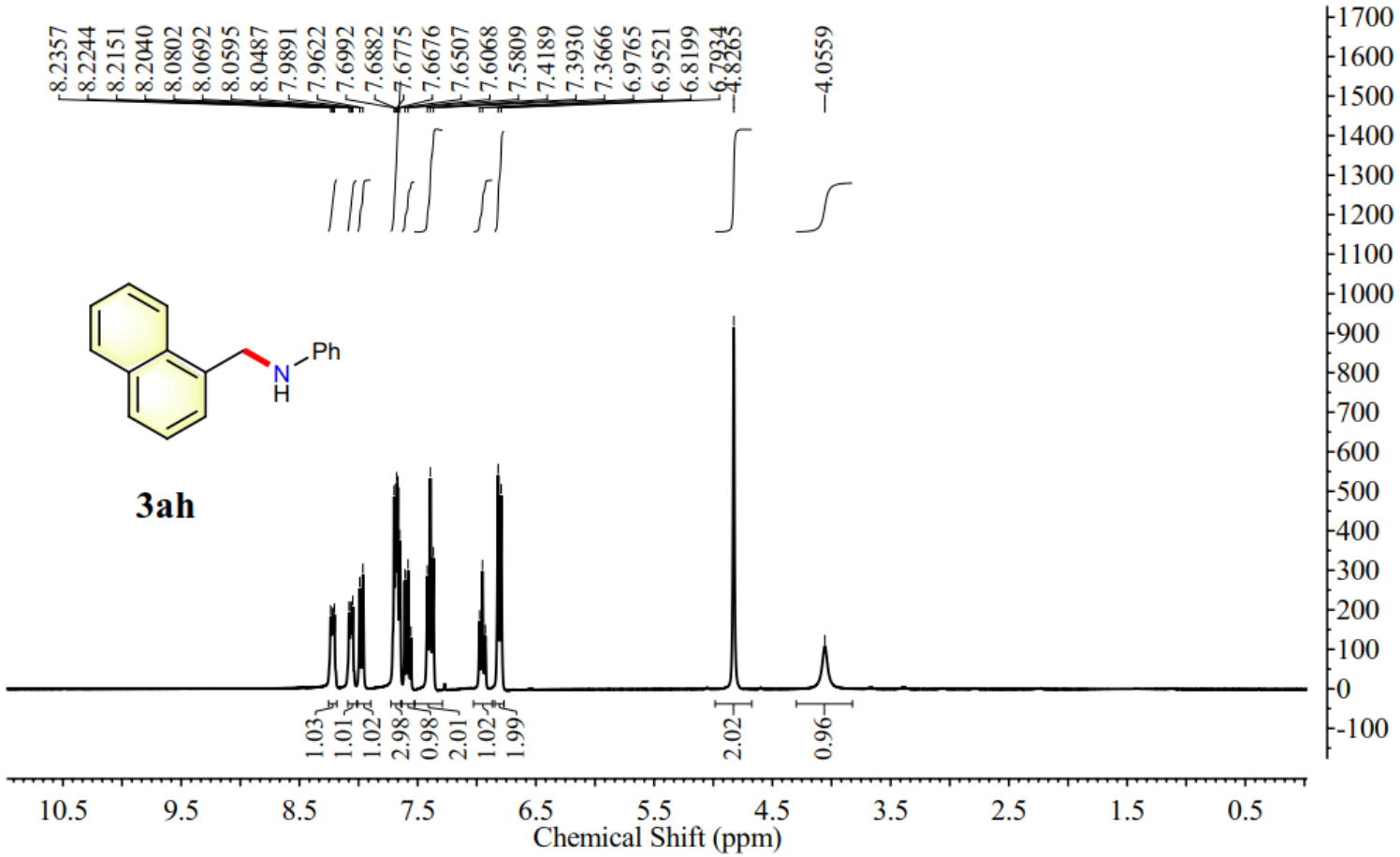
Chemical Shift (ppm)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7.6882
7.6775
7.6676
7.6507
7.6068
7.5809
7.4189
7.3930
7.3666
6.9765
6.9521
6.8199
4.0559
Ph
N
H
3ah
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1.01
1.02
2.98
0.98
2.01
1.02
1.99
2.02
0.96
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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7.5
6.5
5.5
4.5
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2.5
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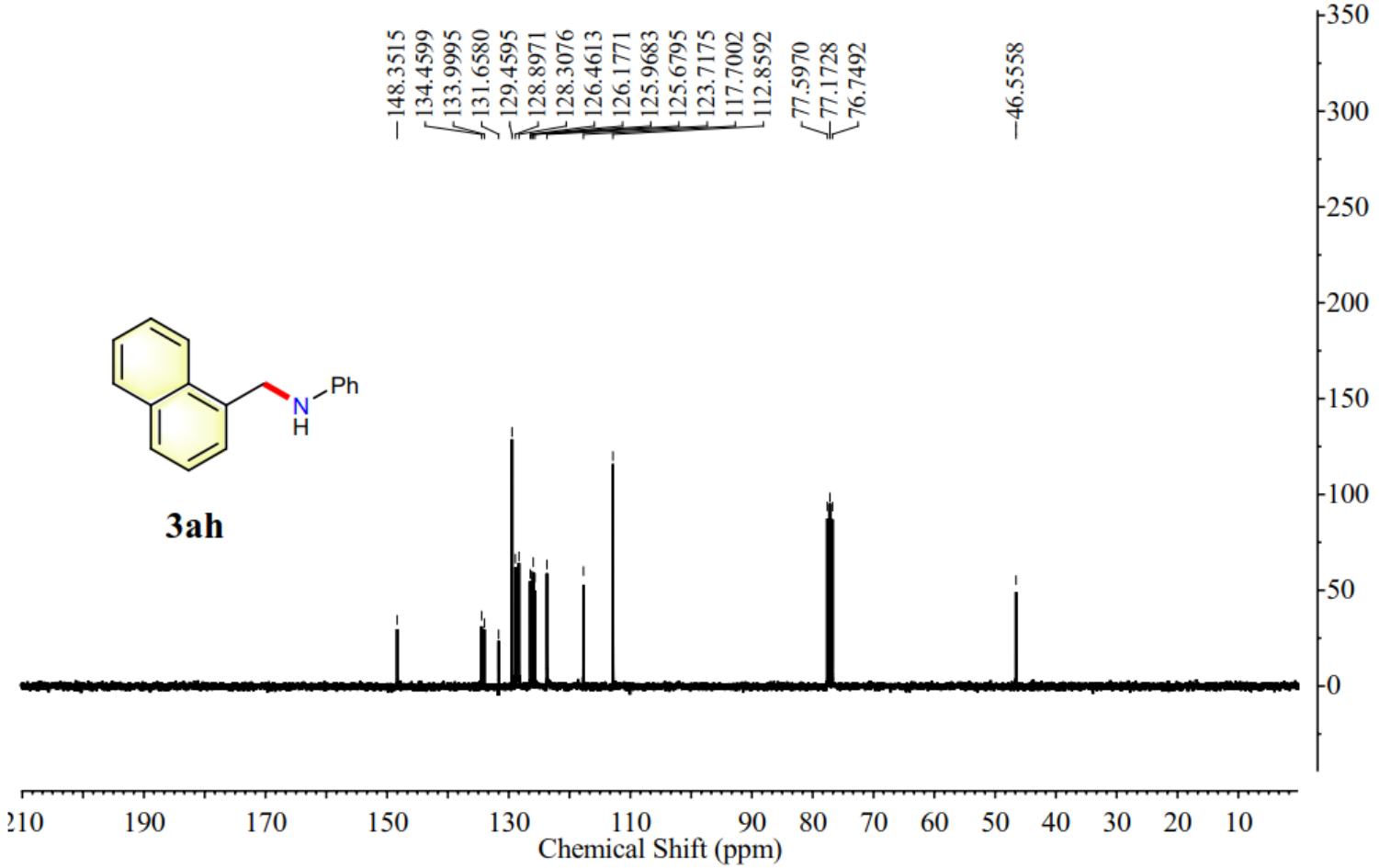
Chemical Shift (ppm)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125.6795
123.7175
117.7002
112.8592
77.5970
77.1728
76.7492
46.5558
N
H
Ph
3ah
350
300
250
200
150
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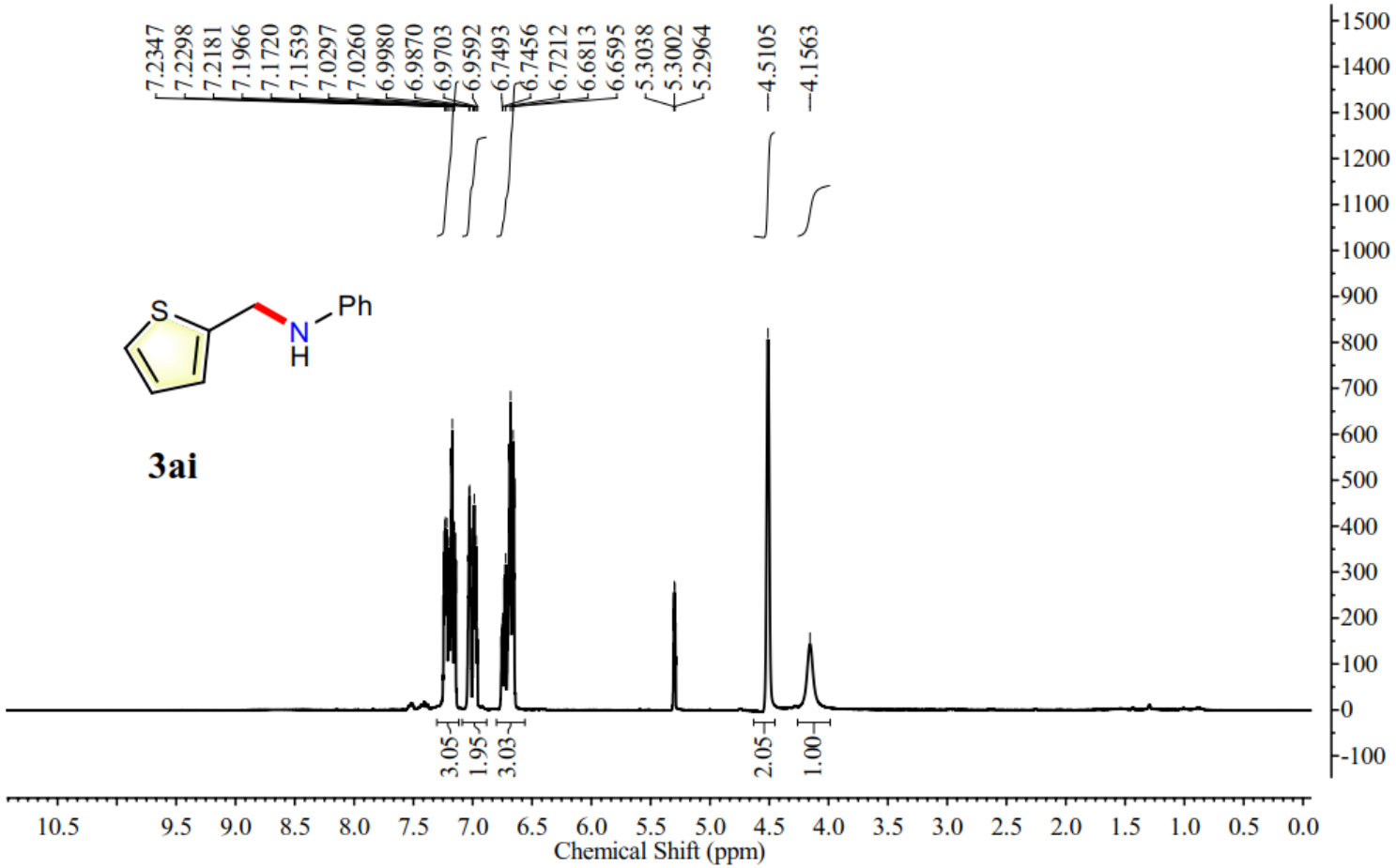
Chemical Shift (ppm)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6.7493
6.7456
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6.6813
6.6595
5.3038
5.3002
5.2964
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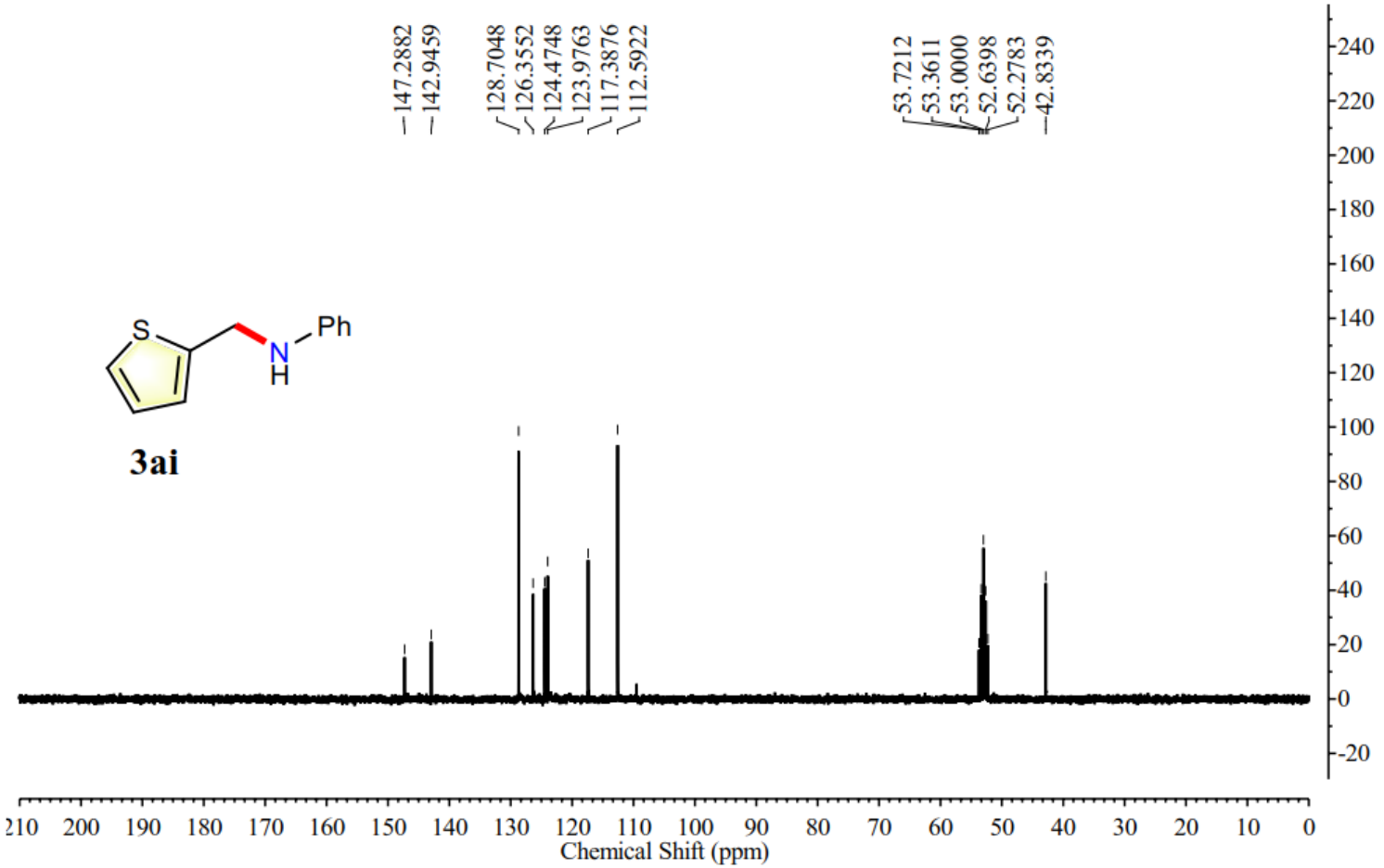
S
N
H
Ph
3ai
3.05
1.95
3.03
2.05
1.00
Chemical Shift (ppm)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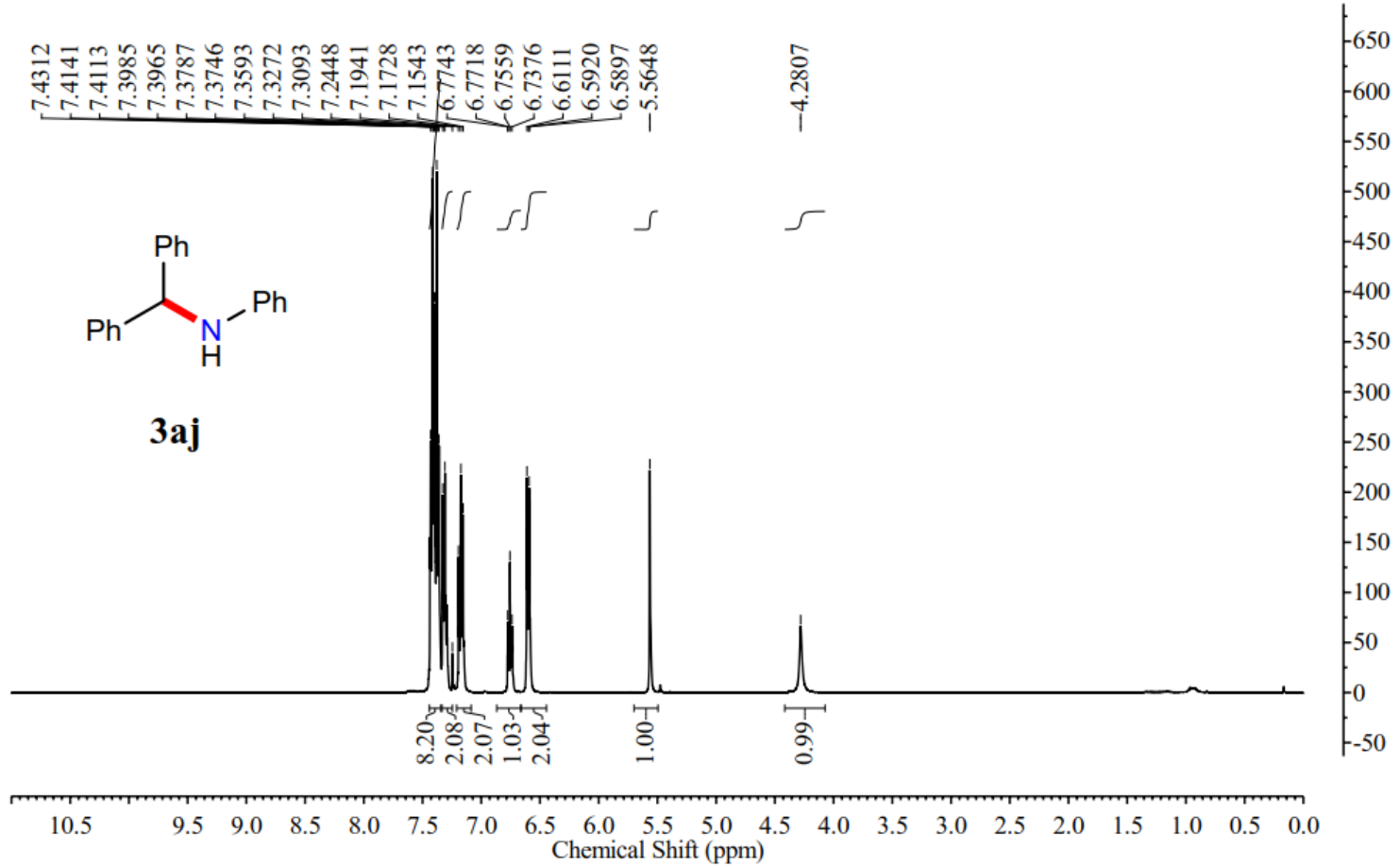
124.4748
123.9763
117.3876
112.5922
53.7212
53.3611
53.0000
52.6398
52.2783
42.8339
S
N
H
Ph
3ai
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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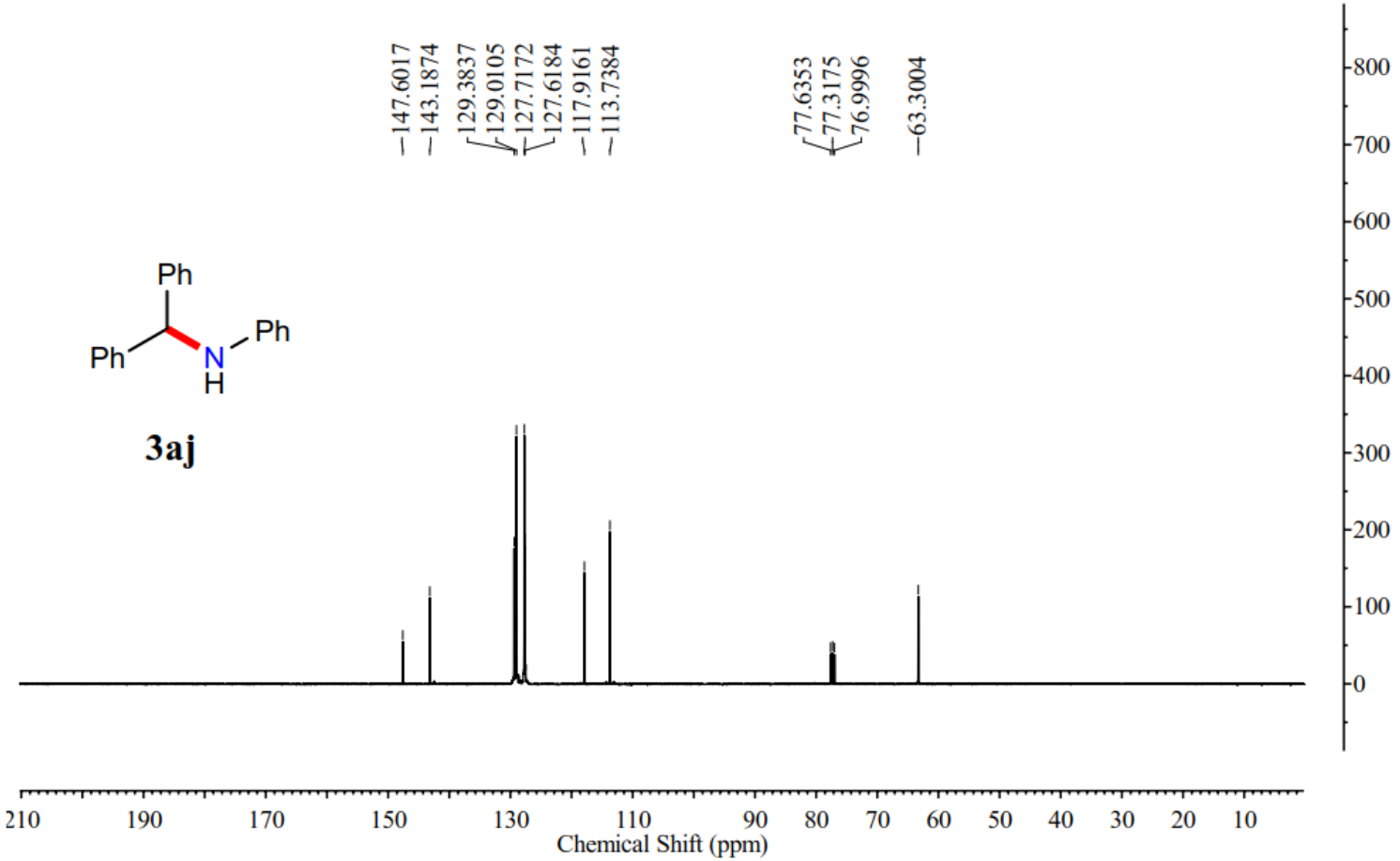
7.2448
7.1941
7.1728
7.1543
6.7743
6.7718
6.7559
6.7376
6.6111
6.5920
6.5897
5.5648
4.2807
Ph
Ph
Ph
N
H
3aj
8.20
2.08
2.07
1.03
2.04
1.00
0.99
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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127.6184
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77.6353
77.3175
76.9996
63.3004
Ph
Ph
Ph
N
H
3aj
800
700
600
500
400
300
200
100
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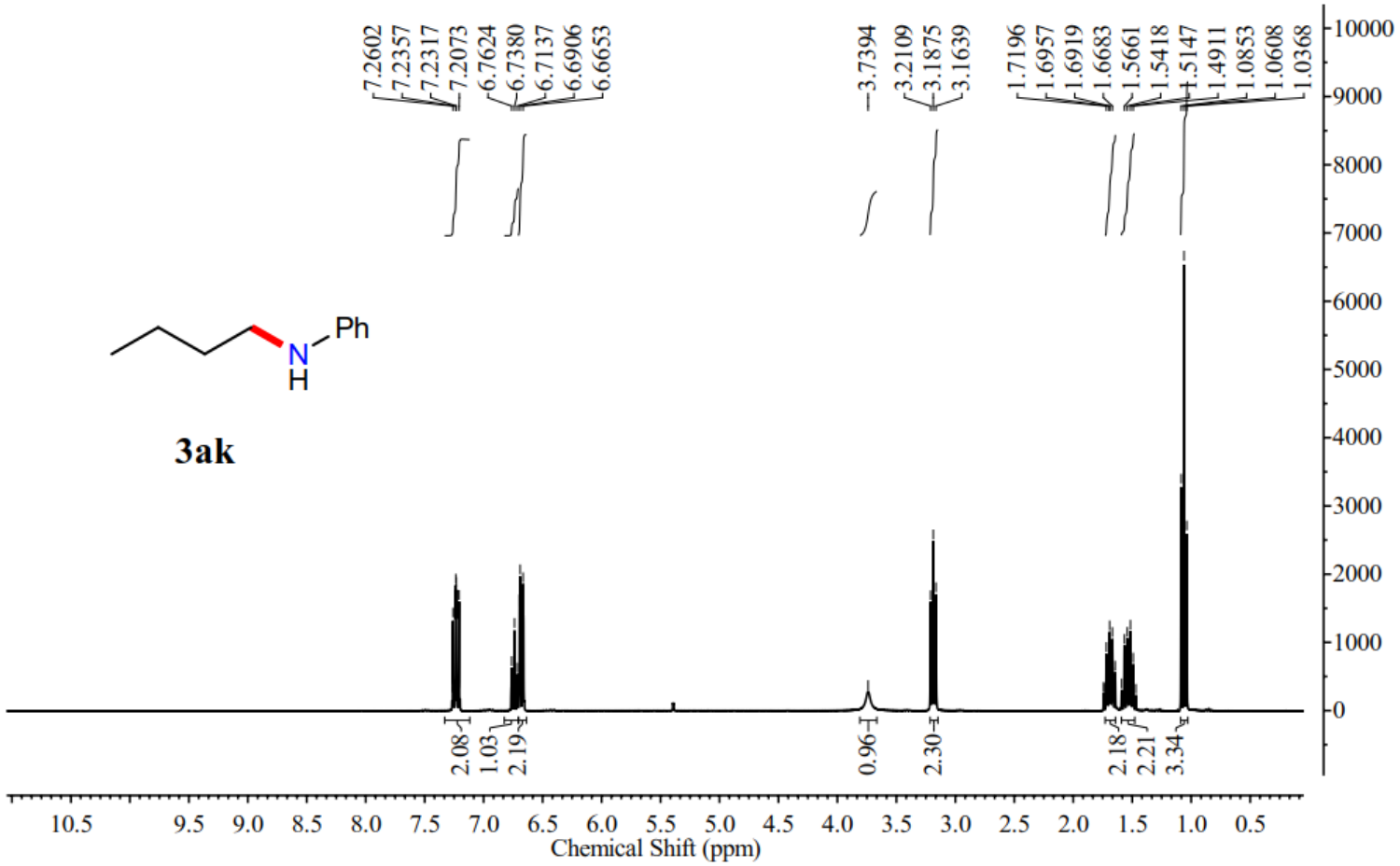
150
130
110
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)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6.7137
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3.2109
3.1875
3.1639
1.7196
1.6957
1.6919
1.6683
1.5661
1.5418
1.5147
1.4911
1.0853
1.0608
1.0368
Ph
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H
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2.08
1.03
2.19
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2.30
2.18
2.21
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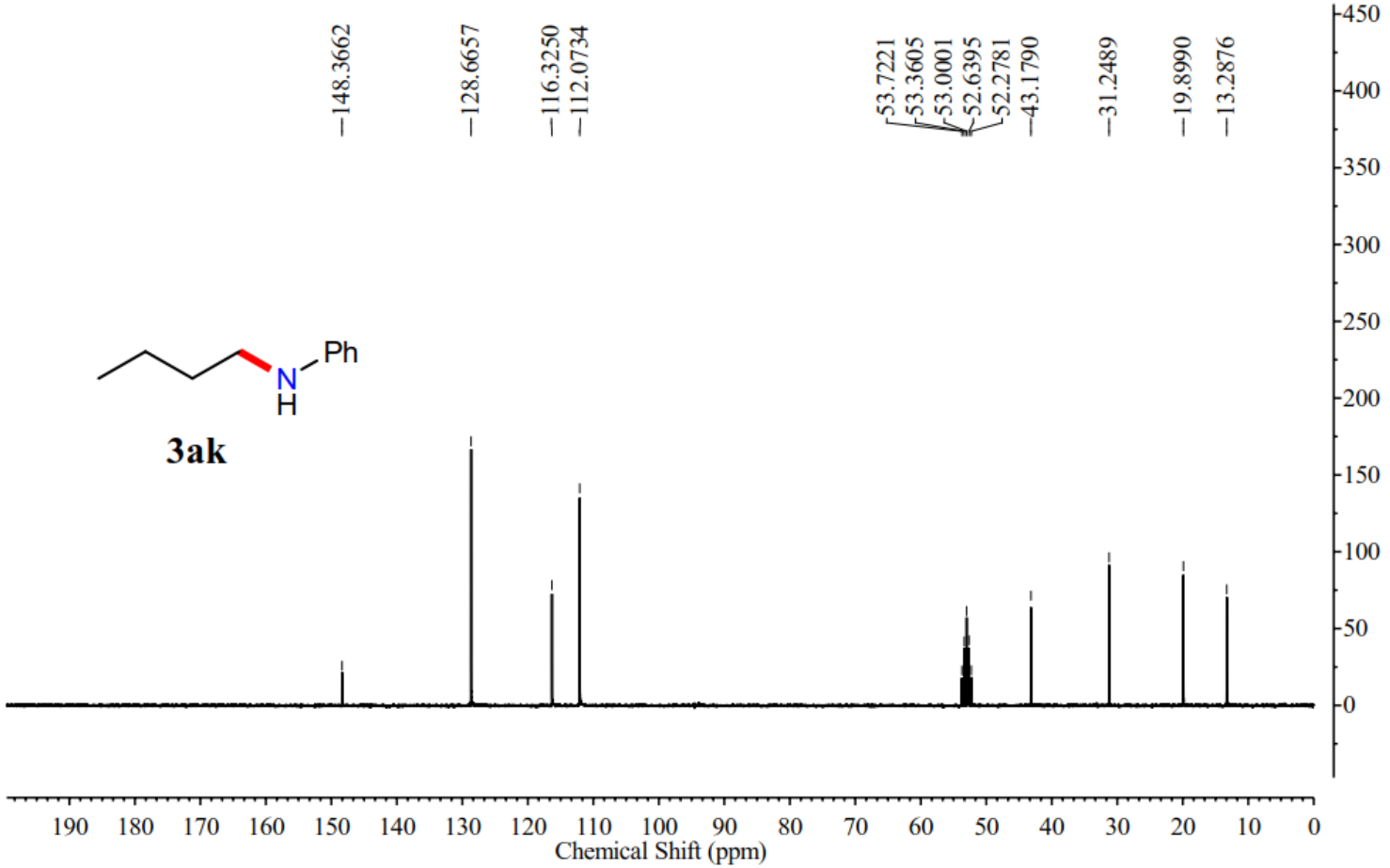
Chemical Shift (ppm)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31.2489
19.8990
13.2876
Ph
N
H
3ak
450
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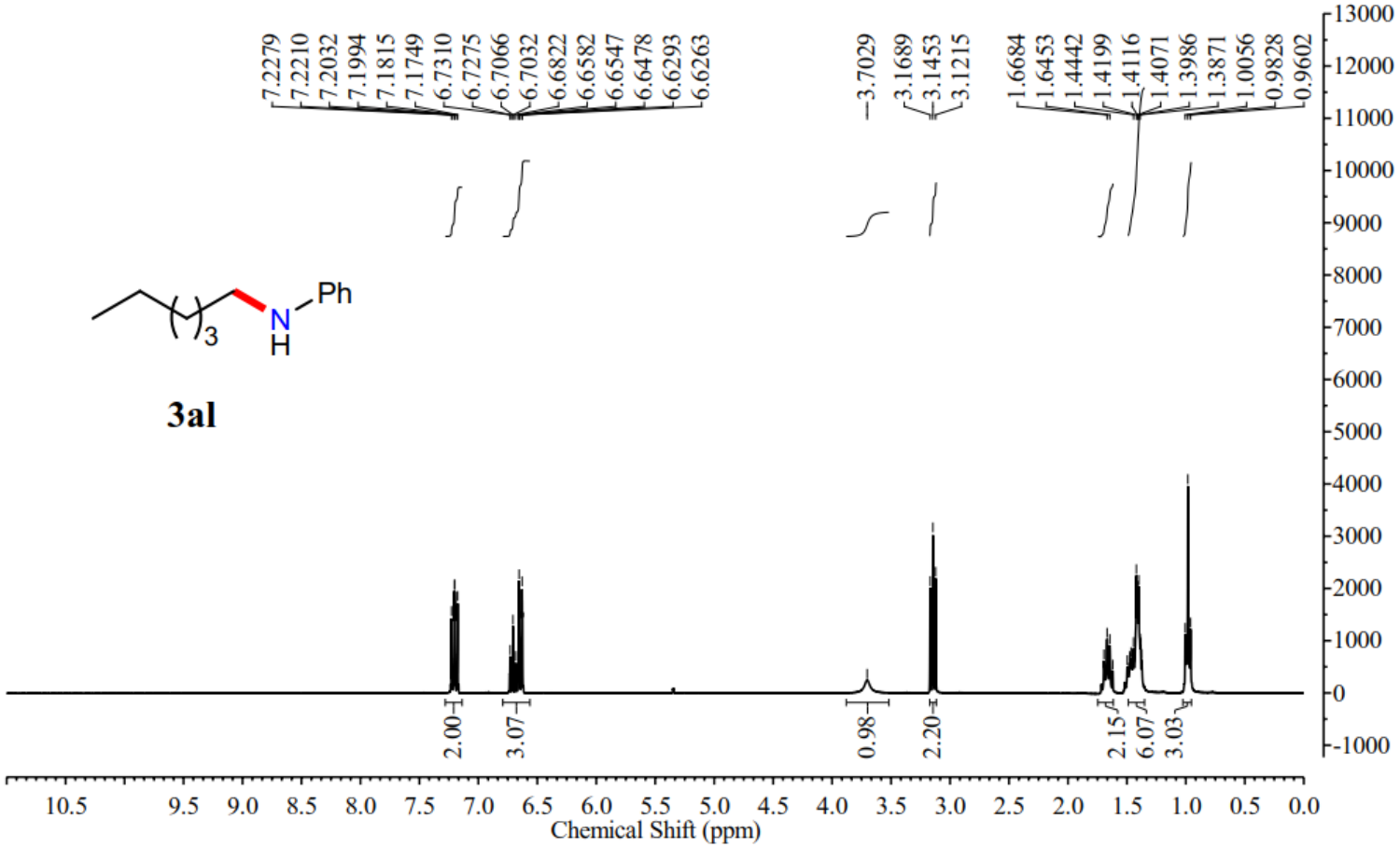
300
250
200
150
100
50
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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6.6547
6.6478
6.6293
6.6263
3.7029
3.1689
3.1453
3.1215
1.6684
1.6453
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1.4199
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1.4071
1.3986
1.3871
1.0056
0.9828
0.9602
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H
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2.15
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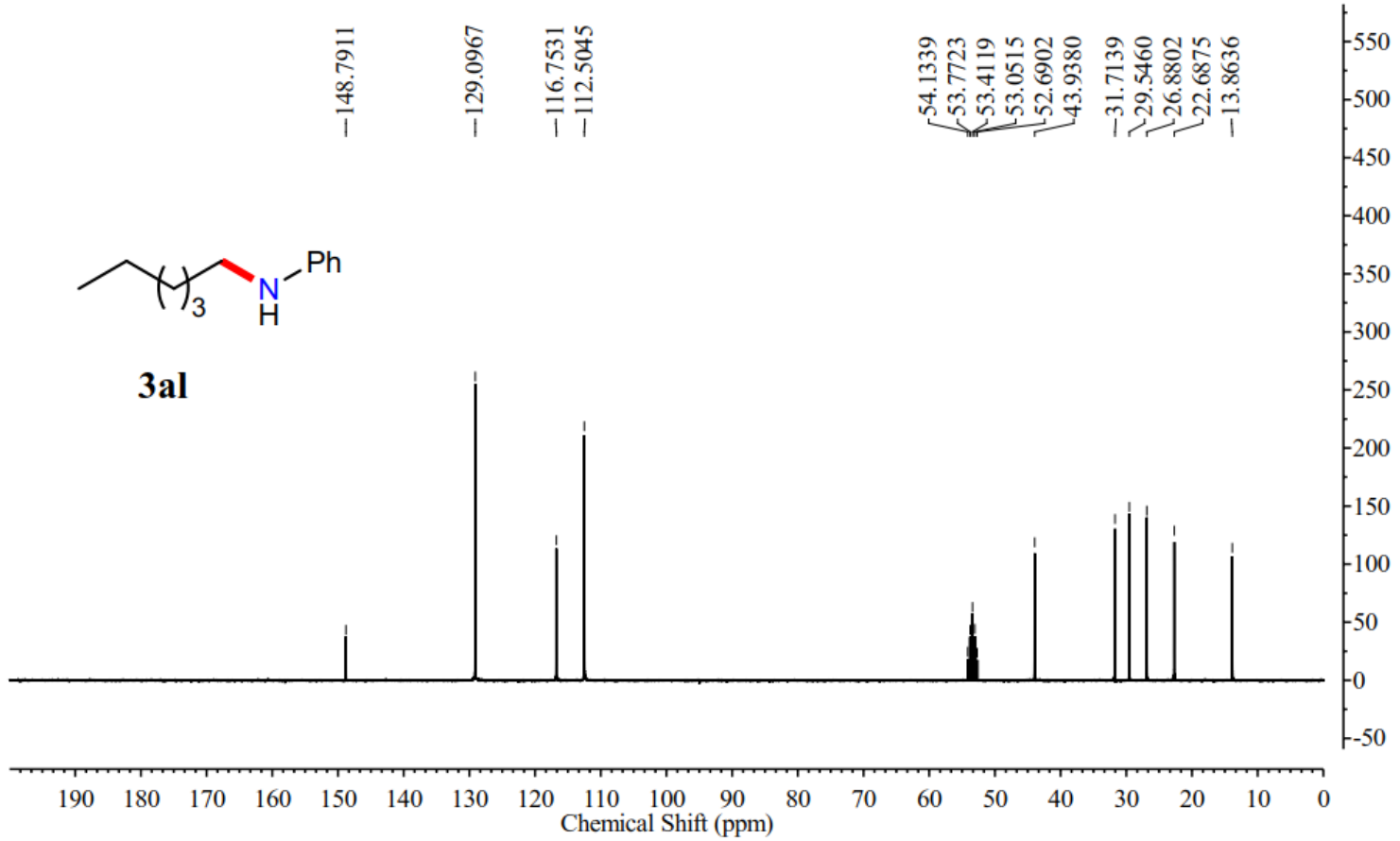
Chemical Shift (ppm)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53.4119
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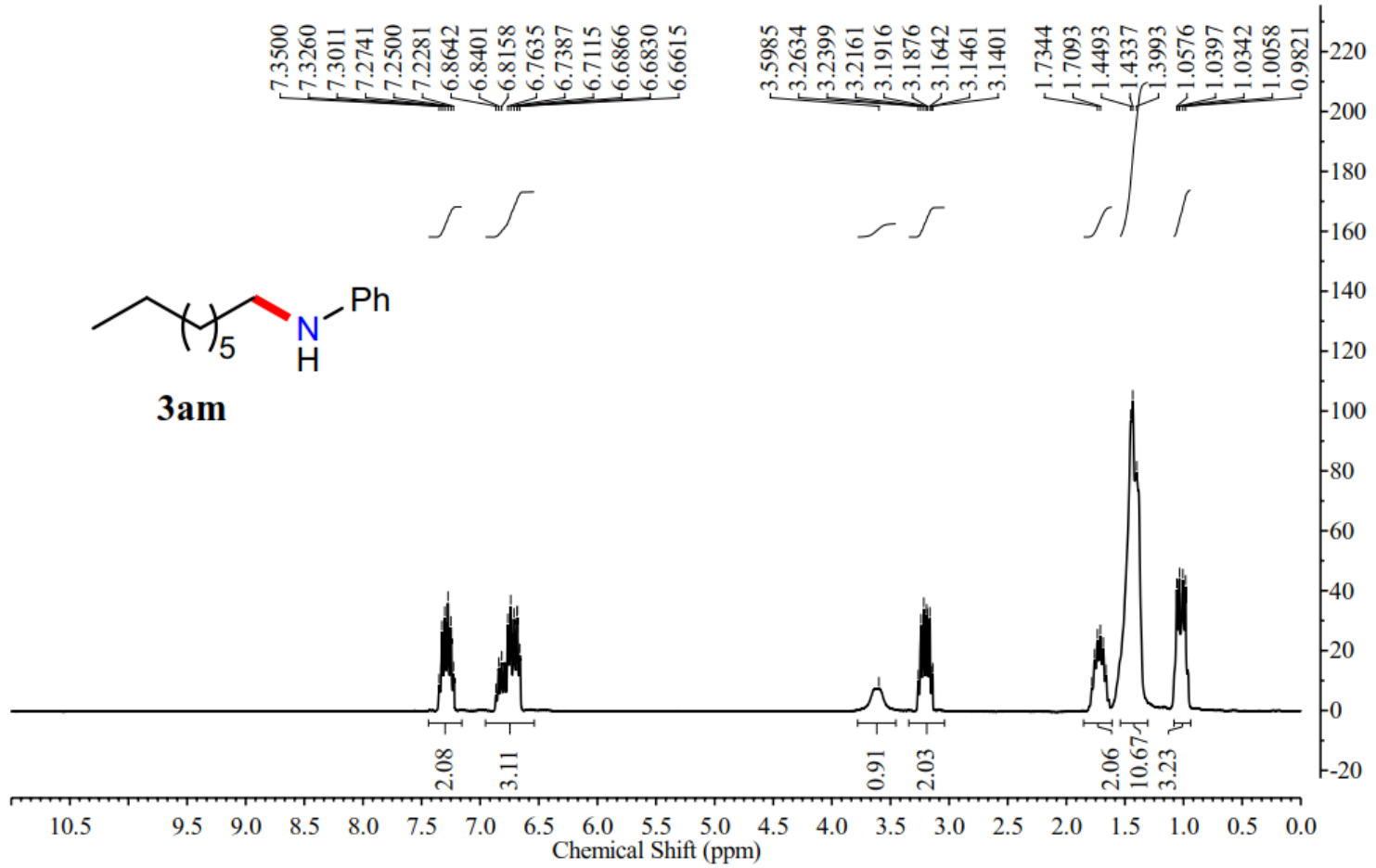
29.5460
26.8802
22.6875
13.8636
Ph
N
H
3
3al
Chemical Shift (ppm)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6.7387
6.7115
6.6866
6.6830
6.6615
3.5985
3.2634
3.2399
3.2161
3.1916
3.1876
3.1642
3.1461
3.1401
1.7344
1.7093
1.4493
1.4337
1.3993
1.0576
1.0397
1.0342
1.0058
0.9821
Ph
N
H
5
3am
2.08
3.11
0.91
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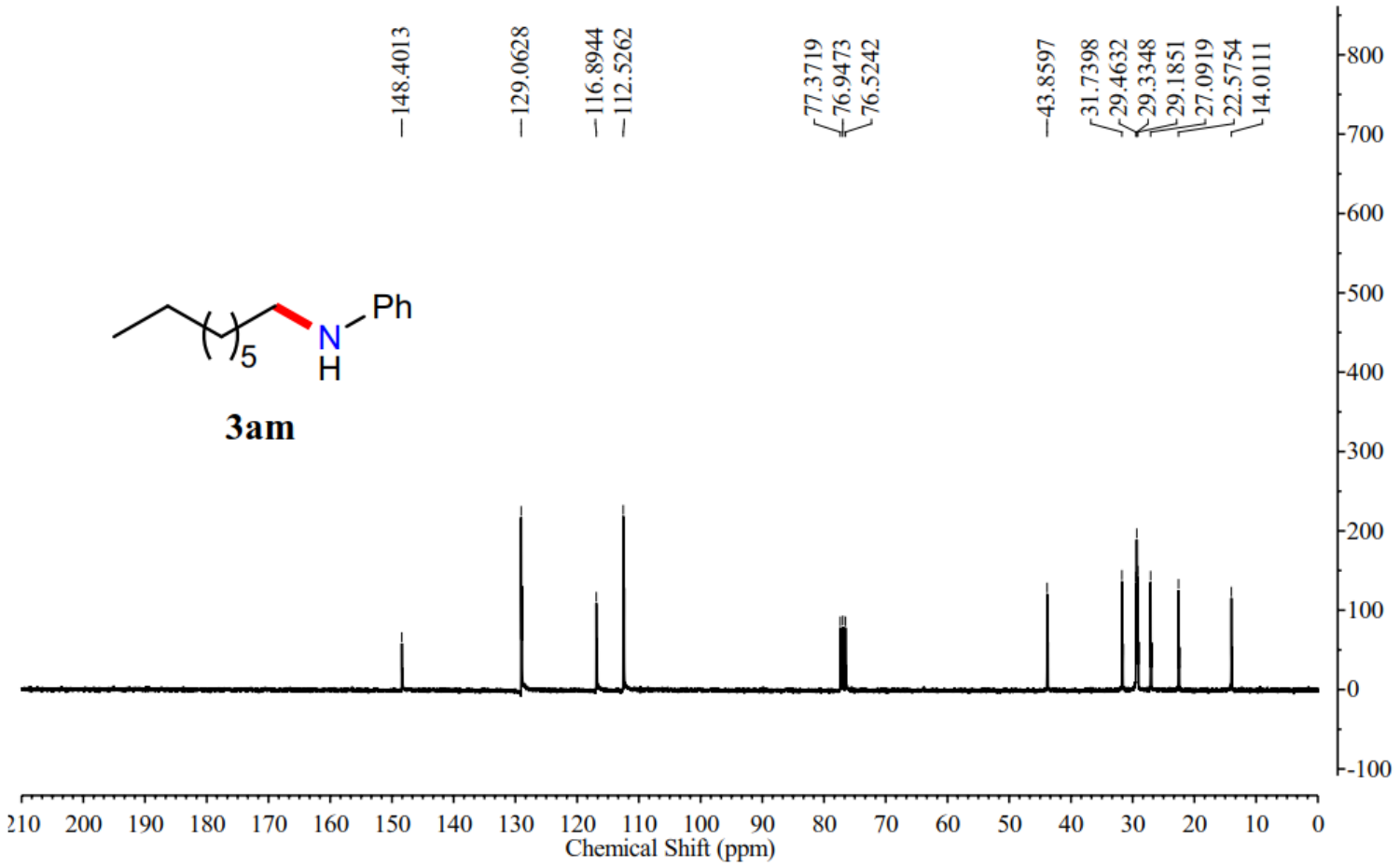
2.06
10.67
3.23
Chemical Shift (ppm)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76.5242
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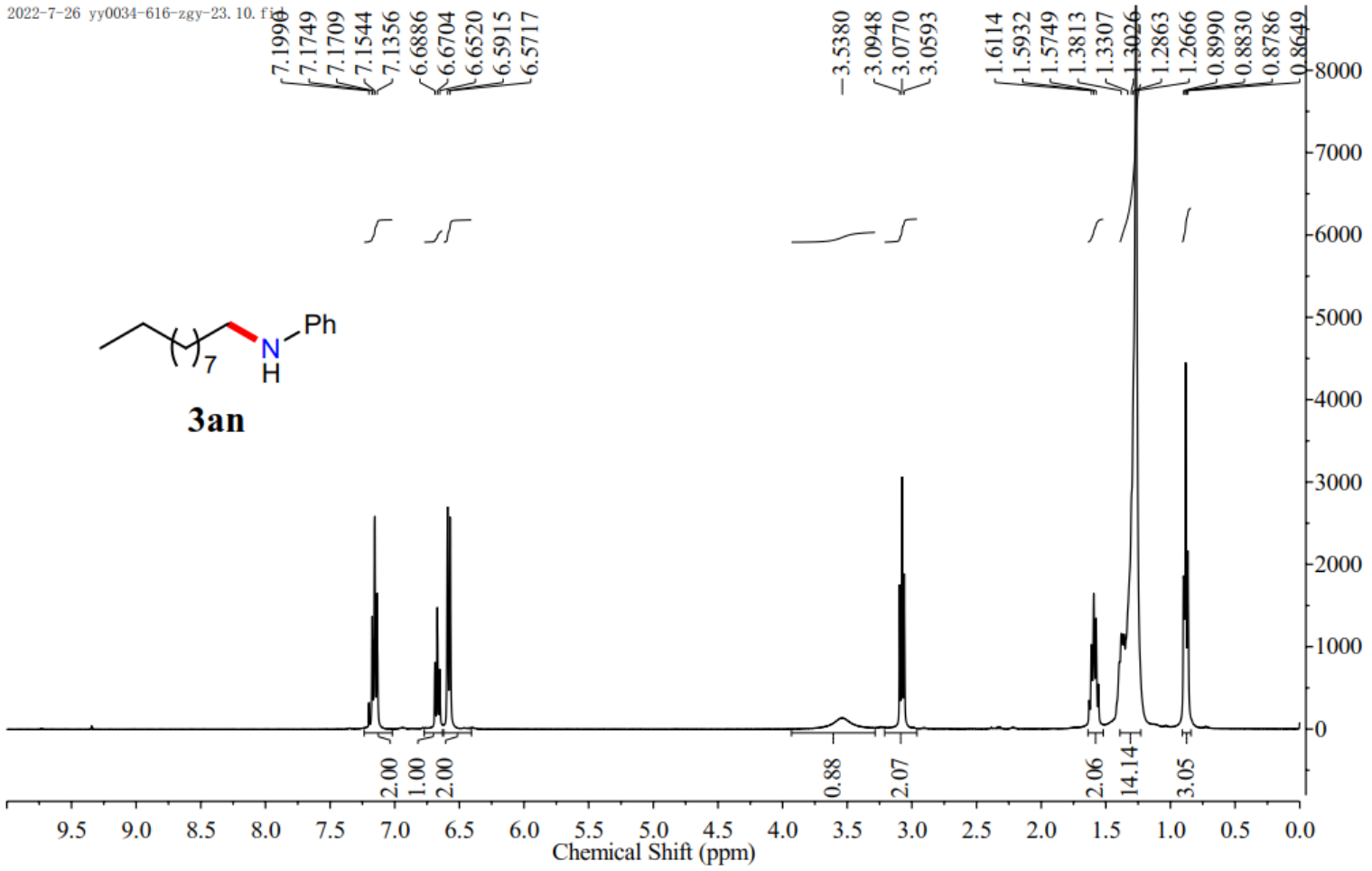
29.4632
29.3348
29.1851
27.0919
22.5754
14.0111
Ph
N
H
5
3am
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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6.6704
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6.5915
6.5717
3.5380
3.0948
3.0770
3.0593
1.6114
1.5932
1.5749
1.3813
1.3307
1.3026
1.2863
1.2666
0.8990
0.8830
0.8786
0.8649
Ph
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1.00
2.00
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2.06
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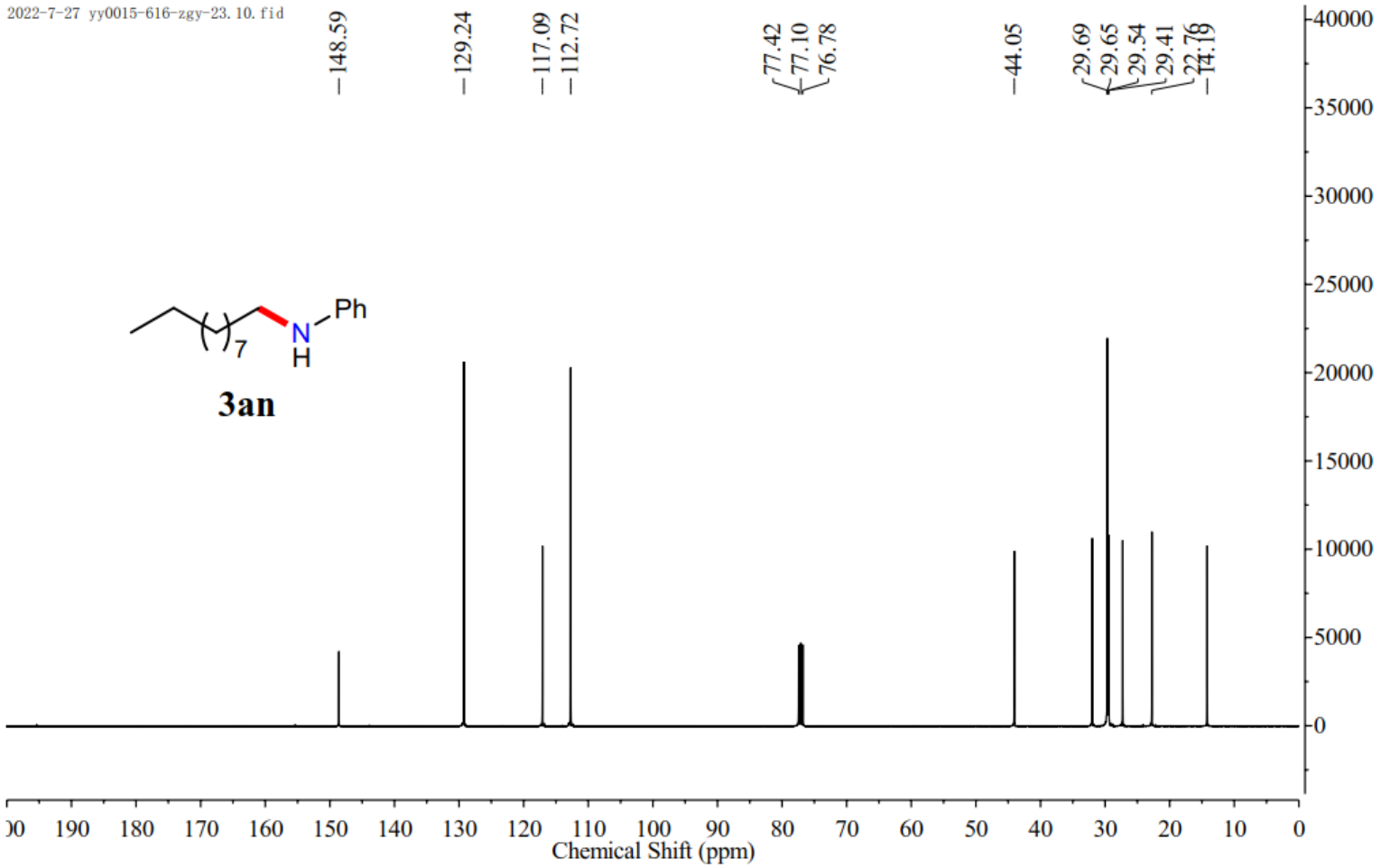
3.05
Chemical Shift (ppm)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77.10
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44.05
29.69
29.65
29.54
29.41
22.76
14.19
Ph
N
H
7
3an
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20000
15000
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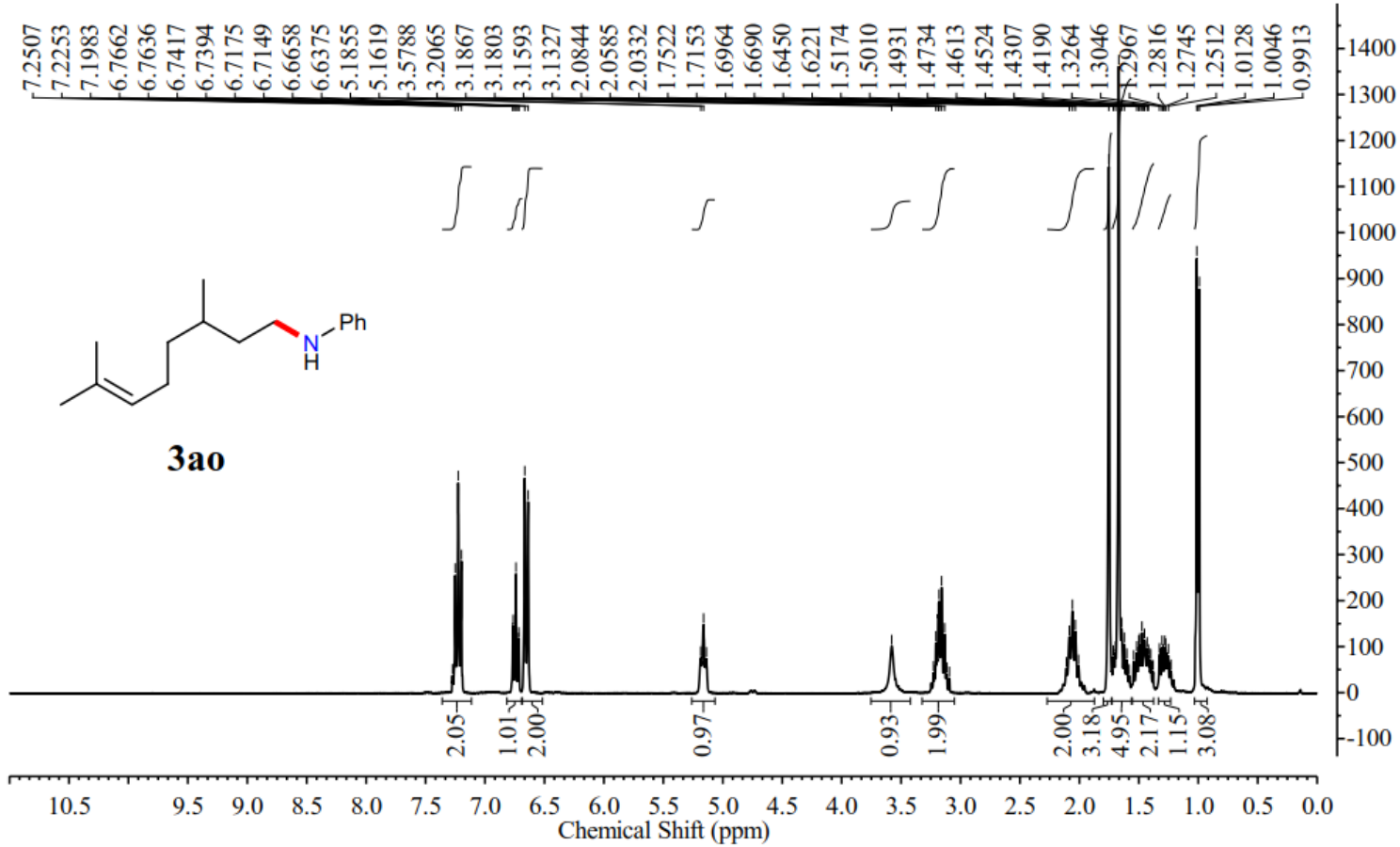
Chemical Shift (ppm)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3.1867
3.1803
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3.1327
2.0844
2.0585
2.0332
1.7522
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1.6964
1.6690
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1.6221
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1.2967
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1.0046
0.9913
Ph
N
H
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2.05
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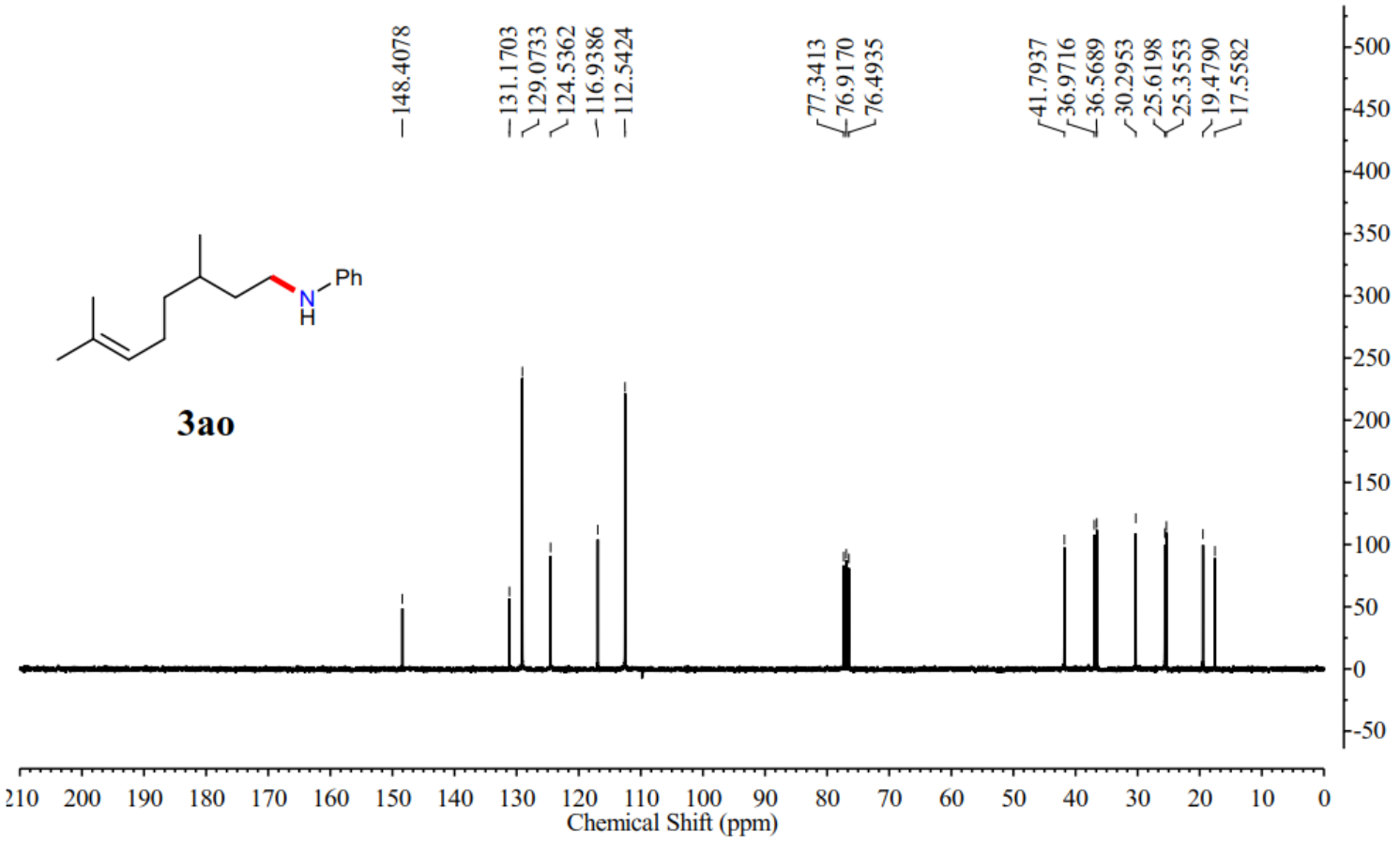
3.08
Chemical Shift (ppm)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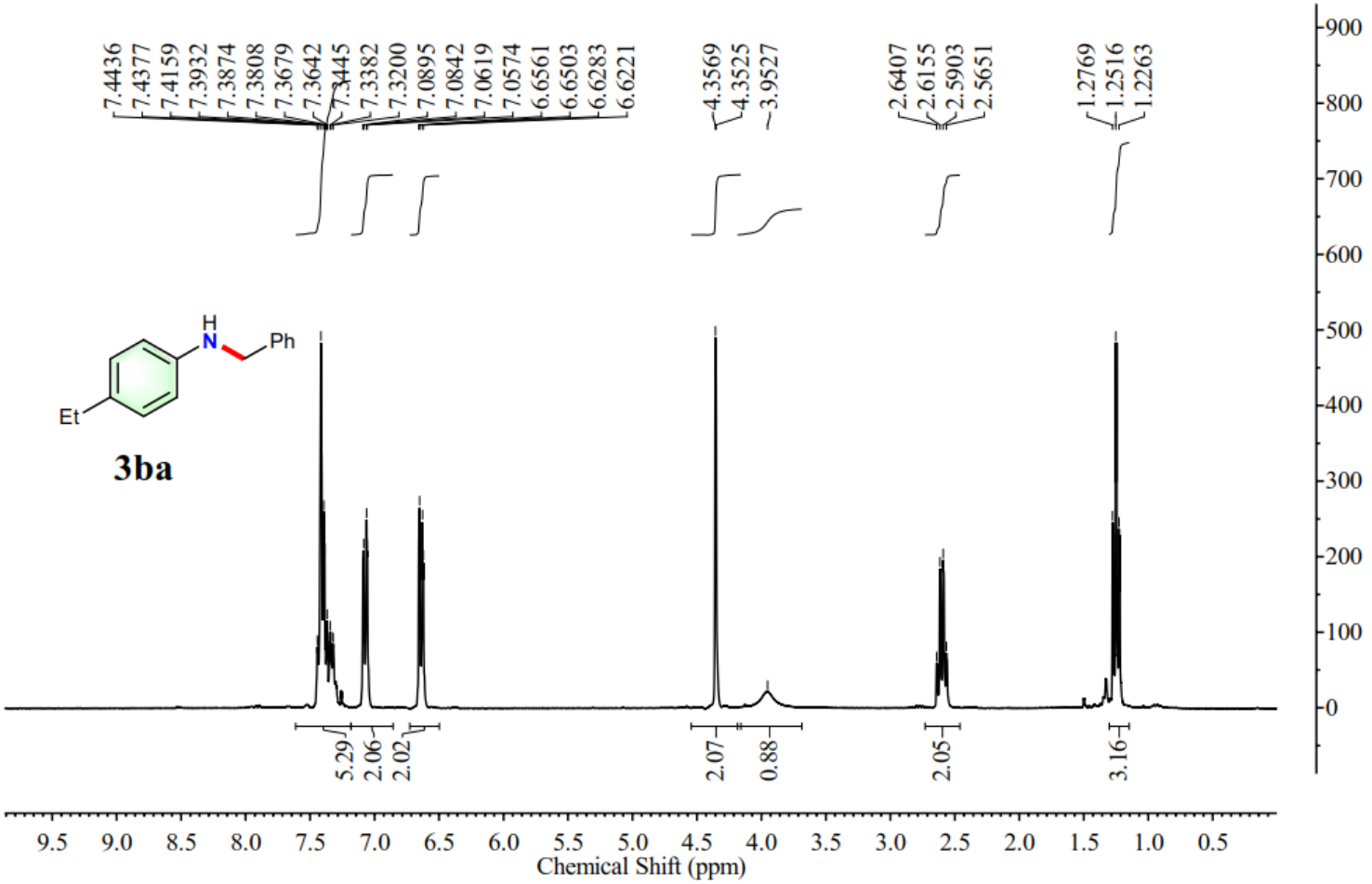
Ph
N
H
3ao
Chemical Shift (ppm)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7.0895
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6.6221
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1.2516
1.2263
H
N
Ph
Et
3ba
5.29
2.06
2.02
2.07
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2.05
3.16
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800
700
600
500
400
300
200
100
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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1.5
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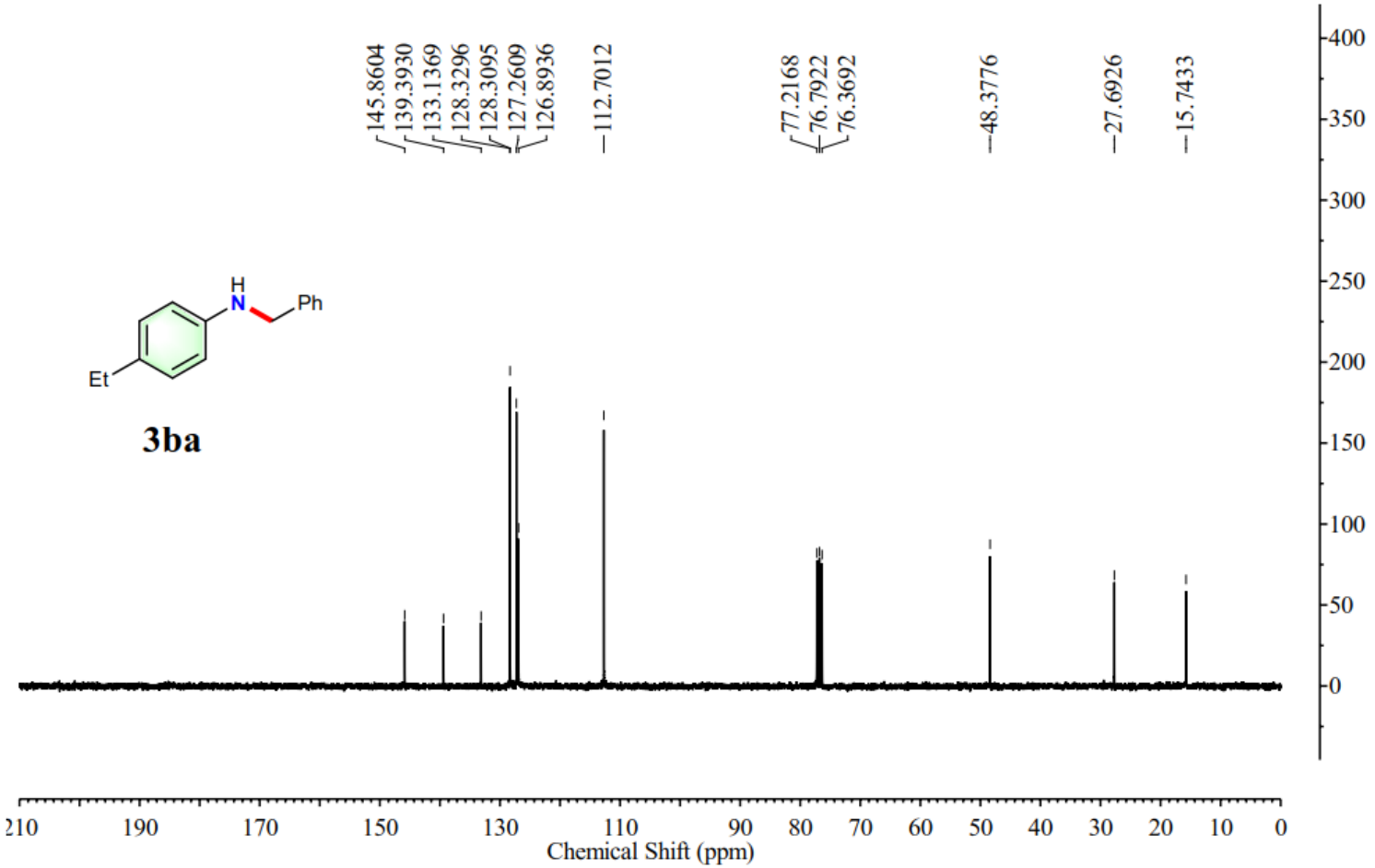
Chemical Shift (ppm)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48.3776
27.6926
15.7433
H
N
Ph
Et
3ba
400
350
300
250
200
150
100
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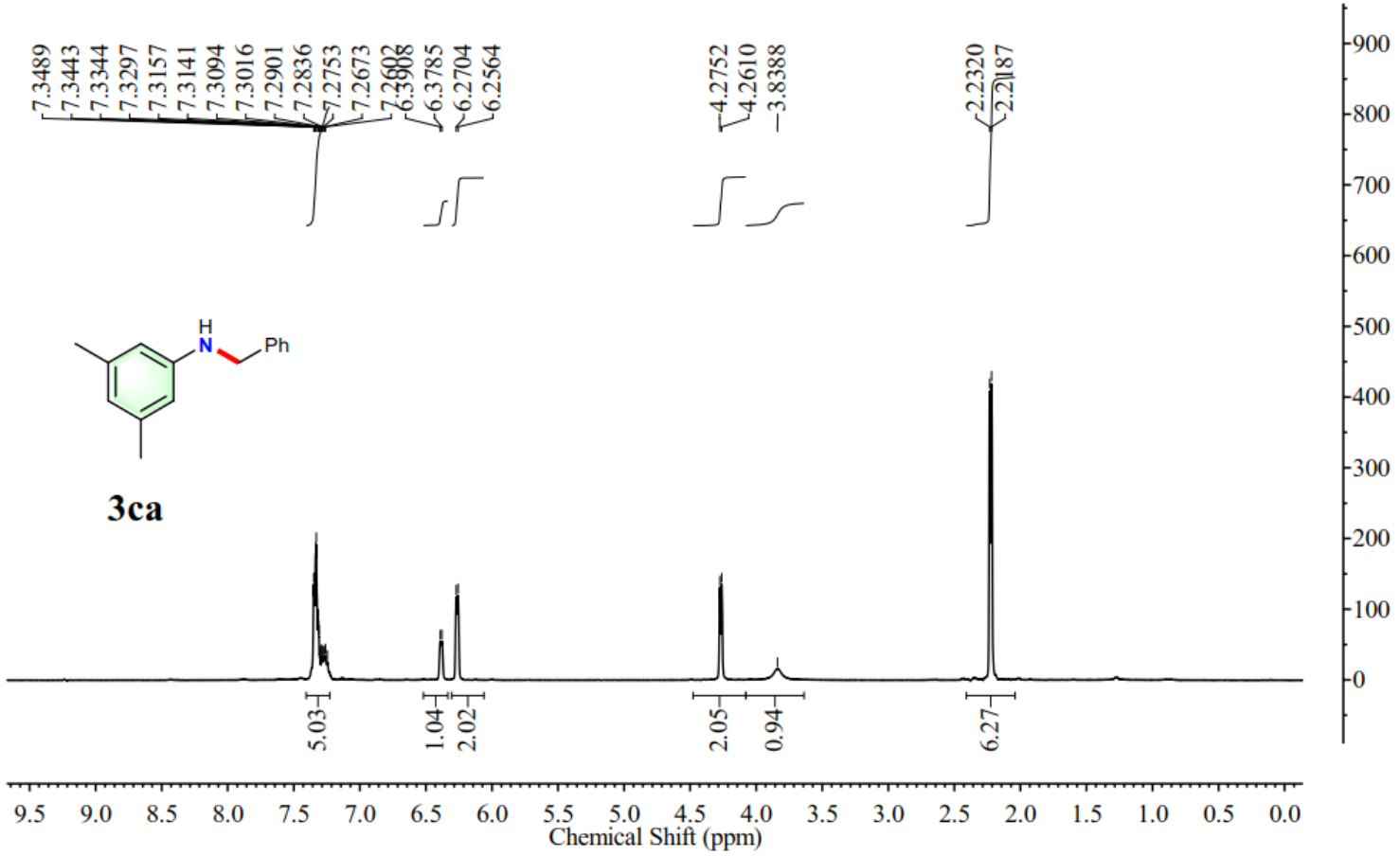
Chemical Shift (ppm)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7.2602
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6.3785
6.2704
6.2564
4.2752
4.2610
3.8388
2.2320
2.2187
H
N
Ph
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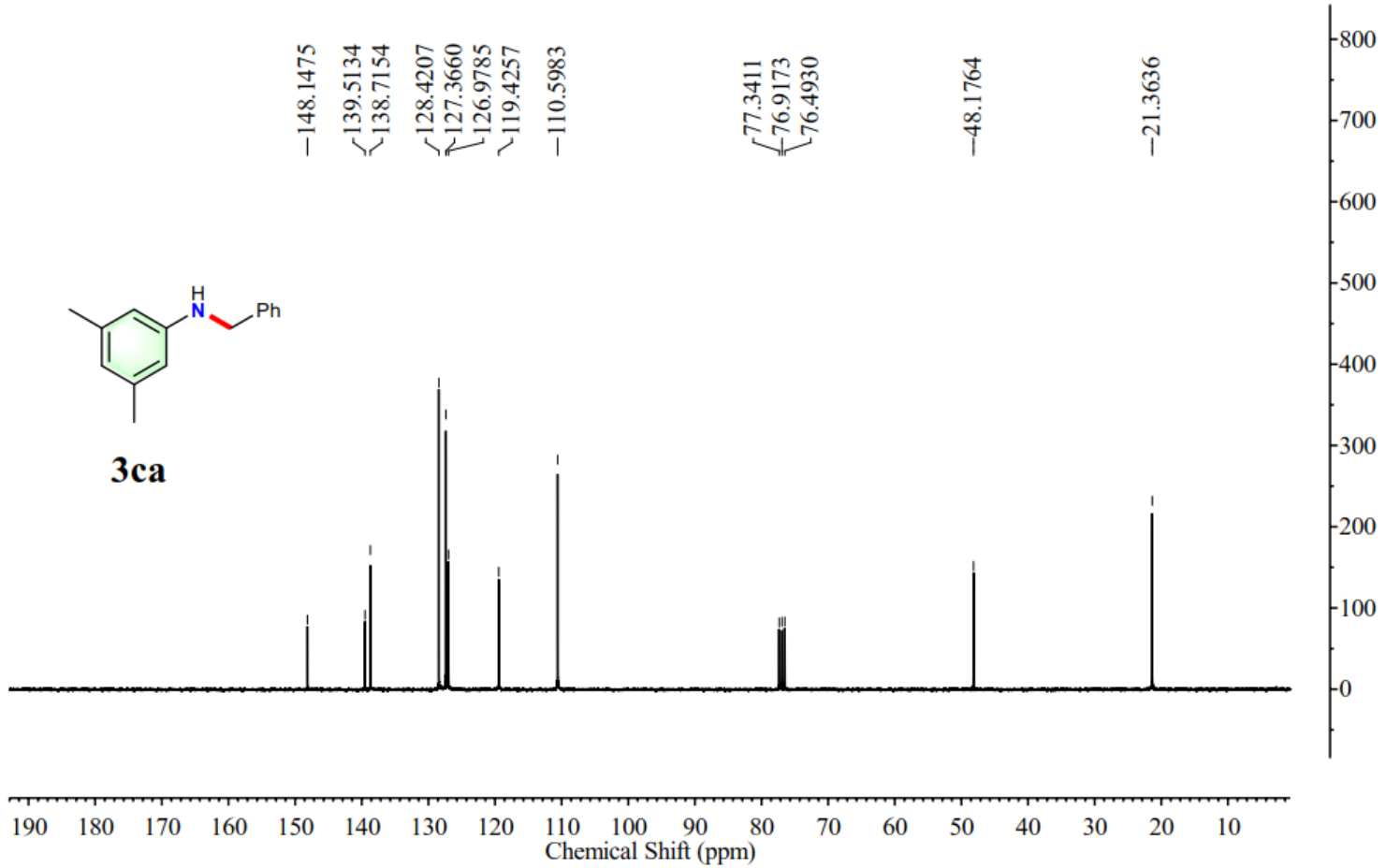
1.04
2.02
2.05
0.94
6.27
900
800
700
600
500
400
300
200
100
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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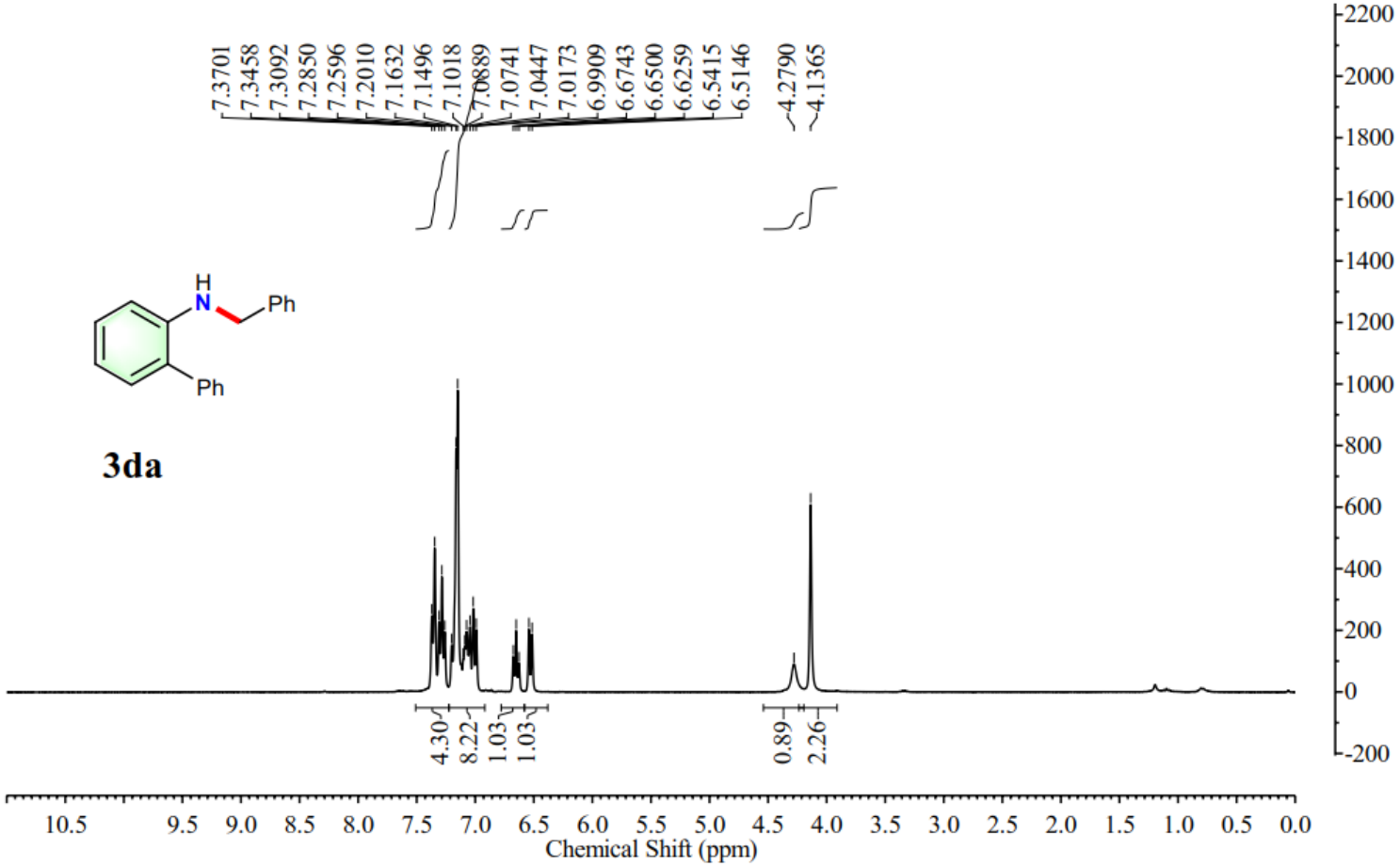
21.3636
H
N
Ph
3ca
800
700
600
500
400
300
200
100
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)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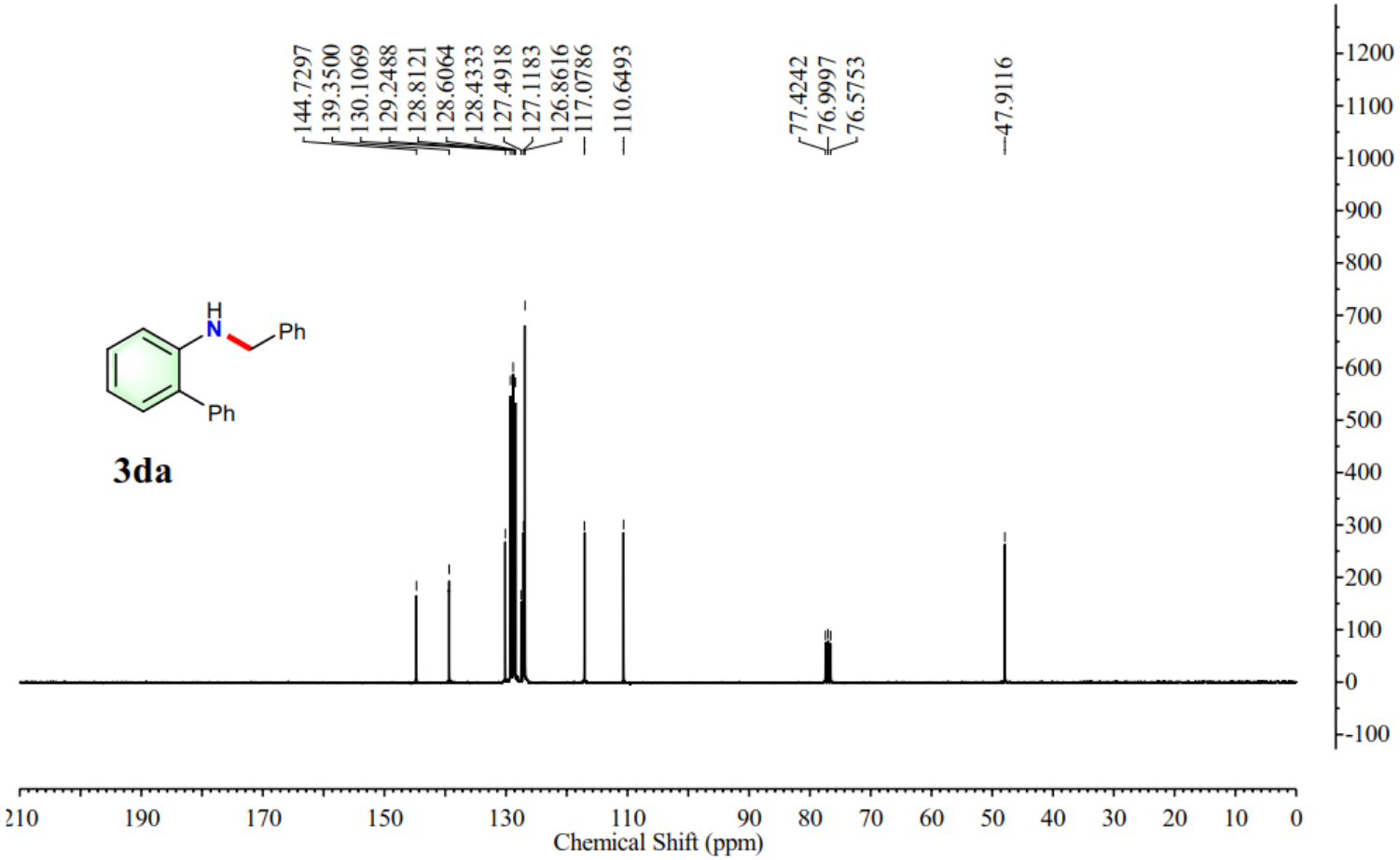
7.3458
7.3092
7.2850
7.2596
7.2010
7.1632
7.1496
7.1018
7.0889
7.0741
7.0447
7.0173
6.9909
6.6743
6.6500
6.6259
6.5415
6.5146
4.2790
4.1365
H
N
Ph
Ph
3da
4.30
8.22
1.03
1.03
0.89
2.26
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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128.6064
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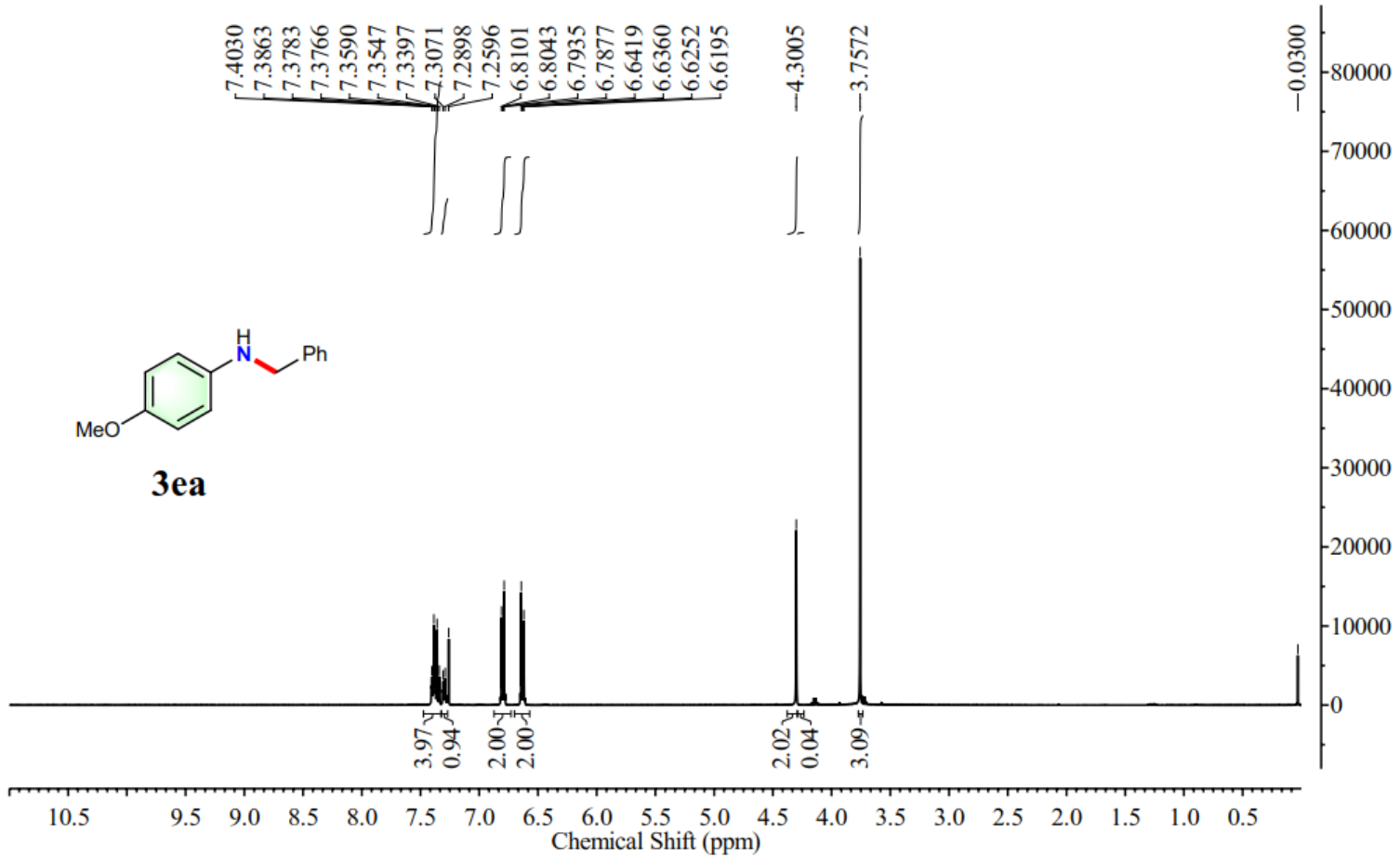
127.1183
126.8616
117.0786
110.6493
77.4242
76.9997
76.5753
47.9116
H
N
Ph
Ph
3da
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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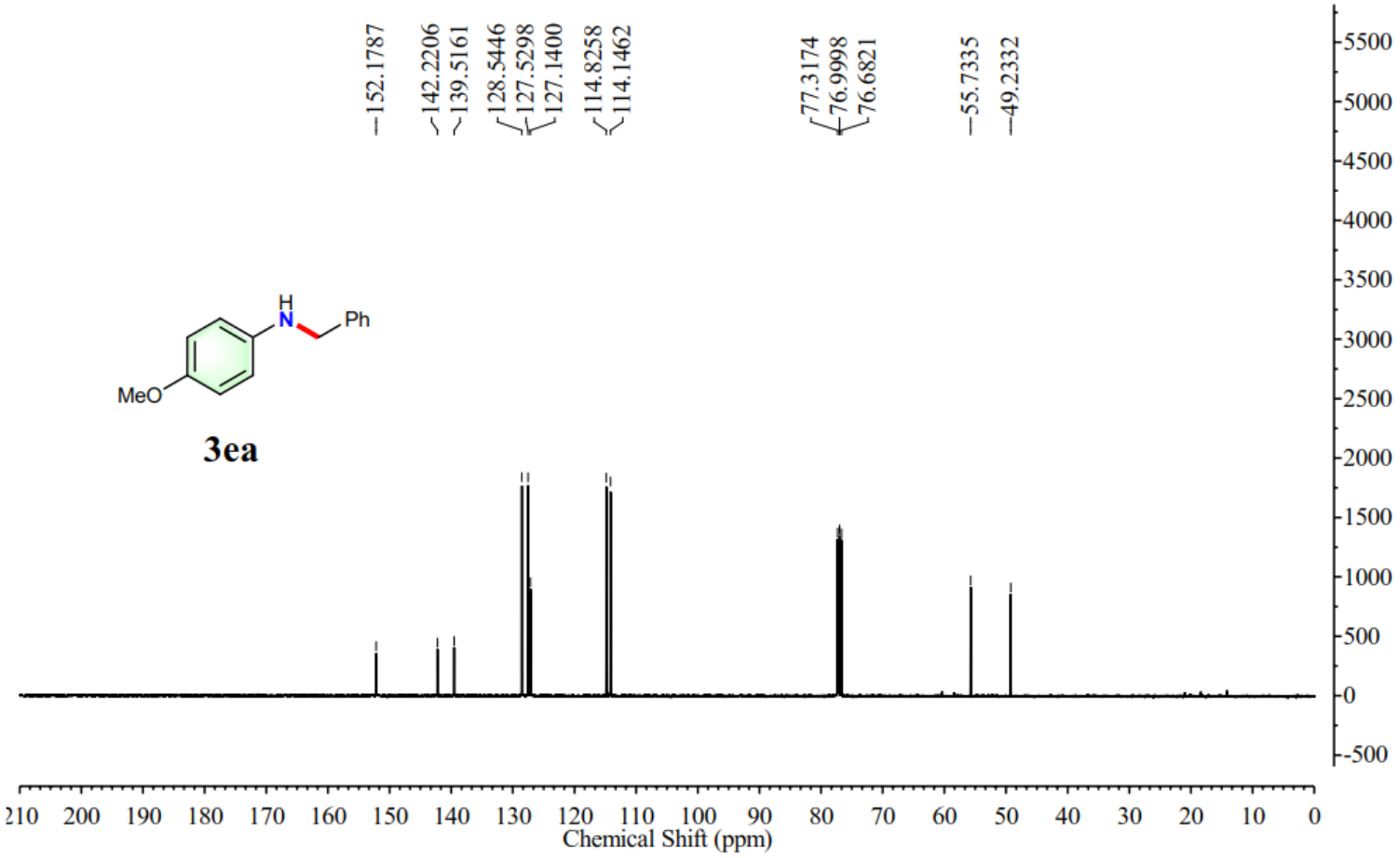
7.3863
7.3783
7.3766
7.3590
7.3547
7.3397
7.3071
7.2898
7.2596
6.8101
6.8043
6.7935
6.7877
6.6419
6.6360
6.6252
6.6195
4.3005
3.7572
0.0300
H
N
Ph
MeO
3ea
3.97
0.94
2.00
2.00
2.02
0.04
3.09
Chemical Shift (ppm)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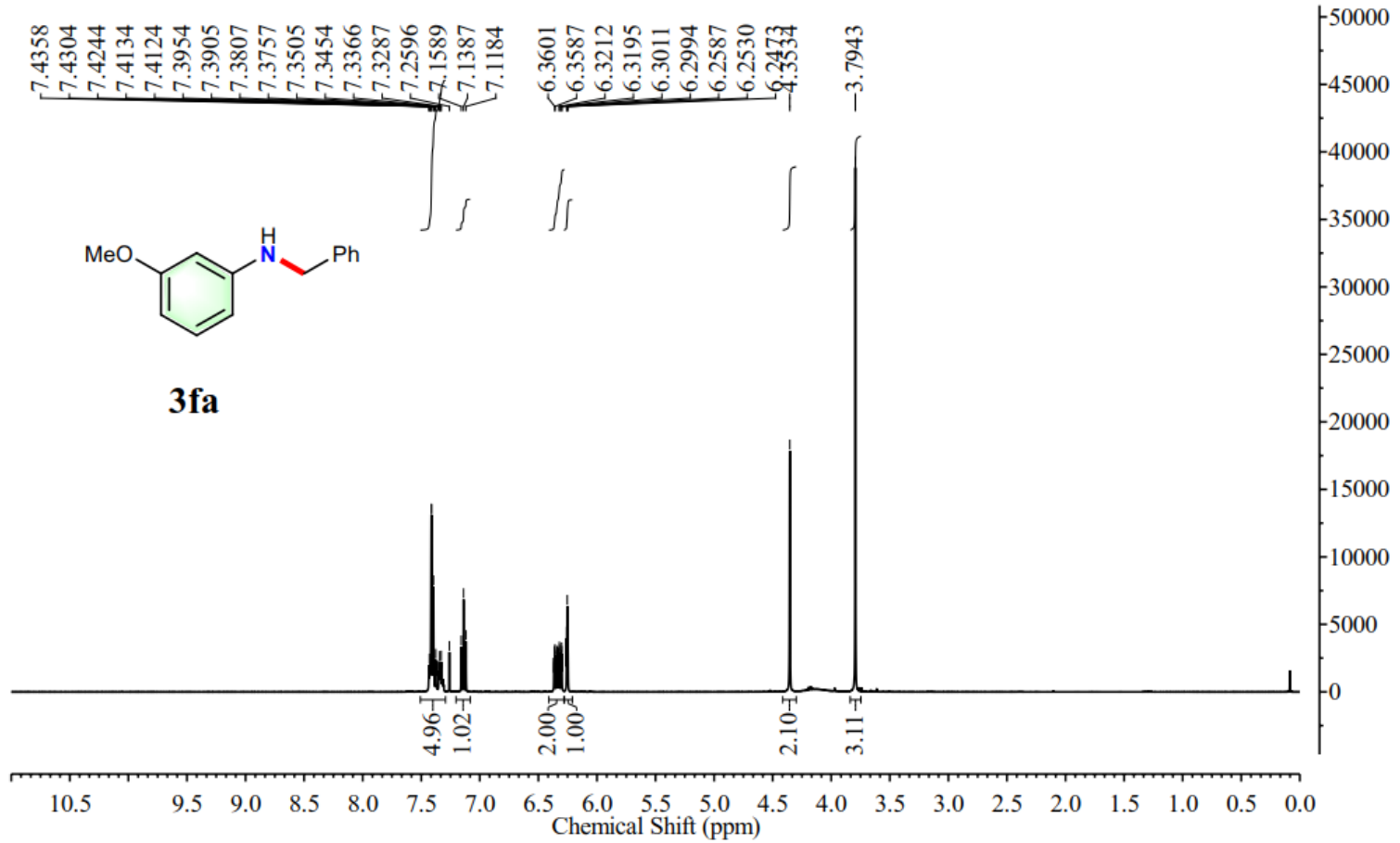
142.2206
139.5161
128.5446
127.5298
127.1400
114.8258
114.1462
77.3174
76.9998
76.6821
55.7335
49.2332
MeO
H
N
Ph
3ea
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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7.4244
7.4134
7.4124
7.3954
7.3905
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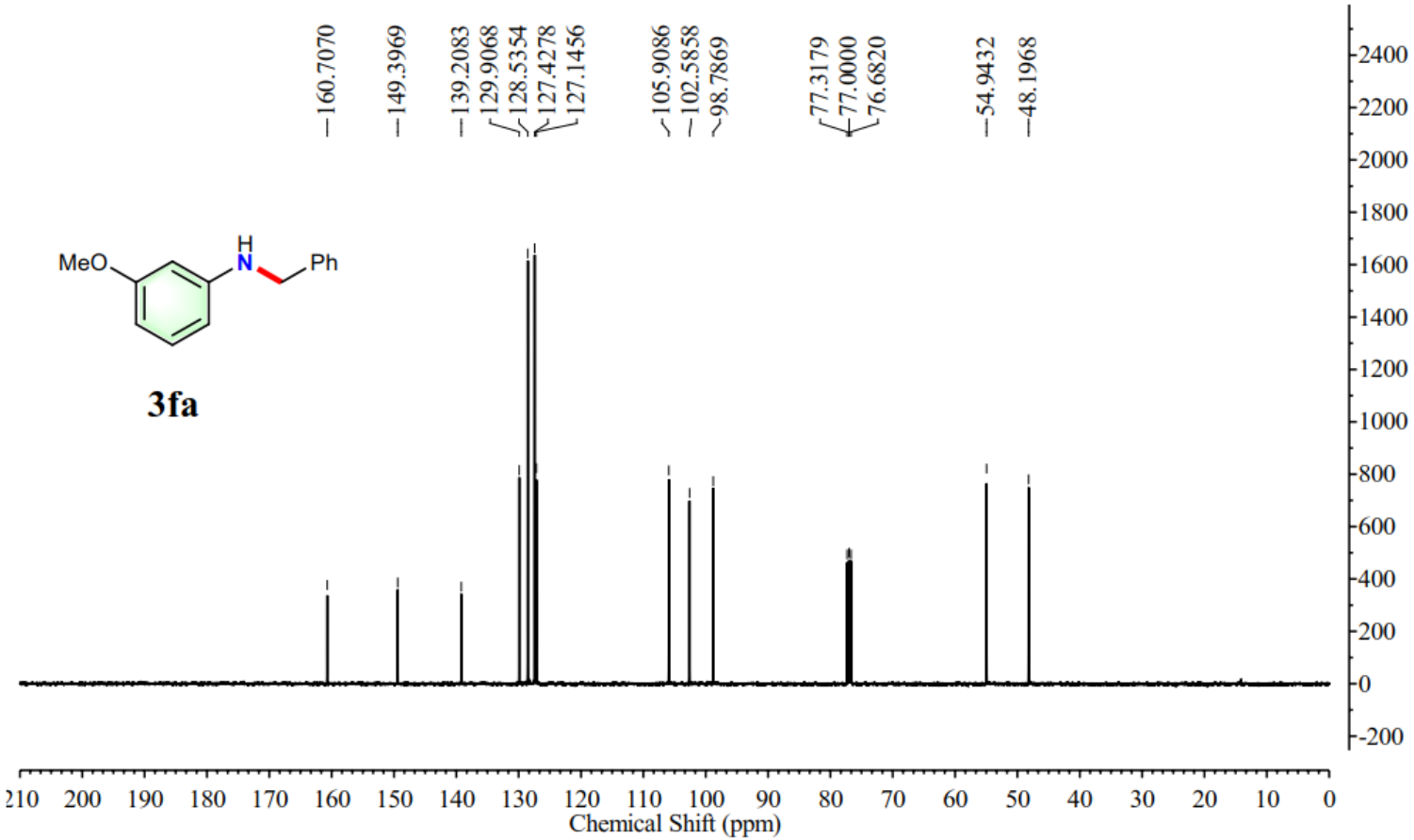
7.3757
7.3505
7.3454
7.3366
7.3287
7.2596
7.1589
7.1387
7.1184
6.3601
6.3587
6.3212
6.3195
6.3011
6.2994
6.2587
6.2530
6.2473
4.3534
3.7943
MeO
H
N
Ph
3fa
4.96
1.02
2.00
1.00
2.10
3.11
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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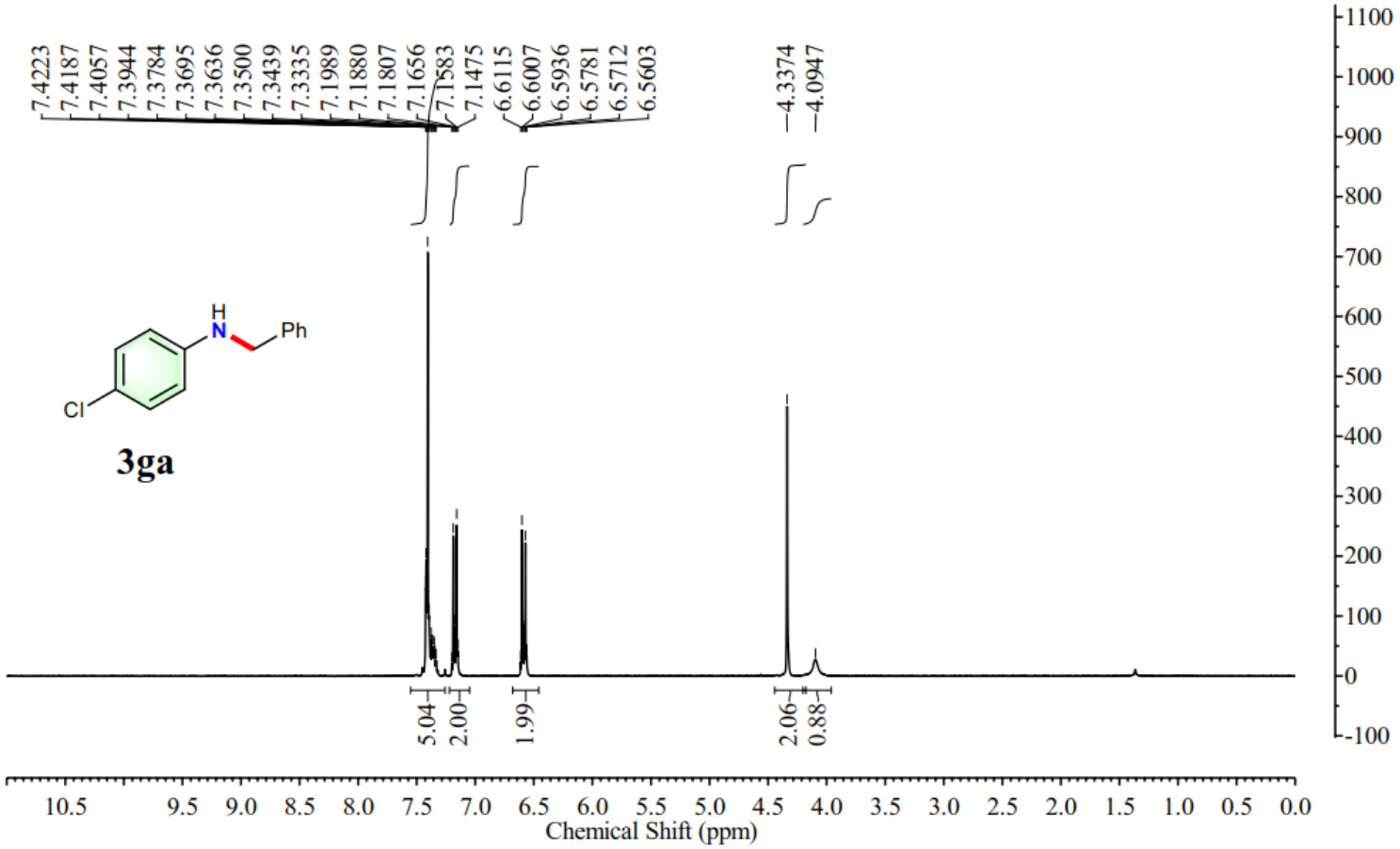
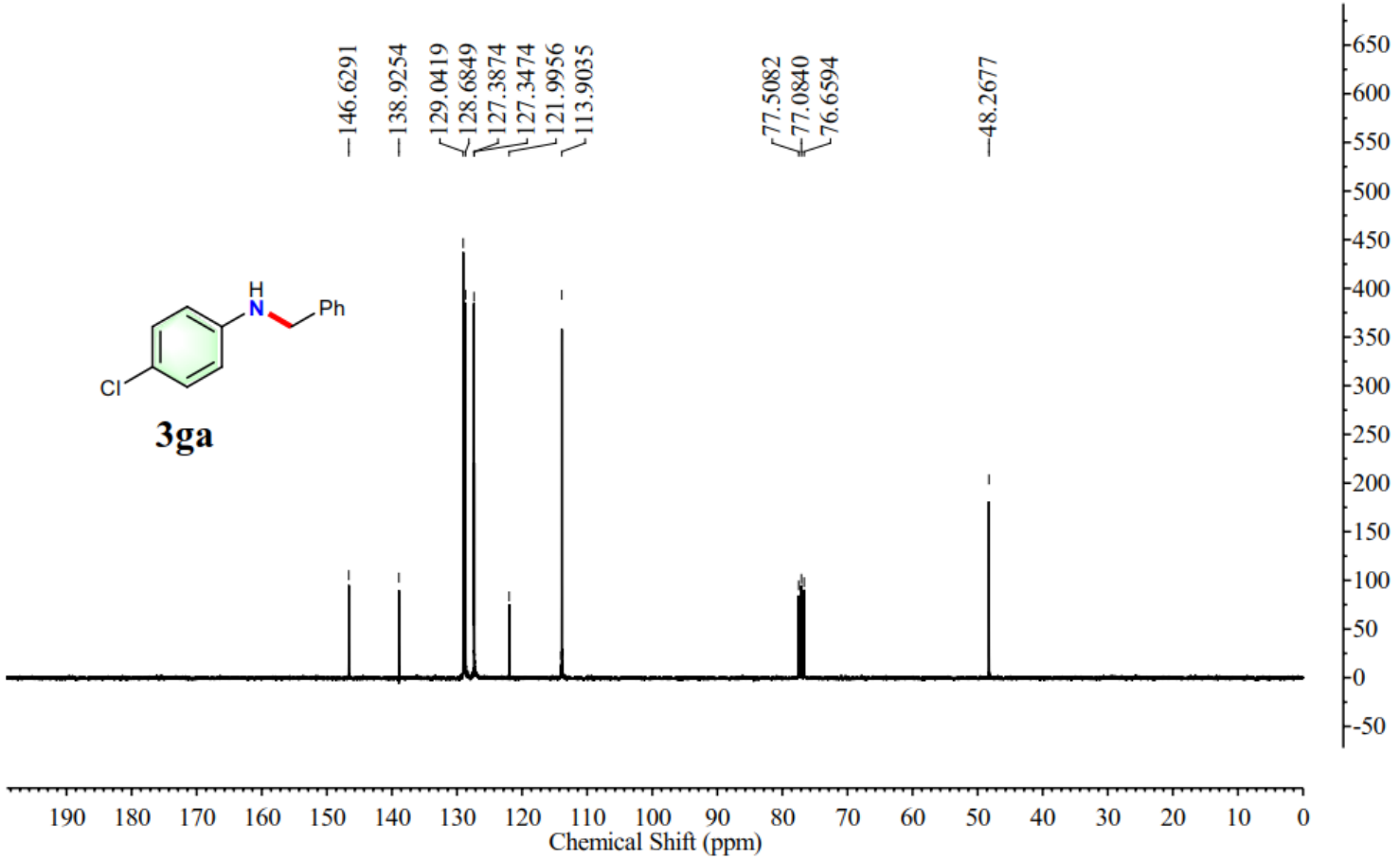
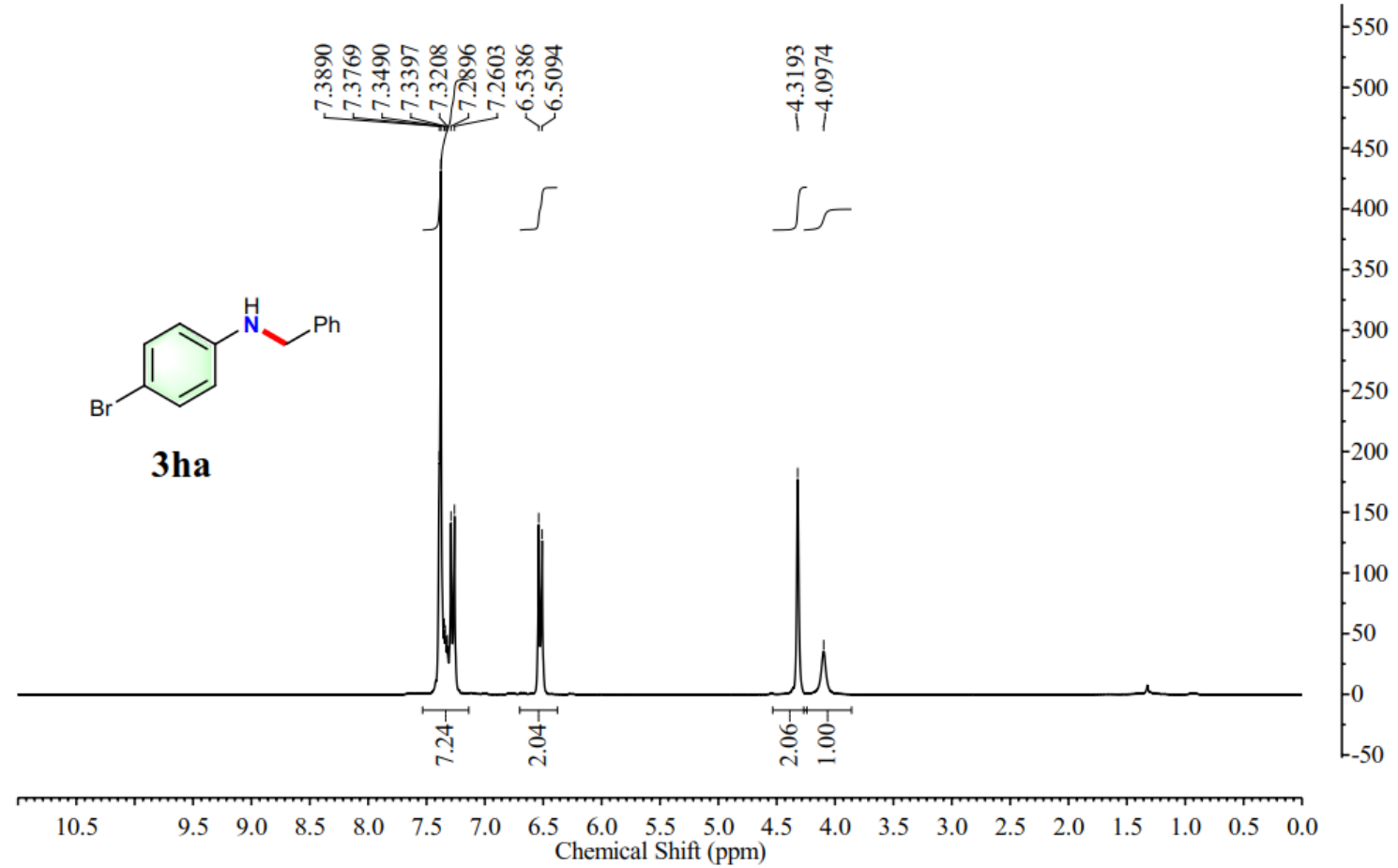
149.3969
139.2083
129.9068
128.5354
127.4278
127.1456
105.9086
102.5858
98.7869
77.3179
77.0000
76.6820
54.9432
48.1968
MeO
H
N
Ph
3fa
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


7.4223
7.4187
7.4057
7.3944
7.3784
7.3695
7.3636
7.3500
7.3439
7.3335
7.1989
7.1880
7.1807
7.1656
7.1583
7.1475
6.6115
6.6007
6.5936
6.5781
6.5712
6.5603
4.3374
4.0947
H
N
Ph
Cl
3ga
5.04
2.00
1.99
2.06
0.88
Chemical Shift (ppm)


146.6291
138.9254
129.0419
128.6849
127.3874
127.3474
121.9956
113.9035
77.5082
77.0840
76.6594
48.2677
H
N
Ph
Cl
3ga
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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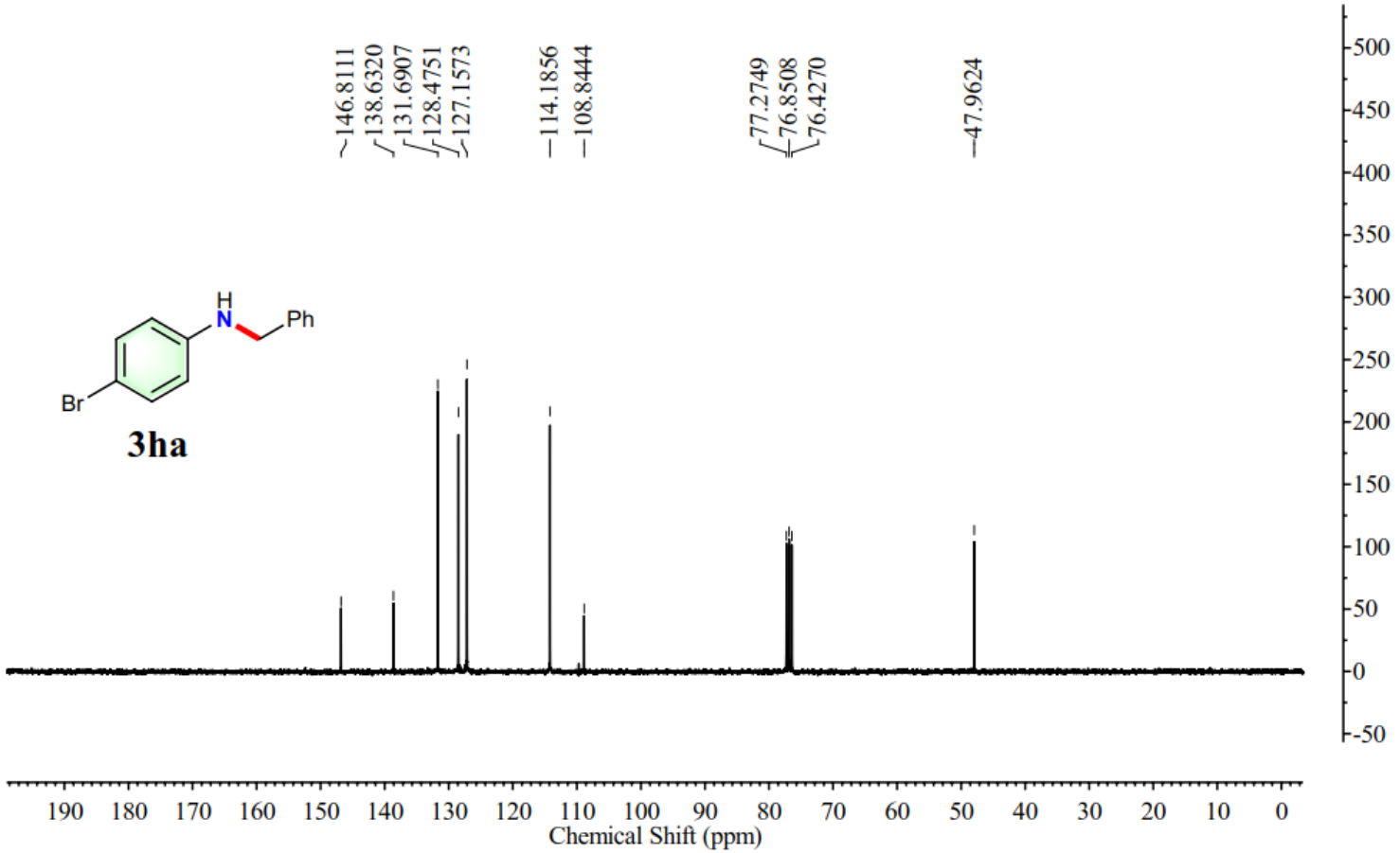
7.3769
7.3490
7.3397
7.3208
7.2896
7.2603
6.5386
6.5094
4.3193
4.0974
H
N
Ph
Br
3ha
7.24
2.04
2.06
1.00
Chemical Shift (ppm)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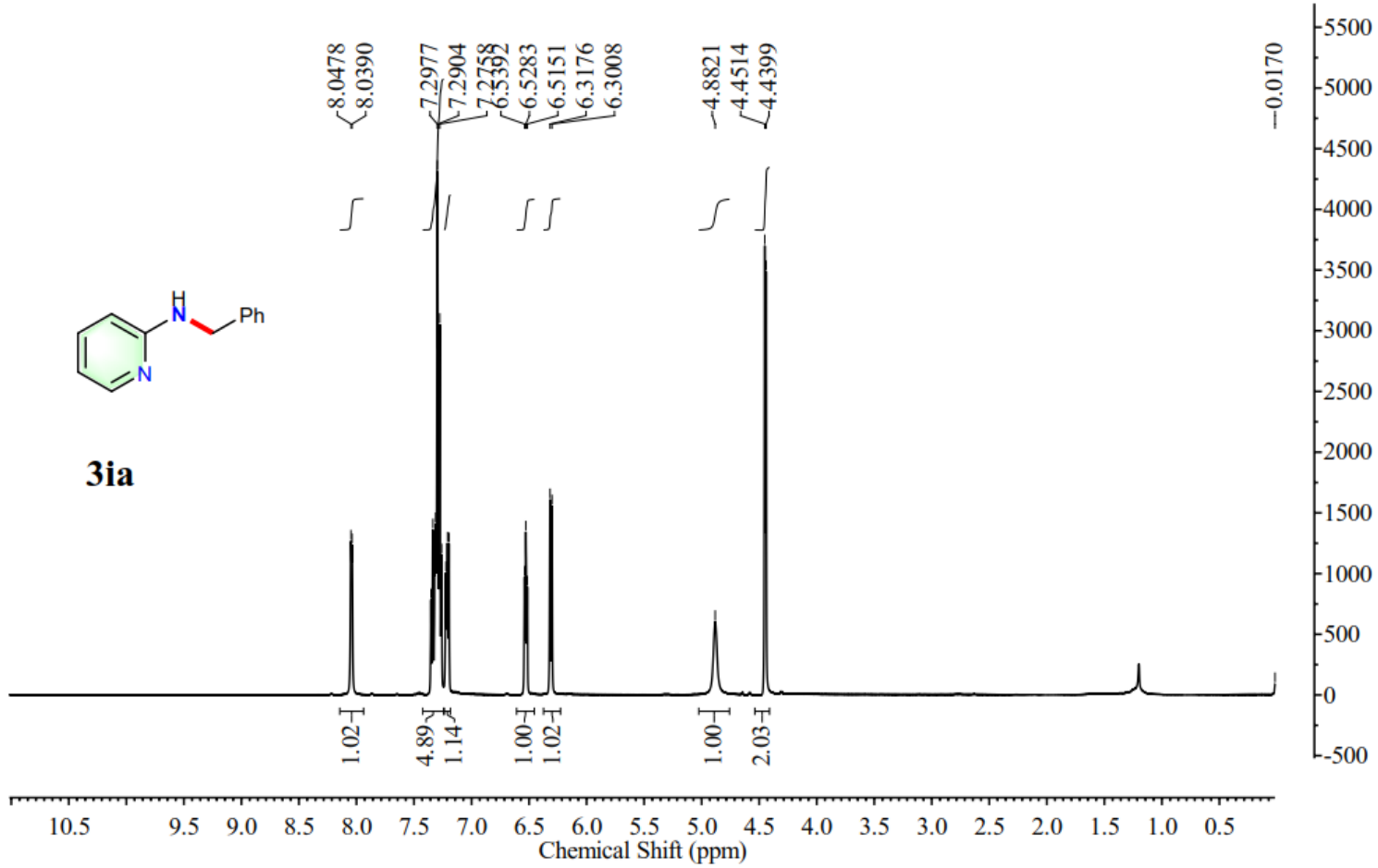
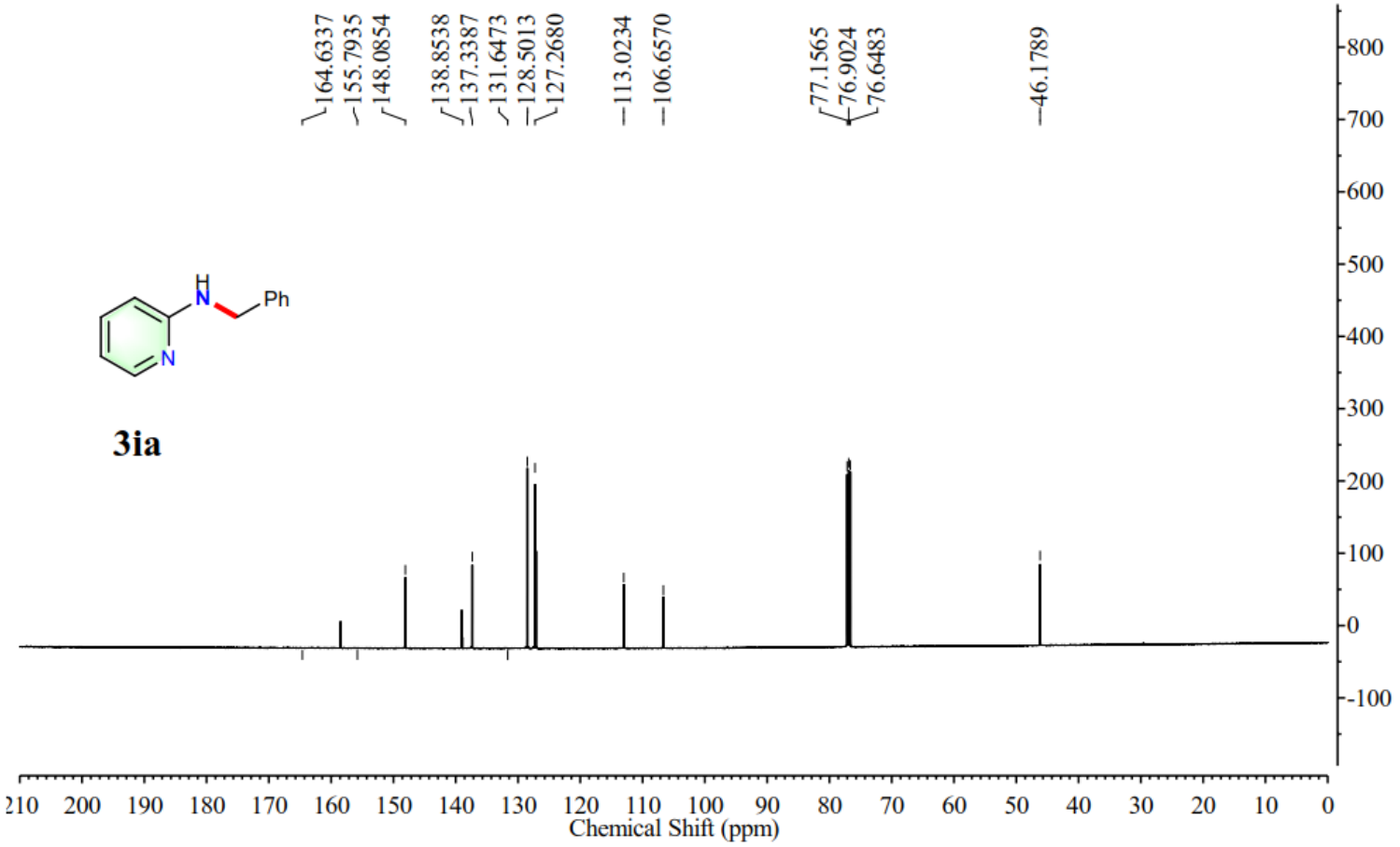
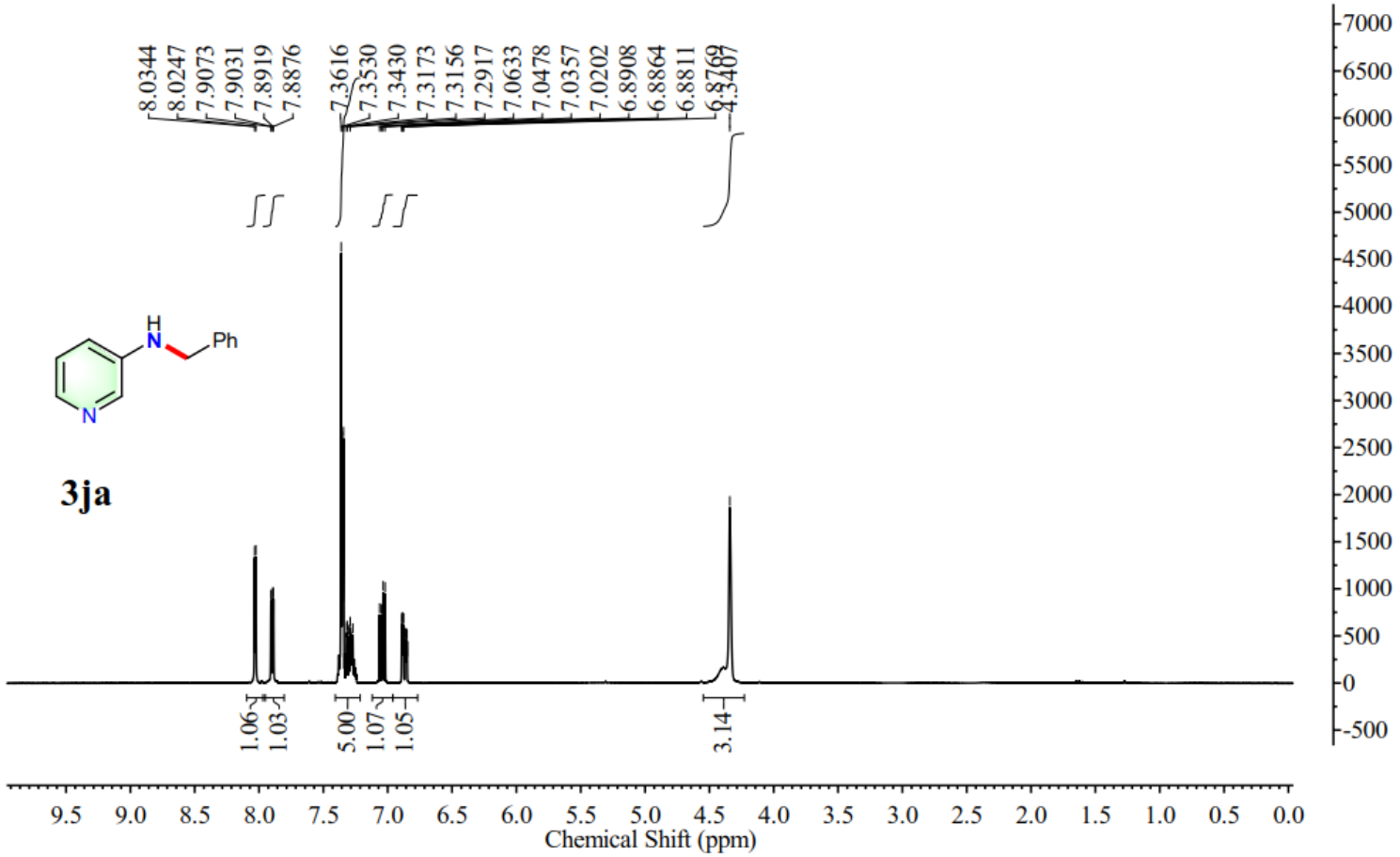
138.6320
131.6907
128.4751
127.1573
114.1856
108.8444
77.2749
76.8508
76.4270
47.9624
H
N
Ph
Br
3ha
500
450
400
350
300
250
200
150
100
50
0
-50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


8.0478
8.0390
7.2977
7.2904
7.2758
6.5392
6.5283
6.5151
6.3176
6.3008
4.8821
4.4514
4.4399
0.0170
H
N
Ph
N
3ia
1.02
4.89
1.14
1.00
1.02
1.00
2.03
Chemical Shift (ppm)


164.6337
155.7935
148.0854
138.8538
137.3387
131.6473
128.5013
127.2680
113.0234
106.6570
77.1565
76.9024
76.6483
46.1789
H
N
Ph
N
3ia
800
700
600
500
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


8.0344
8.0247
7.9073
7.9031
7.8919
7.8876
7.3616
7.3530
7.3430
7.3173
7.3156
7.2917
7.0633
7.0478
7.0357
7.0202
6.8908
6.8864
6.8811
6.8769
6.8707
4.3407
H
N
Ph
N
3ja
1.06
1.03
5.00
1.07
1.05
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)
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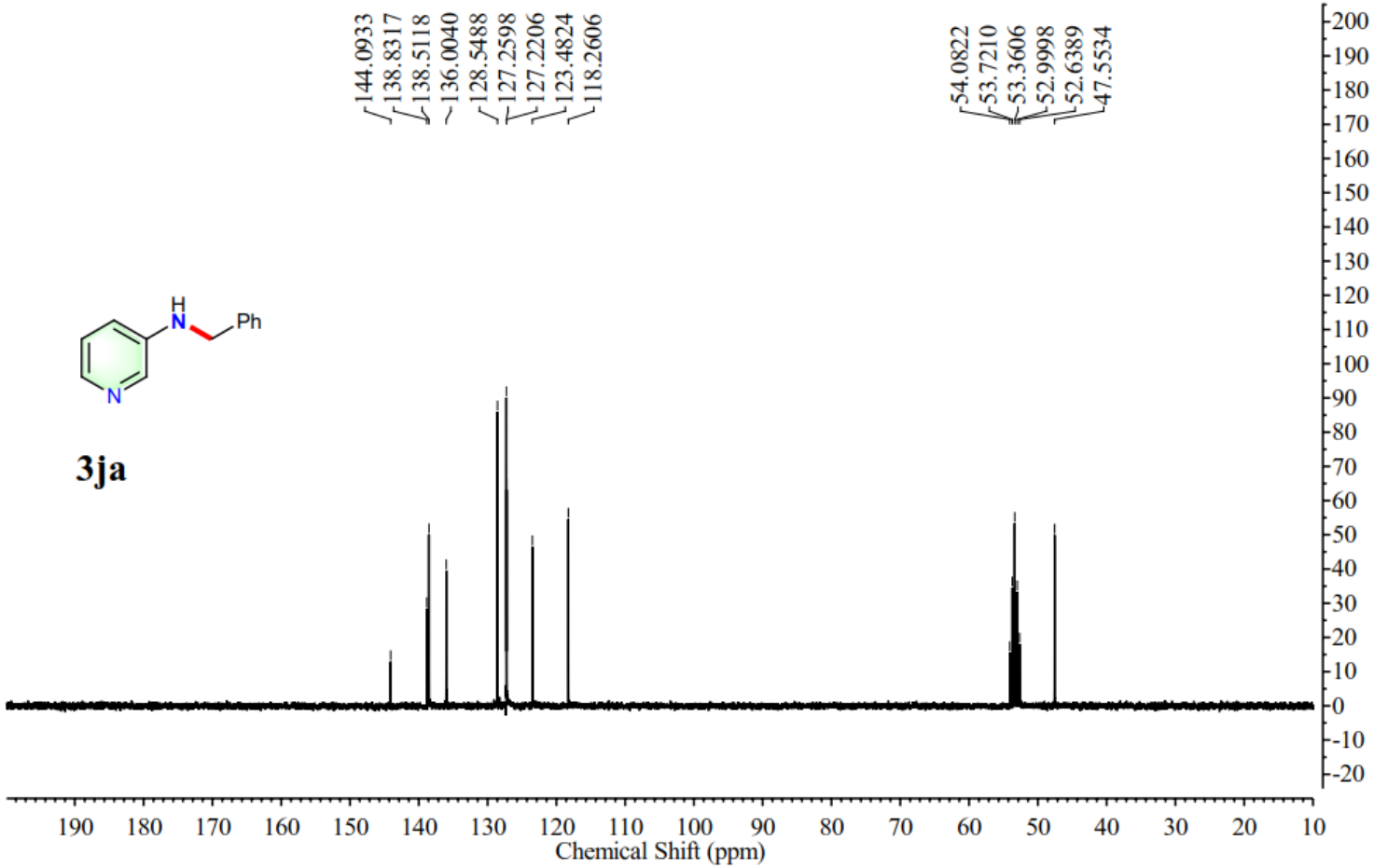
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


144.0933
138.8317
138.5118
136.0040
128.5488
127.2598
127.2206
123.4824
118.2606
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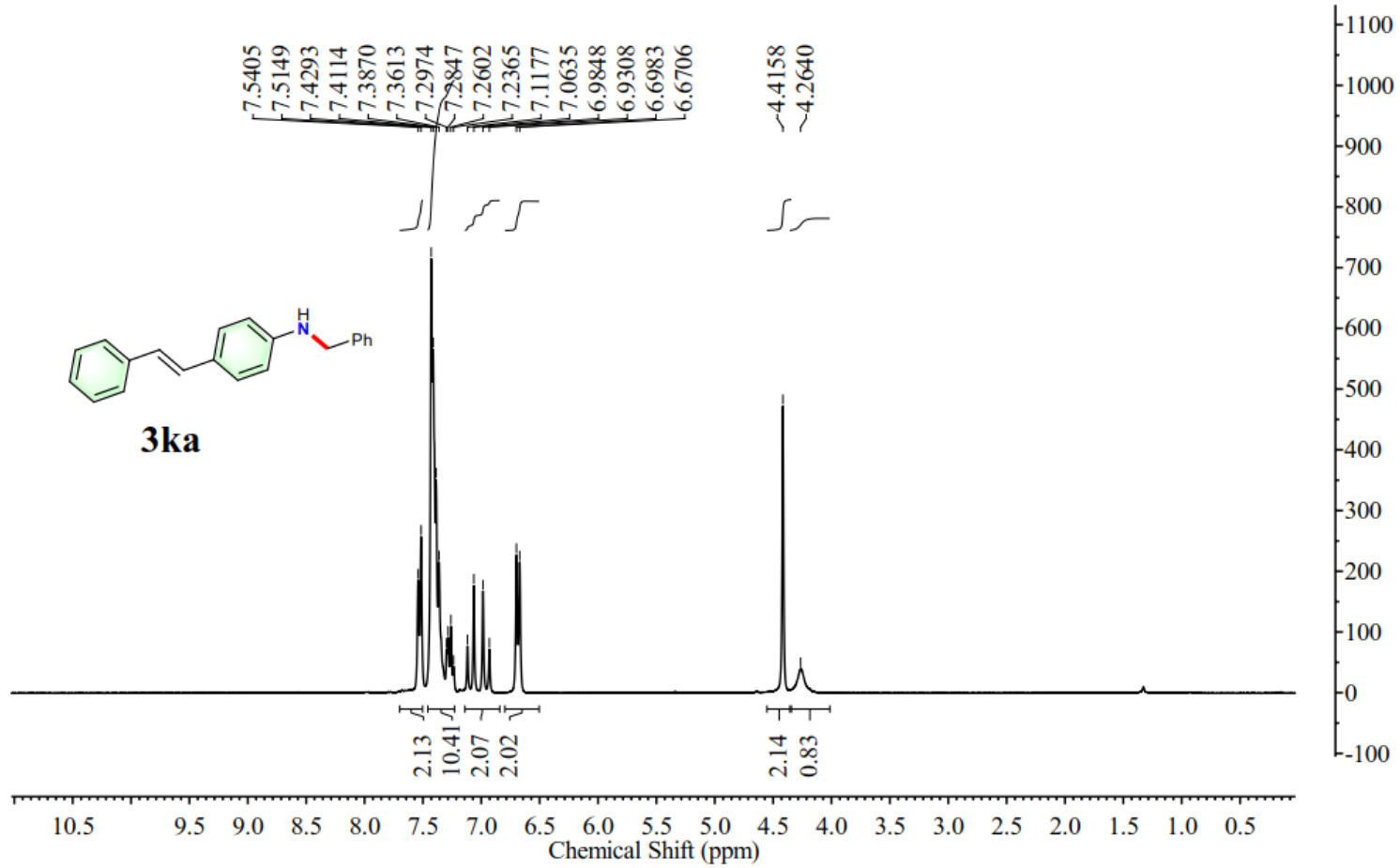
53.7210
53.3606
52.9998
52.6389
47.5534
H
N
Ph
N
3ja
Chemical Shift (ppm)


7.5405
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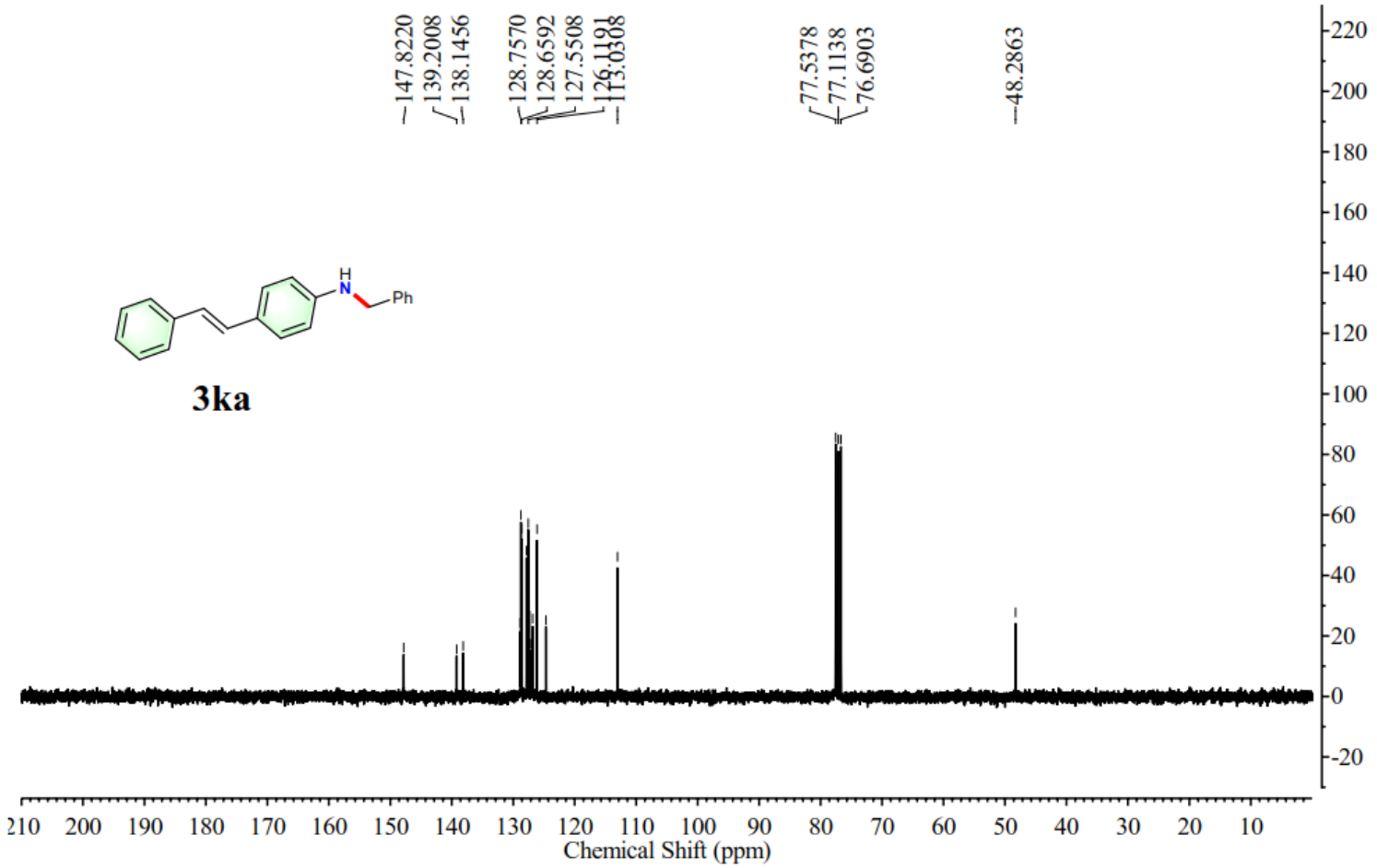
7.4293
7.4114
7.3870
7.3613
7.2974
7.2847
7.2602
7.2365
7.1177
7.0635
6.9848
6.9308
6.6983
6.6706
4.4158
4.2640
Ph
3ka
2.13
10.41
2.07
2.02
2.14
0.83
Chemical Shift (ppm)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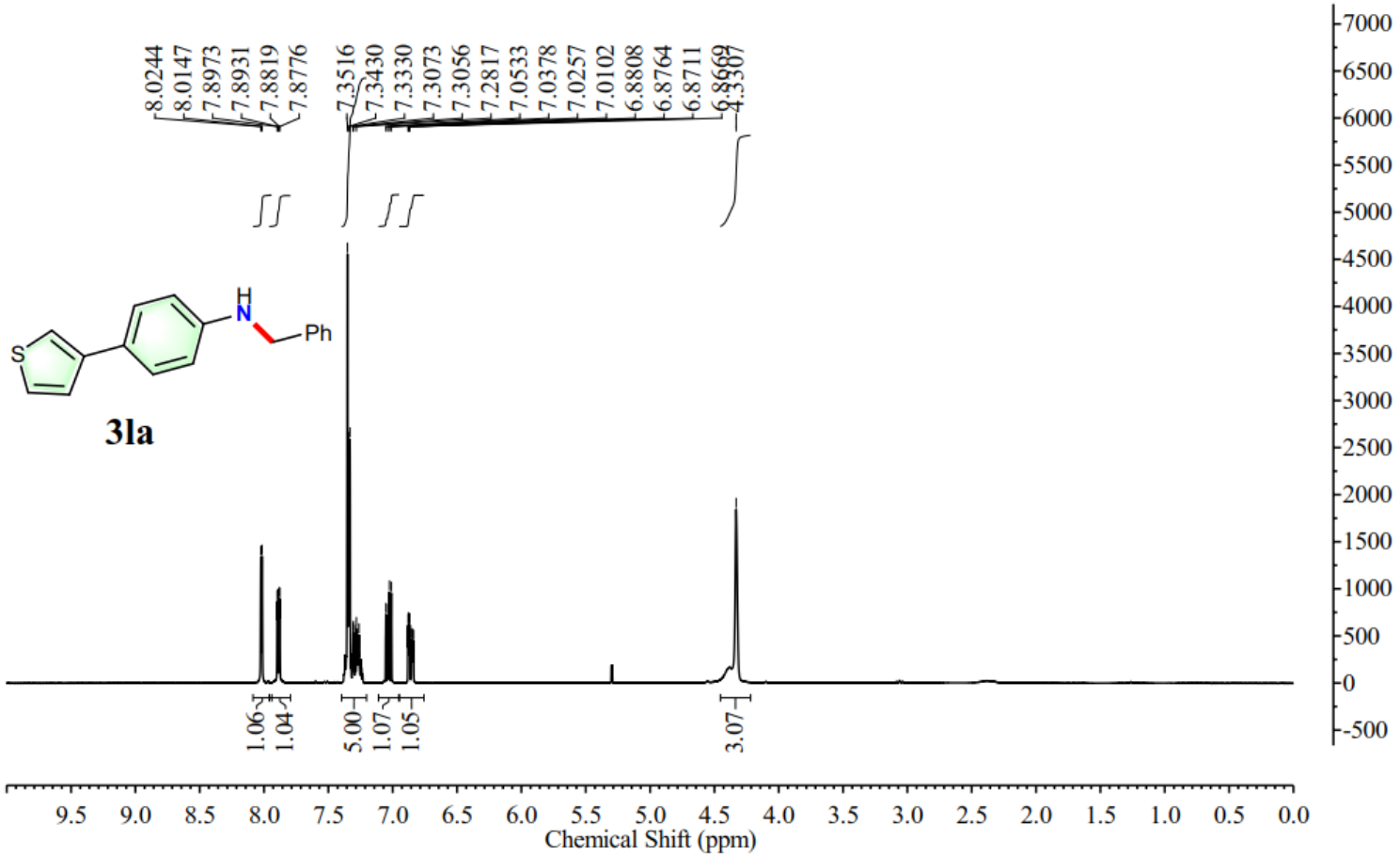
138.1456
128.7570
128.6592
127.5508
126.1191
113.0308
77.5378
77.1138
76.6903
48.2863
H
N
Ph
3ka
220
200
180
160
140
120
100
80
60
40
20
0
-20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)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8.0147
7.8973
7.8931
7.8819
7.8776
7.3516
7.3430
7.3330
7.3073
7.3056
7.2817
7.0533
7.0378
7.0257
7.0102
6.8808
6.8764
6.8711
4.3307
S
N
H
Ph
3la
1.06
1.04
5.00
1.07
1.05
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)
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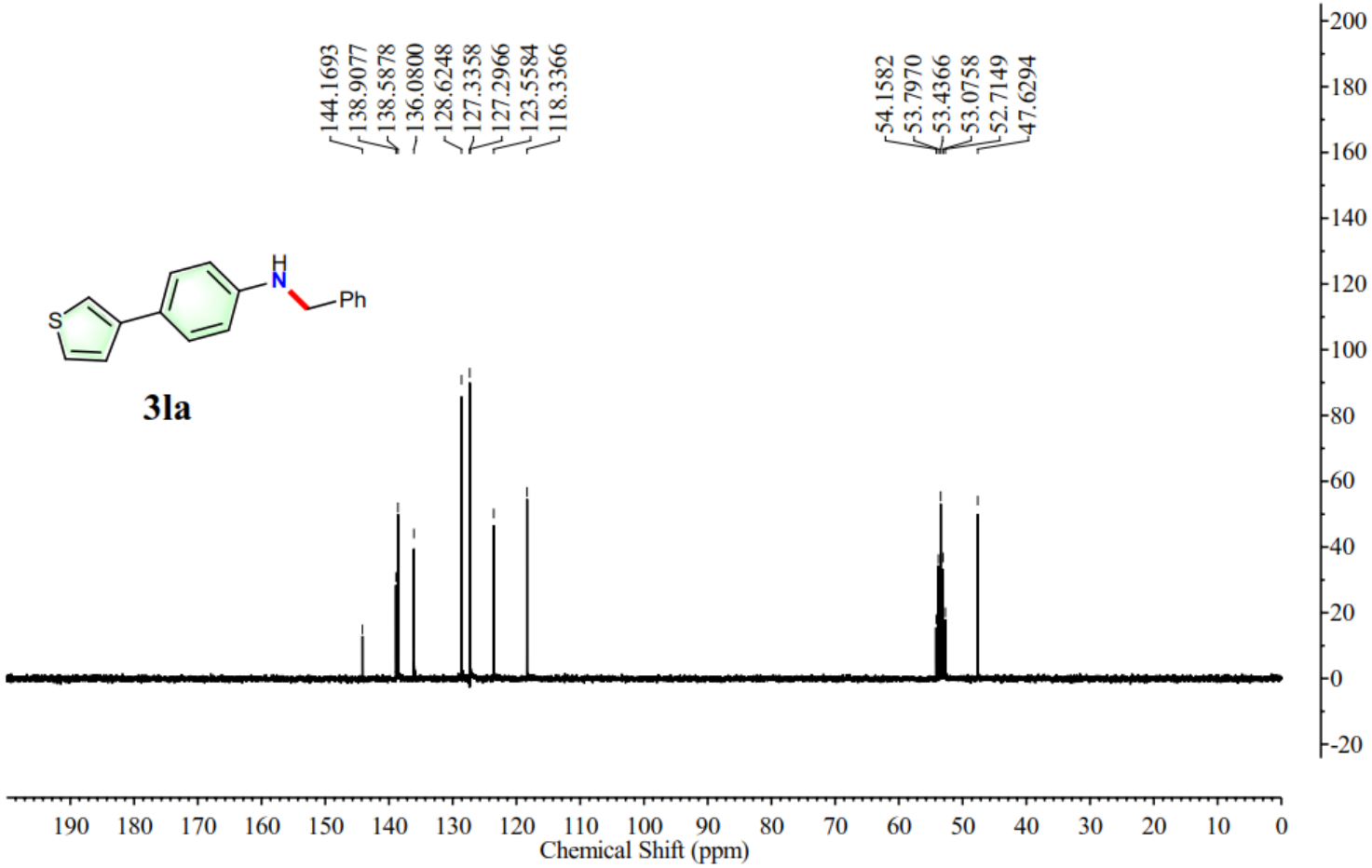
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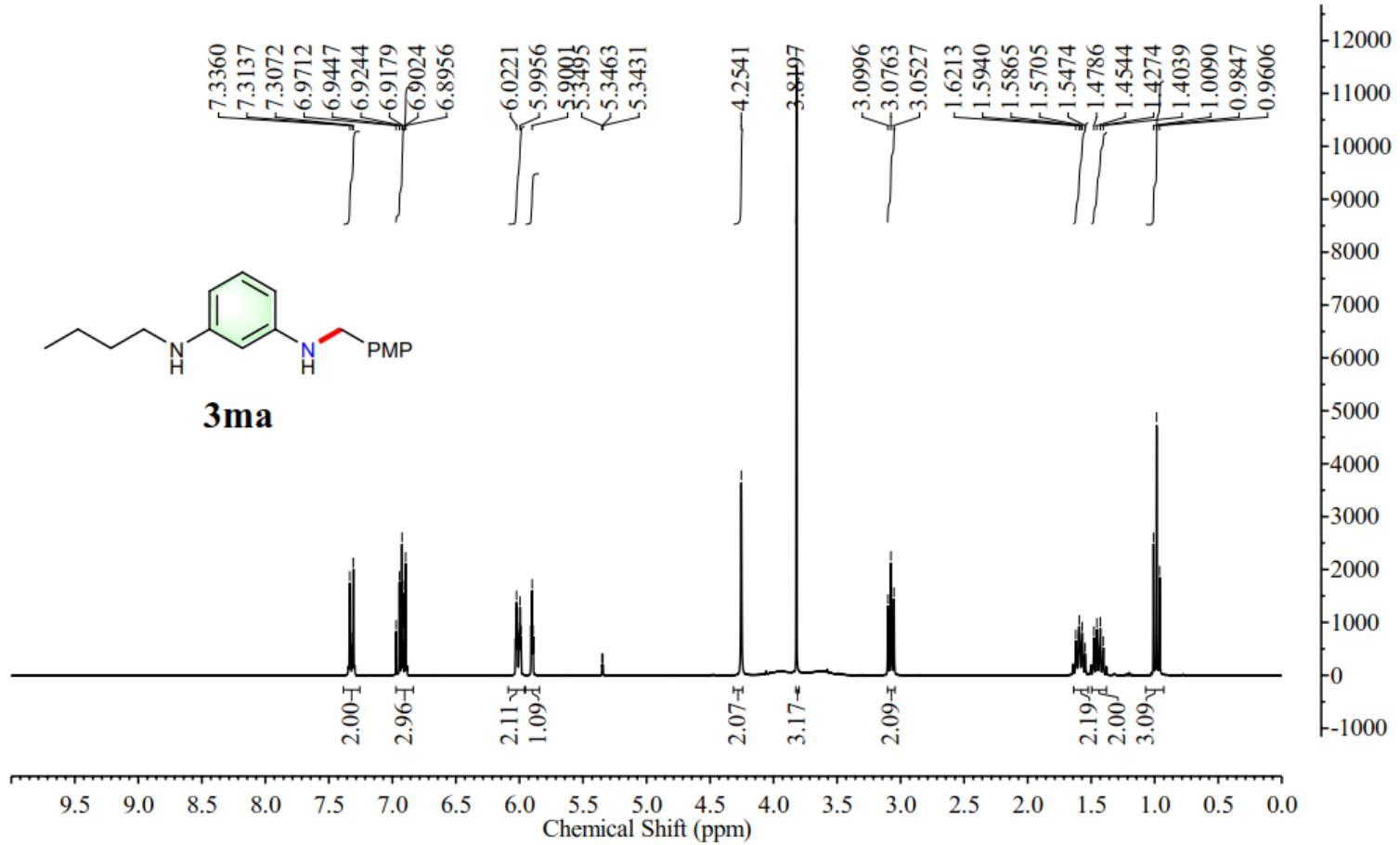
138.5878
136.0800
128.6248
127.3358
127.2966
123.5584
118.3366
54.1582
53.7970
53.4366
53.0758
52.7149
47.6294
H
N
Ph
S
3la
200
180
160
140
120
100
80
60
40
20
0
-20
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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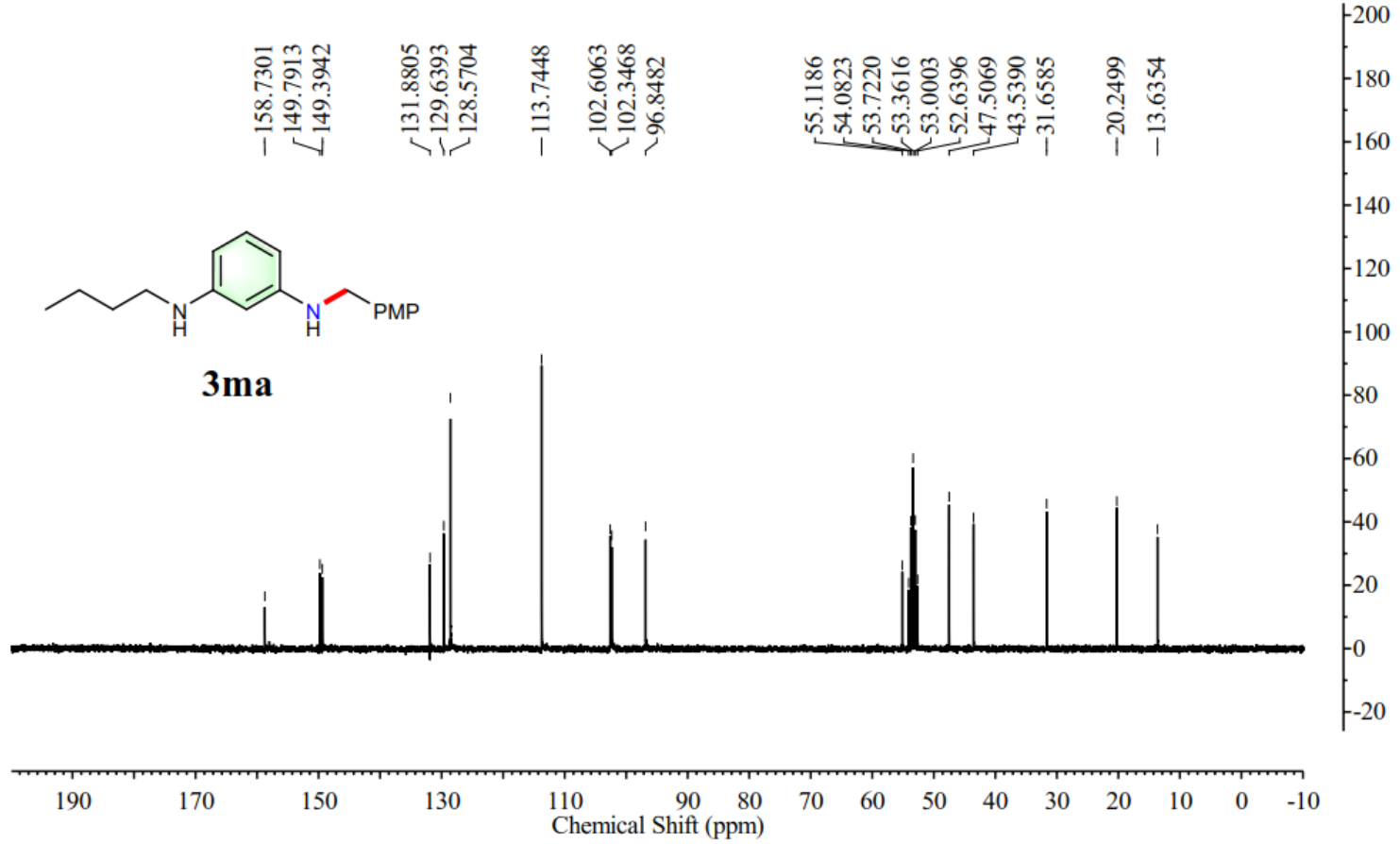
6.0221
5.9956
5.3463
5.3431
4.2541
3.8497
3.0996
3.0763
3.0527
1.6213
1.5940
1.5865
1.5705
1.5474
1.4786
1.4544
1.4274
1.4039
1.0090
0.9847
0.9606
N
H
N
H
PMP
3ma
2.00
2.96
2.11
1.09
2.07
3.17
2.09
2.19
2.00
3.09
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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113.7448
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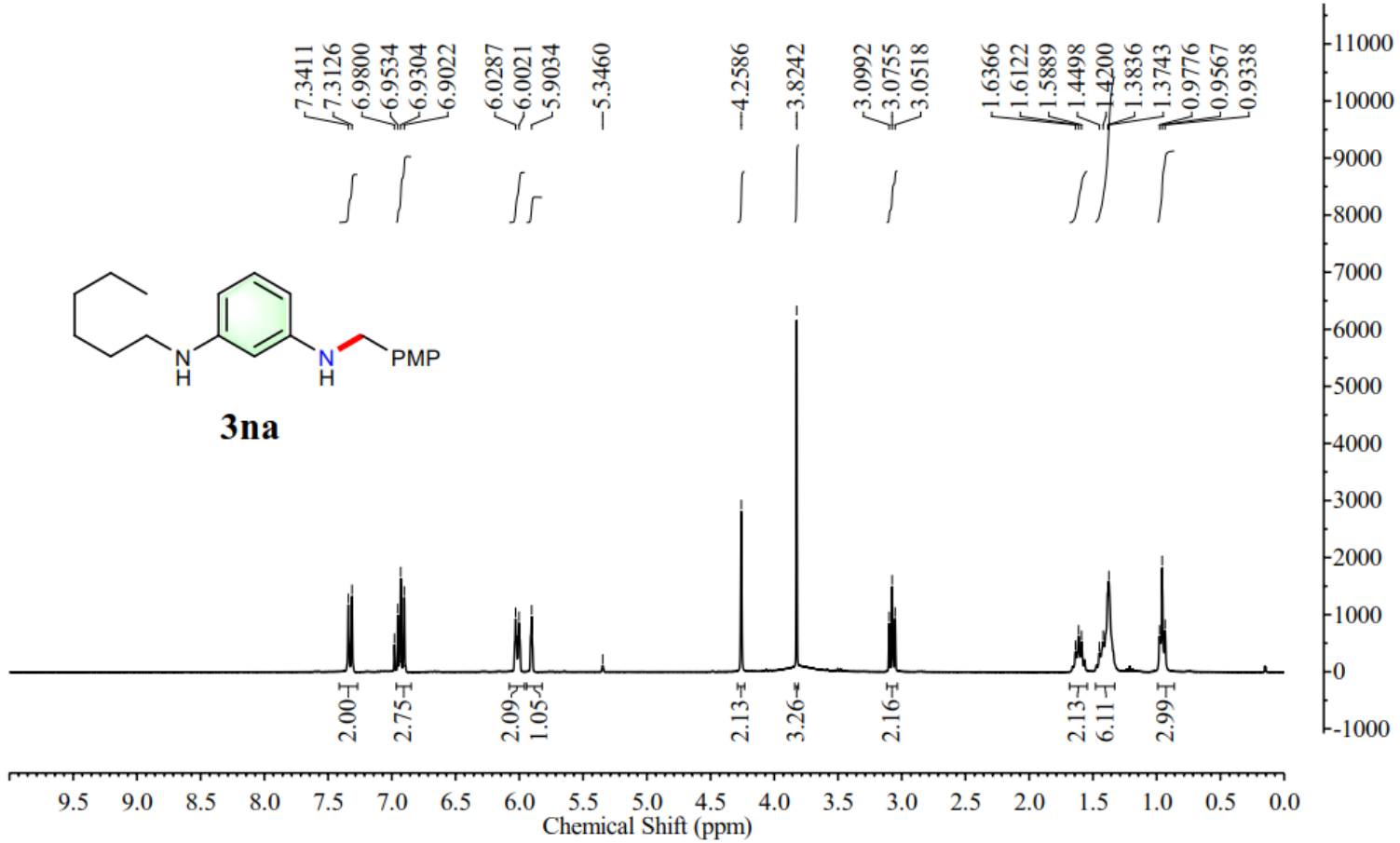
102.3468
96.8482
55.1186
54.0823
53.7220
53.3616
53.0003
52.6396
47.5069
43.5390
31.6585
20.2499
13.6354
N
H
N
H
PMP
3ma
200
180
160
140
120
100
80
60
40
20
0
-20
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)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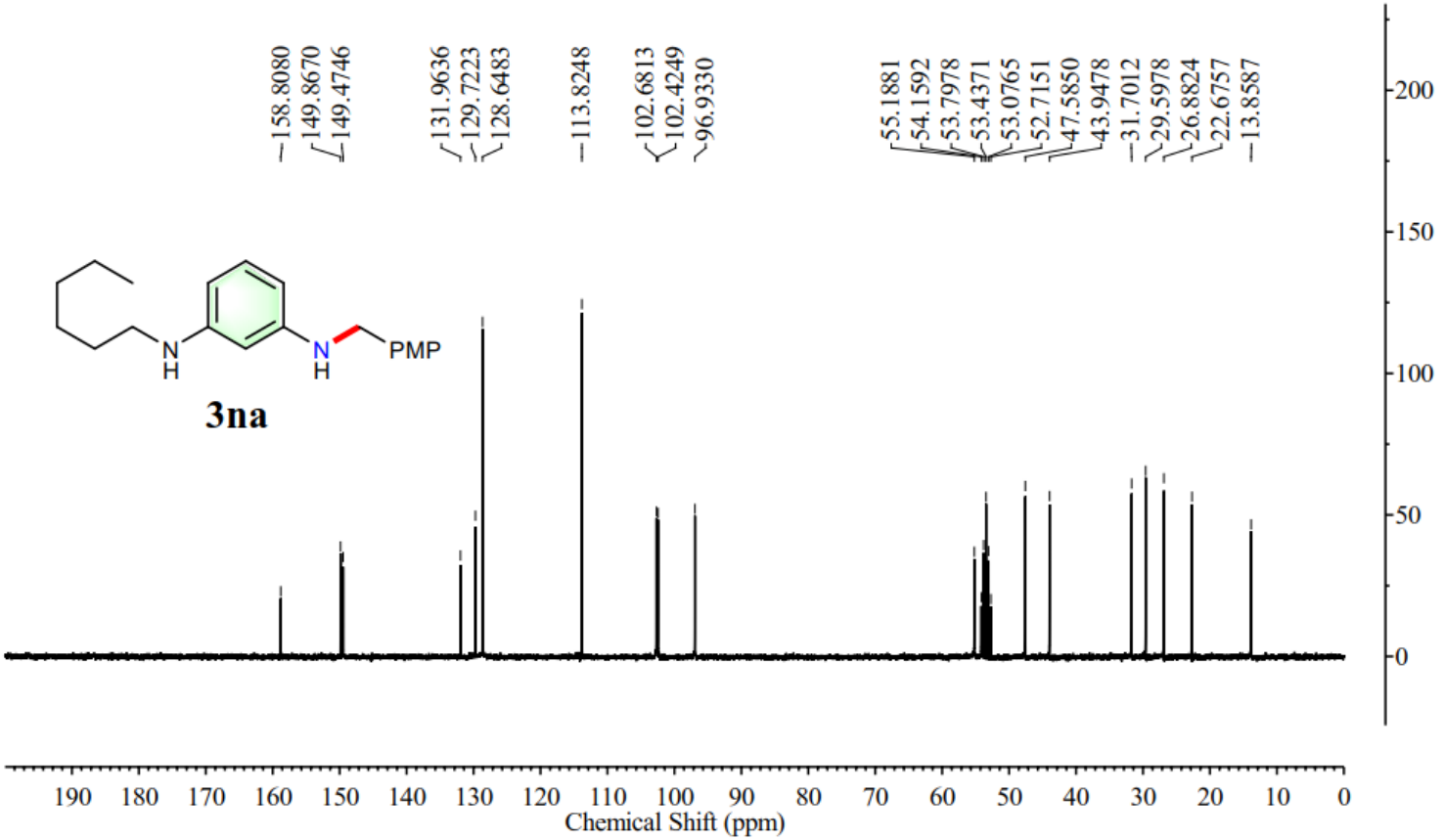
6.9800
6.9534
6.9304
6.9022
6.0287
6.0021
5.9034
5.3460
4.2586
3.8242
3.0992
3.0755
3.0518
1.6366
1.6122
1.5889
1.4498
1.4200
1.3836
1.3743
0.9776
0.9567
0.9338
N
H
N
H
PMP
3na
2.00
2.75
2.09
1.05
2.13
3.26
2.16
2.13
6.11
2.99
Chemical Shift (ppm)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113.8248
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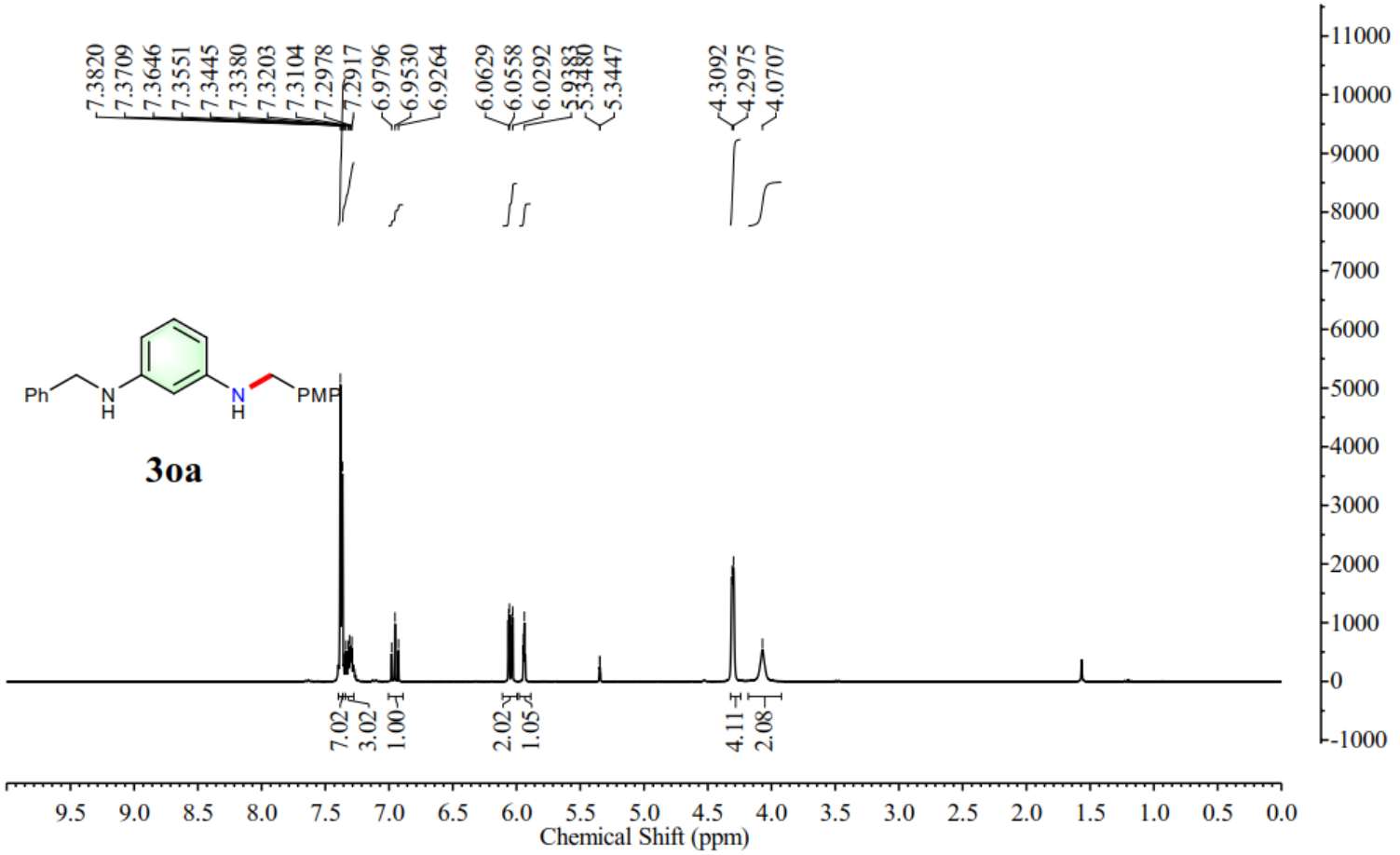
102.4249
96.9330
55.1881
54.1592
53.7978
53.4371
53.0765
52.7151
47.5850
43.9478
31.7012
29.5978
26.8824
22.6757
13.8587
N
H
N
H
PMP
3na
200
150
100
50
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)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7.3445
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7.3203
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7.2978
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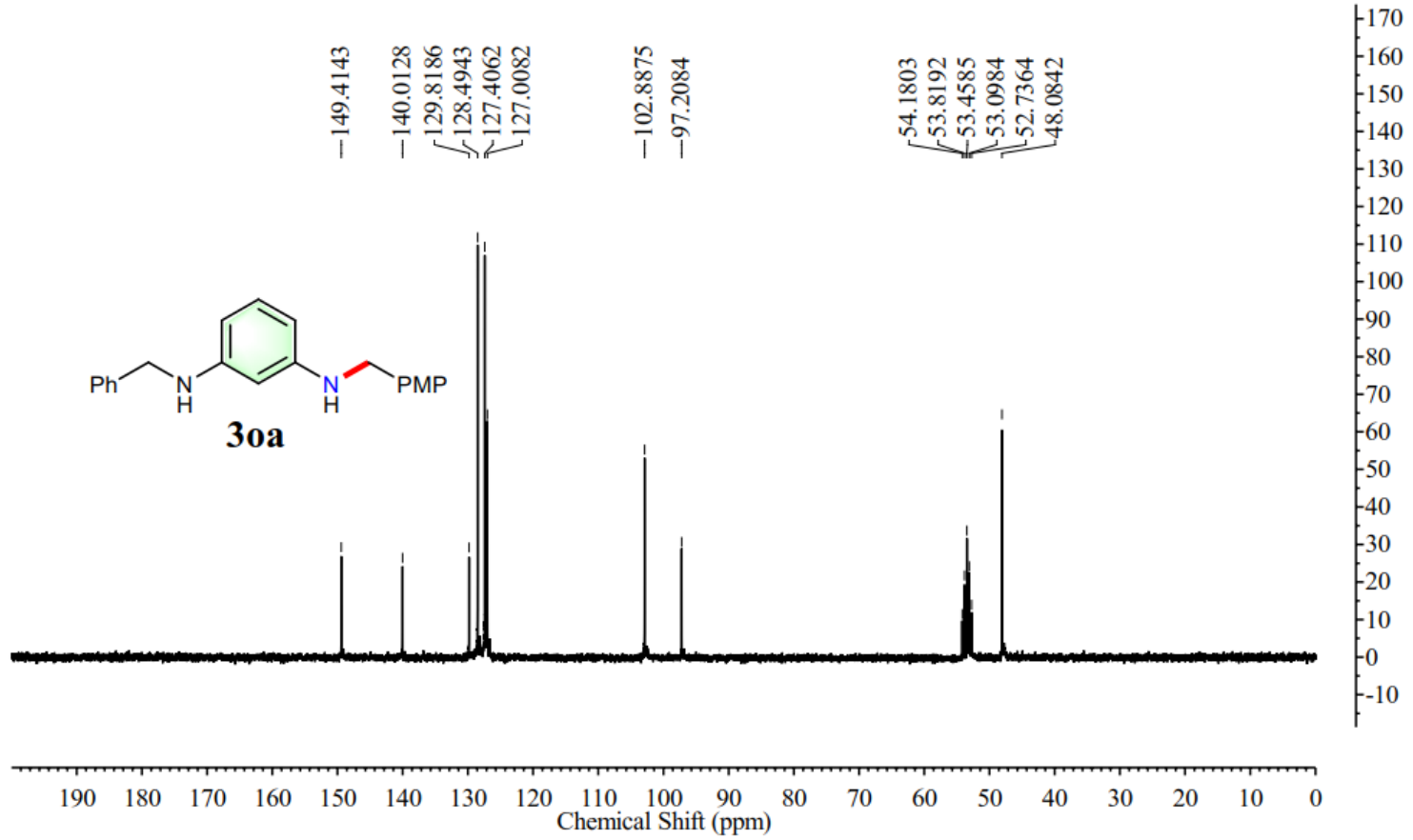
6.9530
6.9264
6.0629
6.0558
6.0292
5.9383
5.3480
5.3447
4.3092
4.2975
4.0707
Ph
N
H
N
H
PMP
3oa
7.02
3.02
1.00
2.02
1.05
4.11
2.08
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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129.8186
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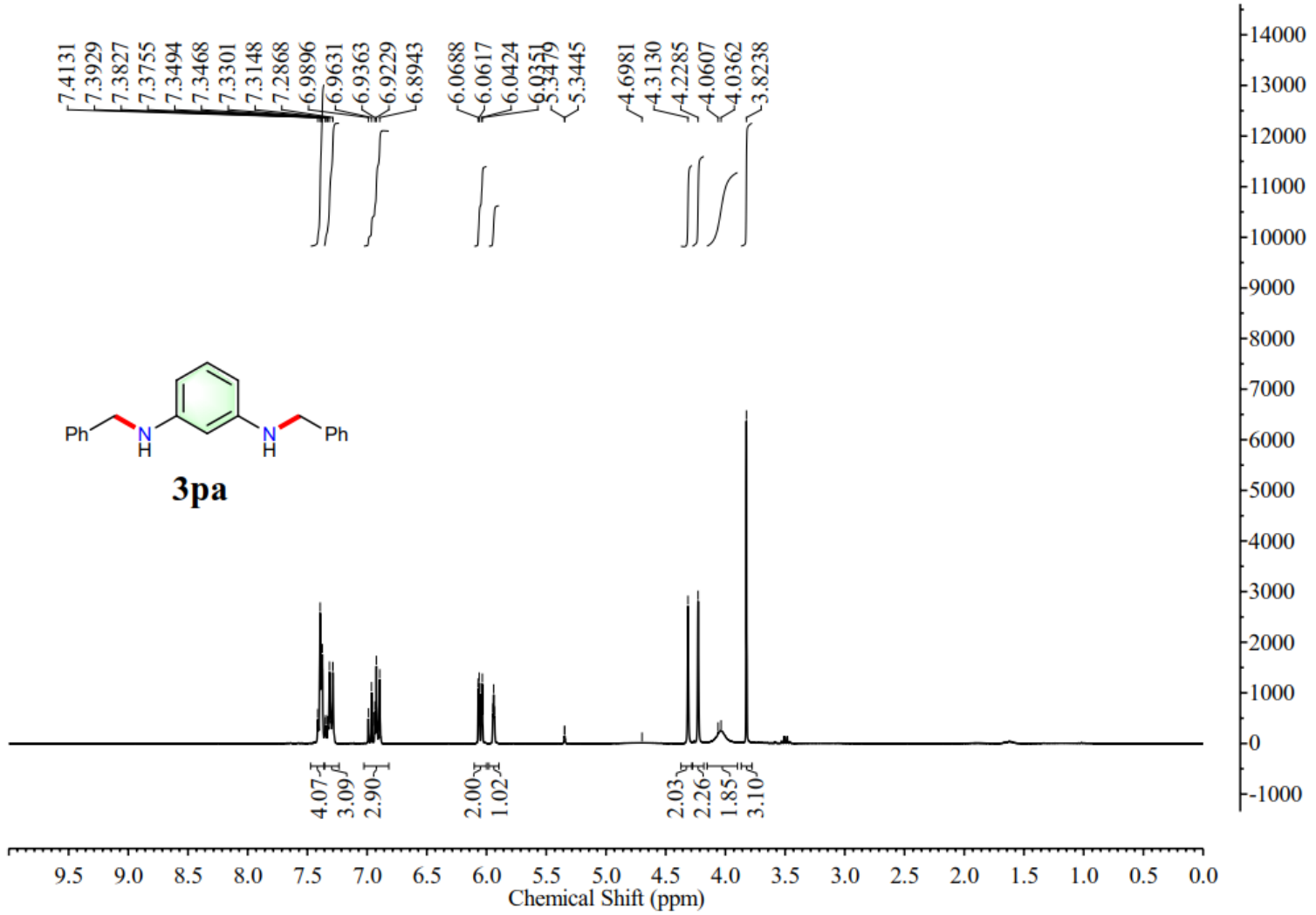
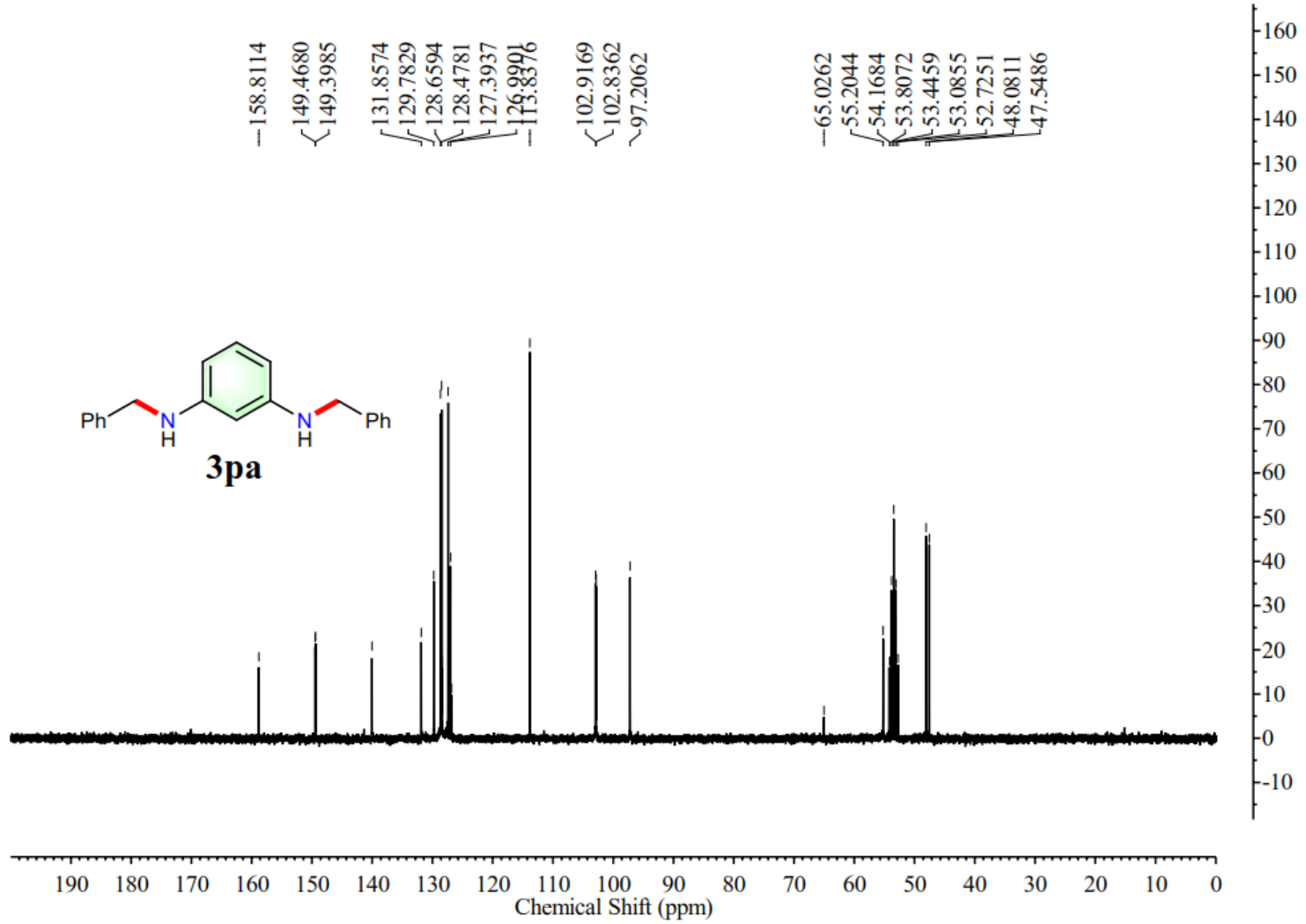
127.0082
102.8875
97.2084
54.1803
53.8192
53.4585
53.0984
52.7364
48.0842
Ph
N
H
N
H
PMP
3oa
Chemical Shift (ppm)


7.4131
7.3929
7.3827
7.3755
7.3494
7.3468
7.3301
7.3148
7.2868
6.9896
6.9631
6.9363
6.9229
6.8943
6.0688
6.0617
6.0424
6.0351
5.3479
5.3445
4.6981
4.3130
4.2285
4.0607
4.0362
3.8238
Ph
N
H
N
H
Ph
3pa
4.07
3.09
2.90
2.00
1.02
2.03
2.26
1.85
3.10
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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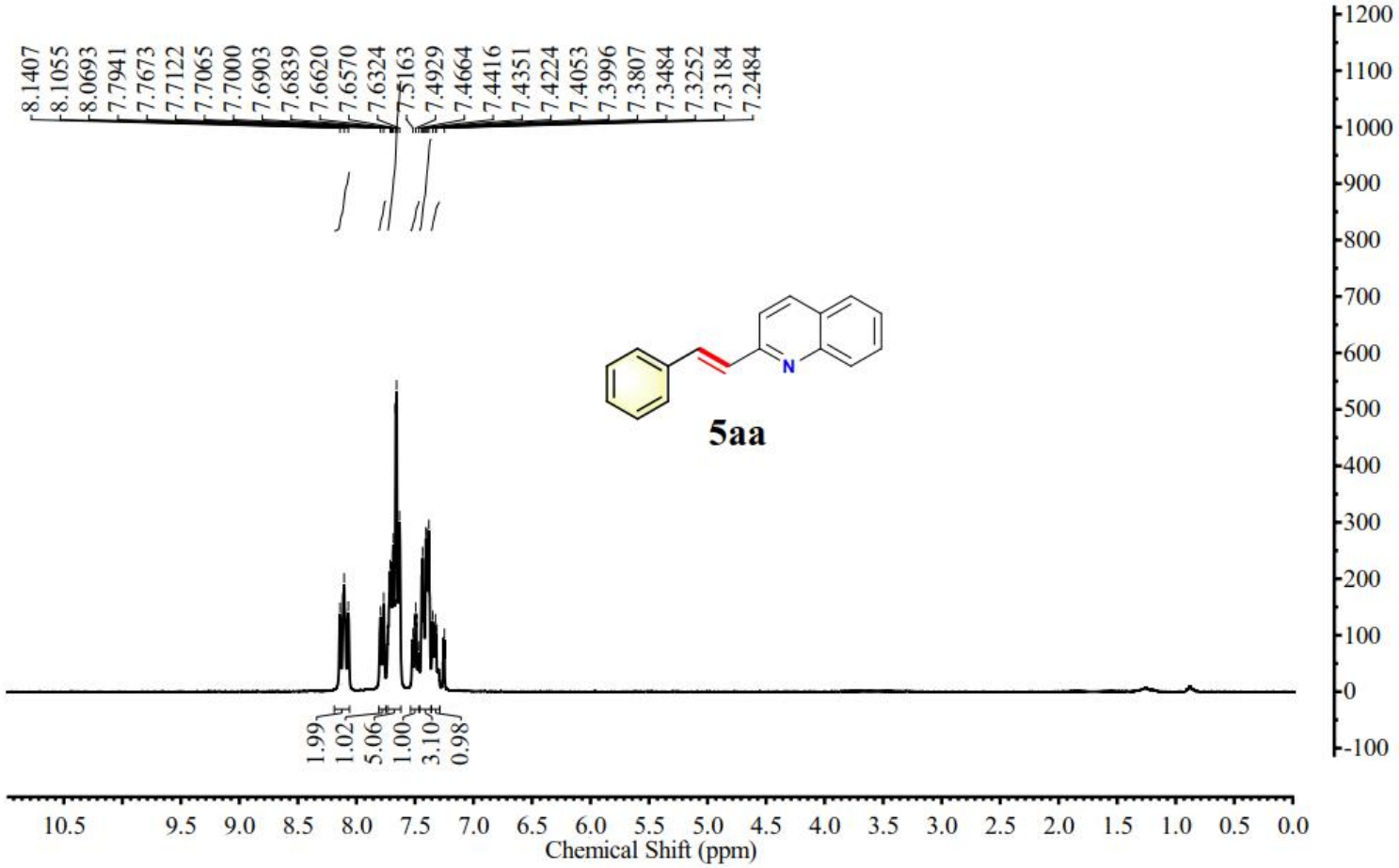
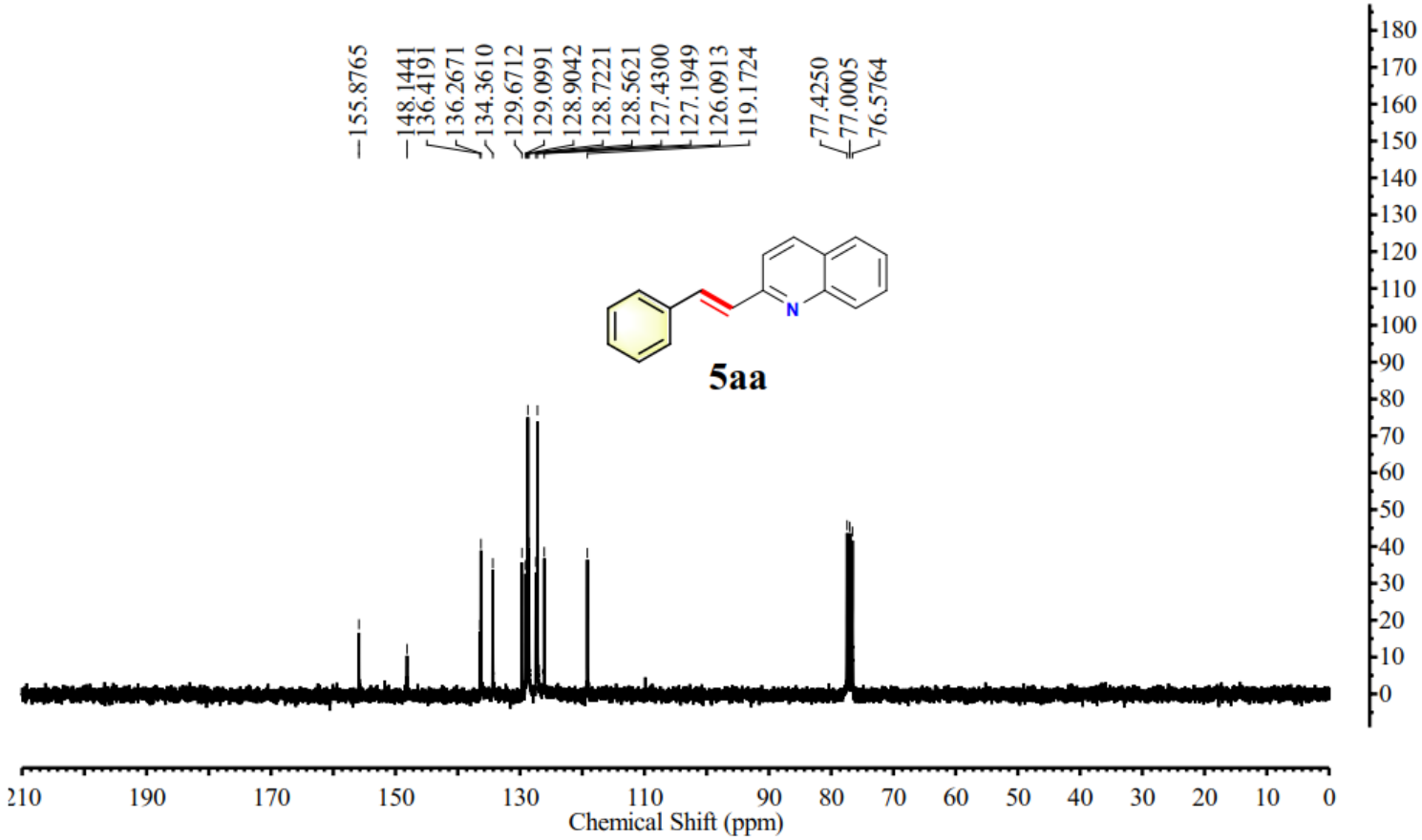
149.3985
131.8574
129.7829
128.6594
128.4781
127.3937
126.9991
113.8376
102.9169
102.8362
97.2062
65.0262
55.2044
54.1684
53.8072
53.4459
53.0855
52.7251
48.0811
47.5486
Ph
N
H
N
H
Ph
3pa
Chemical Shift (ppm)


8.1407
8.1055
8.0693
7.7941
7.7673
7.7122
7.7065
7.7000
7.6903
7.6839
7.6620
7.6570
7.6324
7.5163
7.4929
7.4664
7.4416
7.4351
7.4224
7.4053
7.3996
7.3807
7.3484
7.3252
7.3184
7.2484
N
5aa
1.99
1.02
5.06
1.00
3.10
0.98
Chemical Shift (ppm)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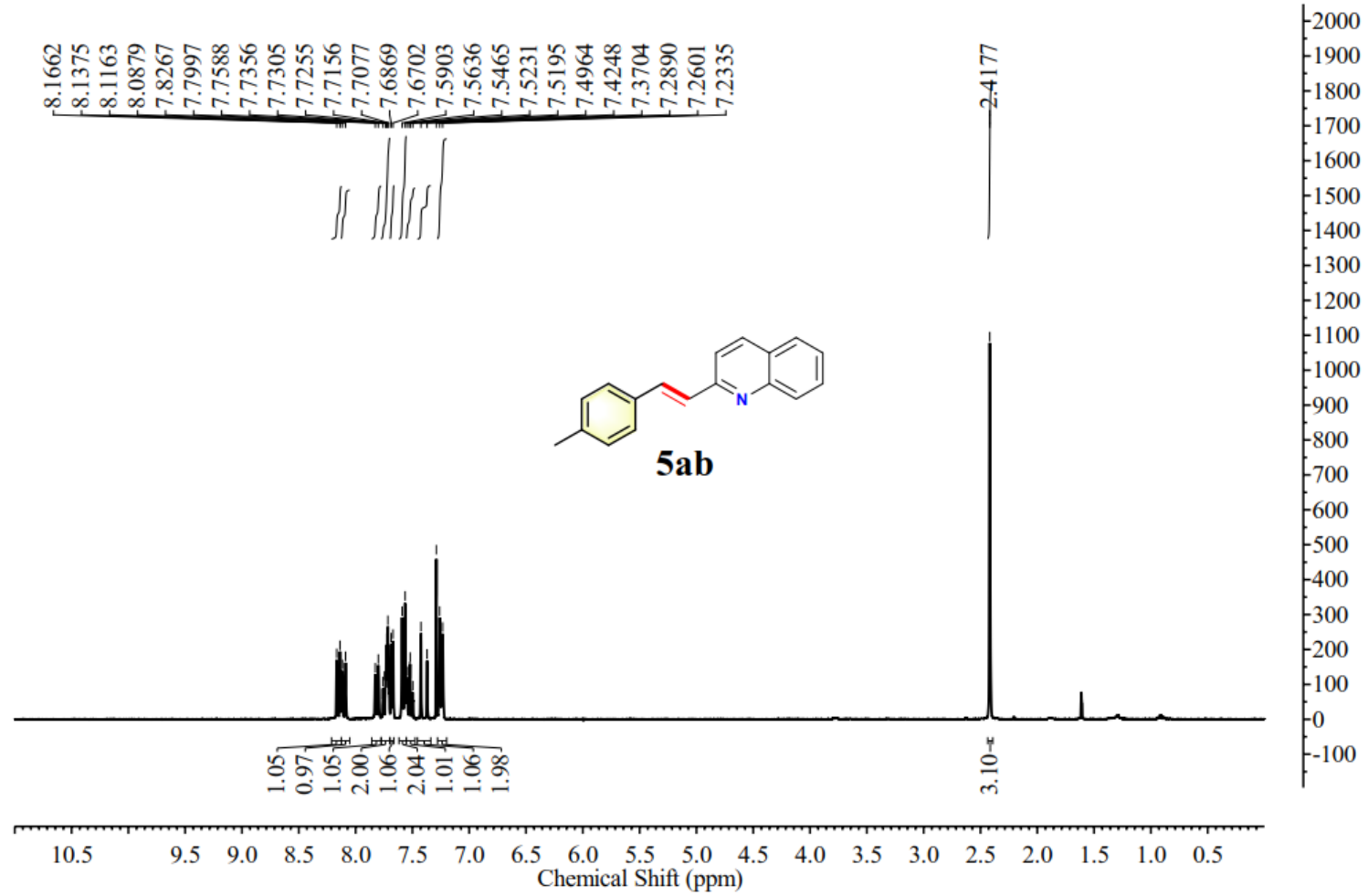
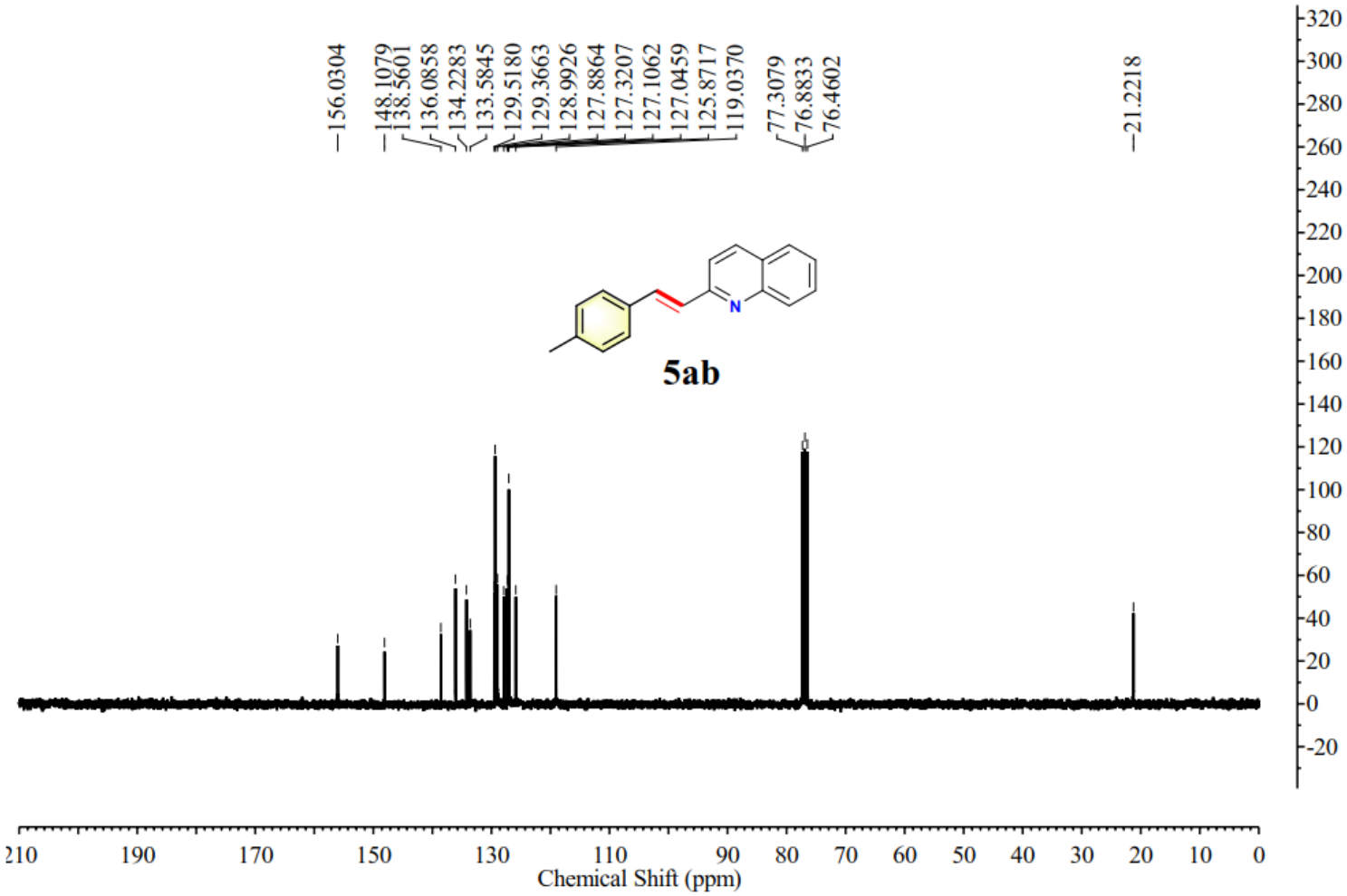
148.1441
136.4191
136.2671
134.3610
129.6712
129.0991
128.9042
128.7221
128.5621
127.4300
127.1949
126.0913
119.1724
77.4250
77.0005
76.5764
N
5aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.1662
8.1375
8.1163
8.0879
7.8267
7.7997
7.7588
7.7356
7.7305
7.7255
7.7156
7.7077
7.6869
7.6702
7.5903
7.5636
7.5465
7.5231
7.5195
7.4964
7.4248
7.3704
7.2890
7.2601
7.2335
2.4177
N
5ab
1.05
0.97
1.05
2.00
1.06
2.04
1.01
1.06
1.98
3.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100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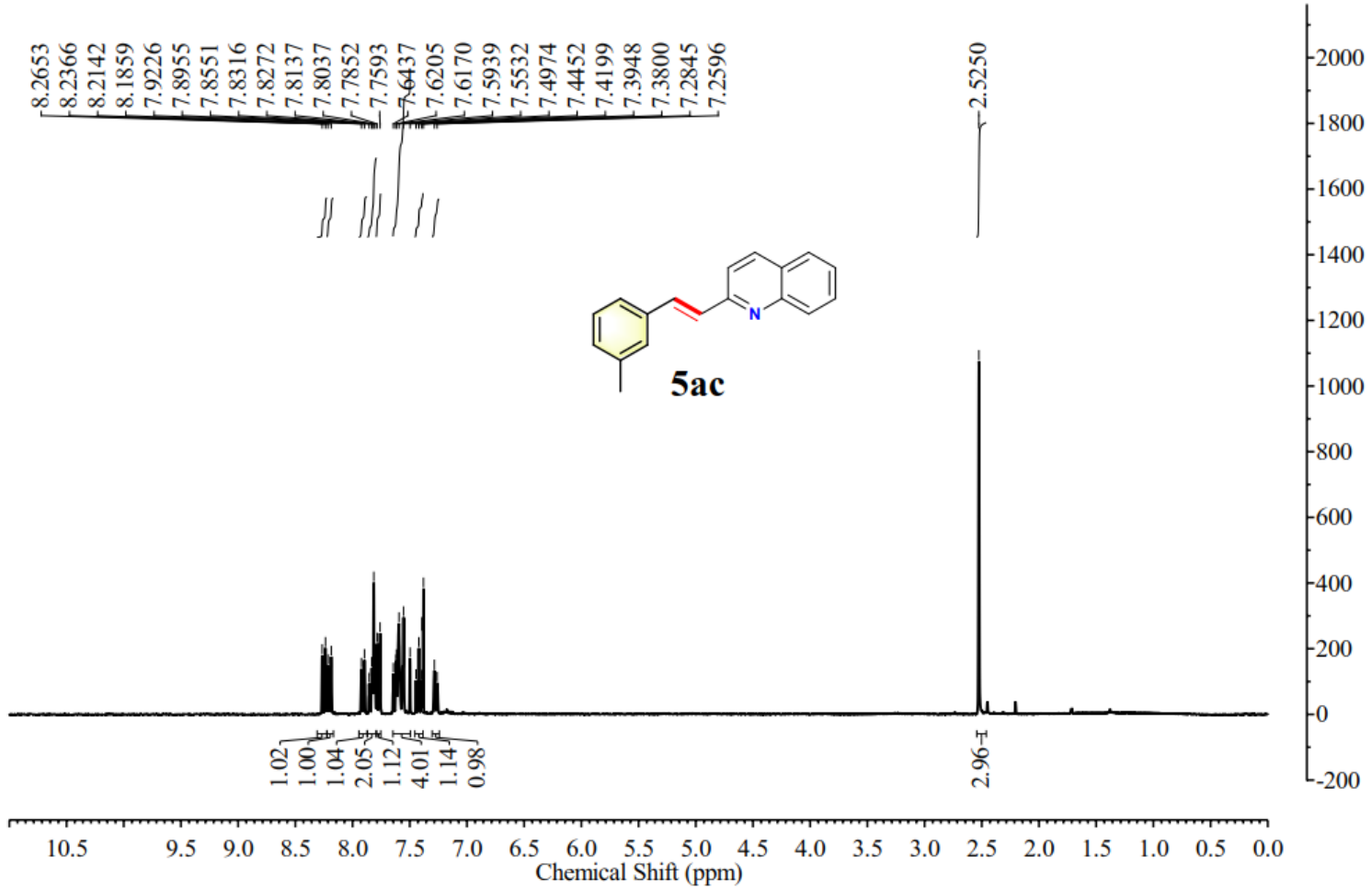
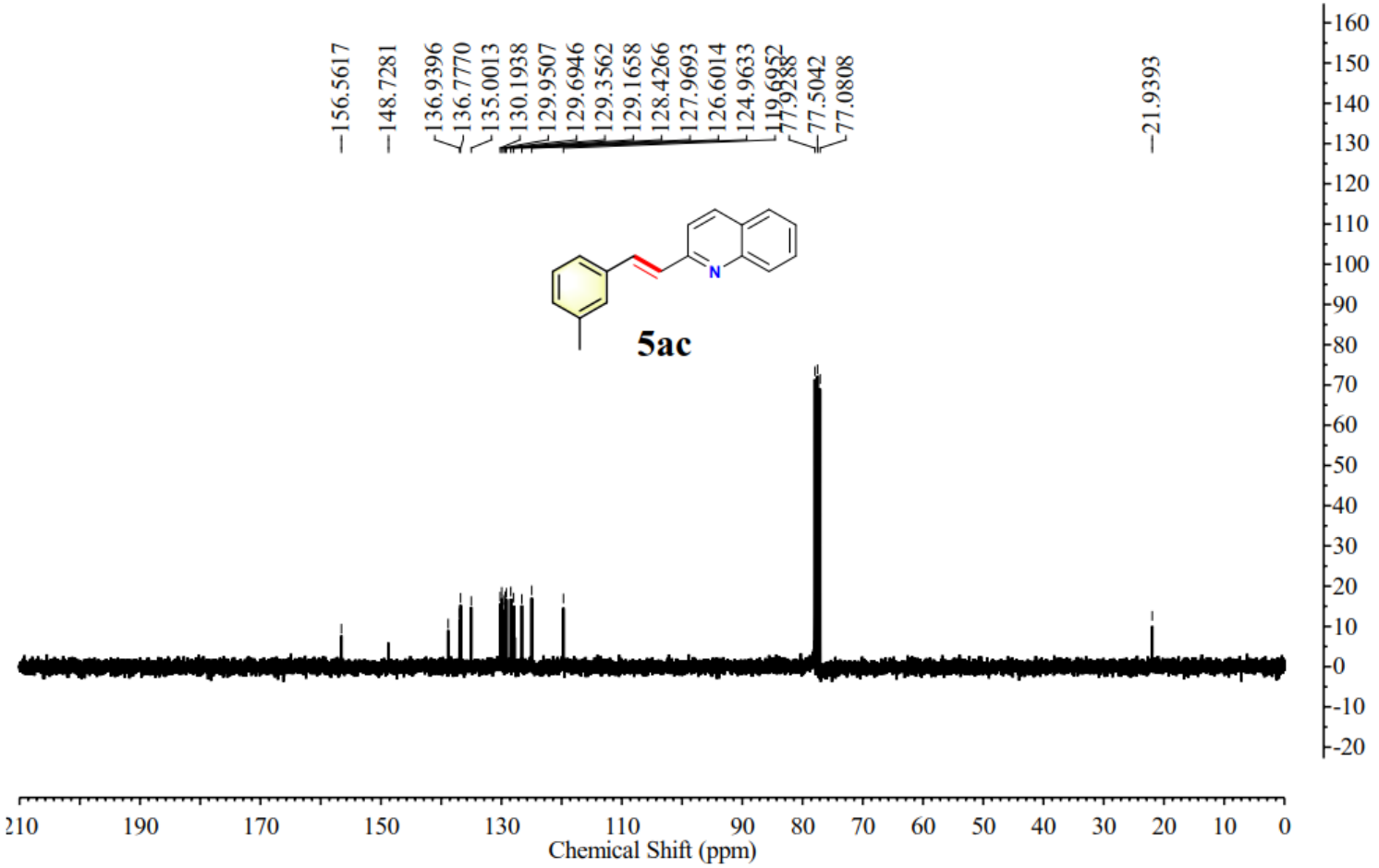
148.1079
138.5601
136.0858
134.2283
133.5845
129.5180
129.3663
128.9926
127.8864
127.3207
127.1062
127.0459
125.8717
119.0370
77.3079
76.8833
76.4602
21.2218
N
5ab
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.2653
8.2366
8.2142
8.1859
7.9226
7.8955
7.8551
7.8316
7.8272
7.8137
7.8037
7.7852
7.7593
7.6437
7.6205
7.6170
7.5939
7.5532
7.4974
7.4452
7.4199
7.3948
7.3800
7.2845
7.2596
2.5250
N
5ac
1.02
1.00
1.04
2.05
1.12
4.01
1.14
0.98
2.96
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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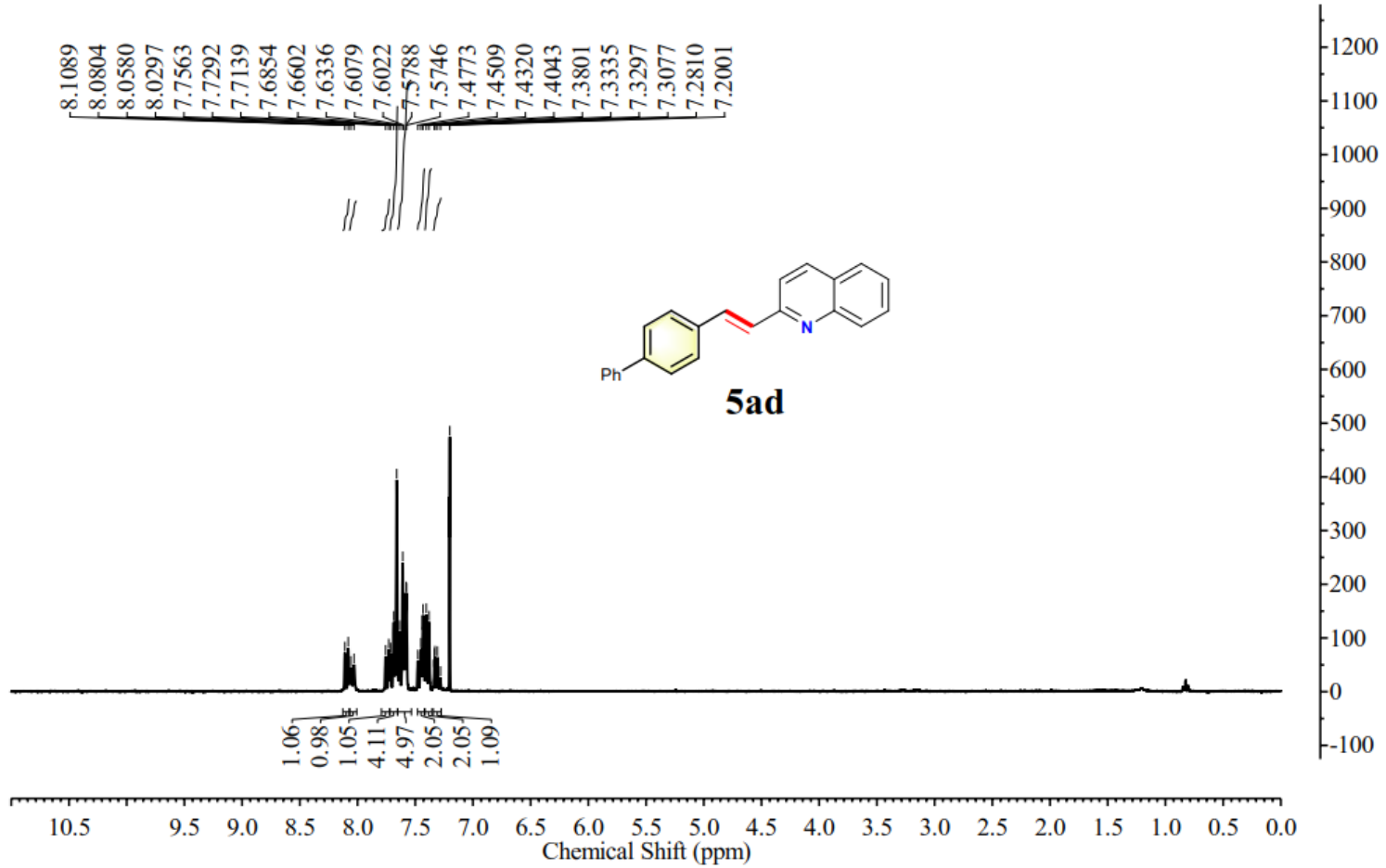
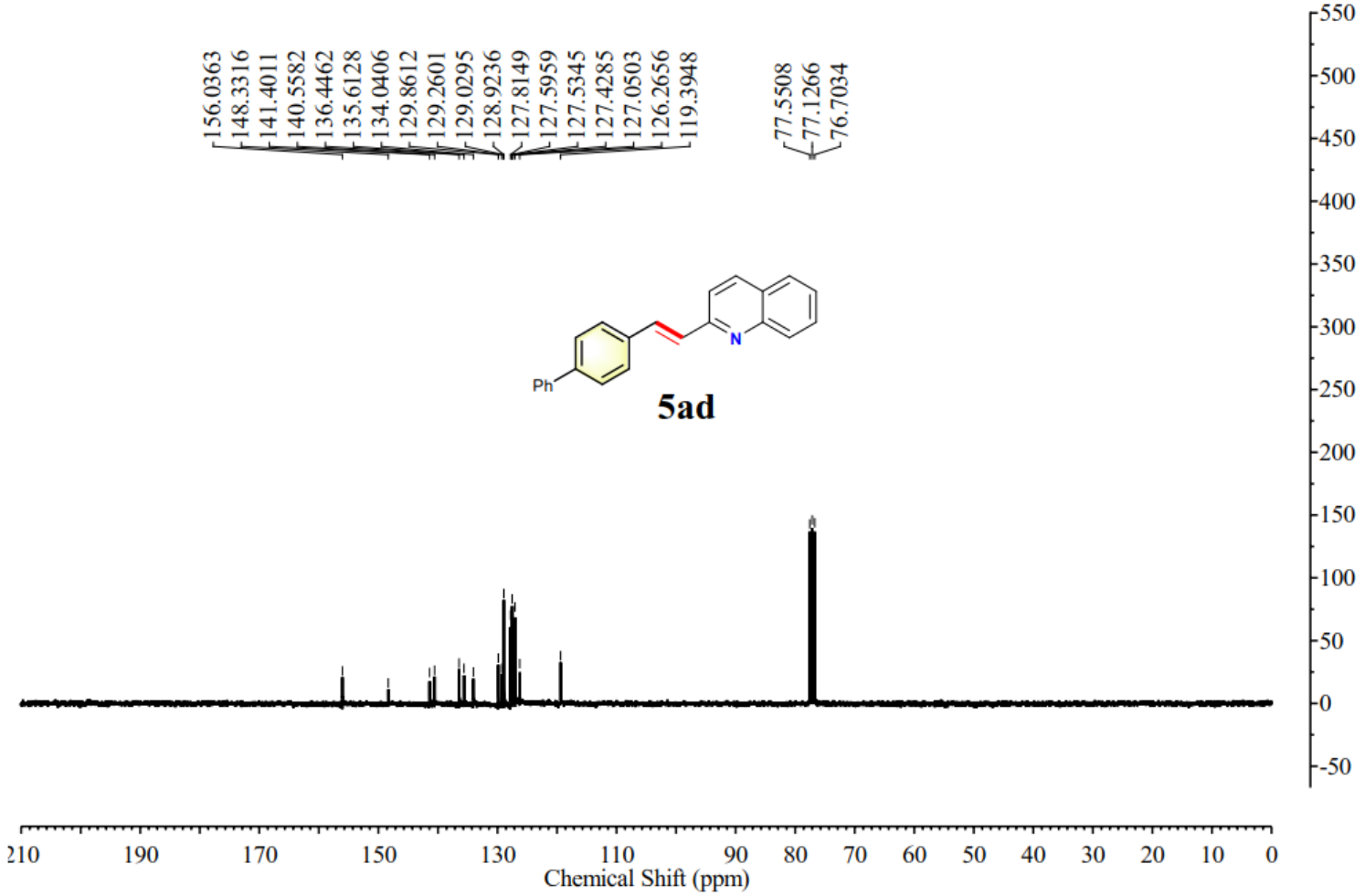
136.9396
136.7770
135.0013
130.1938
129.9507
129.6946
129.3562
129.1658
128.4266
127.9693
126.6014
124.9633
119.6952
77.9288
77.5042
77.0808
21.9393
N
5ac
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.1089
8.0804
8.0580
8.0297
7.7563
7.7292
7.7139
7.6854
7.6602
7.6336
7.6079
7.6022
7.5788
7.5746
7.4773
7.4509
7.4320
7.4043
7.3801
7.3335
7.3297
7.3077
7.2810
7.2001
Ph
N
5ad
1.06
0.98
1.05
4.11
4.97
2.05
2.05
1.09
Chemical Shift (ppm)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141.4011
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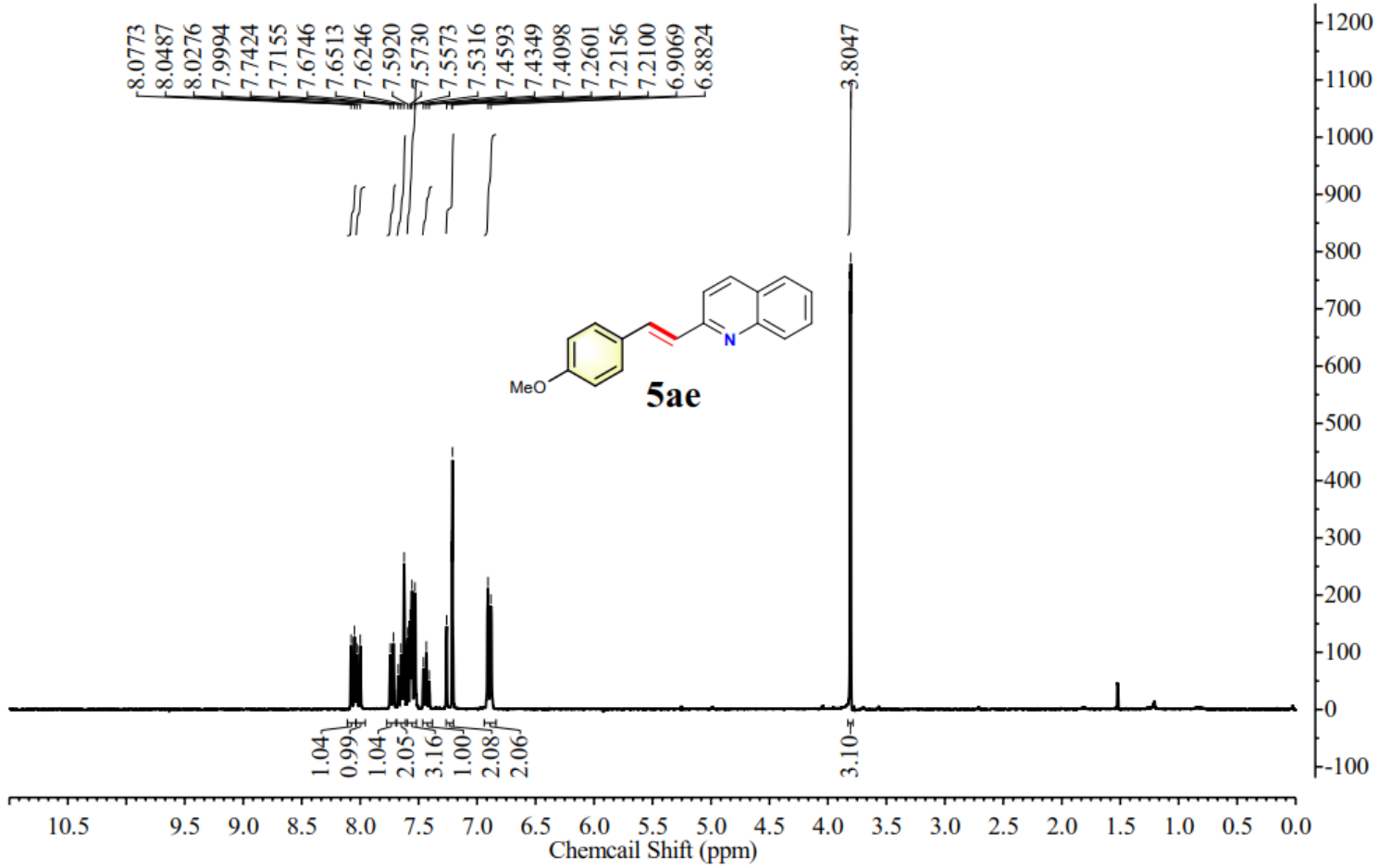
136.4462
135.6128
134.0406
129.8612
129.2601
129.0295
128.9236
127.8149
127.5959
127.5345
127.4285
127.0503
126.2656
119.3948
77.5508
77.1266
76.7034
N
Ph
5ad
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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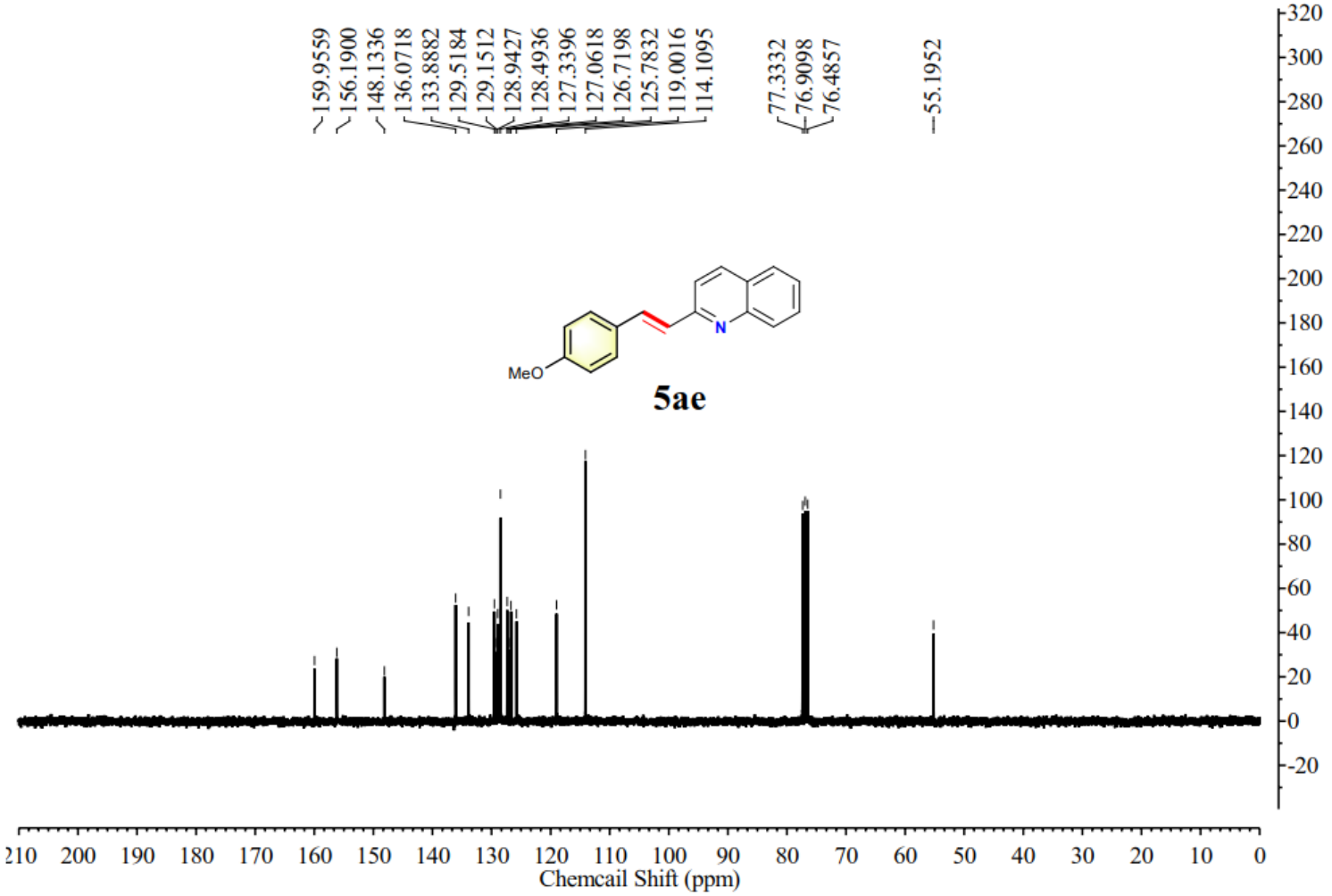
8.0487
8.0276
7.9994
7.7424
7.7155
7.6746
7.6513
7.6246
7.5920
7.5730
7.5573
7.5316
7.4593
7.4349
7.4098
7.2601
7.2156
7.2100
6.9069
6.8824
3.8047
MeO
N
5ae
1.04
0.99
1.04
2.05
3.16
1.00
2.08
2.06
3.10
Chemcail Shift (ppm)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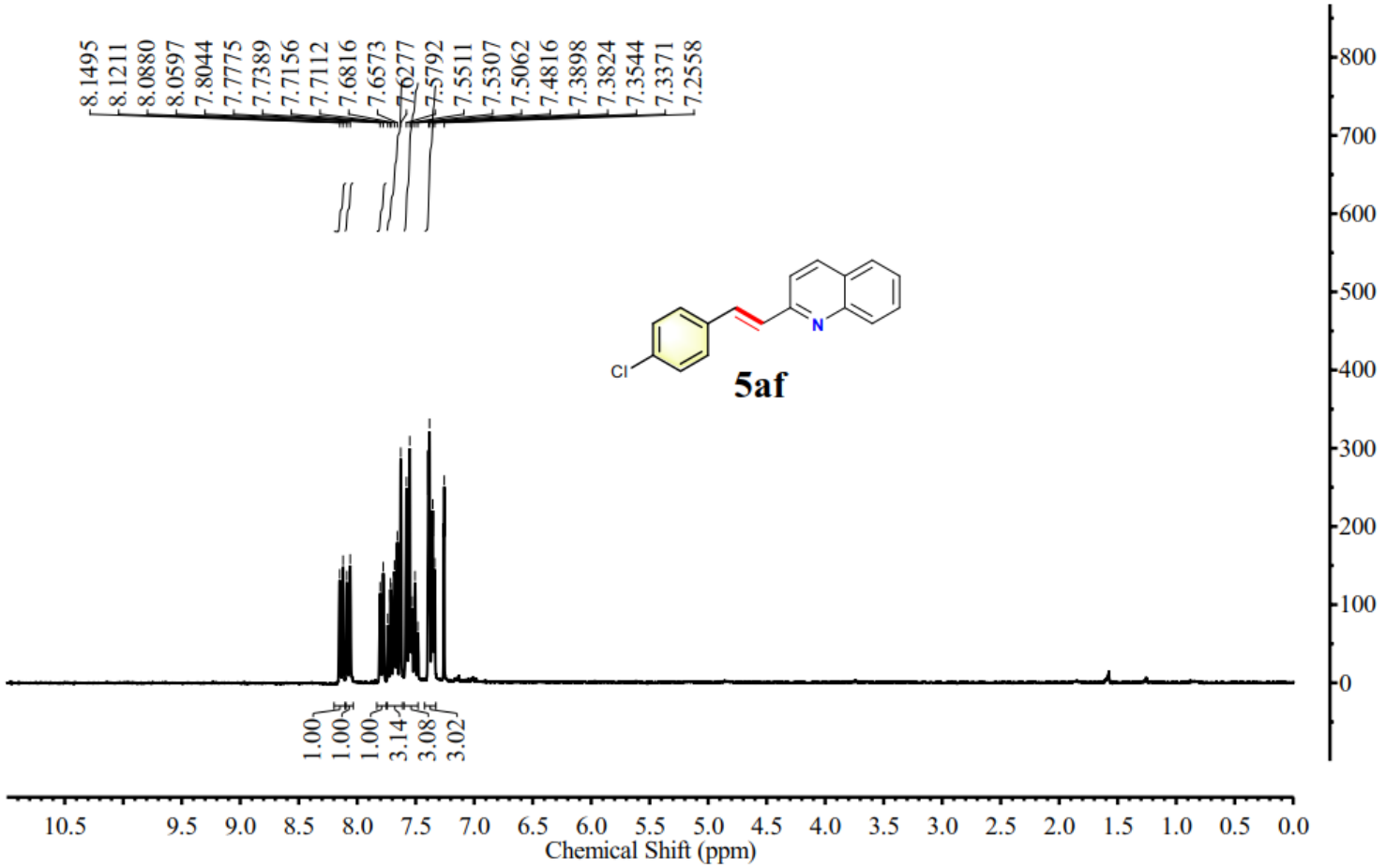
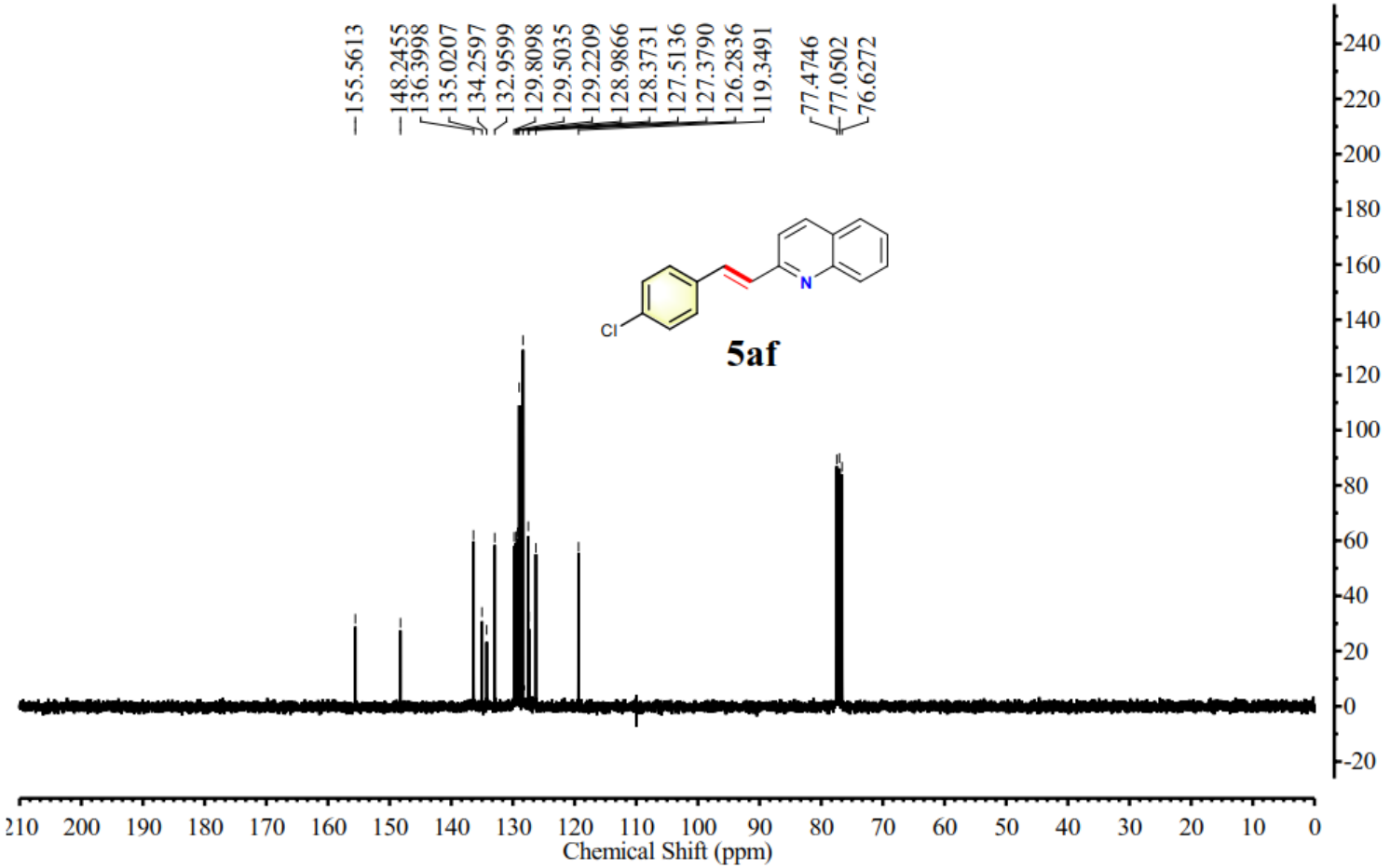
148.1336
136.0718
133.8882
129.5184
129.1512
128.9427
128.4936
127.3396
127.0618
126.7198
125.7832
119.0016
114.1095
77.3332
76.9098
76.4857
55.1952
MeO
N
5ae
Chemcail Shift (ppm)


8.1495
8.1211
8.0880
8.0597
7.8044
7.7775
7.7389
7.7156
7.7112
7.6816
7.6573
7.6277
7.5792
7.5511
7.5307
7.5062
7.4816
7.3898
7.3824
7.3544
7.3371
7.2558
Cl
N
5af
1.00
1.00
1.00
3.14
3.08
3.02
800
700
600
500
400
300
200
100
0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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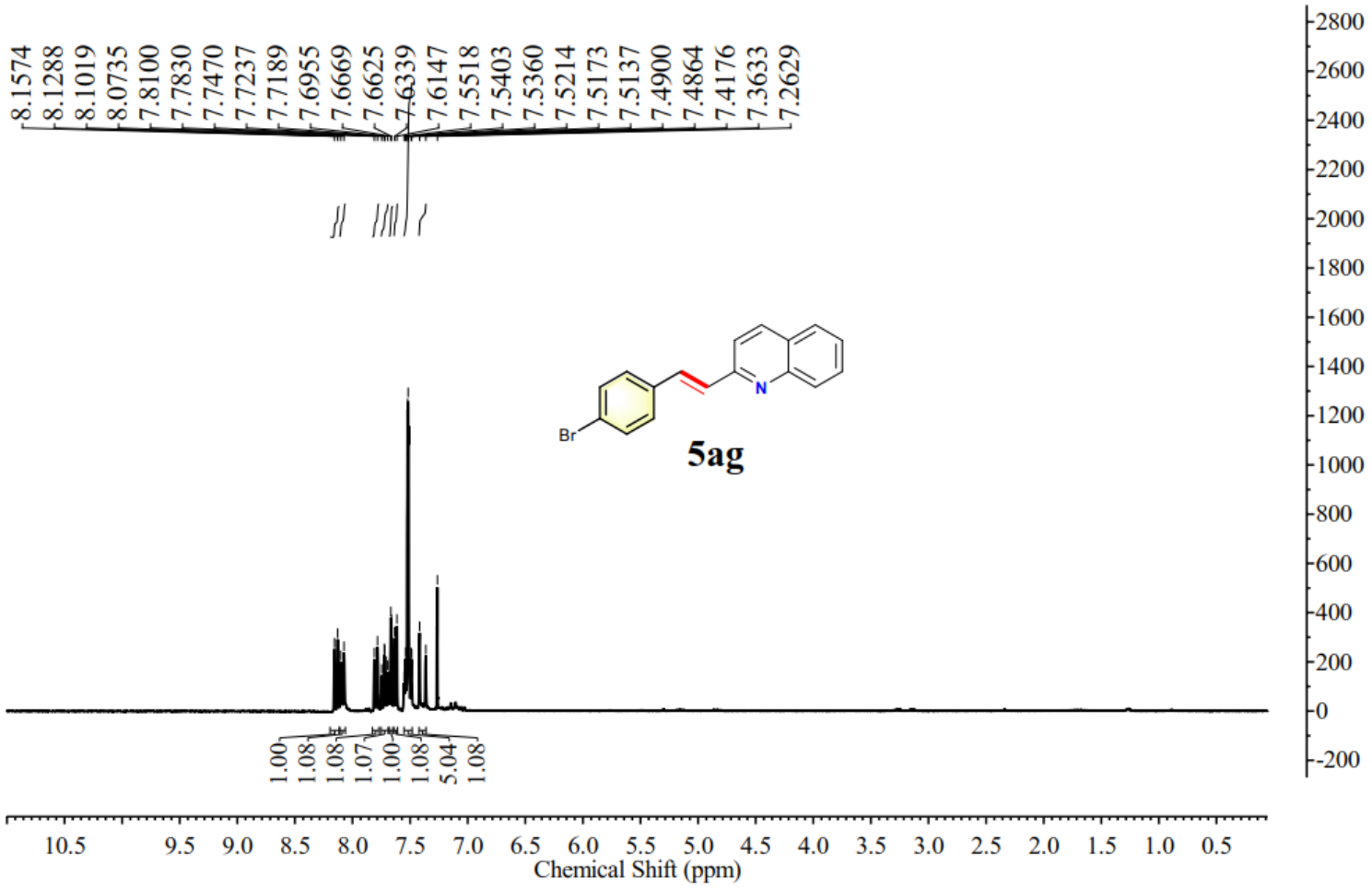
135.0207
134.2597
132.9599
129.8098
129.5035
129.2209
128.9866
128.3731
127.5136
127.3790
126.2836
119.3491
77.4746
77.0502
76.6272
N
Cl
5af
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


8.1574
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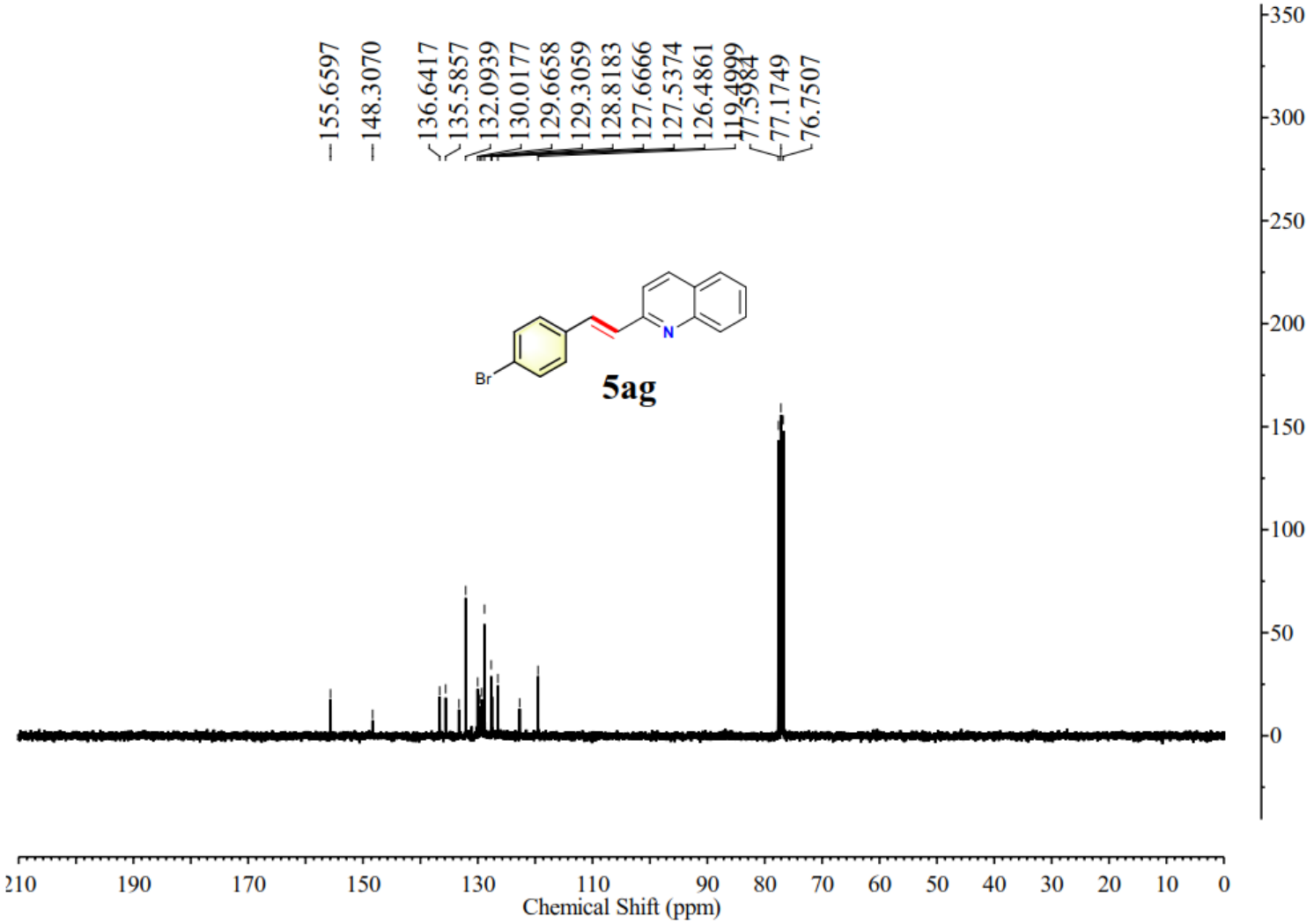
8.1019
8.0735
7.8100
7.7830
7.7470
7.7237
7.7189
7.6955
7.6669
7.6625
7.6339
7.6147
7.5518
7.5403
7.5360
7.5214
7.5173
7.5137
7.4900
7.4864
7.4176
7.3633
7.2629
Br
N
5ag
1.00
1.08
1.08
1.07
1.00
1.08
5.04
1.08
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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129.6658
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127.5374
126.4861
119.4999
77.5984
77.1749
76.7507
Br
N
5ag
350
300
250
200
150
100
50
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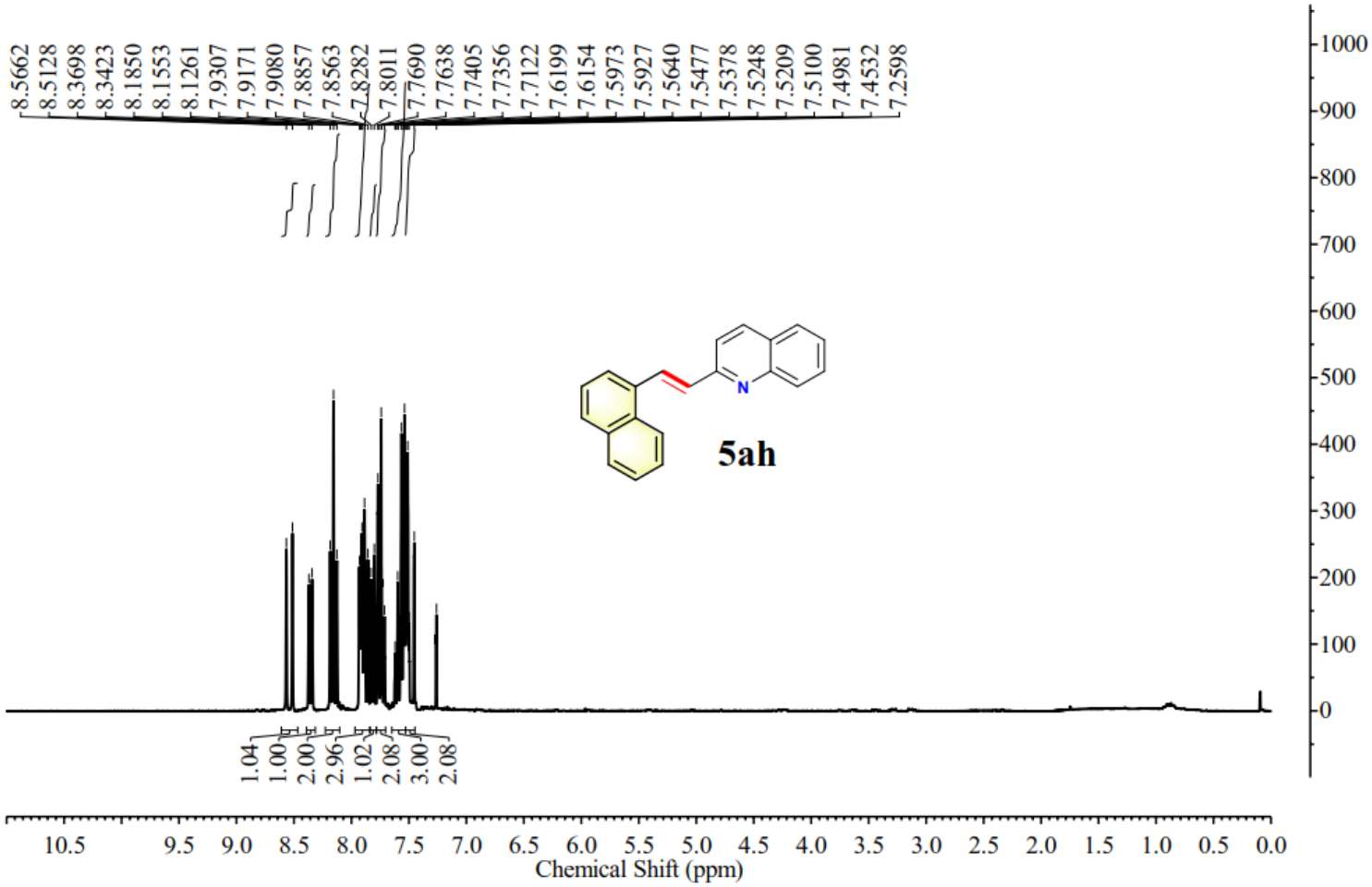
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.5662
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8.1261
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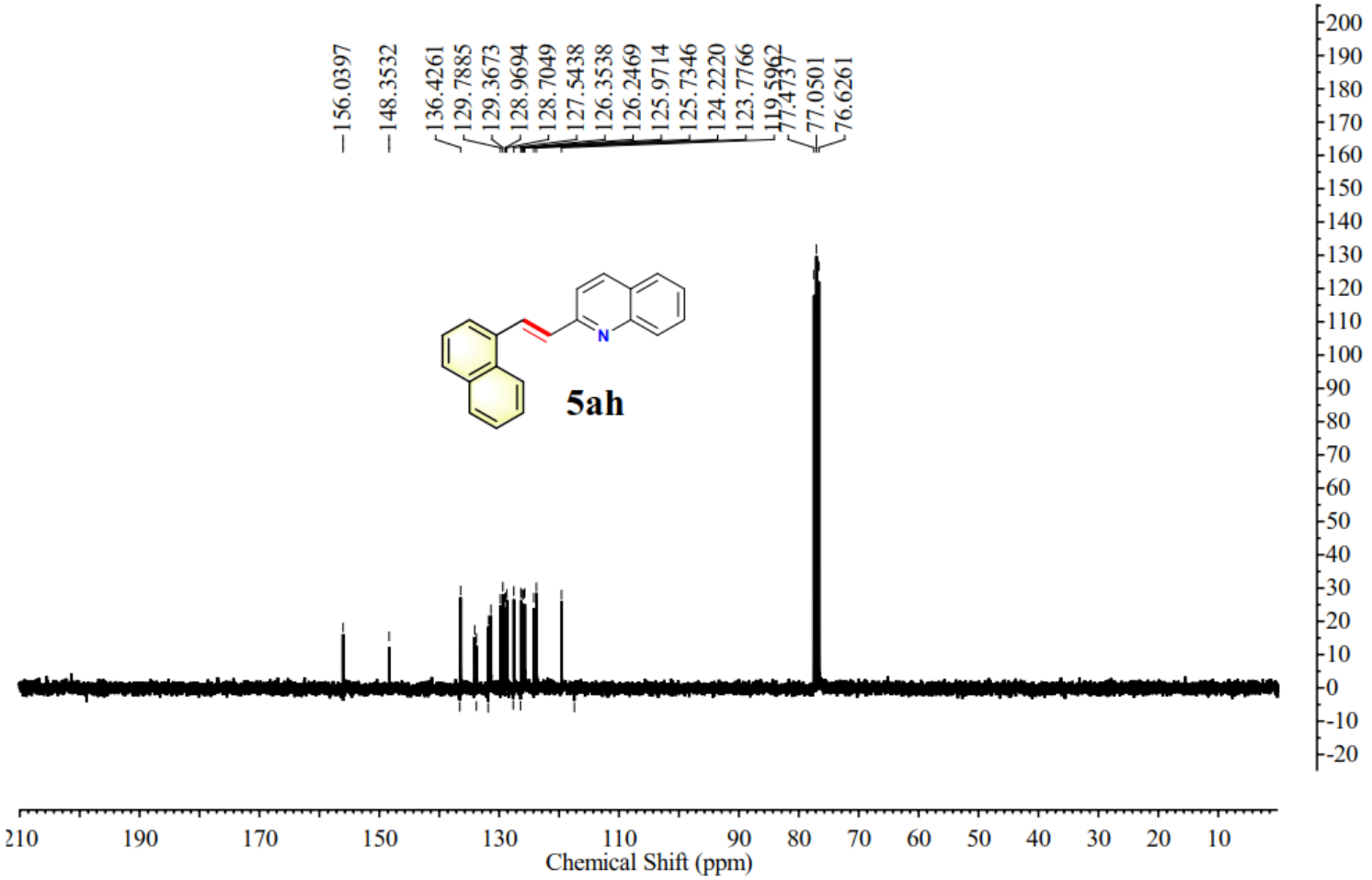
7.9171
7.9080
7.8857
7.8563
7.8282
7.8011
7.7690
7.7638
7.7405
7.7356
7.7122
7.6199
7.6154
7.5973
7.5927
7.5640
7.5477
7.5378
7.5248
7.5209
7.5100
7.4981
7.4532
7.2598
N
5ah
1.04
1.00
2.00
2.96
1.02
2.08
3.00
2.08
1000
900
800
700
600
500
400
300
200
100
0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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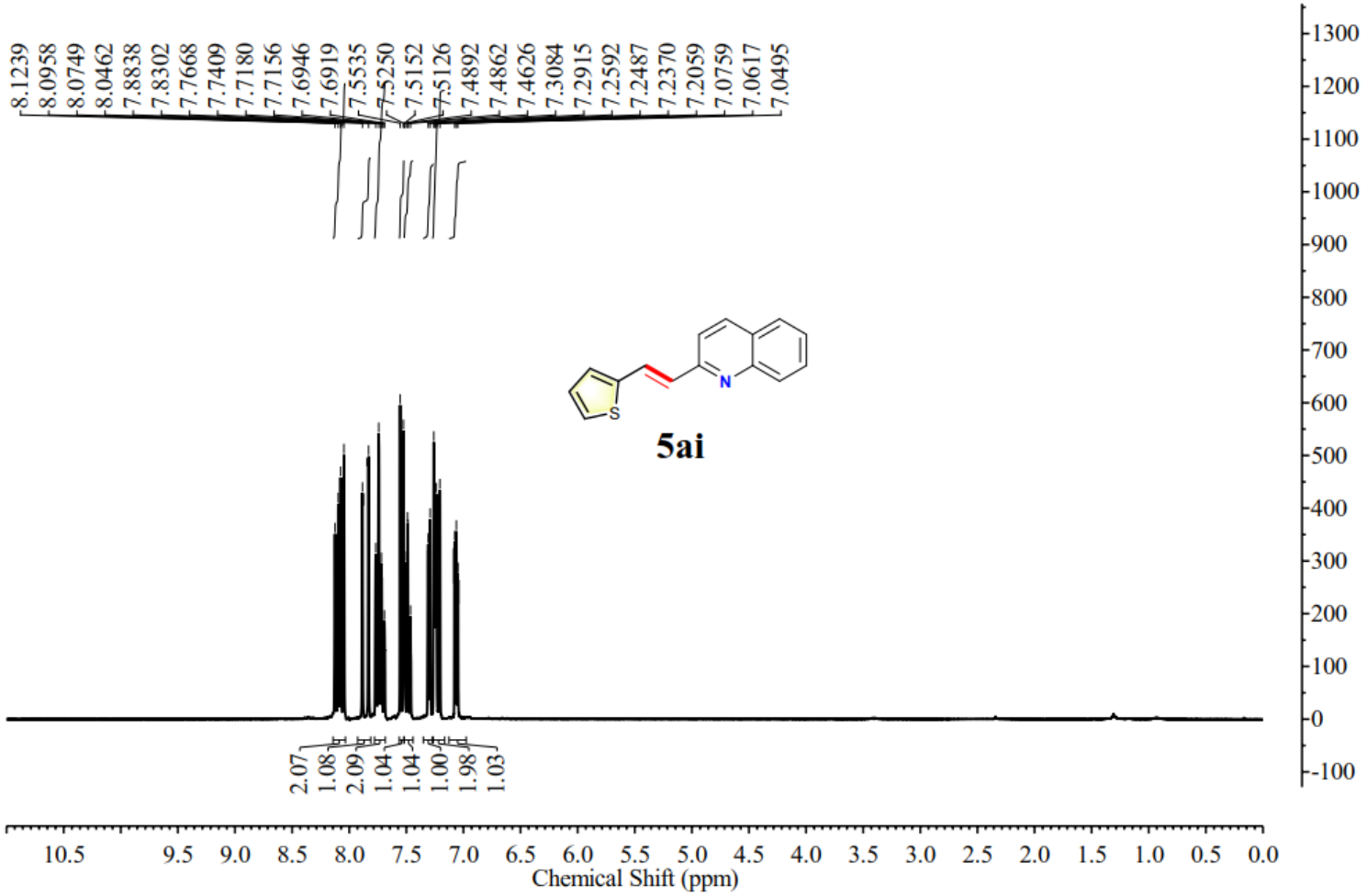
129.7885
129.3673
128.9694
128.7049
127.5438
126.3538
126.2469
125.9714
125.7346
124.2220
123.7766
119.5962
77.4737
77.0501
76.6261
N
5ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)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8.0749
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7.8302
7.7668
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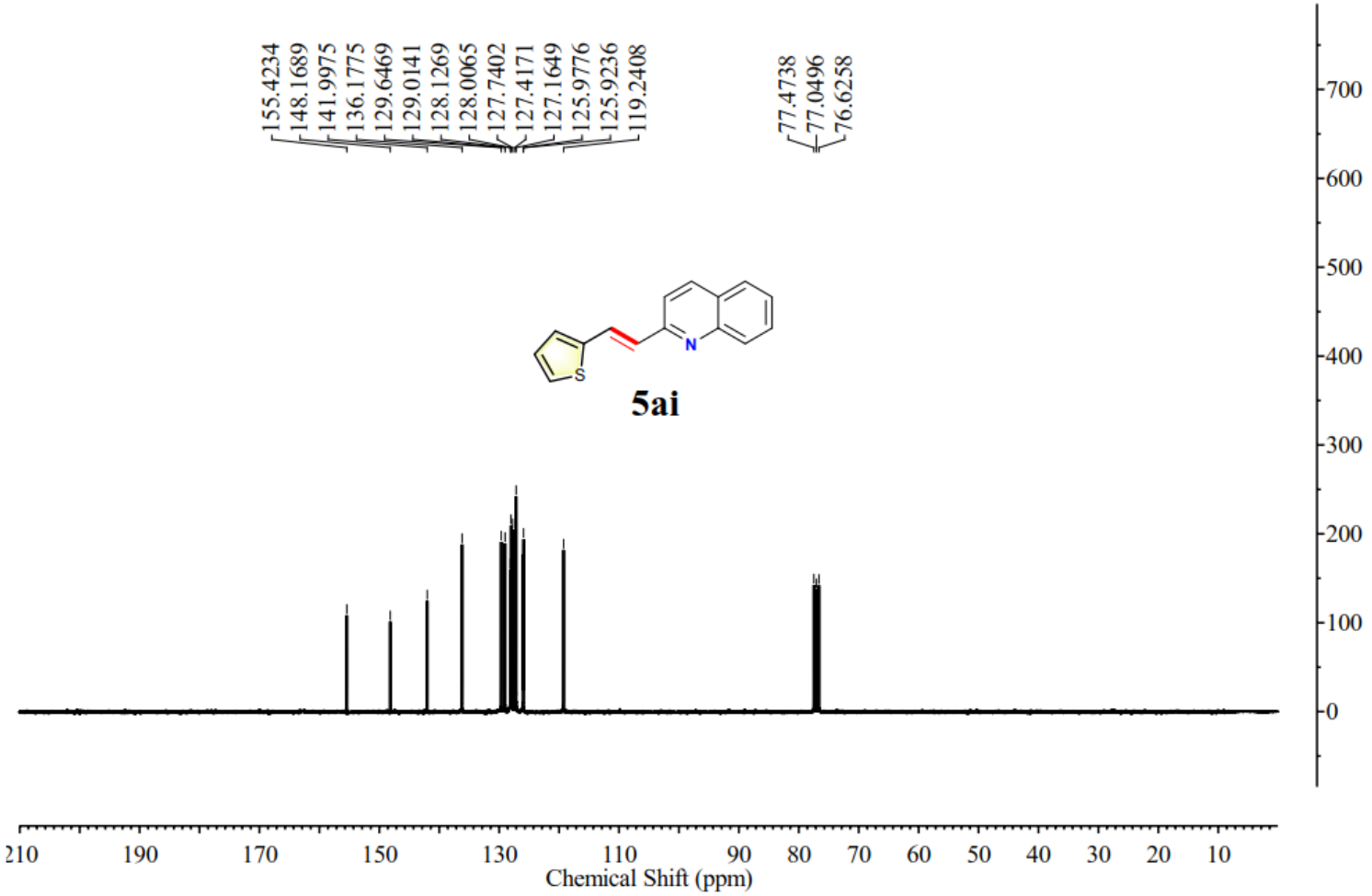
7.7180
7.7156
7.6946
7.6919
7.5535
7.5250
7.5152
7.5126
7.4892
7.4862
7.4626
7.3084
7.2915
7.2592
7.2487
7.2370
7.2059
7.0759
7.0617
7.0495
5ai
2.07
1.08
2.09
1.04
1.04
1.00
1.98
1.03
Chemical Shift (ppm)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129.0141
128.1269
128.0065
127.7402
127.4171
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125.9776
125.9236
119.2408
77.4738
77.0496
76.6258
N
S
5ai
700
600
500
400
300
200
100
0
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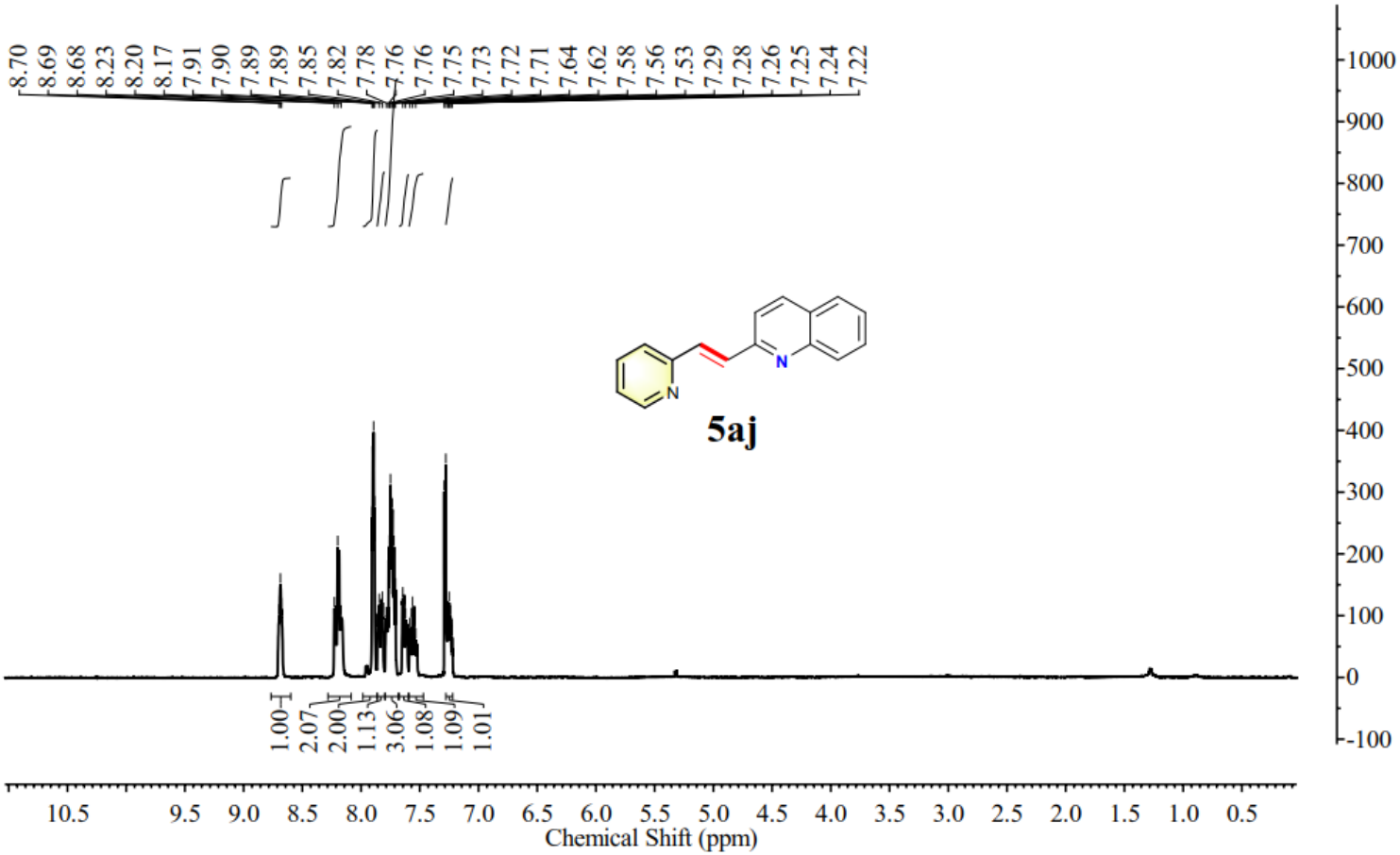
190
170
150
130
110
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


8.70
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8.23
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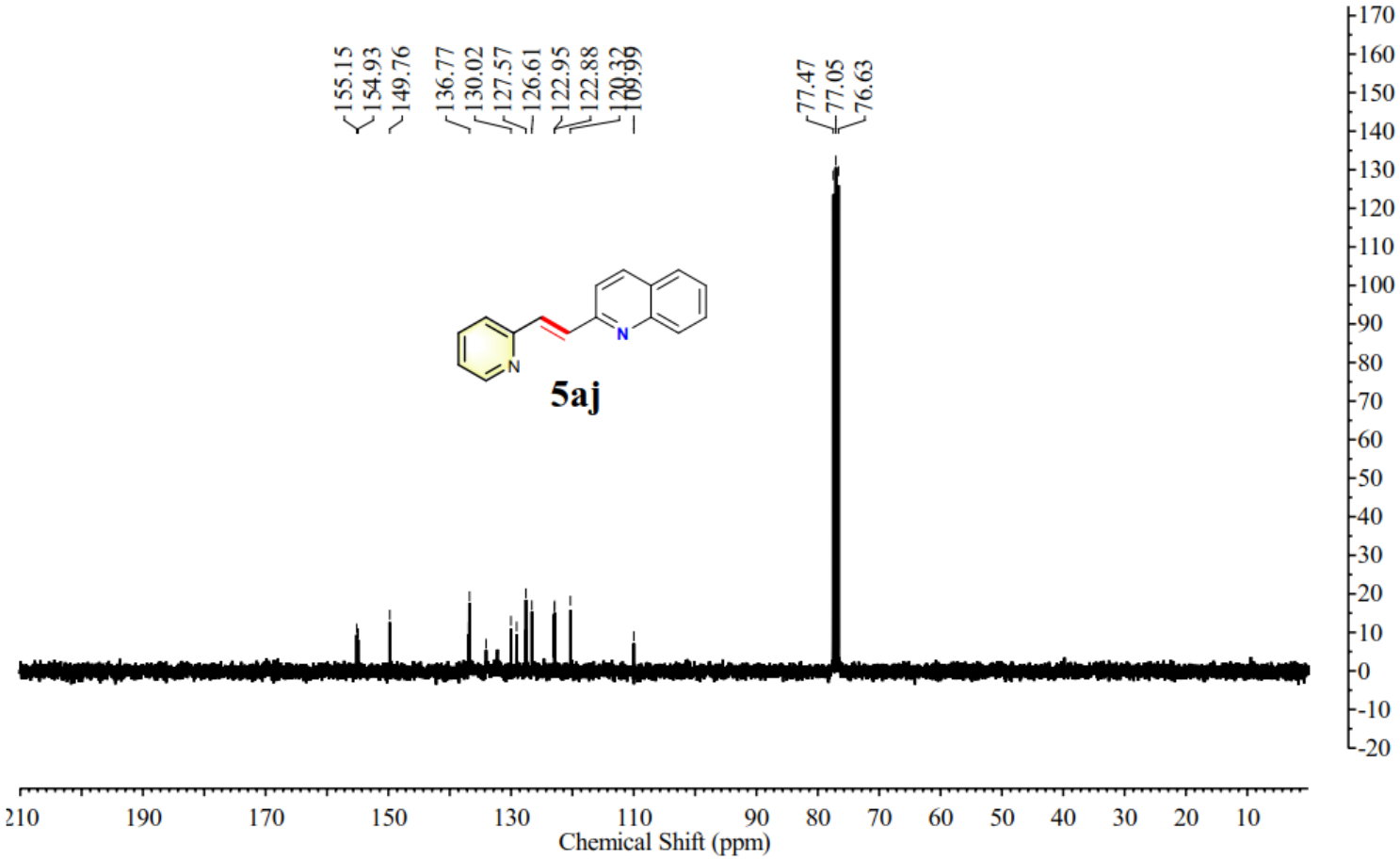
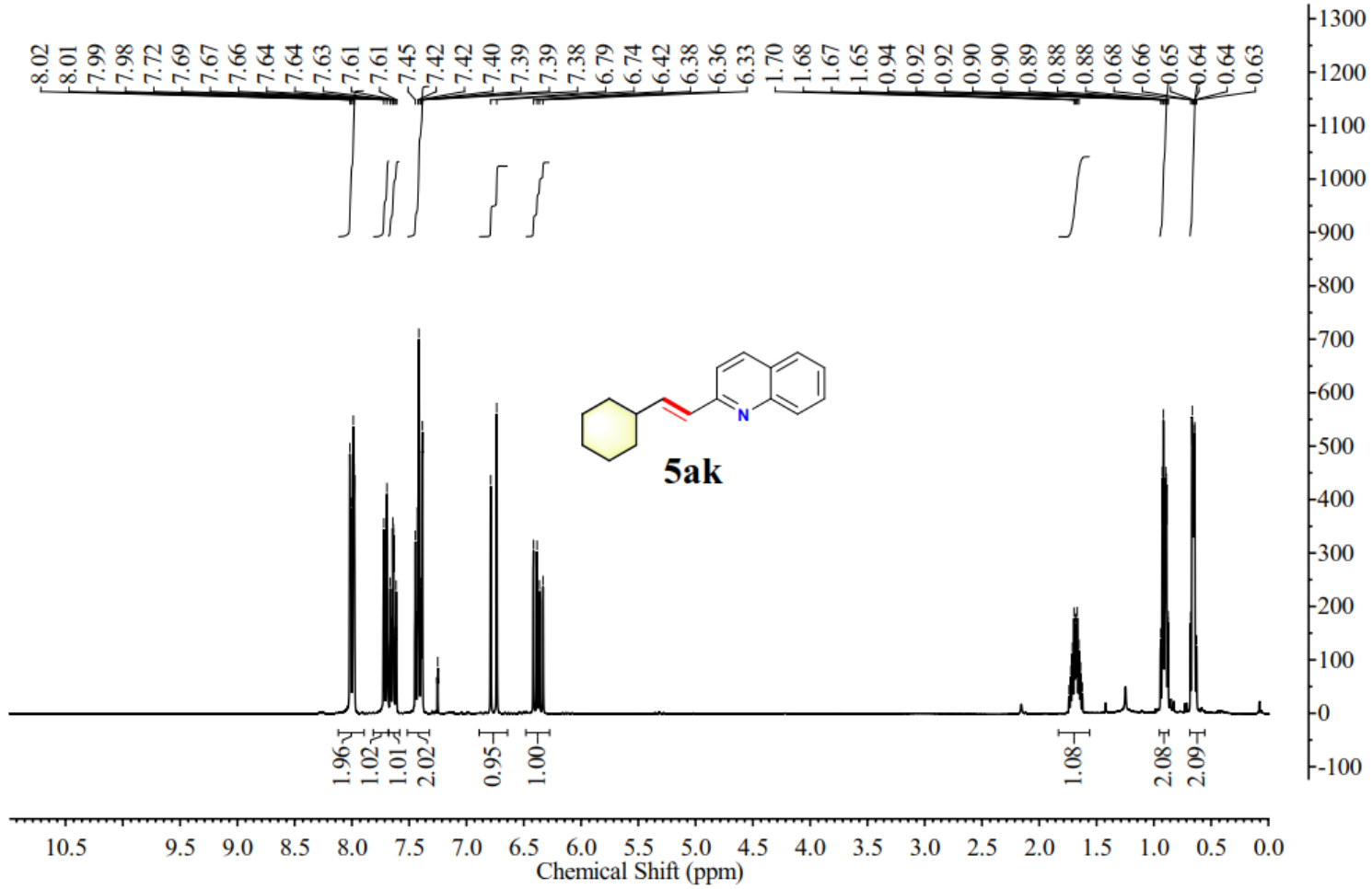
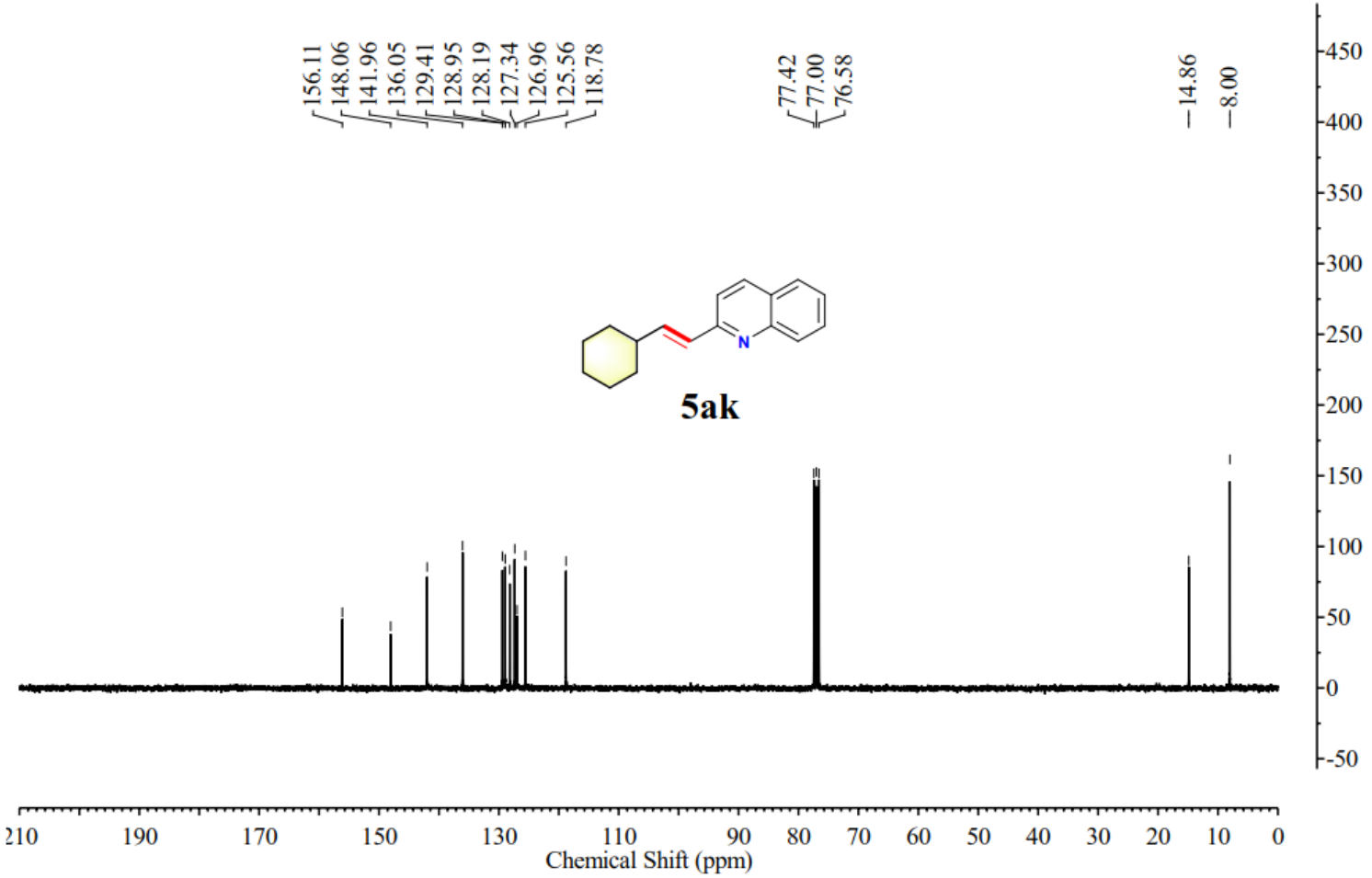
8.17
7.91
7.90
7.89
7.89
7.85
7.82
7.78
7.76
7.76
7.75
7.73
7.72
7.71
7.64
7.62
7.58
7.56
7.53
7.29
7.28
7.26
7.25
7.24
7.22
N
N
5aj
1.00
2.07
2.00
1.13
3.06
1.08
1.09
1.01
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


155.15
154.93
149.76
136.77
130.02
127.57
126.61
122.95
122.88
77.47
77.05
76.63
5aj
Chemical Shift (ppm)


8.02
8.01
7.99
7.98
7.72
7.69
7.67
7.66
7.64
7.64
7.63
7.61
7.61
7.45
7.42
7.42
7.40
7.39
7.39
7.38
6.79
6.74
6.42
6.38
6.36
6.33
1.70
1.68
1.67
1.65
0.94
0.92
0.92
0.90
0.90
0.89
0.88
0.88
0.68
0.66
0.65
0.64
0.64
0.63
N
5ak
1.96
1.02
1.01
2.02
0.95
1.00
1.08
2.08
2.09
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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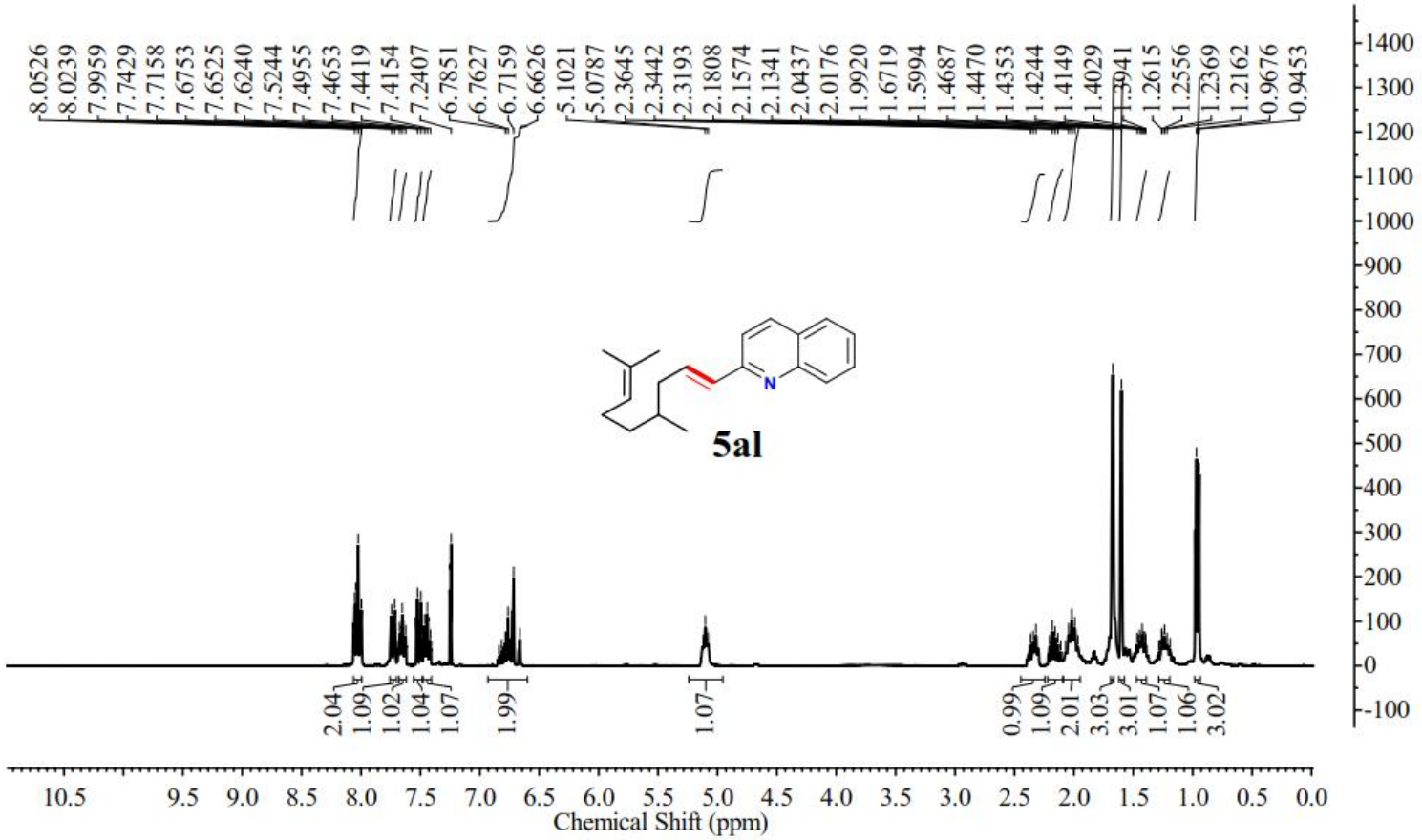
148.06
141.96
136.05
129.41
128.95
128.19
127.34
126.96
125.56
118.78
77.42
77.00
76.58
14.86
8.00
N
5ak
450
400
350
300
250
200
150
100
50
0
-50
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.0526
8.0239
7.9959
7.7429
7.7158
7.6753
7.6525
7.6240
7.5244
7.4955
7.4653
7.4419
7.4154
7.2407
6.7851
6.7627
6.7159
6.6626
5.1021
5.0787
2.3645
2.3442
2.3193
2.1808
2.1574
2.1341
2.0437
2.0176
1.9920
1.6719
1.5994
1.4687
1.4470
1.4353
1.4244
1.4149
1.4029
1.3941
1.2615
1.2556
1.2369
1.2162
0.9676
0.9453
N
5al
2.04
1.09
1.02
1.04
1.07
1.99
1.07
0.99
1.09
2.01
3.03
3.01
1.07
1.06
3.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)
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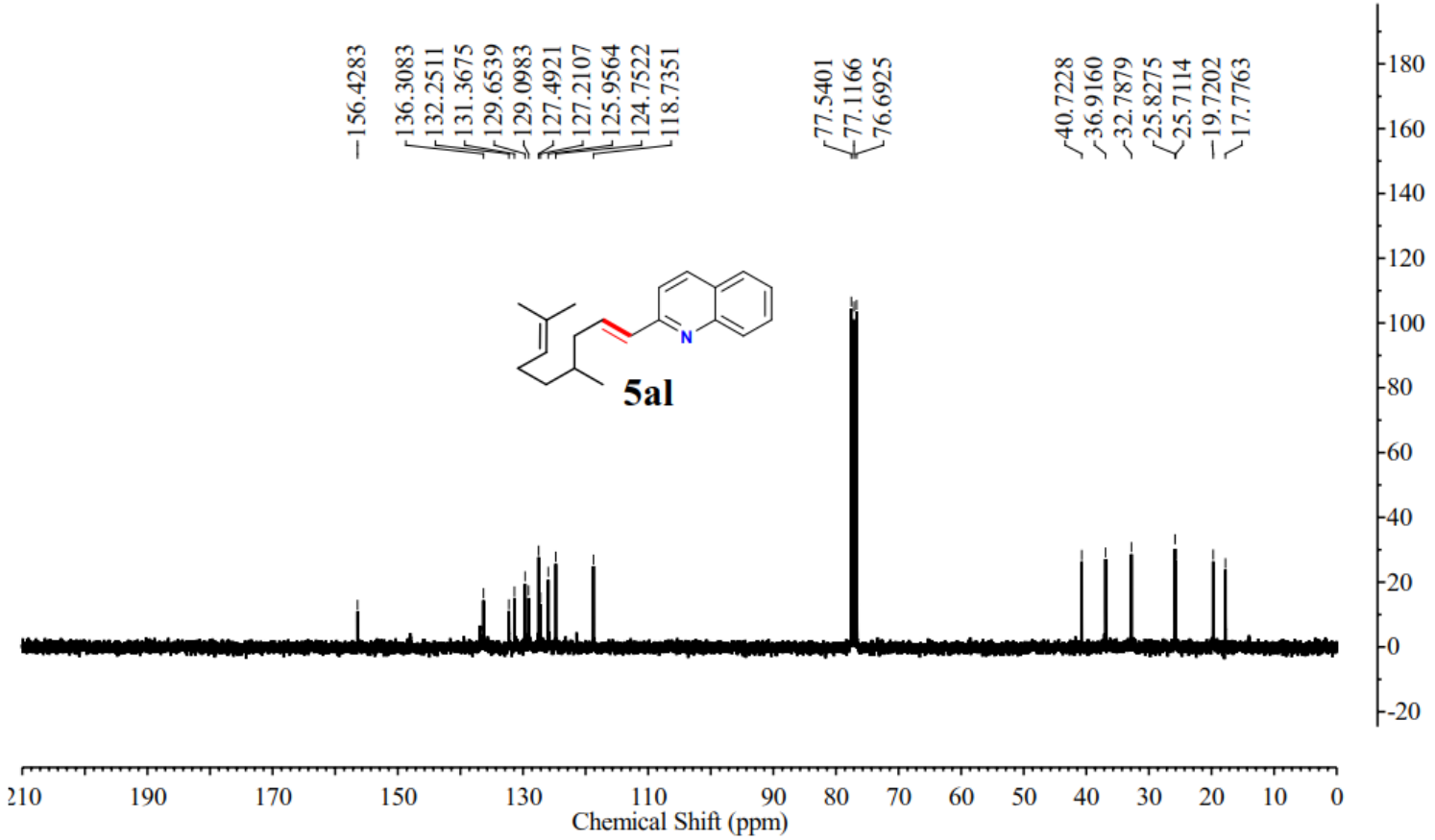
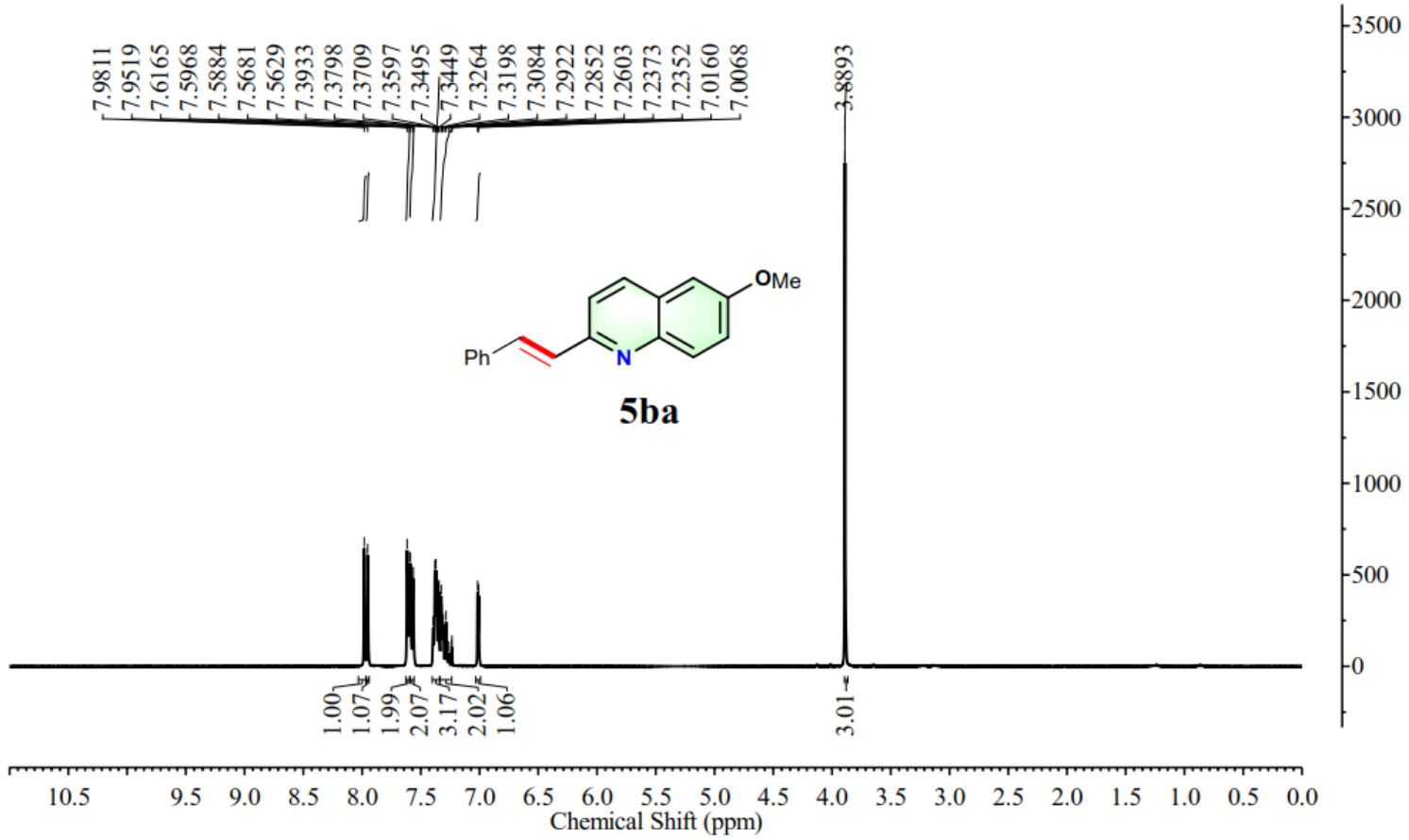
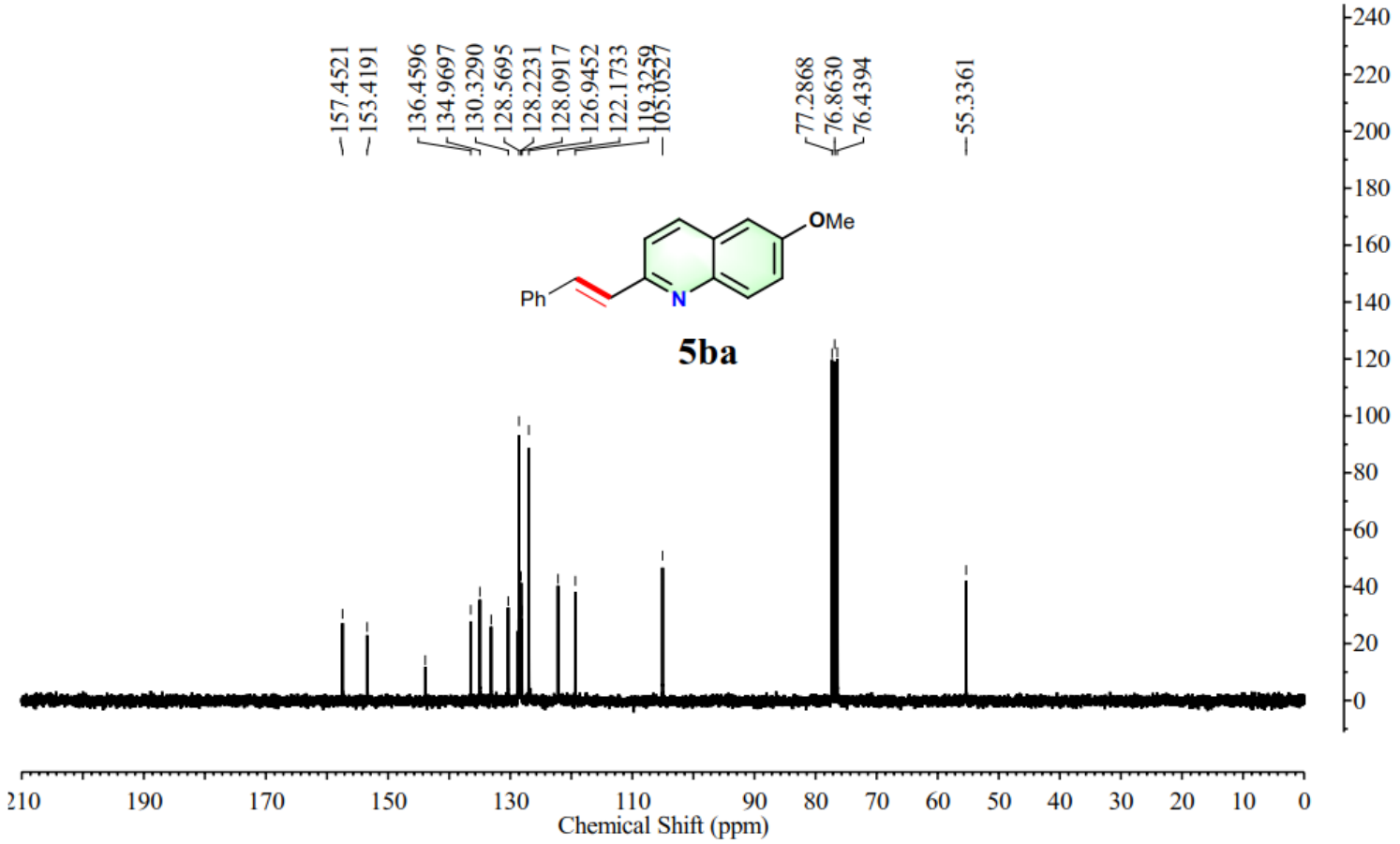
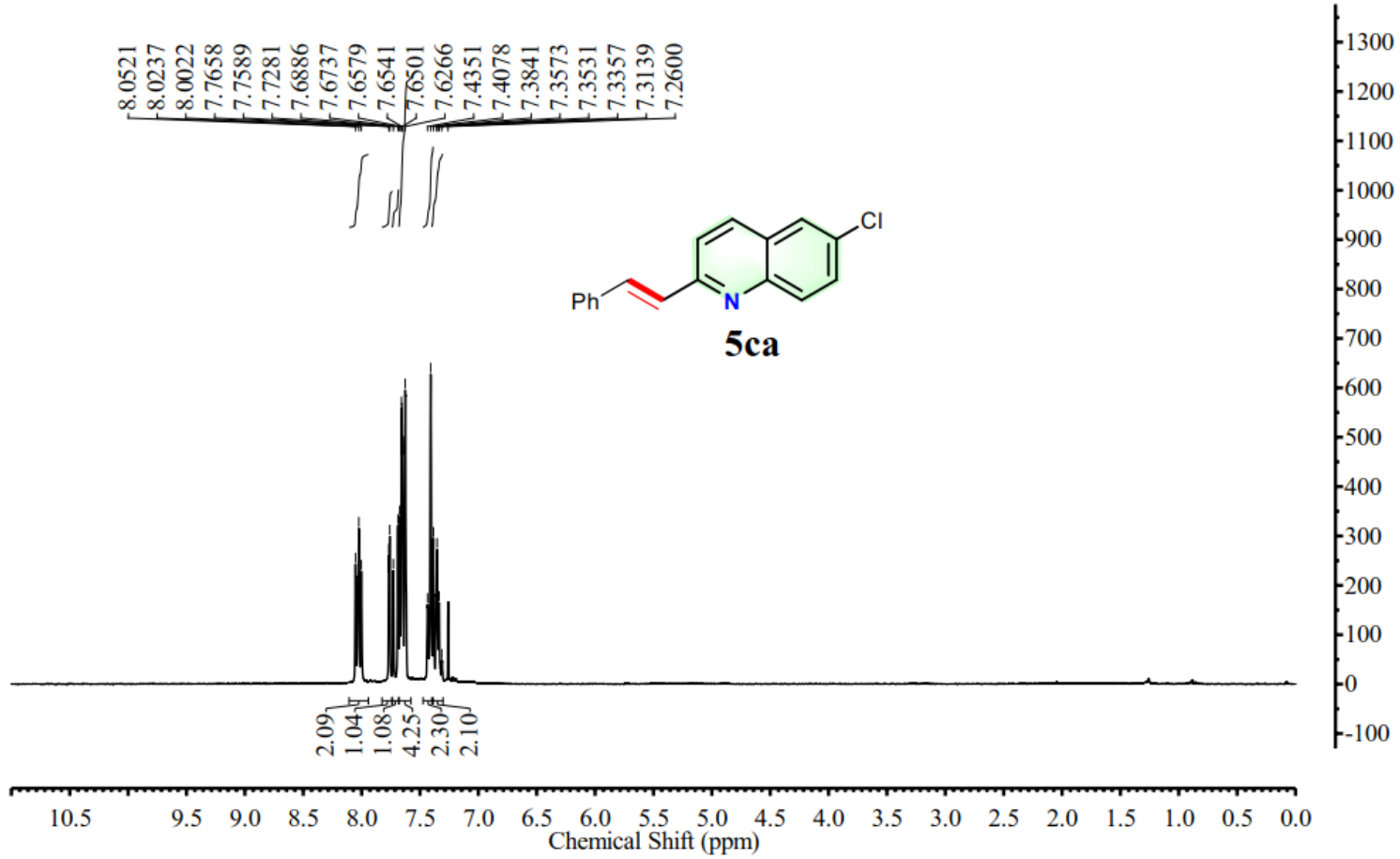
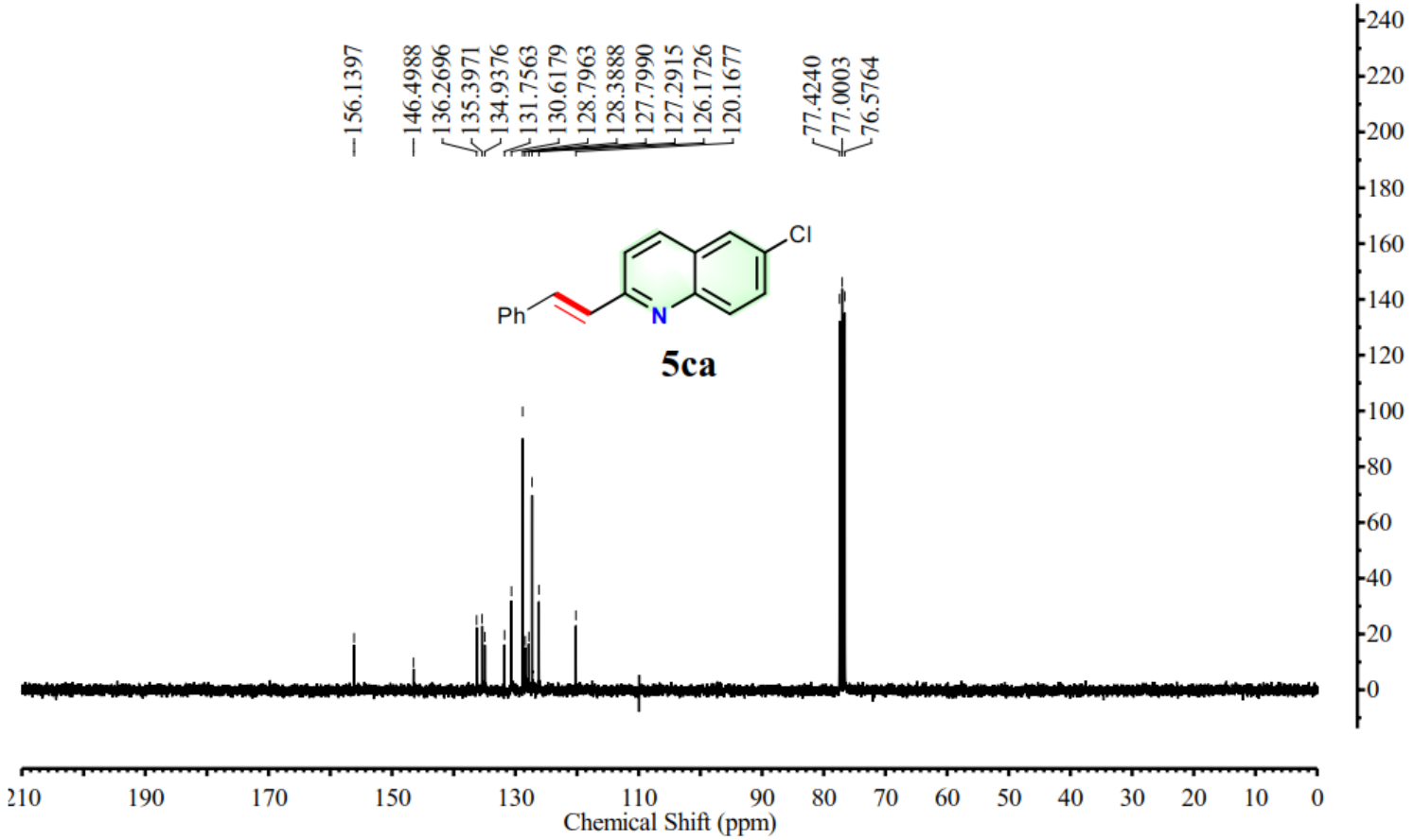
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

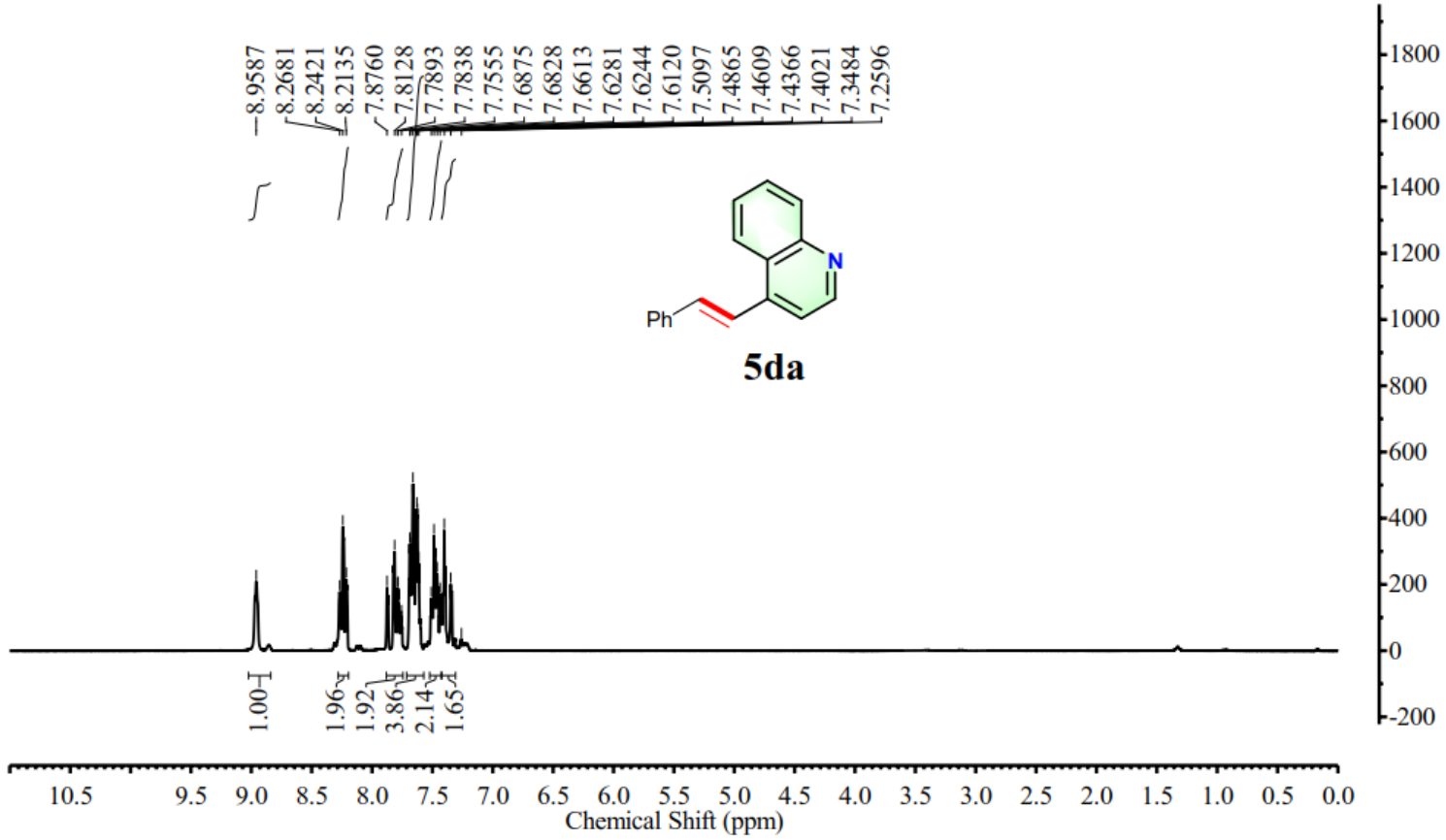

156.4283
136.3083
132.2511
131.3675
129.6539
129.0983
127.4921
127.2107
125.9564
124.7522
118.7351
77.5401
77.1166
76.6925
40.7228
36.9160
32.7879
25.8275
25.7114
19.7202
17.7763
N
5al
180
160
140
120
100
80
60
40
20
0
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

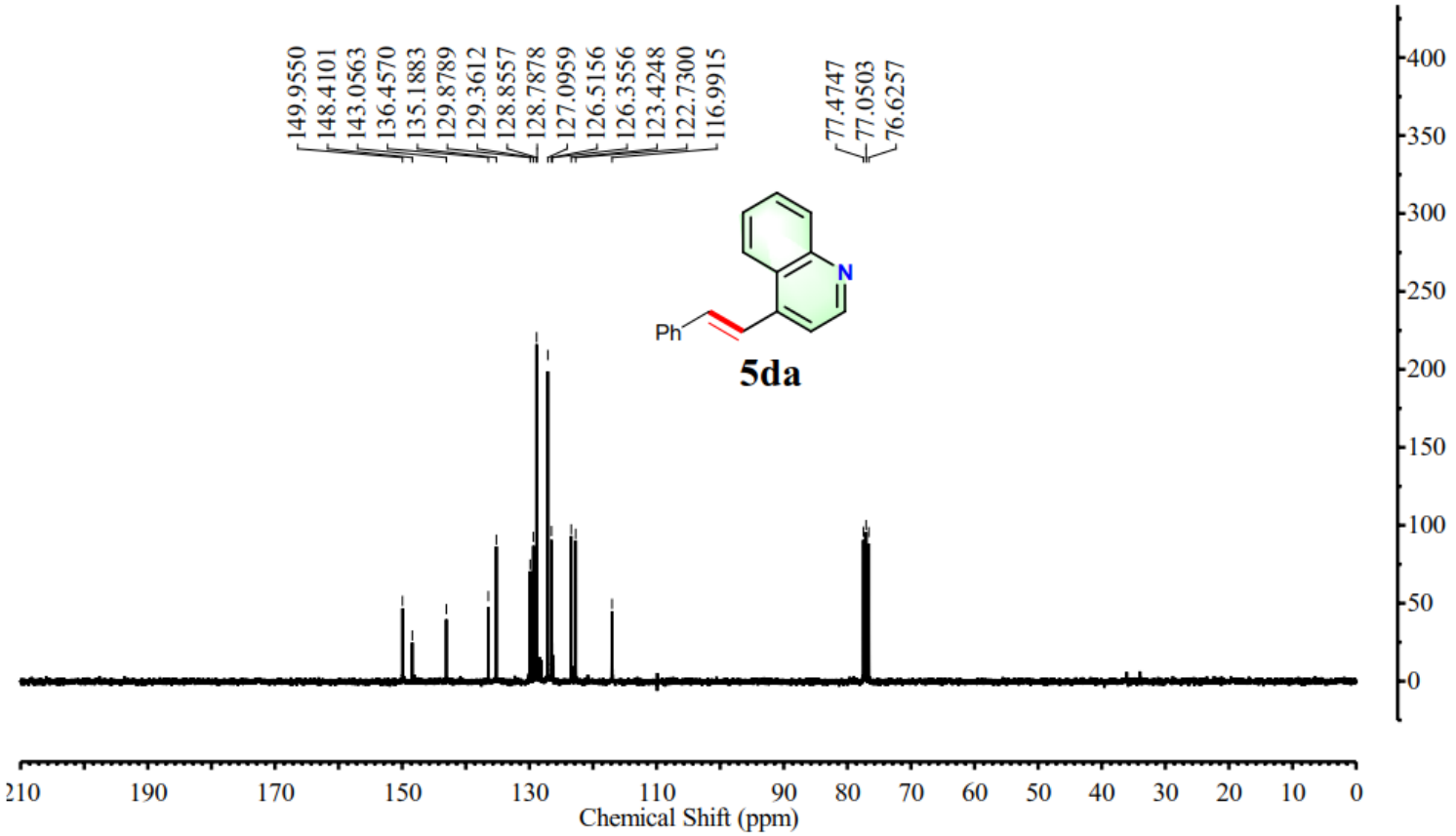

7.9811
7.9519
7.6165
7.5968
7.5884
7.5681
7.5629
7.3933
7.3798
7.3709
7.3597
7.3495
7.3449
7.3264
7.3198
7.3084
7.2922
7.2852
7.2603
7.2373
7.2352
7.0160
7.0068
3.8893
OMe
Ph
N
5ba
1.00
1.07
1.99
2.07
3.17
2.02
1.06
3.01
3500
3000
2500
2000
1500
1000
500
0
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


157.4521
153.4191
136.4596
134.9697
130.3290
128.5695
128.2231
128.0917
126.9452
122.1733
119.3259
105.0527
77.2868
76.8630
76.4394
55.3361
OMe
Ph
N
5ba
240
220
200
180
160
140
120
100
80
60
40
20
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.0521
8.0237
8.0022
7.7658
7.7589
7.7281
7.6886
7.6737
7.6579
7.6541
7.6501
7.6266
7.4351
7.4078
7.3841
7.3573
7.3531
7.3357
7.3139
7.2600
Cl
Ph
N
5ca
2.09
1.04
1.08
4.25
2.30
2.10
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


156.1397
146.4988
136.2696
135.3971
134.9376
131.7563
130.6179
128.7963
128.3888
127.7990
127.2915
126.1726
120.1677
77.4240
77.0003
76.5764
Cl
Ph
N
5ca
240
220
200
180
160
140
120
100
80
60
40
20
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.9587
8.2681
8.2421
8.2135
7.8760
7.8128
7.7893
7.7838
7.7555
7.6875
7.6828
7.6613
7.6281
7.6244
7.6120
7.5097
7.4865
7.4609
7.4366
7.4021
7.3484
7.2596
N
Ph
5da
1.00
1.96
1.92
3.86
2.14
1.65
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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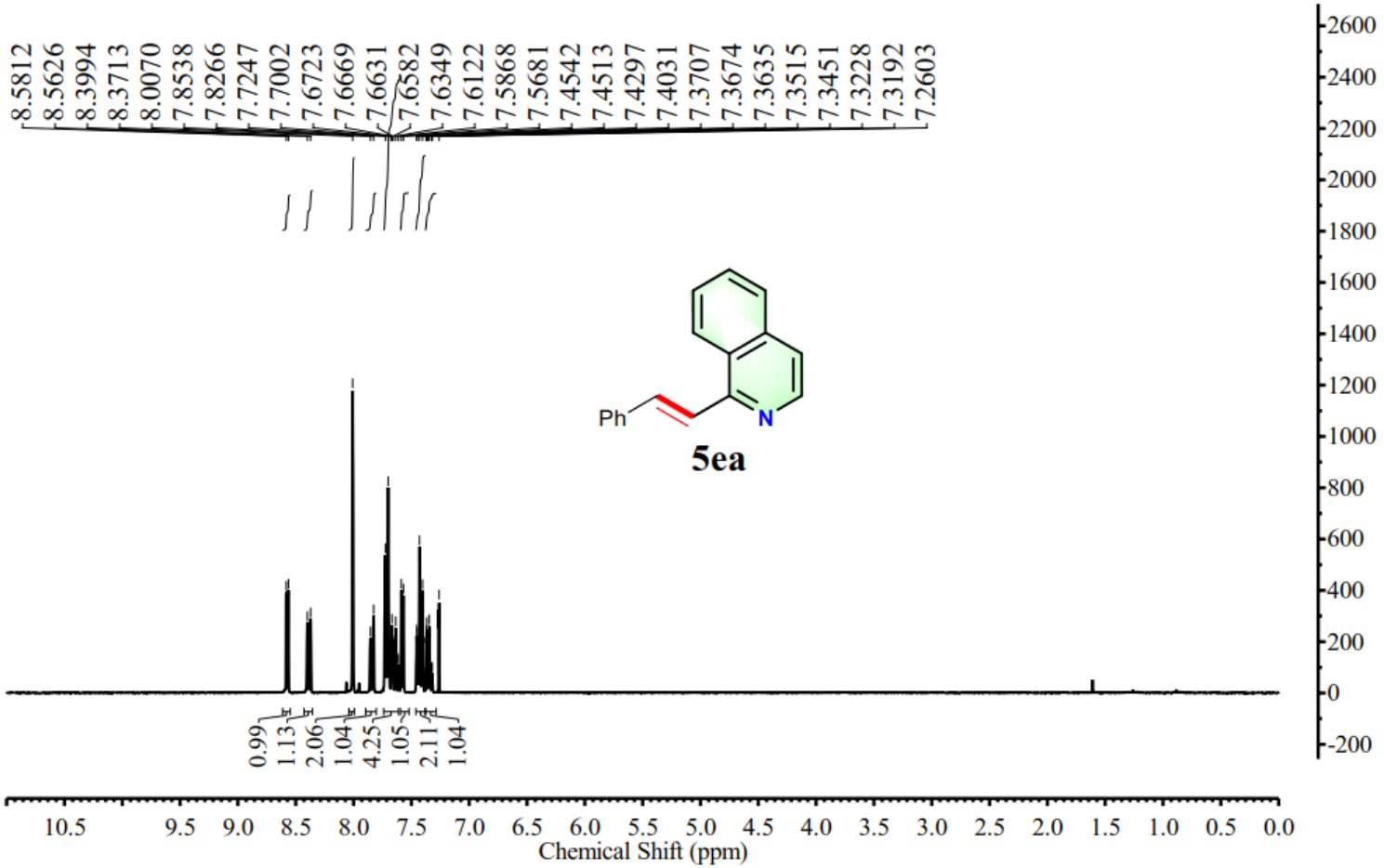
148.4101
143.0563
136.4570
135.1883
129.8789
129.3612
128.8557
128.7878
127.0959
126.5156
126.3556
123.4248
122.7300
116.9915
77.4747
77.0503
76.6257
N
Ph
5da
400
350
300
250
200
150
100
50
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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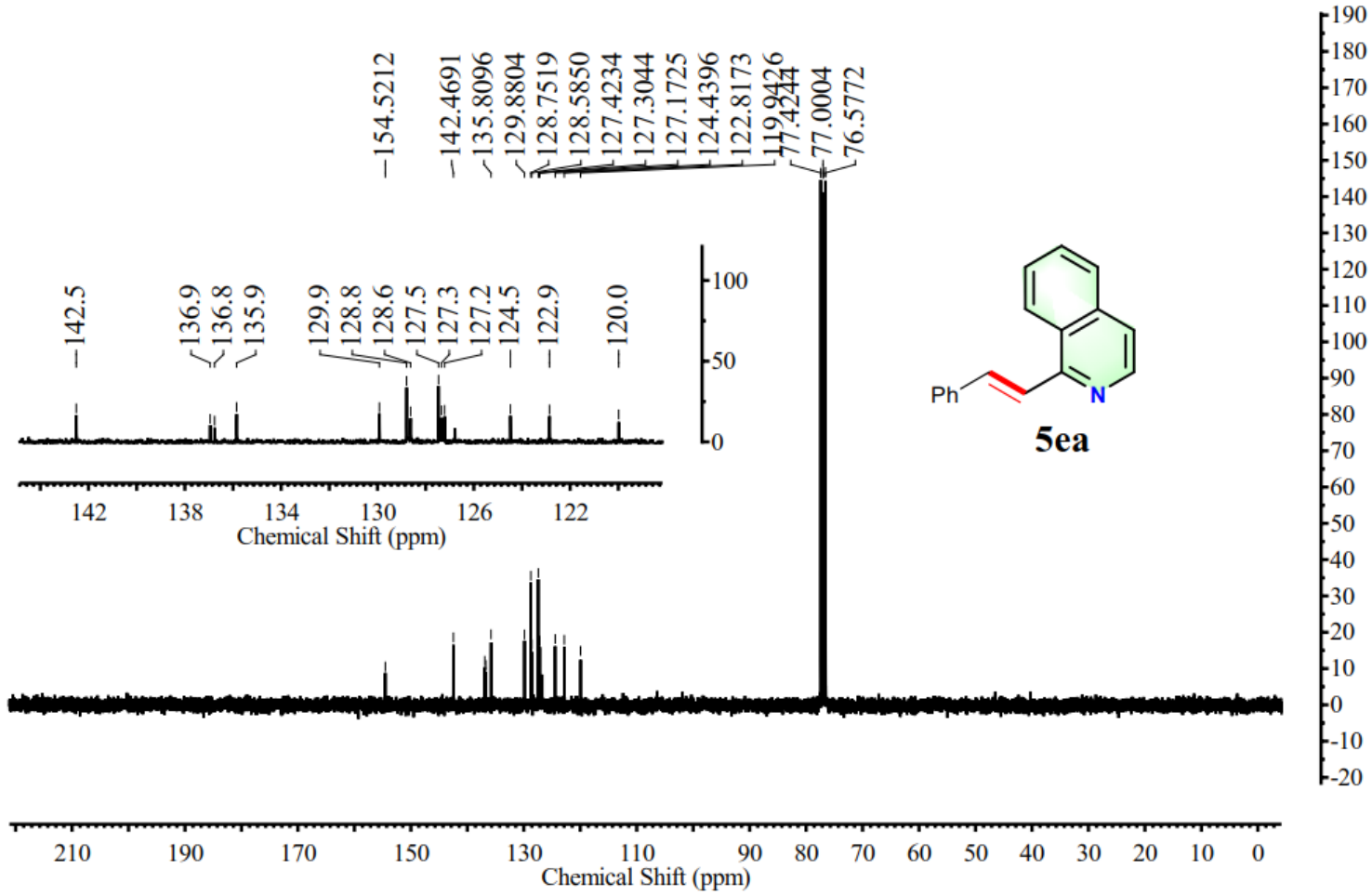
8.3994
8.3713
8.0070
7.8538
7.8266
7.7247
7.7002
7.6723
7.6669
7.6631
7.6582
7.6349
7.6122
7.5868
7.5681
7.4542
7.4513
7.4297
7.4031
7.3707
7.3674
7.3635
7.3515
7.3451
7.3228
7.3192
7.2603
Ph
N
5ea
0.99
1.13
2.06
1.04
4.25
1.05
2.11
1.04
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)


154.5212
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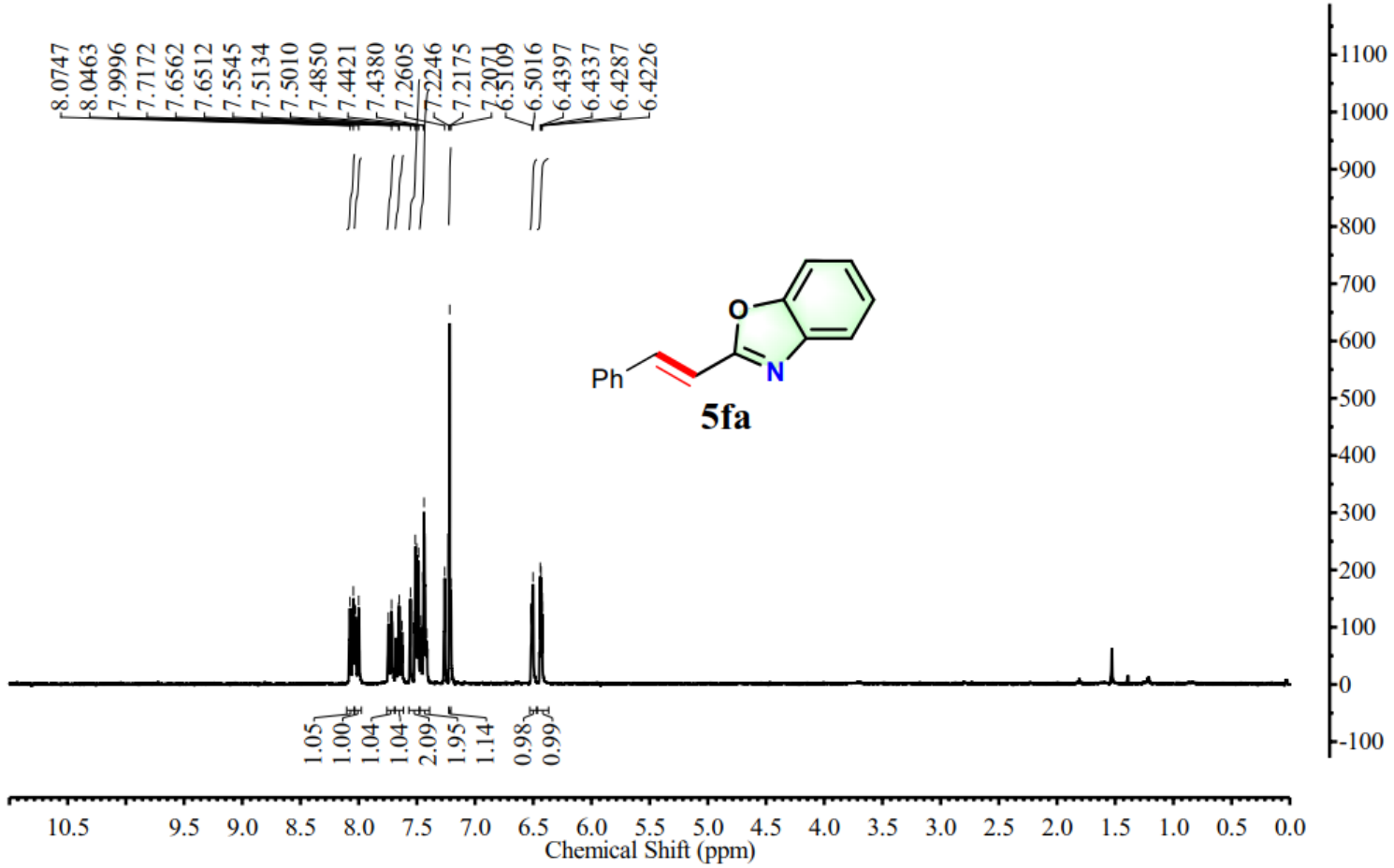
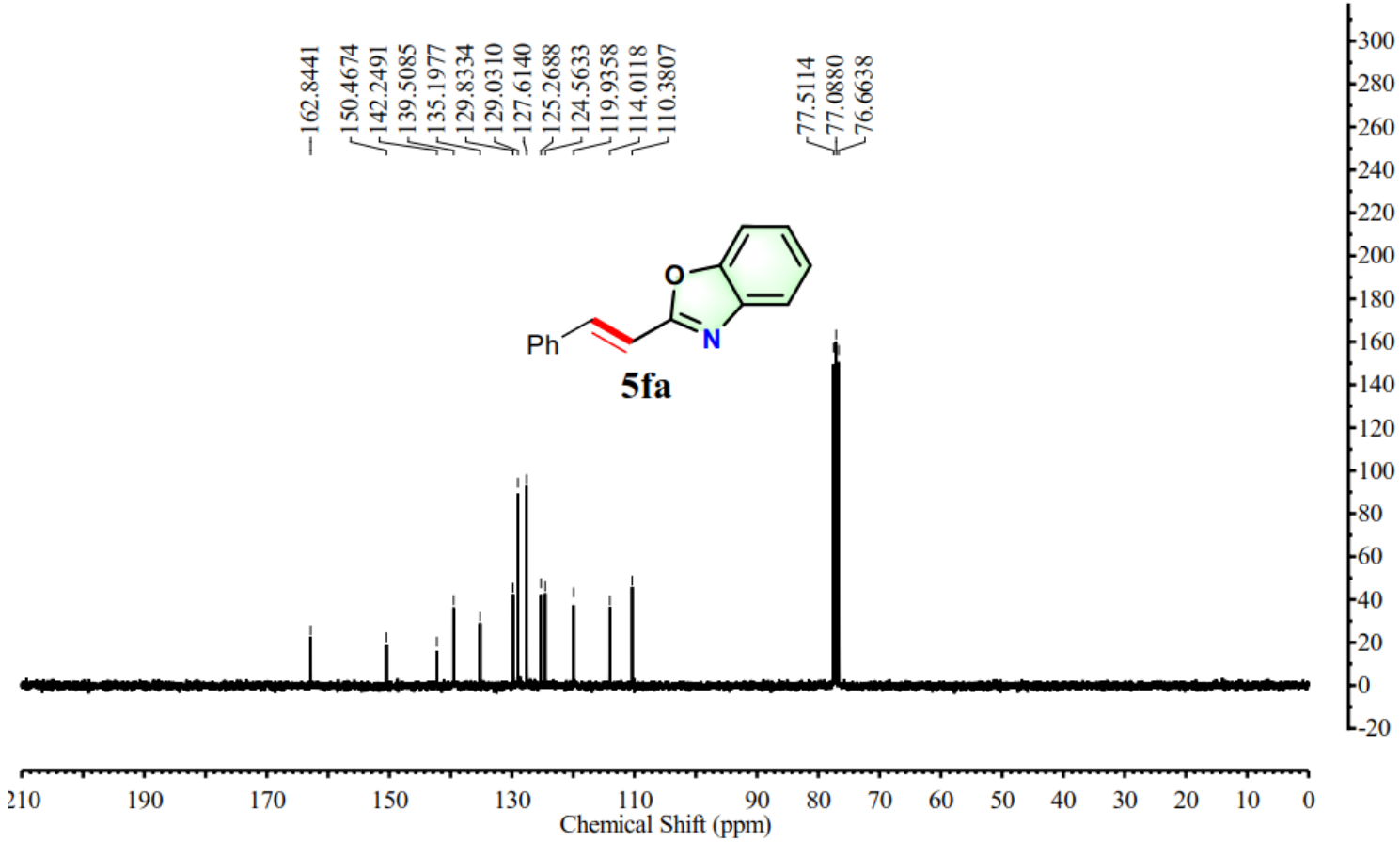
129.8804
128.7519
128.5850
127.4234
127.3044
127.1725
124.4396
122.8173
119.9426
77.4244
77.0004
76.5772
142.5
136.9
136.8
135.9
129.9
128.8
128.6
127.5
127.3
127.2
124.5
122.9
120.0
Chemical Shift (ppm)
Ph
N
5ea
Chemical Shift (ppm)


8.0747
8.0463
7.9996
7.7172
7.6562
7.6512
7.5545
7.5134
7.5010
7.4850
7.4421
7.4380
7.2605
7.2246
7.2175
7.2071
6.5109
6.5016
6.4397
6.4337
6.4287
6.4226
O
N
Ph
5fa
1.05
1.00
1.04
1.04
2.09
1.95
1.14
0.98
0.99
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical Shift (ppm)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135.1977
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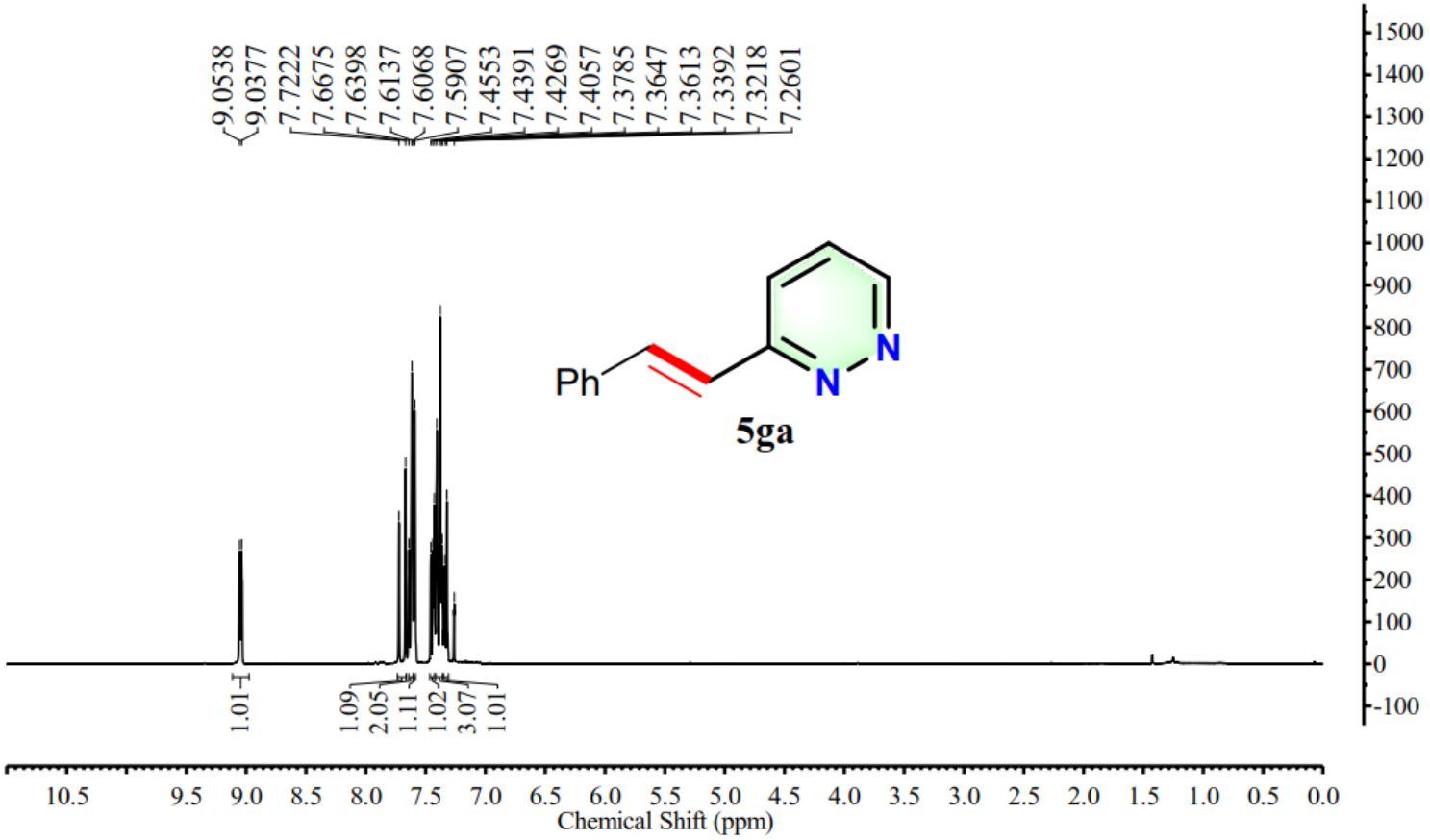
127.6140
125.2688
124.5633
119.9358
114.0118
110.3807
77.5114
77.0880
76.6638
O
N
Ph
5fa
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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9.0377
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7.6398
7.6137
7.6068
7.5907
7.4553
7.4391
7.4269
7.4057
7.3785
7.3647
7.3613
7.3392
7.3218
7.2601
Ph
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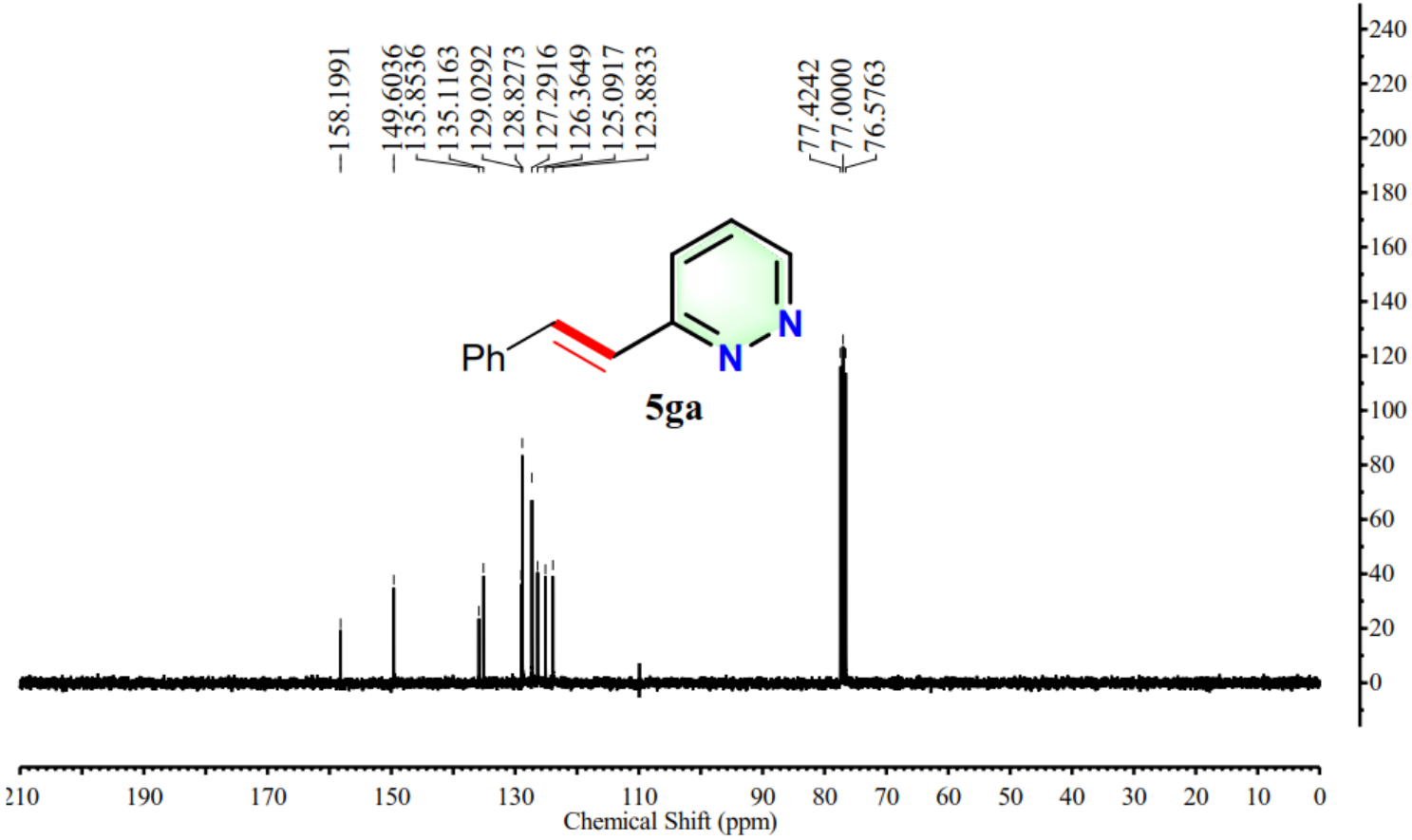
N
5ga
1.01
1.09
2.05
1.11
1.02
3.07
1.01
Chemical Shift (ppm)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135.8536
135.1163
129.0292
128.8273
127.2916
126.3649
125.0917
123.8833
77.4242
77.0000
76.5763
Ph
N
N
5ga
240
220
200
180
160
140
120
100
80
60
40
20
0
210
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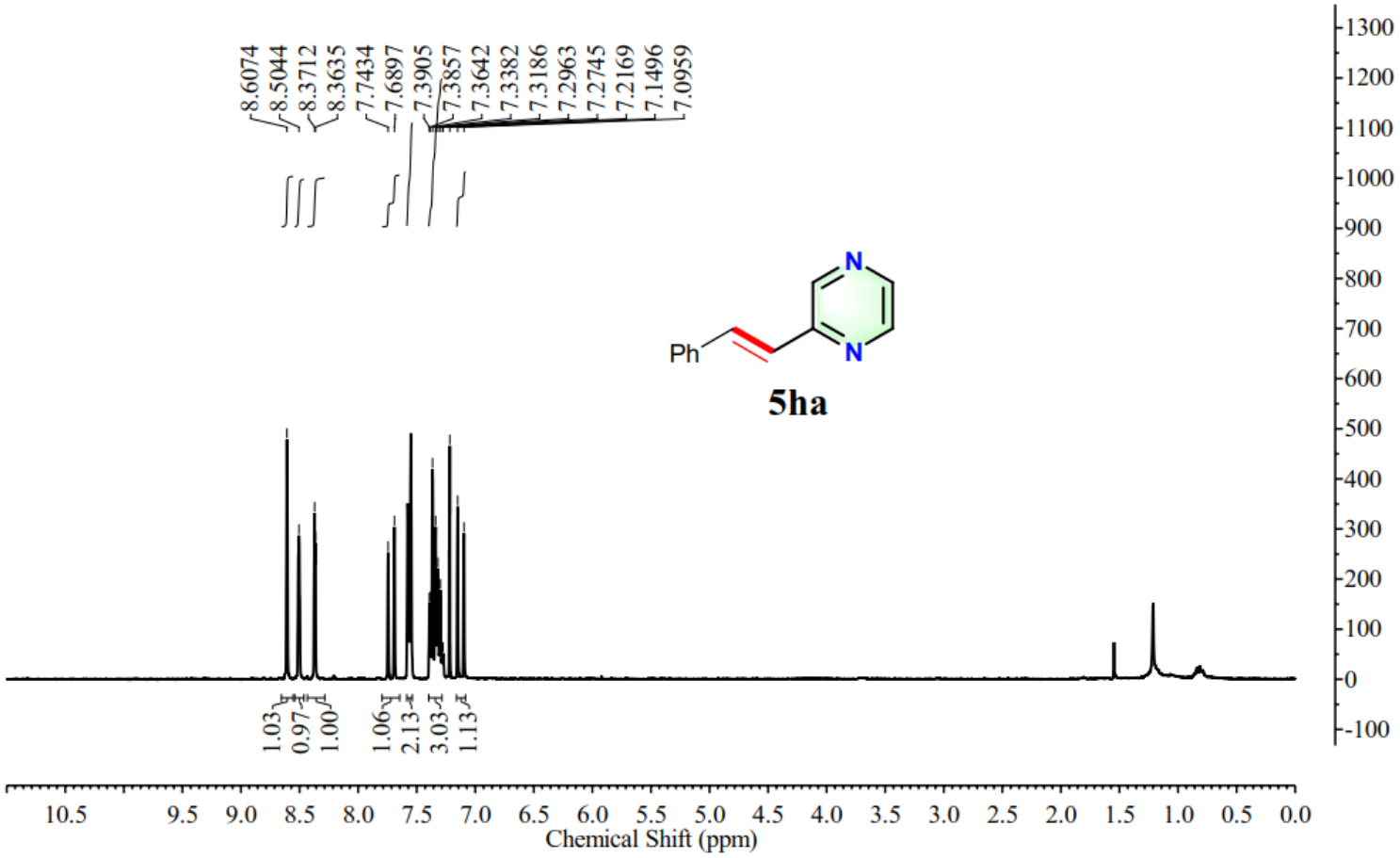
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.6074
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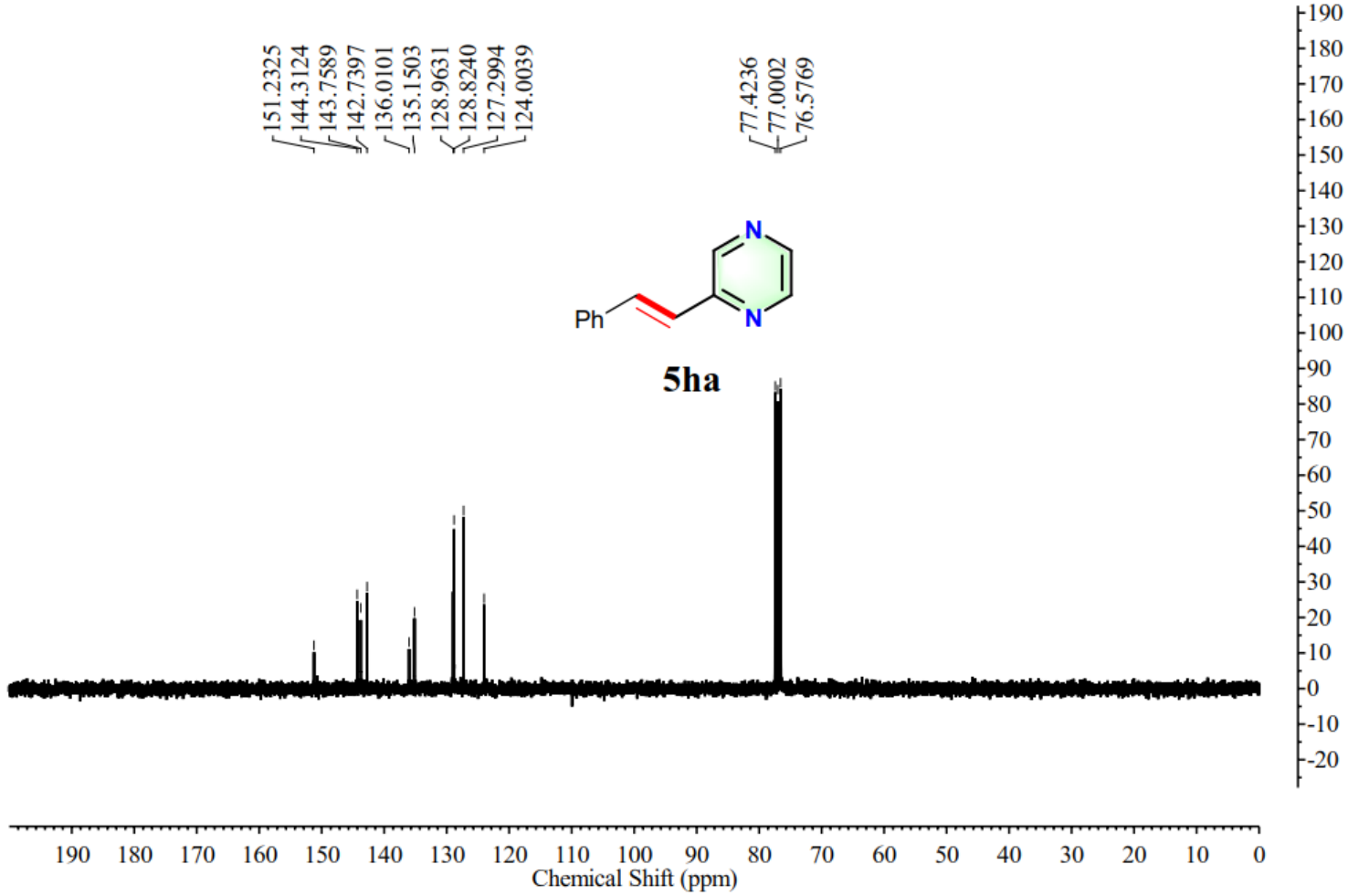
8.3712
8.3635
7.7434
7.6897
7.3905
7.3857
7.3642
7.3382
7.3186
7.2963
7.2745
7.2169
7.1496
7.0959
N
N
Ph
5ha
1.03
0.97
1.00
1.06
2.13
3.03
1.13
Chemical Shift (ppm)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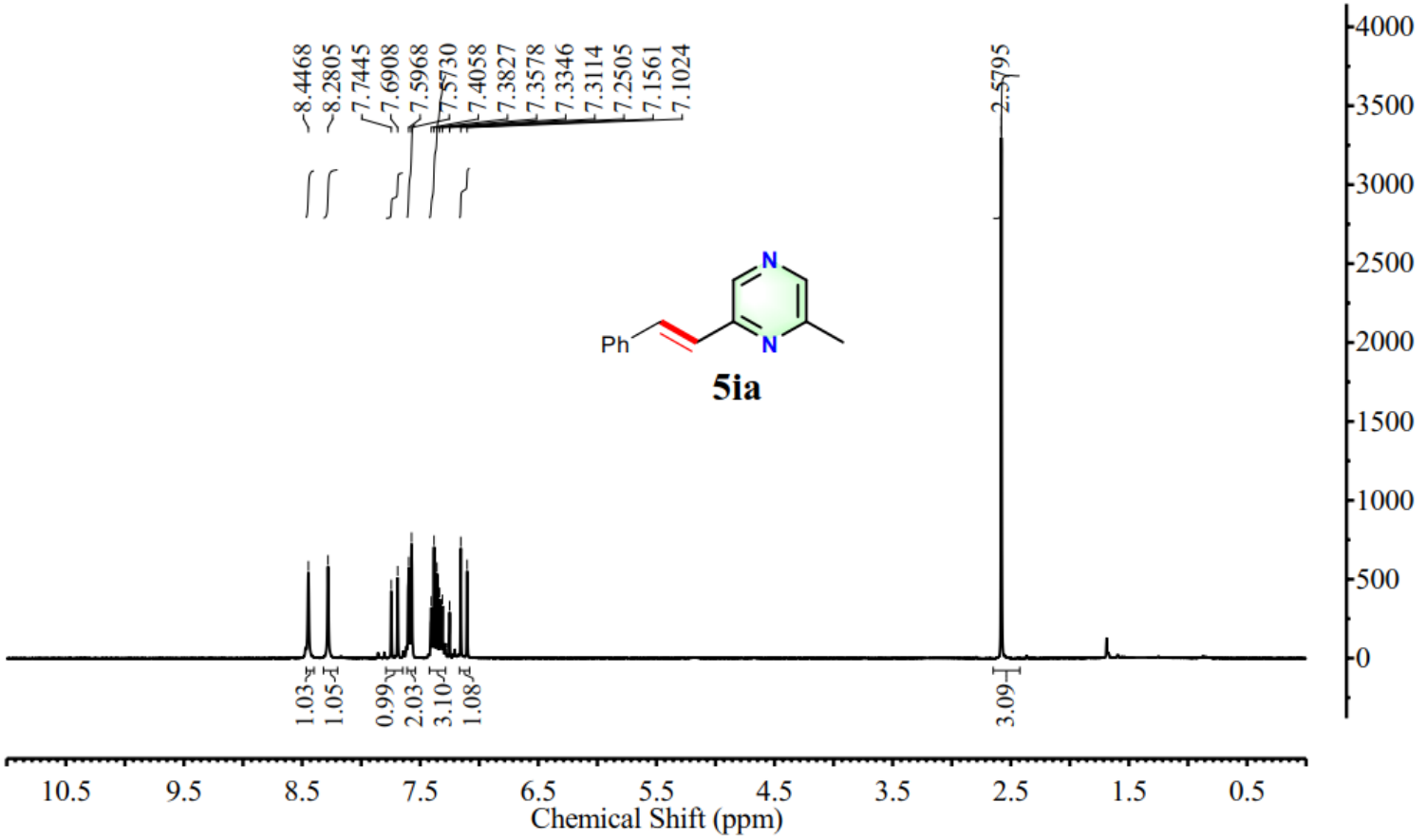
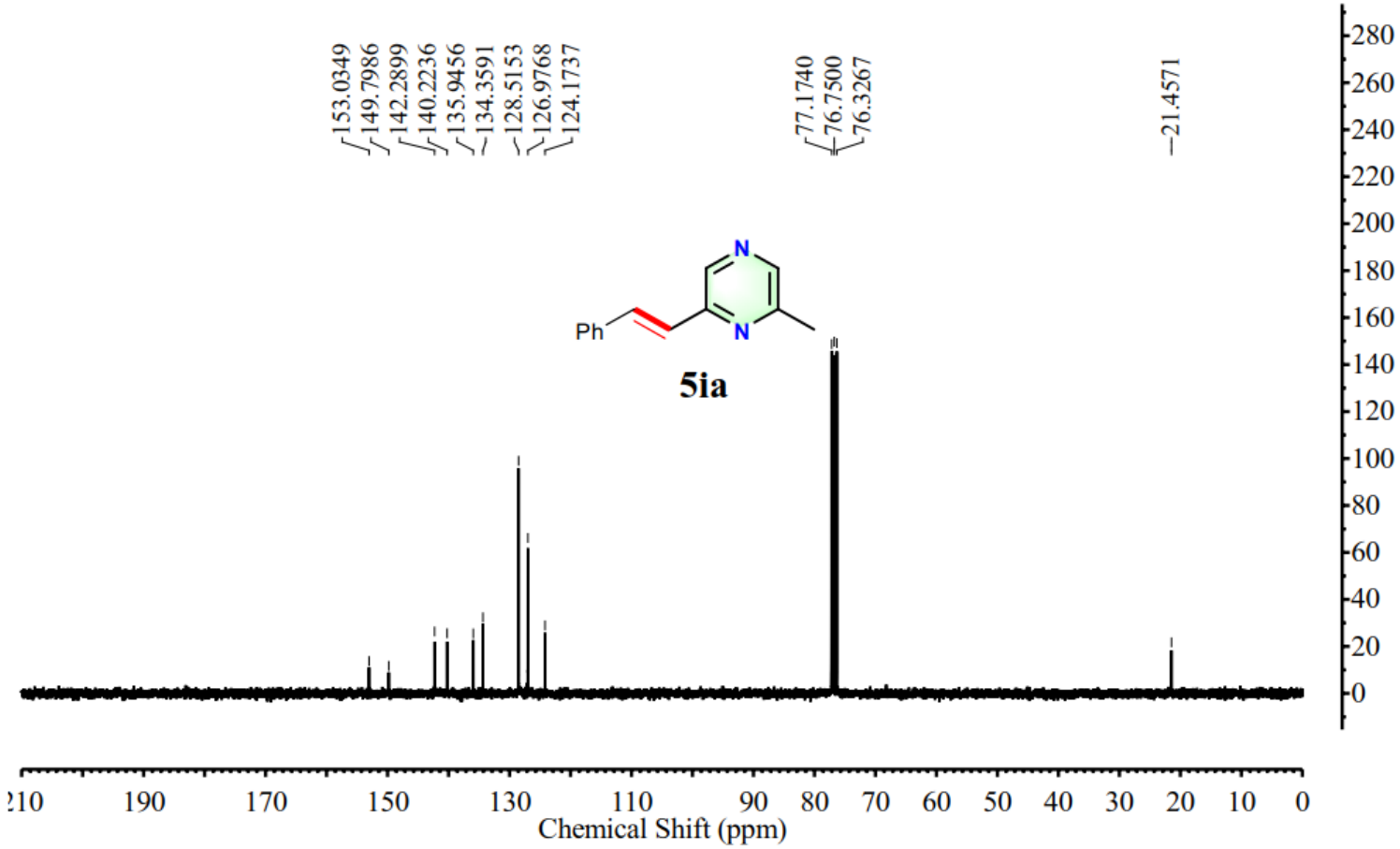
144.3124
143.7589
142.7397
136.0101
135.1503
128.9631
128.8240
127.2994
124.0039
77.4236
77.0002
76.5769
N
N
Ph
5ha
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


8.4468
8.2805
7.7445
7.6908
7.5968
7.5730
7.4058
7.3827
7.3578
7.3346
7.3114
7.2505
7.1561
7.1024
2.5795
N
N
Ph
5ia
1.03
1.05
0.99
2.03
3.10
1.08
3.09
4000
3500
3000
2500
2000
1500
1000
500
0
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)


153.0349
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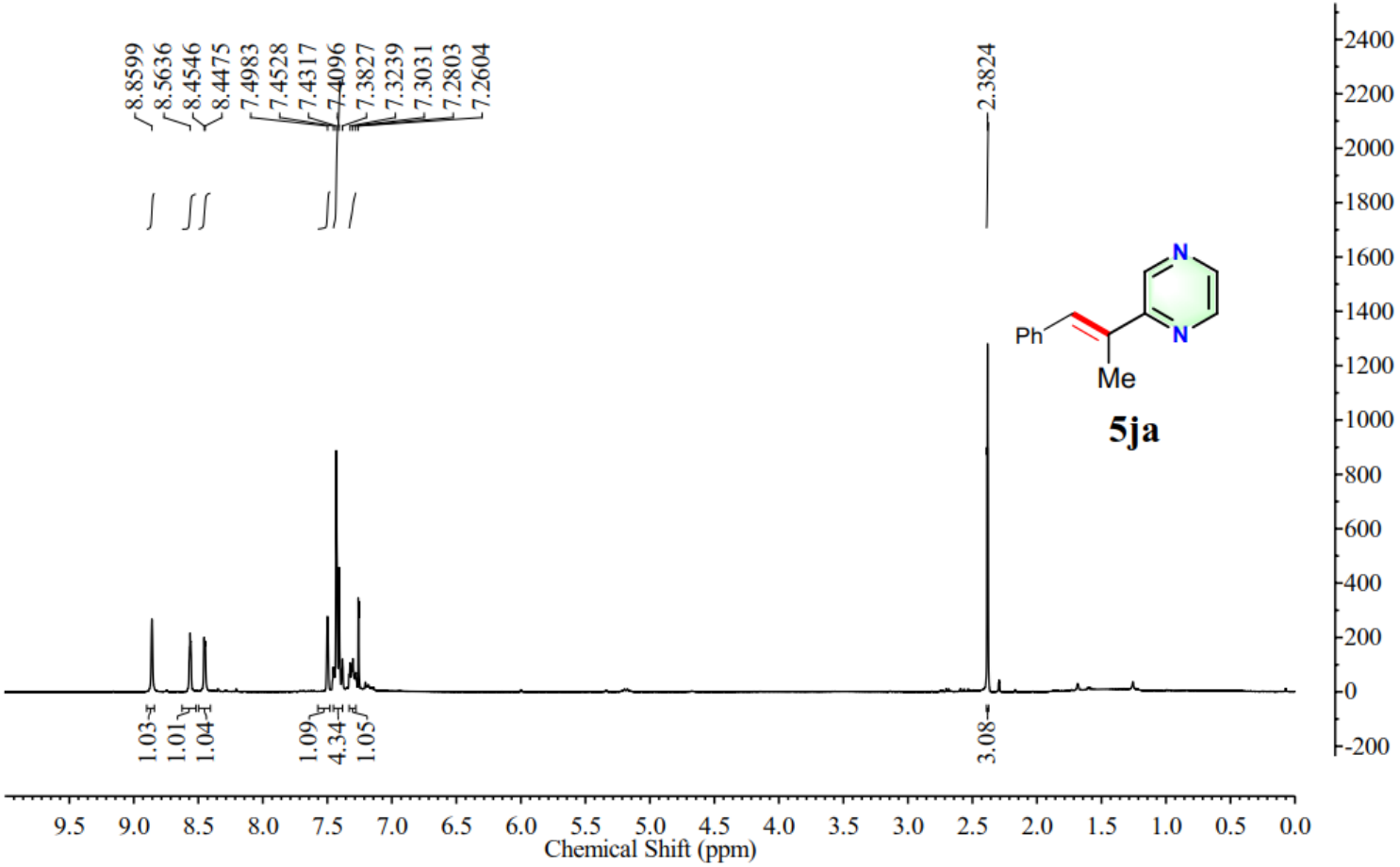
142.2899
140.2236
135.9456
134.3591
128.5153
126.9768
124.1737
77.1740
76.7500
76.3267
21.4571
Ph
N
N
5ia
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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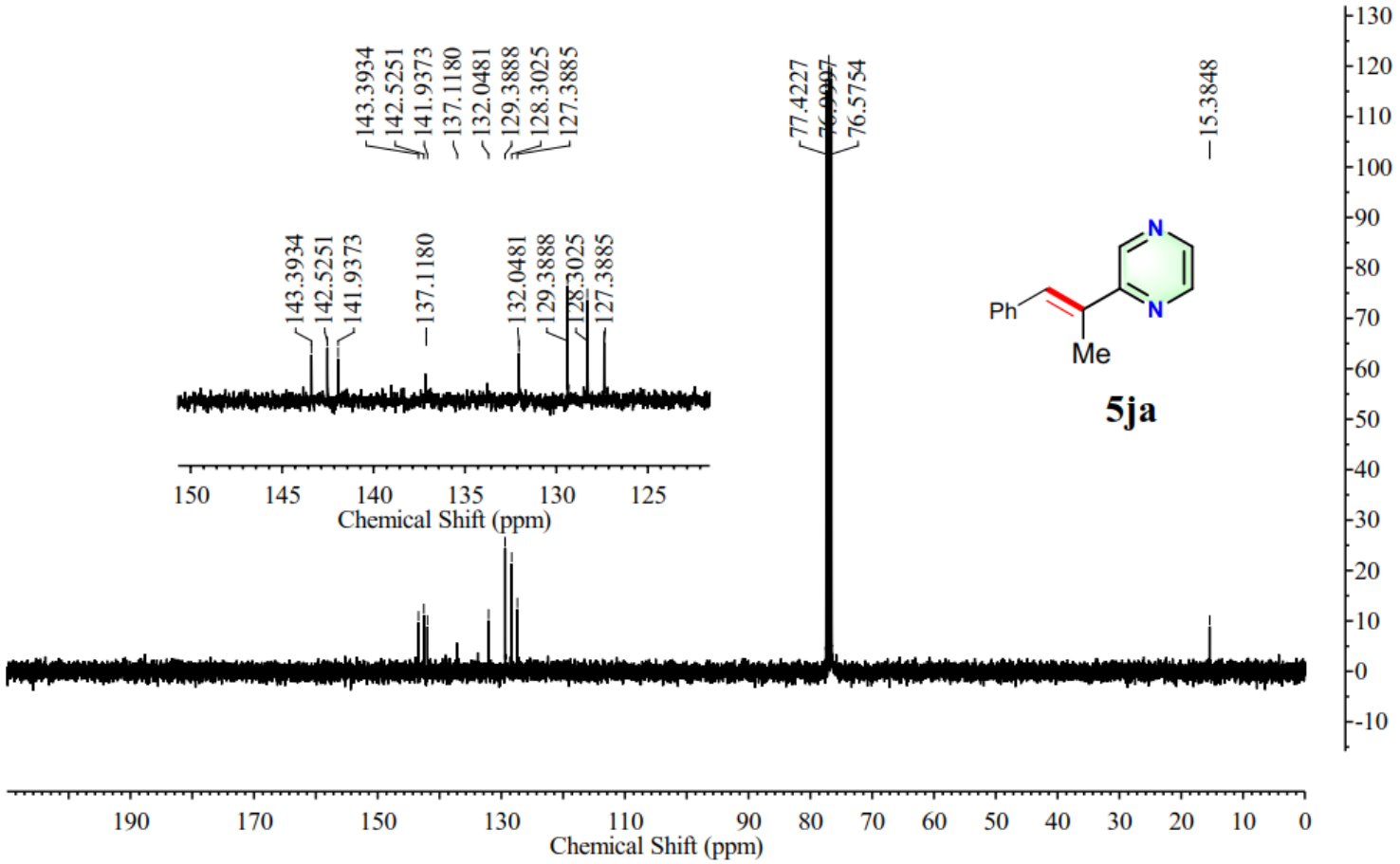
8.5636
8.4546
8.4475
7.4983
7.4528
7.4317
7.4096
7.3827
7.3239
7.3031
7.2803
7.2604
2.3824
1.03
1.01
1.04
1.09
4.34
1.05
3.08
N
N
Ph
Me
5ja
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)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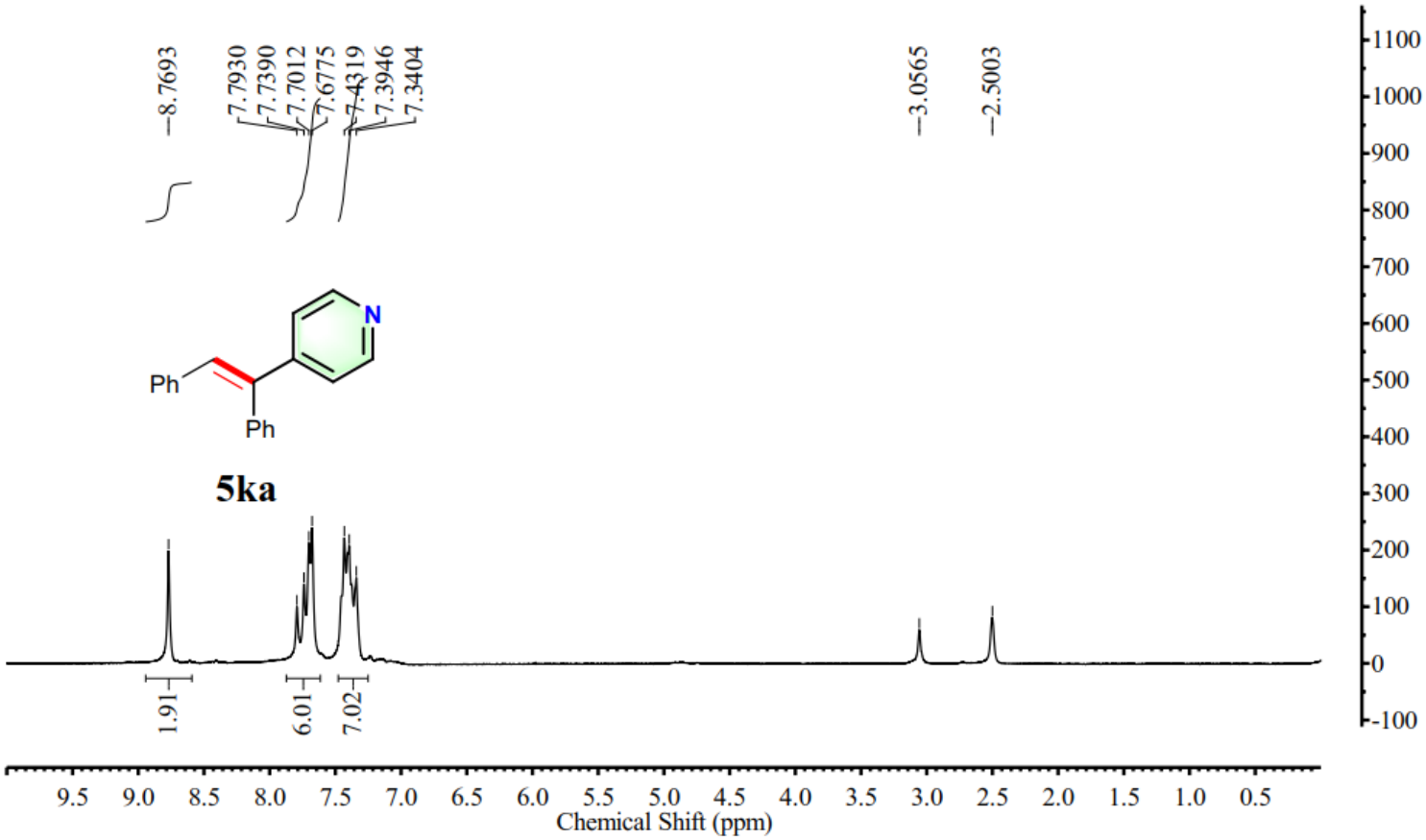
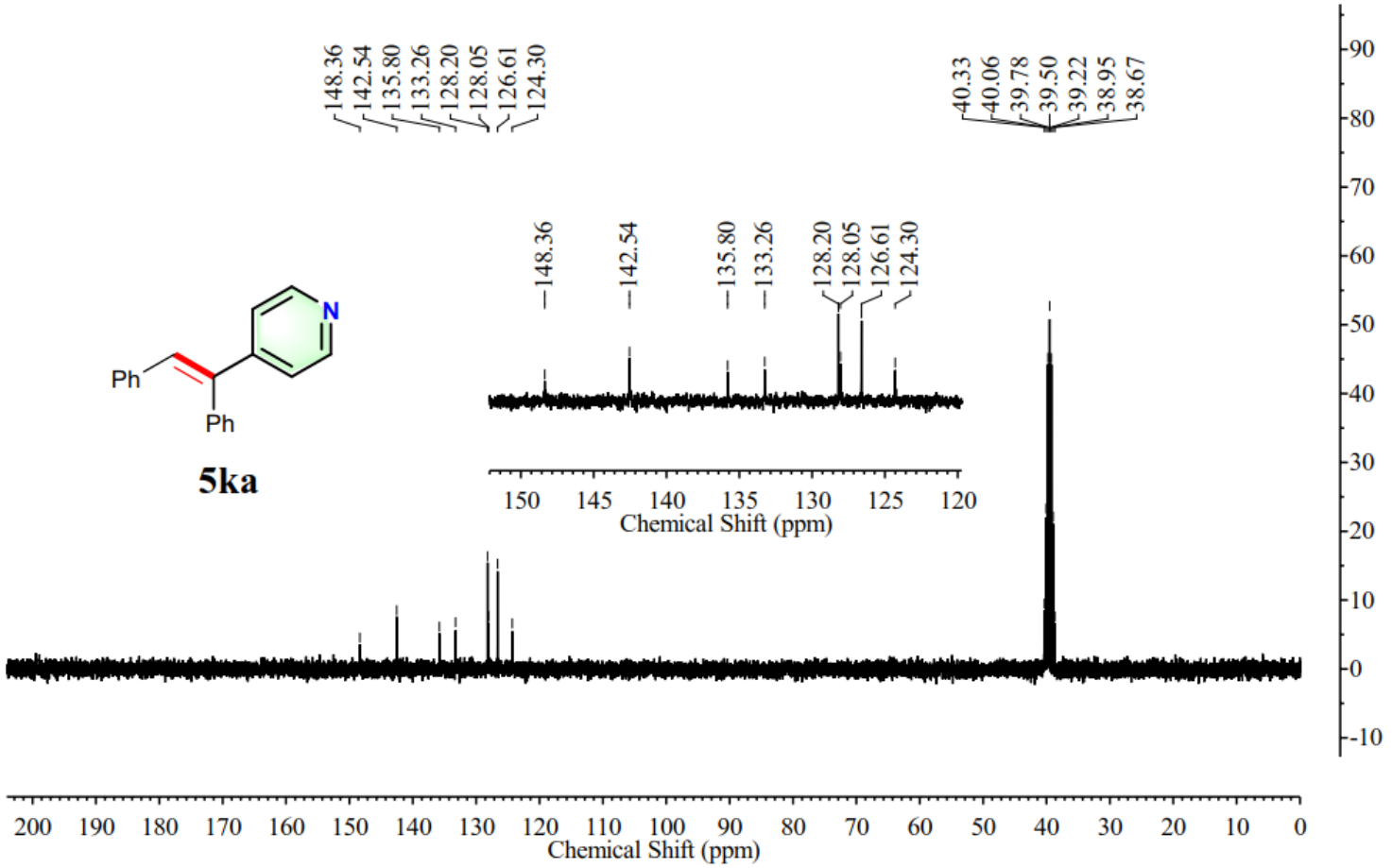
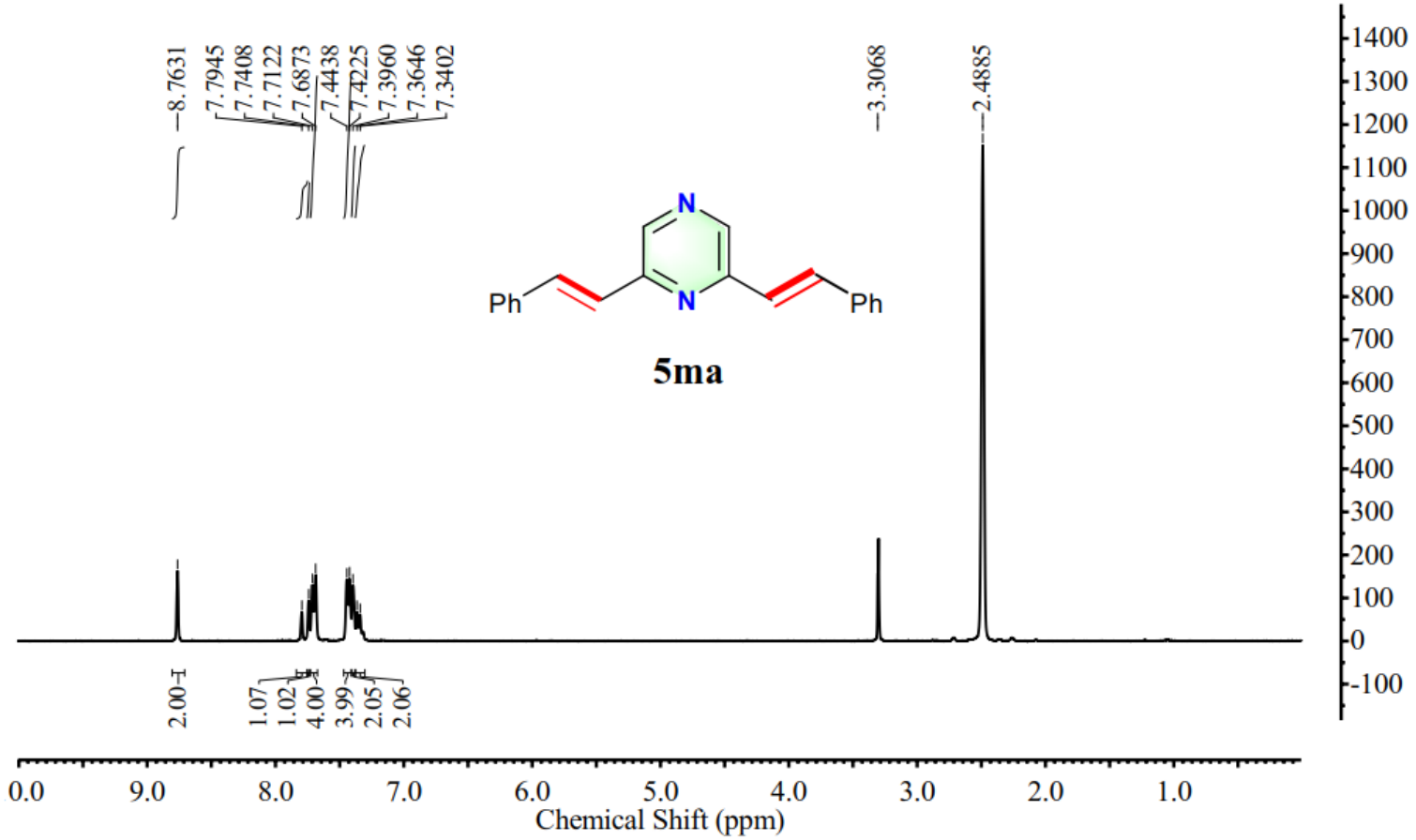
142.5251
141.9373
137.1180
132.0481
129.3888
128.3025
127.3885
77.4227
76.9997
76.5754
15.3848
Ph
Me
N
N
5ja
150
145
140
135
130
125
Chemical Shift (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


8.7693
7.7930
7.7390
7.7012
7.6775
7.4319
7.3946
7.3404
3.0565
2.5003
N
Ph
Ph
5ka
1.91
6.01
7.02
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)


148.36
142.54
135.80
133.26
128.20
128.05
126.61
124.30
40.33
40.06
39.78
39.50
39.22
38.95
38.67
N
Ph
Ph
5ka
Chemical Shift (ppm)
Chemical Shift (ppm)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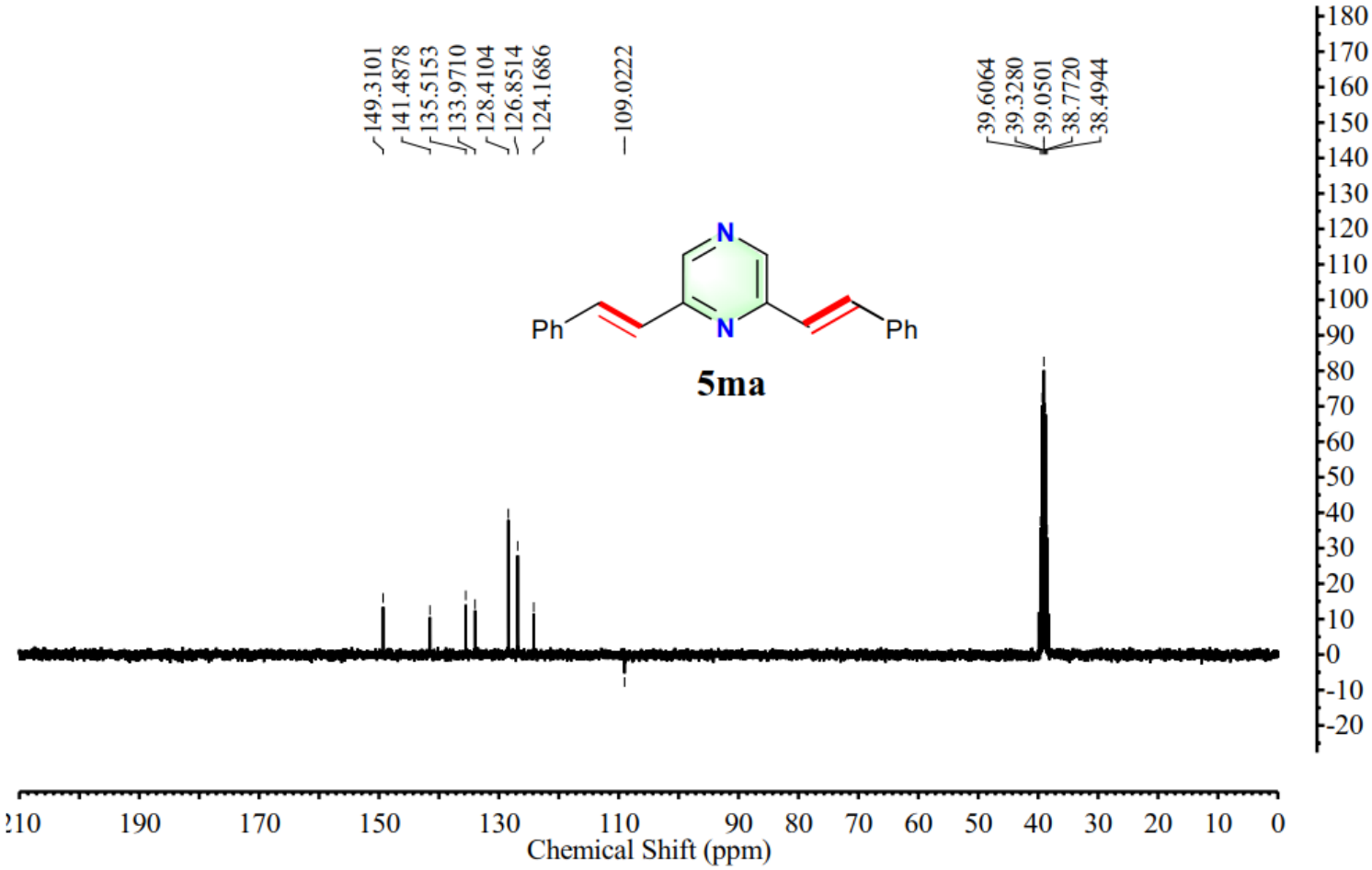
7.7945
7.7408
7.7122
7.6873
7.4438
7.4225
7.3960
7.3646
7.3402
3.3068
2.4885
N
N
Ph
Ph
5ma
2.00
1.07
1.02
4.00
3.99
2.05
2.06
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)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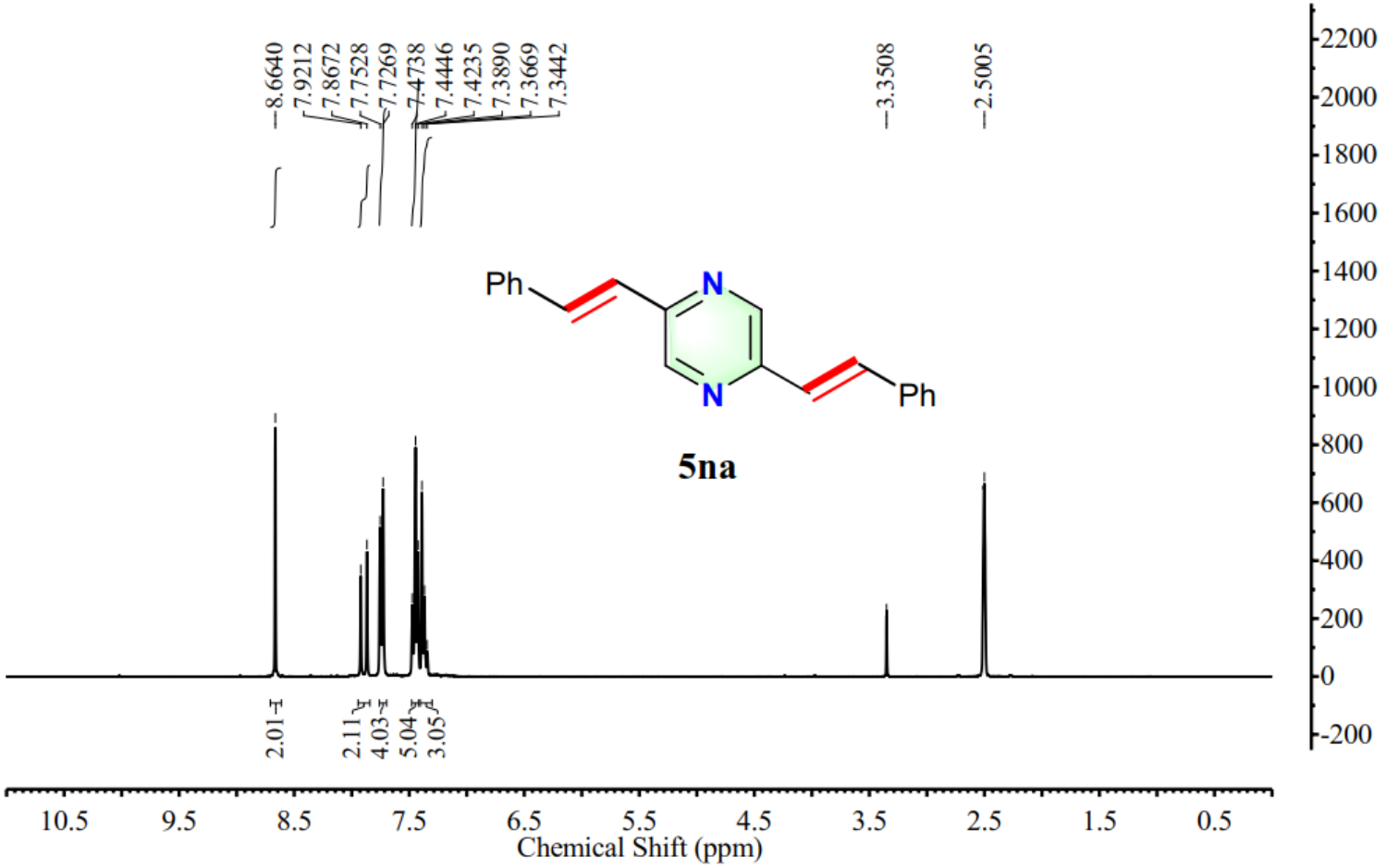
141.4878
135.5153
133.9710
128.4104
126.8514
124.1686
109.0222
39.6064
39.3280
39.0501
38.7720
38.4944
N
N
Ph
Ph
5ma
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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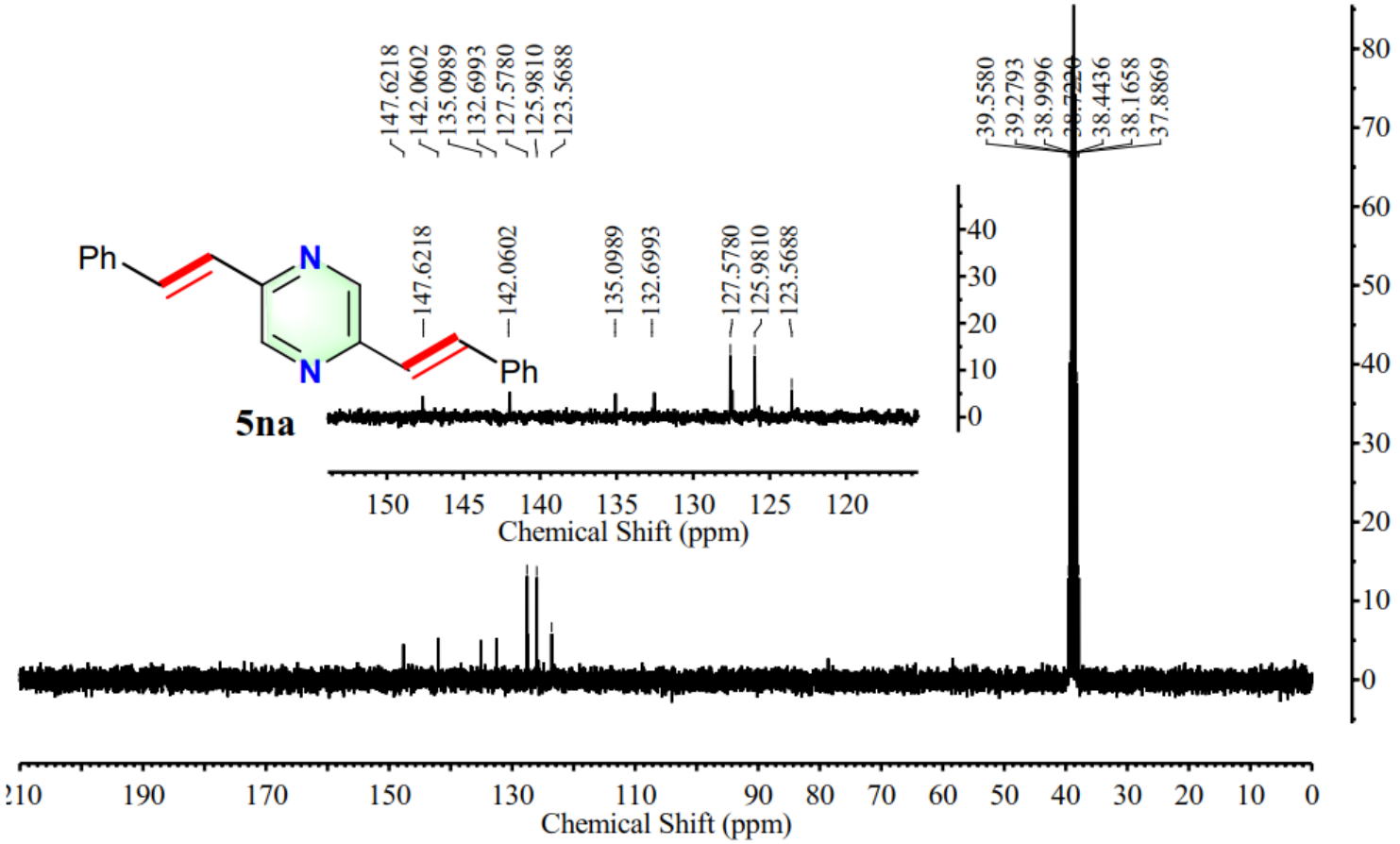
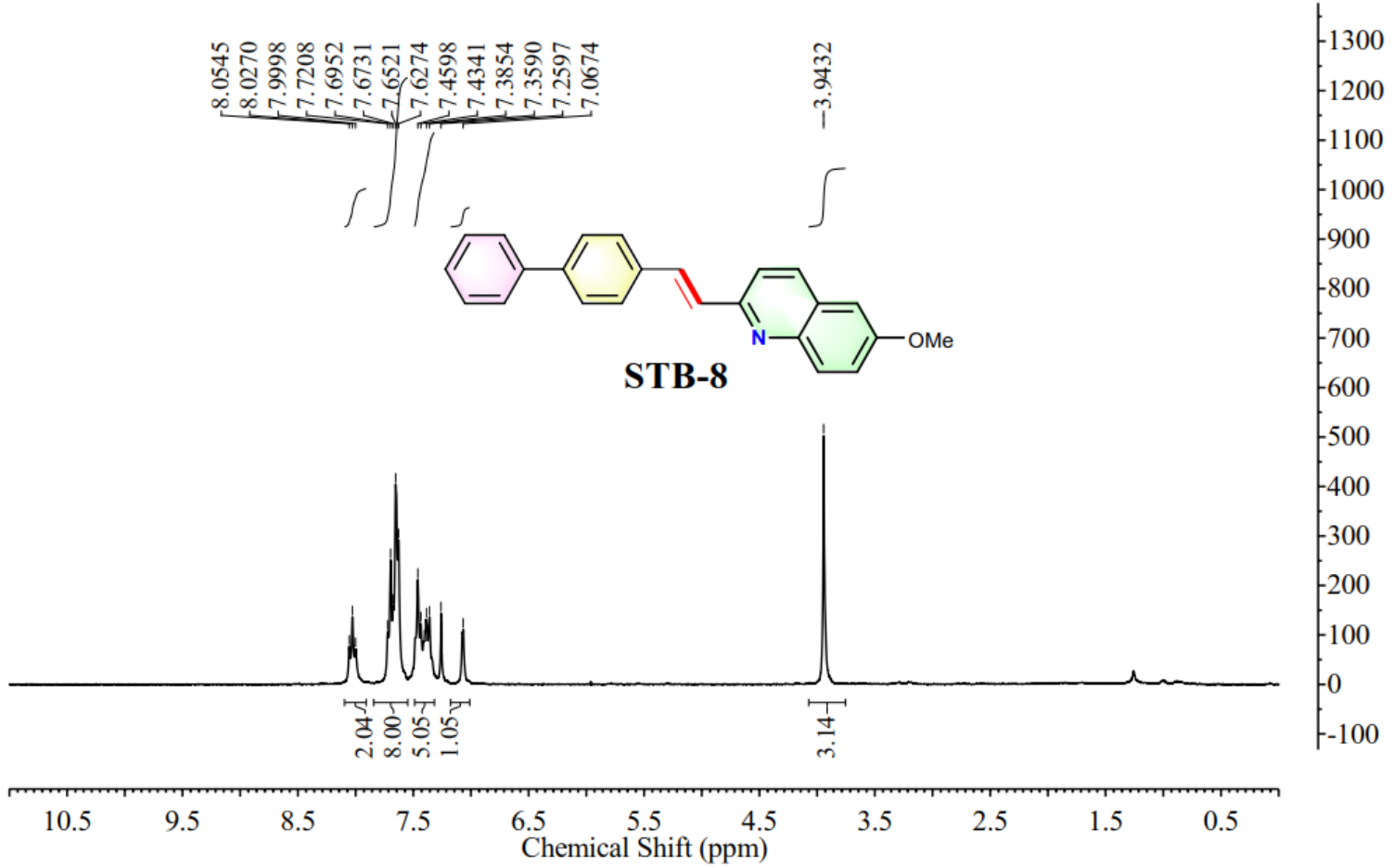
7.9212
7.8672
7.7528
7.7269
7.4738
7.4446
7.4235
7.3890
7.3669
7.3442
3.3508
2.5005
Ph
N
N
Ph
5na
2.01
2.11
4.03
5.04
3.05
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


147.6218
142.0602
135.0989
132.6993
127.5780
125.9810
123.5688
39.5580
39.2793
38.9996
38.4436
38.1658
37.8869
Ph
N
N
Ph
5na
Chemical Shift (ppm)
Chemical Shift (ppm)


8.0545
8.0270
7.9998
7.7208
7.6952
7.6731
7.6521
7.6274
7.4598
7.4341
7.3854
7.3590
7.2597
7.0674
3.9432
N
OMe
STB-8
2.04
8.00
5.05
1.05
3.14
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
Chemical Shift (ppm)