Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of 3-Aminotetrahydro-1*H*-carbazols by Visible-Light Photocatalyzed Cycloaddition of Cyclopropylanilines with 2-Alkenylarylisocyanides

Table of content

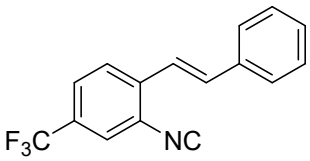
I. General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Flash chromatography was carried out using silica gel (200- 300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a JEOL 400 MHz and 100 MHz NMR spectrometers or Bruker 600 MHz and 150 MHz NMR spectrometers. For ^{1}H NMR, tetramethyl silane (TMS) served as internal standard (δ=0) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS (δ=0) was used as internal standard and spectra were obtained with complete proton decoupling. High resolution mass spectra (HRMS) were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. Crystal measurement was recorded on Bruker D8 QUEST.

II. Experimental Procedures

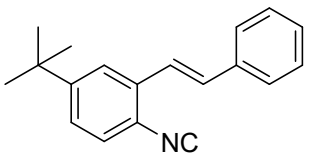
(1). General Procedure for the Synthesis of Aryl Isocyanides

Aryl isocyanides were synthesized according to literature reports. **1a-1c**[1], **1e**[1], **1g-1i**[1], **1k**[1], **1l**[1], **1m**[2], **1s**[2] , **1p**[3], **1q**[3], **1t**[4] are known compounds. The characterization data of new isocyanides **1d**, **1f**, **1j**, **1n**, **1o**, **1r** are as following:



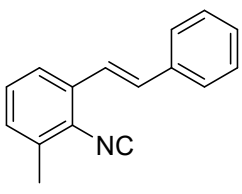
(*E*)-2-isocyano-1-styryl-4-(trifluoromethyl)benzene (**1d**)

White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 30/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.49 – 7.38 (m, 4H), 7.37 – 7.29 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.3, 137.2, 135.8, 135.3, 130.1 (C-F, $^2J_{C\text{-}F}$ = 33.8 Hz), 129.4, 129.0, 127.4, 126.2, 126.1, 126.1, 126.1, 124.6 (C-F, $^3J_{C\text{-}F}$ = 4.1 Hz), 121.8, 120.8. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{16}H_{11}F_3N$ 274.0838; found 274.0833.



(*E*)-4-(tert-butyl)-1-isocyano-2-styrylbenzene (**1f**)

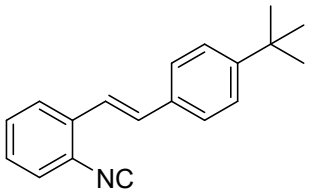
White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 30/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 1.7 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.54–7.44 (m, 3H), 7.42–7.35 (m, 3H), 7.28 (d, *J* = 16.3 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 152.9, 136.6, 133.1, 132.2, 128.9, 128.6, 127.1, 127.0, 125.6, 122.9, 122.3, 35.1, 31.2. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{19}H_{20}N$ 262.1590; found 262.1587.



(*E*)-2-isocyano-1-methyl-3-styrylbenzene (**1j**)

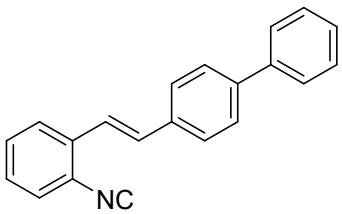
White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 30/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.58 (m, 3H), 7.53 – 7.40 (m, 3H), 7.39 – 7.29 (m, 2H), 7.26 – 7.18 (m, 2H), 2.50 (s, 3H). **^{13}C**

NMR (101 MHz, CDCl3) δ 169.3, 136.7, 135.5, 133.9, 132.6, 129.1, 128.9, 128.9, 128.5, 127.0, 122.9, 122.9, 19.1. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{16}H_{14}N$ 220.1121; found 220.1116.



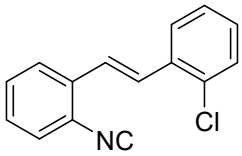
(*E*)-1-(4-(tert-butyl)styryl)-2-isocyanobenzene (**1n**)

White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 30/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82–7.75 (m, 1H), 7.59 – 7.54 (m, 2H), 7.49 – 7.39 (m, 5H), 7.32 – 7.29 (m, 1H), 7.24 (d, *J* = 16.2 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.9, 152.0, 134.0, 133.7, 132.6, 129.5, 127.9, 127.4, 126.9, 125.8, 125.4, 121.5, 34.8, 31.3. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{19}H_{20}N$ 262.1590; found 262.1585.



(*E*)-4-(2-isocyanostyryl)-1,1'-biphenyl (**1o**)

White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 20/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 – 7.78 (m, 1H), 7.69 (dd, *J* = 7.1, 1.2 Hz, 6H), 7.55 – 7.49 (m, 3H), 7.48 – 7.41 (m, 3H), 7.35 – 7.28 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 141.4, 140.5, 135.5, 133.8, 132.2, 129.5, 129.0, 128.1, 127.6, 127.6, 127.6, 127.4, 127.1, 125.5, 125.0, 122.2. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{21}H_{16}N$ 282.1277; found 282.1270.



(*E*)-1-chloro-2-(2-isocyanostyryl)benzene (**1r**)

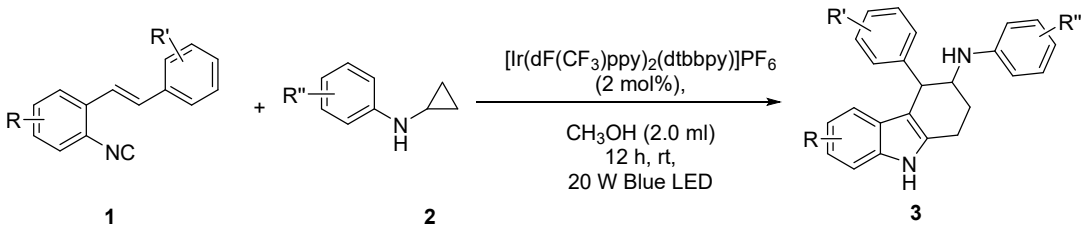
White solid, Column chromatography on silica gel (Eluent: petroleum ether/ethyl acetate, 20/1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85–7.80 (m, 2H), 7.66 (d, *J* = 16.3 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.39 – 7.26 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 134.6, 133.9, 133.5, 130.0, 129.6, 129.6, 128.7, 128.6, 127.4, 127.2,

127.0, 125.9, 125.2, 124.7. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{15}H_{11}ClN$ 240.0575; found 240.0567.

(2). General Procedure for the Synthesis of *N*-Aryl Aminocyclopropane

Aryl halide derivatives and Cyclopropylamine are commercial available and used directly without purification. *N*-aryl aminocyclopropane **2a**-**2m** were prepared according to literature procedures [5].

(3). General Procedure for Preparation of 3



A pressure tube was charged with **1** (0.2 mmol, 1 equiv.), **2** (0.4 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.004 mmol, 2 mol %), CH_3OH (2.0 mL). The reaction mixture was then stirred and irradiation with a 20 W blue LED at room temperature for 12 h under Ar atmosphere. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the corresponding products.

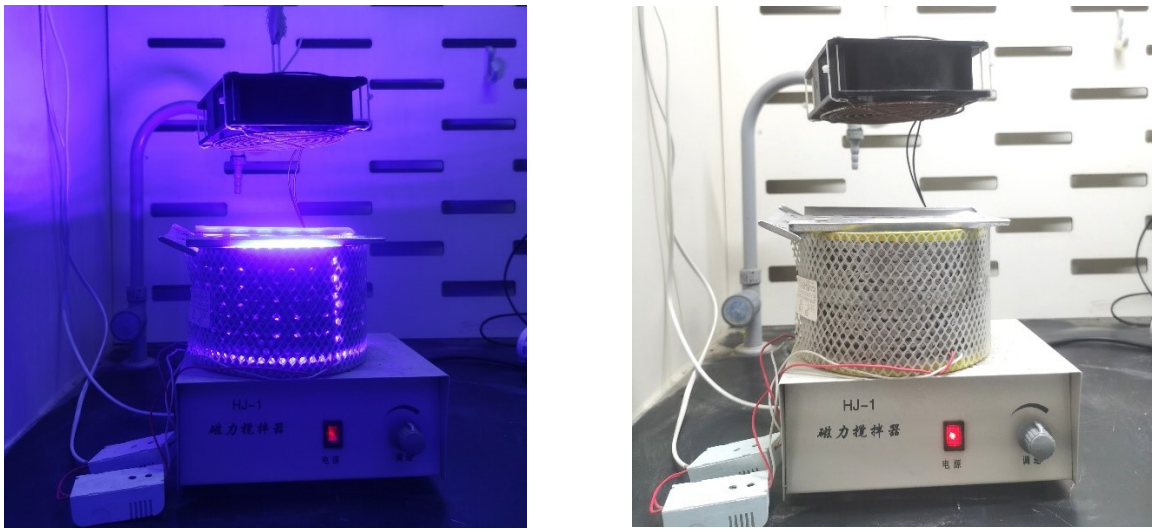
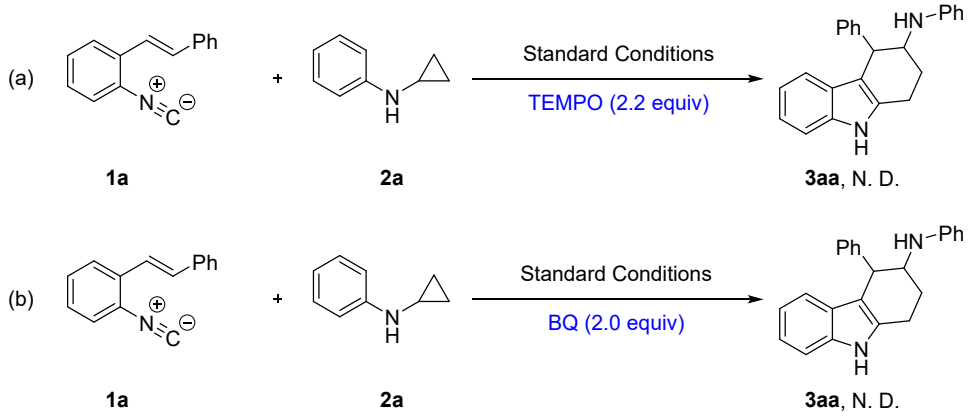


Figure S1. Reaction setup for photocatalyzed cycloaddition

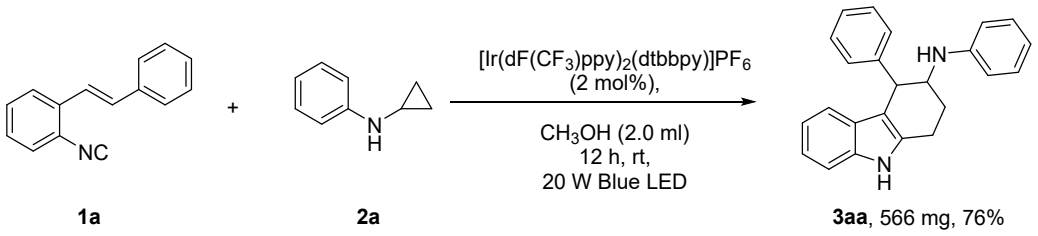
(4) Control Experiments [6]



(a) A pressure tube was charged with **1** (0.2 mmol, 1 equiv.), **2** (0.4 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.04 mmol, 2 mol %), TEMPO (0.44 mmol, 2.0 equiv.) and CH_3OH (2.0 mL). The reaction mixture was then stirred and irradiation with a 20 W blue LED at room temperature for 12 h under Ar atmosphere. No **3aa** was detected by TLC.

(b) A pressure tube was charged with **1** (0.2 mmol, 1 equiv.), **2** (0.4 mmol, 2 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.04 mmol, 2 mol %), BQ (0.40 mmol, 2.0 equiv.) and CH_3OH (2.0 mL). The reaction mixture was then stirred and irradiation with a 20 W blue LED at room temperature for 12 h under Ar atmosphere. No **3aa** was detected by TLC.

(5) Scale-up synthesis of product 3aa



1a **2a** **3aa**, 566 mg, 76%

A pressure tube was charged with **1a** (2.4 mmol, 1.0 equiv.), **2a** (4.8 mmol, 2.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), CH_3OH (20 mL). The reaction mixture was then stirred and irradiation with a 20 W blue LED at room temperature for 24 h under Ar atmosphere. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:1 (v/v) to give the corresponding products **3aa** (566 mg, 76%).

III. Crystal Data for 3aa (CCDC: 2265600)

Single crystal of *N*,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-amine (**3aa**) suitable for X-ray analysis was obtained by slow evaporation of 0.02 M solution in 20:1 mixture of petroleum hexane/ethyl acetate at room temperature. A suitable crystal was measured on a Bruker APEX-II CCD diffractometer. The crystal was kept at 276(2) K during data collection.

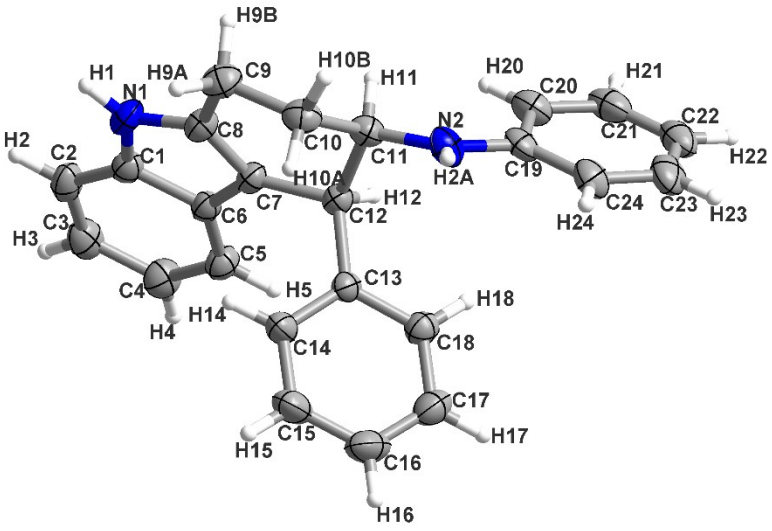


Figure S1 X-Ray crystal structure of **3aa (CCDC: 2265600)**, ellipsoids are drawn at the 30% probability level.

Table S1 Crystal data, data collection, and structure refinement for compound **3aa**

Empirical formula	$C_{24}H_{22}N_2$
Formula weight	338.43
Temperature/K	276(2) K
Crystal system	monoclinic
Space group	$P2_{(1)/n}$

a/Å	9.4607(7)
b/Å	10.9217(8)
c/Å	17.9906(14)
α/°	90
β/°	96.556(2)
γ/°	90
Volume/Å^3	1846.8(2)
Z	4
ρ_{calc}g/cm^3	1.217
μ/mm^{-1}	0.071
F(000)	720.0
Crystal size/mm^3	0.120 x 0.110 x 0.100
Radiation	MoKα (λ = 0.71073)
Range for data collection	2.185 to 25.100
Limiting indices	-11<=h<=11, -13<=k<=13, -21<=l<=21
Reflections collected	52227
Independent reflections	3280 [R(int) = 0.5287]
Data/restraints/parameters	3280 / 0 / 236
Goodness-of-fit on F^2	0.828
Final R indices [I>2sigma(I)]	R_1 = 0.0419, wR_2 = 0.0816
R indices (all data)	R_1 = 0.1220, wR_2 = 0.0978

Table S2. Bond lengths [A] and angles [deg] for **3aa**

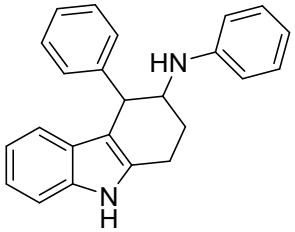
Atom	**Length**
C(1)-N(1)	1.376(2)
C(1)-C(2)	1.385(3)
C(1)-C(6)	1.411(3)
C(2)-C(3)	1.372(3)
C(3)-C(4)	1.391(3)
C(4)-C(5)	1.370(2)
C(5)-C(6)	1.390(3)
C(6)-C(7)	1.434(3)
C(7)-C(8)	1.354(2)
C(7)-C(12)	1.491(3)
C(8)-N(1)	1.378(2)
C(8)-C(9)	1.492(3)
C(9)-C(10)	1.522(3)
C(10)-C(11)	1.527(2)
C(11)-N(2)	1.444(2)
C(11)-C(12)	1.562(3)
C(12)-C(13)	1.508(2)
C(13)-C(14)	1.384(2)
C(13)-C(18)	1.387(3)
C(14)-C(15)	1.382(3)
C(15)-C(16)	1.376(3)
C(16)-C(17)	1.376(3)
C(17)-C(18)	1.380(3)

C(19)-N(2)	1.386(2)
C(19)-C(20)	1.388(3)
C(19)-C(24)	1.394(3)
C(20)-C(21)	1.389(3)
C(21)-C(22)	1.369(3)
C(22)-C(23)	1.373(3)
C(23)-C(24)	1.373(3)
N(1)-C(1)-C(2)	131.1(2)
N(1)-C(1)-C(6)	106.90(19)
C(2)-C(1)-C(6)	122.0(2)
C(3)-C(2)-C(1)	117.5(2)
C(2)-C(3)-C(4)	121.6(2)
C(5)-C(4)-C(3)	120.7(2)
C(4)-C(5)-C(6)	119.6(2)
C(5)-C(6)-C(1)	118.5(2)
C(5)-C(6)-C(7)	134.4(2)
C(1)-C(6)-C(7)	107.00(19)
C(8)-C(7)-C(6)	107.16(19)
C(8)-C(7)-C(12)	124.05(19)
C(6)-C(7)-C(12)	128.79(19)
C(7)-C(8)-N(1)	109.55(19)
C(7)-C(8)-C(9)	126.4(2)
N(1)-C(8)-C(9)	124.0(2)
C(8)-C(9)-C(10)	109.00(18)
C(9)-C(10)-C(11)	112.04(16)
N(2)-C(11)-C(10)	109.62(16)
N(2)-C(11)-C(12)	114.52(17)
C(10)-C(11)-C(12)	111.17(17)

C(7)-C(12)-C(13)	113.87(17)
C(7)-C(12)-C(11)	107.28(16)
C(13)-C(12)-C(11)	113.72(15)
C(14)-C(13)-C(18)	117.82(19)
C(14)-C(13)-C(12)	122.3(2)
C(18)-C(13)-C(12)	119.86(19)
C(15)-C(14)-C(13)	121.0(2)
C(16)-C(15)-C(14)	120.3(2)
C(17)-C(16)-C(15)	119.6(2)
C(16)-C(17)-C(18)	119.8(2)
C(17)-C(18)-C(13)	121.5(2)
N(2)-C(19)-C(20)	123.2(2)
N(2)-C(19)-C(24)	118.45(19)
C(20)-C(19)-C(24)	118.4(2)
C(19)-C(20)-C(21)	119.8(2)
C(22)-C(21)-C(20)	121.6(2)
C(21)-C(22)-C(23)	118.3(3)
C(24)-C(23)-C(22)	121.5(3)
C(23)-C(24)-C(19)	120.4(2)
C(1)-N(1)-C(8)	109.37(18)
C(19)-N(2)-C(11)	124.73(16)

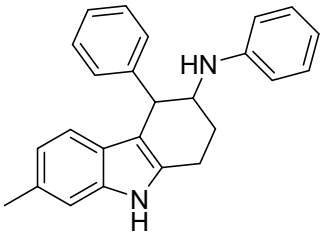
IV. Characterization Data for Products

_N_,4-diphenyl-2,3,4,9-tetrahydro-1_H_-carbazol-3-amine (3aa)



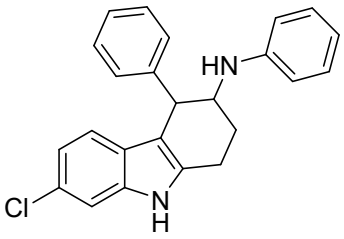
Colorless semisolid (26.4 mg, 78% yield, d.r. = 2.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.21 (m, 5H), 7.18 – 7.08 (m, 4H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.72 (d, *J* = 5.3 Hz, 1H), 4.20 (q, *J* = 6.6 Hz, 1H), 3.49 (s, 1H), 3.14 – 2.97 (m, 2H), 2.01 (h, *J* = 6.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 140.1, 136.8, 134.3, 130.3, 129.6, 128.0, 127.3, 126.8, 121.6, 119.5, 118.5, 117.3, 113.5, 111.7, 110.5, 52.4, 41.0, 24.7, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{22}N_2$ 339.1856; found 339.1865.

7-methyl-_N_,4-diphenyl-2,3,4,9-tetrahydro-1_H_-carbazol-3-amine (3ba)



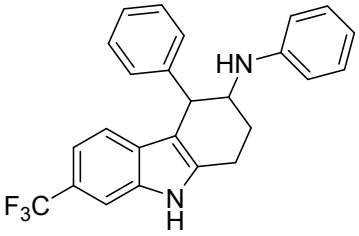
Colorless semisolid (27.5 mg, 78% yield, d.r. = 1.4:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate solvents. (14.1 mg，40% yield). ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (s, 1H), 7.31 (s, 2H), 7.25 (d, *J* = 8.3 Hz, 3H), 7.14 (d, *J* = 4.7 Hz, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.83 – 6.74 (m, 2H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.69 (d, *J* = 5.3 Hz, 1H), 4.20 (q, *J* = 6.8 Hz, 1H), 3.06 (q, *J* = 7.0, 4.5 Hz, 2H), 2.46 (s, 3H), 2.08 – 1.97 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.2, 137.3, 133.6, 131.4, 130.3, 129.6, 128.0, 126.8, 125.2, 121.2, 118.2, 117.5, 113.7, 111.6, 110.7, 52.6, 41.2, 24.8, 23.0, 21.8. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2022.

7-chloro-_N_,4-diphenyl-2,3,4,9-tetrahydro-1_H_-carbazol-3-amine (3ca)



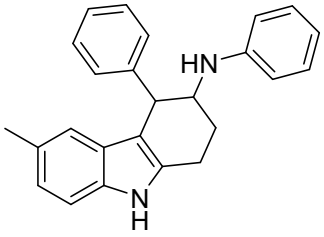
Colorless semisolid (28.6 mg, 77% yield, d.r. = 1.8:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.30 (d, *J* = 9.4 Hz, 3H), 7.22 (d, *J* = 7.5 Hz, 3H), 7.08 (dd, *J* = 6.8, 2.9 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 5.3 Hz, 1H), 4.18 (dt, *J* = 9.7, 4.9 Hz, 1H), 3.14 – 2.97 (m, 2H), 2.07 – 1.93 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 139.9, 137.3, 135.1, 130.2, 129.6, 128.1, 127.5, 127.0, 126.1, 120.2, 119.3, 117.5, 113.6, 112.1, 110.6, 52.5, 41.1, 24.7, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1479.

***N*,4-diphenyl-7-(trifluoromethyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3da)**



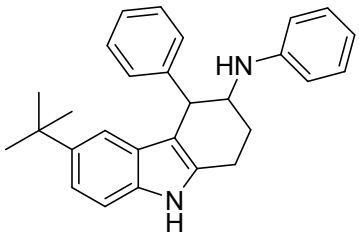
colorless semisolid (26.4 mg, 65% yield, d.r. = 1.7:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 7.58 (s, 1H), 7.26 – 7.10 (m, 7H), 7.04 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.68 (d, *J* = 5.3 Hz, 1H), 4.17 (m, 1H), 3.18 – 2.94 (m, 2H), 2.09 – 1.84 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.9, 139.7, 137.3, 135.7, 130.1, 129.7, 129.5, 128.7, 128.1, 127.1, 123.6 (q, C-F, $^{2}J_{C\text{-}F}$ = 31.6 Hz), 118.7, 117.5, 116.4, 113.5, 112.3, 108.0, 108.0, 52.2, 40.8, 24.5, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{21}F_3N_2$ 407.1730; found 407.1742.

6-methyl-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ea)



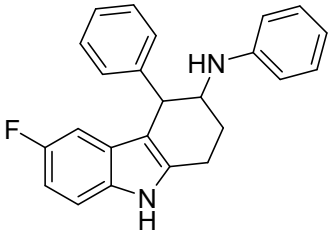
Colorless semisolid (27.4 mg, 78% yield, d.r. = 3.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (s, 1H), 7.25 – 7.16 (m, 6H), 7.12 – 7.05 (m, 2H), 6.91 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.86 (s, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.66 – 6.58 (m, 2H), 4.65 (d, *J* = 5.3 Hz, 1H), 4.14 (q, *J* = 6.4 Hz, 1H), 3.11 – 2.92 (m, 2H), 2.28 (s, 3H), 1.97 (dd, *J* = 7.7, 5.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.2, 140.3, 135.2, 134.4, 130.3, 129.6, 128.7, 128.0, 127.7, 126.8, 123.2, 118.3, 117.4, 113.6, 111.5, 110.2, 52.6, 41.1, 24.8, 23.1, 21.5. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2025.

6-(tert-butyl)-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3fa)



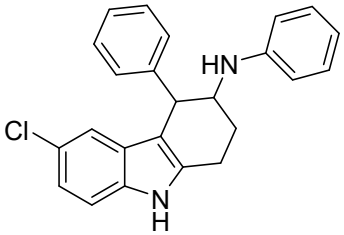
Colorless semisolid (31.5 mg, 80% yield, d.r. = 1.5:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (s, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.22 (m, 4H), 7.22 – 7.11 (m, 4H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 4.1 Hz, 1H), 3.96 (ddd, *J* = 6.7, 4.4, 2.4 Hz, 1H), 2.88 (t, *J* = 6.5 Hz, 2H), 2.17 (m, 1H), 2.01 (m, 1H), 1.21 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 142.5, 134.7, 134.3, 129.5, 128.8, 128.5, 127.7, 126.6, 119.7, 117.6, 115.0, 113.8, 110.0, 109.8, 56.1, 45.8, 34.6, 32.0, 23.6, 19.9. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{28}H_{30}N_2$ 395.2482; found 395.2498.

6-fluoro-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ga)



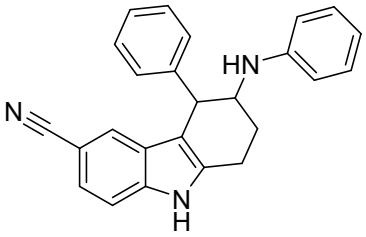
Colorless semisolid (25.6 mg, 72% yield, d.r. = 2.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 7.33 – 7.18 (m, 6H), 7.11 – 7.05 (m, 2H), 6.85 (m, 1H), 6.80 – 6.70 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 5.4 Hz, 1H), 4.18 (m, 1H), 3.46 (s, 1H), 3.16 – 2.98 (m, 2H), 2.00 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 139.9, 136.3, 133.3, 130.3, 129.7, 128.2, 127.1, 117.6, 113.7, 111.0 (d, C-F, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 109.7 (d, C-F, $^{2}J_{C\text{-}F}$ = 26.1 Hz), 103.8(d, C-F, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 52.5, 41.2, 24.8, 23.1. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}FN_2$ 357.1762; found 357.1775.

6-chloro-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ha)



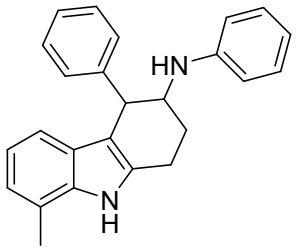
Colorless semisolid (27.9 mg, 75% yield, d.r. = 1.9:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.25 – 7.18 (m, 6H), 7.05 (m, *J* = 7.4, 2.3 Hz, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 4.62 (d, *J* = 5.4 Hz, 1H), 4.15 (q, *J* = 7.6, 7.1 Hz, 1H), 3.39 (d, *J* = 8.8 Hz, 1H), 3.10 – 2.94 (m, 2H), 1.97 (m, *J* = 10.3, 9.0, 5.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 139.8, 135.9, 135.2, 130.2, 129.6, 128.6, 128.1, 127.1, 125.3, 121.9, 118.0, 117.5, 113.6, 111.8, 111.5, 52.4, 41.0, 24.6, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1480.

4-phenyl-3-(phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazole-6-carbonitrile (3ia)



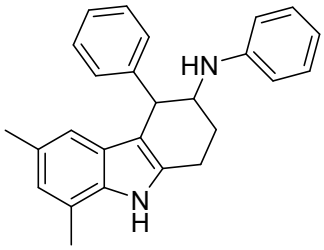
Colorless semisolid (18.9 mg, 52% yield, d.r. = 1.3:1), purified by flash chromatography using petroleum ether/ethyl acetate, (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.38 (s, 1H), 7.35 – 7.32 (m, 2H), 7.25 (d, J = 3.4 Hz, 3H), 7.21 (dd, J = 8.5, 7.3 Hz, 2H), 7.04 (dd, J = 6.6, 3.0 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.9 Hz, 2H), 4.66 (d, J = 5.4 Hz, 1H), 4.15 (m, 1H), 3.05 (m, 2H), 2.08 – 2.01 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 146.8, 139.3, 138.5, 136.8, 130.06, 129.7, 128.3, 127.3, 127.2, 124.9, 123.9, 117.6, 113.5, 112.8, 111.3, 102.6, 52.2, 40.7, 24.5, 22.9. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{21}N_3$ 364.1808; found 364.1821.

8-methyl-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ja)



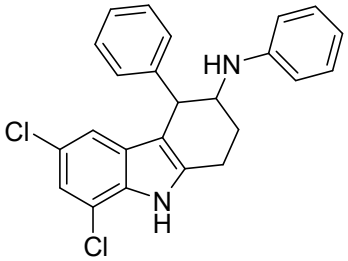
Colorless oil (23.9mg, 68% yield, d.r. = 2.5:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. **^{1}H NMR (*cis* isomer, 400 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.24 (m, 4H), 7.12 (d, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.75 (q, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.71 (d, *J* = 5.4 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 1H), 3.09 (q, *J* = 6.2, 4.0 Hz, 2H), 2.54 (d, *J* = 4.3 Hz, 3H), 2.02 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 147.4, 147.1, 143.6, 140.2, 136.2, 135.9, 134.0, 133.9, 130.3, 129.6, 129.5, 128.6, 128.5, 128.0, 127.3, 126.8, 126.8, 126.6, 122.3, 119.7, 119.6, 117.4, 117.3, 116.6, 116.2, 113.6, 113.5, 112.2, 109.9, 60.6, 55.6, 52.4, 45.4, 41.1, 24.7, 23.01, 22.8, 21.2, 19.5, 16.8, 14.3. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2022.

6,8-dimethyl-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ka)



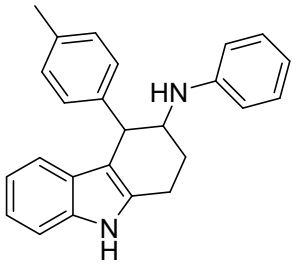
Colorless oil (24.8mg, 68% yield, d.r. = 2.1:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. **^{1}H NMR (*cis* isomer, 400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.21 (m, 7H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.74 (m, 4H), 4.72 – 4.57 (m, 1H), 4.17 – 4.06 (m, 1H), 3.04 (q, *J* = 8.2 Hz, 2H), 2.57 – 2.39 (m, 3H), 2.28 – 2.20 (m, 3H), 2.00 – 1.90 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.5, 147.2, 140.3, 134.6, 134.3, 134.1, 134.0, 130.3, 129.6, 129.5, 129.0, 129.0, 128.7, 128.5, 128.0, 127.7, 127.2, 126.7, 126.5, 124.1, 119.4, 119.3, 117.4, 117.3, 116.2, 115.9, 113.6, 113.5, 111.9, 109.3, 60.6, 55.5, 52.5, 45.2, 41.1, 29.8, 24.7, 23.1, 22.3, 21.4, 19.3, 16.7. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{26}H_{26}N_2$ 367.2169; found 367.2181.

6,8-dichloro-*N*,4-diphenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3la)



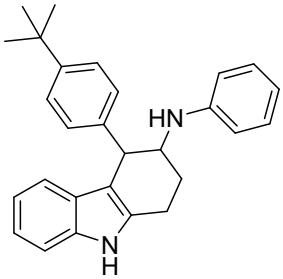
Colorless oil (27.6mg, 68% yield, d.r. = 1.9:1), purified by flash chromatography using petroleum ether/ethyl acetate (10:1) as eluants. **^{1}H NMR (*cis* isomer, 400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 19.7 Hz, 1H), 7.36 – 7.22 (m, 7H), 7.11 (s, 1H), 6.96 (s, 1H), 6.75 (m, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 4.61 (d, *J* = 5.3 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.05 (d, *J* = 6.8 Hz, 2H), 1.99 (q, *J* = 10.7, 9.4 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 146.8, 142.7, 139.3, 136.7, 136.4, 132.5, 132.2, 130.1, 129.6, 129.5, 129.2, 128.7, 128.5, 128.2, 127.2, 127.0, 125.2, 125.2, 121.0, 117.7, 117.5, 117.1, 116.8, 116.4, 116.3, 113.6, 113.5, 112.8, 110.7, 77.5, 55.4, 52.1, 45.2, 40.7, 24.4, 23.0, 22.8, 19.5. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{20}Cl_2N_2$ 407.1076; found 407.1072.

***N*-phenyl-4-(*p*-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ma)**



Colorless semisolid (24.9mg, 71% yield, d.r. = 1.5:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.30 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.09 – 7.06 (m, 2H), 7.05 – 7.01 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.92 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.64 (d, *J* = 5.3 Hz, 1H), 4.19 – 4.05 (m, 1H), 3.08 – 2.93 (m, 2H), 2.30 (s, 3H), 1.98 (dt, *J* = 9.1, 4.2 Hz, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.5, 140.6, 136.1, 134.1, 129.5, 129.2, 128.5, 127.9, 121.6, 119.5, 118.9, 117.4, 113.6, 110.5, 109.7, 55.7, 45.0, 22.9, 21.2, 19.5. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2022.

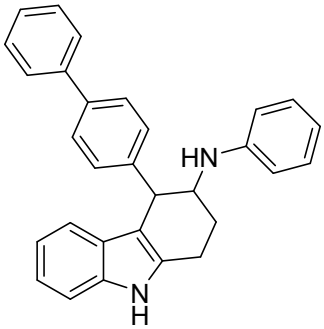
4-(4-(tert-butyl)phenyl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3na)



Colorless semisolid (26.4mg, 67% yield, d.r. = 7.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.06 – 7.02 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.78 – 6.72 (m, 1H), 6.68 – 6.65 (m, 2H), 4.66 (d, *J* = 5.2 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.06 (q, *J* = 6.2, 4.1 Hz, 2H), 2.01 (dd, *J* = 7.6, 4.8 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.6, 147.3, 137.0, 134.2, 129.9, 129.6, 127.5, 124.9, 121.6, 119.5, 118.7, 117.3, 113.6, 112.3, 110.5, 52.6, 40.8, 34.5, 31.6, 24.8, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{28}H_{30}N_2$ 395.2482; found 395.2495.

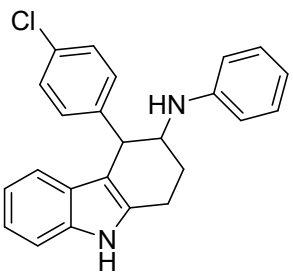
E isomer：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 3H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.33 (d, *J* = 3.3 Hz, 1H), 3.99 (p, *J* = 2.7 Hz, 1H), 2.87 (t, *J* = 6.3 Hz, 2H), 2.15 – 1.97 (m, 2H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.2, 147.4, 140.4, 136.4, 134.1, 129.4, 128.1, 127.9, 125.3, 121.5, 119.4, 118.9, 117.3, 113.5, 110.5, 109.5, 55.2, 44.6, 34.5, 31.5, 22.3, 19.2.

4-([1,1'-biphenyl]-4-yl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3oa)



Colorless oil (24.8mg, 60% yield, d.r. = 1.9:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. **^{1}H NMR (*cis* isomer, 400 MHz, $CDCl_3$)** δ 7.89 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.42 (m, 4H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 4H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.77 (d, *J* = 5.2 Hz, 1H), 4.23 (q, *J* = 6.7 Hz, 1H), 3.10 (q, *J* = 6.2, 4.0 Hz, 2H), 2.06 (q, *J* = 8.7, 6.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 141.0, 139.5, 139.3, 136.8, 134.4, 130.7, 129.6, 128.9, 127.3, 127.2, 127.1, 126.7, 121.7, 119.5, 118.5, 117.4, 113.6, 111.7, 110.6, 52.5, 40.6, 24.8, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{30}H_{26}N_2$ 415.2169; found 415.2182.

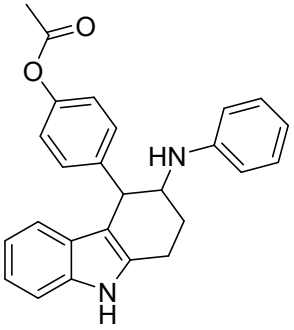
4-(4-chlorophenyl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3pa)



Colorless semisolid (24.8mg, 67% yield, d.r. = 1.4:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 4H), 7.11 (t, *J* =

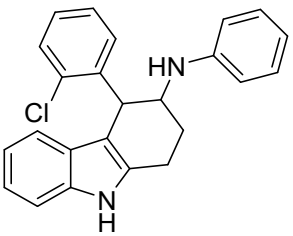
7.6 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 7.01 – 6.91 (m, 3H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.66 – 6.57 (m, 2H), 4.68 (d, *J* = 5.4 Hz, 1H), 4.15 (dt, *J* = 14.3, 5.6 Hz, 1H), 3.09 – 2.98 (m, 2H), 2.01 – 1.88 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.0, 138.9, 137.0, 134.4, 132.8, 131.6, 129.7, 128.1, 127.3, 121.9, 119.7, 118.4, 117.6, 113.6, 111.5, 110.6, 52.5, 40.5, 25.0, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1479.

4-(3-(phenylamino)-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)phenyl acetate (3qa)



Colorless semisolid (24.5mg, 62% yield, d.r. = 1:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 7.8 Hz, 2H), 7.08 (m, 4H), 6.94 (m, 3H), 6.73 (t, J = 7.4 Hz, 1H), 6.64 (d, J = 7.9 Hz, 2H), 4.70 (d, J = 5.2 Hz, 1H), 4.22 – 4.09 (m, 1H), 3.03 (m, 2H), 2.27 (s, 3H), 1.96 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.5, 149.7, 146.9, 137.7, 136.9, 134.3, 131.1, 129.7, 127.3, 121.8, 120.9, 119.7, 118.5, 117.6, 113.7, 111.7, 110.6, 52.7, 40.4, 24.8, 23.1, 21.3. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{26}H_{24}N_2O_2$ 397.1911; found 397.1924.

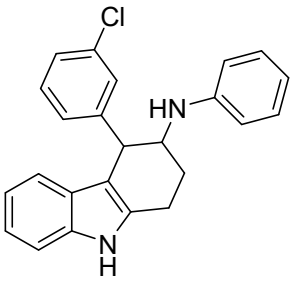
4-(2-chlorophenyl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ra)



Colorless semisolid (23.8mg, 64% yield, d.r. = 13:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.18 – 7.05 (m, 6H), 6.96 – 6.87 (m, 2H), 6.68 – 6.61 (m, 1H), 6.58 – 6.49 (m, 2H), 5.24 (d, *J* = 5.3

Hz, 1H), 4.31 (ddd, *J* = 8.5, 5.4, 2.6 Hz, 1H), 3.04 (dtd, *J* = 16.8, 6.0, 1.3 Hz, 1H), 2.94 (dddd, *J* = 16.7, 7.6, 6.2, 1.4 Hz, 1H), 2.34 – 2.22 (m, 1H), 2.11 (dtd, *J* = 13.1, 6.1, 2.6 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 147.4, 137.8, 136.6, 135.1, 134.6, 131.9, 129.7, 129.3, 128.1, 127.1, 126.5, 121.7, 119.5, 119.2, 117.3, 113.4, 110.6, 110.5, 51.8, 39.5, 25.6, 21.1. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1478.

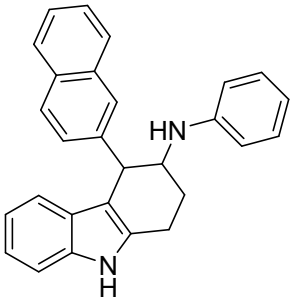
4-(3-chlorophenyl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3sa)



Yellow semisolid (22.3mg, 60% yield, d.r. = 6.7:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.06 (m, 7H), 7.00 – 6.95 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 4.69 (d, *J* = 5.4 Hz, 1H), 4.24 – 4.12 (m, 1H), 3.37 (d, *J* = 9.4 Hz, 1H), 3.12 – 2.98 (m, 2H), 2.09 – 1.89 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.0, 142.6, 137.0, 134.4, 134.1, 130.1, 129.7, 129.1, 128.6, 127.3, 127.1, 121.8, 119.7, 118.4, 117.7, 113.7, 111.2, 110.7, 52.5, 40.9, 24.9, 22.9.

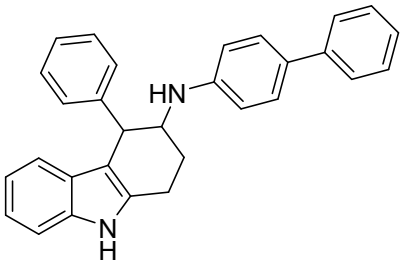
E isomer：^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.15 (m, 5H), 7.12 (ddd, *J* = 8.4, 4.8, 2.4 Hz, 2H), 7.02 – 6.92 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 2H), 4.29 (d, *J* = 3.6 Hz, 1H), 3.94 (p, *J* = 2.9 Hz, 1H), 2.89 (dd, *J* = 7.6, 5.1 Hz, 2H), 2.13 – 1.99 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.1, 145.9, 136.4, 134.4, 134.3, 129.8, 129.5, 128.6, 127.5, 126.9, 121.8, 119.6, 118.7, 117.6, 113.6, 110.7, 108.7, 55.5, 45.1, 22.8, 19.4. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1476.

4-(naphthalen-2-yl)-*N*-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ta)



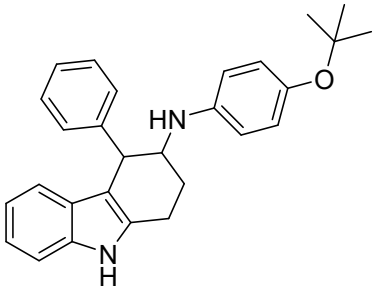
Yellow semisolid (22.3mg, 71% yield, d.r. = 1.8:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (s, 1H), 7.73 – 7.57 (m, 3H), 7.44 – 7.29 (m, 2H), 7.25 – 7.18 (m, 4H), 7.15 – 7.04 (m, 4H), 6.95 (d, *J* = 6.5 Hz, 2H), 6.78 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.80 (d, *J* = 5.3 Hz, 1H), 4.30 (q, *J* = 6.8 Hz, 1H), 3.65 (s, 1H), 3.09 (qd, *J* = 16.7, 10.4 Hz, 2H), 2.04 (h, *J* = 4.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.7, 140.1, 136.8, 135.5, 134.4, 130.3, 129.4, 128.0, 127.8, 127.6, 127.3, 126.8, 126.5, 126.0, 122.1, 121.7, 119.6, 118.6, 118.5, 111.7, 110.6, 105.1, 52.5, 40.4, 24.6, 23.1. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{28}H_{24}N_2$ 389.2012; found 389.2023.

***N*-([1,1'-biphenyl]-4-yl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ab)**



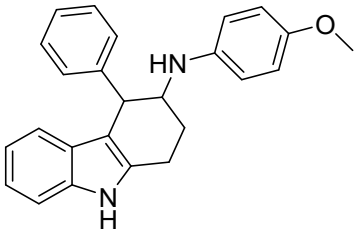
Yellow semisolid (35.2mg, 85% yield, d.r. = 2.1:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (s, 4H), 7.10 (m, 4H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 4.71 (d, *J* = 5.4 Hz, 1H), 4.27 – 4.15 (m, 1H), 3.53 (d, *J* = 9.4 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.05 – 1.99 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.7, 141.4, 140.2, 137.0, 134.3, 130.3, 130.3, 128.8, 128.3, 128.1, 127.5, 126.9, 126.4, 126.2, 121.7, 119.6, 118.6, 113.8, 111.9, 11.6, 52.6, 41.4, 24.9, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{30}H_{26}N_2$ 415.2169; found 415.2180.

***N*-(4-(tert-butoxy)phenyl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ac)**



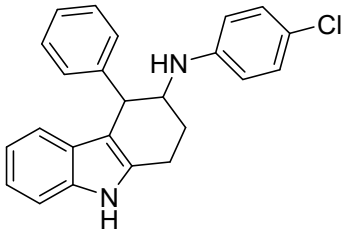
Colorless semisolid (33.6mg, 82% yield, d.r. = 5.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 5.0 Hz, 3H), 7.08 (q, *J* = 6.0 Hz, 4H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.53 (d, *J* = 7.5 Hz, 2H), 4.68 (d, *J* = 5.5 Hz, 1H), 4.13 – 4.06 (m, 1H), 3.02 (d, *J* = 9.3 Hz, 2H), 2.07 – 1.87 (m, 2H), 1.33 – 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.2, 136.9, 134.3, 130.3, 128.1, 127.5, 126.9, 125.7, 121.7, 119.6, 118.6, 114.2, 112.0, 110.5, 53.4, 41.2, 29.0, 26.6, 24.8, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{28}H_{30}N_2O$ 411.2431; found 411.2442.

***N*-(4-methoxyphenyl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ad)**



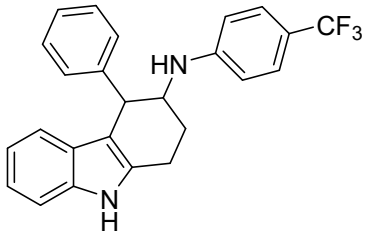
Colorless semisolid (28.7mg, 78% yield, d.r. = 2.4:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 3H), 7.10 (q, *J* = 7.7 Hz, 5H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 1H), 6.19 (s, 1H), 4.68 (d, *J* = 5.4 Hz, 1H), 4.20 – 4.09 (m, 1H), 3.78 (s, 3H), 3.45 (d, *J* = 9.8 Hz, 1H), 3.03 (q, *J* = 6.5 Hz, 2H), 1.99 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3, 148.6, 140.2, 136.9, 134.3, 130.3, 128.0, 127.4, 126.9, 121.7, 119.6, 118.6, 111.9, 110.5, 106.7, 102.6, 99.6, 55.3, 52.6, 41.3, 24.9, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2O$ 369.1961; found 369.1972.

***N*-(4-chlorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ae)**



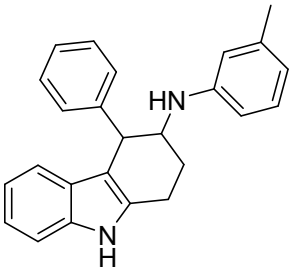
Yellow semisolid (33.4mg, 90% yield, d.r. = 1.6:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 3H), 7.20 – 7.07 (m, 6H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.64 – 6.51 (m, 2H), 4.69 (d, *J* = 5.2 Hz, 1H), 4.13 (m, 1H), 3.07 (q, *J* = 6.2 Hz, 2H), 2.10 – 1.91 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.8, 140.0, 136.9, 134.2, 130.2, 129.4, 128.1, 127.4, 127.0, 121.9, 121.8, 119.6, 118.5, 114.7, 111.7, 110.6, 52.8, 41.1, 24.8, 22.9. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1478.

4-phenyl-*N*-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3af)



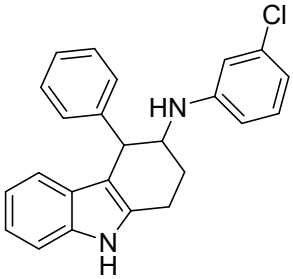
Yellow semisolid (30.4mg, 75% yield, d.r. = 4.9:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.23 (p, *J* = 2.9, 2.4 Hz, 3H), 7.15 – 7.03 (m, 4H), 6.97 – 6.90 (m, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.65 (d, *J* = 5.4 Hz, 1H), 4.16 (tt, *J* = 12.3, 5.8 Hz, 1H), 3.78 (s, 1H), 3.13 – 2.98 (m, 2H), 2.09 – 1.91 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.6, 139.8, 135.4 (q, C-F, $^{1}J_{C\text{-}F}$ = 262.5 Hz), 130.1, 128.2, 127.1, 127.0, 126.9 (q, C-F, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 121.7, 120.0, 118.5, 112.4, 111.3, 110.6, 52.1, 40.9, 24.6, 22.8. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{21}F_3N_2$ 407.1730; found 407.1741.

4-phenyl-*N*-(m-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ag)



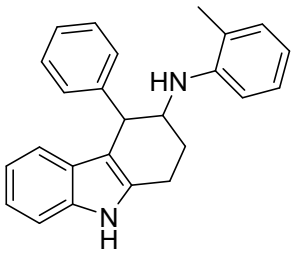
Colorless semisolid (24.6mg, 70% yield, d.r. = 1.0:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 6.5 Hz, 3H), 7.10 (m, 5H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 9.8 Hz, 2H), 4.67 (d, *J* = 5.4 Hz, 1H), 4.19 – 4.12 (m, 1H), 3.37 (d, *J* = 9.0 Hz, 1H), 3.13 – 2.97 (m, 2H), 2.29 (s, 3H), 1.98 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.3, 140.3, 139.4, 136.9, 134.4, 130.3, 129.5, 128.0, 127.5, 126.8, 121.7, 119.6, 118.6, 118.3, 114.3, 112.0, 110.8, 110.5, 52.5, 41.3, 24.9, 23.0, 21.8. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2023.

***N*-(3-chlorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ah)**



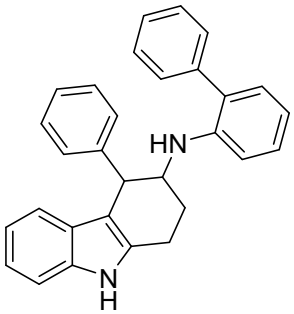
Yellow semisolid (31.2mg, 84% yield, d.r. = 1.2:1), purified by flash chromatography using (petroleum ether/ethyl acetate, 8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 3H), 7.12 – 7.05 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.67 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.59 (d, *J* = 2.2 Hz, 1H), 6.45 (dd, *J* = 8.3, 2.3 Hz, 1H), 4.65 (d, *J* = 5.4 Hz, 1H), 4.11 (tt, *J* = 9.9, 5.6 Hz, 1H), 3.51 (d, *J* = 9.9 Hz, 1H), 3.20 – 2.92 (m, 2H), 2.06 – 1.89 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.5, 140.0, 136.9, 135.4, 134.2, 130.5, 130.2, 128.2, 127.4, 127.0, 121.8, 119.7, 118.6, 117.2, 113.1, 111.8, 111.7, 110.6, 52.5, 41.3, 24.8, 22.9. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{24}H_{21}ClN_2$ 373.1466; found 373.1444.

4-phenyl-*N*-(o-tolyl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ai)



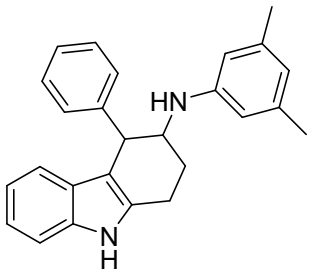
Colorless semisolid (27.4mg, 78% yield, d.r. = 2.3:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.22 – 7.09 (m, 6H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 5.3 Hz, 1H), 4.27 (h, *J* = 5.2, 4.7 Hz, 1H), 3.32 (d, *J* = 9.7 Hz, 1H), 3.17 – 3.00 (m, 2H), 2.14 – 1.98 (m, 2H), 1.89 (d, *J* = 2.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.0, 140.3, 136.9, 134.4, 130.6, 130.1, 128.1, 127.5, 127.4, 126.9, 122.3, 121.7, 119.6, 118.6, 116.8, 111.9, 110.6, 110.3, 52.1, 41.1, 24.9, 22.9, 17.4. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{25}H_{24}N_2$ 353.2012; found 353.2022.

***N*-([1,1'-biphenyl]-2-yl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3aj)**



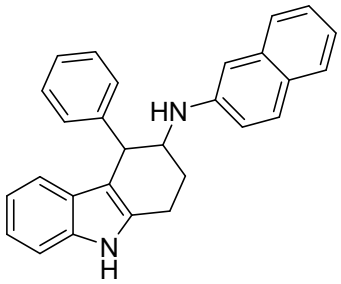
Colorless semisolid (18.6mg, 45% yield, d.r. = 99:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, CDl_3)** δ 7.73 (s, 1H), 7.33 – 7.28 (m, 5H), 7.19 – 7.08 (m, 8H), 7.02 – 6.93 (m, 3H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 4.66 (d, *J* = 5.5 Hz, 1H), 4.20 (m, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.05 – 2.84 (m, 2H), 2.07 – 1.87 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.0, 140.1, 139.4, 136.8, 134.2, 129.8, 129.3, 128.8, 128.2, 128.1, 127.4, 127.0, 126.6, 121.6, 119.5, 118.6, 116.7, 111.9, 110.8, 110.5, 52.6, 41.5, 42.6, 22.7. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{30}H_{26}N_2$ 415.2169; found 415.2181.

***N*-(3,5-dimethylphenyl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3ak)**



Colorless semisolid (27.4mg, 75% yield, d.r. = 1.4:1), purified by flash chromatography using petroleum ether/ethyl acetate (15:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28 (m, 4H), 7.13 (t, *J* = 8.6 Hz, 4H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.42 (s, 1H), 6.30 (s, 2H), 4.69 (d, *J* = 5.3 Hz, 1H), 4.18 (q, *J* = 6.7 Hz, 1H), 3.08 (q, *J* = 6.8 Hz, 2H), 2.28 (s, 6H), 2.04 – 1.97 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.2, 140.3, 139.2, 136.9, 134.4, 130.4, 128.0, 127.5, 126.8, 121.7, 119.6, 119.5, 118.6, 114.8, 111.6, 110.5, 52.6, 41.4, 24.9, 23.1, 21.7. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{26}H_{26}N_2$ 367.2196; found 367.2197.

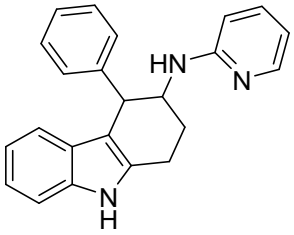
***N*-(naphthalen-2-yl)-4-phenyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3al)**



Yellow semisolid (33.3mg, 86% yield, d.r. = 2.8:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 12.6, 8.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.13 (dt, *J* = 8.9, 5.3 Hz, 4H), 6.98 (t, *J* = 3.4 Hz, 2H), 6.80 (dt, *J* = 8.9, 1.6 Hz, 1H), 4.82 (d, *J* = 5.4 Hz, 1H), 4.32 (h, *J* = 6.5, 5.7 Hz, 1H), 3.63 (d, *J* = 9.8 Hz, 1H), 3.17 – 2.98 (m, 2H), 2.07 (h, *J* = 4.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.9, 140.2, 136.9, 135.6, 134.4, 130.3, 129.3, 128.0, 127.8, 127.7, 127.5, 126.9, 126.5, 126.0, 122.1, 121.7, 119.6, 118.6, 118.5, 111.8, 110.6, 105.3, 52.6, 40.8, 24.8, 23.0. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{28}H_{24}N_2$

389.2012; found 389.2023.

4-phenyl-*N*-(pyridin-2-yl)-2,3,4,9-tetrahydro-1*H*-carbazol-3-amine (3am)



Yellow semisolid (18.3mg, 54% yield, d.r. = 1.0:1), purified by flash chromatography using petroleum ether/ethyl acetate (8:1) as eluants. The *cis* isomer was separated by crystallization with hexane and ethyl acetate as solvents. ***cis* isomer：^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 5.0 Hz, 1H), 7.96 (s, 1H), 7.46 – 7.36 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 3H), 7.12 – 7.00 (m, 4H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.57 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 4.64 (d, *J* = 5.5 Hz, 1H), 4.54 (dd, *J* = 10.8, 6.5 Hz, 1H), 4.28 (s, 1H), 3.17 – 2.94 (m, 2H), 2.00 (pt, *J* = 9.4, 4.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.9, 140.3, 137.7, 136.7, 134.3, 130.1, 128.2, 127.3, 126.9, 121.5, 119.4, 118.6, 112.8, 111.5, 110.5, 107.9, 50.8, 41.6, 24.9, 22.7. **HRMS (ESI) m/z** $[M + H]^+$ calcd for $C_{23}H_{21}N_3$ 340.1808; found 340.1818.

V. References

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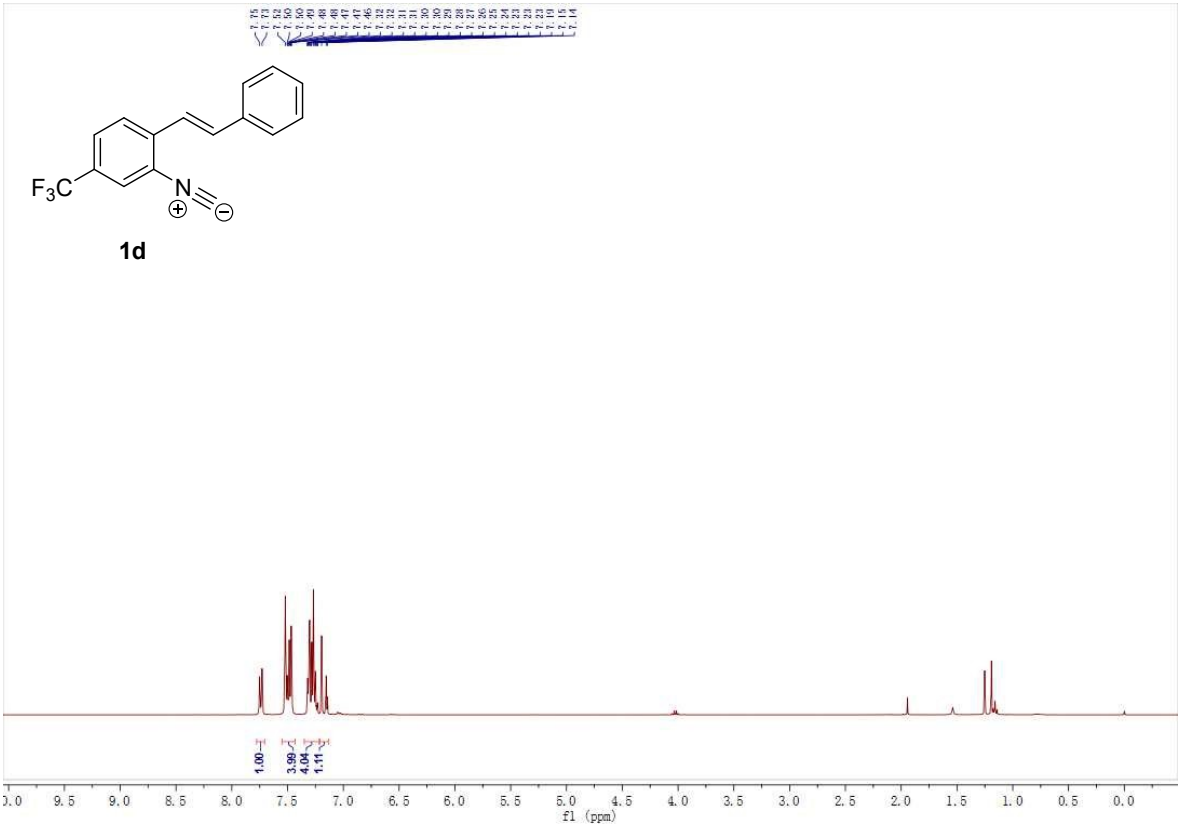
3. Hu, Z.; Dong, J.; Li, Z., et al. Metal-Free Triple Annulation of Ene-Yne-Ketones with Isocyanides: Domino Access to Furan-Fused Heterocycles via Furoketenimine. *Org. Lett*. **2018**, *20(21)*, 6750-6754.

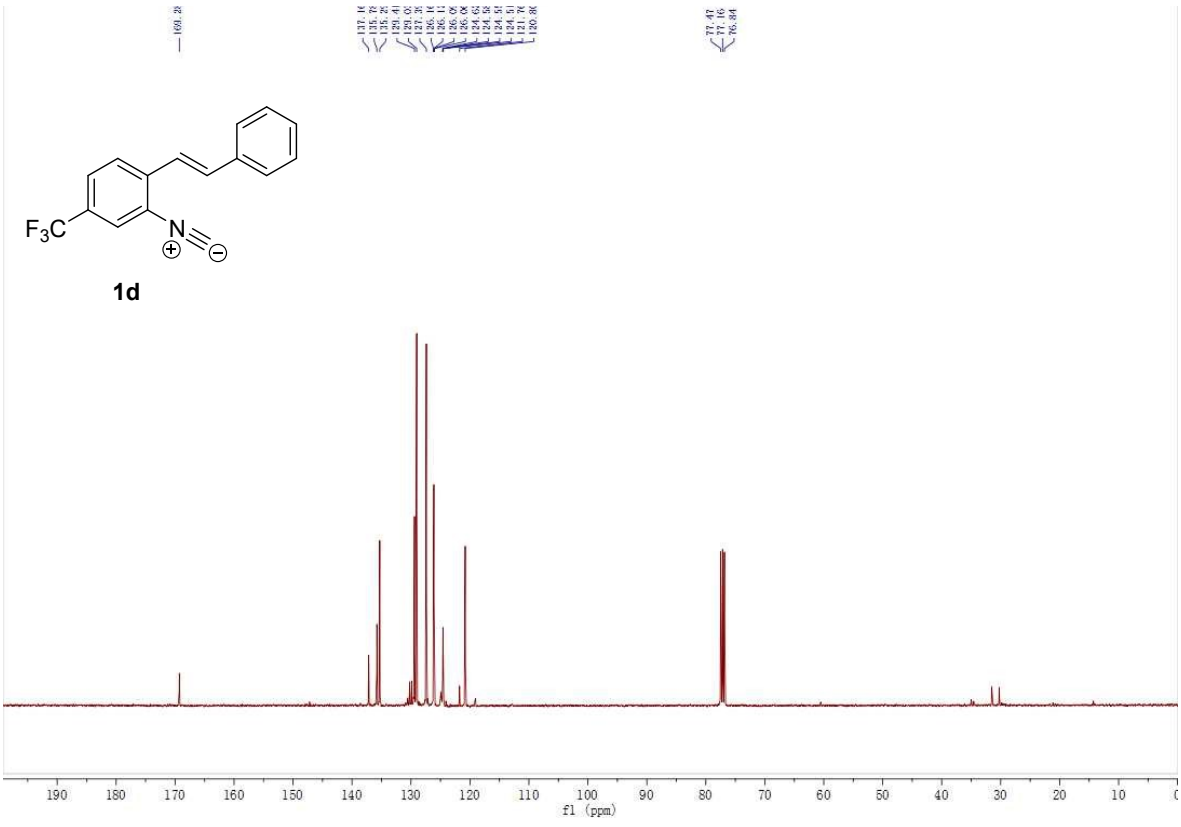
4. Yoshihisa, K. and Thru, F. Development of a Novel Indole Synthesis and Its Application to Natural Products Synthesis. *J. Heterocyclic Chem*. **1998**, *35*, 1043-1055.

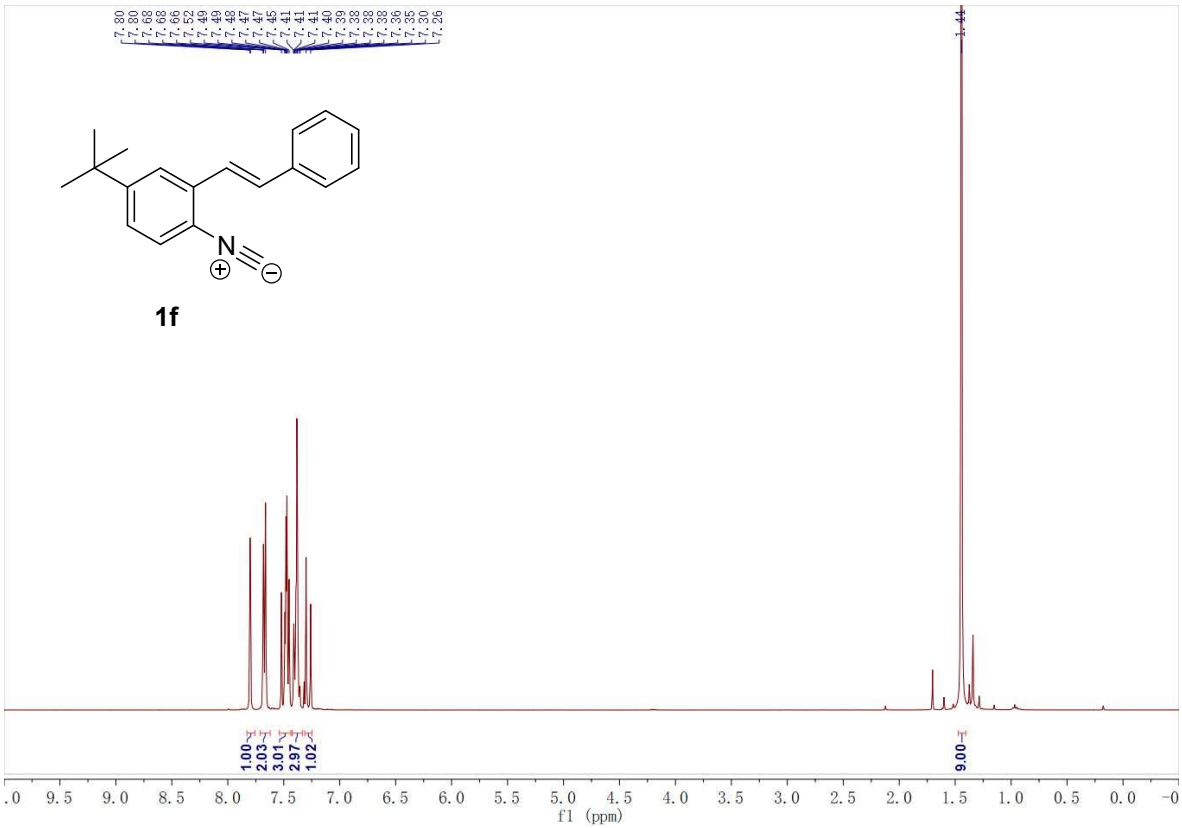
5. Kuang, Y.; Ning, Y.; Zhu, J., et al. Dirhodium(II)-Catalyzed (3 + 2) Cycloaddition of the N-Arylaminocyclopropane with Alkene Derivatives. *Org. Lett*. **2018**, *20(9)*, 2693-2697.

6. Pei, C.; Liu, Y.; Chen, X.; et al. Visible-Light-Induced Oxidative Carboazidation of Arylacrylamides. *Adv. Synth. Catal.* **2023**, *365*, 860-864.

VI. NMR Spectra of All Compound



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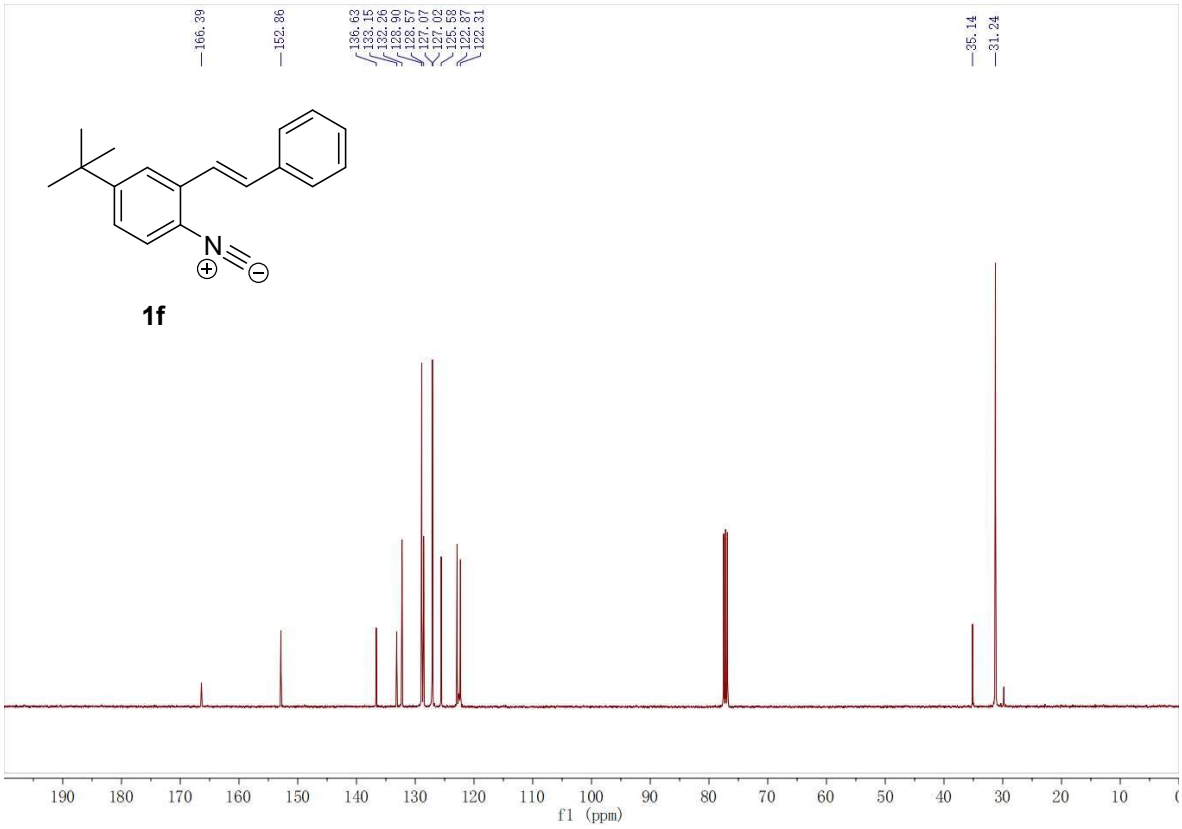
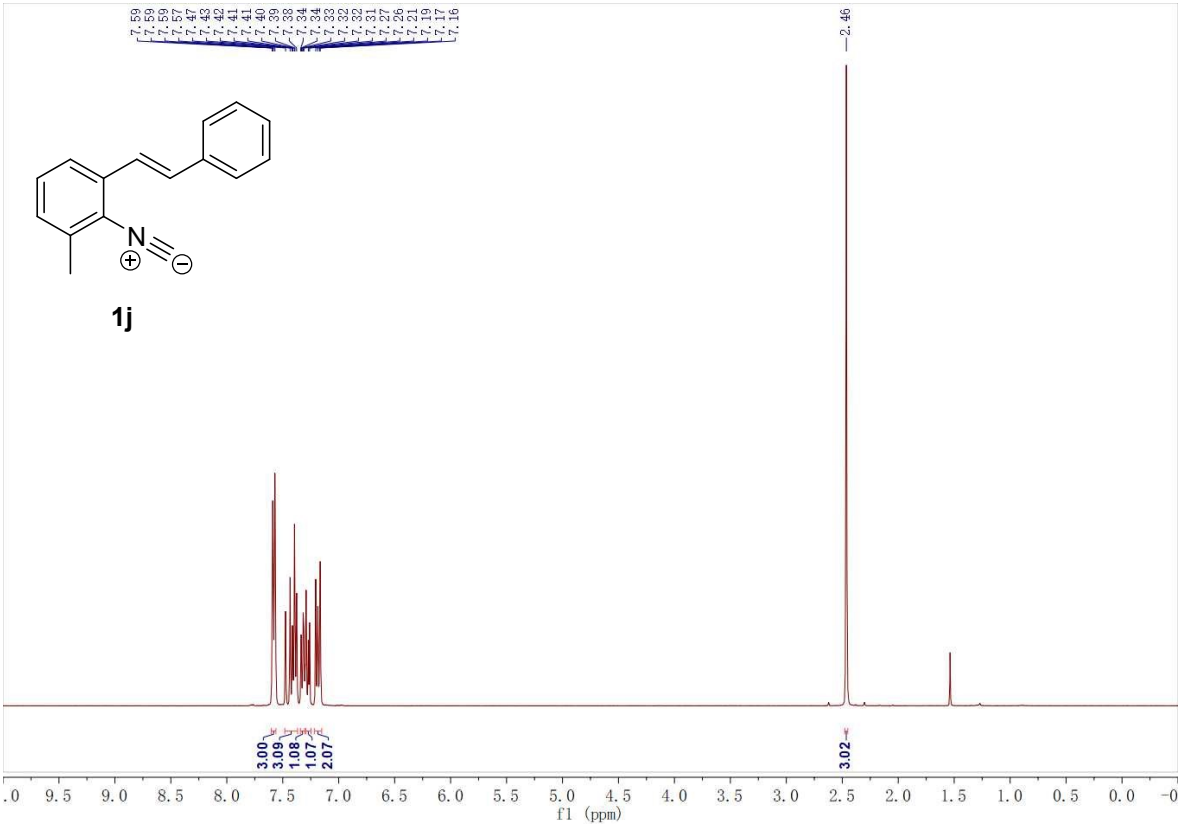
3.01
2.97
1.02
9.00
f1 (ppm)


1f
f1 (ppm)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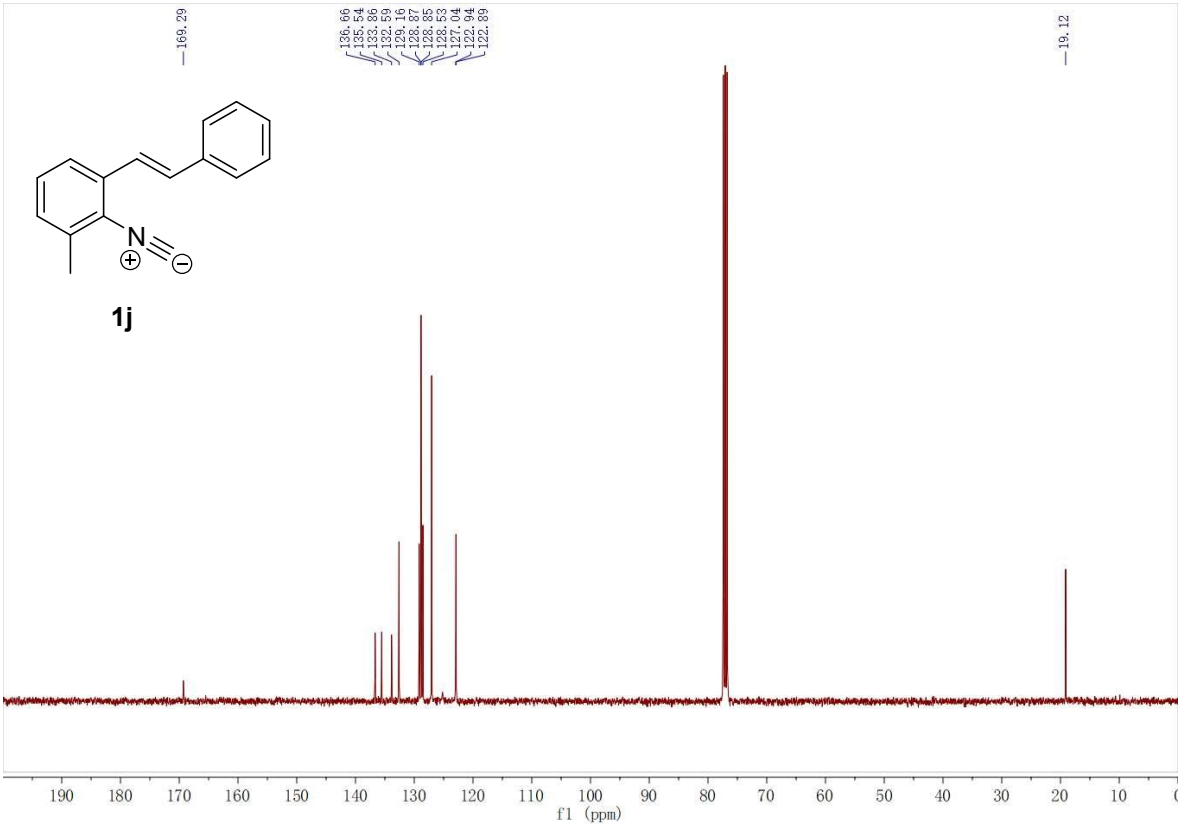
7.59
7.59
7.57
7.47
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.34
7.34
7.33
7.32
7.32
7.31
7.27
7.26
7.21
7.19
7.17
7.16
2.46
3.00
3.09
1.08
1.07
2.07
3.02
f1 (ppm)

1j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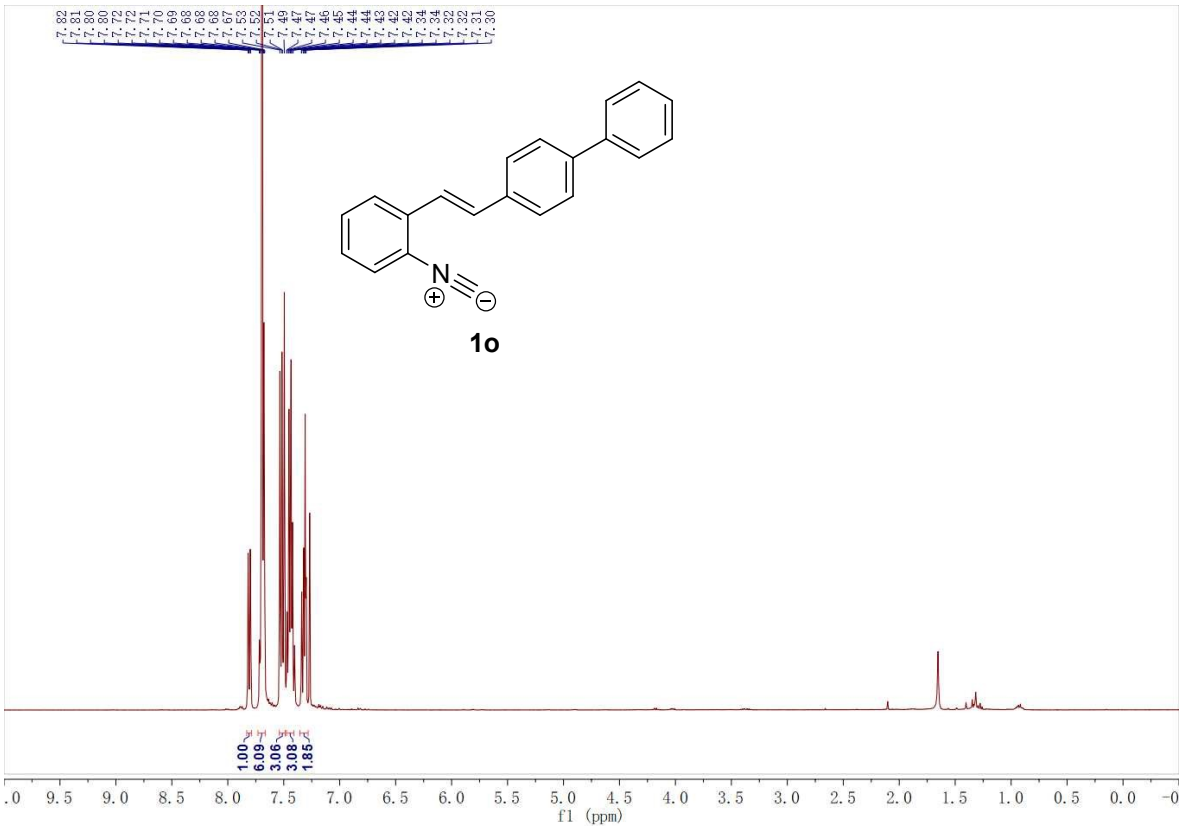
136.66
135.54
133.86
132.59
129.16
128.87
128.85
128.53
127.04
122.94
122.89
19.12
f1 (ppm)

1j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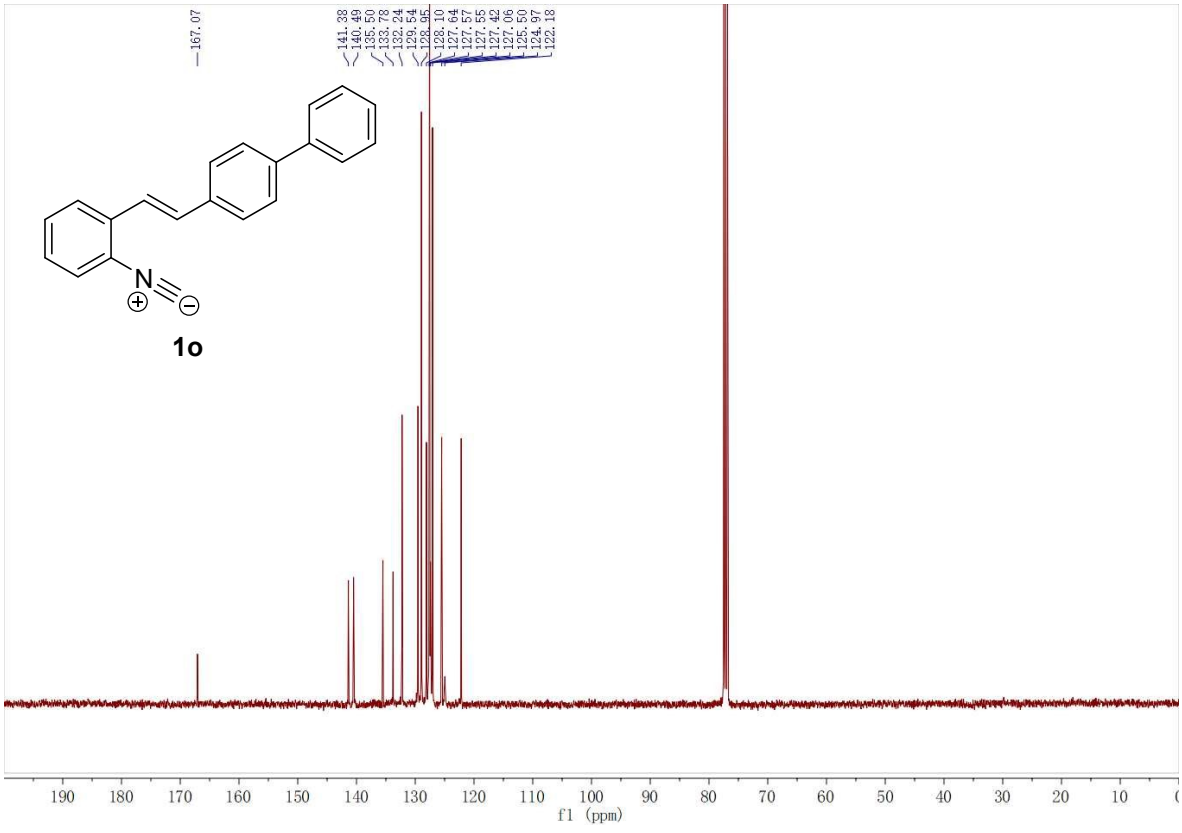
7.81
7.80
7.80
7.72
7.72
7.71
7.70
7.69
7.68
7.68
7.67
7.53
7.51
7.49
7.47
7.47
7.46
7.45
7.44
7.43
7.42
7.34
7.32
7.31
7.30
1o
1.00
6.09
3.06
3.08
1.85
f1 (ppm)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140.49
135.50
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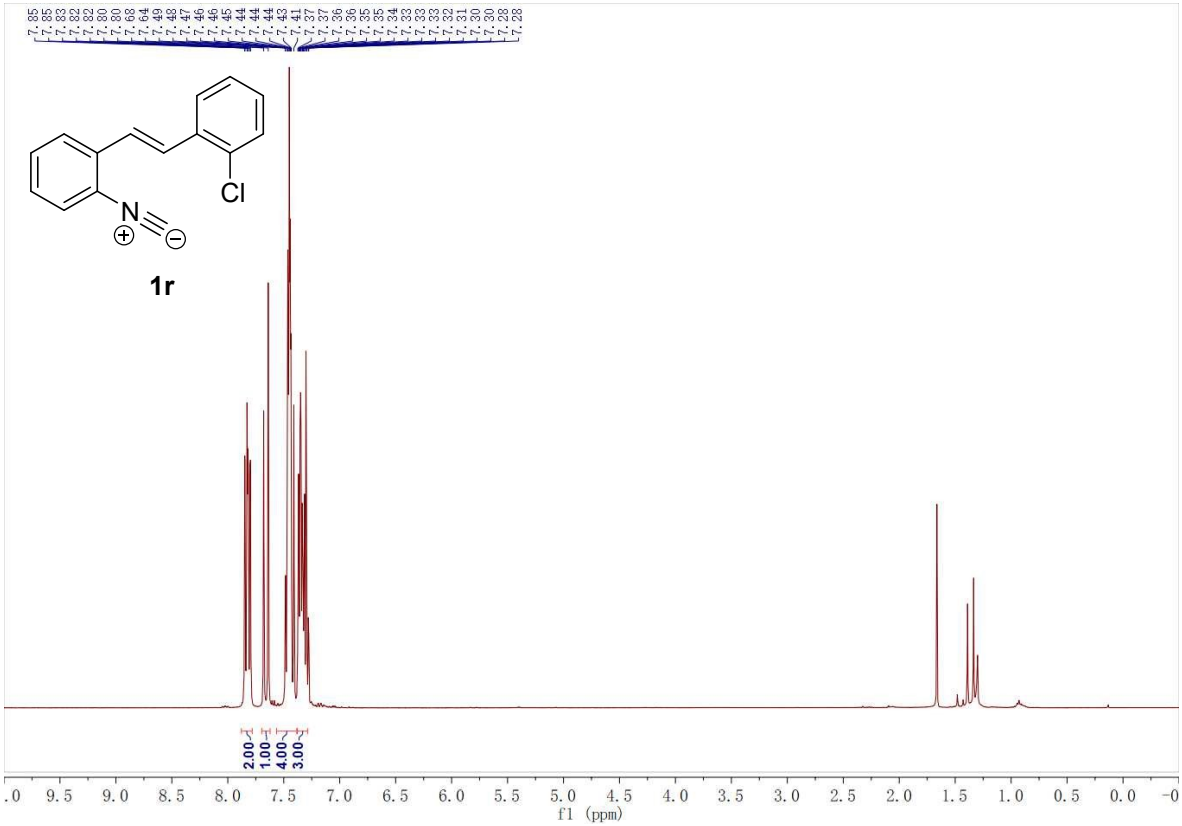
132.24
129.54
128.95
128.10
127.64
127.57
127.55
127.42
127.06
125.50
124.97
122.18
1o
f1 (ppm)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7.85
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7.82
7.82
7.80
7.80
7.68
7.64
7.49
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.41
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
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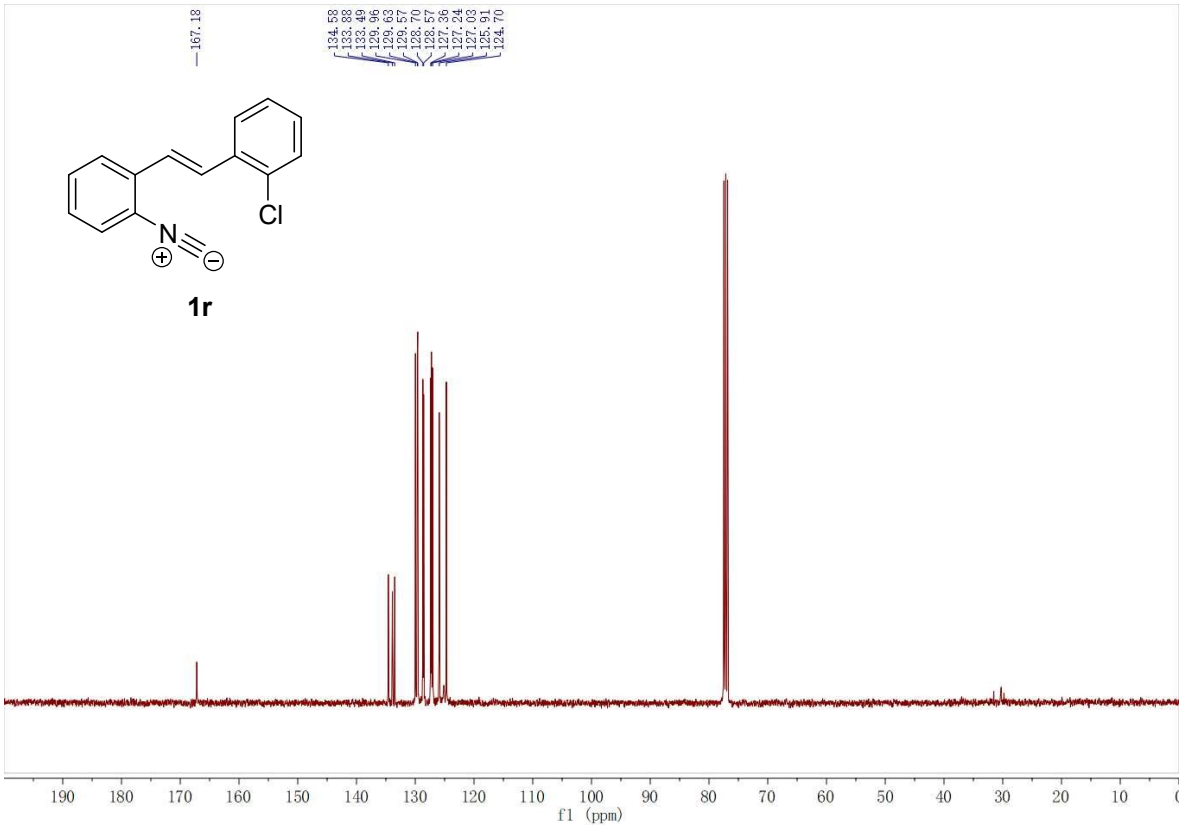
1.00
4.00
3.00
f1 (ppm)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133.88
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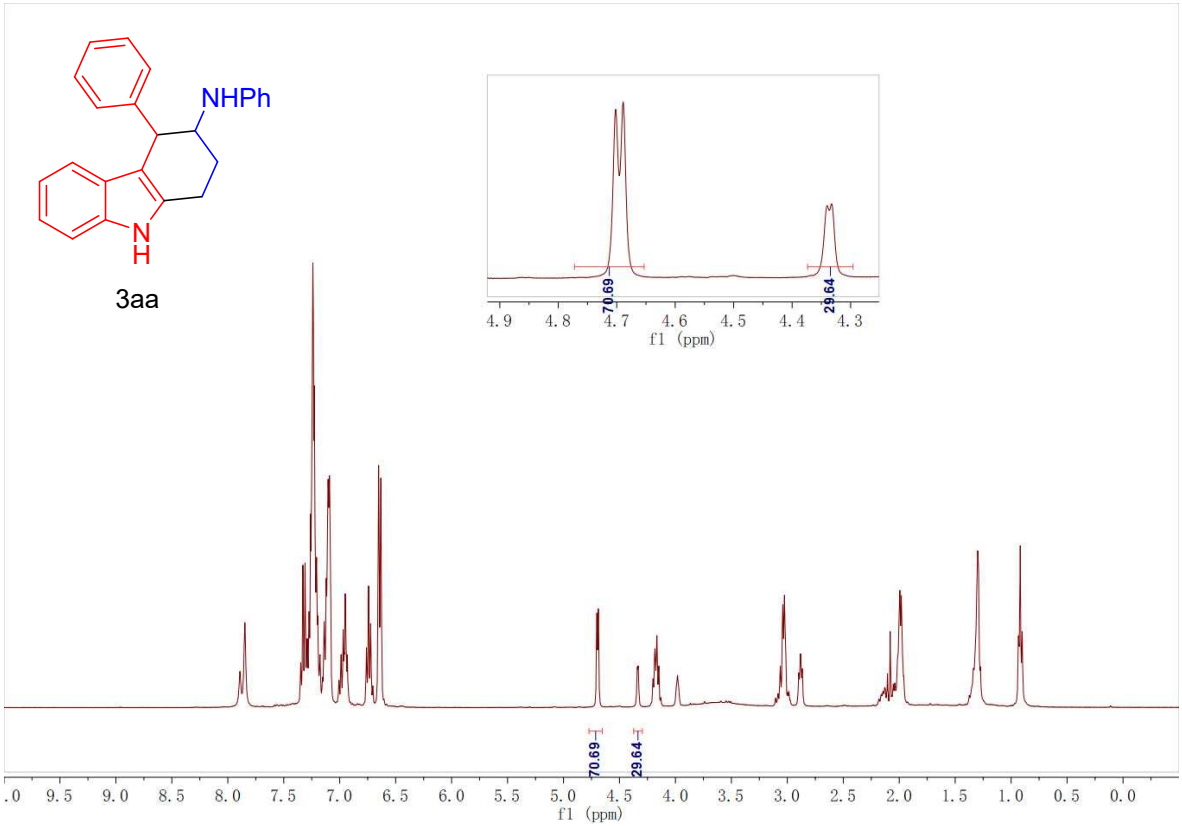
129.96
129.63
129.57
128.70
128.57
127.36
127.24
127.03
125.91
124.70
Cl
N
1r
f1 (ppm)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N
H
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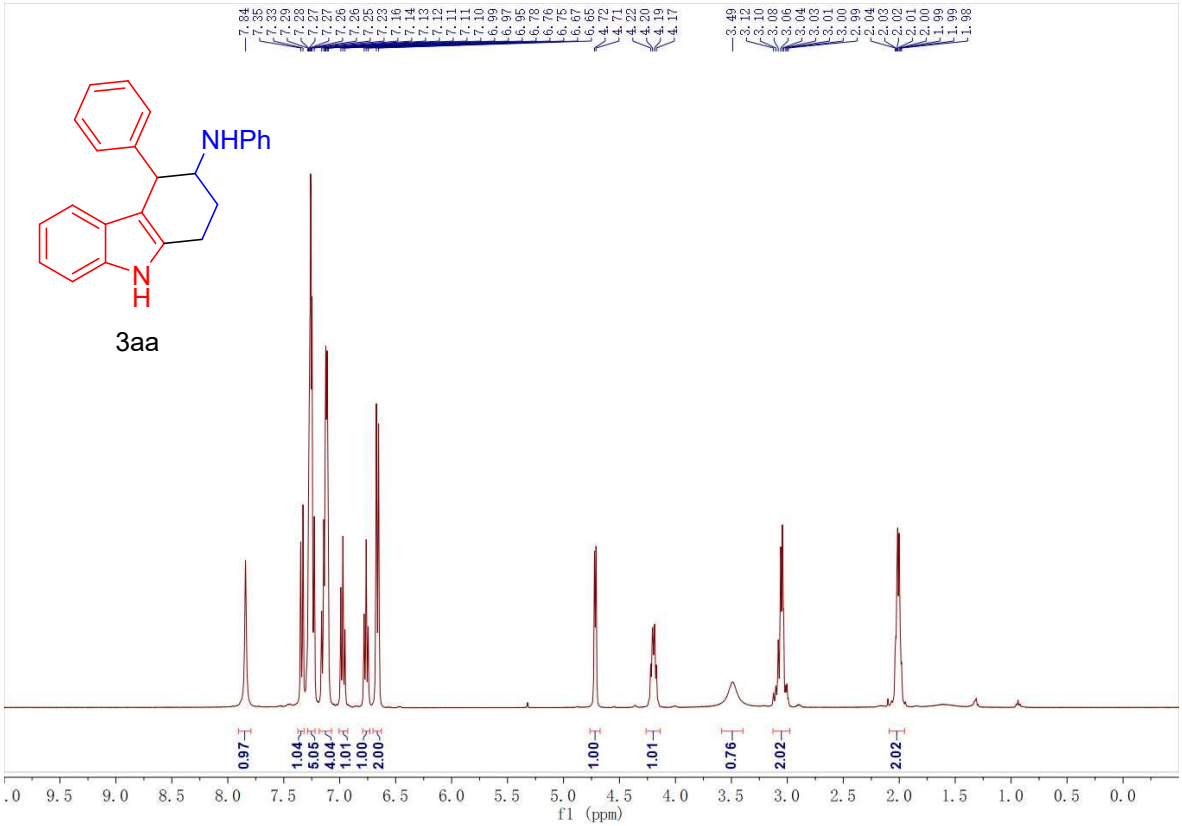
29.64
f1 (ppm)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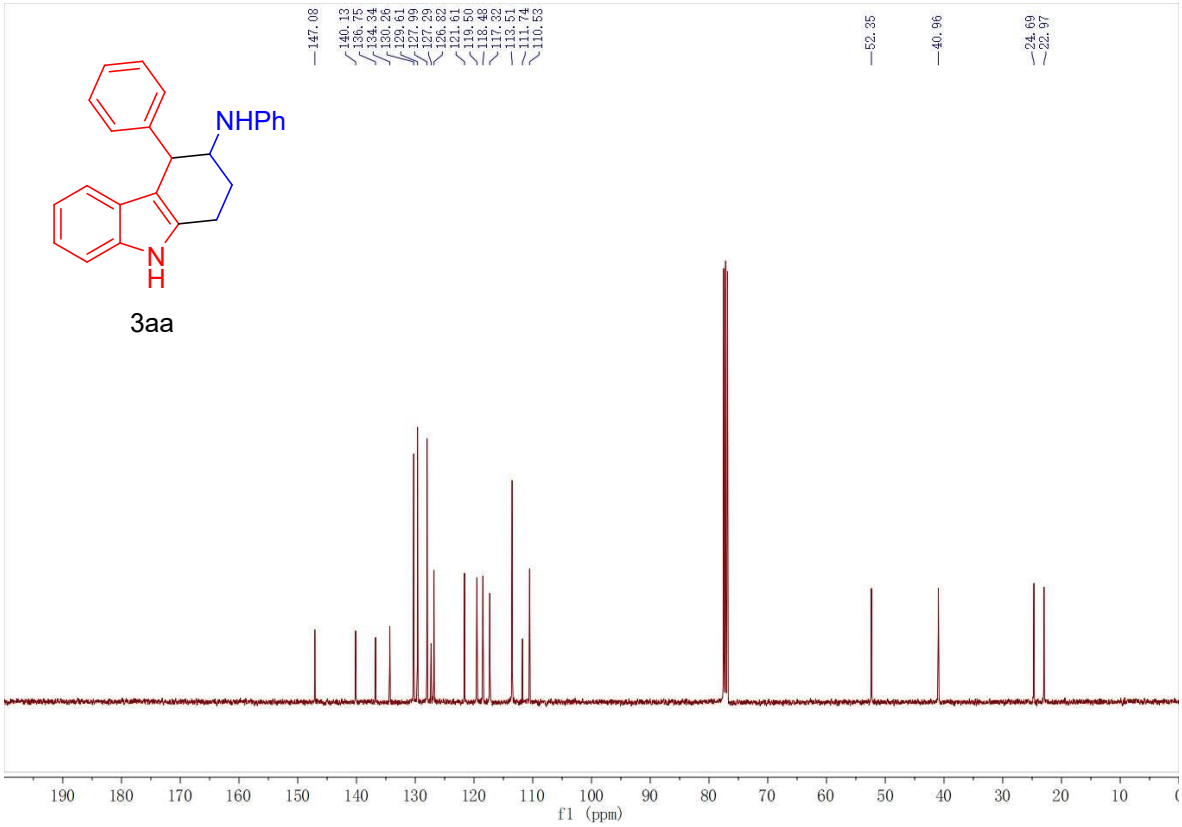
2.02
f1 (ppm)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127.29
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121.61
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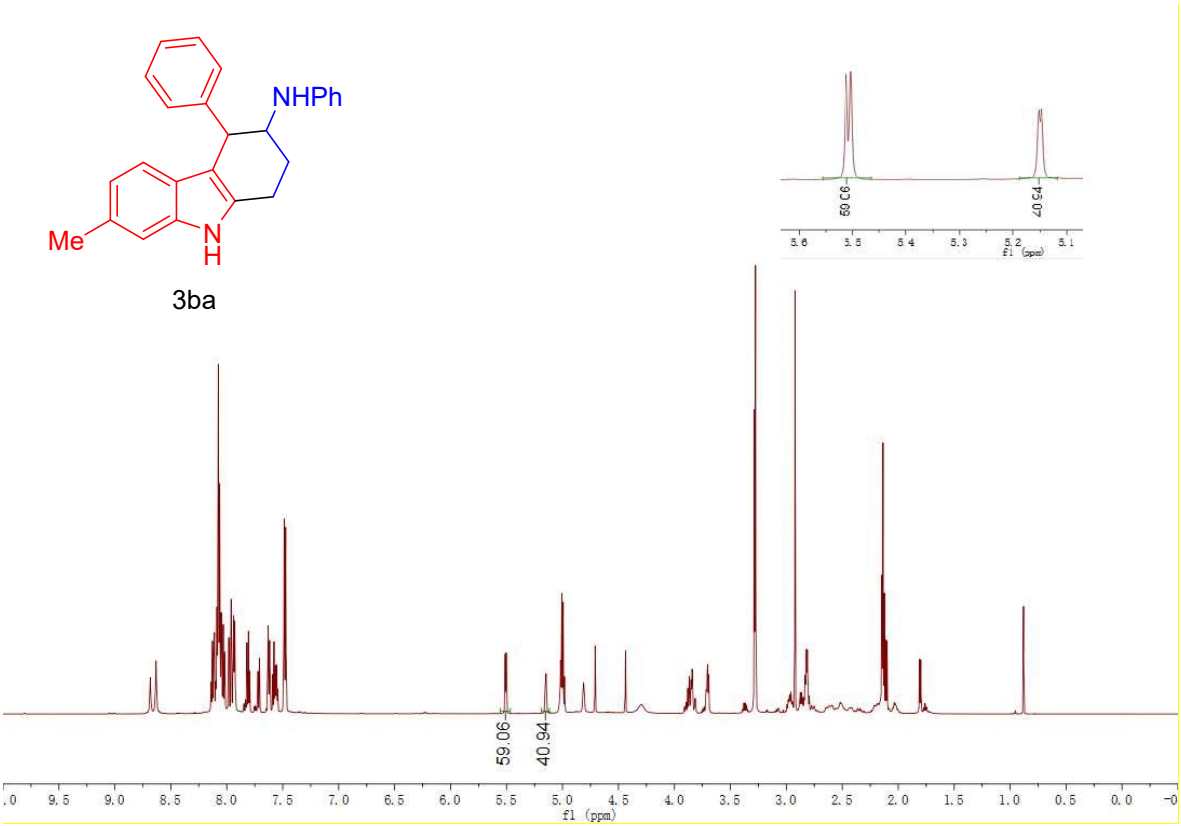
118.48
117.32
113.51
111.74
110.53
52.35
40.96
24.69
22.97
NHPh
N
H
3aa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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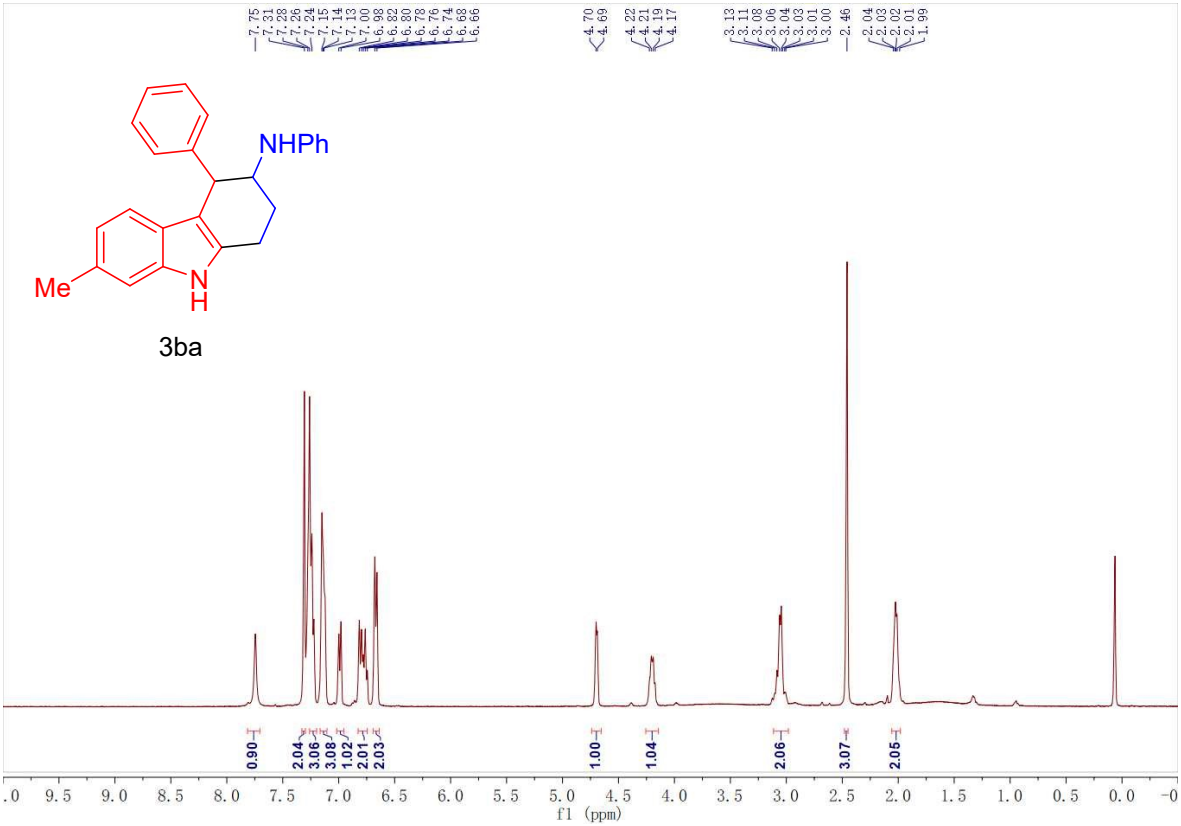
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Me
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H
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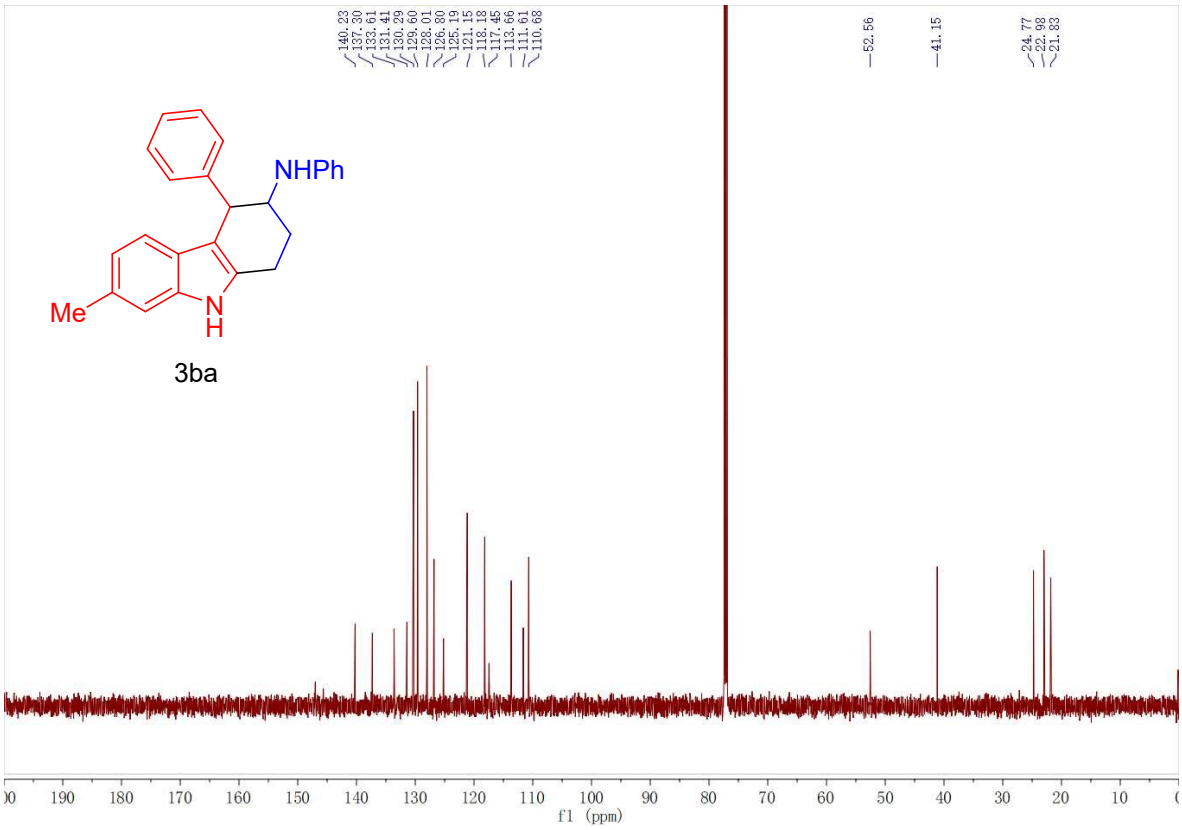
2.01
2.03
1.00
1.04
2.06
3.07
2.05
f1 (ppm)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113.66
111.61
110.68
52.56
41.15
24.77
22.98
21.83
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Me
N
H
3ba
190
180
170
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140
130
120
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90
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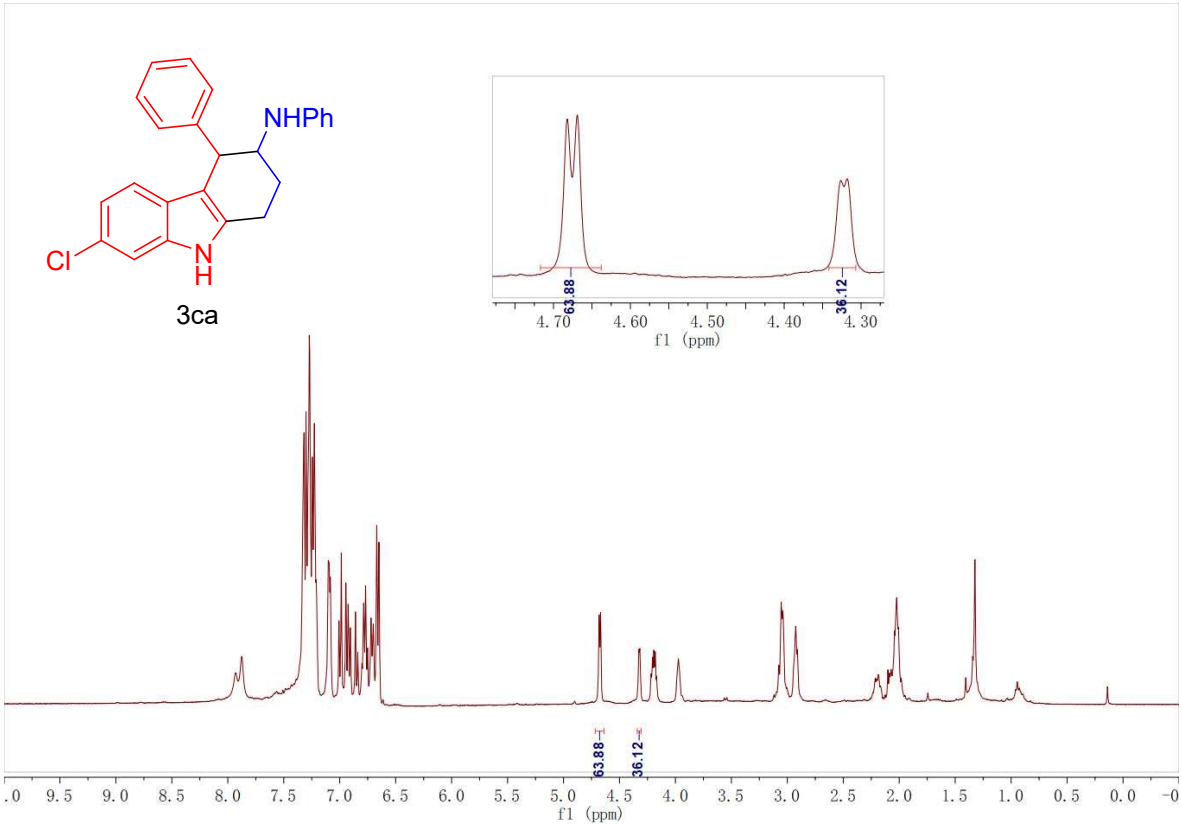
60
50
40
30
20
10
f1 (ppm)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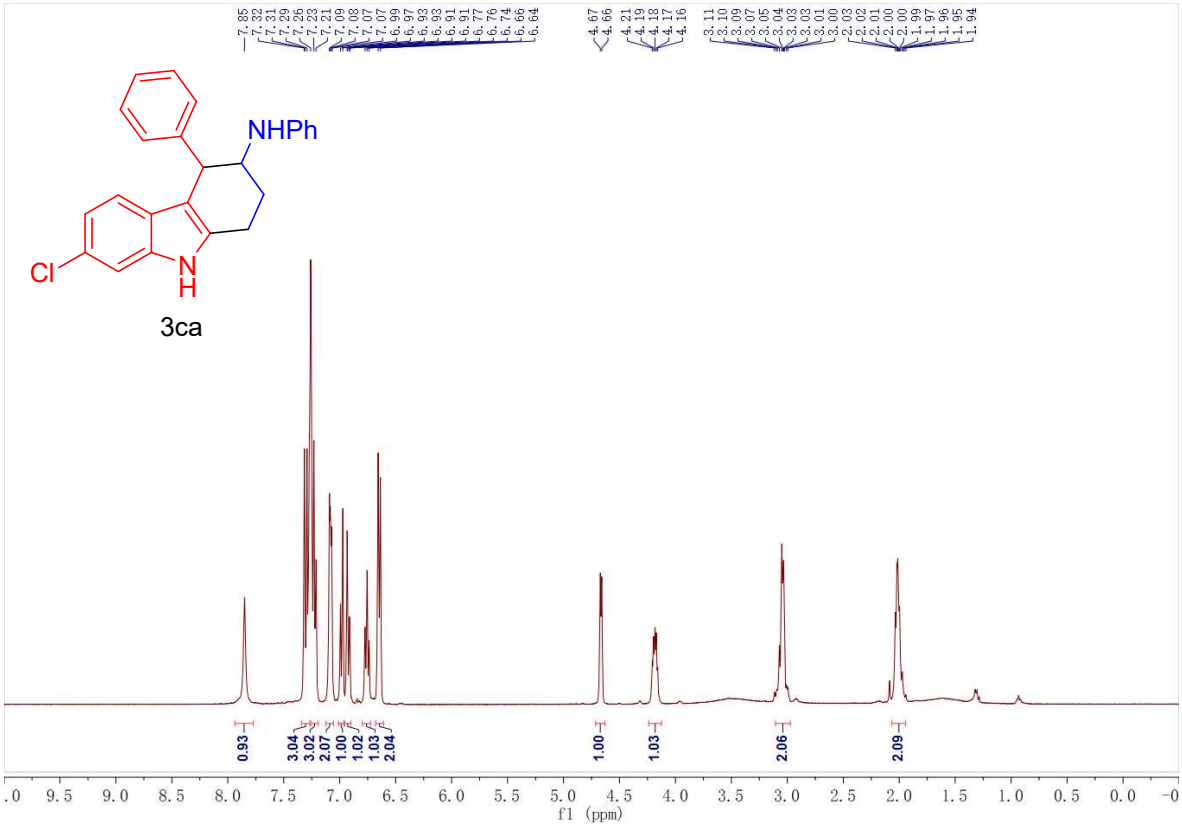
f1 (ppm)
63.88
36.12
f1 (ppm)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H
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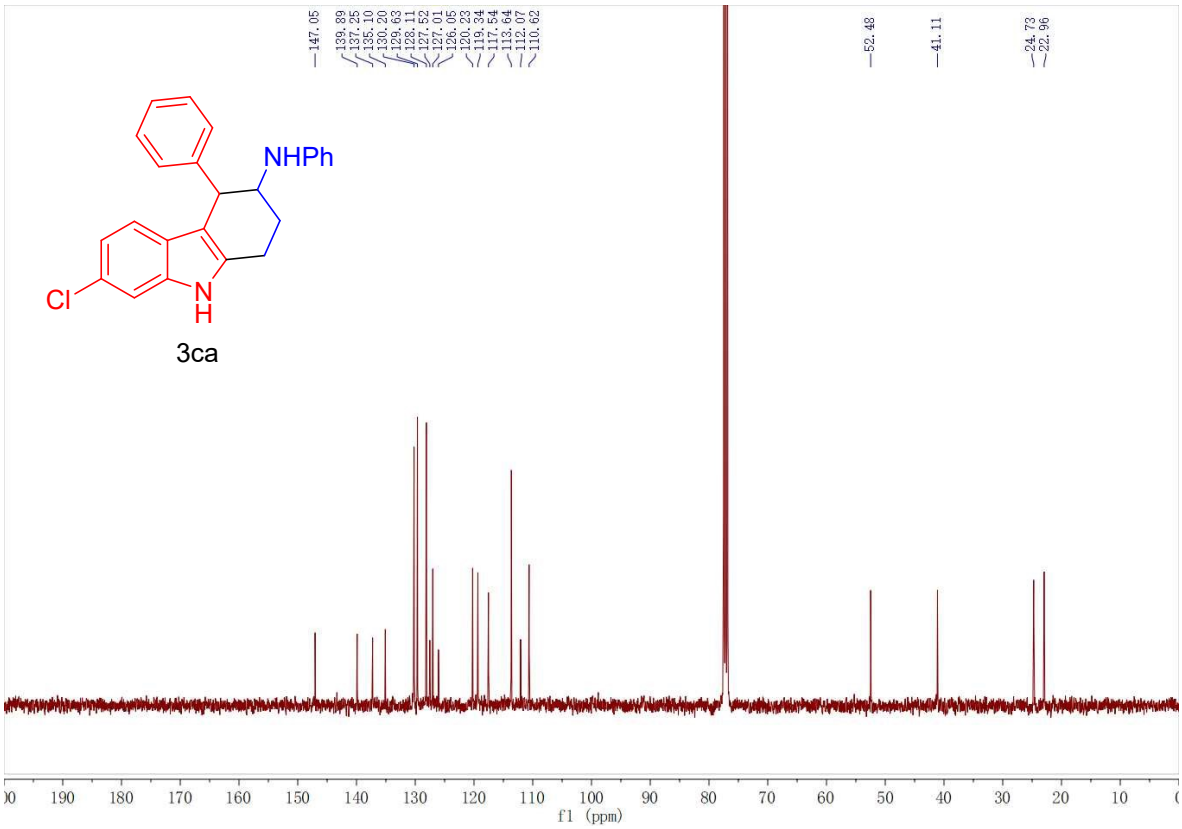
1.03
2.06
2.09
f1 (ppm)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129.63
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127.52
127.01
126.05
120.23
119.34
117.54
113.64
112.07
110.62
52.48
41.11
24.73
22.96
NHPh
Cl
N
H
3ca
190
180
170
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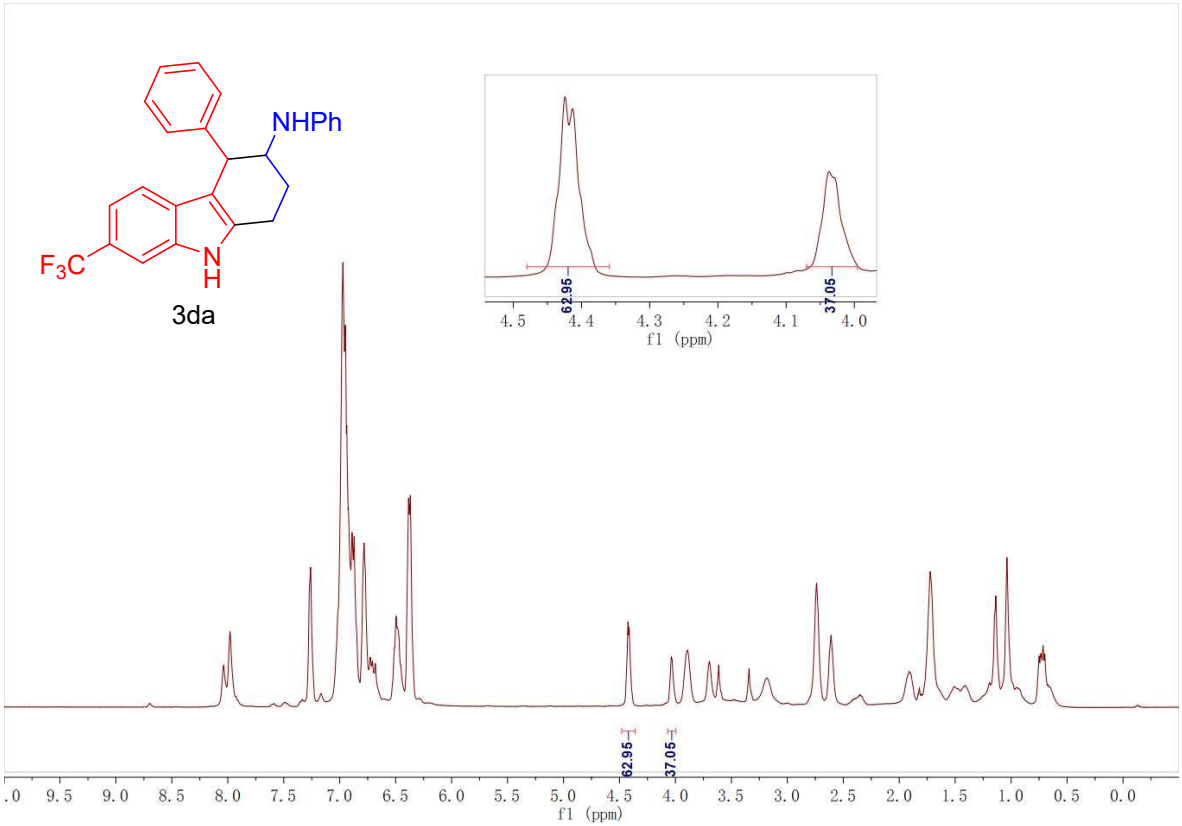
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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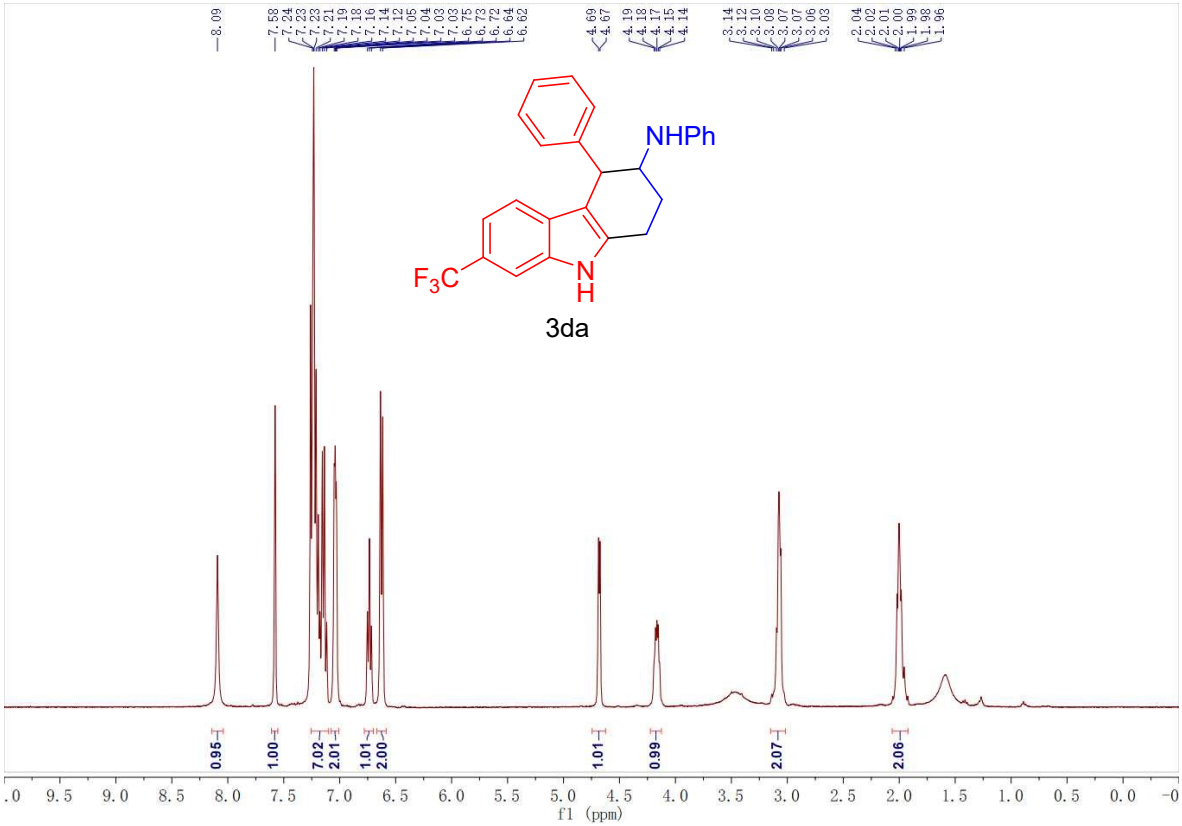
F3C
N
H
3da
62.95
37.05
f1 (ppm)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F3C
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H
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1.00
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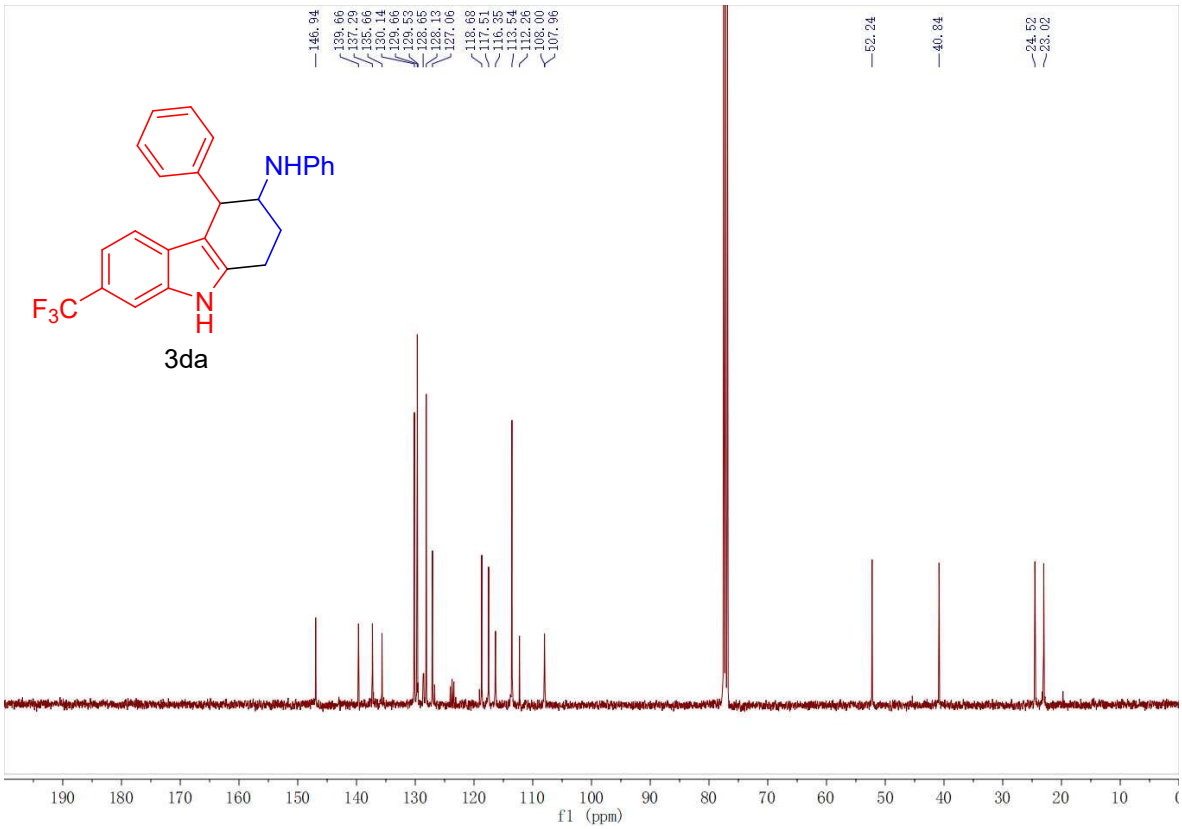
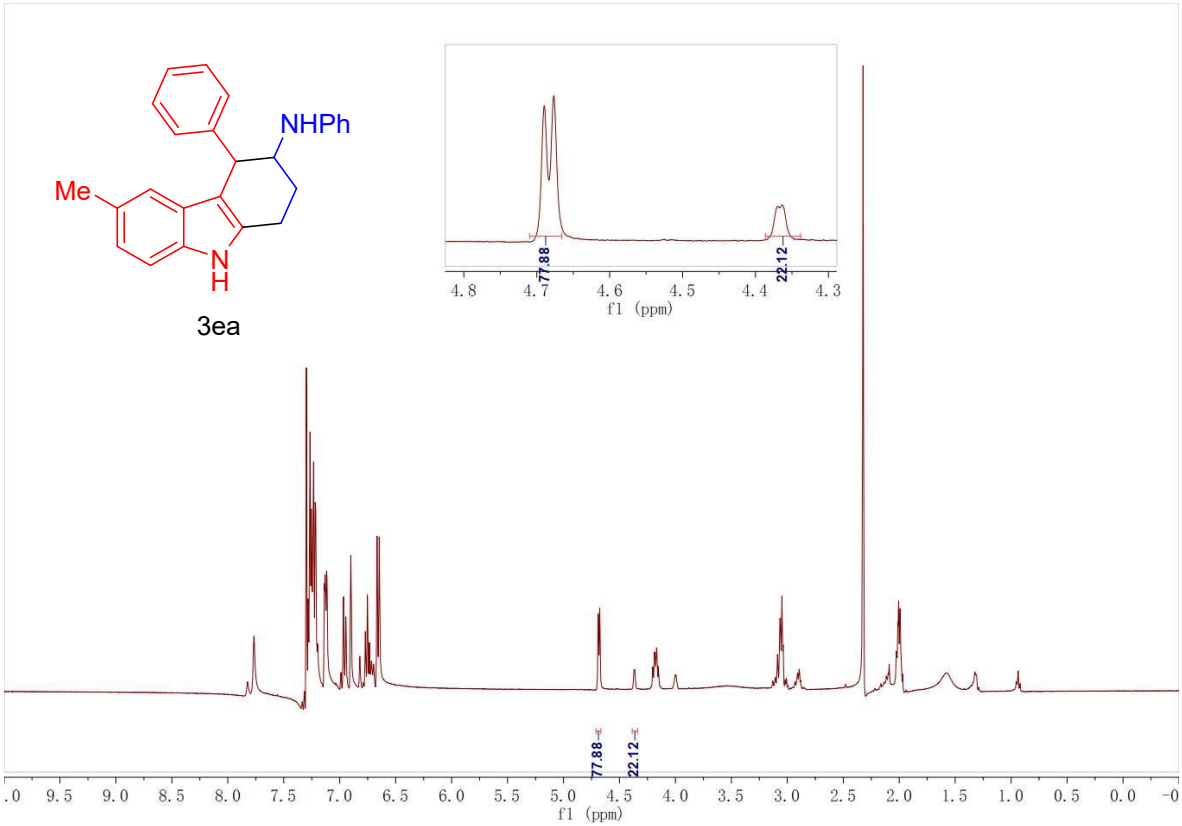
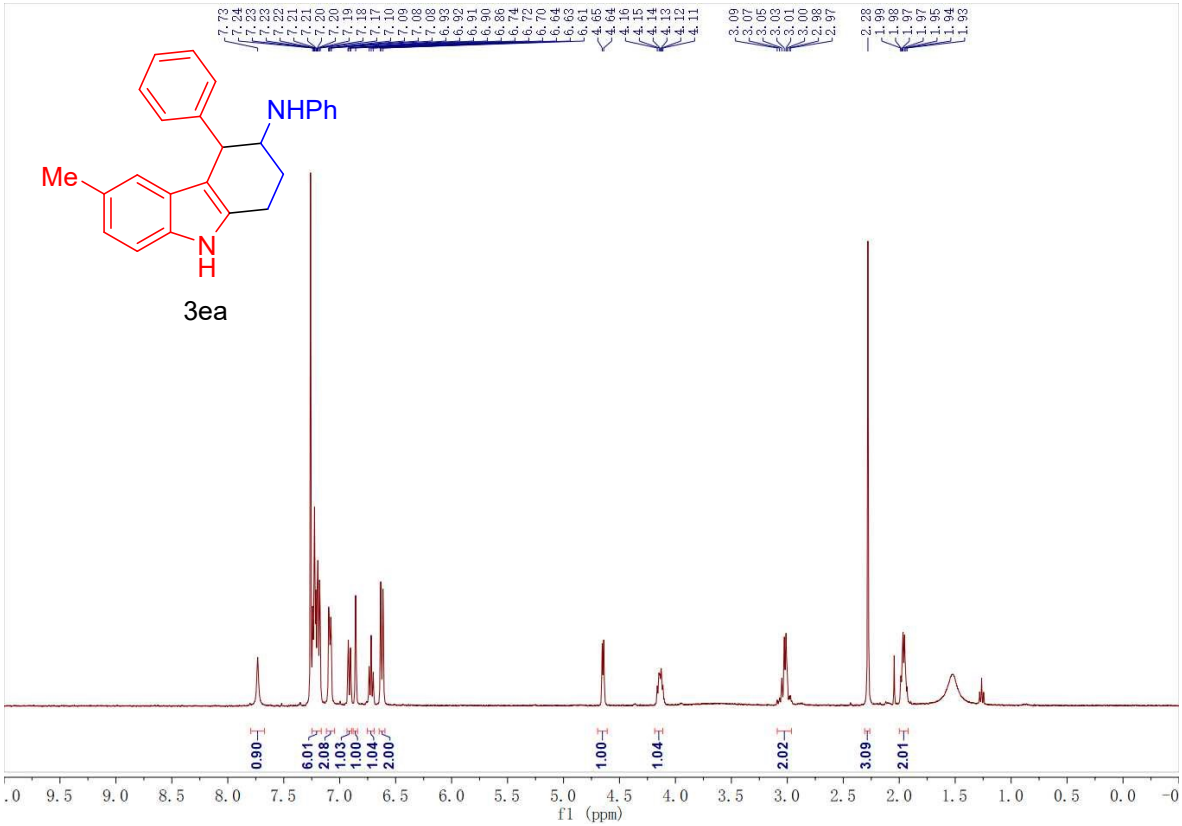
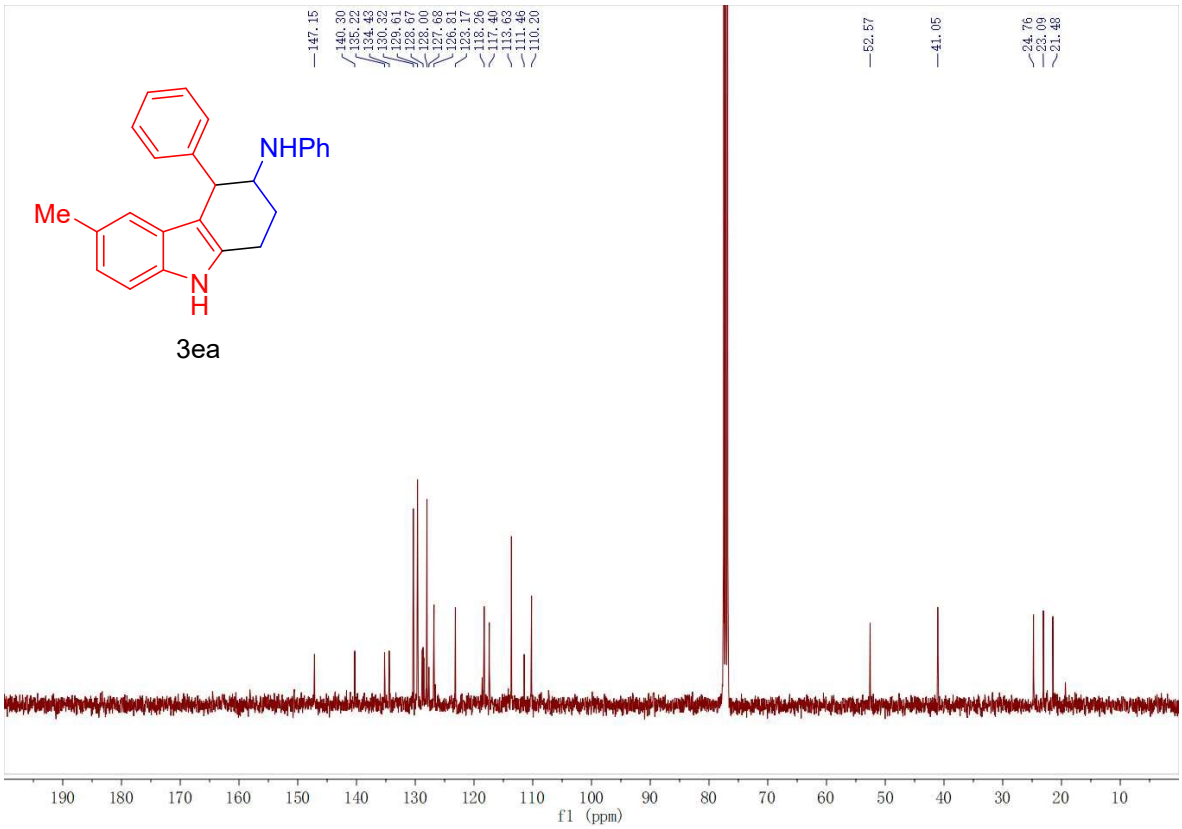
1.01
2.00
1.01
0.99
2.07
2.06
f1 (ppm)


146.94
139.66
137.29
135.66
130.14
129.66
129.53
128.65
128.13
127.06
118.68
117.51
116.35
113.54
112.26
108.00
107.96
52.24
40.84
24.52
23.02
NHPh
F3C
N
H
3da
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NHPh
Me
N
H
3ea
77.88
22.12
f1 (ppm)


NHPh
Me
N
H
3ea
0.90
6.01
2.08
1.03
1.00
1.04
2.00
1.00
1.04
2.02
3.09
2.01
f1 (ppm)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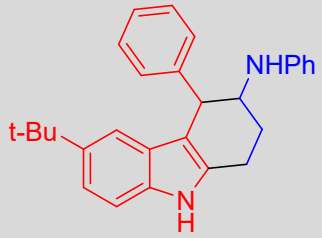
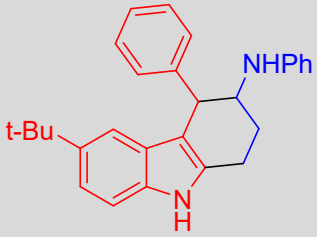
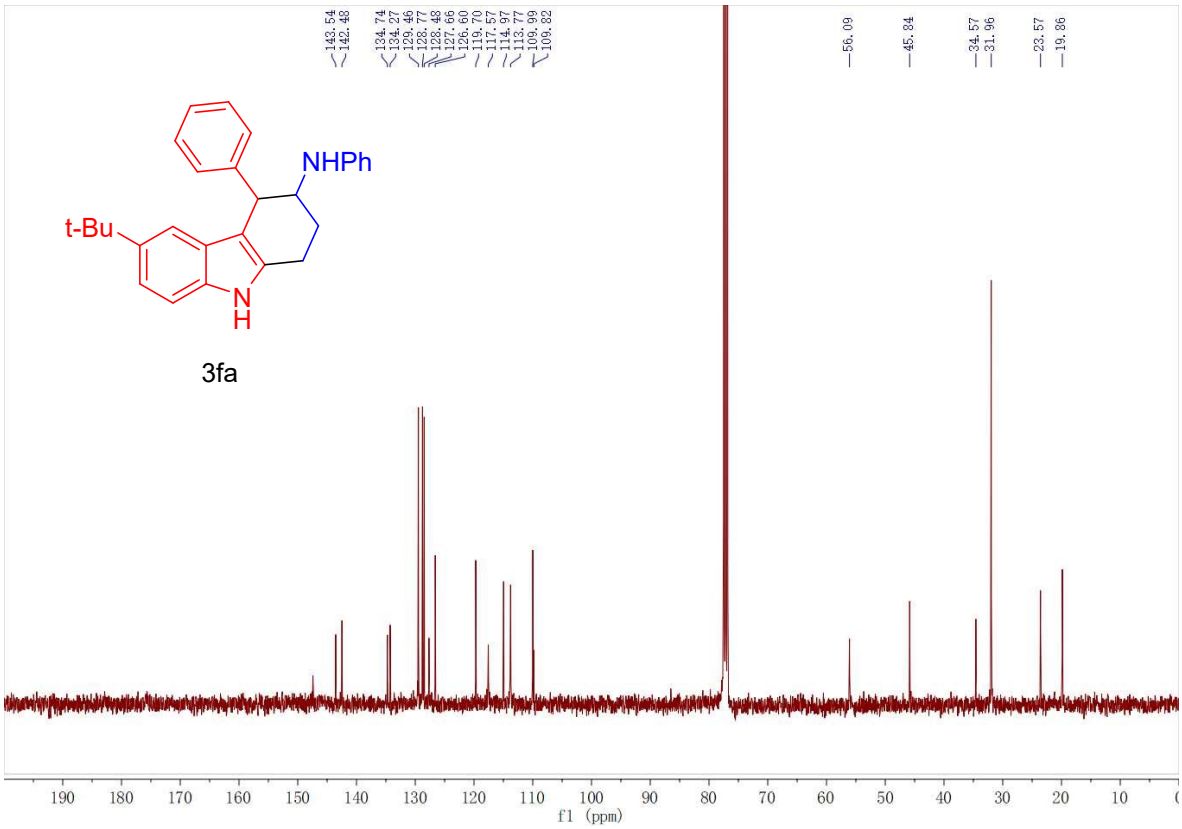
140.30
135.22
134.43
130.32
129.61
128.67
128.00
127.68
126.81
126.17
118.26
117.40
113.63
111.46
110.20
52.57
41.05
24.76
23.09
21.48
NHPh
Me
N
H
3ea
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3fa



3fa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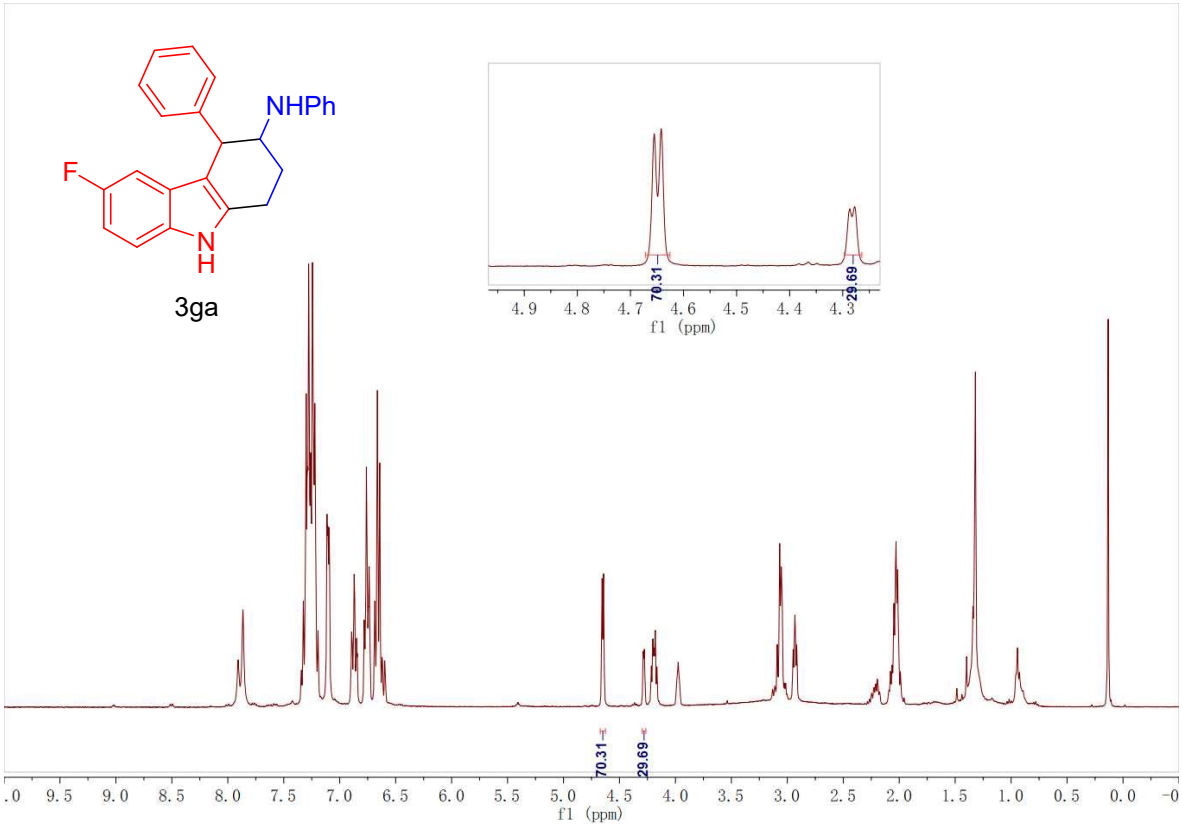
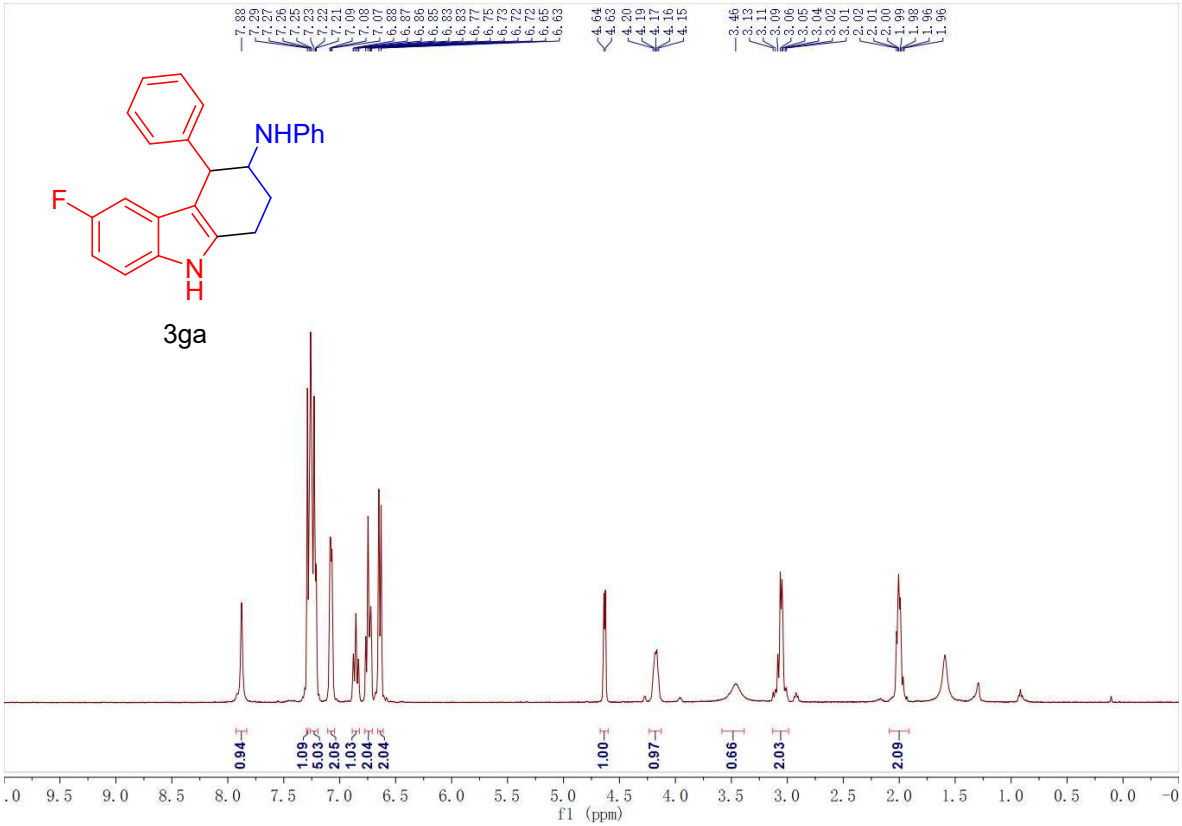
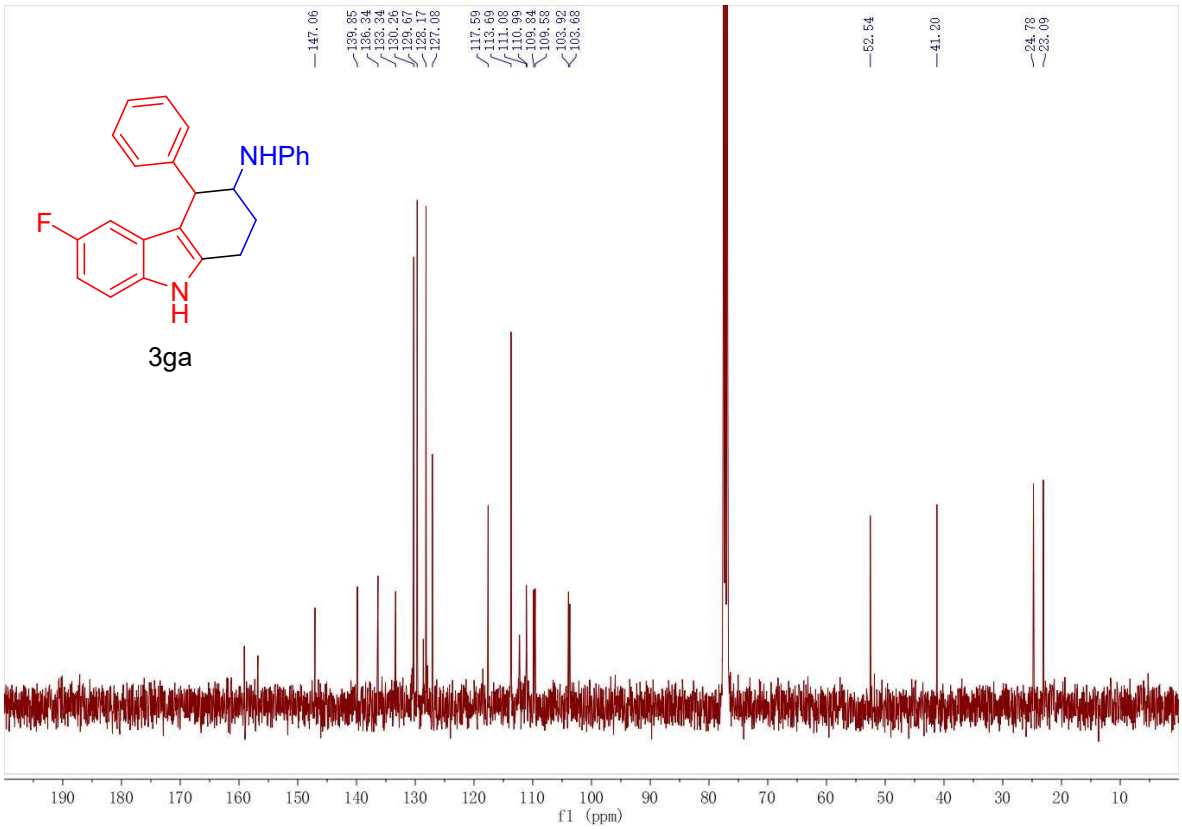
142.48
134.74
134.27
129.46
128.77
128.48
127.66
126.60
119.70
117.57
114.97
113.77
109.99
109.82
56.09
45.84
34.57
31.96
23.57
19.86
NHPh
t-Bu
N
H
3fa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NHPh
F
N
H
3ga
70.31
29.69
4.9 4.8 4.7 4.6 4.5 4.4 4.3
f1 (ppm)
70.31
29.69
f1 (ppm)


NHPh
F
N
H
3ga
0.94
1.09
5.03
2.05
1.03
2.04
2.04
1.00
0.97
0.66
2.03
2.09
f1 (ppm)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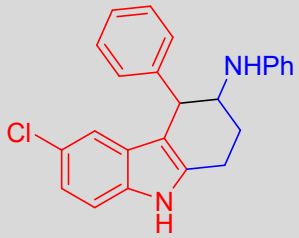
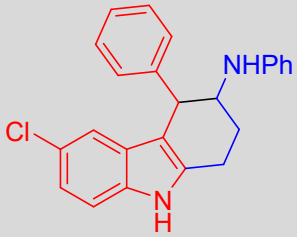
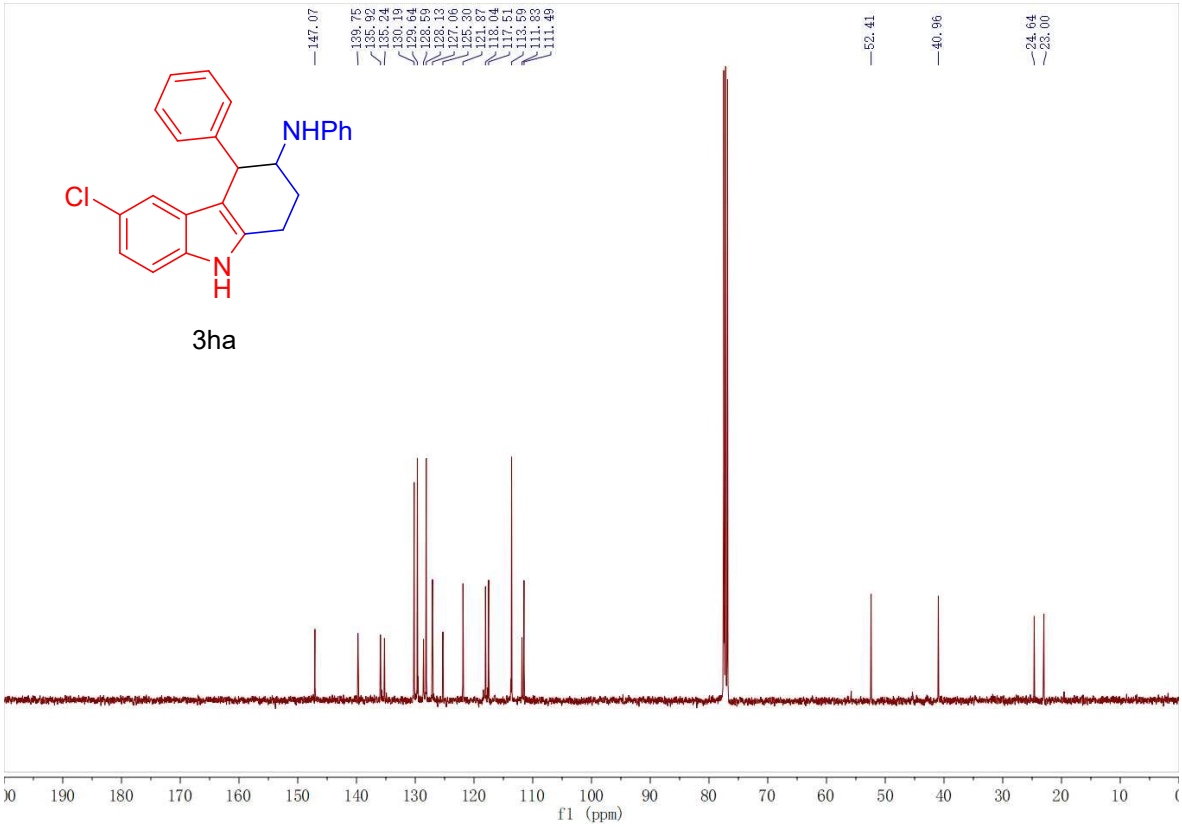
139.85
136.34
133.34
130.26
129.67
128.17
127.08
117.59
113.69
111.08
110.99
109.84
109.58
103.92
103.68
52.54
41.20
24.78
23.09
NHPh
F
N
H
3ga
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3ha



3ha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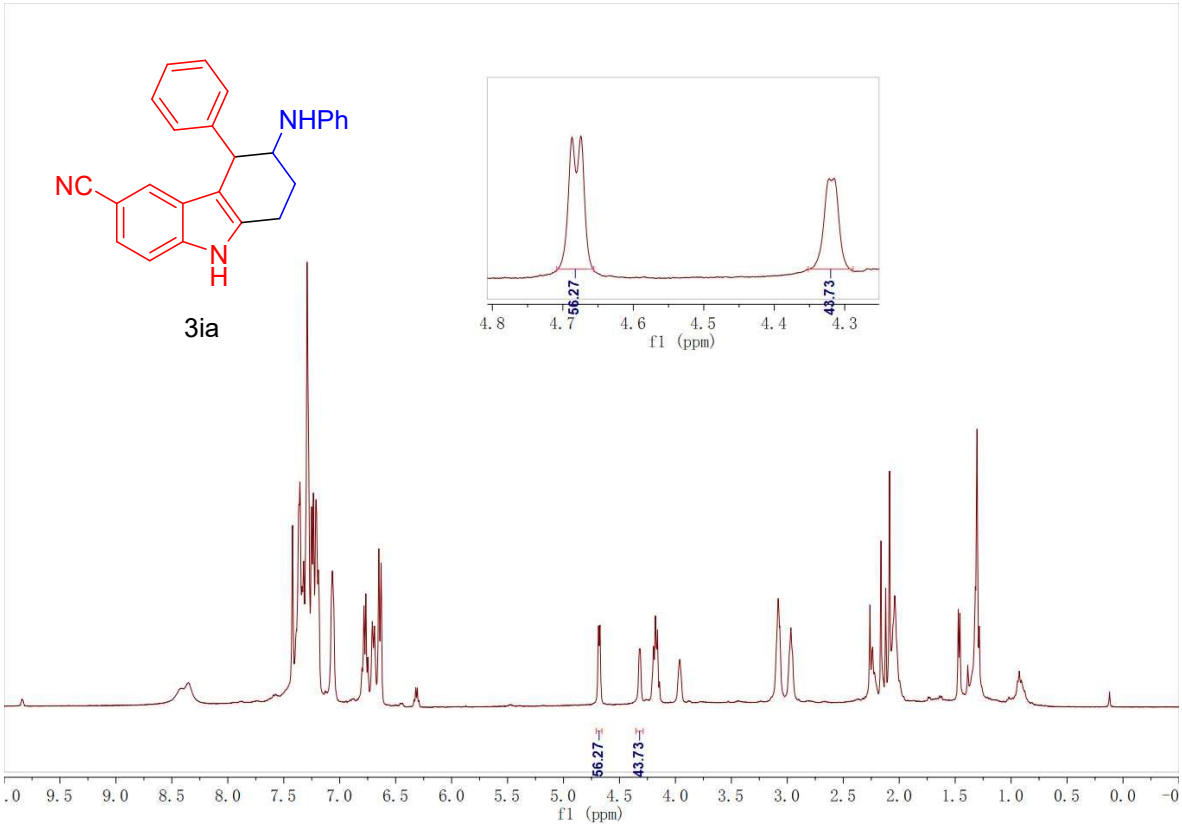
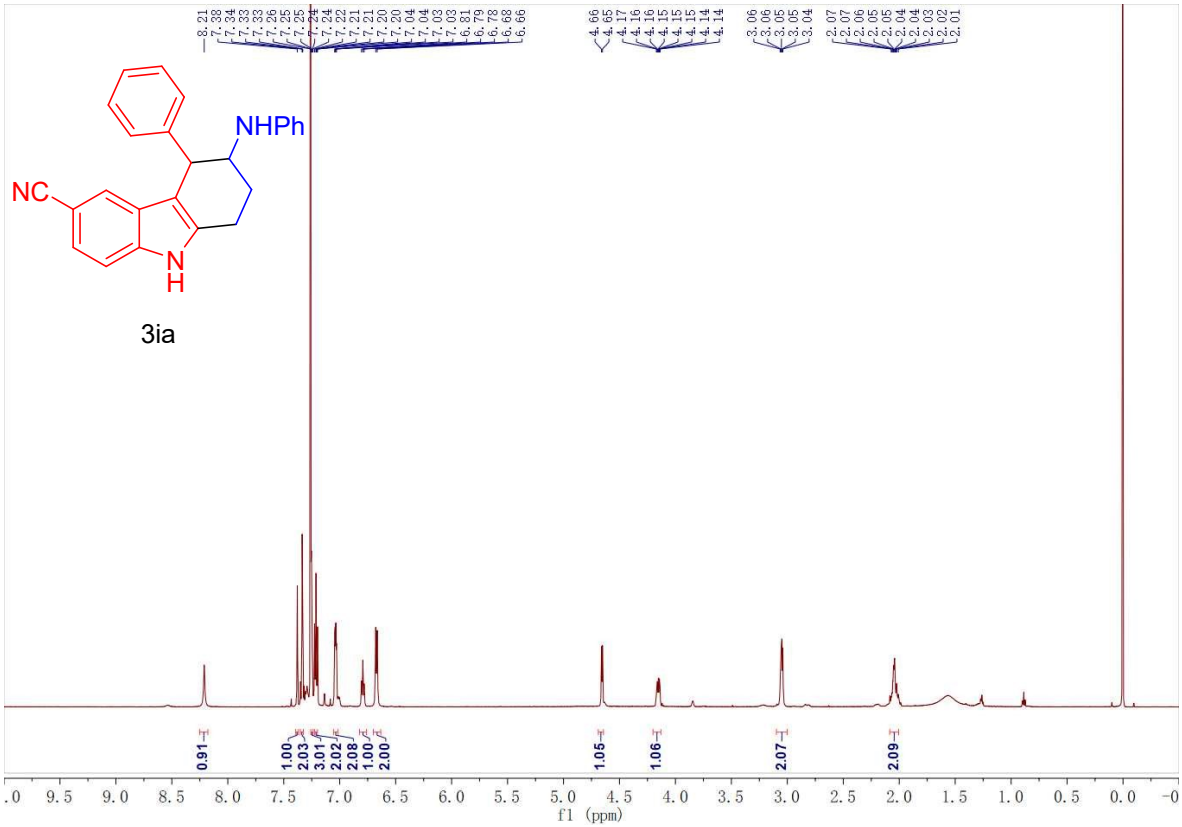
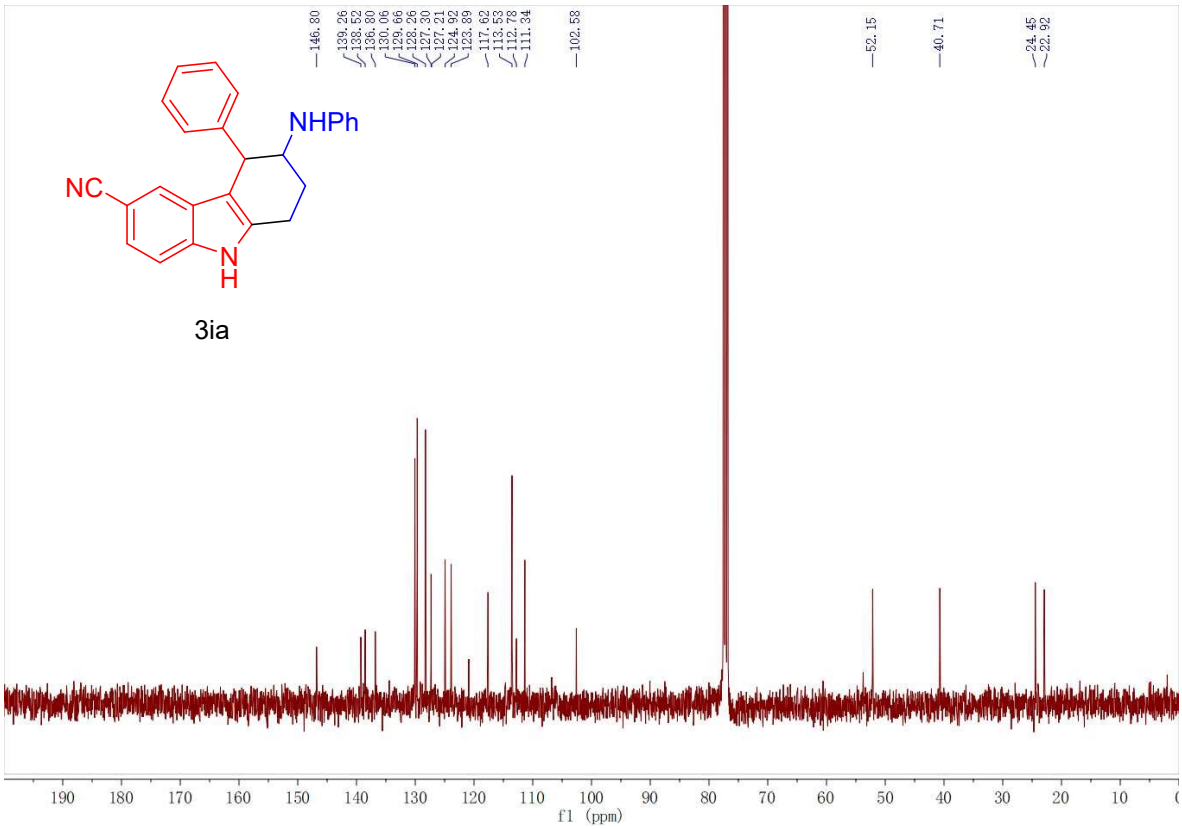
139.75
135.92
135.24
130.19
129.64
128.59
128.13
127.06
125.30
121.87
118.04
117.51
113.69
111.83
111.49
52.41
40.96
24.64
23.00
NHPh
Cl
N
H
3ha
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NHPh
NC
N
H
3ia
56.27
43.73
f1 (ppm)


NHPh
NC
N
H
3ia
f1 (ppm)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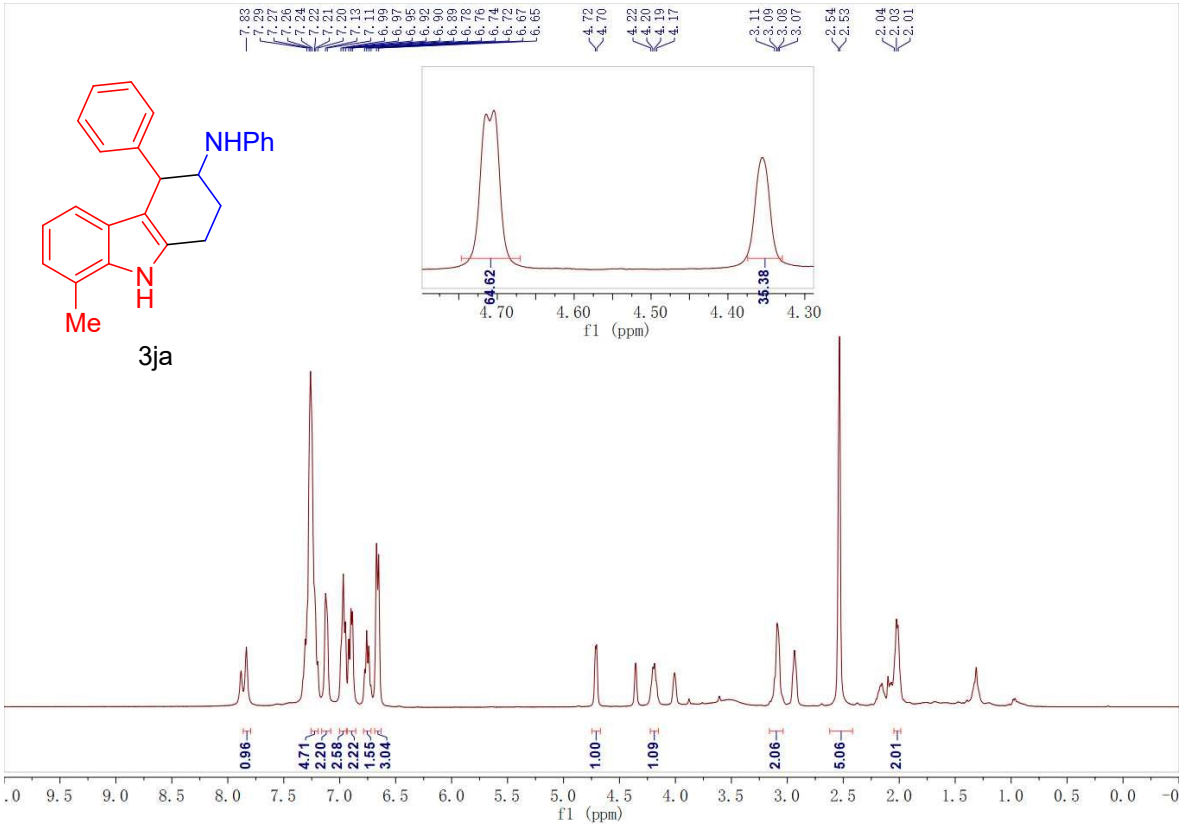
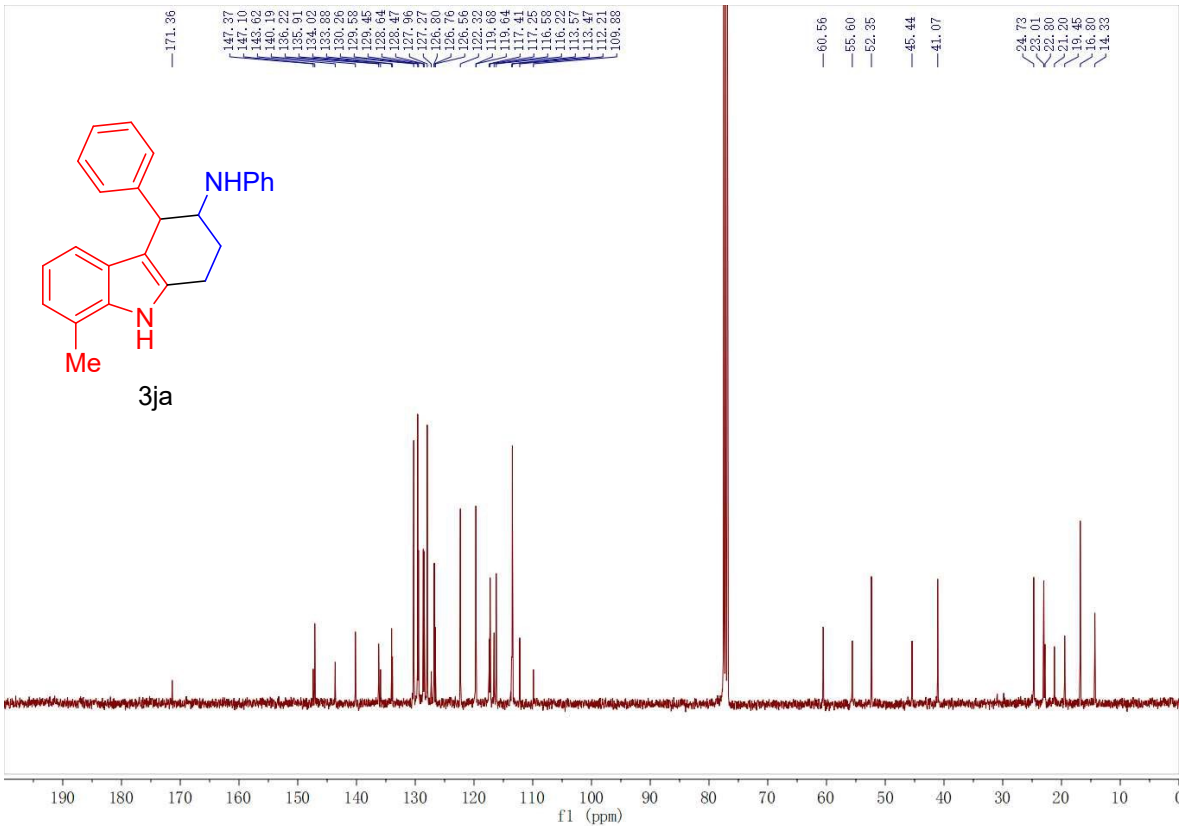
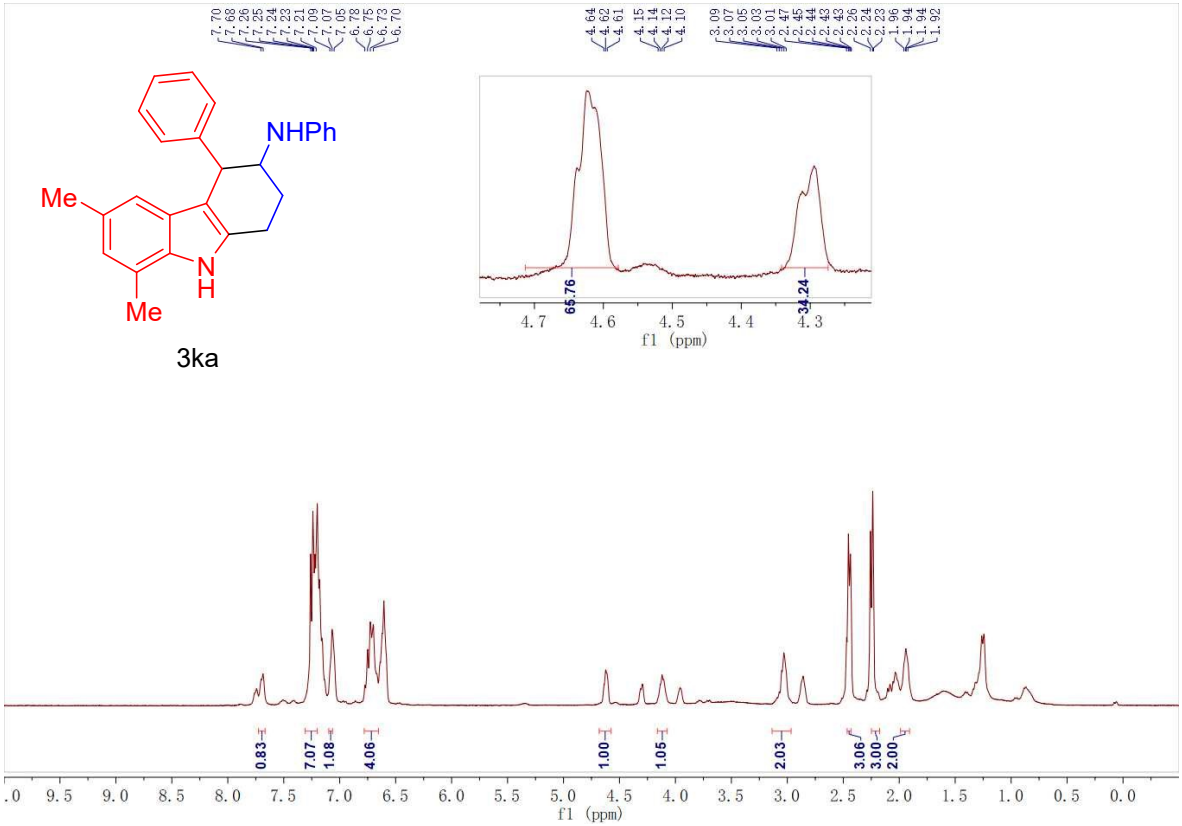
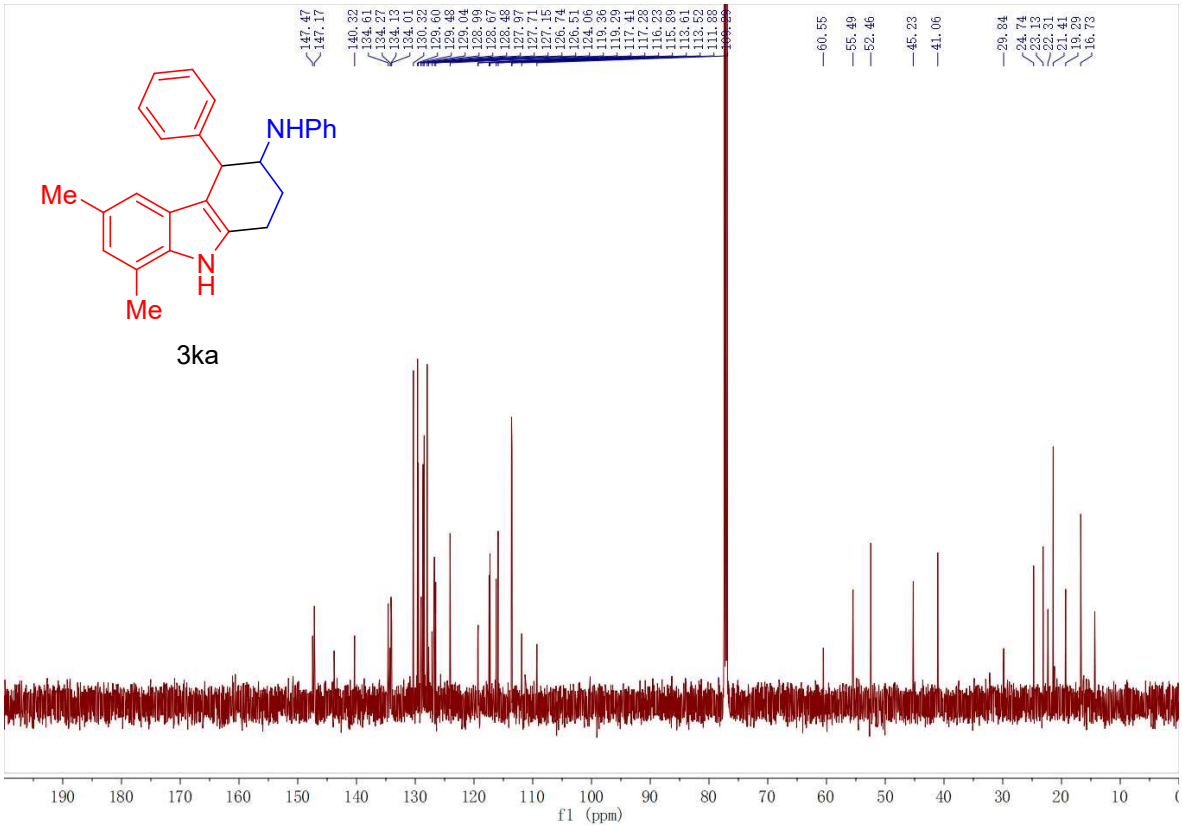
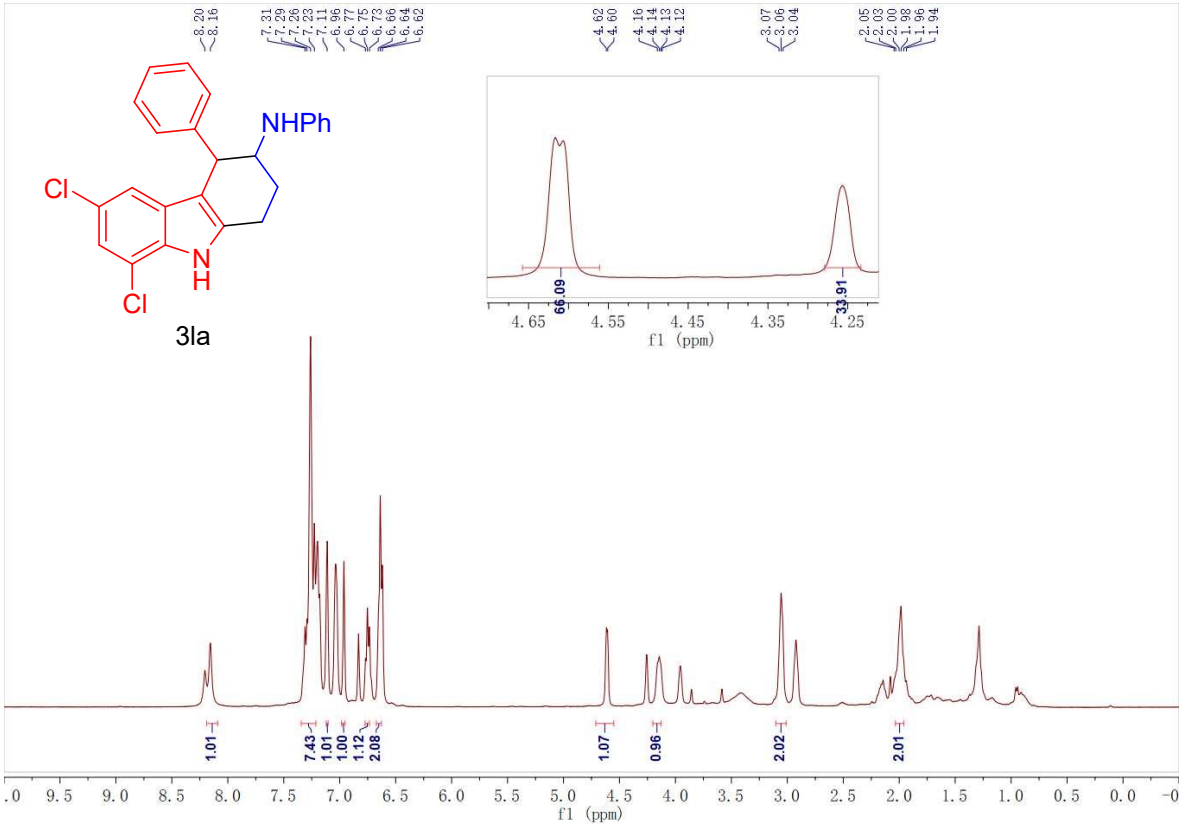
139.26
138.52
136.80
130.06
129.66
128.26
127.30
127.21
124.92
123.89
117.62
113.53
112.78
111.34
102.58
52.15
40.71
24.45
22.92
NHPh
NC
N
H
3ia
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

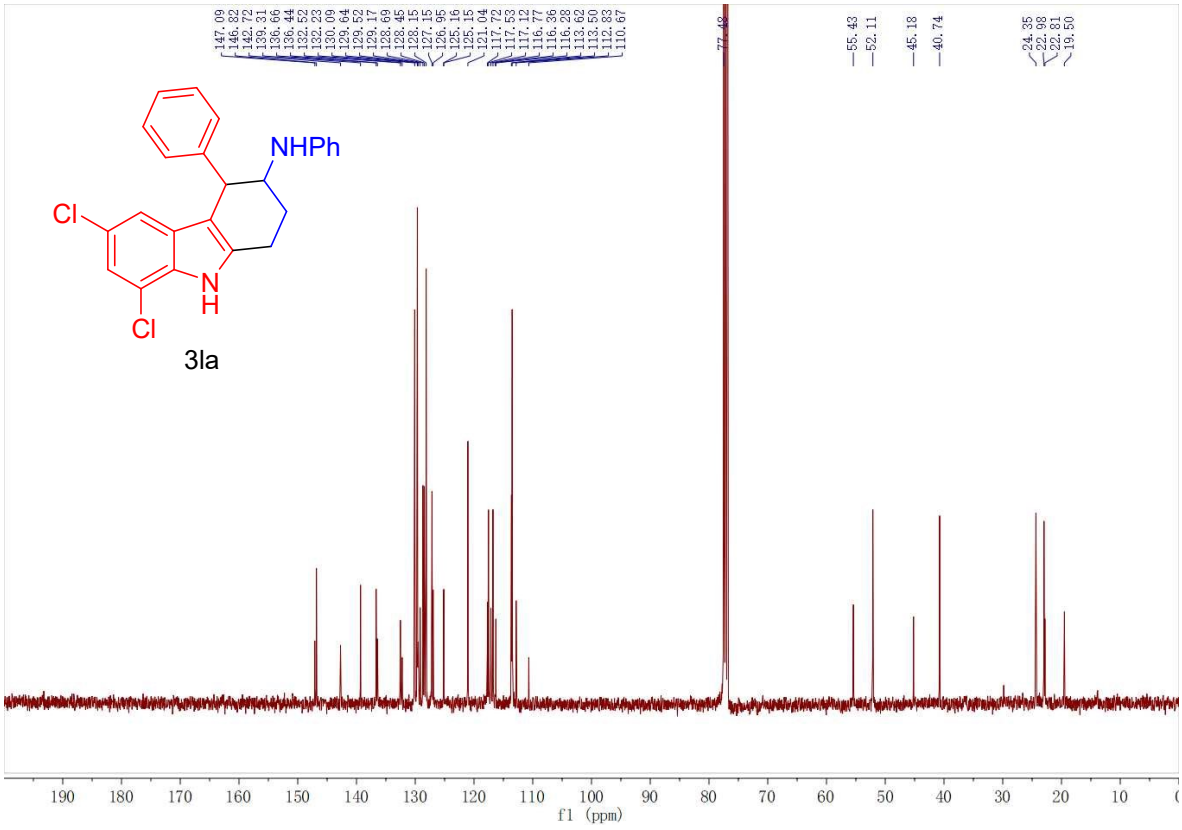

NHPh
N
H
Me
3ja
f1 (ppm)

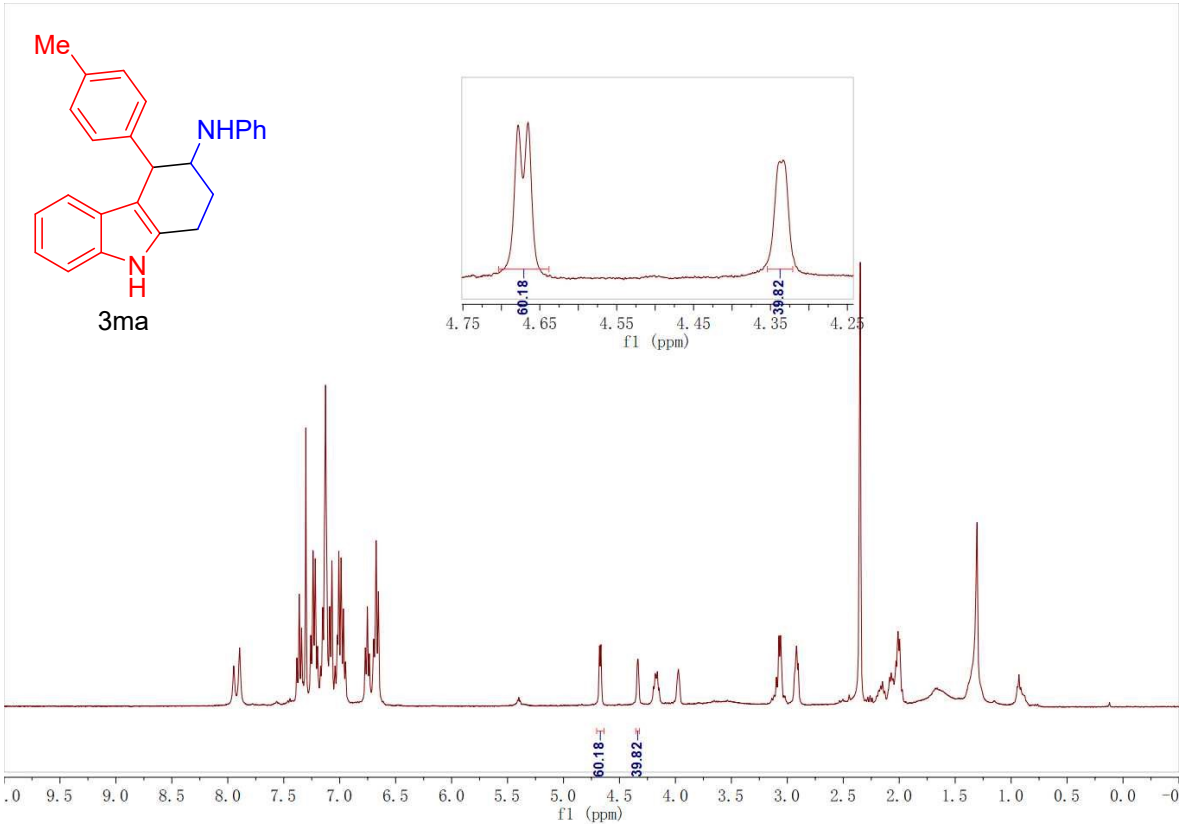

NHPh
N
H
Me
3ja
f1 (ppm)

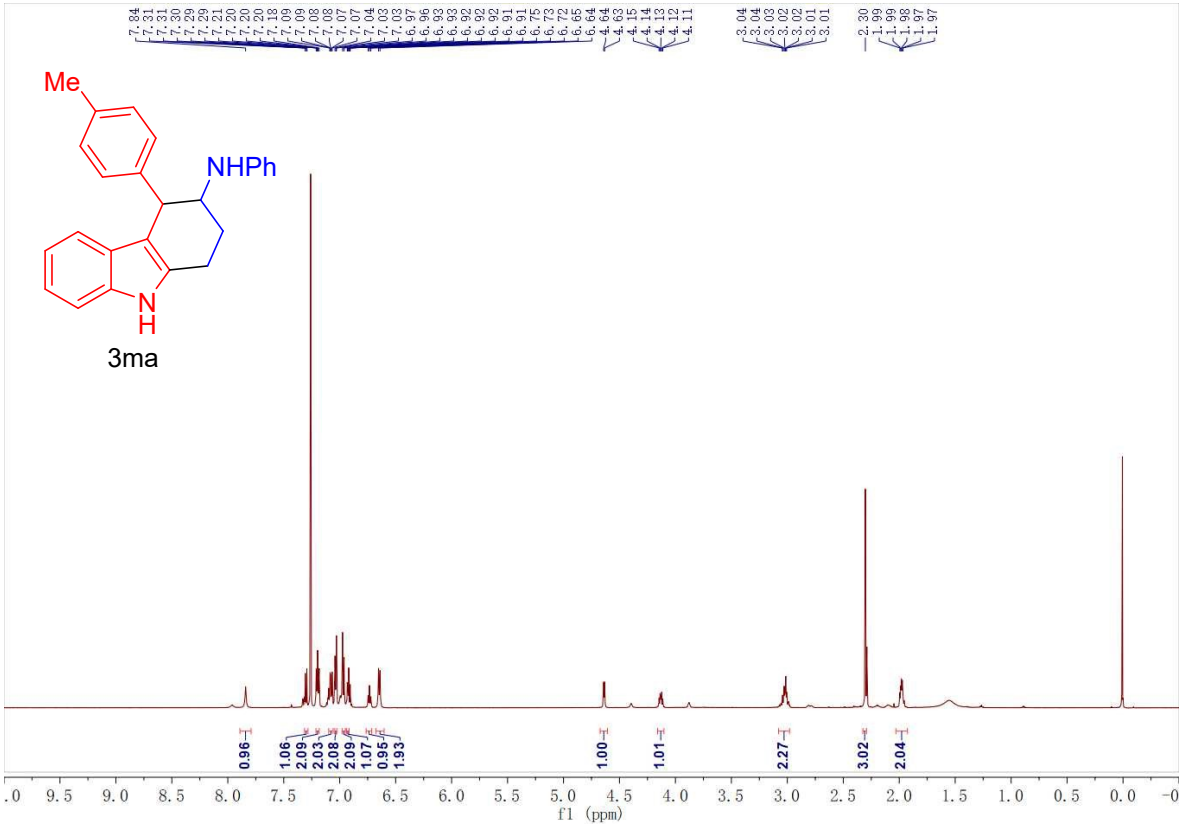

NHPh
Me
N
H
Me
3ka
65.76
34.24
f1 (ppm)
0.83
7.07
1.08
4.06
1.00
1.05
2.03
3.06
3.00
2.00
f1 (ppm)

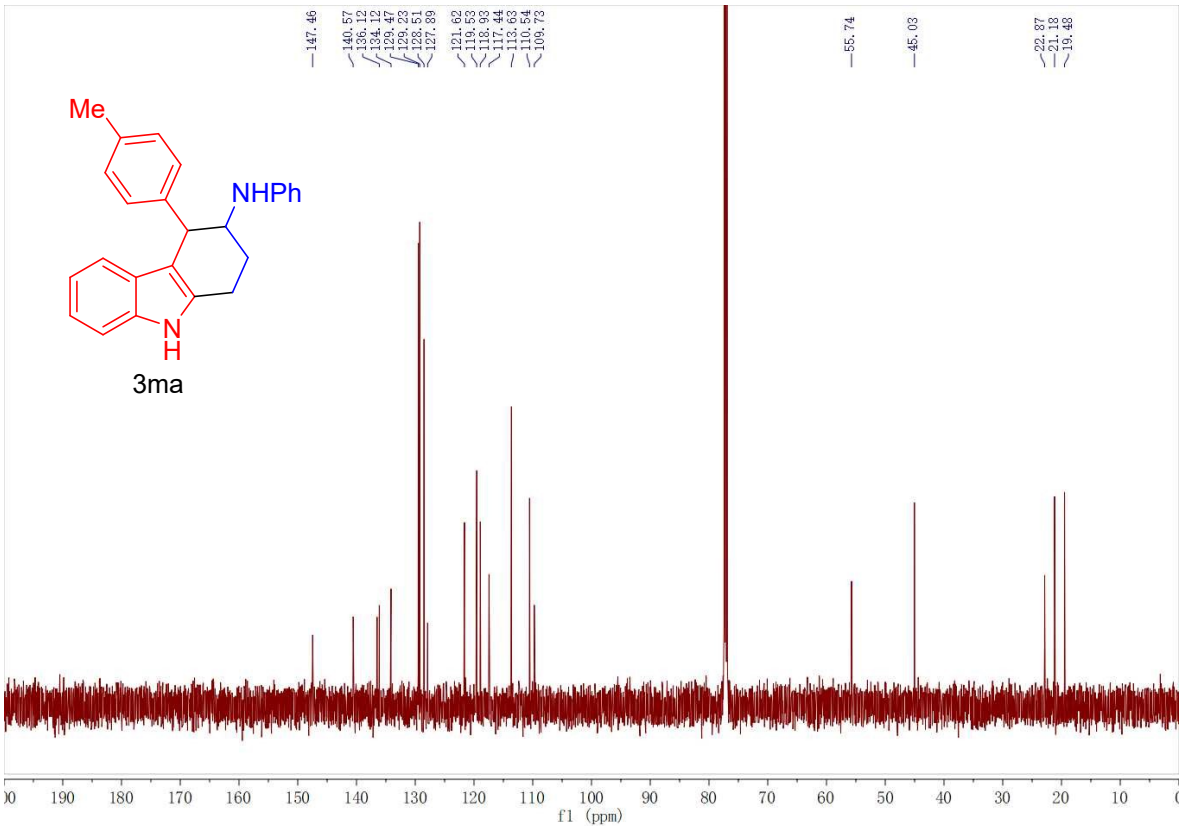

NHPh
Me
N
H
Me
3ka
f1 (ppm)


NHPh
Cl
N
H
Cl
3la
66.09
33.91
4.65
4.55
4.45
4.35
4.25
f1 (ppm)
1.01
7.43
1.01
1.00
1.12
2.08
1.07
0.96
2.02
2.01
f1 (ppm)


NHPh
Cl
N
H
Cl
3la
77.48
f1 (ppm)


Me
NHPh
N
H
3ma
60.18
39.82
f1 (ppm)


Me
NHPh
N
H
3ma
0.96
1.06
2.09
2.03
2.08
2.09
1.07
0.95
1.93
1.00
1.01
2.27
3.02
2.04
f1 (ppm)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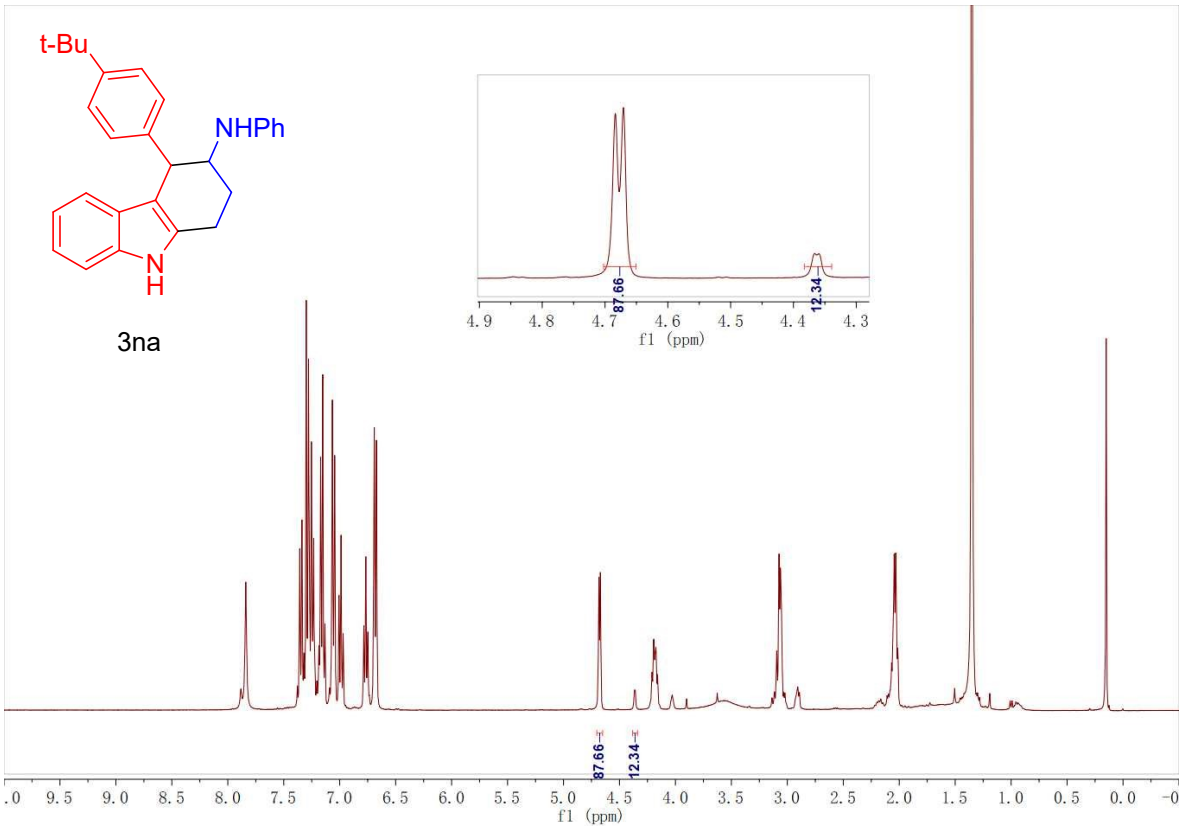
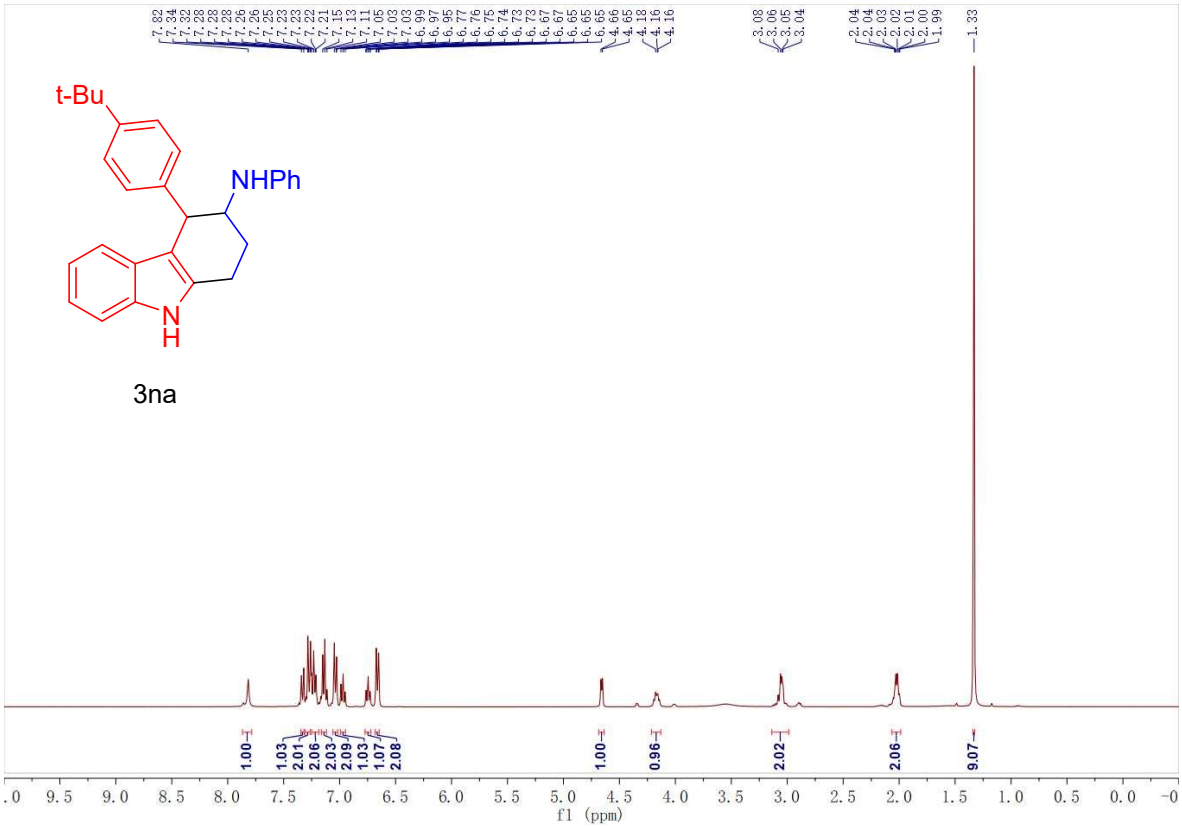
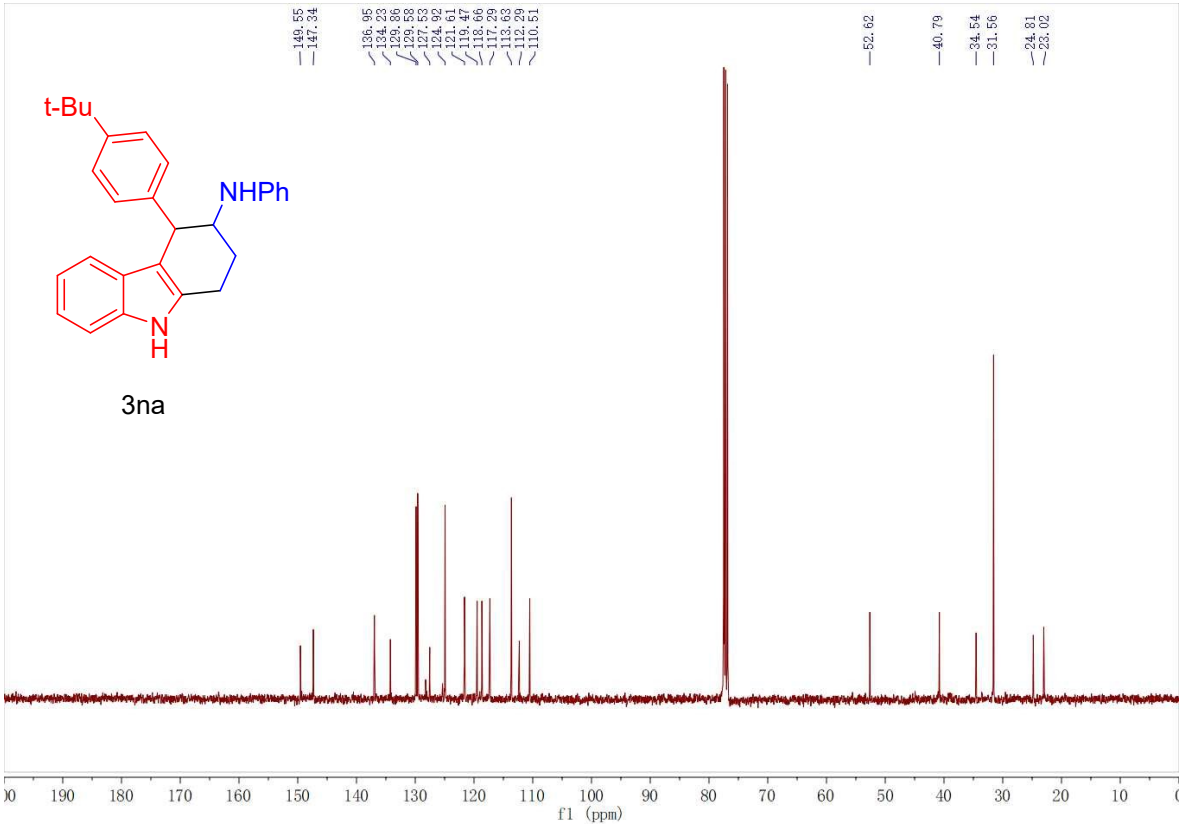
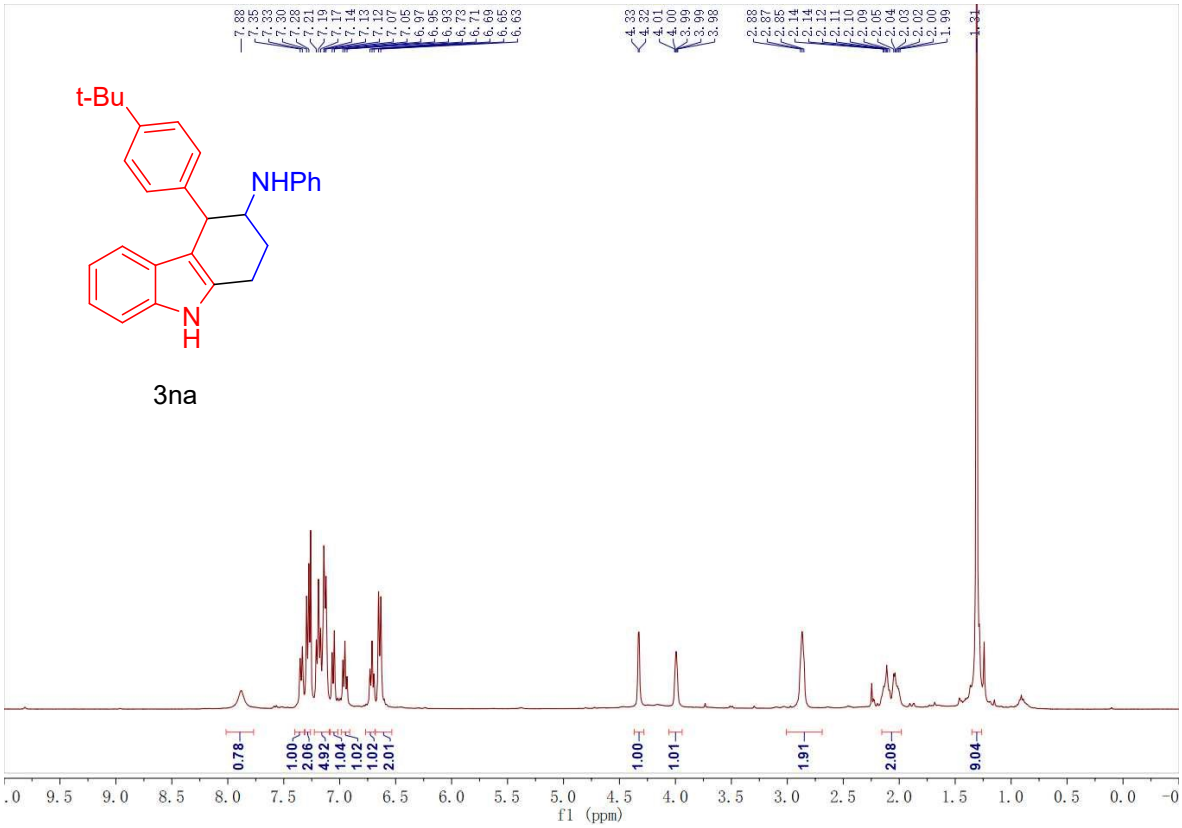
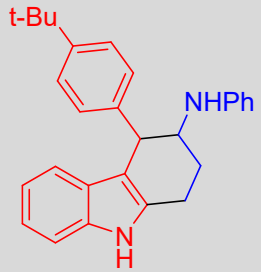
140.57
136.12
134.12
129.47
129.23
128.51
127.89
121.62
119.53
118.93
117.44
113.63
110.54
109.73
55.74
45.03
22.87
21.18
19.48
Me
NHPh
N
H
3ma
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


t-Bu
NHPh
N
H
3na
87.66
12.34
f1 (ppm)

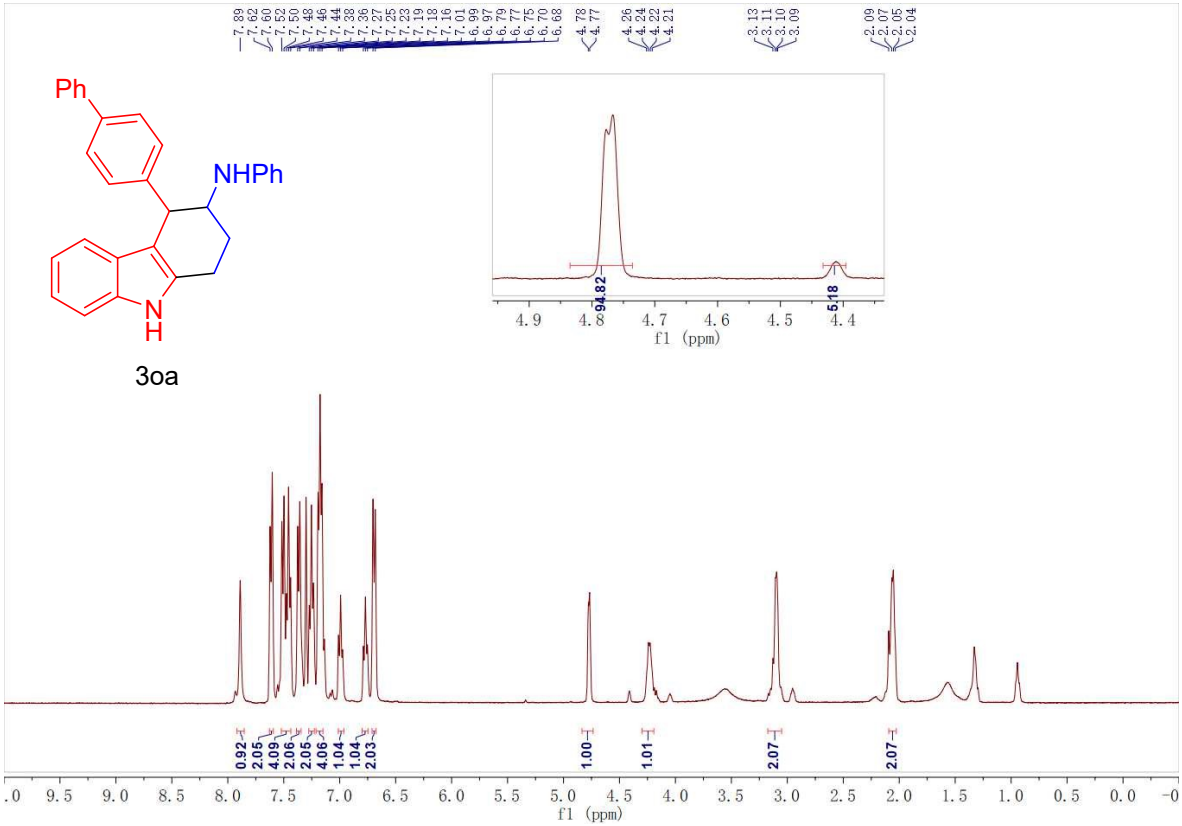

t-Bu
NHPh
N
H
3na
f1 (ppm)

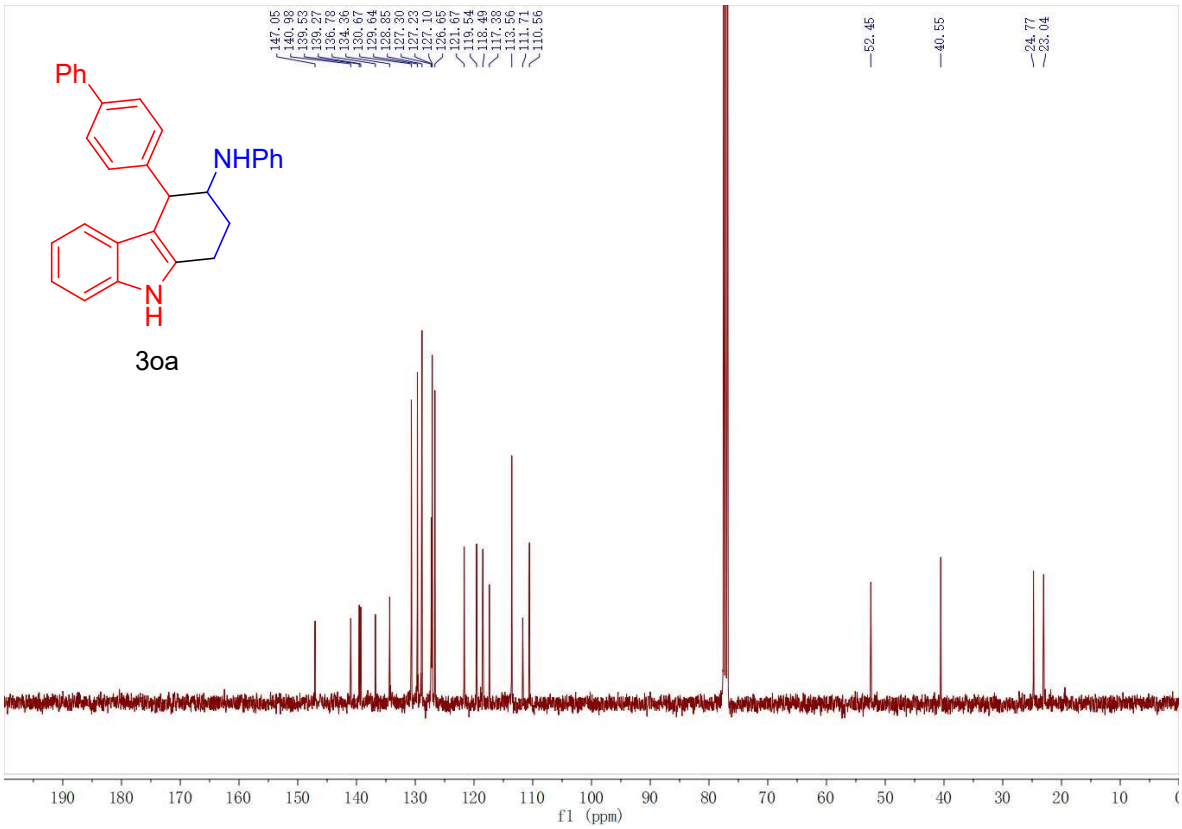

t-Bu
NHPh
N
H
3na
149.55
147.34
126.95
124.23
123.86
120.58
117.53
114.92
111.61
110.47
118.66
117.29
113.63
112.29
110.51
52.62
40.79
34.54
31.56
24.81
23.02
f1 (ppm)

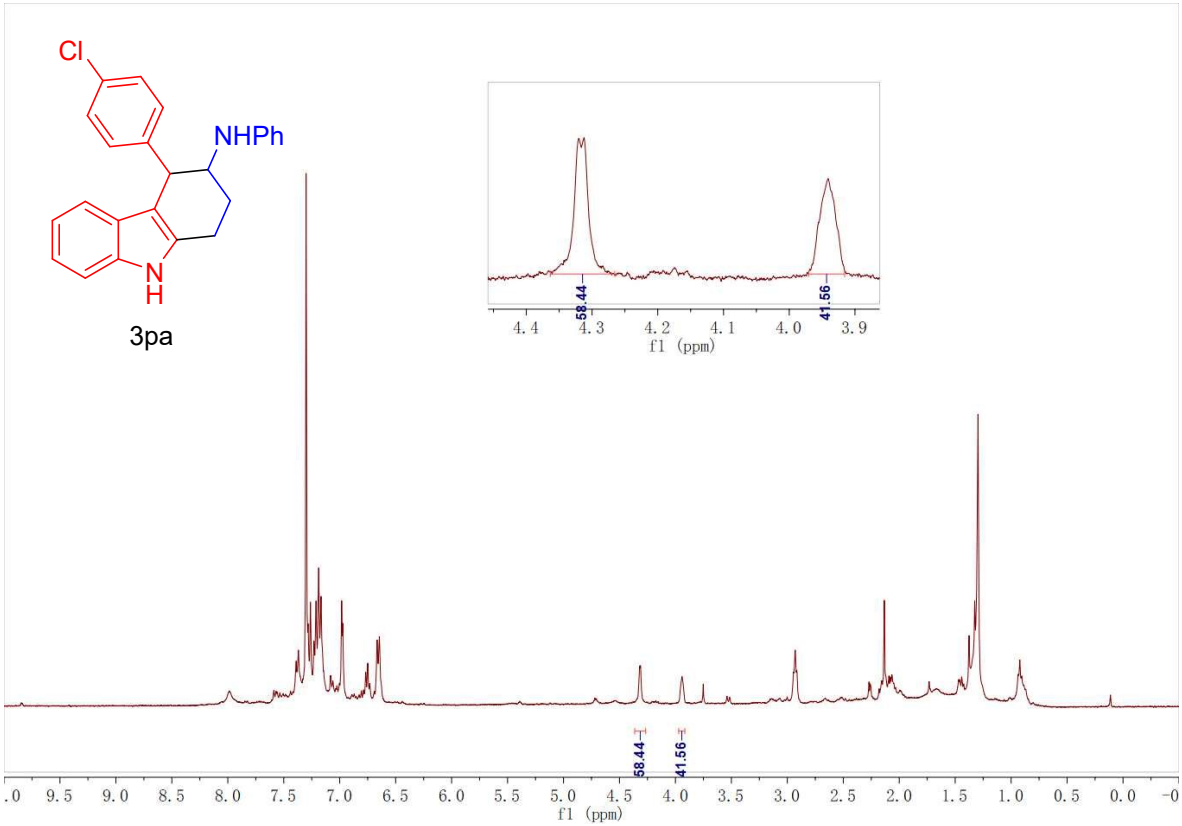

t-Bu
NHPh
N
H
3na
7.88
7.35
7.33
7.30
7.28
7.21
7.19
7.17
7.14
7.13
7.12
7.07
7.05
6.97
6.95
6.93
6.73
6.71
6.69
6.65
6.63
4.33
4.32
4.01
4.00
3.99
3.99
3.98
2.88
2.87
2.85
2.14
2.12
2.11
2.10
2.09
2.05
2.04
2.03
2.02
2.00
1.99
1.34
0.78
1.00
2.06
4.92
1.04
1.02
1.02
2.01
1.00
1.01
1.91
2.08
9.04
f1 (ppm)

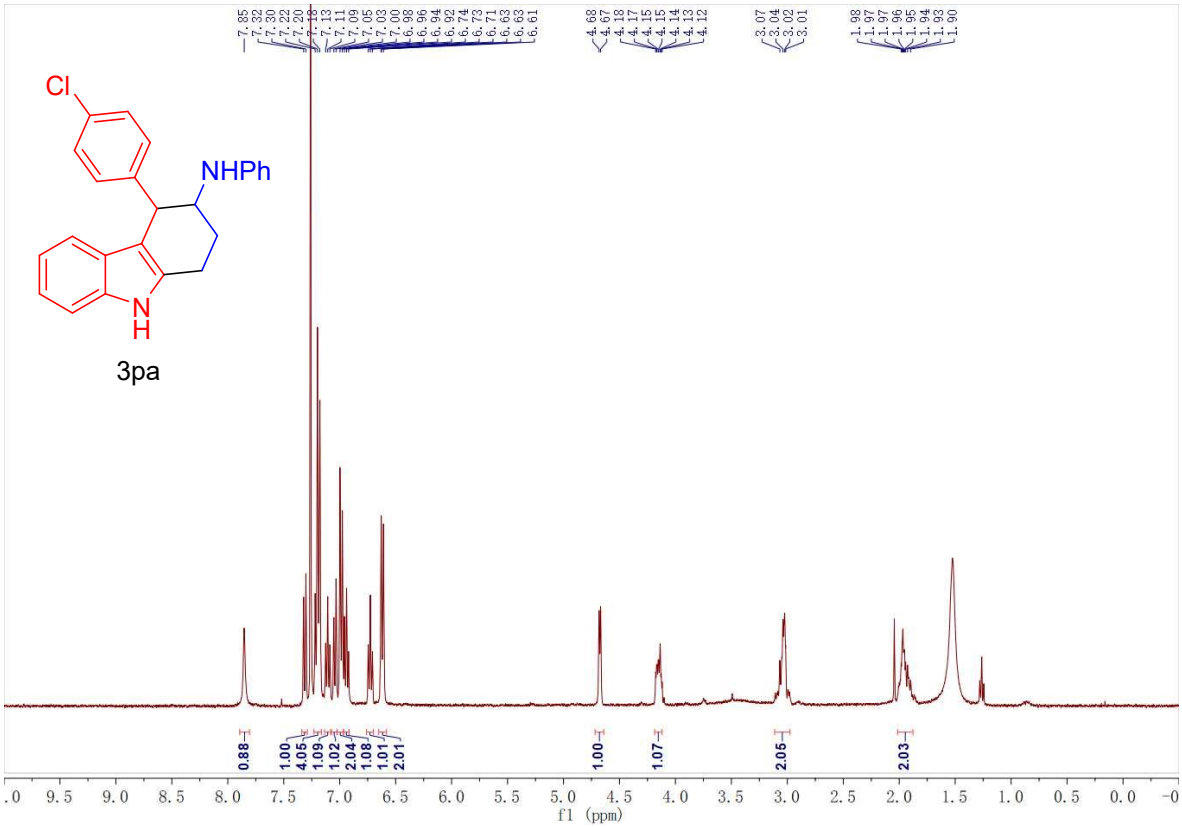


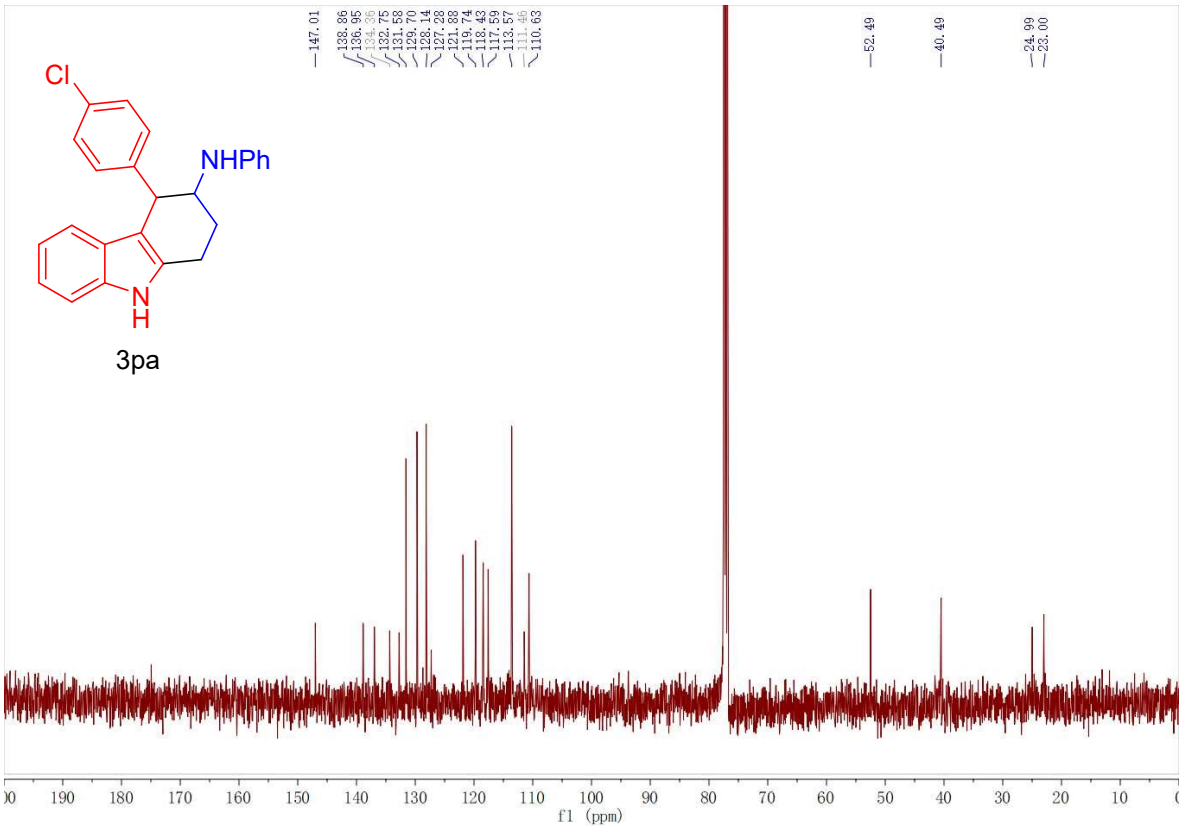
3na

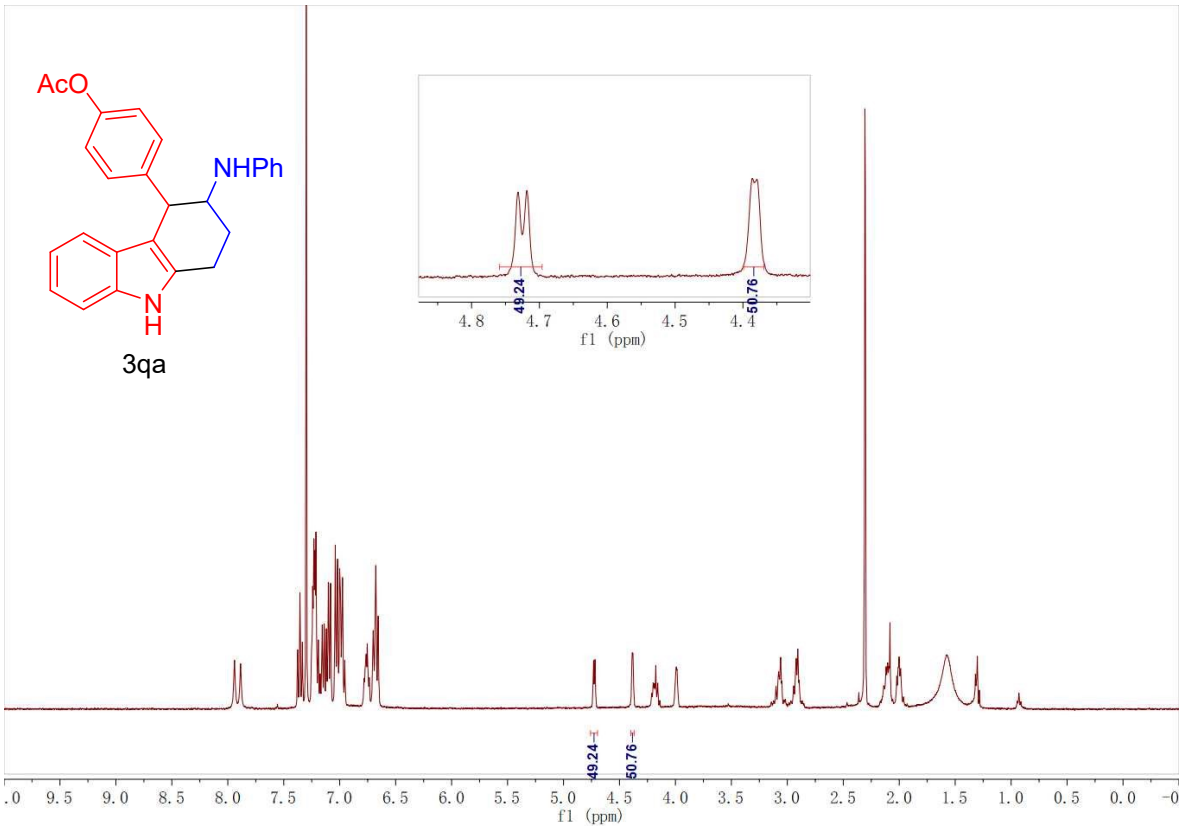

Ph
NHPh
N
H
3oa
f1 (ppm)

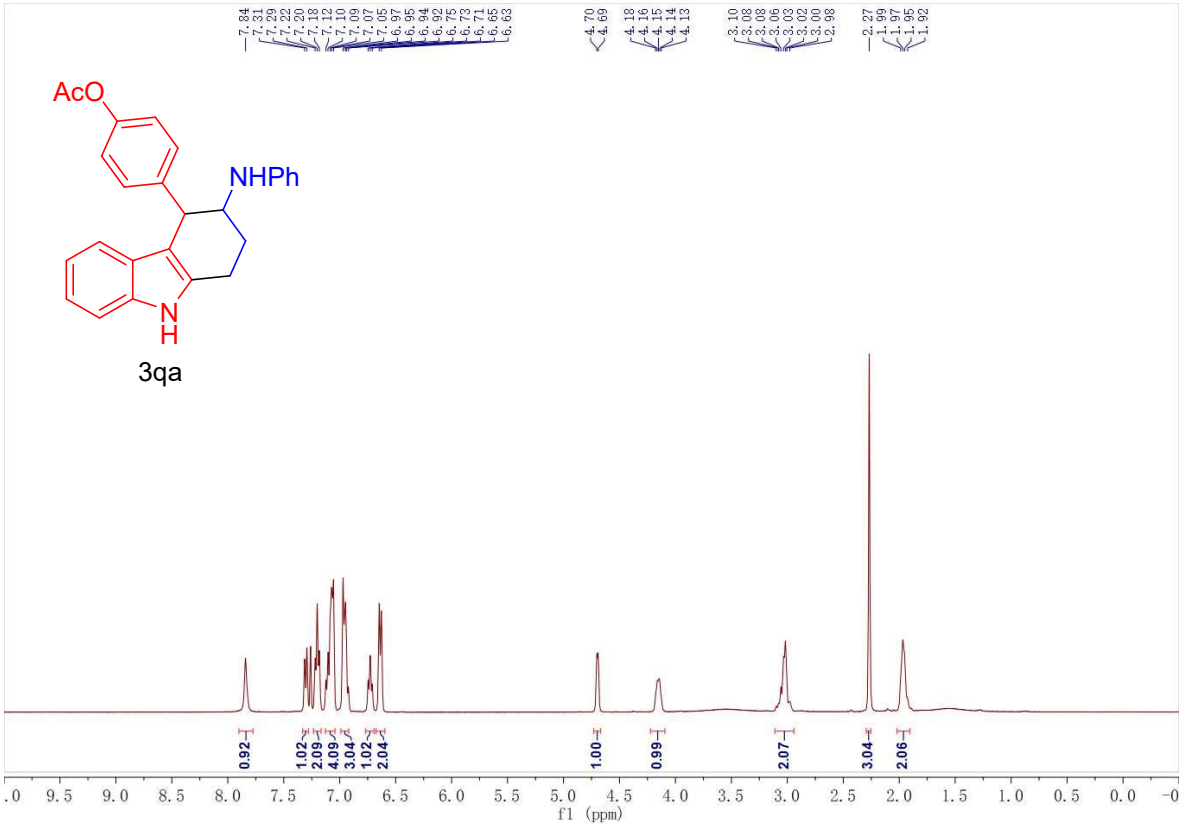

Ph
NHPh
N
H
3oa
f1 (ppm)

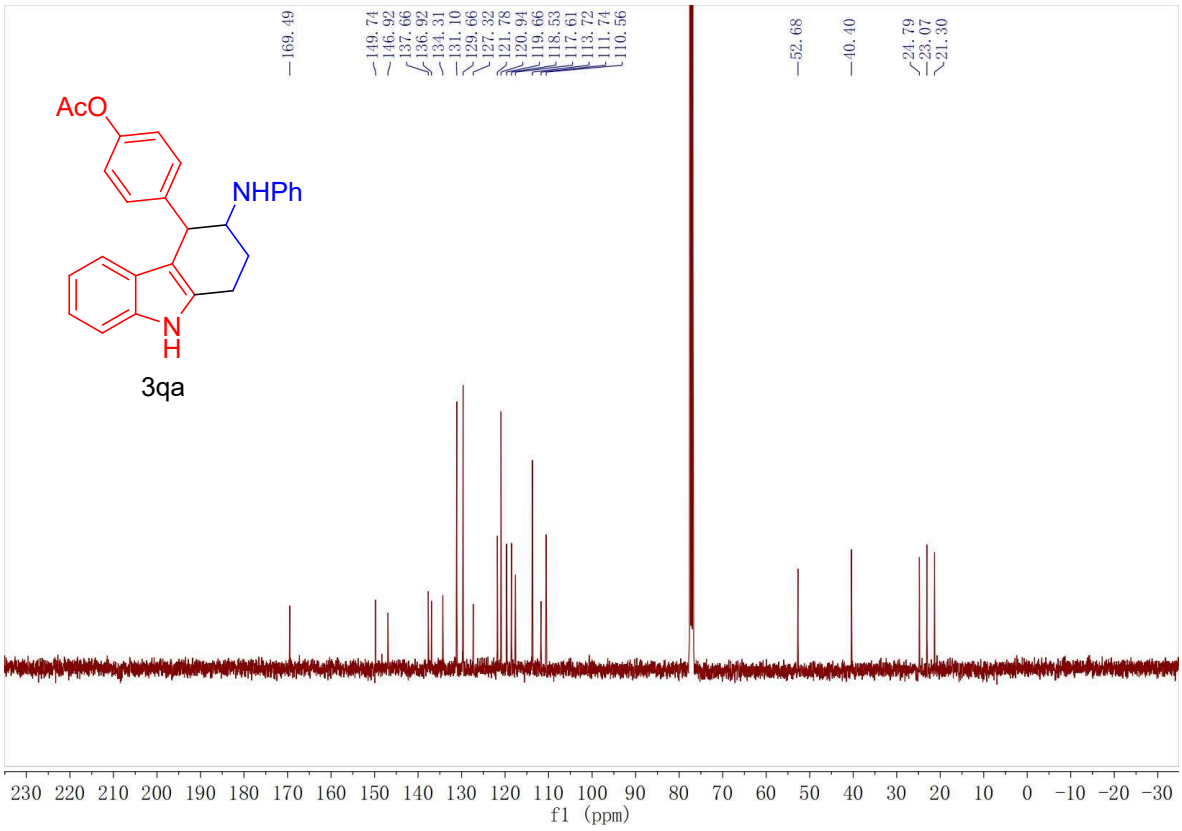

Cl
NHPh
N
H
3pa
58.44
41.56
f1 (ppm)

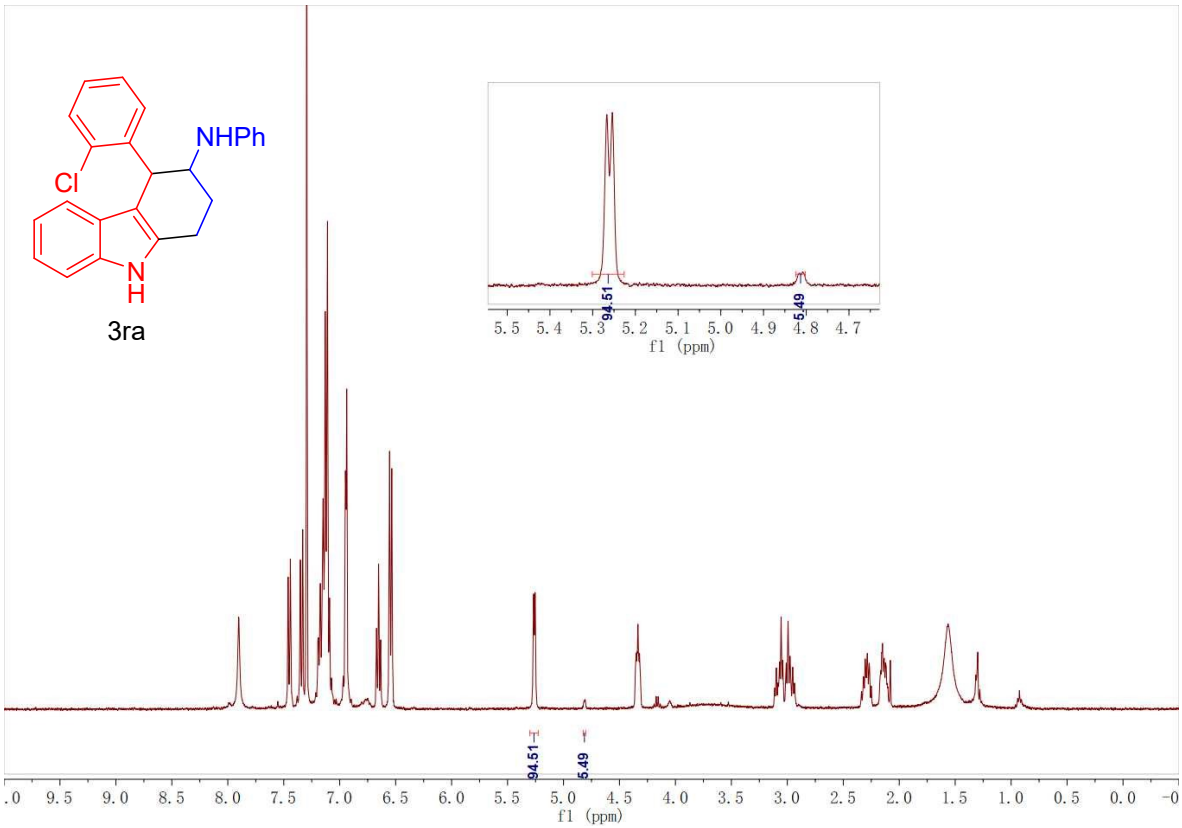

Cl
NHPh
N
H
3pa
0.88
1.00
4.05
1.09
1.02
2.04
1.08
1.01
2.01
1.00
1.07
2.05
2.03
f1 (ppm)

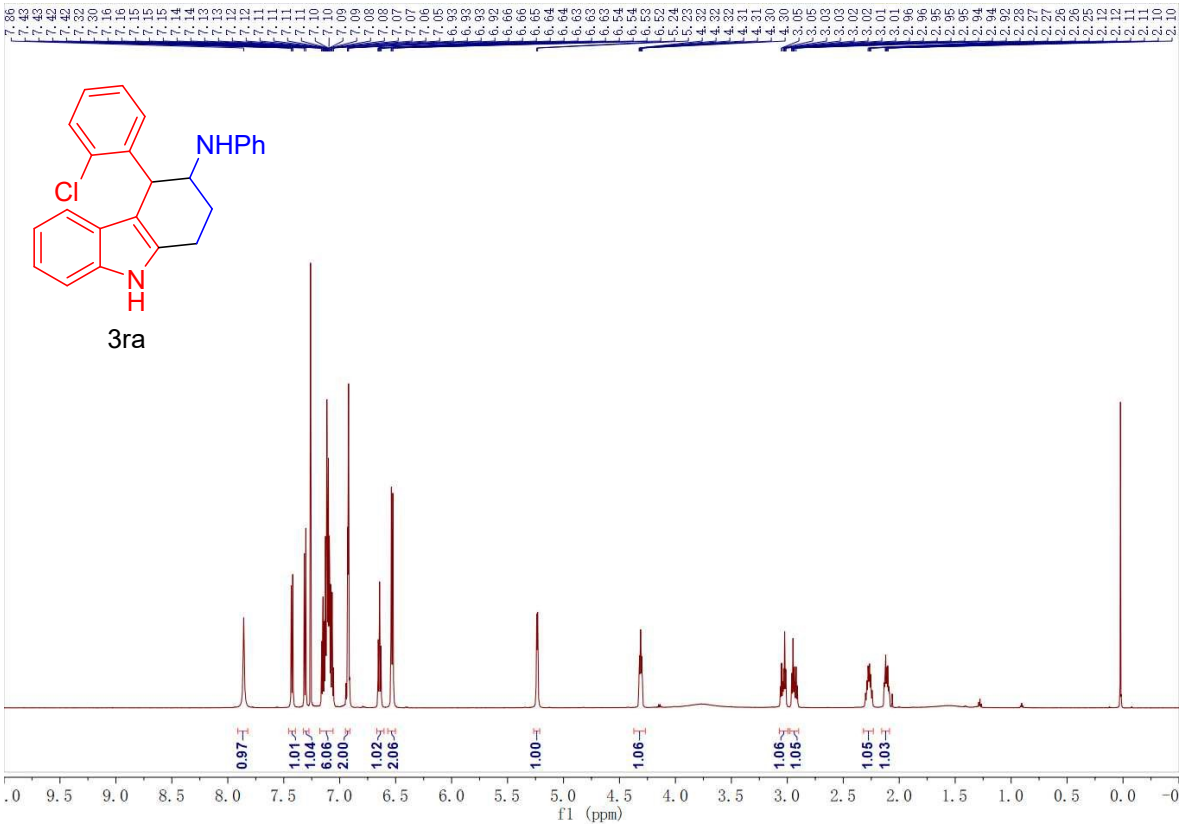

Cl
NHPh
N
H
3pa
147.01
138.86
136.95
134.30
132.75
131.58
129.70
128.14
127.28
121.88
119.74
118.43
117.59
113.57
111.46
110.63
52.49
40.49
24.99
23.00
f1 (ppm)

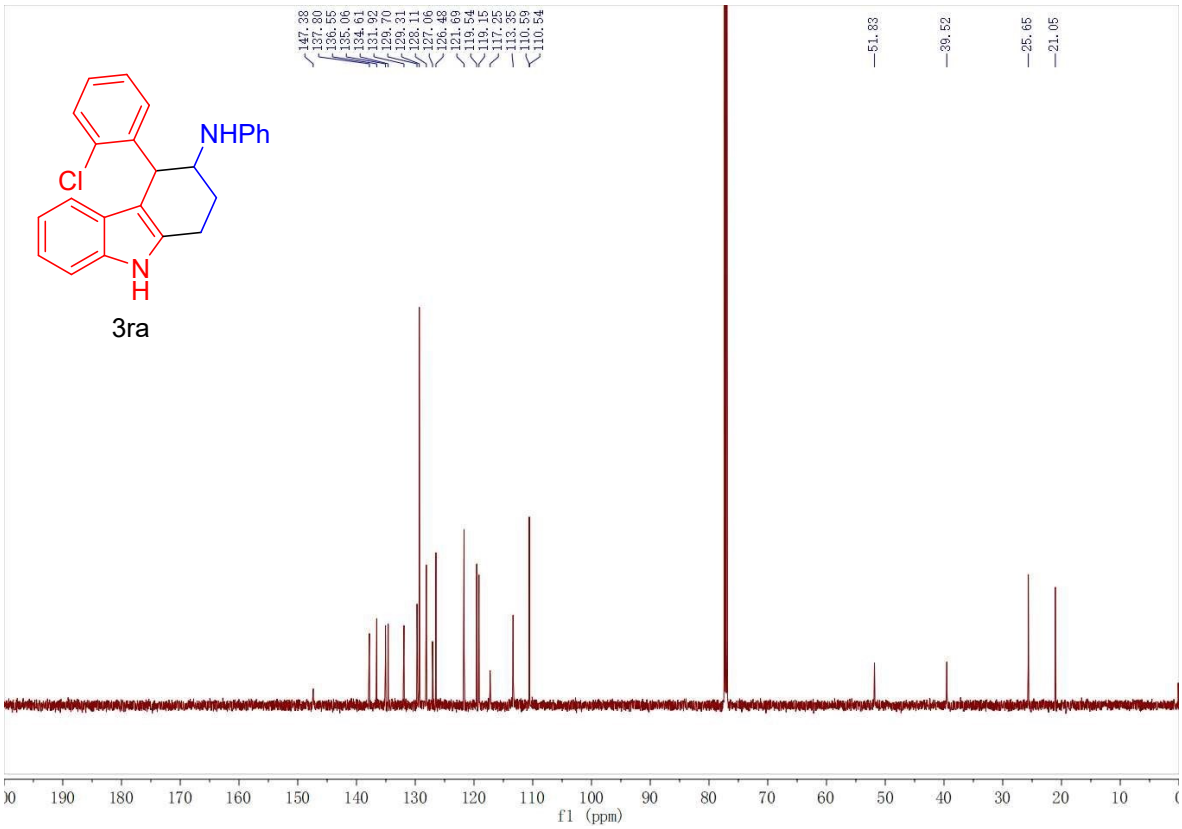

AcO
NHPh
N
H
3qa
49.24
50.76
f1 (ppm)

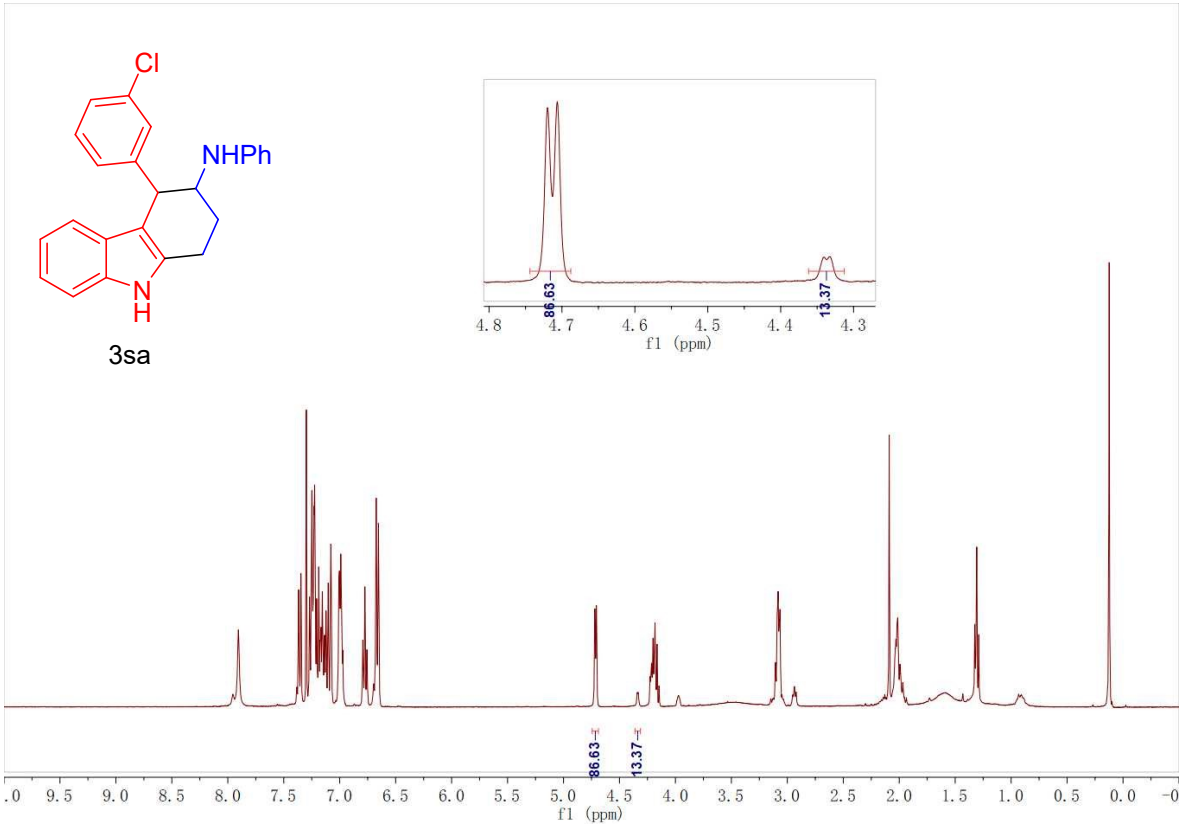

AcO
NHPh
N
H
3qa
f1 (ppm)

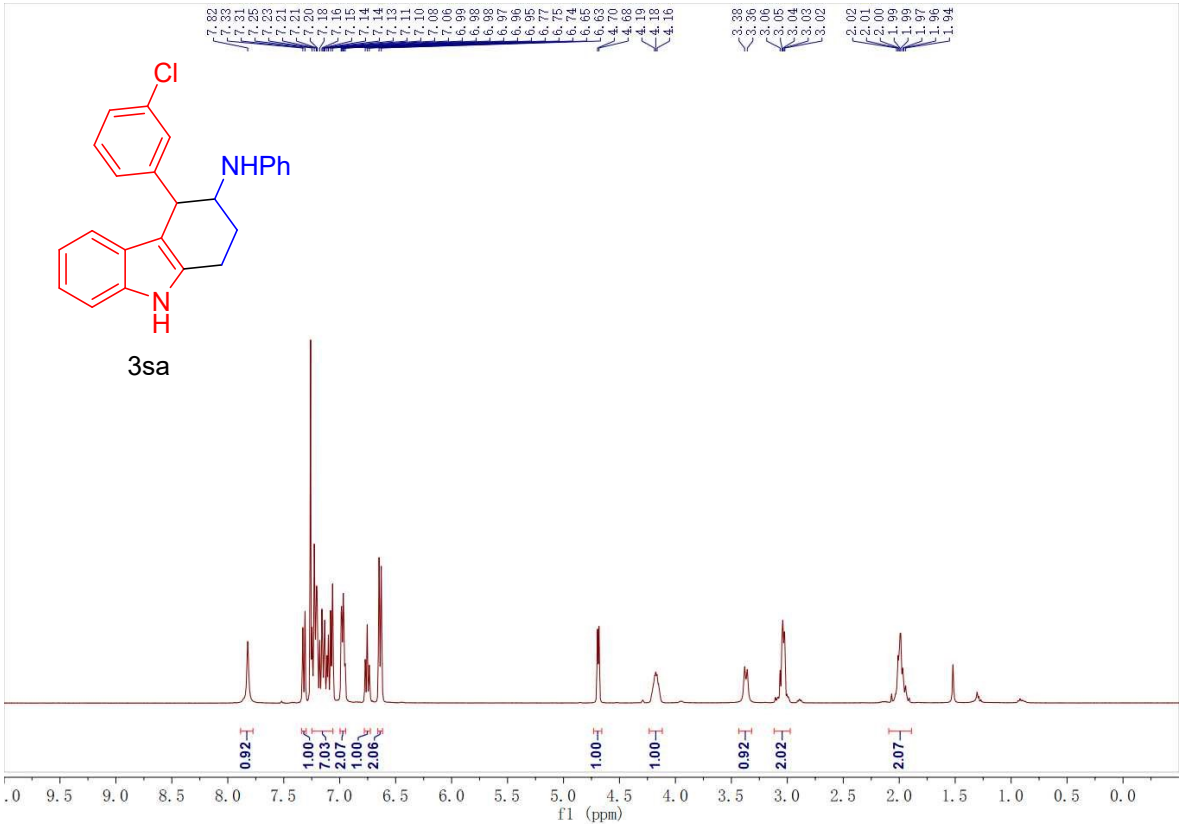

169.49
149.74
146.92
137.66
136.92
134.31
131.10
129.66
127.32
121.78
120.94
119.66
118.53
117.61
113.72
111.74
110.56
52.68
40.40
24.79
23.07
21.30
AcO
NHPh
N
H
3qa
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

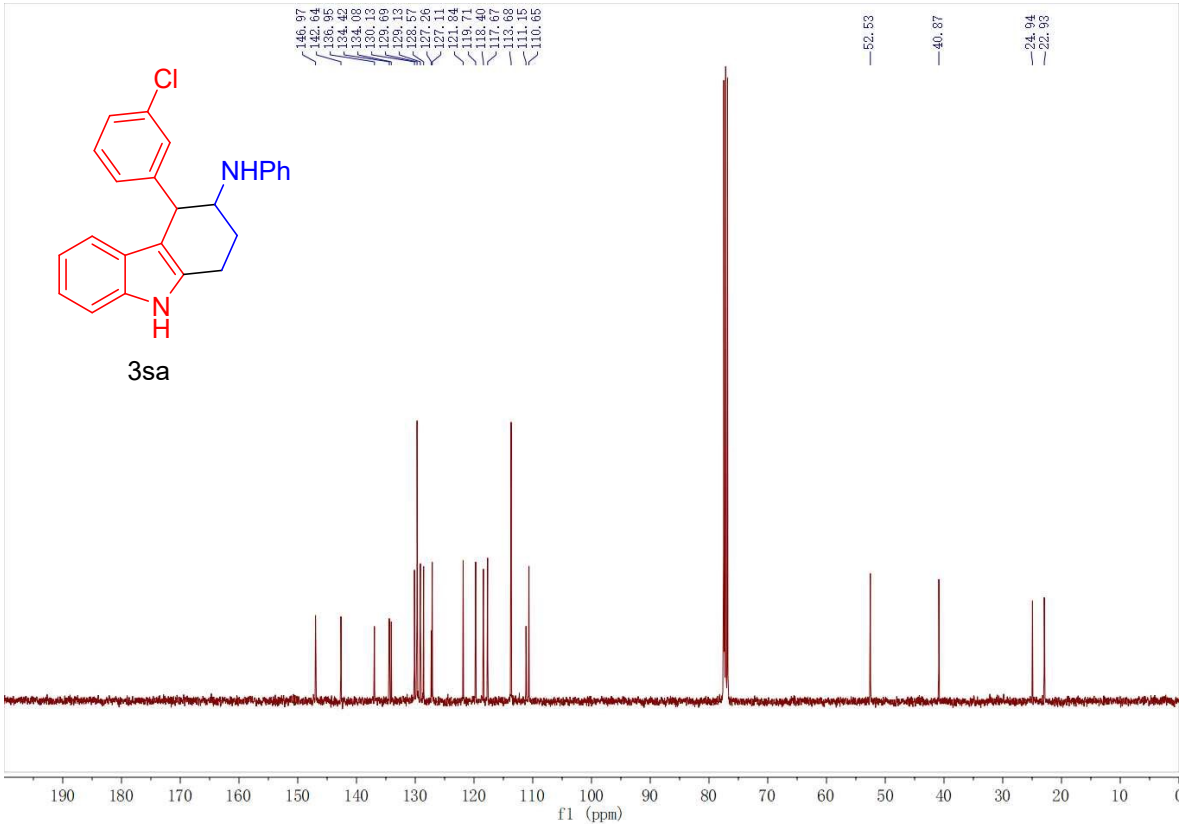

NHPh
Cl
N
H
3ra
94.51
5.49
f1 (ppm)

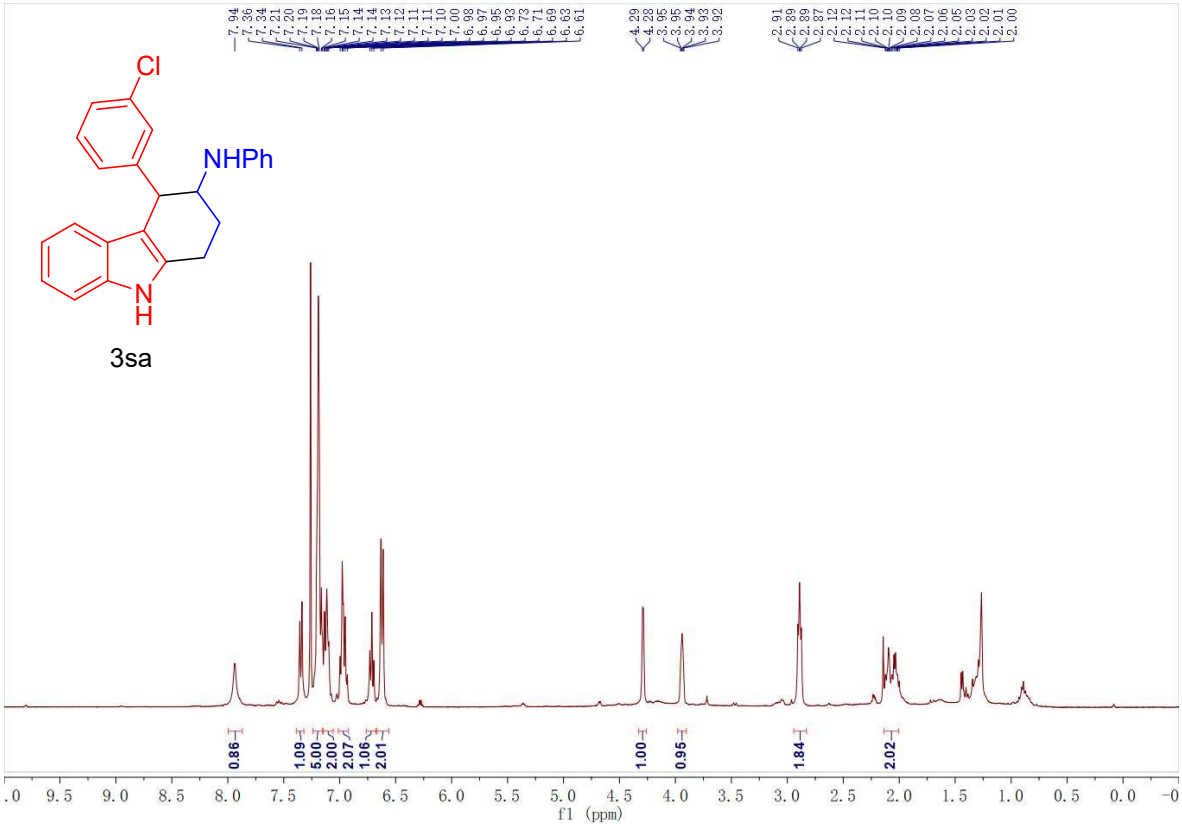

NHPh
Cl
N
H
3ra
0.97
1.01
1.04
6.06
2.00
1.02
2.06
1.00
1.06
1.06
1.05
1.05
1.03
f1 (ppm)


147.38
137.80
136.55
135.06
134.61
131.92
129.70
129.31
128.11
127.06
126.48
121.69
119.54
119.15
117.25
113.35
110.59
110.54
51.83
39.52
25.65
21.05
NHPh
Cl
N
H
3ra
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
NHPh
N
H
3sa
86.63
13.37
f1 (ppm)


Cl
NHPh
N
H
3sa
0.92
1.00
7.03
2.07
1.00
2.06
1.00
1.00
0.92
2.02
2.07
f1 (ppm)


Cl
NHPh
N
H
3sa
146.97
142.64
136.95
134.42
134.08
130.13
129.69
129.13
128.57
127.26
127.11
121.84
119.71
118.40
117.67
113.68
111.15
110.65
52.53
40.87
24.94
22.93
f1 (ppm)


Cl
NHPh
N
H
3sa
7.94
7.36
7.34
7.21
7.20
7.19
7.18
7.16
7.15
7.14
7.13
7.12
7.11
7.10
7.00
6.98
6.97
6.95
6.93
6.73
6.71
6.69
6.63
6.61
4.29
4.28
3.95
3.95
3.94
3.93
3.92
2.91
2.89
2.89
2.87
2.12
2.12
2.11
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.03
2.02
2.01
2.00
0.86
1.09
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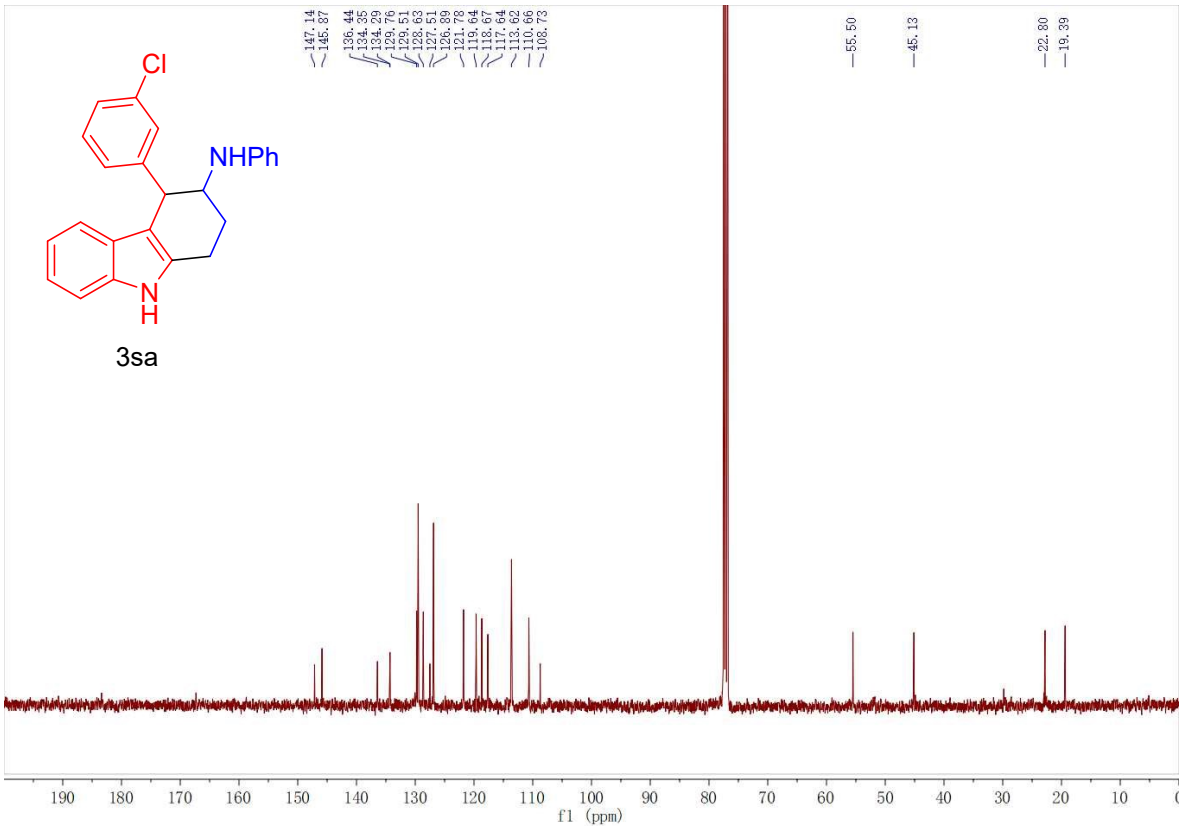
2.00
2.07
1.06
2.01
1.00
0.95
1.84
2.02
f1 (ppm)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NHPh
N
H
3sa
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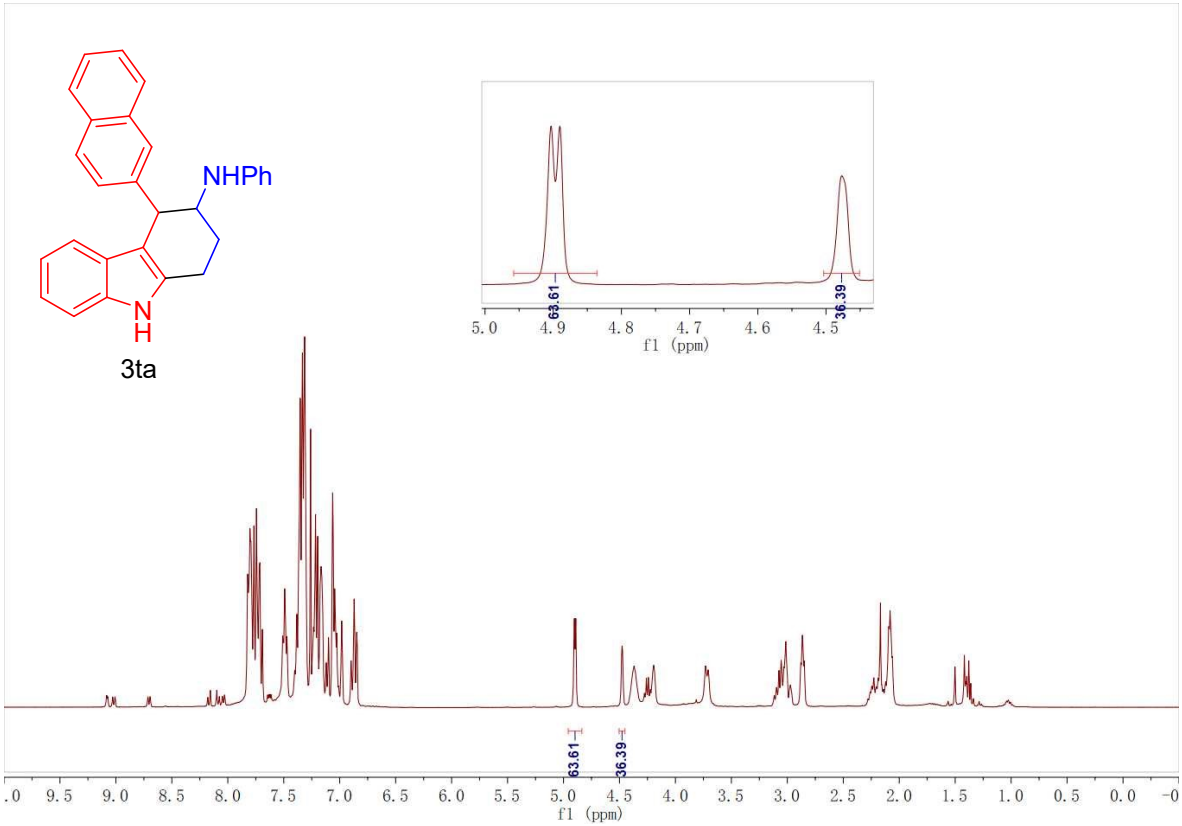
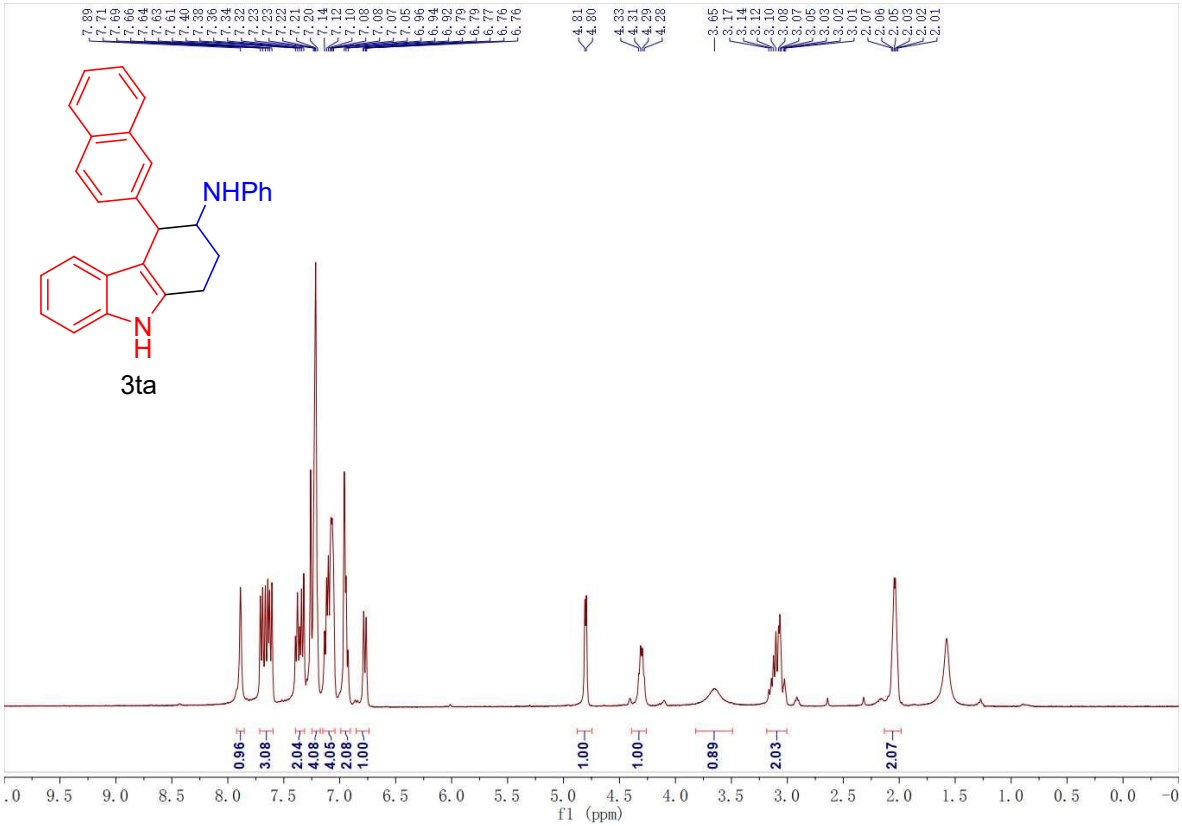
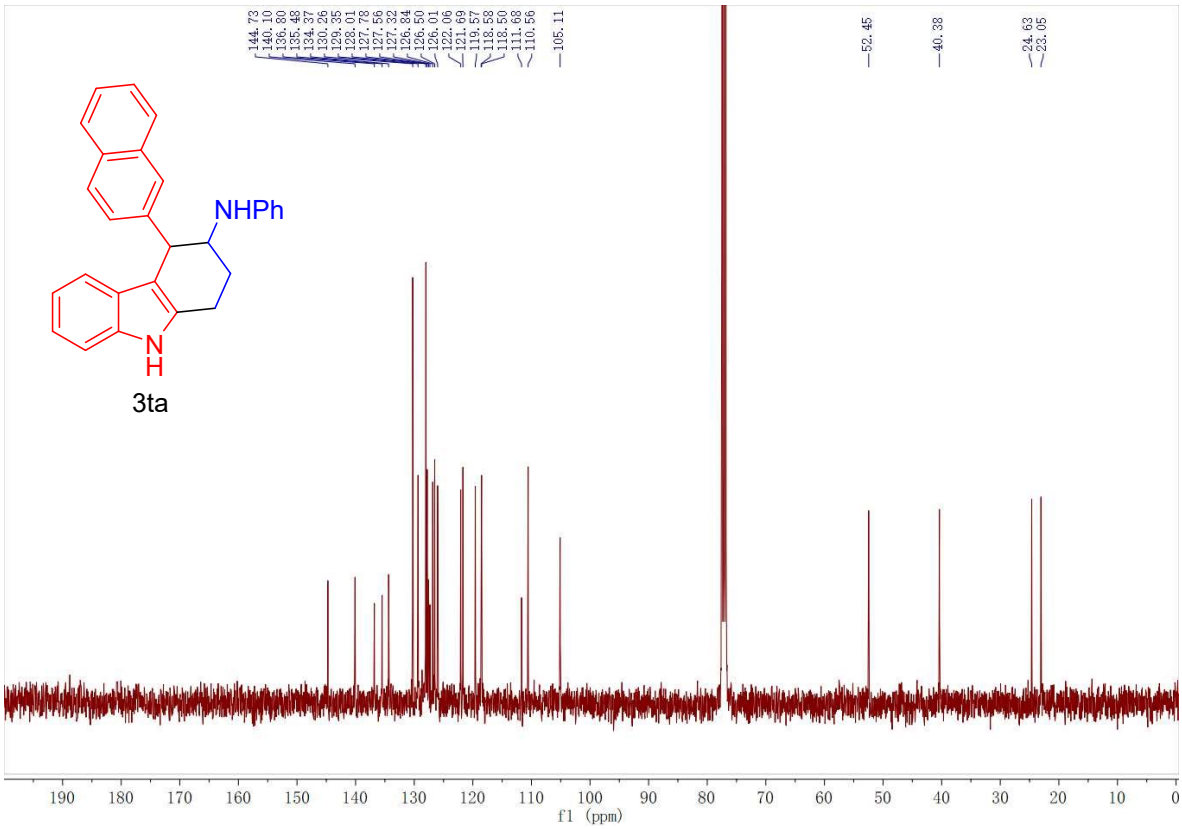
145.87
136.44
134.35
134.29
129.76
129.51
128.63
127.51
126.89
121.78
119.64
118.67
117.64
113.62
110.66
108.73
55.50
45.13
22.80
19.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


NHPh
N
H
3ta
63.61
36.39
f1 (ppm)


NHPh
N
H
3ta
0.96
3.08
2.04
4.08
4.05
2.08
1.00
1.00
1.00
0.89
2.03
2.07
f1 (ppm)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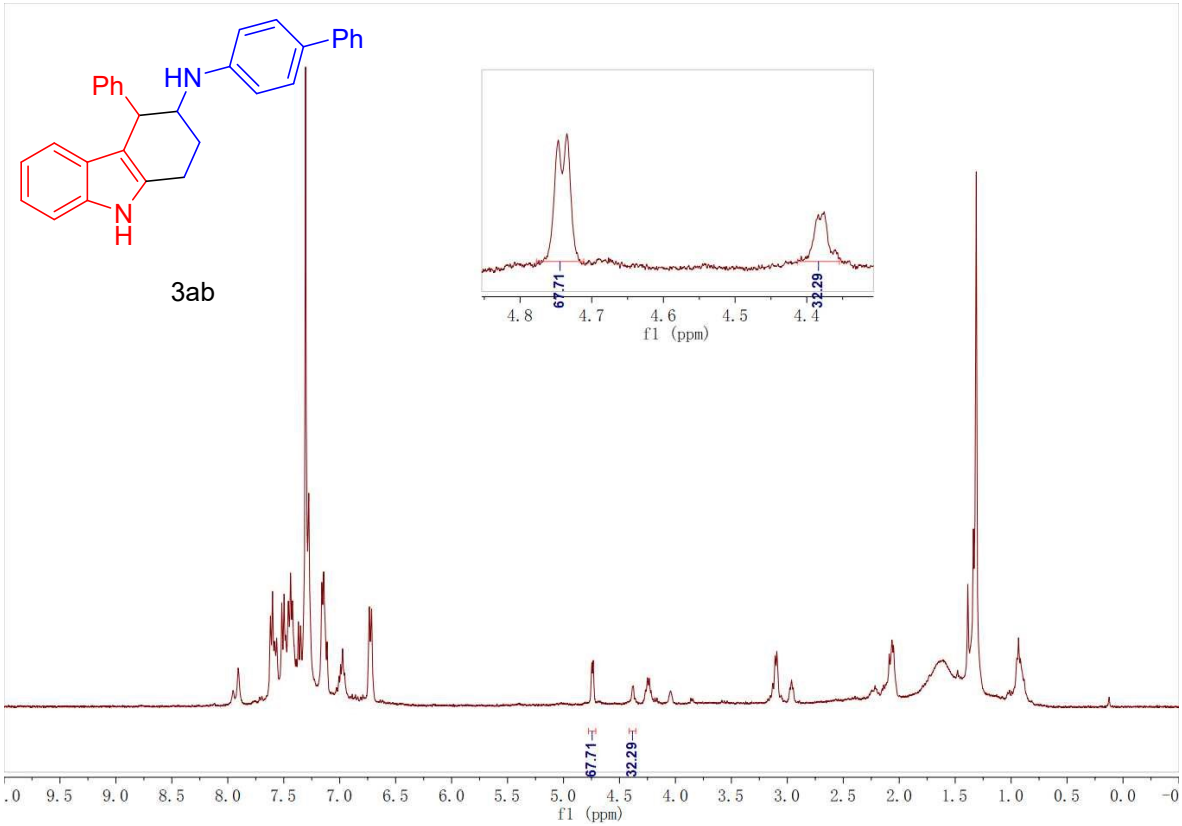
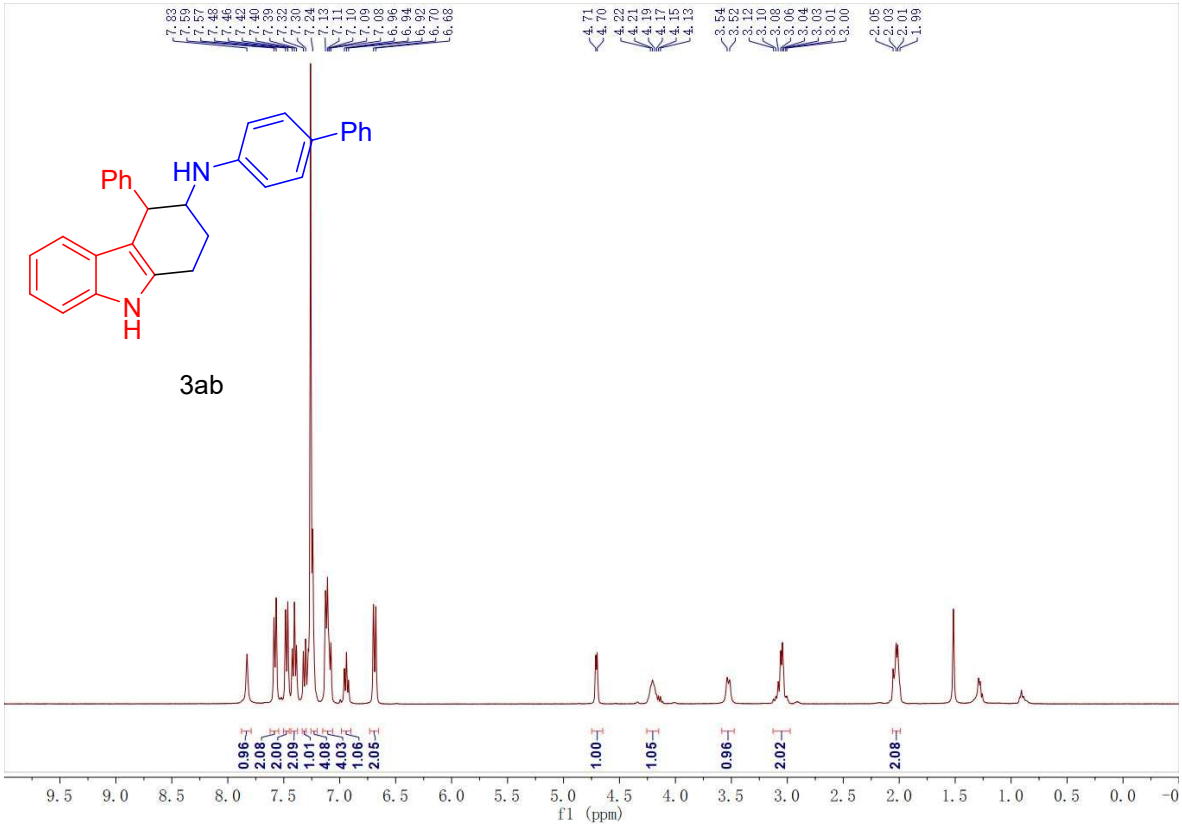
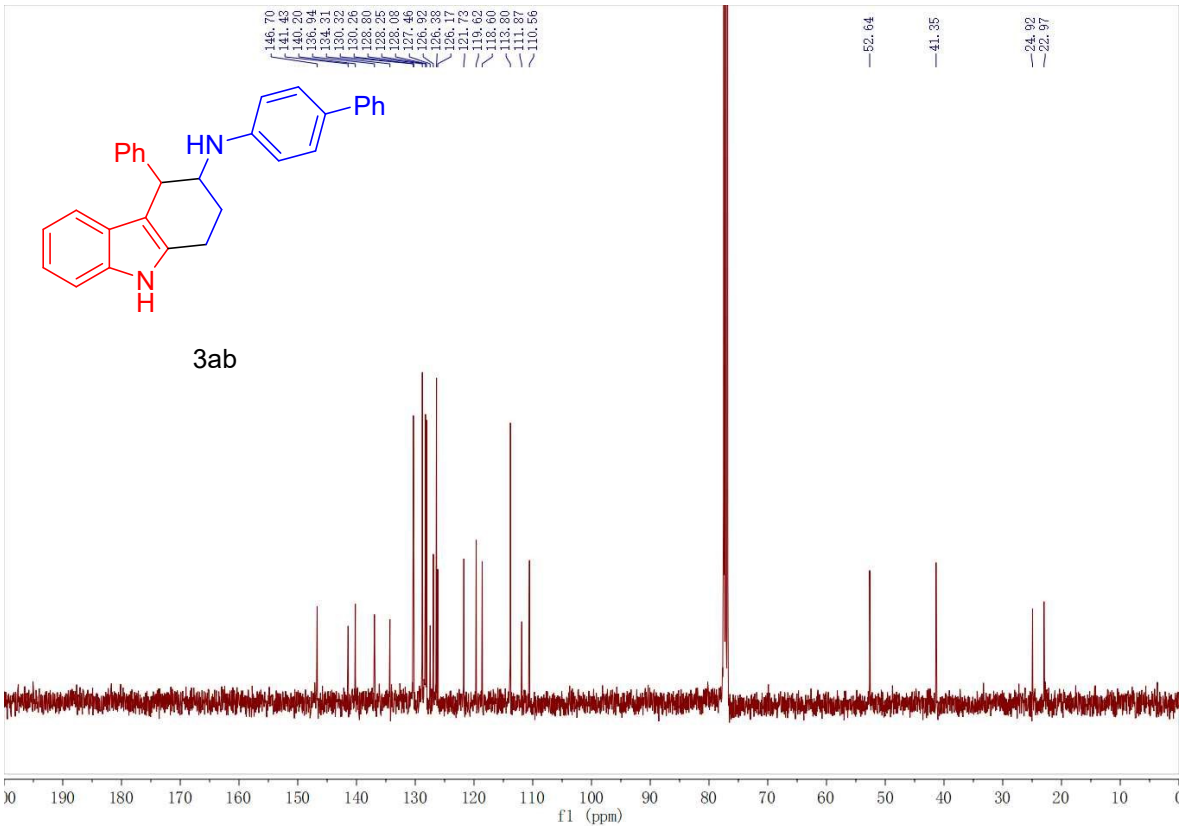
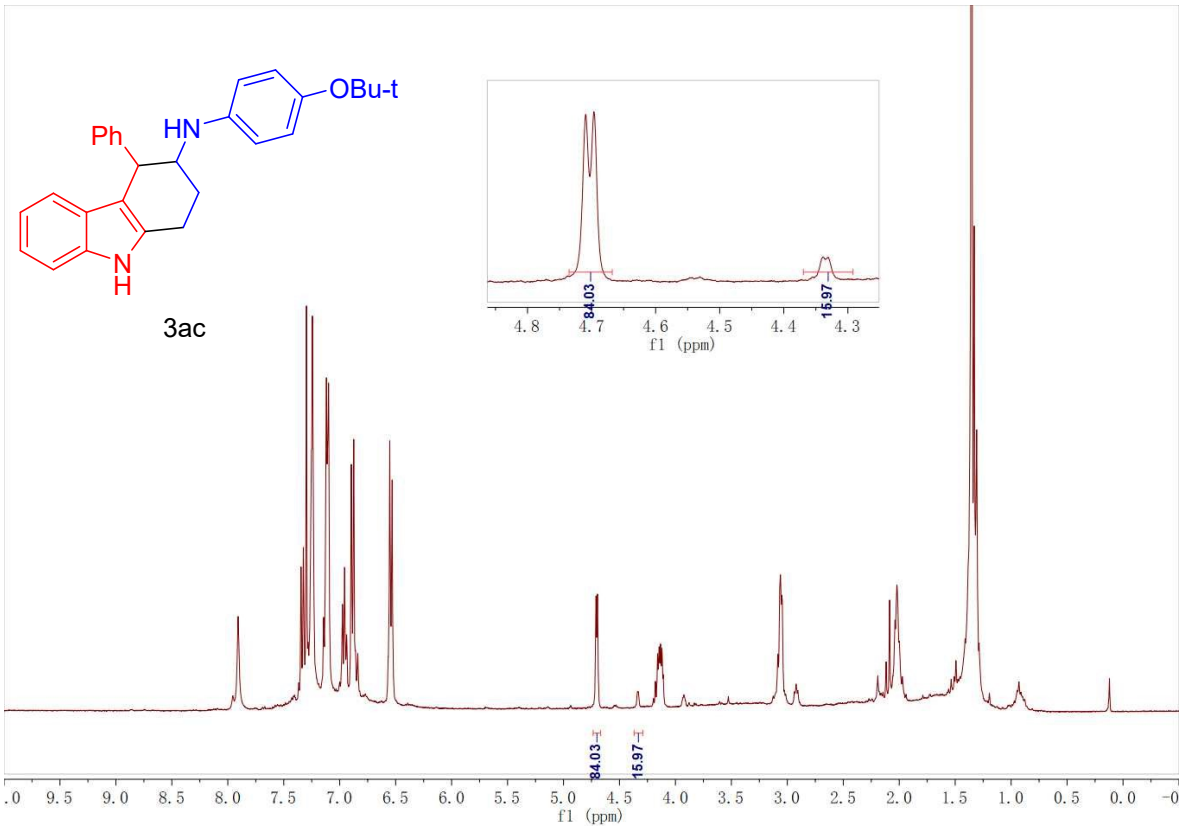
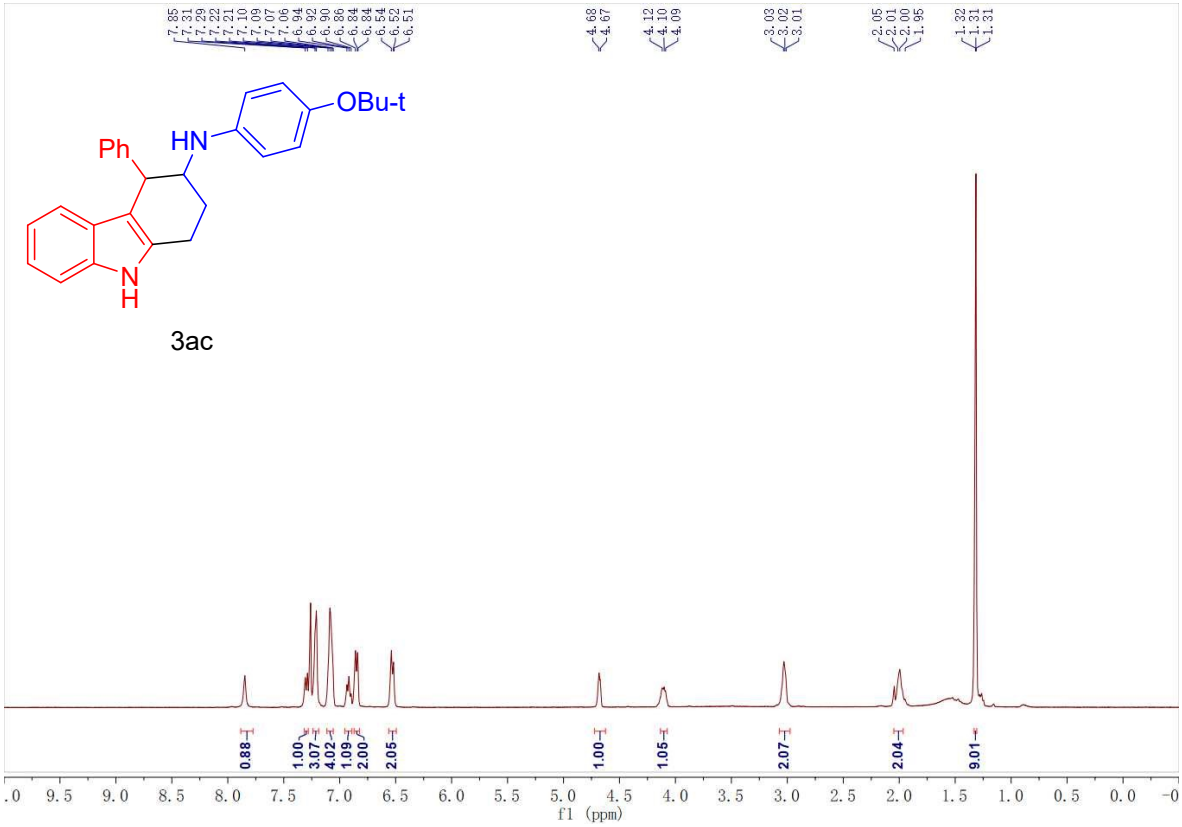
140.10
136.80
135.48
134.37
130.26
129.35
128.01
127.78
127.56
127.32
126.84
126.50
126.01
122.06
121.69
119.57
118.58
118.50
111.68
110.56
105.11
52.45
40.38
24.63
23.05
NHPh
N
H
3ta
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

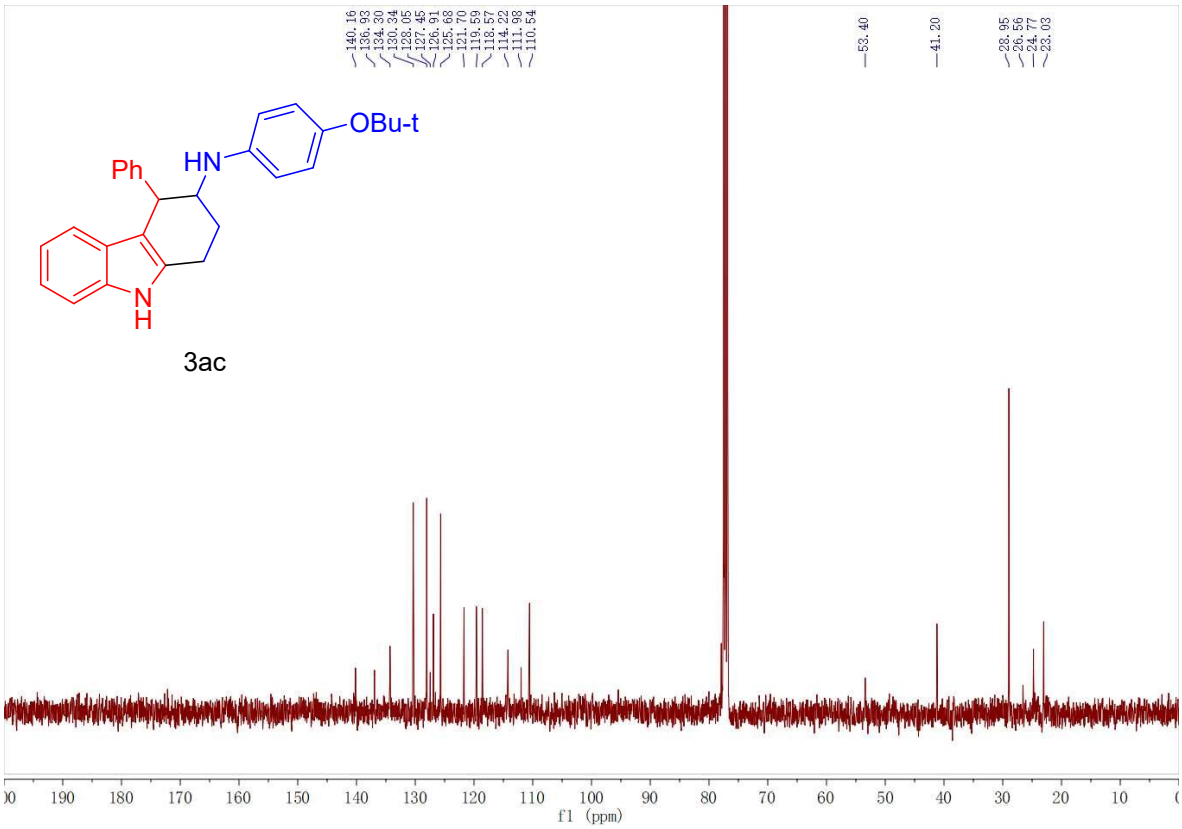

Ph
HN
Ph
N
H
3ab
67.71
32.29
f1 (ppm)

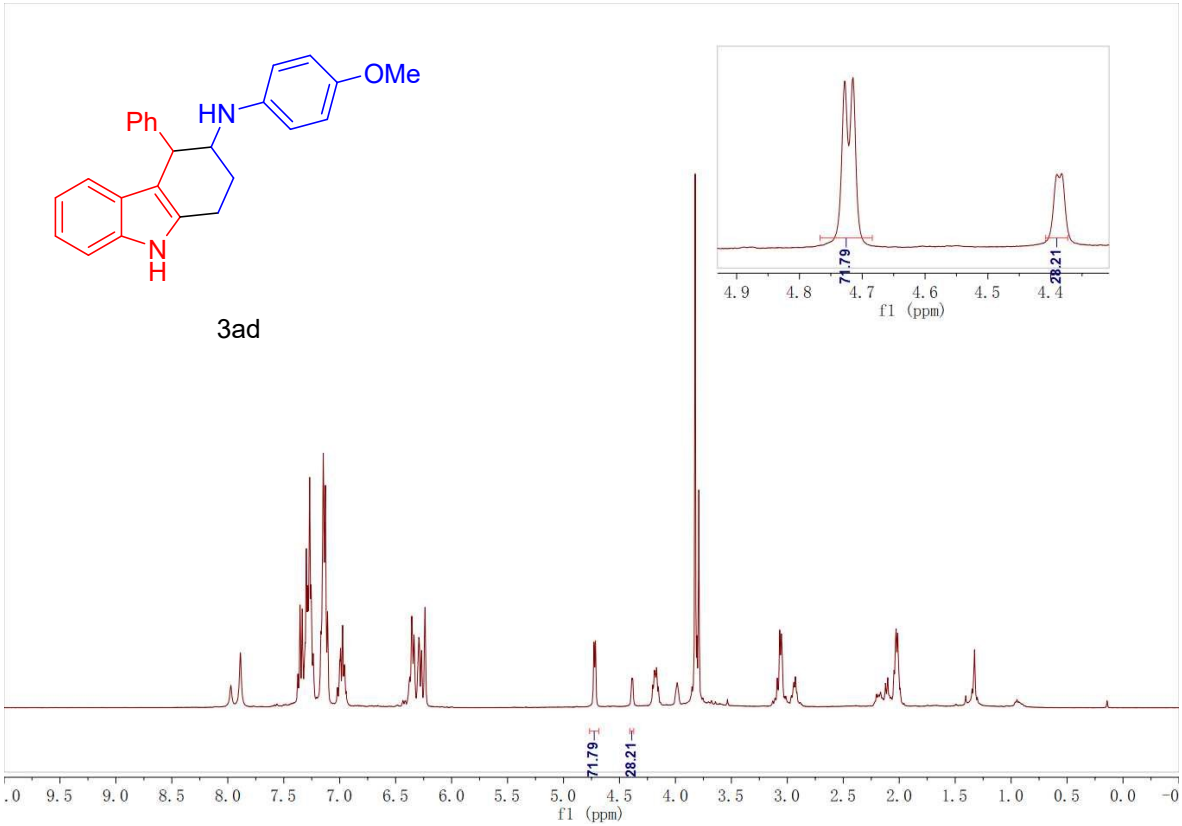

Ph
HN
Ph
N
H
3ab
f1 (ppm)

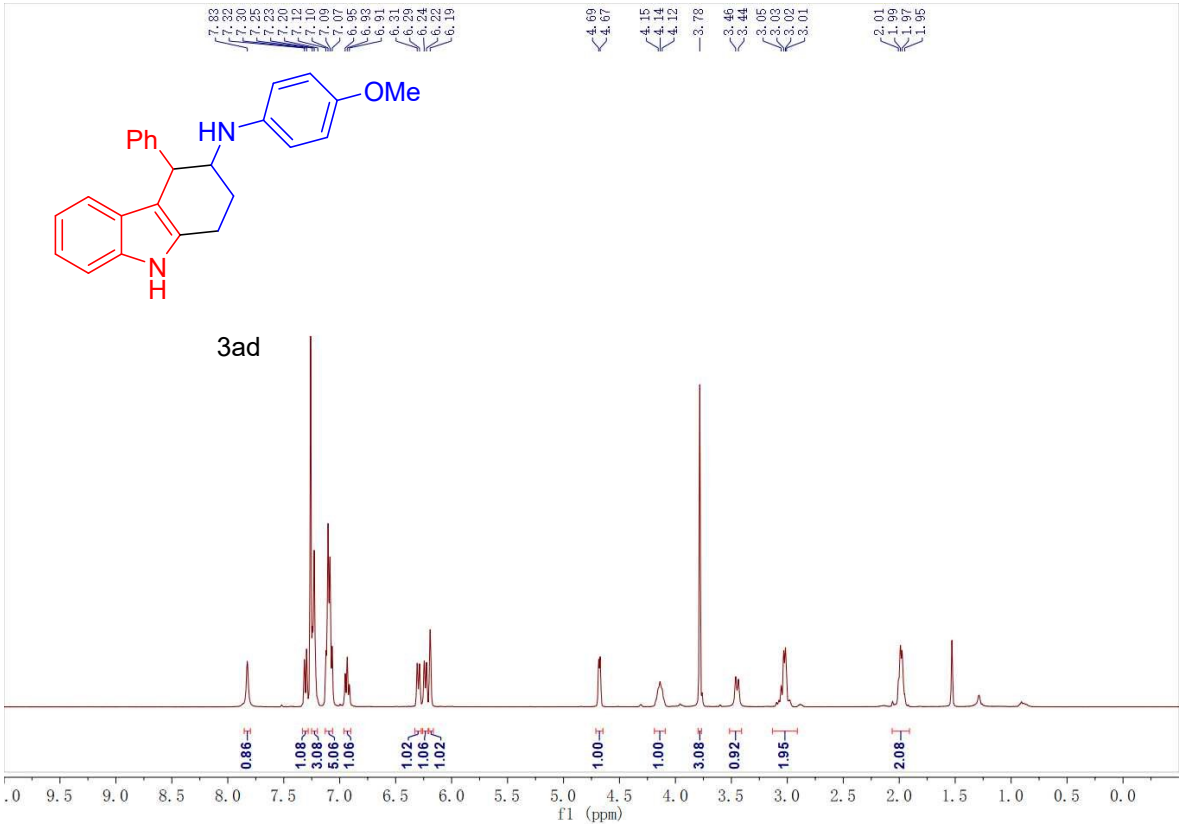

146.70
141.43
140.20
136.64
134.31
130.32
130.26
128.80
128.25
128.08
127.46
126.92
126.38
126.17
121.73
119.62
118.60
113.80
111.87
110.56
52.64
41.35
24.92
22.97
Ph
HN
Ph
N
H
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

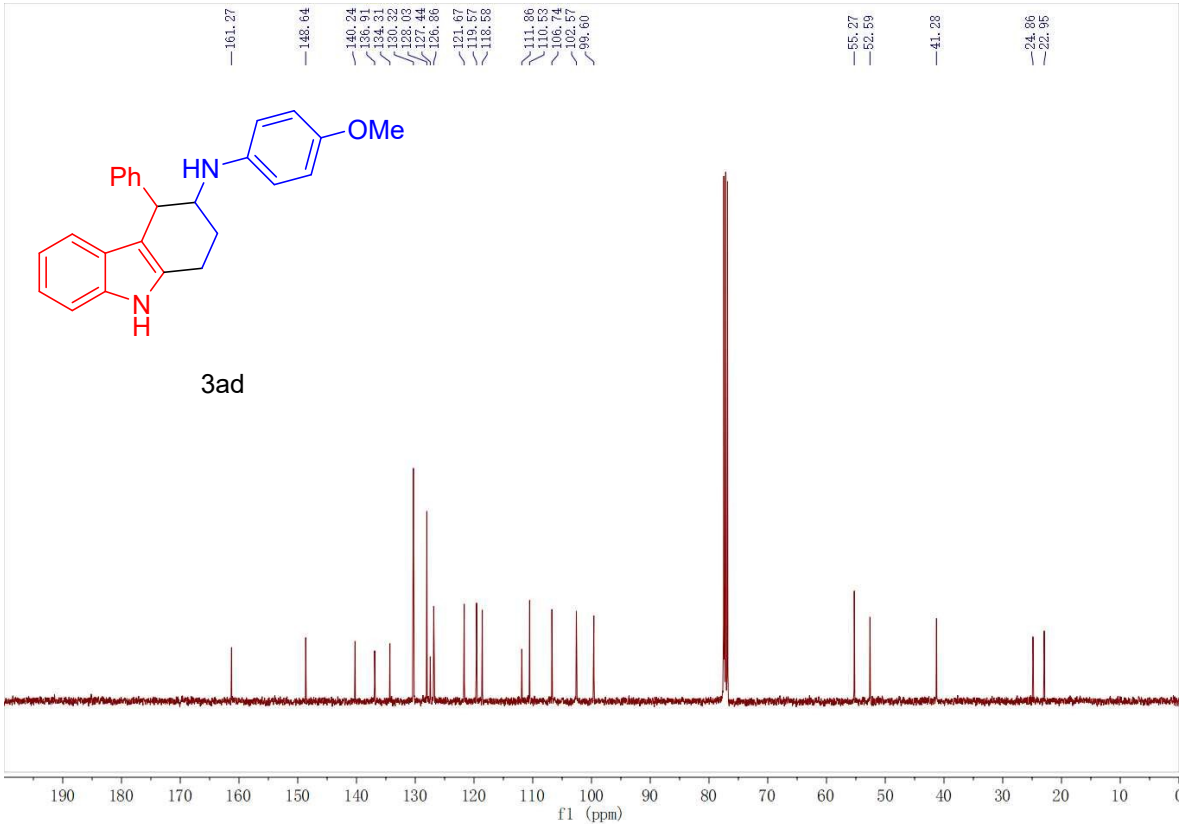

OBu-t
HN
Ph
N
H
3ac
84.03
15.97
f1 (ppm)


OBu-t
HN
Ph
N
H
3ac
f1 (ppm)


140.16
136.93
134.30
130.34
128.05
127.45
126.91
125.68
121.70
119.59
118.57
114.22
111.98
110.54
53.40
41.20
28.95
26.56
24.77
23.03
OBu-t
HN
Ph
N
H
3ac
f1 (ppm)


OMe
HN
Ph
N
H
3ad
71.79
28.21
f1 (ppm)


OMe
HN
Ph
N
H
3ad
f1 (ppm)


161.27
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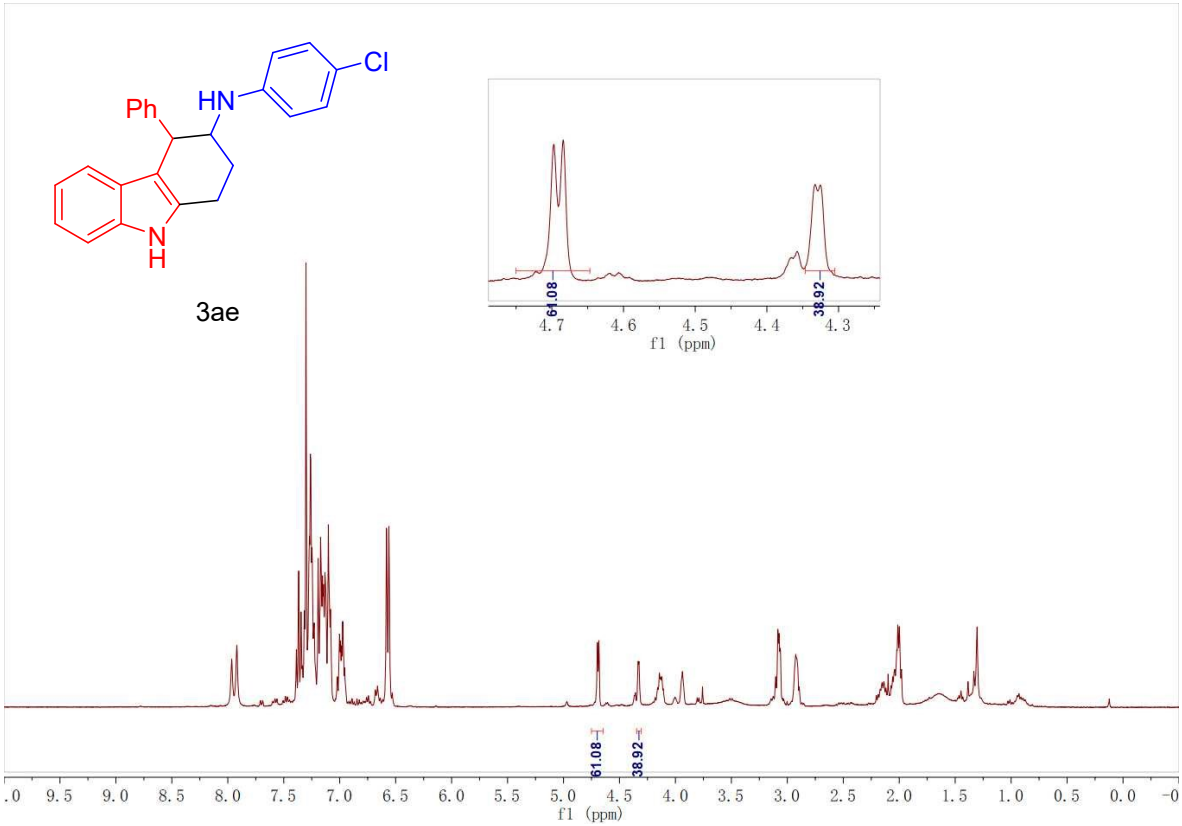
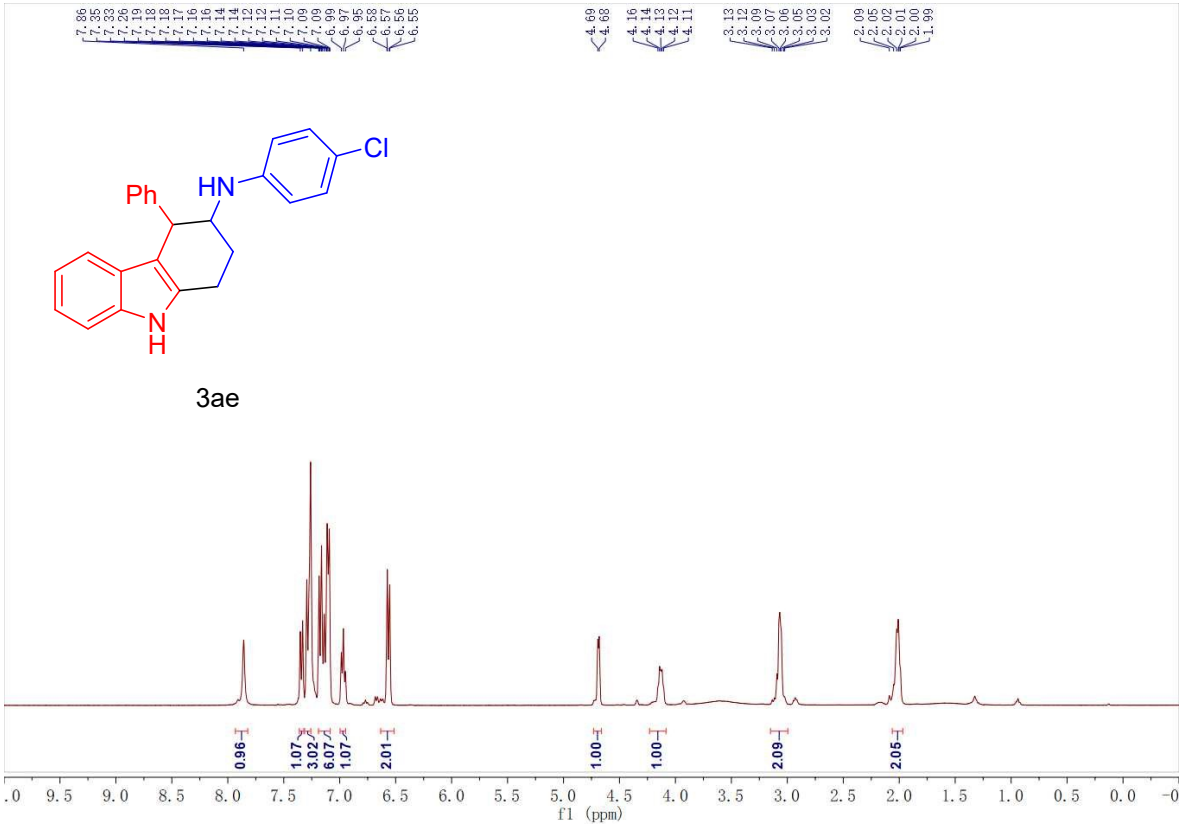
140.24
136.91
134.31
130.32
128.03
127.44
126.86
121.67
119.57
118.58
111.86
110.53
106.74
102.57
99.60
55.27
52.59
41.28
24.86
22.95
OMe
HN
Ph
N
H
3ad
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Cl
HN
Ph
N
H
3ae
61.08
38.92
4.7
4.6
4.5
4.4
4.3
f1 (ppm)
61.08
38.92
f1 (ppm)


Cl
HN
Ph
N
H
3ae
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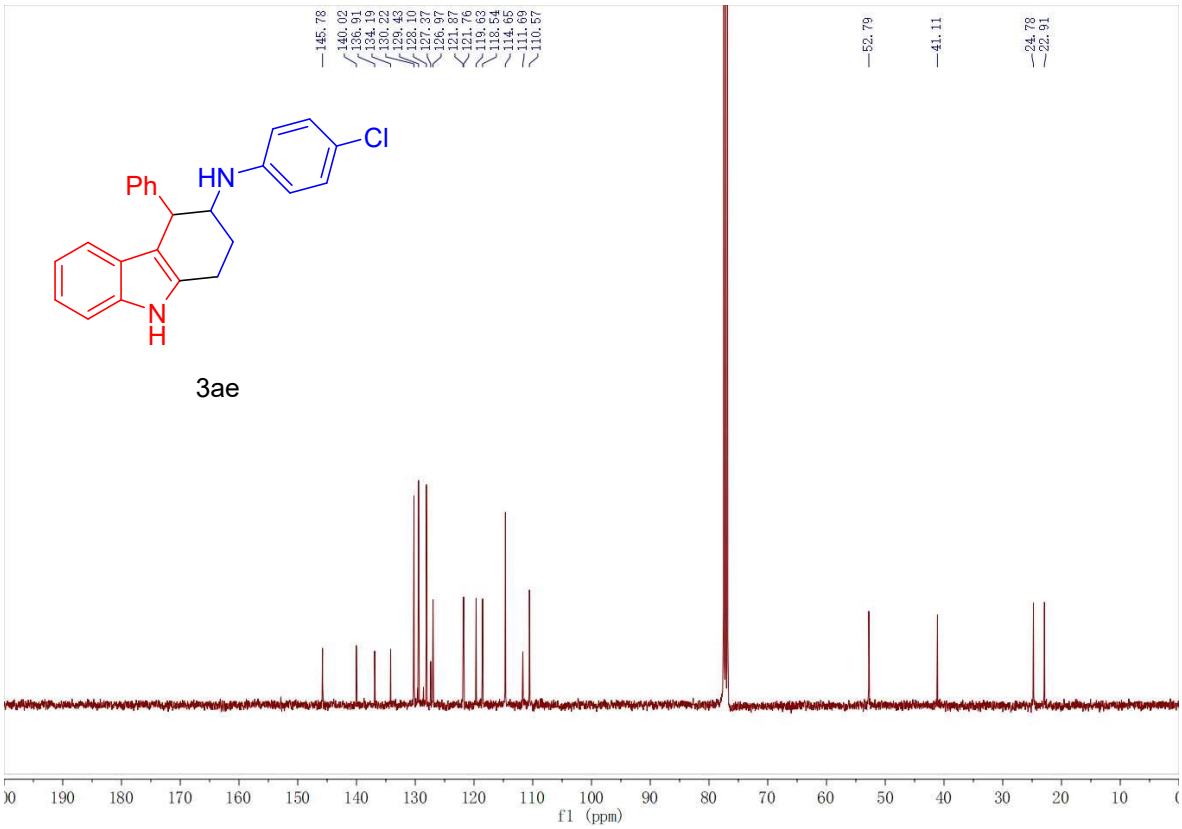
3.02
6.07
1.07
2.01
1.00
1.00
2.09
2.05
f1 (ppm)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140.02
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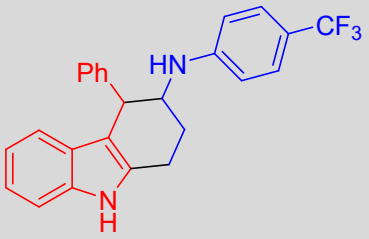
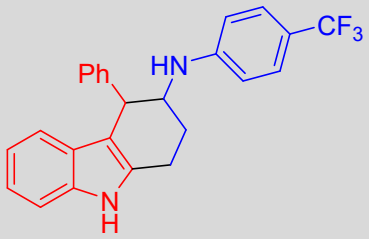
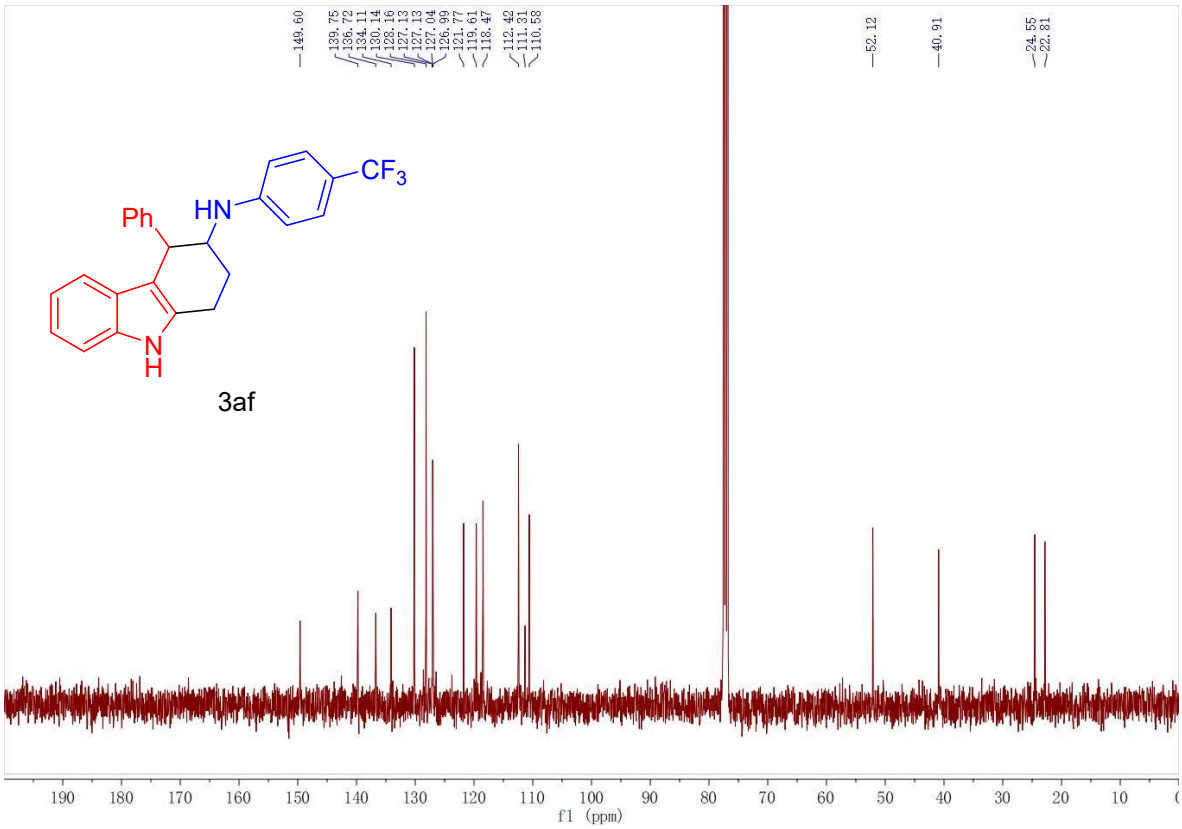
134.19
130.22
129.43
128.10
127.37
126.97
121.87
121.76
119.63
118.54
114.65
111.69
110.57
52.79
41.11
24.78
22.91
Cl
HN
Ph
N
H
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



3af



3af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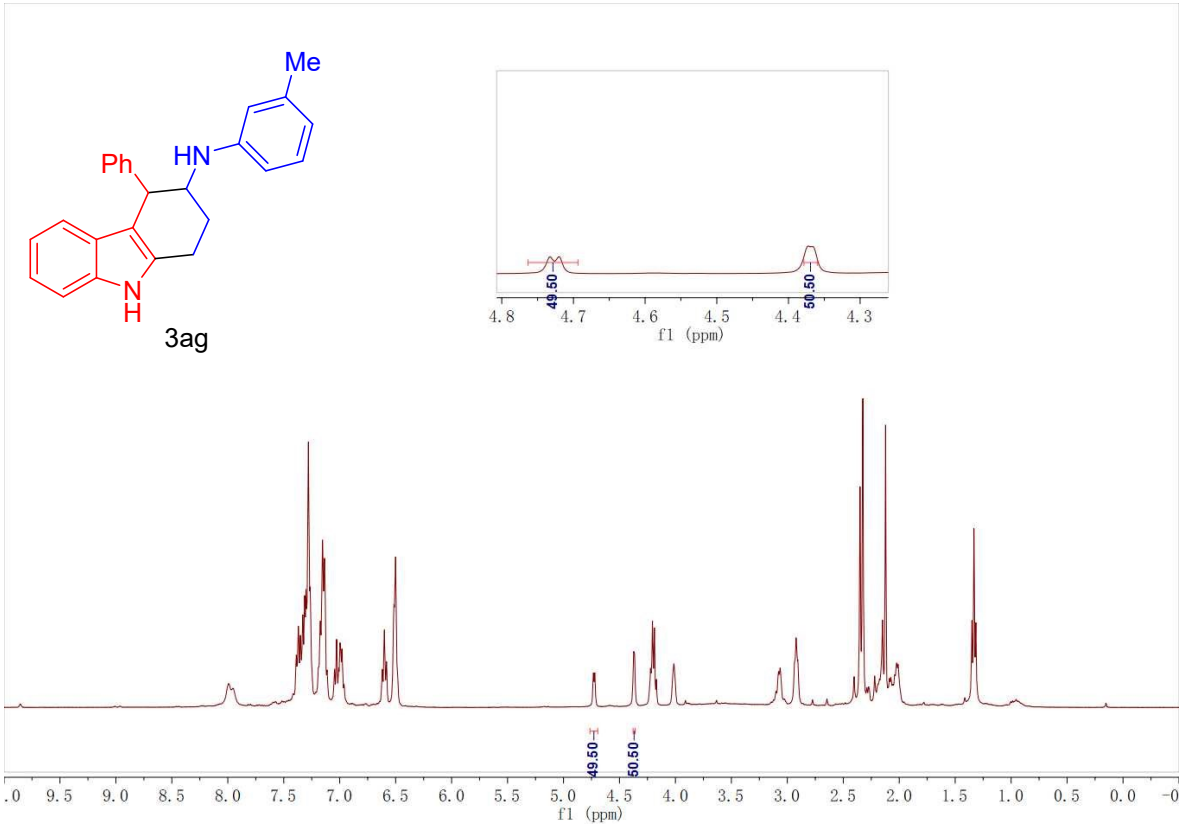
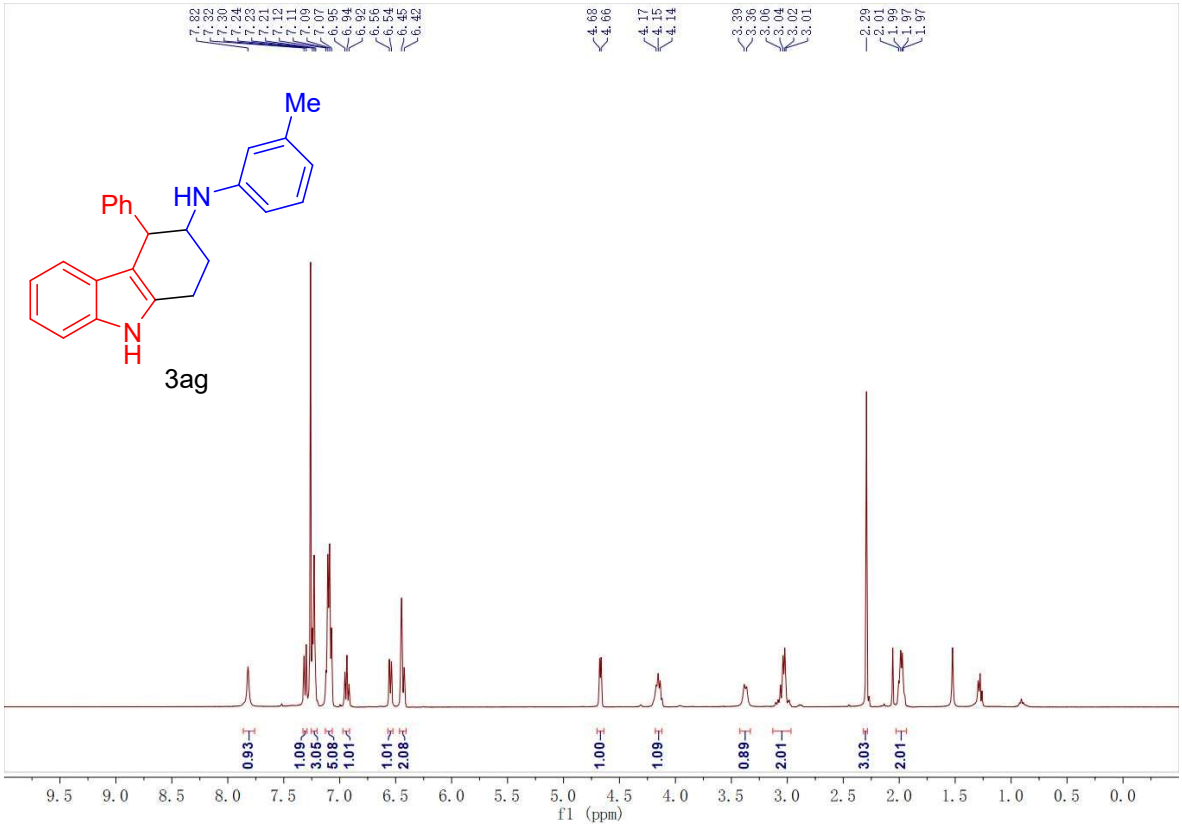
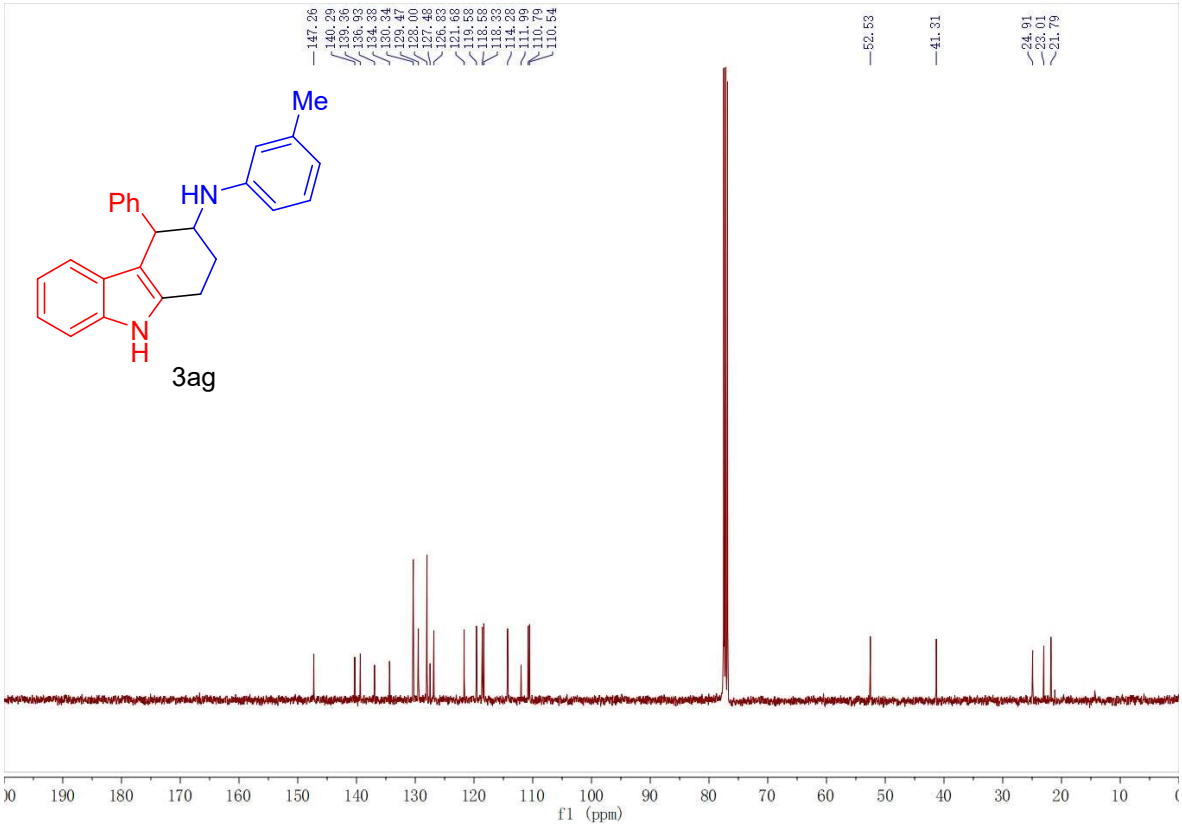
127.13
127.04
126.99
121.77
119.61
118.47
112.42
111.31
110.58
52.12
40.91
24.55
22.81
Ph
HN
CF3
N
H
3af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
HN
Ph
N
H
3ag
49.50
50.50
f1 (ppm)


Me
HN
Ph
N
H
3ag
f1 (ppm)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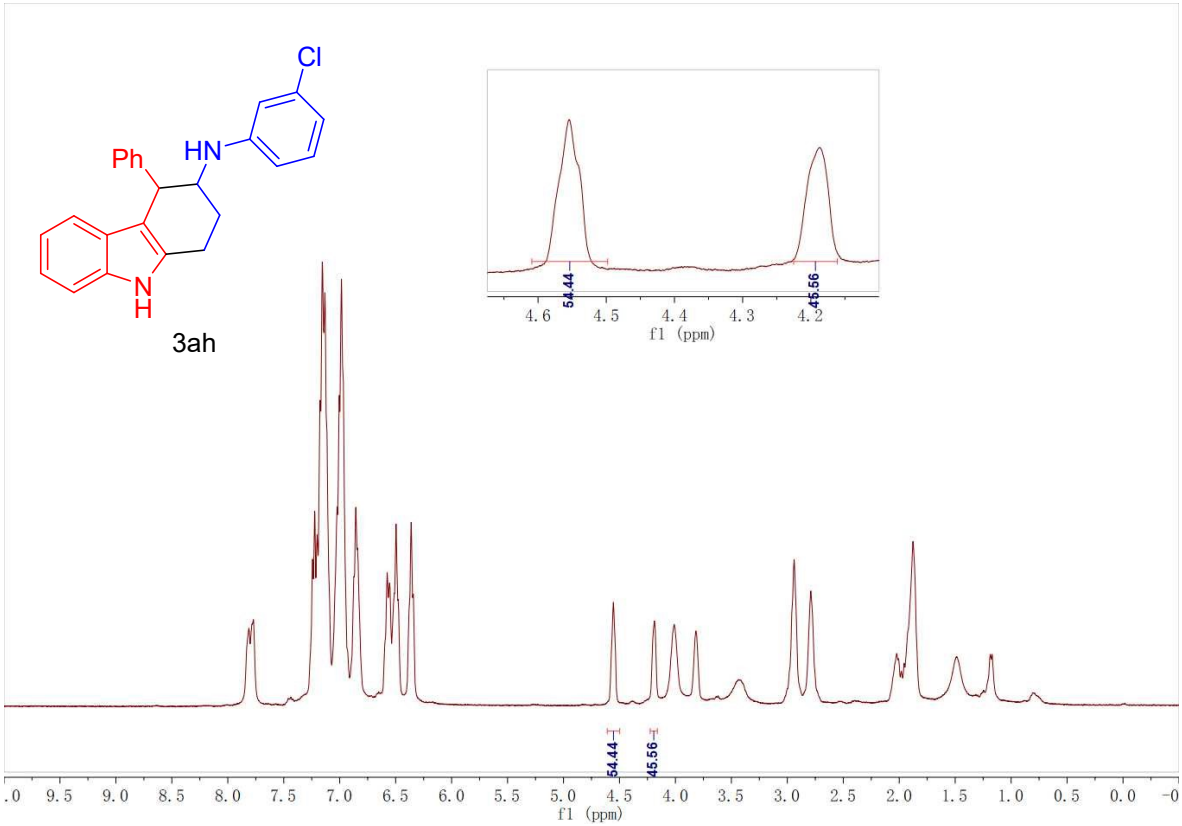
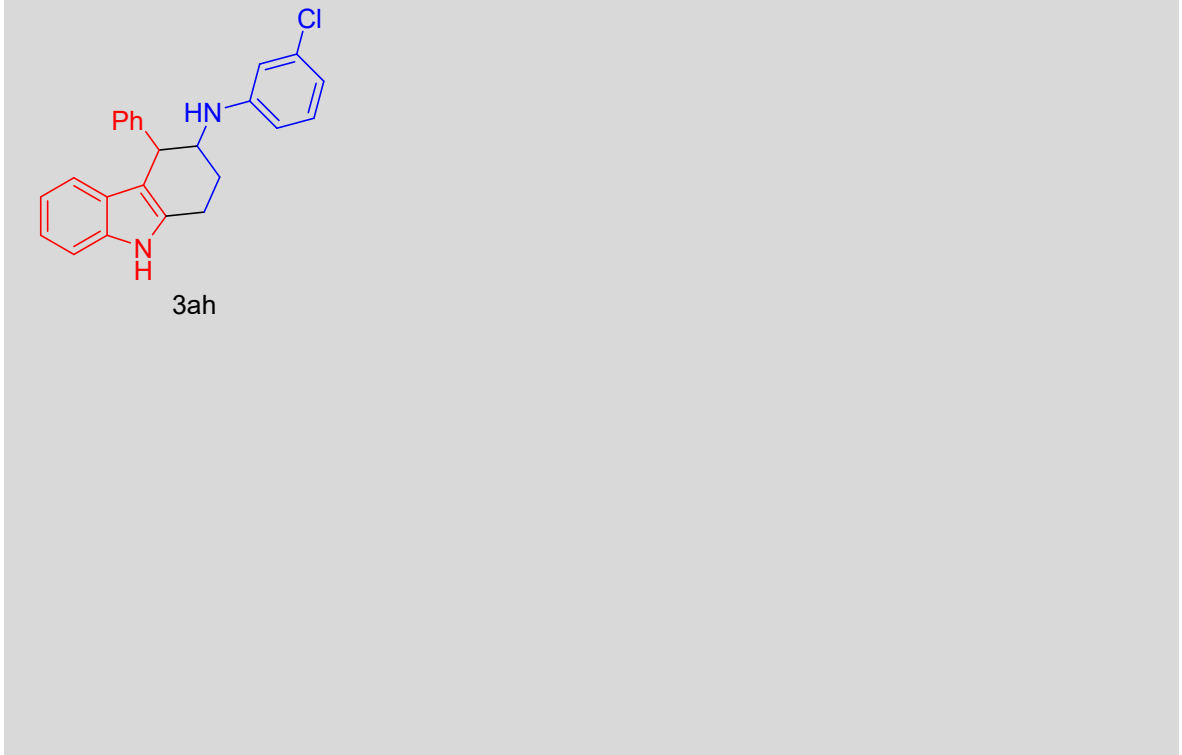
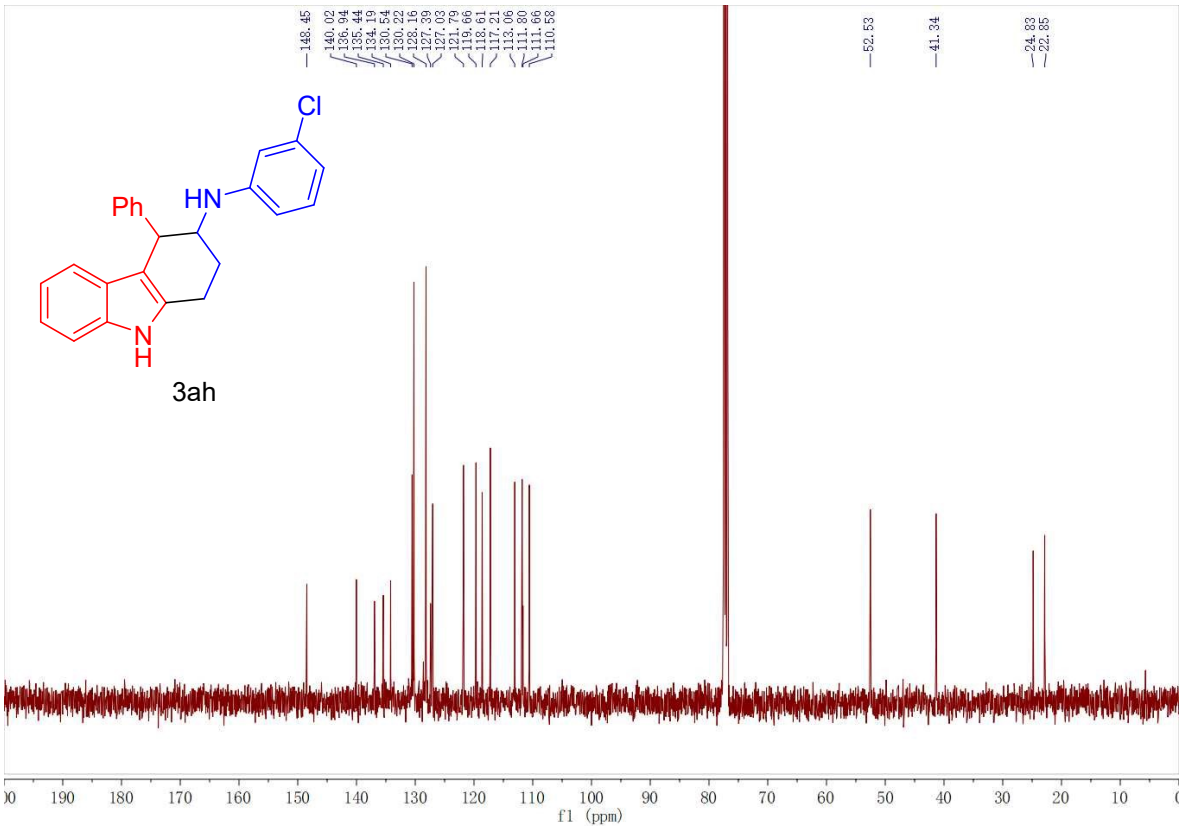
136.93
134.38
130.34
129.47
128.00
127.48
126.83
121.68
119.58
118.58
118.33
114.28
111.99
110.79
110.54
52.53
41.31
24.91
23.91
21.79
Me
HN
Ph
N
H
3ag
f1 (ppm)


Cl
HN
Ph
N
H
3ah
54.44
45.56
4.6
4.5
4.4
4.3
4.2
f1 (ppm)
54.44
45.56
f1 (ppm)


Cl
HN
Ph
N
H
3ah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140.02
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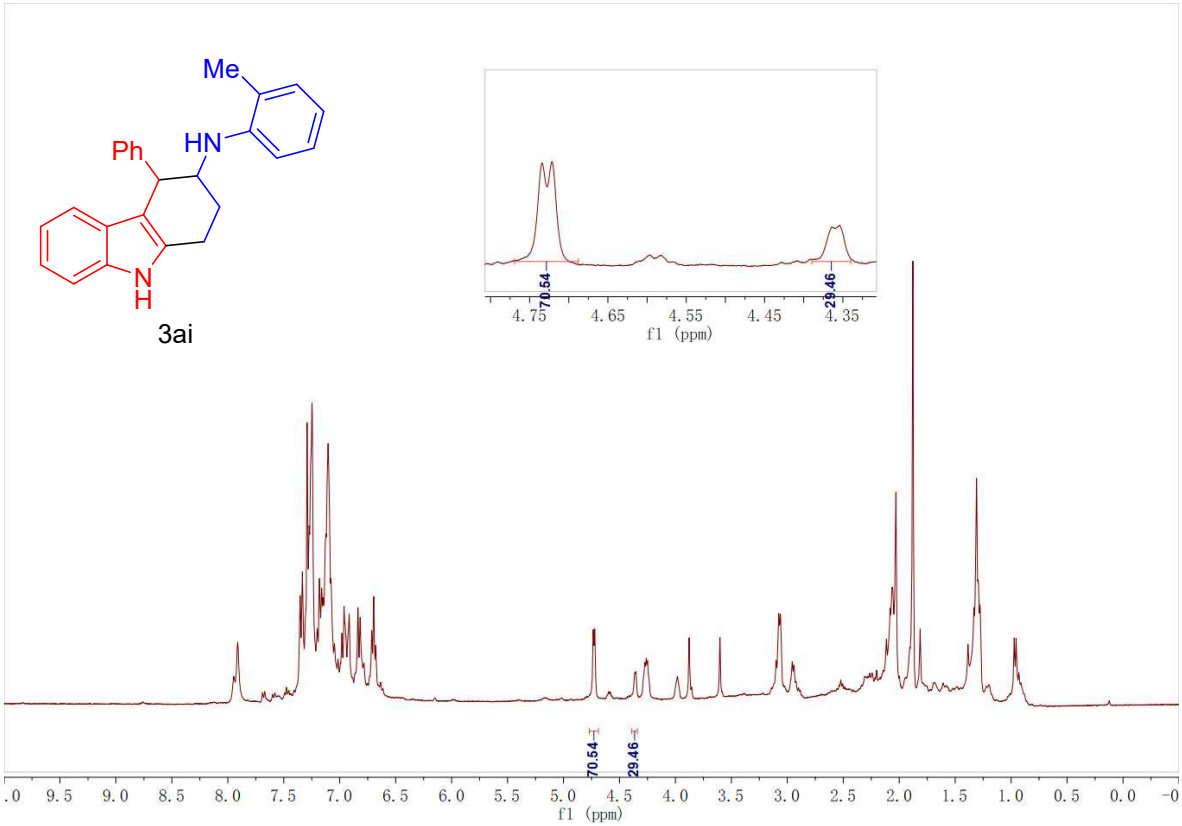
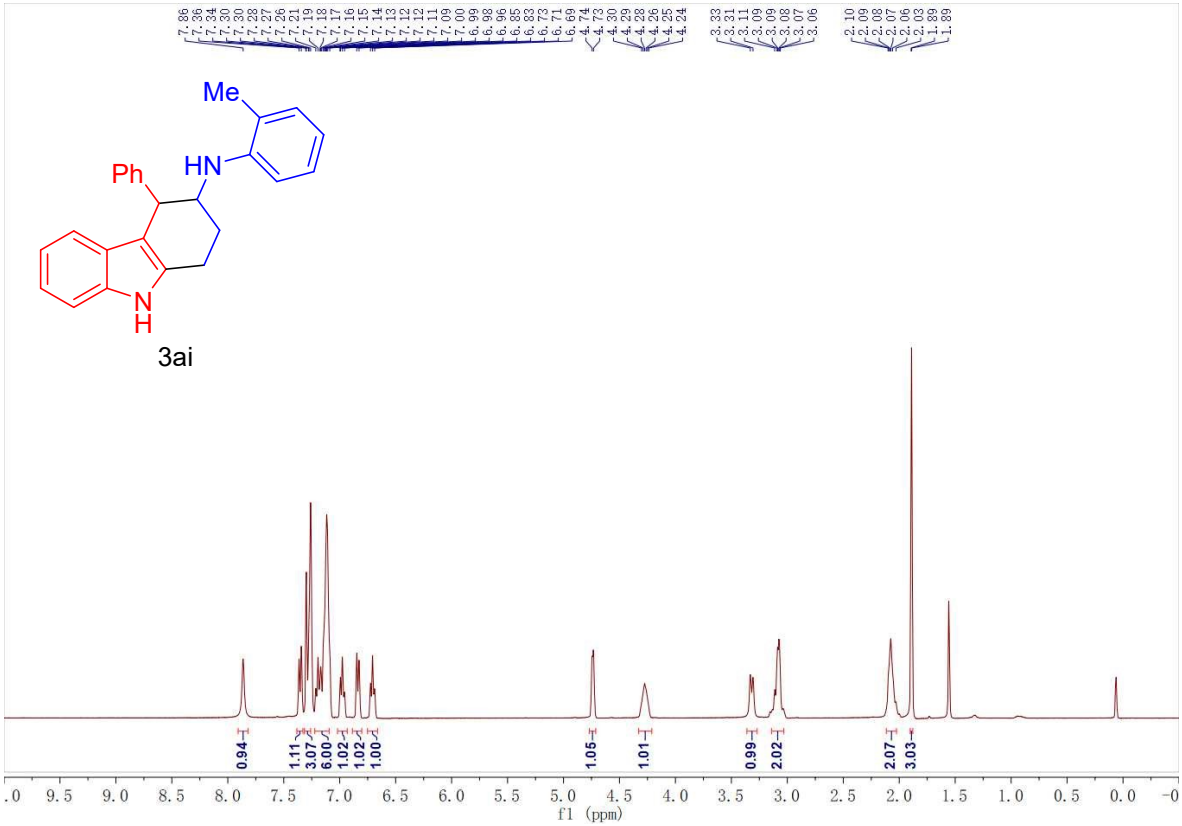
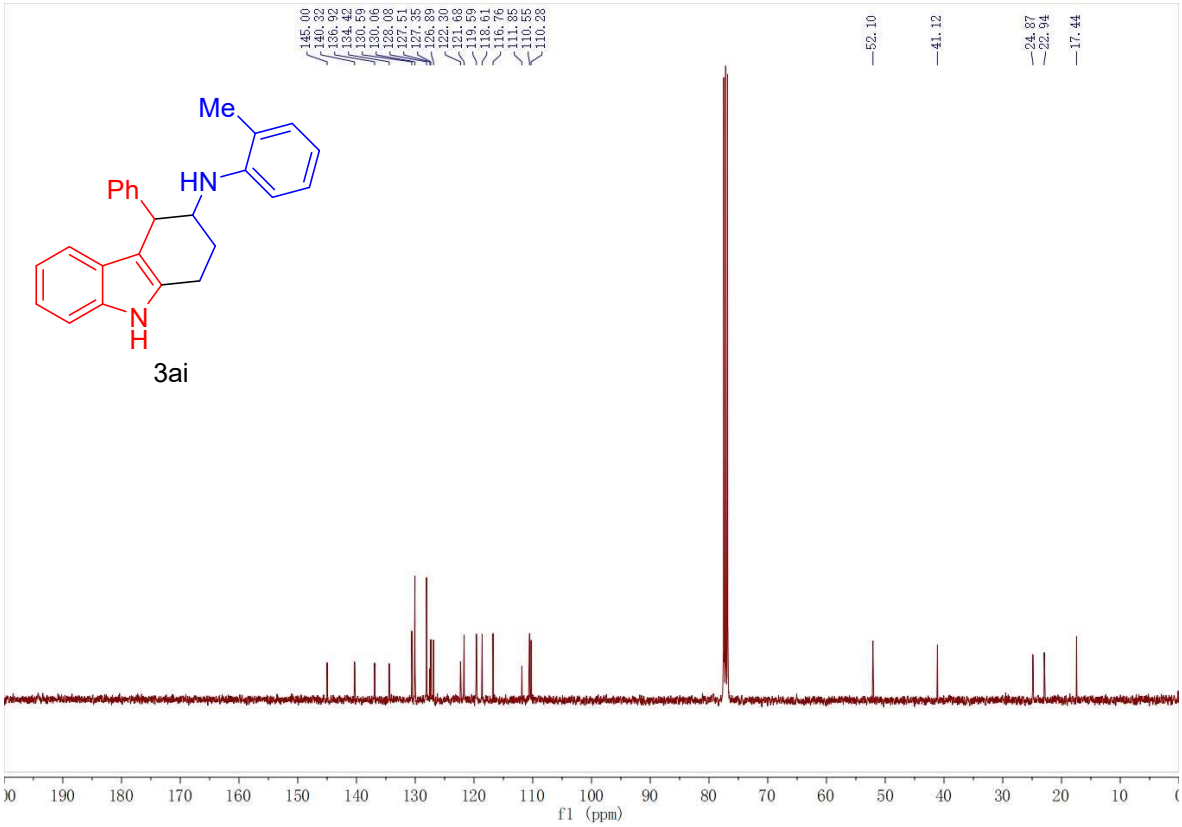
135.44
134.19
130.54
130.22
128.16
127.39
127.03
121.79
119.66
118.61
117.21
113.06
111.80
111.66
110.58
52.53
41.34
24.83
22.85
Cl
HN
Ph
N
H
3ah
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
HN
Ph
N
H
3ai
70.54
29.46
4.75
4.65
4.55
4.45
4.35
f1 (ppm)
70.54
29.46
f1 (ppm)


Me
HN
Ph
N
H
3ai
0.94
1.11
3.07
6.00
1.02
1.02
1.00
1.05
1.01
0.99
2.02
2.07
3.03
f1 (ppm)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130.06
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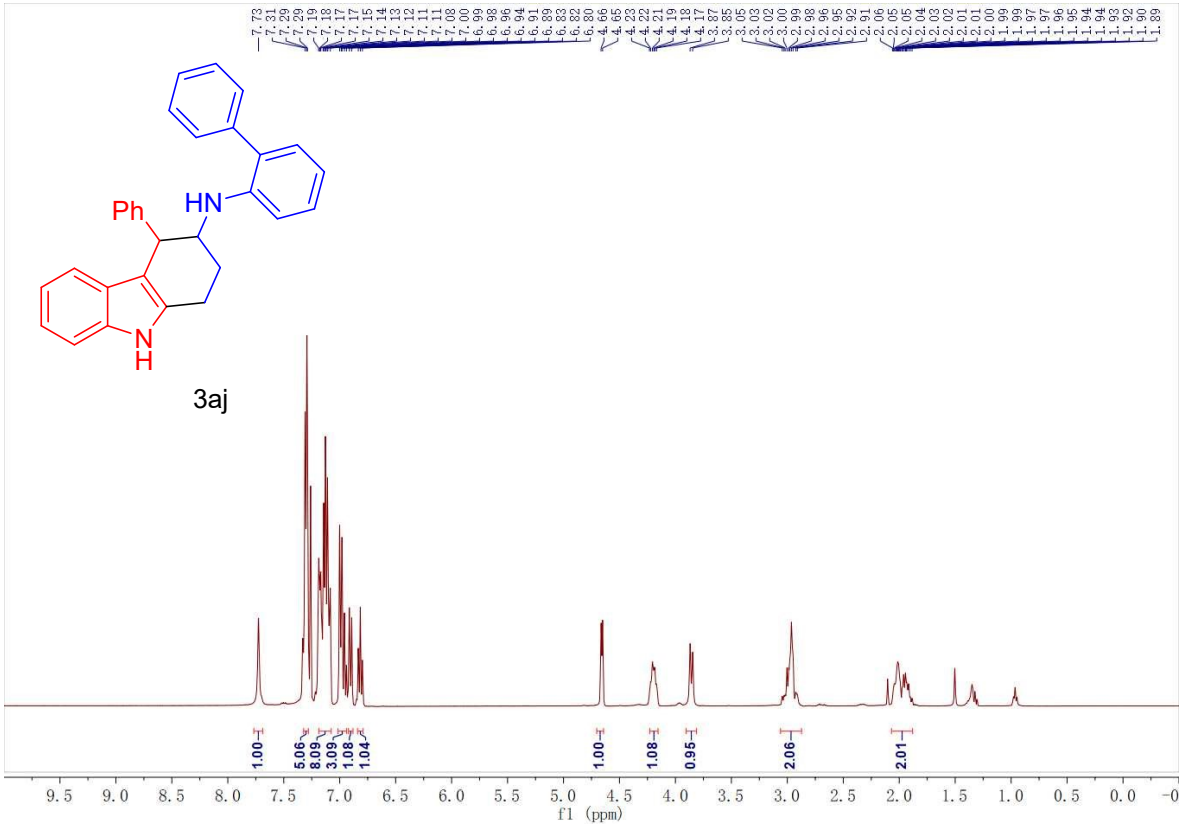
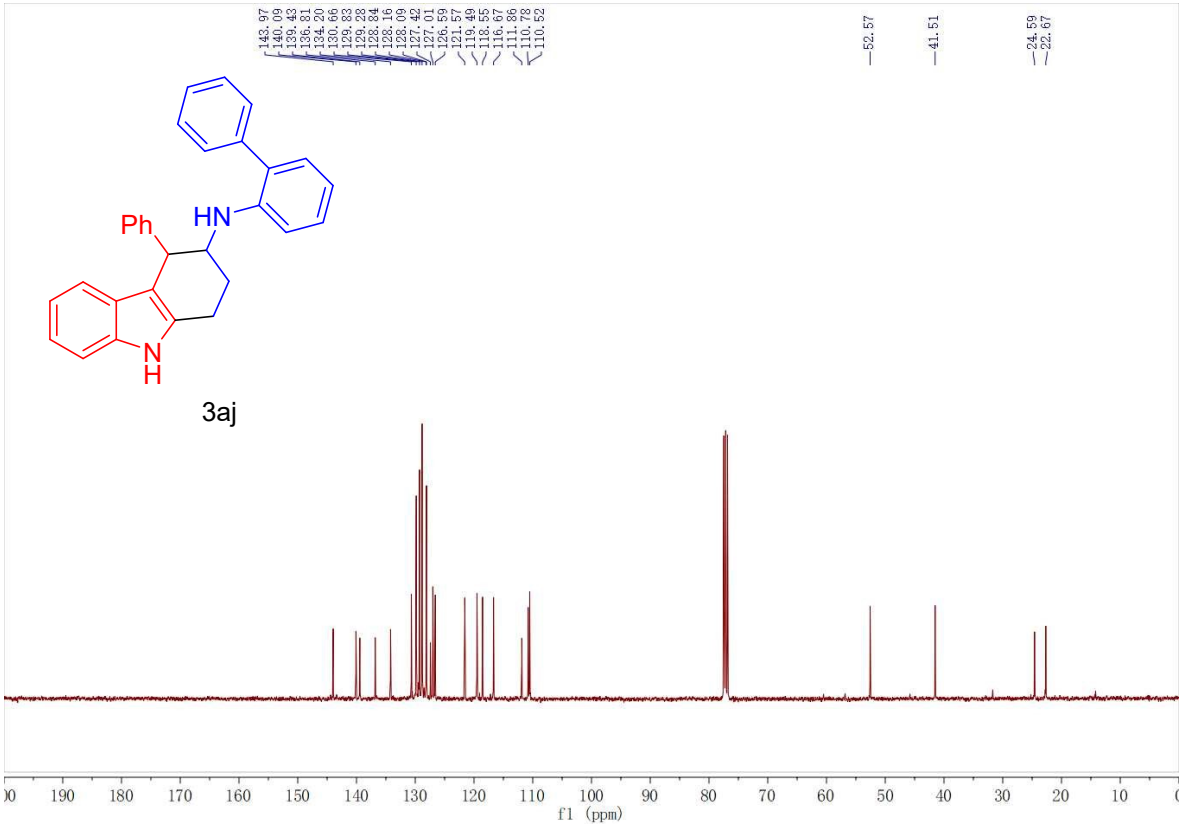
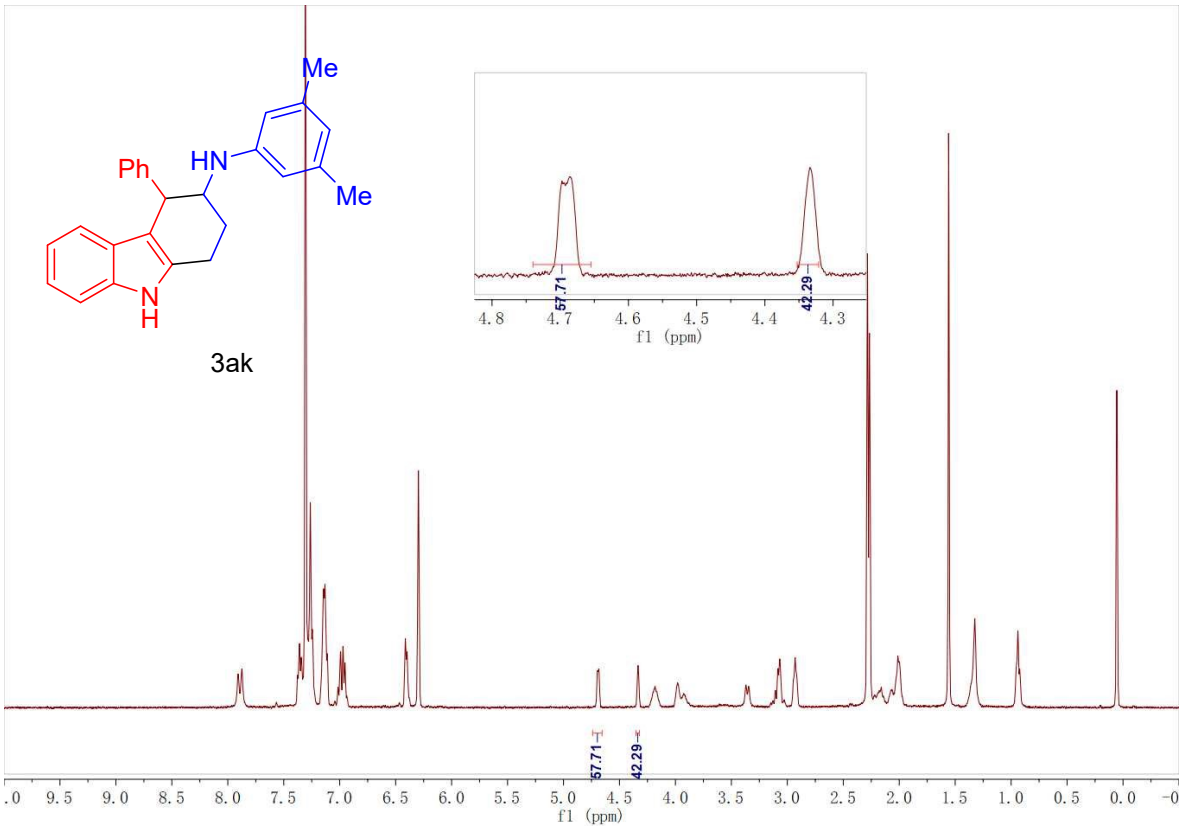
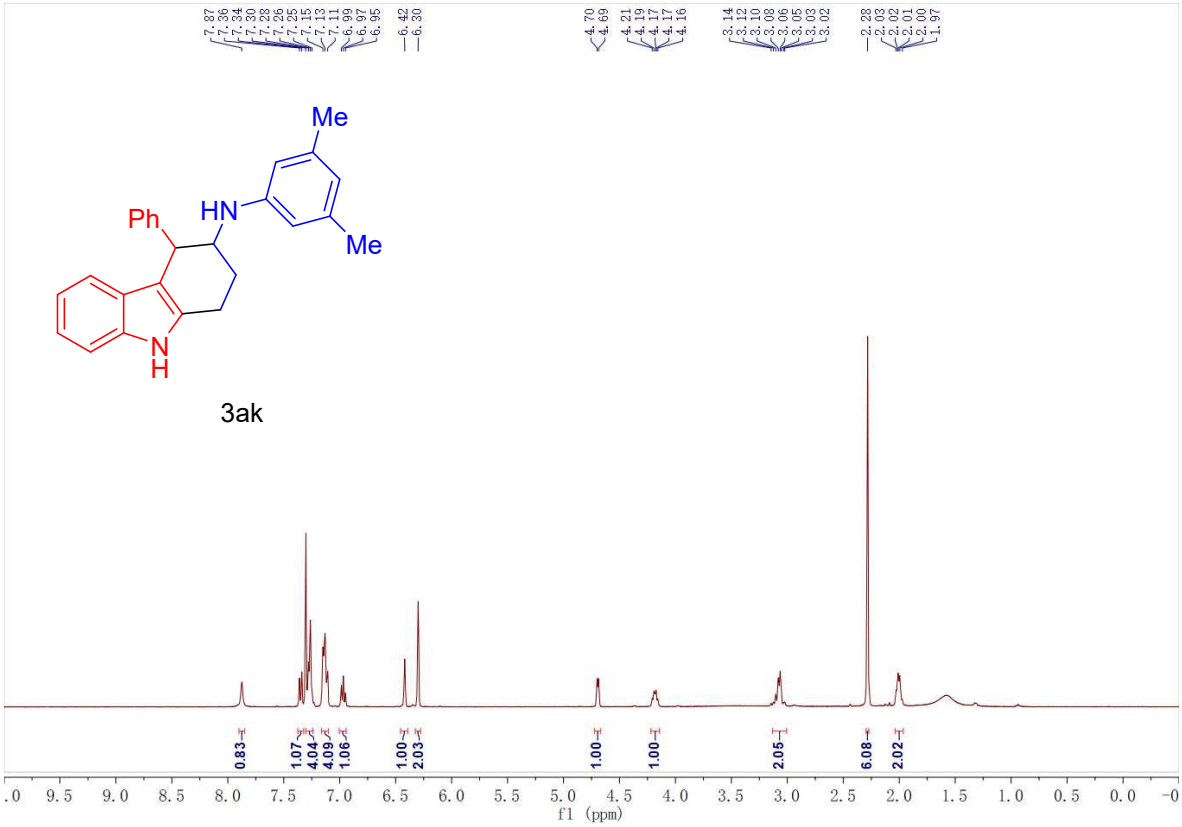
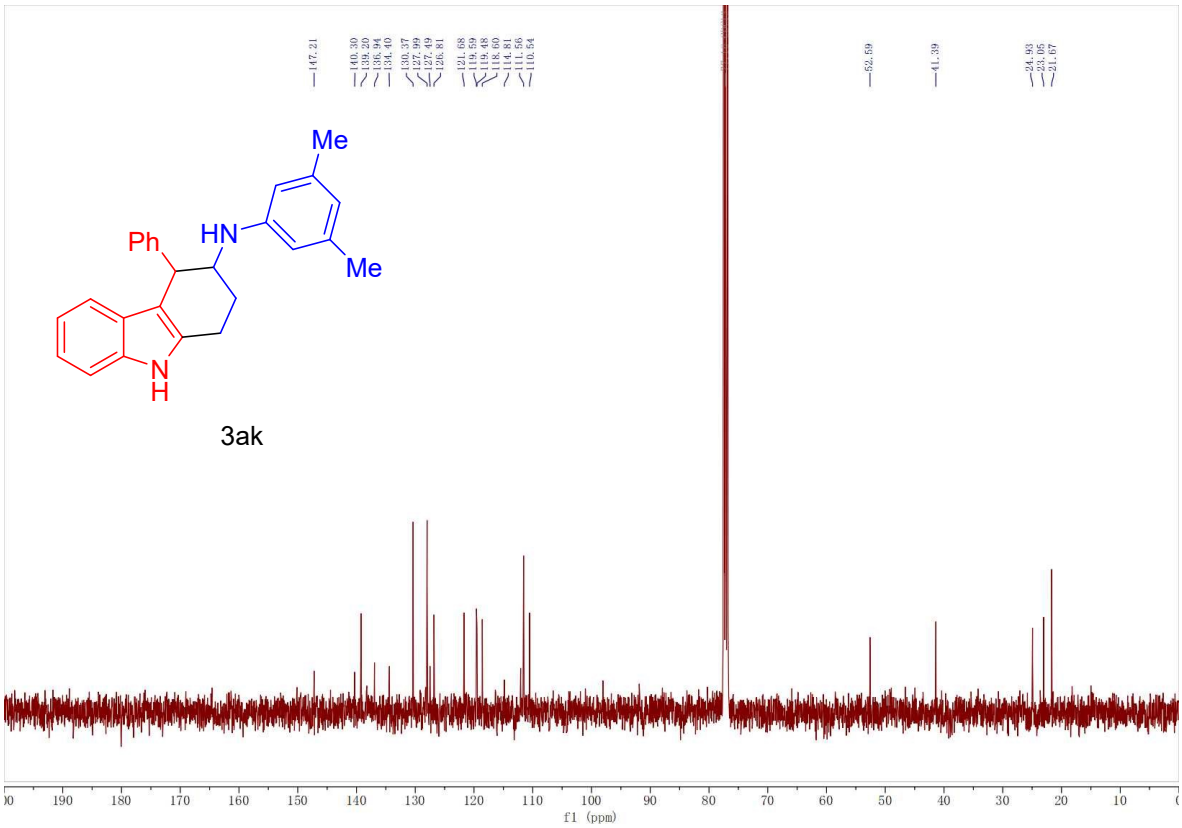
127.51
127.35
126.89
122.30
121.68
119.59
118.61
116.76
111.85
110.55
110.28
52.10
41.12
24.87
22.94
17.44
Me
HN
Ph
N
H
3ai
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

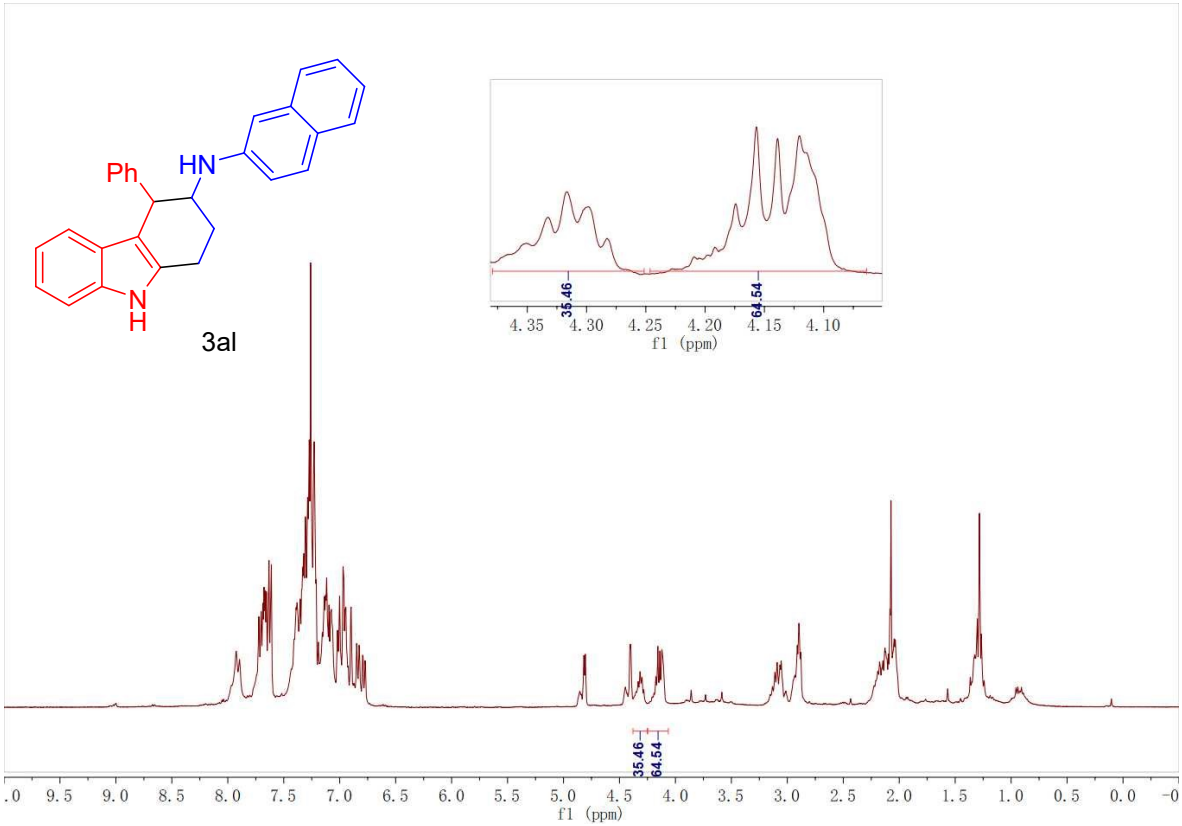

Ph
HN
N
H
3aj
1.00
5.06
8.09
3.09
1.08
1.04
1.00
1.08
0.95
2.06
2.01
f1 (ppm)

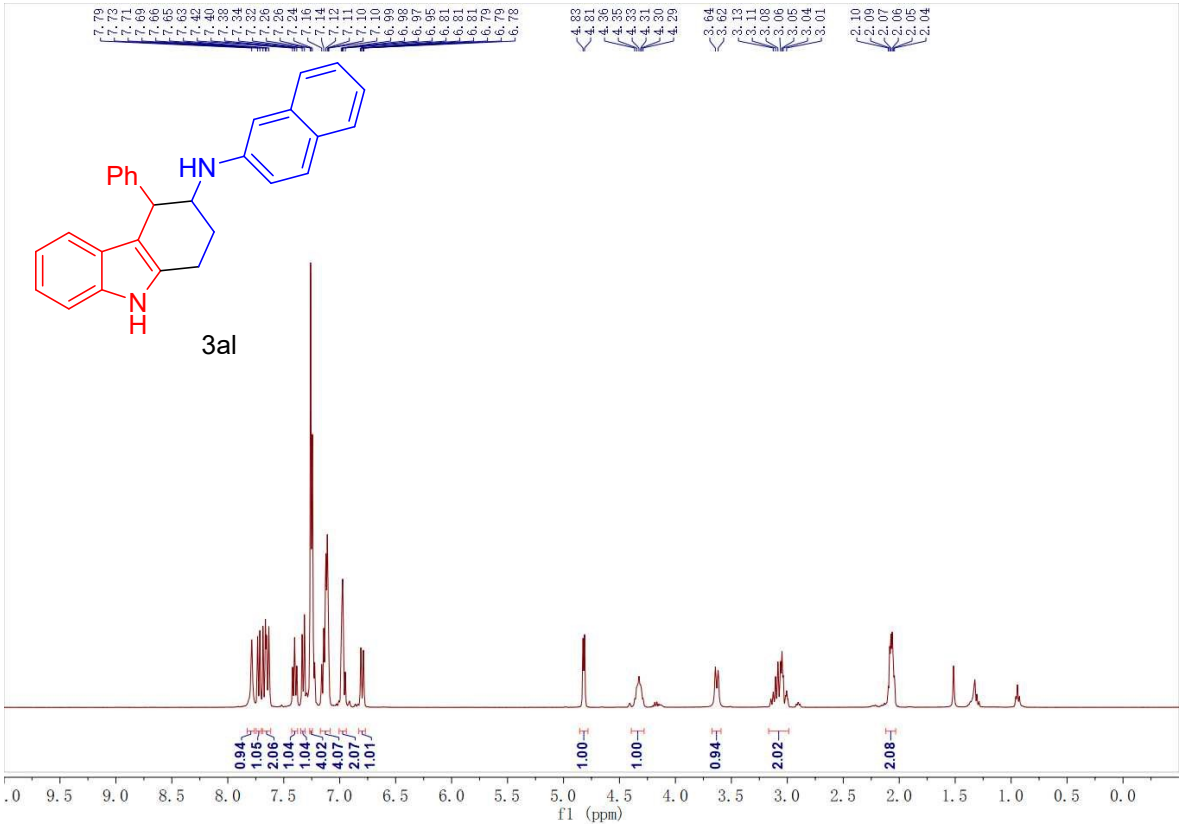

Ph
HN
N
H
3aj
f1 (ppm)

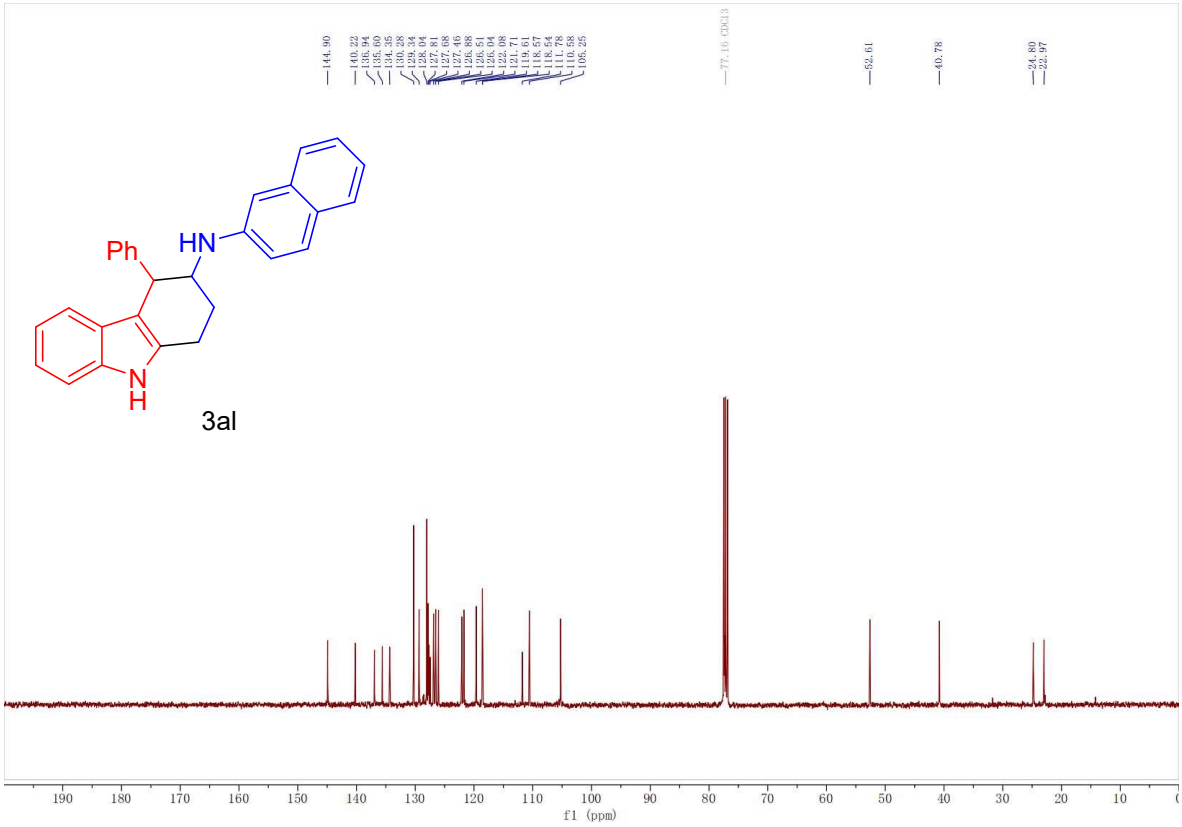

Me
HN
Ph
Me
N
H
3ak
57.71
42.29
4.8
4.7
4.6
4.5
4.4
4.3
f1 (ppm)
57.71
42.29
f1 (ppm)

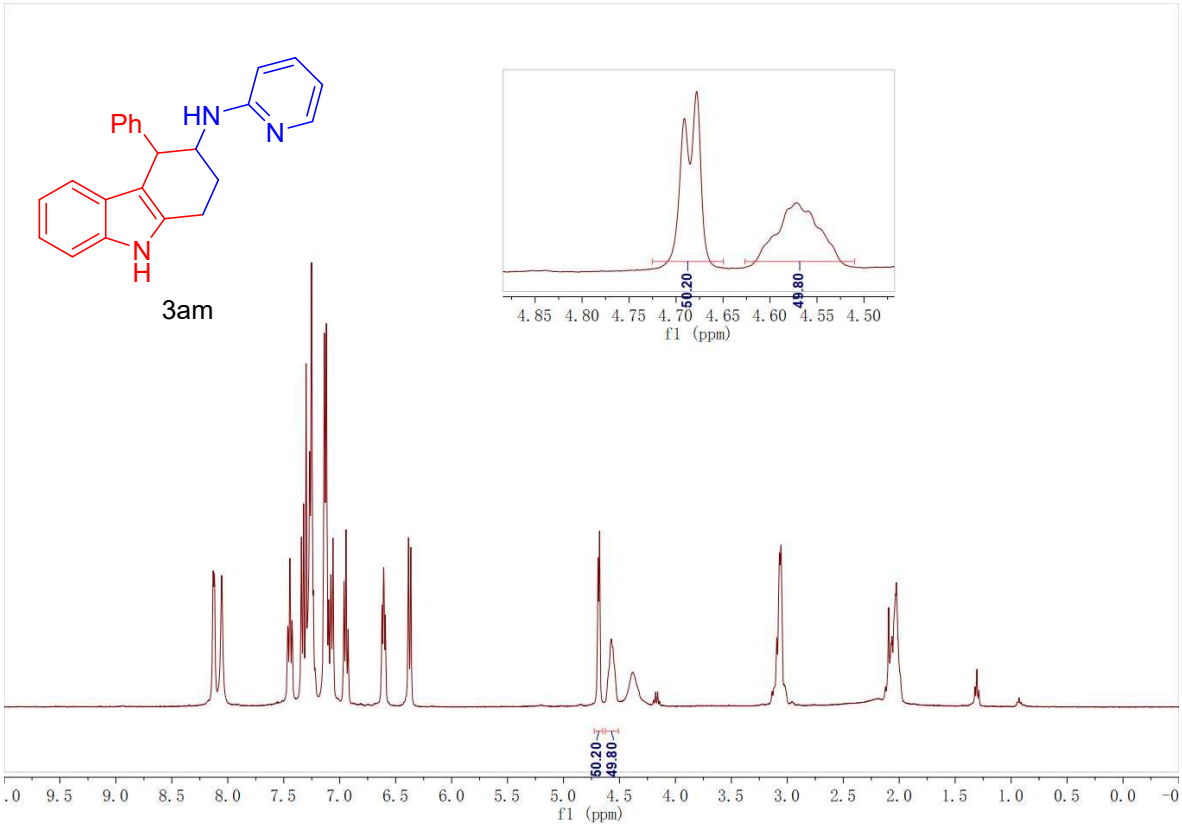

7.87
7.36
7.34
7.30
7.28
7.26
7.25
7.15
7.13
7.11
6.99
6.97
6.95
6.42
6.30
4.70
4.69
4.21
4.19
4.17
4.17
4.16
3.14
3.12
3.10
3.08
3.06
3.05
3.03
3.02
2.28
2.03
2.02
2.01
2.00
1.97
Me
HN
Ph
Me
N
H
3ak
0.83
1.07
4.04
4.09
1.06
1.00
2.03
1.00
1.00
2.05
6.08
2.02
f1 (ppm)

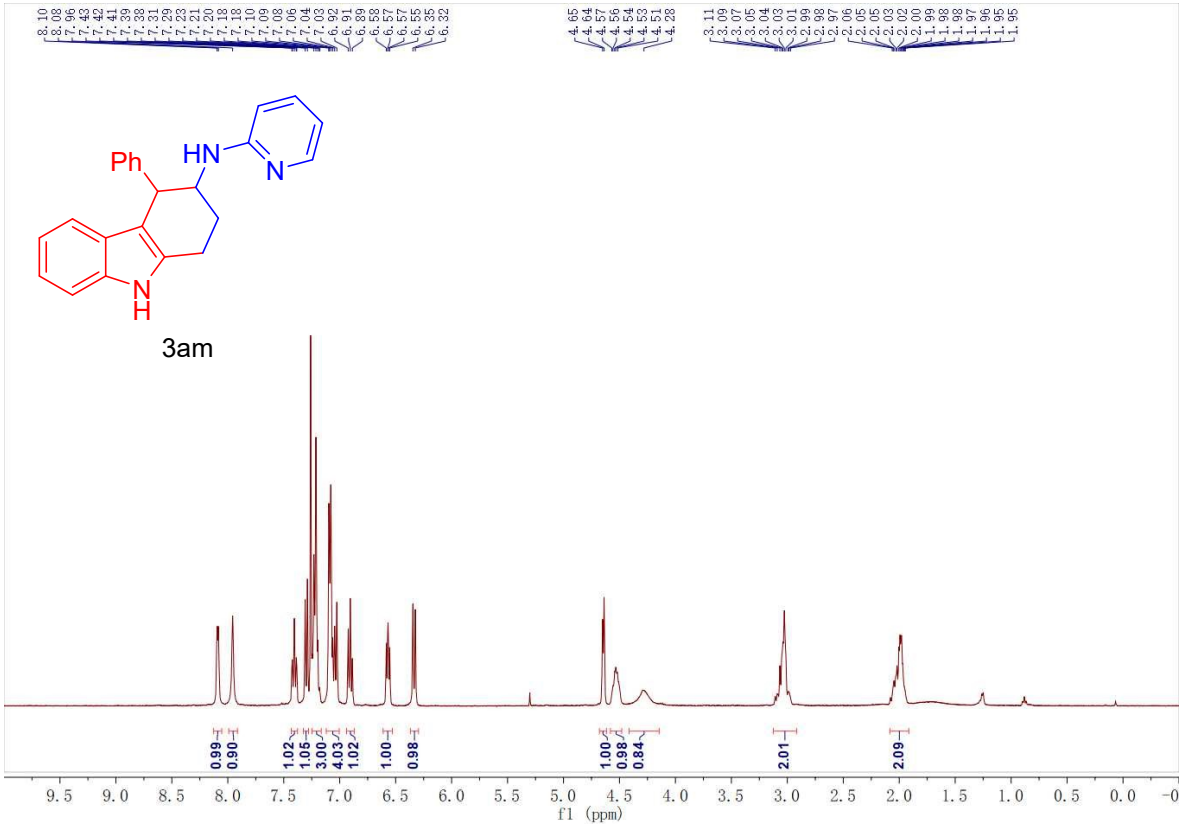

147.21
140.30
139.20
136.94
134.46
130.37
127.99
127.49
126.81
121.68
119.59
119.48
118.60
114.81
111.56
110.54
52.59
41.39
24.93
23.95
21.67
Me
HN
Me
Ph
N
H
3ak
f1 (ppm)

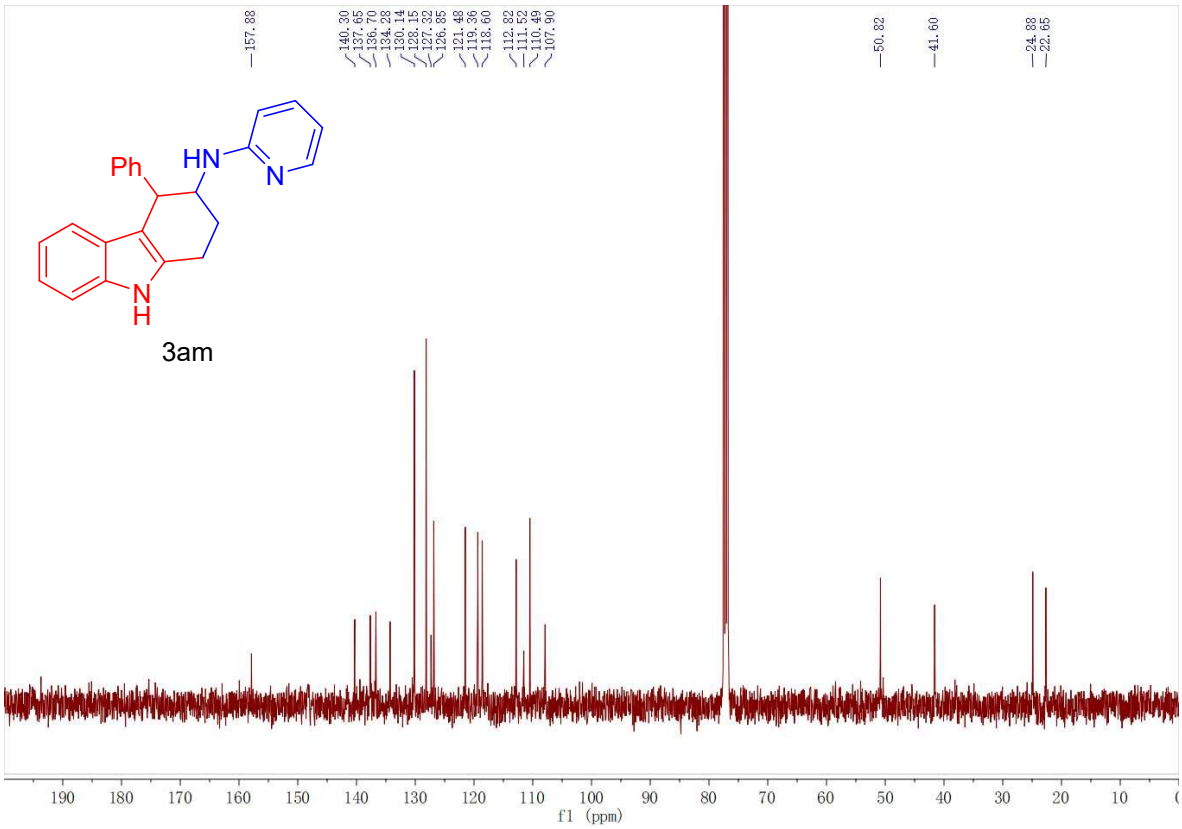

Ph
HN
N
H
3al
35.46
64.54
4.35 4.30 4.25 4.20 4.15 4.10
f1 (ppm)
35.46
64.54
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


7.79 7.73 7.71 7.69 7.66 7.65 7.63 7.42 7.40 7.38 7.34 7.32 7.26 7.24 7.16 7.14 7.12 7.11 7.10 6.99 6.98 6.97 6.95 6.81 6.81 6.81 6.79 6.79 6.78
4.83 4.81 4.36 4.35 4.33 4.31 4.30 4.29
3.64 3.62 3.13 3.11 3.08 3.06 3.05 3.04 3.01
2.10 2.09 2.07 2.06 2.05 2.04
Ph
HN
N
H
3al
0.84 1.05 2.06 1.04 1.04 4.02 4.07 2.07 1.01
1.00 1.00 0.94 2.02 2.08
.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
f1 (ppm)


144.90
140.22
136.94
135.60
134.35
130.28
129.34
129.04
127.81
127.68
127.46
126.88
126.51
126.04
122.08
121.71
119.61
118.57
111.54
111.78
110.58
108.25
77.16 CDCl3
52.61
40.78
24.89
22.97
Ph
HN
N
H
3al
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
HN
N
N
H
3am
50.20
49.80
4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50
f1 (ppm)
50.20
49.80
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
f1 (ppm)


8.10 8.08 7.96 7.43 7.42 7.41 7.39 7.38 7.31 7.29 7.23 7.21 7.20 7.18 7.10 7.09 7.08 7.06 7.04 7.03 6.92 6.91 6.89 6.58 6.57 6.57 6.55 6.35 6.32
4.65 4.64 4.57 4.56 4.54 4.53 4.51 4.28
3.11 3.09 3.07 3.05 3.04 3.03 3.01 2.99 2.98 2.97 2.06 2.05 2.05 2.03 2.02 2.00 1.99 1.98 1.98 1.97 1.96 1.95 1.95
Ph
HN
N
N
H
3am
0.99 0.90 1.02 1.05 3.00 4.03 1.02 1.00 0.98 1.00 0.98 0.84 2.01 2.09
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
f1 (ppm)


157.88
140.30
137.65
136.70
134.28
130.14
128.15
127.32
126.85
121.48
119.36
118.60
112.82
111.52
110.49
107.90
50.82
41.60
24.88
22.65
Ph
HN
N
N
H
3am
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)