Supporting Information

Organophotocatalytic pyridination of *N*-arylglycines with 4-cyanopyridines by decarboxylative and decyanative radical-radical coupling

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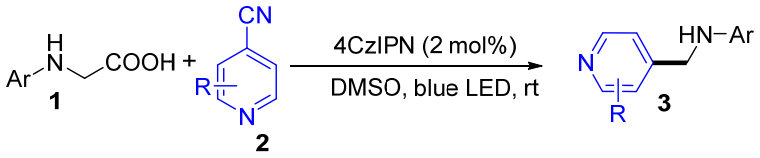
1. General Considerations

General Information: Unless otherwise noted, all chemicals were purchased and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer (101 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm). The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Emission intensities were recorded using a FS5 spectrophotometer. Cyclic voltammetry was performed on the CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).

2. General Synthetic Procedures

All substrates are known compounds. *N*-aryl glycine **1b-1r** were synthesized according to the literature.[1] 4-cyanopyridine **2h-2o** were prepared according to the literature.[2]

General procedure for photoredox-catalyzed decarboxylative pyridination of *N*-aryl glycines with 4-cyanopyridine:



The mixture of *N*-phenyl glycine **1** (0.3 mmol, 1.5 equiv), **2** (0.2 mmol, 1 equiv.), 4CzIPN (2 mol%, 0.004 mmol, 3.2 mg) and DMSO (2 mL, 0.1M) was added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times). The reaction mixture was irradiated with 6 W blue LEDs at ambient temperature for 12 h. Then, the reaction mixture was diluted with sat. $NaHCO_3$ (10 mL) and extracted by ethyl acetate (10 mL×2). After drying over sodium sulfate, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate) to obtain the product **3**. The photoreactor is shown in Figure S1.

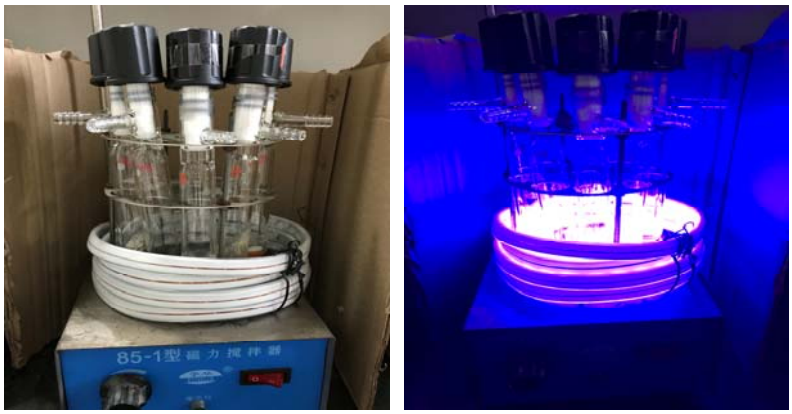


Figure S1. Photoreactor used in this work.

The Light Source and the Material of the Irradiation Vessel:

The photochemical reaction was carried out under visible light irradiation by a 6W blue LED at room temperature. This blue LED was purchased from taobao (link:

https://m.tb.cn/h.gYNqadS?sm=38a27d?tk=BDtaWH5ZZZP). The blue LED's energy peak wavelength is 476 nm and irradiance@6W is 2.1 mW/cm^2. The reaction vessel is a borosilicate glass tube. The distance between the tube and lamp is about 1 cm, and no filter is applied.

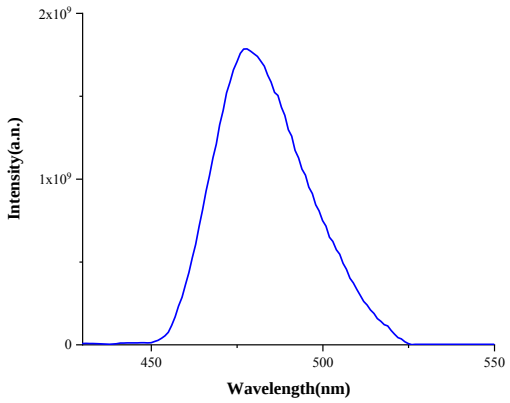


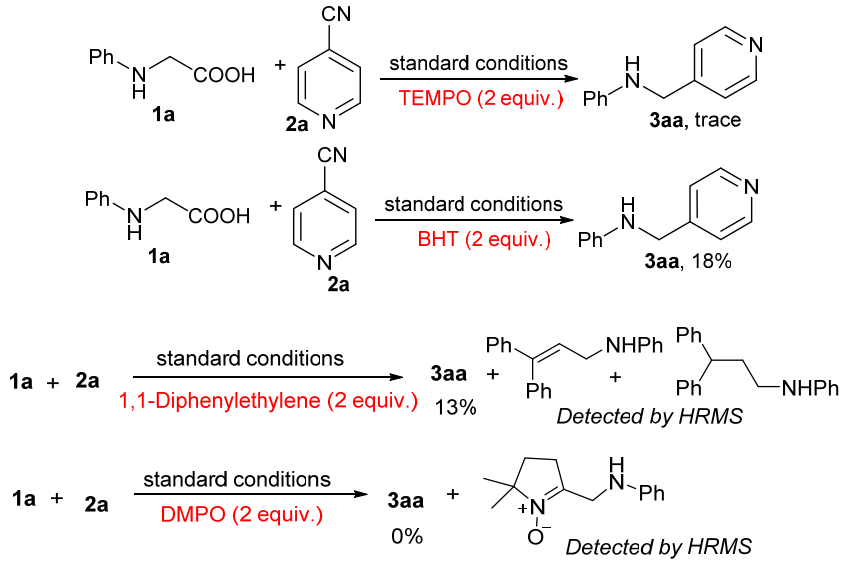
Figure S2. The spectral distribution of 6W blue LED

1 mmol scale preparation of 3aa

The mixture of *N*-phenyl glycine **1a** (1.5 mmol, 226.5 mg, 1.5 equiv.), **2a** (1 mmol, 104 mg, 1 equiv.), 4CzIPN (2 mol%, 0.02 mmol, 15.8 mg) and DMSO (10 mL, 0.1M) was added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times). The reaction mixture was irradiated with 6 W blue LEDs at ambient temperature for 12 h. Then, the reaction mixture was diluted with sat. $NaHCO_3$ (30 mL) and extracted by ethyl acetate (20×2 mL). After drying over sodium sulfate, the solvent was evaporated under reduced pressure, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 2/1, v/v) to obtain the product **3aa** (77%, 141.8 mg).

3. Mechanism studies

3.1 Radical inhibition experiment for the reaction of 1a with 2a



The mixture of **1a** (0.15 mmol, 22.7 mg, 1.5 equiv.), **2a** (0.1 mmol, 10.4 mg, 1 equiv.), 4CzIPN (2 mol%, 1.6 mg), radical inhibitor (BHT (0.2 mmol, 44 mg, 2 equiv.), TEMPO (0.2 mmol, 31.2 mg, 2 equiv.), 1,1-Diphenylethylene (0.2 mmol, 36.5 mg, 2 equiv.) or DMPO (0.2 mmol, 22.6 mg, 2 equiv.) and DMSO (1 mL, 0.1M) was added to a Schlenk tube. The tube was evacuated and backfilled with nitrogen (repeated five times). The reaction mixture was irradiated with 6 W blue LEDs at ambient temperature for 12 h.

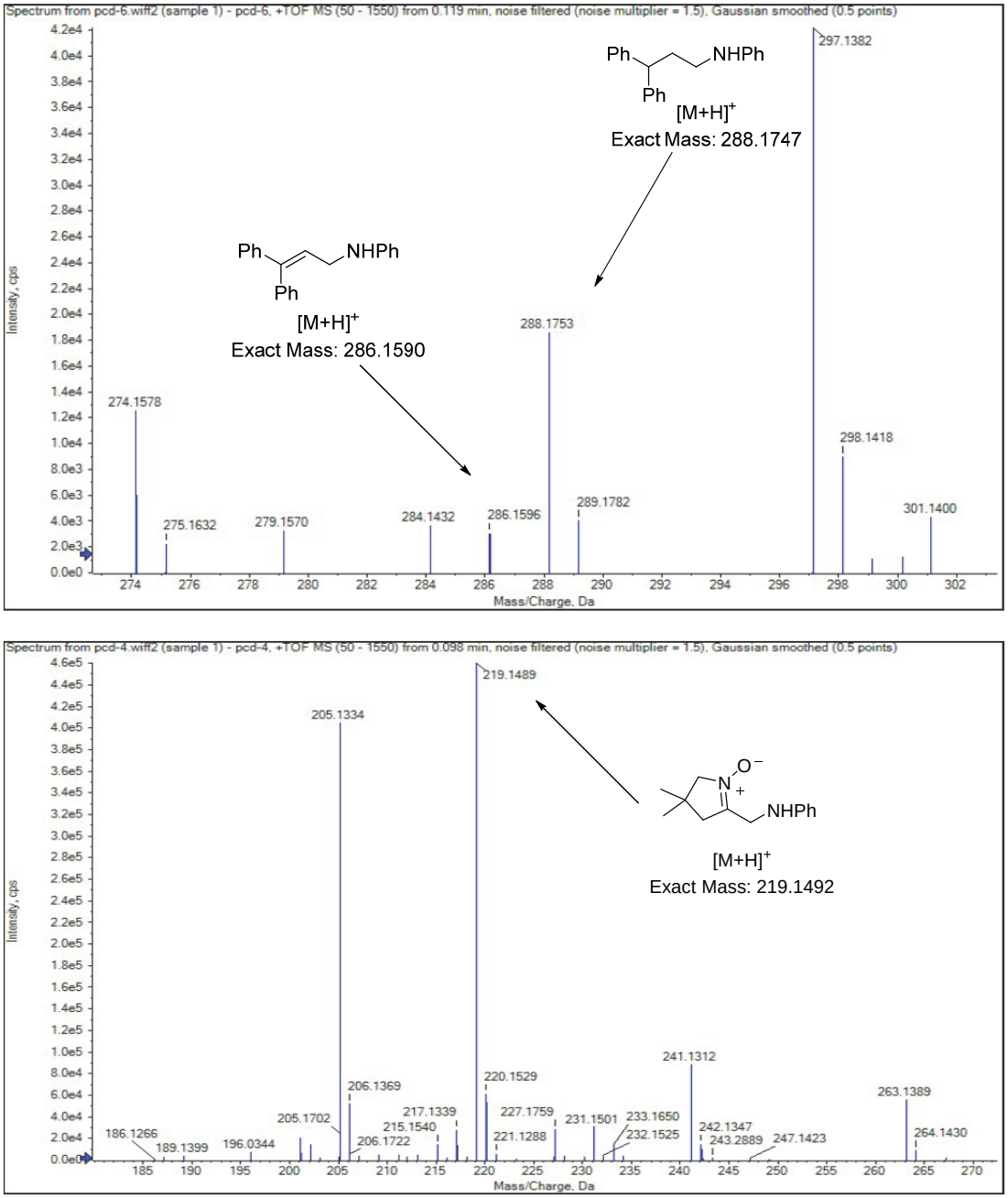


Figure S3. The detection of phenylaminomethyl radical by HRMS

3.2 HRMS analysis of model reaction solution

After **1a** reacted with **2a** under the standard conditions, the reaction mixture was detected by HRMS. The ***N***-phenylmethanimine was detected by HRMS.

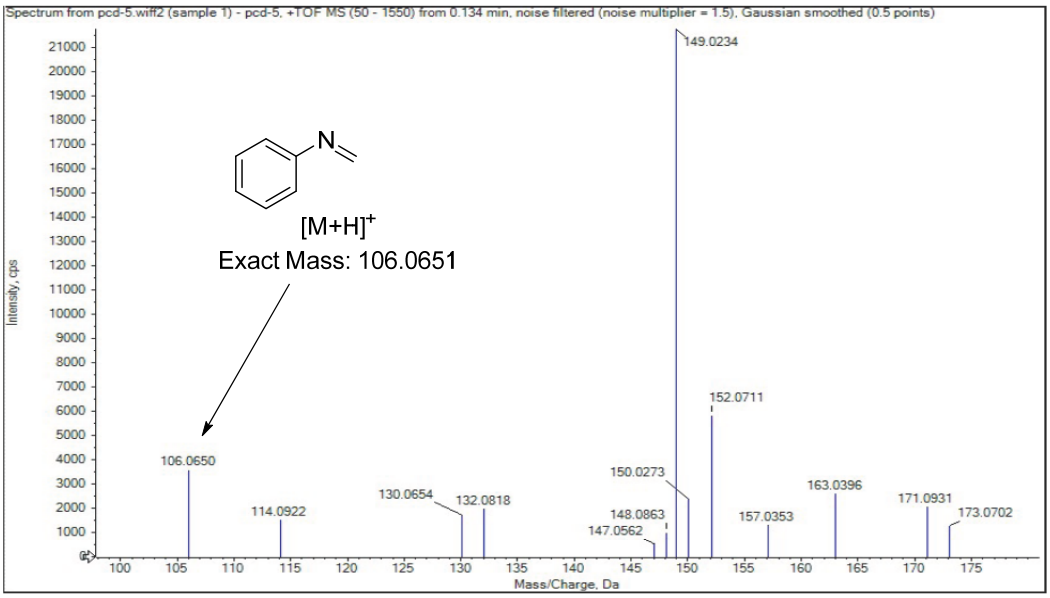


Figure S4. HRMS analysis of model reaction solution

3.3 Stern–Volmer luminescence-quenching experiments

Fluorescence quenching experiments were measured on an Agilent Cary Eclipse Spectrophotometer. The excitation wavelength of 4CzIPN was fixed at 330 nm with emission spectrum λ_{max} = 550 nm. The emission spectrum of a 3 × 10^{-5} M solution of 4CzIPN in DMSO was collected.

1a: A stock solution of **1a** (0.01 M) was prepared. The emission intensity of 4CzIPN (3 × 10^{-5} M in DMSO) was collected with the gradient concentration of **1a** and the results were presented.

2a: A stock solution of **2a** (0.01 M) was prepared. The emission intensity of 4CzIPN (3 × 10^{-5} M in DMSO) was collected with the gradient concentration of **2a** and the results were presented.

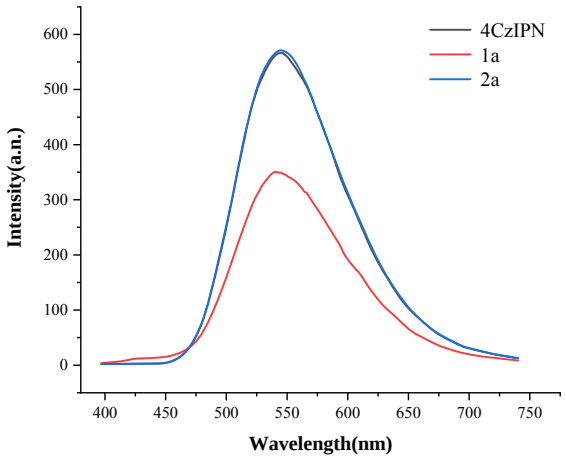


Figure S5. Fluorescence quenching of 4CzIPN by **1a or 2a**

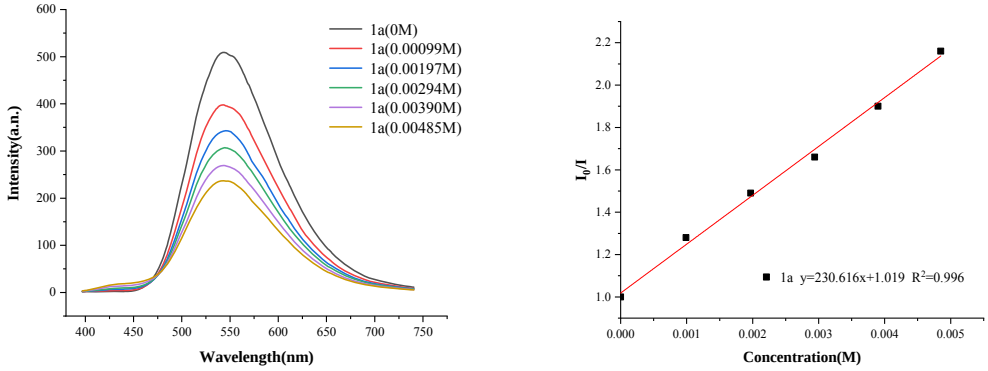


Figure S6. Luminescence quenching of 4CzIPN by **1a** and the Stern-Volmer plots.

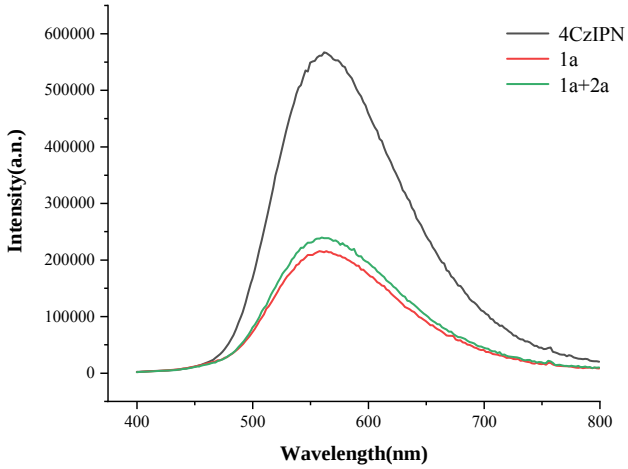


Figure S7. Luminescence quenching of 4CzIPN by **1a** and **2a**

3.4 Cyclic voltammetry study

Cyclic voltammetric investigations were performed on the ChenhuaCHI400C electrochemical workstation with the conventional three-electrode system. The measurements were conducted in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN. The solutions were kept under positive pressure of nitrogen. Cyclic voltammetry (CV) with the following settings: Scan Rates = 0.1 V/s, Sweep Segments = 10, Sample Interval = 0.001 V, Quiet Time = 2 sec. CV recording is based on the traditional IUPAC (positive anode current and negative cathode current).

Supporting electrolyte: $TBAPF_6$ was purchased from Energy Chemical and used without further purification. The concentration of electrolyte is 0.1 M.

Solvent: Anhydrous CH_3CN was purchased from Energy Chemical and exhausted via a nitrogen blast for 30 min before using.

Electrodes: The working electrode is a glassy carbon electrode (Φ3 mm, $7x10^{-6}$ cm^2). It was first polished with sandpaper in steps (3000 mesh–2000 mesh–1000 mesh); then with 1.0 μm, 0.3 μm, and 0.05 μm alumina powder until the surface of the

electrode is mirror-like, then, the electrodes are washed with distilled water and acetone before air drying. Saturated calomel electrode (SCE) was used as the reference electrode. Pt column (Φ1 mm x 5 mm) was used as the counter electrode.

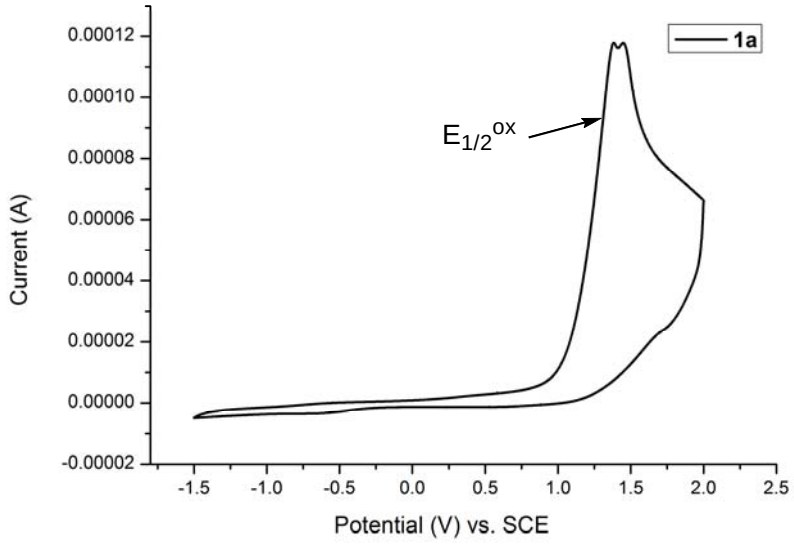


Figure S8. The CV experiment of **1a** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. $E_{1/2}^{ox}$ = +1.11 V SCE for **1a**.

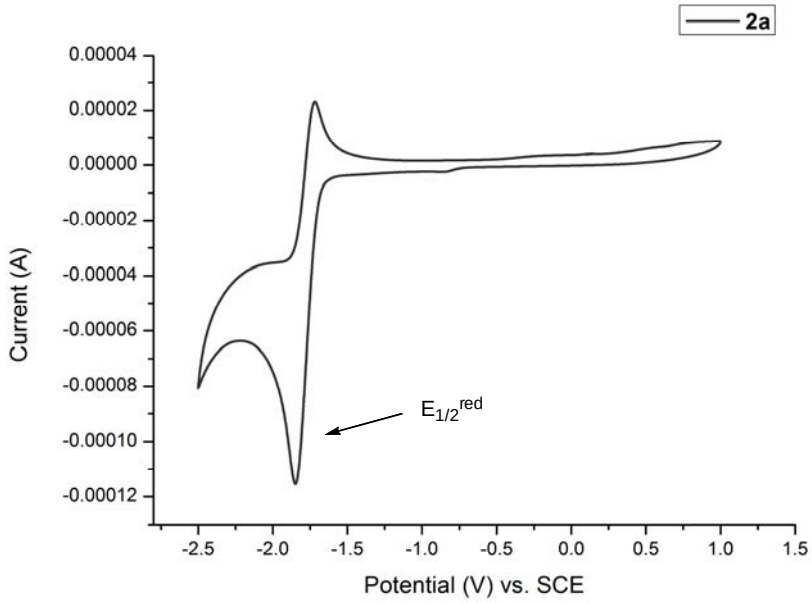


Figure S9. The CV experiment of **2a** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. $E_{1/2}^{red}$ = −1.8 V SCE for **2a**.

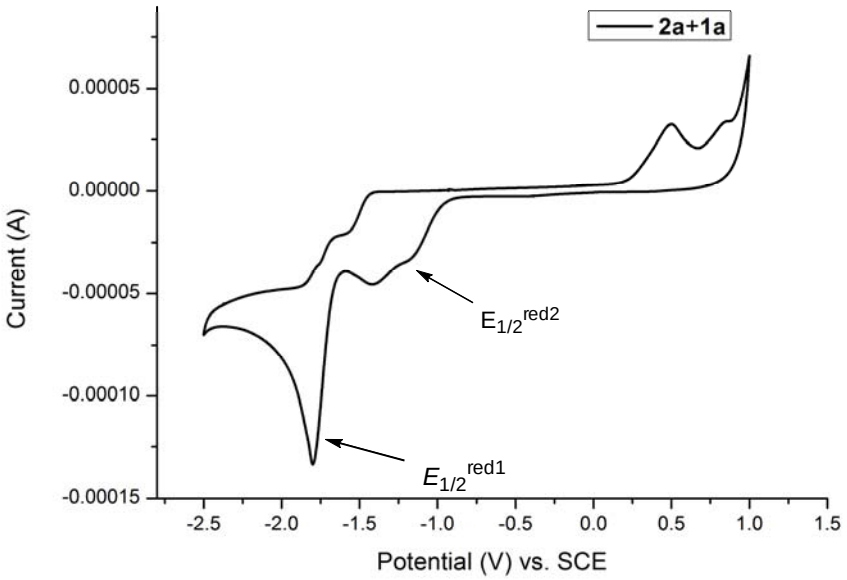


Figure S10. The CV experiment of **1a** (1.0×10^{-3} M) with **2a** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1a** was firstly oxidized and then **2a** was reduced, $E_{1/2}^{red1} = -1.8$ V SCE, $E_{1/2}^{red2} = -1.11$ V SCE.

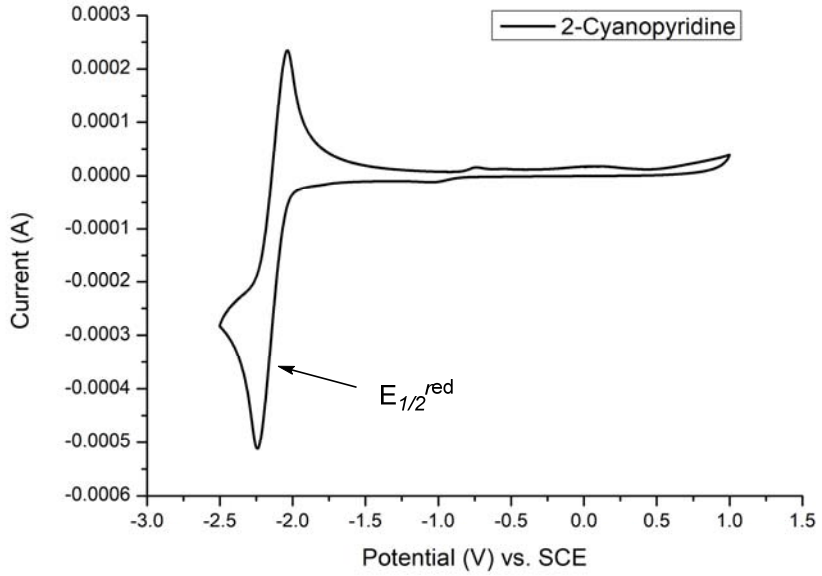


Figure S11. The CV experiment of 2-cyanopyridine **2q** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. $E_{1/2}^{red} = -2.06$ V SCE for **2q**.

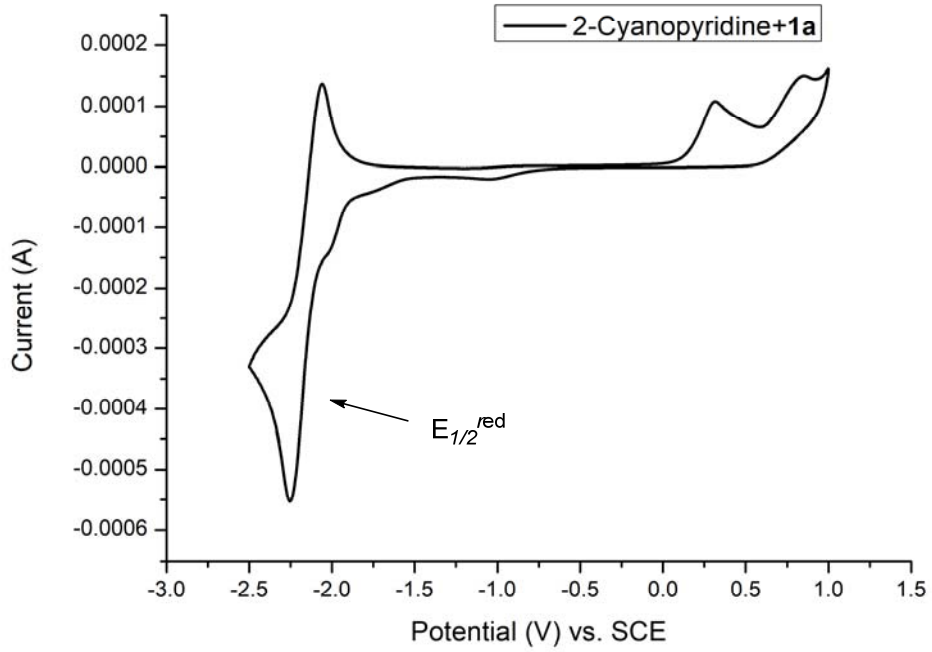


Figure S12. The CV experiment of 2-cyanopyridine **2q** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN in the presence of **1a,** plotting based on IUPAC. No new obvious reductive peak appeared in the CV spectra.

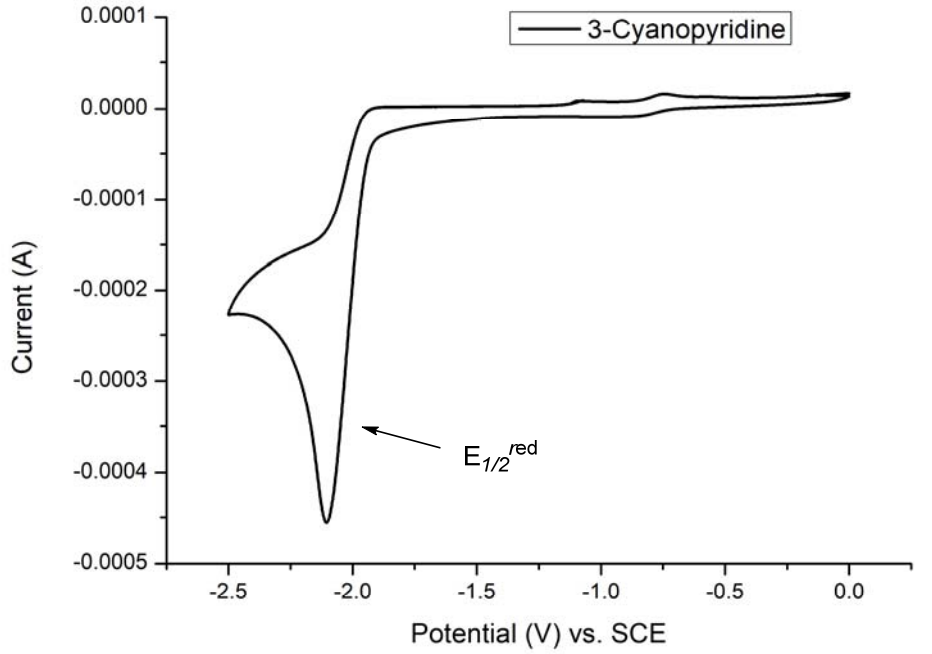


Figure S13. The CV experiment of 3-cyanopyridine **2r** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. $E_{1/2}^{red}$ = −2.04 V SCE for **2r**.

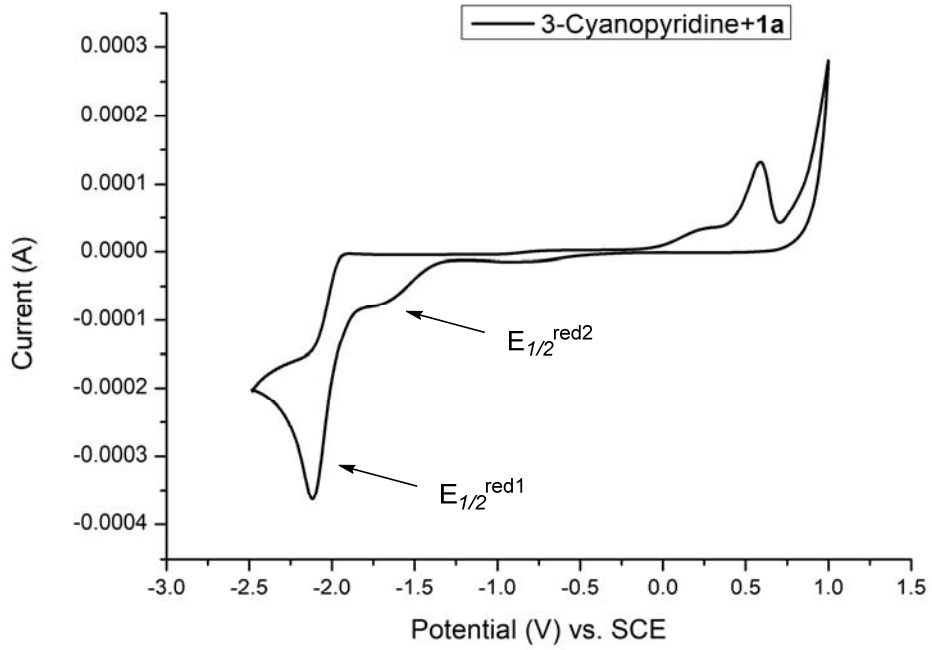


Figure S14. The CV experiment of 3-cyanopyridine **2r** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN in the presence of **1a,** plotting based on IUPAC. $E_{1/2}^{red1} = -2.04$ V SCE, $E_{1/2}^{red2} = -1.57$ V SCE.

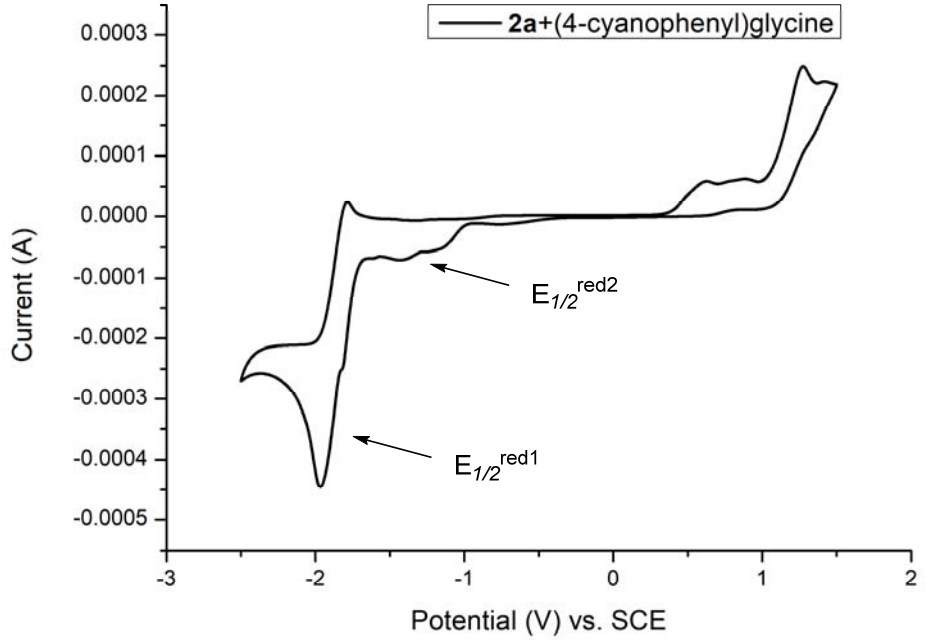


Figure S15. The CV experiment of (4-cyanophenyl)glycine **1v** (1.0×10^{-3} M) with **2a** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1v** was firstly oxidized and then **2a** was reduced, $E_{1/2}^{red1} = -1.81$ V SCE, $E_{1/2}^{red2} = -1.31$ V SCE.

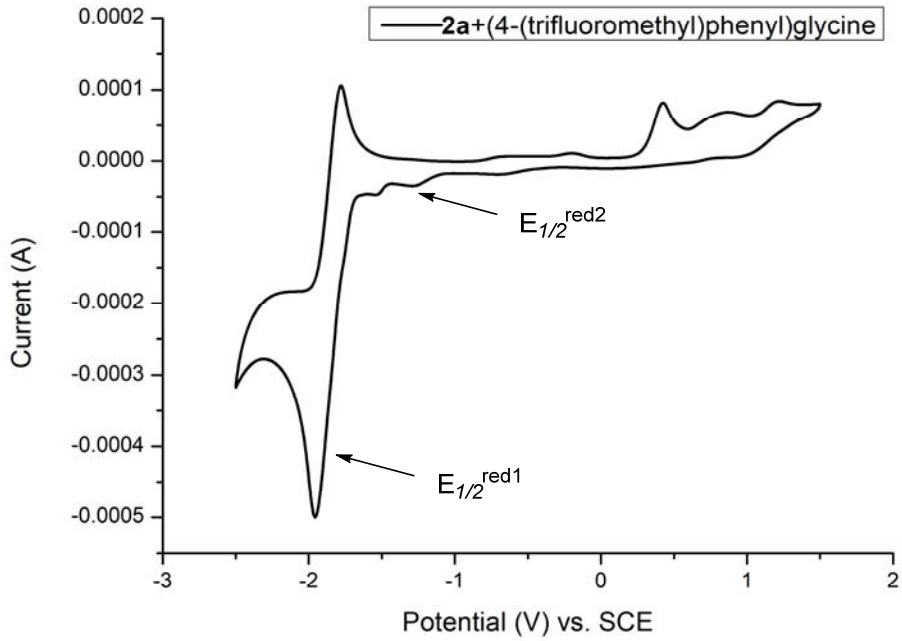


Figure S16. The CV experiment of (4-(trifluoromethyl)phenyl)glycine **1w** (1.0×10^{-3} M) with **2a** (1.0×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1w** was firstly oxidized and then **2a** was reduced, $E_{1/2}^{red1} = -1.8$V SCE, $E_{1/2}^{red2} = -1.28$ V SCE.

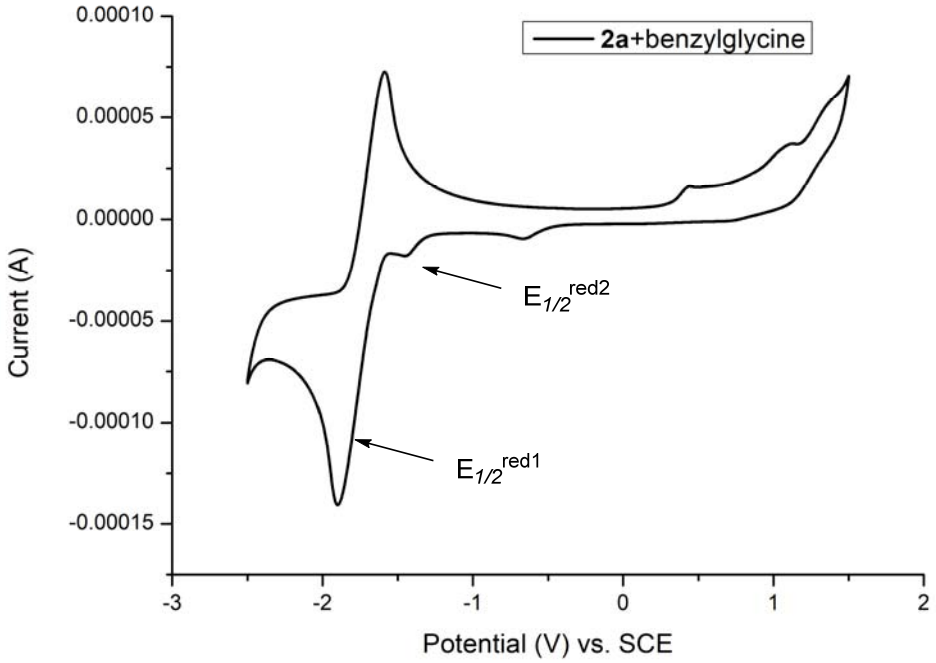


Figure S17. The CV experiment of benzylglycine **1x** (3×10^{-3} M) with **2a** (3×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1x** was firstly oxidized and then **2a** was reduced, $E_{1/2}^{red1} = -1.81$V SCE, $E_{1/2}^{red2} = -1.40$ V SCE.

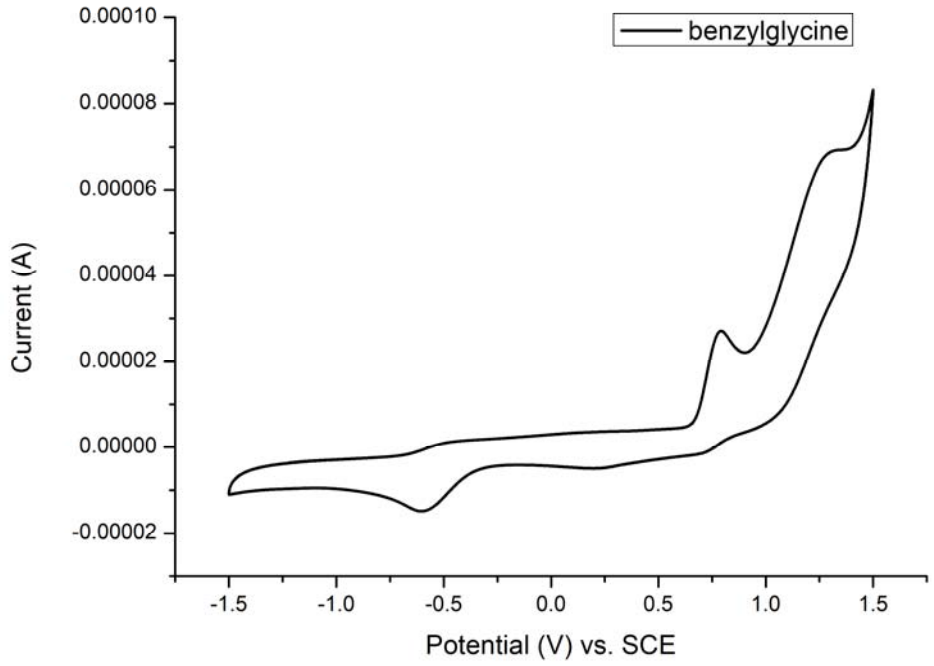


Figure S18. The CV experiment of benzylglycine **1x** (3×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC.

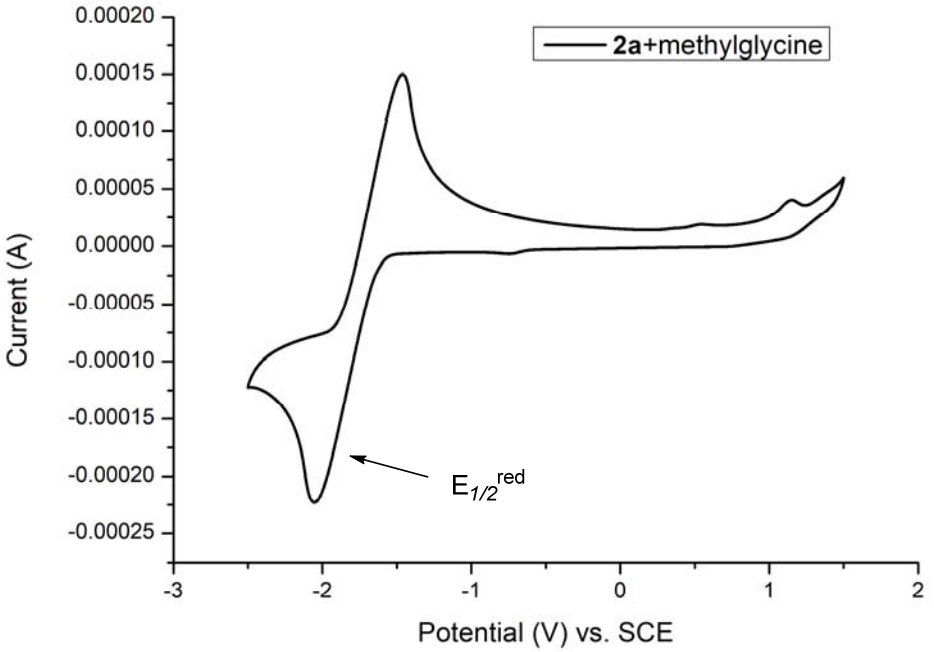


Figure S19. The CV experiment of benzylglycine **1y** (2×10^{-3} M) with **2a** (2×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1y** was firstly oxidized and then **2a** was reduced. No reductive peak shift was found.

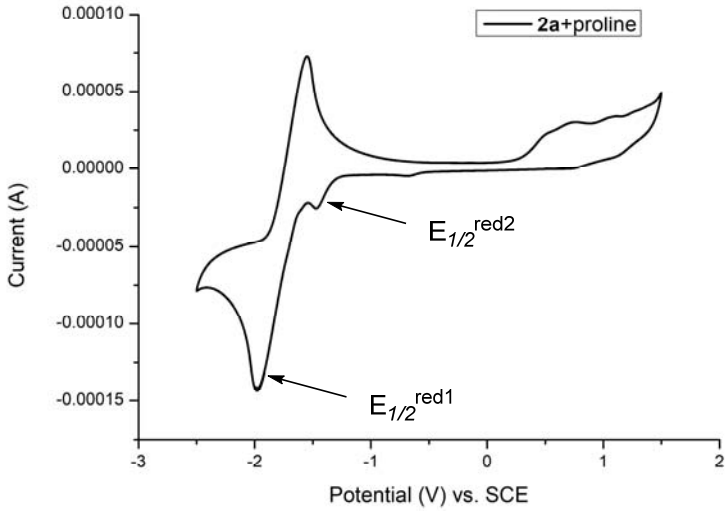


Figure S20. The CV experiment of proline **1z** (3×10^{-3} M) with **2a** (3×10^{-3} M) and NBu_4PF_6 (0.1 M) in degassed CH_3CN, plotting based on IUPAC. **1z** was firstly oxidized and then **2a** was reduced. $E_{1/2}^{red1}$ = −1.81V SCE, $E_{1/2}^{red2}$ = −1.41V SCE.

3.5 ^{1}HNMR of the mixture of *N*-phenyl glycine 1a and 4-cyanopyridine 2a

The mixture of *N*-phenyl glycine **1a** and 4-cyanopyridine **2a** was tested by ^{1}HNMR. The chemical shift of **1a** has decreased about 0.025 ppm. The chemical shift of **2a** has increased about 0.02 ppm. The N−H signal of **1a** shifted from 6.34 to 7.37 ppm after the addition of **2a**. However, no obvious N-H signal shift was observed in the ^{1}H NMR spectrum of the mixture (**1a**+**2q**).

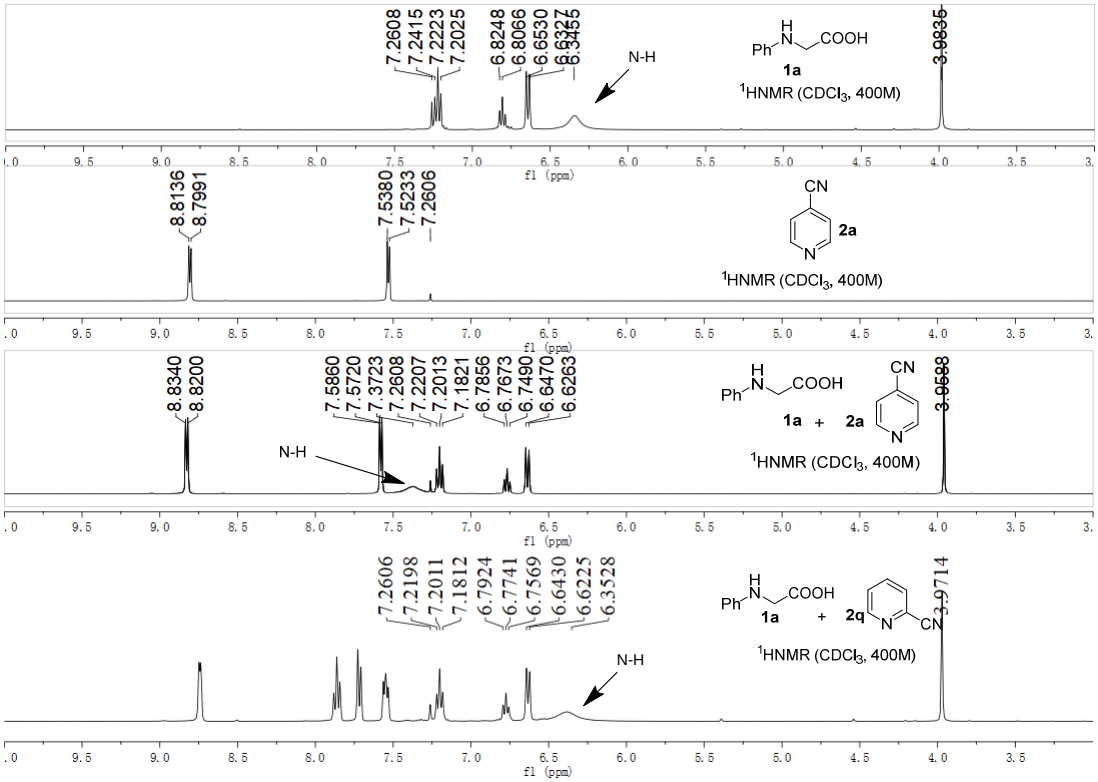


Figure S21. The ^{1}HNMR spectra of the mixture of **1a** and **2a** or **2q**

3.6 Evidence for no 4CzIPN photo-conversion by ^{1}H NMR Spectra

To a dry NMR tube, 3.2 mg of 4CzIPN added. Then 0.6 mL DMSO-d_6 was added. a) The solution was bubbled 5 minutes with nitrogen at room temperature. The ^{1}H NMR spectrum was recorded. b) Then *N*-phenyl glycine **1a** (0.1 mmol, 15.1 mg) was added. The solution was bubbled 5 minutes with nitrogen at room temperature. The ^{1}H NMR spectrum was recorded. c) After the solution (4CzIPN+**1a**+DMSO-d_6) was irradiated with 6 W blue light for 2 hours, the ^{1}H NMR spectrum was recorded.

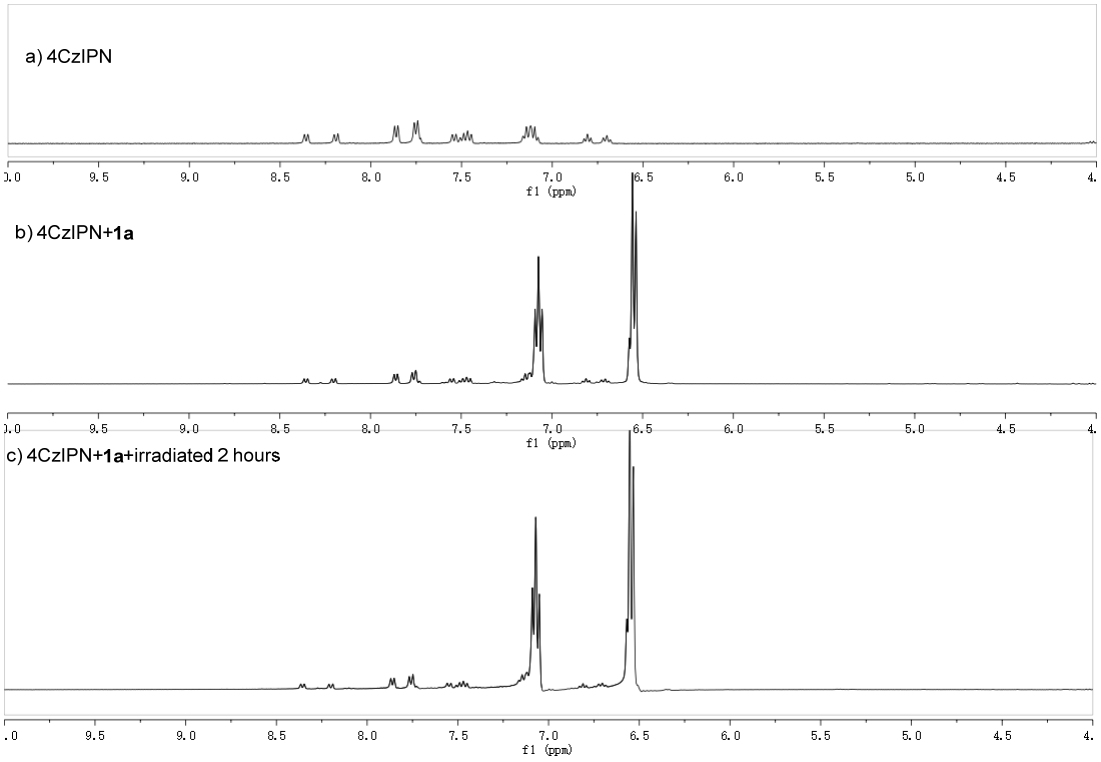
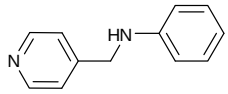


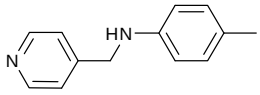
Figure S22. Evidence for no 4CzIPN photo-conversion by ^{1}H NMR measurement

4. Characterization Data for the Products



(CAS: 3034-32-0)

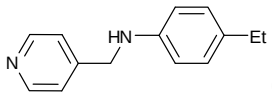
N-(pyridin-4-ylmethyl)aniline (**3aa**, 31.3 mg, 85%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.28 (d, J = 5.9 Hz, 2H), 7.19-7.15 (m, 2H), 6.74 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 4.38 (s, 2H), 4.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.0, 147.4, 129.4, 122.1, 118.1, 112.9, 47.1.



(CAS: 16552-48-0)

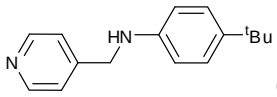
4-methyl-N-(pyridin-4-ylmethyl)aniline (**3ba**, 28.1 mg, 71%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H),

6.98 (t, J = 8.0 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 4.35 (s, 2H), 4.12 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.2, 145.1, 129.9, 127.3, 122.1, 112.9, 47.4, 20.4.



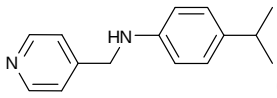
(CAS: 27048-23-3)

4-ethyl-N-(pyridin-4-ylmethyl)aniline (**3ca**, 32.3 mg, 76%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 8.5 Hz, 2H), 4.35 (s, 2H), 4.20 (s, 1H), 2.54 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.3, 145.4, 133.9, 128.7, 122.1, 112.9, 47.4, 27.9, 15.9.



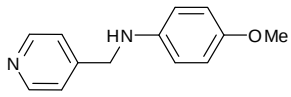
(CAS: 847735-93-7)

4-(tert-butyl)-N-(pyridin-4-ylmethyl)aniline (**3da**, 31.7 mg, 66%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.30 (d, J = 6.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.54 (d, J = 8.7 Hz, 2H), 4.36 (s, 2H), 4.17 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.4, 145.2, 140.9, 126.1, 122.2, 112.6, 47.4, 33.9, 31.5.



(CAS: 1019576-41-0)

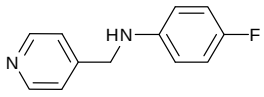
4-isopropyl-N-(pyridin-4-ylmethyl)aniline (**3ea**, 29.4 mg, 65%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.30 (d, J = 5.7 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 4.35 (s, 2H), 4.18 (s, 1H), 2.84-2.77 (m, 1H), 1.20 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.3, 145.5, 138.6, 127.2, 122.1, 112.9, 47.4, 33.2, 24.2.



(CAS: 16552-49-1)

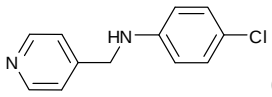
4-methoxy-N-(pyridin-4-ylmethyl)aniline (**3fa**, 29.8 mg, 70%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 1/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0 Hz, 2H), 7.28 (d, J = 5.9 Hz, 2H), 6.75 (d, J = 8.9 Hz, 2H), 6.53 (d, J = 8.9 Hz, 2H), 4.31 (s, 2H), 3.96 (s, 1H), 3.72 (s,

4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 149.9, 149.3, 141.6, 122.2, 114.9, 114.1, 55.8, 47.9.



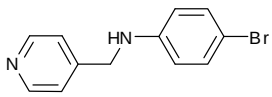
(CAS: 193339-01-4)

4-fluoro-N-(pyridin-4-ylmethyl)aniline (**3ga**, 22.2 mg, 55%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 6.0 Hz, 2H), 7.28 (d, J = 5.9 Hz, 2H), 6.87 (t, J = 8.6 Hz, 2H), 6.52-6.48 (m, 2H), 4.34 (s, 2H), 4.11 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (d, $J_{C\text{-}F}$ = 236.4 Hz), 149.9, 148.8, 143.7 (d, $J_{C\text{-}F}$ = 1.9 Hz), 122.1, 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 113.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 47.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -127.2.



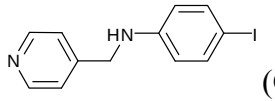
(CAS: 29083-47-4)

4-chloro-N-(pyridin-4-ylmethyl)aniline (**3ha**, 29.7 mg, 68%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 5.8 Hz, 2H), 7.26 (d, J = 5.2 Hz, 2H), 7.09 (d, J = 8.9 Hz, 2H), 6.48 (d, J = 8.9 Hz, 2H), 4.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.6, 145.9, 129.2, 127.3, 122.6, 122.0, 113.9, 47.0.



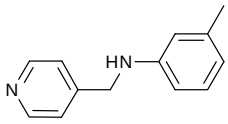
(CAS: 166110-81-2)

4-bromo-N-(pyridin-4-ylmethyl)aniline (**3ia**, 29.9 mg, 57%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.26-7.21 (m, 4H), 6.44 (d, J = 8.9 Hz, 2H), 4.39 (s, 1H), 4.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 148.4, 146.4, 132.0, 121.9, 114.4, 109.6, 46.9.

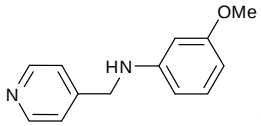


(CAS: 1018075-45-0)

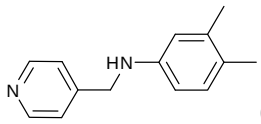
4-iodo-N-(pyridin-4-ylmethyl)aniline (**3ja**, 31.6 mg, 51%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 6.0 Hz, 2H), 6.34 (d, J = 8.8 Hz, 2H), 4.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 148.4, 146.9, 137.9, 121.9, 115.1, 78.8, 46.8.


(CAS: 355395-76-5)

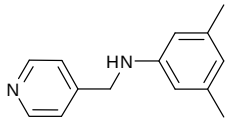
3-methyl-N-(pyridin-4-ylmethyl)aniline (**3ka**, 26.1 mg, 66%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 5.8 Hz, 2H), 7.06 (t, J = 7.7 Hz, 1H), 6.57 (d, J = 7.5 Hz, 1H), 6.41 (s, 1H), 6.38 (d, J = 8.0 Hz, 1H), 4.36 (s, 2H), 4.22 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.2, 147.5, 139.2, 129.3, 122.1, 119.0, 113.7, 109.9, 47.1, 21.7.


(CAS: 1021084-69-4)

3-methoxy-N-(pyridin-4-ylmethyl)aniline (**3la**, 24 mg, 56%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 1/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 6.0 Hz, 2H), 7.27 (d, J = 6.0 Hz, 2H), 7.07 (t, J = 8.1 Hz, 1H), 6.29 (dd, J = 8.1, 2.0 Hz, 1H), 6.20 (dd, J = 8.0, 1.8 Hz, 1H), 6.11 (d, J = 2.3 Hz, 1H), 4.35 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 149.9, 148.9, 148.9, 130.2, 122.1, 105.9, 102.9, 99.0, 55.1, 47.0.

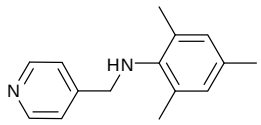

(CAS: 332108-35-7)

3,4-dimethyl-N-(pyridin-4-ylmethyl)aniline (**3ma**, 25.9 mg, 61%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.6 Hz, 2H), 7.29 (d, J = 4.8 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.42 (s, 1H), 6.33 (d, J = 8.0 Hz, 1H), 4.35 (s, 2H), 4.07 (s, 1H), 2.17 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.4, 147.6, 137.5, 126.2, 122.1, 114.7, 110.2, 47.4, 20.1, 18.7.

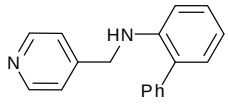

(CAS: 331970-83-3)

3,5-dimethyl-N-(pyridin-4-ylmethyl)aniline (**3na**, 27.6 mg, 65%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 6.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 2H), 6.41 (s, 1H), 6.22 (s, 2H), 4.35 (s, 2H), 4.18 (s, 1H), 2.22 (s, 6H); ^{13}C NMR (101

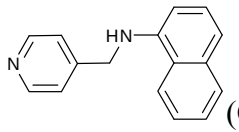
MHz, $CDCl_3$) δ 149.8, 149.2, 147.5, 138.9, 121.9, 119.9, 110.6, 46.9, 21.4.



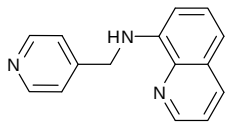
2,4,6-trimethyl-N-(pyridin-4-ylmethyl)aniline (**3oa**, 24.9 mg, 55%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 7.33 (d, J = 3.8 Hz, 2H), 6.85 (s, 2H), 4.08 (s, 2H), 2.94 (s, 1H), 2.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.4, 142.6, 132.2, 130.2, 129.6, 122.8, 51.7, 20.6, 18.2; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2$ 227.1543; Found 227.1539.


(CAS: 1019543-05-5)

N-(pyridin-4-ylmethyl)-[1,1'-biphenyl]-2-amine (**3pa**, 30.2 mg, 58%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 6.0 Hz, 2H), 7.39-7.38 (m, 4H), 7.32-7.26 (m, 1H), 7.15 (d, J = 5.8 Hz, 2H), 7.08-7.04 (m, 2H), 6.73-6.69 (m, 1H), 6.38 (d, J = 8.0 Hz, 1H), 4.42 (s, 1H), 4.25 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.1, 144.2, 139.2, 130.4, 129.4, 129.1, 128.7, 127.9, 127.5, 121.9, 117.7, 110.6, 47.0.

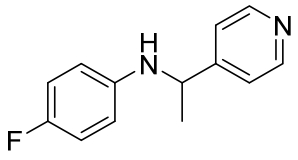

(CAS: 351992-06-8)

N-(pyridin-4-ylmethyl)naphthalen-1-amine (**3qa**, 30.9 mg, 66%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 6.0 Hz, 2H), 7.89-7.87 (m, 1H), 7.84-7.81 (m, 1H), 7.52-7.46 (m, 2H), 7.34 (d, J = 5.8 Hz, 2H), 7.28-7.26 (m, 2H), 6.47-6.42 (m, 1H), 4.93 (s, 1H), 4.56 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 148.6, 142.4, 134.3, 128.8, 126.4, 125.9, 125.1, 123.3, 122.2, 119.8, 118.2, 105.1, 47.2.


(CAS: 1020949-97-6)

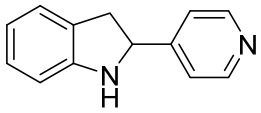
N-(pyridin-4-ylmethyl)quinolin-8-amine (**3ra**, 24.9 mg, 53%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 1.7 Hz, 1H), 8.54 (d, J = 6.1 Hz, 2H),

8.08 (dd, J = 8.3, 1.7 Hz, 1H), 7.42-7.39 (m, 1H), 7.34 (d, J = 6.0 Hz, 2H), 7.29 (t, J = 7.9 Hz, 1H), 7.09 (dd, J = 8.2, 1.0 Hz, 1H), 6.75 (s, 1H), 6.48 (d, J = 7.6 Hz, 1H), 4.60 (d, J = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 148.8, 147.2, 143.9, 138.1, 136.2, 128.6, 127.6, 122.1, 121.6, 114.9, 105.3, 46.6.



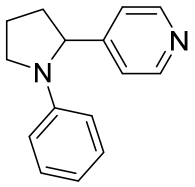
(CAS: 152127-32-7)

4-fluoro-N-(1-(pyridin-4-yl)ethyl)aniline (**3sa**, 13.4 mg, 31%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 4.5 Hz, 2H), 7.28 (d, J = 5.0 Hz, 2H), 6.69 (t, J = 8.6 Hz, 2H), 6.39-6.35 (m, 2H), 4.38 (q, J = 6.8 Hz, 1H), 3.97 (s, 1H), 1.50 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9 (d, $J_{C\text{-}F}$ = 236.5 Hz), 154.3, 150.1, 142.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 121.2, 115.6 (d, $J_{C\text{-}F}$ = 22.4 Hz), 114.1 (d, $J_{C\text{-}F}$ = 7.4 Hz), 53.3, 24.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -127.5.



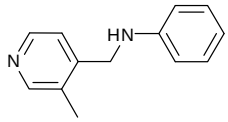
(CAS: 595548-63-3)

2-(pyridin-4-yl)indoline (**3ta**, 9.0 mg, 23%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 5.8 Hz, 2H), 7.35 (d, J = 5.8 Hz, 2H), 7.09-7.07 (m, 2H), 6.76 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.95 (t, J = 9.2 Hz, 1H), 4.20 (s, 1H), 3.53-3.47 (m, 1H), 2.95-2.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 150.6, 150.0, 127.8, 127.3, 124.7, 121.4, 119.3, 109.1, 62.3, 39.2.



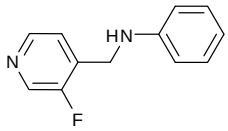
(CAS: 1352088-26-6)

4-(1-phenylpyrrolidin-2-yl)pyridine (**3ua**, 12.1 mg, 27%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 7.18-1.44 (m, 4H), 6.68 (t, J = 7.1 Hz, 1H), 6.45 (d, J = 7.8 Hz, 2H), 4.68 (t, J = 8.6 Hz, 1H), 3.73-3.71 (m, 1H), 3.45-3.39 (m, 1H), 2.45-2.39 (m, 1H), 2.01-1.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 149.9, 146.8, 129.2, 121.3, 116.5, 112.4, 62.1, 49.2, 35.6, 23.2.



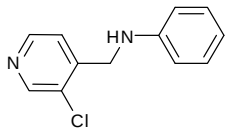
(CAS: 1880363-75-6)

N-((3-methylpyridin-4-yl)methyl)aniline (**3ab**, 25 mg, 63%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.7 Hz, 2H), 7.27 (d, J = 5.0 Hz, 1H), 7.20-7.16 (m, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.6 Hz, 2H), 4.31 (s, 2H), 4.13 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 147.9, 147.6, 146.4, 130.9, 129.4, 121.5, 118.0, 112.8, 45.1, 15.8.



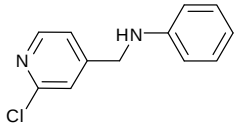
(CAS: 1477544-73-2)

N-((3-fluoropyridin-4-yl)methyl)aniline (**3ac**, 22.2 mg, 55%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 1.6 Hz, 1H), 8.33 (d, J = 4.8 Hz, 1H), 7.35 (d, J = 5.7 Hz, 1H), 7.20-7.16 (m, 2H), 6.76 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.7 Hz, 2H), 4.47 (s, 2H), 4.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (d, $J_{C\text{-}F}$ = 255.9 Hz), 147.1, 146.0 (d, $J_{C\text{-}F}$ = 5.2 Hz), 137.6 (d, $J_{C\text{-}F}$ = 23.5 Hz), 135.6 (d, $J_{C\text{-}F}$ = 12.1 Hz), 129.4, 123.1 (d, $J_{C\text{-}F}$ = 1.7 Hz), 118.3, 112.8, 40.9 (d, $J_{C\text{-}F}$ = 4.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -133.1.



(CAS: 1522712-20-4)

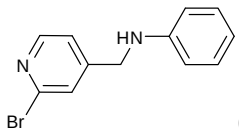
N-((3-chloropyridin-4-yl)methyl)aniline (**3ad**, 24.9 mg, 57%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.40 (d, J = 5.0 Hz, 1H), 7.35 (d, J = 4.8 Hz, 1H), 7.20-7.16 (m, 2H), 6.76 (t, J = 7.4 Hz, 1H), 6.55 (d, J = 7.6 Hz, 2H), 4.46 (s, 2H), 4.29 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 148.1, 147.0, 146.1, 130.8, 129.4, 122.8, 118.3, 112.8, 45.0.



(CAS: 2018446-00-7)

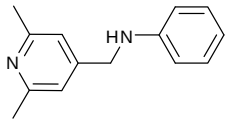
N-((2-chloropyridin-4-yl)methyl)aniline (**3ae**, 16.6 mg, 38%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 5/1, v/v) gave colorless

oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 5.1 Hz, 1H), 7.35 (s, 1H), 7.23-7.16 (m, 3H), 6.76 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.8 Hz, 2H), 4.38 (s, 2H), 4.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 152.0, 149.8, 147.1, 129.4, 122.4, 120.8, 118.4, 112.9, 46.8.

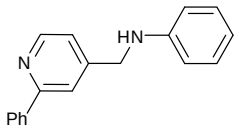


(CAS: 1780955-02-3)

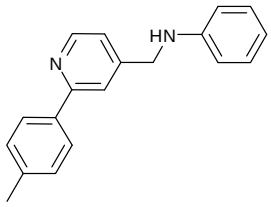
N-((2-bromopyridin-4-yl)methyl)aniline (**3af**, 16.3 mg, 31%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 5/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 5.0 Hz, 1H), 7.50 (s, 1H), 7.25 (d, J = 4.8 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 6.76 (d, J = 7.3 Hz, 1H), 6.55 (d, J = 8.3 Hz, 2H), 4.36 (s, 2H), 4.27 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 150.3, 147.0, 142.7, 138.7, 129.4, 126.2, 121.2, 118.4, 112.9, 46.7.



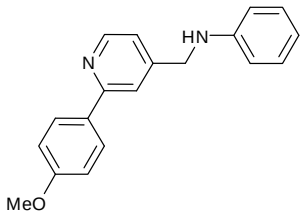
N-((2,6-dimethylpyridin-4-yl)methyl)aniline (**3ag,** 32.7 mg, 77%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.15 (m, 2H), 6.96 (s, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H), 4.27 (s, 2H), 4.19(s, 1H), 2.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 149.5, 147.7, 129.3, 118.7, 117.9, 112.9, 47.2, 24.5; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2$ 213.1386; Found 213.1379.



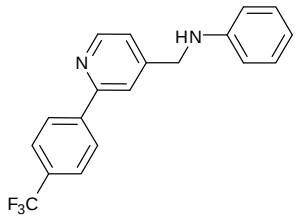
N-((2-phenylpyridin-4-yl)methyl)aniline (**3ah**, 44.8 mg, 86%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 5.0 Hz, 1H), 7.99 (d, J = 7.0 Hz, 1H), 7.73 (s, 1H), 7.50-7.41 (m, 3H), 7.24-7.18 (m, 3H), 6.77 (d, J = 7.3 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 4.40 (s, 2H), 4.32 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 149.9, 147.6, 139.3, 129.4, 129.1, 128.8, 127.0, 120.7, 118.9, 118.1, 112.9, 47.4; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2$ 261.1386; Found 261.1376.



N-((2-(p-tolyl)pyridin-4-yl)methyl)aniline (**3ai**, 40.1 mg, 73%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 5.0 Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.69 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.22-7.17 (m, 3H), 6.76 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 4.39 (s, 2H), 4.30 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 149.8, 149.7, 147.6, 139.1, 136.5, 129.5, 129.4, 126.9, 120.4, 118.6, 118.1, 112.9, 47.4, 21.4; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2$ 275.1543; Found 275.1542.

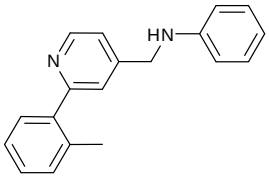


N-((2-(4-methoxyphenyl)pyridin-4-yl)methyl)aniline (**3aj**, 44.1 mg, 76%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 5.0 Hz, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.66 (s, 1H), 7.18 (t, J = 7.2 Hz, 3H), 6.98 (d, J = 8.8 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 4.39 (s, 2H), 4.28 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 157.4, 149.8, 149.7, 147.6, 131.9, 129.4, 128.3, 120.0, 118.2, 118.1, 114.1, 112.9, 55.4, 47.5; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2O$ 291.1492; Found 291.1494.

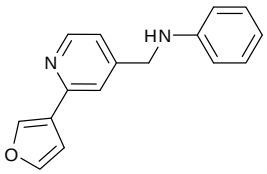


N-((2-(4-(trifluoromethyl)phenyl)pyridin-4-yl)methyl)aniline (**3ak**, 40 mg, 61%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 5.0 Hz, 1H), 8.08 (d, J = 8.2 Hz, 2H), 7.77 (s, 1H), 7.71 (t, J = 8.2 Hz, 2H), 7.31 (d, J = 4.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 6.77 (d, J = 7.3 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 4.45 (s, 2H), 4.30 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 150.3, 150.1, 147.4, 142.6, 142.6,

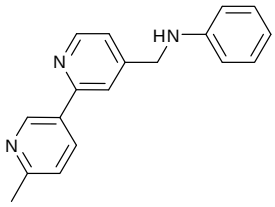
130.8 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.4, 127.3, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 273.1 Hz), 121.4, 119.2, 118.3, 112.9, 55.4, 47.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{16}F_3N_2$ 329.1260; Found 329.1233.



N-((2-(o-tolyl)pyridin-4-yl)methyl)aniline (**3al**, 27.9 mg, 51%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 5/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.1 Hz, 1H), 7.38-7.36 (m, 2H), 7.30-7.23 (m, 4H), 7.19-7.15 (m, 2H), 6.73 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 4.41 (s, 2H), 4.25 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 149.4, 149.2, 147.5, 140.3, 135.8, 130.8, 129.6, 129.4, 128.3, 125.9, 122.4, 120.1, 118.1, 112.9, 47.2, 20.3; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2$ 275.1543; Found 275.1540.

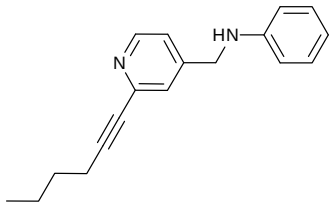


N-((2-(furan-3-yl)pyridin-4-yl)methyl)aniline (**3am**, 31 mg, 62%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 4/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 5.0 Hz, 1H), 8.02 (s, 1H), 7.48 (t, J = 1.7 Hz, 1H), 7.46 (s, 1H), 7.20-7.15 (m, 3H), 6.88 (d, J = 1.1 Hz, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.6 Hz, 2H), 4.38 (s, 2H), 4.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 149.9, 149.7, 147.5, 143.9, 141.4, 129.4, 126.9, 120.3, 118.4, 118.1, 112.9, 108.7, 47.3; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O$ 251.1179; Found 251.1172.

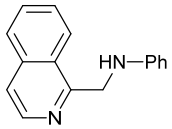


N-((6'-methyl-[2,3'-bipyridin]-4-yl)methyl)aniline (**3an**, 30.8 mg, 56%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 1/2, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 2.1 Hz, 1H), 8.65 (d, J = 5.0

Hz, 1H), 8.21 (dd, J = 8.1, 2.3 Hz, 1H), 7.73 (s, 1H), 7.30-7.28 (m, 2H), 7.22-7.18 (m, 2H), 6.77 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 4.46 (s, 3H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 155.3, 150.2, 150.1, 147.5, 147.4, 134.8, 132.1, 129.4, 123.3, 121.0, 118.6, 118.1, 112.9, 47.3, 24.3; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3$ 276.1495; Found 276.1503.



N-((2-(hex-1-yn-1-yl)pyridin-4-yl)methyl)aniline (**3ao**, 42.4 mg, 80%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 5/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 5.1 Hz, 1H), 7.38 (s, 1H), 7.18-7.15 (m, 3H), 6.74 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.6 Hz, 2H), 4.33 (s, 3H), 4.25 (s, 1H), 2.42 (t, J = 7.0 Hz, 2H), 1.64-1.56 (m, 2H), 1.52-1.42 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.3, 147.4, 144.1, 129.4, 124.9, 120.7, 118.1, 112.9, 91.2, 80.4, 46.9, 30.4, 22.1, 19.1, 13.7; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{21}N_2$ 265.1699; Found 265.1697.

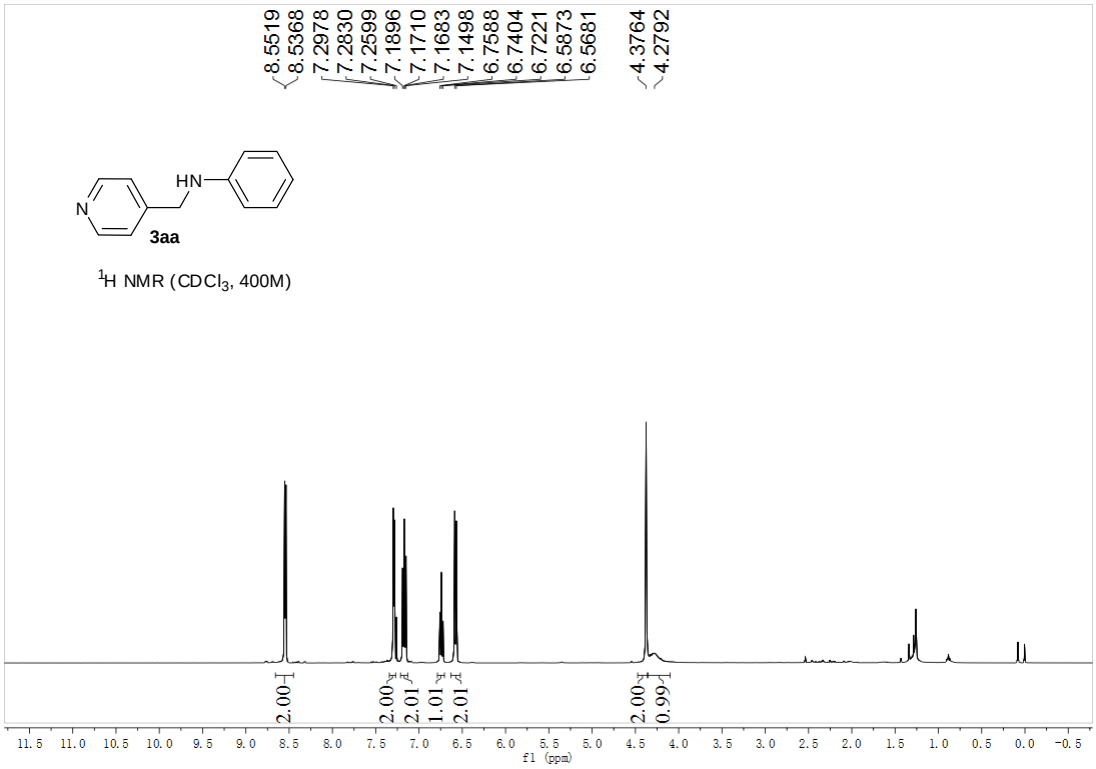


N-(isoquinolin-1-ylmethyl)aniline (**3ap**, 29.5 mg, 63%). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 2/1, v/v) gave colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.65 (s, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 2H), 4.70 (s, 2H), 3.96 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 147.9, 142.8, 134.5, 130.9, 129.4, 128.5, 128.4, 127.7, 127.4, 123.0, 118.1, 112.9, 44.1; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2$ 235.1230; Found 235.1225.

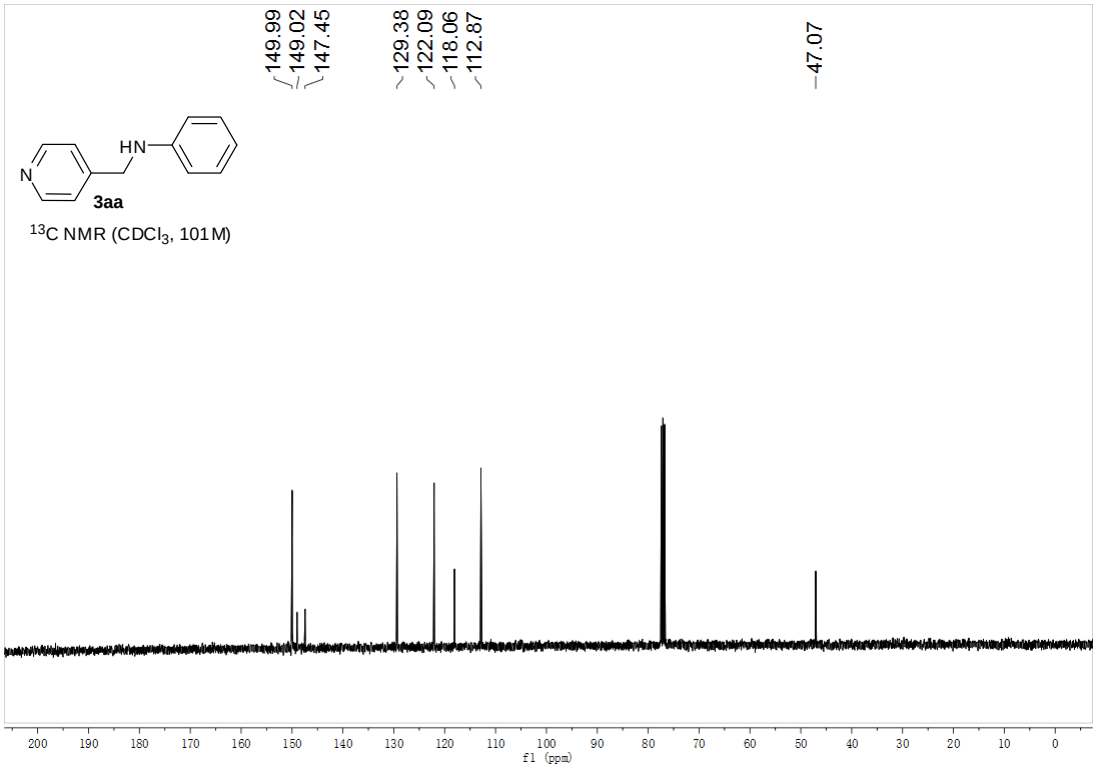
5. References

1. L. Chen, Y.-D. Li, Y. Lv, Z.-H. Lu and S.-J. Yan, *Chem. Commun.,* 2022, **58**, 10194.
2. E. Bergamaschi, V. J. Mayerhofe and C. J. Teskey, *ACS Catal.,* 2022, **12**, 14806.

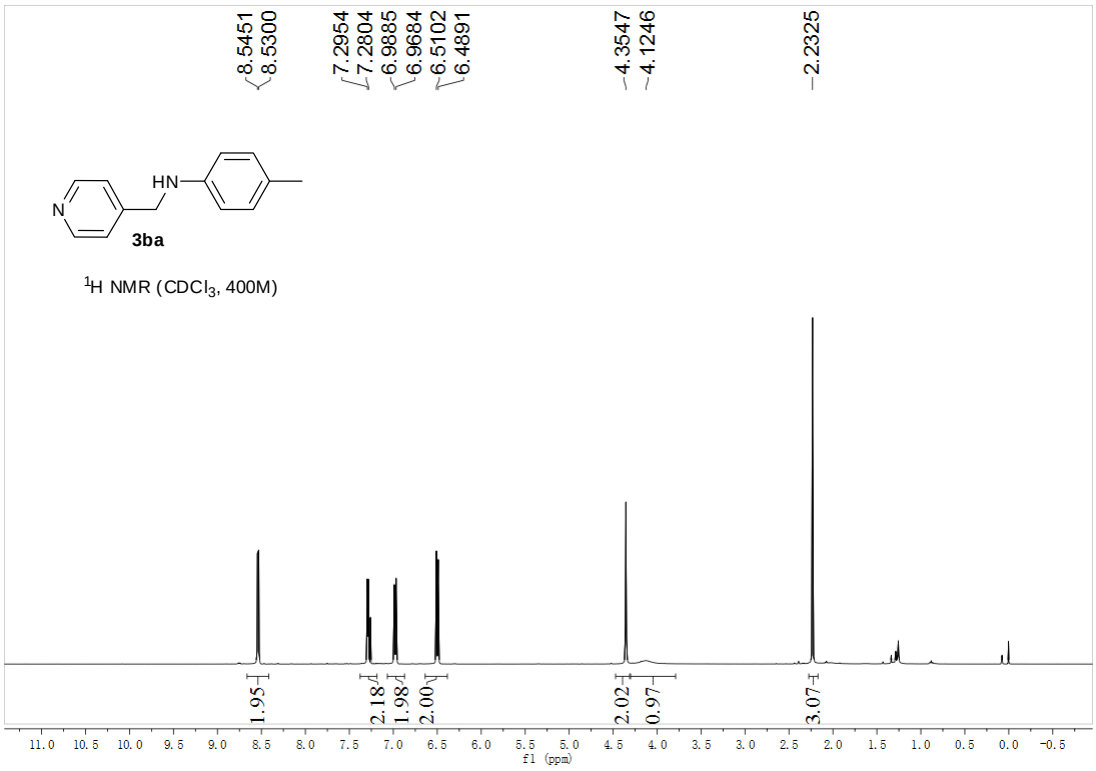
6. Copies of the ^{1}H NMR and ^{13}C NMR Spectra



^{1}H NMR ($CDCl_3$, 400M)



^{13}C NMR ($CDCl_3$, 101M)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HN
N
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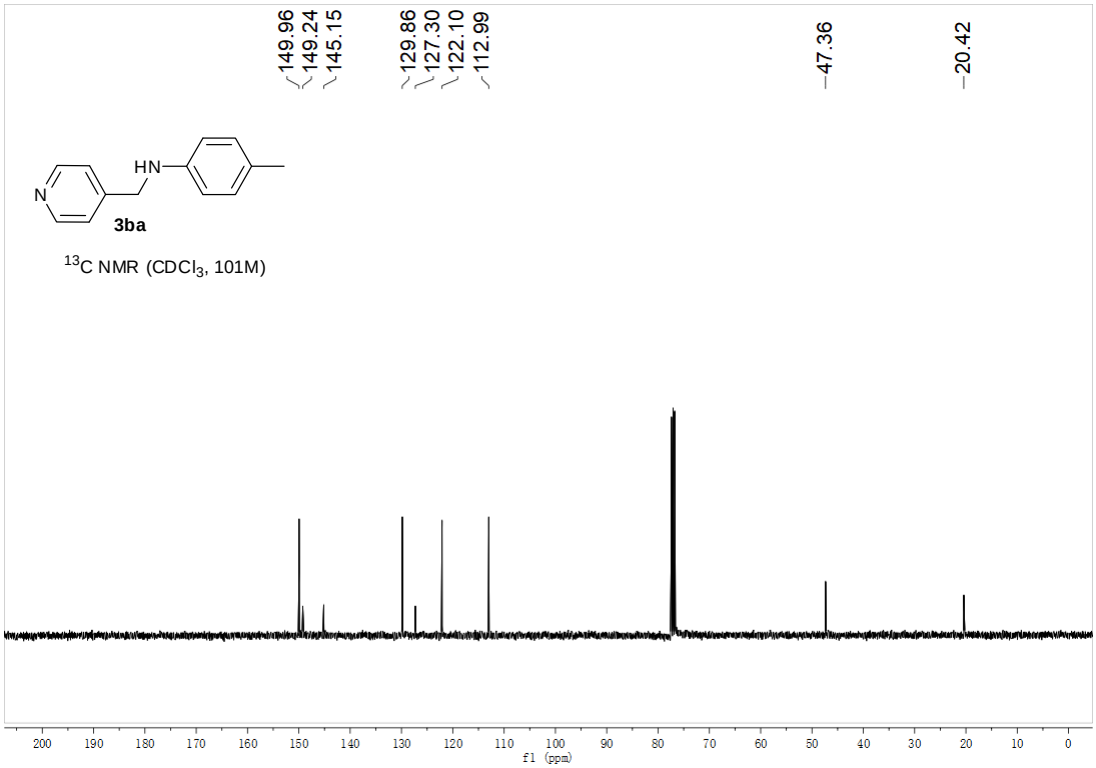
2.02
0.97
3.07
f1 (ppm)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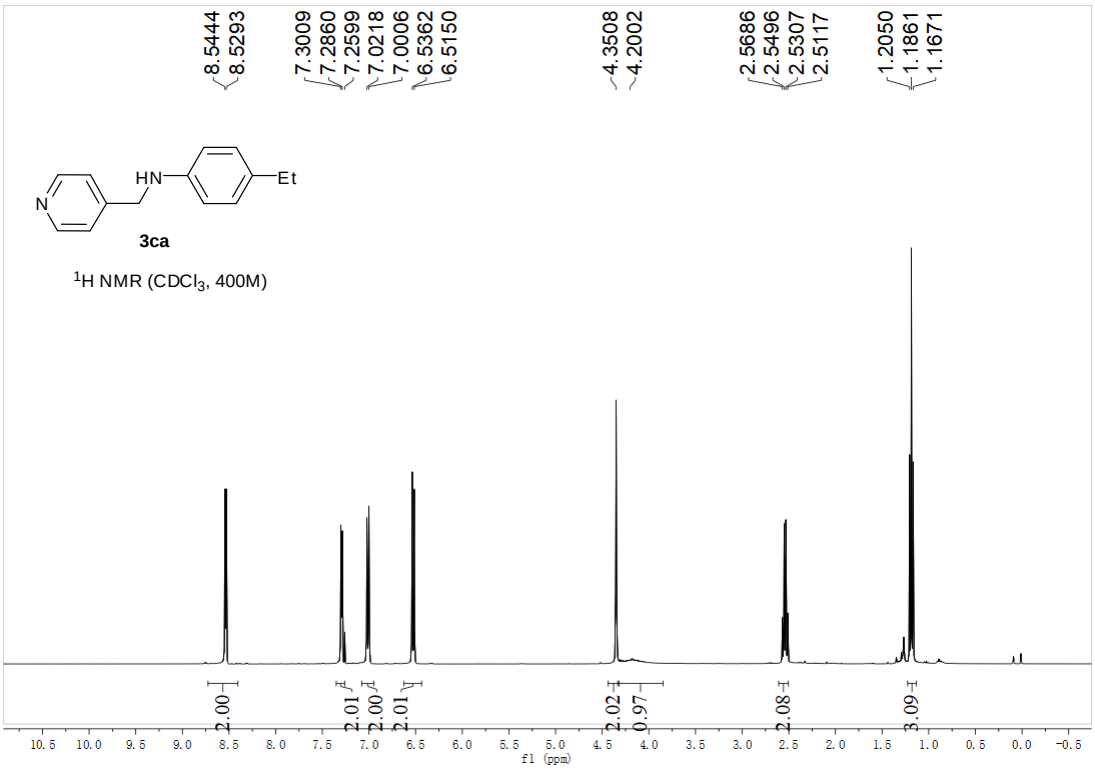
N
3ba
13C NMR (CDCl3, 101M)
f1 (ppm)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Et
N
3ca
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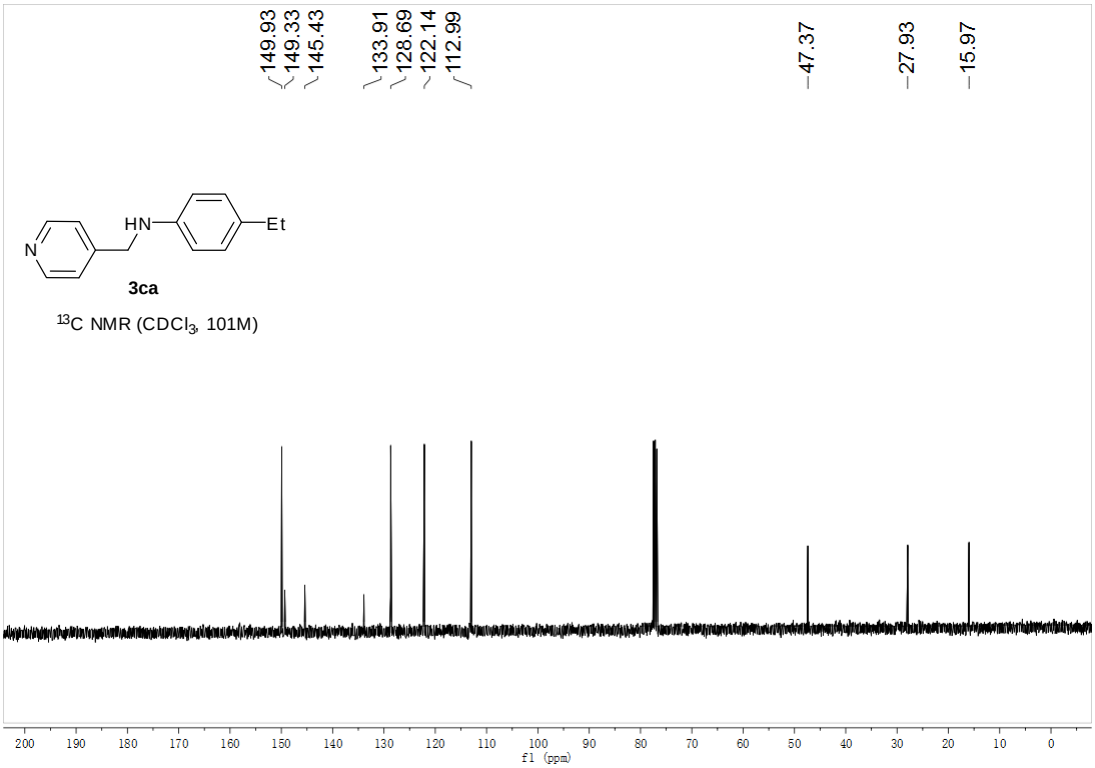
f1 (ppm)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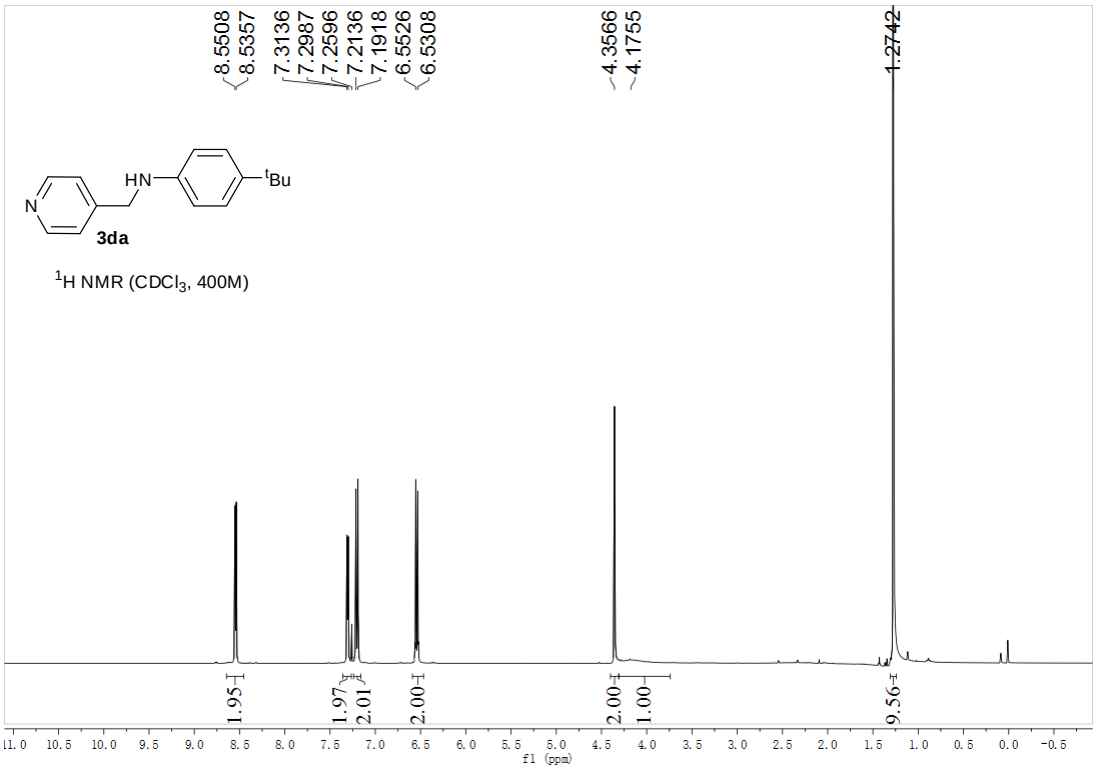
f1 (ppm)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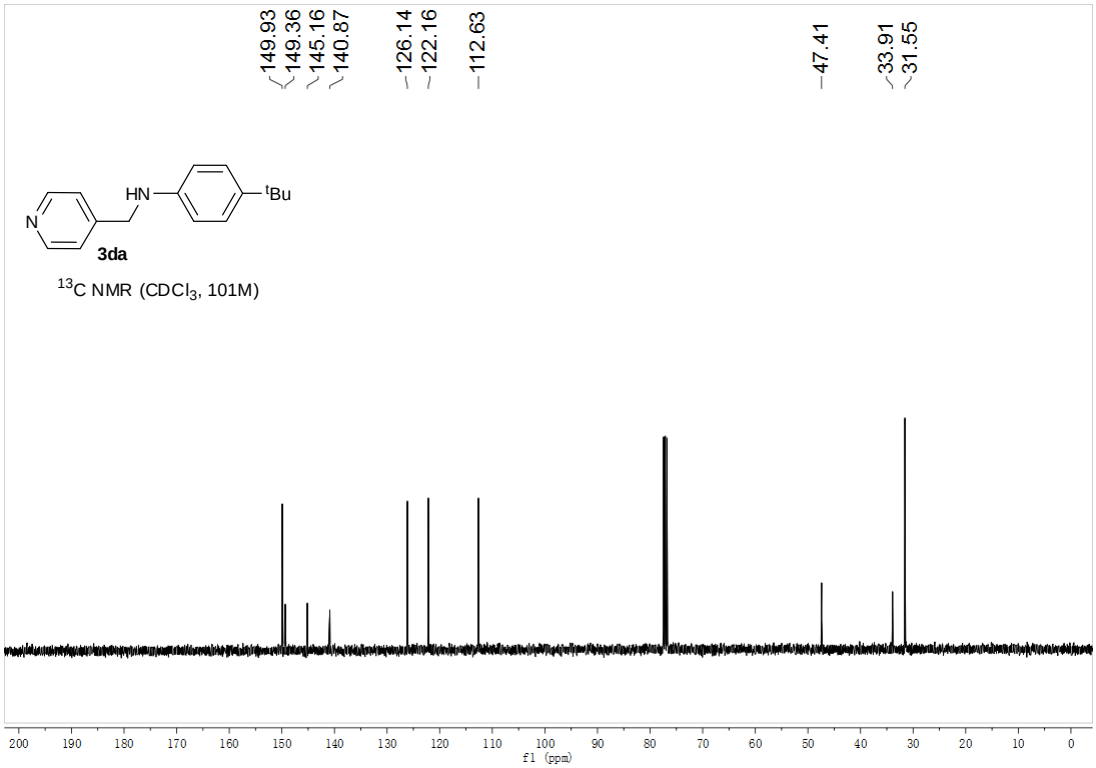
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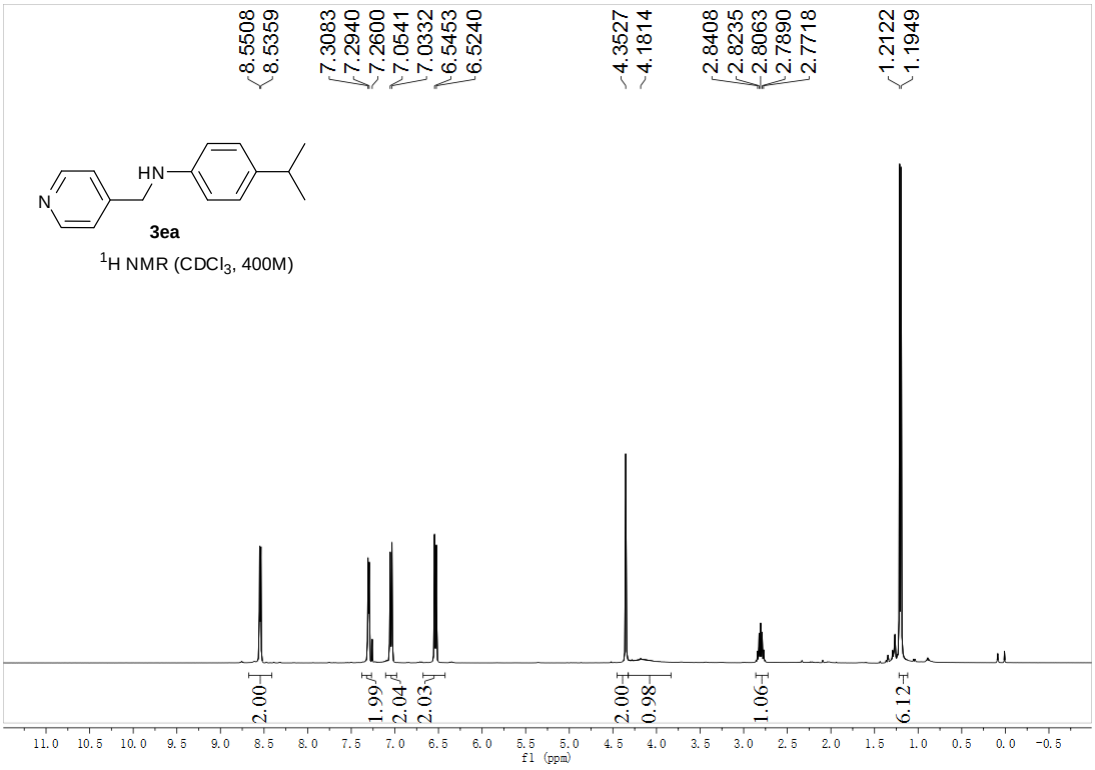
f1 (ppm)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HN
N
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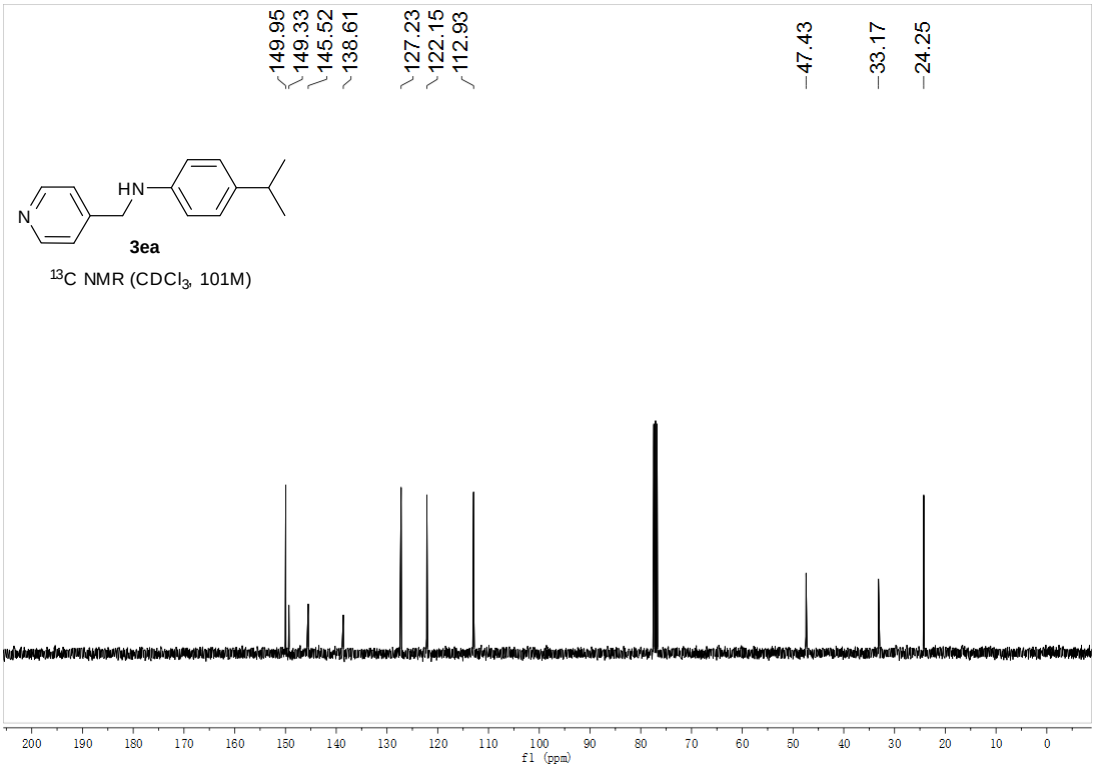
f1 (ppm)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33.17
24.25
HN
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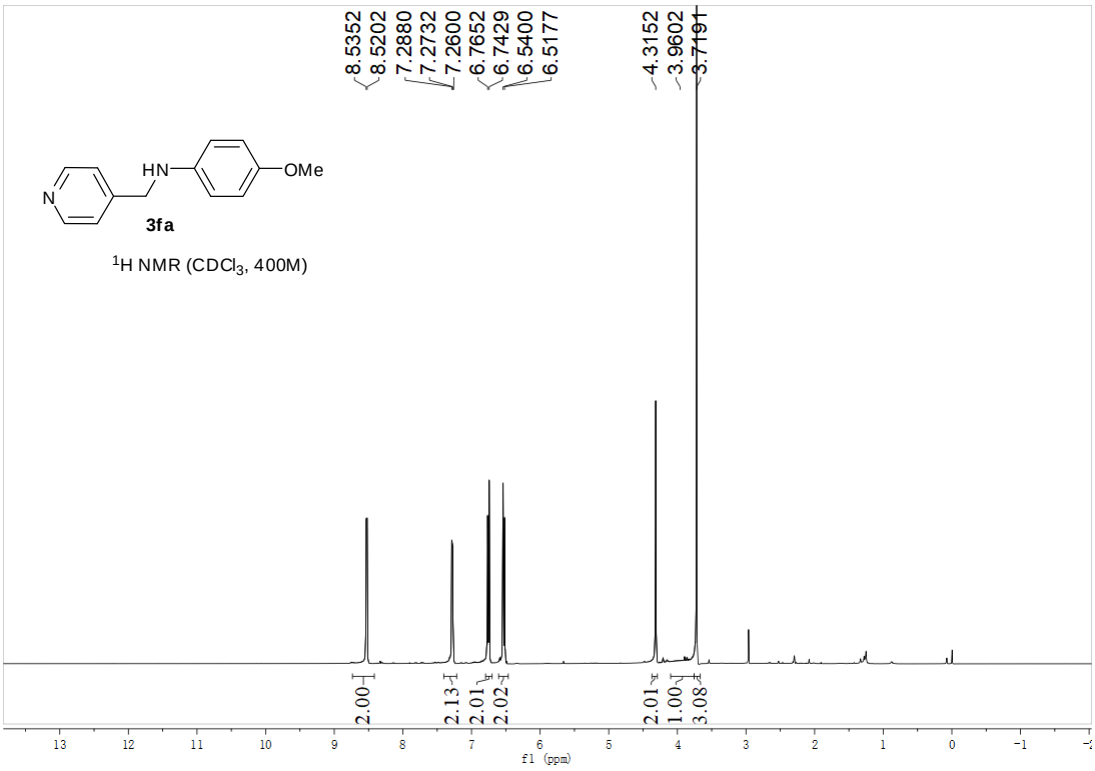
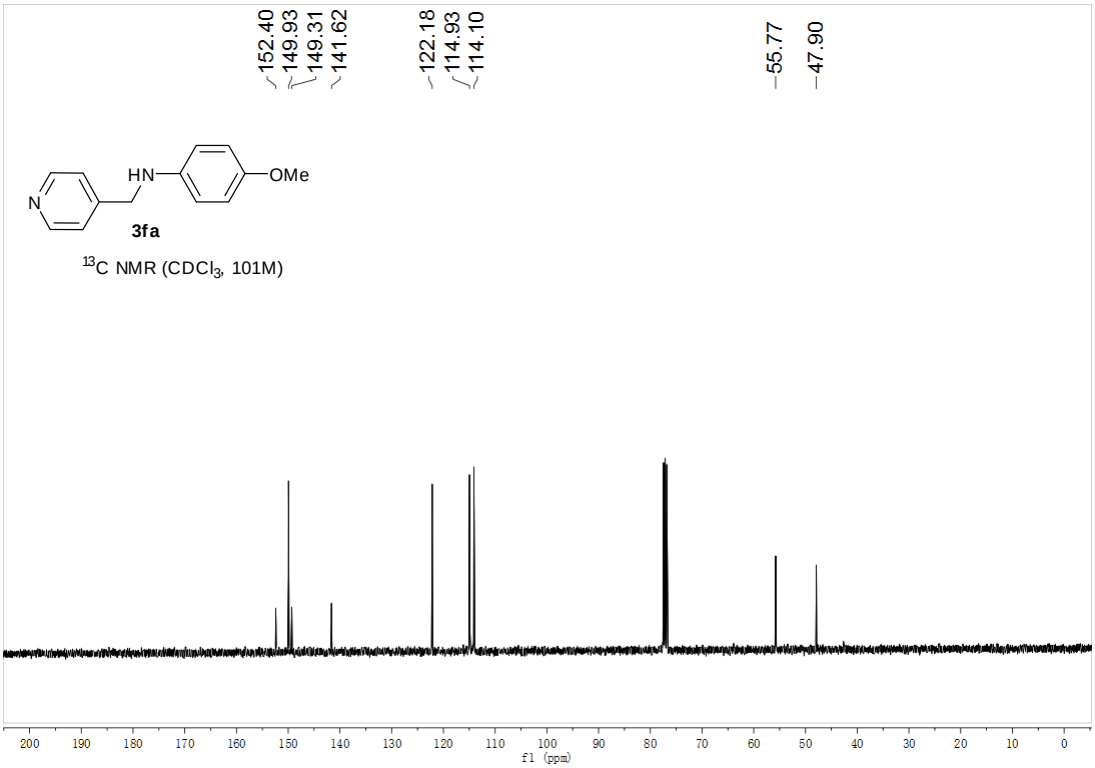
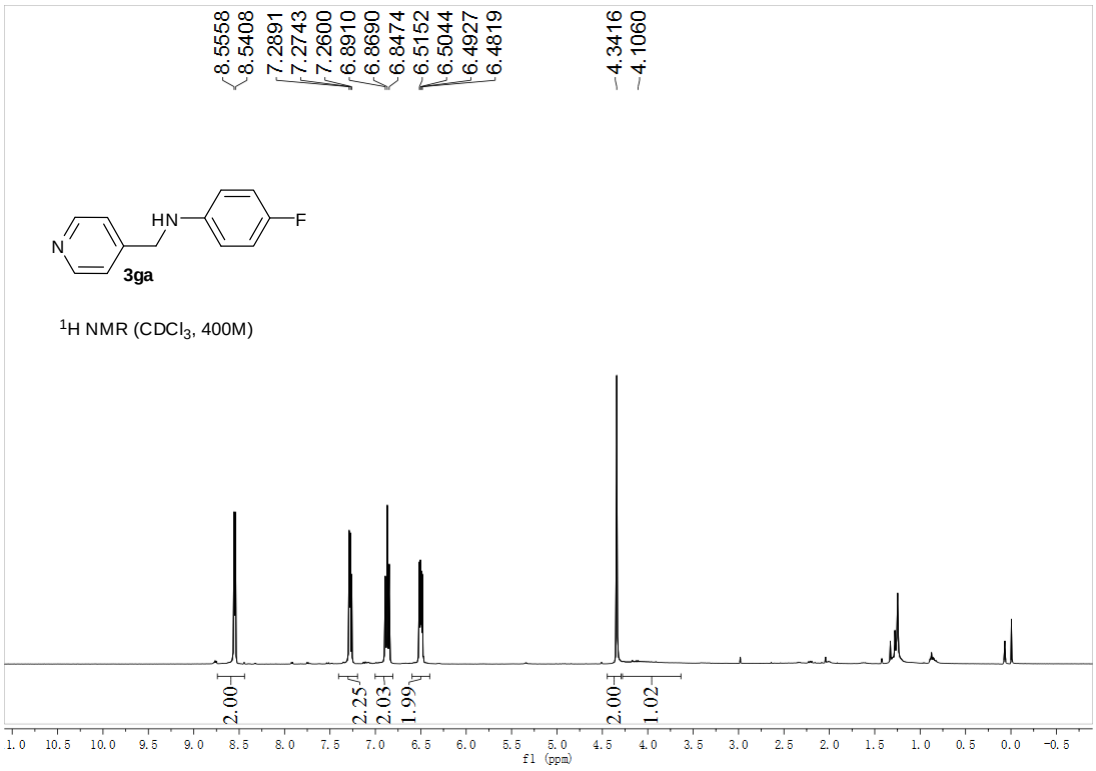
13C NMR (CDCl3, 101M)
f1 (ppm)



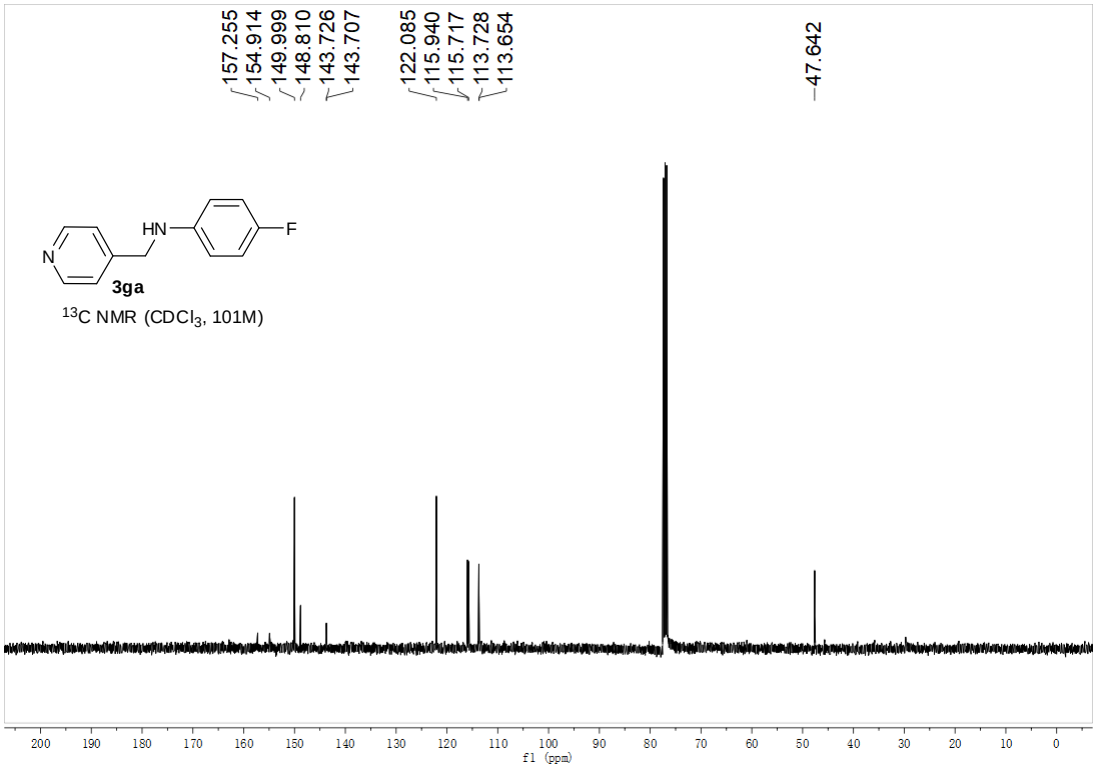
^{1}H NMR ($CDCl_3$, 400M)



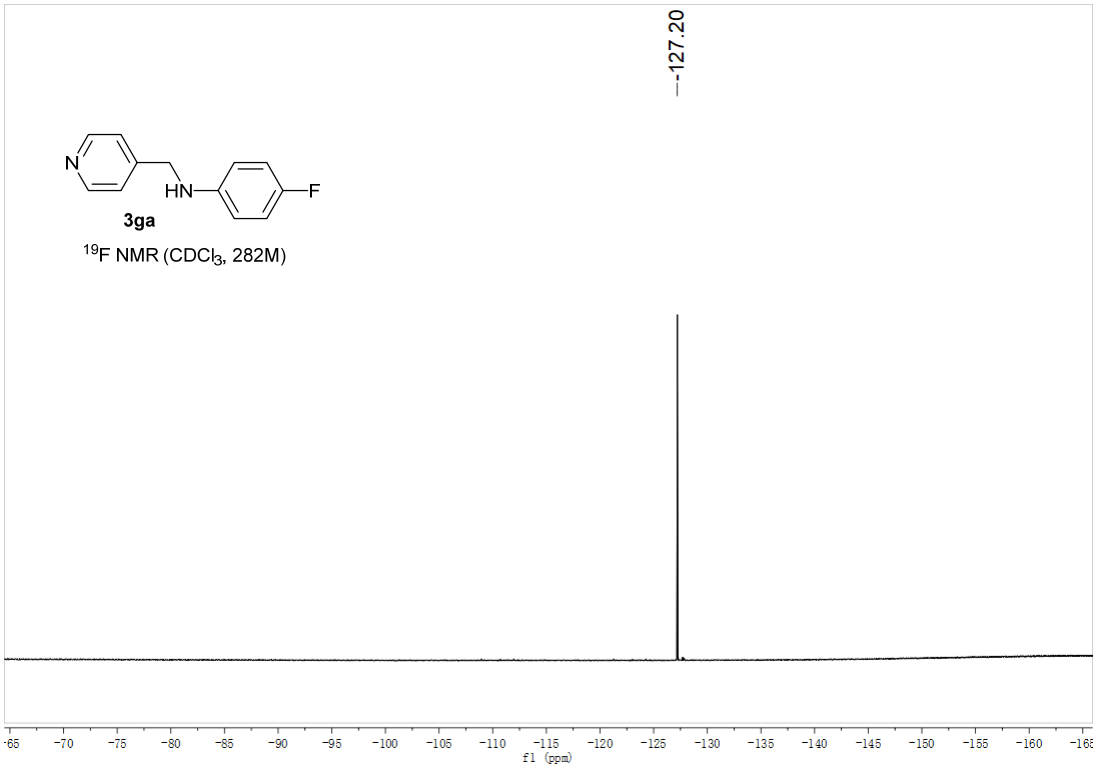
^{13}C NMR ($CDCl_3$, 101M)

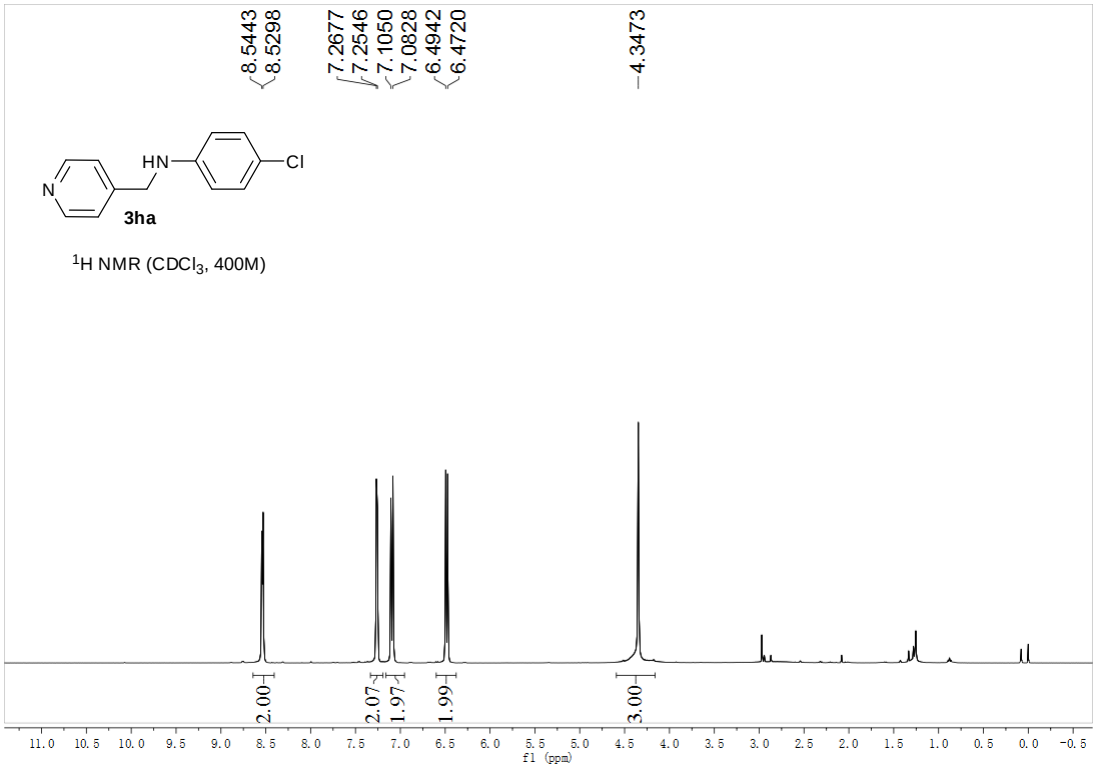


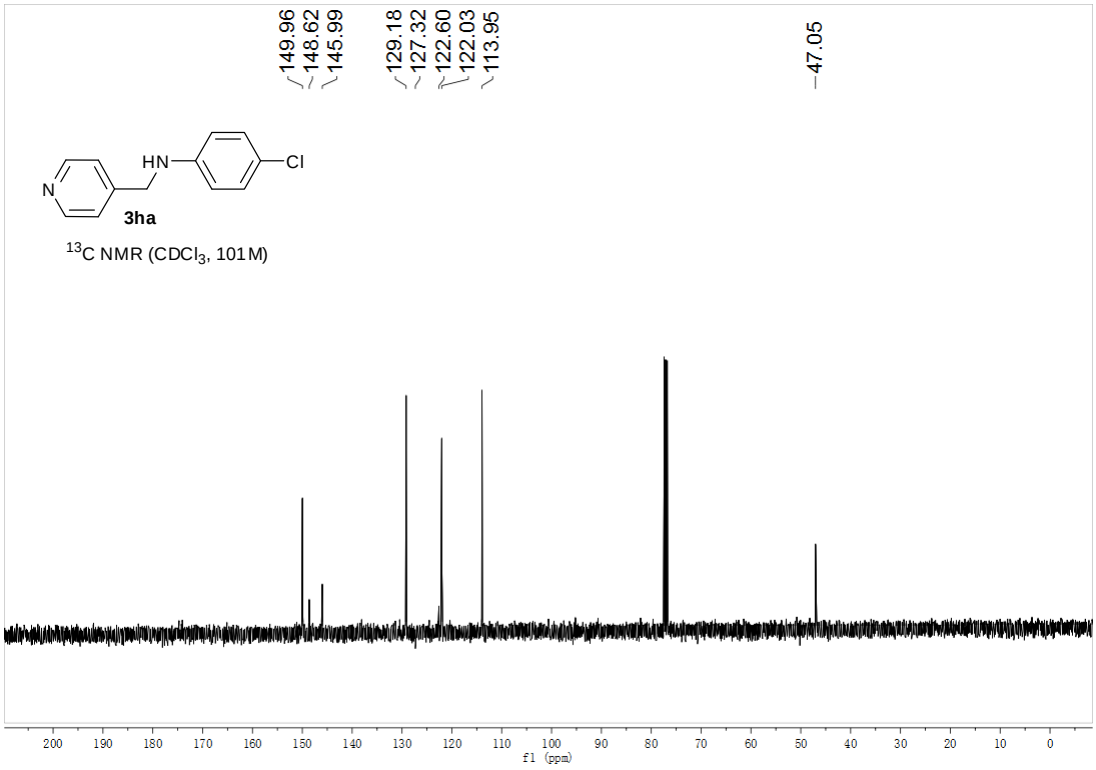
^{1}H NMR ($CDCl_3$, 400M)

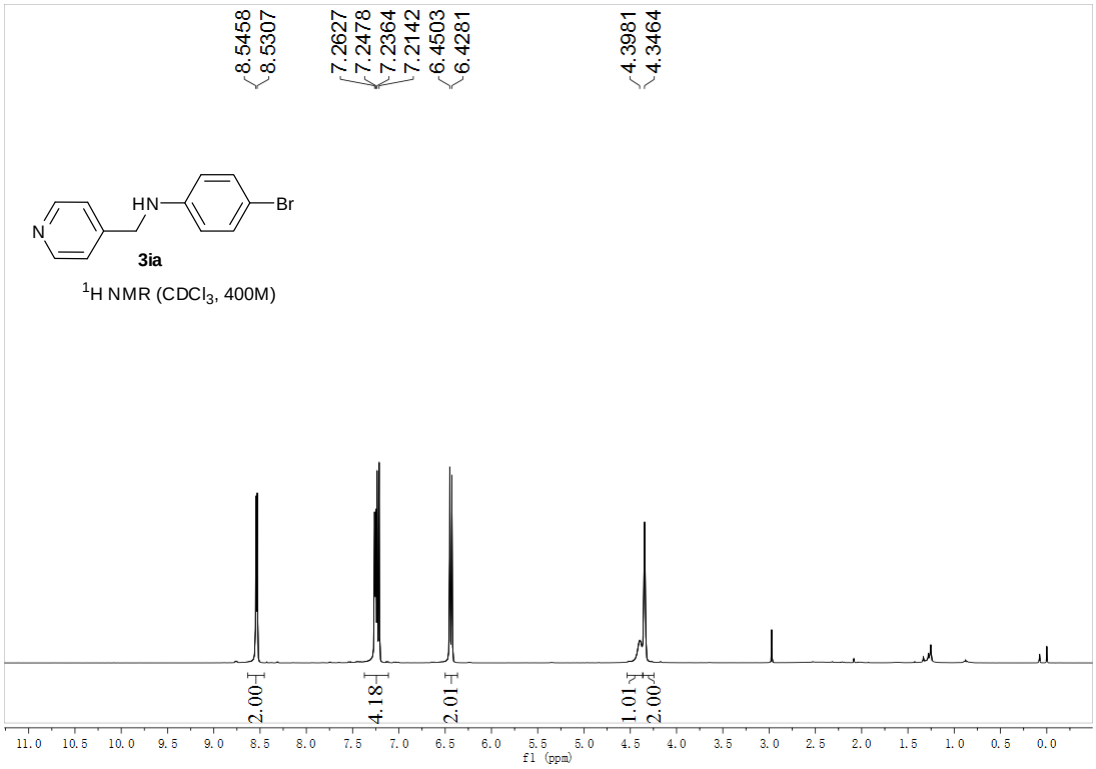


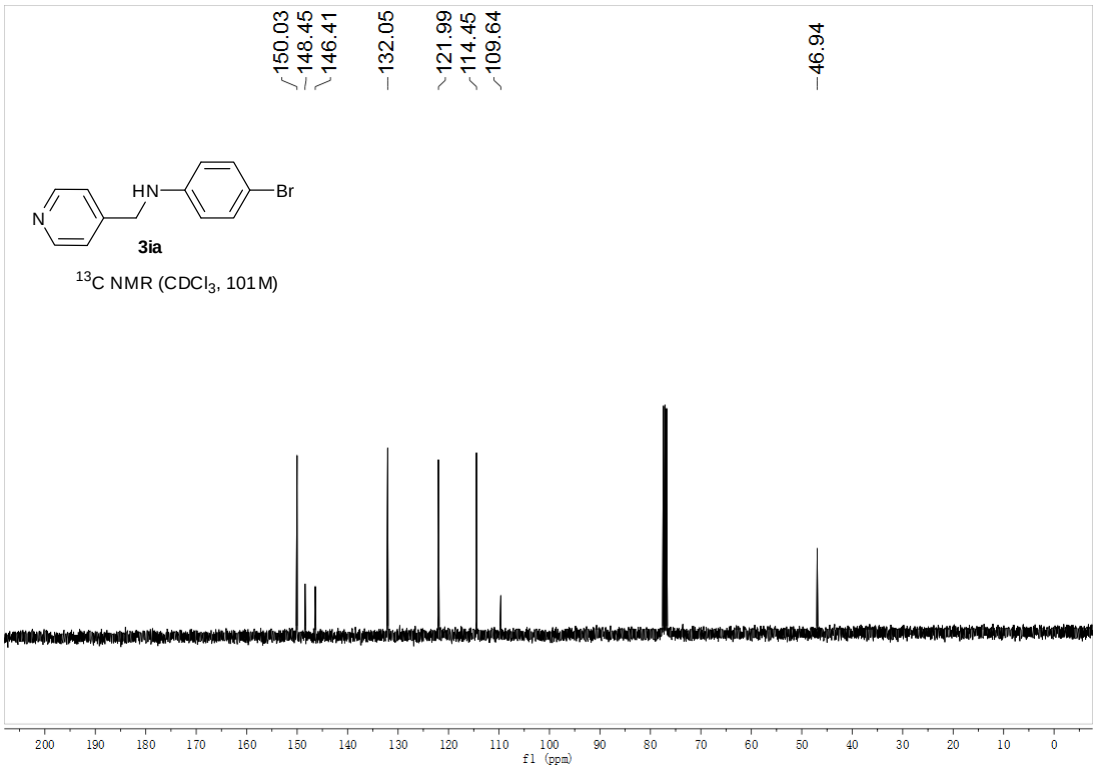
^{13}C NMR ($CDCl_3$, 101M)

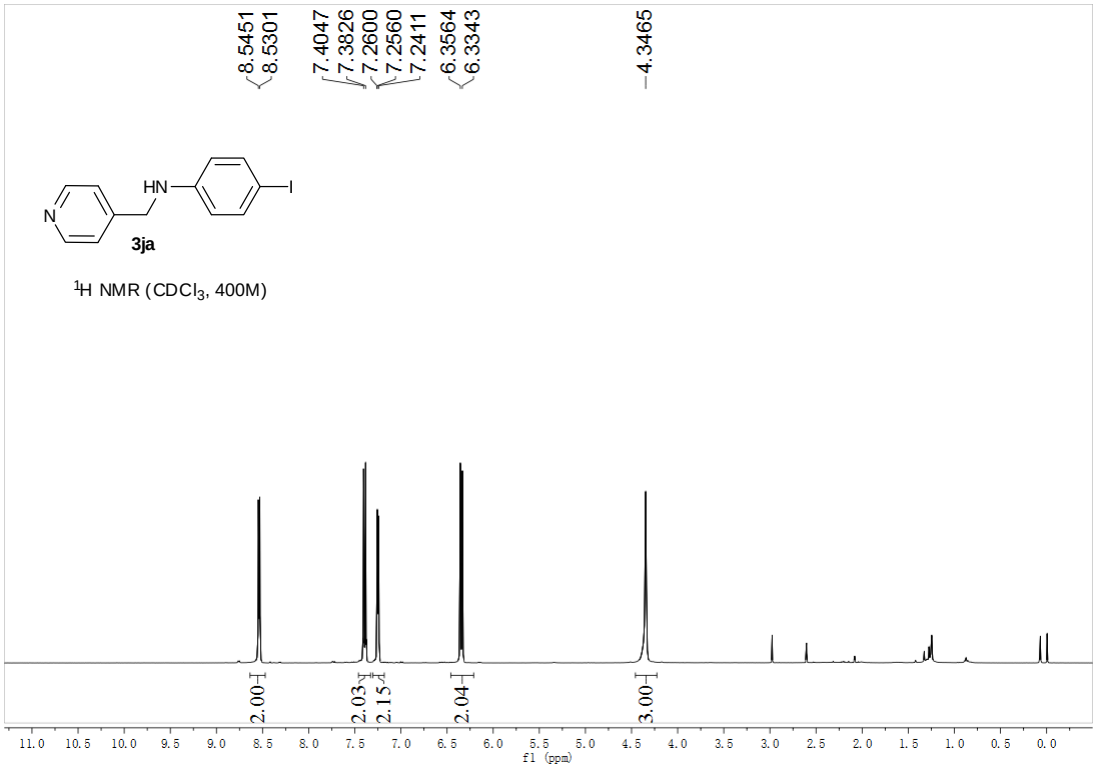

-127.20
N
HN
F
3ga
^{19}F NMR ($CDCl_3$, 282M)
f1 (ppm)

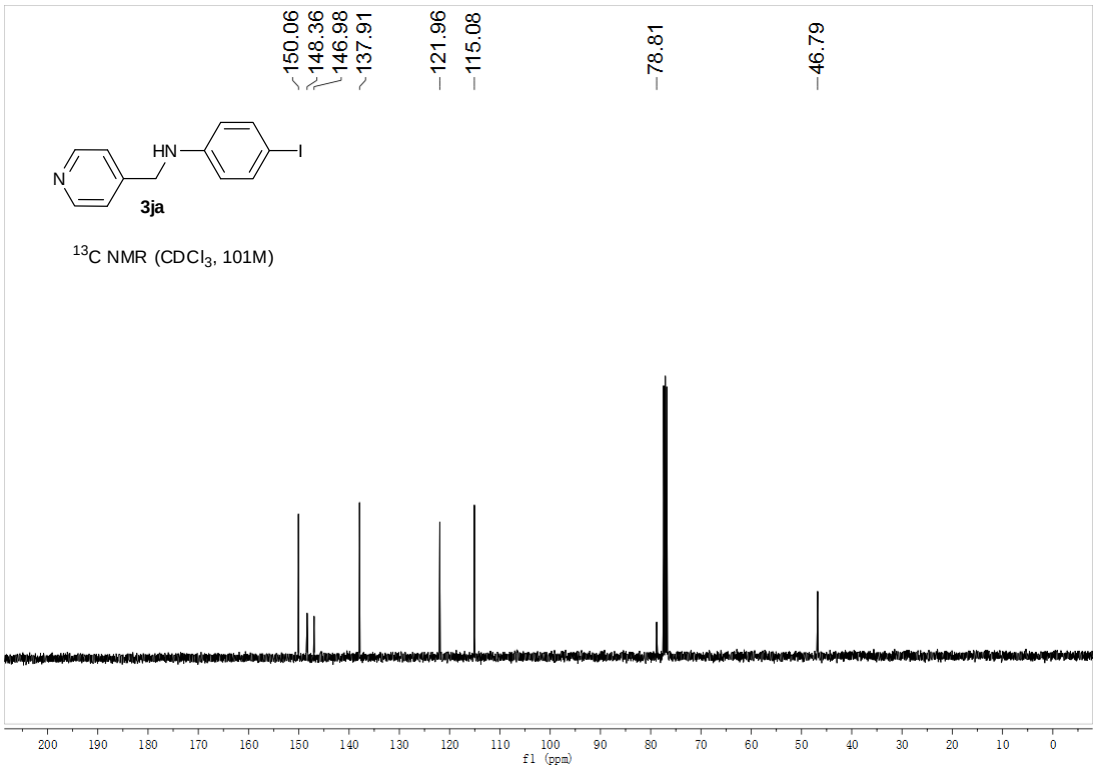

8.5443
8.5298
7.2677
7.2546
7.1050
7.0828
6.4942
6.4720
4.3473
HN
Cl
N
3ha
^{1}H NMR ($CDCl_3$, 400M)
2.00
2.07
1.97
1.99
3.00
f1 (ppm)

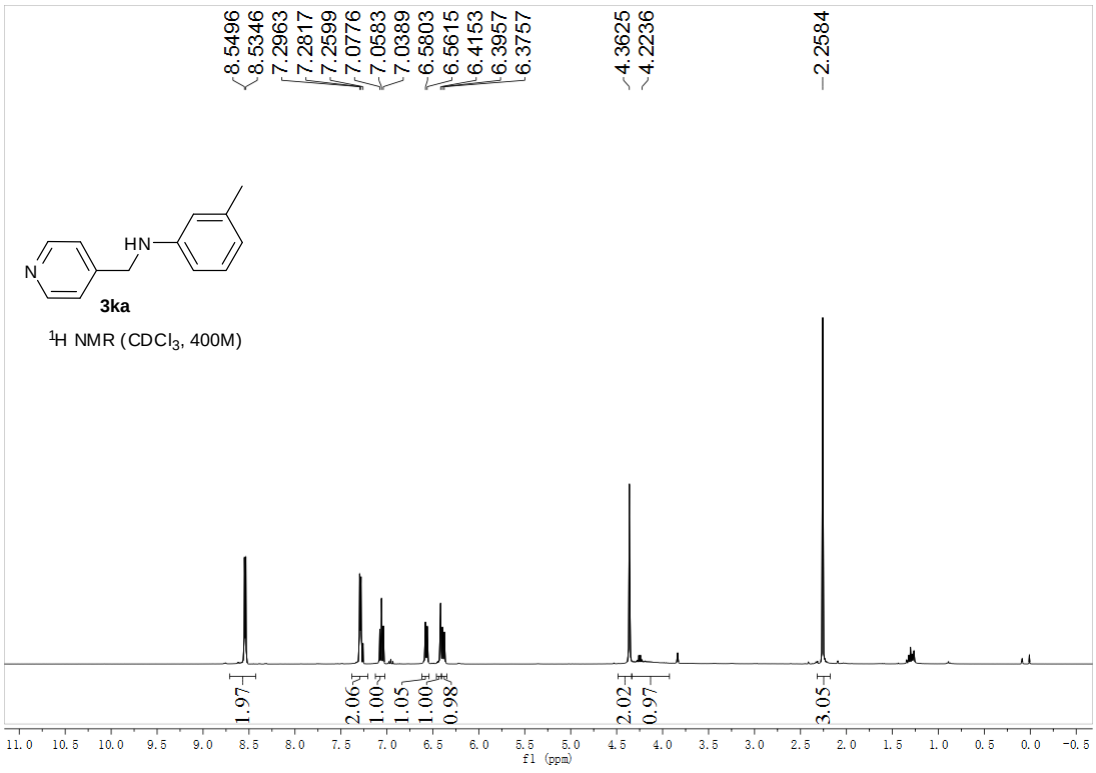

149.96
148.62
145.99
129.18
127.32
122.60
122.03
113.95
47.05
HN
Cl
N
3ha
^{13}C NMR ($CDCl_3$, 101M)
f1 (ppm)

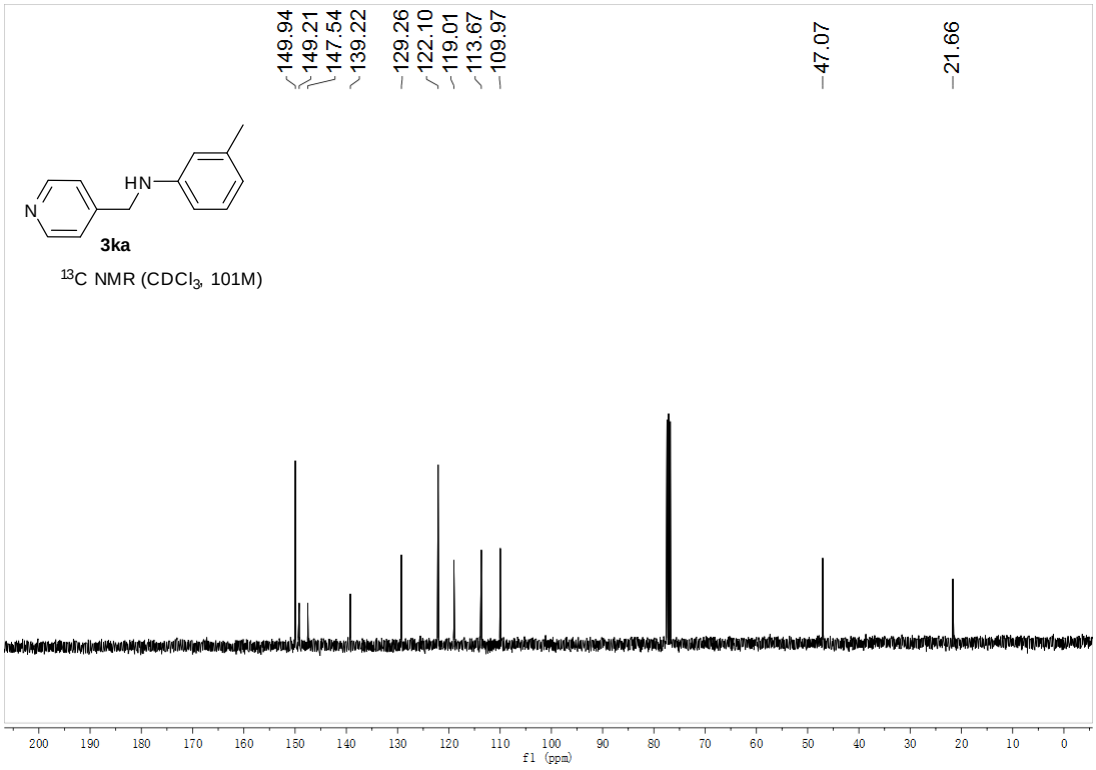

8.5458
8.5307
7.2627
7.2478
7.2364
7.2142
6.4503
6.4281
4.3981
4.3464
HN
Br
N
3ia
^{1}H NMR ($CDCl_3$, 400M)
2.00
4.18
2.01
1.01
2.00
f1 (ppm)

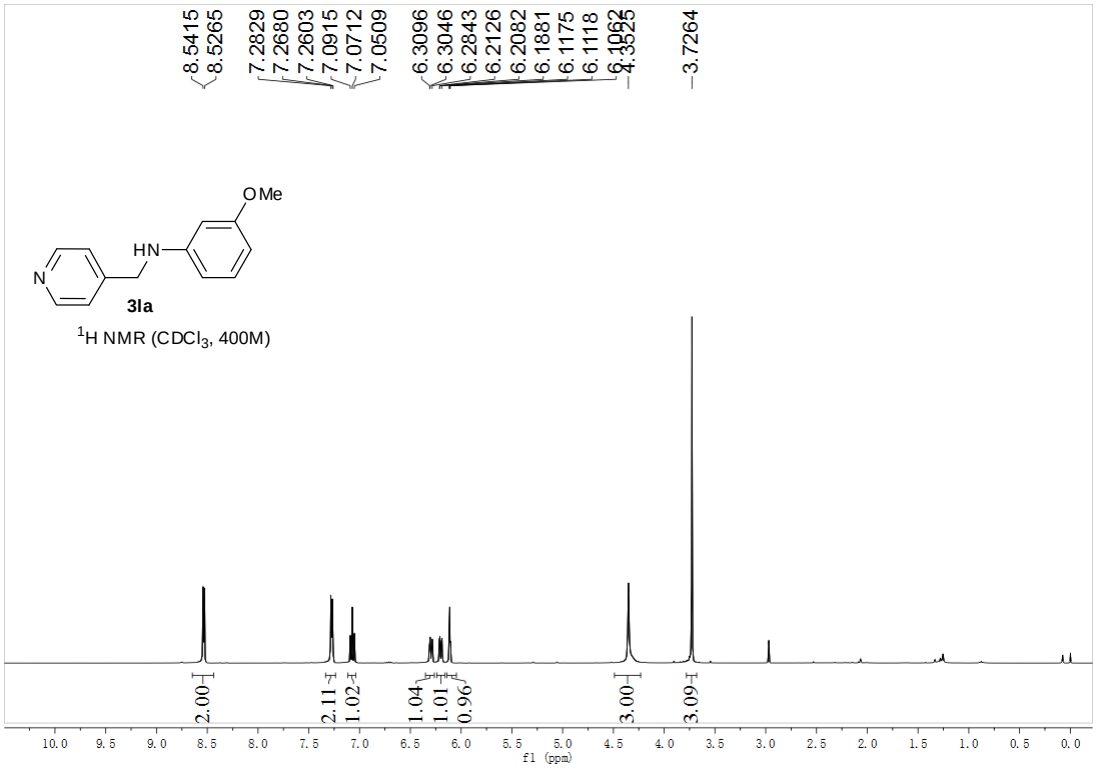

150.03
148.45
146.41
132.05
121.99
114.45
109.64
46.94
HN
Br
N
3ia
^{13}C NMR ($CDCl_3$, 101M)
f1 (ppm)

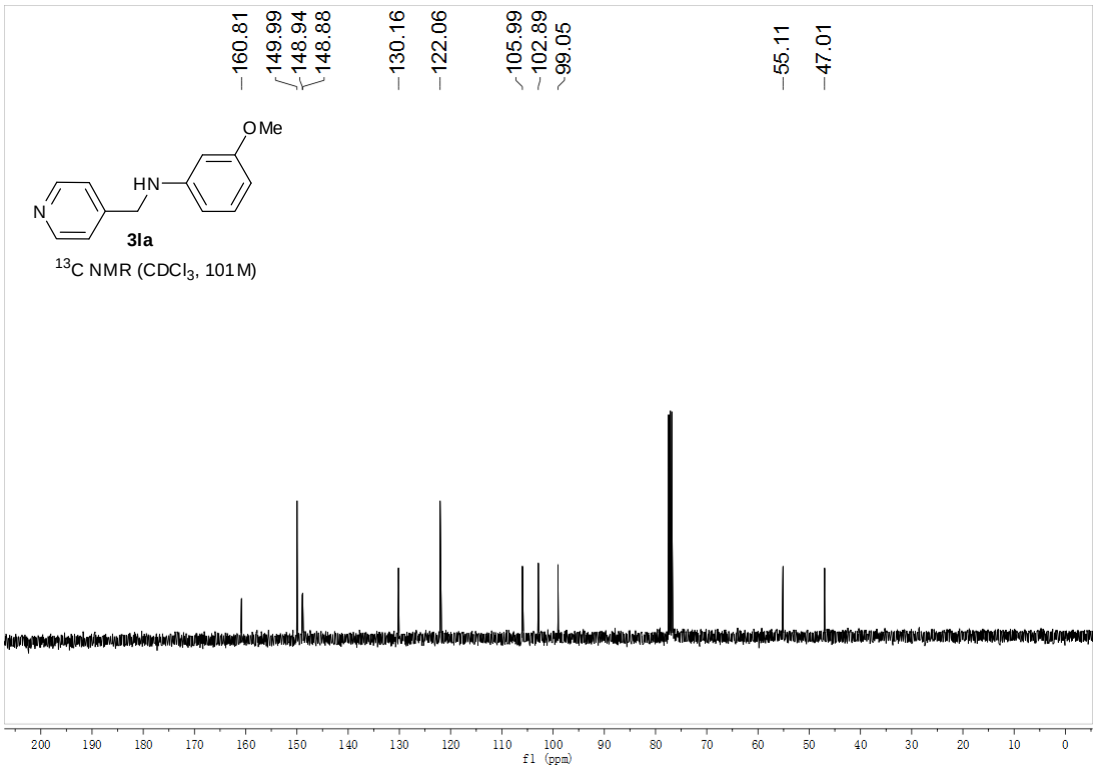

8.5451
8.5301
7.4047
7.3826
7.2600
7.2560
7.2411
6.3564
6.3343
4.3465
HN
I
N
3ja
^{1}H NMR ($CDCl_3$, 400M)
2.00
2.03
2.15
2.04
3.00
f1 (ppm)

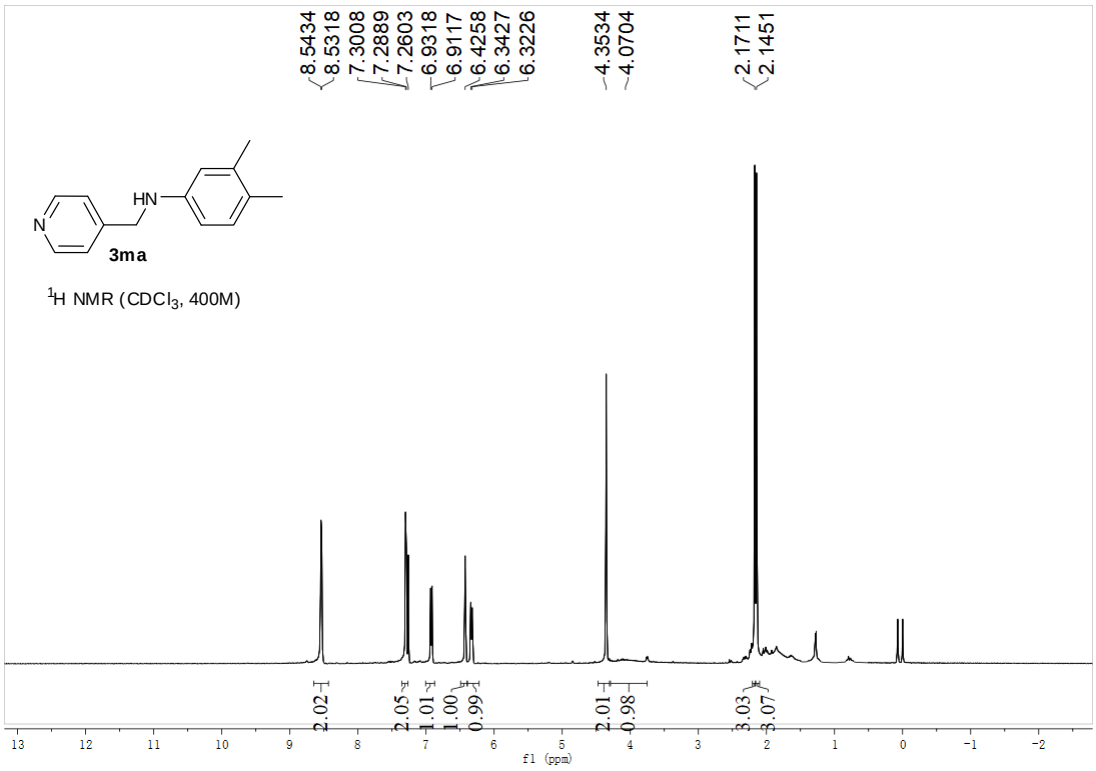

150.06
148.36
146.98
137.91
121.96
115.08
78.81
46.79
HN
I
N
3ja
^{13}C NMR ($CDCl_3$, 101M)
f1 (ppm)

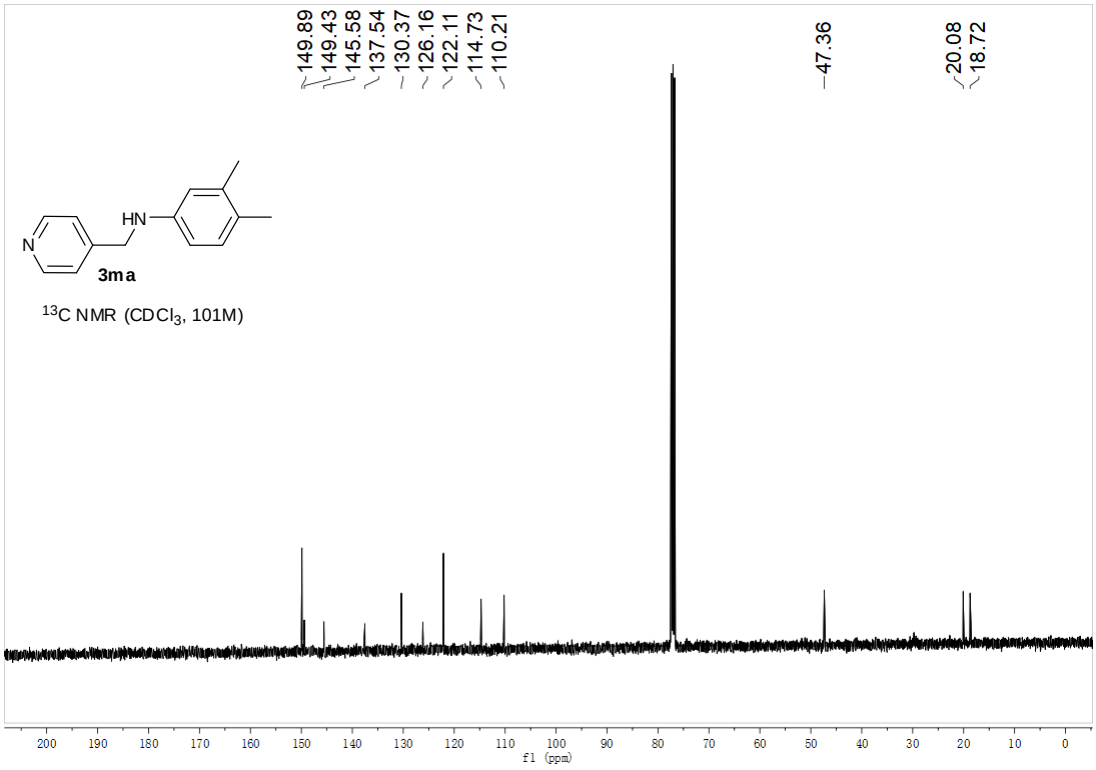

8.5496
8.5346
7.2963
7.2817
7.2599
7.0776
7.0583
7.0389
6.5803
6.5615
6.4153
6.3957
6.3757
4.3625
4.2236
2.2584
HN
N
3ka
^{1}H NMR ($CDCl_3$, 400M)
1.97
2.06
1.00
1.05
1.00
0.98
2.02
0.97
3.05
f1 (ppm)

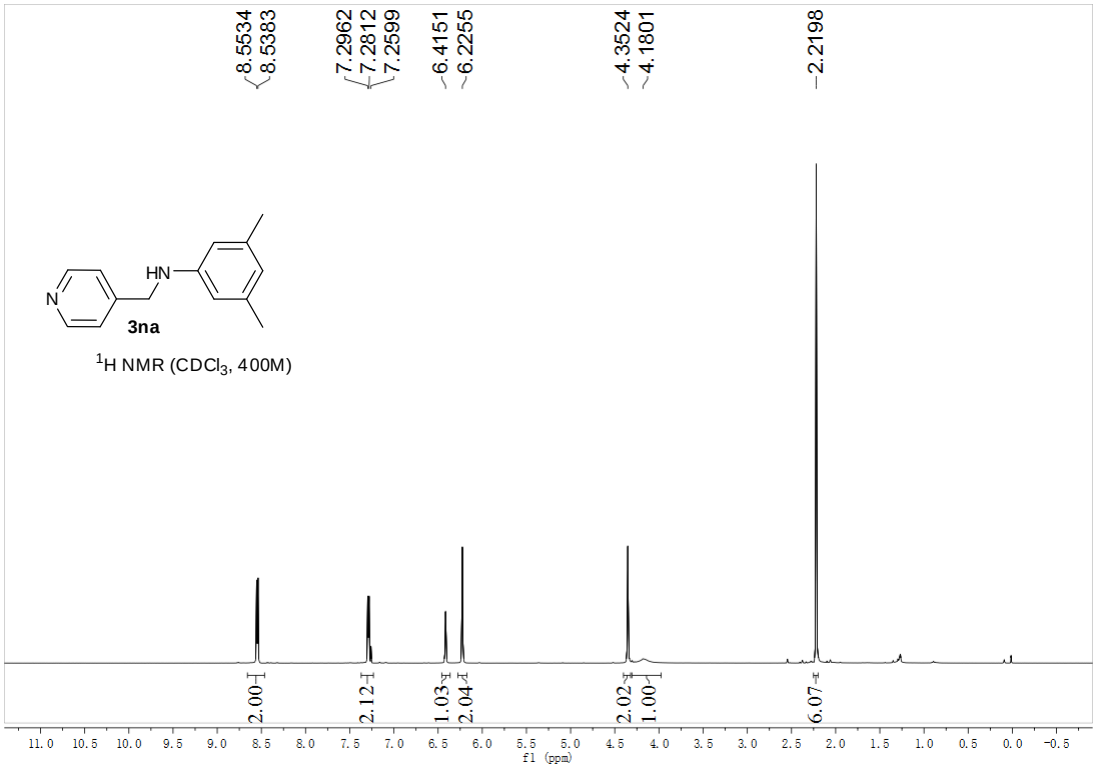

149.94
149.21
147.54
139.22
129.26
122.10
119.01
113.67
109.97
47.07
21.66
HN
N
3ka
13C NMR (CDCl3, 101M)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

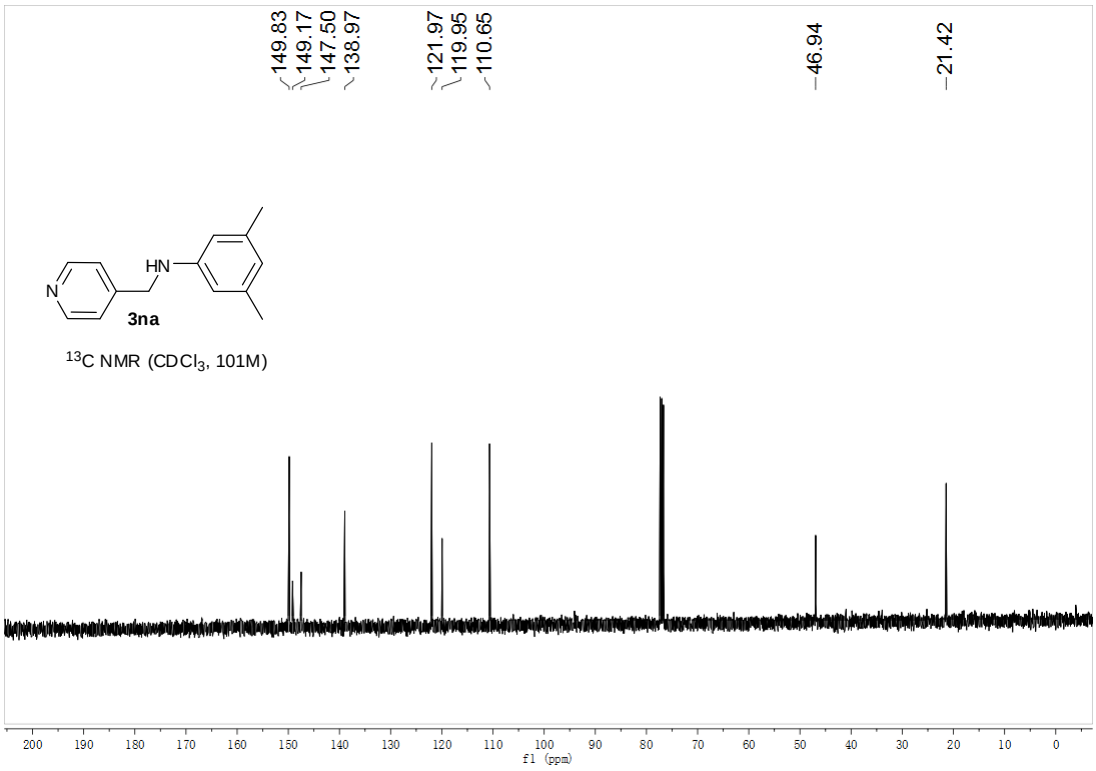

8.5415
8.5265
7.2829
7.2680
7.2603
7.0915
7.0712
7.0509
6.3096
6.3046
6.2843
6.2126
6.2082
6.1881
6.1175
6.1118
6.1062
4.3525
3.7264
OMe
HN
N
3la
1H NMR (CDCl3, 400M)
2.00
2.11
1.02
1.04
1.01
0.96
3.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.81
149.99
148.94
148.88
130.16
122.06
105.99
102.89
99.05
55.11
47.01
OMe
HN
N
3la
13C NMR (CDCl3, 101M)
f1 (ppm)

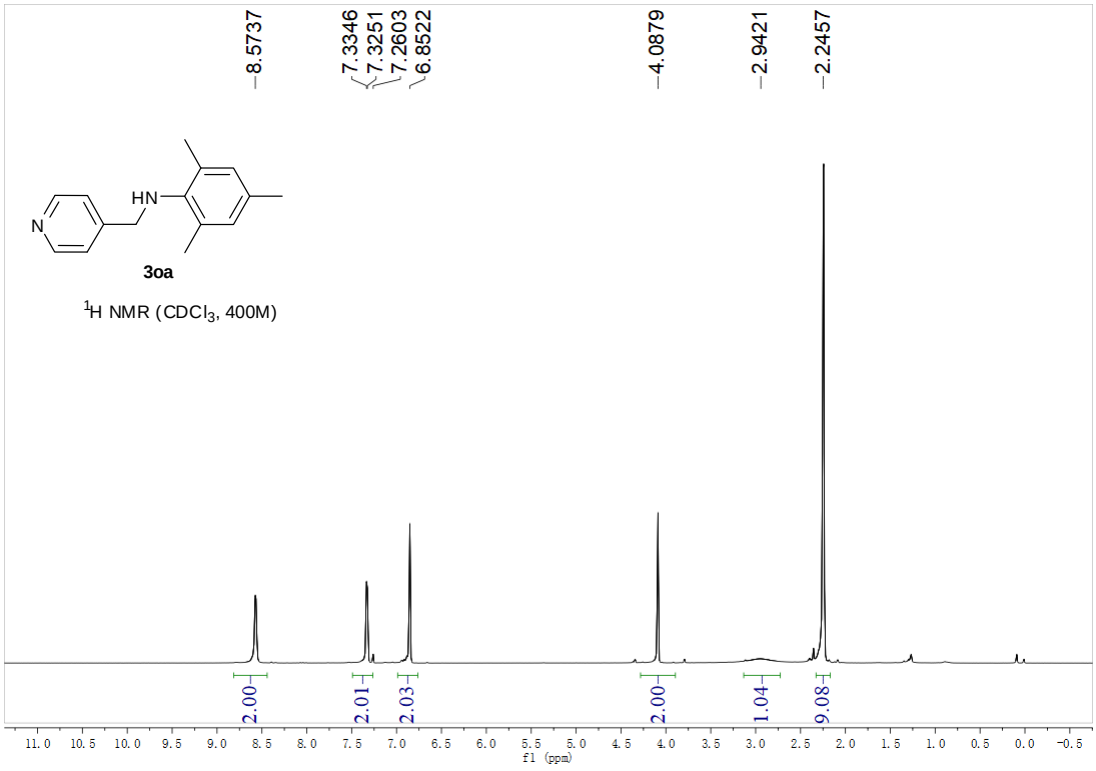

8.5434
8.5318
7.3008
7.2889
7.2603
6.9318
6.9117
6.4258
6.3427
6.3226
4.3534
4.0704
2.1711
2.1451
HN
N
3ma
1H NMR (CDCl3, 400M)
2.02
2.05
1.01
1.00
0.99
2.01
0.98
3.03
3.07
f1 (ppm)


149.89
149.43
145.58
137.54
130.37
126.16
122.11
114.73
110.21
47.36
20.08
18.72
HN
N
3ma
13C NMR (CDCl3, 101M)
f1 (ppm)

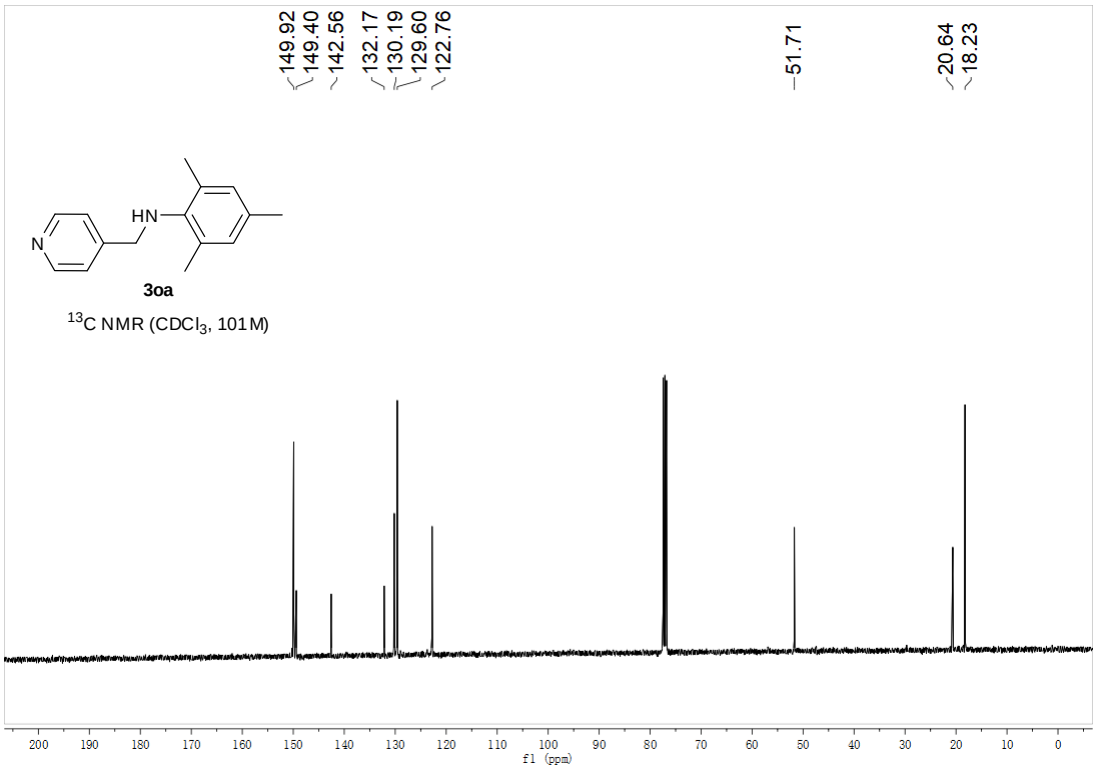

8.5534
8.5383
7.2962
7.2812
7.2599
6.4151
6.2255
4.3524
4.1801
2.2198
2.00
2.12
1.03
2.04
2.02
1.00
6.07
HN
N
3na
1H NMR (CDCl3, 400M)
f1 (ppm)

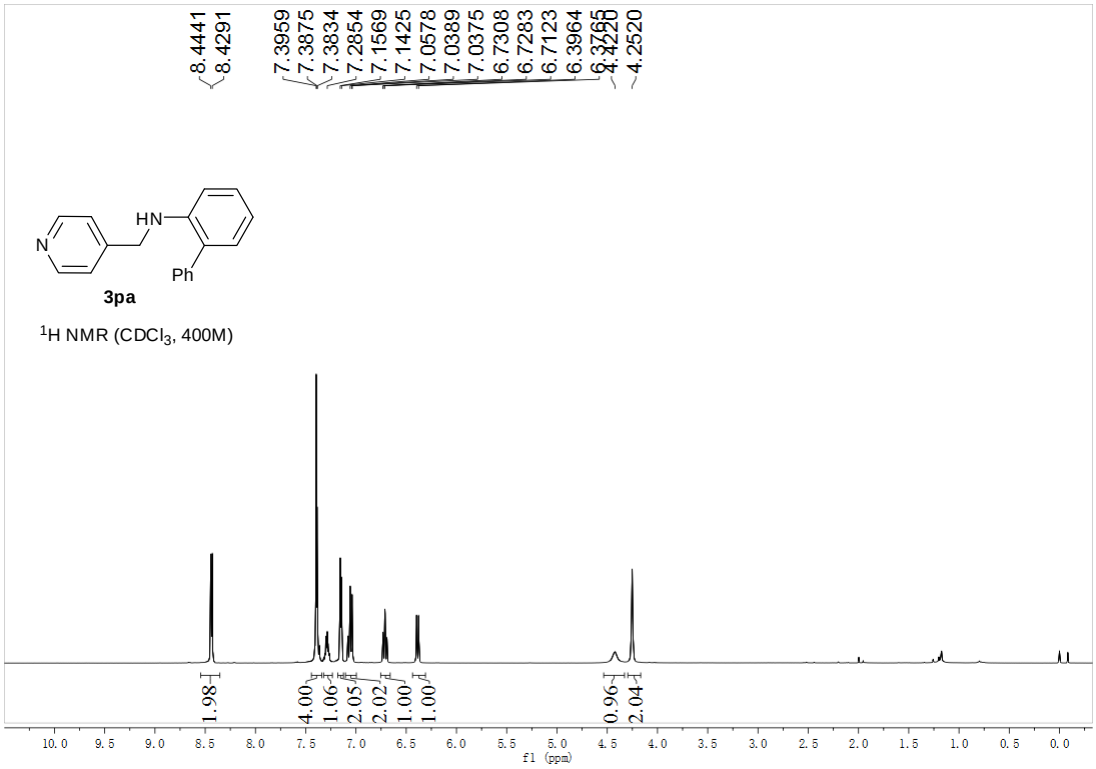


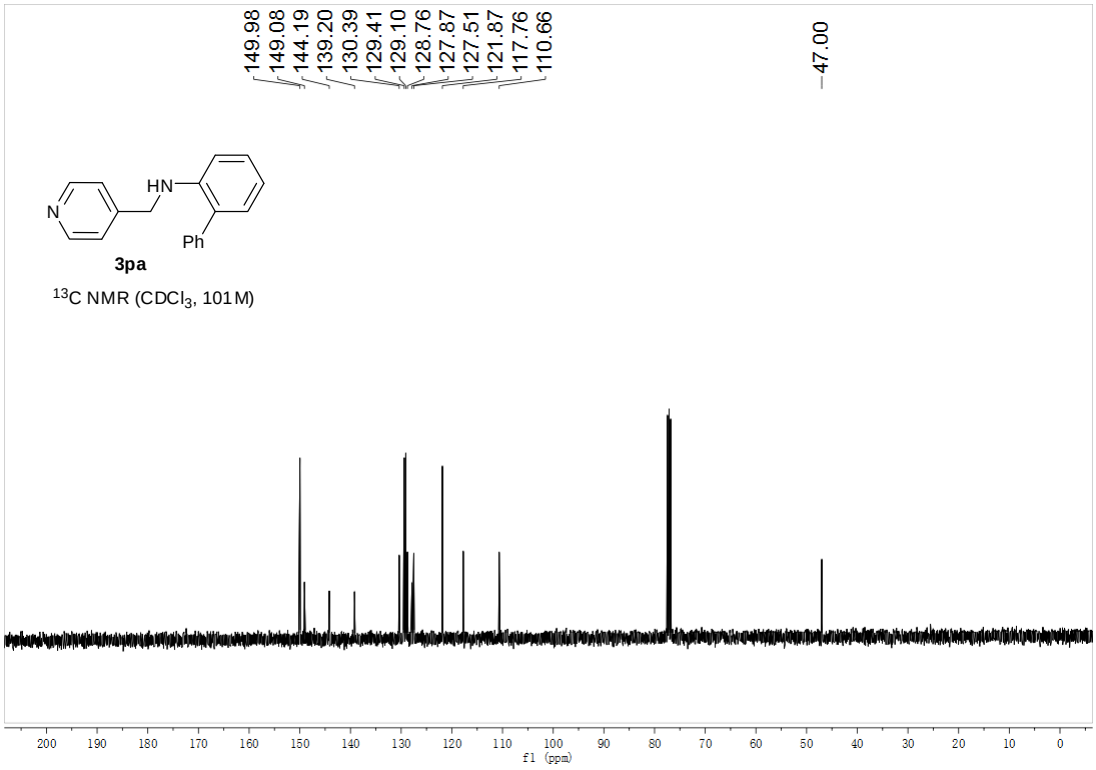
^{13}C NMR ($CDCl_3$, 101M)

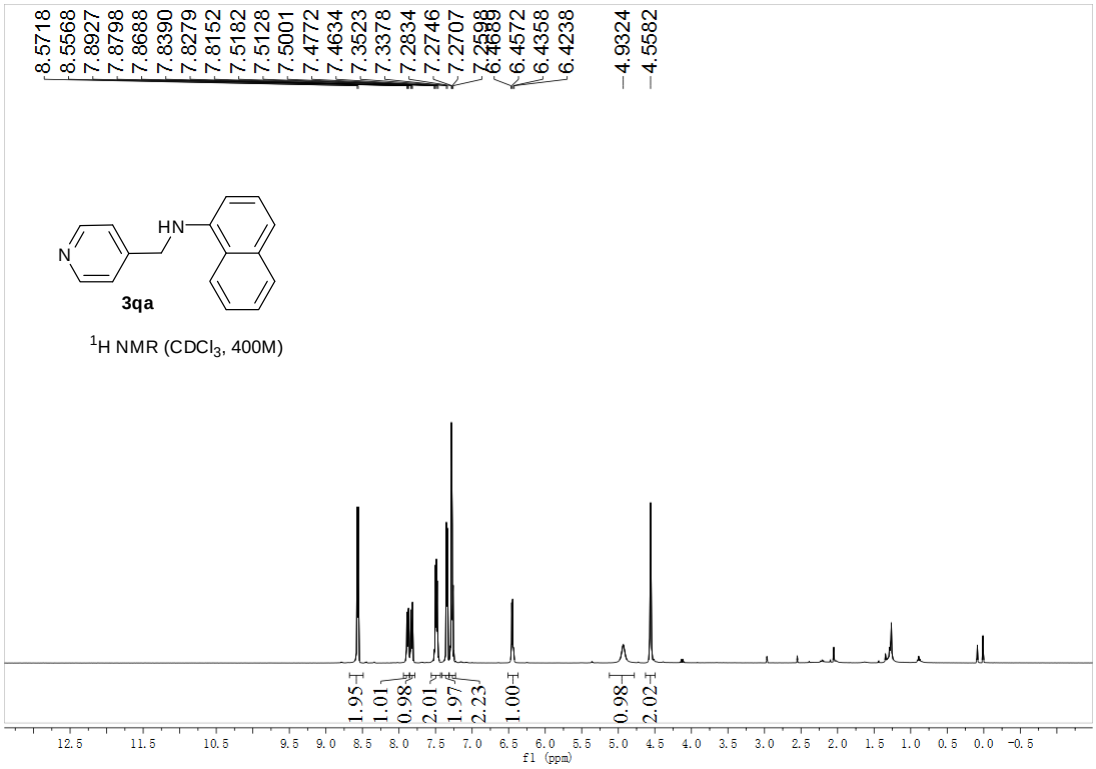


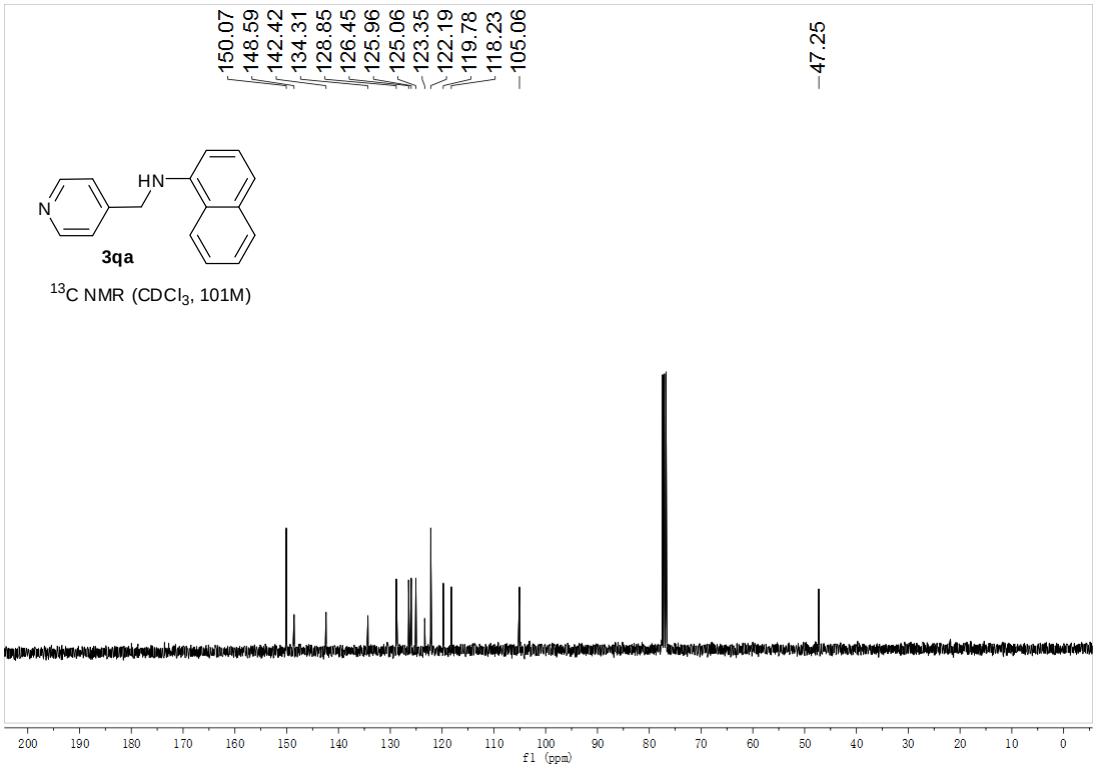
^{1}H NMR ($CDCl_3$, 400M)

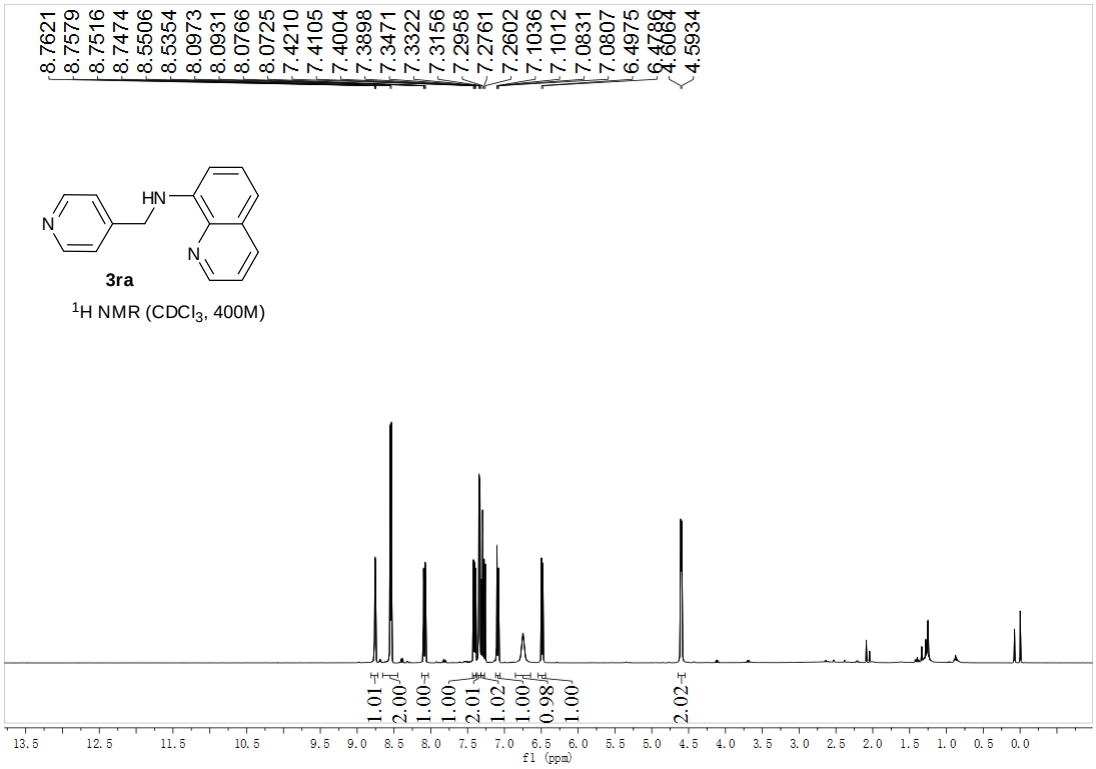

149.92
149.40
142.56
132.17
130.19
129.60
122.76
51.71
20.64
18.23
HN
N
3oa
13C NMR (CDCl3, 101M)
f1 (ppm)

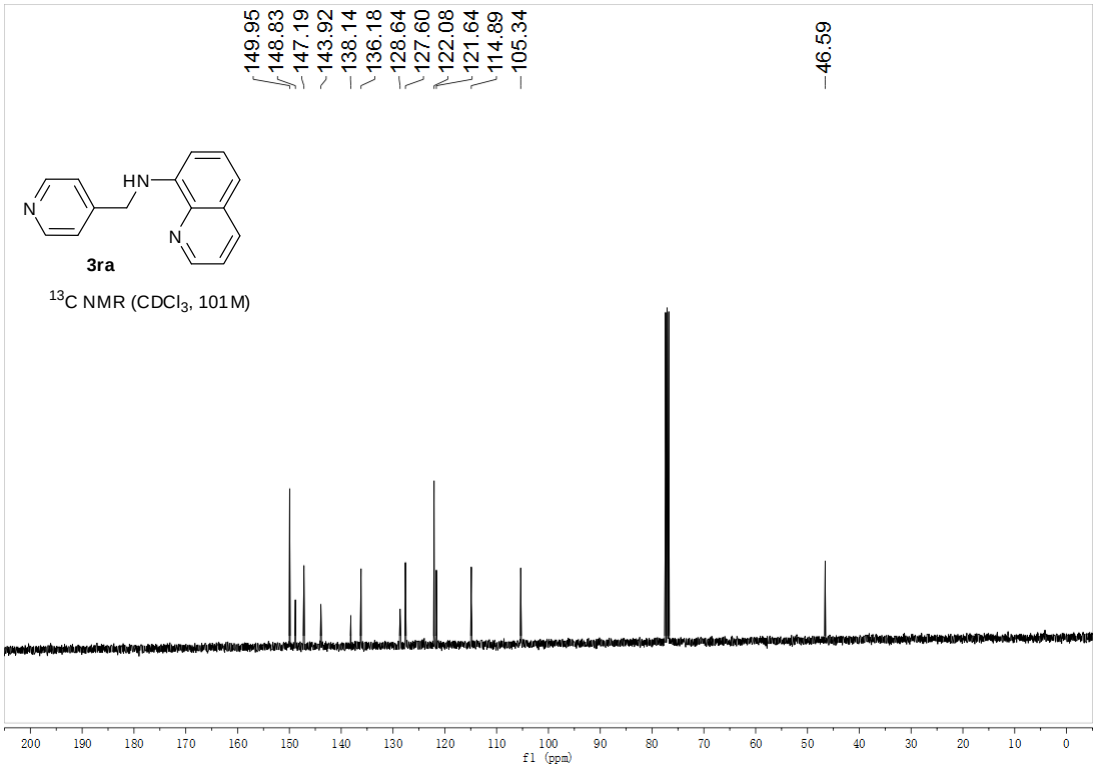

8.4441
8.4291
7.3959
7.3875
7.3834
7.2854
7.1569
7.1425
7.0578
7.0389
7.0375
6.7308
6.7283
6.7123
6.3964
4.2520
HN
N
Ph
3pa
1H NMR (CDCl3, 400M)
1.98
4.00
1.06
2.05
2.02
1.00
1.00
0.96
2.04
f1 (ppm)

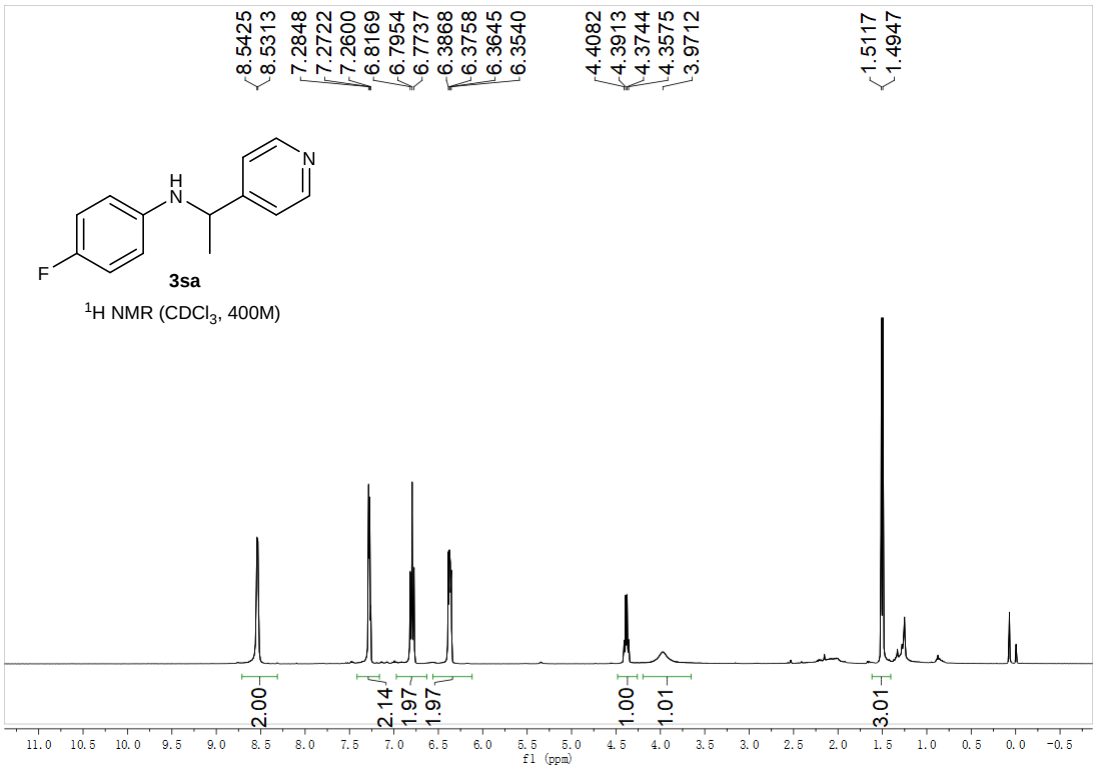

149.98
149.08
144.19
139.20
130.39
129.41
129.10
128.76
127.87
127.51
121.87
117.76
110.66
47.00
HN
N
Ph
3pa
13C NMR (CDCl3, 101M)
f1 (ppm)

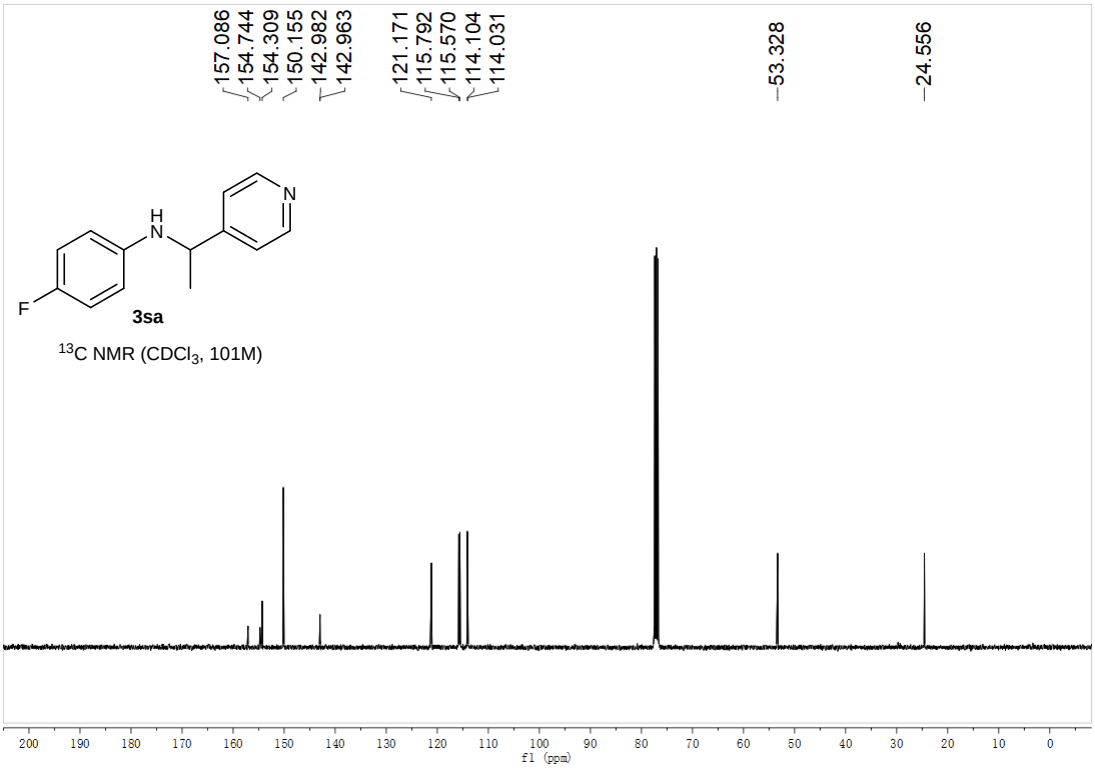

8.5718
8.5568
7.8927
7.8798
7.8688
7.8390
7.8279
7.8152
7.5182
7.5128
7.5001
7.4772
7.4634
7.3523
7.3378
7.2834
7.2746
7.2707
6.4572
6.4358
6.4238
4.9324
4.5582
HN
N
3qa
1H NMR (CDCl3, 400M)
1.95
1.01
0.98
2.01
1.97
2.23
1.00
0.98
2.02
f1 (ppm)

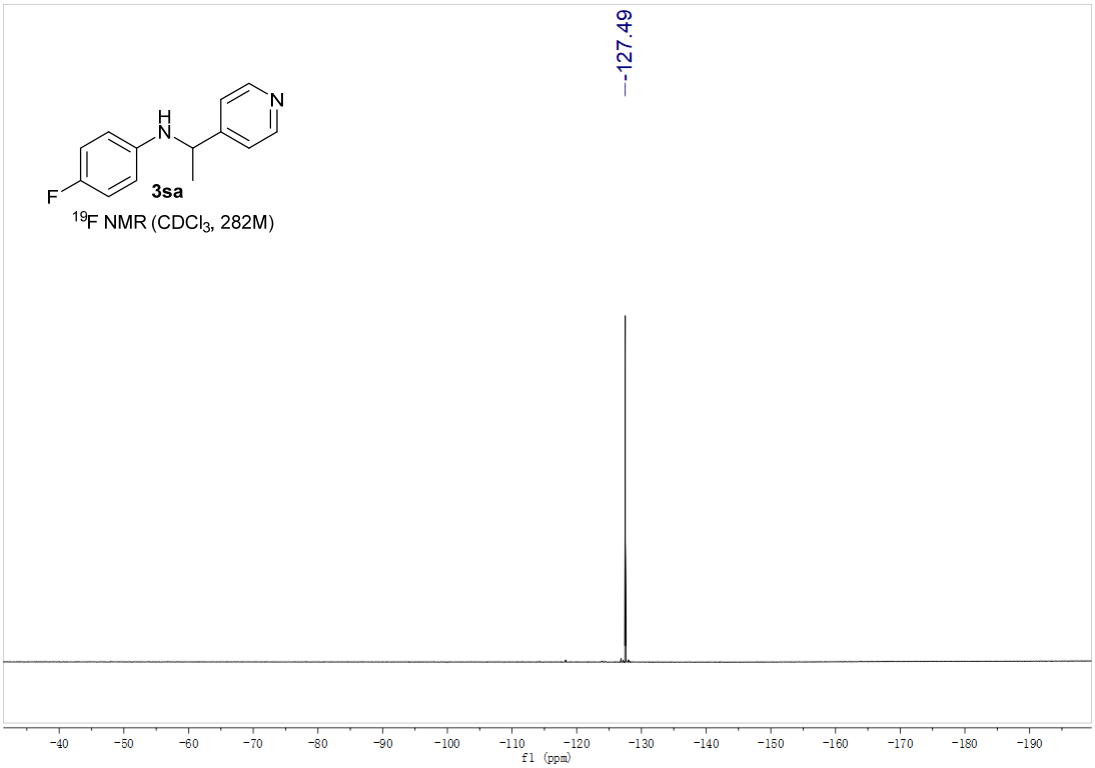

150.07
148.59
142.42
134.31
128.85
126.45
125.96
125.06
123.35
122.19
119.78
118.23
105.06
47.25
HN
N
3qa
13C NMR (CDCl3, 101M)
f1 (ppm)

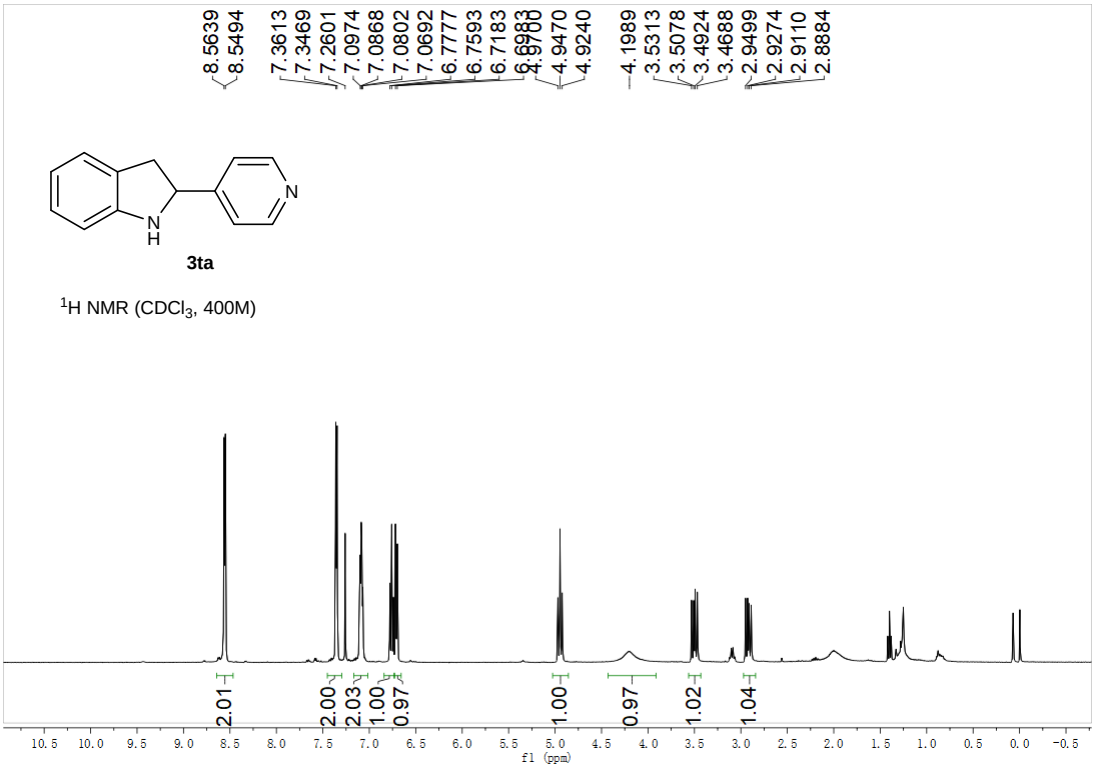

8.7621
8.7579
8.7516
8.7474
8.5506
8.5354
8.0973
8.0931
8.0766
8.0725
7.4210
7.4105
7.4004
7.3898
7.3471
7.3322
7.3156
7.2958
7.2761
7.2602
7.1036
7.1012
7.0831
7.0807
6.4975
6.4786
6.4064
4.5934
HN
N
N
3ra
1H NMR (CDCl3, 400M)
1.01
2.00
1.00
1.00
2.01
1.02
1.00
0.98
1.00
2.02
f1 (ppm)


149.95
148.83
147.19
143.92
138.14
136.18
128.64
127.60
122.08
121.64
114.89
105.34
46.59
HN
N
N
3ra
13C NMR (CDCl3, 101M)
f1 (ppm)


8.5425
8.5313
7.2848
7.2722
7.2600
6.8169
6.7954
6.7737
6.3868
6.3758
6.3645
6.3540
4.4082
4.3913
4.3744
4.3575
3.9712
1.5117
1.4947
H
N
N
F
3sa
1H NMR (CDCl3, 400M)
2.00
2.14
1.97
1.97
1.00
1.01
3.01
f1 (ppm)

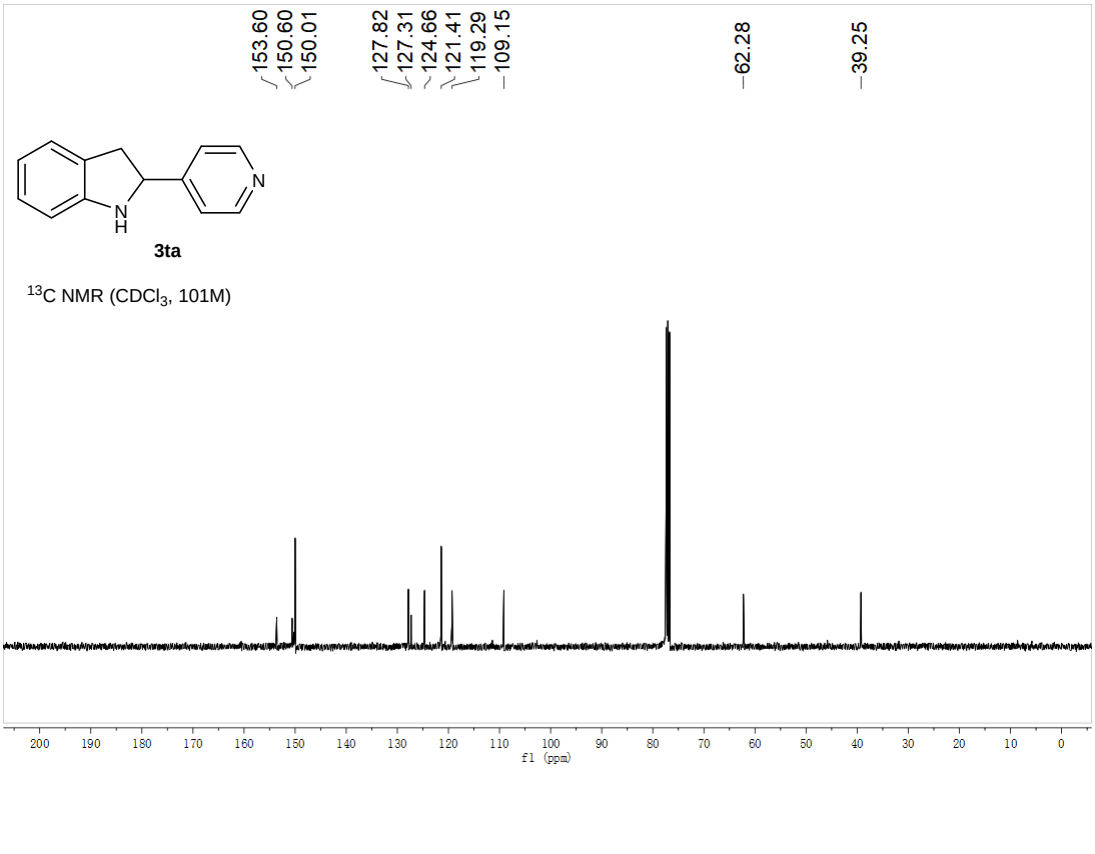

157.086
154.744
154.309
150.155
142.982
142.963
121.171
115.792
115.570
114.104
114.031
53.328
24.556
H
N
N
F
3sa
13C NMR (CDCl3, 101M)
f1 (ppm)


-127.49
H
N
N
F
3sa
19F NMR (CDCl3, 282M)
f1 (ppm)



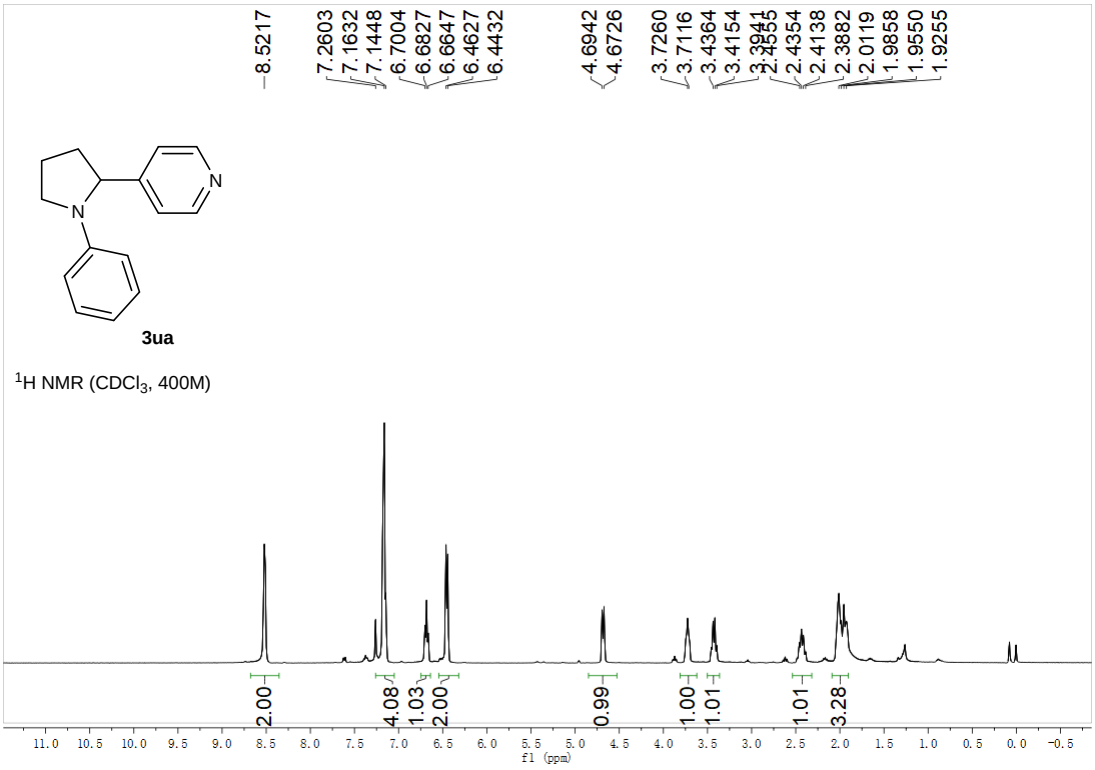
3ta

^{1}H NMR ($CDCl_3$, 400M)



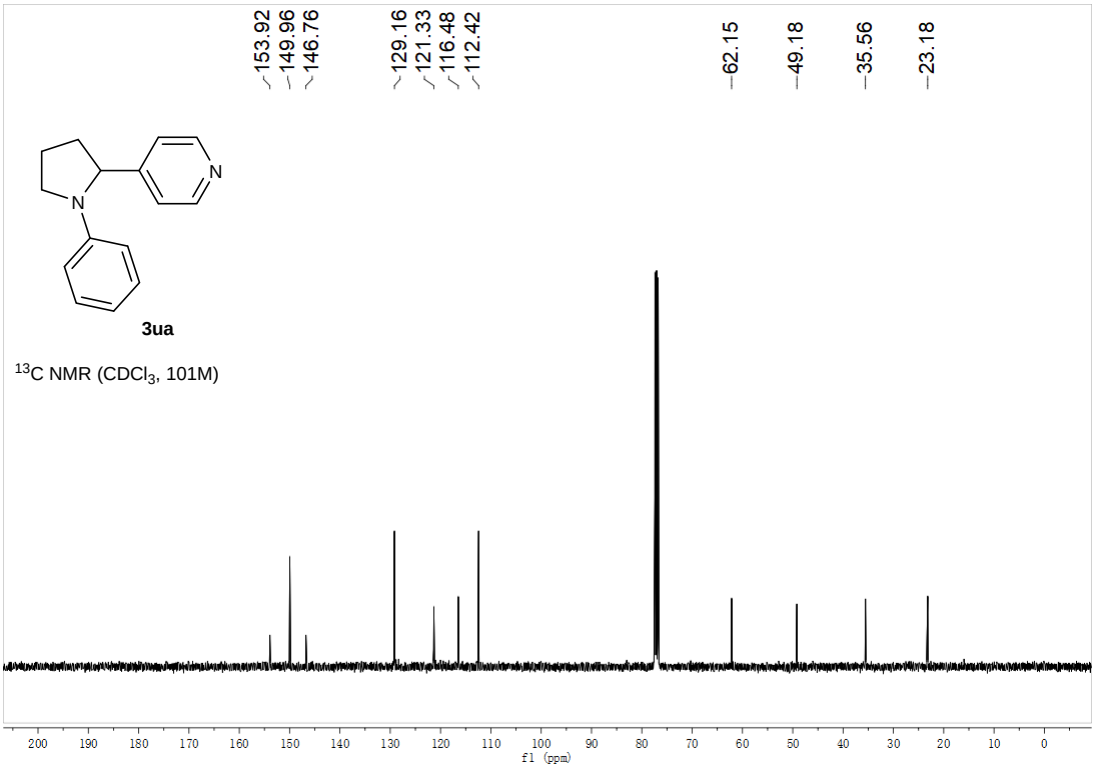
3ta

^{13}C NMR ($CDCl_3$, 101M)



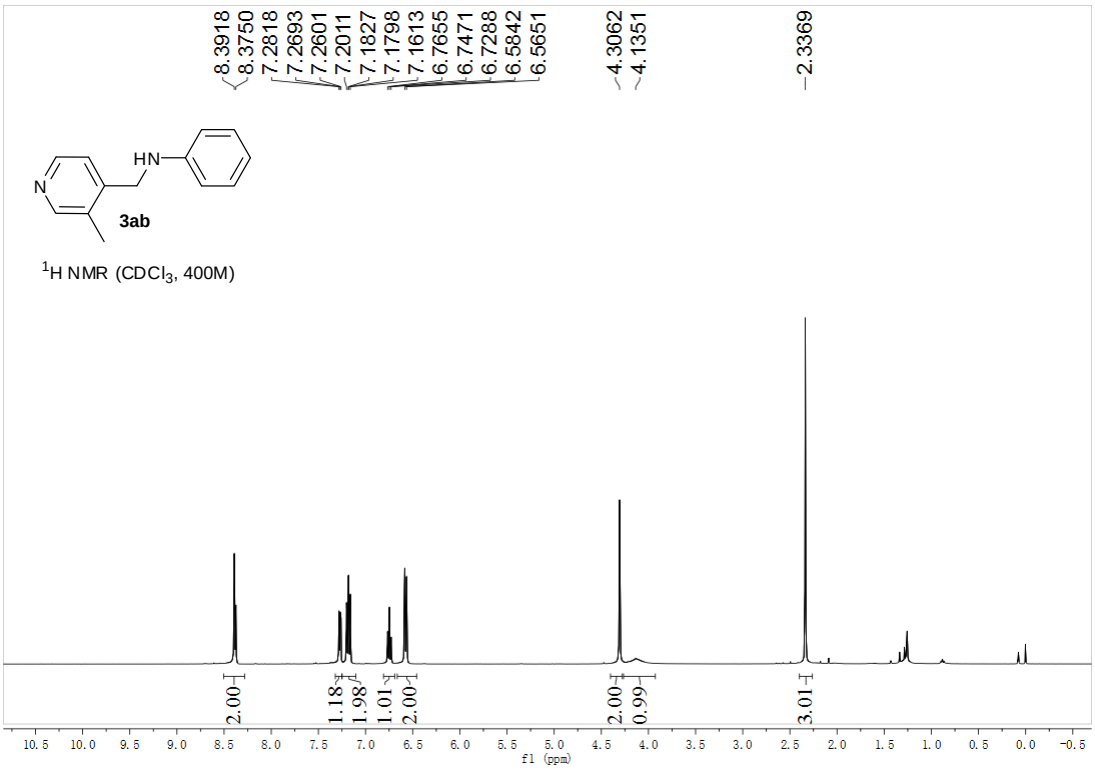
3ua

^{1}H NMR ($CDCl_3$, 400M)

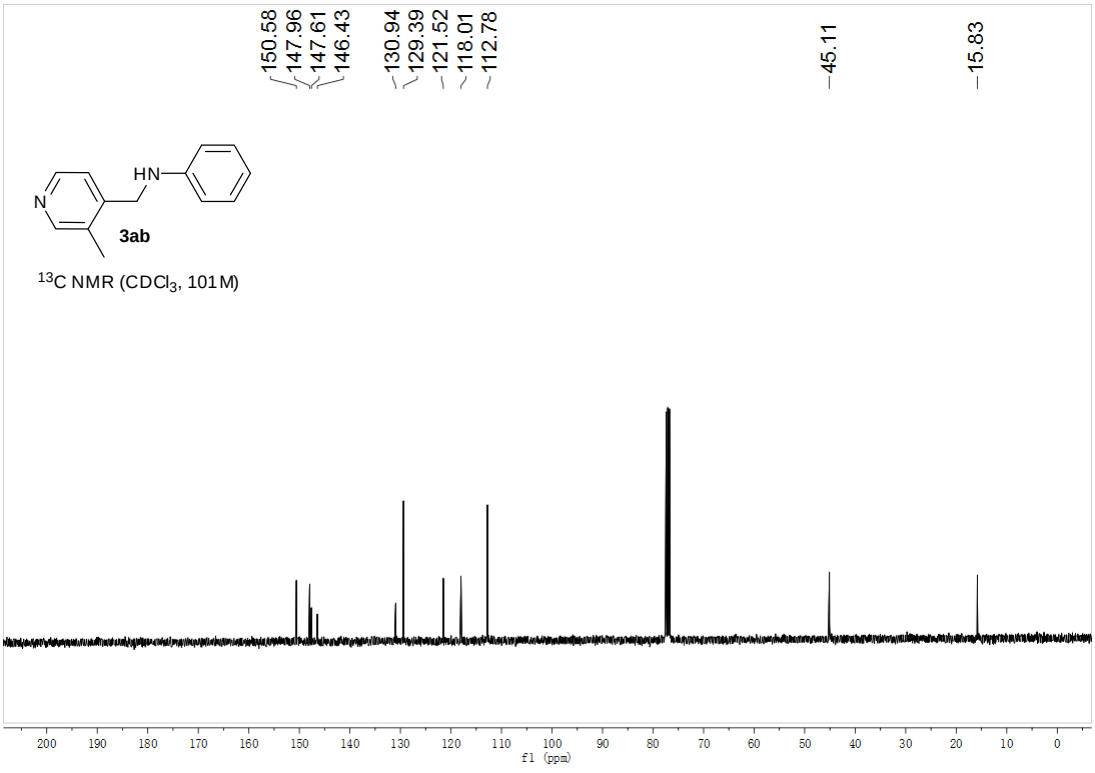


3ua

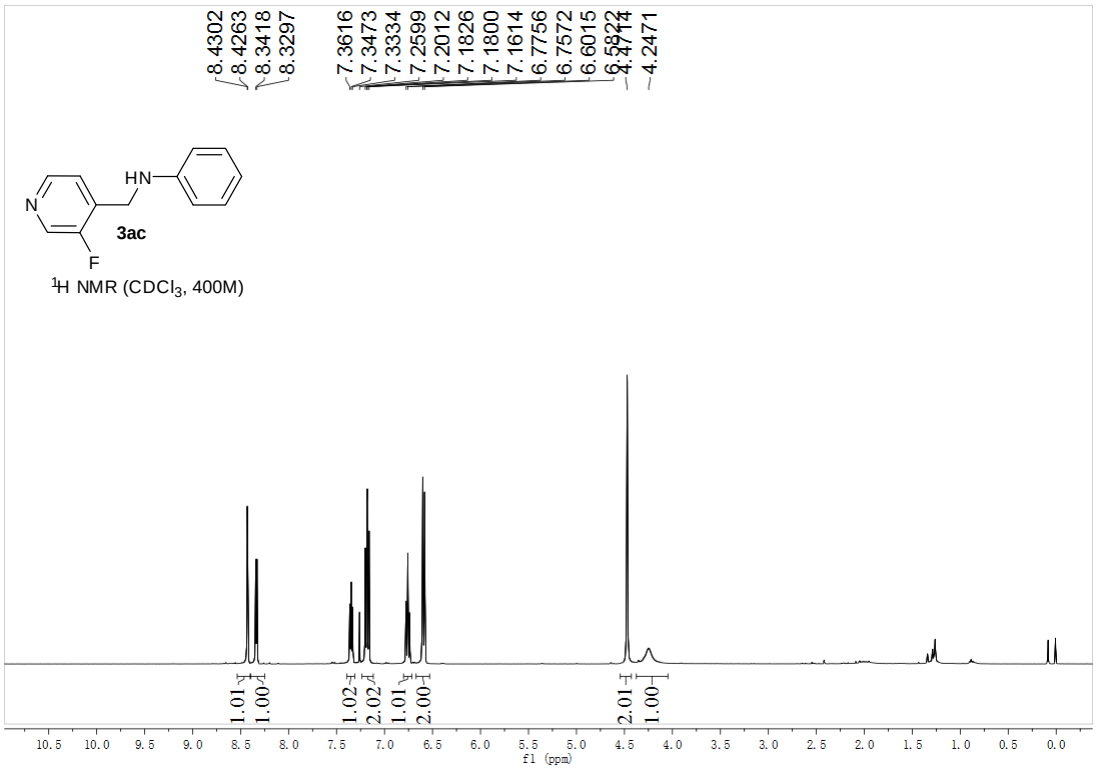
^{13}C NMR ($CDCl_3$, 101M)

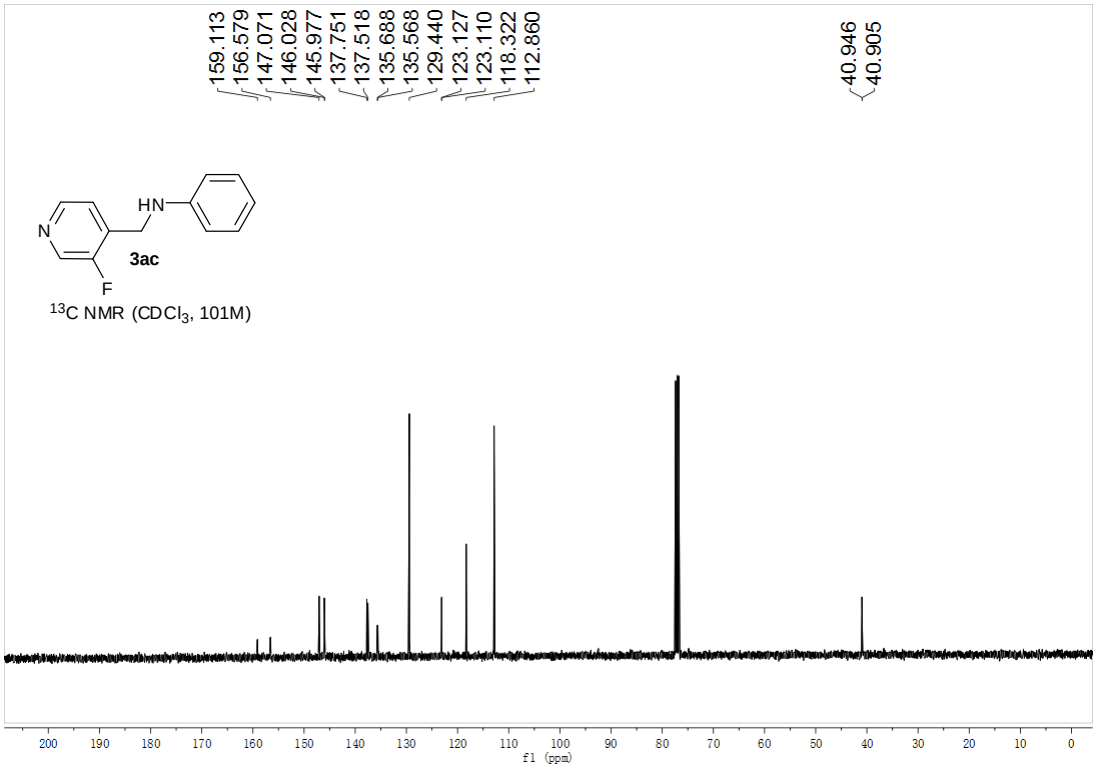


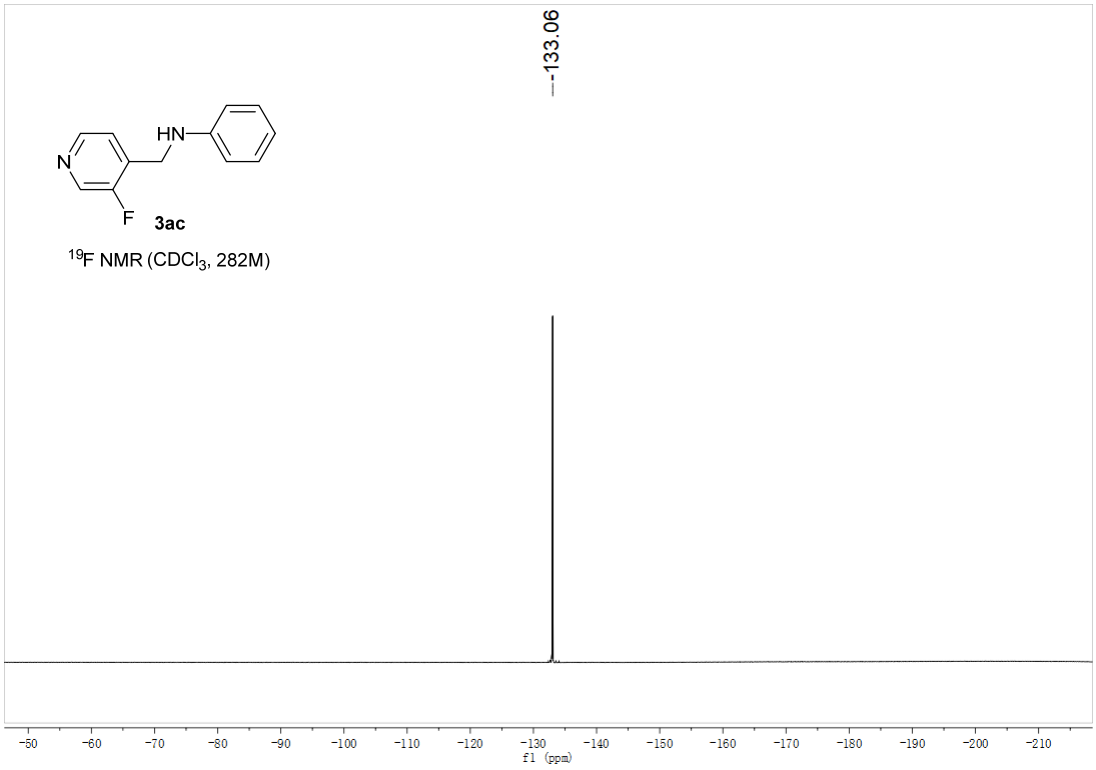
^{1}H NMR ($CDCl_3$, 400M)

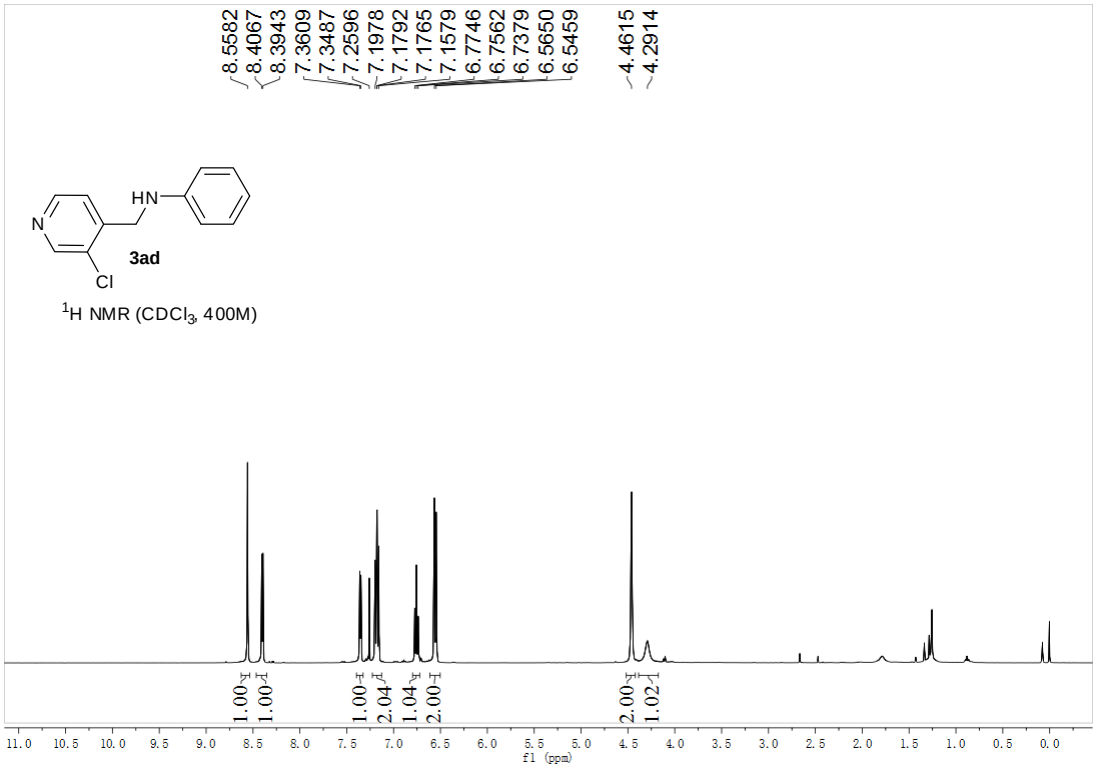


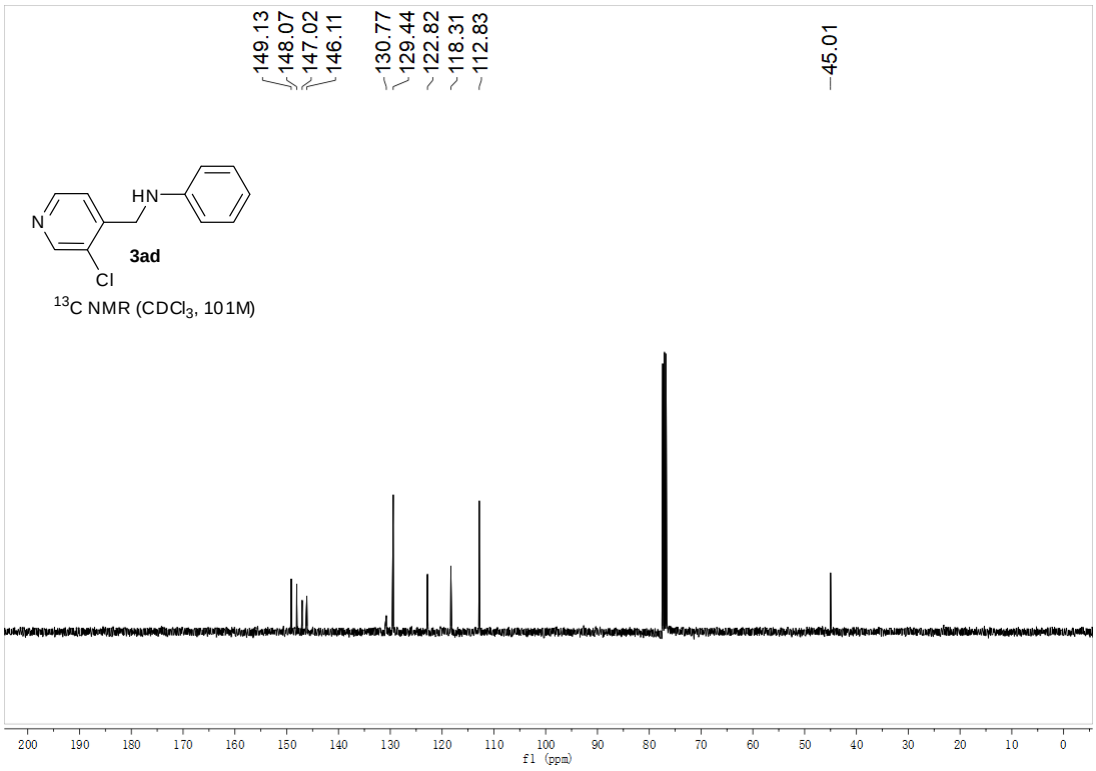
^{13}C NMR ($CDCl_3$, 101M)

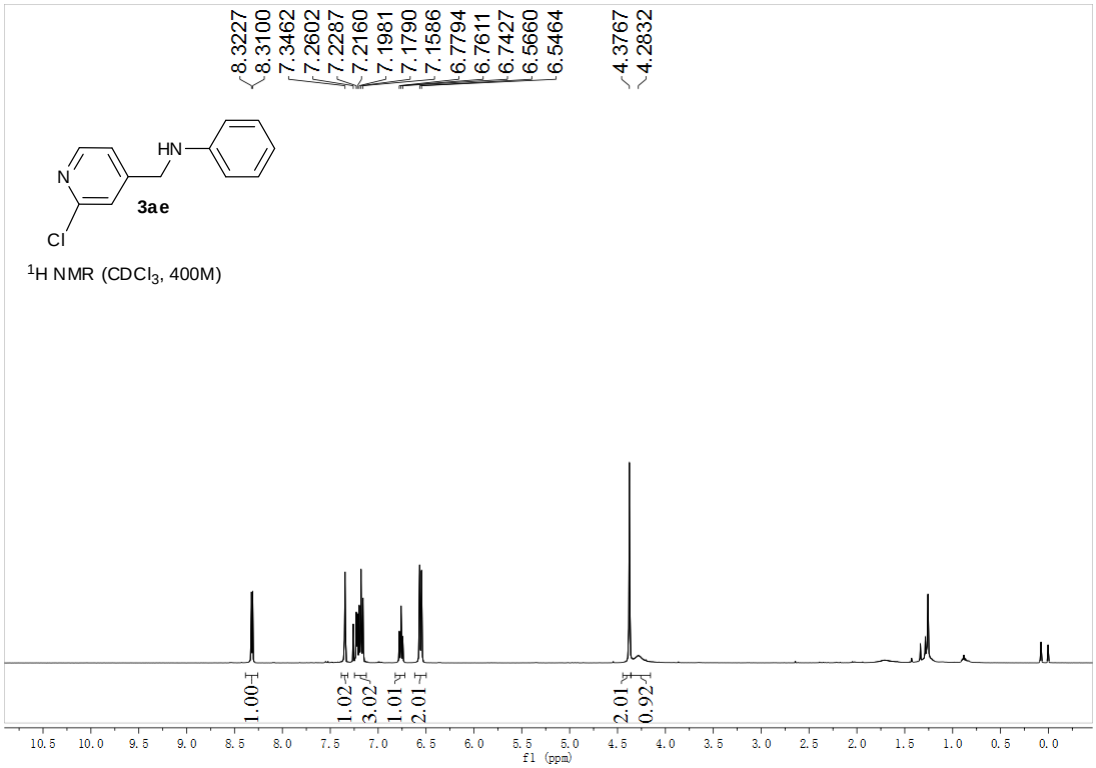

8.4302
8.4263
8.3418
8.3297
7.3616
7.3473
7.3334
7.2599
7.2012
7.1826
7.1800
7.1614
6.7756
6.7572
6.6015
6.5822
4.4714
4.2471
HN
N
F
3ac
1H NMR (CDCl3, 400M)
1.01
1.00
1.02
2.02
1.01
2.00
2.01
1.00
f1 (ppm)

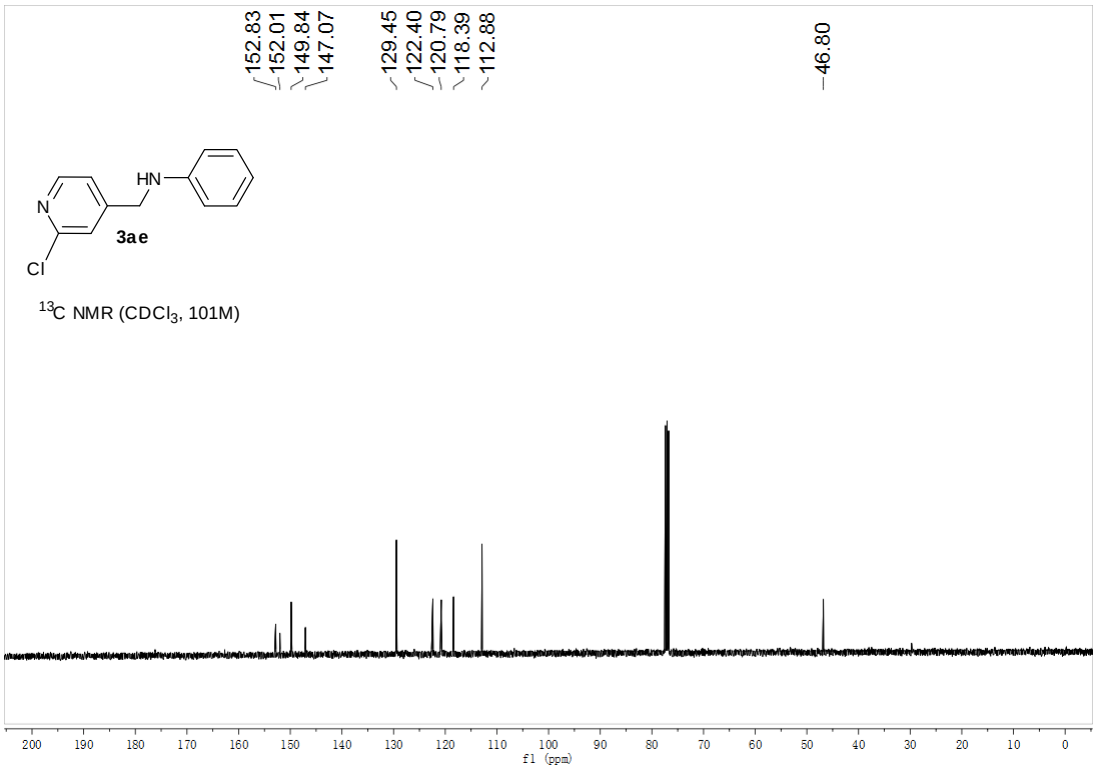

159.113
156.579
147.071
146.028
145.977
137.751
137.518
135.688
135.568
129.440
123.127
123.110
118.322
112.860
40.946
40.905
HN
N
F
3ac
13C NMR (CDCl3, 101M)
f1 (ppm)

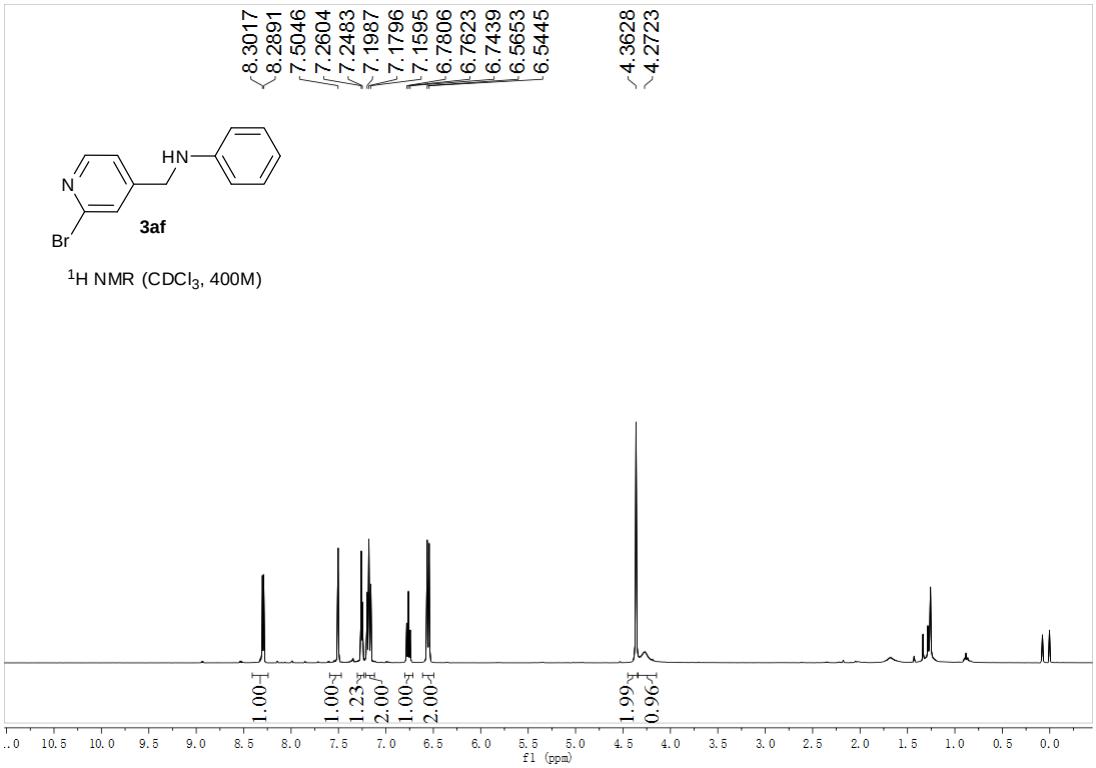

-133.06
HN
N
F
3ac
^{19}F NMR ($CDCl_3$, 282M)
f1 (ppm)

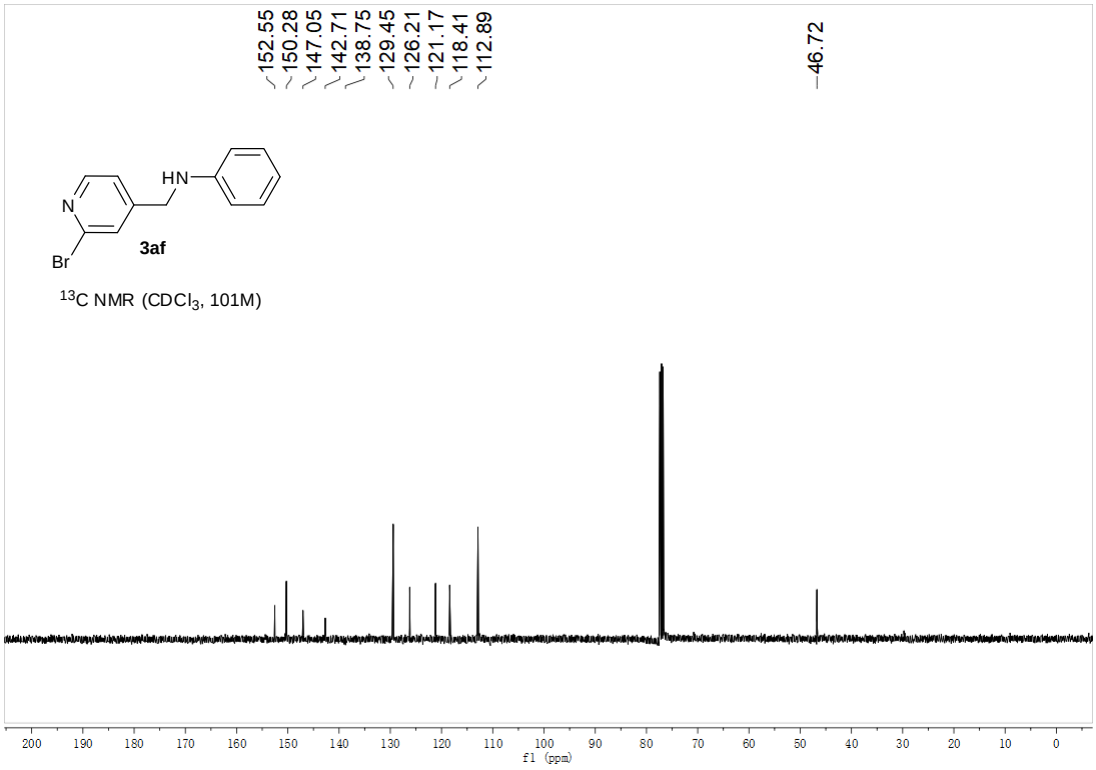

8.5582
8.4067
8.3943
7.3609
7.3487
7.2596
7.1978
7.1792
7.1765
7.1579
6.7746
6.7562
6.7379
6.5650
6.5459
4.4615
4.2914
HN
N
Cl
3ad
^{1}H NMR ($CDCl_3$, 400M)
1.00
1.00
1.00
2.04
1.04
2.00
2.00
1.02
f1 (ppm)

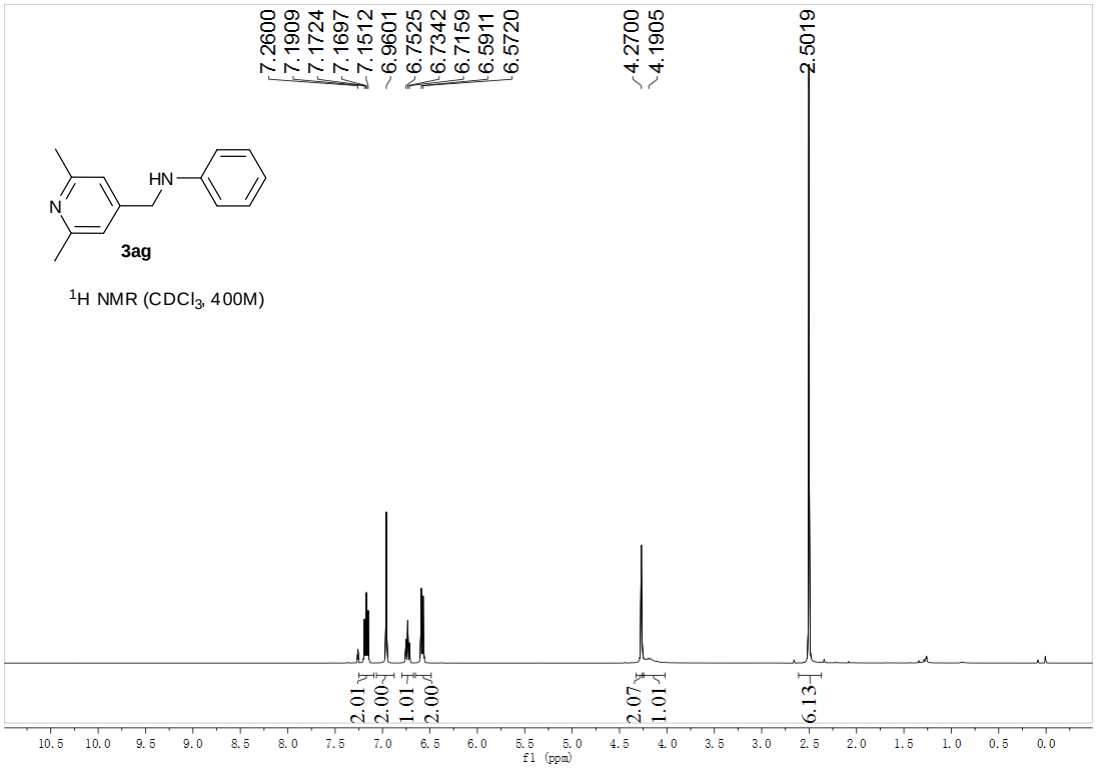

149.13
148.07
147.02
146.11
130.77
129.44
122.82
118.31
112.83
45.01
HN
N
Cl
3ad
^{13}C NMR ($CDCl_3$, 101M)
f1 (ppm)

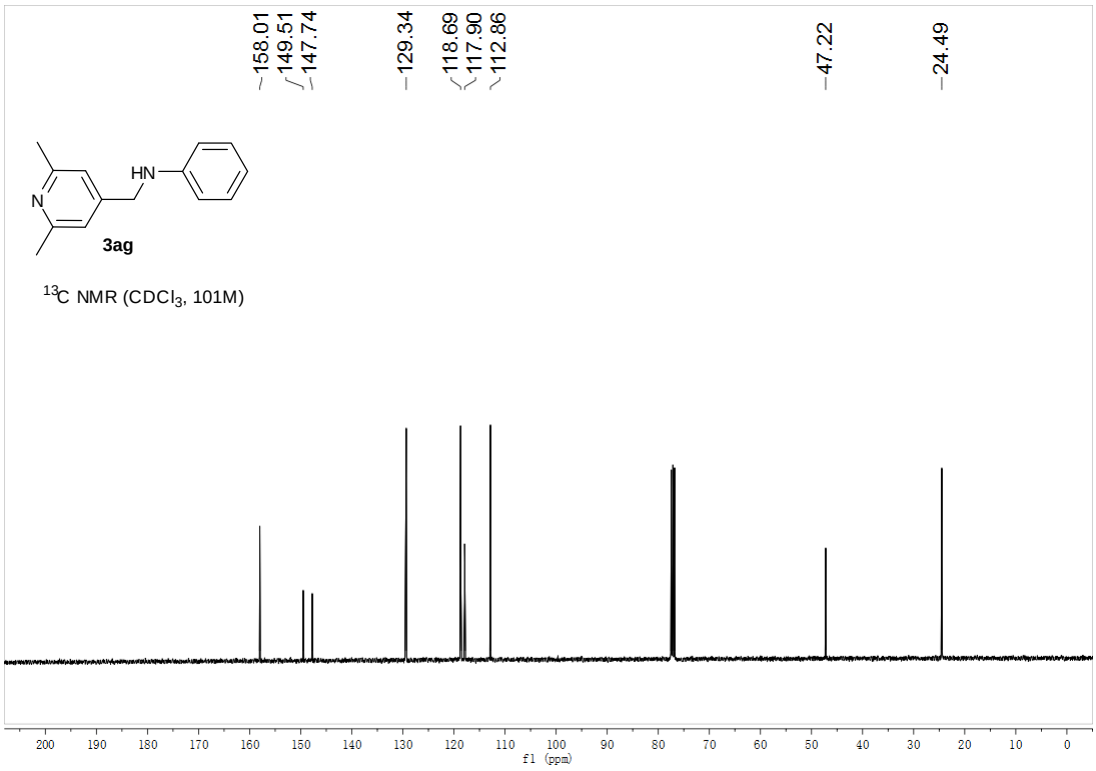

8.3227
8.3100
7.3462
7.2602
7.2287
7.2160
7.1981
7.1790
7.1586
6.7794
6.7611
6.7427
6.5660
6.5464
4.3767
4.2832
HN
N
Cl
3ae
^{1}H NMR ($CDCl_3$, 400M)
1.00
1.02
3.02
1.01
2.01
2.01
0.92
f1 (ppm)

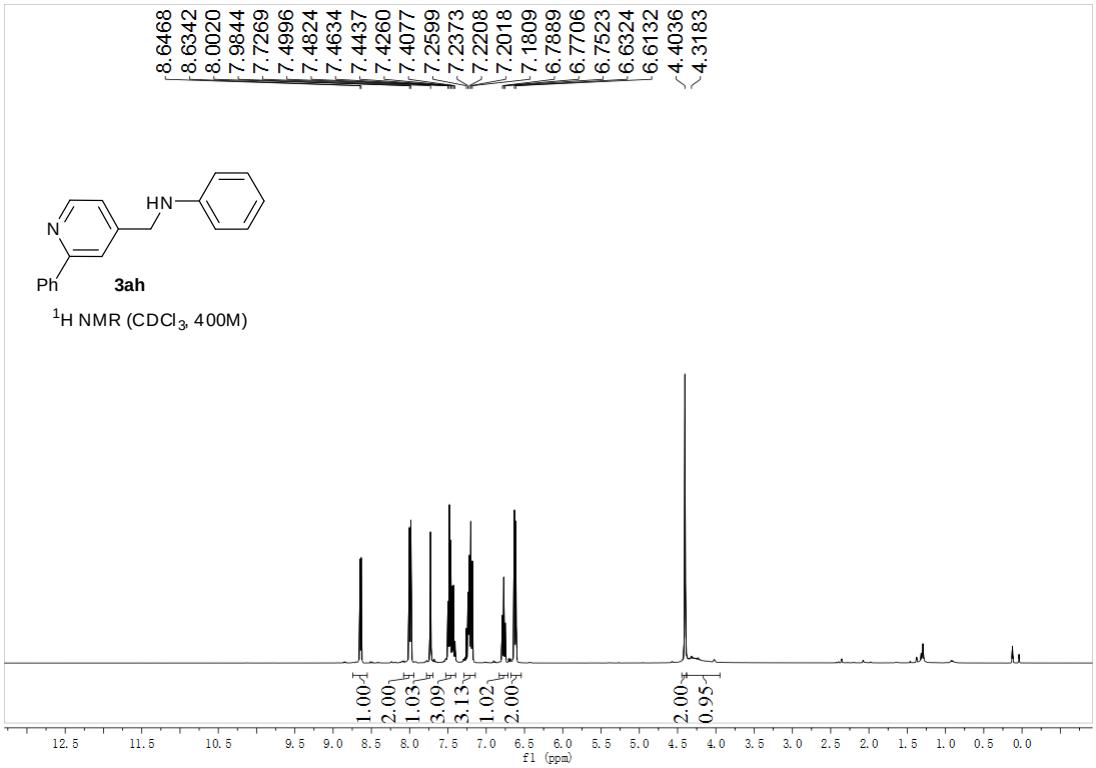

152.83
152.01
149.84
147.07
129.45
122.40
120.79
118.39
112.88
46.80
HN
N
Cl
3ae
^{13}C NMR (CDCl$_3$, 101M)
f1 (ppm)

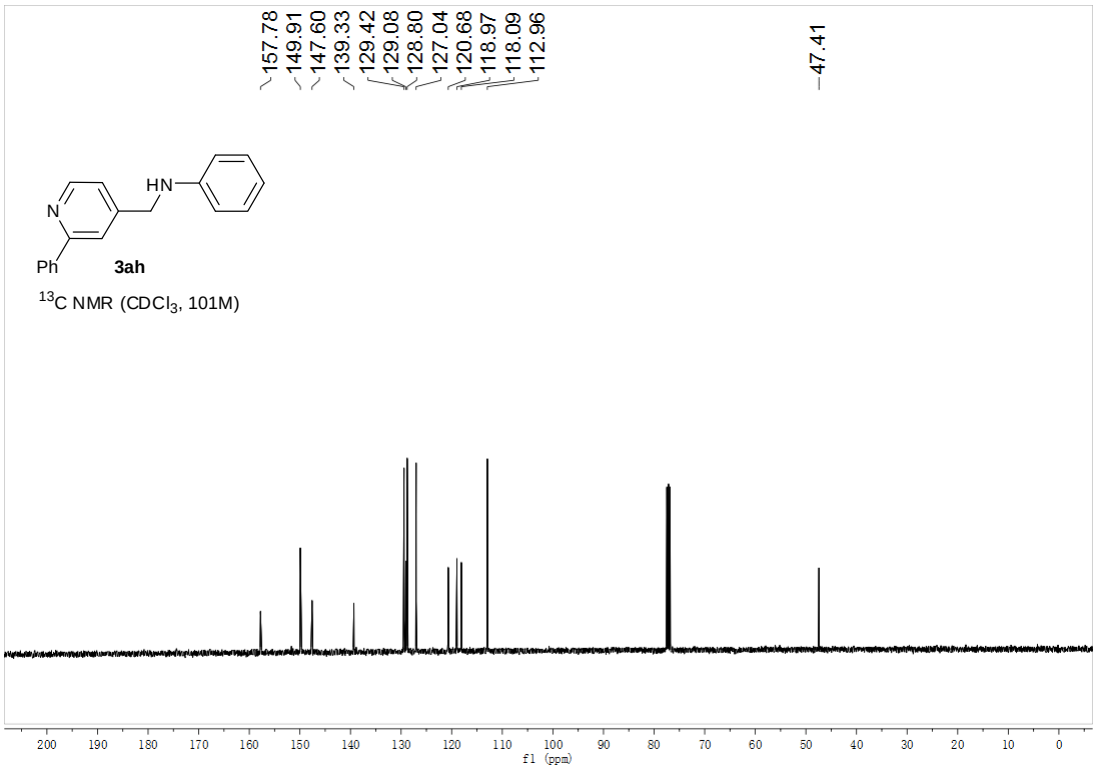

8.3017
8.2891
7.5046
7.2604
7.2483
7.1987
7.1796
7.1595
6.7806
6.7623
6.7439
6.5653
6.5445
4.3628
4.2723
HN
N
Br
3af
^{1}H NMR (CDCl$_3$, 400M)
1.00
1.00
1.23
2.00
1.00
2.00
1.99
0.96
f1 (ppm)

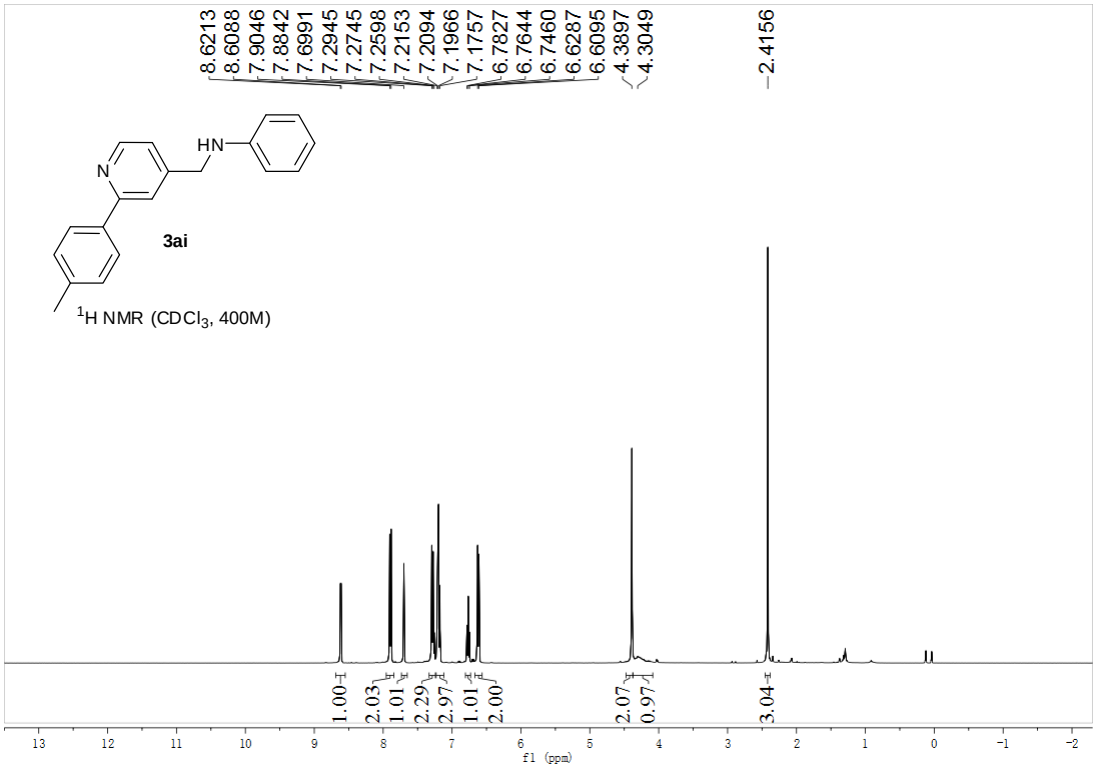

152.55
150.28
147.05
142.71
138.75
129.45
126.21
121.17
118.41
112.89
46.72
HN
N
Br
3af
13C NMR (CDCl3, 101M)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

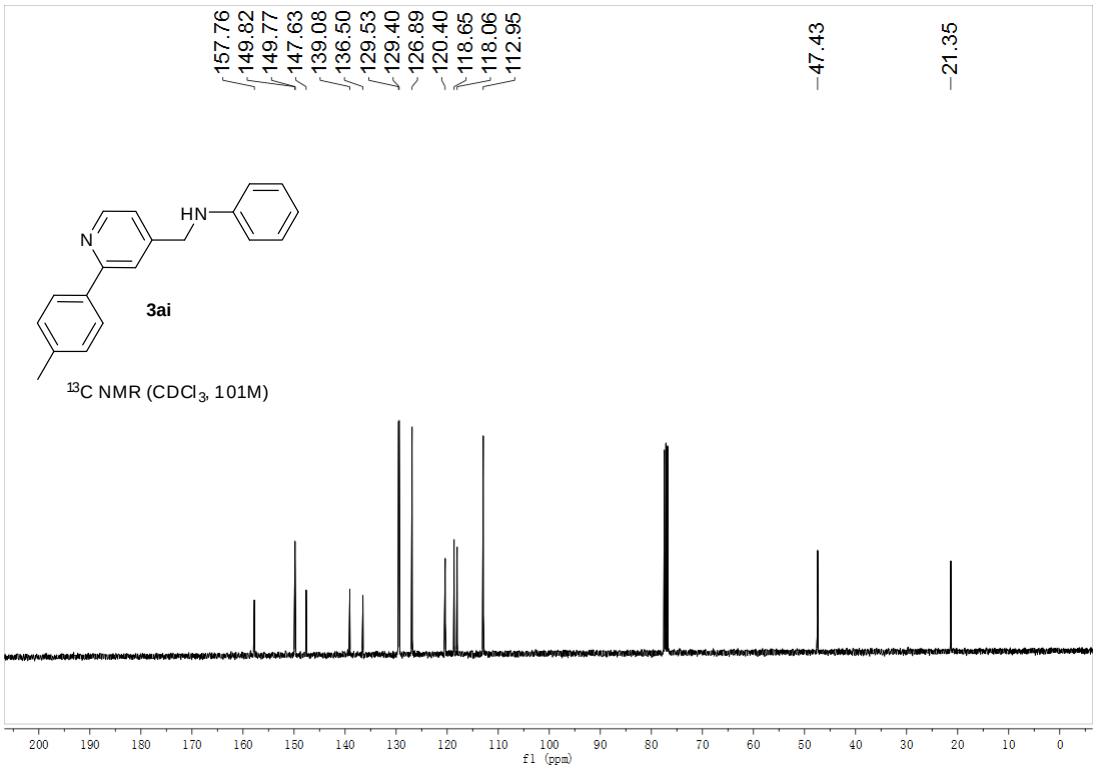

7.2600
7.1909
7.1724
7.1697
7.1512
6.9601
6.7525
6.7342
6.7159
6.5911
6.5720
4.2700
4.1905
2.5019
HN
N
3ag
1H NMR (CDCl3, 400M)
2.01
2.00
1.01
2.00
2.07
1.01
6.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

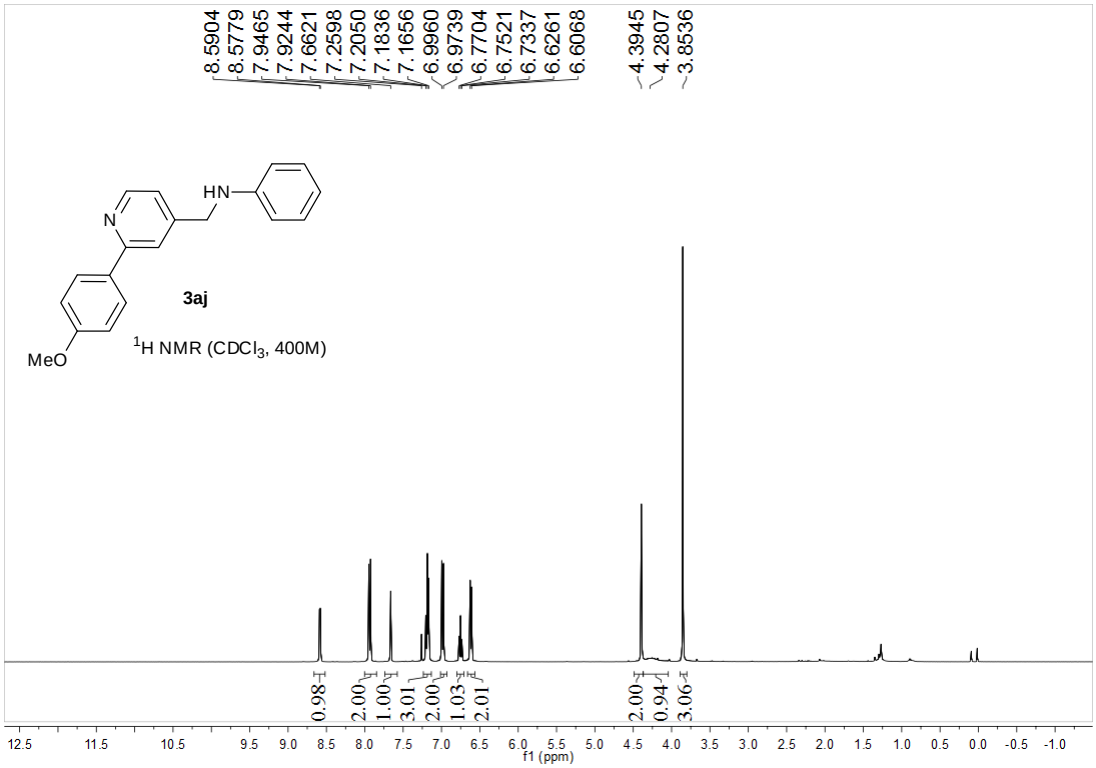

158.01
149.51
147.74
129.34
118.69
117.90
112.86
47.22
24.49
HN
N
3ag
13C NMR (CDCl3, 101M)
f1 (ppm)


8.6468
8.6342
8.0020
7.9844
7.7269
7.4996
7.4824
7.4634
7.4437
7.4260
7.4077
7.2599
7.2373
7.2208
7.2018
7.1809
7.7889
7.7706
7.7523
6.6324
6.6132
4.4036
4.3183
HN
N
Ph
3ah
1H NMR (CDCl3, 400M)
1.00
2.00
1.03
3.09
3.13
1.02
2.00
2.00
0.95
f1 (ppm)


157.78
149.91
147.60
139.33
129.42
129.08
128.80
127.04
120.68
118.97
118.09
112.96
47.41
HN
N
Ph
3ah
13C NMR (CDCl3, 101M)
f1 (ppm)


8.6213
8.6088
7.9046
7.8842
7.6991
7.2945
7.2745
7.2598
7.2153
7.2094
7.1966
7.1757
6.7827
6.7644
6.7460
6.6287
6.6095
4.3897
4.3049
2.4156
HN
N
3ai
1H NMR (CDCl3, 400M)
1.00
2.03
1.01
2.29
2.97
1.01
2.00
2.07
0.97
3.04
f1 (ppm)


157.76
149.82
149.77
147.63
139.08
136.50
129.53
129.40
126.89
120.40
118.65
118.06
112.95
47.43
21.35
HN
N
3ai
13C NMR (CDCl3, 101M)
f1 (ppm)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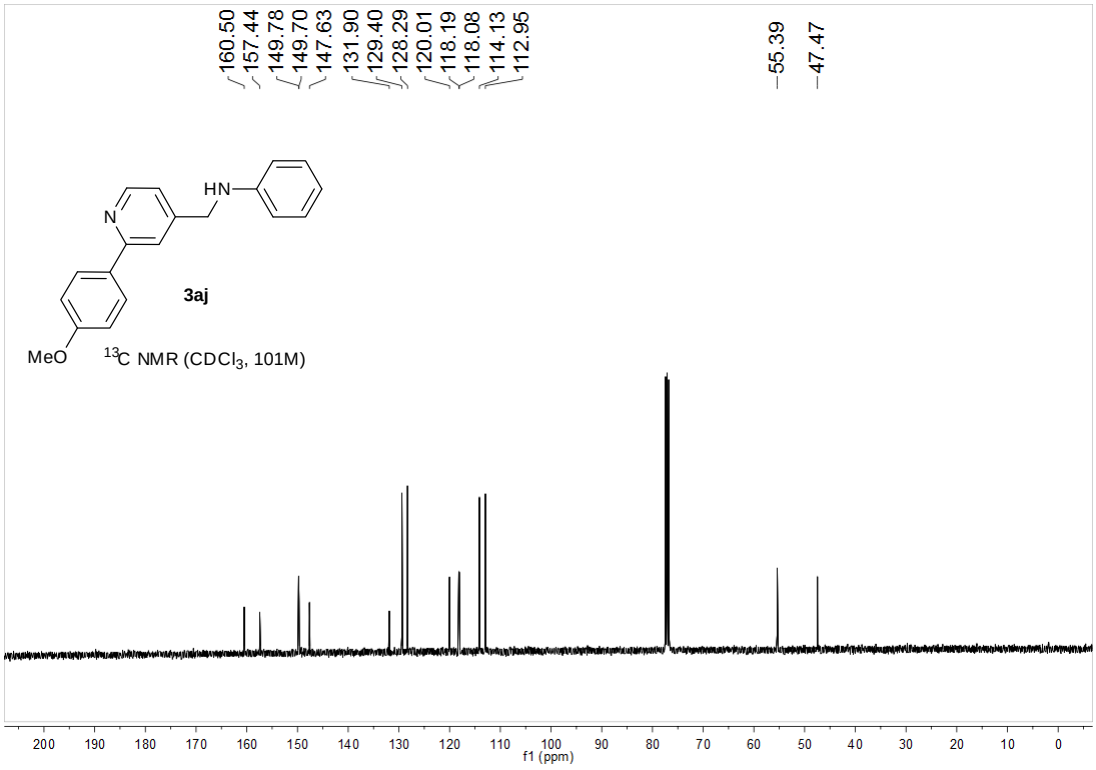
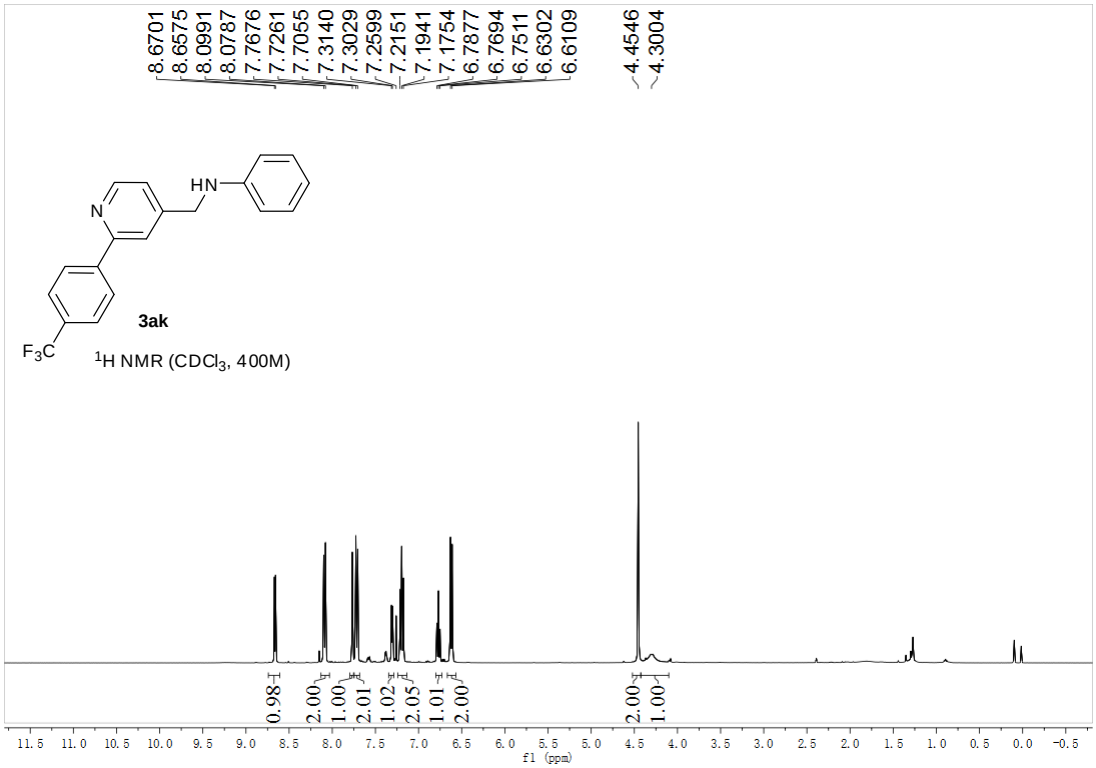
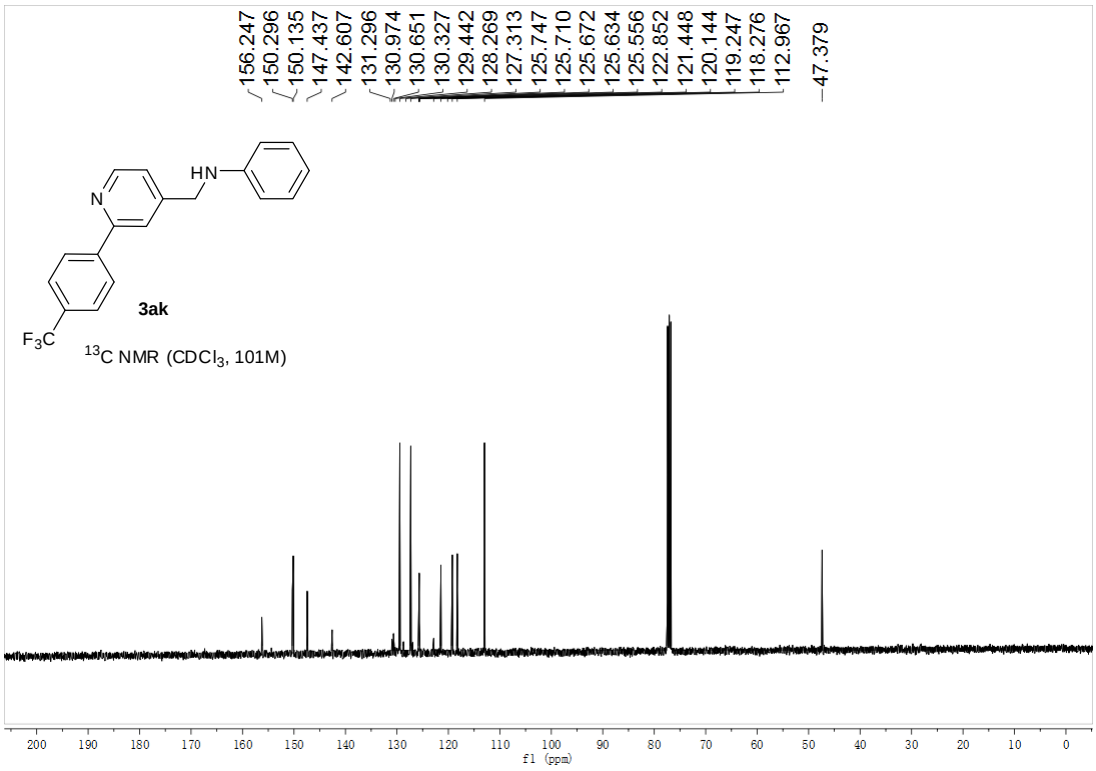
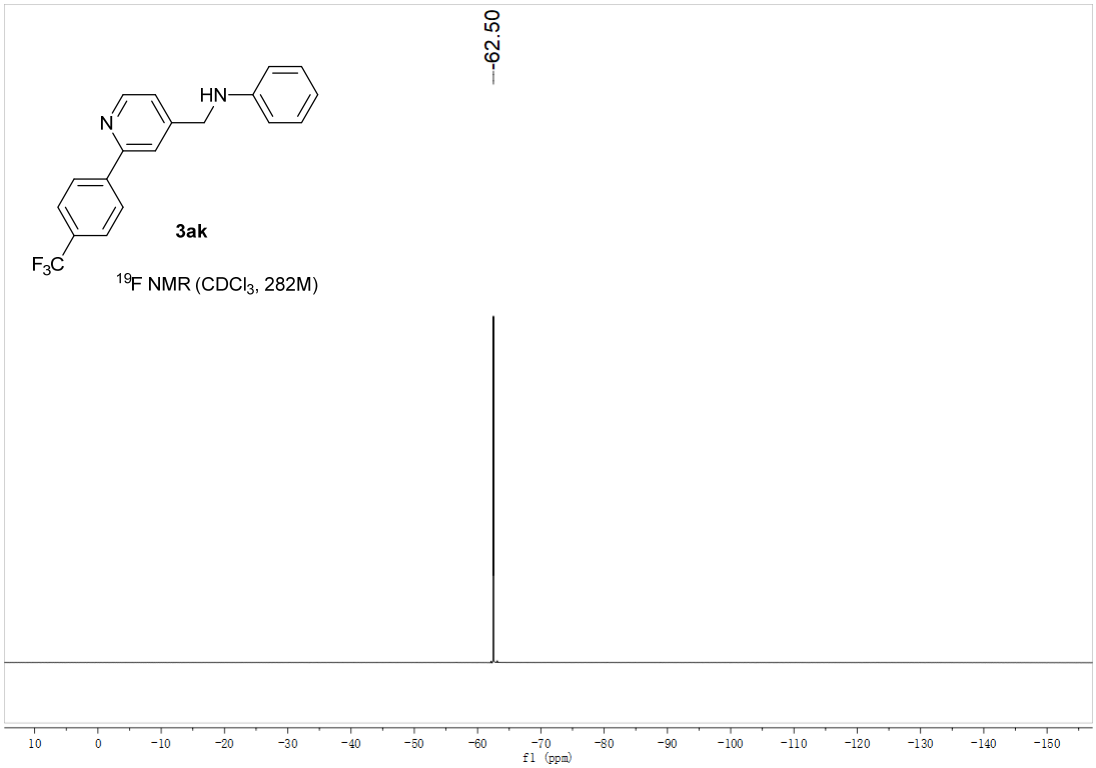
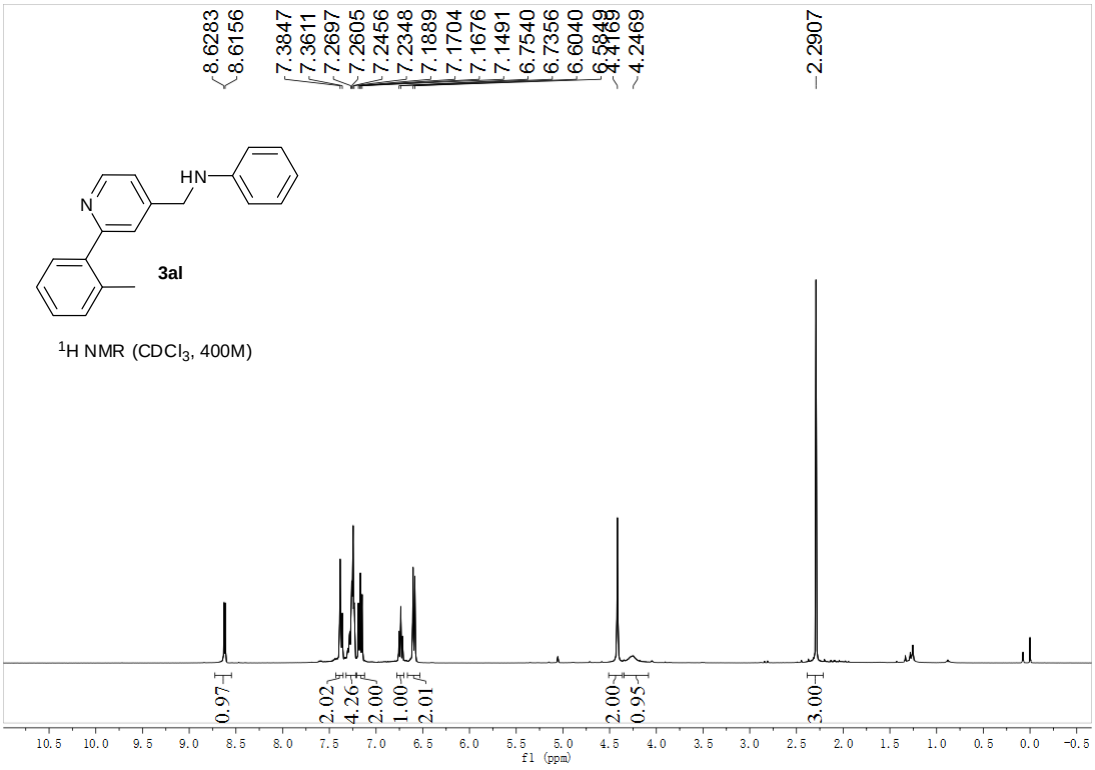
8.5779
7.9465
7.9244
7.6621
7.2598
7.2050
7.1836
7.1656
6.9960
6.9739
6.7704
6.7521
6.7337
6.6261
6.6068
4.3945
4.2807
3.8536
HN
N
MeO
3aj
1H NMR (CDCl3, 400M)
0.98
2.00
1.00
3.01
2.00
1.03
2.01
2.00
0.94
3.06
f1 (ppm)


160.50
157.44
149.78
149.70
147.63
131.90
129.40
128.29
120.01
118.19
118.08
114.13
112.95
55.39
47.47
HN
N
MeO
3aj
13C NMR (CDCl3, 101M)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

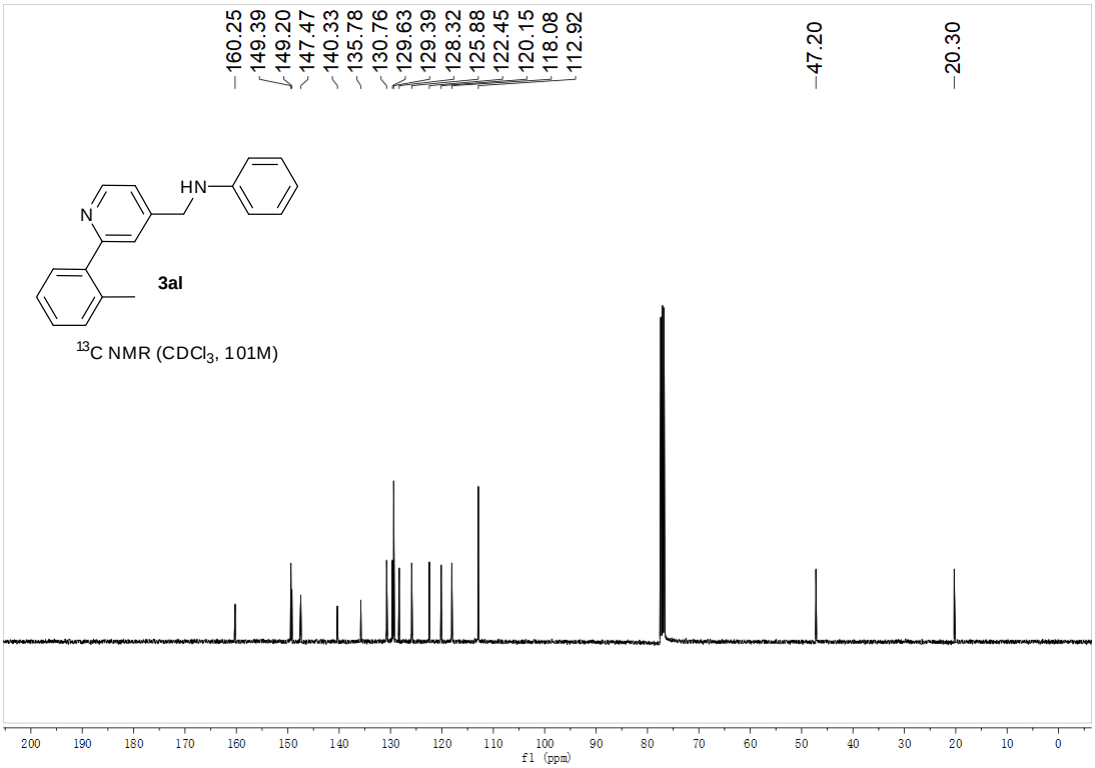

8.6701
8.6575
8.0991
8.0787
7.7676
7.7261
7.7055
7.3140
7.3029
7.2599
7.2151
7.1941
7.1754
6.7877
6.7694
6.7511
6.6302
6.6109
4.4546
4.3004
HN
N
F3C
3ak
1H NMR (CDCl3, 400M)
0.98
2.00
1.00
2.01
1.02
2.05
1.01
2.00
2.00
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


156.247
150.296
150.135
147.437
142.607
131.296
130.974
130.651
130.327
129.442
128.269
127.313
125.747
125.710
125.672
125.634
125.556
122.852
121.448
120.144
119.247
118.276
112.967
47.379
HN
N
3ak
F3C
13C NMR (CDCl3, 101M)
f1 (ppm)

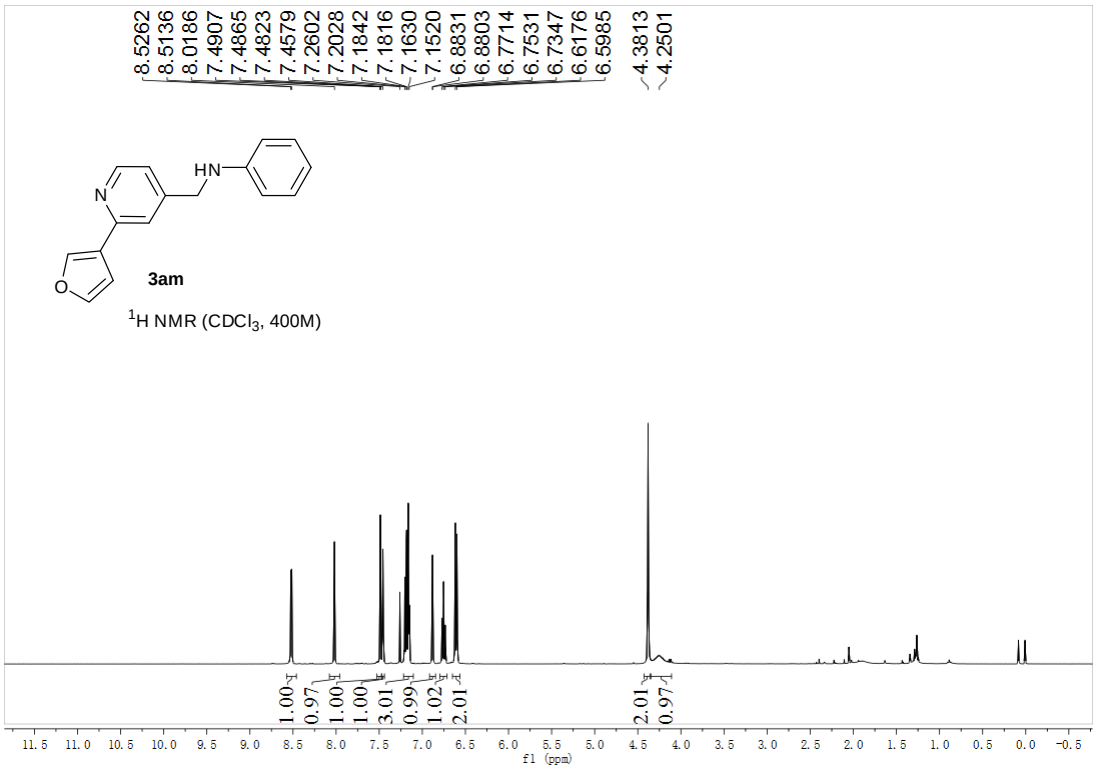

-62.50
HN
N
3ak
F3C
19F NMR (CDCl3, 282M)
f1 (ppm)



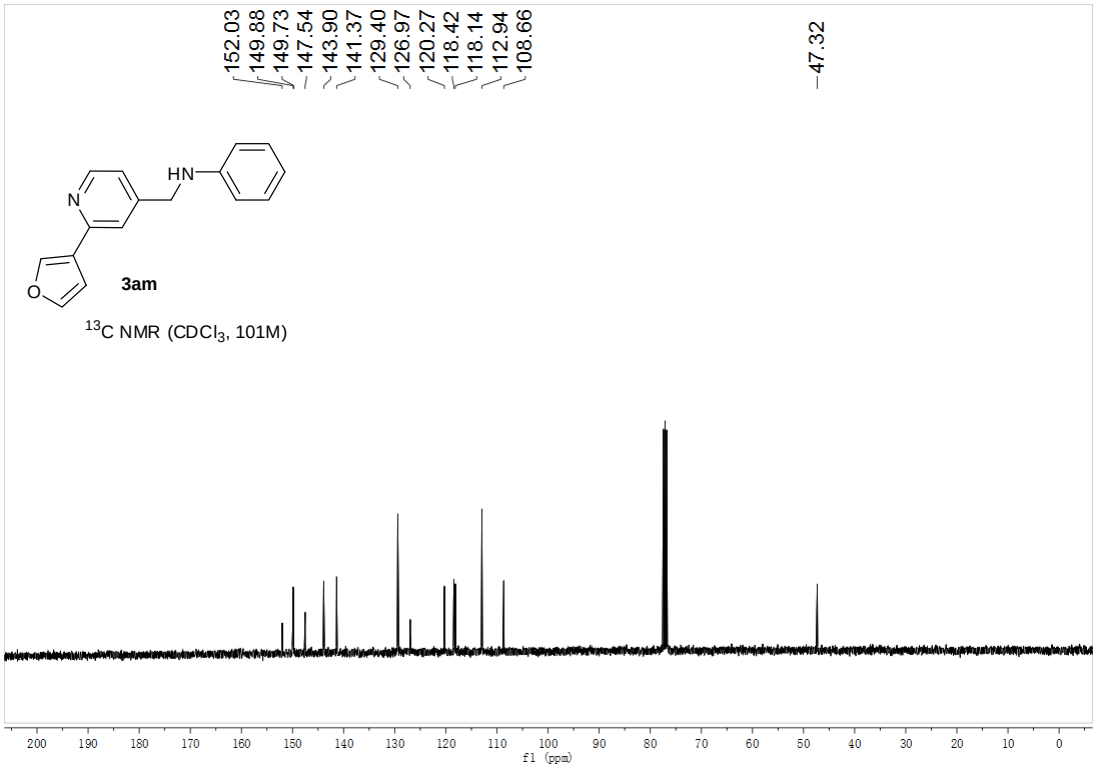
^{1}H NMR ($CDCl_3$, 400M)



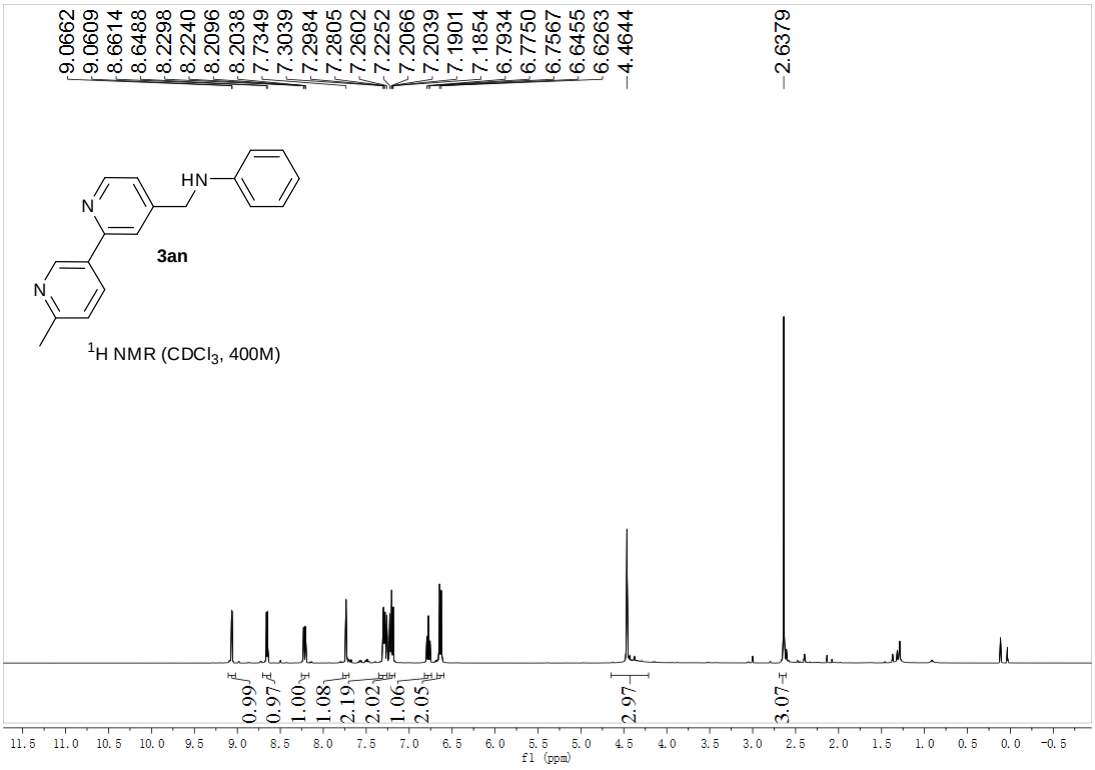
^{13}C NMR ($CDCl_3$, 101M)

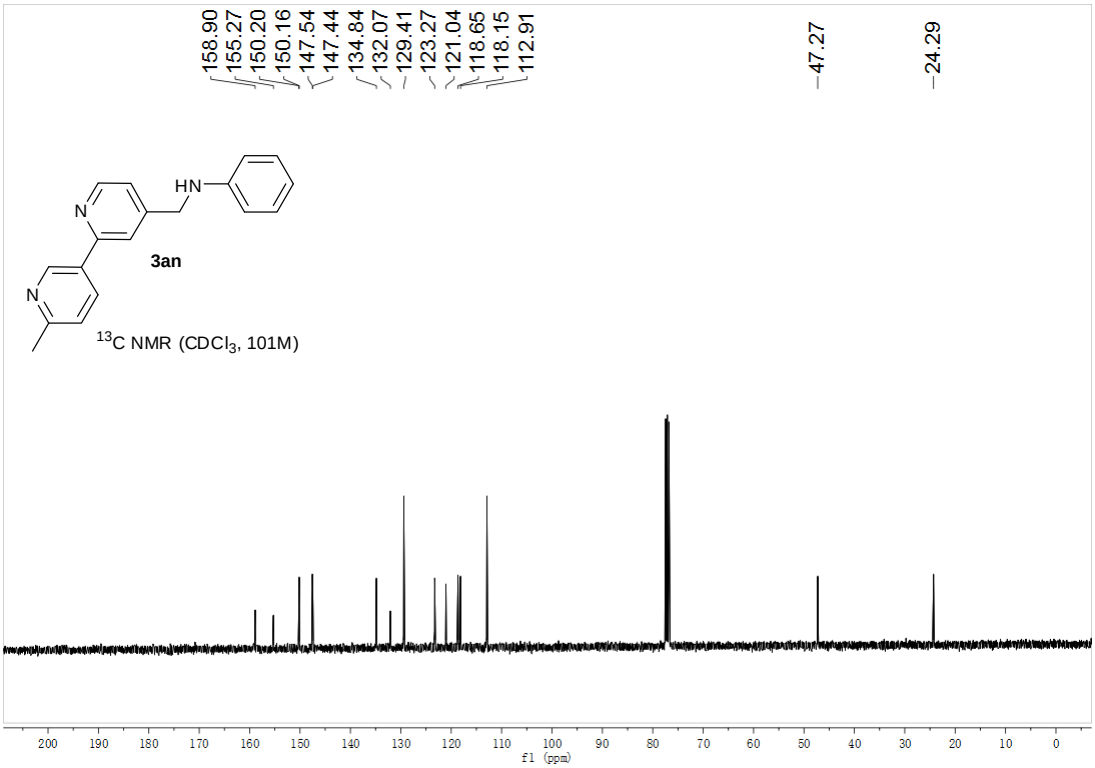


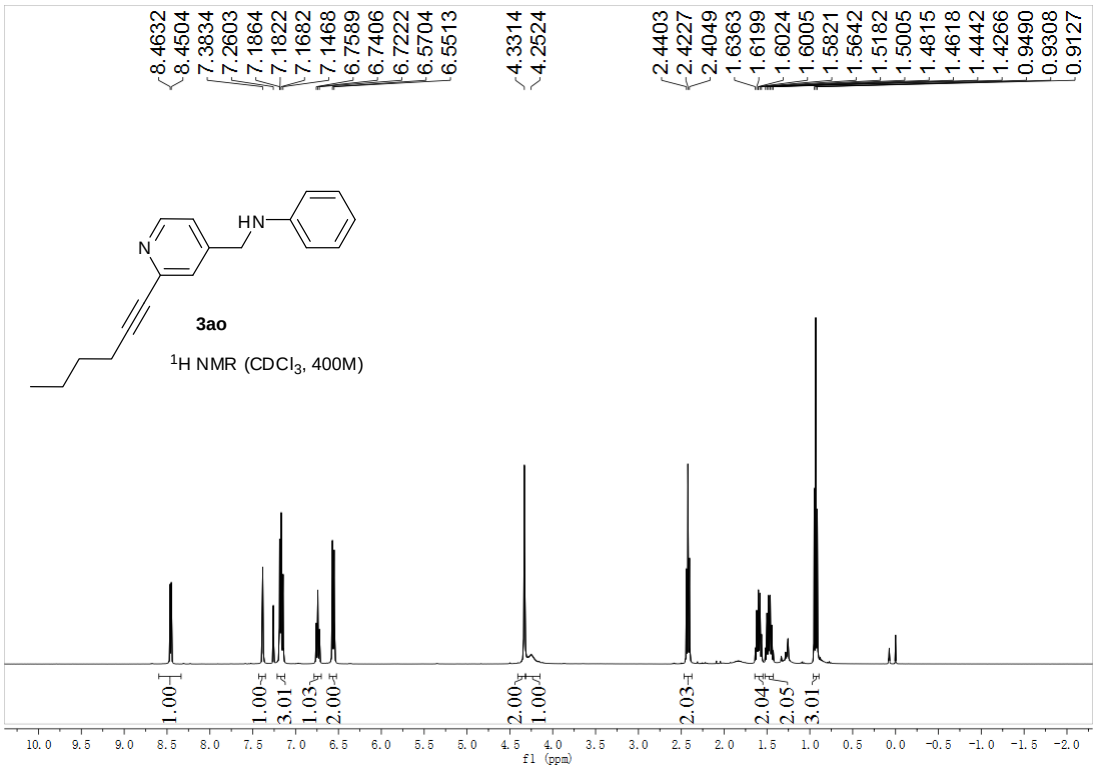
^{1}H NMR ($CDCl_3$, 400M)

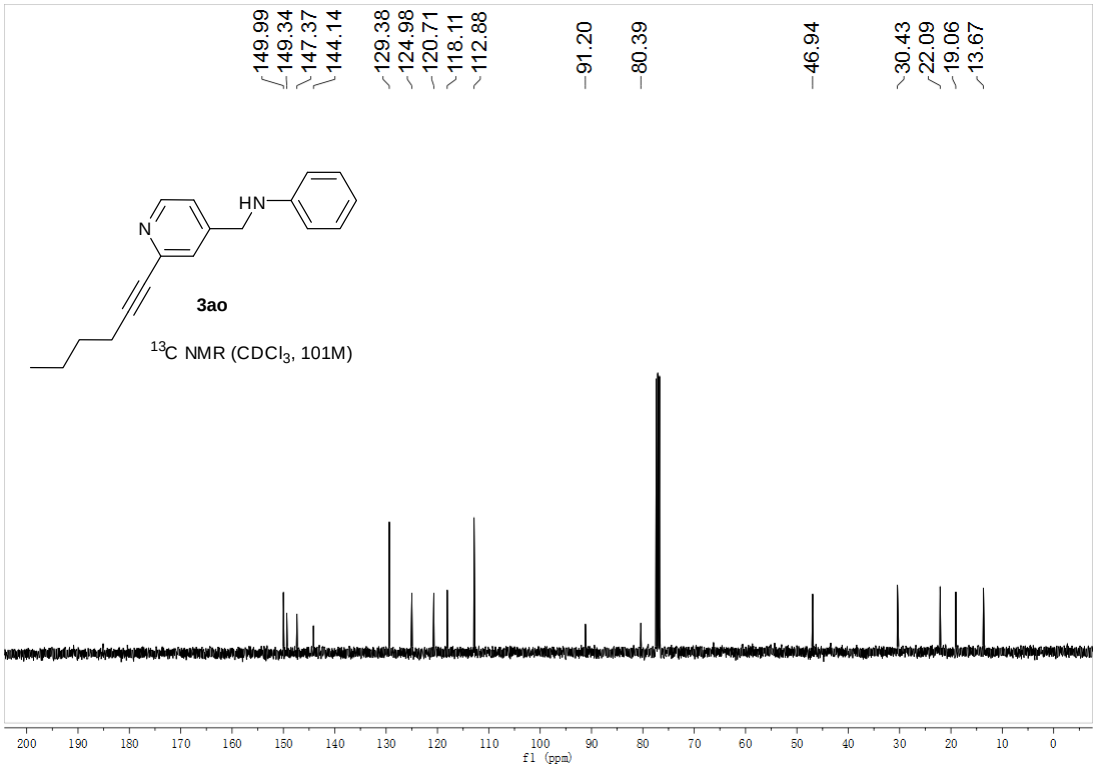


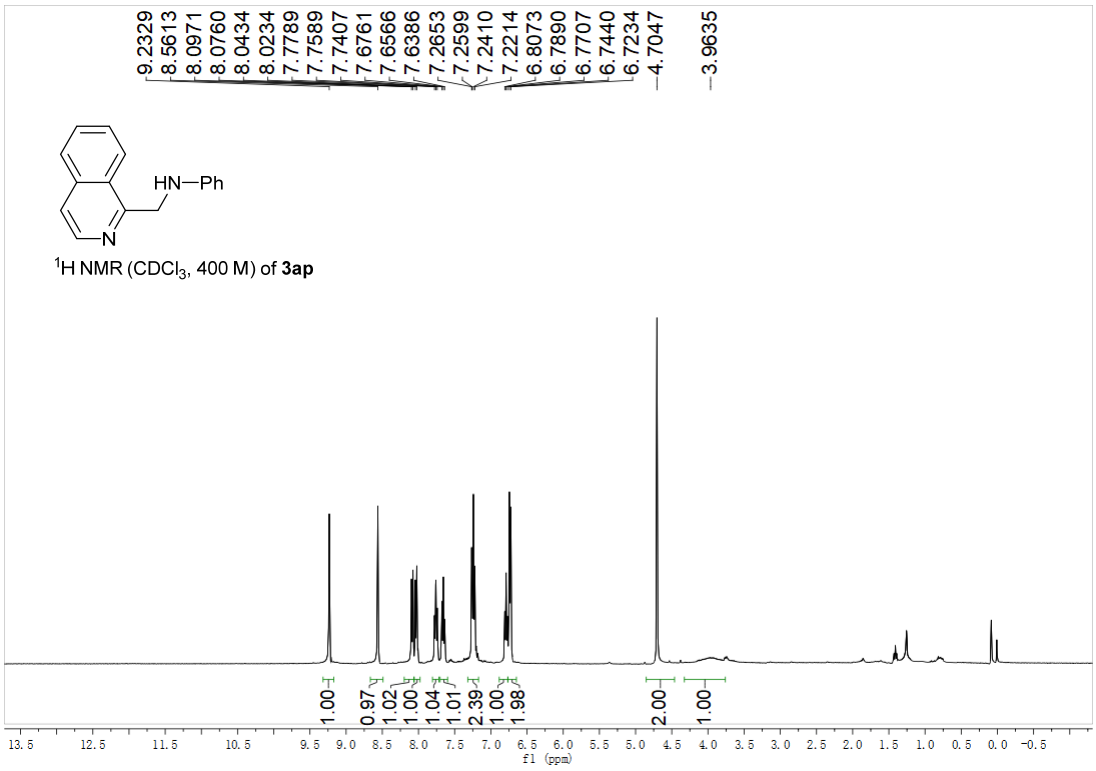
^{13}C NMR ($CDCl_3$, 101M)


9.0662
9.0609
8.6614
8.6488
8.2298
8.2240
8.2096
8.2038
7.7349
7.3039
7.2984
7.2805
7.2602
7.2252
7.2066
7.2039
7.1901
7.1854
6.7934
6.7750
6.7567
6.6455
6.6263
4.4644
2.6379
HN
N
N
3an
1H NMR (CDCl3, 400M)
0.99
0.97
1.00
1.08
2.19
2.02
1.06
2.05
2.97
3.07
f1 (ppm)

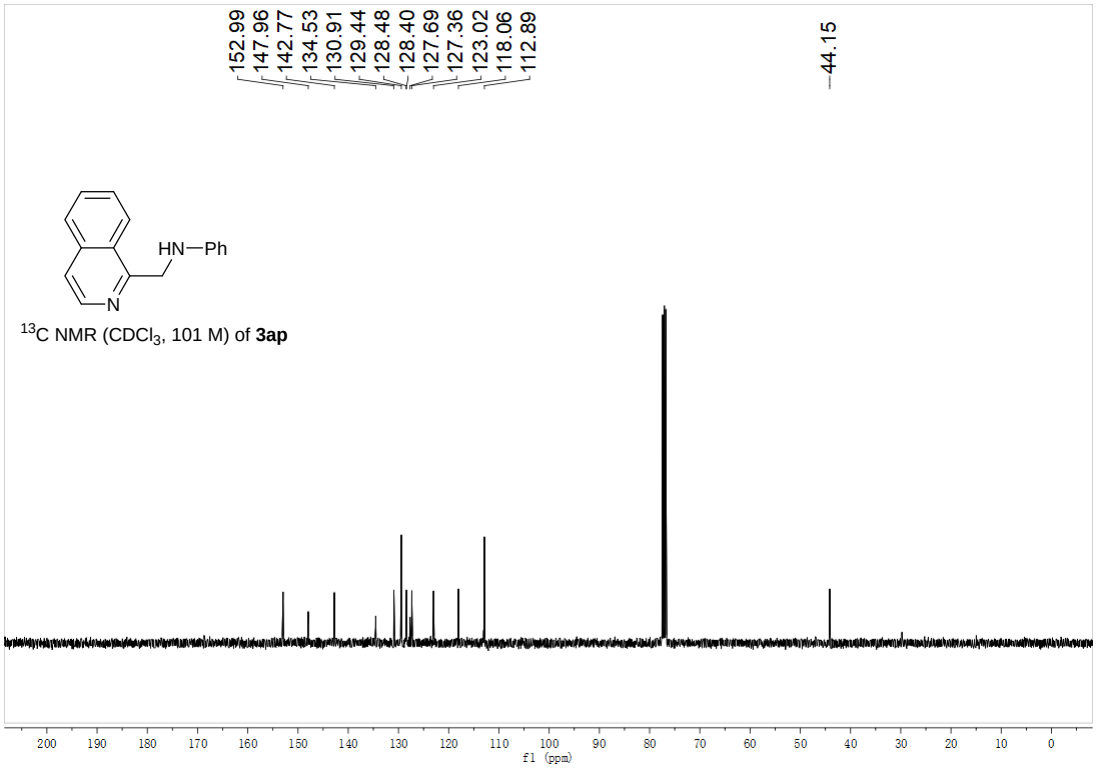

158.90
155.27
150.20
150.16
147.54
147.44
134.84
132.07
129.41
123.27
121.04
118.65
118.15
112.91
47.27
24.29
HN
N
N
3an
13C NMR (CDCl3, 101M)
f1 (ppm)


8.4632
8.4504
7.3834
7.2603
7.1864
7.1822
7.1682
7.1468
6.7589
6.7406
6.7222
6.5704
6.5513
4.3314
4.2524
2.4403
2.4227
2.4049
1.6363
1.6199
1.6024
1.6005
1.5821
1.5642
1.5182
1.5005
1.4815
1.4618
1.4442
1.4266
0.9490
0.9308
0.9127
HN
N
3ao
1H NMR (CDCl3, 400M)
1.00
1.00
3.01
1.03
2.00
2.00
1.00
2.03
2.04
2.05
3.01
f1 (ppm)


149.99
149.34
147.37
144.14
129.38
124.98
120.71
118.11
112.88
91.20
80.39
46.94
30.43
22.09
19.06
13.67
HN
N
3ao
13C NMR (CDCl3, 101M)
f1 (ppm)



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



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