

Supporting Information

Benzophenone-catalyzed alkenylative pyridylation of vinylarenes with alkenylboronic esters

Yuhui Ying, Zixiang Li, and Bin Liu*

School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi 330031, P. R. China.

*Corresponding author, E-mail: liubin@ncu.edu.cn

Table of Contents

Supporting Information	S1
1. General Information.....	S3
2. Experimental Equipments	S4
3. Synthesis of alkene	S6
Method A ^[1]	S6
4. Optimization Studies	S10
Table S1 Optimization of Time.....	S10
Table S2 Optimization of Solvent.....	S10
Table S3 Optimization of Wavelength	S11
Table S4 Optimization of concentration.....	S11
Table S5 Optimization of ratio.....	S12
Table S6 Control Experiment	S12
5. General procedures for alkene difunctionalization.....	S13
General Procedure 1	S13
6. Proposed mechanism	S14
7. Alkylboronic Esters	S15
8. Experimental data for isolated products	S16
9. Mechanistic investigation experimental procedures.....	S44
Radical trapping experiment.....	S44
10. Gram-Scale reaction.....	S45
11. NMR Spectra of Substrates and Products.....	S46
12. Reference	S106

1. General Information

All air and water-sensitive reactions were carried out in oven-dried glassware under nitrogen atmosphere using standard Schlenk manifold technique. Commercially available compounds and solvents were purchased from Leyan, Adamas-beta, Bidepharm and used as received. All reactions were followed by thin-layer chromatography (TLC) and visualized under UV light. If the reaction product is not fluorescent under UV light, it is placed in an iodine bath for 5 minutes before observation. Flash column chromatography (FCC) was carried out using silica gel (200 – 300 mesh). ^1H NMR, ^{13}C NMR, ^{19}F NMR, spectra were recorded on an Agilent 400MR DD2 (400 MHz) or AVANCE III HD (400MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to incompletely deuterated CDCl_3 (s, 7.26 ppm). ^{13}C NMR data was acquired on an Agilent 400MR DD2 (101 MHz) or AVANCE III HD (101 MHz) spectrometer. ^{19}F NMR data was acquired on an Agilent 400MR DD2 (376 MHz) spectrum Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), q (quartet). HRMS ESI measurements were tested by an Agilent 1260HpLC-6545Q-TOF LC-MS. The microanalyte was dissolved in chromatography-grade methanol before the test. High resolution mass values are given in m/z.

2. Experimental Equipments

We used the RLH-18-bit photoreaction system, which was produced by Beijing Rogertech Ltd. The photoreactor has eight same 10 W LEDs. This blue light 10 W LEDs energy peak wavelength is 395 nm, 12.6 nm in half-height, and the irradiance of sample position is 18.78 mW/cm². The irradiation vessel is a borosilicate glass test tube, and the LED reaches the test tube through a high-reflection channel with a path length of 2 cm. There is no filter between the LED and the test tube. The spectra are as follows :

Parameter							
Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm ²)	0.0019	SDCM	100.00	Peak Signal	53986		
Euvc(mW/cm ²)	0.0000	Ra	-84.7	Dark Signal	2501		
Euvb(mW/cm ²)	0.0000	Ee(mW/cm ²)	67.03522	Compensate level	2900		
Euva(mW/cm ²)	47.6198	S/P	59.239				
Euvm(mW/cm ²)	47.62	Dominant(nm)	411.10				
Eb(mW/cm ²)	18.78	Purity(%)	99.9				
Eg(mW/cm ²)	0.00	HalfWidth(nm)	12.6				
Er(mW/cm ²)	0.00	Peak(nm)	395.9				
Eir(mW/cm ²)	2.73	Center(nm)	395.5				
E(lx)	184.10	Centroid(nm)	413.0				
Candle E(fc)	17.10	Color Ratio(RGB)	0.5,0.0,99.5				
CCT(K)	100000	CIE1931 X	9223.617				
Duv	-0.13447	CIE1931 Y	269.540				
CIE x,y	0.1726,0.0050	CIE1931 Z	43946.301				
CIE u,v	0.2543,0.0111	TLCI-2012	0				
CIE u',v'	0.2543,0.0167	Integral Time(ms)	0.2				

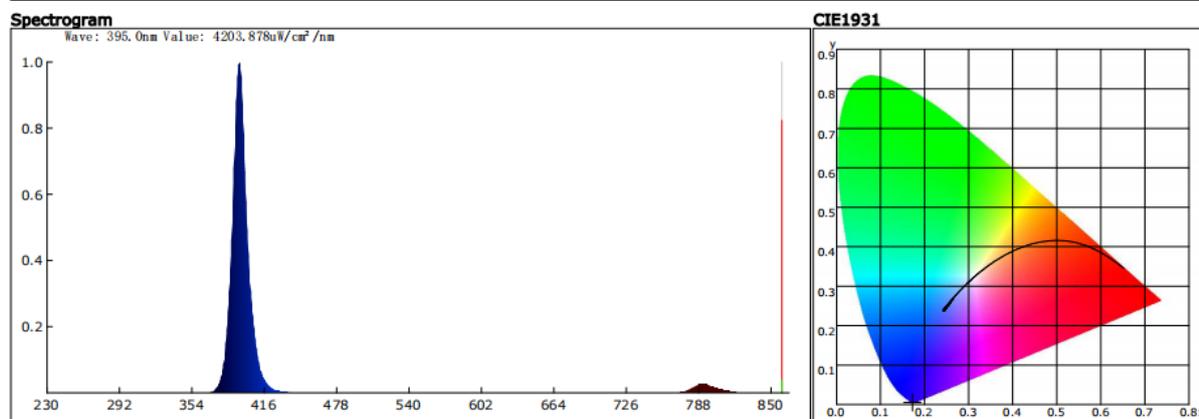


Figure S1 Light Source Test Report

The main experimental equipment during the reaction is the photoreactor and magnetic stirrer, as shown in the figure below :

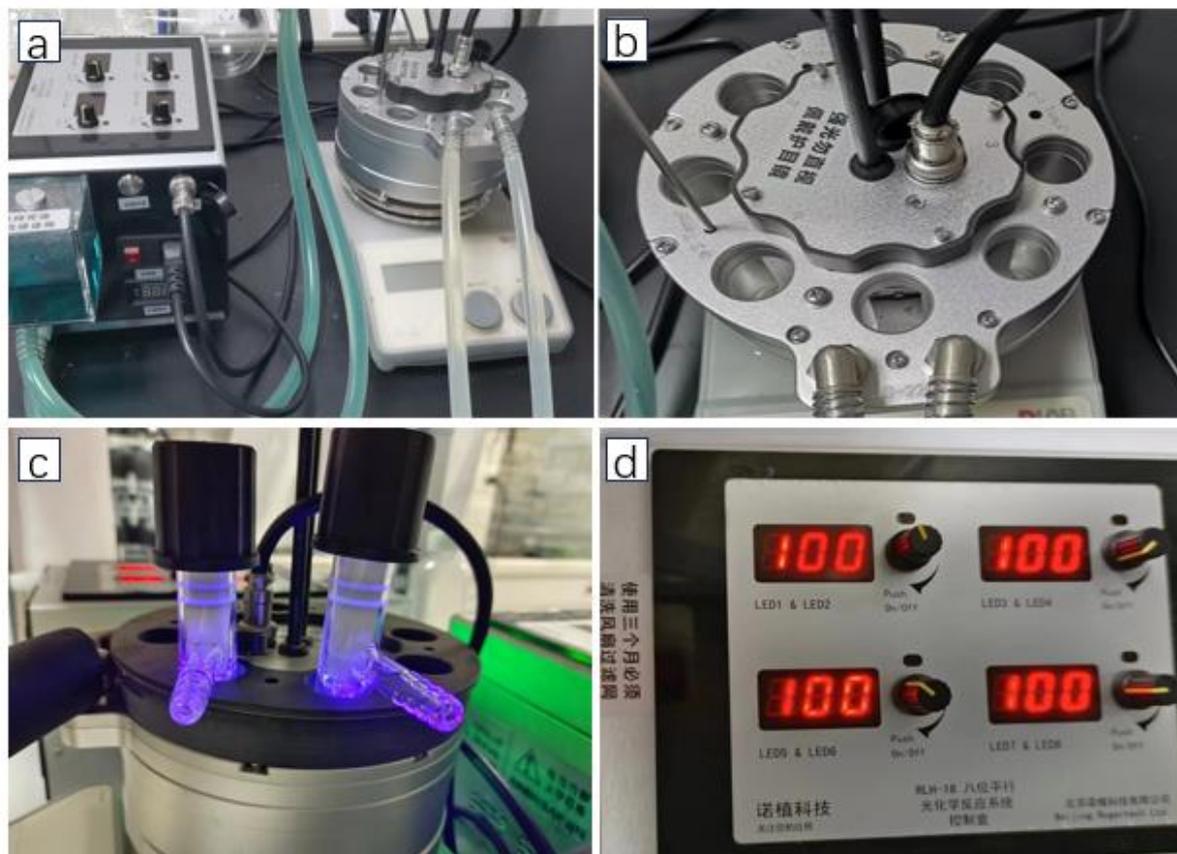
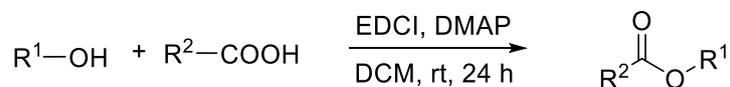


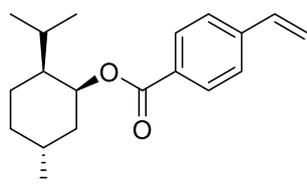
Figure S2 a). General view of photoreactor and agitator; b). Top view of reaction tube module; c). Operation status of the reaction tube module; d). Control switch

3. Synthesis of alkene

Method A^[1]



To a stirred solution of carboxylic acid (2 mmol, 1 equiv.) and EDCI (1.15 g, 6 mmol, 3 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and alcohol (2 mmol, 1 equiv.). The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction (TLC), the reaction was quenched with water and the mixture was extracted with EtOAc. The combined organic layer dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo and the residue was purified by flash column chromatography afford the product.

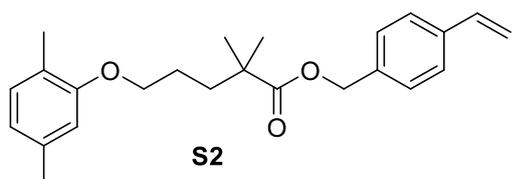


S1

Synthesized according to Method A. To a stirred solution of 4-vinylbenzoic acid (0.3 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and Menthol (0.31 g, 2.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO₂, PE: EA = 10:1) afford **S1** (0.49 g, 85%) as a colorless liquid.

TLC: (SiO₂): R_f (PE: EA= 10: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.5 Hz, 1H), 5.29 (d, *J* = 11.0 Hz, 1H), 4.85 (td, *J* = 10.9, 4.4 Hz, 1H), 2.05 (d, *J* = 10.5 Hz, 1H), 1.92 – 1.84 (m, 1H), 1.65 (d, *J* = 11.6 Hz, 2H) 1.51 – 1.44 (m, 2H), 1.08 – 0.97 (m, 2H), 0.84 (dd, *J* = 6.8, 4.5 Hz, 7H), 0.71 (d, *J* = 6.9 Hz, 3H).

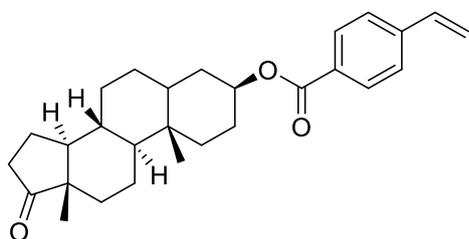


S2

Synthesized according to Method A. Synthesized according to Method A. To a stirred solution of (4-vinylphenyl) methanol (0.27 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and Gemfibrozil (0.31 g, 2.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO₂, PE: EA = 10:1) afford **S2** (0.61 g, 71%) as a colorless liquid.

TLC: (SiO₂): R_f (PE: EA= 10: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.67 – 6.61 (m, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 5.02 (s, 2H), 3.83 – 3.77 (m, 2H), 2.23 (s, 3H), 2.08 (s, 3H), 1.65 (dd, *J* = 3.4, 1.9 Hz, 4H), 1.17 (s, 6H).

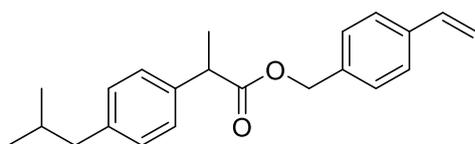


S3

Synthesized according to Method A. Synthesized according to Method A. To a stirred solution of 4-vinylbenzoic acid (0.3 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and Epiandrosterone (0.58 g, 2.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO₂, PE: EA = 5:1) afford **S3** (0.59 g, 70%) as a white solid.

TLC: (SiO₂): R_f (PE: EA= 5: 1) = 0.6

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 4.91 – 4.81 (m, 1H), 2.37 (dd, *J* = 19.3, 8.8 Hz, 1H), 2.00 (dt, *J* = 19.0, 9.0 Hz, 1H), 1.93 – 1.82 (m, 2H), 1.76 – 1.66 (m, 4H), 1.64 – 1.52 (m, 2H), 1.52 – 1.37 (m, 3H), 1.32 – 1.16 (m, 6H), 1.08 – 0.86 (m, 2H), 0.82 (s, 3H), 0.79 (s, 3H), 0.72 – 0.63 (m, 1H).

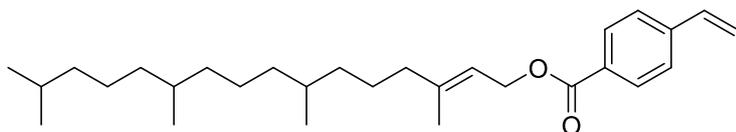


S4

Synthesized according to Method A. Synthesized according to Method A. To a stirred solution of (4-vinylphenyl) methanol (0.27 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and Ibuprofen (0.41 g, 2.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO₂, PE: EA = 10:1) afford **S4** (0.59 g, 91%) as a white solid.

TLC: (SiO₂): R_f (PE: EA= 10: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.8 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.30 – 5.23 (m, 1H), 5.10 (s, 2H), 3.77 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.87 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H).

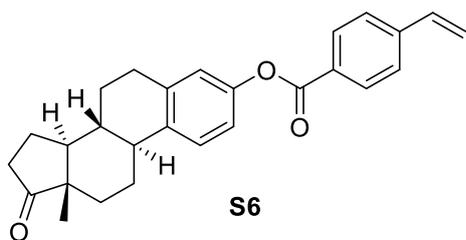


S5

Synthesized according to Method A. Synthesized according to Method A. To a stirred solution of 4-vinylbenzoic acid (0.3 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and phytol (0.98 g, 2.0 mmol, 1.0 equiv.). Purification by flash column chromatography (SiO₂, PE: EA = 10:1) afford **S5** (0.68 g, 80%) as a colorless liquid.

TLC: (SiO₂): R_f (PE: EA= 10: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (d, *J* = 17.6 Hz, 1H), 5.38 (t, *J* = 7.1 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 7.1 Hz, 2H), 1.96 (t, *J* = 8.1 Hz, 2H), 1.67 (s, 3H), 1.50 – 1.42 (m, 1H), 1.38 – 1.26 (m, 4H), 1.25 – 1.12 (m, 7H), 1.09 – 1.03 (m, 2H), 1.03 – 0.90 (m, 4H), 0.82 – 0.73 (m, 13H).



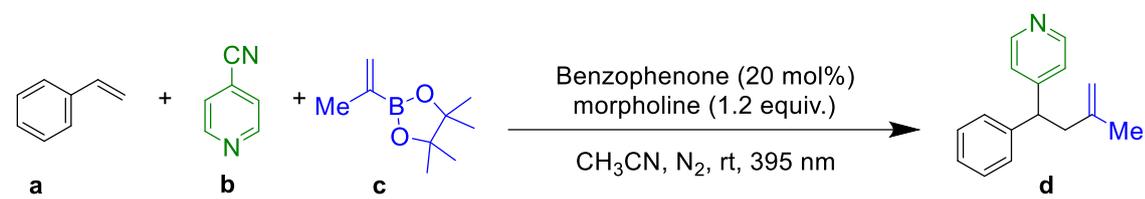
Synthesized according to Method A. To a stirred solution of 4-vinylbenzoic acid (0.3 g, 2.0 mmol, 1.0 equiv.) and EDCI (1.15 g, 6 mmol, 3.0 equiv.) in DCM (8 mL) were added DMAP (4-dimethylaminepyridine) (0.29 g, 2.4 mmol, 1.2 equiv.) and Estrone (0.98 g, 2.0 mmol, 1.0 equiv.) Purification by flash column chromatography (SiO₂, PE: EA = 5: 1) afford **S6** (0.6 g, 75%) as a white solid.

TLC: (SiO₂): R_f (PE: EA= 5: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.79 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.91 (d, *J* = 18.3 Hz, 1H), 5.43 (d, *J* = 11.5 Hz, 1H), 2.95 (dd, *J* = 8.6, 3.9 Hz, 2H), 2.52 (dd, *J* = 18.9, 8.3 Hz, 1H), 2.48 – 2.40 (m, 1H), 2.39 – 2.27 (m, 1H), 2.21 – 2.10 (m, 1H), 2.09 – 2.00 (m, 2H), 2.00 – 1.95 (m, 1H), 1.71 – 1.59 (m, 2H), 1.58 – 1.49 (m, 3H), 1.49 – 1.41 (m, 1H), 0.93 (s, 3H).

4. Optimization Studies

Table S1 Optimization of Time

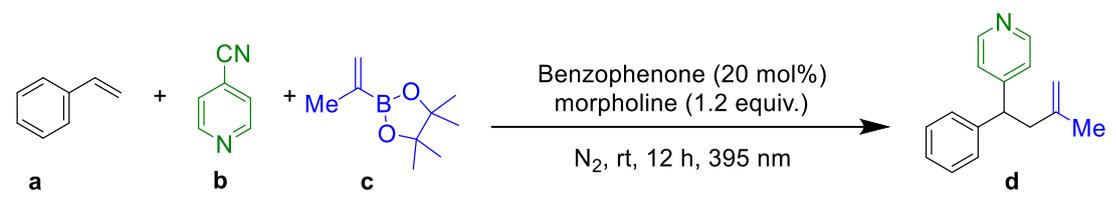


Reaction scheme for Table S1: Styrene (**a**) reacts with 4-cyanopyridine (**b**) and a pinacol boronate ester (**c**) in the presence of Benzophenone (20 mol%) and morpholine (1.2 equiv.) in CH₃CN, N₂, rt, 395 nm to form product **d**.

Entry	Time (h)	Yield (%)
1	12	71
2	24	56
3	36	57

Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), CH₃CN (4 mL), 395 nm blue LEDs, room temperature, under a nitrogen atmosphere. isolated yield.

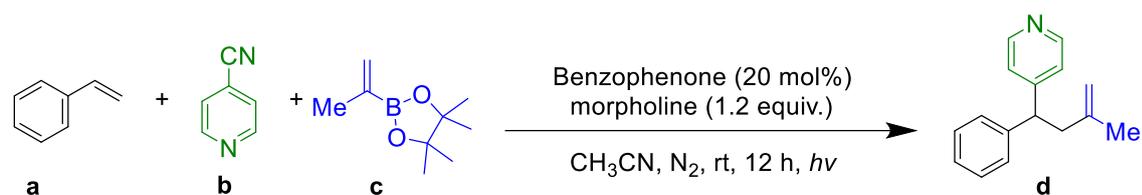
Table S2 Optimization of Solvent



Reaction scheme for Table S2: Styrene (**a**) reacts with 4-cyanopyridine (**b**) and a pinacol boronate ester (**c**) in the presence of Benzophenone (20 mol%) and morpholine (1.2 equiv.) under N₂, rt, 12 h, 395 nm to form product **d**.

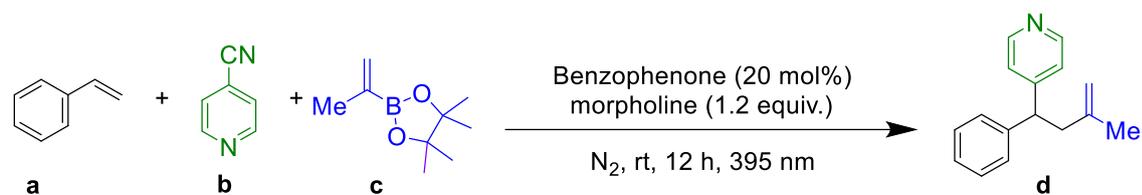
Entry	Solvent	Yield (%)
1	BTF	33
2	CH ₃ CN	71
3	Toluene	20
4	DMSO	68
5	DMA	25
6	DMF	34

Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), solvent (4 mL), 12 h, 395 nm blue LEDs, room temperature, under a nitrogen atmosphere. isolated yield.

Table S3 Optimization of Wavelength

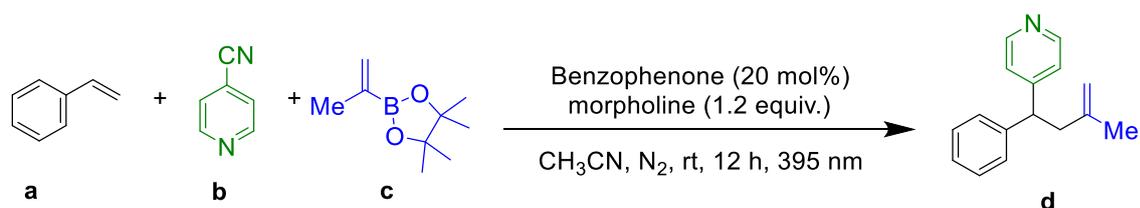
Entry	Wavelength (nm)	Yield (%)
1	365	61
2	395	71
3	425	n.d.

Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), CH₃CN (4 mL), 12 h, 395 nm blue LEDs, room temperature, under a nitrogen atmosphere. isolated yield.

Table S4 Optimization of concentration

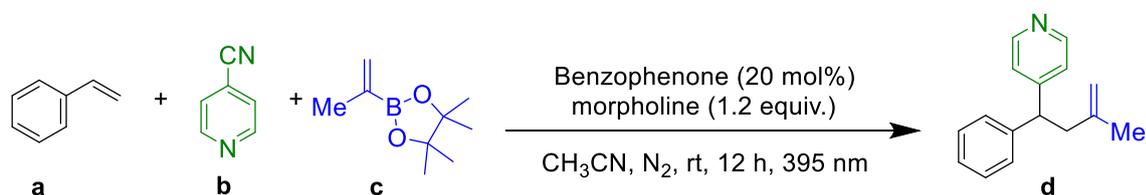
Entry	CH ₃ CN (mL)	Yield (%)
1	1	59
2	2	63
4	4	71
8	8	52

Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), CH₃CN, 12 h, 395 nm blue LEDs, room temperature, under a nitrogen atmosphere. isolated yield.

Table S5 Optimization of ratio

Entry	Deviation from the standard conditions	Yield (%)
1	1.0 equiv a ; 2.0 equiv c	52
2	1.0 equiv a ; 2.0 equiv b	38
3	1.0 equiv a	38
4	2.0 equiv a	71
5	4.0 equiv a	72
6	0.6 equiv morpholine	43
7	1.8 equiv morpholine	56

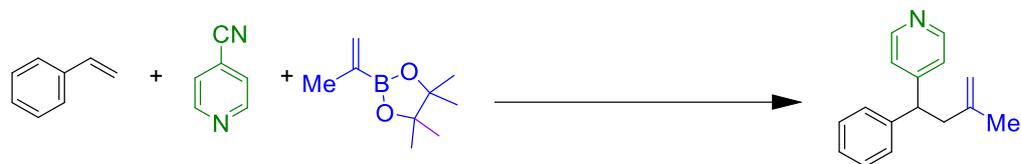
Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), CH₃CN (4 mL), 12 h, 395 nm blue LEDs, room temperature, under a nitrogen atmosphere. isolated yield.

Table S6 Control Experiment

Entry	Variation from the standard conditions	Yield (%)
1	None	71
2	Without BP	n.d.
3	Without light	n.d.
4	Without morpholine	n.d.

Reaction conditions: 0.2 mmol scale, **a** (2.0 equiv.), **b** (1.0 equiv.), **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.), CH₃CN (4 mL), 395 nm blue LEDs, room temperature, 12 h, under a nitrogen atmosphere. isolated yield.

5. General procedures for alkene difunctionalization



General Procedure 1

A 10 mL Schlenk tube was equipped with a magnetic stir bar and dried using a heat gun. The Schlenk tube was then charged with 4-cyanopyridine (0.2 mmol, 1.0 equiv), Benzophenone (20 mol%). The reaction mixture was evacuated and purged with nitrogen gas three times. Styrene (0.4 mmol, 2.0 equiv.), BPin (0.2 mmol, 1.0 equiv.), morpholine (0.24 mmol, 1.2 equiv.) and CH₃CN (4 mL) were added under a nitrogen atmosphere. The reaction was irradiated with 10 W 395 nm blue LEDs at room temperature. After 12 hours, the reaction mixture was concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using the specified solvent system to yield the desired product.

6. Proposed mechanism

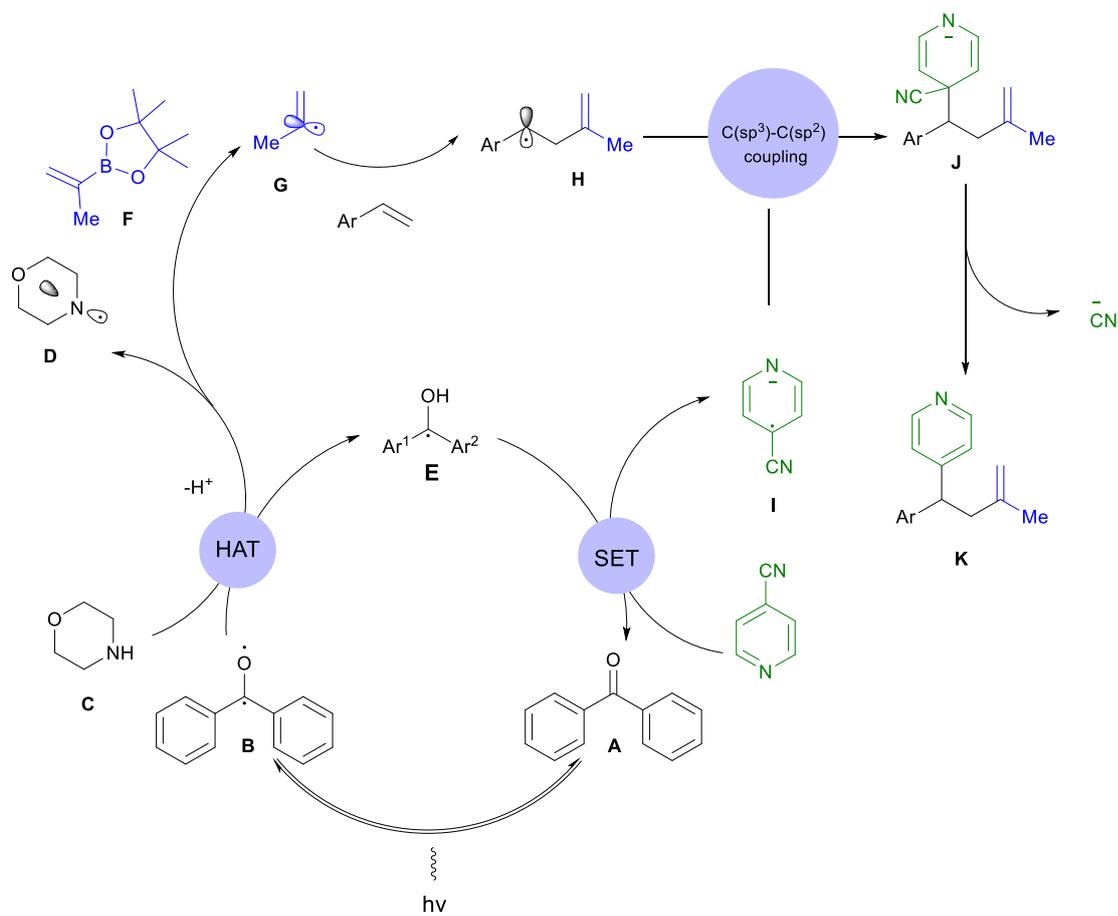


Figure S3 Proposed mechanism

7. Alkylboronic Esters

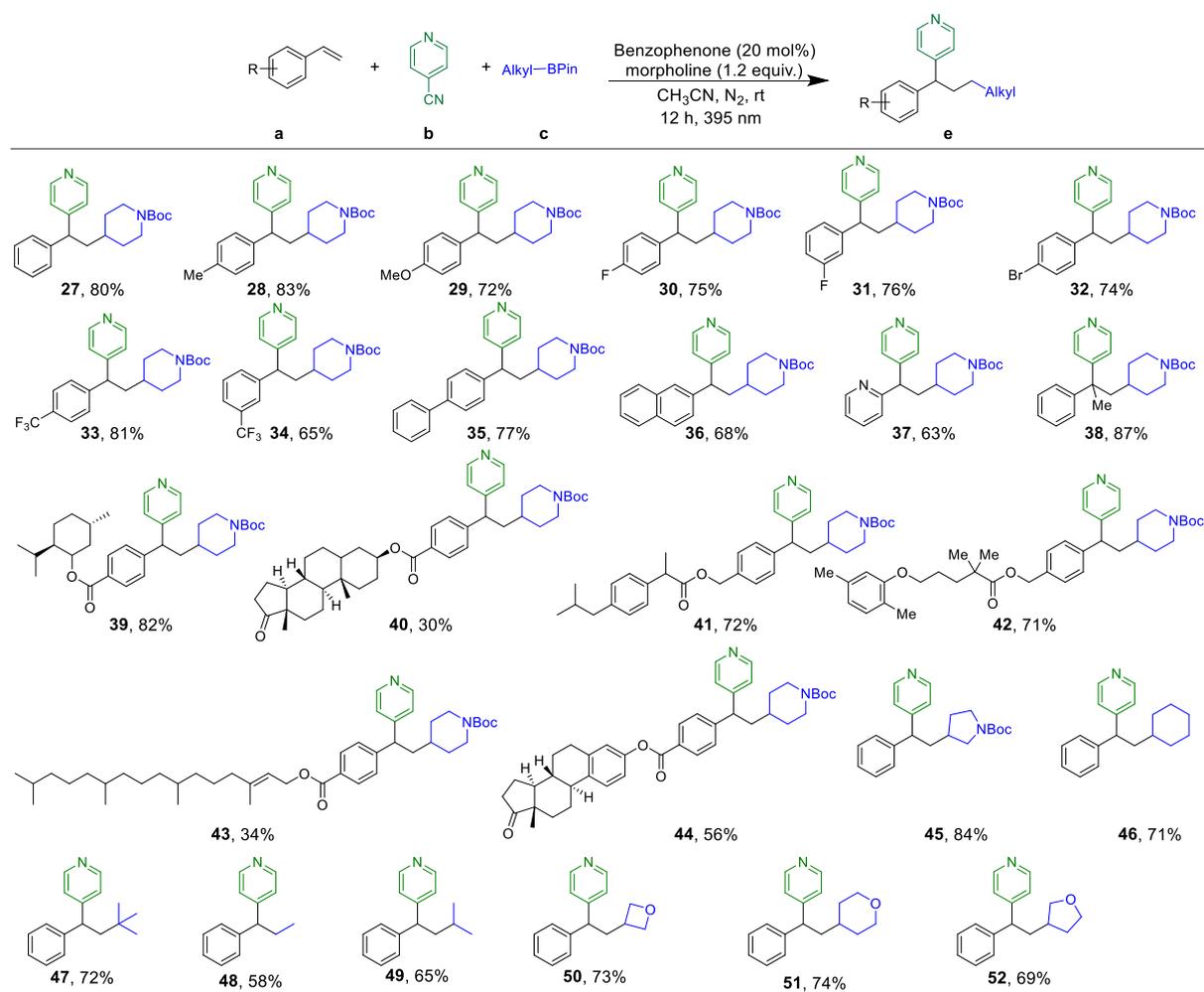
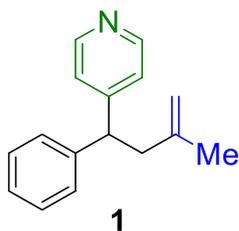


Figure S4. Substrate scope. Reaction conditions: 0.2 mmol scale, compound **a** (2.0 equiv.), compound **b** (1.0 equiv.), compound **c** (1.0 equiv.), Benzophenone (20 mol%), morpholine (1.2 equiv.) in CH₃CN (0.05 M), 395 nm blue LEDs, room temperature, 12 h, under a nitrogen atmosphere. isolated yield.

8. Experimental data for isolated products

4-(3-methyl-1-phenylbut-3-en-1-yl) pyridine (1)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 31.5 mg, 71% yield.

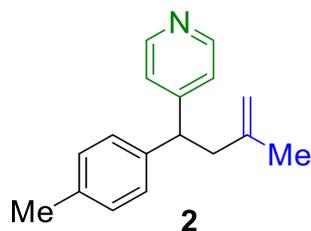
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.3 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.16 – 7.11 (m, 3H), 7.08 (d, *J* = 6.1 Hz, 2H), 4.58 (d, *J* = 48.5 Hz, 2H), 4.08 (t, *J* = 7.9 Hz, 1H), 2.69 (d, *J* = 7.9 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.6, 149.7, 142.8, 142.4, 128.7, 127.9, 126.8, 123.4, 113.2, 48.7, 43.1, 22.5.

HRMS (ESI): C₁₆H₁₇NH⁺ [M+H]⁺ Calcd 224.1434, Found 224.1439.

4-(3-methyl-1-(p-tolyl) but-3-en-1-yl) pyridine (2)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 30.2 mg, 64% yield.

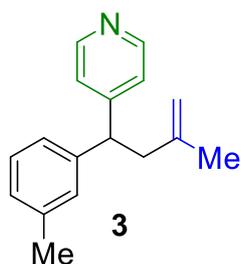
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 6.3 Hz, 2H), 7.07 (d, *J* = 6.3 Hz, 2H), 7.03 (s, 4H), 4.58 (d, *J* = 46.3 Hz, 2H), 4.04 (t, *J* = 7.9 Hz, 1H), 2.67 (d, *J* = 7.9 Hz, 2H), 2.23 (s, 3H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.0, 149.6, 142.5, 139.8, 136.4, 129.4, 127.7, 123.3, 113.2, 48.3, 43.2, 22.5, 21.0.

HRMS (ESI): C₁₇H₁₉NH⁺ [M+H]⁺ Calcd 238.1590, Found 238.1600.

4-(3-methyl-1-(m-tolyl) but-3-en-1-yl) pyridine (3)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 27.9 mg, 59% yield.

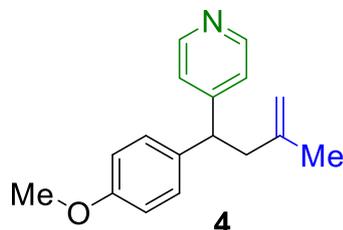
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.1 Hz, 2H), 7.10 – 7.08 (m, 3H), 6.96 (s, 1H), 6.94 (s, 2H), 4.64 (s, 1H), 4.51 (s, 1H), 4.04 (t, *J* = 7.9 Hz, 1H), 2.68 (d, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 149.6, 142.8, 142.5, 138.3, 128.7, 128.5, 127.6, 124.8, 123.4, 113.2, 48.6, 43.1, 22.6, 21.5.

HRMS (ESI): C₁₇H₁₉NH⁺ [M+H]⁺ Calcd 238.1590, Found 238.1601

4-(1-(4-methoxyphenyl)-3-methylbut-3-en-1-yl) pyridine (4)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 24 mg, 47% yield.

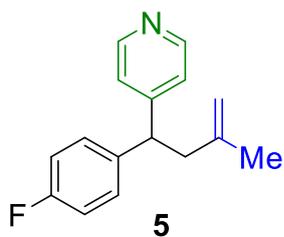
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.3 Hz, 2H), 7.11 – 7.01 (m, 4H), 6.78 – 6.74 (m, 2H), 4.57 (d, *J* = 50.5 Hz, 2H), 4.03 (t, *J* = 7.9 Hz, 1H), 3.69 (s, 3H), 2.66 (d, *J* = 7.4 Hz, 2H), 1.61 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.3, 154.4, 149.4, 142.5, 134.8, 128.9, 123.3, 114.0, 113.2, 55.2, 47.8, 43.3, 22.5.

HRMS (ESI): C₁₇H₁₉NOH⁺ [M+H]⁺ Calcd 254.1539, Found 254.1549.

4-(1-(4-fluorophenyl)-3-methylbut-3-en-1-yl) pyridine (5)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 31.0 mg, 64% yield.

TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

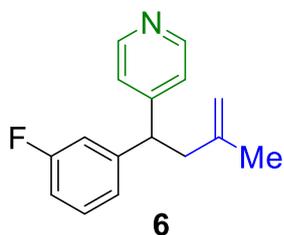
¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 6.1 Hz, 2H), 7.12 – 7.06 (m, 4H), 6.94 – 6.89 (m, 8.7 Hz, 2H), 4.58 (d, *J* = 58.4 Hz, 2H), 4.08 (t, *J* = 7.9 Hz, 1H), 2.67 (d, *J* = 7.9 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 162.9, 160.4, 154.2, 149.2, 142.0, 138.2 (d, *J* = 3.3 Hz), 129.4 (d, *J* = 8.0 Hz), 123.4, 115.5 (d, *J* = 21.4 Hz), 113.5, 47.9, 43.3, 22.5.

HRMS (ESI): C₁₆H₁₆FNH⁺ [M+H]⁺ Calcd 242.1340, Found 242.1332.

¹⁹F NMR (376 MHz, CDCl₃) δ -115.84.

4-(1-(3-fluorophenyl)-3-methylbut-3-en-1-yl) pyridine (6)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 28.0 mg, 58% yield.

TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

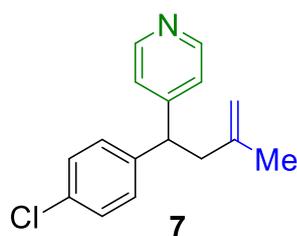
¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 5.6 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.07 (d, *J* = 6.3 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.87 – 6.80 (m, 2H), 4.58 (d, *J* = 55.5 Hz, 2H), 4.08 (t, *J* = 7.9 Hz, 1H), 2.67 (d, *J* = 7.9 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 164.1, 161.7, 153.0, 149.7, 145.3 (d, *J* = 6.9 Hz), 141.9, 130.1 (d, *J* = 8.4 Hz), 123.7 (d, *J* = 2.5 Hz), 114.8 (d, *J* = 21.8 Hz), 113.7 (d, *J* = 21.1 Hz), 113.5, 48.3 (d, *J* = 1.8 Hz), 43.0, 22.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -112.69.

HRMS (ESI): C₁₆H₁₆FNH⁺ [M+H]⁺ Calcd 242.1340, Found 242.1345.

4-(1-(4-chlorophenyl)-3-methylbut-3-en-1-yl) pyridine (7)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 28.3 mg, 55% yield.

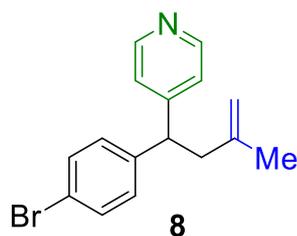
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 6.0 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.09 – 7.04 (m, 4H), 4.58 (d, *J* = 58.2 Hz, 2H), 4.06 (t, *J* = 7.9 Hz, 1H), 2.66 (d, *J* = 8.0 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.2, 149.8, 142.0, 141.2, 132.6, 129.3, 128.8, 123.2, 113.5, 48.0, 43.1, 22.5.

HRMS (ESI): C₁₆H₁₆ClNH⁺ [M+H]⁺ Calcd 258.1044, Found 258.1048.

4-(1-(4-bromophenyl)-3-methylbut-3-en-1-yl) pyridine (8)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 38.0 mg, 63% yield.

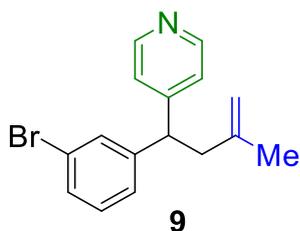
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, *J* = 6.1 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.57 (d, *J* = 58.2 Hz, 2H), 4.05 (t, *J* = 7.9 Hz, 1H), 2.65 (d, *J* = 8.0 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.2, 149.6, 141.9, 141.7, 131.8, 129.7, 123.3, 120.7, 113.6, 48.0, 43.0, 22.5.

HRMS (ESI): C₁₆H₁₆BrNH⁺ [M+H]⁺ Calcd 302.0539, Found 302.0540.

4-(1-(3-bromophenyl)-3-methylbut-3-en-1-yl) pyridine (9)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 30.4 mg, 51% yield.

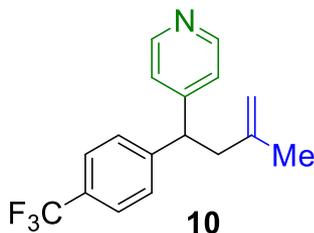
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 6.1 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.20 – 7.14 (m, 2H), 7.13 (d, *J* = 6.1 Hz, 2H), 4.66 (d, *J* = 57.4 Hz, 2H), 4.11 (t, *J* = 7.9 Hz, 1H), 2.74 (d, *J* = 8.0 Hz, 2H), 1.69 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 152.6, 149.9, 145.1, 141.9, 131.0, 130.2, 129.9, 126.6, 123.3, 122.7, 113.6, 48.3, 42.9, 22.5.

HRMS (ESI): C₁₆H₁₆BrNH⁺ [M+H]⁺ Calcd 302.0539, Found 302.0549.

4-(3-methyl-1-(4-(trifluoromethyl) phenyl) but-3-en-1-yl) pyridine (10)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 35.2 mg, 61% yield.

TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

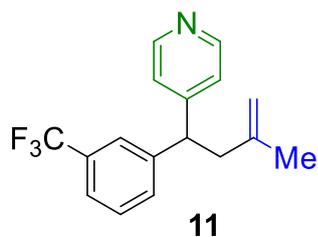
¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 4.8 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 6.3 Hz, 2H), 4.58 (d, *J* = 56.9 Hz, 2H), 4.14 (t, *J* = 7.9 Hz, 1H), 2.69 (d, *J* = 8.0 Hz, 2H), 1.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 152.5, 149.9, 146.8 (d, *J* = 1.5 Hz), 141.8, 129.1 (q, *J* = 32.5 Hz), 128.3, 125.6 (q, *J* = 3.6 Hz), 123.3, 122.7, 113.6, 48.4, 42.9, 22.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.44.

HRMS (ESI): C₁₇H₁₆F₃NH⁺ [M+H]⁺ Calcd 292.1308, Found 292.1314.

4-(3-methyl-1-(3-(trifluoromethyl) phenyl) but-3-en-1-yl) pyridine (11)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 17.6 mg, 30% yield.

TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

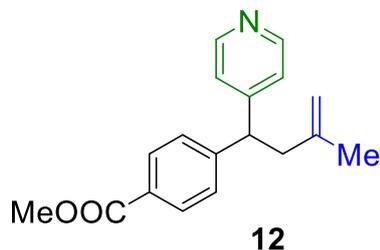
¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 6.0 Hz, 2H), 7.44 – 7.29 (m, 4H), 7.08 (d, *J* = 6.3 Hz, 2H), 4.59 (d, *J* = 58.8 Hz, 2H), 4.15 (t, *J* = 7.9 Hz, 1H), 2.71 (dd, *J* = 8.0, 4.0 Hz, 2H), 1.63 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.1, 149.4, 143.5, 141.6, 131.1 (q, *J* = 32.0 Hz), 129.2, 125.4, 124.6 (q, *J* = 4.0 Hz), 123.8 (t, *J* = 3.6 Hz), 123.4, 122.7, 113.8, 48.4, 43.0, 22.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.56.

HRMS (ESI): C₁₇H₁₆F₃NH⁺ [M+H]⁺ Calcd 292.1308, Found 292.1317.

methyl 4-(3-methyl-1-(pyridin-4-yl) but-3-en-1-yl) benzoate (12)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 27.1 mg, 48% yield.

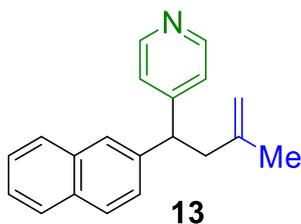
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 6.3 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.3 Hz, 2H), 4.65 (d, *J* = 54.7 Hz, 2H), 4.21 (t, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 2.78 (d, *J* = 8.0 Hz, 2H), 1.70 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.8, 152.6, 149.9, 148.0, 141.9, 130.0, 128.7, 128.0, 123.3, 113.6, 52.1, 48.6, 42.9, 22.5.

HRMS (ESI): C₁₈H₁₉NO₂H⁺ [M+H]⁺ Calcd 282.1489, Found 282.1495.

4-(3-methyl-1-(naphthalen-2-yl) but-3-en-1-yl) pyridine (13)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 16.2 mg, 34% yield.

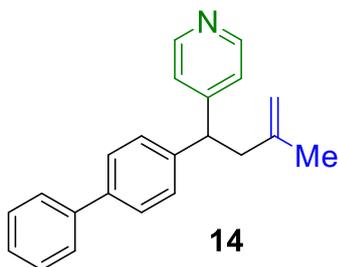
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.1 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.59 (s, 1H), 7.40 – 7.32 (m, 2H), 7.20 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.11 (d, *J* = 6.3 Hz, 2H), 4.58 (d, *J* = 36.5 Hz, 2H), 4.23 (t, *J* = 7.9 Hz, 1H), 2.77 (dd, *J* = 7.9, 3.9 Hz, 2H), 1.63 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.6, 149.7, 142.3, 140.2, 133.5, 132.4, 128.4, 127.8, 127.7, 126.4, 126.3, 126.3, 125.8, 123.5, 113.4, 48.7, 43.0, 22.6.

HRMS (ESI): C₂₀H₁₉NH⁺ [M+H]⁺ Calcd 274.1590, Found 274.1582.

4-(1-([1,1'-biphenyl]-4-yl)-3-methylbut-3-en-1-yl) pyridine (14)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 37 mg, 62% yield.

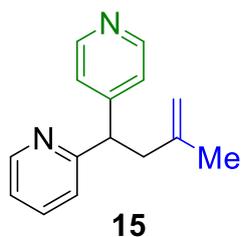
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 6.0 Hz, 2H), 7.51 – 7.42 (m, 4H), 7.36 – 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 7.13 (d, *J* = 6.1 Hz, 2H), 4.60 (d, *J* = 46.0 Hz, 2H), 4.13 (t, *J* = 7.9 Hz, 1H), 2.73 (d, *J* = 7.9 Hz, 2H), 1.65 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.1, 148.5, 142.1, 141.5, 140.5, 139.8, 128.8, 128.3, 127.4, 127.4, 127.0, 123.8, 113.5, 48.4, 43.1, 22.6.

HRMS (ESI): C₂₂H₂₁NNa⁺ [M+Na]⁺ Calcd 322.1566, Found 322.1566.

2-(3-methyl-1-(pyridin-4-yl)but-3-en-1-yl) pyridine (15)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 19.3 mg, 43% yield.

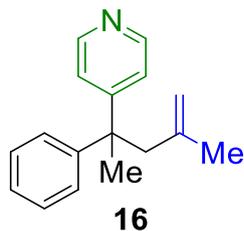
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, *J* = 4.9 Hz, 1H), 8.44 (d, *J* = 4.8 Hz, 2H), 7.54 (td, *J* = 7.7, 1.9 Hz, 1H), 7.27 (d, *J* = 4.8 Hz, 2H), 7.14 – 7.04 (m, 2H), 4.57 (d, *J* = 40.4 Hz, 2H), 4.23 (t, *J* = 7.8 Hz, 1H), 2.91 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.73 (dd, *J* = 14.6, 7.9 Hz, 1H), 1.63 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 161.4, 153.3, 149.6, 148.8, 142.3, 136.7, 123.8, 122.9, 122.0, 113.1, 51.1, 42.5, 22.6.

HRMS (ESI): C₁₅H₁₆N₂H⁺ [M+H]⁺ Calcd 225.1386, Found 225.1393.

4-(4-methyl-2-phenylpent-4-en-2-yl) pyridine (16)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a pale yellow oil in 30 mg, 64% yield.

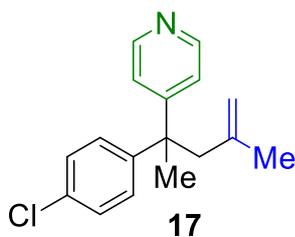
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 6.0 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.15 – 7.09 (m, 5H), 4.61 (d, *J* = 105.1 Hz, 2H), 2.82 (s, 2H), 1.58 (s, 3H), 1.11 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 149.0, 147.6, 141.9, 128.2, 127.5, 126.4, 123.0, 116.0, 48.7, 45.9, 26.7, 24.4.

HRMS (ESI): C₁₇H₁₉NH⁺ [M+H]⁺ Calcd 238.1590, Found 238.1585.

4-(2-(4-chlorophenyl)-4-methylpent-4-en-2-yl) pyridine (17)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 28.8 mg, 53% yield.

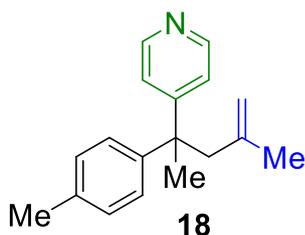
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 6.3 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.07 – 7.03(m, 4H), 4.61 (d, *J* = 109.4 Hz, 2H), 2.79 (s, 2H), 1.56 (s, 3H), 1.13 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.9, 149.4, 146.2, 141.5, 132.2, 128.9, 128.3, 122.7, 116.3, 48.7, 45.6, 26.7, 24.5.

HRMS (ESI): C₁₇H₁₈NClH⁺ [M+H]⁺ Calcd 272.1201, Found 272.1198.

4-(4-methyl-2-(p-tolyl) pent-4-en-2-yl) pyridine (18)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 25 mg, 50% yield.

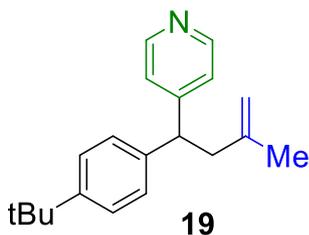
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 5.8 Hz, 2H), 7.12 (d, *J* = 6.1 Hz, 2H), 7.04 – 6.97 (m, 4H), 4.60 (d, *J* = 104.6 Hz, 2H), 2.81 (s, 2H), 2.24 (s, 3H), 1.57 (s, 3H), 1.12 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 160.3, 148.6, 144.6, 142.0, 136.0, 128.9, 127.3, 123.1, 115.9, 48.7, 45.6, 26.7, 24.5, 20.9.

HRMS (ESI): C₁₈H₂₁NH⁺ [M+H]⁺ Calcd 252.1747, Found 252.1743.

4-(1-(4-(tert-butyl) phenyl)-3-methylbut-3-en-1-yl) pyridine (19)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 28.6 mg, 49% yield.

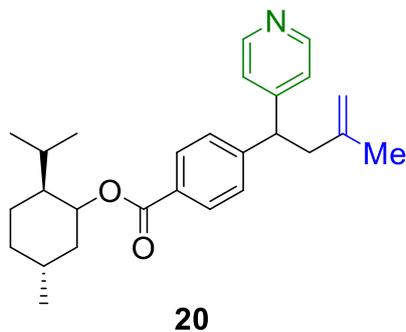
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.1 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.11 – 7.03 (m, 4H), 4.57 (d, *J* = 47.5 Hz, 2H), 4.05 (t, *J* = 7.9 Hz, 1H), 2.68 (d, *J* = 7.5 Hz, 2H), 1.62 (s, 3H), 1.21 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 153.8, 149.6, 142.5, 139.8, 127.4, 125.5, 123.5, 113.1, 48.3, 43.2, 34.4, 31.4, 22.6.

HRMS (ESI): C₂₀H₂₅NNa⁺ [M+Na]⁺ Calcd 302.1879, Found 302.1876.

(2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(3-methyl-1-(pyridin-4-yl) but-3-en-1-yl) benzoate (20)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a pale yellow oil in 49.0 mg, 60% yield.

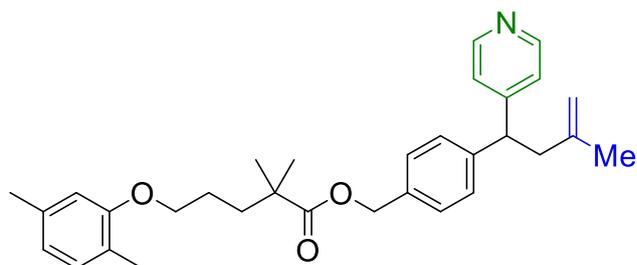
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 5.8 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 4.4 Hz, 2H), 4.83 (td, *J* = 10.9, 4.4 Hz, 1H), 4.59 (d, *J* = 51.9 Hz, 2H), 4.14 (t, *J* = 7.9 Hz, 1H), 2.70 (d, *J* = 7.9 Hz, 2H), 2.05 – 1.99 (m, 1H), 1.92 – 1.83 (m, 1H), 1.69 – 1.59 (m, 5H), 1.50 – 1.41 (m, 2H), 1.20 – 0.94 (m, 3H), 0.88 – 0.79 (m, 6H), 0.70 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.8, 152.9, 152.8, 149.8, 147.7, 141.9, 130.0, 129.5, 127.9, 123.3, 113.5, 74.8, 48.6, 47.2, 42.9, 42.9, 41.0, 34.3, 31.4, 26.4, 23.6, 22.5, 22.1, 20.8, 16.5.

HRMS (ESI): C₂₇H₃₅NO₂H⁺ [M+H]⁺ Calcd 406.2741, Found 406.2748.

4-(3-methyl-1-(pyridin-4-yl) but-3-en-1-yl) benzyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (21)



21

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 54.0 mg, 57% yield.

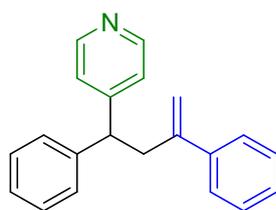
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.1 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 4.99 (s, 2H), 4.56 (d, *J* = 50.9 Hz, 2H), 4.06 (t, *J* = 7.9 Hz, 1H), 3.79 (t, *J* = 5.8 Hz, 2H), 2.66 (d, *J* = 7.9 Hz, 2H), 2.22 (s, 3H), 2.06 (s, 3H), 1.68 – 1.62 (m, 4H), 1.61 (s, 3H), 1.15 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 177.6, 156.9, 153.4, 149.7, 142.7, 142.2, 136.5, 134.9, 130.3, 128.1, 128.0, 123.6, 123.4, 120.7, 113.3, 111.9, 67.9, 65.8, 48.4, 43.1, 42.2, 37.1, 25.2, 25.2, 22.5, 21.5, 15.8.

HRMS (ESI): C₃₂H₃₉NO₃H⁺ [M+H]⁺ Calcd 486.3003, Found 486.3013.

4-(1,3-diphenylbut-3-en-1-yl) pyridine (22)



22

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 25.0 mg, 44% yield.

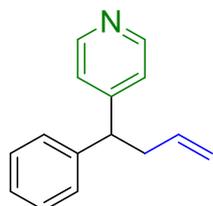
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 6.3 Hz, 2H), 7.28 – 7.22 (m, 4H), 7.22 – 7.10 (m, 4H), 7.08 – 7.05 (m, 2H), 7.00 (d, *J* = 6.3 Hz, 2H), 4.92 (d, *J* = 121.6 Hz, 2H), 3.96 (t, *J* = 7.8 Hz, 1H), 3.24 – 3.10 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.7, 149.3, 145.5, 142.6, 140.6, 128.7, 128.6, 128.0, 127.7, 126.9, 126.4, 123.6, 115.6, 48.6, 41.0.

HRMS (ESI): $\text{C}_{21}\text{H}_{19}\text{NH}^+$ $[\text{M}+\text{H}]^+$ Calcd 286.1590, Found 286.1585.

4-(1-phenylbut-3-en-1-yl) pyridine (23)



23

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 8.0 mg, 20% yield.

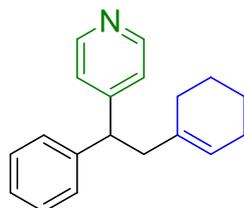
TLC: (SiO_2): R_f (PE: EA= 4: 1) = 0.4

^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, J = 6.1 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.12 (m, 3H), 7.10 (d, J = 6.3 Hz, 2H), 5.66 – 5.56 (m, 1H), 5.00 – 4.88 (m, 2H), 3.92 (t, J = 7.8 Hz, 1H), 2.76 – 2.72 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.7, 149.5, 142.5, 135.7, 128.7, 128.0, 126.9, 123.5, 117.2, 50.6, 39.2.

HRMS (ESI): $\text{C}_{15}\text{H}_{15}\text{NH}^+$ $[\text{M}+\text{H}]^+$ Calcd 210.1277, Found 210.1280.

4-(2-(cyclohex-1-en-1-yl)-1-phenylethyl) pyridine (24)



24

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 16.8 mg, 32% yield.

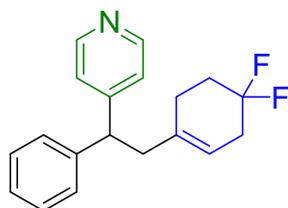
TLC: (SiO_2): R_f (PE: EA= 4: 1) = 0.4

^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, J = 5.4 Hz, 2H), 7.23 – 7.19(m, 2H), 7.15 – 7.11 (m, 3H), 7.07 (d, J = 6.1 Hz, 2H), 5.20 – 5.18 (m, 1H), 4.04 (t, J = 7.9 Hz, 1H), 2.59 (d, J = 8.0 Hz, 2H), 1.81 – 1.75 (m, 4H), 1.52 – 1.42 (m, 2H), 1.41 – 1.31 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.2, 149.4, 143.2, 134.4, 128.5, 128.0, 126.6, 124.4, 123.6, 48.8, 43.5, 28.5, 25.2, 22.9, 22.3.

HRMS (ESI): $\text{C}_{19}\text{H}_{21}\text{NH}^+$ $[\text{M}+\text{H}]^+$ Calcd 264.1747, Found 264.1747.

4-(2-(4,4-difluorocyclohex-1-en-1-yl)-1-phenylethyl) pyridine (25)



25

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 23.1 mg, 39% yield.

TLC: (SiO_2): R_f (PE: EA= 4: 1) = 0.4

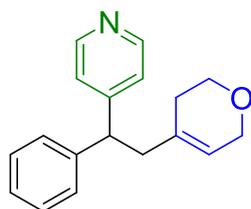
^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, J = 5.3 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.08 (m, 3H), 7.05 (d, J = 5.9 Hz, 2H), 5.06 – 5.00 (m, 1H), 4.01 (t, J = 7.9 Hz, 1H), 2.66 (d, J = 7.9 Hz, 2H), 2.29 (t, J = 16.4 Hz, 2H), 2.12 – 2.05 (m, 2H), 1.91 – 1.80 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.4, 149.7, 142.6, 134.2, 128.7, 127.9, 126.9, 125.1, 123.0 (d, J = 58.5 Hz), 119.3 (t, J = 5.3 Hz), 49.0, 42.3, 34.5 (t, J = 26.5 Hz), 30.3 (t, J = 24.3 Hz), 26.8 (t, J = 5.4 Hz).

^{19}F NMR (376 MHz, CDCl_3) δ -96.78 – -97.03 (m).

HRMS (ESI): $\text{C}_{19}\text{H}_{19}\text{F}_2\text{NH}^+$ $[\text{M}+\text{H}]^+$ Calcd 300.1558, Found 300.1566.

4-(2-(3,6-dihydro-2H-pyran-4-yl)-1-phenylethyl) pyridine (26)



26

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 3:2) as a colorless oil in 17.6 mg, 33% yield.

TLC: (SiO_2): R_f (PE: EA= 3: 2) = 0.4

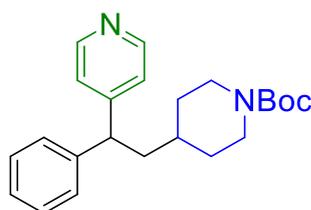
^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, J = 5.8 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.16 – 7.11 (m,

3H), 7.08 (d, $J = 6.3$ Hz, 2H), 5.23 – 5.19 (m, 1H), 4.05 (t, $J = 7.8$ Hz, 1H), 3.91 – 3.90 (m, 2H), 3.62 (t, $J = 5.4$ Hz, 2H), 2.66 (d, $J = 7.9$ Hz, 2H), 1.97 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.3, 149.6 (d, $J = 96.6$ Hz), 142.5, 132.5, 128.9 (d, $J = 38.5$ Hz), 127.8 (d, $J = 21.1$ Hz), 126.9, 123.2 (d, $J = 63.9$ Hz), 118.4, 65.5 (d, $J = 51.6$ Hz), 64.1, 48.4 (d, $J = 23.3$ Hz), 42.1 (d, $J = 80.7$ Hz), 28.3 (d, $J = 58.1$ Hz).

HRMS (ESI): $\text{C}_{18}\text{H}_{19}\text{NOH}^+$ $[\text{M}+\text{H}]^+$ Calcd 266.1539, Found 266.1545.

tert-butyl 4-(2-phenyl-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (27)



27

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 58.6 mg, 80% yield.

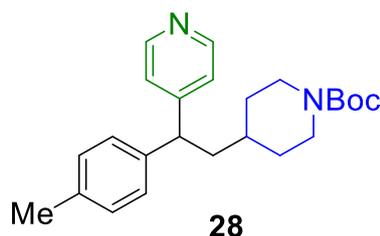
TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

^1H NMR (400 MHz, CDCl_3) δ 8.42 (d, $J = 5.6$ Hz, 2H), 7.27 – 7.21 (m, 2H), 7.18 – 7.11 (m, 3H), 7.10 (d, $J = 6.1$ Hz, 2H), 3.96 (t, $J = 8.0$ Hz, 3H), 2.49 (s, 2H), 1.95 – 1.83 (m, 2H), 1.65 – 1.53 (m, 2H), 1.37 (s, 9H), 1.25 – 1.19 (m, 1H), 1.09 – 1.03 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 154.2, 149.7, 142.7, 128.9, 127.8, 126.9, 123.3, 79.4, 47.4, 41.8, 33.4, 32.0, 28.5.

HRMS (ESI): $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 367.2380, Found 367.2386.

tert-butyl 4-(2-(pyridin-4-yl)-2-(p-tolyl) ethyl) piperidine-1-carboxylate (28)



28

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 63.1 mg, 83% yield.

TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

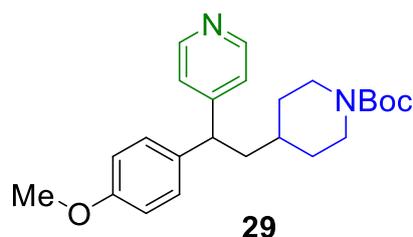
^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, $J = 5.4$ Hz, 2H), 7.08 (d, $J = 4.5$ Hz, 2H), 7.04 – 7.01(m,

4H), 3.97 (s, 1H), 3.92 (t, $J = 8.0$ Hz, 2H), 2.49 (s, 2H), 2.24 (s, 3H), 1.97 – 1.78 (m, 2H), 1.65 – 1.52 (m, 2H), 1.37 (s, 9H), 1.25 – 1.21 (m, 1H), 1.10 – 1.02 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 154.3, 149.8, 139.7, 136.5, 129.5, 127.7, 123.2, 79.3, 47.0, 41.9, 33.4, 32.0, 28.5, 24.9, 21.0.

HRMS (ESI): $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 381.2537, Found 381.2540.

tert-butyl 4-(2-(4-methoxyphenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (29)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 56.7 mg, 72% yield.

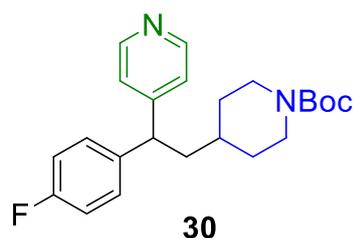
TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

^1H NMR (400 MHz, CDCl_3) δ 8.41 (d, $J = 6.0$ Hz, 2H), 7.08 – 7.02 (m, 4H), 6.78 (d, $J = 8.8$ Hz, 2H), 3.97 (s, 1H), 3.90 (t, $J = 8.1$ Hz, 2H), 3.71 (s, 3H), 2.49 (s, 2H), 1.92 – 1.80 (m, 2H), 1.64 – 1.58 (m, 2H), 1.37 (s, 9H), 1.23 – 1.18 (m, 1H), 1.11 – 1.03 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 158.4, 154.8, 154.5, 149.8, 134.7, 128.8, 123.1, 114.2, 79.3, 55.3, 46.5, 42.0, 33.4, 32.3, 28.5.

HRMS (ESI): $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_3\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 397.2486, Found 397.2494.

tert-butyl 4-(2-(4-fluorophenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (30)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 58.3 mg, 75% yield.

TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

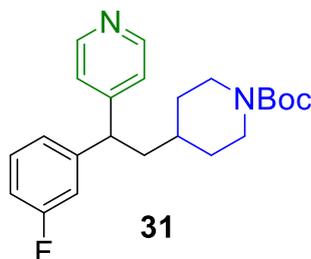
^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 6.3$ Hz, 2H), 7.13 – 7.03 (m, 4H), 6.97 – 6.90 (m, 2H), 3.95 (t, $J = 8.0$ Hz, 3H), 2.49 (s, 2H), 1.94 – 1.82 (m, 2H), 1.63 – 1.56 (m, 2H), 1.37 (s, 9H), 1.22 – 1.15 (m, 1H), 1.10 – 1.03 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.9, 160.4, 154.8, 153.8, 149.8, 138.4, 129.2 (d, $J = 8.0$ Hz), 123.1, 115.7 (d, $J = 21.1$ Hz), 79.4, 46.6, 41.9, 33.4, 32.2, 28.5.

^{19}F NMR (376 MHz, CDCl_3) δ -115.69.

HRMS (ESI): $\text{C}_{23}\text{H}_{29}\text{FN}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 385.2286, Found 385.2282.

tert-butyl 4-(2-(3-fluorophenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (31)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 59 mg, 76% yield.

TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

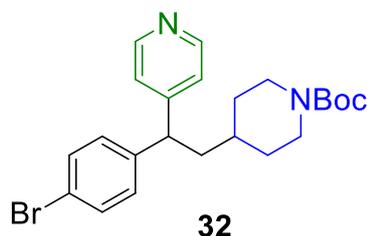
^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $J = 6.4$ Hz, 2H), 7.23 – 7.17 (m, 1H), 7.09 (s, 2H), 6.95 – 6.80 (m, 3H), 4.10 – 3.99 (m, 1H), 3.95 (t, $J = 8.1$ Hz, 2H), 2.42 (d, $J = 53.4$ Hz, 2H), 1.92 – 1.84 (m, 2H), 1.63 – 1.57 (m, 2H), 1.37 (s, 9H), 1.24 – 1.17 (m, 1H), 1.14 – 1.02 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 164.2, 161.8, 154.8, 153.2, 149.9, 145.3 (d, $J = 6.5$ Hz), 130.3 (d, $J = 8.0$ Hz), 123.6 (d, $J = 2.9$ Hz), 114.7 (d, $J = 21.1$ Hz), 113.9 (d, $J = 21.1$ Hz), 79.4, 47.1, 41.7, 33.3, 28.5.

^{19}F NMR (376 MHz, CDCl_3) δ -112.34.

HRMS (ESI): $\text{C}_{23}\text{H}_{29}\text{FN}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 385.2286, Found 385.2284.

tert-butyl 4-(2-(4-bromophenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (32)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 65.8 mg, 74% yield.

TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

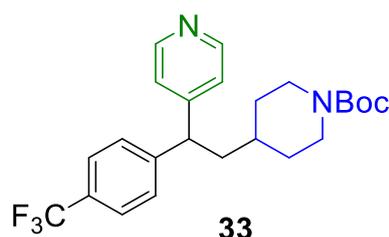
^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 5.6$ Hz, 2H), 7.38 – 7.34 (m, 2H), 7.05 (d, $J = 6.1$

Hz, 2H), 7.01 (d, $J = 8.5$ Hz, 2H), 4.06 – 3.96 (m, 1H), 3.92 (t, $J = 8.0$ Hz, 2H), 2.48 (s, 2H), 1.91 – 1.82 (m, 2H), 1.62 – 1.55 (m, 2H), 1.37 (s, 9H), 1.22 – 1.11 (m, 1H), 1.13 – 1.01 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) (101 MHz, CDCl_3) δ 154.8, 153.2, 150.0, 141.8, 131.9, 129.5, 123.1, 120.7, 79.4, 46.8, 41.7, 33.3, 31.9, 28.5, 24.9

HRMS (ESI): $\text{C}_{23}\text{H}_{29}\text{BrN}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 445.1485, Found 445.1480.

tert-butyl 4-(2-(pyridin-4-yl)-2-(4-(trifluoromethyl) phenyl) ethyl) piperidine-1-carboxylate (33)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 70.2 mg, 81% yield.

TLC: (SiO_2): R_f (PE: EA= 1: 1) = 0.5

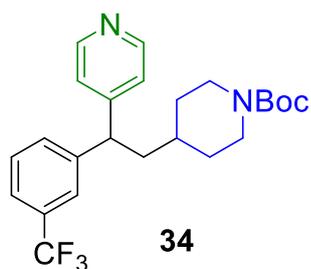
^1H NMR (400 MHz, CDCl_3) δ 8.45 (d, $J = 5.3$ Hz, 2H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 6.3$ Hz, 2H), 4.03 (t, $J = 7.9$ Hz, 3H), 2.49 (s, 2H), 1.92 (t, $J = 7.3$ Hz, 2H), 1.63 – 1.53 (m, 2H), 1.37 (s, 9H), 1.23 – 1.16 (d, $J = 14.6$ Hz, 1H), 1.11 – 1.08 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 154.8, 153.0, 149.9, 146.8, 129.1, 128.2, 125.8 (t, $J = 3.6$ Hz), 123.2, 79.5, 47.2, 41.7, 33.3, 32.2, 28.5.

^{19}F NMR (376 MHz, CDCl_3) δ -62.46.

HRMS (ESI): $\text{C}_{24}\text{H}_{29}\text{F}_3\text{N}_2\text{O}_2\text{H}^+$ $[\text{M}+\text{H}]^+$ Calcd 435.2254, Found 435.2252.

tert-butyl 4-(2-(pyridin-4-yl)-2-(3-(trifluoromethyl) phenyl) ethyl) piperidine-1-carboxylate (34)



According to the general procedure 1, the product was isolated by flash chromatography

(PE: EA = 1:1) as a colorless oil in 56.7 mg, 65% yield.

TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

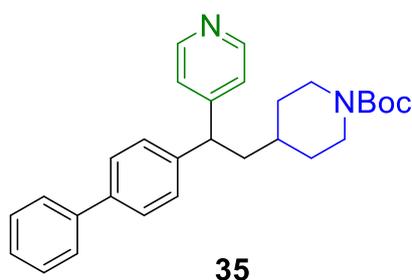
¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 5.0 Hz, 2H), 7.45 – 7.30 (m, 4H), 7.09 (d, *J* = 6.3 Hz, 2H), 4.03 (t, *J* = 8.0 Hz, 3H), 2.49 (s, 2H), 1.99 – 1.87 (m, 2H), 1.62 – 1.59 (m, 2H), 1.37 (s, 9H), 1.22 – 1.17 (m, 1H), 1.14 – 1.04 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.8, 152.9, 150.0, 143.8, 131.2, 129.4, 125.3, 124.4 (t, *J* = 4.0 Hz), 123.9 (t, *J* = 3.6 Hz), 123.1, 122.6, 79.4, 47.2, 41.7, 33.4, 32.1, 28.5.

HRMS (ESI): C₂₄H₂₉F₃N₂O₂H⁺ [M+H]⁺ Calcd 435.2254, Found 435.2251.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.51.

tert-butyl 4-(2-([1,1'-biphenyl]-4-yl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (35)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 68 mg, 77% yield.

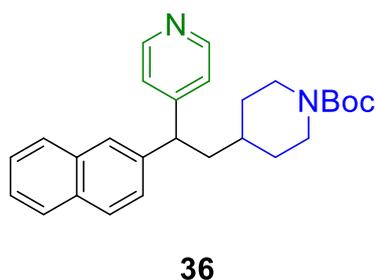
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, *J* = 6.0 Hz, 2H), 7.50 – 7.46 (m, 4H), 7.38 – 7.33 (m, 2H), 7.29 – 7.19 (m, 3H), 7.13 (d, *J* = 6.3 Hz, 2H), 4.00 (t, *J* = 8.0 Hz, 3H), 2.50 (s, 2H), 2.01 – 1.86 (m, 2H), 1.67 – 1.60 (m, 2H), 1.37 (s, 9H), 1.30 – 1.20 (m, 1H), 1.16 – 1.03 (m, 2H).

¹³C NMR (101 MHz, CDCl₃). δ 154.8, 154.0, 149.8, 141.8, 140.5, 139.8, 128.8, 128.2, 127.5, 127.4, 127.0, 123.2, 79.4, 47.1, 41.9, 33.4, 32.0, 28.5.

HRMS (ESI): C₂₉H₃₄N₂O₂H⁺ [M+H]⁺ Calcd 443.2693, Found 443.2700.

tert-butyl 4-(2-(naphthalen-2-yl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (36)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 57 mg, 68% yield.

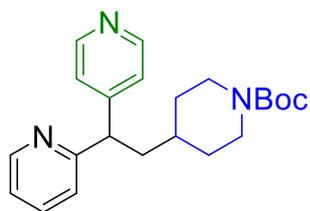
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 6.1 Hz, 2H), 7.76 – 7.58 (m, 4H), 7.43 – 7.36 (m, 1.6 Hz, 2H), 7.22 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.13 (d, *J* = 6.3 Hz, 2H), 4.12 (t, *J* = 8.0 Hz, 1H), 3.97 (s, 2H), 2.47 (s, 2H), 2.22 (s, 1H), 2.09 – 2.02 (m, 1H), 1.70 – 1.59 (m, 2H), 1.36 (s, 9H), 1.26 – 1.20 m, 1H), 1.18 – 1.06 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.8, 153.9, 149.8, 140.1, 133.5, 132.4, 128.6, 127.7, 127.7, 126.4, 126.3, 126.2, 125.9, 123.3, 79.4, 47.4, 41.6, 33.4, 32.0, 28.5.

HRMS (ESI): C₂₇H₃₂N₂O₂H⁺ [M+H]⁺ Calcd 417.2537, Found 417.2539.

tert-butyl 4-(2-(pyridin-2-yl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (37)



37

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 3:1) as a colorless oil in 46.3 mg, 63% yield.

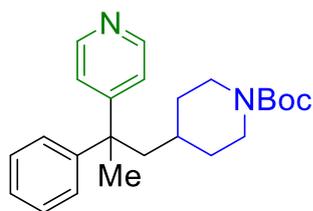
TLC: (SiO₂): R_f (PE: EA= 3: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.53 – 8.48 (m, 1H), 8.43 (d, *J* = 5.9 Hz, 2H), 7.53 (td, *J* = 7.7, 1.9 Hz, 1H), 7.21 (dd, *J* = 3.9, 2.4 Hz, 2H), 7.12 – 7.05 (m, 2H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.96 (s, 2H), 2.48 (s, 2H), 2.17 – 1.89 (m, 2H), 1.67 – 1.55 (m, 2H), 1.36 (s, 9H), 1.20 – 1.14 (m, 1H), 1.13 – 0.98 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 161.7, 154.8, 152.6, 149.8, 149.6, 136.8, 123.4, 122.8, 121.9, 79.3, 49.8, 41.2, 33.5, 32.1, 28.5.

HRMS (ESI): C₂₂H₂₉N₃O₂H⁺ [M+H]⁺ Calcd 368.2333, Found 368.2335.

tert-butyl 4-(2-phenyl-2-(pyridin-4-yl) propyl) piperidine-1-carboxylate (38)



38

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 66.4 mg, 87% yield.

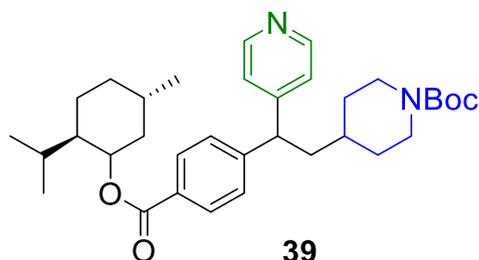
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.48 – 8.35 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.17 – 7.08 (m, 3H), 7.06 (d, *J* = 4.6 Hz, 2H), 3.82 (s, 2H), 2.43 (q, *J* = 13.5 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.59 (s, 3H), 1.35 (s, 9H), 1.29 – 1.19 (m, 2H), 1.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.4, 154.8, 149.3, 147.4, 128.3, 127.3, 126.4, 122.7, 79.3, 47.3, 46.4, 34.3, 32.5, 28.4, 27.4.

HRMS (ESI): C₂₄H₃₂N₂O₂H⁺ [M+H]⁺ Calcd 381.2537, Found 381.2540.

tert-butyl 4-(2-(4-(((2R,5S)-2-isopropyl-5-methylcyclohexyl) oxy) carbonyl) phenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (39)



39

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 89.8 mg, 82% yield.

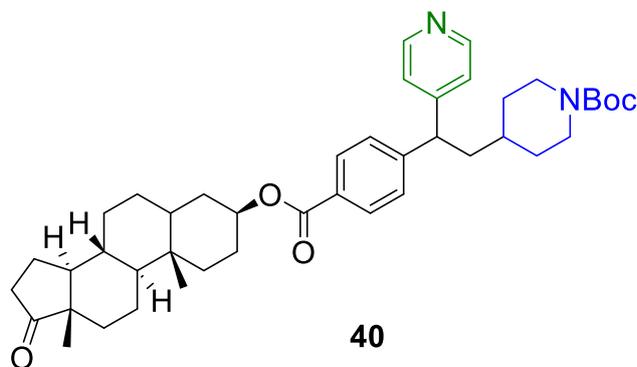
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.37 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.84 (td, *J* = 10.9, 4.4 Hz, 1H), 4.02 (t, *J* = 8.1 Hz, 3H), 2.48 (s, 2H), 2.15 (s, 1H), 2.05 – 1.84 (m, 4H), 1.69 – 1.61 (m, 3H), 1.52 – 1.42 (m, 2H), 1.37 (s, 9H), 1.21 – 1.18 (m, 1H), 1.14 – 0.94 (m, 5H), 0.85 – 0.82 (m, 6H), 0.71 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.7, 154.8, 148.6, 147.2, 130.3, 129.8, 127.9, 123.5, 79.4, 74.9, 47.5, 47.2, 41.6, 41.0, 34.3, 33.4, 31.4, 28.5, 26.5, 24.9, 23.5, 22.1, 20.8, 16.5.

HRMS (ESI): C₃₄H₄₈N₂O₄H⁺ [M+H]⁺ Calcd 549.3687, Found 549.3683.

tert-butyl 4-(2-(4-(((3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl) oxy) carbonyl) phenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (40)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 74.2 mg, 30% yield.

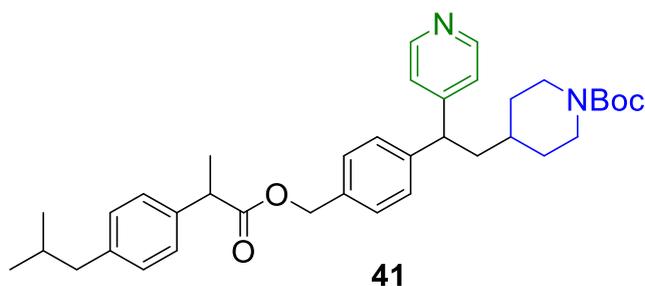
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, *J* = 6.3 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.07 (d, *J* = 6.0 Hz, 2H), 4.90 – 4.82 (m, 1H), 4.10 – 3.90 (m, 3H), 3.90 – 3.69 (m, 1H), 2.41 – 2.34 (m, 1H), 2.04 – 1.83 (m, 7H), 1.77 – 1.52 (m, 9H), 1.51 – 1.44 (m, 2H), 1.44 – 1.41 (m, 2H), 1.37 (s, 9H), 1.31 – 1.22 (m, 4H), 1.11 – 0.90 (m, 4H), 0.82 (s, 3H), 0.80 (s, 3H), 0.72 – 0.63 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 165.8, 154.8, 153.2, 149.9, 147.7, 130.1, 129.6, 127.8, 123.1, 79.4, 74.2, 68.1, 54.3, 51.4, 47.8, 47.4, 46.3, 44.7, 41.6, 36.7, 35.9, 35.7, 35.0, 34.0, 33.4, 32.3, 31.5, 30.8, 28.5, 28.3, 27.5, 21.8, 20.5, 13.8, 12.3.

HRMS (ESI): C₄₃H₅₈N₂O₅H⁺ [M+H]⁺ Calcd 683.4418, Found 683.4412.

tert-butyl 4-(2-(4-(((2-(4-isobutylphenyl) propanoyl) oxy) methyl) phenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (41)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 84.4 mg, 72% yield.

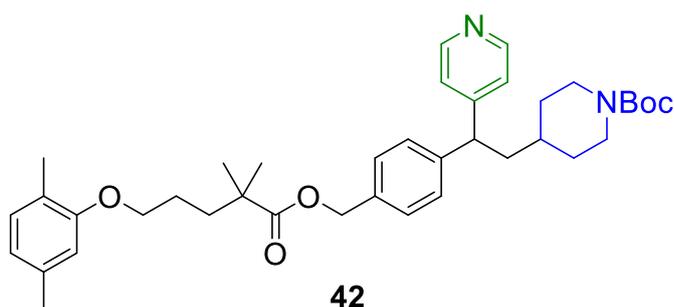
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 6.3 Hz, 2H), 7.13 – 7.04 (m, 8H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.03 – 4.95 (m, 2H), 4.04 (s, 1H), 3.93 (t, *J* = 8.0 Hz, 2H), 3.66 (q, *J* = 7.2 Hz, 1H), 2.50 (s, 2H), 2.36 (d, *J* = 7.1 Hz, 2H), 1.94 – 1.82 (m, 2H), 1.81 – 1.71 (m, 1H), 1.64 – 1.51 (m, 2H), 1.42 (d, *J* = 7.1 Hz, 3H), 1.37 (s, 9H), 1.26 – 1.21 (m, 1H), 1.11 – 1.00 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 174.6, 154.8, 154.5, 149.2, 142.3, 140.6, 137.6, 134.9, 129.3, 128.2, 127.9, 127.2, 123.3, 79.4, 65.9, 47.1, 45.1, 45.0, 41.8, 33.3, 30.2, 28.5, 22.4, 18.5.

HRMS (ESI): C₃₇H₄₈N₂O₄H⁺ [M+H]⁺ Calcd 585.3687, Found 585.3685.

tert-butyl 4-(2-(4-(((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl) oxy) methyl) phenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (42)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 90.0 mg, 71% yield.

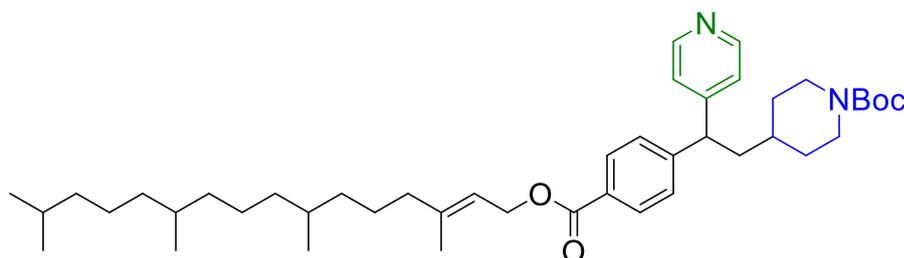
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 6.0 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 1.5 Hz, 1H), 4.99 (s, 2H), 3.93 (t, *J* = 8.0 Hz, 3H), 3.79 (t, *J* = 5.6 Hz, 2H), 2.47 (s, 2H), 2.22 (s, 3H), 2.05 (s, 3H), 1.90 – 1.84 (m, 2H), 1.69 – 1.53 (m, 6H), 1.36 (s, 9H), 1.18 (d, *J* = 5.8 Hz, 1H), 1.15 (s, 6H), 1.12 – 1.00 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 177.6, 156.9, 154.8, 153.6, 149.9, 142.7, 136.5, 135.0, 130.3, 128.2, 127.9, 123.5, 123.2, 120.7, 111.9, 79.3, 67.8, 65.7, 47.1, 42.2, 41.8, 37.1, 33.4, 32.2, 29.7, 28.5, 25.2, 24.9, 21.5, 15.8.

HRMS (ESI): C₃₉H₅₂N₂O₅Na⁺ [M+Na]⁺ Calcd 651.3768, Found 651.3774.

tert-butyl (E)-4-(2-(pyridin-4-yl)-2-(4-(((3,7,11,15-tetramethylhexadec-2-en-1-yl) oxy) carbonyl) phenyl) ethyl) piperidine-1-carboxylate (43)



43

According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 47.0 mg, 34% yield.

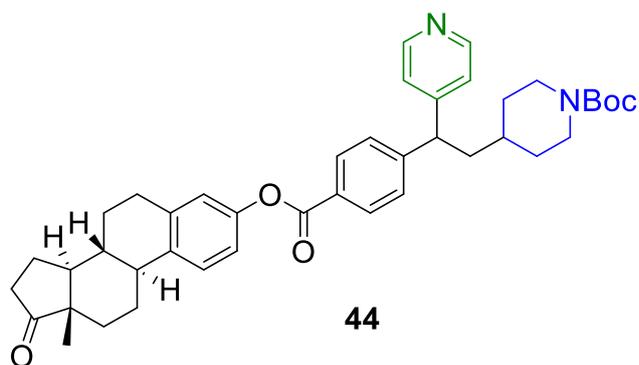
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.43 (s, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.06 (d, *J* = 6.3 Hz, 2H), 5.39 – 5.34 (m, 1H), 4.75 (d, *J* = 7.1 Hz, 2H), 4.03 – 3.99 (m, 3H), 2.47 (s, 2H), 1.97 – 1.87 (m, 4H), 1.67 (s, 3H), 1.62 – 1.48 (m, 2H), 1.47 – 1.39 (m, 2H), 1.37 (s, 9H), 1.33 – 1.23 (m, 4H), 1.22 – 1.12 (m, 8H), 1.12 – 1.04 (m, 4H), 1.04 – 0.92 (m, 4H), 0.82 – 0.72 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 166.3, 154.8, 153.0, 150.0, 147.8, 143.0, 130.2, 129.3, 127.8, 123.1, 118.0, 79.4, 62.0, 47.3, 41.6, 39.9, 39.4, 37.4, 37.4, 37.3, 36.6, 33.4, 32.8, 32.7, 32.3, 28.5, 28.0, 25.0, 24.8, 24.5, 22.8, 22.7, 19.8, 19.7, 16.5.

HRMS (ESI): C₄₄H₆₈N₂O₄H⁺ [M+H]⁺ Calcd 689.5252, Found 689.5249.

tert-butyl 3-(2-(4-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl) oxy) carbonyl) phenyl)-2-(pyridin-4-yl) ethyl) piperidine-1-carboxylate (44)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a colorless oil in 74.2 mg, 56% yield.

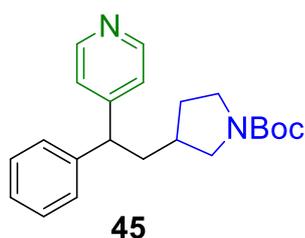
TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

¹H NMR (400 MHz, CDCl₃) δ 8.45 (s, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.25 (m, 3H), 7.10 (d, *J* = 6.0 Hz, 2H), 6.90 – 6.82 (m, 2H), 4.10 – 3.97 (m, 3H), 2.88 – 2.84 (m, 2H), 2.48 – 2.33 (m, 3H), 2.28 – 2.18 (m, 1H), 2.13 – 1.99 (m, 2H), 1.97 (s, 3H), 1.94 – 1.86 (m, 2H), 1.62 – 1.49 (m, 4H), 1.49 – 1.40 (m, 4H), 1.37 (s, 9H), 1.26 – 1.21 (m, 1H), 1.11 – 1.05 (m, 2H), 0.84 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 171.2, 165.1, 154.8, 152.9, 150.0, 148.7, 138.1, 137.5, 130.8, 128.4, 128.1, 126.5, 123.1, 121.7, 118.8, 79.4, 60.4, 50.4, 48.0, 47.4, 44.2, 41.6, 38.0, 35.9, 33.5, 32.3, 31.5, 29.7, 29.4, 28.5, 26.3, 25.8, 21.6, 21.1, 14.2, 13.8.

HRMS (ESI): C₄₂H₅₀N₂O₅H⁺ [M+H]⁺ Calcd 663.3792, Found 663.3787.

tert-butyl 3-(2-phenyl-2-(pyridin-4-yl) ethyl) pyrrolidine-1-carboxylate (45)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 1:1) as a pale yellow oil in 50.1 mg, 84% yield.

TLC: (SiO₂): R_f (PE: EA= 1: 1) = 0.5

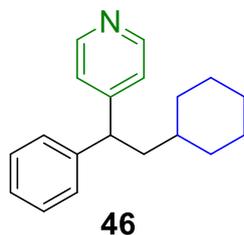
¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 5.8 Hz, 2H), 7.27 – 7.11 (m, 5H), 7.09 (d, *J* = 6.4 Hz, 2H), 3.84 – 3.79 (m, 1H), 3.55 – 3.28 (m, 2H), 3.16 – 3.02 (m, 1H), 2.96 – 2.74 (m, 1H), 2.15 – 1.99 (m, 2H), 1.96 – 1.79 (m, 2H), 1.52 – 1.40 (m, 1H), 1.36 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 154.5, 153.6, 149.9, 142.6, 128.9, 127.8, 127.0, 123.0, 79.1,

51.5, 51.0, 49.3, 45.6, 45.3, 38.5, 36.9, 35.9, 31.8, 31.0, 28.5.

HRMS (ESI): C₂₂H₂₈N₂O₂H⁺ [M+H]⁺ Calcd 353.2224, Found 353.2222.

4-(2-cyclohexyl-1-phenylethyl) pyridine (46)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 37.6 mg, 71% yield.

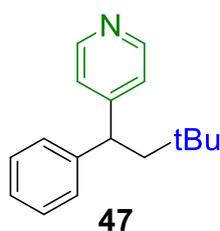
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 4.5 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 3H), 7.08 (d, *J* = 6.0 Hz, 2H), 3.96 (t, *J* = 8.0 Hz, 1H), 1.83 (td, *J* = 7.6, 3.2 Hz, 2H), 1.73 – 1.62 (m, 2H), 1.60 – 1.50 (m, 2H), 1.56 – 1.52 (m, 1H), 1.11 – 0.96 (m, 4H), 0.93 – 0.80 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 154.4, 149.8, 143.4, 128.7, 127.9, 126.6, 123.4, 47.5, 42.8, 34.8, 33.4, 33.3, 26.5, 26.1, 26.1.

HRMS (ESI): C₁₉H₂₃NH⁺ [M + H]⁺ Calcd 266.1903, found, 266.1901^[2]

4-(3,3-dimethyl-1-phenylbutyl) pyridine (47)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 34.7 mg, 72% yield.

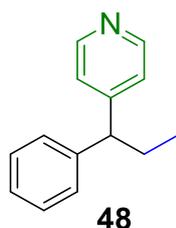
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, *J* = 5.8 Hz, 2H), 7.20 (d, *J* = 6.4 Hz, 4H), 7.18 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 3.95 (t, *J* = 6.6 Hz, 1H), 2.07 – 1.96 (m, 2H), 0.76 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 155.6, 149.8, 144.8, 128.7, 127.8, 126.5, 123.2, 48.7, 47.9, 31.6, 30.2.

HRMS (ESI): C₁₇H₂₁NH⁺ [M + H]⁺ Calcd 240.1747; found, 240.1745^[2]

4-(1-phenylpropyl) pyridine (48)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 22.7 mg, 58% yield.

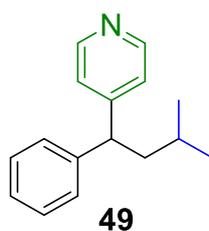
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 5.9 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 7.12 – 7.09 (m, 2H), 3.71 (t, *J* = 7.8 Hz, 1H), 2.04 – 1.97 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.6, 149.3, 143.0, 128.7, 127.9, 126.7, 123.5, 52.7, 27.9, 12.6.

HRMS (ESI): C₁₄H₁₅NH⁺ [M + H]⁺ Calcd 198.1277, found, 198.1277.^[2]

4-(3-methyl-1-phenylbutyl) pyridine (49)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 4:1) as a colorless oil in 29.2 mg, 65% yield.

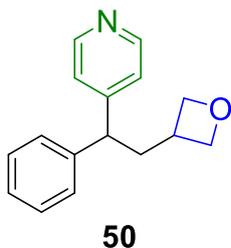
TLC: (SiO₂): R_f (PE: EA= 4: 1) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 5.8 Hz, 2H), 7.27 – 7.14 (m, 5H), 7.12 (s, 2H), 3.93 (t, *J* = 8.0 Hz, 1H), 1.92 – 1.77 (m, 2H), 1.41 – 1.31 (m, 1H), 0.86 (d, *J* = 2.3 Hz, 3H), 0.84 (d, *J* = 2.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.0, 149.2, 143.0, 128.7, 127.9, 126.7, 123.5, 48.4, 44.2, 25.5, 22.7, 22.4.

HRMS (ESI): C₁₆H₁₉NH⁺ [M + H]⁺ Calcd 226.1590, found, 226.1589^[2]

4-(2-(oxetan-3-yl)-1-phenylethyl) pyridine (50)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 3:2) as a colorless oil in 35.0 mg, 73% yield.

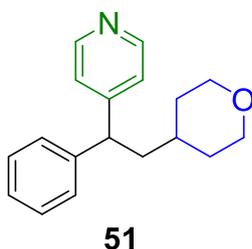
TLC: (SiO₂): R_f (PE: EA= 3: 2) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 6.1 Hz, 2H), 7.25 – 7.07 (m, 5H), 7.05 (d, *J* = 6.3 Hz, 2H), 4.60 – 4.48 (m, 2H), 4.23 (dt, *J* = 38.5, 6.3 Hz, 2H), 3.68 (t, *J* = 7.8 Hz, 1H), 2.90 – 2.76 (m, 1H), 2.36 (t, *J* = 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 153.1, 150.0, 142.2, 128.9, 127.8, 127.1, 123.0, 77.2, 48.8, 38.8, 33.8.

HRMS (ESI): C₁₆H₁₇NOH⁺ [M+H]⁺ Calcd 240.1383, Found 240.1389.

4-(1-phenyl-2-(tetrahydro-2H-pyran-4-yl) ethyl) pyridine (51)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 3:2) as a colorless oil in 39.6.1 mg, 74% yield.

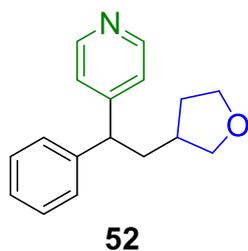
TLC: (SiO₂): R_f (PE: EA= 3: 2) = 0.4

¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 6.1 Hz, 2H), 7.22 (q, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 3H), 7.09 (d, *J* = 6.1 Hz, 2H), 3.96 (t, *J* = 8.1 Hz, 1H), 3.87 – 3.79 (m, 2H), 3.17 (t, *J* = 11.3 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.57 – 1.50 (m, 2H), 1.31 – 1.19 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.1, 149.7, 142.8, 128.8, 127.8, 126.9, 123.2, 67.8, 47.1, 42.2, 33.2, 32.9, 32.4.

HRMS (ESI): C₁₈H₂₁NOH⁺ [M+H]⁺ Calcd 268.1696, found, 268.1693^[2]

4-(1-phenyl-2-(tetrahydrofuran-3-yl) ethyl) pyridine (52)



According to the general procedure 1, the product was isolated by flash chromatography (PE: EA = 3:2) as a colorless oil in 35.1 mg, 69% yield.

TLC: (SiO₂): R_f (PE: EA= 3: 2) = 0.4

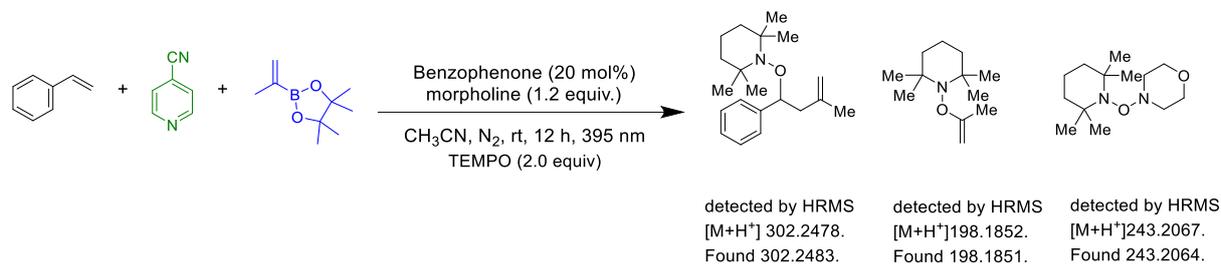
¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 6.3 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.09 (d, *J* = 4.4 Hz, 2H), 3.85 – 3.70 (m, 3H), 3.65 – 3.57 (m, 1H), 3.36 – 3.24 (m, 1H), 2.13 – 2.02 (m, 2H), 2.01 – 1.86 (m, 2H), 1.54 – 1.43 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 153.7, 149.9, 142.6, 128.9, 127.8, 127.0, 123.1, 73.2, 67.9, 49.7, 38.5, 37.2, 32.5.

HRMS (ESI): C₁₇H₁₉NOH⁺ [M+H]⁺ Calcd 254.1539, Found 254.1548.

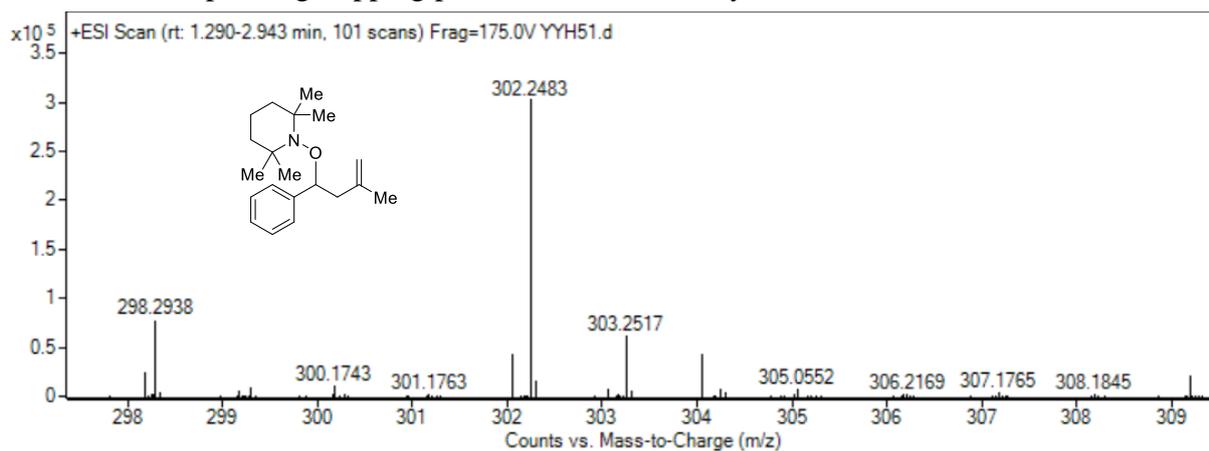
9. Mechanistic investigation experimental procedures

Radical trapping experiment

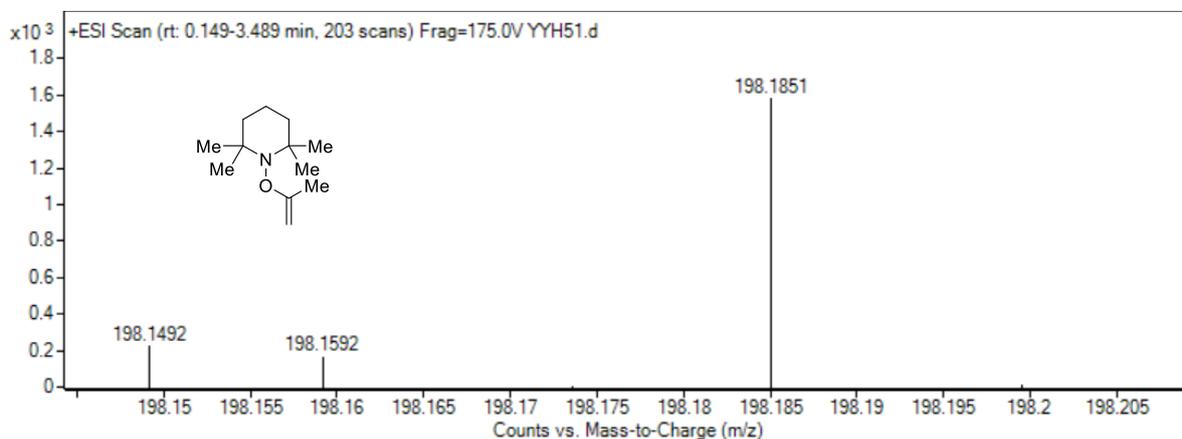


Synthesized according to general procedure 1: 4-Cyanopyridine (0.2 mmol, 1.0 equiv.), benzophenone (0.04 mmol, 0.2 equiv.), TEMPO (0.4 mmol, 2 equiv.) and Alkene (0.4 mmol, 2.0 equiv), BPiN (0.2 mmol, 1equiv.) in MeCN (0.05 M, 4 mL), room temperature, 12 h, 10 W 395 nm blue LEDs.

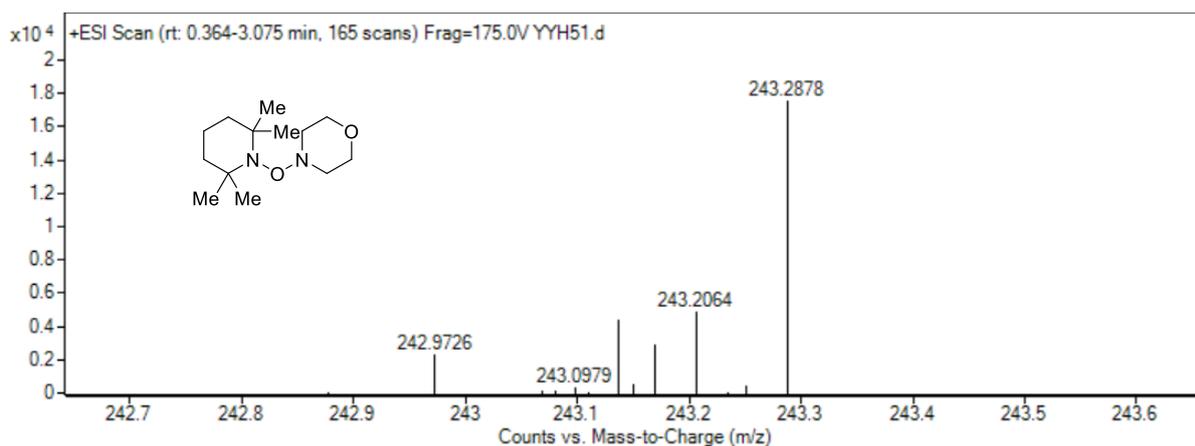
The corresponding trapping product was detected by HRMS.



HRMS (ESI): m/z calcd. For [C₂₀H₃₁NO+H]⁺; [M+H]⁺: 302.2478; found: 302.2483.

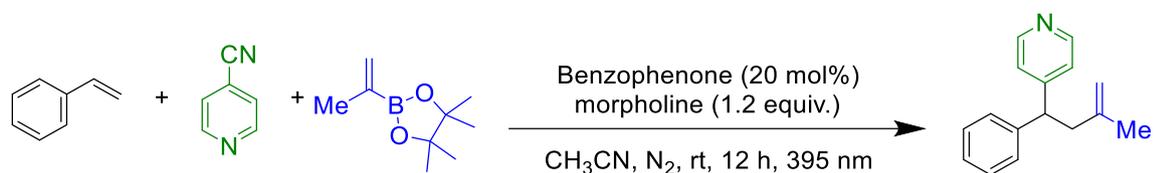


HRMS (ESI): m/z calcd. For [C₁₂H₂₃NO+H]⁺; [M+H]⁺: 198.1852; found: 198.1851.



HRMS (ESI): m/z calcd. For $[C_{13}H_{26}N_2O_2+H]^+$; $[M+H]^+$: 243.2067; found: 243.2064.

10. Gram-Scale reaction

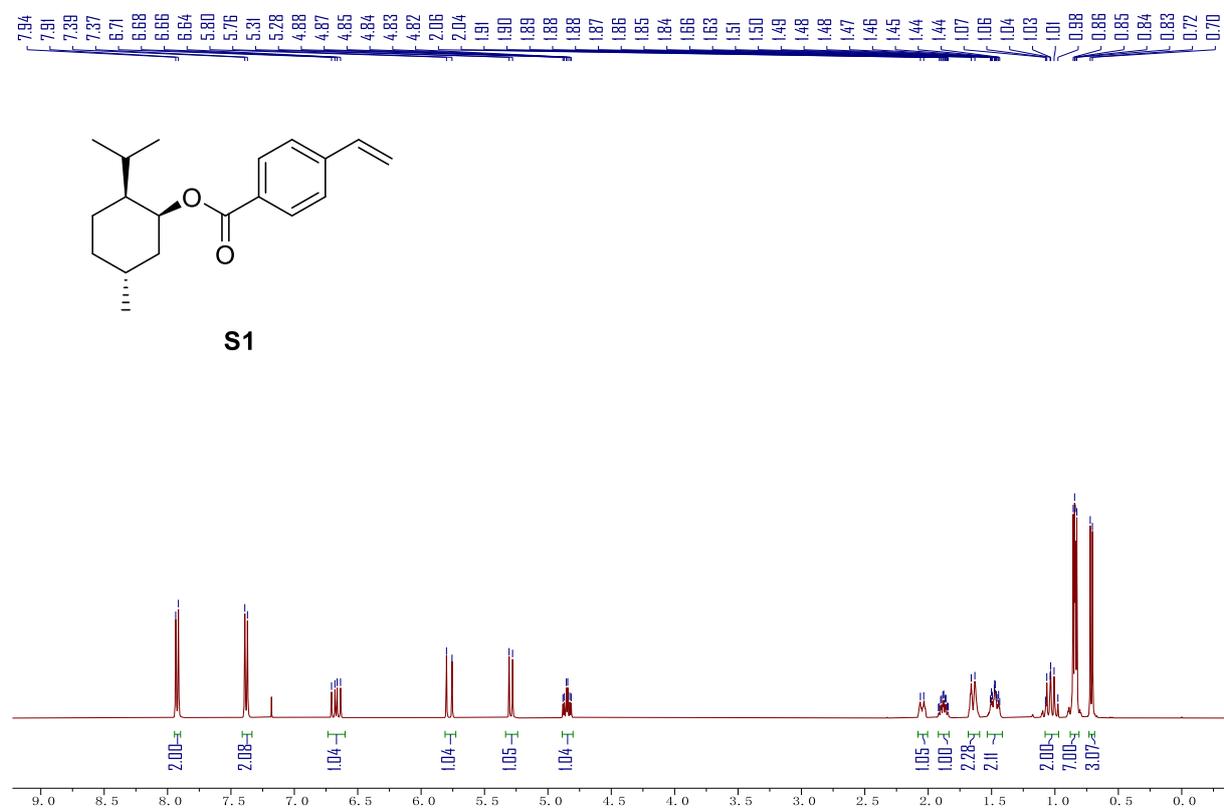


Synthesized according to General Procedure 1: 4-Cyanopyridine (5 mmol, 0.5205g, 1.0 equiv.), Benzophenone (1 mmol, 0.1825 g, 0.2 equiv.). Styrene (10 mmol, 1.16mL 2.0 equiv.), BPin (5 mmol, 0.95mL, 1.0 equiv.), morpholine (6 mmol, 0.52 mL, 1.2 equiv.) in CH_3CN (0.05 M). The reaction was irradiated with 10 W 395 nm blue LEDs, at room temperature. After 12 hours, the reaction mixture was concentrated under vacuum. Purification by flash chromatography (SiO_2 , PE: EA=4:1) afforded **1** (0.7810 g, 70%), as a yellow liquid, as shown in the figure below:

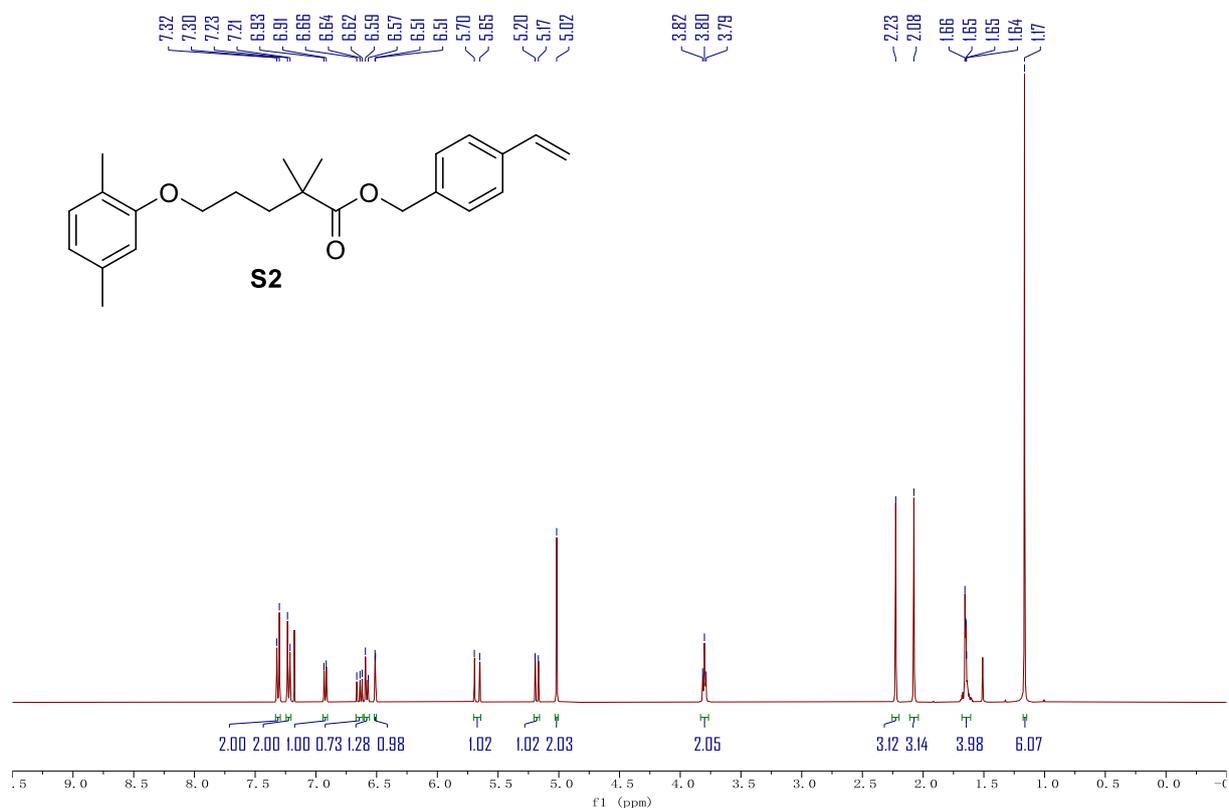


11. NMR Spectra of Substrates and Products

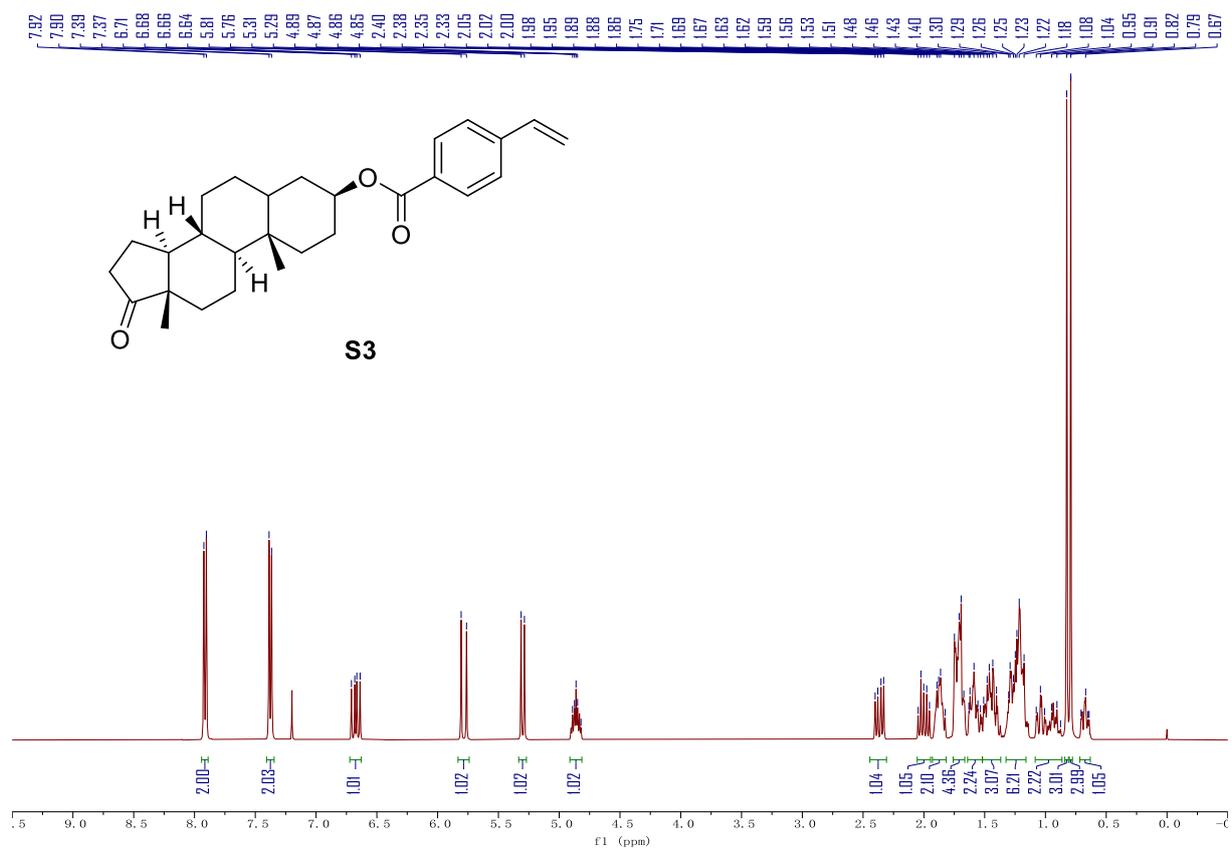
¹H NMR spectra of compound **S1** (400 MHz, Chloroform-*d*)



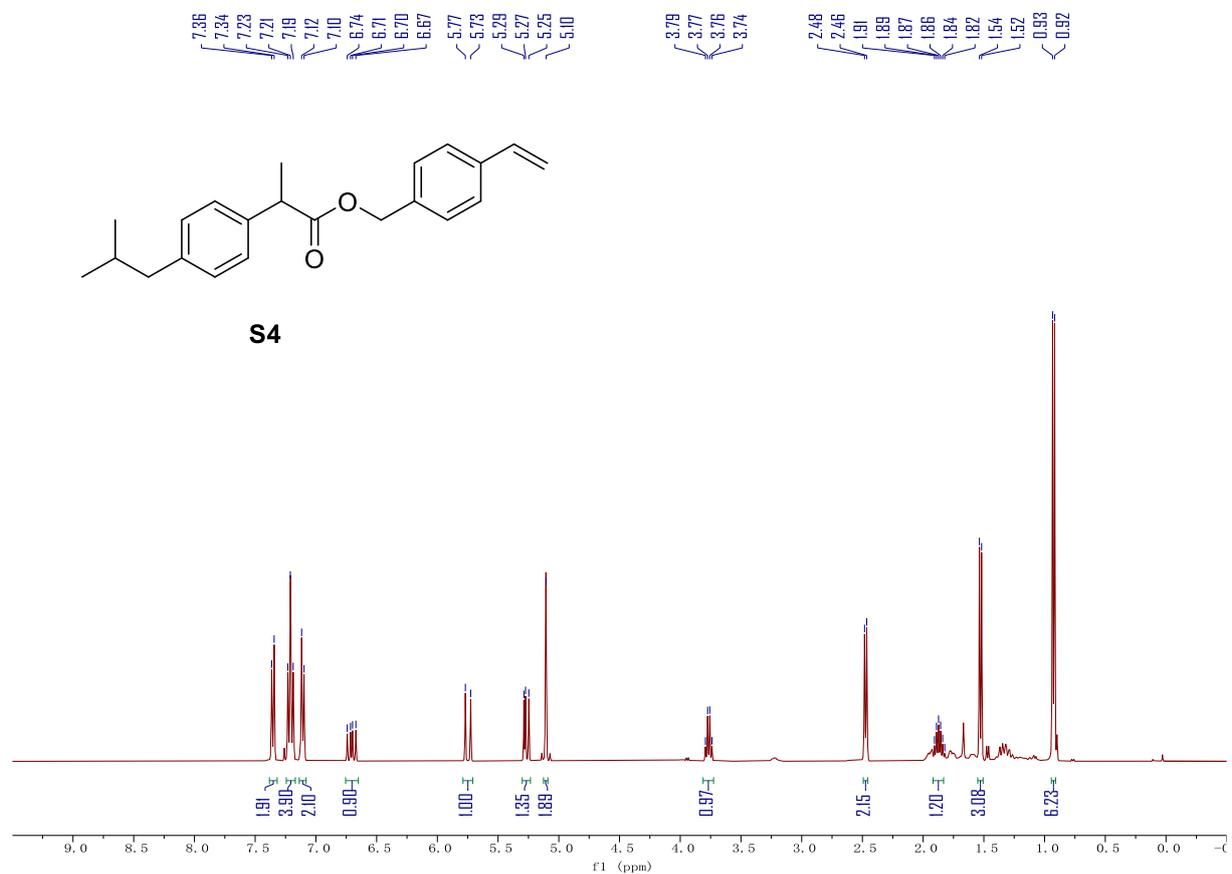
¹H NMR spectra of compound **S2** (400 MHz, Chloroform-*d*)



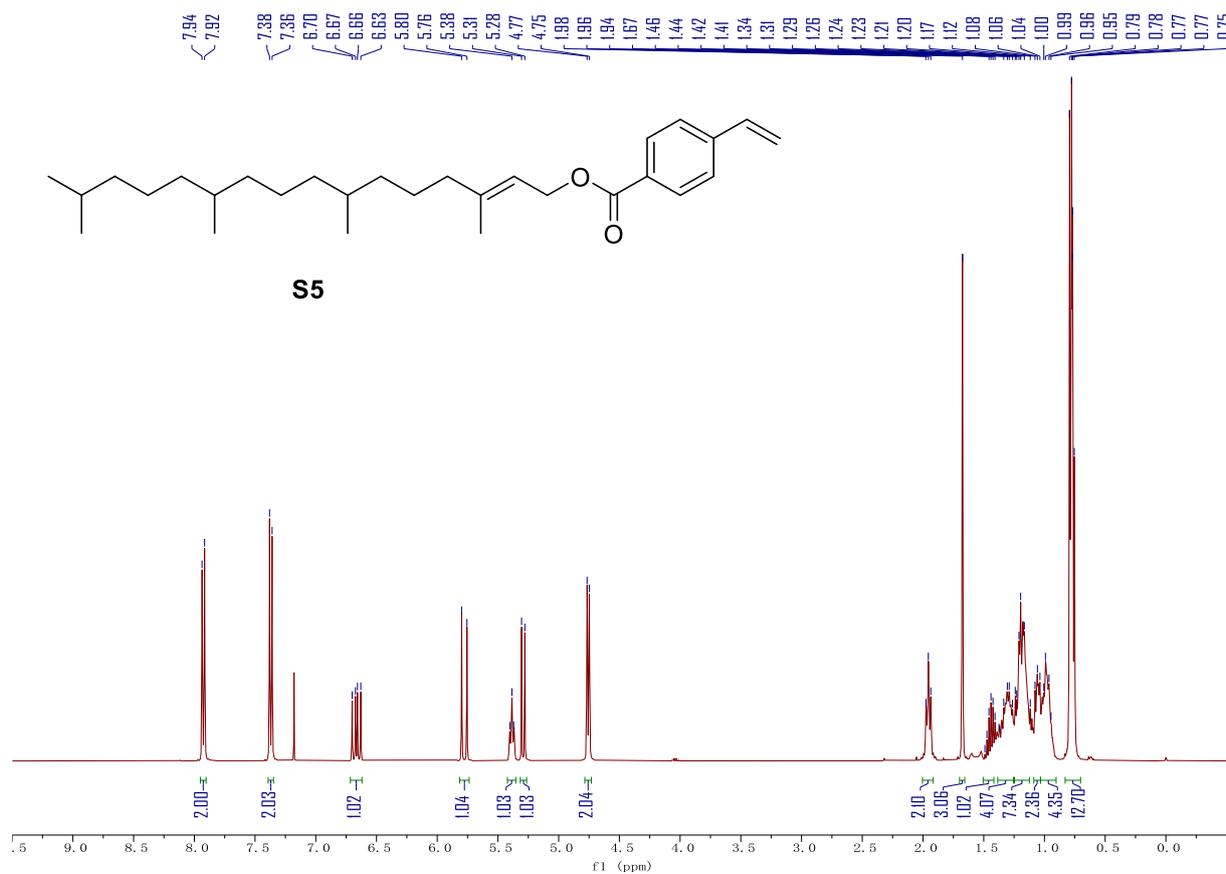
¹H NMR spectra of compound S3 (400 MHz, Chloroform-d)



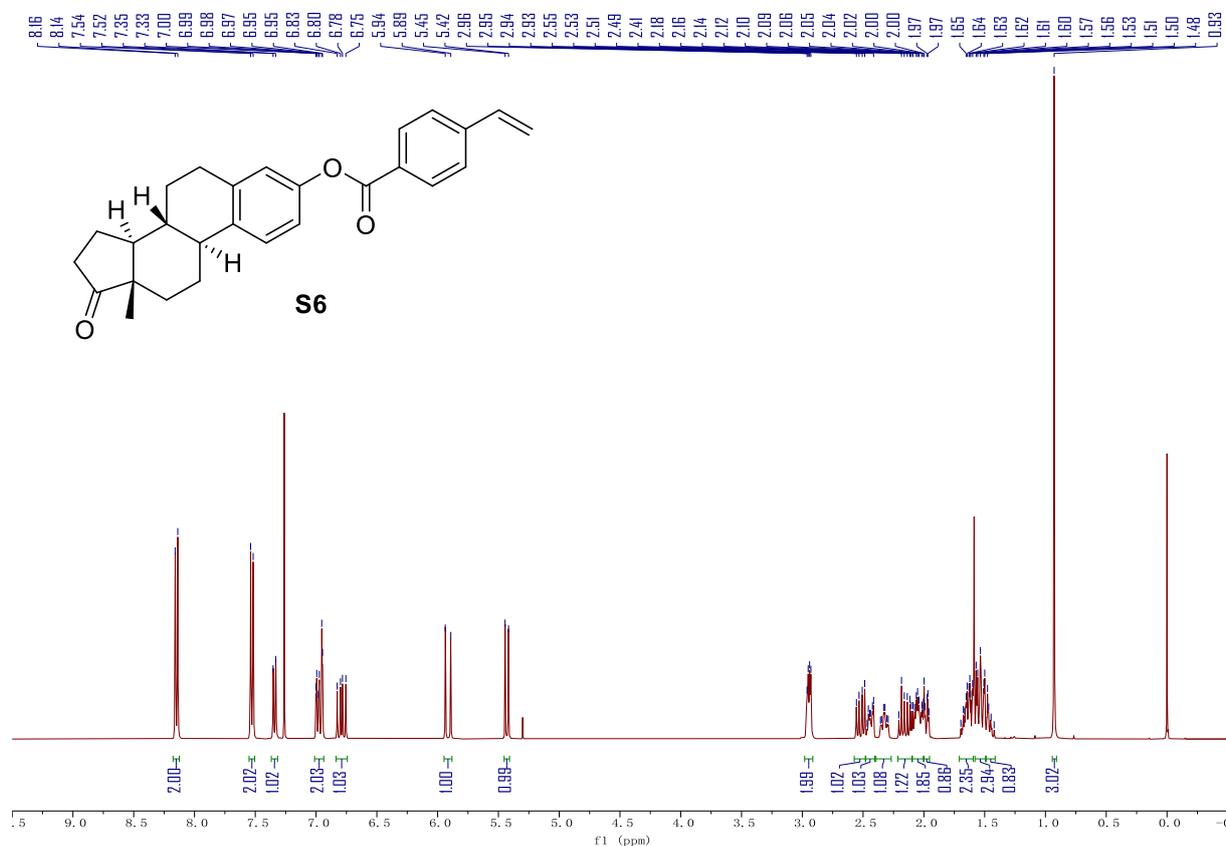
¹H NMR spectra of compound S4 (400 MHz, Chloroform-d)



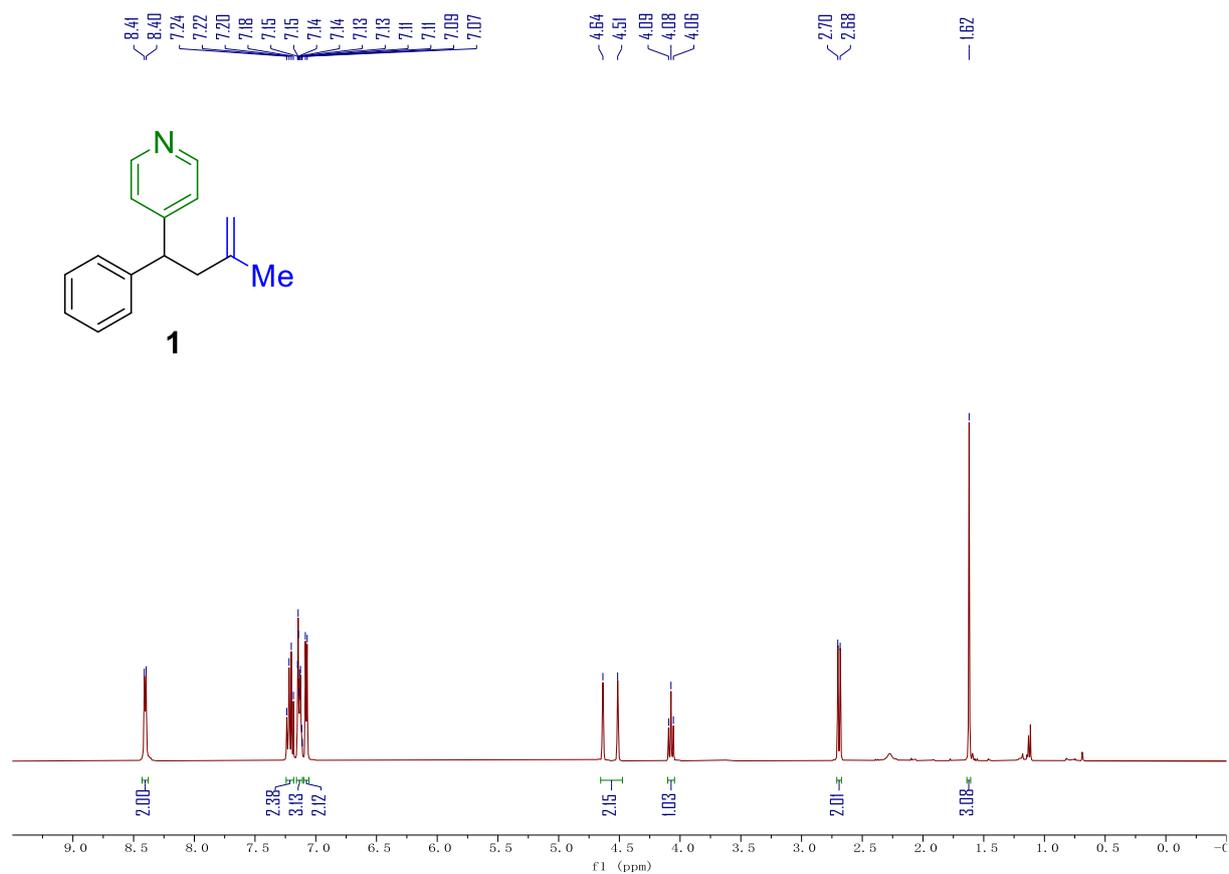
¹H NMR spectra of compound S5 (400 MHz, Chloroform-d)



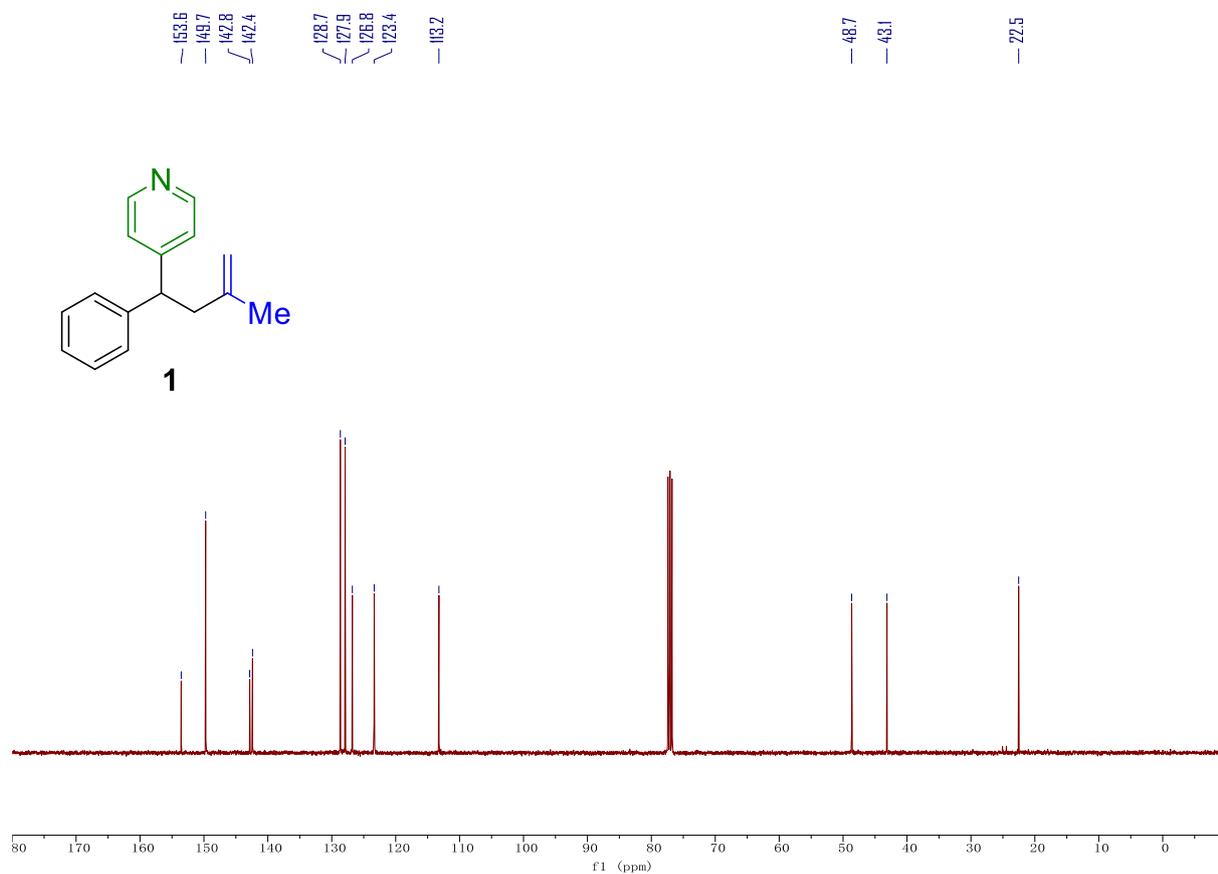
¹H NMR spectra of compound S6 (400 MHz, Chloroform-d)



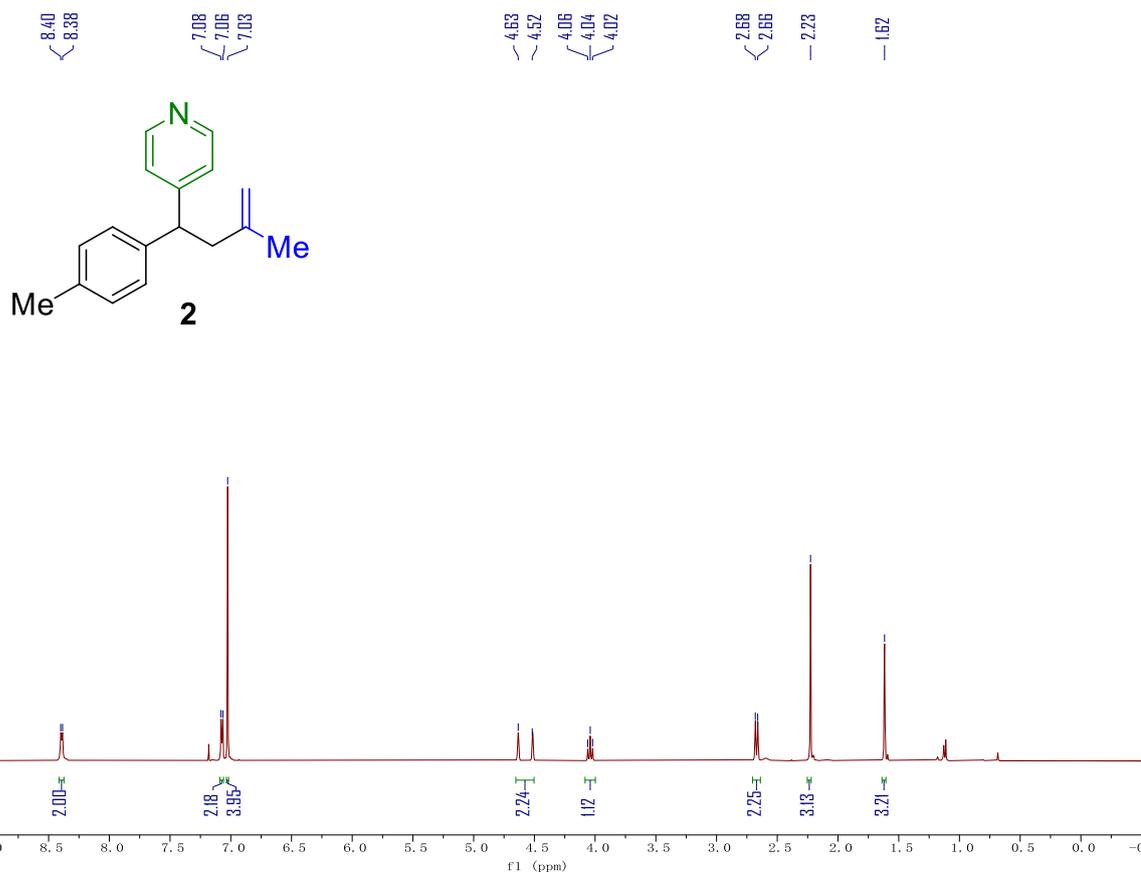
^1H NMR spectra of compound **1** (400 MHz, Chloroform-*d*)



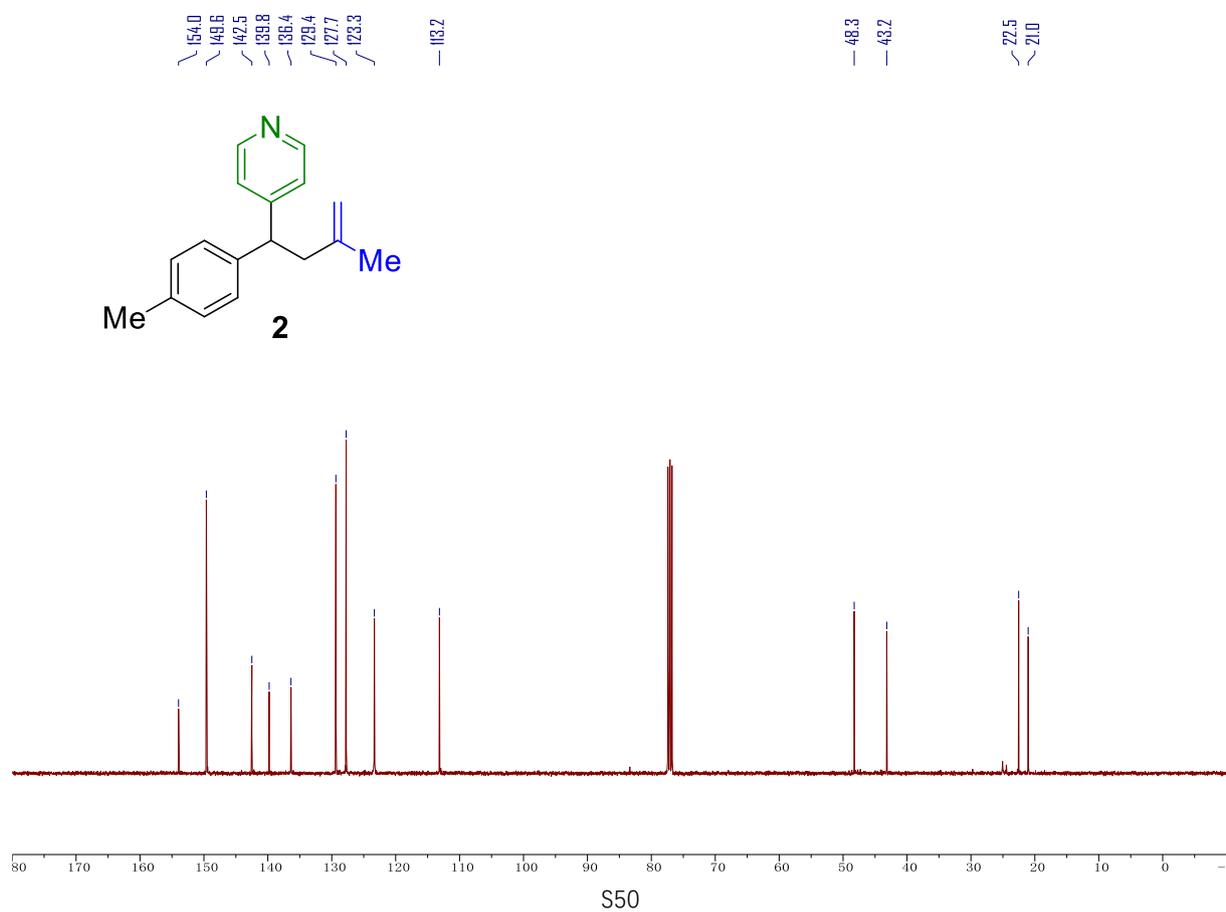
^{13}C NMR spectra of compound **1** (101 MHz, Chloroform-*d*)



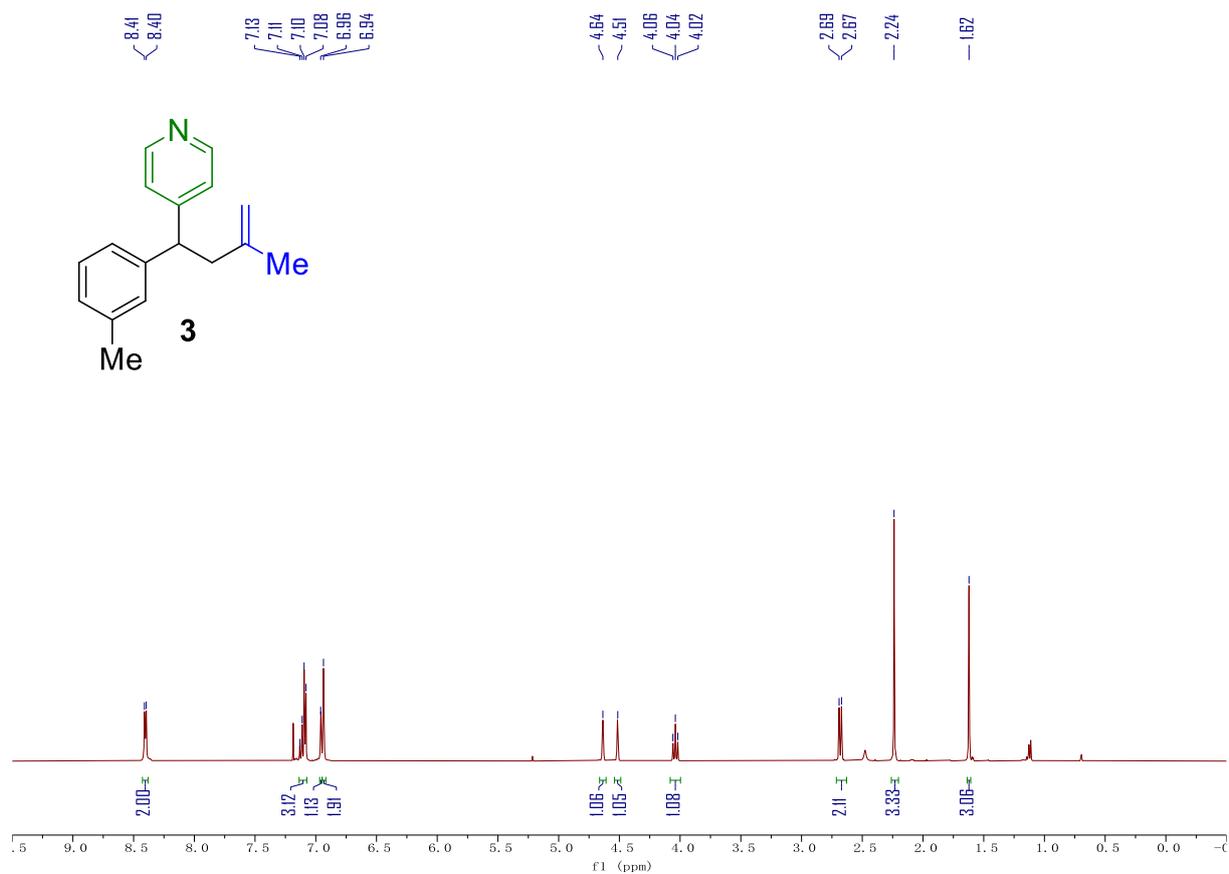
¹H NMR spectra of compound 2 (400 MHz, Chloroform-*d*)



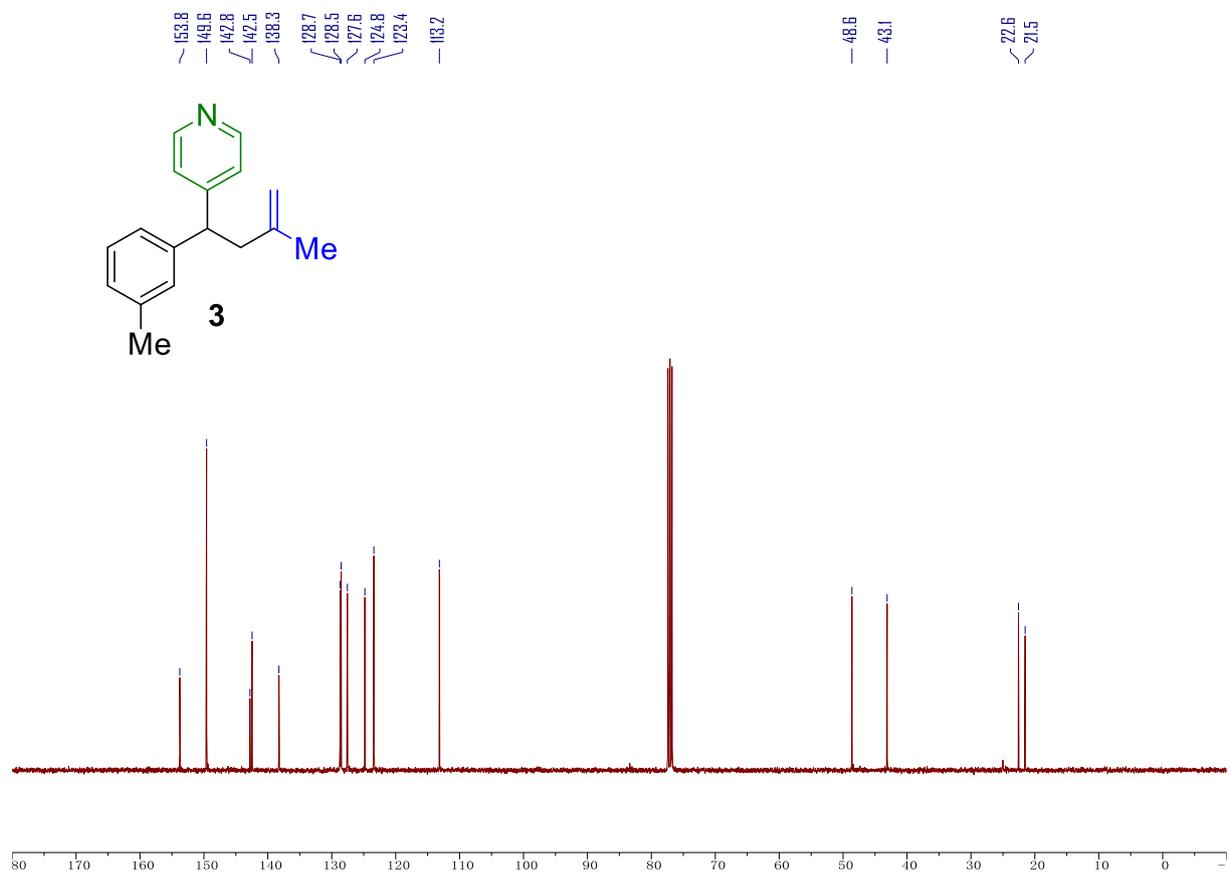
¹³C NMR spectra of compound 2 (101 MHz, Chloroform-*d*)



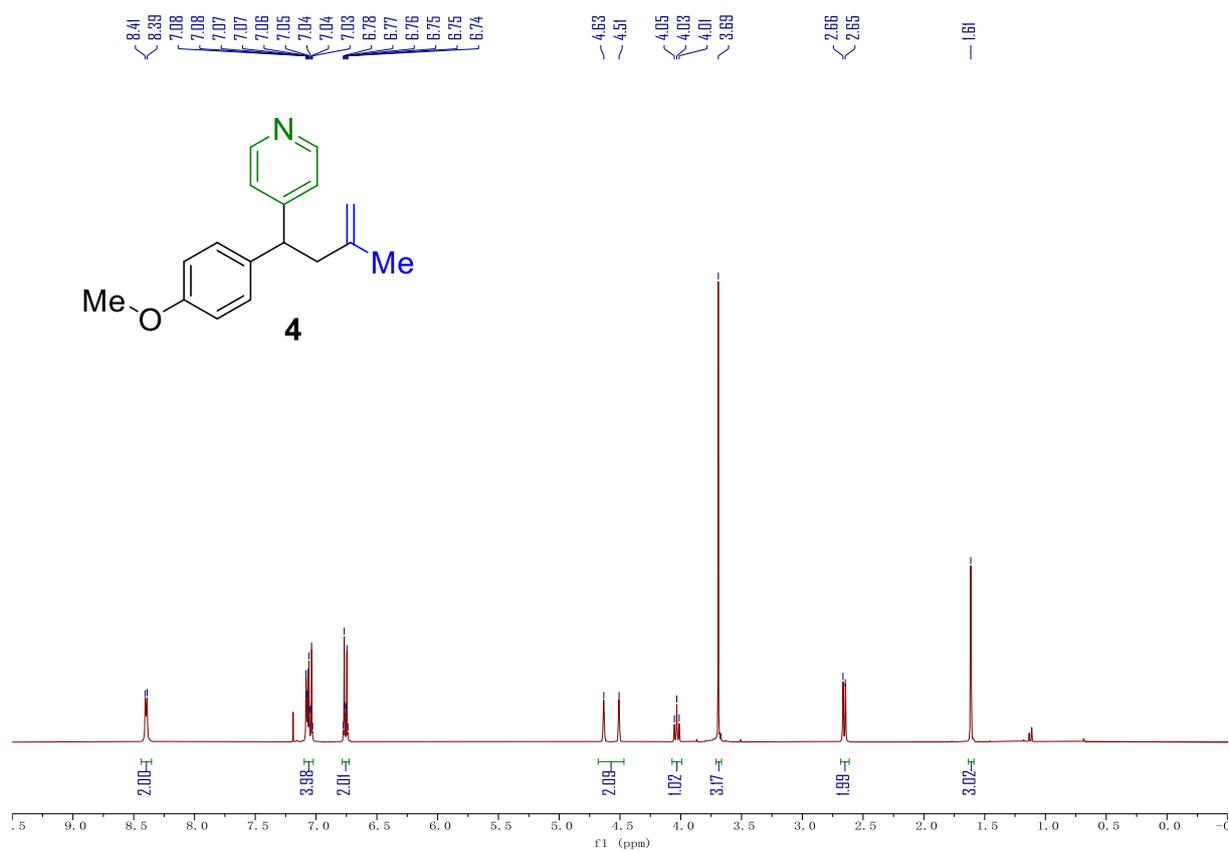
¹H NMR spectra of compound 3 (400 MHz, Chloroform-*d*)



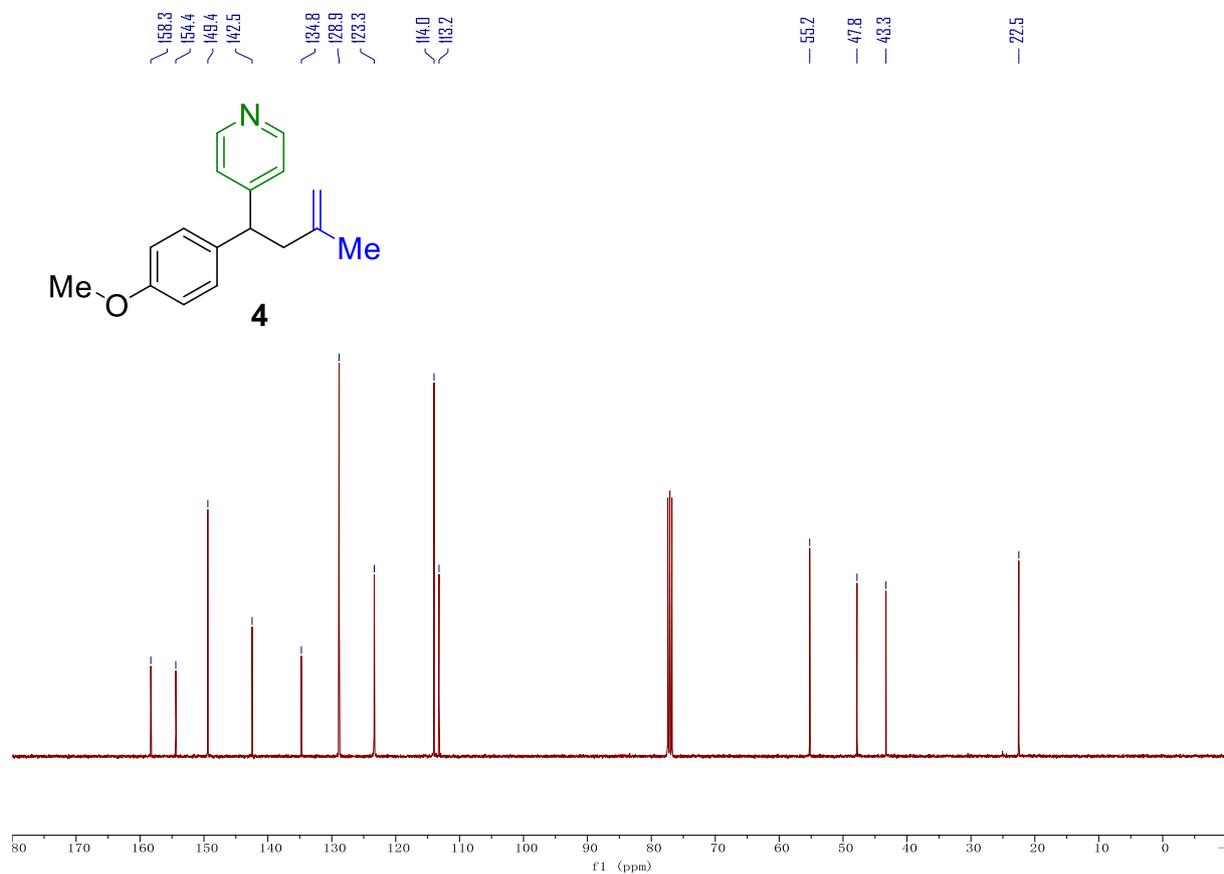
¹³C NMR spectra of compound 3 (101 MHz, Chloroform-*d*)



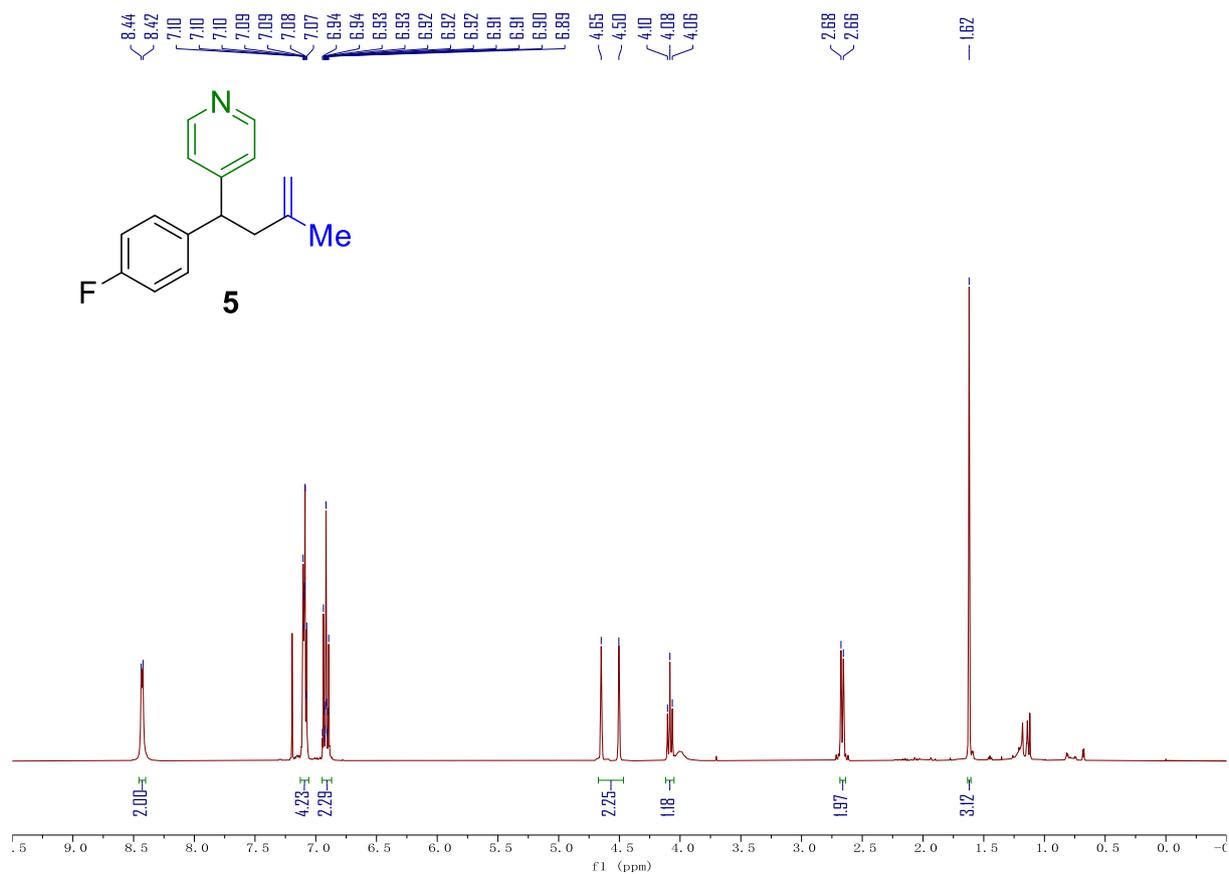
^1H NMR spectra of compound **4** (400 MHz, Chloroform-*d*)



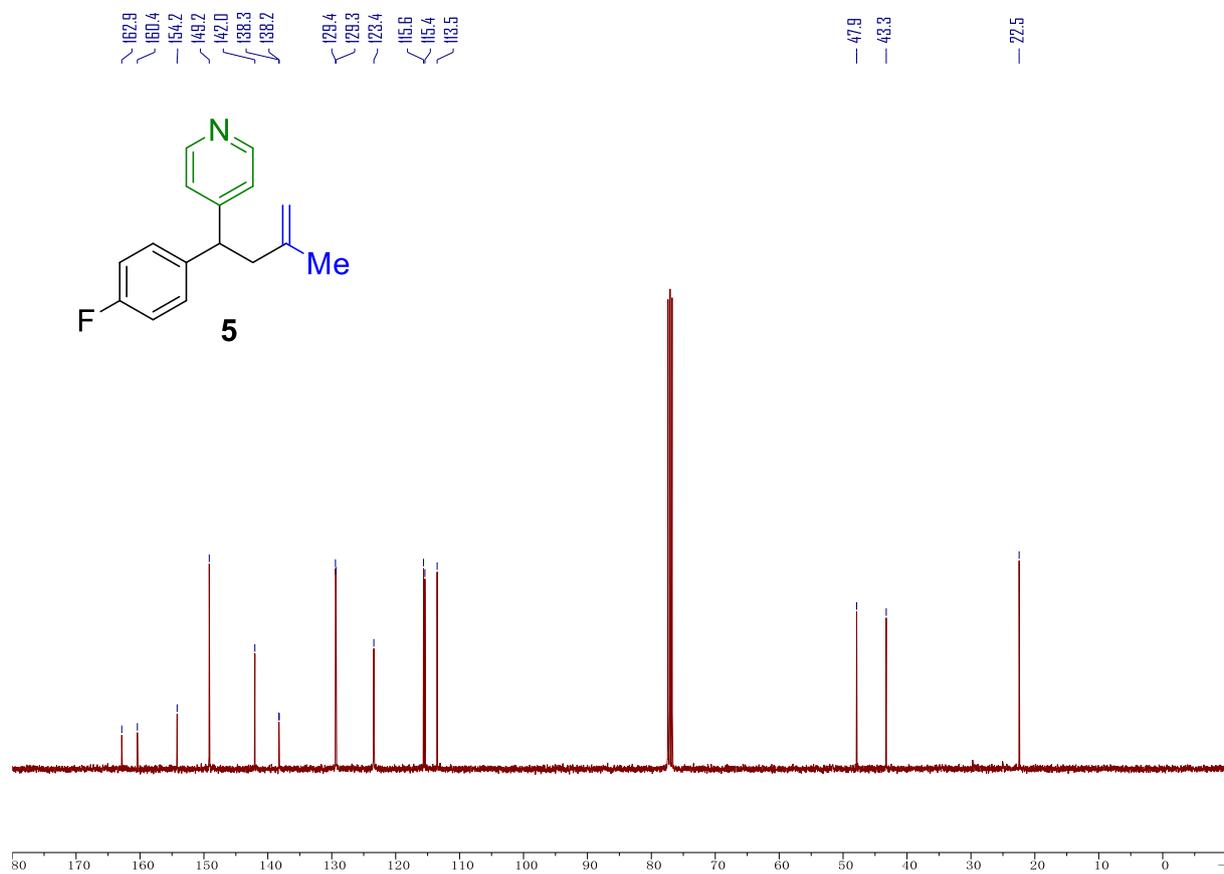
^{13}C NMR spectra of compound **4** (101 MHz, Chloroform-*d*)



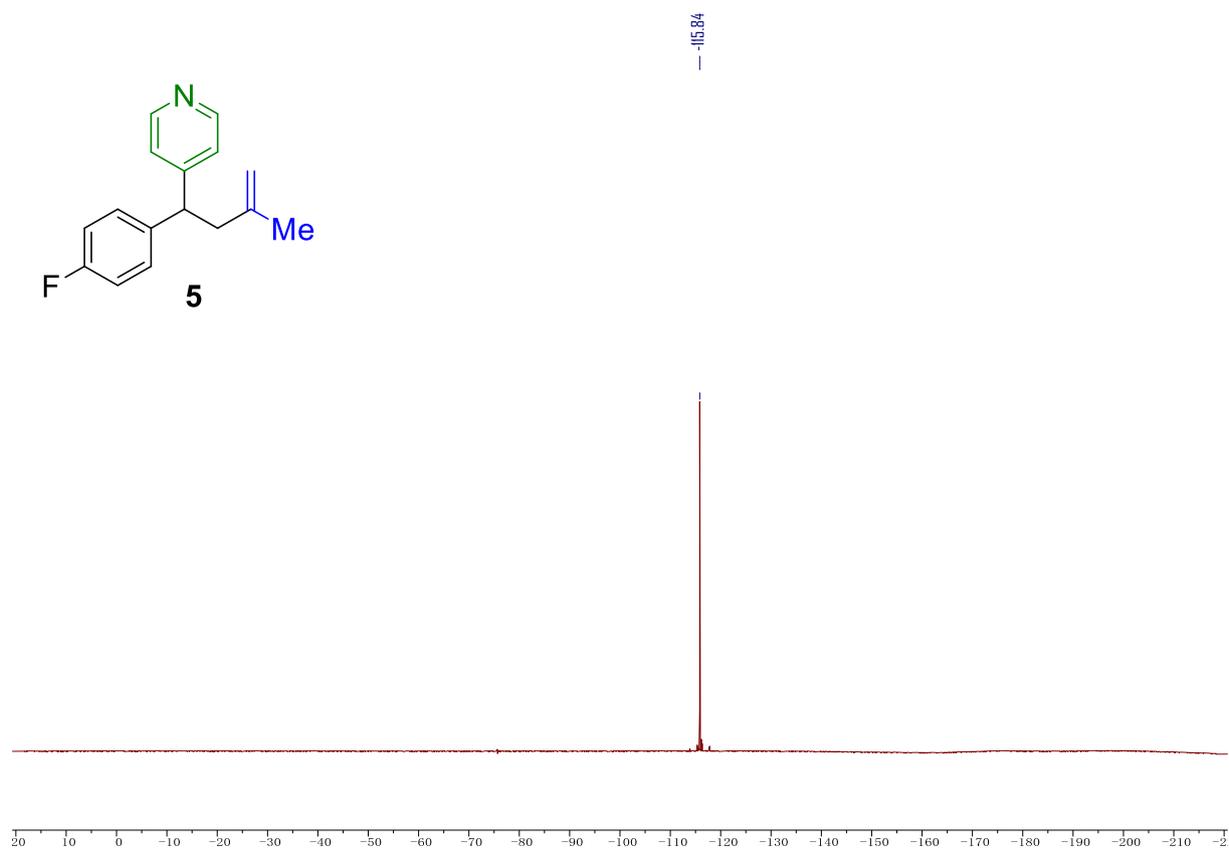
¹H NMR spectra of compound **5** (400 MHz, Chloroform-*d*)



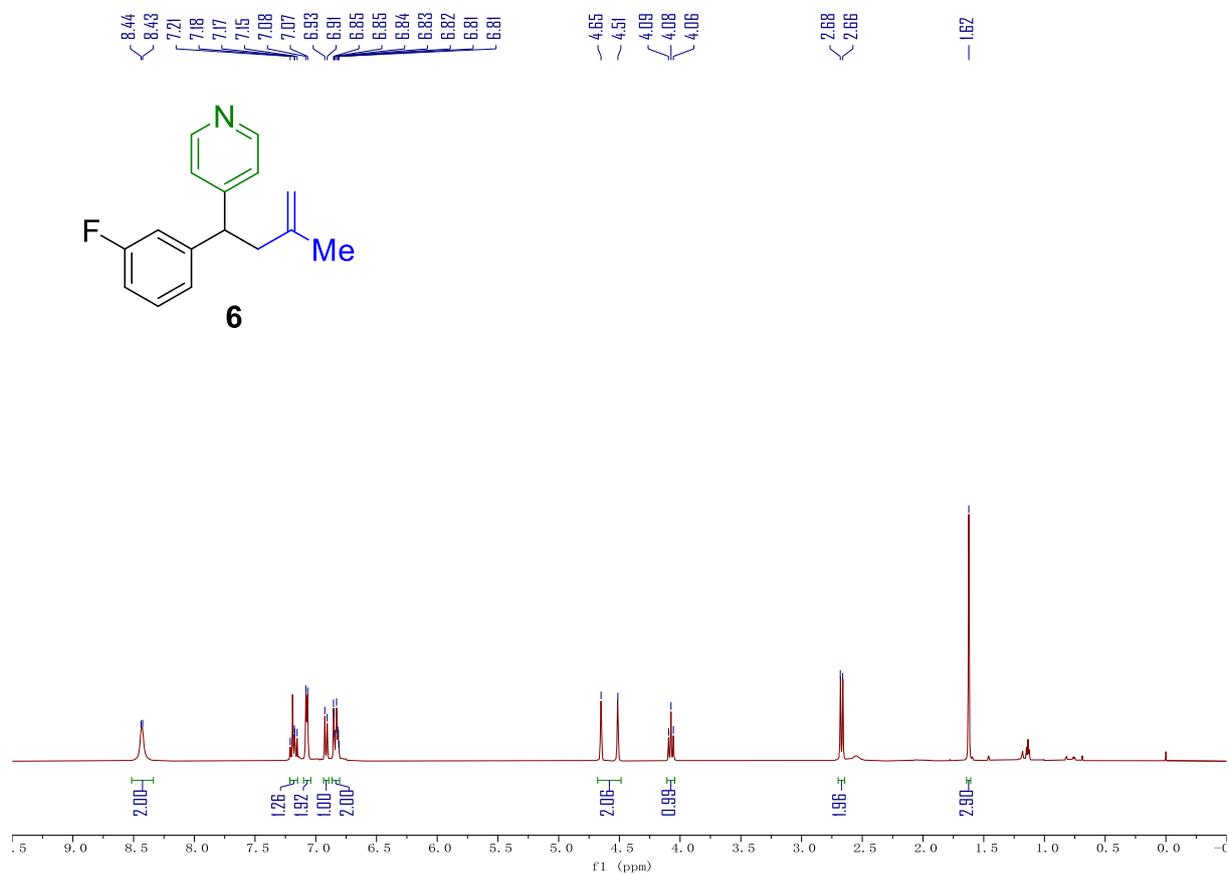
¹³C NMR spectra of compound **5** (101 MHz, Chloroform-*d*)



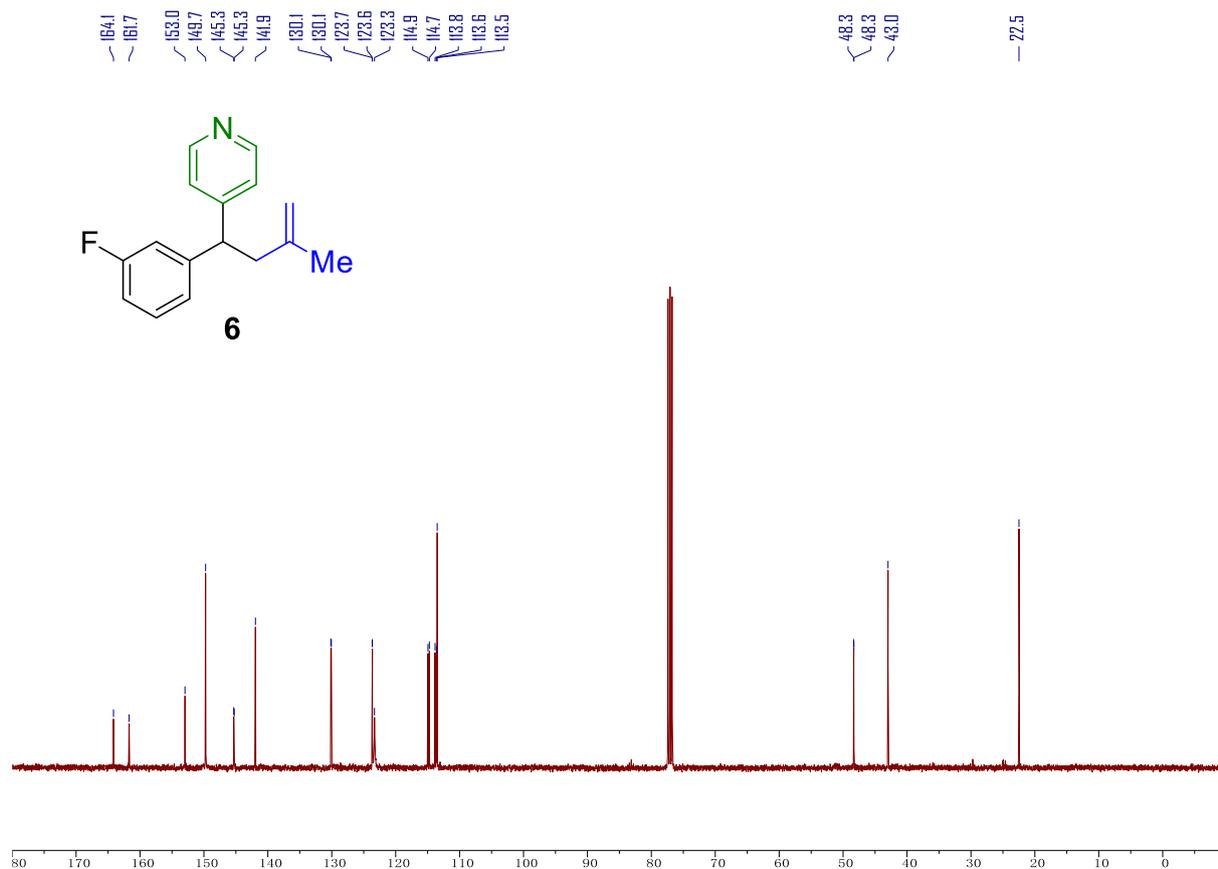
^{19}F NMR spectra of compound 5 (376 MHz, Chloroform-*d*)



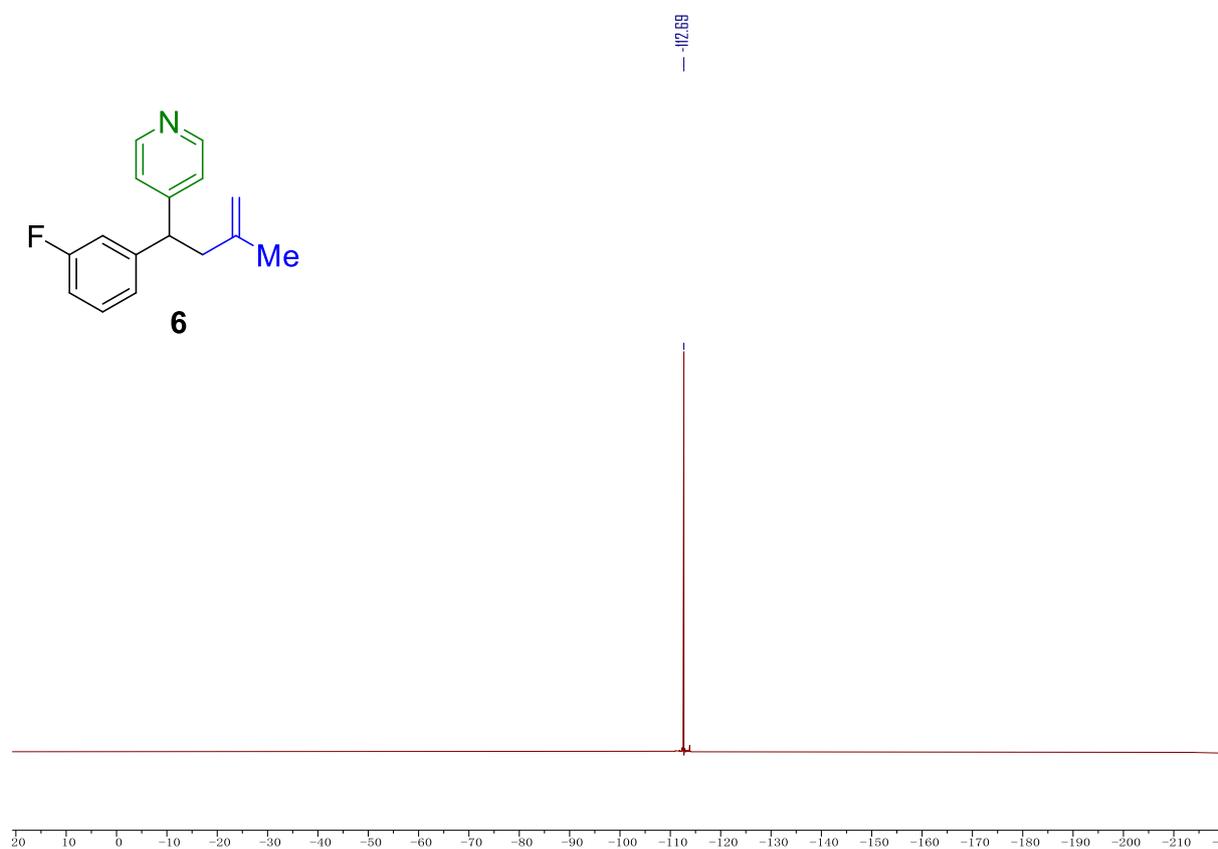
^1H NMR spectra of compound 6 (400 MHz, Chloroform-*d*)



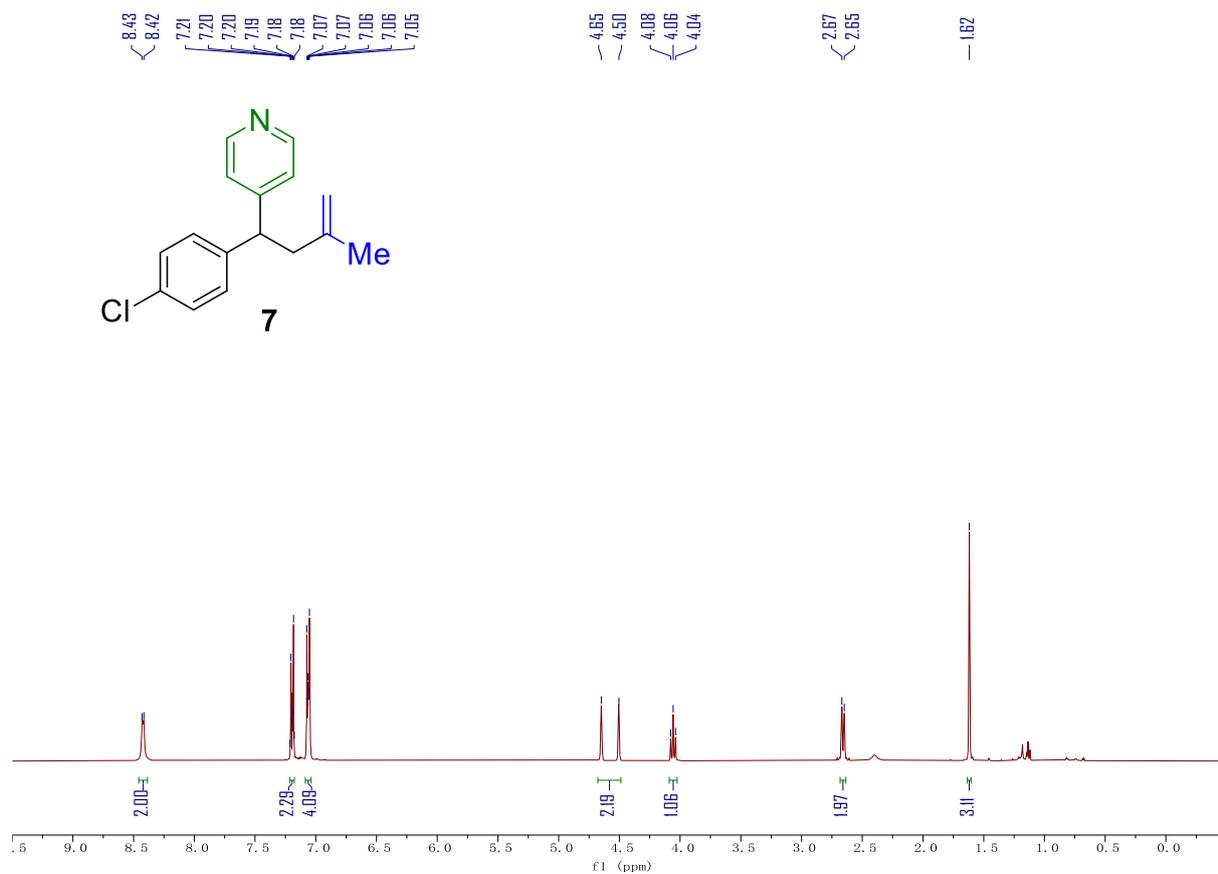
¹³C NMR spectra of compound **6** (101 MHz, Chloroform-*d*)



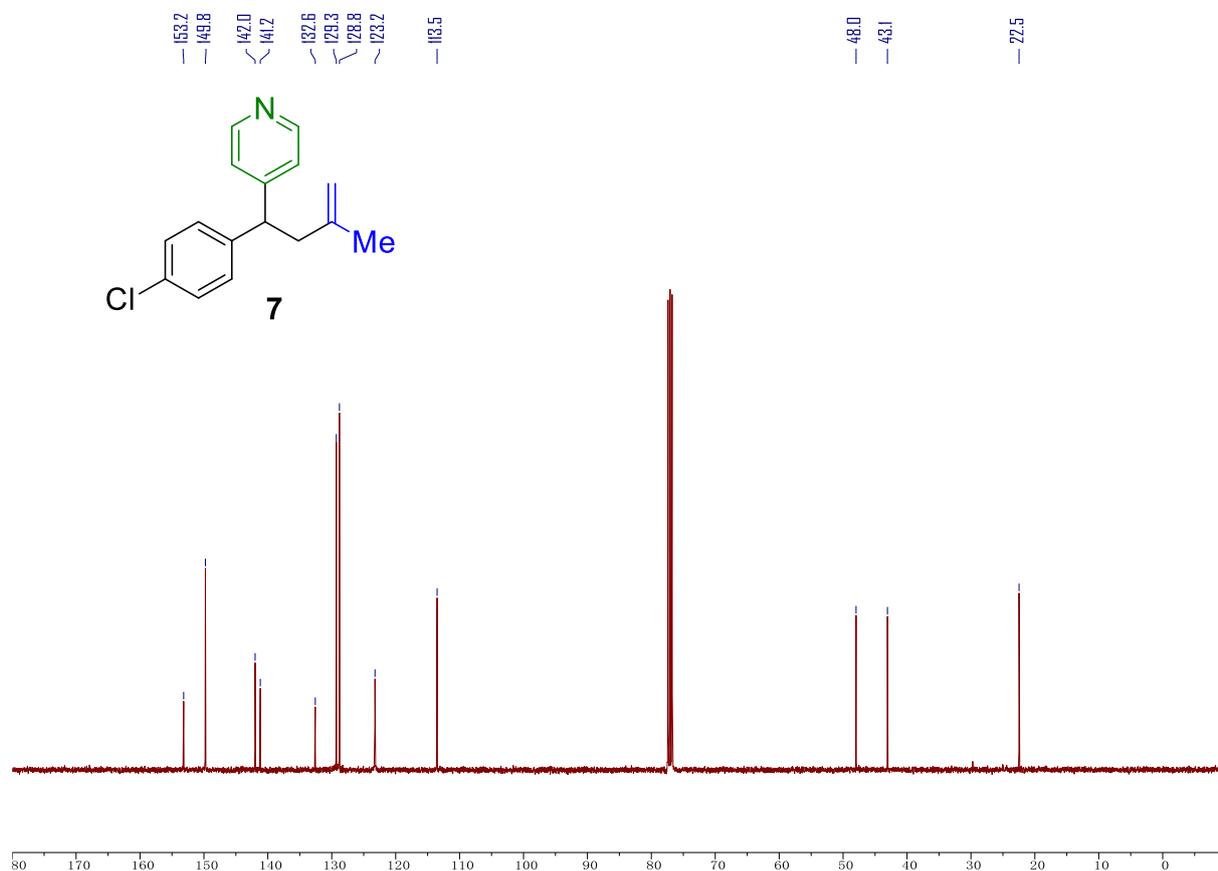
¹⁹F NMR spectra of compound **6** (376 MHz, Chloroform-*d*)



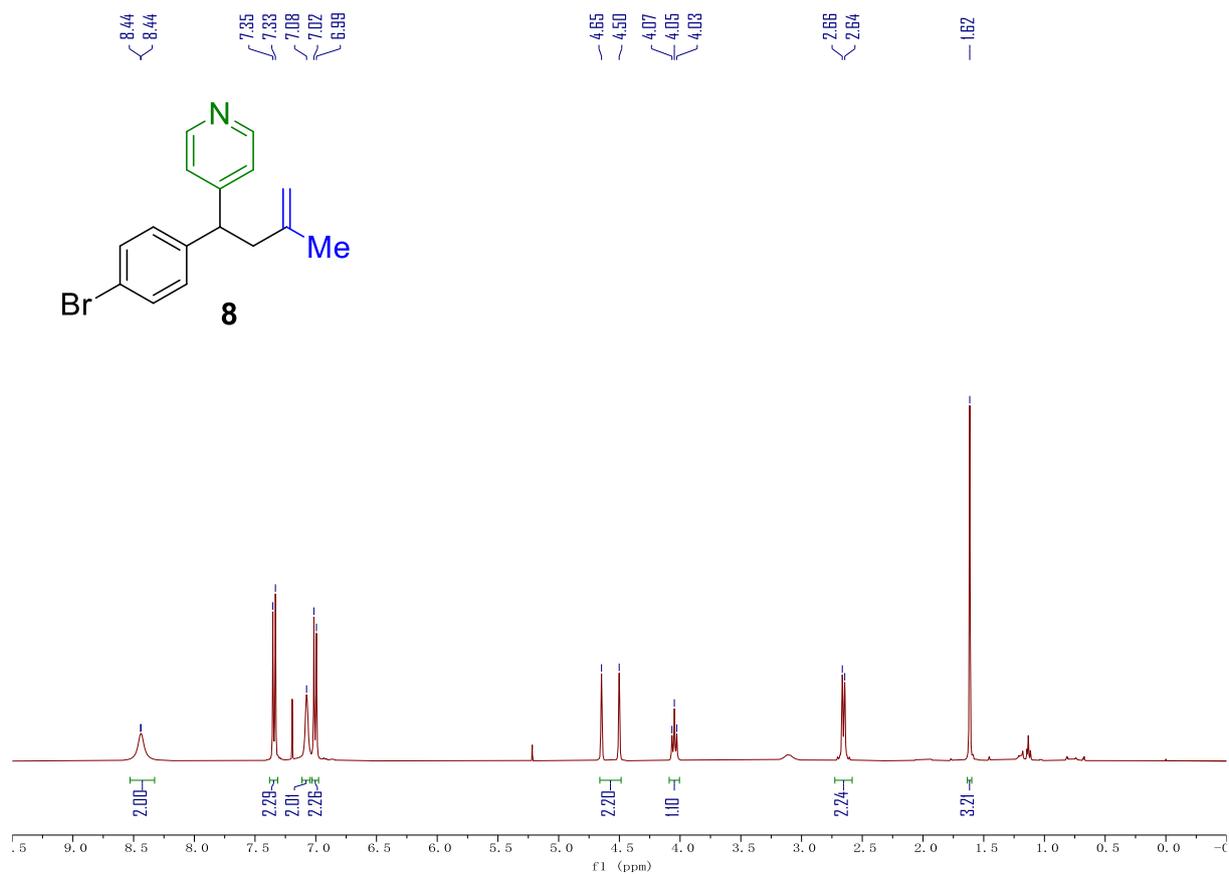
¹H NMR spectra of compound 7 (400 MHz, Chloroform-*d*)



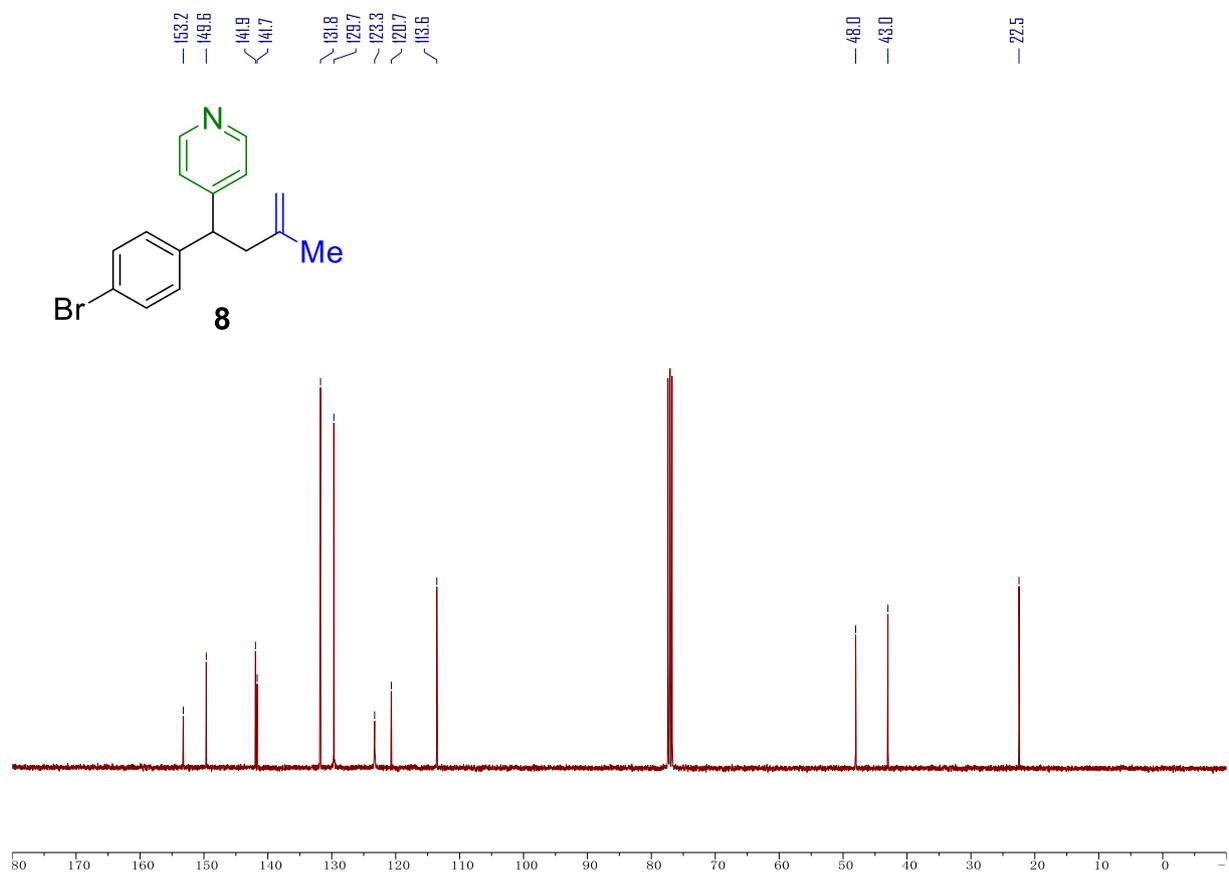
¹³C NMR spectra of compound 7 (101 MHz, Chloroform-*d*)



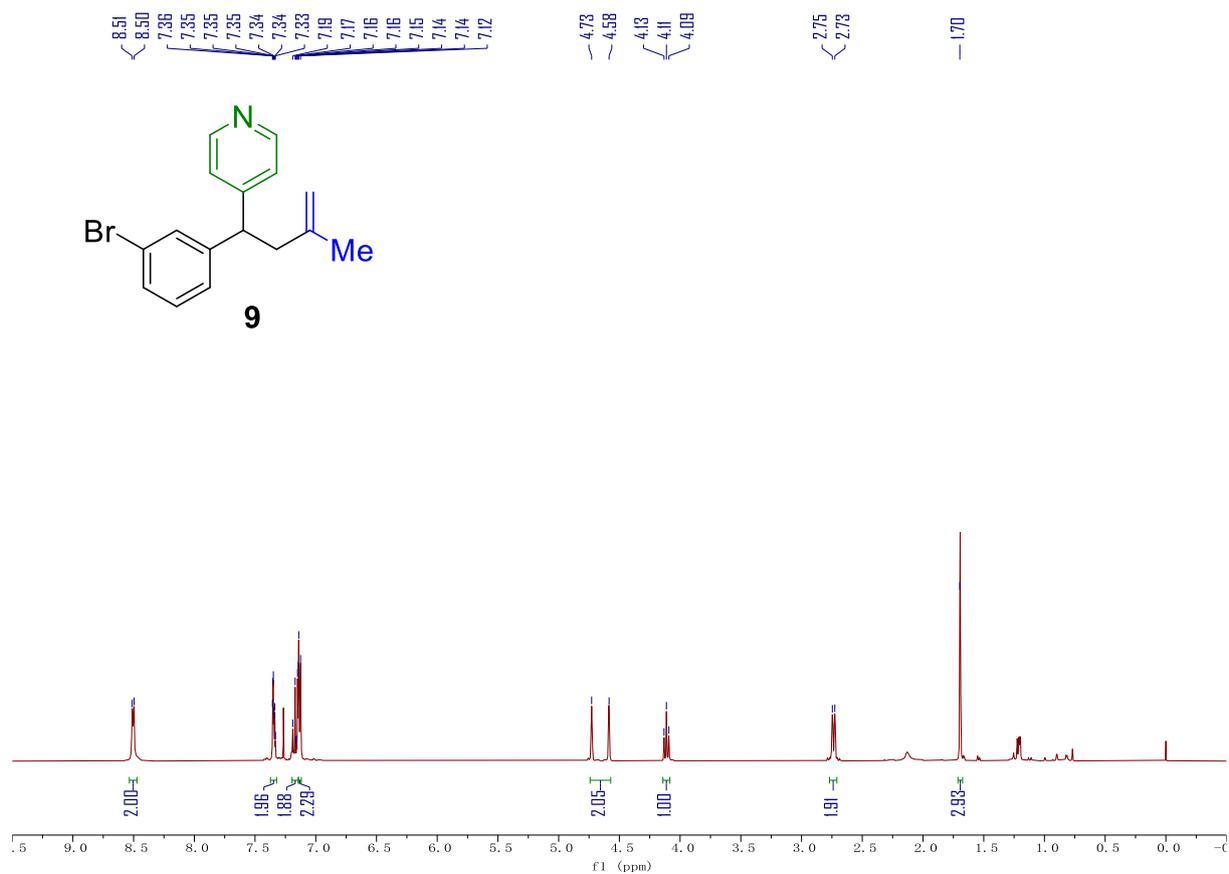
¹H NMR spectra of compound **8 (400 MHz, Chloroform-*d*)**



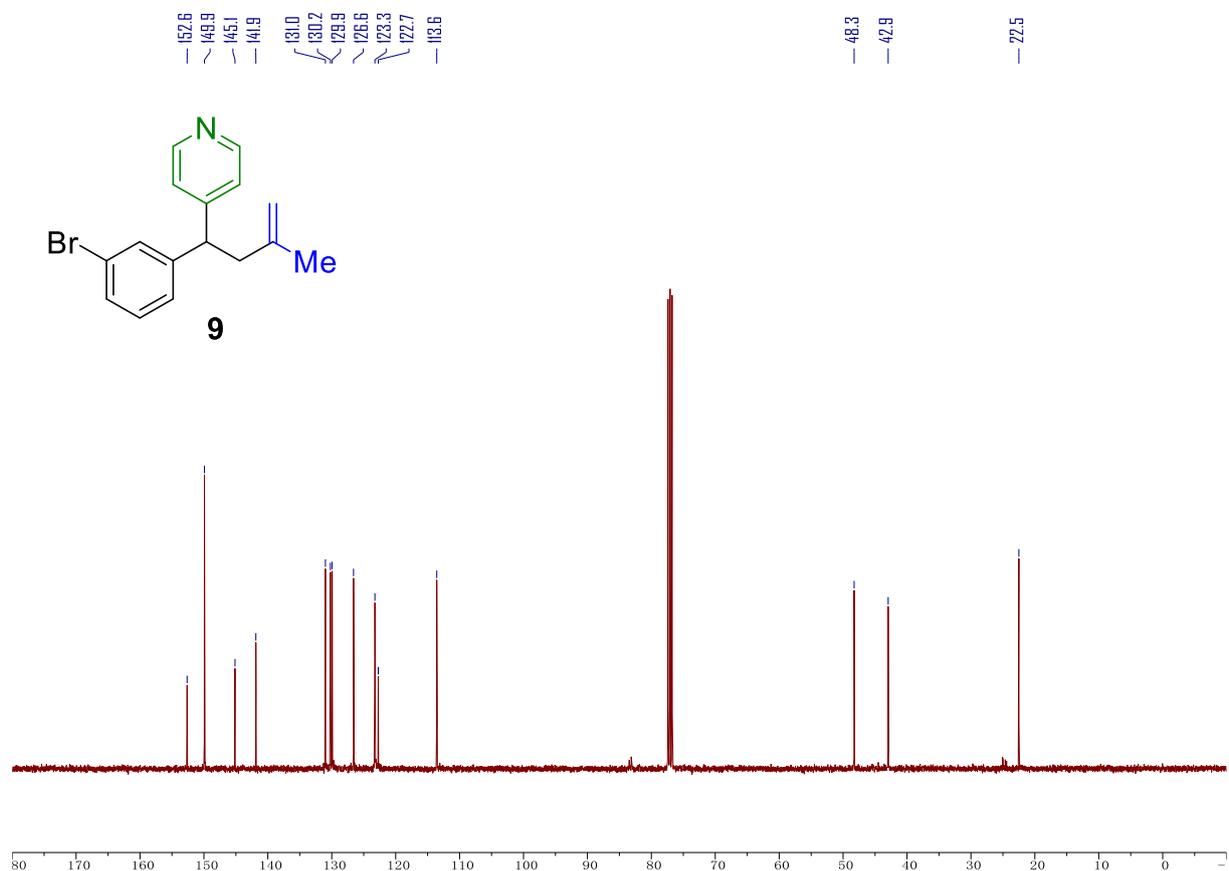
¹³C NMR spectra of compound **8 (101 MHz, Chloroform-*d*)**



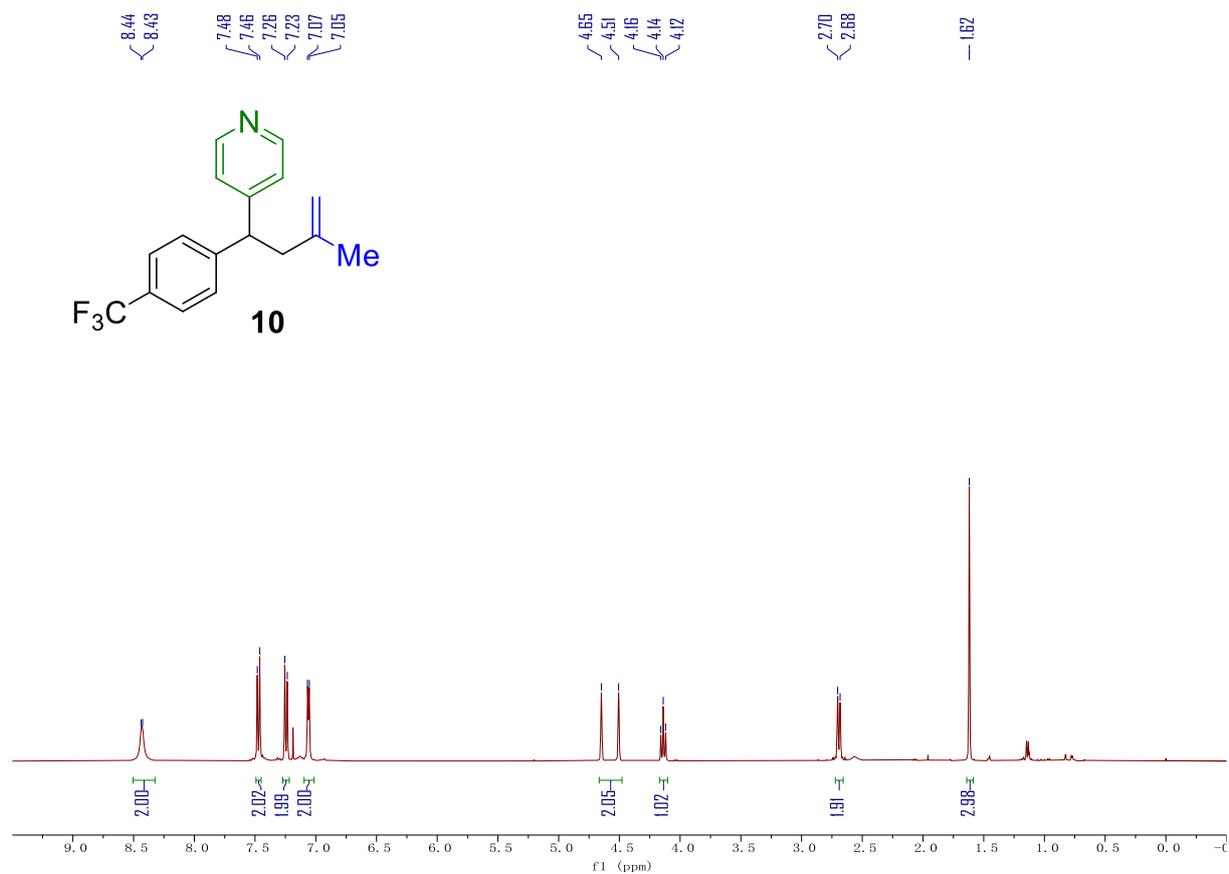
¹H NMR spectra of compound 9 (400 MHz, Chloroform-*d*)



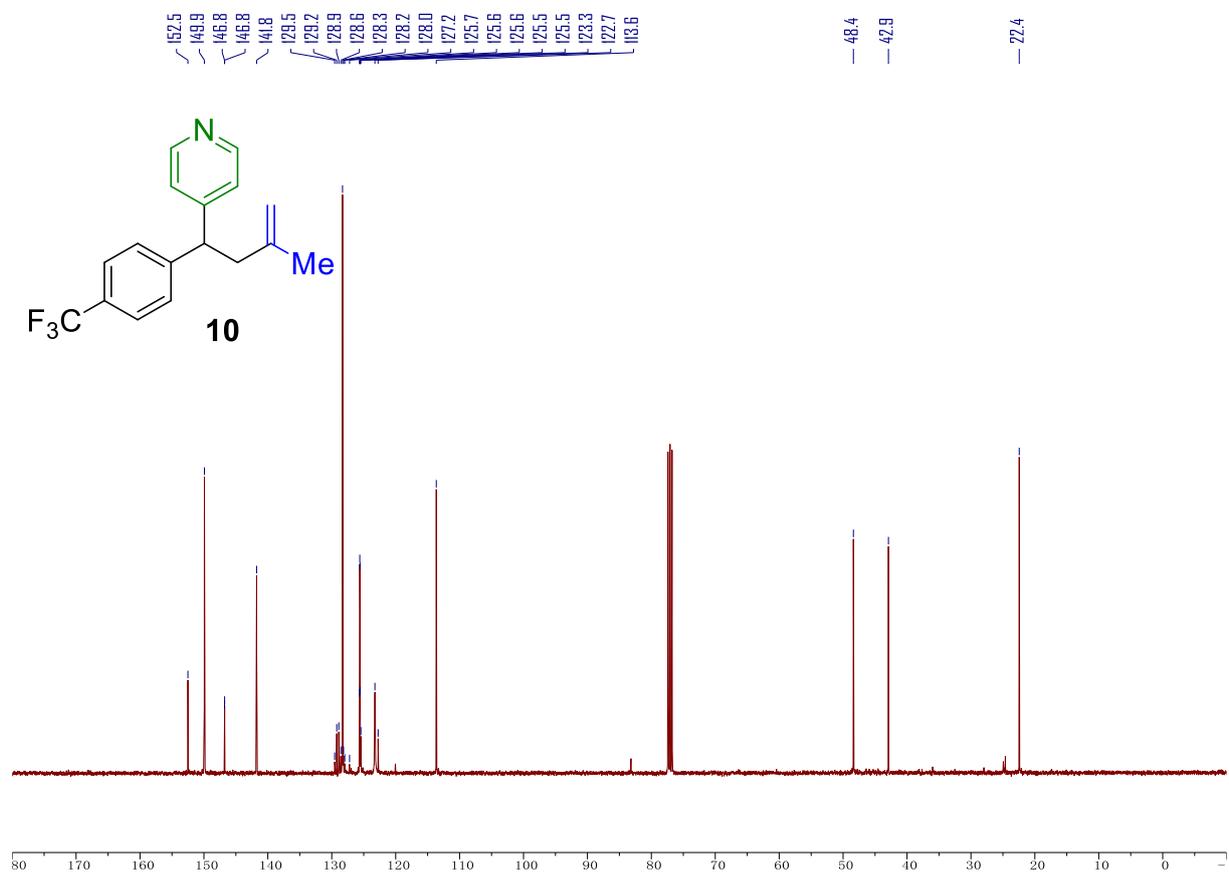
¹³C NMR spectra of compound 9 (101 MHz, Chloroform-*d*)



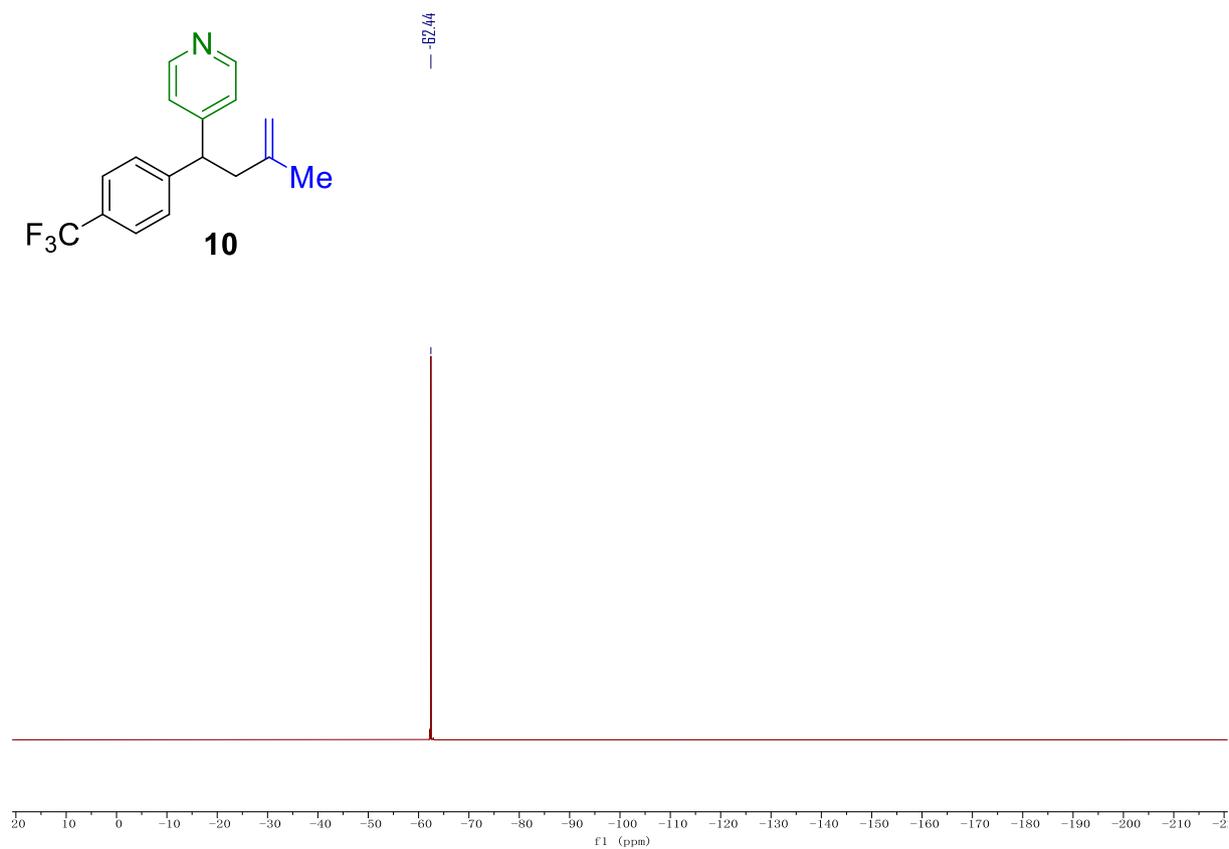
¹H NMR spectra of compound 10 (400 MHz, Chloroform-*d*)



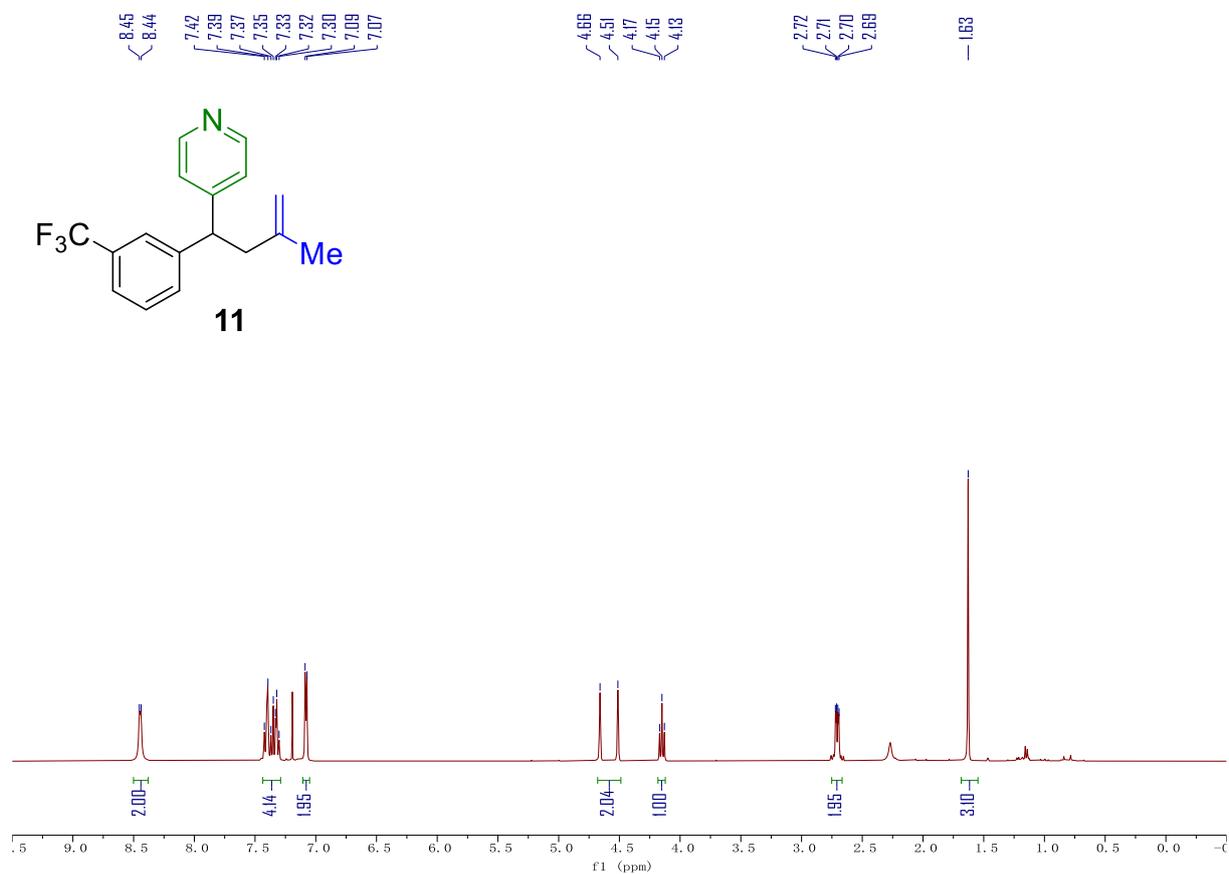
¹³C NMR spectra of compound 10 (101 MHz, Chloroform-*d*)



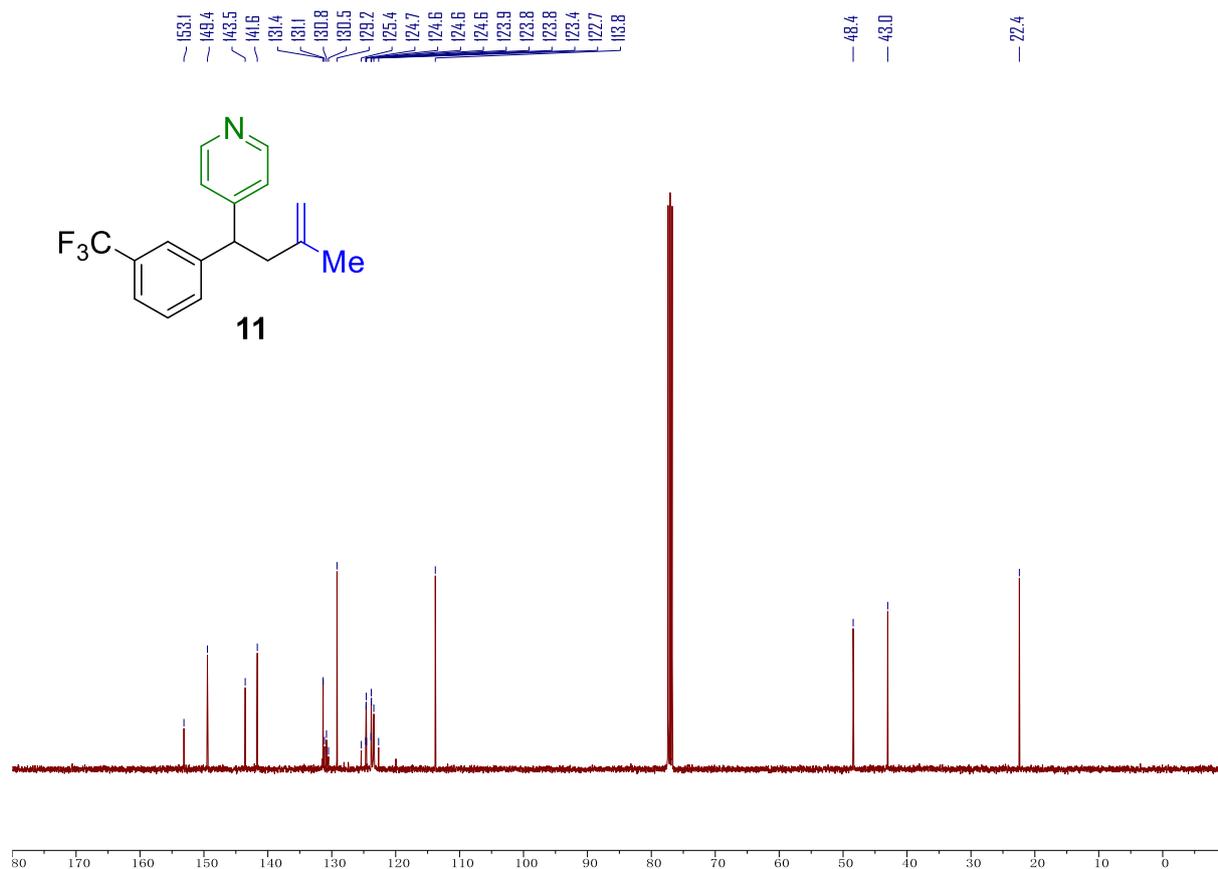
¹⁹F NMR spectra of compound 10 (376 MHz, Chloroform-*d*)



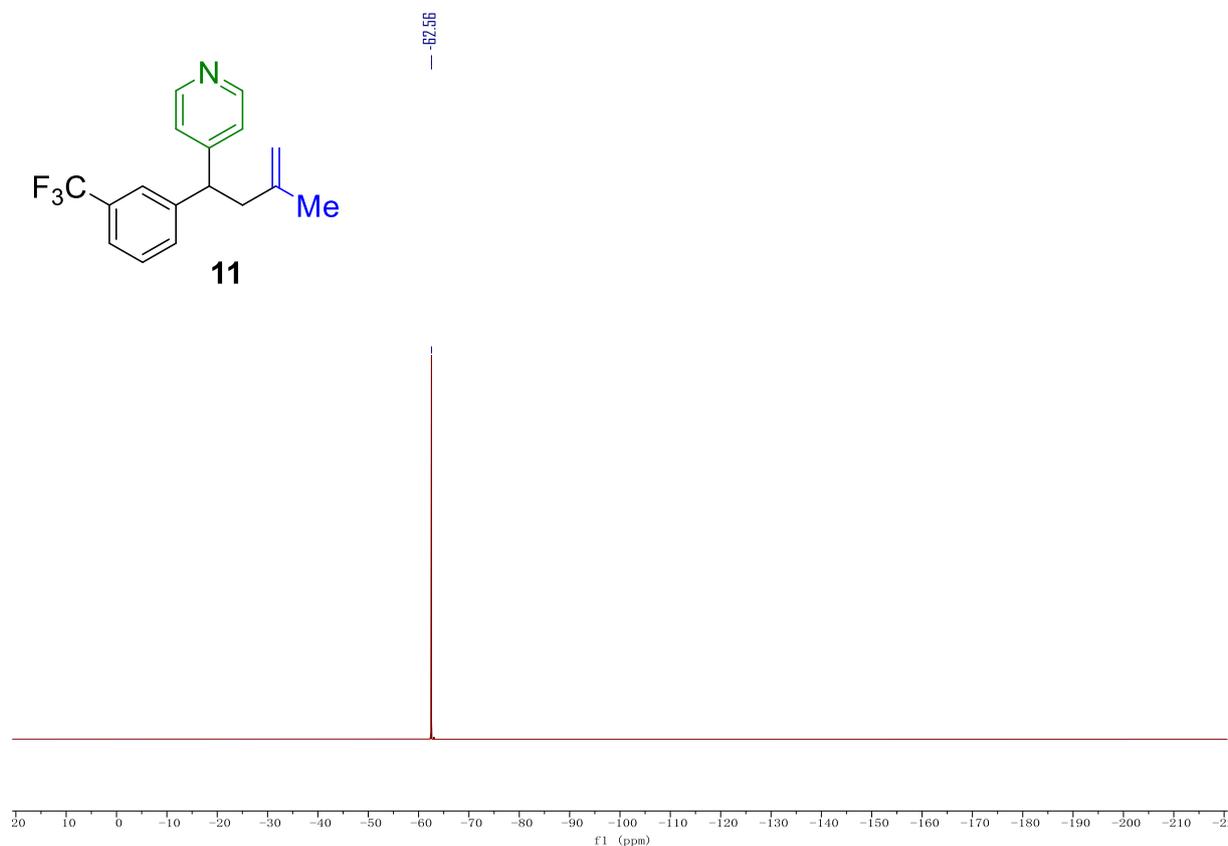
¹H NMR spectra of compound 11 (400 MHz, Chloroform-*d*)



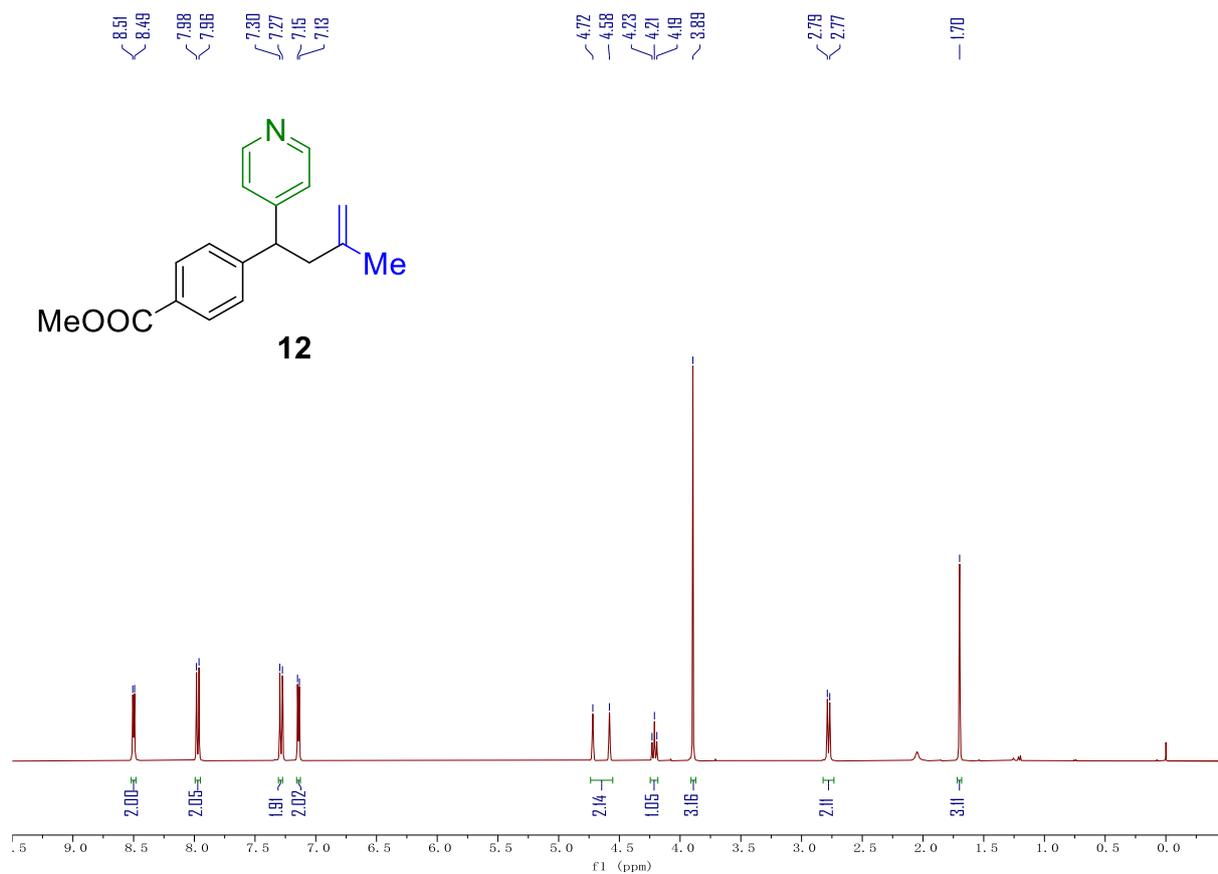
¹³C NMR spectra of compound **11** (101 MHz, Chloroform-*d*)



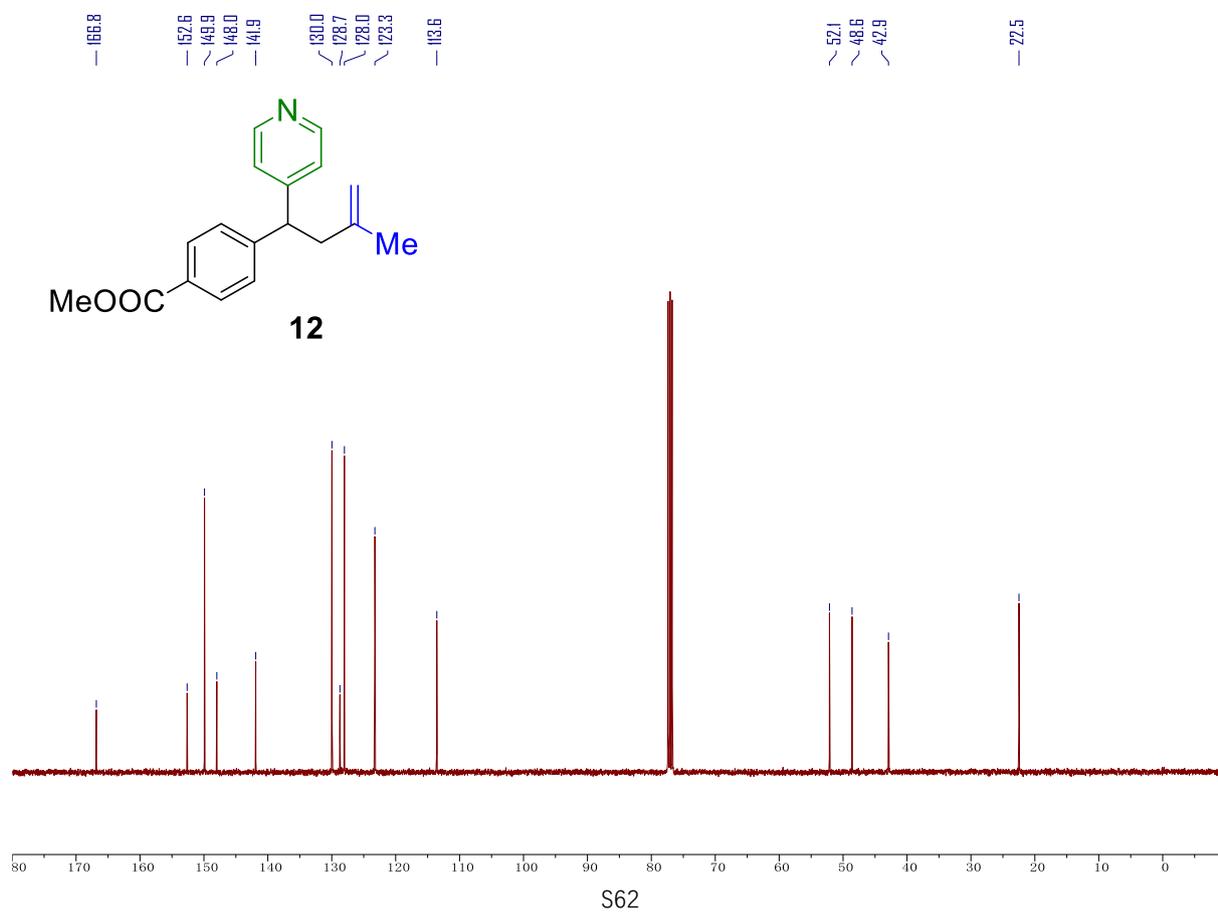
¹⁹F NMR spectra of compound **11** (376 MHz, Chloroform-*d*)



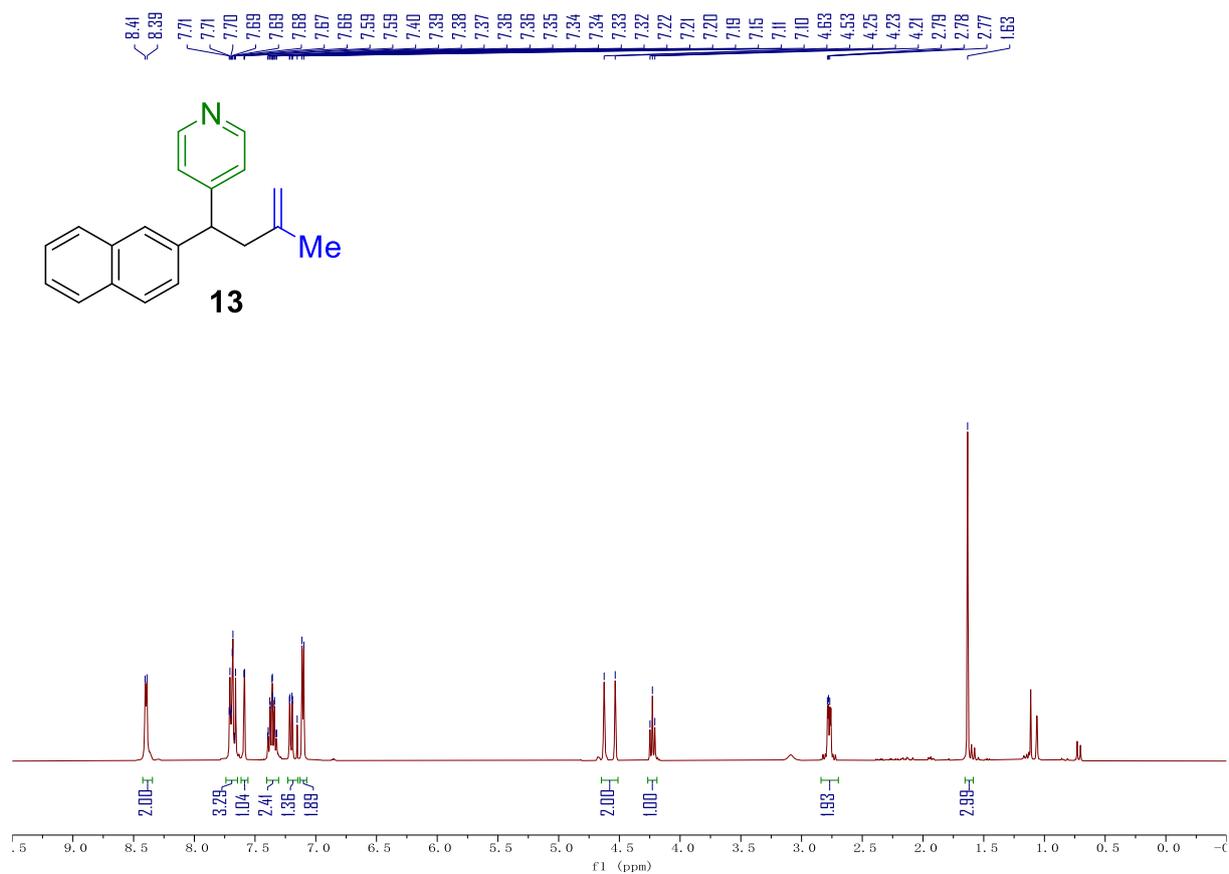
¹H NMR spectra of compound 12 (400 MHz, Chloroform-*d*)



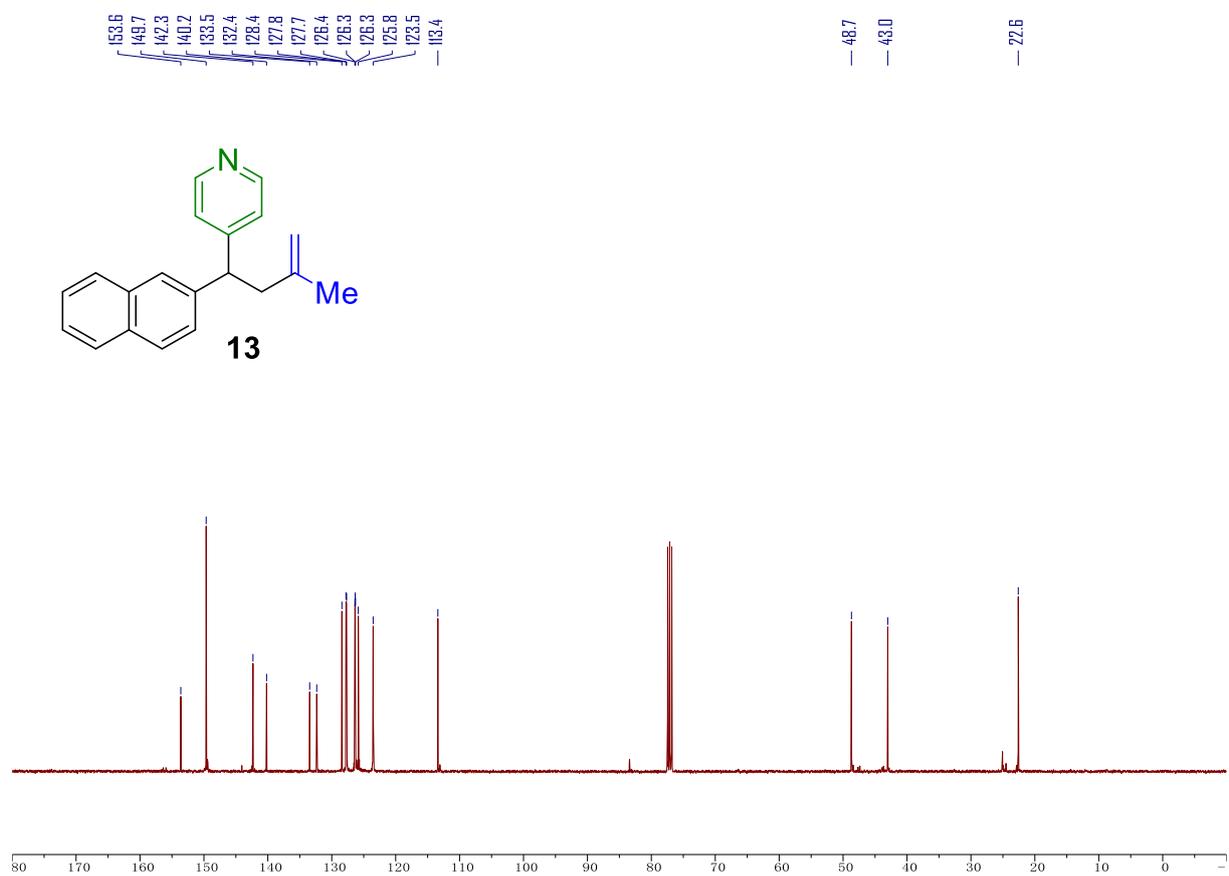
¹³C NMR spectra of compound 12 (101 MHz, Chloroform-*d*)



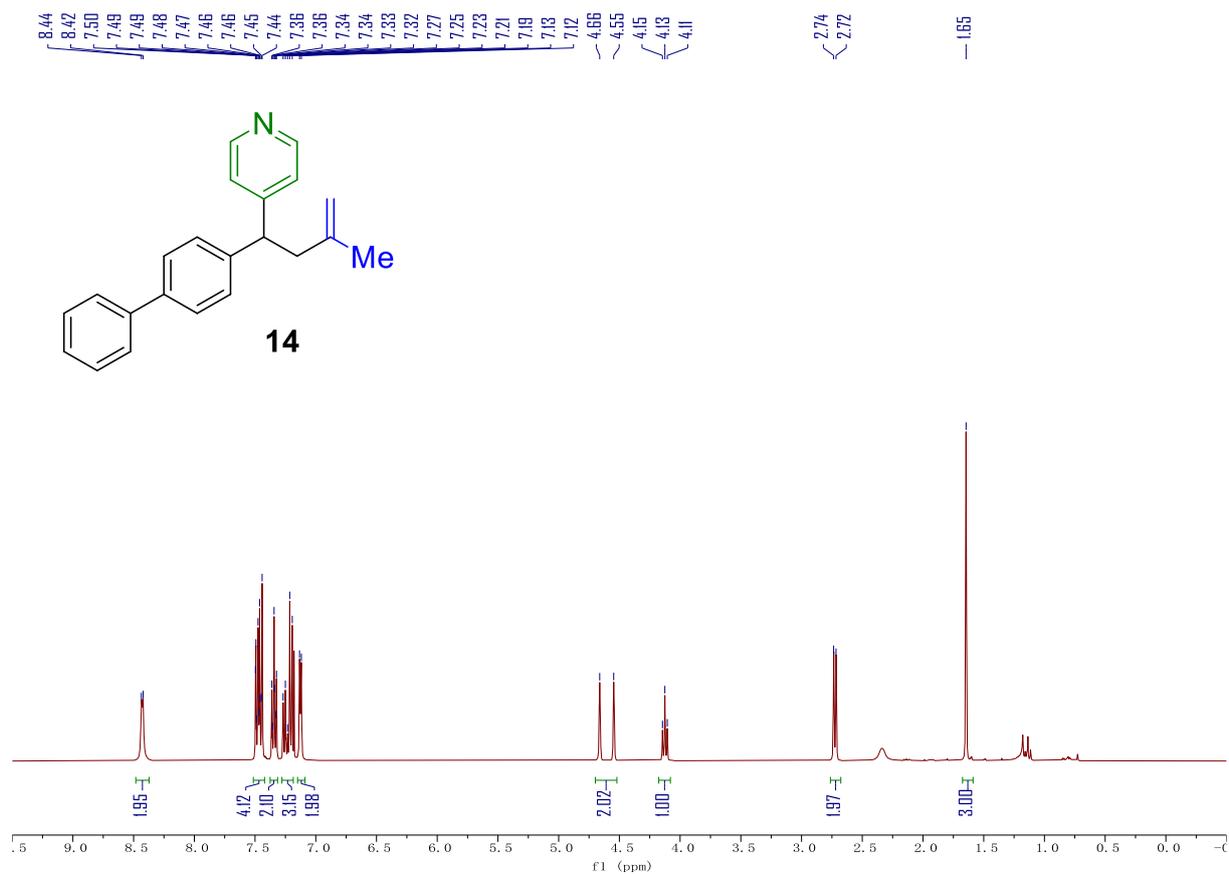
¹H NMR spectra of compound 13 (400 MHz, Chloroform-*d*)



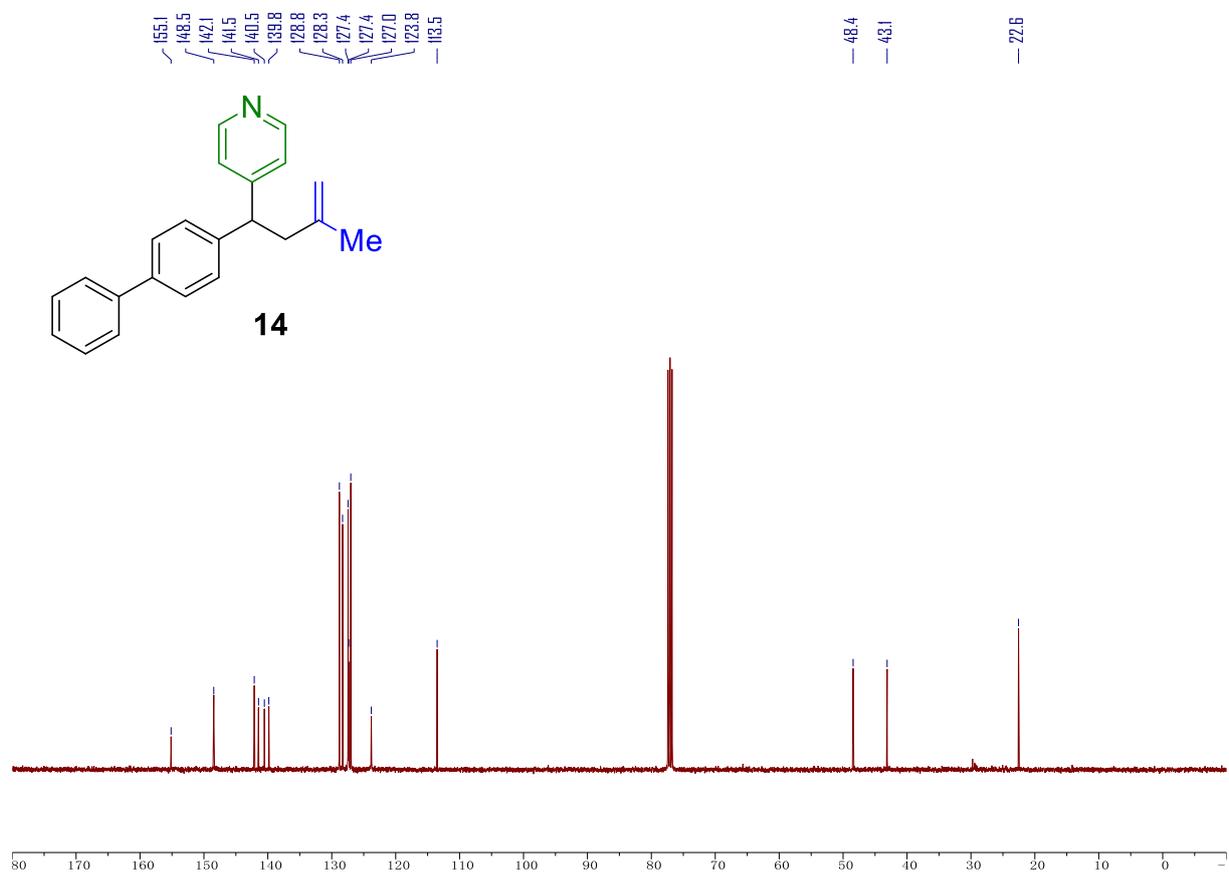
¹³C NMR spectra of compound 13 (101 MHz, Chloroform-*d*)



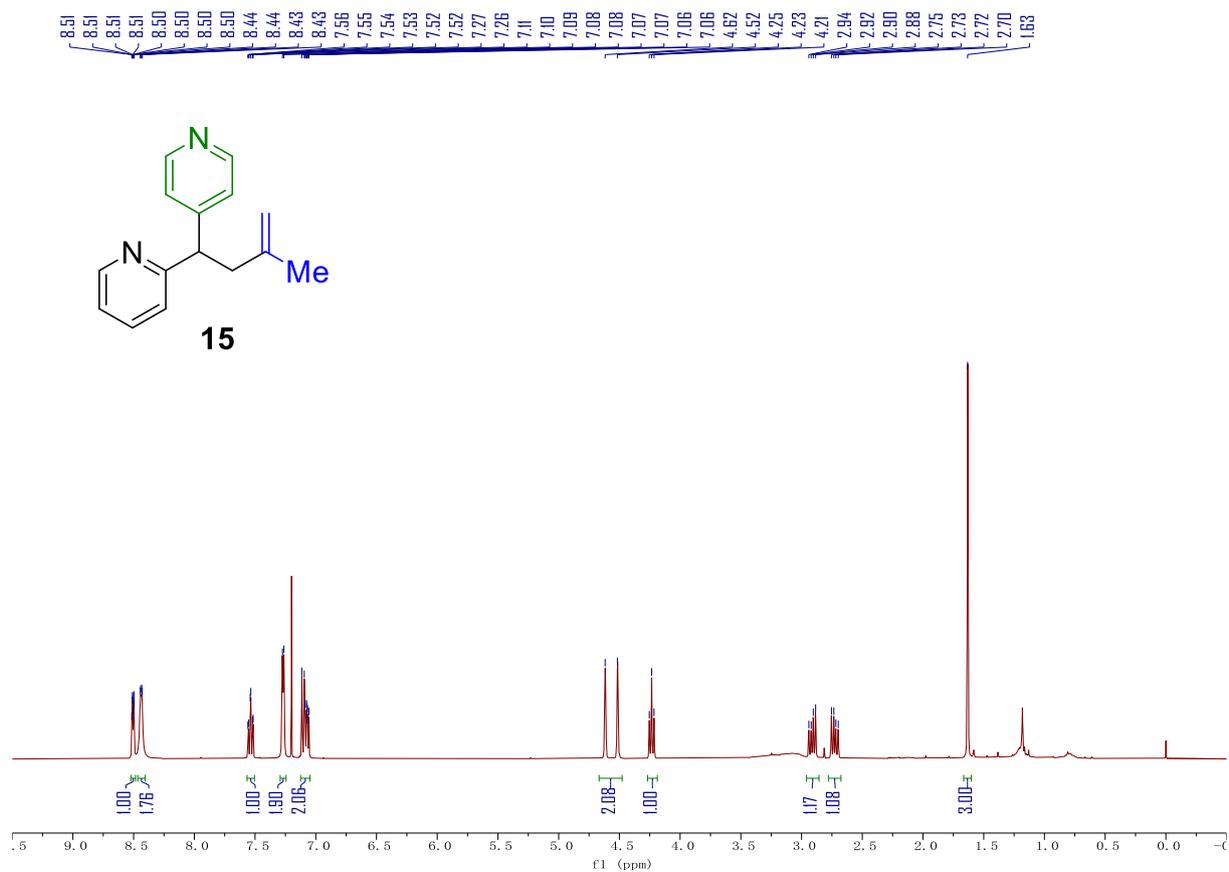
¹H NMR spectra of compound 14 (400 MHz, Chloroform-*d*)



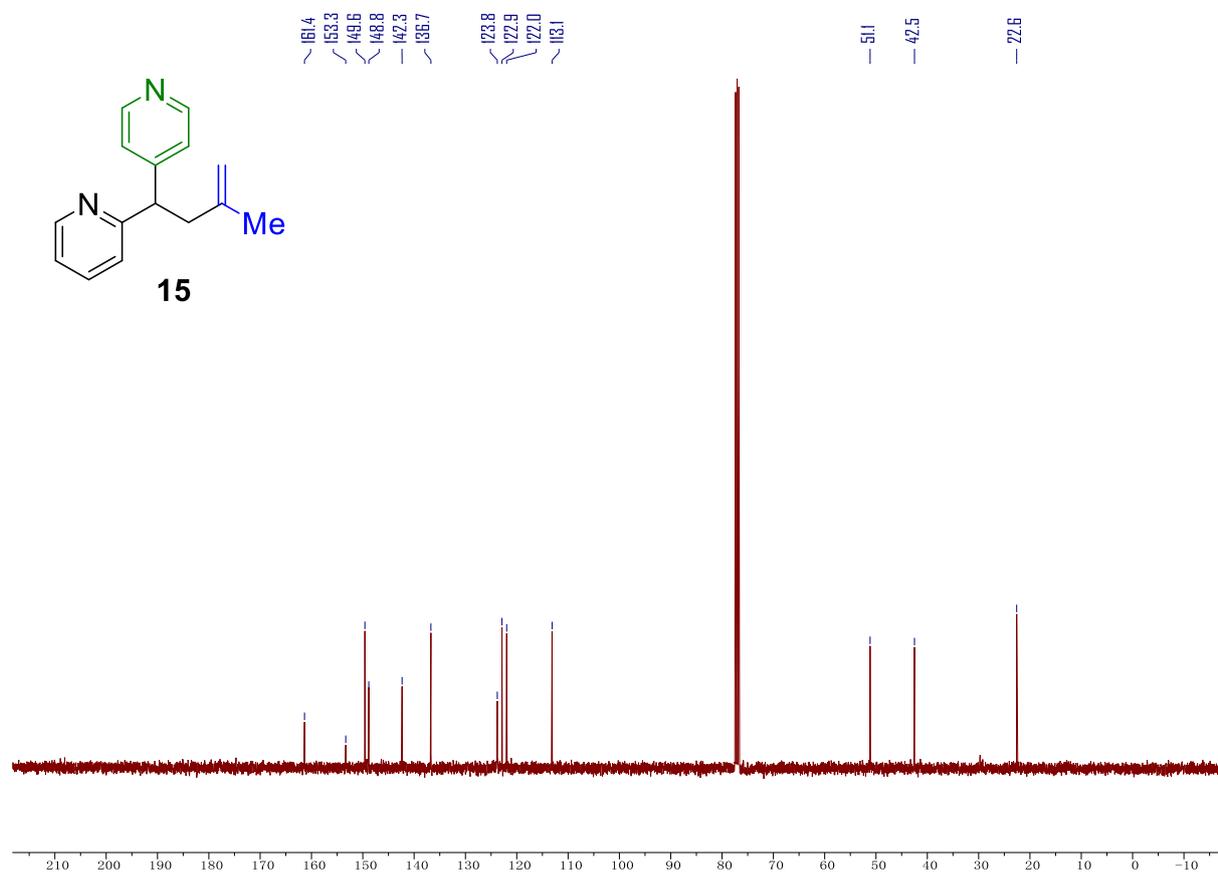
¹³C NMR spectra of compound 14 (101 MHz, Chloroform-*d*)



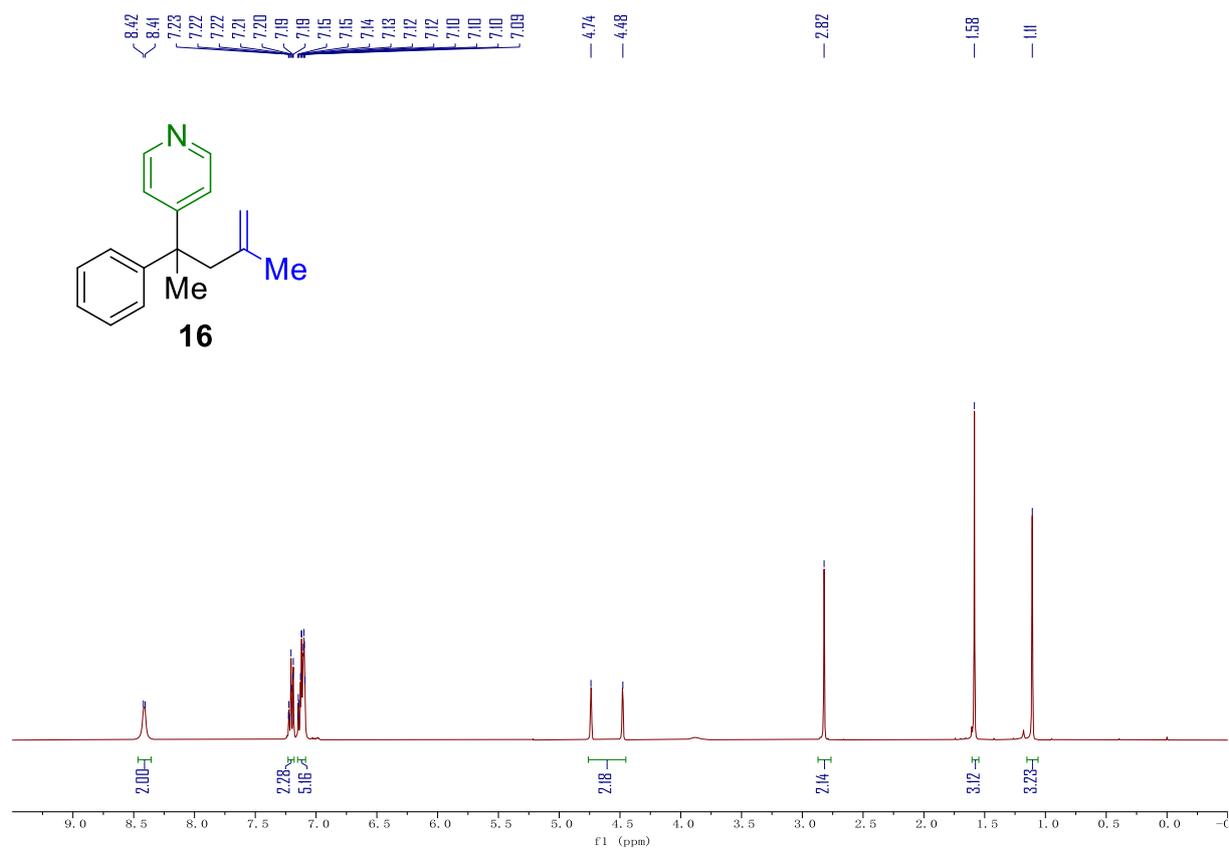
¹H NMR spectra of compound **15** (400 MHz, Chloroform-*d*)



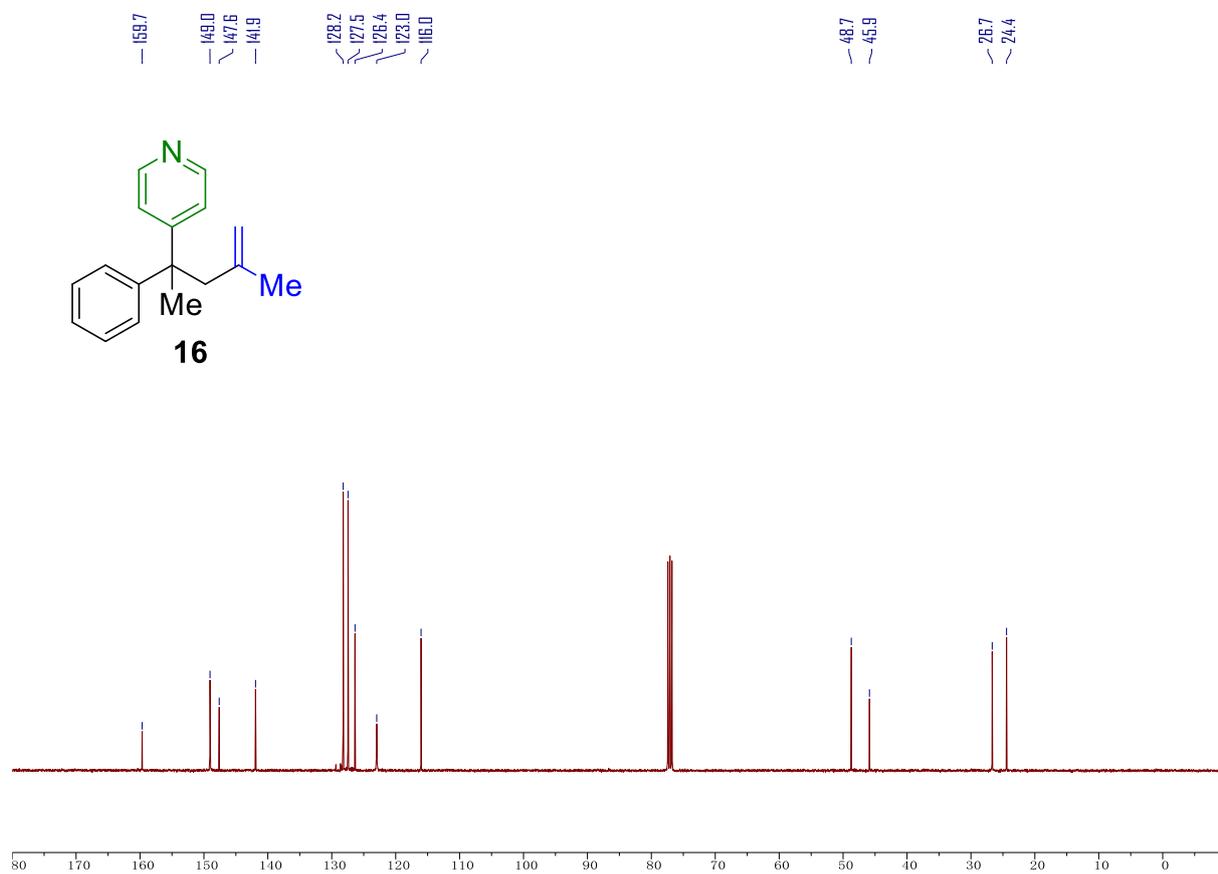
¹³C NMR spectra of compound **15** (101 MHz, Chloroform-*d*)



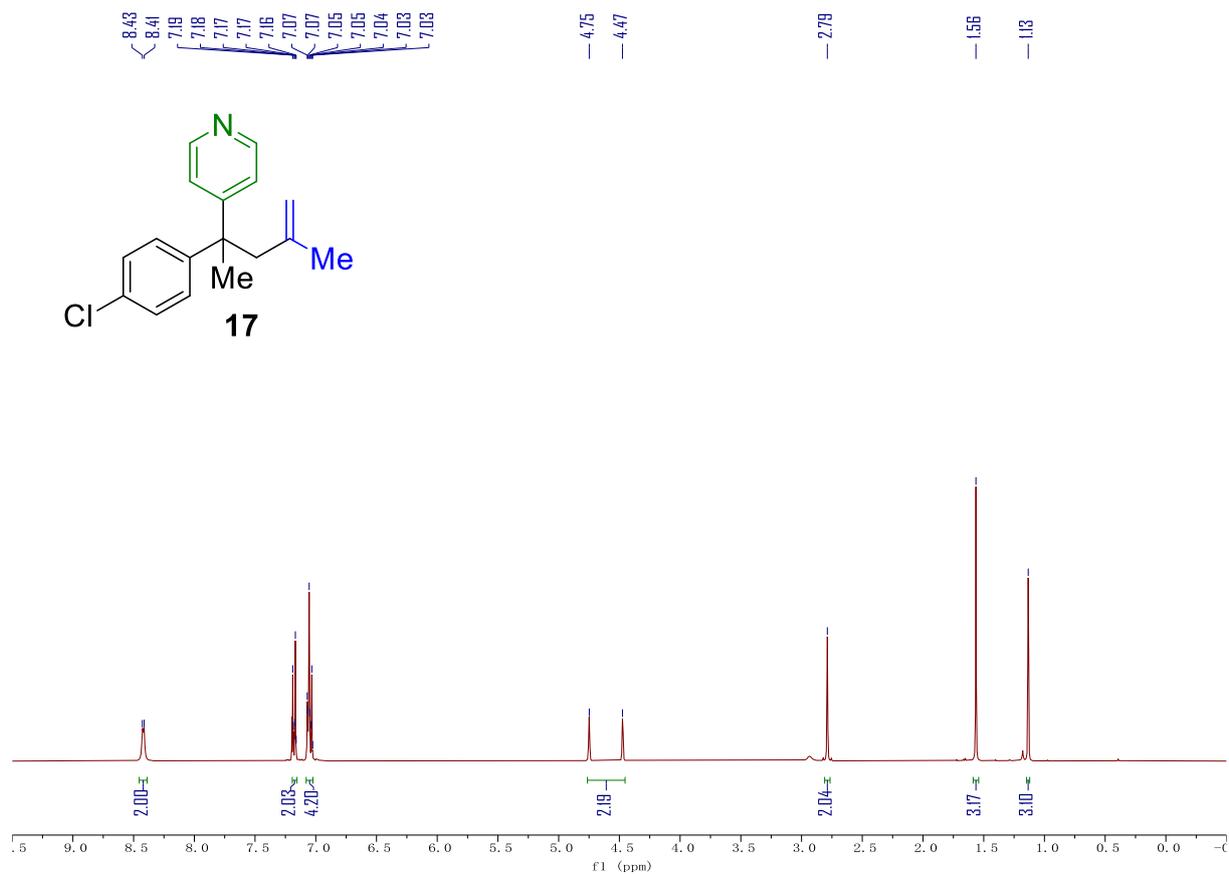
¹H NMR spectra of compound 16 (400 MHz, Chloroform-*d*)



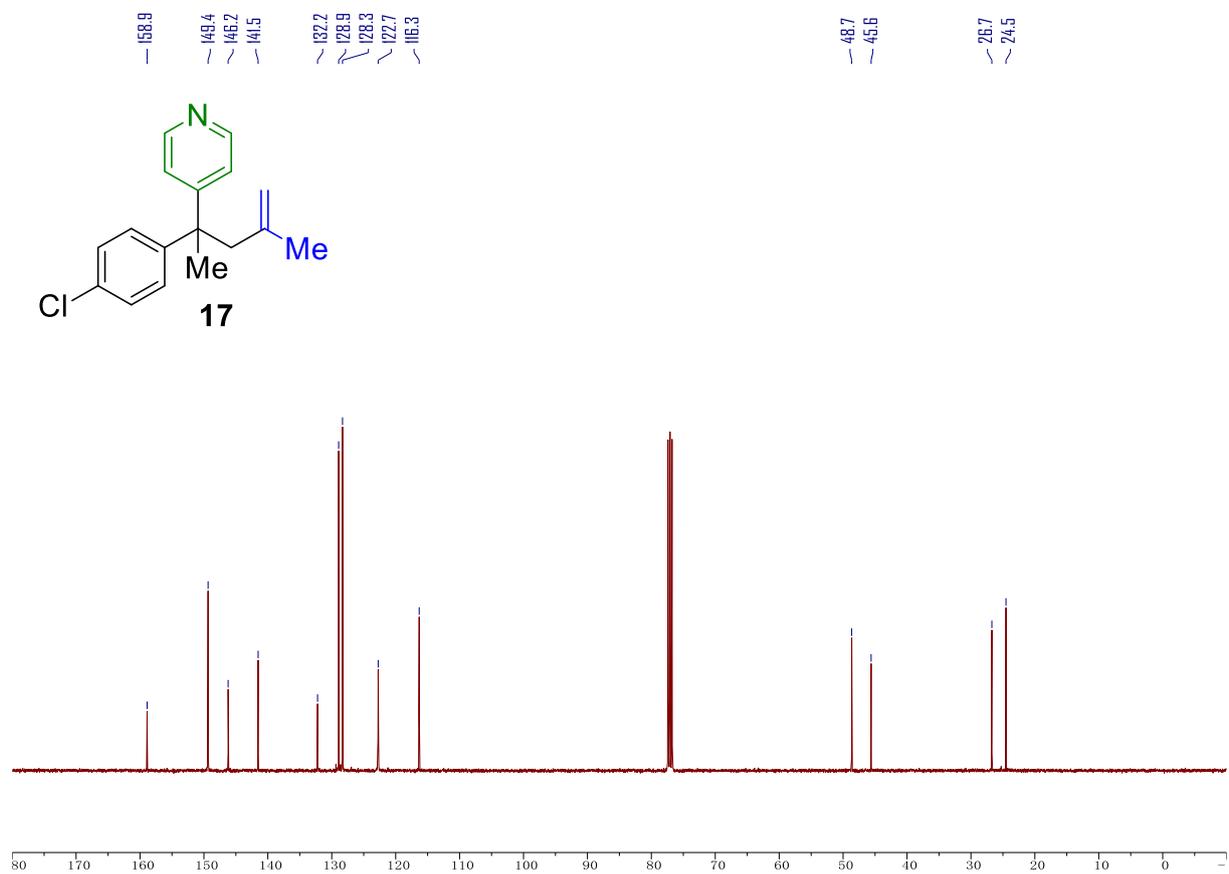
¹³C NMR spectra of compound 16 (101 MHz, Chloroform-*d*)



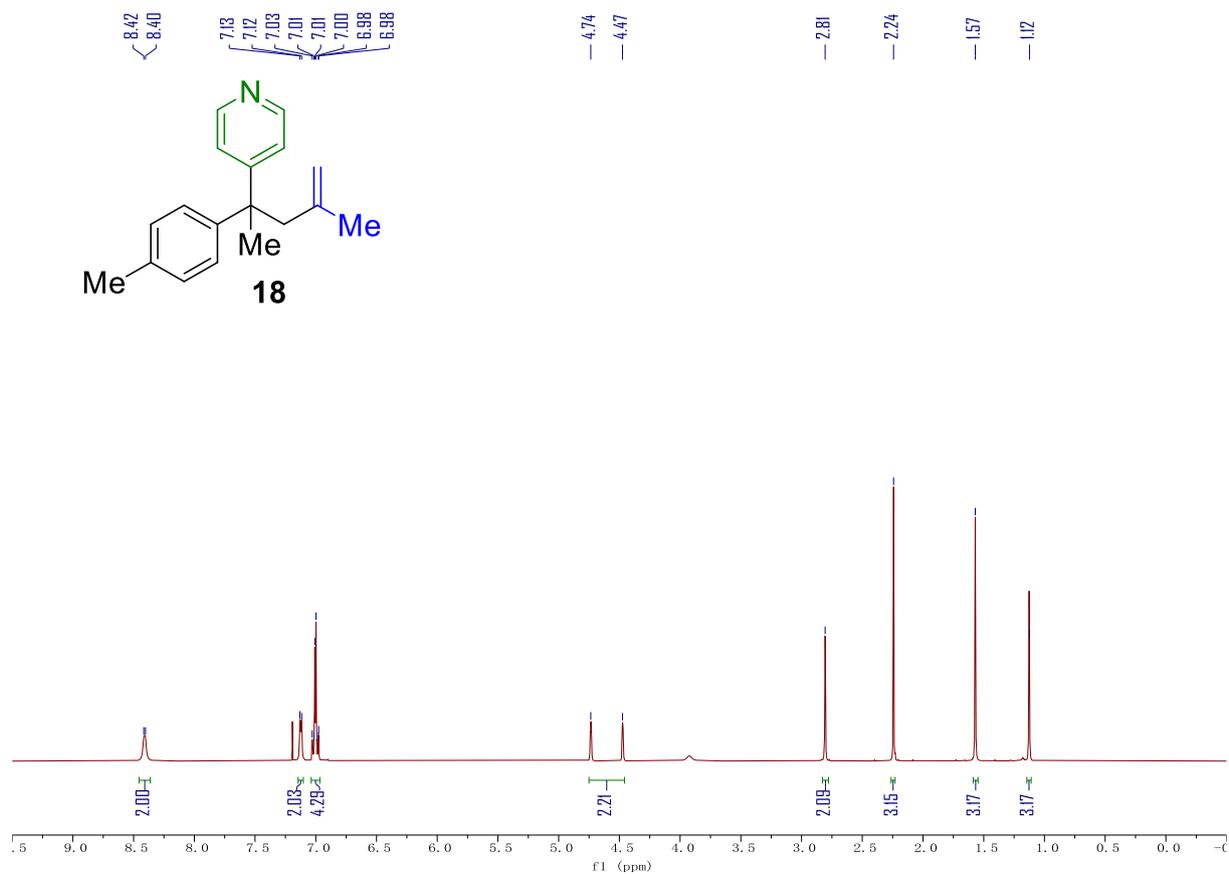
¹H NMR spectra of compound 17 (400 MHz, Chloroform-*d*)



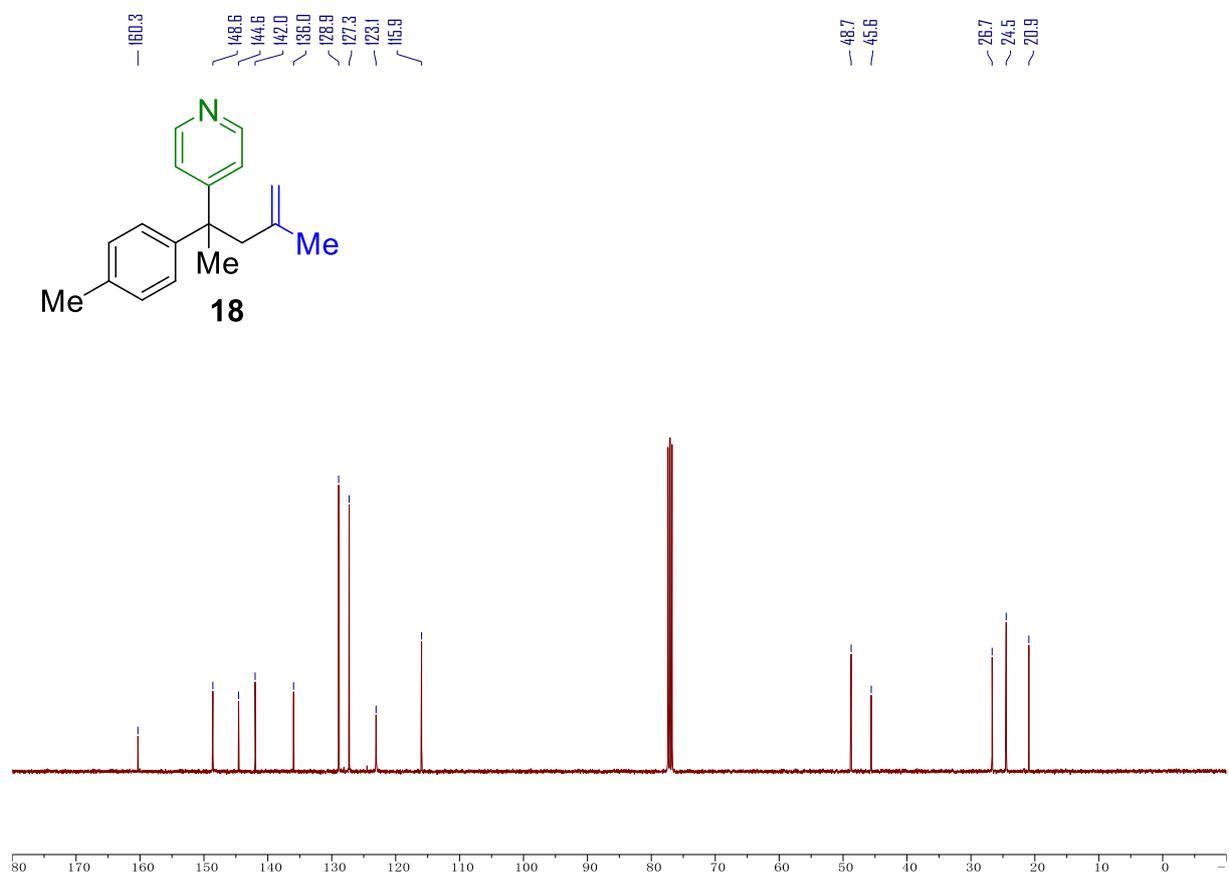
¹³C NMR spectra of compound 17 (101 MHz, Chloroform-*d*)



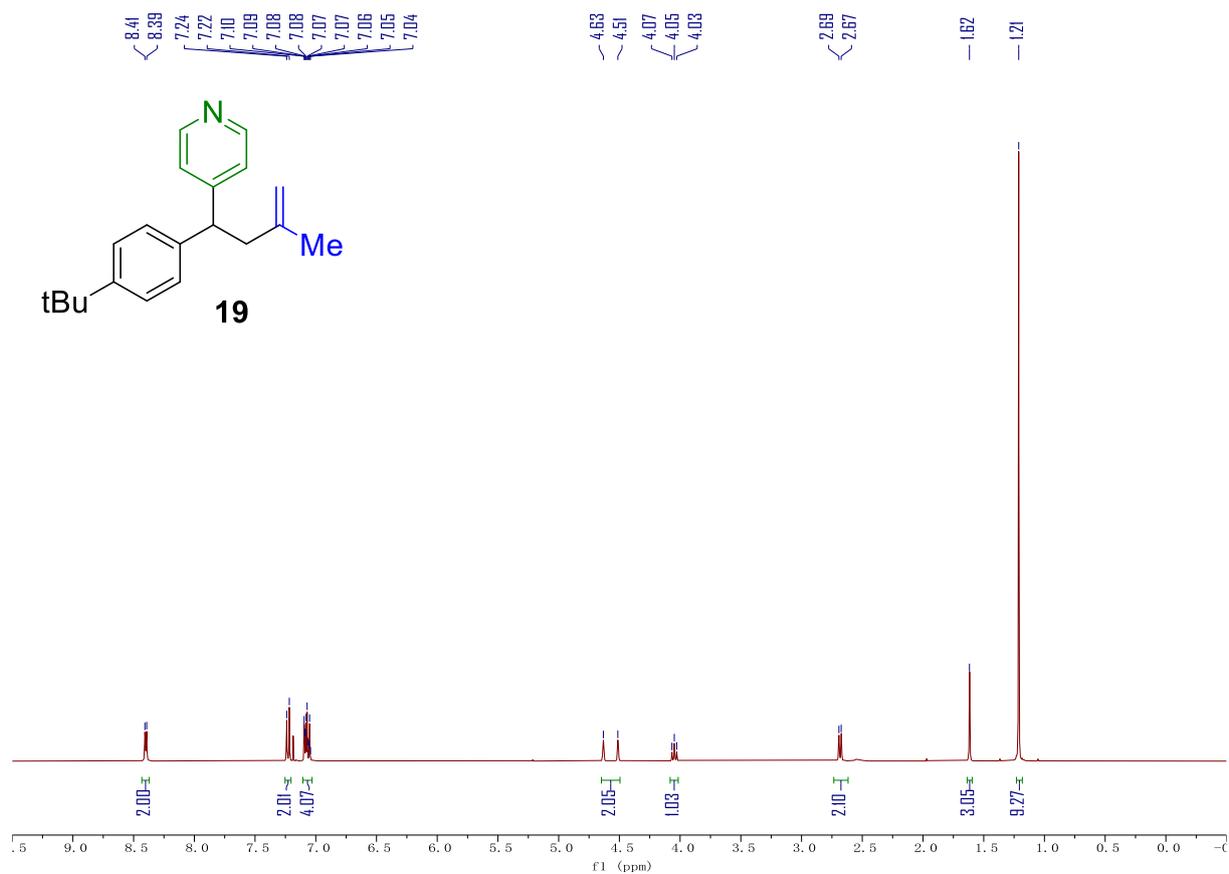
¹H NMR spectra of compound 18 (400 MHz, Chloroform-*d*)



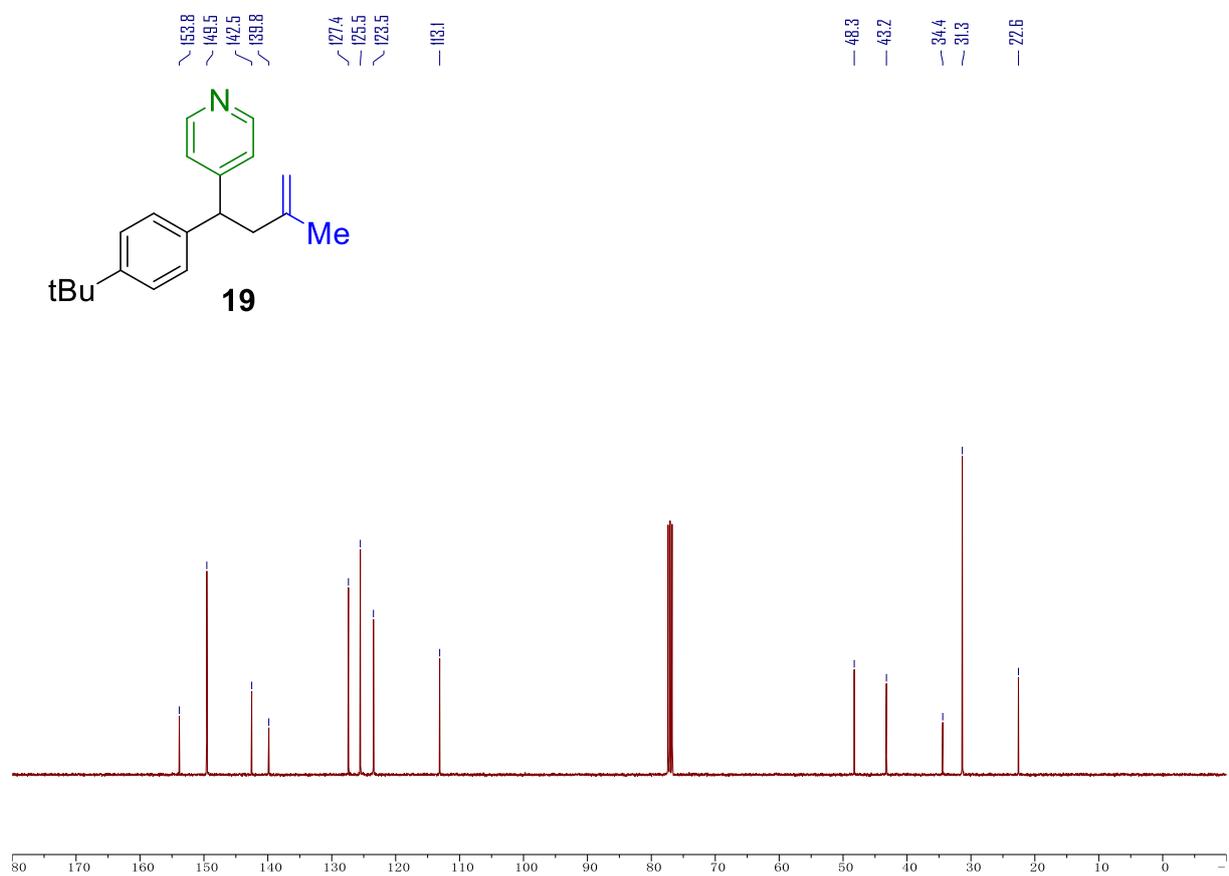
¹³C NMR spectra of compound 18 (101 MHz, Chloroform-*d*)



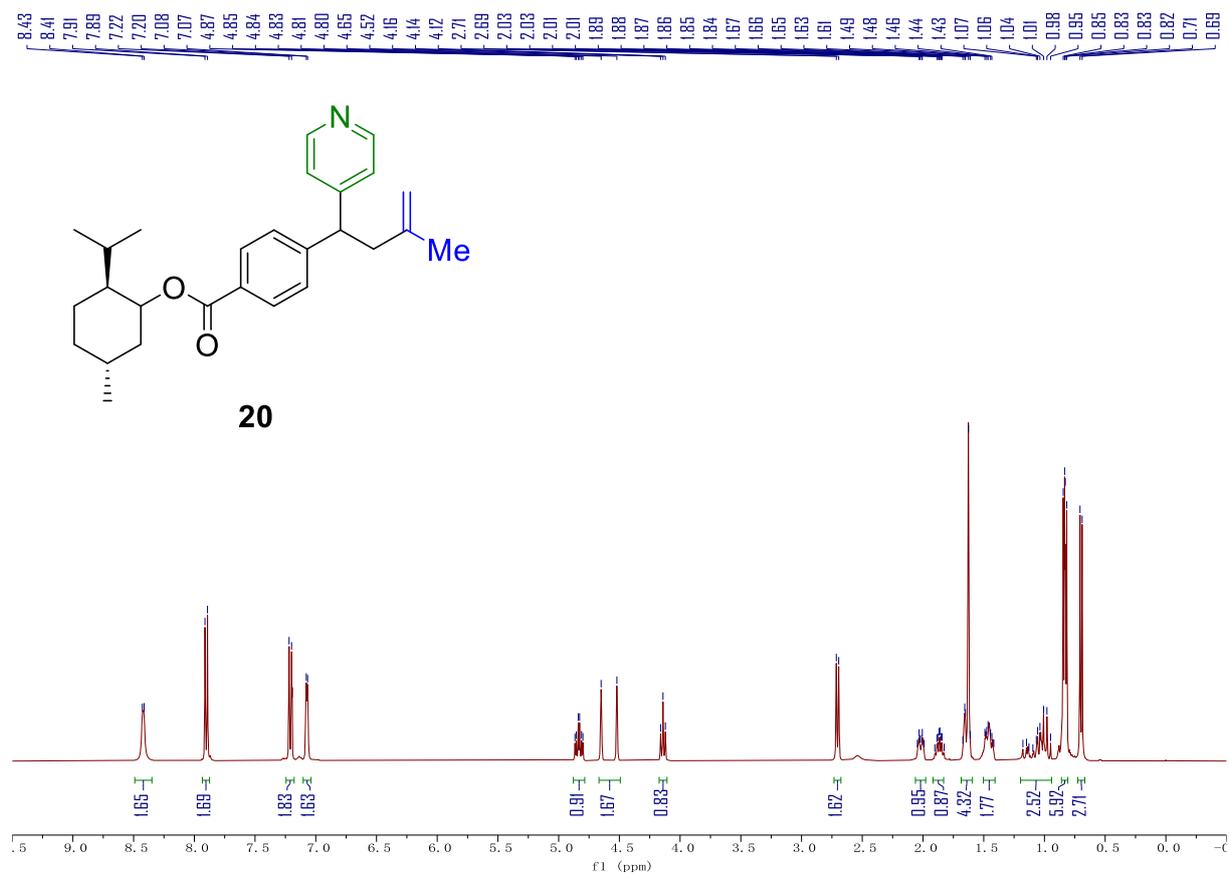
¹H NMR spectra of compound 19 (400 MHz, Chloroform-*d*)



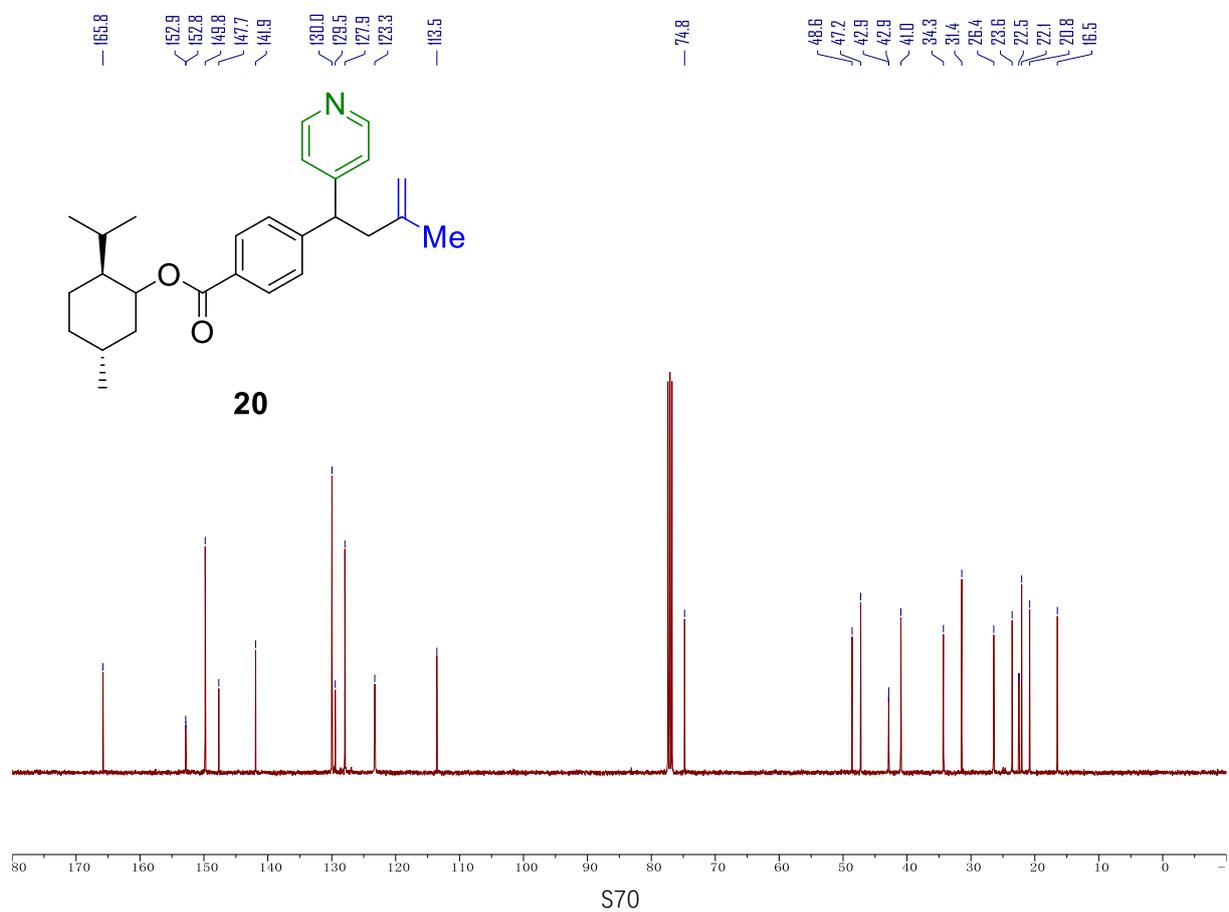
¹³C NMR spectra of compound 19 (101 MHz, Chloroform-*d*)



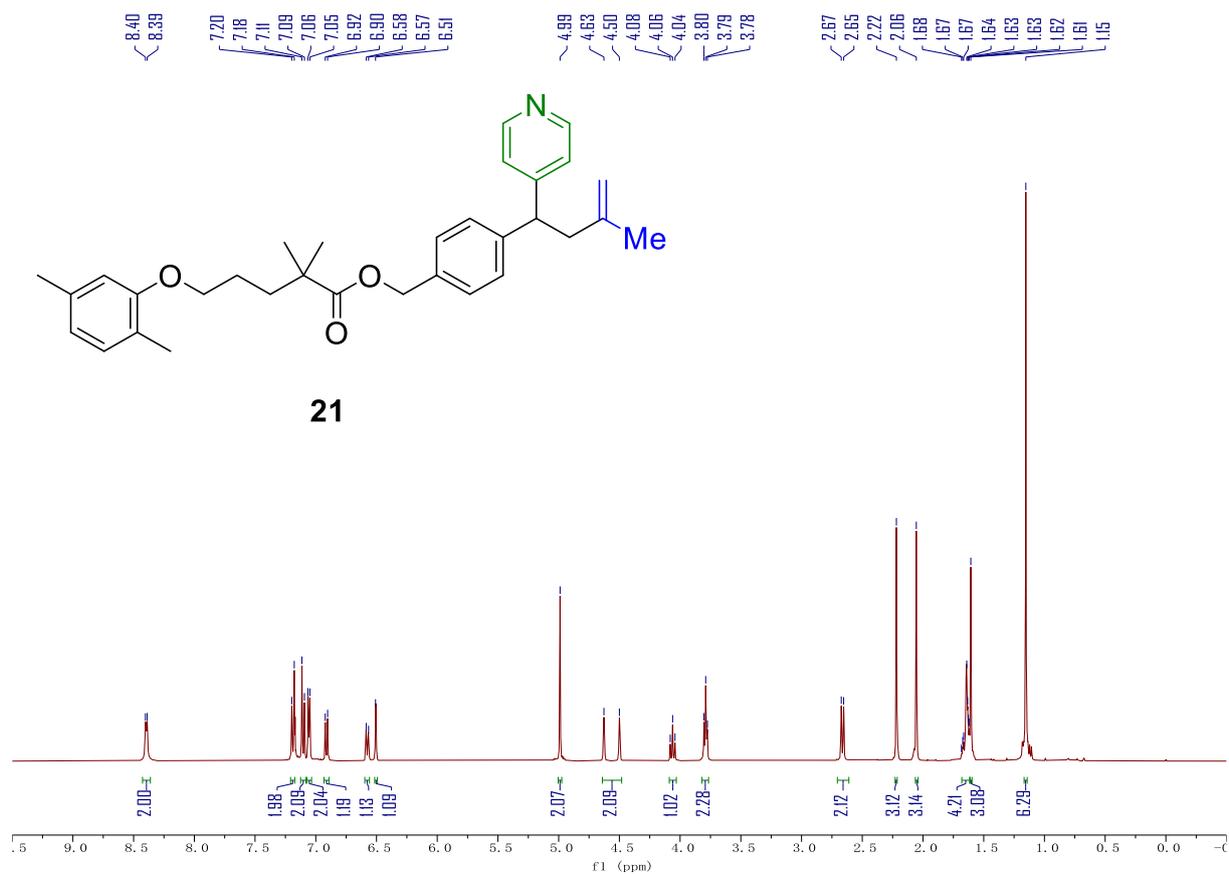
¹H NMR spectra of compound **20** (400 MHz, Chloroform-*d*)



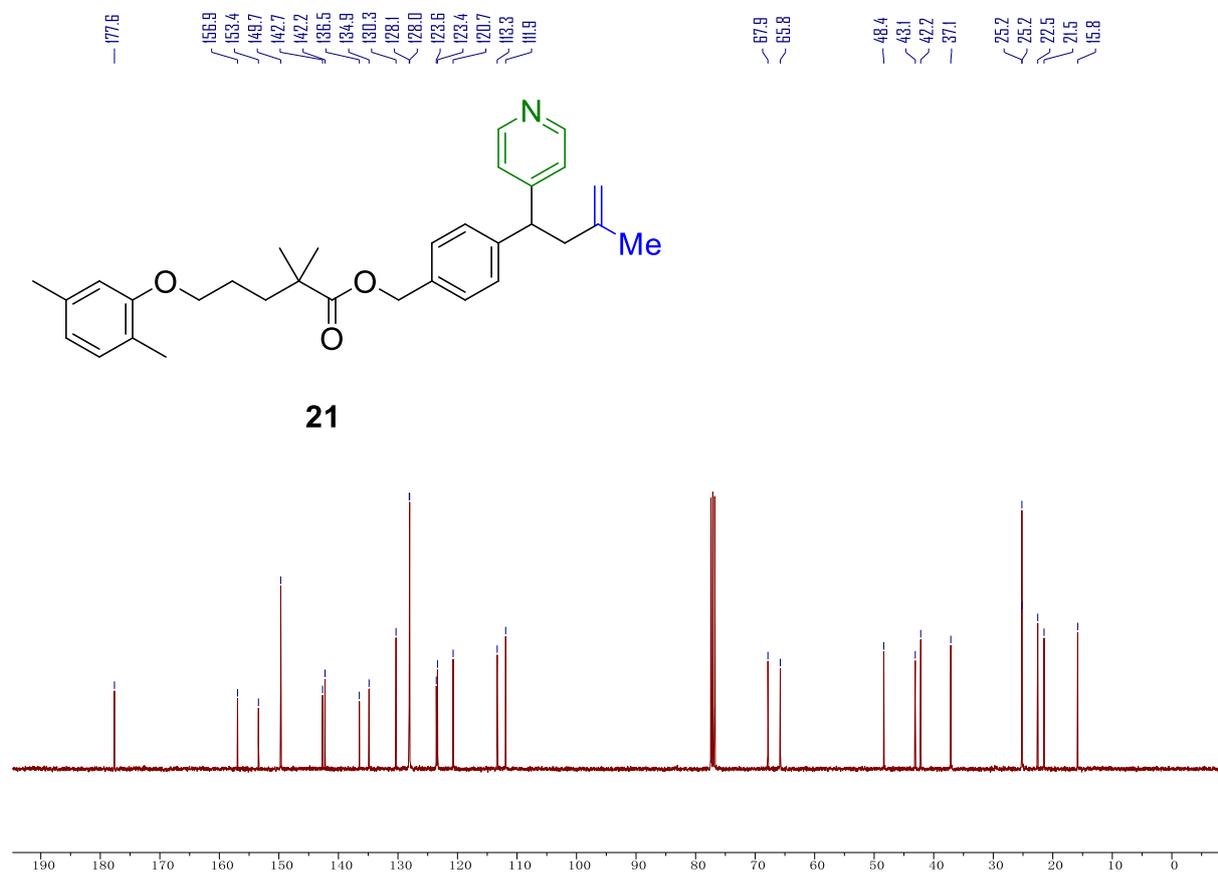
¹³C NMR spectra of compound **20** (101 MHz, Chloroform-*d*)



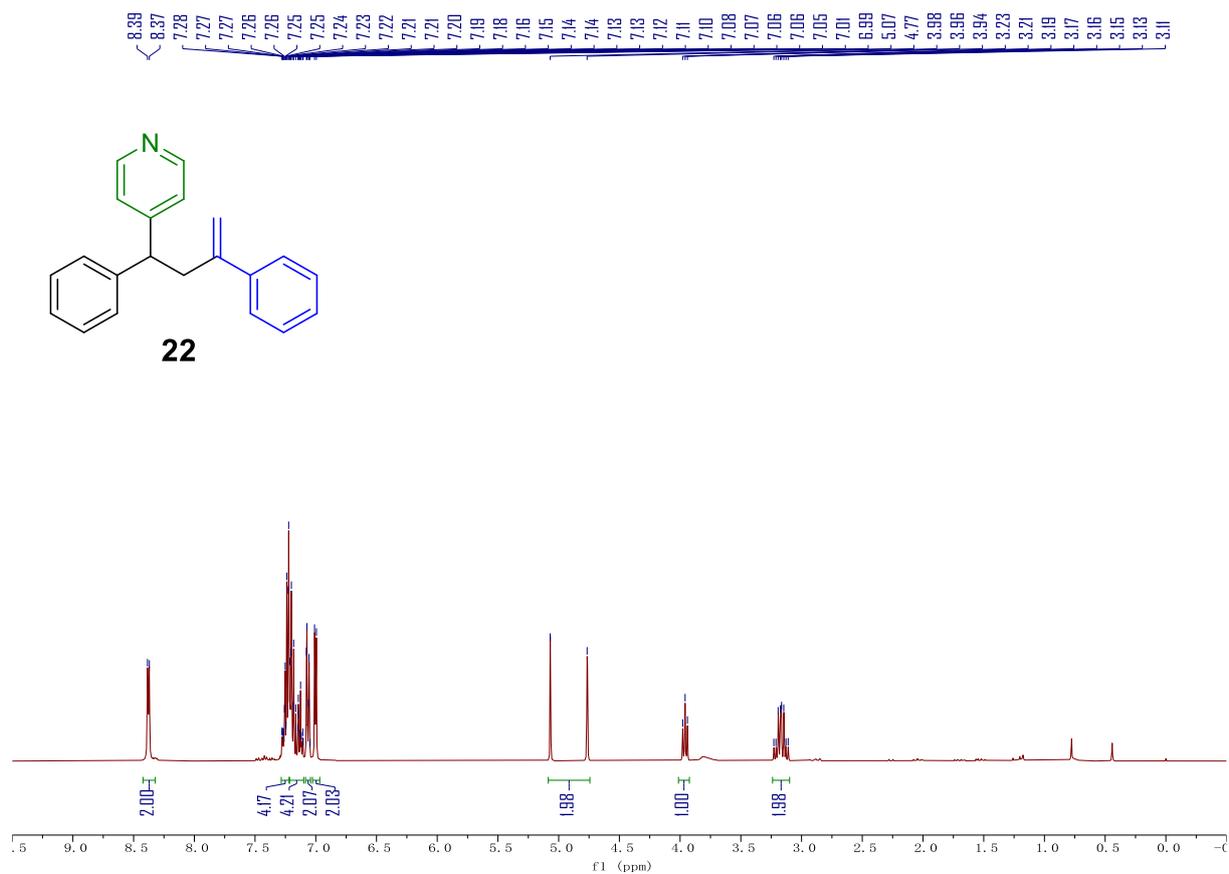
¹H NMR spectra of compound 21 (400 MHz, Chloroform-*d*)



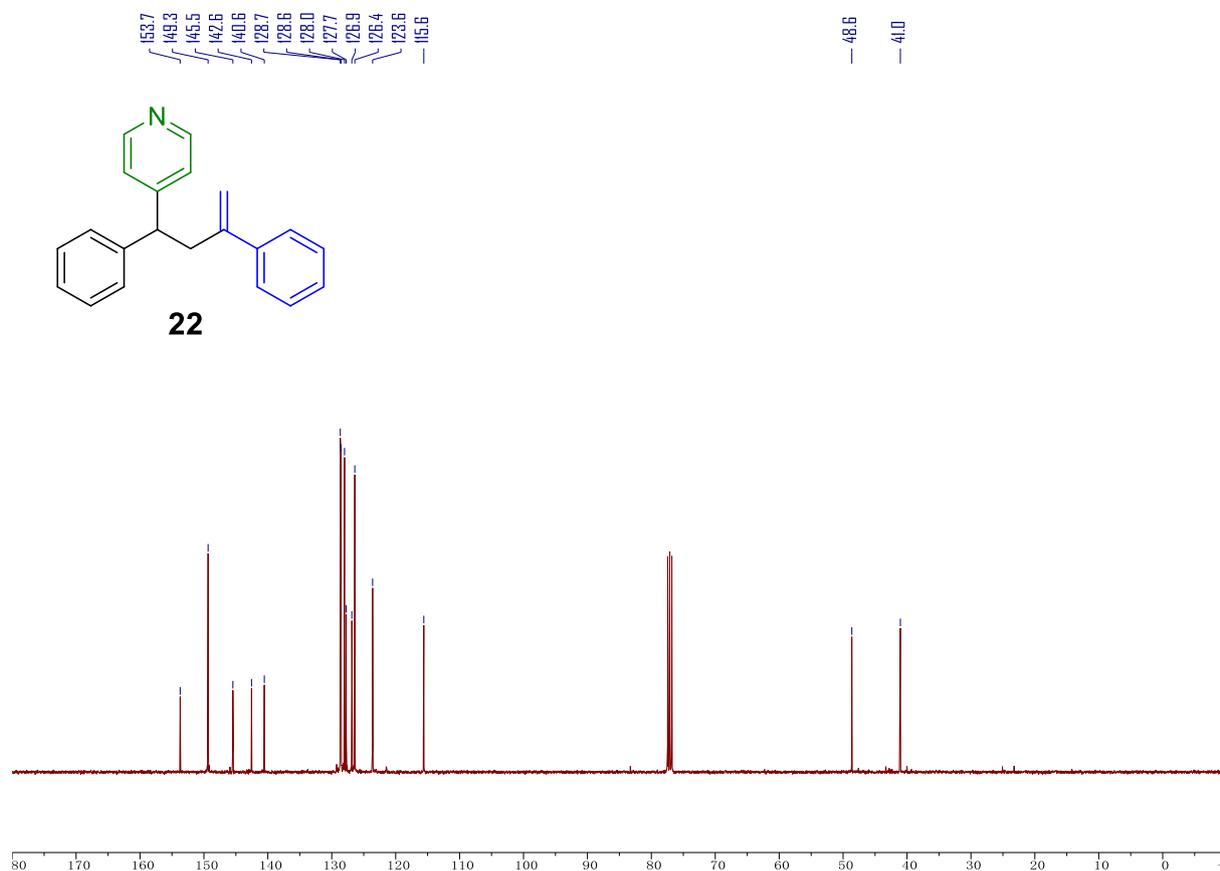
¹³C NMR spectra of compound 21 (101 MHz, Chloroform-*d*)



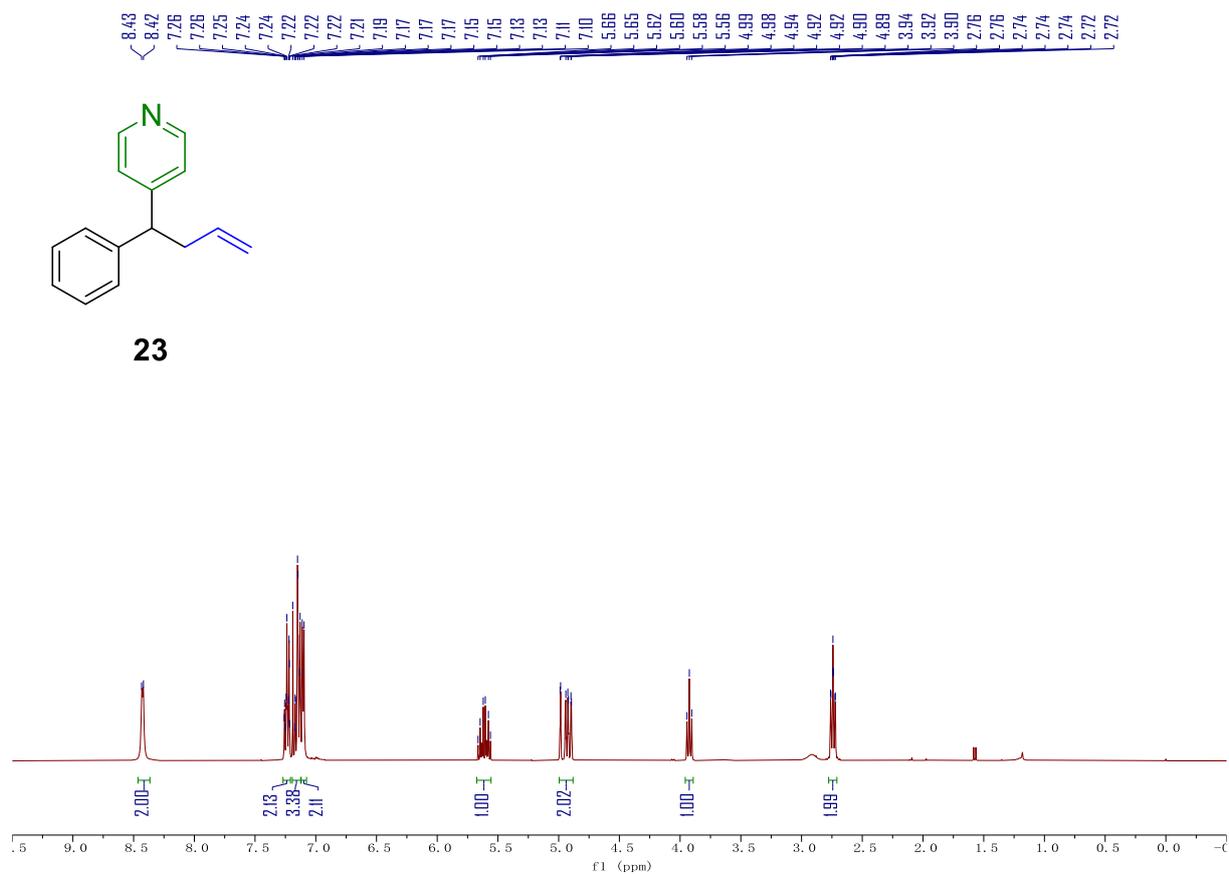
¹H NMR spectra of compound 22 (400 MHz, Chloroform-*d*)



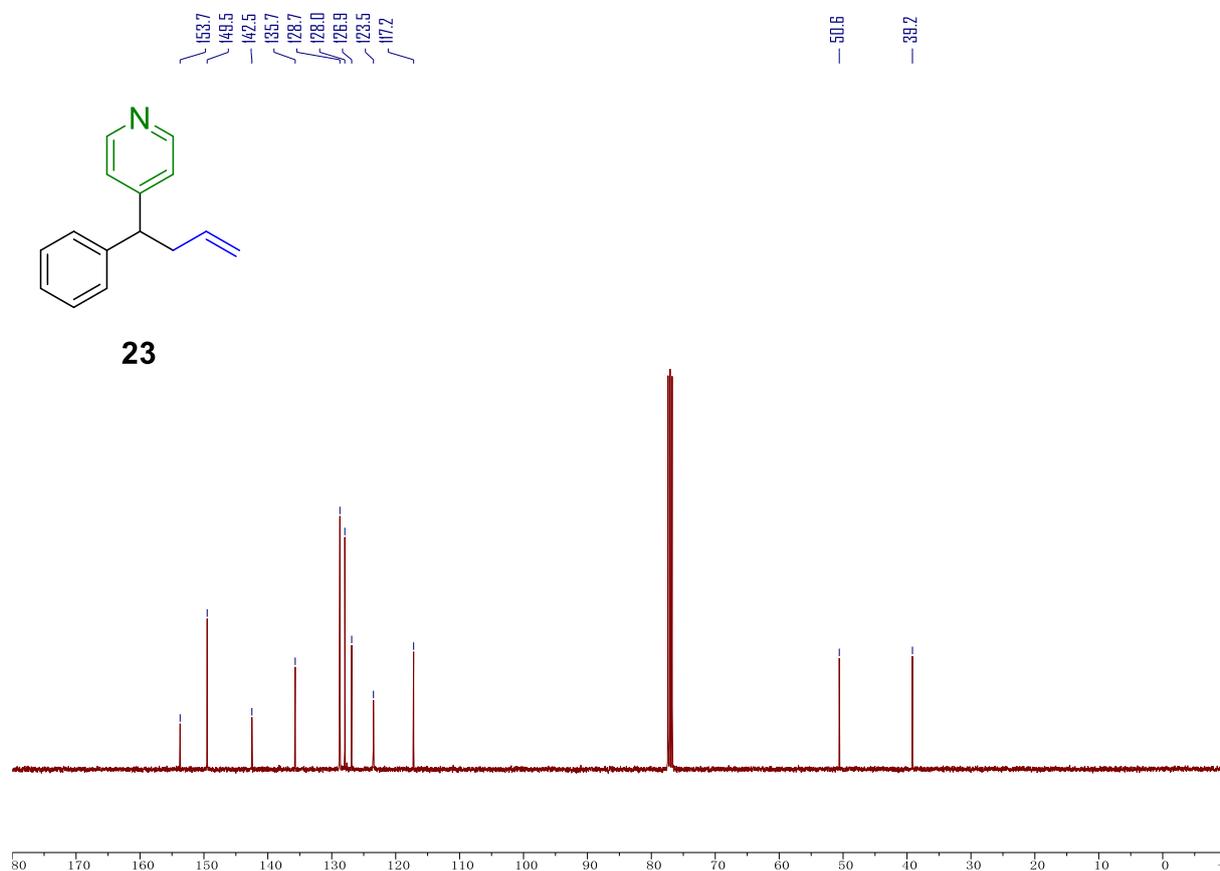
¹³C NMR spectra of compound 22 (101 MHz, Chloroform-*d*)



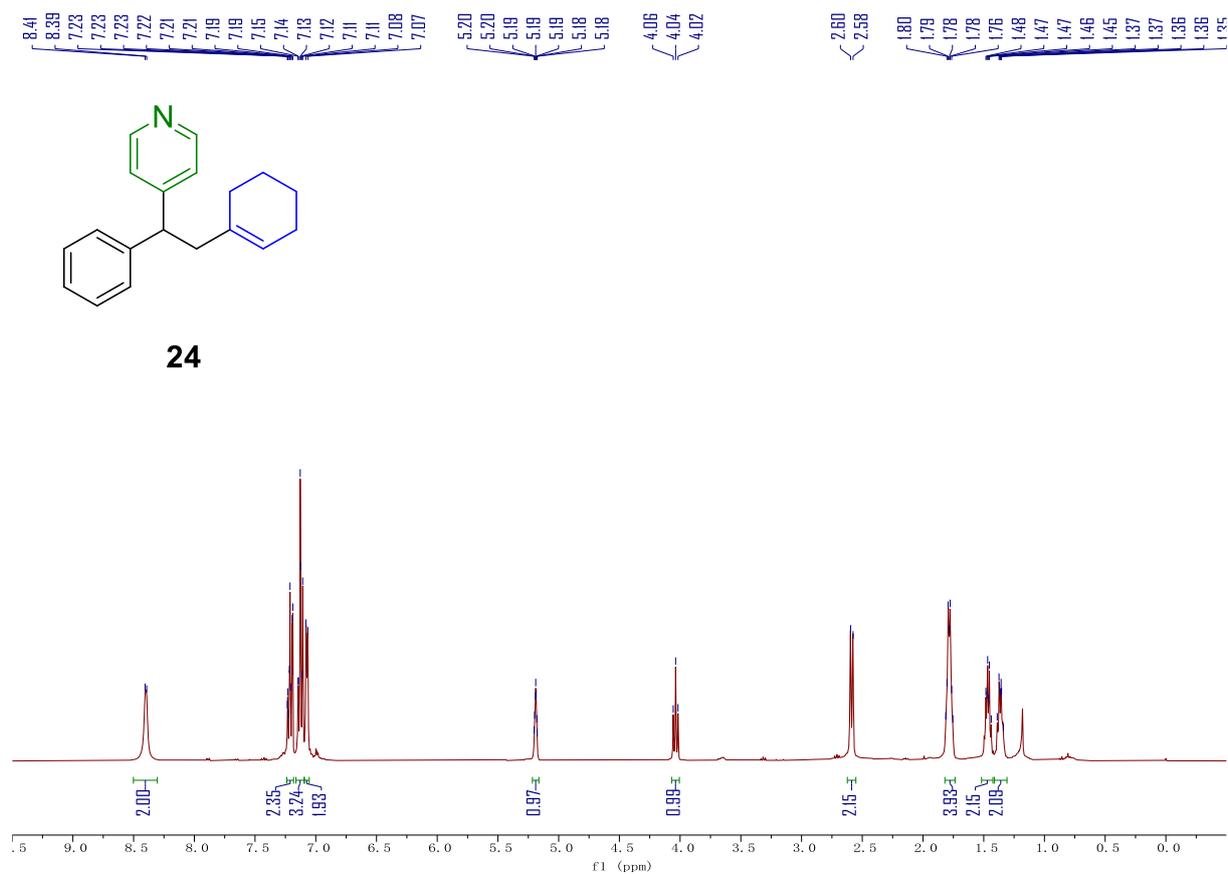
¹H NMR spectra of compound 23 (400 MHz, Chloroform-*d*)



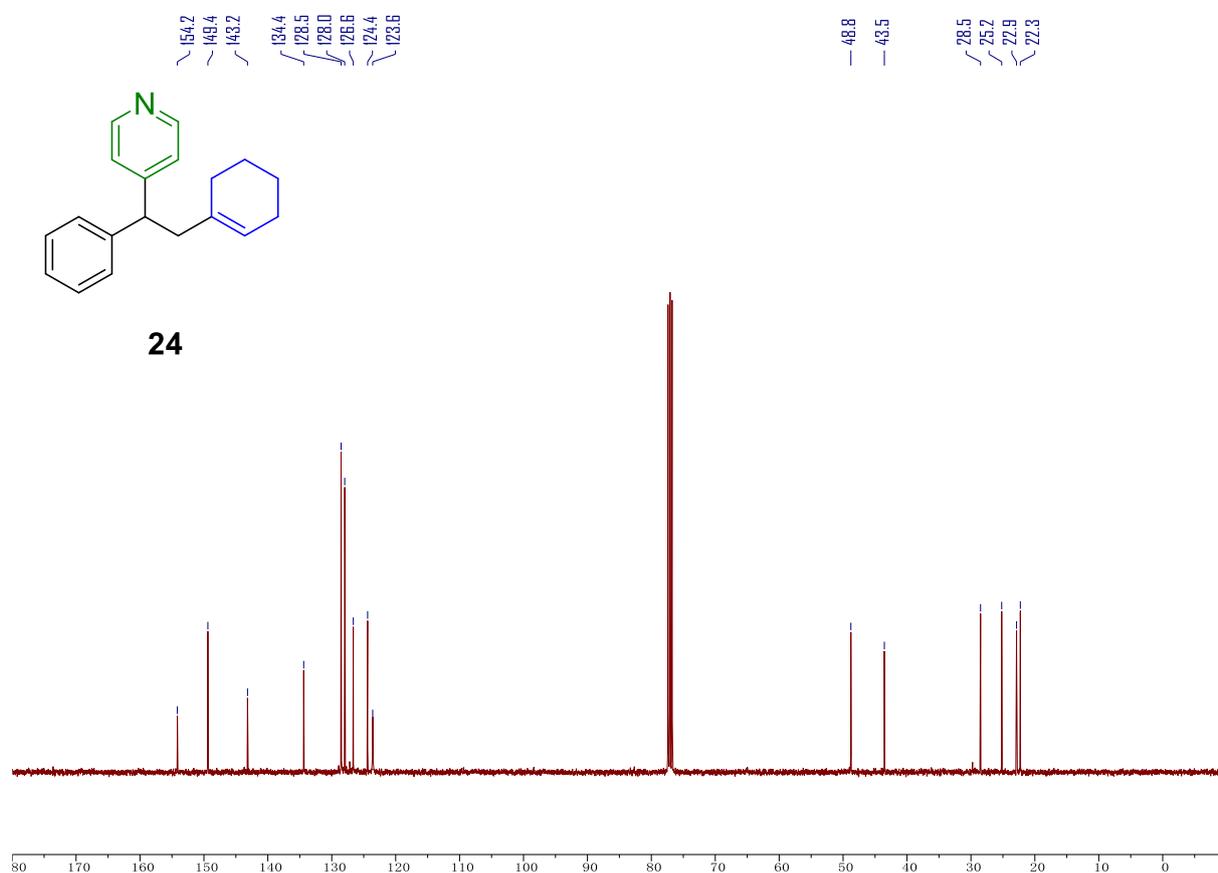
¹³C NMR spectra of compound 23 (101 MHz, Chloroform-*d*)



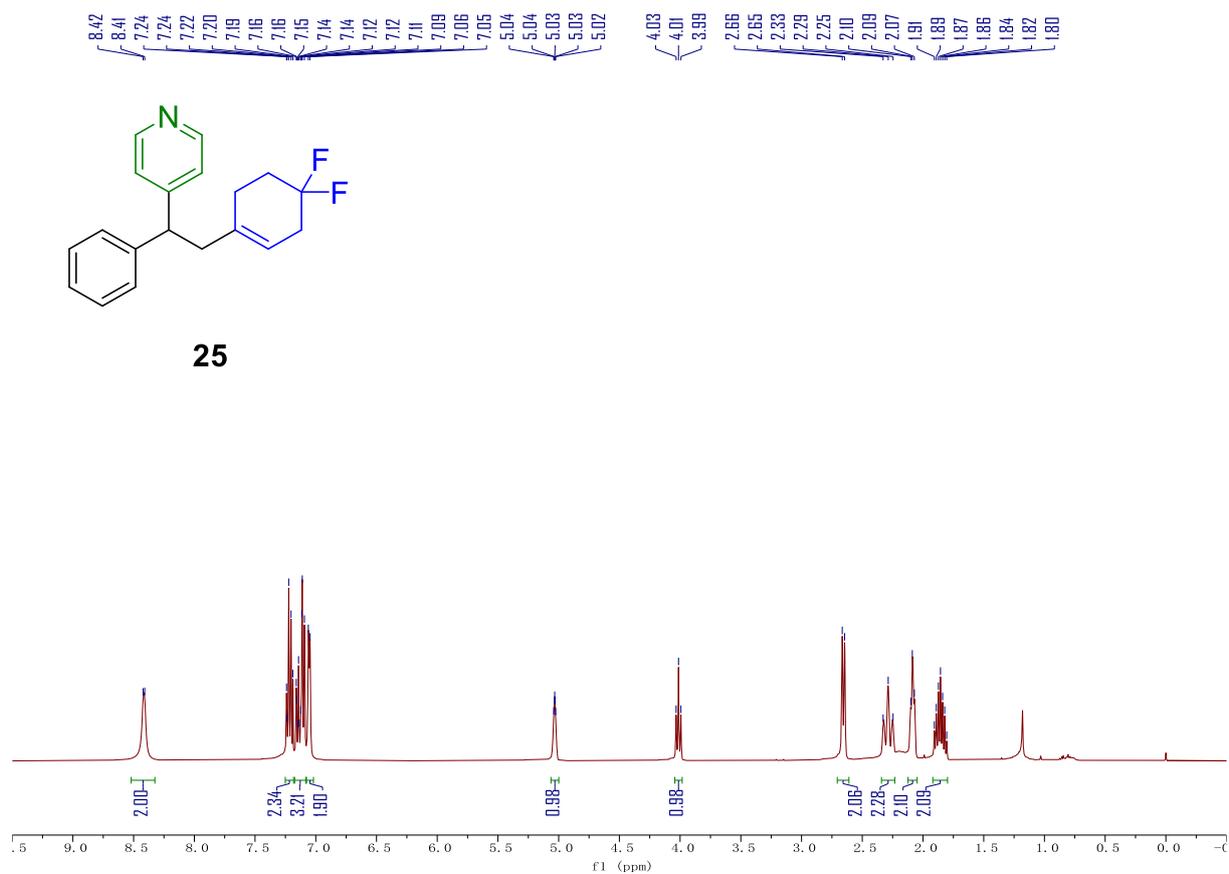
¹H NMR spectra of compound 24 (400 MHz, Chloroform-*d*)



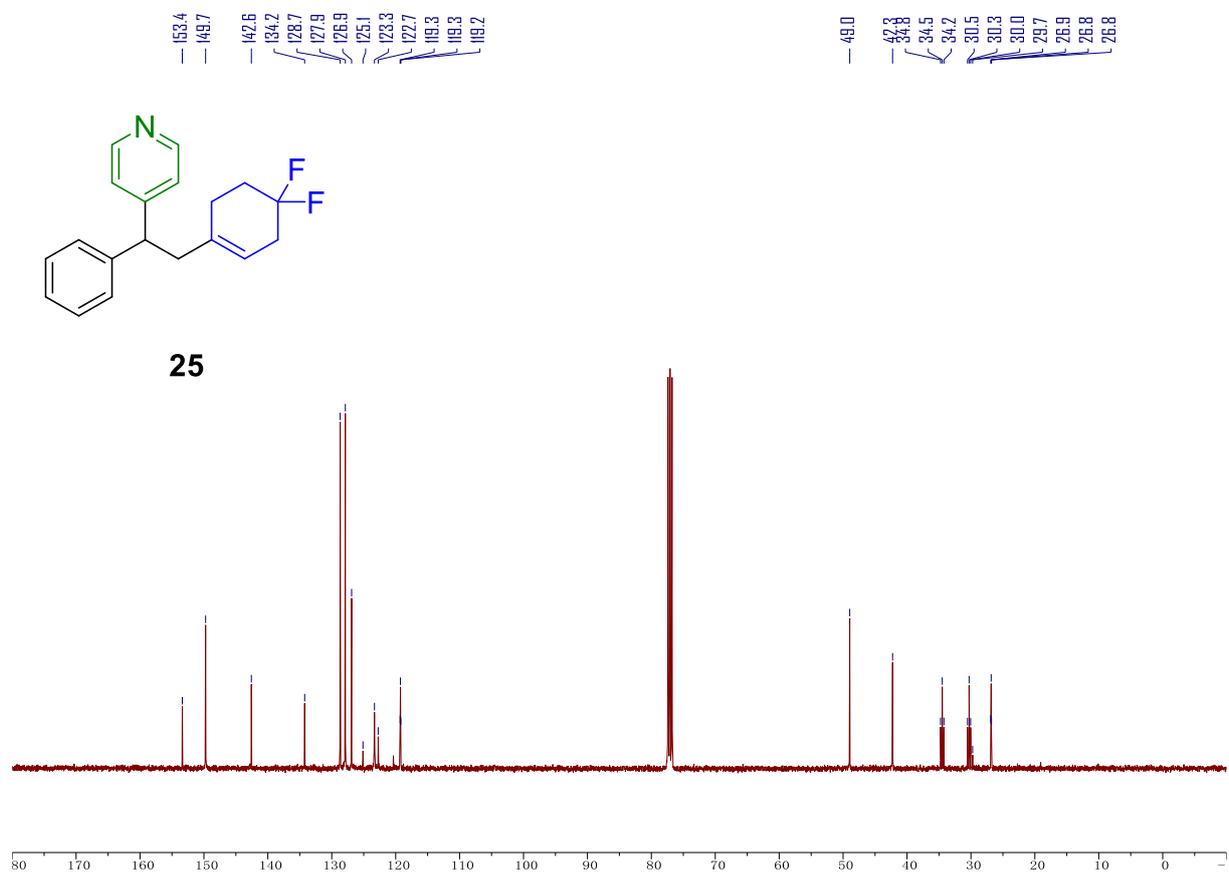
¹³C NMR spectra of compound 24 (101 MHz, Chloroform-*d*)



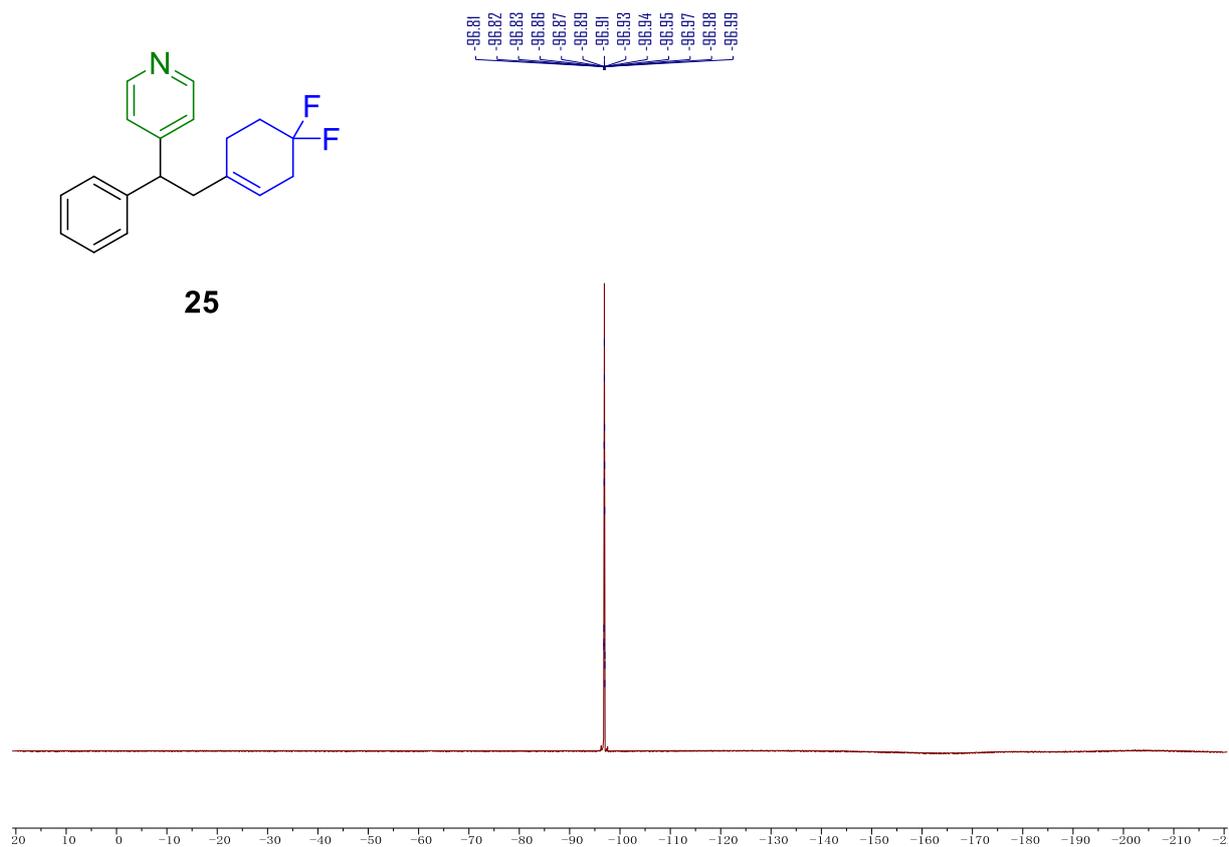
¹H NMR spectra of compound 25 (400 MHz, Chloroform-*d*)



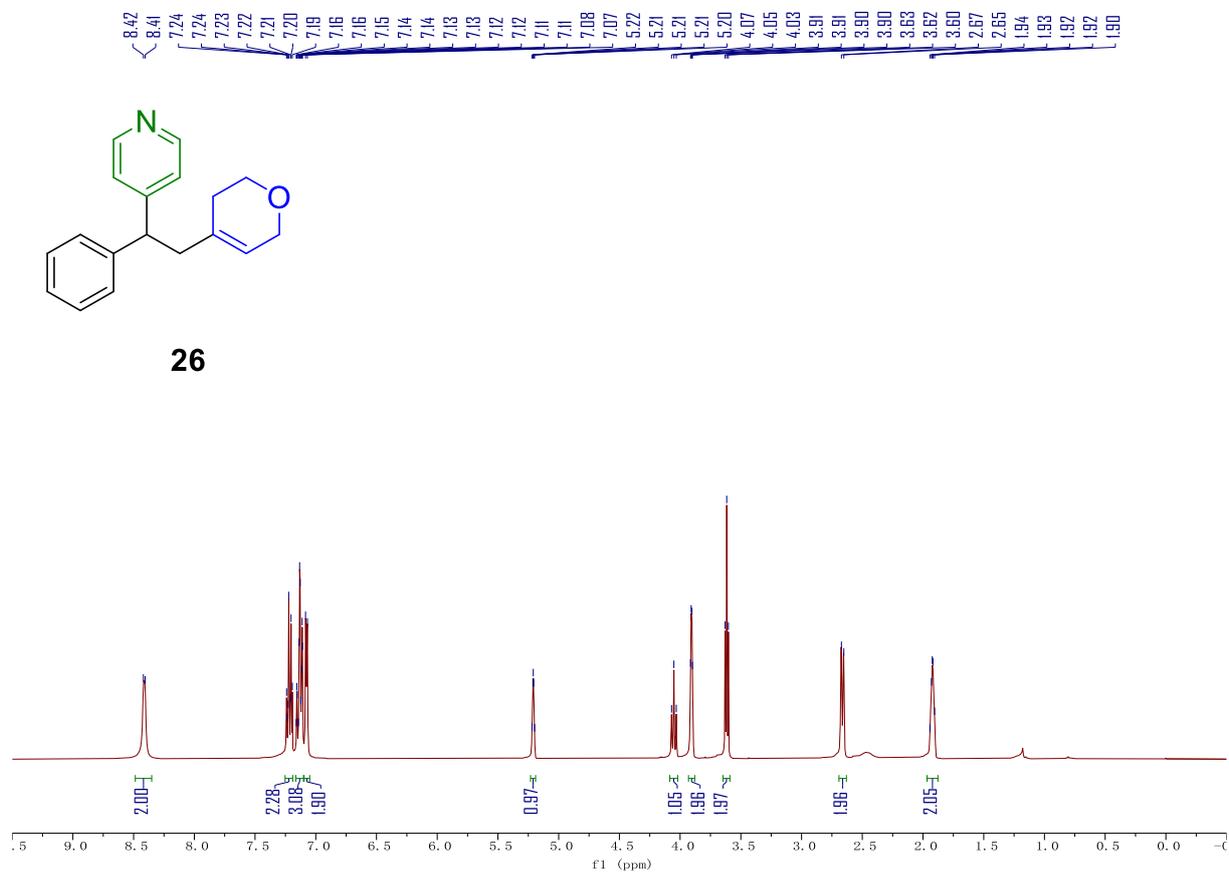
¹³C NMR spectra of compound 25 (101 MHz, Chloroform-*d*)



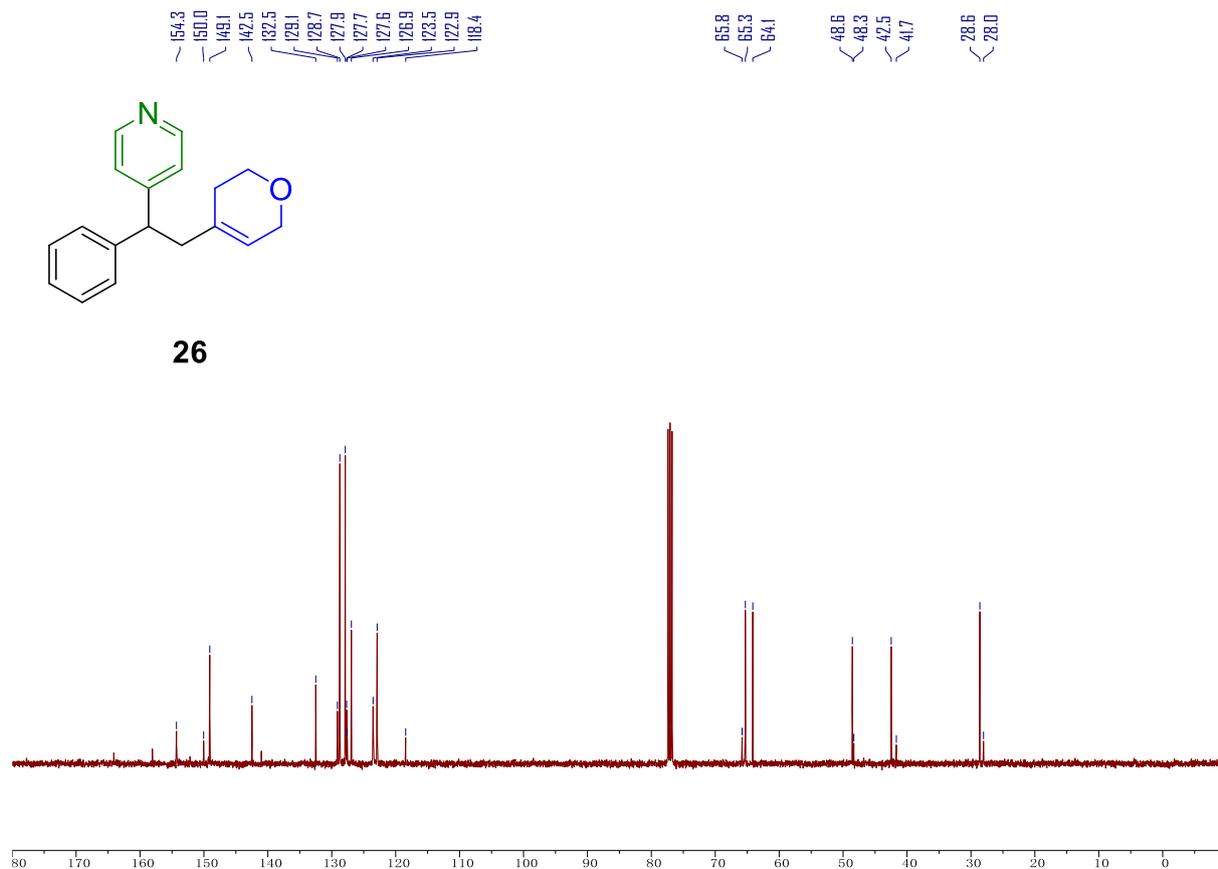
¹⁹F NMR spectra of compound **25** (376 MHz, Chloroform-*d*)



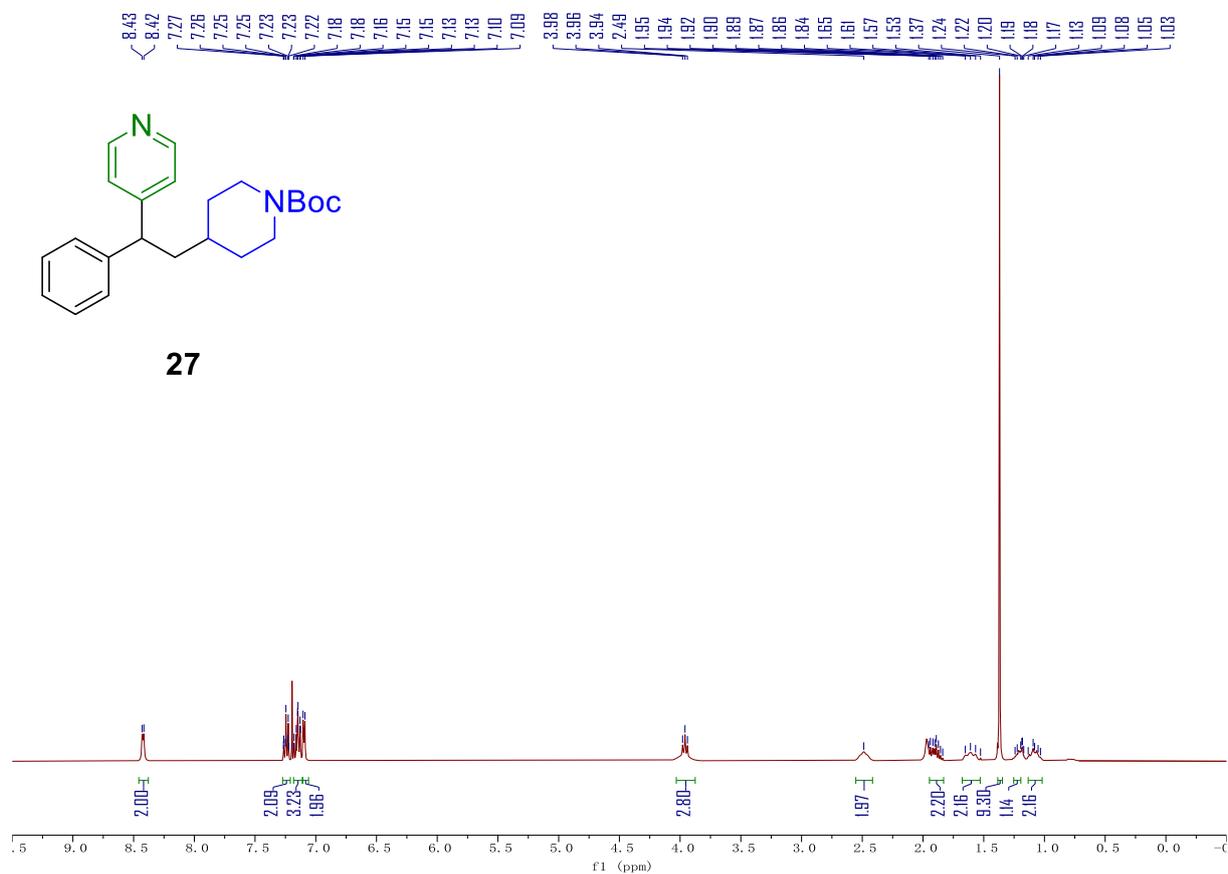
¹H NMR spectra of compound **26** (400 MHz, Chloroform-*d*)



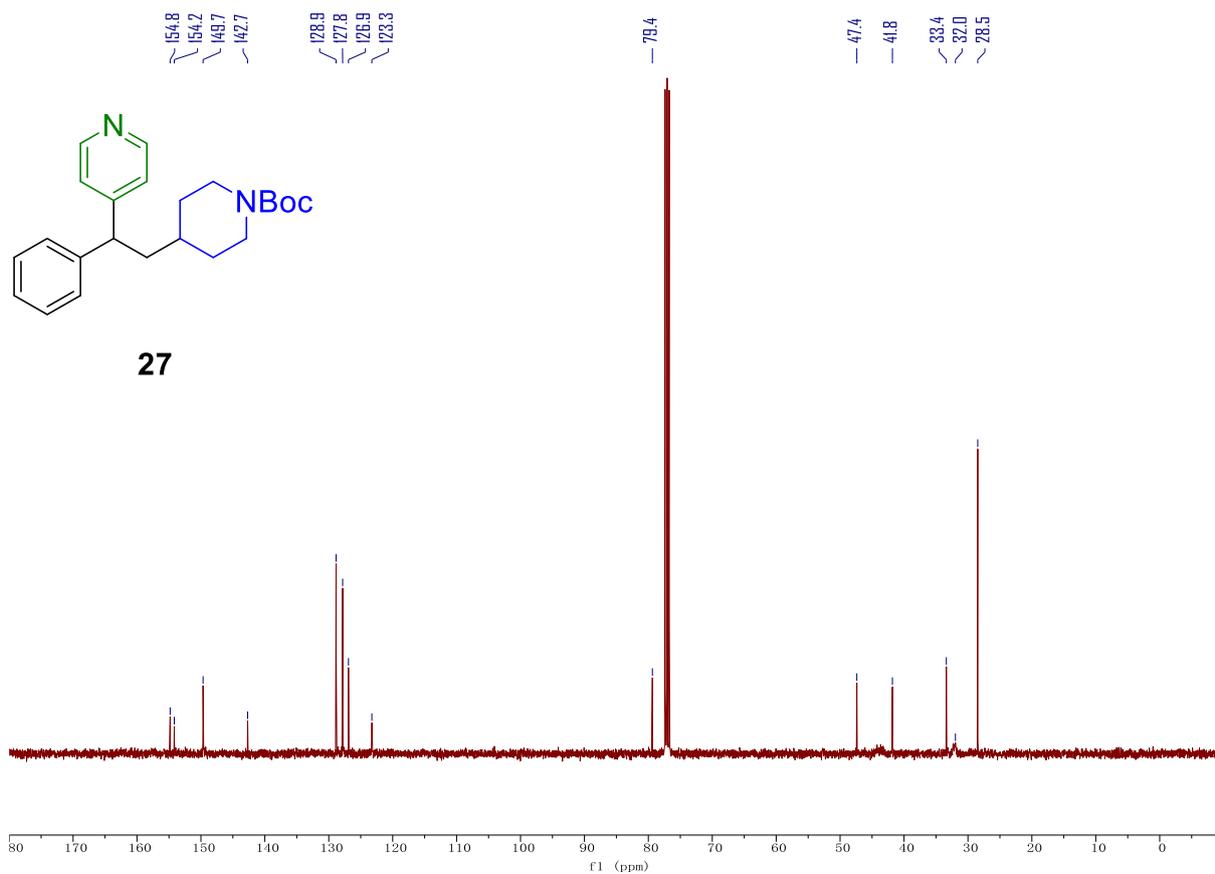
¹³C NMR spectra of compound **26** (101 MHz, Chloroform-*d*)



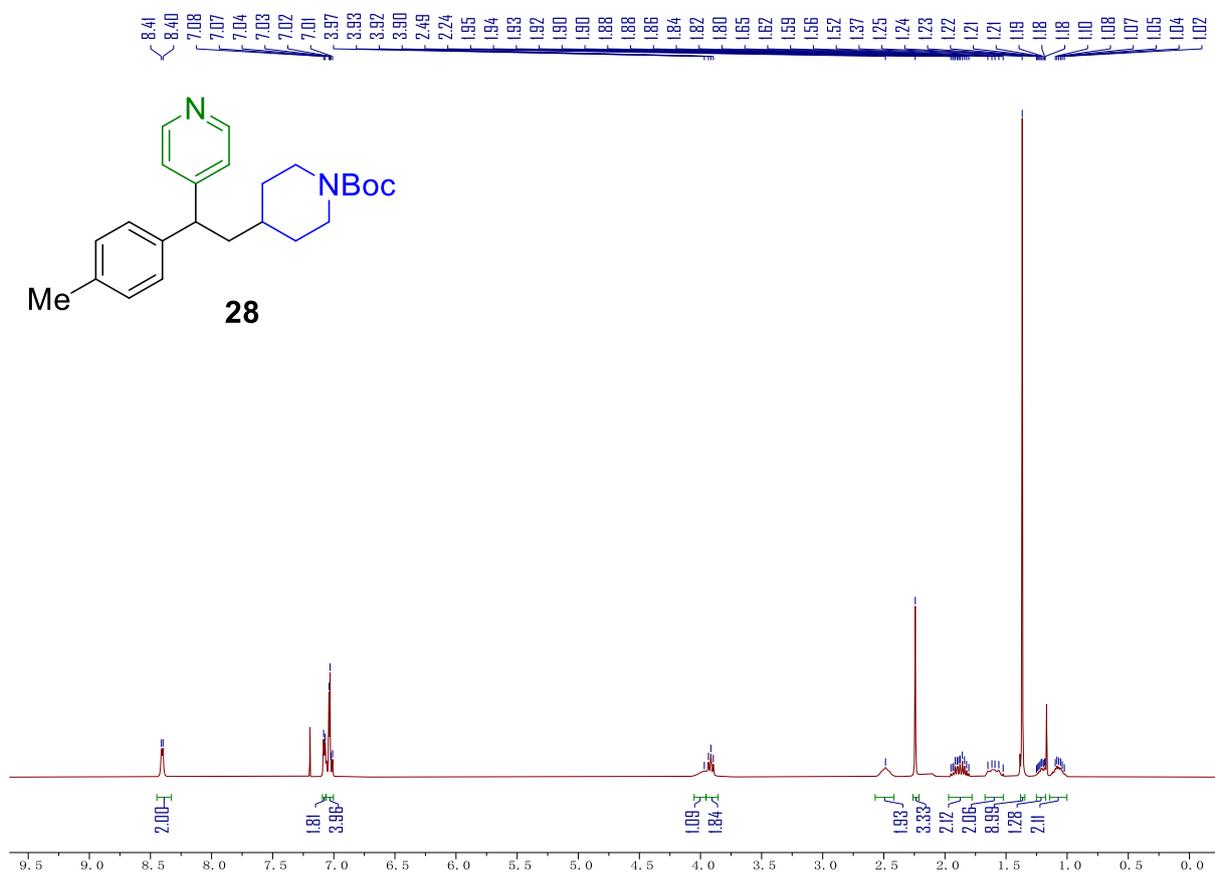
¹H NMR spectra of compound **27** (400 MHz, Chloroform-*d*)



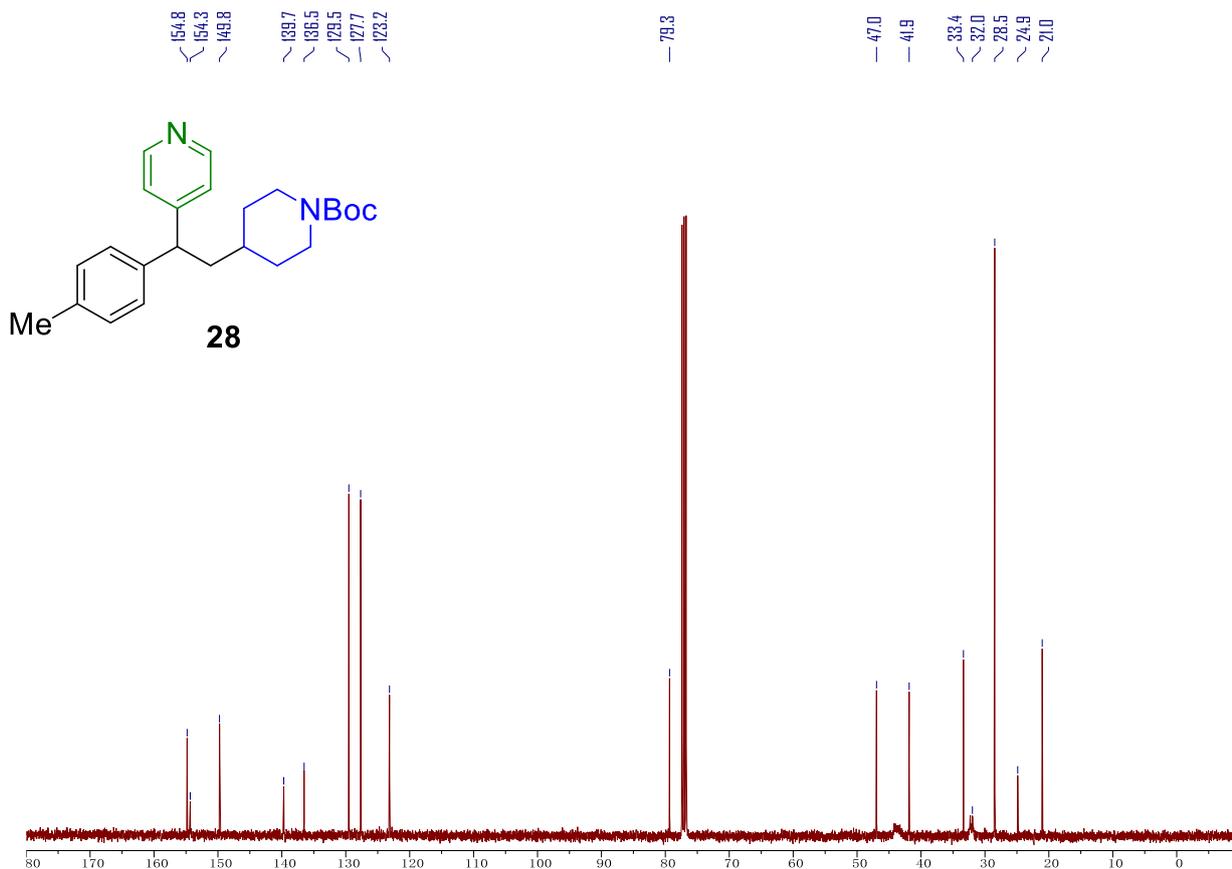
¹³C NMR spectra of compound **27** (101 MHz, Chloroform-*d*)



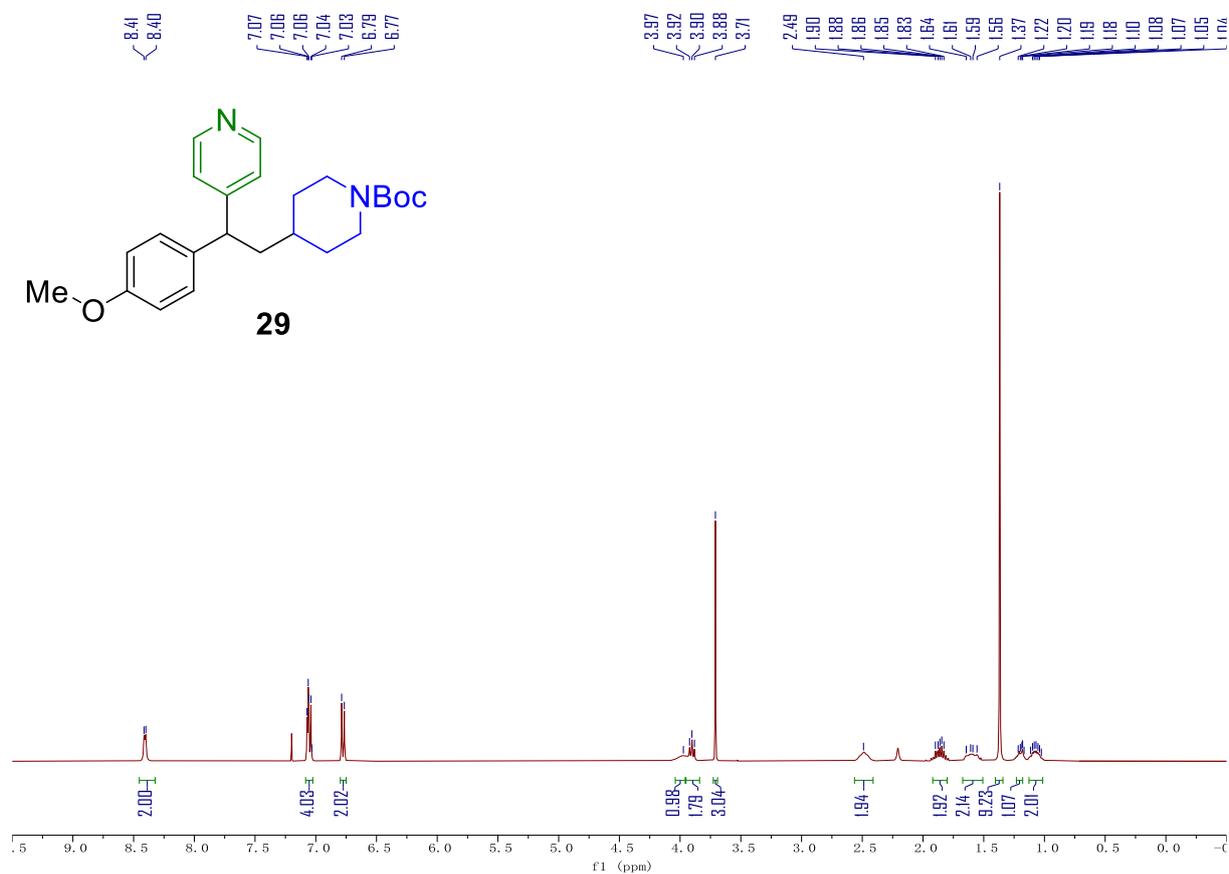
¹H NMR spectra of compound **28** (400 MHz, Chloroform-*d*)



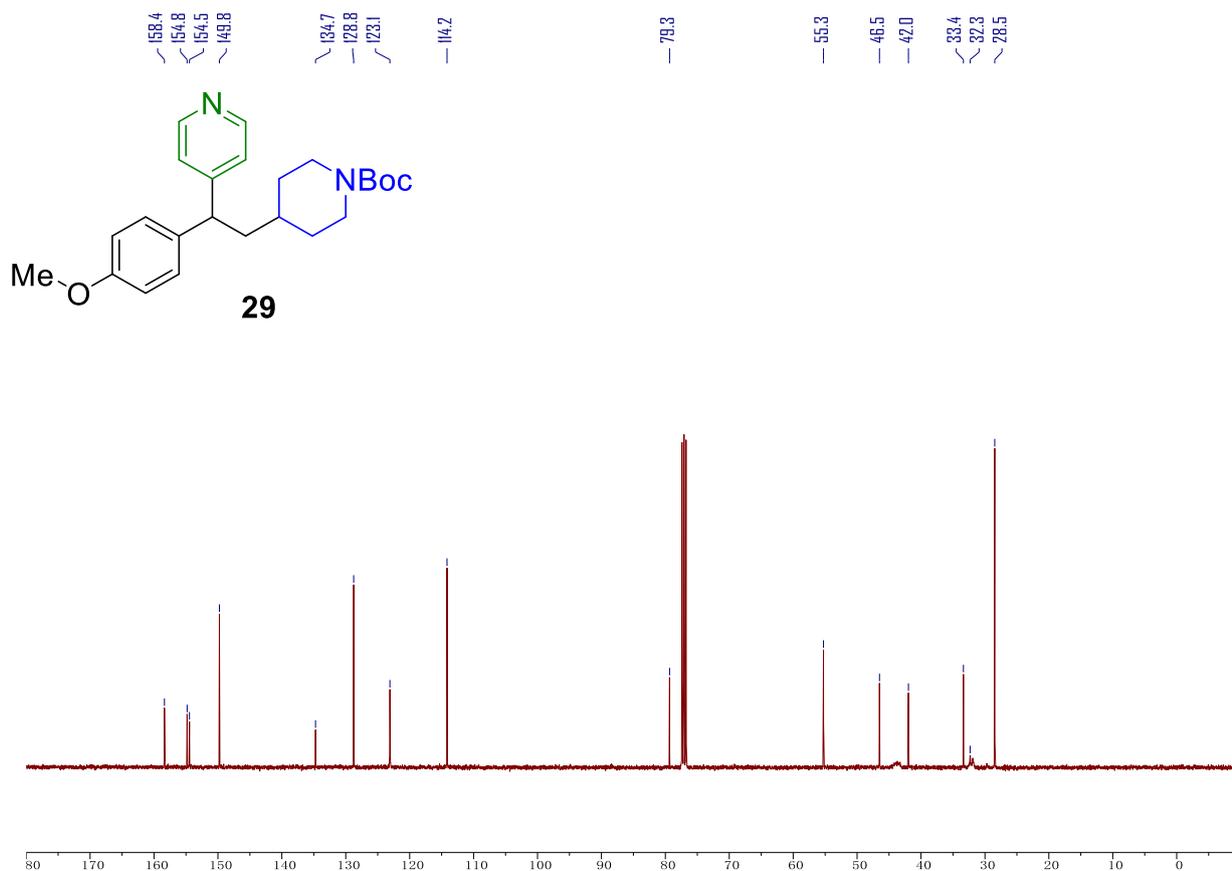
¹³C NMR spectra of compound **28** (101 MHz, Chloroform-*d*)



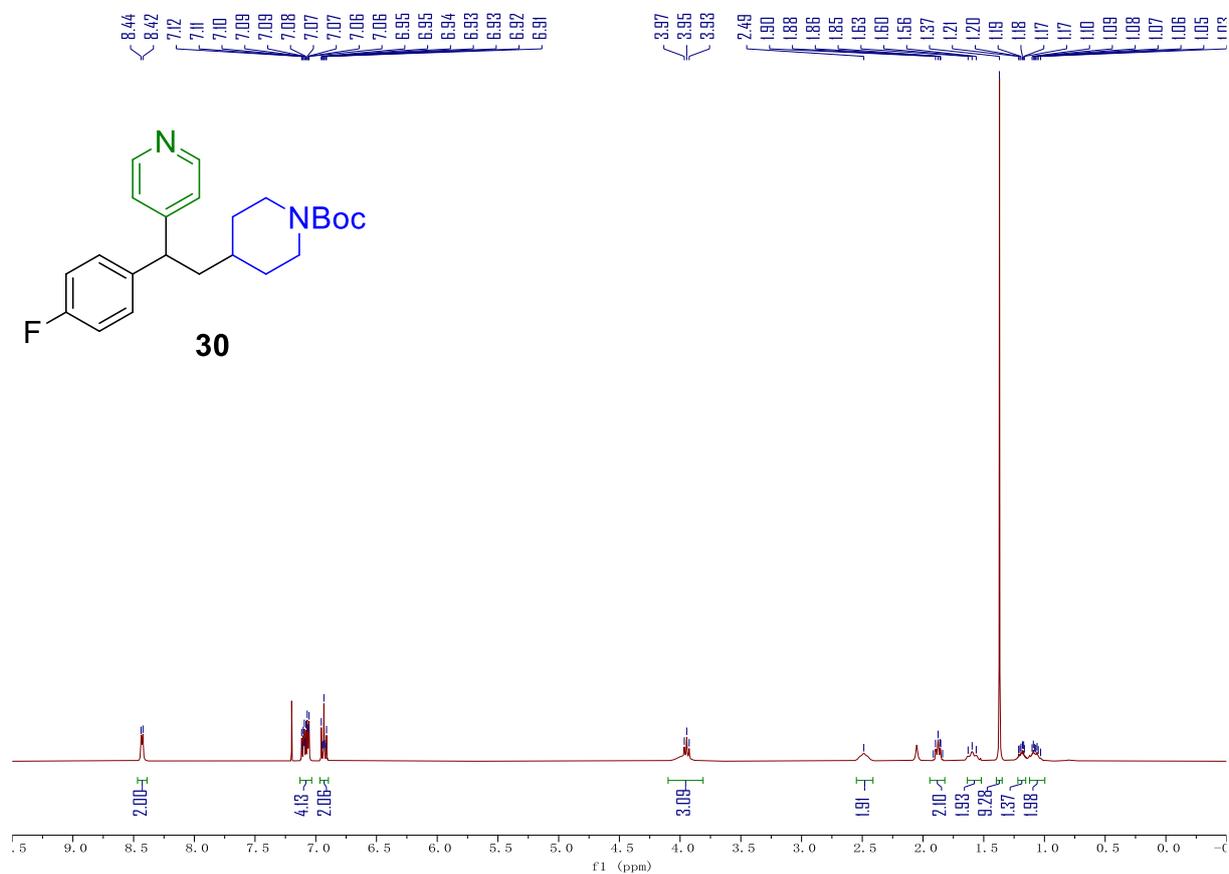
¹H NMR spectra of compound **29** (400 MHz, Chloroform-*d*)



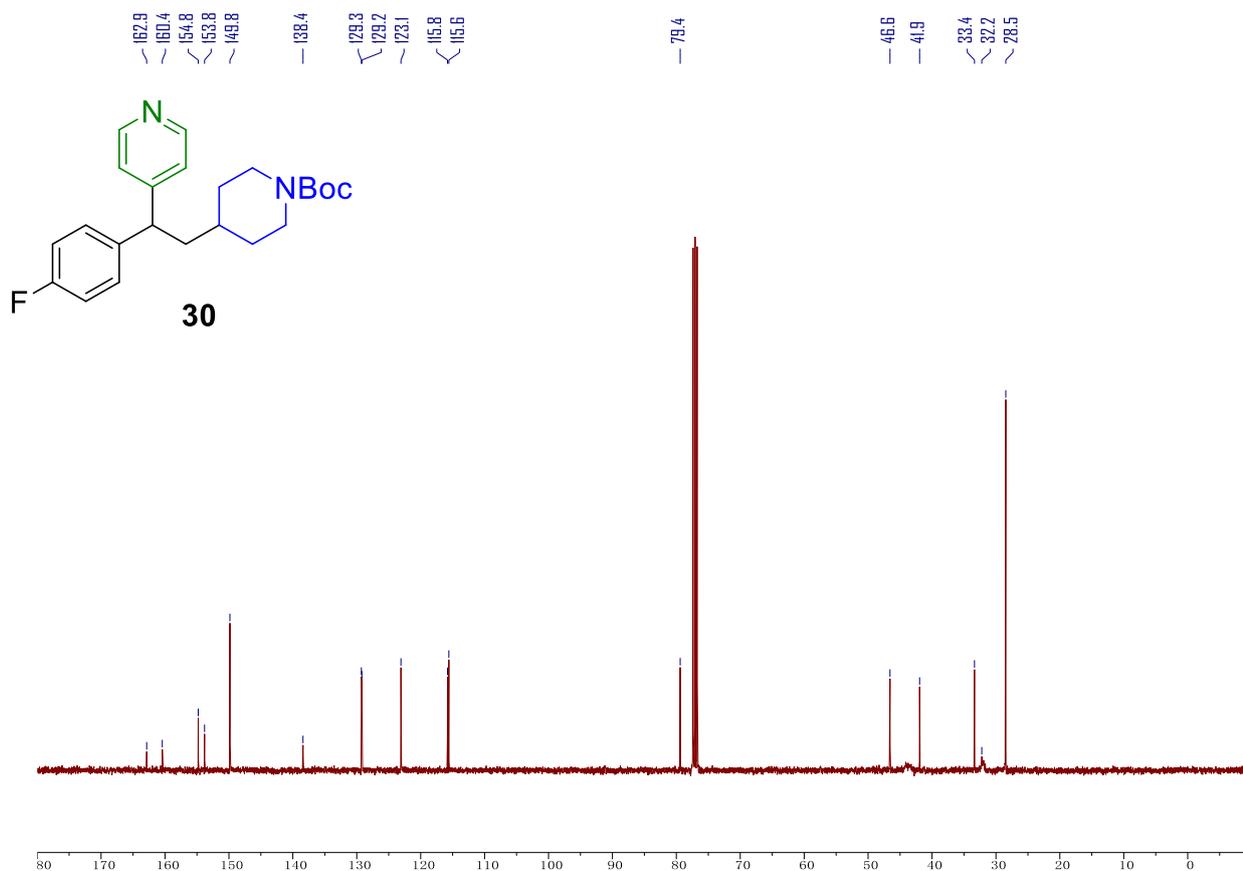
¹³C NMR spectra of compound **29** (101 MHz, Chloroform-*d*)



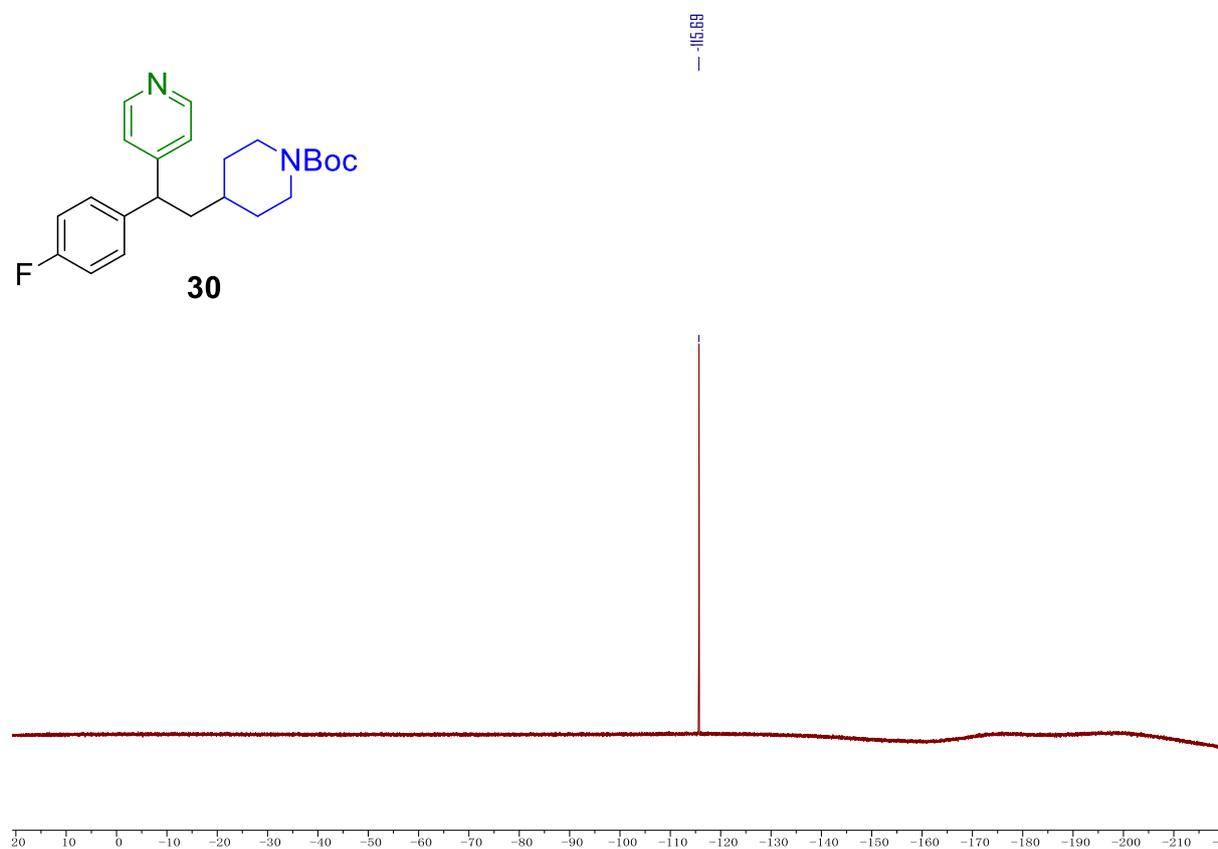
¹H NMR spectra of compound **30** (400 MHz, Chloroform-*d*)



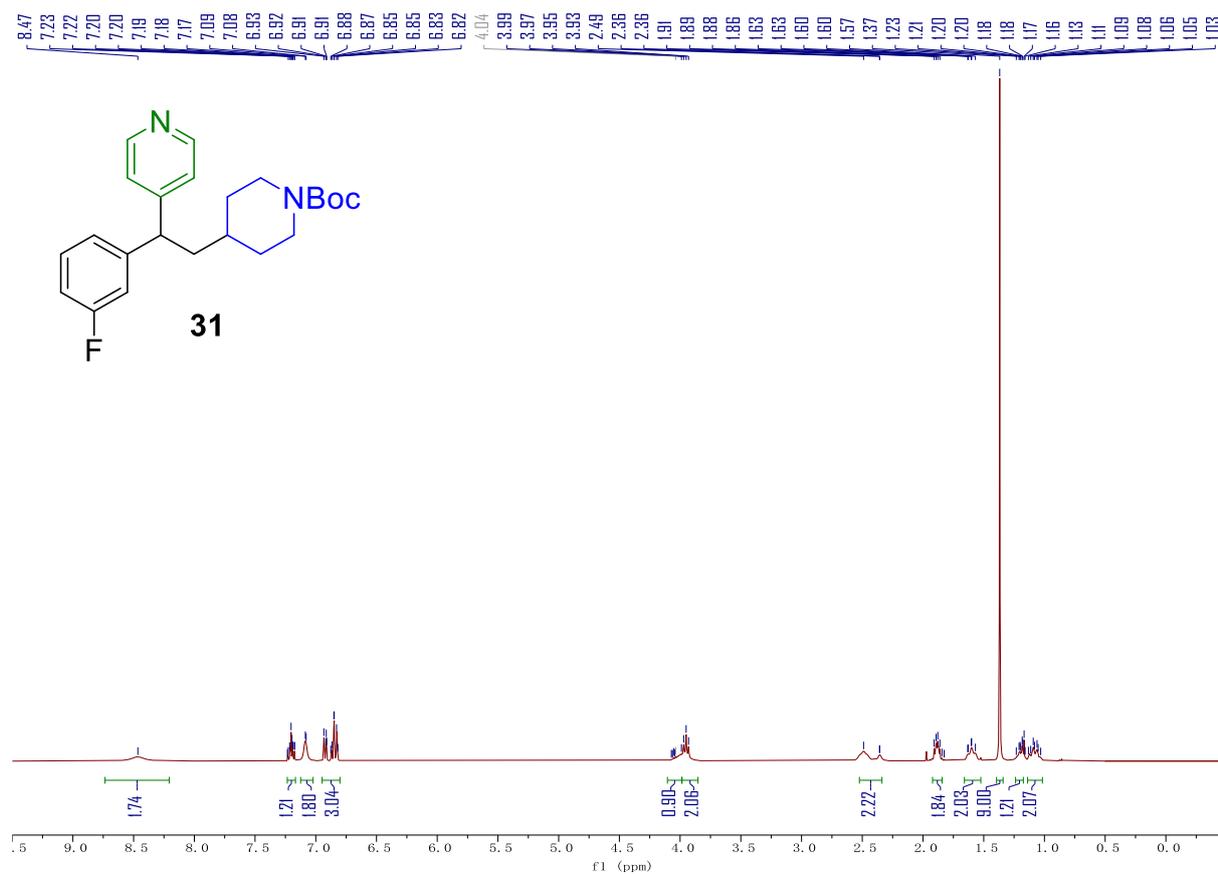
¹³C NMR spectra of compound **30** (101 MHz, Chloroform-*d*)



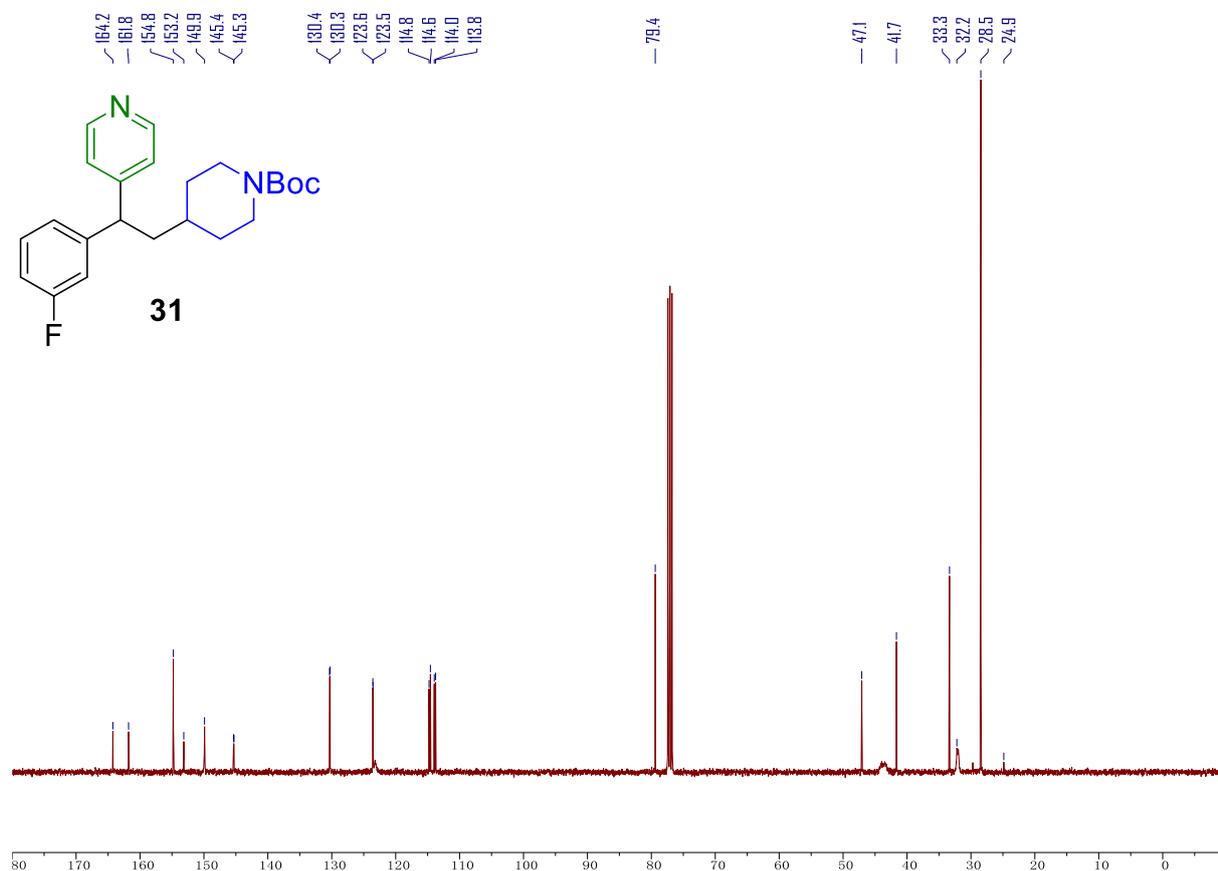
¹⁹F NMR spectra of compound **30** (376 MHz, Chloroform-*d*)



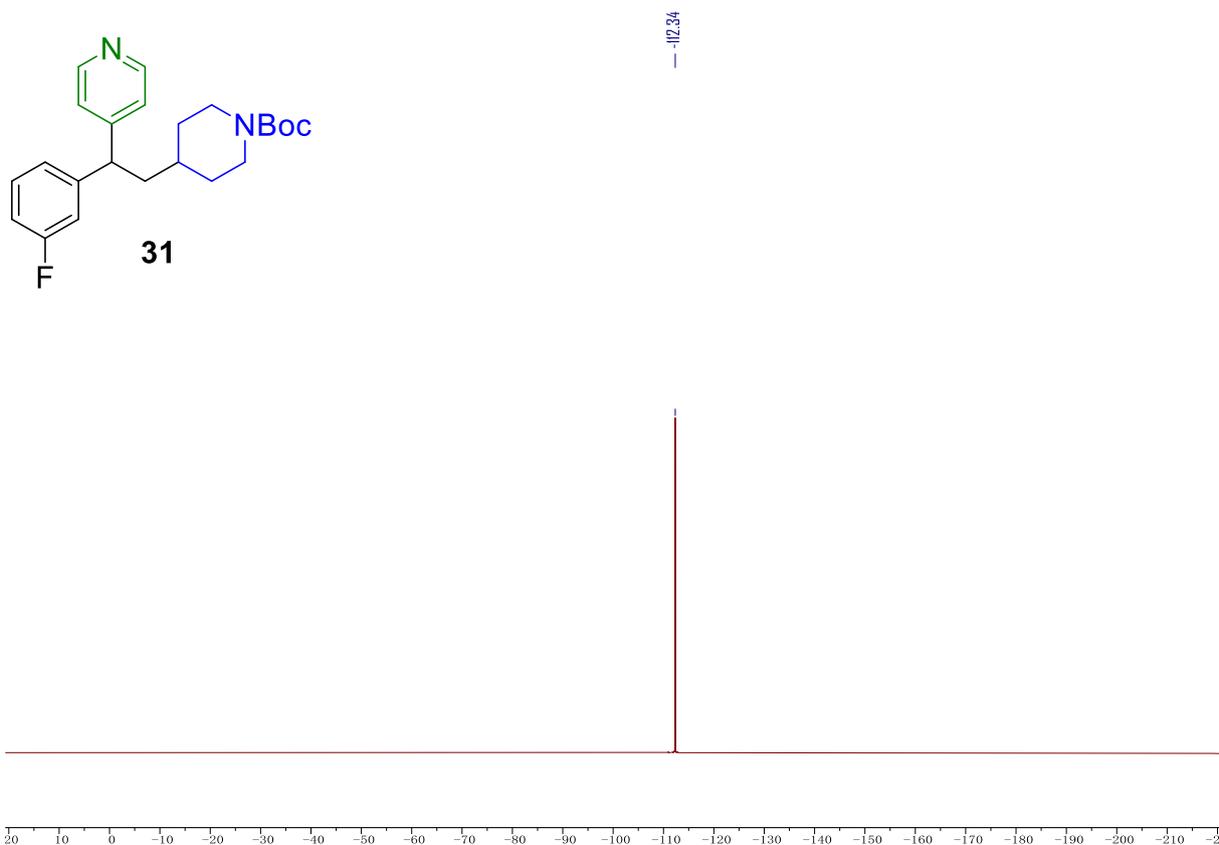
¹H NMR spectra of compound 31 (400 MHz, Chloroform-*d*)



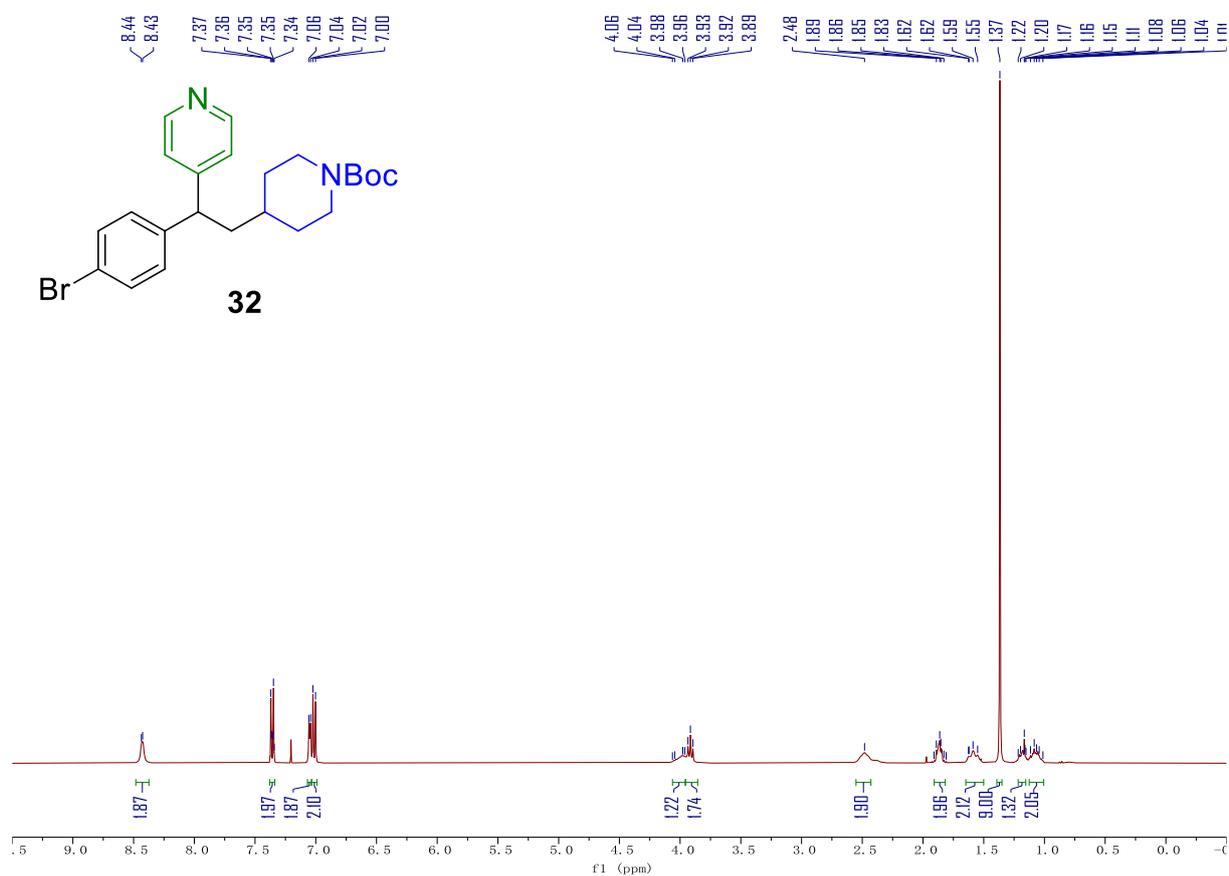
¹³C NMR spectra of compound 31 (101 MHz, Chloroform-*d*)



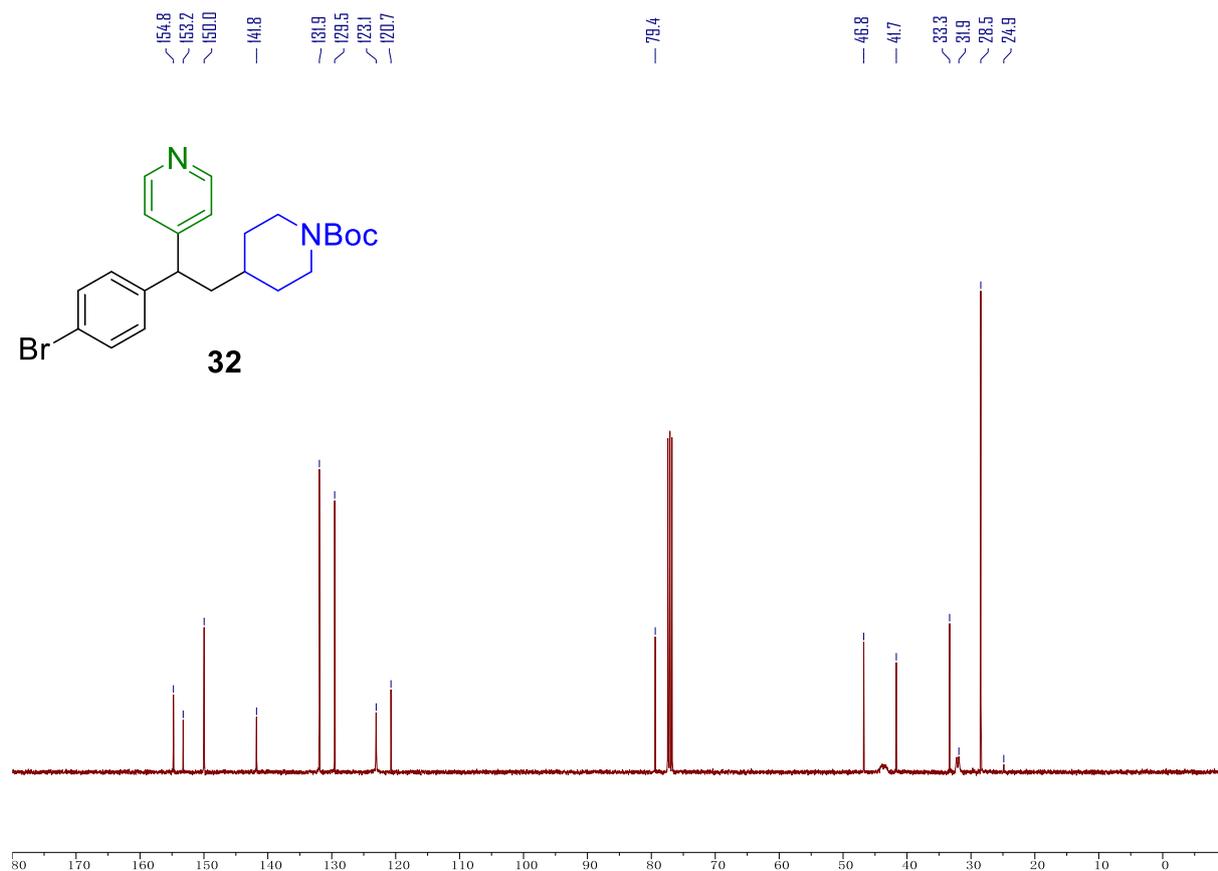
¹⁹F NMR spectra of compound 31 (376 MHz, Chloroform-*d*)



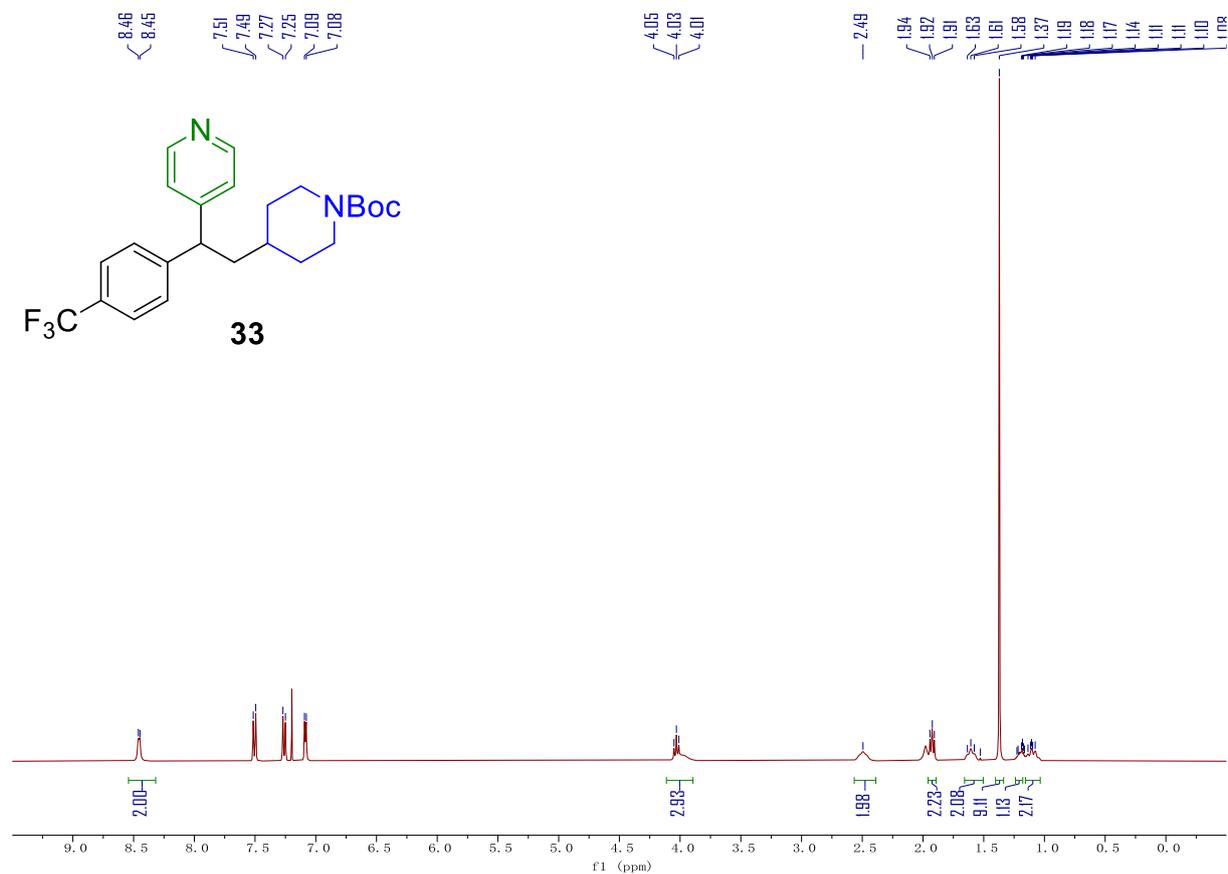
¹H NMR spectra of compound 32 (400 MHz, Chloroform-*d*)



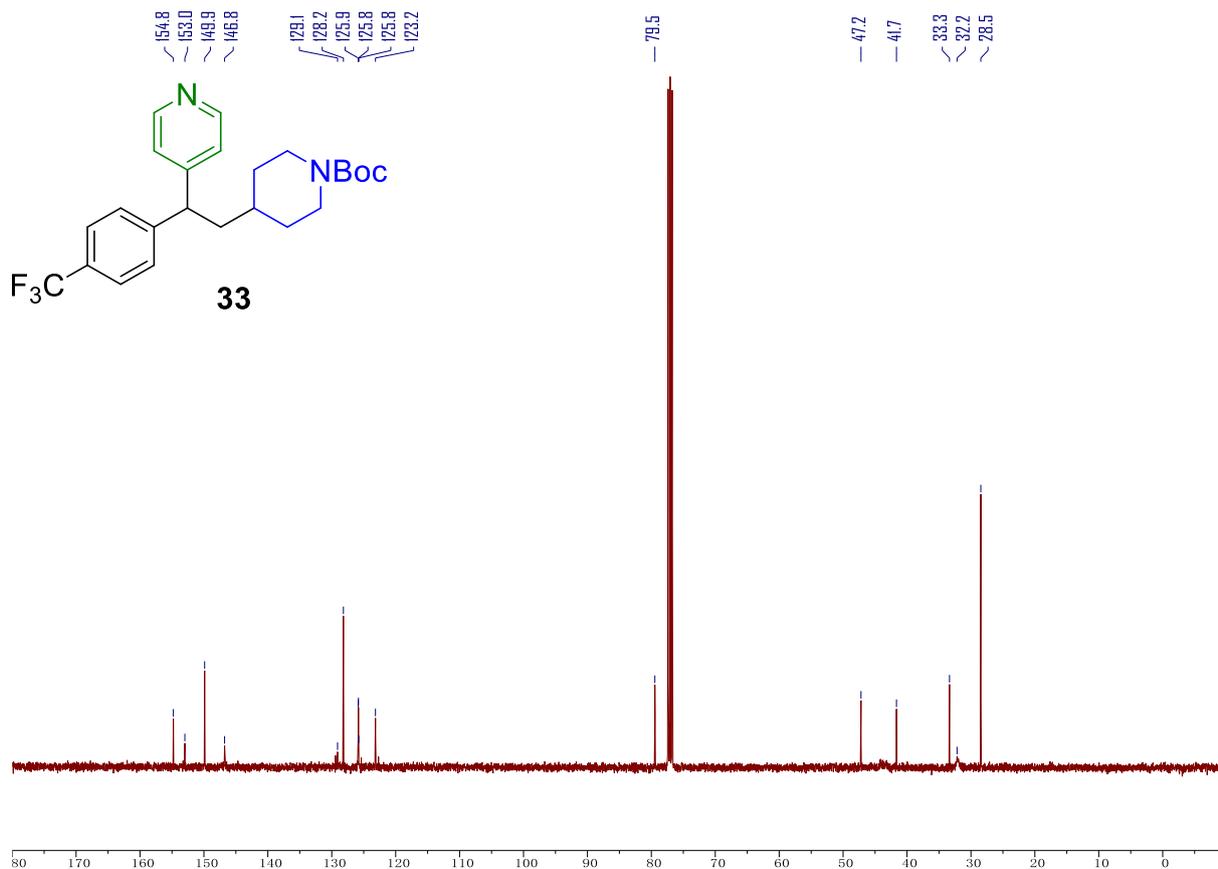
¹³C NMR spectra of compound **32** (101 MHz, Chloroform-*d*)



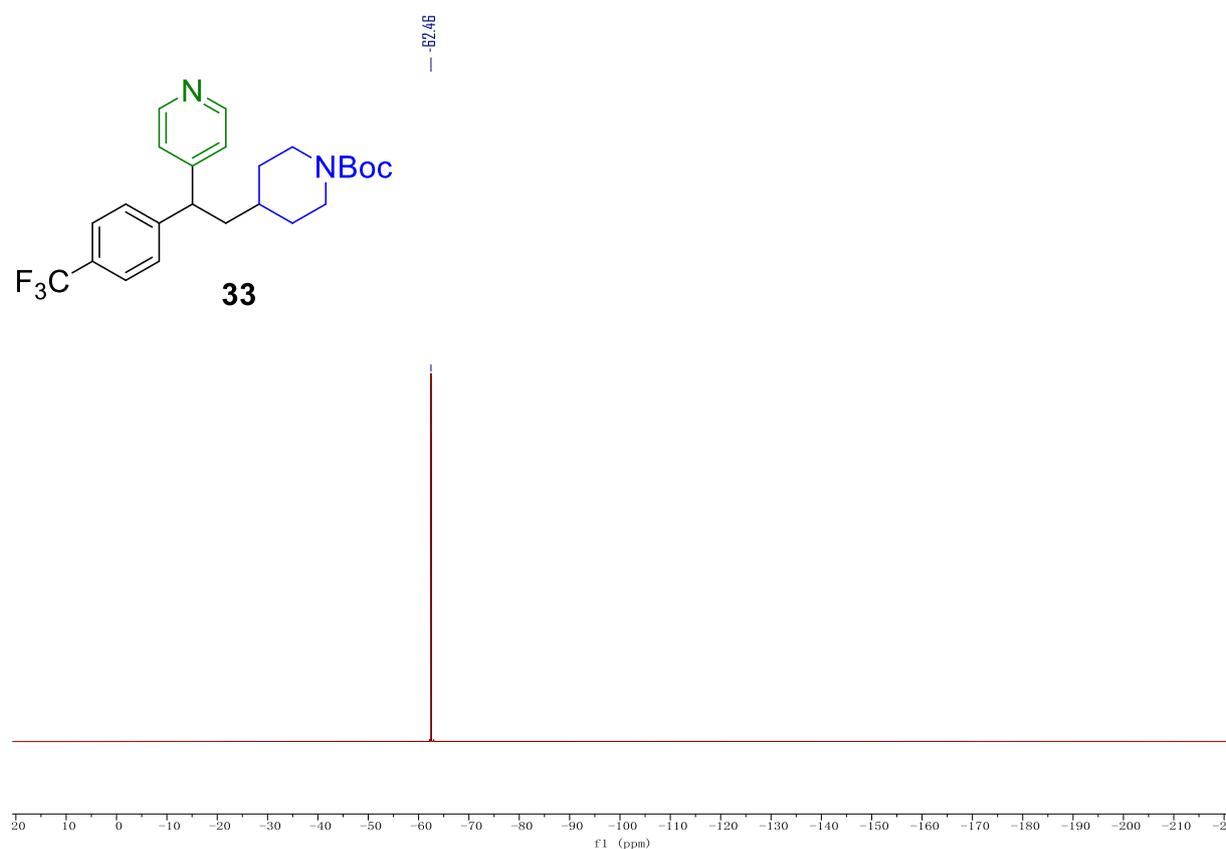
¹H NMR spectra of compound **33** (400 MHz, Chloroform-*d*)



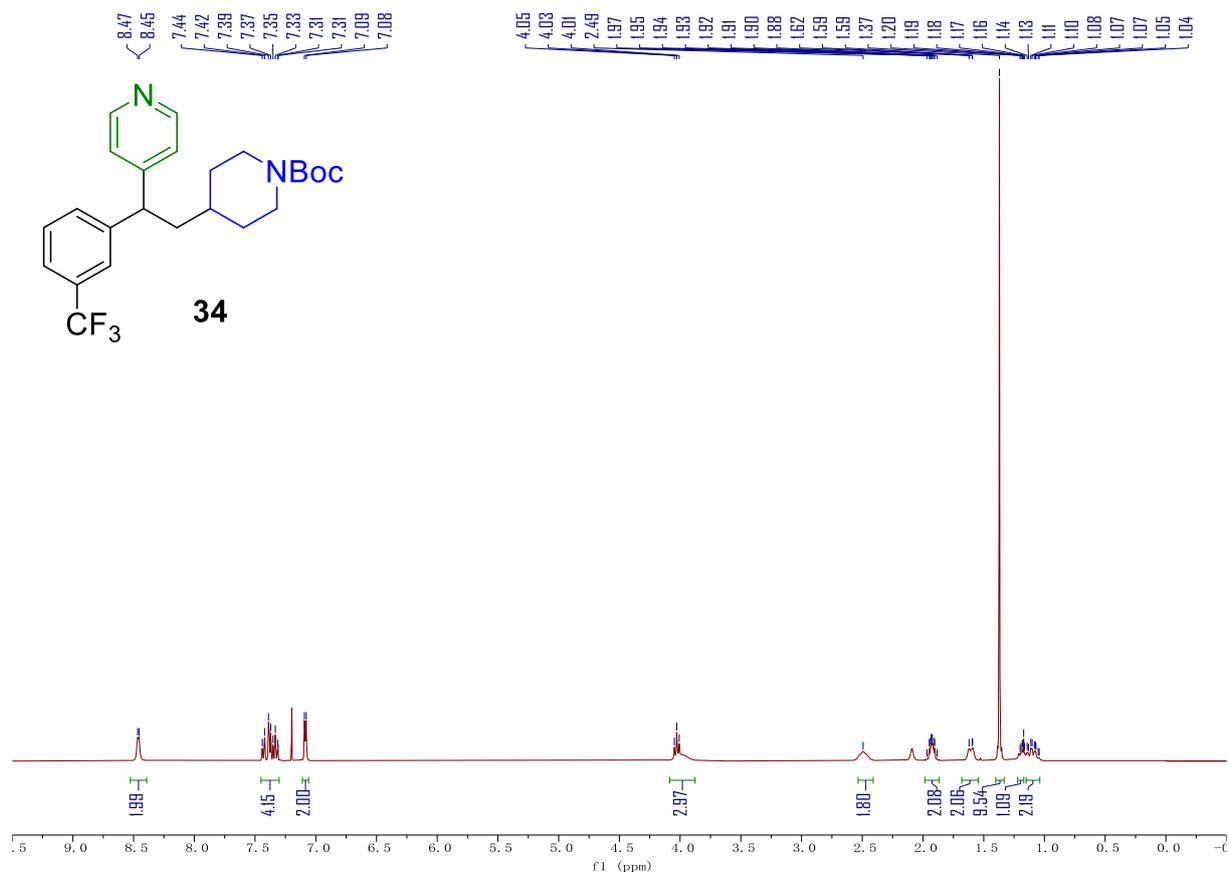
¹³C NMR spectra of compound **33** (101 MHz, Chloroform-*d*)



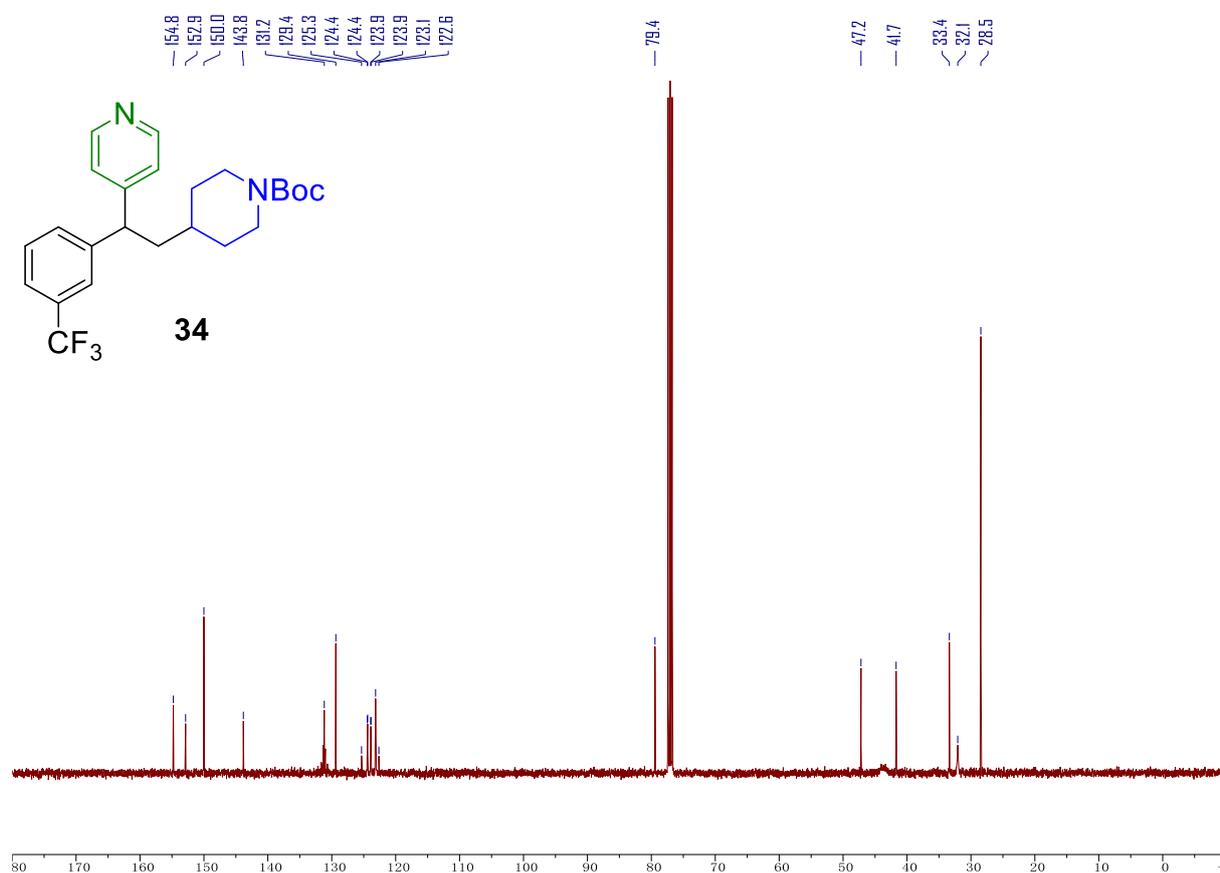
¹⁹F NMR spectra of compound **33** (376 MHz, Chloroform-*d*)



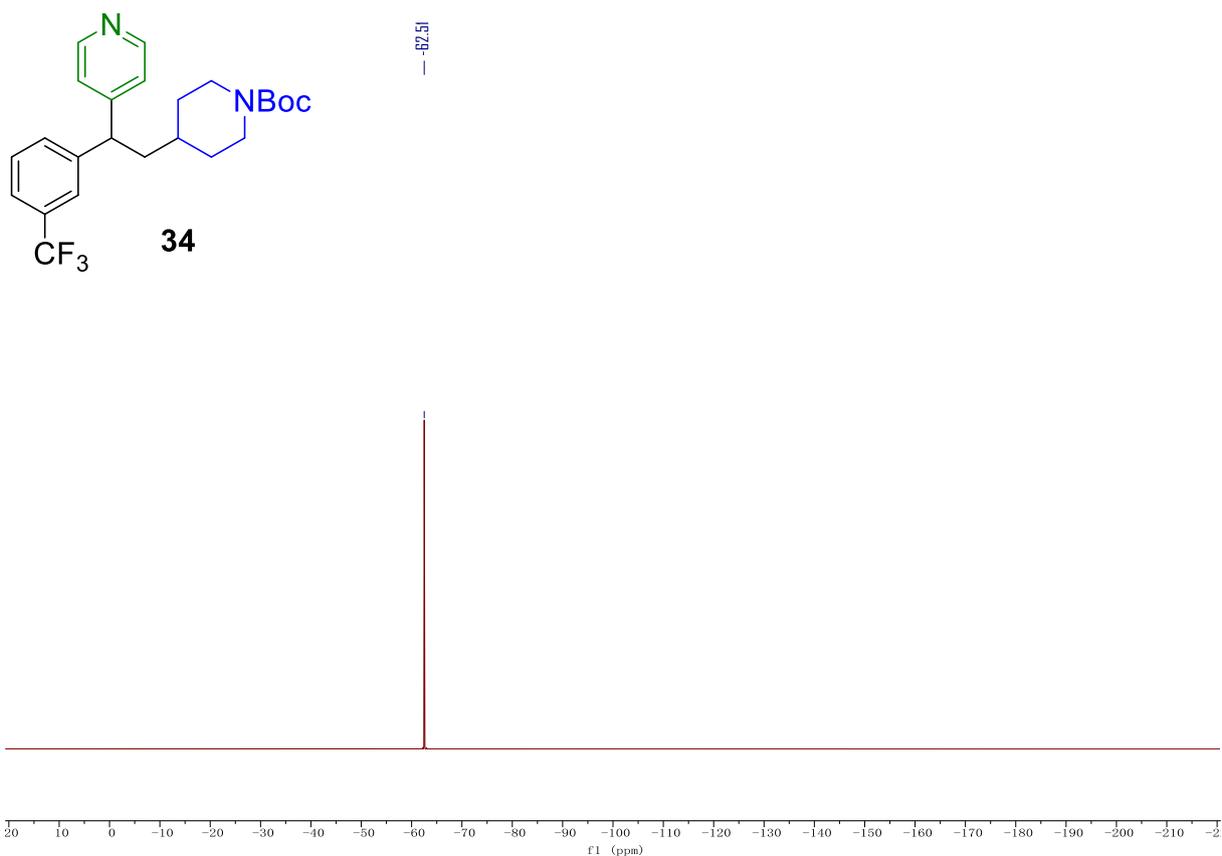
¹H NMR spectra of compound 34 (400 MHz, Chloroform-*d*)



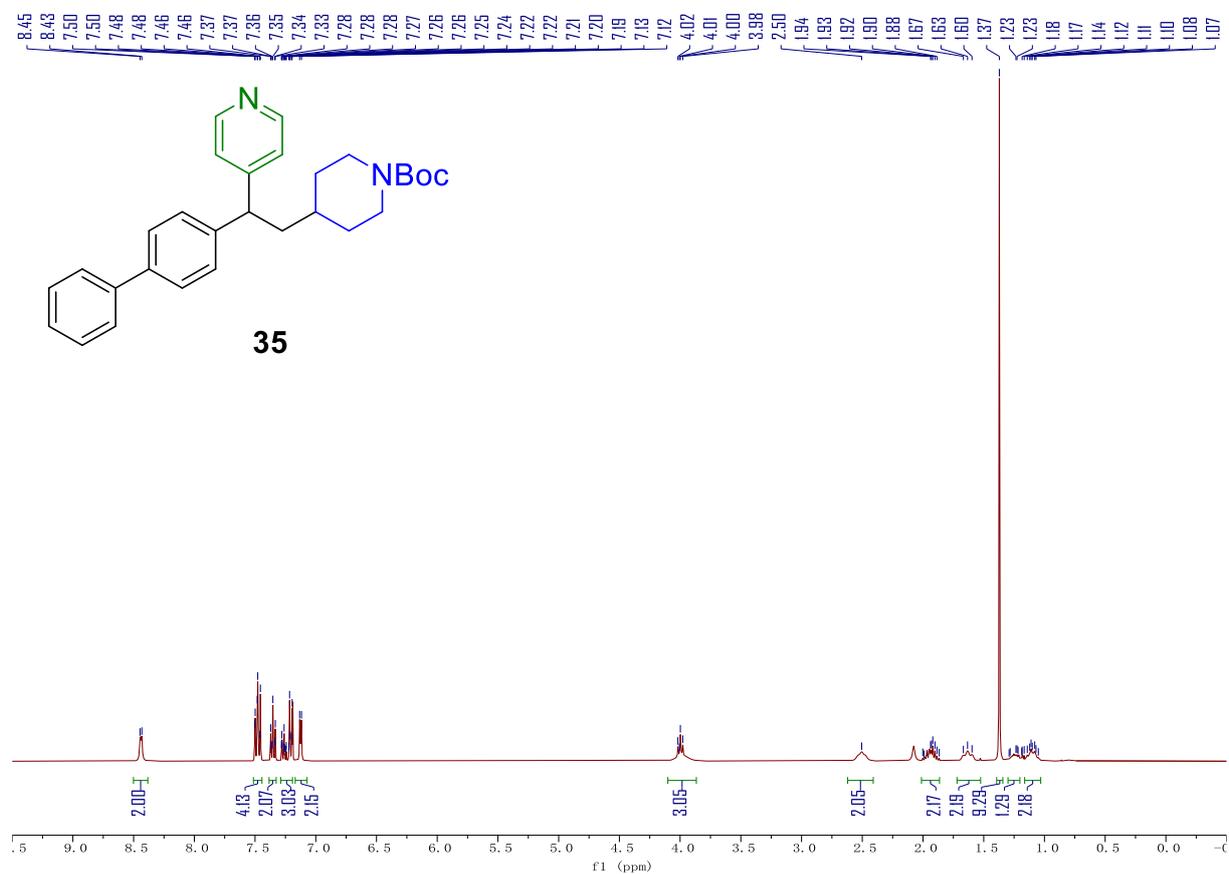
¹³C NMR spectra of compound 34 (101 MHz, Chloroform-*d*)



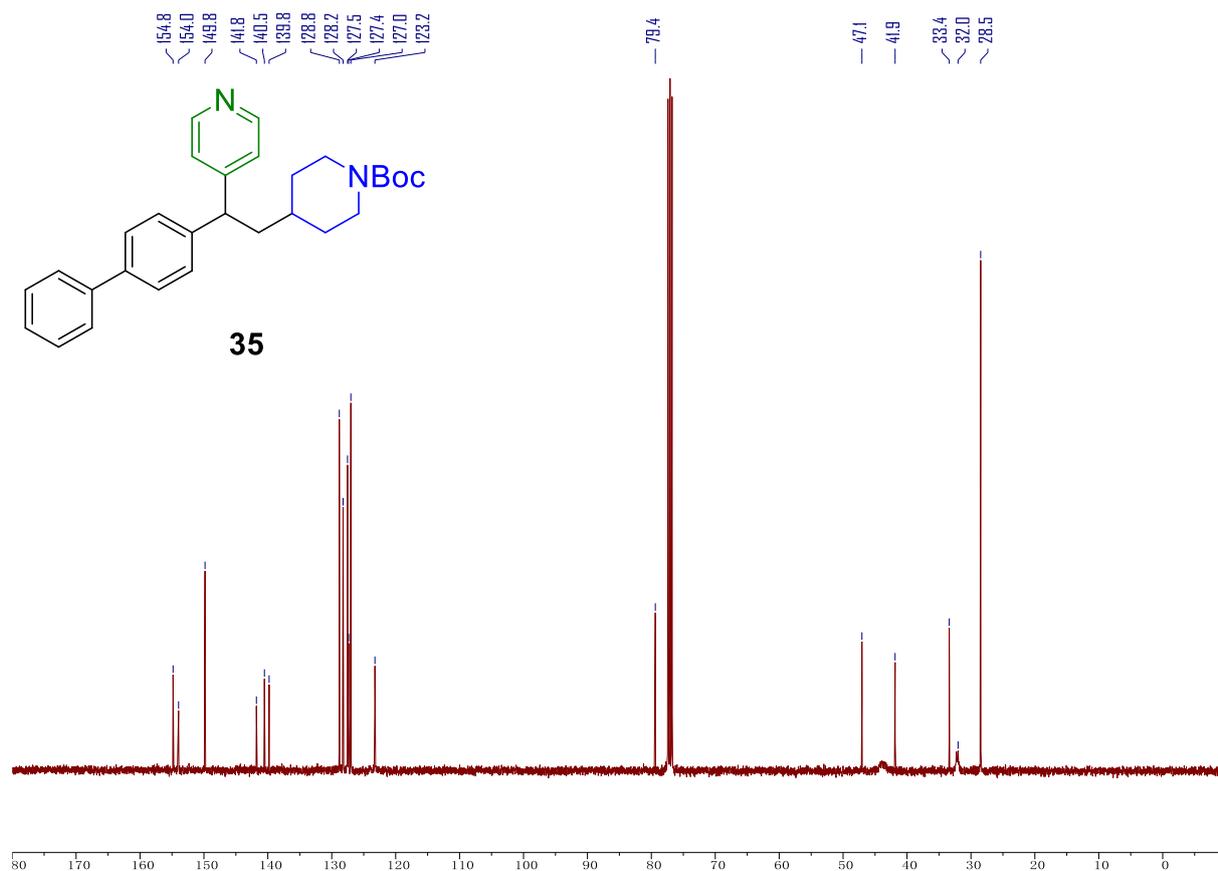
¹⁹F NMR spectra of compound 34 (376 MHz, Chloroform-*d*)



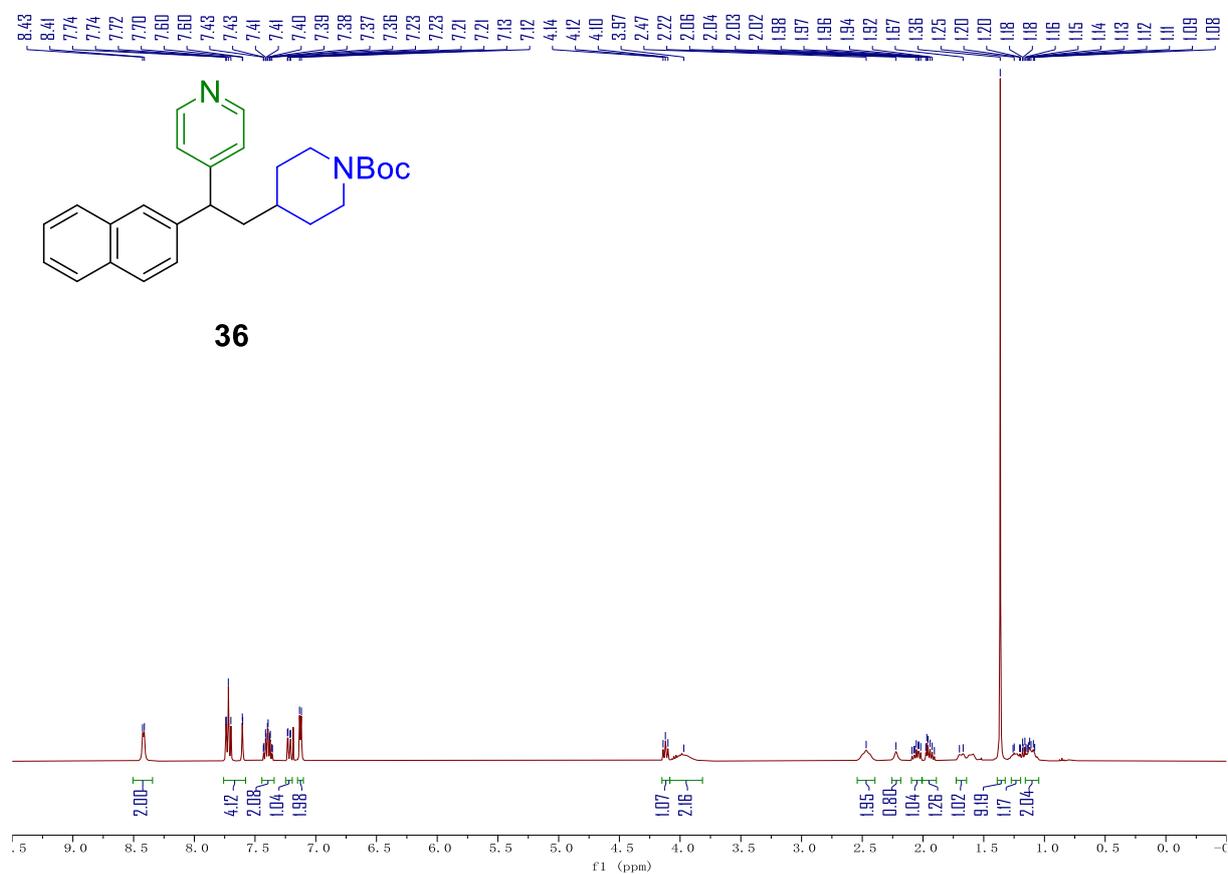
¹H NMR spectra of compound 35 (400 MHz, Chloroform-*d*)



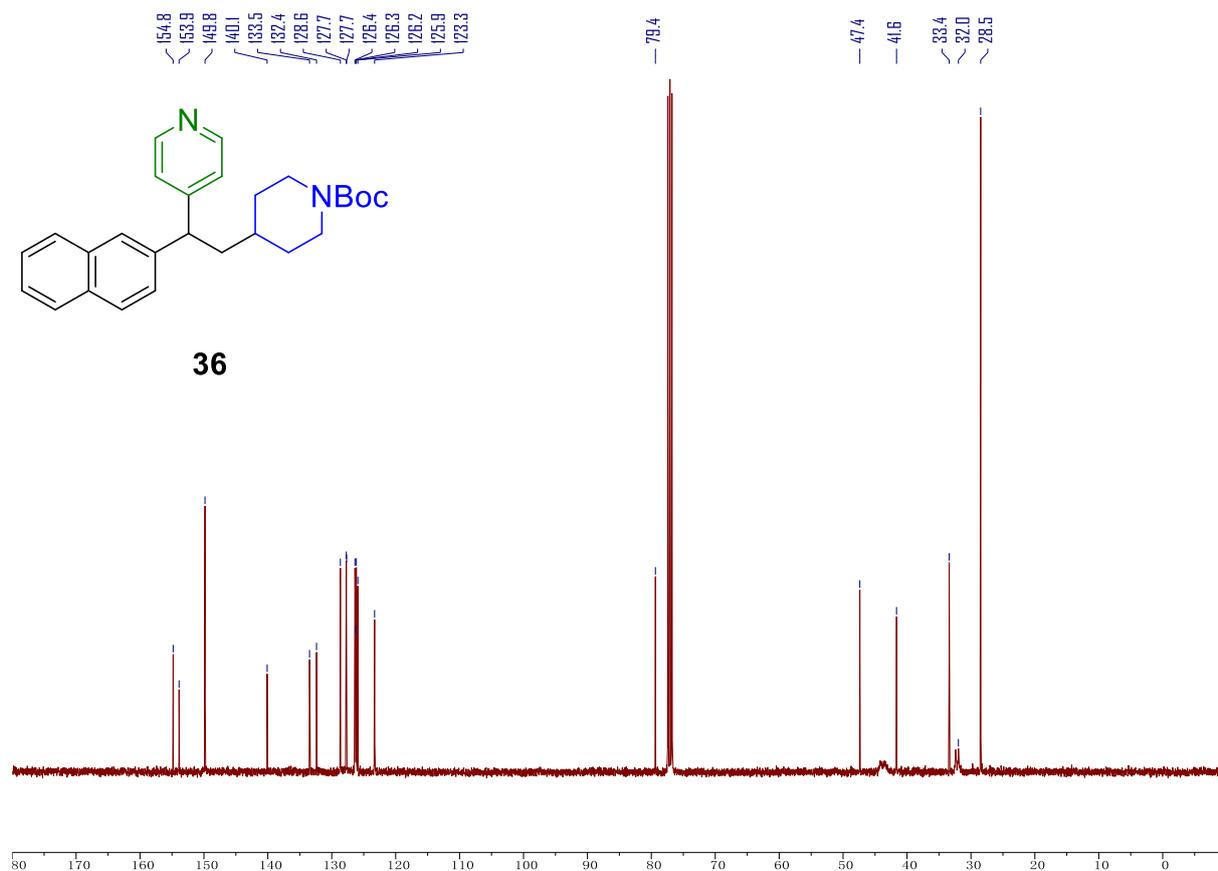
¹³C NMR spectra of compound **35** (101 MHz, Chloroform-*d*)



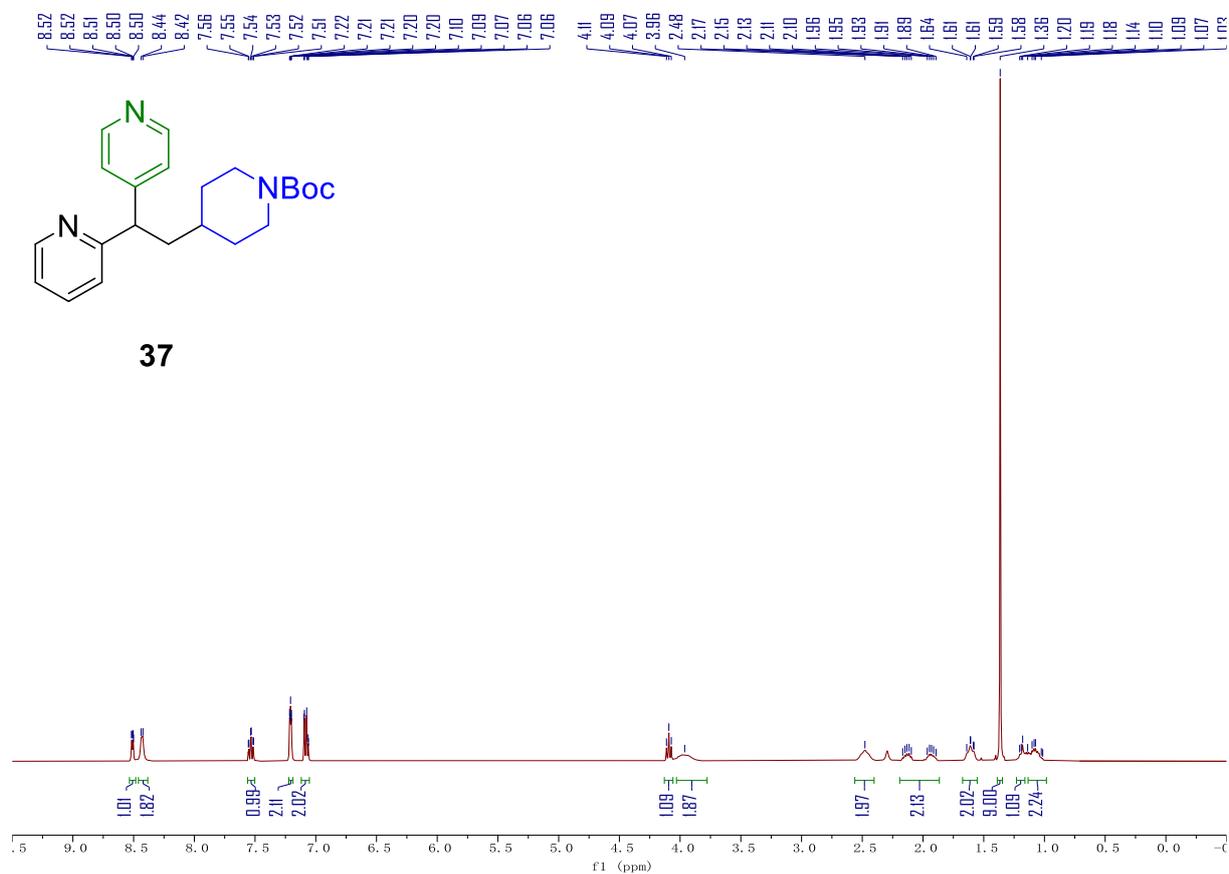
¹H NMR spectra of compound **36** (400 MHz, Chloroform-*d*)



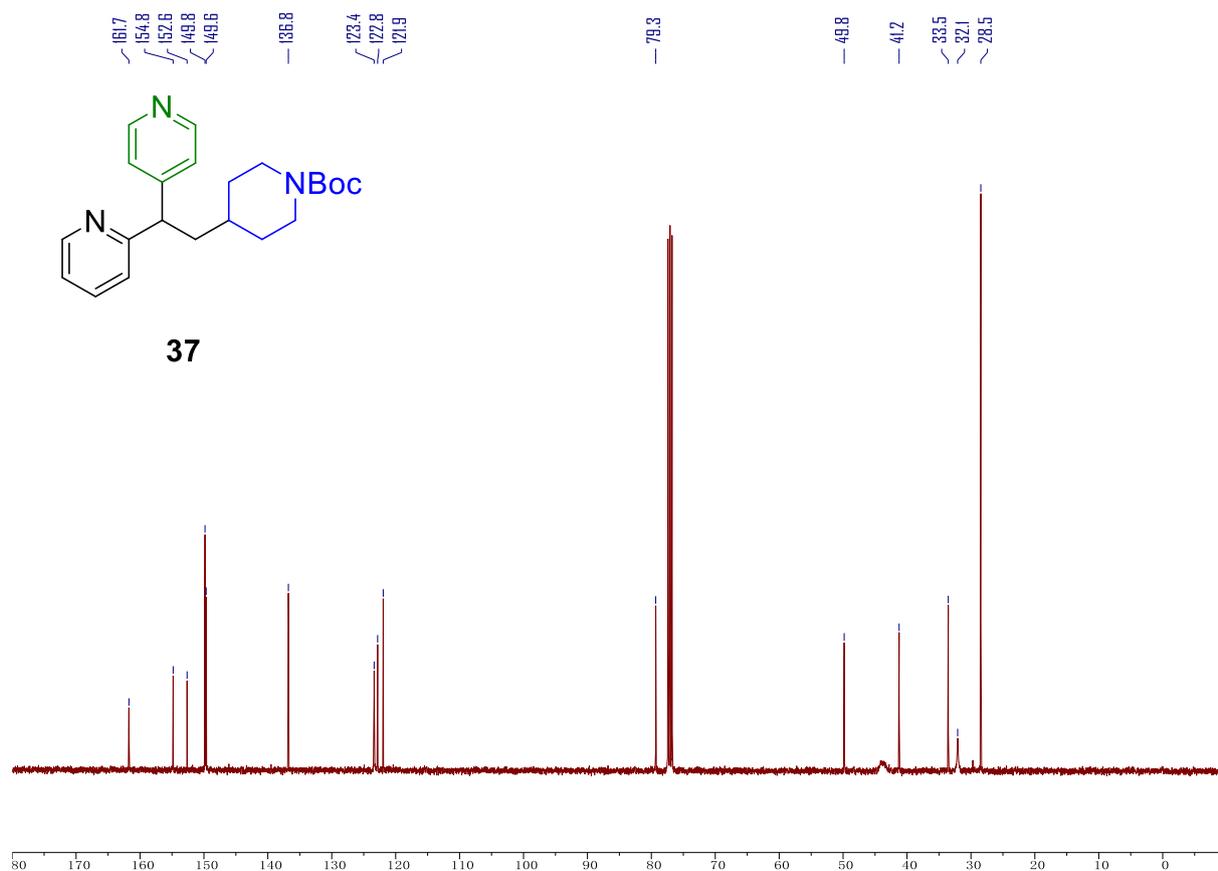
¹³C NMR spectra of compound **36** (101 MHz, Chloroform-*d*)



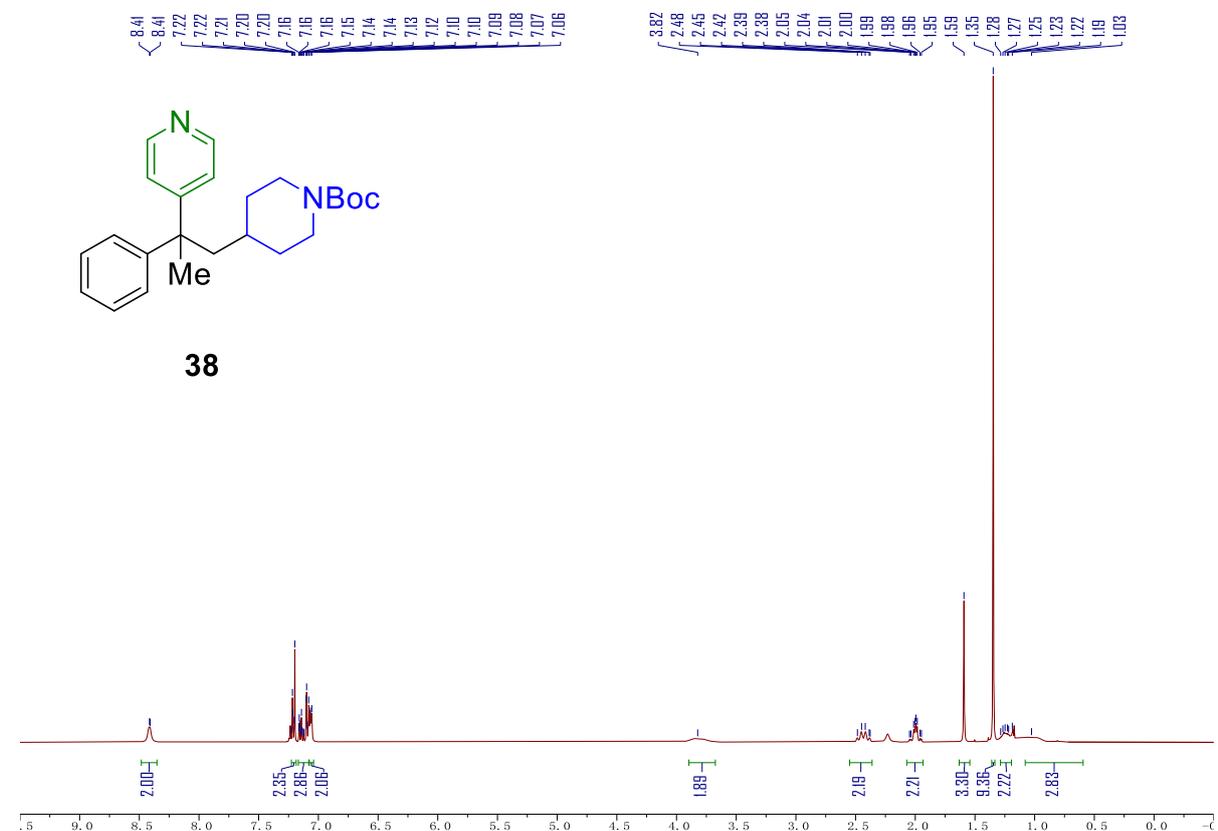
¹H NMR spectra of compound **37** (400 MHz, Chloroform-*d*)



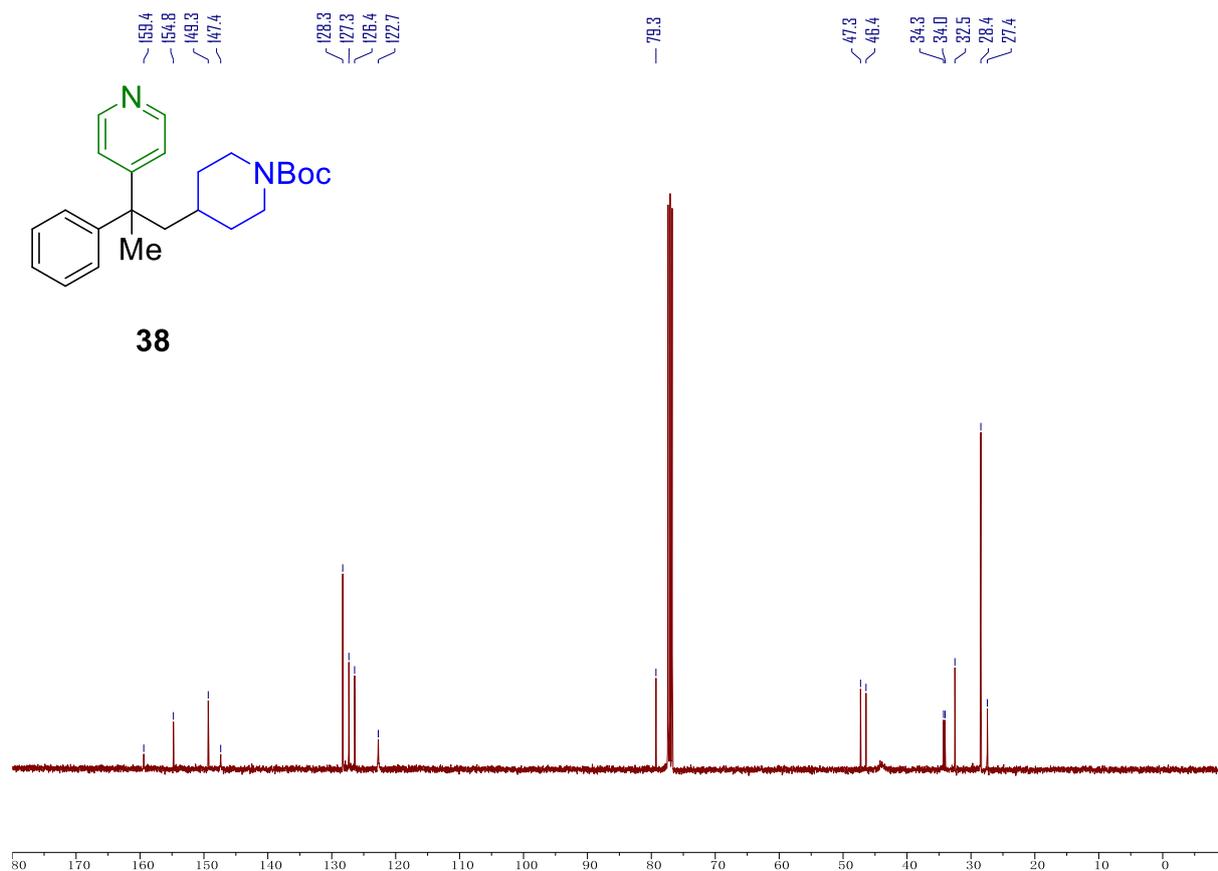
¹³C NMR spectra of compound **37** (101 MHz, Chloroform-*d*)



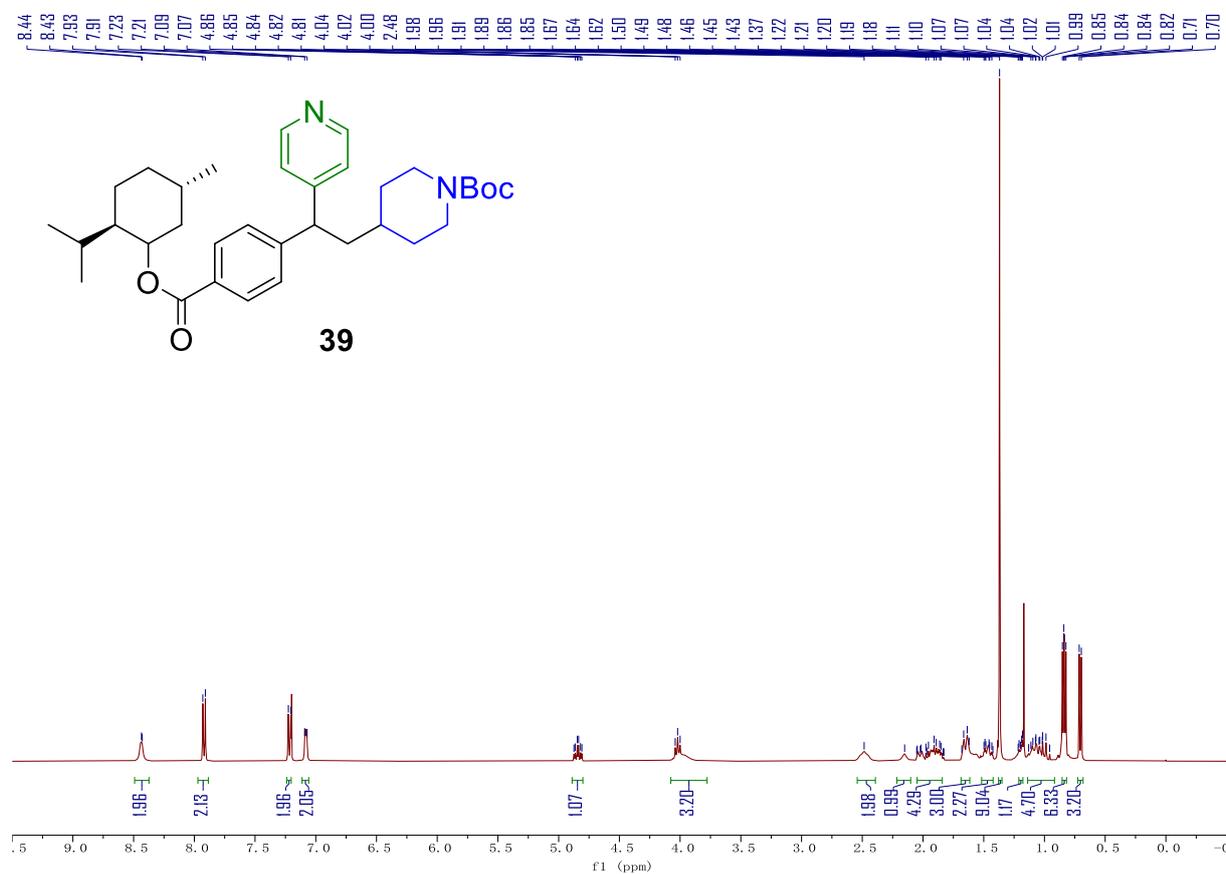
¹H NMR spectra of compound **38** (400 MHz, Chloroform-*d*)



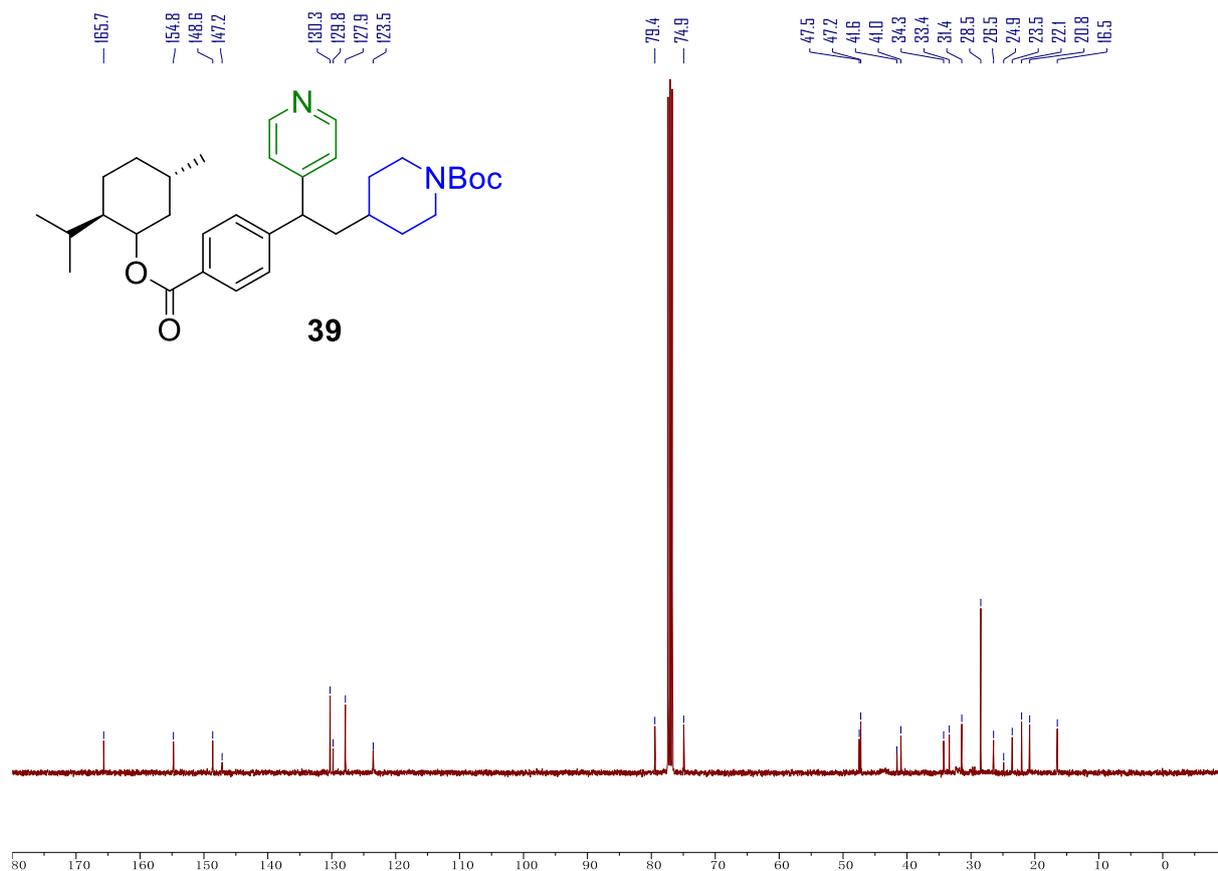
¹³C NMR spectra of compound **38** (101 MHz, Chloroform-*d*)



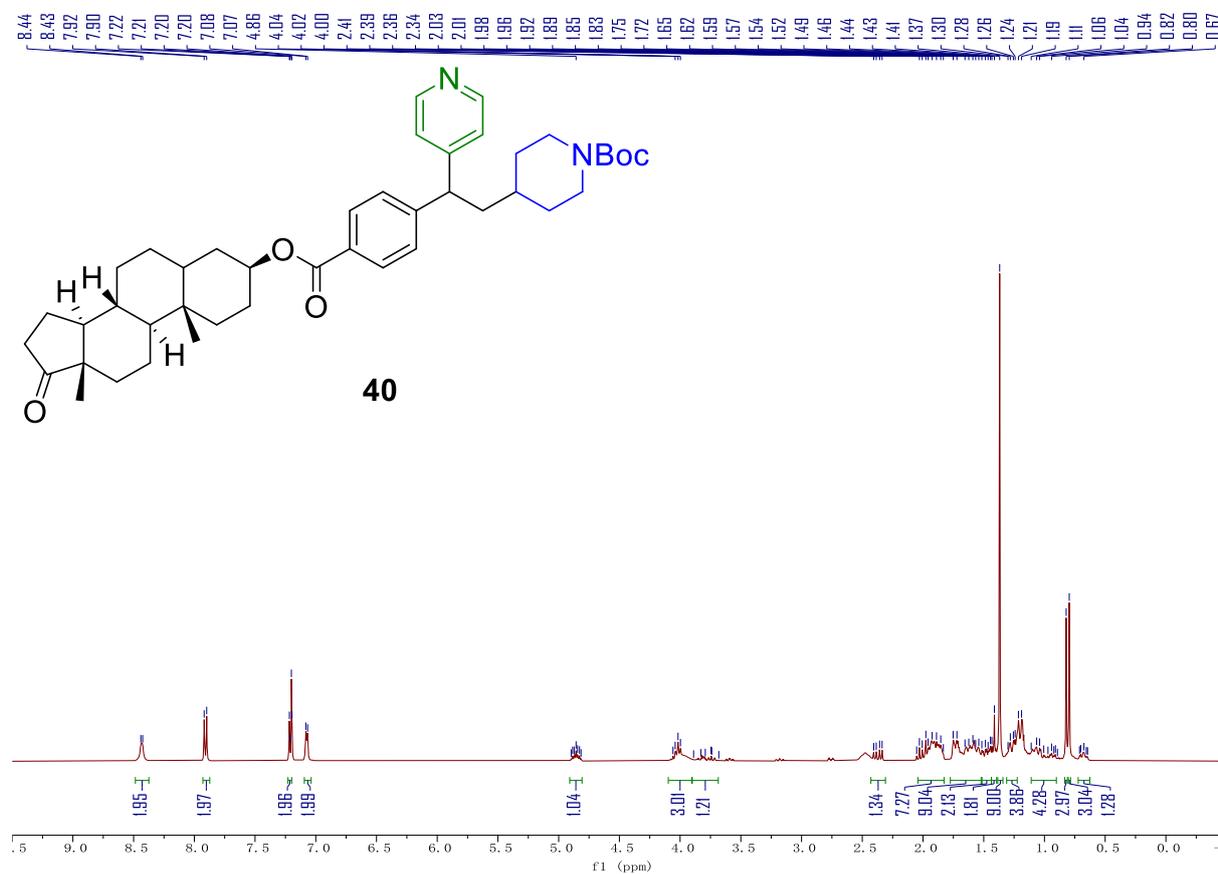
¹H NMR spectra of compound **39** (400 MHz, Chloroform-*d*)



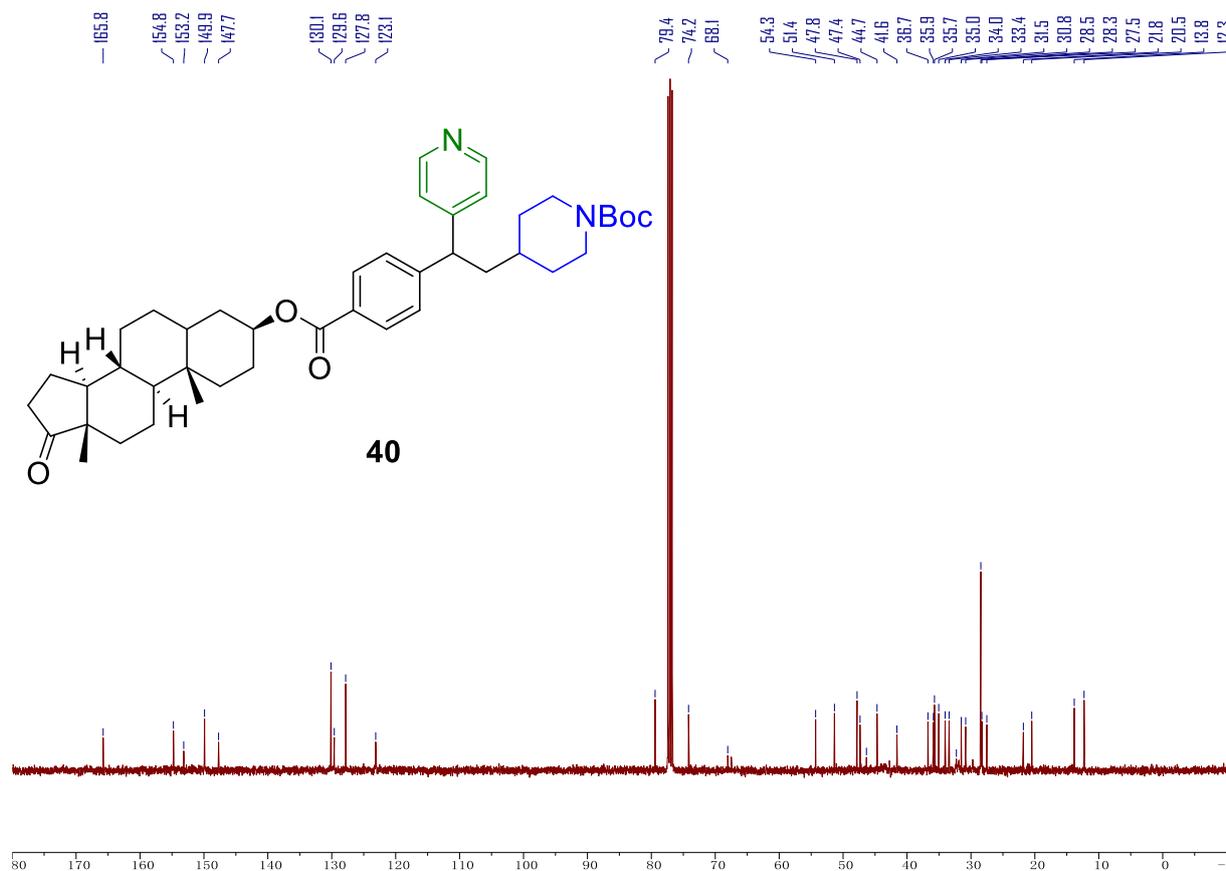
¹³C NMR spectra of compound **39** (101 MHz, Chloroform-*d*)



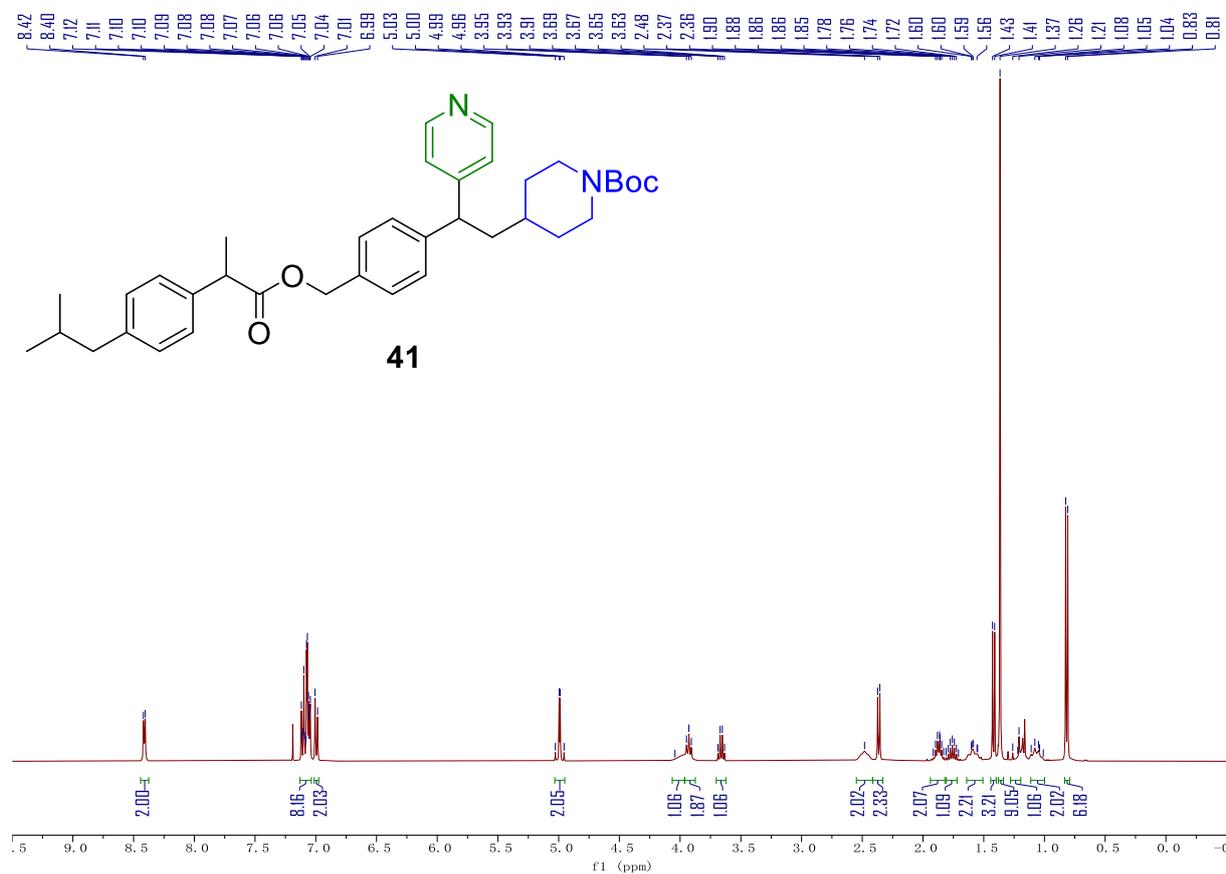
¹H NMR spectra of compound **40** (400 MHz, Chloroform-*d*)



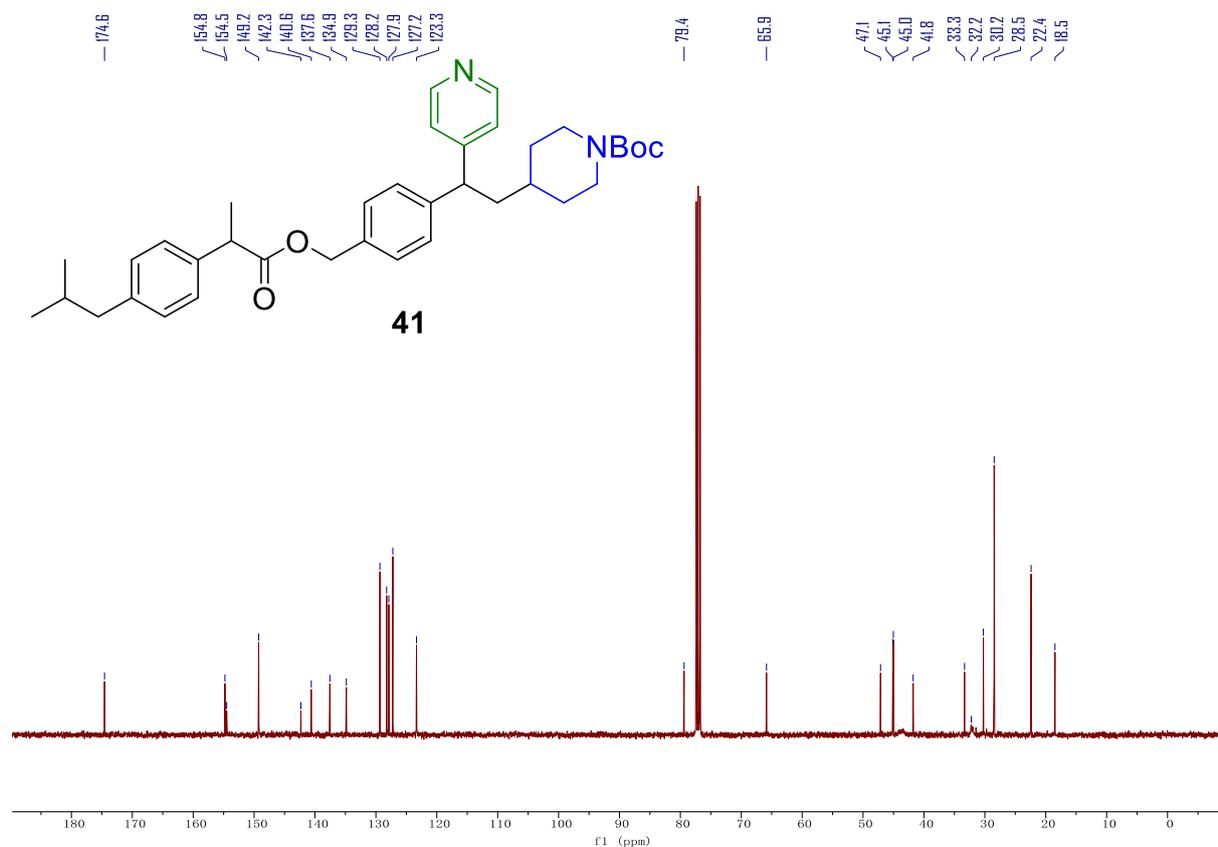
¹³C NMR spectra of compound **40** (101 MHz, Chloroform-*d*)



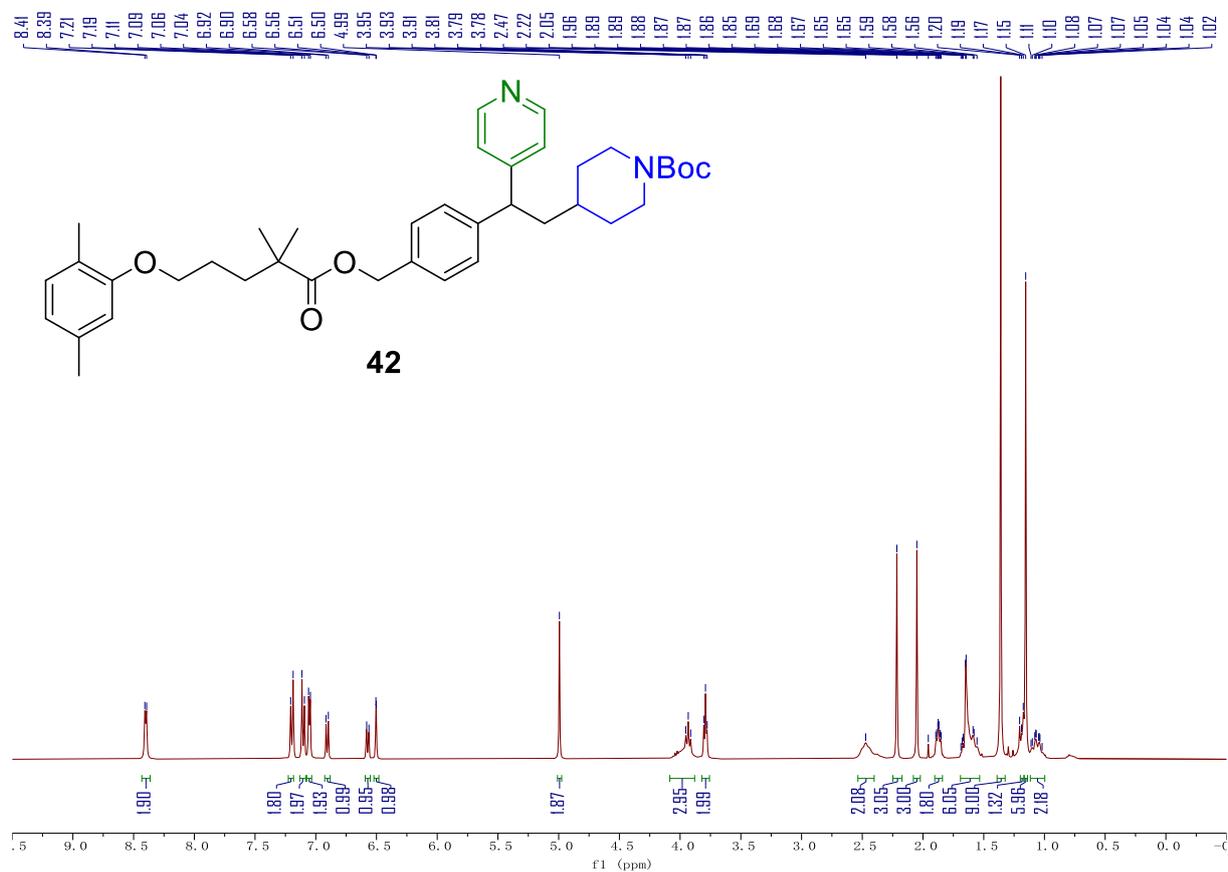
¹H NMR spectra of compound **41** (400 MHz, Chloroform-*d*)



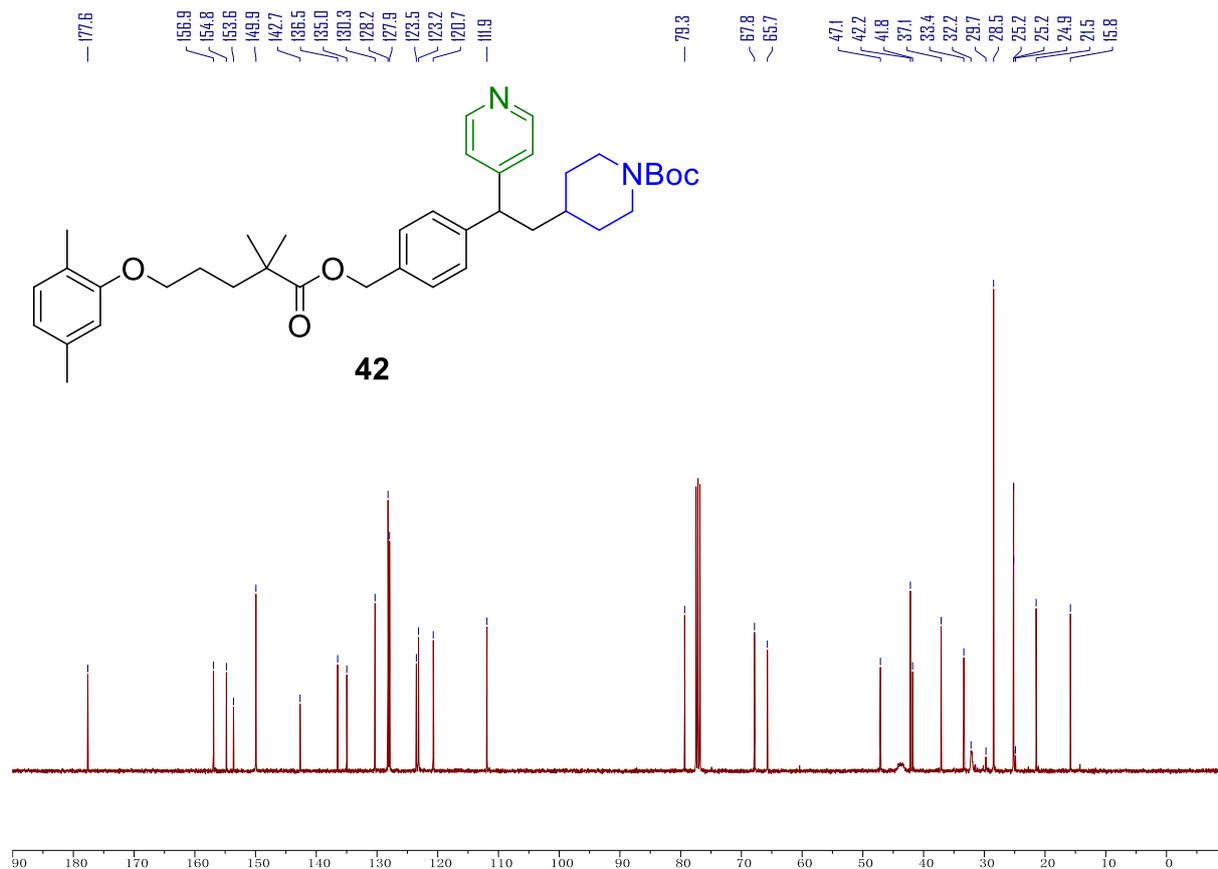
¹³C NMR spectra of compound **41** (101 MHz, Chloroform-*d*)



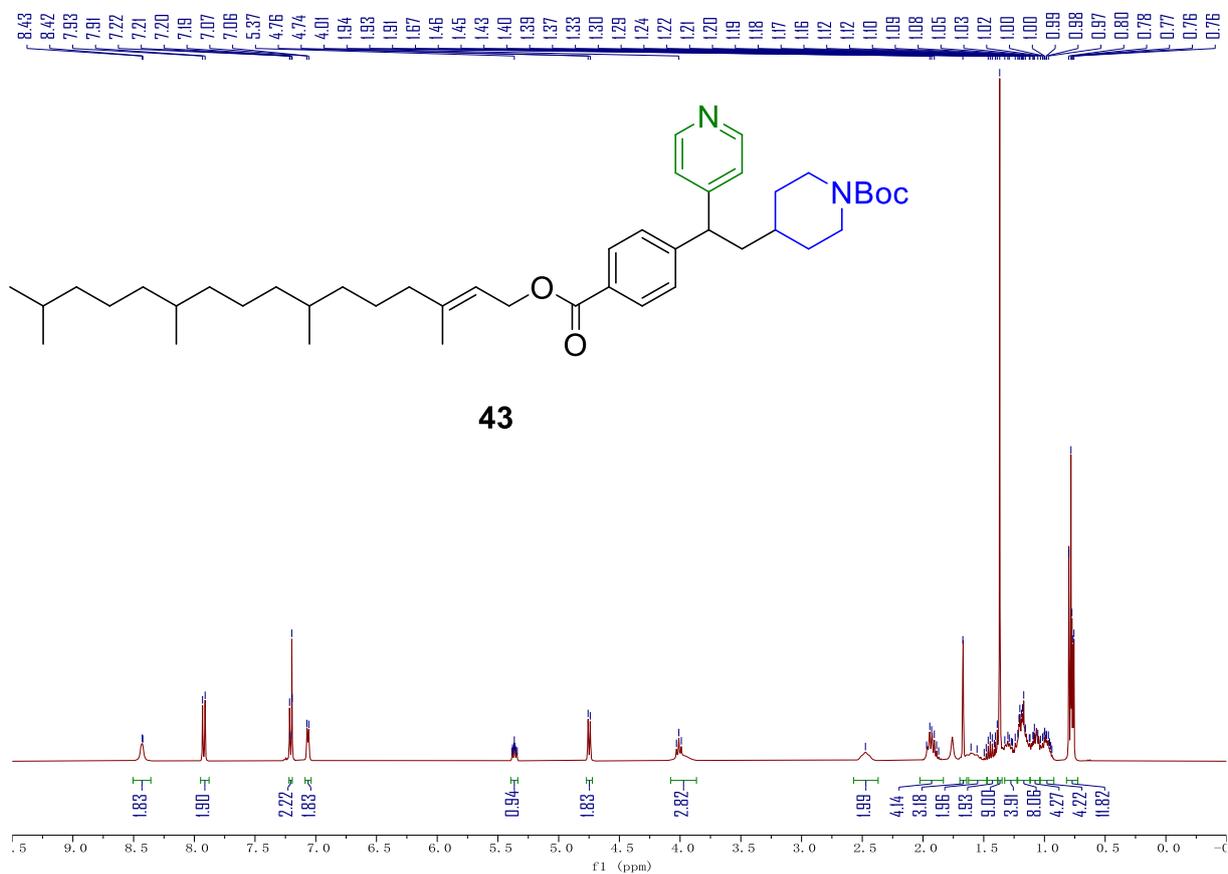
¹H NMR spectra of compound **42** (400 MHz, Chloroform-*d*)



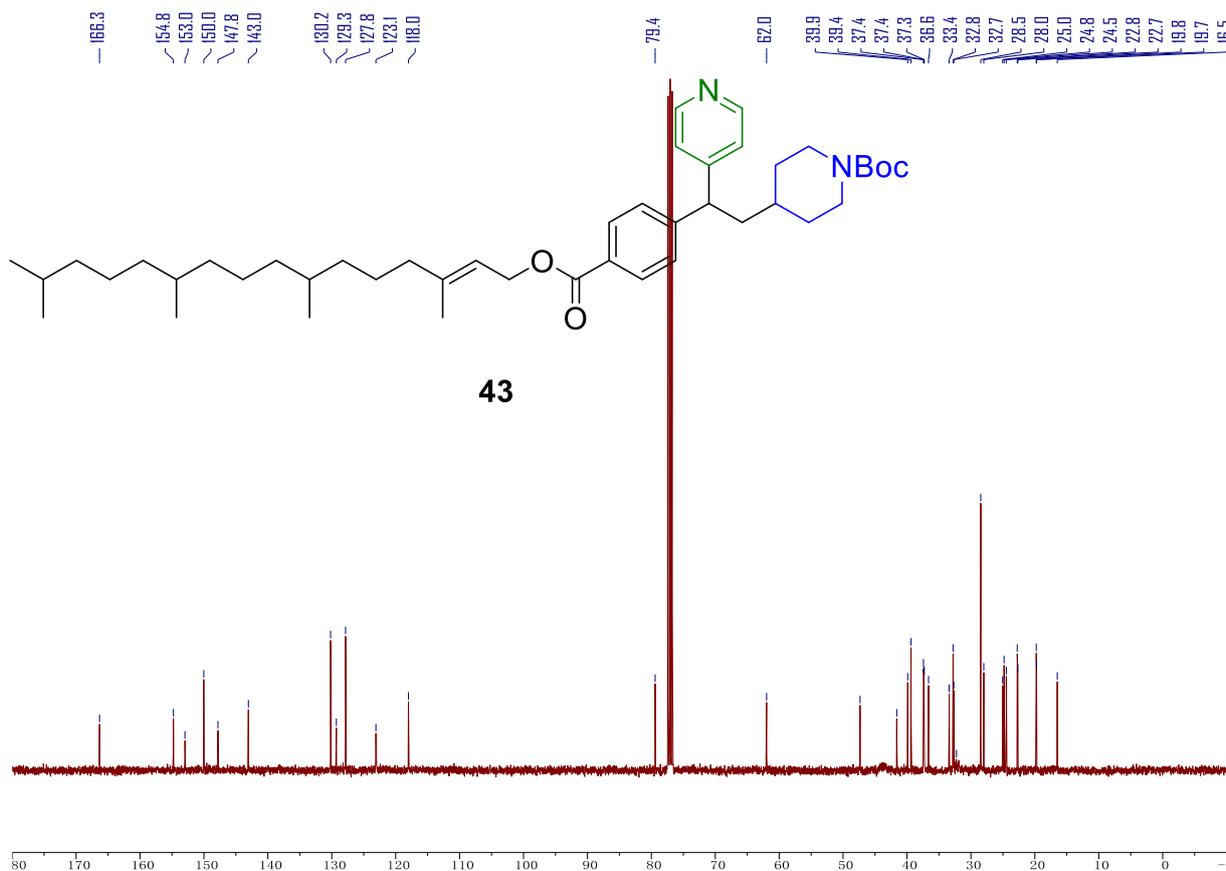
¹³C NMR spectra of compound **42** (101 MHz, Chloroform-*d*)



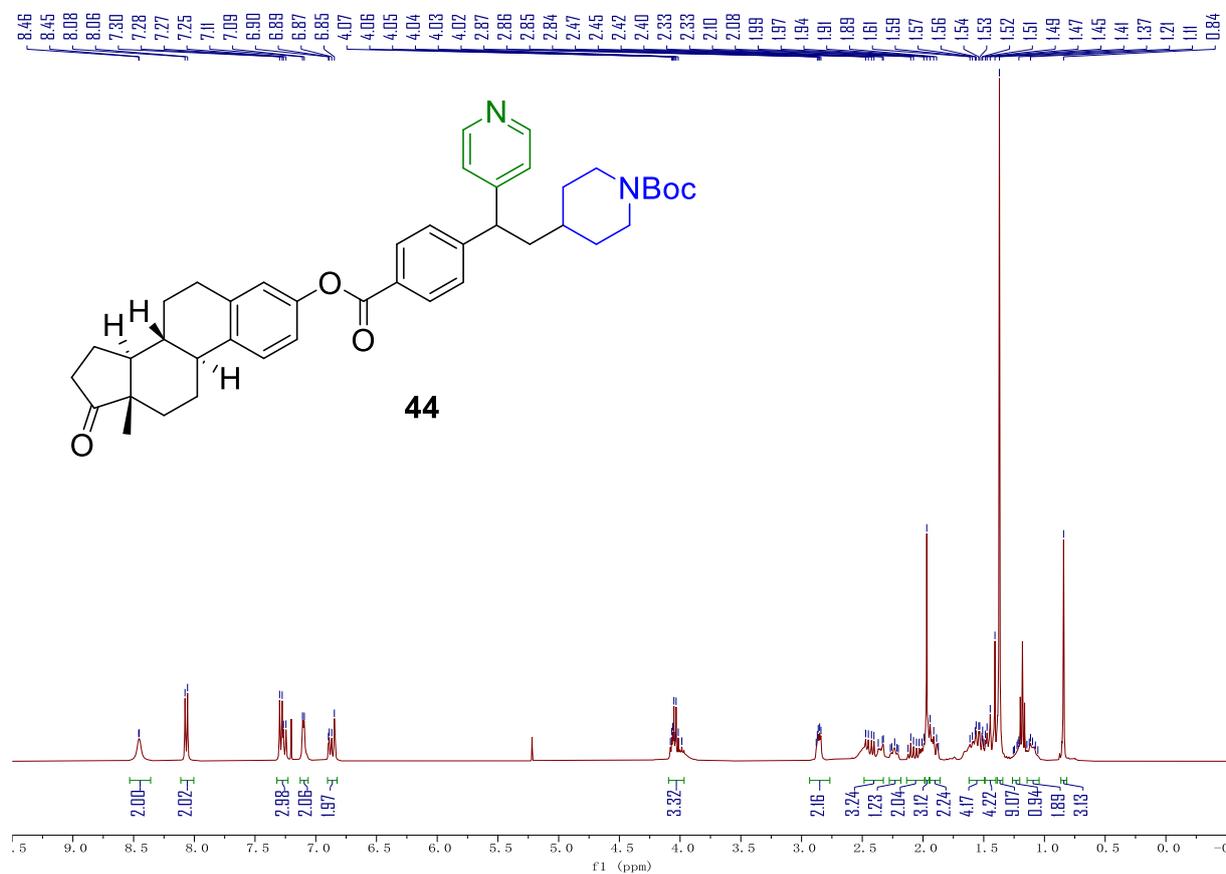
¹H NMR spectra of compound **43** (400 MHz, Chloroform-*d*)



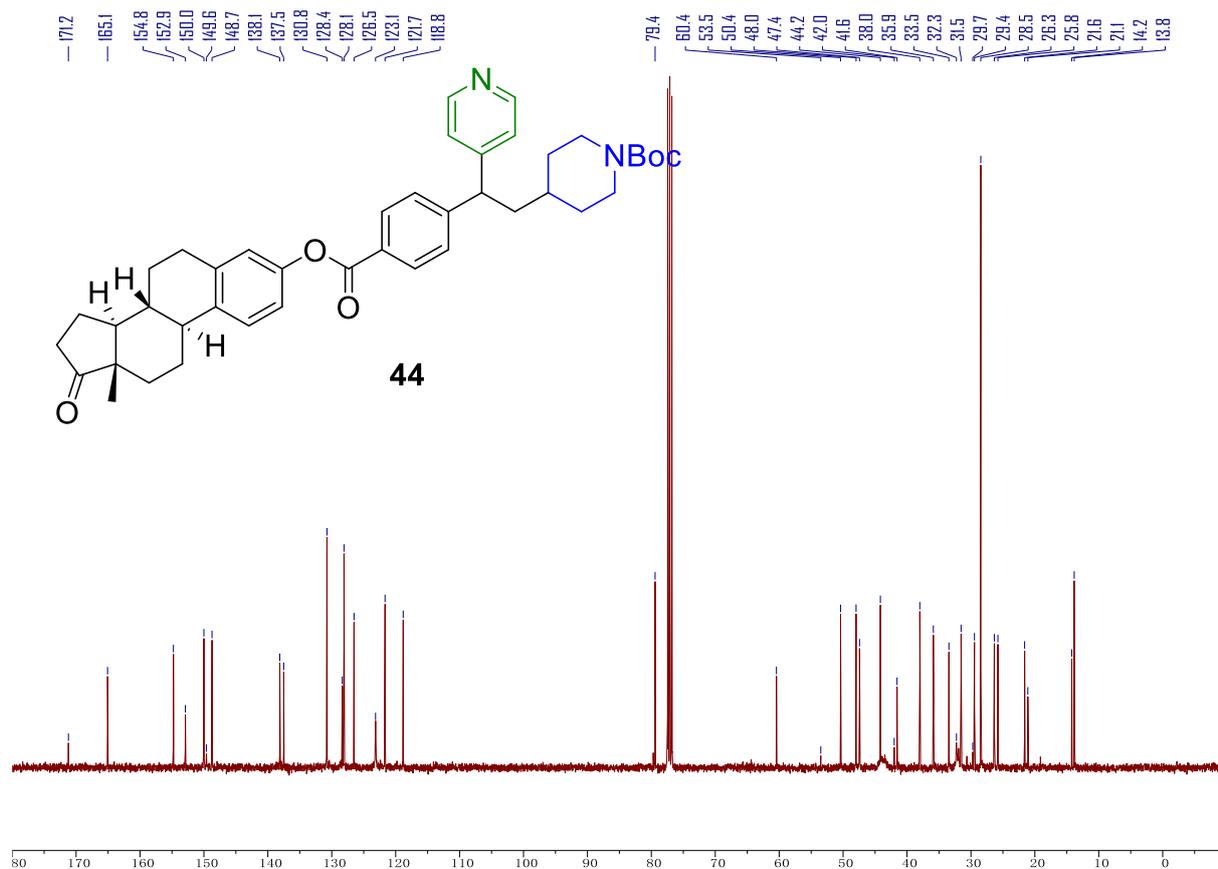
¹³C NMR spectra of compound **43** (101 MHz, Chloroform-*d*)



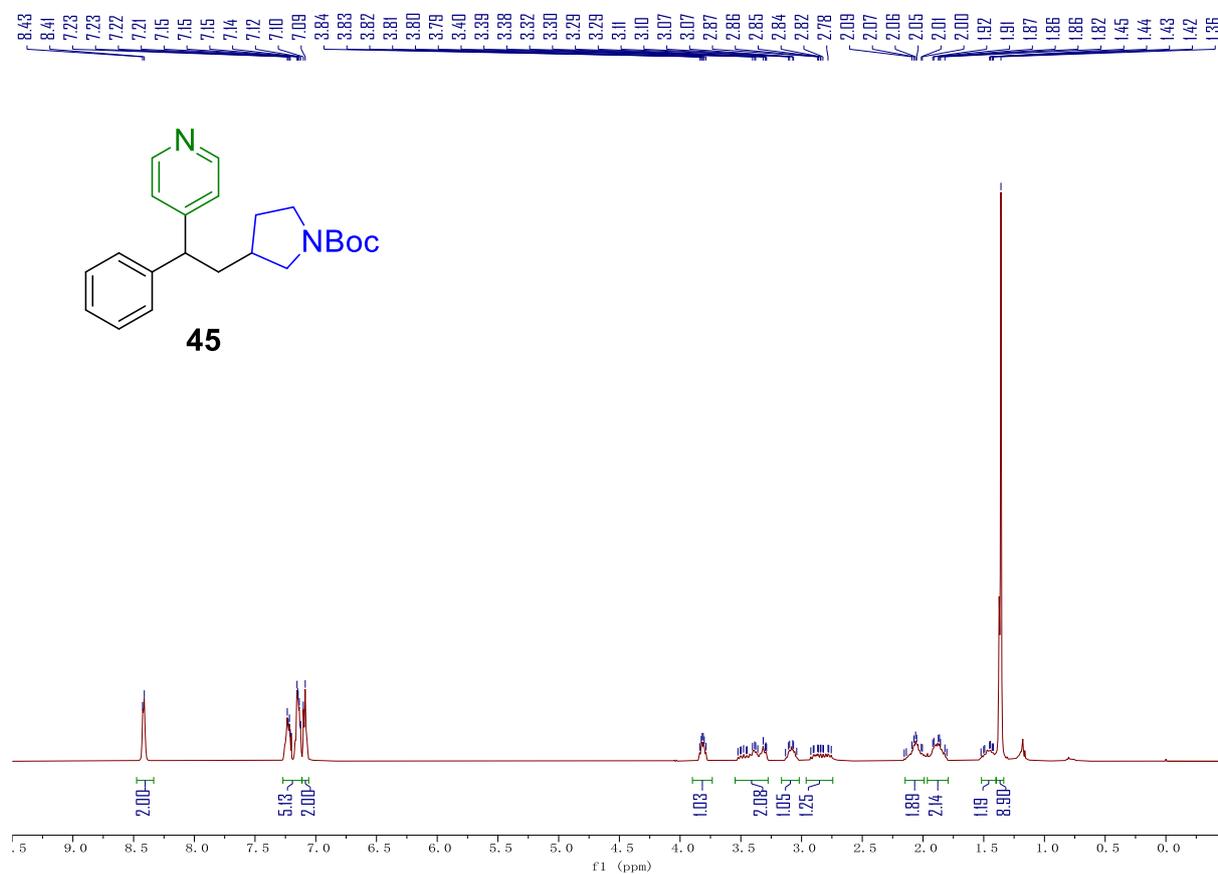
¹H NMR spectra of compound **44** (400 MHz, Chloroform-*d*)



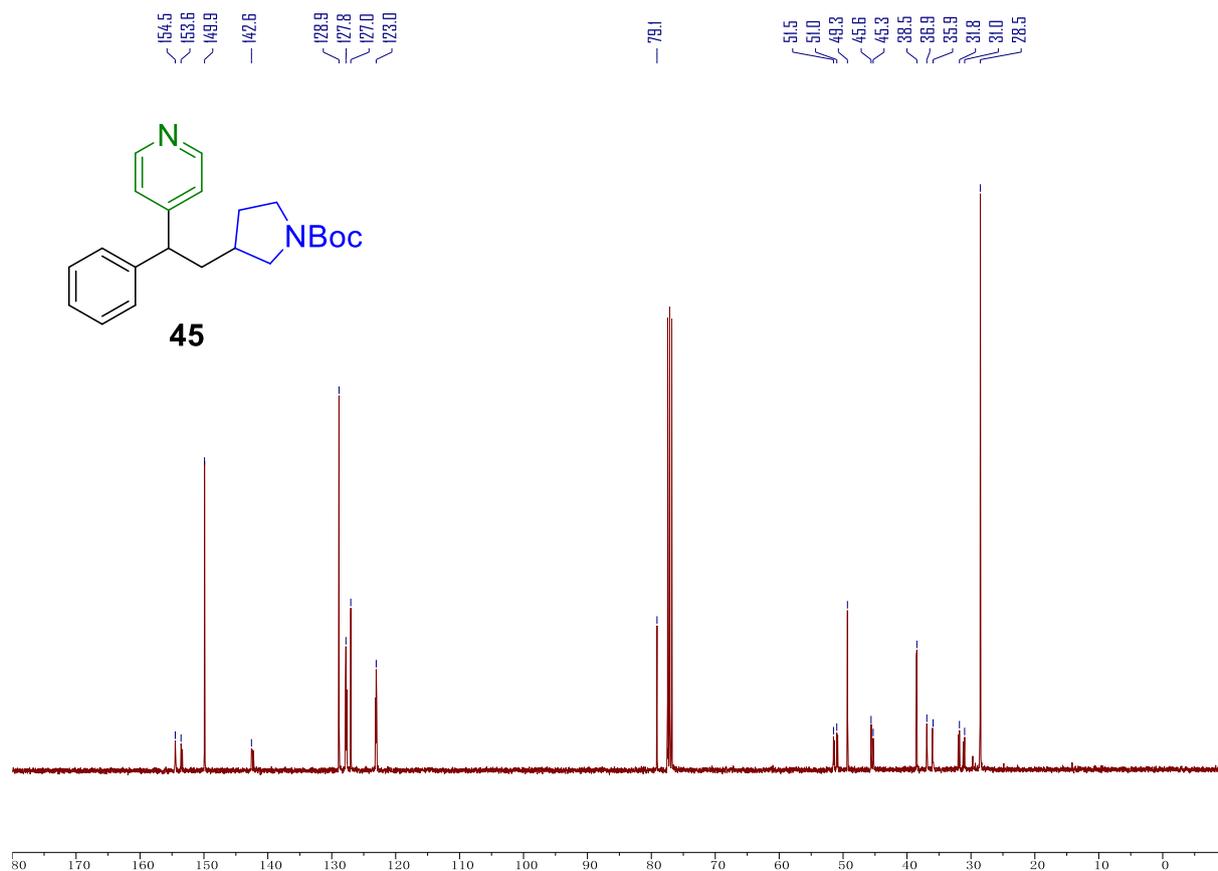
¹³C NMR spectra of compound **44** (101 MHz, Chloroform-*d*)



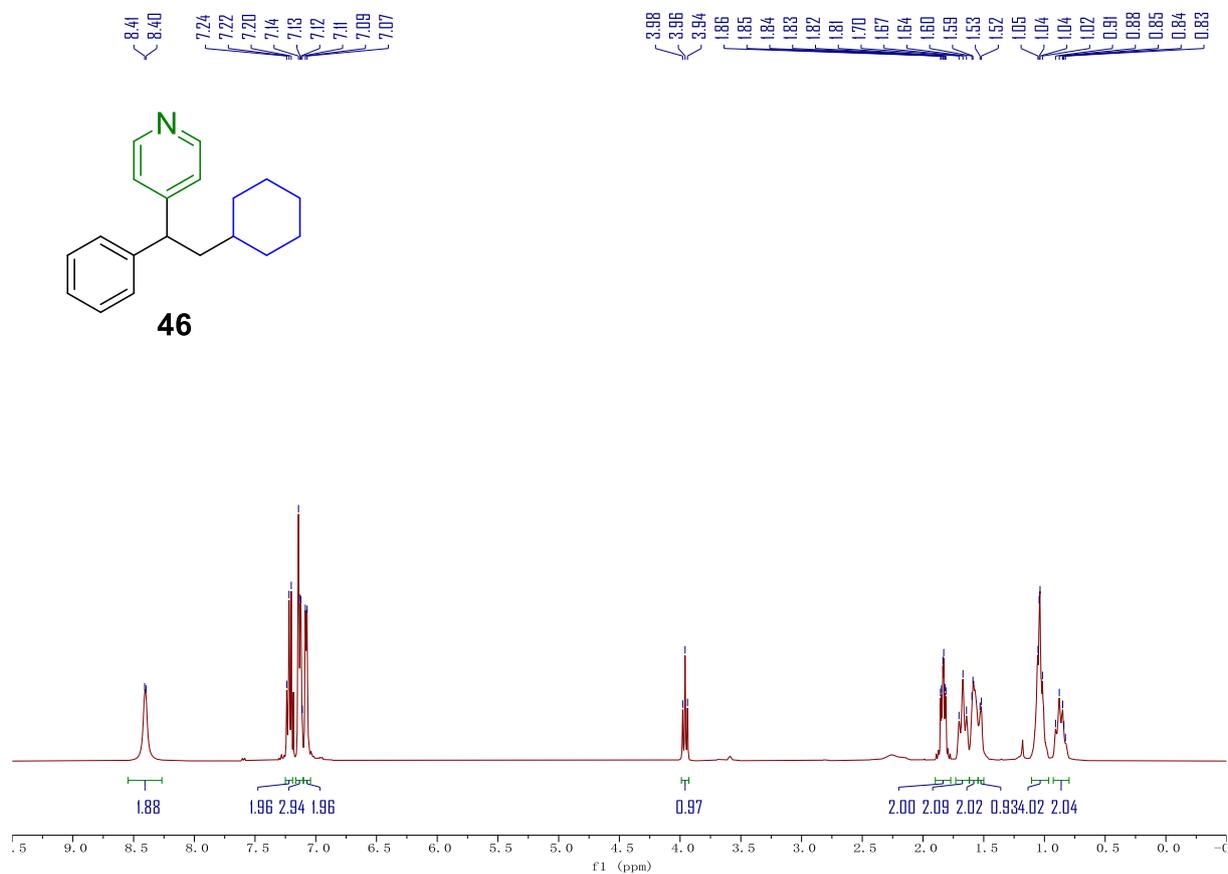
¹H NMR spectra of compound **45** (400 MHz, Chloroform-*d*)



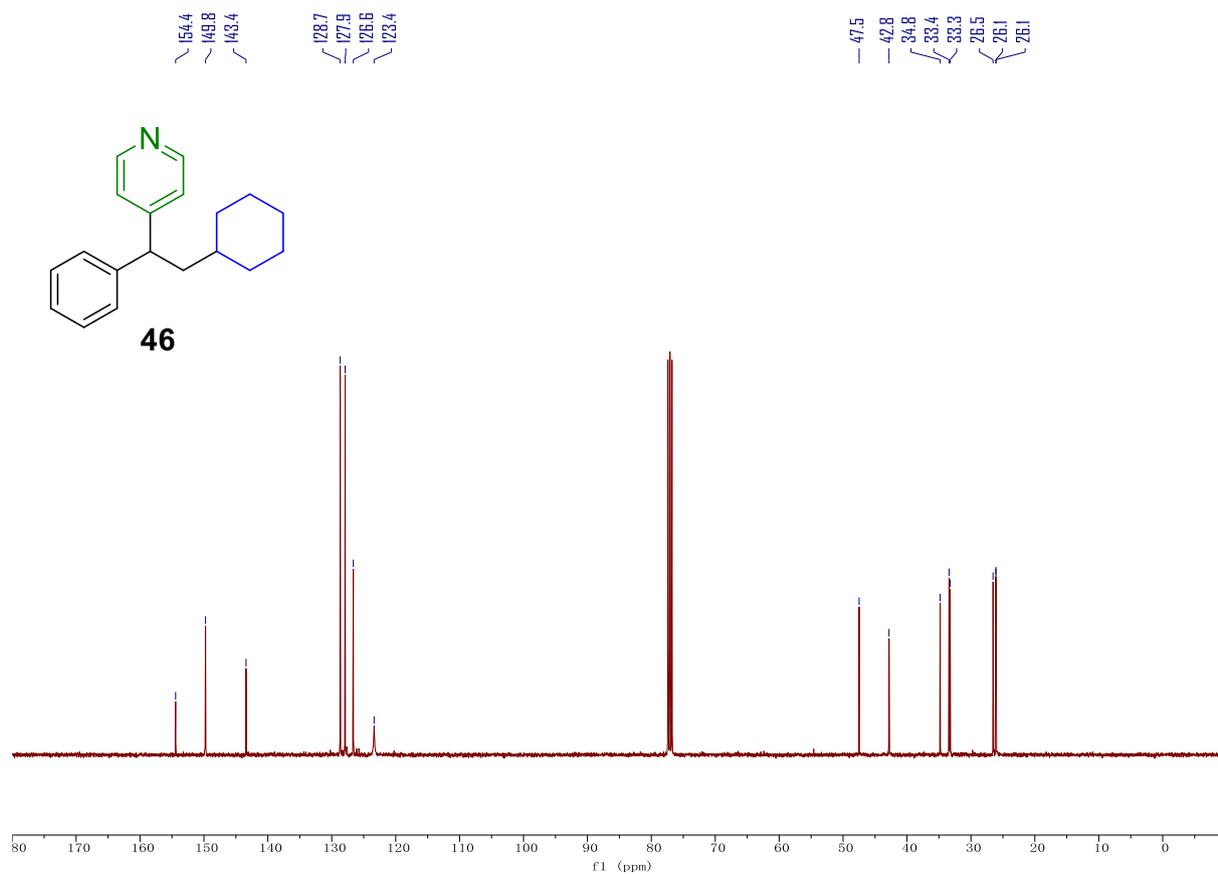
¹³C NMR spectra of compound **45** (101 MHz, Chloroform-*d*)



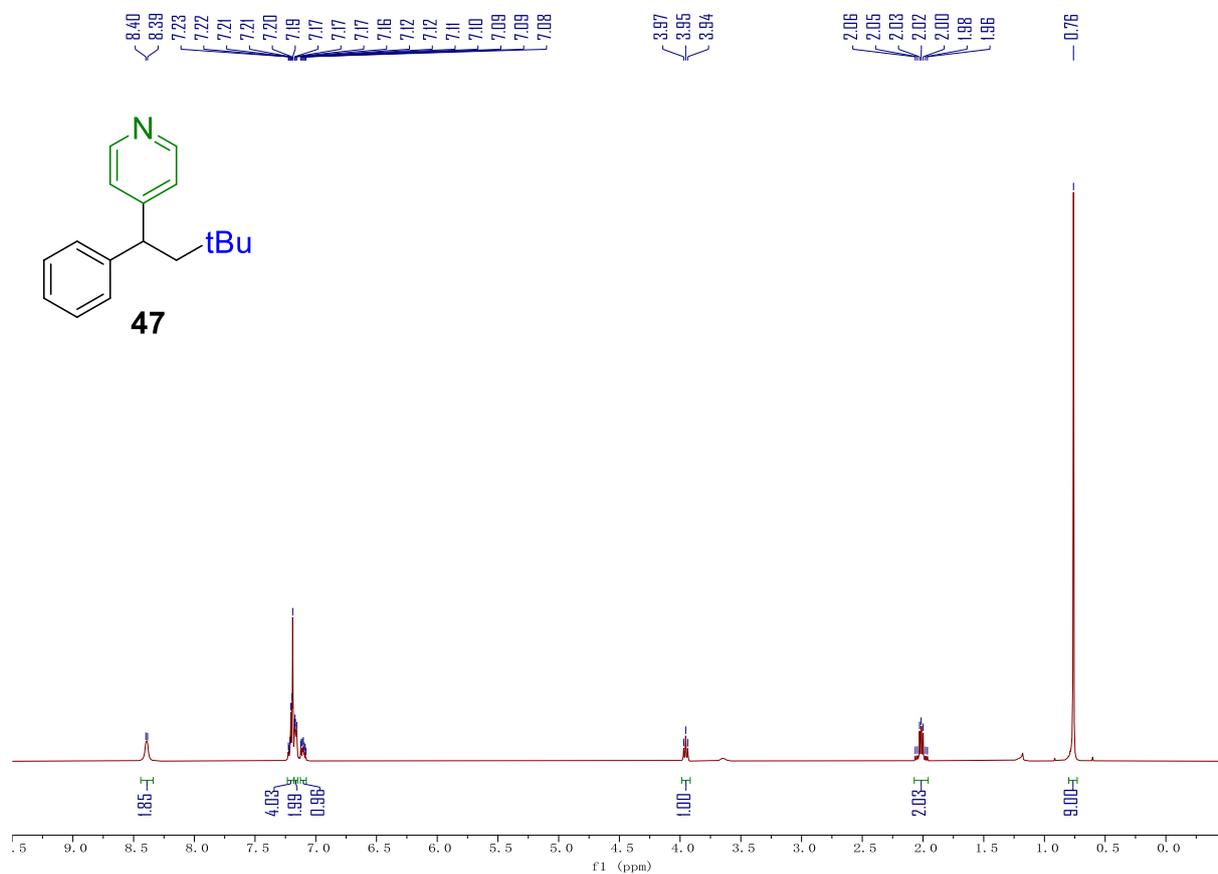
¹H NMR spectra of compound **46** (400 MHz, Chloroform-*d*)



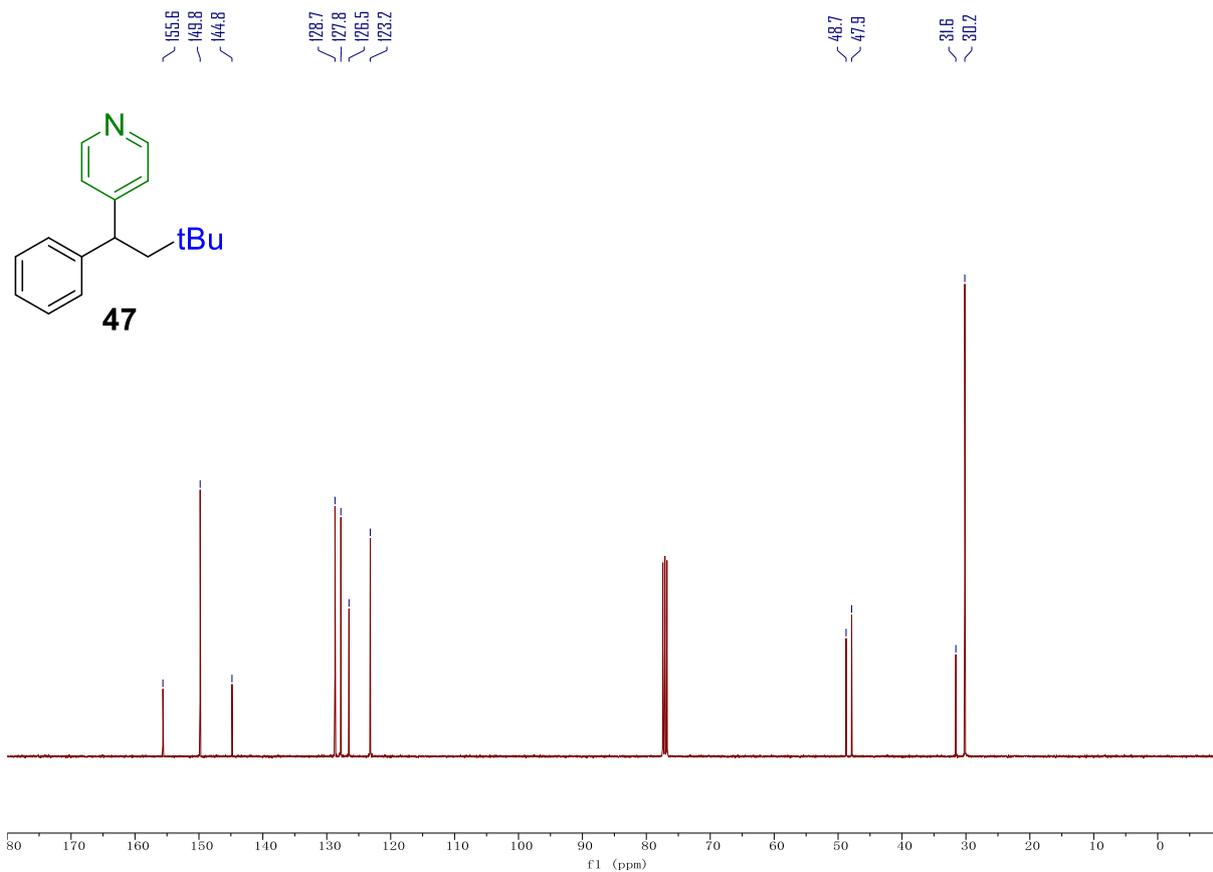
¹³C NMR spectra of compound **46** (101 MHz, Chloroform-*d*)



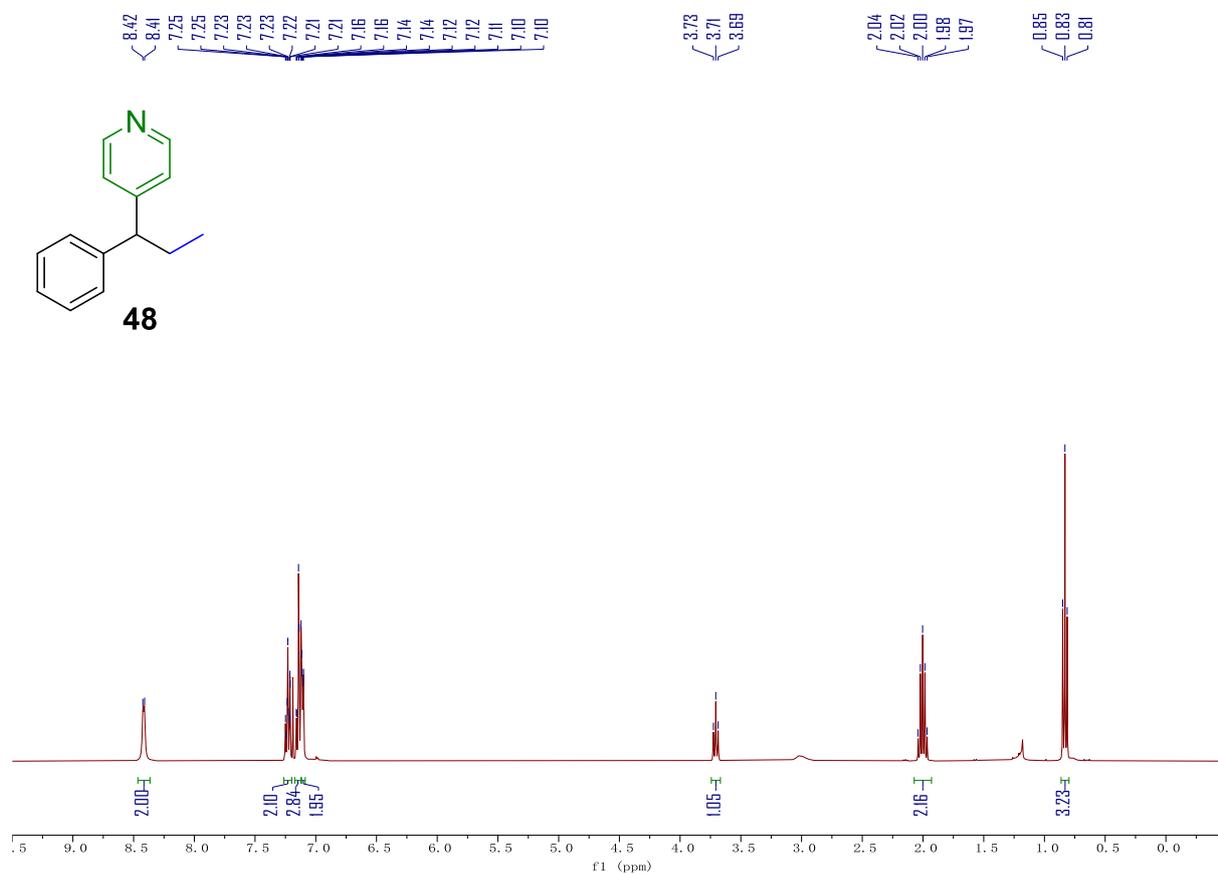
¹H NMR spectra of compound **47** (400 MHz, Chloroform-*d*)



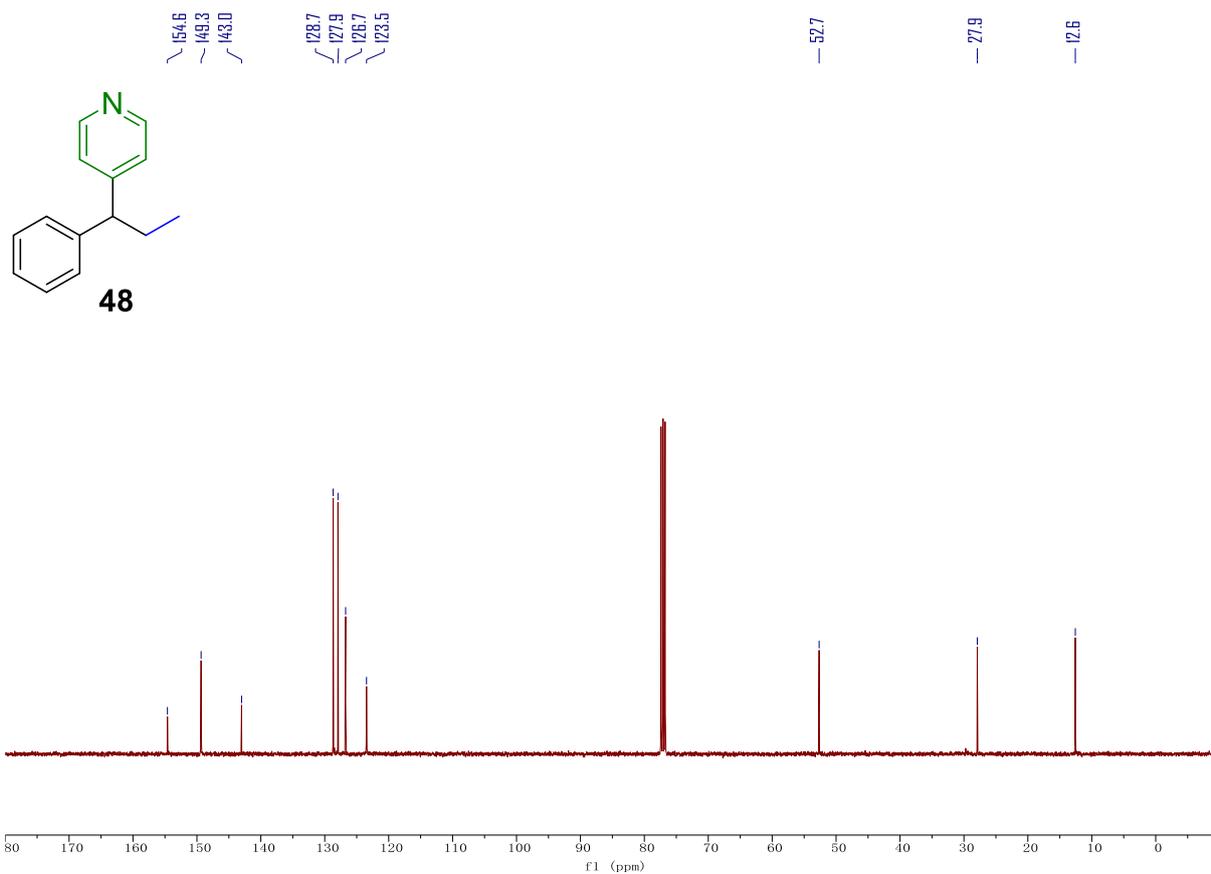
¹³C NMR spectra of compound **47** (101 MHz, Chloroform-*d*)



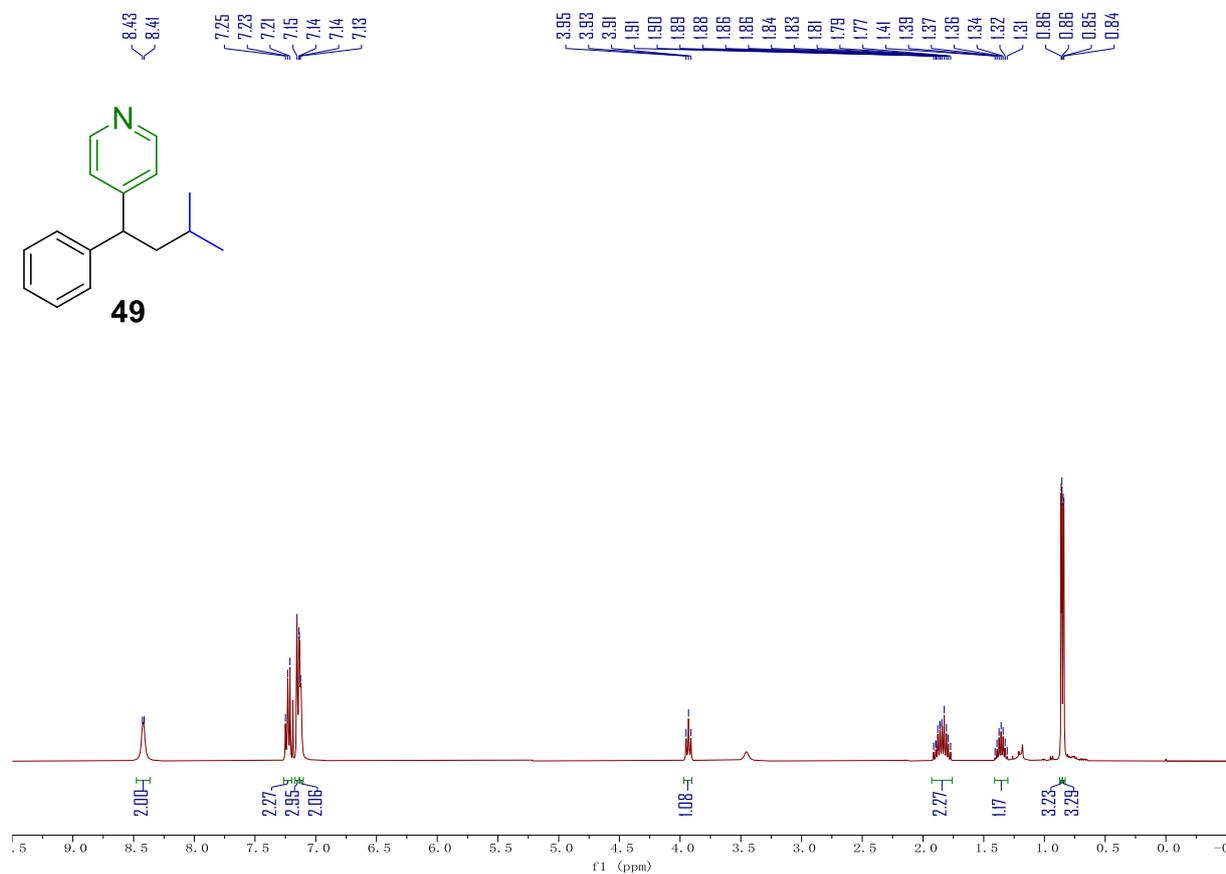
¹H NMR spectra of compound **48** (400 MHz, Chloroform-*d*)



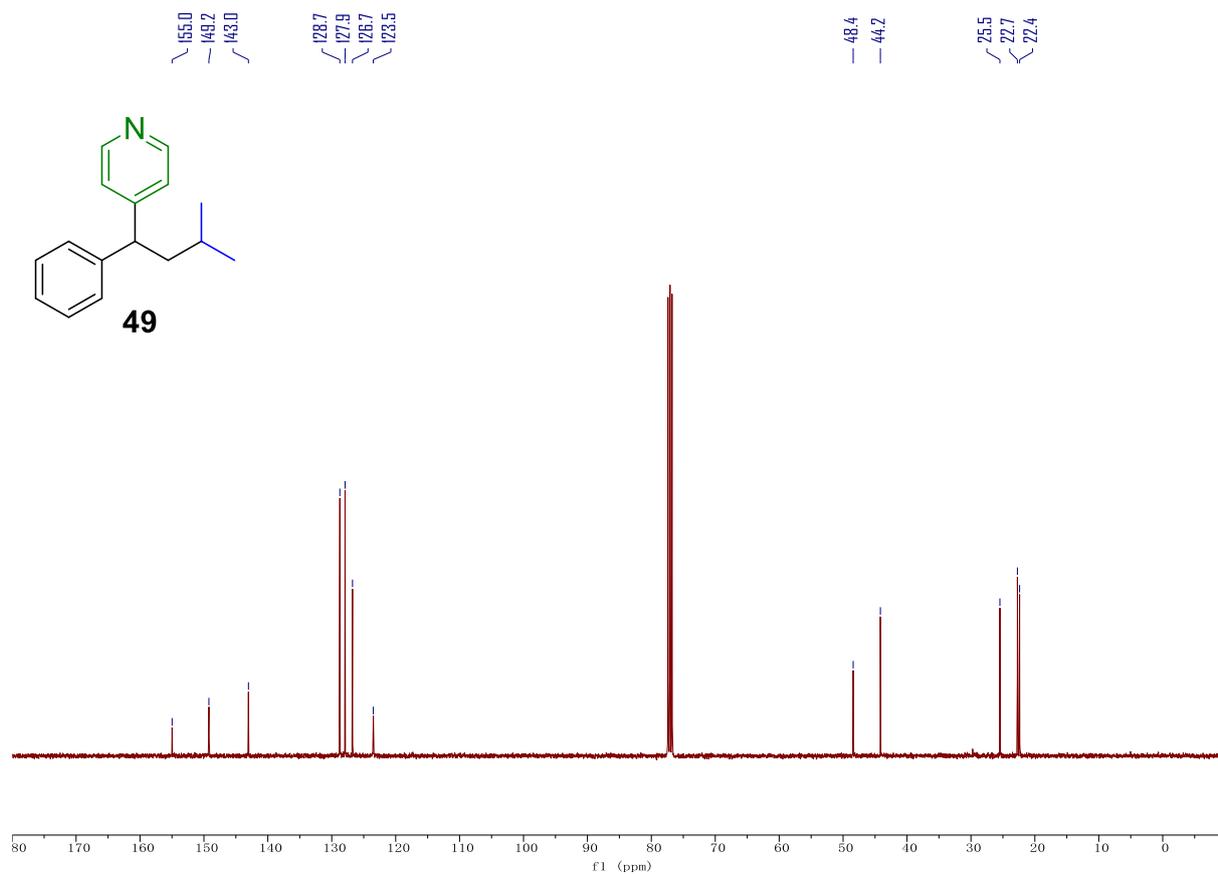
¹³C NMR spectra of compound **48** (101 MHz, Chloroform-*d*)



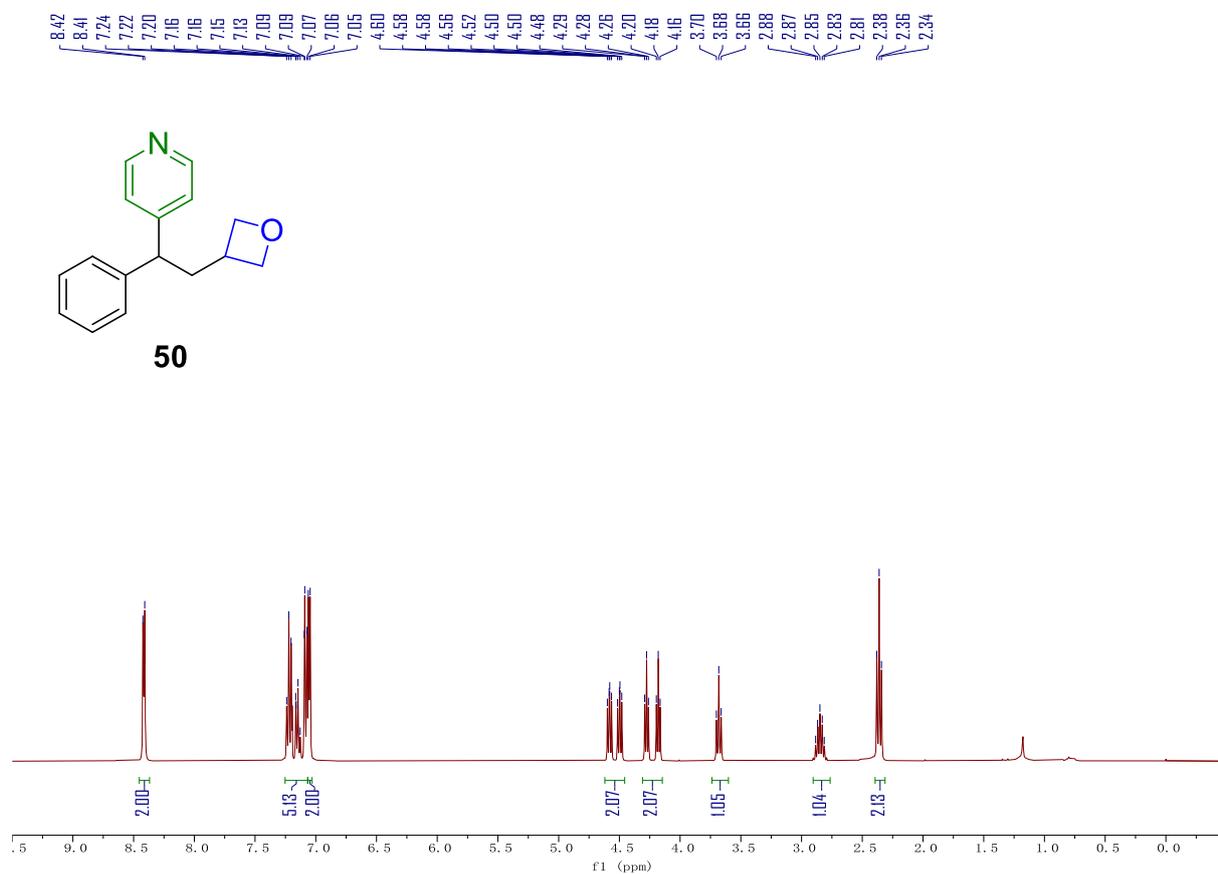
¹H NMR spectra of compound **49** (400 MHz, Chloroform-*d*)



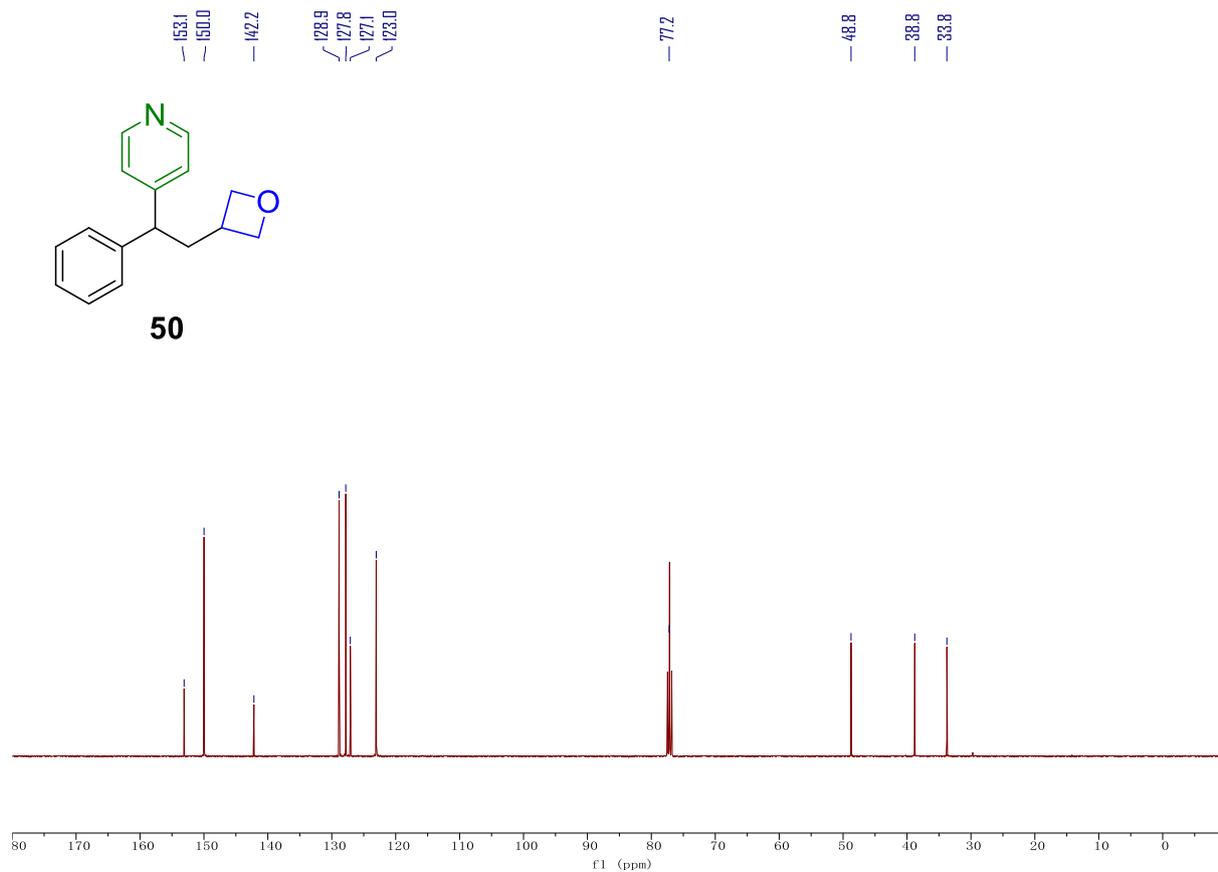
¹³C NMR spectra of compound **49** (101 MHz, Chloroform-*d*)



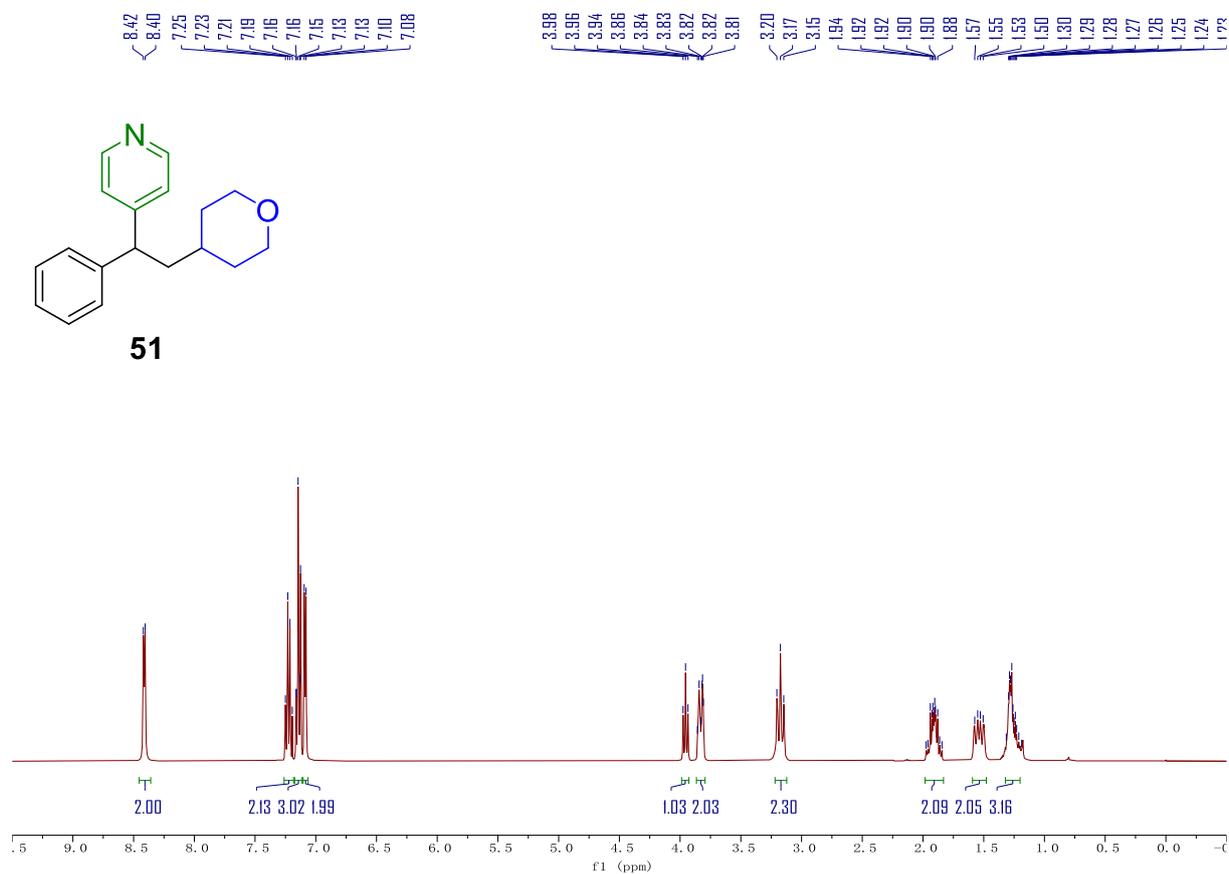
¹H NMR spectra of compound **50** (400 MHz, Chloroform-*d*)



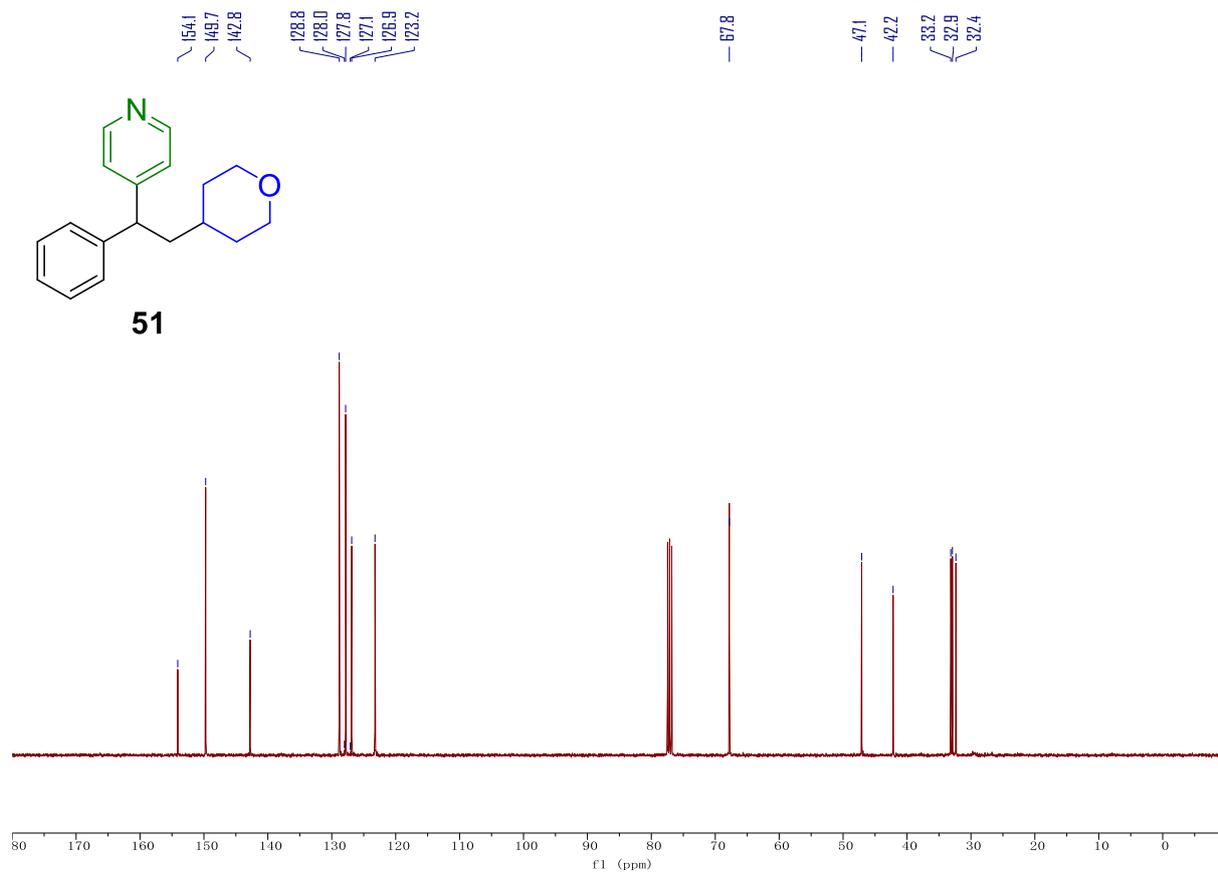
¹³C NMR spectra of compound **50** (101 MHz, Chloroform-*d*)



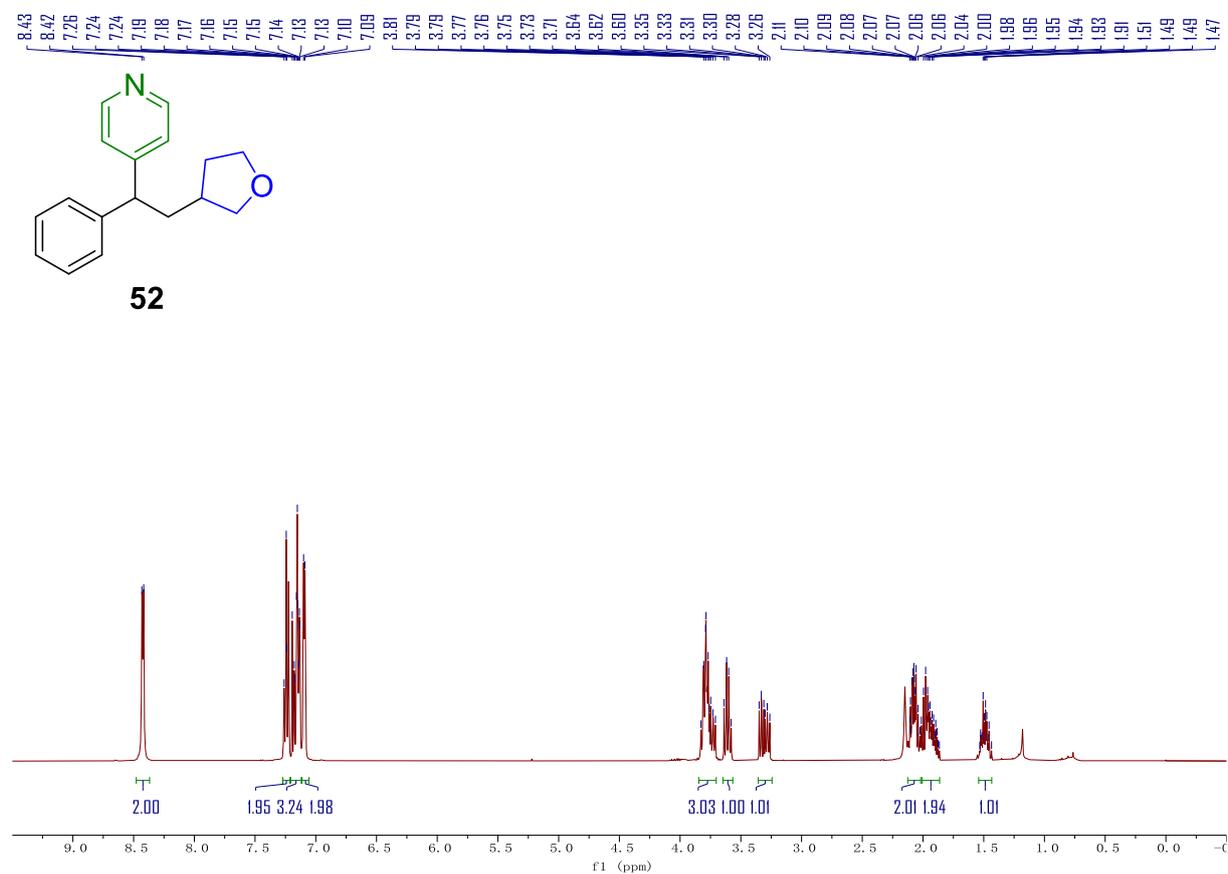
¹H NMR spectra of compound **51** (400 MHz, Chloroform-*d*)



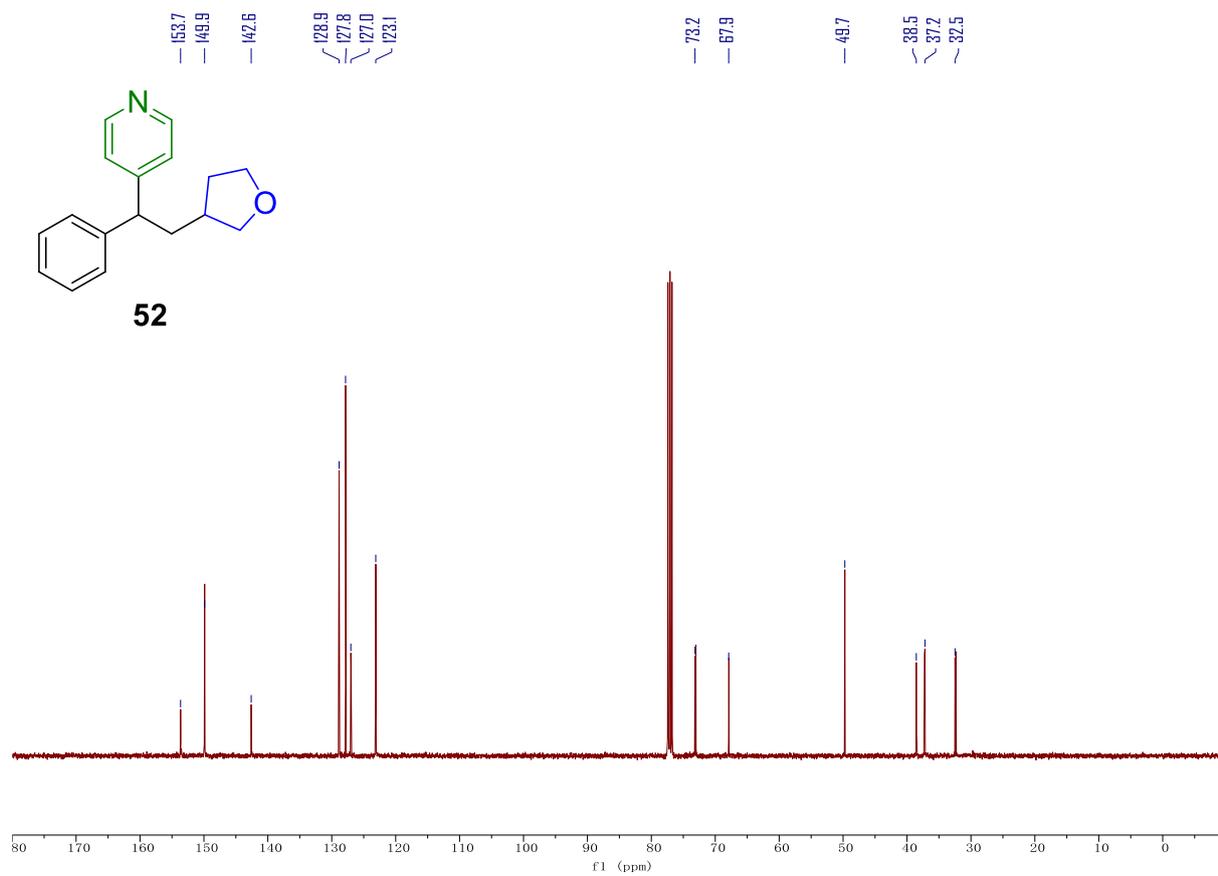
¹³C NMR spectra of compound **51** (101 MHz, Chloroform-*d*)



¹H NMR spectra of compound **52** (400 MHz, Chloroform-*d*)



¹³C NMR spectra of compound **52** (101 MHz, Chloroform-*d*)



12. Reference

- [1] J. Xu and B Liu, Metal Free Functionalization of Saturated Heterocycles with Vinylarenes and Pyridine Enabled by Photocatalytic Hydrogen Atom Transfer, *Chem. Eur. J.*, 2024, **30**, e202400612.
- [2] D. D. Tang, Y.-Z. Wang, C. Liu, Y. Xia and Y. Li, Photoredox-Catalyzed Amino-Radical-Transfer Mediated Three-Component Alkylarylation of Alkenes, *Org. Lett.*, 2024, **26**, 6477–6481.