Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Deoxygenation of oximes for the synthesis of pyrrolines via hydroimination cyclization

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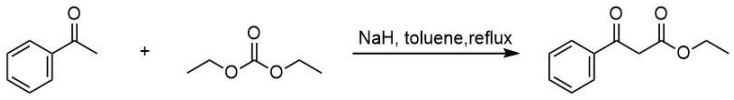
1. General information

CH_2Cl_2 was freshly distilled over CaH prior to use. All other reagents were used as received from commercial sources. PPh_3 and $(4\text{-}MeOC_6H_4)_3P$ were purchased from Energy Chemical. $(4\text{-}MeC_6H_4)_3P$ and Ph_2POEt were purchased from Adamas-beta. $(4\text{-}FC_6H_4)_3P$ was purchased from Aladdin. Reactions were monitored through thin layer chromatography (TLC) on 0.25-mm silica gel plates and visualized under UV light (254 nm). Flash column chromatography (FCC) was performed using silica gel. NMR spectra were recorded using Bruker Avance II 400 and Vaian DL G400 instruments, calibrated to $CD(H)Cl_3$ as the internal reference (7.26 and 77.0 ppm for ^1H and ^{13}C NMR spectra, respectively). ^1H NMR spectral data are reported in terms of chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectral data are reported in terms of chemical shift (δ, ppm). The following abbreviations indicate the multiplicities: s, singlet. d, doublet. t, triplet. q, quartet. m, multiplet. High-resolution mass spectra were obtained using Agilent 6224 TOF LC/MS Mass Spectrometer and Thermo Scientific Q Exactive Plus MS with electrospray ionization (ESI) probe operating in positive ion mode. The fluorescence spectra were measured with Edinburgh Analytical Instruments FLS 920. The photocatalysts 4-CzIPN,[1] $[Ru(bpy)_3]PF_6$,[2] and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$[3] were prepared according to previous reports. The oximes **1a**[4], **1q**[5], **1s**[4], **1t**[6] and **1v**[7] were prepared according to previous reports.

2. Substrate preparation

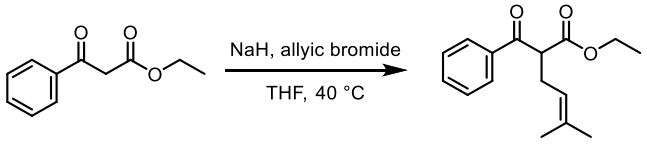
2.1 General Procedure 1 (GP1)



S1 **S2**

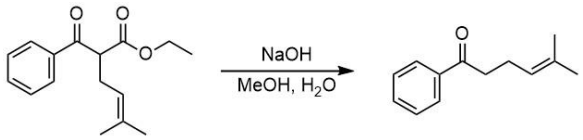
To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (70 mmol), diethyl carbonate (50 mmol), and toluene (25 mL). The mixture was heated to reflux. A solution of ketone **S1** (25 mmol) in toluene (15 mL) was added dropwise from the dropping funnel over 1-2 h. After the addition, the mixture was heated to reflux until the evolution of hydrogen ceased (15-20 min). When the reaction was cooled to room temperature, glacial acetic acid (8 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was

added until the solid was dissolved completely. The toluene layer was separated, and the aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic solution was washed with water (100 mL) and brine (100 mL), then dried over Na_2SO_4. After evaporation of the solvent, the mixture was distilled under reduced pressure or subjected chromatography to give the desired ß-keto esters **S2** in 32-95% yield.[8]



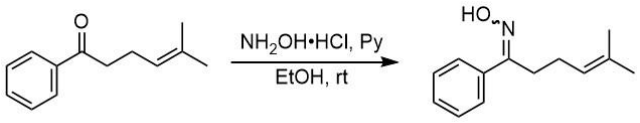
S2 **S3**

A solution of ethyl benzoylacetate **S2** (20 mmol) in THF (0.17M) was treated with NaH (20 mmol), stirred for 1h and treated with the allylic bromide (22 mmol). The mixture was warmed to 40 ºC and stirred overnight. The mixture was cooled to room temperature and MeOH was added. The crude product was purified by column chromatography on silica gel eluting with petroleum ether–Et_2O (95:5) to give the **S3** in 48-99% yield.[9]



S3 **S4**

A solution of the β-ketoester **S3** (20 mmol) in MeOH–H_2O (0.01M, 2:1) was treated with NaOH (80 mmol) and heated under reflux for 2 h. The mixture was cooled to room temperature and the volatiles were removed in vacuo. EtOAc was added and the organic layers were separated. The aqueous layer was then washed with EtOAc (50 mL × 3) and the combined organic fractions were dried (Na_2SO_4), filtered and evaporated. Purification by column chromatography on silica gel, eluting with petroleum ether–Et_2O (99:1) to give the **S4** in 51-86% yield.[9]



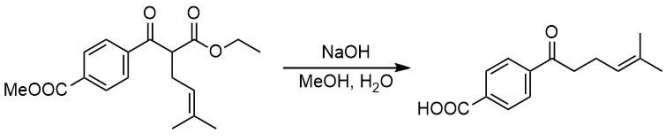
S4 **S5**

To a stirred solution of **S4** (10 mmol) in EtOH (15 mL), was added hydroxylamine hydrochloride (11 mmol) and pyridine (11 mmol). The reaction mixture was stirred for 2~4 hours at room temperature. Then the reaction was quenched with saturated aqueous NH_4Cl, extracted with EtOAc (50 mL × 3). The organic layers were separated and dried over Na_2SO_4. Finally, the crude product

was purified by column chromatography on silica gel, eluting with petroleum ether–Et_2O (20:1) to give the **S5** in 69-92% yield.[9]

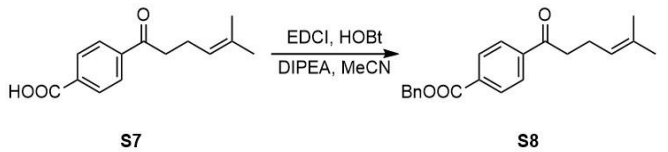
Following **GP1**, oximes (**1a**–**1h**, **1k**–**1l, 1q**–**1s**, **1u**–**1v**) were synthesized.

2.2 General Procedure 2 (GP2)



S6 **S7**

A solution of the β-ketoester **S6** (2 mmol) in MeOH–H_2O (100 mL, 2:1) was treated with NaOH (8 mmol) and heated under reflux for 2 h. The mixture was cooled to room temperature and the volatiles were removed in vacuo. EtOAc was added and the organic layers were separated. The aqueous layer was then washed with EtOAc (10 mL × 3) and the combined organic fractions were dried (Na_2SO_4), filtered and evaporated. Purification by column chromatography on silica gel, eluting with petroleum ether–Et_2O (2:1) to give the **S7** in 98% yield.

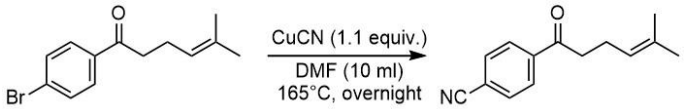


S7 **S8**

S7 (2 mmol), EDCI (3 mmol) and HOBt (3 mmol) were dissolved in MeCN at 0 °C. Then DIPEA (3 mmol) and benzyl alcohol (3 mmol) was added. The reaction was stirred at room temperature overnight. The volatiles were removed and the residue was dissolved in DCM. The reaction was quenched by 1N HCl and extracted with DCM. The combined organic fractions were dried (Na_2SO_4), filtered and evaporated. Purification by column chromatography on silica gel, eluting with petroleum ether–Et_2O (99:1) to give the **S8** in 99% yield.

Following **GP1** and **GP2**, oxime (**1j**) was synthesized.

2.3 General Procedure 3 (GP3)

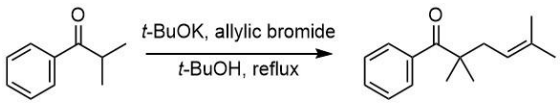


S9 **S10**

CuCN (11 mmol) was added portionwise to a stirred solution of **S9** (10 mmol) in DMF (10 mL). The resultant suspension was heated at 165 ºC overnight. Following cooling, H_2O and CH_2Cl_2 were added. The aqueous phase was washed with CH_2Cl_2 and the combined organic phase was washed with 10% aqueous NaCN solution, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography gave **S10** in 35% yield.[4]

Following **GP1** and **GP3**, oxime (**1i**) was synthesized.

2.4 General Procedure 4 (GP4)

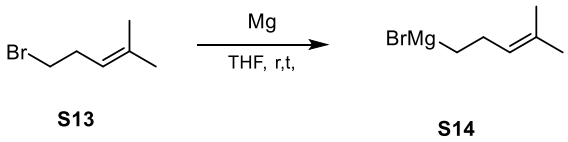


S11 **S12**

To a solution of **S11** (20 mmol) in anhydrous *t*-BuOH (60 mL) was added *t*-BuOK (100 mmol) and the mixture was stirred at room temperature for 5 minutes. Then, allylic bromide (30 mmol) was added via syringe and the mixture was heated at 90 °C for 16 hours. The mixture was cooled to room temperature and H_2O was added. The mixture was extracted with EtOAc. The organic extracts were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **S12** in 66% yield.[10]

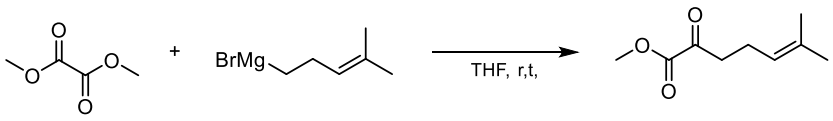
Following **GP1** and **GP4**, oxime (**1t**) was synthesized.

2.5 General Procedure 5 (GP5)



S13 **S14**

A dry three necked flask equipped with a stirring bar was charged with Mg turnings (0.4 g, 16.5 mmol) and then the flask was evacuated and refilled with N_2 (× 3). Dry THF (2 mL) was added and then **S13** (5 mmol) was added. Once the Grignard reaction started, the remaining **S13** (11.5 mmol) were added as a solution in THF (23 mL). The corresponding mixture was stirred for another hour.

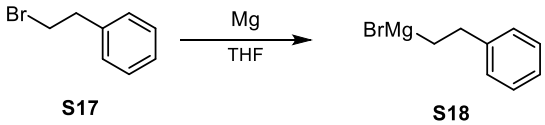


S15 **S14** **S16**

A dry flask equipped with a stirring bar was charged with **S15** (1.18 g, 15 mmol) and then the flask was evacuated and refilled with N_2 (× 3). Dry THF (20 mL) was added and the mixture was cooled to –78 ºC. A freshly prepared solution of **S14** (1.05 equiv.) was added by dropwise. The mixture was allowed to warm to room temperature overnight. Then NH_4Cl was added and the mixture was extracted with Et_2O (10 mL × 3). The organic extracts were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **S16** in 25% yield.[9]

Following **GP1** and **GP5**, oxime **(1z)** was synthesized.

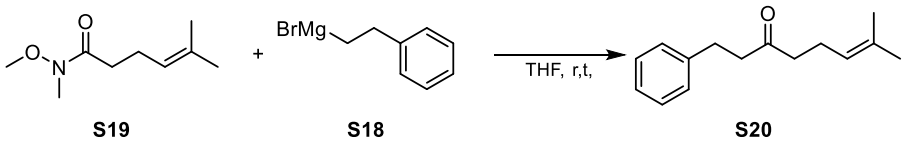
2.6 General Procedure 6 (GP6)



S17 **S18**

A dry three necked flask equipped with a stirring bar was charged with Mg turnings (0.181 g, 7.45 mmol) and then the flask was evacuated and refilled with N_2 (× 3). Dry THF (2 mL) was added and then **S17** (2 mmol) was added. Once the Grignard reaction started, the remaining **S17** (4.25

mmol) were added as a solution in THF (8.5 mL). The corresponding mixture was stirred for another hour.

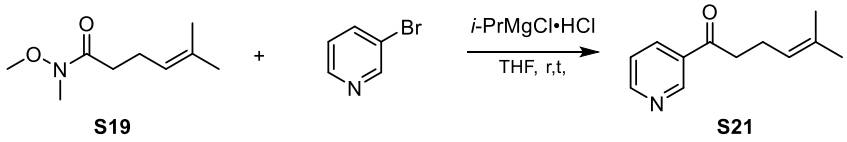


S19 **S18** **S20**

A dry flask equipped with a stirring bar was charged with **S19**[8] (0.856 g, 5 mmol) and then the flask was evacuated and refilled with N_2 (× 3). Dry THF (10 mL) was added and the mixture was cooled to –10 ºC. A freshly prepared solution of **S18** (1.25 equiv.) was added by dropwise. The mixture was allowed to warm to room temperature for 1 hour. Then NH_4Cl was added and the mixture was extracted with Et_2O (10 mL × 3). The organic extracts were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **S20** in 90% yield.[11]

Following **GP1** and **GP6**, oxime **(1n**–**1p**, **1x**–**1y)** was synthesized.

2.7 General Procedure 7 (GP7)



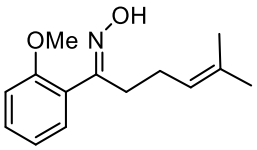
S19 **S21**

A dry flask equipped with a stirring bar was charged with 3-bromopyridine (0.79 g, 5 mmol) and then the flask was evacuated and refilled with N_2 (× 3). Dry THF (5 mL) was added and the mixture was cooled to 0 ºC and *i*-PrMgCl•LiCl (3.85 mL, 5 mmol, 1.3 M in THF) was added by dropwise. The mixture was allowed to stir at 0 ºC for 4 hours and then **S19** (5 mmol) was added as a solution in THF (4 ml). The mixture was allowed to warm to room temperature overnight. Then H_2O (10 ml) was added and the mixture was extracted with Et_2O (10 mL × 3). The organic extracts were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography to give **S21** in 48% yield.[11]

Following **GP1** and **GP7**, oxime **(1m)** was synthesized.

2.8 Characterization data of substrates

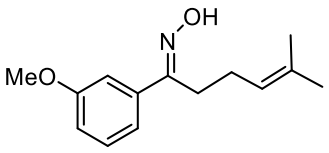
(*E*)-1-(2-methoxyphenyl)-5-methylhex-4-en-1-one oxime



1b

Synthesized according to **GP1**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (br, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1 H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.07 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.15 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.63 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 157.4, 132.2, 130.1, 130.0, 125.9, 123.8, 120.6, 110.8, 55.4, 28.5, 25.7, 24.3, 17.6. HRMS-ESI: calcd for $C_{14}H_{20}NO_2^+$ ([M + H^+]) *m*/*z* 234.1489, found 234.1480.

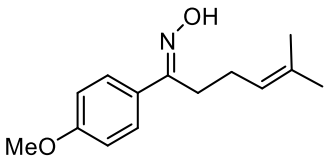
(*E*)-1-(3-methoxyphenyl)-5-methylhex-4-en-1-one oxime



1c

Synthesized according to **GP1**. White solid, m.p. = 45.9 – 46.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (br, 1H), 7.33 – 7.27 (m, 1H), 7.23 – 7.12 (m, 2H), 6.92 (d, *J* =7.2 Hz, 1H), 5.18 (t, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.26 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.5, 137.3, 132.8, 129.5, 123.3, 118.9, 115.0, 111.6, 55.3, 26.6, 25.7, 24.9, 17.7. HRMS-ESI: calcd for $C_{14}H_{20}NO_2^+$ ([M + H^+]) *m*/*z* 234.1489, found 234.1483.

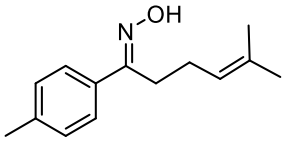
(*E*)-1-(4-methoxyphenyl)-5-methylhex-4-en-1-one oxime



1d

Synthesized according to **GP1**. White solid, m.p. = 82.6 – 83.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.18 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.26 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.1, 132.7, 128.3, 127.7, 123.4, 113.9, 55.3, 26.4, 25.6, 25.0, 17.7. HRMS-ESI: calcd for $C_{14}H_{20}NO_2^+$ ([M + H^+]) *m*/*z* 234.1489, found 234.1485.

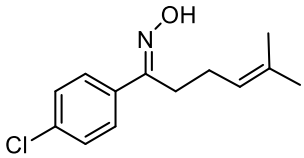
(*E*)-5-methyl-1-(*p*-tolyl)hex-4-en-1-one oxime



1e

Synthesized according to **GP1**. White solid, m.p. = 49.2 – 49.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.18 (t, *J* = 7.2 Hz, 1H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.26 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.66 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 139.2, 133.0, 132.7, 129.3, 126.3, 123.4, 26.6, 25.7, 24.9, 21.3, 17.7. HRMS-ESI: calcd for $C_{14}H_{20}NO^+$ ([M + H^+]) *m*/*z* 218.1539, found 218.1539.

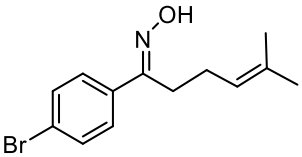
(*E*)-1-(4-chlorophenyl)-5-methylhex-4-en-1-one oxime



1f

Synthesized according to **GP1**. White solid, m.p. = 84.1 – 85.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 5.15 (t, *J* = 7.2 Hz, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.24 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.66 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 135.2, 134.3, 133.0, 128.7, 127.6, 123.0, 26.3, 25.6, 24.8, 17.7. HRMS-ESI: calcd for $C_{13}H_{17}ClNO^+$ ([M + H^+]) *m*/*z* 238.0993, found 238.0985.

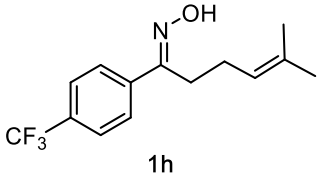
(*E*)-1-(4-bromophenyl)-5-methylhex-4-en-1-one oxime



1g

Synthesized according to **GP1**. White solid, m.p. = 101.0 – 102.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.60 – 7.42 (m, 4H), 5.15 (t, *J* = 7.2 Hz, 1H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.24 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.66 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 134.7, 133.0, 131.7, 127.9, 123.5, 123.0, 26.3, 25.7, 24.8, 17.7. HRMS-ESI: calcd for $C_{13}H_{17}BrNO^+$ ([M + H^+]) *m*/*z* 282.0488, found 282.0482.

(*E*)-5-methyl-1-(4-(trifluoromethyl)phenyl)hex-4-en-1-one oxime

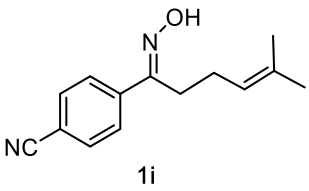


1h

Synthesized according to **GP1**. White solid, m.p. = 83.2 – 84.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 5.15 (t, *J* = 6.8 Hz, 1H), 2.85 (t, *J* = 8.0 Hz, 2H), 2.27 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.65 (s, 3H), 1.55 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 158.8, 139.3, 133.2, 131.1 (q, J = 32.7 Hz), 126.7, 125.5 (q, J = 3.6 Hz), 124.0 (q, J = 270.4 Hz), 122.9, 26.5, 25.6, 24.9, 17.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ 62.75. HRMS-ESI: calcd for $C_{14}H_{17}F_3NO_3^+$ ([M + H^+]) *m*/*z* 272.1257, found 272.1251.

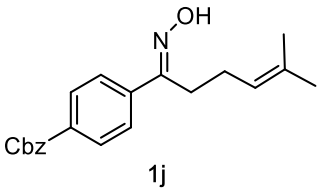
(*E*)-4-(1-(hydroxyimino)-5-methylhex-4-en-1-yl)benzonitrile



1i

Synthesized according to **GP1** and **GP3**. White solid, m.p. = 56.3 – 58.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 7.6 Hz, 1H), 7.62 (q, J = 8.4 Hz, 4H), 5.05 (t, J = 7.2 Hz, 1H), 2.75 (t, J = 8.0 Hz, 2H), 2.27 (dd, J = 15.2, 7.6 Hz, 2H), 1.57 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 140.2, 133.3, 132.3, 126.9, 122.7, 118.6, 112.6, 26.2, 25.6, 24.7, 17.7. HRMS-ESI: calcd for $C_{14}H_{17}N_2O^+$ ([M + H^+]) *m*/*z* 229.1335, found 229.1330.

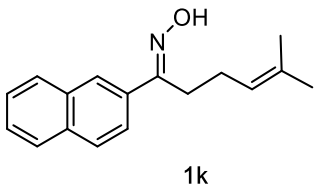
benzyl (*E*)-4-(1-(hydroxyimino)-5-methylhex-4-en-1-yl)benzoate



1j

Synthesized according to **GP1** and **GP2**. White solid, m.p. = 80.6 – 81.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (br, 1H), 8.13 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 6.8 Hz, 2H), 7.47 – 7.30 (m, 3H), 5.42 (s, 2H), 5.19 (t, J = 6.4 Hz, 1H), 2.88 (t, J = 7.6 Hz, 2H), 2.30 (dd, J = 15.2, 7.6 Hz, 2H), 1.69 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.9, 140.4, 136.0, 133.0, 130.5, 130.0, 128.7, 128.3, 128.2, 126.4, 123.0, 66.9, 26.4, 25.7, 24.8, 17.7. HRMS-ESI: calcd for $C_{21}H_{24}NO_3^+$ ([M + H^+]) *m*/*z* 338.1751, found 338.1742.

(*E*)-5-methyl-1-(naphthalen-2-yl)hex-4-en-1-one oxime

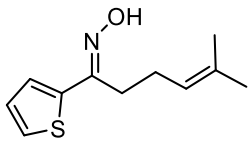


1k

Synthesized according to **GP1**. White solid, m.p. = 137.6 – 138.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.02 (s, 1H), 7.92 – 7.77 (m, 4H), 7.56 – 7.44 (m, 2H), 5.24 (t, J = 7.2 Hz, 1H), 2.94 (t, J = 8.0 Hz, 2H), 2.34 (dd, J = 15.6, 7.6 Hz, 2H), 1.68 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 133.7, 133.2, 133.1, 132.9, 128.5,

128.2, 127.7, 126.7, 126.4, 126.1, 123.7, 123.3, 26.3, 25.7, 25.1, 17.7. HRMS-ESI: calcd for $C_{17}H_{19}NO^+$ ([M + H^+]) *m/z* 254.1539, found 254.1542.

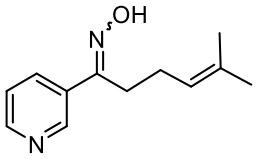
(*E*)-5-methyl-1-(thiophen-2-yl)hex-4-en-1-one oxime



1l

Synthesized according to **GP1**. White solid, m.p. = 60.1 – 60.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.28 (d, *J* = 5.2 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.22 (t, *J* = 7.2 Hz, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.34 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.68 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 139.7, 133.0, 127.2, 126.8, 126.4, 123.1, 27.1, 25.7, 25.2, 17.7. HRMS-ESI: calcd for $C_{11}H_{16}NOS^+$ ([M + H^+]) *m/z* 210.0947, found 210.0956.

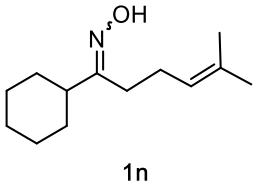
5-methyl-1-(pyridin-3-yl)hex-4-en-1-one oxime



1m

Synthesized according to **GP1** and **GP7**. Colorless oil, *E:Z* = 70:30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 0.7H), 9.99 (s, 0.3H), 8.92 (s, 0.7H), 8.75 (s, 0.3H), 8.66 – 8.51 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 0.7H), 7.84 (d, *J* = 8.0 Hz, 0.3H), 7.38 (dd, *J* = 8.0, 4.8 Hz, 0.3H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 0.7H), 5.17 (t, *J* = 7.2 Hz, 0.7H), 5.09 (t, *J* = 7.2 Hz, 0.3H), 2.84 (t, *J* = 7.6 Hz, 1.4H), 2.62 (t, *J* = 7.6 Hz, 0.6H), 2.29 (dd, *J* = 15.2, 7.6 Hz, 1.4H), 2.17 (dd, *J* = 15.2, 7.6 Hz, 0.6H), 1.66 (s, 3H), 1.57 (s, 2.1H), 1.50 (s, 0.9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.9, 149.4, 149.3, 148.8, 147.5, 136.2, 133.9, 133.1, 133.0, 132.3, 129.7, 123.4, 123.2, 123.0, 122.5, 35.0, 26.0, 25.7, 25.6, 25.3, 24.7, 17.7, 17.7. HRMS-ESI: calcd for $C_{12}H_{17}N_2O^+$ ([M + H^+]) *m/z* 205.1335, found 205.1337.

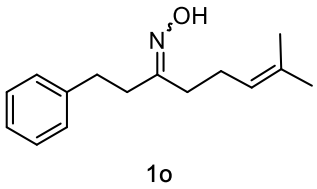
1-cyclohexyl-5-methylhex-4-en-1-one oxime



1n

Synthesized according to **GP1** and **GP6**. Colorless oil, *E:Z* = 80:20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 5.22 – 5.06 (m, 1H), 3.25 – 3.07 (m, 0.2H), 2.40 – 2.28 (m, 1.8H), 2.26 – 2.08 (m, 3H), 1.87 – 1.74 (m, 4H), 1.72 – 1.65 (m, 4H), 1.63 (s, 2.4H), 1.61 (s, 0.6H), 1.34 – 1.15 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.9, 132.3, 132.3, 123.8, 123.6, 43.9, 36.8, 30.9, 30.3, 28.9, 27.4, 26.3, 26.2, 26.1, 26.1, 25.7, 24.9, 24.5, 17.7, 17.7. HRMS-ESI: calcd for $C_{13}H_{24}NO^+$ ([M + H^+]) *m/z* 210.1852, found 210.1851.

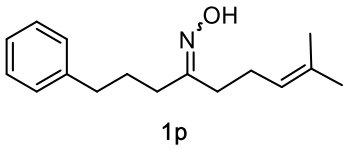
7-methyl-1-phenyloct-6-en-3-one oxime



1o

Synthesized according to **GP1** and **GP6**. Colorless oil, *E:Z* = 50:50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (br, 1H), 7.33 – 7.08 (m, 5H), 5.20 – 5.00 (m, 1H), 2.95 – 2.78 (m, 2H), 2.70 – 2.58 (m, 1H), 2.55 – 2.45 (m, 1H), 2.43 – 2.33 (m, 1H), 2.28 – 2.07 (m, 3H), 1.69 (s, 1.5H), 1.68 (s, 1.5H), 1.62 (s, 1.5H), 1.59 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.8, 141.5, 141.4, 132.8, 132.6, 128.5, 128.5, 128.4, 128.4, 126.1, 126.1, 123.3, 123.1, 36.4, 34.7, 32.6, 31.6, 30.1, 28.2, 25.7, 25.7, 24.8, 24.2, 17.8, 17.7. HRMS-ESI: calcd for $C_{15}H_{22}NO^+$ ([M + H^+]) *m/z* 232.1696, found 232.1697.

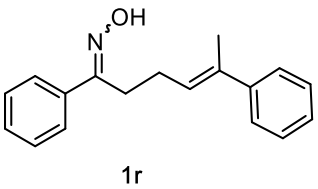
8-methyl-1-phenylnon-7-en-4-one oxime



1p

Synthesized according to **GP1** and **GP6**. Colorless oil, *E:Z* = 50:50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 – 8.10 (m, 1H), 7.35 – 7.25 (m, 2H), 7.22 – 7.08 (m, 3H), 5.18 – 5.00 (m, 1H), 2.78 – 2.57 (m, 2H), 2.46 – 2.29 (m, 2H), 2.28 – 2.10 (m, 4H), 1.92 – 1.78 (m, 2H), 1.68 (s, 3H), 1.62 – 1.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 141.9, 141.9, 132.7, 132.6, 128.5, 128.4, 128.4, 125.9, 125.9, 123.4, 123.1, 36.1, 35.4, 34.2, 33.9, 27.9, 27.8, 27.4, 27.3, 25.7, 25.7, 24.9, 24.2, 17.7, 17.7. HRMS-ESI: calcd for $C_{16}H_{24}NO^+$ ([M + H^+]) *m/z* 246.1852, found 246.1848.

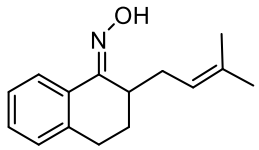
(4*E*)-1,5-diphenylhex-4-en-1-one oxime



1r

Synthesized according to **GP1**. White solid, m.p. = 74.3 – 74.9 ℃, *E:Z* = 82:18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.75 – 7.55 (m, 1.64H), 7.50 – 7.42 (m, 0.36H), 7.41 – 7.08 (m, 8H), 5.79 (t, *J* = 7.2 Hz, 0.82H), 5.52 (t, *J* = 7.2 Hz, 0.18H), 2.97 (t, *J* = 8.0 Hz, 1.64H), 2.82 (t, *J* = 8.0 Hz, 0.36H), 2.49 (dd, *J* = 15.6, 7.6 Hz, 1.64H), 2.26 (dd, *J* = 15.6, 7.6 Hz, 0.36H), 1.99 (s, 0.54H), 1.95 (s, 2.46H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.2, 143.9, 141.9, 137.8, 136.0, 135.9, 135.7, 129.4, 129.3, 128.8, 128.7, 128.3, 128.2, 128.0, 127.0, 126.8, 126.7, 126.6, 126.4, 126.2, 125.8, 26.9, 26.5, 26.0, 25.7, 16.0. HRMS-ESI: calcd for $C_{18}H_{20}NO^+$ ([M + H^+]) *m*/*z* 266.1539, found 266.1531.

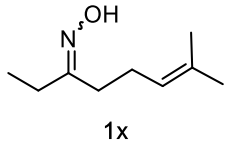
(*E*)-2-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2*H*)-one oxime



1u

Synthesized according to **GP1**. White solid, m.p. = 134.5 – 136.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (br, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.22 (t, *J* = 7.2 Hz, 1H), 3.57 (td, *J* = 8.8, 4.4 Hz, 1H), 2.92 (ddd, *J* = 16.8, 12.0, 5.2 Hz, 1H), 2.67 (dt, *J* = 16.8, 4.4 Hz, 1H), 2.45 – 2.30 (m, 1H), 2.16 (dt, *J* = 14.4, 9.2 Hz, 1H), 1.98 – 1.80 (m, 2H), 1.72 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 138.9, 133.4, 130.1, 129.1, 128.9, 126.3, 124.5, 122.0, 32.2, 27.2, 25.9, 25.1, 24.4, 17.9. HRMS-ESI: calcd for $C_{15}H_{20}NO^+$ ([M + H^+]) *m*/*z* 230.1539, found 230.1533.

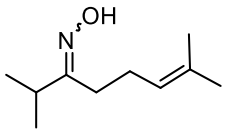
7-methyloct-6-en-3-one oxime



1x

Synthesized according to **GP1** and **GP6**. Colorless oil, *E:Z* = 50:50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (br, 1H), 5.25 – 5.00 (m, 1H), 2.55 – 2.32 (m, 2H), 2.28 – 2.15 (m, 4H), 1.69 (s, 3H), 1.63 (s, 1.5H), 1.62 (s, 1.5H), 1.10 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 162.2, 132.5, 132.5, 123.5, 123.2, 33.8, 27.9, 27.7, 25.6, 25.0, 24.2, 21.0, 17.7, 17.6, 10.7, 10.0. HRMS-ESI: calcd for $C_{10}H_{20}NO^+$ ([M + H^+]) *m*/*z* 170.1539, found 170.1536.

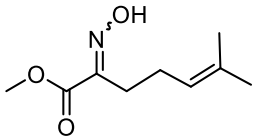
2,7-dimethyloct-6-en-3-one oxime



1y

Synthesized according to **GP1** and **GP6**. Colorless oil, *E:Z* = 84:16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (br, 1H), 5.40 – 5.00 (m, 1H), 3.44 (dt, *J* = 14.0, 6.8 Hz, 0.16H), 2.50 (dt, *J* = 14.0, 6.8 Hz, 0.84H), 2.37 – 2.14 (m, 4H), 1.69 (s, 3H), 1.63 (s, 2.52H), 1.61 (s, 0.48H), 1.11 (d, *J* = 6.8 Hz, 5.04H) , 1.08 (d, *J* = 6.8 Hz, 0.96H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.6, 132.3, 123.7, 123.6, 33.8, 30.1, 27.1, 26.3, 25.6, 24.9, 24.5, 19.9, 18.9, 17.6, 17.6. HRMS-ESI: calcd for $C_9H_{18}NO_3^+$ ([M + H^+]) *m*/*z* 186.1125, found 186.1122.

methyl 2-(hydroxyimino)-6-methylhept-5-enoate



1z

Synthesized according to **GP1** and **GP5**. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (br, 1H), 5.15 (t, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.23 (dd, *J* = 15.6, 7.6 Hz, 2H), 1.68 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 152.5, 133.1, 122.7, 52.6, 25.6, 24.9, 24.3, 17.5. HRMS-ESI: calcd for $C_9H_{16}NO_3^+$ ([M + H^+]) *m*/*z* 186.1125, found 186.1122.

3. Deoxygenation of oximes for the synthesis of pyrrolines

3.1 Reaction setup

We use RLH-18 8-position Photo Reaction System, which is manufactured by Beijing Rogertech Co. (**Figure S1**). The photo reactor was equipped with 8 blue light LED (10 W) and a cooling fan was used to keep reactions around room temperature. All the reactions were performed in borosilicate glassware while irradiating with a 455 nm 10 W blue light LED (**Figure S2**), at a distance of 2 cm, without the use of any filter.

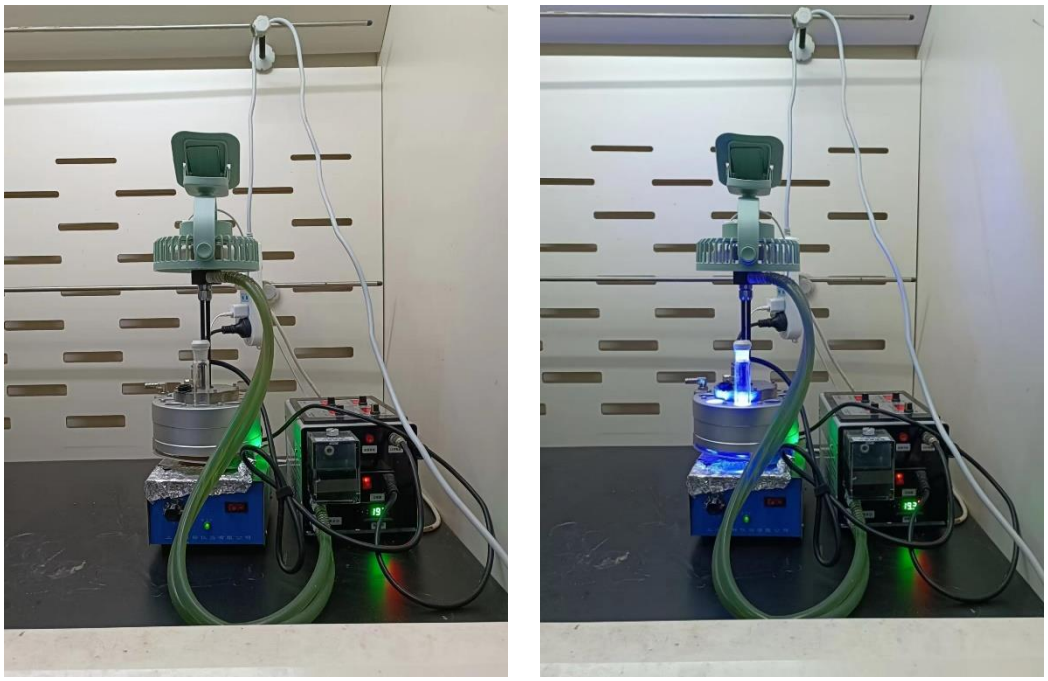


Figure S1. Integrated photoreactor and associated equipment.

Beijing Rogertech Ltd
http://www.rogertech.cn
Tel: +86(10)62966884
Fax:

RLH-18 10WLED Test report

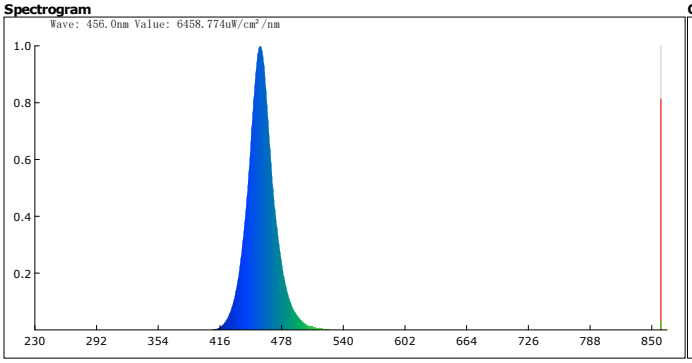
Product Mark

Model: 1-455nm(456.7)@10W
Manufacture: Beijing Rogertech Ltd
Temperature: 20°C
Humidity: 65%
Tester: Wu
Test Date: 2022-06-21,15:34:31

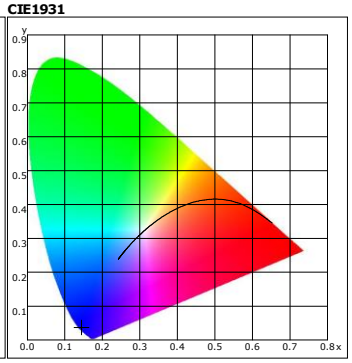
Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm²)	0.0000	CIE u,v	0.1839,0.0693	CIE1931 Y	130873.648		
Euvc(mW/cm²)	0.0000	CIE u',v'	0.1839,0.1039	CIE1931 Z	2949318.500		
Euvb(mW/cm²)	0.0000	SDCM	100.00	TLCI-2012	1		
Euva(mW/cm²)	0.0000	Ra	-63.7	Integral Time(ms)	0.1		
Euv(mW/cm²)	0.00	Ee(mW/cm²)	194.23262	Peak Signal	53258		
Eb(mW/cm²)	190.91	S/P	20.108	Dark Signal	2045		
Eg(mW/cm²)	1.67	Dominant(nm)	461.30	Compensate level	2878		
Er(mW/cm²)	0.00	Purity(%)	98.5				
Eir(mW/cm²)	0.00	HalfWidth(nm)	25.2				
E(lx)	89386.70	Peak(nm)	456.7				
Candle E(fc)	8304.23	Center(nm)	457.4				
CCT(K)	100000	Centroid(nm)	458.5				
Duv	-0.05186	Color Ratio(RGB)	0.0,12.1,87.9				
CIE x,y	0.1446,0.0363	CIE1931 X	520893.188				

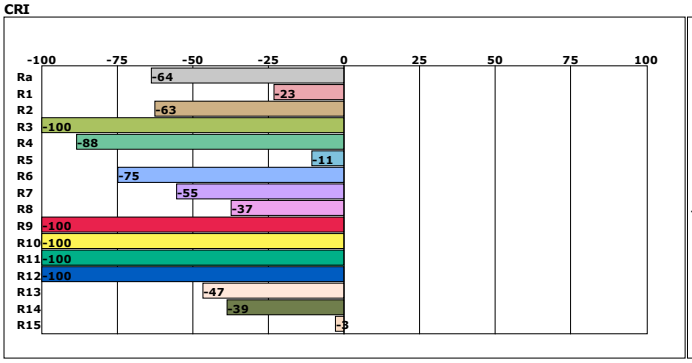
Spectrogram

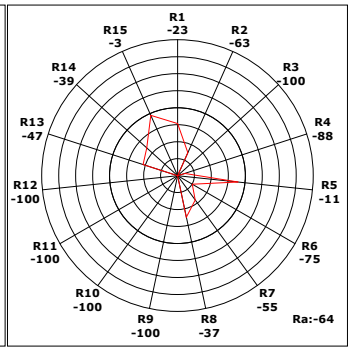


CIE1931



CRI





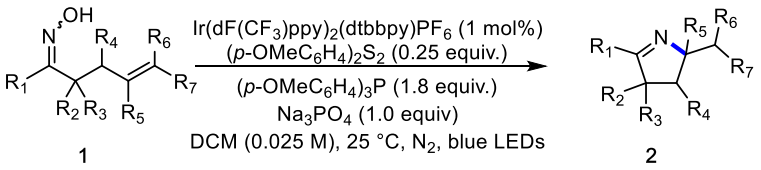
Instrument Status

Type: OHSP-350UV
SN: 0
Scan Range: 230-850nm
Integral Time: 0.077ms
VPeak: 53258
VDark: 2045

Remark:

Figure S2. Spectrophotocolormeter analysis report.

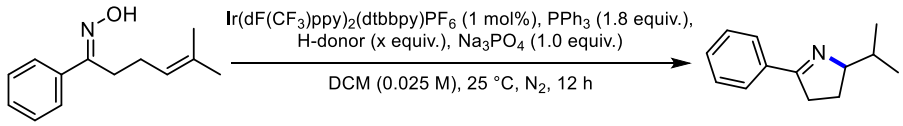
3.2 General procedure



To an oven-dried reaction tube equipped with a stir bar was added oximes (0.1 mmol, 1.0 equiv.), (p-$OMeC_6H_4)_2S_2$ (0.025 mmol, 0.25 equiv.), (p-$OMeC_6H_4)_3P$ (0.18 mmol, 1.8 equiv.), Na_3PO_4 (1.0 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol%). The tube was sealed and placed under nitrogen before DCM (4 mL) was added. The reaction mixture was irradiated by a 10 W blue LED at 25 °C for 12 hours. Then the reaction mixture was concentrated and purified through column chromatography to afford the desired product.

3.3 Optimization details

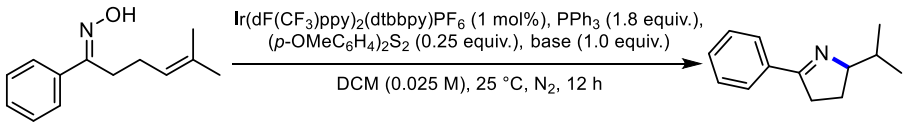
Table S1. Screening of the H-donor.



entry	H-donor (x equiv.)	yield (%)[a]
1	(p-$OMeC_6H_4)_2S_2$ (0.25 equiv.)	82
2	Ph_2S_2 (0.25 equiv.)	68
3	TRIP-SH (0.5 equiv.)	68
4	(p-$OMeC_6H_4)_2S_2$ (0.05 equiv.)	36
5	(p-$OMeC_6H_4)_2S_2$ (0.15 equiv.)	72
6	(p-$OMeC_6H_4)_2S_2$ (0.35 equiv.)	78

[a]Yields were calculated by ^1H NMR using 1,3,5-trimethoxybenzene as internal standards.

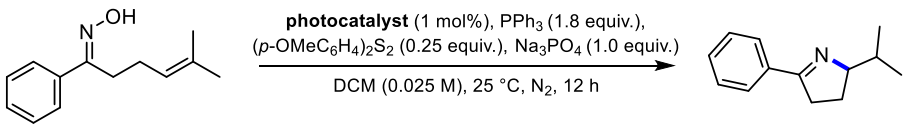
Table S2. Screening of the base.



entry	**Base**	yield (%)[a]
1	Na_3PO_4	82
2	no base	58
3	Na_2CO_3	77
4	NaOAc	50
5	$NaHCO_3$	77
6	Na_2HPO_4	69
7	NaH_2PO_4	68
8	K_3PO_4	79
9	K_2HPO_4	77
10	KH_2PO_4	66
11	2,6-lutidine	47
12	2,4,6-collidine	41

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

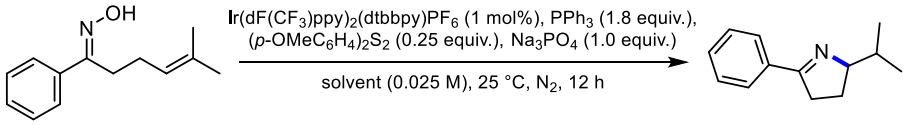
Table S3. Screening of the photocatalysts.



entry	**photocatalyst**	yield (%)[a]
1	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	82
2	$Ir(dF(CF_3)ppy)_2(phen)PF_6$	65
3	$[Ir(ppy)_2(dtbbpy)]PF_6$	2
4	$[Ru(bpz)_3](PF_6)_2$	trace
5	$Ir(ppy)_3$	6
6	4-CzIPN (5 mol%)	10

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

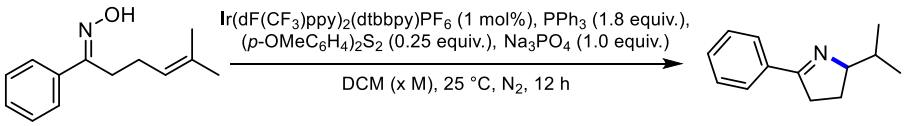
Table S4. Screening of the solvent.



entry	**solvent**	yield (%)[a]
1	DCM	82
2	THF	0
3	MeCN	4
4	PhMe	6
5	DMF	0
6	DMSO	0

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

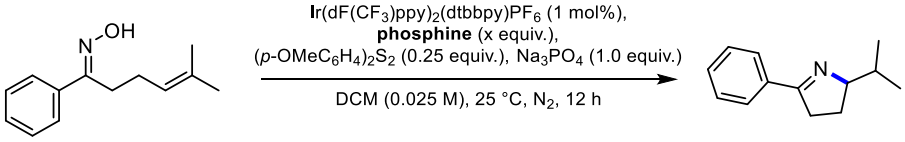
Table S5. Screening of the concentration.



entry	**concentration**	yield (%)[a]
1	DCM (0.1 M)	60
2	DCM (0.05 M)	71
3	DCM (0.025 M)	82
4	DCM (0.013 M)	69

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

Table S6. Screening of the phosphine.



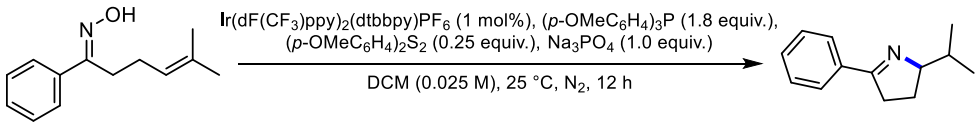
entry	phosphine (x equiv.)	yield (%)[a]
1	PPh_3 (1.2 equiv.)	74
2	PPh_3 (1.4 equiv.)	78
3	PPh_3 (1.6 equiv.)	78
4	PPh_3 (1.8 equiv.)	82
5	PPh_3 (2.0 equiv.)	81
6	(p-MeC_6H_4)$_3$P (1.8 equiv.)	88

7	(p-FC_6H_4)$_3$P (1.8 equiv.)	55
8	(p-$OMeC_6H_4$)$_3$P (1.8 equiv.)	94
9	Ph_2POEt (1.8 equiv.)	52

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

3.4 Control experiments

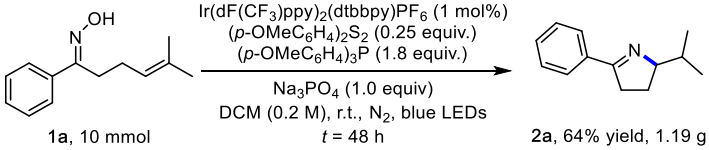
Table S7. Control experiments for the synthesis of pyrrolines.



entry	**deviation from standard conditions**	yield (%)[a]
1	none	94
2	no (p-$OMeC_6H_4$)$_3$P	0
3	no photocatalyst	0
4	no light	0
5	no (p-$OMeC_6H_4$)$_2S_2$	47

[a]Yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standards.

3.5 Gram-scale reaction



To a 250 mL round-bottomed flask equipped with a stir bar was added **1a** (10.0 mmol, 2.033 g, 1.0 equiv.), (p-$OMeC_6H_4)_2S_2$ (2.5 mmol, 696 mg, 0.25 equiv.), (p-$OMeC_6H_4)_3P$ (18.0 mmol, 6.34 g, 1.8 equiv.), Na_3PO_4 (10.0 mmol, 1.64 g, 1.0 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (116.6 mg, 1 mol%). The flask was sealed and placed under nitrogen before DCM (50 mL) was added. The reaction mixture was irradiated by a 50 W blue LED at room temperature for 48 hours. Then the reaction mixture was concentrated and purified through column chromatography to afford **2a** (1.19 g, 64% yield).

3.6 Gram-scale synthesis in continuous-flow

Flow reactor setup

The outline diagram of the assembled flow photoreactor was shown in **Figure S3**. The flow photoreactor was mainly consisted of a syringe pump (TYB01-01), an RLH-18 octet photocatalytic parallel reaction system with eight 10W blue LEDs, and a cylindrical coil continuous-flow reaction system (RLR-18CF, **Figure S4**), which were purchased from Beijing Roger tech Ltd. FEP tubing (1 mm inner diameter) was selected, and the calculated residence volume of the tubing was about 12 mL. The reaction temperature was controlled by an aluminum cooling block, which was connected to a chiller (2 °C).

Figure S3. Picture of the Flow Photoreactor

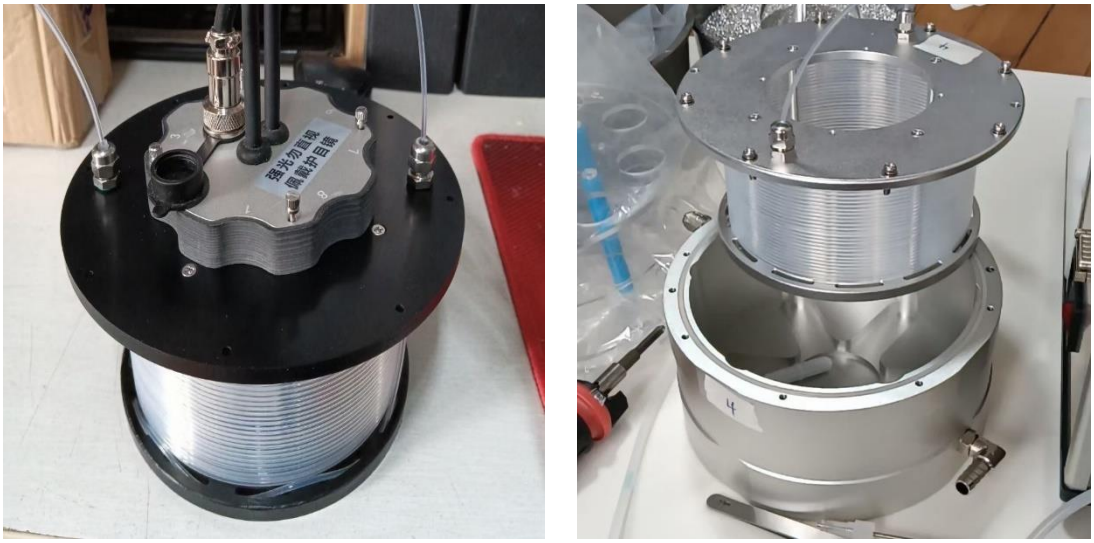
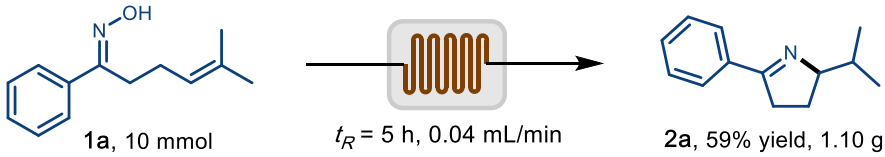


Figure S4. Pictures of the cylindrical coil

General procedure

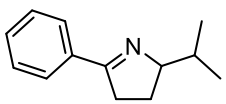


To a 250 mL round-bottomed flask was added **1a** (10.0 mmol, 2.033 g, 1.0 equiv.), (*p*-

$OMeC_6H_4)_2S_2$ (2.5 mmol, 696 mg, 0.25 equiv.), (p-$OMeC_6H_4)_3P$ (18.0 mmol, 6.34 g, 1.8 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (116.6 mg, 1 mol%). The flask was sealed and placed under nitrogen before DCM (50 mL) was added. The mixture solution was transferred to syringe and pumped via a syringe pump to pass through the flow photoredox system with a flow rate of 0.04 mL/min. The outlet solution was collected, concentrated, and purified through column chromatography to afford **2a** (1.10 g, 59% yield).

3.7 Characterization data for all the products

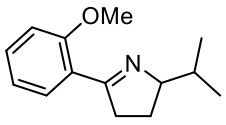
2-isopropyl-5-phenyl-3,4-dihydro-2*H*-pyrrole



2a

Purified by column chromatography (PE/EA = 20:1), colorless oil (16.1 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.65 (m, 2H), 7.50 – 7.23 (m, 3H), 3.95 (dd, J = 14.4, 6.8 Hz, 1H), 3.01 – 2.71 (m, 2H), 2.10 – 1.94 (m, 1H), 1.94 – 1.80 (m, 1H), 1.68 – 1.50 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 134.9, 130.1, 128.3, 127.6, 79.2, 35.3, 33.5, 25.2, 20.0, 18.4. HRMS-ESI: calcd for $C_{13}H_{18}N^+$ ([M + H$^+$]) m/z 188.1434, found 188.1438.

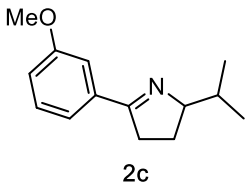
2-isopropyl-5-(2-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole



2b

Purified by column chromatography (PE/EA = 20:1), colorless oil (10.9 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 3.85 (dd, J = 13.6, 6.8 Hz, 1H), 3.76 (s, 3H), 2.90 (t, J = 7.6 Hz, 2H), 2.00 – 1.84 (m, 2H), 1.64 – 1.45 (m, 1H), 1.00 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 158.1, 130.9, 130.1, 125.2, 120.6, 111.2, 77.8, 55.4, 38.8, 33.3, 25.5, 20.1, 18.3. HRMS-ESI: calcd for $C_{14}H_{20}NO^+$ ([M + H$^+$]) m/z 218.1539, found 218.1532.

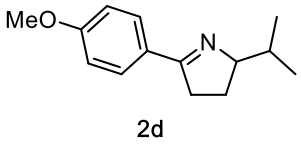
2-isopropyl-5-(3-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole



2c

Purified by column chromatography (PE/EA = 20:1), colorless oil (17.5 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.16 (m, 1H), 6.88 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.93 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.77 (s, 3H), 3.01 – 2.68 (m, 2H), 2.10 – 1.93 (m, 1H), 1.93 – 1.80 (m, 1H), 1.68 – 1.50 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 159.6, 136.3, 129.3, 120.4, 116.5, 112.1, 79.1, 55.4, 35.4, 33.5, 25.1, 20.1, 18.3. $C_{14}H_{20}NO^+$ ([M + H^+]) *m*/*z* 218.1539, found 218.1531.

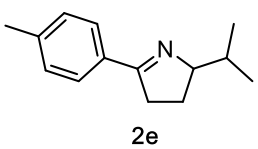
2-isopropyl-5-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyrrole



2d

Purified by column chromatography (PE/EA = 20:1), light yellow solid (21.1 mg, 97% yield), m.p. = 45.6 – 46.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 3.98 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.83 (s, 3H), 3.05 – 2.70 (m, 2H), 2.12 – 1.97 (m, 1H), 1.97 – 1.85 (m, 1H), 1.75 – 1.55 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 161.2, 129.2, 127.8, 113.6, 78.9, 55.3, 35.2, 33.5, 25.2, 20.1, 18.3. $C_{14}H_{20}NO^+$ ([M + H^+]) *m*/*z* 218.1539, found 218.1531.

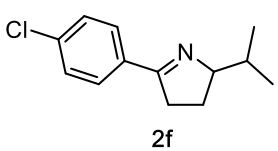
2-isopropyl-5-(*p*-tolyl)-3,4-dihydro-2*H*-pyrrole



2e

Purified by column chromatography (PE/EA = 20:1), colorless oil (19.1 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.00 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.01 – 2.75 (m, 2H), 2.37 (s, 3H), 2.12 – 2.00 (m, 1H), 2.00 – 1.86 (m, 1H), 1.74 – 1.56 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 140.3, 132.2, 129.0, 127.6, 79.0, 35.3, 33.5, 25.1, 21.4, 20.0, 18.3. HRMS-ESI: calcd for $C_{14}H_{20}N^+$ ([M + H^+]) *m*/*z* 202.1590, found 202.1617.

5-(4-chlorophenyl)-2-isopropyl-3,4-dihydro-2*H*-pyrrole

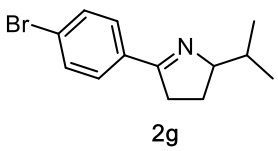


2f

Purified by column chromatography (PE/EA = 20:1), white solid (18.9 mg, 85% yield), m.p. = 49.1 – 50.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.90 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.95 – 2.62 (m, 2H), 2.10 – 1.92 (m, 1H), 1.92 – 1.74 (m, 1H), 1.66 – 1.43

(m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 136.2, 133.3, 129.0, 128.6, 79.3, 35.2, 33.6, 25.3, 20.0, 18.4. HRMS-ESI: calcd for $C_{13}H_{17}ClN^+$ ([M + H^+]) m/z 222.1044, found 222.1036.

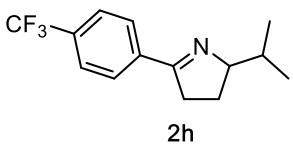
5-(4-bromophenyl)-2-isopropyl-3,4-dihydro-2*H*-pyrrole



2g

Purified by column chromatography (PE/EA = 20:1), light yellow solid (22.2 mg, 83% yield), m.p. = 60.2 – 61.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 3.92 (dd, J = 14.4, 6.8 Hz, 1H), 2.97 – 2.60 (m, 2H), 2.10 – 1.92 (m, 1H), 1.91 – 1.80 (m, 1H), 1.68 – 1.45 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 133.8, 131.5, 129.2, 124.6, 79.3, 35.2, 33.5, 25.3, 20.0, 18.4. HRMS-ESI: calcd for $C_{13}H_{17}BrN^+$ ([M + H^+]) m/z 266.0539, found 266.0531.

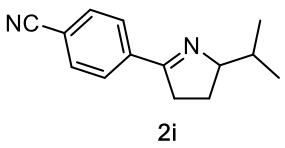
2-isopropyl-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyrrole



2h

Purified by column chromatography (PE/EA = 20:1), light yellow solid (23.0 mg, 90% yield), m.p. = 51.0 – 51.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 4.04 (dd, J = 14.4, 6.8 Hz, 1H), 3.10 – 2.65 (m, 2H), 2.18 – 2.02 (m, 1H), 2.02 – 1.89 (m, 1H), 1.78 – 1.60 (m, 1H), 1.09 (dd, J = 6.8, 1.6 Hz, 3H), 0.93 (d, J = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.0, 131.8 (q, J = 32.3 Hz), 127.9, 125.3 (q, J = 3.7 Hz), 124.0 (q, J = 270.6 Hz), 79.4, 35.4, 33.5, 25.2, 20.0, 18.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ 62.74. HRMS-ESI: calcd for $C_{14}H_{17}F_3N^+$ ([M + H^+]) m/z 256.1308, found 256.1307.

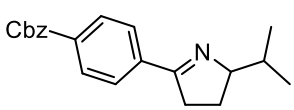
4-(2-isopropyl-3,4-dihydro-2*H*-pyrrol-5-yl)benzonitrile



2i

Purified by column chromatography (PE/EA = 20:1), light yellow solid (13.1 mg, 62% yield), m.p. = 75.6 – 76.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 3.96 (dd, J = 14.4, 6.8 Hz, 1H), 3.05 – 2.65 (m, 2H), 2.15 – 2.00 (m, 1H), 1.92 – 1.79 (m, 1H), 1.68 – 1.62 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 138.8, 132.2, 128.2, 118.7, 113.5, 79.6, 35.3, 33.6, 25.4, 19.9, 18.5. HRMS-ESI: calcd for $C_{14}H_{17}N_2^+$ ([M + H^+]) m/z 213.1386, found 213.1379.

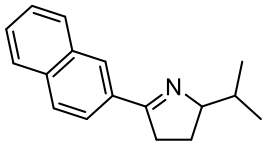
benzyl 4-(2-isopropyl-3,4-dihydro-2*H*-pyrrol-5-yl)benzoate



2j

Purified by column chromatography (PE/EA = 20:1), colorless oil (24.7 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.13 (m, 3H), 5.25 (s, 2H), 3.90 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.00 – 2.65 (m, 2H), 2.05 – 1.90 (m, 1H), 1.90 – 1.73 (m, 1H), 1.65 – 1.45 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 166.1, 139.0, 136.0, 131.4, 129.8, 128.7, 128.4, 128.3, 127.7, 79.5, 66.9, 35.4, 33.6, 25.3, 20.0, 18.5. HRMS-ESI: calcd for $C_{21}H_{24}NO_2^+$ ([M + H$^+$]) *m*/*z* 322.1802, found 322.1790.

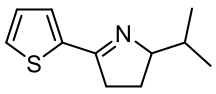
2-isopropyl-5-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyrrole



2k

Purified by column chromatography (PE/EA = 20:1), light yellow solid (22.1 mg, 93% yield), m.p. = 70.6 – 71.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.95 (m, 2H), 7.90 – 7.65 (m, 3H), 7.50 – 7.25 (m, 2H), 3.99 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.10 – 2.70 (m, 2H), 2.12 – 1.95 (m, 1H), 1.95 – 1.79 (m, 1H), 1.70 – 1.50 (m, 1H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 134.3, 133.0, 132.4, 128.7, 128.0, 128.0, 127.8, 126.9, 126.3, 124.8, 79.3, 35.3, 33.6, 25.3, 20.1, 18.4. HRMS-ESI: calcd for $C_{17}H_{20}N^+$ ([M + H$^+$]) *m*/*z* 238.1590, found 238.1581.

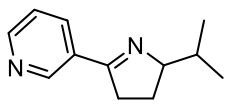
2-isopropyl-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole



2l

Purified by column chromatography (PE/EA = 20:1), colorless oil (14.5 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7. 05 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.13 – 3.85 (m, 1H), 3.10 – 2.75 (m, 2H), 2.13 – 1.99 (m, 1H), 1.99 – 1.90 (m, 1H), 1.76 – 1.62 (m, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 139.9, 128.8, 128.7, 127.4, 78.9, 36.0, 33.3, 25.2, 20.0, 18.1. HRMS-ESI: calcd for $C_{11}H_{16}NS^+$ ([M + H$^+$]) *m*/*z* 194.0998, found 194.0991.

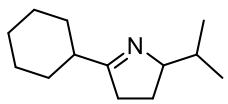
3-(2-isopropyl-3,4-dihydro-2*H*-pyrrol-5-yl)pyridine



2m

Purified by column chromatography (PE/EA = 2:1), colorless oil (13.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.65 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.02 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.10 – 2.77 (m, 2H), 2.25 – 2.04 (m, 1H), 2.00 – 1.86 (m, 1H), 1.75 – 1.63 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 151.1, 149.1, 134.8, 130.5, 123.4, 79.3, 35.2, 33.5, 25.2, 19.9, 18.5. HRMS-ESI: calcd for $C_{12}H_{17}N_2^+$ ([M + H$^+$]) *m*/*z* 189.1386, found 189.1388.

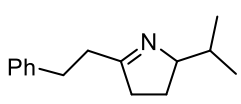
5-cyclohexyl-2-isopropyl-3,4-dihydro-2*H*-pyrrole



2n

Purified by column chromatography (PE/EA = 4:1), colorless oil (7.1 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.58 – 2.28 (m, 3H), 1.93 – 1.72 (m, 6H), 1.72 – 1.64 (m, 1H), 1.55 – 1.42 (m, 1H), 1.39 – 1.19 (m, 5H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 77.9, 42.8, 34.8, 33.0, 30.7, 30.6, 26.1, 26.0, 24.4, 19.8, 17.9. HRMS-ESI: calcd for $C_{13}H_{24}N^+$ ([M + H$^+$]) *m*/*z* 194.1903, found 194.1904.

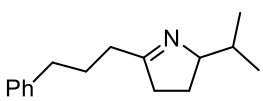
2-isopropyl-5-phenethyl-3,4-dihydro-2*H*-pyrrole



2o

Purified by column chromatography (PE/EA = 4:1), colorless oil (11.4 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.14 (m, 5H), 3.84 – 3.72 (m, 1H), 3.00 – 2.84 (m, 2H), 2.72 – 2.56 (m, 2H), 2.46 – 2.30 (m, 2H), 1.96 – 1.75 (m, 2H), 1.55 – 1.42 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 141.5, 128.4, 128.3, 126.0, 78.5, 37.7, 35.5, 33.1, 32.9, 25.0, 19.9, 18.2. HRMS-ESI: calcd for $C_{15}H_{22}N^+$ ([M + H$^+$]) *m*/*z* 216.1747, found 216.1748.

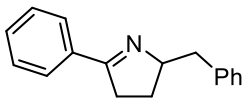
2-isopropyl-5-(3-phenylpropyl)-3,4-dihydro-2*H*-pyrrole



2p

Purified by column chromatography (PE/EA = 4:1), colorless oil (9.6 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.22 – 7.13 (m, 3H), 3.77 (dd, *J* = 7.6, 6.4 Hz, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.31 (m, 4H), 1.99 – 1.77 (m, 4H), 1.55 – 1.43 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 142.0, 128.5, 128.3, 125.8, 78.5, 37.3, 35.8, 33.5, 33.1, 28.6, 25.0, 19.9, 18.2. HRMS-ESI: calcd for $C_{16}H_{24}N^+$ ([M + H^+]) *m*/*z* 230.1903, found 230.1897.

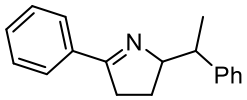
2-benzyl-5-phenyl-3,4-dihydro-2*H*-pyrrole



2q

Purified by column chromatography (PE/EA = 20:1), light yellow solid (22.2 mg, 94% yield), m.p. = 77.4 – 78.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.78 (m, 2H), 7.45 – 7.35 (m, 3H), 7.33 – 7.23 (m, 4H), 7.23 – 7.14 (m, 1H), 4.50 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.30 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.90 – 2.75 (m, 2H), 2.72 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.10 – 1.95 (m, 1H), 1.80 – 1.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 139.5, 134.7, 130.4, 129.5, 128.4, 128.3, 127.7, 126.1, 74.2, 42.5, 34.9, 27.9. HRMS-ESI: calcd for $C_{17}H_{18}N^+$ ([M + H^+]) *m*/*z* 236.1434, found 236.1441.

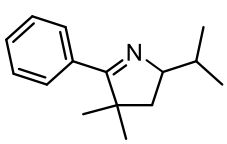
5-phenyl-2-(1-phenylethyl)-3,4-dihydro-2*H*-pyrrole



2r

Purified by column chromatography (PE/EA = 20:1), colorless oil (16.9 mg, 68% yield), d.r. = 1.5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 2H), 7.45 – 7.32 (m, 3H), 7.31 – 7.23 (m, 4H), 7.22 – 7.12 (m, 1H), 4.49 (dd, *J* = 14.4, 6.8 Hz, 0.6H), 4.36 (dd, *J* = 14.4, 6.8 Hz, 0.4H), 3.35 – 3.20 (m, 0.6H), 2.94 – 2.56 (m, 2.4H), 2.00 – 1.84 (m, 1H), 1.77 – 1.65 (m, 0.6H), 1.60 – 1.48 (m, 1.6H), 1.34 (d, *J* = 6.8 Hz, 1.8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 172.6, 144.9, 144.4, 134.9, 134.8, 130.3, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 126.2, 126.1, 78.8, 78.5, 46.1, 44.3, 35.3, 34.9, 27.0, 25.0, 19.9, 16.4. HRMS-ESI: calcd for $C_{18}H_{20}N^+$ ([M + H^+]) *m*/*z* 250.1590, found 250.1581.

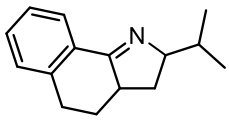
2-isopropyl-4,4-dimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrole



2t

Purified by column chromatography (PE/EA = 20:1), colorless oil (10.1 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 2H), 7.35 – 7.25 (m, 3H), 3.70 (dt, *J* = 9.2, 6.8 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.51 (dd, *J* = 12.4, 9.2 Hz, 1H), 1.28 (s, 3H), 1.23 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 134.2, 128.2, 127.1, 126.9, 72.9, 49.2, 43.9, 32.3, 26.0, 25.0, 19.2, 17.6. HRMS-ESI: calcd for $C_{15}H_{22}N^+$ ([M + H^+]) *m*/*z* 216.1747, found 216.1740.

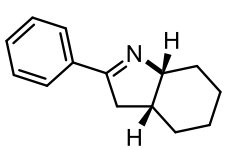
2-isopropyl-3,3a,4,5-tetrahydro-2*H*-benzo[*g*]indole



2u

Purified by column chromatography (PE/EA = 20:1), light yellow oil (19.4 mg, 91% yield), d.r. = 2.4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.94 (m, 1H), 7.35 – 7.02 (m, 3H), 4.11 (t, *J* = 7.2 Hz, 0.3H), 3.65 – 3.53 (m, 0.7H), 3.03 – 2.87 (m, 1H), 2.87 – 2.73 (m, 2H), 2.23 – 2.09 (m, 1.7H), 2.08 – 1.96 (m, 0.3H), 1.94 – 1.74 (m, 1H), 1.60 – 1.48 (m, 1.3H), 1.23 – 1.16 (m, 0.6H), 1.07 (d, *J* = 6.8 Hz, 2H), 0.92 (d, *J* = 6.8 Hz, 1H), 0.85 (d, *J* = 6.8 Hz, 2H), 0.81 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.7, 140.9, 140.9, 130.5, 130.4, 130.4, 130.3, 128.8, 126.4, 126.3, 126.1, 125.9, 77.4, 77.2, 47.3, 46.7, 33.8, 33.4, 32.9, 31.9, 30.5, 30.1, 30.0, 29.7, 20.6, 19.8, 18.7, 18.4. HRMS-ESI: calcd for $C_{15}H_{20}N^+$ ([M + H^+]) *m*/*z* 214.1590, found 214.1582.

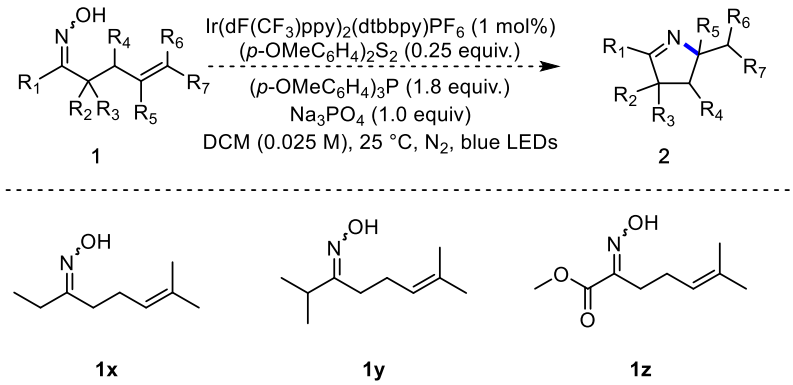
(3a*R*)-2-phenyl-3a,4,5,6,7,7a-hexahydro-3*H*-indole



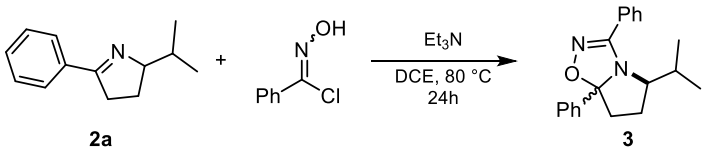
2v

Purified by column chromatography (PE/EA = 20:1), colorless oil (17.3 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.65 (m, 2H), 7.45 – 7.25 (m, 3H), 3.91 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.82 (ddd, *J* = 16.0, 7.2, 1.6 Hz, 1H), 2.64 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.40 – 2.20 (m, 1H), 1.83 (dd, *J* = 12.0, 5.6 Hz, 2H), 1.72 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.32 – 1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 135.3, 130.3, 128.4, 127.4, 70.0, 41.5, 36.9, 29.2, 27.4, 23.0, 22.1. HRMS-ESI: calcd for $C_{14}H_{18}N^+$ ([M + H^+]) *m*/*z* 200.1434, found 200.1425.

3.8 Unsuccessful oximes

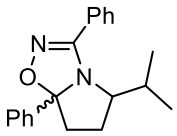


3.9 Further transformation of the products



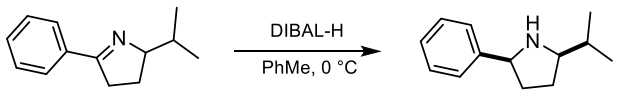
To an oven-dried tube, was added **2a** (56.1 mg, 0.3 mmol), *N*-hydroxybenzimidoyl chloride (93.3 mg, 0.6 mmol) and triethylamine (60.6 mg, 0.6 mmol). The system was evacuated and backfilled with N_2 for 3 time. Dry 1,2-dichloroethane (DCE) (3 mL) was added. The reaction mixture was stirred for 24 hours at 80 ºC. Then the crude product was purified by column chromatography on silica gel, eluting with petroleum ether–EtOAc (20:1) to give the **3** (68.9 mg, 75% yield), d.r. > 19:1.

5-isopropyl-3,7a-diphenyl-5,6,7,7a-tetrahydropyrrolo[1,2-*d*][1,2,4]oxadiazole



3

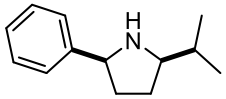
Purified by column chromatography (PE/EA = 20:1), yellow oil (68.9 mg, 75% yield), d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 8. Hz, 2H), 7.52 – 7.35 (m, 5H), 7.34 – 7.26 (m, 1H), 3.27 (t, *J* = 7.6 Hz, 1H), 2.67 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.52 – 2.33 (m, 1H), 2. 10 – 1.93 (m, 2H), 1.88 – 1.73 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 142.8, 130.6, 128.6, 128.6, 128.4, 128.2, 127.3, 125.5, 109.7, 71.7, 38.6, 31.2, 26.6, 21.2, 19.0. HRMS-ESI: calcd for $C_{20}H_{23}N_2O^+$ ([M + H^+]) *m*/*z* 307.1805, found 307.1806.



2a **4**

A dry tube equipped with a stirring bar was charged with **2a** (37.4 mg, 0.2 mmol) and then the tube was evacuated and refilled with N_2 (× 3). Dry toluene (2.8 mL) was added and the mixture was cooled to 0 ºC. Then diisobutylaluminium hydride (1.0 M solution in hexane, 0.6 mL, 0.6 mmol) was added by dropwise. The mixture was stirred for 1 hour at 0 ºC. Then the reaction was quenched with saturated aqueous NH_4Cl, extracted with DCM (5 mL × 3). The organic layers were separated and dried over Na_2SO_4. Finally, the crude product was purified by column chromatography on silica gel, eluting with petroleum ether–EtOAc (1:1) to give the **4** (37.1 mg, 98% yield).

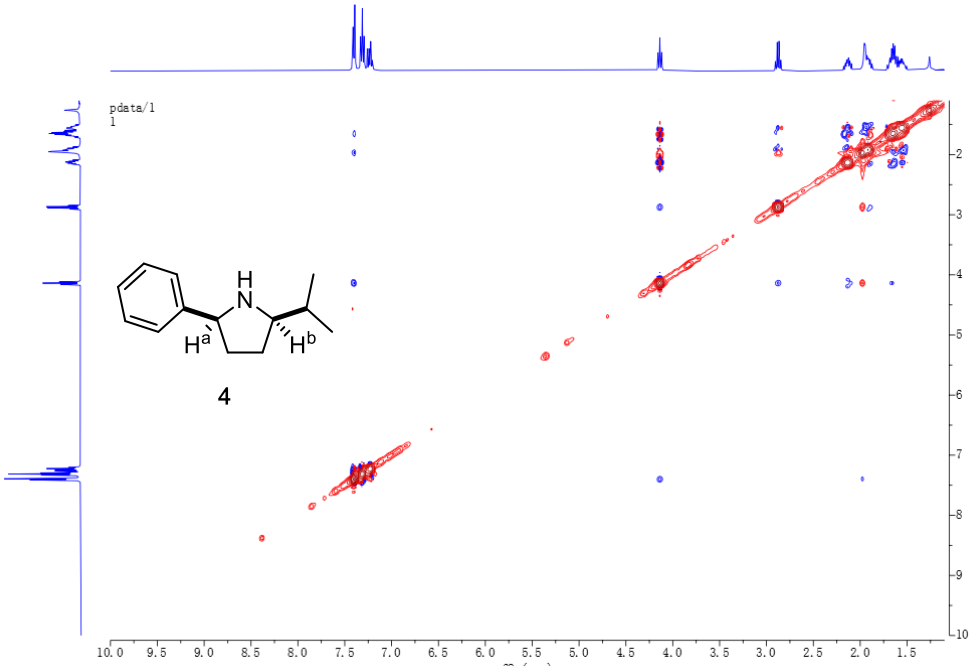
2-isopropyl-5-phenylpyrrolidine

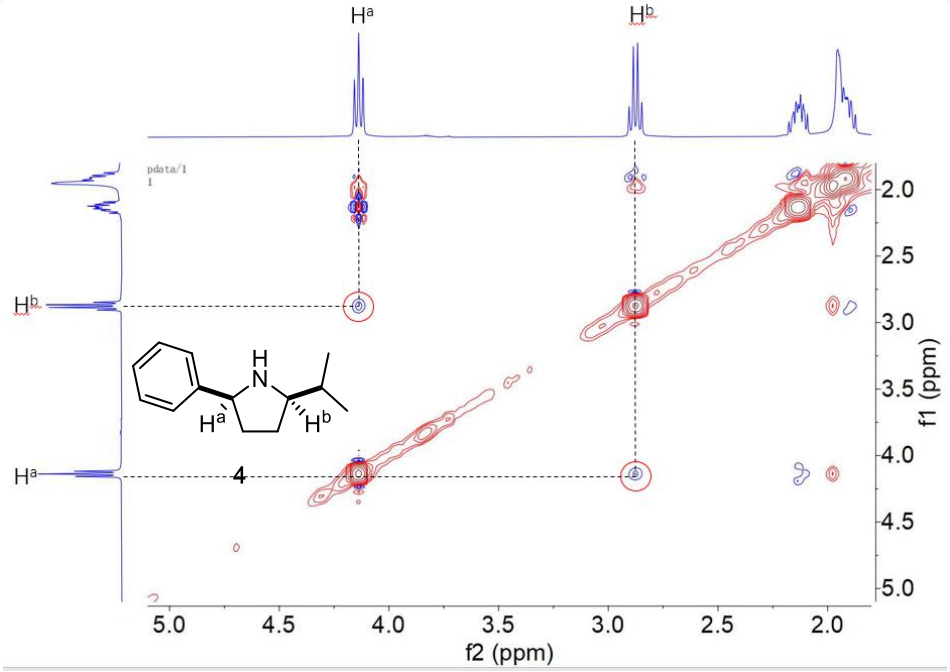


4

Purified by column chromatography (PE/EA = 1:1), colorless oil (37.1 mg, 98% yield), d.r. > 19:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.13 (t, *J* = 7.6 Hz, 1H), 2.87 (q, *J* = 7.6 Hz, 1H), 2.23 – 2.06 (m, 1H), 1.99 – 1.86 (m, 2H), 1.70 – 1.59 (m, 2H), 1.58 – 1.48 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 128.3, 126.8, 126.7, 65.8, 62.6, 34.1, 29.3, 20.4, 19.8. HRMS-ESI: calcd for $C_{13}H_{20}N^+$ ([M + H^+]) *m*/*z* 190.1590, found 190.1588.

2D NOESY ^{1}H NMR reveals that there is a correlation between H^a/H^b.





4. Mechanistic studies

4.1 Cyclic voltammetry experiments

Cyclic voltammograms were recorded using a CH Instruments 656E potentiostat and a glassy carbon working electrode, a Ag/AgCl reference electrode, and a Pt counter electrode. The voltammograms were recorded at room temperature under nitrogen atmosphere in 0.1 M tetrabutylammonium hexafluorophosphate in MeCN containing triaryl phosphines or oxime **1a** (1 mM). The scan rate was 100 mV s^{-1}. All potentials are reported in V vs SCE. The potential of the Fc/Fc^{+} redox couple, which was used as a standard, is 0.40 V vs SCE in acetonitrile under our conditions.[12]

Table S8. Oxidation potentials of compounds[a]

entry	**Compounds**	$E_{p/2}$
1	Ph_3P	1.16
2	$(4\text{-}OMeC_6H_4)_3P$	0.87
3	$(4\text{-}MeC_6H_4)_3P$	1.05
4	$(4\text{-}FC_6H_4)_3P$	1.23
5	**1a**	1.43
6[b]	**1a** + Na_3PO_4	1.44

[a] All potentials are given in volts versus the saturated calomel electrode (SCE). Measurements were performed in MeCN at room temperature. [b] 1.0 equiv. of Na_3PO_4 was added to the solution of **1a** in MeCN.

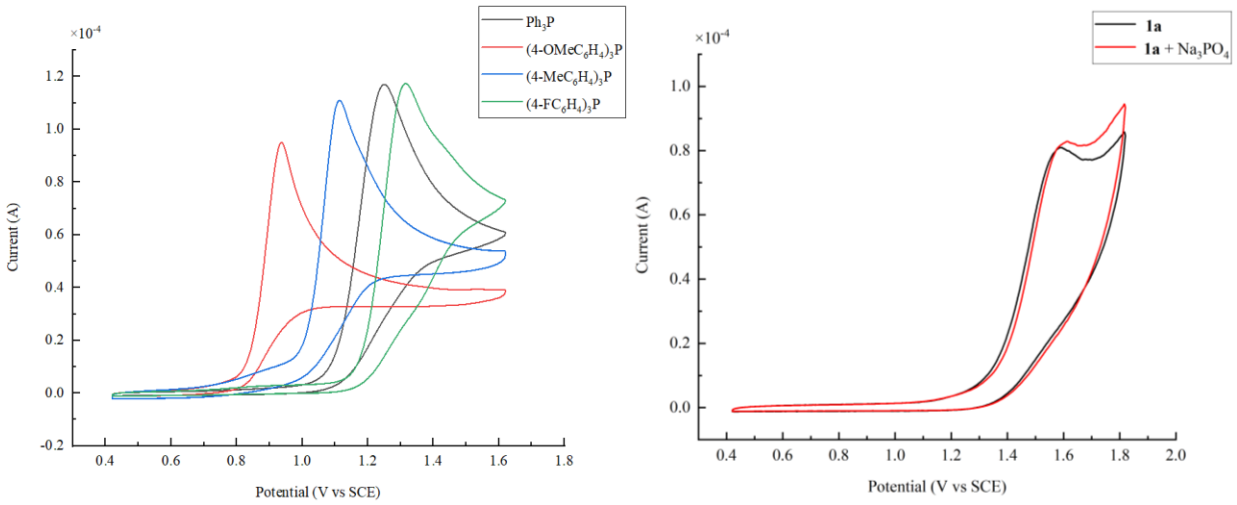


Figure S5. Cyclic voltammogram of triaryl phosphines and oxime **1a**.

4.2 Luminescence quenching experiments

Emission spectra were recorded on an Edinburgh Analytical Instruments FLS 920 fluorescence spectrophotometer. Rigorously degassed solutions of each component were prepared under nitrogen atmosphere prior to each set of experiments. In a typical experiment, a 2.5 × 10^{-6} M solution of Ir(dF(CF_3)ppy)$_2$(dtbbpy)PF_6 in DCM was added the appropriate amount of quencher in a quartz cuvette. The solutions were irradiated as a function of quencher concentration.[13]

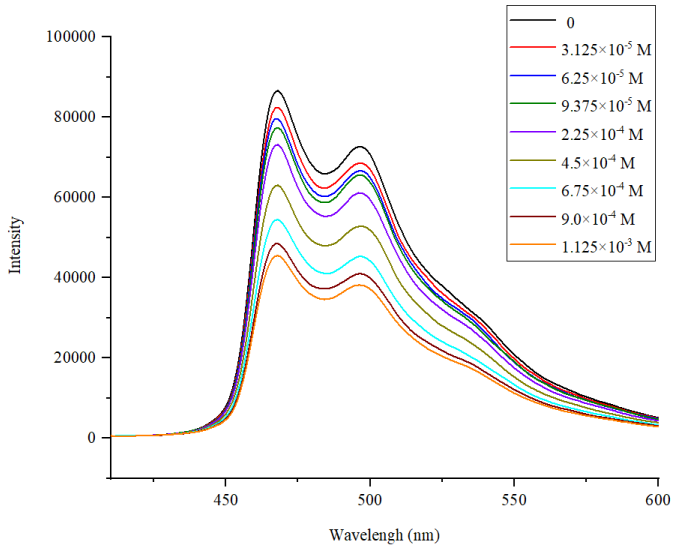


Figure S6. Luminescence quenching of Ir(dF(CF_3)ppy)$_2$(dtbbpy)PF_6 by (*p*-$OMeC_6H_4$)$_2S_2$.

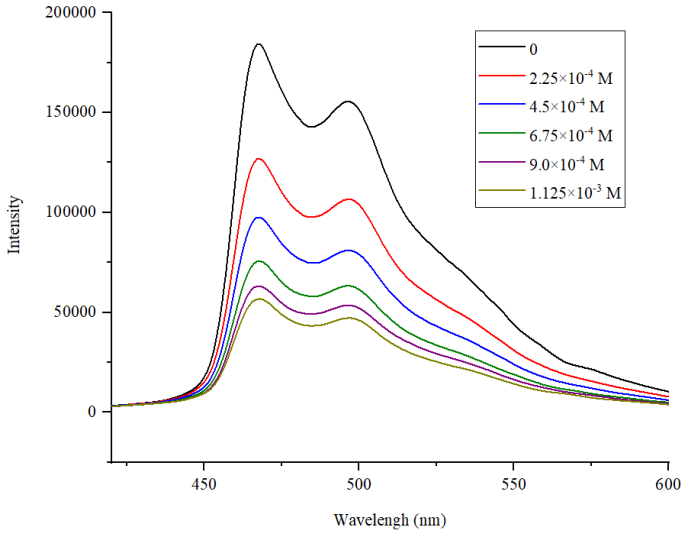


Figure S7. Luminescence quenching of $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ by (p-OMePh)$_3$P.

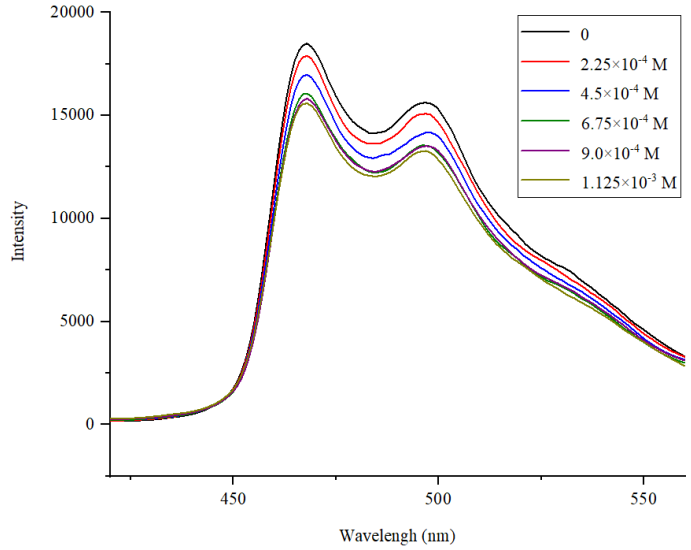


Figure S8. Luminescence quenching of $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ by **1a**.

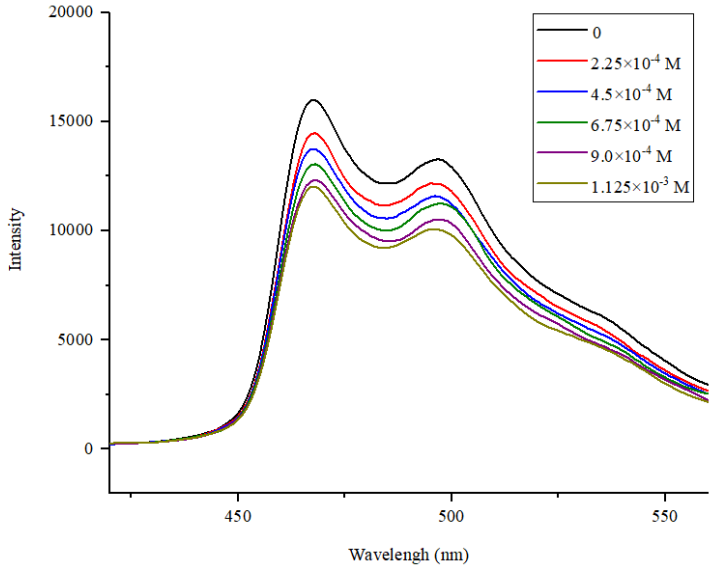


Figure S9. Luminescence quenching of Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$ by **1a** + Na$_3$PO$_4$.

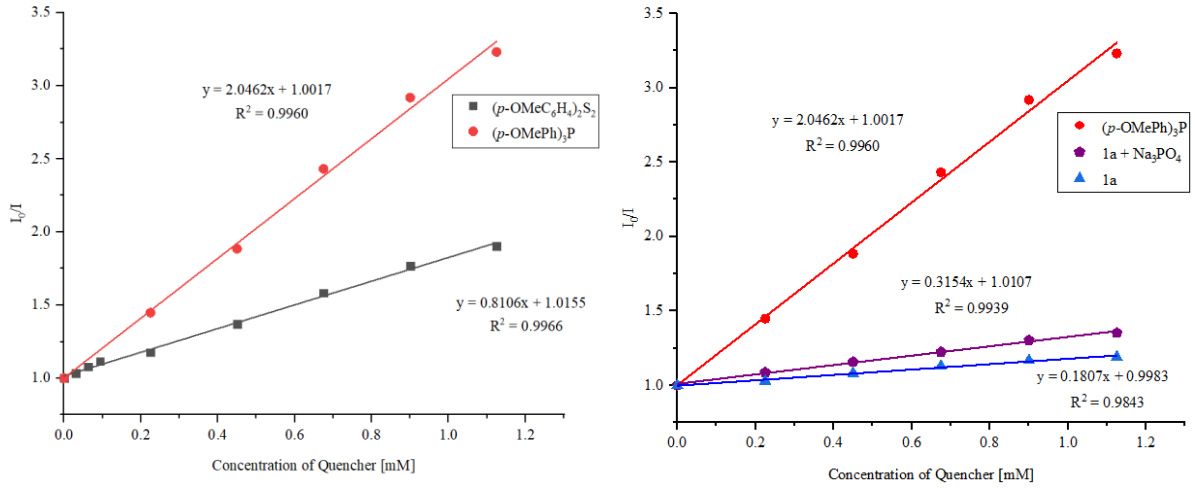
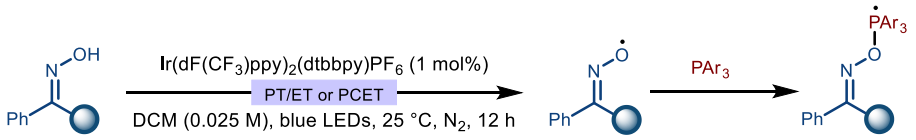


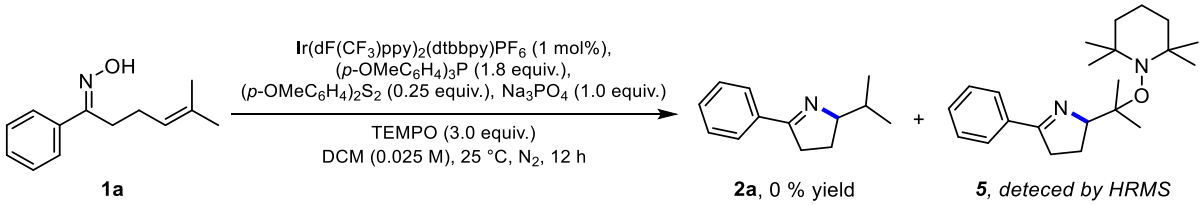
Figure S10. Stern-Volmer emission quenching of Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$.

These results suggested that (*p*-OMePh)$_3$P could decrease the luminescence significantly compared with other components (**Figure S10**). In addition, we found that the solutions containing varying concentrations of oxime **1a** and Na$_3$PO$_4$ (1:1), also resulted in a slight decrease in the emission intensity. These results suggested that O-centered radical may generated via PT/ET or PCET in the catalytic system (Scheme S1). According to a recent example, we could not rule out the formation of phosphoranyl radical via the addition of O-centered radical to PAr$_3$.[14]



Scheme S1. The formation of phosphoranyl radical from O-centered radical.

4.3 Radical inhibiting experiment



To an oven-dried reaction tube equipped with a stir bar was added **1a** (0.1 mmol, 1.0 equiv.), (*p*-$OMeC_6H_4)_2S_2$ (0.025 mmol, 0.25 equiv.), (*p*-$OMeC_6H_4)_3P$ (0.18 mmol, 1.8 equiv.), Na_3PO_4 (1.0 equiv.), TEMPO (0.3 mmol, 3.0 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol%). The tube was sealed and placed under nitrogen before DCM (4 mL) was added. The reaction mixture was irradiated by a 10 W blue LED at 25 °C for 12 hours. ESI-MS analysis of the crude reaction mixture was performed and the radical trapped product was successfully detected (**Figure S11**). HRMS-ESI: calcd for $C_{22}H_{35}N_2O^+$ ([M + H^+]) *m*/*z* 343.2744, found 343.2747.

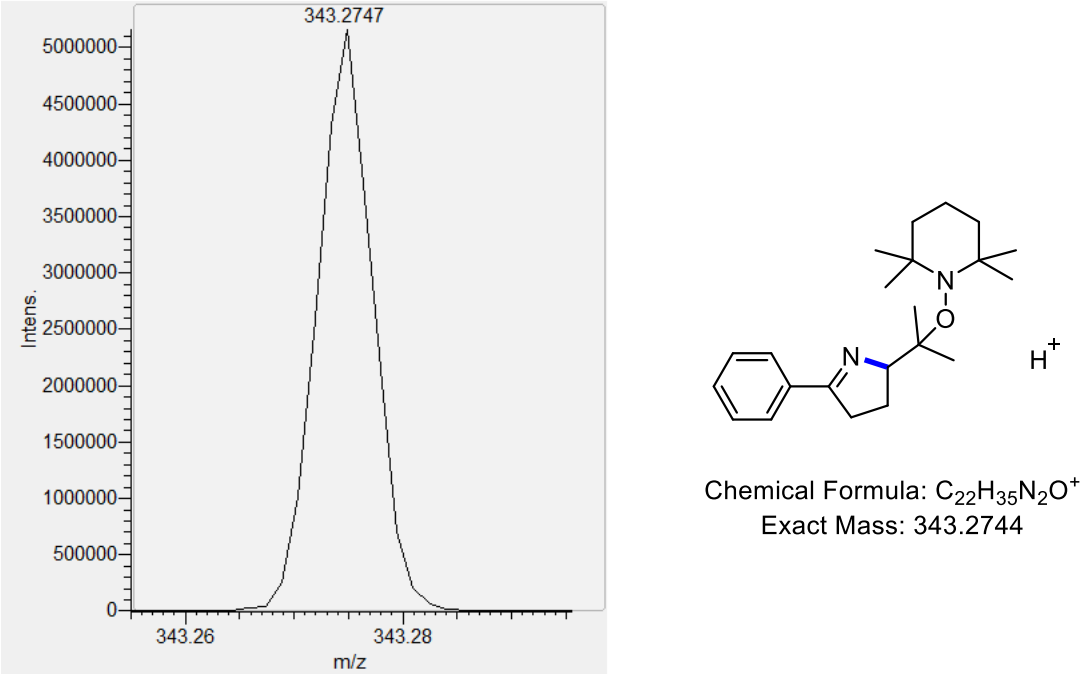
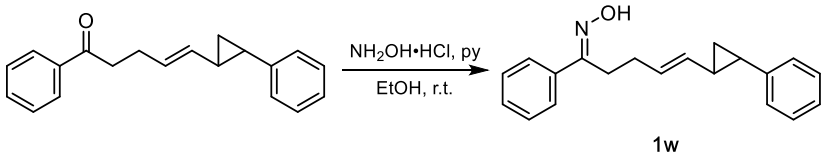


Figure S11. Crude ESI-MS of the TEMPO-trapping experiment.

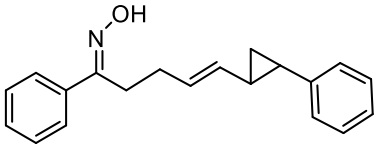
4.4 Radical clock experiments

4.4.1 Synthesis of (1*E*,4*E*)-1-phenyl-5-(2-phenylcyclopropyl)pent-4-en-1-one oxime



Add hydroxylamine hydrochloride (0.9 mmol) followed by pyridine (0.9 mmol) to a stirred solution of (*E*)-1-phenyl-5-(2-phenylcyclopropyl)pent-4-en-1-one[15] (0.83 mmol, 230 mg) in EtOH (2 mL). The reaction mixture was stired for 2~4 hours at room temperature. Then the reaction was quenched with saturated aqueous NH_4Cl, extracted with EtOAc (5 mL × 3). The organic layers were separated and dried over Na_2SO_4. Finally, the crude product was purified by column chromatography on silica gel, eluting with petroleum ether–Et_2O (20:1) to give the **1w** (180 mg, 95% yield).

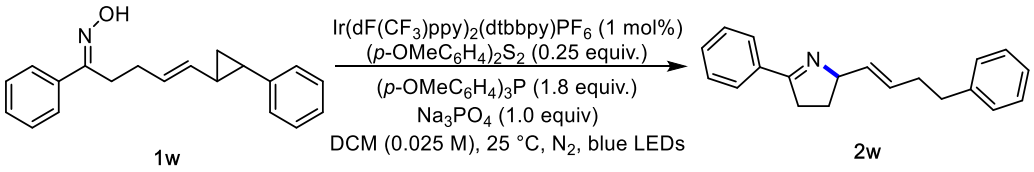
(1*E*,4*E*)-1-phenyl-5-(2-phenylcyclopropyl)pent-4-en-1-one oxime



1w

Purified by column chromatography (PE/EA = 20:1), white solid (180 mg, 95% yield), m.p. = 87.4 – 88.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (br, 1H), 7.70 – 7.50 (m, 2H), 7.48 – 7.30 (m, 3H), 7.30 – 7.18 (m, 2H), 7.18 – 7.08 (m, 1H), 7.06 – 6.95 (m, 2H), 5.68 – 5.45 (m, 1H), 5.32 – 5.08 (m, 1H), 2.97 – 2.76 (m, 2H), 2.40 – 2.20 (m, 2H), 1.90 – 1.75 (m, 1H), 1.67 – 1.55 (m, 1H), 1.18 – 1.05 (m, 1H), 1.05 – 0.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.6, 135.8, 133.1, 129.2, 128.6, 128.3, 127.6, 126.4, 125.7, 125.5, 29.1, 26.4, 26.3, 25.0, 16.6. HRMS-ESI: calcd for $C_{20}H_{22}NO^+$ ([M + H$^+$]) *m*/*z* 292.1696, found 292.1689.

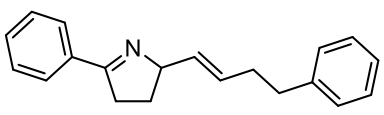
4.4.2 General procedure



1w 2w

To an oven-dried reaction tube equipped with a stir bar was added **1w** (0.1 mmol, 1.0 equiv.), (*p*-$OMeC_6H_4)_2S_2$ (0.025 mmol, 0.25 equiv.), (*p*-$OMeC_6H_4)_3P$ (0.18 mmol, 1.8 equiv.), Na_3PO_4 (1.0 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1 mol%). The tube was sealed and placed under nitrogen before DCM (4 mL) was added. The reaction mixture was irradiated by a 10 W blue LED at 25 °C for 12 hours. Then the reaction mixture was concentrated and purified through column chromatography to afford the desired product **2w** (2.7 mg, 10% yield).

(*E*)-5-phenyl-2-(4-phenylbut-1-en-1-yl)-3,4-dihydro-2*H*-pyrrole



2w

Purified by column chromatography (PE/EA = 20:1), light yellow oil (2.7 mg, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.70 (m, 2H), 7.45 – 7.28 (m, 3H), 7.25 – 7.17 (m, 2H), 7.15 – 7.05 (m, 3H), 5.80 – 5.60 (m, 1H), 5.58 – 5.40 (m, 1H), 4.62 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.05 – 2.90 (m, 1H), 2.90 – 2.75 (m, 1H), 2.73 – 2.57 (m, 2H), 2.42 – 2.25 (m, 2H), 2.25 – 2.11 (m, 1H), 1.72 – 1.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 142.1, 134.4, 132.4, 130.6, 130.5, 128.5, 128.4, 128.3, 127.9, 125.8, 74.4, 35.7, 35.1, 34.4, 29.7. HRMS-ESI: calcd for $C_{20}H_{22}N^+$ ([M + H$^+$]) *m*/*z* 276.1747, found 276.1738.

4.5 Oxidative quenching cycle

Given the fact that the disulfide could also quench the excited state of the iridium photocatalyst (**Figure S12**), an oxidative quenching cycle was proposed.

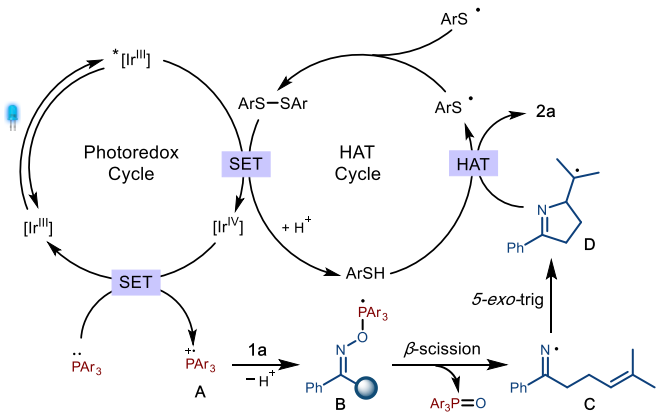


Figure S12. Oxidative quenching cycle.

5. References

[1] Y. Liu, X.-L. Chen, X.-Y. Li, S.-S. Zhu, S.-J. Li, Y. Song, L.-B. Qu and B. Yu, *J. Am. Chem. Soc.,* 2021, **143**, 964−972.

[2] X. Li, Y. Zhang, H. Chen, J. Sun and F. Feng, *ACS Appl. Mater. Interfaces,* 2016, **8**, 22756−22761.

[3] M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Complex. Chem. Mater.,* 2005, **17**, 5712−5719.

[4] K. Usami, E. Yamaguchi, N. Tada and A. Itoh, *Org. Lett.,* 2018, **20**, 5714−5717.

[5] X. Peng, B. M. K. Tong, H. Hirao and S. Chiba, *Angew. Chem.* 2014, **126**, 1990−1993.

[6] F. Chen, X.-L. Yang, Z.-W. Wu and B. Han, *J. Org. Chem.*, 2016, **81**, 3042−3050.

[7] X.-X. Peng, Y.-J. Deng, X.-L. Yang, L. Zhang, W. Yu and B. Han, *Org. Lett.,* 2014, **16**, 4650−4653.

[8] T. Cheng, S. Meng and Y. Huang, *Org. Lett.,* 2013, **15**, 1958−1961.

[9] J. Davies, N. S. Sheikh and D. Leonori, *Angew. Chem. Int. Ed.,* 2017, **56**, 13361−13365.

[10] C. Chen, Y. Bao, J. Zhao and B. Zhu, *Chem. Commun.,* 2019, **55**, 14697–14700.

[11] J. Davies, S. G. Booth, S. Essafi, R. A. W. Dryfe and D. Leonori, *Angew. Chem. Int. Ed.,* 2015, **54**, 14017−14021.

[12] L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil and D. Martin, *Angew. Chem. Int. Ed.,* 2021, **60**, 26783–26789.

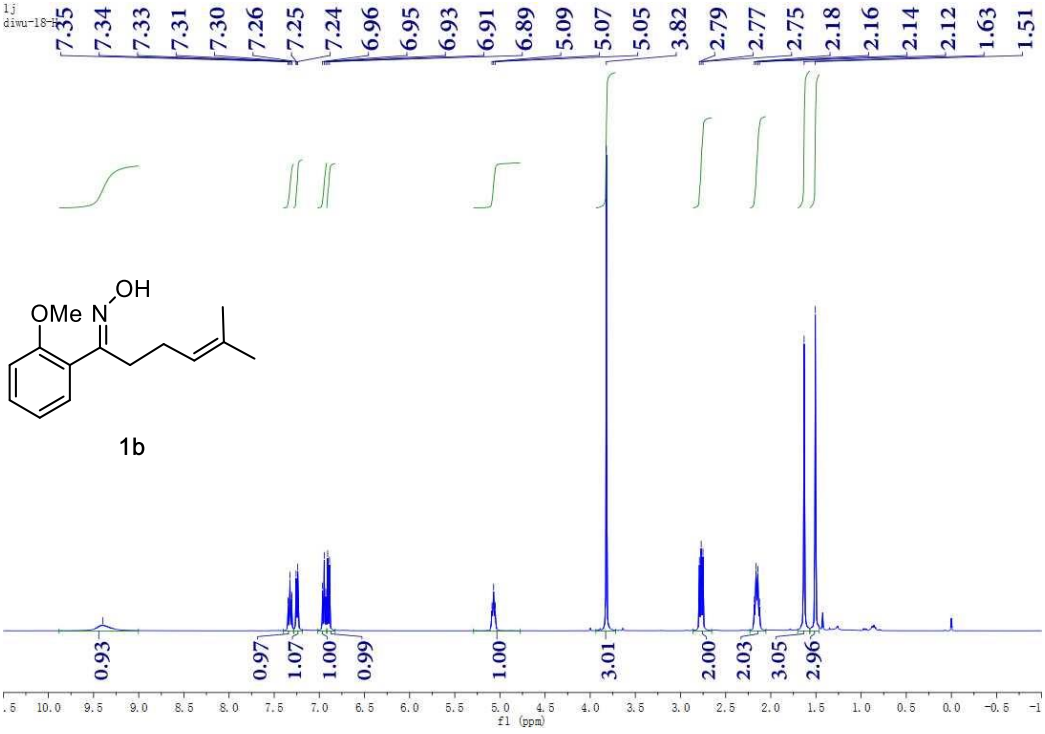
[13] M. Jiang, H. Li, H. Yang and H. Fu, *Angew. Chem. Int. Ed.*, 2017, **129**, 892 –897.

[14] J.-B. Han, A. Guo and X.-Y. Tang, *Chem. Eur. J.* 2019, **25**, 2989 – 2994.

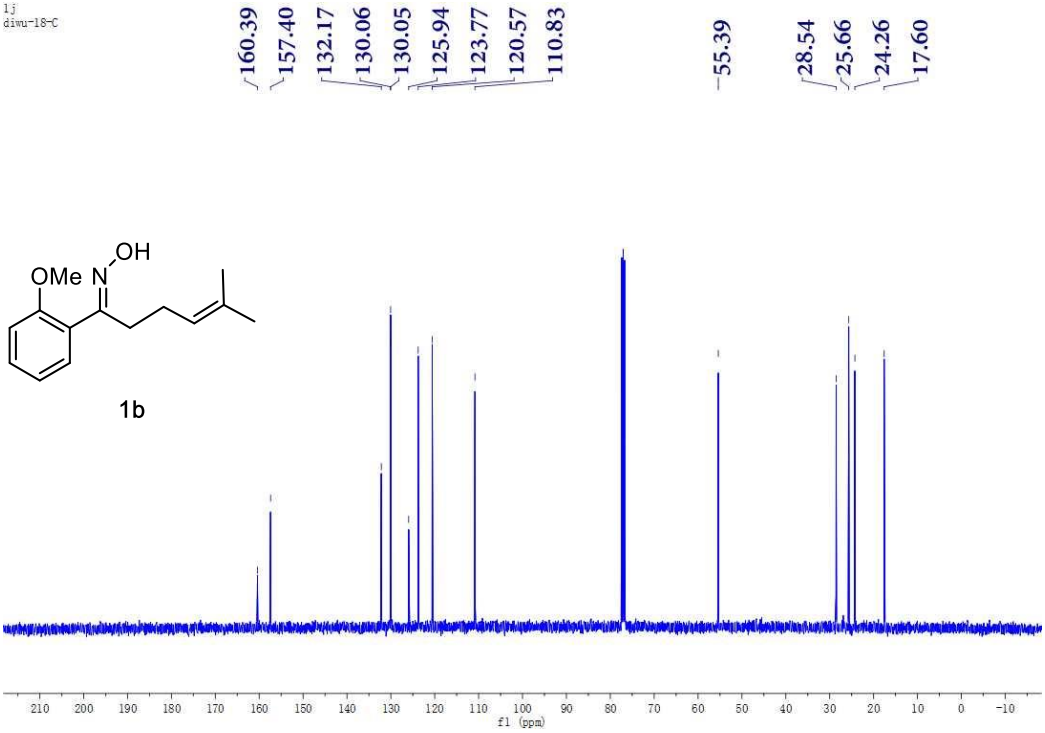
[15] W.-D. Liu, W. Lee, H. Shu, C. Xiao, H. Xu, X. Chen, Kendall N. Houk and J. Zhao, *J. Am. Chem. Soc.,* 2022, **144**, 22767–22777.

6. Copy of ^{1}H NMR, ^{13}C and ^{19}F NMR spectra

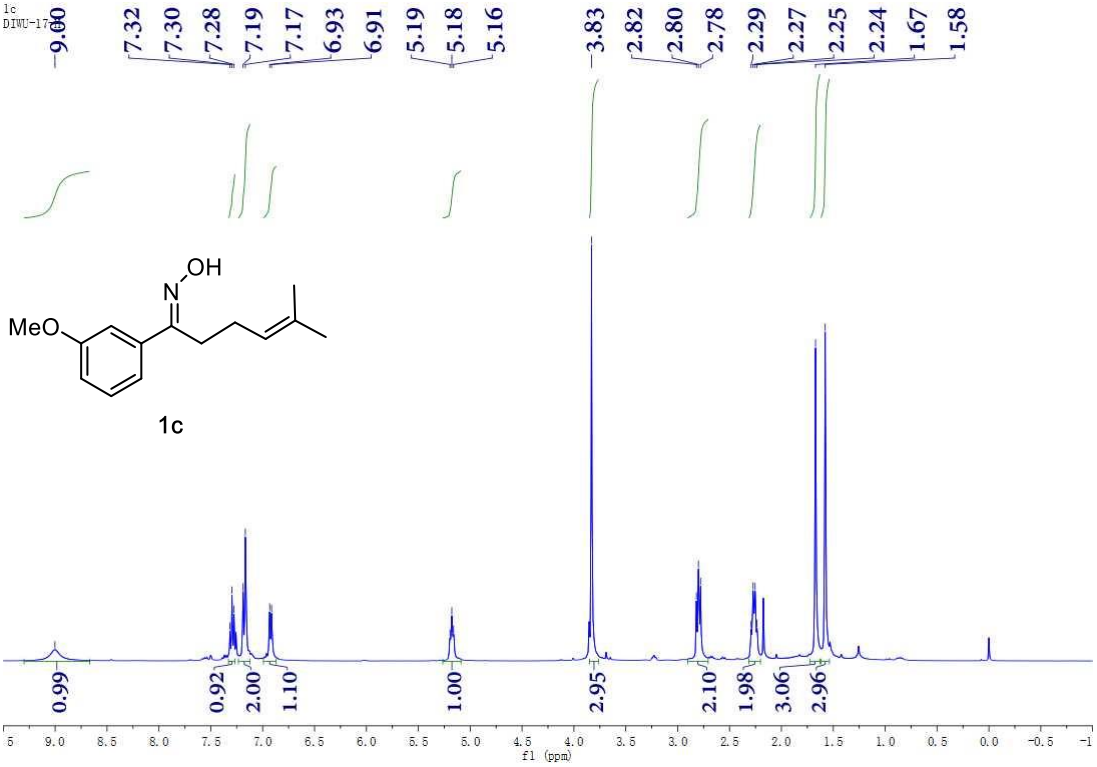
^{1}H NMR Spectrum of **1b** (400 MHz; $CDCl_3$)



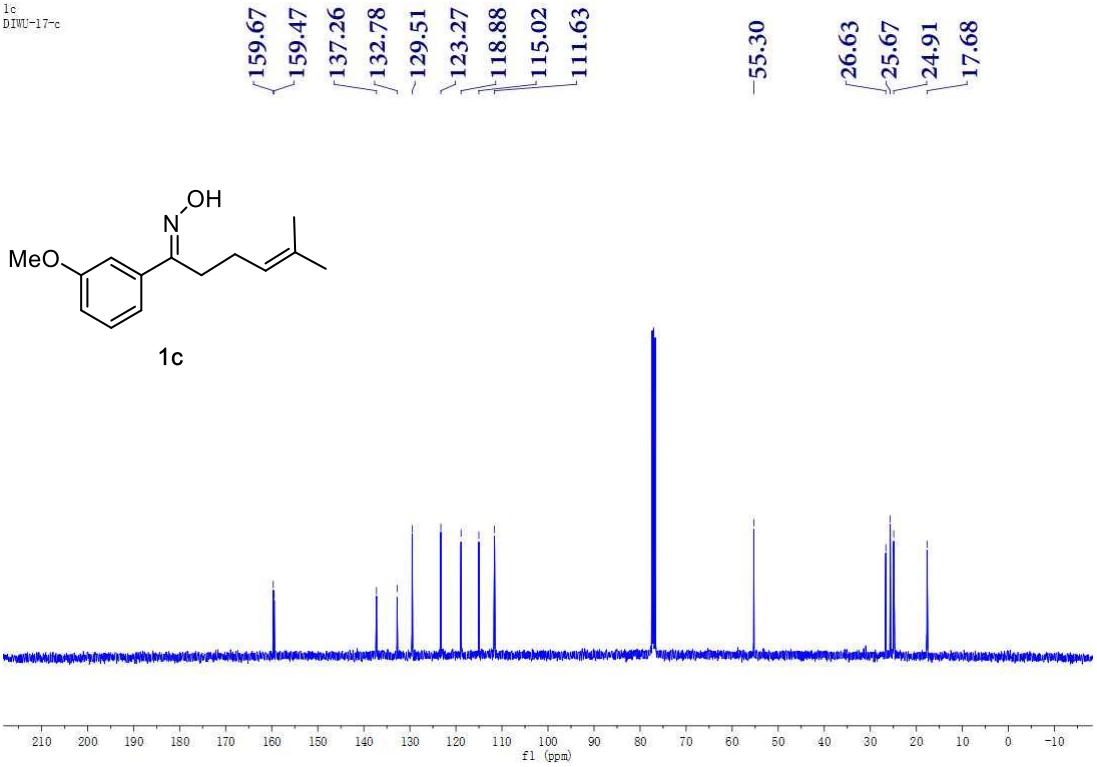
^{13}C NMR Spectrum of **1b** (100 MHz; $CDCl_3$)



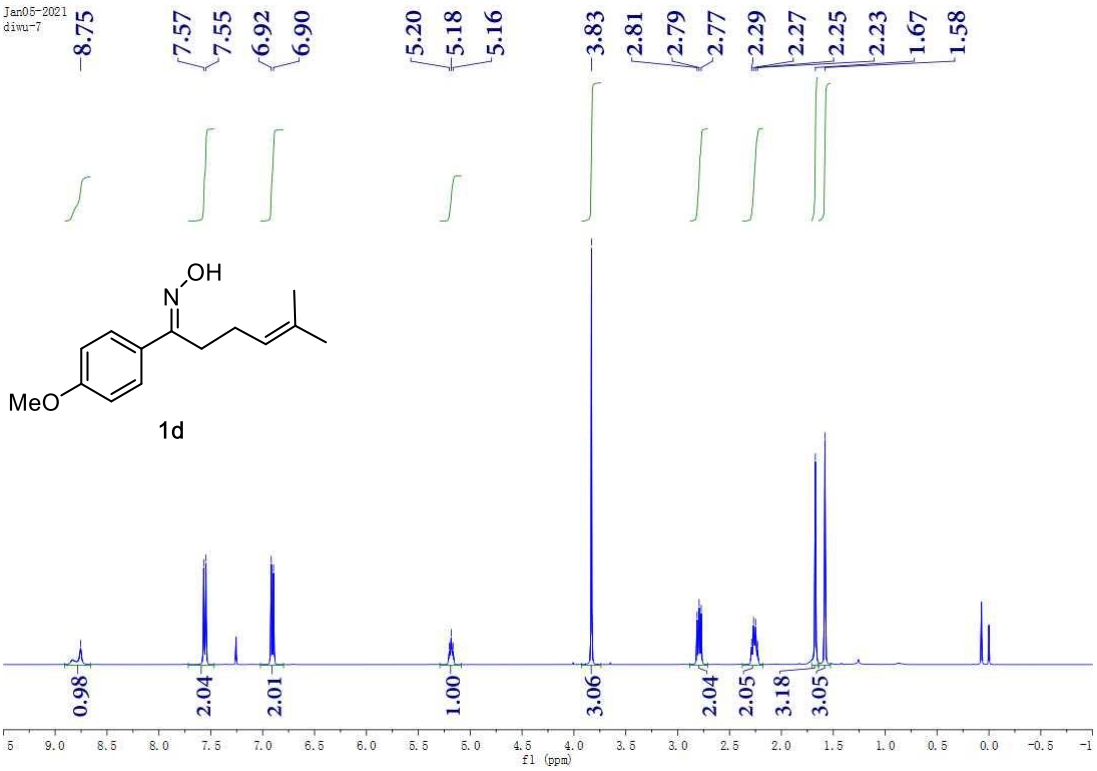
^{1}H NMR Spectrum of **1c** (400 MHz; $CDCl_3$)



^{13}C NMR Spectrum of **1c** (100 MHz; $CDCl_3$)



^{1}H NMR Spectrum of **1d** (400 MHz; $CDCl_3$)



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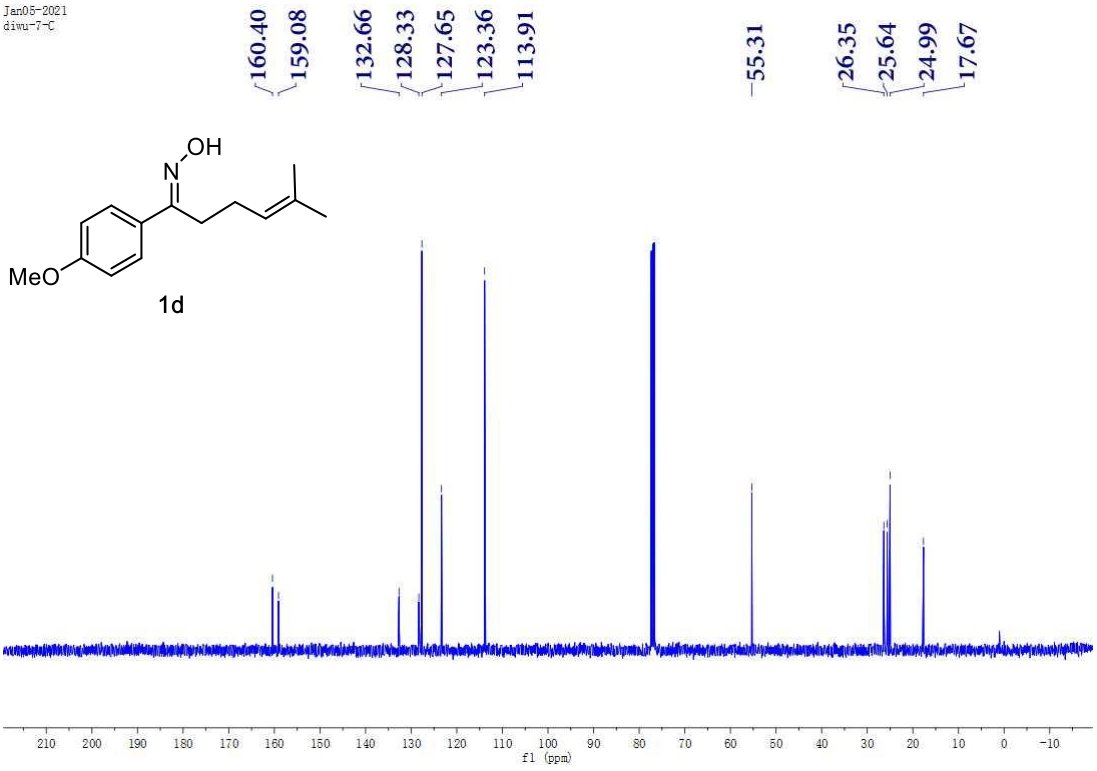
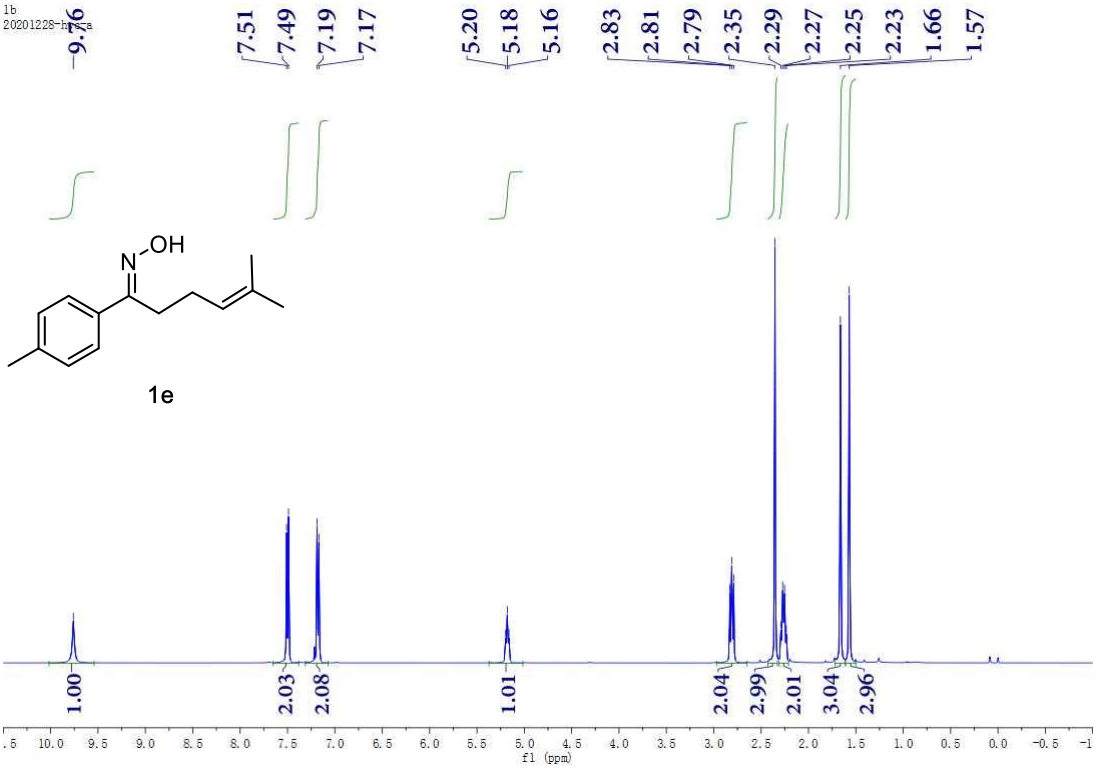
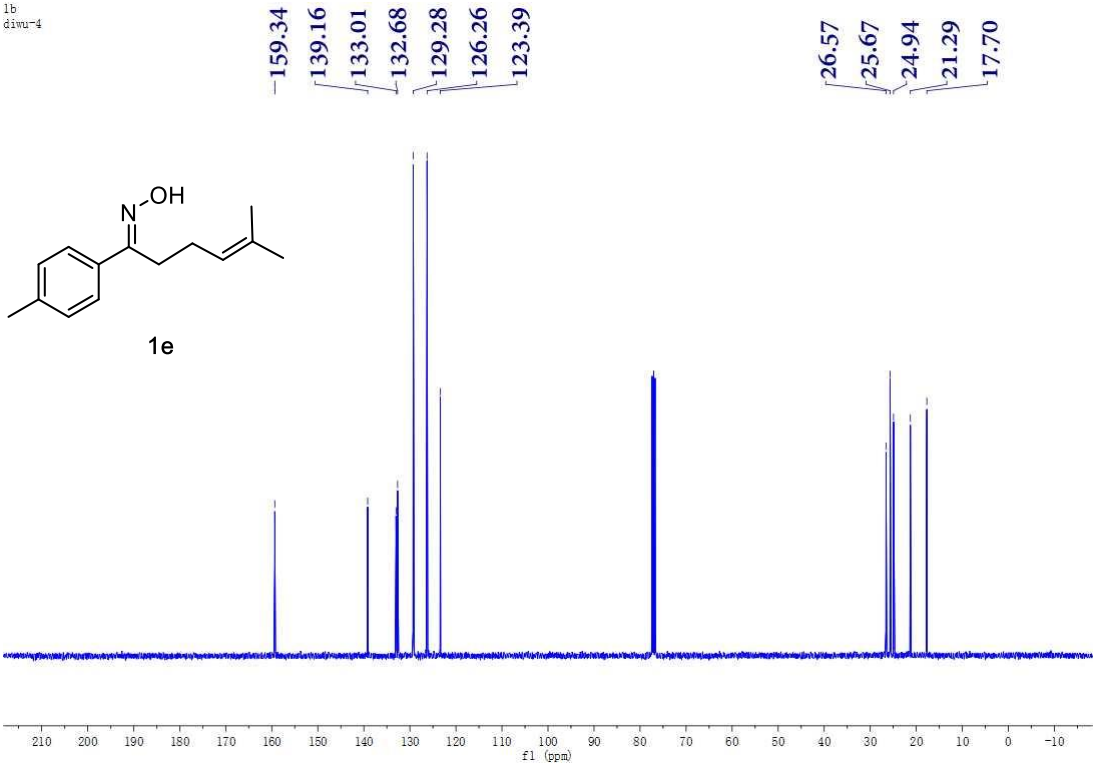


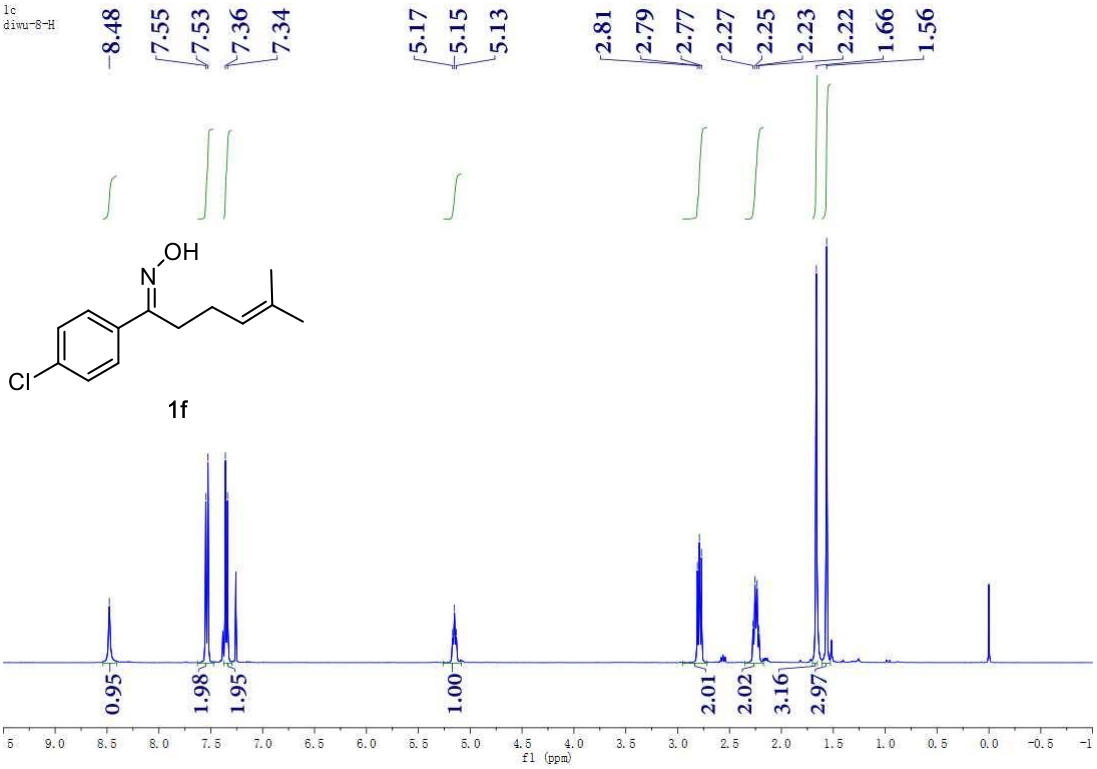
^{1}H NMR Spectrum of **1e** (400 MHz; $CDCl_3$)



^{13}C NMR Spectrum of **1e** (100 MHz; $CDCl_3$)



^{1}H NMR Spectrum of **1f** (400 MHz; $CDCl_3$)



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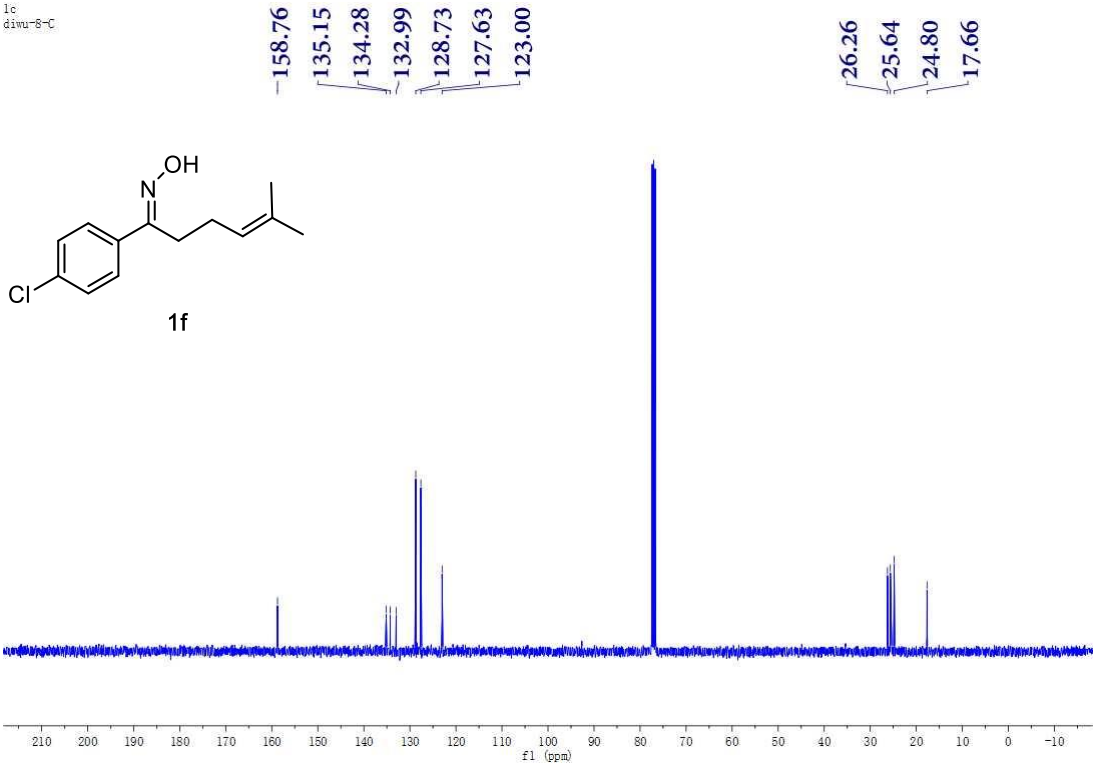

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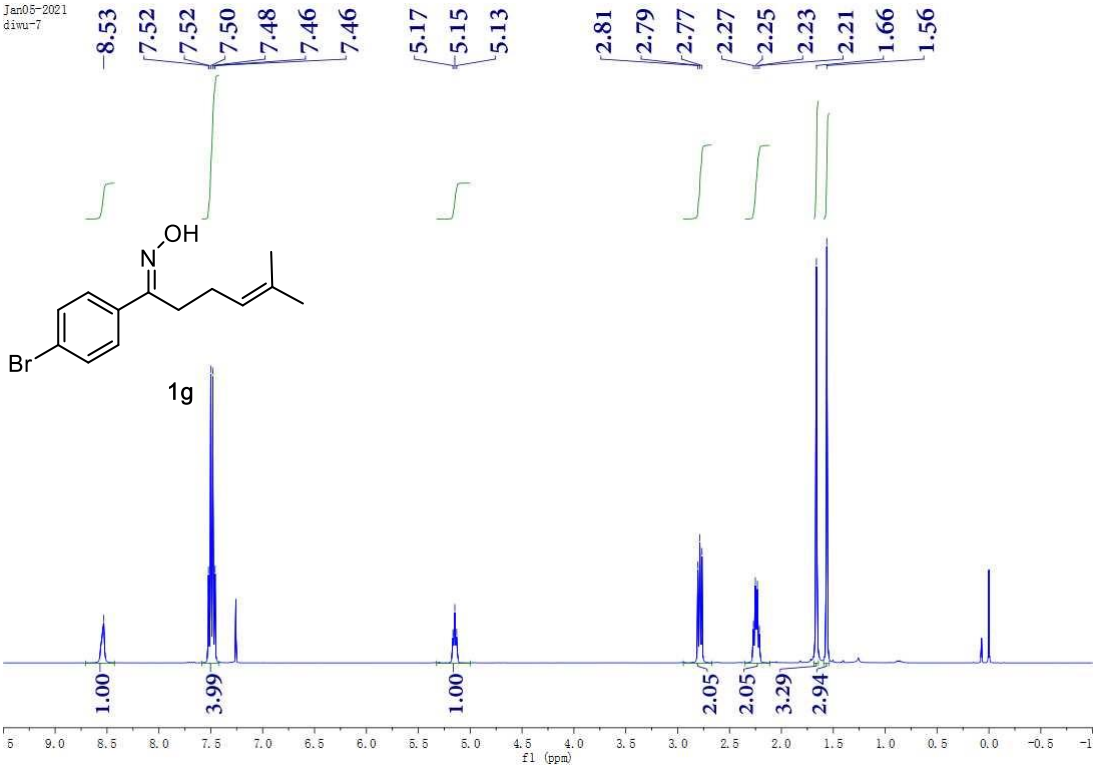

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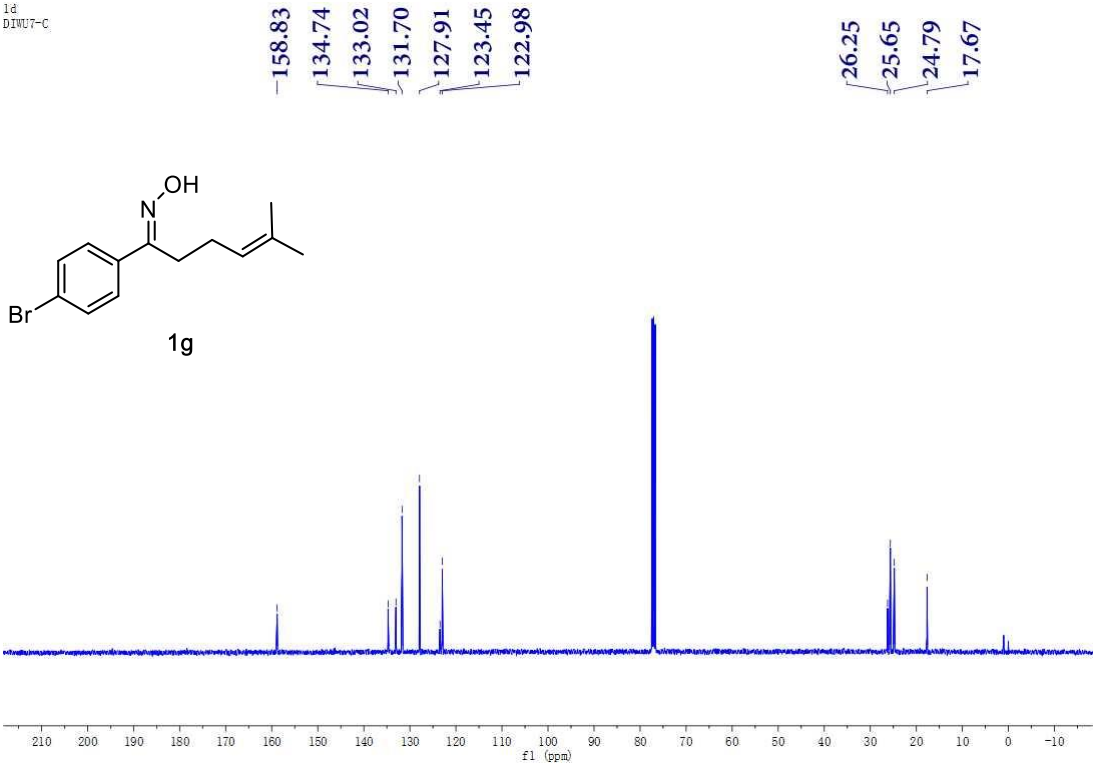
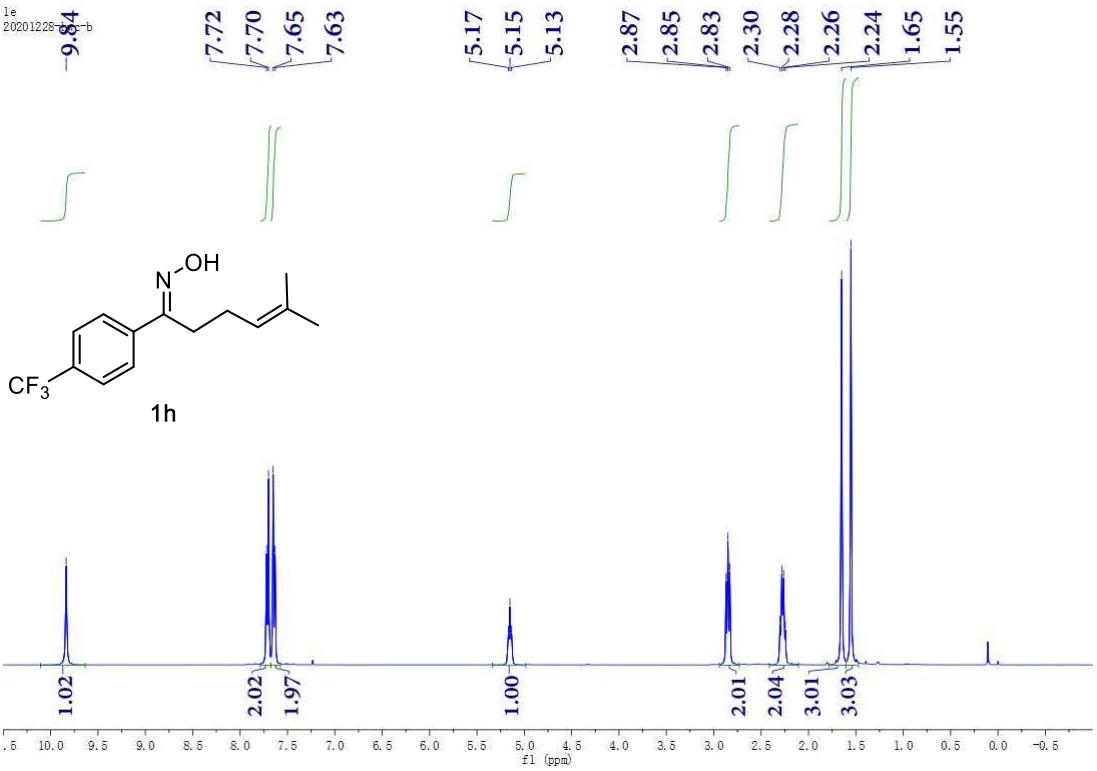


^{1}H NMR Spectrum of **1h** (400 MHz; $CDCl_3$)



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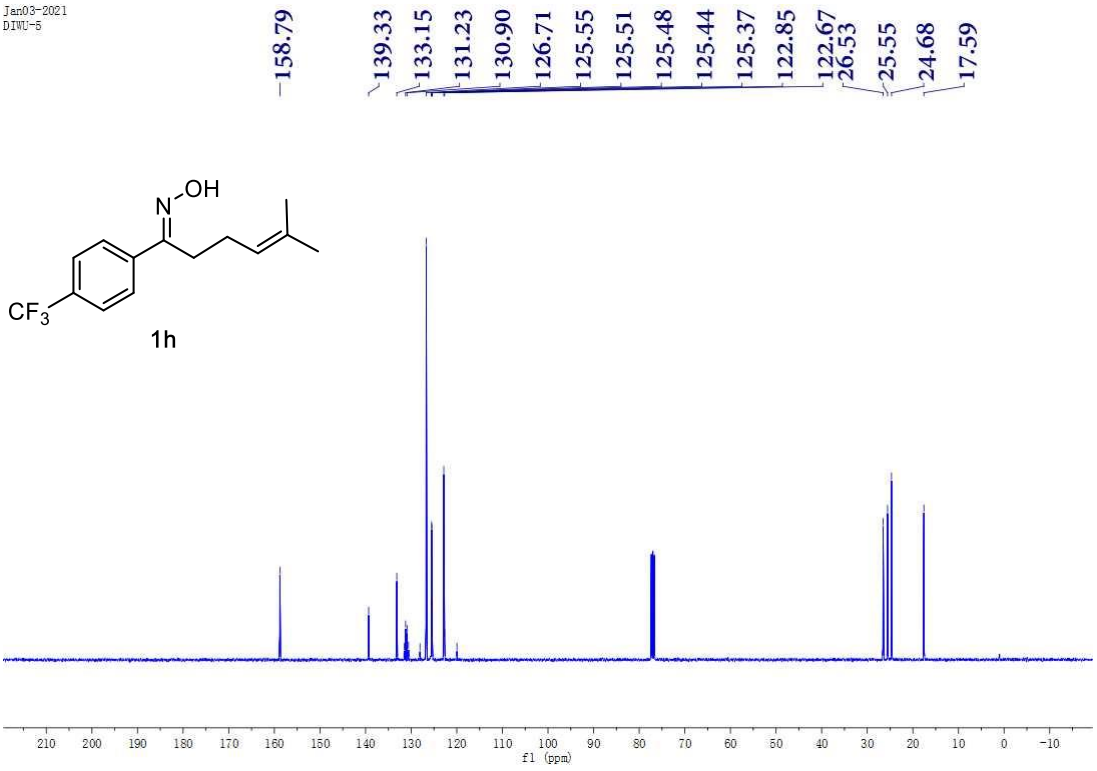
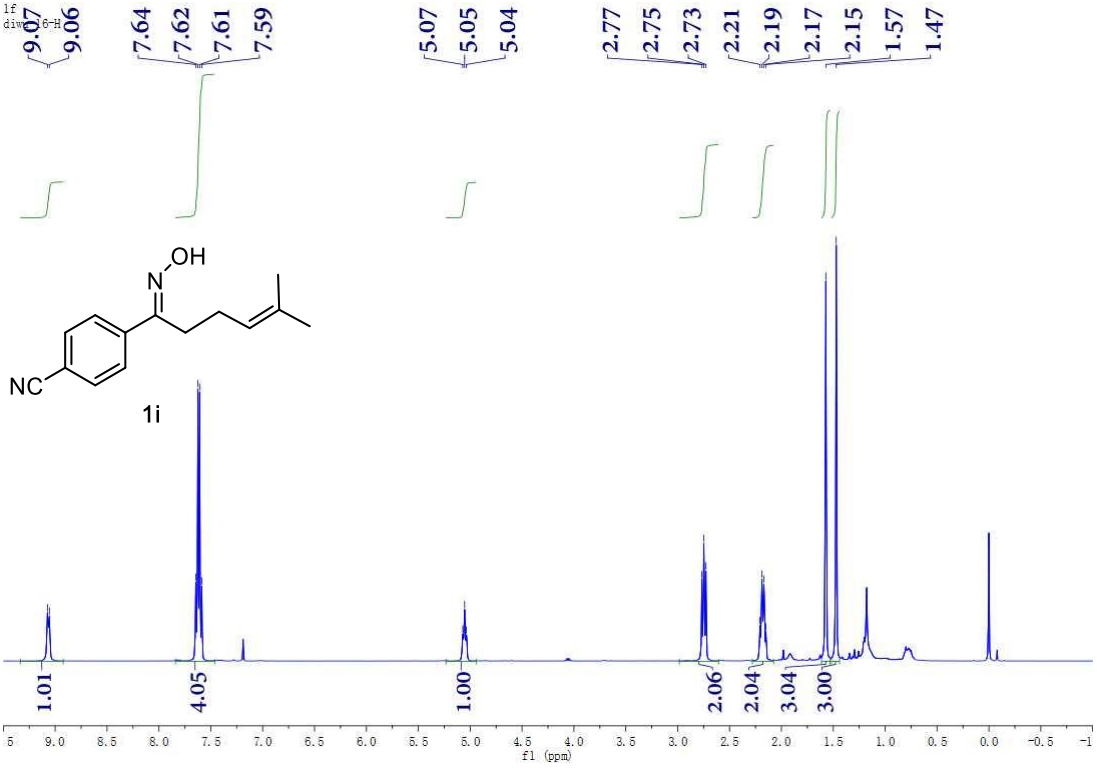
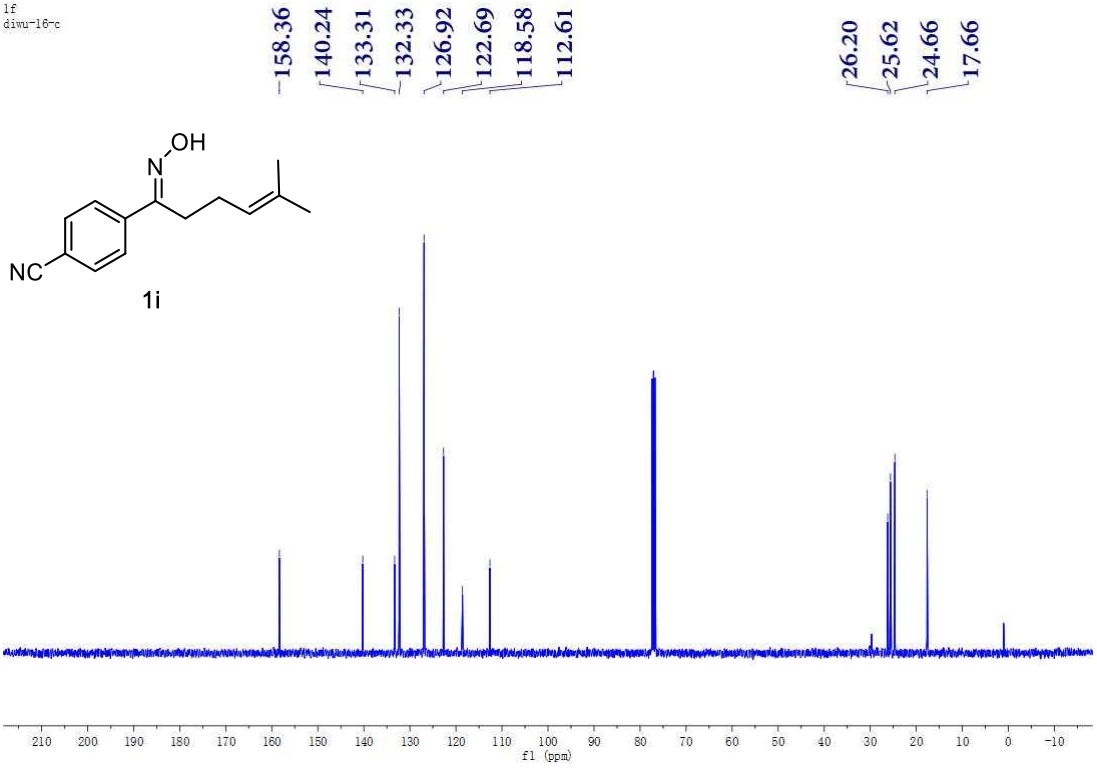


^{19}F NMR Spectrum of **1h** (376 MHz; $CDCl_3$)

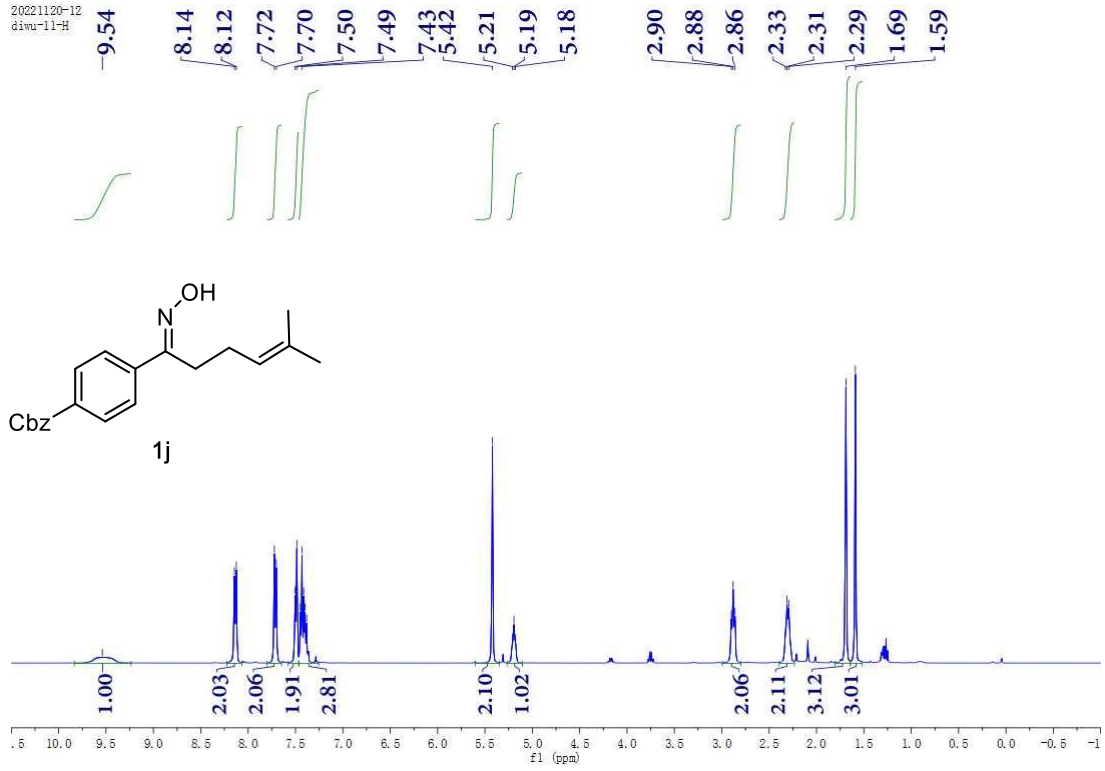
^{1}H NMR Spectrum of **1i** (400 MHz; $CDCl_3$)]\



^{13}C NMR Spectrum of **1i** (100 MHz; $CDCl_3$)



^{1}H NMR Spectrum of **1j** (400 MHz; $CDCl_3$)



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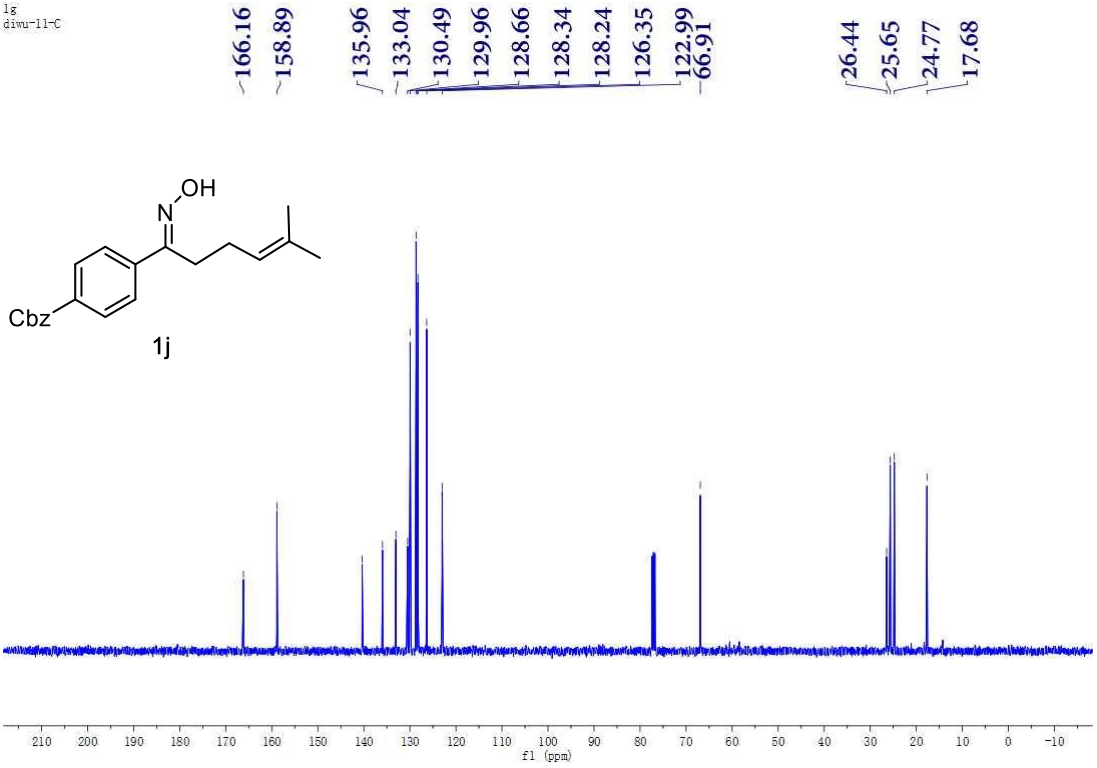
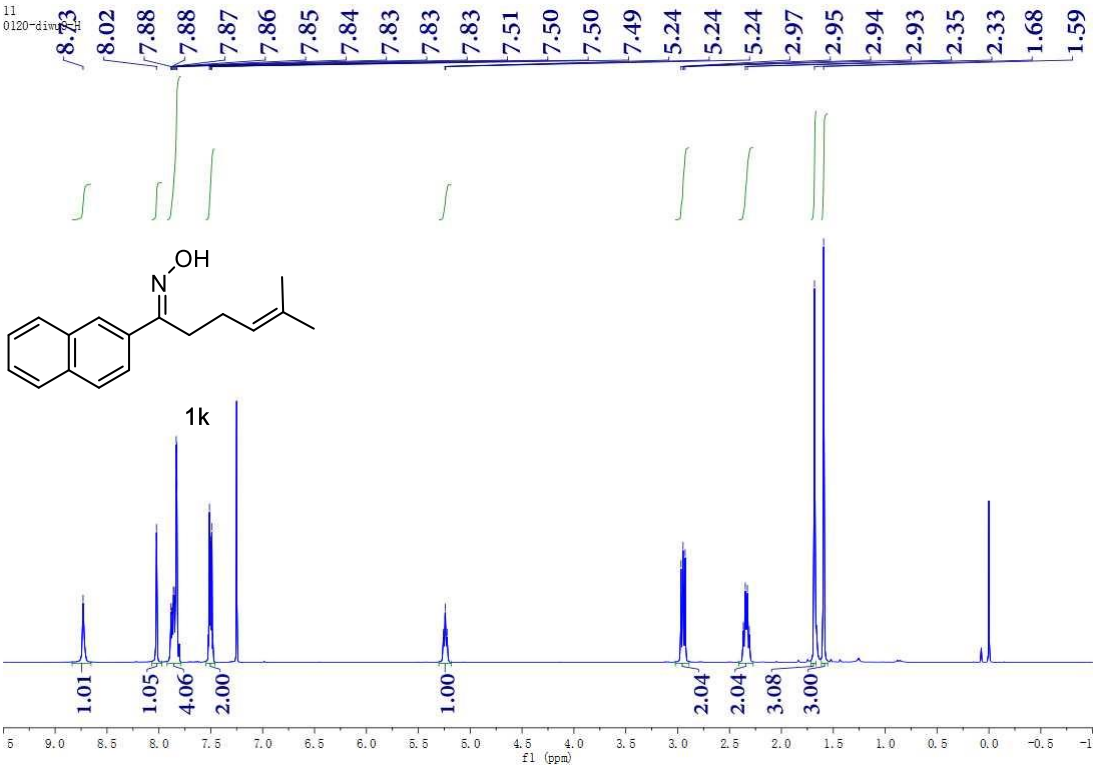
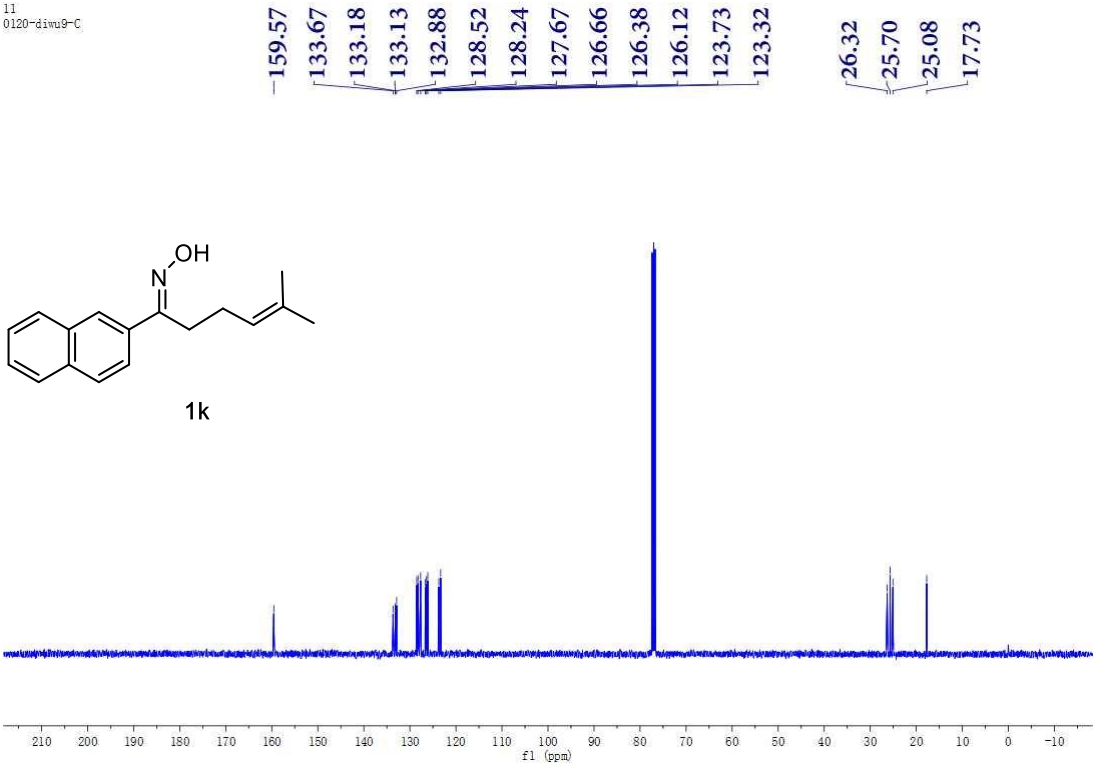


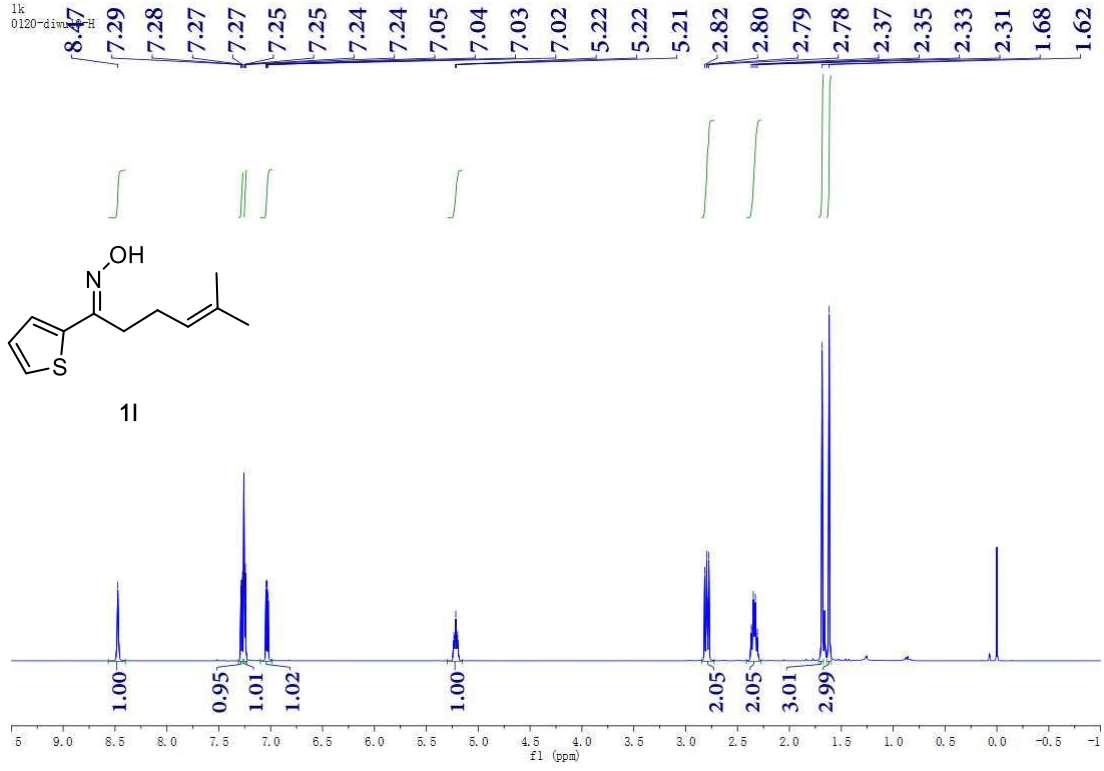
^{1}H NMR Spectrum of **1k** (400 MHz; $CDCl_3$)



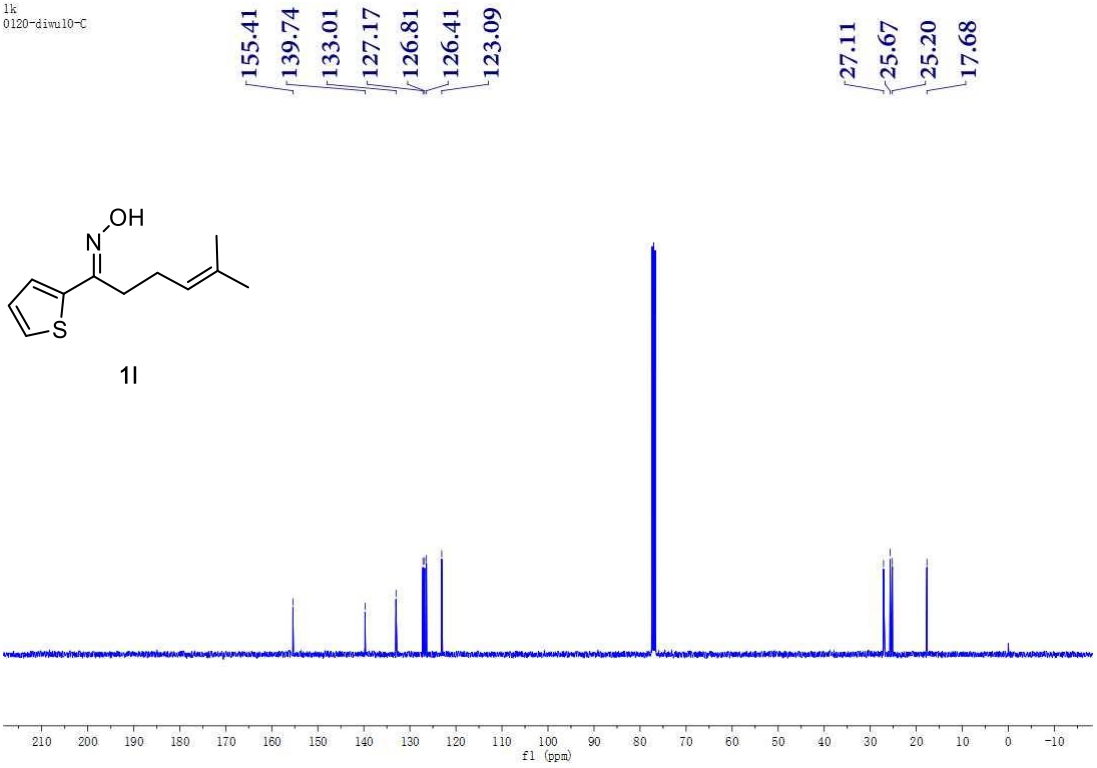
^{13}C NMR Spectrum of **1k** (100 MHz; $CDCl_3$)



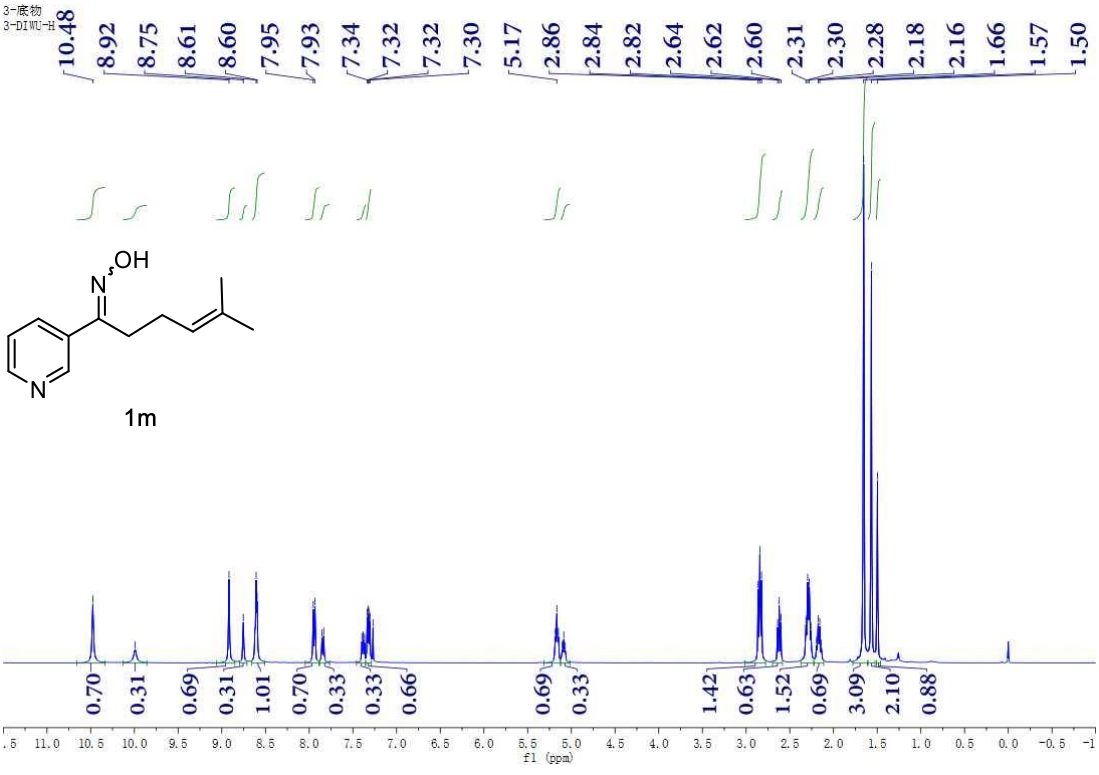
^{1}H NMR Spectrum of **1l** (400 MHz; $CDCl_3$)



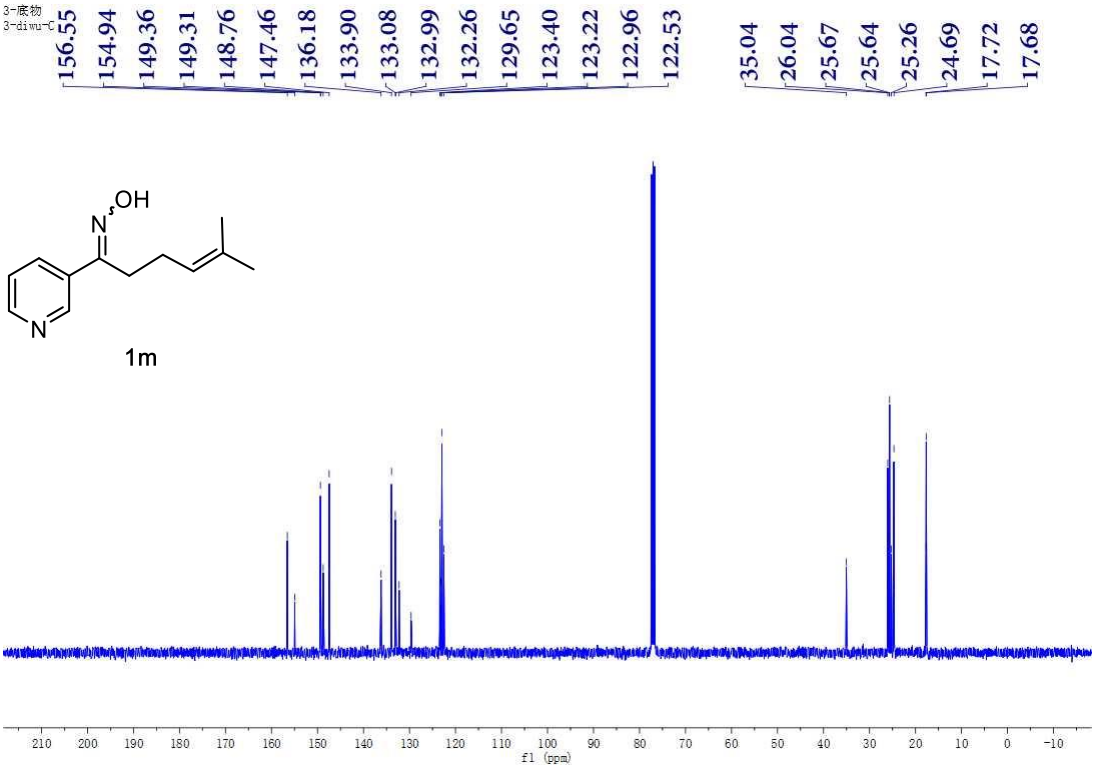
^{13}C NMR Spectrum of **1l** (100 MHz; $CDCl_3$)



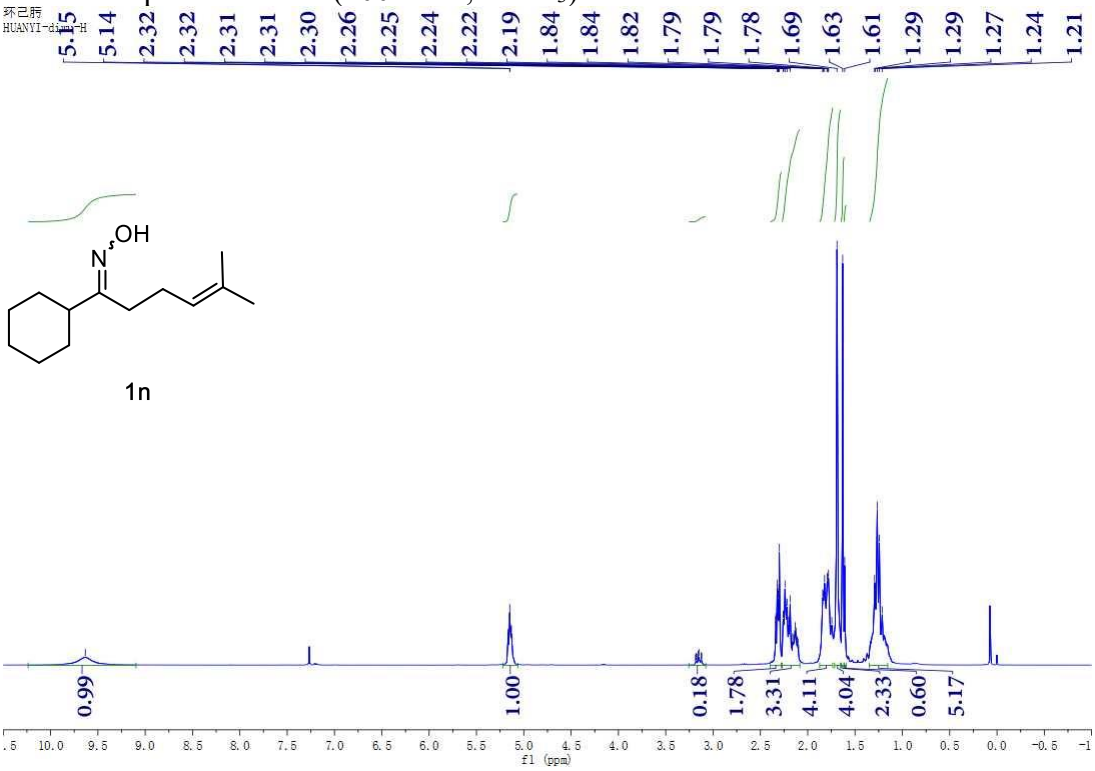
^{1}H NMR Spectrum of **1m** (400 MHz; $CDCl_3$)



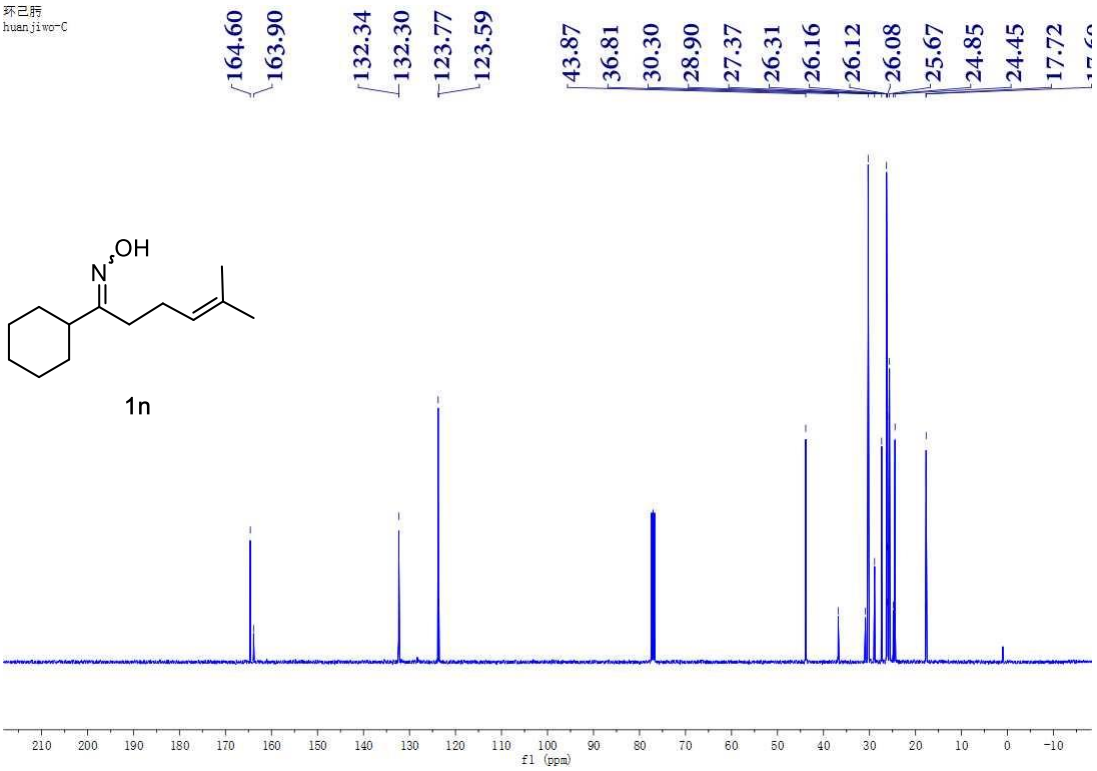
^{13}C NMR Spectrum of **1m** (100 MHz; $CDCl_3$)



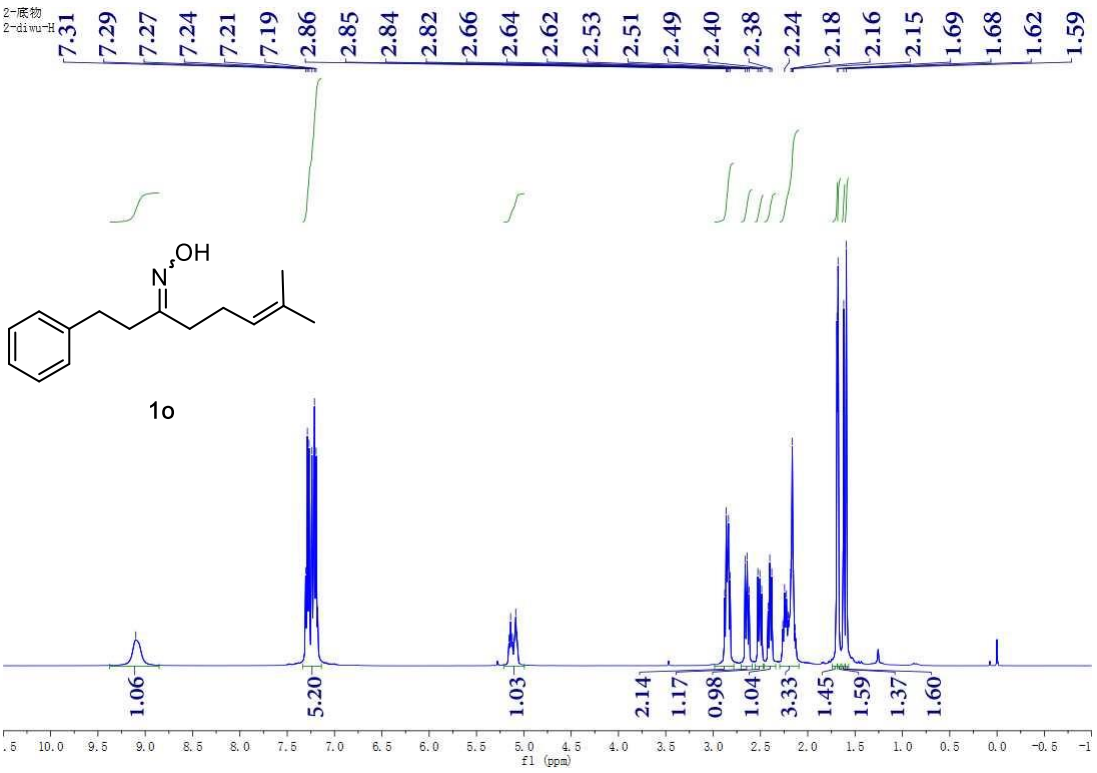
^{1}H NMR Spectrum of **1n** (400 MHz; $CDCl_3$)



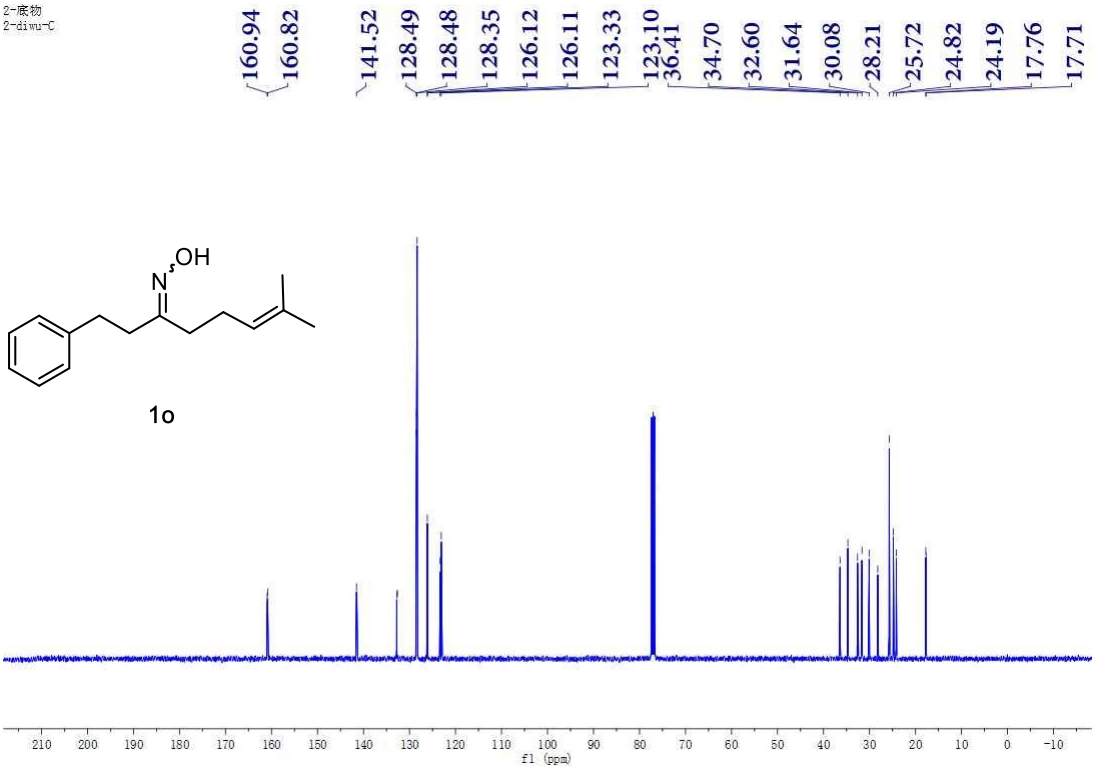
^{13}C NMR Spectrum of **1n** (100 MHz; $CDCl_3$)



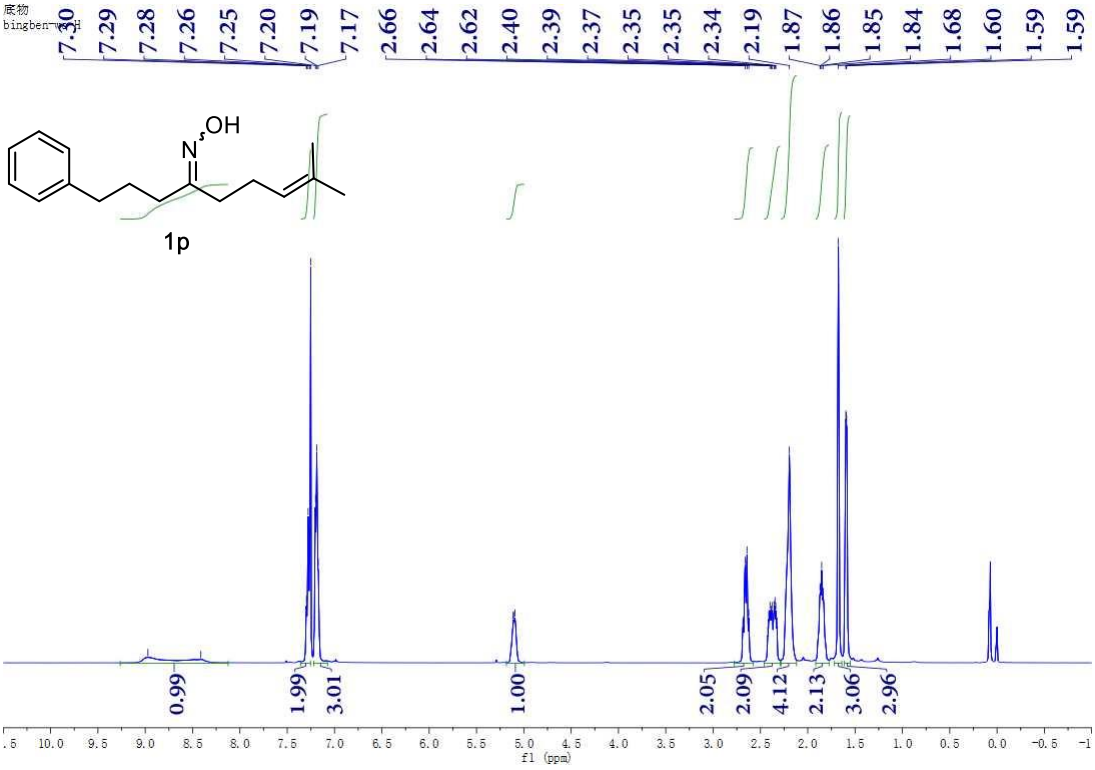
^{1}H NMR Spectrum of **1o** (400 MHz; $CDCl_3$)



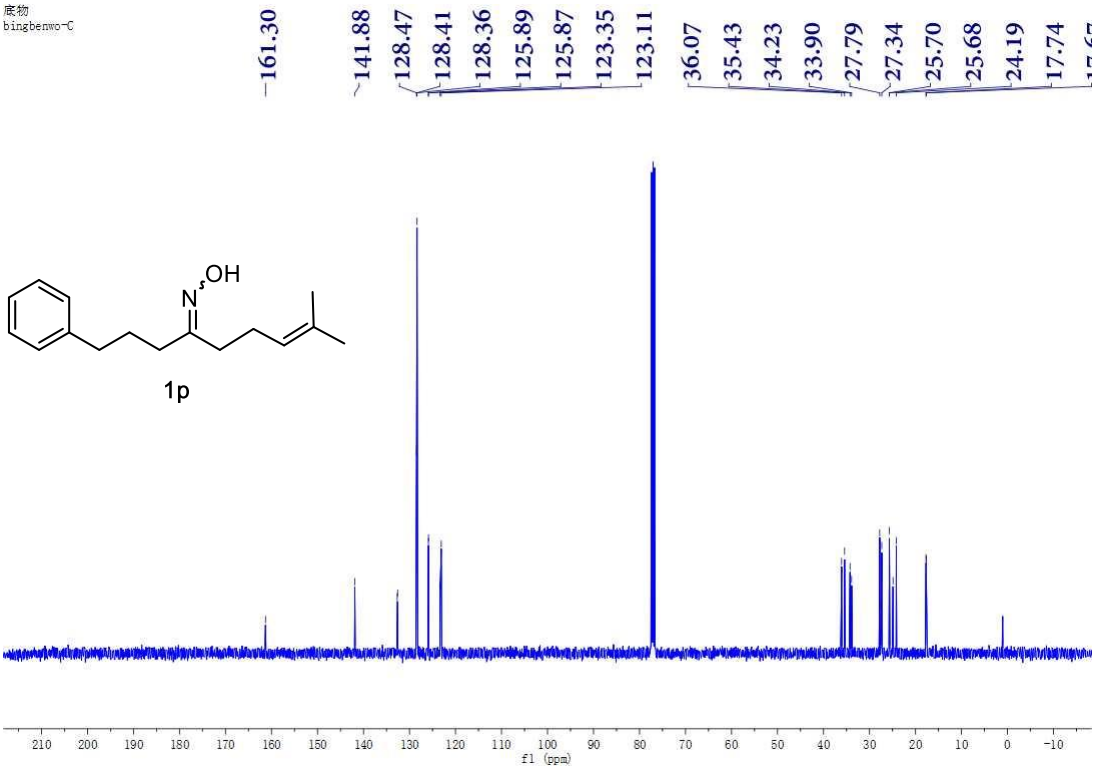
^{13}C NMR Spectrum of **1o** (100 MHz; $CDCl_3$)



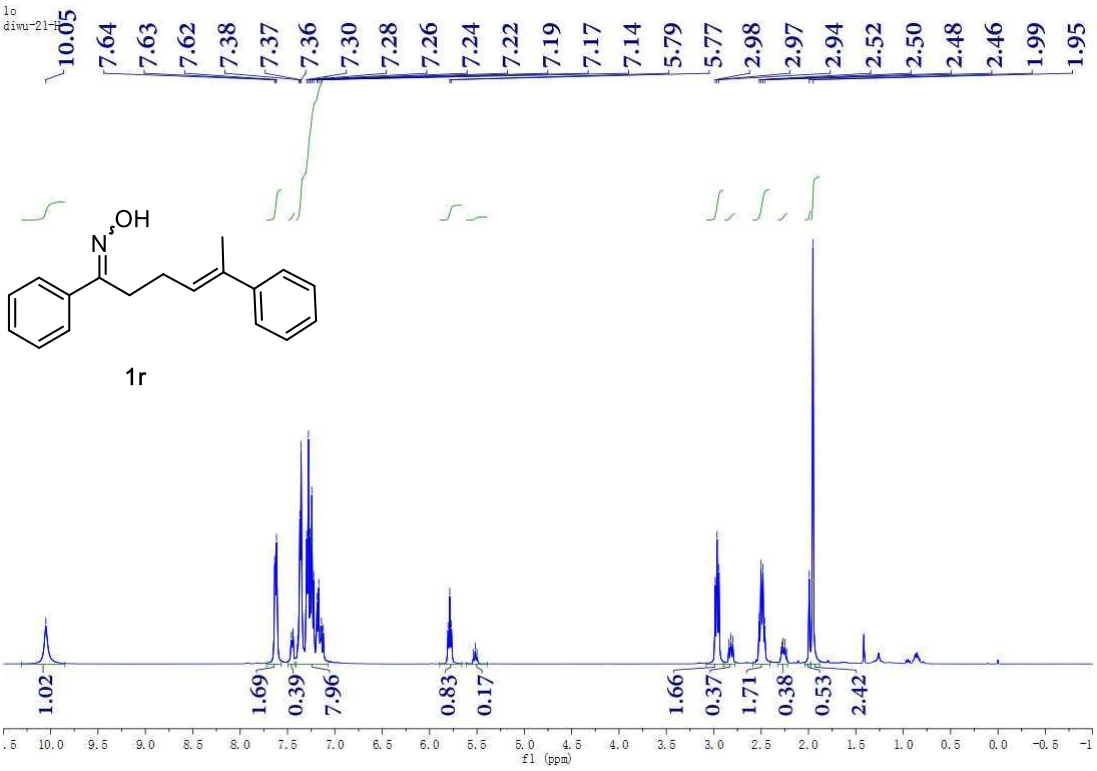
^{1}H NMR Spectrum of **1p** (400 MHz; $CDCl_3$)



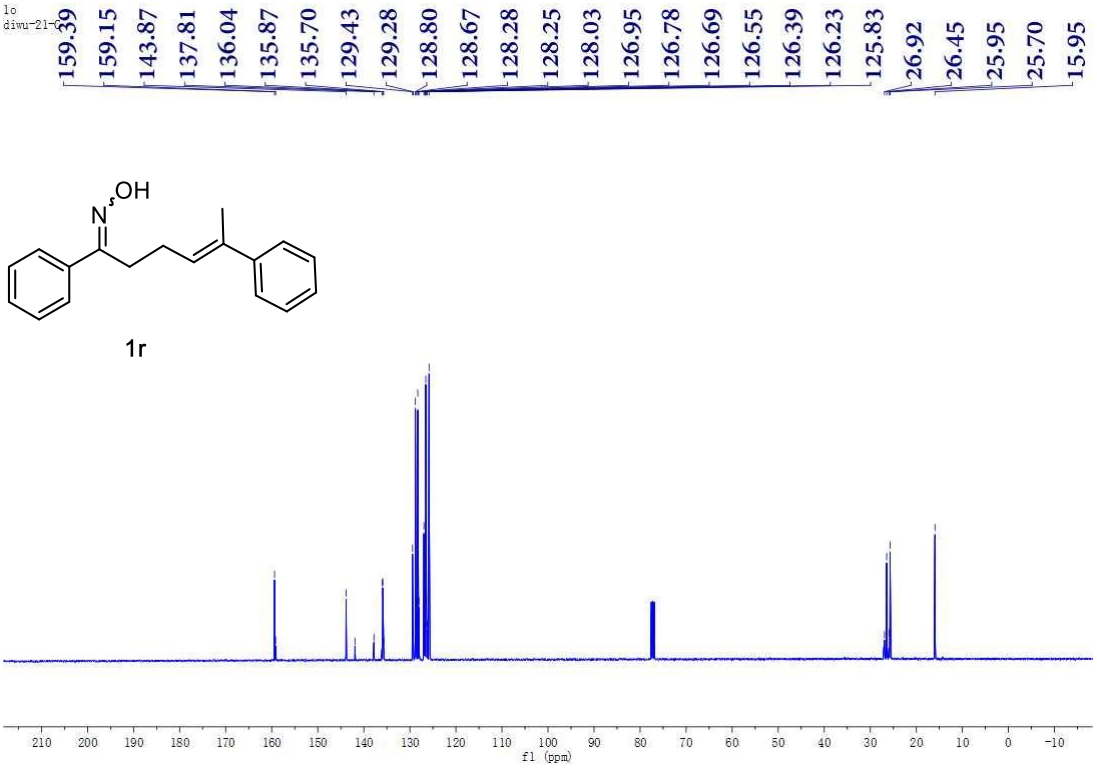
^{13}C NMR Spectrum of **1p** (100 MHz; $CDCl_3$)



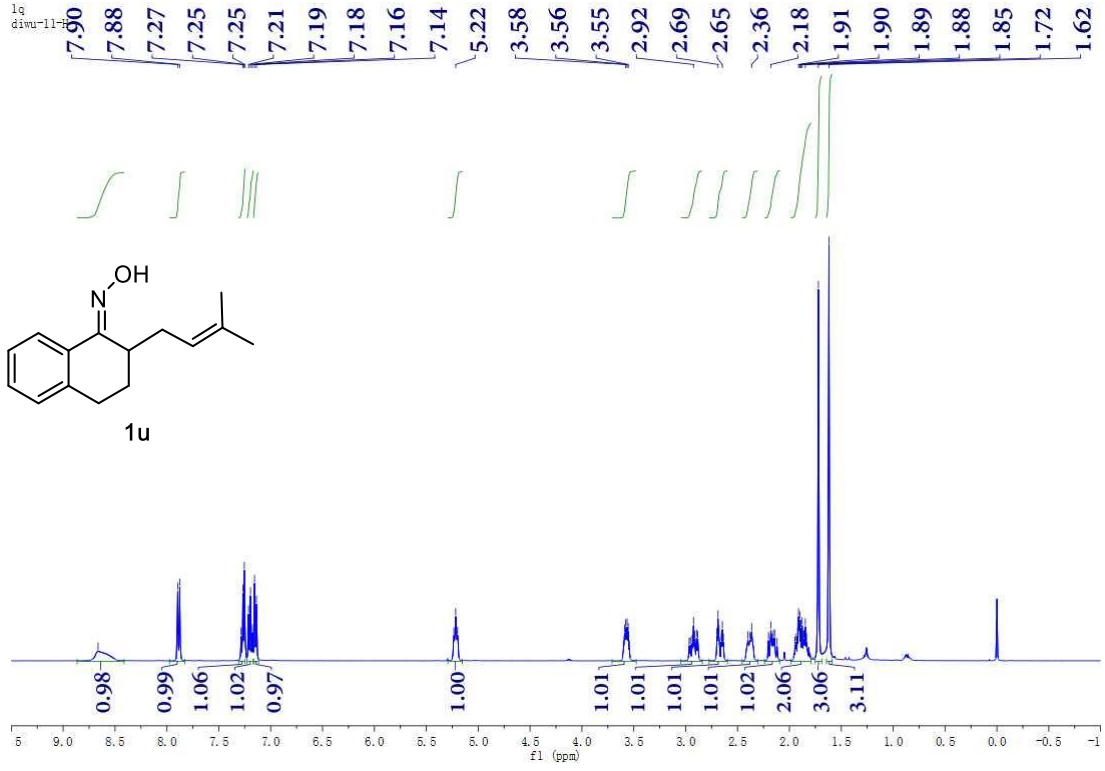
^{1}H NMR Spectrum of **1r** (400 MHz; $CDCl_3$)



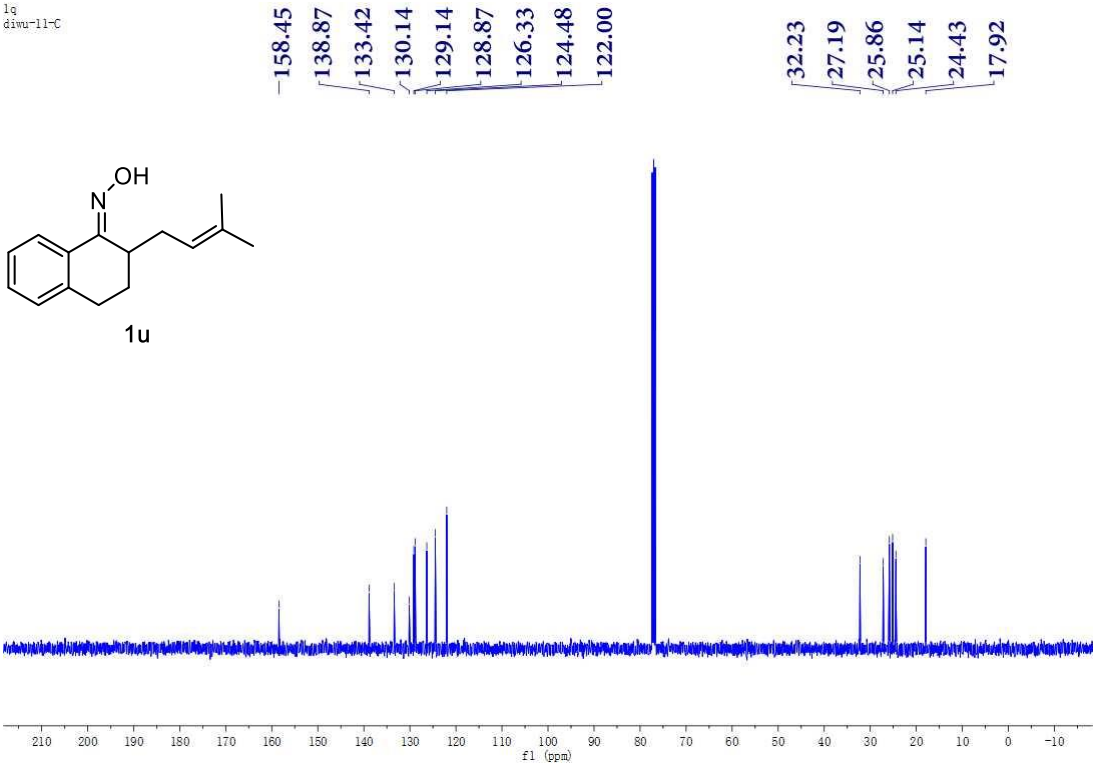
^{13}C NMR Spectrum of **1r** (100 MHz; $CDCl_3$)



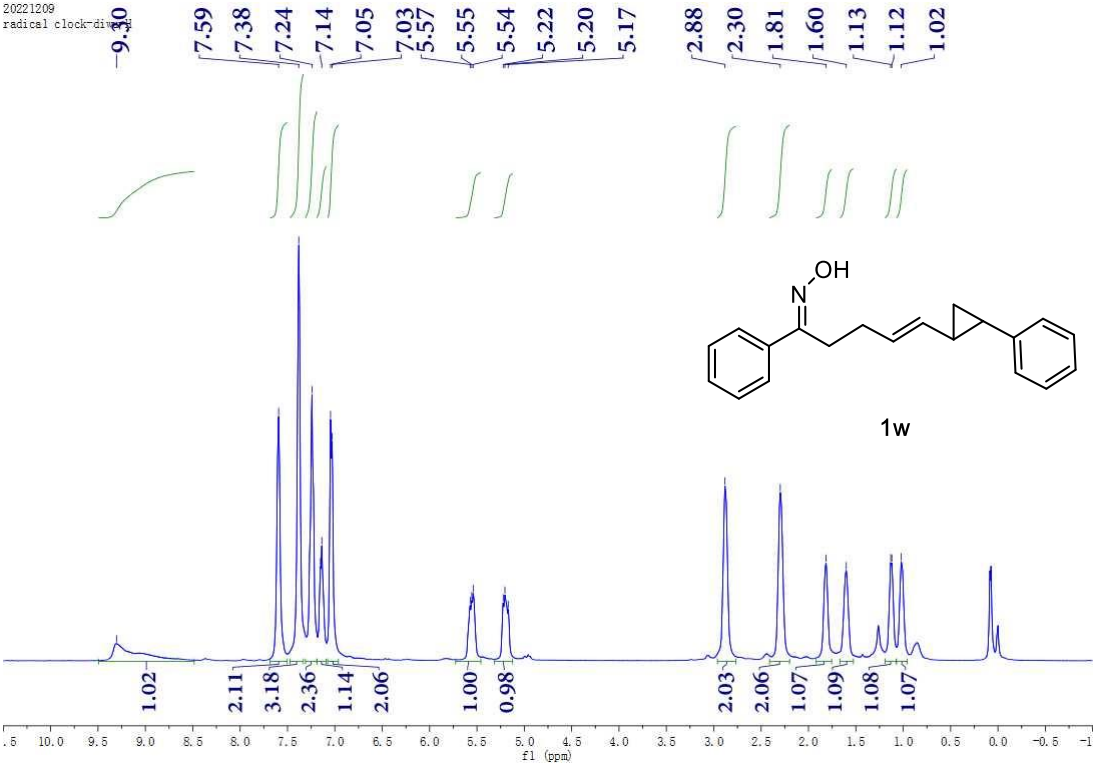
^{1}H NMR Spectrum of **1u** (400 MHz; $CDCl_3$)



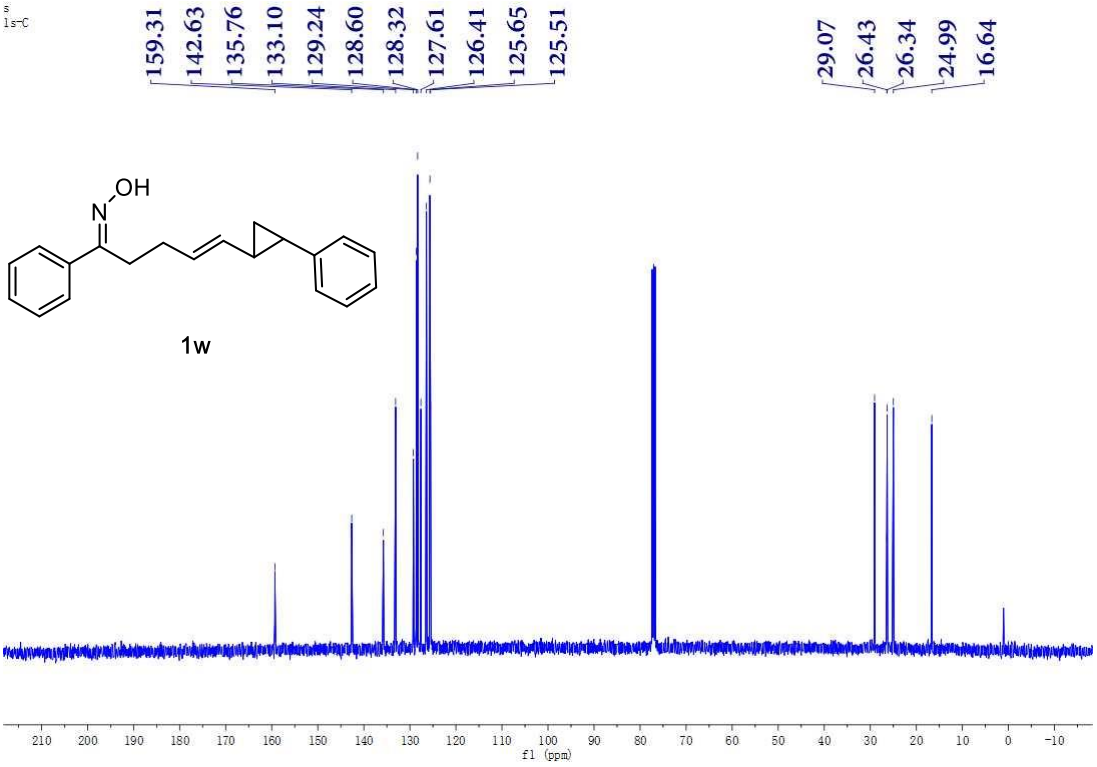
^{13}C NMR Spectrum of **1u** (100 MHz; $CDCl_3$)



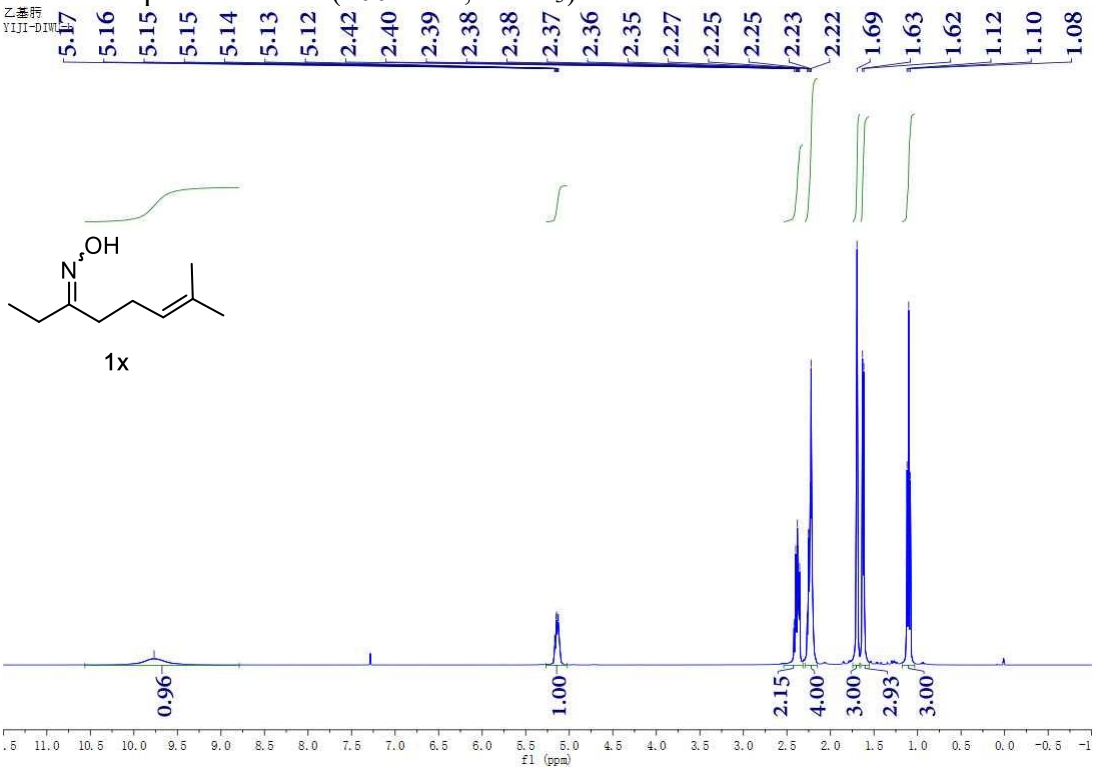
^{1}H NMR Spectrum of **1w** (400 MHz; $CDCl_3$)



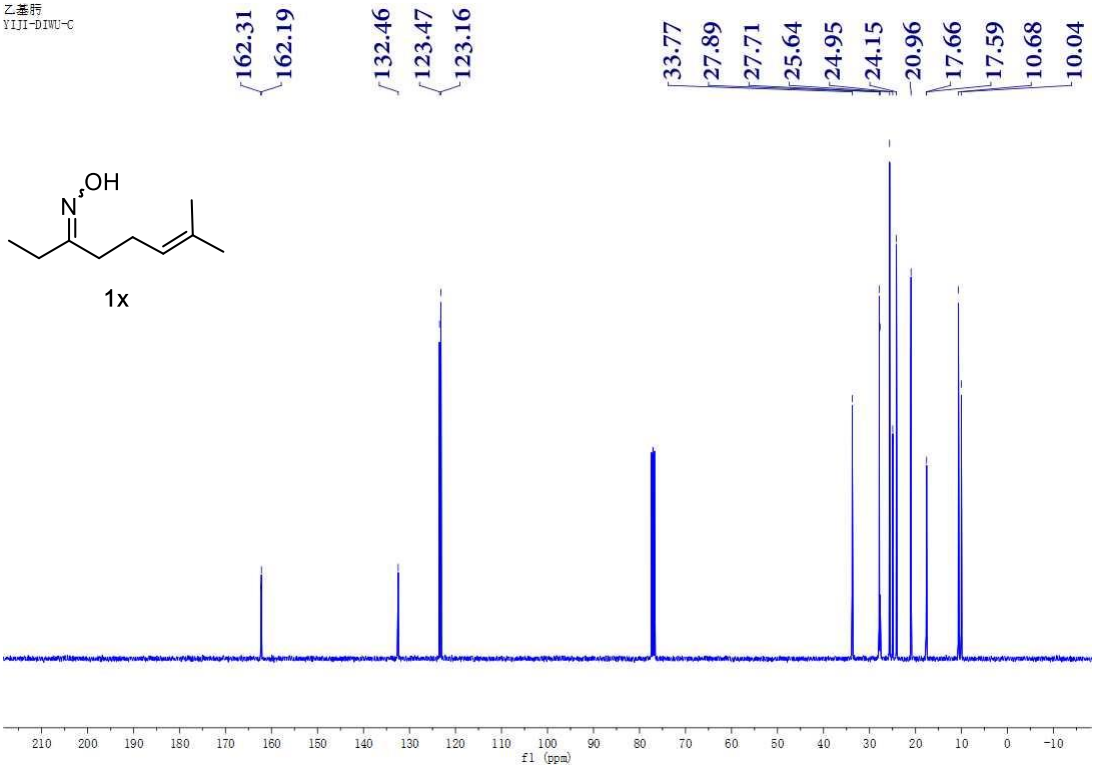
^{13}C NMR Spectrum of **1w** (100 MHz; $CDCl_3$)



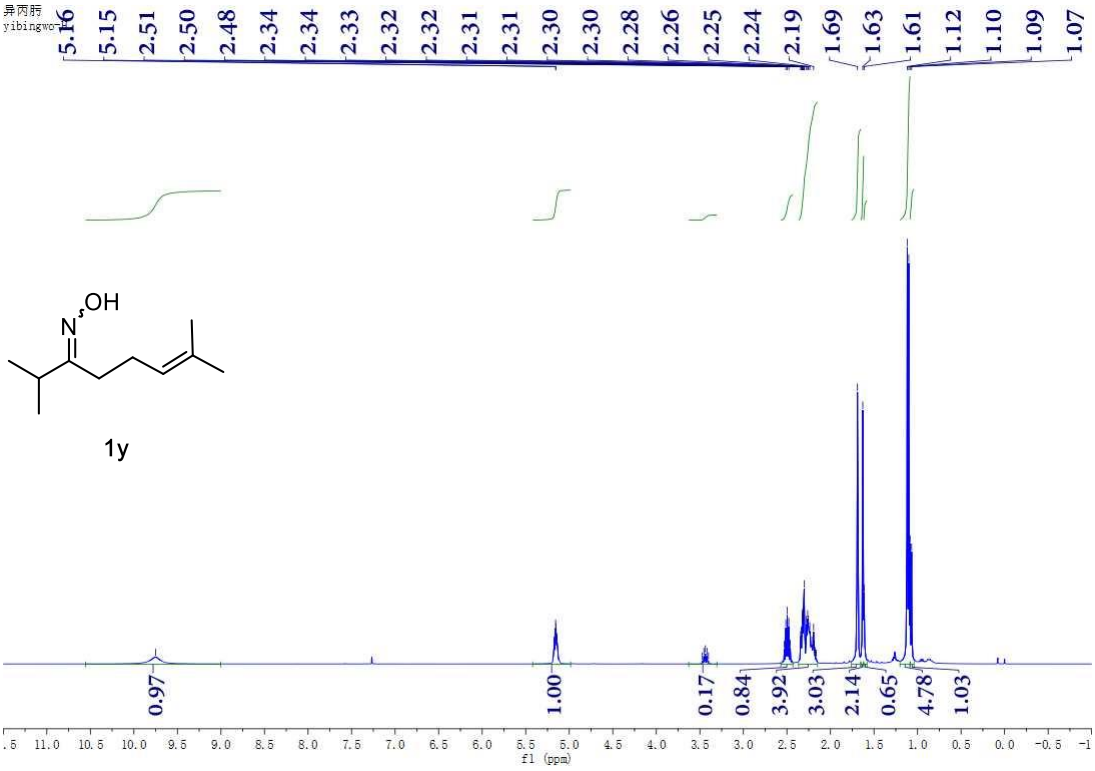
^{1}H NMR Spectrum of **1x** (400 MHz; $CDCl_3$)



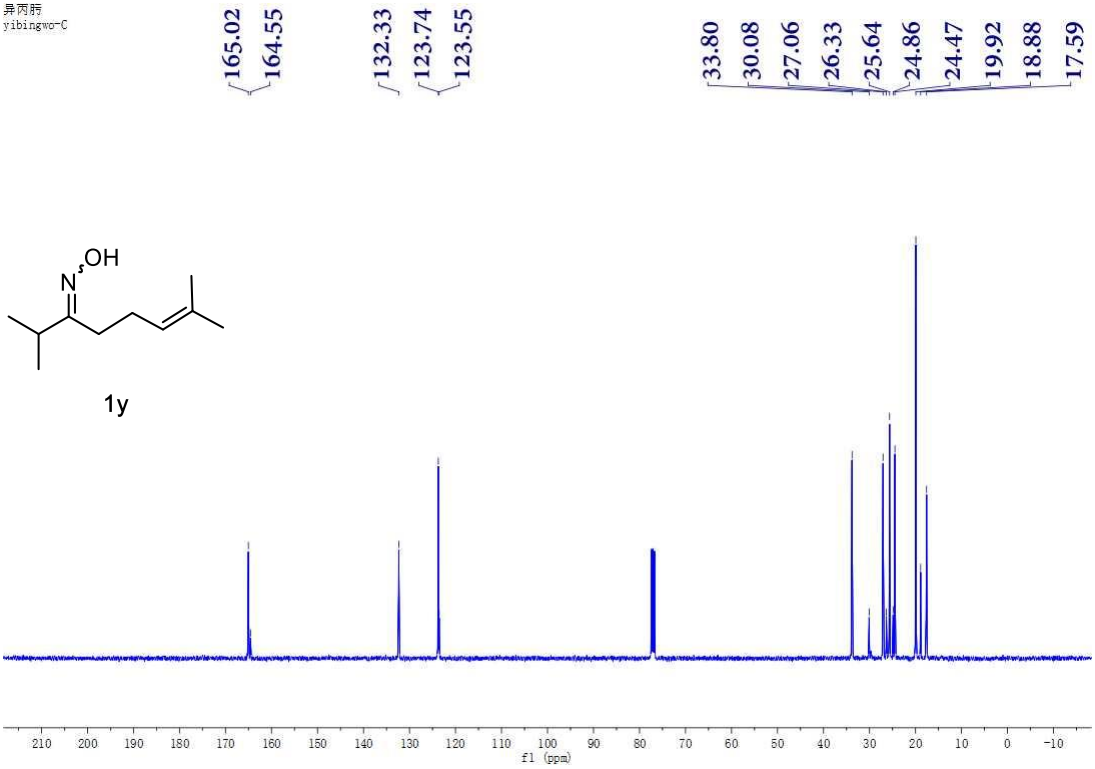
^{13}C NMR Spectrum of **1x** (100 MHz; $CDCl_3$)



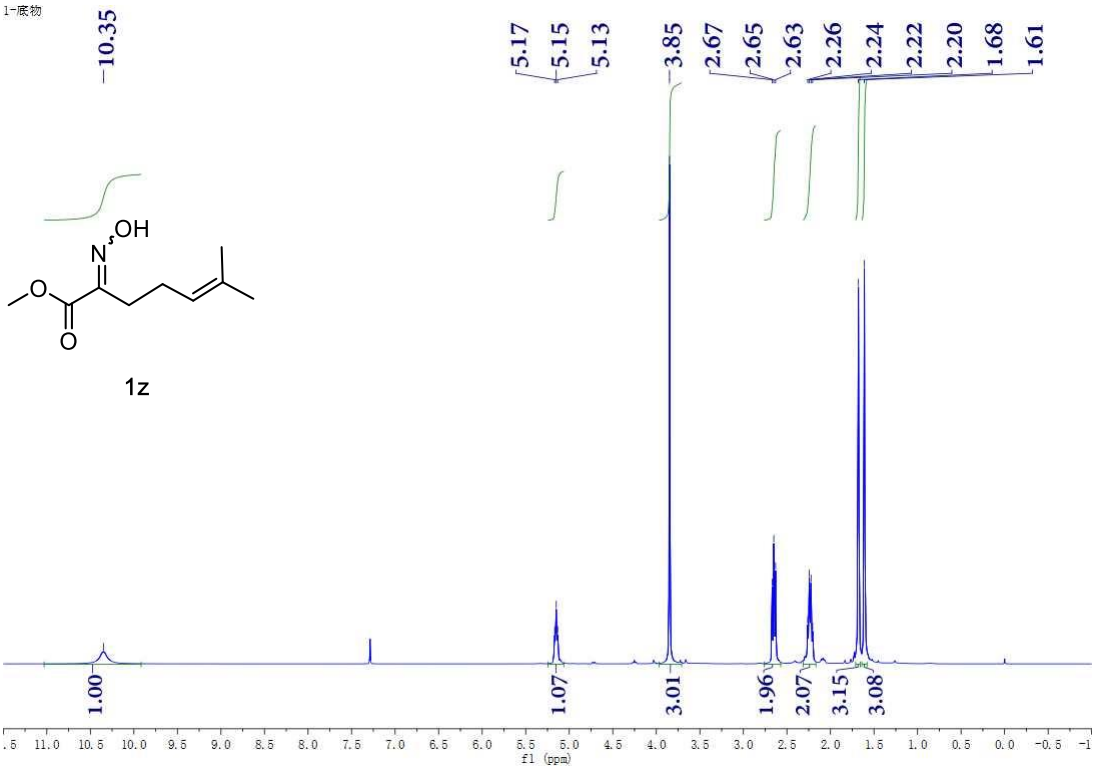
^{1}H NMR Spectrum of **1y** (400 MHz; $CDCl_3$)



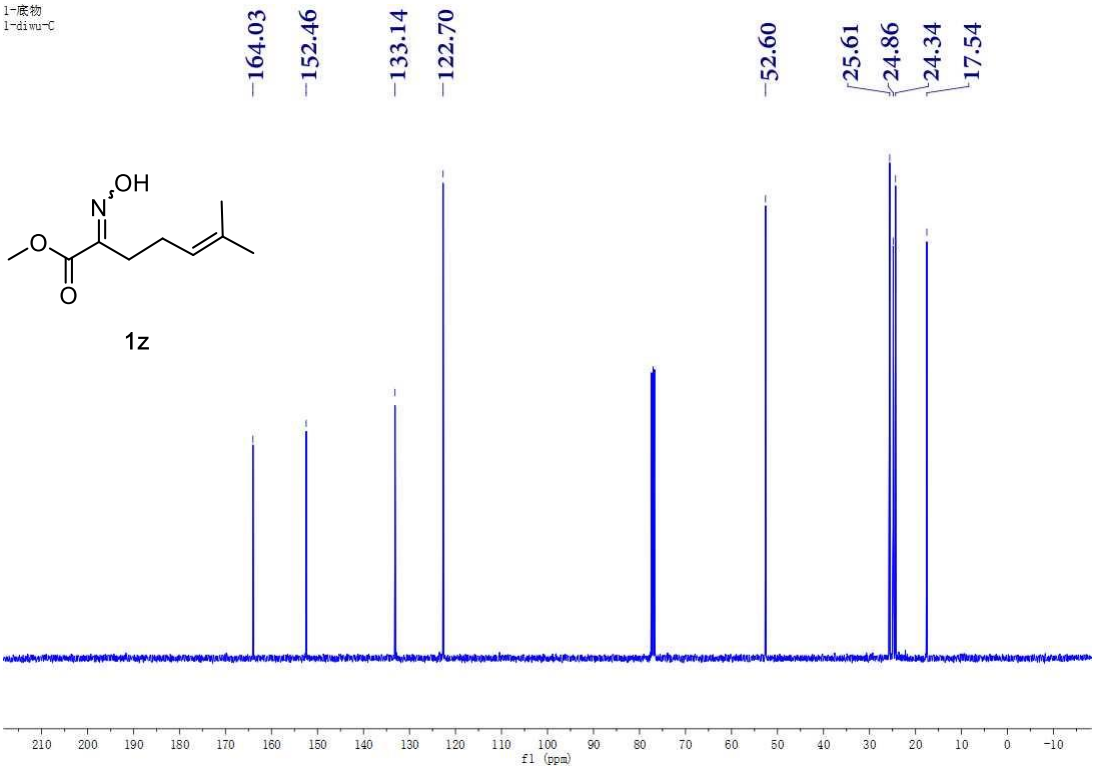
^{13}C NMR Spectrum of **1y** (100 MHz; $CDCl_3$)



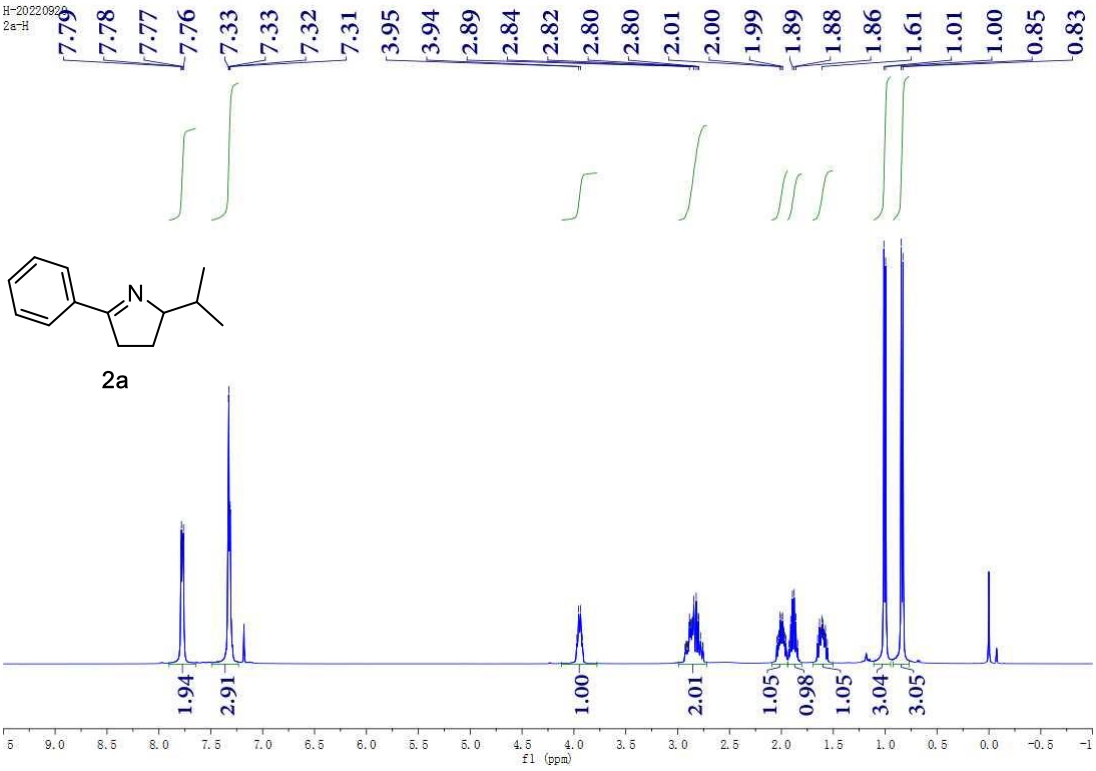
^{1}H NMR Spectrum of **1z** (400 MHz; $CDCl_3$)



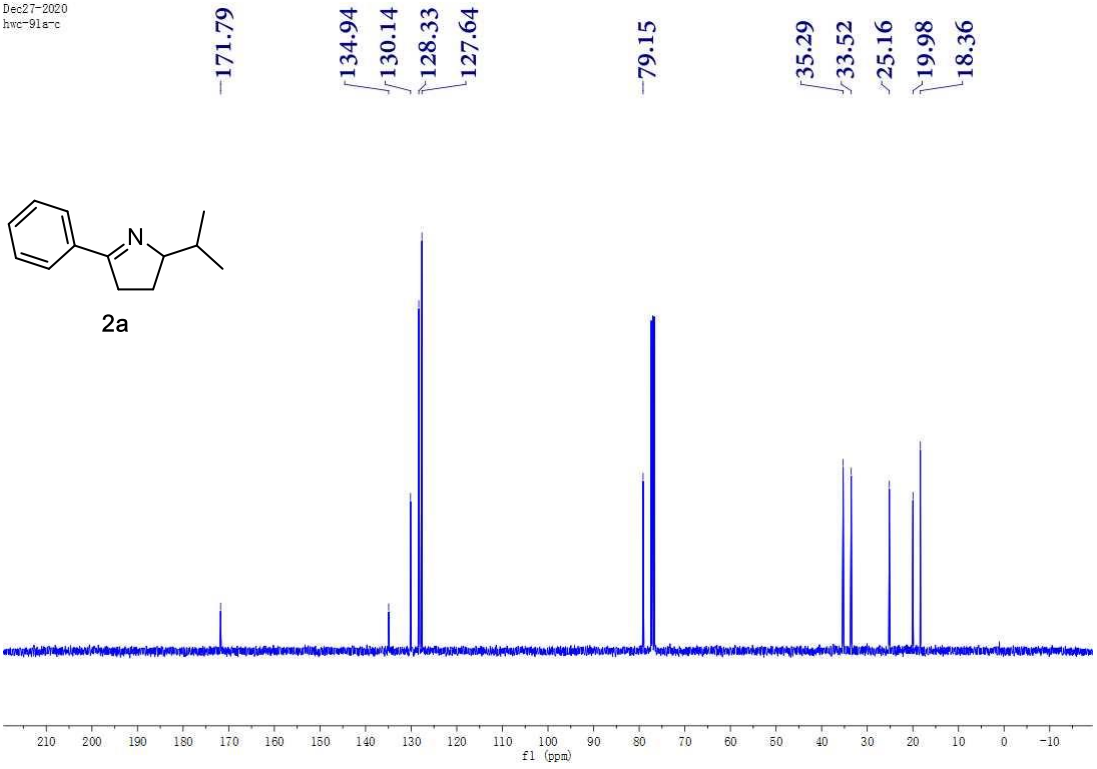
^{13}C NMR Spectrum of **1z** (100 MHz; $CDCl_3$)



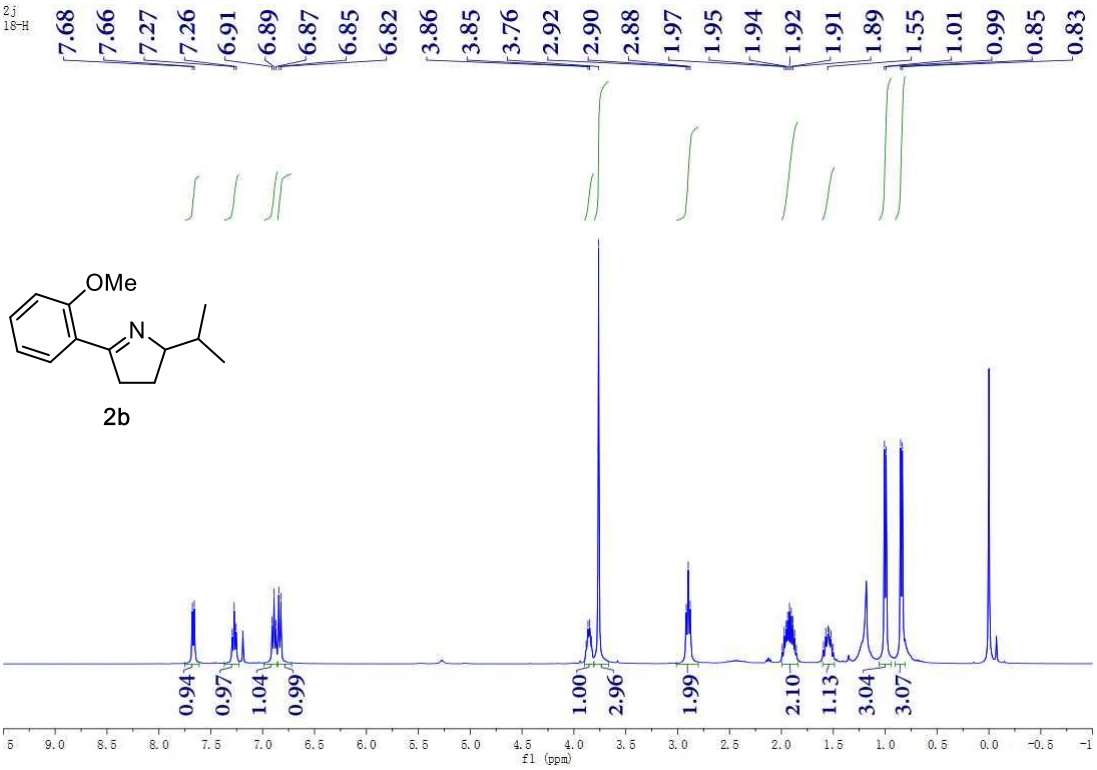
^{1}H NMR Spectrum of **2a** (400 MHz; $CDCl_3$)



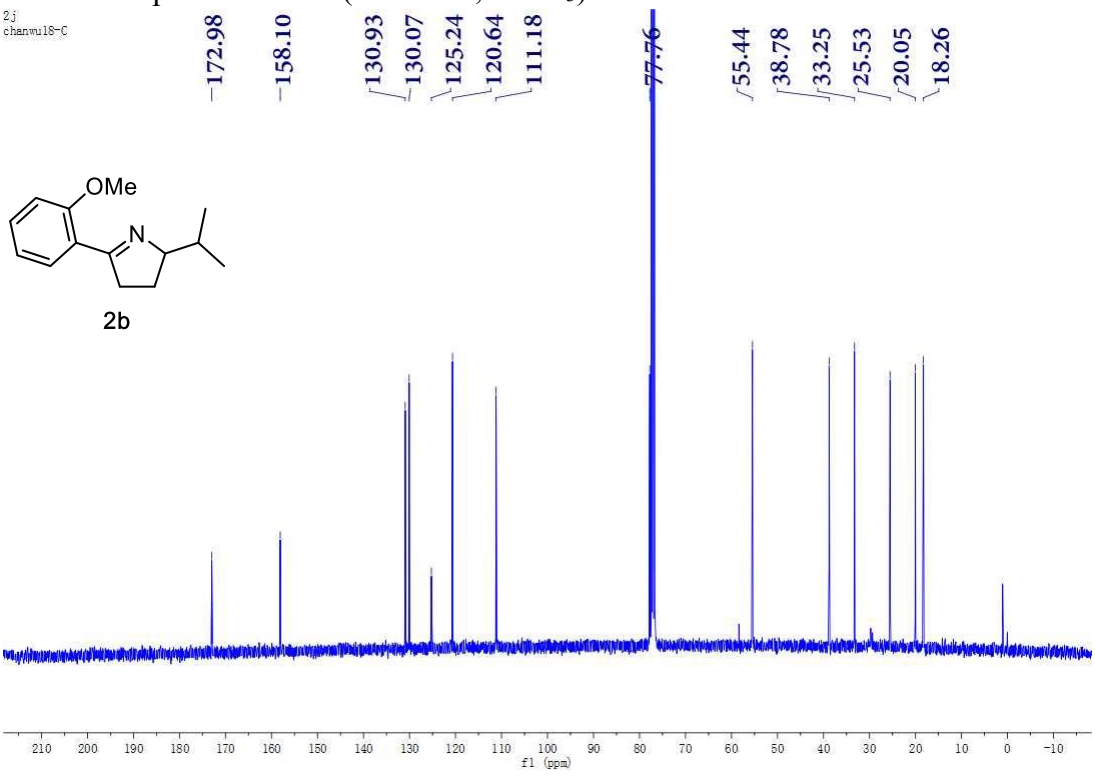
^{13}C NMR Spectrum of **2a** (100 MHz; $CDCl_3$)



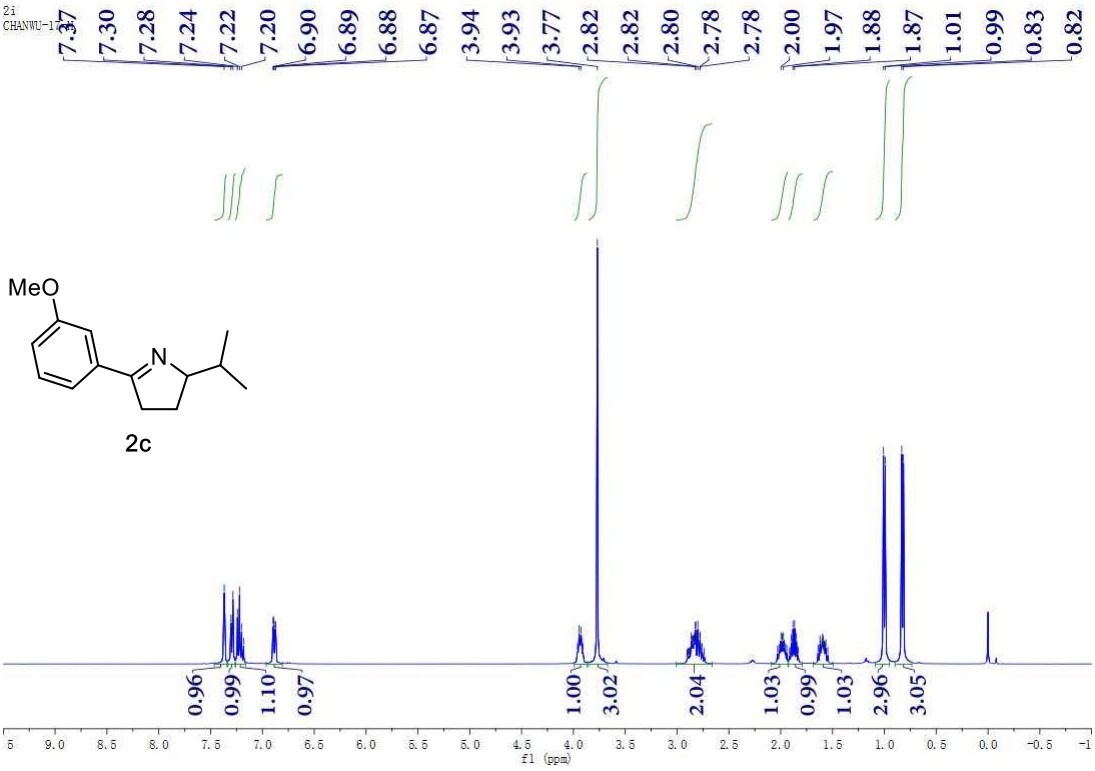
^{1}H NMR Spectrum of **2b** (400 MHz; $CDCl_3$)



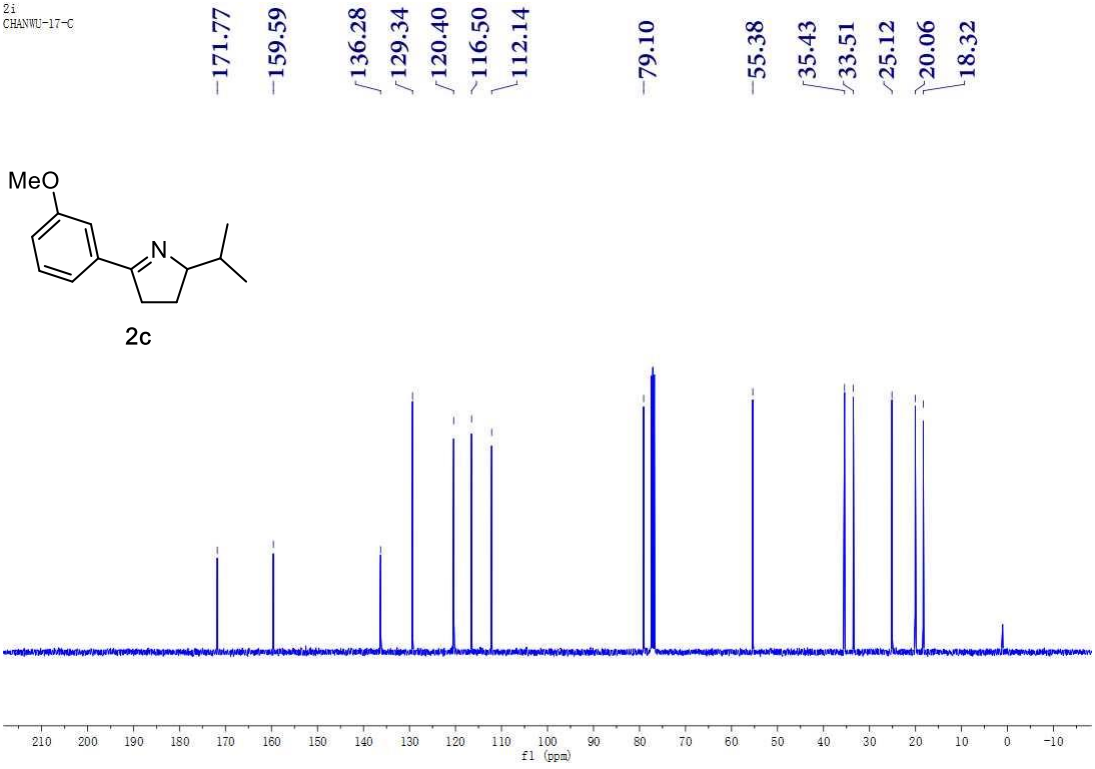
^{13}C NMR Spectrum of **2b** (100 MHz; $CDCl_3$)



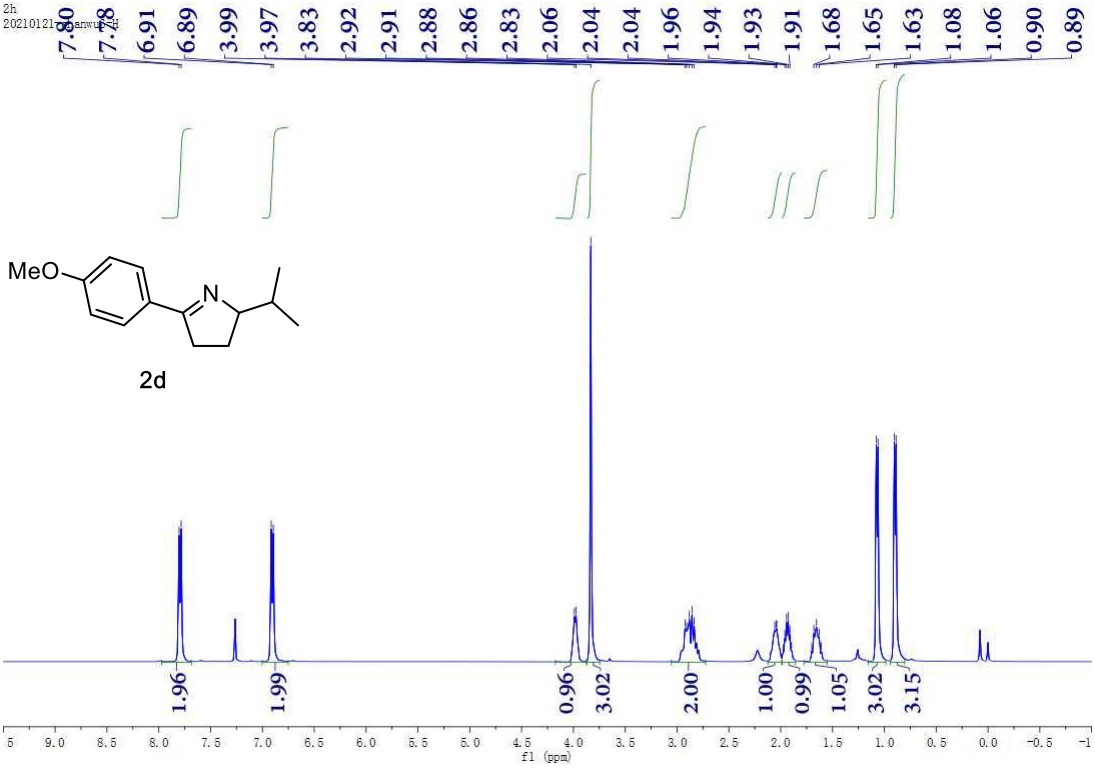
^{1}H NMR Spectrum of **2c** (400 MHz; $CDCl_3$)



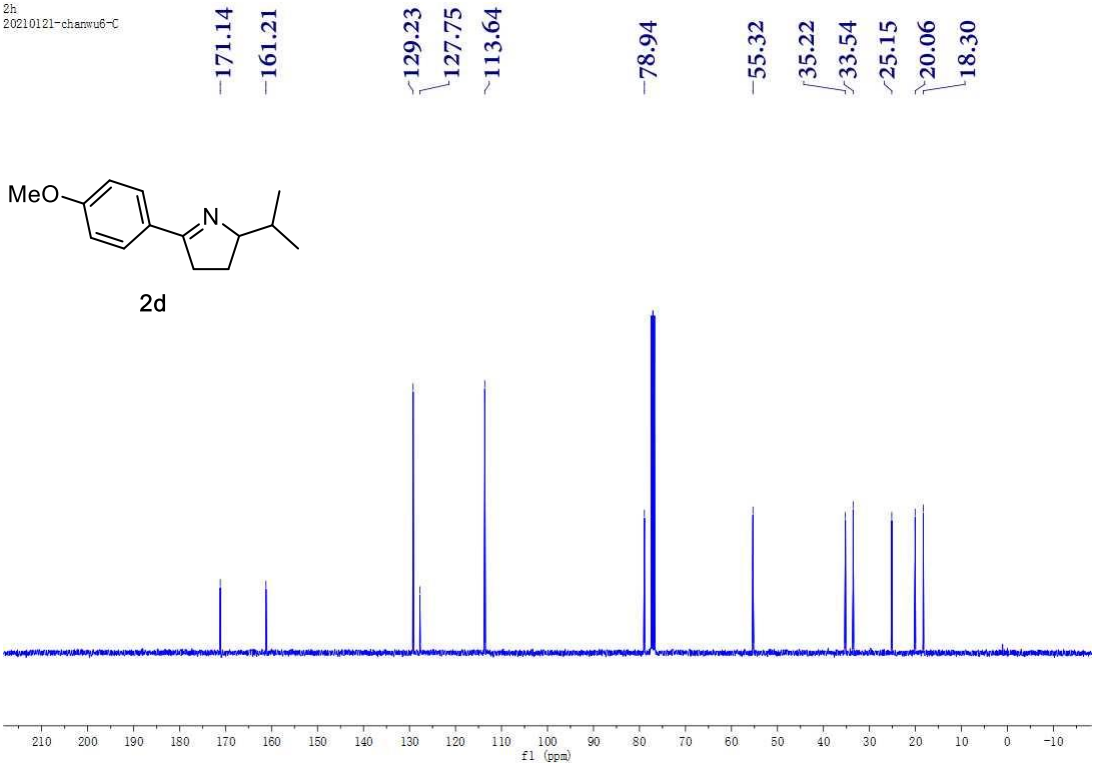
^{13}C NMR Spectrum of **2c** (100 MHz; $CDCl_3$)



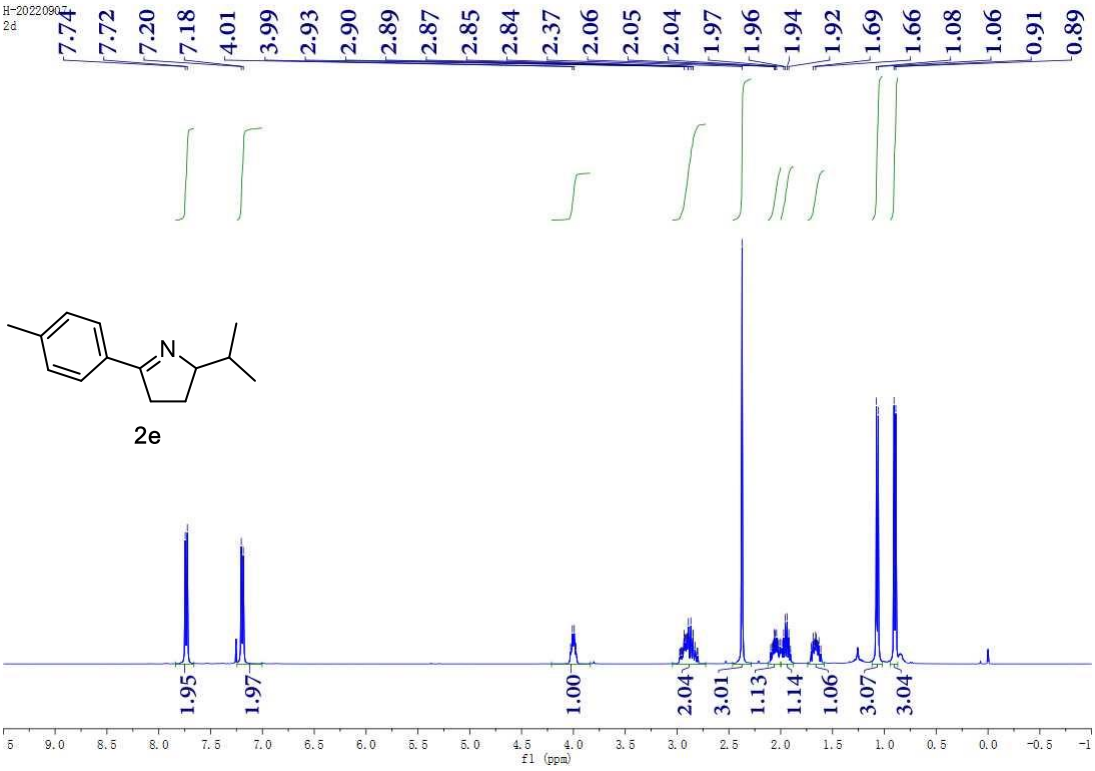
^{1}H NMR Spectrum of **2d** (400 MHz; $CDCl_3$)



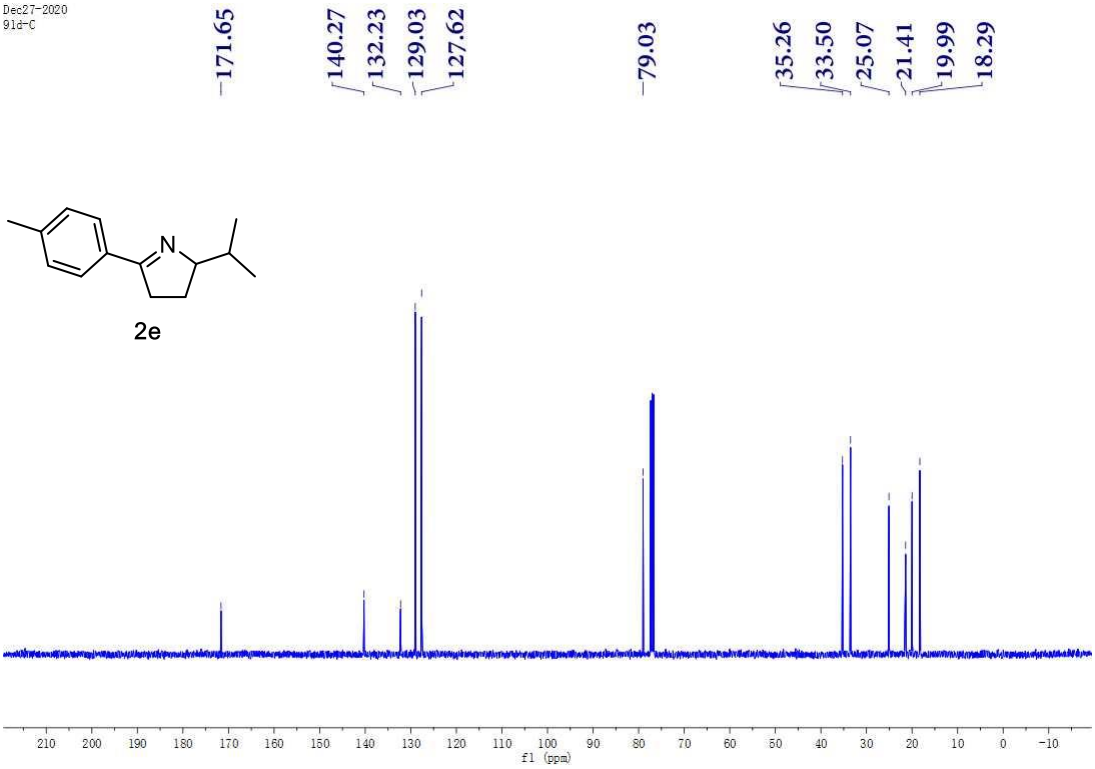
^{13}C NMR Spectrum of **2d** (100 MHz; $CDCl_3$)



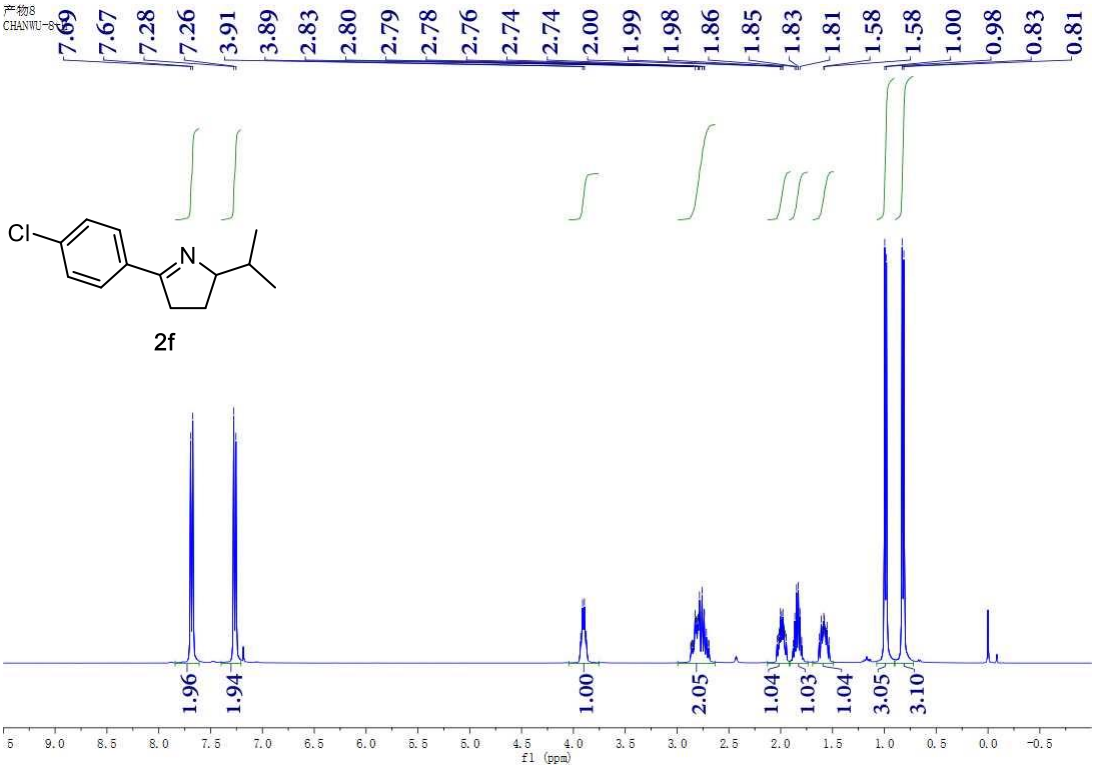
^{1}H NMR Spectrum of **2e** (400 MHz; $CDCl_3$)



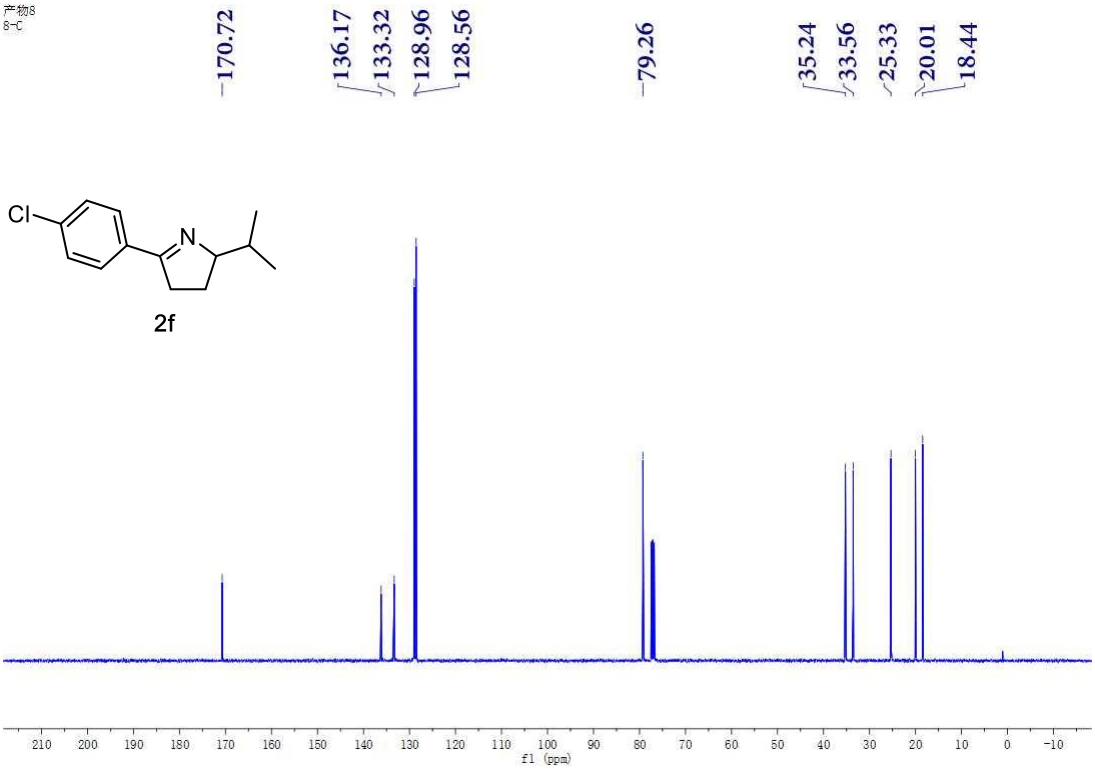
^{13}C NMR Spectrum of **2e** (100 MHz; $CDCl_3$)



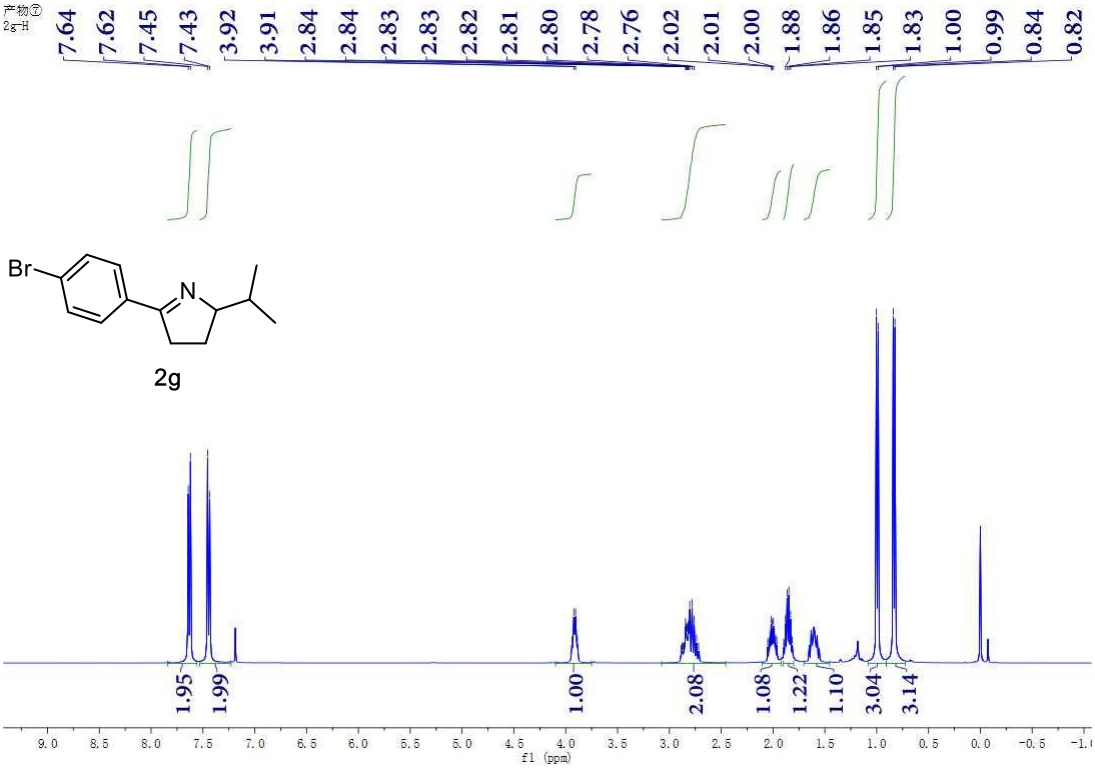
^{1}H NMR Spectrum of **2f** (400 MHz; $CDCl_3$)



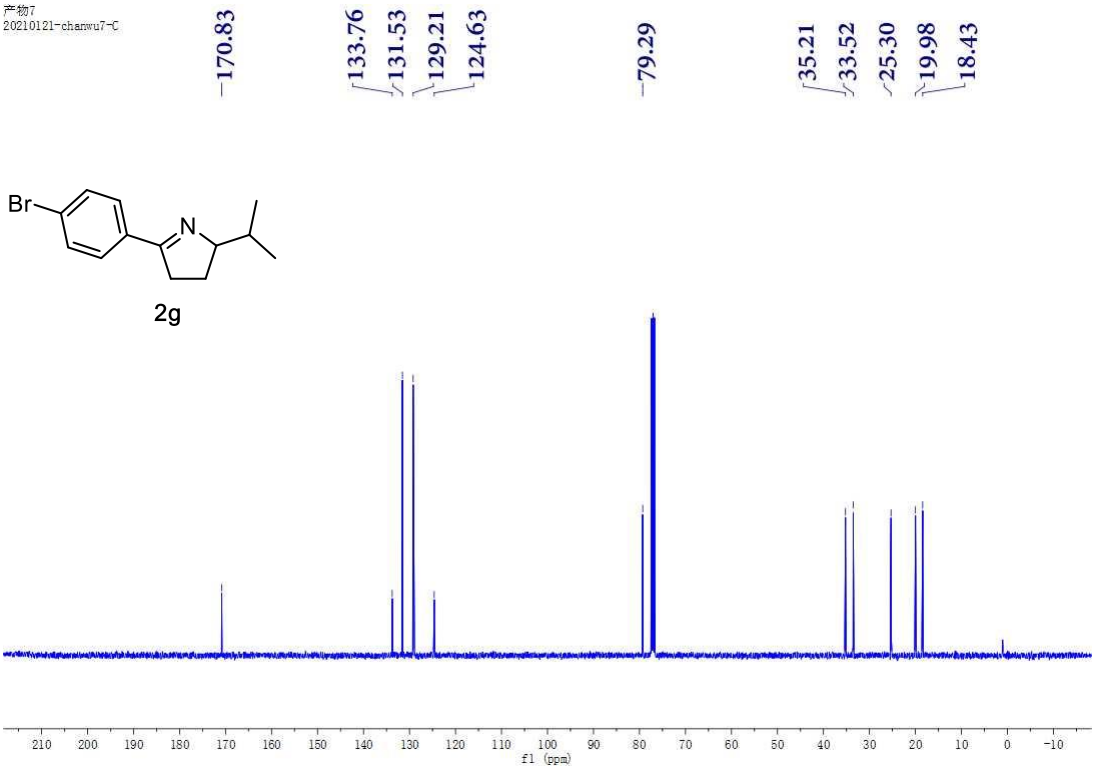
^{13}C NMR Spectrum of **2f** (100 MHz; $CDCl_3$)



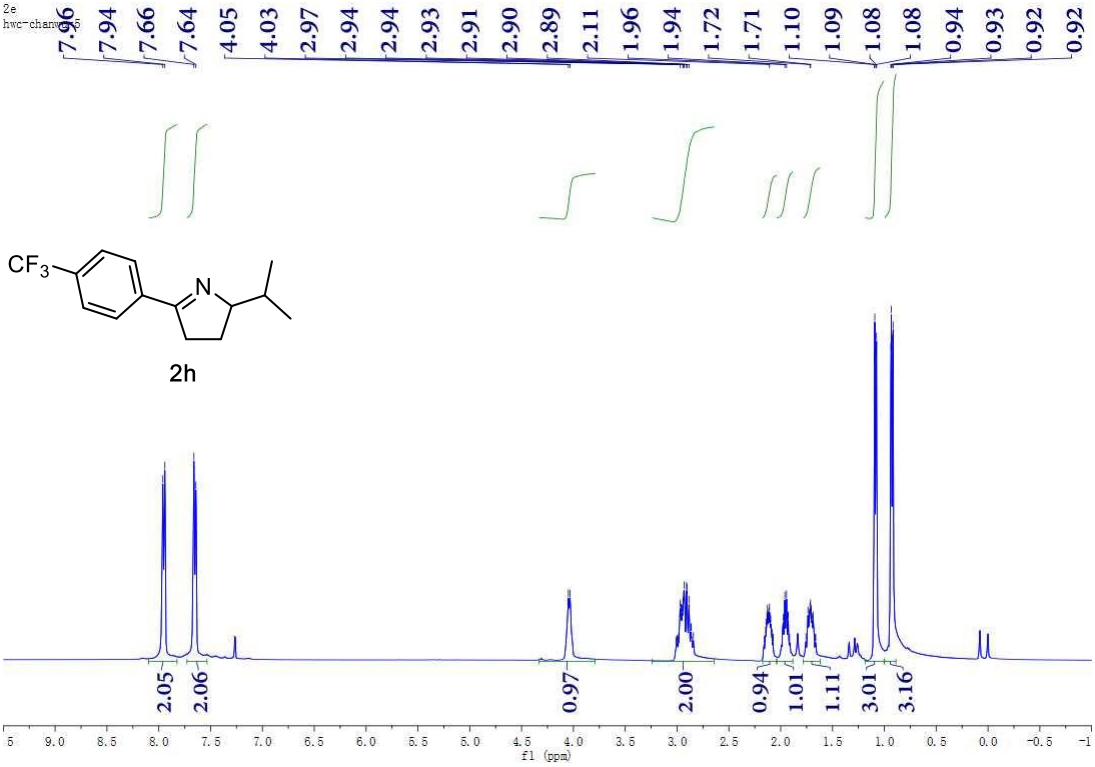
^{1}H NMR Spectrum of **2g** (400 MHz; $CDCl_3$)



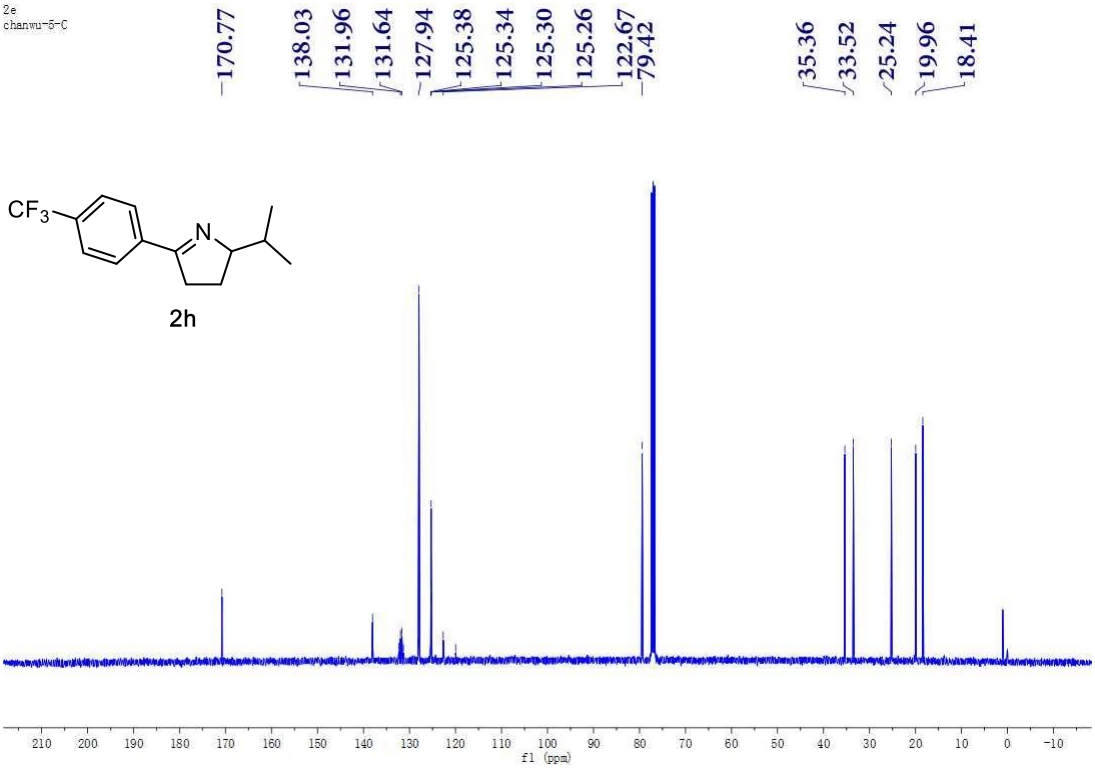
^{13}C NMR Spectrum of **2g** (100 MHz; $CDCl_3$)



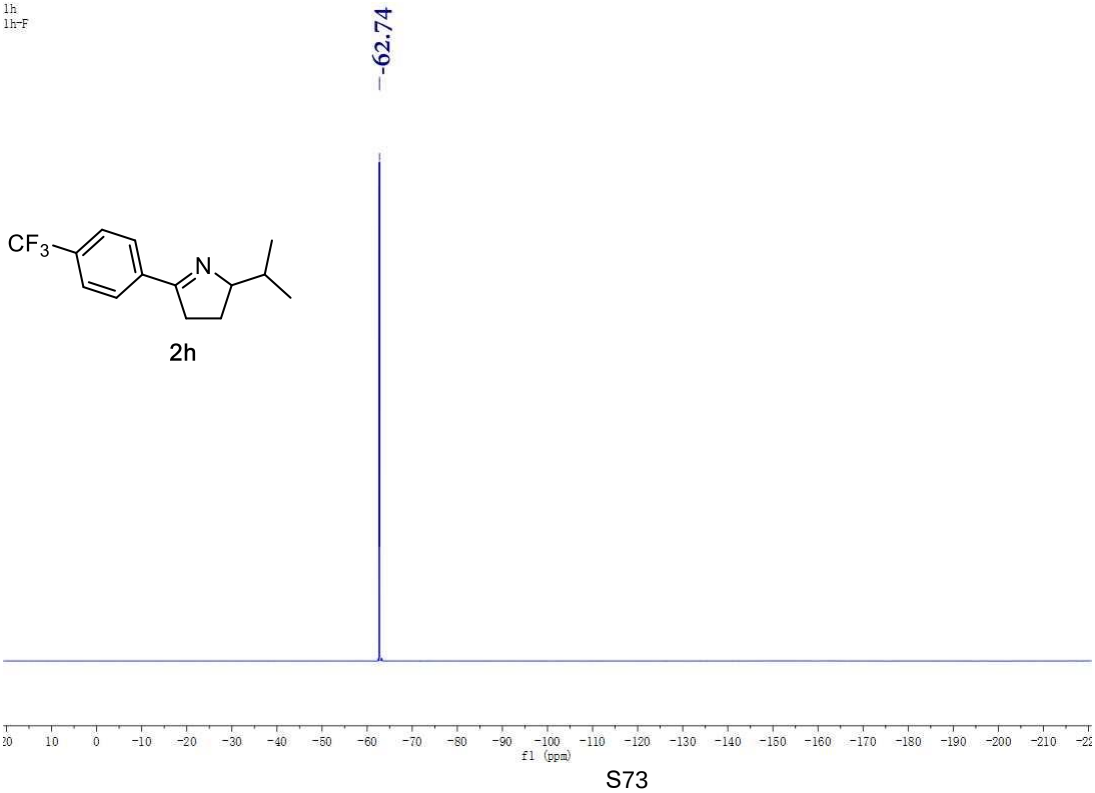
^{1}H NMR Spectrum of **2h** (400 MHz; $CDCl_3$)



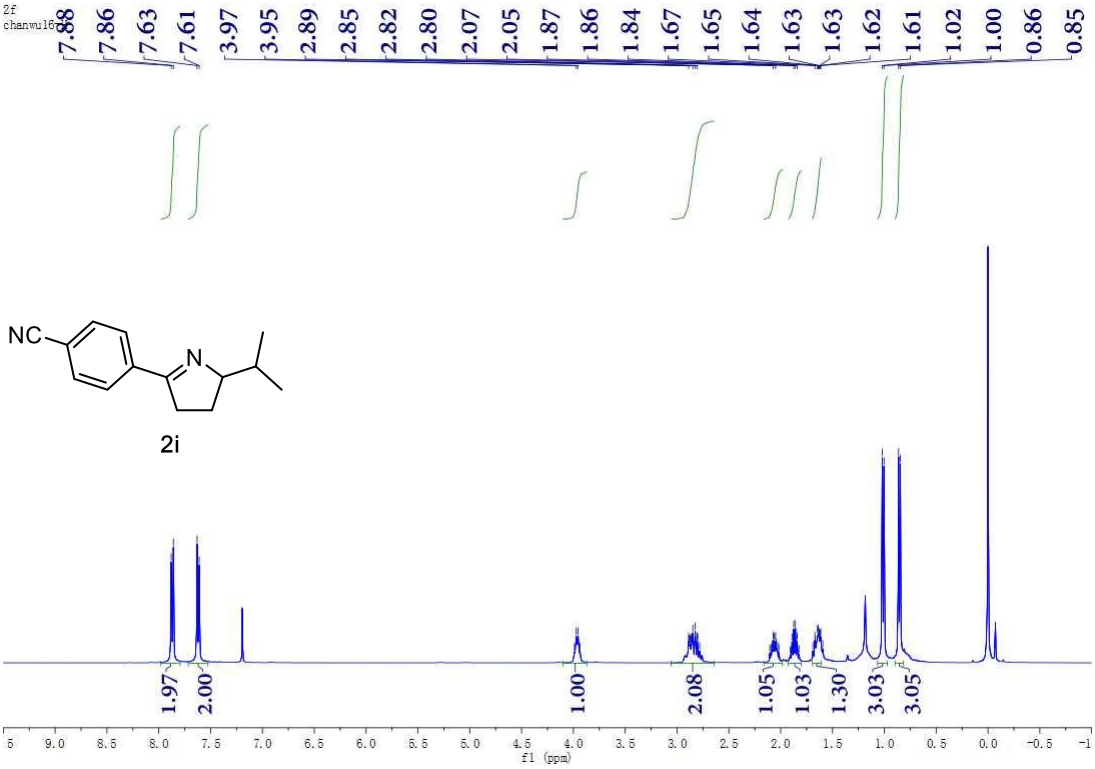
^{13}C NMR Spectrum of **2h** (100 MHz; $CDCl_3$)



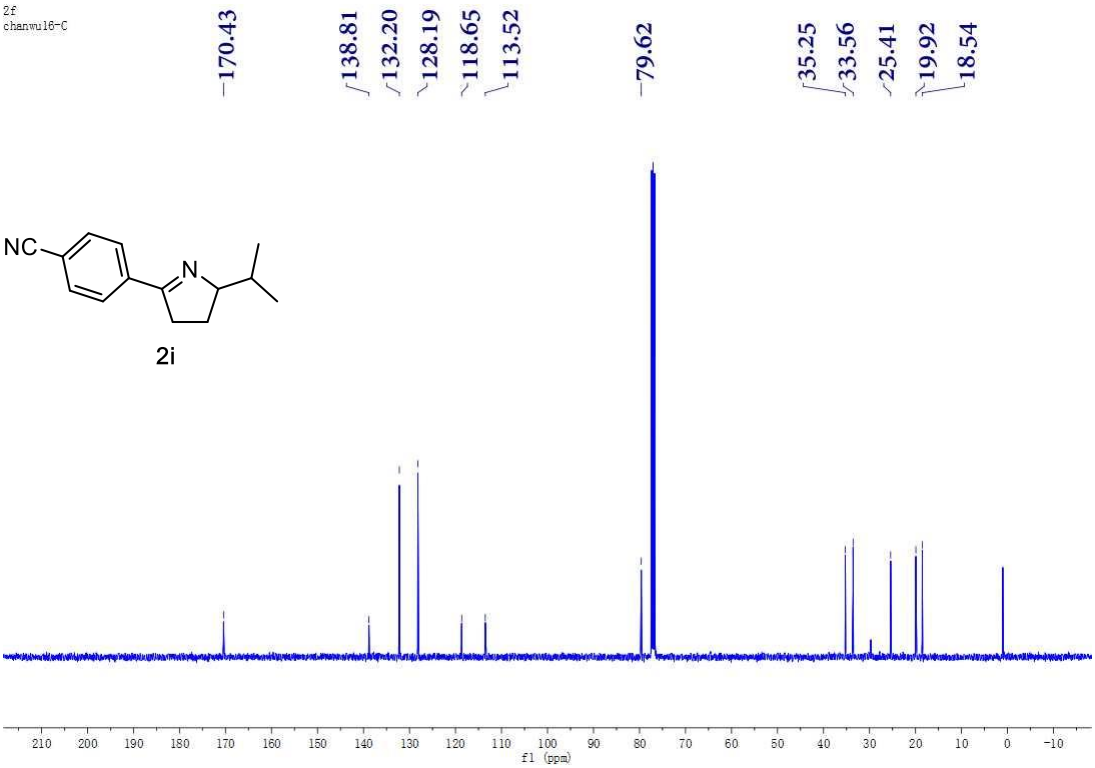
^{19}F NMR Spectrum of **2h** (376 MHz; $CDCl_3$)



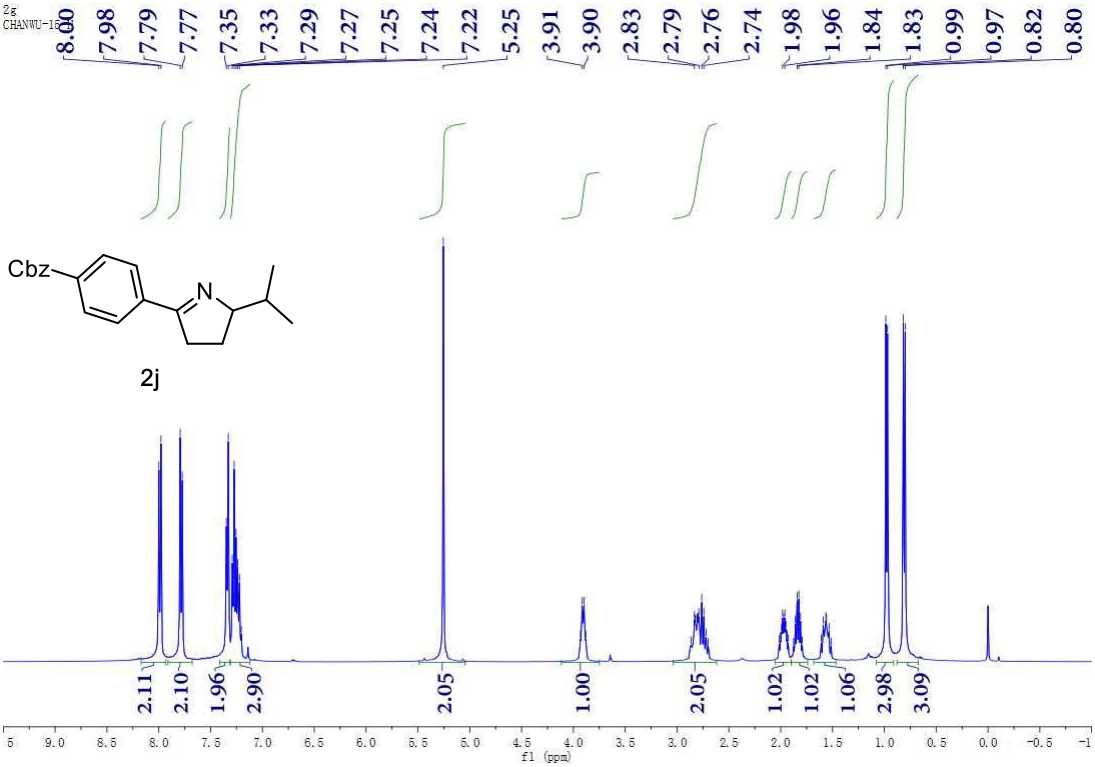
^{1}H NMR Spectrum of **2i** (400 MHz; $CDCl_3$)



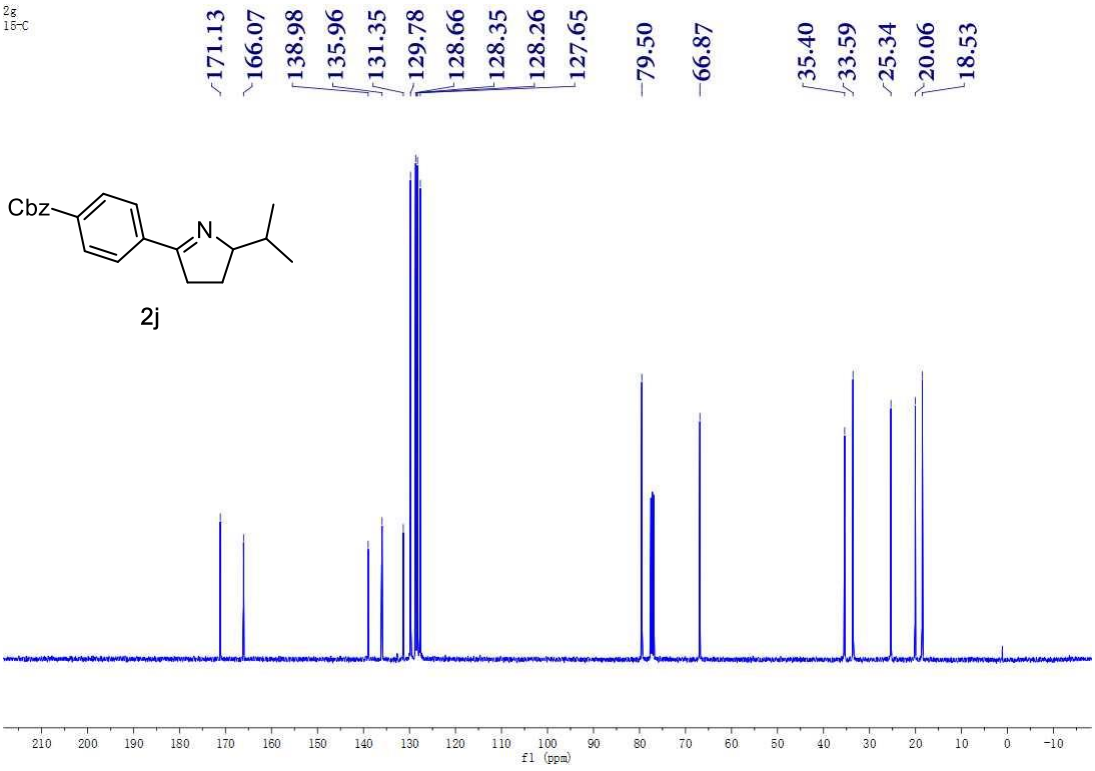
^{13}C NMR Spectrum of **2i** (100 MHz; $CDCl_3$)



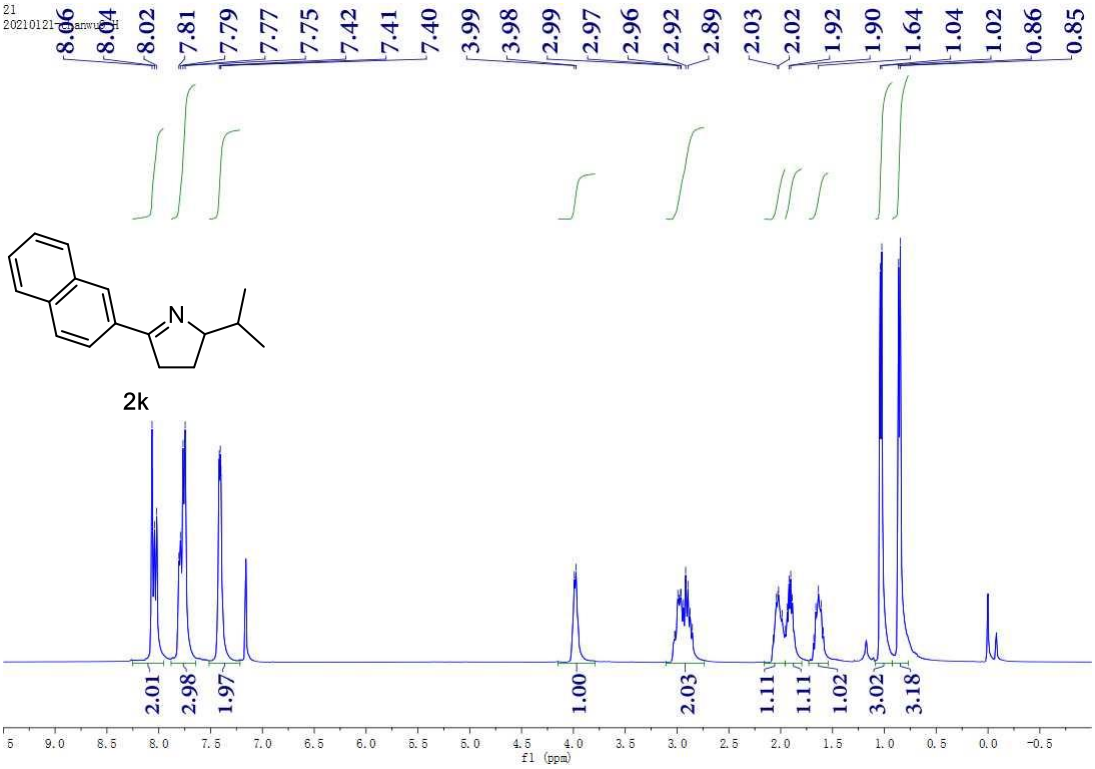
^{1}H NMR Spectrum of **2j** (400 MHz; $CDCl_3$)



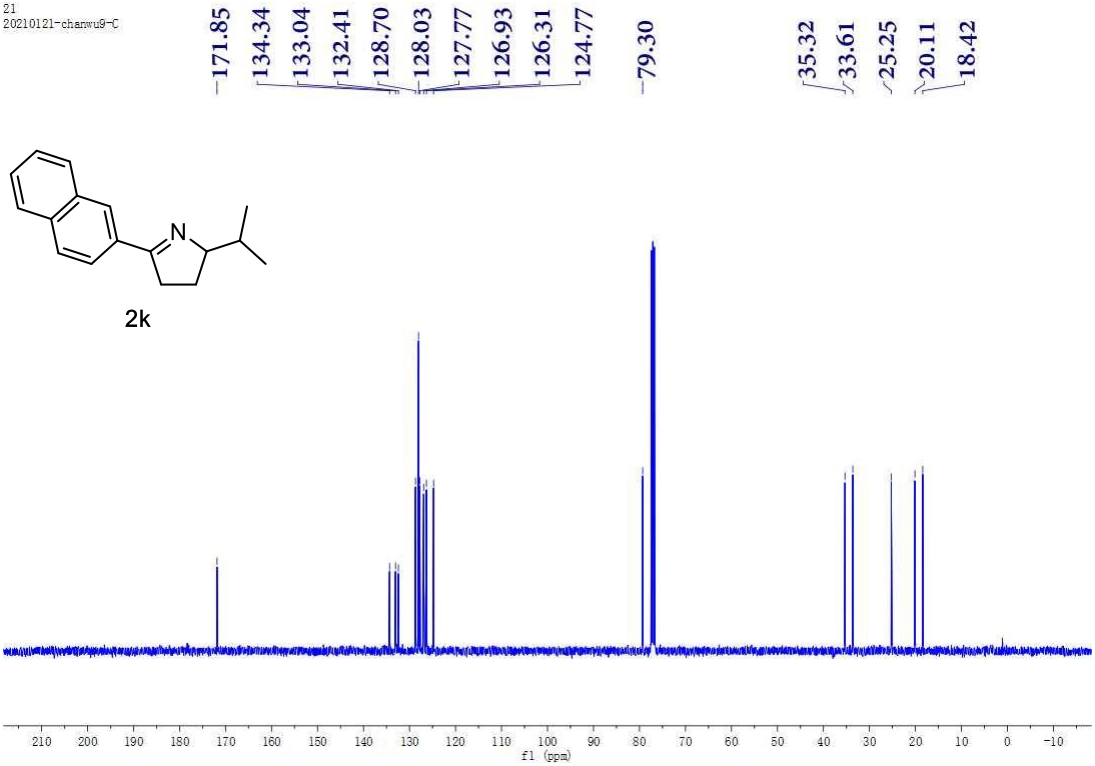
^{13}C NMR Spectrum of **2j** (100 MHz; $CDCl_3$)



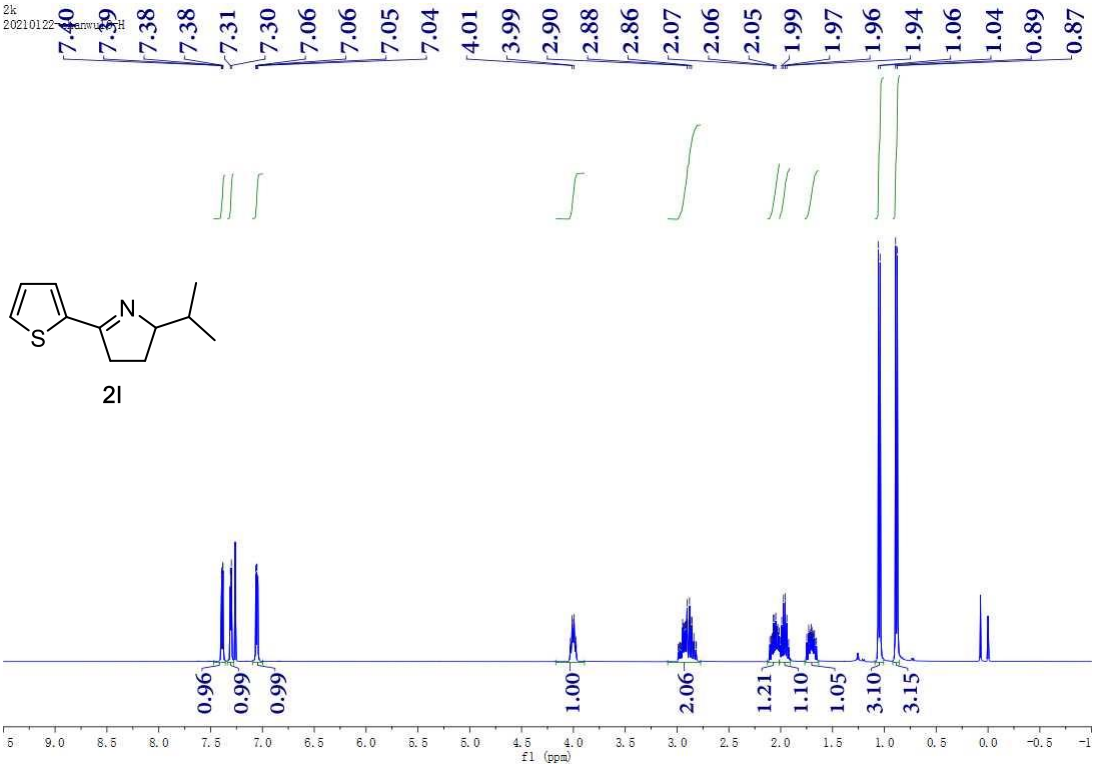
^{1}H NMR Spectrum of **2k** (400 MHz; $CDCl_3$)



^{13}C NMR Spectrum of **2k** (100 MHz; $CDCl_3$)

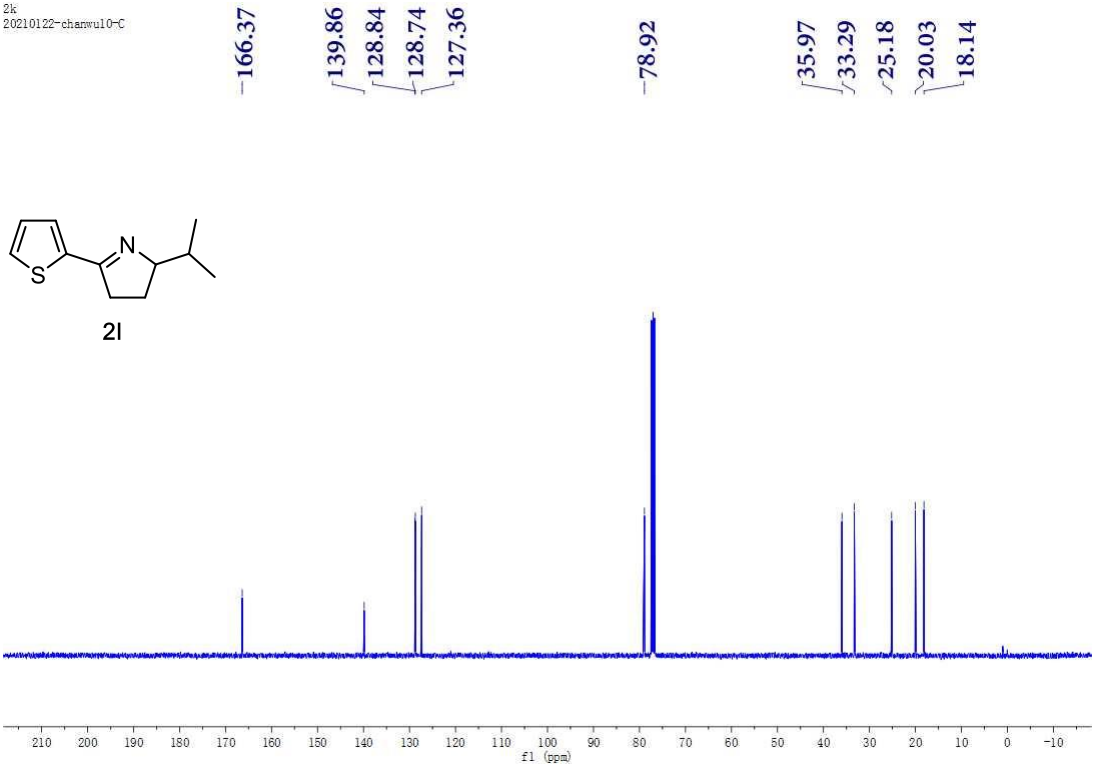


^{1}H NMR Spectrum of **2l** (400 MHz; $CDCl_3$)



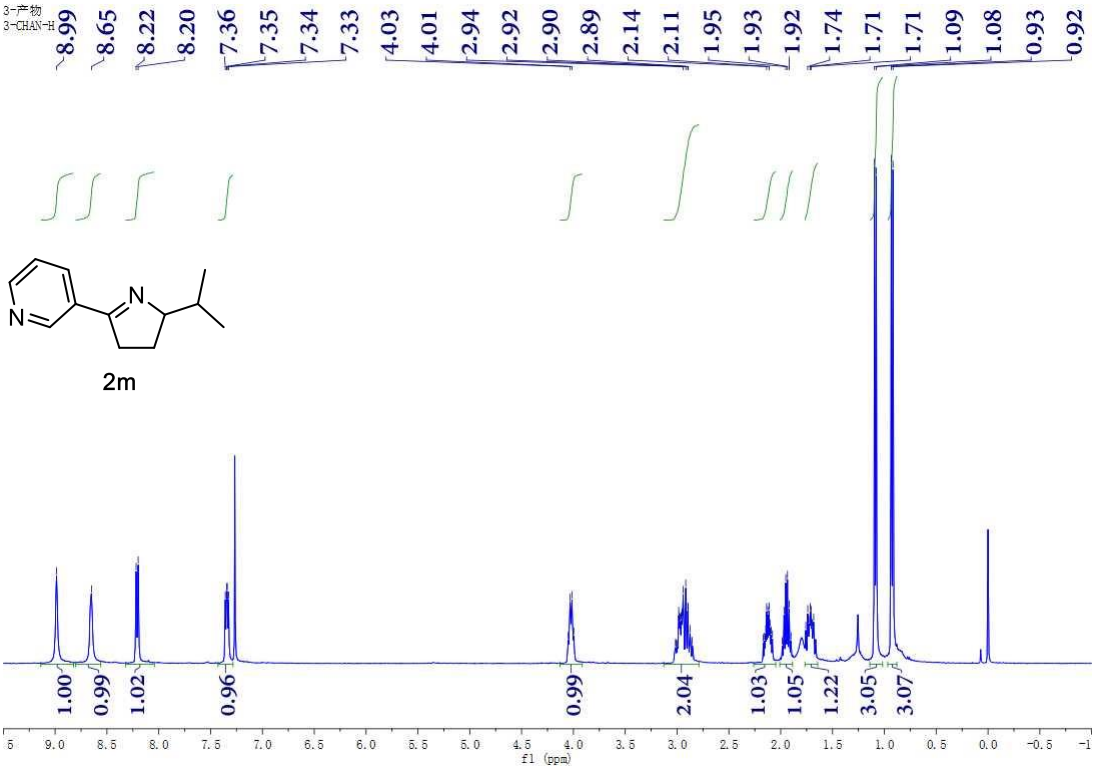
2l

^{13}C NMR Spectrum of **2l** (100 MHz; $CDCl_3$)

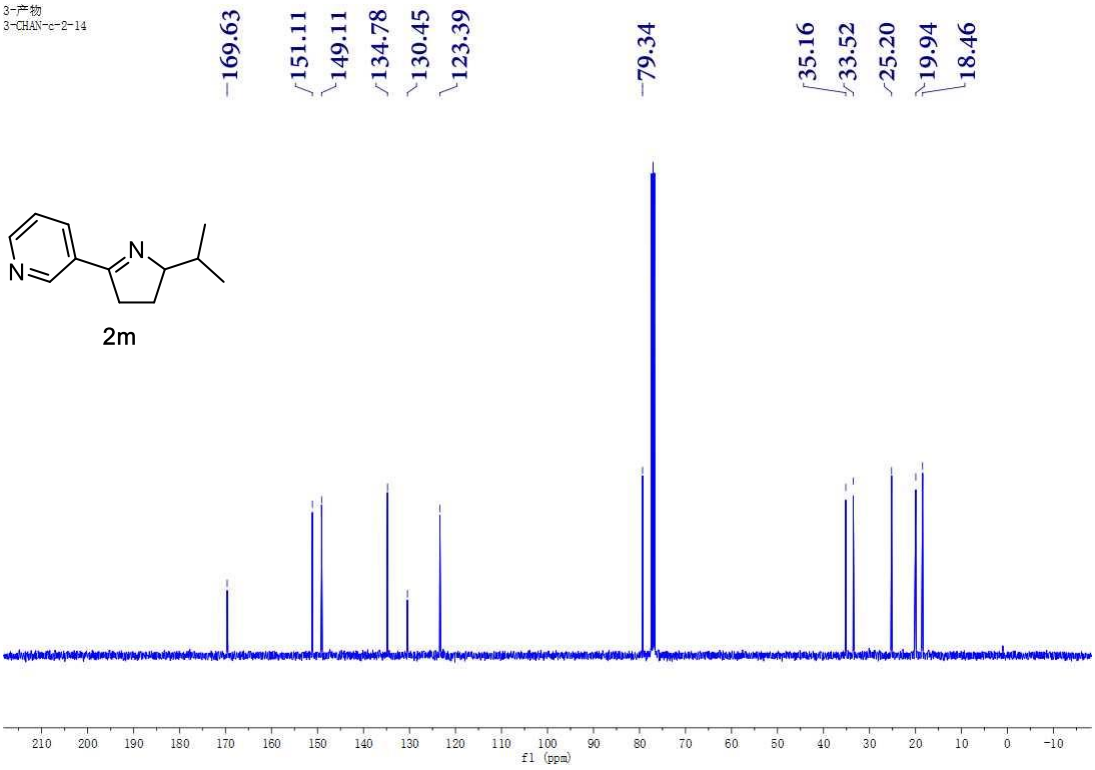


2l

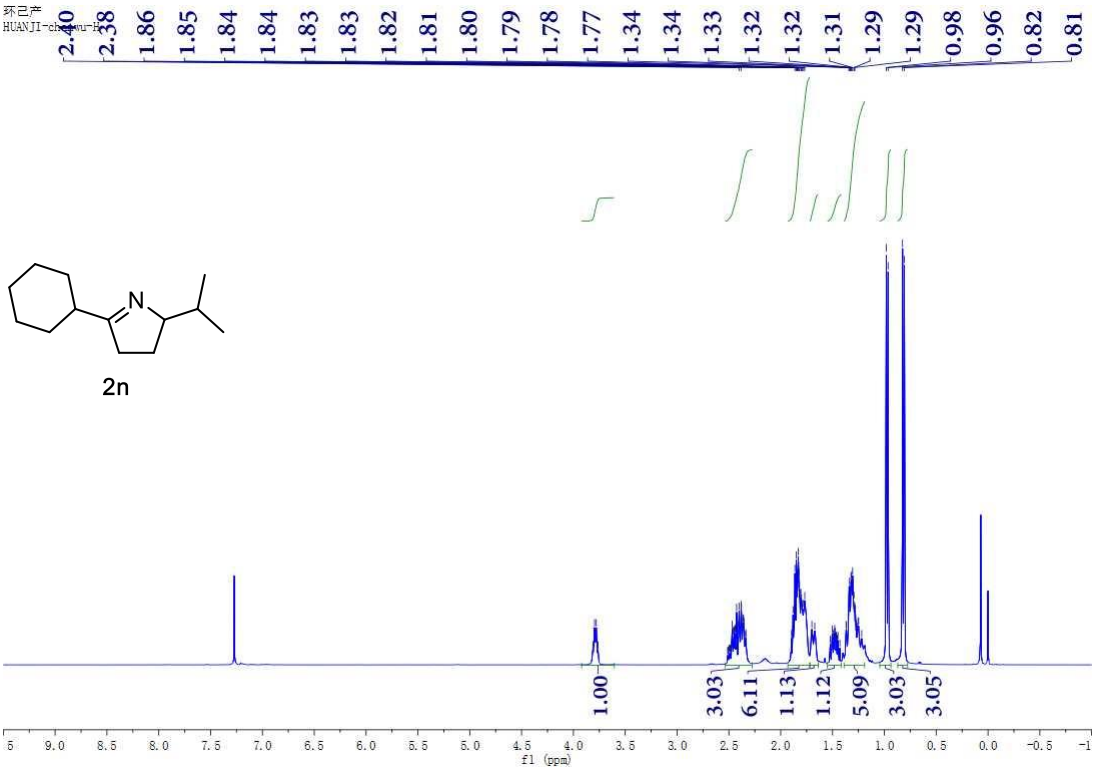
^{1}H NMR Spectrum of **2m** (400 MHz; $CDCl_3$)



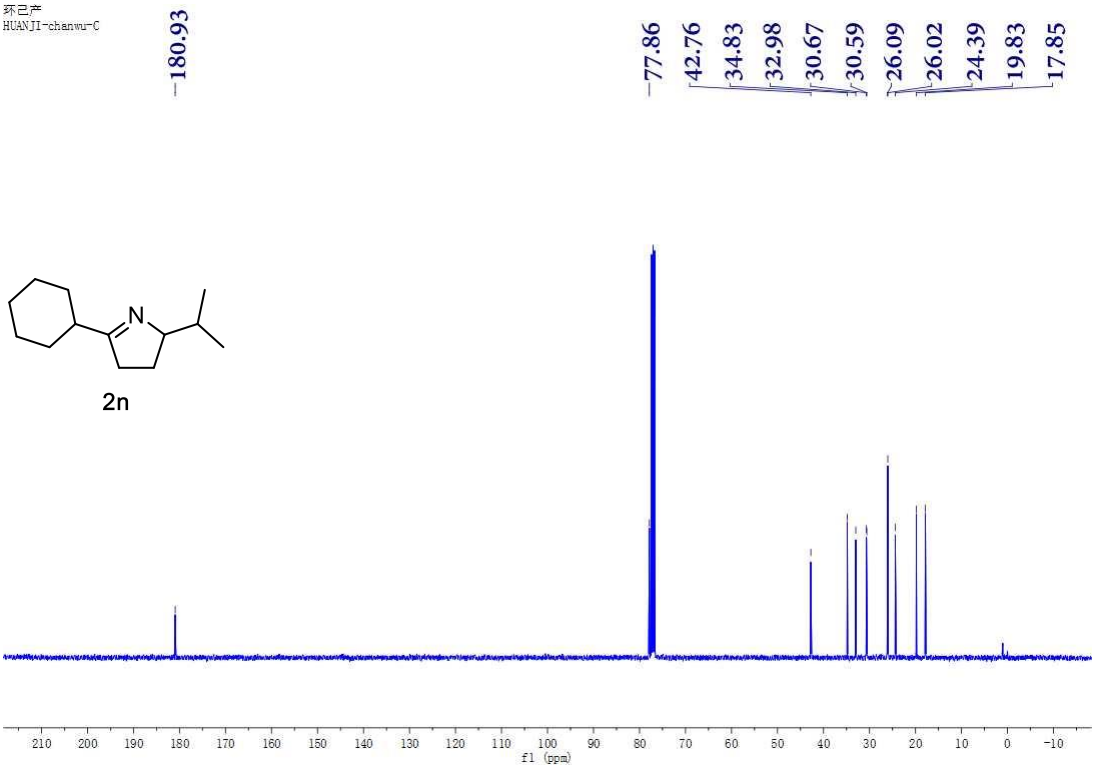
^{13}C NMR Spectrum of **2m** (100 MHz; $CDCl_3$)



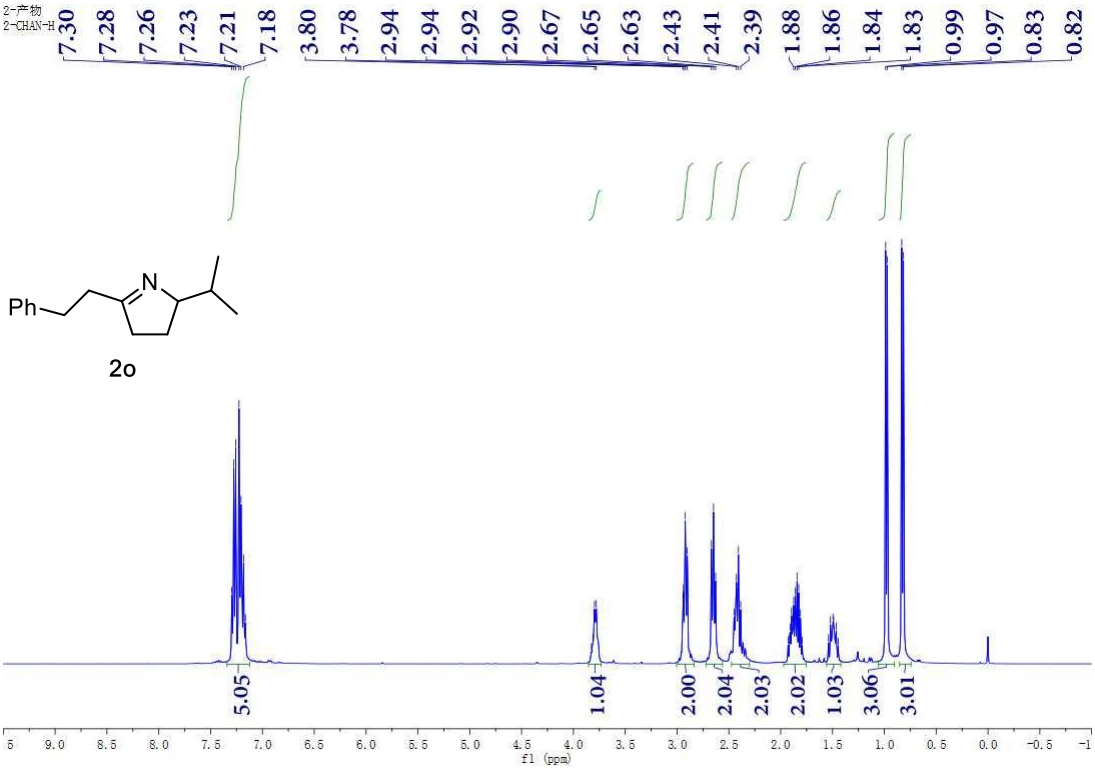
^{1}H NMR Spectrum of **2n** (400 MHz; $CDCl_3$)



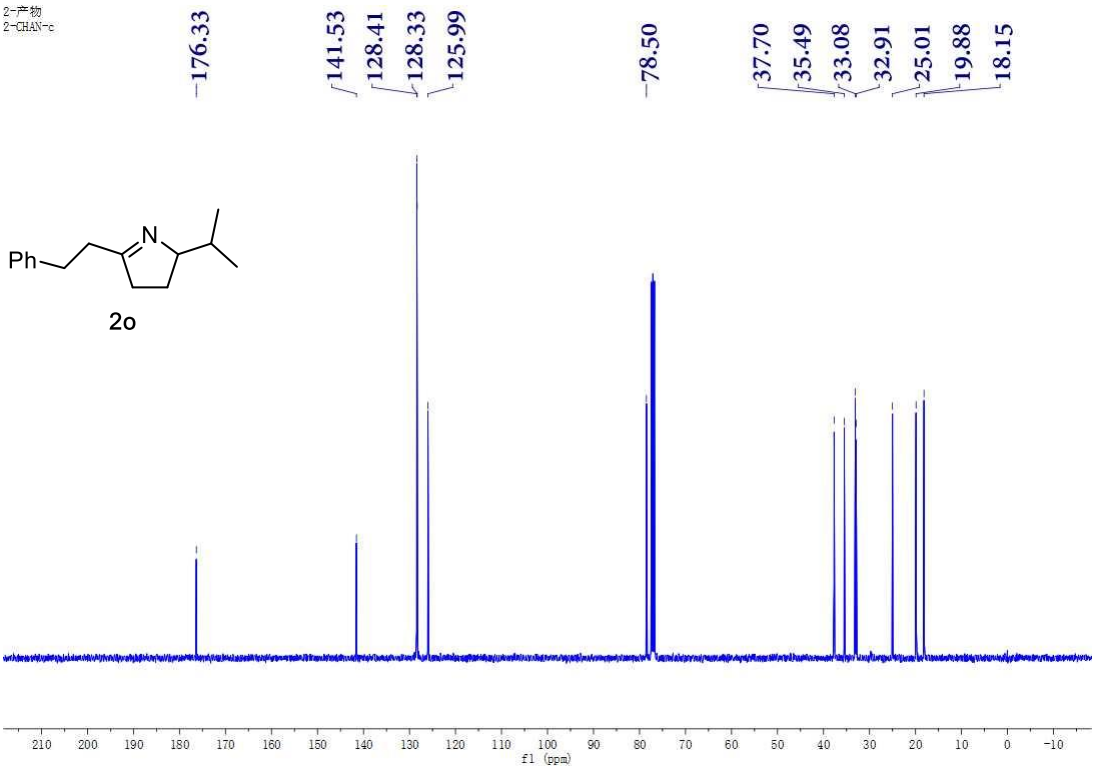
^{13}C NMR Spectrum of **2n** (100 MHz; $CDCl_3$)



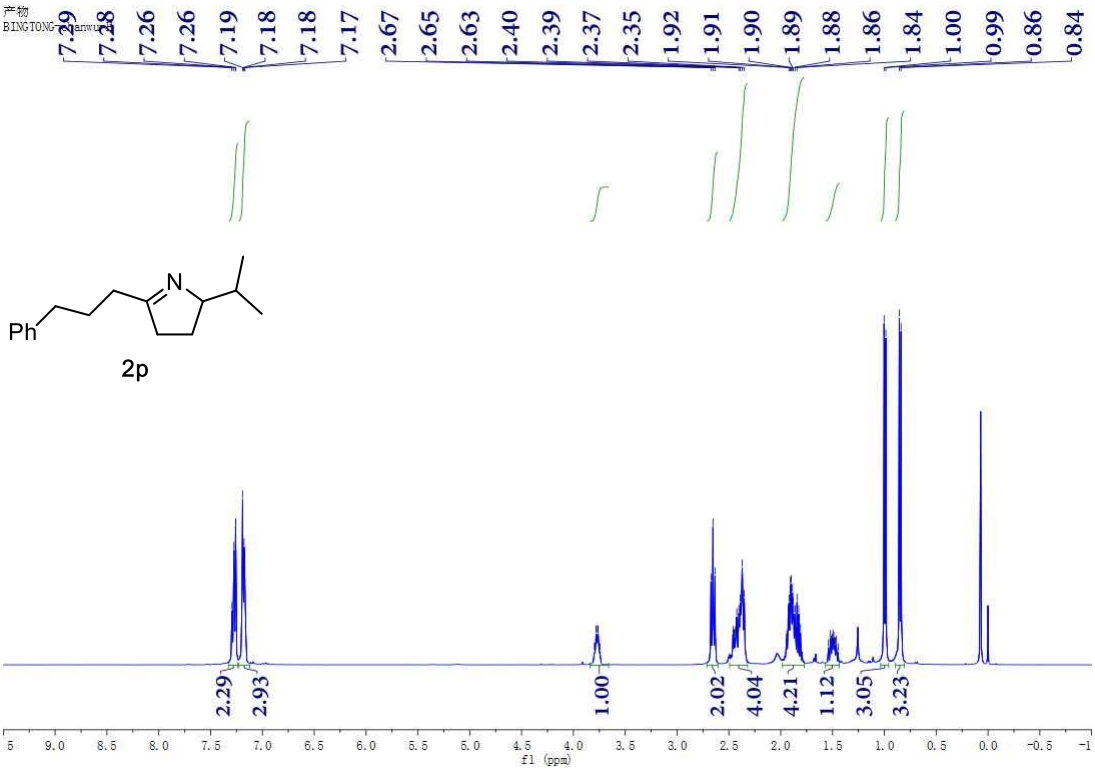
^{1}H NMR Spectrum of **2o** (400 MHz; $CDCl_3$)



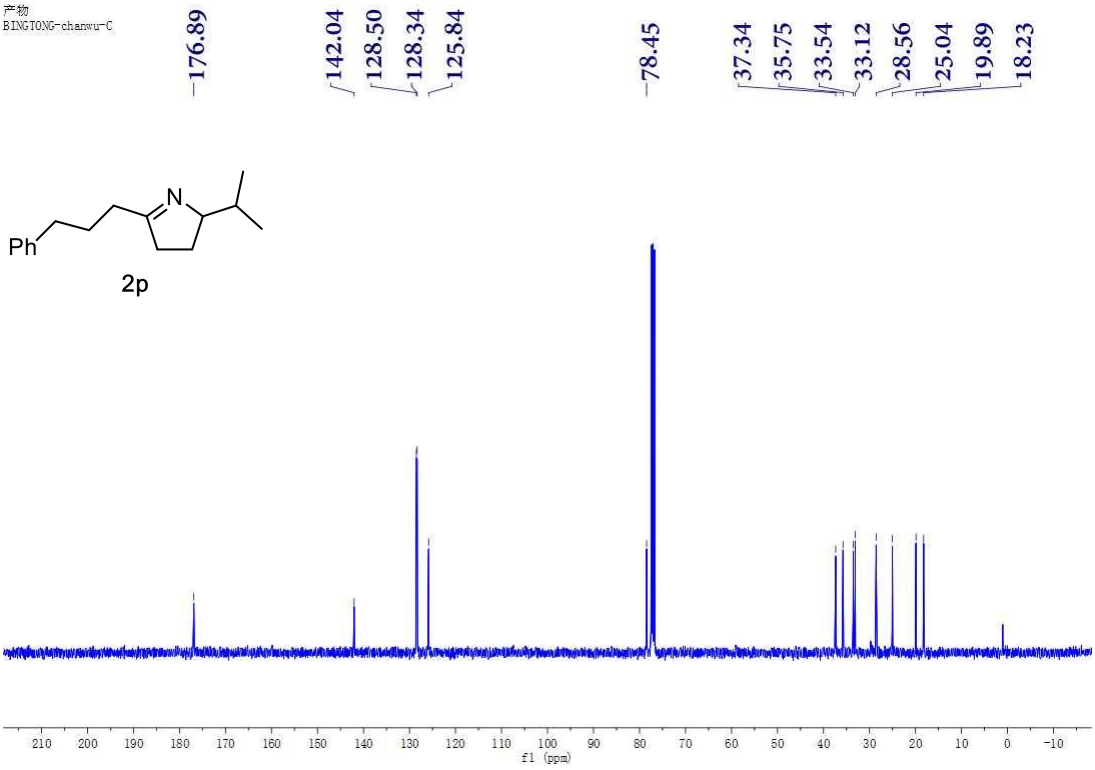
^{13}C NMR Spectrum of **2o** (100 MHz; $CDCl_3$)



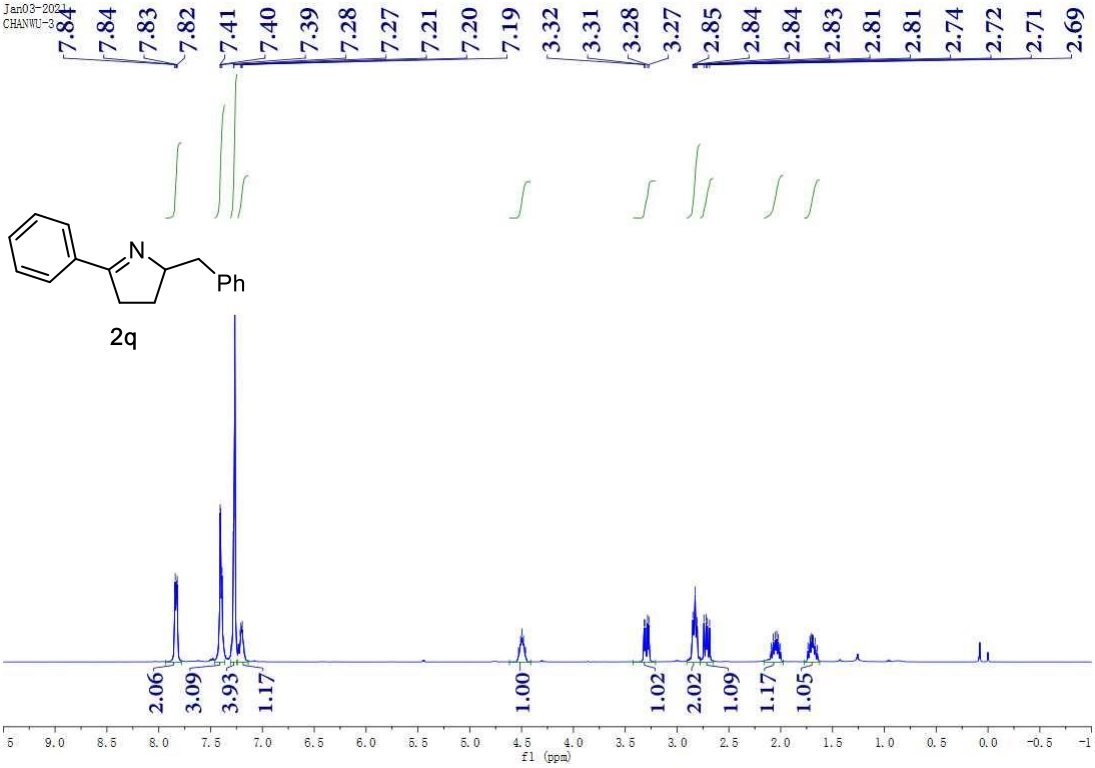
^{1}H NMR Spectrum of **2p** (400 MHz; $CDCl_3$)



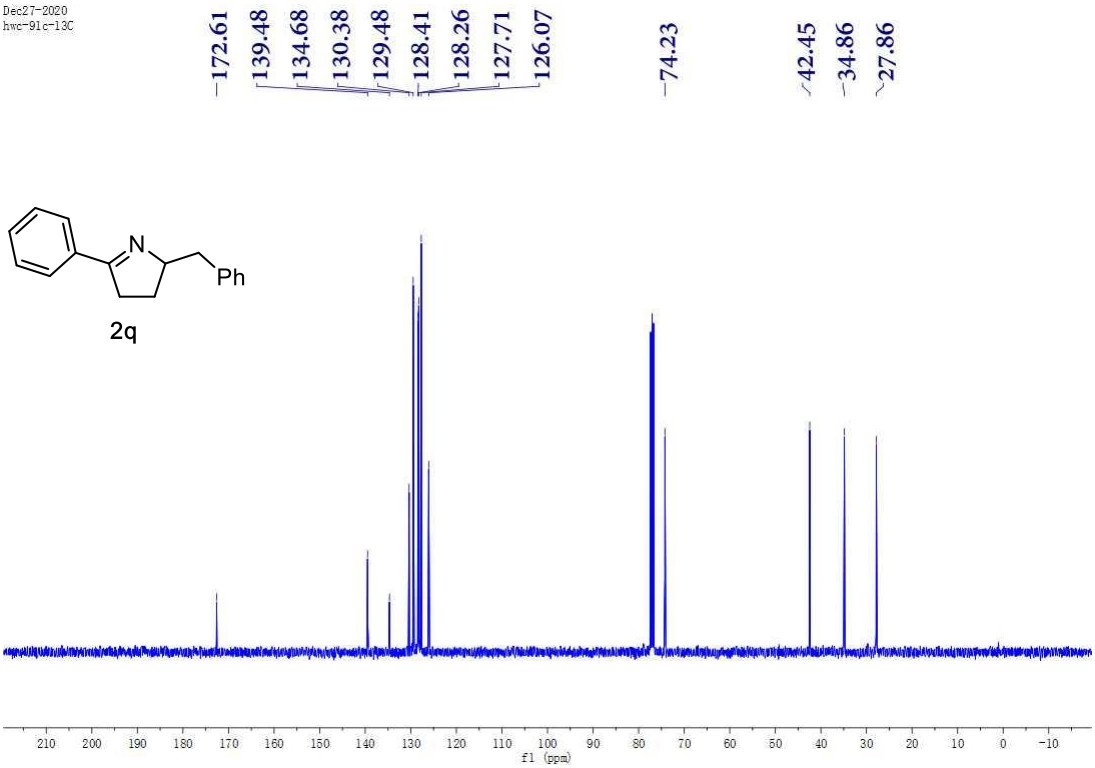
^{13}C NMR Spectrum of **2p** (100 MHz; $CDCl_3$)



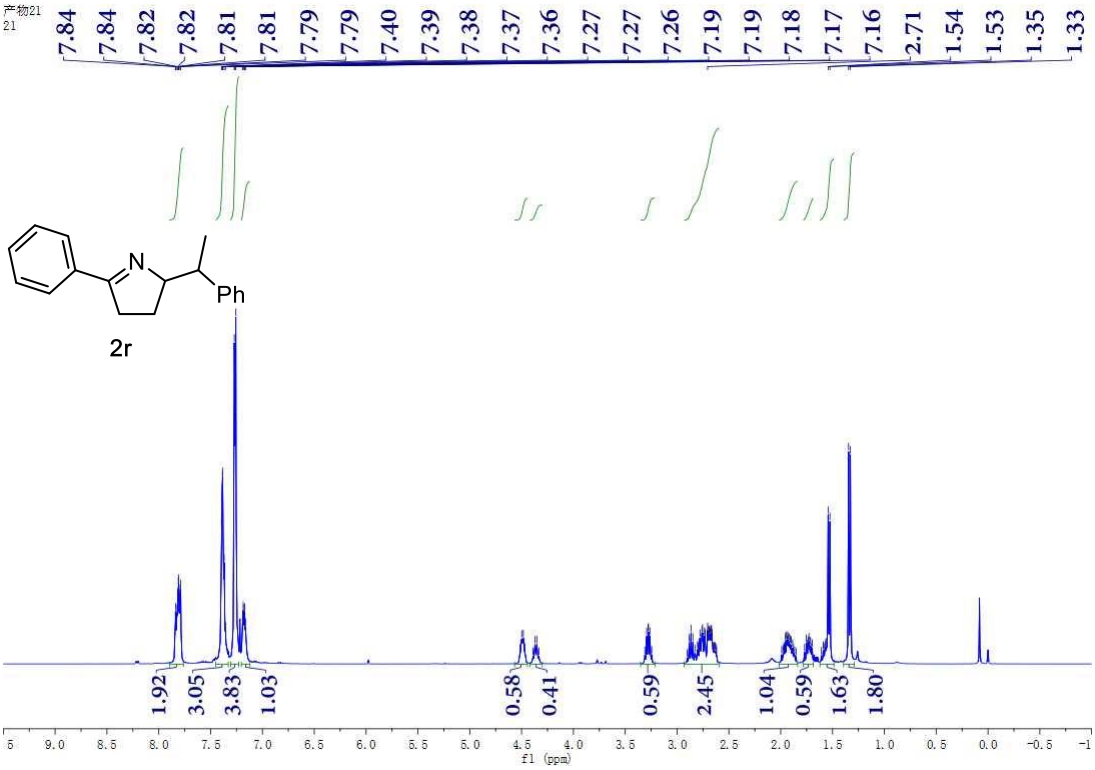
^{1}H NMR Spectrum of **2q** (400 MHz; $CDCl_3$)



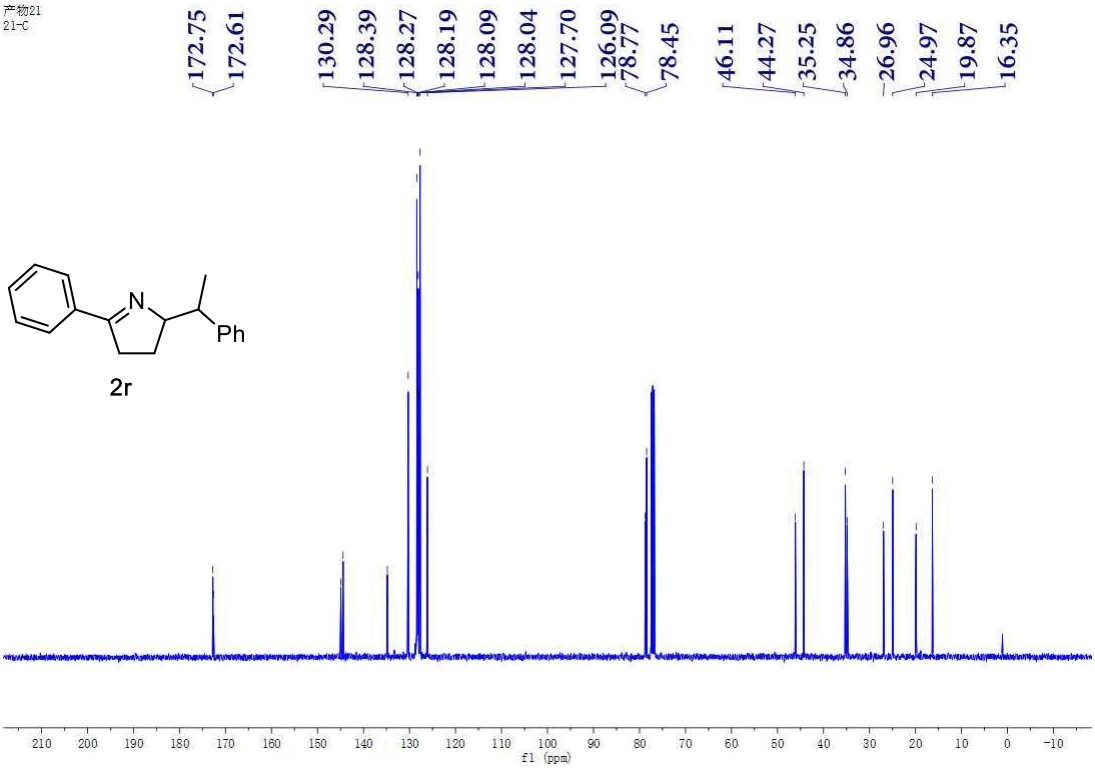
^{13}C NMR Spectrum of **2q** (100 MHz; $CDCl_3$)



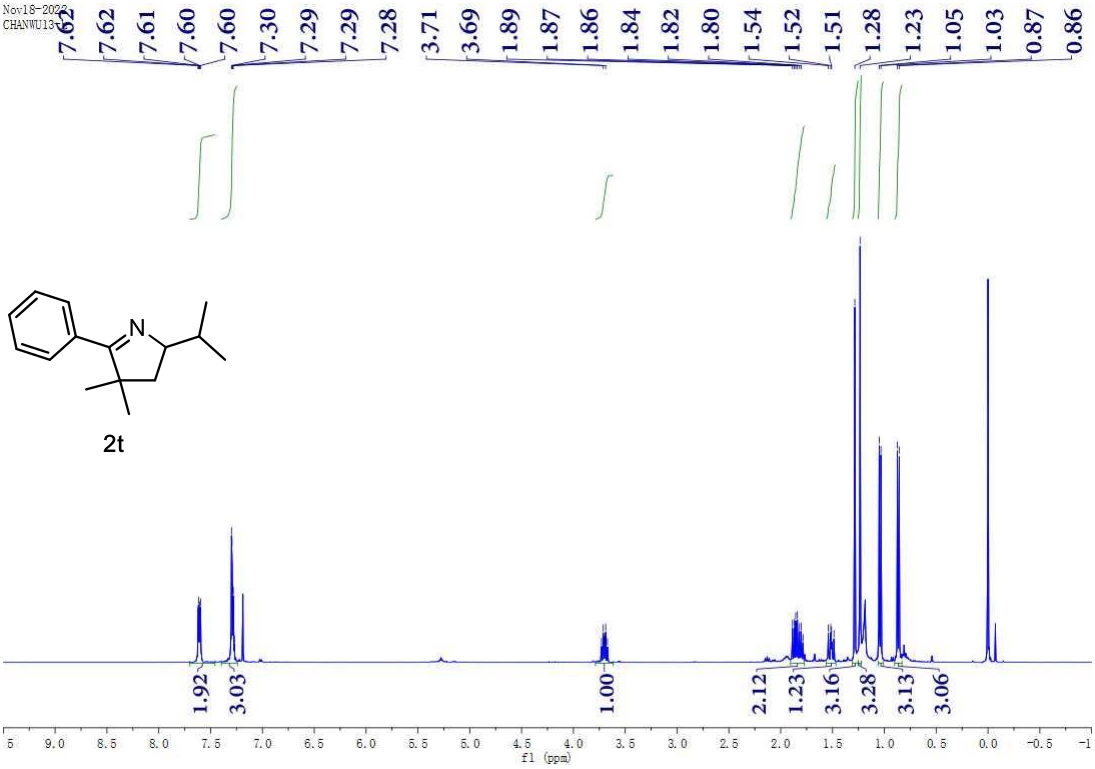
^{1}H NMR Spectrum of **2r** (400 MHz; $CDCl_3$)



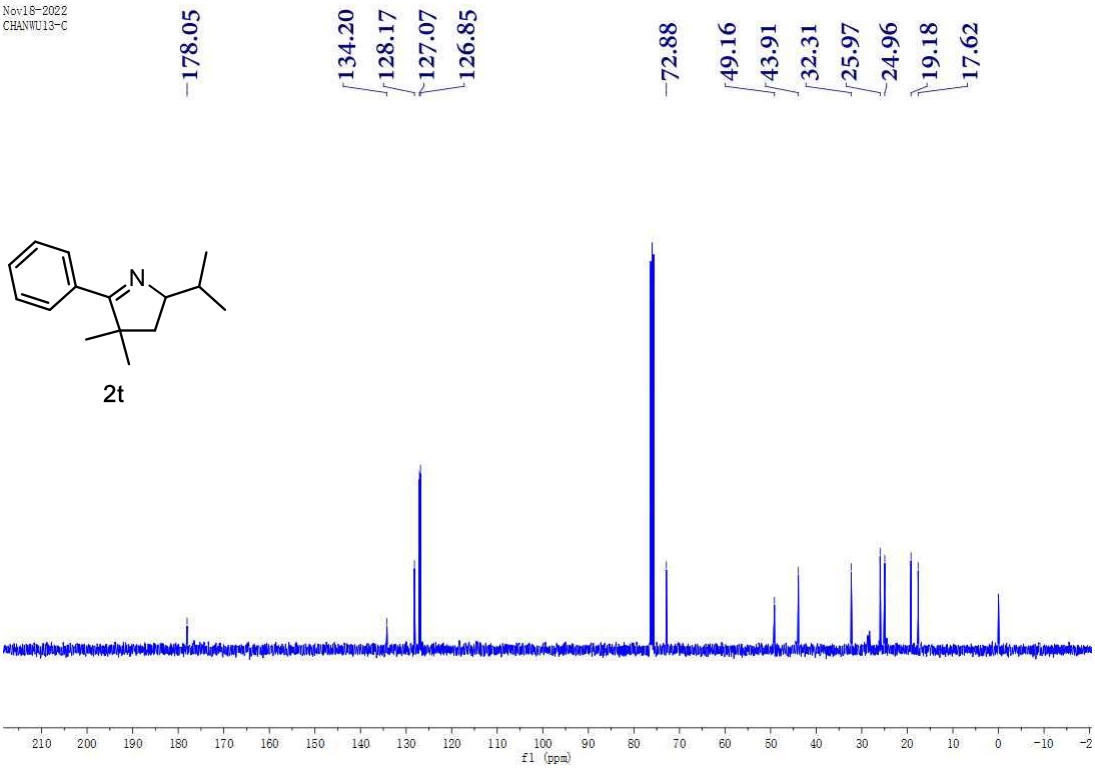
^{13}C NMR Spectrum of **2r** (100 MHz; $CDCl_3$)



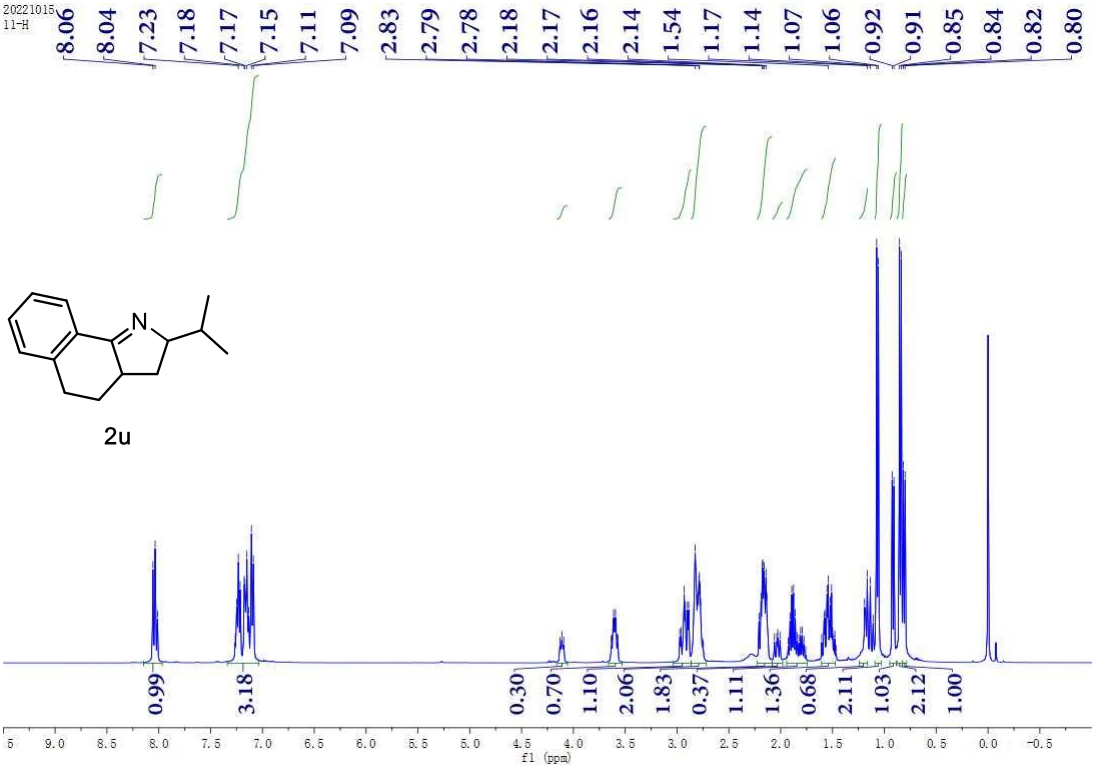
^{1}H NMR Spectrum of **2t** (400 MHz; $CDCl_3$)



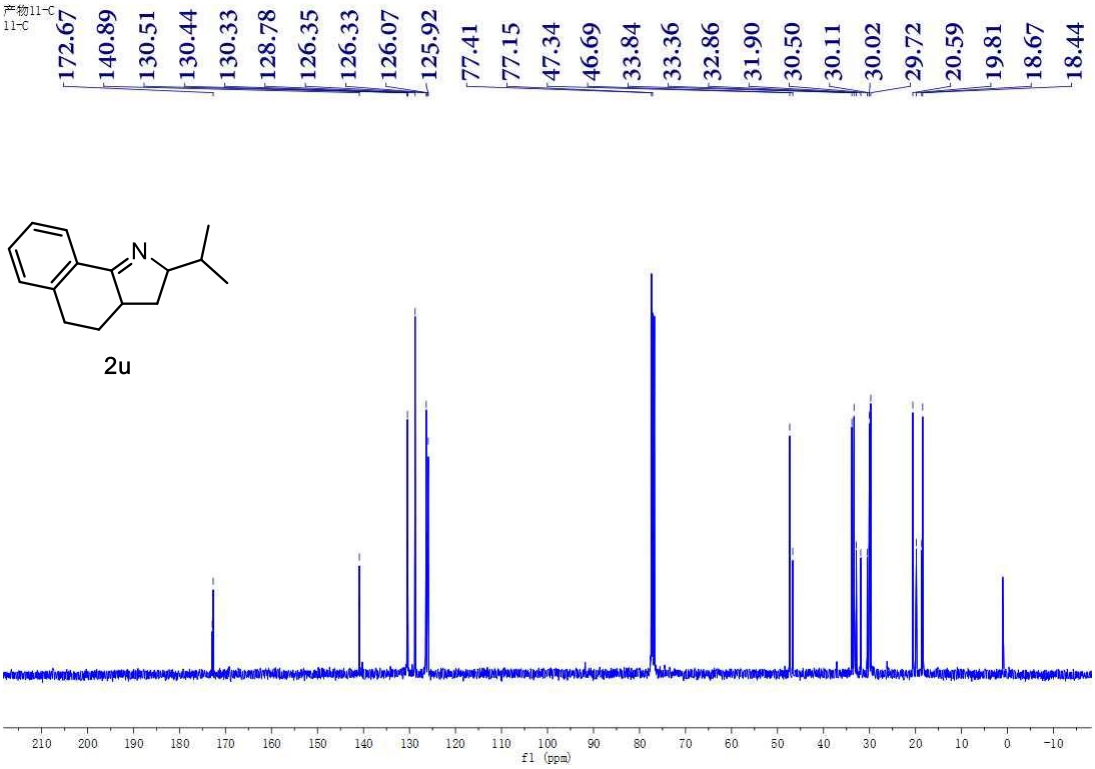
^{13}C NMR Spectrum of **2t** (100 MHz; $CDCl_3$)



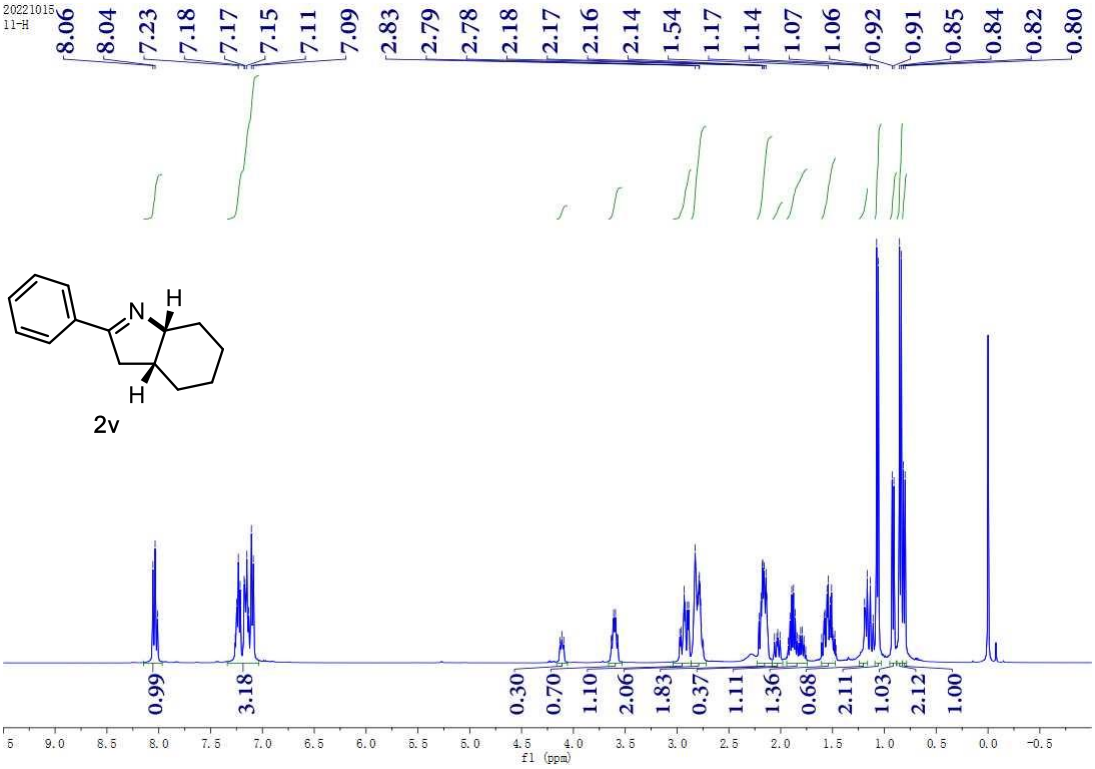
^{1}H NMR Spectrum of **2u** (400 MHz; $CDCl_3$)



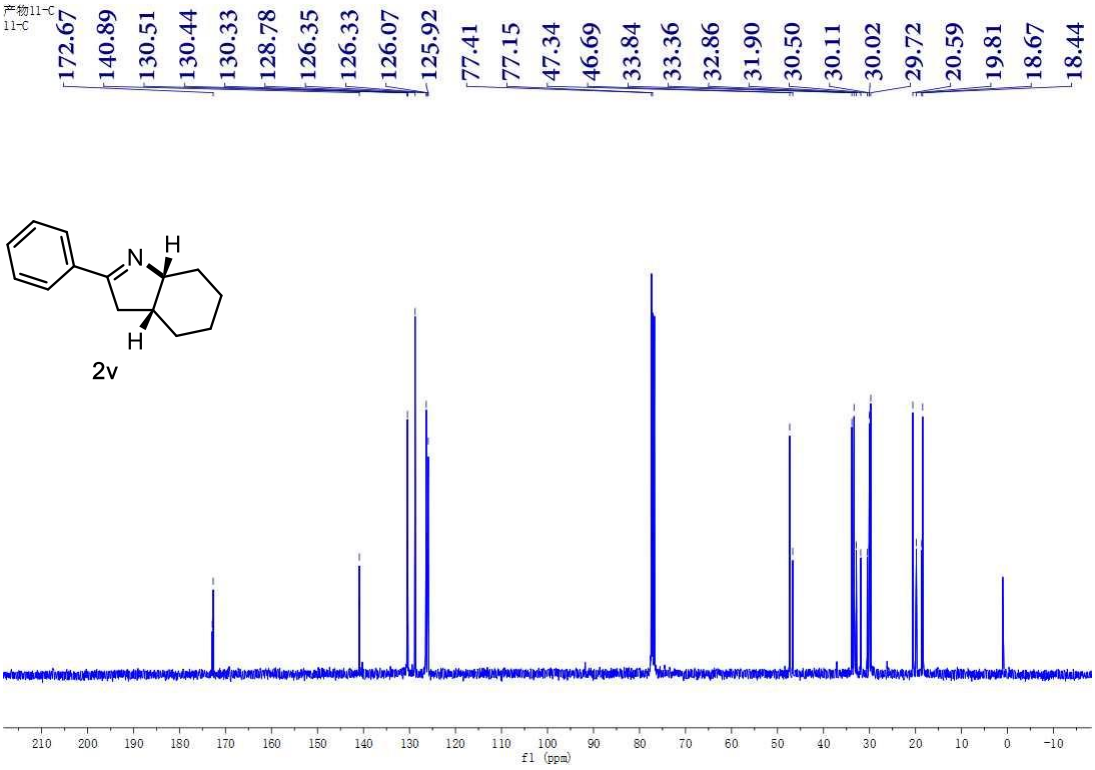
^{13}C NMR Spectrum of **2u** (100 MHz; $CDCl_3$)



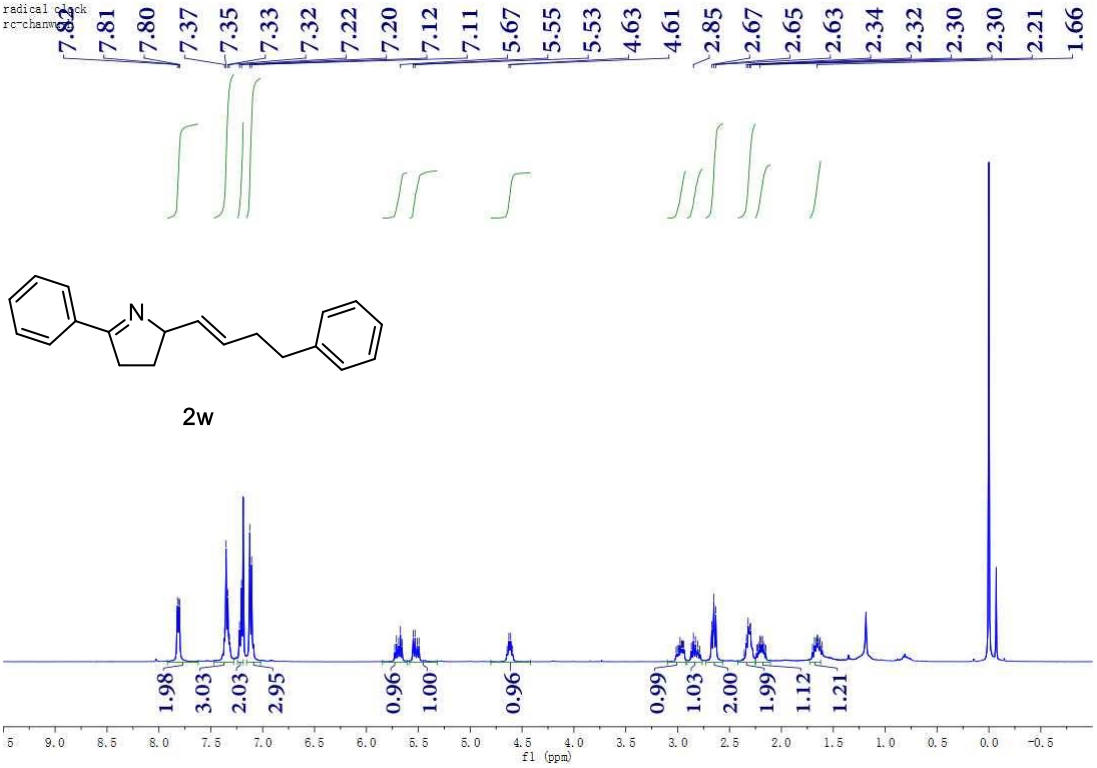
^{1}H NMR Spectrum of **2v** (400 MHz; $CDCl_3$)



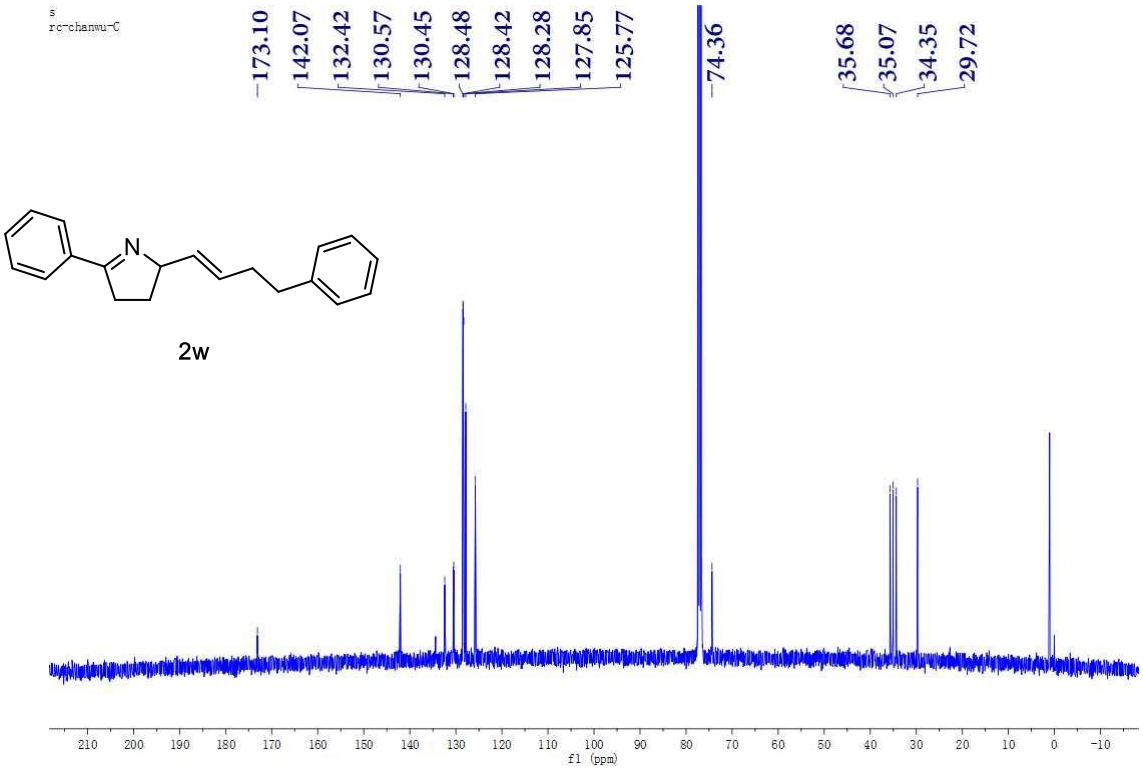
^{13}C NMR Spectrum of **2v** (100 MHz; $CDCl_3$)



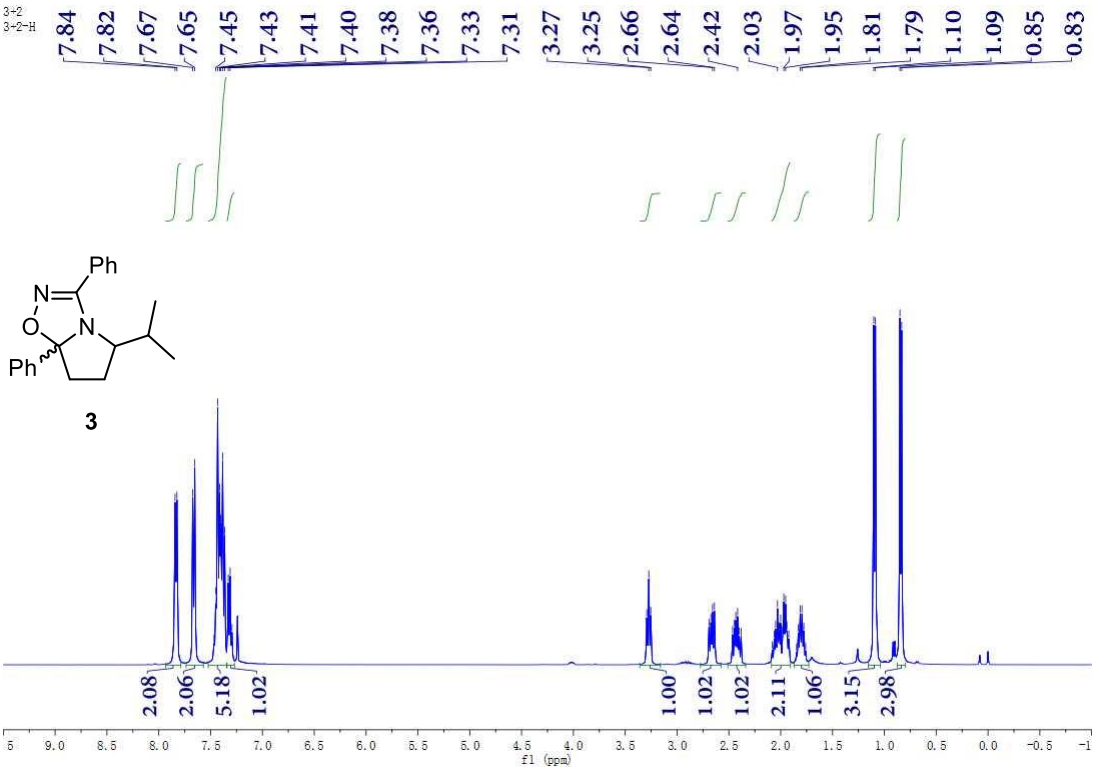
^{1}H NMR Spectrum of **2w** (400 MHz; $CDCl_3$)



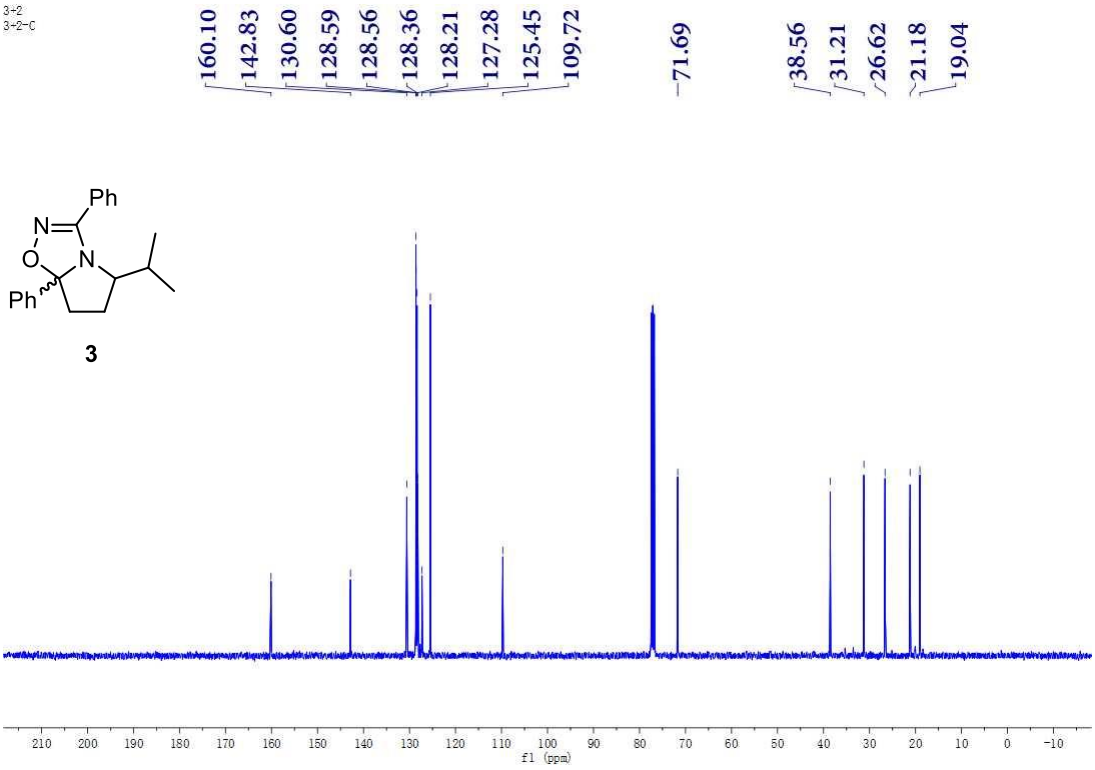
^{13}C NMR Spectrum of **2w** (100 MHz; $CDCl_3$)



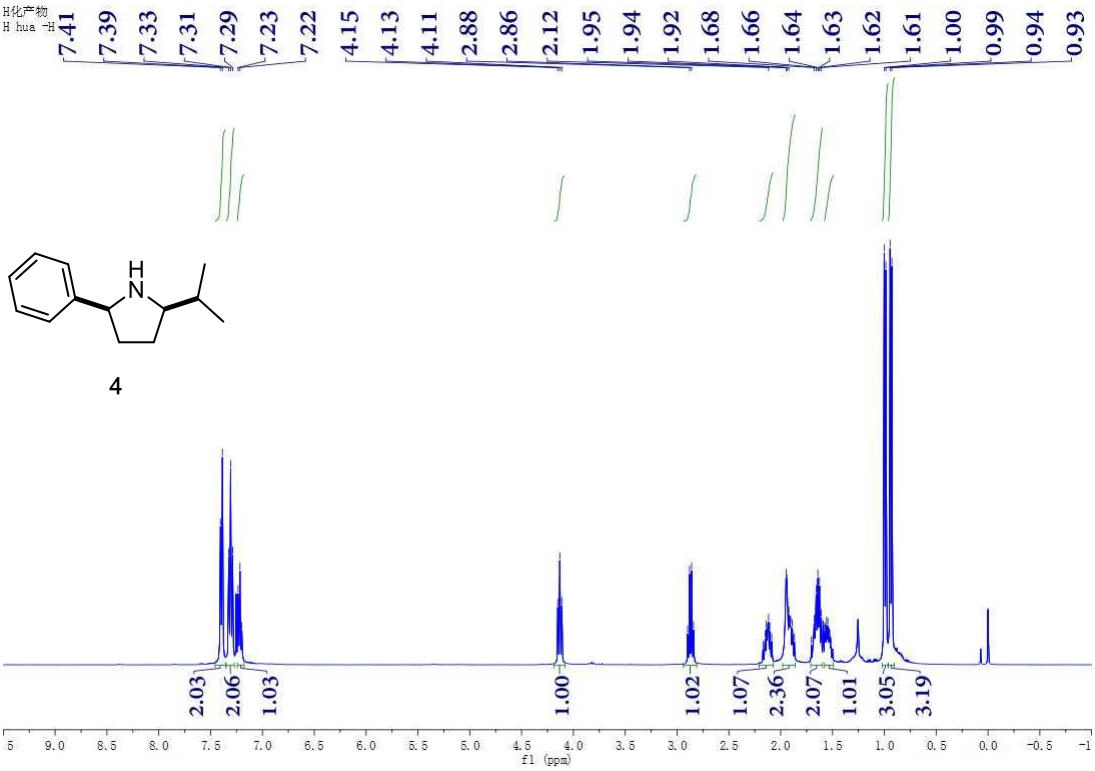
^{1}H NMR Spectrum of **3** (400 MHz; $CDCl_3$)



^{13}C NMR Spectrum of **3** (100 MHz; $CDCl_3$)



^{1}H NMR Spectrum of **4** (400 MHz; $CDCl_3$)



^{13}C NMR Spectrum of **4** (100 MHz; $CDCl_3$)