Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dearomative Pyrrole (3 + 2) Reaction with Geminal Bromonitroalkane: Synthesis of 2,3-Dihydropyrroles

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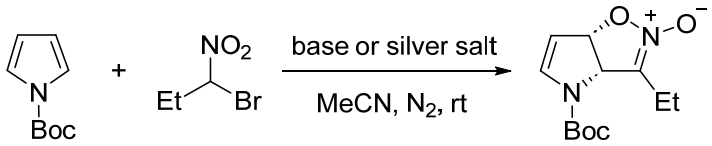
Table of contents

1. General information

All the solvents and reagents were obtained from commercial sources and used without purification unless stated otherwise. THF, Et_2O and 1,4-dioxane were distilled over CaH_2 and $LiAlH_4$ under N_2 atmosphere. Toluene, CH_2Cl_2 and CH_3CN were distilled over CaH_2 under N_2. Acetone, AcOEt, DMSO, DMA, DMF, DME, $CHCl_3$, $C_2H_5NO_2$, CH_3NO_2 and DBU were dried over activated 4A molecular sieves. All glassware was dried overnight at 100 °C prior to use. Thin-layer chromatography (TLC) was performed on silica gel plates (0.2–0.25 mm thickness). Visualization of TLC was achieved by the use of UV light (254 nm). Flash column chromatography was performed on a silica gel (Qingdao Haiyang, 200–300 mesh) column. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECZ 400 MHz or 600 MHz spectrometer. The chemical shift (δ) values are given in ppm and are referenced to TMS or residual solvent peaks. Chemical shifts of ^{19}F NMR are referred to $CFCl_3$ (δ = 0). Infrared spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRX-4 (Shanghai Yice) micro melting point apparatus. Mass spectra were obtained on an AB Sciex TripleTOF 5600+ mass spectrometer. X-ray diffraction experiment was performed on a Rigaku XtalLAB Synergy diffractometer using Cu Kα radiation. Visible light promoted reactions were conducted in a tube irradiated with blue light LEDs (456 nm, 15 W, approximately 3.0 cm distance from the tube). For reactions that require heating, a silicone oil bath was used.

2. Optimization of reaction conditions

Table S1 Effect of base or Ag(I) salt.



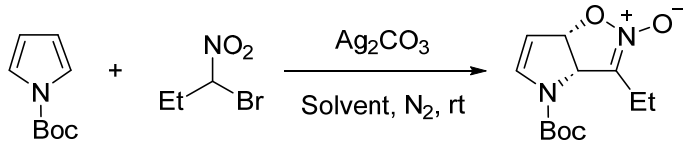
1a **2a** **(±)-3aa**

Entry	Base or Ag salt	Yield (%)[a]	Entry	Base or Ag salt	Yield (%)[a]
1	Na_2CO_3	trace	14	Ag_2CO_3	50[b]
2	$NaHCO_3$	0	15		0[c]
3	NaH_2PO_4	0	16		75[d]
4	CH_3CO_2Na	0	17		0[e]
5	$KF·2H_2O$	0	18	$Cu(OH)_2$	0
6	Ag_2O	12	19	DABCO	0
7	AgF	31	20	DBU	0

8	$AgPF_6$	17	21	Et_3N	0
9	Ag_2SO_4	0	22	DIPEA	0
10	AgOAc	0	23	2,6-lutidine	0
11	$AgNO_2$	0	24	pyridine	0
12	$AgNO_3$	0	25	none	0
13	Ag_2CO_3	0	26	TBSCl/Et_3N	0[f]

[a] Isolated yield. [b] The mixture was irradiated with blue light LEDs (456 nm). [c] 10 mol % PPh_3 was added. [d] 10 mol % PPh_3 was added. The mixture was irradiated with blue light LEDs (456 nm). [e] 10 mol % (*R*)-BINAP was added. The mixture was irradiated with blue light LEDs (456 nm). [f] Reaction time: 7 days.

Table S2 Effect of solvent.

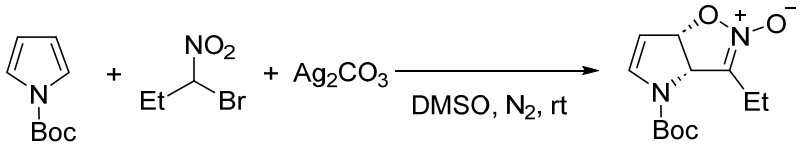


1a **2a** **(±)-3aa**

Entry	Solvent	Yield (%)[a]	Entry	Solvent	Yield (%)[a]
1	THF	0	9	AcOEt	0
2	DME	0	10	Acetone	0
3	Et_2O	0	11	DMF	20
4	1,4-Dioxane	12	12	DMA	33
5	Benzene	31	13	DMSO	80
6	Toluene	17	14	Methanol	0
7	DCM	0	15	Ethanol	0
8	Chloroform	0			

[a] Isolated yield.

Table S3 Effect of the molar ratio.



1a **2a** **(±)-3aa**

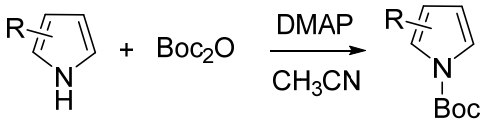
1a : **2a** : Ag_2CO_3	Yield (%)[a]	**1a** : **2a** : Ag_2CO_3	Yield (%)[a]
1.0 : 1.0 : 2.0	31	1.0 : 2.0 : 1.0	63
1.0 : 2.0 : 2.0	80	1.0 : 2.0 : 1.5	75
1.0 : 3.0 : 2.0	78	1.0 : 2.0 : 3.0	82

[a] Isolated yield.

3. Preparation of pyrroles

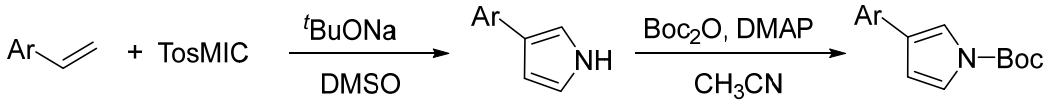
3.1 Preparation of pyrroles

General procedure A[1]



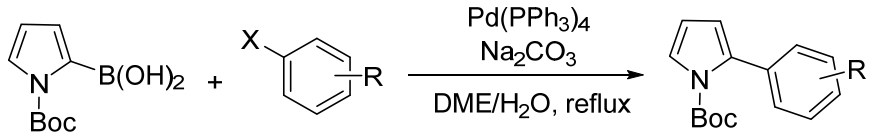
Boc_2O (1.4 mL, 6.0 mmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol) were added to a solution of pyrrole (5.0 mmol) in acetonitrile. The solution was stirred at rt overnight, diluted with Et_2O, washed with $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the corresponding product.

General procedure B[2]



To a suspension of ^{t}BuONa (384 mg, 4.0 mmol) in dry DMSO (10 mL) at room temperature was added a solution of arylalkene (2.0 mmol) and tosylmethyl isocyanate (508 mg, 2.6 mmol) in DMSO (10 mL) via cannular. The beige solution was stirred at room temperature for 2 h whereupon it was diluted with EtOAc (50 mL) and brine (50 mL). The aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the 3-arylpyrrole. *N*-Boc-3-arylpyrrole was synthesized according to General procedure A.

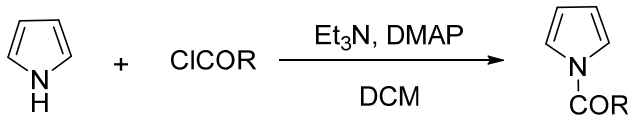
General procedure C[3]



To a stirred solution of the appropriate aryl iodide or bromide (3.6 mmol), *N*-Boc-pyrrole-2-boronic acid (1.06 g, 5.0 mmol) and *tetrakis*-(triphenylphosphine)palladium (0.21 g, 0.18 mmol) in 1,2-dimethoxyethane (20 mL) at room temperature under argon was added a solution of sodium carbonate (1.6 g, 15 mmol) in water (8 mL). The mixture was heated at reflux for 4 h, cooled, then partitioned

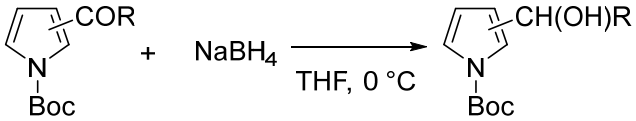
between water (50 mL) and dichloromethane (4 × 20 mL). The combined extracts were dried over Na_2SO_4 and evaporated in vacuo to give an oil. The residue was purified by flash chromatography on silica gel to give the *N*-Boc-2-arylpyrrole.

General procedure D[4]



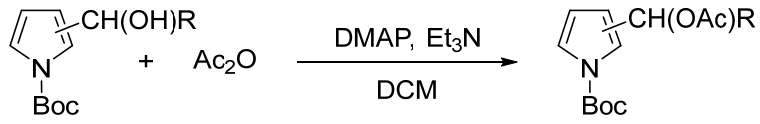
Triethylamine (1.0 mL, 7.5 mmol) was added to a stirred solution of pyrrole (0.4 mL, 5.0 mmol) and chloroformate, acyl chloride or sulfonyl chloride (7.5 mmol) in dry DCM at 0 °C. DMAP (61 mg, 0.5 mmol) was added to the mixture. After stirring the reaction mixture at room temperature for 5 min, the reaction was completed. Water was added to the mixture. The aqueous layer was extracted with 3 portions of EtOAc. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel to give the corresponding product.

General procedure E[5]



To a solution of acyl-substituted pyrrole (10 mmol) in 30 mL THF at 0 °C, $NaBH_4$ (379 mg, 10 mmol) was added in portions, and the mixture was stirred for 1.5 h at 0 °C. The reaction mixture was supplemented with 100 mL Et_2O, poured onto 50 mL ice water and extracted with Et_2O (3 × 100 mL). The combined organic phase was washed with brine (3 × 50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography to give the corresponding product.

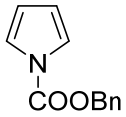
General procedure F



The hydroxyalkyl-substituted pyrrole (10 mmol) and Ac_2O (0.95 mL, 10 mmol) in CH_2Cl_2 (30 mL) were treated with Et_3N (2 mL, 10 mmol) and DMAP (122 mg, 1 mmol), and the mixture was stirred at rt overnight. The mixture was diluted with CH_2Cl_2. The organic layer was washed with brine (3 × 50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by silica gel chromatography to give the corresponding product.

3.2 Physical data

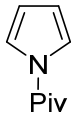
Phenylmethyl-1*H*-pyrrole-1-carboxylate (1b)[6]



General procedure D

Clear oil (0.9 g, 90% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.05 (m, 7H), 6.33 (d, *J* = 2.5 Hz, 2H), 5.43 (d, *J* = 3.1 Hz, 2H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 134.8, 134.8, 128.5, 128.2, 120.0, 112.4, 68.7 ppm.

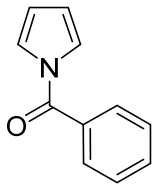
2,2-Dimethyl-1-(1*H*-pyrrol-1-yl)-1-propanone (1c)[7]



General procedure D

Clear oil (0.7 g, 97% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 2.4 Hz, 2H), 6.08 (t, *J* = 2.4 Hz, 2H), 1.29 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.8, 120.5, 111.8, 40.5, 28.4 ppm.

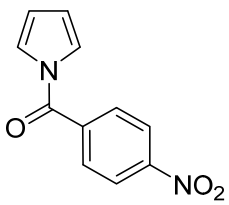
Phenyl-*H*-pyrrole-1-ylmethanone (1d)[8]



General procedure D

White solid (0.7 g, 80% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.28 (m, 2H), 6.35 (t, *J* = 2.3 Hz, 2H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.5, 133.1, 132.1, 129.3, 128.3, 121.1, 113.0 ppm.

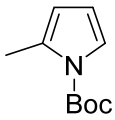
(4-Nitrophenyl)-1*H*-pyrrole-1-ylmethanone (1e)[9]



General procedure D

White solid (0.8 g, 75% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.20 (m, 2H), 6.41 – 6.37 (m, 2H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.6, 149.8, 138.9, 130.3, 123.7, 121.0, 114.2 ppm.

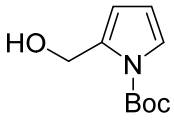
1,1-Dimethylethyl 2-methyl-1*H*-pyrrole-1-carboxylate (1f)



General procedure A

Clear oil (0.8 g, 91% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.08 (t, *J* = 3.3 Hz, 1H), 5.99 – 5.74 (m, 1H), 2.46 (s, 3H), 1.62 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.6, 131.4, 120.4, 111.7, 109.8, 83.1, 27.9, 15.3 ppm.

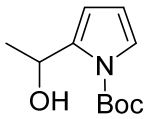
1,1-Dimethylethyl 2-(hydroxymethyl)-1*H*-pyrrole-1-carboxylate (1g)



General procedure E

Clear oil (0.9 g, 93% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.17 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.09 (t, *J* = 3.3 Hz, 1H), 4.64 (d, *J* = 6.4 Hz, 2H), 1.61 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.0, 134.7, 121.8, 113.4, 110.2, 84.4, 57.6, 27.8 ppm.

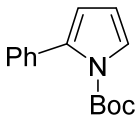
***tert*-Butyl 2-(1-hydroxyethyl)-1*H*-pyrrole-1-carboxylate (1h)**



General procedure E

Clear oil (0.9 g, 90% yield); R_f = 0.5 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.25 – 6.16 (m, 1H), 6.09 (t, *J* = 3.4 Hz, 1H), 5.08 – 5.05 (m, 1H), 4.16 (d, *J* = 3.4 Hz, 1H), 1.61 (s, 9H), 1.57 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.3, 139.1, 121.9, 110.9, 110.2, 84.5, 62.0, 28.0, 20.3 ppm; IR (film) ν_{max} 3428, 1366, 1130, 788 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{17}NO_3Na$ 234.1101; Found 234.1106.

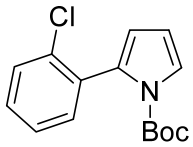
1,1-Dimethylethyl-2-phenyl-1*H*-pyrrole-1-carboxylate (1i)[10]



General procedure C

Clear oil (0.9 g, 78% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 4.5 Hz, 6H), 6.23 (t, *J* = 3.3 Hz, 1H), 6.21 – 6.18 (m, 1H), 1.35 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 135.0, 134.4, 129.1, 127.5, 127.1, 122.5, 114.3, 110.5, 83.5, 27.5 ppm.

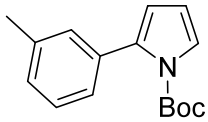
***tert*-Butyl 2-(2-chlorophenyl)-1*H*-pyrrole-1-carboxylate (1j)**



General procedure C

Clear oil (0.7 g, 54% yield); R_f = 0.5 (50:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.35 – 7.29 (m, 1H), 7.29 – 7.18 (m, 2H), 6.26 (d, *J* = 3.3 Hz, 1H), 6.15 (dd, *J* = 3.3, 1.8 Hz, 1H), 1.29 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 135.0, 134.4, 131.4, 131.1, 128.9, 128.8, 126.2, 121.9, 114.5, 110.4, 83.4, 27.4 ppm; IR (film) ν_{max} 1738, 1312, 1137, 851, 739 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{17}ClNO_2$ 278.0942; Found 278.0940.

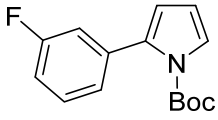
1,1-Dimethylethyl 2-(3-methylphenyl)-1*H*-pyrrole-1-carboxylate (1k)[11]



General procedure C

White solid (1.0 g, 82% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.08 (m, 3H), 6.23 (t, *J* = 3.3 Hz, 1H), 6.19 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.38 (d, *J* = 0.8 Hz, 3H), 1.36 (d, *J* = 0.8 Hz, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 136.9, 135.1, 134.3, 129.9, 127.9, 127.5, 126.2, 122.4, 114.2, 110.5, 83.4, 27.6, 21.3 ppm.

1,1-Dimethylethyl 2-(3-fluorophenyl)-1*H*-pyrrole-1-carboxylate (1l)

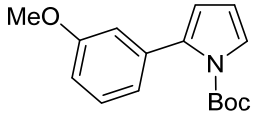


General procedure C

Yellow oil (0.7 g, 57% yield); R_f = 0.5 (50:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 2H), 7.18 – 6.92 (m, 3H), 6.23 (dq, *J* = 5.2, 3.2 Hz, 2H), 1.39 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 245.0 Hz), 149.2, 136.4 (d, *J* = 8.6 Hz), 133.6, 128.9 (d, *J* = 8.4 Hz), 124.9 (d, *J* = 2.8 Hz), 123.0, 116.2 (d, *J* = 22.0 Hz), 114.9, 113.9 (d, *J* = 21.0 Hz), 110.6, 83.8,

27.6 ppm; ^{19}F NMR (565 MHz, Chloroform-*d*) δ −115.04 ppm; IR (film) ν_{max} 1750, 1501, 1301, 1150, 809, 752 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{16}NO_2FNa$ 284.1057; Found 284.1052.

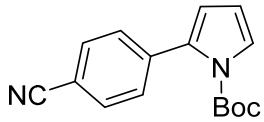
1,1-Dimethylethyl 2-(3-methoxyphenyl)-1*H*-pyrrole-1-carboxylate (1m)



General procedure C

Yellow oil (1.2 g, 88% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dd, *J* = 3.4, 1.8 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.02 – 6.69 (m, 3H), 6.51 – 5.89 (m, 3H), 3.80 (s, 3H), 1.36 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 149.3, 135.6, 134.8, 128.5, 122.5, 121.8, 114.8, 114.3, 112.8, 110.5, 83.5, 55.2, 27.5 ppm.

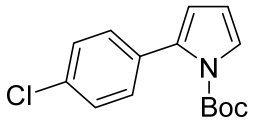
1,1-Dimethylethyl 2-(4-cyanophenyl)-1*H*-pyrrole-1-carboxylate (1n)[12]



General procedure C

White solid (1.2 g, 89% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (dt, *J* = 3.2, 1.6 Hz, 1H), 6.27 (tt, *J* = 6.5, 2.1 Hz, 2H), 1.42 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.9, 138.8, 133.1, 131.4, 129.6, 123.9, 119.0, 116.1, 111.0, 110.5, 84.4, 27.7 ppm.

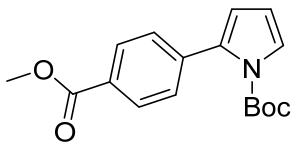
1,1-Dimethylethyl 2-(4-chlorophenyl)-1*H*-pyrrole-1-carboxylate (1o)[12]



General procedure C

White solid (1.1 g, 78% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.01 (m, 5H), 6.37 – 5.91 (m, 2H), 1.39 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.2, 133.8, 133.1, 132.8, 130.5, 127.7, 122.8, 114.8, 110.6, 83.9, 27.7 ppm.

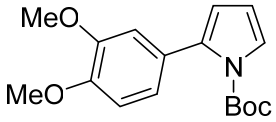
1,1-Dimethylethyl 2-[4-(methoxycarbonyl)phenyl]-1*H*-pyrrole-1-carboxylate (1p)[13]



General procedure C

White solid (1.2 g, 81% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 – 7.82 (m, 2H), 7.66 – 7.33 (m, 3H), 6.62 – 5.89 (m, 2H), 3.93 (s, 3H), 1.37 (d, *J* = 1.8 Hz, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 149.1, 138.9, 133.9, 128.9, 128.9, 128.5, 123.5, 115.4, 110.8, 84.0, 52.0, 27.6 ppm.

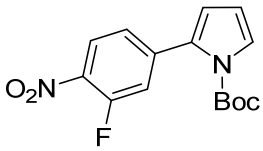
1,1-Dimethylethyl 2-(3,4-dimethoxyphenyl)-1*H*-pyrrole-1-carboxylate (1q)[14]



General procedure C

Yellow oil (0.9 g, 65% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.90 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.20 (t, *J* = 3.3 Hz, 1H), 6.15 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.87 (d, *J* = 13.2 Hz, 6H), 1.38 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.3, 148.4, 148.0, 134.9, 127.1, 122.2, 121.6, 114.0, 112.9, 110.4, 110.4, 83.4, 55.9, 55.8, 27.7 ppm.

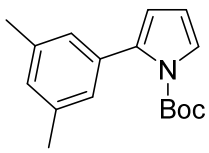
2-(3-Fluoro-4-nitrophenyl)-1*H*-pyrrole (1r)



General procedure C

Yellow solid (0.7 g, 44% yield); R_f = 0.4 (50:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (t, *J* = 8.3 Hz, 1H), 7.41 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.35 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.27 (t, *J* = 3.4 Hz, 1H), 1.47 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 153.8, 148.8,142.1 (d, *J* = 9.3 Hz), 131.7, 125.5 (d, *J* = 2.4 Hz), 124.9, 124.9, 118.5 (d, *J* = 22.0 Hz), 117.2, 111.4, 85.0, 27.8 ppm; ^{19} F NMR (565 MHz, Chloroform-*d*) δ -116.9 ppm; IR (film) ν_{max} 1700, 1605, 1520, 1356, 1172, 809, 665 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{15}N_2O_4FNa$ 329.0908; Found 329.0912.

***tert*-Butyl 2-(3,5-dimethylphenyl)-1*H*-pyrrole-1-carboxylate (1s)**[15]

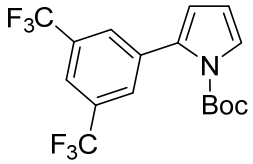


General procedure C

White solid (0.9 g, 67% yield); R_f = 0.3 (100:1 hexanes/AcOEt); m.p. 55.1–56.3 °C ; ^{1}H NMR (400 MHz,

Chloroform-*d*) δ 7.36 (dt, *J* = 3.3, 1.7 Hz, 1H), 7.07 – 6.91 (m, 3H), 6.23 (td, *J* = 3.3, 1.1 Hz, 1H), 6.19 (dt, *J* = 3.2, 1.6 Hz, 1H), 2.36 (dd, *J* = 1.4, 0.7 Hz, 6H), 1.38 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.5, 136.8, 135.3, 134.2, 128.8, 127.0, 122.3, 114.0, 110.4, 83.3, 27.5, 21.2 ppm; IR (film) ν_{max} 1739, 1315, 1150, 849, 729 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_2NO_2Na$ 294.1465; Found 294.1461.

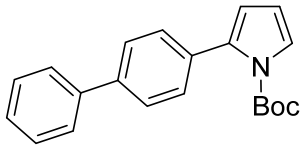
1,1-Dimethylethyl 2-[3,5-bis(trifluoromethyl)phenyl]-1*H*-pyrrole-1-carboxylate (1t)[16]



General procedure C

Clear oil (1.4 g, 72% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (s, 3H), 7.43 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.49 – 5.90 (m, 2H), 1.37 (d, *J* = 1.9 Hz, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.9, 136.4, 131.6, 131.0 (q, *J* = 33.3 Hz), 129.2, 124.0, 123.3 (q, *J* = 272.6 Hz), 120.6, 116.3, 111.0, 84.6, 27.5 ppm.

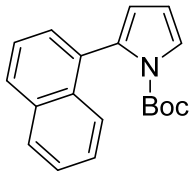
1,1-Dimethylethyl 2-[1,1′-biphenyl]-4-yl-1*H*-pyrrole-1-carboxylate (1u)[17]



General procedure C

White solid (1.3 g, 79% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.64 (m, 2H), 7.63 – 7.60 (m, 2H), 7.51 – 7.43 (m, 4H), 7.42 – 7.36 (m, 2H), 6.28 (td, *J* = 3.2, 2.2 Hz, 2H), 1.42 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4, 140.9, 140.0, 134.7, 133.3, 129.5, 128.8, 127.2, 127.0, 126.3, 122.7, 114.5, 110.7, 83.7, 27.6 ppm.

1,1-Dimethylethyl 2-(2-naphthalenyl)-1*H*-pyrrole-1-carboxylate (1v)[18]

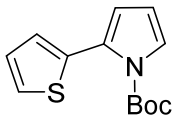


General procedure C

White solid (1.3 g, 90% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 – 7.77 (m, 4H), 7.47 (ddd, *J* = 8.0, 3.6, 1.7 Hz, 3H), 7.40 (dd, *J* = 3.3, 1.8 Hz, 3H), 6.29 (dd, *J* = 3.3, 1.8 Hz, 3H), 6.27 (t, *J* = 3.3 Hz,

3H), 1.32 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.4, 135.0, 133.0, 132.5, 131.9, 127.9, 127.9, 127.6, 127.3, 126.7, 126.1, 125.9, 122.7, 114.9, 110.7, 83.7, 77.2, 77.0, 76.8, 27.6 ppm.

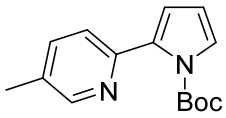
1,1-Dimethylethyl 2-(2-thienyl)-1*H*-pyrrole-1-carboxylate (1w)[19]



General procedure C

Yellow oil (0.9 g, 96% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 3.4, 1.8 Hz, 1H), 7.31 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.07 (dd, *J* = 3.5, 1.3 Hz, 1H), 7.03 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.33 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.23 (dd, *J* = 4.2, 2.5 Hz, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 134.9, 127.7, 126.8, 126.3, 125.5, 123.1, 116.5, 110.5, 83.7, 27.6 ppm.

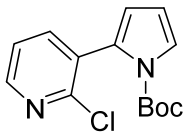
***tert*-Butyl 2-(5-methylpyridin-2-yl)-1*H*-pyrrole-1-carboxylate (1x)**[20]



General procedure C

White solid (0.9 g, 70% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.65 – 7.41 (m, 1H), 7.33 (dd, *J* = 3.3, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.37 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (t, *J* = 3.3 Hz, 1H), 2.35 (s, 3H), 1.37 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 149.3, 149.2, 136.2, 134.1, 131.2, 123.2, 123.1, 115.2, 110.5, 83.5, 27.6, 18.2 ppm.

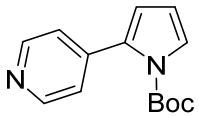
1,1-Dimethylethyl 2-(5-methyl-2-pyridinyl)-1*H*-pyrrole-1-carboxylate (1y)[21]



General procedure C

White solid (0.9 g, 66% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 2H), 7.66 (ddd, *J* = 7.5, 1.9, 0.7 Hz, 2H), 7.53 – 7.40 (m, 2H), 7.28 (dd, *J* = 4.8, 0.7 Hz, 1H), 6.32 – 6.26 (m, 2H), 6.21 (dd, *J* = 3.3, 1.8 Hz, 1H), 1.32 (s, 12H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 148.7, 148.3, 139.4, 131.2, 128.8, 122.6, 121.9, 115.4, 110.7, 84.0, 27.4 ppm.

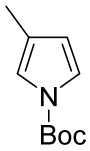
***tert*-Butyl 2-(pyridin-4-yl)-1*H*-pyrrole-1-carboxylate (1z)**



General procedure C

Yellow oil (1.0 g, 80% yield); R_f = 0.4 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.67 – 8.42 (m, 2H), 7.39 (dd, *J* = 3.4, 1.7 Hz, 1H), 7.30 – 7.14 (m, 2H), 6.30 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.25 (t, *J* = 3.3 Hz, 1H), 1.40 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 141.8, 132.3, 124.2, 116.2, 111.0, 84.4, 27.6 ppm; IR (film) ν_{max} 1719, 1697, 1411, 1293, 849 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}N_2O_2$ 245.1285; Found 245.1278.

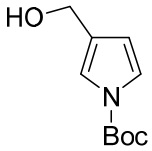
1,1-Dimethylethyl 3-methyl-1*H*-pyrrole-1-carboxylate (1a′)[22]



General procedure A

Clear oil (0.9 g, 96% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.14 (s, 1H), 6.97 (s, 1H), 6.05 (dd, *J* = 3.3, 1.7 Hz, 1H), 2.06 (s, 3H), 1.58 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.9, 122.3, 119.8, 117.1, 113.9, 82.9, 82.9, 27.8, 11.7 ppm.

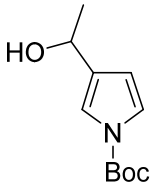
1,1-Dimethylethyl 3-(hydroxymethyl)-1*H*-pyrrole-1-carboxylate (1b′)



General procedure E

Clear oil (0.9 g, 92% yield); R_f = 0.4 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 1.9 Hz, 2H), 6.23 (q, *J* = 2.0, 1.5 Hz, 1H), 4.52 (d, *J* = 1.7 Hz, 2H), 3.73 (d, *J* = 1.0 Hz, 1H), 1.58 (d, *J* = 0.6 Hz, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 127.2, 120.4, 117.4, 111.5, 83.4, 57.9, 27.7 ppm; IR (film) ν_{max} 3387, 1735, 1481, 1350, 1165, 972 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{15}NO_3Na$ 220.0944; Found 220.0948.

***tert*-Butyl 3-(1-hydroxyethyl)-1*H*-pyrrole-1-carboxylate (1c′)**

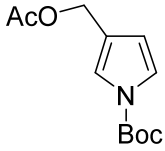


General procedure E

Clear oil (0.9 g, 85% yield); R_f = 0.5 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 –

7.09 (m, 2H), 6.47 – 5.96 (m, 1H), 4.81 (d, *J* = 6.7 Hz, 1H), 1.57 (s, 9H), 1.47 (dd, *J* = 6.5, 2.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.7, 132.4, 120.2, 115.8, 110.1, 83.4, 63.9, 27.7, 23.8 ppm; IR (film) ν_{max} 3341, 1726, 1470, 972 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{17}NO_3Na$ 234.1101; Found 234.1107.

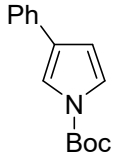
***tert*-Butyl 3-(acetoxymethyl)-1*H*-pyrrole-1-carboxylate (1d′)**



General procedure F

Clear oil (1.1 g, 91% yield); R_f = 0.4 (10:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (s, 1H), 7.20 – 7.16 (m, 1H), 6.42 – 6.08 (m, 1H), 4.94 (s, 2H), 2.05 (s, 3H), 1.57 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 148.5, 122.0, 120.5, 119.4, 112.3, 83.8, 59.5, 27.8, 20.9 ppm; IR (film) ν_{max} 1736, 1474, 1351, 972 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{17}NO_4Na$ 262.1050; Found 262.1050.

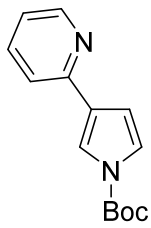
1,1-Dimethylethyl-3-phenyl-1*H*-pyrrole-1-carboxylate (1e′)[23]



General procedure B

Clear oil (0.80 g, 63% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.51 (s, 1H), 7.36 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.55 (dd, *J* = 3.3, 1.8 Hz, 1H), 1.62 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.8, 134.3, 128.7, 127.8, 126.6, 125.5, 120.9, 115.7, 110.4, 83.8, 28.0 ppm.

1,1-Dimethylethyl 3-(2-pyridinyl)-1*H*-pyrrole-1-carboxylate (1f′)[24]

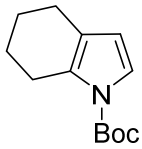


General procedure B

Yellow oil (0.70 g, 54% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.57 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.81 (d, *J* = 1.9 Hz, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 – 7.43 (m, 1H), 7.31 (dd, *J* = 3.3, 2.1

Hz, 1H), 7.11 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 6.74 (dd, *J* = 3.3, 1.7 Hz, 1H), 1.62 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.0, 149.3, 148.5, 136.2, 127.9, 121.0, 120.9, 119.4, 118.0, 110.1, 83.8, 27.7 ppm.

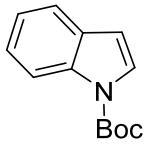
1,1-Dimethylethyl 4,5,6,7-tetrahydro-1*H*-indole-1-carboxylate (1g′)[25]



General procedure A

Clear oil (1.1 g, 94% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 3.7 Hz, 1H), 6.29 – 5.64 (m, 1H), 3.07 – 2.67 (m, 2H), 2.56 – 2.28 (m, 2H), 1.78 (dt, *J* = 6.1, 2.4 Hz, 2H), 1.70 (d, *J* = 6.1 Hz, 2H), 1.57 (s, 9H) ppm.

***tert*-Butyl 1*H*-indole-1-carboxylate (1h′)**[26]

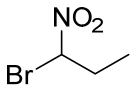


General procedure A

Clear oil (1.1 g, 96% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 3.7 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.40 (tt, *J* = 7.1, 1.2 Hz, 1H), 7.34 – 7.27 (m, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 1.75 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.8, 130.5, 125.8, 124.1, 122.6, 120.9, 115.1, 107.2, 83.5, 28.1 ppm.

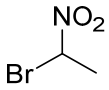
4. Physical data of *gem*-bromonitroalkanes

1-Bromo-1-nitropropane (2a)[27]



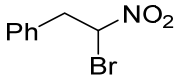
Yellow oil (4.2 g, 86% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.93 – 5.80 (m, 1H), 2.53 – 2.19 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 81.2, 31.0, 10.4 ppm.

1-Bromo-1-nitroethane (2b)



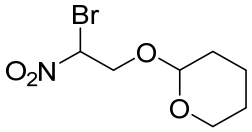
Yellow oil (4.3 g, 94% yield); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.04 (q, *J* = 6.4 Hz, 1H), 2.14 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 74.5, 24.2 ppm.

(2-Bromo-2-nitroethyl)benzene (2c)



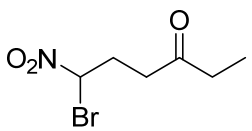
Yellow oil (1.1 g, 75% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 3H), 7.21 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.06 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.76 (dd, *J* = 14.5, 8.2 Hz, 1H), 3.52 (dd, *J* = 14.5, 6.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.2, 129.1, 129.0, 128.3, 79.2, 43.4 ppm.

2-(2-Bromo-2-nitroethoxy)tetrahydro-2*H*-pyran (2d)



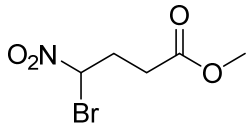
Clear oil (1.3 g, 71% yield); R_f = 0.1 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.02 (ddd, *J* = 12.6, 9.4, 3.6 Hz, 1H), 4.70 (dd, *J* = 33.0, 2.9 Hz, 1H), 4.47 – 4.20 (m, 1H), 4.01 (dddd, *J* = 50.0, 11.7, 3.7, 1.8 Hz, 1H), 3.85 – 3.69 (m, 1H), 3.60 – 3.49 (m, 1H), 1.99 – 1.14 (m, 6H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 100.5, 75.4, 69.7, 62.6, 30.0, 25.0, 18.9 ppm; IR (film) ν_{max} 1540, 1483, 1241, 556 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_7H_{13}NO_4Br$ 254.0022; Found 254. 0020.

6-Bromo-6-nitrohexan-3-one (2e)



Clear oil (1.3 g, 76% yield); R_f = 0.1 (20:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.41 – 5.81 (m, 1H), 2.71 – 2.52 (m, 4H), 2.45 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.3, 78.9, 37.5, 36.0, 31.2, 7.7 ppm; IR (film) ν_{max} 2915, 1630, 1560, 1033, 656 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_6H_{10}NO_3BrNa$ 245.9736; Found 245.9737.

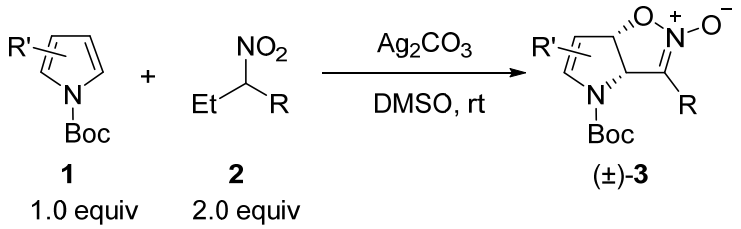
Methyl 4-bromo-4-nitrobutanoate (2f)



Clear oil (0.7 g, 41% yield); R_f = 0.2 (20:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.29 – 5.92 (m, 1H), 3.96 – 3.09 (m, 3H), 2.77 – 2.64 (m, 1H), 2.61 – 2.44 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 78.5, 52.1, 32.1, 29.8 ppm; IR (film) ν_{max} 2950, 1731, 1569, 1270, 1225, 858, 650 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_5H_8BrNO_4Na$ 247. 9529; Found 247.9527.

5. Cycloaddition reactions

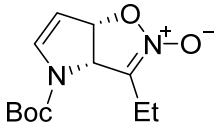
5.1 Typical procedure



A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). Substituted 1-Boc-pyrrole (**1**, 0.50 mmol), 1-bromo-1-nitroalkane (**2**, 1.00 mmol), Ag_2CO_3 (275 mg, 1.00 mmol) and anhydrous DMSO (6.0 mL) were added under N_2 atmosphere. After stirring at rt under N_2 for 12 h, the mixture was diluted with AcOEt, washed with brine (3 × 50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5:1 hexanes/AcOEt) to give **3aa**.

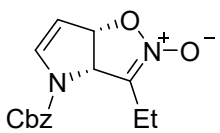
5.2 Physical data

4-(*tert*-Butoxycarbonyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3aa)



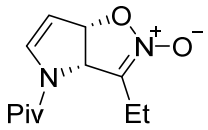
White solid (101 mg, 80% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 110.6–111.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 61.8 Hz, 1H), 5.98 – 5.74 (m, 1H), 5.56 (t, *J* = 9.5 Hz, 1H), 5.21 (d, *J* = 23.9 Hz, 1H), 2.58 – 2.41 (m, 2H), 1.48 (s, 9H), 1.13 (td, *J* = 7.5, 2.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 135.2, 115.5, 105.9, 82.2, 79.4, 65.8, 28.1, 19.0, 9.3 ppm; IR (film) ν_{max} 1709, 1636, 1458, 1354, 1138, 899, 786 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{18}N_2O_4Na$ 277.1159; Found 277.1156.

4-((Benzyloxy)carbonyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ba)



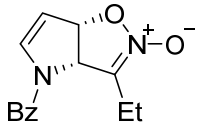
Yellow oil (78 mg, 54% yield); R_f = 0.2 (5:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (s, 5H), 7.02 – 6.81 (m, 1H), 5.79 (d, *J* = 9.5 Hz, 1H), 5.69 – 5.52 (m, 1H), 5.23 (d, *J* = 24.7 Hz, 2H), 2.53 (ddd, *J* = 52.7, 14.3, 7.2 Hz, 2H), 1.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.6, 134.9, 134.3, 128.6, 128.1, 115.1, 107.1, 79.1, 68.1, 66.1, 18.9, 9.3 ppm; IR (film) ν_{max} 1735, 1609, 1594, 1441, 809 cm^{-1}; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{15}H_{17}N_2O_4$ 289.1183; Found 289.1185.

3-Ethyl-4-pivaloyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ca)



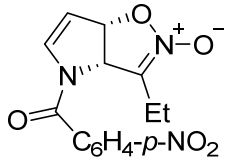
Yellow oil (62 mg, 52% yield); R_f = 0.2 (5:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 4.2 Hz, 1H), 5.92 (d, *J* = 9.5 Hz, 1H), 5.70 (d, *J* = 9.6 Hz, 1H), 5.38 (d, *J* = 2.9 Hz, 1H), 3.06 – 1.99 (m, 2H), 1.29 (s, 9H), 1.13 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.0, 134.4, 116.0, 108.6, 77.1, 67.4, 39.3, 27.6, 19.4, 9.5 ppm; IR (film) ν_{max} 1713, 1612, 1474, 1120, 768 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{19}N_2O_3$ 239.1390; Found 239.1387.

4-Benzoyl-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3da)



Yellow oil (77 mg, 60% yield); R_f = 0.1 (5:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.5 Hz, 3H), 7.47 (dd, *J* = 8.3, 6.9 Hz, 2H), 6.82 (d, *J* = 4.4 Hz, 1H), 6.06 (d, *J* = 9.6 Hz, 1H), 5.82 (dd, *J* = 9.5, 2.3 Hz, 1H), 5.37 (dd, *J* = 4.5, 2.3 Hz, 1H), 2.79 – 2.44 (m, 2H), 1.22 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 135.9, 133.9, 131.6, 128.9, 127.8, 115.5, 108.9, 78.4, 66.1, 19.4, 9.5 ppm; IR (film) ν_{max} 1715, 1604, 1466, 1322, 856 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{14}H_{14}N_2O_3Na$ 281.0897; Found 281. 0894.

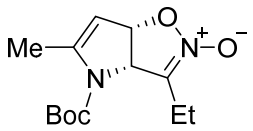
3-Ethyl-4-(4-nitrobenzoyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ea)



White solid (71 mg, 47% yield); R_f = 0.1 (3:1 hexanes/AcOEt); m.p. 190.6–191.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 – 8.16 (m, 2H), 7.85 – 7.58 (m, 1H), 6.68 (d, *J* = 4.4 Hz, 1H), 6.06 (dd, *J* =

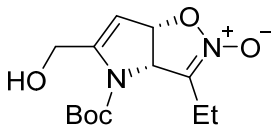
9.5, 0.9 Hz, 1H), 5.88 – 5.80 (m, 1H), 5.48 (ddd, *J* = 4.5, 2.4, 0.8 Hz, 1H), 2.72 – 2.48 (m, 2H), 1.23 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 149.4, 139.6, 134.6, 128.9, 124.2, 114.9, 110.6, 78.1, 66.4, 19.4, 9.6 ppm; IR (film) ν_{max} 1717, 1632, 1609, 1524, 1346, 829 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{13}N_3O_5Na$ 326.0747; Found 326.0751.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-methyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3fa)



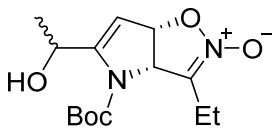
White solid (36 mg, 27% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 83.6–85.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.01 – 5.40 (m, 2H), 5.09 – 4.72 (m, 1H), 2.75 – 2.36 (m, 2H), 2.13 (s, 3H), 1.49 (s, 9H), 1.13 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 146.3, 116.0, 106.4, 82.3, 77.8, 68.1, 28.2, 19.0, 16.3, 9.5 ppm; IR (film) ν_{max} 1715, 1630, 1401, 1170, 864 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2O_4$ 269.1495; Found 269.1489.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(hydroxymethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ga)



Clear oil (100 mg, 71% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.92 – 5.52 (m, 2H), 5.28 (s, 1H), 4.36 (s, 2H), 2.92 – 2.02 (m, 2H), 1.54 (s, 9H), 1.14 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.2, 148.7, 115.4, 106.8, 83.0, 77.7, 67.9, 58.2, 27.8, 18.6, 9.1 ppm; IR (film) ν_{max} 3448, 1715, 1603, 1391, 972 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2O_5$ 285.1444; Found 285.1447.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(1-hydroxyethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxidee (3ha)



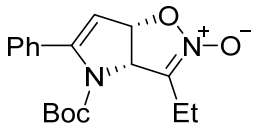
Total 92 mg, 62% yield, dr = 1:1.

Clear oil (48 mg, 33% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.99 – 5.54 (m, 2H), 5.21 (s, 1H), 4.84 – 4.37 (m, 1H), 2.70 – 2.17 (m, 2H), 1.53 (s, 9H), 1.39 (dd, *J* = 6.5,

1.8 Hz, 3H), 1.11 (td, J = 7.5, 1.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 151.7, 115.1, 106.3, 83.6, 77.8, 68.5, 62.4, 28.2, 20.4, 18.8, 9.5 ppm; IR (film) ν_{max} 3426, 1710, 1596, 1397, 992 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{23}N_2O_5$ 299.1601; Found 299.1603.

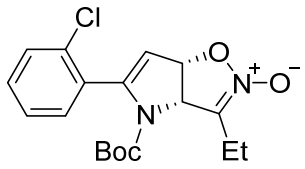
Clear oil (43 mg, 29% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.81 – 5.61 (m, 1H), 5.33 – 5.27 (m, 1H), 4.69 (d, J = 6.8 Hz, 1H), 2.56 – 2.25 (m, 2H), 1.50 (s, 9H), 1.39 (dd, J = 6.0, 1.8 Hz, 3H), 1.14 – 1.06 (m, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.7, 115.1, 106.3, 83.6, 77.8, 68.5, 62.4, 28.2, 20.4, 18.8, 9.5 ppm.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-phenyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ia)



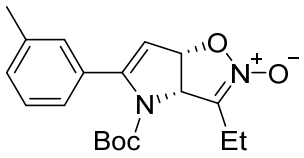
White solid (137 mg, 83% yield); R_f = 0.1 (5:1 hexanes/AcOEt); m.p. 113.9–115.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (d, J = 4.7 Hz, 3H), 7.29 (d, J = 6.1 Hz, 2H), 5.90 (d, J = 3.7 Hz, 2H), 5.35 (s, 1H), 2.80 – 2.37 (m, 2H), 1.27 (dt, J = 9.5, 5.7 Hz, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.5, 148.8, 133.0, 128.9, 127.9, 126.8, 115.5, 110.0, 82.2, 78.7, 69.7, 27.7, 18.8, 9.5 ppm; IR (film) ν_{max} 1720, 1373, 1257, 1150, 709 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{23}N_2O_4$ 331.1652; Found 331.1654.

4-(*tert*-Butoxycarbonyl)-5-(2-chlorophenyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ja)



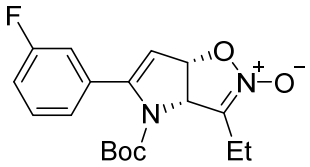
Yellow oil (114 mg, 63% yield); R_f = 0.2 (5:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, J = 7.7 Hz, 1H), 7.33 – 7.19 (m, 3H), 5.90 (s, 2H), 5.28 (s, 1H), 2.66 – 2.49 (m, 2H), 1.24 (t, J = 7.4 Hz, 3H), 1.13 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.3, 132.6, 132.4, 129.9, 129.7, 129.2, 126.4, 115.7, 110.5, 81.8, 77.8, 77.2, 68.3, 27.4, 18.8, 9.3 ppm; IR (film) ν_{max} 1715, 1649, 1490, 1370, 1128, 845 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{22}N_2O_4Cl$ 365.1262; Found 365.1259.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(*m*-tolyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ka)



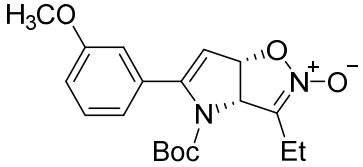
White solid (103 mg, 60% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 119.6–121.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.09 – 7.05 (m, 2H), 5.88 (d, *J* = 1.5 Hz, 2H), 5.33 (d, *J* = 1.3 Hz, 1H), 2.73 – 2.47 (m, 2H), 2.35 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 148.9, 137.4, 132.7, 129.6, 127.8, 127.4, 123.9, 115.6, 109.7, 82.1, 78.7, 69.6, 27.6, 21.3, 18.7, 9.5 ppm; IR (film) ν_{max} 1717, 1615, 1474, 1348, 1119, 766 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{19}H_{25}N_2O_4$ 345.1808; Found 345.1809.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(3-fluorophenyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3la)



White solid (93 mg, 54% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 153.6–154.4 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 8.1, 5.7 Hz, 1H), 7.07 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.03 (td, *J* = 8.4, 2.6 Hz, 1H), 6.98 (dd, *J* = 9.6, 2.1 Hz, 1H), 5.89 (s, 2H), 5.38 (s, 1H), 2.85 – 2.22 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.21 (s, 6H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3 (d, *J* = 246.0 Hz), 152.3, 147.6, 135.0 (d, *J* = 8.0 Hz), 129.5 (d, *J* = 8.2 Hz), 122.6, 122.5, 115.7 (d, *J* = 21.3 Hz), 115.3, 114.0 (d, *J* = 23.0 Hz), 110.9, 82.5, 78.5, 70.0, 27.7, 18.7, 9.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −113.3ppm; IR (film) ν_{max} 1705, 1643, 1342, 1141, 849 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{22}FN_2O_4$ 349.1558; Found 349.1564.

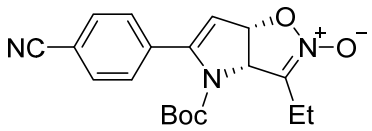
4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(3-methoxyphenyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ma)



White solid (119 mg, 66% yield); R_f = 0.2 (3:1 hexanes/AcOEt); m.p. 128.6–130.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.07 (m, 1H), 6.93 – 6.86 (m, 2H), 6.83 (p, *J* = 1.1 Hz, 1H), 5.89 (s, 2H), 5.36 (s, 1H), 3.80 (s, 3H), 2.62 – 2.53 (m, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.21 (s, 9H) ppm; ^{13}C NMR (101

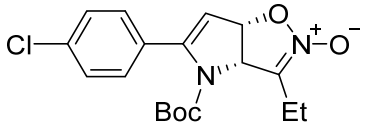
MHz, Chloroform-*d*) δ 159.1, 152.4, 148.5, 134.1, 128.9, 119.2, 115.6, 114.1, 112.6, 110.0, 82.1, 78.6, 69.5, 55.2, 27.6, 18.6, 9.4 ppm; IR (film) v_{max} 1701, 1639, 1369, 1342, 1049, 698 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{25}N_2O_5$ 361.1758; Found 361.1768.

4-(*tert*-Butoxycarbonyl)-5-(4-cyanophenyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3na)



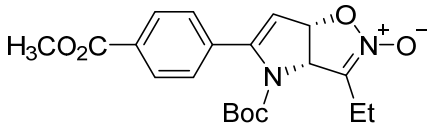
White solid (137 mg, 77% yield); R_f = 0.2 (3:1 hexanes/AcOEt); m.p. 93.8–94.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.92 (d, *J* = 1.0 Hz, 2H), 5.47 (s, 1H), 3.07 – 2.20 (m, 2H), 1.29 – 1.19 (m, 12H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 147.1, 137.4, 131.8, 127.5, 118.3, 115.0, 112.5, 112.4, 83.1, 78.3, 69.7, 27.7, 18.7, 9.5 ppm; IR (film) v_{max} 2147, 1725, 1674, 1378, 1119, 776 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{22}N_3O_4$ 356.1604; Found 356.1608.

4-(*tert*-Butoxycarbonyl)-5-(4-chlorophenyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3oa)



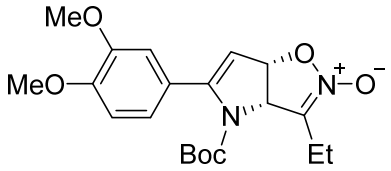
White solid (129 mg, 71% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 98.6–99.3 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.89 (s, 2H), 5.36 (s, 1H), 2.60 – 2.54 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.24 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.3, 147.8, 134.8, 131.3, 128.2, 128.1, 115.3, 110.5, 82.6, 78.5, 69.6, 53.4, 27.7, 18.7, 9.5 ppm; IR (film) v_{max} 1705, 1639, 1474, 1489, 1369, 1146, 1092, 845 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{22}N_2O_4Cl$ 365.1262; Found 365.1259.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(4-(methoxycarbonyl)phenyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3pa)



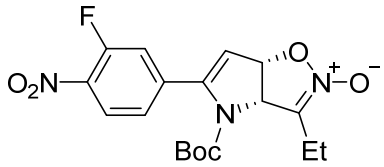
White solid (157 mg, 81% yield); R_f = 0.1 (5:1 hexanes/AcOEt); m.p. 88.3–89.5 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 – 7.75 (m, 2H), 7.57 – 7.03 (m, 2H), 5.90 (d, *J* = 1.1 Hz, 2H), 5.43 (s, 1H), 3.91 (s, 3H), 2.85 – 2.15 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.17 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.4, 152.3, 147.9, 137.4, 130.3, 129.2, 126.8, 115.2, 111.5, 82.7, 78.5, 70.0, 52.2, 27.7, 18.7, 9.5 ppm; IR (film) ν_{max} 1720, 1639, 1369, 1280, 1149, 1111, 771 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{25}N_2O_6$ 389.1707; Found 389.1708.

4-(*tert*-Butoxycarbonyl)-5-(3,4-dimethoxyphenyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3qa)



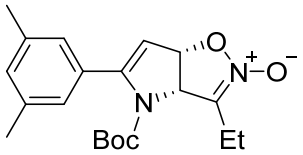
White solid (132 mg, 68% yield); R_f = 0.2 (3:1 hexanes/AcOEt); m.p. 123.6–125.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.90 – 6.80 (m, 2H), 6.78 (t, *J* = 1.7 Hz, 1H), 5.86 (d, *J* = 1.5 Hz, 2H), 5.30 (d, *J* = 1.5 Hz, 1H), 3.86 (dd, *J* = 9.9, 1.4 Hz, 6H), 2.70 – 2.44 (m, 2H), 1.24 (t, *J* = 1.9 Hz, 12H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 149.6, 148.5, 148.3, 125.3, 119.6, 115.6, 110.4, 110.1, 109.1, 82.1, 78.7, 69.6, 55.9, 55.8, 27.8, 18.7, 9.5 ppm; IR (film) ν_{max} 1739, 1505, 1474, 1379, 1171, 765 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_6$ 391.1863; Found 391.1860.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(3-fluoro-4-nitrophenyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ra)



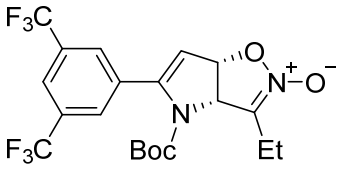
Yellow solid (84 mg, 43% yield); R_f = 0.2 (3:1 hexanes/AcOEt); m.p. 133.6–134.9 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 5.91 (d, *J* = 23.1 Hz, 2H), 5.56 (s, 1H), 2.6 – 2.50 (m, 2H), 1.30 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1 (d, *J* = 265.4 Hz), 151.9, 145.8, 140.5 (d, *J* = 8.6 Hz), 136.8, 125.9, 122.9 (d, *J* = 3.8 Hz), 116.8 (d, *J* = 22.4 Hz), 114.8, 113.6, 83.5, 78.2, 69.8, 27.8, 18.7, 9.5 ppm; ^{19}F NMR (565 MHz, Chloroform-*d*) δ −116.94 ppm; IR (film) ν_{max} 1714, 1505, 1494, 1258, 1019, 759 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}N_3O_6F$ 394.1408; Found 394.1404.

4-(*tert*-Butoxycarbonyl)-5-(3,5-dimethylphenyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3sa)



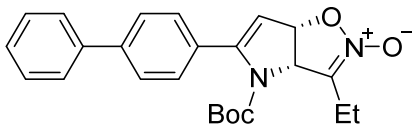
White solid (116 mg, 65% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 127.6–128.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 (s, 1H), 6.87 (s, 2H), 5.86 (d, *J* = 1.8 Hz, 2H), 5.31 (d, *J* = 1.6 Hz, 1H), 2.74 – 2.47 (m, 2H), 2.30 (s, 6H), 1.26 (m, 3H), 1.19 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 148.9, 137.1, 132.5, 130.3, 124.5, 115.6, 109.3, 81.8, 78.6, 69.4, 27.5, 21.0, 18.6, 9.4 ppm; IR (film) ν_{max} 1724, 1642, 1152, 844, 732 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_4$ 359.1965; Found 359.1960.

5-(3,5-Bis(trifluoromethyl)phenyl)-4-(*tert*-butoxycarbonyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ta)



White solid (137 mg, 59% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 146.9–150.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dt, *J* = 1.6, 0.9 Hz, 1H), 7.98 – 7.37 (m, 2H), 6.72 – 5.81 (m, 2H), 5.53 (d, *J* = 1.6 Hz, 1H), 3.40 – 2.18 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 4H), 1.18 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.0, 146.1, 135.1, 131.6 (q, *J* = 33.3 Hz), 127.1, 124.4, 122.4, 121.6, 114.9, 112.6, 83.3, 78.1, 69.7, 27.6, 18.8, 9.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ −62.9 ppm; IR (film) ν_{max} 1717, 1643, 1281, 1173, 1134, 991, 845 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O_4F_6$ 467.1400; Found 467.1394.

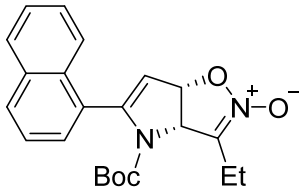
5-([1,1'-Biphenyl]-4-yl)-4-(*tert*-butoxycarbonyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ua)



Yellow solid (148 mg, 73% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 89.6–90.6 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.54 (m, 4H), 7.51 – 7.41 (m, 2H), 7.40 – 7.34 (m, 2H), 5.92 (d, *J* = 1.0

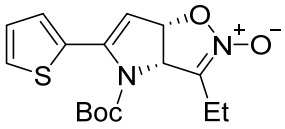
Hz, 2H), 5.42 (d, *J* = 1.0 Hz, 1H), 2.69 – 2.49 (m, 2H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.23 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 148.5, 141.8, 140.4, 131.7, 128.8, 127.6, 127.3, 127.0, 126.6, 115.6, 110.0, 82.4, 78.7, 69.7, 27.7, 18.7, 9.6 ppm; IR (film) ν_{max} 1713, 1643, 1366, 1150, 741 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{24}H_{27}N_2O_4$ 407.1965; Found 407.1964.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(naphthalen-1-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3va)



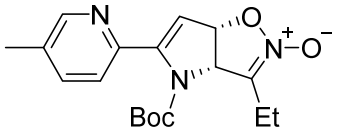
White solid (146 mg, 77% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 151.6–152.4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.69 (m, 4H), 7.58 – 7.45 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 5.94 (d, *J* = 1.9 Hz, 2H), 5.58 – 5.36 (m, 1H), 2.89 – 2.21 (m, 2H), 1.30 (td, *J* = 7.6, 2.0 Hz, 3H), 1.13 (d, *J* = 2.1 Hz, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.5, 148.9, 133.4, 132.7, 130.3, 128.0, 127.7, 127.4, 126.6, 126.5, 125.9, 124.7, 115.6, 110.3, 82.4, 78.7, 69.7, 27.6, 18.8, 9.6 ppm; IR (film) ν_{max} 1701, 1639, 1380, 1342, 1165, 1138, 844, 748 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{22}H_{25}N_2O_4$ 381.1808; Found 381.1803.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(thiophen-2-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3wa)



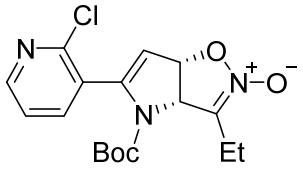
White solid (96 mg, 57% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 97.1–99.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 3.7, 1.2 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.21 – 5.66 (m, 2H), 5.44 (d, *J* = 1.6 Hz, 1H), 2.61 – 2.49 (m, 2H), 1.31 (s, 9H), 1.24 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 142.1, 133.8, 127.0, 126.7, 126.2, 115. 5, 110.63, 82.5, 78.4, 70.0, 27.8, 18.7, 9.5 ppm; IR (film) ν_{max} 1721, 1625, 1366, 1250, 1150, 845, 733 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{21}N_2O_4S$ 337.1217; Found 337.1215.

4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(5-methylpyridin-2-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3xa)



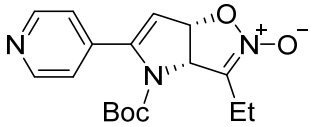
White solid (81 mg, 47% yield); R_f = 0.1 (3:1 hexanes/AcOEt);); m.p. 168.6–169.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 – 8.25 (m, 1H), 7.48 (ddd, *J* = 8.0, 2.2, 0.8 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.15 – 5.83 (m, 2H), 5.61 (d, *J* = 1.6 Hz, 1H), 2.61 – 2.52 (m, 2H), 2.34 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H), 1.20 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 149.3, 148.7, 148.0, 136.2, 133.2, 121.9, 115.5, 111.7, 82.3, 78.7, 69.7, 27.7, 18.7, 18.3, 9.4 ppm; IR (film) ν_{max} 1710, 1641, 1561, 1482, 1331, 1151, 843 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{24}N_3O_4$ 346.1761; Found 346.1770.

4-(*tert*-Butoxycarbonyl)-5-(2-chloropyridin-3-yl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ya)



White solid (100 mg, 55% yield); R_f = 0.1 (3:1 hexanes/AcOEt);); m.p. 147.3–148.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 5.0 Hz, 1H), 7.64 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.44 – 7.17 (m, 1H), 5.93 (s, 2H), 5.36 (s, 1H), 2.68 – 2.49 (m, 2H), 1.24 (t, *J* = 7.4 Hz, 4H), 1.17 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 149.2, 143.9, 137.9, 129.2, 128.7, 122.0, 115.2, 111.4, 82.3, 77.5, 68.2, 27.4, 18.8, 9.2 ppm; IR (film) ν_{max} 1704, 1640, 1395, 1136, 842 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{21}N_3O_4Cl$ 366.1215; Found 366.1202.

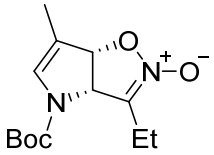
4-(*tert*-Butoxycarbonyl)-3-ethyl-5-(pyridin-4-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3za)



White solid (58 mg, 35% yield); R_f = 0.1 (3:1 hexanes/AcOEt); m.p. 140.1–141.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 5.1 Hz, 2H), 7.20 – 7.14 (m, 2H), 5.89 (s, 2H), 5.48 (s, 1H), 2.64 – 2.43 (m, 2H), 1.26 – 1.06 (m, 12H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 149.6, 146.6, 140.7, 121.3, 115.0, 112.6, 83.2, 78.3, 69.8, 27.7, 18.7, 9.5 ppm; IR (film) ν_{max} 1705, 1639, 1597, 1401,

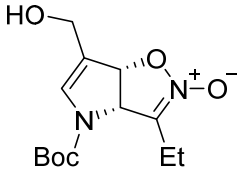
1293, 1138, 841 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{22}N_3O_4$ 332.1604; Found 332.1603.

4-(*tert*-Butoxycarbonyl)-3-ethyl-6-methyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3a′a)



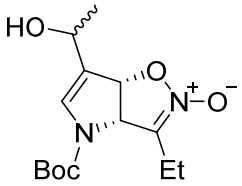
White solid (68 mg, 51% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 81.1–83.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.43 (d, *J* = 57.9 Hz, 1H), 5.53 (d, *J* = 16.6 Hz, 2H), 2.54 – 2.37 (m, 2H), 1.73 (s, 3H), 1.45 (s, 9H), 1.11 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 128.4, 116.2, 115.9, 82.5, 81.4, 65.8, 28.1, 18.9, 10.8, 9.3 ppm; IR (film) ν_{max} 1705, 1628, 1396, 1165, 864 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2O_4$ 269.1495; Found 269.1493.

4-(*tert*-Butoxycarbonyl)-3-ethyl-6-(hydroxymethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3b′a)



Clear oil (90 mg, 64% yield); R_f = 0.2 (2:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.77 (d, *J* = 59.8 Hz, 1H), 5.84 (d, *J* = 19.2 Hz, 1H), 5.66 (d, *J* = 9.5 Hz, 1H), 4.29 (s, 2H), 2.75 – 2.42 (m, 2H), 2.12 (s, 1H), 1.48 (s, 9H), 1.15 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 131.1, 119.6, 116.1, 82.3, 78.9, 66.4, 57.0, 28.1, 19.0, 9.3 ppm; IR (film) ν_{max} 3441, 1705, 1643, 1381, 1165, 902 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2O_5$ 285.1444; Found 285.1439.

4-(*tert*-Butoxycarbonyl)-3-ethyl-6-(1-hydroxyethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3c′a)



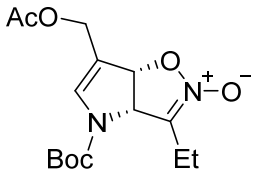
Total 103 mg, 70% yield, dr = 1:1.

Clear oil (50 mg, 35% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.62 (d, *J* = 24.2 Hz, 1H), 5.98 – 5.73 (m, 1H), 5.61 (d, *J* = 10.0 Hz, 1H), 4.56 (s, 1H), 2.87 – 2.21 (m, 2H),

1.47 (s, 9H), 1.38 (dd, J = 13.9, 6.6 Hz, 3H), 1.14 (d, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 129.6, 123.8, 116.1, 82.1, 79.1, 66.5, 63.6, 28.1, 22.2, 19.0, 9.3 ppm; IR (film) ν_{max} 3223, 1696, 1401, 1048, 904 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{23}N_2O_5$ 299.1601; Found 299.1603.

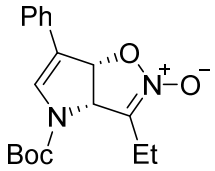
Clear oil (53 mg, 35% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.95 – 6.73 (m, 1H), 5.49 (d, J = 22.1 Hz, 1H), 5.18 – 5.04 (m, 1H), 4.15 – 3.77 (m, 1H), 2.65 – 2.42 (m, 2H), 1.52 (s, 9H), 1.15 (q, J = 7.5, 6.6 Hz, 6H) ppm.

6-(Acetoxymethyl)-4-(*tert*-butoxycarbonyl)-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3d′a)



Clear oil (93 mg, 57% yield); R_f = 0.2 (5:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.83 (d, J = 92.0 Hz, 1H), 5.74 (dd, J = 36.3, 9.9 Hz, 1H), 5.59 (dd, J = 32.8, 10.2 Hz, 1H), 4.72 (dd, J = 13.1, 2.9 Hz, 1H), 4.60 (d, J = 13.0 Hz, 1H), 2.54 – 2.40 (m, 2H), 2.03 (d, J = 2.9 Hz, 3H), 1.46 (s, 9H), 1.11 (t, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 150.5, 134.0, 115.3, 114.6, 82.5, 78.8, 66.5, 58.1, 28.0, 20.8, 19.0, 9.3 ppm; IR (film) ν_{max} 1745, 1566, 1203, 748, 694 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{22}N_2O_6$ 327.1551; Found 327.1555.

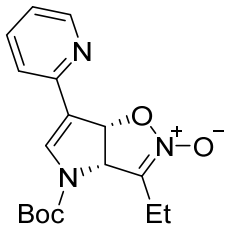
4-(*tert*-Butoxycarbonyl)-3-ethyl-6-phenyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3e′a)



White solid (48 mg, 29% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 133.1–135.0 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.09 (s, 1H), 6.10 (dd, J = 34.0, 10.0 Hz, 1H), 5.71 (dd, J = 33.7, 9.9 Hz, 1H), 2.64 – 2.50 (m, 2H), 1.53 (s, 9H), 1.18 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.8, 131.7, 128.7, 128.6, 127.4, 125.0, 120.0, 115.5, 82.6, 79.0, 66.4, 28.2, 19.2, 9.4 ppm; IR (film) ν_{max} 1609, 1366, 1103, 848, 732 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{23}N_2O_4$ 331.1652; Found 331.1655.

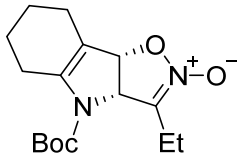
4-(*tert*-Butoxycarbonyl)-3-ethyl-6-(pyridin-2-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-

oxide (3f′a)



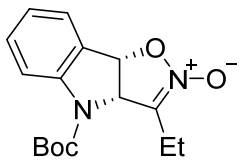
White solid (28 mg, 17% yield); R_f = 0.1 (3:1 hexanes/AcOEt); m.p. 136.1–138.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.9 Hz, 1H), 7.62 (dd, *J* = 15.9, 8.0 Hz, 1H), 7.26 (s, 1H), 7.12 (s, 1H), 6.18 (d, *J* = 9.8 Hz, 1H), 5.81 (d, *J* = 9.8 Hz, 1H), 2.66 – 2.48 (m, 2H), 1.54 (s, 9H), 1.19 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.3, 150.7, 149.6, 136.6, 132.9, 121.7, 120.4, 120.0, 115.4, 83.0, 78.1, 67.0, 28.2, 19.2, 9.4 ppm; IR (film) ν_{max} 1713, 1636, 1389, 1311, 1165, 795 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{22}N_3O_4$ 332.1605; Found 332.1610.

4-(*tert*-Butoxycarbonyl)-3-ethyl-6-(pyridin-2-yl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3g′a)



Clear oil (140 mg, 91% yield); R_f = 0.2 (7:1 hexanes/AcOEt); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.59 (d, *J* = 9.5 Hz, 1H), 5.52 – 5.40 (m, 1H), 2.51 (dd, *J* = 14.0, 7.3 Hz, 2H), 2.45 – 2.30 (m, 2H), 2.27 – 2.15 (m, 1H), 1.99 – 1.91 (m, 1H), 1.81 – 1.64 (m, 2H), 1.60 – 1.50 (m, 2H), 1.47 (s, 9H), 1.12 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.6, 140.9, 116.3, 116.0, 81.8, 80.0, 66.4, 28.2, 25.2, 22.4, 22.0, 21.6, 18.9, 9.4 ppm; IR (film) ν_{max} 1719, 1646, 1350, 1148, 890, 784 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{25}N_2O_4$ 309.1809; Found 309.1818.

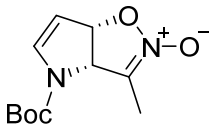
4-(*tert*-Butoxycarbonyl)-3-ethyl-3a,8b-dihydro-4*H*-isoxazolo[4,5-*b*]indole 2-oxide (3h′a)



White solid (81 mg, 53% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 130.8–131.9 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 – 7.43 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.08 (d, *J* = 9.4 Hz, 1H), 5.90 (s, 1H), 3.07 – 2.21 (m, 2H), 1.57 (s, 9H), 1.13 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.3, 131.0, 127.7, 126.3, 123.8, 116.2, 82.8, 67.8,

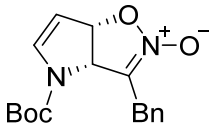
28.2, 18.9, 9.3 ppm; IR (film) ν_{max} 3010, 1460, 1390, 1304, 1290, 720 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2O_4$ 305.1496; Found 305.1501.

4-(*tert*-Butoxycarbonyl)-3-methyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ab)



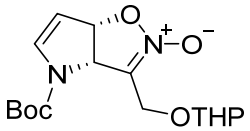
White solid (88 mg, 74% yield); R_f = 0.3 (5:1 hexanes/AcOEt); m.p. 131.1–132.0 °C; ^1H NMR (600 MHz, Chloroform-*d*) δ 6.85 (d, *J* = 98.0 Hz, 1H), 5.82 (t, *J* = 19.3 Hz, 1H), 5.66 – 5.33 (m, 1H), 5.22 (d, *J* = 37.8 Hz, 1H), 2.09 (s, 3H), 1.50 (s, 9H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.6, 135.1, 111.4, 105.6, 82.2, 79.4, 66.6, 28.1, 28.0, 11.4 ppm; IR (film) ν_{max} 1707, 1642, 1370, 1171, 895, 765 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}N_2O_4$ 241.1183; Found 241.1185.

3-Benzyl-4-(*tert*-butoxycarbonyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ac)



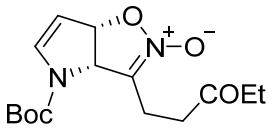
White solid (35 mg, 22% yield); R_f = 0.2 (5:1 hexanes/AcOEt); m.p. 111.3–113.0 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.27 (dt, *J* = 17.7, 7.3 Hz, 3H), 6.74 (s, 1H), 5.77 (d, *J* = 9.7 Hz, 1H), 5.60 (d, *J* = 9.8 Hz, 1H), 5.19 (s, 1H), 3.83 (s, 2H), 1.44 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6, 135.5, 135.3, 128.8, 128.6, 126.9, 113.6, 105.8, 82.2, 79.8, 65.7, 30.9, 28.1 ppm; IR (film) ν_{max} 1705, 1636, 1381, 1357, 1142, 718 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}N_2O_4$ 317.1495; Found 317.1495.

4-(*tert*-Butoxycarbonyl)-3-(2-((tetrahydro-2*H*-pyran-2-yl)oxy)ethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ad)



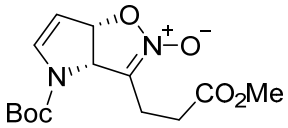
Yellow oil (97 mg, 57% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^1H NMR (600 MHz, Chloroform-*d*) δ 6.80 (s, 1H), 5.99 – 5.54 (m, 2H), 5.19 (s, 1H), 4.83 – 4.24 (m, 4H), 4.09 – 3.28 (m, 3H), 2.11 – 1.69 (m, 4H), 1.48 (s, 11H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 135.7, 105.1, 99.2, 99.0, 82.2, 80.2, 65.23, 61.9, 59.7, 30.3, 28.1, 25.2, 19.0 ppm; IR (film) ν_{max} 1731, 1636, 1450, 1269, 1241, 1098, 813, 780 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}N_2O_6$ 355.1863; Found 355.1853.

4-(*tert*-Butoxycarbonyl)-3-(3-oxopentyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3ae)



Yellow oil (62 mg, 40% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.77 (s, 1H), 5.79 (d, *J* = 11.1 Hz, 1H), 5.66 (d, *J* = 9.7 Hz, 1H), 5.18 (s, 1H), 3.32 – 2.88 (m, 2H), 2.71 (ddd, *J* = 41.4, 16.2, 7.0 Hz, 2H), 2.43 (qd, *J* = 7.4, 2.6 Hz, 2H), 1.47 (s, 9H), 1.03 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.5, 150.8, 135.4, 114.2, 105.6, 82.3, 79.9, 66.4, 36.3, 35.5, 28.1, 19.8, 7.7 ppm; IR (film) ν_{max} 1730, 1715, 1670, 1483, 1362, 1242, 740 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{23}N_2O_5$ 311.1601; Found 311.1598.

4-(*tert*-Butoxycarbonyl)-3-(3-methoxy-3-oxopropyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole 2-oxide (3af)



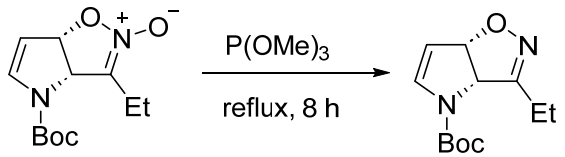
Yellow oil (84 mg, 54% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.99 – 6.71 (m, 1H), 5.81 (d, *J* = 9.8 Hz, 1H), 5.64 (d, *J* = 9.7 Hz, 1H), 5.19 (s, 1H), 3.67 (s, 3H), 2.92 – 2.70 (m, 3H), 2.55 (d, *J* = 17.2 Hz, 1H), 1.48 (s, 9H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 150.7, 135.4, 113.4, 105.5, 82.3, 79.9, 66.1, 51.7, 28.5, 28.0, 20.8 ppm; IR (film) ν_{max} 1735, 1448, 1330, 1275, 1140, 540 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}N_2O_6$ 313.1399; Found 313.1405.

6. Gram-scale reaction

A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). *tert*-Butyl 1*H*-pyrrole-1-carboxylate (**1a**, 1.0 g, 6.0 mmol), 1-bromo-1-nitropropane (**2a**, 1.3 mL, 12 mmol), Ag_2CO_3 (3.3 g, 12.0 mmol) and anhydrous DMSO (20 mL) were added under N_2 atmosphere. The reaction mixture was degassed by freeze-pump-thaw method, and stirred at rt (approximately 25 °C). The reaction was monitored by TLC. Upon completion (12 h), the mixture was diluted with AcOEt and washed with brine (3 × 50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5:1 hexanes/AcOEt) to give **3aa** (white solid, 1.13 g, 73% yield).

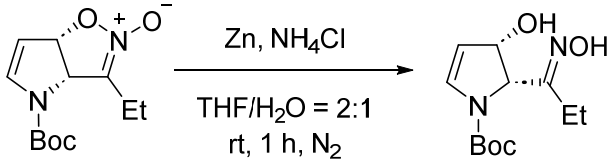
7. Conversions of 3aa

7.1 Conversions of 3aa



(±)-**3aa** **4a**

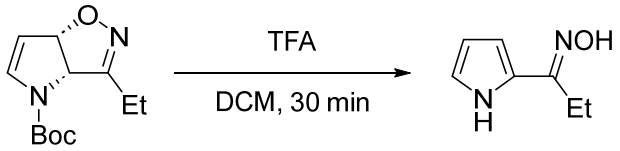
According to a literature procedure[28], a solution of **3aa** (254 mg, 1 mmol) in $P(OMe)_3$ (3 mL) was stirred in a closed vial at 100 °C for 5 h, diluted with Et_2O (10 mL), washed with three times with 1 M HCl (3 × 10 mL), once with brine and water, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by column chromatography on silica gel (10:1 hexanes/AcOEt) gave a yellow oil (225 mg, 95% yield).



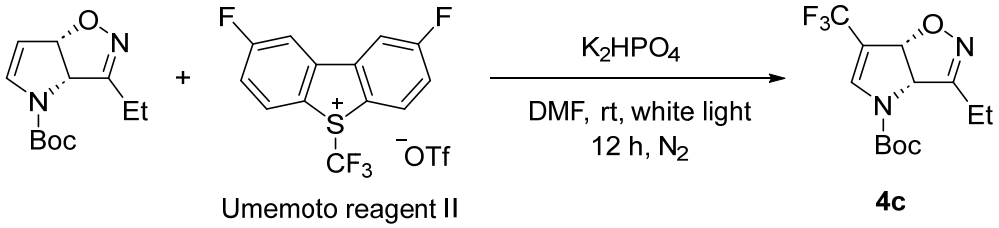
3aa **4b**

According to a literature procedure[29], **3aa** (41 mg, 0.16 mmol) was added to a solution of NH_4Cl (26 mg, 0.48 mmol) in THF (2 mL) and water (1 mL) at room temperature. The reaction mixture was stirred for 5 min, and then Zn powder (158 mg, 2.42 mmol) was added in portions. The reaction was stirred at room temperature for 1 h. At the end, the reaction mixture was concentrated under vacuum, and the

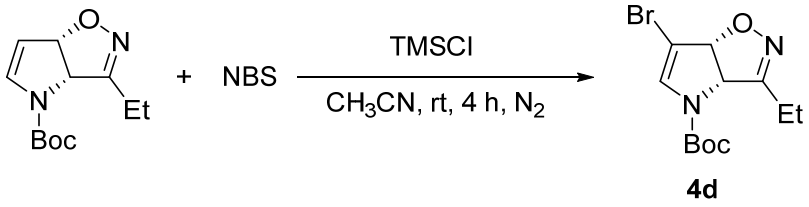
residue was purified by chromatography on silica gel (2:1 hexanes/AcOEt) to give the product (clear oil, 33 mg, 81% yield).



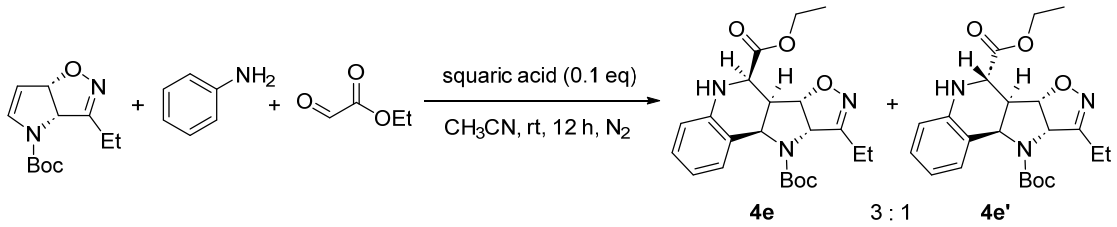
3aa (38 mg, 0.16 mmol) was added to a solution of TFA (0.16 mmol) in DCM (2 mL) at room temperature. The reaction mixture was stirred for 30 min, concentrated under vacuum, and purified by chromatography on silica gel (7:1 hexanes/AcOEt) to give the product (white solid, 19 mg, 87% yield).



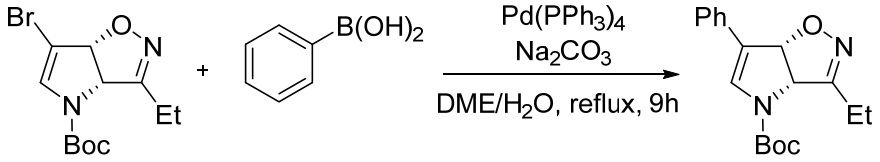
K_2HPO_4 (174 mg, 1.0 mmol) and Umemoto reagent II (438 mg, 1.0 mmol) were added to a solution of **3aa** (119 mg, 0.5 mmol) in DMF (4 mL). The reaction mixture was stirred under irradiation with white LEDs (approximately 3.0 cm distance from the tube) at room temperature for 12 hours. The mixture was extracted with ethyl acetate, washed with saturated brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by chromatography on silica gel (10:1 hexanes/AcOEt) gave the product (clear oil, 92 mg, 60% yield).



NBS (133 mg, 0.75 mmol) and Trimethylchlorosilane (108 mg, 1.0 mmol) were added in one potion to a solution of **3aa** (119 mg, 0.5 mmol) in CH_3CN (4 mL). The reaction mixture was stirred at room temperature for 4 h, concentrated under vacuum, and purified by chromatography on silica gel (7:1 hexanes/AcOEt) to give the product (clear oil, 142 mg, 90% yield).



Squaric acid (11 mg, 0.1 mmol), aniline (97 mg, 1.05 mmol) and ethyl glyoxylate solution (102 mg, 1.05 mmol, 50% in toluene) were added to a solution of **3aa** (238 mg, 1 mmol) in CH_3CN (4 mL). The reaction mixture was stirred under N_2 at room temperature for 12 hours, concentrated in vacuo, and purified by chromatography on silica gel (7:1 hexanes/AcOEt) to give the major isomer (white solid, 232mg, 56% yield) and the minor isomer (white solid, 78mg, 19% yield). The total yield was 75%. The isomer ratio was determined to be 3:1.

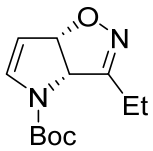


4f

To a stirred solution of the **4d** (0.5 mmol), Phenylboronicacid (72 mg, 0.6 mmol) and tetrakis-(triphenylphosphine)palladium (57 mg, 0.05 mmol) in 1,2-dimethoxyethane (10 mL) at room temperature under argon was added a solution of sodium carbonate (159 mg, 1.5 mmol) in water (5 mL). The mixture was heated at reflux for 9 h, cooled, then partitioned between water (50 mL) and dichloromethane (4 × 20 mL). The combined extracts were dried over Na_2SO_4 and evaporated in vacuo to give an oil. The residue was purified by flash chromatography on silica gel to give **4f** (110 mg, 71% yield).

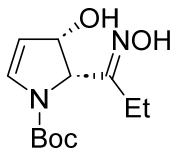
7.2 Physical data

***tert*-Butyl 3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole-4-carboxylate (4a)**



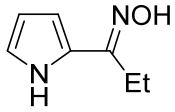
Clear oil (225 mg, 95% yield); R_f = 0.1 (7:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 – 6.37 (m, 1H), 5.67 (t, *J* = 8.4 Hz, 1H), 5.35 (dd, *J* = 31.0, 9.9 Hz, 1H), 5.09 (d, *J* = 15.2 Hz, 1H), 2.33 (m, 2H), 1.38 (s, 9H), 1.11 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.4, 150.7, 132.4, 107.1, 85.2, 81.4, 69.4, 27.9, 20.3, 10.4 ppm; IR (film) ν_{max} 1709, 1393, 1362, 1138, 930 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}N_2O_3$ 239.1390; Found 239.1391.

***tert*-Butyl 3-hydroxy-2-(1-(hydroxyimino)propyl)-2,3-dihydro-1*H*-pyrrole-1-carboxylate (4b)**



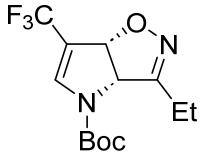
Clear oil (33 mg, 81% yield); R_f = 0.1 (3:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (s, 1H), 6.74 (d, *J* = 61.3 Hz, 1H), 5.35 – 4.89 (m, 2H), 4.56 (s, 1H), 3.74 (s, 1H), 2.31 (m, 2H), 1.41 (s, 9H), 1.09 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.3, 151.5, 150.8, 133.3, 108.9, 81.3, 75.9, 74.9, 63.9, 63.4, 28.3, 28.2, 28.0, 27.8, 21.4, 10.0, 9.6 ppm; IR (film) ν_{max} 3391, 1705, 1396, 1146, 1049, 764 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{21}N_2O_4$ 257.1495; Found 257.1493.

1-(1*H*-pyrrol-2-yl)propan-1-one oxime



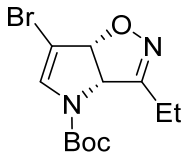
White solid (23 mg, 91% yield); R_f = 0.1 (5:1 hexanes/AcOEt); m.p. 99.1–101.0 °C; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.63 (s, 1H), 6.97 (q, *J* = 2.3 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 6.27 (q, *J* = 2.8 Hz, 1H), 2.63 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3, 125.1, 120.9, 113.0, 108.6, 25.8, 12.7 ppm; IR (film) ν_{max} 3414, 3237, 1423, 1381, 926, 733 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_7H_{11}N_2O$ 139.0865; Found 139.0864.

***tert*-Butyl 3-ethyl-6-(trifluoromethyl)-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole-4-carboxylate (4c)**



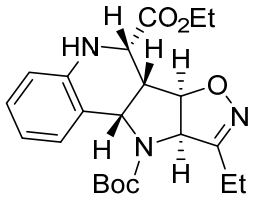
Clear oil (92 mg, 60% yield); R_f = 0.2 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (s, 1H), 5.89 (d, *J* = 10.4 Hz, 2H), 5.67 (d, *J* = 10.1 Hz, 1H), 2.48 (td, *J* = 21.1, 18.7, 10.9 Hz, 2H), 1.53 (s, 9H), 1.25 (t, *J* = 7.4 Hz, 3H). ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2, 150.3, 136.0, 122.6 (q, *J* = 267.2 Hz), 110.7 (q, *J* = 35.9 Hz), 83.9, 82.8, 71.8, 28.1, 20.6, 10.7 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}F_3N_2O_3$ 307.1264; Found 307.1261.

***tert*-Butyl 6-bromo-3-ethyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole-4-carboxylate (4d)**



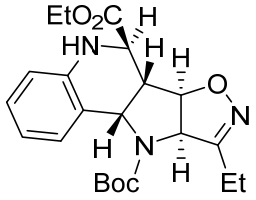
Clear oil (142 mg, 90% yield); R_f = 0.1 (5:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.74 (s, 1H), 5.67 (d, *J* = 10.5 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H), 2.70 – 2.16 (m, 2H), 1.50 (s, 9H), 1.23 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 150.3, 131.5, 100.4, 86.8, 82.6, 70.3, 28.1, 20.4, 10.6 ppm; IR (film) ν_{max} 1740, 1630, 1311, 1356, 1242, 709 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}BrN_2O_3$ 317.0495; Found 317.0504.

10-(*tert*-Butyl) 6-ethyl (6*S*,6a*S*,6b*R*,9a*R*,10a*S*)-9-ethyl-5,6,6a,6b,9a,10a-hexahydro-10*H*-isoxazolo[5',4':4,5]pyrrolo[3,2-*c*]quinoline-6,10-dicarboxylate (4e)



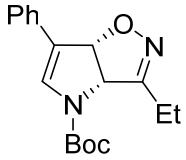
White solid (186 mg, 45% yield); R_f = 0.15 (5:1 hexanes/AcOEt, less polar); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 5.50 – 5.04 (m, 3H), 4.77 – 4.08 (m, 4H), 2.97 (d, *J* = 34.1 Hz, 1H), 2.51 (s, 2H), 1.59 (s, 9H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (d, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 142.4, 129.0, 128.5, 118.6, 115.2, 81.2, 79.7, 79.3, 69.2, 62.0, 55.9, 52.3, 46.0, 28.4, 21.8, 14.1, 11.1 ppm; IR (film) ν_{max} 3101, 1750, 1660, 1380, 1377, 1142, 718 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{30}N_3O_5$ 416.2179; Found 416.2187.

10-(*tert*-Butyl) 6-ethyl (6*R*,6a*S*,6b*R*,9a*R*,10a*S*)-9-ethyl-5,6,6a,6b,9a,10a-hexahydro-10*H*-isoxazolo[5',4':4,5]pyrrolo[3,2-*c*]quinoline-6,10-dicarboxylate (4e′)



White solid (124 mg, 30% yield); R_f = 0.13 (5:1 hexanes/AcOEt, more polar); m.p. 156.1–158.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.17 – 6.98 (m, 1H), 6.77 – 6.66 (m, 1H), 6.60 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.32 – 4.94 (m, 3H), 4.40 (s, 1H), 4.17 (dq, *J* = 7.2, 3.7 Hz, 2H), 4.07 (t, *J* = 2.6 Hz, 1H), 2.88 (td, *J* = 7.4, 3.3 Hz, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.55 (s, 9H), 1.24 (td, *J* = 7.2, 2.2 Hz, 6H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 161.3, 154.6, 142.1, 129.5, 128.9, 119.0, 115.2, 81.8, 81.3, 68.8, 61.7, 52.9, 44.1, 28.4, 21.6, 14.1, 10.9 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{30}N_3O_5$ 416.2179; Found 416.2187.

***tert*-Butyl (3a*S*,6a*S*)-3-ethyl-6-phenyl-3a,6a-dihydro-4*H*-pyrrolo[2,3-*d*]isoxazole-4-carboxylate (4f)**



Clear oil (110 mg, 71% yield); R_f = 0.3 (10:1 hexanes/AcOEt); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.14 (m, 2H), 6.10 (dd, *J* = 15.9, 9.8 Hz, 1H), 5.61 (dd, *J* = 40.4, 9.9 Hz, 1H), 2.50 (tt, *J* = 16.9, 8.3 Hz, 2H), 1.55 (s, 9H), 1.26 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.0, 151.0, 132.3, 128.6, 127.0, 126.4, 125.1, 121.2, 85.0, 82.2, 70.2, 28.2, 20.5, 10.7 ppm; IR (film) ν_{max} 1740, 1370, 1270, 1180, 701 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{23}N_2O_3$ 315.1703; Found 315.1698.

8. Mechanism experiments

8.1 Radical trapping experiment using TEMPO

A dry Schlenk tube charged with a stirring bar was evacuated and backfilled with N_2 (three times). 1-Boc-pyrrole (**1a**, 1.00 mmol, 167 mg), 1-bromo-1-nitropropane (**2a**, 2.0 mmol, 0.20 mL), TEMPO (2.00 mmol, 312 mg), Ag_2CO_3 (2.00 mmol, 551 mg) and anhydrous DMSO (6.0 mL) were added under N_2 atmosphere. After stirring at rt under N_2 for 12 h, the mixture was diluted with AcOEt, washed with brine (3 × 50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5:1 hexanes/AcOEt) to give **3aa** (76 mg, 30% yield).

8.2 Powder X-ray diffraction spectrum

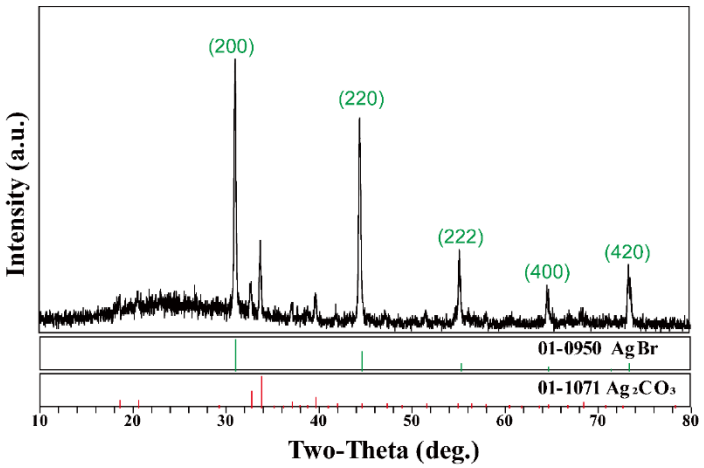


Figure S1 XRD patterns of the precipitate in the mechanism experiment.

9. DFT calculations

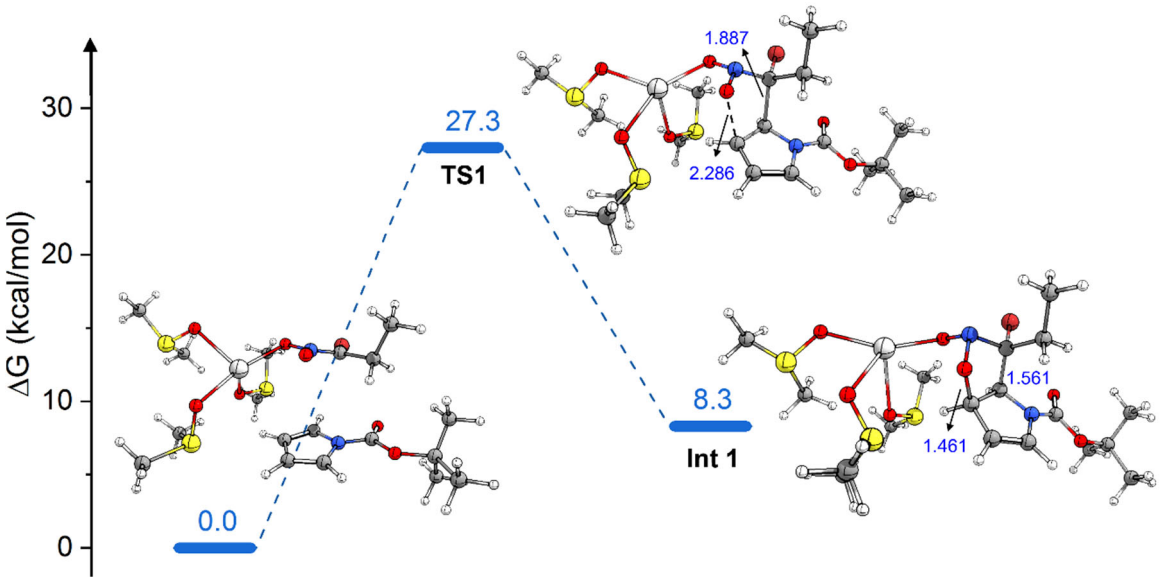


Figure S2. Free energy profile for the [3+2] cycloaddition between **1a** and the Ag(I) nitronate of **2a**. Three explicit DMSO molecules and implicit PCM model are included to account for the solvent effect. Energies and selected bond distances are given in kcal/mol and angstrom, respectively.

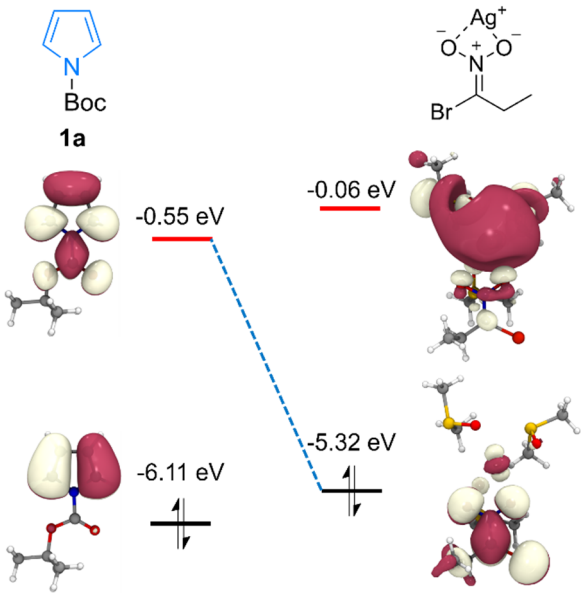
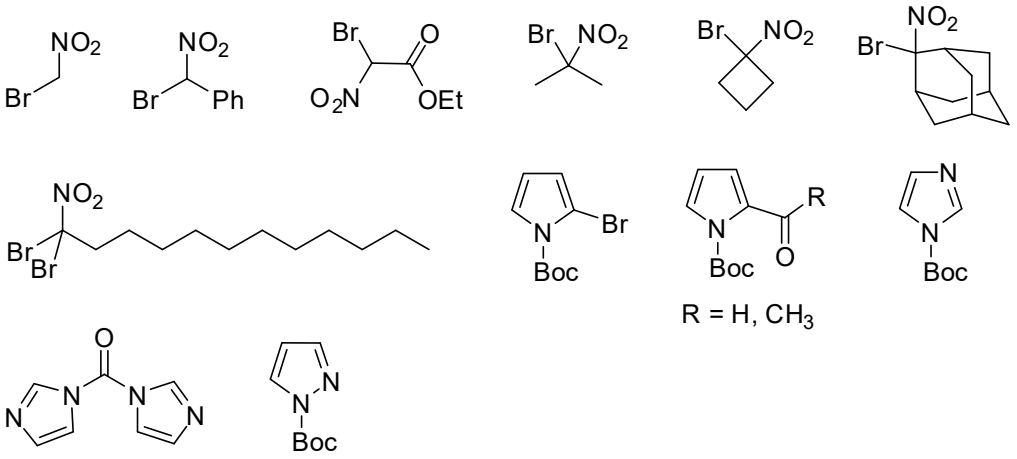


Figure S3. The HOMO and LUMO orbitals along with their energies (in eV) of **1a** and the Ag(I) nitronate of **2a** calculated at the B3LYP-D3/6-31G*&SDD level. Three DMSO coordinate with the Ag^{+}.

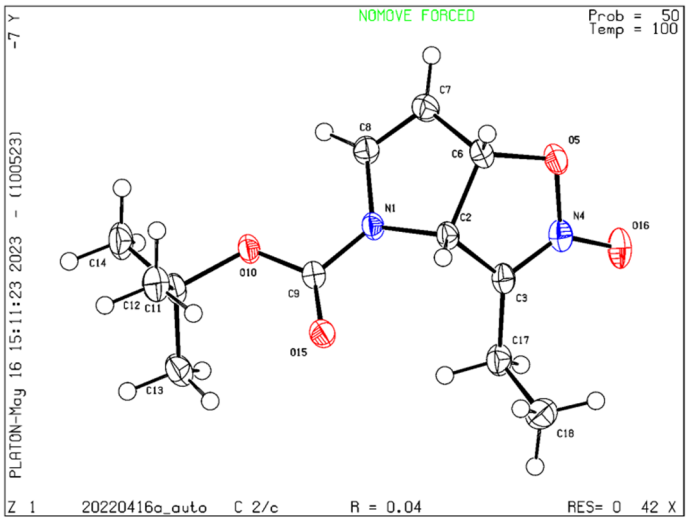
10. Unsuccessful reactants



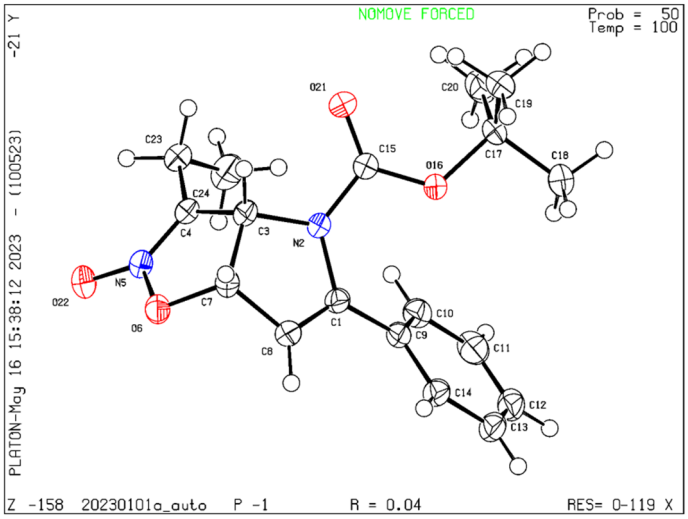
11. Crystal data

CCDC numbers: 2268832 (**3aa**); 2268866 (**3ia**); 2306811 (**3e′a**); 2306810 (**4e′**).

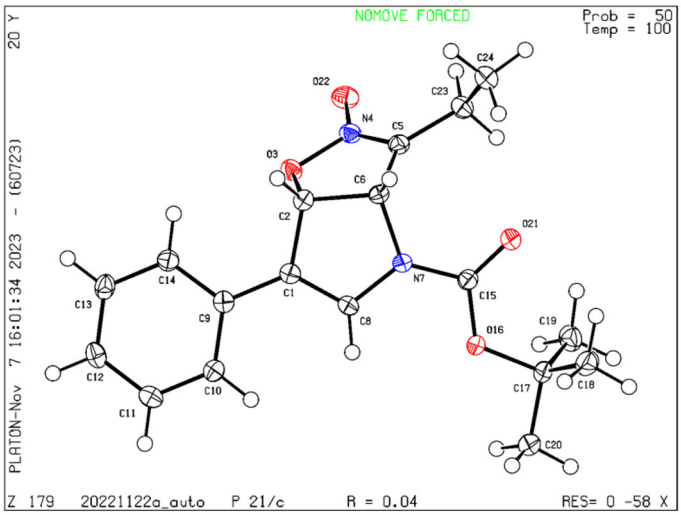
Single crystals of **3aa**, **3ia**, **3e′a** and **4e′** were obtained by layering an ethyl acetate solution with *n*-hexane and subsequent slow evaporation of the solvents at rt. The ellipsoid contour probability level is 50%.



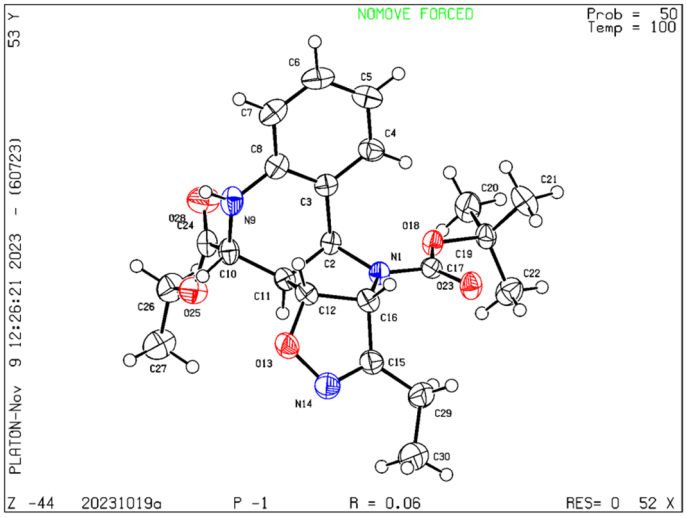
Crystal data and structure refinement for **3aa**.	
Temperature/K	100(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	23.2511(5)
b/Å	6.0802(7)
c/Å	18.4786(9)
α/°	90
β/°	97.790(3)
γ/°	90
Volume/Å^3	2588.2(3)
Z	8
ρcalcg/cm^3	1.305
μ/mm^{-1}	0.820
F(000)	1088.0
Crystal size/mm^3	0.500 × 0.500 × 0.200
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.676 to 152.408
Index ranges	-28 ≤ h ≤ 28, -5 ≤ k ≤ 7, -23 ≤ l ≤ 21
Reflections collected	12333
Independent reflections	2612 [Rint = 0.0436, Rsigma = 0.0283]
Data/restraints/parameters	2612/0/168
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0392, wR2 = 0.1039
Final R indexes [all data]	R1 = 0.0434, wR2 = 0.1070
Largest diff. peak/hole / e Å-3	0.25/-0.23



Crystal data and structure refinement for **3ia**.	
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.5021(8)
b/Å	9.6751(5)
c/Å	10.0293(9)
α/°	77.914(6)
β/°	71.586(8)
γ/°	89.936(6)
Volume/Å^3	853.33(12)
Z	2
ρcalcg/cm^3	1.286
μ/mm^{-1}	0.749
F(000)	352.0
Crystal size/mm^3	0.100 × 0.100 × 0.100
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.372 to 151.894
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12
Reflections collected	22766
Independent reflections	3413 [Rint = 0.0860, Rsigma = 0.0477]
Data/restraints/parameters	3413/0/222
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R1 = 0.0439, wR2 = 0.1074
Final R indexes [all data]	R1 = 0.0581, wR2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.19/-0.21



Crystal data and structure refinement for **3e′a**.	
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.1005(18)
b/Å	9.9090(10)
c/Å	11.5159(15)
α/°	90
β/°	93.934(11)
γ/°	90
Volume/Å^3	1719.1(4)
Z	4
ρcalcg/cm^3	1.269
μ/mm^{-1}	0.724
F(000)	700.0
Crystal size/mm^3	0.150 × 0.100 × 0.100
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.686 to 153.67
Index ranges	-19 ≤ h ≤ 19, -11 ≤ k ≤ 12, -14 ≤ l ≤ 13
Reflections collected	23697
Independent reflections	3496 [Rint = 0.0780, Rsigma = 0.0496]
Data/restraints/parameters	3496/0/222
Goodness-of-fit on F2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0390, wR2 = 0.0949
Final R indexes [all data]	R1 = 0.0491, wR2 = 0.1004
Largest diff. peak/hole / e Å^{-3}	0.24/-0.21



Crystal data and structure refinement for **4e′**.	
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6012(7)
b/Å	10.4718(6)
c/Å	11.4984(9)
α/°	86.861(6)
β/°	70.637(7)
γ/°	79.609(5)
Volume/Å^3	1072.78(14)
Z	2
ρcalcg/cm^3	1.286
μ/mm^{-1}	0.092
F(000)	444.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.404 to 59.594
Index ranges	-13 ⩽ h ⩽ 13, -13 ⩽ k ⩽ 14, -14 ⩽ l ⩽ 15
Reflections collected	9167
Independent reflections	4892 [Rint = 0.0487, Rsigma = 0.0692]
Data/restraints/parameters	4892/0/276
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R1 = 0.0622, wR2 = 0.1522
Final R indexes [all data]	R1 = 0.0831, wR2 = 0.1740
Largest diff. peak/hole / e Å^{-3}	0.38/-0.37

12. References

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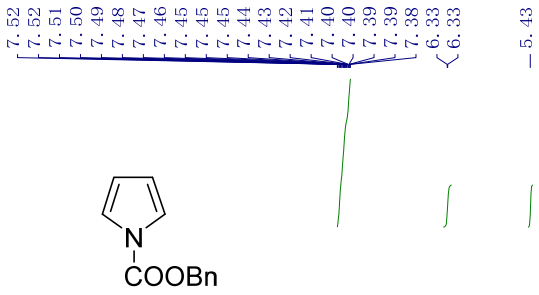
13.NMR spectra



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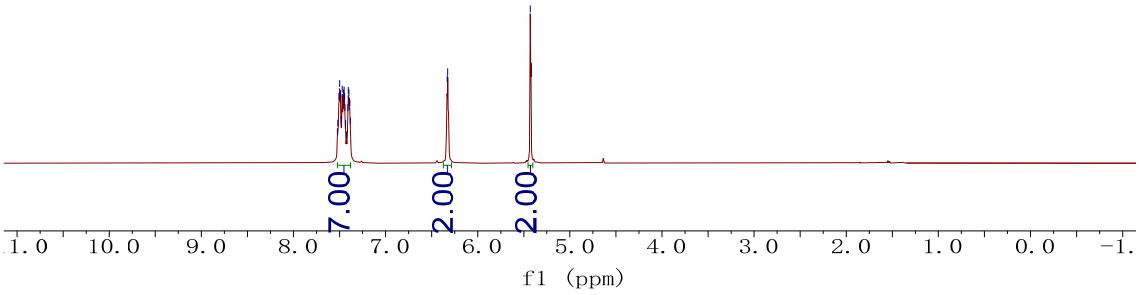

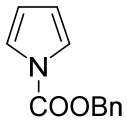

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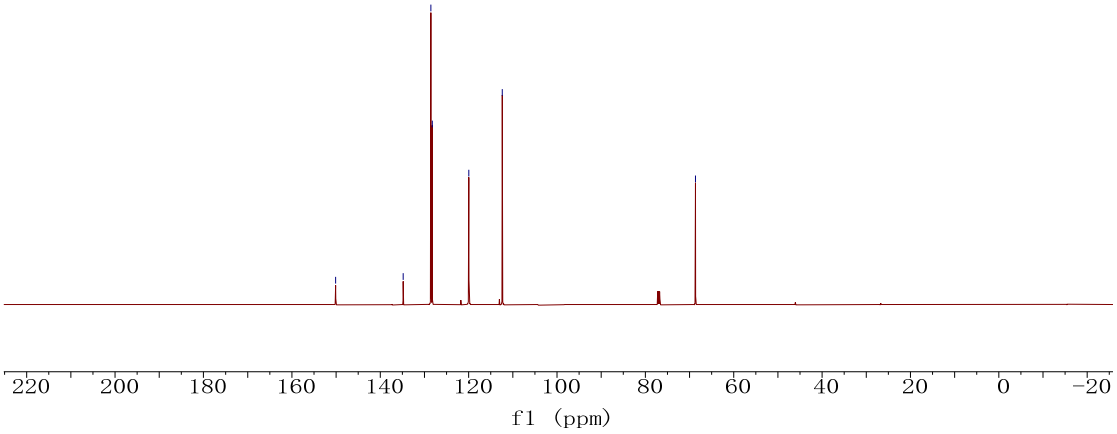

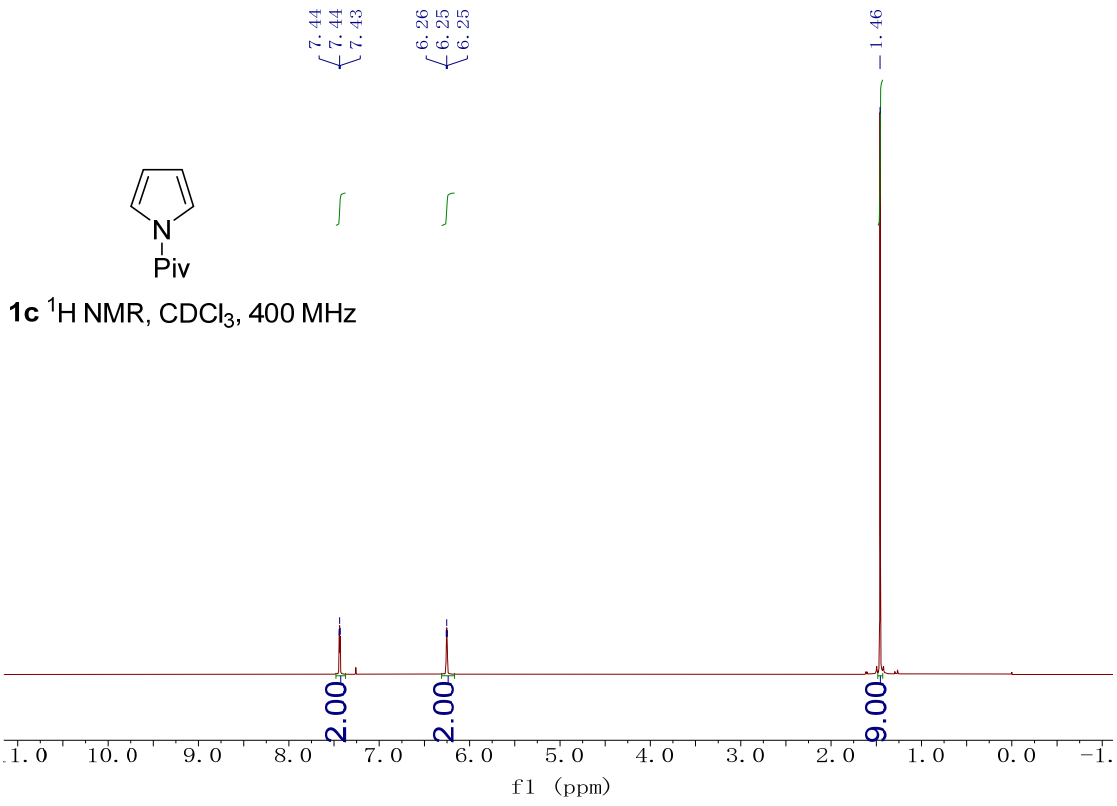

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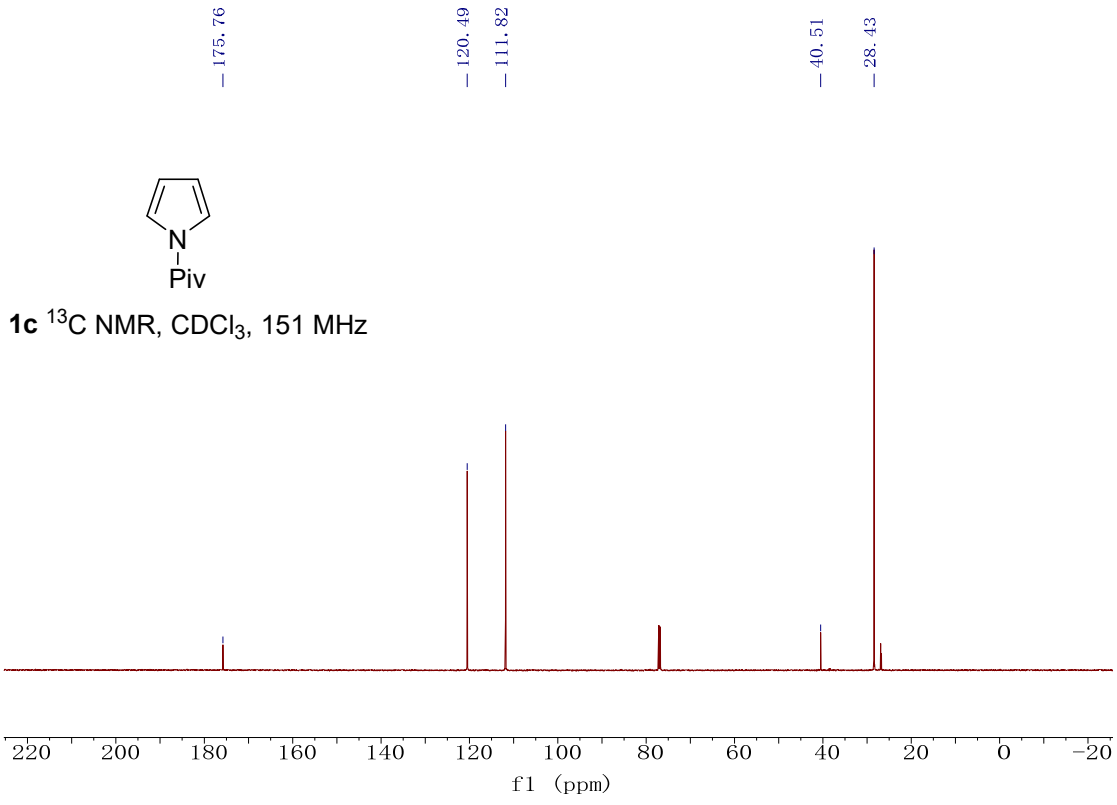

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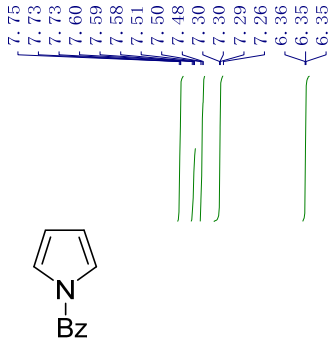

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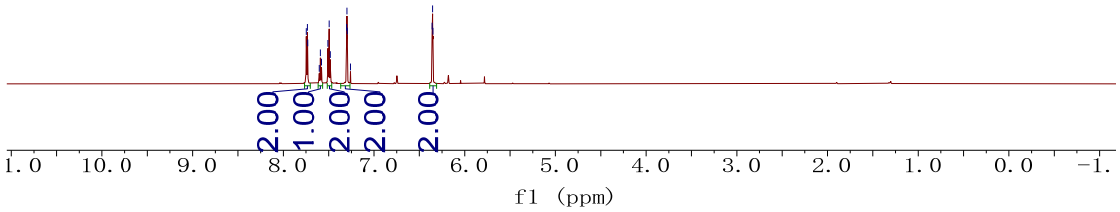

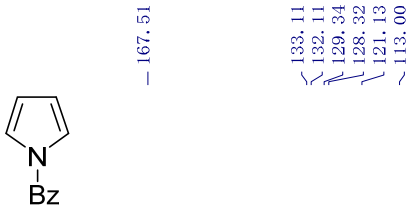

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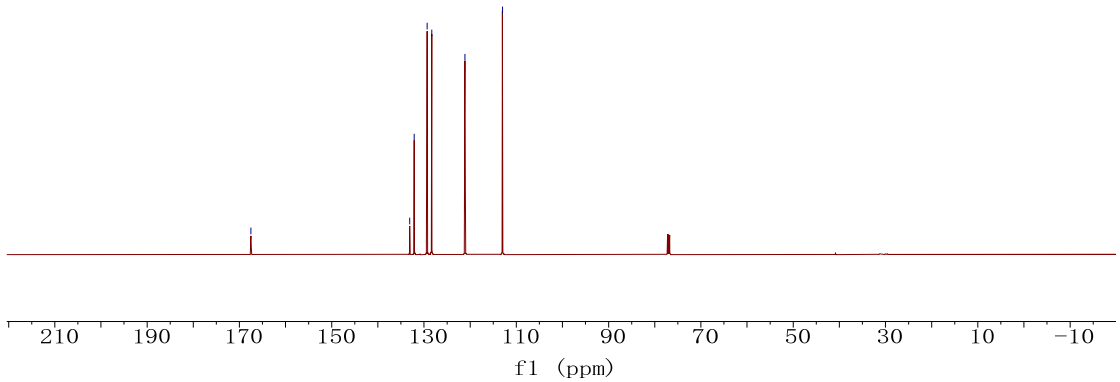

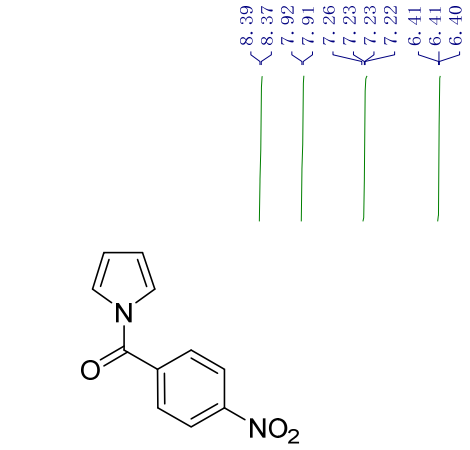

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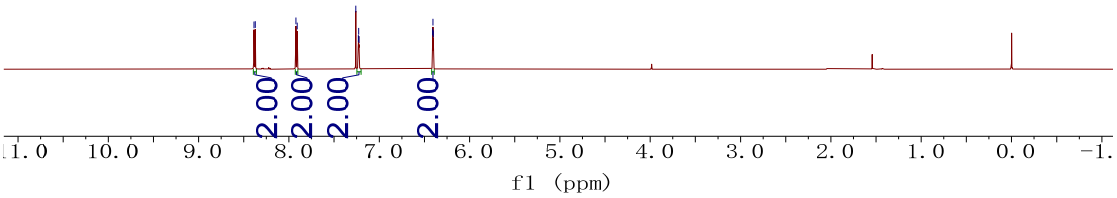

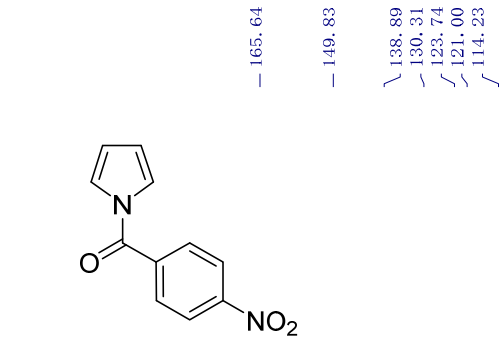

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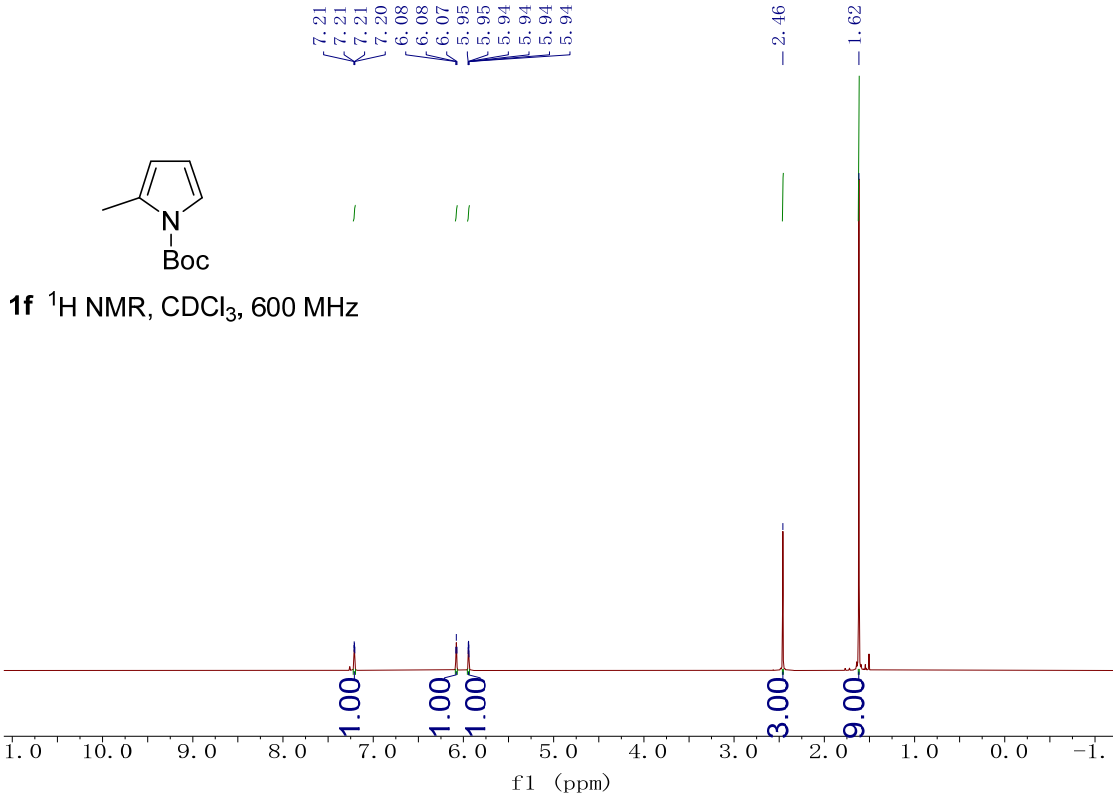

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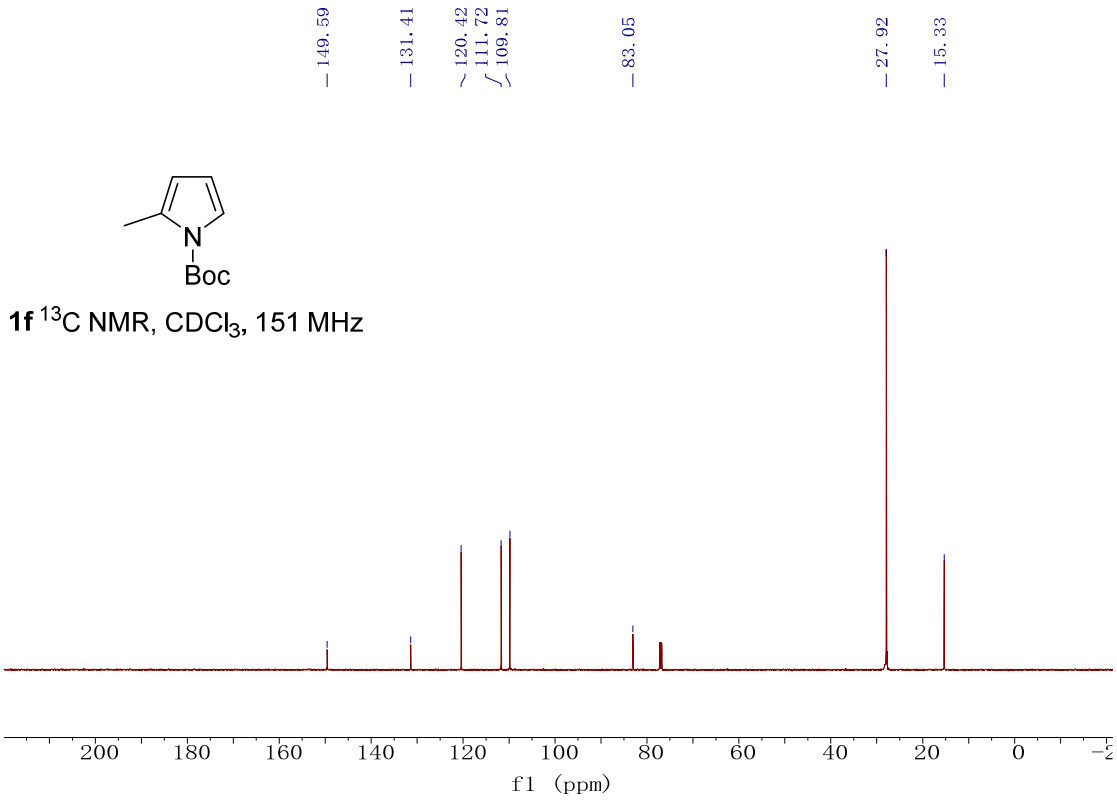

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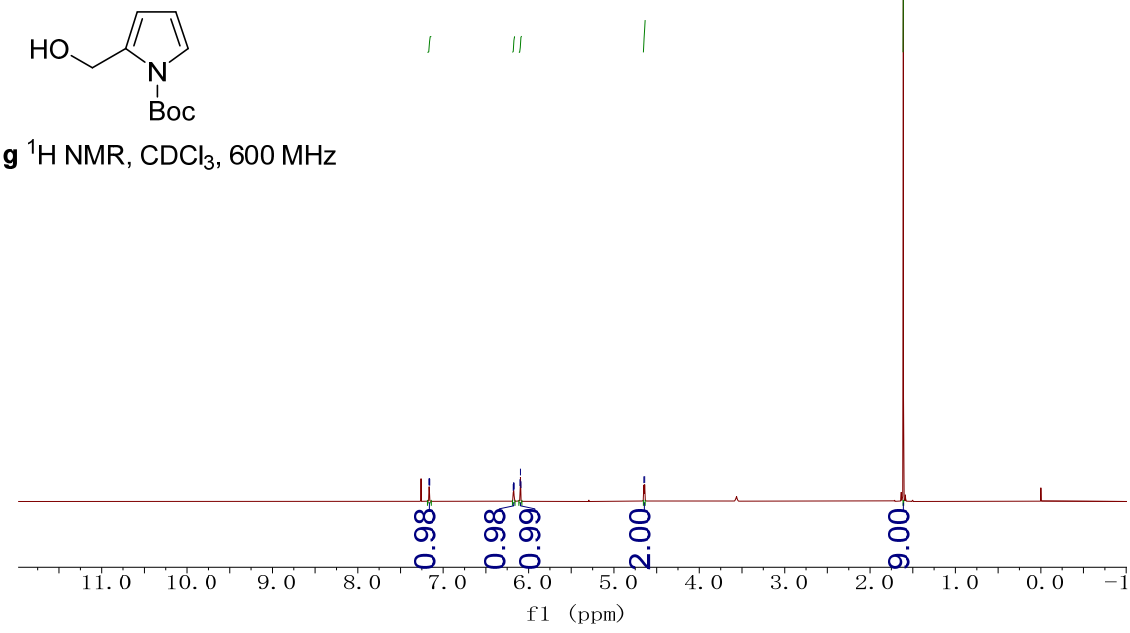

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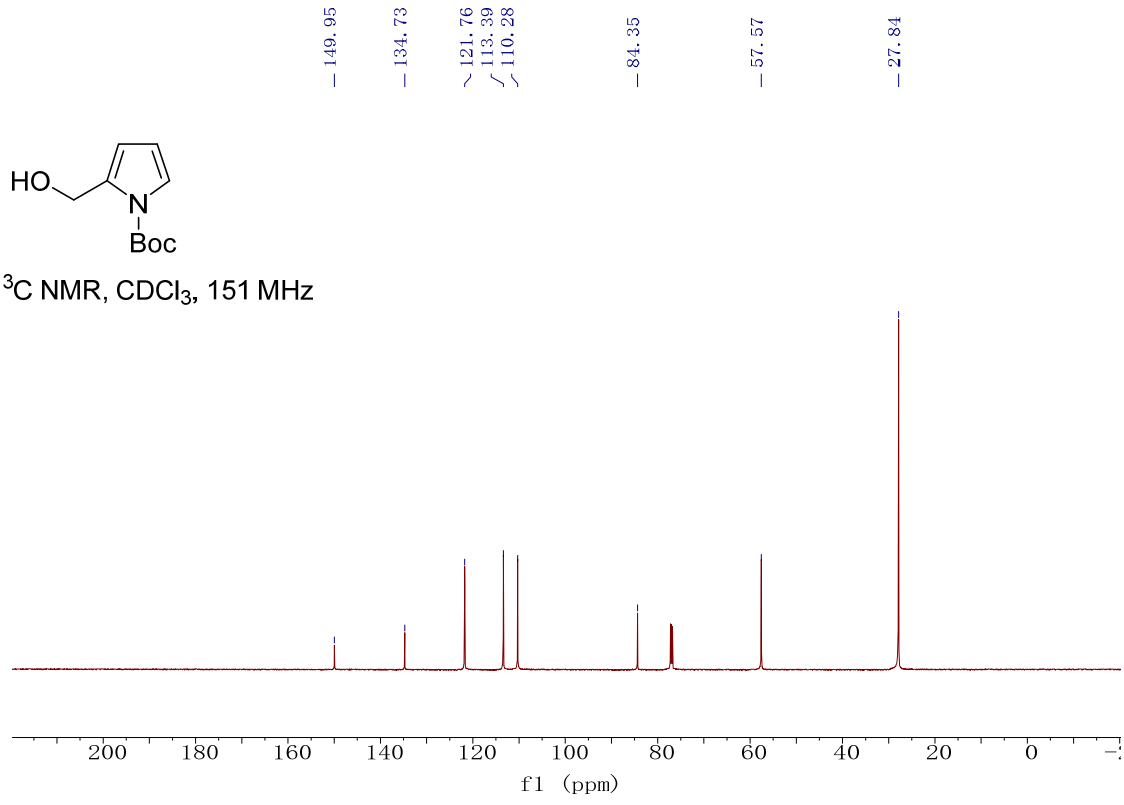

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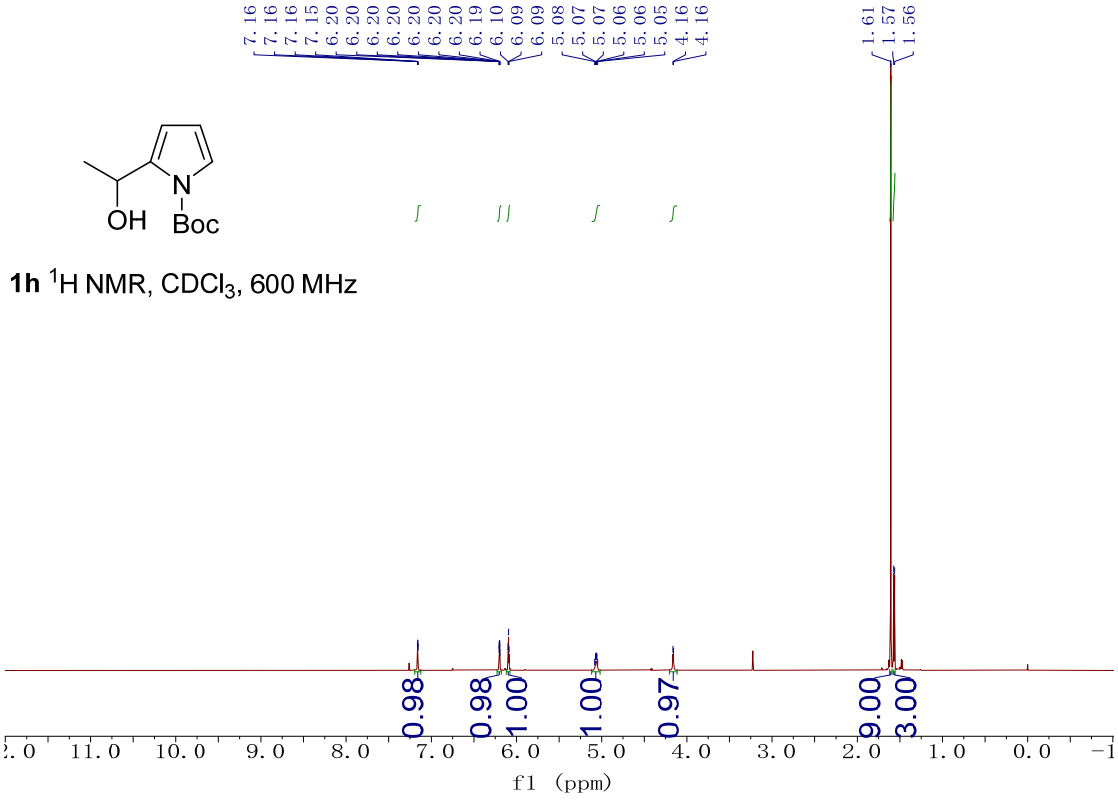

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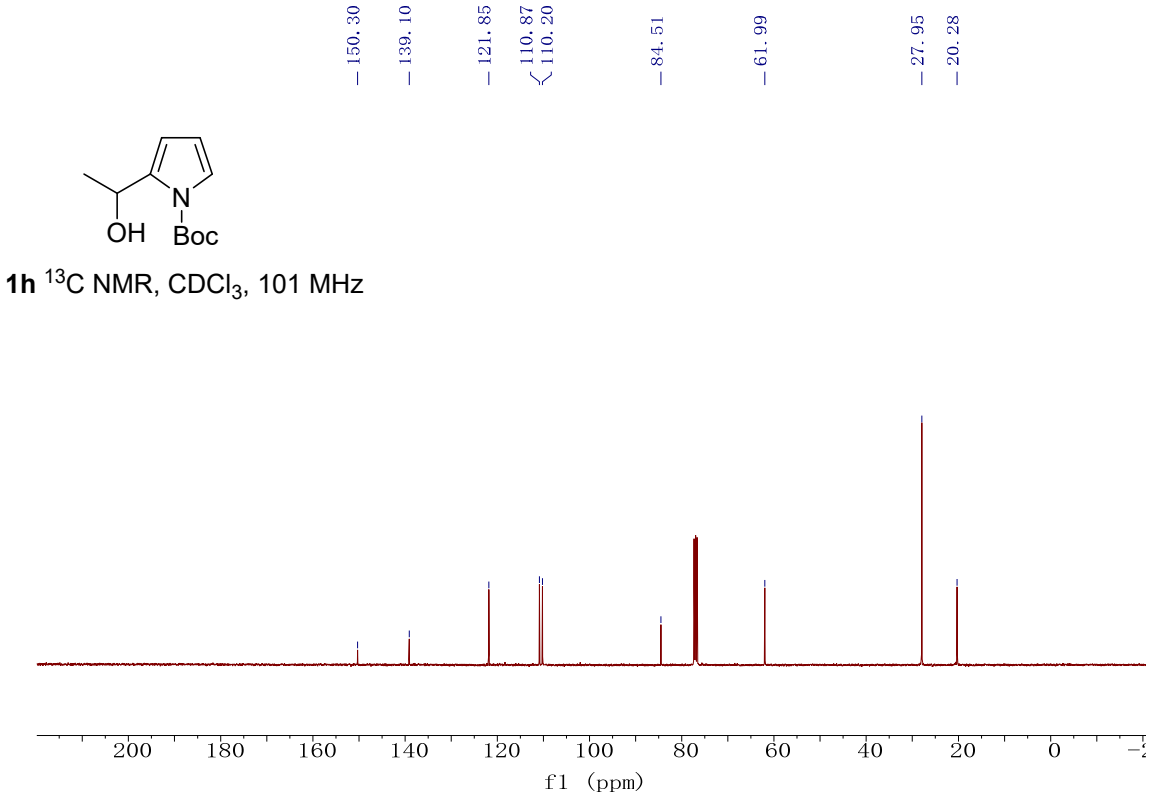

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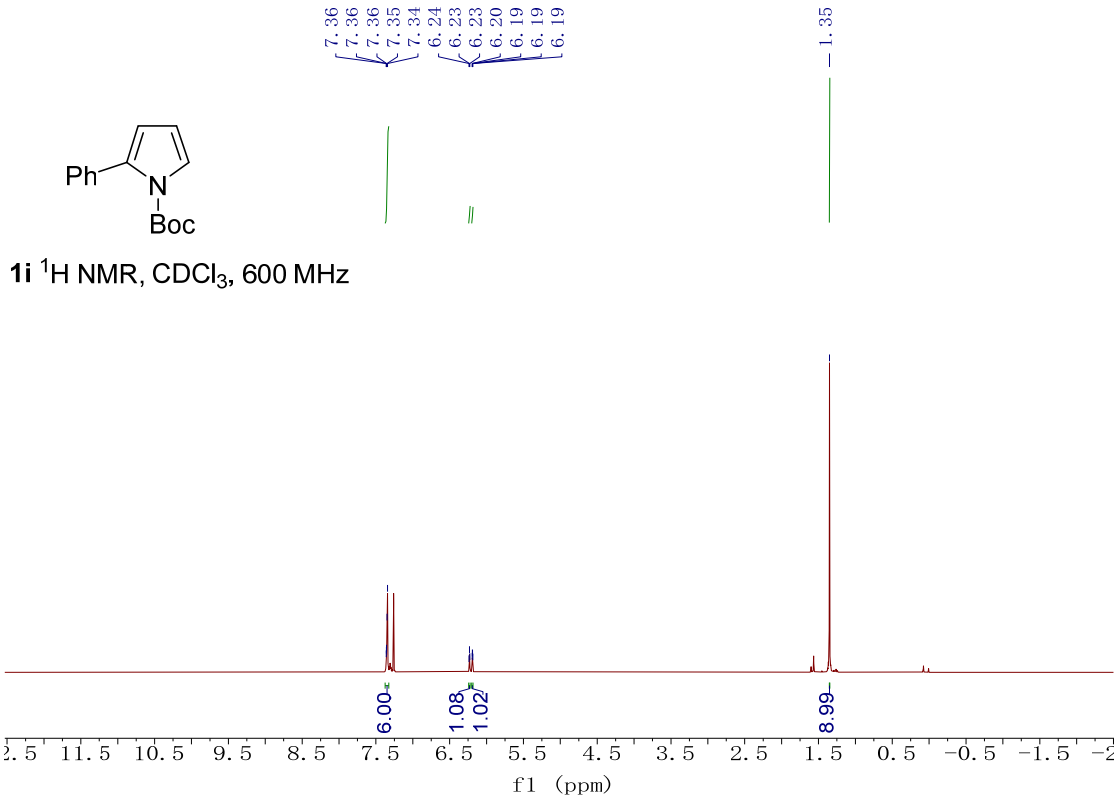

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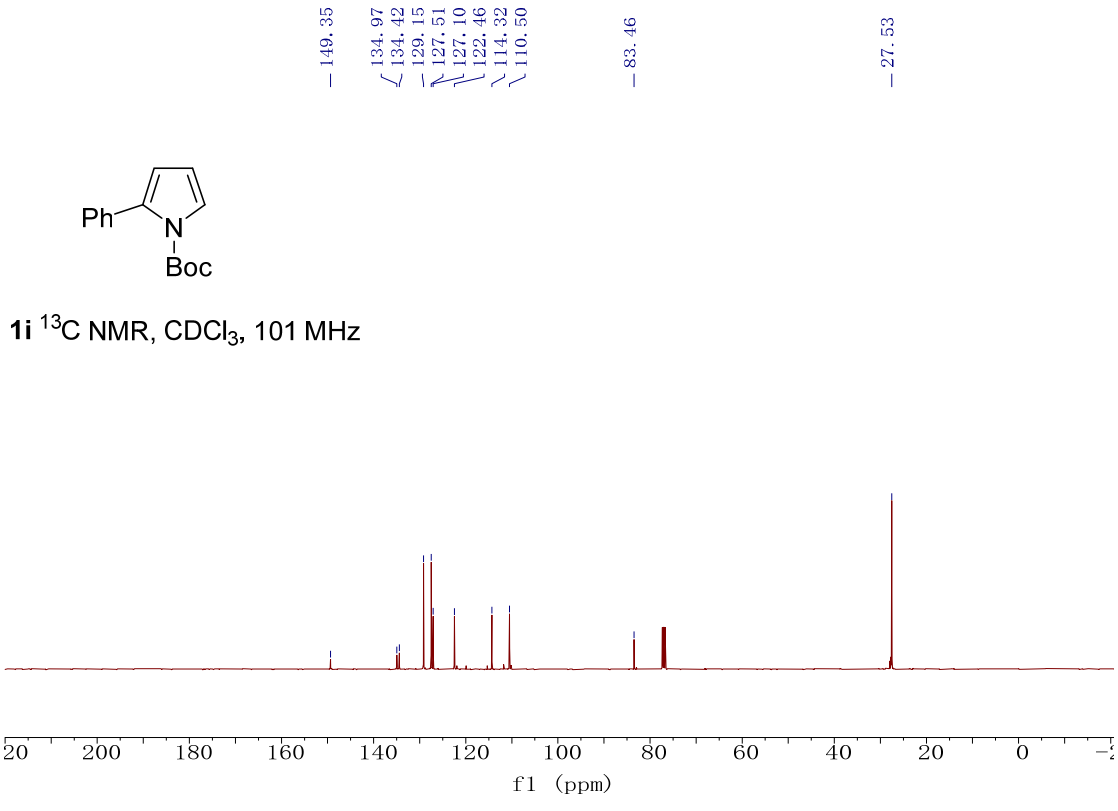

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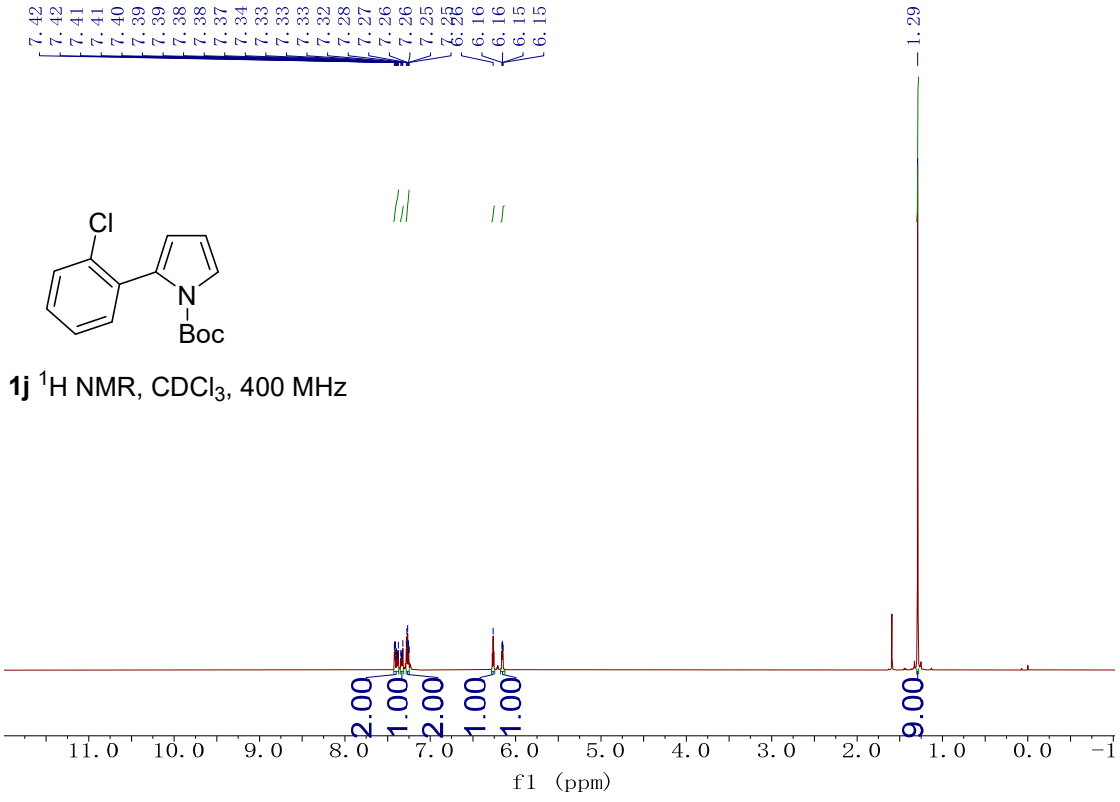

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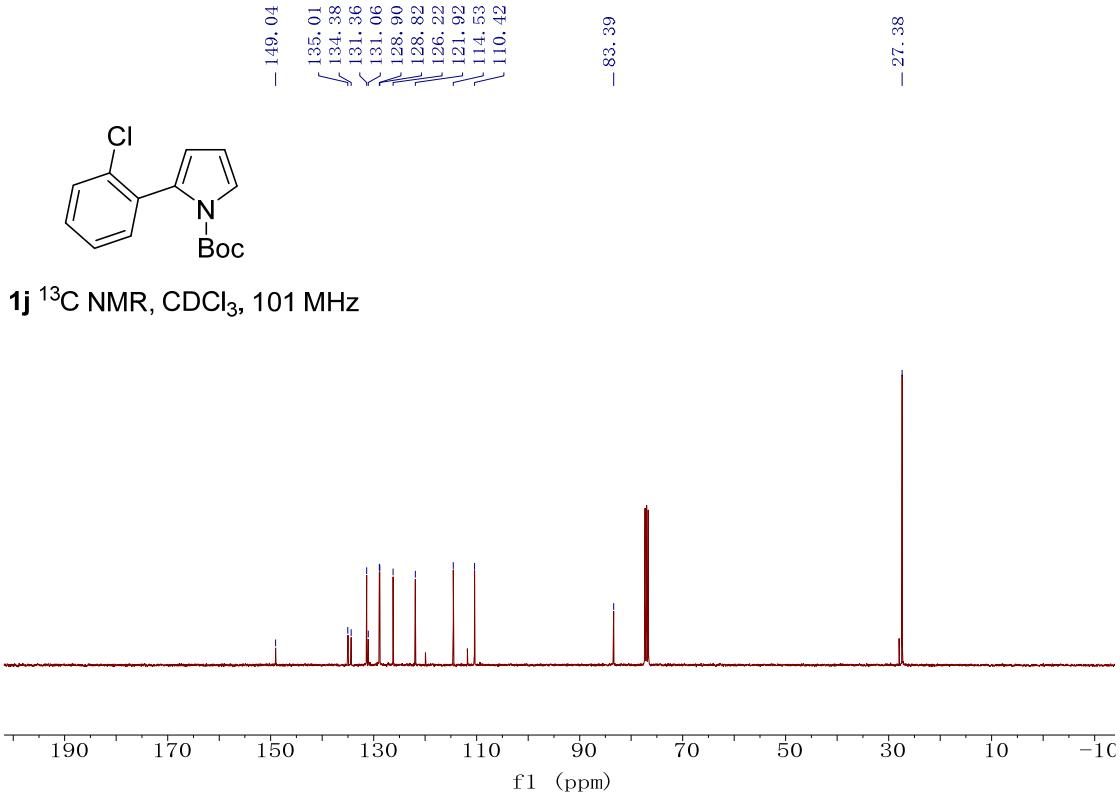

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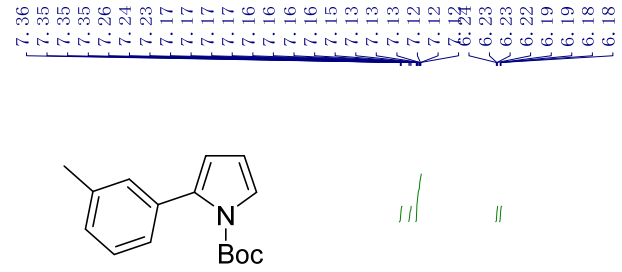

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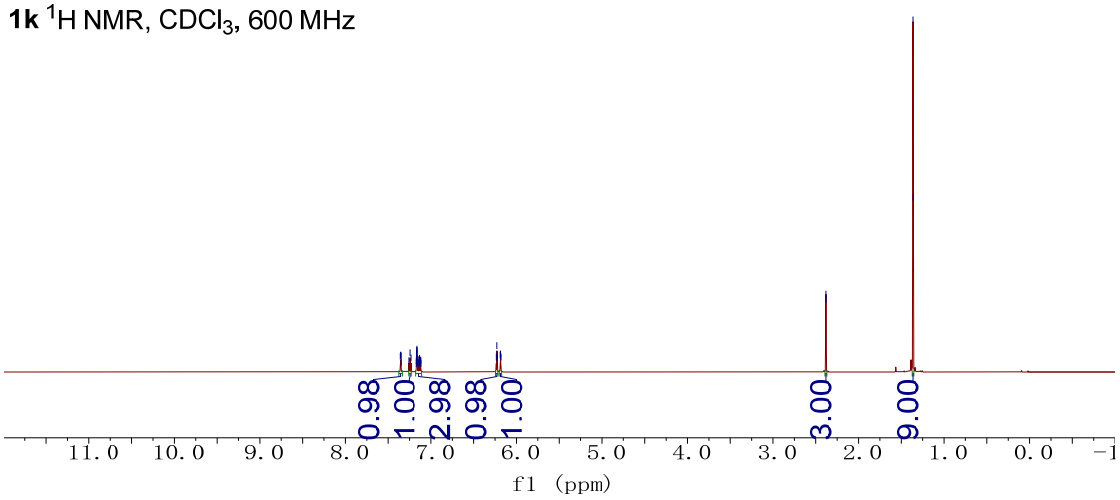

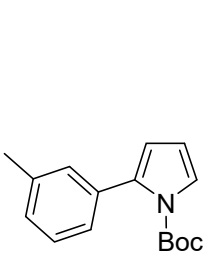

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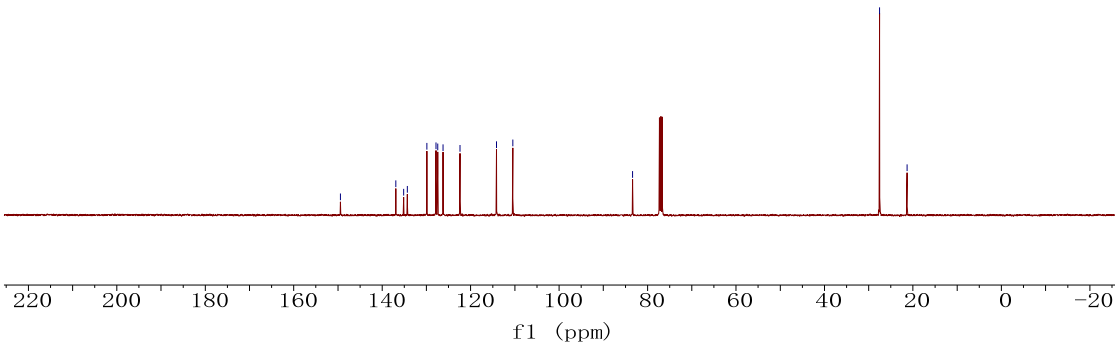

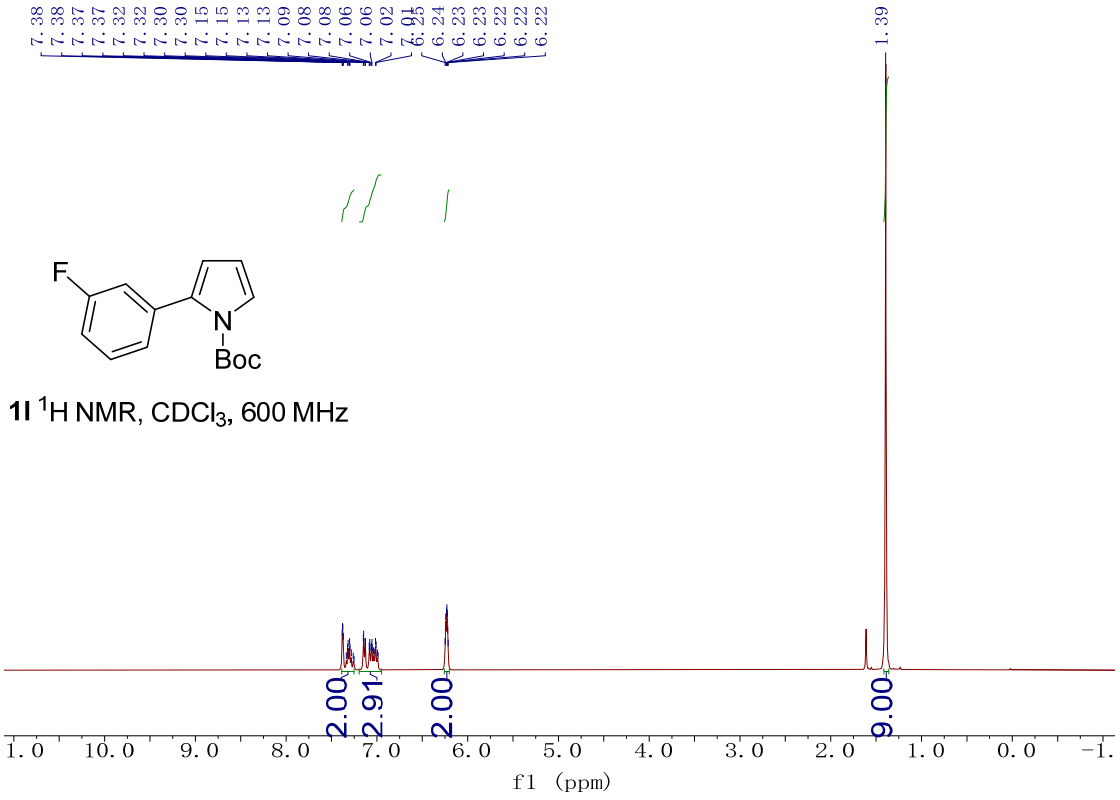

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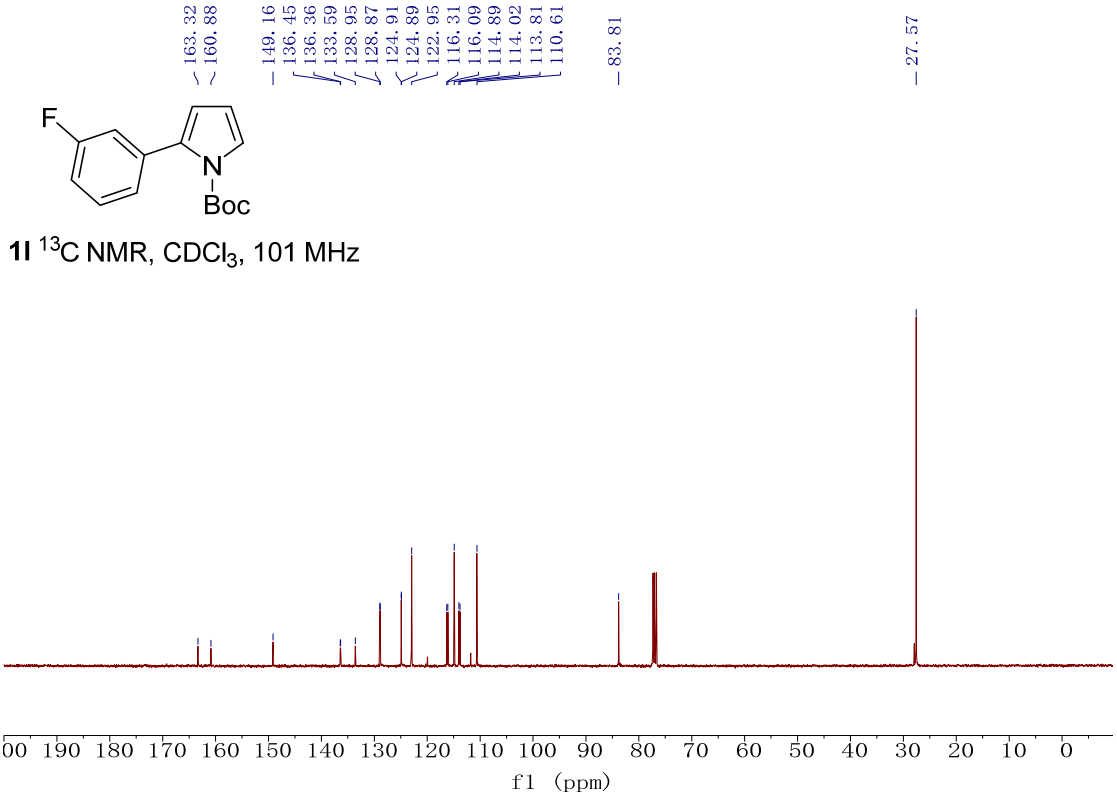

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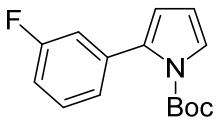

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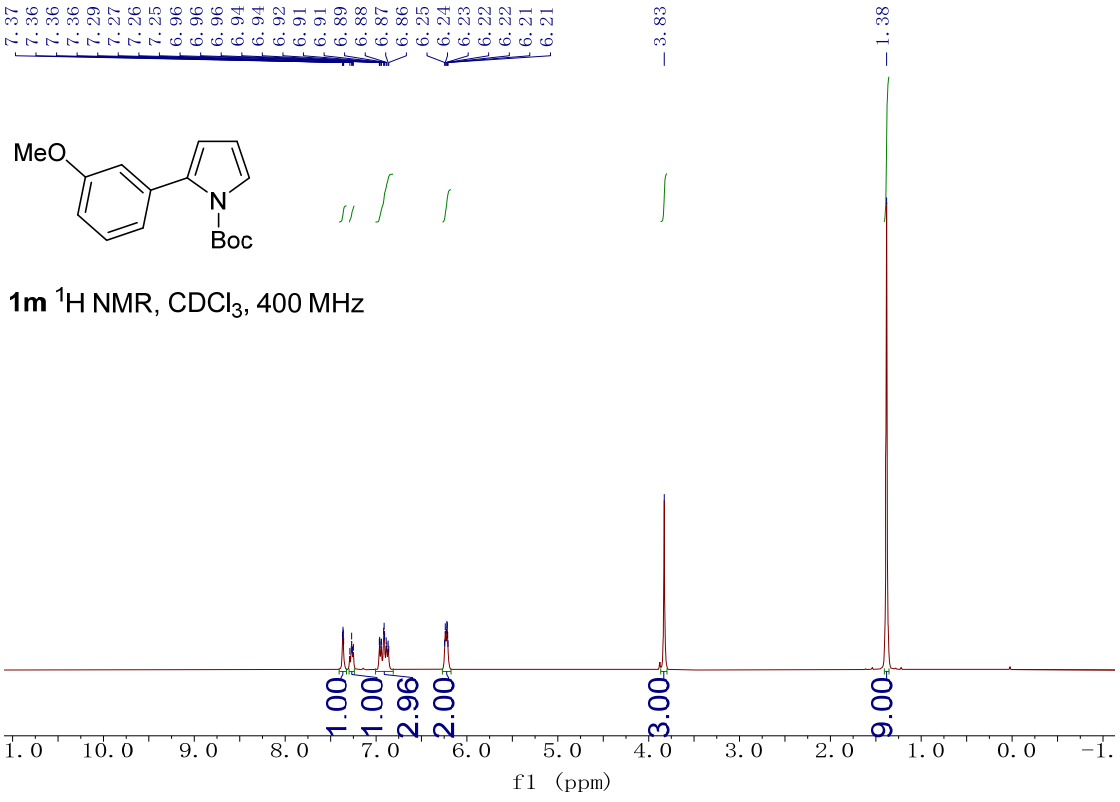

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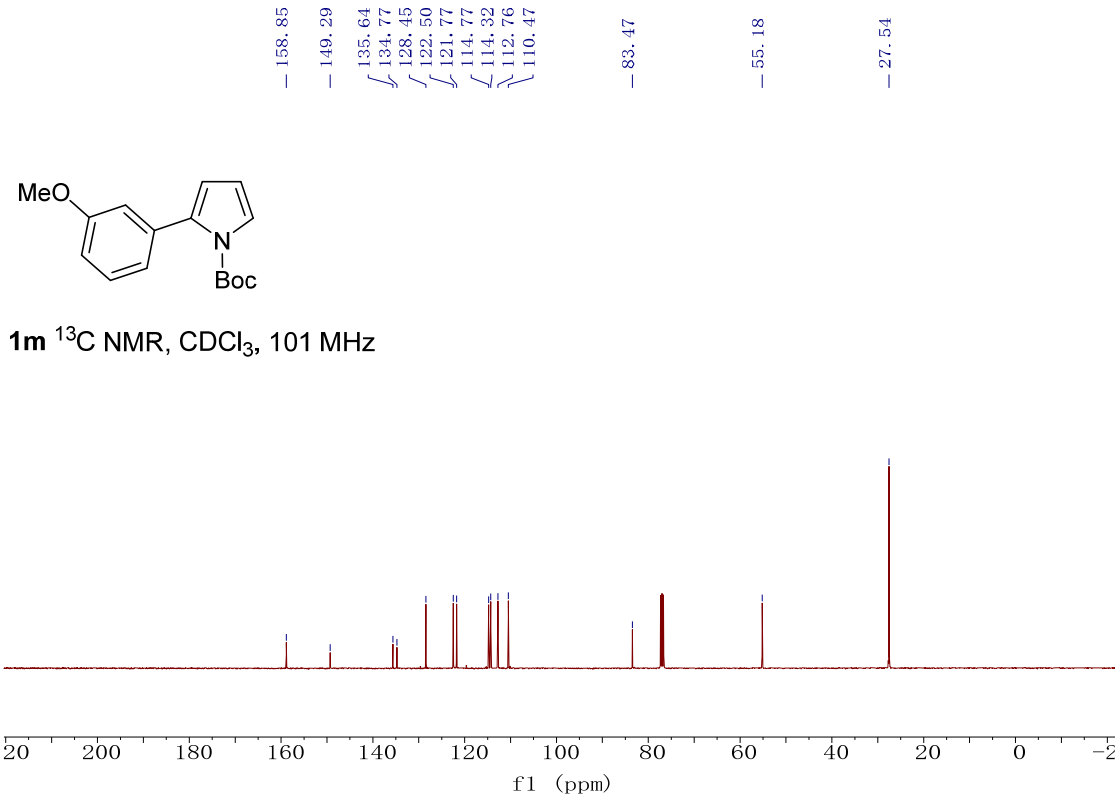
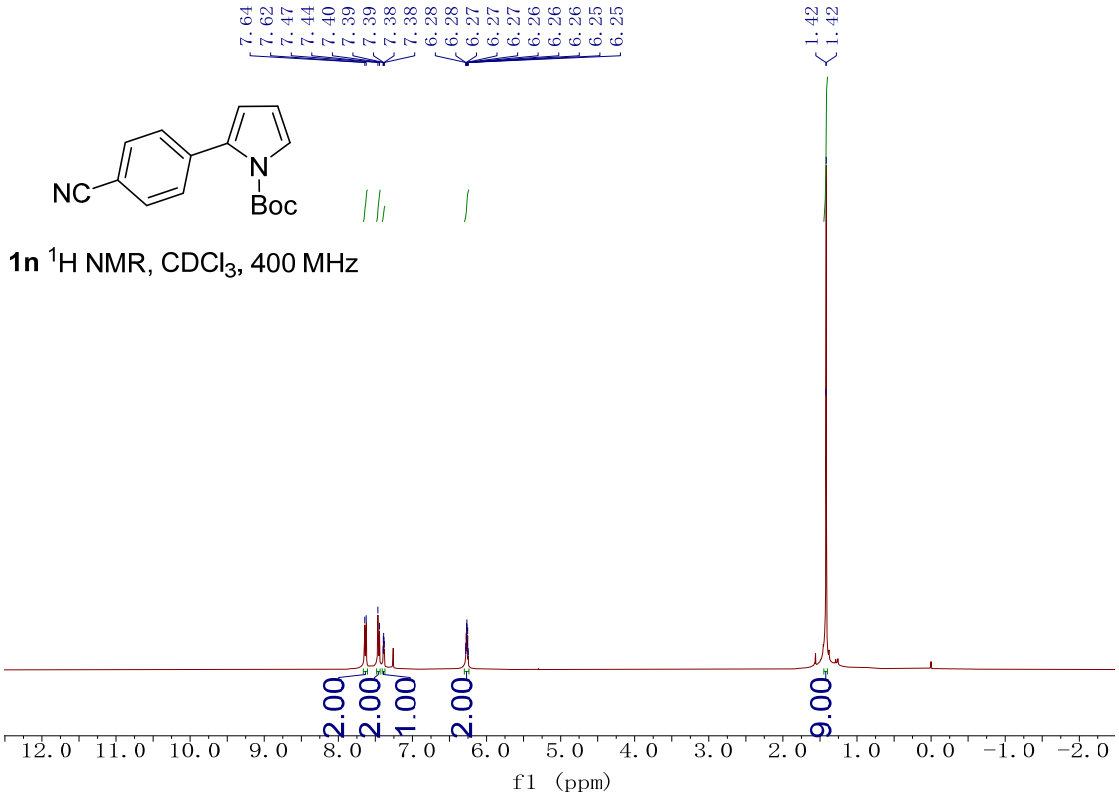
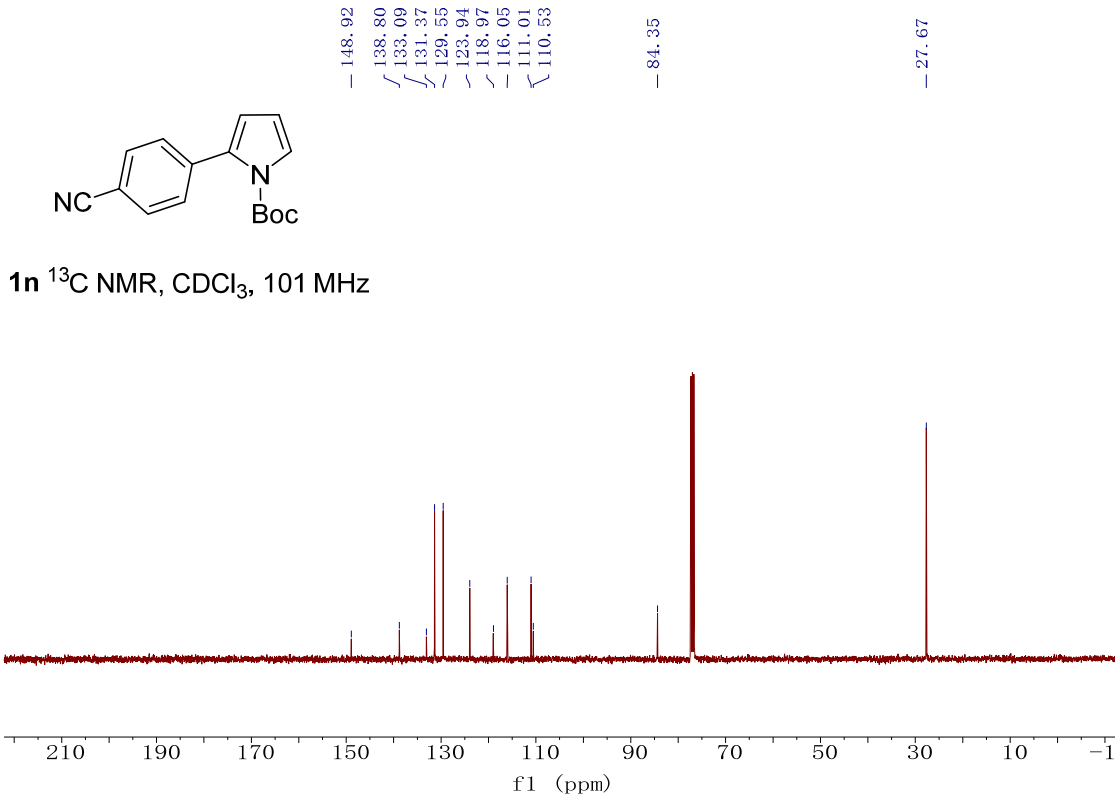


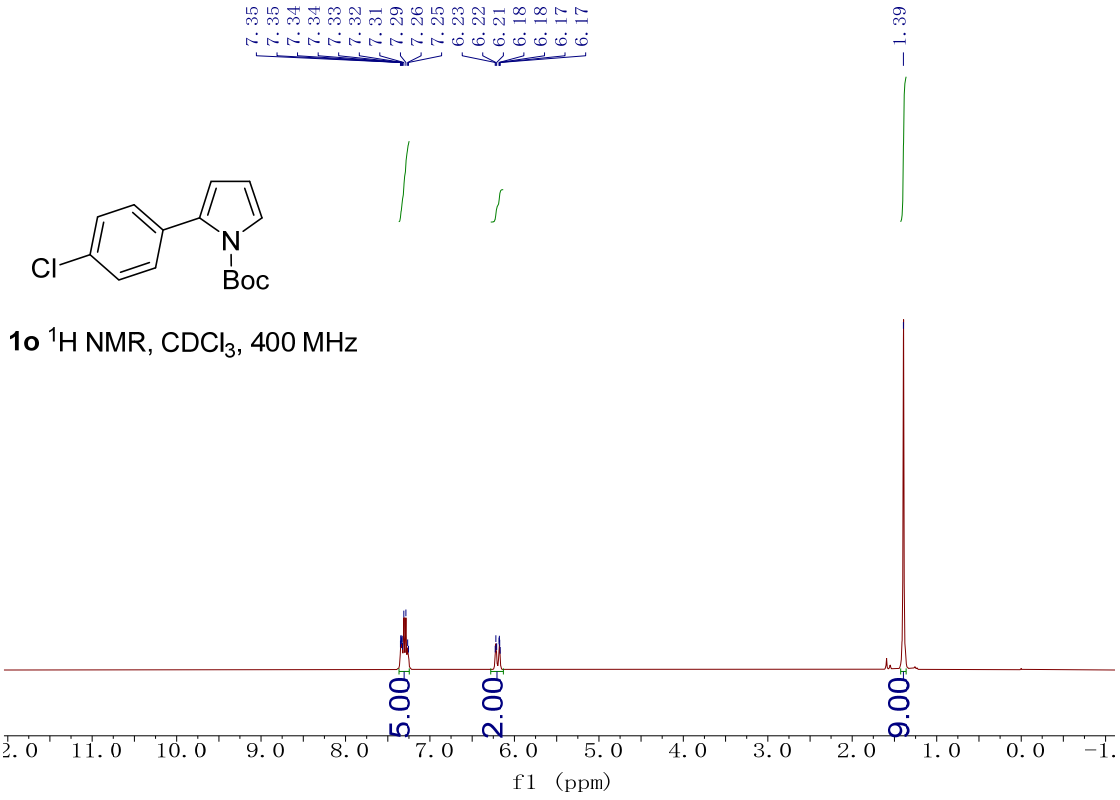
1m ^{13}C NMR, $CDCl_3$, 101 MHz



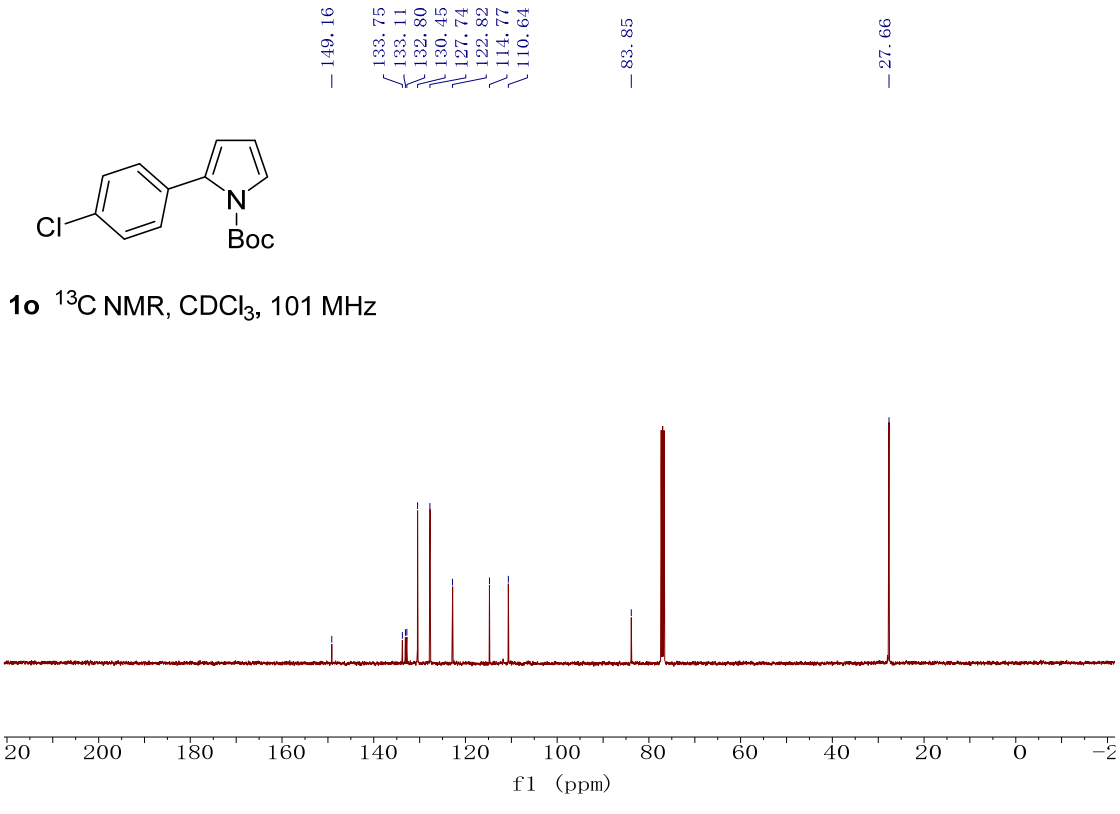
1n ^{1}H NMR, $CDCl_3$, 400 MHz



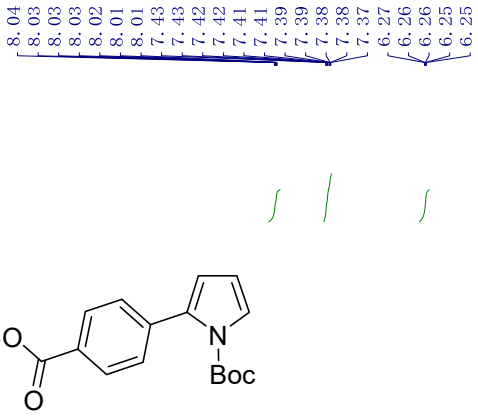
1n ^{13}C NMR, $CDCl_3$, 101 MHz



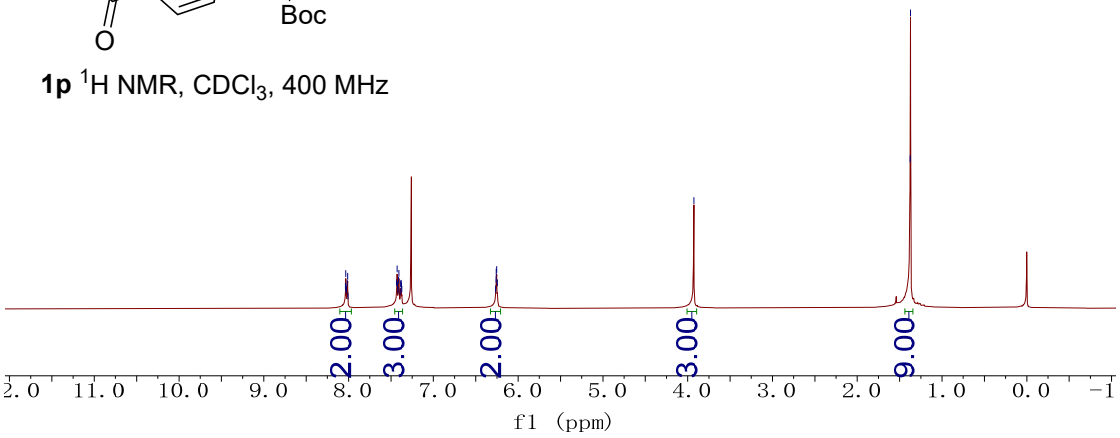
1o ^{1}H NMR, $CDCl_3$, 400 MHz

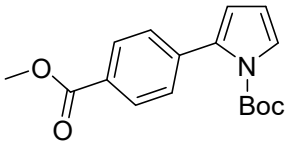


1o ^{13}C NMR, $CDCl_3$, 101 MHz

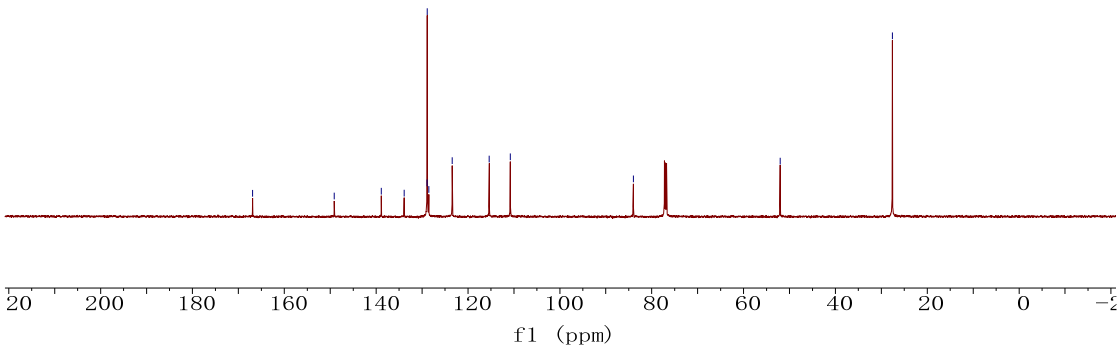


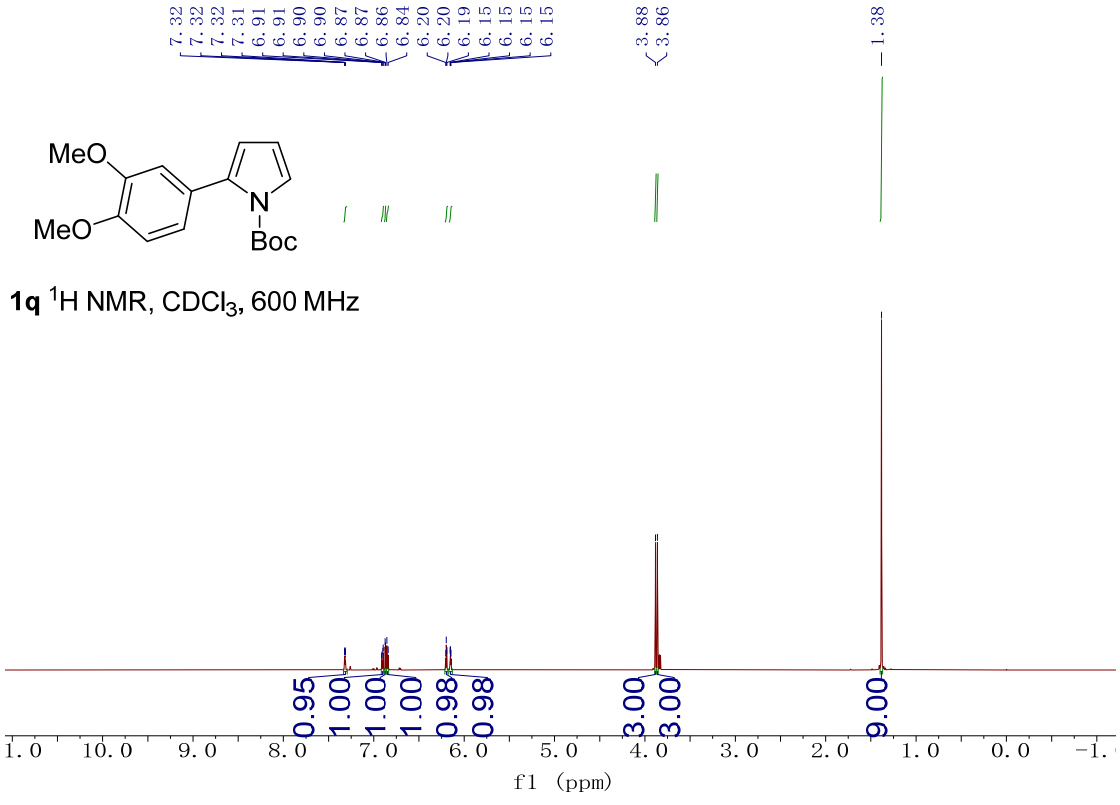
1p ^{1}H NMR, $CDCl_3$, 400 MHz



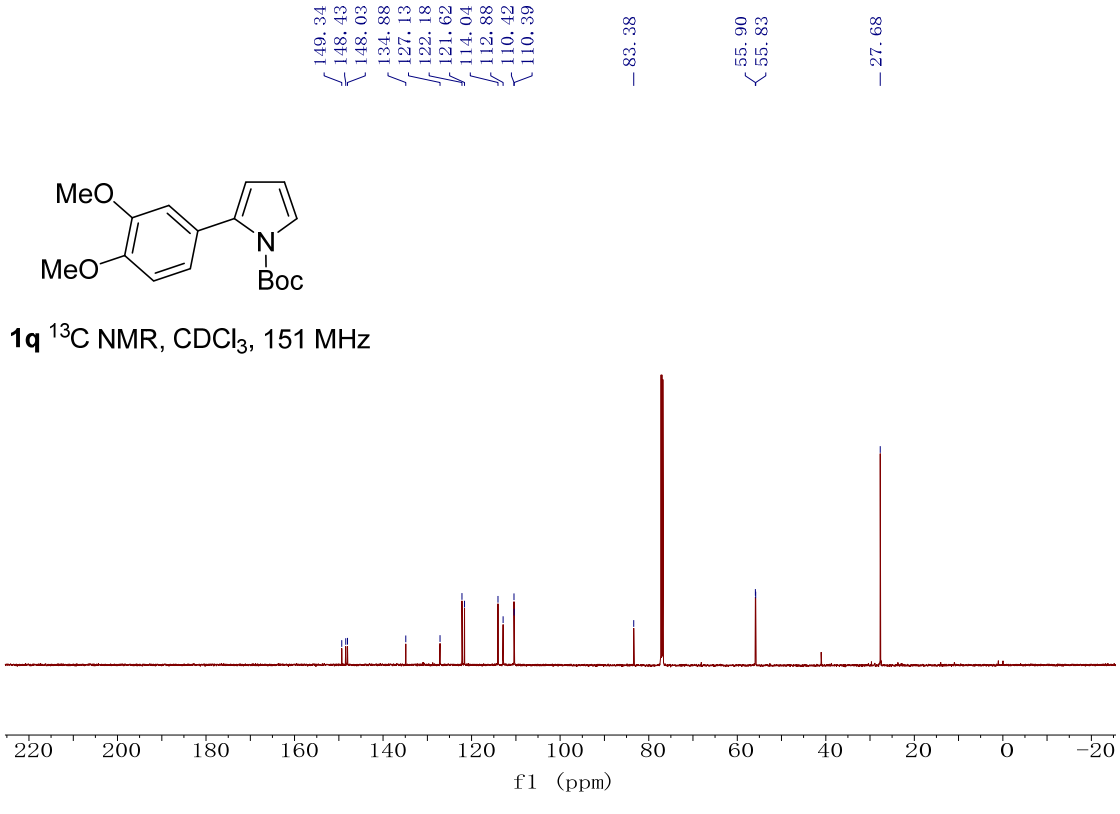


1p ^{13}C NMR, $CDCl_3$, 151 MHz

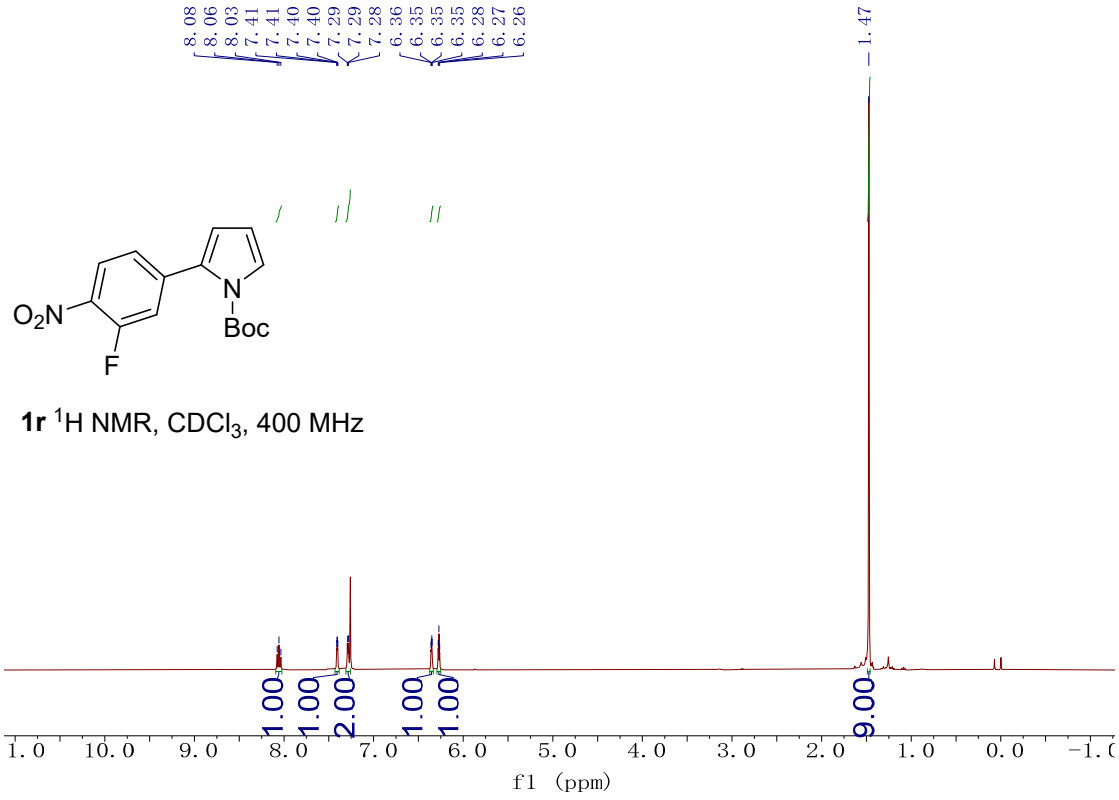




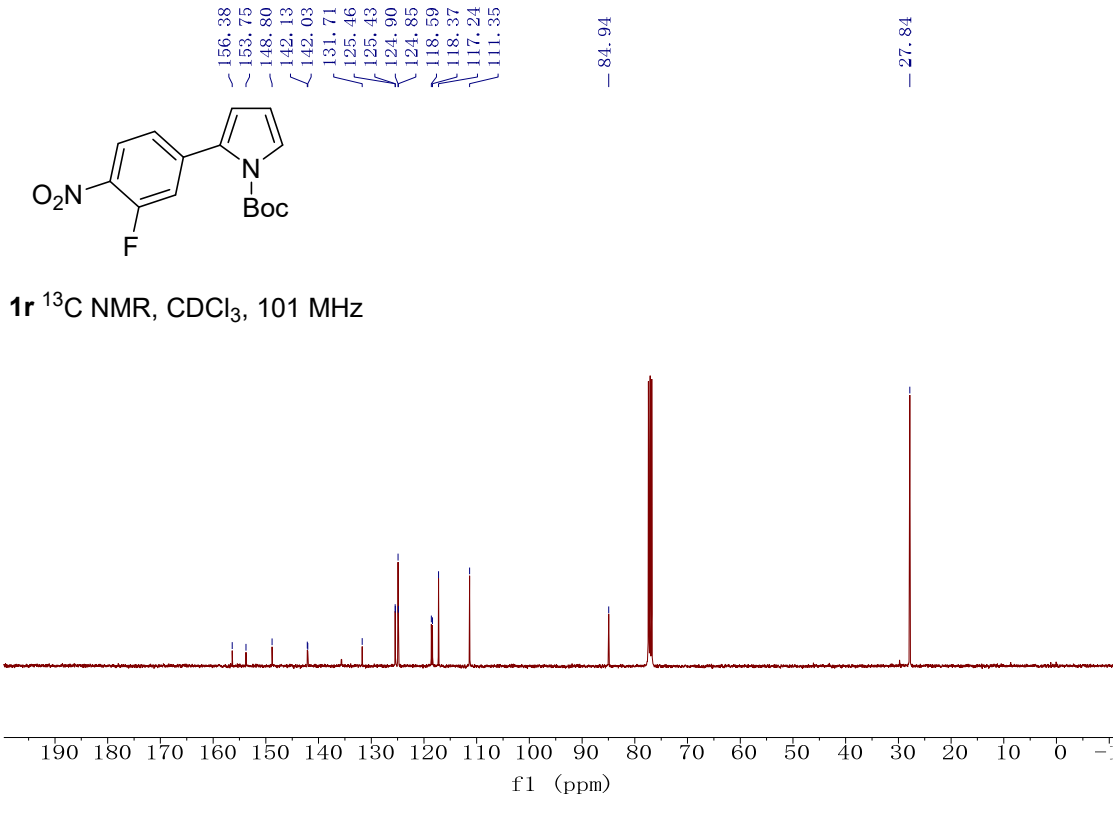
1q ^{1}H NMR, $CDCl_3$, 600 MHz



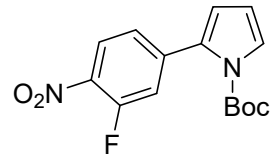
1q ^{13}C NMR, $CDCl_3$, 151 MHz



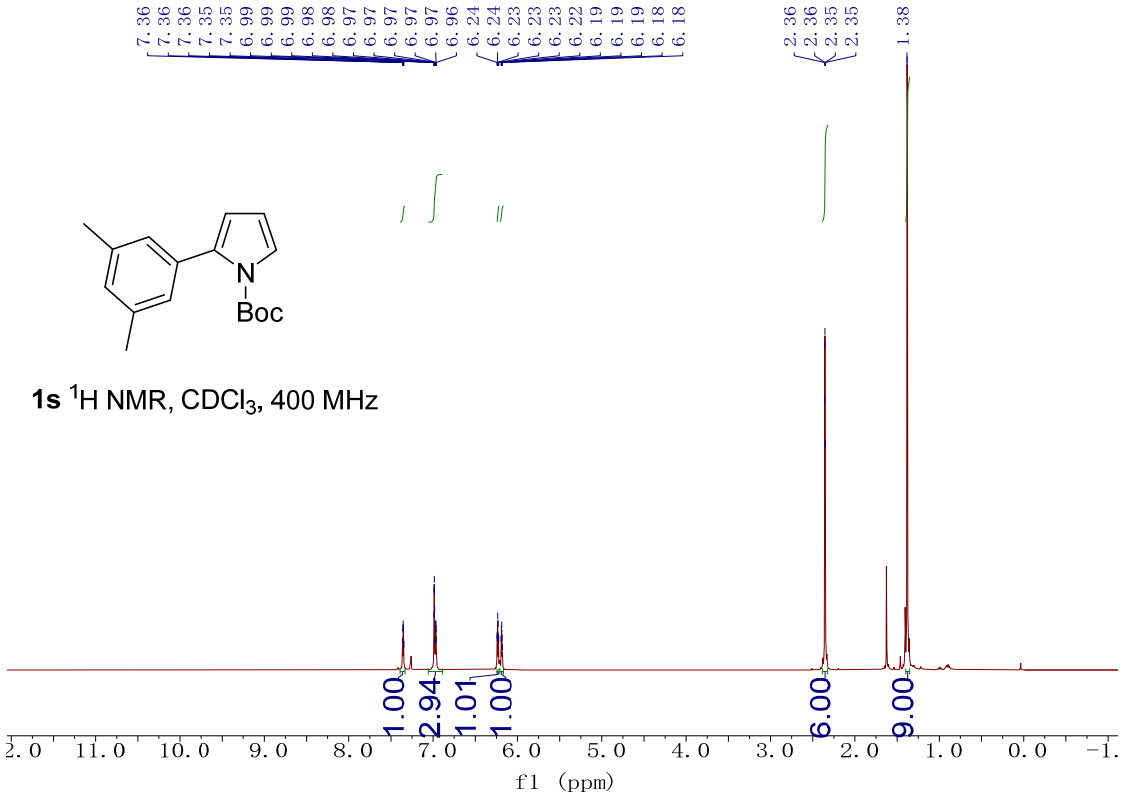
1r ^{1}H NMR, $CDCl_3$, 400 MHz



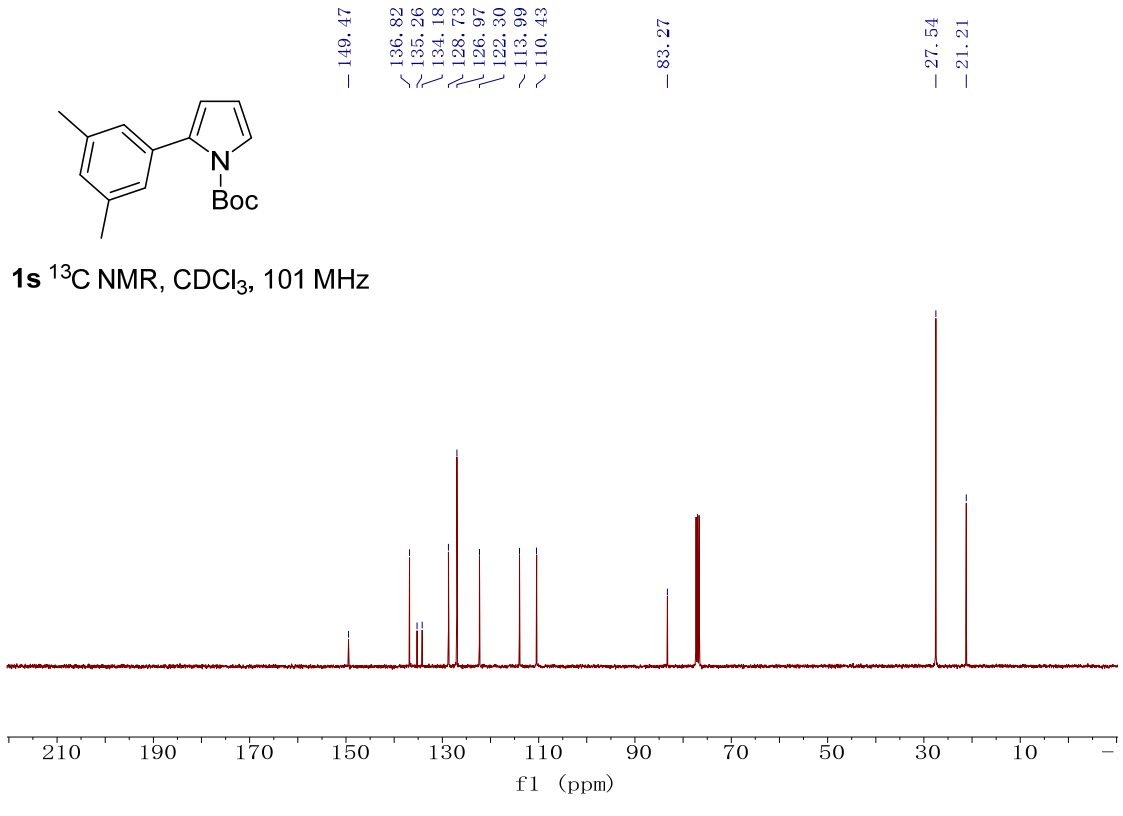
1r ^{13}C NMR, $CDCl_3$, 101 MHz



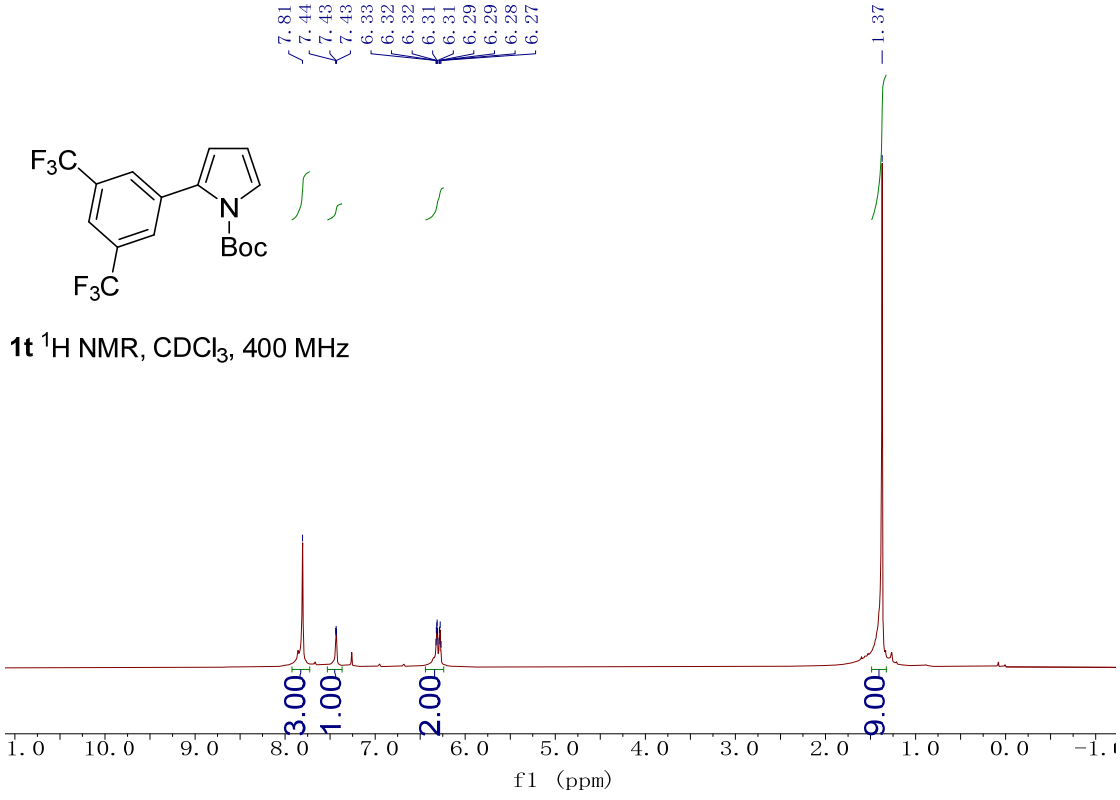
1r ^{19}F NMR, $CDCl_3$, 565MHz



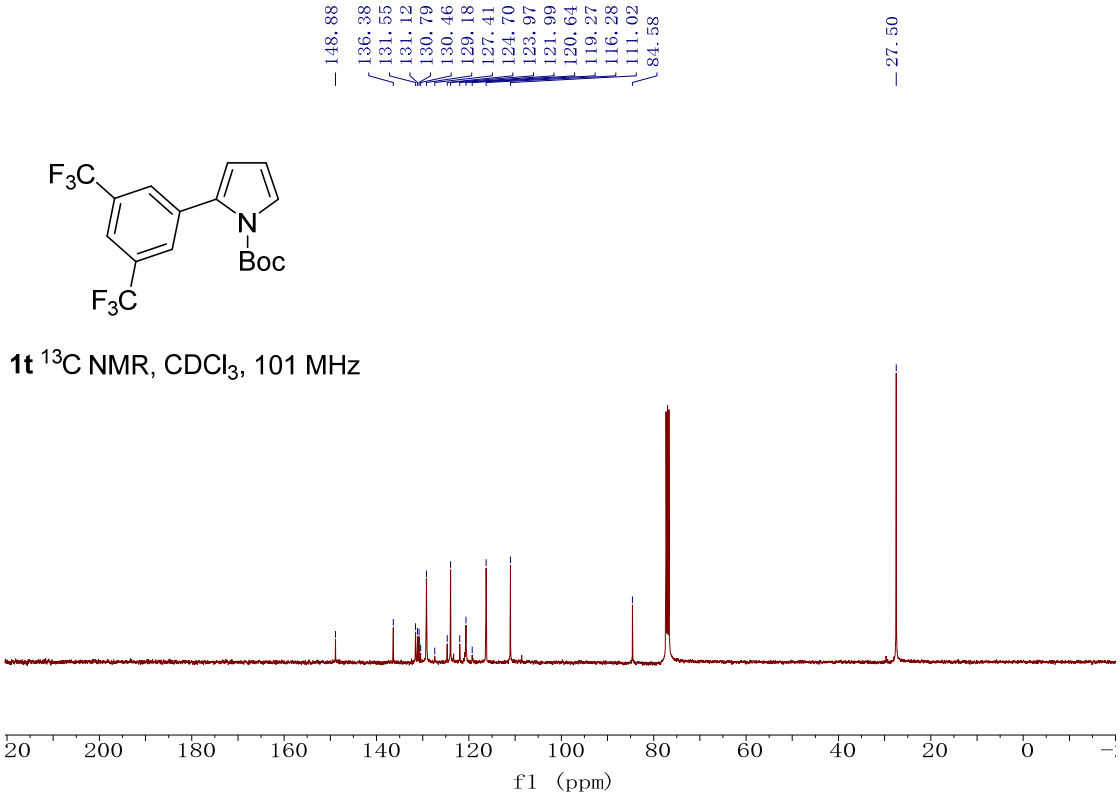
1s ^{1}H NMR, $CDCl_3$, 400 MHz



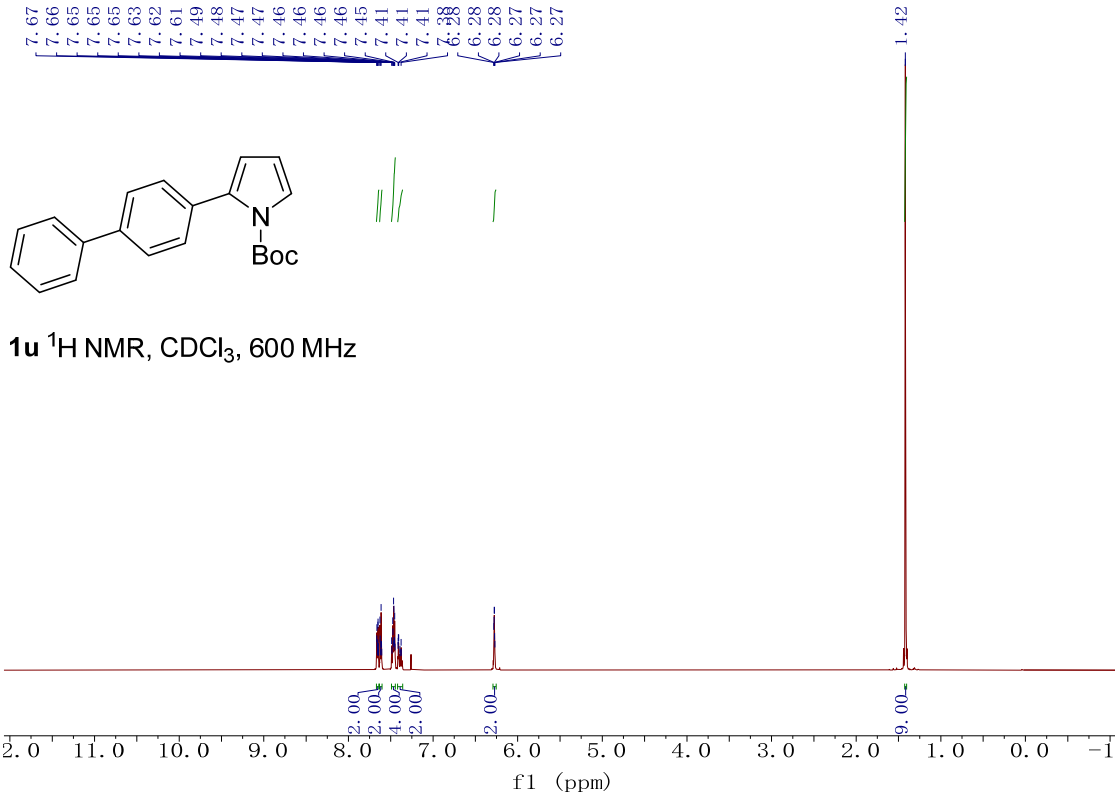
1s ^{13}C NMR, $CDCl_3$, 101 MHz



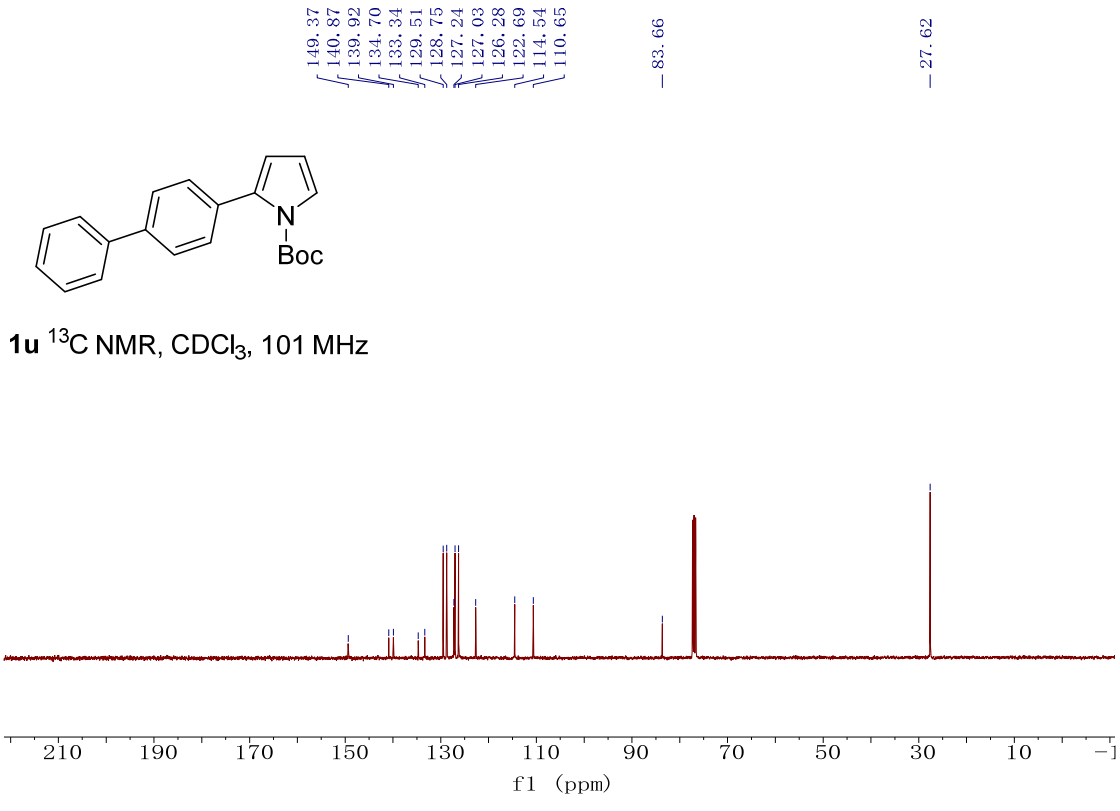
1t ^{1}H NMR, $CDCl_3$, 400 MHz



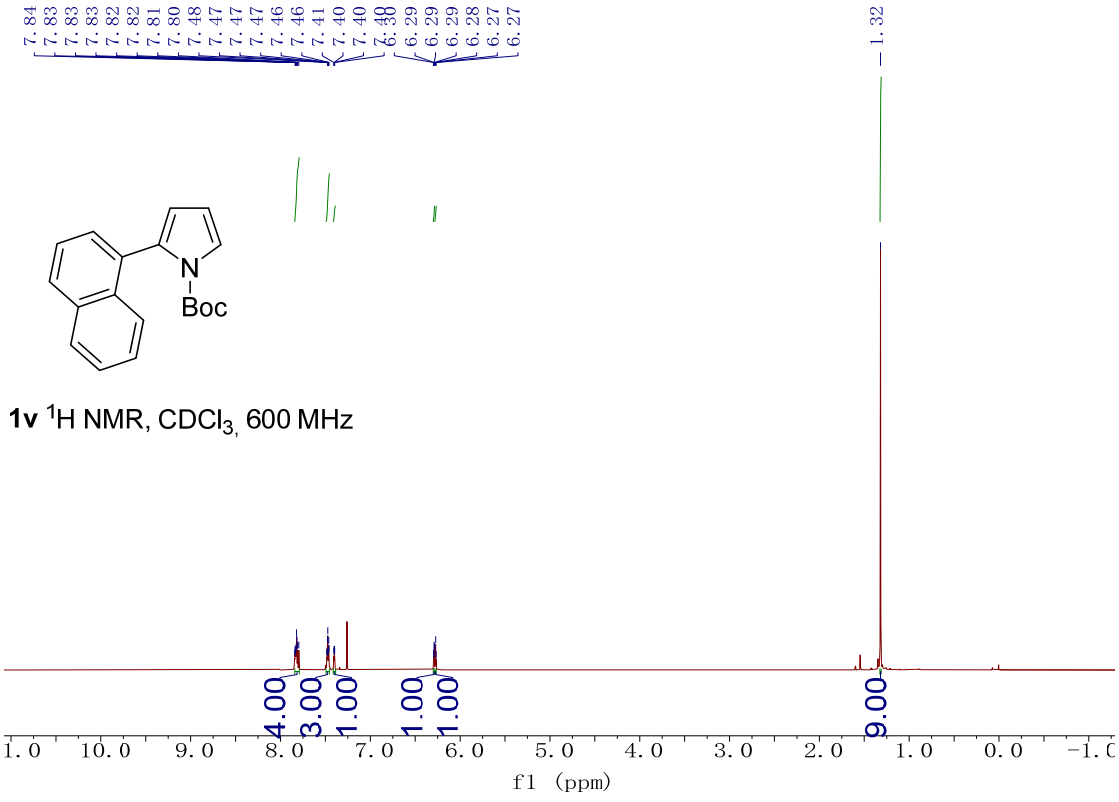
1t ^{13}C NMR, $CDCl_3$, 101 MHz



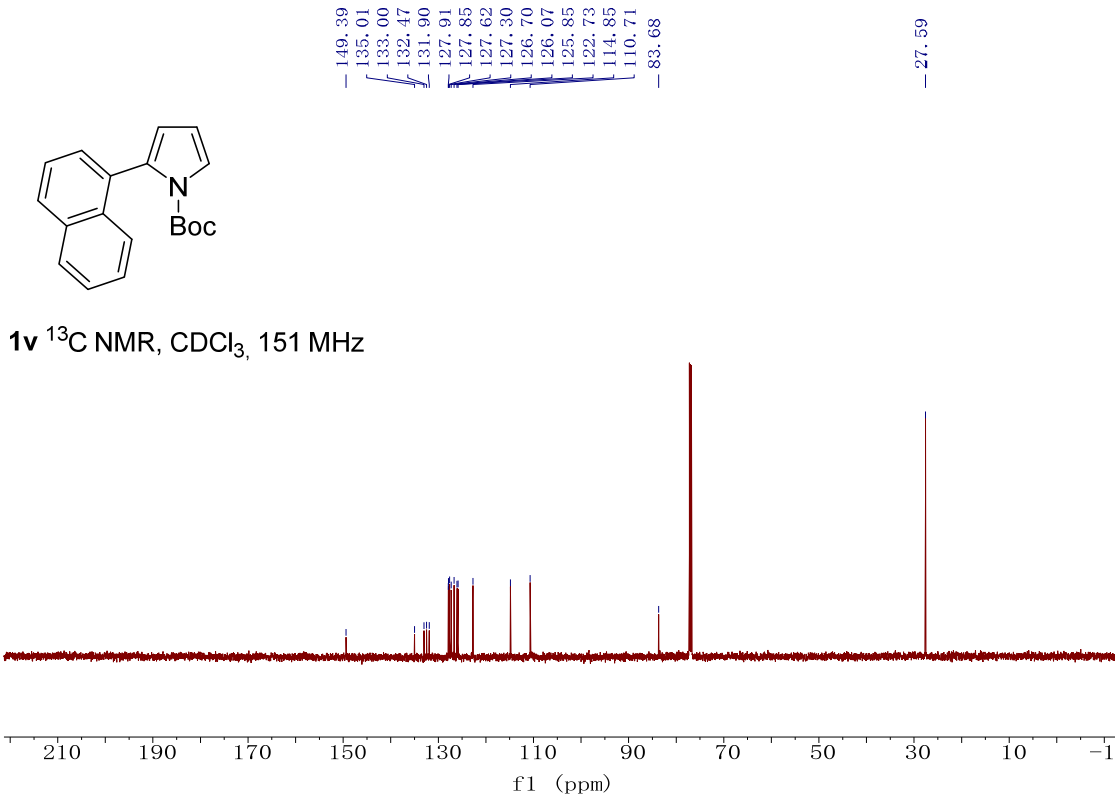
1u ^{1}H NMR, $CDCl_3$, 600 MHz



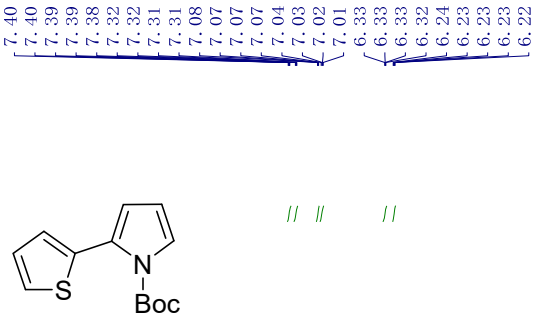
1u ^{13}C NMR, $CDCl_3$, 101 MHz



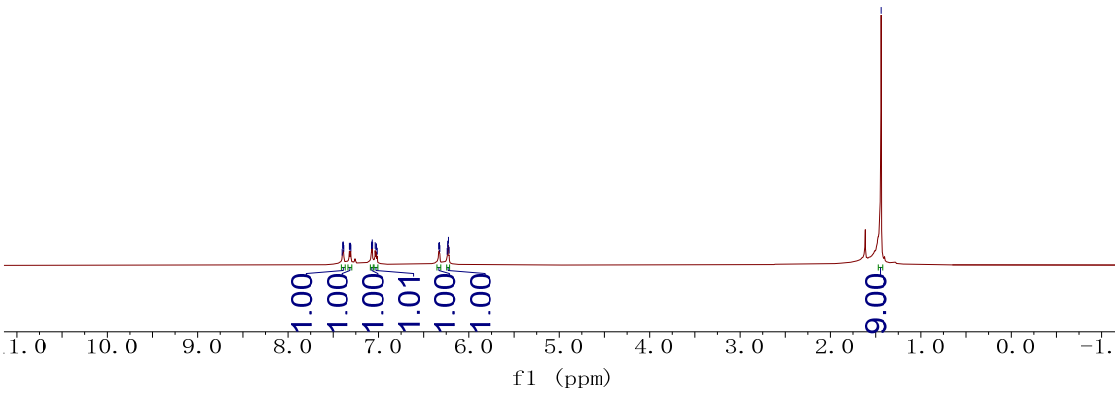
1v ^{1}H NMR, $CDCl_3$, 600 MHz

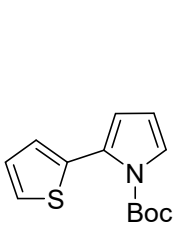


1v ^{13}C NMR, $CDCl_3$, 151 MHz

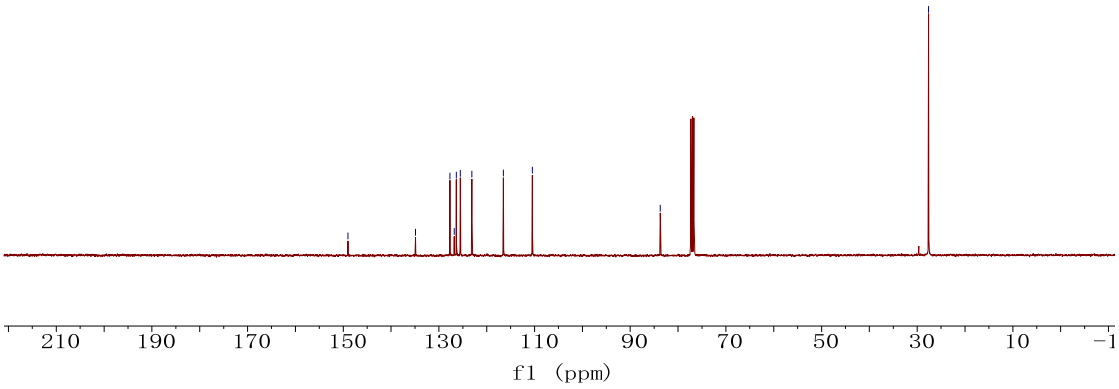


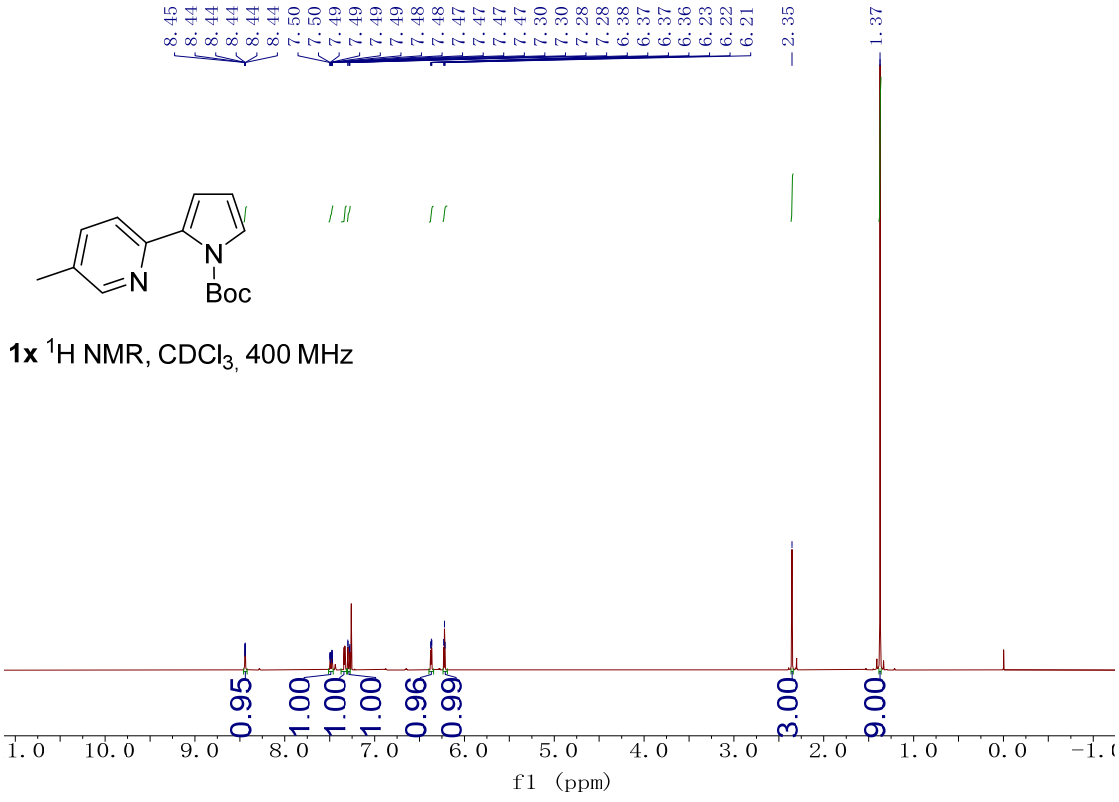
1w ^{1}H NMR, $CDCl_3$, 400 MHz



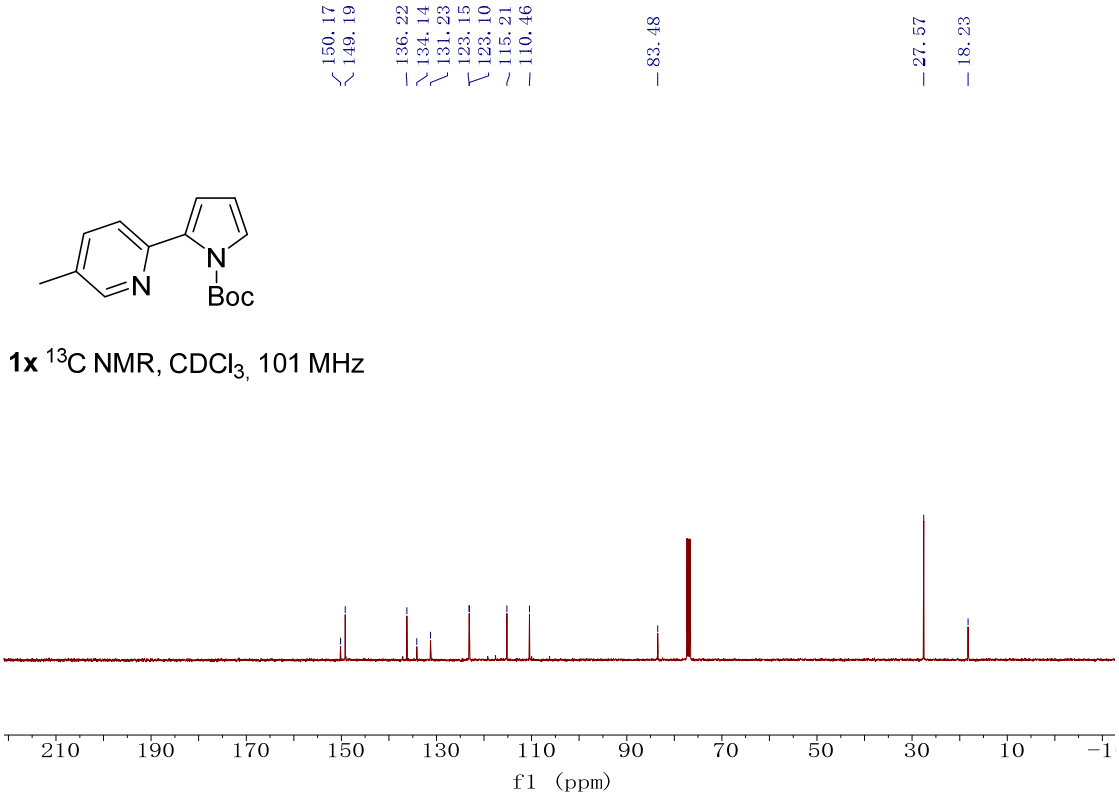


1w ^{13}C NMR, $CDCl_3$, 101 MHz

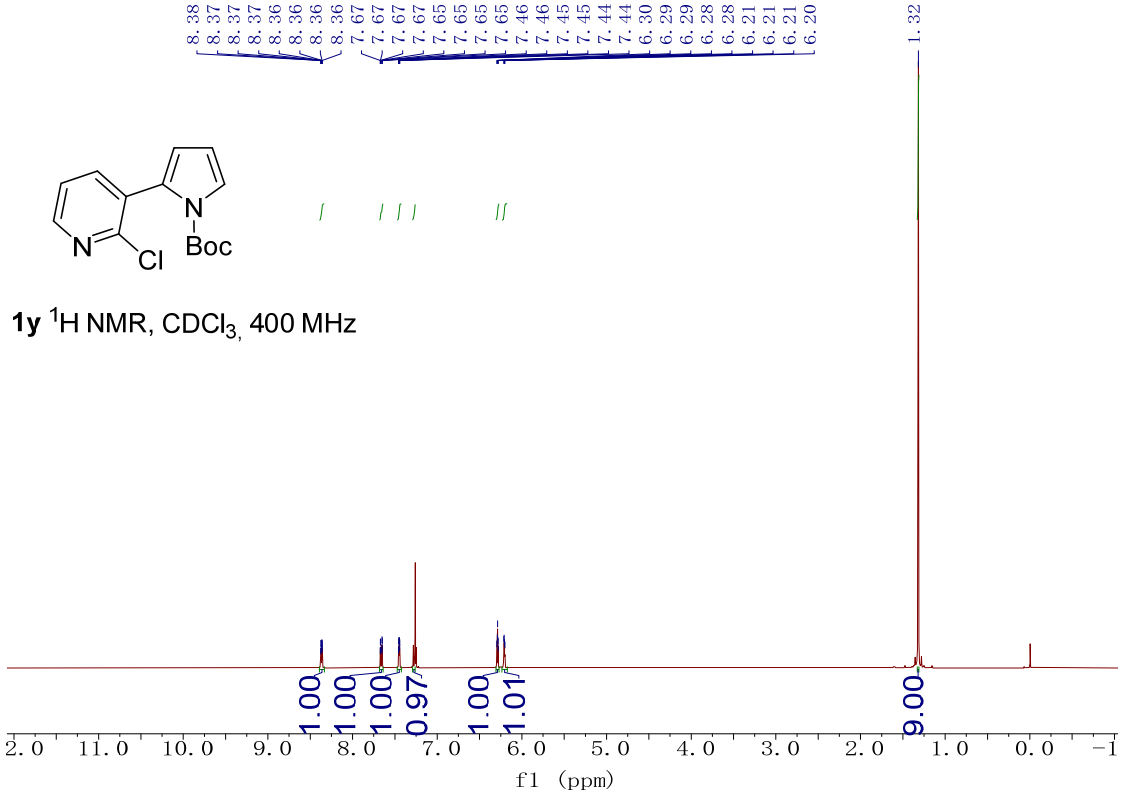




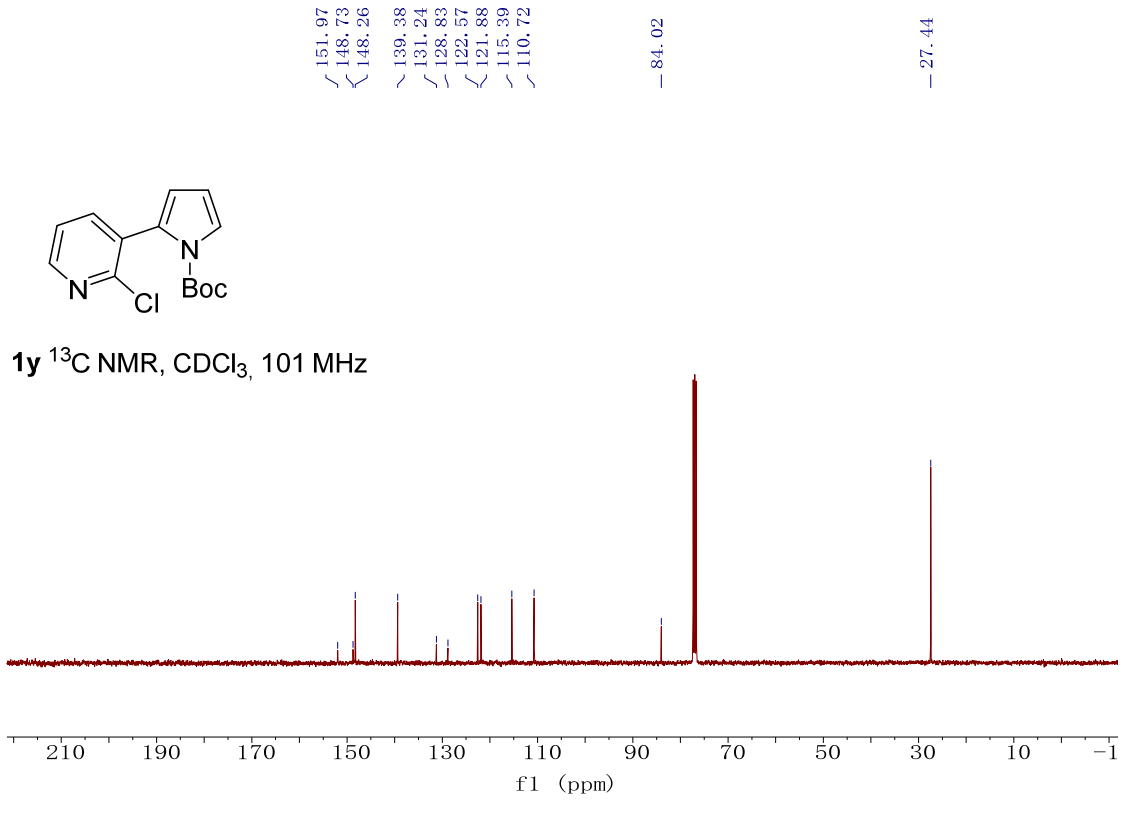
1x ^{1}H NMR, $CDCl_3$, 400 MHz



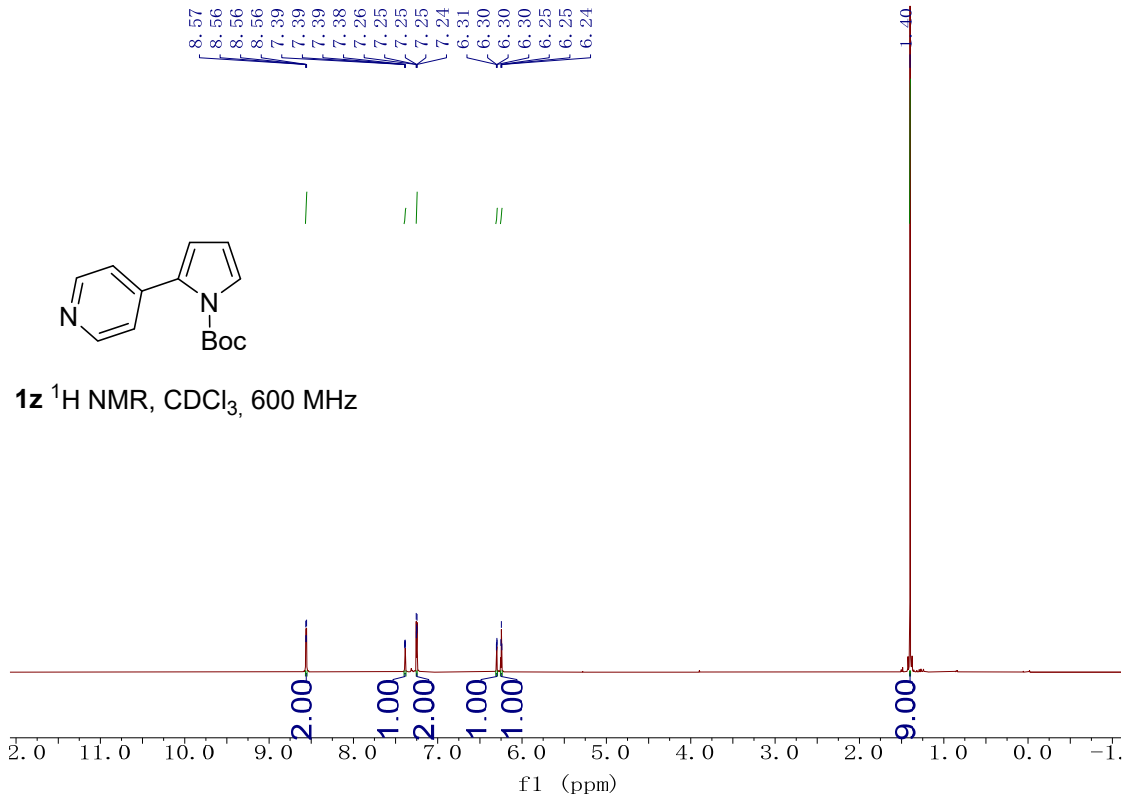
1x ^{13}C NMR, $CDCl_3$, 101 MHz



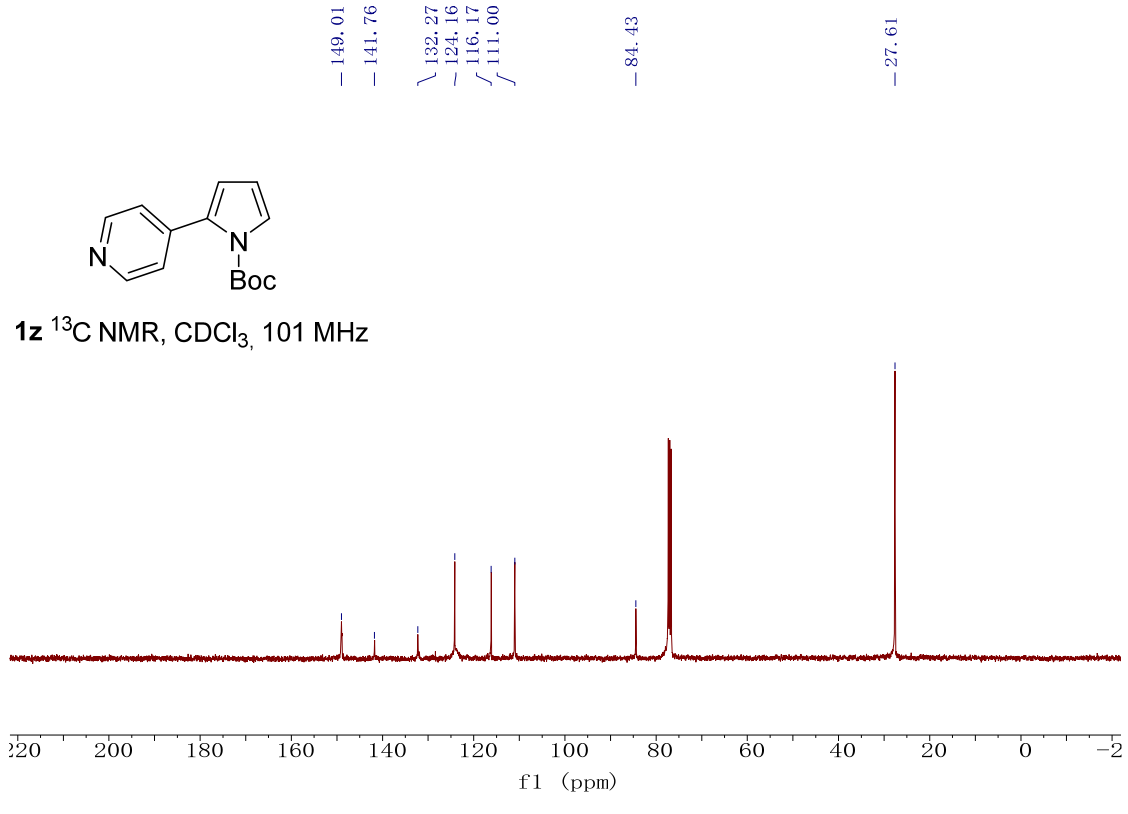
1y ^{1}H NMR, $CDCl_3$, 400 MHz



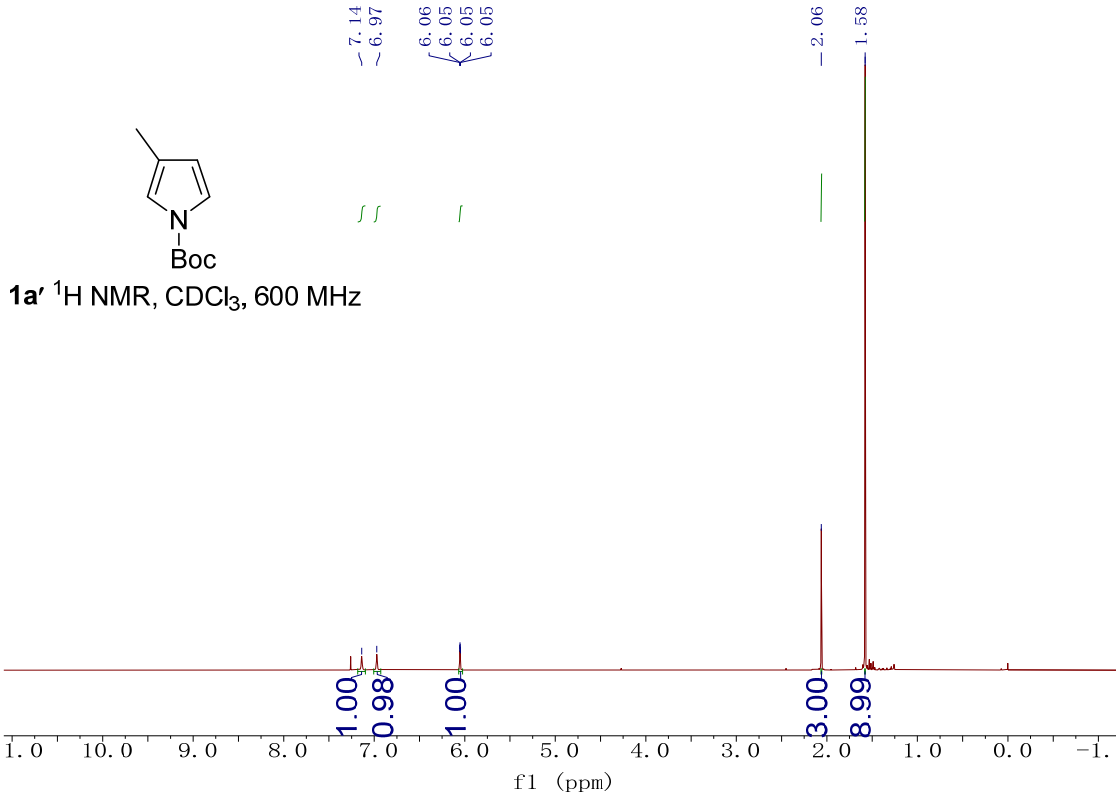
1y ^{13}C NMR, $CDCl_3$, 101 MHz



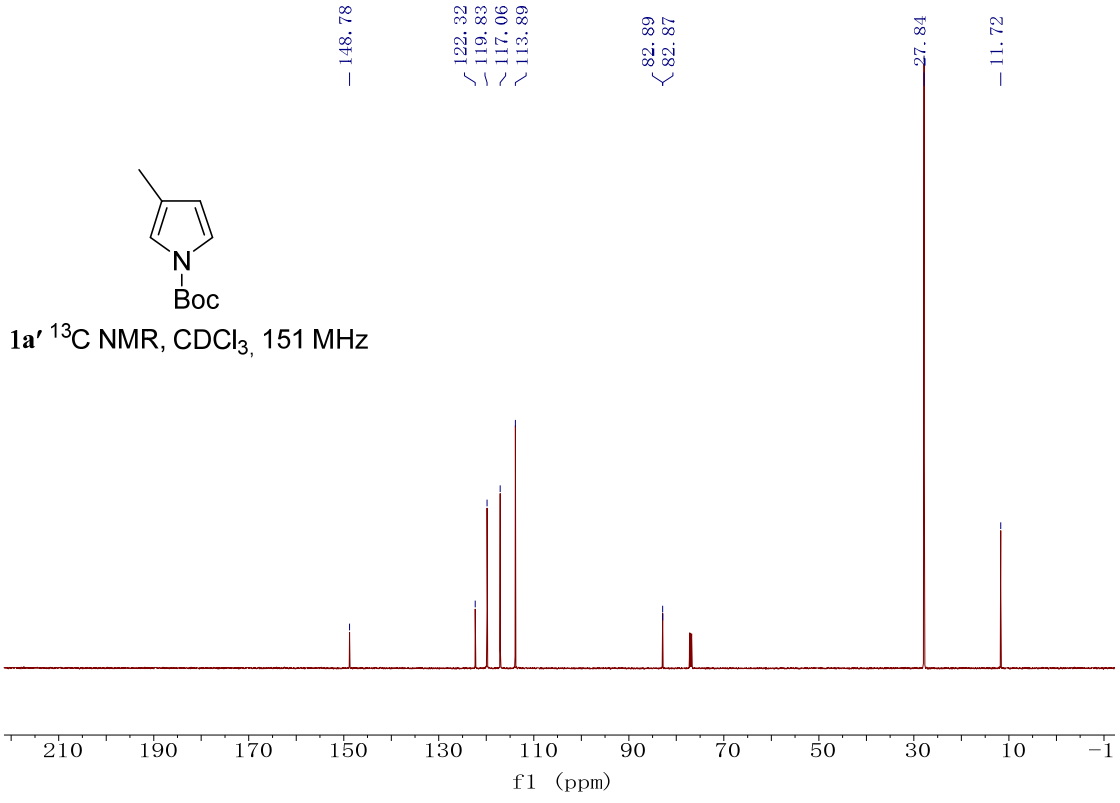
1z ^{1}H NMR, $CDCl_3$, 600 MHz



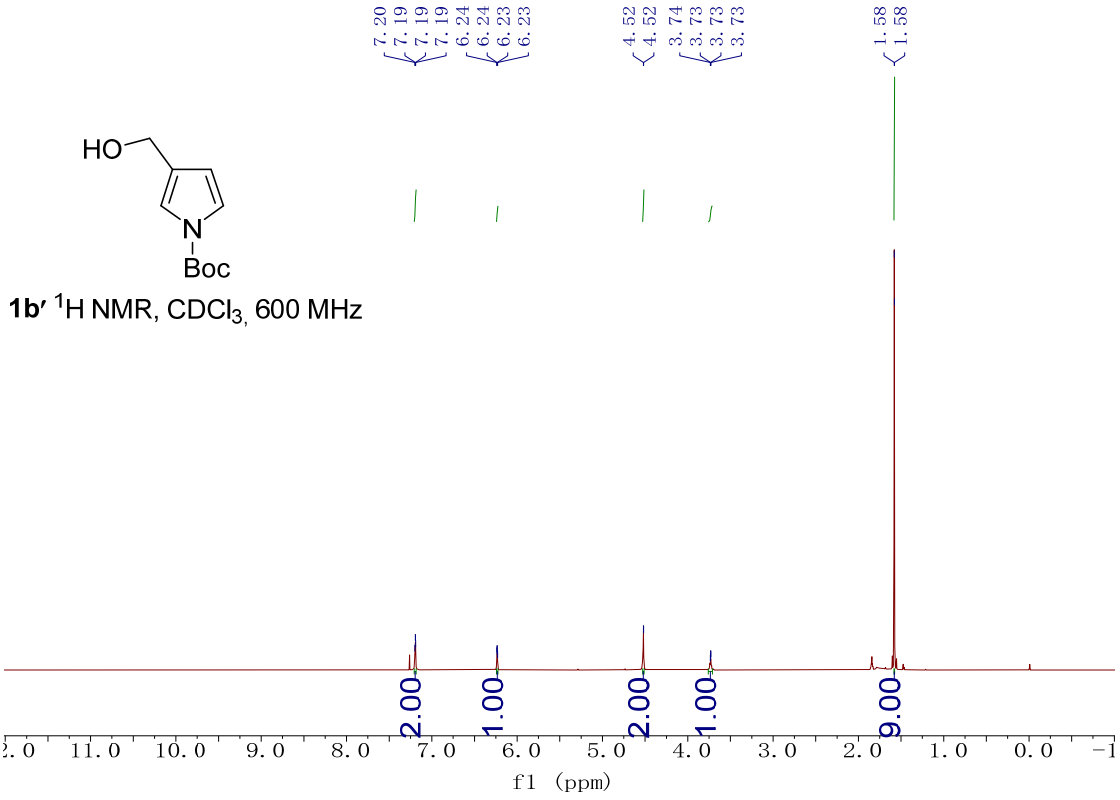
1z ^{13}C NMR, $CDCl_3$, 101 MHz



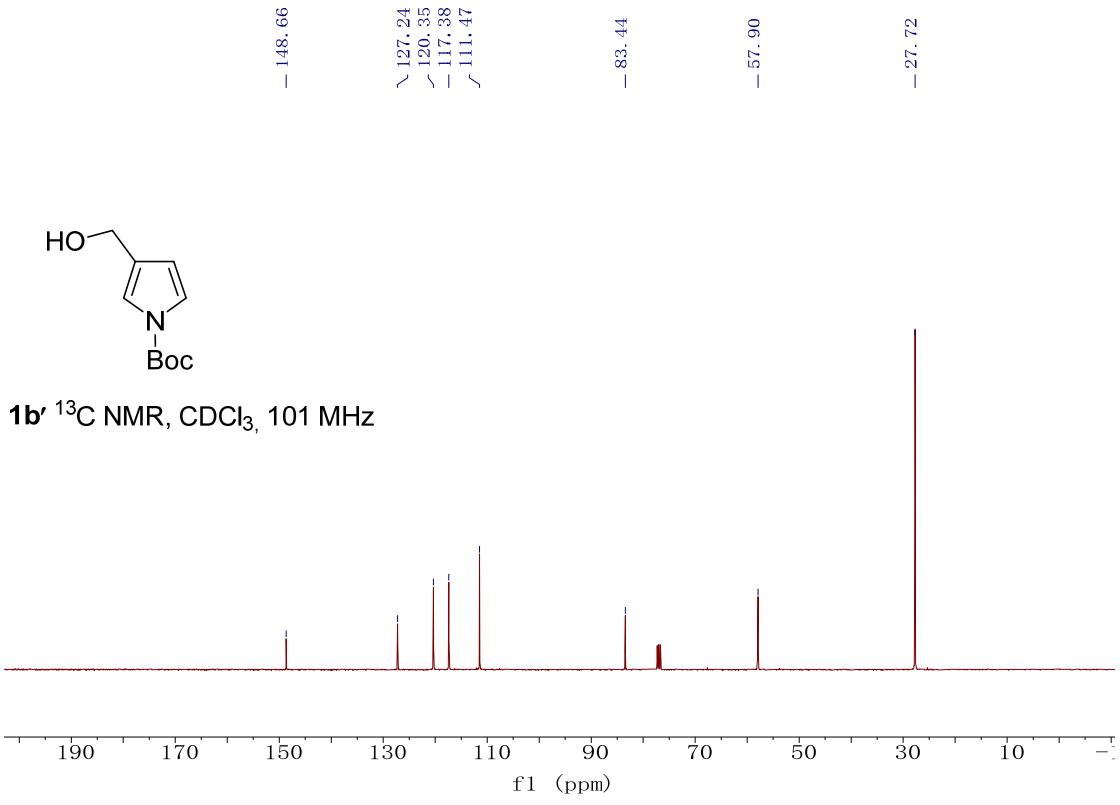
1a′ ^{1}H NMR, $CDCl_3$, 600 MHz



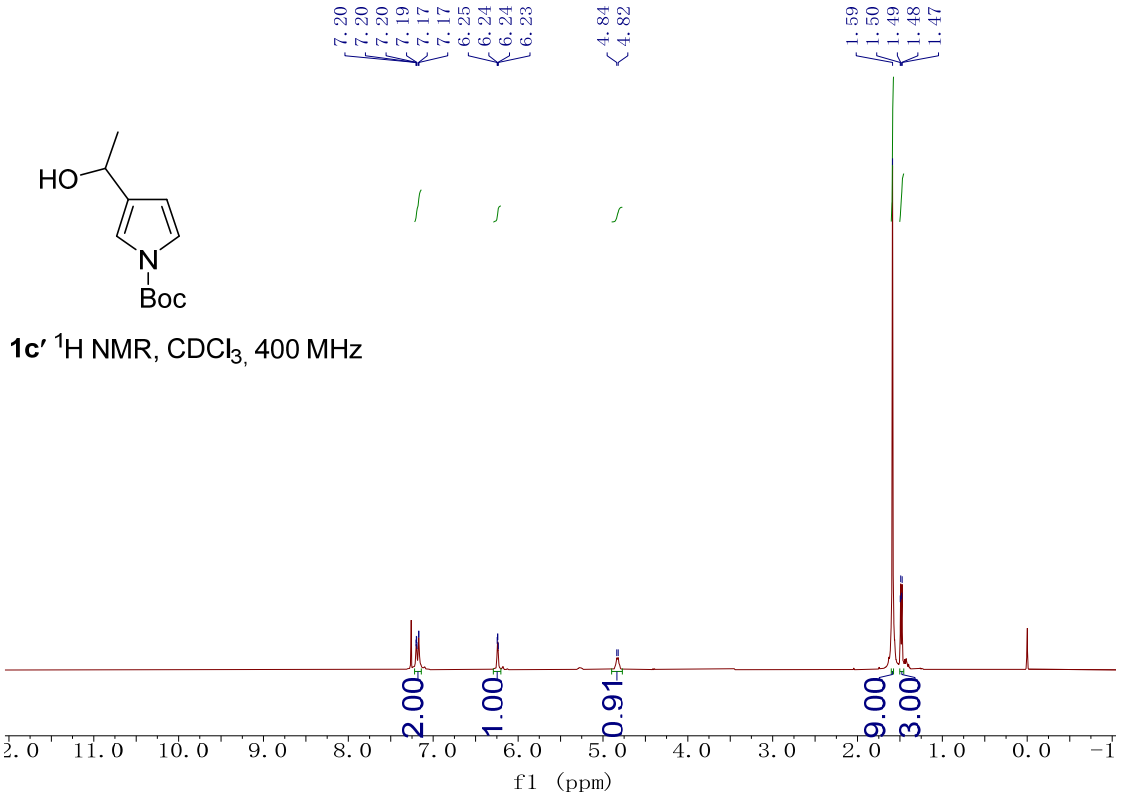
1a′ ^{13}C NMR, $CDCl_3$, 151 MHz



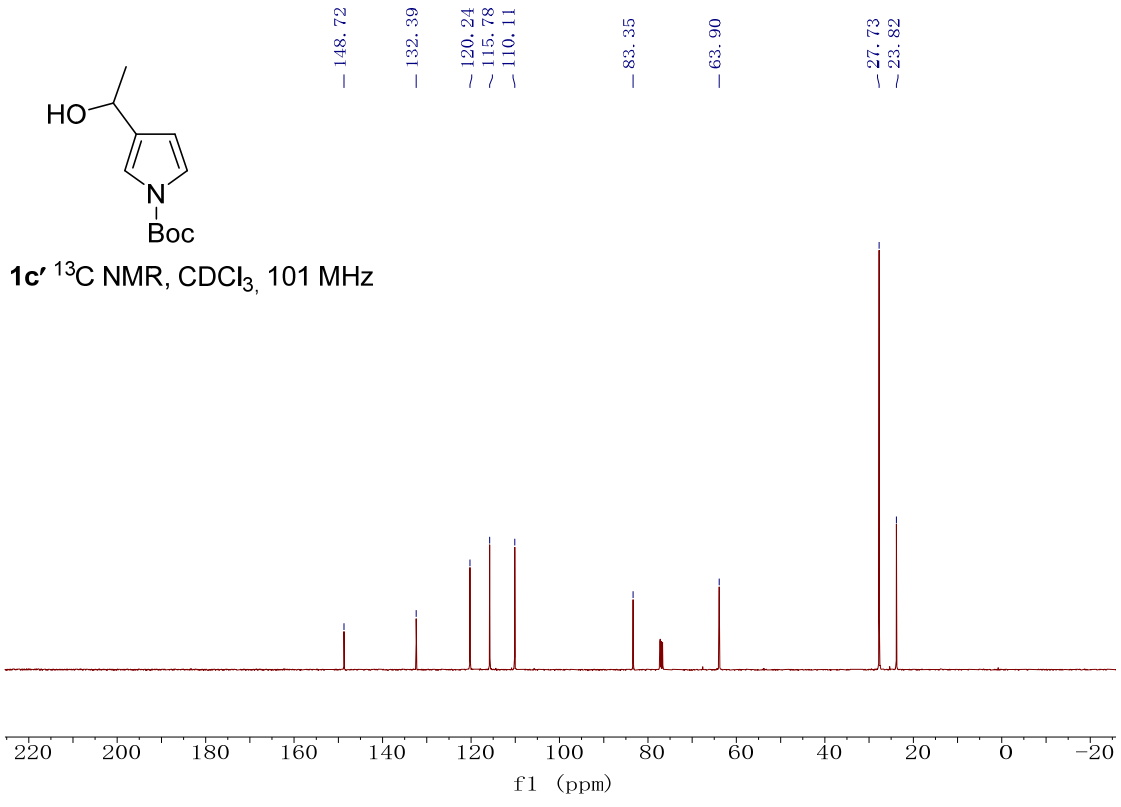
1b′ ^{1}H NMR, $CDCl_3$, 600 MHz



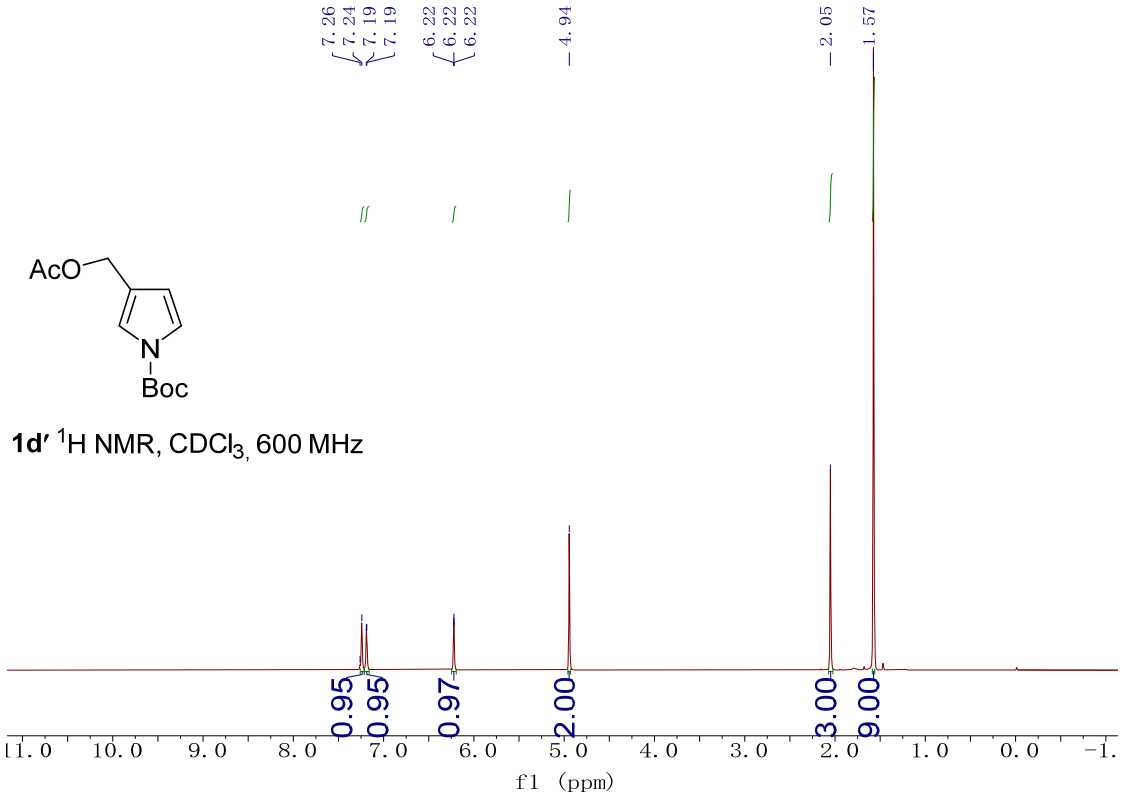
1b′ ^{13}C NMR, $CDCl_3$, 101 MHz



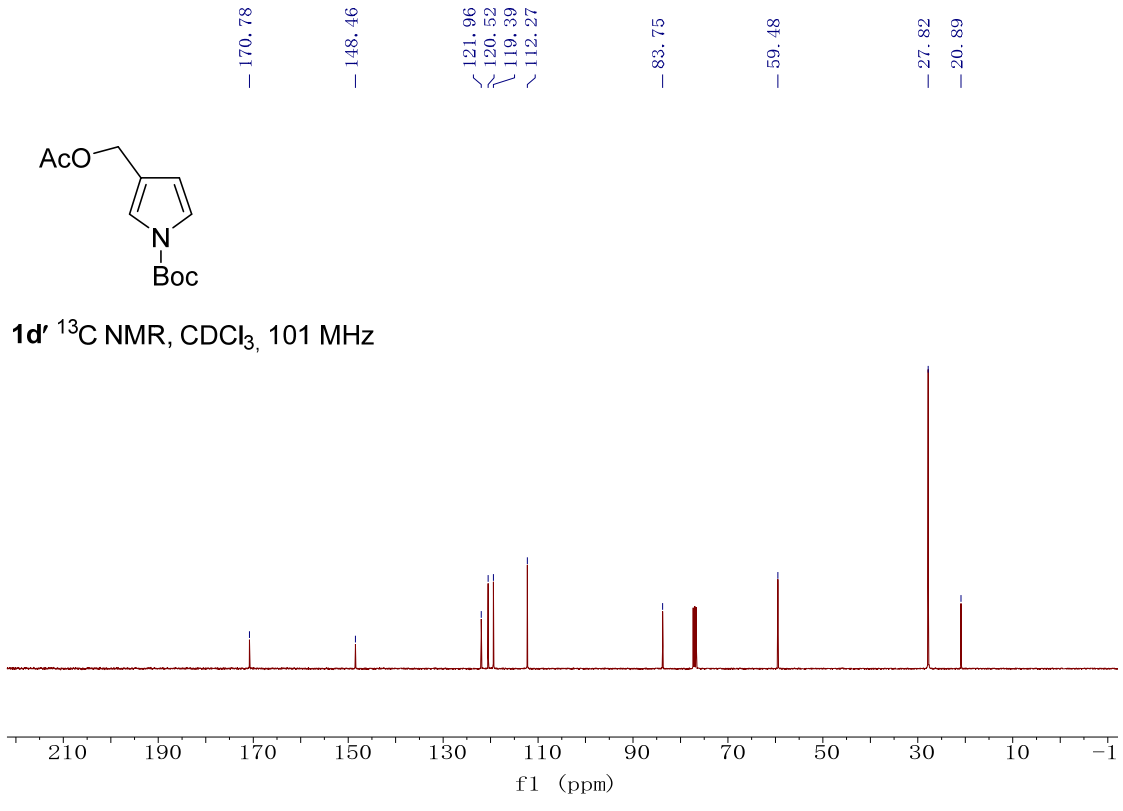
1c′ ^{1}H NMR, $CDCl_3$, 400 MHz



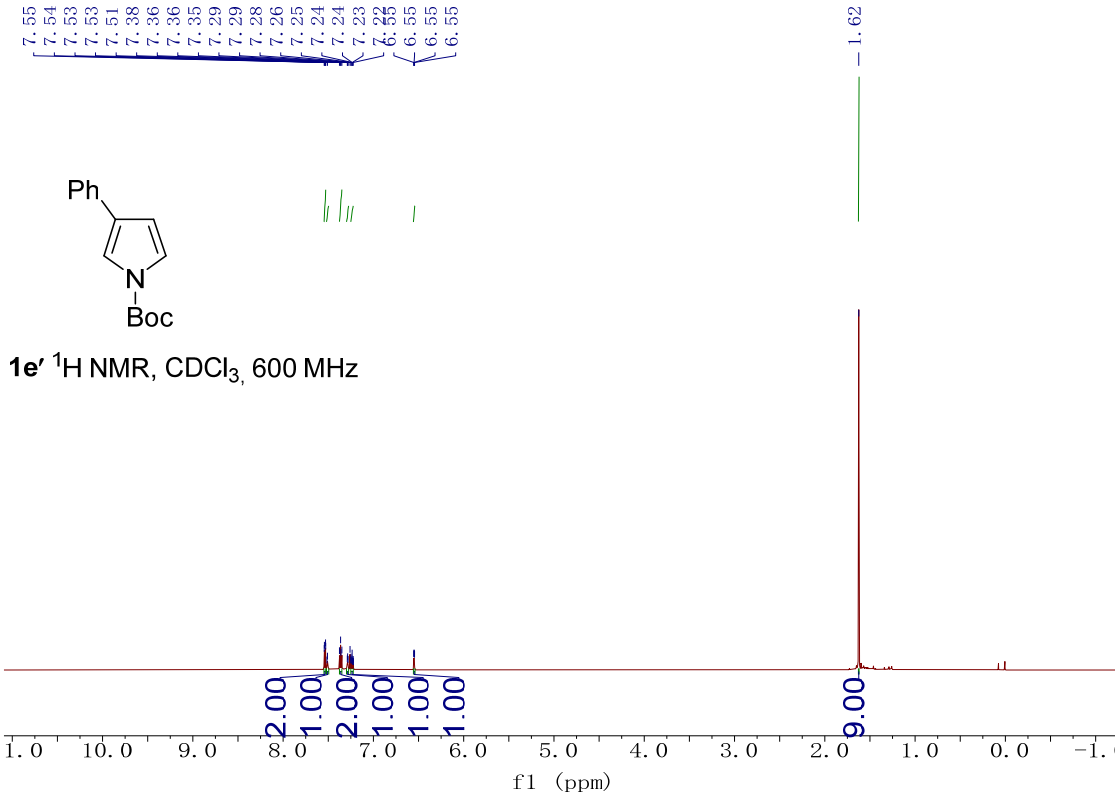
1c′ ^{13}C NMR, $CDCl_3$, 101 MHz



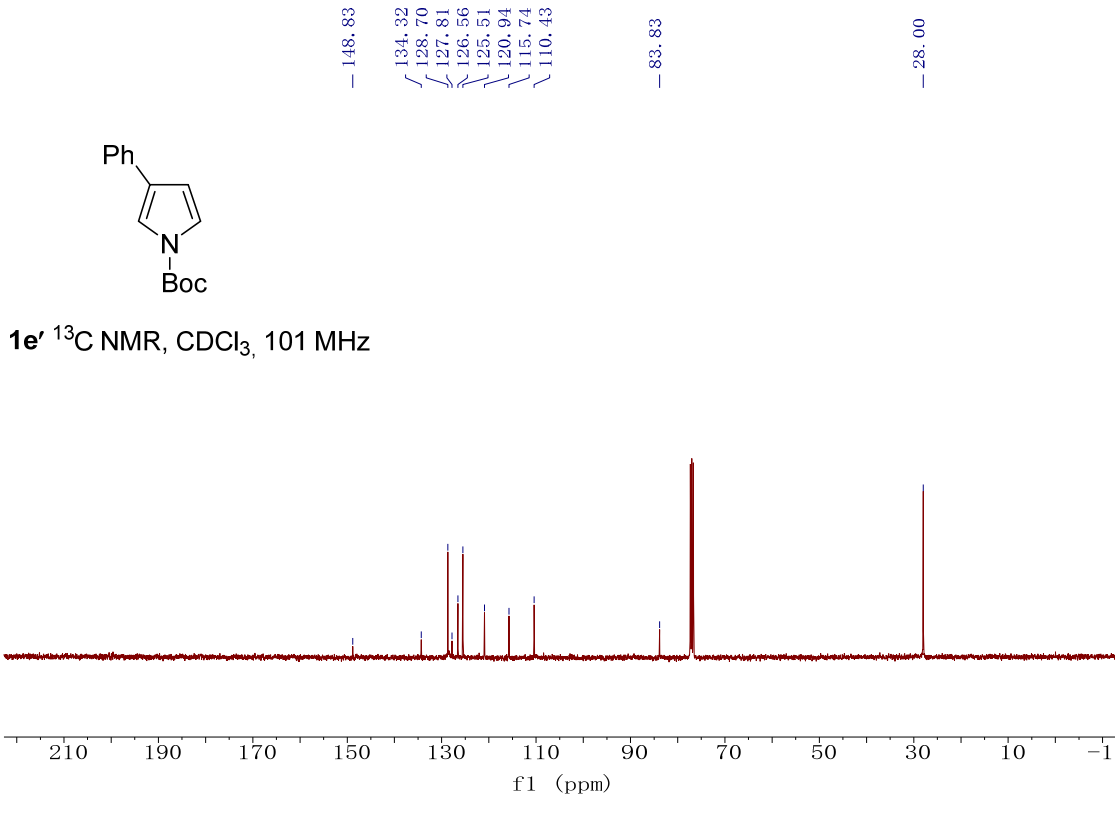
1d′ ^{1}H NMR, $CDCl_3$, 600 MHz



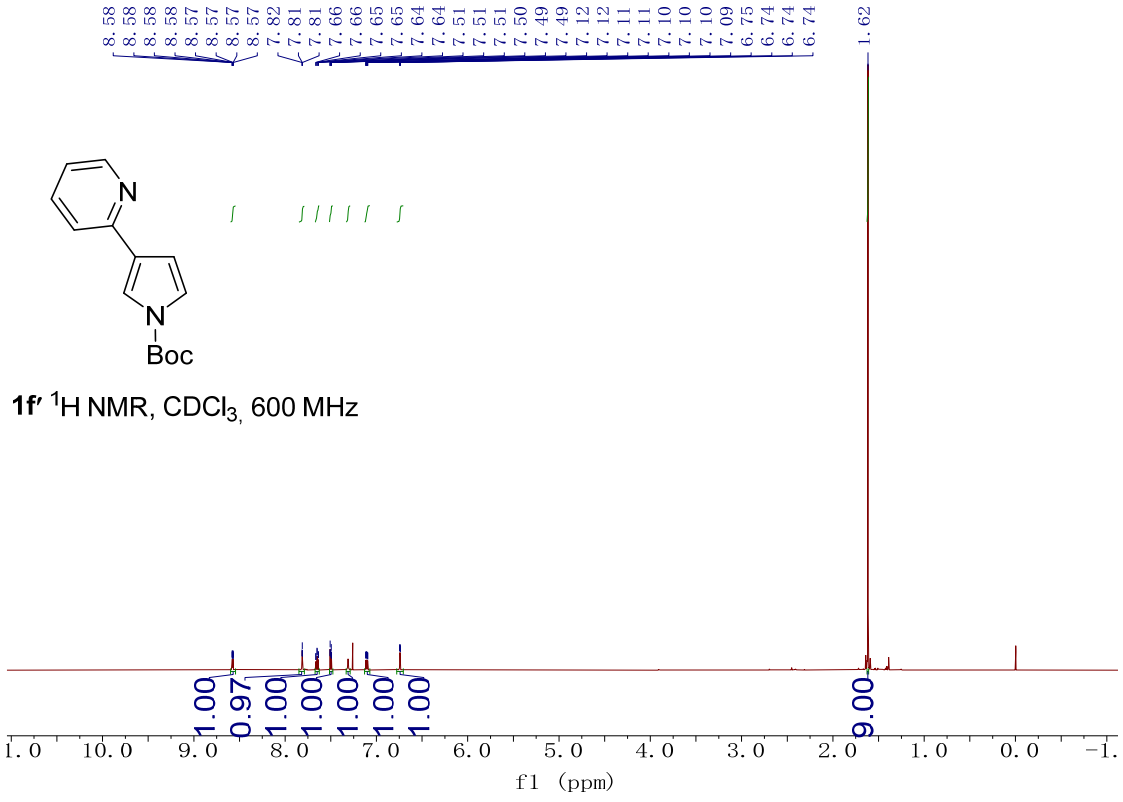
1d′ ^{13}C NMR, $CDCl_3$, 101 MHz



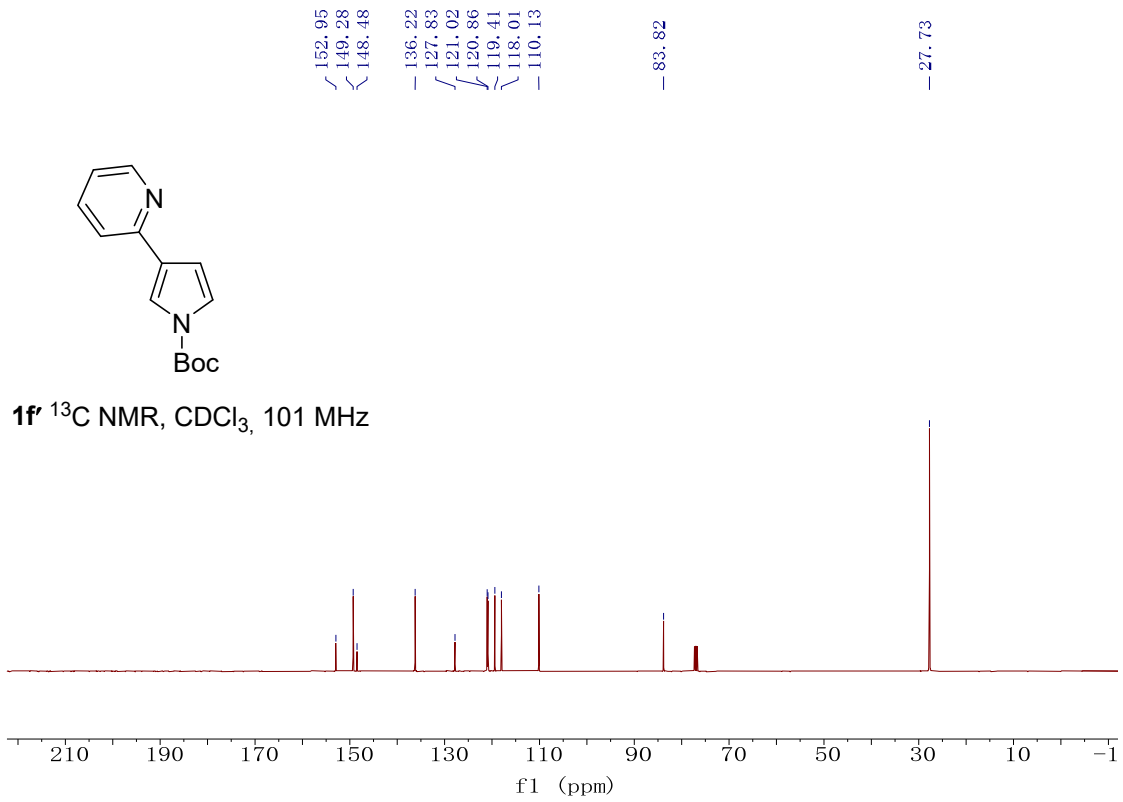
1e′ ^{1}H NMR, $CDCl_3$, 600 MHz



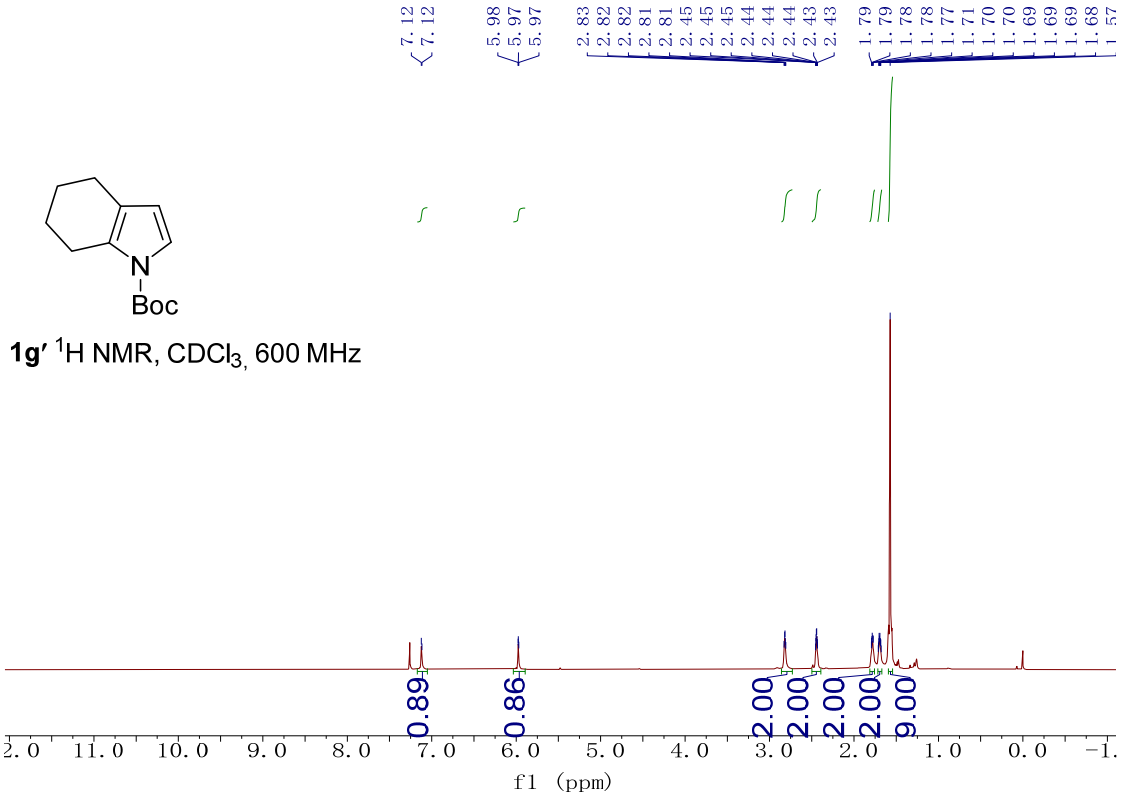
1e′ ^{13}C NMR, $CDCl_3$, 101 MHz



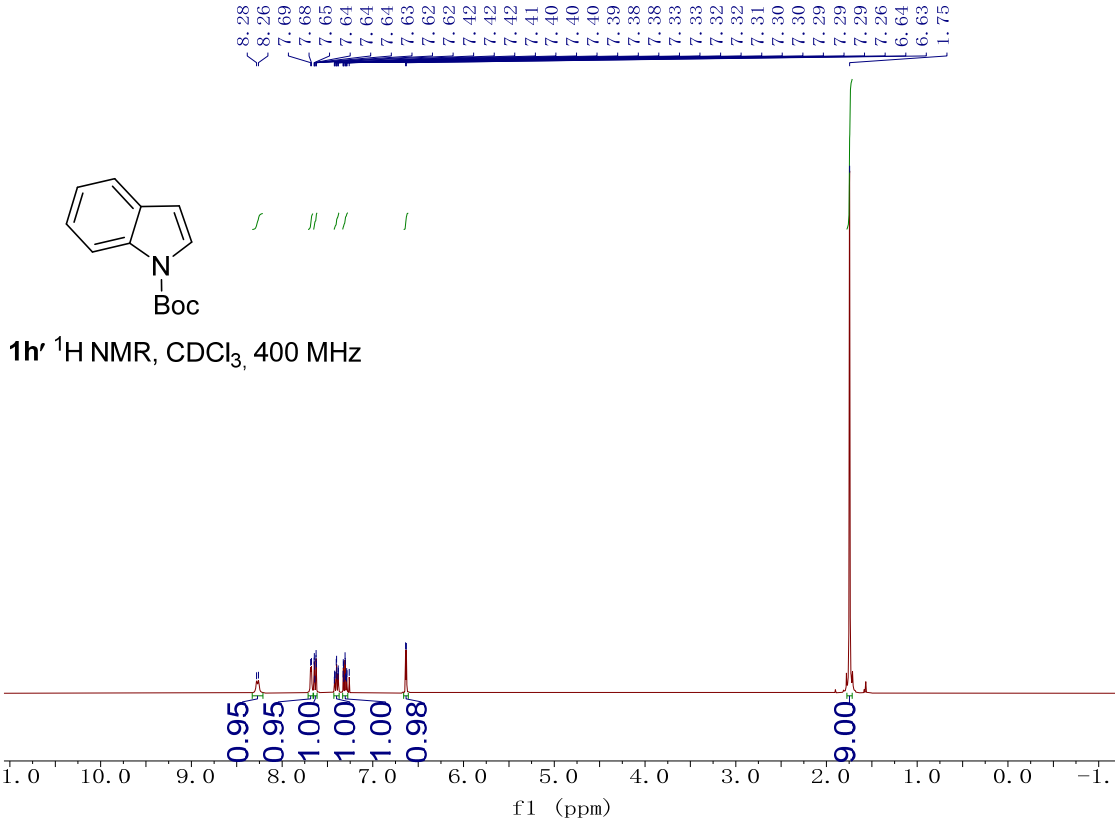
1f′ ^{1}H NMR, $CDCl_3$, 600 MHz



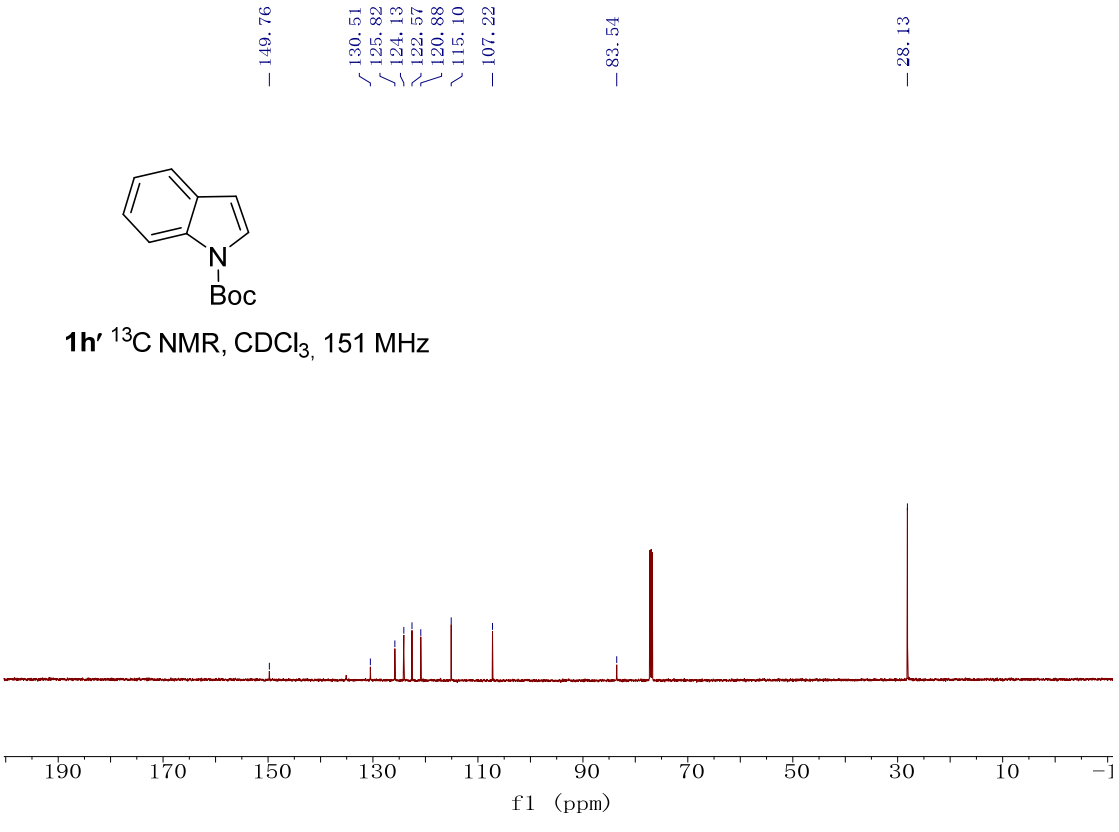
1f′ ^{13}C NMR, $CDCl_3$, 101 MHz



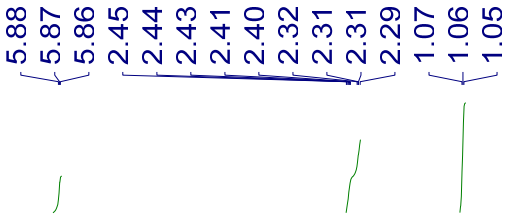
1g′ ^{1}H NMR, $CDCl_3$, 600 MHz

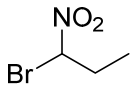


1h′ ^{1}H NMR, $CDCl_3$, 400 MHz

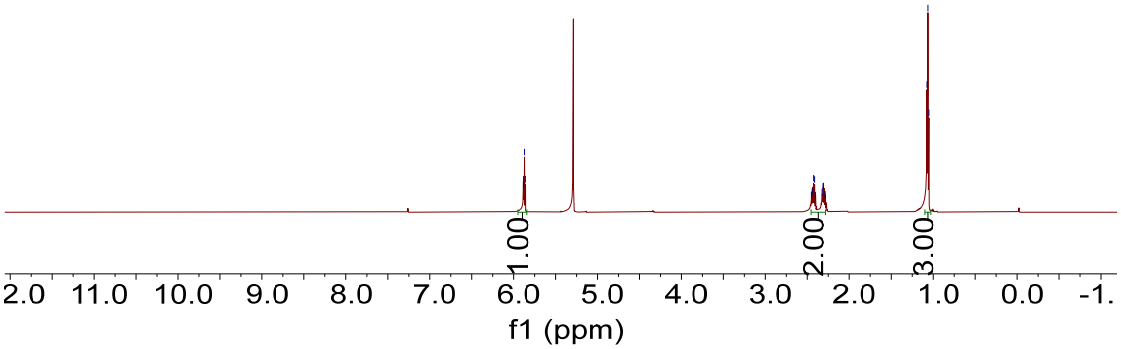


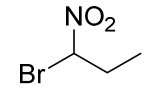
1h′ ^{13}C NMR, $CDCl_3$, 151 MHz



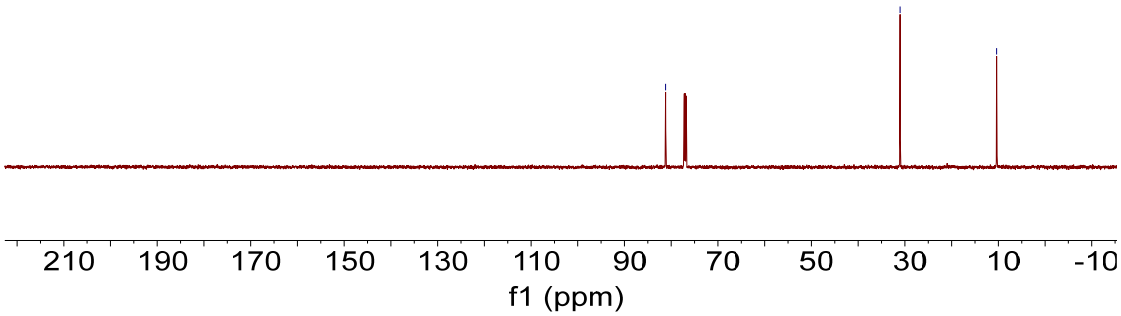


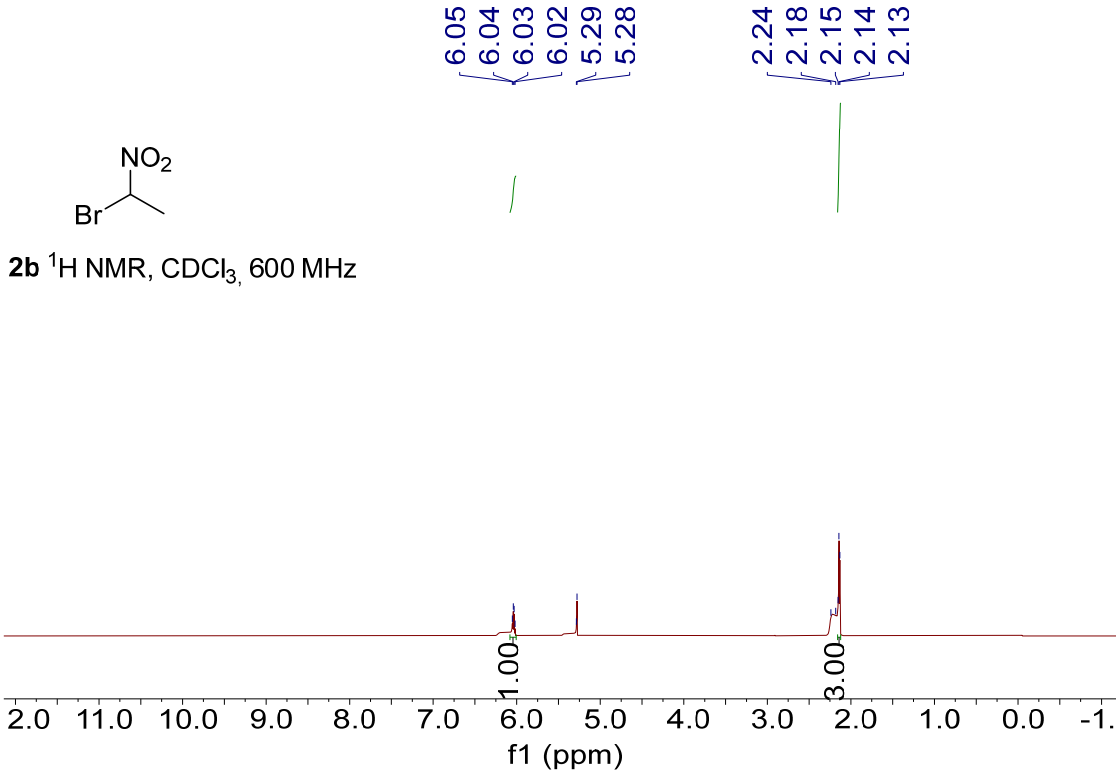
2a ^{1}H NMR, $CDCl_3$, 600 MHz



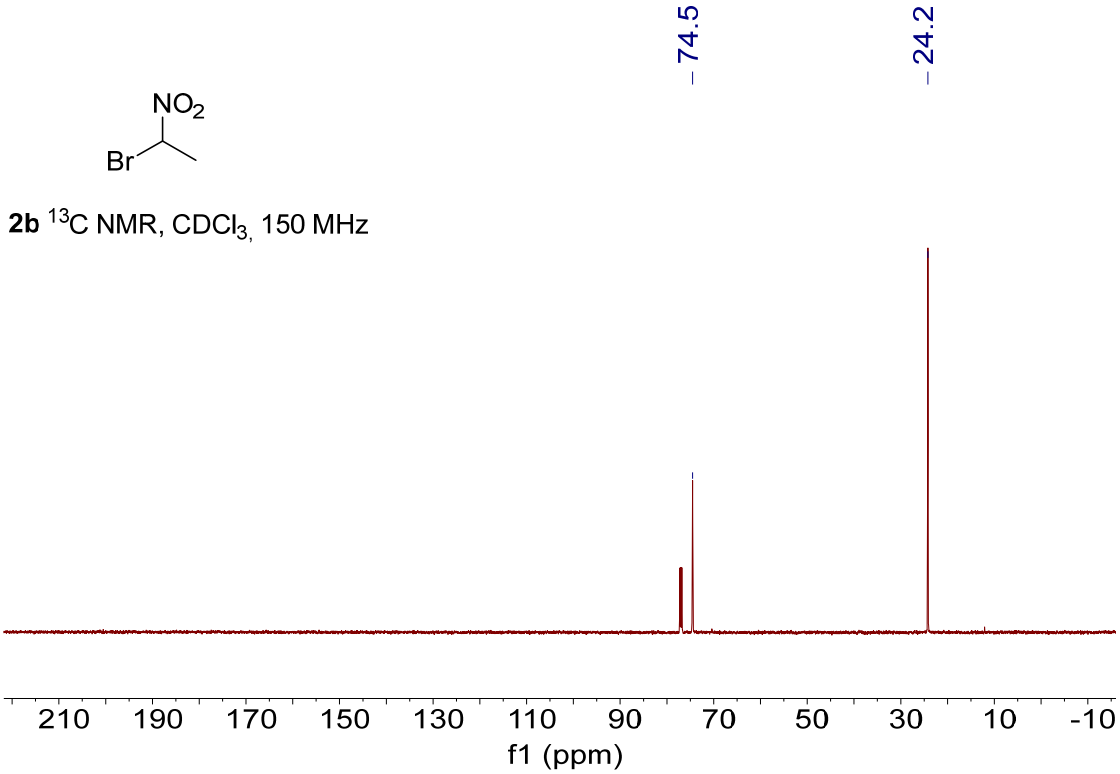


2a ^{13}C NMR, $CDCl_3$, 150 MHz

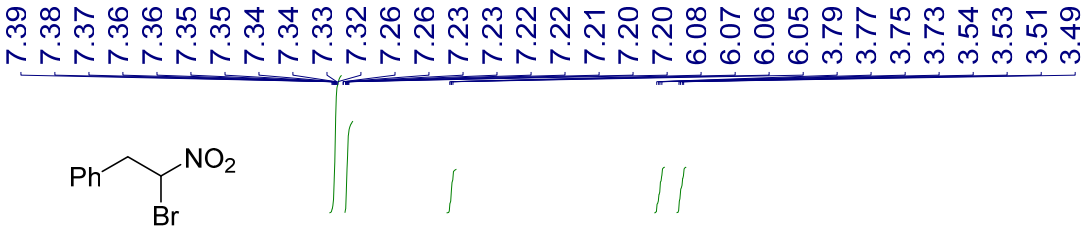




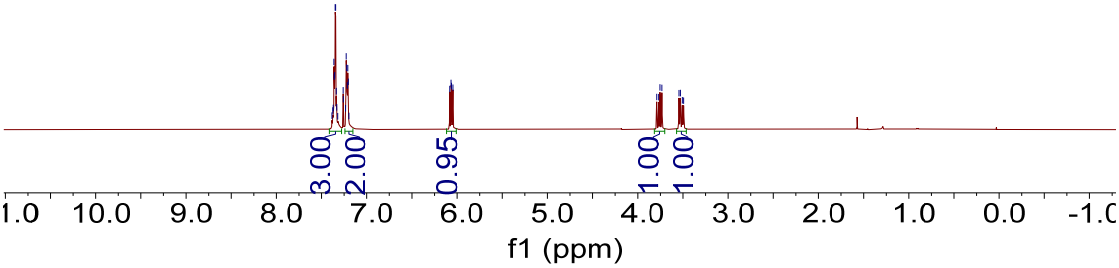
2b ^{1}H NMR, $CDCl_3$, 600 MHz

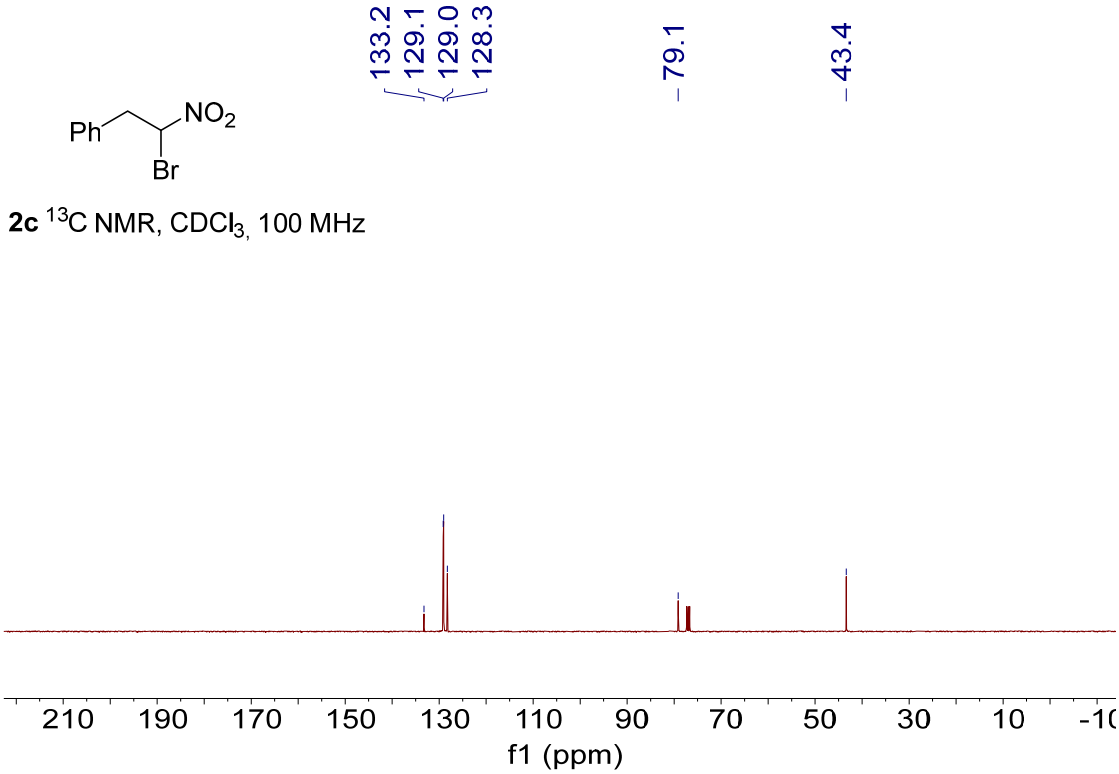


2b ^{13}C NMR, $CDCl_3$, 150 MHz

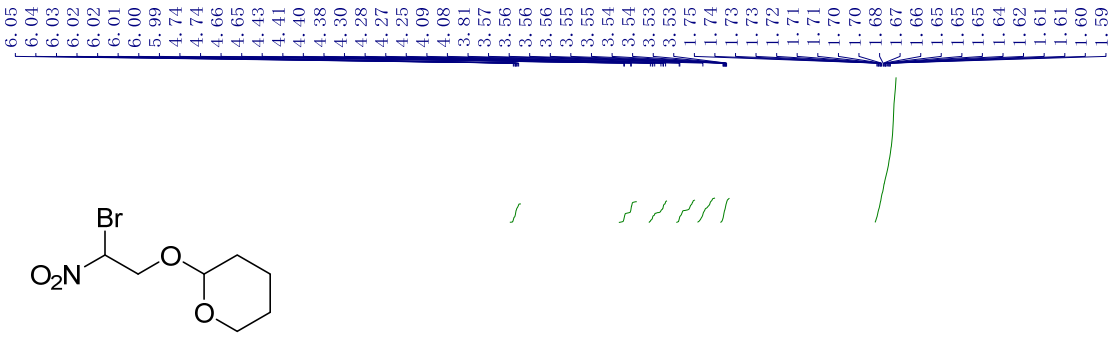


2c ^{1}H NMR, $CDCl_3$, 400 MHz

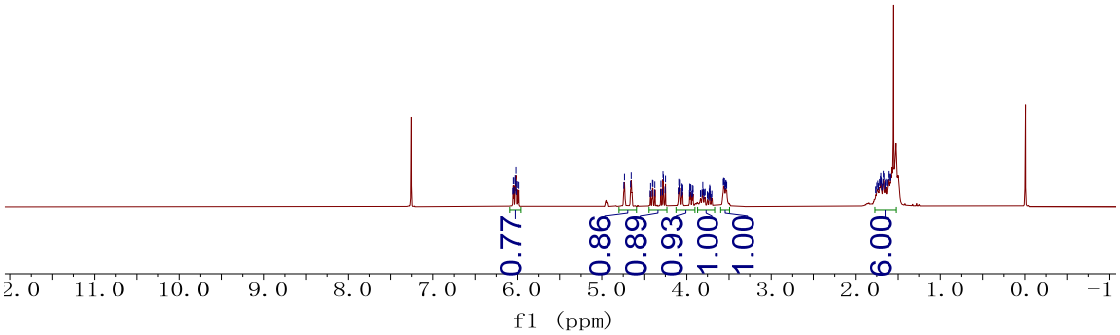


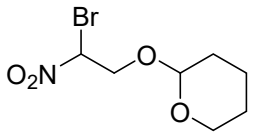


2c ^{13}C NMR, $CDCl_3$, 100 MHz

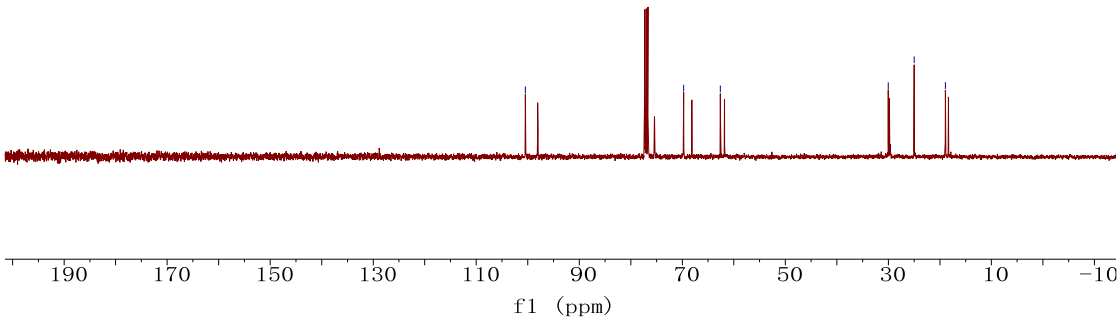


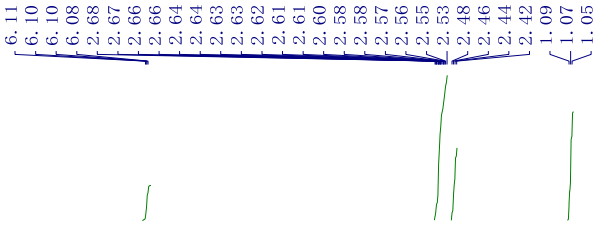
2d ^{1}H NMR, $CDCl_3$, 400 MHz

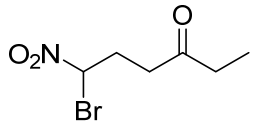




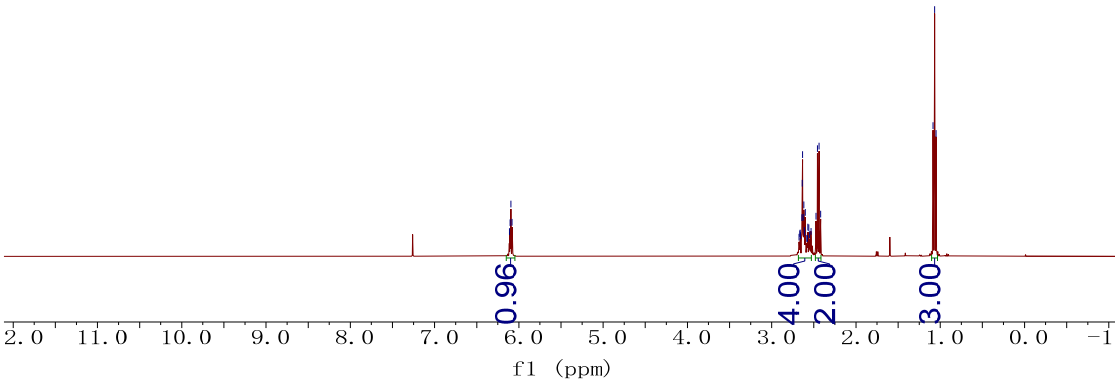
2d ^{13}C NMR, $CDCl_3$, 101 MHz

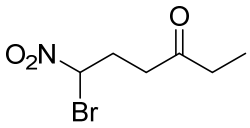




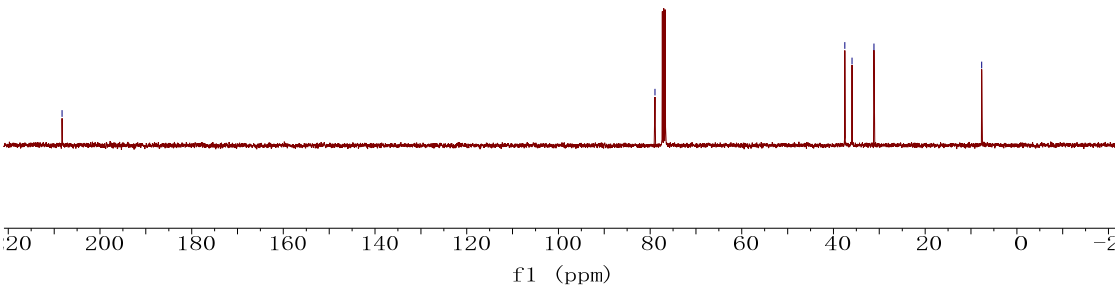


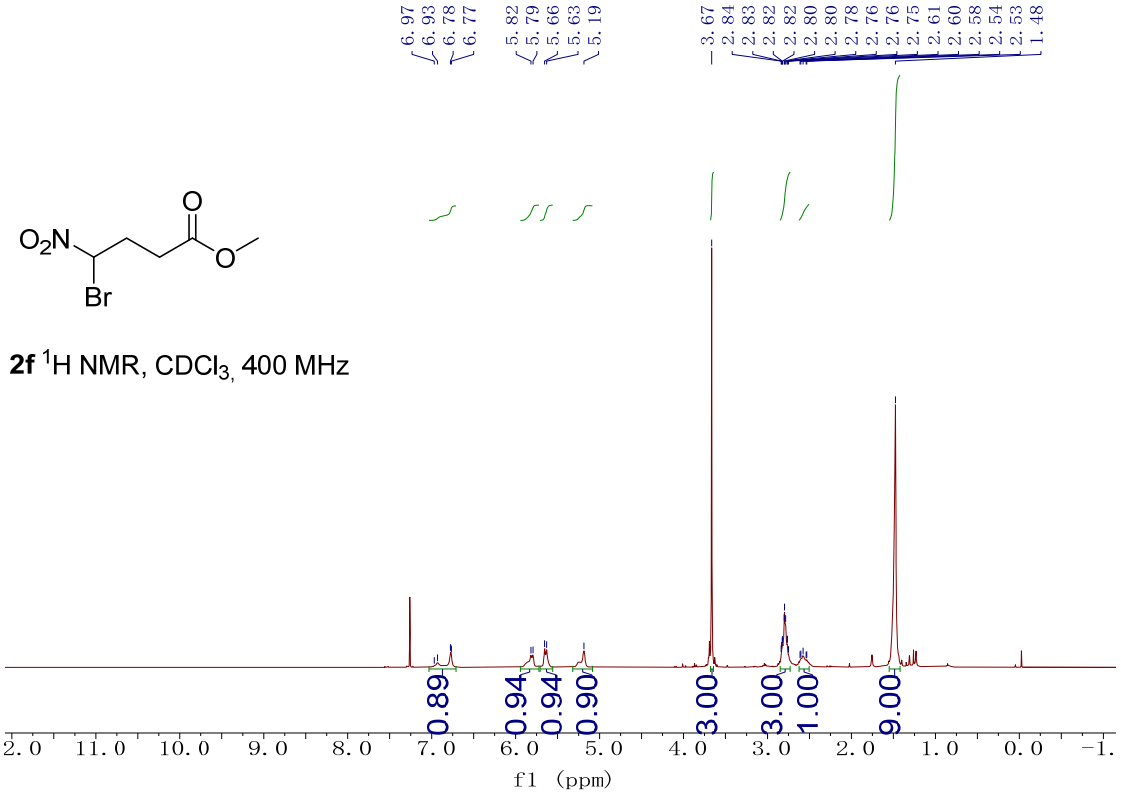
2e ^{1}H NMR, $CDCl_3$, 400 MHz



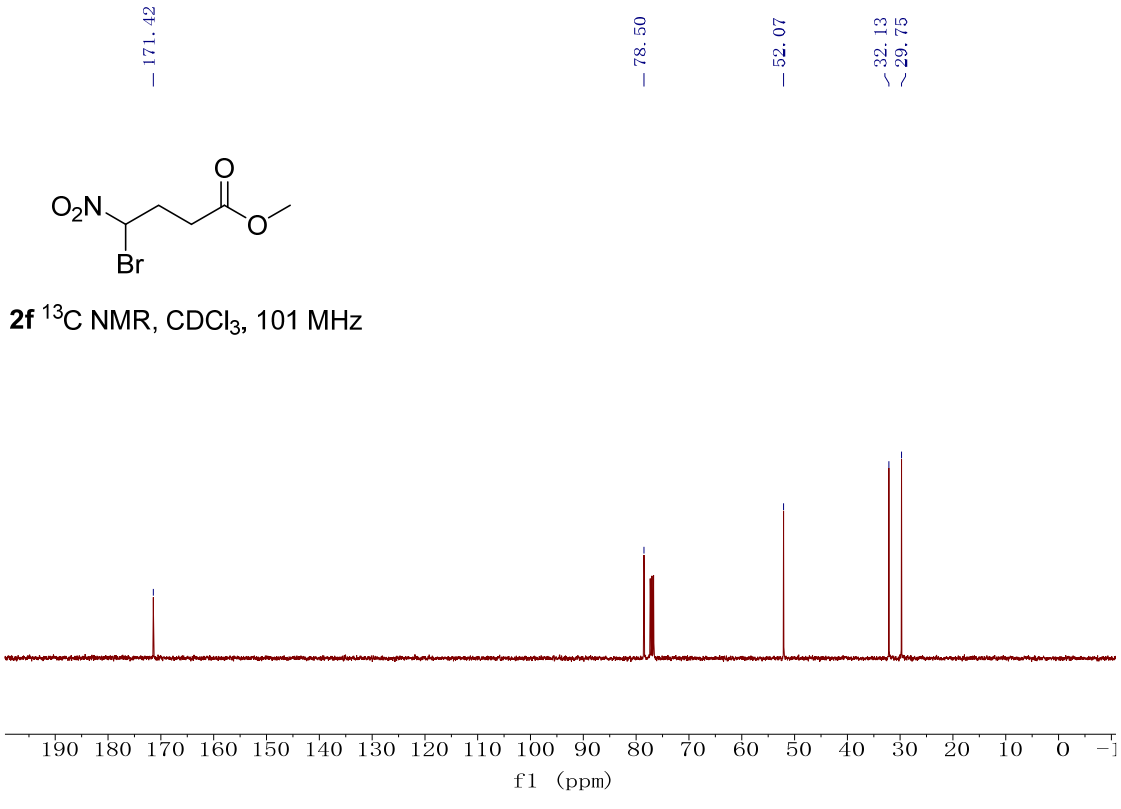


2e ^{13}C NMR, $CDCl_3$, 101 MHz

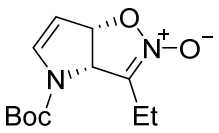




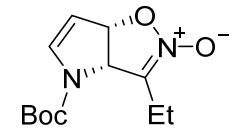
2f ^{1}H NMR, $CDCl_3$, 400 MHz



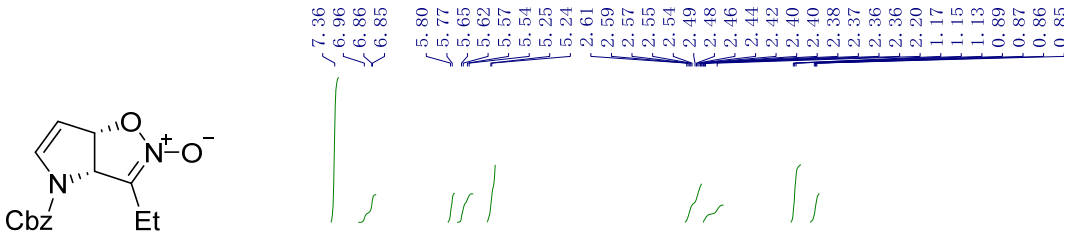
2f ^{13}C NMR, $CDCl_3$, 101 MHz



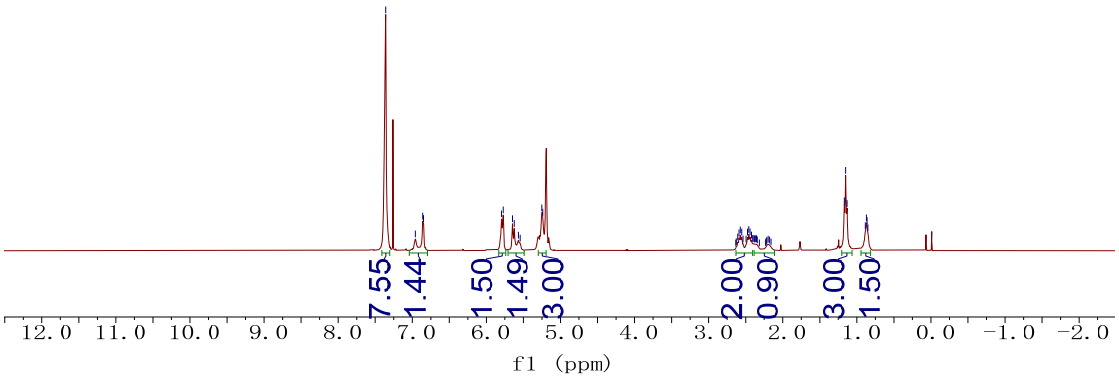
3aa ^{1}H NMR, $CDCl_3$, 400 MHz

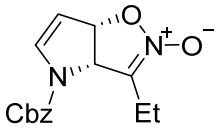


3aa ^{13}C NMR, $CDCl_3$, 101 MHz

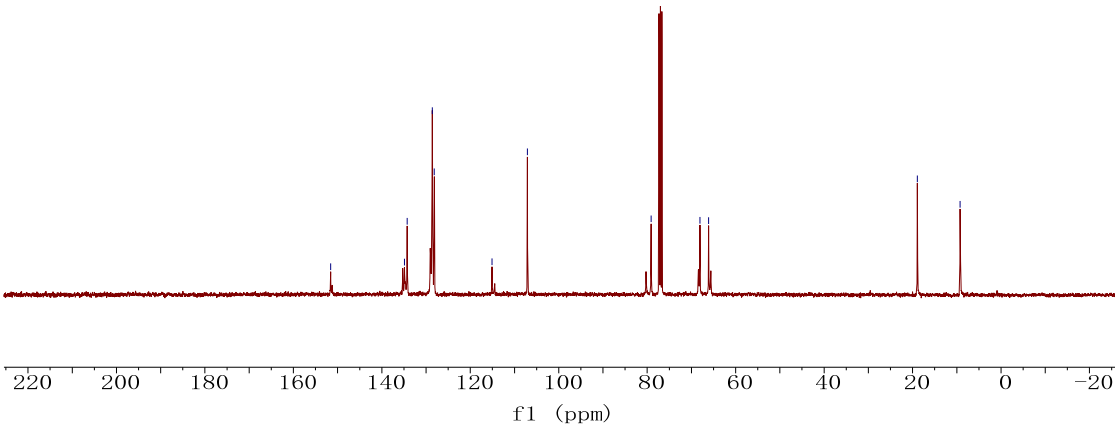


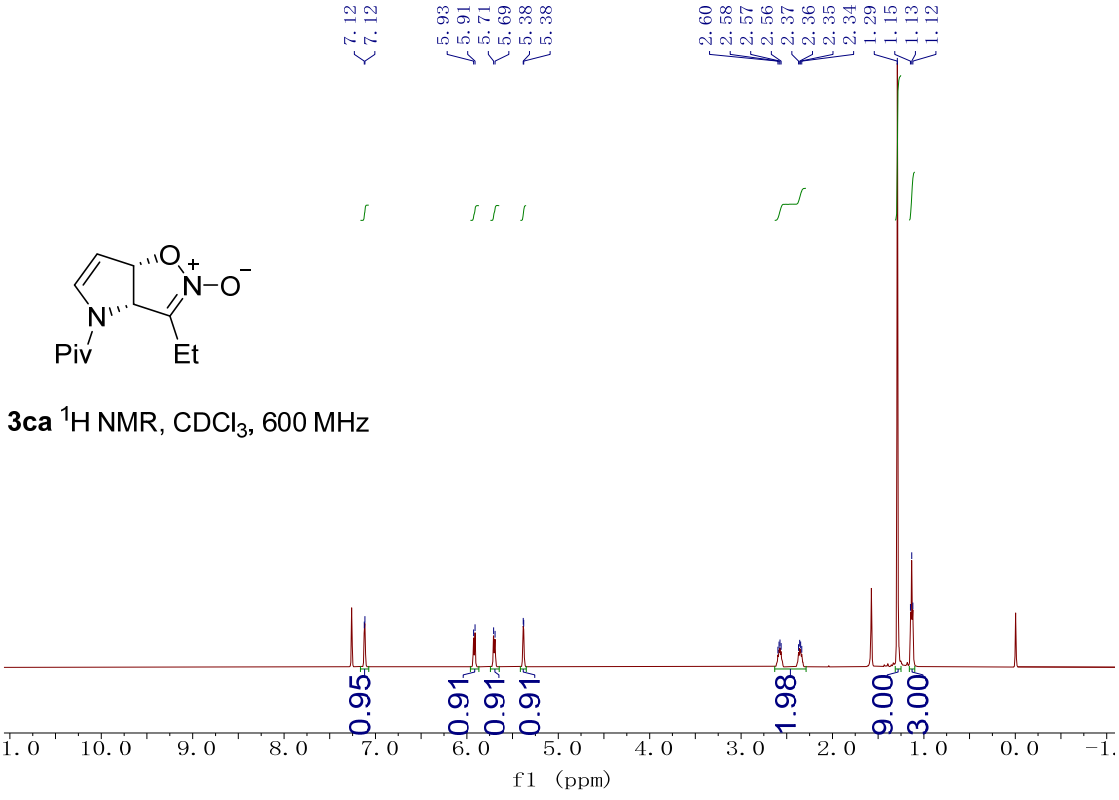
3ba ^{1}H NMR, $CDCl_3$, 400 MHz



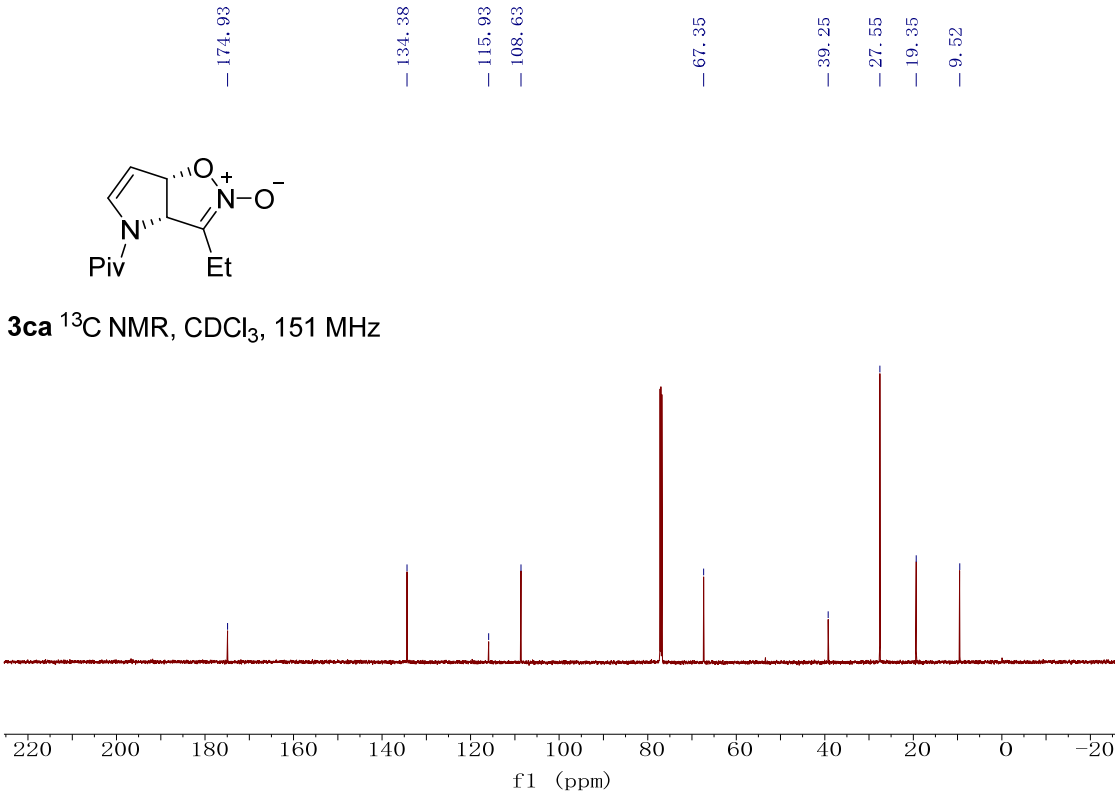


3ba ^{13}C NMR, $CDCl_3$, 101 MHz

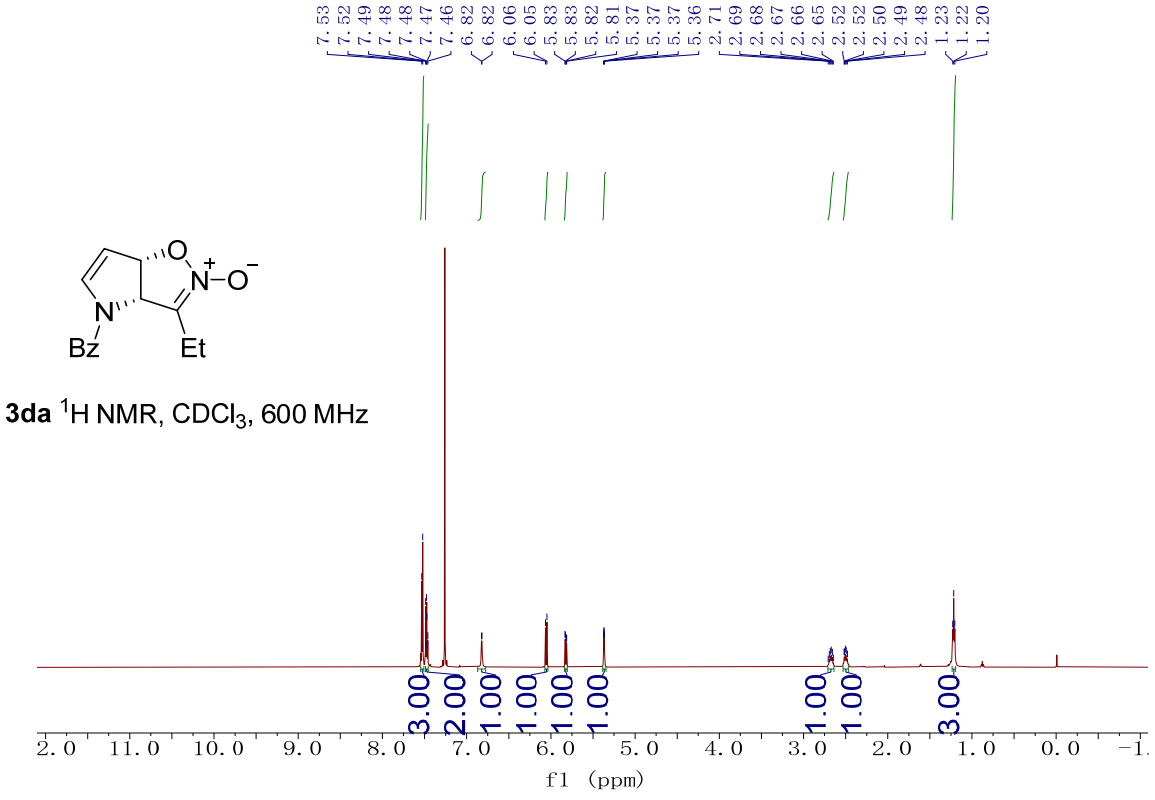




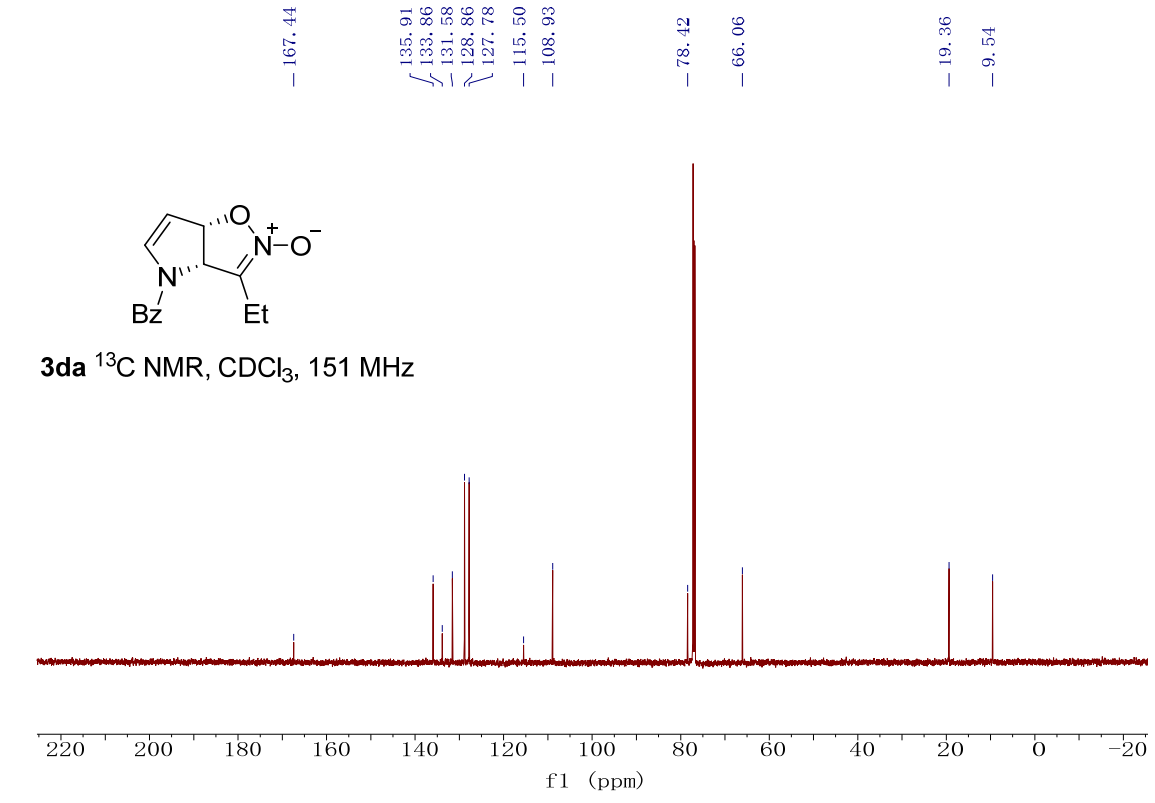
3ca ^{1}H NMR, $CDCl_3$, 600 MHz



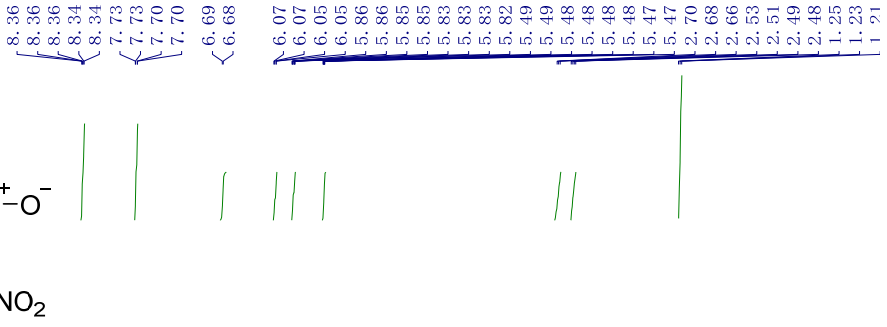
3ca ^{13}C NMR, $CDCl_3$, 151 MHz



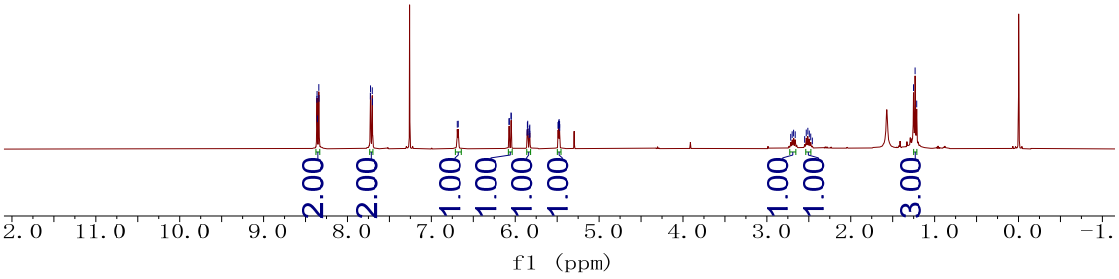
3da ^{1}H NMR, $CDCl_3$, 600 MHz

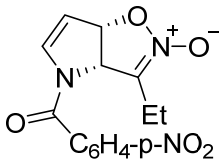


3da ^{13}C NMR, $CDCl_3$, 151 MHz

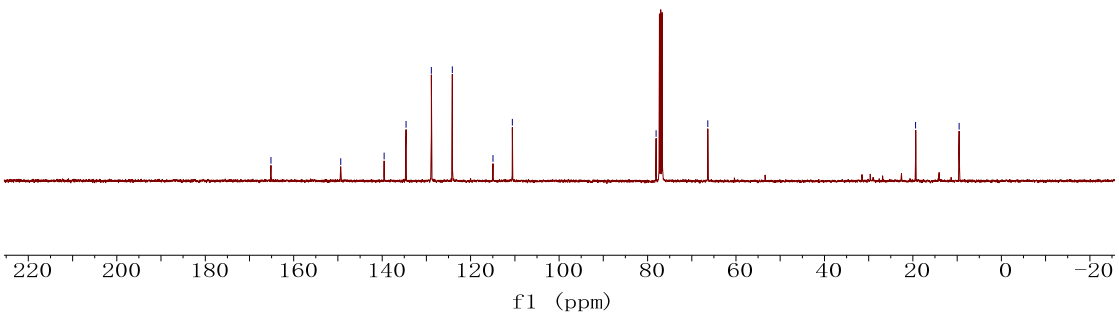


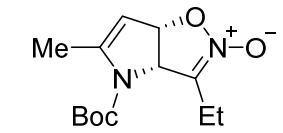
3ea ^{1}H NMR, $CDCl_3$, 400 MHz



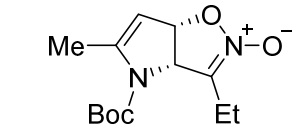


3ea ^{13}C NMR, $CDCl_3$, 101 MHz

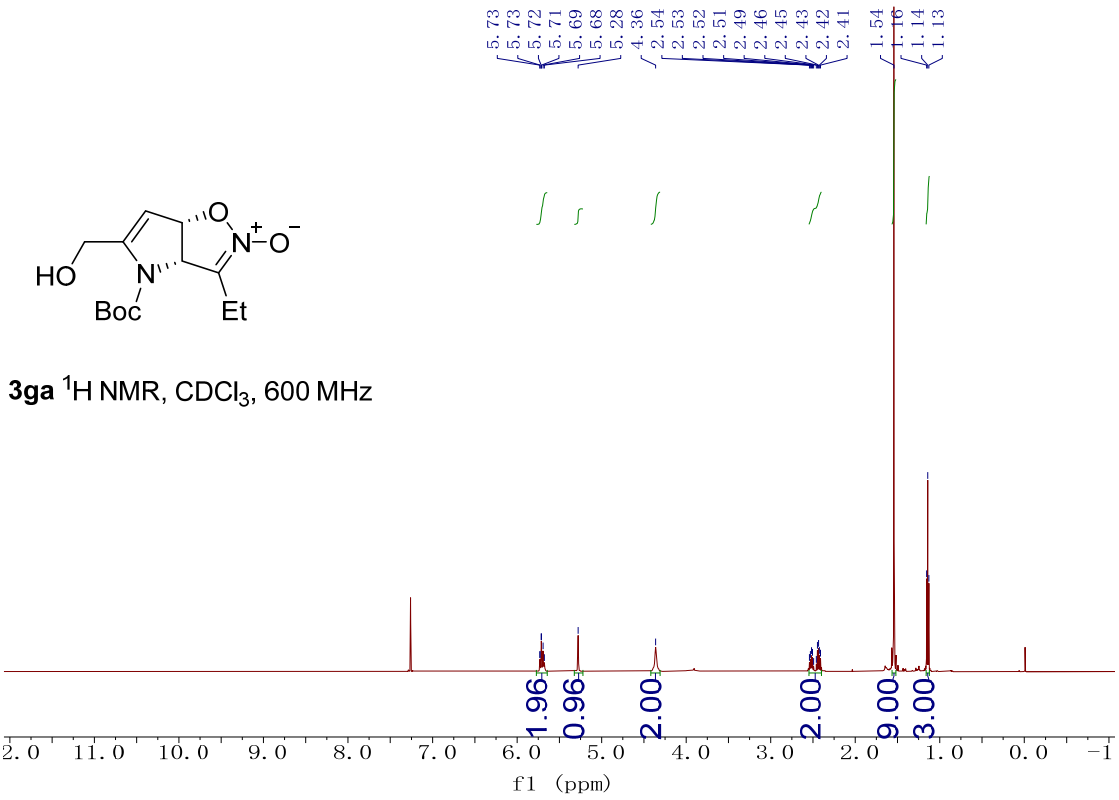




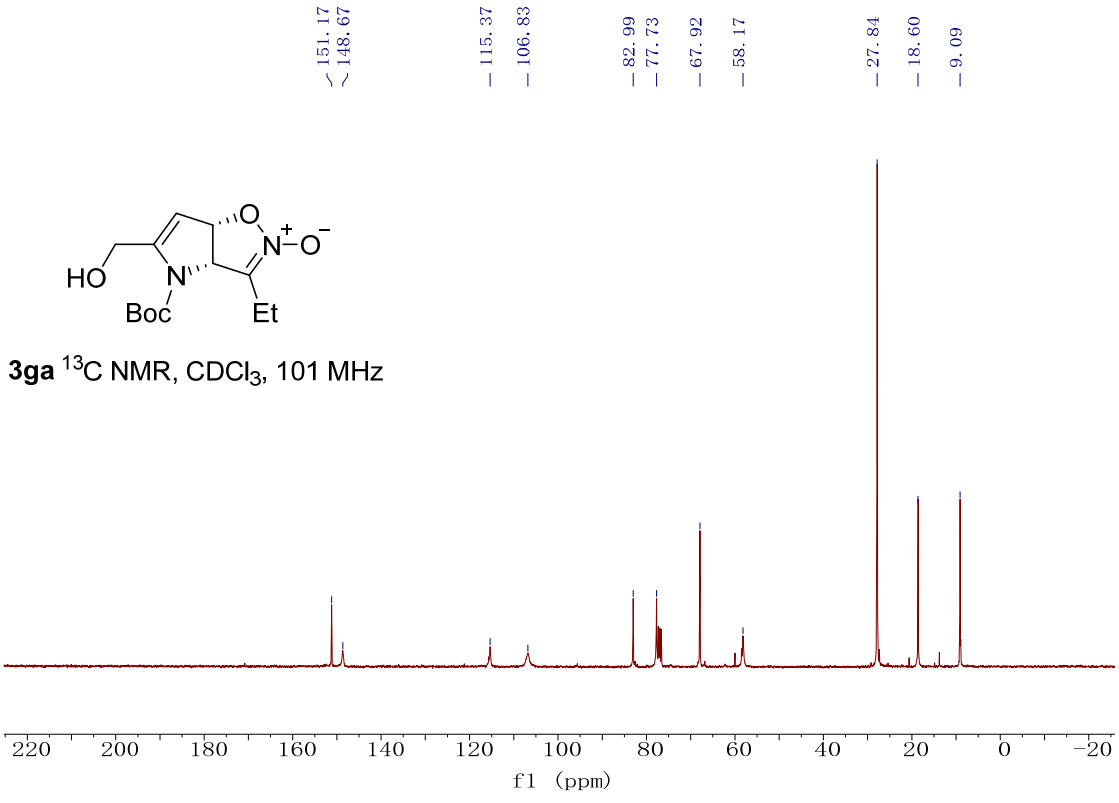
3fa ^{1}H NMR, $CDCl_3$, 400 MHz



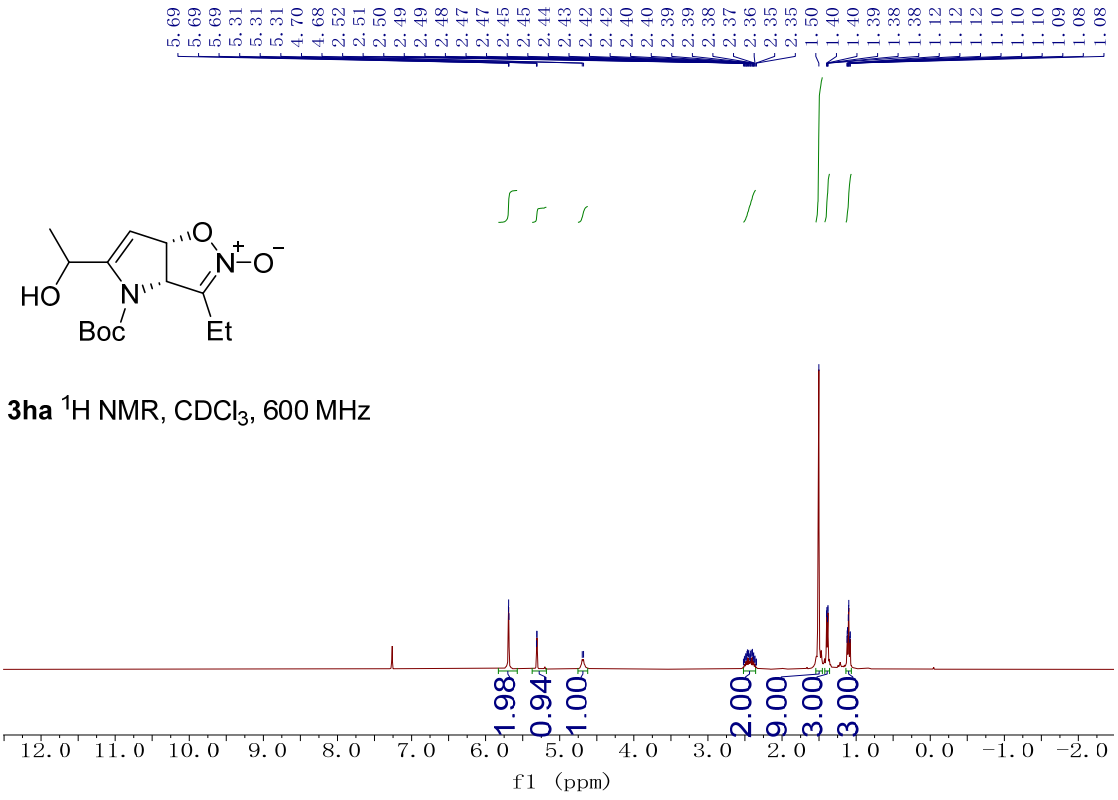
3fa ^{13}C NMR, $CDCl_3$, 151 MHz



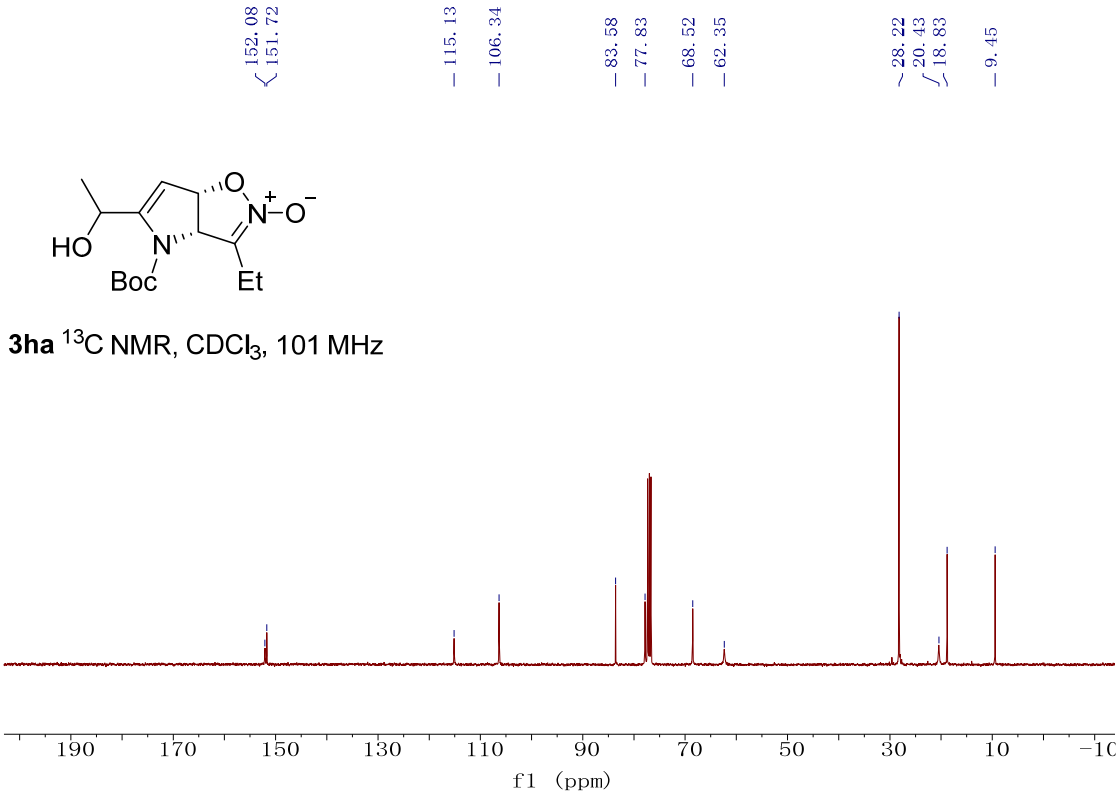
3ga ^{1}H NMR, $CDCl_3$, 600 MHz



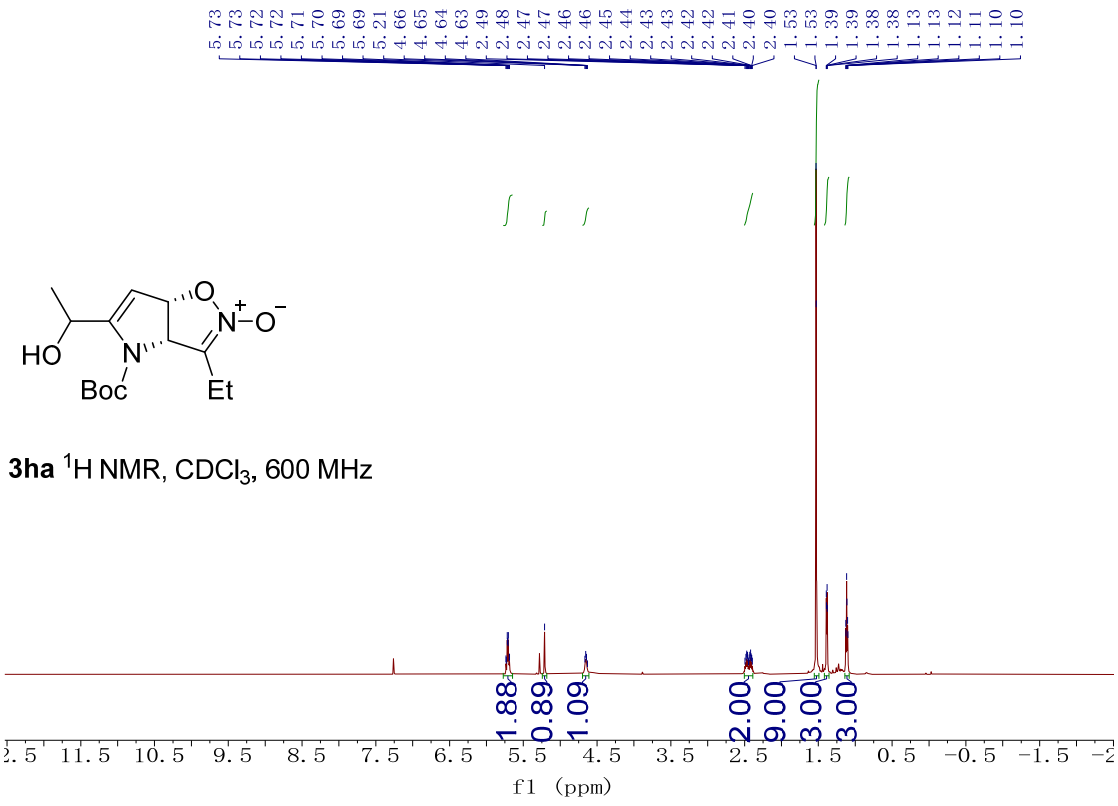
3ga ^{13}C NMR, $CDCl_3$, 101 MHz



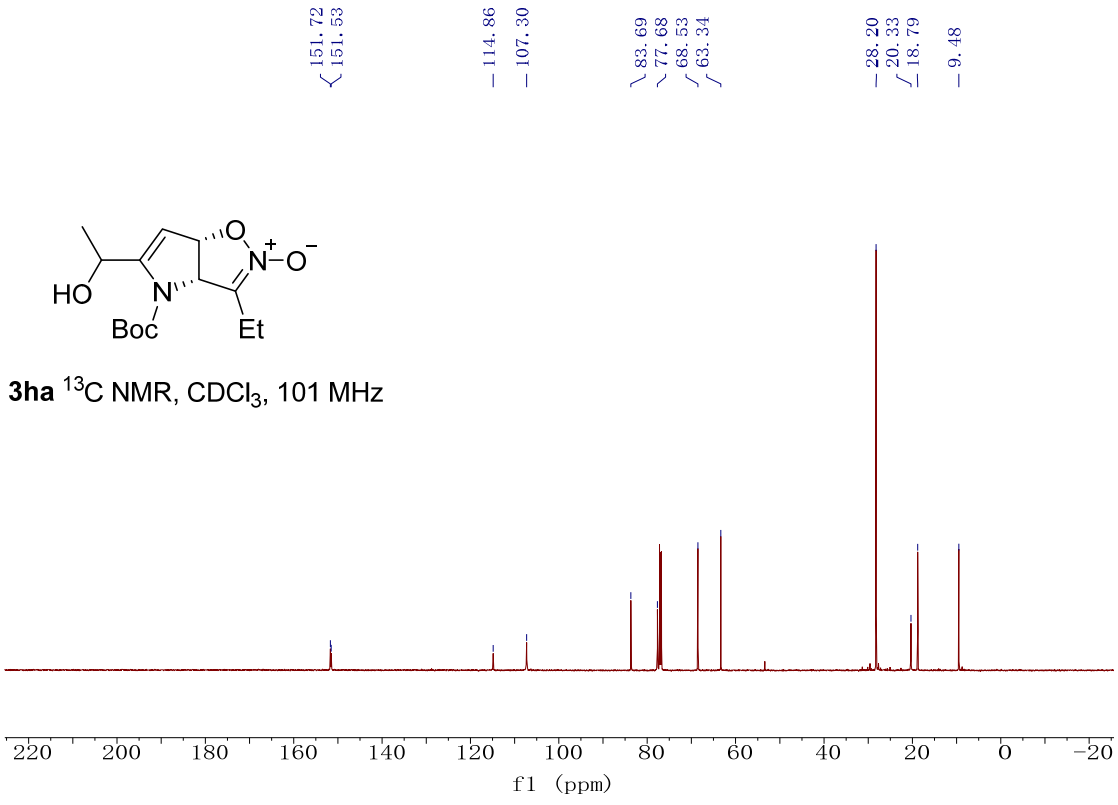
3ha ^{1}H NMR, $CDCl_3$, 600 MHz



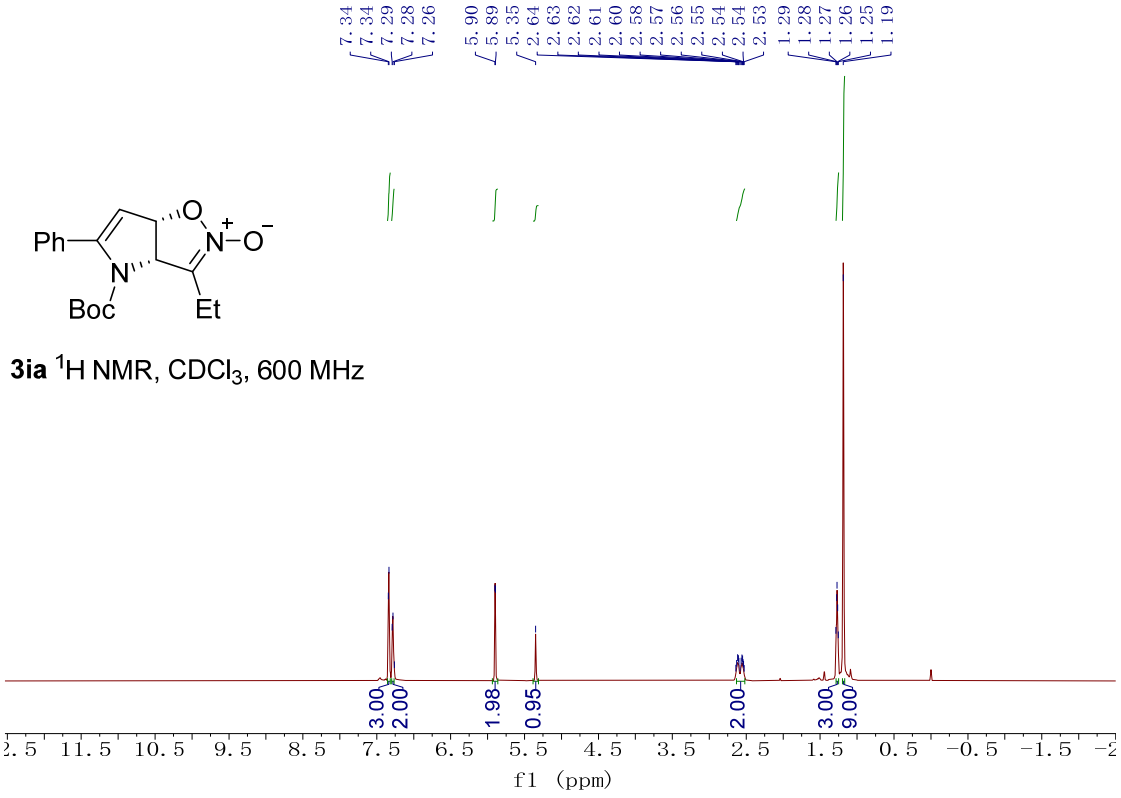
3ha ^{13}C NMR, $CDCl_3$, 101 MHz



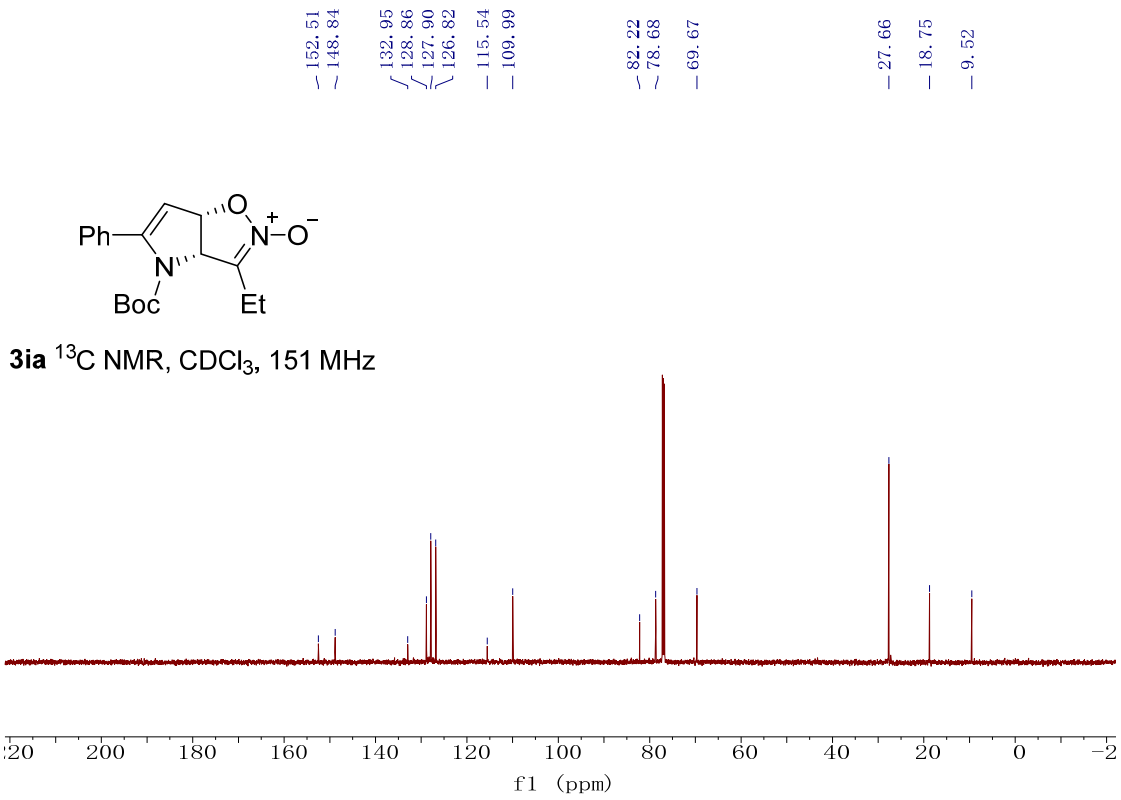
3ha ^{1}H NMR, $CDCl_3$, 600 MHz



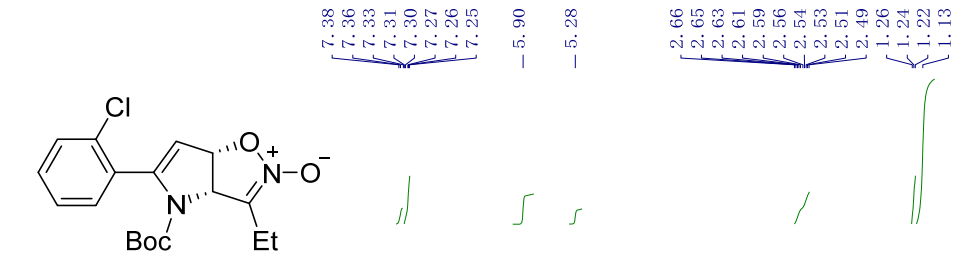
3ha ^{13}C NMR, $CDCl_3$, 101 MHz



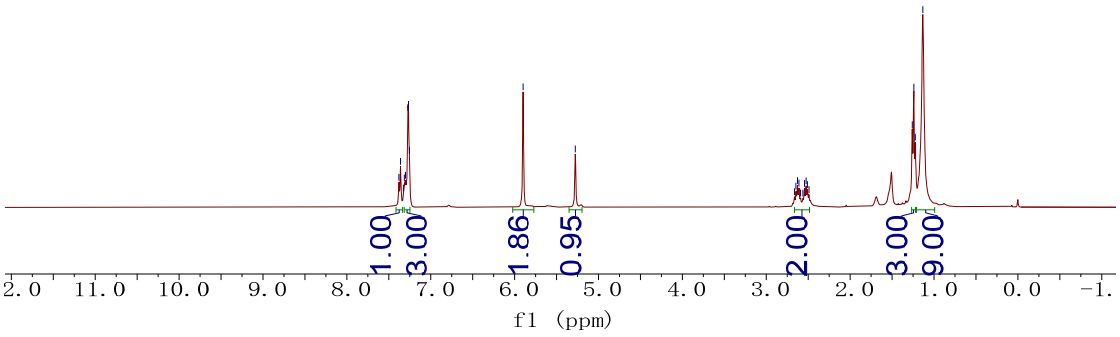
3ia ^{1}H NMR, $CDCl_3$, 600 MHz

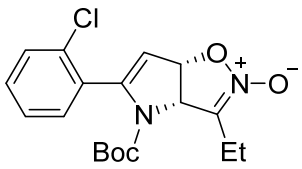


3ia ^{13}C NMR, $CDCl_3$, 151 MHz

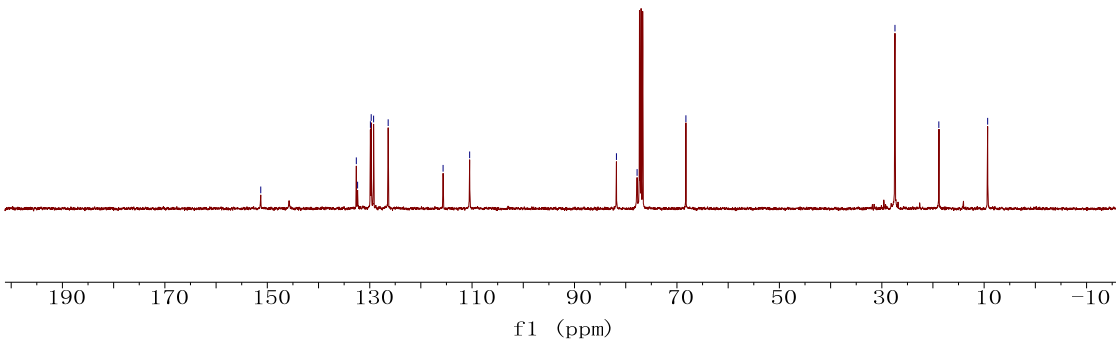


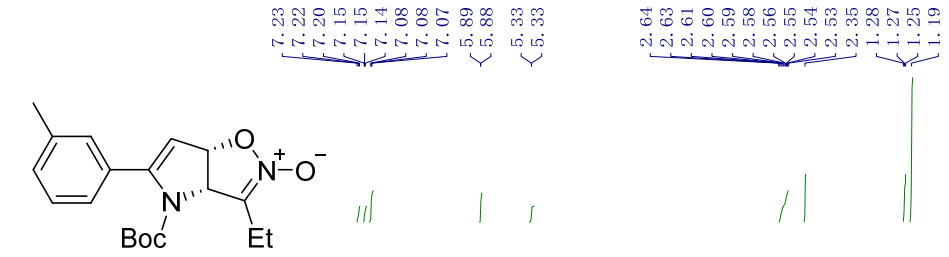
3ja ^{1}H NMR, $CDCl_3$, 400 MHz



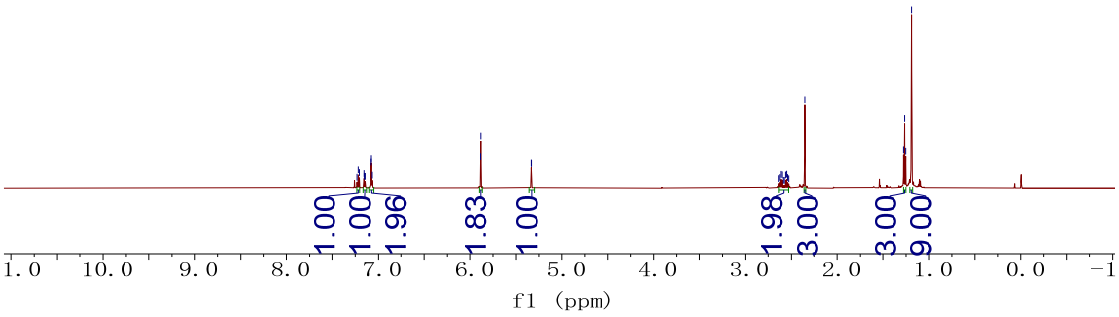


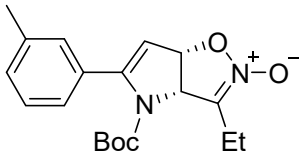
3ja ^{13}C NMR, $CDCl_3$, 101 MHz



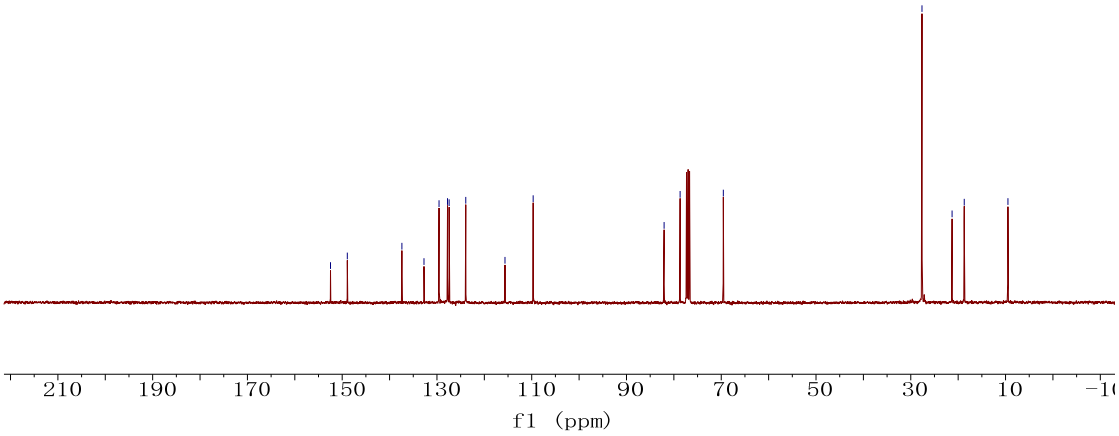


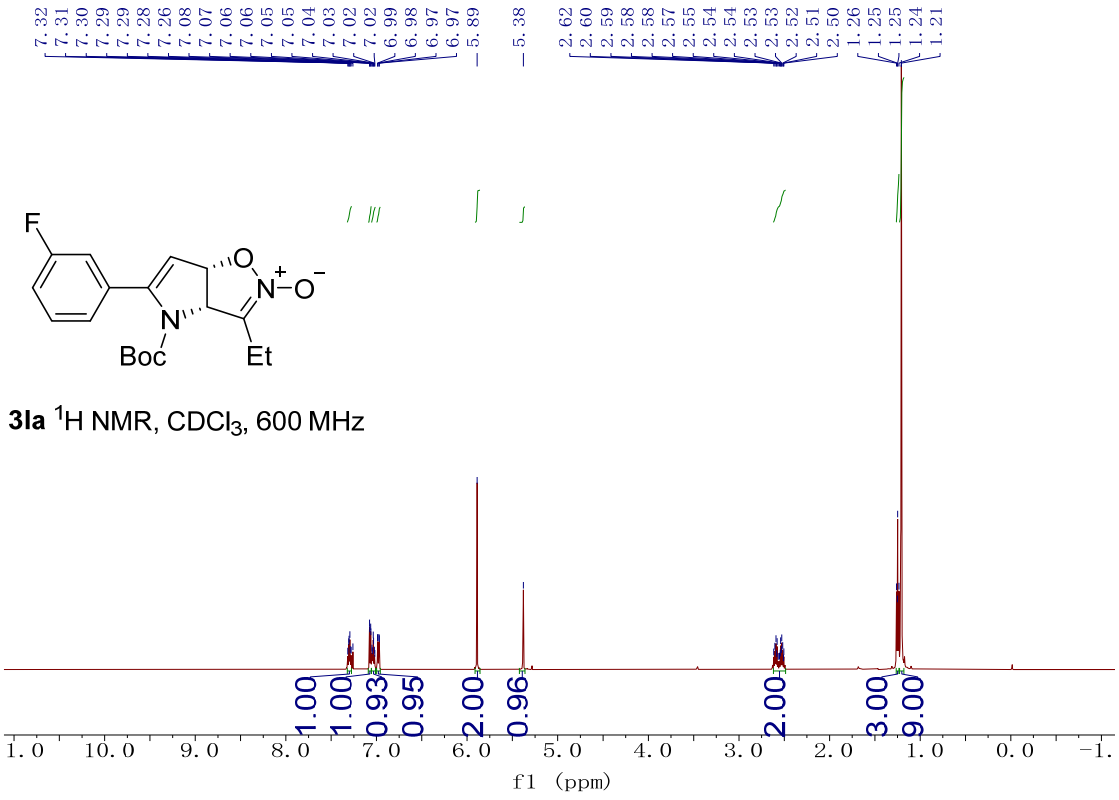
3ka ^{1}H NMR, $CDCl_3$, 600 MHz



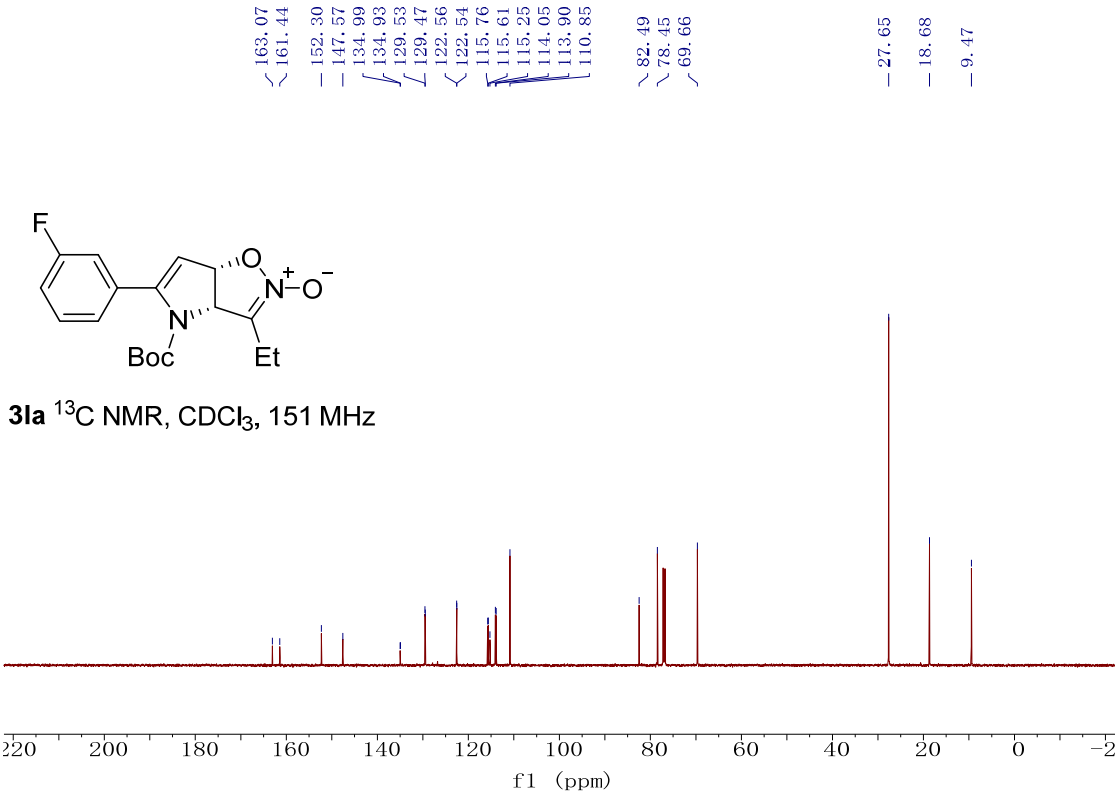


3ka ^{13}C NMR, $CDCl_3$, 101 MHz

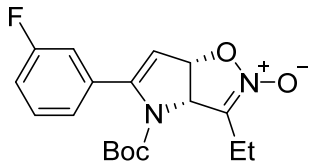




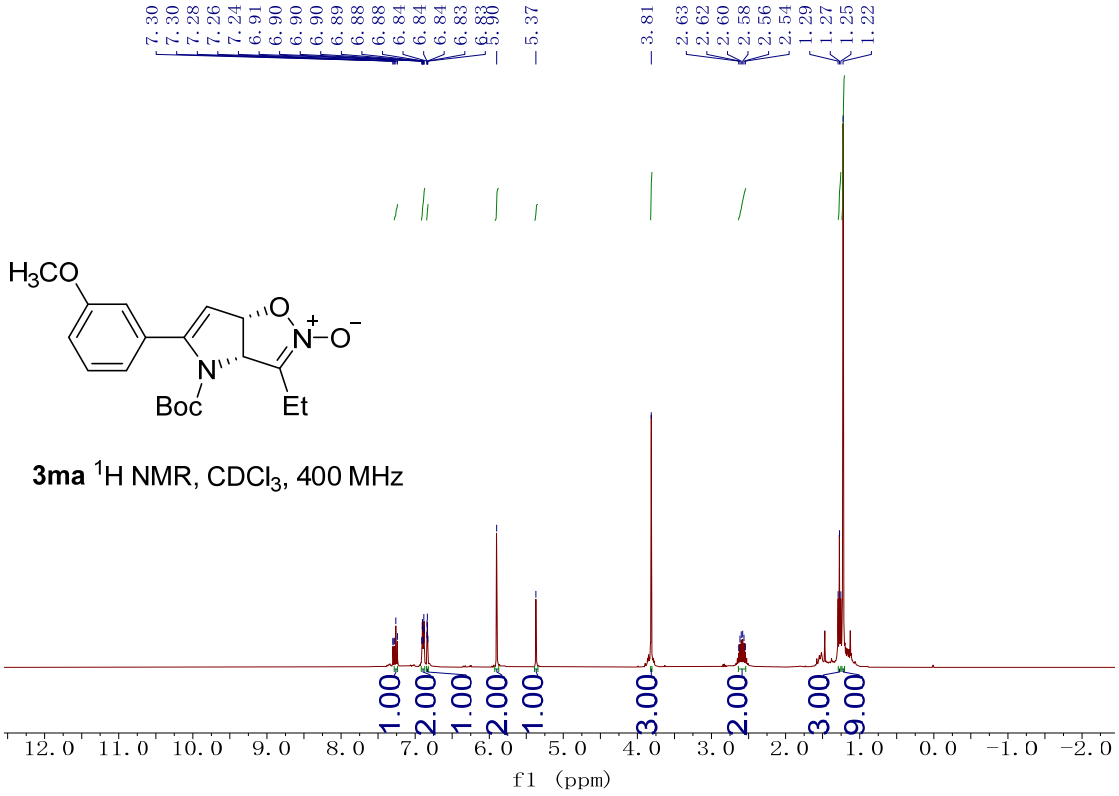
3la ^{1}H NMR, $CDCl_3$, 600 MHz



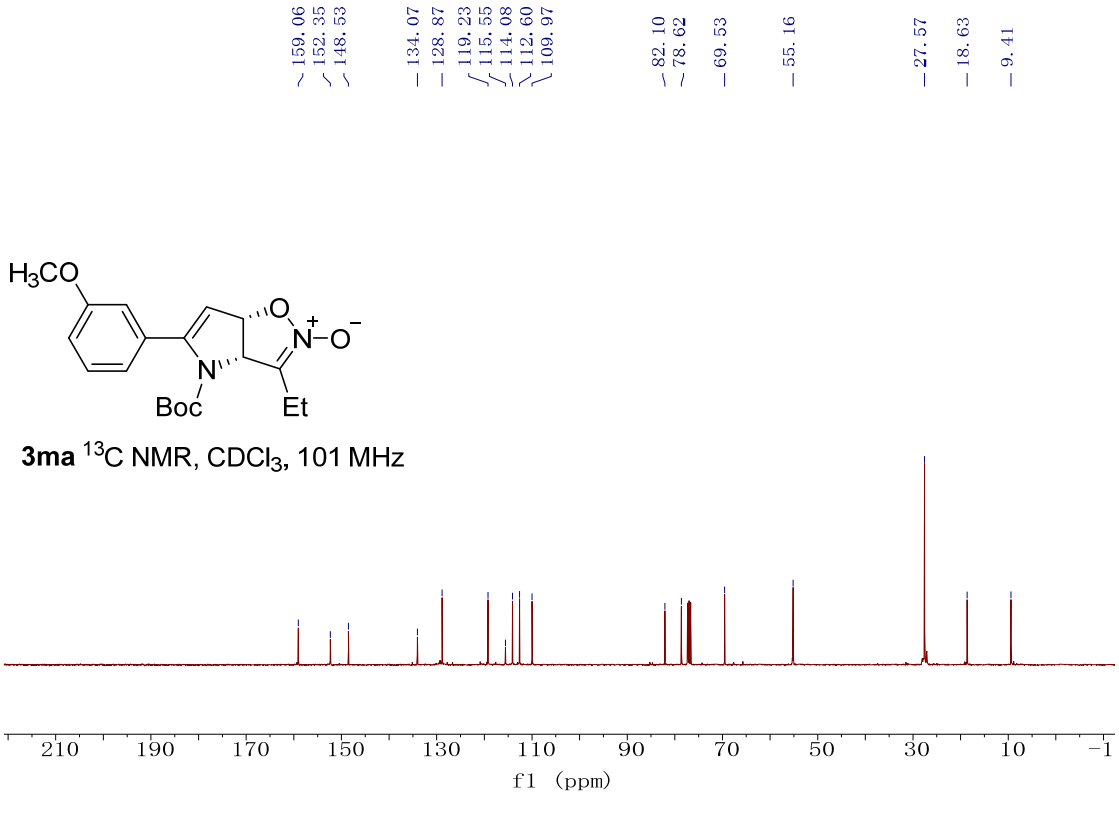
3la ^{13}C NMR, $CDCl_3$, 151 MHz



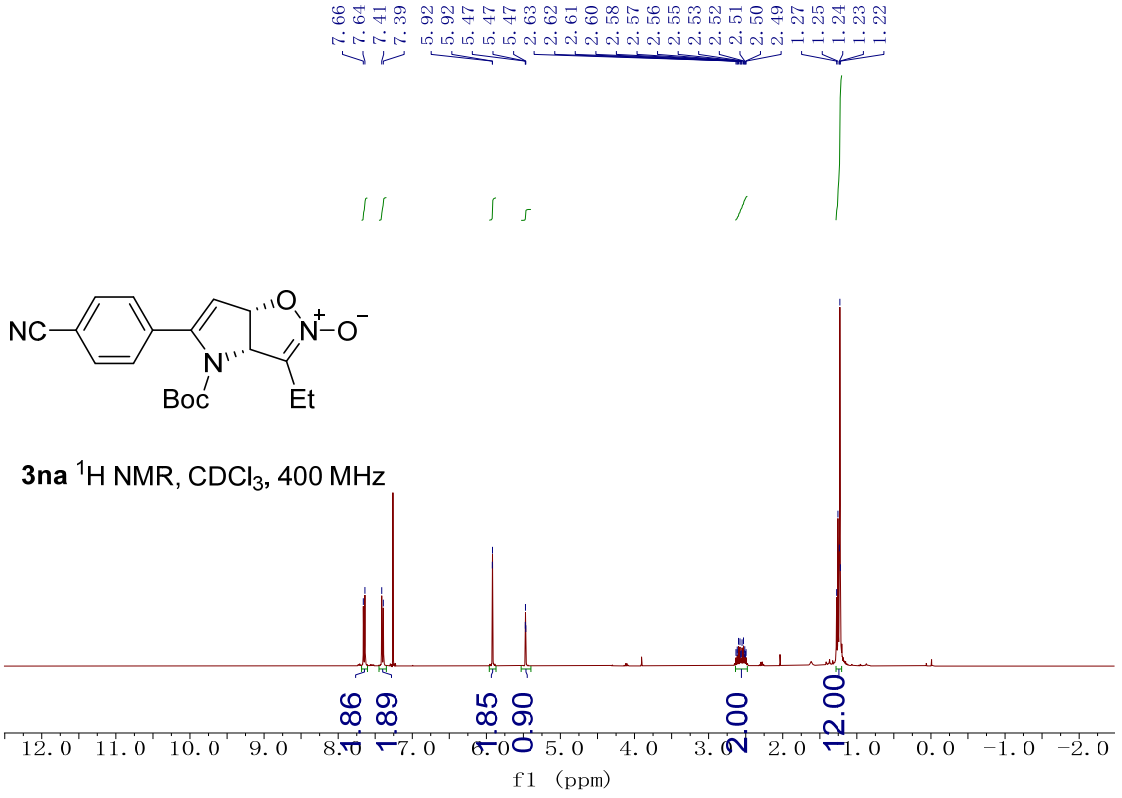
3la ^{19}F NMR, $CDCl_3$, 565 MHz



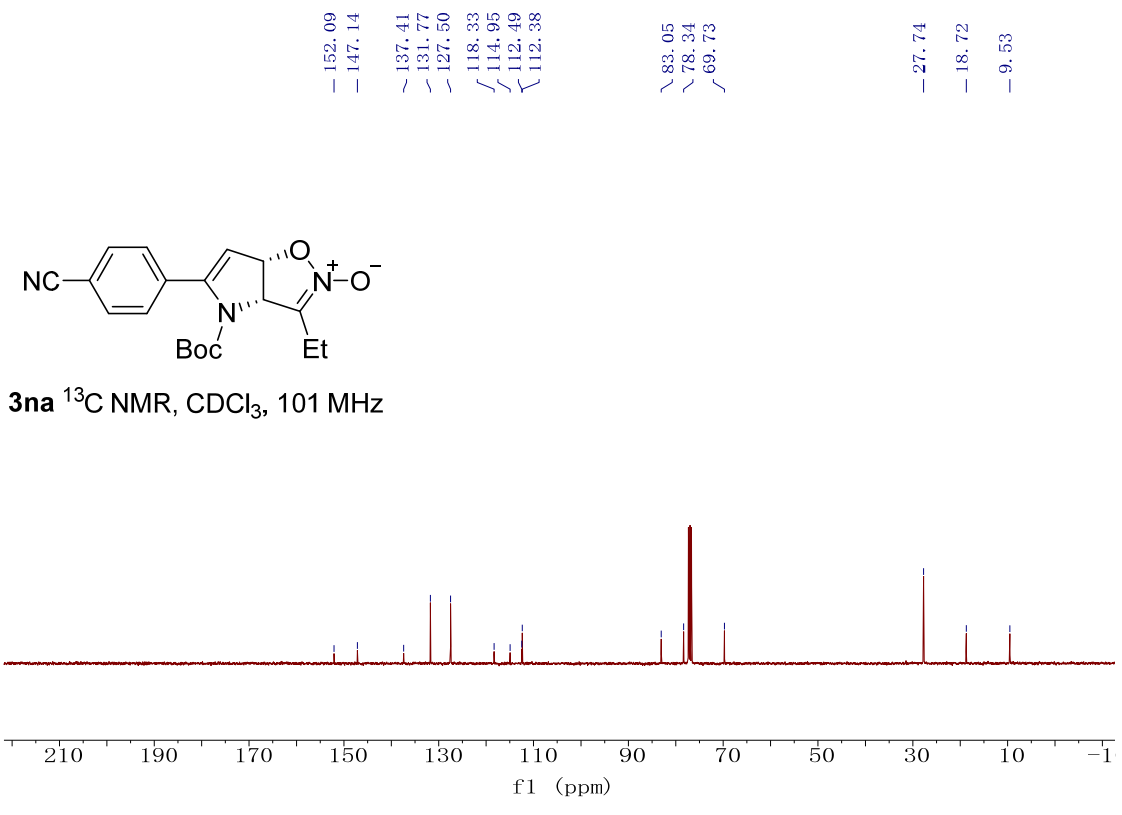
3ma ^{1}H NMR, $CDCl_3$, 400 MHz



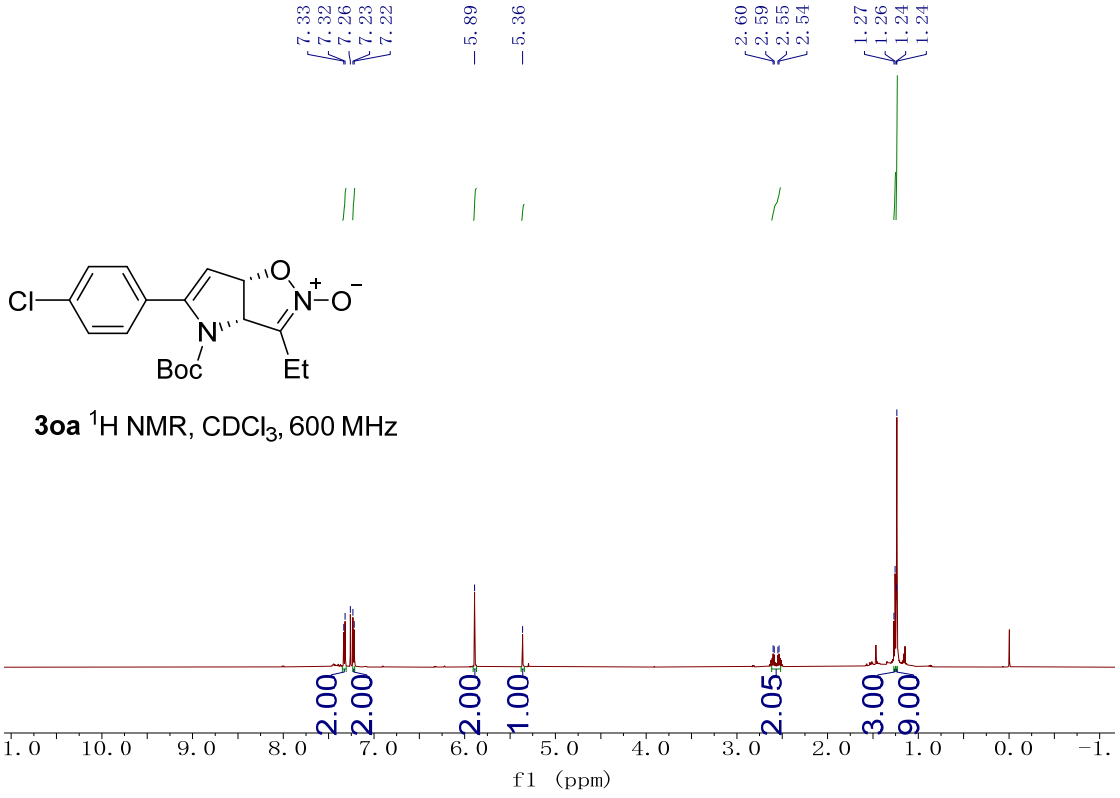
3ma ^{13}C NMR, $CDCl_3$, 101 MHz



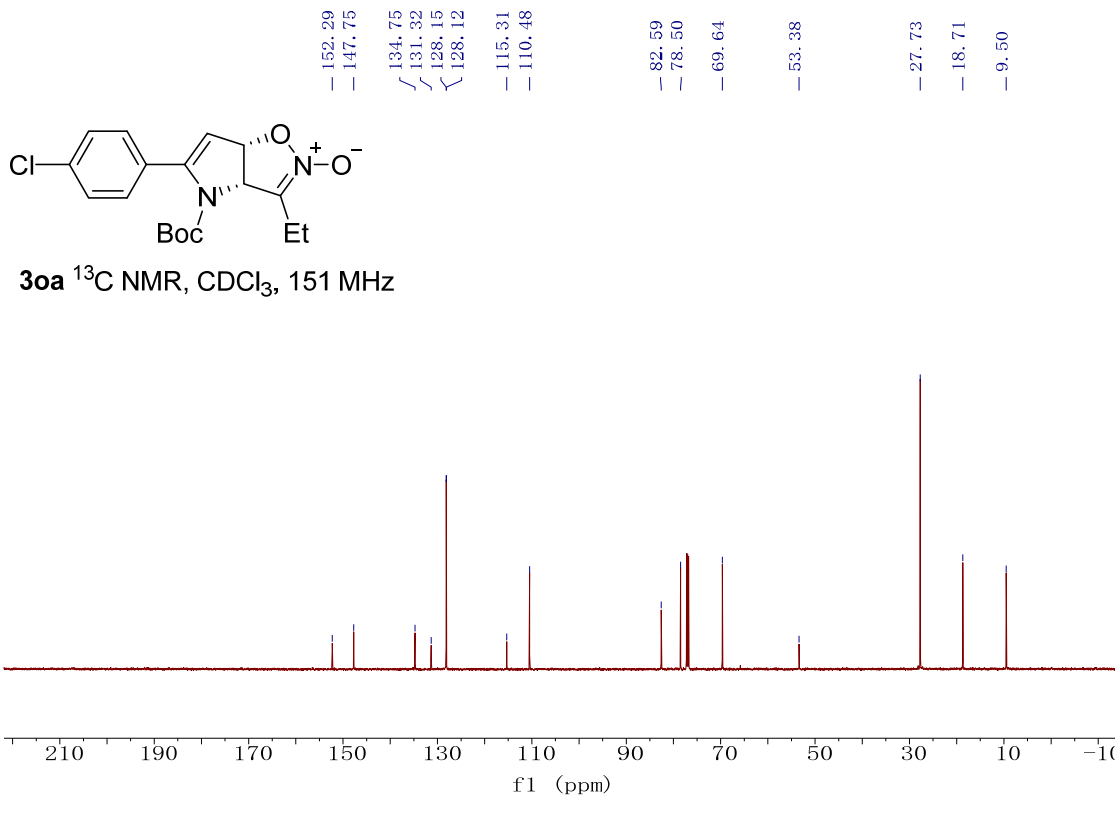
3na ^{1}H NMR, $CDCl_3$, 400 MHz



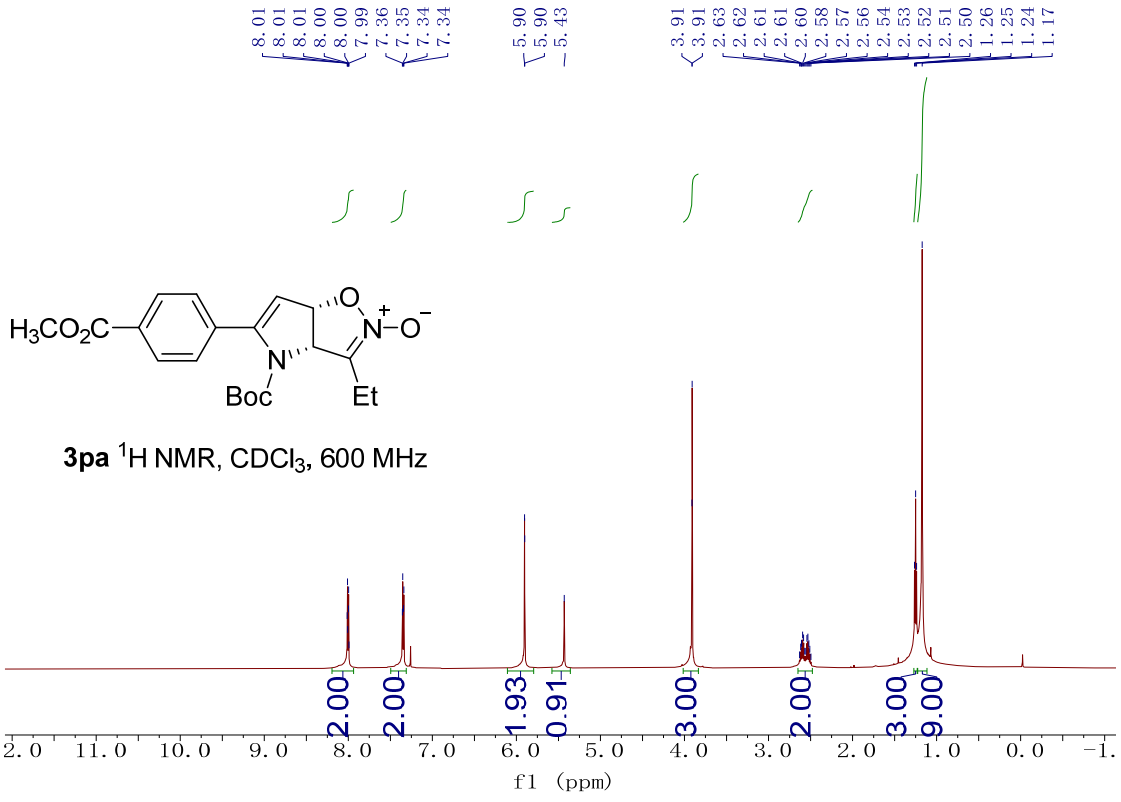
3na ^{13}C NMR, $CDCl_3$, 101 MHz



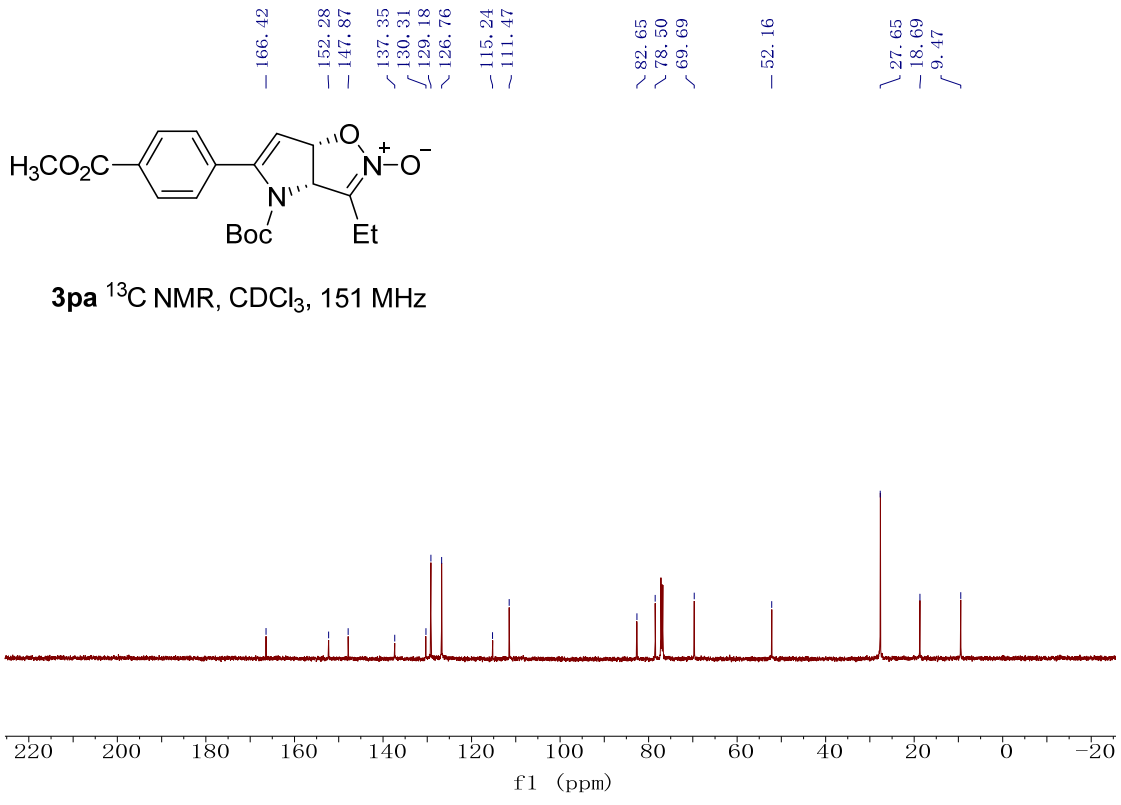
3oa ^{1}H NMR, $CDCl_3$, 600 MHz



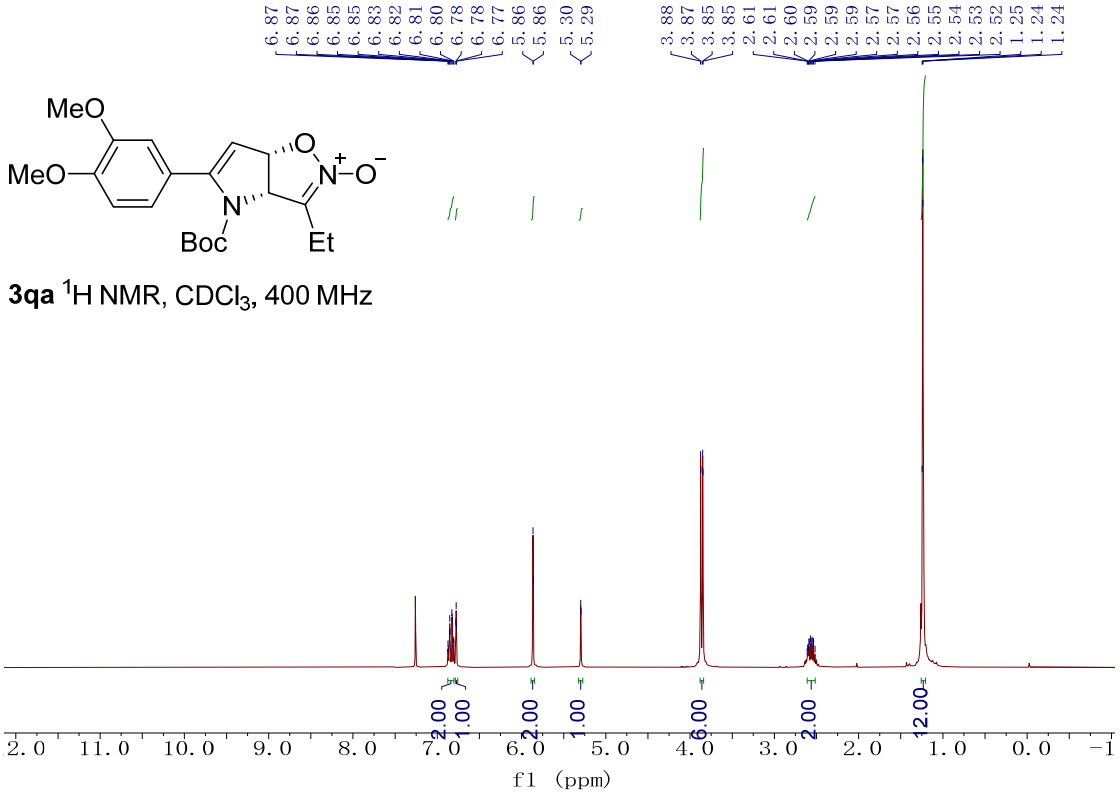
3oa ^{13}C NMR, $CDCl_3$, 151 MHz



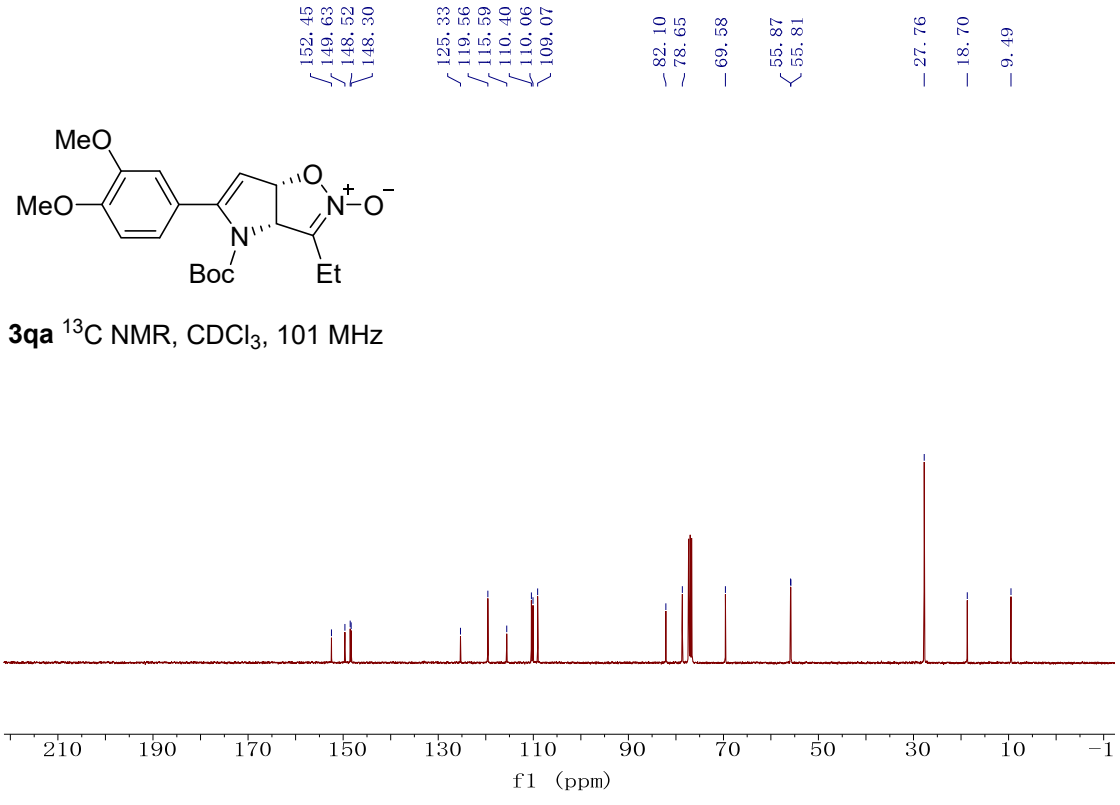
3pa ^{1}H NMR, $CDCl_3$, 600 MHz



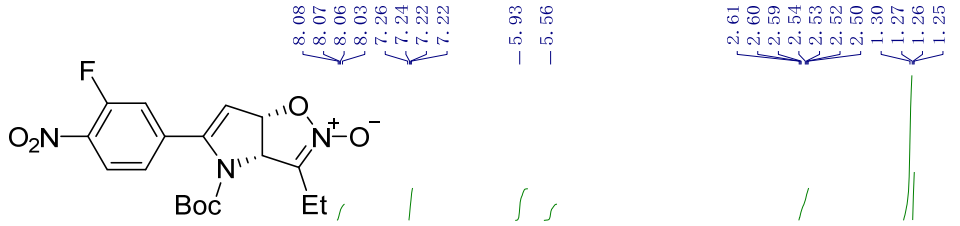
3pa ^{13}C NMR, $CDCl_3$, 151 MHz



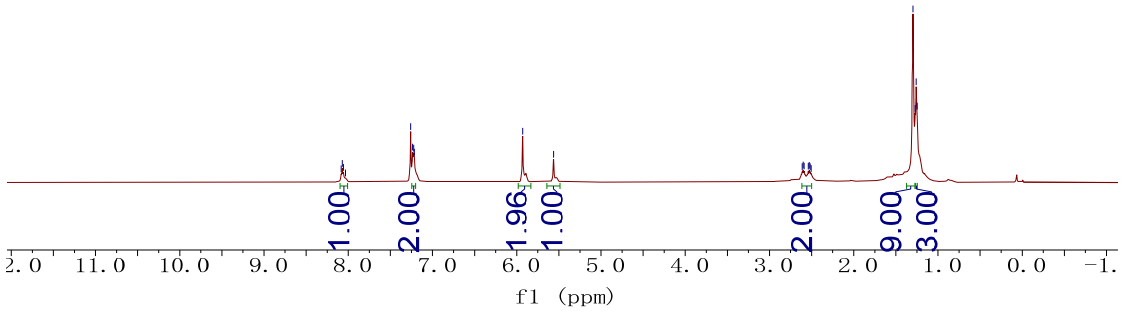
3qa ^{1}H NMR, $CDCl_3$, 400 MHz

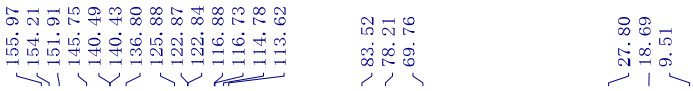


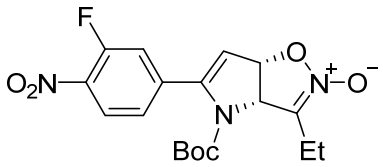
3qa ^{13}C NMR, $CDCl_3$, 101 MHz



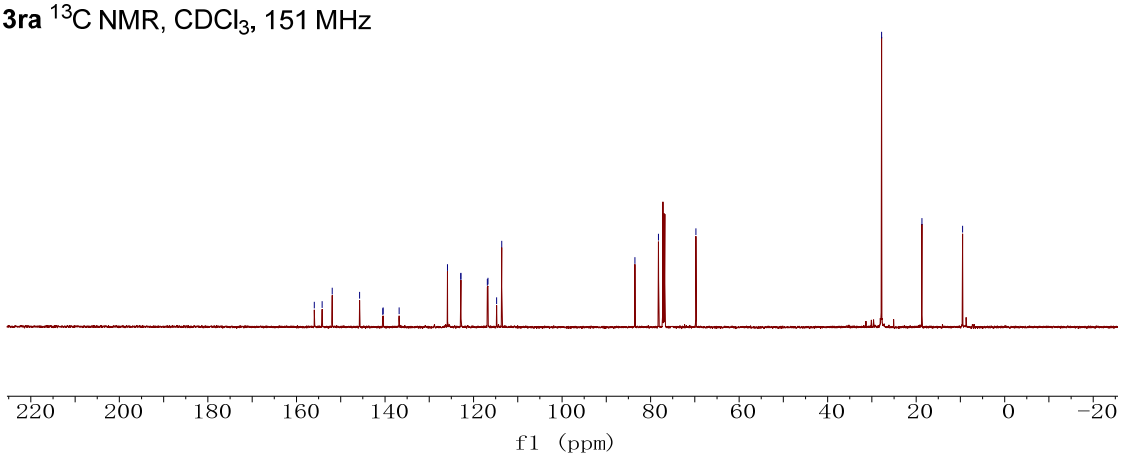
3ra ^{1}H NMR, $CDCl_3$, 600 MHz

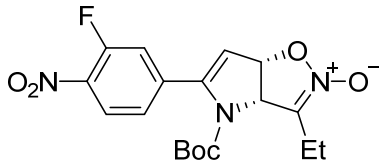




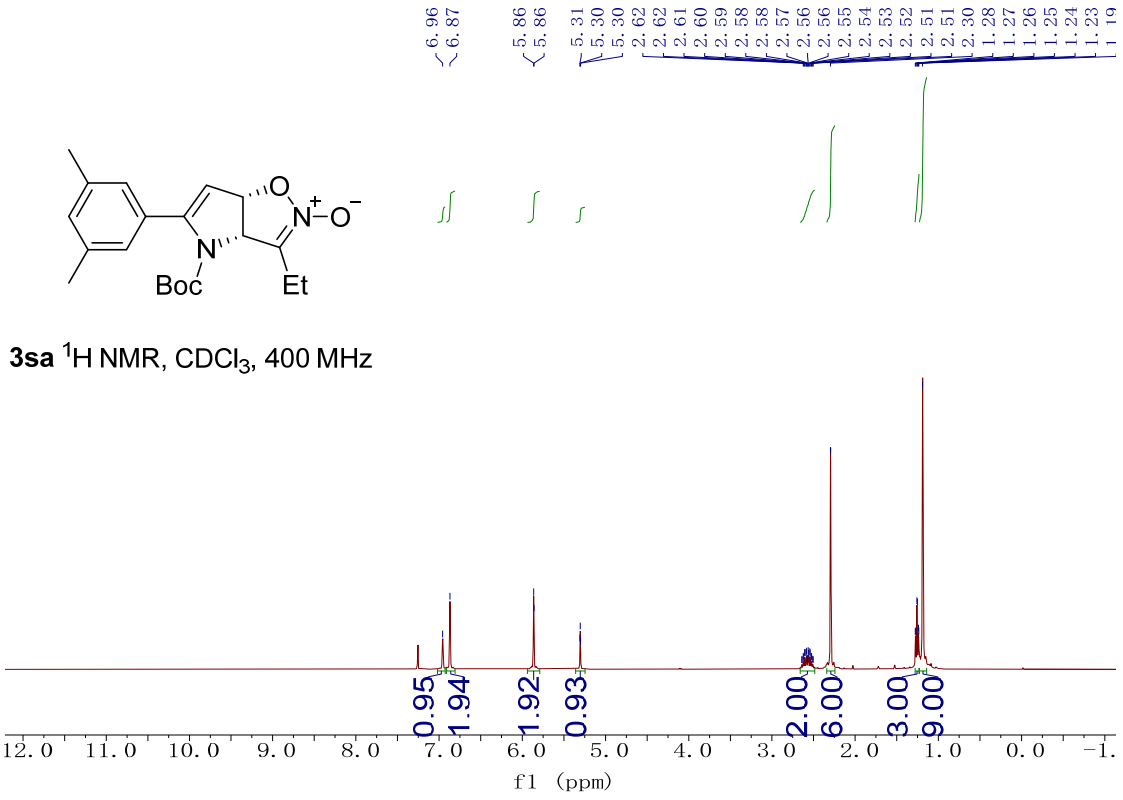


3ra ^{13}C NMR, $CDCl_3$, 151 MHz

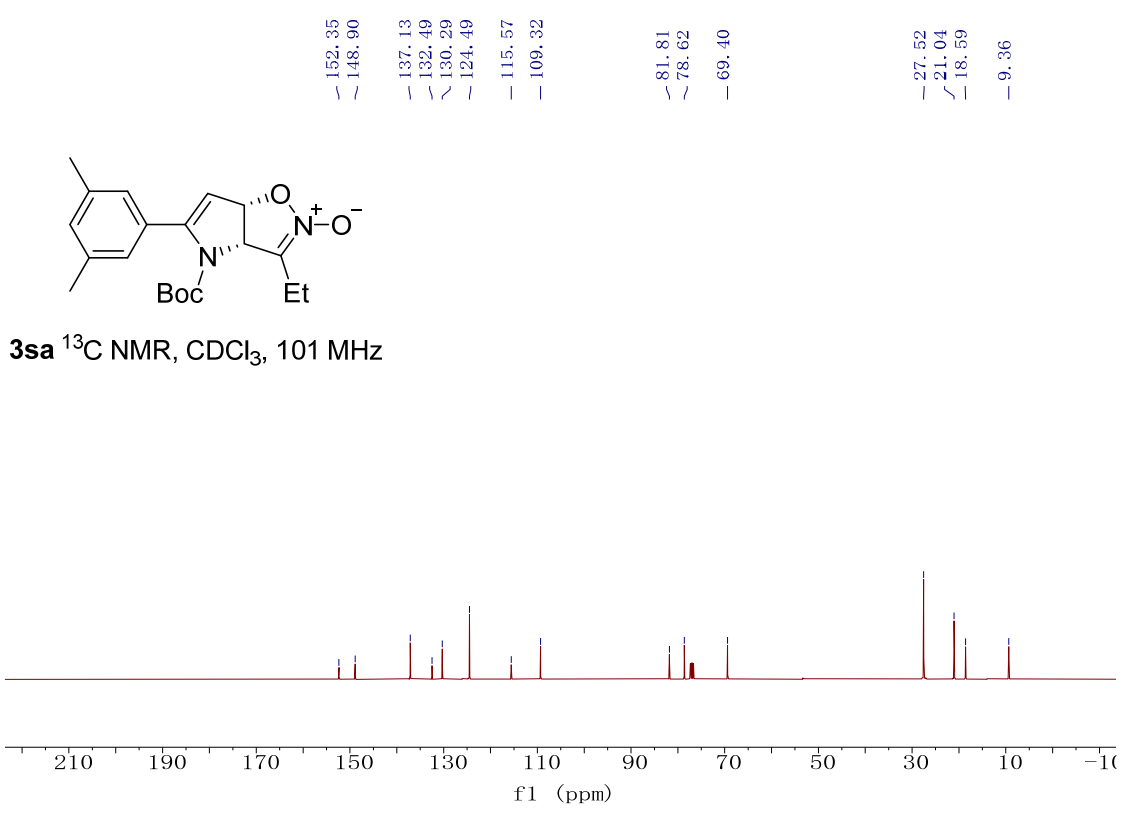




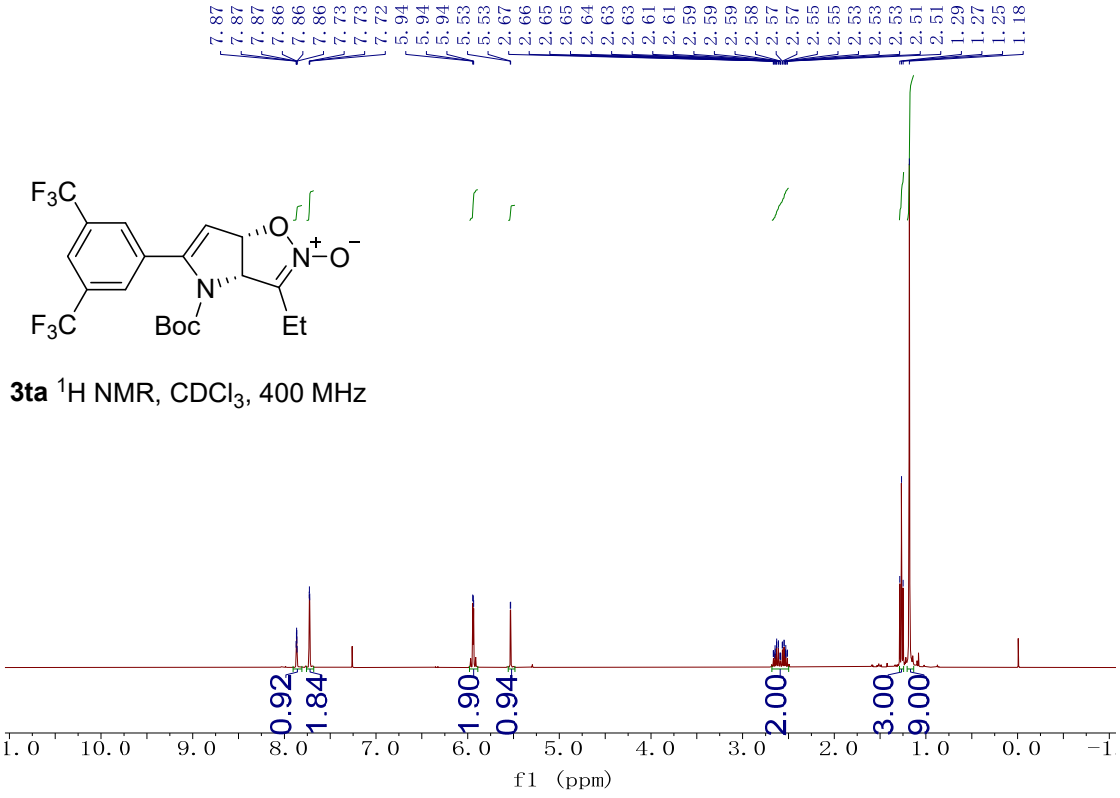
3ra ^{19}F NMR, $CDCl_3$, 565 MHz



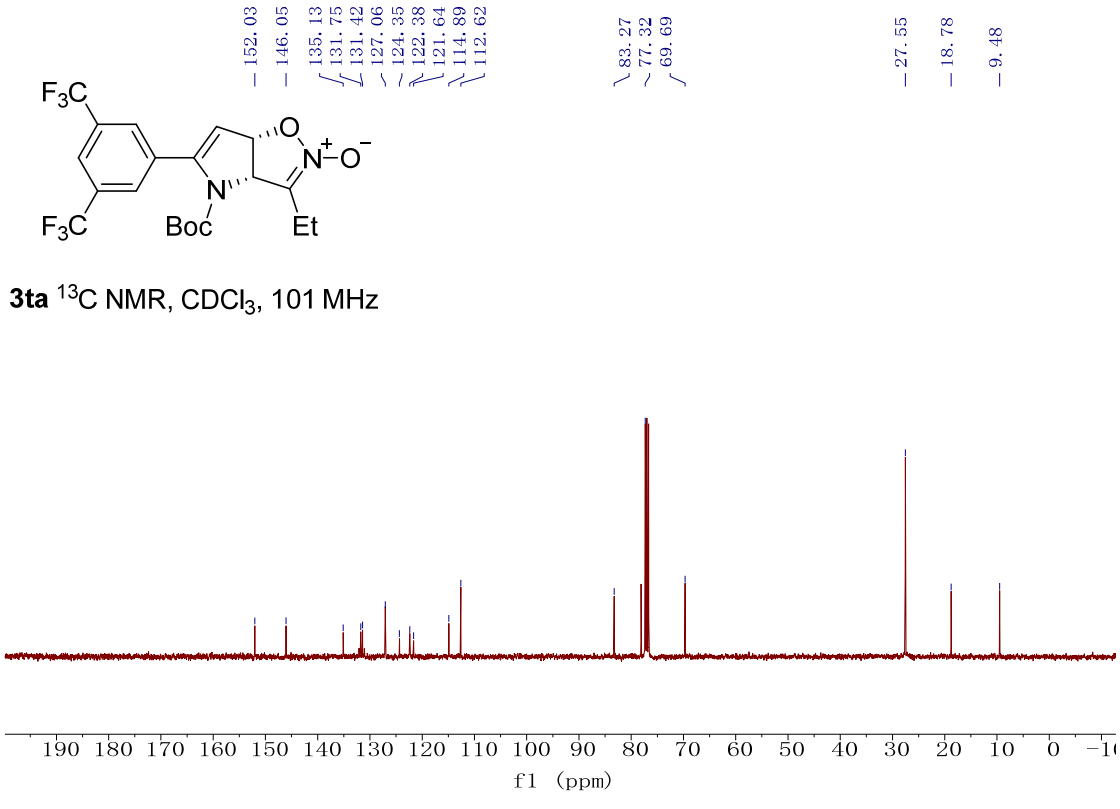
3sa ^{1}H NMR, $CDCl_3$, 400 MHz



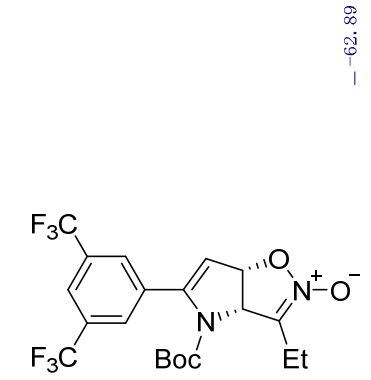
3sa ^{13}C NMR, $CDCl_3$, 101 MHz



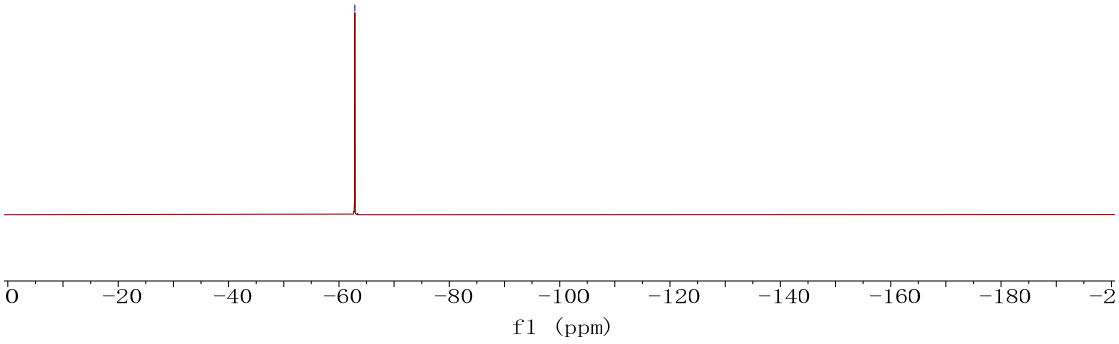
3ta ^{1}H NMR, $CDCl_3$, 400 MHz

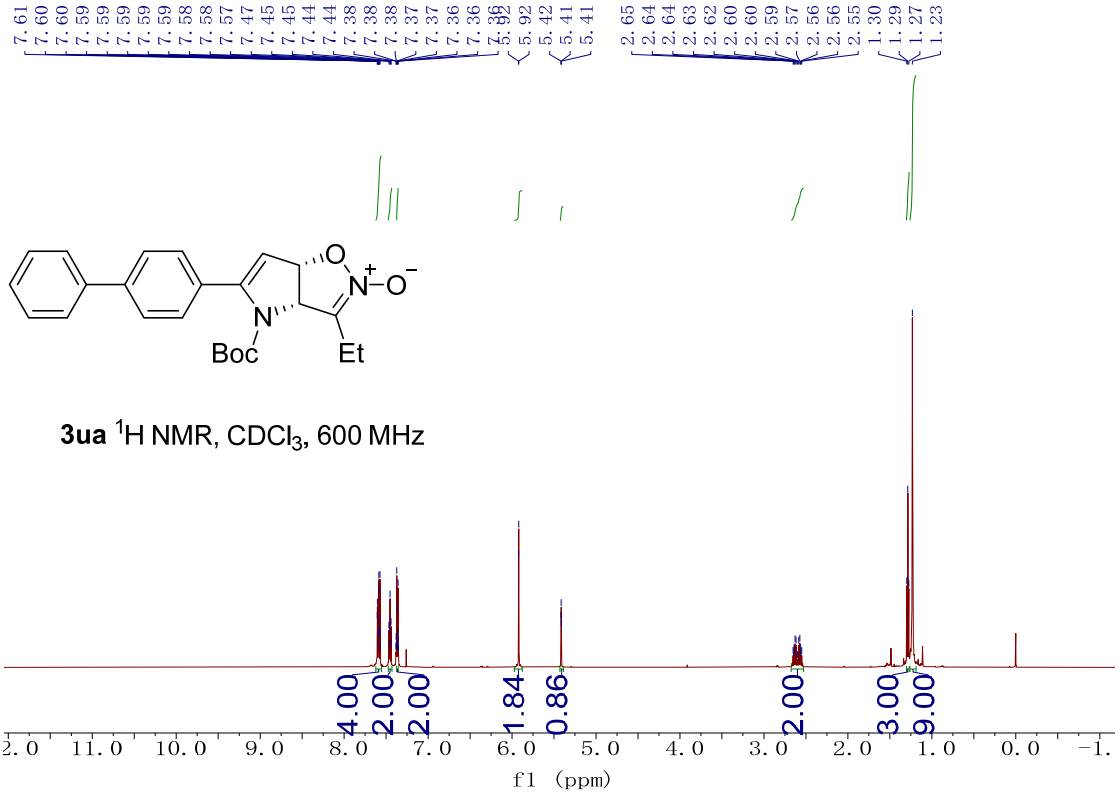


3ta ^{13}C NMR, $CDCl_3$, 101 MHz

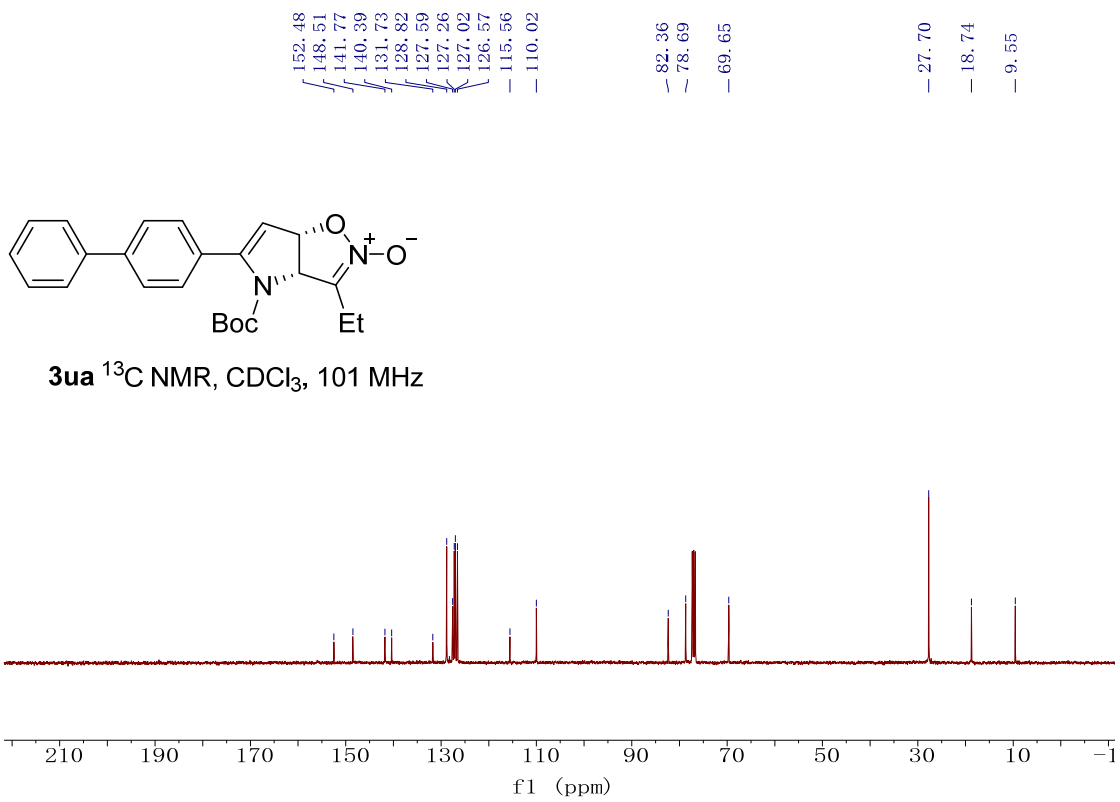


3ta ^{19}F NMR, $CDCl_3$, 565 MHz

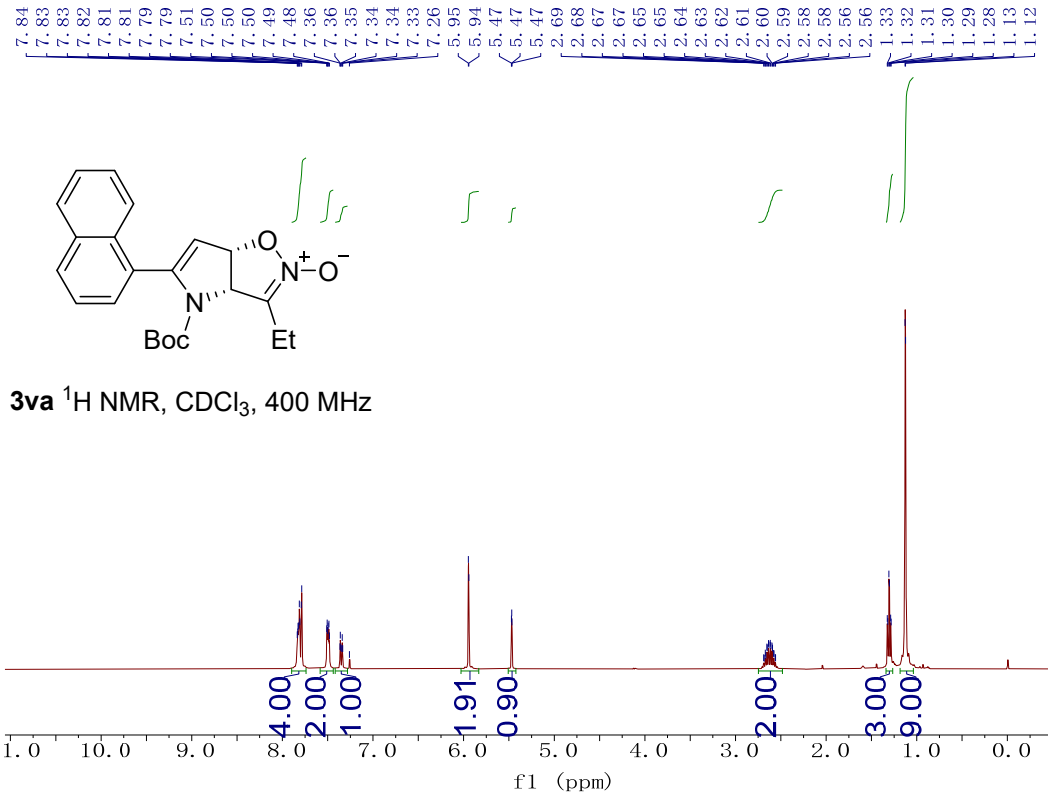




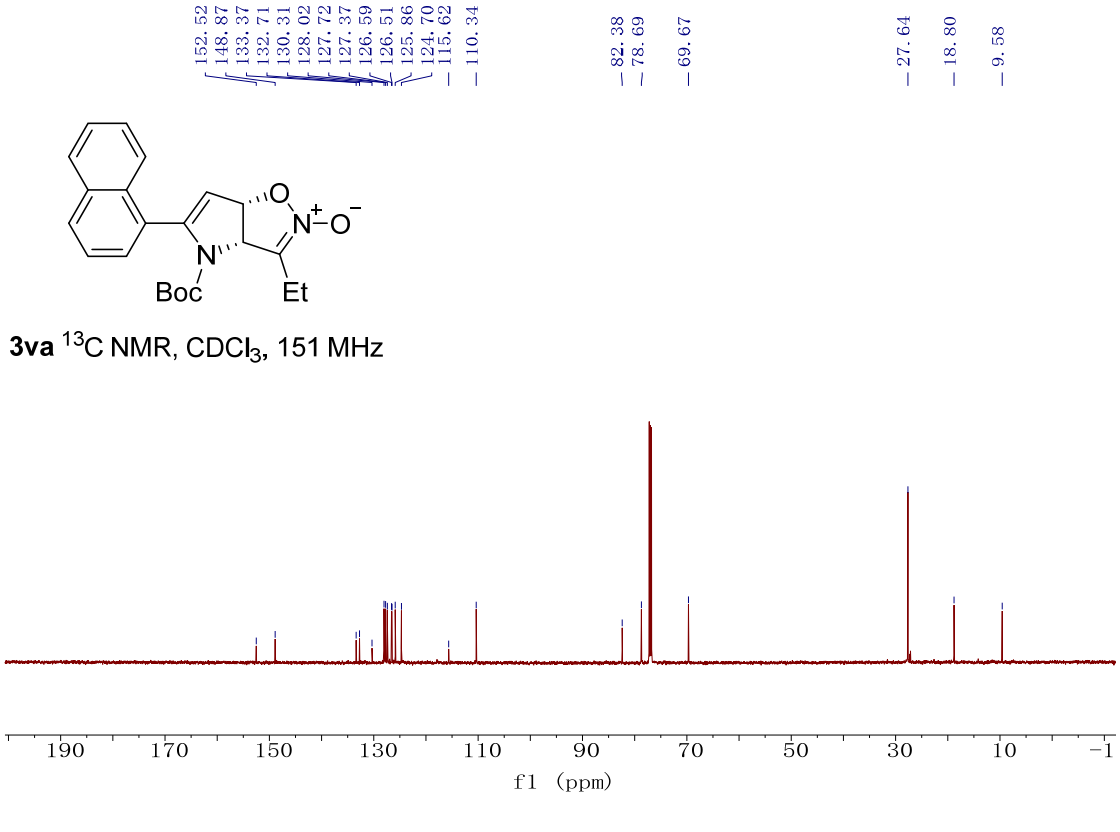
3ua ^{1}H NMR, $CDCl_3$, 600 MHz



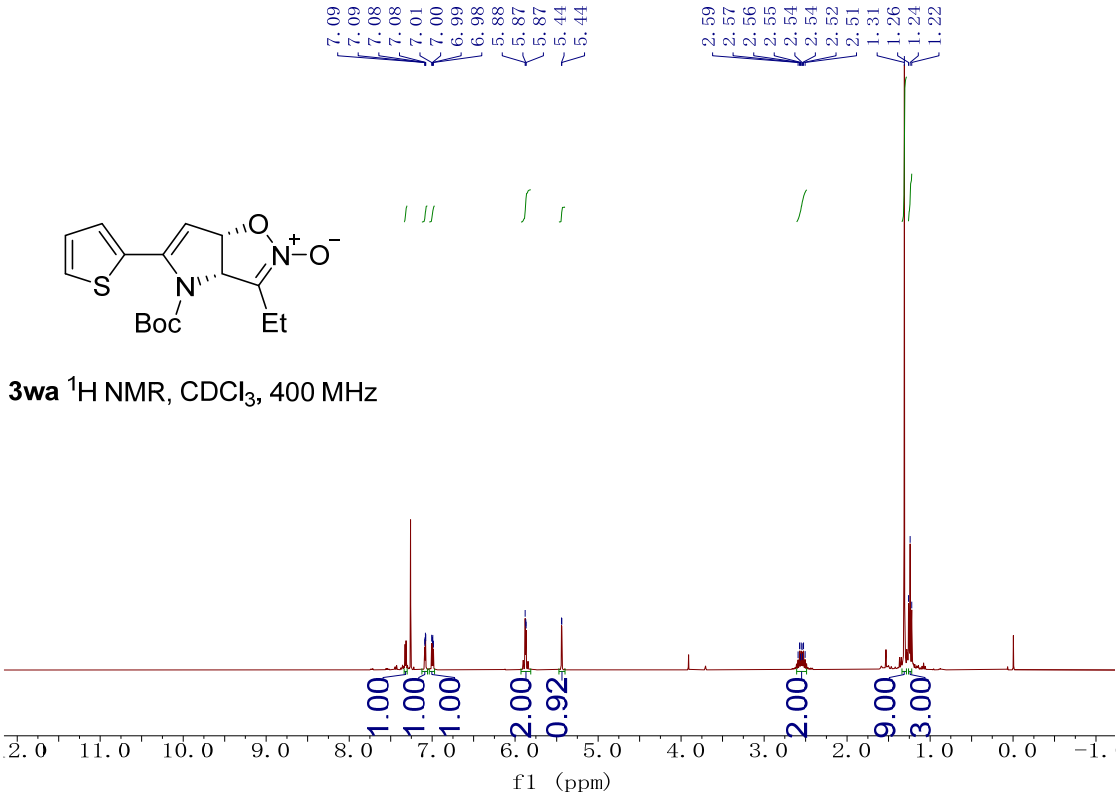
3ua ^{13}C NMR, $CDCl_3$, 101 MHz



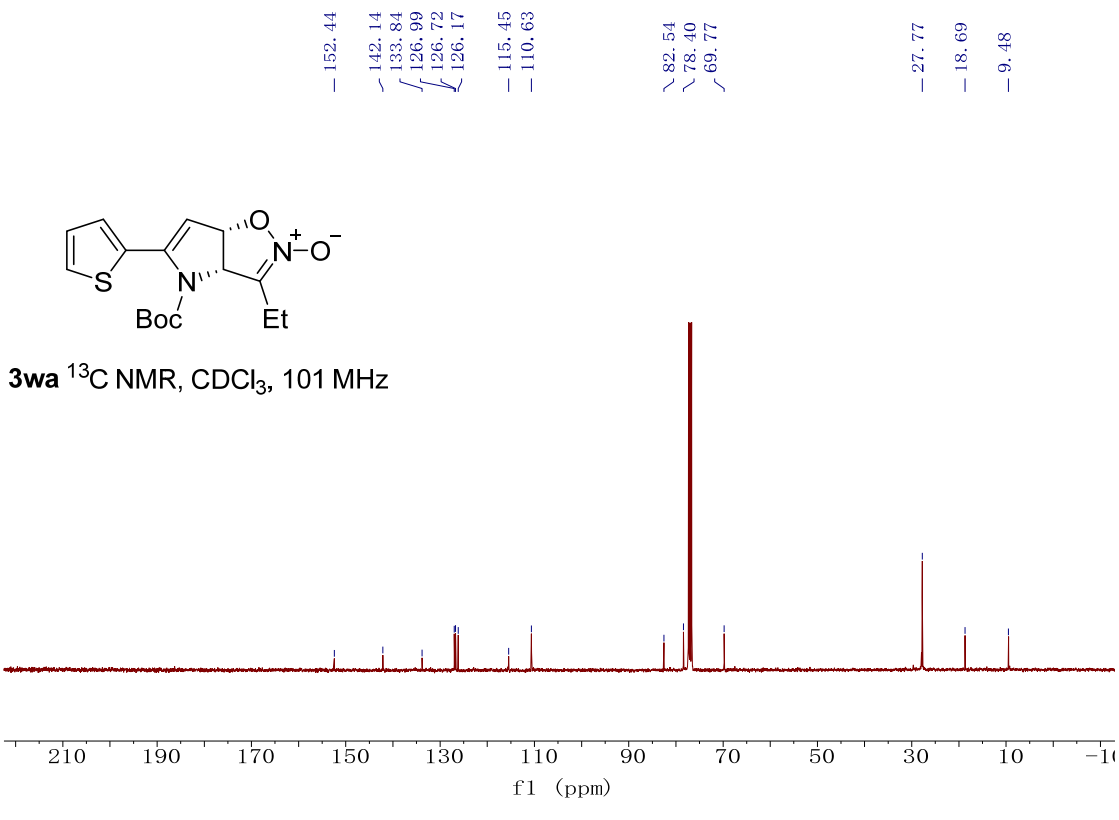
3va ^{1}H NMR, $CDCl_3$, 400 MHz



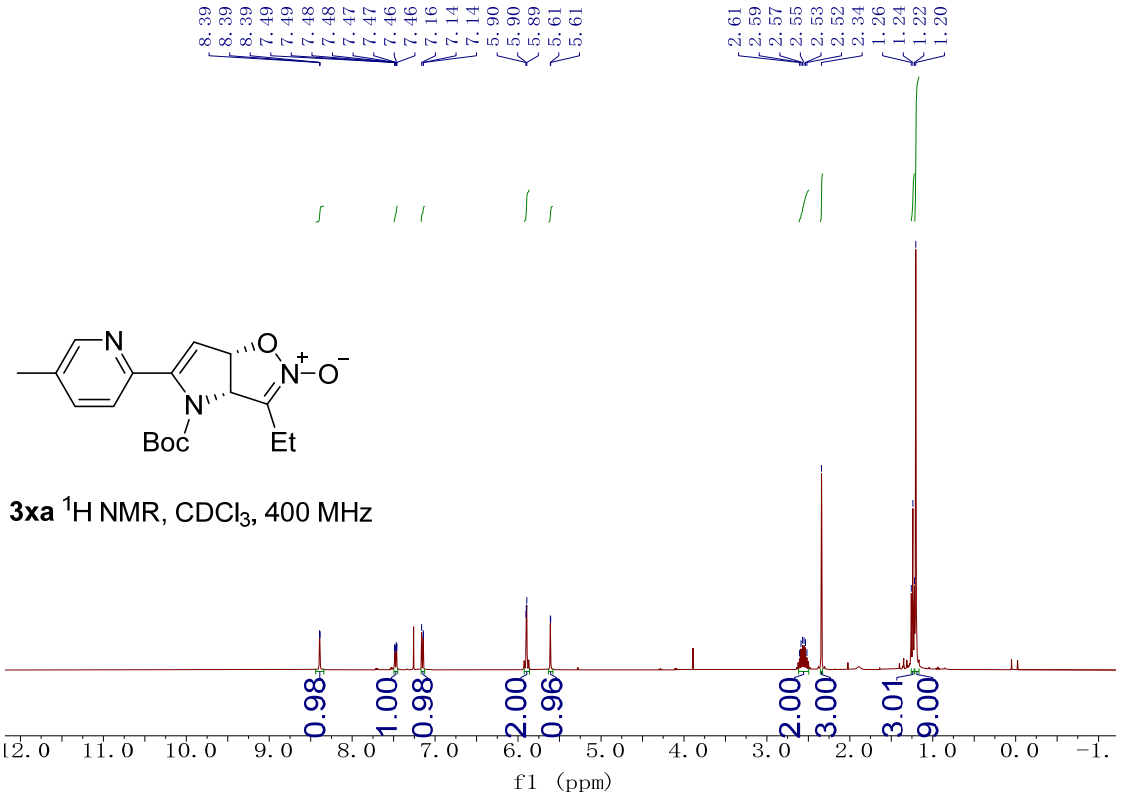
3va ^{13}C NMR, $CDCl_3$, 151 MHz



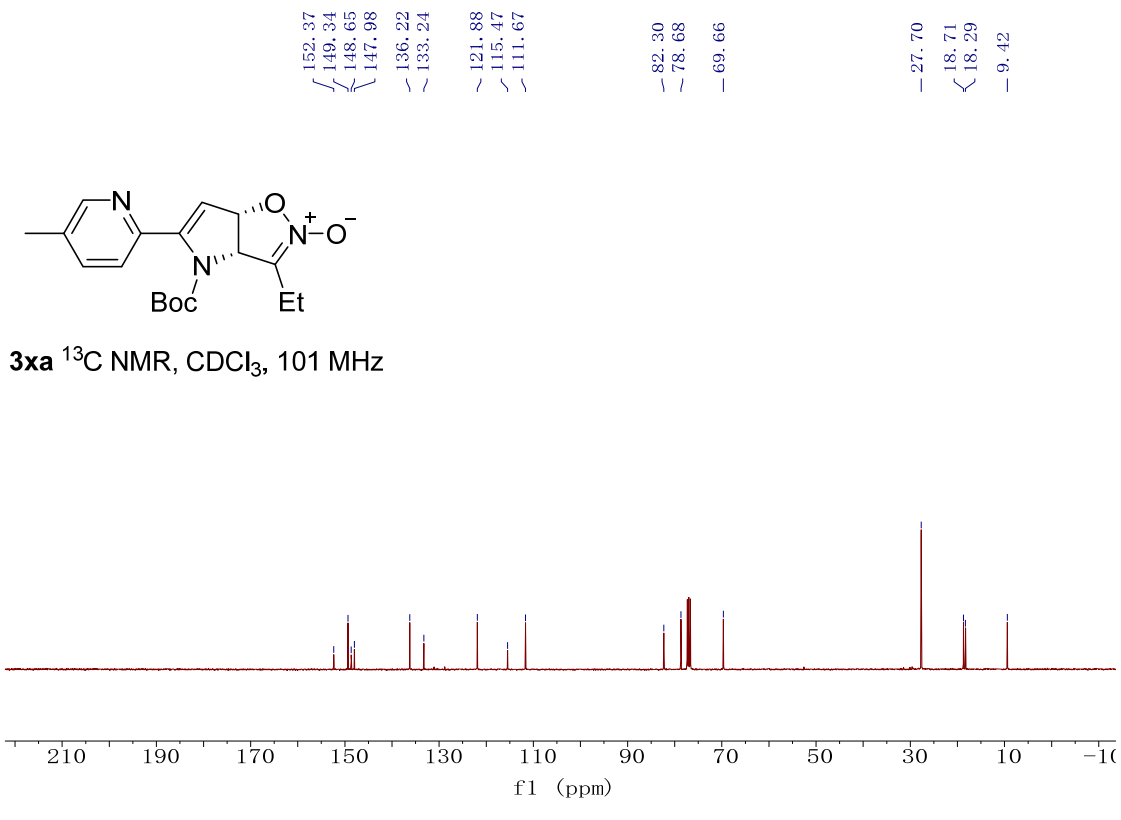
3wa ^{1}H NMR, $CDCl_3$, 400 MHz



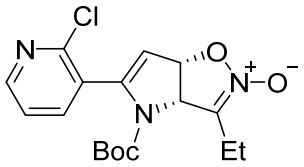
3wa ^{13}C NMR, $CDCl_3$, 101 MHz



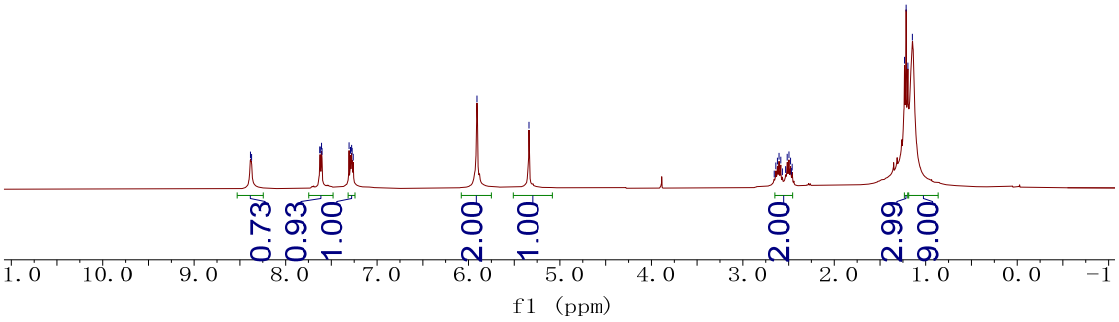
3xa ^{1}H NMR, $CDCl_3$, 400 MHz

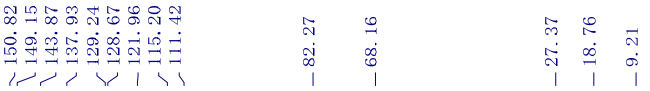


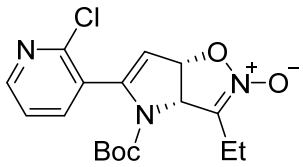
3xa ^{13}C NMR, $CDCl_3$, 101 MHz



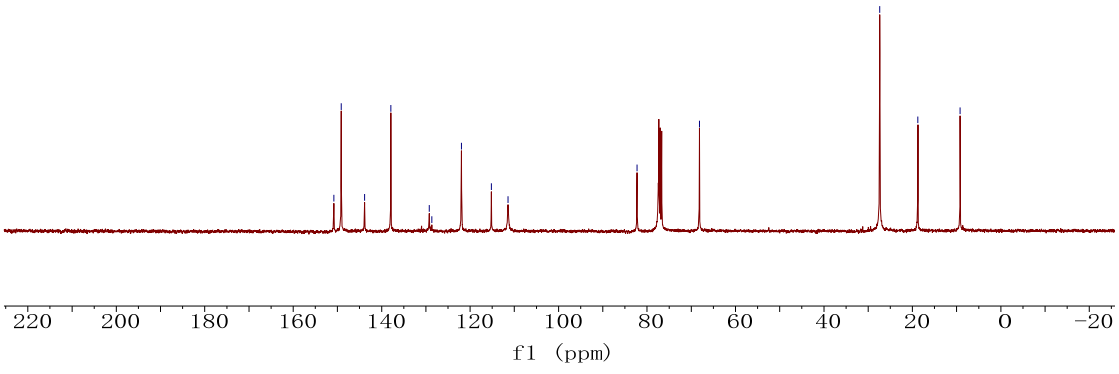
3ya ^{1}H NMR, $CDCl_3$, 400 MHz

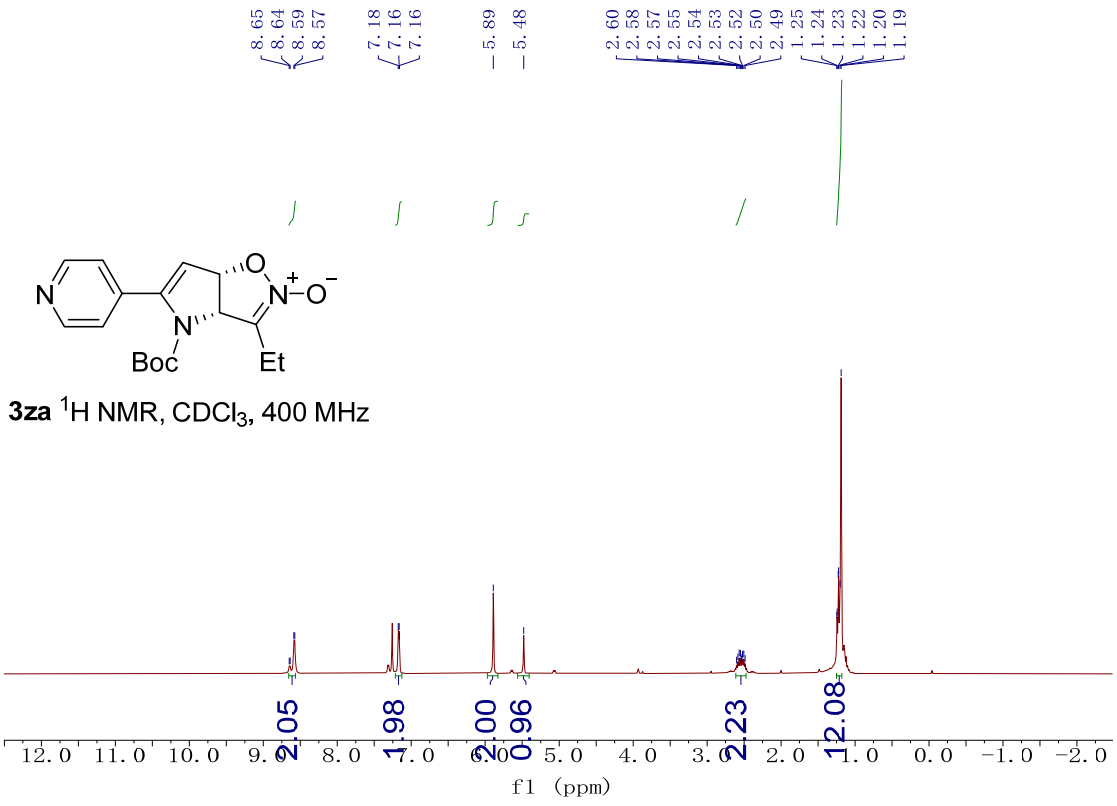




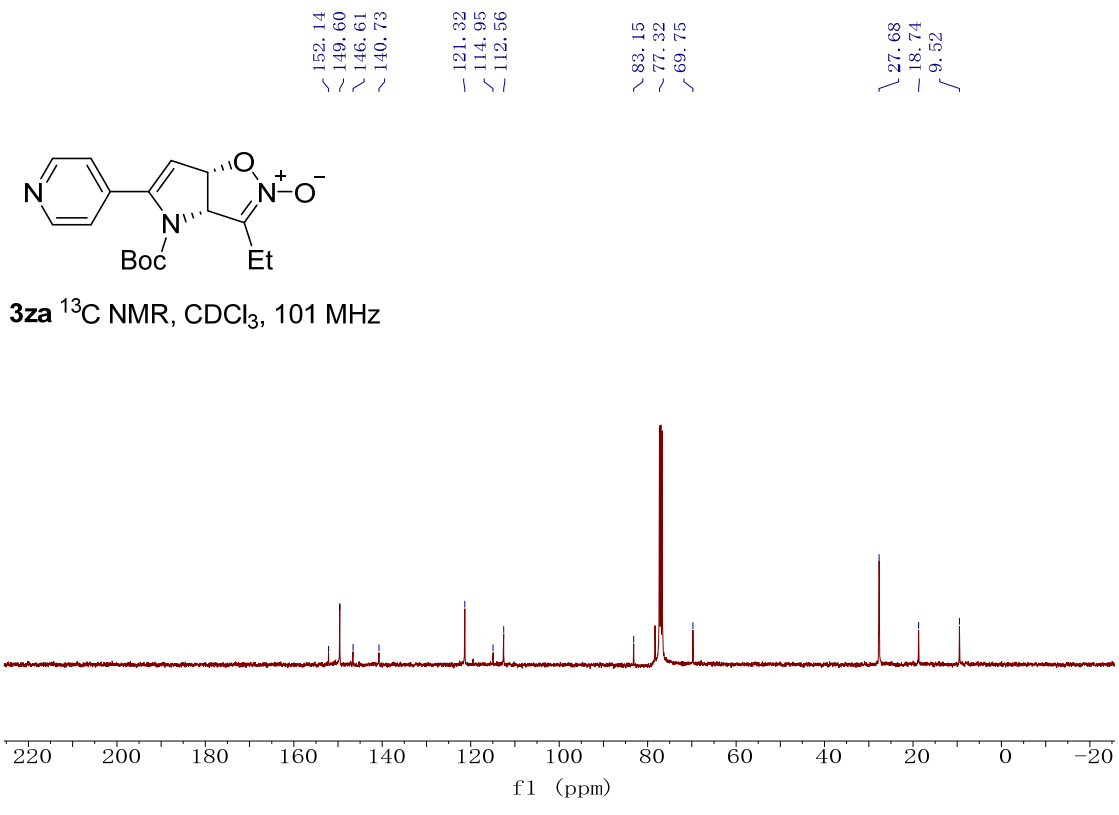


3ya ^{13}C NMR, $CDCl_3$, 101 MHz

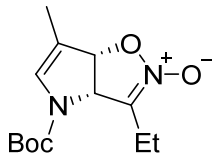


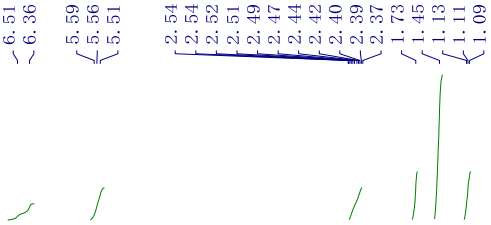


3za ^{1}H NMR, $CDCl_3$, 400 MHz

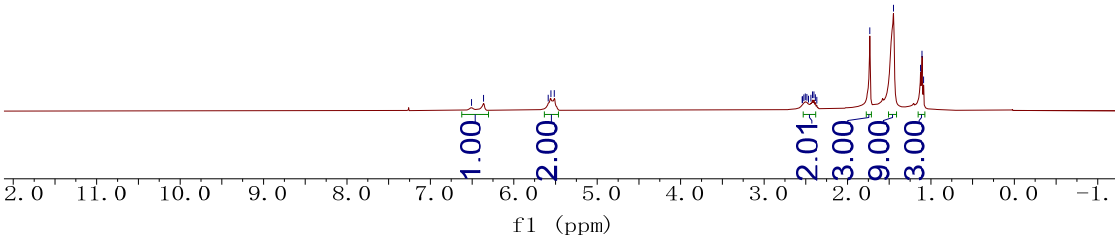


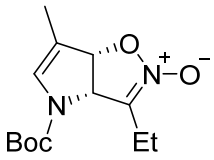
3za ^{13}C NMR, $CDCl_3$, 101 MHz



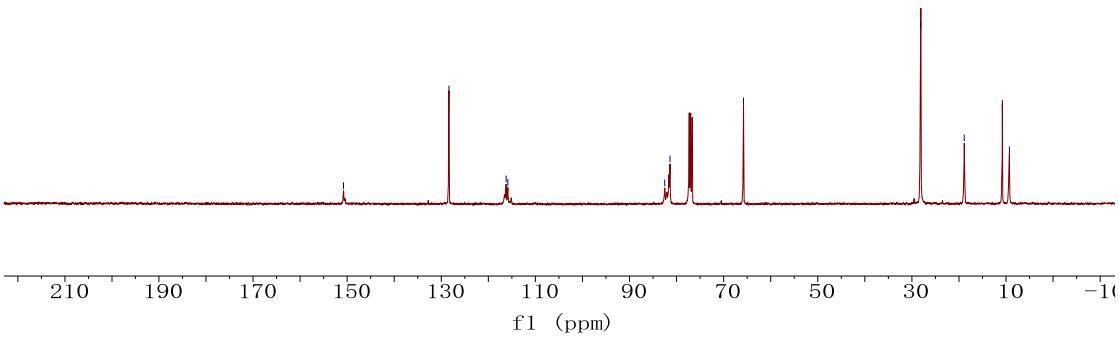


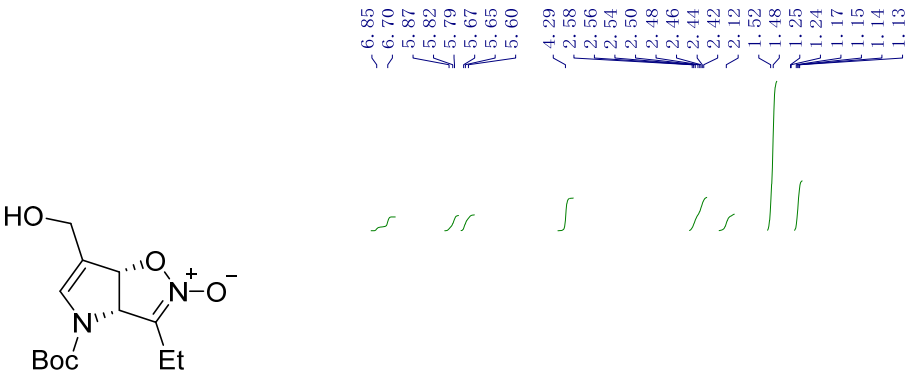
3a′a ^{1}H NMR, $CDCl_3$, 400 MHz



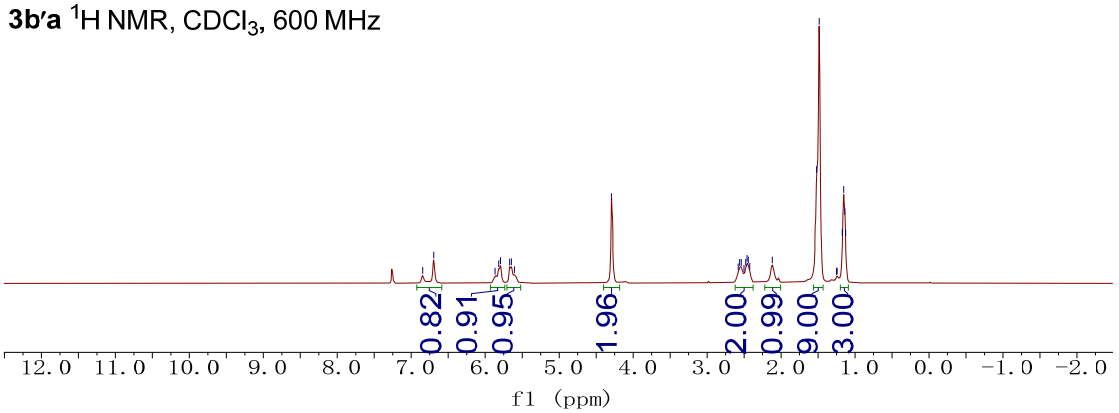


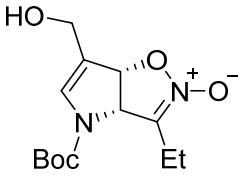
3a′a ^{13}C NMR, $CDCl_3$, 101 MHz



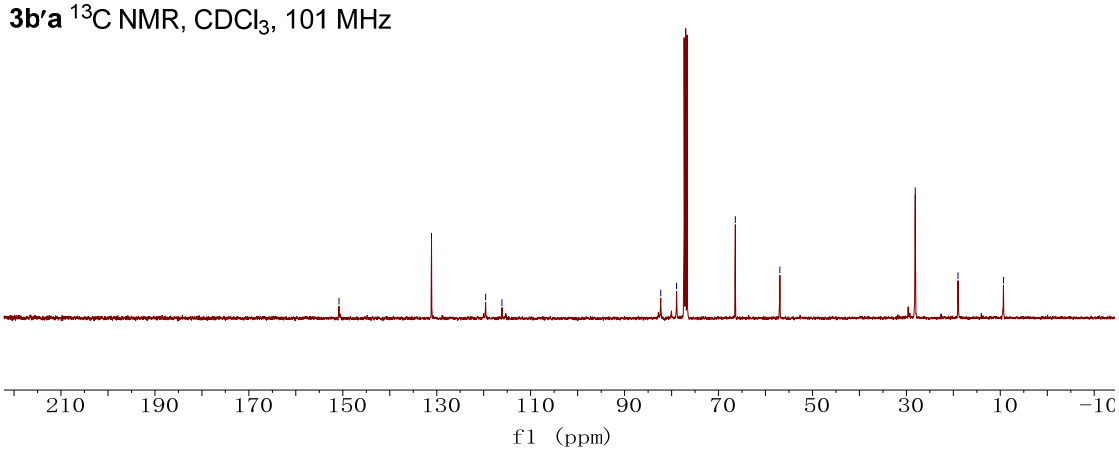


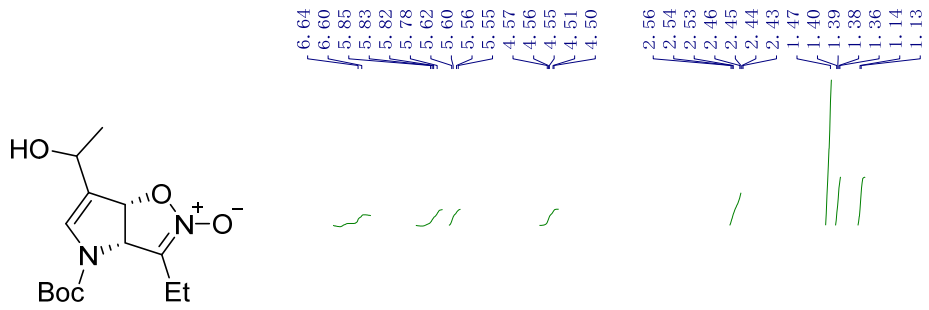
3b′a ^{1}H NMR, $CDCl_3$, 600 MHz



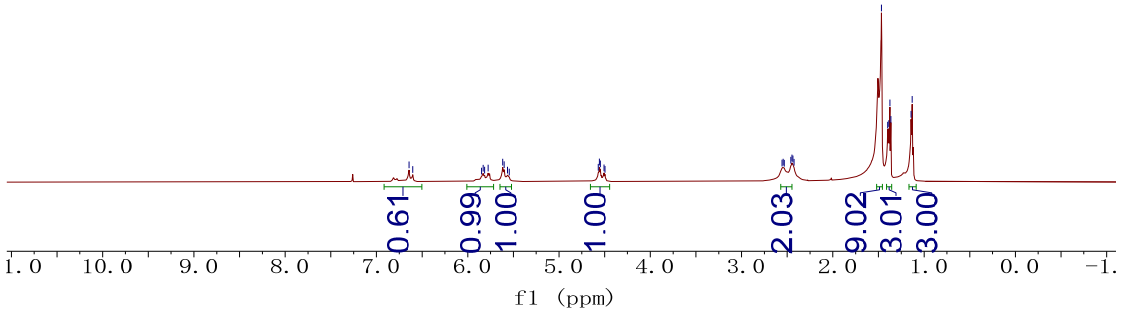


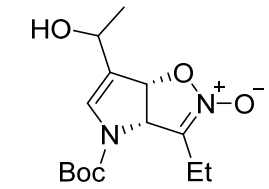
3b′a ^{13}C NMR, $CDCl_3$, 101 MHz



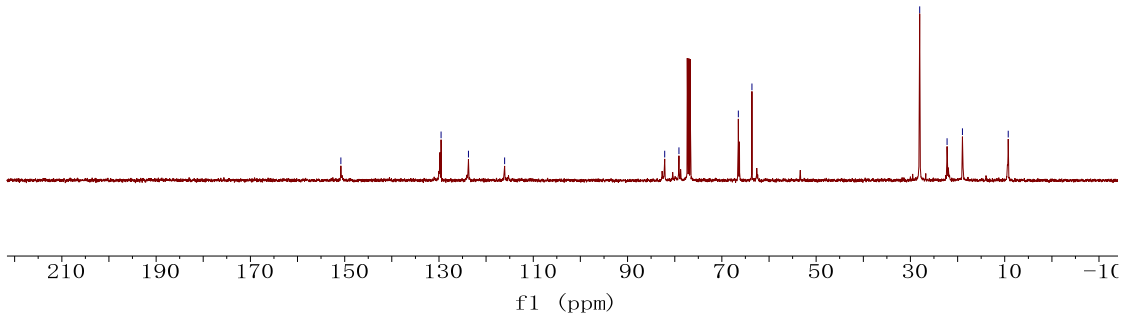


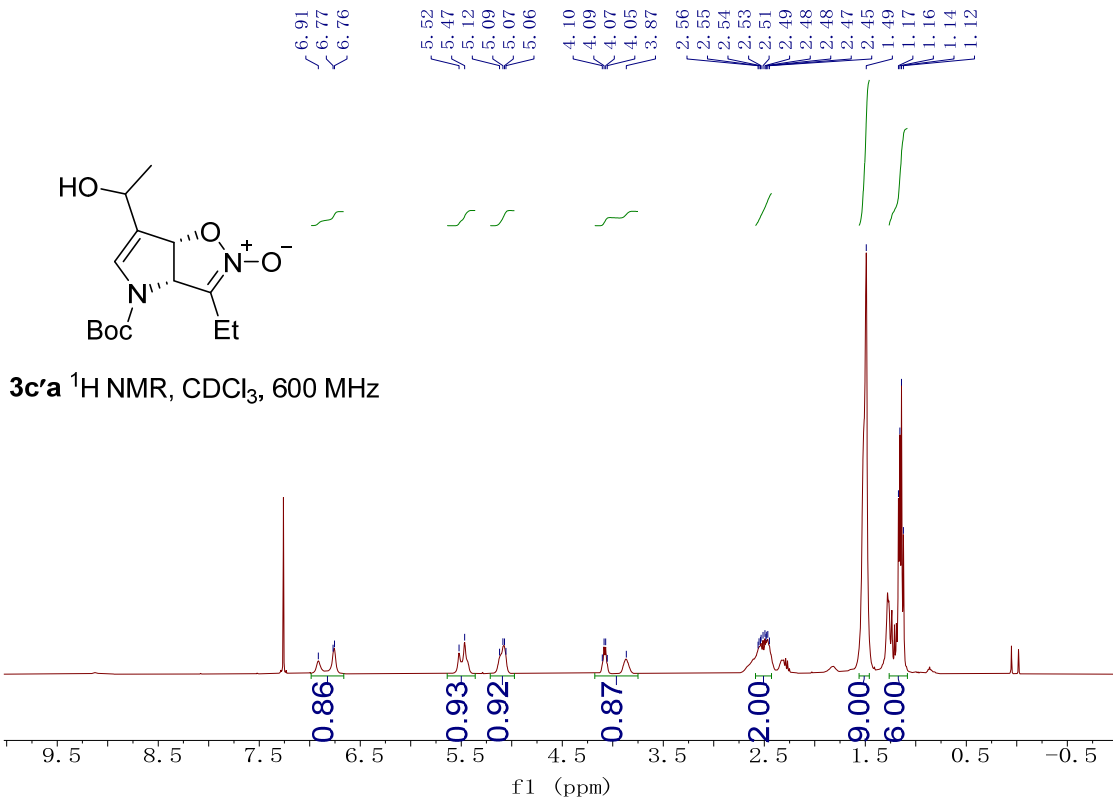
3c′a ^{1}H NMR, $CDCl_3$, 600 MHz



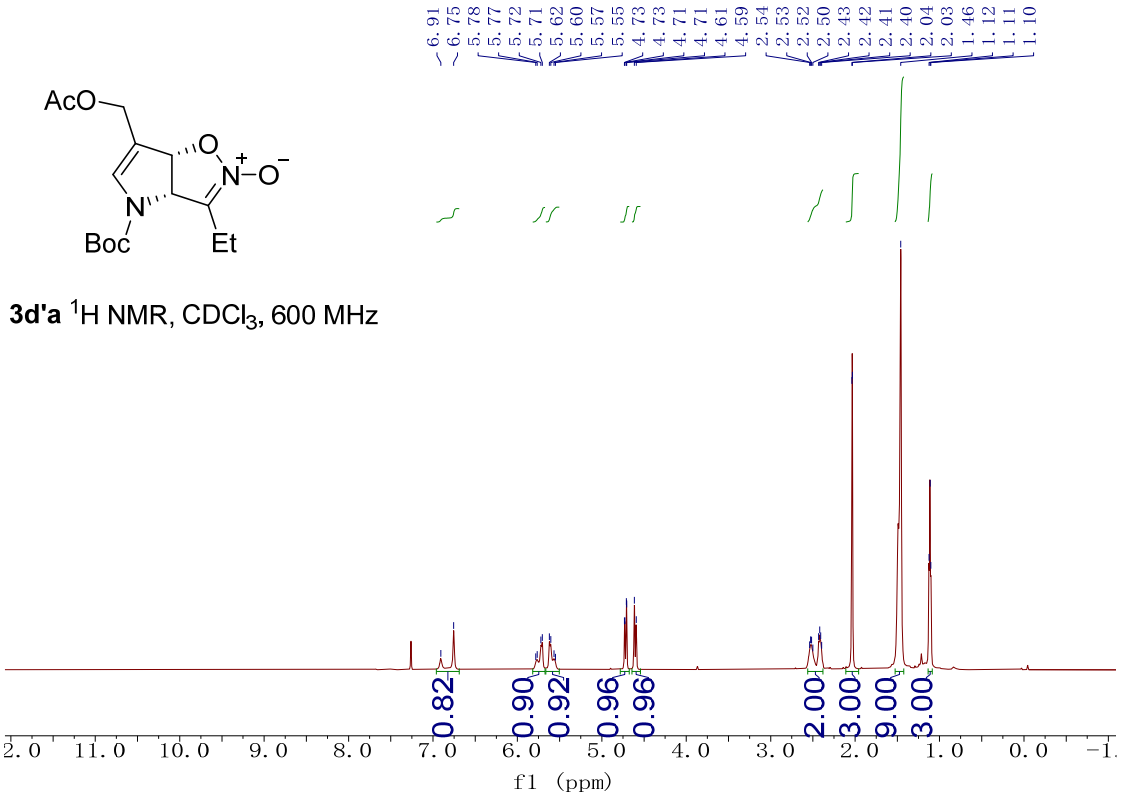


3c′a ^{13}C NMR, $CDCl_3$, 101 MHz

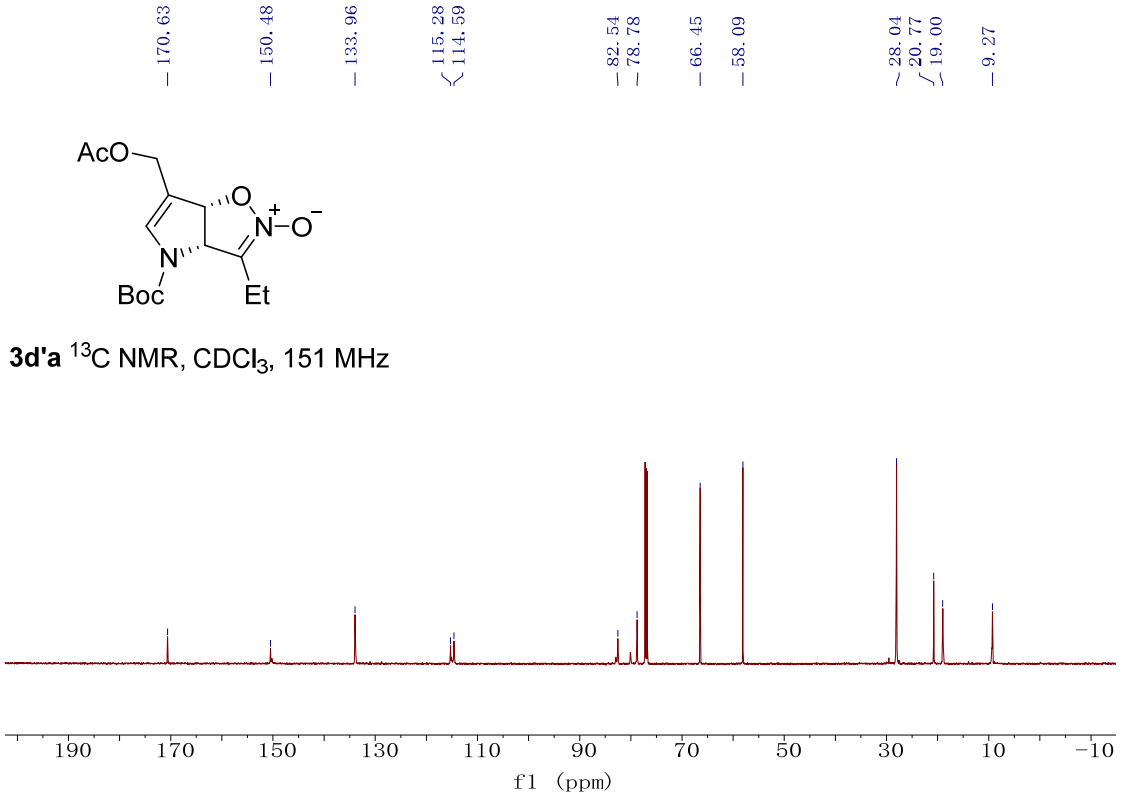




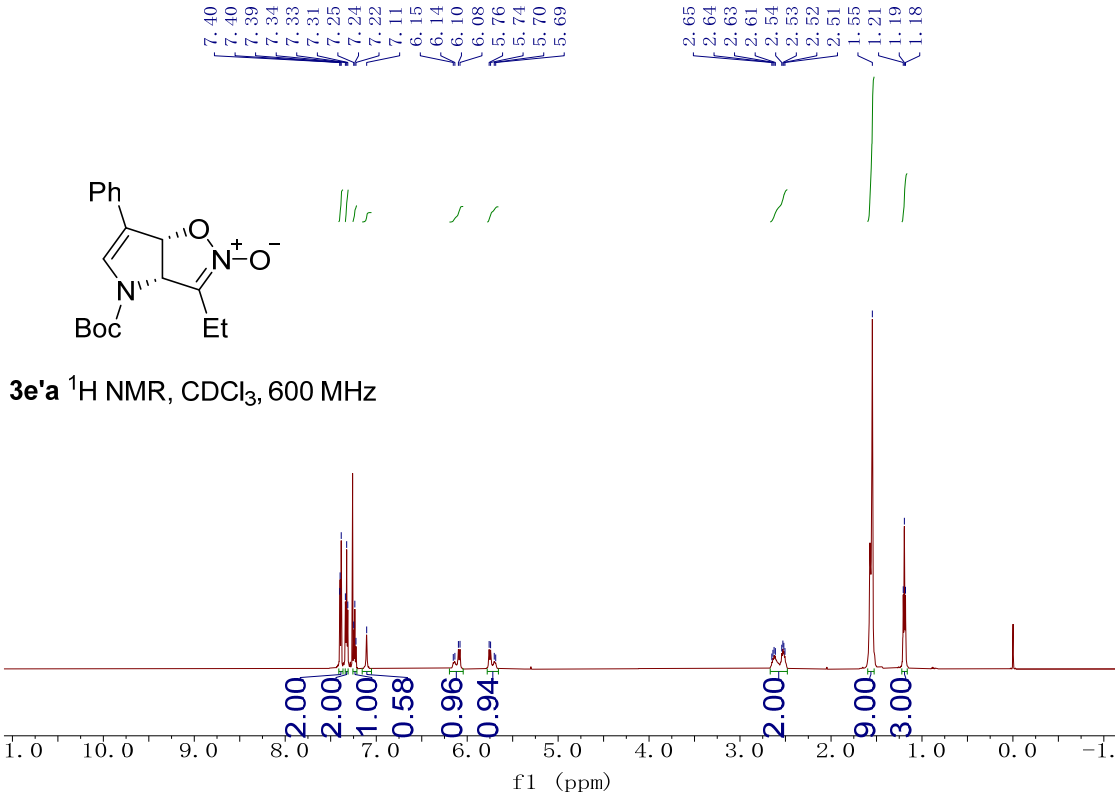
3c′a ^{1}H NMR, $CDCl_3$, 600 MHz



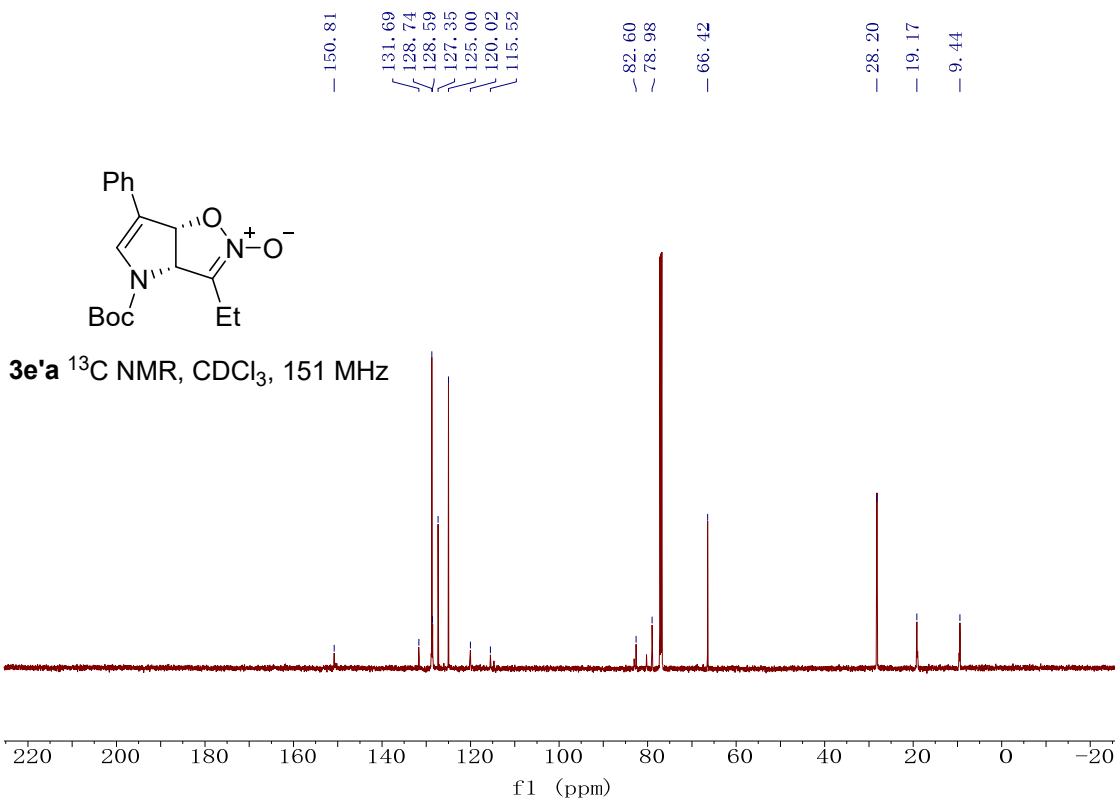
3d'a ^{1}H NMR, $CDCl_3$, 600 MHz



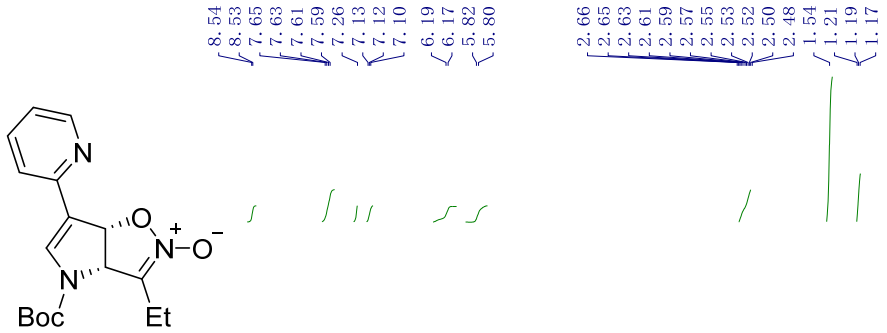
3d'a ^{13}C NMR, $CDCl_3$, 151 MHz



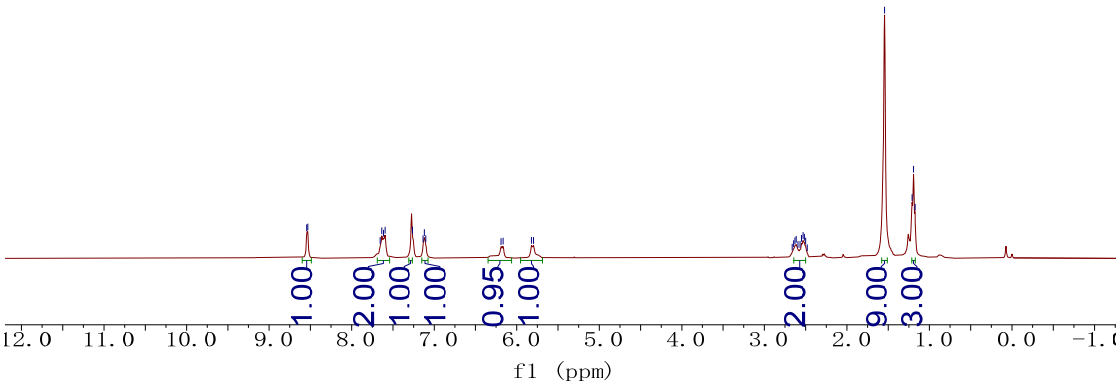
3e'a ^{1}H NMR, $CDCl_3$, 600 MHz



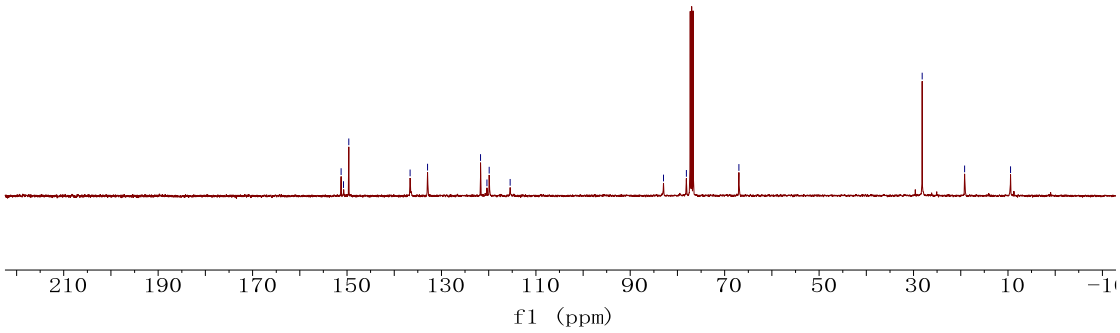
3e'a ^{13}C NMR, $CDCl_3$, 151 MHz

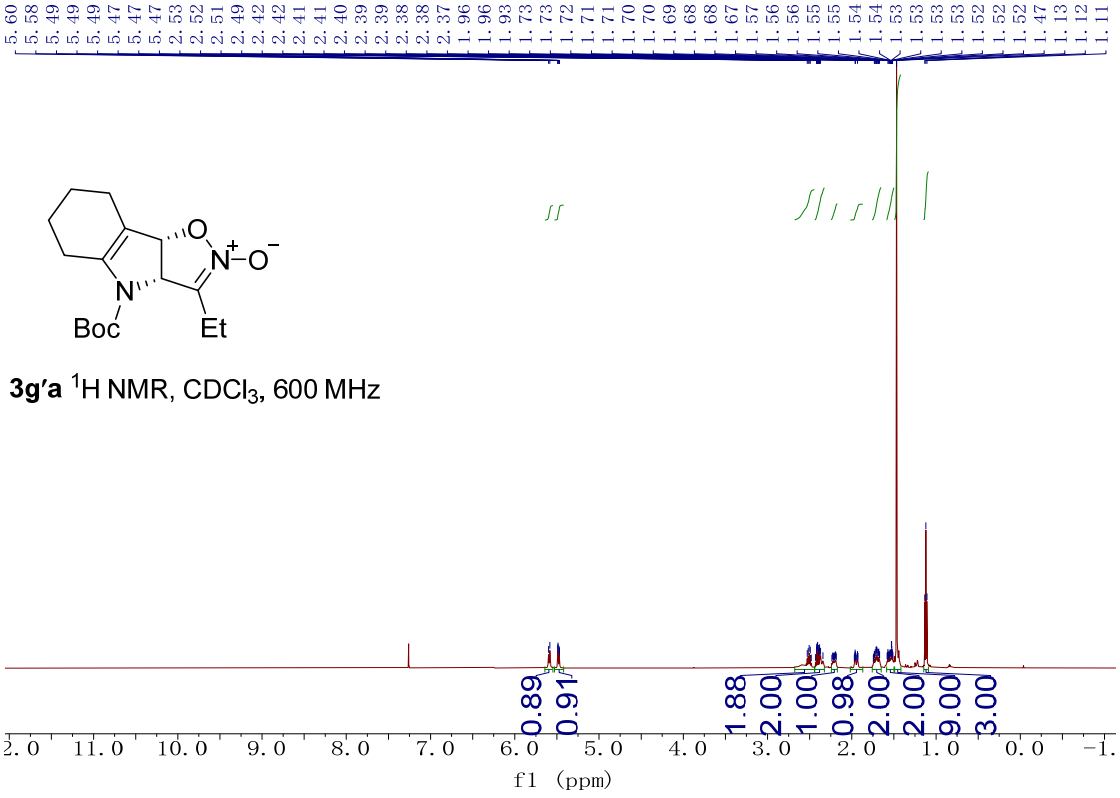


3f′a ^{1}H NMR, $CDCl_3$, 400 MHz

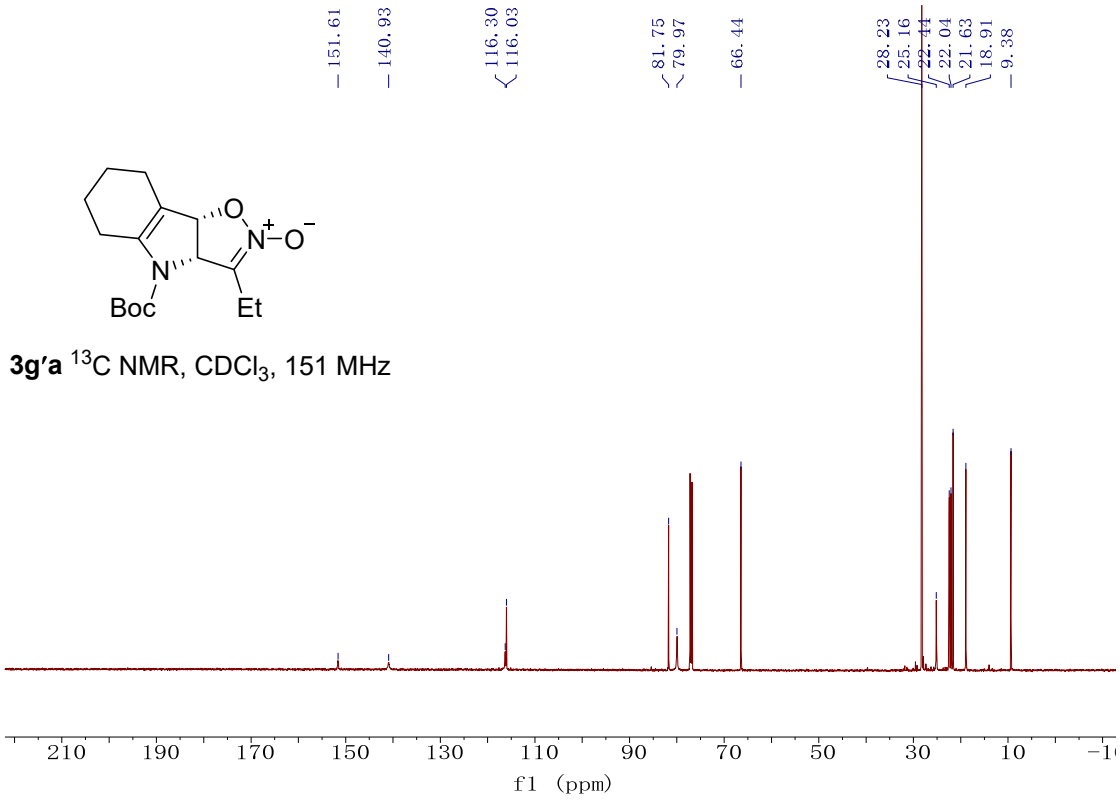


3f′a ^{13}C NMR, $CDCl_3$, 101 MHz

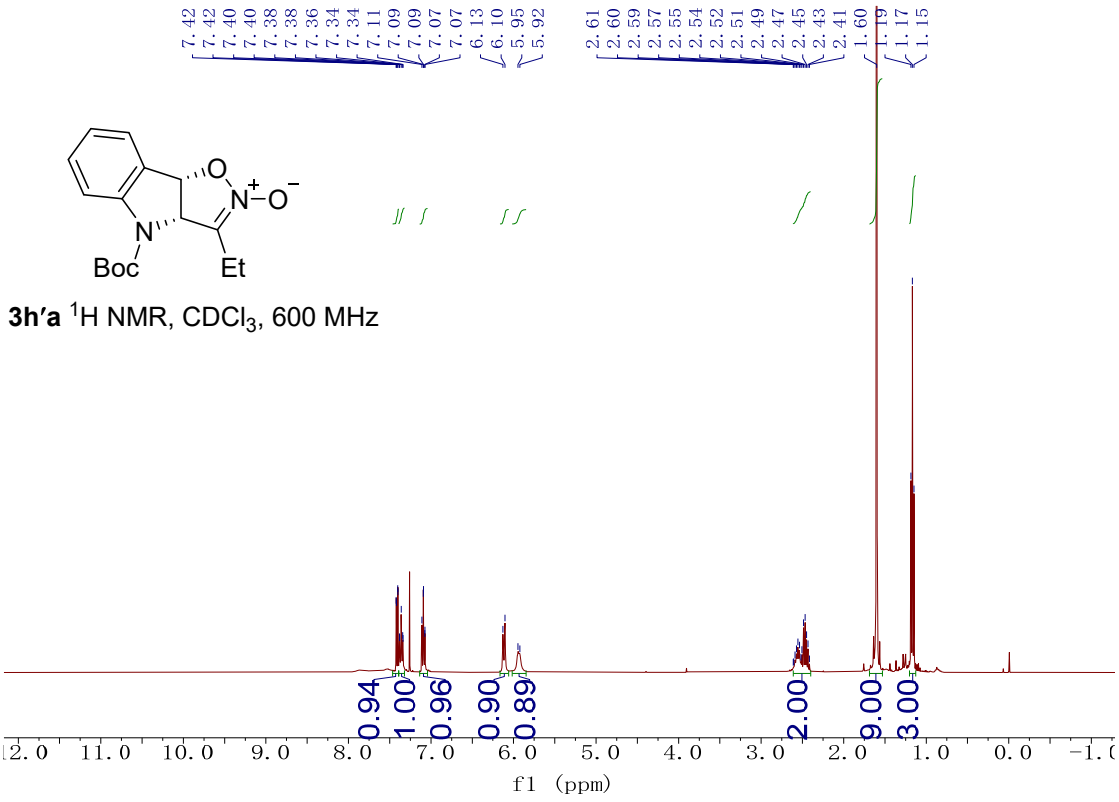




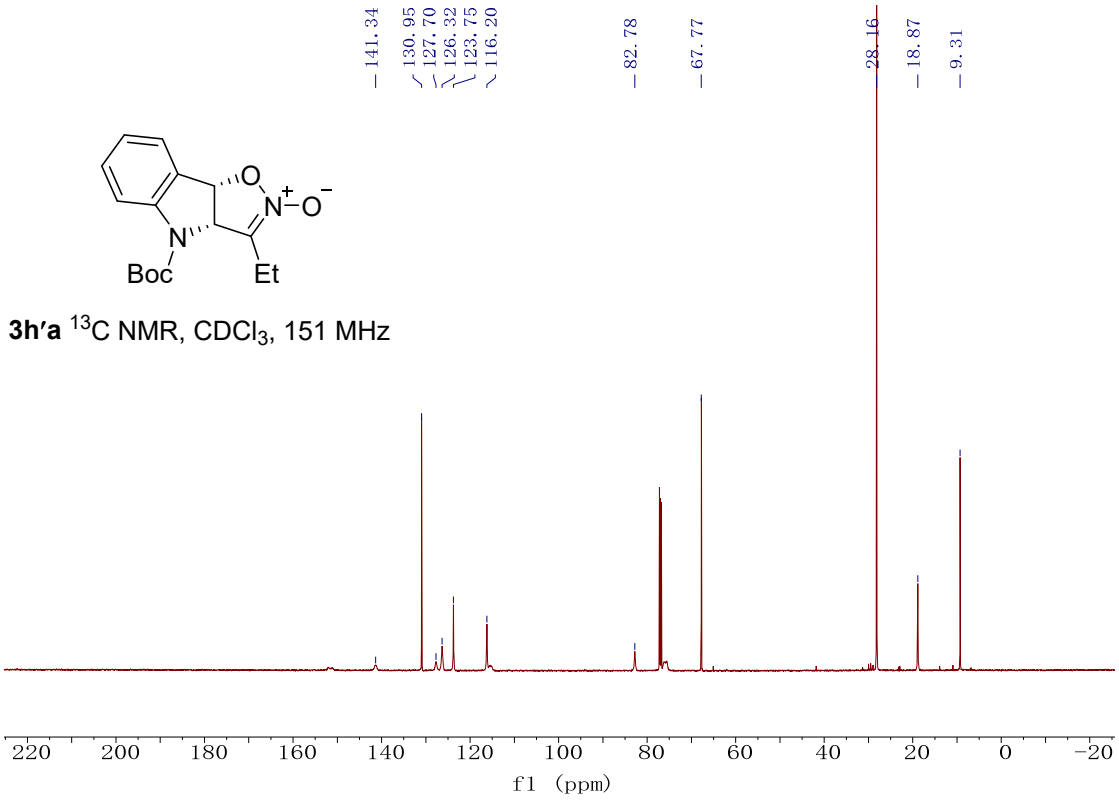
3g′a ^{1}H NMR, $CDCl_3$, 600 MHz



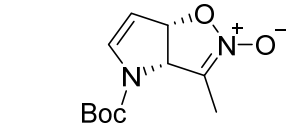
3g′a ^{13}C NMR, $CDCl_3$, 151 MHz



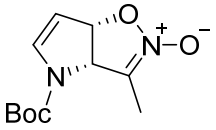
3h′a ^{1}H NMR, $CDCl_3$, 600 MHz



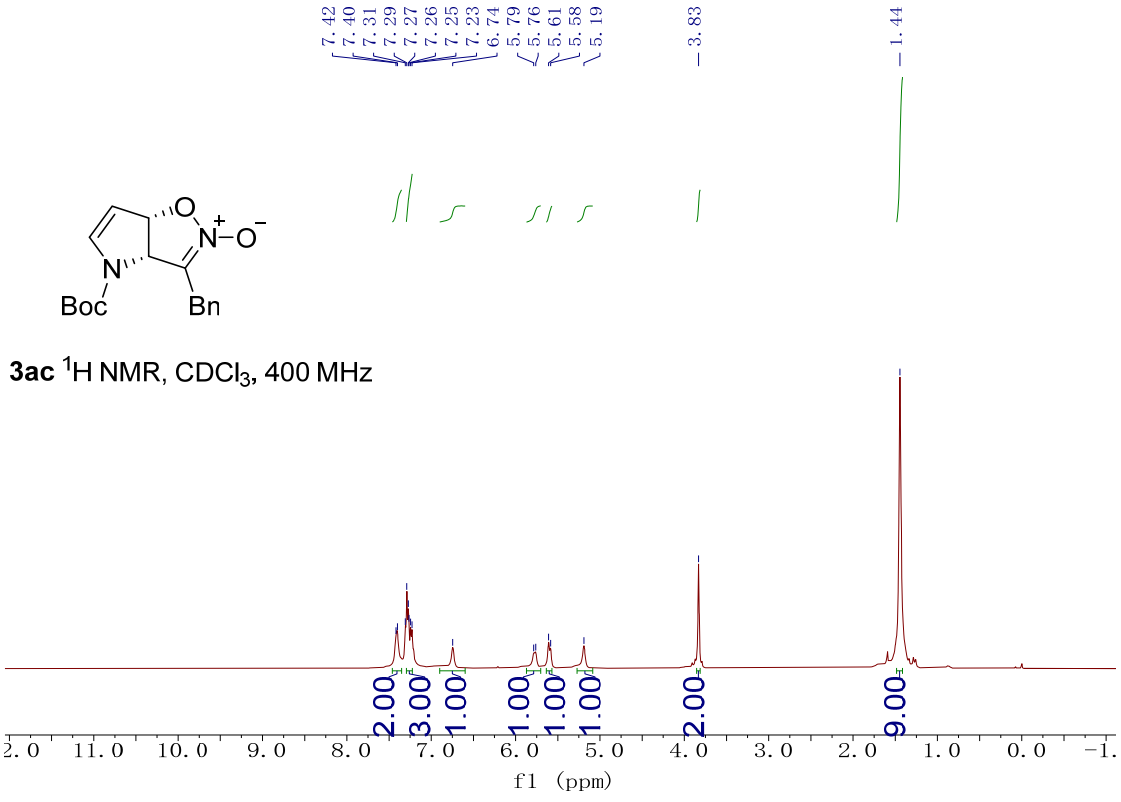
3h′a ^{13}C NMR, $CDCl_3$, 151 MHz



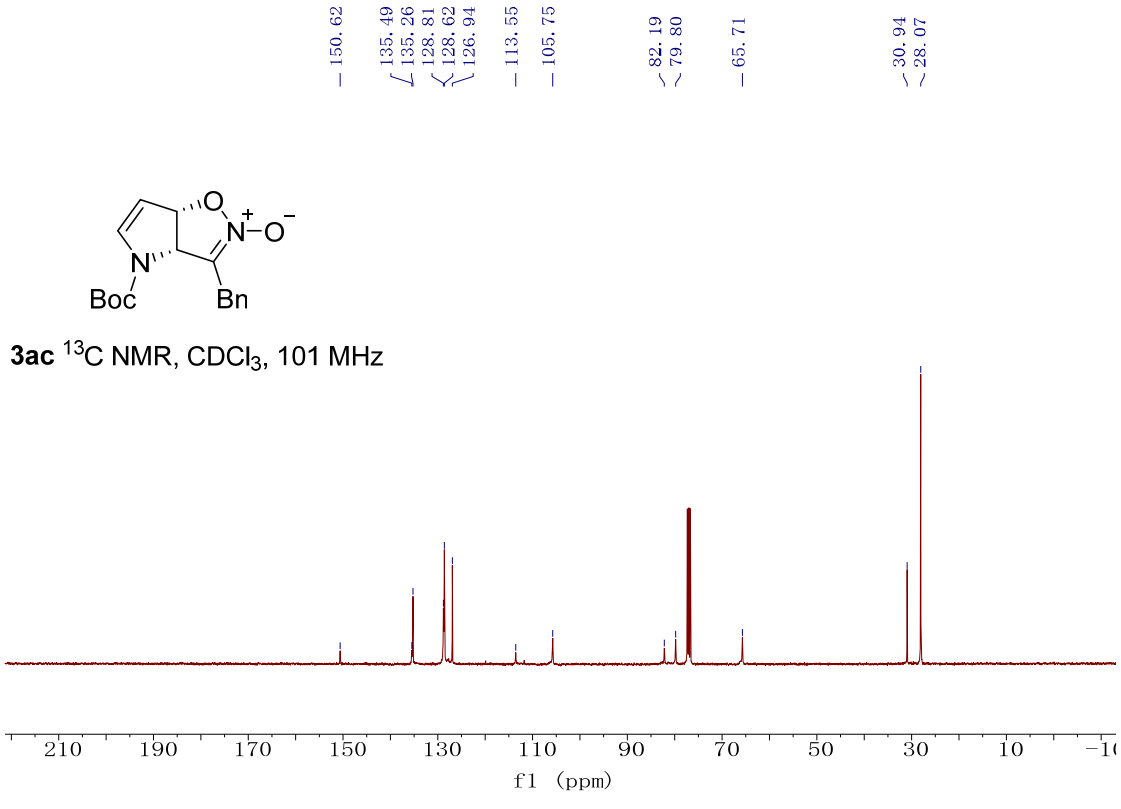
3ab ^{1}H NMR, $CDCl_3$, 600 MHz



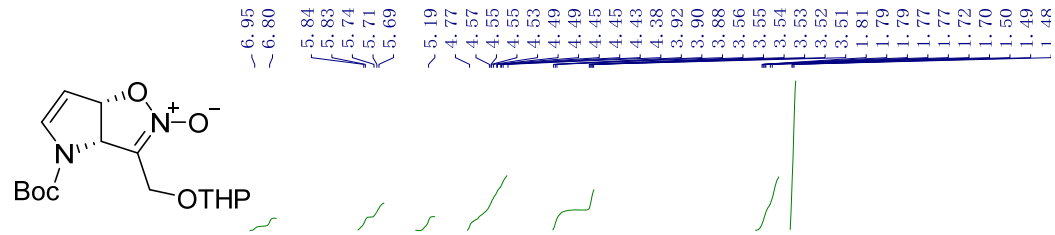
3ab ^{13}C NMR, $CDCl_3$, 151 MHz



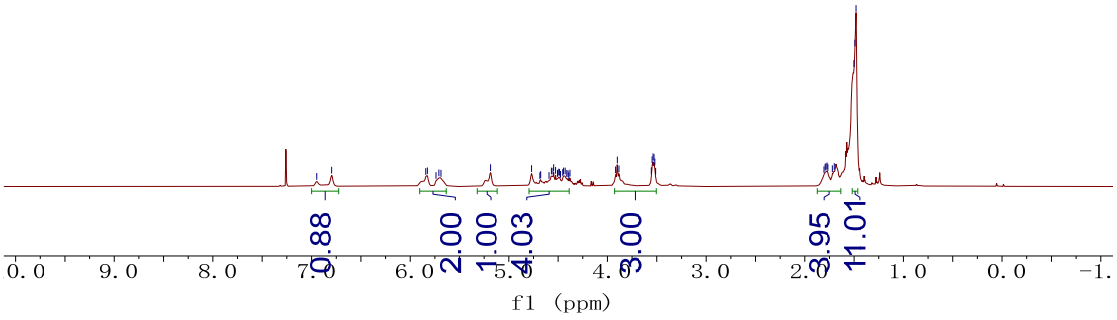
3ac ^{1}H NMR, $CDCl_3$, 400 MHz

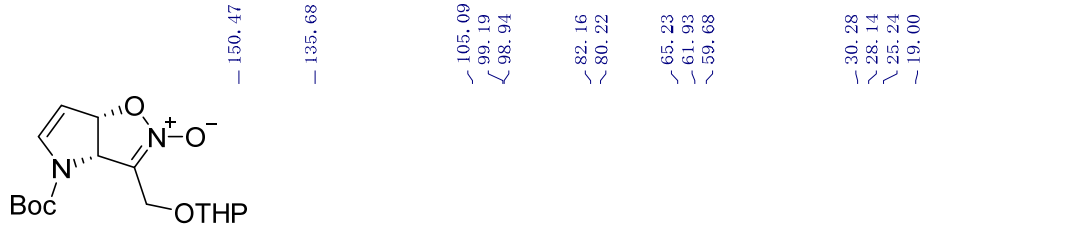


3ac ^{13}C NMR, $CDCl_3$, 101 MHz

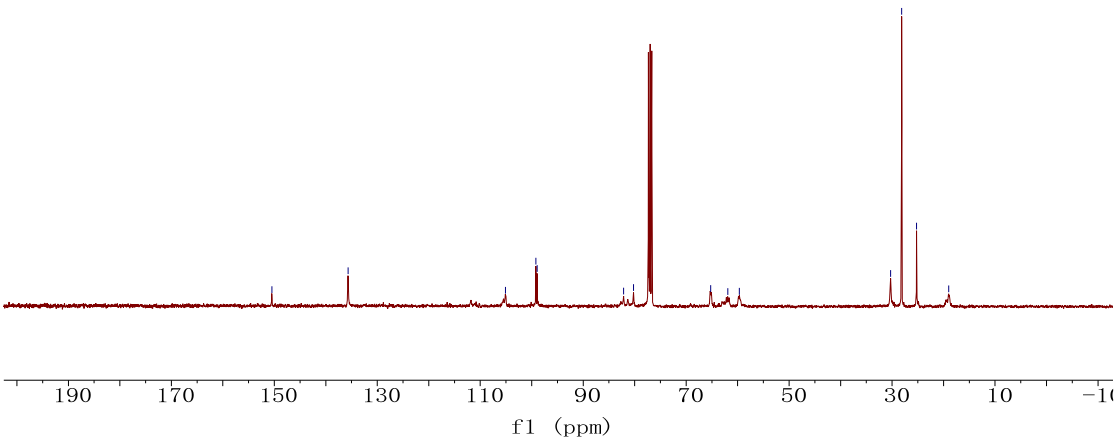


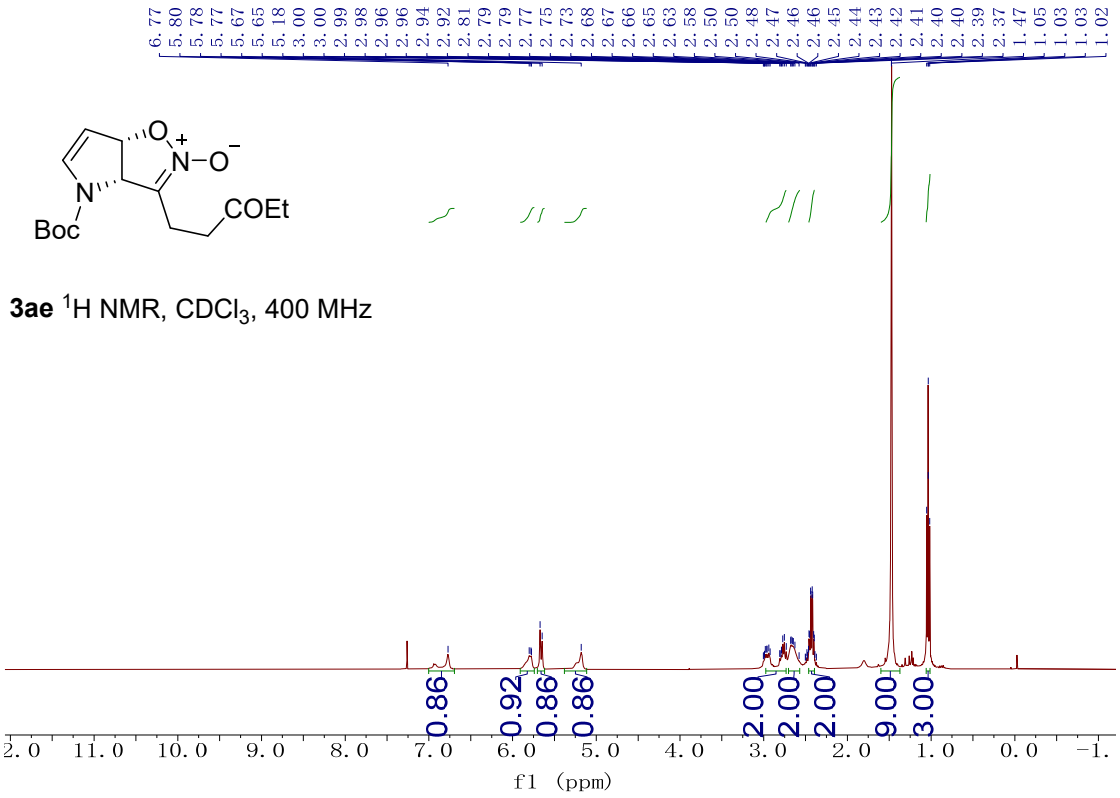
3ad ^{1}H NMR, $CDCl_3$, 400 MHz



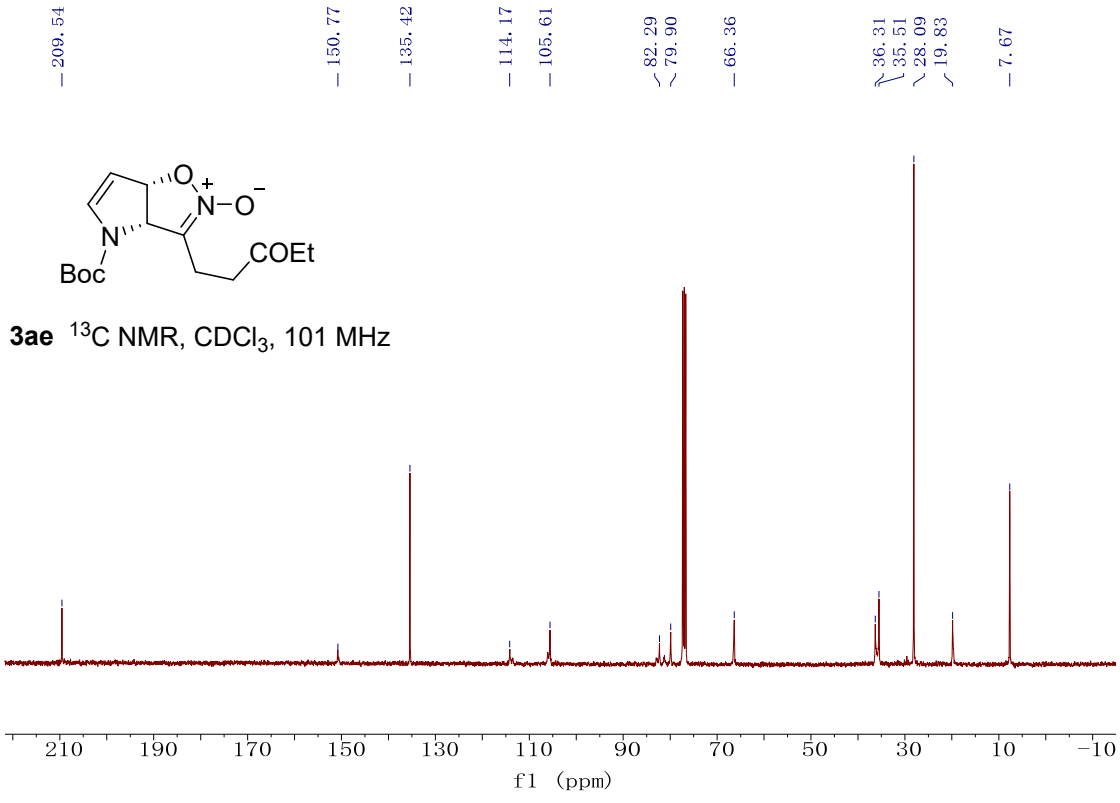


3ad ^{13}C NMR, $CDCl_3$, 101 MHz

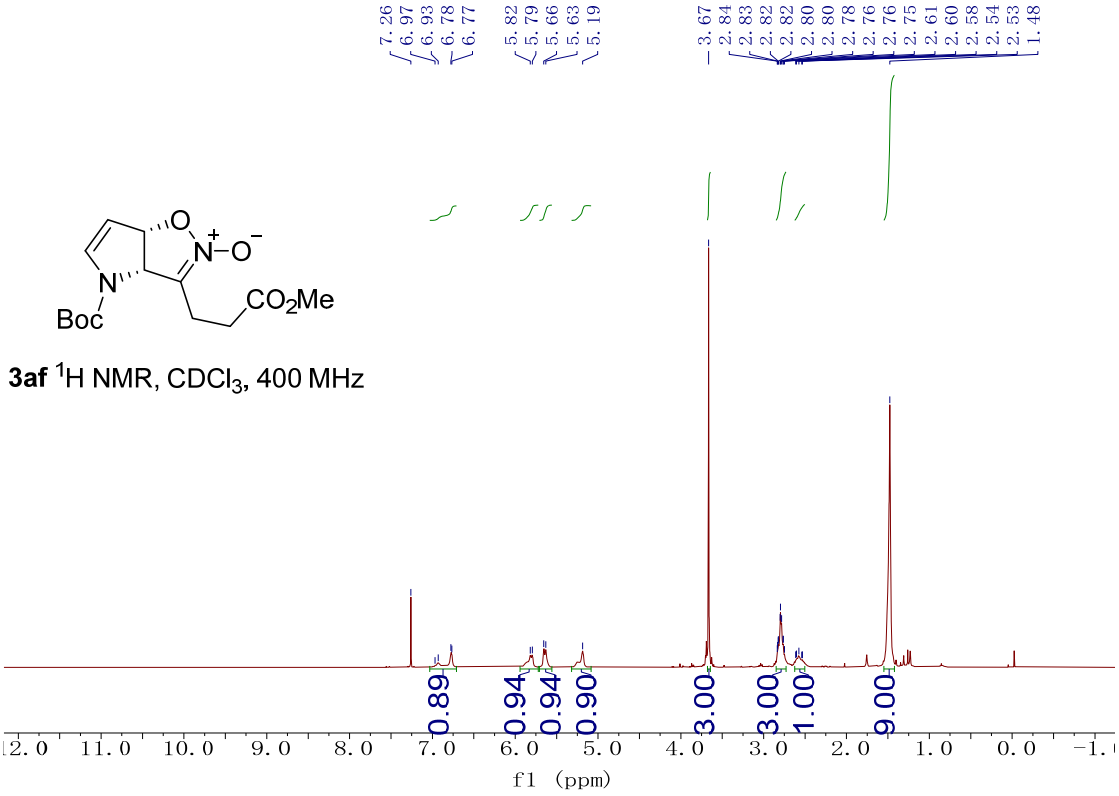




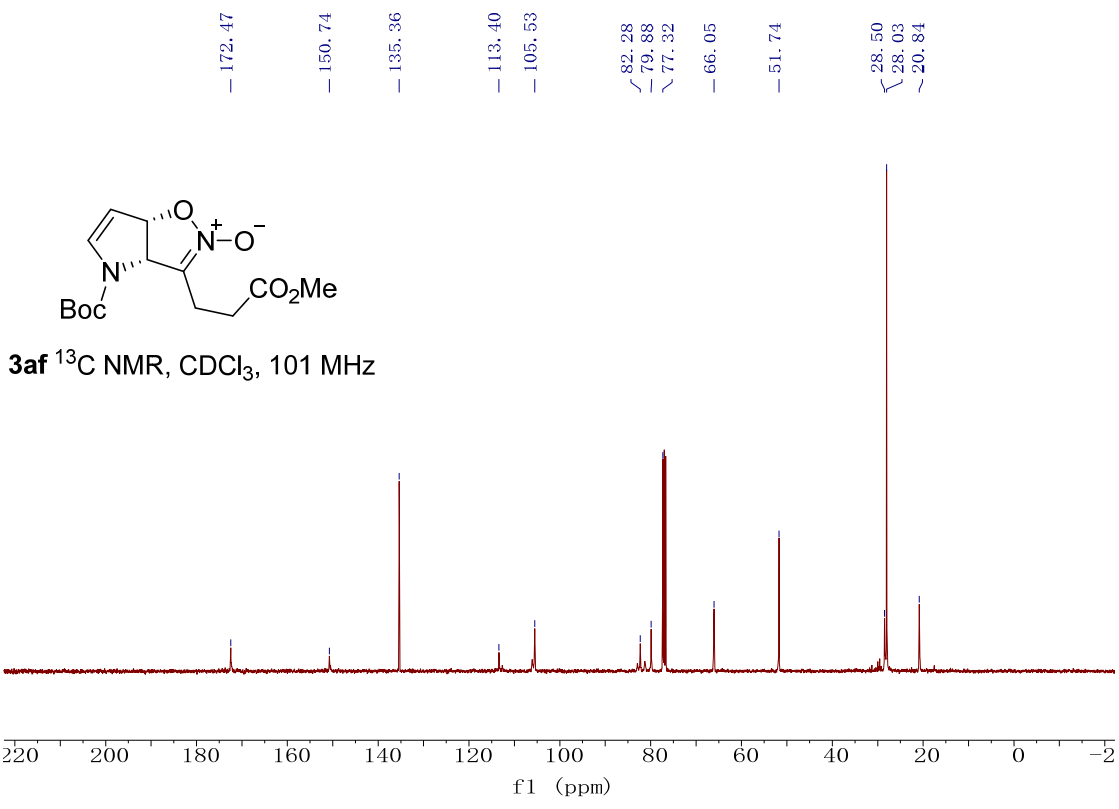
3ae ^{1}H NMR, $CDCl_3$, 400 MHz



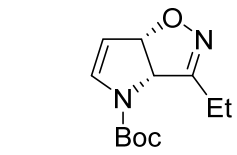
3ae ^{13}C NMR, $CDCl_3$, 101 MHz



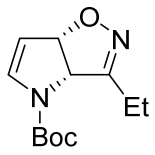
3af ^{1}H NMR, $CDCl_3$, 400 MHz



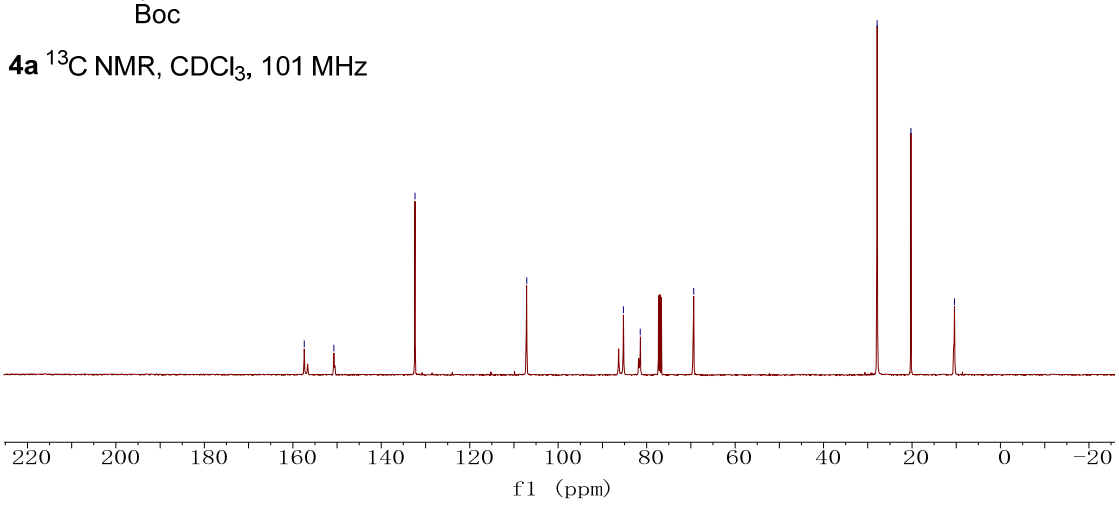
3af ^{13}C NMR, $CDCl_3$, 101 MHz

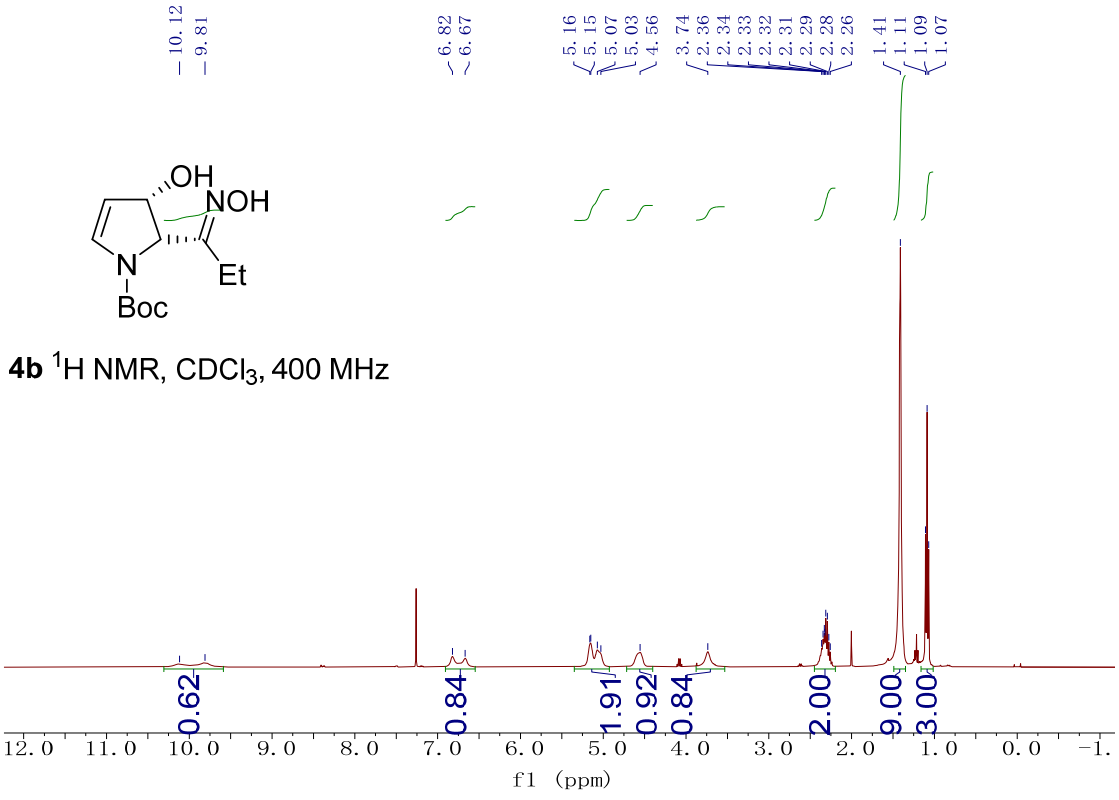


4a ^{1}H NMR, $CDCl_3$, 400 MHz

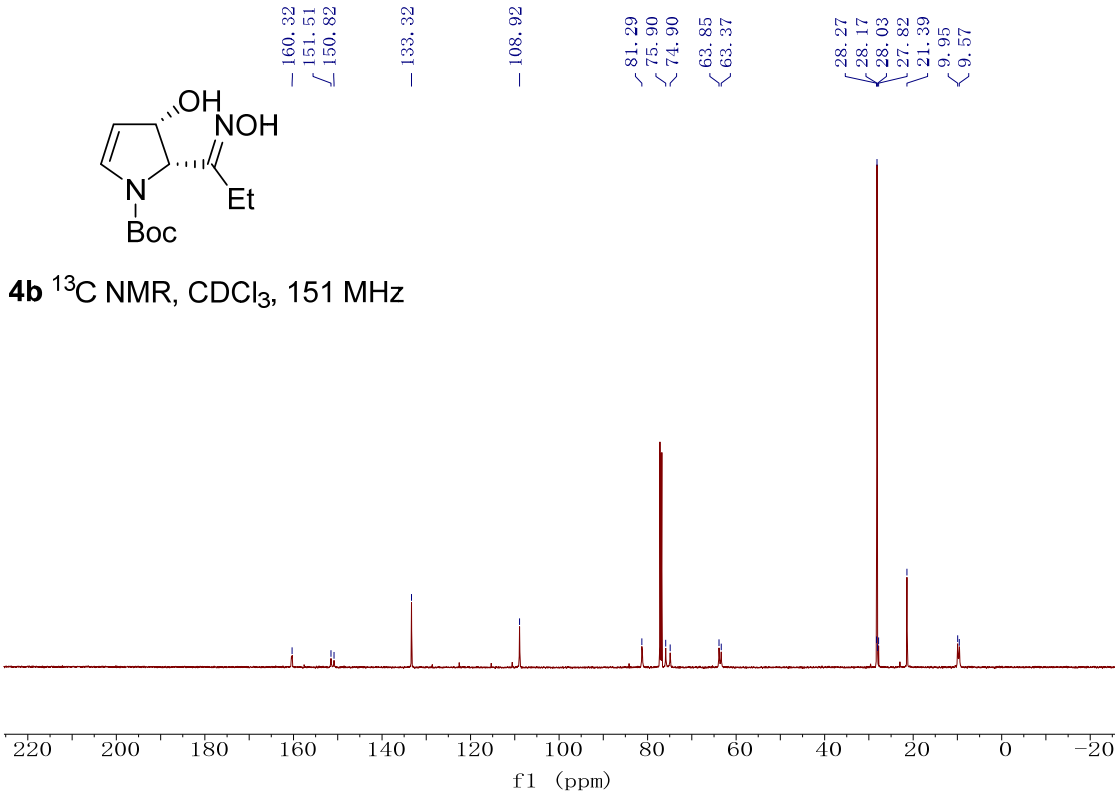


4a ^{13}C NMR, $CDCl_3$, 101 MHz

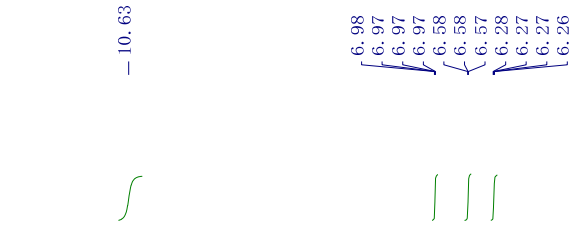


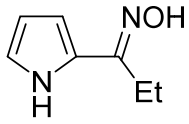


4b ^{1}H NMR, $CDCl_3$, 400 MHz

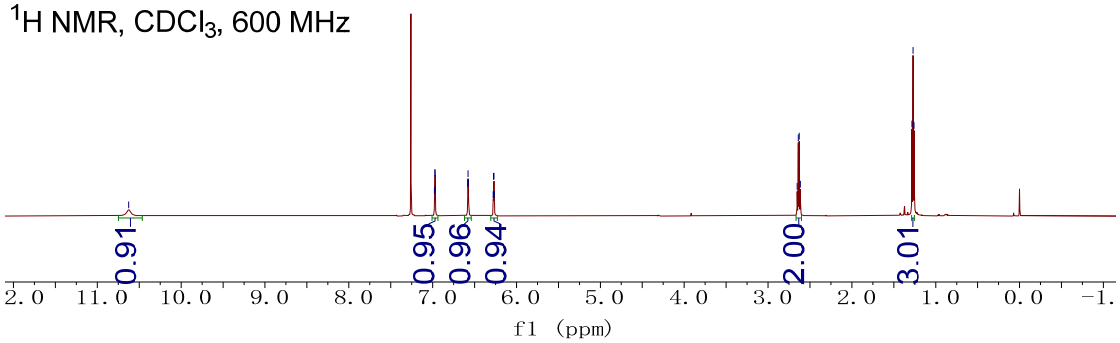


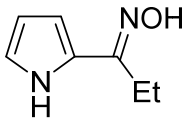
4b ^{13}C NMR, $CDCl_3$, 151 MHz



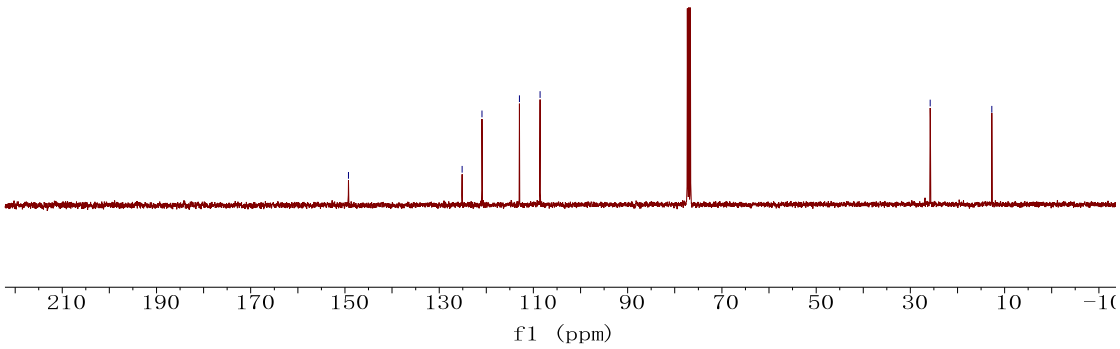


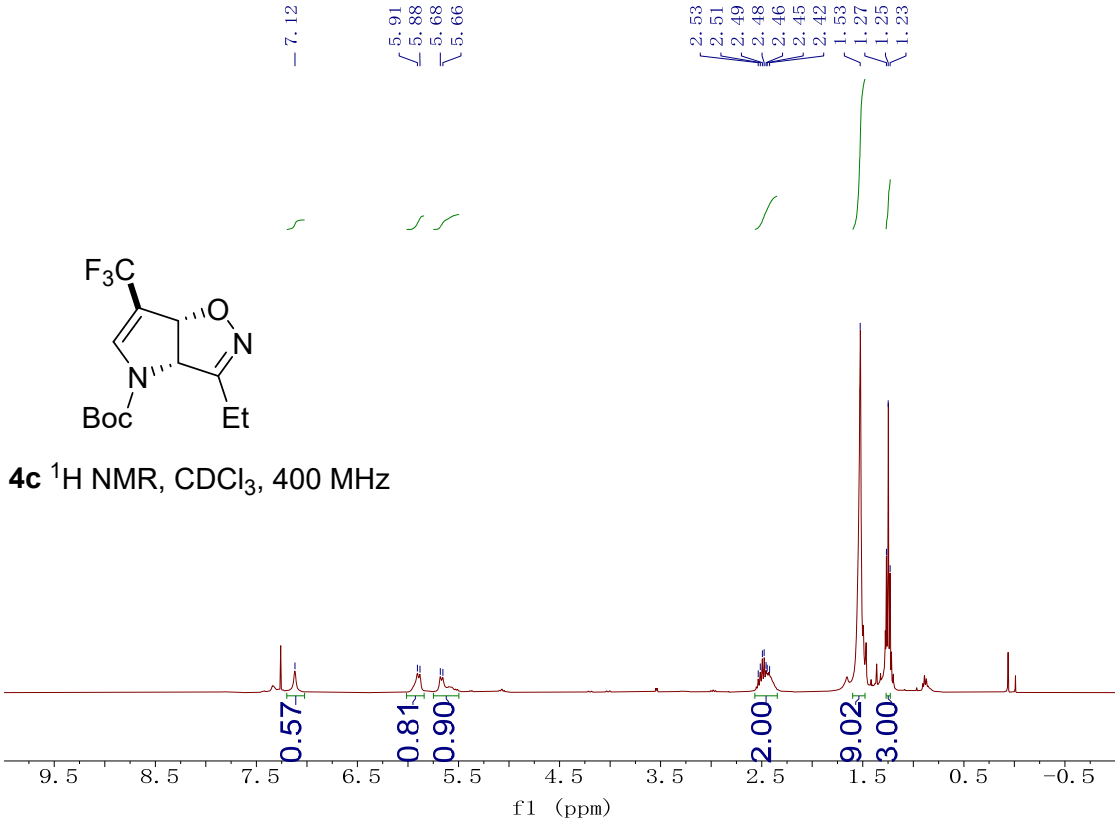
^{1}H NMR, $CDCl_3$, 600 MHz



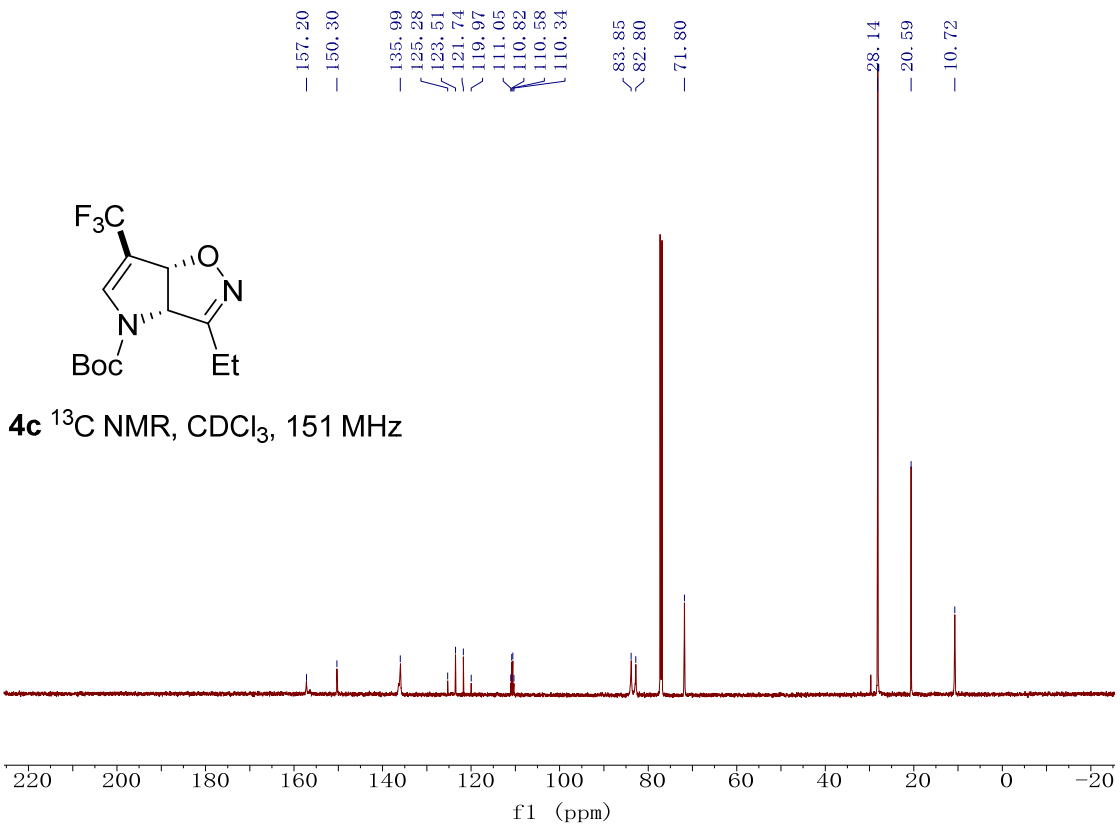


^{13}C NMR, $CDCl_3$, 101 MHz



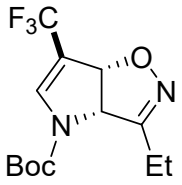


4c ^{1}H NMR, $CDCl_3$, 400 MHz

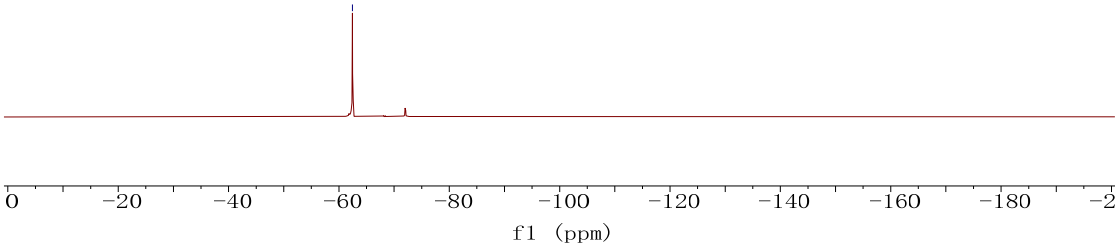


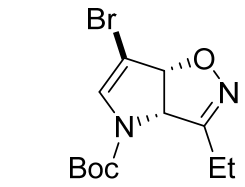
4c ^{13}C NMR, $CDCl_3$, 151 MHz

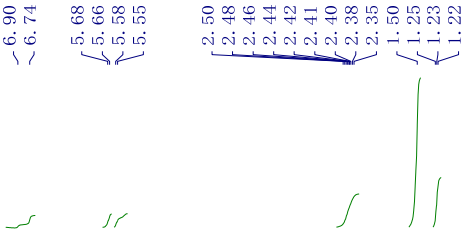
−62.46



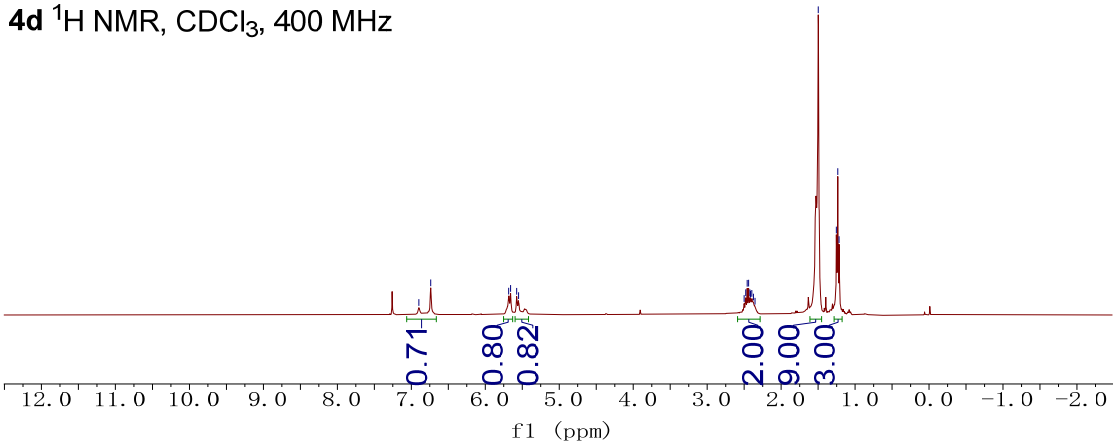
4c ^{19}F NMR, $CDCl_3$, 565 MHz

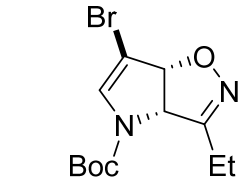


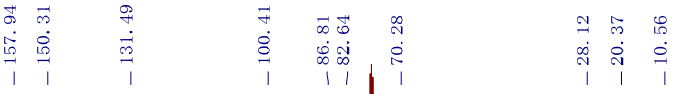




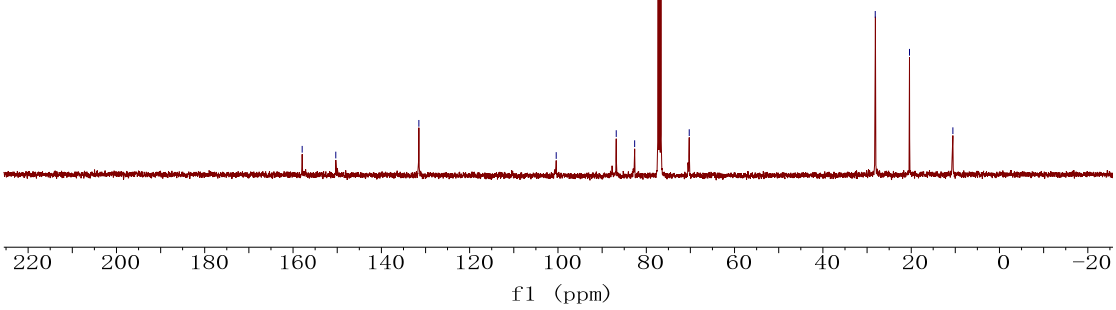
4d ^{1}H NMR, $CDCl_3$, 400 MHz

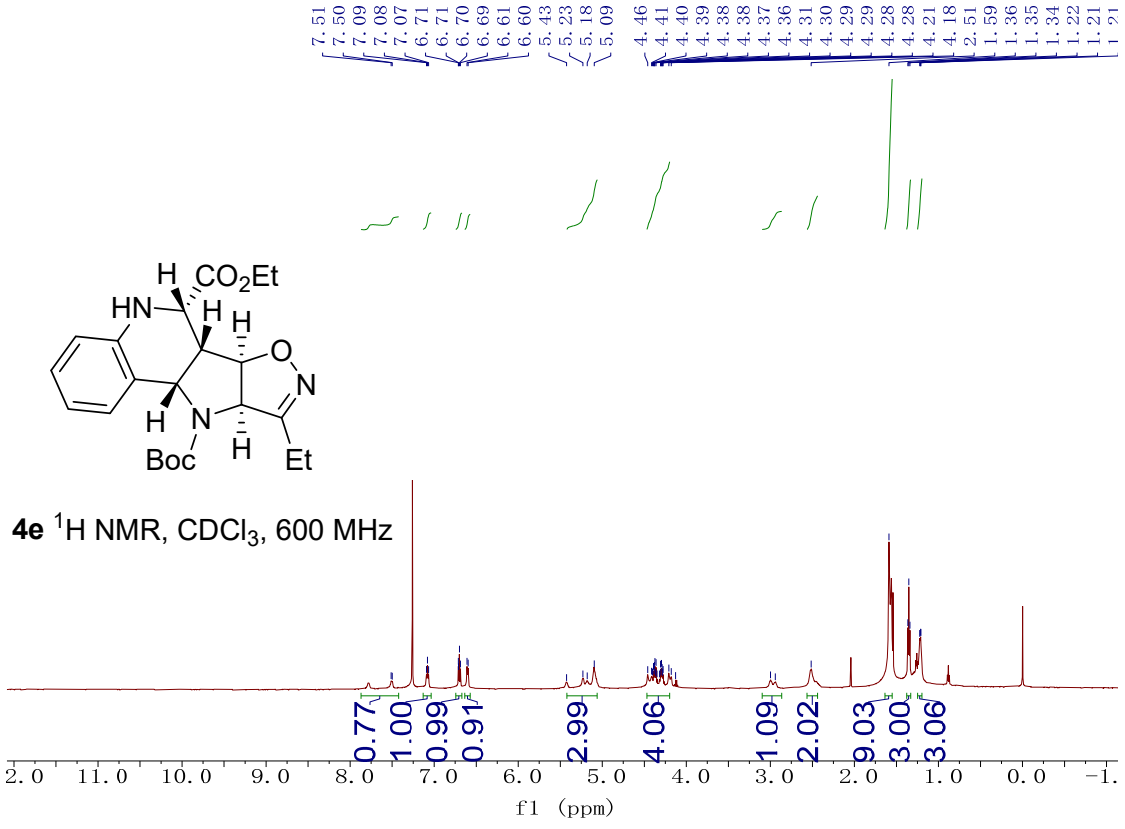


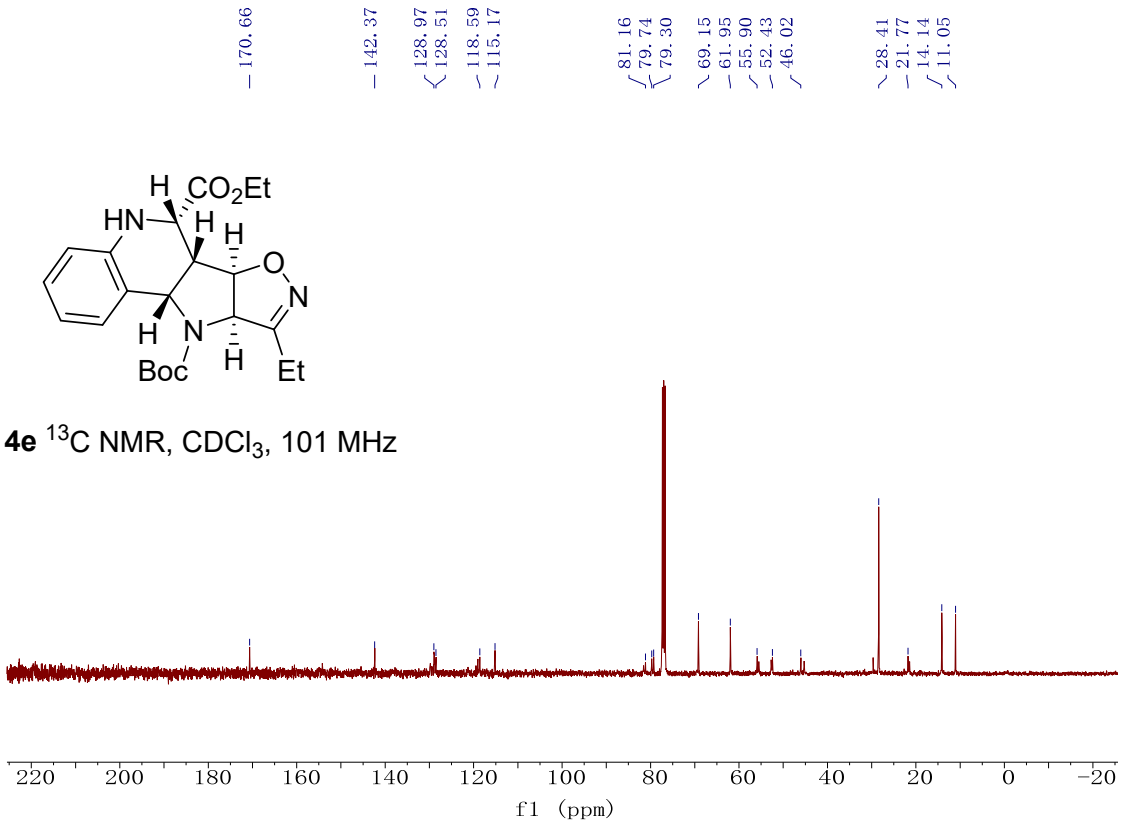


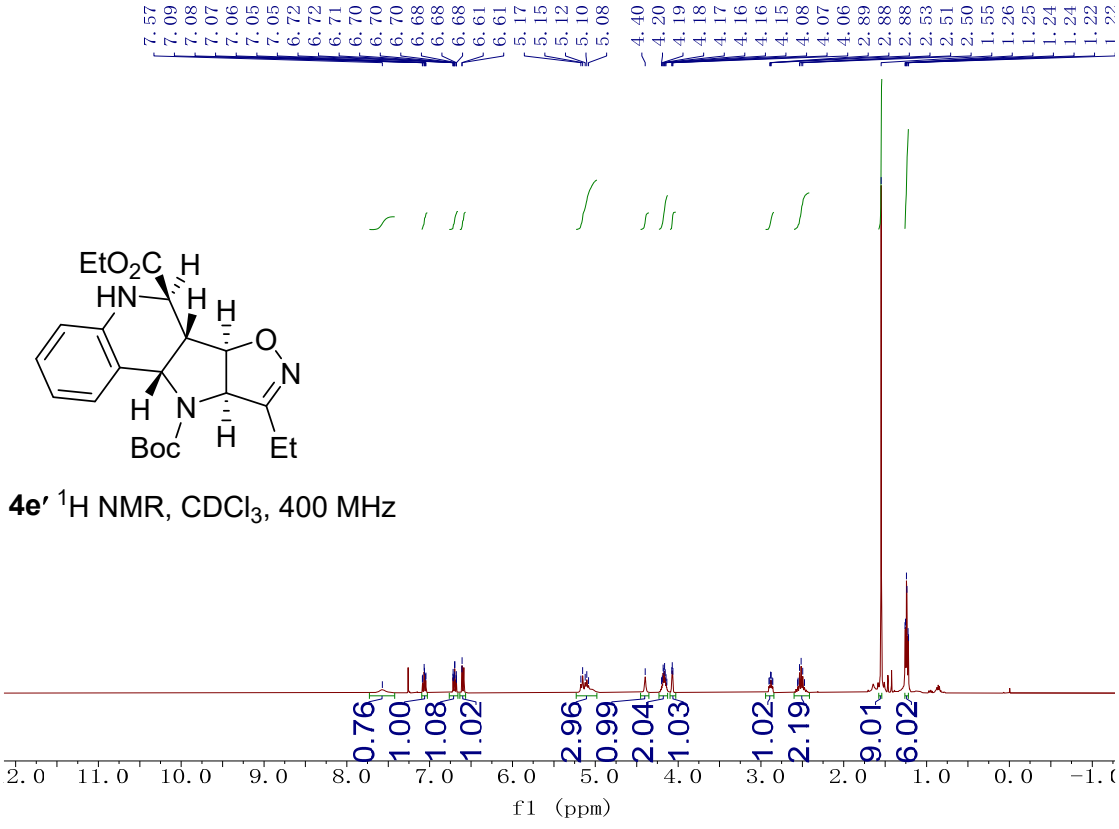


4d ^{13}C NMR, $CDCl_3$, 101 MHz

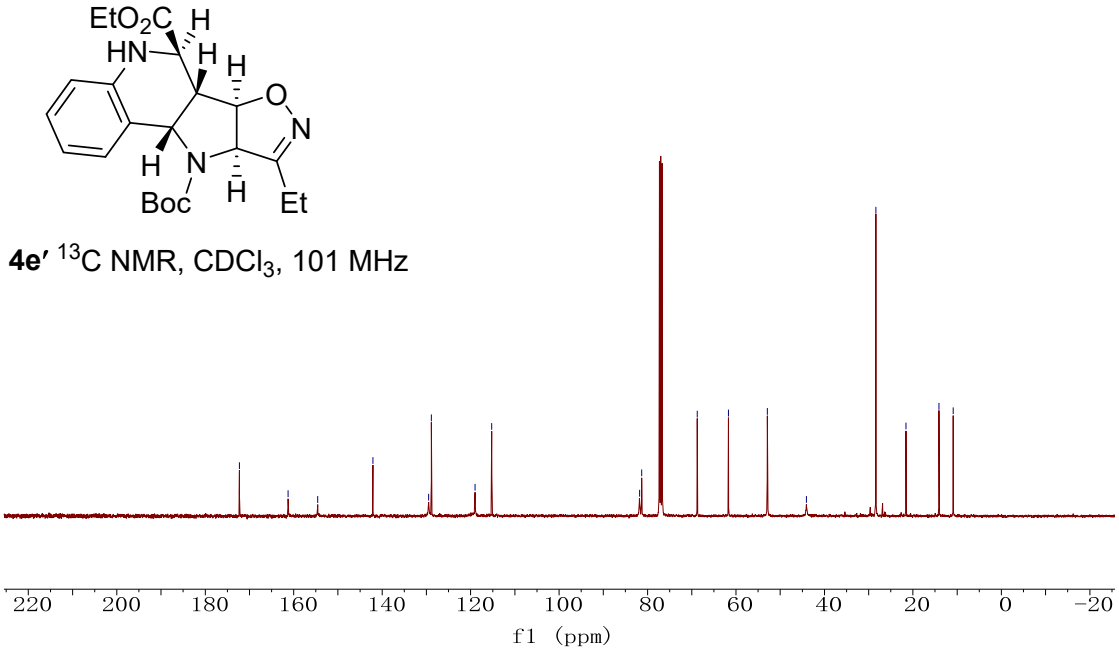



7.51
7.50
7.09
7.08
7.07
6.71
6.70
6.69
6.61
6.60
5.43
5.23
5.18
5.09
4.46
4.41
4.40
4.39
4.38
4.38
4.37
4.36
4.31
4.30
4.29
4.29
4.28
4.28
4.21
4.18
2.51
1.59
1.36
1.35
1.34
1.22
1.21
1.21
H
CO2Et
HN
H
H
O
N
H
N
H
Boc
Et
4e 1H NMR, CDCl3, 600 MHz
0.77
1.00
0.99
0.91
2.99
4.06
1.09
2.02
9.03
3.00
3.06
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.
f1 (ppm)

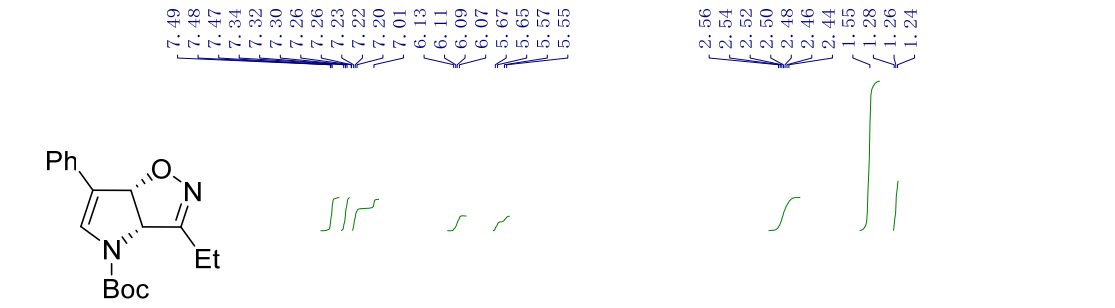

170.66
142.37
128.97
128.51
118.59
115.17
81.16
79.74
79.30
69.15
61.95
55.90
52.43
46.02
28.41
21.77
14.14
11.05
H
CO2Et
HN
H
H
O
N
H
N
H
Boc
Et
4e 13C NMR, CDCl3, 101 MHz
220
200
180
160
140
120
100
80
60
40
20
0
−20
f1 (ppm)



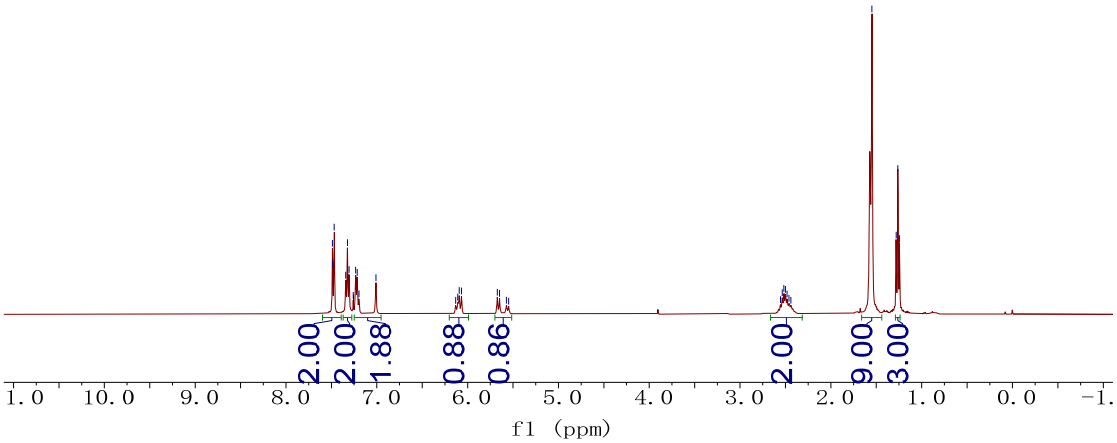
4e′ ^{1}H NMR, $CDCl_3$, 400 MHz

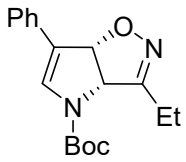


4e′ ^{13}C NMR, $CDCl_3$, 101 MHz



4f ^{1}H NMR, $CDCl_3$, 400 MHz





4f ^{13}C NMR, $CDCl_3$, 101 MHz