Supplementary Information

Nitrogen radical-triggered trifunctionalizing *ipso*-spirocyclization of unactivated alkenes with vinyl azides towards new spiroaminal frameworks

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Contents

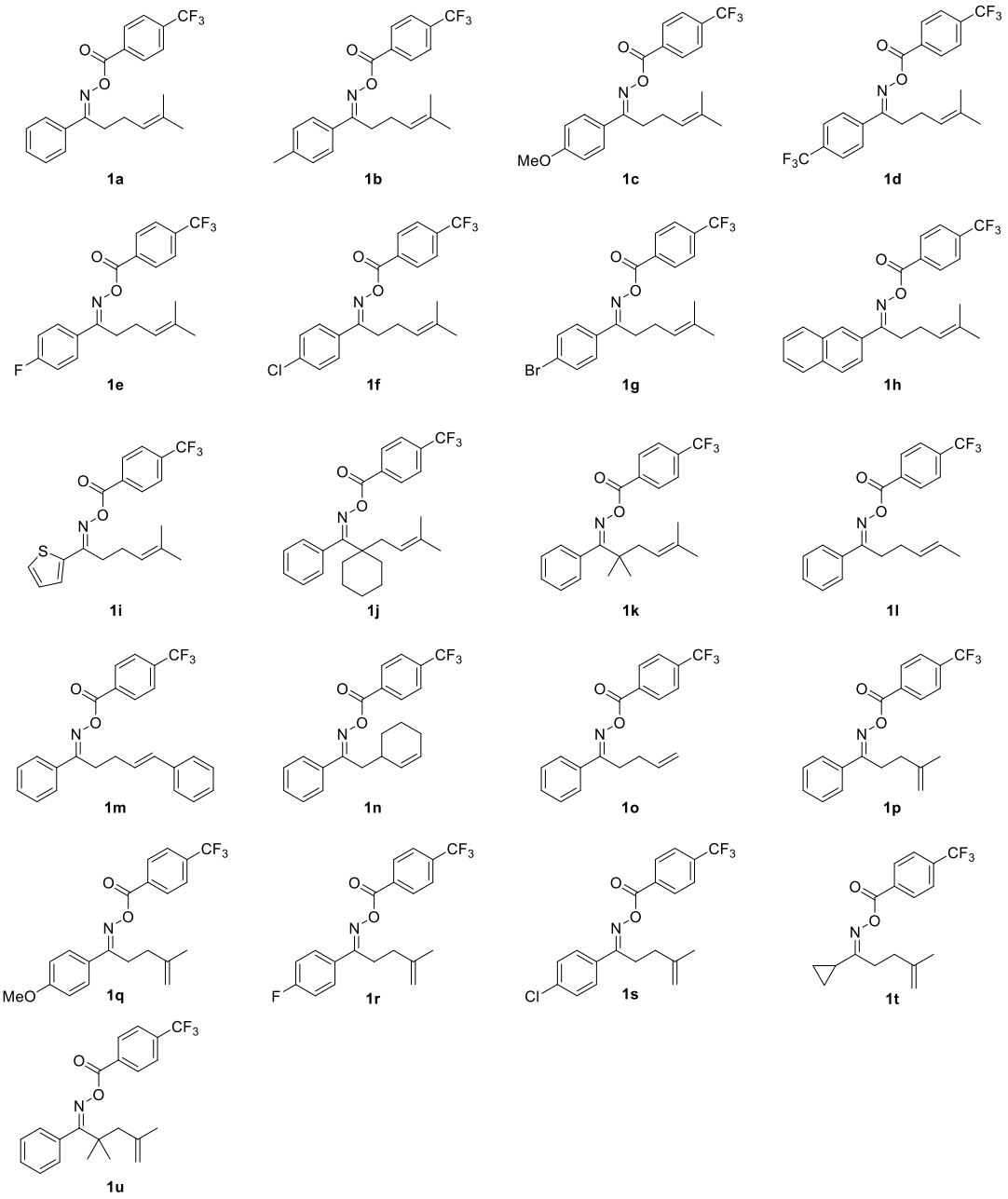
1. General remarks

All reagents and starting materials, unless otherwise noted, were purchased from Energy, J&K, TCI, Alfa, Sigma-Aldrich, Innochem, and Adamas-beta® Chemical company as reagent grade and used without further purification. Anhydrous solvents (including DMSO, MeCN, DME, MeOH, CH_2Cl_2, DMF, $ClCH_2CH_2Cl$, THF, Water < 0.005%) were purchased from J&K and Energy, and used as received. Unless otherwise indicated, all syntheses and manipulations were carried out under argon atmosphere.

^1H, ^{13}C and ^{19}F NMR spectra NMR spectra were obtained with a Bruker AV II-400 spectrometer (^1H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). The ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, ddd = doublet of doublet of doublets. TLC was performed using commercially prepared silica gel plates (GF254), and visualization was effected at 254 nm. Melting points were measured using a Hanon MP470 apparatus and were uncorrected. Flash column chromatography was performed on silica gel (100-200 mesh). Emission intensities were recorded using Hitachi F-7000 Fluorescence Spectrometer. Cyclic voltammetry tests were carried out with a CHI700E electrochemical workstation. Mass analysis data were acquired on a SCIEX UPLC (EXion) – QTOF (X500R).

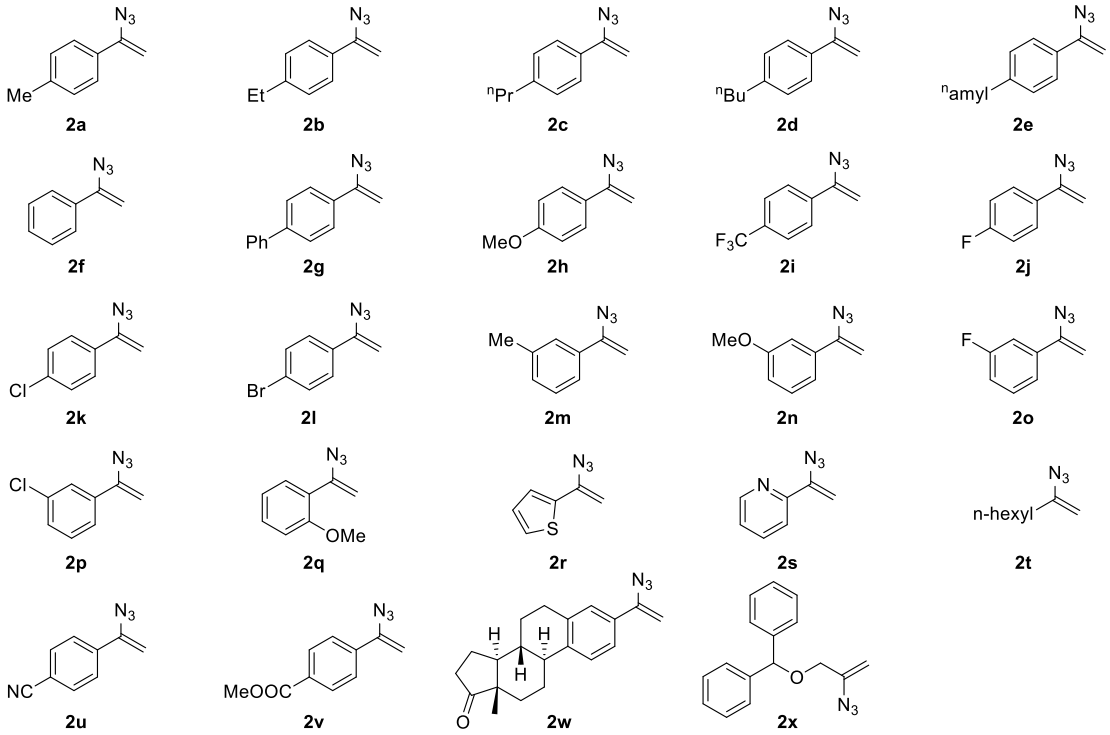
2. The synthesis of starting materials

2.1 The preparation of olefinic oxime esters



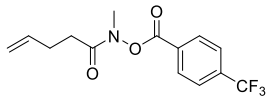
Olefinic oxime esters were synthesized according to the literature procedures.[1]

2.2 The preparation of vinyl azides

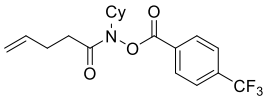


Vinyl azides were synthesized according to the literature procedures.[2]

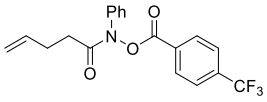
2.3 The preparation of olefinic amides



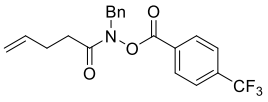
4a



4b



4c



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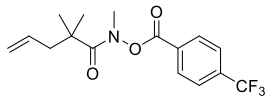
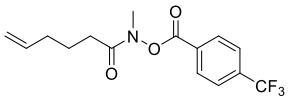
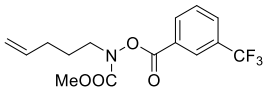


4e



4f

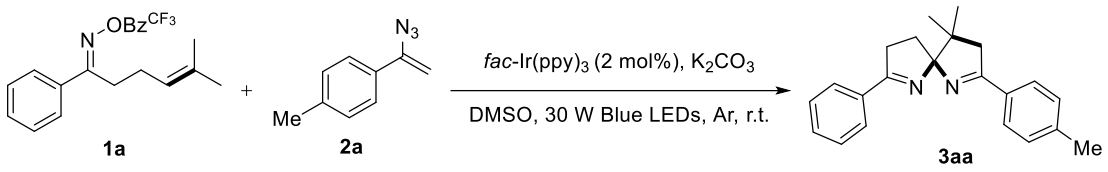


4g

Olefinic amides were synthesized according to the literature procedures.[3]

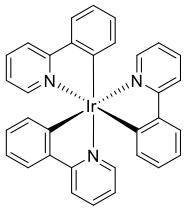
3. Optimization of reaction conditions

3.1 Photoredox-catalyzed, iminyl radical-triggered trifunctionalizing *ipso*-spirocyclization

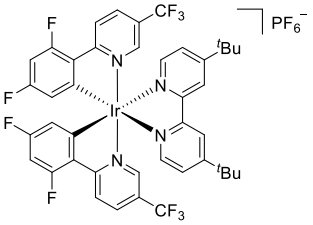


An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (0.1 mmol), base, and photocatalyst. The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** and solvent (1 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (2.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, then dibromomethane (17.4 mg, 0.1 mmol) and $CDCl_3$ (0.5 mL) were added and the mixture was analysed by ^1H NMR spectroscopy to determine the NMR yield of **3aa**.

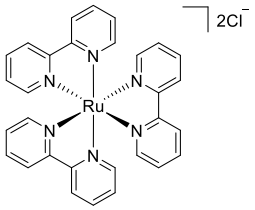
Table S1. Optimization of reaction conditions with olefinic oxime esters[a]



fac-Ir(ppy)$_3$ (**1**)



Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ (**2**)



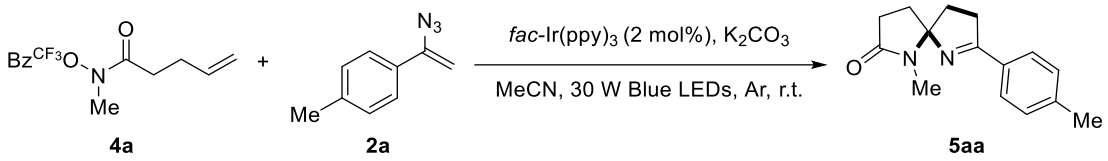
Ru(bpy)$_3$Cl$_2$ (**3**)

Entry	Variation from the standard conditions	Yield (%)[b]
1	**none**	**76 (71)**
2	LG = $C_6F_5CO_2$-	10
3	LG = 2,4-NO_2-C_6H_3O-	n.d.
4	**PC-2** instead of *fac*-Ir(ppy)$_3$	30
5	**PC-3** instead of *fac*-Ir(ppy)$_3$	n.d.
6	DMF instead of DMSO	34
7	MeCN instead of DMSO	46
8	DME instead of DMSO	n.d.
9	MeOH instead of DMSO	n.d.
10	**1a**:**2a** = 1:2	61
11	**1a**:**2a** = 1:3	74
12	*fac*-Ir(ppy)$_3$ (4 mol%)	69
13	*fac*-Ir(ppy)$_3$ (1 mol%)	60
14	no base	54
15	no argon protection	53
16	no light	n.d.
17	no photocatalyst	n.d.

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), K_2CO_3 (0.15 mmol), DMSO (1 mL) were carried out in a sealed tube under Ar atmosphere upon irradiation of 30 W blue LEDs at room temperature for 6 h. LG = *p*-CF_3-$C_6H_4CO_2$- (OBz^{CF_3}). n.d.= no detection.

[b] Yields were determined by ^{1}H NMR using dibromomethane as an internal standard. Isolated yields in parentheses.

3.2 Photoredox-catalyzed, amidyl radical-triggered trifunctionalizing *ipso*-spirocyclization



An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic amides **4a** (0.1 mmol), base (0.15 mmol), and photocatalyst (2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (0.25 mmol) and solvent (1 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction mixture was filtered and concentrated under reduced pressure. Then, dibromomethane (17.4 mg, 0.1 mmol) and $CDCl_3$ (0.5 mL) were added and the mixture was analyzed by ^1H NMR spectroscopy to determine the NMR yield of **5aa**.

Table S2. Optimization of reaction conditions with olefinic amides[a]

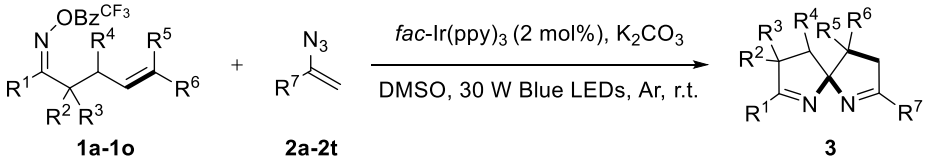
Entry	Variation from the standard conditions	Yield (%)[b]
1	**none**	**75 (69)**
2	$Ir(ppy)_2(dtbbpy)PF_6$ instead of *fac*-$Ir(ppy)_3$	17.
3	4CzIPN instead of *fac*-$Ir(ppy)_3$	n.d.
4	$Ru(bpy)_3BF_4$ instead of *fac*-$Ir(ppy)_3$	trace
5	^{i}PvONa instead of K_2CO_3	41
6	CH_2Cl_2 instead of MeCN	50
7	DMSO instead of MeCN	44
8	DMF instead of MeCN	trace
9	$ClCH_2CH_2Cl$ instead of MeCN	56

[a] Reaction conditions: **4a** (0.1 mmol), **2a** (0.25 mmol), *fac*-$Ir(ppy)_3$ (2 mol%), K_2CO_3 (0.15 mmol), MeCN (1 mL) were carried out in a sealed tube under Ar atmosphere upon irradiation of 30 W blue LEDs at room temperature for 6 h. n.d.= no detection.

[b] Yields were determined by ^1H NMR using dibromomethane as an internal standard. Isolated yields in parentheses.

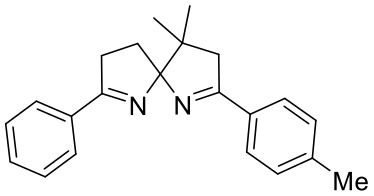
4. Trifunctionalizing *ipso*-spirocyclization products

4.1 General procedure and product characterizations for the photoredox-catalyzed, iminyl radical-triggered trifunctionalizing *ipso*-spirocyclization



An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1** (0.2 mmol, 1.0 equiv.), K_2CO_3 (0.3 mmol, 1.5 equiv.), and *fac*-Ir(ppy)$_3$ (2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2** (0.5 mmol, 2.5 equiv.) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (4.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel to afford the desired product **3**.

4,4-dimethyl-7-phenyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3aa)



Yield: 71%.

Appearance: white solid.

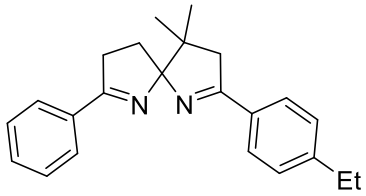
Melting Point: 111.0-112.1 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.32 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.24 (d, *J* = 15.9 Hz, 1H), 3.00 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.85 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.30 (ddd, *J* = 12.3, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.3, 8.1 Hz, 1H), 1.16 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.2, 140.9, 134.9, 132.2, 130.4, 129.0, 128.3, 128.0, 127.9, 110.5, 50.0, 44.8, 35.4, 28.6, 25.1, 21.8, 21.5.

HRMS (ESI) calcd for $C_{22}H_{24}N_2$ $[M+H]^+$: 317.2012, found: 317.2001.

2-(4-ethylphenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ab)



Yield: 54%.

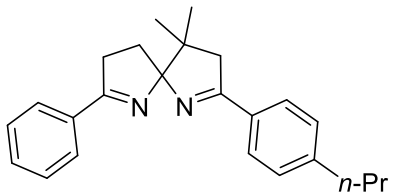
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.31 (ddd, *J* = 16.8, 8.9, 7.9 Hz, 1H), 3.24 (d, *J* = 15.9 Hz, 1H), 3.00 (ddd, *J* = 16.9, 9.4, 3.3 Hz, 1H), 2.86 (d, *J* = 16.0 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.29 (ddd, *J* = 13.3, 8.9, 3.3 Hz, 2H), 2.12 (ddd, *J* = 13.3, 9.4, 7.9 Hz, 1H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.16 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.0, 147.2, 134.9, 132.5, 130.4, 128.2, 127.9, 127.9, 127.8, 110.5, 49.9, 44.9, 35.4, 28.8, 28.5, 25.1, 21.9, 15.5.

HRMS (ESI) calcd for $C_{23}H_{26}N_2$ $[M+H]^+$: 331.2169, found: 331.2165.

4,4-dimethyl-7-phenyl-2-(4-propylphenyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ac)



Yield: 62%.

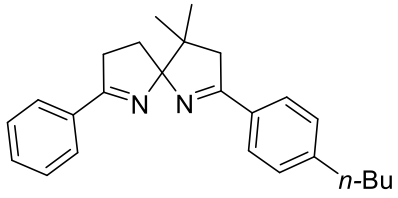
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.32 (ddd, *J* = 16.8, 8.9, 7.9 Hz, 1H), 3.25 (d, *J* = 15.9 Hz, 1H), 3.00 (ddd, *J* = 16.8, 9.4, 3.3 Hz, 1H), 2.86 (d, *J* = 15.9 Hz, 1H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.30 (ddd, *J* = 13.2, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.71 – 1.56 (m, 2H), 1.16 (s, 3H), 1.05 (s, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 173.1, 145.7, 134.9, 132.5, 130.4, 128.4, 128.3, 128.0, 127.9, 110.5, 50.0, 44.9, 37.9, 35.4, 28.6, 25.1, 24.4, 21.9, 13.8.

HRMS (ESI) calcd for $C_{24}H_{28}N_2$ $[M+H]^+$: 345.2325, found: 345.2317.

2-(4-butylphenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ad)



Yield: 69%.

Appearance: colorless oil.

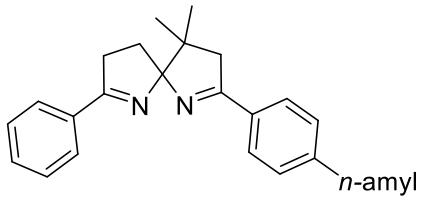
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.78 (d,

J = 8.2 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.32 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.25 (d, *J* = 15.9 Hz, 1H), 3.00 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.86 (d, *J* = 15.9 Hz, 1H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.30 (ddd, *J* = 12.3, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.3, 8.0 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.40 – 1.28 (m, 2H), 1.16 (s, 3H), 1.05 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.1, 145.9, 134.9, 132.4, 130.4, 128.4, 128.2, 128.0, 127.9, 110.5, 49.9, 44.8, 35.6, 35.4, 33.4, 28.5, 25.1, 22.3, 21.8, 13.9.

HRMS (ESI) calcd for $C_{25}H_{30}N_2$ $[M+H]^+$: 359.2482, found: 359.2477.

4,4-dimethyl-2-(4-pentylphenyl)-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ae)



Yield: 62%.

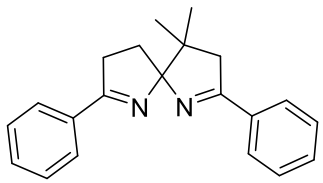
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.32 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.32 (dt, *J* = 17.0, 8.5 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.00 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.86 (d, *J* = 15.9 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.30 (ddd, *J* = 12.3, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.3, 8.1 Hz, 1H), 1.67 – 1.55 (m, 2H), 1.38 – 1.24 (m, 4H), 1.16 (s, 3H), 1.05 (s, 3H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 173.1, 146.0, 134.9, 132.4, 130.4, 128.4, 128.3, 128.0, 127.9, 110.5, 50.0, 44.8, 35.8, 35.4, 31.4, 31.0, 28.5, 25.1, 22.5, 21.8, 14.0.

HRMS (ESI) calcd for $C_{26}H_{32}N_2$ $[M+H]^+$: 373.2638, found: 373.2632.

4,4-dimethyl-2,7-diphenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3af)



Yield: 53%.

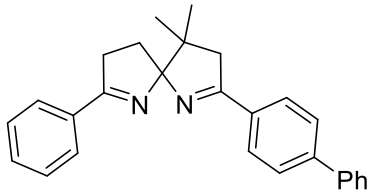
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 7.51 – 7.33 (m, 6H), 3.38 – 3.23 (m, 2H), 3.01 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.31 (ddd, *J* = 12.2, 8.9, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.18 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 173.2, 135.0, 134.8, 130.6, 130.4, 128.3, 128.0, 127.8, 110.6, 50.0, 44.9, 35.4, 28.5, 25.1, 21.8.

HRMS (ESI) calcd for $C_{21}H_{22}N_2$ $[M+H]^+$: 303.1856, found: 303.1853.

2-([1,1'-biphenyl]-4-yl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ag)



Yield: 44%.

Appearance: white solid.

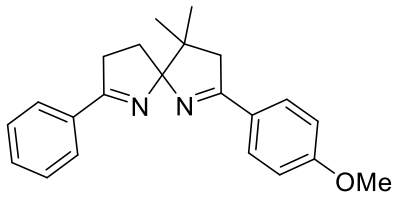
Melting Point: 127.4-129.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.67 – 7.58 (m, 4H), 7.50 – 7.33 (m, 6H), 3.34 (dt, *J* = 16.9, 8.7 Hz, 1H), 3.30 (d, *J* = 15.8 Hz, 1H), 3.02 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.90 (d, *J* = 16.0 Hz, 1H), 2.33 (ddd, *J* = 12.1, 8.9, 3.2 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.19 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.3, 143.3, 140.4, 134.8, 133.8, 130.5, 128.8, 128.34, 128.26, 128.0, 127.7, 127.1, 126.9, 110.6, 50.0, 44.9, 35.4, 28.5, 25.1, 21.8.

HRMS (ESI) calcd for $C_{27}H_{26}N_2$ $[M+H]^+$: 379.2169, found: 379.2161.

2-(4-methoxyphenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ah)



Yield: 62%.

Appearance: white soild.

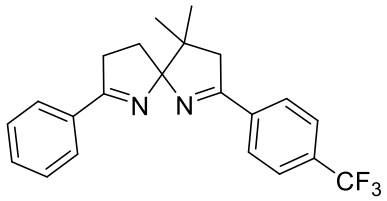
Melting Point: 128.2-129.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.84 – 7.79 (m, 2H), 7.44 – 7.34 (m, 3H), 6.93 – 6.86 (m, 2H), 3.83 (s, 3H), 3.32 (dt, *J* = 16.8, 8.5 Hz, 1H), 3.23 (d, *J* = 15.9 Hz, 1H), 3.00 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 1H), 2.30 (ddd, *J* = 12.2, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.3, 8.1 Hz, 1H), 1.16 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.1, 161.7, 134.9, 130.4, 129.6, 128.3, 128.0, 127.7, 113.6, 110.5, 55.4, 49.9, 44.9, 35.5, 28.6, 25.2, 21.8

HRMS (ESI) calcd for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961, found: 333.1960.

4,4-dimethyl-7-phenyl-2-(4-(trifluoromethyl)phenyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ai)



Yield: 42%.

Appearance: colorless oil.

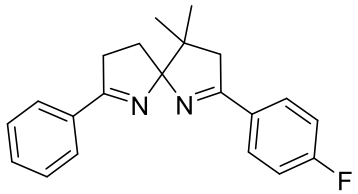
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.91– 7.85 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.35 (m, 3H), 3.38 – 3.25 (m, 2H), 3.04 (ddd, *J* = 16.9, 9.4, 3.1 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.32 (ddd, *J* = 13.3, 8.8, 3.0 Hz, 1H), 2.20 – 2.03 (m, 1H), 1.19 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.3, 138.2, 134.6, 132.1 (q, *J* = 32.5 Hz), 130.6, 128.3, 128.1, 128.0, 125.2 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.9 Hz), 110.8, 50.0, 45.0, 35.4, 28.5, 25.1, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74.

HRMS (ESI) calcd for $C_{22}H_{21}F_3N_2$ $[M+H]^+$: 371.1730, found: 371.1719.

2-(4-fluorophenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3aj)



Yield: 56%.

Appearance: colorless oil.

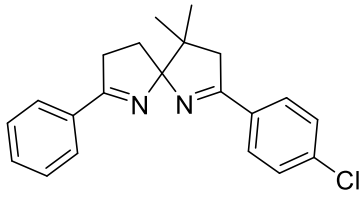
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 4H), 7.44 – 7.35 (m, 3H), 7.10 – 7.02 (m, 2H), 3.32 (dt, *J* = 17.0, 8.6 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.01 (ddd, *J* = 16.8, 9.4, 3.1 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.30 (ddd, *J* = 13.1, 8.8, 3.1 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.3, 8.2 Hz, 1H), 1.17 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.3, 164.4 (d, *J* = 250.7 Hz), 134.8, 131.3 (d, *J* = 3.1 Hz), 130.5, 130.0 (d, *J* = 8.6 Hz), 128.3, 128.0, 115.3 (d, *J* = 21.7 Hz), 110.6, 50.0, 45.0, 35.5, 28.6, 25.2, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.75.

HRMS (ESI) calcd for $C_{21}H_{21}FN_2$ $[M+H]^+$: 321.1762, found: 321.1759.

2-(4-chlorophenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ak)



Yield: 45%.

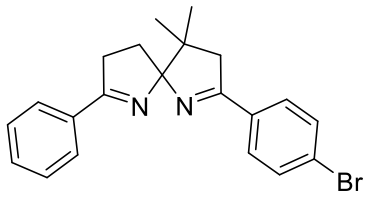
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.82 – 7.76 (m, 2H), 7.46 – 7.33 (m, 5H), 3.32 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.01 (ddd, *J* = 16.9, 9.4, 3.1 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.30 (ddd, *J* = 13.3, 8.8, 3.1 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 8.1 Hz, 1H), 1.17 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.3, 136.6, 134.7, 133.4, 130.5, 129.2, 128.5, 128.3, 128.0, 110.6, 49.9, 45.0, 35.4, 28.5, 25.1, 21.7.

HRMS (ESI) calcd for $C_{21}H_{21}ClN_2$ $[M+H]^+$: 337.1466, found: 337.1460.

2-(4-bromophenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3al)



Yield: 46%.

Appearance: brown solid.

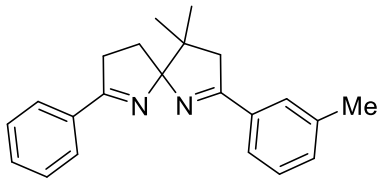
Melting Point: 120.2-122.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.32 (m, 3H), 3.32 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 3.02 (ddd, *J* = 16.9, 9.4, 3.1 Hz, 1H), 2.82 (d, *J* = 16.0 Hz, 1H), 2.34 – 2.25 (m, 1H), 2.17 – 2.07 (m, 1H), 1.17 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.4, 134.7, 133.8, 131.5, 130.5, 129.4, 128.3, 128.0, 125.1, 110.7, 49.8, 45.0, 35.4, 28.5, 25.1, 21.7.

HRMS (ESI) calcd for $C_{21}H_{21}BrN_2$ $[M+H]^+$: 380.0961, found: 380.0956.

4,4-dimethyl-7-phenyl-2-(*m*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3am)



Yield: 62%.

Appearance: colorless oil.

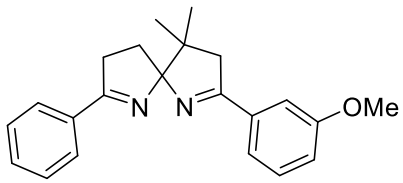
Melting Point: 87.8-90.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.73 (s, 1H), 7.64 – 7.58 (m, 1H), 7.46 – 7.34 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.20 (m, 1H), 3.39 – 3.26 (m, 1H), 3.26 (d, *J* = 15.9 Hz, 1H), 3.01 (ddd, *J* = 16.9, 9.4, 3.2 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 2.31 (ddd, *J* = 13.3, 8.9, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.17 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 173.2, 138.0, 134.9, 131.5, 130.4, 128.3, 128.24, 128.18, 128.0, 125.2, 110.5, 50.1, 44.8, 35.4, 28.5, 25.1, 21.8, 21.3.

HRMS (ESI) calcd for $C_{22}H_{24}N_2$ $[M+H]^+$: 317.2012, found: 317.2010.

2-(3-methoxyphenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3an)



Yield: 52%.

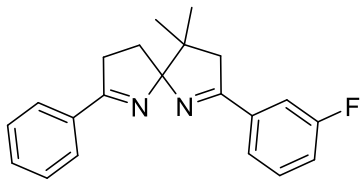
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.46 (s, 1H), 7.44 – 7.34 (m, 4H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.97 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.84 (s, 3H), 3.32 (dt, *J* = 17.3, 8.6 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.01 (ddd, *J* = 16.8, 9.4, 3.3 Hz, 1H), 2.86 (d, *J* = 16.0 Hz, 1H), 2.30 (ddd, *J* = 12.4, 8.8, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.3, 9.3, 8.0 Hz, 1H), 1.17 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.3, 159.5, 136.4, 134.8, 130.5, 129.2, 128.3, 128.0, 120.6, 117.2, 112.1, 110.6, 55.4, 50.1, 44.9, 35.4, 28.6, 25.0, 21.9.

HRMS (ESI) calcd for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961, found: 333.1952.

2-(3-fluorophenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ao)



Yield: 53%.

Appearance: colorless oil.

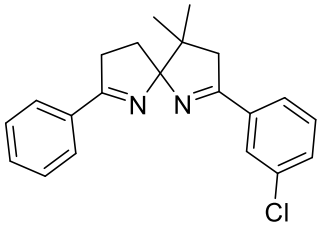
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.64 – 7.54 (m, 2H), 7.48 – 7.31 (m, 4H), 7.17 – 7.03 (m, 1H), 3.39 – 3.26 (m, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 3.02 (ddd, *J* = 16.9, 9.4, 3.1 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.31 (ddd, *J* = 13.3, 8.8, 3.0 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 8.1 Hz, 1H), 1.18 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.5 (d, *J* = 2.6 Hz), 162.7 (d, *J* = 246.0 Hz), 137.3 (d, *J* = 7.4 Hz), 134.7, 130.6, 129.8 (d, *J* = 8.0 Hz), 128.3, 128.0, 123.7 (d, *J* = 2.9 Hz), 117.5 (d, *J* = 21.4 Hz), 114.6 (d, *J* = 22.3 Hz), 110.7, 50.0, 45.0, 35.5, 28.5, 25.1, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.11.

HRMS (ESI) calcd for $C_{21}H_{21}FN_2$ $[M+H]^+$: 321.1762, found: 321.1762.

2-(3-chlorophenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ap)



Yield: 44%.

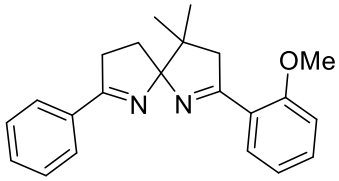
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 3H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.32 (t, *J* = 7.8 Hz, 1H), 3.39 – 3.28 (m, 1H), 3.26 (d, *J* = 16.5 Hz, 1H), 3.03 (ddd, *J* = 16.9, 9.4, 3.0 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.31 (ddd, *J* = 11.9, 8.8, 3.0 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 8.1 Hz, 1H), 1.18 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.3, 136.8, 134.7, 134.4, 130.6, 130.5, 129.6, 128.3, 128.0, 127.8, 126.0, 110.7, 50.0, 44.9, 35.4, 28.5, 25.1, 21.7.

HRMS (ESI) calcd for $C_{21}H_{21}ClN_2$ $[M+H]^+$: 337.1466, found: 337.1454.

2-(2-methoxyphenyl)-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3aq)



Yield: 70%.

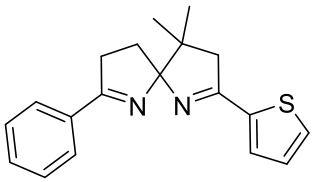
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.79 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.44 – 7.30 (m, 4H), 6.94 (td, *J* = 7.5, 0.9 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.85 (s, 3H), 3.39 – 3.20 (m, 2H), 2.99 (ddd, *J* = 16.8, 9.4, 3.1 Hz, 1H), 2.92 (d, *J* = 16.6 Hz, 1H), 2.28 (ddd, *J* = 12.0, 8.8, 3.1 Hz, 1H), 2.12 (ddd, *J* = 13.2, 9.3, 8.2 Hz, 1H), 1.14 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 173.2, 158.4, 135.0, 131.3, 130.4, 129.9, 128.3, 128.0, 125.2, 120.6, 111.1, 109.4, 55.4, 53.7, 45.0, 35.4, 28.5, 24.8, 21.7.

HRMS (ESI) calcd for $C_{22}H_{24}N_2O$ $[M+H]^+$: 333.1961, found: 333.1961.

4,4-dimethyl-7-phenyl-2-(thiophen-2-yl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ar)



Yield: 45%.

Appearance: colorless oil.

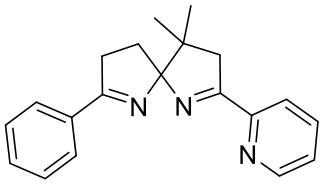
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.47 – 7.31 (m,

5H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.38 – 3.27 (m, 1H), 3.28 (d, *J* = 15.5 Hz, 1H), 2.99 (ddd, *J* = 16.9, 9.5, 3.2 Hz, 1H), 2.84 (d, *J* = 15.8 Hz, 1H), 2.32 (ddd, *J* = 12.4, 8.8, 3.1 Hz, 1H), 2.11 (ddd, *J* = 13.3, 9.5, 8.0 Hz, 1H), 1.16 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 168.8, 139.8, 134.8, 130.5, 130.0, 129.5, 128.3, 128.0, 127.4, 110.6, 50.6, 45.2, 35.5, 28.4, 25.0, 21.7.

HRMS (ESI) calcd for $C_{19}H_{20}N_2S$ $[M+H]^+$: 309.1420, found: 309.1419.

4,4-dimethyl-7-phenyl-2-(pyridin-2-yl)-1,6-diazaspiro[4.4]nona-1,6-diene (3as)



Yield: 65%.

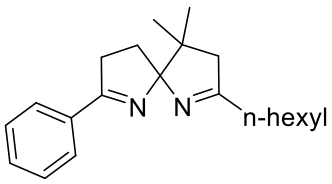
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.64 (m, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.33 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 3.42 – 3.28 (m, 2H), 3.16 (d, *J* = 16.8 Hz, 1H), 3.05 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.35 (ddd, *J* = 13.3, 8.9, 3.2 Hz, 1H), 2.18 (ddd, *J* = 13.3, 9.4, 7.9 Hz, 1H), 1.21 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 173.6, 153.4, 149.2, 136.3, 134.7, 130.6, 128.3, 128.0, 124.9, 122.4, 111.2, 49.7, 44.7, 35.4, 28.5, 25.0, 21.9.

HRMS (ESI) calcd for $C_{20}H_{21}N_3$ $[M+H]^+$: 304.1808, found: 304.1804.

2-hexyl-4,4-dimethyl-7-phenyl-1,6-diazaspiro[4.4]nona-1,6-diene (3at)



Yield: 44%.

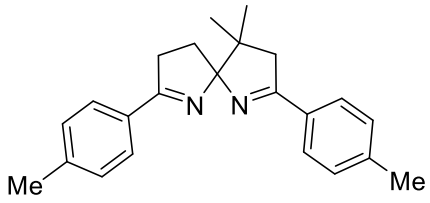
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.39 – 7.24 (m, 3H), 3.16 (dt, *J* = 17.0, 8.6 Hz, 1H), 2.88 (ddd, *J* = 16.8, 9.5, 2.7 Hz, 1H), 2.79 (d, *J* = 16.3 Hz, 1H), 2.36 – 2.24 (m, 2H), 2.11 (ddd, *J* = 13.2, 8.7, 2.7 Hz, 1H), 2.01 – 1.87 (m, 2H), 1.58 – 1.34 (m, 2H), 1.37 – 1.08 (m, 6H), 1.01 (s, 3H), 0.90 (s, 3H), 0.80 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.8, 171.9, 133.9, 129.3, 127.2, 126.9, 108.9, 50.7, 43.6, 34.2, 33.7, 30.6, 28.2, 27.3, 25.5, 24.1, 21.5, 20.4, 13.0.

HRMS (ESI) calcd for $C_{21}H_{30}N_2$ $[M+H]^+$: 311.2482, found: 311.2473.

4,4-dimethyl-2,7-di-*p*-tolyl-1,6-diazaspiro[4.4]nona-1,6-diene (3ba)



Yield: 67%.

Appearance: white solid.

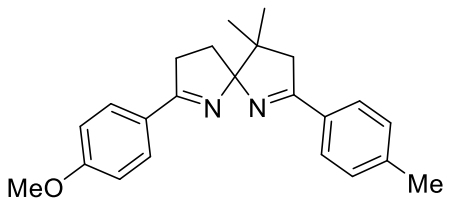
Melting Point: 115.5-117.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.18 (d, *J* = 7.7 Hz, 4H), 3.34 – 3.23 (m, 1H), 3.23 (d, *J* = 15.9 Hz, 1H), 2.97 (ddd, *J* = 16.8, 9.4, 3.4 Hz, 1H), 2.84 (d, *J* = 15.9 Hz, 1H), 2.36 (s, 6H), 2.27 (ddd, *J* = 12.6, 8.9, 3.4 Hz, 1H), 2.11 (ddd, *J* = 13.3, 9.4, 7.8 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.9, 140.8, 140.6, 132.3, 132.2, 129.0, 128.9, 128.0, 127.8, 110.5, 50.0, 44.9, 35.4, 28.6, 25.1, 21.9, 21.5.

HRMS (ESI) calcd for $C_{23}H_{26}N_2$ $[M+H]^+$: 331.2169, found: 331.2158.

7-(4-methoxyphenyl)-4,4-dimethyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ca)



Yield: 58%.

Appearance: white solid.

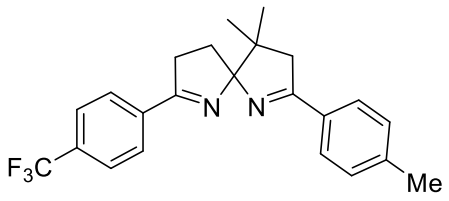
Melting Point: 107.8-109.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.33 – 3.19 (m, 2H), 2.97 (ddd, *J* = 16.7, 9.4, 3.4 Hz, 1H), 2.84 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 2.26 (ddd, *J* = 12.6, 8.9, 3.4 Hz, 1H), 2.11 (ddd, *J* = 13.2, 9.4, 7.8 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 172.4, 161.3, 140.8, 132.3, 129.6, 129.0, 127.8, 127.7, 113.5, 110.4, 55.3, 49.9, 44.8, 35.3, 28.7, 25.1, 21.9, 21.5.

HRMS (ESI) calcd for $C_{23}H_{26}N_2$ $[M+H]^+$: 347.2118, found: 347.2113.

4,4-dimethyl-2-(*p*-tolyl)-7-(4-(trifluoromethyl)phenyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3da)



Yield: 59%.

Appearance: colorless oil.

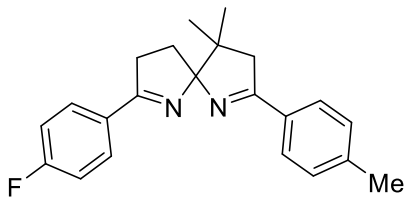
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.33 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 3.01 (ddd, *J* = 16.9, 9.5, 3.2 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.36 – 2.30 (m, 1H), 2.15 (ddd, *J* = 13.3, 9.4, 8.1 Hz, 1H), 1.16 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 171.9, 141.1, 138.1, 132.0 (q, *J* = 32.4 Hz), 132.1, 129.1, 128.3, 127.9, 125.2 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 110.7, 50.0, 44.9, 35.5, 28.5, 25.1, 21.8, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.77.

HRMS (ESI) calcd for $C_{23}H_{23}F_3N_2$ $[M+H]^+$: 385.1886, found: 385.1876.

7-(4-fluorophenyl)-4,4-dimethyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ea)



Yield: 73%.

Appearance: colorless oil.

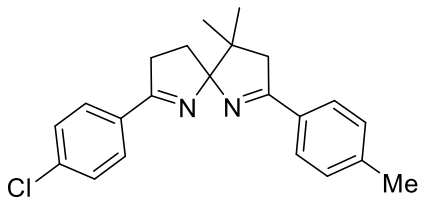
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 3.34 – 3.23 (m, 1H), 3.23 (d, *J* = 15.9 Hz, 1H), 2.97 (ddd, *J* = 16.8, 9.4, 3.2 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 2.29 (ddd, *J* = 13.3, 8.9, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 171.9, 164.2 (d, *J* = 250.1 Hz), 140.9, 132.2, 131.1 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 8.6 Hz), 129.0, 127.8, 115.2 (d, *J* = 21.6 Hz), 110.5, 49.9, 44.8, 35.4, 28.7, 25.1, 21.8, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.09.

HRMS (ESI) calcd for $C_{22}H_{24}FN_2$ $[M+H]^+$: 335.1918, found: 335.1916.

7-(4-chlorophenyl)-4,4-dimethyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3fa)



Yield: 70%.

Appearance: colorless oil.

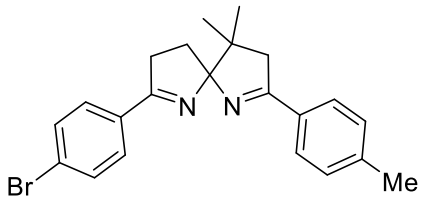
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.75

(d, *J* = 8.2 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.35 – 3.18 (m, 2H), 2.97 (ddd, *J* = 16.9, 9.4, 3.2 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 2.30 (ddd, *J* = 13.3, 8.9, 3.2 Hz, 1H), 2.13 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 172.0, 141.0, 136.4, 133.3, 132.1, 129.3, 129.0, 128.5, 127.9, 110.6, 50.0, 44.8, 35.3, 28.6, 25.1, 21.8, 21.5

HRMS (ESI) calcd for $C_{22}H_{23}ClN_2$ $[M+H]^+$: 351.1623, found: 351.1615.

7-(4-bromophenyl)-4,4-dimethyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ga)



Yield: 57%.

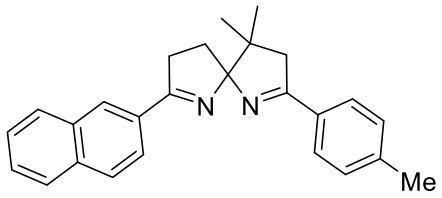
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 4H), 7.55 – 7.47 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.33 – 3.19 (m, 2H), 2.96 (ddd, *J* = 16.8, 9.5, 3.2 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 2.30 (ddd, *J* = 13.2, 8.9, 3.2 Hz, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 8.0 Hz, 1H), 1.14 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 172.1, 141.0, 133.7, 132.1, 131.4, 129.5, 129.0, 127.8, 124.9, 110.6, 50.0, 44.8, 35.3, 28.6, 25.1, 21.8, 21.5

HRMS (ESI) calcd for $C_{22}H_{23}BrN_2$ $[M+H]^+$: 395.1117, found: 395.1118.

4,4-dimethyl-7-(naphthalen-2-yl)-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ha)



Yield: 64%.

Appearance: white solid.

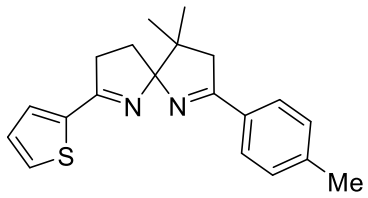
Melting Point: 143.5-145.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.11 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.85 – 7.80 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.43 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.43 (dt, *J* = 16.7, 8.6 Hz, 1H), 3.27 (d, *J* = 15.9 Hz, 1H), 3.13 (ddd, *J* = 16.7, 9.4, 3.4 Hz, 1H), 2.88 (d, *J* = 15.9 Hz, 1H), 2.39 – 2.29 (m, 4H), 2.18 (ddd, *J* = 13.3, 9.4, 7.8 Hz, 1H), 1.20 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 173.1, 140.9, 134.5, 132.9, 132.5, 132.3, 129.0, 128.8, 128.4, 127.9, 127.9, 127.8, 127.0, 126.3, 125.1, 110.7, 50.0, 45.0, 35.5, 28.7, 25.2, 22.0, 21.5.

HRMS (ESI) calcd for $C_{26}H_{26}N_2$ $[M+H]^+$: 367.2169, found: 367.2160.

4,4-dimethyl-7-(thiophen-2-yl)-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ia)



Yield: 68%.

Appearance: white solid.

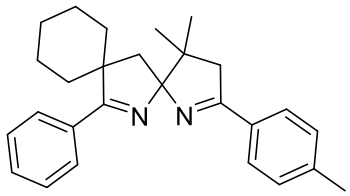
Melting Point: 142.8-145.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.34 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.05 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.32 – 3.21 (m, 1H), 3.21 (d, *J* = 16.1 Hz, 1H), 3.00 (ddd, *J* = 16.6, 9.4, 3.5 Hz, 1H), 2.82 (d, *J* = 15.9 Hz, 1H), 2.37 (s, 3H), 2.28 (ddd, *J* = 12.6, 8.9, 3.5 Hz, 1H), 2.14 (ddd, *J* = 13.2, 9.4, 7.9 Hz, 1H), 1.14 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 167.2, 140.9, 139.8, 132.2, 129.4, 129.2, 129.0, 127.9, 127.3, 110.4, 49.9, 44.8, 36.0, 28.9, 25.1, 21.9, 21.5

HRMS (ESI) calcd for $C_{20}H_{22}N_2S$ $[M+H]^+$: 323.1576, found: 323.1573.

4,4-dimethyl-13-phenyl-2-(*p*-tolyl)-1,14-diazadispiro[4.1.5^7.2^5]tetradeca-1,13-diene (3ja)



Yield: 45%.

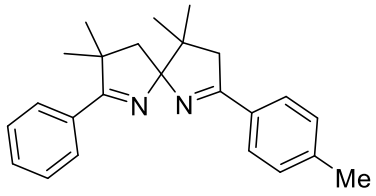
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.83 (d, *J* = 16.0 Hz, 1H), 2.52 (d, *J* = 13.4 Hz, 1H), 2.39 (s, 3H), 2.34 (d, *J* = 12.9 Hz, 1H), 1.90 – 1.70 (m, 6H), 1.63 (ddd, *J* = 20.0, 13.1, 3.9 Hz, 2H), 1.41 (ddd, *J* = 13.9, 10.4, 4.1 Hz, 2H), 1.22 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 174.2, 140.6, 136.2, 132.6, 128.9, 128.8, 128.3, 128.0, 127.8, 107.1, 56.9, 49.4, 44.7, 39.5, 36.1, 33.0, 25.7, 25.5, 23.7, 23.4, 21.5, 21.2.

HRMS (ESI) calcd for $C_{27}H_{32}N_2$ $[M+H]^+$: 385.2638, found: 385.2636.

3,3,9,9-tetramethyl-2-phenyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ka)



Yield: 58%.

Appearance: white solid.

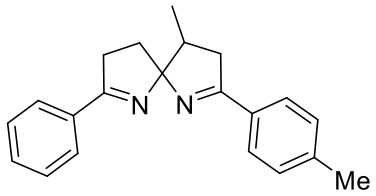
Melting Point: 105.0-108.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.38 – 7.33 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.81 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 2.24 (d, *J* = 13.1 Hz, 1H), 1.99 (d, *J* = 13.1 Hz, 1H), 1.75 (s, 3H), 1.32 (s, 3H), 1.20 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 174.3, 140.7, 135.3, 132.5, 129.3, 128.9, 128.2, 128.1, 127.8, 106.2, 51.0, 49.3, 45.9, 44.6, 27.7, 27.5, 25.3, 21.5, 21.1.

HRMS (ESI) calcd for $C_{24}H_{28}N_2$ $[M+H]^+$: 345.2325, found: 345.2314.

4-methyl-7-phenyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3la)



Yield: 48%.

Appearance: colorless oil.

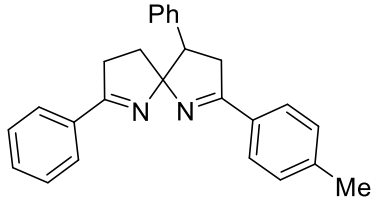
d.r. = 1:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.33 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.32 (ddd, *J* = 16.6, 9.6, 6.6 Hz, 1H), 3.22 (dd, *J* = 16.4, 8.1 Hz, 1H), 3.08 – 2.90 (m, 2H), 2.55 – 2.39 (m, 2H), 2.38 (s, 3H), 2.13 – 2.02 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.9, 140.9, 134.8, 132.0, 130.5, 129.0, 128.3, 128.0, 127.9, 108.9, 43.0, 43.0, 35.5, 34.1, 21.5, 13.5.

HRMS (ESI) calcd for $C_{21}H_{22}N_2$ $[M+H]^+$: 303.1856, found: 303.1855.

4,7-diphenyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3ma)



Yield: 37%.

Appearance: colorless oil.

d.r. = 1.3:1.

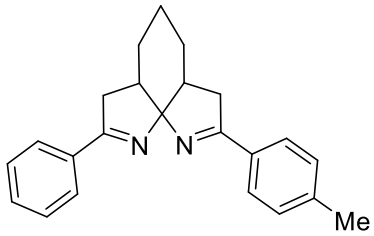
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.84 – 7.80 (m, 1H), 7.70 – 7.66 (m, 1H), 7.49 – 7.38 (m, 3H), 7.36 – 7.28 (m, 2H), 7.25 – 7.20 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.91 (t, *J* = 8.6 Hz, 0.46H), 3.72 – 3.61 (m, 054H), 3.59 – 3.37 (m, 2H), 3.23 (ddd, *J* = 16.2, 9.8, 6.7 Hz, 0.58H), 2.92 (ddd, *J* = 16.8, 9.1, 4.3 Hz, 0.46H), 2.73 – 2.56 (m,

1H), 2.41 (s, 1.31H), 2.39 (s, 1.65H), 2.23 – 2.16 (m, 0.46H), 2.15 – 2.04 (m, 0.58H), 2.00 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 174.3, 173.9, 172.5, 141.3, 141.2, 139.5, 138.1, 134.6, 134.2, 131.7, 131.4, 130.7, 130.4, 128.4, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 126.8, 126.7, 110.7, 108.6, 55.5, 52.6, 42.8, 40.1, 35.5, 35.5, 33.8, 30.2, 21.5.

HRMS (ESI) calcd for $C_{26}H_{24}N_2$ $[M+H]^+$: 365.2012, found: 365.2008.

2-phenyl-8-(*p*-tolyl)-3a,4,5,6,6a,7-hexahydro-3*H*-pyrrolo[3,2-h]indole (3na)



Yield: 60%.

Appearance: colorless oil.

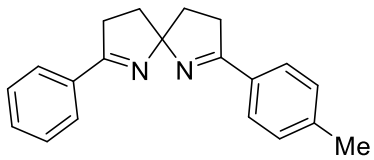
d.r. > 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.33 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.39 (ddd, *J* = 16.6, 7.9, 5.8 Hz, 2H), 2.80 (dt, *J* = 16.6, 5.6 Hz, 2H), 2.65 – 2.53 (m, 2H), 2.38 (s, 3H), 1.75 – 1.61 (m, 2H), 1.55 – 1.29 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.21, 174.16, 140.9, 134.8, 132.0, 130.6, 129.0, 128.3, 128.0, 106.3, 42.03, 42.01, 41.3, 27.3, 27.2, 21.5, 18.9.

HRMS (ESI) calcd for $C_{23}H_{24}N_2$ $[M+H]^+$: 329.2012, found: 329.2007.

2-phenyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene (3oa)



Yield: 55%.

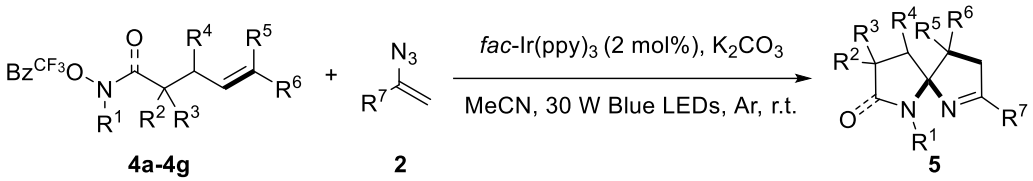
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.35 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.34 – 3.18 (m, 2H), 3.14 – 3.00 (m, 2H), 2.47 – 2.25 (m, 5H), 2.20 – 2.07 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.30, 173.29, 140.9, 134.4, 131.6, 130.7, 129.0, 128.3, 128.1, 128.1, 108.7, 35.48, 35.46, 35.4, 21.5.

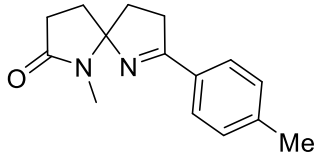
HRMS (ESI) calcd for $C_{20}H_{20}N_2$ $[M+H]^+$: 289.1699, found: 289.1699.

4.2 General procedure and product characterizations for the photoredox-catalyzed, amidyl radical-triggered trifunctionalizing *ipso*-spirocyclization



An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **4** (0.2 mmol, 1.0 equiv.), K_2CO_3 (0.3 mmol, 1.5 equiv.), and *fac*-Ir(ppy)$_3$ (2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2** (0.5 mmol, 2.5 equiv.) and CH_3CN (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction mixture was filtered and concentrated under reduced pressure. Then, the resulting residue was purified by column chromatography on silica gel to afford the desired product **5**.

1-methyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5aa)



Yield: 69%.

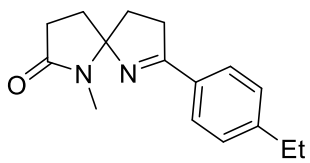
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.23 – 2.94 (m, 2H), 2.77 – 2.59 (m, 4H), 2.48 (ddd, *J* = 16.7, 9.6, 6.1 Hz, 1H), 2.41 (s, 3H), 2.30 – 2.19 (m, 2H), 2.17 – 2.04 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.2, 141.8, 130.7, 129.3, 128.0, 96.2, 34.8, 32.9, 31.6, 30.1, 24.5, 21.5.

HRMS (ESI) calcd for $C_{15}H_{18}N_2O$ $[M+H]^+$: 243.1492, found: 243.1491.

7-(4-ethylphenyl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5ab)



Yield: 48%.

Appearance: colorless oil.

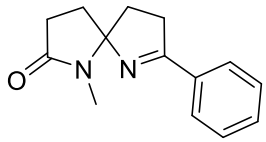
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.26

(m, 2H), 3.18 – 2.95 (m, 2H), 2.76 – 2.60 (m, 6H), 2.48 (ddd, *J* = 16.4, 9.6, 5.9 Hz, 1H), 2.31 – 2.18 (m, 2H), 2.17 – 2.04 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.2, 148.1, 130.9, 128.15, 128.09, 96.2, 34.8, 32.9, 31.6, 30.1, 28.9, 24.5, 15.4.

HRMS (ESI) calcd for $C_{16}H_{20}N_2O$ $[M+H]^+$: 257.1648, found: 257.1647.

1-methyl-7-phenyl-1,6-diazaspiro[4.4]non-6-en-2-one (5af)



Yield: 75%.

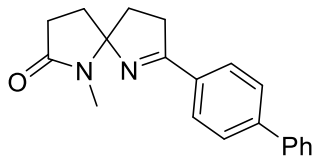
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 2H), 7.55 – 7.36 (m, 3H), 3.22 – 2.97 (m, 2H), 2.81 – 2.56 (m, 4H), 2.49 (ddd, *J* = 16.6, 9.3, 5.9 Hz, 1H), 2.39 – 2.18 (m, 2H), 2.19 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.3, 133.4, 131.4, 128.6, 128.0, 96.2, 34.9, 32.8, 31.6, 30.1, 24.5.

HRMS (ESI) calcd for $C_{14}H_{16}N_2O$ $[M+H]^+$: 229.1335, found: 229.1333.

7-([1,1'-biphenyl]-4-yl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5ag)



Yield: 56%.

Appearance: white solid.

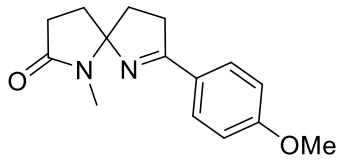
Melting Point: 138.6-140.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.53 – 7.43 (m, 2H), 7.43 – 7.34 (m, 1H), 3.29 – 2.98 (m, 2H), 2.80 – 2.59 (m, 4H), 2.51 (ddd, *J* = 17.5, 9.6, 5.9 Hz, 1H), 2.35 – 2.21 (m, 2H), 2.20 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.0, 144.1, 140.1, 132.2, 128.9, 128.5, 128.0, 127.3, 127.1, 96.2, 34.9, 32.9, 31.6, 30.1, 24.6.

HRMS (ESI) calcd for $C_{20}H_{20}N_2O$ $[M+H]^+$: 305.1648, found: 305.1643.

7-(4-methoxyphenyl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5ah)



Yield: 48%.

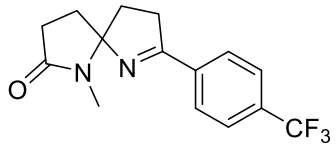
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.68 (m, 2H), 7.08 – 6.84 (m, 2H), 3.86 (s, 3H), 3.23 – 2.90 (m, 2H), 2.73 – 2.60 (m, 4H), 2.48 (ddd, *J* = 16.5, 9.2, 6.1 Hz, 1H), 2.32 – 2.16 (m, 2H), 2.18 – 2.02 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 172.6, 162.1, 129.7, 126.1, 113.9, 96.1, 55.4, 34.8, 32.9, 31.7, 30.2, 24.5.

HRMS (ESI) calcd for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441, found: 259.1440.

1-methyl-7-(4-(trifluoromethyl)phenyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5ai)



Yield: 52%.

Appearance: colorless oil.

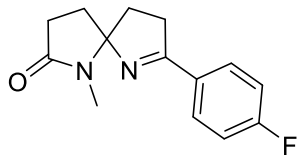
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 3.26 – 2.97 (m, 2H), 2.76 – 2.61 (m, 4H), 2.58 – 2.43 (m, 1H), 2.35 – 2.20 (m, 2H), 2.21 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 172.1, 136.6, 132.9 (q, *J* = 32.5 Hz), 128.4, 125.6 (q, *J* = 3.7 Hz),123.8 (q, *J* = 272.4 Hz) 96.4, 35.0, 32.8, 31.5, 30.1, 24.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.92.

HRMS (ESI) calcd for $C_{15}H_{15}F_3N_2O_3$ $[M+H]^+$: 297.1209, found: 297.1209.

7-(4-fluorophenyl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5aj)



Yield: 63%.

Appearance: colorless oil.

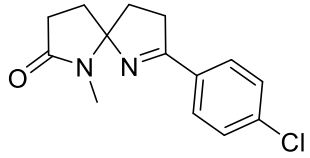
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.79 (m, 2H), 7.19 – 7.04 (m, 2H), 3.27 – 2.94 (m, 2H), 2.75 – 2.62 (m, 4H), 2.49 (ddd, *J* = 16.5, 9.6, 5.9 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.19 – 2.07 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 172.0, 164.7 (d, *J* = 252.1 Hz), 130.1 (d, *J* = 8.8 Hz), 129.7 (d, *J* = 3.1 Hz), 115.7 (d, *J* = 21.8 Hz), 96.2, 34.9, 32.9, 31.6, 30.1, 24.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.76.

HRMS (ESI) calcd for $C_{14}H_{15}FN_2O$ $[M+H]^+$: 247.1241, found: 247.1238.

7-(4-chlorophenyl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5ak)



Yield: 57%.

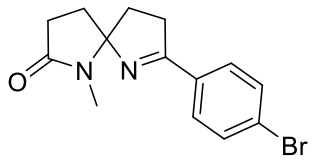
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.48 – 7.36 (m, 2H), 3.17 – 2.95 (m, 2H), 2.73 – 2.63 (m, 4H), 2.49 (ddd, *J* = 16.4, 9.4, 5.7 Hz, 1H), 2.31 – 2.19 (m, 2H), 2.19 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 172.2, 137.5, 131.8, 129.3, 128.9, 96.3, 34.8, 32.8, 31.6, 30.1, 24.5.

HRMS (ESI) calcd for $C_{14}H_{15}ClN_2O$ $[M+H]^+$: 263.0946, found: 263.0940

7-(4-bromophenyl)-1-methyl-1,6-diazaspiro[4.4]non-6-en-2-one (5al)



Yield: 54%.

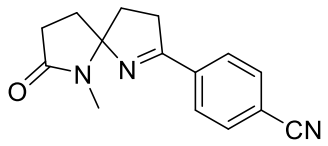
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 2H), 7.63 – 7.53 (m, 2H), 3.15 – 2.98 (m, 2H), 2.77 – 2.59 (m, 4H), 2.50 (ddd, *J* = 16.9, 9.7, 5.8 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.20 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 172.3, 132.2, 131.8, 129.5, 126.0, 96.3, 34.8, 32.8, 31.6, 30.1, 24.6.

HRMS (ESI) calcd for $C_{14}H_{15}BrN_2O$ $[M+H]^+$: 307.0441, found: 307.0436.

4-(6-methyl-7-oxo-1,6-diazaspiro[4.4]non-1-en-2-yl)benzonitrile (5au)



Yield: 48%.

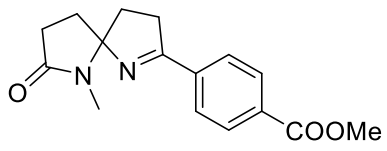
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 3.20 – 3.02 (m, 2H), 2.75 – 2.64 (m, 4H), 2.56 – 2.46 (m, 1H), 2.35 – 2.21 (m, 2H), 2.20 – 2.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 171.7, 137.3, 132.4, 128.6, 118.3, 114.6, 96.4, 34.9, 32.8, 31.5, 30.1, 24.6.

HRMS (ESI) calcd for $C_{15}H_{15}N_3O$ $[M+H]^+$: 254.1288, found: 254.1287.

methyl 4-(6-methyl-7-oxo-1,6-diazaspiro[4.4]non-1-en-2-yl)benzoate (5av)



Yield: 70%.

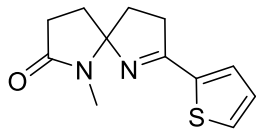
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 3.21 – 3.03 (m, 2H), 2.75 – 2.63 (m, 4H), 2.49 (ddd, *J* = 16.7, 9.5, 5.6 Hz, 1H), 2.33 – 2.22 (m, 2H), 2.19 – 2.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 172.6, 166.4, 137.3, 132.4, 129.8, 128.0, 96.4, 52.4, 35.0, 32.8, 31.5, 30.1, 24.6.

HRMS (ESI) calcd for $C_{16}H_{18}N_2O_3$ $[M+H]^+$: 287.1390, found: 287.1381.

1-methyl-7-(thiophen-2-yl)-1,6-diazaspiro[4.4]non-6-en-2-one (5ar)



Yield: 39%.

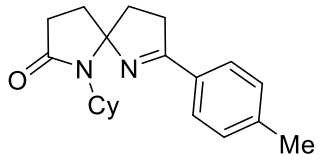
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.43 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.18 – 2.98 (m, 2H), 2.71 – 2.61 (m, 4H), 2.47 (ddd, *J* = 16.5, 9.4, 6.0 Hz, 1H), 2.32 – 2.18 (m, 2H), 2.18 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 167.6, 138.1, 130.5, 130.4, 127.7, 96.1, 35.5, 32.7, 31.9, 30.1, 24.6.

HRMS (ESI) calcd for $C_{12}H_{14}N_2OS$ $[M+H]^+$: 235.0900, found: 235.0897.

1-cyclohexyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5ba)



Yield: 80%.

Appearance: white solid.

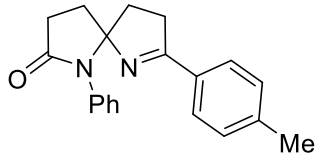
Melting Point: 167.5-169.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.09 (ddd, *J* = 17.2, 9.0, 4.8 Hz, 1H), 2.99 (dt, *J* = 17.1, 8.3 Hz, 1H), 2.71 (tt, *J* = 12.0, 3.6 Hz, 1H), 2.56 (ddd, *J* = 16.5, 9.6, 5.7 Hz, 1H), 2.45 – 2.30 (m, 5H), 2.28 – 2.01 (m, 6H), 1.81 – 1.65 (m, 2H), 1.64 – 1.50 (m, 2H), 1.31 – 0.98 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 172.2, 141.6, 131.1, 129.3, 127.9, 97.6, 53.6, 34.6, 33.5, 33.3, 30.8, 30.2, 29.8, 26.5, 26.3, 25.2, 21.5.

HRMS (ESI) calcd for $C_{20}H_{26}N_2O$ $[M+H]^+$: 311.2118, found: 311.2110.

1-phenyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5ca)



Yield: 29%.

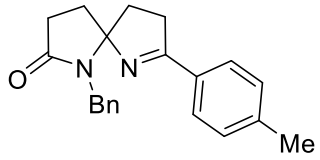
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.20 (m, 5H), 7.19 – 7.12 (m, 2H), 2.97 (dt, *J* = 17.1, 9.1 Hz, 1H), 2.84 (ddd, *J* = 17.1, 9.5, 5.5 Hz, 1H), 2.63 (ddd, *J* = 17.0, 9.3, 3.7 Hz, 1H), 2.50 – 2.27 (m, 6H), 2.20 (ddd, *J* = 14.9, 9.4, 5.5 Hz, 1H), 2.08 (ddd, *J* = 13.8, 9.5, 5.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 173.4, 141.6, 136.2, 131.0, 129.3, 129.1, 128.9, 127.9, 127.7, 97.8, 34.7, 34.2, 32.7, 30.6, 21.5.

HRMS (ESI) calcd for $C_{20}H_{20}N_2O$ $[M+H]^+$: 305.1648, found: 305.1641.

1-benzyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5da)



Yield: 38%.

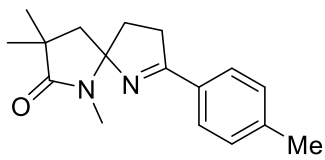
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.18 (m, 7H), 4.69 (d, *J* = 15.7 Hz, 1H), 3.92 (d, *J* = 15.7 Hz, 1H), 2.95 – 2.86 (m, 2H), 2.76 (ddd, *J* = 16.7, 9.4, 7.2 Hz, 1H), 2.57 (ddd, *J* = 16.9, 9.2, 5.4 Hz, 1H), 2.40 (s, 3H), 2.31 – 2.23 (m, 1H), 2.21 – 2.10 (m, 1H), 2.02 – 1.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 173.3, 141.7, 138.6, 130.8, 129.2, 128.4, 128.0, 127.5, 127.0, 96.6, 43.0, 34.7, 33.8, 32.6, 30.0, 21.5.

HRMS (ESI) calcd for $C_{21}H_{22}N_2O$ $[M+H]^+$: 319.1805, found: 319.1800.

1,3,3-trimethyl-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-en-2-one (5ea)



Yield: 72%.

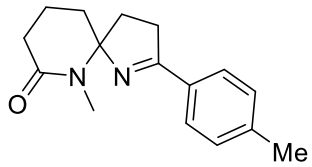
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.18 – 2.95 (m, 2H), 2.65 (s, 3H), 2.40 (s, 3H), 2.30 – 2.15 (m, 2H), 2.10 (ddd, *J* = 13.9, 9.2, 5.4 Hz, 1H), 2.02 (d, *J* = 13.0 Hz, 1H), 1.35 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 172.8, 141.6, 130.8, 129.3, 127.9, 93.5, 48.4, 40.6, 34.8, 32.3, 26.4, 26.0, 24.7, 21.5.

HRMS (ESI) calcd for $C_{17}H_{22}N_2O$ $[M+H]^+$: 271.1805, found: 271.1800.

6-methyl-2-(*p*-tolyl)-1,6-diazaspiro[4.5]dec-1-en-7-one (5fa)



Yield: 50%.

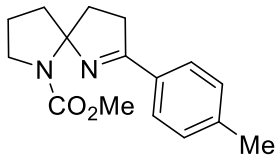
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.15 (ddd, *J* = 17.5, 9.5, 4.3 Hz, 1H), 2.99 (dt, *J* = 17.4, 8.6 Hz, 1H), 2.76 (s, 3H), 2.55 – 2.49 (m, 2H), 2.41 (s, 3H), 2.23 – 2.08 (m, 2H), 2.08 – 1.96 (m, 2H), 1.86 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 170.3, 141.7, 130.8, 129.3, 127.9, 93.4, 35.3, 34.7, 32.5, 32.1, 28.1, 21.5, 18.1.

HRMS (ESI) calcd for $C_{16}H_{20}N_2O$ $[M+H]^+$: 257.1648, found: 257.1649.

methyl 2-oxo-7-(*p*-tolyl)-1,6-diazaspiro[4.4]non-6-ene-1-carboxylate (5ga)



Yield: 52%.

Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.27 – 7.16 (m, 2H), 3.83 – 3.70 (m, 1H), 3.68 – 3.49 (m, 4H), 3.43 (ddd, *J* = 16.5, 10.2, 5.8 Hz, 0.78H), 3.13 (ddd, *J* = 15.5, 10.3, 5.1 Hz, 0.36H), 2.98 – 2.86 (m, 1H), 2.61 (ddd, *J* = 14.4, 10.3, 4.4 Hz, 0.7H), 2.50 – 2.35 (m, 3.42H), 2.27 – 2.15 (m, 2H), 2.10 – 1.98 (m, 1.43H), 1.94 – 1.86 (m, 1H).

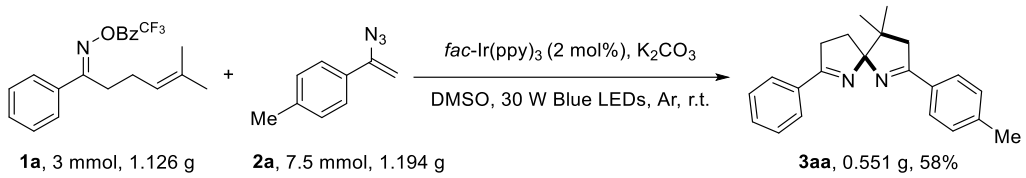
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.00, 171.88, 154.39, 140.98, 140.76, 131.58, 131.49, 129.13, 128.97, 128.01, 127.78, 96.14, 95.65, 52.24, 51.79, 48.67, 47.90, 42.52, 41.82, 35.84, 35.43, 33.66, 32.32, 22.94, 22.57, 21.49.

HRMS (ESI) calcd for $C_{16}H_{18}N_2O_3$ $[M+H]^+$: 273.1598, found: 273.1589.

5. Synthetic applications of the reaction

5.1 Gram-scale reaction

The synthesis of 4,4-dimethyl-7-phenyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4]nona-1,6-diene

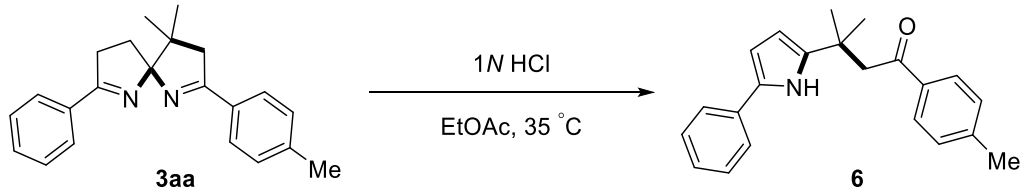


1a, 3 mmol, 1.126 g **2a**, 7.5 mmol, 1.194 g **3aa**, 0.551 g, 58%

An oven-dried Schlenk tube (100 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (1.126 g, 3 mmol), K_2CO_3 (621.9 mg, 4.5 mmol), and *fac*-Ir(ppy)$_3$ (39.3 mg, 0.06 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (1.194 g, 7.5 mmol) and DMSO (30 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (30 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as eluent to afford the desired product **3aa** (551 mg, 58%).

5.2 Product derivatizations

(a) The synthesis of 3-methyl-3-(5-phenyl-1*H*-pyrrol-2-yl)-1-(*p*-tolyl)butan-1-one[4]



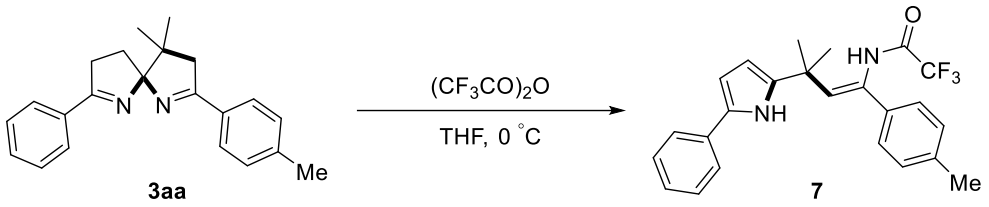
3aa **6**

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with **3aa** (31.6 mg, 0.1 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, EtOAc (1.5 mL) and HCl aqueous solution (500 μL, 1 *N*) were added in turn under Ar flow. The reaction mixture was stirred at 35 °C for 8 h. After completion, the reaction was quenched with saturated solution of $NaHCO_3$ and extracted with EtOAc. The

organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1 ~ 20:1) as eluent to afford the desired product **6** (23.8 mg, 75%). **Appearance:** colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.11 (m, 1H), 6.37 (t, *J* = 3.1 Hz, 1H), 6.00 (t, *J* = 3.2 Hz, 1H), 3.32 (s, 2H), 2.39 (s, 3H), 1.52 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.9, 144.2, 140.9, 135.2, 133.1, 131.0, 129.2, 128.7, 128.2, 125.5, 123.4, 104.9, 104.6, 50.8, 33.9, 29.1, 21.6. **HRMS (ESI)** calcd for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1852, found: 318.1851.

(b) The synthesis of

2,2,2-trifluoro-*N*-(3-methyl-3-(5-phenyl-1*H*-pyrrol)-1-(*p*-tolyl)but-1-en-1-yl)acetamide[5]

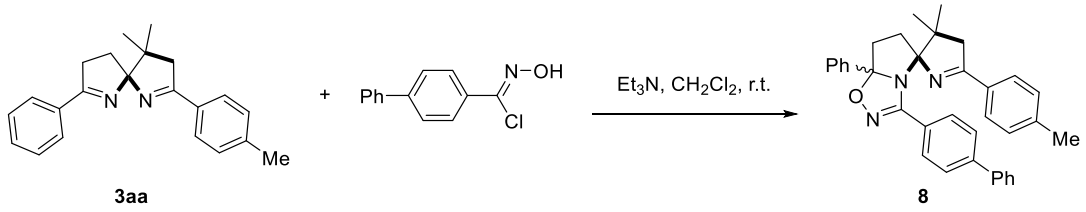


An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with **3aa** (31.6 mg, 0.1 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Anhydrous THF (2 mL) was added under Ar flow. Next, the solution was stirred in ice bath and $(CF_3CO)_2O$ (13.9 μL, 0.1 mmol) was added under Ar flow. The resulting mixture was stirred at 0 °C for 12 h. After completion, the reaction was quenched with saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1 ~ 20:1) as eluent to afford the desired product **7** (28.0 mg, 68%). **Appearance:** colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 7.49 – 7.41 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.07 (m, 5H), 6.47 (t, *J* = 4.0 Hz, 1H), 6.18 (t, *J* = 4.0 Hz, 1H), 5.84 (s, 1H), 2.33 (s, 3H), 1.56 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.2 (q, *J* = 37.4 Hz), 138.5, 138.3, 133.4, 132.7, 132.6,

132.3, 132.2, 129.3, 128.8, 126.3, 125.5, 123.7, 115.4 (q, J = 288.9 Hz), 106.2, 105.8, 36.1, 29.1, 21.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -75.55. **HRMS (ESI)** calcd for $C_{24}H_{23}F_3N_2O$ $[M+H]^+$: 413.1835, found: 413.1834.

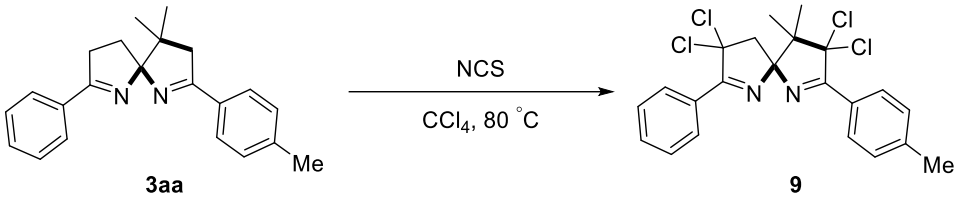
(c) The synthesis of

3'-([1,1'-biphenyl]-4-yl)-3,3-dimethyl-7a'-phenyl-5-(*p*-tolyl)-3,4,7',7a'-tetra-Hydro-6'*H*-spiro[pyrrole-2,5'-pyrrole[1,2-*d*][1,2,4]oxadiazole][6]



An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with **3aa** (31.6 mg, 0.1 mmol) and *N*-hydroxy-[1,1'-biphenyl]-4-carbimidoyl chloride (60.0 mg, 0.22 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, CH_2Cl_2 (2 mL) and Et_3N (35.0 μL, 0.25 mmol) were added in turn under Ar flow. The reaction mixture was stirred at room temperature for 8 h. After completion, the reaction was quenched with saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1 ~ 20:1) as eluent to afford the desired product **8** (43.5 mg, 85%). **Appearance:** colorless oil. **d.r. >** 20:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, J = 6.6 Hz, 2H), 7.74 (dd, J = 8.2, 1.4 Hz, 4H), 7.59 – 7.38 (m, 9H), 7.38 – 7.29 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 2.82 (ddd, J = 17.3, 9.3, 3.9 Hz, 1H), 2.76 – 2.56 (m, 3H), 2.32 (s, 3H), 2.08 – 1.80 (m, 2H), 1.18 (s, 3H), 0.98 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 158.0, 143.2, 141.4, 140.1, 137.4, 134.3, 130.9, 128.8, 128.6, 128.5, 128.3, 128.0, 127.8, 127.2, 127.1, 127.0, 125.5, 108.3, 105.8, 51.1, 49.0, 35.4, 25.4, 24.1, 23.0, 21.1. **HRMS (ESI)** calcd for $C_{35}H_{33}N_3O$ $[M+H]^+$: 512.2696, found: 512.2694.

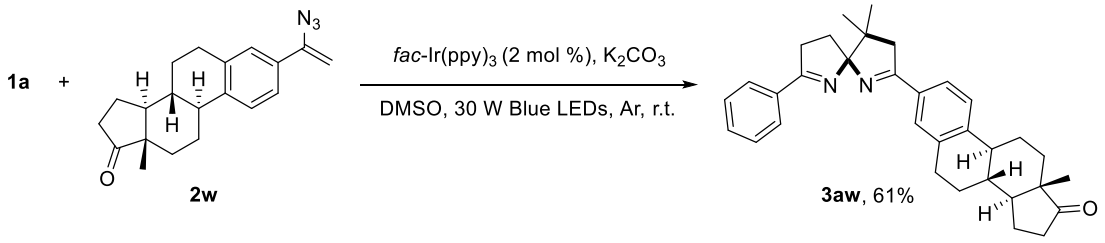
(d) The synthesis of 3,3,8,8-tetrachloro-4,4-dimethyl-7-phenyl-2-(*p*-tolyl)-1,6-diazaspiro[4.4] Nona-1,6-diene[7]



3aa **9**

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with **3aa** (31.6 mg, 0.1 mmol) and *N*-chlorosuccinimide (NCS) (80.1 mg, 0.6 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, CCl_4 (1 mL) was added under Ar flow. The reaction mixture was stirred at 80 °C for 8 h. After completion, the reaction was quenched with water and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1 ~ 20:1) as eluent to afford the desired product **9** (41.6 mg, 92%). **Appearance:** colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36 – 8.31 (m, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.42 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.57 (d, *J* = 15.6 Hz, 1H), 3.21 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H), 1.39 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 169.4, 142.0, 131.8, 130.0, 129.3, 129.0, 128.9, 128.3, 127.3, 102.7, 95.5, 85.8, 56.9, 55.4, 22.5, 21.7, 21.5 **HRMS (ESI)** calcd for $C_{22}H_{20}Cl_4N$ $[M+H]^+$: 453.0453, found: 453.0453.

5.3. Late-stage functionalization

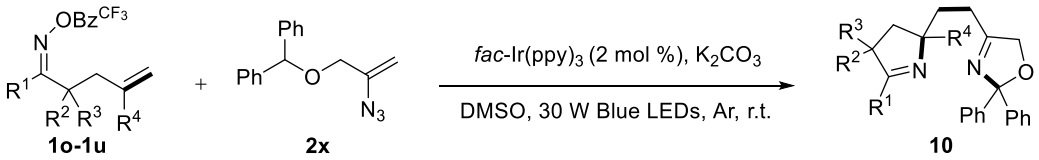


2w

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with oxime ester **1a** (28.2 mg, 0.075 mmol), K_2CO_3 (15.5 mg, 0.1125 mmol), and *fac*-Ir(ppy)$_3$ (1.0 mg, 0.0015 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar

for three times. Next, vinyl azide **2w** (60.3 mg, 0.1875 mmol) and DMSO (0.75 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (2.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel to afford the desired product **3aw** (21.9 mg, 61%). **Appearance:** yellow oil. **d.r. =** 1:1. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.66 (d, *J* = 9.3 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.48 – 7.33 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 1H), 3.31 (dt, *J* = 16.9, 8.5 Hz, 1H), 3.24 (d, *J* = 15.9 Hz, 1H), 3.08 – 2.89 (m, 3H), 2.86 (d, *J* = 15.9 Hz, 1H), 2.61 – 2.40 (m, 2H), 2.37 – 2.23 (m, 2H), 2.22 – 1.90 (m, 5H), 1.84 – 1.37 (m, 6H), 1.16 (s, 3H), 1.04 (s, 3H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 221.0, 174.4, 174.3, 173.15, 173.12, 142.63, 142.61, 136.58, 136.55, 134.9, 132.5, 130.5, 128.3, 128.25, 128.15, 128.0, 125.5, 125.4, 125.3, 110.6, 50.5, 50.0, 48.0, 44.94, 44.93, 44.59, 44.58, 38.0, 35.9, 35.5, 31.6, 29.3, 28.6, 26.4, 25.7, 25.1, 21.92, 21.89, 21.6, 13.9. **HRMS (ESI)** calcd for $C_{33}H_{38}N_2O$ $[M+H]^+$: 479.3057, found: 479.3051.

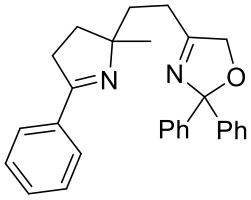
5.4 Exploration of other vinyl azides and olefinic oxime esters



An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1o-1u** (0.2 mmol, 1.0 equiv.), K_2CO_3 (0.3 mmol, 1.5 equiv.), and *fac*-Ir(ppy)$_3$ (2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, 2-azidoallyl diphenylmethyl ether **2x** (0.5 mmol, 2.5 equiv.) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (4.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and

dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel to afford the desired product **10**.

4-(2-(2-methyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,2-diphenyl-2,5-dihydrooxazole (10px)



Yield: 48%.

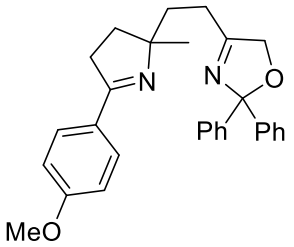
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.52 – 7.45 (m, 4H), 7.44 – 7.35 (m, 3H), 7.34 – 7.20 (m, 6H), 4.76 – 4.61 (m, 2H), 3.13 – 2.90 (m, 2H), 2.56 (ddd, *J* = 16.9, 11.7, 5.4 Hz, 1H), 2.45 (ddd, *J* = 15.9, 11.6, 5.0 Hz, 1H), 2.17 – 2.00 (m, 2H), 2.00 – 1.90 (m, 1H), 1.88 – 1.77 (m, 1H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 170.5, 144.01, 143.99, 134.5, 130.4, 128.4, 128.04, 128.03, 127.7, 127.51, 127.49, 126.08, 126.06, 113.1, 75.9, 75.5, 37.9, 35.4, 33.8, 27.2, 25.7.

HRMS (ESI) calcd for $C_{28}H_{28}N_2O$ $[M+H]^+$: 409.2274, found: 409.2267.

4-(2-(5-(4-methoxyphenyl)-2-methyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,2-diphenyl-2,5-dihydrooxazole (10qx)



Yield: 35%.

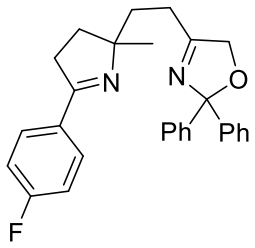
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.35 – 7.19 (m, 6H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.70 (d, *J* = 2.3 Hz, 2H), 3.83 (s, 3H), 3.15 – 2.84 (m, 2H), 2.55 (ddd, *J* = 16.9, 11.6, 5.5 Hz, 1H), 2.44 (ddd, *J* = 15.9, 11.6, 5.0 Hz, 1H), 2.13 – 1.99 (m, 2H), 1.94 (ddd, *J* = 12.9, 9.6, 5.1 Hz, 1H), 1.80 (ddd, *J* = 12.9, 9.6, 5.9 Hz, 1H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 169.9, 161.4, 144.01, 143.98, 129.3, 128.04, 128.03, 127.51, 127.49, 126.06, 126.08, 113.7, 113.1, 75.9, 75.2, 55.3, 38.0, 35.3, 33.8, 27.3, 25.8.

HRMS (ESI) calcd for $C_{29}H_{30}N_2O_2$ $[M+H]^+$: 439.2380, found: 439.2376.

4-(2-(5-(4-fluorophenyl)-2-methyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,2-diphenyl-2,5-dihydrooxazole (10rx)



Yield: 45%.

Appearance: colorless oil.

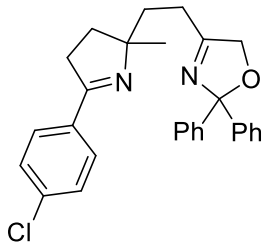
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 2H), 7.54 – 7.44 (m, 4H), 7.36 – 7.18 (m, 6H), 7.09 – 7.02 (m, 2H), 4.77 – 4.63 (m, 2H), 3.09 – 2.89 (m, 2H), 2.56 (ddd, *J* = 16.8, 11.5, 5.5 Hz, 1H), 2.44 (ddd, *J* = 16.0, 11.5, 5.0 Hz, 1H), 2.15 – 1.89 (m, 3H), 1.83 (ddd, *J* = 12.9, 9.5, 5.9 Hz, 1H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 169.3, 164.1 (d, *J* = 250.4 Hz), 143.99, 143.96, 130.7 (d, *J* = 3.1 Hz), 129.7 (d, *J* = 8.7 Hz), 128.1, 128.0, 127.53, 127.51, 126.1, 126.0, 115.4 (d, *J* = 21.7 Hz), 113.1, 75.9, 75.5, 37.9, 35.4, 33.9, 27.1, 25.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.07.

HRMS (ESI) calcd for $C_{28}H_{27}FN_2O$ $[M+H]^+$: 427.2180, found: 427.2175.

4-(2-(5-(4-chlorophenyl)-2-methyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,2-diphenyl-2,5-dihydrooxazole (10sx)



Yield: 32%.

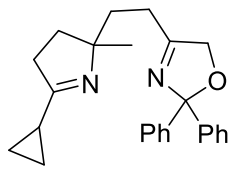
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.39 – 7.18 (m, 8H), 4.75 – 4.66 (m, 2H), 3.06 – 3.08 (m, 2H), 2.56 (ddd, *J* = 16.7, 11.5, 5.5 Hz, 1H), 2.44 (ddd, *J* = 16.0, 11.5, 5.1 Hz, 1H), 2.15 – 1.89 (m, 3H), 1.83 (ddd, *J* = 12.9, 9.5, 5.9 Hz, 1H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 169.4, 143.99, 143.95, 136.4, 132.9, 129.0, 128.6, 128.1, 128.0, 127.53, 127.51, 126.1, 126.0, 113.1, 75.9, 75.6, 37.9, 35.3, 33.9, 27.1, 25.7.

HRMS (ESI) calcd for $C_{28}H_{27}ClN_2O$ $[M+H]^+$: 443.1885, found: 443.1882.

4-(2-(5-cyclopropyl-2-methyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,2-diphenyl-2,5-dihydrooxazole (10tx)



Yield: 30%.

Appearance: colorless oil.

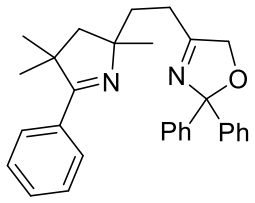
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 4H), 7.39 – 7.20 (m, 6H),

4.75 – 4.63 (m, 2H), 2.60 – 2.39 (m, 2H), 2.38 – 2.28 (m, 2H), 2.03 – 1.84 (m, 2H), 1.83 – 1.70 (m, 2H), 1.62 (ddd, *J* = 12.9, 9.5, 6.0 Hz, 1H), 1.21 (s, 3H), 0.90 – 0.82 (m, 2H), 0.81 – 0.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 144.0, 128.0, 127.52, 127.51, 126.1, 113.1, 75.9, 74.4, 37.7, 34.2, 33.4, 27.0, 25.7, 14.3, 7.3, 7.2.

HRMS (ESI) calcd for $C_{25}H_{28}N_2O$ $[M+H]^+$: 373.2274, found: 373.2262.

2,2-diphenyl-4-(2-(2,4,4-trimethyl-5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,5-dihydroox azole (10ux)



Yield: 32%.

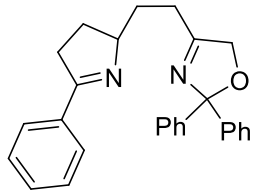
Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.53 – 7.47 (m, 4H), 7.41 – 7.35 (m, 3H), 7.34 – 7.22 (m, 6H), 4.77 – 4.66 (m, 2H), 2.59 (ddd, *J* = 16.9, 11.7, 5.3 Hz, 1H), 2.48 (ddd, *J* = 15.9, 11.7, 5.0 Hz, 1H), 2.14 – 1.97 (m, 2H), 1.95 (d, *J* = 13.1 Hz, 1H), 1.82 (d, *J* = 13.2 Hz, 1H), 1.42 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 172.4, 143.99, 143.97, 134.9, 129.3, 128.2, 128.1, 128.0, 127.54, 127.53, 126.1, 113.1, 76.0, 71.3, 51.58, 51.56, 39.0, 29.2, 28.7, 28.5, 25.8.

HRMS (ESI) calcd for $C_{30}H_{32}N_2O$ $[M+H]^+$: 437.2587, found: 437.2587.

2,2-diphenyl-4-(2-(5-phenyl-3,4-dihydro-2*H*-pyrrol-2-yl)ethyl)-2,5-dihydrooxazole (10ox)



Yield: 25%.

Appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.54 – 7.47 (m, 4H), 7.46 – 7.36 (m, 3H), 7.35 – 7.16 (m, 6H), 4.81 – 4.68 (m, 2H), 4.29 – 4.19 (m, 1H), 3.10 – 2.98 (m, 1H), 2.95 – 2.85 (m, 1H), 2.73 (ddd, *J* = 16.0, 9.9, 6.2 Hz, 1H), 2.62 (ddd, *J* = 15.9, 9.6, 6.0 Hz, 1H), 2.31 – 2.17 (m, 1H), 2.14 – 1.98 (m, 2H), 1.71 – 1.53 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 172.2, 144.05, 144.02, 134.4, 130.4, 128.4, 128.0,127.7, 127.5, 126.06, 126.05, 113.1, 76.0, 72.5, 35.1, 32.9, 28.5, 27.6.

HRMS (ESI) calcd for $C_{27}H_{26}N_2O$ $[M+H]^+$: 395.2118, found: 395.2108.

6. Mechanistic Studies

6.1 Stern-Volmer quenching studies

A Schlenck quartz cuvette was charged with 0.1 mM solution of *fac*-Ir(ppy)$_3$ in dry MeCN (2.0 mL) and the initial emission of the sample was collected. Then, the appropriate amount of olefinic amide **4a** as a 0.3 M solution in dry MeCN was added and the emission of the sample was collected again after the sample was shaken. All of solutions were kept oxygen-free during the operation. Linear regression of I_0/I against concentration was performed in Origin.

Species	Concentration (mM)
fac-Ir(ppy)$_3$	0.1
4a	Varied

Substrate (mM)	0.000	0.750	1.500	2.250	3.000	3.750
I_0/I	1.000	3.850	6.798	9.722	12.556	15.570

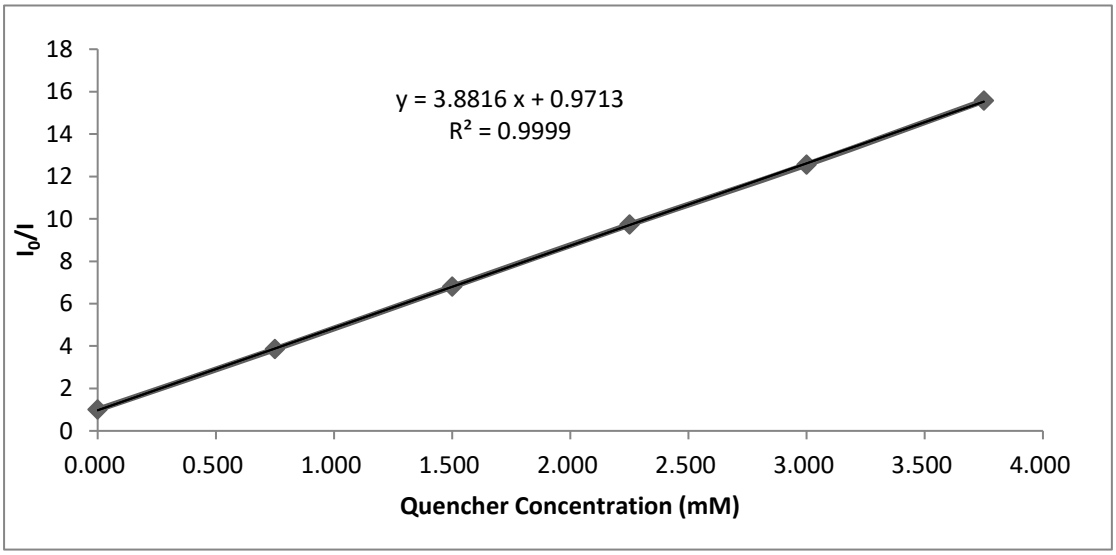


Figure S1. Stern-Volmer quenching experiments with *fac*-Ir(ppy)$_3$ (0.1 mM, λ_{ex} = 420 nm, λ_{em} = 516 nm).

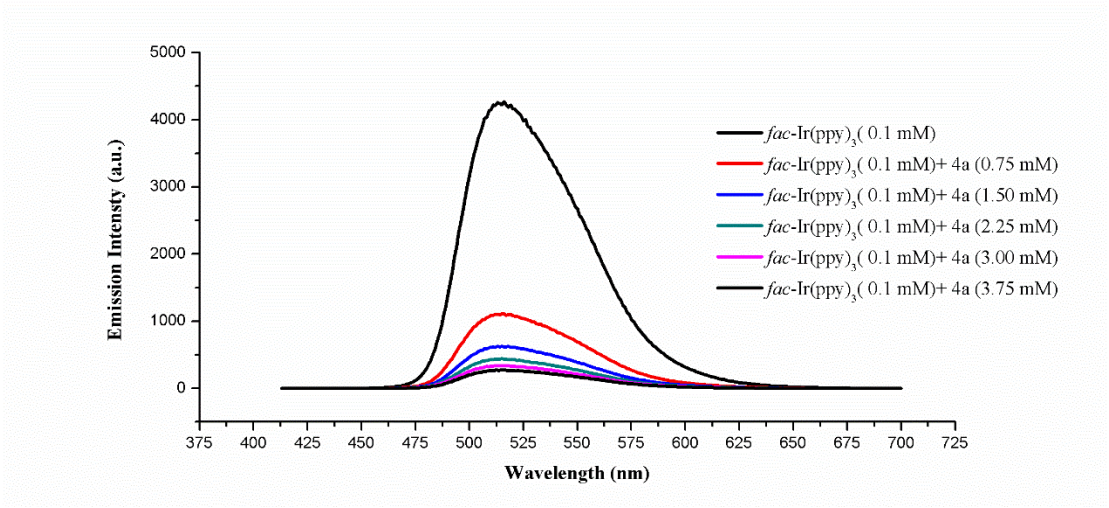


Figure S2. Emission spectra of *fac*-Ir(ppy)$_3$ (0.1 mM, λ_{ex} = 420 nm) in the presence of **4a**.

6.2 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell under argon at room temperature. All cyclic voltammograms were measured using Ag/Ag$^+$ (0.01 M $AgNO_3$ in MeCN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M hexafluorophosphate (^{n}Bu$_4$NPF$_6$) in CH_3CN at a scan rate of 50 mV/s; Prior to each measurement, solutions were purged with argon (Ar) for 10 minutes to ensure the oxygen-free conditions.

Measuring the Fc/Fc$^+$ redox couple afforded $E_{1/2}$ = +0.12 V *vs.* Ag/Ag$^+$ under our experimental conditions. The obtained value was referenced to Ag/Ag$^+$ and converted to SCE by subtracting 0.30 V, providing a value of +0.42 V for the Fc/Fc$^+$ couple[8]. The reduction half-peak potential of **1a** and **4a** in MeCN was measured as -1.91 V and -1.79 V (*vs.* Ag/Ag$^+$), and calculated to -1.61 V and -1.49 V (*vs.* SCE), respectively. The corresponding oxidation peak of **1a** was measured as +1.46 V (*vs.* Ag/Ag$^+$), and calculated to +1.76 V (*vs.* SCE) and the oxidation peak of **4a** was not observed.

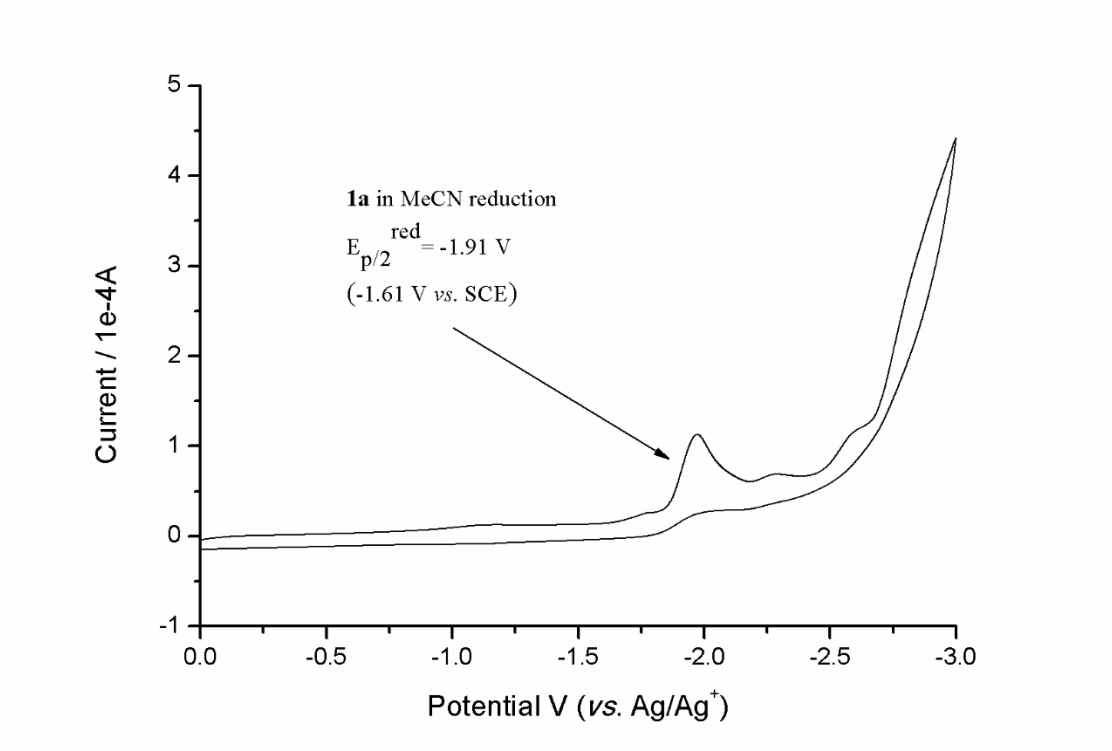


Figure S3. Cyclic voltammetry of **1a** (5 mM) in MeCN (*vs.* Ag/Ag$^+$) with ^{n}Bu$_4$NPF$_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

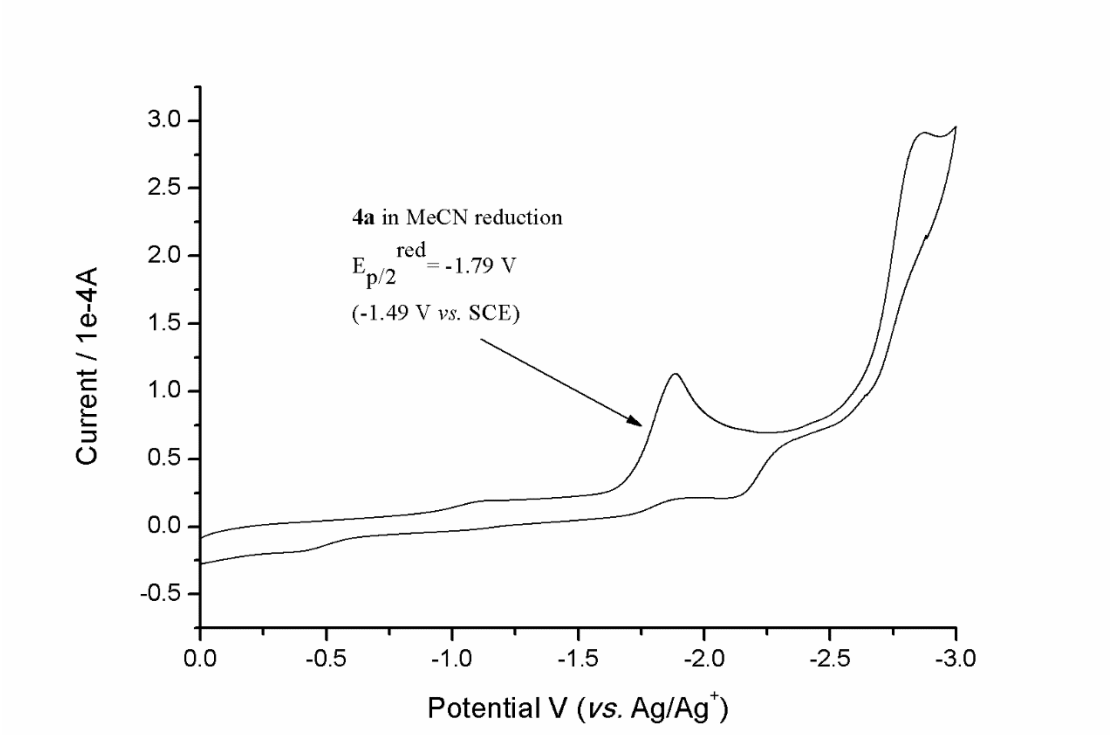
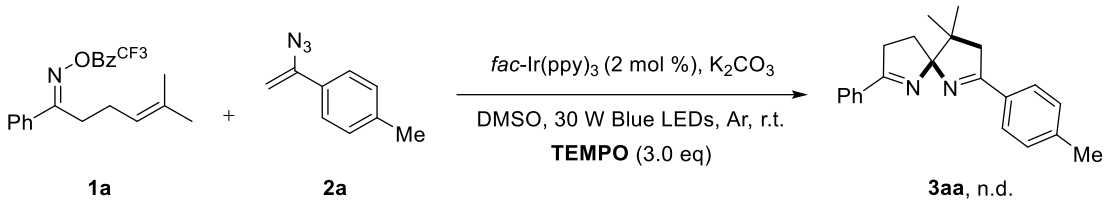


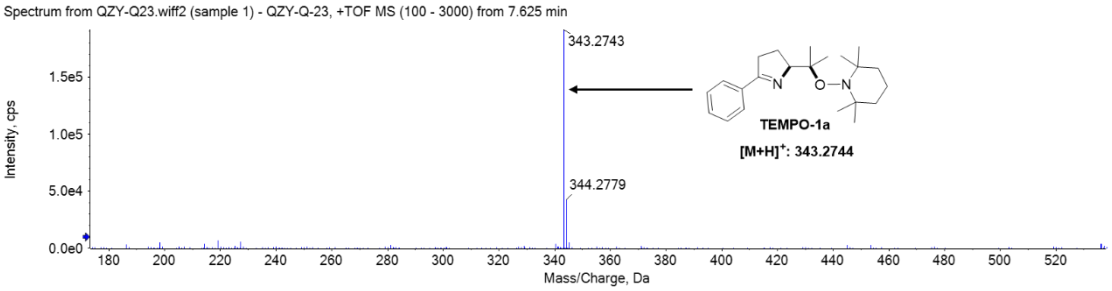
Figure S4. Cyclic voltammetry of **4a** (5 mM) in MeCN (*vs.* Ag/Ag$^+$) with ^{n}Bu$_4$NPF$_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

6.3 Radical trapping experiment and LC-MS analysis

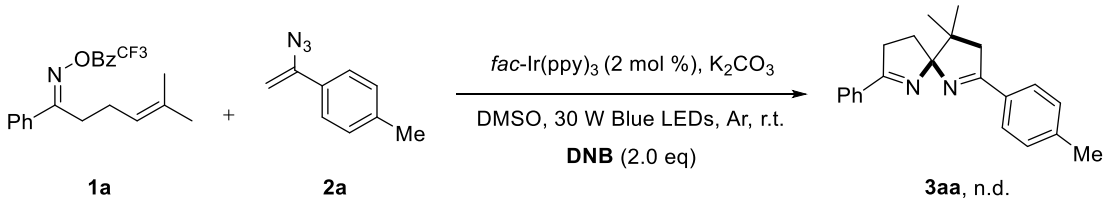


1a **2a** **3aa**, n.d.

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (75.1 mg, 0.2 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), 2,2,6,6-tetramethyl-piperidinyloxyl (TEMPO) (93.8 mg, 0.6 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (79.6 mg, 0.5 mmol) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the corresponding **1a**-derived TEMPO-trapped adduct was detected through LC-MS analysis and the desired product **3aa** was not detected.



6.4 Electron-transfer scavenging experiment

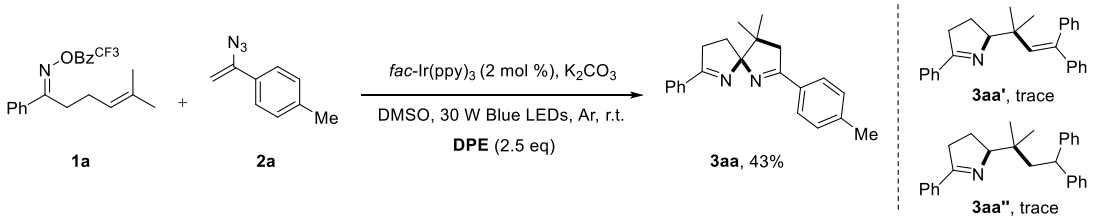


1a **2a** **3aa**, n.d.

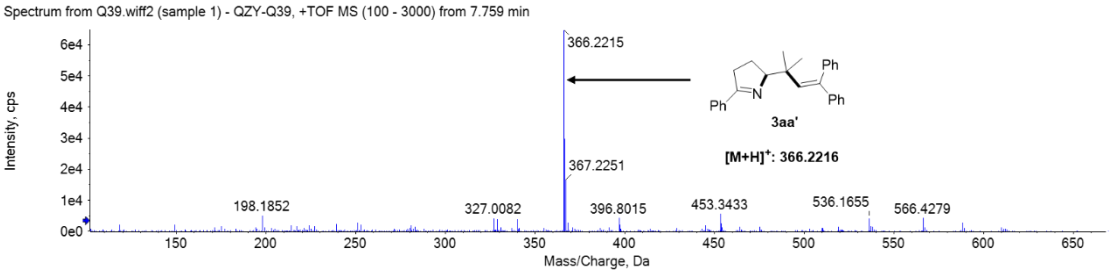
An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (75.1 mg, 0.2 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), *p*-dinitrobenzene (DNB) (67.2 mg, 0.4 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (79.6 mg, 0.5 mmol) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm

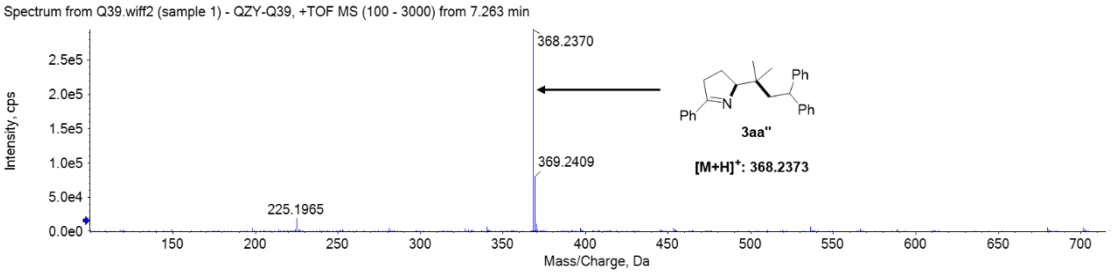
from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the desired product **3aa** was not detected.

6.5 Competitive experiment

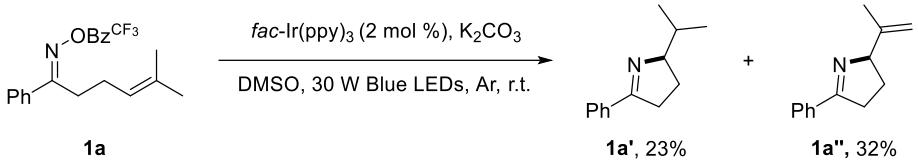


An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (75.1 mg, 0.2 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (79.6 mg, 0.5 mmol), 1,1-diphenylethylene (DPE) (88 μL, 0.5 mmol), and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, a trace amount of addition products **3aa'** and **3aa''** were captured by LC-MS analysis. Then, the reaction was quenched with H_2O (4.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (6:1) as eluent to afford the desired product **3aa** (43%).





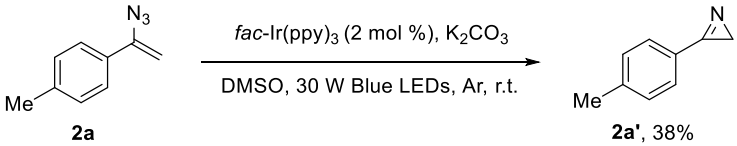
6.6 Auxiliary analysis of the nitrogen radical process



1a **1a'**, 23% **1a''**, 32%

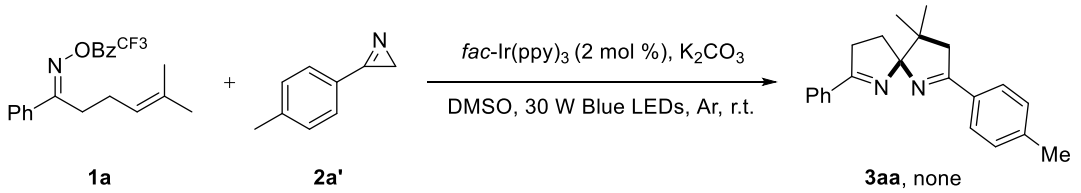
An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (187.7 mg, 0.5 mmol), K_2CO_3 (103.7 mg, 0.75 mmol), and *fac*-Ir(ppy)$_3$ (6.5 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, DMSO (5 mL) was added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (10 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel to afford products **1a'** and **1a''**. **2-isopropyl-5-phenyl-3,4-dihydro-2*H*-pyrrole** (**1a'**, 21.4 mg, 23%), **Appearance:** colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.81 (m, 2H), 7.43 – 7.39 (m, 3H), 4.08 – 3.95 (m, 1H), 3.06 – 2.79 (m, 2H), 2.14 – 2.02 (m, 1H), 2.03 – 1.88 (m, 1H), 1.77 – 1.61 (m, 1H), 1.08 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 134.8, 130.2, 128.4, 127.7, 79.1, 35.3, 33.5, 25.1, 20.1, 18.3. **HRMS (ESI)** calcd for $C_{13}H_{17}N$ $[M+H]^+$: 188.1434, found: 188.1424. **5-phenyl-2-(prop-1-en-2-yl)-3,4-dihydro-2*H*-pyrrole** (**1a''**, 29.5 mg, 32%), **Appearance:** colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.87 (m, 2H), 7.52 – 7.35 (m, 3H), 4.96 – 4.93 (m, 1H), 4.86 – 4.81 (m, 1H), 4.76 – 4.69 (m, 1H), 3.09 – 3.00 (m, 1H), 2.99 – 2.89 (m, 1H), 2.37 – 2.20 (m, 1H), 1.86 – 1.78 (m, 1H), 1.77 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.2, 146.8, 134.5, 130.5, 128.4, 127.8, 110.3, 77.6, 35.2, 28.3, 19.5. **HRMS (ESI)** calcd for $C_{13}H_{15}N$ $[M+H]^+$: 186.1277, found: 186.1269.

6.7 Analysis of the key intermediate: 2*H*-azirine (2a')



2a **2a'**, 38%

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with K_2CO_3 (41.5 mg, 0.3 mmol) and *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, vinyl azide **2a** (79.6 mg, 0.5 mmol) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the reaction was quenched with H_2O (4.5 mL) and extracted with EtOAc. The organic layer was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and then the resulting residue was purified by column chromatography on silica gel to afford the product **2a'** (24.9 mg, 38%). **Appearance:** colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 2.46 (s, 3H), 1.76 (s, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.3, 143.8, 129.8, 129.6, 122.7, 21.9, 19.5.



1a **2a'** **3aa**, none

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with olefinic oxime ester **1a** (75.1 mg, 0.2 mmol), K_2CO_3 (41.5 mg, 0.3 mmol), and *fac*-Ir(ppy)$_3$ (2.6 mg, 2 mol%). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Next, **2a'** (65.5 mg, 0.5 mmol) and DMSO (2 mL) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs, and then stirred at room temperature for 6 h. After completion, the desired product **3aa** was not detected. The result suggested that 2*H*-azirine **2a'** was not the key intermediate in this cyclization reaction.

7. Computational details of mechanistic studies

7.1 General setup

All calculations were performed with the Gaussian 16 C.01 version[9] for all calculations and GaussView 6.0 was used to build up input structure, if not otherwise stated. For optimization, the functional M06-2X[10] was applied, as well as Grimme's D3 dispersion correction[11]. The basis set def2-SVP[12] was used for all optimization, and all final structure were re-calculated in a single-point calculation with the def2-TZVP basis set[12] with SMD solvation model (DMSO)[13]. Redox potentials were then calculated from the Free Energies of the respective oxidized and reduced species; the values were referenced to saturated calomel electrode (SCE) by subtraction of its absolute potential in acetonitrile (E_{ref} = 4.422 V).[14]

7.2 Input keywords

The following keywords were applied for different calculation types:

For Geometry Optimization

#p um062x/def2svp opt freq EmpiricalDispersion=GD3

For Single-Point Calculations:

#p um062x/def2tzvp scrf=(smd, solvent=dmso) EmpiricalDispersion=GD3

For Transition States:

#p um062x/def2svp opt=(calcfc,ts,noeigentest) freq EmpiricalDispersion=GD3

7.3 M06-2X calculated absolute energies and free energies of all structures

Geometry	G[1]	Thermal Correction to Free Energy	Single[2]	G1[3]	IF[4]
1a	-1315.154945	0.309105	-1316.975162	-1316.666057	
1a+1e$^-$	-1315.184331	0.307305	-1317.063951	-1316.756646	
CF_3_Phen_carboxylate	-756.410185	0.070302	-757.449700	-757.379398	
A	-558.811393	0.212508	-559.658401	-559.445893	
TS_A_B	-558.793079	0.213285	-559.640670	-559.427385	-598.45
B	-558.829914	0.216364	-559.674521	-559.458157	

B+2f	-1031.401335	0.338298	-1032.900363	-1032.562065	
TS_B_2f	-1031.393988	0.341176	-1032.893717	-1032.552541	-379.52
C (1)	-1031.444939	0.348672	-1032.948568	-1032.599896	
C (2)	-1031.448687	0.347225	-1032.959961	-1032.612736	
TS_C	-1031.449067	0.346817	-1032.959267	-1032.612450	-226.26
D_N_2	-1031.518935	0.340204	-1033.022883	-1032.682679	
D (1)	922.110968	0.341905	923.489135	923.147230	
D (2)	-922.112935	0.340514	-923.488330	-923.147816	
TS_D_E	-922.096376	0.336848	-923.466469	-923.129621	-1833.71
E (1)	-922.134000	0.340497	-923.509738	-923.169241	
E (2)	-922.132723	0.339990	-923.509776	-923.169786	
TS_E_F	-922.107297	0.341787	-923.481379	-923.139592	-711.76
E_cation	-921.912252	0.345825	-923.358677	-923.012852	
F	-922.147196	0.344954	-923.525501	-923.180547	
F_cation (H)	-921.964780	0.348564	-923.408755	-923.060191	
CF_3_Phen_carboxylate	-756.410185	0.070302	-757.449700	-757.379398	
H	-921.581441	0.335945	-922.949914	-922.613969	
CF_3_Phen_carboxylate acid	-756.949589	0.084018	-757.924551	-757.840533	
Fac-Ir-S_0	-1538.509805	0.424692	-1540.539443	-1540.114751	
Fac-Ir-T	-1538.410922	0.419645	-1540.438270	-1540.018625	
Fac-Ir+1	-1538.279734	0.424126	-1540.351086	-1539.926960	
DMSO	-552.786970	0.051209	-553.201619	-553.150410	
TS_B_DMSO	-1111.588805	0.286193	-1112.854037	-1112.567844	-1470.52
1a'	-559.474724	0.233104	-560.337769	-560.104665	
DMSO_radical	-552.130734	0.071929	-552.528028	-552.491896	

7.4 Coordinates of DFT computed stationary points

1a

0 1

C	-6.57914100	-0.54766600	-0.06069300
C	-6.80425100	-1.91927900	0.00261800
C	-5.71629200	-2.79494400	0.02315400
C	-4.41758900	-2.30349700	-0.01957600
C	-4.17885000	-0.92060300	-0.08637900
C	-5.27626000	-0.05035700	-0.10588400
C	-2.76946200	-0.40745500	-0.12650300
C	-2.59594400	1.08634300	-0.28958300
N	-1.89103400	-1.32554000	-0.00091500
C	-1.20909600	1.71318400	-0.47238400
C	-1.33585700	3.18903600	-0.73454000
C	-1.17665000	4.18368700	0.15014200
C	-1.35063300	5.62202100	-0.25770000
C	-0.81902400	3.98343500	1.59852400
O	-0.58194900	-0.89587800	-0.02806100
H	-7.42040900	0.14665500	-0.07517500
H	-7.82331800	-2.30741200	0.03603700
H	-5.88244500	-3.87203300	0.07301300
H	-3.56372700	-2.98017100	-0.00027500
H	-5.13270100	1.02871700	-0.15212700
H	-3.22469000	1.37664000	-1.14709900
H	-3.07967900	1.55677600	0.58354800
H	-0.59267400	1.51772500	0.41283100
H	-0.70357300	1.23305800	-1.32279800
H	-1.61714700	3.46522400	-1.75777100
H	-1.60496100	5.71658800	-1.32132200
H	-2.14568000	6.10183300	0.33525900
H	-0.42754900	6.19319900	-0.06873800
H	-0.73275500	2.92865100	1.88447600

H	0.13509600	4.48287800	1.83111200
H	-1.58108500	4.44915600	2.24323500
C	0.30722100	-1.91110000	0.15935700
O	0.00740000	-3.04707800	0.35700000
C	1.71668100	-1.40916500	0.09109900
C	2.03772300	-0.08092700	-0.20138300
C	2.72979200	-2.34130200	0.33513400
C	3.37184800	0.31364500	-0.24901300
H	1.24464100	0.64054000	-0.39016600
C	4.06216300	-1.94838800	0.28931700
H	2.44801400	-3.36990600	0.56238800
C	4.37709500	-0.62108700	-0.00556800
H	3.63397300	1.34892500	-0.46888900
H	4.86000900	-2.66471800	0.48796800
C	5.82210000	-0.20563500	-0.10807900
F	6.29136500	-0.38113100	-1.34548100
F	6.59706500	-0.91834900	0.71018100
F	5.98610700	1.08286100	0.19497000

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C	-6.74674200	-0.14201000	0.00568200
C	-7.04441500	-1.50049400	0.03835100
C	-5.99632600	-2.42712400	0.03218300
C	-4.67544300	-2.00216900	-0.00845900
C	-4.36022100	-0.62940400	-0.04632700
C	-5.41958100	0.29038800	-0.03575000
C	-2.93340800	-0.19378300	-0.08633300
C	-2.67540000	1.29873600	-0.13440700

N	-2.09340400	-1.16362300	-0.05263500
C	-1.24350900	1.81624600	-0.27800300
C	-1.21632900	3.31861700	-0.33310200
C	-0.25614700	4.12749700	0.13637200
C	-0.36453700	5.62383900	0.00188500
C	1.00362400	3.64794600	0.80663500
O	-0.79783000	-0.84280500	-0.07412000
H	-7.55150600	0.59595500	0.01340000
H	-8.08174100	-1.83856400	0.07028400
H	-6.21442600	-3.49661700	0.06079500
H	-3.84871200	-2.71327200	-0.00835300
H	-5.21970600	1.36158500	-0.05635500
H	-3.27589500	1.70289300	-0.96897200
H	-3.12385700	1.73957800	0.77466200
H	-0.62771900	1.44182700	0.54667600
H	-0.80030500	1.39224300	-1.19351700
H	-2.07530400	3.79368500	-0.82599100
H	-1.29917400	5.92226200	-0.49219600
H	-0.32381600	6.10902900	0.99128100
H	0.48054800	6.02680200	-0.58047600
H	1.06887600	2.55649800	0.88843900
H	1.88564000	3.99053000	0.24104200
H	1.09235000	4.07954000	1.81713300
C	0.07673400	-1.96430800	0.08138200
O	-0.37876800	-3.07771100	0.25449100
C	1.43965000	-1.54201900	0.02628700
C	1.86948500	-0.19728800	-0.23124300
C	2.46251600	-2.52237900	0.25149000
C	3.20557100	0.13202500	-0.24175700

H	1.12477300	0.57085700	-0.43353200
C	3.79278500	-2.18261000	0.23943300
H	2.14583400	-3.54836300	0.44433300
C	4.20162500	-0.84381600	0.00204100
H	3.50603600	1.16437900	-0.43687000
H	4.55223600	-2.94552600	0.42578600
C	5.63313100	-0.49725000	-0.08332500
F	6.17340100	-0.64184100	-1.32114500
F	6.40498700	-1.26106600	0.71528700
F	5.88095700	0.78516700	0.24915700

CF_3_Phen_carboxylate

-1 1

O	3.85430000	1.12944400	0.01685700
C	3.34117300	-0.00002800	0.01092900
O	3.85425700	-1.12945700	0.01647400
C	1.77794200	0.00005200	-0.00592800
C	1.07025800	1.20465800	-0.01582900
C	1.07031400	-1.20459000	-0.01568600
C	-0.32212600	1.21247700	-0.03268400
H	1.66432100	2.12035800	-0.01336500
C	-0.32208600	-1.21252000	-0.03252200
H	1.66438900	-2.12028600	-0.01310400
C	-1.01795700	-0.00004200	-0.04021700
H	-0.87863600	2.15204600	-0.04833400
H	-0.87852200	-2.15213200	-0.04805100
C	-2.51301800	-0.00001100	0.00294600
F	-2.99415400	0.00059200	1.25853100
F	-3.04443000	-1.07715700	-0.59374700

F	-3.04441600	1.07658100	-0.59476700

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C	-3.31746500	1.81090500	-0.07588300
C	-4.48487400	1.08596000	0.14872100
C	-4.42432500	-0.30353500	0.27773200
C	-3.20363400	-0.96140800	0.18264000
C	-2.02380600	-0.23764600	-0.04340400
C	-2.09076600	1.15330300	-0.17200100
C	-0.71605200	-0.96700300	-0.14209100
C	0.55595500	-0.17454200	-0.40467900
N	-0.66197100	-2.21354700	-0.00861300
C	1.81731700	-1.03690900	-0.47988900
C	3.03413500	-0.21147400	-0.79293600
C	3.90522600	0.30462900	0.08579700
C	5.07426600	1.13503600	-0.37136600
C	3.81352700	0.11719800	1.57633000
H	-3.35745700	2.89630400	-0.17759000
H	-5.44339600	1.60159300	0.22354400
H	-5.33590000	-0.87653300	0.45342600
H	-3.14668300	-2.04637800	0.28184800
H	-1.18608200	1.73595000	-0.34780400
H	0.41985700	0.39012800	-1.34186600
H	0.66337900	0.57760300	0.39444800
H	1.93120300	-1.58704000	0.46457400
H	1.67505100	-1.80251300	-1.25725400
H	3.19818300	0.01222400	-1.85358800
H	5.09583400	1.24191200	-1.46372100

H	5.03776400	2.14109600	0.07671000
H	6.02425100	0.67975000	-0.04804300
H	2.94544900	-0.47686200	1.88519000
H	4.72191100	-0.37563900	1.95829900
H	3.75339900	1.09614800	2.07828400

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C	3.97642600	0.73247700	-0.04106200
C	4.39040600	-0.58388600	0.14563200
C	3.43931700	-1.60346300	0.23476100
C	2.08486100	-1.30691700	0.13720800
C	1.65926500	0.01658000	-0.04525600
C	2.61678400	1.03269800	-0.13296400
C	0.19461200	0.31350700	-0.16156400
C	-0.28923400	1.75745700	-0.14314400
N	-0.63706900	-0.62224600	-0.31647700
C	-1.77858700	1.69766600	0.18156800
C	-2.37840200	0.51281900	-0.52578400
C	-3.37727300	-0.29926900	-0.03403500
C	-3.77227000	-0.34199900	1.41066200
C	-3.92947700	-1.39216800	-0.89476300
H	4.71365600	1.53333700	-0.11542600
H	5.45338800	-0.81782500	0.22180200
H	3.75907300	-2.63638400	0.38123000
H	1.32842300	-2.09023000	0.19953800
H	2.30728700	2.06789500	-0.28379000
H	0.27170200	2.36853400	0.57803500
H	-0.11119900	2.19148500	-1.14237500

H	-1.90433000	1.59197600	1.26748000
H	-2.28100600	2.62922600	-0.12259500
H	-2.25555900	0.51413200	-1.61475300
H	-3.58936100	0.60043700	1.94082000
H	-4.83845400	-0.59219900	1.51625100
H	-3.20426700	-1.13574300	1.92943700
H	-3.54129200	-2.36741600	-0.55027300
H	-5.02814500	-1.44325500	-0.83124500
H	-3.63900600	-1.27125700	-1.94635300

B

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C	3.93486300	-0.74364200	-0.19398100
C	4.31240100	0.59560100	-0.13156500
C	3.33878400	1.58673900	0.02025200
C	1.99606800	1.23945300	0.10861600
C	1.60695500	-0.10621400	0.04231000
C	2.58714800	-1.09328400	-0.10893100
C	0.17282300	-0.46305500	0.14192200
C	-0.33068800	-1.89349500	0.05134200
N	-0.72912100	0.40922300	0.35784200
C	-1.83785600	-1.67015300	-0.09962900
C	-2.03577800	-0.24110000	0.46253400
C	-3.14084200	0.54445100	-0.18176200
C	-4.48554800	-0.10395500	-0.24207900
C	-3.05984100	2.03450000	-0.18342800
H	4.69116100	-1.52132500	-0.30959600
H	5.36626300	0.87002700	-0.19996900
H	3.63291100	2.63624300	0.07064000

H	1.21881100	1.99434500	0.23191300
H	2.30027000	-2.14516200	-0.15581800
H	0.11921700	-2.45239400	-0.78065800
H	-0.07266300	-2.42759800	0.98170500
H	-2.11381300	-1.67128500	-1.16531100
H	-2.44644200	-2.42617500	0.41230000
H	-2.25418900	-0.30684600	1.55450900
H	-4.42723900	-1.15621800	-0.55900100
H	-4.98396800	-0.09676400	0.74906300
H	-5.15344000	0.42576800	-0.93699900
H	-3.79216000	2.46937400	-0.87955500
H	-3.27949500	2.45194500	0.82043700
H	-2.05230500	2.37643200	-0.45215300

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C	6.96918500	-0.80968300	-0.16993300
C	7.42121200	0.37329000	0.40996900
C	6.50098500	1.33478300	0.83693700
C	5.13755100	1.11343300	0.68427200
C	4.67419300	-0.07313800	0.09756100
C	5.60095900	-1.03150800	-0.32724100
C	3.21750900	-0.29632100	-0.05596800
C	2.63793300	-1.53049900	-0.72744600
N	2.35658600	0.51779200	0.41144200
C	1.17348700	-1.11670600	-0.89788800
C	0.99590000	0.01643300	0.14122900
C	-2.40153900	-0.27246700	-1.95067100
C	-0.86638700	1.70961200	0.74064300

H	7.68330200	-1.56458100	-0.50223200
H	8.49138700	0.54839000	0.53132300
H	6.85332900	2.26162700	1.29241300
H	4.39856800	1.84515100	1.01270000
H	5.25481900	-1.96231200	-0.77985400
H	3.14334200	-1.77805500	-1.67144900
H	2.75783300	-2.39783800	-0.05625800
H	1.01748300	-0.71525400	-1.91067100
H	0.45077700	-1.92697900	-0.74274400
H	0.62089600	-0.40877400	1.08957600
H	-1.41522100	-0.64791300	-2.22315600
H	-2.95004400	0.35539300	-2.65165000
H	-1.77773500	2.10089800	0.25764800
H	-1.16314900	0.96265100	1.49183500
H	-0.40076500	2.55538800	1.28361800
C	0.07018800	1.12579000	-0.26298600
C	0.43403700	1.96949900	-1.44033500
H	1.07654600	2.81652000	-1.13222400
H	0.99576300	1.40938700	-2.20252100
H	-0.46197900	2.39869100	-1.91660700
C	-2.91779500	-0.54882000	-0.74625200
C	-4.25376300	-0.06969800	-0.30143000
C	-4.43533900	0.46236300	0.98333400
C	-5.34791500	-0.12363400	-1.17439400
C	-5.68257000	0.93873500	1.37972700
H	-3.58960600	0.52692500	1.67117700
C	-6.59352800	0.35567400	-0.77658900
H	-5.21597900	-0.56085200	-2.16547600
C	-6.76428400	0.88725100	0.50133200

H	-5.80771000	1.35723400	2.37920500
H	-7.43808000	0.30441800	-1.46524600
H	-7.74133600	1.25781700	0.81440200
N	-2.11833000	-1.28968600	0.16412000
N	-2.66005200	-1.85530200	1.11141900
N	-3.03571100	-2.40484100	2.01772700

TS_B_2f

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C	6.36815800	0.75321600	-0.78660200
C	6.69255900	-0.52275800	-1.24130200
C	5.72326800	-1.52967000	-1.23884300
C	4.43791200	-1.26090900	-0.78407300
C	4.10421300	0.01990300	-0.32042400
C	5.07939800	1.02335100	-0.32625100
C	2.72930500	0.29358900	0.15839200
C	2.30119700	1.63841000	0.71952100
N	1.80175400	-0.57668000	0.08492600
C	0.94116900	1.29129300	1.33454200
C	0.54398000	-0.00588900	0.59989100
C	-2.16899300	0.18607300	1.93365100
C	-0.80748300	-2.13873400	0.53759600
H	7.12031300	1.54342300	-0.78923700
H	7.70107100	-0.73518400	-1.59962900
H	5.97537000	-2.52943200	-1.59591600
H	3.66275900	-2.02791900	-0.77630200
H	4.83241300	2.02647600	0.02548300
H	3.02257200	2.04847700	1.43984900
H	2.21760300	2.36449700	-0.10692500

H	1.06361700	1.09702000	2.40967900
H	0.18444100	2.07551800	1.21260100
H	-0.07196600	0.24680500	-0.28584400
H	-1.58938300	0.81984200	2.60532400
H	-2.54261300	-0.76483300	2.31040200
H	-1.47306700	-2.79318600	1.12097700
H	-1.37803300	-1.72607500	-0.30864800
H	-0.00129000	-2.76455900	0.11245000
C	-0.21511600	-1.05054400	1.37686800
C	0.28758600	-1.44592400	2.73061100
H	1.26864500	-1.95097400	2.64328400
H	0.42321800	-0.58986400	3.40748000
H	-0.40201900	-2.15349700	3.21449400
C	-2.68826500	0.71016500	0.79099400
C	-3.59799400	-0.03933000	-0.10329500
C	-3.45803100	0.02720100	-1.49981500
C	-4.59768000	-0.86750300	0.43072100
C	-4.28718100	-0.71945500	-2.33300500
H	-2.67253700	0.64423200	-1.94162100
C	-5.42202700	-1.61536300	-0.40423300
H	-4.73559600	-0.90621300	1.51253400
C	-5.27100100	-1.54449500	-1.78960500
H	-4.15669200	-0.66185600	-3.41452800
H	-6.19583300	-2.25075900	0.02921200
H	-5.92028700	-2.12819600	-2.44337600
N	-2.21519800	1.98547600	0.39040800
N	-2.86528600	2.65500000	-0.40684500
N	-3.36449200	3.35056000	-1.13902900

C (1)

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C	6.19223300	0.74731900	0.05780200
C	6.50203800	0.04970300	-1.10736300
C	5.48320800	-0.55588200	-1.84795800
C	4.16266700	-0.46472200	-1.42447100
C	3.84218300	0.23688300	-0.25328500
C	4.86701400	0.84225200	0.48241500
C	2.43191200	0.32227100	0.19169800
C	2.00561400	1.10403200	1.41998600
N	1.49293300	-0.28710700	-0.41471000
C	0.47666500	1.04752800	1.30835000
C	0.21758500	-0.07046200	0.26358100
C	-1.73708600	-1.22083900	1.43407000
C	-0.36785400	-2.44745100	-0.29516400
H	6.98414600	1.22105200	0.63967800
H	7.53825400	-0.02323400	-1.44134500
H	5.72441500	-1.10179600	-2.76136300
H	3.35012100	-0.92875400	-1.98463200
H	4.63246000	1.38997100	1.39678800
H	2.39316500	0.60664700	2.32481700
H	2.40505100	2.12823900	1.41776100
H	-0.00910600	0.85922800	2.27511700
H	0.08431000	2.00123500	0.93001400
H	-0.50849600	0.26326700	-0.49526600
H	-1.68250100	-0.48361800	2.24878200
H	-2.02750800	-2.17668800	1.89518300
H	-0.85916200	-3.36989000	0.04982700
H	-0.93451000	-2.06547900	-1.15743100

H	0.64631900	-2.68443400	-0.64050500
C	-0.31568900	-1.41234900	0.83306100
C	0.59913500	-1.92615200	1.94903100
H	1.63044100	-2.04395500	1.58460900
H	0.60946000	-1.24703600	2.81598900
H	0.25311400	-2.90916900	2.30222500
C	-2.80946100	-0.83700300	0.46050700
C	-3.08259900	0.53400700	0.06566500
C	-3.57528300	0.86203100	-1.21920300
C	-2.82452700	1.60281100	0.95473600
C	-3.80685600	2.18386800	-1.58276200
H	-3.73808500	0.08393600	-1.96477600
C	-3.06195000	2.92005800	0.58450300
H	-2.45492300	1.39305800	1.95834600
C	-3.55671200	3.22266900	-0.68593500
H	-4.17543900	2.40453800	-2.58565300
H	-2.86436500	3.72113400	1.29875200
H	-3.74031700	4.25791100	-0.97502300
N	-3.46871700	-1.91849900	-0.07596800
N	-4.48497200	-1.83905200	-0.76542200
N	-5.41214100	-1.91814000	-1.41068400

C (2)

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C	5.95214700	1.14341800	0.00559000
C	6.45830400	0.12962200	-0.80462900
C	5.59585400	-0.83308600	-1.33607700
C	4.23517900	-0.78205200	-1.05755200
C	3.71757200	0.23551300	-0.24324600

C	4.58658500	1.19724600	0.28411600
C	2.26663900	0.27754400	0.05190400
C	1.63559200	1.37078300	0.89184200
N	1.46595200	-0.62085000	-0.36290900
C	0.14039400	1.04193800	0.77823700
C	0.10699800	-0.35451200	0.09647900
C	-1.83993700	-1.27010600	1.48492900
C	-0.36910900	-2.81846200	0.14924200
H	6.62160800	1.89684400	0.42299800
H	7.52628000	0.08769500	-1.02424000
H	5.99078900	-1.62706200	-1.97173900
H	3.54253200	-1.52157700	-1.46075600
H	4.19804500	1.99454400	0.92008300
H	2.01659600	1.31185400	1.92461400
H	1.89060800	2.37117000	0.51310800
H	-0.36178300	1.05123500	1.75437600
H	-0.38024300	1.77906700	0.15061900
H	-0.53629900	-0.33375800	-0.79936700
H	-1.81955300	-0.47532300	2.24515200
H	-2.19296300	-2.19179100	1.96869800
H	-0.69588800	-3.67335200	0.76003000
H	-1.04233300	-2.75181800	-0.71710200
H	0.64827700	-3.00597500	-0.21628600
C	-0.39555200	-1.52986800	0.97683000
C	0.50461800	-1.69484700	2.20500400
H	1.52783700	-1.95537500	1.89951300
H	0.54565100	-0.77296500	2.80676300
H	0.12601900	-2.50021400	2.85199900
C	-2.83680400	-0.89615300	0.41311500

C	-3.00889600	0.54888600	0.07833400
C	-2.90653700	0.99954200	-1.24401200
C	-3.22562500	1.47849600	1.10198200
C	-3.00376200	2.35811800	-1.53285000
H	-2.72869700	0.28265700	-2.04711800
C	-3.34701000	2.83495000	0.80882000
H	-3.31380100	1.13882700	2.13574200
C	-3.22622200	3.27797500	-0.50760500
H	-2.90839200	2.69919800	-2.56441000
H	-3.53047700	3.54881500	1.61282500
H	-3.30701700	4.34164600	-0.73602500
N	-3.44670600	-1.86971600	-0.14934100
N	-4.45581900	-1.43609000	-1.13719200
N	-4.71476400	-2.07106200	-2.06944300

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C	5.95741100	1.13396900	0.00555900
C	6.46178300	0.12064200	-0.80635800
C	5.59771900	-0.84000200	-1.33891300
C	4.23722300	-0.78736500	-1.05981600
C	3.72140400	0.22972700	-0.24378500
C	4.59203400	1.18938000	0.28469500
C	2.27060800	0.27349400	0.05187500
C	1.64153800	1.36614400	0.89404200
N	1.46839300	-0.62273700	-0.36463100
C	0.14580800	1.03919600	0.78155200
C	0.10984800	-0.35490800	0.09514900
C	-1.83887400	-1.27147700	1.48064000

C	-0.37249500	-2.81779200	0.13886300
H	6.62813300	1.88579300	0.42383200
H	7.52961500	0.07747400	-1.02643000
H	5.99125400	-1.63361700	-1.97589400
H	3.54333200	-1.52525000	-1.46387900
H	4.20489100	1.98630500	0.92197700
H	2.02356900	1.30548600	1.92632400
H	1.89729200	2.36674500	0.51633700
H	-0.35470000	1.04552000	1.75858100
H	-0.37525400	1.77902500	0.15748700
H	-0.53287200	-0.32973700	-0.80092300
H	-1.81830400	-0.47693800	2.24121800
H	-2.19219400	-2.19287100	1.96466600
H	-0.70207300	-3.67404900	0.74621900
H	-1.04509500	-2.74572300	-0.72757300
H	0.64447500	-3.00689900	-0.22700200
C	-0.39569900	-1.53217100	0.97112500
C	0.50434500	-1.70382000	2.19858400
H	1.52702200	-1.96494500	1.89180200
H	0.54720900	-0.78445900	2.80404300
H	0.12441600	-2.51111200	2.84239000
C	-2.83847500	-0.89465000	0.40972500
C	-3.00380400	0.55266600	0.07798500
C	-2.88874500	1.00651700	-1.24211900
C	-3.22222400	1.48013000	1.10272000
C	-2.97526400	2.36636400	-1.52754900
H	-2.71031400	0.29010500	-2.04563300
C	-3.33276100	2.83848800	0.81283300
H	-3.32002400	1.13785200	2.13478900

C	-3.19934400	3.28475400	-0.50106600
H	-2.87031300	2.70995200	-2.55736300
H	-3.51756400	3.55097700	1.61776300
H	-3.27159100	4.34959500	-0.72685900
N	-3.45188300	-1.86730500	-0.14697900
N	-4.48672500	-1.39959600	-1.15619700
N	-4.81308900	-2.06964100	-2.03366700

D_N_2

0 2

C	5.99082800	1.52328000	0.43299300
C	6.62432700	0.78758700	-0.56587400
C	5.88503100	-0.10131900	-1.35101200
C	4.52024000	-0.25378600	-1.13705300
C	3.87481100	0.48348800	-0.13394700
C	4.62084600	1.37316400	0.64718000
C	2.42086700	0.30945800	0.08995400
C	1.65314300	1.10614400	1.12695700
N	1.73387100	-0.54347700	-0.55878200
C	0.20550000	0.67616500	0.85269200
C	0.34369500	-0.53200900	-0.11481500
C	-1.51525500	-1.92624700	0.93962500
C	0.15755500	-2.98712300	-0.60548100
H	6.56382500	2.21808800	1.04863200
H	7.69575500	0.90568300	-0.73523000
H	6.37978400	-0.67725500	-2.13458400
H	3.92204700	-0.94069200	-1.73670900
H	4.13204900	1.95295600	1.43203700
H	2.00410800	0.83486300	2.13632000

H	1.81462800	2.18765100	1.01135700
H	-0.33767700	0.42686500	1.77364800
H	-0.35863100	1.48296300	0.36447500
H	-0.28326600	-0.38644500	-1.01080900
H	-1.62355200	-1.33405100	1.85971300
H	-1.79041000	-2.96294300	1.18084900
H	-0.06344000	-3.98555100	-0.19839800
H	-0.51249000	-2.81428300	-1.46042500
H	1.19270900	-2.97068900	-0.96883600
C	-0.03817400	-1.91724300	0.47280800
C	0.84057300	-2.24493900	1.68400100
H	1.89597000	-2.31978500	1.38546500
H	0.75470900	-1.47705600	2.46917600
H	0.54170800	-3.20796900	2.12452100
C	-2.48972700	-1.39785600	-0.10534300
C	-2.88310400	0.05123300	-0.09648800
C	-2.96758300	0.74600000	-1.30860000
C	-3.19899800	0.70822500	1.09715900
C	-3.35089900	2.08470700	-1.32369900
H	-2.72488100	0.22365800	-2.23558600
C	-3.59121900	2.04548700	1.07863300
H	-3.15617400	0.17080200	2.04627500
C	-3.66299100	2.73720200	-0.13004700
H	-3.40913000	2.62136100	-2.27162100
H	-3.84416400	2.54856300	2.01302400
H	-3.96529900	3.78529300	-0.14291400
N	-2.94498900	-2.14708600	-1.00196500
N	-6.11602800	-0.19023600	-0.09027500
N	-6.31070600	0.60769600	-0.81301300

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C	-5.45760600	-1.47742800	0.50574100
C	-6.11132300	-0.70116300	-0.44836200
C	-5.38406700	0.20265000	-1.22771400
C	-4.01115800	0.32956000	-1.05247700
C	-3.34542500	-0.44842200	-0.09440500
C	-4.07956800	-1.35275300	0.68112900
C	-1.88292700	-0.30080800	0.08949100
C	-1.09632000	-1.13565700	1.08128600
N	-1.20342600	0.55986300	-0.55683100
C	0.34846700	-0.71466600	0.77900500
C	0.19898400	0.51824800	-0.15509800
C	2.10778300	1.86157300	0.87682400
C	0.40543400	2.98178800	-0.59270500
H	-6.02104600	-2.18412000	1.11666000
H	-7.18915400	-0.79907000	-0.58724200
H	-5.89465200	0.81054100	-1.97620900
H	-3.42219300	1.02759300	-1.64839400
H	-3.57495500	-1.96424100	1.43114100
H	-1.41588900	-0.88993600	2.10748400
H	-1.27430300	-2.21142600	0.93918400
H	0.91781100	-0.49297100	1.69116100
H	0.89116300	-1.51538900	0.25755200
H	0.79718500	0.38596300	-1.07260600
H	2.23333100	1.24918800	1.78120600
H	2.40462300	2.88917700	1.13109000
H	0.65329800	3.96690500	-0.16898200

H	1.04698600	2.82000900	-1.47130900
H	-0.64029500	2.98864900	-0.92468400
C	0.61765400	1.88365200	0.45356400
C	-0.22061800	2.19373000	1.69770500
H	-1.28287300	2.29174600	1.43203100
H	-0.12434200	1.40495400	2.46066200
H	0.10575600	3.14080600	2.15308100
C	3.04391700	1.34143900	-0.20777700
C	3.42434000	-0.11175900	-0.22976800
C	3.45941900	-0.79272800	-1.45264600
C	3.74723800	-0.79553800	0.94672600
C	3.79066400	-2.14474200	-1.49337500
H	3.20943700	-0.25078200	-2.36632300
C	4.08983000	-2.14565200	0.90217600
H	3.74056100	-0.27209000	1.90453000
C	4.10412600	-2.82453600	-0.31579700
H	3.80271600	-2.67097700	-2.44887700
H	4.34505900	-2.67010400	1.82409600
H	4.36202900	-3.88407400	-0.34788500
N	3.46581200	2.10141100	-1.11152800

D (2)

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C	-6.20047800	-1.49887000	0.25880800
C	-6.85180100	-0.31850300	-0.09136900
C	-6.10584300	0.81901500	-0.41214000
C	-4.71714700	0.77537200	-0.38192100
C	-4.05344700	-0.40754400	-0.02524200
C	-4.80673700	-1.54297200	0.29319200

C	-2.57320100	-0.44201900	0.00126700
C	-1.77952900	-1.67499000	0.40162200
N	-1.86311700	0.55392400	-0.35485600
C	-0.37693900	-1.08174300	0.56927400
C	-0.44617500	0.20128200	-0.28259300
C	1.84421100	0.94462000	0.52702300
C	0.41446600	2.47077900	-0.89587500
H	-6.77804200	-2.39060000	0.50655300
H	-7.94206300	-0.28280200	-0.11693600
H	-6.61436200	1.74379100	-0.68916600
H	-4.11388000	1.64812100	-0.63405700
H	-4.30432100	-2.47277800	0.56511300
H	-2.16896400	-2.15996200	1.30721700
H	-1.82663600	-2.41609100	-0.41422800
H	-0.20959300	-0.82797000	1.62749800
H	0.42976700	-1.75392100	0.24897500
H	-0.12751800	-0.03168600	-1.31423000
H	1.82982600	0.27159800	1.40124600
H	2.42713600	1.82879200	0.83675100
H	0.96522400	3.36353500	-0.56164300
H	0.87926000	2.09908400	-1.81964800
H	-0.62035800	2.76167300	-1.12305700
C	0.41242700	1.39467600	0.19525800
C	-0.18372200	1.99119500	1.47665800
H	-1.20169000	2.35570900	1.28489100
H	-0.23247100	1.25207700	2.29117000
H	0.42959500	2.83505100	1.82746800
C	2.65584800	0.23685100	-0.55257400
C	4.07178500	-0.15654900	-0.22663000

C	4.85490800	-0.77848400	-1.21042900
C	4.62696400	0.08048700	1.03514500
C	6.16402000	-1.15456300	-0.93485100
H	4.42020800	-0.96079700	-2.19414000
C	5.94159500	-0.29856100	1.30891800
H	4.04064400	0.56224400	1.81749300
C	6.71226100	-0.91565900	0.32740000
H	6.76278300	-1.63680100	-1.70883500
H	6.36260300	-0.10817300	2.29711500
H	7.74013000	-1.21066500	0.54334300
N	2.18196300	-0.02997400	-1.68293600

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C	-6.10116100	-1.29570800	0.52189800
C	-6.57196500	-0.79417700	-0.68973800
C	-5.71079400	-0.08330200	-1.53056100
C	-4.38787400	0.12527700	-1.16134600
C	-3.90600400	-0.37250000	0.05968700
C	-4.77473800	-1.08536200	0.89598700
C	-2.50116800	-0.14683800	0.44202900
C	-1.89296600	-0.64964400	1.73883800
N	-1.66902300	0.46066800	-0.32553400
C	-0.54473800	0.08202500	1.74544100
C	-0.38275500	0.47392600	0.27136400
C	1.94998300	1.27778300	0.32909900
C	0.48667400	1.83756000	-1.63196500
H	-6.76844100	-1.85431300	1.17975500
H	-7.61027600	-0.95780100	-0.98238900

H	-6.07731300	0.30761400	-2.48098900
H	-3.69664500	0.67227200	-1.80319500
H	-4.41284600	-1.48511000	1.84473100
H	-2.52005900	-0.43670500	2.61542700
H	-1.77061100	-1.74437300	1.68044500
H	-0.60489700	0.98290000	2.37752900
H	0.28587100	-0.53564000	2.11305500
H	0.32077200	-0.45774000	-0.22930100
H	2.04094800	1.32742000	1.42933500
H	2.66439600	2.00989100	-0.07690800
H	1.18215900	2.63692900	-1.92918800
H	0.76788400	0.91439400	-2.15873600
H	-0.52692000	2.10953200	-1.95153500
C	0.52696500	1.64148500	-0.11109200
C	0.08099400	2.94162800	0.57009800
H	-0.96610900	3.15741400	0.31049100
H	0.16409200	2.88477000	1.66513600
H	0.70099800	3.78518300	0.23071200
C	2.37120600	-0.12796500	-0.10501800
C	3.84009100	-0.44335700	-0.13775500
C	4.27711900	-1.61599100	-0.76991600
C	4.78267700	0.39474400	0.46766300
C	5.62915000	-1.93772800	-0.79973700
H	3.53330600	-2.26337800	-1.23578400
C	6.13830500	0.06605000	0.44349500
H	4.46622100	1.30730300	0.97399100
C	6.56477700	-1.09732300	-0.19205300
H	5.95811400	-2.84962000	-1.30037400
H	6.86282400	0.72520900	0.92392000

H	7.62573000	-1.35076400	-0.21536600
N	1.54590000	-1.03622300	-0.40579000

E (1)

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C	5.83230000	-1.58070300	-0.63990700
C	6.31295500	-1.26817300	0.63283100
C	5.51788500	-0.51859200	1.50724200
C	4.25925900	-0.08545500	1.11837700
C	3.75961400	-0.39483000	-0.16729300
C	4.57163000	-1.15165900	-1.03940000
C	2.45656600	0.05264000	-0.57442600
C	1.81281300	-0.21264000	-1.91710400
N	1.65719700	0.79336500	0.23193600
C	0.43029500	0.44495200	-1.75362500
C	0.53008100	1.05819600	-0.37091000
C	-1.94362900	1.33696700	-0.04144200
C	-0.31973300	2.10880900	1.74743500
H	6.44672300	-2.16504900	-1.32671200
H	7.30211700	-1.60673900	0.94386200
H	5.88942100	-0.27265200	2.50342900
H	3.62965800	0.49847600	1.78984600
H	4.20703200	-1.40257300	-2.03721500
H	2.40024200	0.23803700	-2.73380700
H	1.74855500	-1.29039100	-2.13192700
H	0.21060200	1.19979400	-2.52437500
H	-0.39012300	-0.29067100	-1.78309400
H	-2.14413000	1.38025100	-1.12698700
H	-2.69038000	2.00570800	0.41791700

H	-1.07900100	2.79552000	2.15007800
H	-0.38548800	1.16289300	2.30119000
H	0.67607500	2.53196900	1.92995100
C	-0.54670300	1.91866200	0.24411700
C	-0.47195500	3.30126300	-0.43765800
H	0.50579000	3.76553600	-0.24674600
H	-0.61447100	3.22364200	-1.52568500
H	-1.25587200	3.96281100	-0.03885700
C	-2.23663700	-0.08361300	0.41192600
C	-3.64809900	-0.56220400	0.22144700
C	-3.99013600	-1.84746700	0.66647800
C	-4.63391100	0.22313600	-0.38860100
C	-5.28309300	-2.33175600	0.50738200
H	-3.21153300	-2.44746500	1.13754000
C	-5.93130900	-0.26435800	-0.55029300
H	-4.40308400	1.22571500	-0.74925100
C	-6.25975400	-1.54097500	-0.10246300
H	-5.53420200	-3.33305200	0.86089600
H	-6.68728100	0.35993300	-1.02887000
H	-7.27490600	-1.92098900	-0.22749300
N	-1.39850200	-0.89970000	0.91042100
H	-0.46724500	-0.48955500	1.00512100

E (2)

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C	-6.00385000	-1.38378600	0.68293200
C	-6.45448000	-1.14663100	-0.61693800
C	-5.61046700	-0.50757200	-1.53297700
C	-4.33590400	-0.10985900	-1.15932400

C	-3.86592100	-0.34240000	0.15451200
C	-4.72763700	-0.98910300	1.06822200
C	-2.54788900	0.06909500	0.54456500
C	-1.93345000	-0.13007900	1.91212700
N	-1.69774500	0.69623200	-0.30690800
C	-0.54159700	0.50450700	1.74035600
C	-0.57057900	0.94939400	0.29247400
C	1.92673400	1.25394800	0.12148100
C	0.44355600	1.58877300	-1.89868300
H	-6.65513500	-1.88194800	1.40322000
H	-7.45626100	-1.45755700	-0.91635400
H	-5.95700700	-0.32072500	-2.55099900
H	-3.66779900	0.38676400	-1.86307800
H	-4.38780900	-1.18124800	2.08769300
H	-2.53115900	0.35713100	2.69914600
H	-1.87794400	-1.19902100	2.17315500
H	-0.37245900	1.35738100	2.41795100
H	0.27611100	-0.21274700	1.90251500
H	2.00127600	1.42751300	1.21119900
H	2.69403500	1.90181800	-0.33252500
H	1.25705000	2.15521500	-2.37774600
H	0.50119000	0.53669600	-2.20435000
H	-0.51885100	1.98606000	-2.24474400
C	0.54441400	1.71389600	-0.37621000
C	0.38180700	3.19664500	0.01815500
H	-0.59427300	3.57055400	-0.32079200
H	0.44643800	3.33456300	1.10834100
H	1.17092100	3.80539300	-0.44972800
C	2.29393600	-0.19285100	-0.13567600

C	3.75258400	-0.53895900	-0.08944700
C	4.24799800	-1.59813900	-0.86122200
C	4.64222800	0.17592300	0.72268100
C	5.59502300	-1.94547300	-0.81122600
H	3.57524300	-2.14046900	-1.52912500
C	5.98841400	-0.17920500	0.78327300
H	4.27990100	1.00930200	1.32622500
C	6.46830300	-1.23982000	0.01657600
H	5.96686600	-2.76539200	-1.42728900
H	6.66637900	0.37766300	1.43159900
H	7.52384200	-1.51216000	0.05814600
N	1.37448600	-1.04462800	-0.34983100
H	1.76291500	-1.98584600	-0.45918800

TS_E_F

0 2

C	-5.40191600	-1.28738700	-0.00952600
C	-5.01439800	-2.62711800	0.01675700
C	-3.66949300	-2.95784600	-0.16580700
C	-2.72479400	-1.96215200	-0.38119300
C	-3.10154500	-0.60598700	-0.41000100
C	-4.45703800	-0.28669800	-0.21497800
C	-2.11380600	0.45211100	-0.65012900
C	-2.22615600	1.84008100	-0.08775700
N	-0.93438400	0.28985600	-1.16762400
C	-0.93046300	1.97420200	0.77515300
C	0.22051200	1.44716500	-0.07692600
C	2.08496800	1.43600500	-1.53210300
H	-6.45014300	-1.01913300	0.13077500

H	-5.75493800	-3.41071700	0.18155200
H	-3.35449400	-4.00191900	-0.13267300
H	-1.67462700	-2.23794100	-0.49872200
H	-4.77367700	0.75695200	-0.24592400
H	-2.20930100	2.59169200	-0.89414600
H	-3.12123600	2.00482500	0.52630800
H	2.99796500	2.01712900	-1.72387100
H	1.88867900	0.82952200	-2.43309200
C	0.87476300	2.29732700	-1.15275800
C	2.19577800	0.53462800	-0.31710600
C	3.31143600	-0.35398300	-0.04926500
C	3.31622700	-1.16649100	1.10375300
C	4.40566900	-0.43315400	-0.93157200
C	4.38031800	-2.01934100	1.36034000
H	2.46385000	-1.10239300	1.78068900
C	5.46867100	-1.29247800	-0.66862700
H	4.42043900	0.18159600	-1.83332000
C	5.46343100	-2.08819300	0.47700900
H	4.37086800	-2.64055000	2.25770300
H	6.30833100	-1.34186700	-1.36388700
H	6.29787100	-2.76020500	0.68240900
N	1.13290500	0.59432900	0.46100900
H	1.21197600	3.24652100	-0.70609600
H	0.19625800	2.52387100	-1.98493200
C	-0.71036900	3.43799700	1.16712700
H	0.23123400	3.55661100	1.72410300
H	-0.67983000	4.09526500	0.28601000
H	-1.53252400	3.77973200	1.81370300
C	-1.07739800	1.11473900	2.03386300

H	-0.17959400	1.19506400	2.65997200
H	-1.95316900	1.44311800	2.61360700
H	-1.19953500	0.05243100	1.77884200
H	-0.66042100	-0.66946600	-1.39022700

E_cation

1 1

C	-4.48477900	-0.28957100	-0.56606000
C	-4.75041700	-1.08019800	0.56064100
C	-3.72549400	-1.76558600	1.22240200
C	-2.42317300	-1.66555000	0.76020900
C	-2.14295900	-0.87498400	-0.37961100
C	-3.18795300	-0.18461400	-1.03759600
C	-0.79788300	-0.75982700	-0.83940600
C	-0.33456500	0.04751400	-2.01035500
N	0.21821400	-1.36392600	-0.18809600
C	1.14872100	-0.30221600	-2.07597600
C	1.34253200	-1.05534900	-0.79704200
C	3.12365800	-0.01436600	0.50661000
C	2.55132100	-2.47831500	0.84831600
H	-5.29630300	0.23899700	-1.06590800
H	-5.77486700	-1.15998900	0.92876200
H	-3.95161100	-2.37303000	2.09865200
H	-1.60136100	-2.18079600	1.25771000
H	-2.97425400	0.43628500	-1.90911600
H	-0.91100300	-0.16383400	-2.92107300
H	-0.47938400	1.11657700	-1.76241100
H	1.39349600	-0.97463500	-2.91681000
H	1.82169800	0.56277200	-2.15263500

H	3.43724000	0.69607200	-0.26991200
H	4.01858400	-0.27076500	1.09315700
H	3.53743800	-2.66863700	1.29460400
H	1.83648300	-2.22256200	1.63969900
H	2.20634100	-3.40654500	0.37185400
C	2.66948200	-1.35725200	-0.18615200
C	3.70222600	-1.71329200	-1.26442000
H	3.43146500	-2.64868400	-1.77493200
H	3.80953100	-0.91777200	-2.01536900
H	4.68255100	-1.86012400	-0.79107500
C	2.06694100	0.58674600	1.41747300
C	1.09786100	1.56799100	0.82414300
C	-0.21488300	1.59627900	1.31987600
C	1.46095000	2.47397800	-0.18094400
C	-1.14935000	2.48722000	0.80021300
H	-0.47652300	0.90525500	2.12325500
C	0.52851600	3.38257500	-0.68862000
H	2.48727800	2.51144200	-0.55161200
C	-0.78054200	3.38358600	-0.20752500
H	-2.16743800	2.49573900	1.19350100
H	0.83207100	4.10071500	-1.45162600
H	-1.50714000	4.09520300	-0.60242000
N	1.90115700	0.25057900	2.63049600
H	2.60884700	-0.42687400	2.92986100

CF_3_Phen_Carboxylate

-1 1

O	3.85430000	1.12944400	0.01685700
C	3.34117300	-0.00002800	0.01092900

O	3.85425700	-1.12945700	0.01647400
C	1.77794200	0.00005200	-0.00592800
C	1.07025800	1.20465800	-0.01582900
C	1.07031400	-1.20459000	-0.01568600
C	-0.32212600	1.21247700	-0.03268400
H	1.66432100	2.12035800	-0.01336500
C	-0.32208600	-1.21252000	-0.03252200
H	1.66438900	-2.12028600	-0.01310400
C	-1.01795700	-0.00004200	-0.04021700
H	-0.87863600	2.15204600	-0.04833400
H	-0.87852200	-2.15213200	-0.04805100
C	-2.51301800	-0.00001100	0.00294600
F	-2.99415400	0.00059200	1.25853100
F	-3.04443000	-1.07715700	-0.59374700
F	-3.04441600	1.07658100	-0.59476700

CF_3_Phen_Carboxylic acid

0 1

O	-3.78344700	-1.10454100	0.01441900
C	-3.20498400	0.10354000	0.00832600
O	-3.83258100	1.12658500	0.01514000
C	-1.71196800	0.03238500	-0.00707800
C	-1.03298200	-1.18878000	-0.01686900
C	-1.00484600	1.23750600	-0.01554000
C	0.35869100	-1.20306800	-0.03210300
H	-1.59920400	-2.11965100	-0.01561100
C	0.38508200	1.22439400	-0.03086400
H	-1.56588700	2.17267900	-0.01303500
C	1.05971700	0.00249700	-0.03569300

H	0.90353900	-2.14741500	-0.04817600
H	0.95045100	2.15672500	-0.04621100
C	2.56648500	-0.01243900	0.00388200
F	3.01810000	0.01038900	1.25992400
F	3.08435300	1.04668500	-0.61889400
F	3.06312900	-1.10746300	-0.57250600
H	-4.74208600	-0.96138600	0.02547700

Fac-Ir-S_0 (Ir^{III})

0 1

Ir	-0.00070400	0.00086200	0.01623100
C	-2.22661400	-0.69804800	-2.15969800
C	-2.78781100	0.94102400	-0.59546200
C	-3.46608600	-0.62271800	-2.78165600
H	-1.45575500	-1.39432100	-2.50147100
C	-4.06048400	1.06611800	-1.17652600
C	-4.39698100	0.28412600	-2.27180600
H	-3.69316900	-1.26114600	-3.63428300
H	-4.78032800	1.76953400	-0.76222700
H	-5.38529900	0.37564200	-2.72514900
C	-2.30949000	1.69927600	0.57407600
C	-3.10602400	2.66399000	1.21120500
C	-1.00234200	1.39138100	1.04136500
C	-2.62847400	3.34597200	2.32175900
H	-4.10843800	2.88863600	0.84186700
C	-0.55047700	2.10405000	2.16757500
C	-1.34459400	3.05934000	2.79668900
H	-3.24924700	4.09427400	2.81595200
H	0.44568900	1.89555100	2.56350000
H	-0.96038000	3.58899600	3.67121900

N	-1.90141600	0.06239900	-1.11256300
C	2.08774400	-0.57702700	2.17574100
C	2.62473700	1.14602100	0.58222500
C	3.31070600	-0.36850700	2.80820600
H	1.40661700	-1.33385200	2.57047900
C	3.85708700	1.35161400	1.22248200
C	4.20435900	0.59752000	2.33472300
H	3.57340800	-0.96546400	3.68435900
H	4.55514000	2.10609900	0.85483300
H	5.16158600	0.75966400	2.83166100
C	2.21223100	1.94067400	-0.58804600
C	2.96230200	2.97648800	-1.16896100
C	0.51438100	2.28255800	-2.15270600
C	2.45701200	3.66149500	-2.26440200
H	3.93283000	3.24293400	-0.75455200
C	1.20431500	3.31527700	-2.77421700
H	-0.47526800	1.96764200	-2.49508000
H	3.03482200	4.46852800	-2.71769600
H	0.76759800	3.83349900	-3.62677300
C	0.58139400	-2.88359900	-0.58971900
C	1.73041200	-1.57976900	-2.14789700
C	1.11208800	-4.04904500	-1.16700600
C	2.28836600	-2.69143600	-2.76564500
H	1.95013100	-0.56435000	-2.48918600
C	1.96437100	-3.95057200	-2.25712600
H	0.85966300	-5.02380900	-0.75374800
H	2.96033800	-2.56979700	-3.61403800
C	-1.55729400	-1.52536500	2.16258300
C	-0.32051100	-2.84711700	0.57502900

C	-1.99108200	-2.69057200	2.78967200
H	-1.87643100	-0.55839500	2.55718900
C	-0.76145900	-4.01901900	1.21001600
C	-1.59609900	-3.94600100	2.31653600
H	-2.64575600	-2.62225100	3.66129400
H	-0.45352100	-4.99969200	0.84238900
H	-1.93670400	-4.85751800	2.80915700
H	2.38138600	-4.85283800	-2.70737100
C	-0.70906700	-1.56069000	1.04008300
C	1.70110000	0.17009300	1.04746600
N	1.00713200	1.61791100	-1.10597200
N	0.90271500	-1.67732500	-1.10596200

Fac-Ir-T

0 3

Ir	-0.08014200	0.06092100	0.09813400
C	2.40518300	-0.64169000	-1.90742500
C	1.68916100	-2.40175100	-0.56147600
C	3.45798800	-1.39112900	-2.42190500
H	2.23262000	0.39297300	-2.21133700
C	2.72547000	-3.21422100	-1.03954900
C	3.61464400	-2.70175100	-1.97562200
H	4.13700800	-0.94742600	-3.14860500
H	2.83888200	-4.23157300	-0.66962800
H	4.43110600	-3.32114400	-2.35019600
C	0.68997800	-2.81235800	0.44362100
C	0.62586600	-4.11620400	0.95478600
C	-0.21739200	-1.82276700	0.87687800
C	-0.33581100	-4.45419000	1.89898200

H	1.32801200	-4.87865200	0.61402600
C	-1.18892700	-2.18810500	1.82236000
C	-1.24288400	-3.48510500	2.33161600
H	-0.38052300	-5.46933200	2.29493900
H	-1.90620100	-1.44576300	2.17867900
H	-2.00210700	-3.74132100	3.07313100
N	1.54997700	-1.14063500	-1.01285600
C	-1.37992300	1.80290000	2.19073100
C	-2.84586500	0.87278300	0.49480100
C	-2.47416600	2.42754100	2.78586000
H	-0.38379500	1.92522700	2.61831800
C	-3.93581200	1.50770900	1.09934900
C	-3.75190500	2.28060600	2.24259000
H	-2.32934000	3.03714300	3.67931700
H	-4.93912600	1.40778100	0.68289000
H	-4.60735300	2.77189800	2.70799300
C	-2.99100700	0.03842400	-0.71652800
C	-4.20138800	-0.22303500	-1.37370900
C	-1.84248800	-1.28533300	-2.25286300
C	-4.20348000	-1.03833300	-2.49810100
H	-5.13058000	0.20747800	-1.00499600
C	-3.00458500	-1.58794500	-2.95271600
H	-0.86883800	-1.68328500	-2.55197300
H	-5.13945300	-1.24820500	-3.01784800
H	-2.96672500	-2.23674700	-3.82660100
C	1.60146900	2.36249300	-0.55974100
C	-0.06838700	2.08168200	-2.25666000
C	2.02222800	3.53571200	-1.20715800
C	0.32570600	3.21484200	-2.90400700

H	-0.89955200	1.47670800	-2.62827000
C	1.42378600	3.97481100	-2.37113700
H	2.83755700	4.10838600	-0.76265600
H	-0.19553200	3.52784500	-3.80792500
C	1.87895300	0.15240400	2.43065500
C	2.11895300	1.83456800	0.68143200
C	2.96701800	0.70081500	3.11822800
H	1.35955600	-0.71458200	2.84745700
C	3.22079700	2.36989500	1.38473200
C	3.63339100	1.81038700	2.58597700
H	3.29419100	0.26244200	4.06240600
H	3.75765300	3.23123500	0.98259400
H	4.48574800	2.24055100	3.11526300
H	1.76068600	4.88676100	-2.86259100
C	1.44096600	0.70379100	1.22706000
C	-1.54037100	1.00941500	1.04242500
N	-1.84518900	-0.49354800	-1.18147600
N	0.54579200	1.61268600	-1.12733300

Fac-Ir+1 (Ir^{IV})

1 2

Ir	0.00124200	-0.00004500	0.11348600
C	2.07580800	1.03523500	-2.10104200
C	2.86105200	-0.58765600	-0.61146500
C	3.30077300	1.11938400	-2.74654000
H	1.22637700	1.65293000	-2.40372600
C	4.12202400	-0.55242900	-1.22225000
C	4.33951000	0.30350900	-2.29315200
H	3.43611800	1.80950000	-3.57795800

H	4.92535800	-1.18773000	-0.85396600
H	5.31889900	0.34020600	-2.77205900
C	2.50257500	-1.43405300	0.54139800
C	3.40321500	-2.32537600	1.13773500
C	1.17940300	-1.32184900	1.03581800
C	3.00487300	-3.10343200	2.21986600
H	4.42328400	-2.41937300	0.76337800
C	0.78910400	-2.12986400	2.11143800
C	1.69962800	-3.00409300	2.70515200
H	3.71233500	-3.79111600	2.68368100
H	-0.22762700	-2.06310000	2.50285400
H	1.38687500	-3.61490100	3.55340900
N	1.86706600	0.20132200	-1.07675700
C	-2.23250200	0.37808000	2.11855700
C	-2.48944100	-1.45079700	0.54588200
C	-3.44274200	0.02427700	2.71525400
H	-1.66595000	1.22505700	2.50984900
C	-3.70941700	-1.78780500	1.14546600
C	-4.18156800	-1.05655100	2.23049300
H	-3.81343300	0.59865200	3.56562800
H	-4.30095000	-2.62429200	0.77143800
H	-5.12895700	-1.32752900	2.69689100
C	-1.93880700	-2.18123400	-0.61048900
C	-2.54059800	-3.28887900	-1.22325500
C	-0.14551500	-2.30742100	-2.10681400
C	-1.91165200	-3.90124900	-2.29846400
H	-3.49131800	-3.66820300	-0.85333500
C	-0.68737100	-3.40787600	-2.75449700
H	0.81304000	-1.87948200	-2.41127900

H	-2.37122600	-4.76603800	-2.77893700
H	-0.16042500	-3.86692200	-3.58961800
C	-0.92597200	2.76910400	-0.60961600
C	-1.93649700	1.27604700	-2.09925900
C	-1.59107900	3.84209600	-1.21850000
C	-2.62554700	2.29339400	-2.74304600
H	-2.04440300	0.23162500	-2.40291400
C	-2.44174600	3.60097700	-2.28855900
H	-1.44518600	4.85552600	-0.84935500
H	-3.29104500	2.06439300	-3.57400700
C	1.45322500	1.75047000	2.10825900
C	-0.01204600	2.88335100	0.54168400
C	1.75370300	2.97677600	2.70141300
H	1.90652200	0.83745600	2.49863600
C	0.30806400	4.10962600	1.13753700
C	1.18329800	4.15562400	2.21771000
H	2.44100000	3.01262600	3.54805100
H	-0.12348500	5.03908400	0.76420100
H	1.42388500	5.11260500	2.68119200
H	-2.96632000	4.42974400	-2.76592300
C	0.55596800	1.68264900	1.03479100
C	-1.73039900	-0.36129000	1.04013500
N	-0.75986900	-1.71352700	-1.07809500
N	-1.10933200	1.51367400	-1.07577100

DMSO

0 1

S	-0.00001100	0.22955400	-0.45304900
O	-0.00029300	1.46865400	0.39221200

C	1.35536900	-0.79842000	0.18655500
H	1.35456900	-1.78757500	-0.28969700
H	2.28196300	-0.26165800	-0.04971800
H	1.23580500	-0.86930800	1.27572000
C	-1.35511300	-0.79885600	0.18652900
H	-2.28187300	-0.26265000	-0.05037100
H	-1.35365100	-1.78828900	-0.28912600
H	-1.23583400	-0.86895600	1.27577600

TS_B_DMSO

0 2

C	4.56529700	-0.48989000	0.69229800
C	4.92009100	-0.45469800	-0.65424200
C	4.00642100	0.01264300	-1.60307200
C	2.74548200	0.44162400	-1.20618000
C	2.37869900	0.40527300	0.14714600
C	3.29854200	-0.06374600	1.09166400
C	1.02691400	0.85232600	0.55636800
C	0.51873100	0.75935600	1.98439400
N	0.19701300	1.34483400	-0.27698400
C	-0.98460900	0.97294700	1.77869300
C	-1.04555600	1.69279000	0.41716900
C	-2.26836800	1.40855600	-0.43892900
C	-3.57571600	1.42631700	0.32275700
C	-2.27867100	2.19214700	-1.73351900
H	5.27634900	-0.85044000	1.43692100
H	5.91008400	-0.79000300	-0.96735500
H	4.28402000	0.04305700	-2.65786100
H	2.01713200	0.81525900	-1.92685100

H	3.02861600	-0.09122800	2.14861500
H	0.76603000	-0.20169000	2.45824500
H	0.98932300	1.55259500	2.59039500
H	-1.50473200	0.00424800	1.70268300
H	-1.45924200	1.54796100	2.58381300
H	-1.02129800	2.79464700	0.56717000
H	-3.60001300	0.63466900	1.08478300
H	-3.72709600	2.40552100	0.81140500
H	-4.42278300	1.26493500	-0.36096400
H	-3.06360800	1.82577100	-2.41253000
H	-2.48556100	3.25803200	-1.53305300
H	-1.30488800	2.12319100	-2.23672600
O	-2.75432800	-1.71613200	1.04802000
S	-2.21777700	-2.32326100	-0.22737600
C	-2.29011000	-1.07043400	-1.49015000
H	-1.49812100	-1.13680100	-2.24527900
H	-3.30179100	-0.99236600	-1.90540200
C	-0.41278200	-2.37383100	-0.04945400
H	0.03213600	-2.85746600	-0.92865600
H	-0.03509100	-1.35062300	0.06685300
H	-0.21955900	-2.96606600	0.85289700
H	-2.14612400	0.18591000	-0.82601500

1a'

0 1

C	3.98397800	-0.73697300	-0.10774400
C	4.35436400	0.60548700	-0.13388100
C	3.37365300	1.59934100	-0.07246800
C	2.03097500	1.25158000	0.01458400

C	1.64921100	-0.09763100	0.03765600
C	2.63639300	-1.08737200	-0.02400400
C	0.21519100	-0.45454700	0.13593300
C	-0.28275400	-1.89007100	0.12432900
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C	-1.78611300	-1.67724600	-0.07554600
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C	-3.19697800	1.98119000	0.13249300
H	4.74579800	-1.51654200	-0.15297400
H	5.40816500	0.88039800	-0.20137200
H	3.66220000	2.65142400	-0.09191500
H	1.24785500	2.00856400	0.06790000
H	2.35486400	-2.14151600	-0.00100700
H	0.18741800	-2.49884100	-0.66016700
H	-0.04689600	-2.36460700	1.09201000
H	-2.03366100	-1.74960100	-1.14682100
H	-2.40894900	-2.40263300	0.46283200
H	-2.27894400	-0.19985500	1.46470900
H	-4.37967800	-1.19056400	-0.70935300
H	-4.74284000	-0.26673000	0.76864400
H	-5.20601000	0.37829700	-0.82138700
H	-3.92761900	2.55055300	-0.46035000
H	-3.53368100	1.99103000	1.18185400
H	-2.22526600	2.48793400	0.08344700
H	-2.76287100	0.57091700	-1.43080400

DMSO radical

0 2

S	-0.10358700	0.15447000	-0.41724000
O	-0.41886700	1.41681500	0.31988900
C	1.51476000	-0.41900900	0.20694500
H	1.74781800	-1.41396100	-0.19268300
H	2.24691700	0.32037000	-0.13917500
H	1.45682600	-0.42030400	1.30190000
C	-1.08853800	-1.13682300	0.23081000
H	-2.01784100	-0.81611300	0.70421400
H	-0.98272400	-2.14102700	-0.18406600

8. X-ray crystal data of 3ka

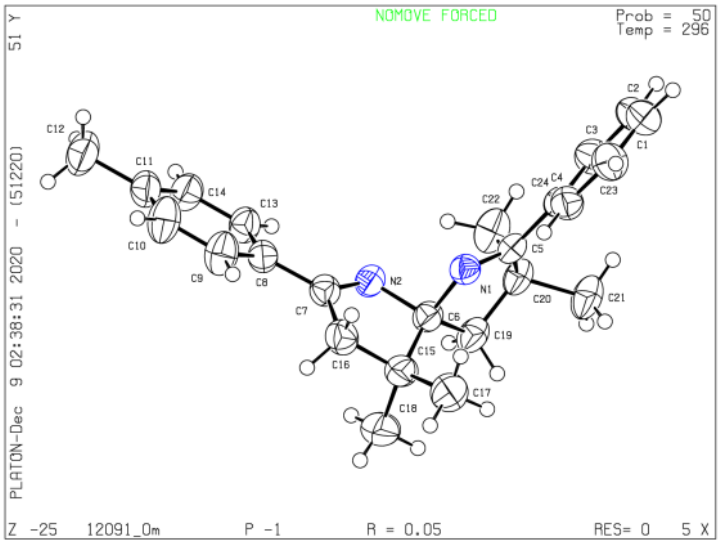

Figure S5: X-Ray crystal structure of **3ka**

(The crystal was obtained by slow evaporation of the solution of CH_2Cl_2 and hexane) (**CCDC 2061499**):

Bond precision:	C-C = 0.0023 Å		Wavelength=0.71073
Cell:	a=9.515 (3)	b=9.721 (3)	c = 11.544 (3)
	alpha=93.268 (4)	beta=107.201 (4)	gamma=91.150 (4)
Temperature:	296 K		
	Calculated		**Reported**
Volume	1017.6 (5)		1017.5 (5)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	$C_{24}H_{28}N_2$		?
Sum formula	$C_{24}H_{28}N_2$		$C_{24}H_{28}N_2$
Mr	344.48		344.48
Dx, g cm^{-3}	1.124		1.124
Z	2		2
Mu (mm^{-1})	0.065		0.065
F000	372.0		372.0
F000′	372.12		
h, k, l_{max}	12, 12, 15		12, 12, 15
Nref	4752		4619
T_{min}, T_{max}	0.988, 0.990		
$T_{min'}$	0.988		
Correction method = Not given			
Data completeness = 0.972	Theta(max) = 27.659		
R(reflections) = 0.0529 (3233)	wR2(reflections) = 0.1728 (4619)		
S = 1.073	Npar = 240		

9. Supplementary references

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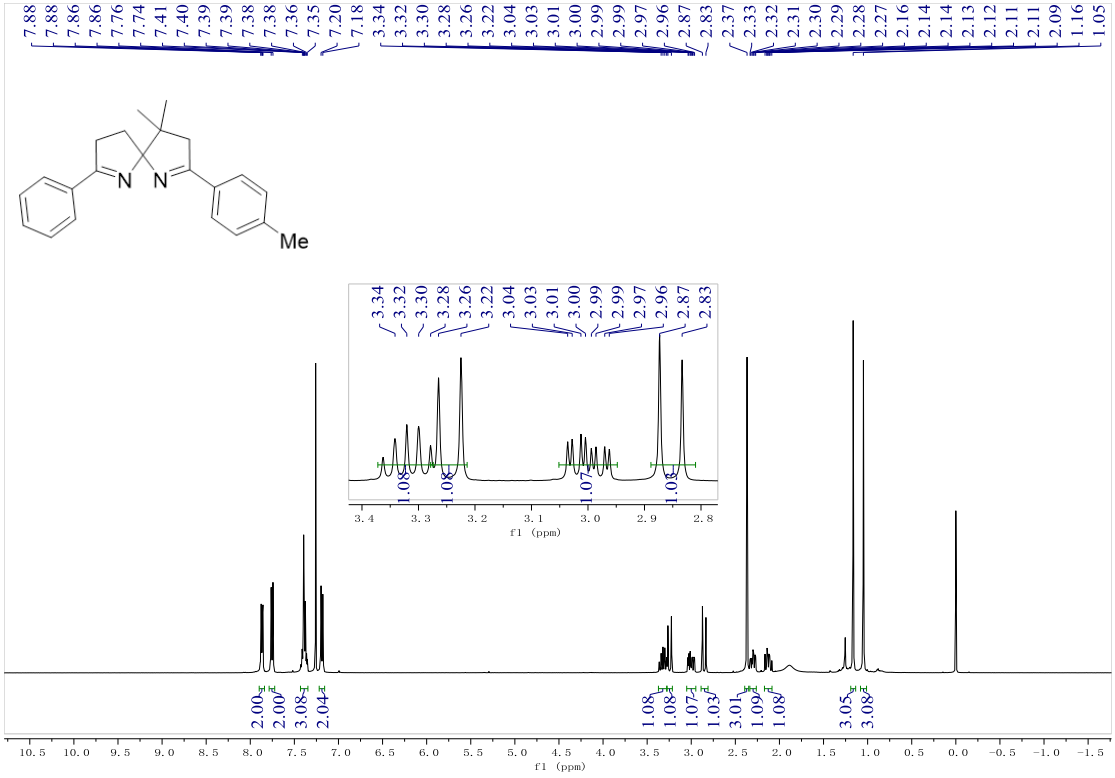
10. Copies of NMR spectra for products

^{1}H NMR spectrum of **3aa**



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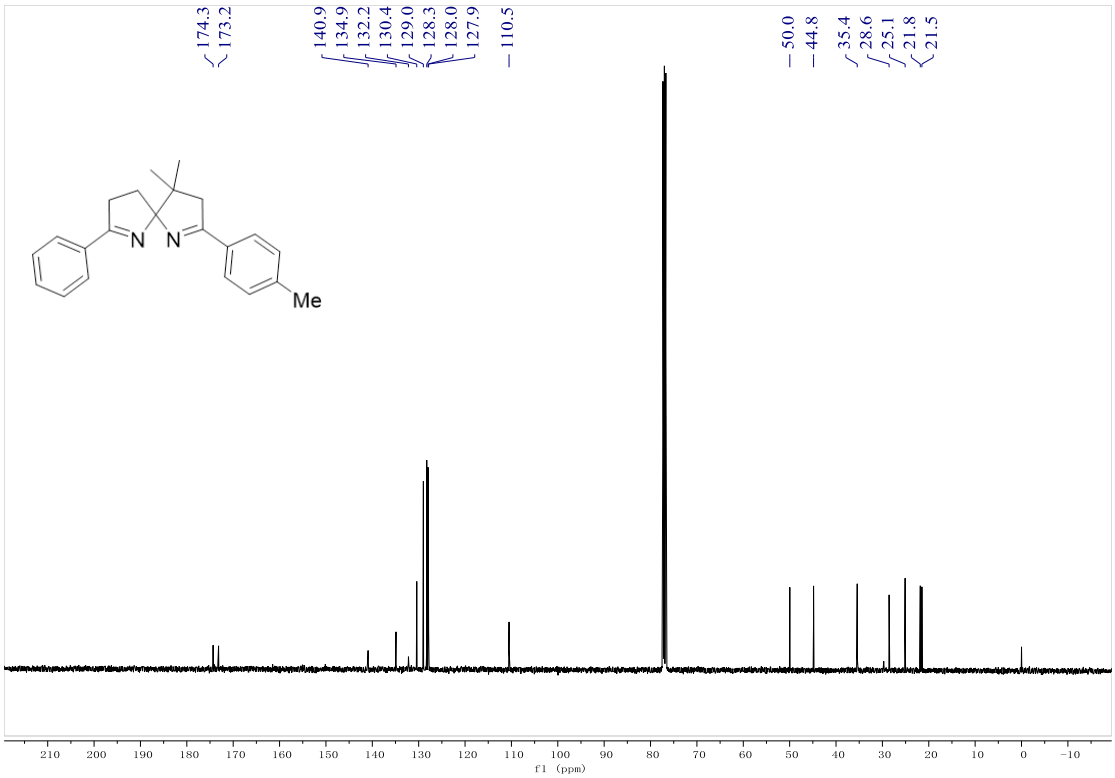
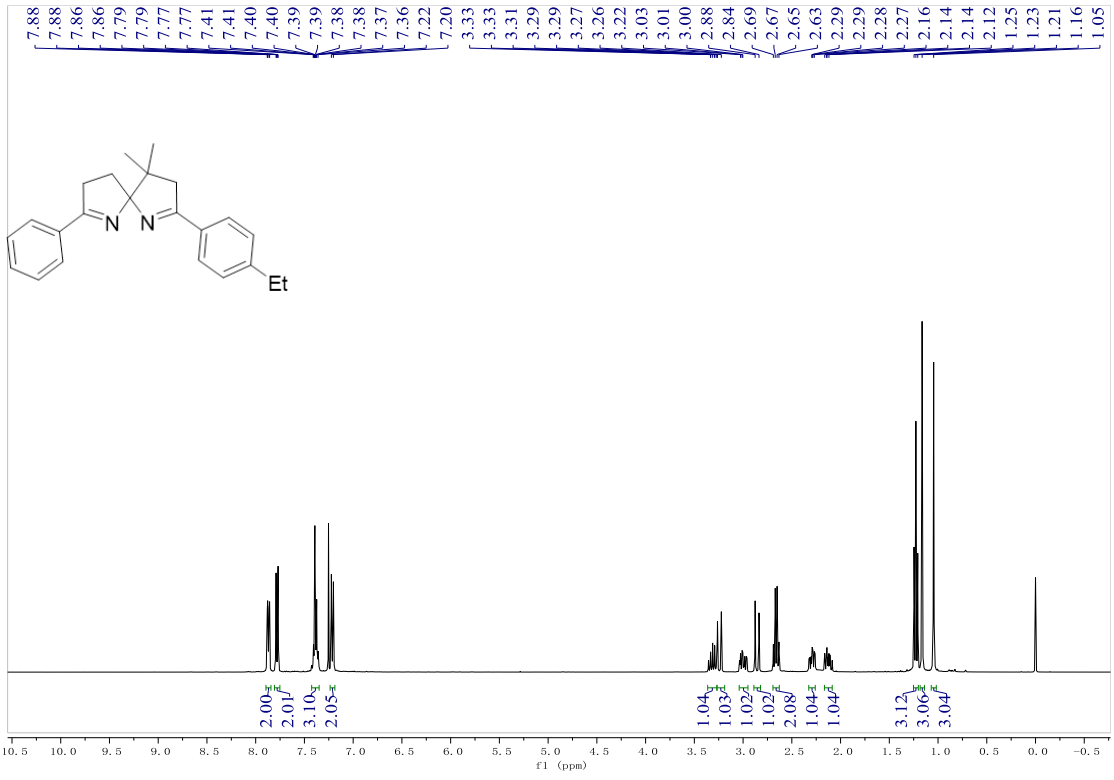


^{1}H NMR spectrum of **3ab**



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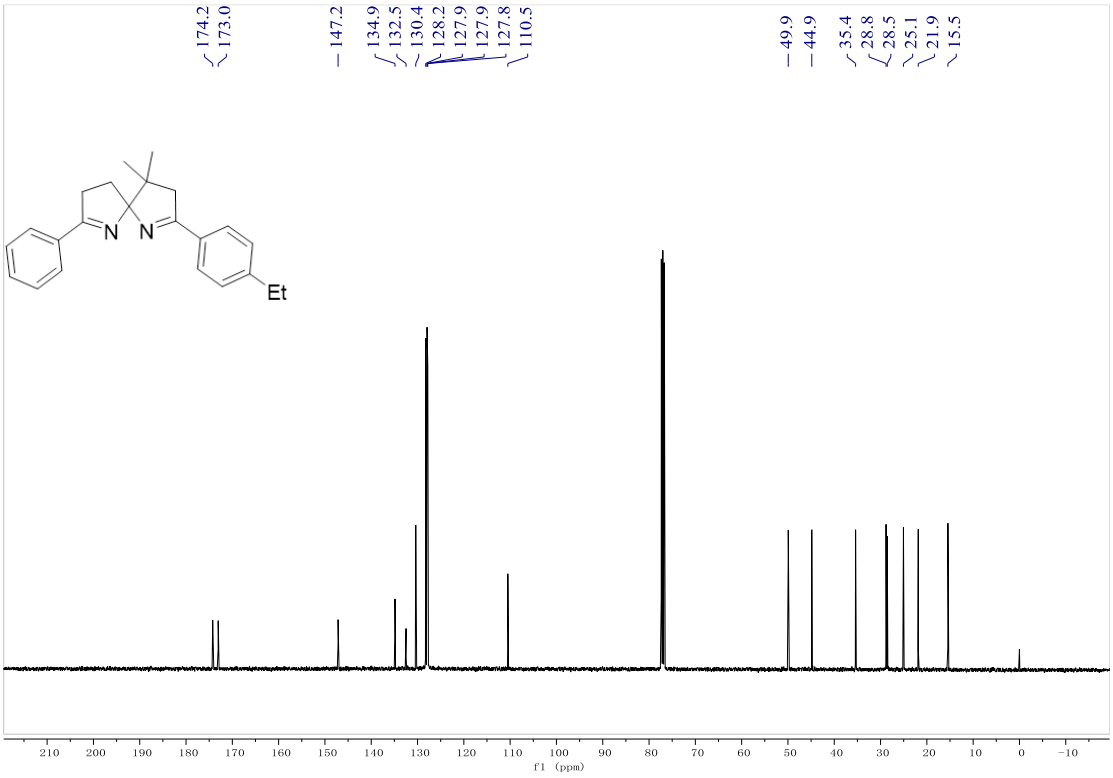
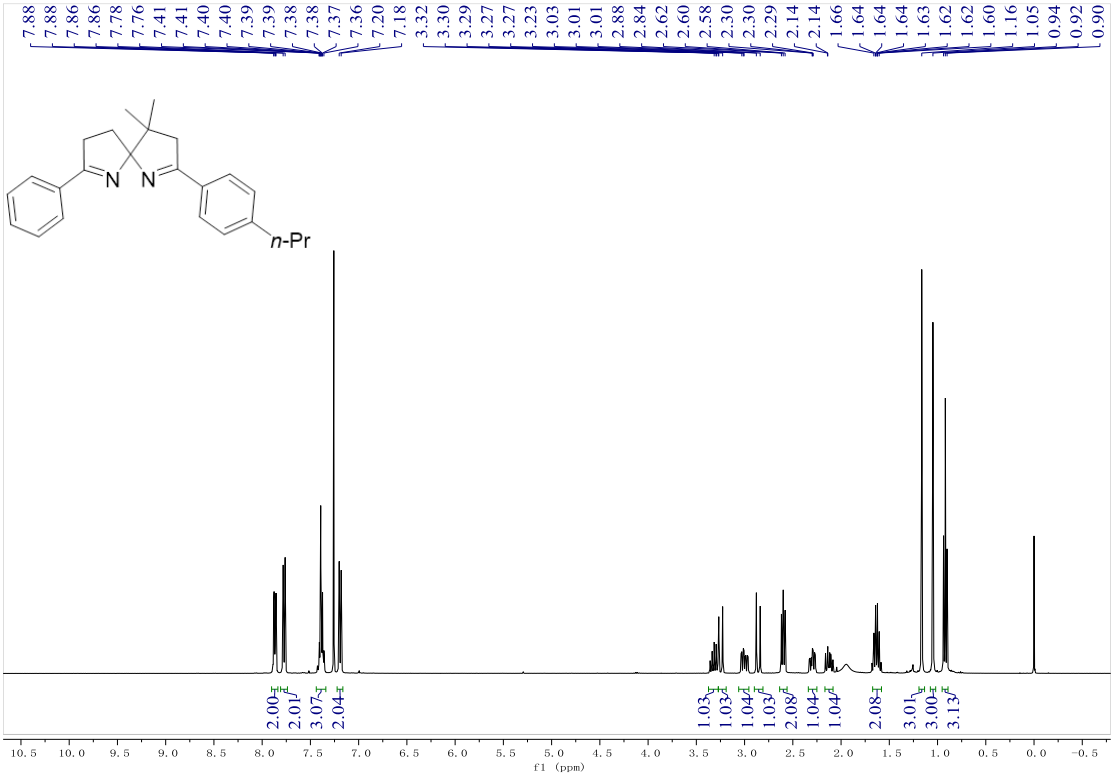
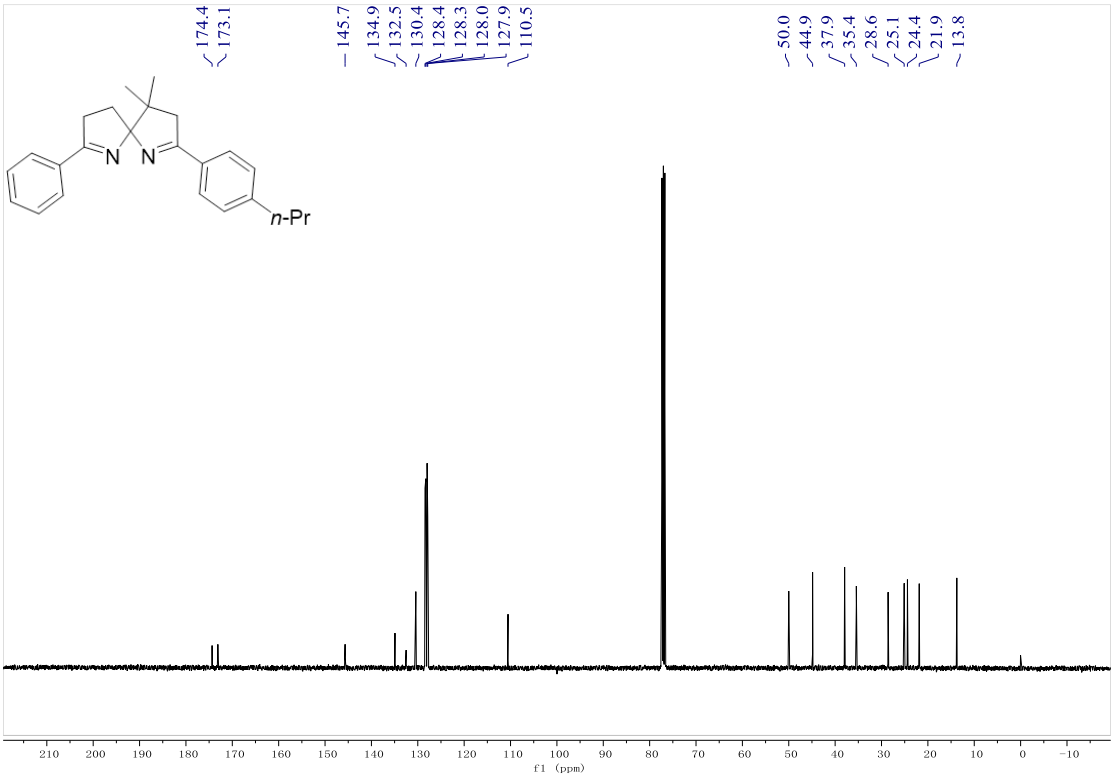


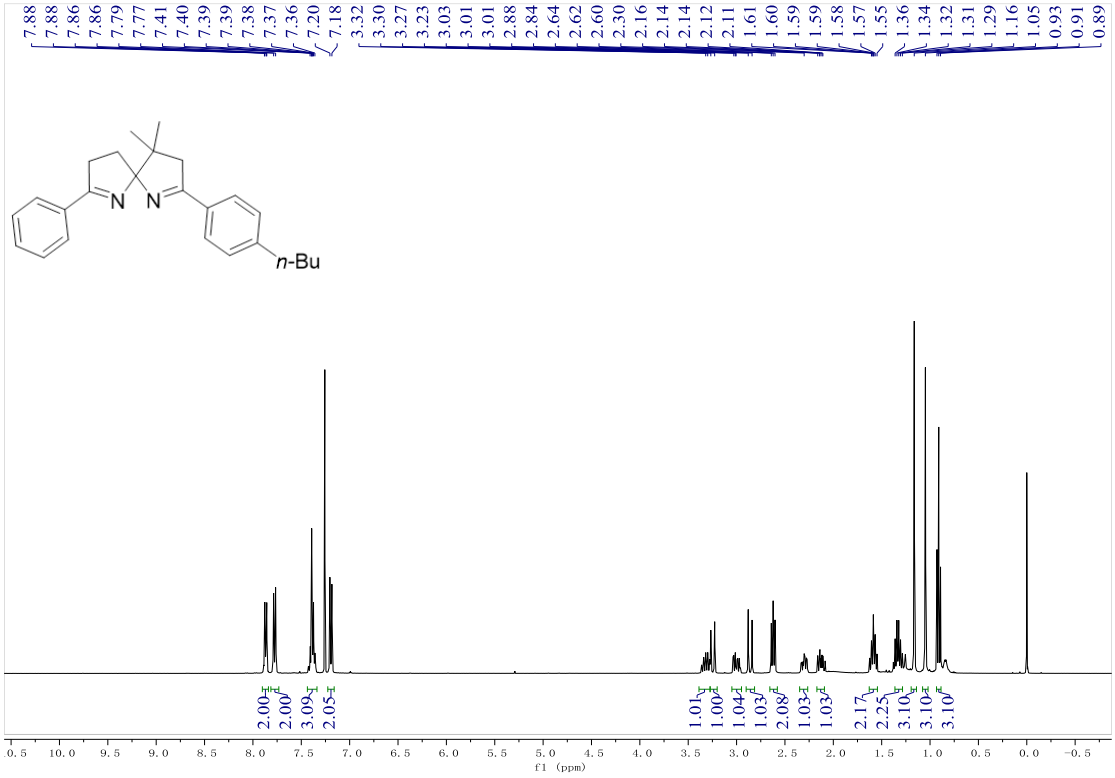
^{1}H NMR spectrum of **3ac**



^{13}C NMR spectrum of **3ac**



^{1}H NMR spectrum of **3ad**



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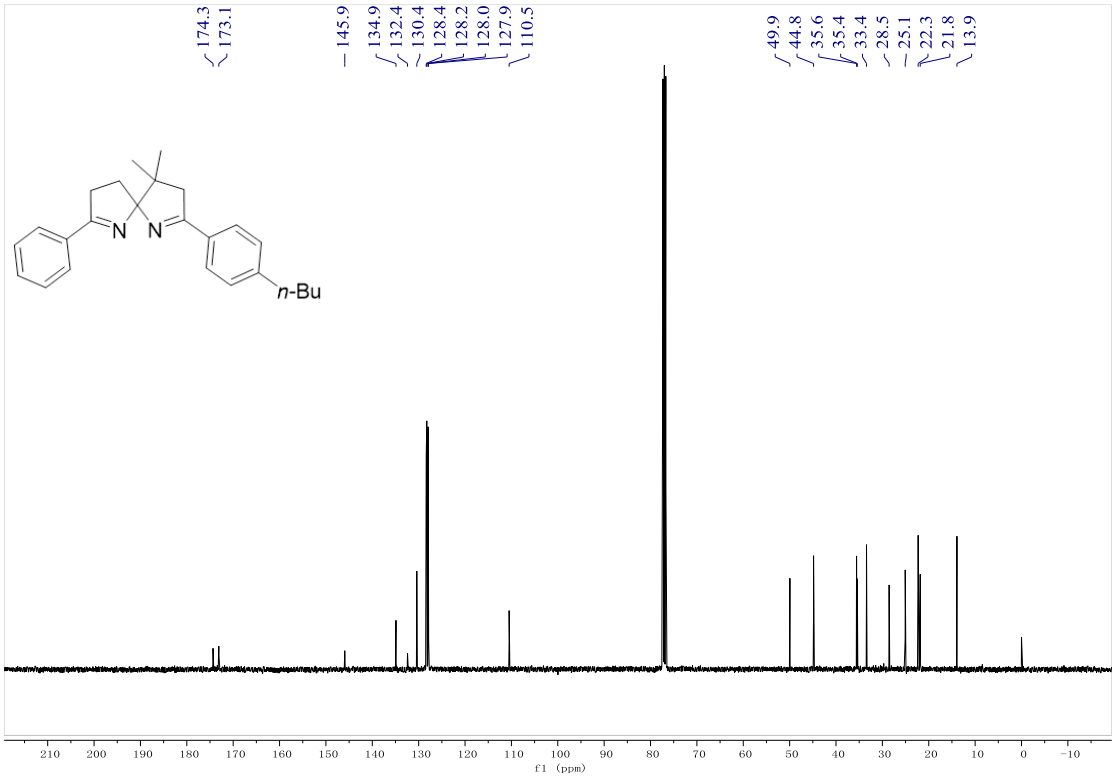
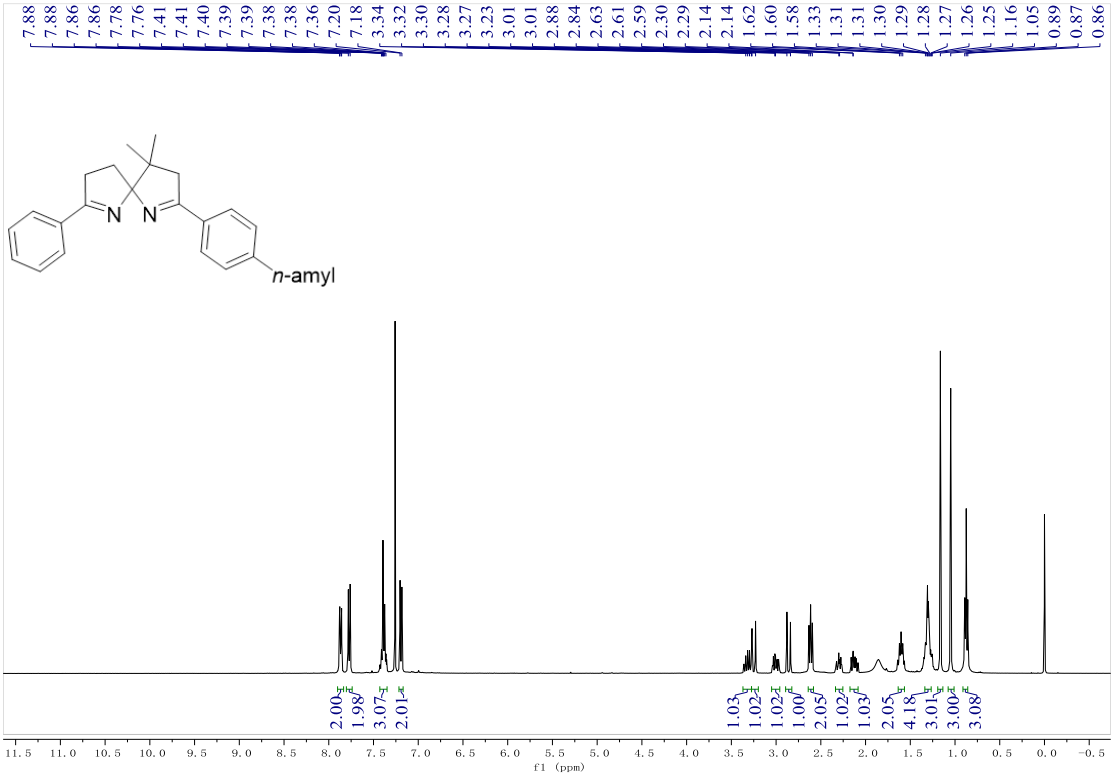
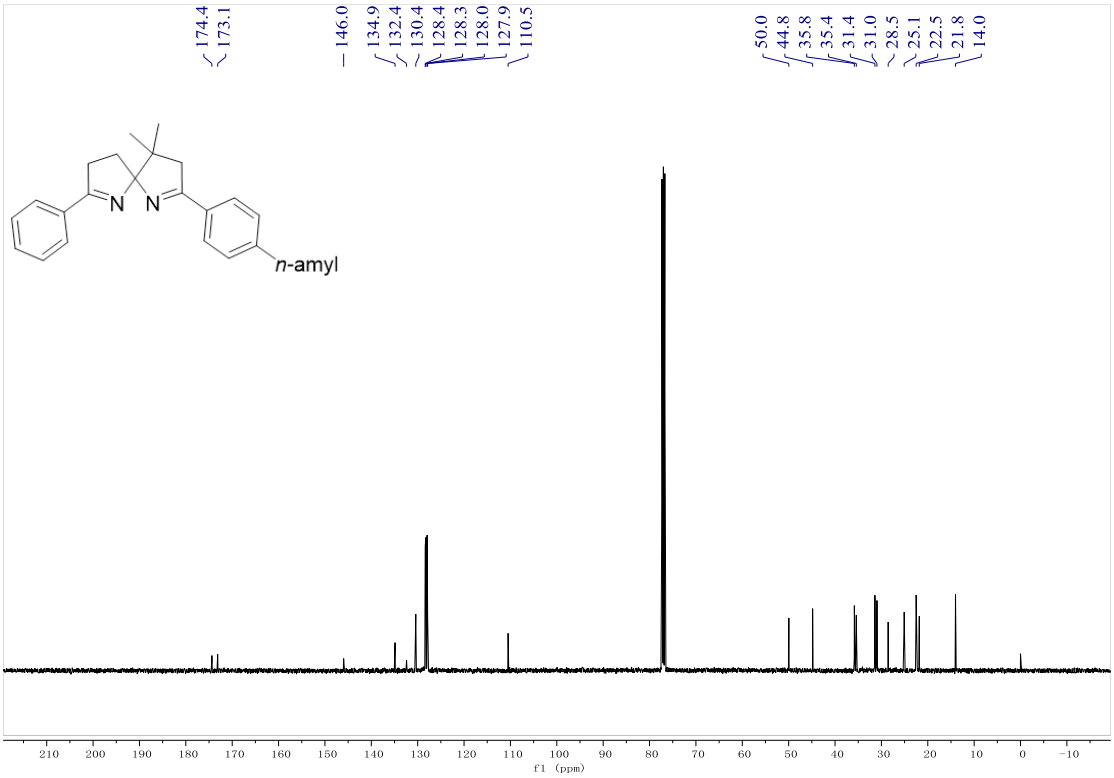


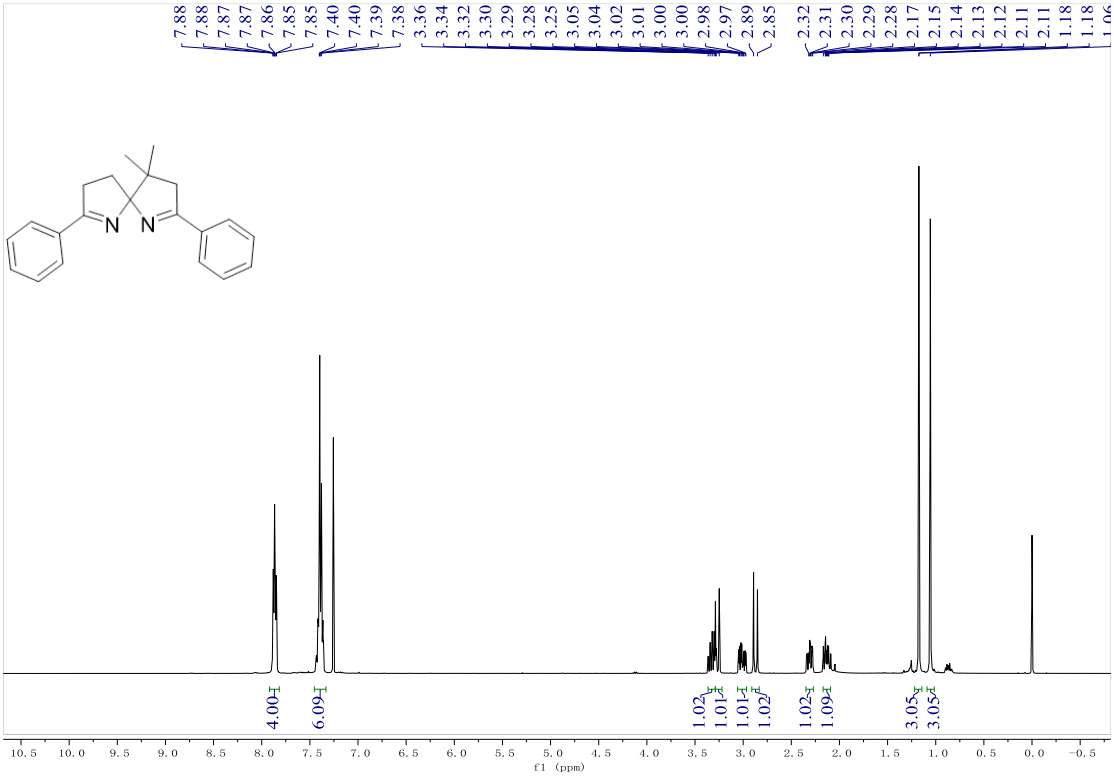
^{1}H NMR spectrum of **3ae**



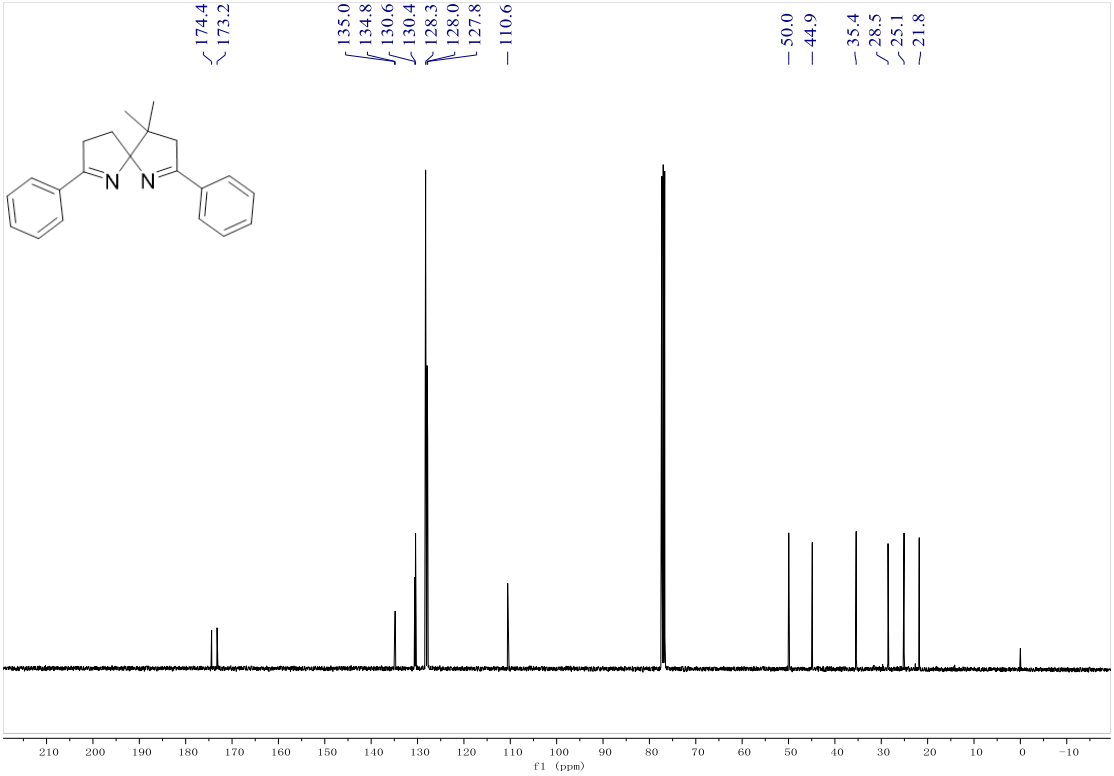
^{13}C NMR spectrum of **3ae**



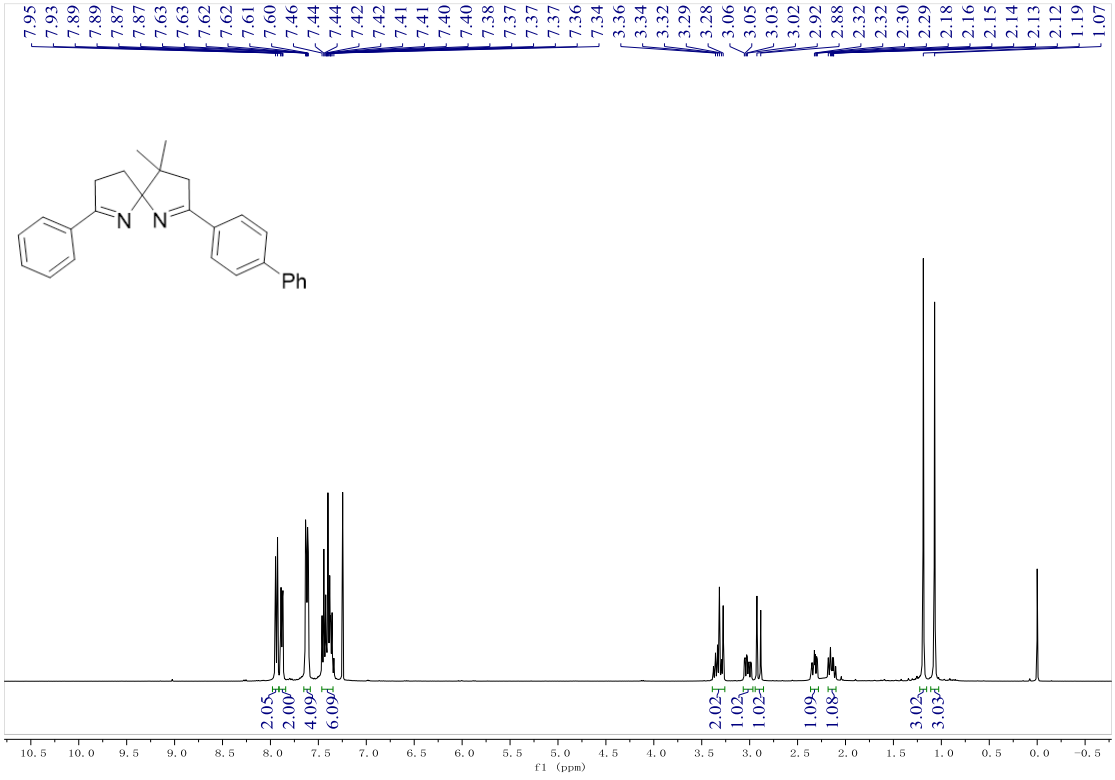
^{1}H NMR spectrum of **3af**



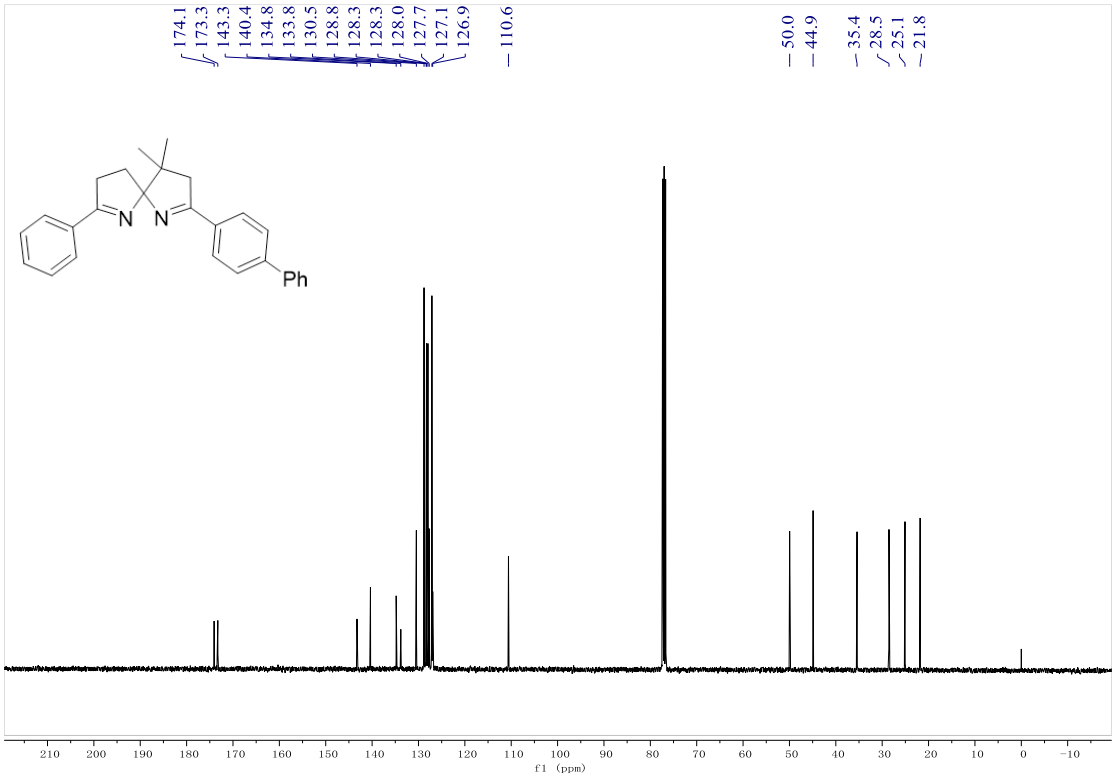
^{13}C NMR spectrum of **3af**



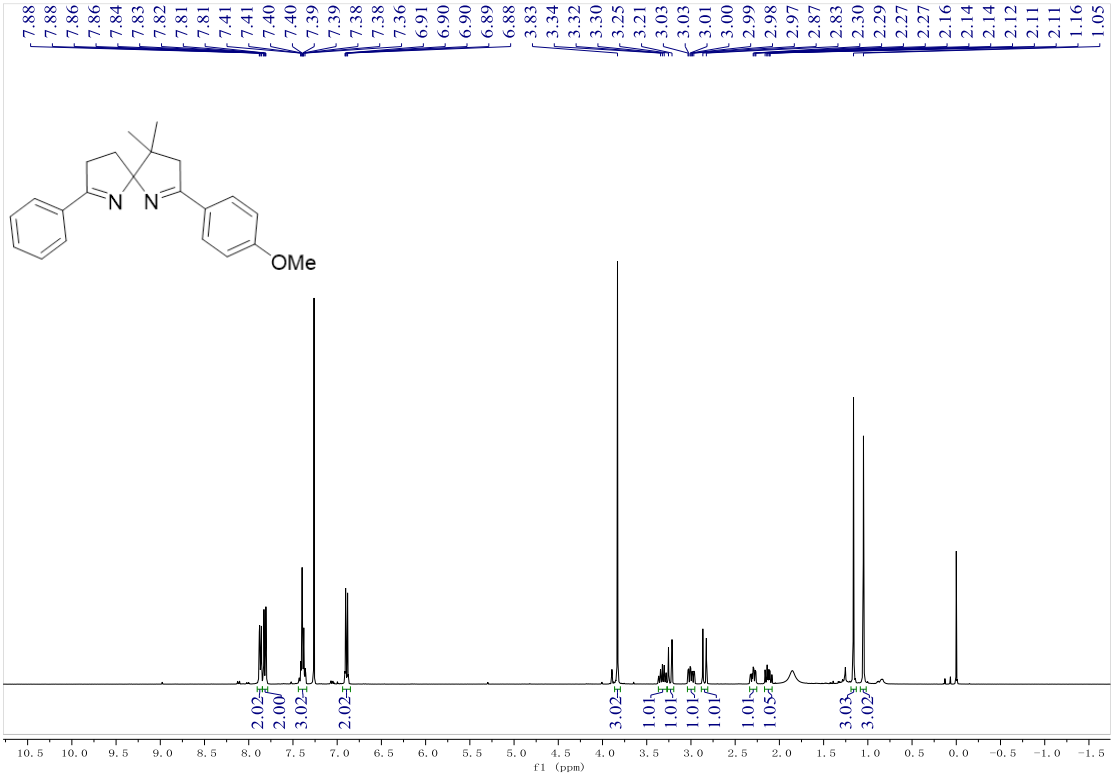
^{1}H NMR spectrum of **3ag**



^{13}C NMR spectrum of **3ag**



^{1}H NMR spectrum of **3ah**



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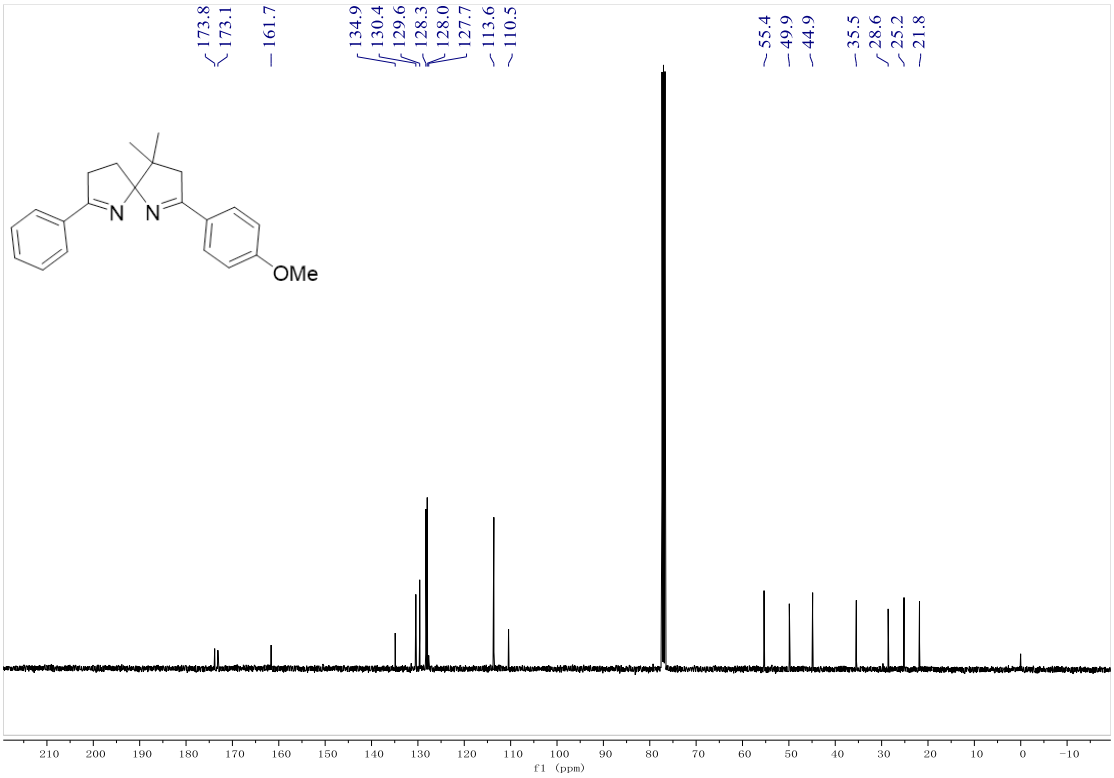

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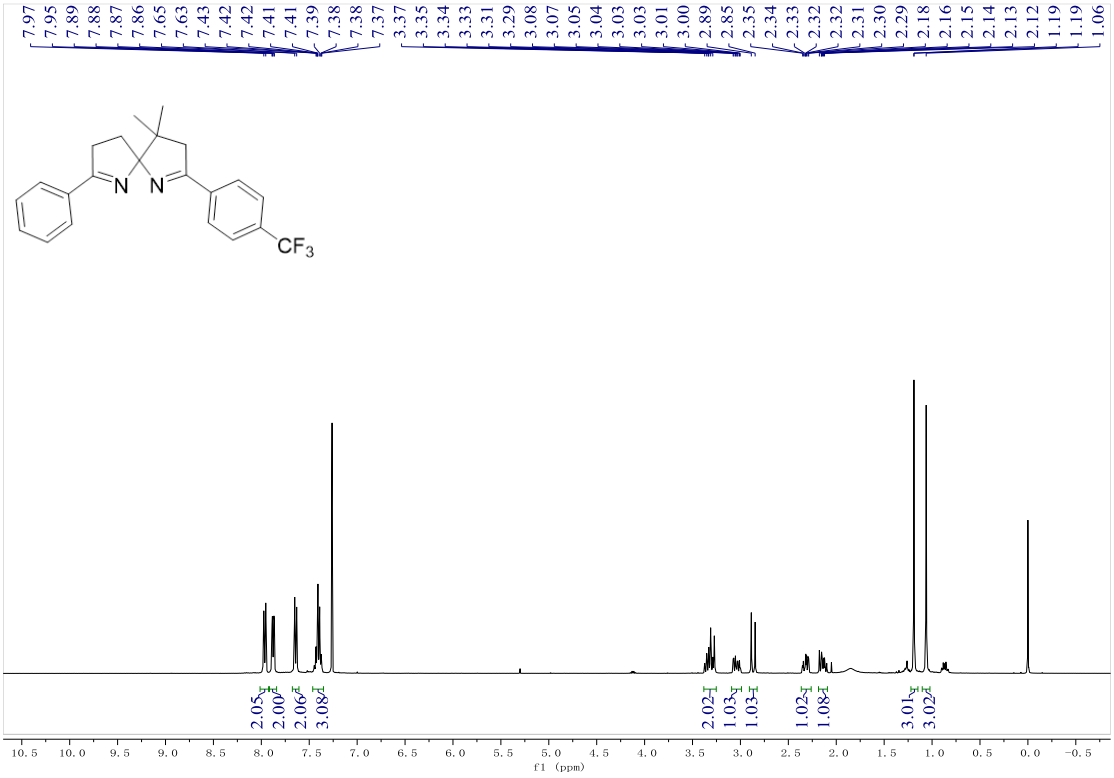

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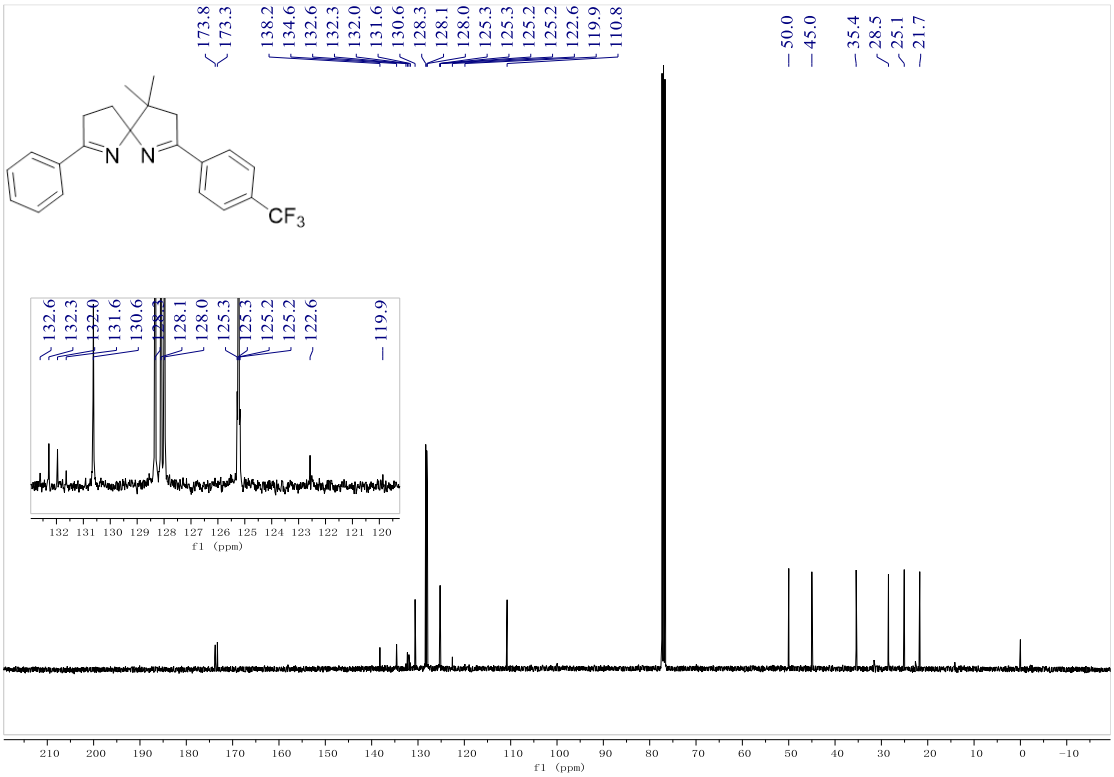
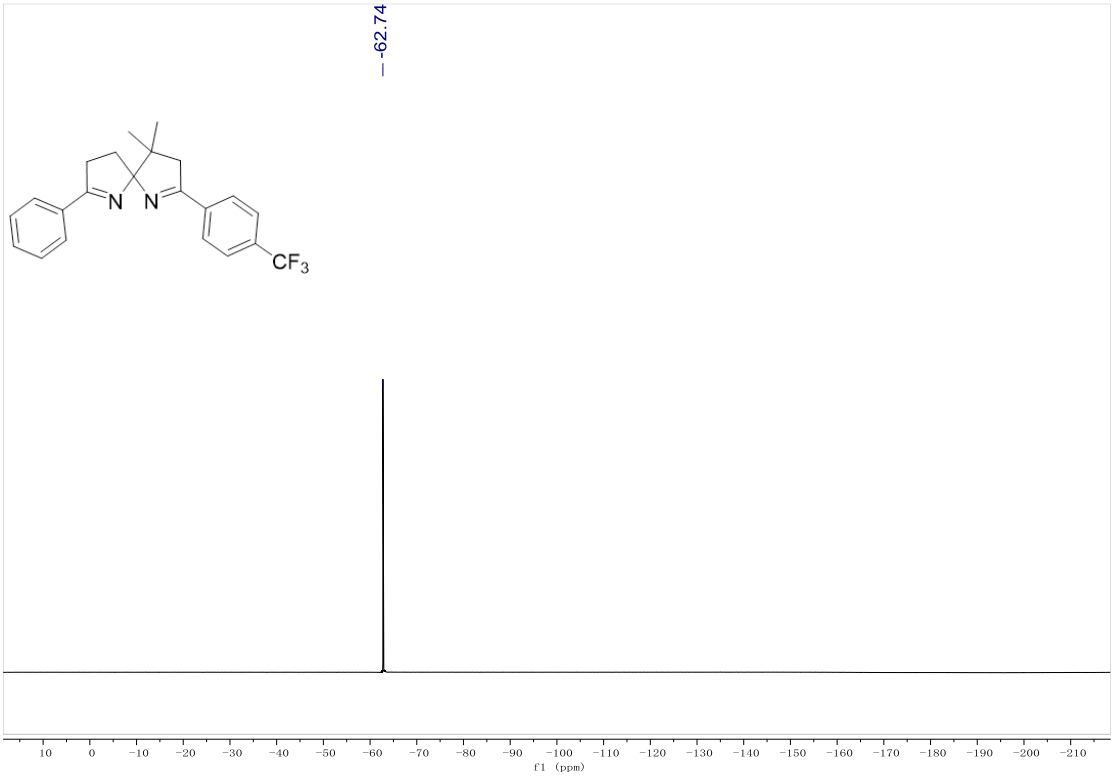


^{19}F NMR spectrum of **3ai**



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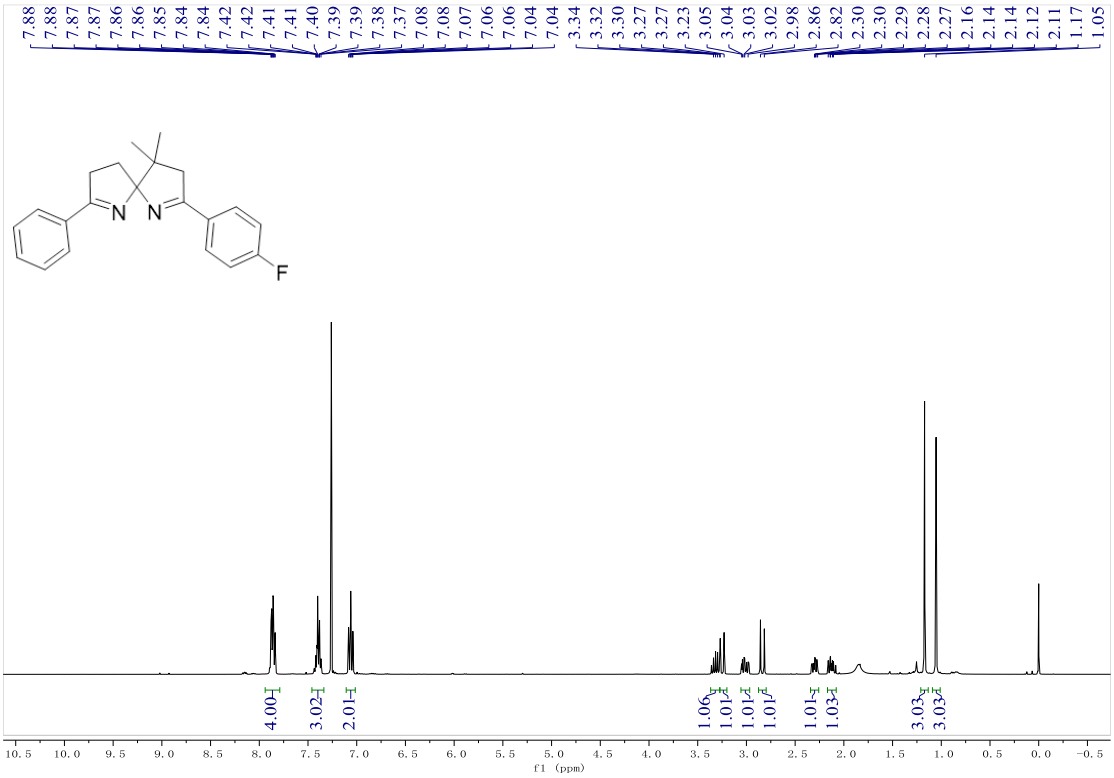

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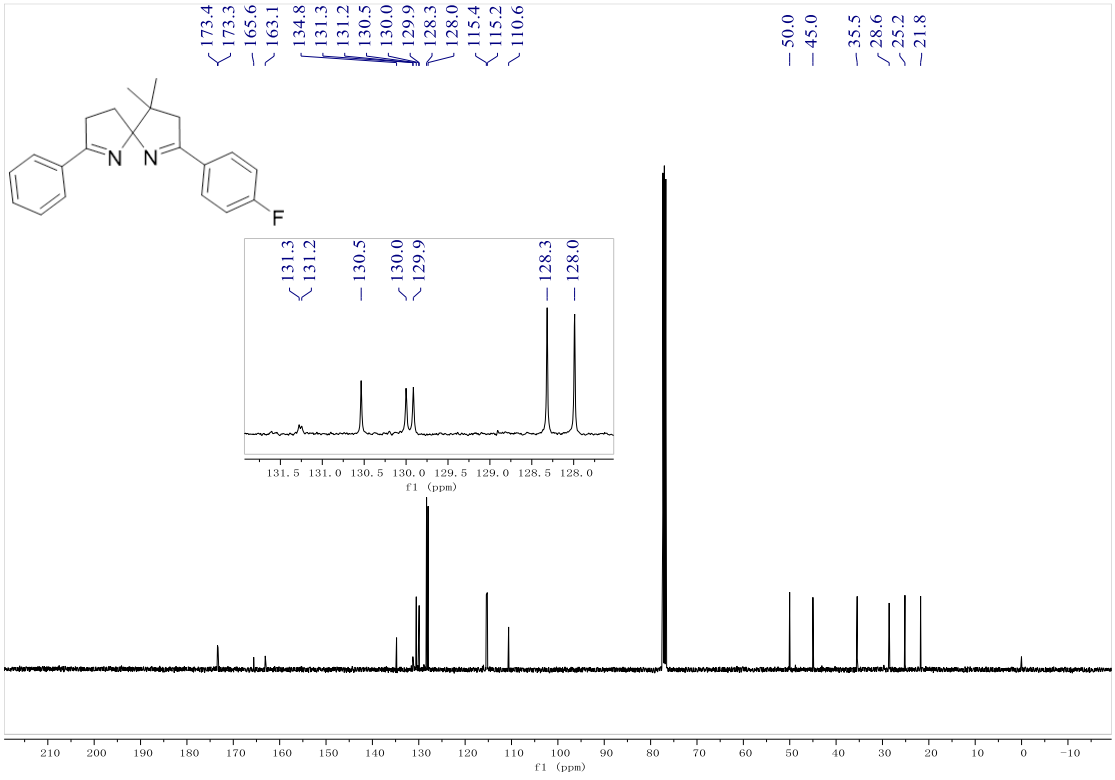
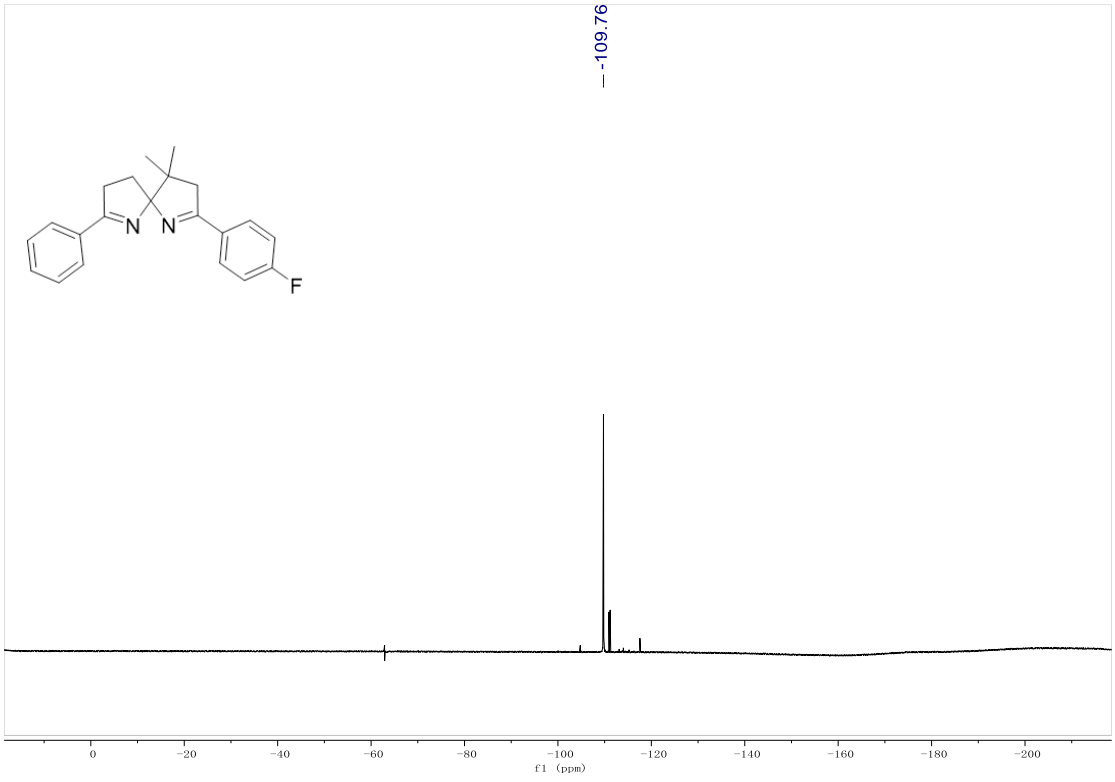
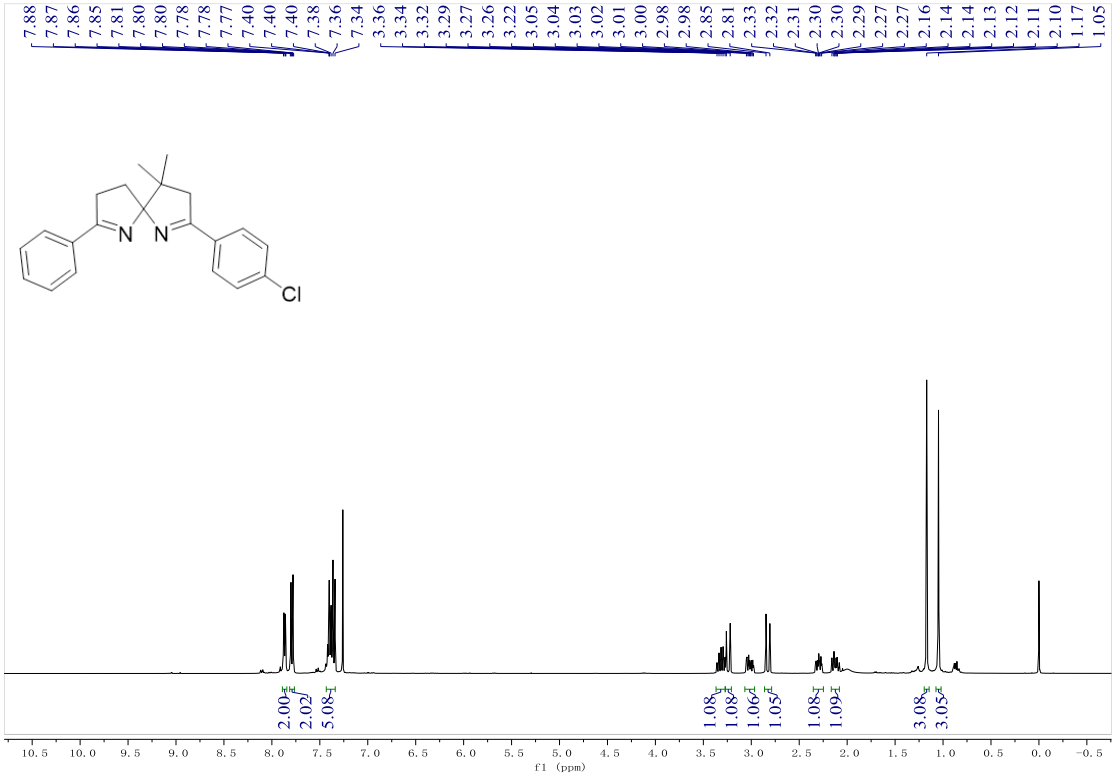


^{19}F NMR spectrum of **3aj**



^{1}H NMR spectrum of **3ak**



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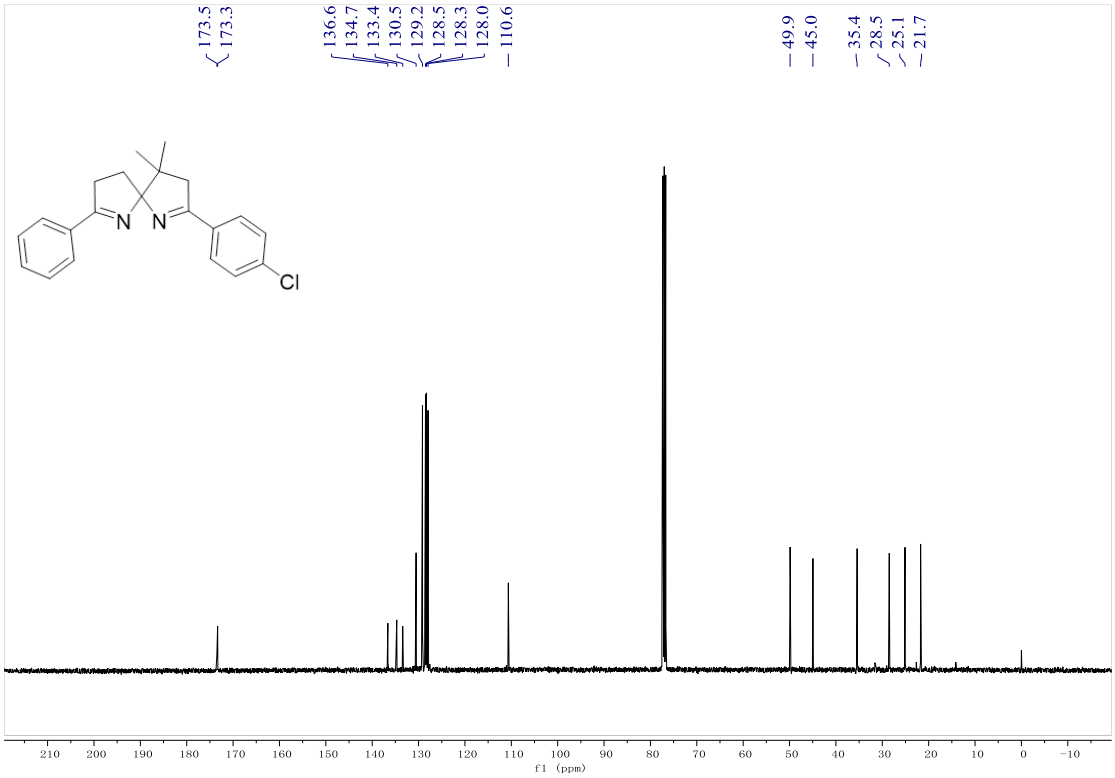
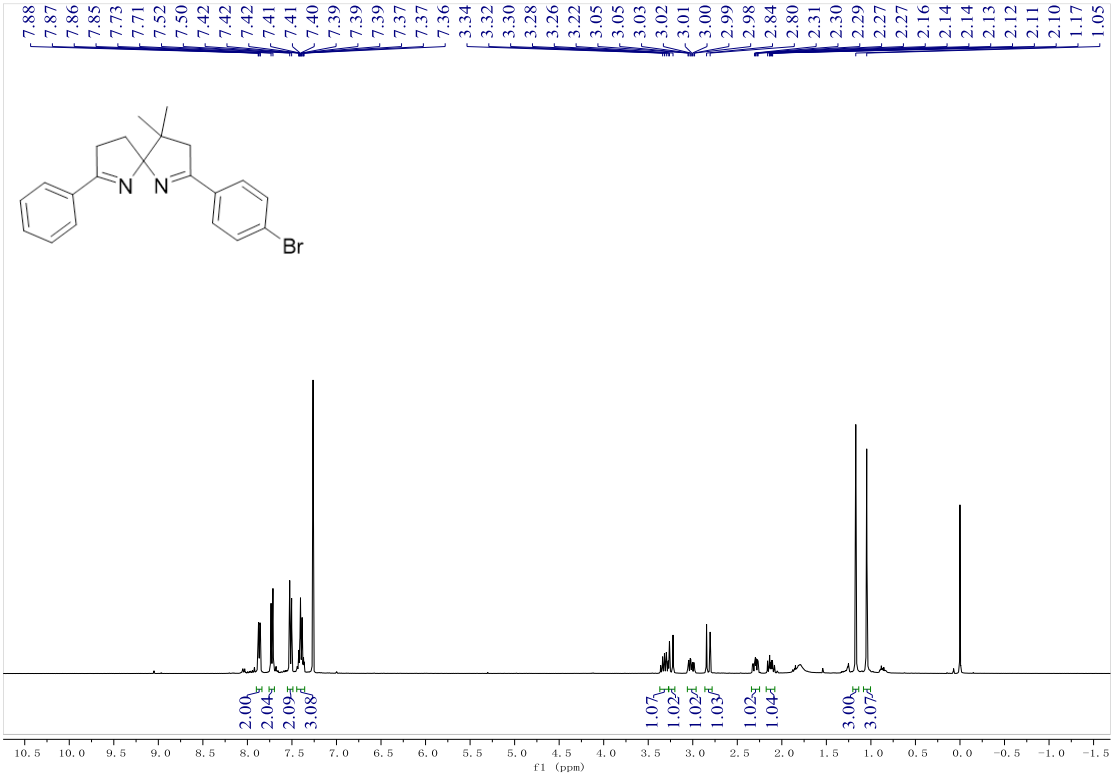
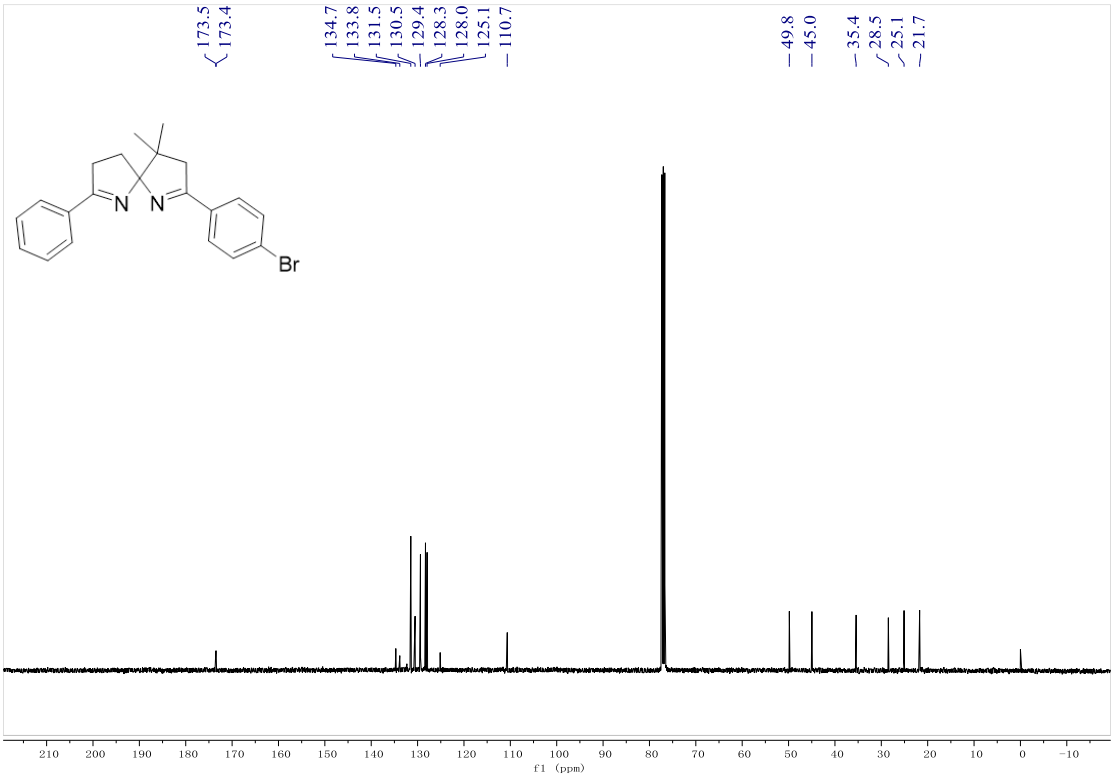


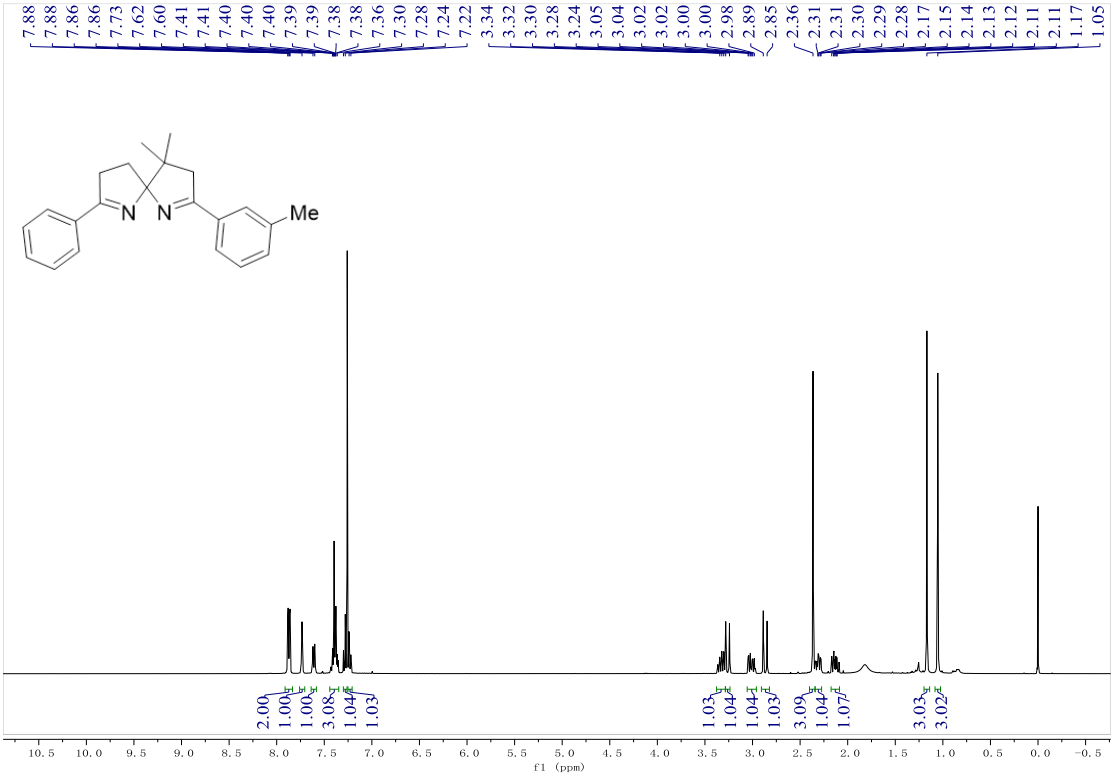
^{1}H NMR spectrum of **3al**



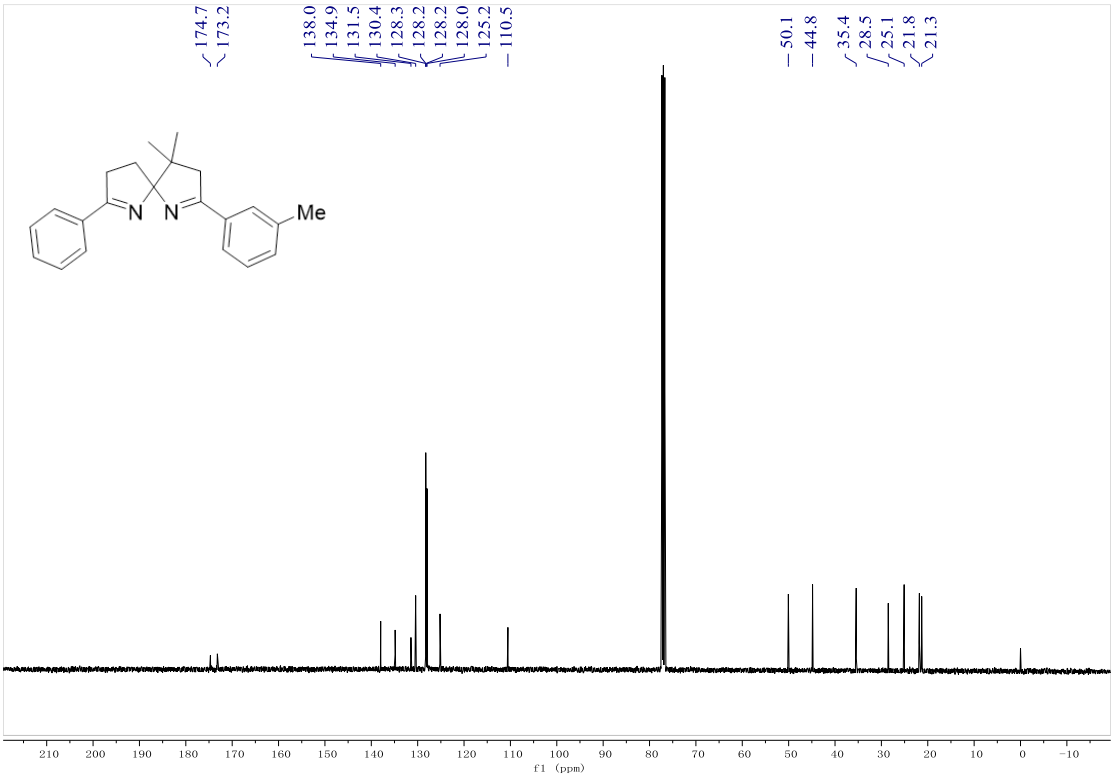
^{13}C NMR spectrum of **3al**



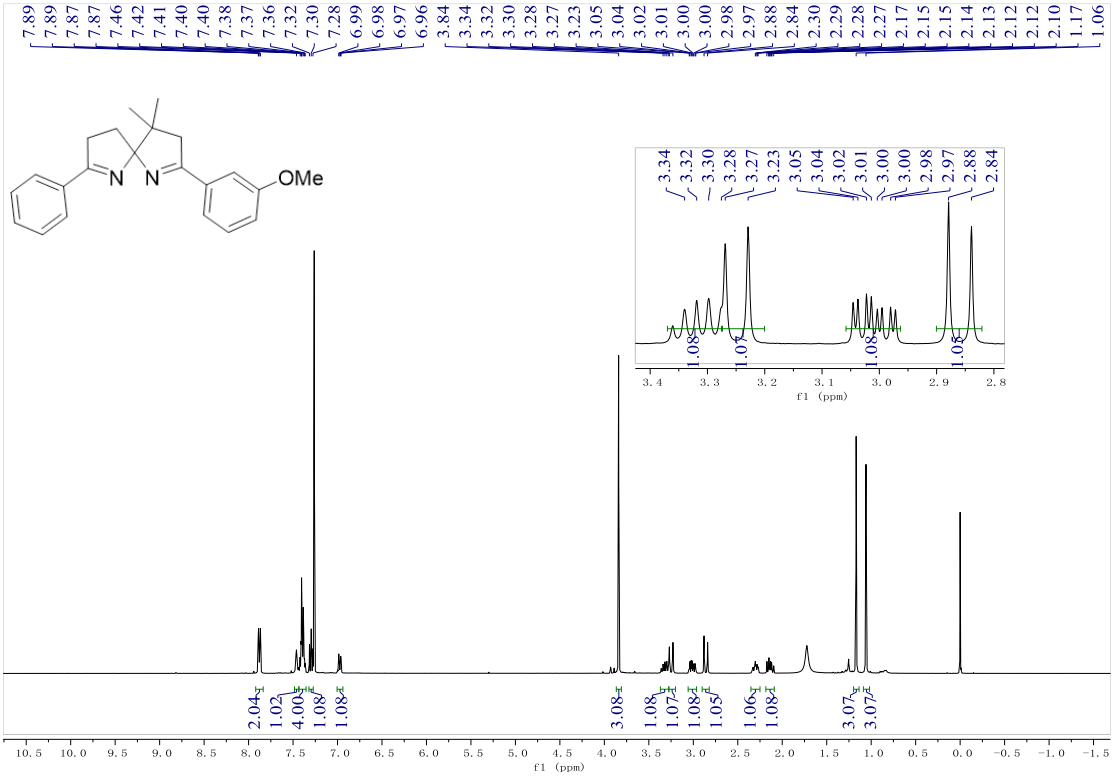
^{1}H NMR spectrum of **3am**



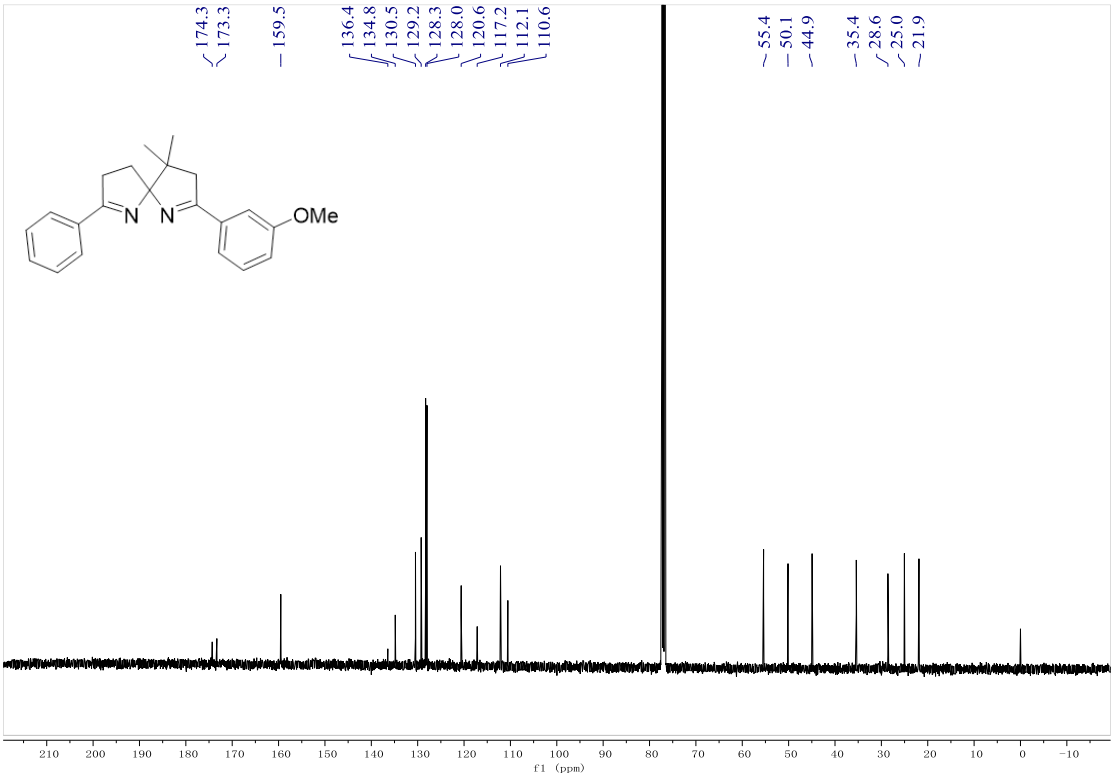
^{13}C NMR spectrum of **3am**



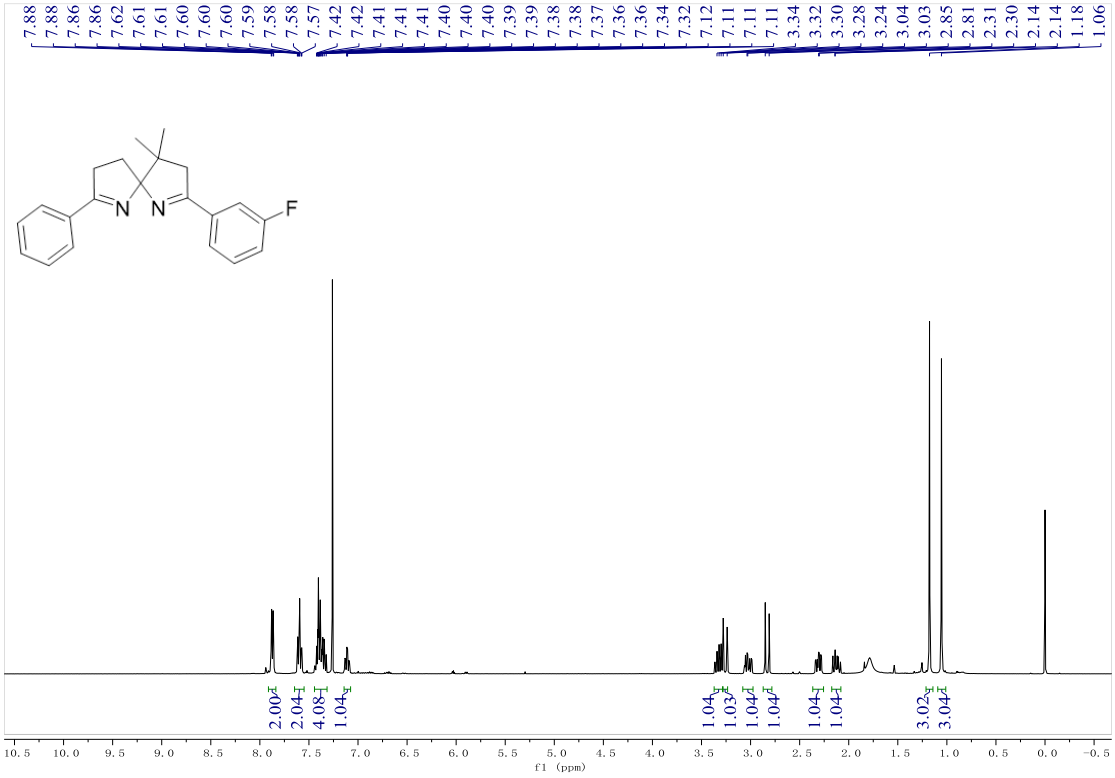
^{1}H NMR spectrum of **3an**



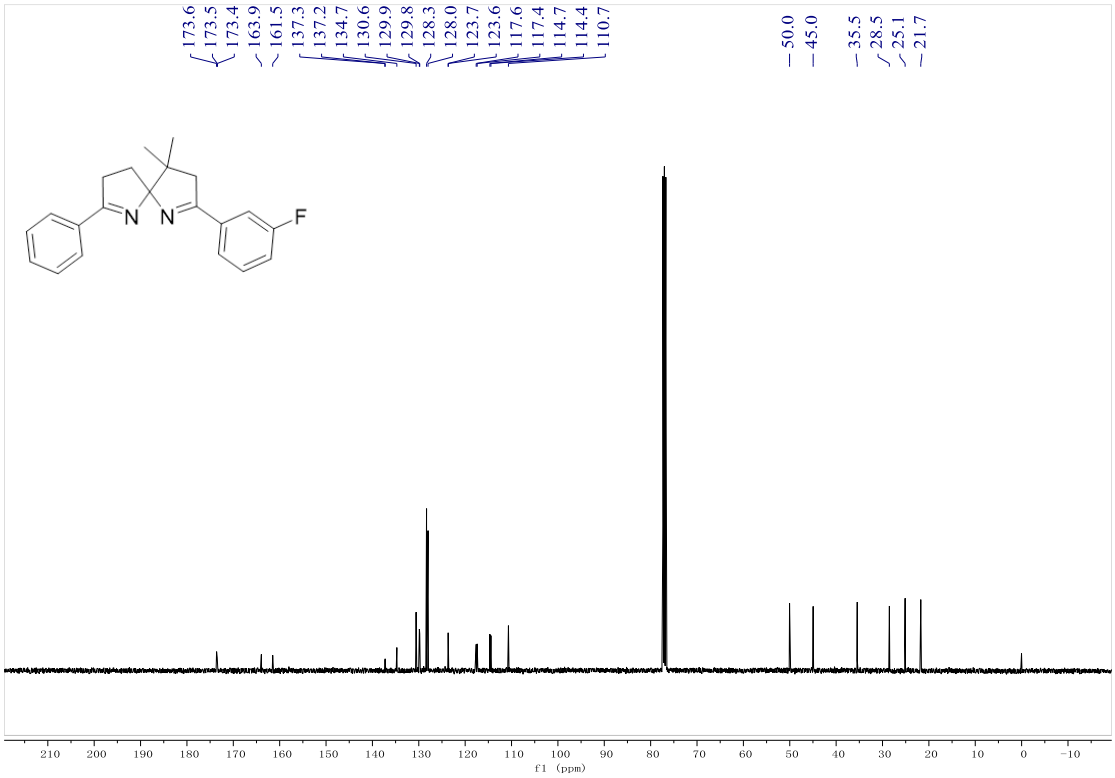
^{13}C NMR spectrum of **3an**



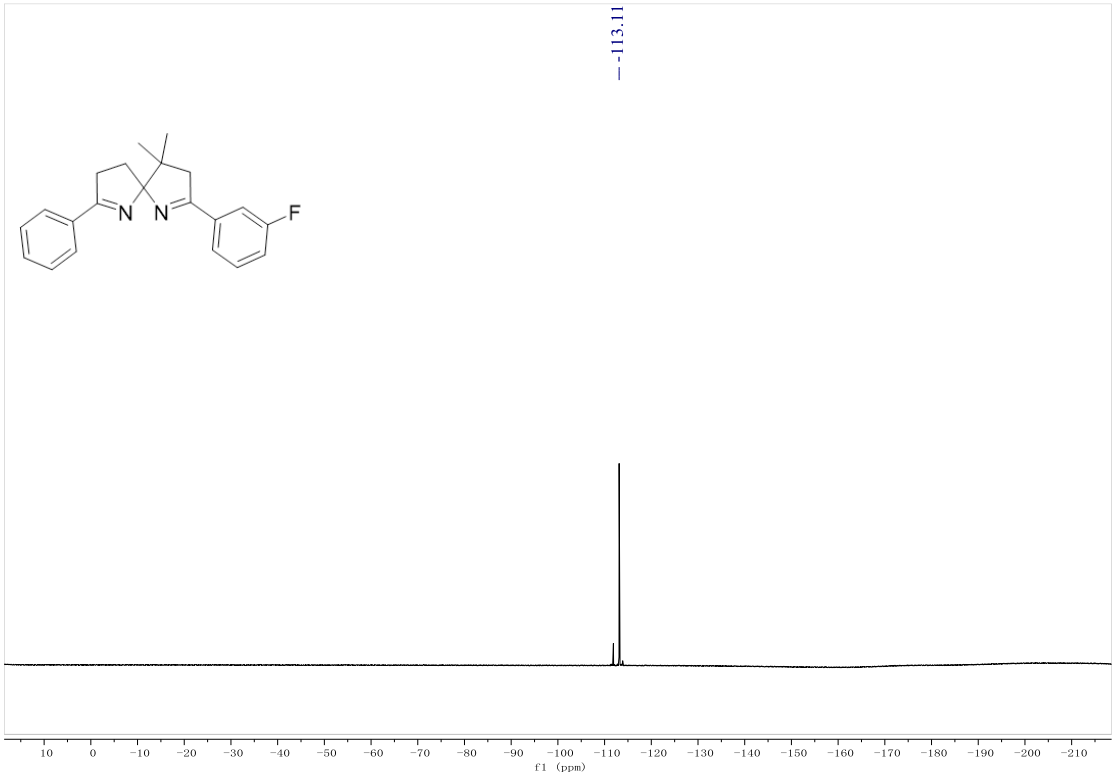
^{1}H NMR spectrum of **3ao**



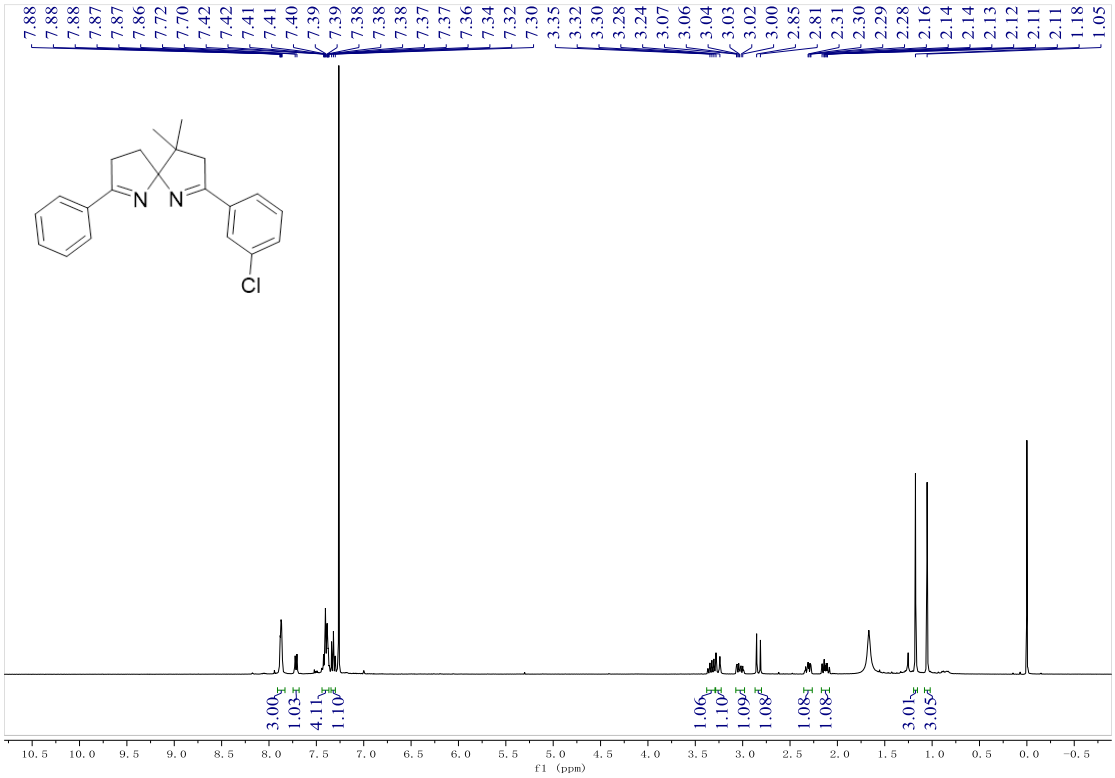
^{13}C NMR spectrum of **3ao**



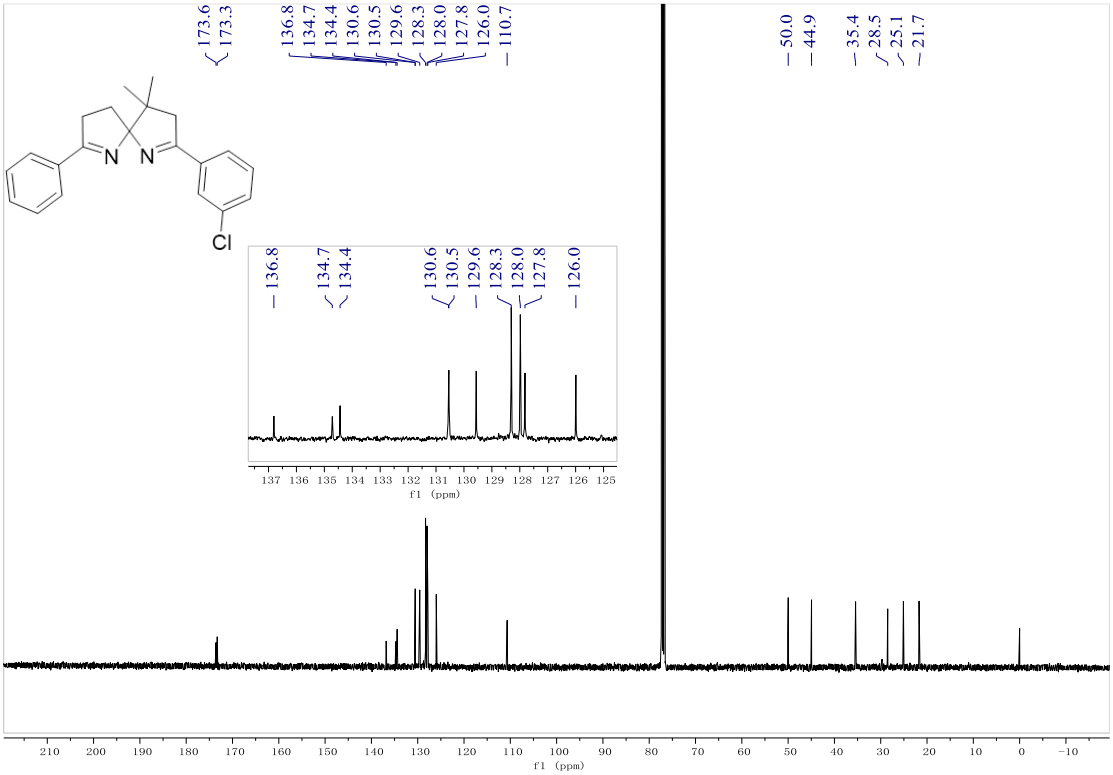
^{19}F NMR spectrum of **3ao**



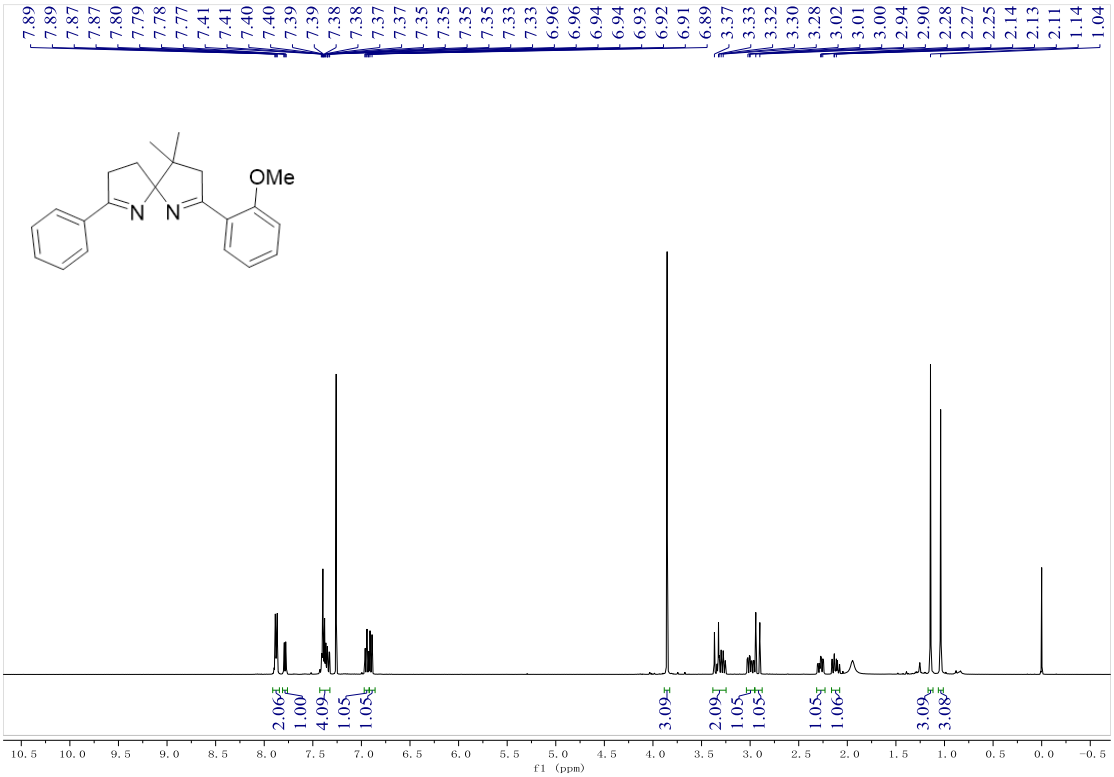
^{1}H NMR spectrum of **3ap**



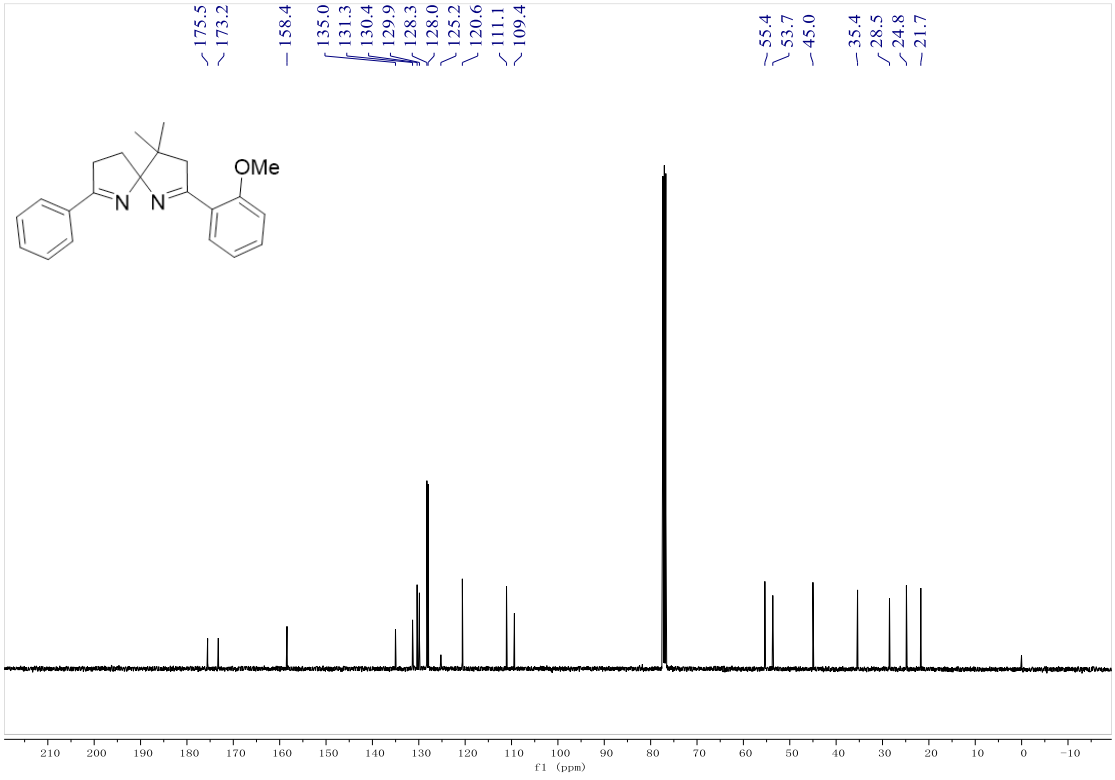
^{13}C NMR spectrum of **3ap**



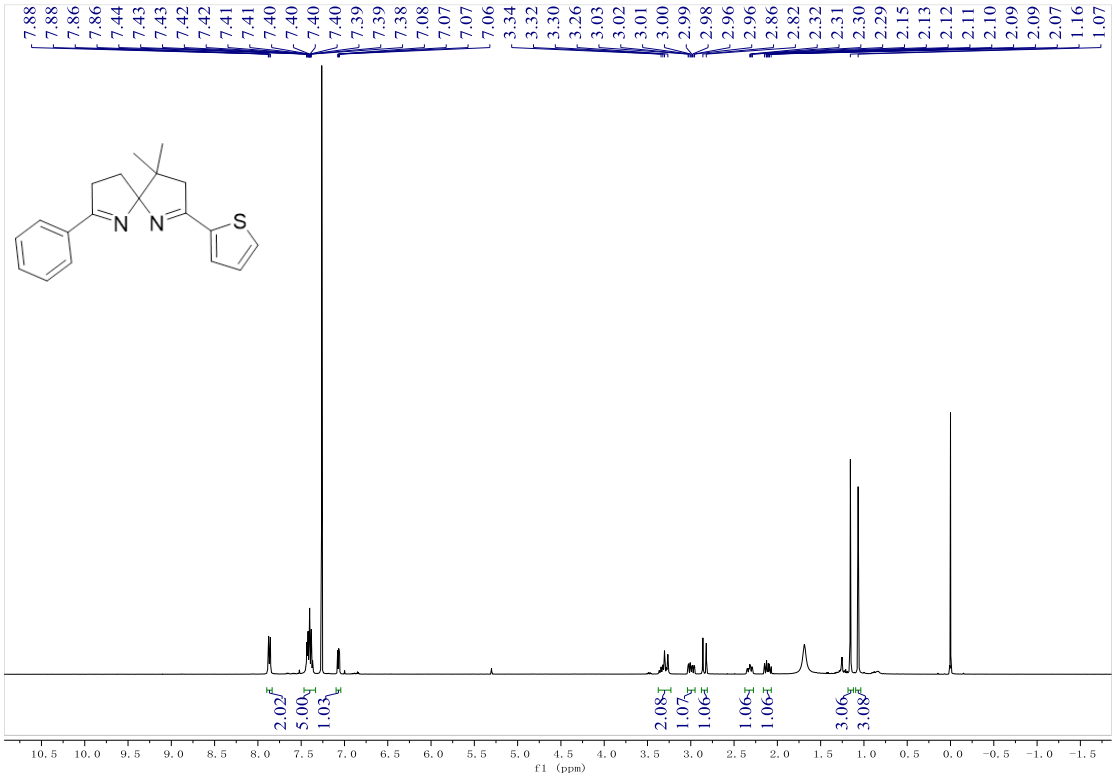
^{1}H NMR spectrum of **3aq**



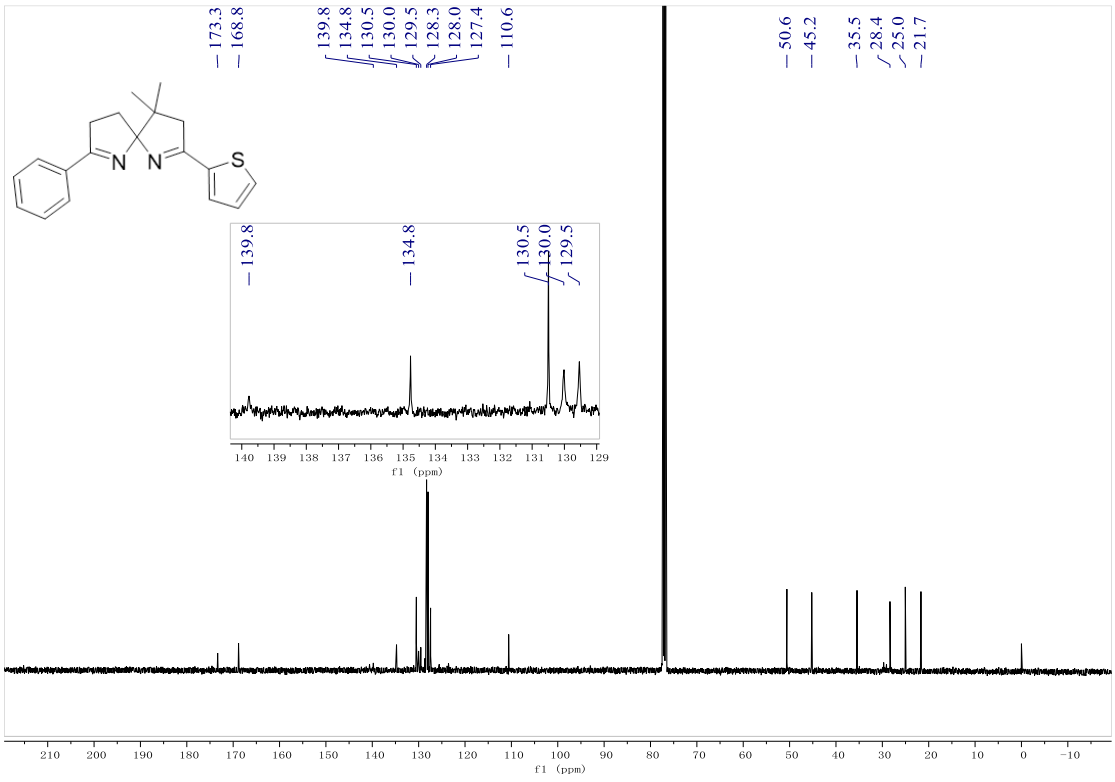
^{13}C NMR spectrum of **3aq**



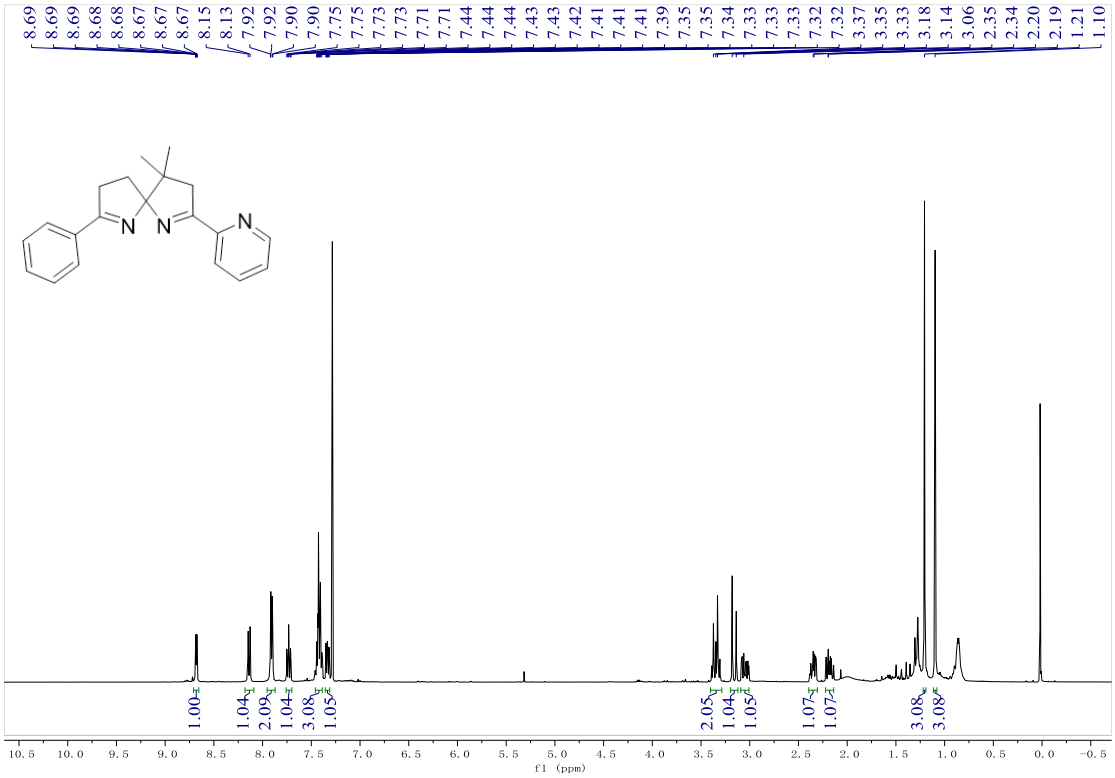
^{1}H NMR spectrum of **3ar**



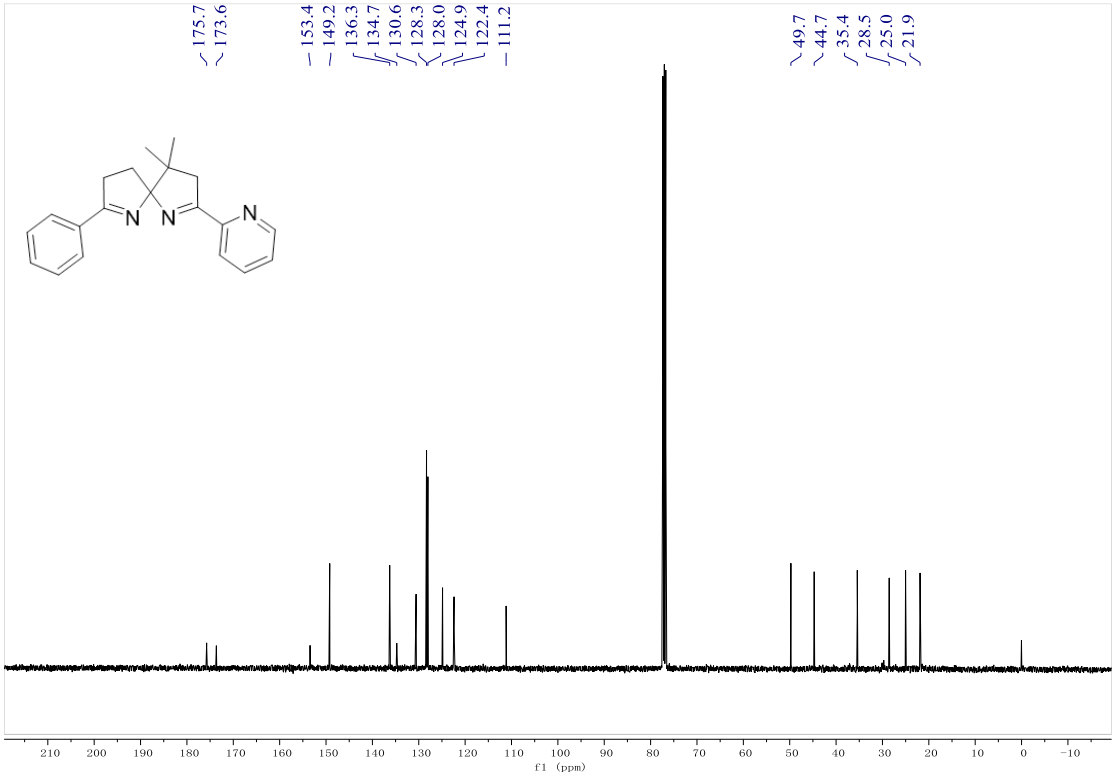
^{13}C NMR spectrum of **3ar**



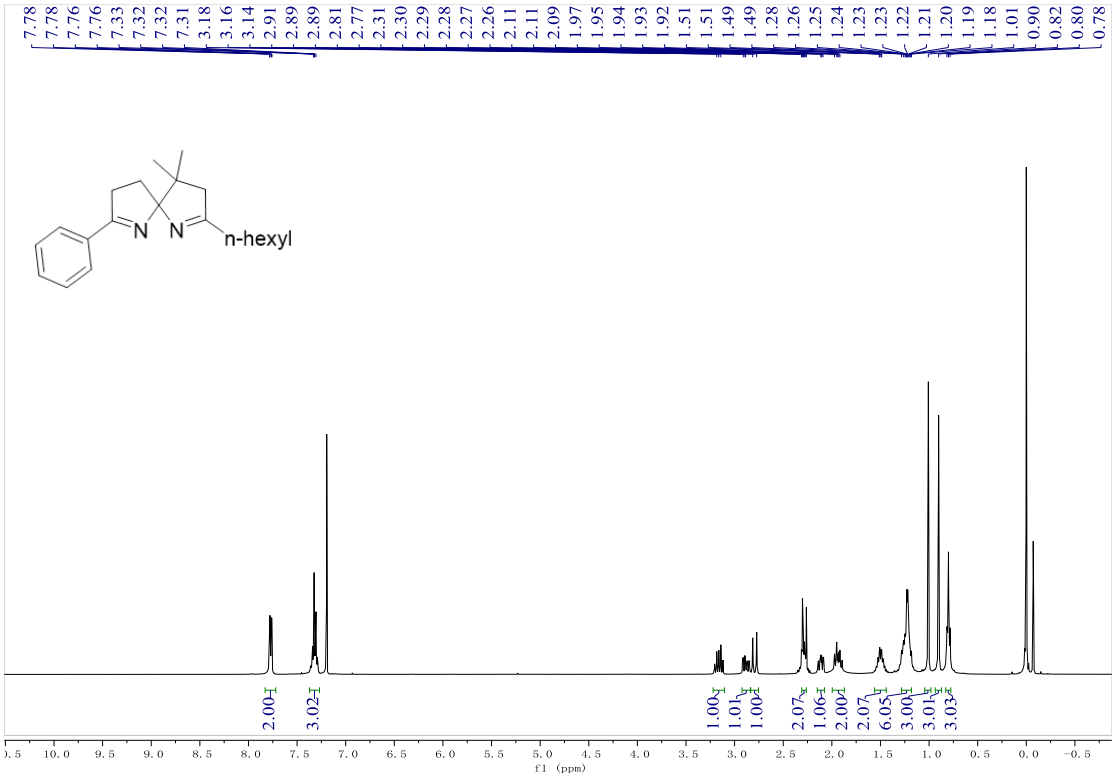
^{1}H NMR spectrum of **3as**



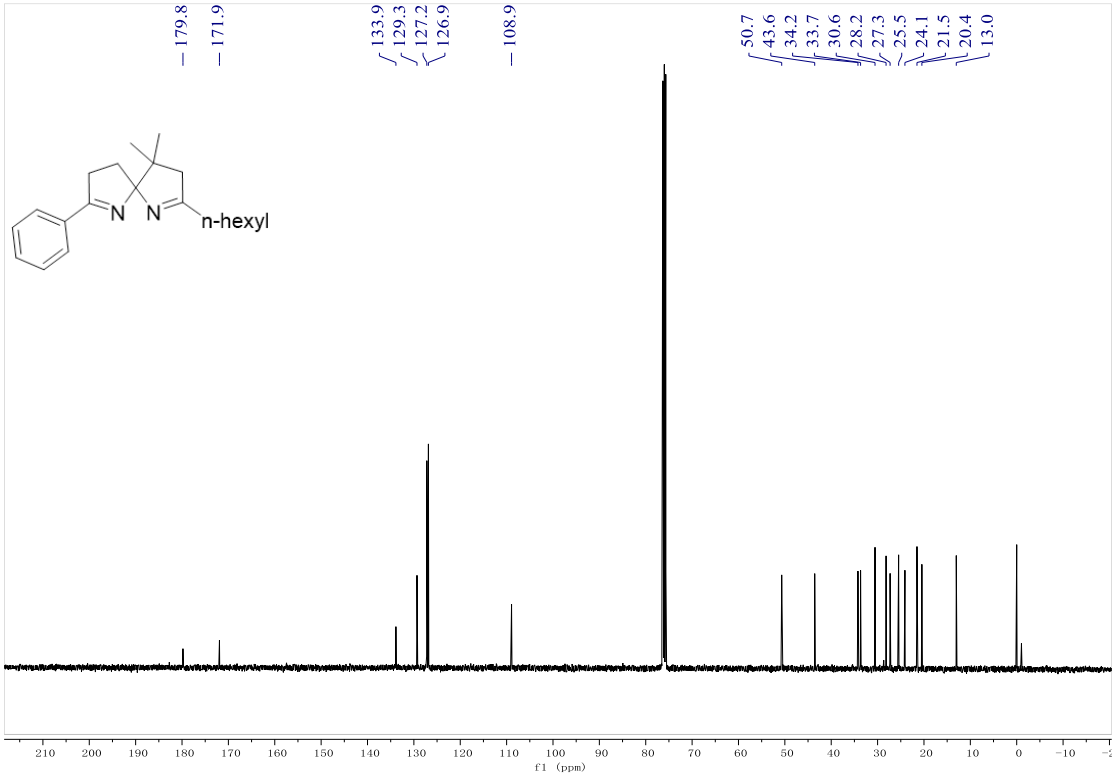
^{13}C NMR spectrum of **3as**



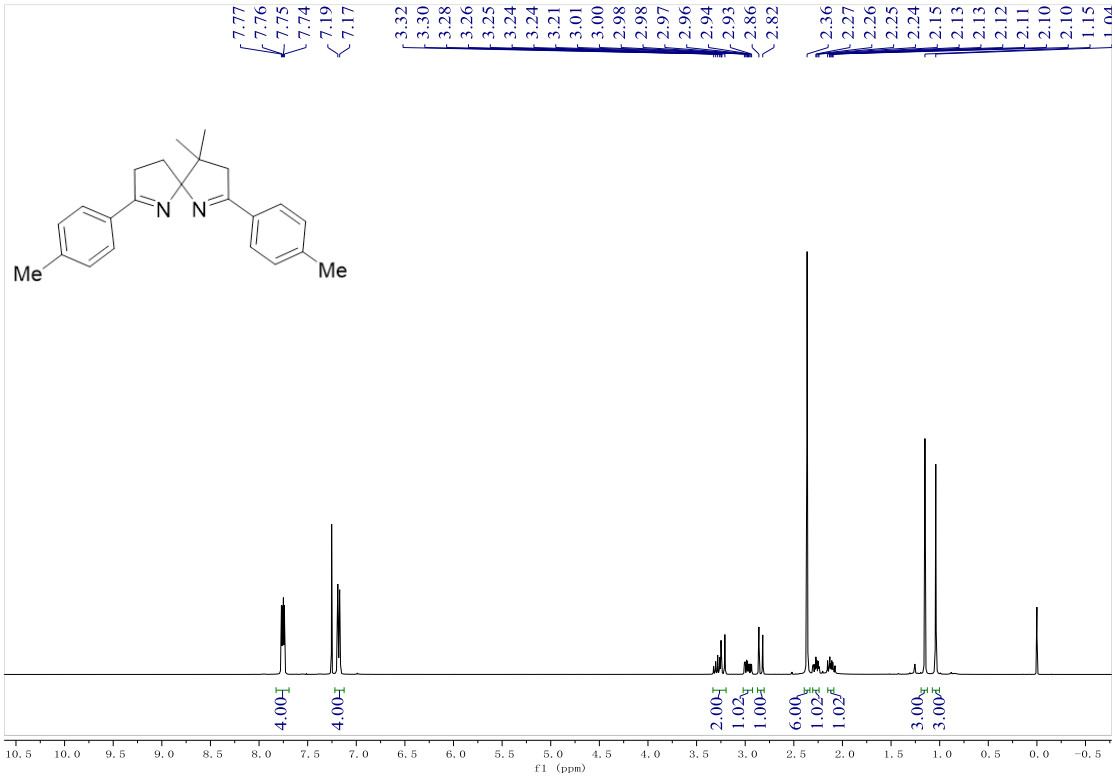
^{1}H NMR spectrum of **3at**



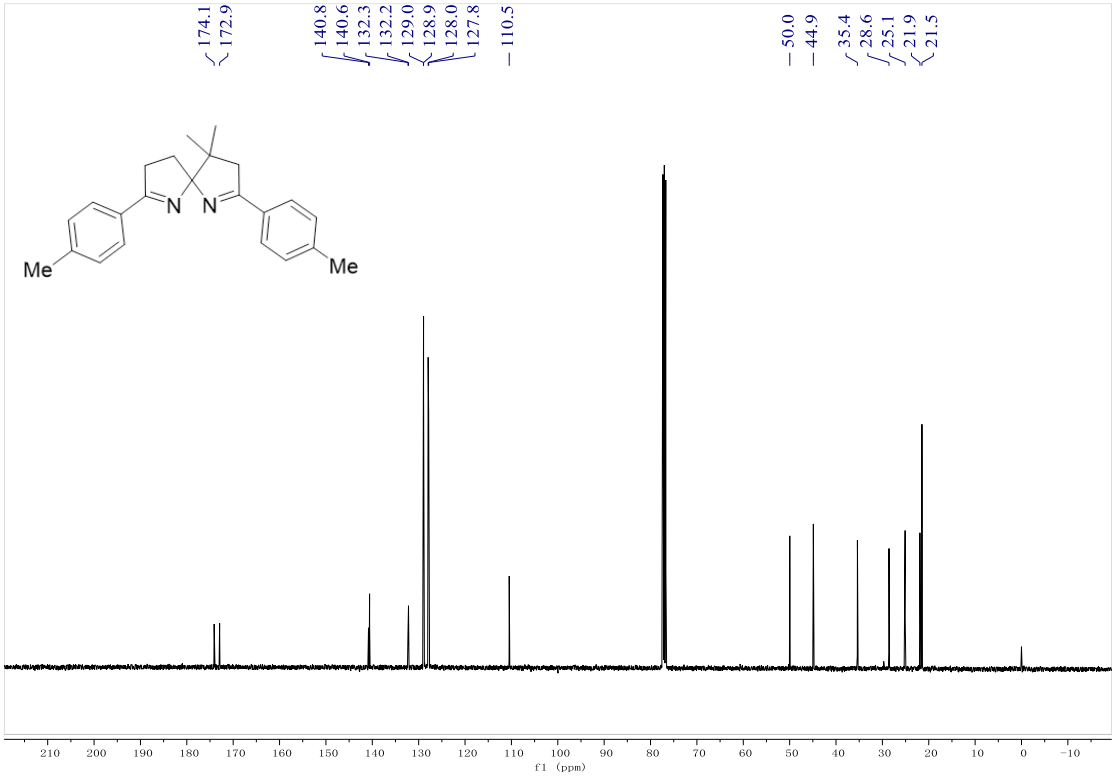
^{13}C NMR spectrum of **3at**



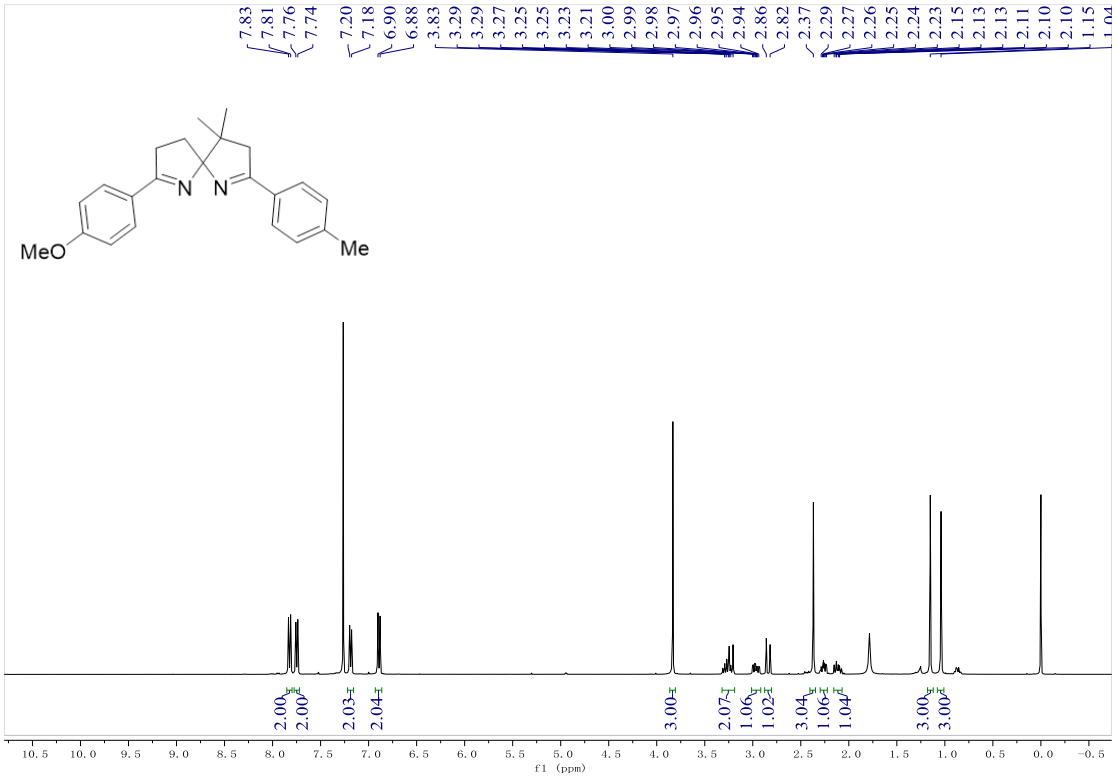
^{1}H NMR spectrum of **3ba**



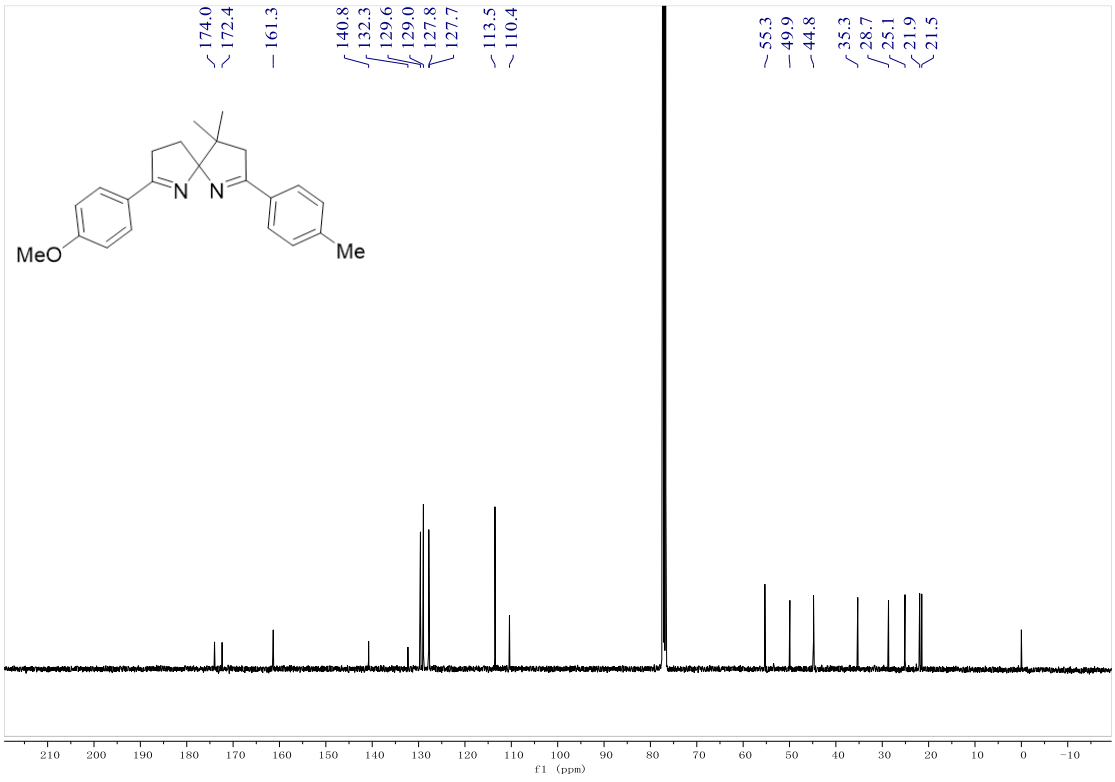
^{13}C NMR spectrum of **3ba**



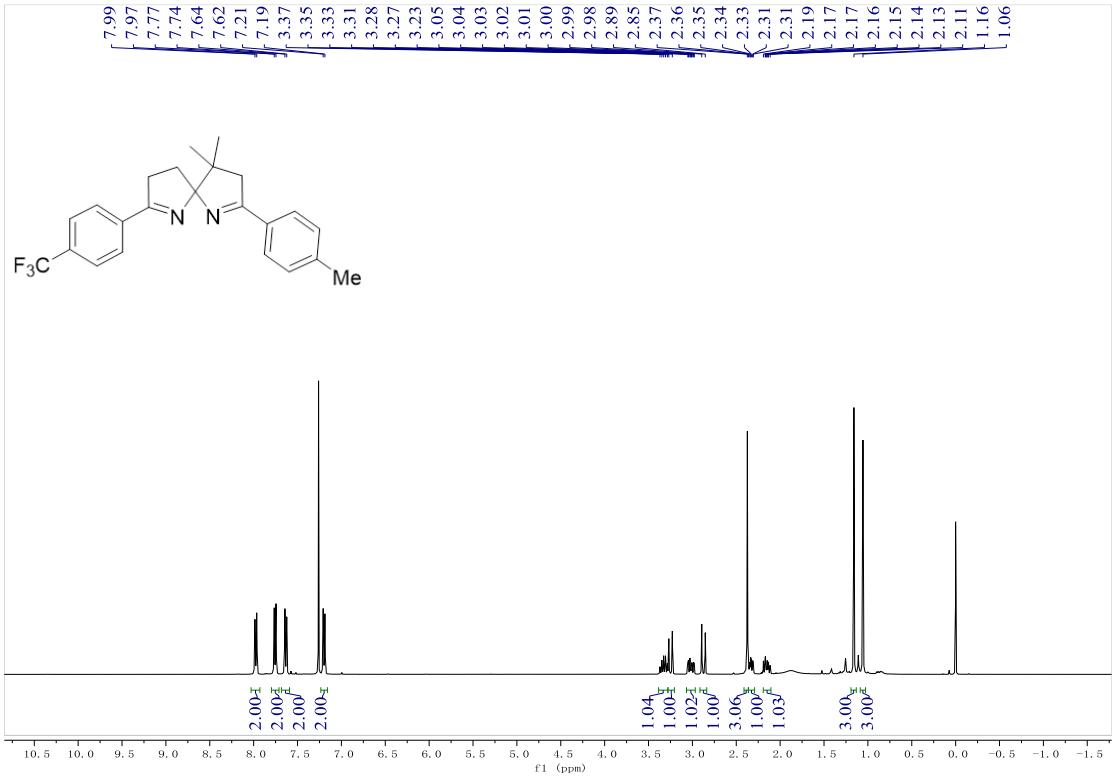
^{1}H NMR spectrum of **3ca**



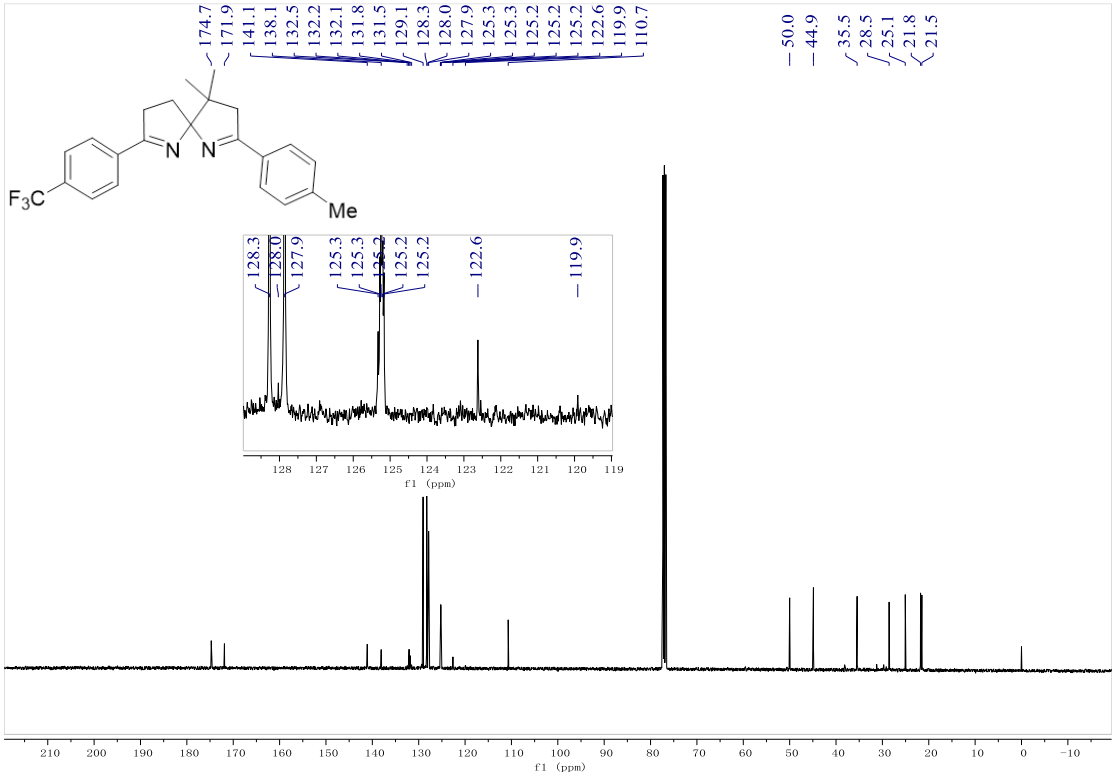
^{13}C NMR spectrum of **3ca**



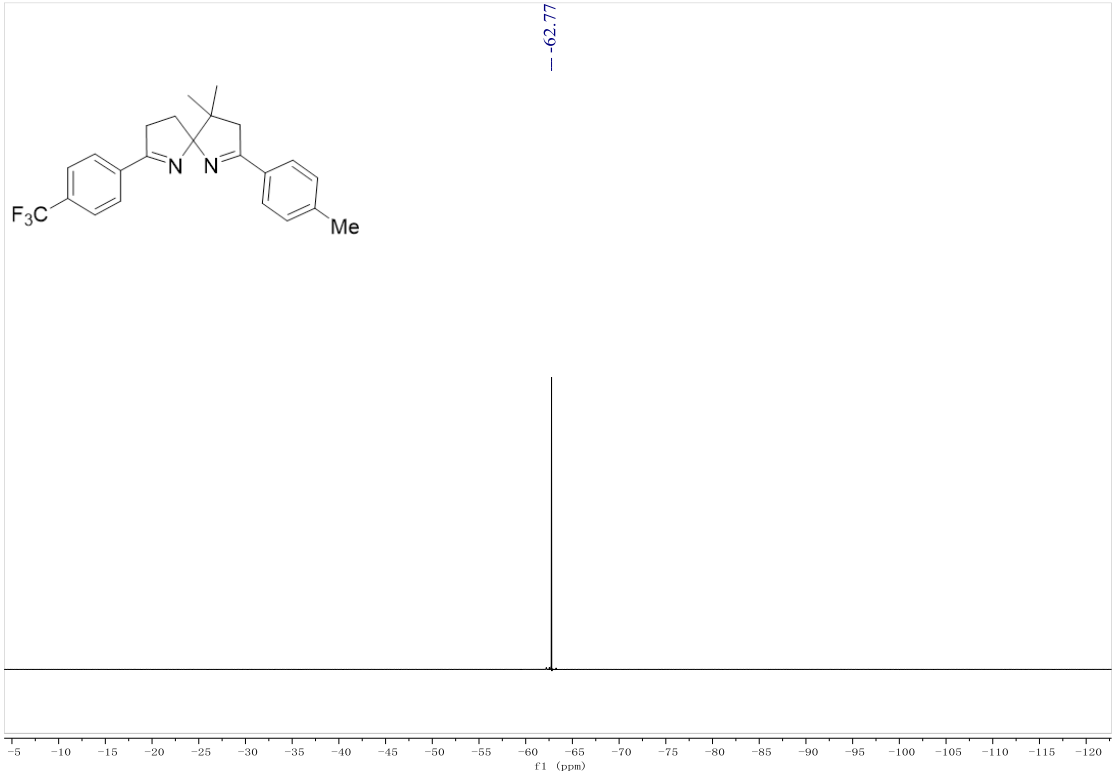
^{1}H NMR spectrum of **3da**



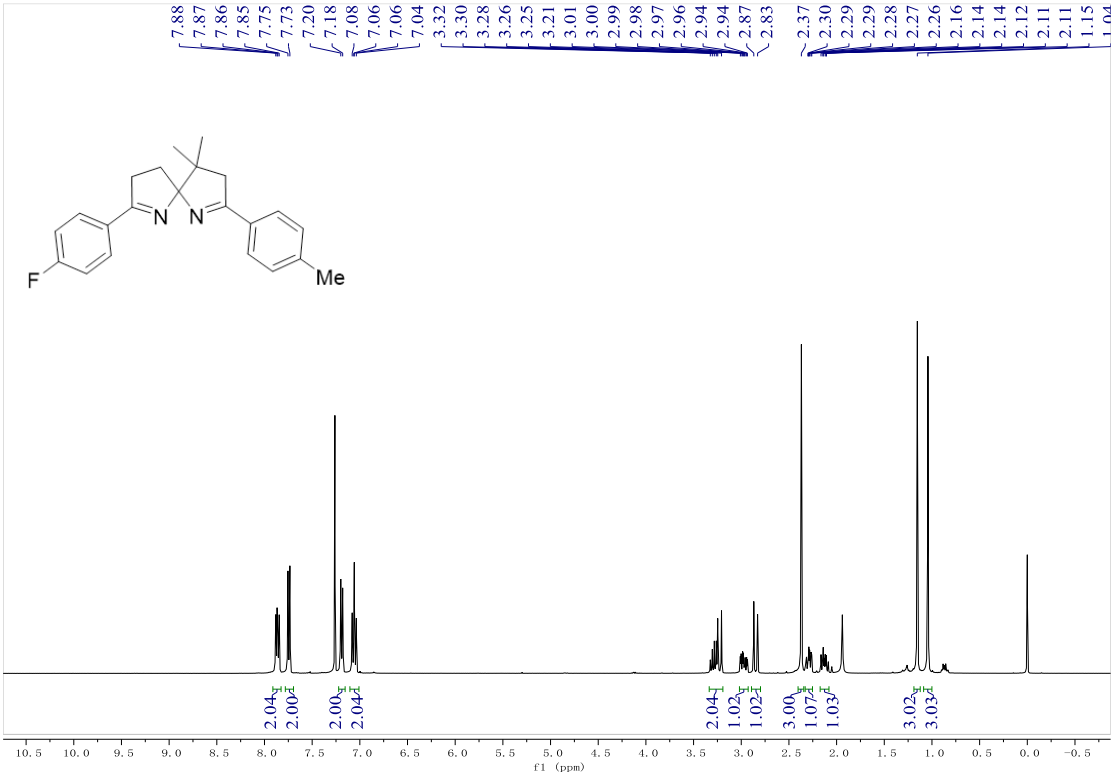
^{13}C NMR spectrum of **3da**



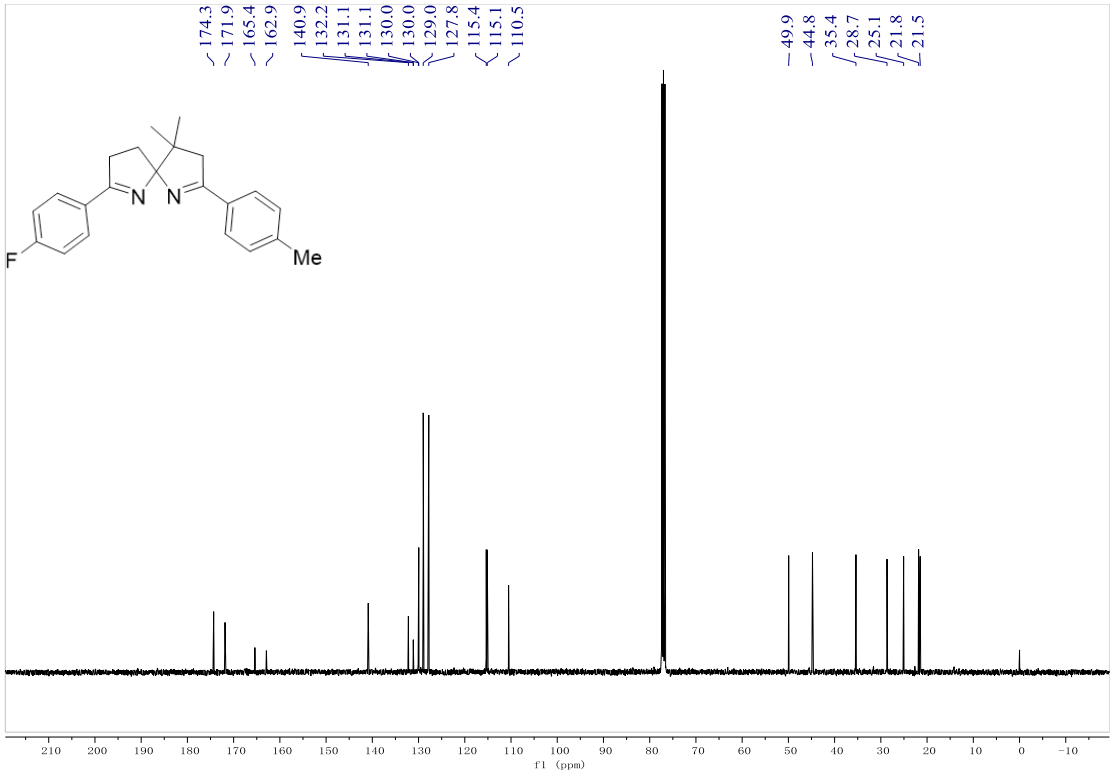
^{19}F NMR spectrum of **3da**



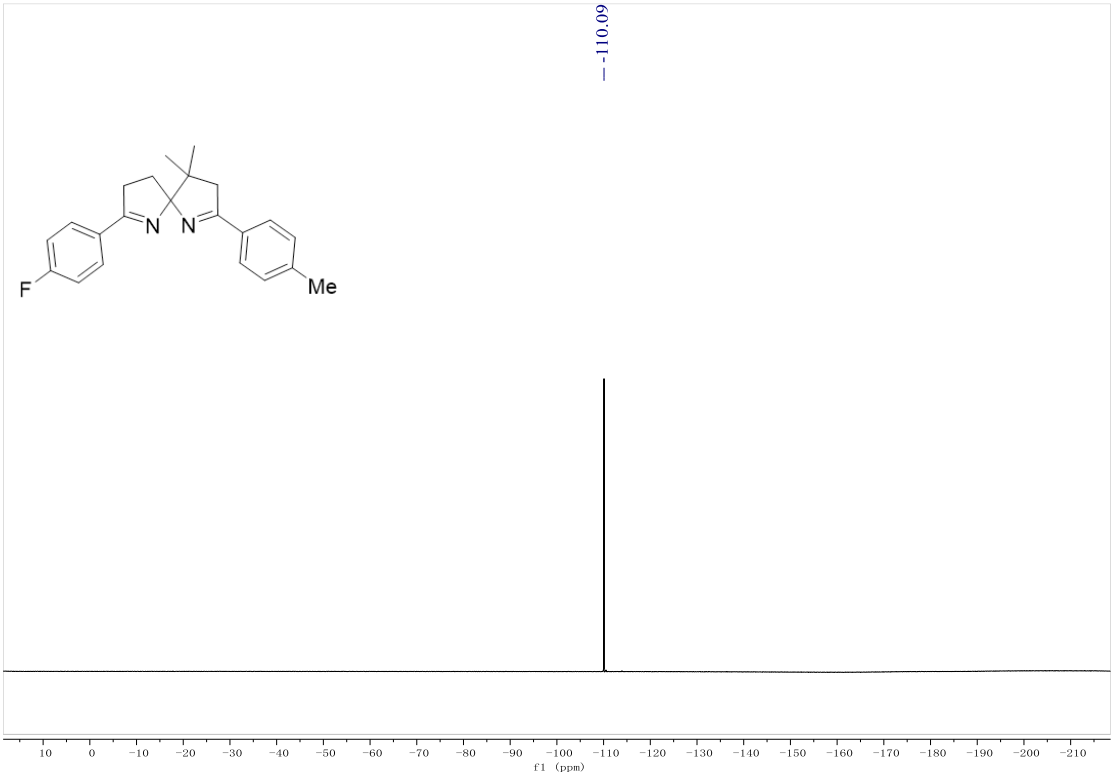
^{1}H NMR spectrum of **3ea**



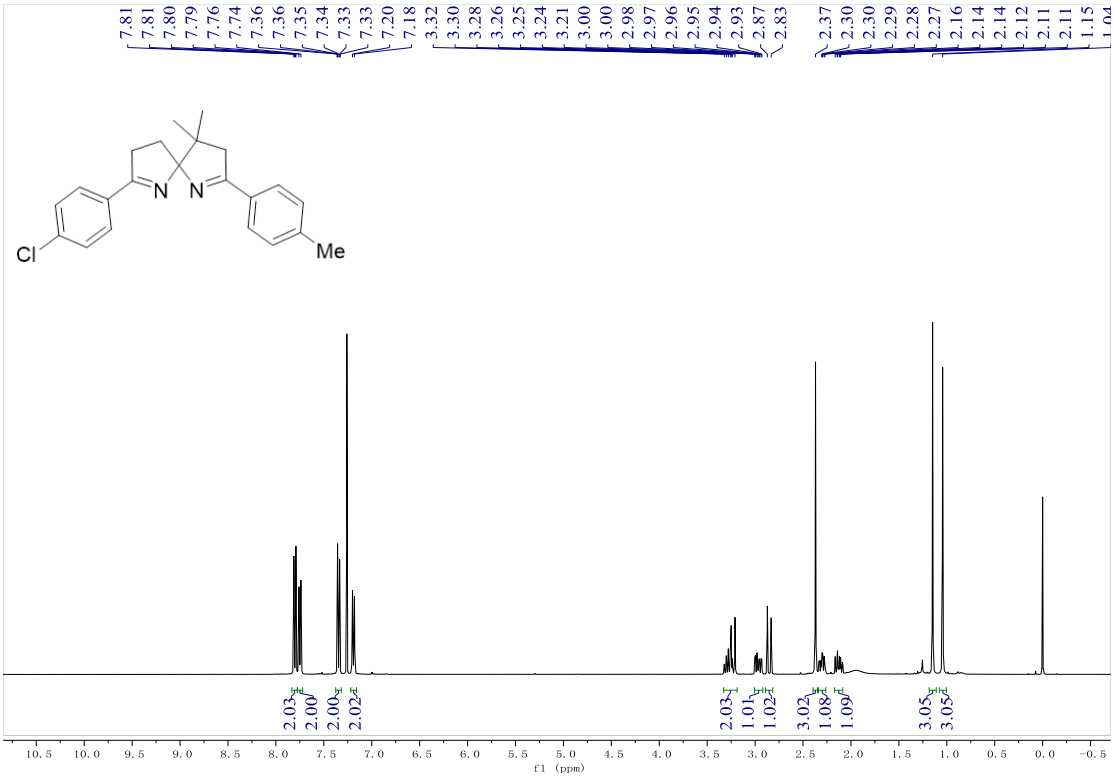
^{13}C NMR spectrum of **3ea**



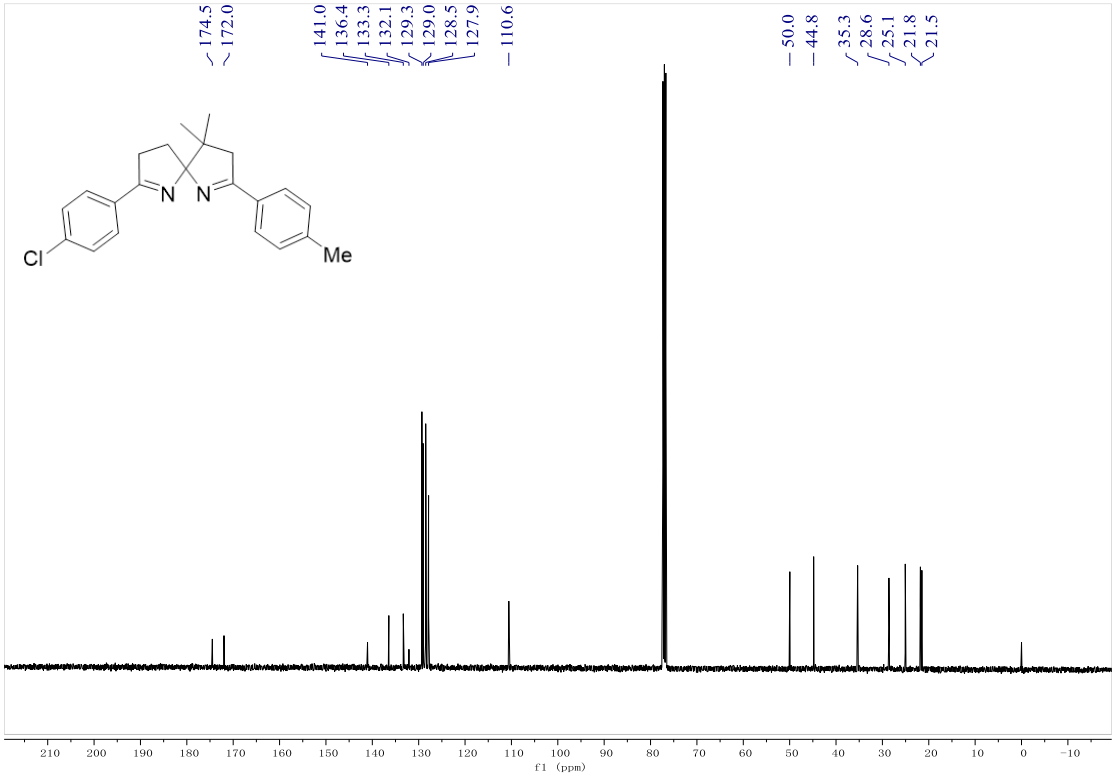
^{19}F NMR spectrum of **3ea**



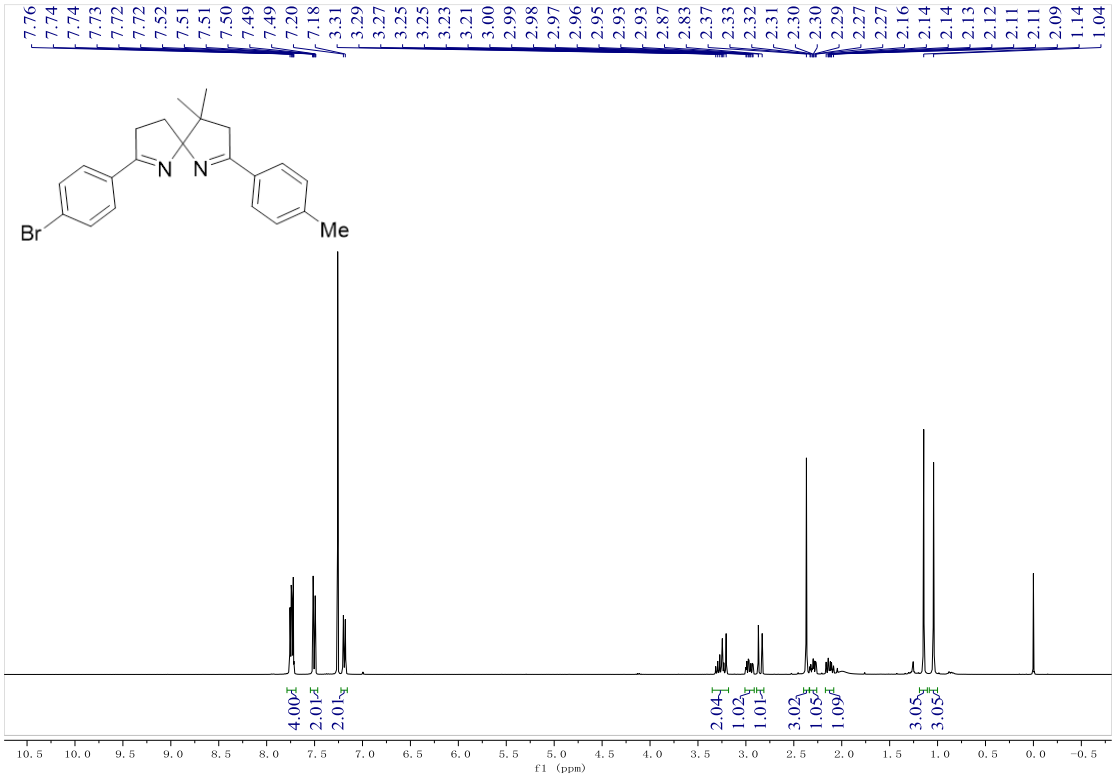
^{1}H NMR spectrum of **3fa**



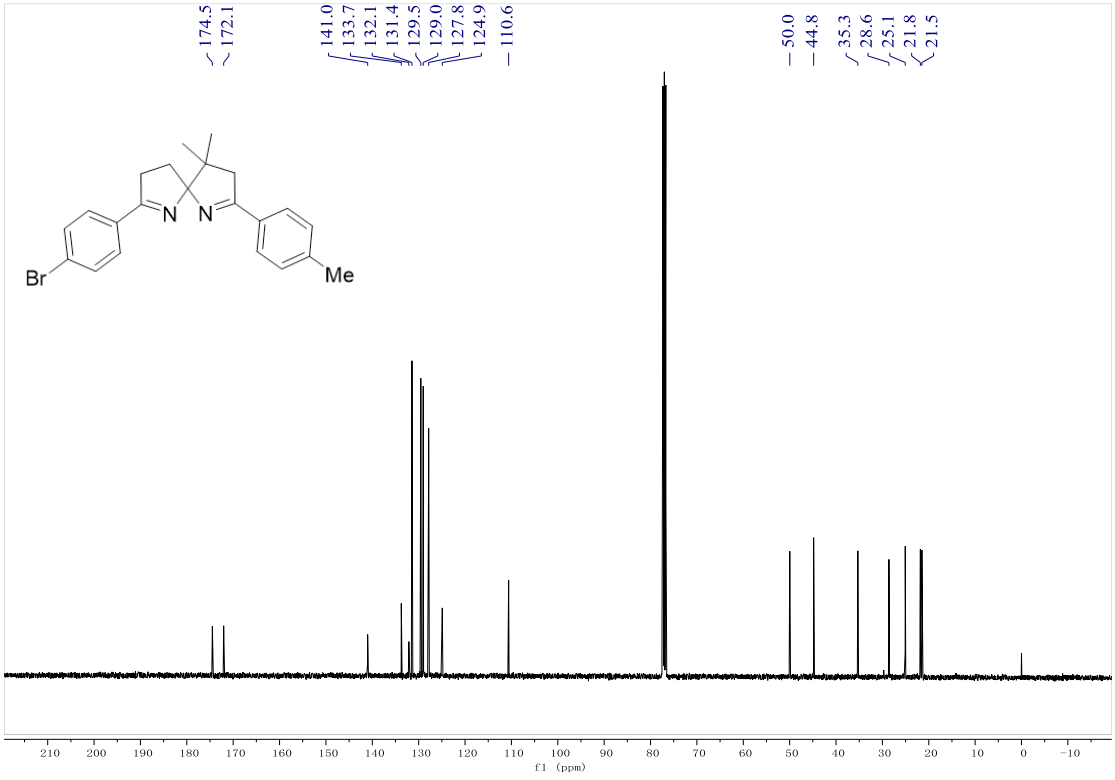
^{13}C NMR spectrum of **3fa**



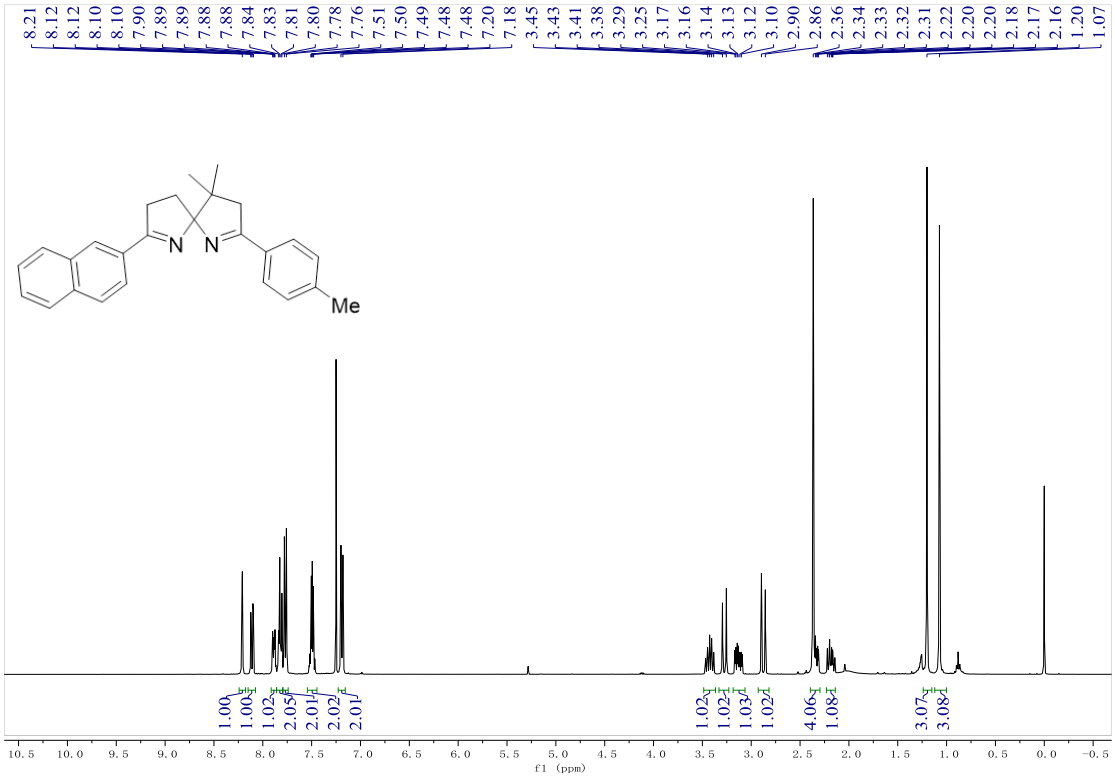
^{1}H NMR spectrum of **3ga**



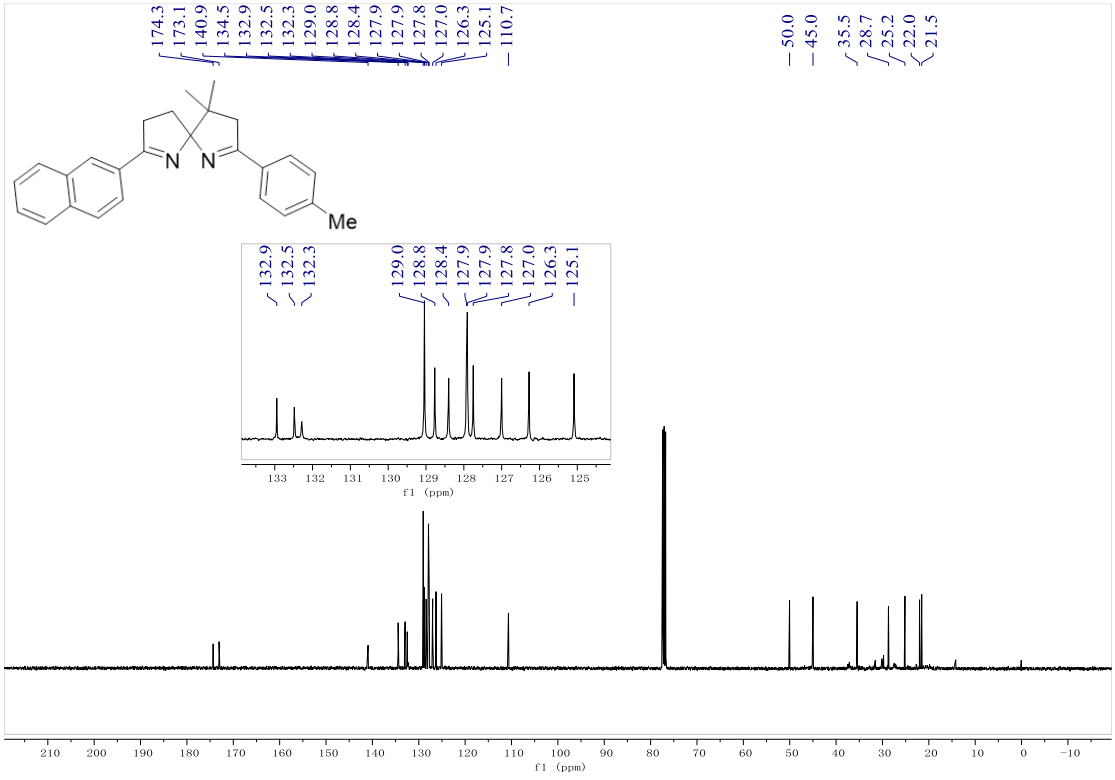
^{13}C NMR spectrum of **3ga**



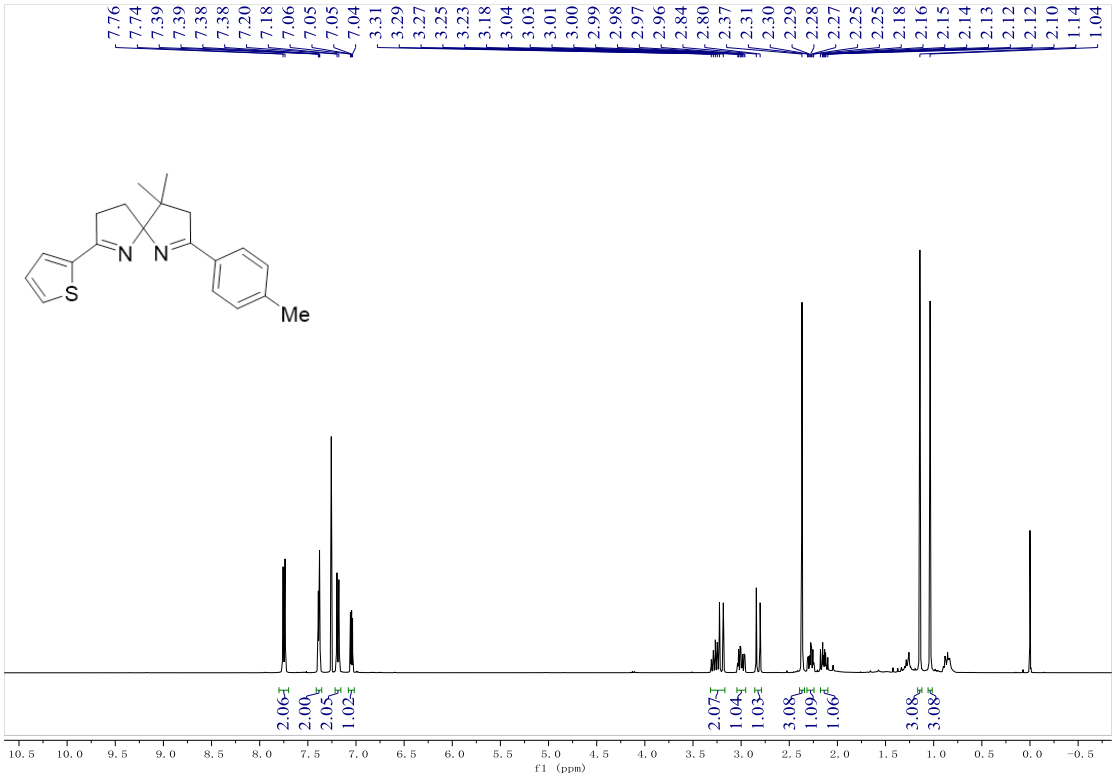
^{1}H NMR spectrum of **3ha**



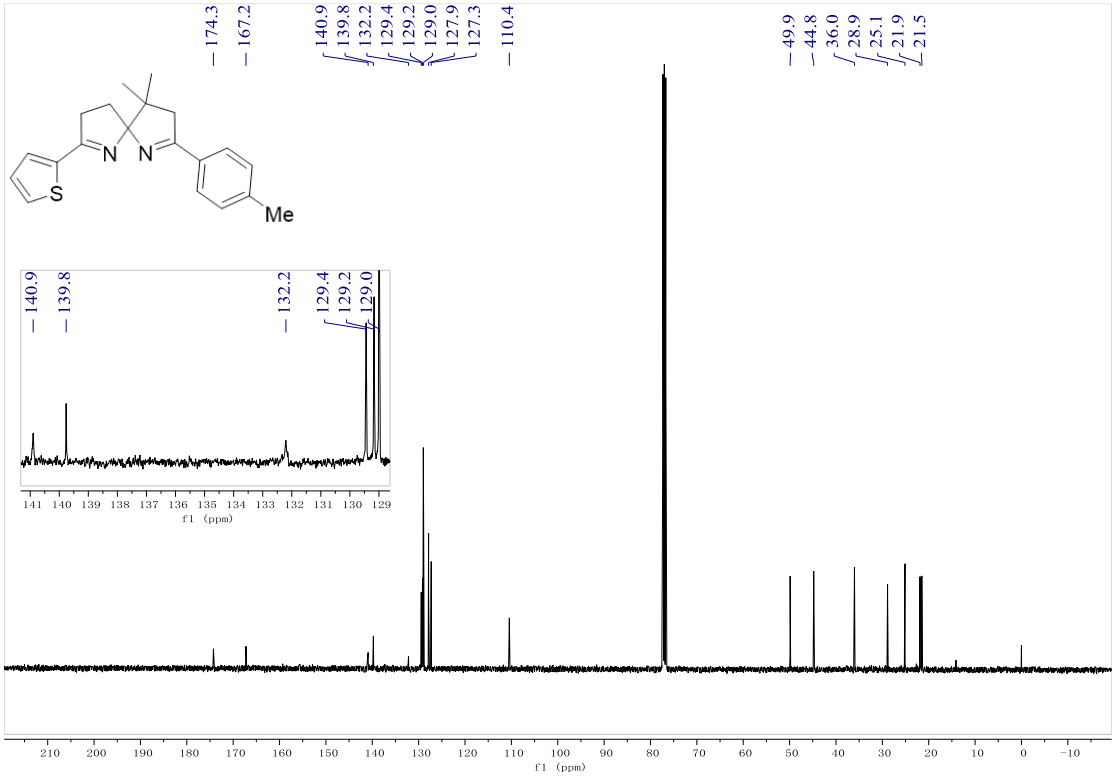
^{13}C NMR spectrum of **3ha**



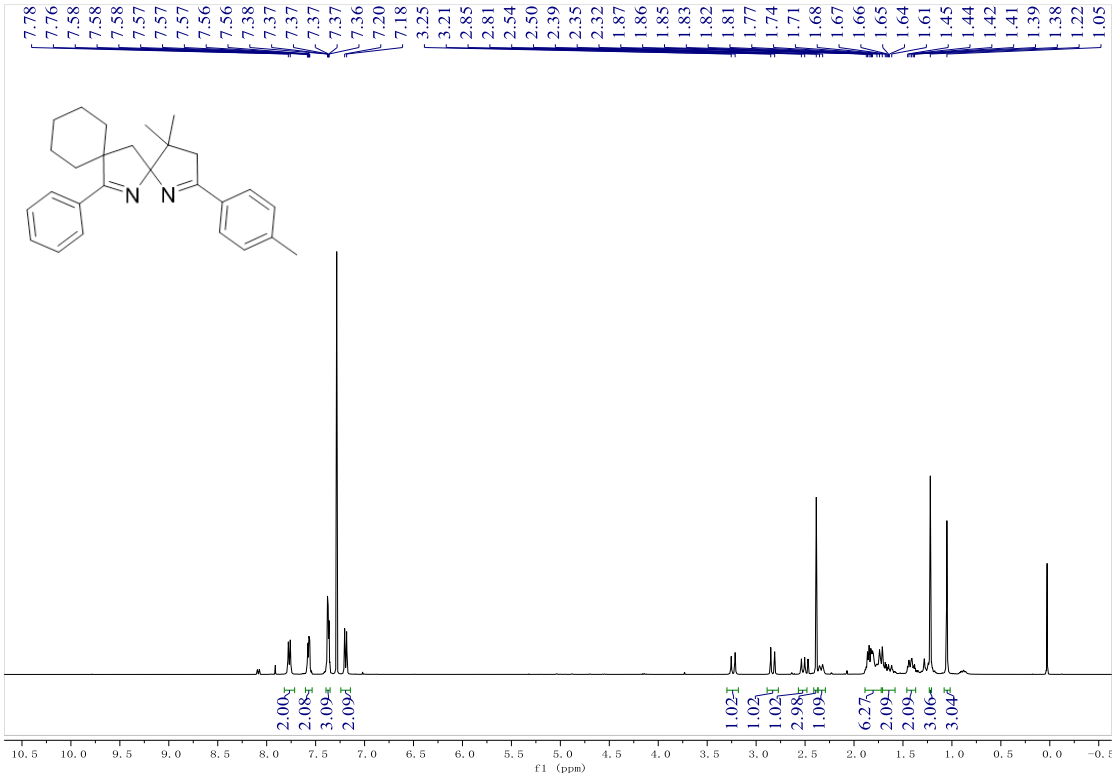
^{1}H NMR spectrum of **3ia**



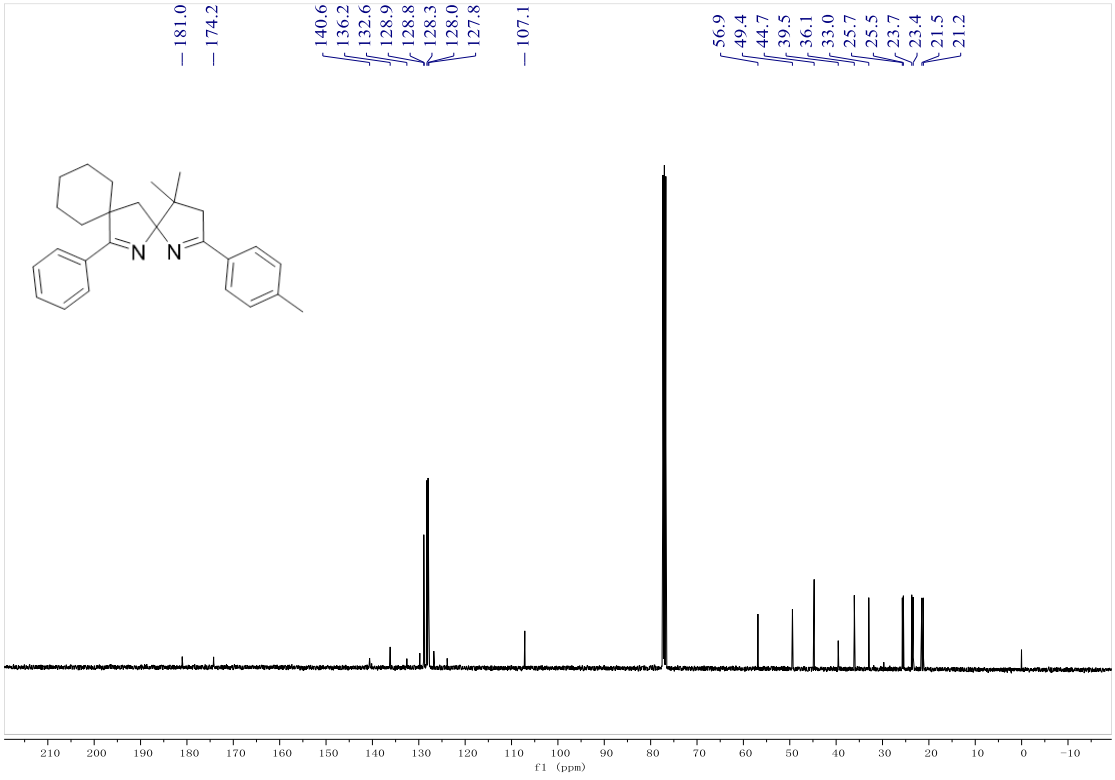
^{13}C NMR spectrum of **3ia**



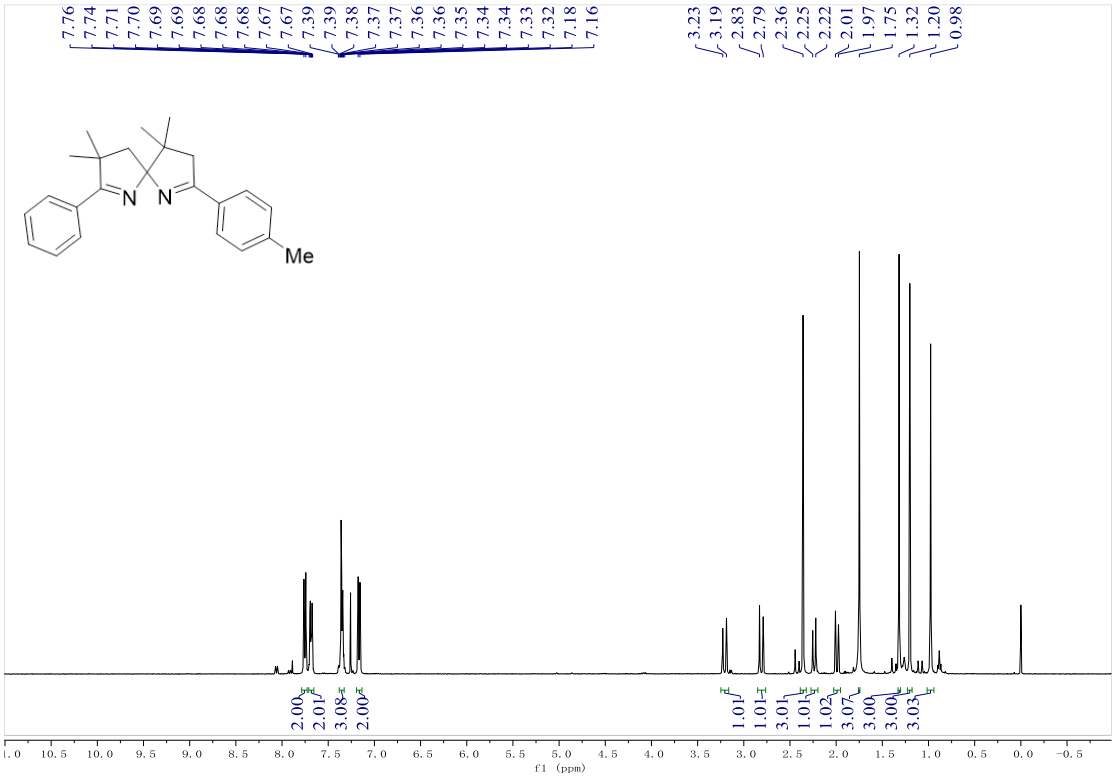
^{1}H NMR spectrum of **3ja**



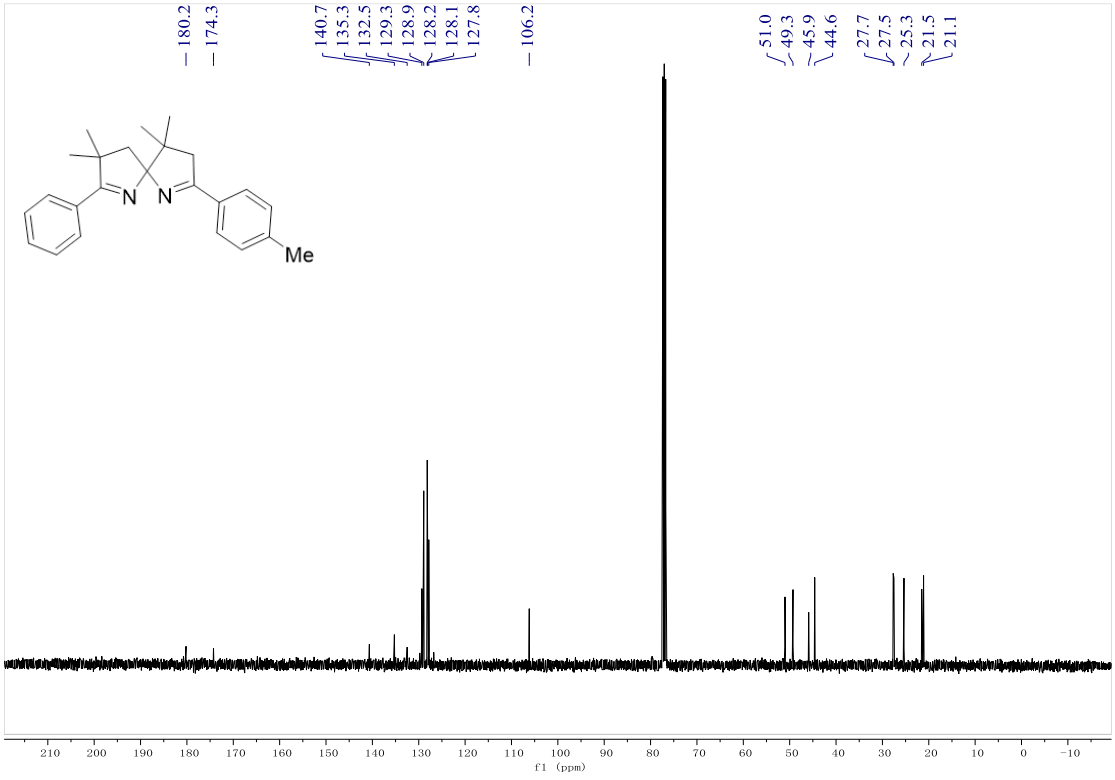
^{13}C NMR spectrum of **3ja**



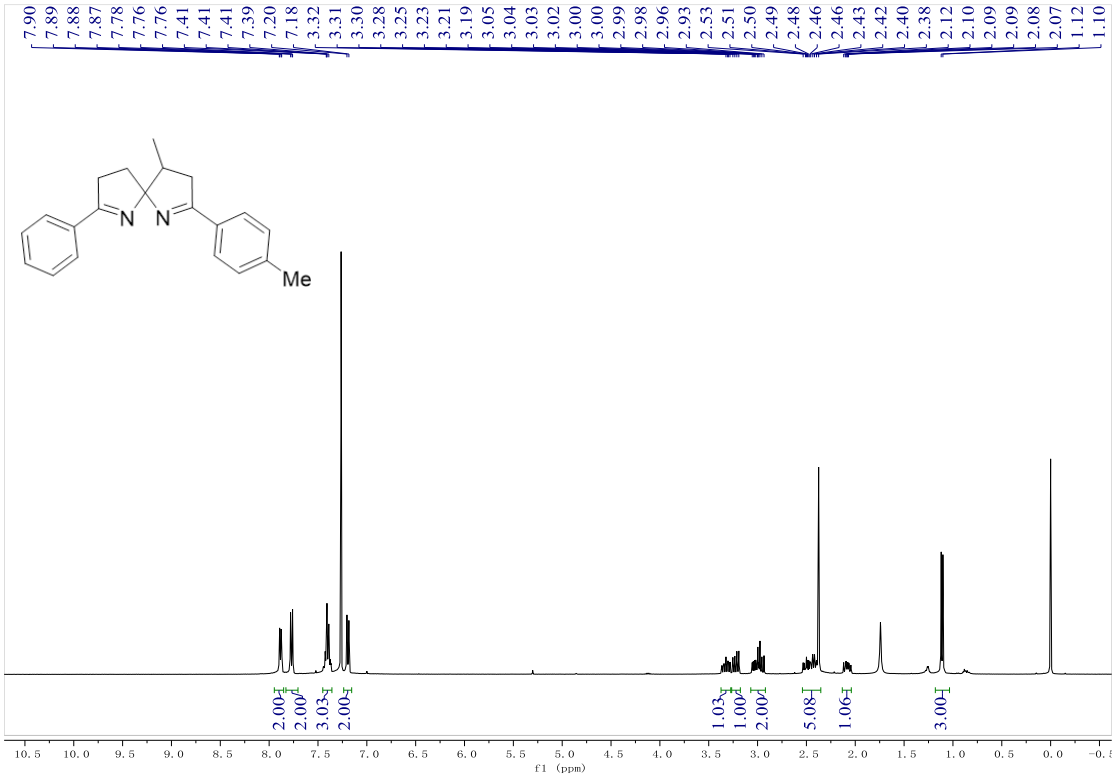
^{1}H NMR spectrum of **3ka**



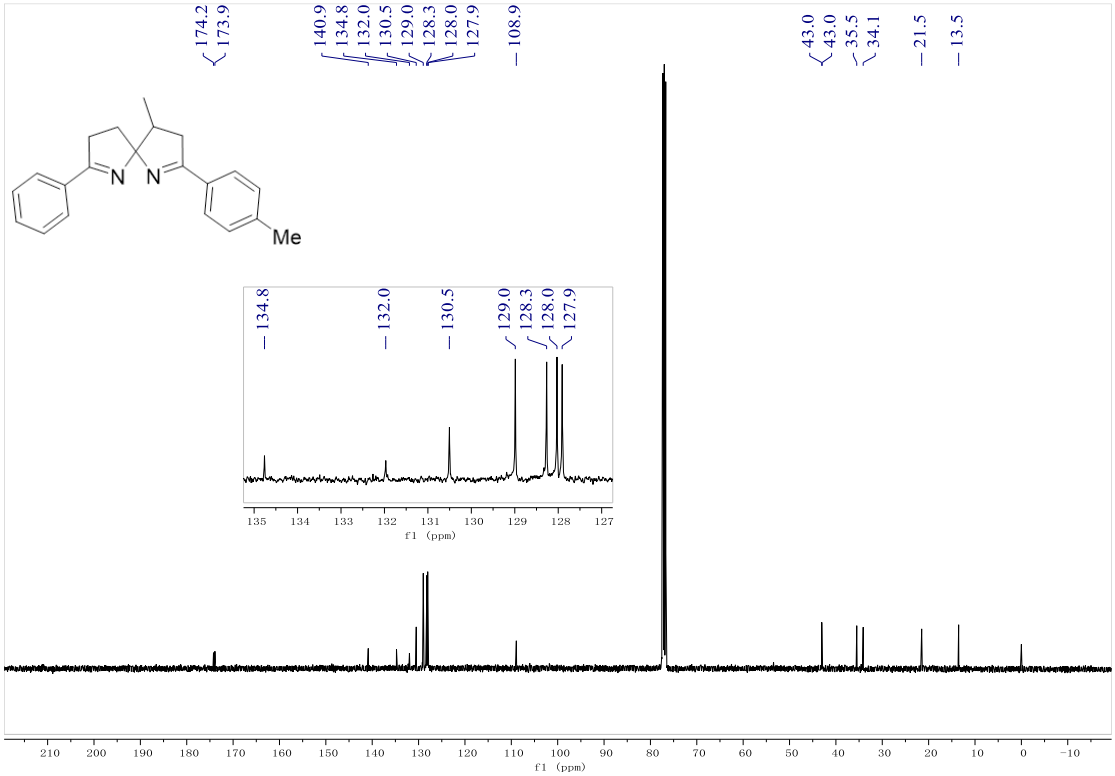
^{13}C NMR spectrum of **3ka**



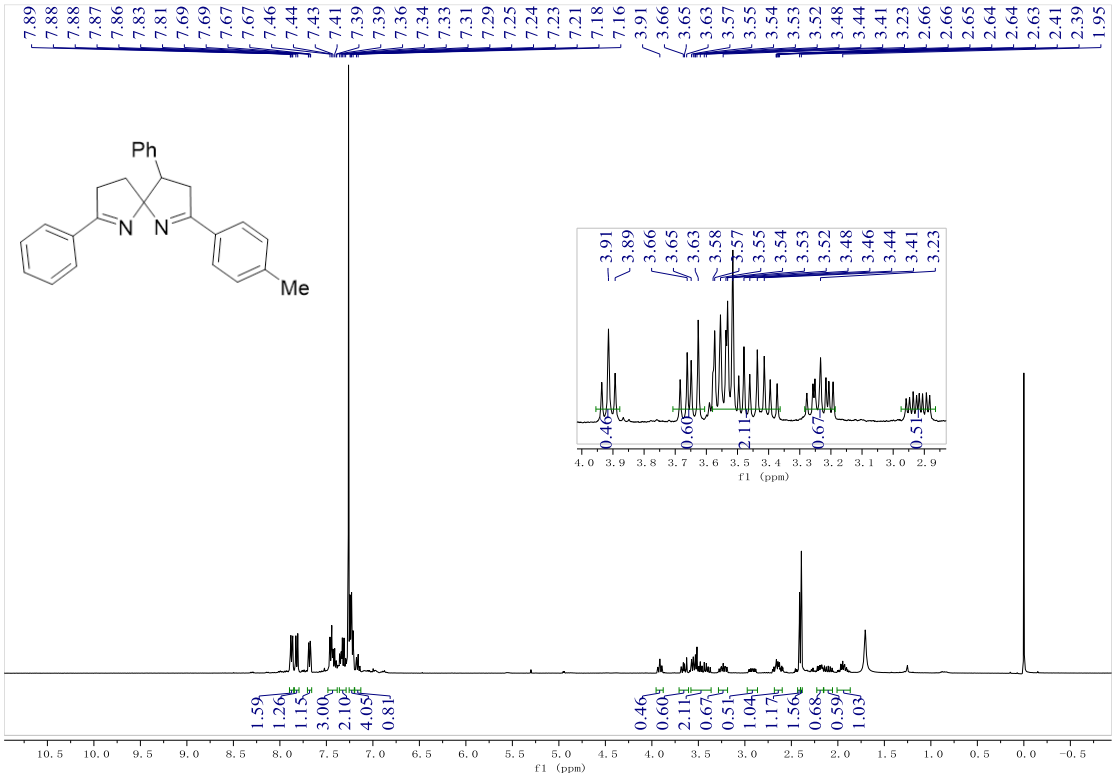
^{1}H NMR spectrum of **3la**



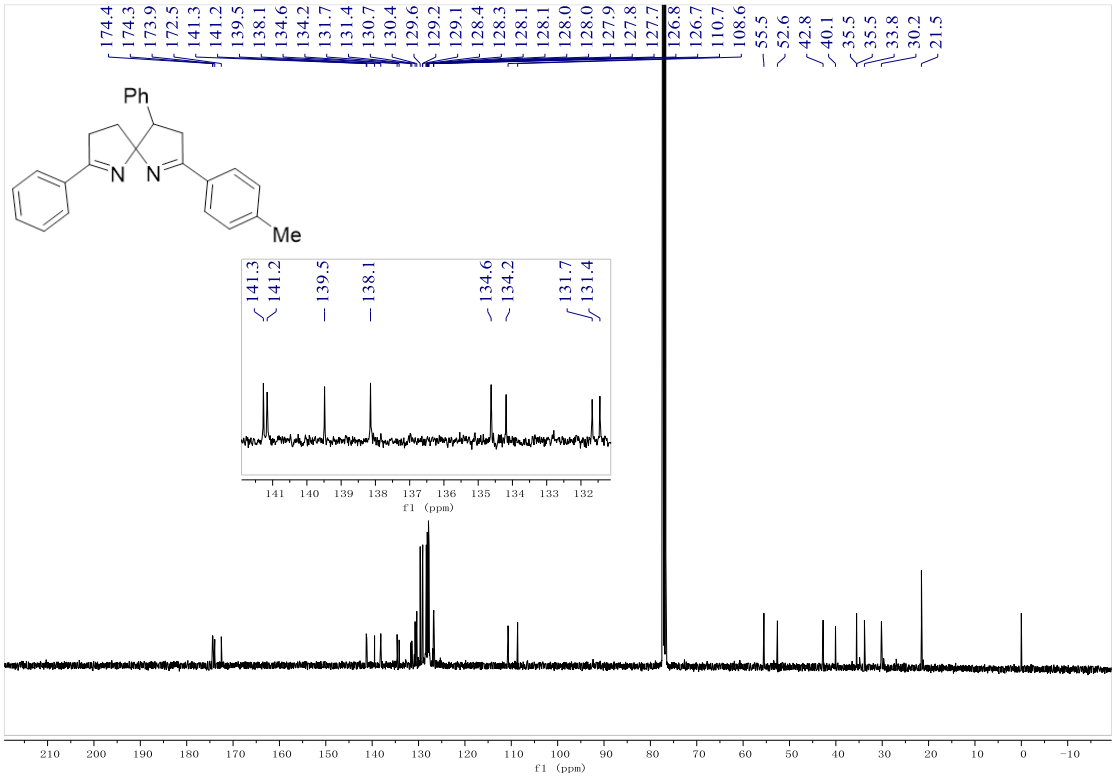
^{13}C NMR spectrum of **3la**



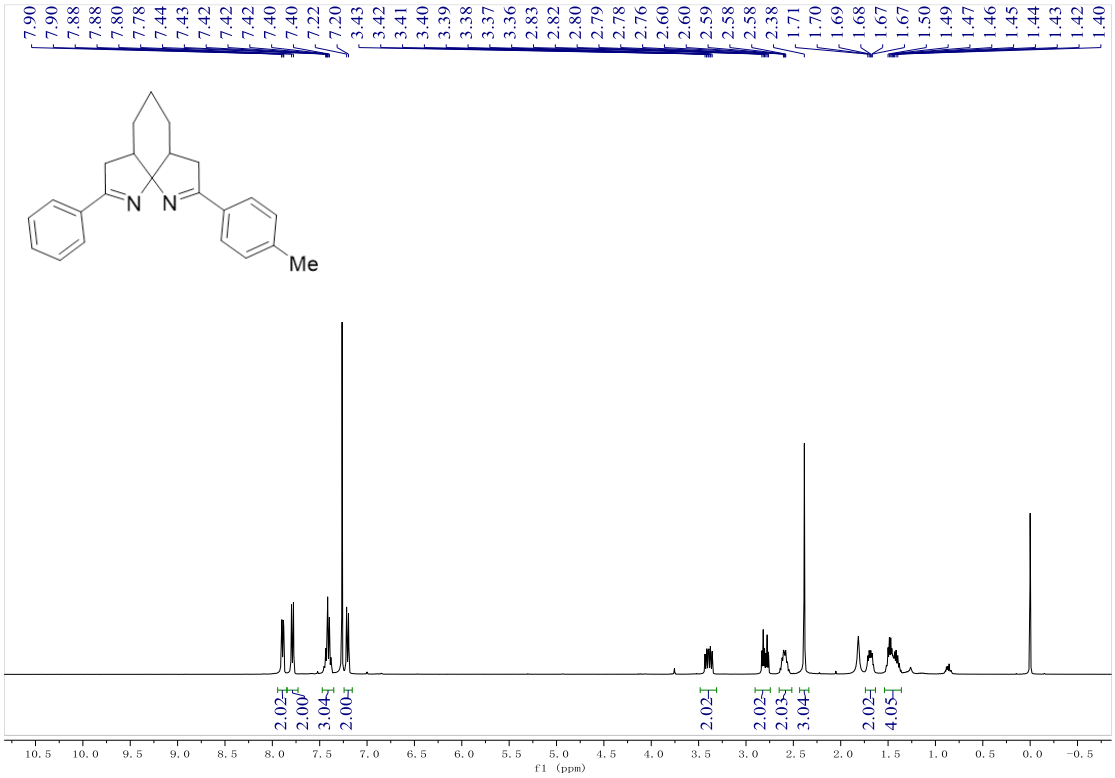
^{1}H NMR spectrum of **3ma**



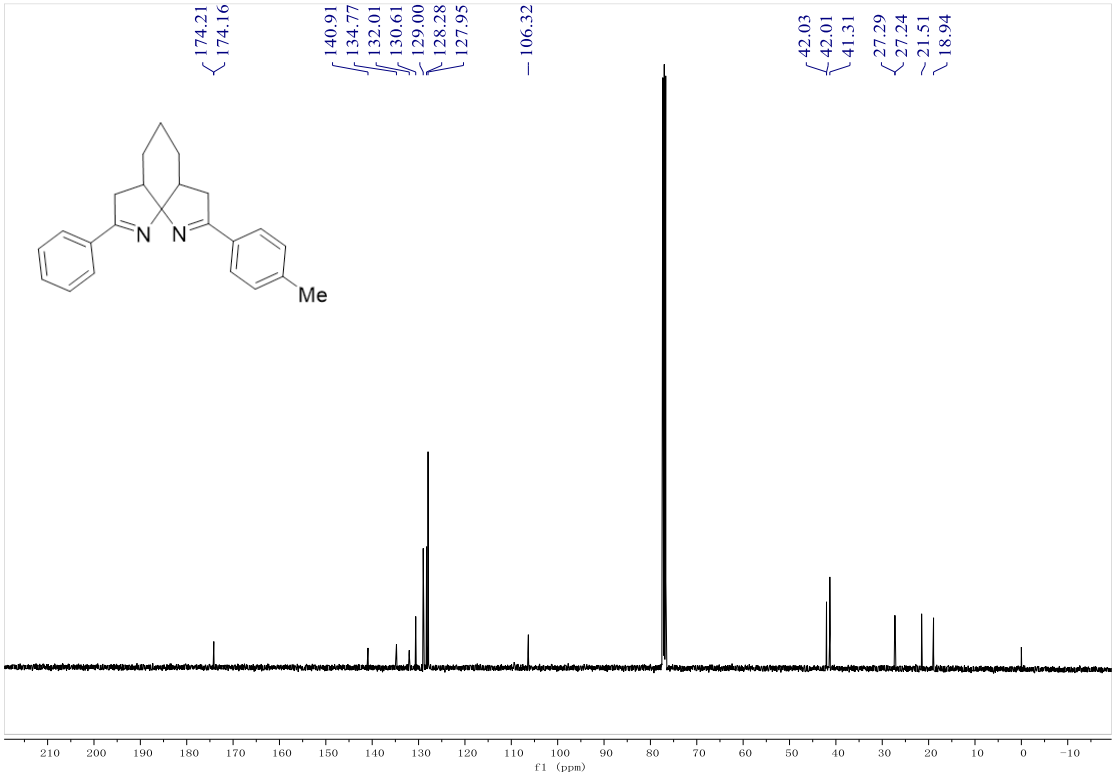
^{13}C NMR spectrum of **3ma**



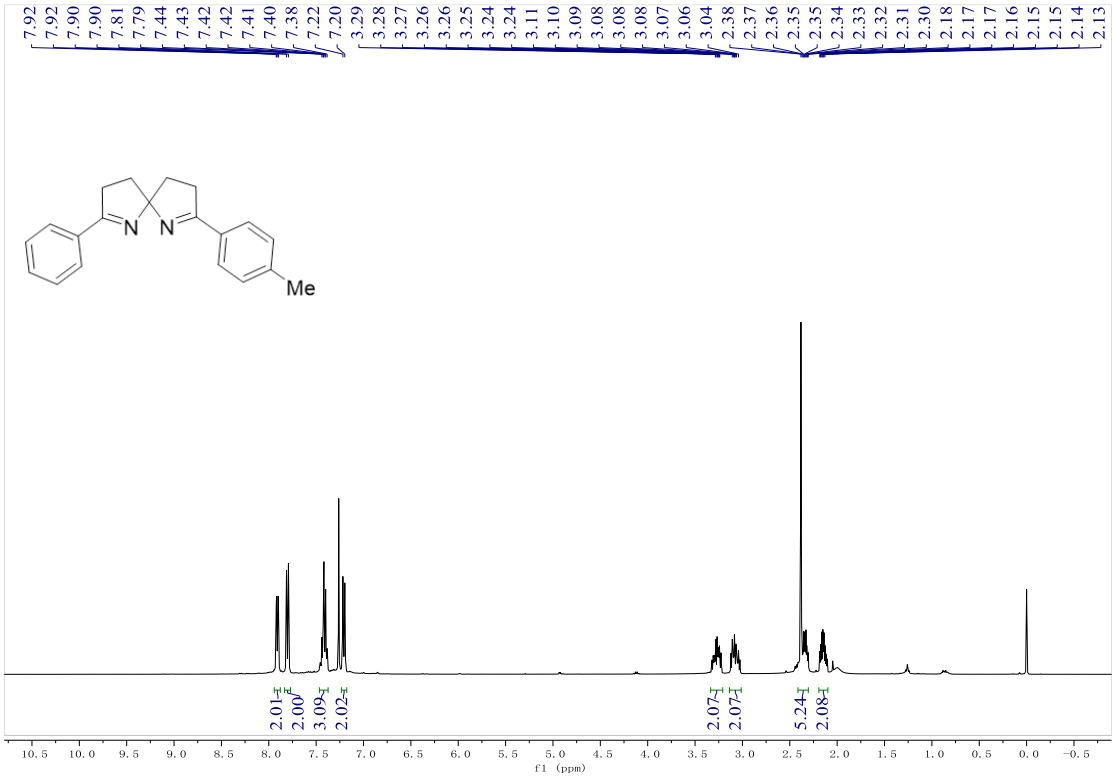
^{1}H NMR spectrum of **3na**



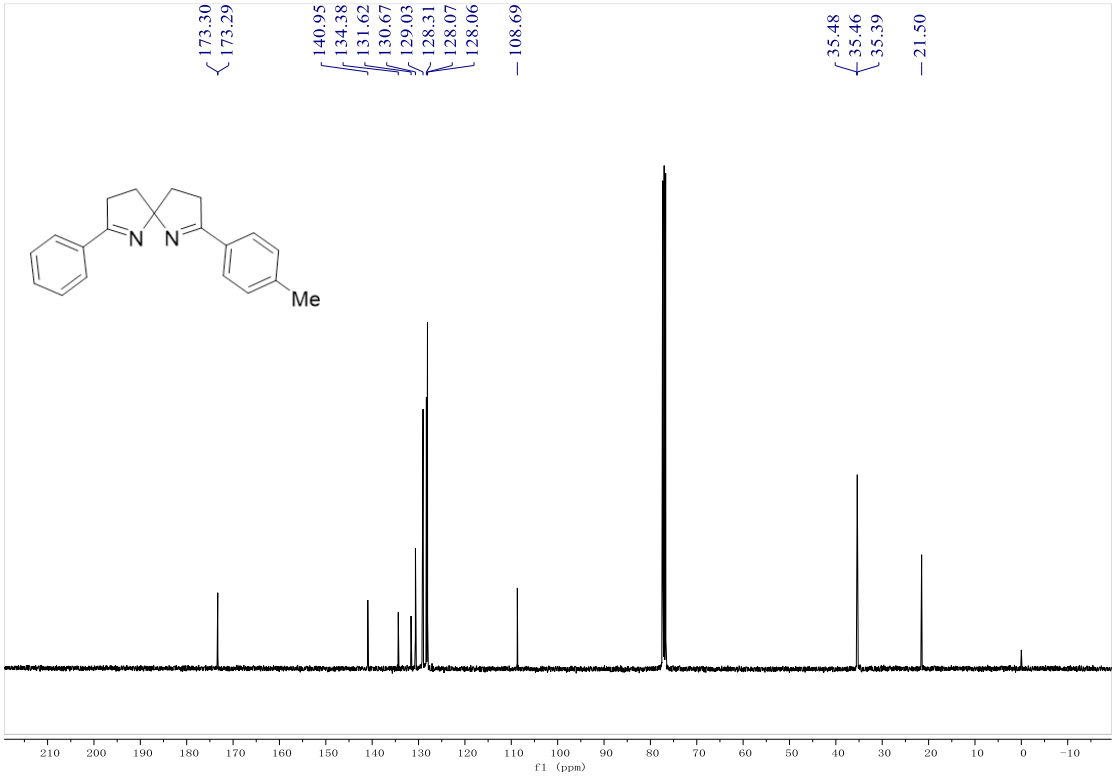
^{13}C NMR spectrum of **3na**



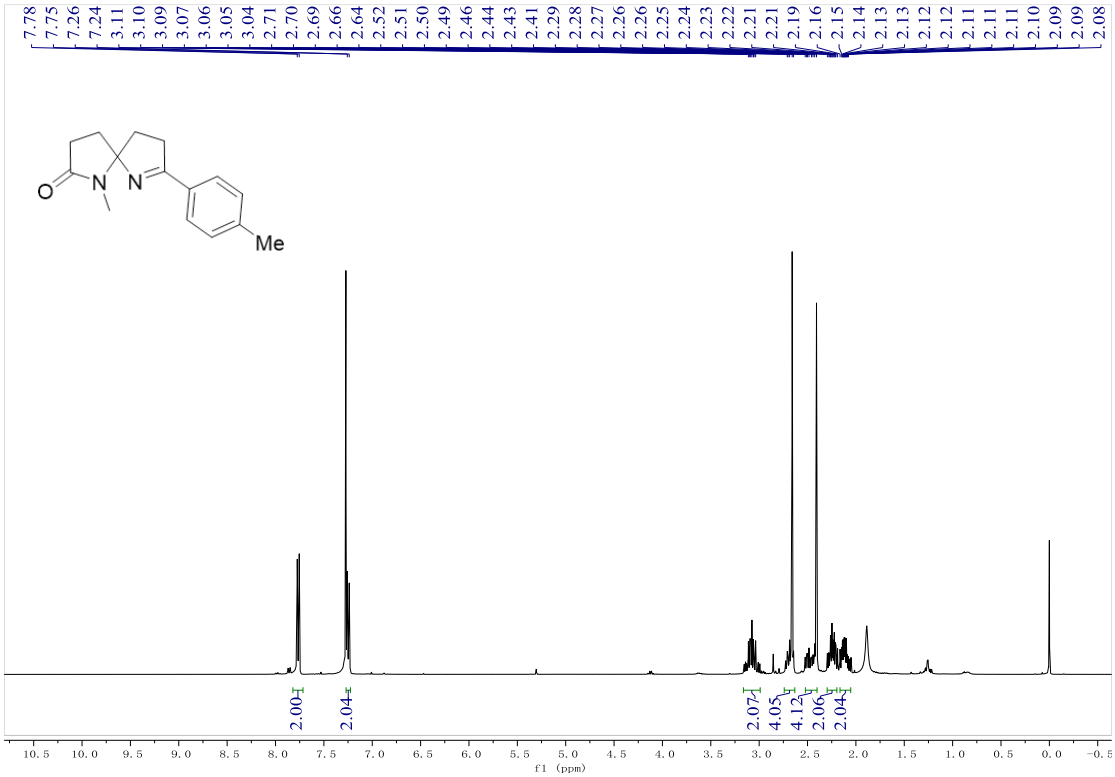
^{1}H NMR spectrum of **3oa**



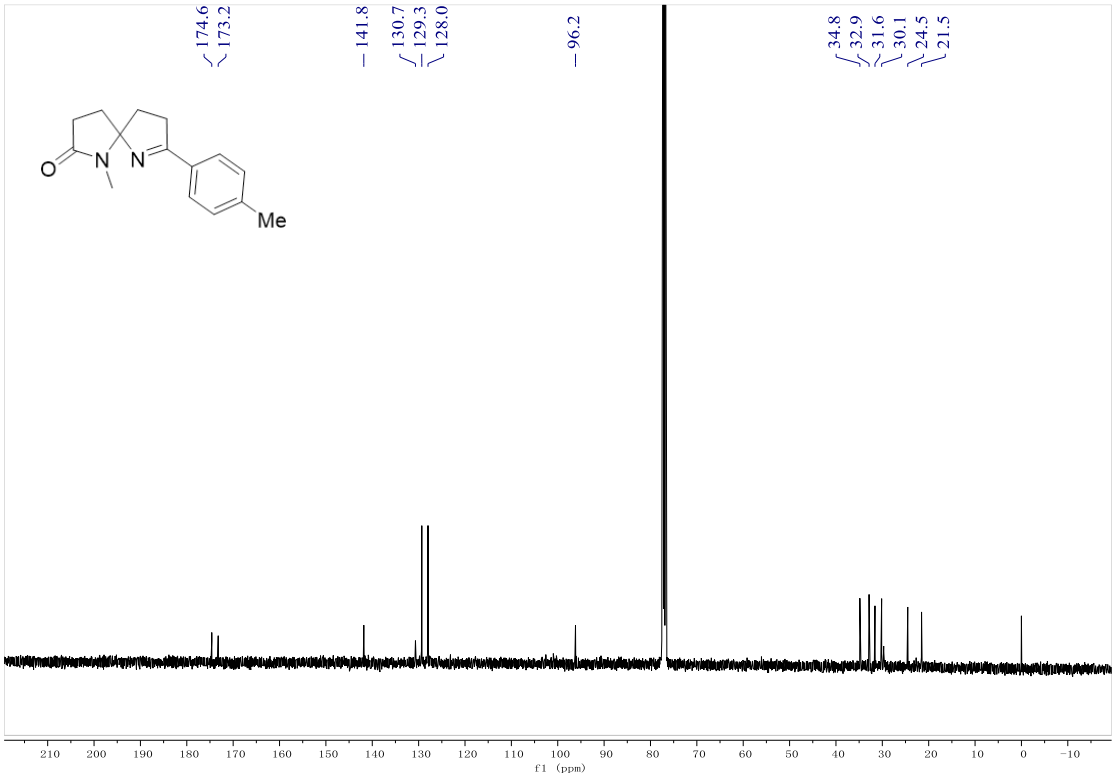
^{13}C NMR spectrum of **3oa**



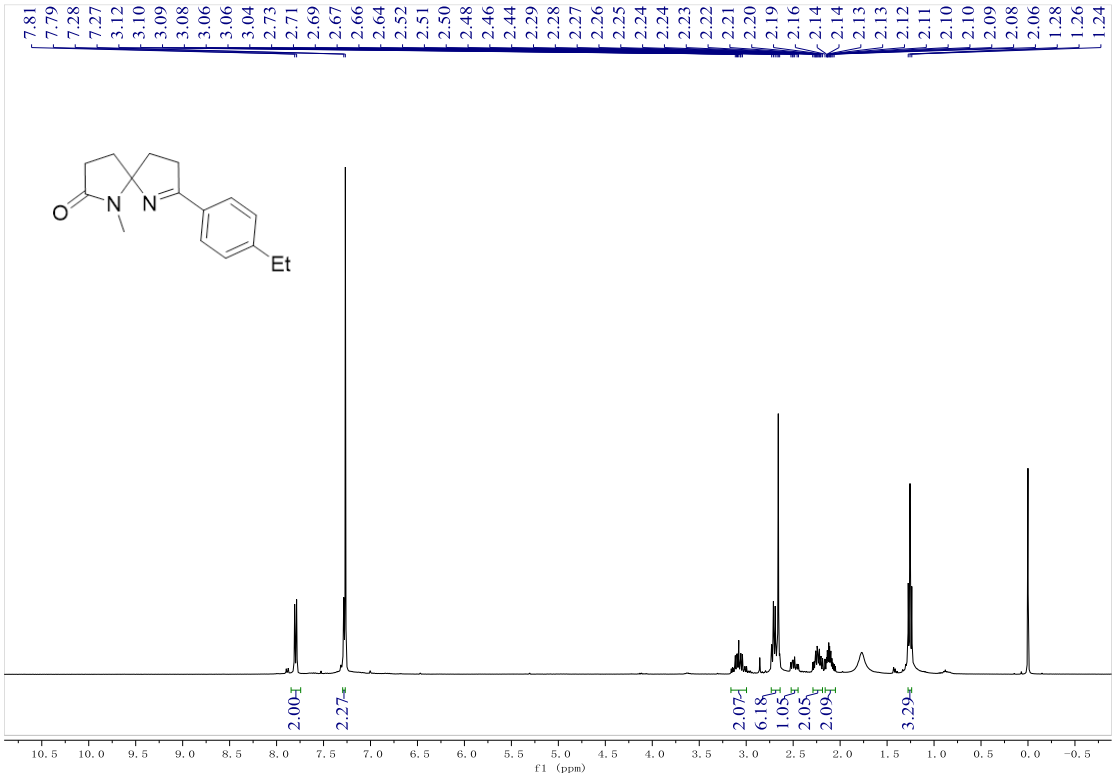
^{1}H NMR spectrum of **5aa**



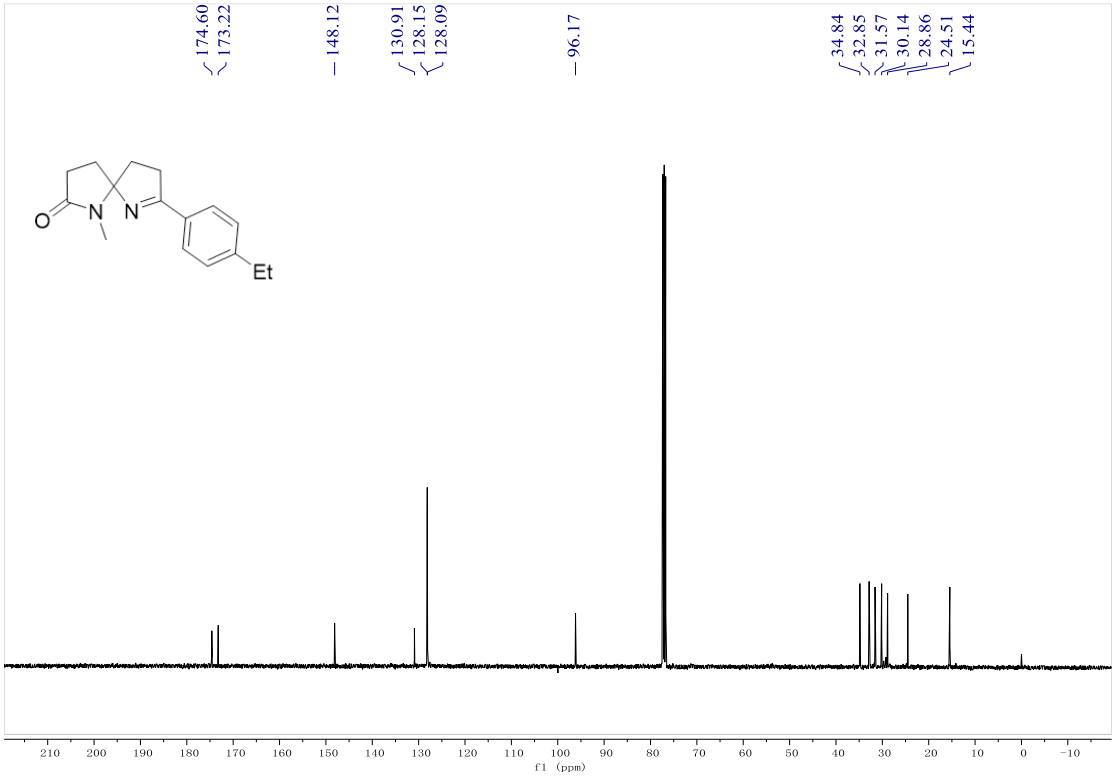
^{13}C NMR spectrum of **5aa**



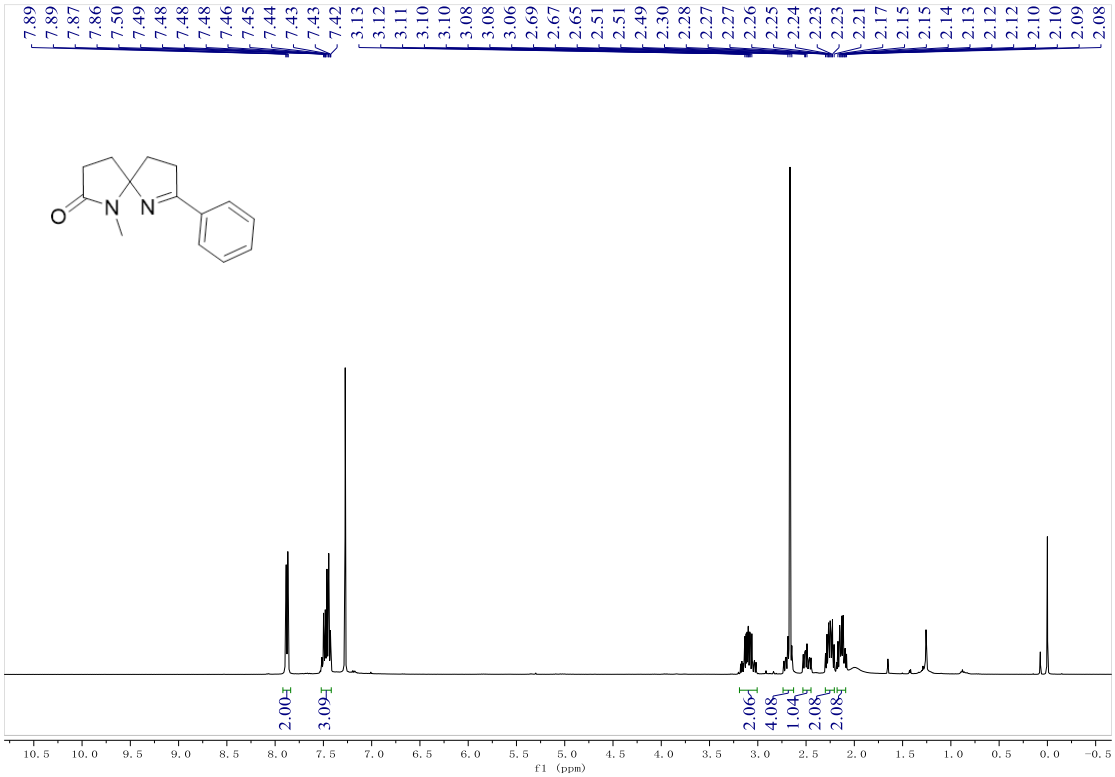
^{1}H NMR spectrum of **5ab**



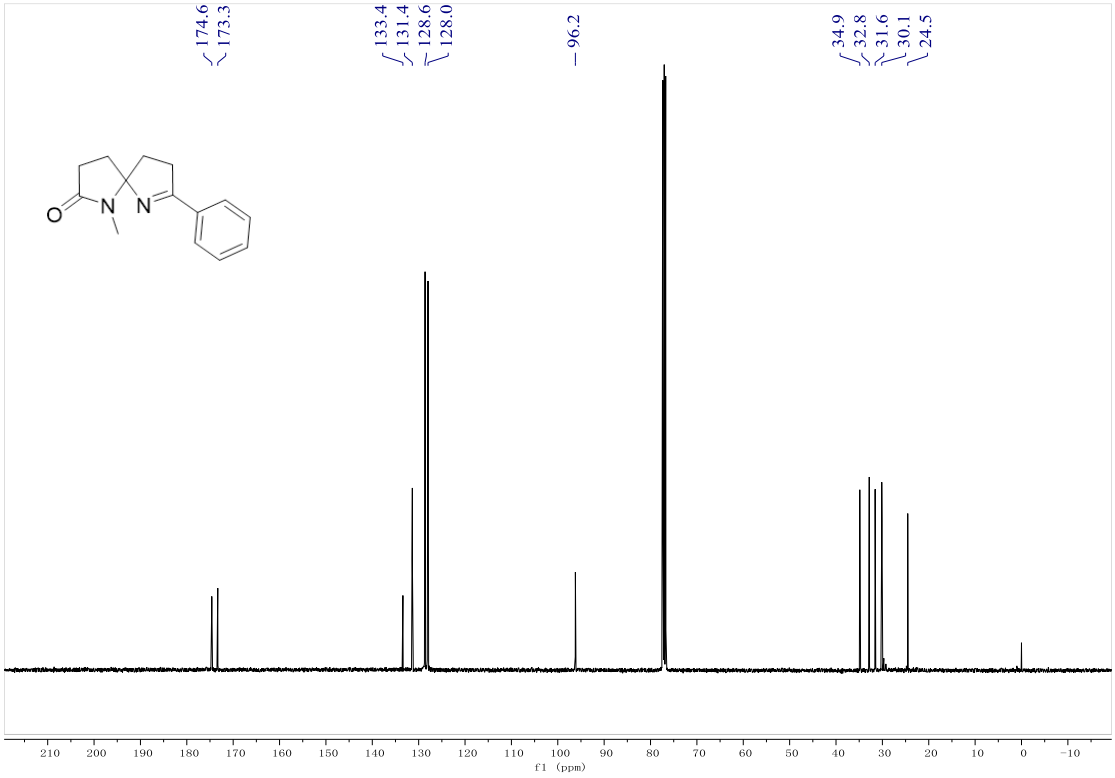
^{13}C NMR spectrum of **5ab**



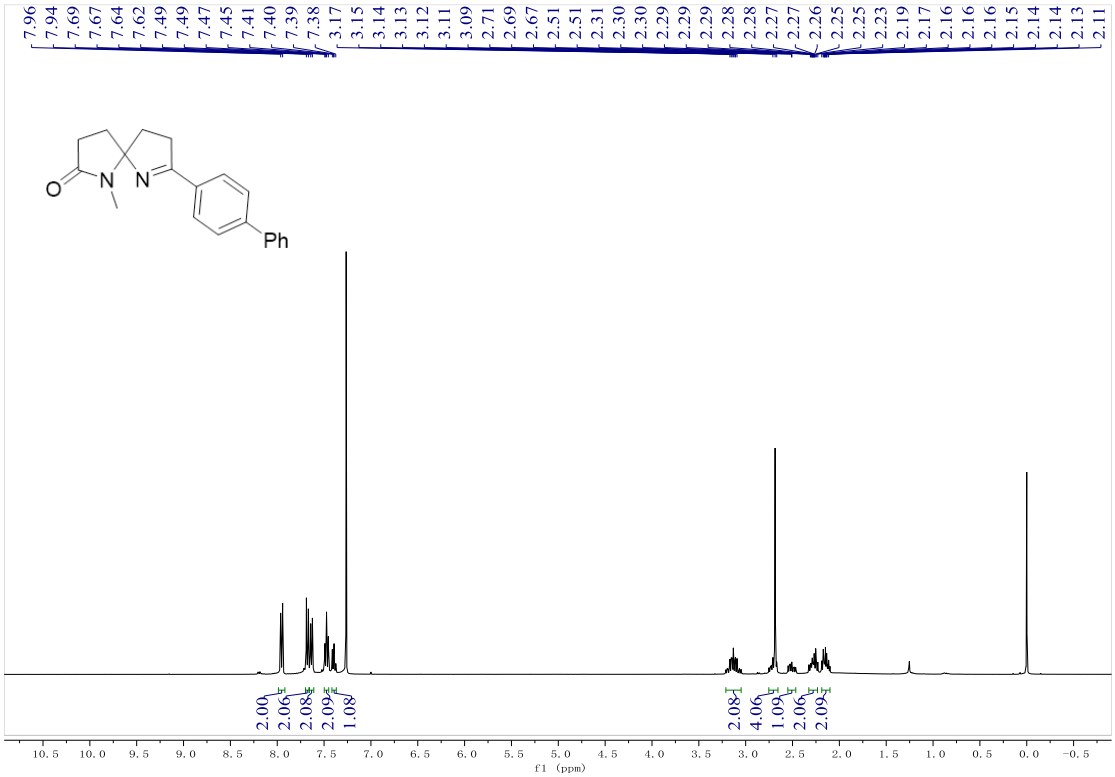
^{1}H NMR spectrum of **5af**



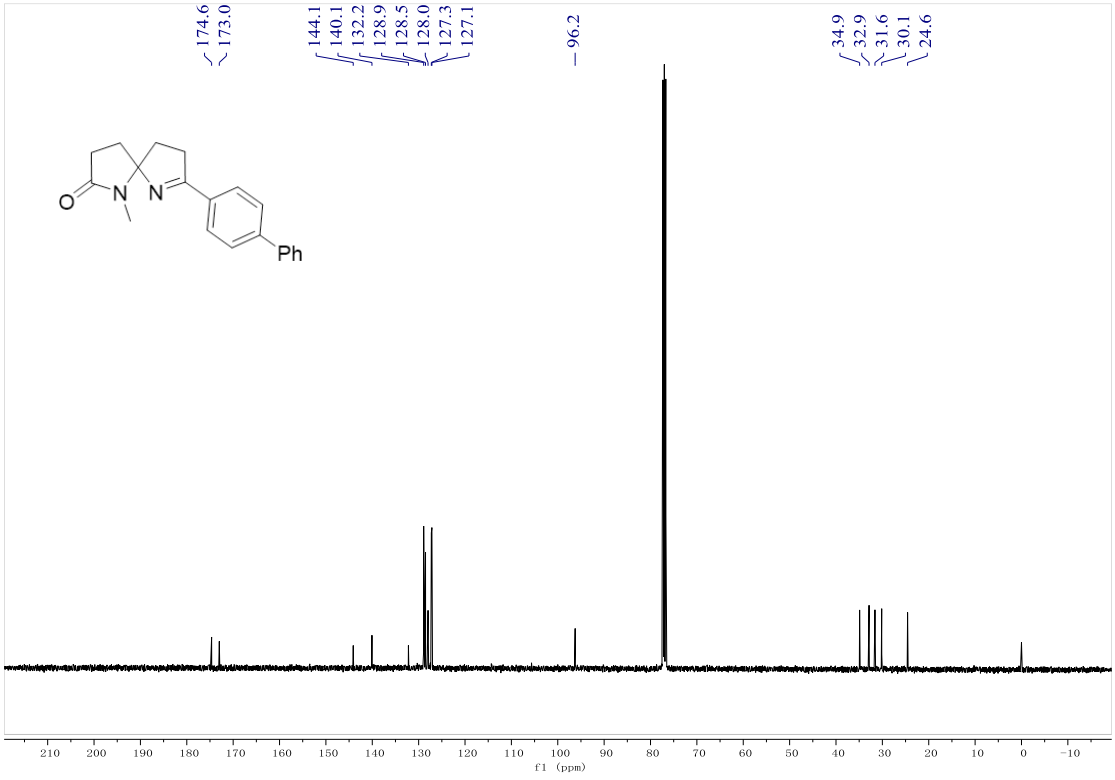
^{13}C NMR spectrum of **5af**



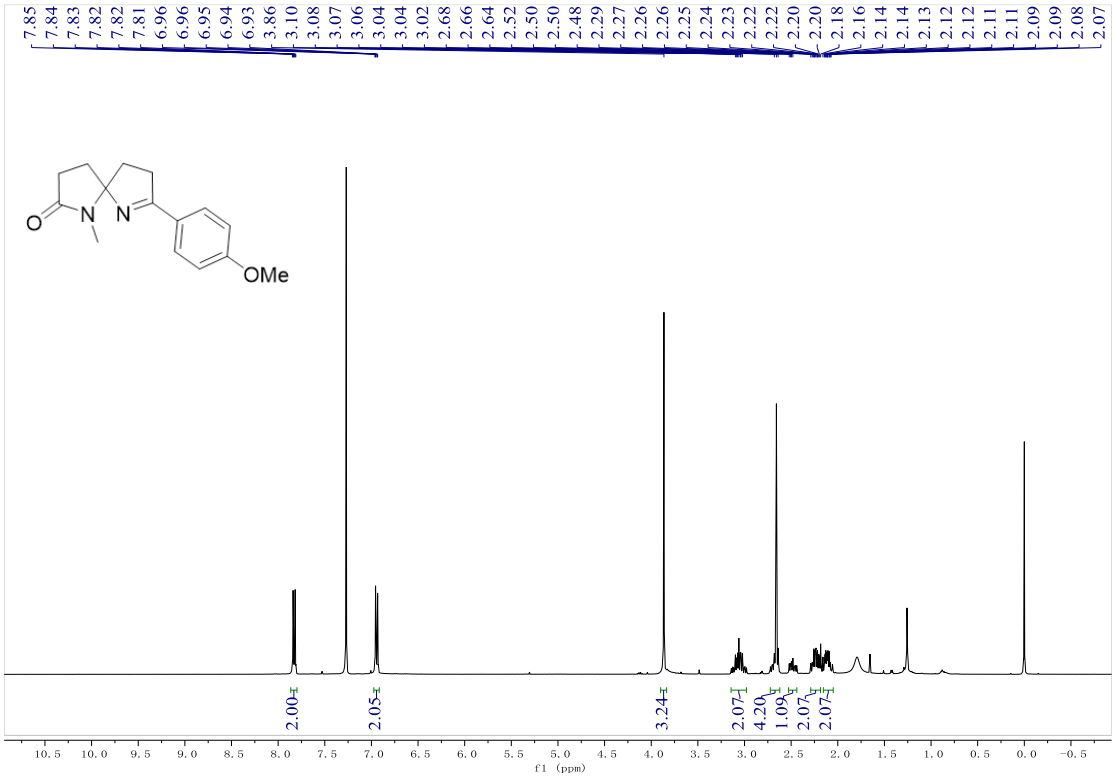
^{1}H NMR spectrum of **5ag**



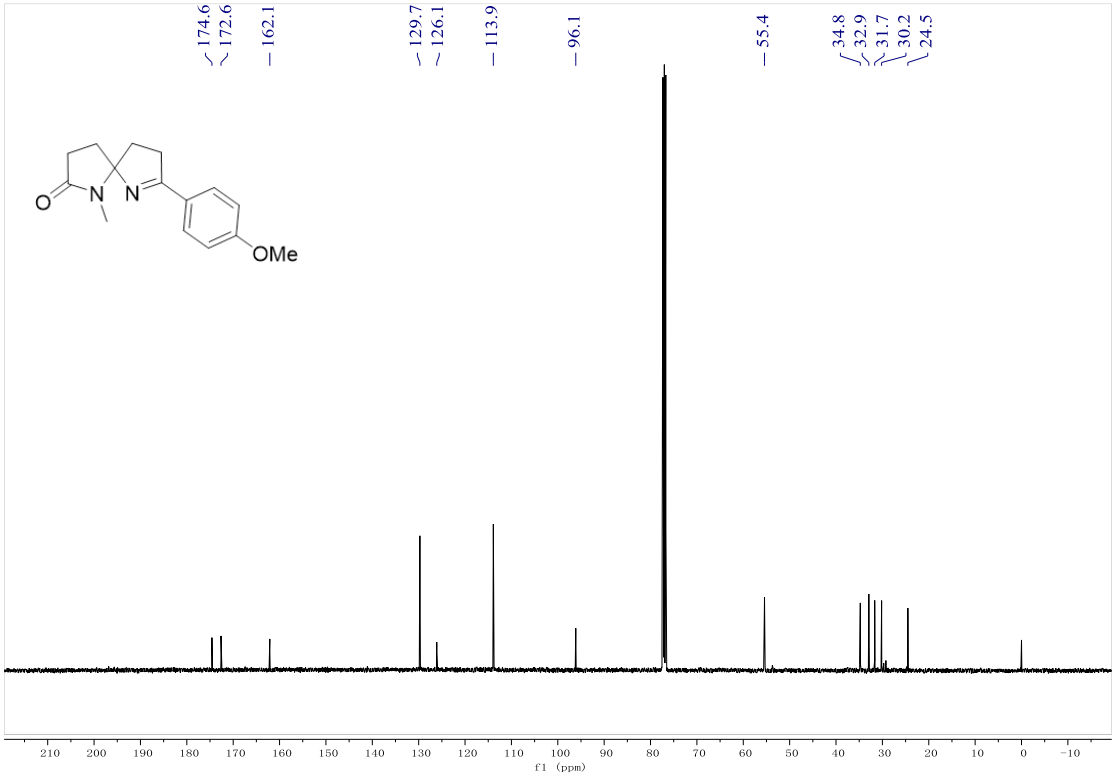
^{13}C NMR spectrum of **5ag**



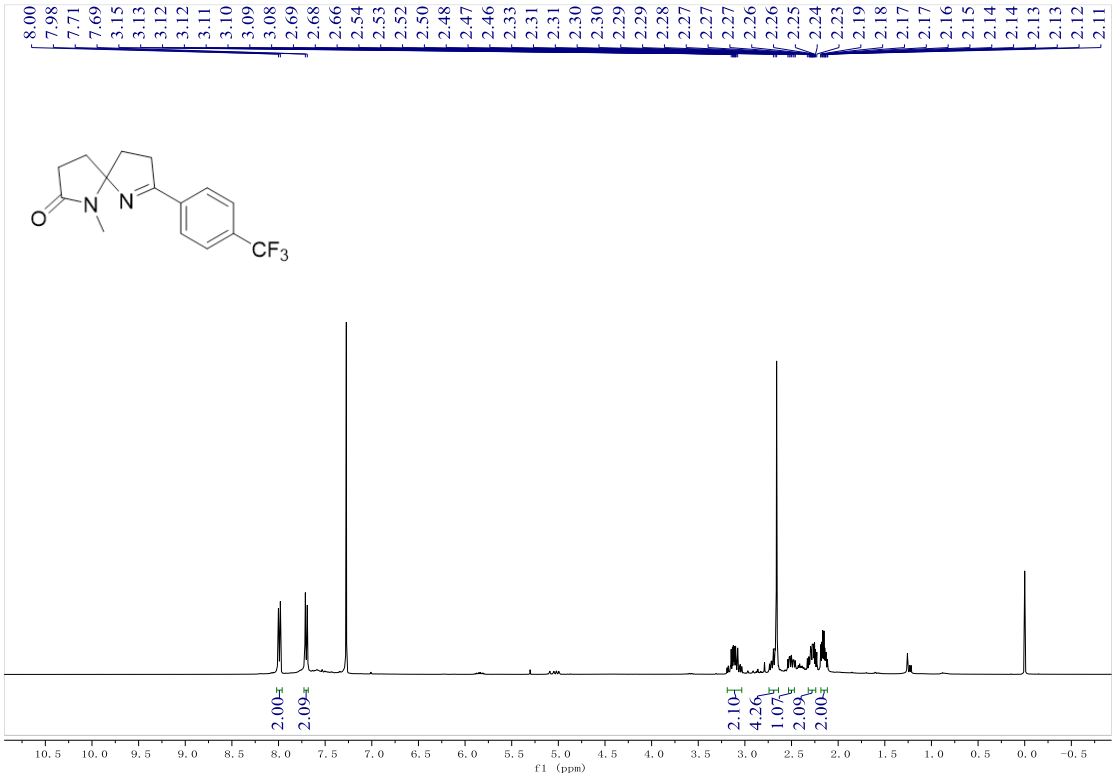
^{1}H NMR spectrum of **5ah**



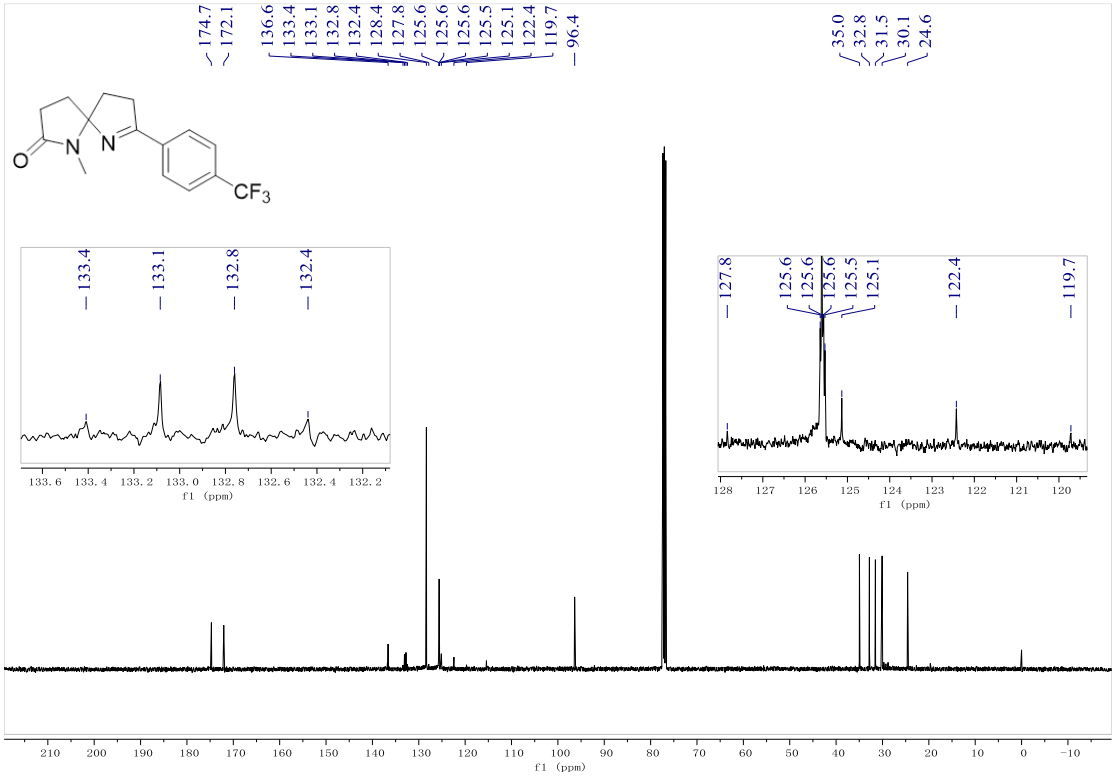
^{13}C NMR spectrum of **5ah**



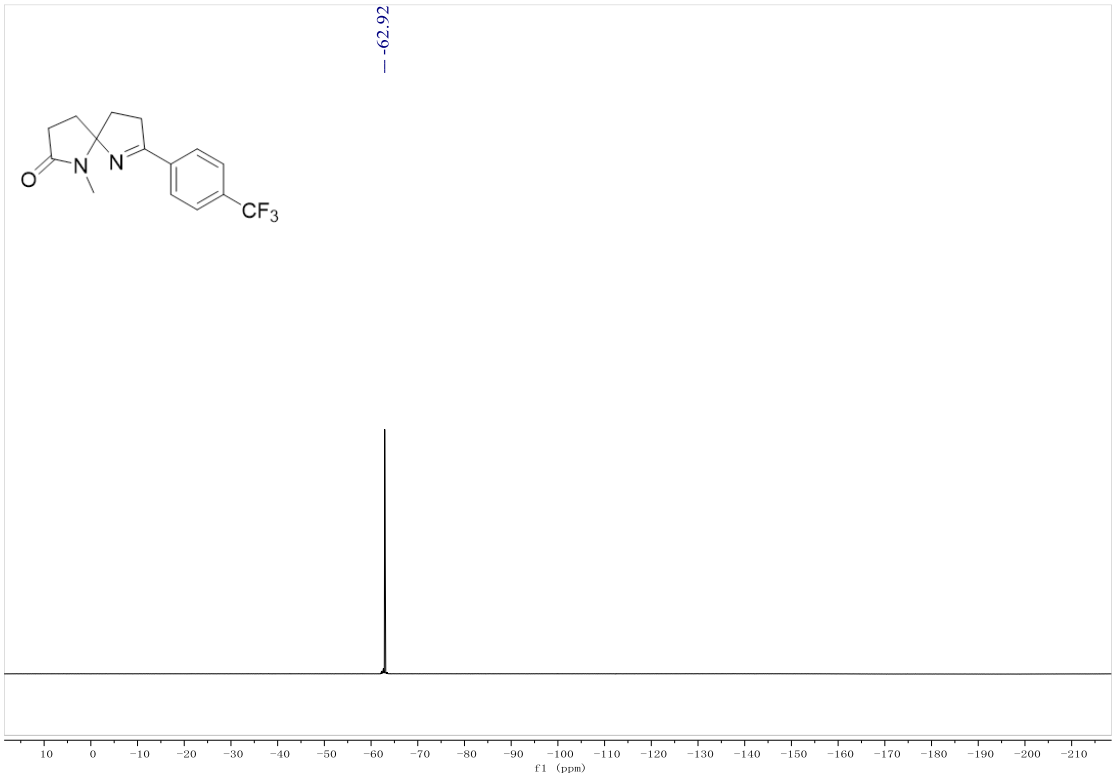
^{1}H NMR spectrum of **5ai**



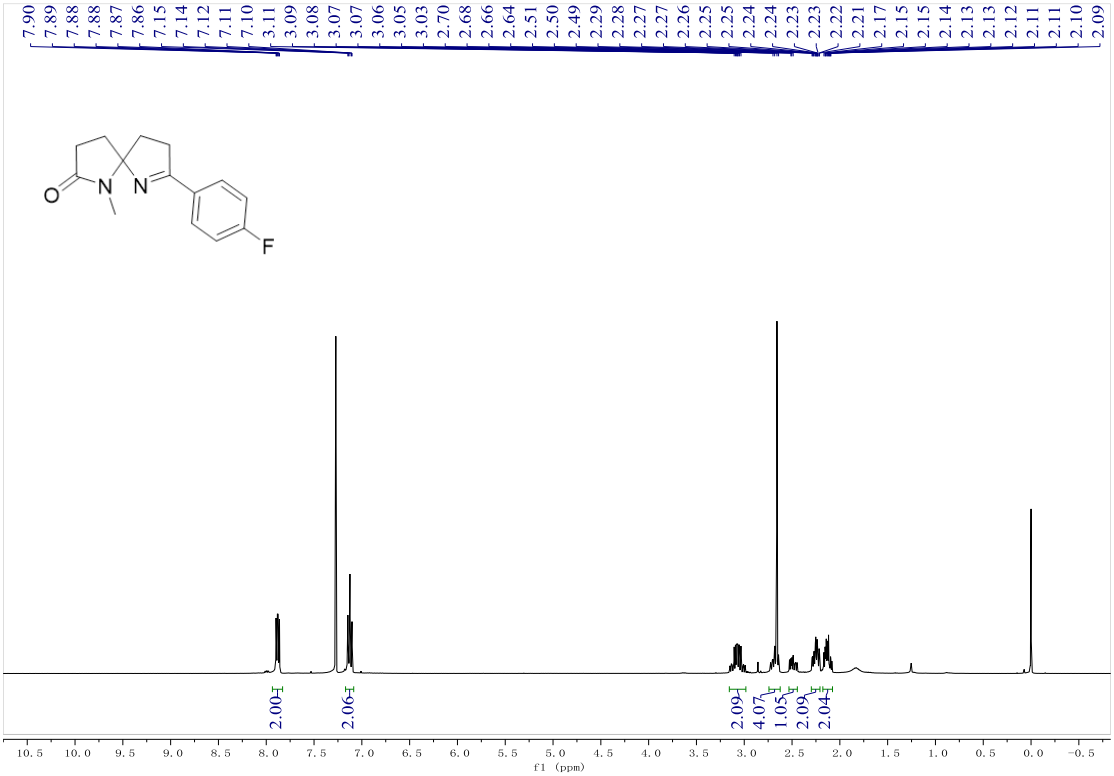
^{13}C NMR spectrum of **5ai**



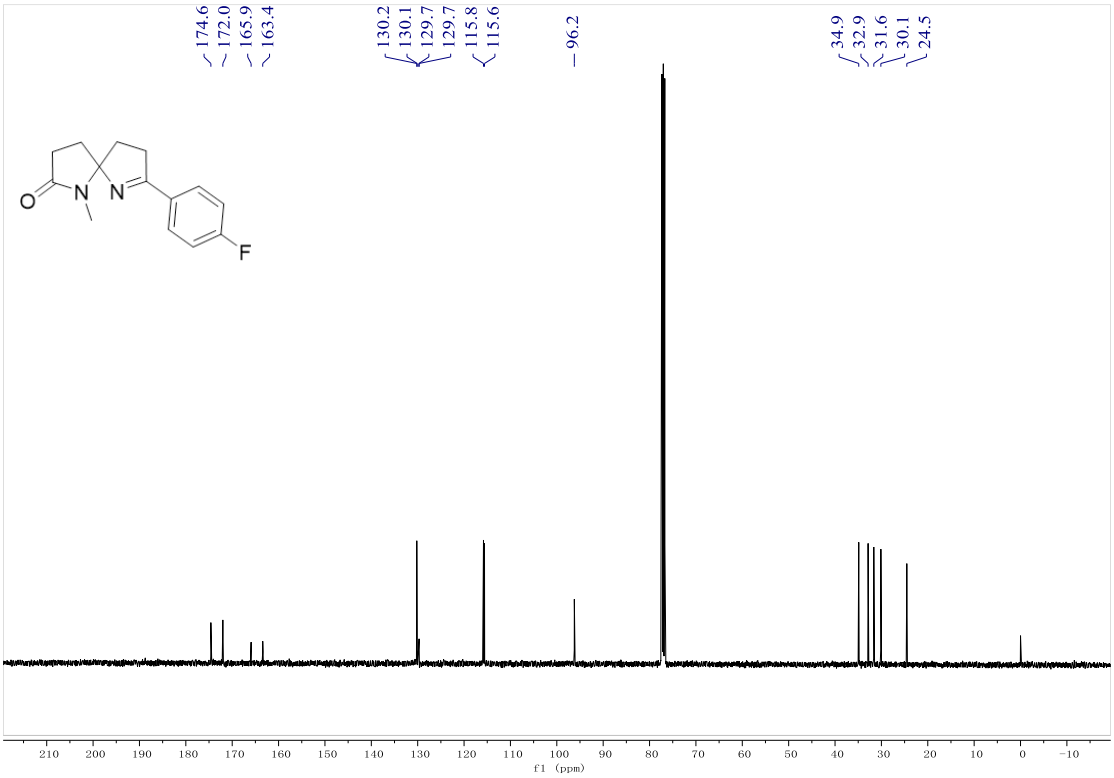
^{19}F NMR spectrum of **5ai**



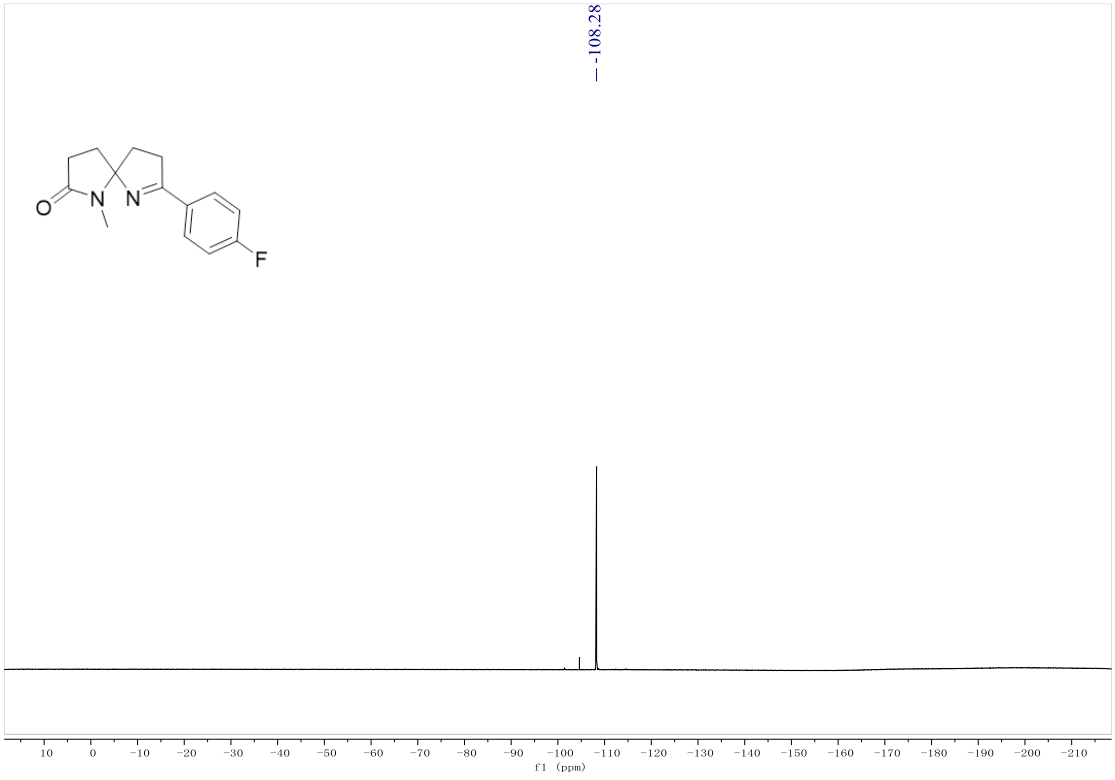
^{1}H NMR spectrum of **5aj**



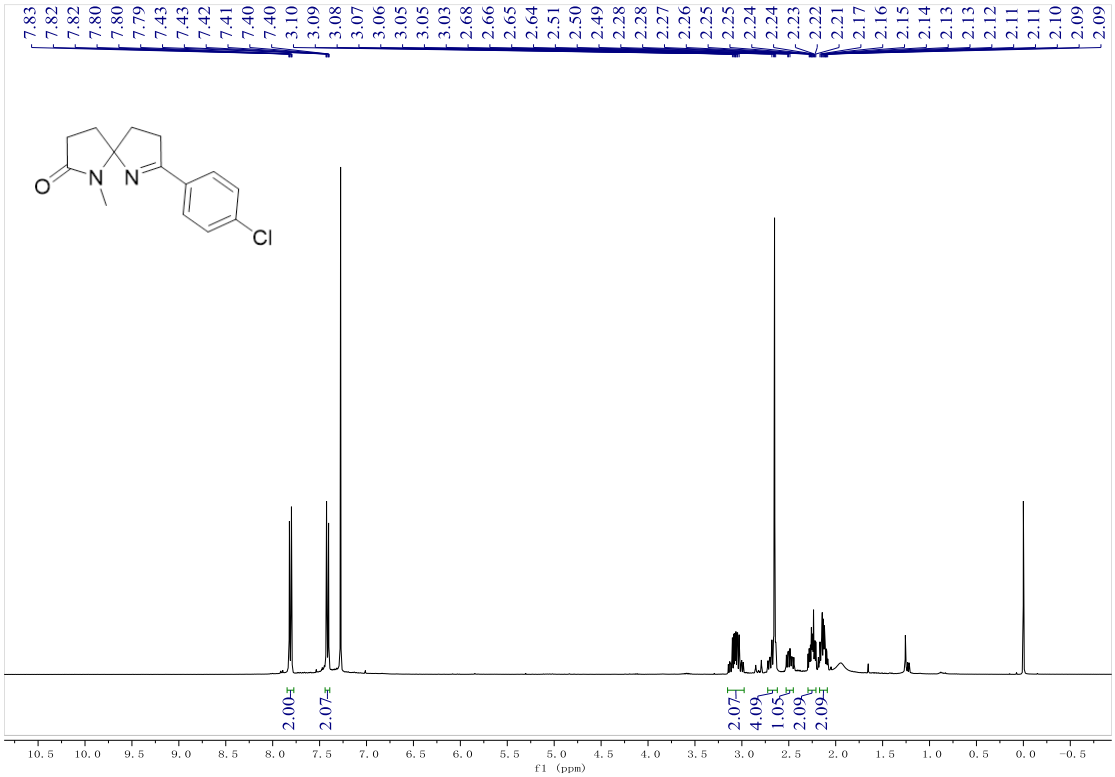
^{13}C NMR spectrum of **5aj**



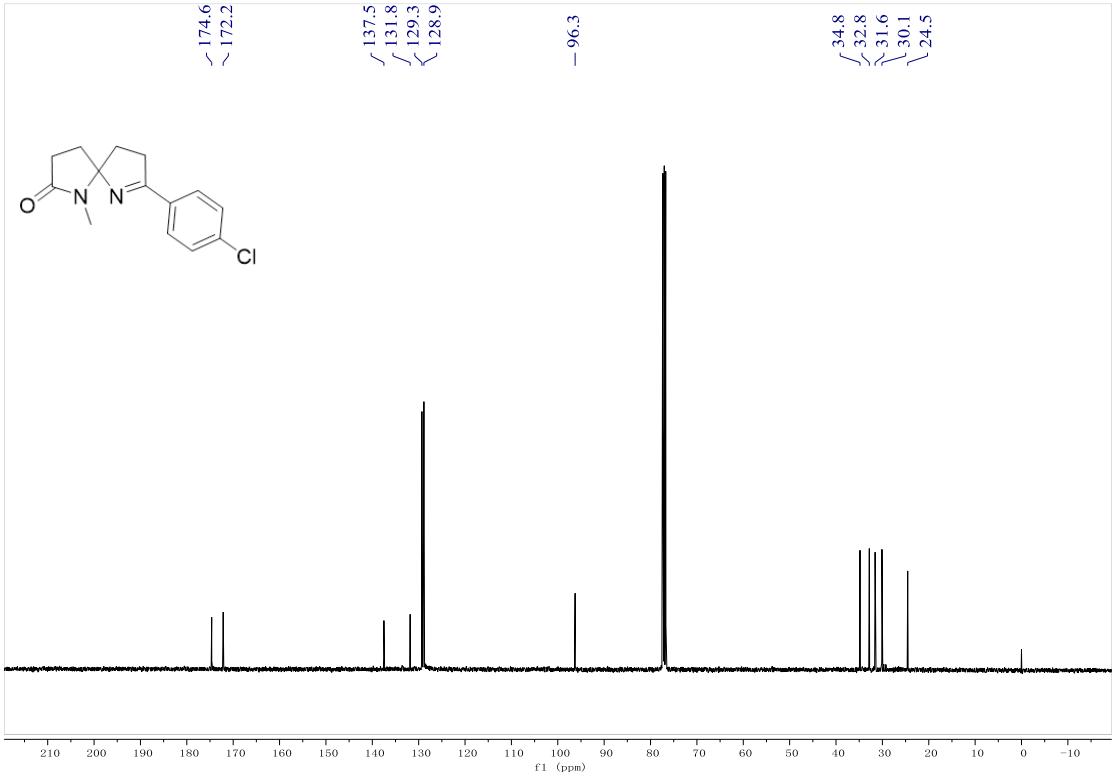
^{19}F NMR spectrum of **5aj**



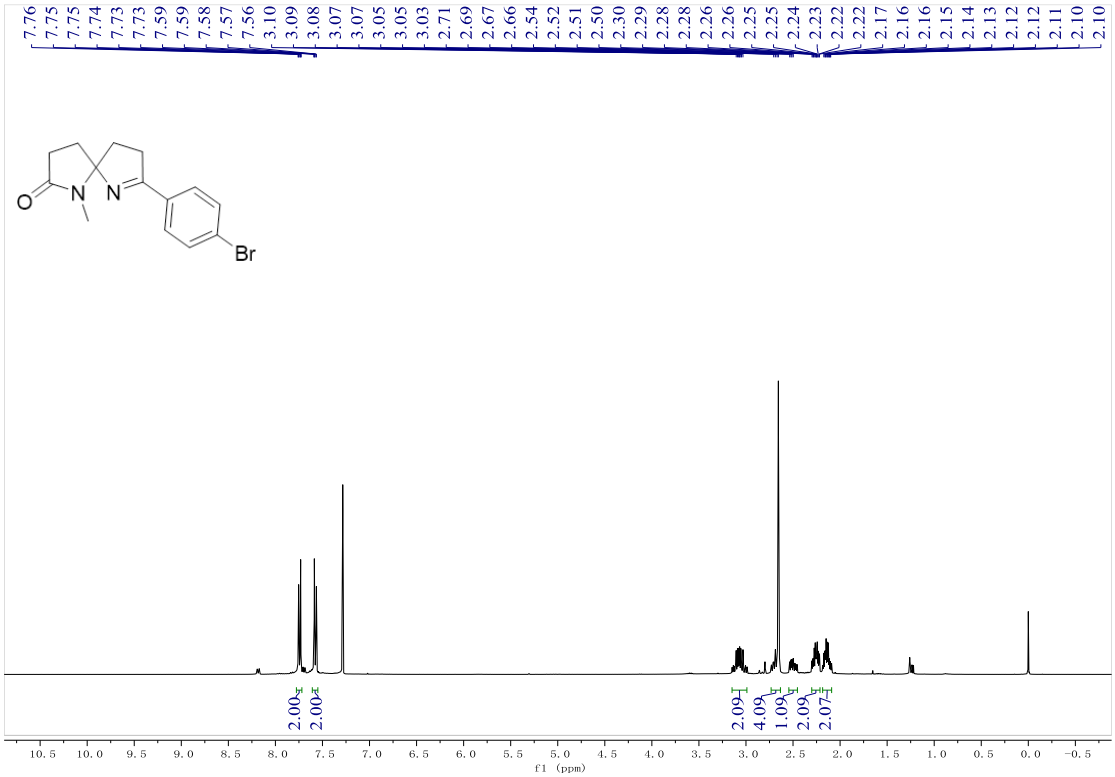
^{1}H NMR spectrum of **5ak**



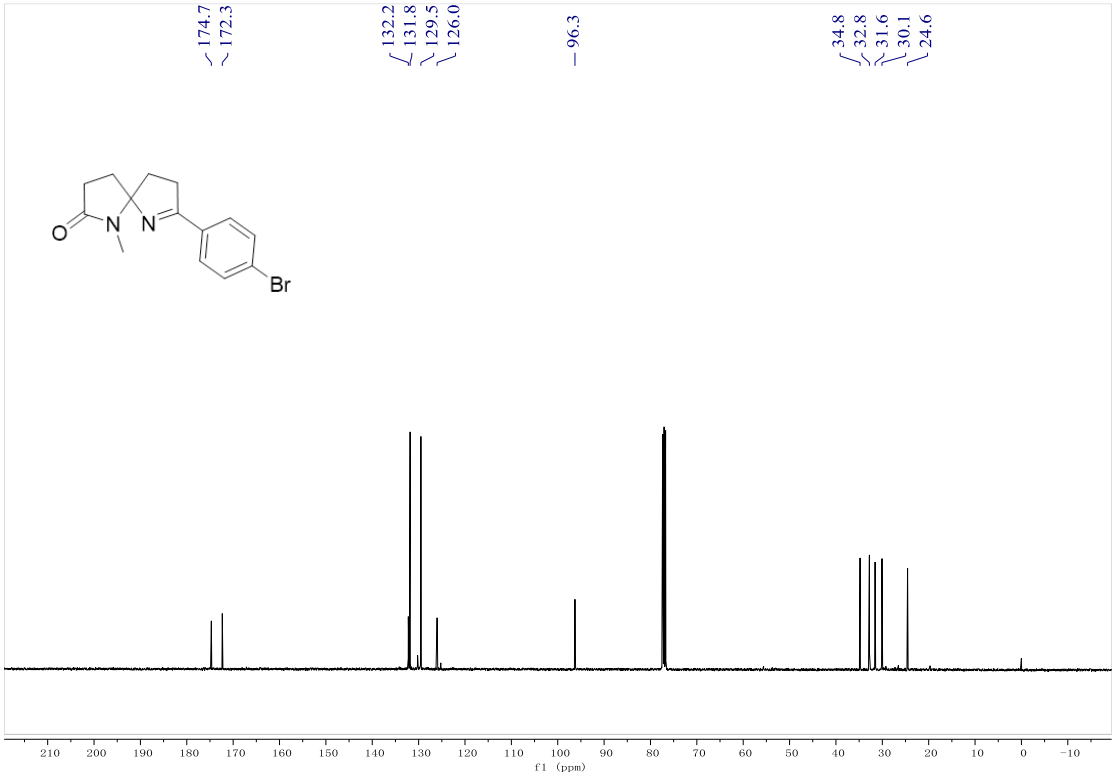
^{13}C NMR spectrum of **5ak**



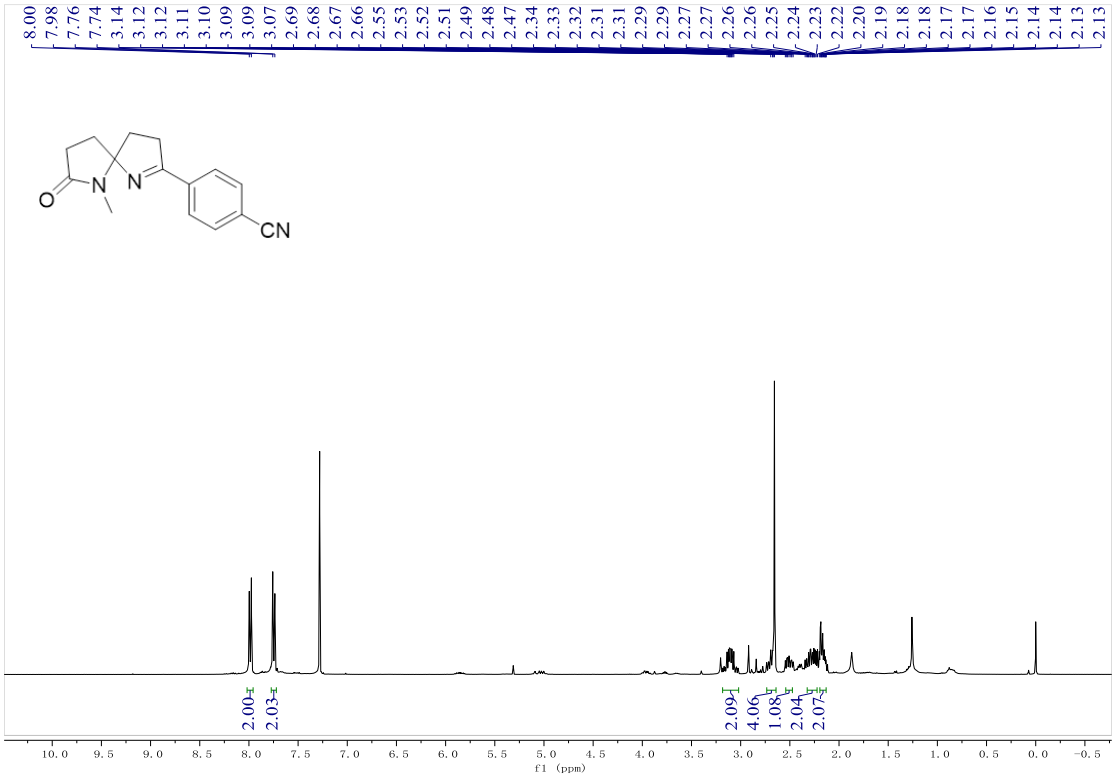
^{1}H NMR spectrum of **5al**



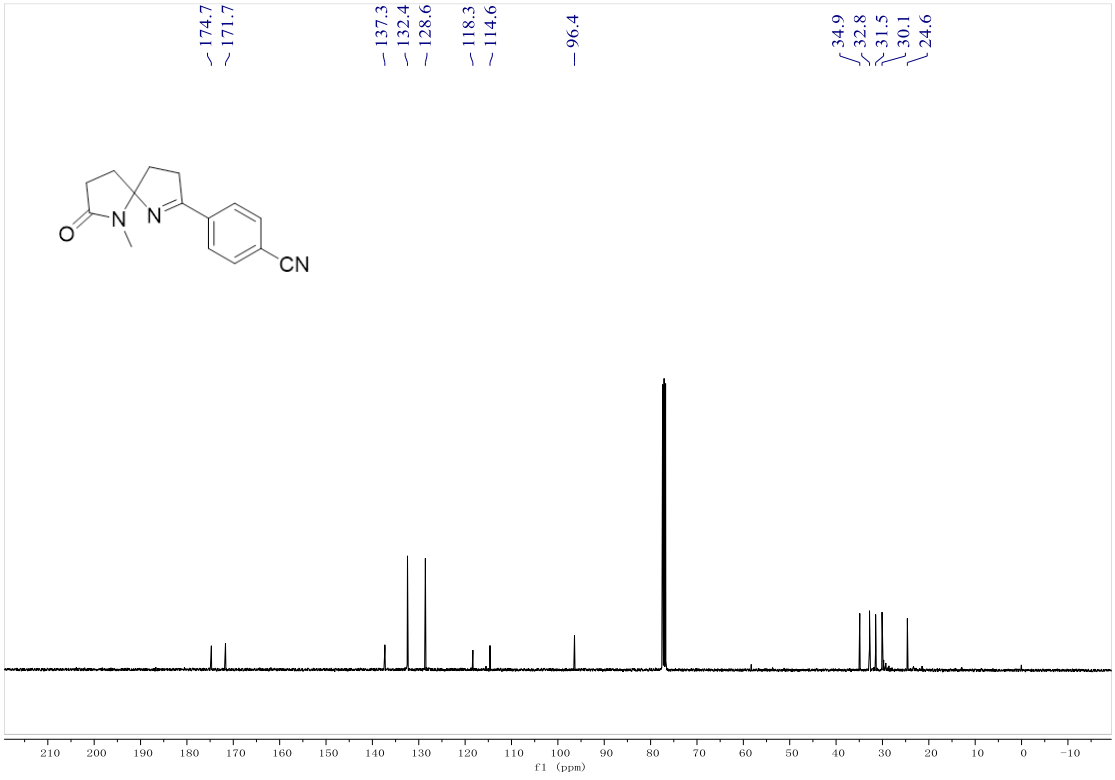
^{13}C NMR spectrum of **5al**



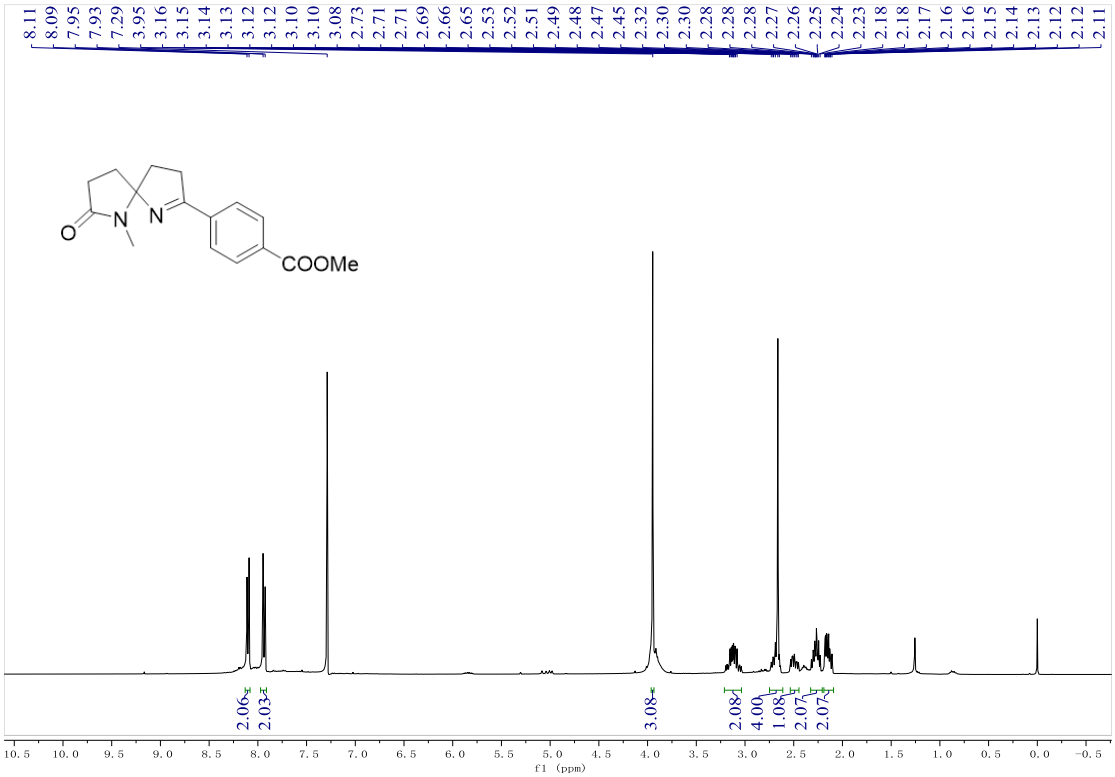
^{1}H NMR spectrum of **5au**



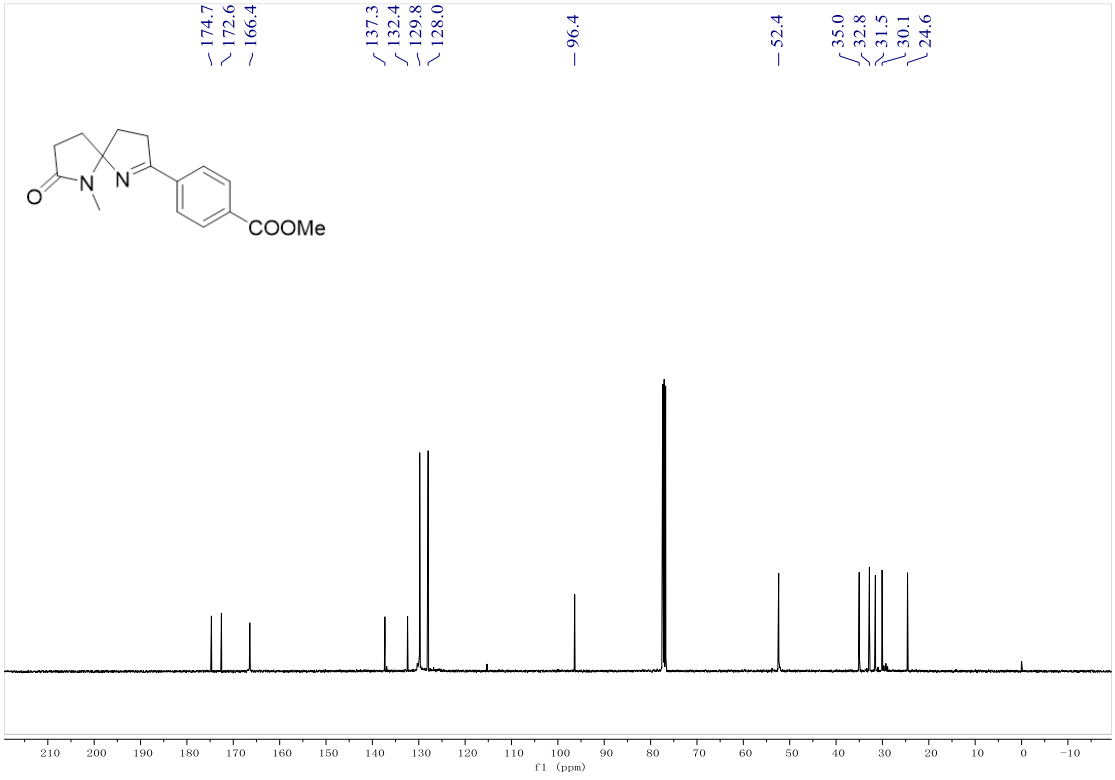
^{13}C NMR spectrum of **5au**



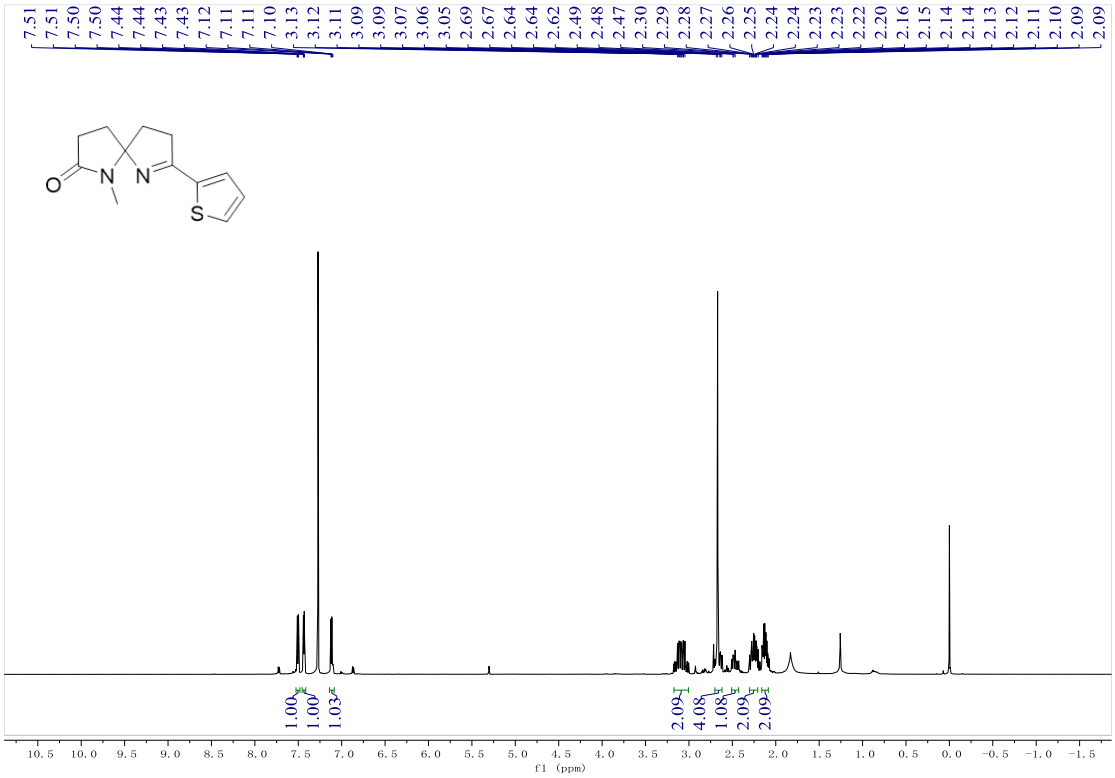
^{1}H NMR spectrum of **5av**



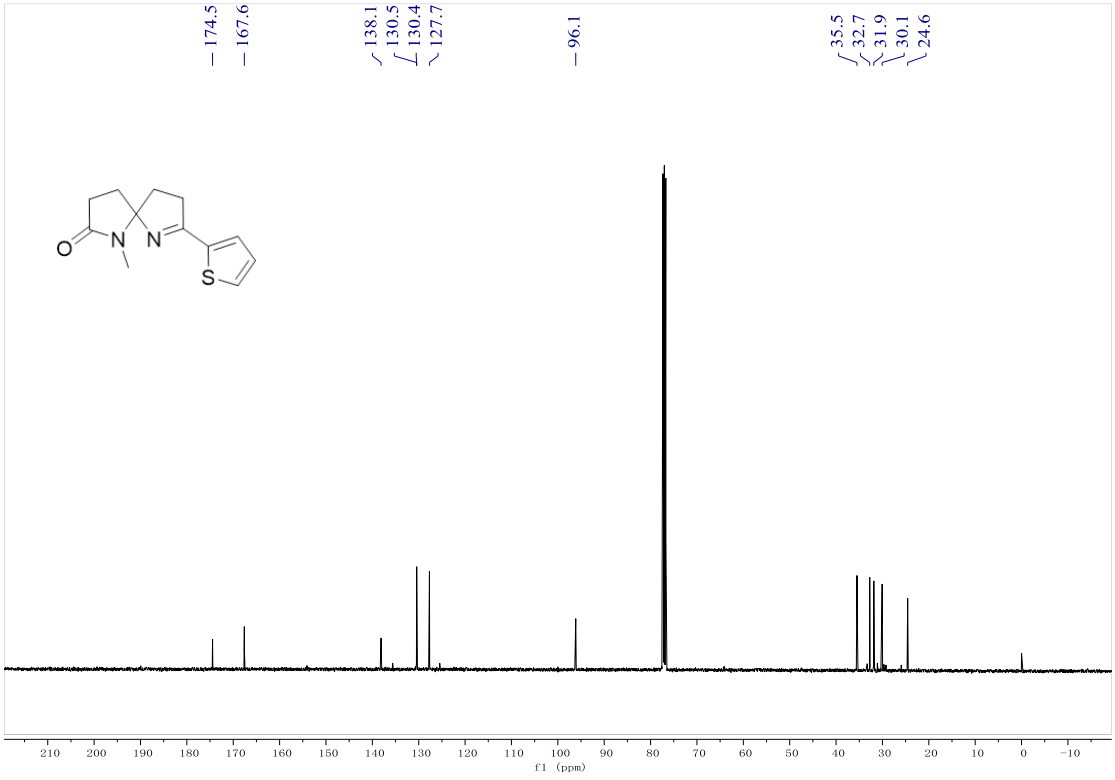
^{1}H NMR spectrum of **5av**



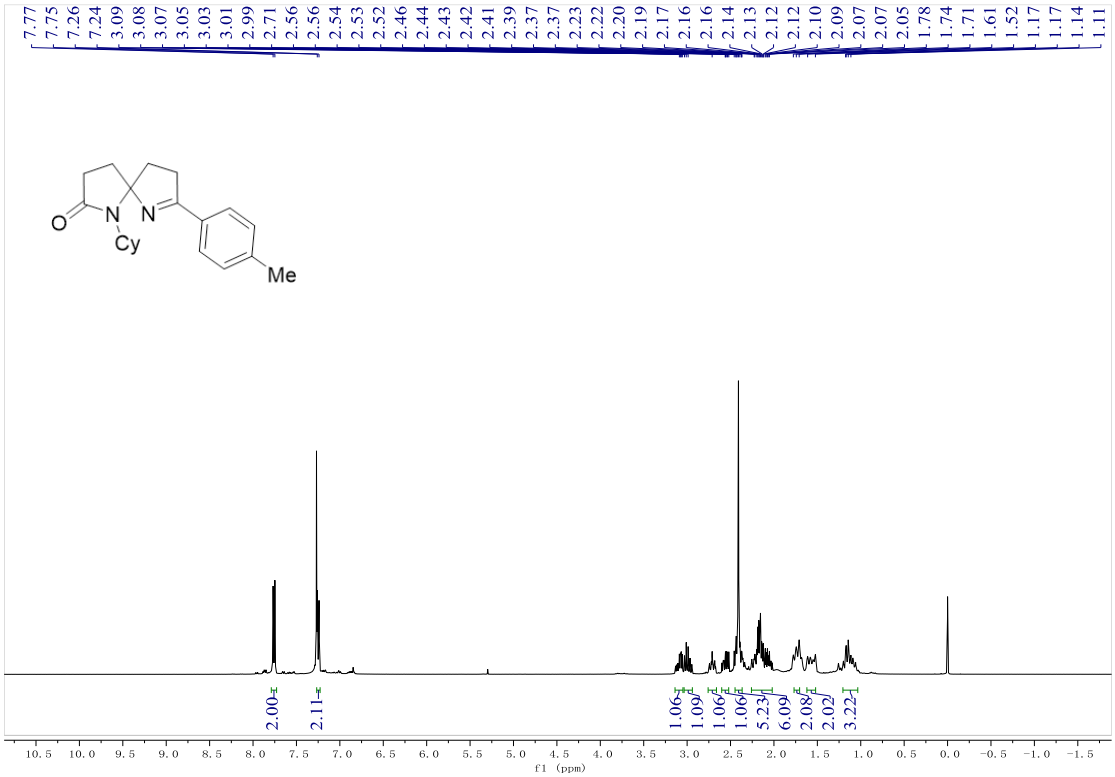
^{1}H NMR spectrum of **5ar**



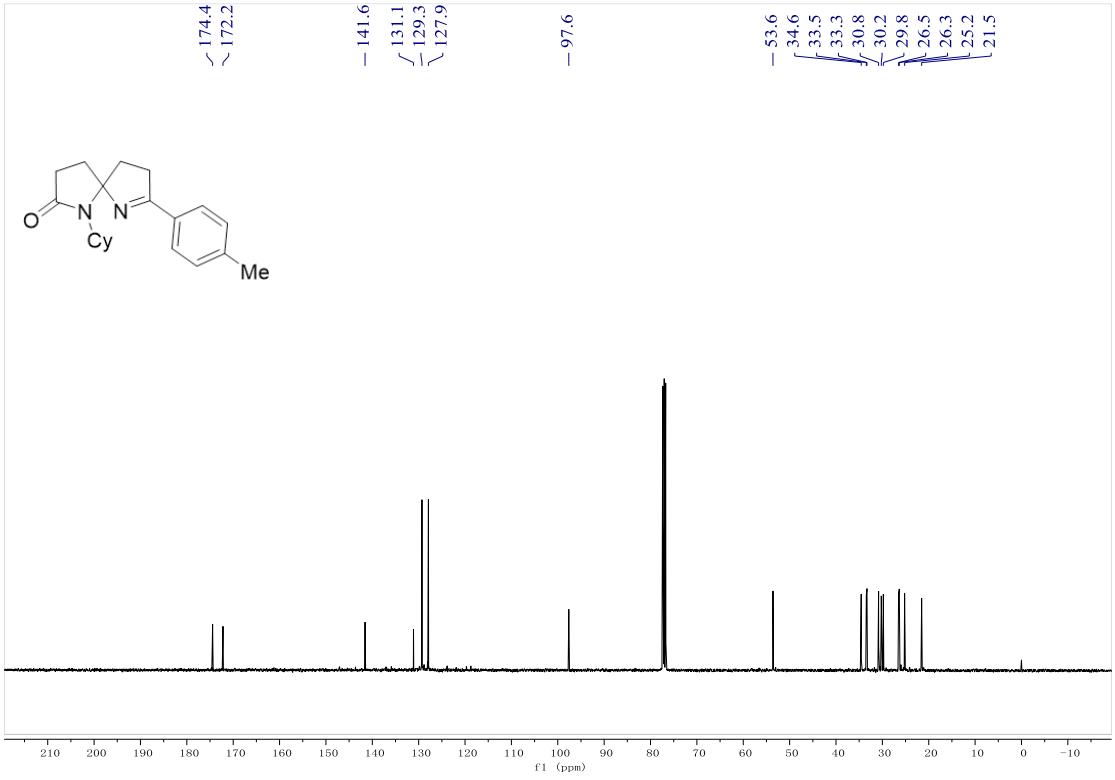
^{13}C NMR spectrum of **5ar**



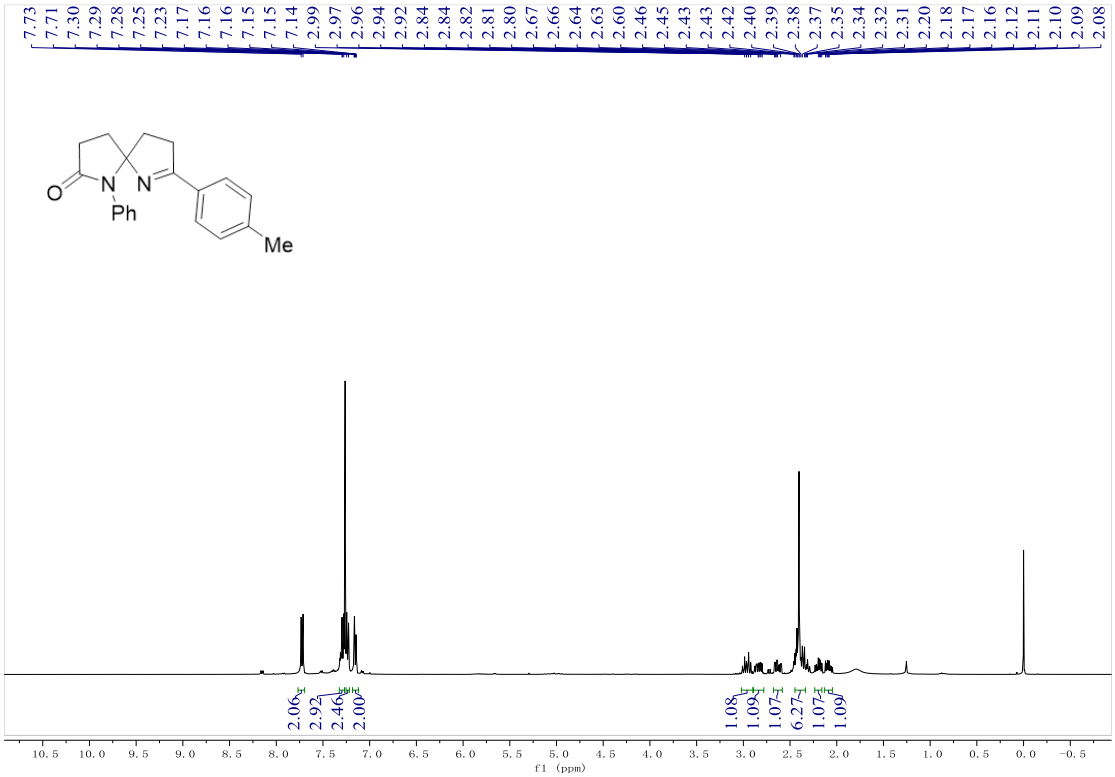
^{1}H NMR spectrum of **5ba**



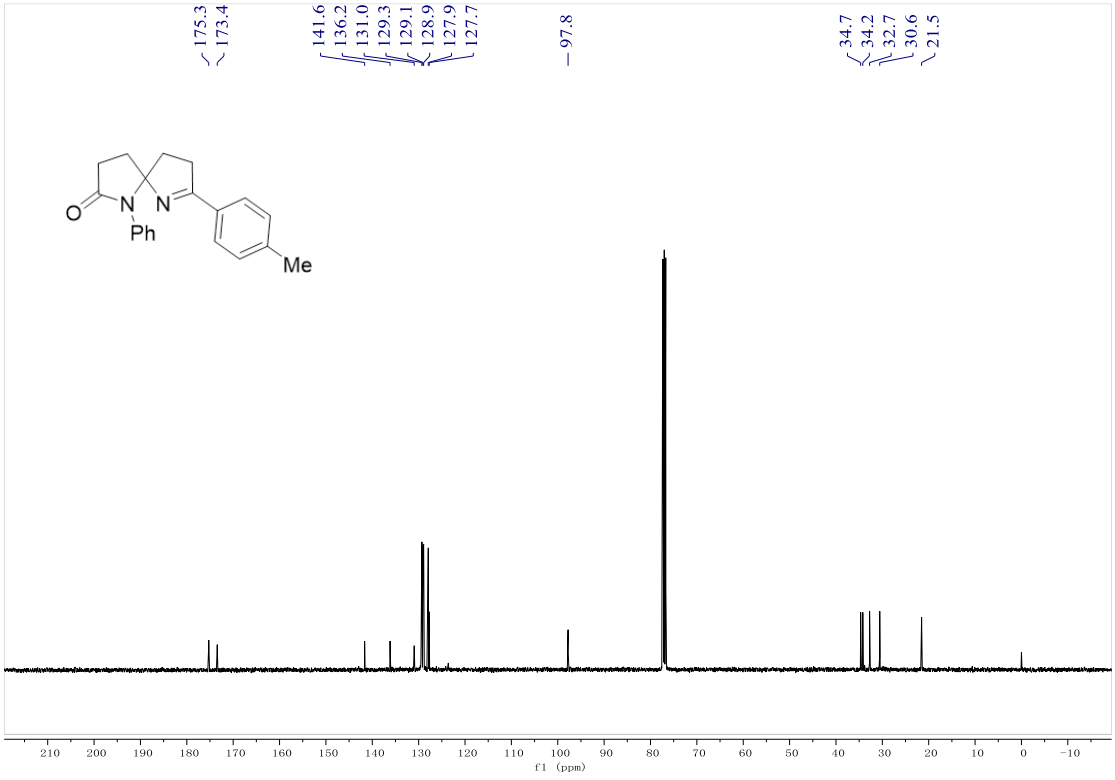
^{13}C NMR spectrum of **5ba**



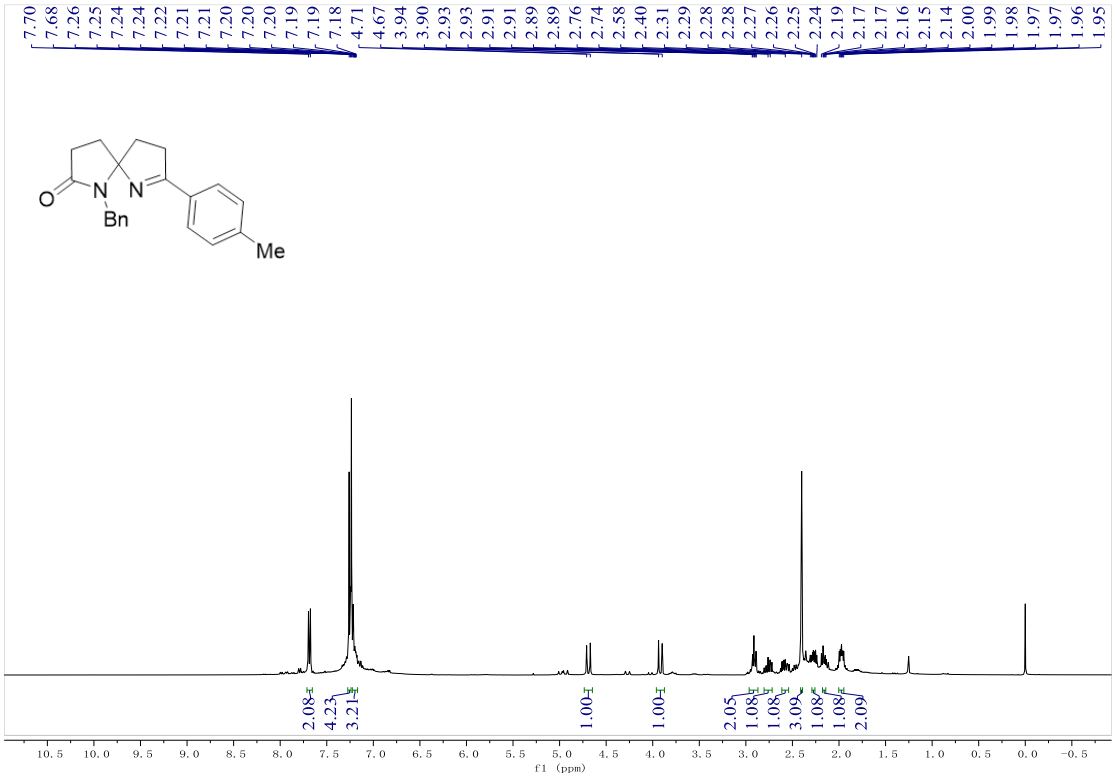
^{1}H NMR spectrum of **5ca**



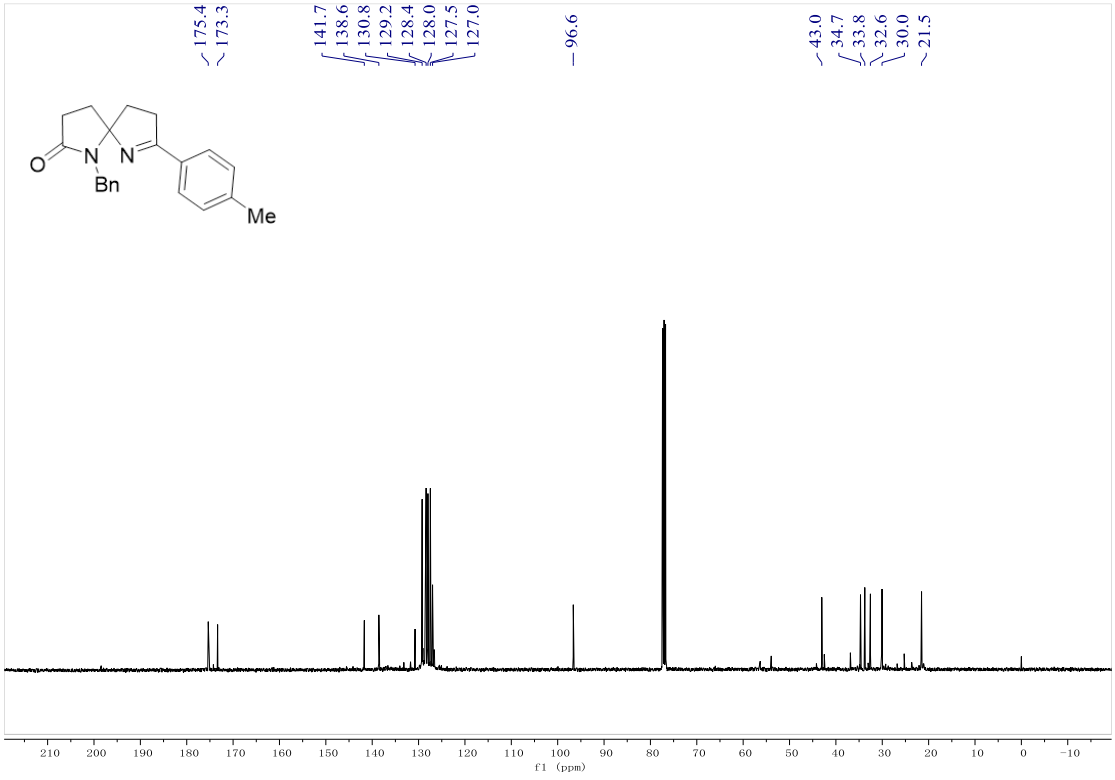
^{13}C NMR spectrum of **5ca**



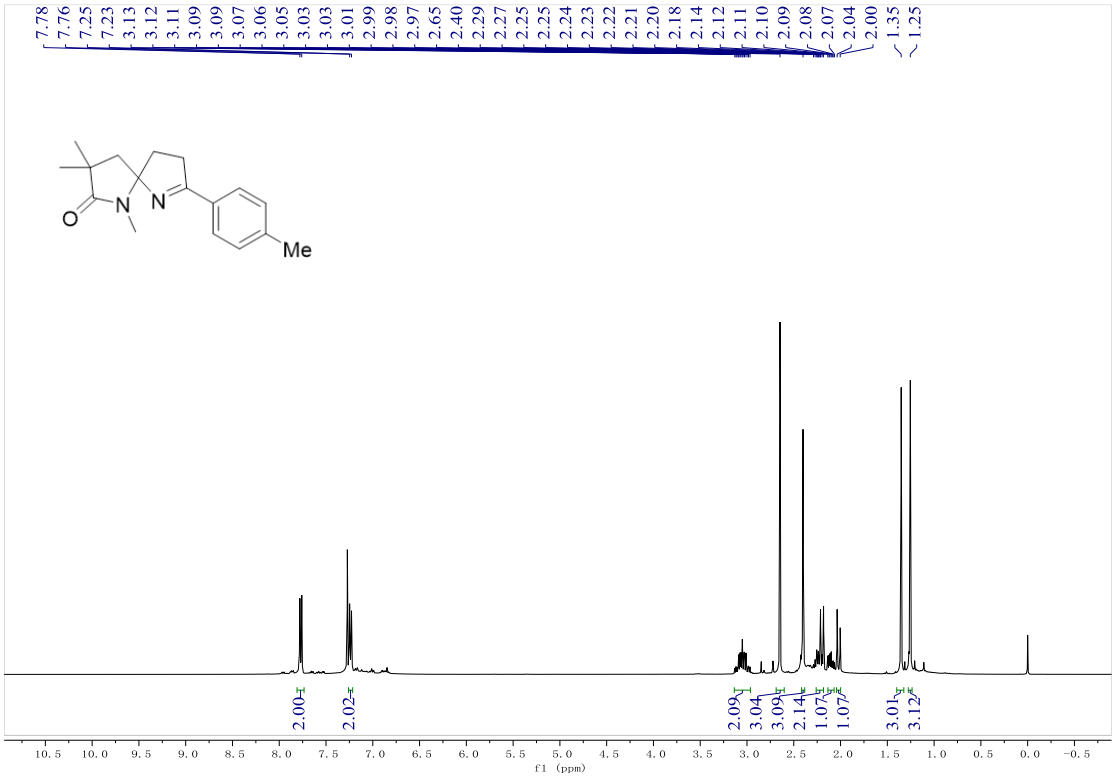
^{1}H NMR spectrum of **5da**



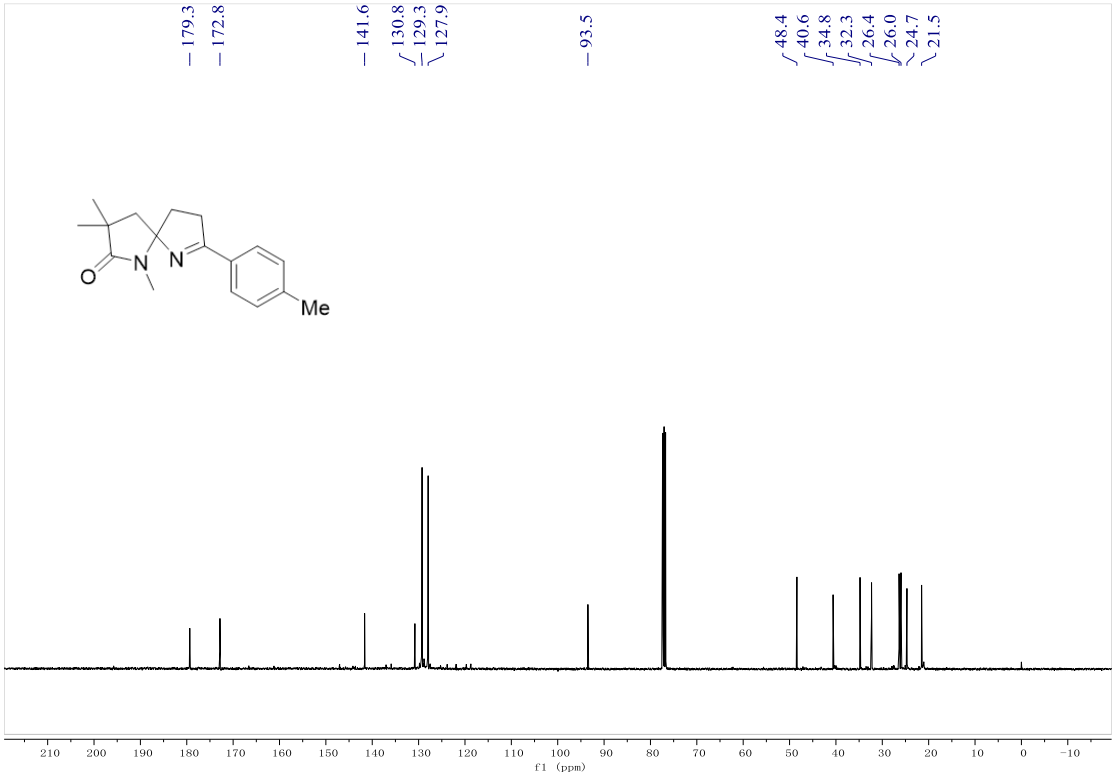
^{13}C NMR spectrum of **5da**



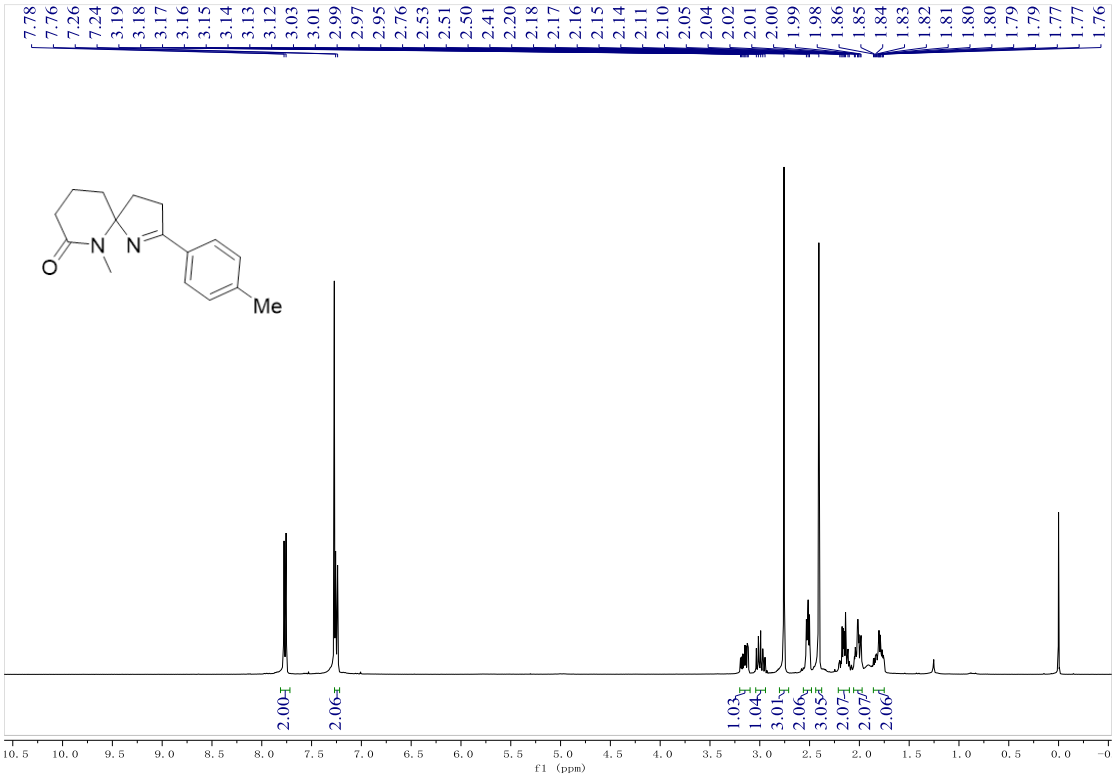
^{1}H NMR spectrum of **5ea**



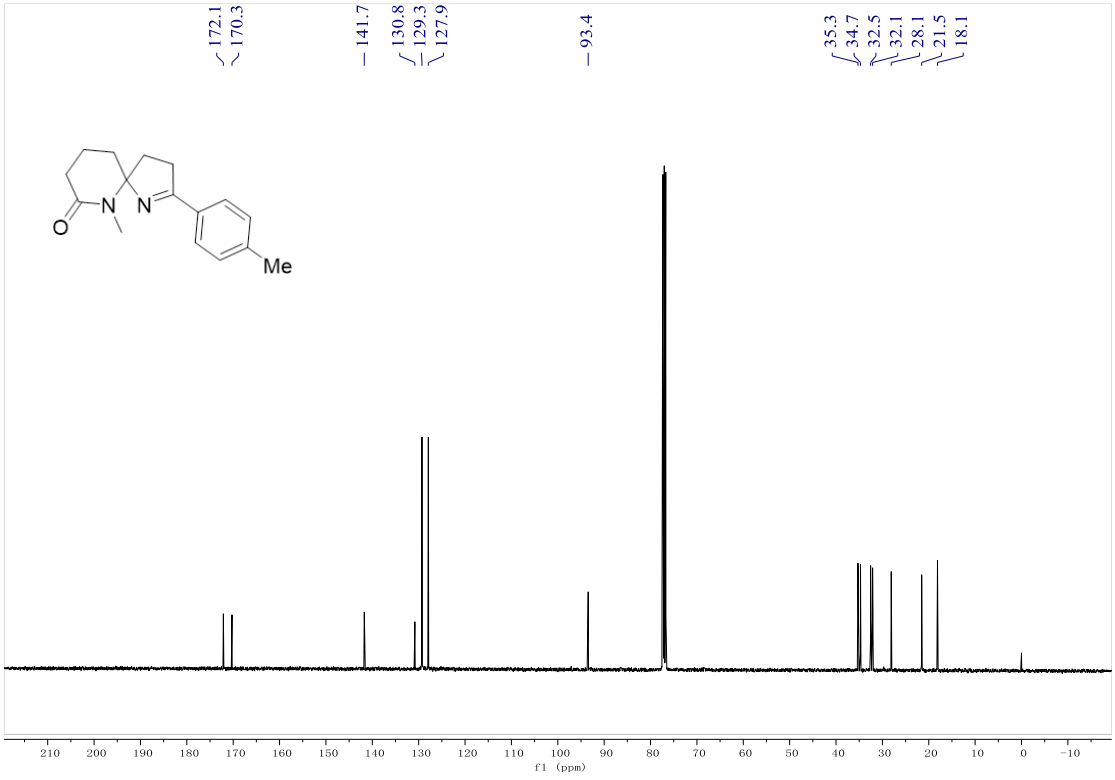
^{13}C NMR spectrum of **5ea**



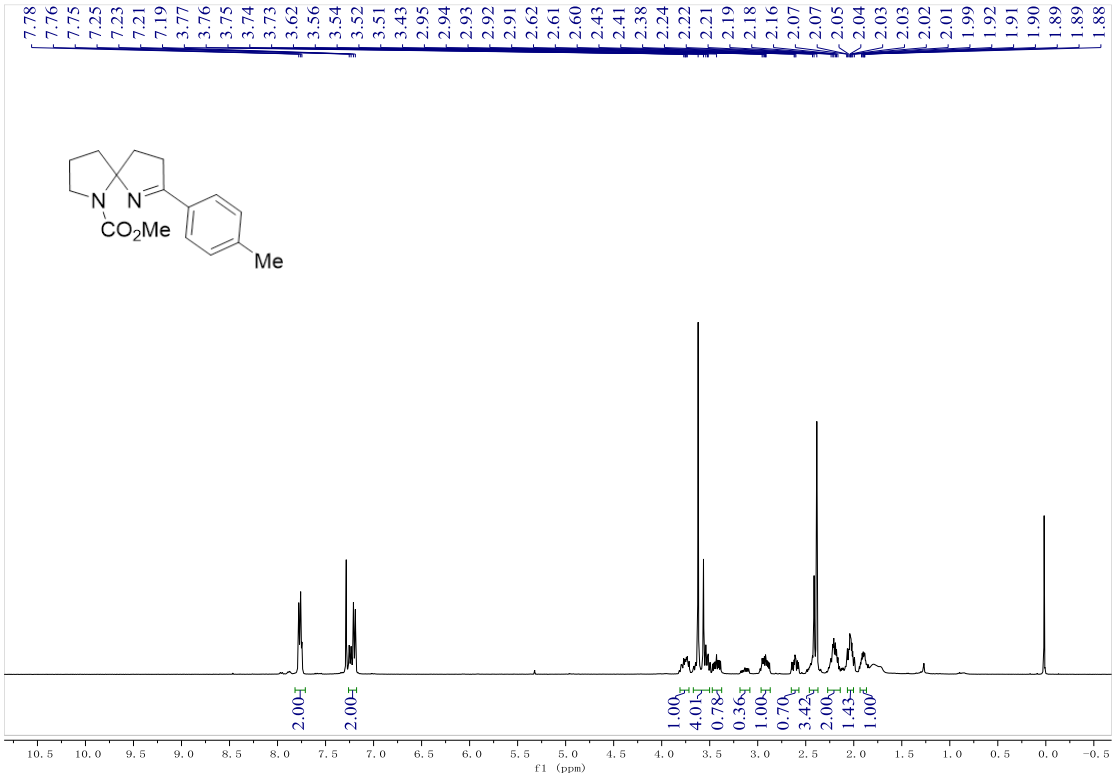
^{1}H NMR spectrum of **5fa**



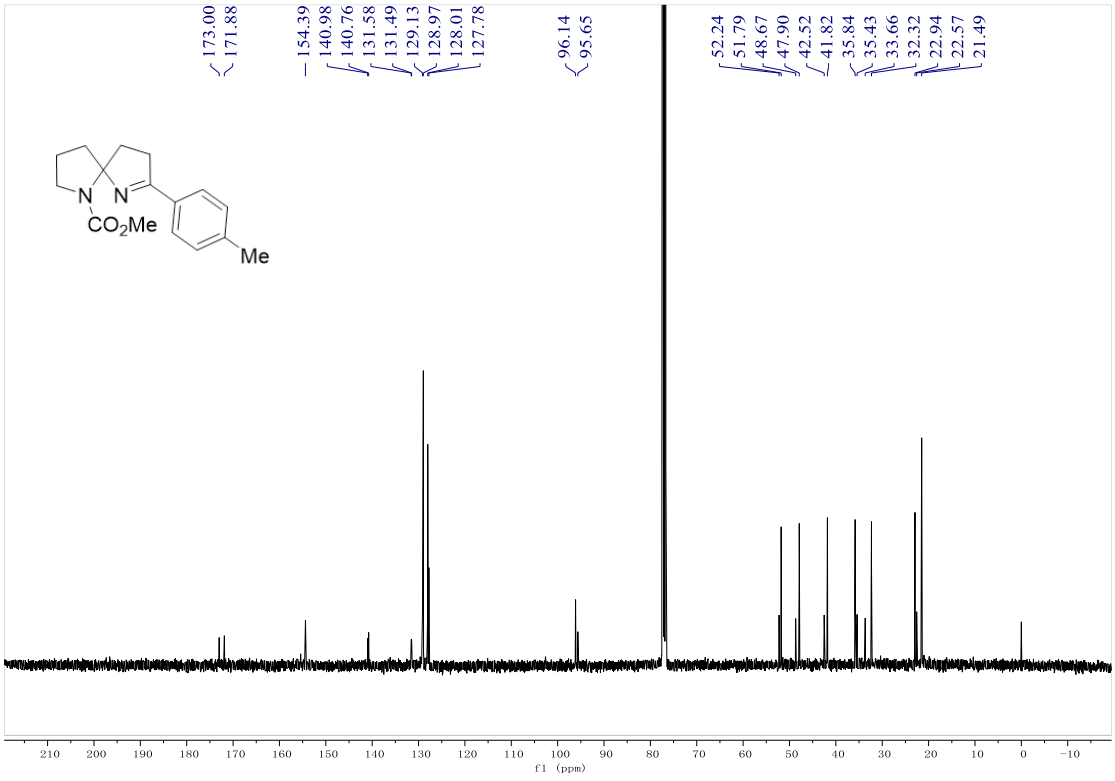
^{13}C NMR spectrum of **5fa**



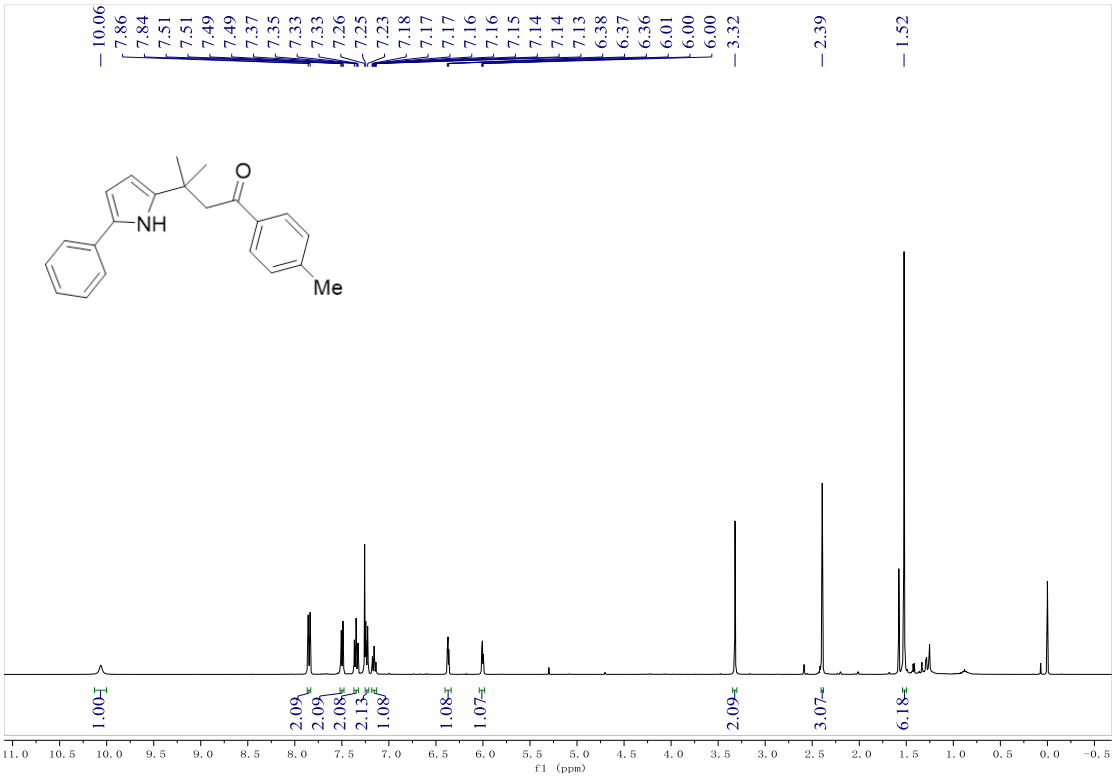
^{1}H NMR spectrum of **5ga**



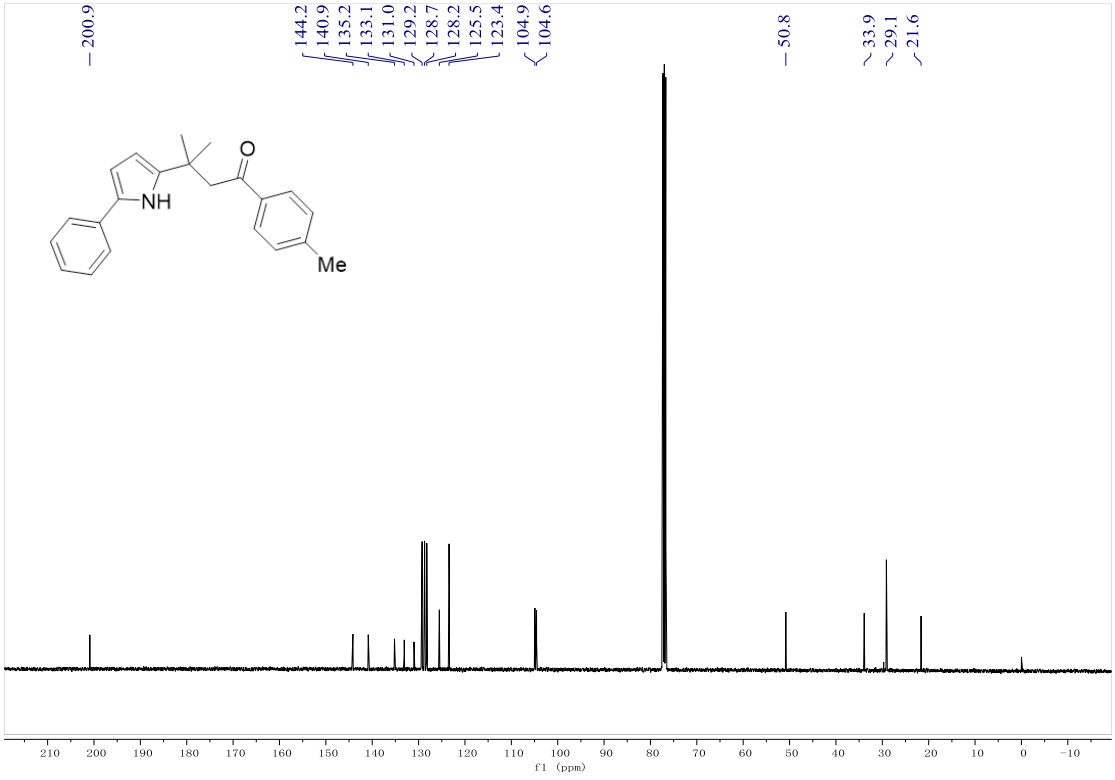
^{13}C NMR spectrum of **5ga**



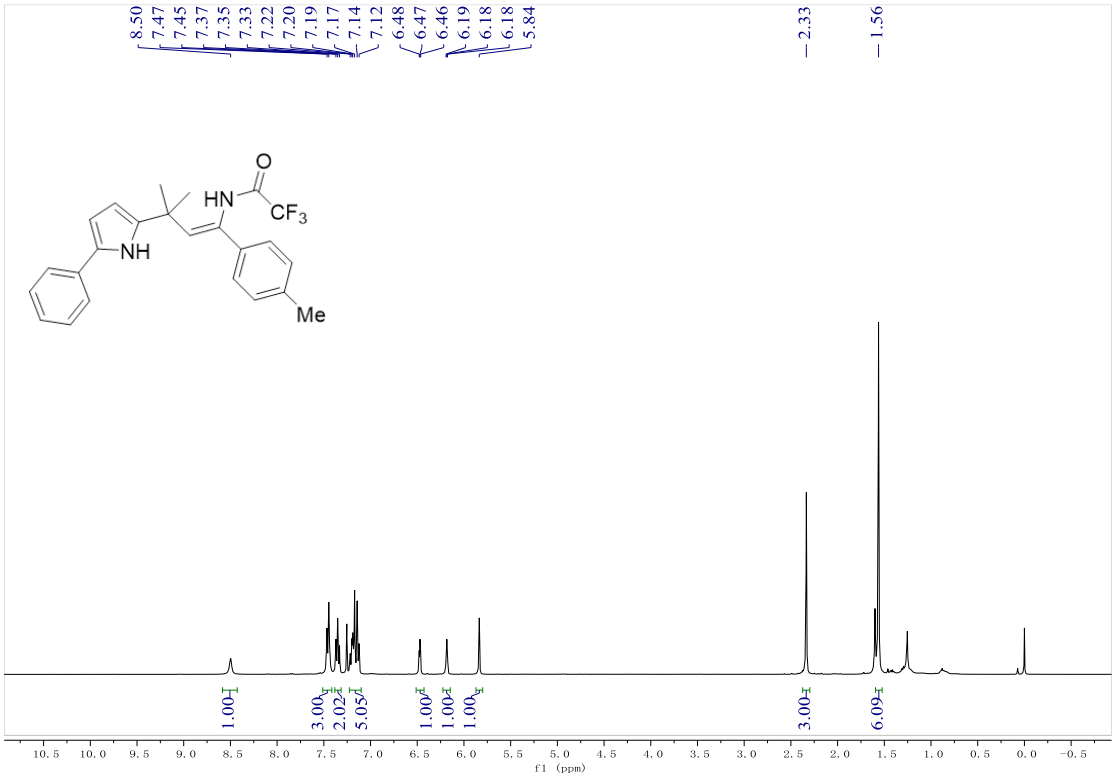
^{1}H NMR spectrum of **6**



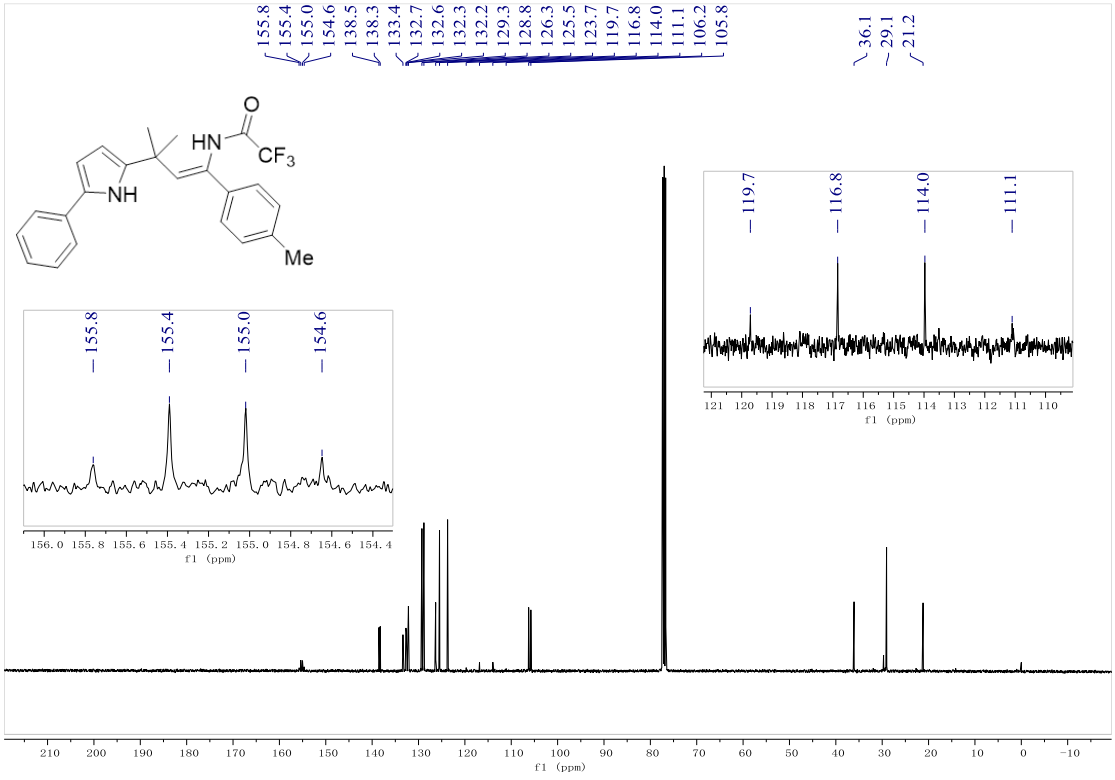
^{13}C NMR spectrum of **6**



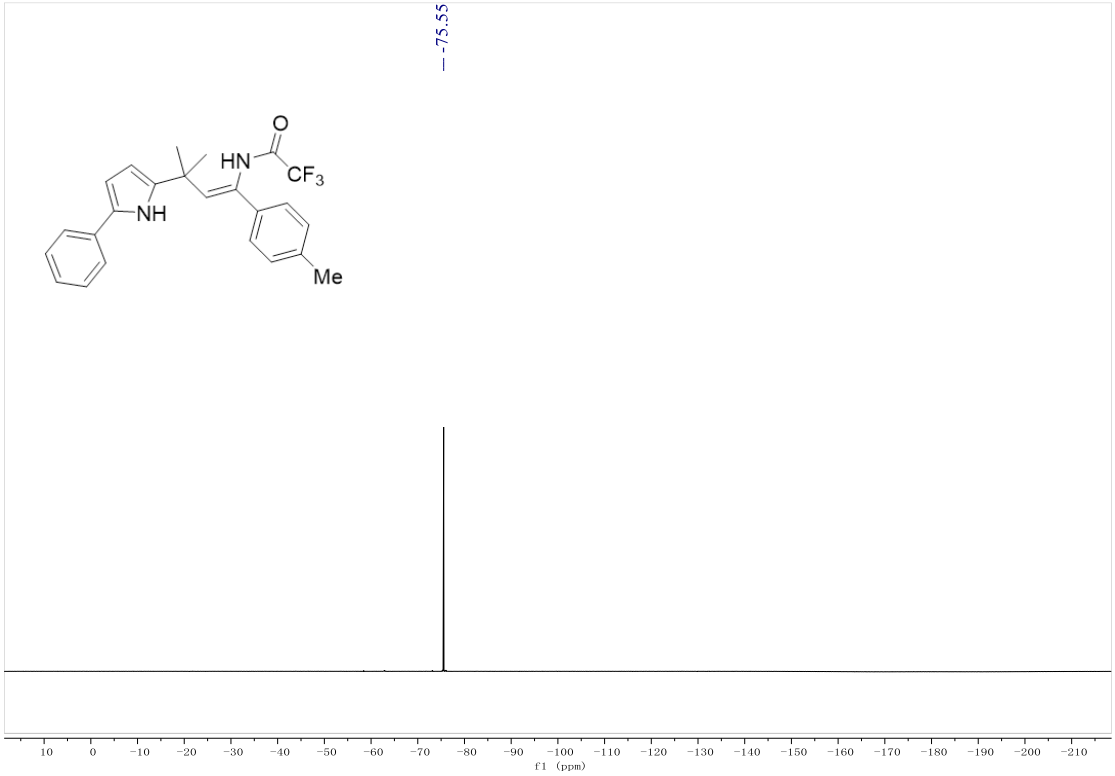
^{1}H NMR spectrum of **7**



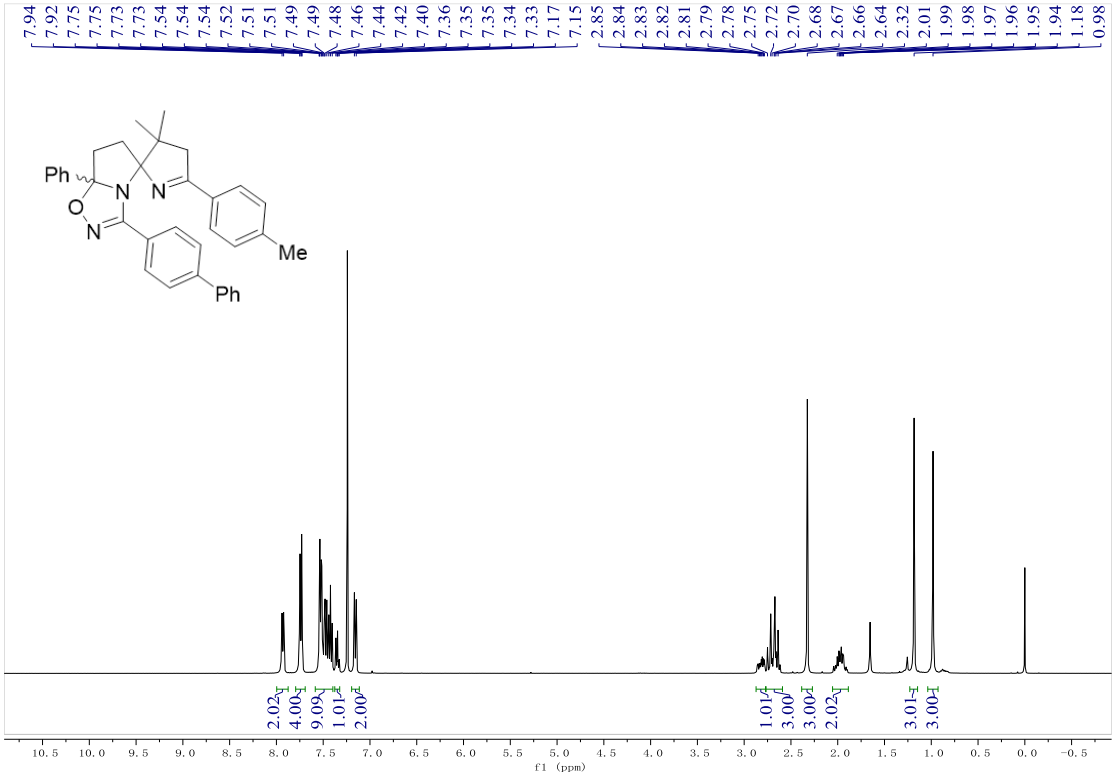
^{13}C NMR spectrum of **7**



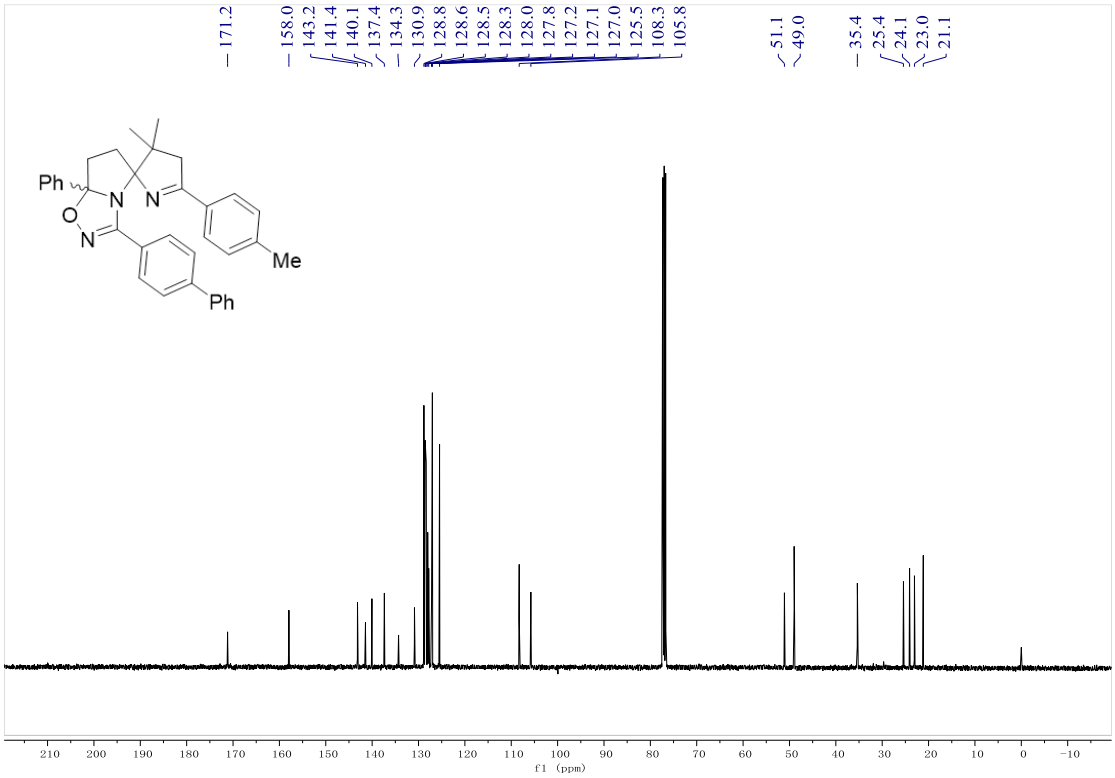
^{19}F NMR spectrum of **7**



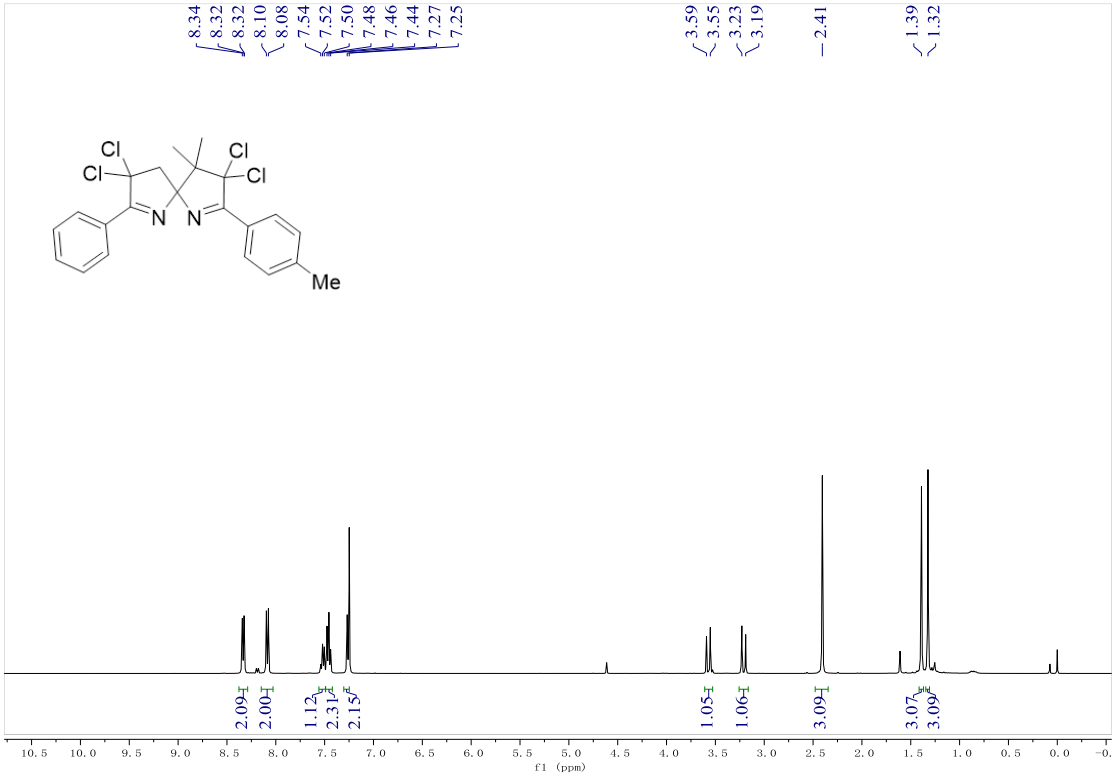
^{1}H NMR spectrum of **8**



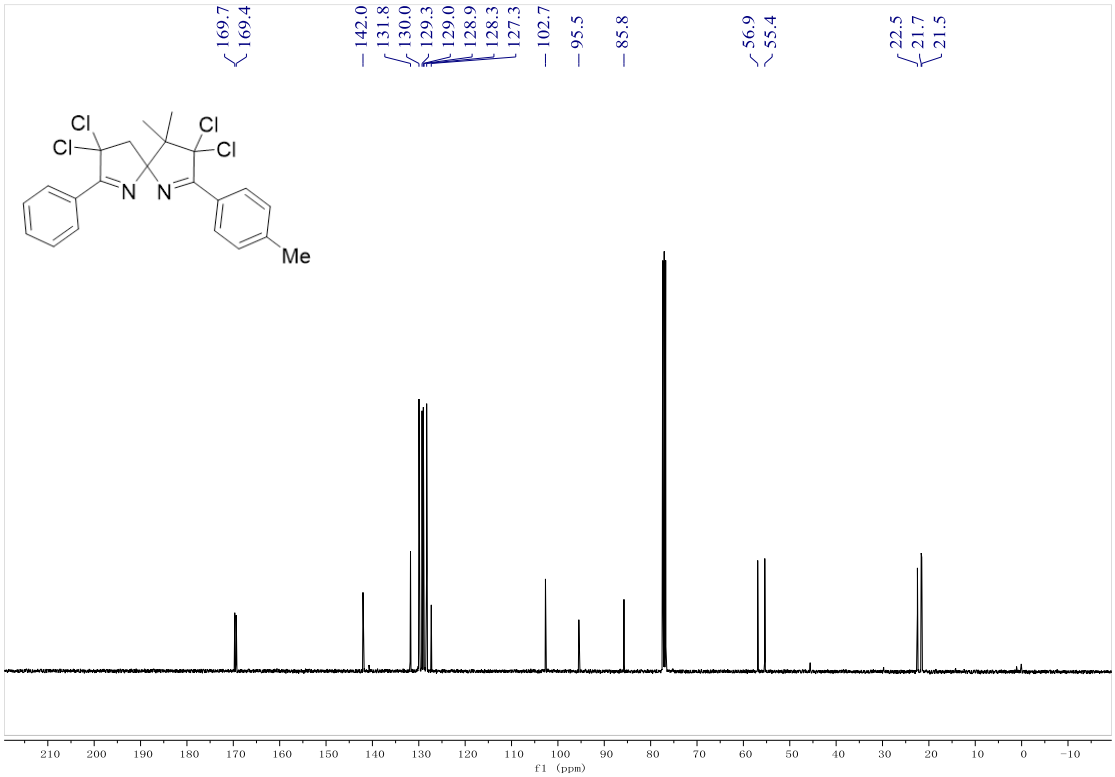
^{13}C NMR spectrum of **8**



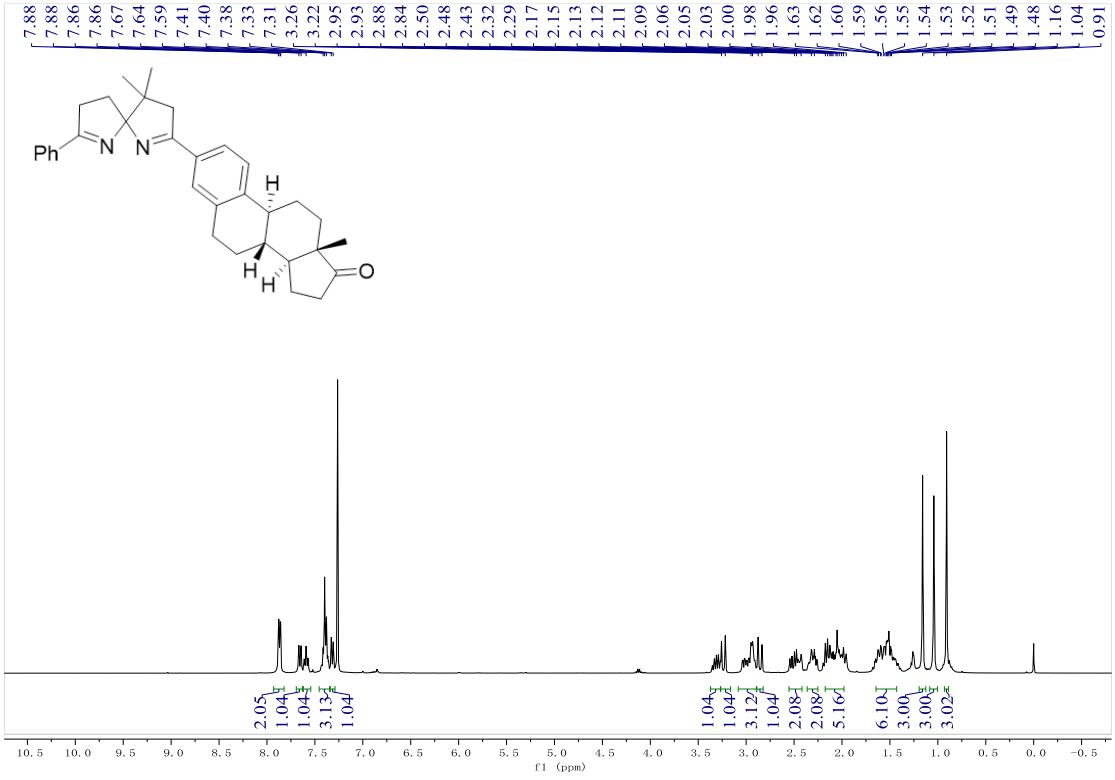
^{1}H NMR spectrum of **9**



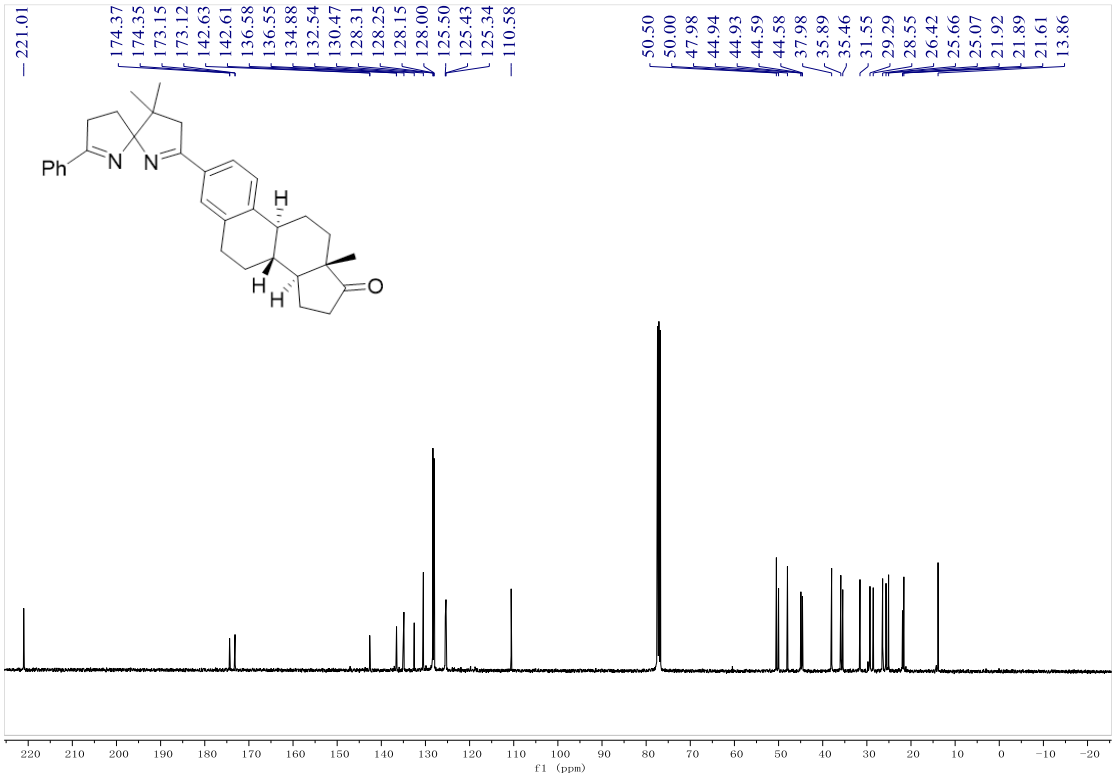
^{13}C NMR spectrum of **9**



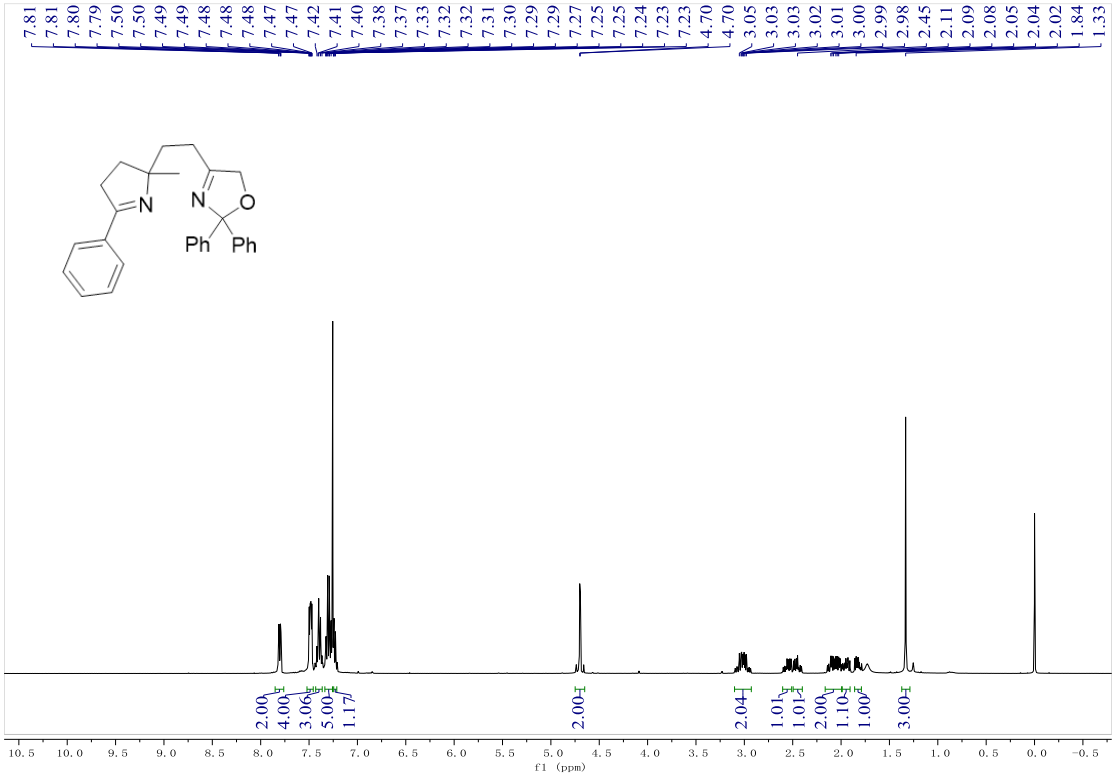
^{1}H NMR spectrum of **3aw**



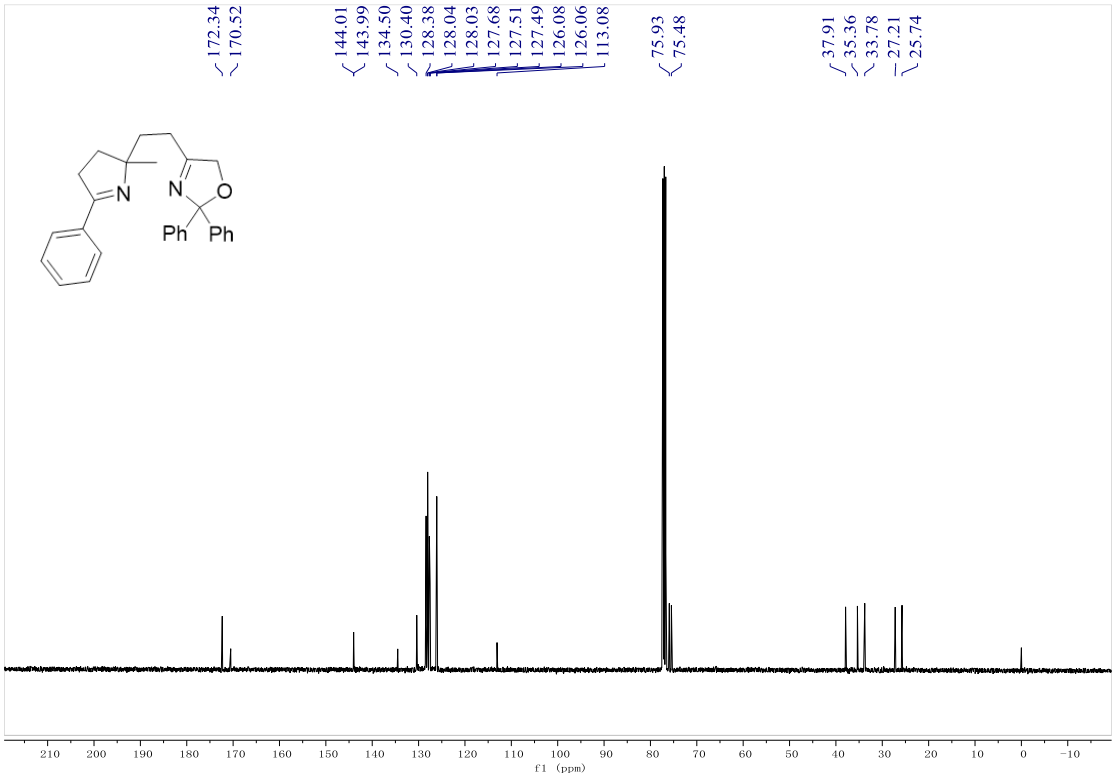
^{13}C NMR spectrum of **3aw**



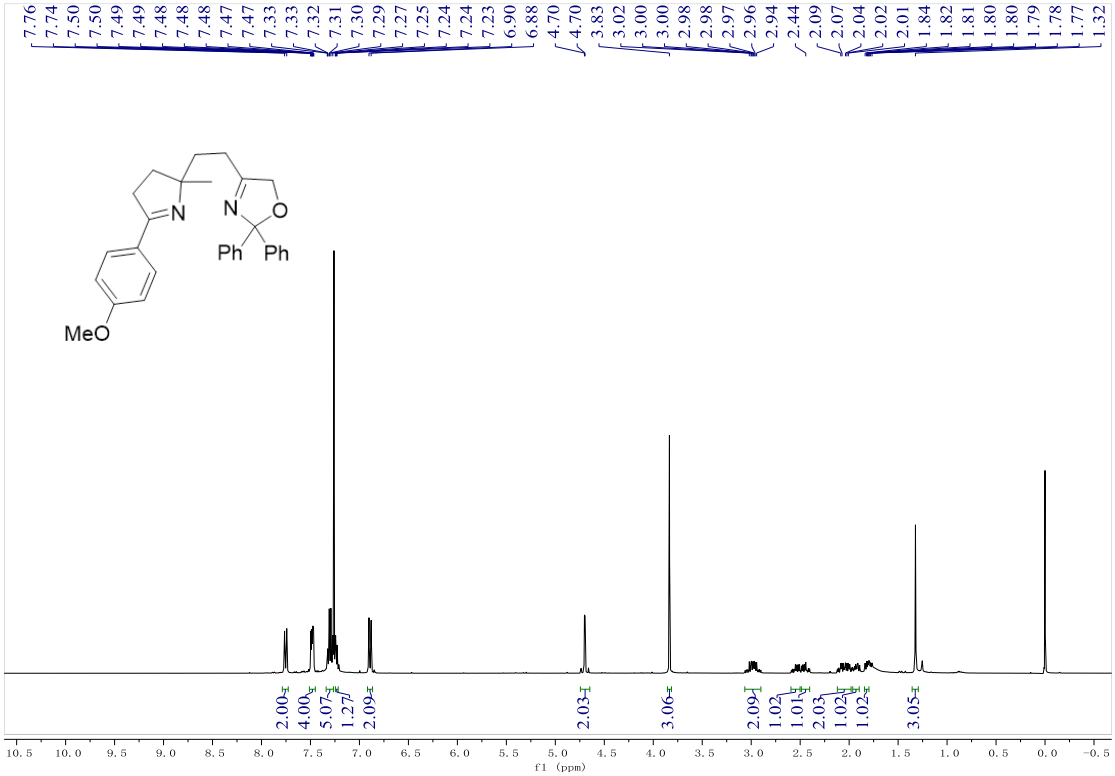
^{1}H NMR spectrum of **10px**



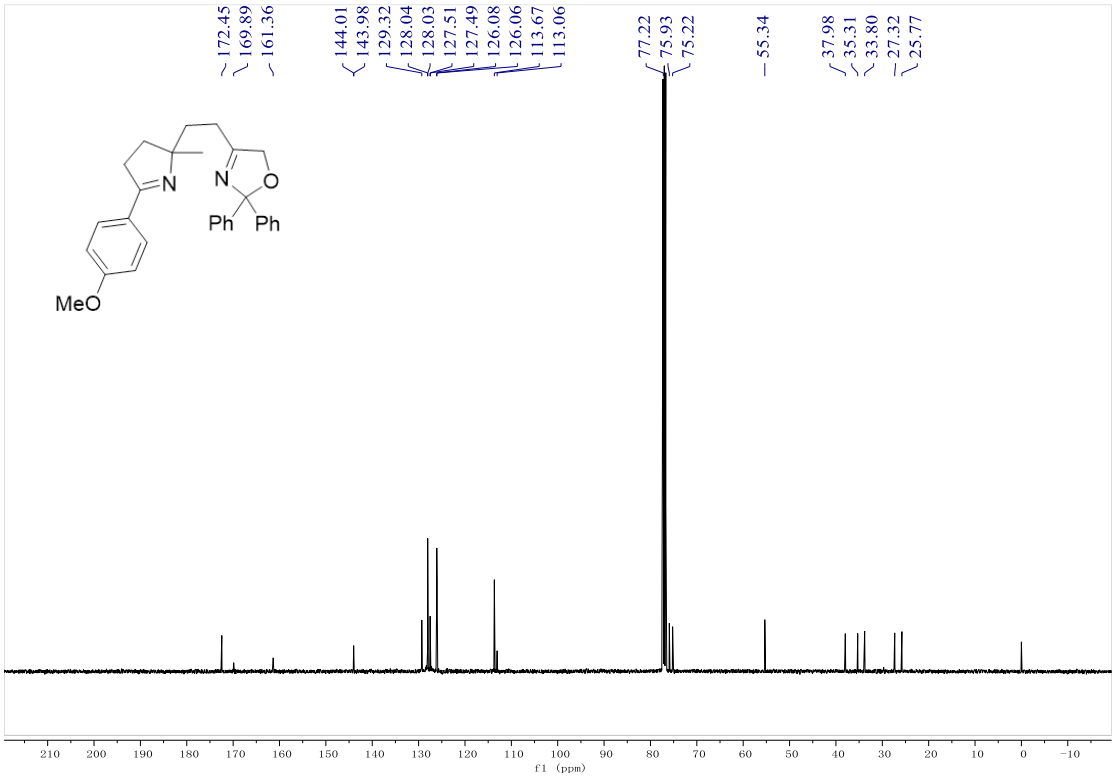
^{13}C NMR spectrum of **10px**



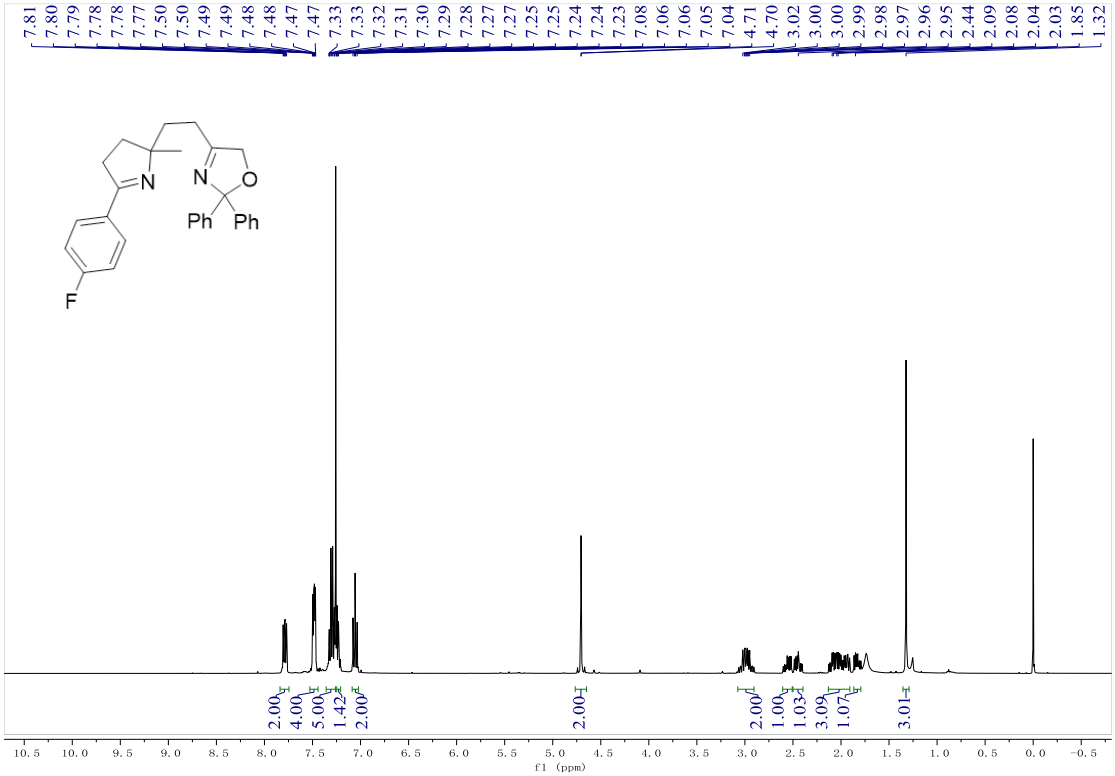
^{1}H NMR spectrum of **10qx**



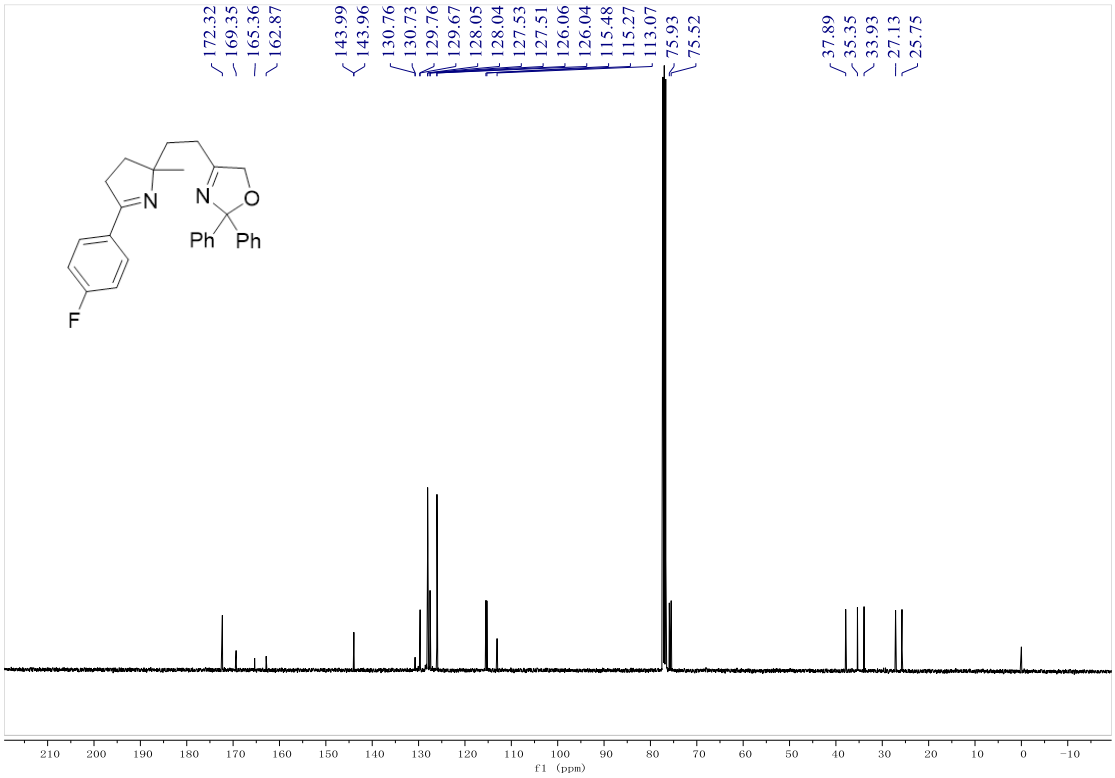
^{13}C NMR spectrum of **10qx**



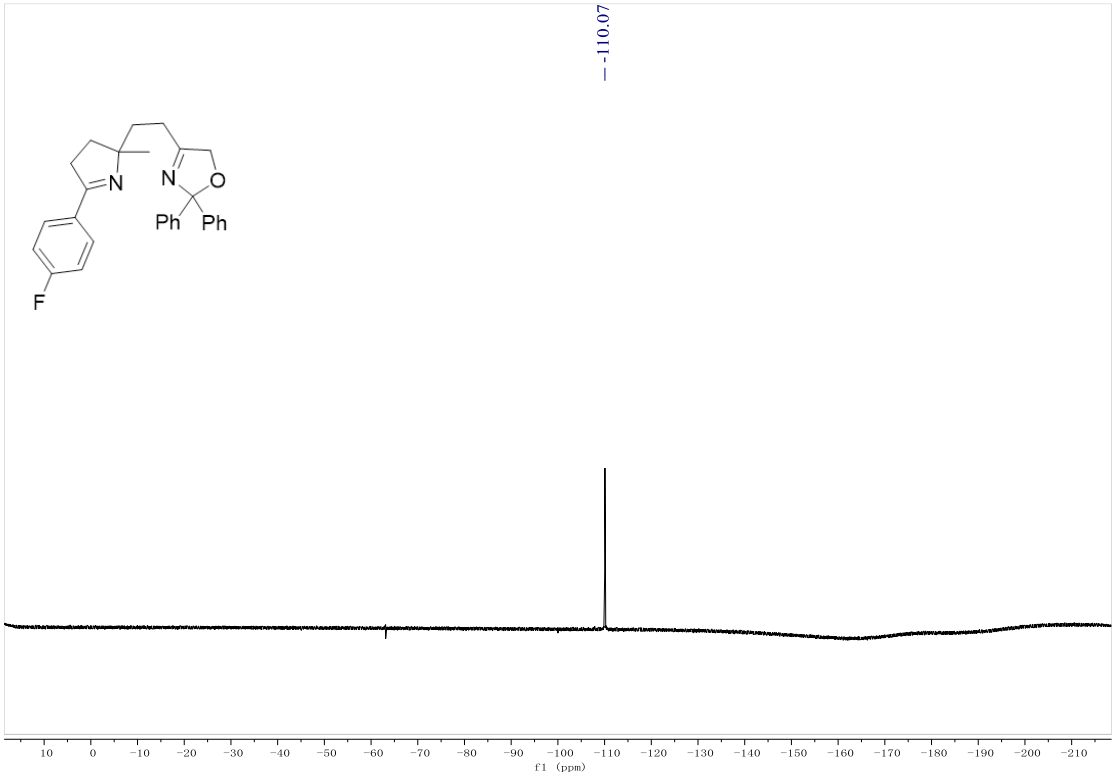
^{1}H NMR spectrum of **10rx**



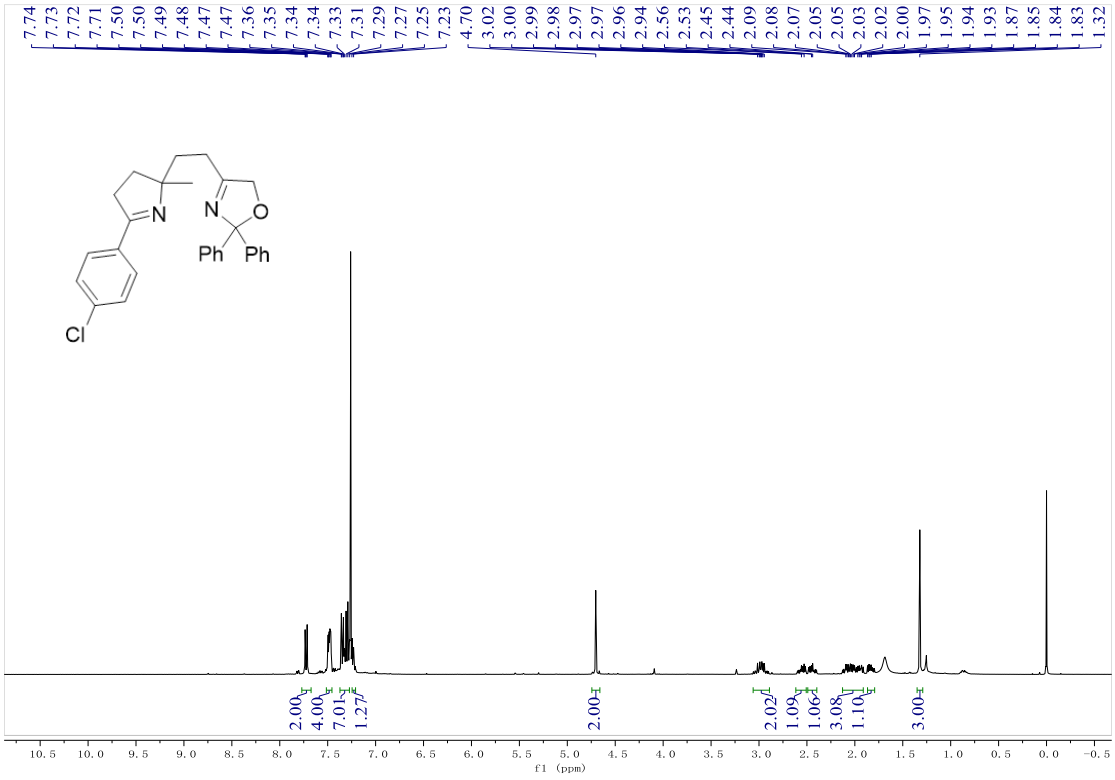
^{13}C NMR spectrum of **10rx**



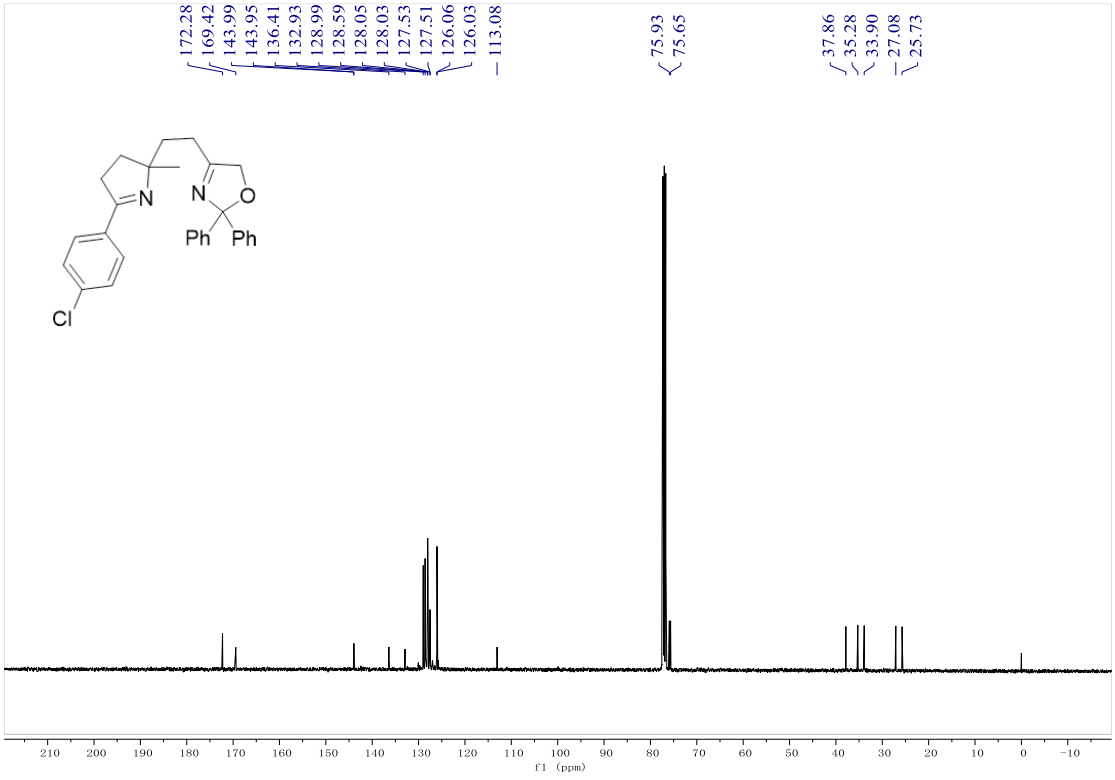
^{19}F NMR spectrum of **10rx**



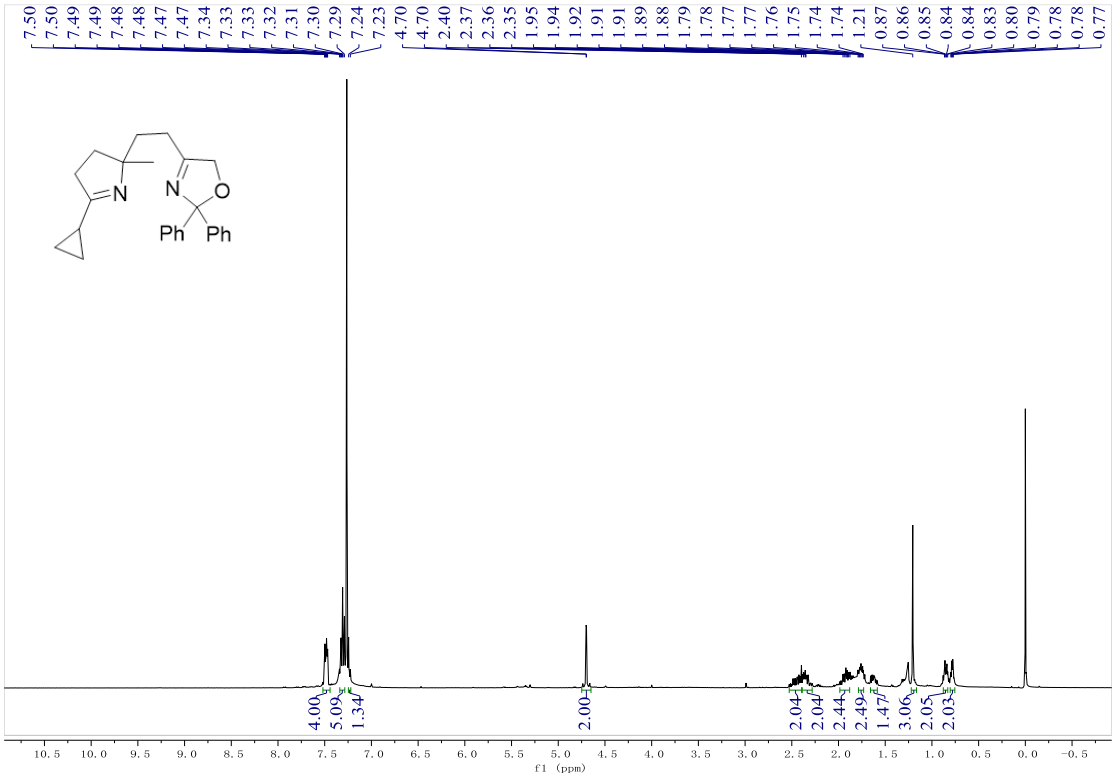
^{1}H NMR spectrum of **10sx**



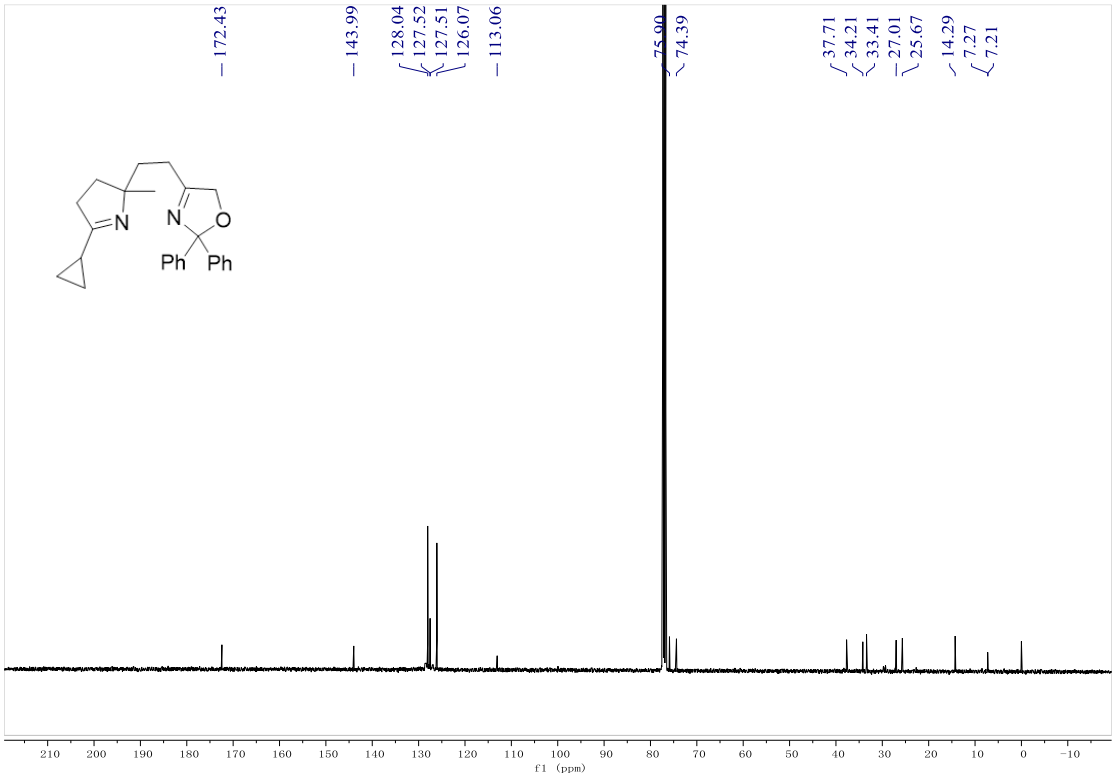
^{13}C NMR spectrum of **10sx**



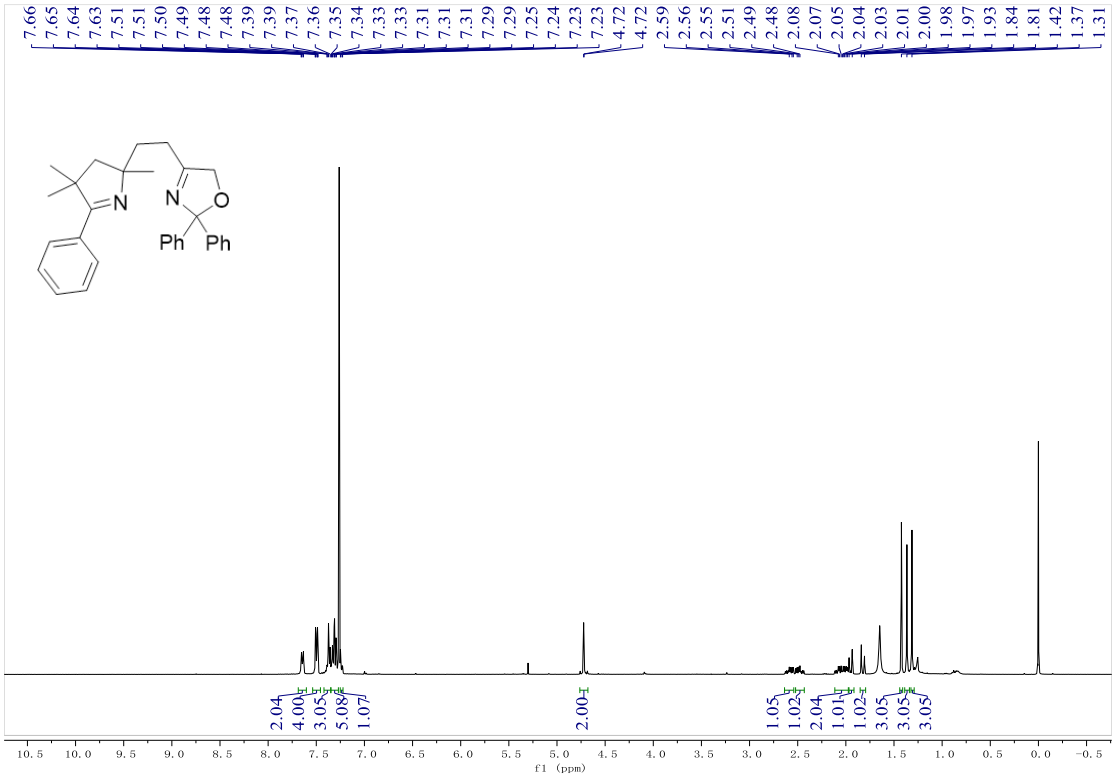
^{1}H NMR spectrum of **10tx**



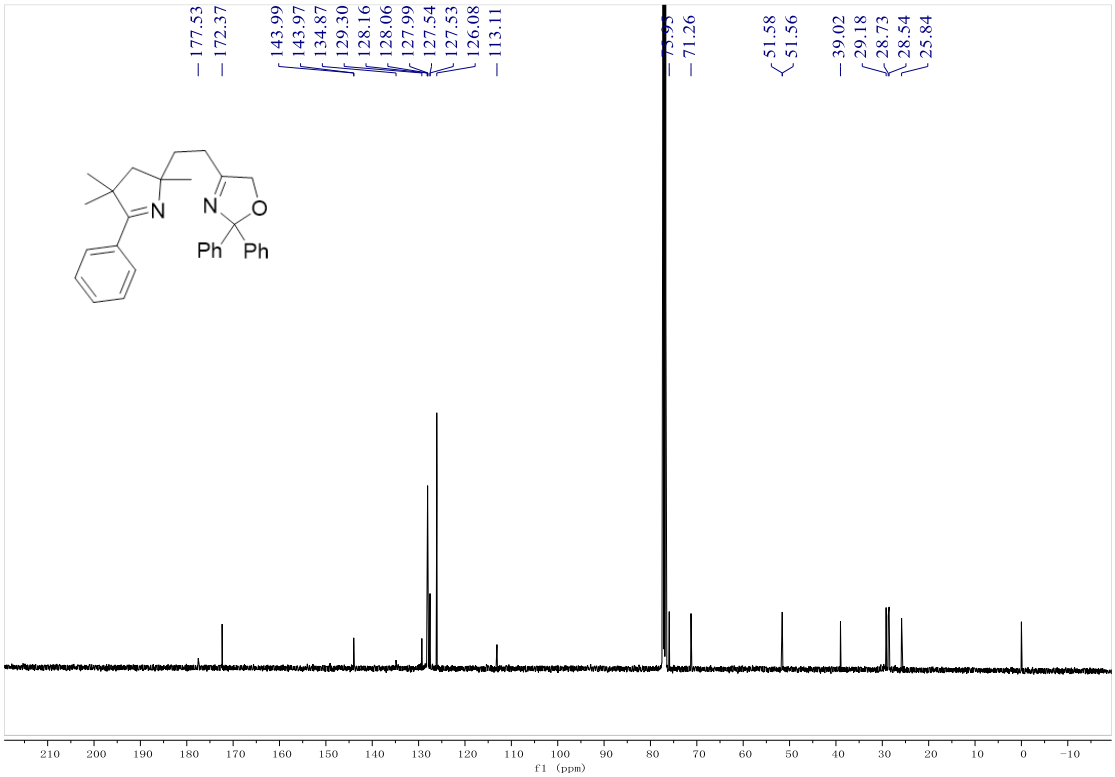
^{13}C NMR spectrum of **10tx**



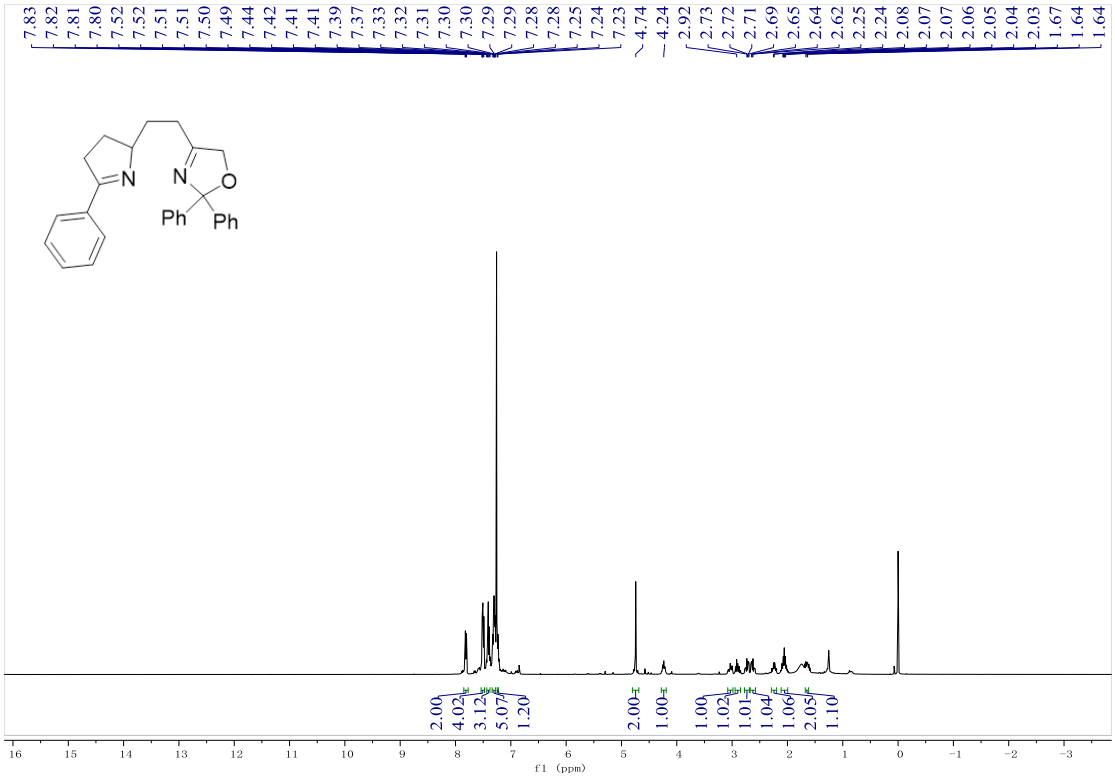
^{1}H NMR spectrum of **10ux**



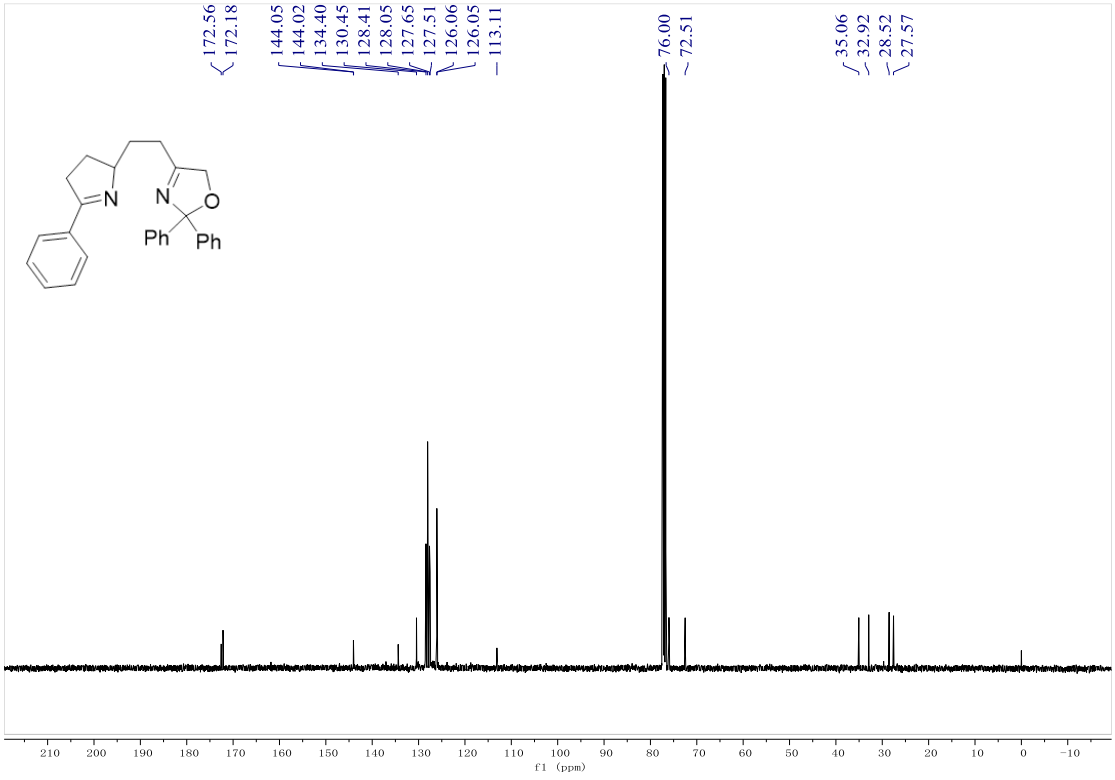
^{13}C NMR spectrum of **10ux**



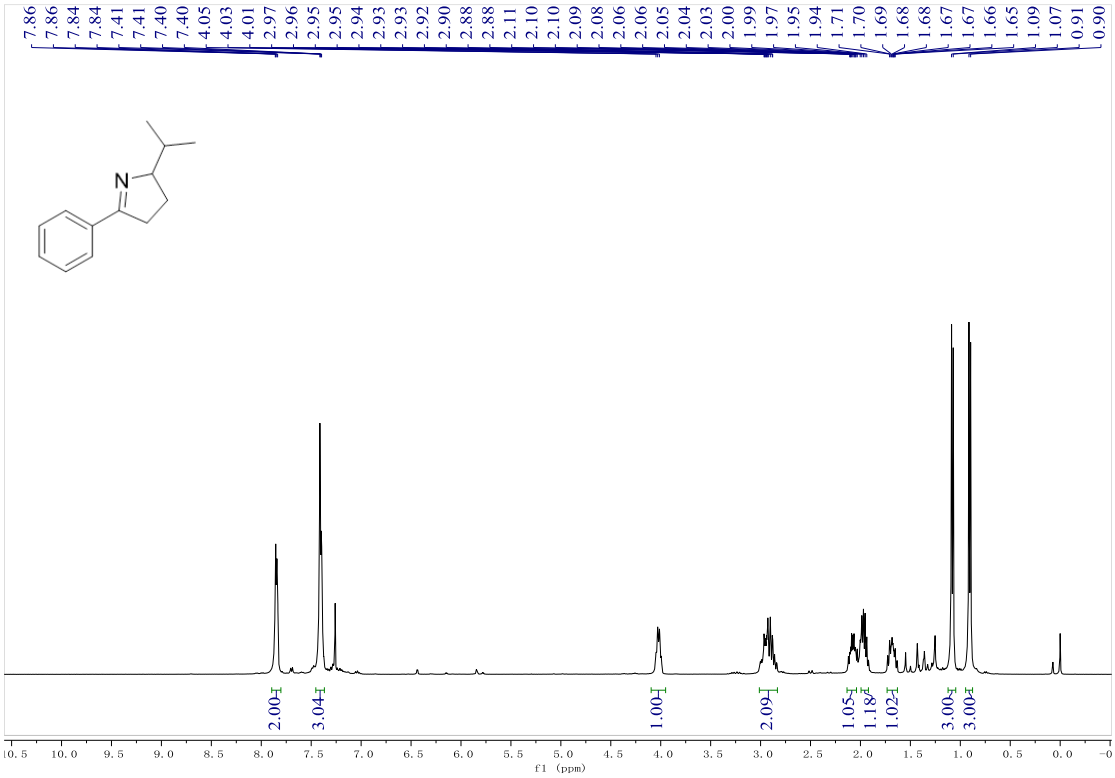
^{1}H NMR spectrum of **10ox**



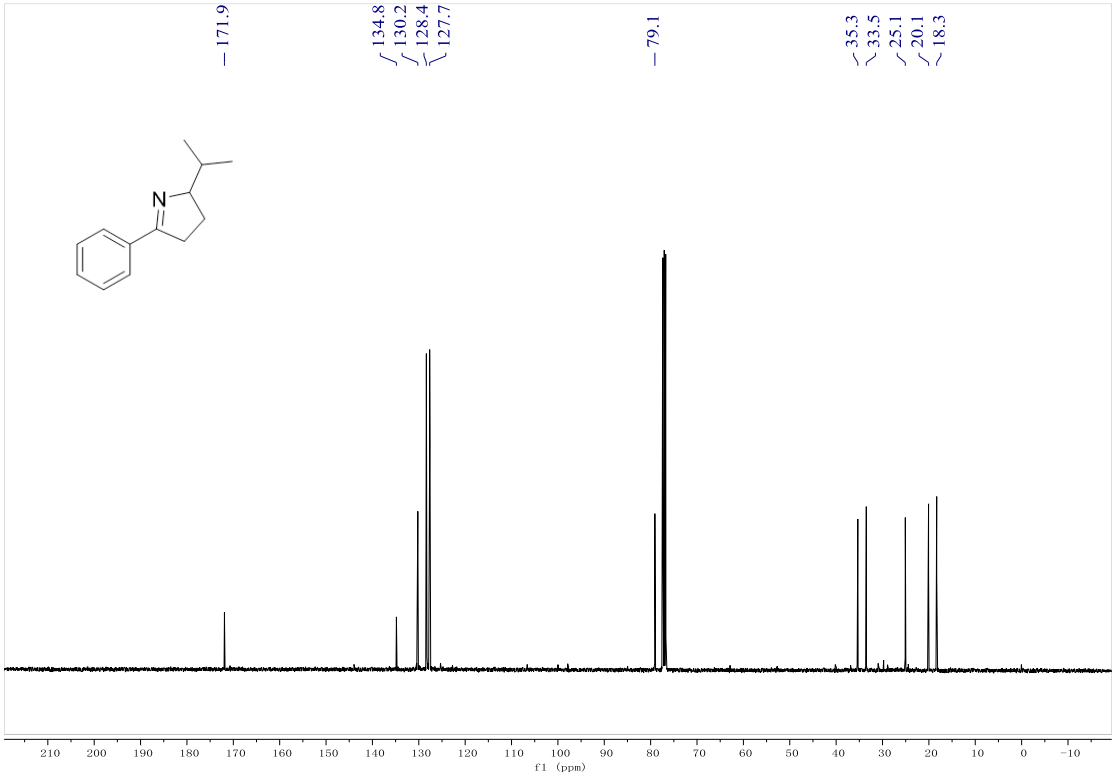
^{13}C NMR spectrum of **10ox**



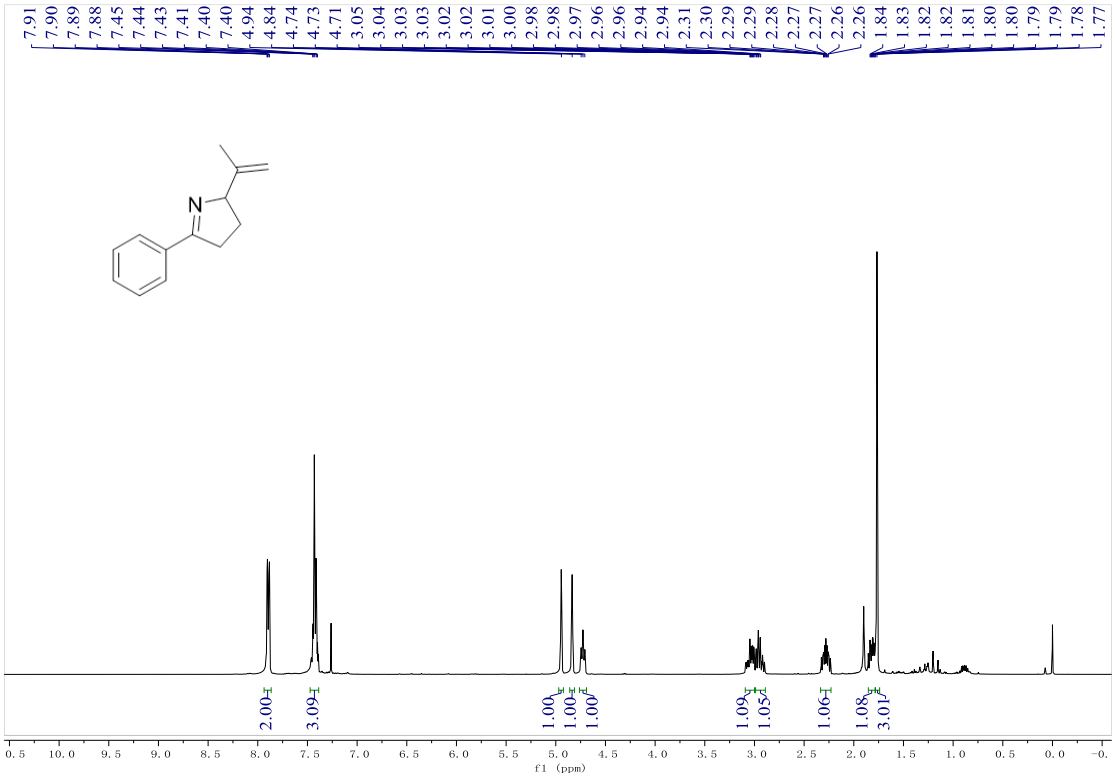
^{1}H NMR spectrum of **1a'**



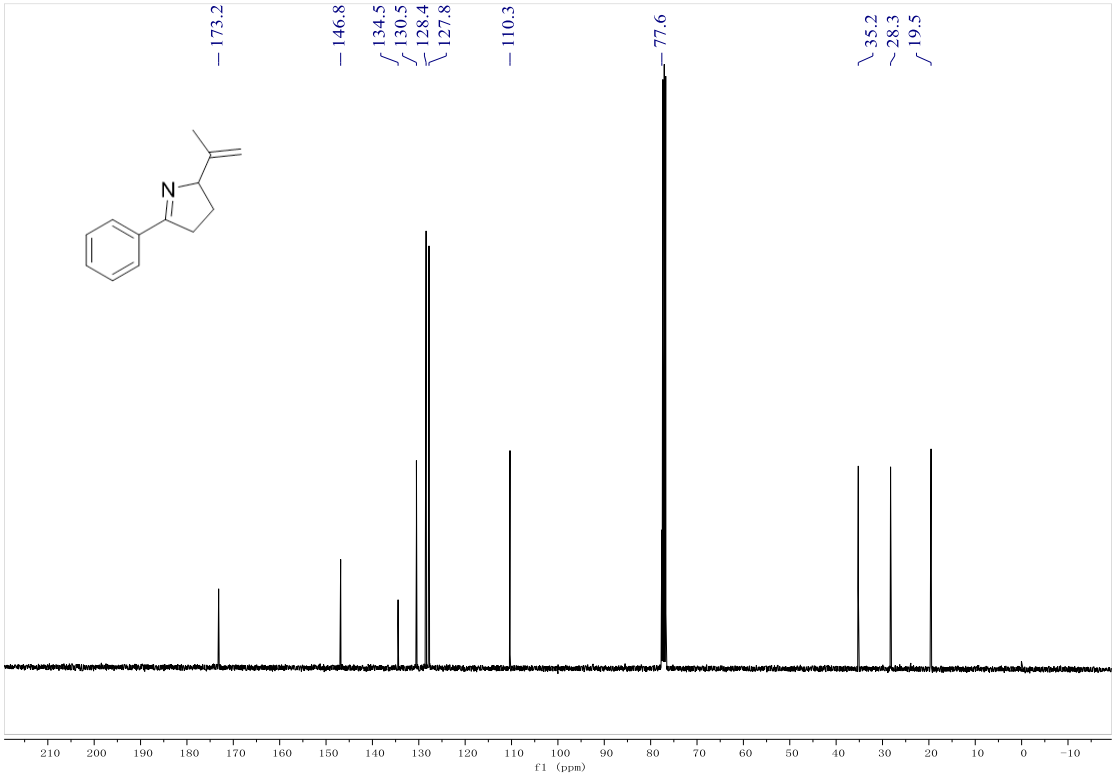
^{13}C NMR spectrum of **1a'**



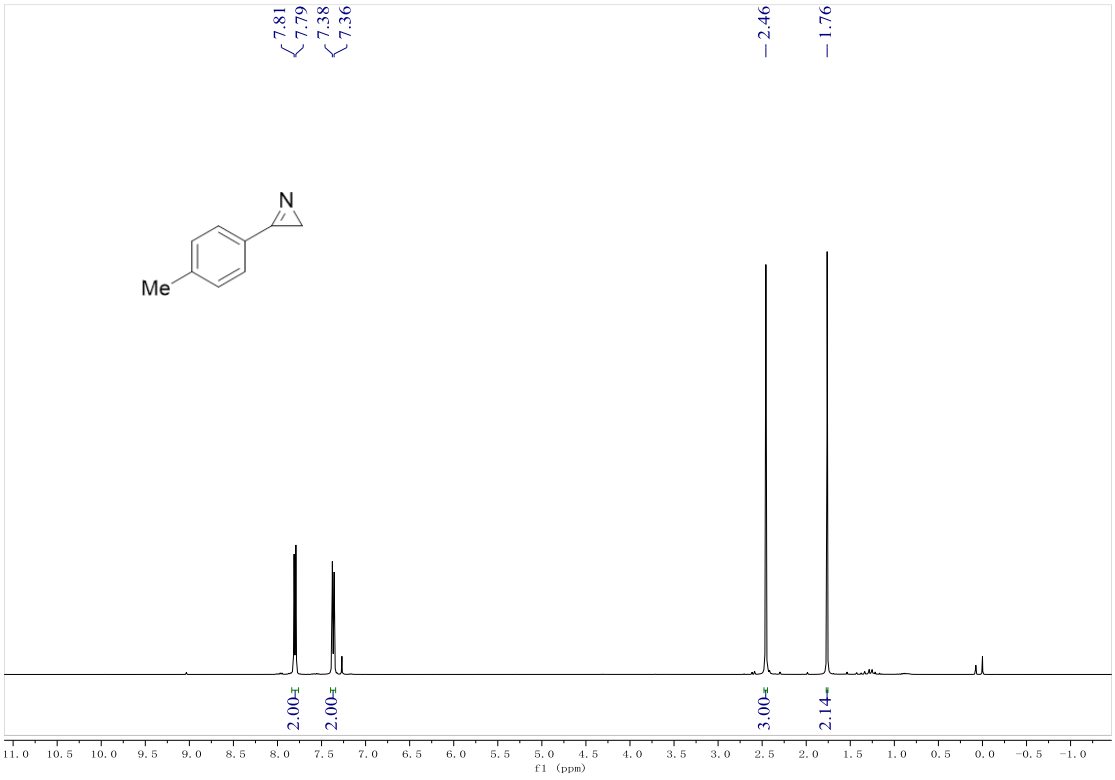
^{1}H NMR spectrum of **1a''**



^{13}C NMR spectrum of **1a''**



^{1}H NMR spectrum of **2a'**



^{13}C NMR spectrum of **2a'**