Supplementary Information for

Synthesis of 1,4-Epoxy-2-aryltetrahydro-1-benzazepines via Rhodium(III)-Catalyzed C-H Allylation/Intramolecular 1,3-dipolar Cycloaddition

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Abbreviations

THF: Tetrahydrofuran

CH_2Cl_2: Dichlormethane

$CHCl_3$: Chloroform

DMSO: Dimethyl sulfoxide

DMF: N,N-Dimethylformamide

PE: Petroleum ether

EA: Ethyl acetate

EtOH: Ethanol

CH_3CN: Acetonitrile

TFEA: 2,2,2-Trifluoroethanol

PhCl: Chlorobenzene

$PhCF_3$:Trifluoromethylbenzene

$CDCl_3$: Deuterated chloroform

equiv: equivalents

TLC: Thin layer chromatography

HRMS: High resolution mass spectrometry

r.t.: room temperature

h: hours

Hz : Hertz

kV : Kilovolt

μA: Microampere

MHz : Megahertz

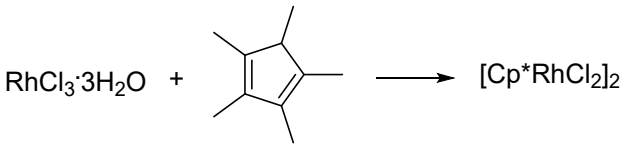
General remarks

Reagents were purchased from commercial suppliers (Macklin, Aladdin, Bidepharm, Energy Chemical, etc.) and used without further purification, unless noted otherwise. Solvents were obtained in analytical grade and used as received for reactions, extractions, eluents, precipitation, solid washing etc. unless indicated otherwise. Dry DCE, benzotrifluoride, chlorobenzene, 1,4-dioxane, CH_3CN，DMSO, DMF for reactions were purchased in a dry form from J&K Scientific,Macklin, Energy Chemical and stored over molecular sieves as well as under an atmosphere of dry N_2. Deuterated solvents for NMR were obtained from Macklin, and Energy Chemical, in the indicated purity grade and used as received for NMR spectroscopy.

^{1}HNMR spectra were recorded on Bruker 600 MHz (with cryoprobe) spectrometers in the indicated deuterated solvents. Data are reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant(s) (*J*, Hz), integration. All signals were referenced to the internal solvent signal as standard ($CDCl_3$, δ 7.26). ^{13}C NMR spectra were recorded with ^{1}H-decoupling on Bruker 151 MHz (with cryoprobe) spectrometers in the indicated deuterated solvent. Mass spectra were recorded on a Thermo LTQ Orbitrap xl with an ESI probe (capillary temperature: 350 °C, sheath gas flow: 40.00 arb, aux gas flow: 10.00 arb, sweep gas flow: 2.00 arb, spray voltage: 5.00 kV, source current: 100 μA, capillary voltage: 6.00 V, tube lens: 90.00 V). Column chromatography (petroleumether/ethyl acetate) was performed on silica gel (200-300 mesh).

General procedure for the preparation of catalysts and nitrones

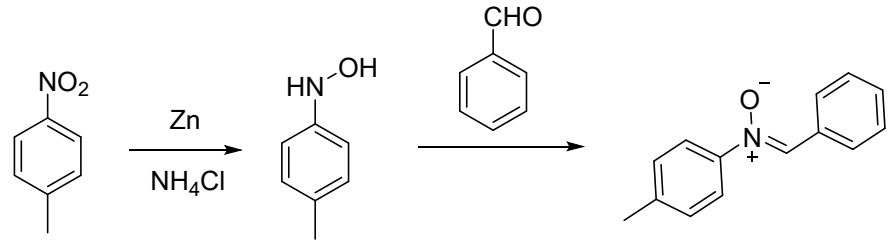
$[Cp^*RhCl_2]_2$,[1] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$,[2] nitrones[3] were synthesized according to published procedures.



$[Cp^*RhCl_2]_2$: The known title complex was prepared as follows. To $RhCl_3 \cdot 3H_2O$ (1.0 g, 3.8 mmol) in 25 mL of methanol was added excess pentamethylcyclopentadiene (0.9 mL, 5.7 mmol, 1.5 equiv). The mixture was stirred under reflux for 20 h. After the mixture was cooled to room temperature, the product was isolated by filtration and washing with ether. Yield 858 mg (73%).

$$[Cp^*RhCl_2]_2 \xrightarrow[CH_3CN]{AgSbF_6} [Cp^*Rh(CH_3CN)_3][SbF_6]_2$$

$[Cp^*Rh(CH_3CN)_3][SbF_6]_2$: To the suspension of $[Cp^*RhCl_2]_2$ (700 mg, 1.13 mmol) in dried CH_3CN (9 mL), the solution of $AgSbF_6$ (1.9 g, 5.53 mmol, 4.9 equiv) in dried CH_3CN (10 mL) was added. Then the white solid precipitated immediately. The reaction was stirred at r.t. for another 3 h. Then the solid was removed by filtration on celite and washed with CH_3CN (10 mL x 3). The filtrate was evaporated in *vacuo* to 10 mL, Et_2O (15 mL) was added dropwise and the pale yellow solid precipitated. The pale yellow solid was collected by filtration, washed with EtOAc (10 mL x 3) and Et_2O (10 mL), dired in *vacuo* to afford $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (858 mg, 76% yield).

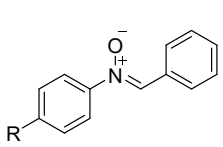


One-pot synthesis

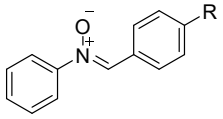
Nitroarene (1.0 equiv), aldehyde (1.1 equiv) and NH_4Cl (1.2 equiv) were added to a mixture of EtOH (2 mL/mmol of starting material) and H_2O (2 mL/mmol of starting material). Then the resulting mixture was cooled to 0 °C. Zinc powder (2.0 equiv) was added with several batches over 4 hours at 0 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 16 hours. The reaction mixture was filtered through a pad of celite and washed with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4, filtered and

concentrated to give the crude nitrones. Pure nitrones were obtained by recrystallization from ethanol or column chromatagraphy with silica gel.

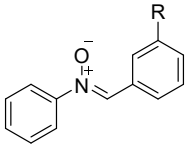
List of nitrones:



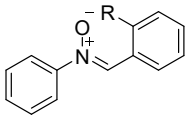
1a, R = Me;
1b, R = H;
1c, R = OMe;
1d, R = SMe;
1e, R = F;
1f, R = Cl;
1g, R = Br;
1h, R = COOEt;
1i, R = COMe



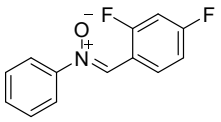
1j, R = Me;
1k, R = OMe;
1l, R =Br;
1m, R = COOMe;
1n, R = CF_3;
1o, R = CN



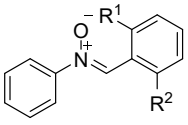
1p, R = Me;
1q, R = OMe;
1r, R = Cl;
1s, R = Br



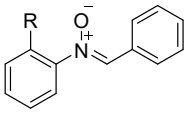
1t, R = Me;
1u, R = OMe



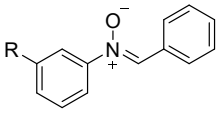
1v



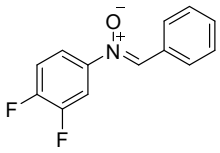
1w, R^1 = F, R^2 = F;
1x, R^1 = Cl, R^2 = Cl



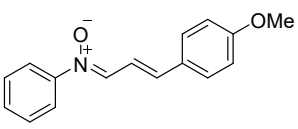
1y, R = Me



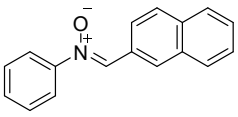
1z, R = F;
1aa, R =Me;
1ab, R = COMe



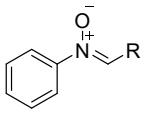
1ac



1ad

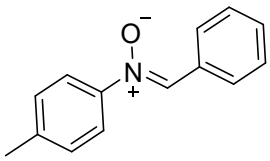


1ae

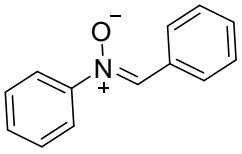


1af, R = 2-furyl;
1ag, R= 3-thienyl

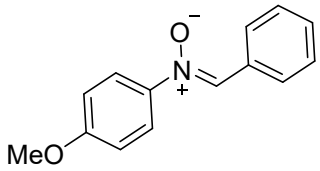
For those nitrones (**1j-1m**, **1o-1q**, **1t-1u**, **1x**, **1ae**) whose analytical data can be easily found in other literature, only ^{1}H-NMR and LRMS data would be supplied below. For others, ^{1}H-NMR, ^{13}C-NMR and HRMS data would be reported in the following part.



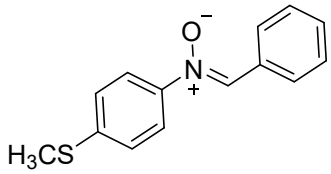
Compound **1a**: Yield 60% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.1, 1.9 Hz, 2H), 7.90 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 140.2, 134.1, 130.8, 130.8, 129.6, 129.0, 128.6, 121.5, 21.1; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{14}H_{14}NO$: 212.1070, found: 212.1076.



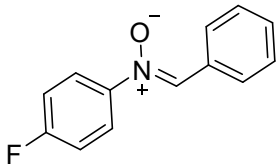
Compound **1b**: Yield 52% from recrystallization; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.34 (m, 2H), 7.92 (s, 1H), 7.82 – 7.70 (m, 2H), 7.47 (dtd, *J* = 8.0, 5.5, 4.9, 2.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 134.6, 130.9, 130.5, 129.9, 129.1, 129.0, 128.6, 121.7; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{12}NO$: 198.0913, found: 198.0909.



Compound **1c**: Yield 55% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 – 8.30 (m, 2H), 7.87 (s, 1H), 7.77 – 7.66 (m, 2H), 7.53 – 7.39 (m, 3H), 6.98 – 6.84 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 141.3, 132.7, 129.7, 129.7, 127.9, 127.6, 121.9, 112.9, 54.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{14}H_{14}NO_2$: 228.1019, found: 228.1011.

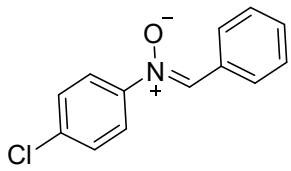


Compound 1**d**: Yield 58% from recrystallization; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 – 8.34 (m, 2H), 7.91 (s, 1H), 7.73 – 7.65 (m, 2H), 7.46 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.32 – 7.24 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 141.3, 133.9, 130.8, 130.5, 128.9, 128.5, 125.9, 121.8, 15.3; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{14}H_{14}NOS$: 244.0791, found: 244.0796.

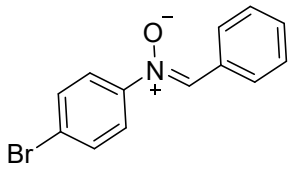


Compound **1e**:Yield 46% from recrystallization; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.33 (m, 2H), 7.87 (s, 1H), 7.82 – 7.72 (m, 2H), 7.51 – 7.41 (m, 3H), 7.19 – 7.06 (m,

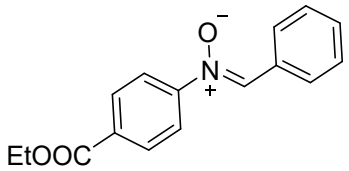
2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9 (d, *J* = 250.7 Hz), 145.1 (d, *J* = 3.0 Hz), 134.5, 131.0, 130.4, 129.0, 128.6, 123.6 (d, *J* = 8.8 Hz),115.9 (d, *J* = 23.3 Hz); HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{11}FNO$: 216.0819, found: 216.0812.



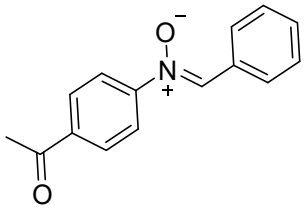
Compound **1f**: Yield 65% from recrystallization, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 – 8.35 (m, 2H), 7.90 (s, 1H), 7.76 – 7.70 (m, 2H), 7.49 – 7.46 (m, 3H), 7.46 – 7.42 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 135.7, 134.6, 131.2, 130.3, 129.2, 129.0, 128.6, 123.0; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{11}ClNO$: 232.0524, found: 232.0518.



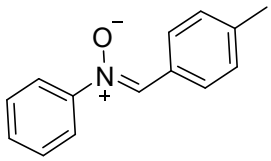
Compound **1g**: Yield 53% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.31 (m, 1H), 7.90 (s, 1H), 7.71 – 7.63 (m, 1H), 7.63 – 7.55 (m, 1H), 7.48 (dd, *J* = 4.8, 1.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 134.6, 132.2, 131.2, 130.3, 129.1, 128.7, 123.8, 123.2; HRMS (ESI^+) m/z:calcd for $[M+H]^+$ $C_{13}H_{11}BrNO$: 276.0019, found: 276.0028.



Compound **1h**: Yield 45% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 2H), 8.18 – 8.08 (m, 2H), 7.98 (s, 1H), 7.88 – 7.81 (m, 2H), 7.47 (dd, *J* = 5.1, 1.9 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 150.7, 134.3, 130.7, 130.4, 129.6, 129.3, 128.2, 127.7, 120.7, 60.5, 13.3;HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{16}H_{15}NO_3$: 270.1125, found: 270.1133.

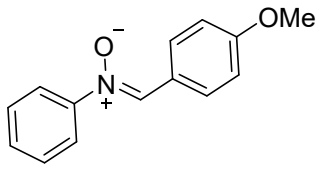


Compound **1i**: Yield 42% from recrystallization;^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 6.8, 2.9 Hz, 2H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.99 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.44 (m, 3H), 2.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 151.7, 137.9, 135.4, 131.5, 130.2, 129.4, 129.3, 128.7, 122.0, 26.8; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{15}H_{14}NO_2$: 240.1019, found: 240.1026.



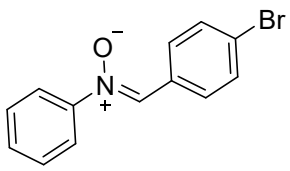
Compound **1j**: Yield 56% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 2H), 7.89 (s, 1H), 7.78 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.48 (qd, *J* = 7.6, 6.5, 3.8 Hz, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+ C_{14}H_{13}NO$: 212.1, found: 212.2.

Analytical data of compound **1j** were identical to previously reported values.[4]



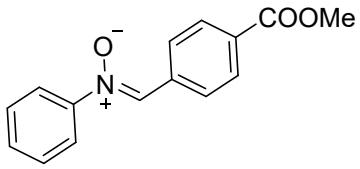
Compound **1k**: Yield 41% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.7 Hz, 2H), 7.85 (s, 1H), 7.76 (dq, *J* = 7.9, 1.5 Hz, 2H), 7.45 (dddd, *J* = 13.7, 7.1, 3.6, 2.0 Hz, 3H), 6.98 (dt, *J* = 9.0, 1.7 Hz, 2H), 3.87 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+ C_{16}H_{14}NO_2$: 228.1, found: 228.1.

Analytical data of compound **1k** were identical to previously reported values.[3]



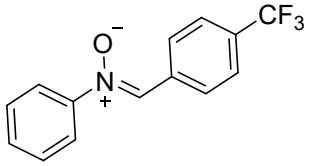
Compound **1l**: Yield 43% from recrystallization, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 – 8.10 (m, 2H), 7.89 (s, 1H), 7.83 – 7.70 (m, 2H), 7.65 – 7.54 (m, 2H), 7.47 (dd, *J* = 5.3, 2.0 Hz, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{11}BrNO$: 276.0, found: 276.1.

Analytical data of compound **1l** were identical to previously reported values.[5]

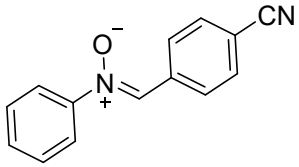


Compound **1m**: Yield 47% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 2H), 8.17 – 8.08 (m, 2H), 7.99 (s, 1H), 7.82 – 7.71 (m, 2H), 7.57 – 7.41 (m, 3H), 3.93 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+C_{16}H_{14}NO_3$: 256.1, found: 256.1.

Analytical data of compound **1m** were identical to previously reported values.[3]

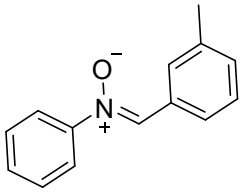


Compound **1n**: Yield 57% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.1 Hz, 2H), 8.00 (s, 1H), 7.83 – 7.65 (m, 4H), 7.58 – 7.35 (m, 3H);^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 133.6, 133.1, 131.7 (q, *J* = 32.5 Hz), 130.4, 129.2, 128.9,125.5 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 121.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{10}F_3NO$: 266.0787, found: 266.0792.



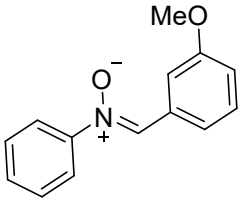
Compound **1o**: Yield 52% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.4 Hz, 2H), 8.00 (s, 1H), 7.92 – 7.71 (m, 4H), 7.52 (h, *J* = 2.7 Hz, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{11}N_2O$: 223.1, found: 223.1.

Analytical data of compound **1n** were identical to previously reported values.[4]



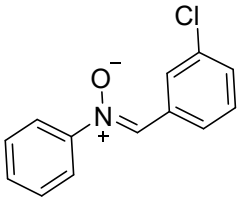
Compound **1p**: Yield 63% from column chromatography (SiO_2, PE/EA = 5:1 v/v),^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.88 (s, 1H), 7.84 – 7.72 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 2.42 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{14}NO$: 212.1, found: 212.2.

Analytical data of compound **1p** were identical to previously reported values.[6]

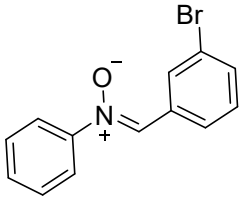


Compound **1q**: Yield 55% from column chromatography (SiO_2, PE/EA = 5:1 v/v),^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.92 (s, 1H), 7.85 – 7.69 (m, 2H), 7.65 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.04 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 3.89 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{14}NO_2$: 228.1, found: 228.3.

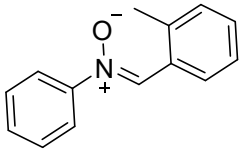
Analytical data of compound **1q** were identical to previously reported values.[4]



Compound **1r**: Yield 49% from recrystallization, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H), 7.80 – 7.69 (m, 2H), 7.47 (d, *J* = 5.3 Hz, 3H), 7.40 (dt, *J* = 15.5, 8.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.8, 134.6, 133.2, 132.1, 130.7, 130.2, 129.7, 129.2, 128.3, 127.0, 121.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{11}ClNO$: 232.0524, found: 232.0521.

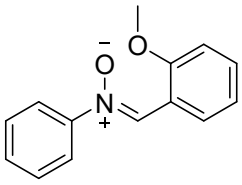


Compound **1s**: Yield 56% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (t, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.88 (s, 1H), 7.78 – 7.68 (m, 2H), 7.63 – 7.52 (m, 1H), 7.47 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.32 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 133.6, 133.0, 132.3, 131.2, 130.2, 130.0, 129.2, 127.4, 122.7, 121.6;HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{13}H_{11}BrNO$: 276.0019, found: 276.0025.



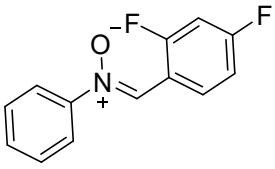
Compound **1t**: Yield 51% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 9.56 – 9.26 (m, 1H), 8.07 (s, 1H), 7.86 – 7.68 (m, 2H), 7.64 – 7.45 (m, 3H), 7.45 – 7.30 (m, 2H), 2.45 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+C_{14}H_{14}NO$: 212.1, found: 212.2.

Analytical data of compound **1t** were identical to previously reported values.[7]



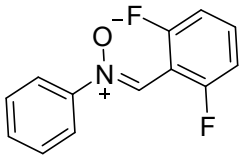
Compound **1u**: Yield 60% from column chromatography (SiO_2, PE/EA = 5:1 v/v),^{1}H NMR (600 MHz, $CDCl_3$) δ 9.48 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.40 (s, 1H), 7.78 (dt, *J* = 6.5, 1.4 Hz, 2H), 7.55 – 7.36 (m, 4H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.00 – 6.76 (m, 1H), 3.87 (s, 3H); LRMS (ESI^+) m/z: calcd for $[M+H]^+ C_{14}H_{14}NO_2$: 228.1, found: 228.2.

Analytical data of compound **1u** were identical to previously reported values.[4]

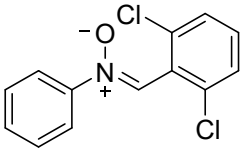


Compound **1v**: Yield 42% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (td, *J* = 8.7, 6.8 Hz, 1H), 8.14 (s, 1H), 7.85 – 7.66 (m, 2H), 7.56 – 7.43 (m, 3H), 7.01 (td, *J* = 8.6, 2.5 Hz, 1H), 6.88 (ddd, *J* = 11.0, 8.5, 2.6 Hz, 1H); ^{13}C NMR (151 MHz,

$CDCl_3$) δ 163.7 (dd, *J* = 256.2, 12.6 Hz), 161.9 (dd, *J* = 256.6, 11.7 Hz), 148.9, 130.2 (dd, *J* = 8.6, 2.3 Hz), 130.2, 129.6, 129.4, 129.2, 125.8 (d, *J* = 6.9 Hz), 121.6,115.9 (dd, *J* = 8.8, 3.9 Hz), 111.6 (dd, *J* = 20.8, 3.6 Hz), 103.6 (dd, *J* = 25.7, 25.7 Hz); HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_9F_2NO$: 234.0725, found: 234.0728.

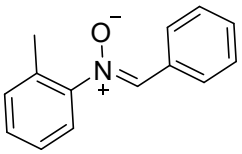


Compound **1w**: Yield 48% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.80 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.39 (tt, *J* = 8.4, 6.2 Hz, 1H), 6.98 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6 (dd, *J* = 255.6, 7.2 Hz), 148.0, 131.7 (t, *J* = 10.4Hz), 130.5, 129.0, 123.9, 121.8, 111.7 (dd, *J* = 21.2, 3.6 Hz), 108.4 (d, *J* = 3.1 Hz); HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_9F_2NO$: 234.0725, found: 234.0726.

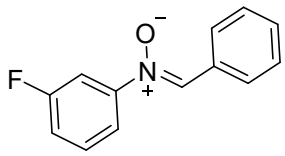


Compound **1x**: Yield 58% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.86 – 7.79 (m, 2H), 7.55 – 7.47 (m, 3H), 7.46 – 7.39 (m, 2H), 7.33 (dd, *J* = 8.7, 7.4 Hz, 1H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{13}H_{10}Cl_2NO$: 266.0, found: 266.3.

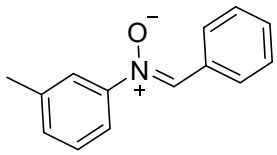
Analytical data of compound **1x** were identical to previously reported values.[8]



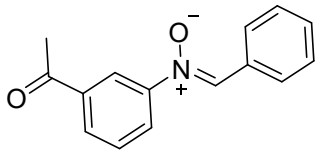
Compound **1y**: Yield 55% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.57 (s, 1H), 7.51 – 7.44 (m, 3H), 7.38 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.32 – 7.25 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 137.5, 131.6, 131.4, 130.8, 130.2, 129.3, 128.7, 128.6, 126.6, 123.3, 17.0; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{14}H_{14}NO$: 212.1070, found: 212.1073.



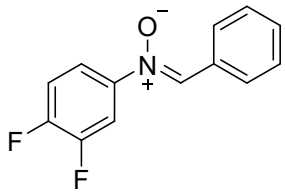
Compound **1z**: Yield 59% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.31 (m, 2H), 7.93 (s, 1H), 7.63 – 7.51 (m, 2H), 7.48 (m, 3H), 7.44 (td, *J* = 8.1, 5.8 Hz, 1H), 7.17 (td, *J* = 8.3, 1.9 Hz, 1H);^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, *J* = 249.2 Hz), 161.7, 150.2 (d, *J* = 9.1 Hz), 134.9, 131.3, 130.4 (d, *J* = 7.6 Hz), 130.2, 129.2, 128.7, 117.1 (d, *J* = 3.0 Hz), 117.0 (d, *J* = 21.1 Hz), 109.9 (d, *J* = 25.7).HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{13}H_{11}FNO$: 216.0819, found: 216.0827.



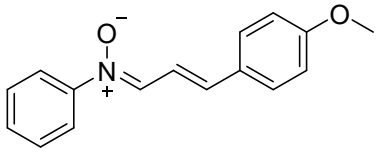
Compound **1aa**: Yield 65% from column chromatography (SiO_2, PE/EA = 5:1 v/v),^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 – 8.34 (m, 2H), 7.90 (s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.52 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 139.3, 134.5, 130.8, 130.5, 128.9, 128.8, 128.5, 122.3, 118.6, 21.3; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+$ $C_{14}H_{14}NO$: 212.1070, found: 212.1076.



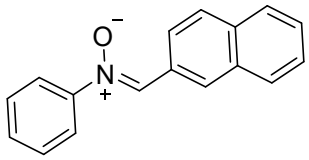
Compound **1ab**: Yield 56% from column chromatography (SiO_2, PE/EA = 2:1 v/v),^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 6.8, 3.1 Hz, 2H), 8.34 (t, *J* = 1.9 Hz, 1H), 8.06 – 8.01 (m, 2H), 8.00 (s, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.46 (m, 3H), 2.65 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 149.1, 137.7, 135.0, 131.3, 130.2, 129.6, 129.5, 129.2, 128.7, 126.1, 121.2, 26.8.; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{15}H_{14}NO_2$: 240.1019, found: 240.1025.



Compound **1ac**: Yield 47% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 – 8.33 (m, 2H), 7.90 (s, 1H), 7.75 (ddd, *J* = 10.4, 6.9, 2.7 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.53 – 7.47 (m, 3H), 7.32 – 7.27 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0 (dd, *J* = 252.8, 12.5 Hz), 150.0 (dd, *J* = 251.2, 12.9 Hz), 145.1 (dd, *J* = 6.6, 3.4 Hz), 134.7, 131.4, 130.1, 129.1, 128.7, 117.6 (dd, *J* = 6.9, 3.9 Hz), 117.5 (d, *J* = 18.9 Hz), 112.1 (d, *J* = 21.1 Hz); HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{13}H_{10}F_2NO$: 234.0725, found:234.0732.

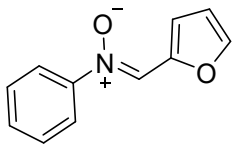


Compound **1ad**: Yield 53% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 9.7, 0.9 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.58 (dd, *J* = 16.2, 9.7 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.48 – 7.39 (m, 3H), 7.10 (d, *J* = 16.2 Hz, 1H), 6.93 – 6.86 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 147.3, 139.9, 136.7, 129.7, 129.1, 129.0, 128.8, 121.3, 116.9, 114.3, 55.3; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{16}H_{16}NO_2$: 254.1176, found: 254.1179.



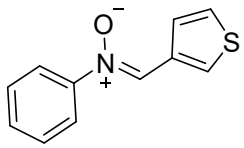
Compound **1ae**: Yield 42% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.04 – 7.97 (m, 2H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.84 (ddd, *J* = 8.0, 6.3, 1.3 Hz, 3H), 7.60 – 7.46 (m, 6H); LRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{17}H_{14}NO$: 248.1, found: 248.3.

Analytical data of compound **1ae** were identical to previously reported values.[4]



Compound **1af**: Yield 51% from recrystallization, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15

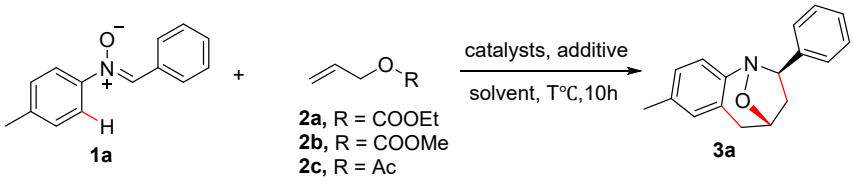
(s, 1H), 8.00 (d, J = 3.6 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.52 – 7.36 (m, 3H), 6.63 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 147.1, 144.6, 129.9, 129.1, 124.3, 120.9, 116.4, 112.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{11}H_9NO_2$: 188.0706, found: 188.0709.



Compound **1ag**: Yield 53% from recrystallization,^{1}H NMR (600 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.06 (s, 1H), 7.76 (d, J = 7.3 Hz, 2H), 7.45 (p, J = 6.3, 5.5 Hz, 4H), 7.36 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.9, 131.4, 129.8, 129.8, 129.1, 128.1, 125.4, 121.4; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{11}H_9NOS$: 204.0478, found: 204.0475.

Optimization of reaction conditions

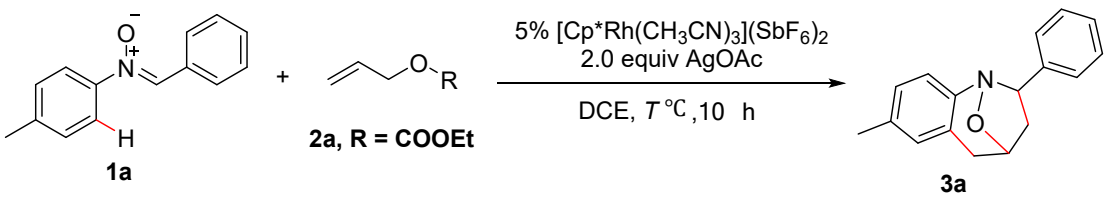
Table S1. Optimization of reaction conditions[a]



Entry	Allyl precursor	Catalysts	Additive (equiv.)	Solvent	T (℃)	Yield (%)[c]
1[b]	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	r.t.	0
2[b]	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	80	43
3[b]	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	120	55
4[b]	**2b**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	120	49
5[b]	**2c**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	120	30
6	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (2.0)	DCE	120	61
7	**2a**	2.5% $[Cp^*RhCl_2]_2$/10% $AgSbF_6$	AgOAc (2.0)	DCE	120	56
8	**2a**	-	AgOAc (2.0)	DCE	120	0
9	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	-	DCE	120	0
10	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	$Cu(OAc)_2$ (2.0)	DCE	120	0
11	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.0)	DCE	120	< 10
12	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2O (2.0)	DCE	120	< 10
13	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgF (2.0)	DCE	120	< 5
14	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	CsOAc (2.0)	DCE	120	20
15	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	PivOH (2.0)	DCE	120	< 10
16	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	NaOAc (2.0)	DCE	120	18
17	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (0.5)	DCE	120	28
18	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.0)	DCE	120	54
19	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	DCE	120	61
20	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	toluene	120	41
21	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	$PhCF_3$	120	47
22	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	PhCl	120	65
23	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	1,4-dioxane	120	46
24	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	CH_3CN	120	< 10
25	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	TFE	120	19
26	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	DMF	120	< 10
27	**2a**	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AgOAc (1.5)	DMSO	120	< 10

[a] Reaction conditions: 1a (0.3 mmol), 2 (0.2 mmol)，additive (0.3 mmol) and solvent (2 mL) was stirred at indicated temperature for 10 h; [b] 1a (0.2 mmol), 2 (0.3 mmol), catalyst (5 mol%), additive (0.4 mmol) and solvent (2 mL) was stirred at indicated temperature for 10 h;[c] Yield of isolated product. $PhCF_3$: benzotrifluoride; PhCl: chlorobenzene.

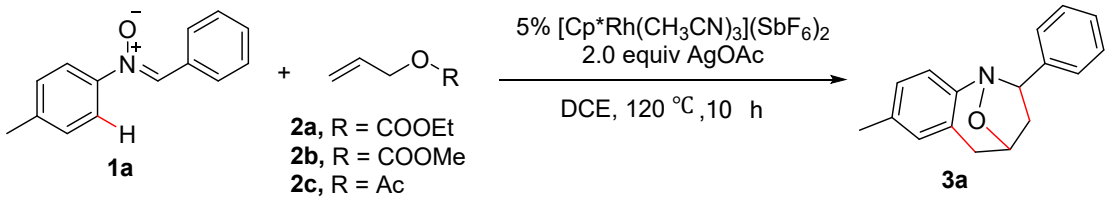
Table S1-1. Screening of temperature[a]



Entry	*T*(℃)	Yield (%)[c]
1	r.t.	0
2	80	43
3	120	55

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.3 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), AgOAc (0.4 mmol) and DCE (2 mL) was stirred at indicated temperature for 10 h; [b] Yield of isolated product.

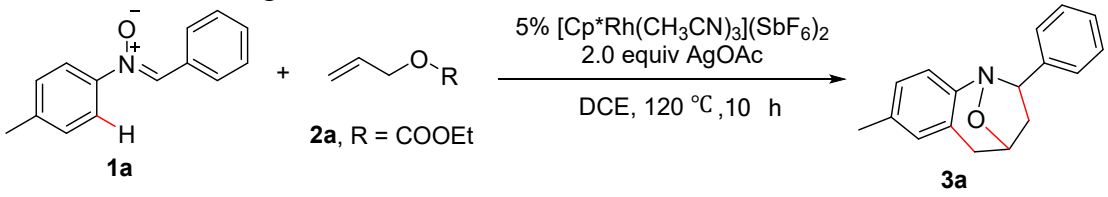
Table S1-2.Screening of allylprecursor[a]



Entry	Allyl precursor	Yield (%)[b]
3	**2a**	55
4	**2b**	49
5	**2c**	30

[a] Reaction conditions: 1a (0.2 mmol), 2 (0.3 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), AgOAc (0.4 mmol) and DCE (2 mL) was stirred at120 ℃ for 10 h; [b] Yield of isolated product.

Table S1-3.Screening of substrate ratio[a]

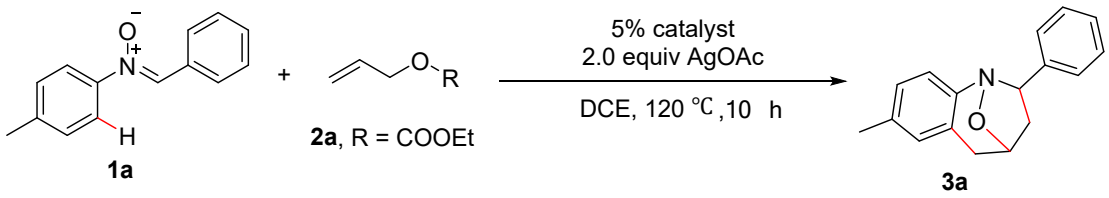


Entry	**1a** (mmol)	**2a** (mmol)	Yield (%)[b]
3	0.2	0.3	55

6	0.3	0.2	61

[a] Reaction conditions: 1a , 2a, $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), AgOAc (0.4 mmol) and DCE (2 mL) was stirred at 120 ℃ for 10 h; [b] Yield of isolated product.

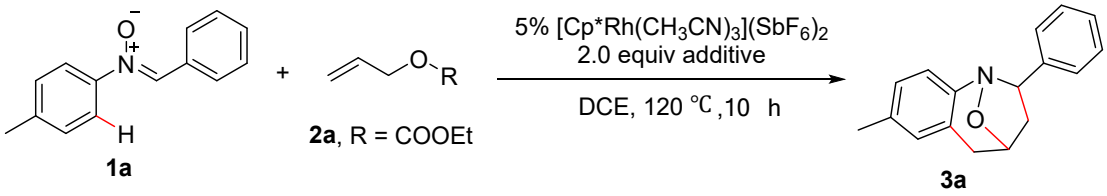
Table S1-4.Screening of catalyst[a]



Entry	Catalyst	Yield (%)[c]
6	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	61
7	2.5% $[Cp^*RhCl_2]_2$/10% $AgSbF_6$	56
8	none	0

[a] Reaction conditions: 1a (0.3 mmol), 2a (0.2 mmol), catalyst(5 mol%), AgOAc (0.4 mmol) and DCE (2 mL) was stirred at 120 ℃ for 10 h; [b] Yield of isolated product.

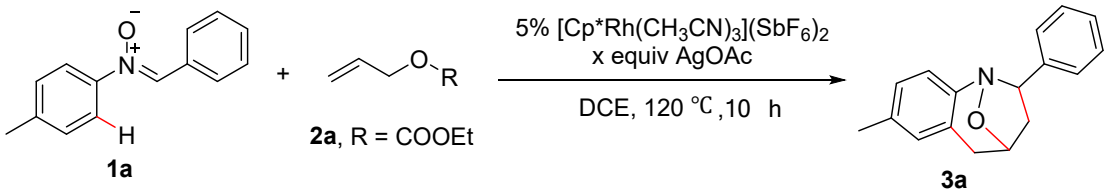
Table S1-5. Screening of additive[a]



Entry	additive	Yield (%)[b]
6	AgOAc	61
9	none	0
10	$Cu(OAc)_2$	0
11	Ag_2CO_3	< 10
12	Ag_2O	< 10
13	AgF	< 5
14	CsOAc	20
15	PivOH	< 10
16	NaOAc	18

[a] Reaction conditions: 1a (0.3 mmol), 2 (0.2 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), additive (0.4 mmol) and DCE (2 mL) was stirred at 120 ℃ for 10 h; [b] Yield of isolated product.

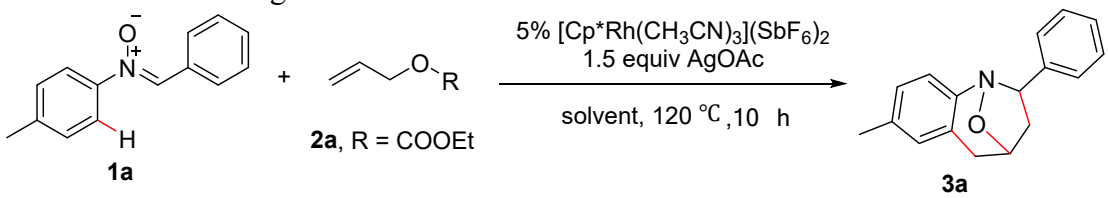
Table S1-6.Screening of AgOAc equivalent[a]



Entry	AgOAc equivalent	Yield (%)[b]
6	2.0	61
17	0.5	28
18	1.0	54
19	1.5	61

[a] Reaction conditions: 1a (0.3 mmol), 2 (0.2 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), AgOAc and DCE (2 mL) was stirred at 120 ℃ for 10 h; [b] Yield of isolated product.

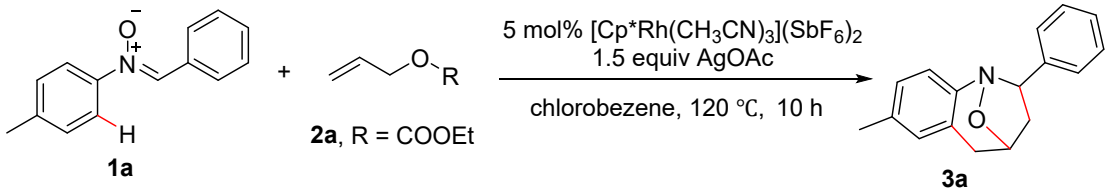
Table S1-7. Screening of solvent[a]



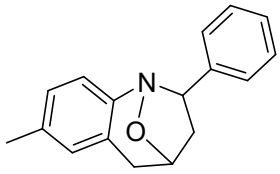
Entry	Solvent	Yield (%)[b]
19	DCE	61
20	toluene	41
21	$PhCF_3$	47
22	PhCl	65
23	1,4-dioxane	46
24	CH_3CN	< 10
25	TFE	19
26	DMF	< 10
27	DMSO	< 10

[a] Reaction conditions: 1a (0.3 mmol), 2 (0.2 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), AgOAc (0.3 mmol) and solvent (2 mL) was stirred at 120 ℃ for 10 h; [b] Yield of isolated product.

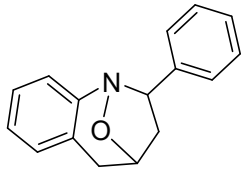
General procedure for the synthesis of 3 (taking 3a as an example):



$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8 mg, 0.01 mmol, 5% equiv), AgOAc (50 mg, 0.3 mmol, 1.5 equiv), nitrone **1a** (63 mg, 0.3 mmol, 1.5 equiv), the allyl precursor **2a** (26 mg, 0.2 mmol, 1.0 equiv) and chlorobenzene (2 mL) were added to a test tube. The reaction mixture was stirred at 120 ℃ for 10 h. After cooling to room temperature, the reaction mixture was filtered through a pad of celite washing with CH_2Cl_2. The solvents was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using PE/EA (20:1) as eluents to afford the title compound **3a**.

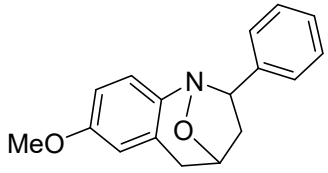


Compound **3a**: Yield 65%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.27 – 7.24 (m, 1H), 6.97 (d, J = 1.2 Hz, 2H), 6.94 (q, J = 1.1 Hz, 1H), 4.98 – 4.90 (m, 1H), 4.63 – 4.53 (m, 1H), 3.38 (dd, J = 16.5, 5.4 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.51 (d, J = 16.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 143.9, 135.5, 130.3, 128.5, 127.2, 126.9, 126.4, 124.9, 121.8, 75.5, 75.1, 42.5, 34.7, 21.0; HRMS (ESI$^+$) m/z: calcd for $[M+Na]^+C_{17}H_{18}NO$: 252.1383, found: 252.1391.

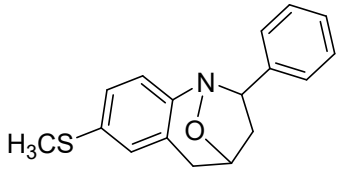


Compound **3b**: Yield 57%,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.21 – 7.11 (m, 3H), 7.11 – 7.06 (m, 1H), 4.97 (ddd, J = 8.0, 4.7, 2.6 Hz, 1H), 4.63 (dd, J = 7.7, 3.6 Hz, 1H), 3.43 (dd, J = 16.5, 5.3 Hz, 1H), 2.66 – 2.58 (m, 2H), 2.56 (d, J = 16.5 Hz, 1H); ^{13}C NMR (151

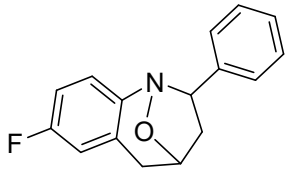
MHz, $CDCl_3$) δ 150.6, 143.7, 129.8, 128.5, 126.9, 126.6, 126.4, 125.9, 125.2, 122.0, 75.4, 75.1, 42.5, 34.7; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{16}H_{16}NO$: 238.1226, found: 238.1253.



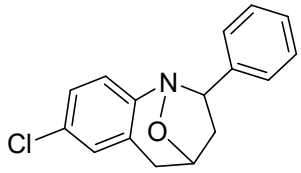
Compound **3c**: Yield 47%, ^1H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.21 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.9 Hz, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 4.94 (td, *J* = 5.8, 3.8 Hz, 1H), 4.56 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.79 (s, 3H), 3.40 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.64 – 2.56 (m, 2H), 2.53 (d, *J* = 16.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 143.8, 143.8, 128.4, 126.9, 126.4, 126.3, 122.9, 114.6, 112.0, 75.5, 74.8, 55.4, 42.5, 35.0;HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{17}H_{18}NO_2$: 268.1332, found: 268.1266.



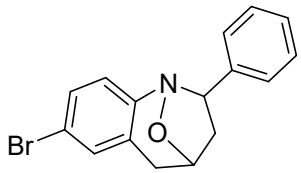
Compound **3d**: Yield 44%, ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.21 (m, 1H), 7.08 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.06 – 6.96 (m, 2H), 4.95 (ddd, *J* = 7.6, 5.4, 2.3 Hz, 1H), 4.58 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.39 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.66 – 2.55 (m, 2H), 2.53 (d, *J* = 16.6 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 143.6, 135.5, 128.5, 128.2, 127.0, 126.4, 126.0, 125.3, 122.5, 75.4, 74.9, 42.5, 34.7, 16.4; HRMS (ESI^+) m/z: calcd for $[M+Na]^+C_{17}H_{17}NOSNa$: 306.0923, found: 306.0934.



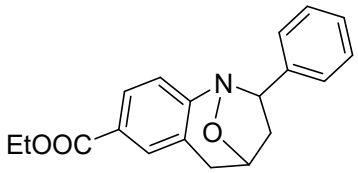
Compound **3e**: Yield 63%,^1H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.36 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.05 (dd, *J* = 8.5, 5.2 Hz, 1H), 6.90 – 6.82 (m, 2H), 5.03 – 4.88 (m, 1H), 4.58 (dd, *J* = 8.3, 3.1 Hz, 1H), 3.41 (dd, *J* = 16.8, 5.5 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.58 – 2.51 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.45(d, *J* = 244.0 Hz*)*,146.4(d, *J* = 2.7 Hz*)*, 143.5, 128.5, 127.3(d, *J* = 8.3 Hz*)*, 127.0, 126.3, 123.5(d, *J* = 8.5 Hz*)*, 116.1(d, *J* = 22.7 Hz*)*, 113.5(d, *J* = 22.7 Hz*)*, 75.4, 74.5, 42.5, 34.8; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{16}H_{15}FNO$: 256.1132, found: 256.1121.



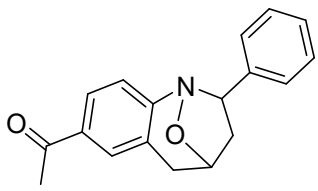
Compound **3f**: Yield 66%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.36 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.17 – 7.11 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 4.95 (ddd, *J* = 7.5, 5.3, 2.0 Hz, 1H), 4.58 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.39 (ddd, *J* = 16.8, 5.5, 1.2 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.53 (d, *J* = 16.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.10, 142.34, 130.12, 128.62, 127.50, 126.22, 126.07, 125.76, 125.33, 122.33, 74.35, 73.60, 41.48, 33.56; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{16}H_{15}ClNO$: 272.0837, found: 272.0842.



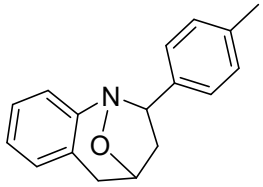
Compound **3g**: Yield 61%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.06 – 6.93 (m, 1H), 5.05 – 4.76 (m, 1H), 4.58 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.40 (ddd, *J* = 16.7, 5.4, 1.2 Hz, 1H), 2.73 – 2.46 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.6, 143.3, 132.6, 129.7, 128.5, 127.7, 127.1, 126.3, 123.7, 118.9, 75.3, 74.6, 42.5, 34.5; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{16}H_{15}BrNO$: 316.0332, found: 316.0338.



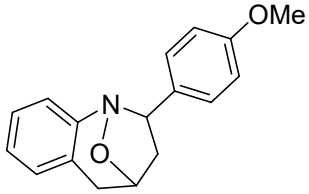
Compound **3h**: Yield 63%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.51 – 7.44 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 4.99 (ddd, *J* = 7.4, 5.3, 1.9 Hz, 1H), 4.64 (dd, *J* = 8.6, 2.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.55 – 3.39 (m, 1H), 2.66 (dddd, *J* = 12.9, 7.7, 2.8, 1.2 Hz, 1H), 2.63 – 2.55 (m, 2H), 1.39 (dd, *J* = 7.4, 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 154.6, 143.2, 131.4, 128.5, 128.2, 128.1, 127.1, 126.3, 125.5, 121.9, 75.3, 74.8, 61.0, 42.5, 34.6, 14.3; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{19}H_{20}NO_3$: 310.1438, found: 310.1483.



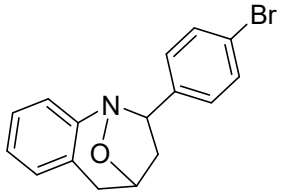
Compound **3i**: Yield 67%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.70 (m, 2H), 7.55 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.25 (m, 1H), 7.21 – 7.12 (m, 1H), 5.00 (ddd, *J* = 7.5, 5.3, 1.9 Hz, 1H), 4.64 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.52 – 3.42 (m, 1H), 2.67 (dddd, *J* = 12.8, 7.7, 2.8, 1.2 Hz, 1H), 2.65 – 2.55 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 154.9, 143.1, 134.9, 130.2, 128.5, 127.2, 127.1, 126.3, 125.8, 122.0, 75.2, 74.8, 42.4, 34.7, 26.6; HRMS (ESI$^+$) m/z: calcd for $[M+Na]^+C_{18}H_{17}NO_2Na$: 302.1152, found: 302.1156.



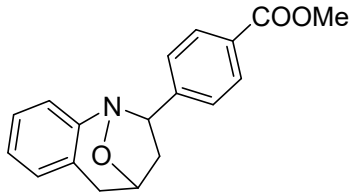
Compound **3j**: Yield 70%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.23 – 7.12 (m, 5H), 7.08 (dd, *J* = 7.3, 1.3 Hz, 1H), 4.97 (ddd, *J* = 7.7, 5.4, 2.4 Hz, 1H), 4.60 (dd, *J* = 8.1, 3.2 Hz, 1H), 3.42 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.55 (d, *J* = 16.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 140.8, 136.6, 129.8, 129.1, 126.5, 126.3, 125.9, 125.2, 121.9, 75.3, 75.0, 42.4, 34.7, 21.0; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{17}H_{18}NO$: 252.1383, found: 252.1358.



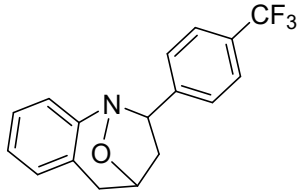
Compound **3k**: Yield 46%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 2H), 7.21 – 7.11 (m, 3H), 7.09 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.95 – 6.81 (m, 2H), 4.98 (ddd, *J* = 7.5, 5.3, 2.3 Hz, 1H), 4.58 (dd, *J* = 8.1, 3.0 Hz, 1H), 3.81 (s, 3H), 3.51 – 3.28 (m, 1H), 2.77 – 2.38 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.57, 150.53, 135.98, 129.88, 129.78, 127.64, 126.53, 125.89, 125.19, 121.94, 113.80, 75.07, 55.31, 42.36, 34.68; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{17}H_{18}NO_2$: 268.3353, found: 268.3368.



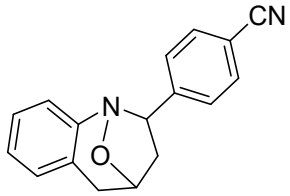
Compound **3l**: Yield 57%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.40 – 7.30 (m, 2H), 7.23 – 7.10 (m, 3H), 7.06 (dd, *J* = 7.2, 1.6 Hz, 1H), 4.95 (ddd, *J* = 7.5, 5.3, 2.0 Hz, 1H), 4.57 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.42 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.65 – 2.50 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 142.8, 131.5, 129.8, 128.2, 126.6, 126.1, 125.2, 121.9, 120.8, 75.1, 74.7, 42.5, 34.6; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{15}BrNO$: 316.0332, found: 316.0349.



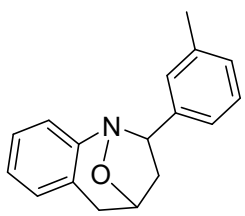
Compound **3m**: Yield 72%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.16 (dtd, *J* = 13.8, 7.1, 4.8 Hz, 3H), 7.11 – 7.03 (m, 1H), 4.96 (ddd, *J* = 7.7, 5.4, 1.7 Hz, 1H), 4.66 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.92 (d, *J* = 0.8 Hz, 3H), 3.43 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.72 – 2.50 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 150.2, 148.8, 129.8, 128.7, 126.6, 126.4, 126.1, 125.2, 121.9, 77.0, 75.1, 74.9, 52.0, 42.6, 34.6; HRMS (ESI^+) m/z: calcd for $[M+Na]^+C_{18}H_{17}NO_3Na$: 318.1101, found: 318.1112.



Compound **3n**: Yield 69%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.54 (m, 4H), 7.22 – 7.11 (m, 3H), 7.07 (dd, *J* = 7.1, 1.8 Hz, 1H), 4.97 (ddd, *J* = 7.5, 5.2, 1.9 Hz, 1H), 4.67 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.43 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.66 (ddd, *J* = 12.7, 8.7, 2.0 Hz, 1H), 2.61 – 2.54 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 147.6, 129.9, 129.1 (**q, *J* = 32.5 Hz**), 126.7, 126.7, 126.2, 125.4 (**q, *J* = 3.8 Hz**), 125.2, 124.2 (**q, *J* = 271.8 Hz**), 121.9, 75.2, 74.7, 42.6, 34.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{17}H_{15}F_3NO$: 306.1101, found: 306.1125.

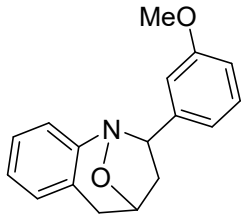


Compound **3o**: Yield 73%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.11 (m, 3H), 7.11 – 7.02 (m, 1H), 4.96 (ddd, *J* = 7.5, 5.3, 1.7 Hz, 1H), 4.65 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.43 (dd, *J* = 16.7, 5.4 Hz, 1H), 2.66 (ddd, *J* = 12.7, 8.8, 1.9 Hz, 1H), 2.60 – 2.51 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 148.9, 132.3, 129.9, 127.1, 126.7, 126.3, 125.1, 121.8, 118.9, 110.7, 75.2, 74.6, 42.6, 34.5; HRMS (ESI^+) m/z: calcd for $[M+H]^+C_{17}H_{15}N_2O$: 263.1179, found: 263.1185.

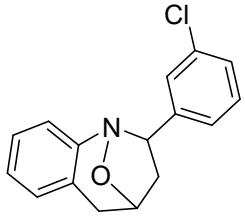


Compound **3p**: Yield 41%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dq, *J* = 1.9, 1.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 7.15 – 7.12 (m, 2H), 7.08 (dd, *J* = 7.2, 1.3 Hz, 2H), 4.97 (ddd, *J* = 7.6, 5.4, 2.4 Hz, 1H), 4.59 (dd, *J* = 8.1, 3.3 Hz, 1H), 3.43

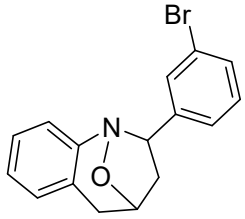
(dd, J = 16.5, 5.4 Hz, 1H), 2.67 – 2.57 (m, 2H), 2.55 (d, J = 16.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 143.7, 138.2, 129.8, 128.4, 127.7, 127.0, 126.6, 125.9, 125.3, 123.5, 122.0, 75.4, 75.1, 42.5, 34.7, 21.5; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{17}H_{18}NO$: 252.1383, found: 252.1326.



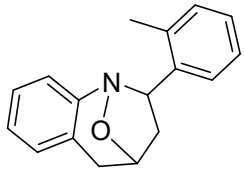
Compound **3q**: Yield 49%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, J = 7.9 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.16 – 7.10 (m, 2H), 7.08 (dt, J = 7.7, 1.5 Hz, 2H), 7.02 (dp, J = 7.6, 0.7 Hz, 1H), 6.81 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 4.96 (ddd, J = 7.9, 5.5, 3.0 Hz, 1H), 4.67 – 4.54 (m, 1H), 3.84 (s, 3H), 3.42 (dd, J = 16.5, 5.4 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.55 (d, J = 16.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 151.6, 146.4, 130.8, 130.5, 127.6, 127.0, 126.2, 123.0, 119.7, 113.5, 113.0, 76.3, 76.0, 56.3, 43.6, 35.6; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{17}H_{18}NO_2$: 268.1333, found: 268.1358.



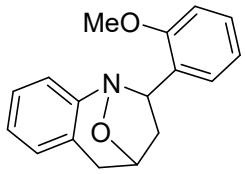
Compound **3r**: Yield 61%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 2.0 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.22 – 7.13 (m, 2H), 7.13 – 7.03 (m, 3H), 6.99 (dd, J = 7.3, 1.6 Hz, 1H), 4.89 (td, J = 7.1, 6.4, 2.5 Hz, 1H), 4.50 (dd, J = 8.1, 3.4 Hz, 1H), 3.35 (dd, J = 16.6, 5.4 Hz, 1H), 2.62 – 2.36 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 145.7, 134.4, 129.8, 129.7, 127.1, 126.7 126.7, 126.1, 125.2, 124.6, 121.9, 75.1, 74.7, 42.5, 34.6; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{15}ClNO$: 272.0837, found: 272.0825.



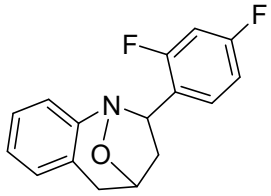
Compound **3s**: Yield 64%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (t, J = 1.9 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.22 (t, J = 7.8 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.07 (dd, J = 7.2, 1.6 Hz, 1H), 4.96 (ddd, J = 7.3, 5.4, 2.4 Hz, 1H), 4.58 (dd, J = 8.1, 3.3 Hz, 1H), 3.42 (dd, J = 16.6, 5.4 Hz, 1H), 2.65 – 2.47 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 146.0, 130.0, 129.8, 129.5, 126.7, 126.1, 125.1, 125.1, 122.6, 121.9, 75.1, 74.7, 42.5, 34.6; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{15}BrNO$: 317.2053, found: 317.2073.



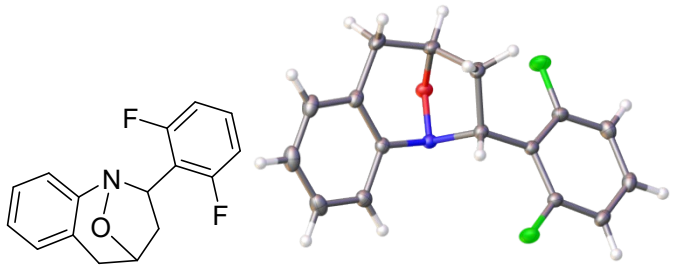
Compound **3t**: Yield 56%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.21 – 7.12 (m, 5H), 7.07 (dd, *J* = 6.8, 1.5 Hz, 1H), 4.94 (ddd, *J* = 7.6, 5.4, 1.9 Hz, 1H), 4.73 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.43 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.63 (ddd, *J* = 12.4, 8.6, 1.9 Hz, 1H), 2.56 (d, *J* = 16.5 Hz, 1H), 2.46 (dddd, *J* = 12.2, 7.8, 2.9, 1.3 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 141.8, 134.0, 130.0, 129.8, 126.8, 126.6, 126.2, 125.9, 125.8, 125.3, 121.9, 75.0, 72.5, 42.1, 34.7, 19.7; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{17}H_{18}NO$: 252.1383, found: 252.1394.



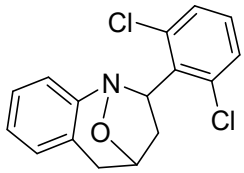
Compound **3u**: Yield 59%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (ddd, *J* = 7.5, 1.8, 0.7 Hz, 1H), 7.25 (td, *J* = 7.8, 1.7 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.07 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.01 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.89 (td, *J* = 7.9, 7.2, 2.0 Hz, 2H), 3.81 (s, 3H), 3.41 (dd, *J* = 16.5, 5.4 Hz, 1H), 2.71 – 2.33 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 150.8, 131.9, 129.7, 127.8, 126.7, 126.4, 125.7, 125.4, 122.0, 120.5, 109.9, 74.8, 70.0, 55.2, 42.1, 34.8; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{14}F_2NO$: 268.1332, found: 268.1354.



Compound **3v**: Yield 68%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (td, *J* = 8.6, 6.5 Hz, 1H), 7.23 – 7.11 (m, 3H), 7.06 (dd, *J* = 7.2, 1.7 Hz, 1H), 6.90 (tdd, *J* = 8.5, 2.6, 1.1 Hz, 1H), 6.78 (ddd, *J* = 10.3, 8.8, 2.5 Hz, 1H), 4.94 (ddd, *J* = 7.5, 5.3, 1.8 Hz, 1H), 4.83 (dt, *J* = 8.7, 1.9 Hz, 1H), 3.50 – 3.34 (m, 1H), 2.63 (ddd, *J* = 12.8, 8.6, 1.9 Hz, 1H), 2.56 (d, *J* = 16.6 Hz, 1H), 2.50 (dddt, *J* = 12.9, 7.7, 2.7, 1.3 Hz, 1H)；^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 **(dd, *J* = 247.6, 12.1 Hz)**, 159.6 **(dd, *J* = 247.6, 12.1 Hz)** , 150.1, 129.8, 128.8 **(dd, *J* = 9.1, 4.5 Hz)**, 126.7 **(dd, *J* = 13.6, 4.5 Hz)**, 126.7, 126.2, 125.1, 122.0, 111.1 **(dd, *J* = 21.1, 3.0 Hz)**, **103.3 (dd, *J* = 25.7, 25.7 Hz)**, 75.0, 68.5 **(d, *J* = 1.5 Hz)** , 41.9, 34.6; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{14}F_2NO$: 274.1038, found: 274.1045.

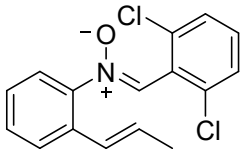


Compound **3w**: Yield 54%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.21 (ddd, *J* = 9.5, 5.8, 2.3 Hz, 1H), 7.18 – 7.13 (m, 3H), 6.98 – 6.85 (m, 2H), 5.12 (ddd, *J* = 7.6, 5.1, 2.2 Hz, 1H), 4.99 (dd, *J* = 8.9, 2.2 Hz, 1H), 3.46 (dd, *J* = 16.4, 5.2 Hz, 1H), 3.14 – 2.99 (m, 1H), 2.58 (d, *J* = 16.3 Hz, 1H), 2.41 (ddq, *J* = 12.9, 8.9, 2.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1 **(dd, *J* = 249.9 ,7.8 Hz)**, 150.1, 129.8, 129.3 **(t, *J* = 10.6 Hz)**, 126.6, 126.1, 125.3, 122.0, 117.7 **(t, *J* = 16.0 Hz)**, 111.8,**(dd, *J* = 22.5, 4.8 Hz)**, 75.4, 66.3, 37.9 **(d, *J* = 2.9 Hz)** , 34.9; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{14}F_2NO$: 274.1038, found: 274.1047.



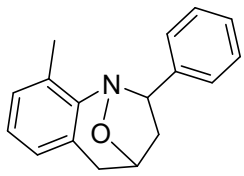
3x

Compound **3x**: Yield <5%, HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{14}Cl_2NO$: 306.0447, found: 306.0451.



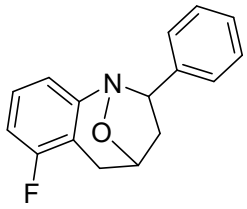
3x'

Compound **3x'**: Yield 60%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.67 – 7.56 (m, 1H), 7.50 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 6.83 (dq, *J* = 15.7, 1.8 Hz, 1H), 6.36 (dq, *J* = 15.7, 6.6 Hz, 1H), 1.91 (dd, *J* = 6.7, 1.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 134.7, 133.0, 130.8, 130.1, 129.0, 128.8, 127.2, 126.8, 126.4, 125.3, 123.9, 123.0, 17.8; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+C_{16}H_{14}Cl_2NO$: 306.0447, found: 306.0453.

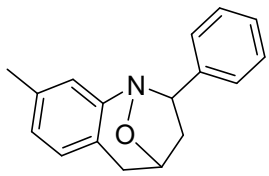


Compound **3y**: Yield 53%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.23 (m, 1H), 7.11 – 6.99 (m, 2H), 6.98 (dd, *J* = 7.0, 2.2 Hz, 1H), 4.96 (ddd, *J* = 7.5, 5.3, 2.1 Hz, 1H), 4.55 (dd, *J* = 8.4, 2.9 Hz, 1H),

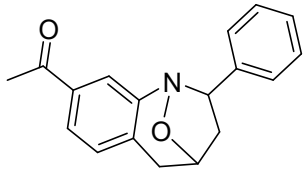
3.42 (dd, J = 16.5, 5.5 Hz, 1H), 2.68 – 2.56 (m, 2H), 2.53 (d, J = 16.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 143.6, 130.6, 128.5, 128.0, 127.3, 126.9, 126.4, 125.3, 124.8, 73.5, 42.6, 34.8, 17.0; HRMS (ESI^+)m/z: calcd for $[M+H]^+C_{17}H_{18}NO$: 252.1383, found: 252.1371.



Compound **3z**: Yield 71%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.33 – 7.26 (m, 1H), 7.16 (td, J = 8.0, 6.0 Hz, 1H), 6.96 – 6.86 (m, 2H), 5.00 (ddd, J = 7.5, 5.3, 1.9 Hz, 1H), 4.63 (dd, J = 8.6, 2.8 Hz, 1H), 3.30 (dd, J = 17.0, 5.5 Hz, 1H), 2.75 – 2.46 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3 (d, J = 246.7 Hz), 152.0 (d, J = 6.0 Hz), 143.3, 128.5, 127.4 (d, J = 9.4 Hz), 127.1, 126.3, 117.5 (d, J = 3.2 Hz), 113.2 (d, J = 20.2 Hz), 112.4(d, J = 21.4 Hz), 75.3, 74.1, 42.7, 29.3 (d, J = 2.3 Hz); HRMS (ESI^+)m/z: calcd for $[M+H]^+C_{16}H_{14}FNO$: 256.1132, found: 256.1148.

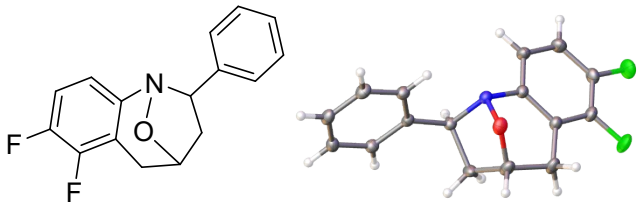


Compound **3aa**: Yield 56%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.02 (d, J = 7.7 Hz, 1H), 6.96 (dd, J = 7.7, 1.7 Hz, 1H), 6.91 (d, J = 1.8 Hz, 1H), 4.96 (ddd, J = 8.4, 4.9, 2.7 Hz, 1H), 4.71 – 4.54 (m, 1H), 3.38 (dd, J = 16.4, 5.4 Hz, 1H), 2.67 – 2.55 (m, 2H), 2.51 (d, J = 16.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 143.8, 136.4, 129.5, 128.4, 126.9, 126.7, 126.4, 122.4, 121.9, 75.4, 75.1, 42.5, 34.3, 21.0; HRMS (ESI^+)m/z: calcd for $[M+H]^+C_{17}H_{18}NO$: 252.1383, found: 252.1401.

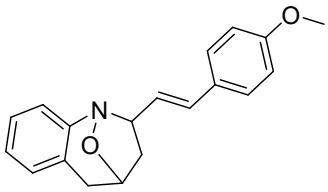


Compound **3ab**: Yield 68%,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.9, 1.8 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 1H), 7.24 (d, J = 7.8 Hz, 1H), 4.99 (ddd, J = 7.6, 5.3, 1.9 Hz, 1H), 4.65 (dd, J = 8.6, 2.8 Hz, 1H), 3.45 (ddt, J = 17.2, 5.4, 1.2 Hz, 1H), 2.69 – 2.59 (m, 3H), 2.57 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.4, 150.7, 143.2, 135.8, 131.4, 130.1, 128.5,

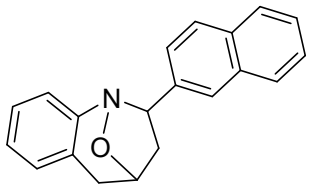
127.1, 126.3, 125.6, 122.2, 75.2, 74.7, 42.7, 34.9, 26.6; HRMS (ESI$^+$) m/z: calcd for [M+Na]$^+$$C_{18}H_{17}NO_2Na$: 302.1152, found: 302.1163.



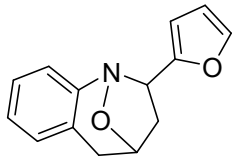
Compound **3ac**: Yield 52%,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.25 (m, 1H), 6.99 (q, *J* = 8.8 Hz, 1H), 6.86 (ddd, *J* = 8.7, 4.2, 1.7 Hz, 1H), 4.99 (t, *J* = 6.2 Hz, 1H), 4.58 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.32 (dd, *J* = 17.2, 5.4 Hz, 1H), 2.71 – 2.48 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9 (**dd, *J* = 247.6, 13.6 Hz**), 148.2(**dd, *J* = 246.1, 13.6 Hz**), 146.7 (**dd, *J* = 3.0, 3.0 Hz**), 143.1, 128.5, 127.2, 126.3,117.4 (**dd, *J* = 3.0, 3.0 Hz**), 115.5 (**d, *J* = 16.6 Hz**), 114.6 (**d, *J* =18.1 Hz**), 75.3, 73.5, 42.7, 29.4;HRMS (ESI$^+$) m/z: calcd for [M+H]$^+$$C_{16}H_{14}F_2NO$: 274.1038, found: 274.1023.



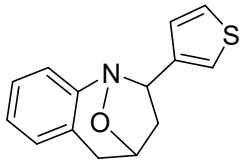
Compound **3ad**: Yield 41%,^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 9.7 Hz, 2H), 7.21 – 7.04 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.6 Hz, 1H), 4.92 (s, 1H), 4.26 – 4.13 (m, 1H), 3.81 (s, 3H), 3.39 (dd, *J* = 16.5, 5.2 Hz, 1H), 2.50 (d, *J* = 16.5 Hz, 1H), 2.38 (tt, *J* = 12.5, 6.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 150.0, 129.8, 129.5, 129.3, 129.2, 127.6, 126.5, 125.9, 125.1, 121.9, 113.9, 74.8, 74.7, 55.2, 40.7, 34.7; HRMS (ESI$^+$) m/z: calcd for [M+H]$^+$ $C_{19}H_{20}NO_2$: 294.1489, found: 294.1502.



Compound **3ae**: Yield 46%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.89 – 7.74 (m, 3H), 7.57 (dt, *J* = 8.5, 1.5 Hz, 1H), 7.47 (dq, *J* = 8.6, 7.0 Hz, 2H), 7.25 – 7.04 (m, 4H), 5.02 (td, *J* = 6.5, 2.4 Hz, 1H), 4.80 (dd, *J* = 8.0, 3.5 Hz, 1H), 3.46 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.79 – 2.64 (m, 2H), 2.59 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 141.0, 133.3, 132.5, 129.8, 128.3, 128.0, 127.5, 126.6, 126.0, 126.0, 125.7, 125.3, 124.8, 124.8, 122.0, 75.5, 75.2, 42.6, 34.7; HRMS (ESI$^+$) m/z:calcd for [M+H]$^+$ $C_{20}H_{18}NO$: 288.1383, found: 288.1372.

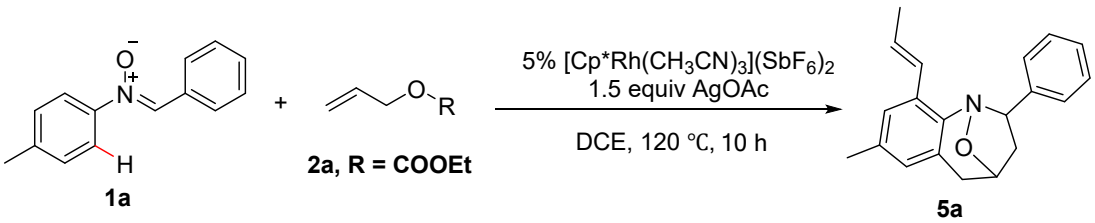


Compound **3af**: Yield 37%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.22 – 7.09 (m, 4H), 6.38 – 6.30 (m, 2H), 4.99 (ddd, *J* = 7.5, 5.3, 1.9 Hz, 1H), 4.64 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.46 – 3.37 (m, 1H), 2.78 (dddd, *J* = 12.8, 7.8, 2.7, 1.2 Hz, 1H), 2.54 (d, *J* = 16.5 Hz, 1H), 2.42 (ddd, *J* = 12.7, 8.7, 2.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 149.9, 142.0, 129.8, 126.7, 126.2, 125.1, 122.1, 110.3, 106.4, 74.8, 69.5, 38.6, 34.6; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{14}NO_2$: 228.1019, found: 228.1025.



Compound **3ag**: Yield 32%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.21 – 7.07 (m, 5H), 4.97 (ddd, *J* = 7.5, 5.2, 2.0 Hz, 1H), 4.67 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.55 – 3.33 (m, 1H), 2.61 (dddd, *J* = 12.6, 7.8, 2.5, 1.2 Hz, 1H), 2.57 – 2.46 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 144.8, 129.8, 126.6, 126.6, 126.0, 126.0, 125.1, 122.0, 120.9, 74.9, 71.9, 41.7, 34.7; HRMS (ESI^+) m/z: calcd for $[M+H]^+$ $C_{14}H_{14}NOS$: 244.0791, found: 244.0801.

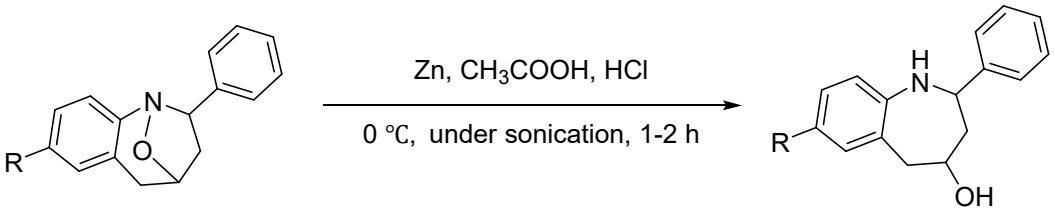
Experimental procedure for the synthesis of double molecular allylation product 5a



$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8 mg, 0.01 mmol, 5% equiv), AgOAc (50 mg, 0.3 mmol, 1.5 equiv), nitrone **1a** (63 mg, 0.2 mmol, 1.0 equiv), the allyl precursor **2a** (53 mg, 0.4 mmol, 2.0 equiv) and DCE (2 mL) were added to a test tube. The reaction mixture was stirred at 120 ℃ for 10 h. After cooling to room temperature, the reaction mixture was filtered through a pad of celite washing with CH_2Cl_2. The solvents was removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel using PE/EA (30:1) as eluents to afford double allylation product **5a**.

Compound **5a**:Yield 20%,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.25 (m, 1H), 7.19 – 7.08 (m, 1H), 6.93 – 6.77 (m, 2H), 6.17 (dq, *J* = 15.8, 6.6 Hz, 1H), 4.96 (ddd, *J* = 7.5, 5.2, 1.9 Hz, 1H), 4.50 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.39 (dd, *J* = 16.4, 5.4 Hz, 1H), 2.64 (dddd, *J* = 12.7, 7.8, 2.7, 1.2 Hz, 1H), 2.54 (ddd, *J* = 12.7, 8.6, 2.0 Hz, 1H), 2.48 (d, *J* = 16.4 Hz, 1H), 2.30 (s, 3H), 1.82 (dd, *J* = 6.6, 1.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 143.5, 134.8, 130.7, 128.8, 128.4, 126.9, 126.8, 126.7, 126.1, 124.7, 123.7, 75.2, 74.2, 42.0, 34.9, 21.1, 18.8; HRMS (ESI^+) m/z: calcd for $[M+Na]^+$: 314.1515, found: 314.1527

Experimental procedure for N-O cleavage of 3a



3a, R = Me;
3f, R = Cl

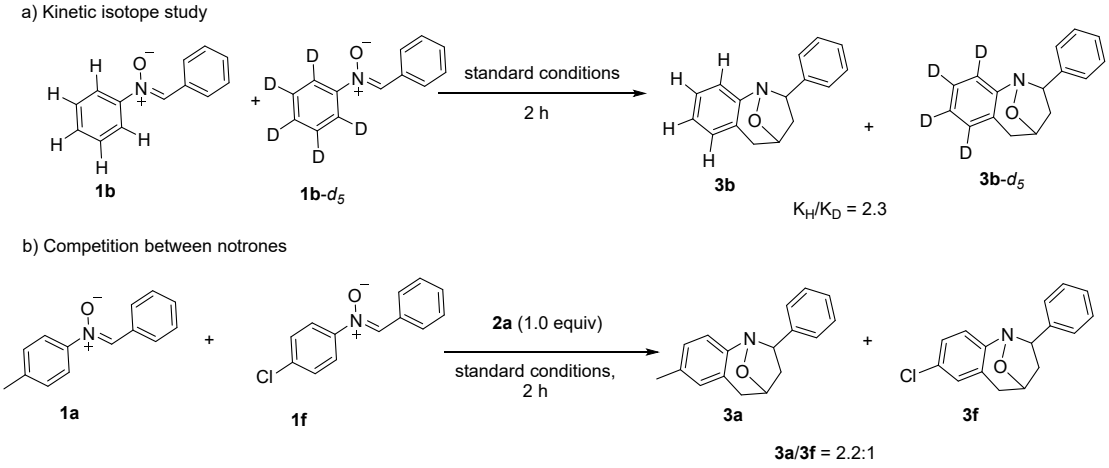
4a, R = Me, yield = 85%;
4f, R = Cl, yield = 80%

To a stirred and cooled (ice-bath) solutions of 1,4-epoxy-cycloadducts **3a**/**3f** (0.1 mmol, 1.0 equiv) in MeOH (1 mL), were added glacial acetic acid (90 μl, 1.5 mmol, 15 equiv), zinc powder (131 mg, 2 mmol, 20 equiv), and hydrochloric acid (37% HCl, 125 μl, 1.5 mmol, 15 equiv). The resulting reaction mixtures were then stirred at 0 ℃ under sonication for additional 1-2 h until the starting material was completely consumed (TLC control: for **3a**, 1 h; for **3f**, 2 h). Afterwards, the reaction mixture was filtered and the filtrate was neutralized with a 25% ammonium hydroxide solution to pH = 8, and then extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure. The remaining crude material was purified by column chromatography on silica gel using PE/EA (4:1) as eluent to afford the desired compound **4a/4f** in a yield of 85%/80%.

Compound **4a**:Yield 85%,^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.89 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 3.93 (dd, *J* = 11.4, 2.1 Hz, 1H), 3.87 (tdd, *J* = 10.1, 3.8, 2.2 Hz, 1H), 3.11 (dd, *J* = 13.5, 10.4 Hz, 1H), 2.97 (dt, *J* = 13.6, 2.3 Hz, 1H), 2.28 (s, 3H), 2.20 (ddt, *J* = 12.9, 4.2, 2.2 Hz, 1H), 2.12 (ddd, *J* = 12.7, 11.3, 9.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 144.8, 132.2, 131.1, 128.9, 127.9, 127.9, 127.8, 126.4, 120.1, 61.4, 48.6, 44.5, 20.5; HRMS (ESI^+) m/z: calcd for $[M+H]^+$: 254.1539, found: 254.1549.

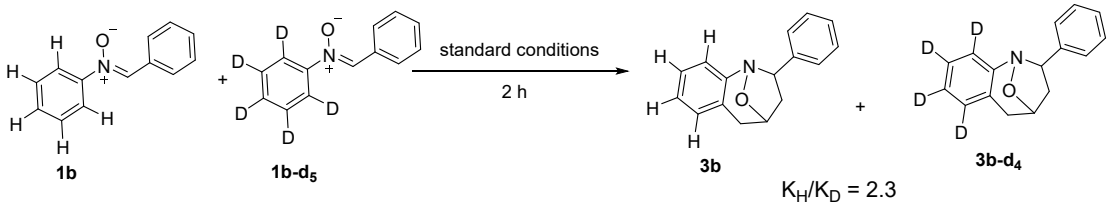
Compound **4f**:Yield 80%, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.34 (ddt, *J* = 6.8, 5.4, 2.4 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 3.91 (dd, *J* = 11.5, 2.1 Hz, 1H), 3.84 (tdd, *J* = 10.1, 4.0, 2.4 Hz, 1H), 3.06 (dd, *J* = 13.6, 10.2 Hz, 1H), 2.95 (dt, *J* = 13.7, 2.3 Hz, 1H), 2.22 – 2.15 (m, 1H), 2.15 – 2.06 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 144.3, 131.1, 129.7, 128.9, 127.9, 127.1, 126.3, 126.2, 121.3, 69.5, 61.1, 48.1, 44.1; HRMS (ESI$^+$) m/z: calcd for $[M+H]^+$: 274.0993, found: 274.0996.

Preliminary mechanistic studies



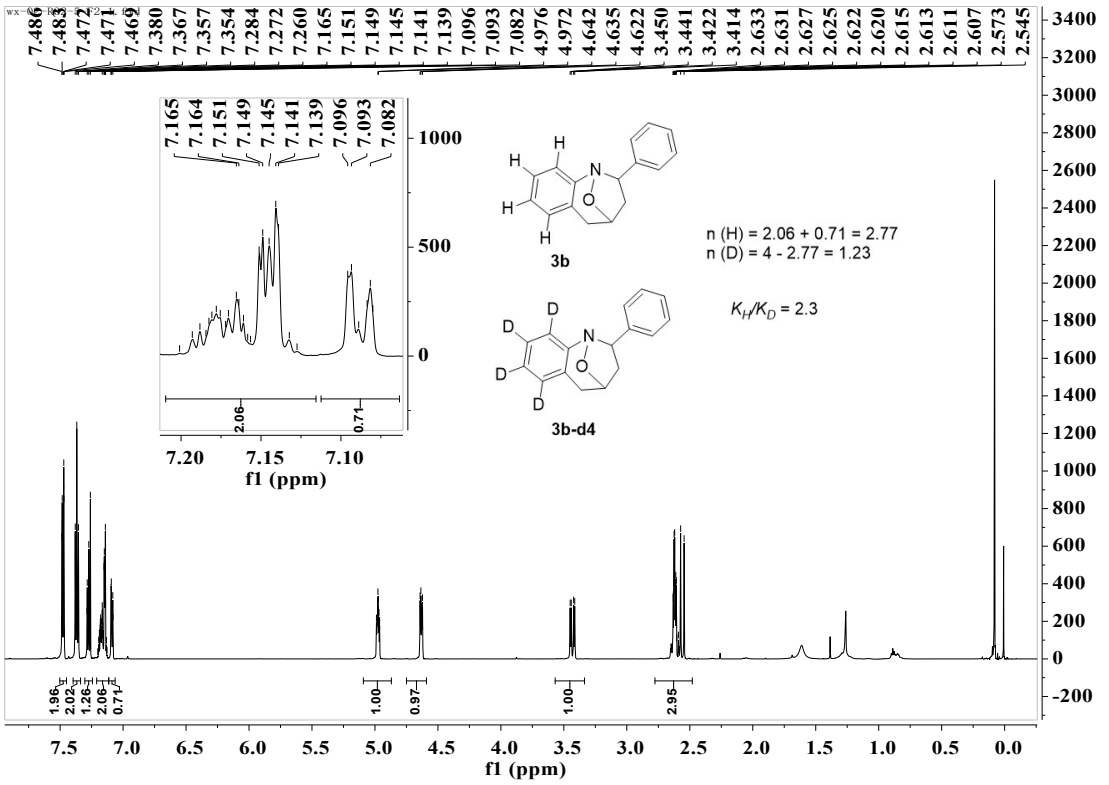
Scheme S1. Experiments for mechanistic studies.

Kinetic Isotope Effect Experiments: intermolecular competitive reactions

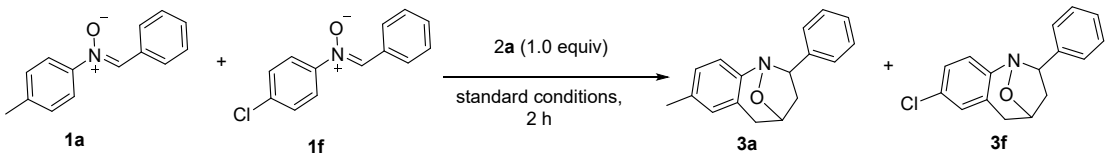


A mixture of nitrone **1b** (0.3 mmol), nitrone **1b**-d_5 (0.3 mmol), [Cp*Rh $(CH_3CN)_3$]$(SbF_6)_2$ (0.01 mmol), and AgOAc (0.3 mmol) were dissolved in chlorobezene (2 mL) in a pressure tube and stirred for seconds, to which was added the allyl precursor **2a** (0.2 mmol). The reaction mixture was stirred at 120 ℃ for 2 h. After that, the reaction mixture was filtered through a pad of celite, and washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed underreduced pressure and the residue was purified by silica gel chromatography using PE/EA (20:1) to afford the mixture of **3b/3b-*d*$_4$** (10 mg, yield: ca. 21%). A KIE value of 2.3 was obtained on the

basis of ^{1}H NMR analysis. This result suggests that the *ortho* C(sp^2)-H bond cleavage might be related to the rate-limiting step.



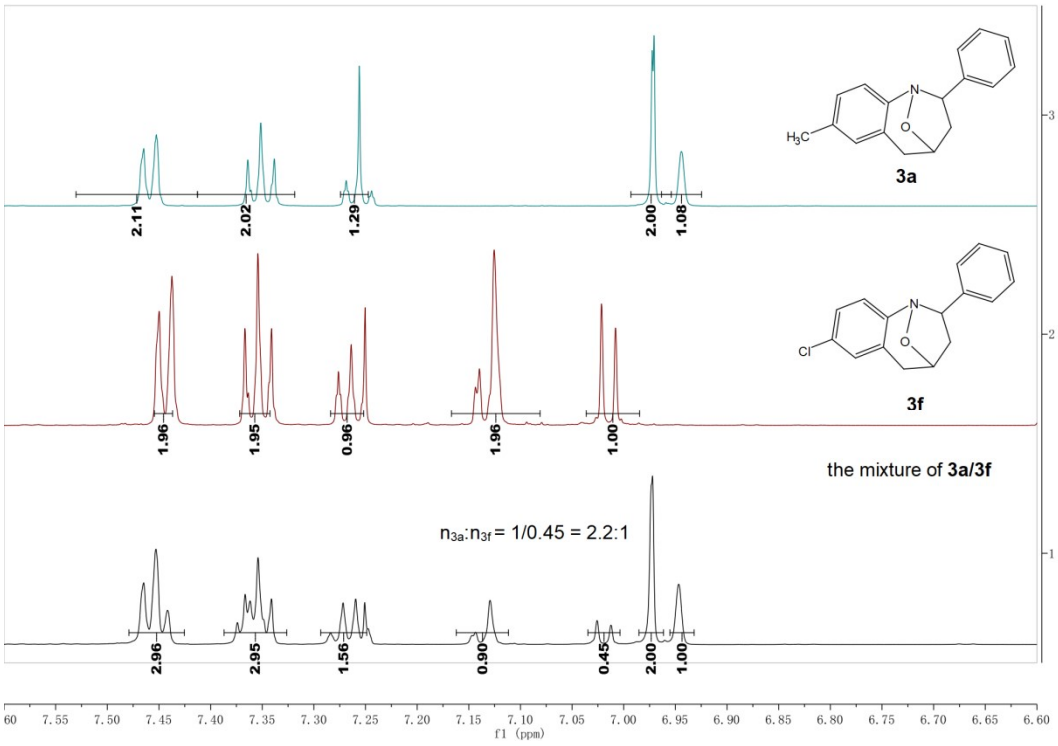
Competition between nitrones

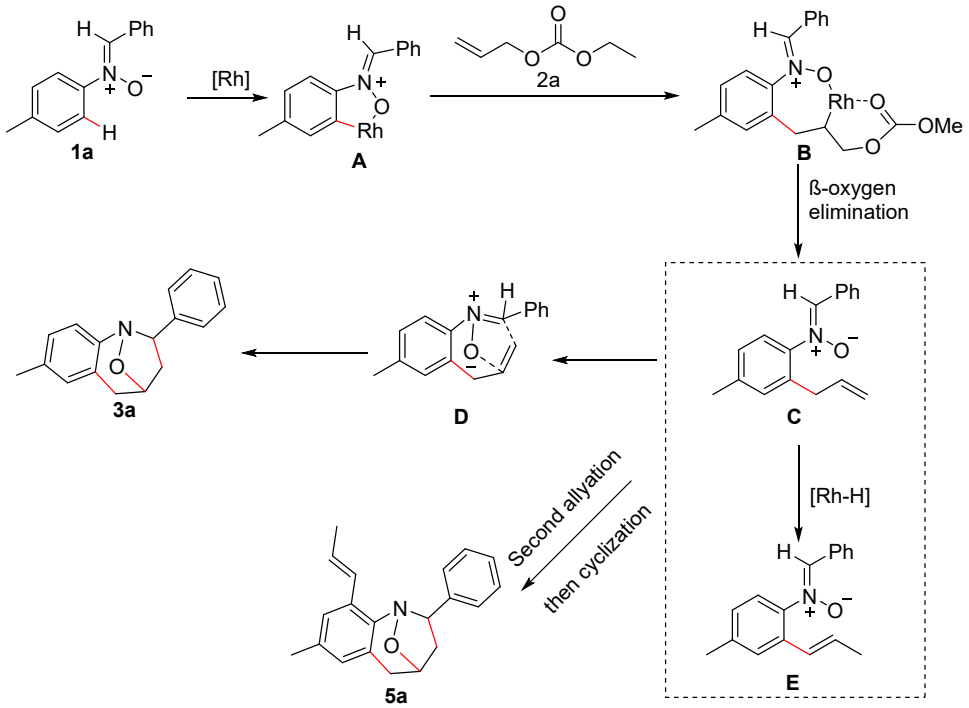


3a/**3f** = 2.2:1

A mixture of nitrone **1a** (0.2 mmol), nitrone **1f** (0.2 mmol), [Cp*Rh $(CH_3CN)_3](SbF_6)_2$ (0.01 mmol), and AgOAc (0.3 mmol) were dissolved in chlorobezene (2 mL) in a pressure tube and stirred for seconds, to which was added the allyl precursor **2a** (0.2 mmol). The reaction mixture was stirred at 120 °C for 2 h. After that, the reaction mixture was filtered through a pad of celite, and washed with CH_2Cl_2 (10 mL x 3). Organic solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (20:1) to afford the mixture of **3a**/**3f** (11 mg, yield: 20-22%). The ratio of **3a**:**3f** = 2.2:1 was determined on the basis of ^{1}H NMR analysis, which indicated that the reaction favored the electron-rich arene, implying that arene activation occurs likely by a variant of the classical electrophilic aromatic substitution mechanism (SEAr), namely electrophilic

metalation.





Scheme S2 Plausible catalytic mechanism

References

[1] Fujita, K.-i.; Takahashi, Y.; Owaki, M.; Yamamoto, K. and Yamaguchi, R., Synthesis of Five-, Six-, and Seven-Membered Ring Lactams by Cp*Rh Complex-Catalyzed Oxidative N-Heterocyclization of Amino Alcohols. *Org. Lett.* **2004,** *6*, 2785-2788.

[2] Li, Y.; Li, B.-J.; Wang, W.-H.; Huang, W.-P.; Zhang, X.-S.; Chen, K. and Shi, Z.-J., Rhodium-Catalyzed Direct Addition of Aryl C□H Bonds to N-Sulfonyl Aldimines. *Angew. Chem. Int. Ed.* **2011,** *50*, 2115-2119.

[3] Duguet, N.; Slawin, A. M. Z. and Smith, A. D., An Asymmetric Hetero-Claisen Approach to 3-Alkyl-3-aryloxindoles. *Org. Lett.* **2009,** *11*, 3858-3861.

[4] Liu, T.; Liu, Z.; Liu, Z.; Hu, D. and Wang, Y., Coupling of N-Nosylhydrazones with Nitrosoarenes: Transition-Metal-Free Approach to (Z)-N-Arylnitrones. *Synthesis* **2018,** *50*, 1728-1736.

[5] a) Choi, M.; Viji, M.; Kim, D.; Lee, Y. H.; Sim, J.; Kwak, Y.-S.; Lee, K.; Lee, H. and Jung, J.-K., Metal-free approach for the L-proline mediated synthesis of nitrones from nitrosobenzene. *Tetrahedron* **2018,** *74*, 4182-4187; b) Tian, Z.; Xu, J.; Liu, B.; Tan, Q. and Xu, B., Copper-Catalyzed Synthesis of Polysubstituted Pyrroles through [3+1+1] Cycloaddition Reaction of Nitrones and Isocyanides. *Org. Lett.* **2018,** *20*, 2603-2606.

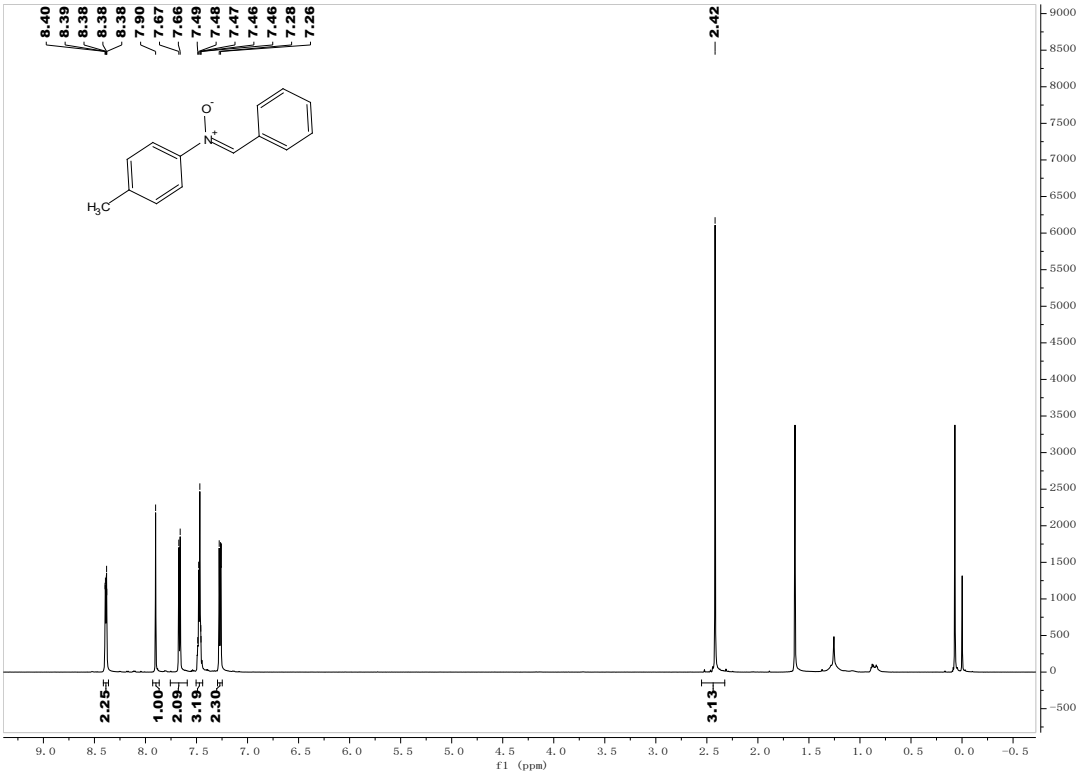
[6] Riesco-Domínguez, A.; van de Wiel, J.; Hamlin, T. A.; van Beek, B.; Lindell, S. D.; Blanco-Ania, D.; Bickelhaupt, F. M. and Rutjes, F. P. J. T., Trifluoromethyl Vinyl Sulfide: A Building Block for the Synthesis of CF3S-Containing Isoxazolidines. *J. Org. Chem.* **2018,** *83*, 1779-1789.

[7] Poulsen, P. H.; Vergura, S.; Monleón, A.; Jørgensen, D. K. B. and Jørgensen, K. A., Controlling Asymmetric Remote and Cascade 1,3-Dipolar Cycloaddition Reactions by Organocatalysis. *J. Am. Chem. Soc.* **2016,** *138*, 6412-6415.

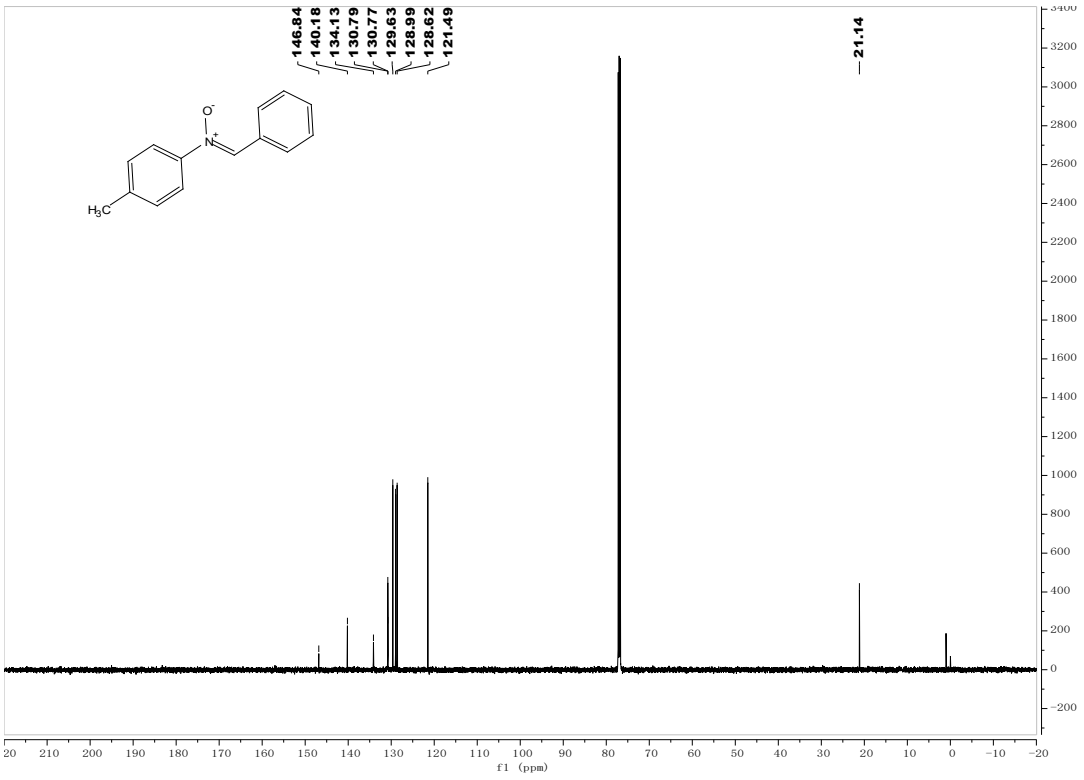
[8] Maiuolo, L.; De Nino, A.; Merino, P.; Russo, B.; Stabile, G.; Nardi, M.; D'Agostino, N. and Bernardi, T., Rapid, efficient and solvent free microwave mediated synthesis of aldo- and ketonitrones. *Arabian Journal of Chemistry* **2016,** *9*, 25-31.

^{1}H NMR and ^{13}C NMR Spectra

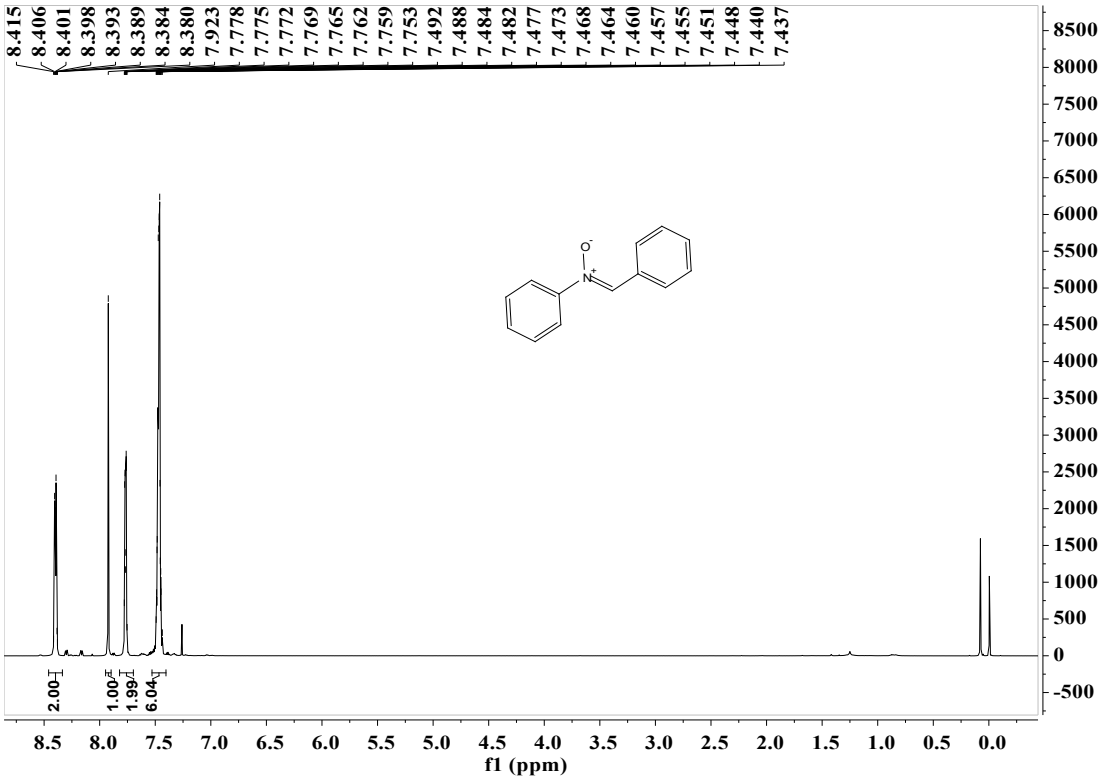
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1a**



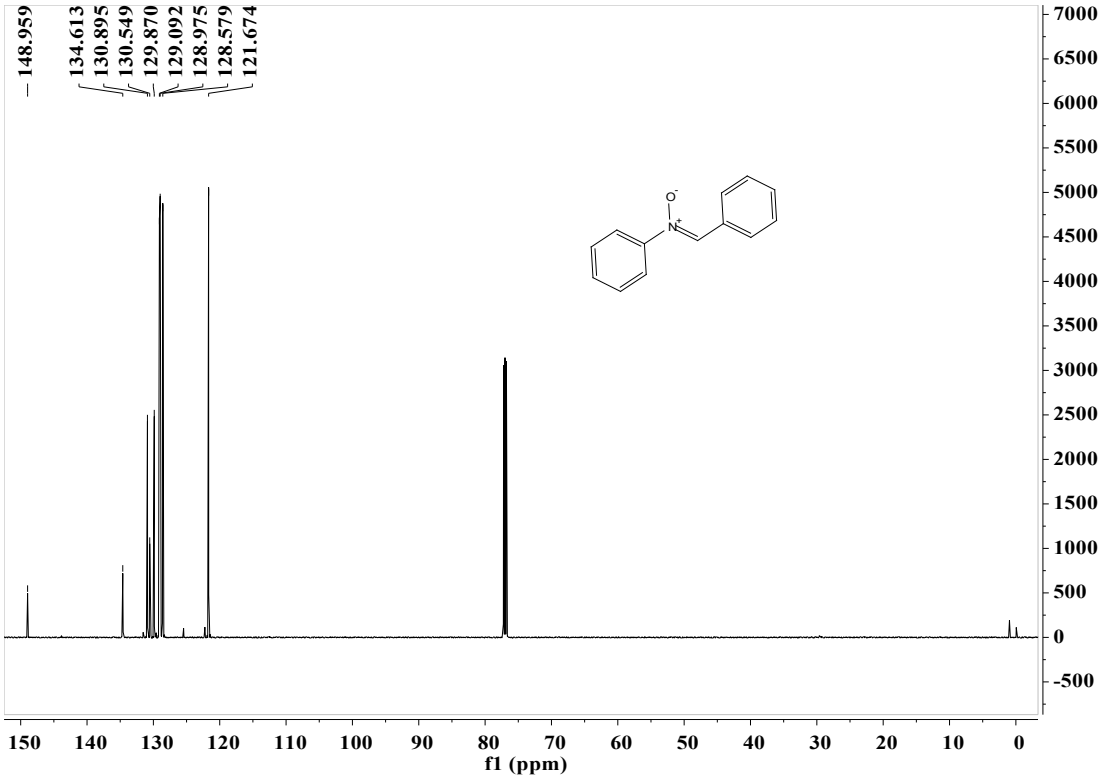
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1a**



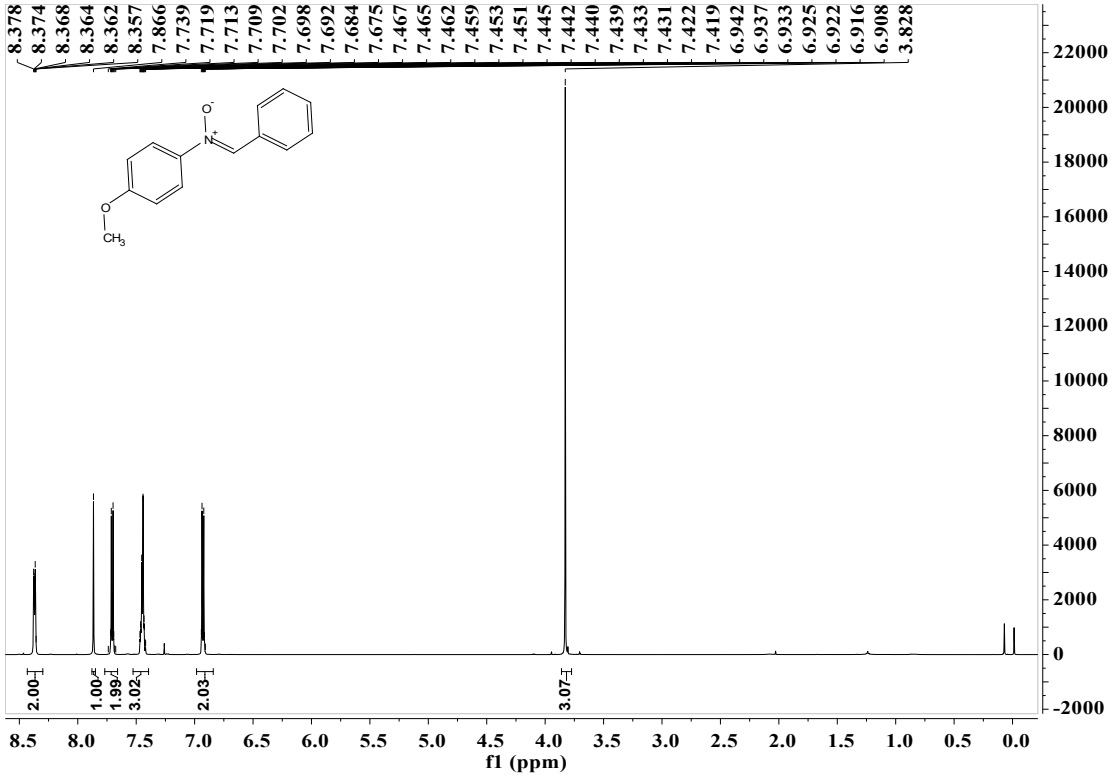
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1b**



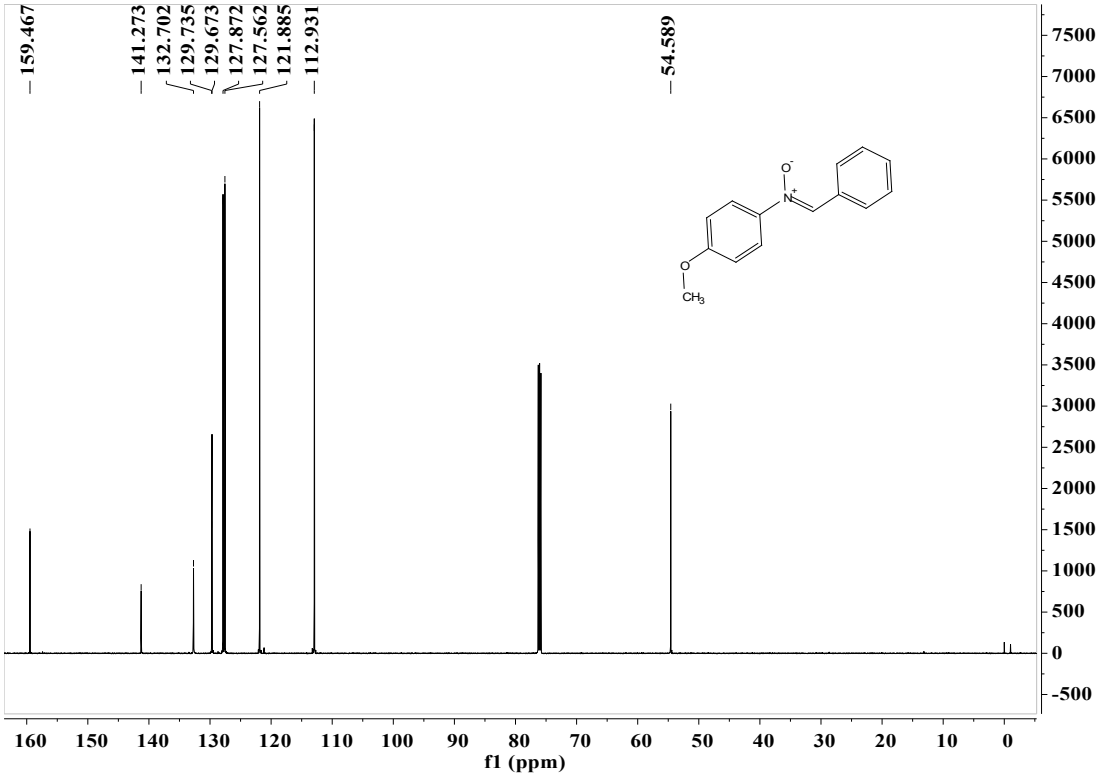
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1b**



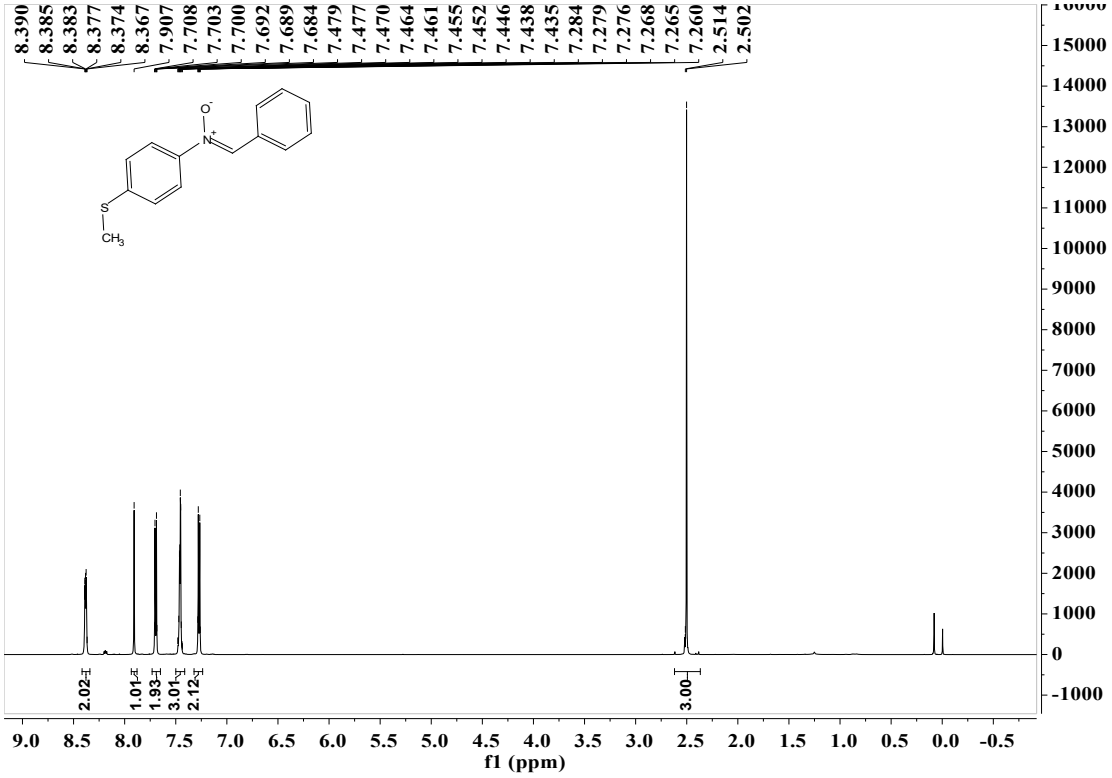
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1c**



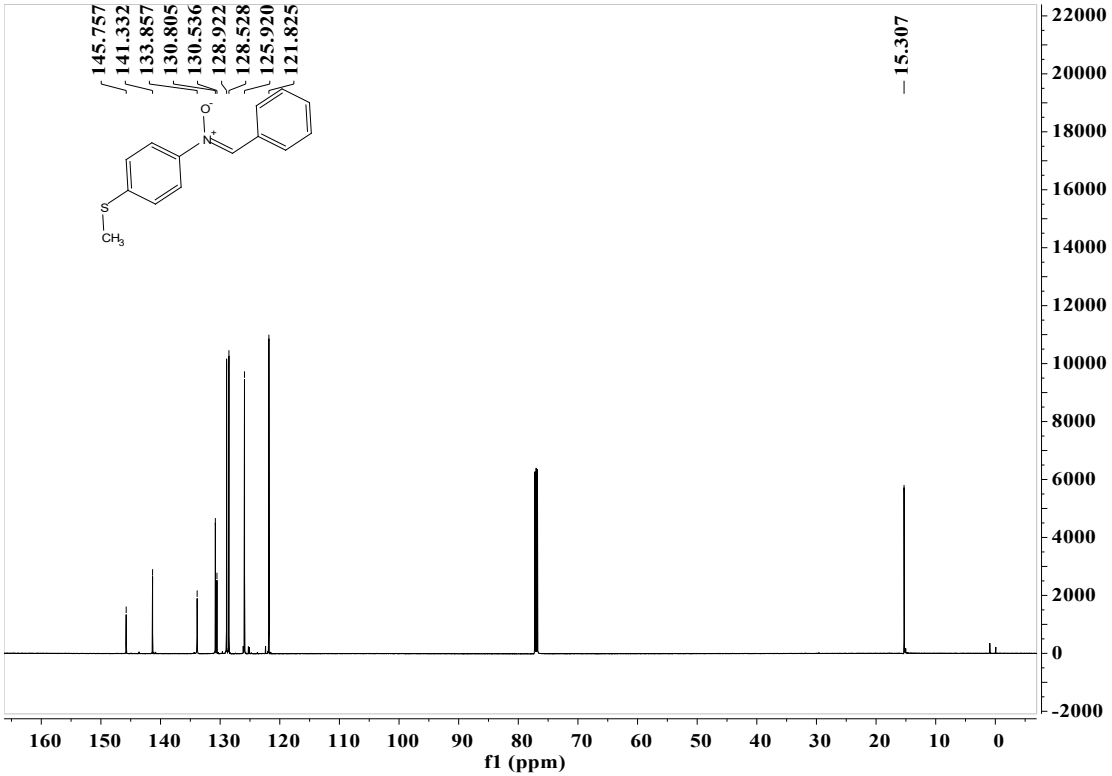
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1c**



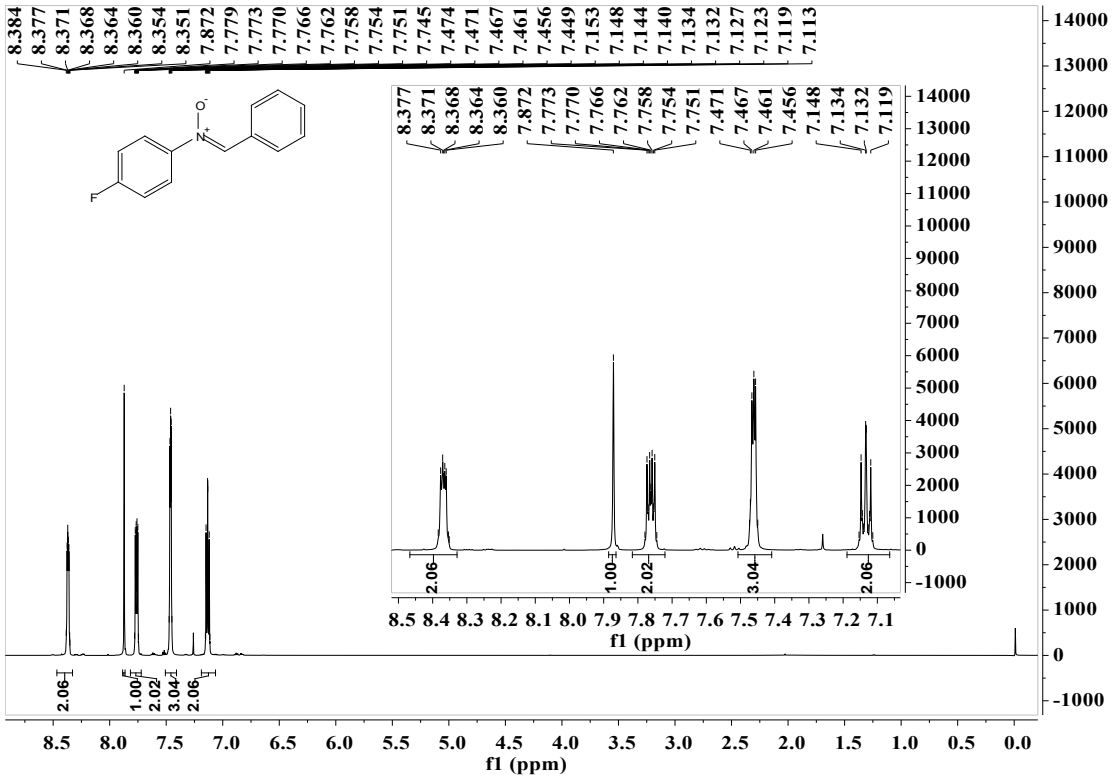
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1d**



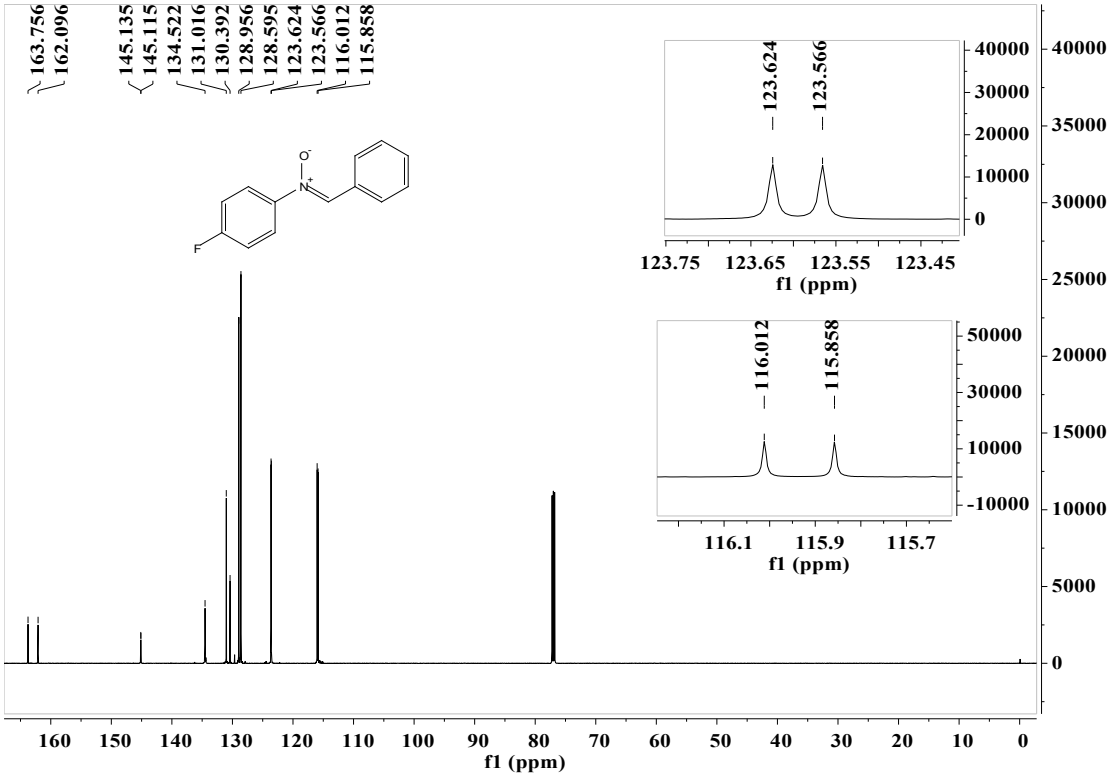
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1d**



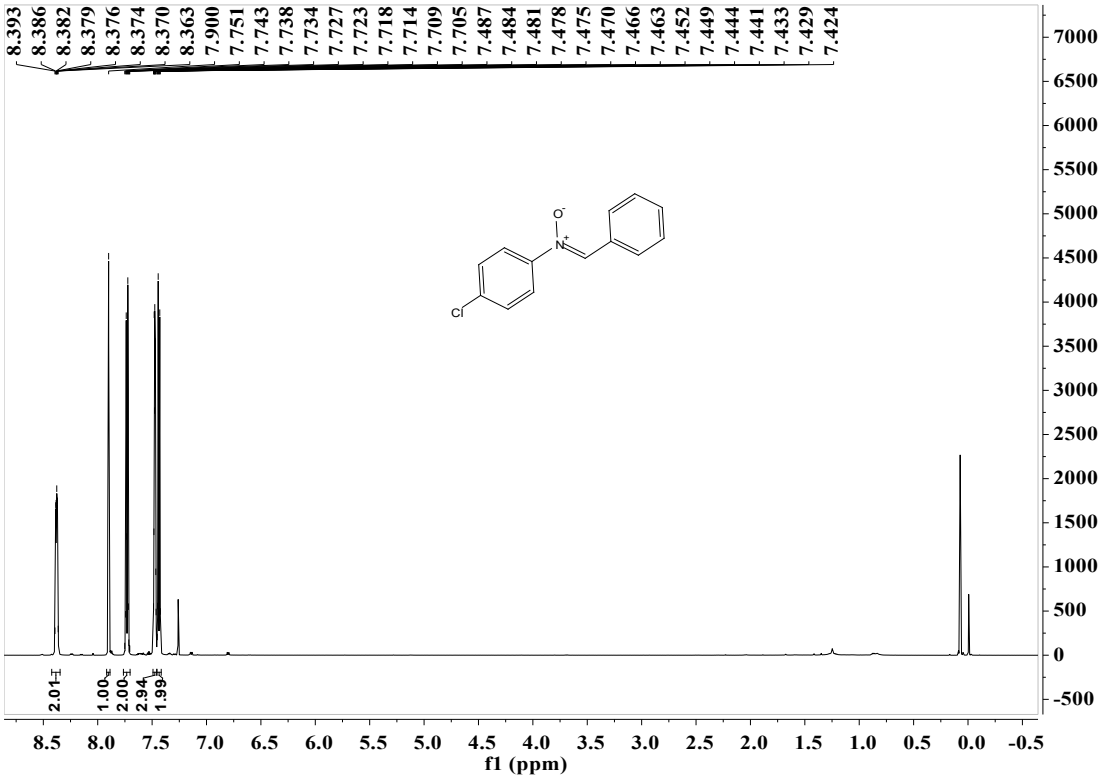
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1e**



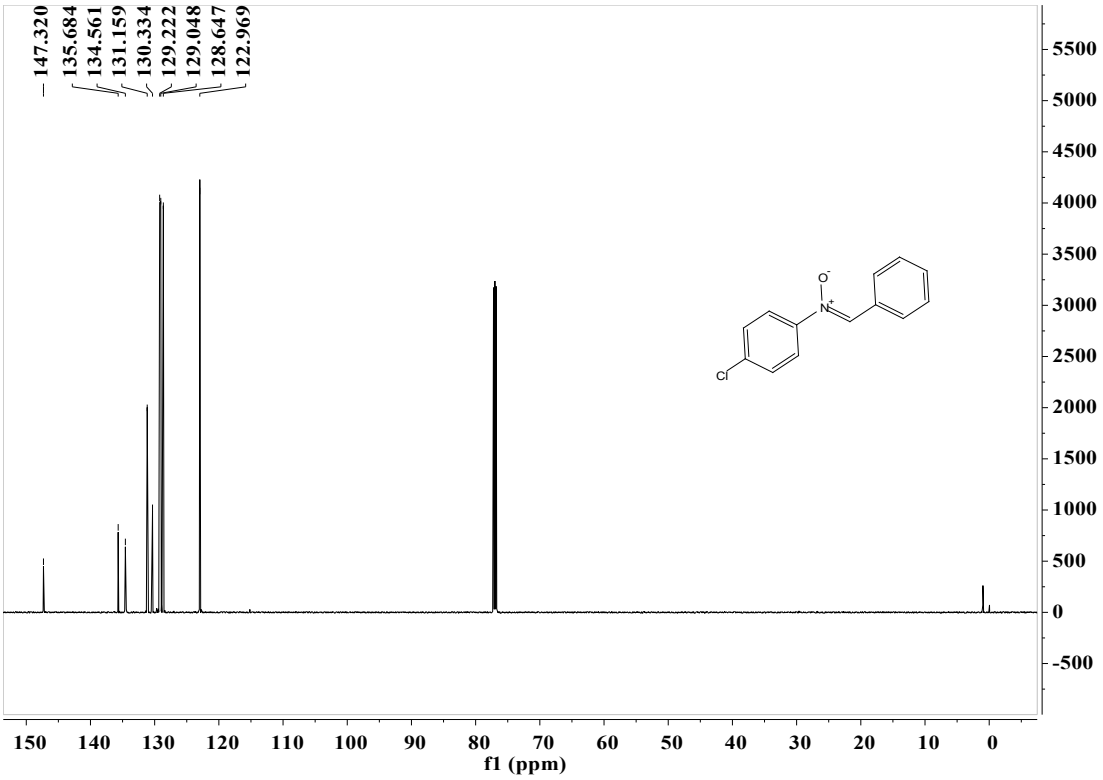
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1e**



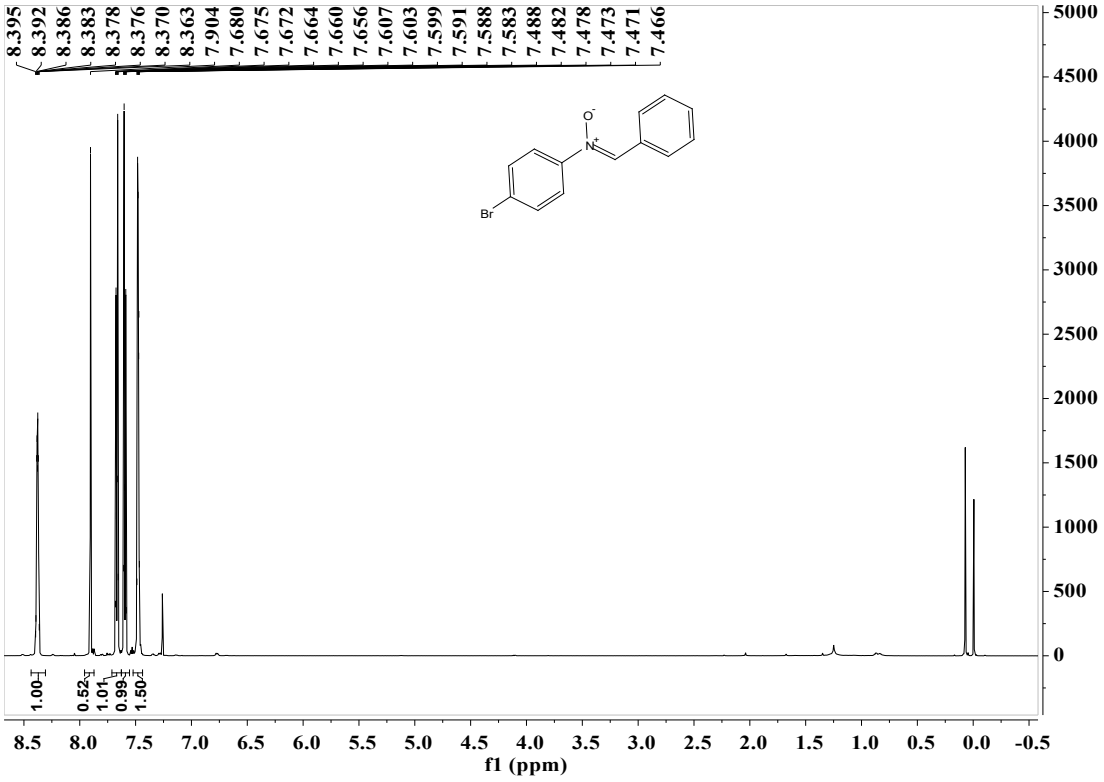
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1f**



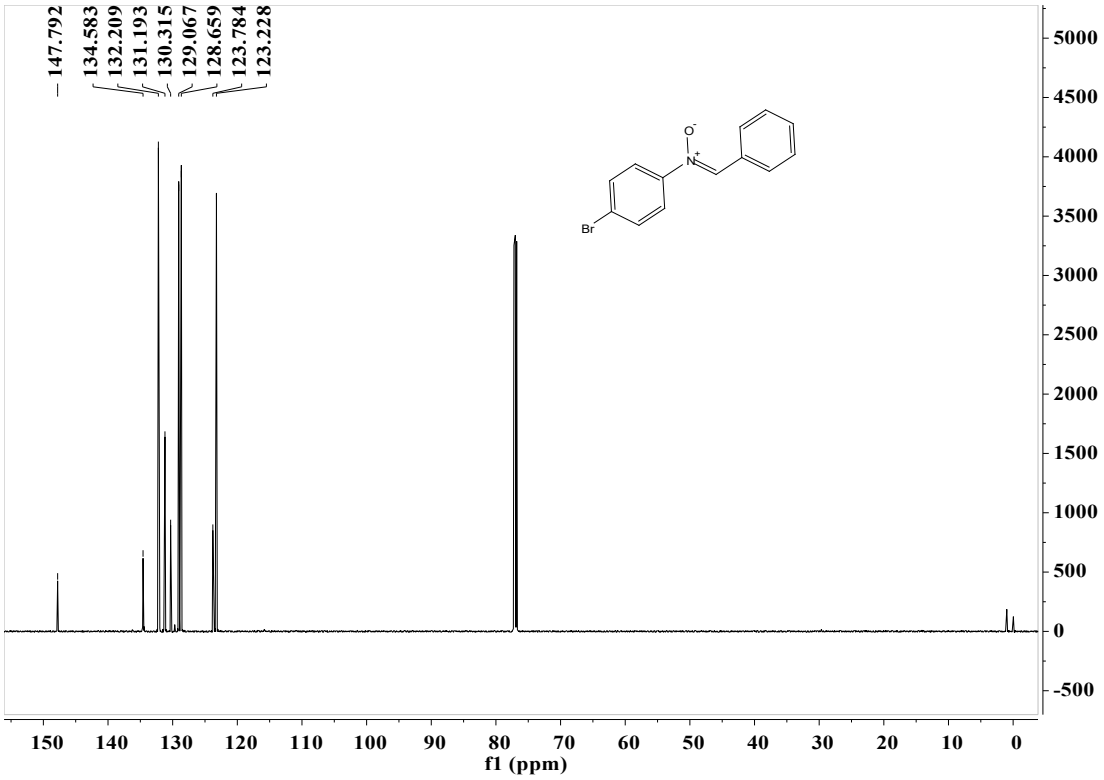
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1f**



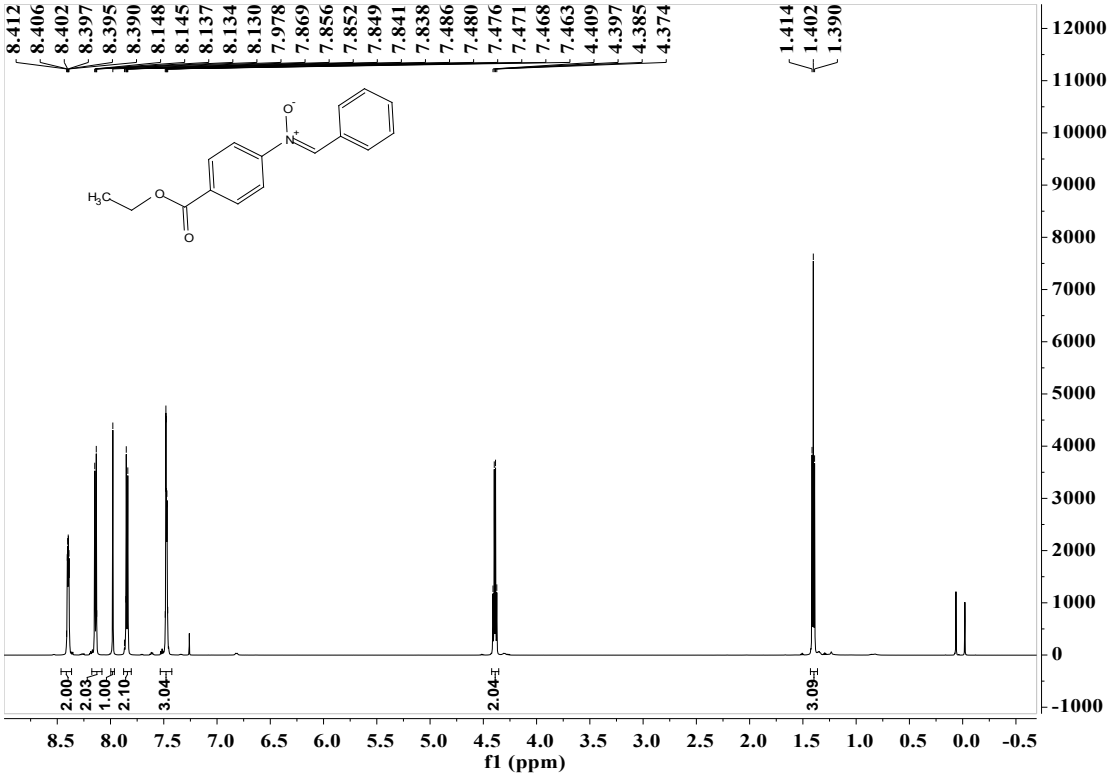
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1g**



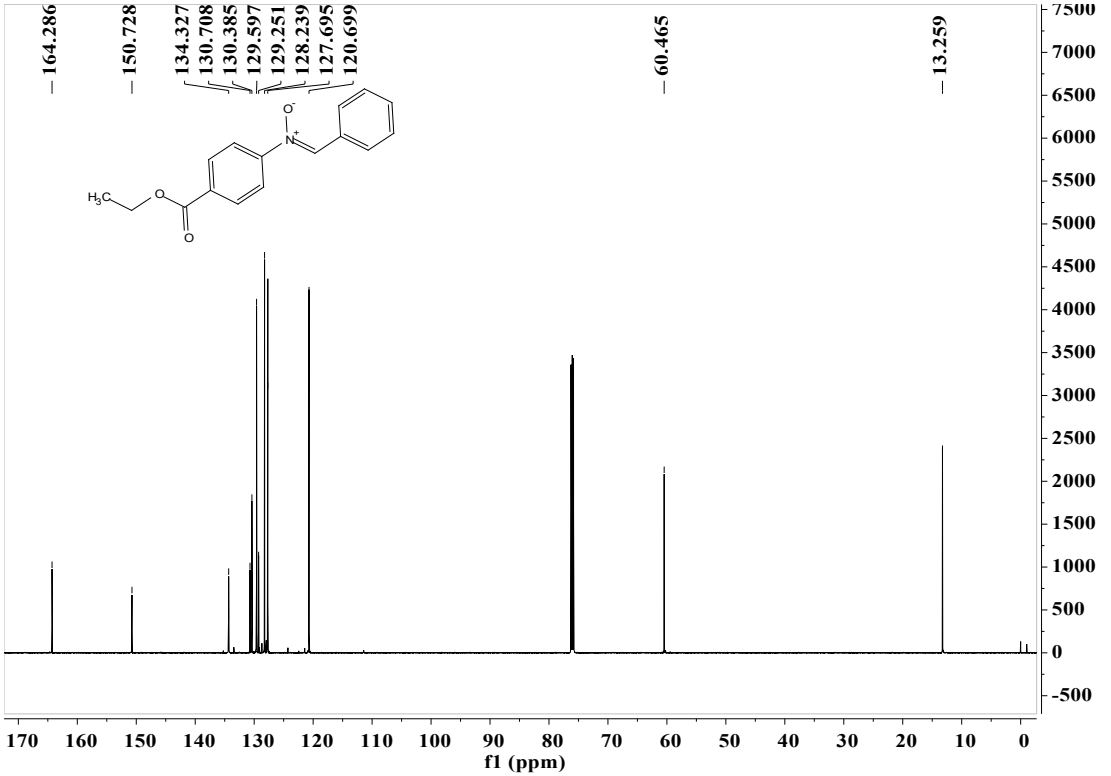
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1g**



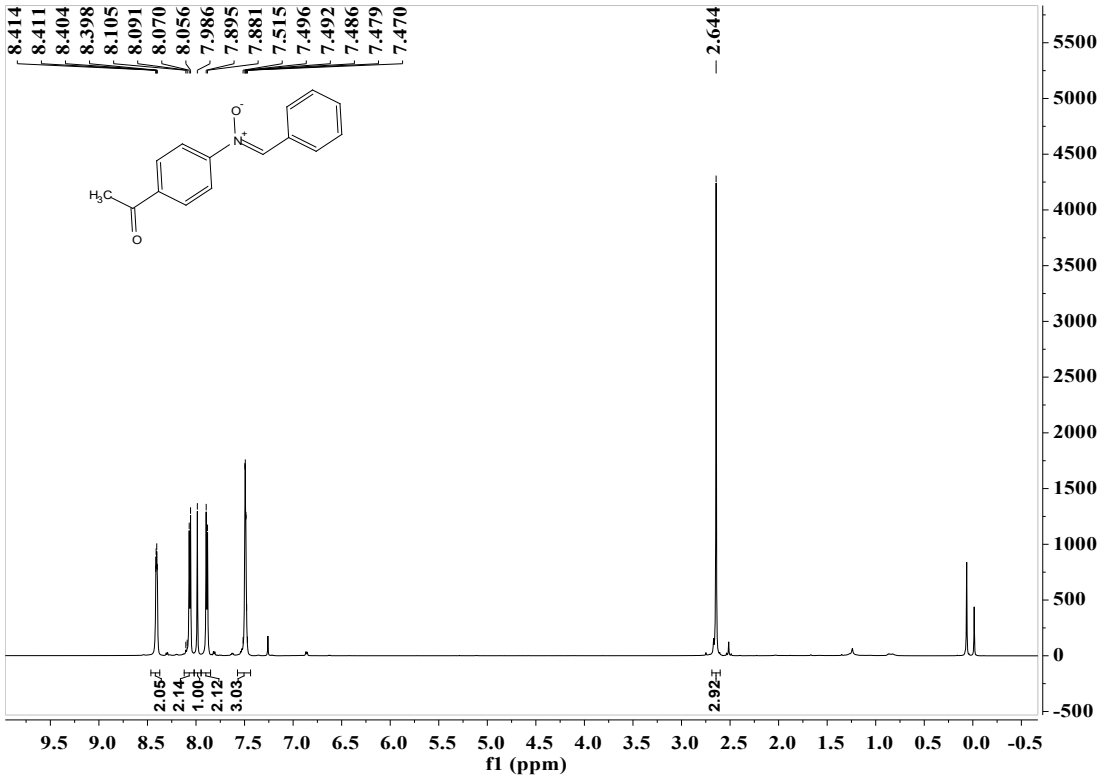
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1h**



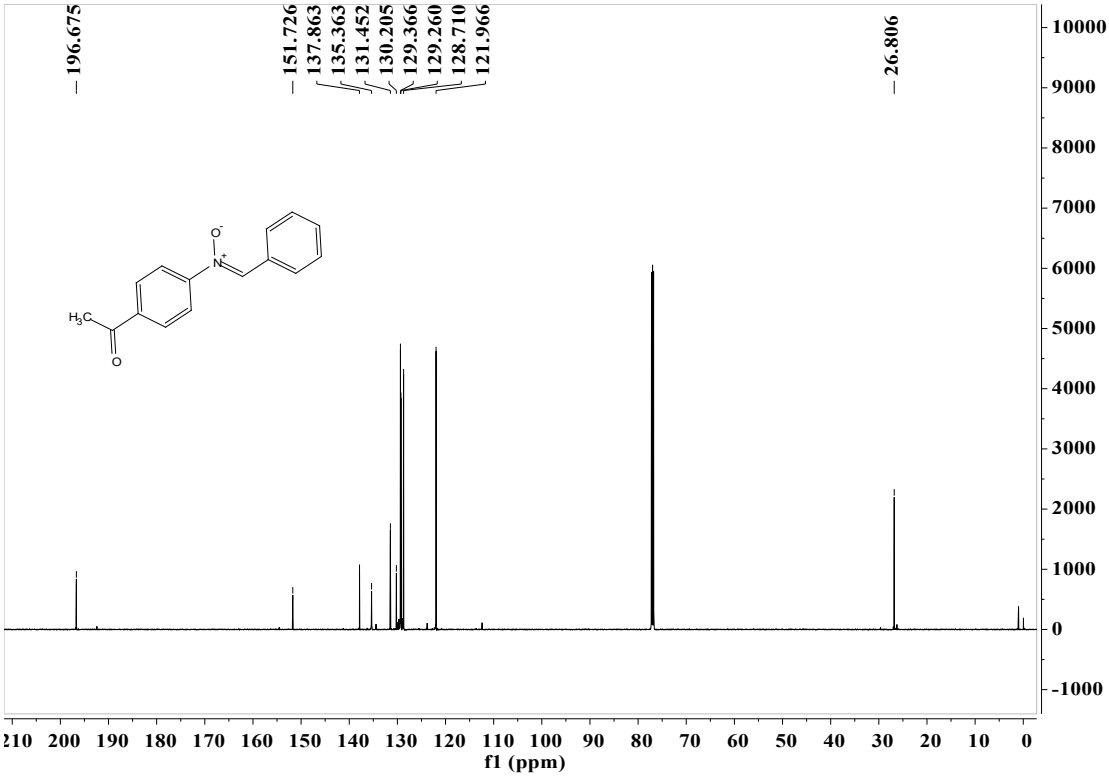
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1h**



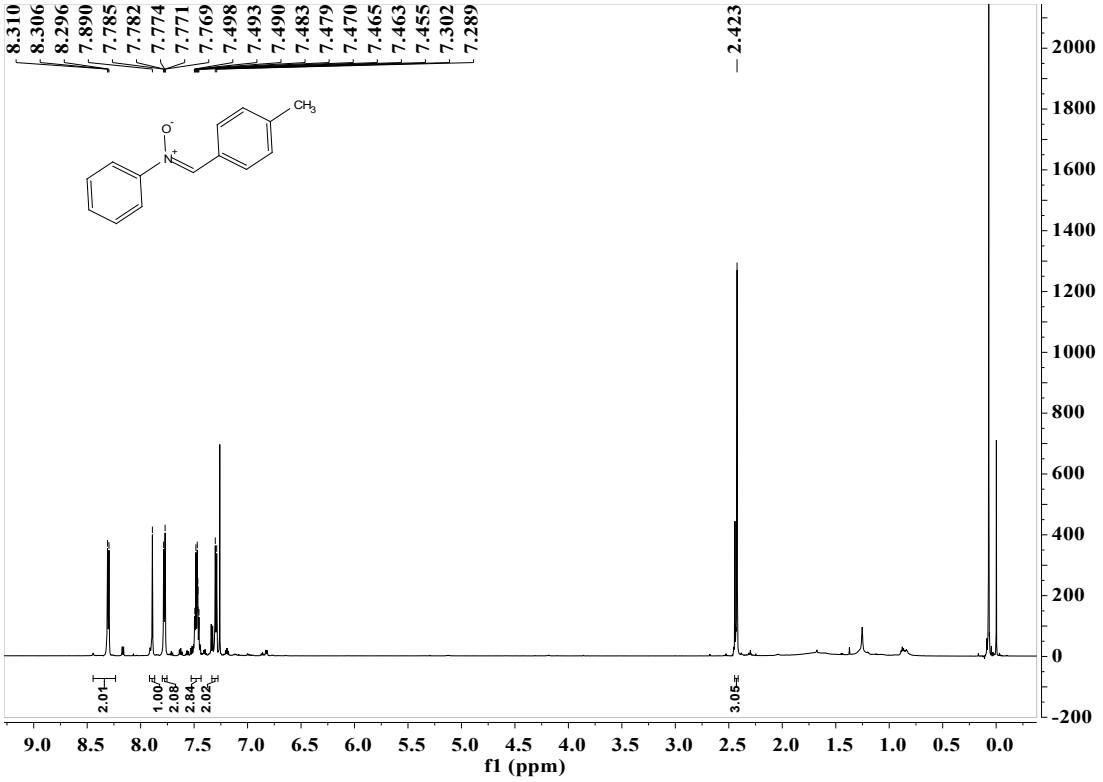
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1i**



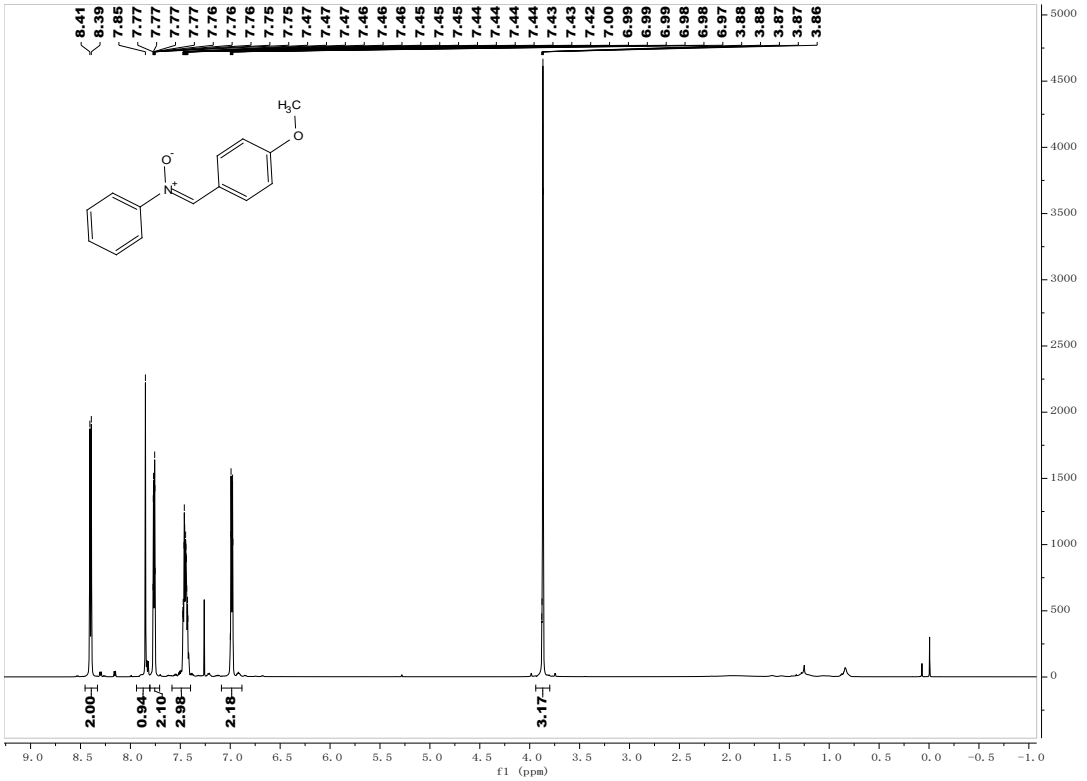
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1i**



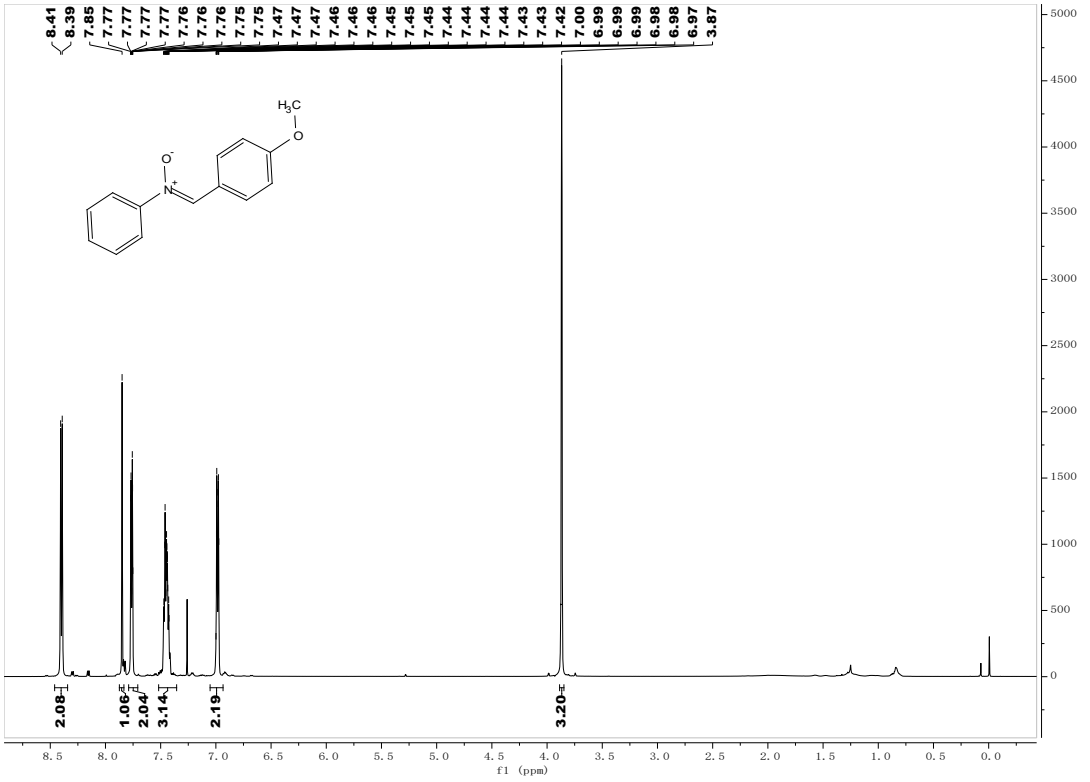
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1j**



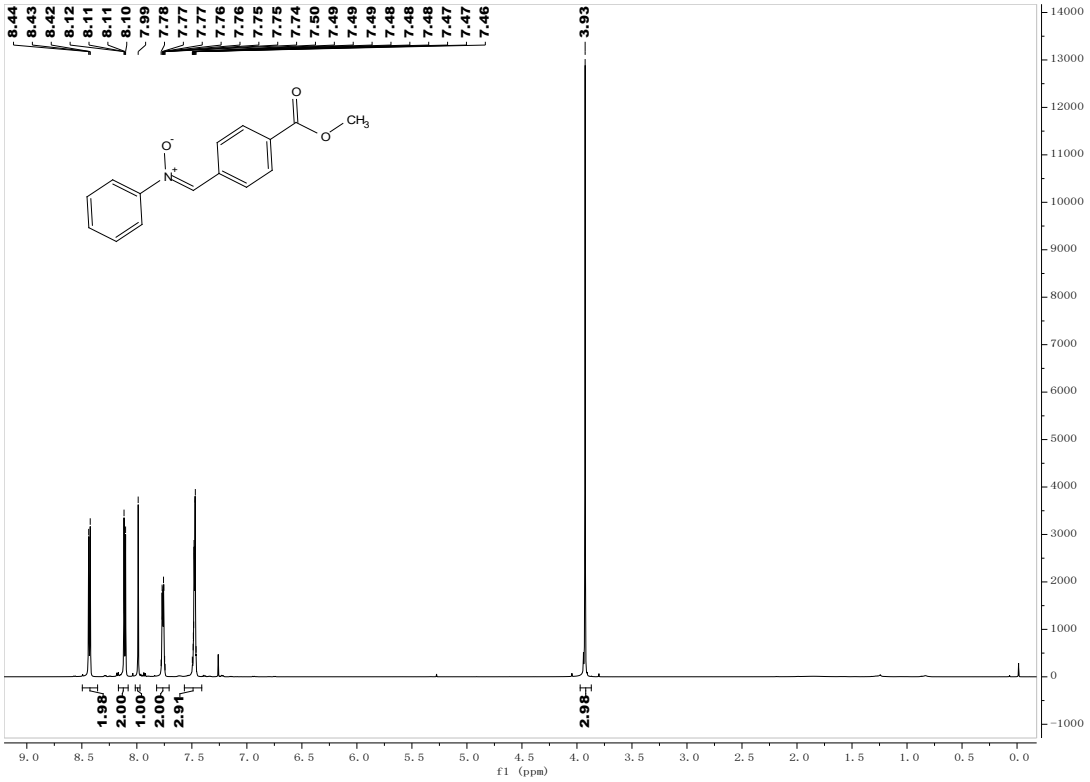
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1k**



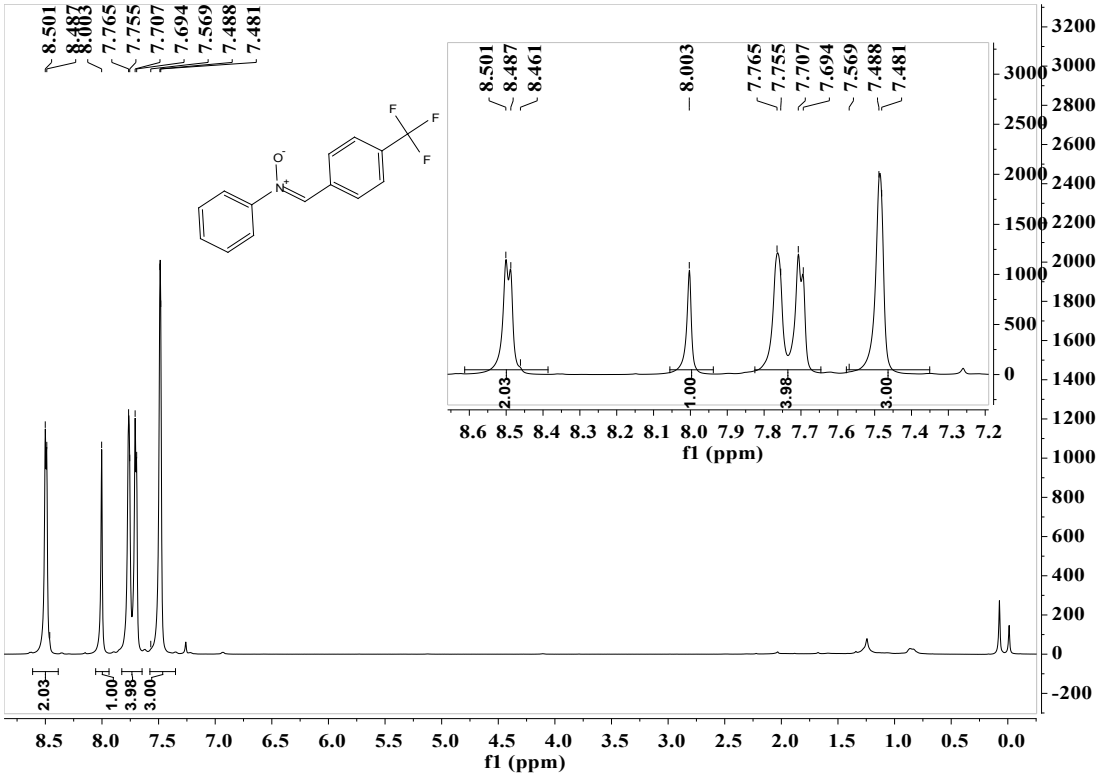
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1l**



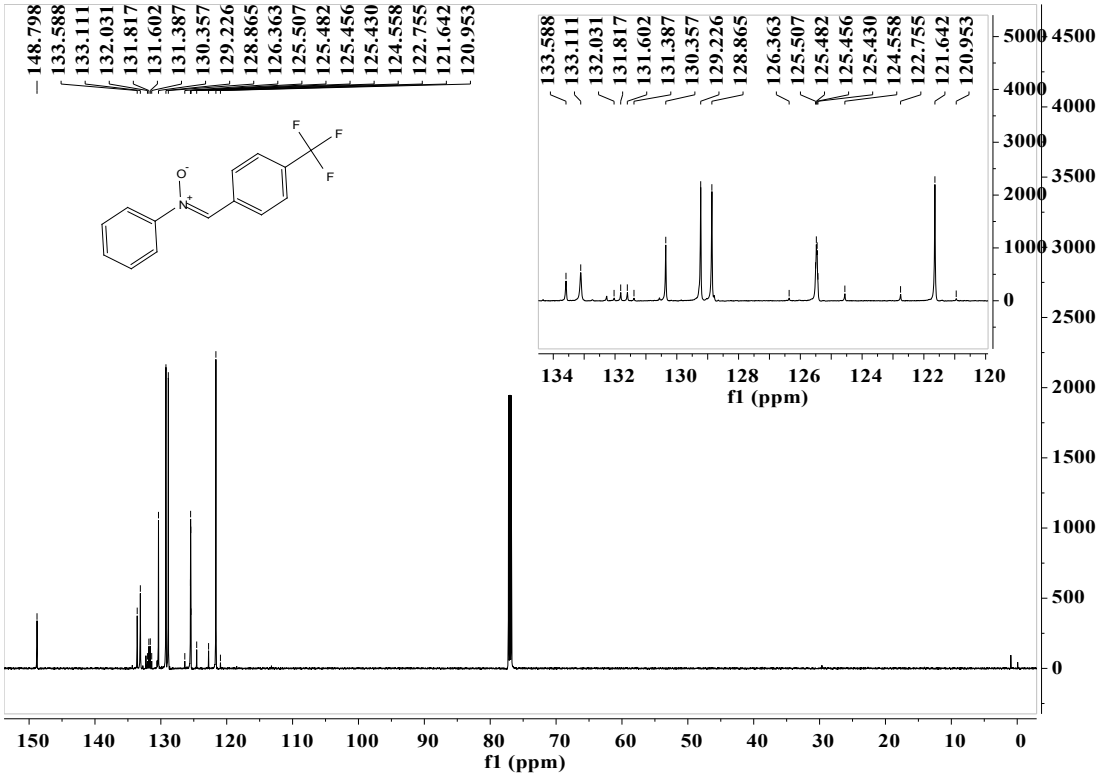
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1m**



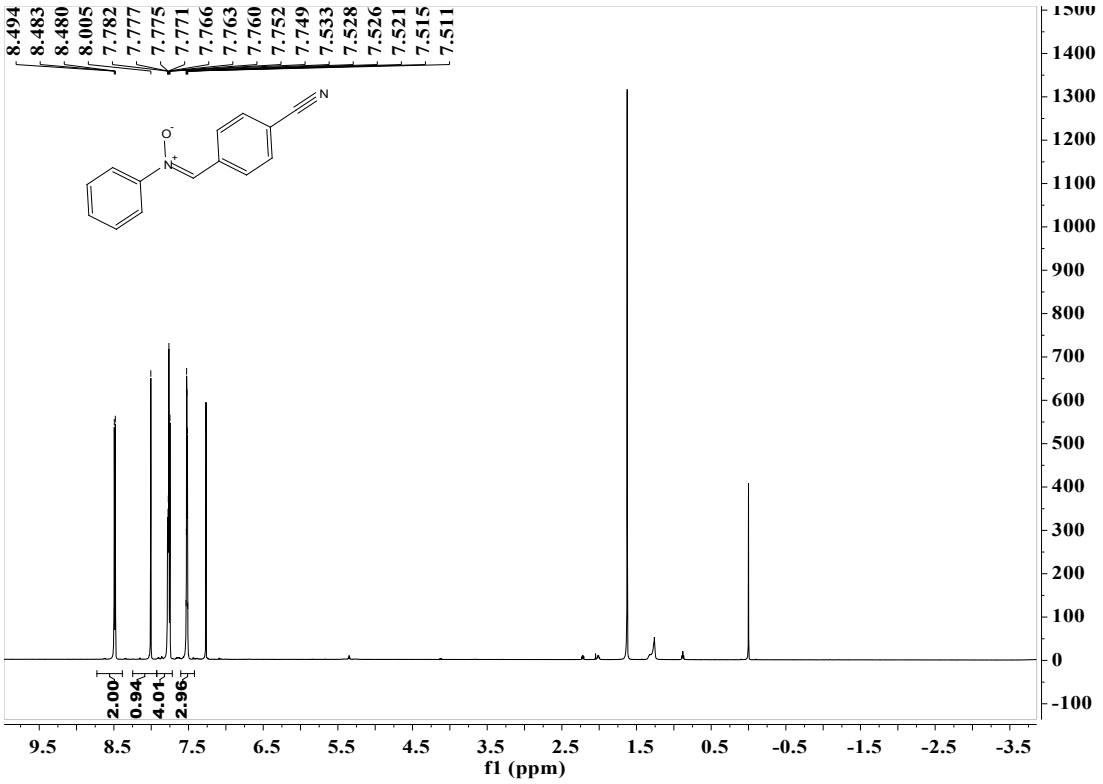
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1n**



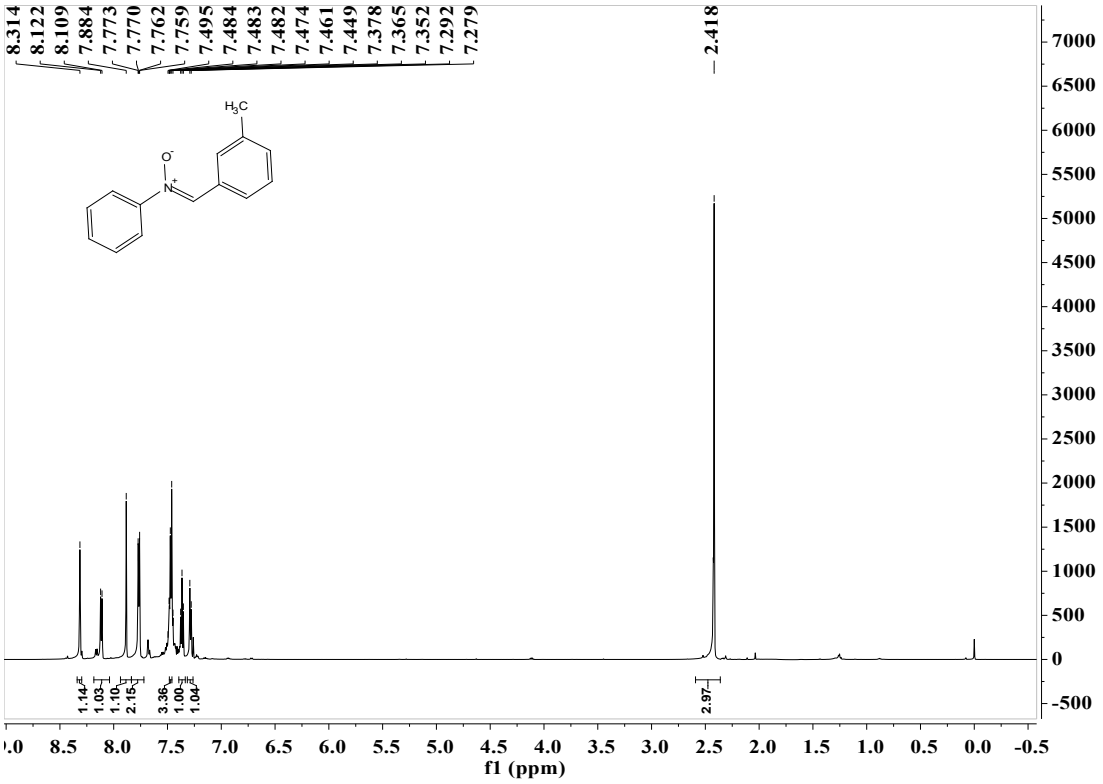
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1n**



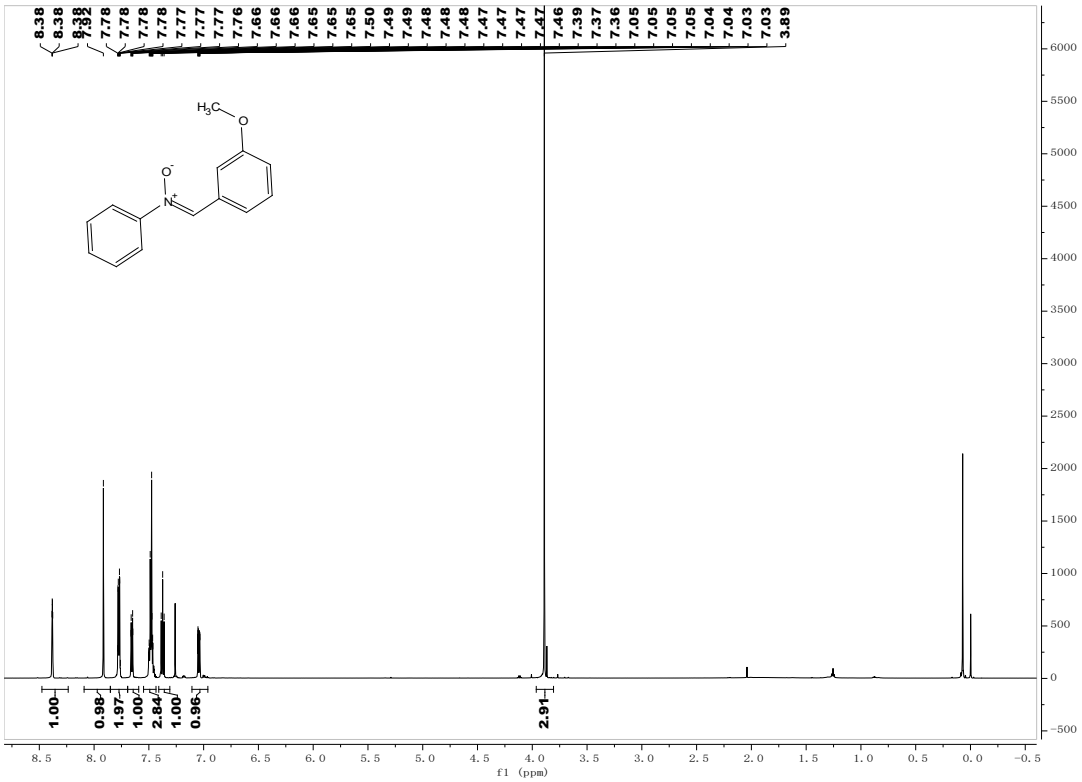
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1o**



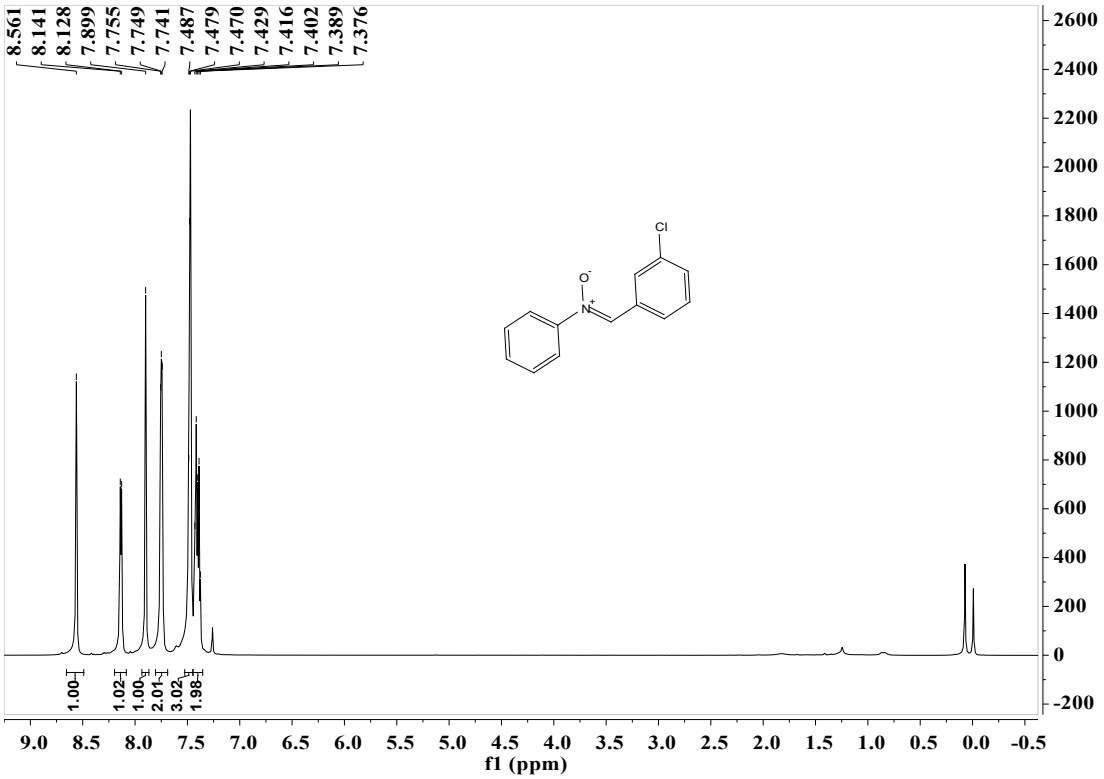
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1p**



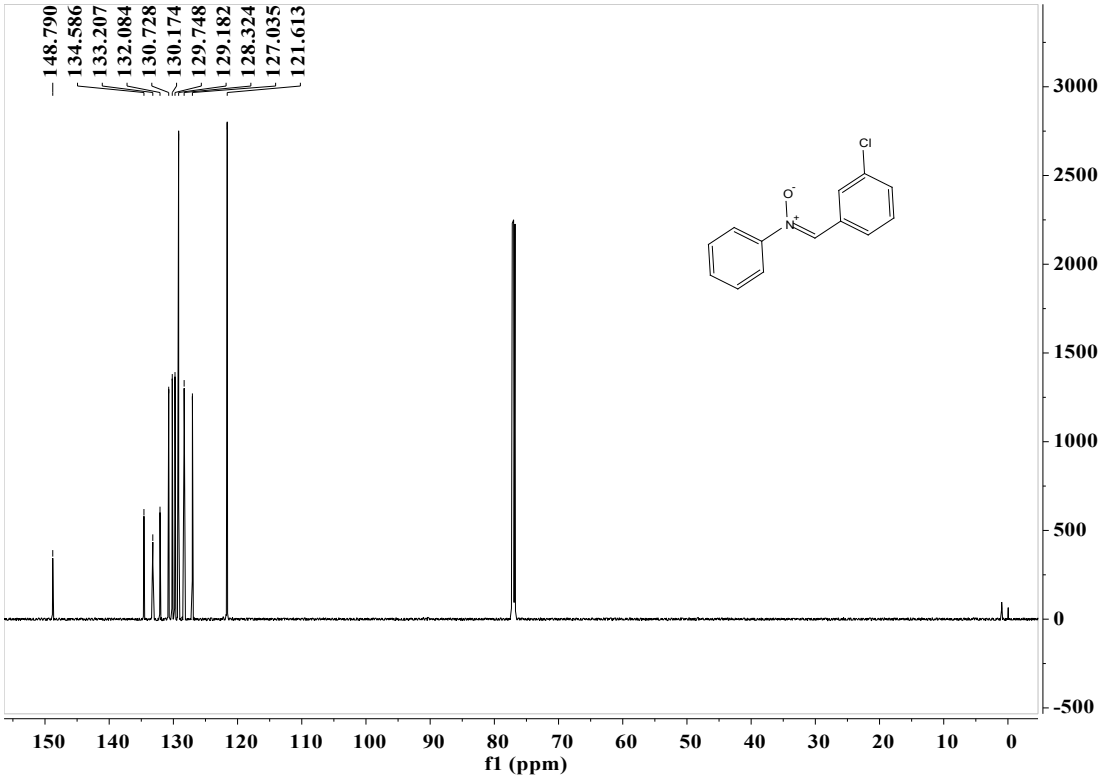
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1q**



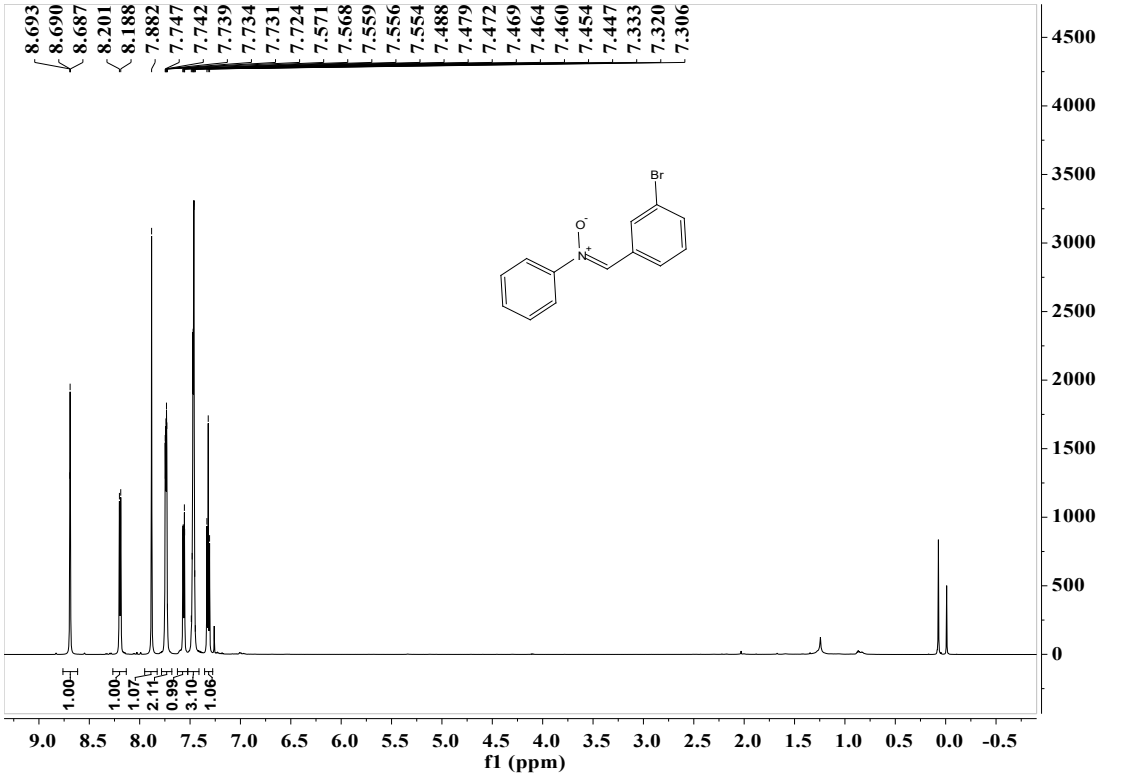
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1r**



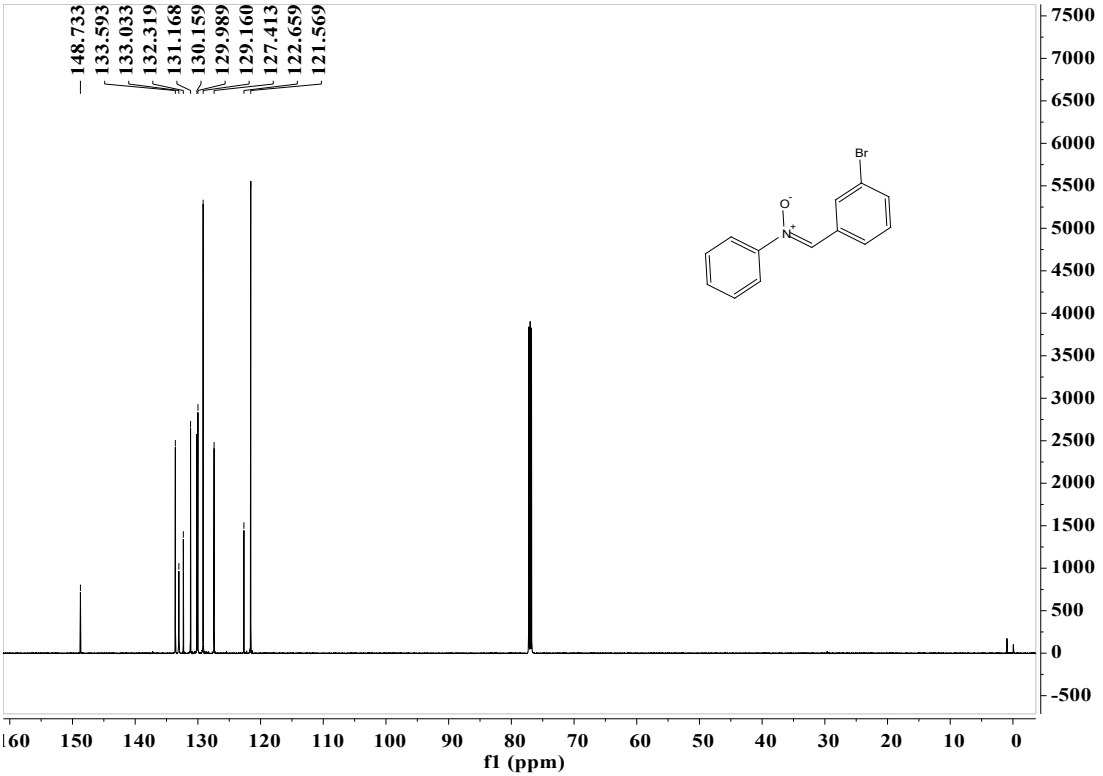
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1r**



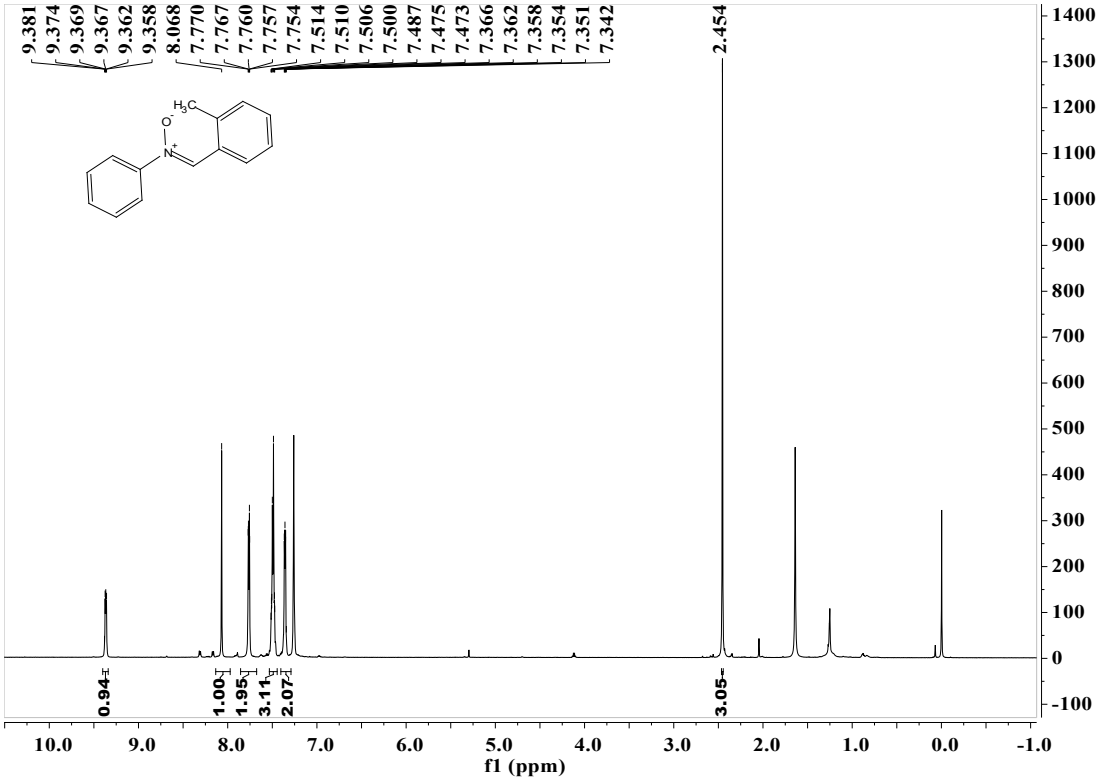
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1s**



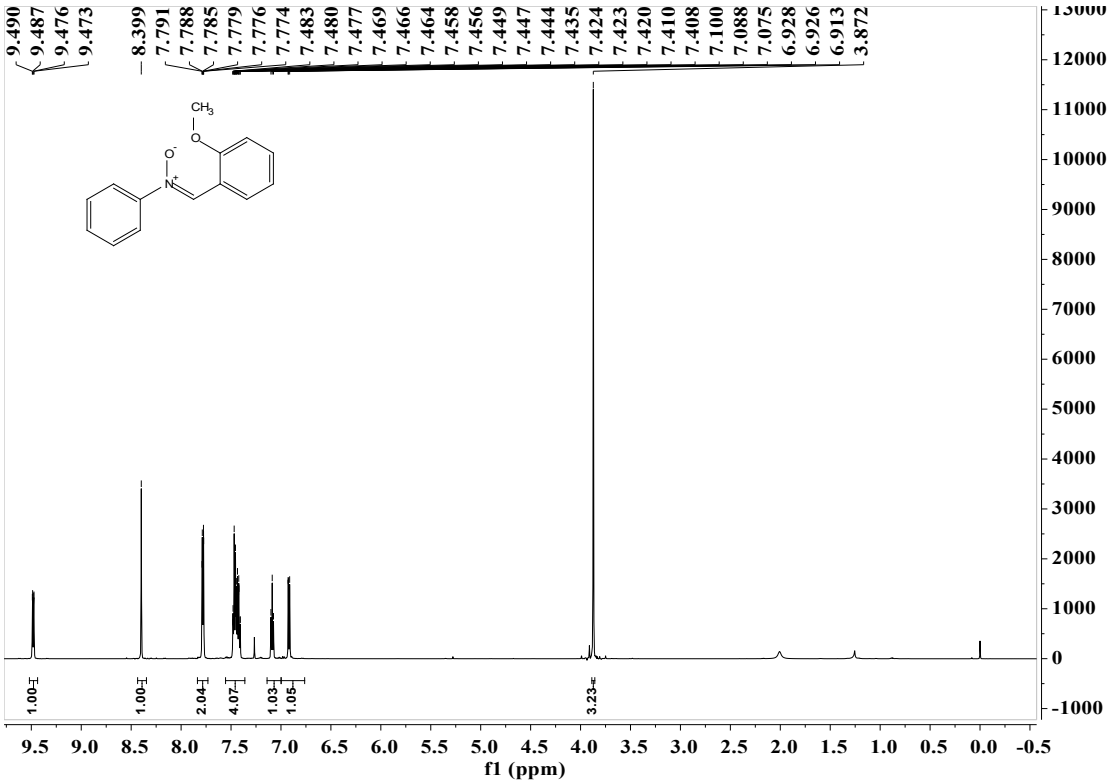
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1s**



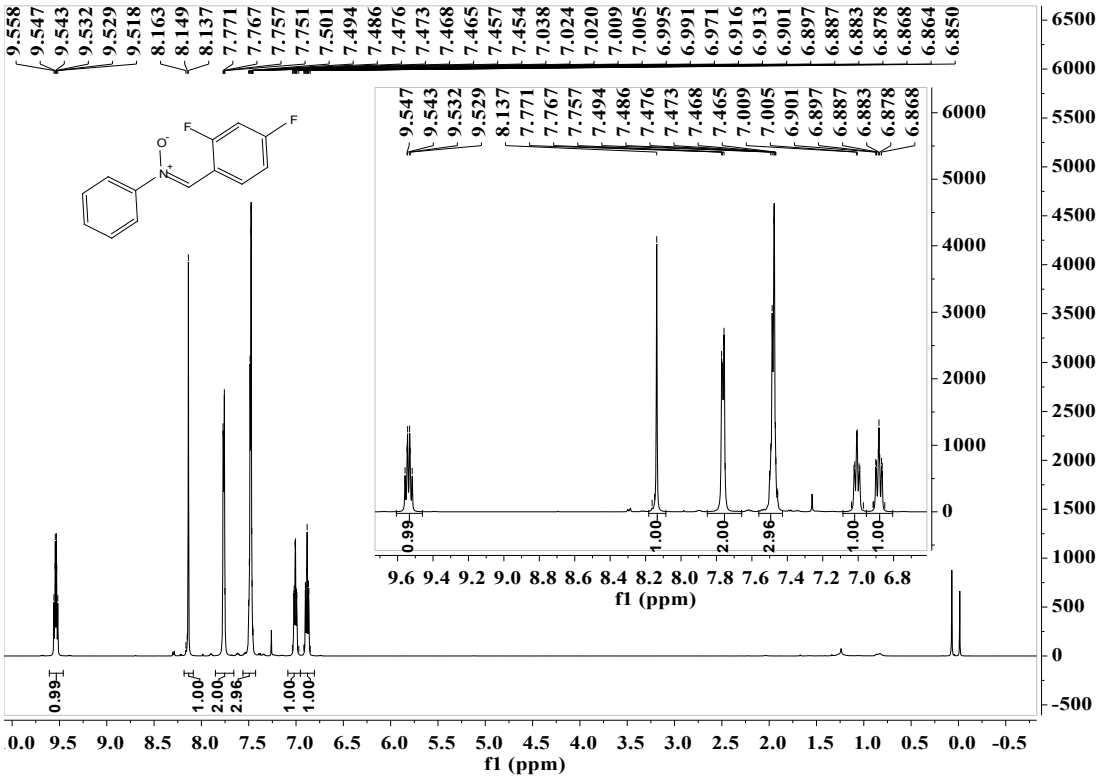
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1t**



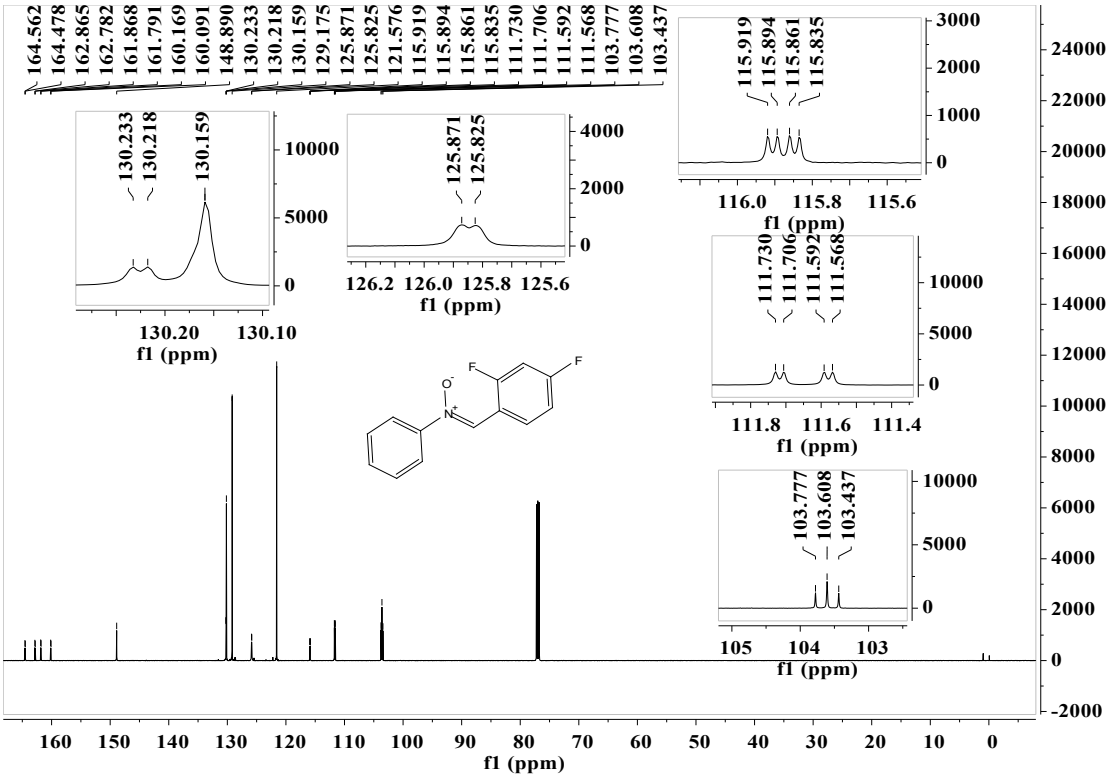
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1u**



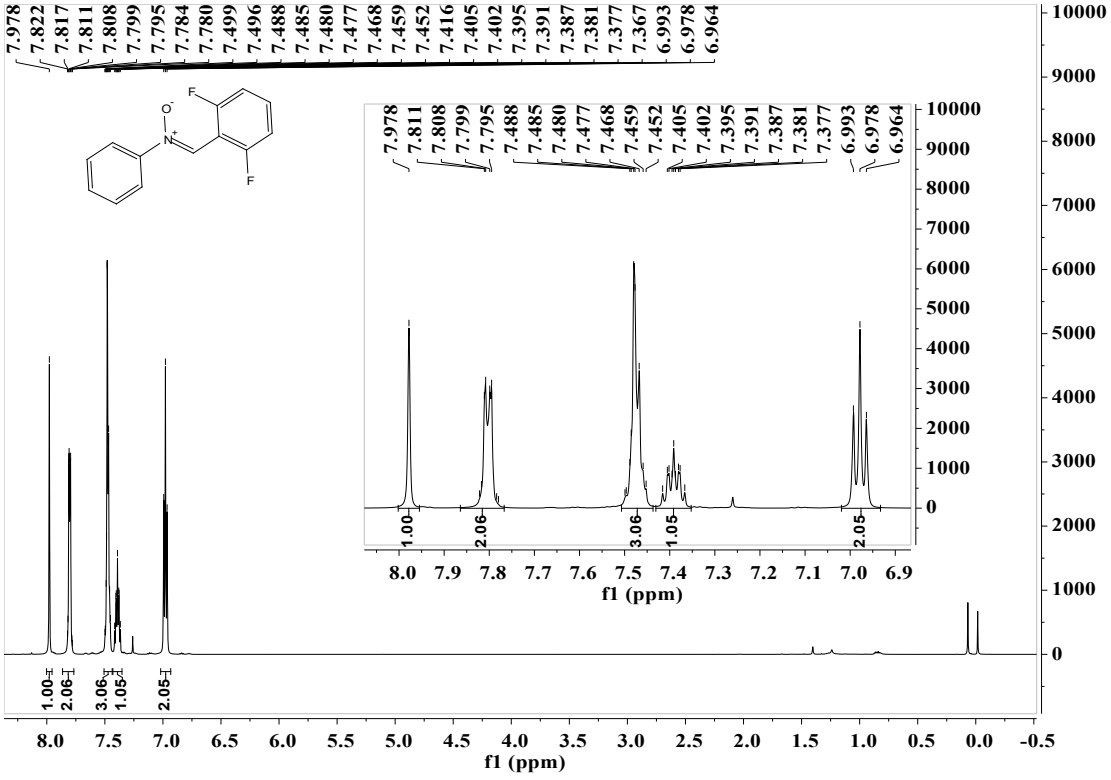
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1v**



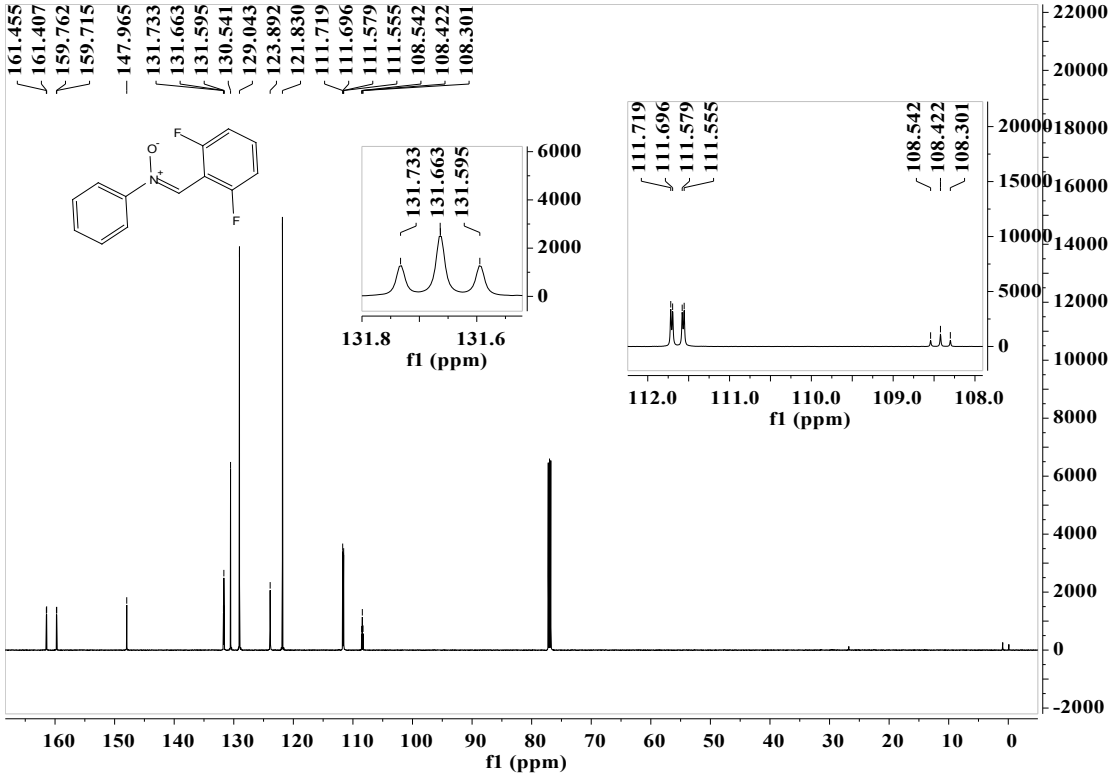
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1v**



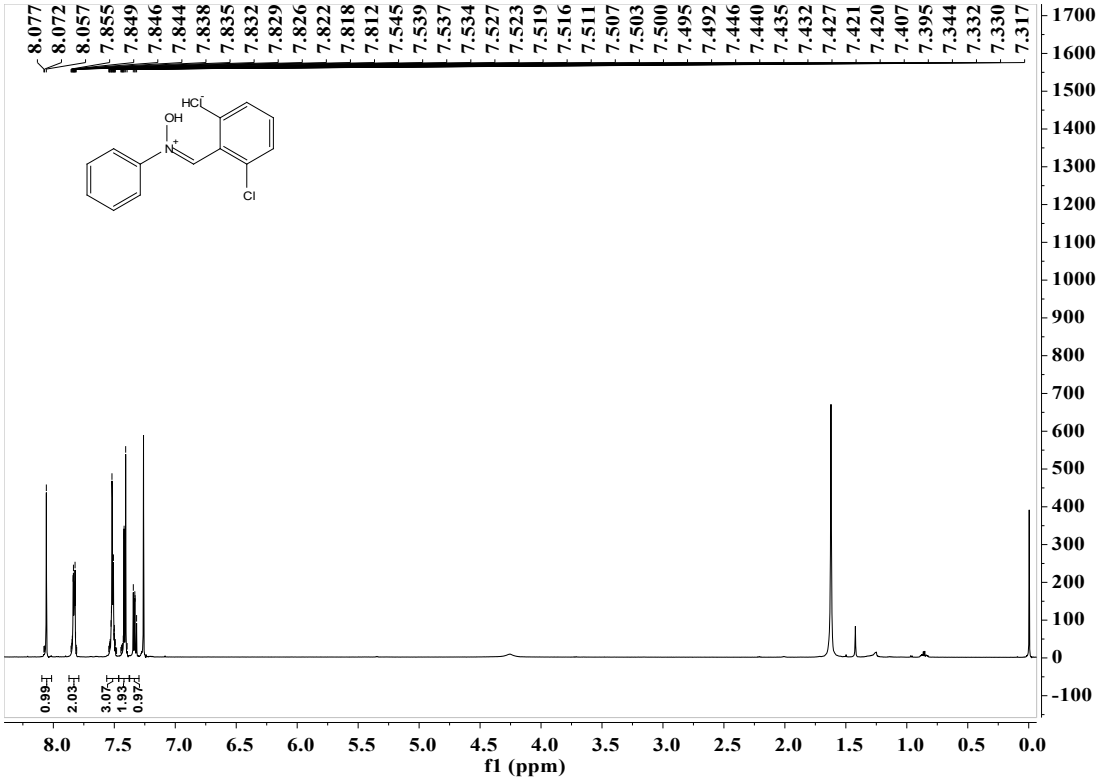
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1w**



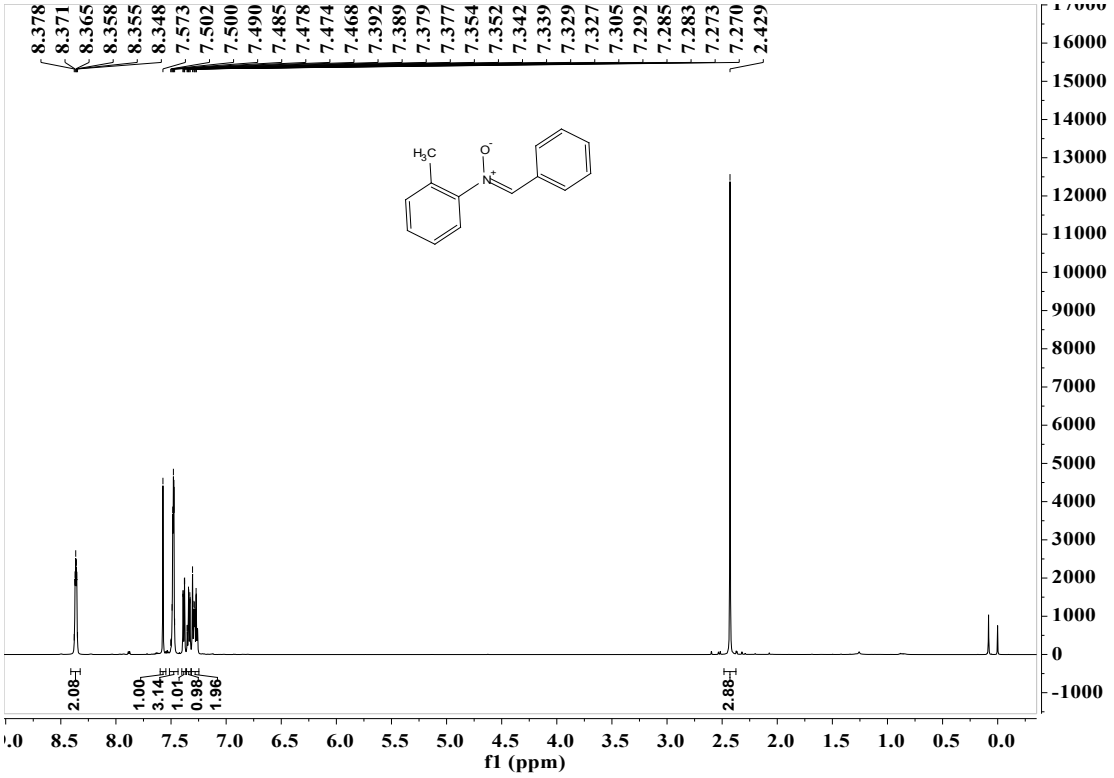
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1w**



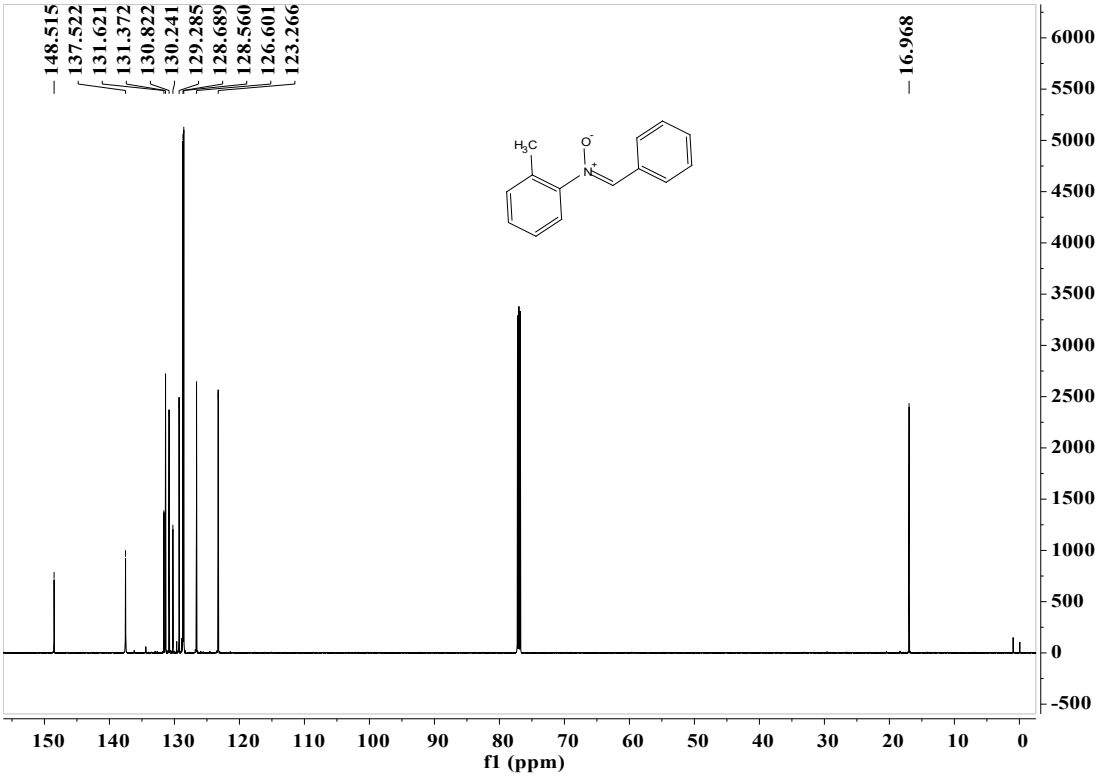
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1x**



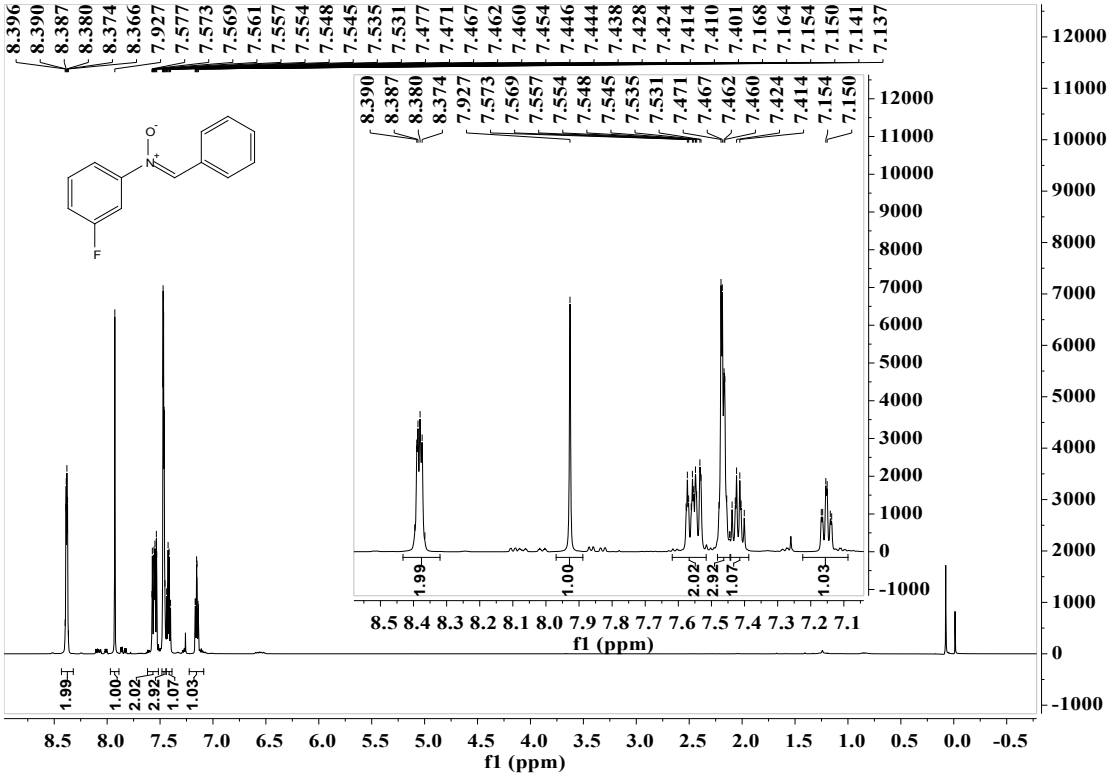
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1y**



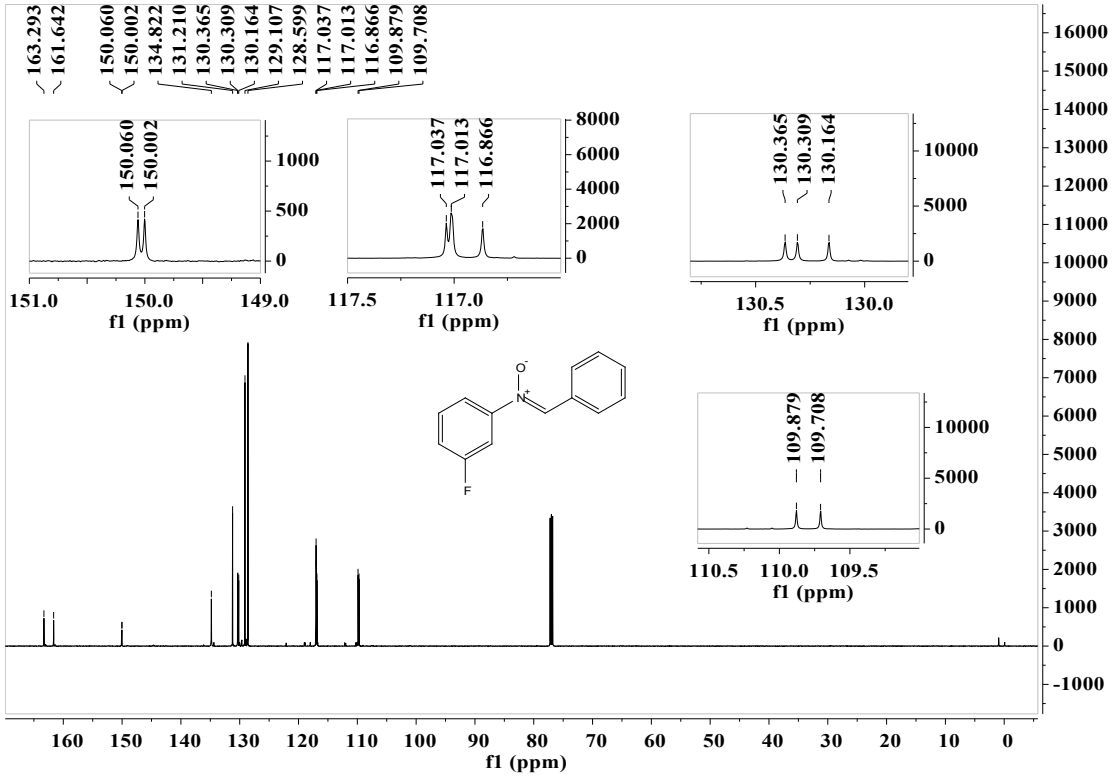
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1y**



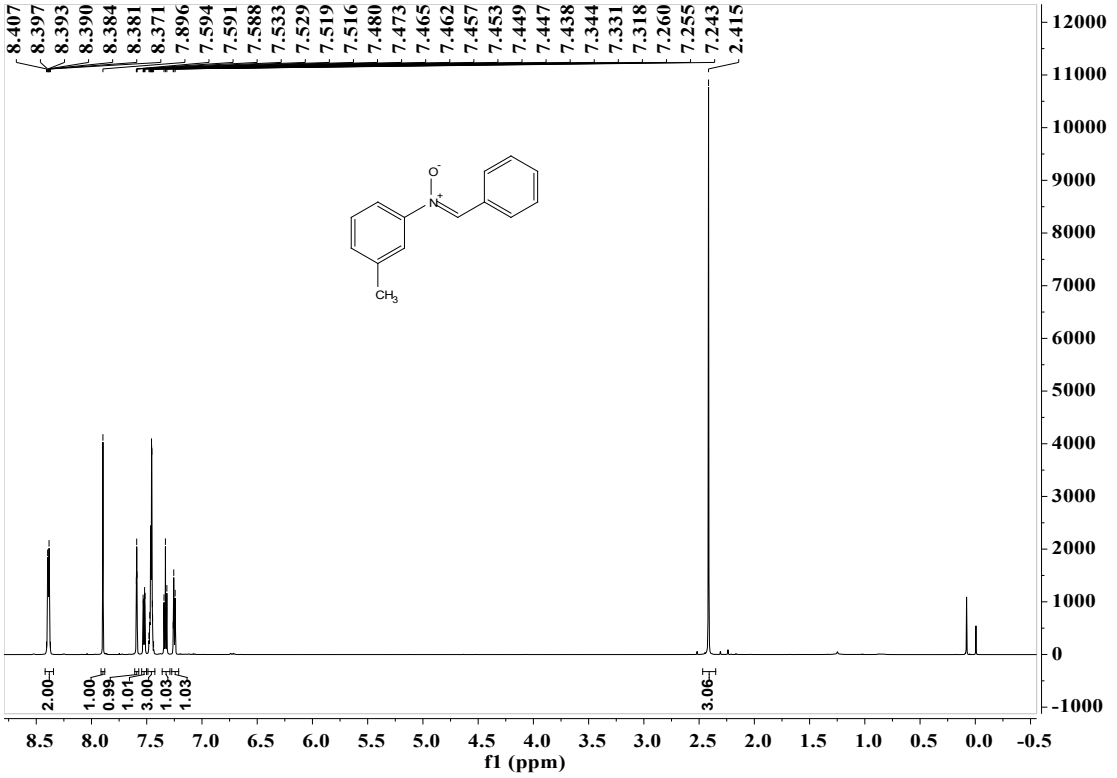
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1z**



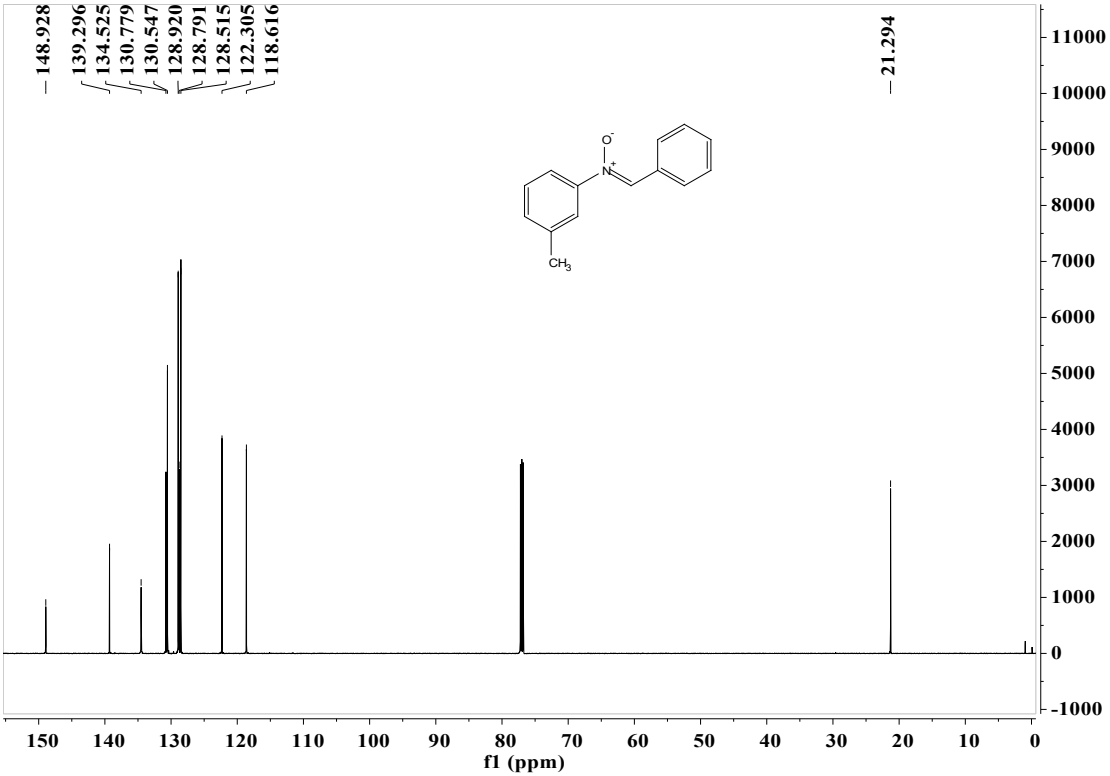
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1z**



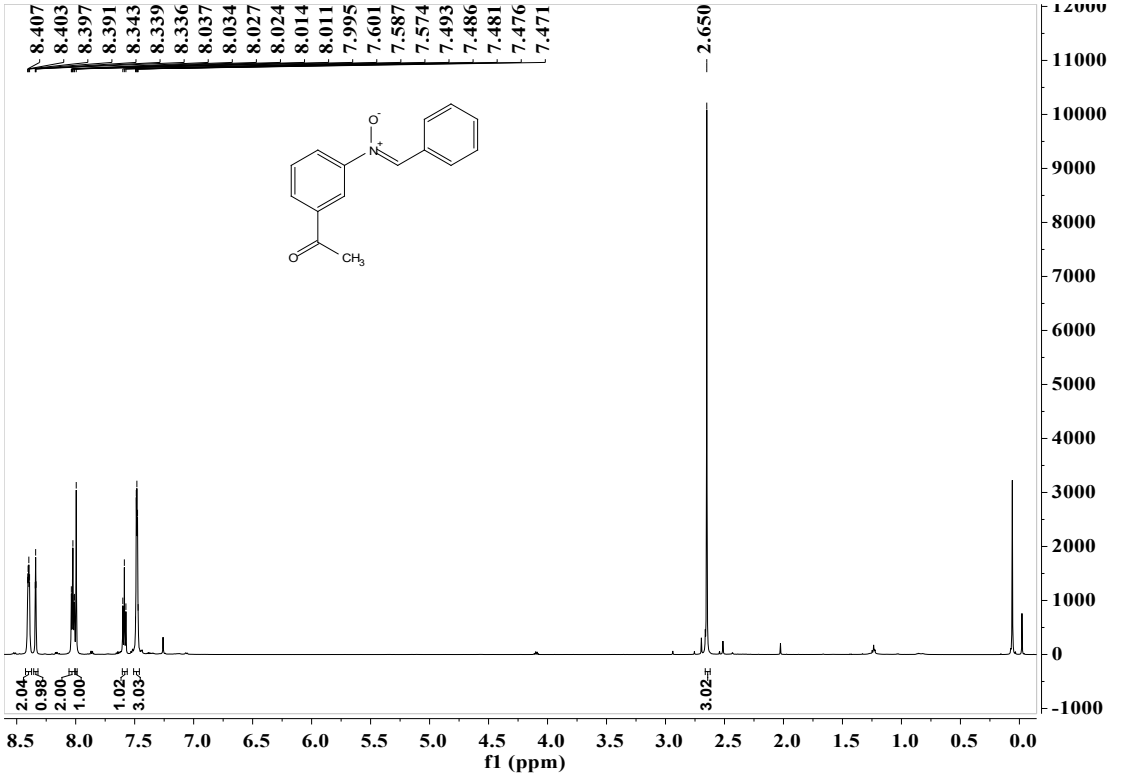
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1aa**



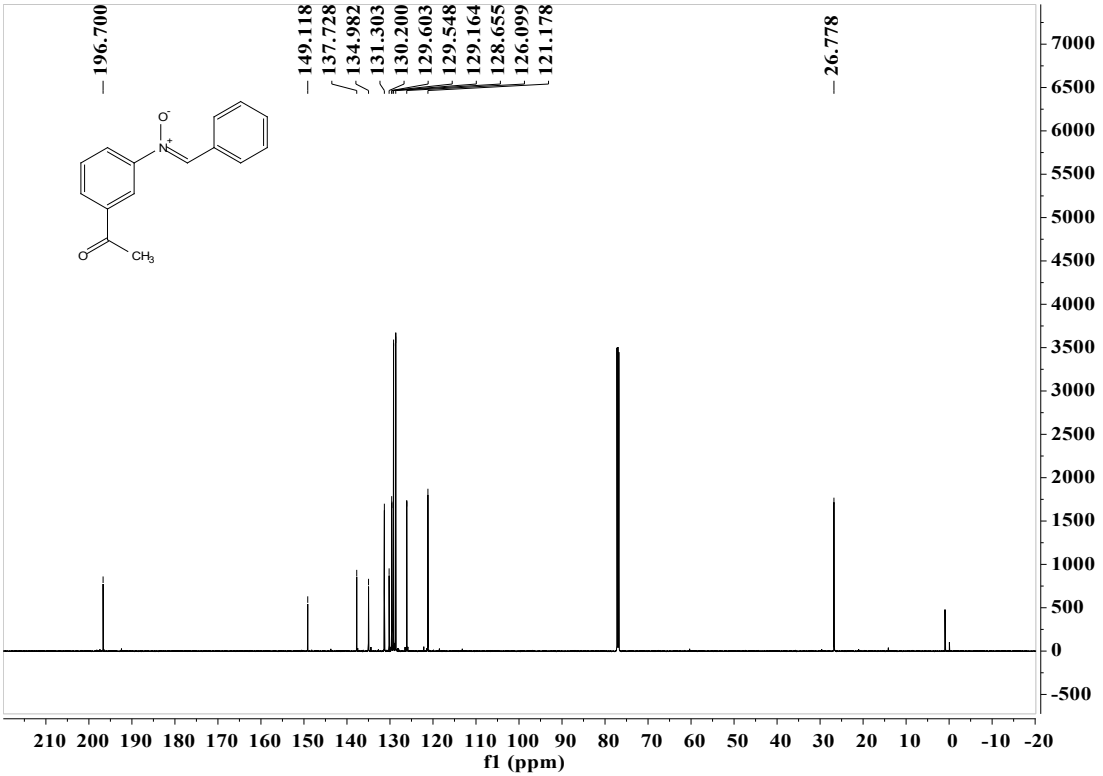
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1aa**



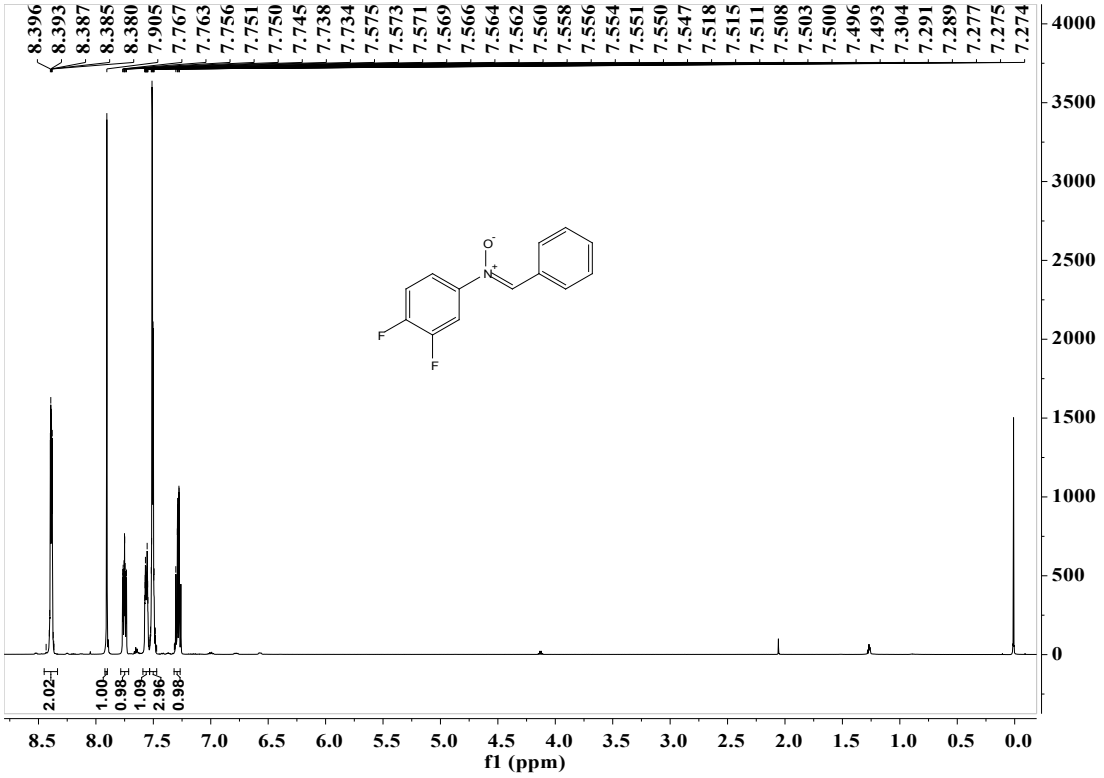
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1ab**



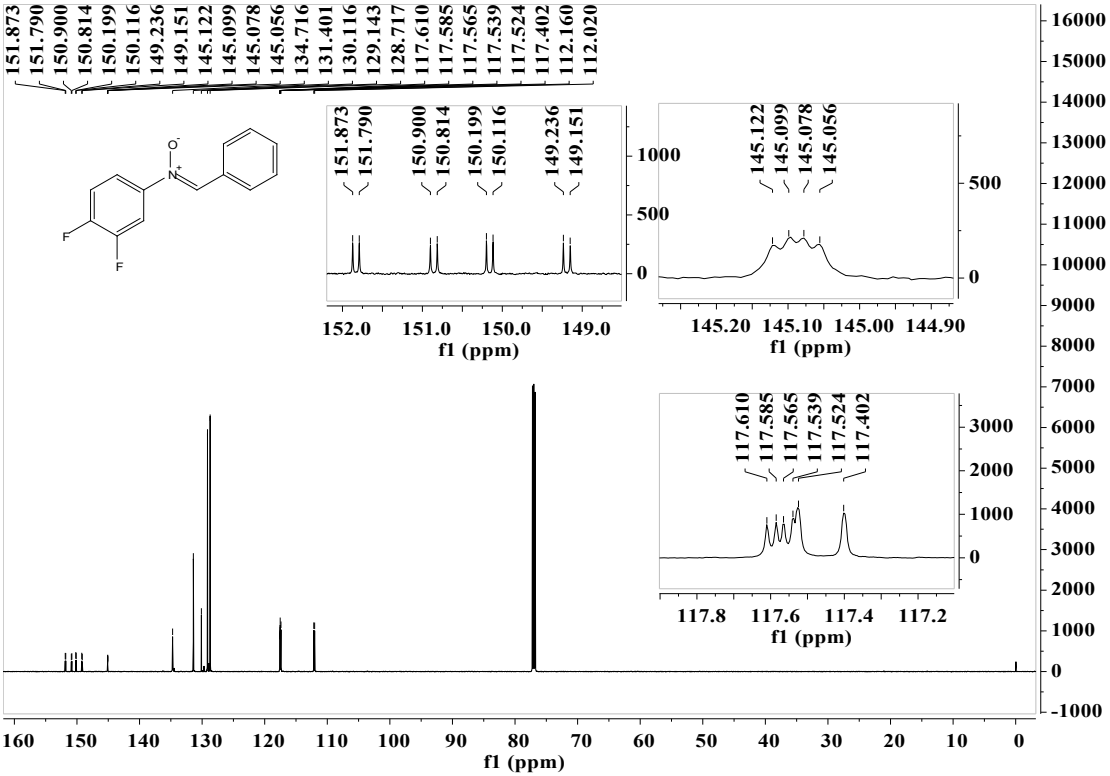
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1ab**



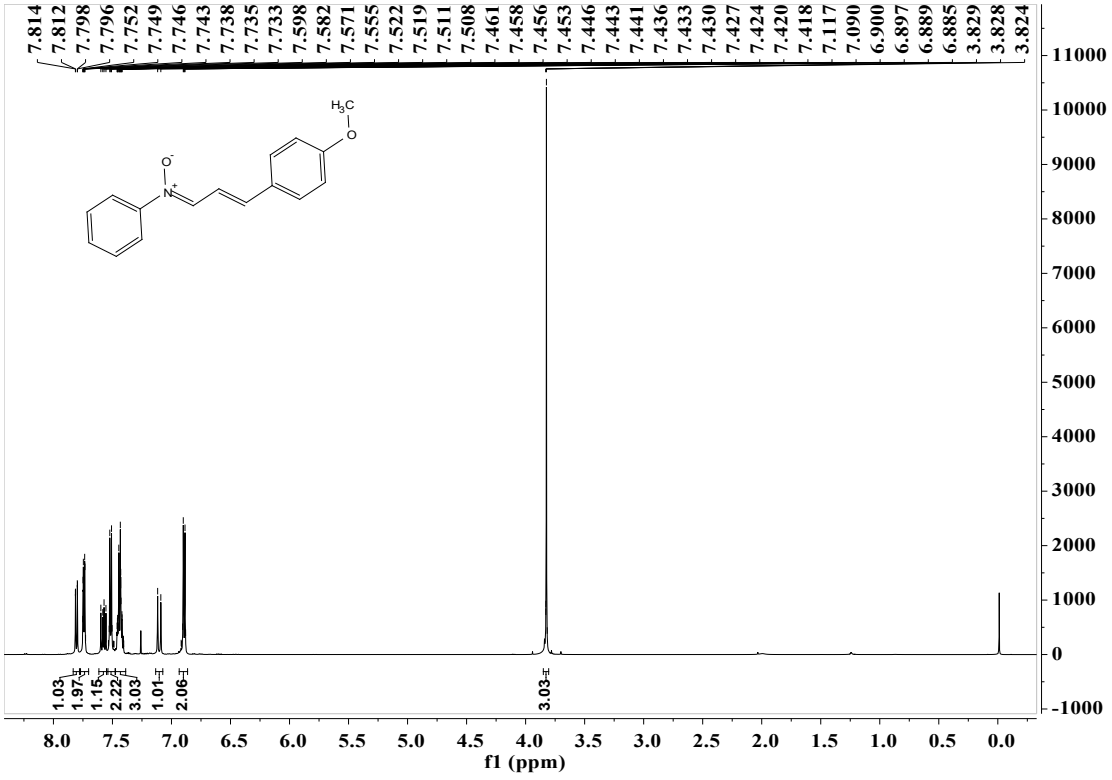
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1ac**



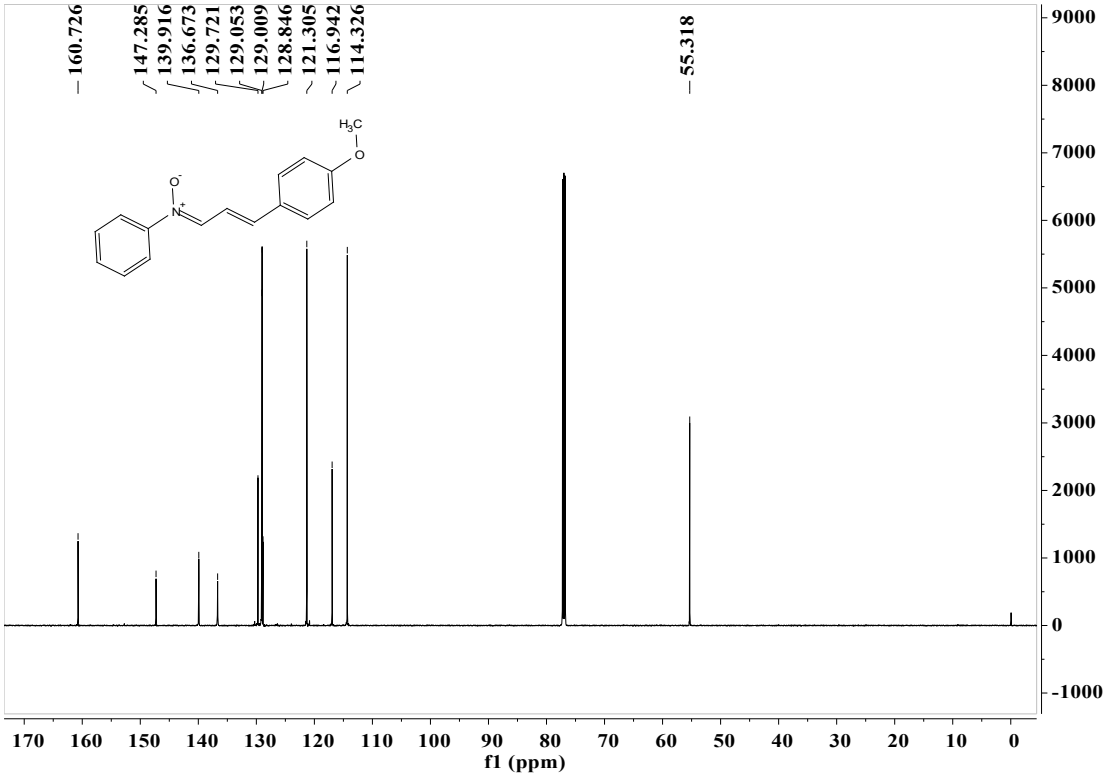
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1ac**



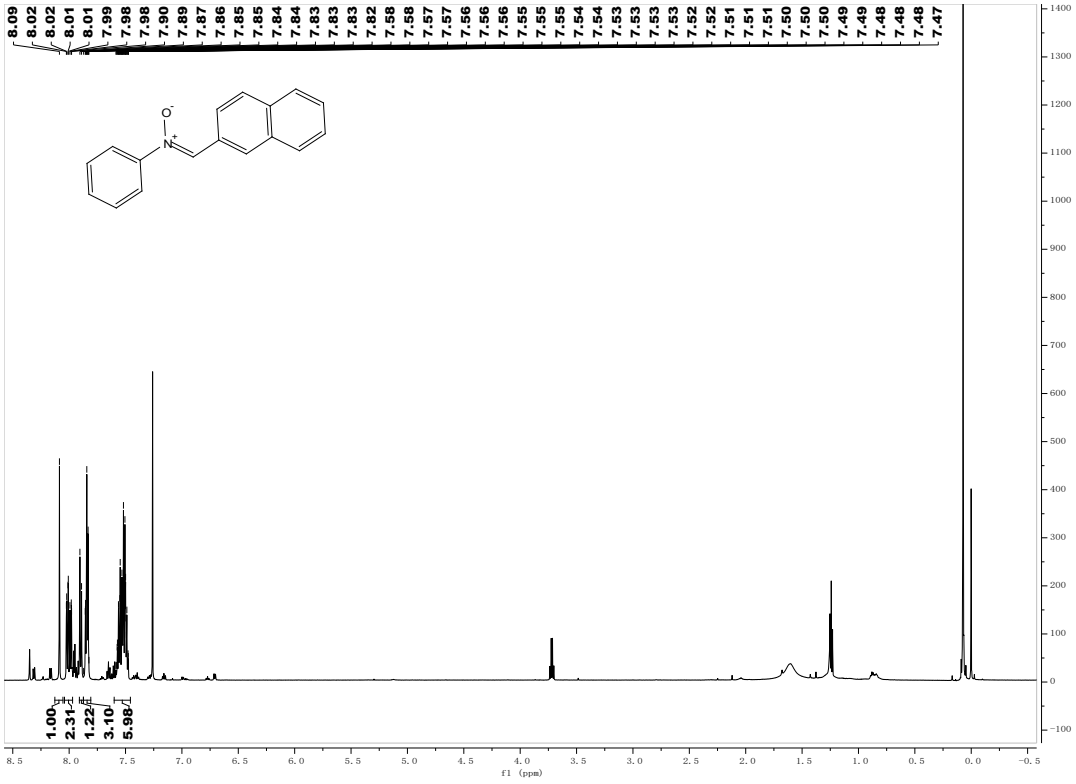
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1ad**



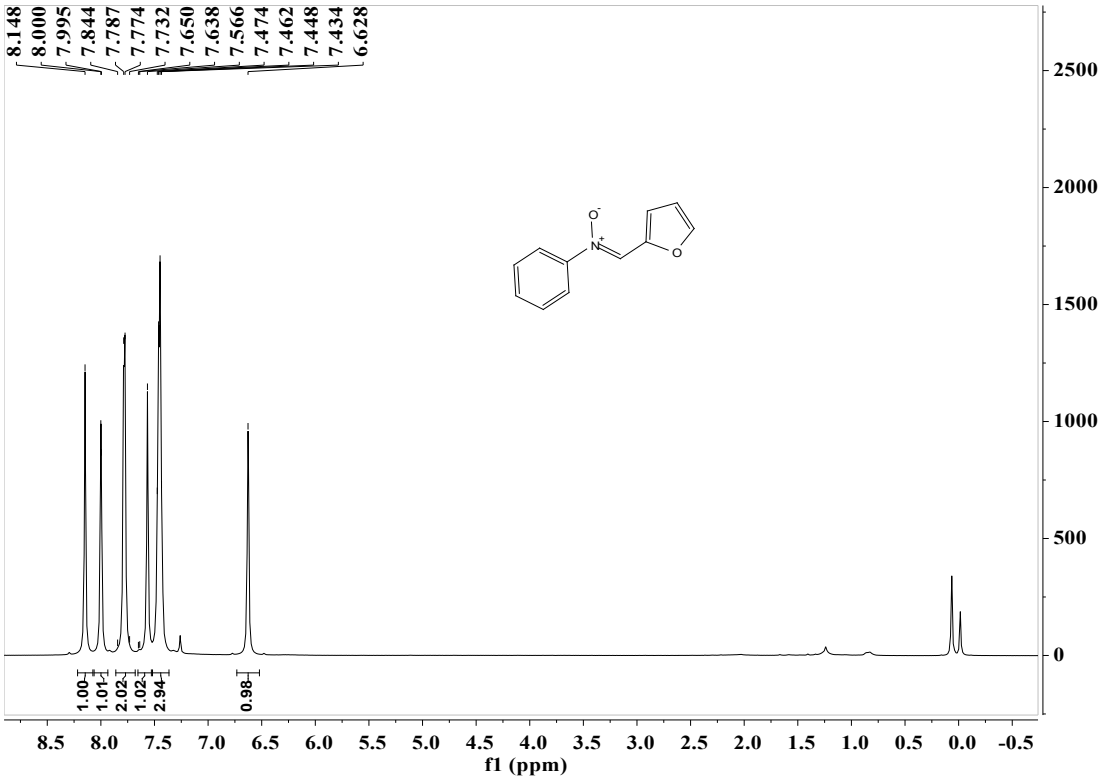
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1ad**



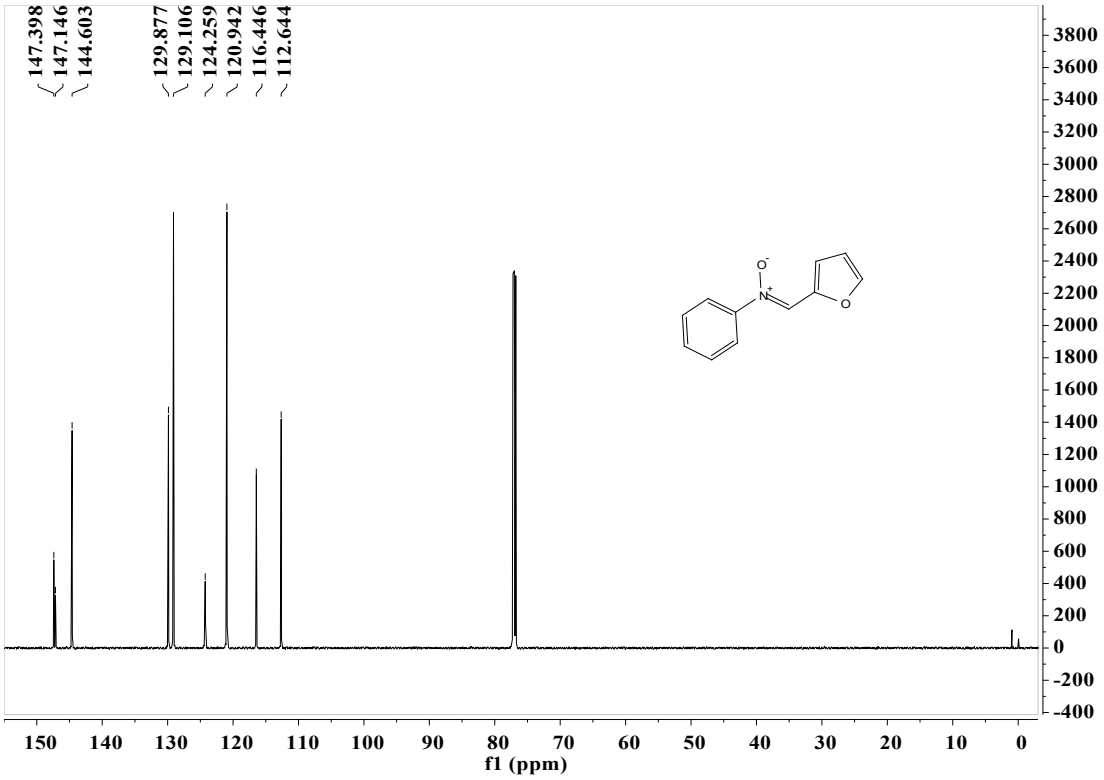
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1ae**



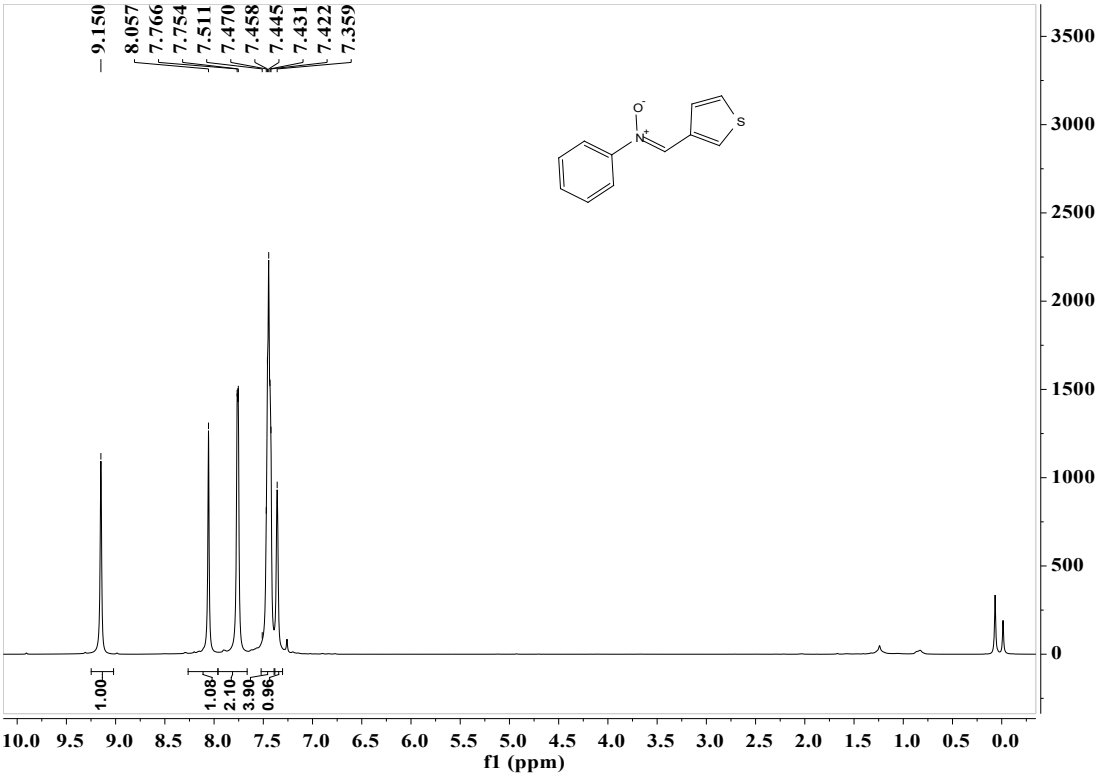
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1af**



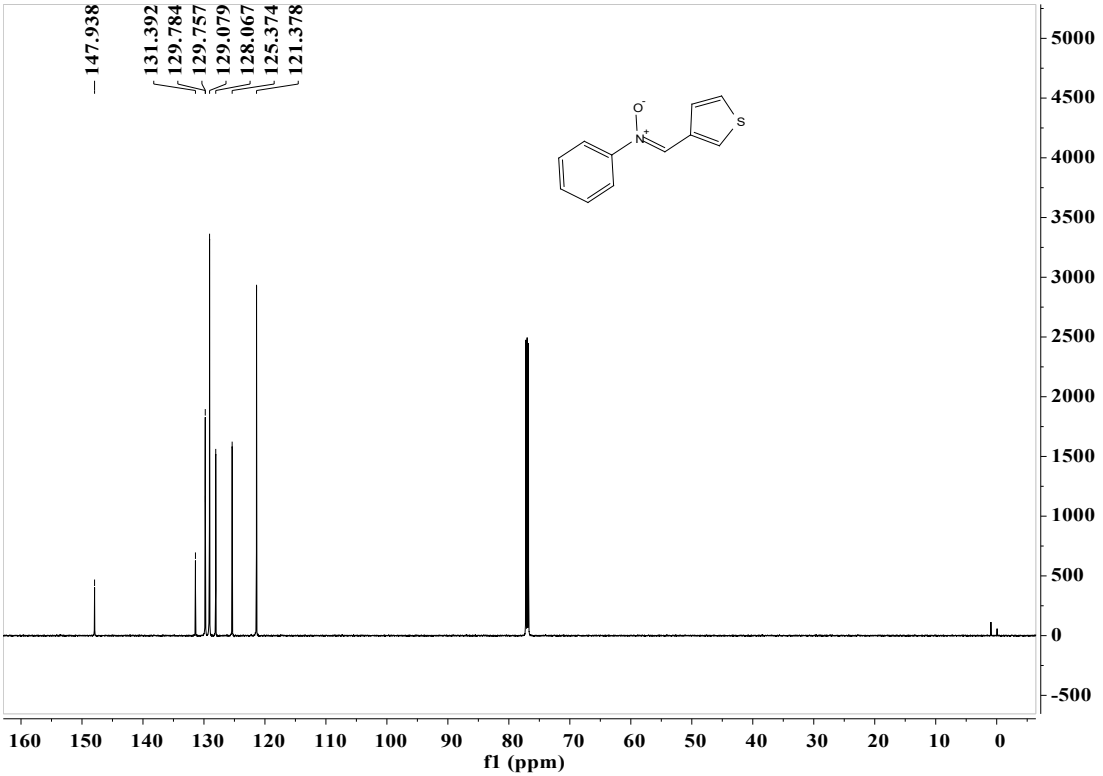
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1af**



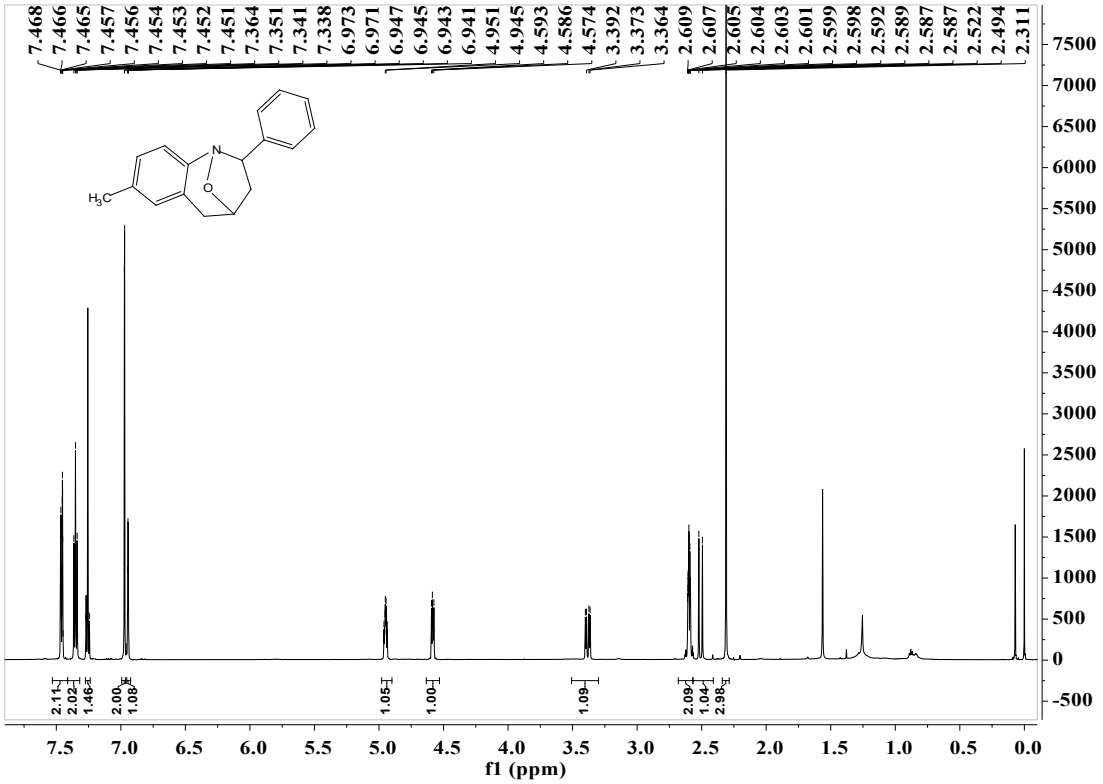
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **1ag**



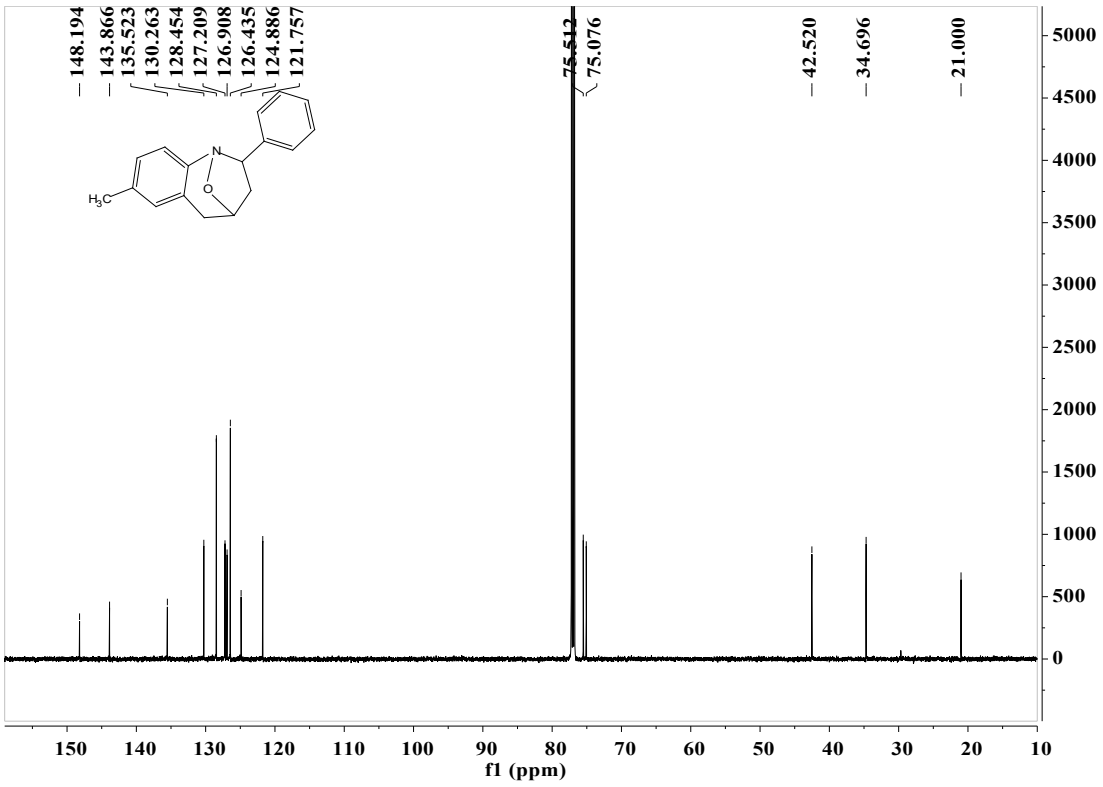
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **1ag**



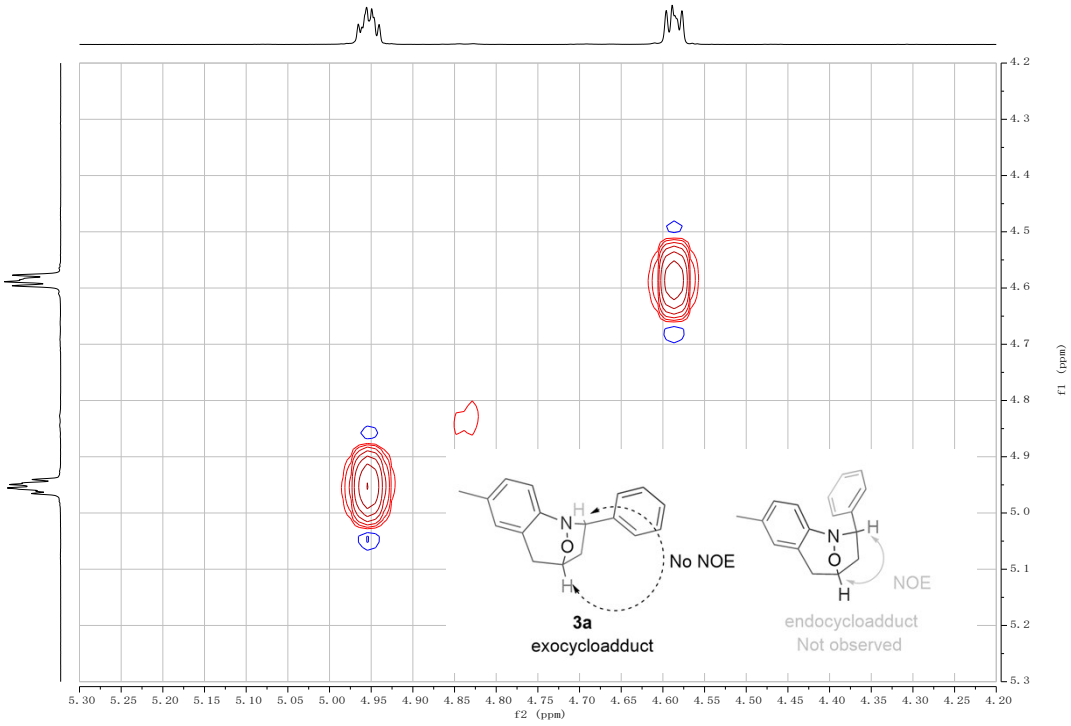
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3a**



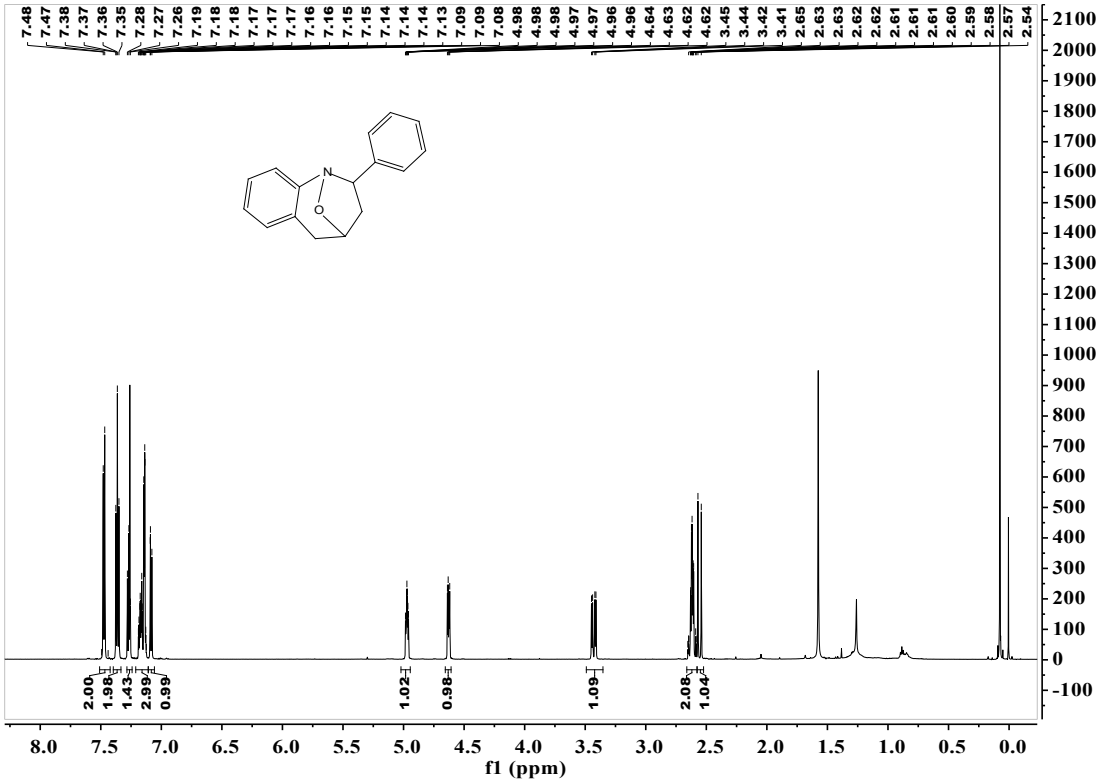
^{13}C NMR (151 MHZ, $CDCl_3$) for compound **3a**



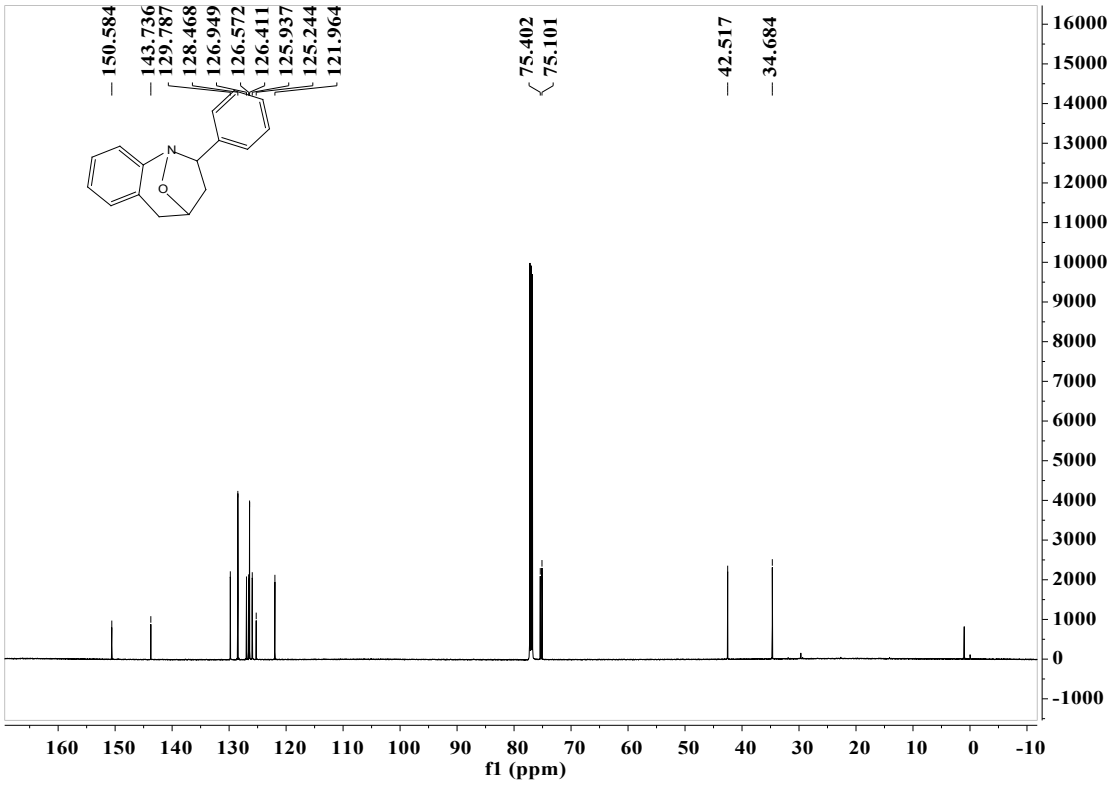
2D NOE experiment of compound **3a**



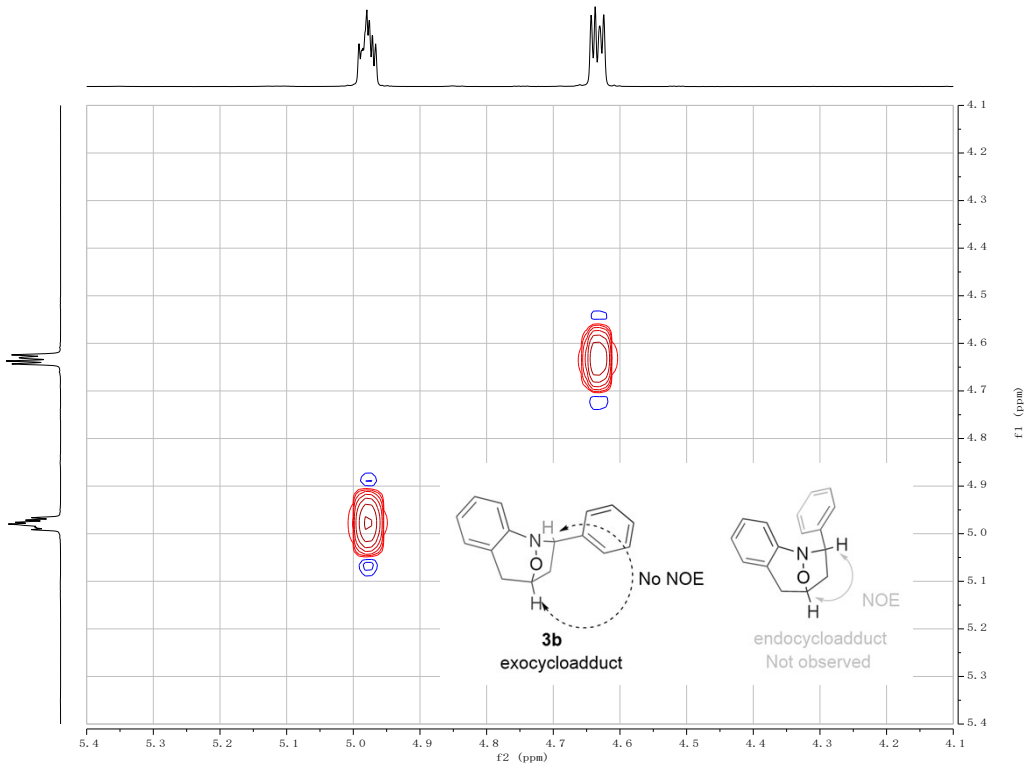
^{1}H NMR (600 MHZ, $CDCl_3$) for compound **3b**



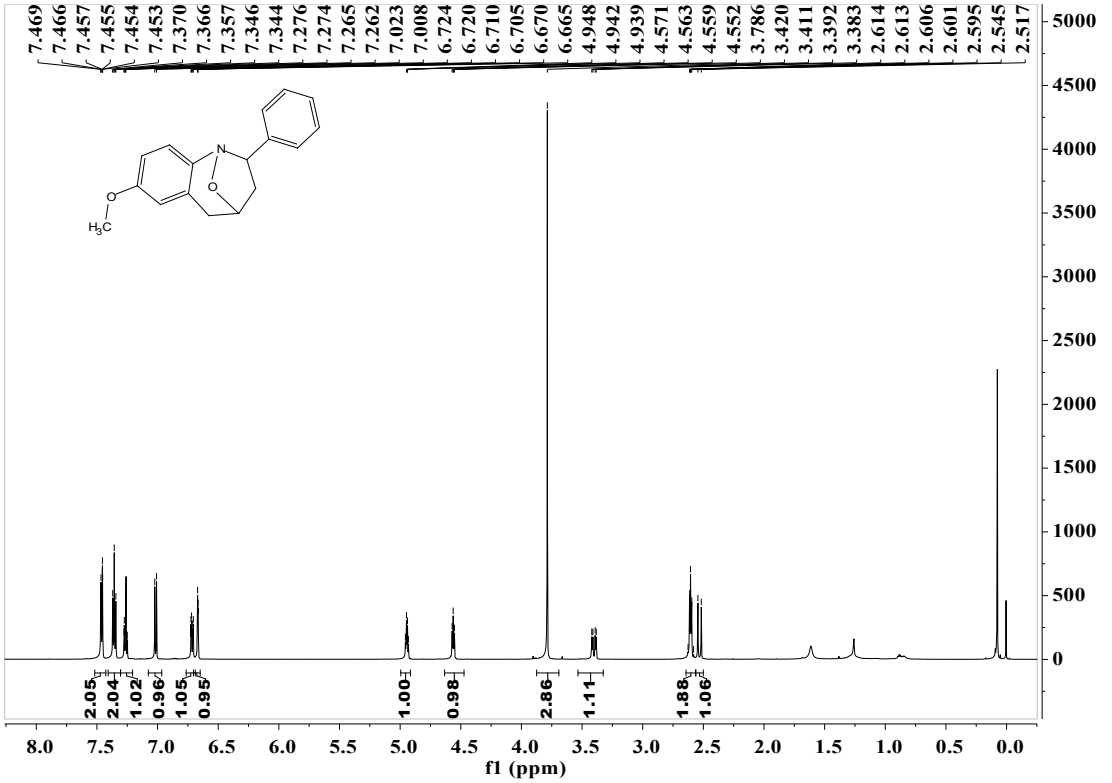
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3b**



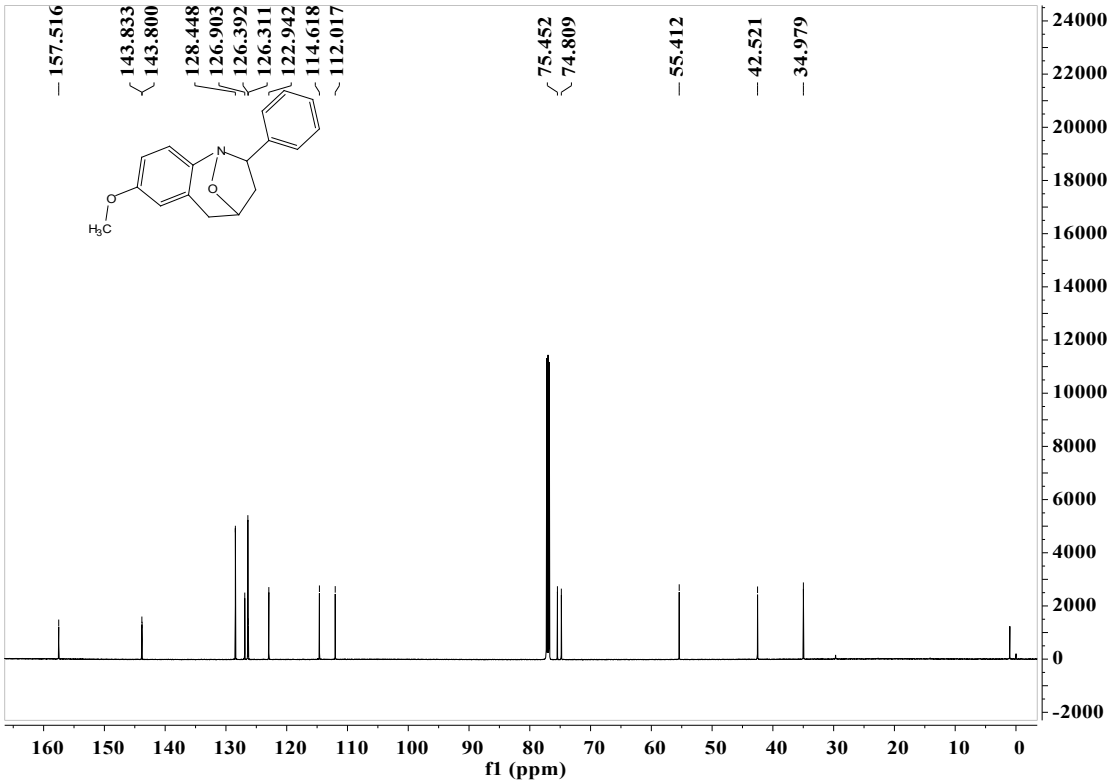
2D NOE experiment of compound **3b**



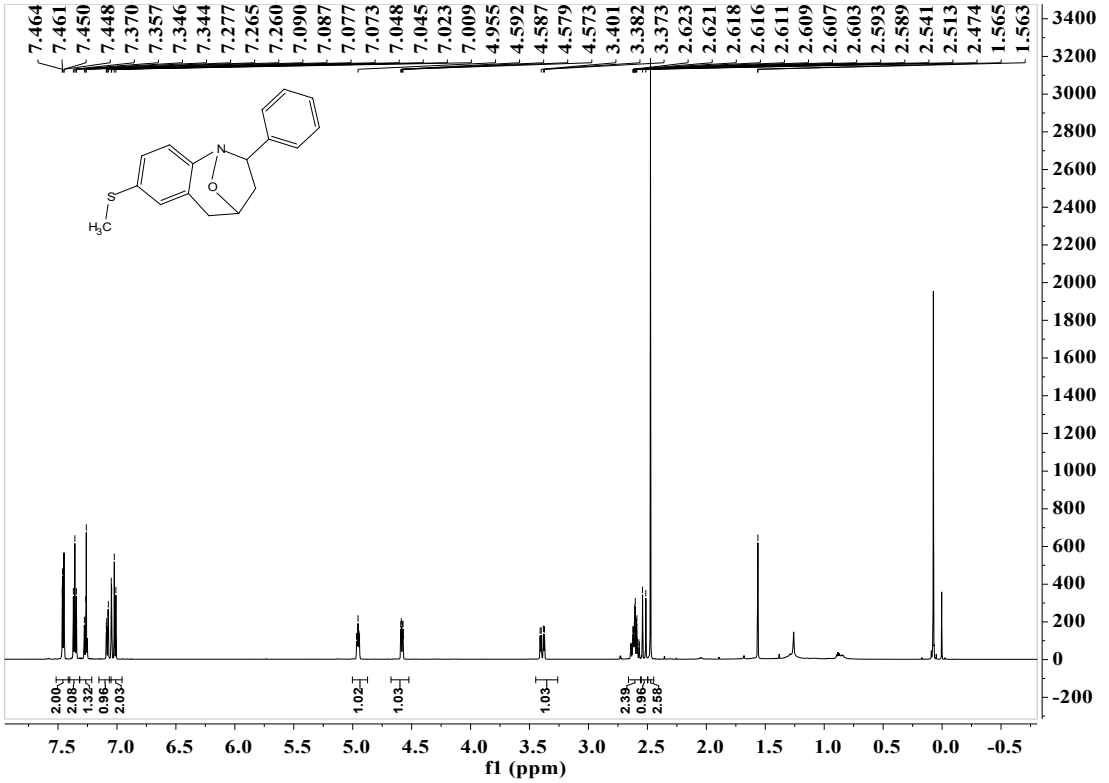
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3c**



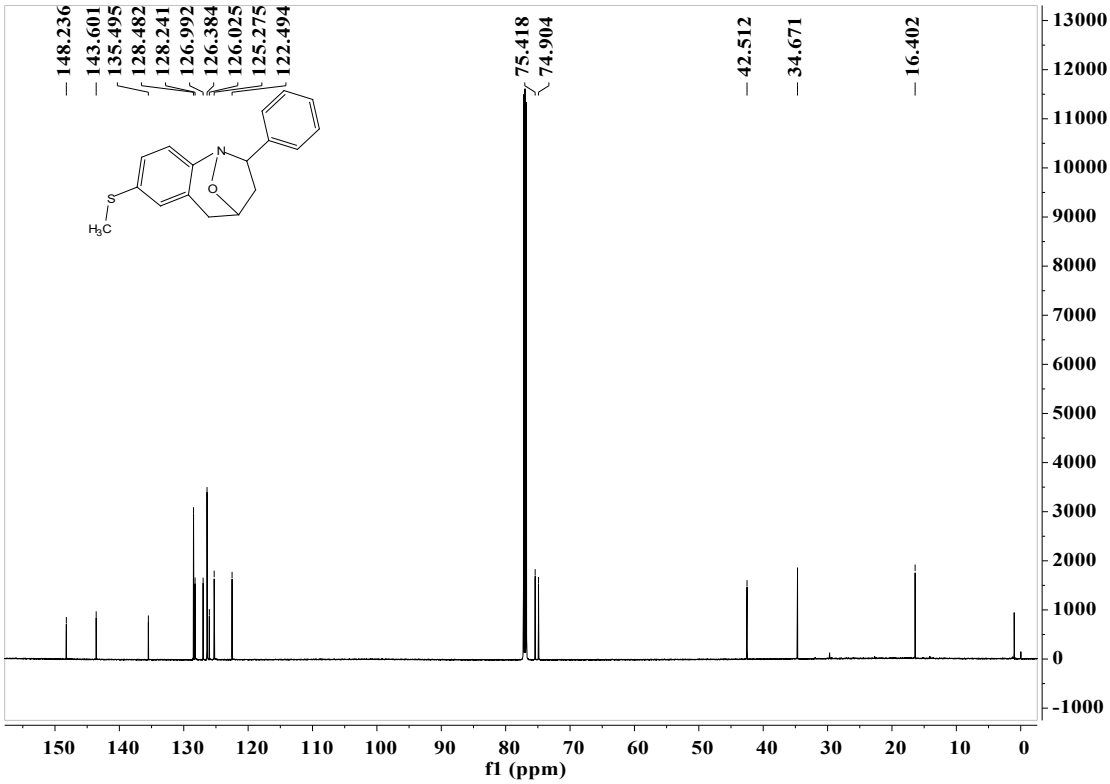
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3c**



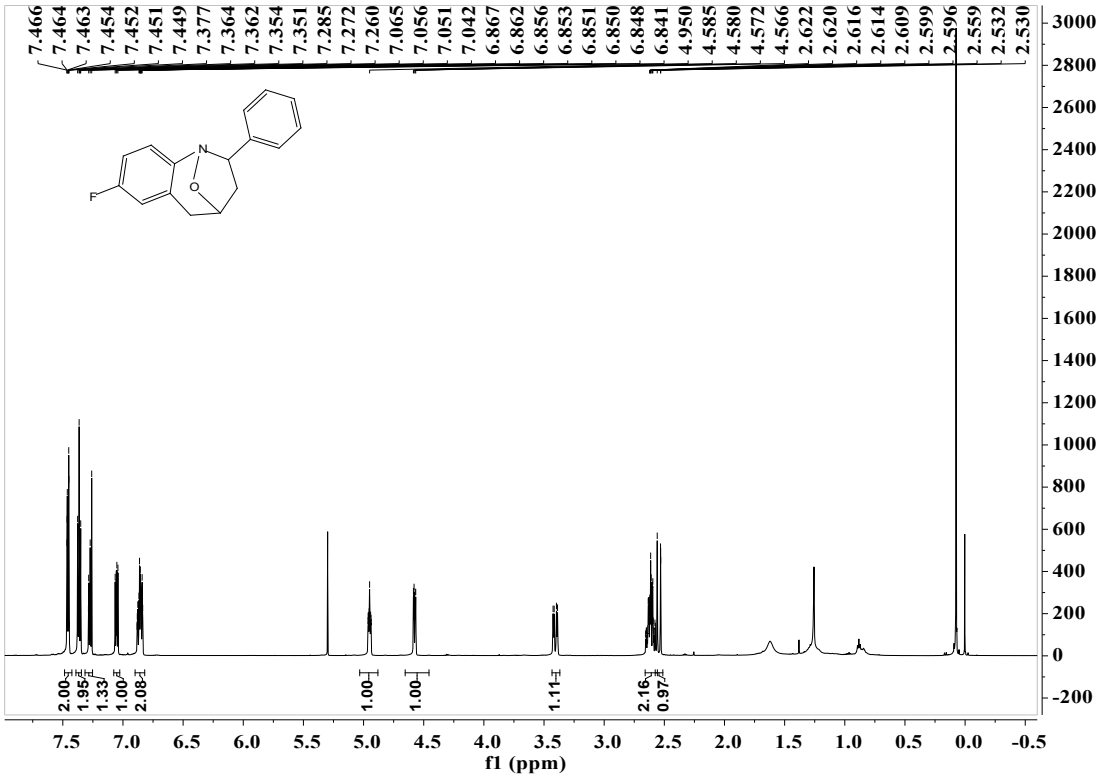
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3d**



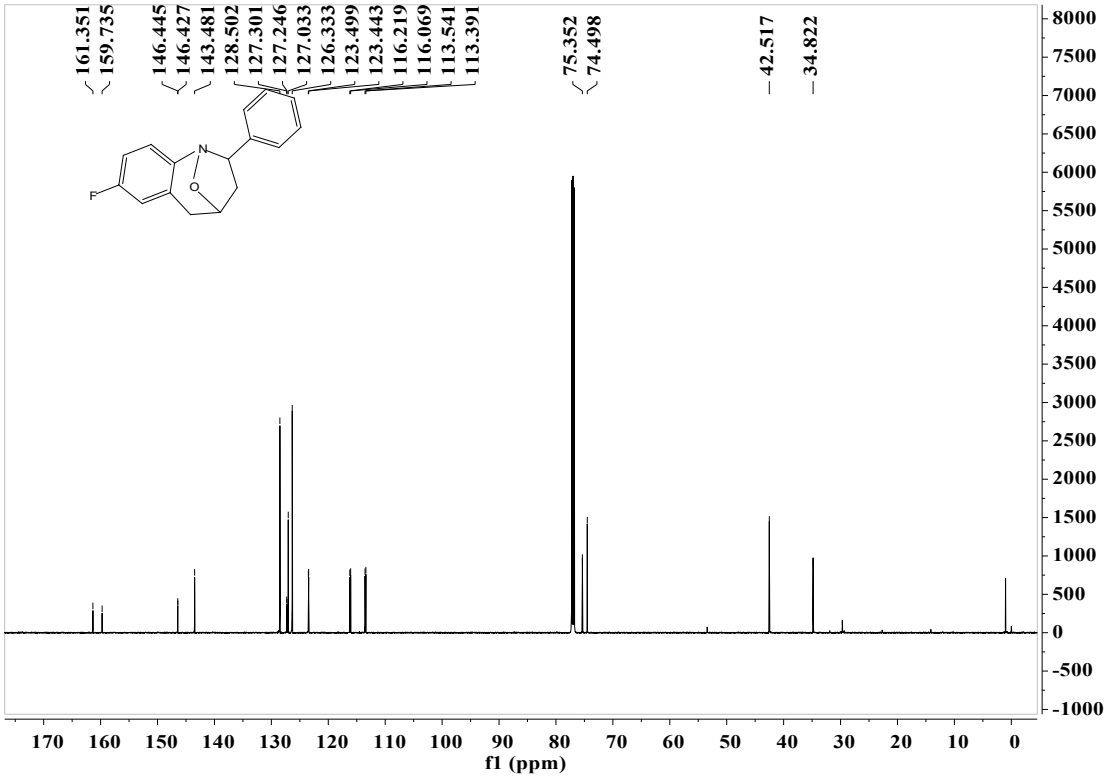
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3d**



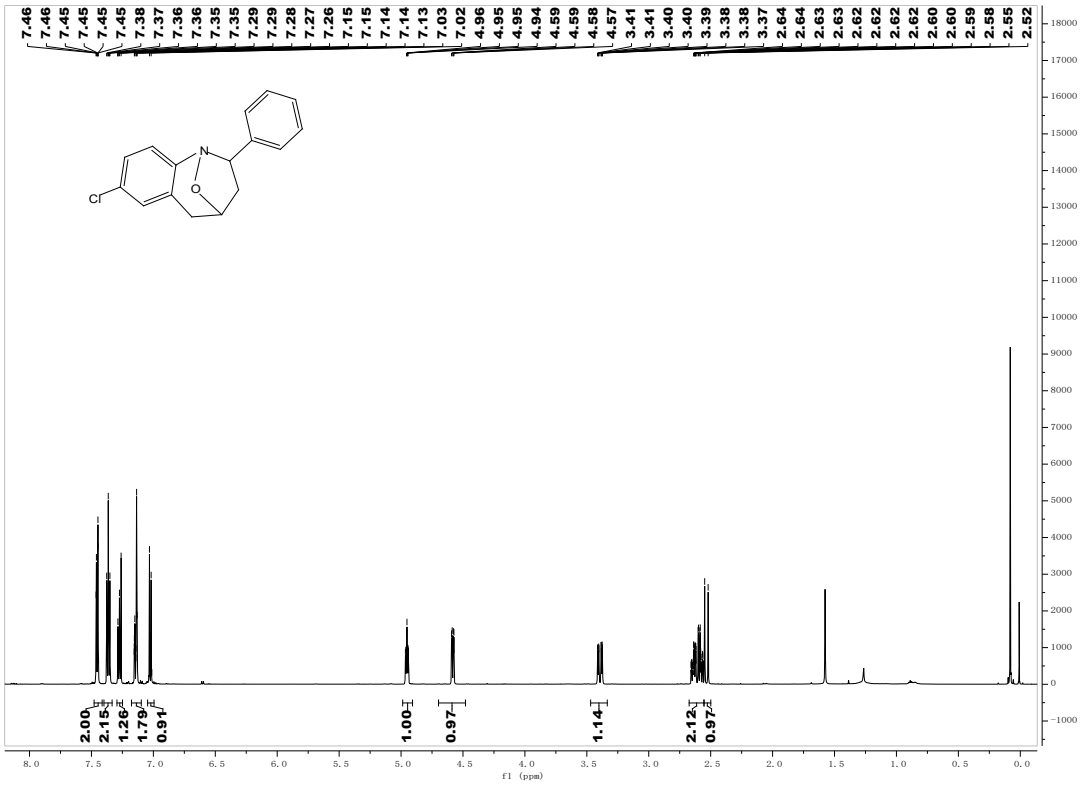
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3e**



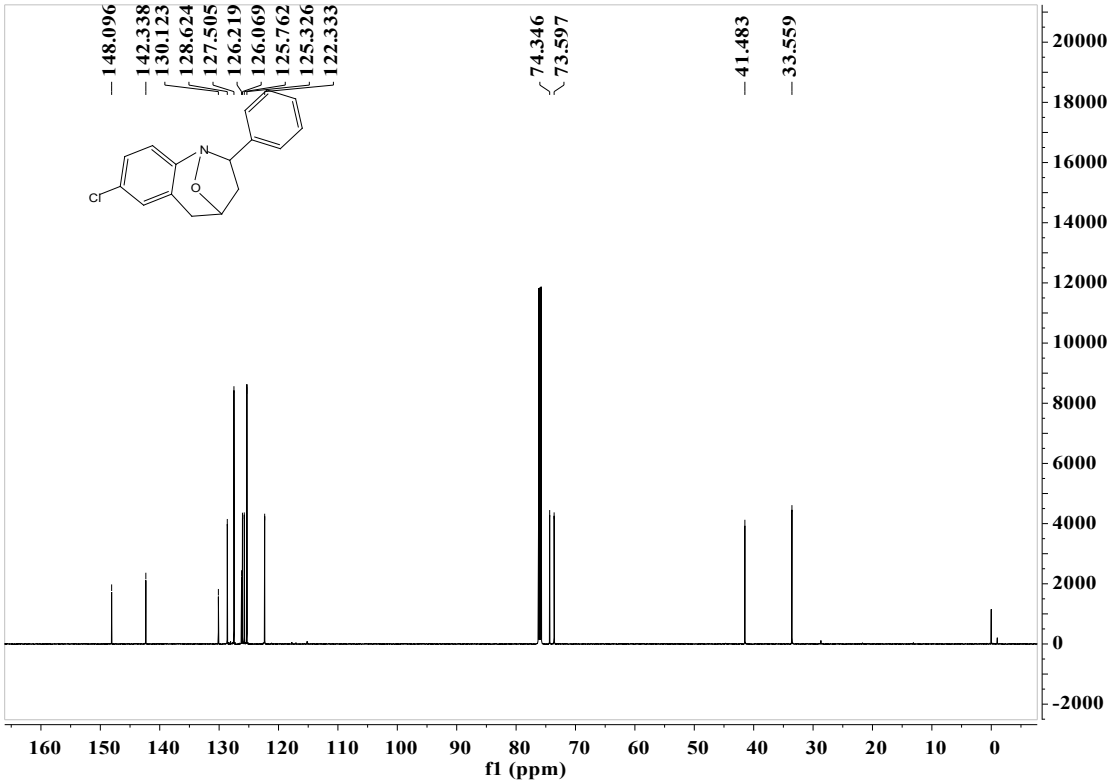
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3e**



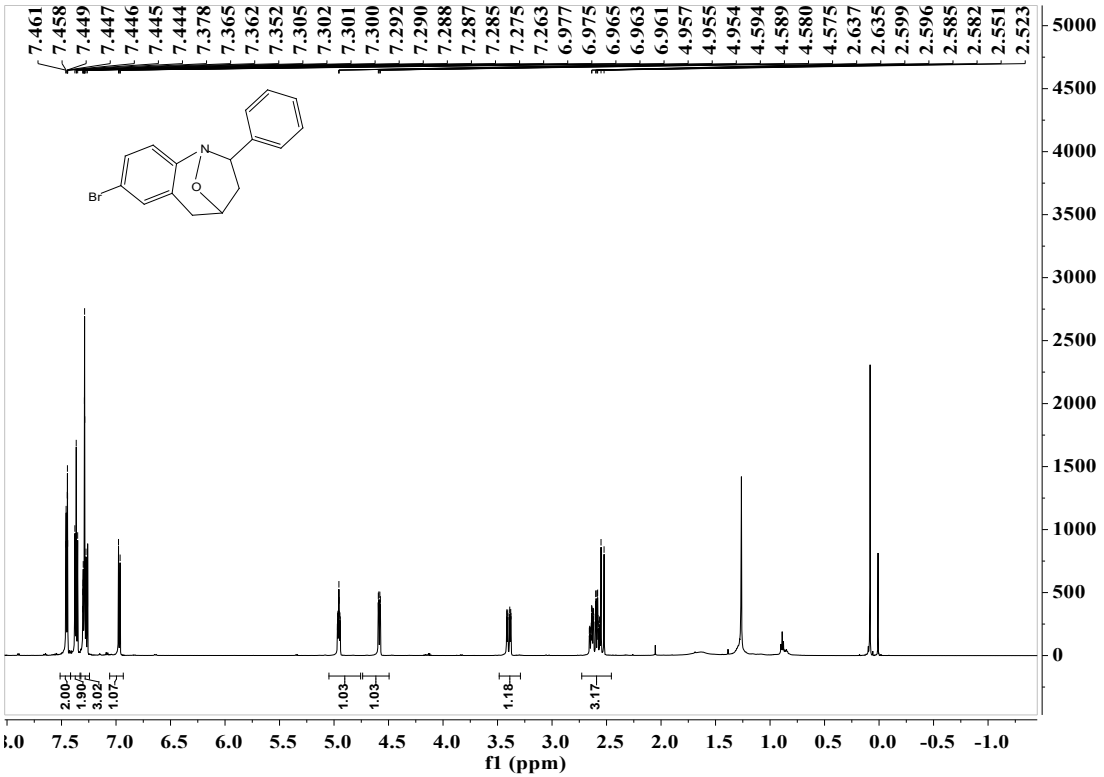
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3f**



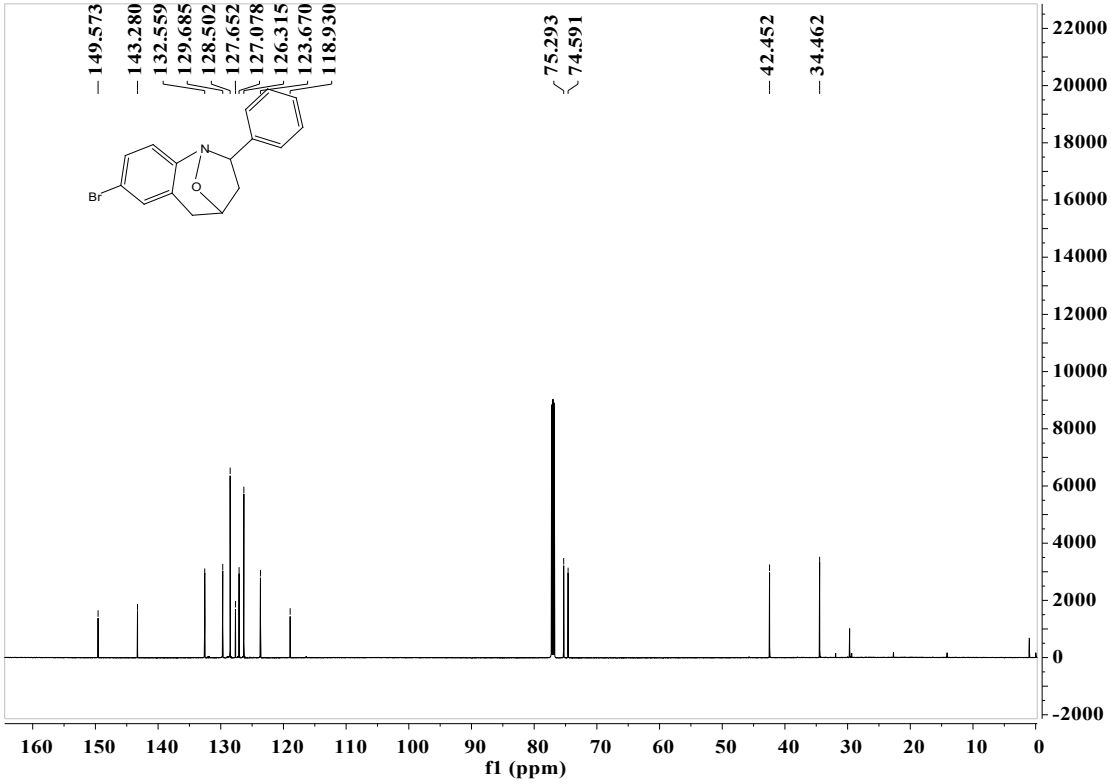
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3f**



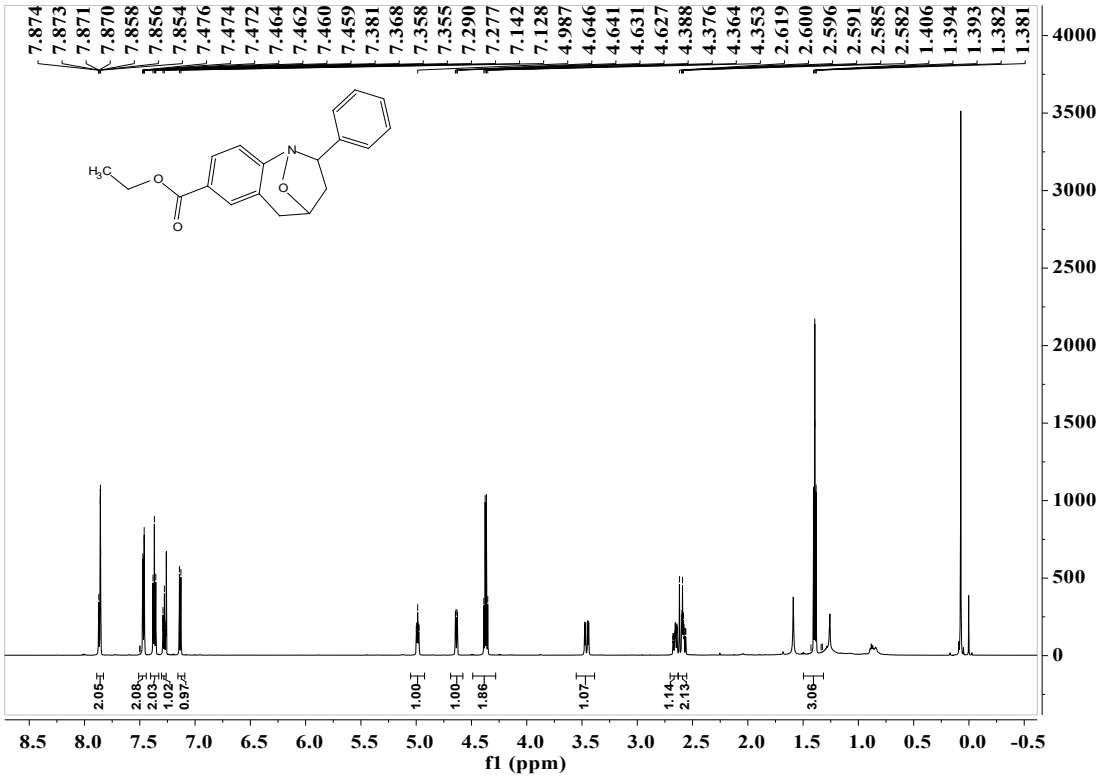
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3g**



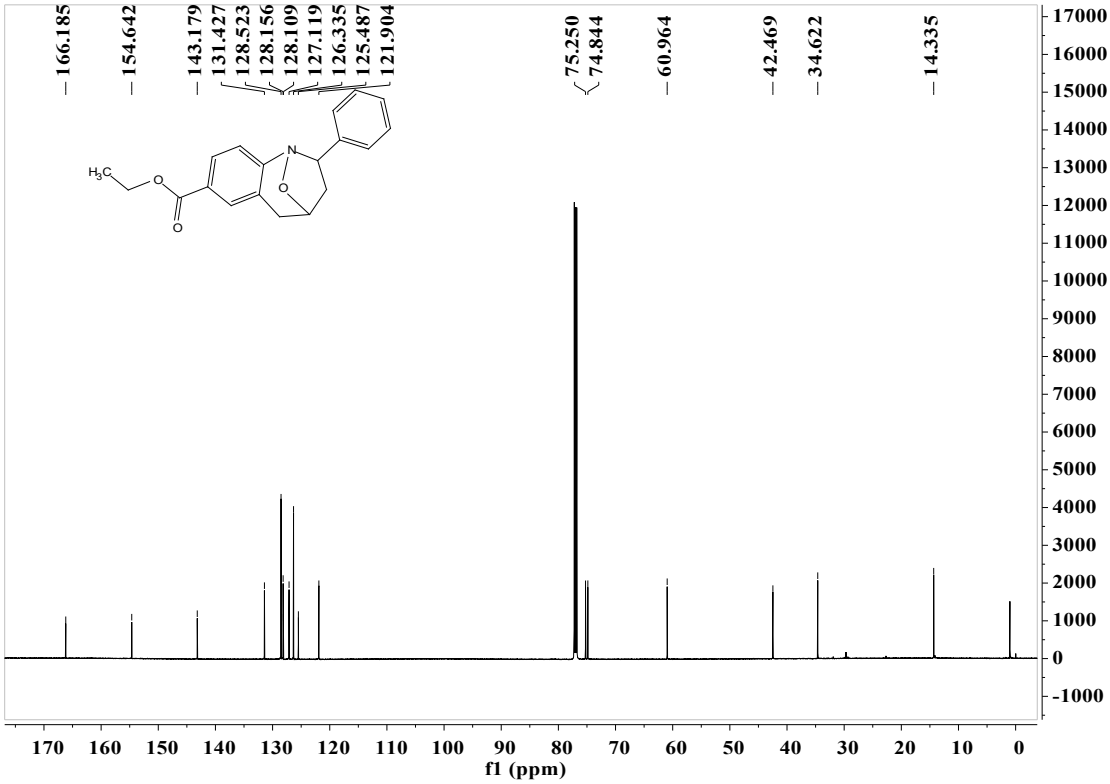
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3g**



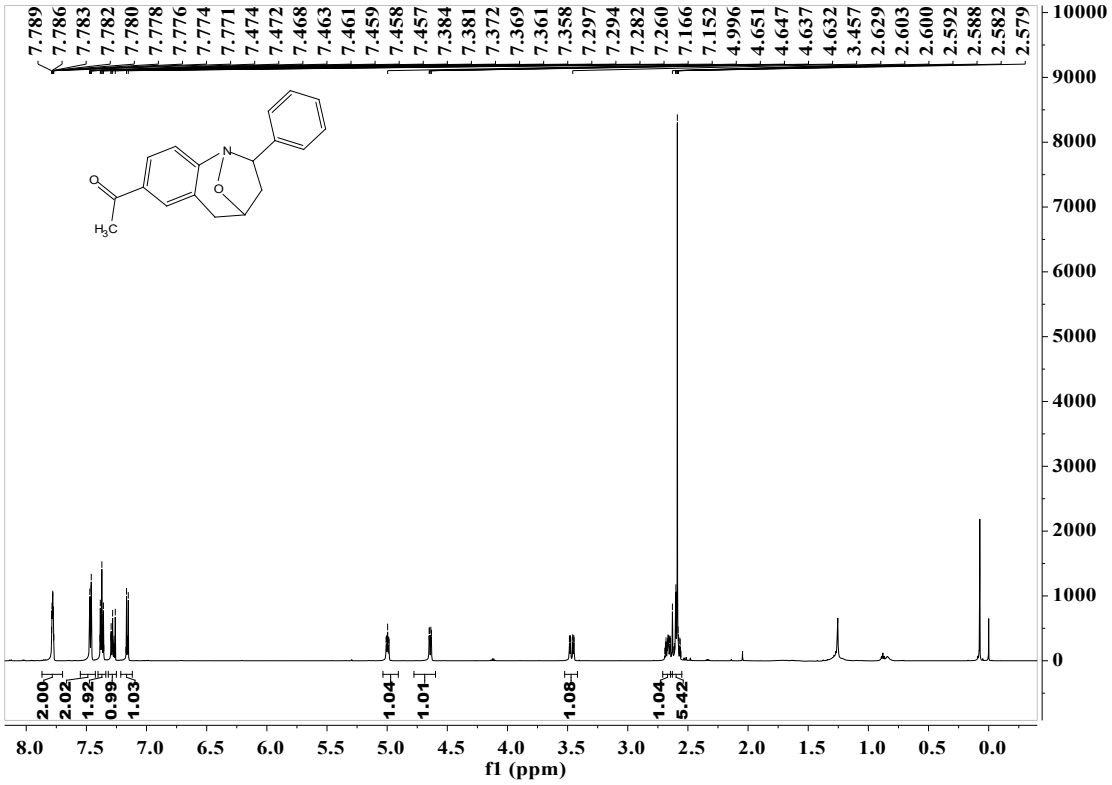
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3h**



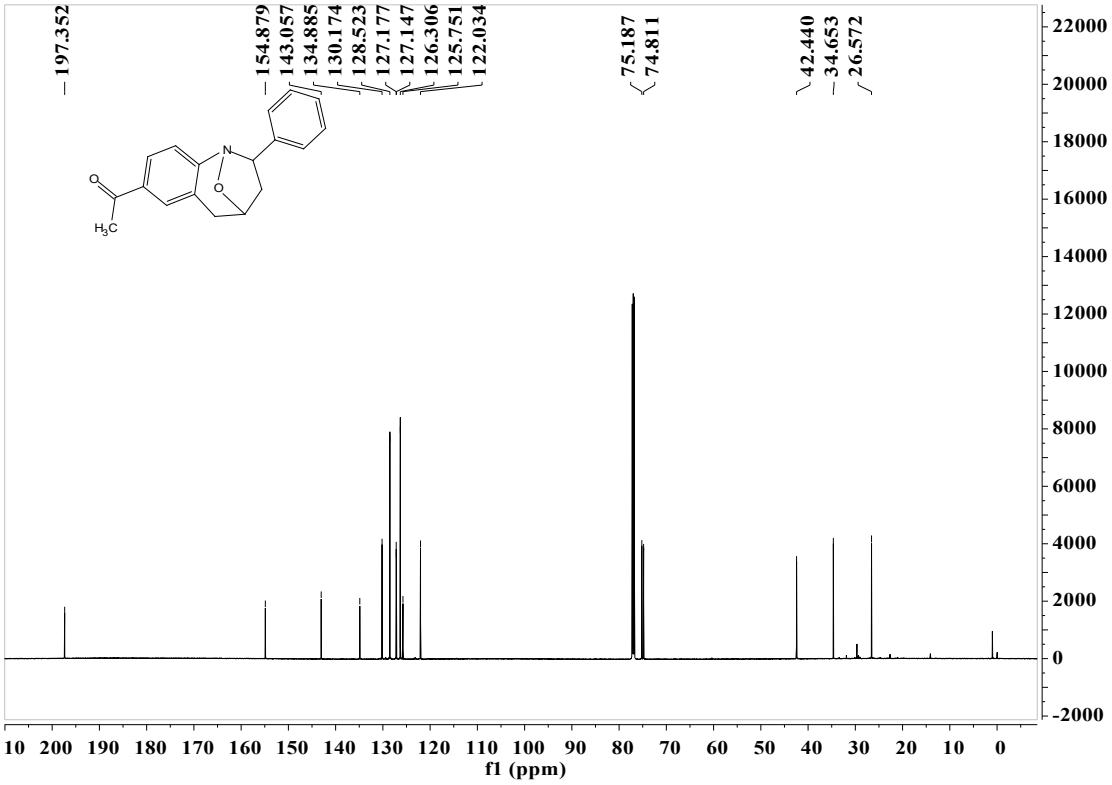
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3h**



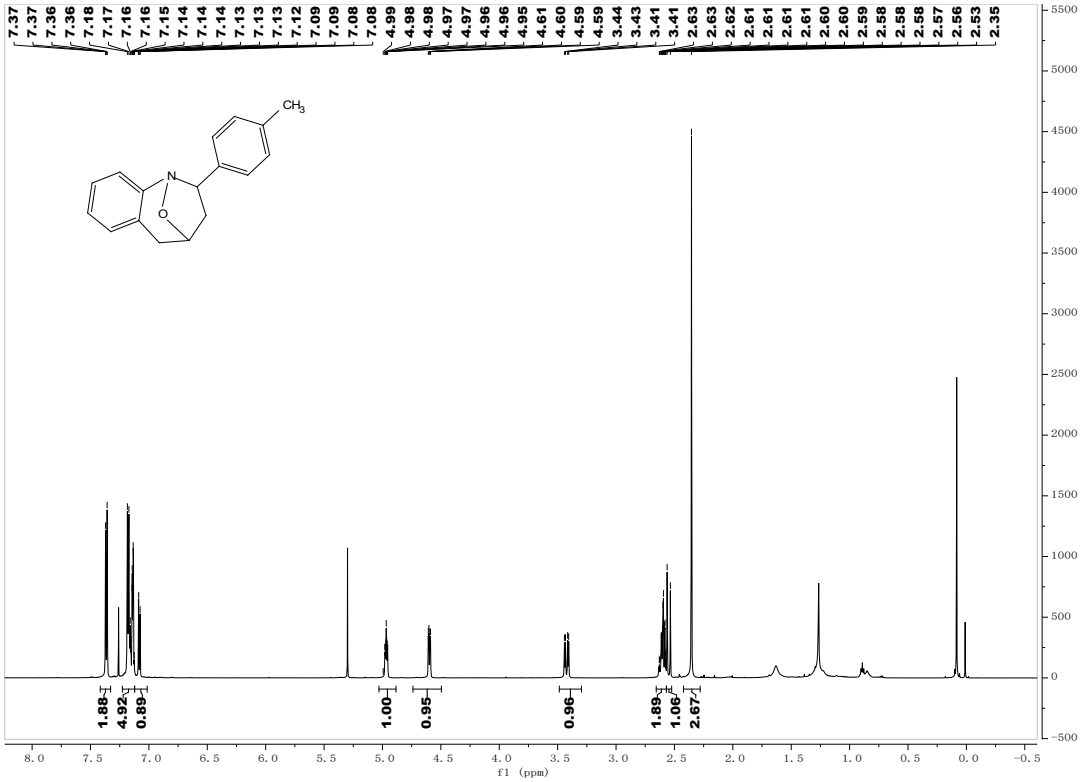
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3i**



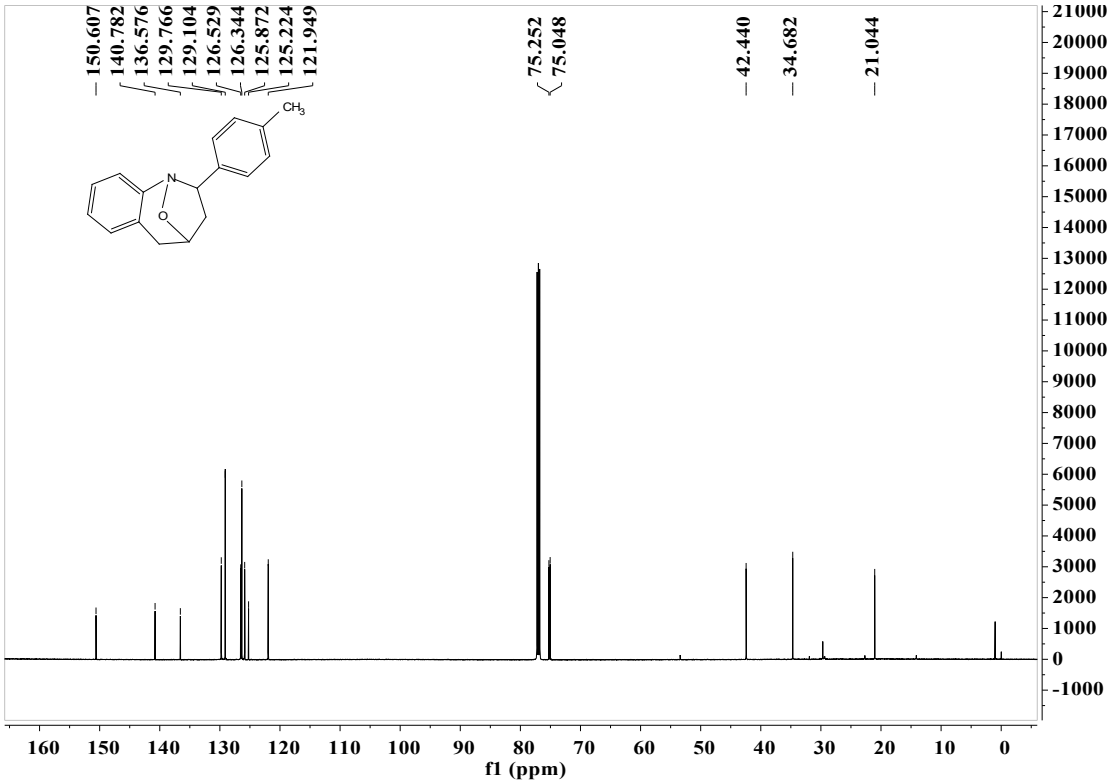
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3i**



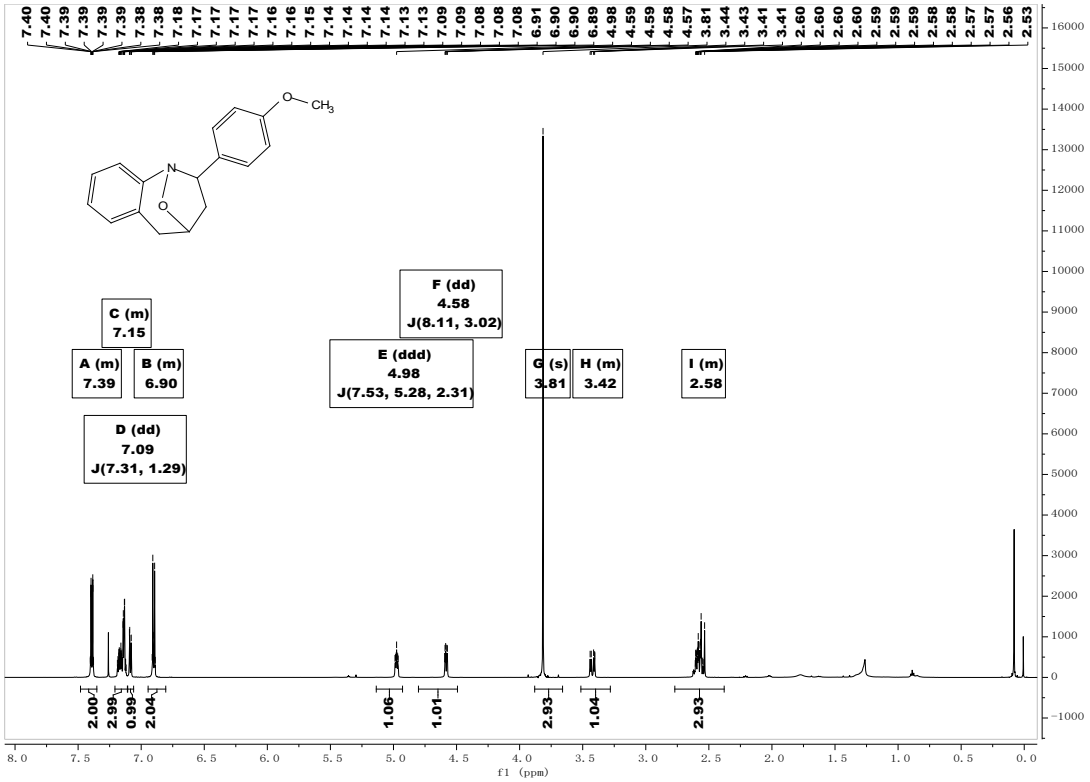
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3j**



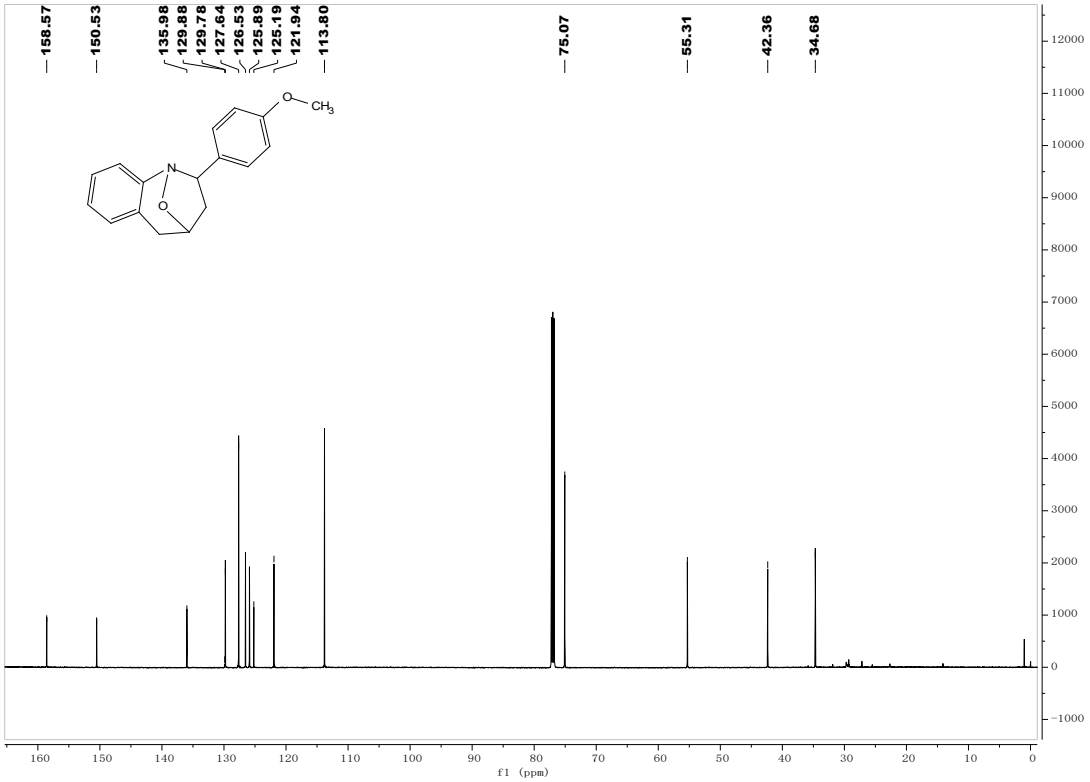
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3j**



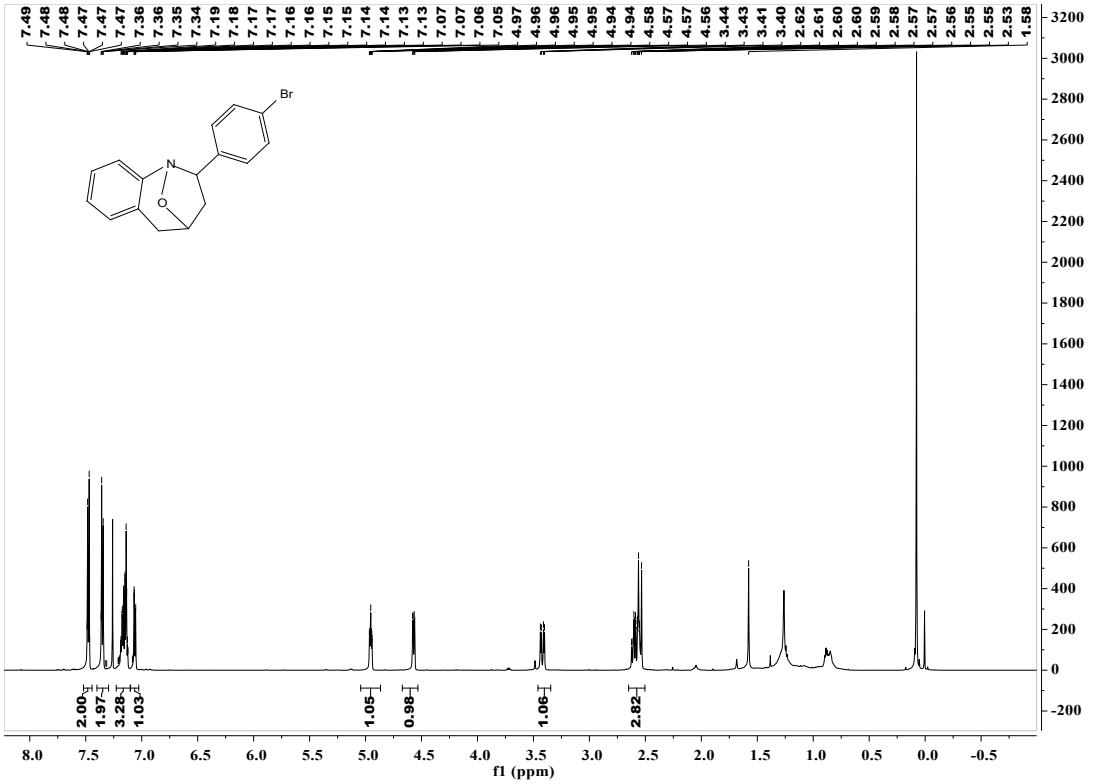
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3k**



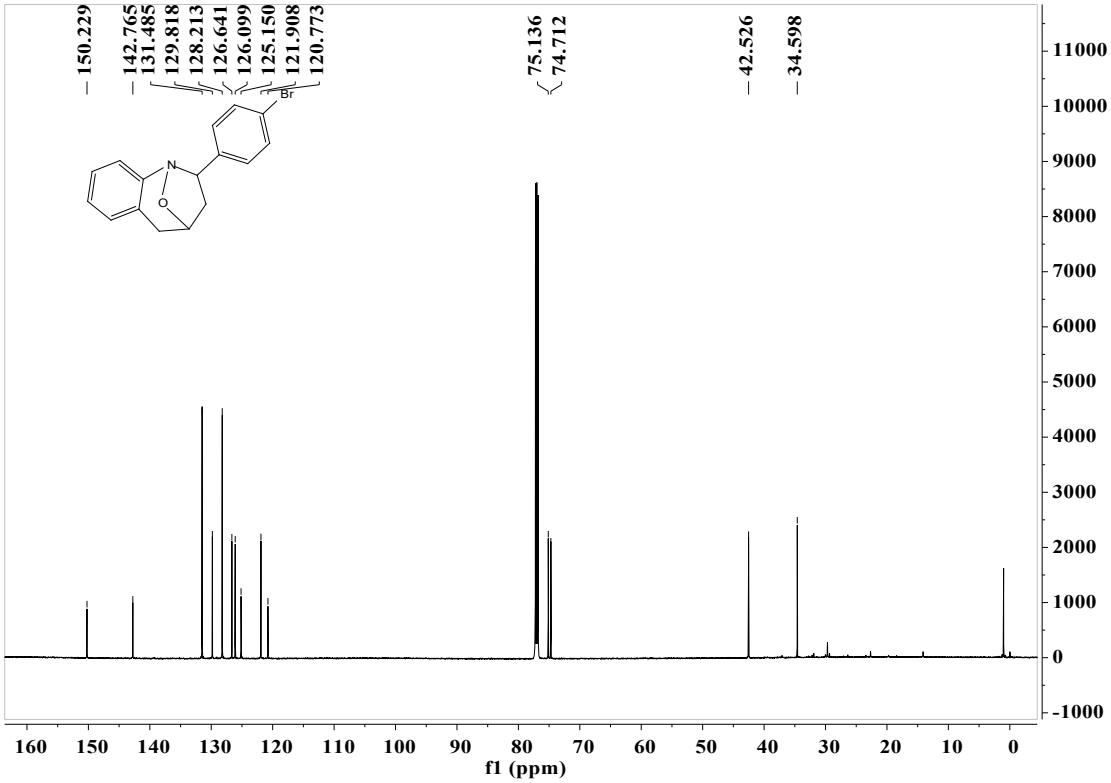
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3k**



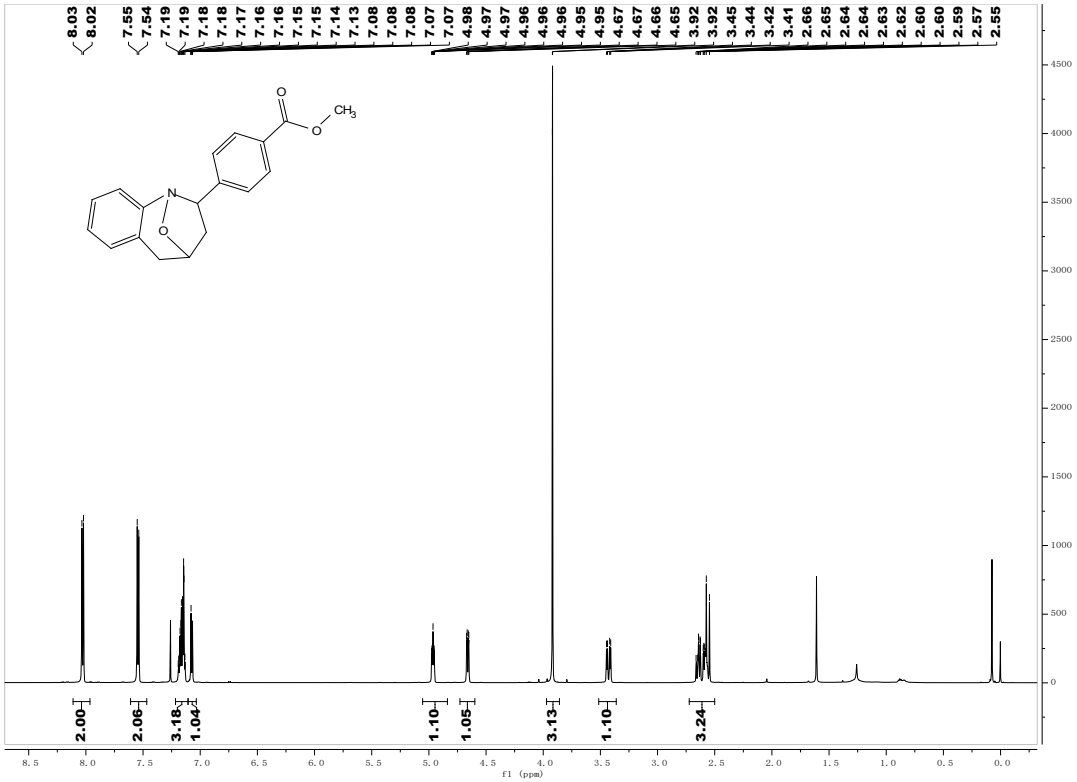
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3l**



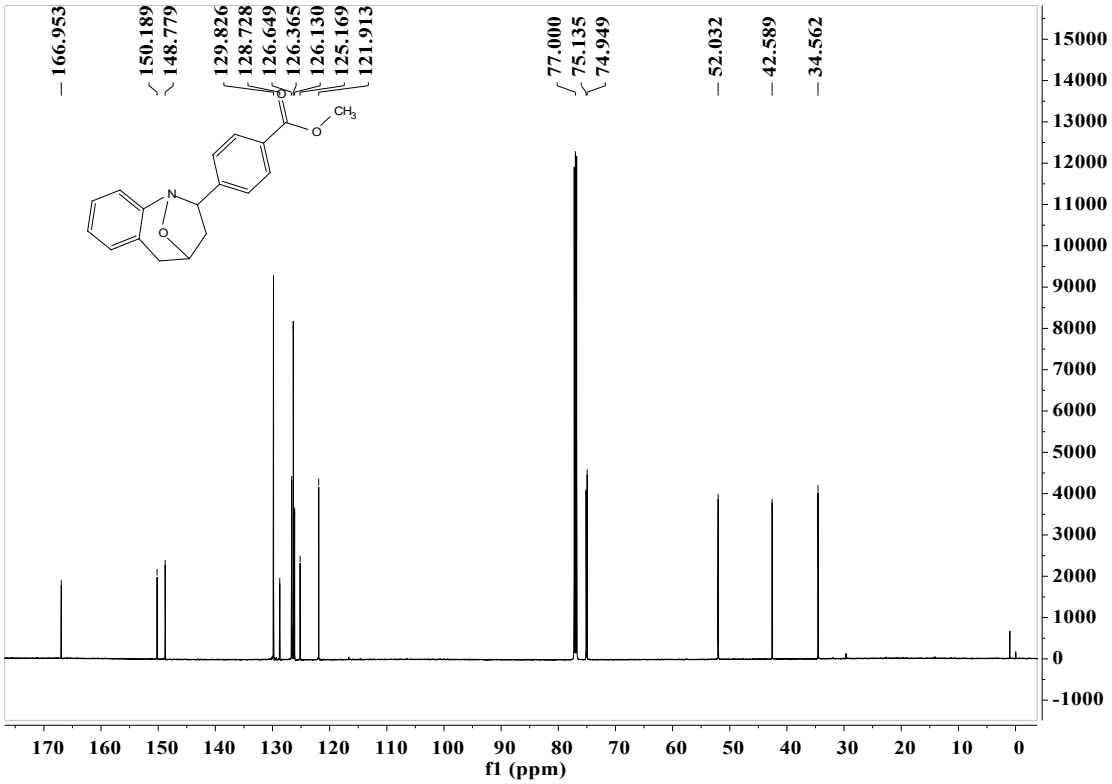
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3l**



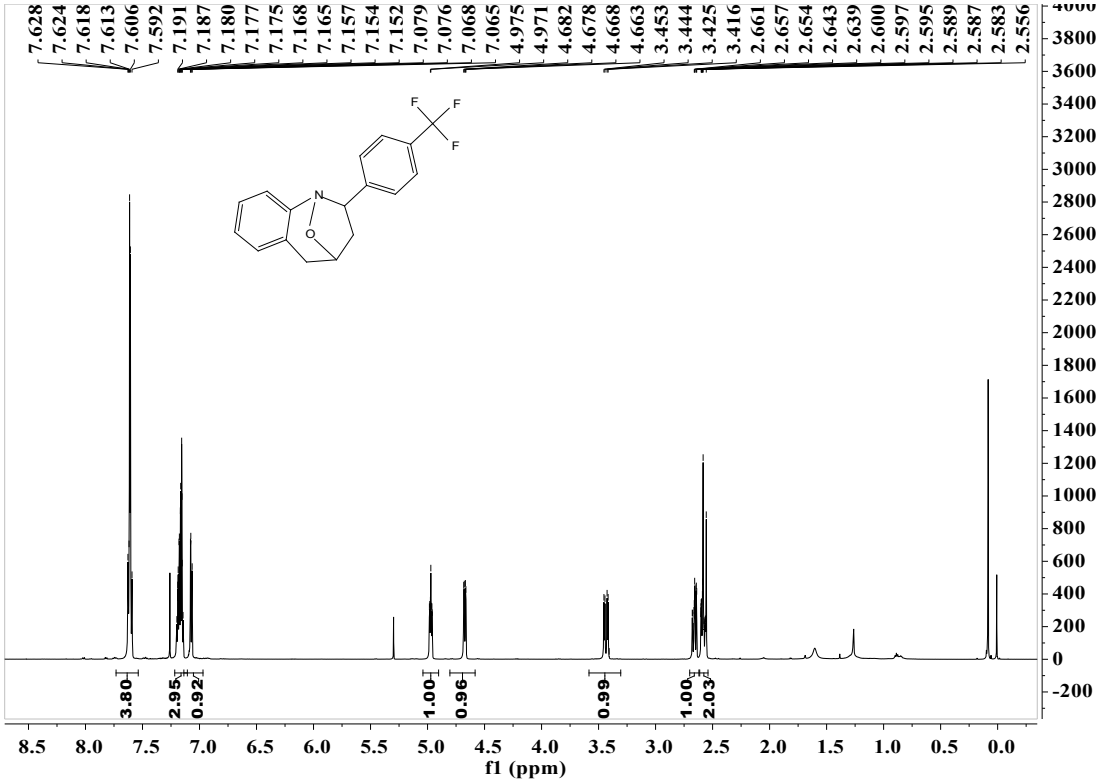
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3m**



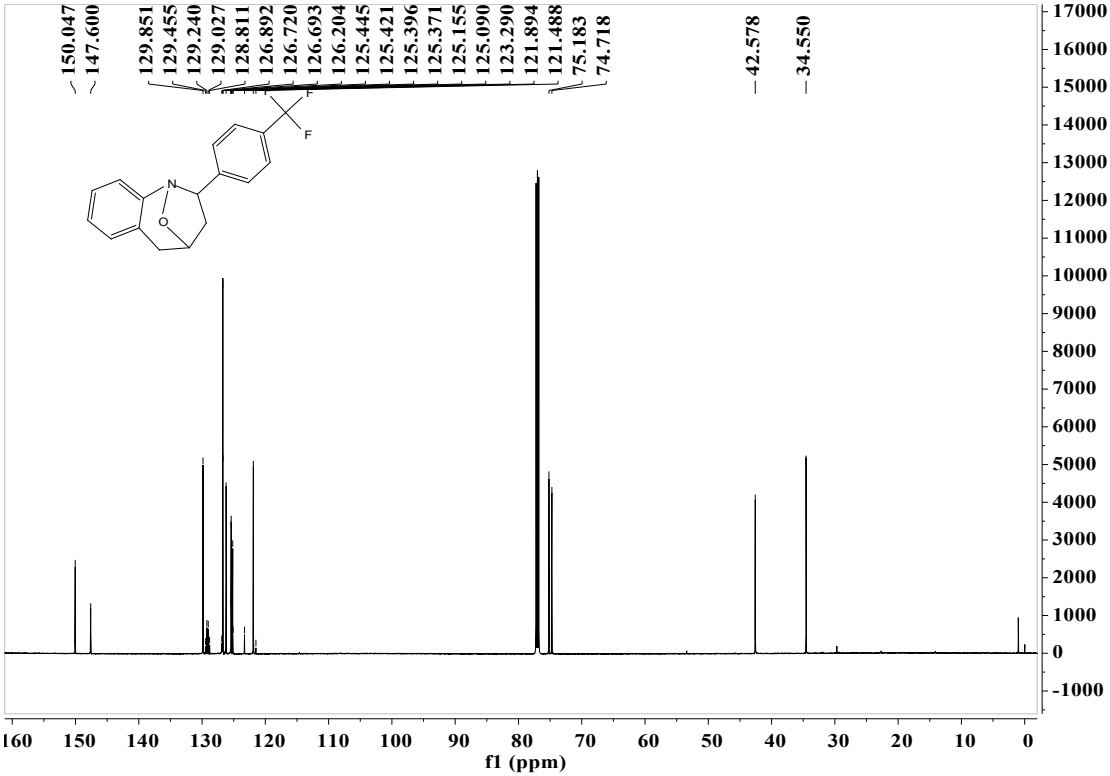
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3m**



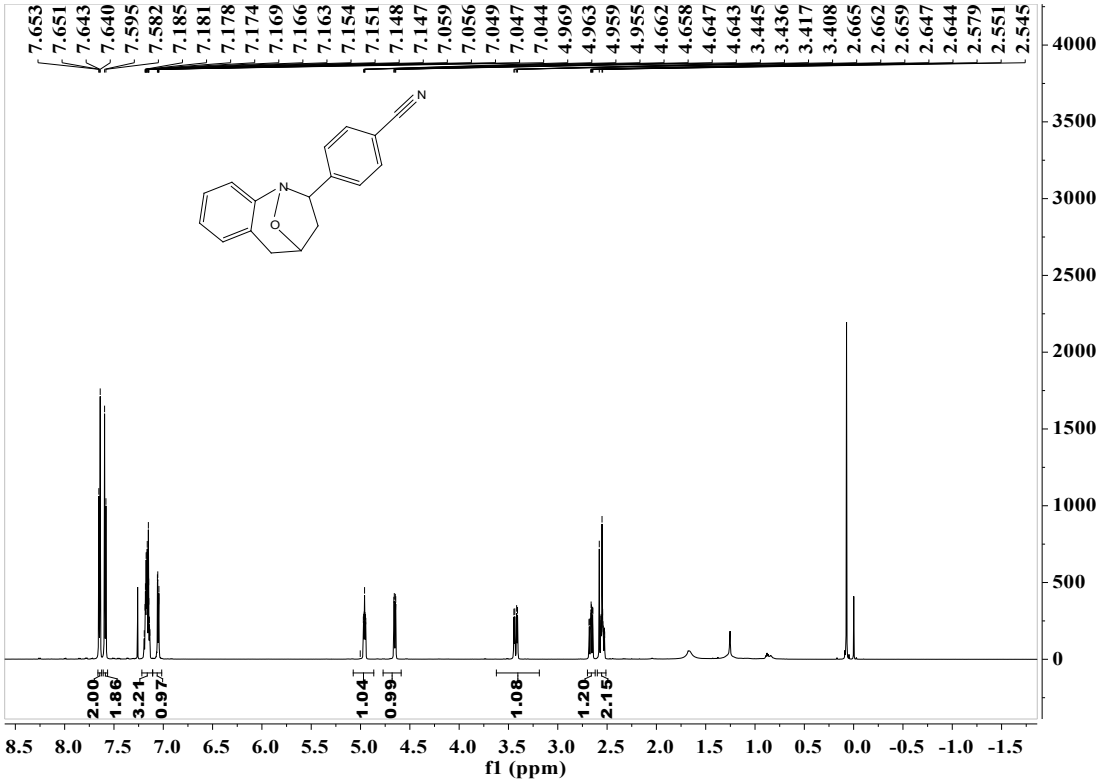
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3n**



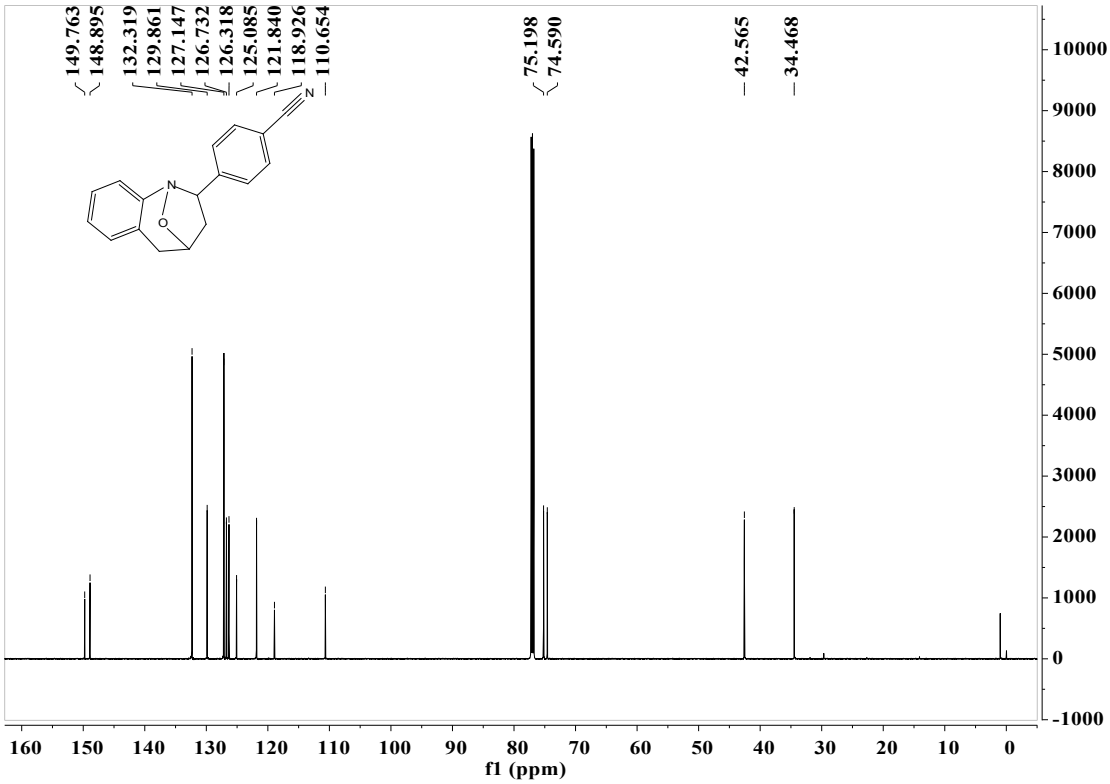
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3n**



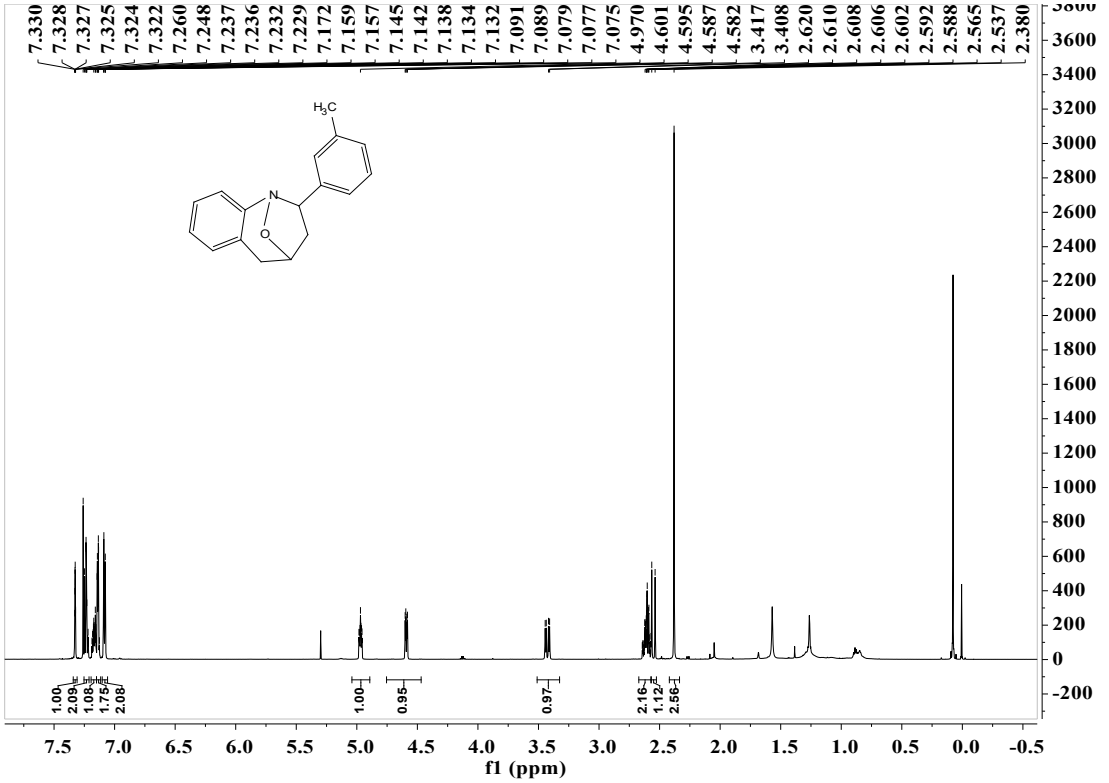
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3o**



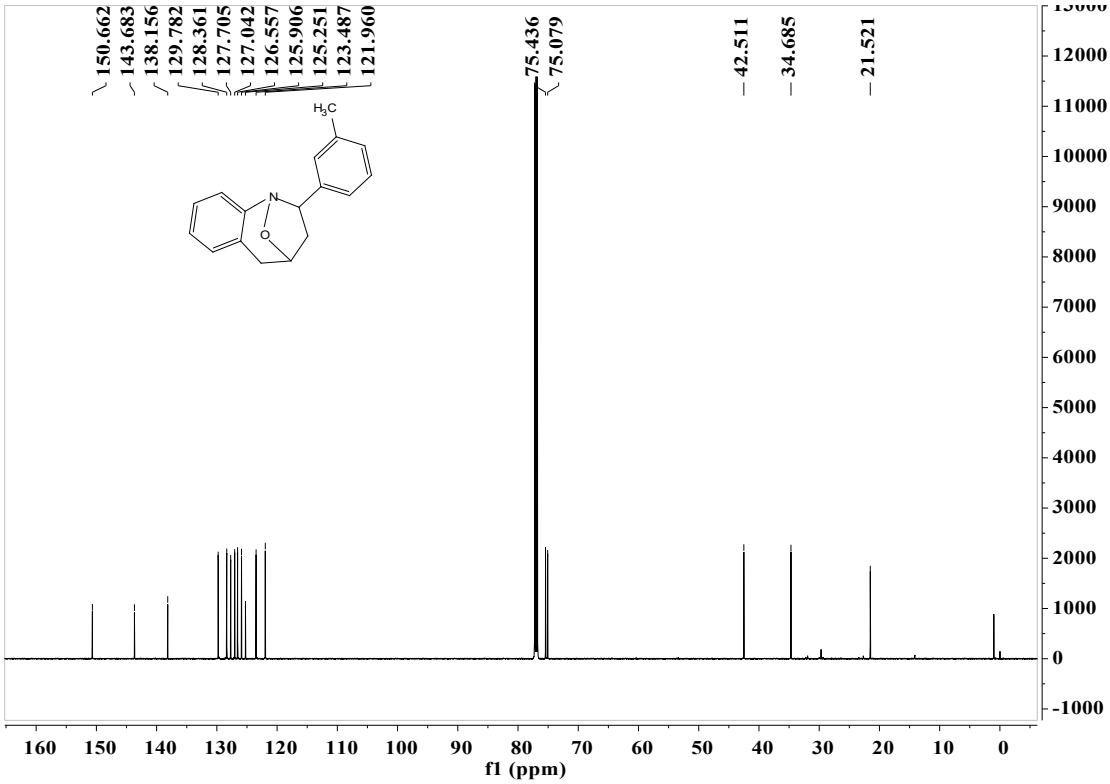
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3o**



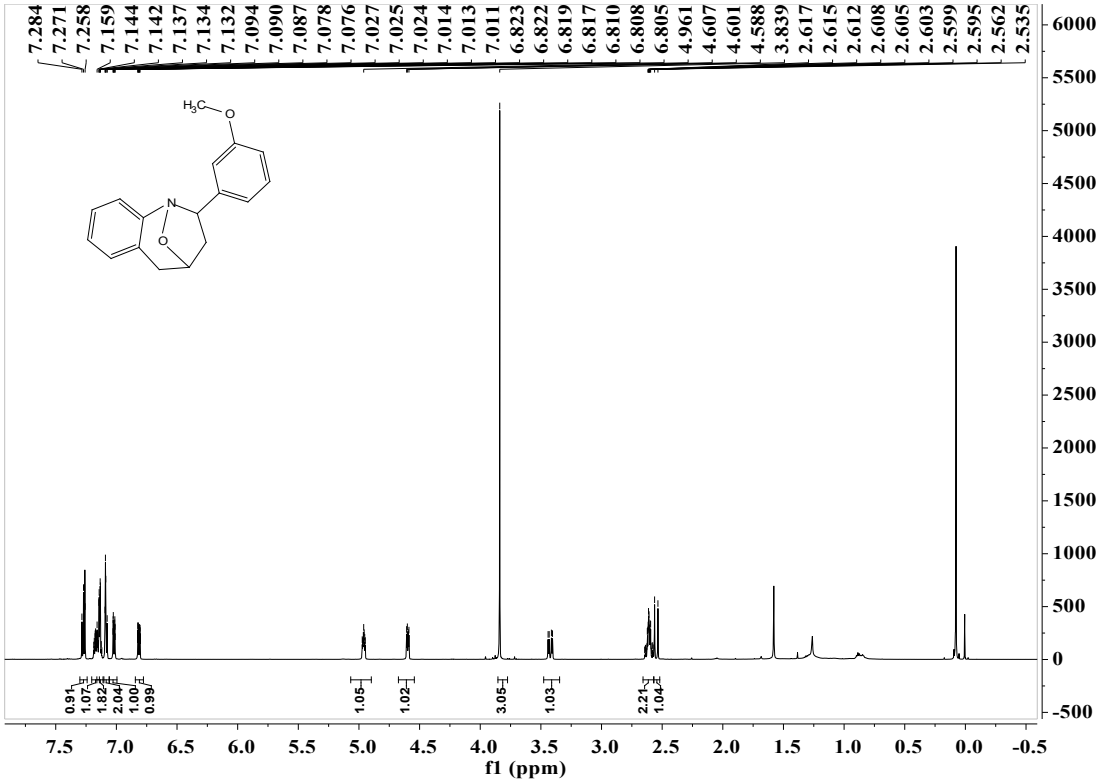
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3p**



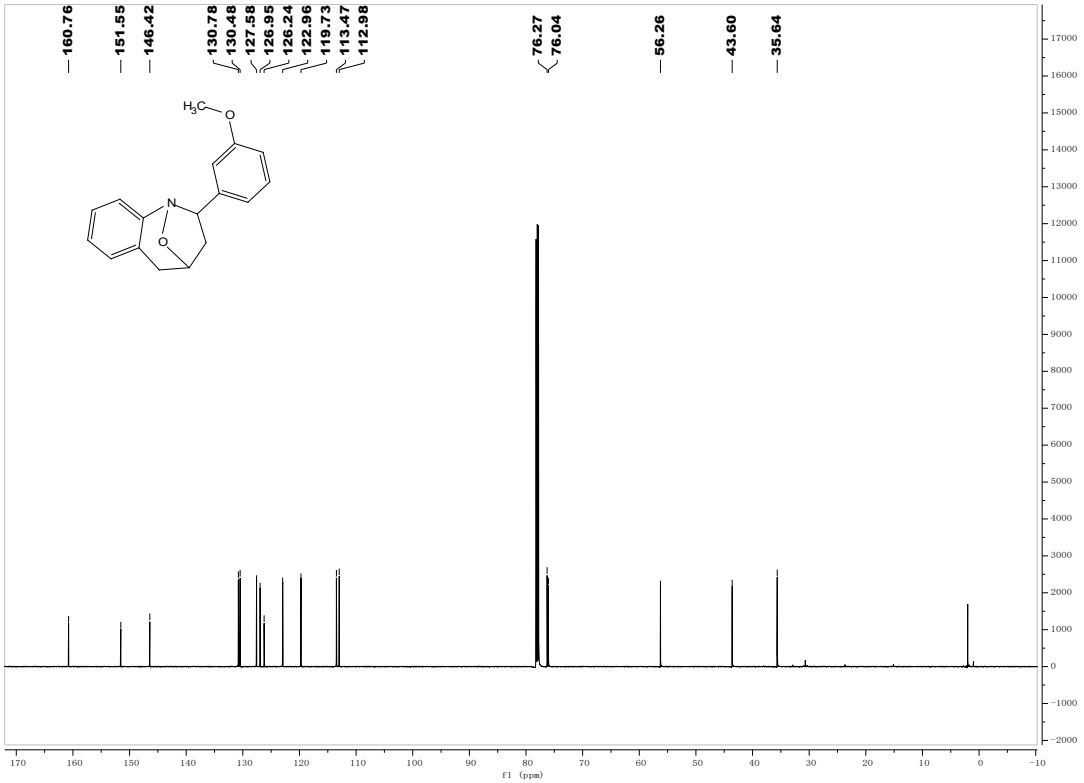
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3p**



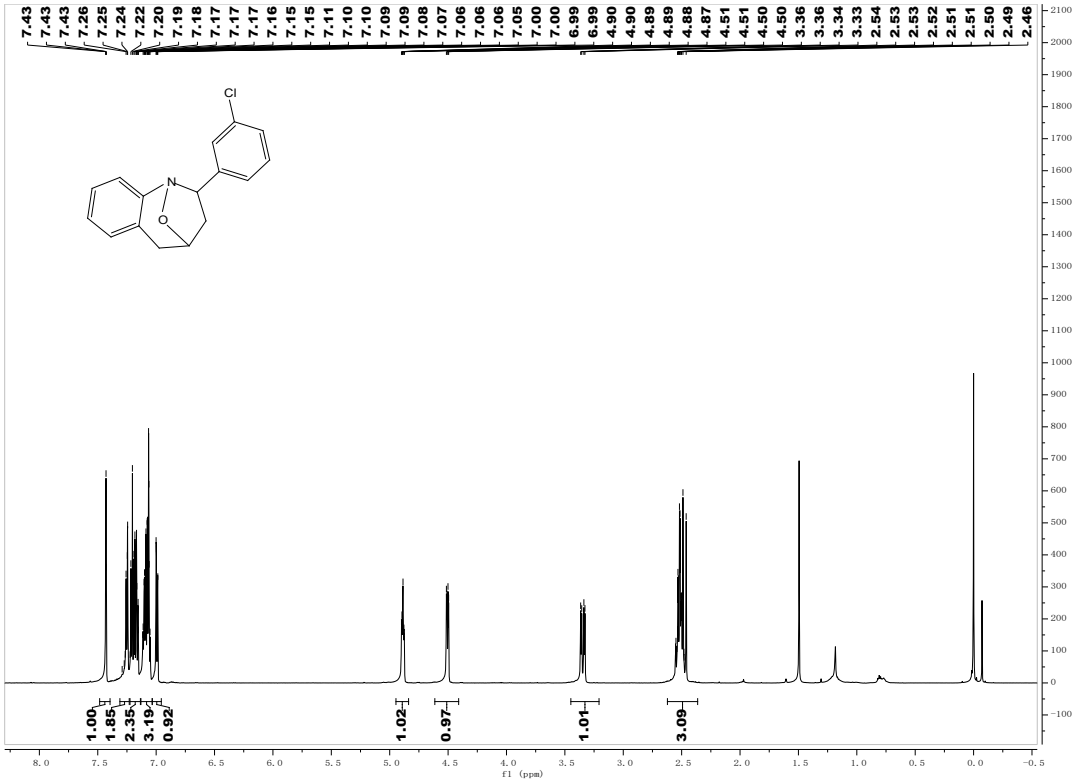
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3q**



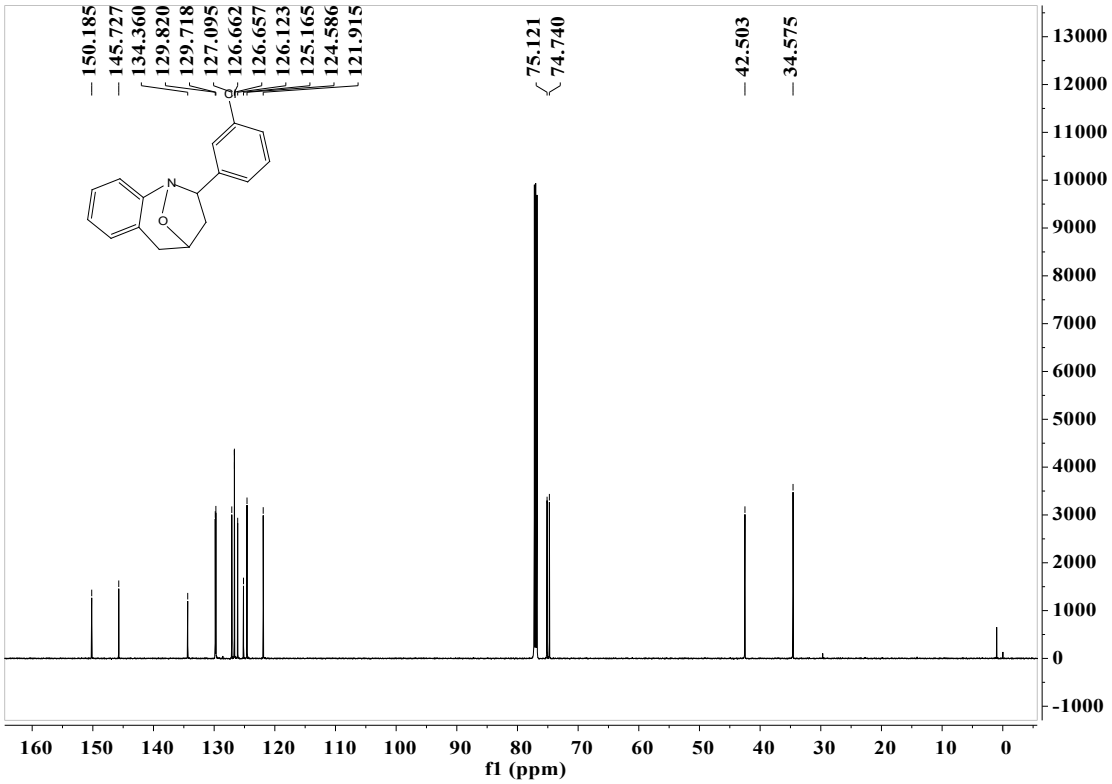
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3q**



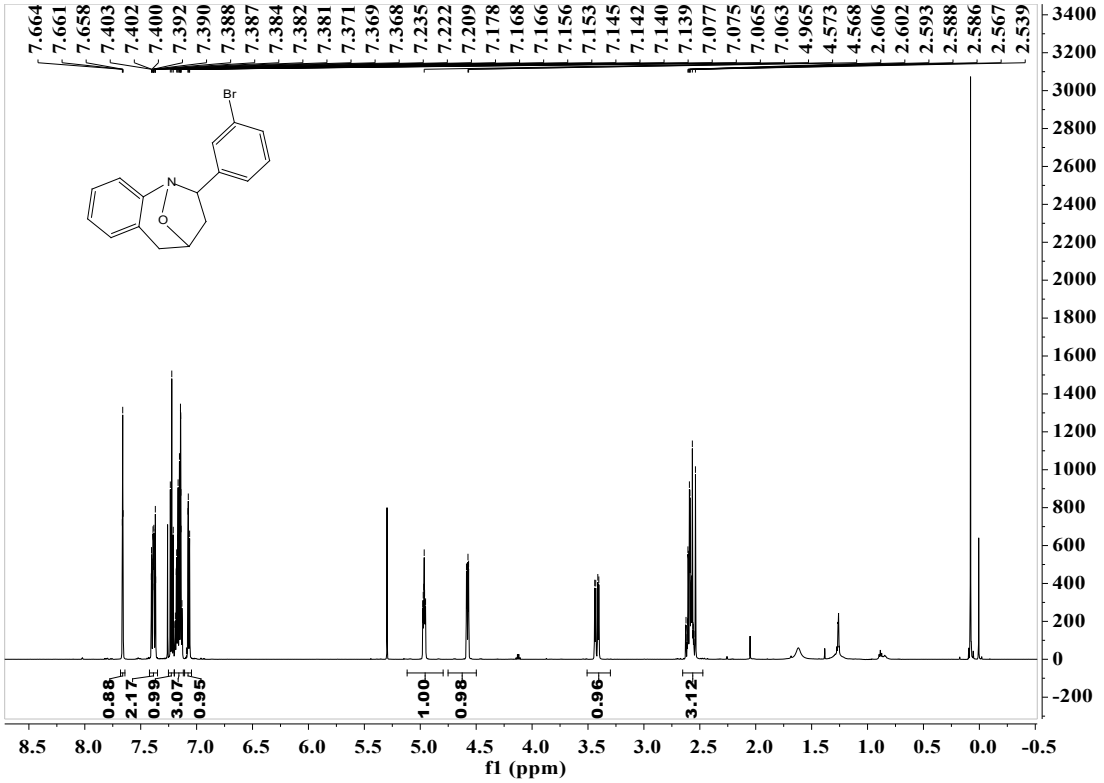
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3r**



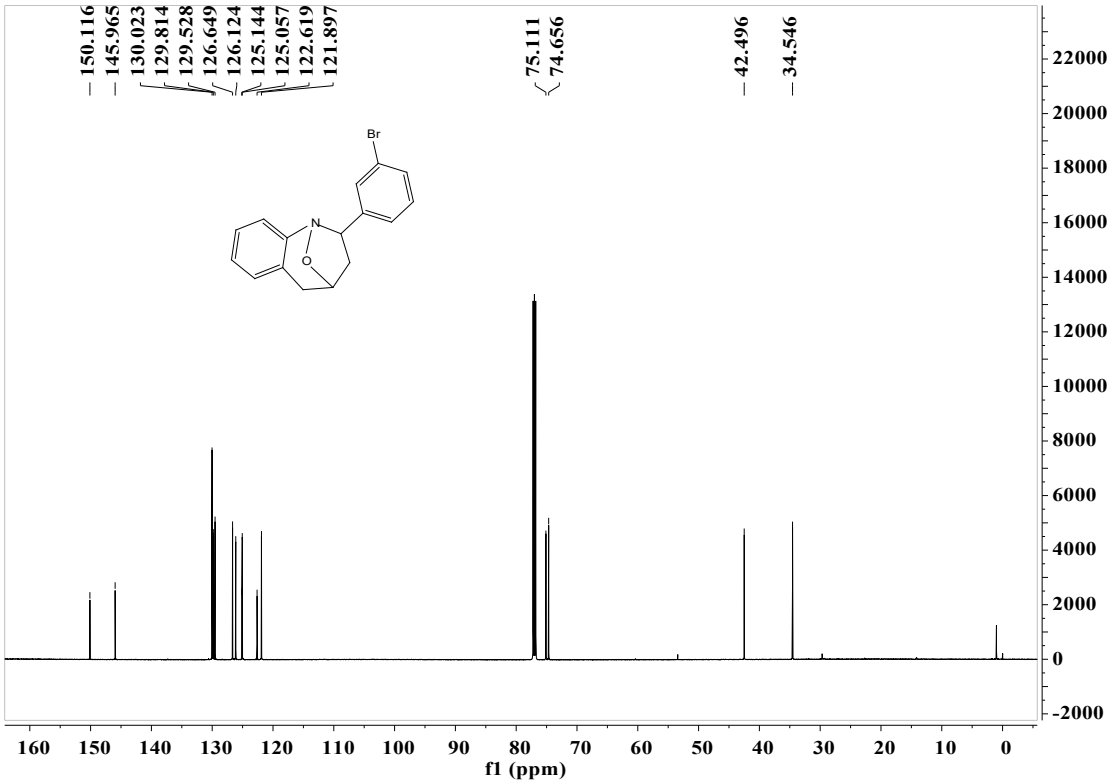
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3r**



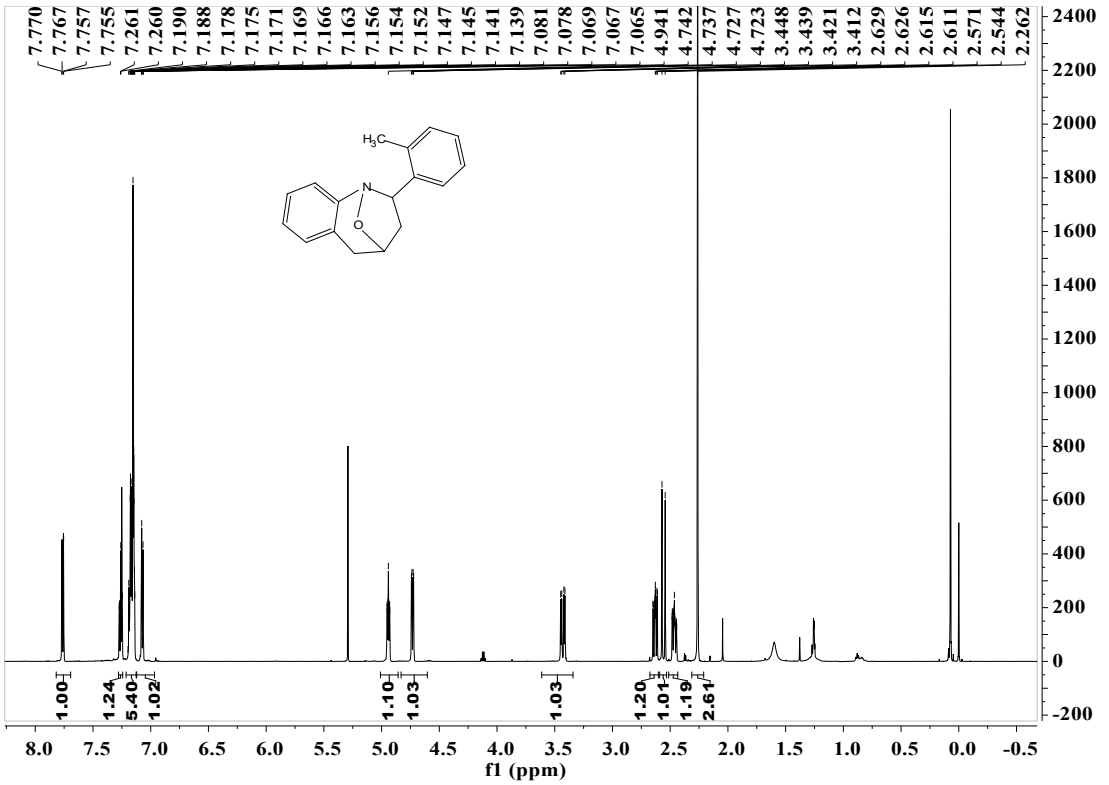
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3s**



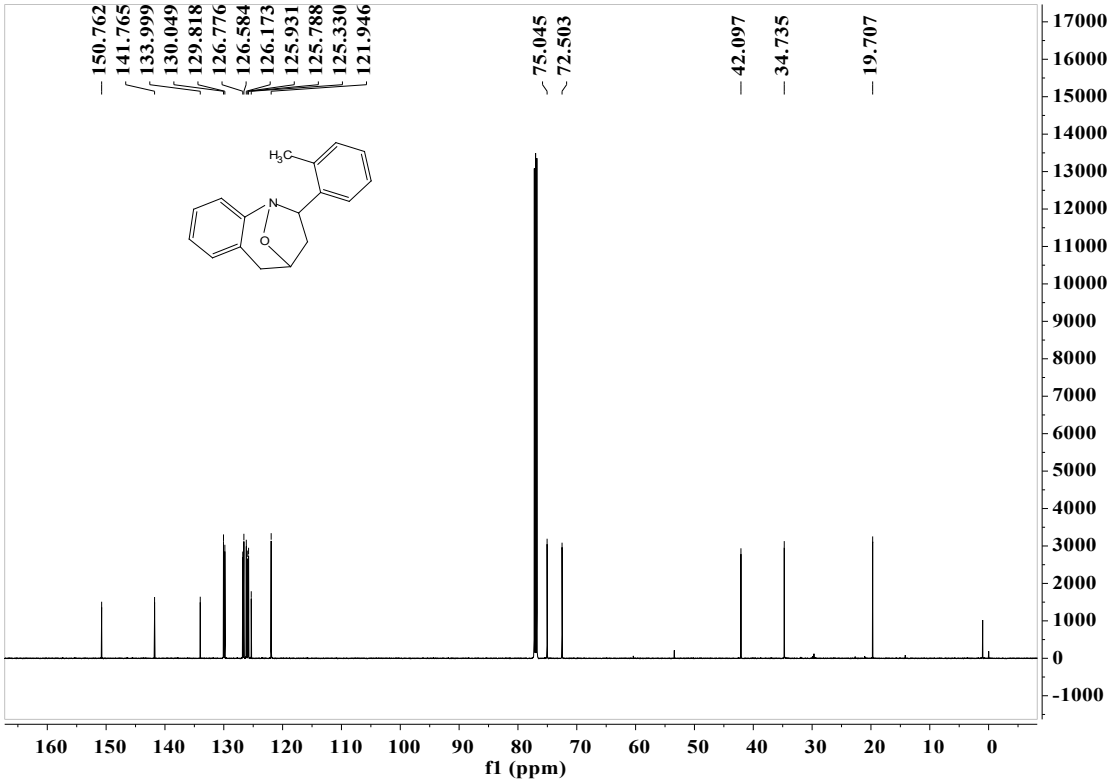
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3s**



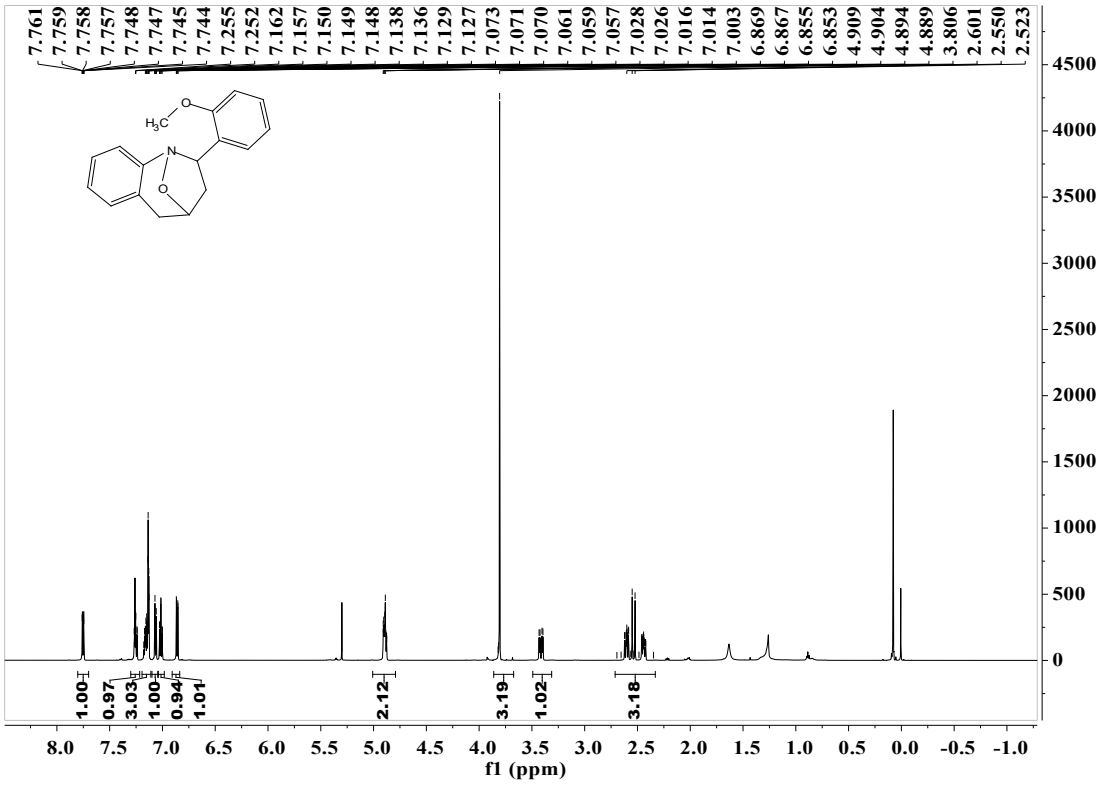
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3t**



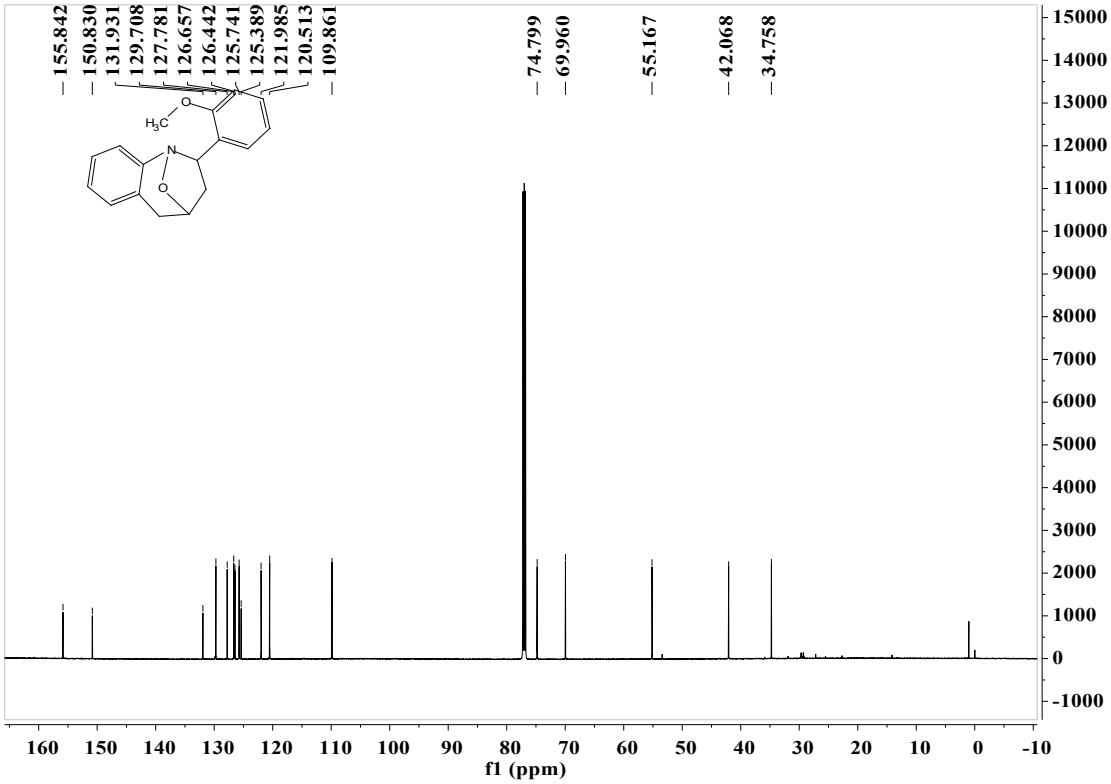
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3t**



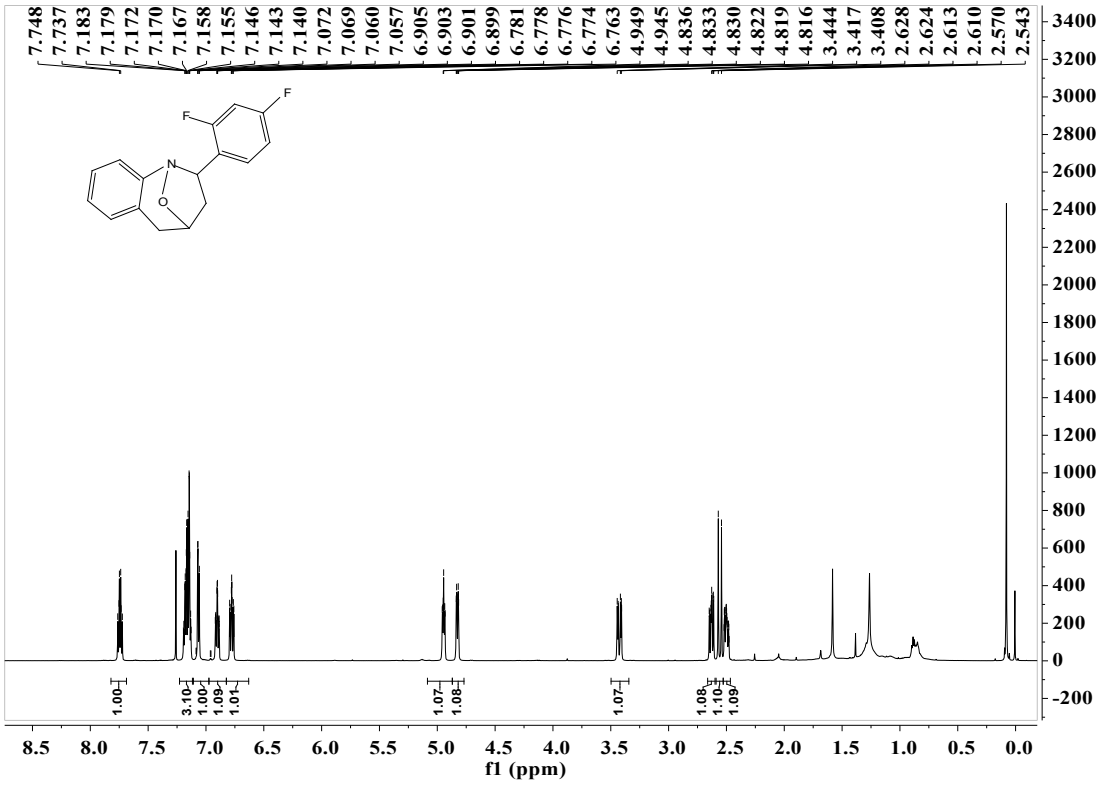
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3u**



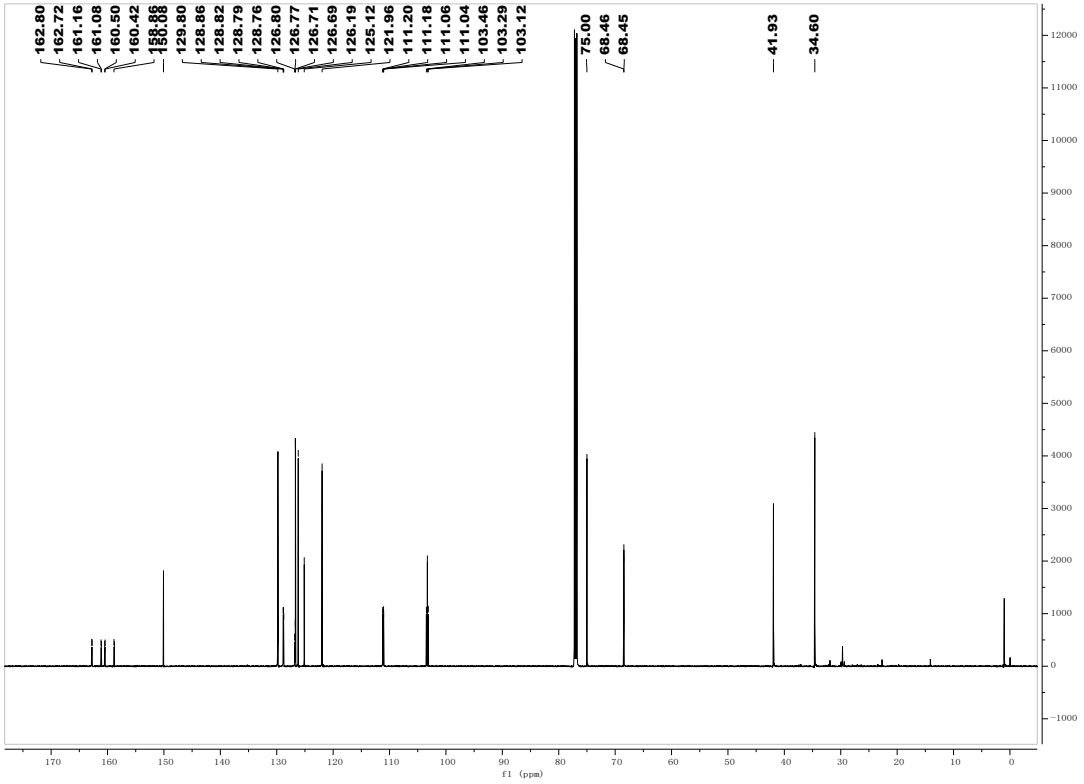
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3u**



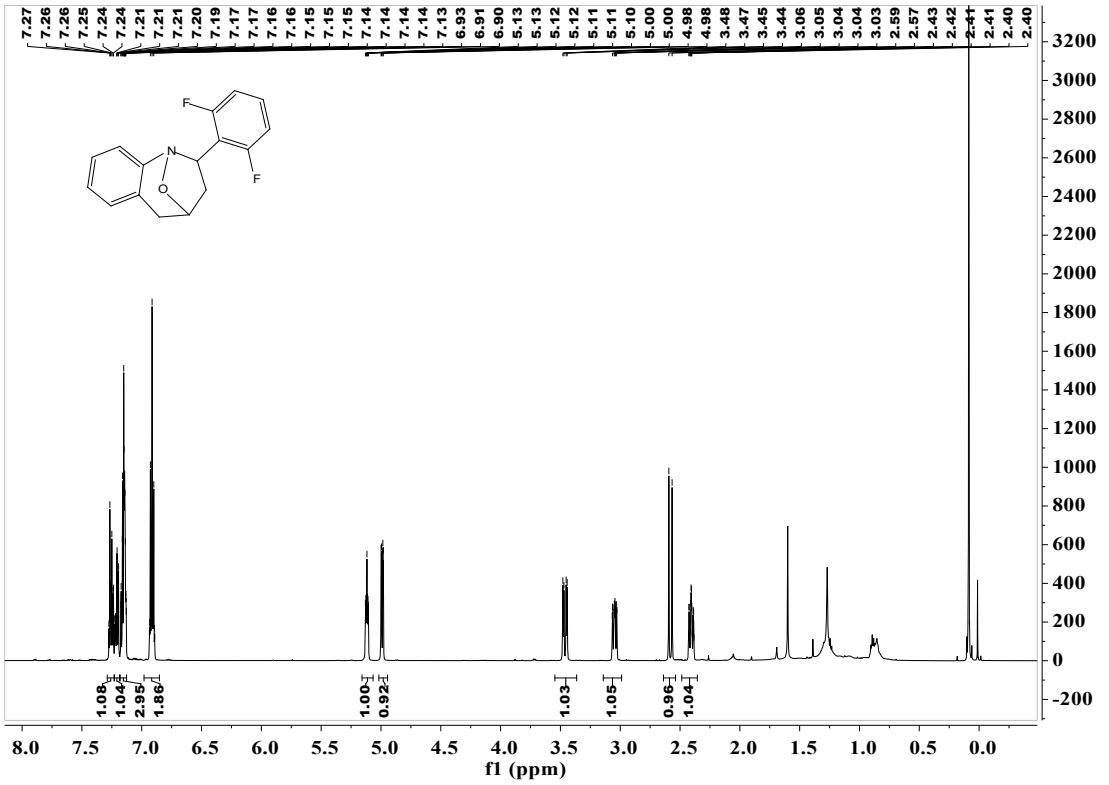
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3v**



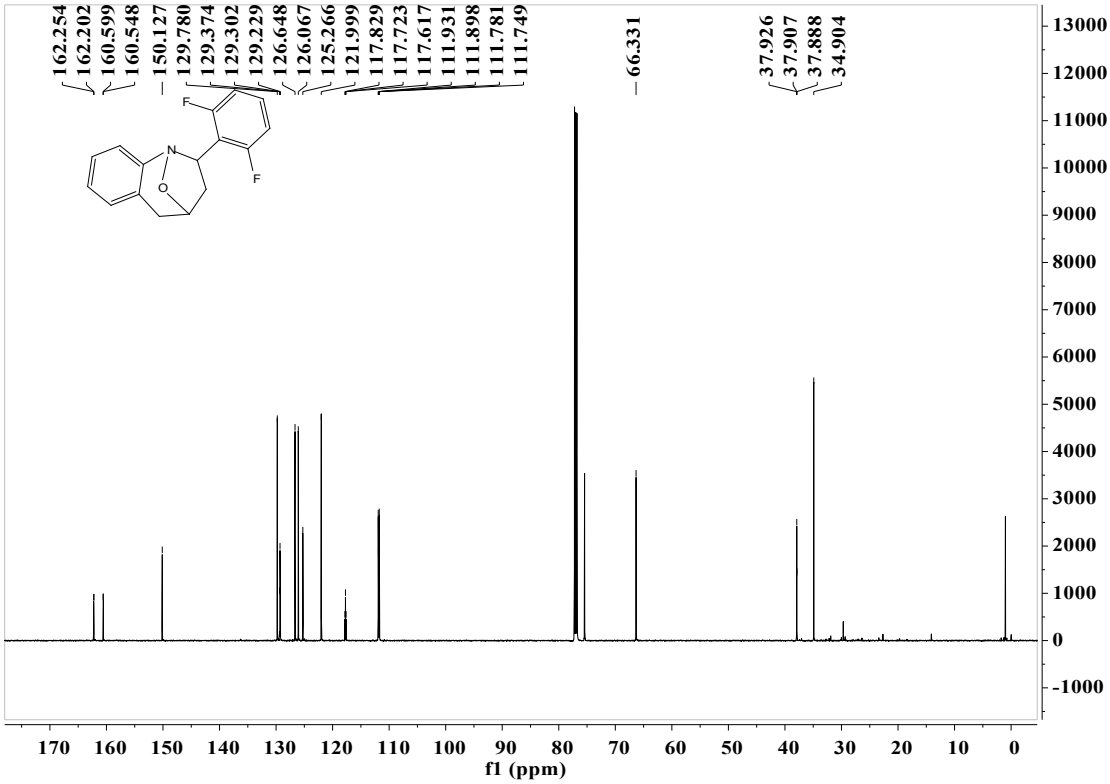
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3v**



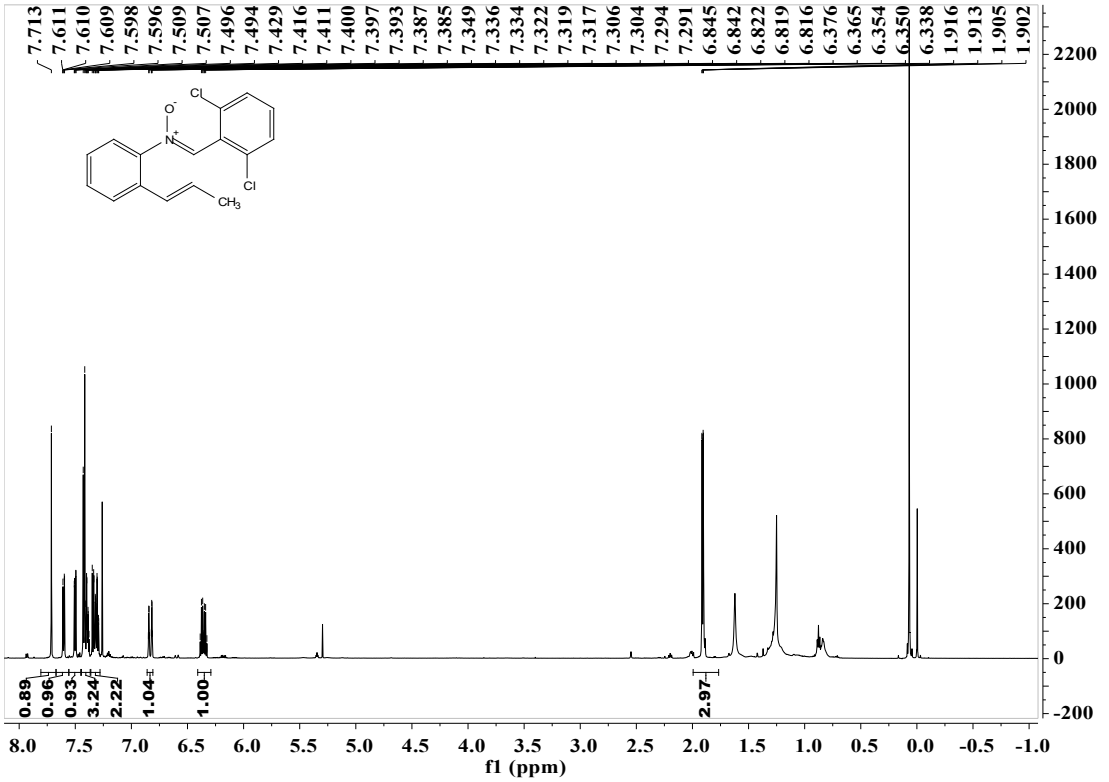
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3w**



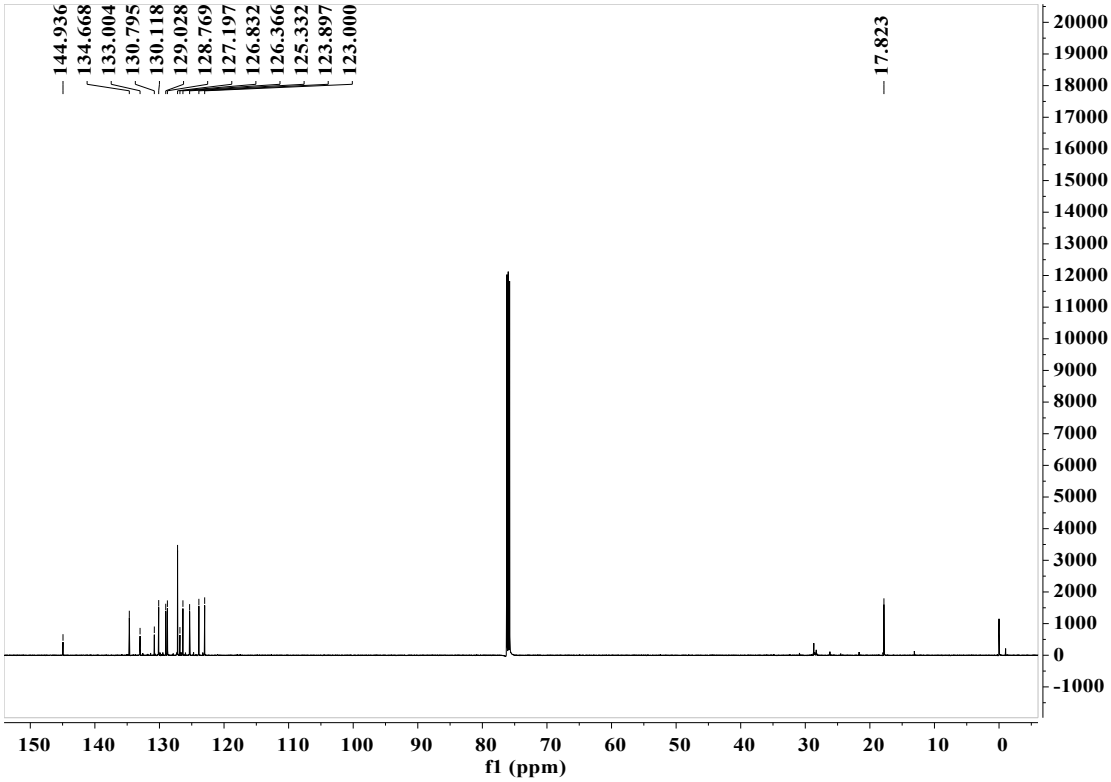
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3w**



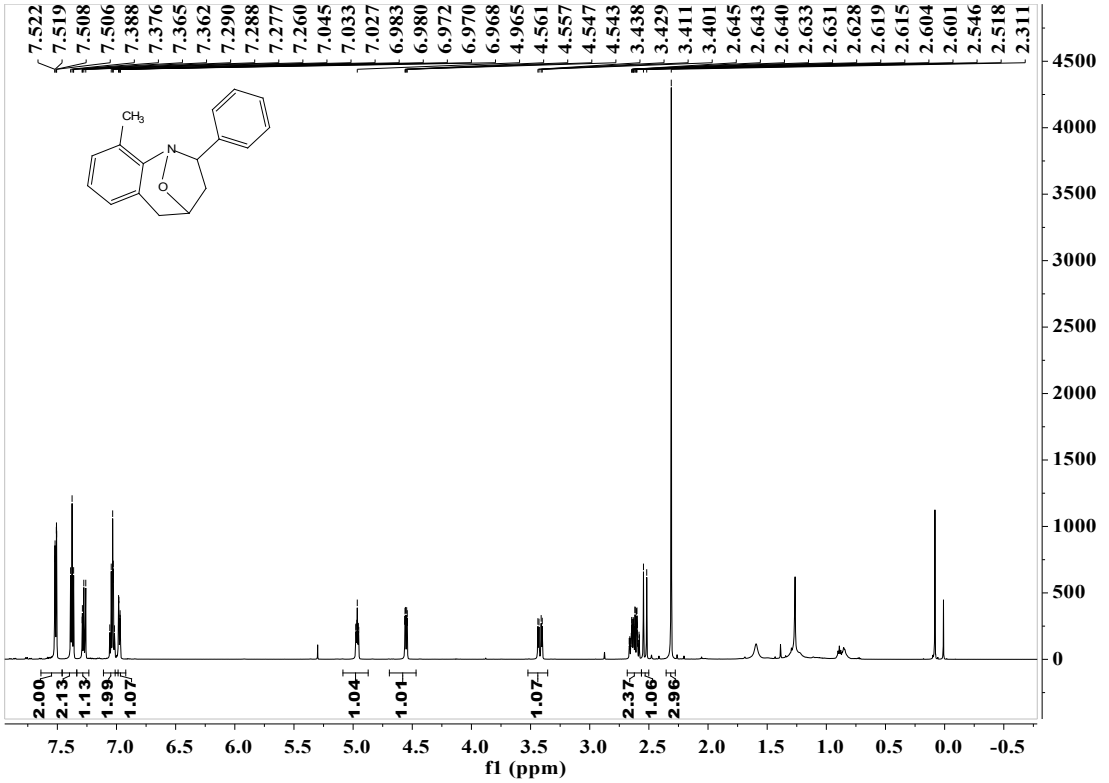
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3x'**



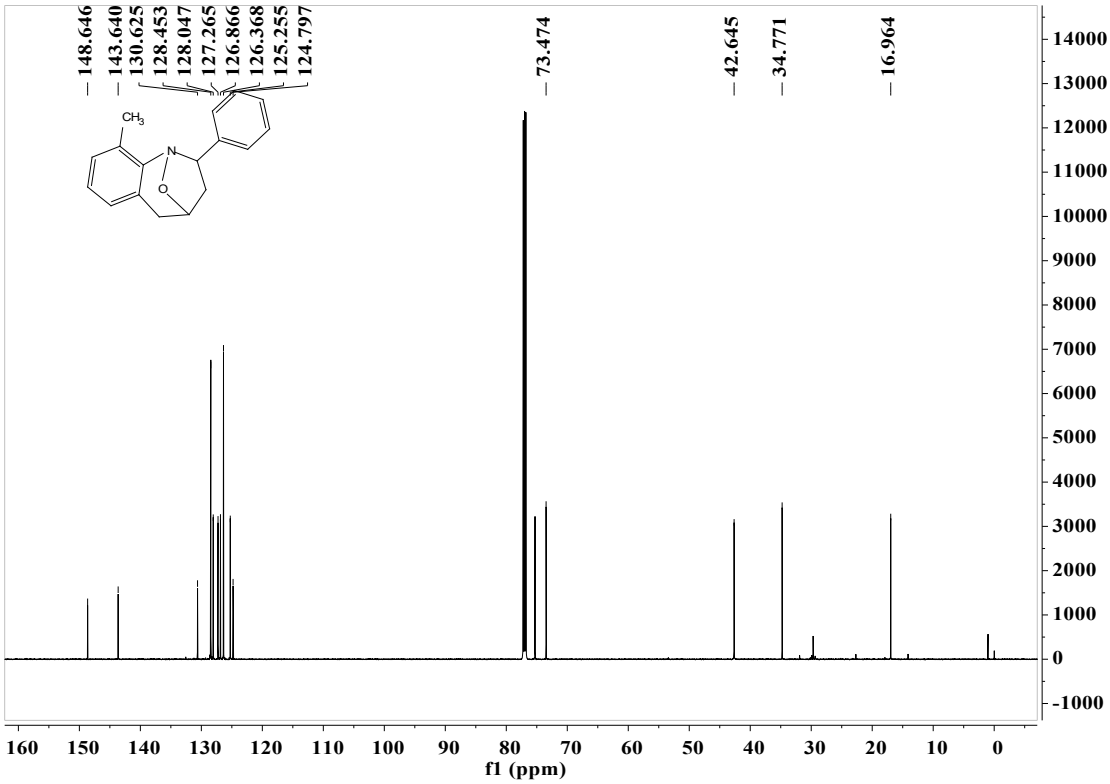
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3x'**



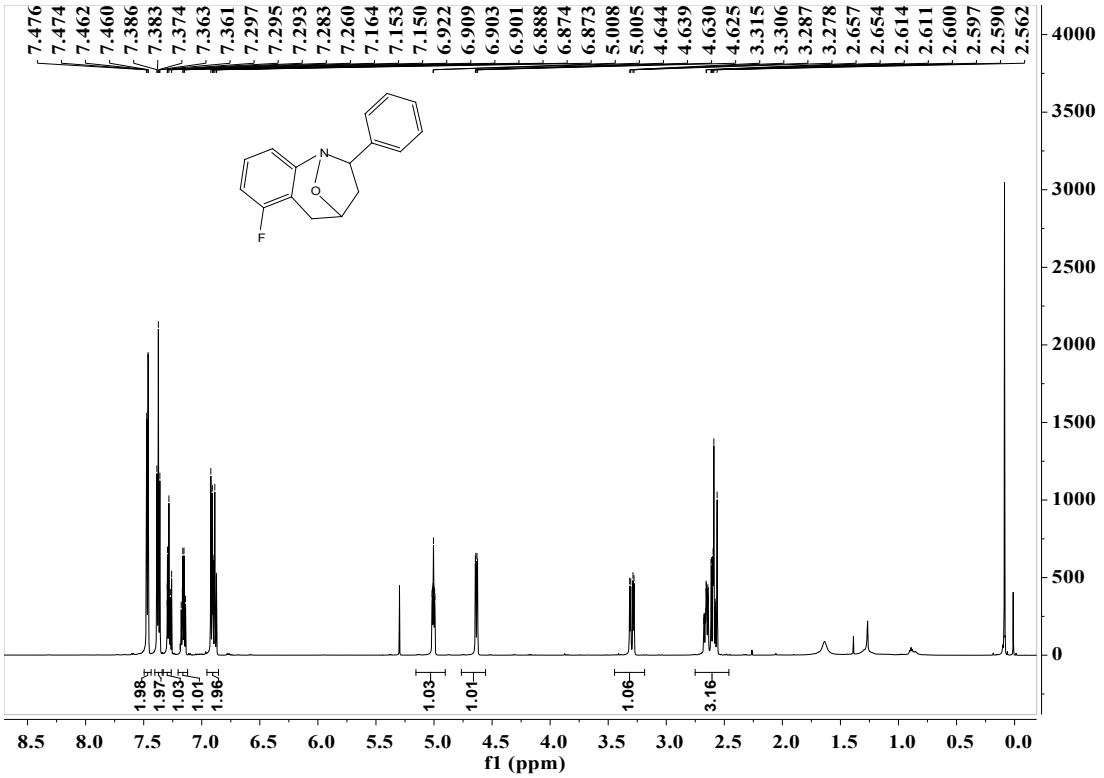
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3y**



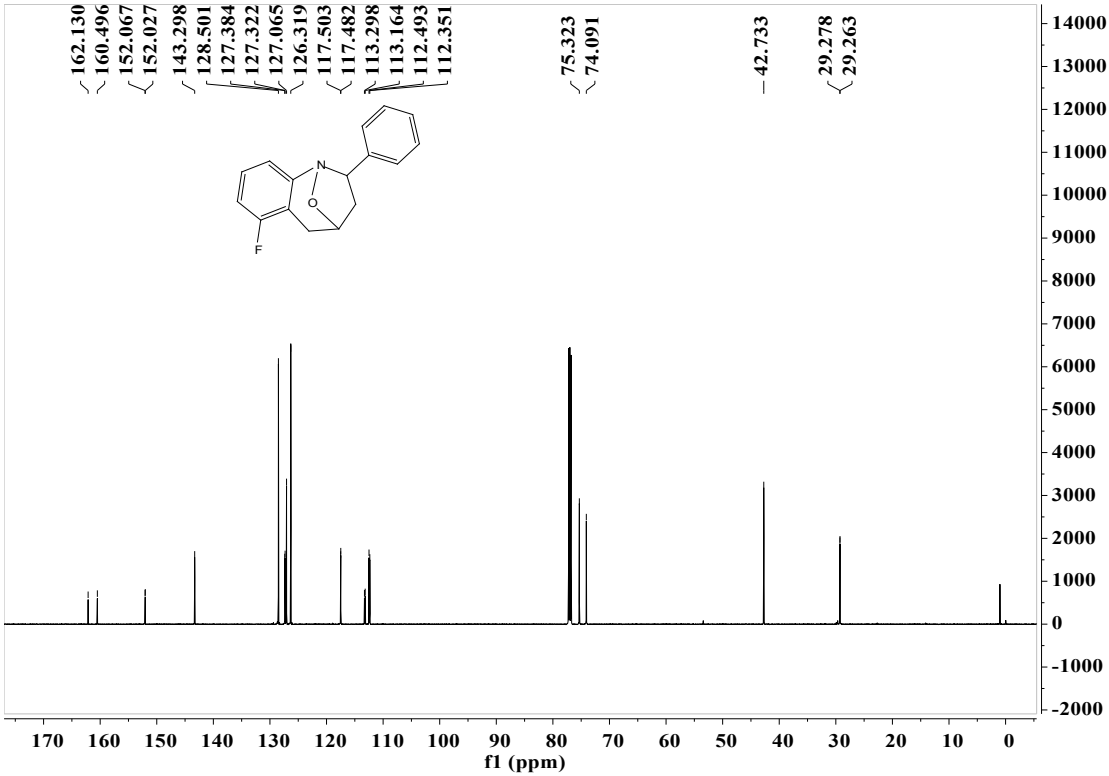
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3y**

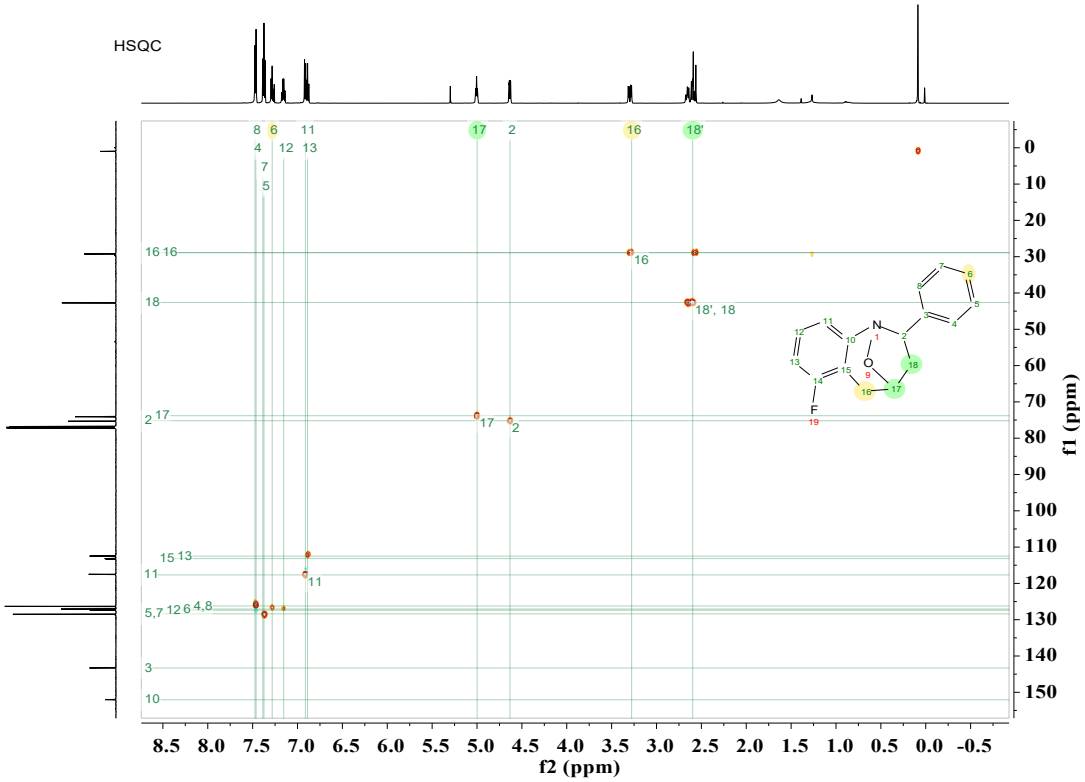


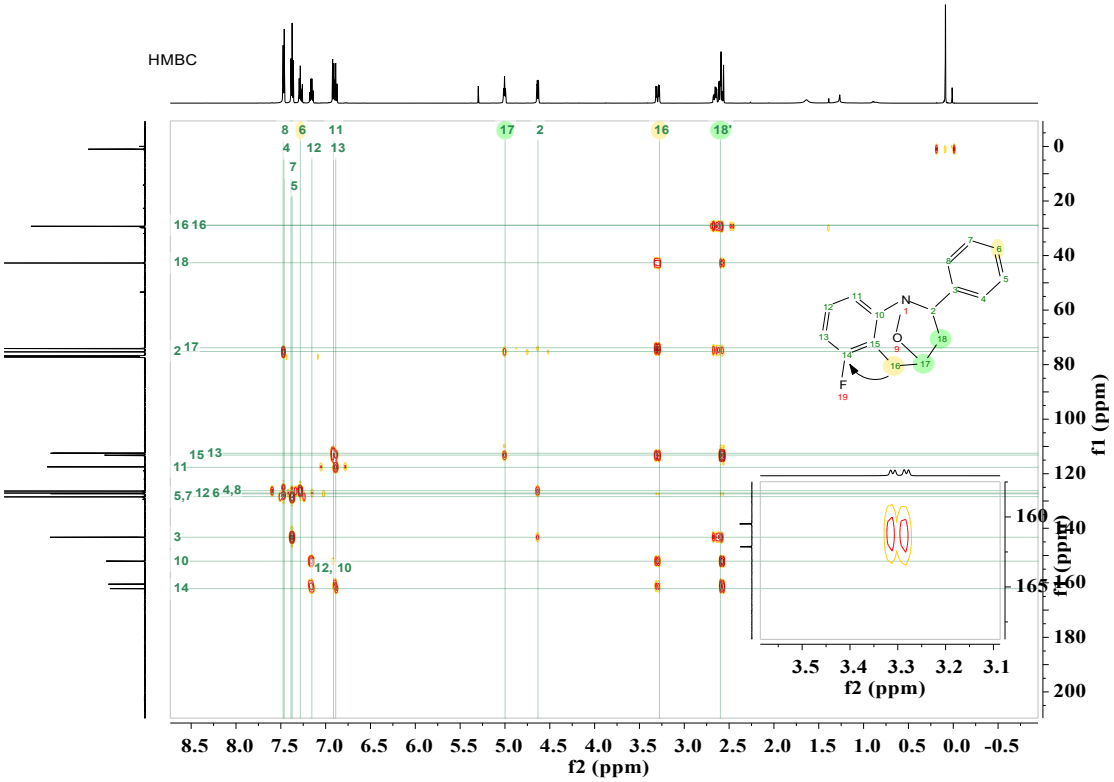
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3z**



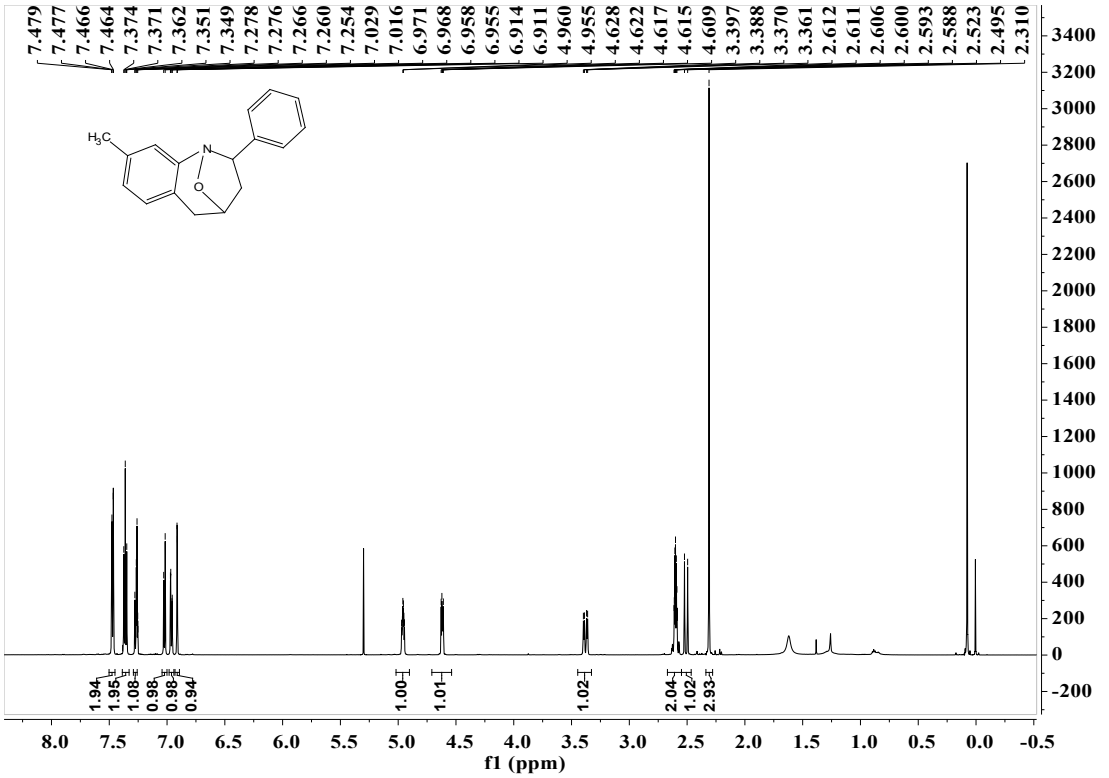
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3z**



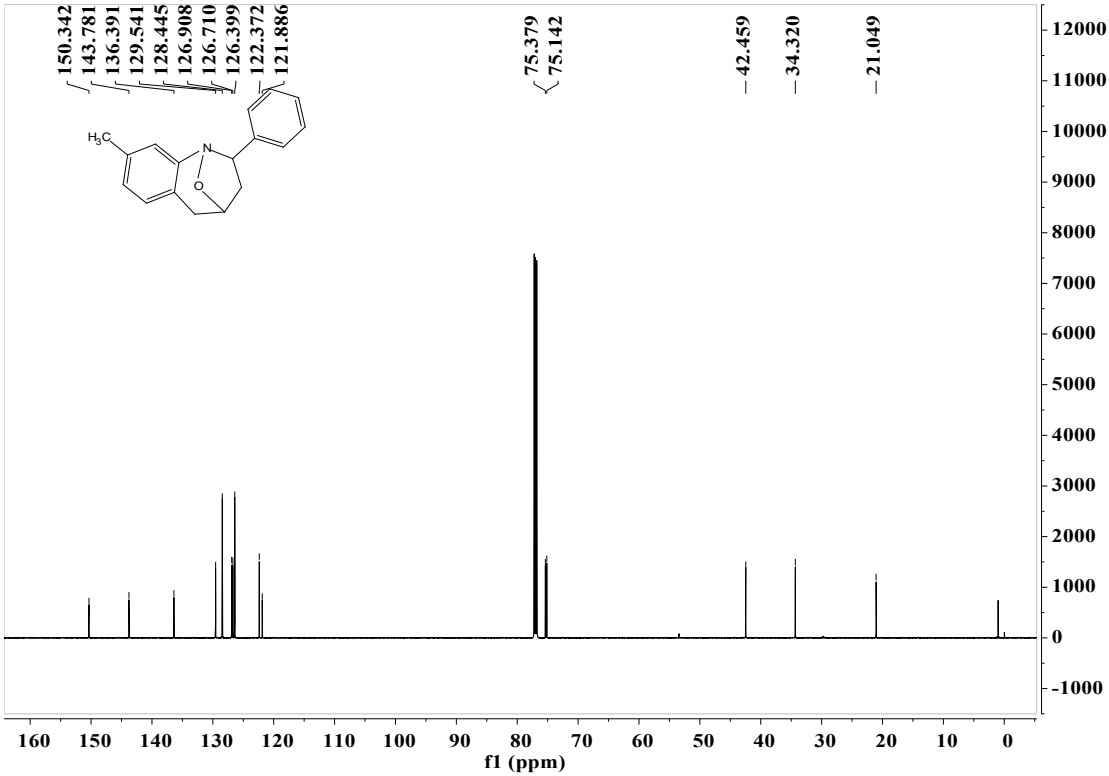

HSQC
f2 (ppm)
f1 (ppm)

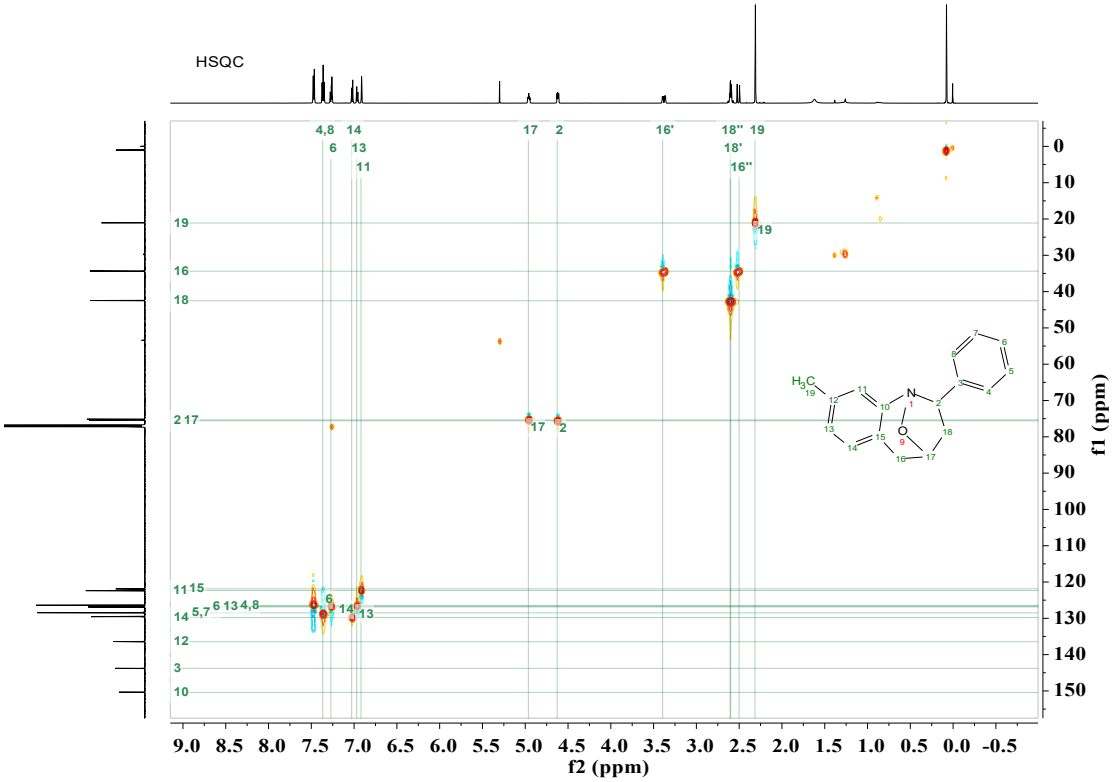

HMBC
f2 (ppm)
f1 (ppm)

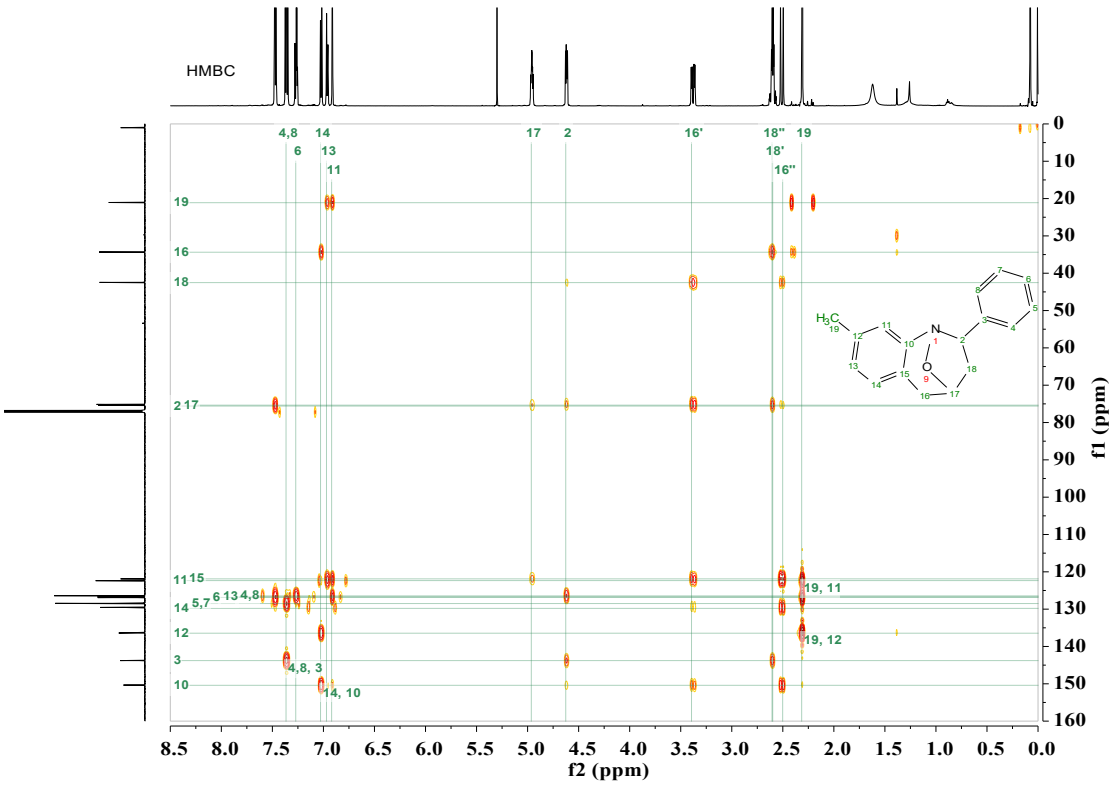
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3aa**



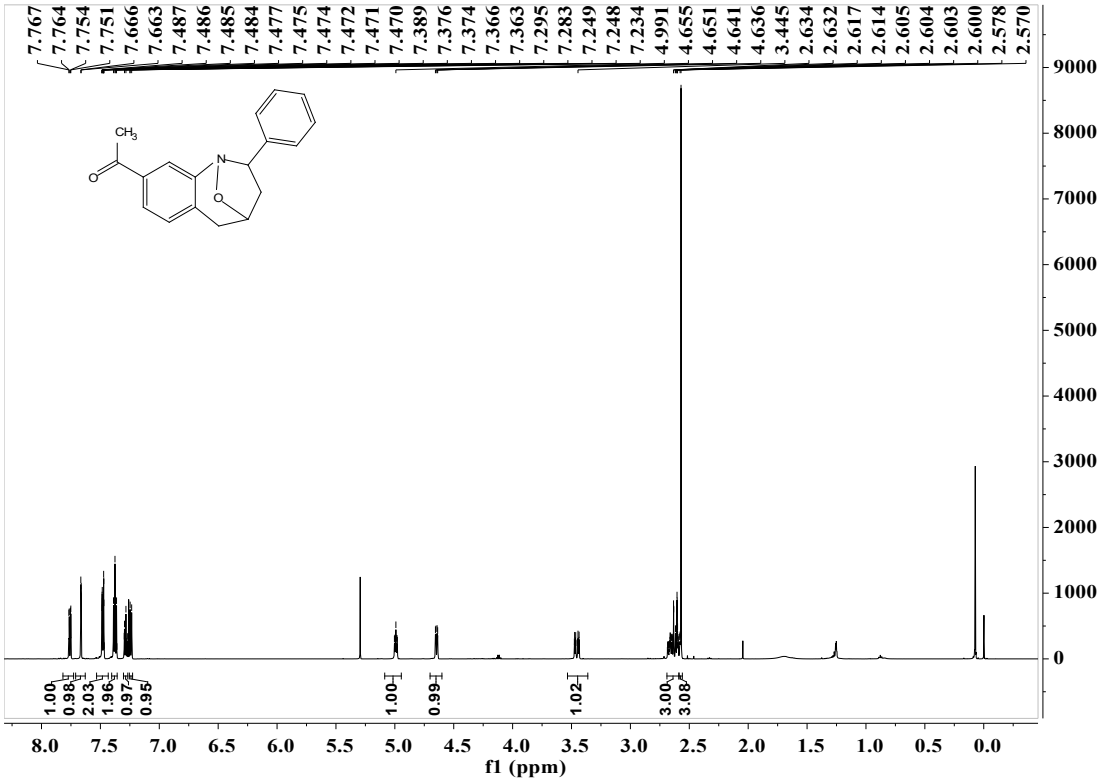
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3aa**



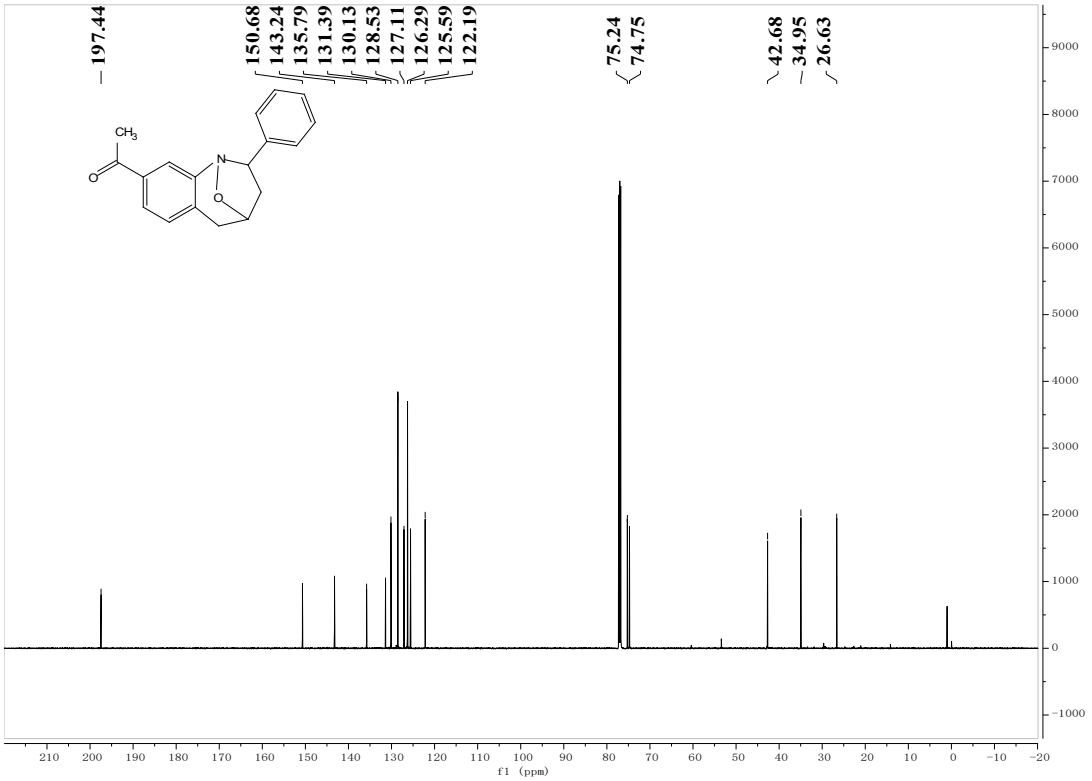

HSQC
f2 (ppm)
f1 (ppm)

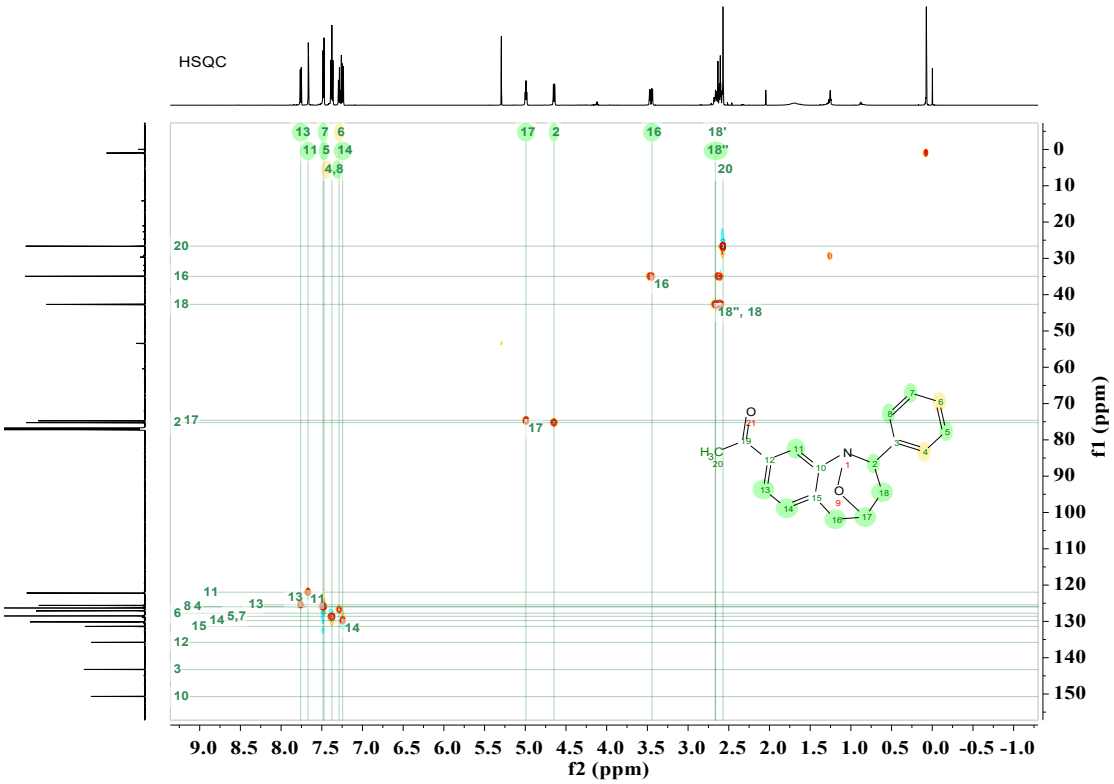

HMBC
f2 (ppm)
f1 (ppm)

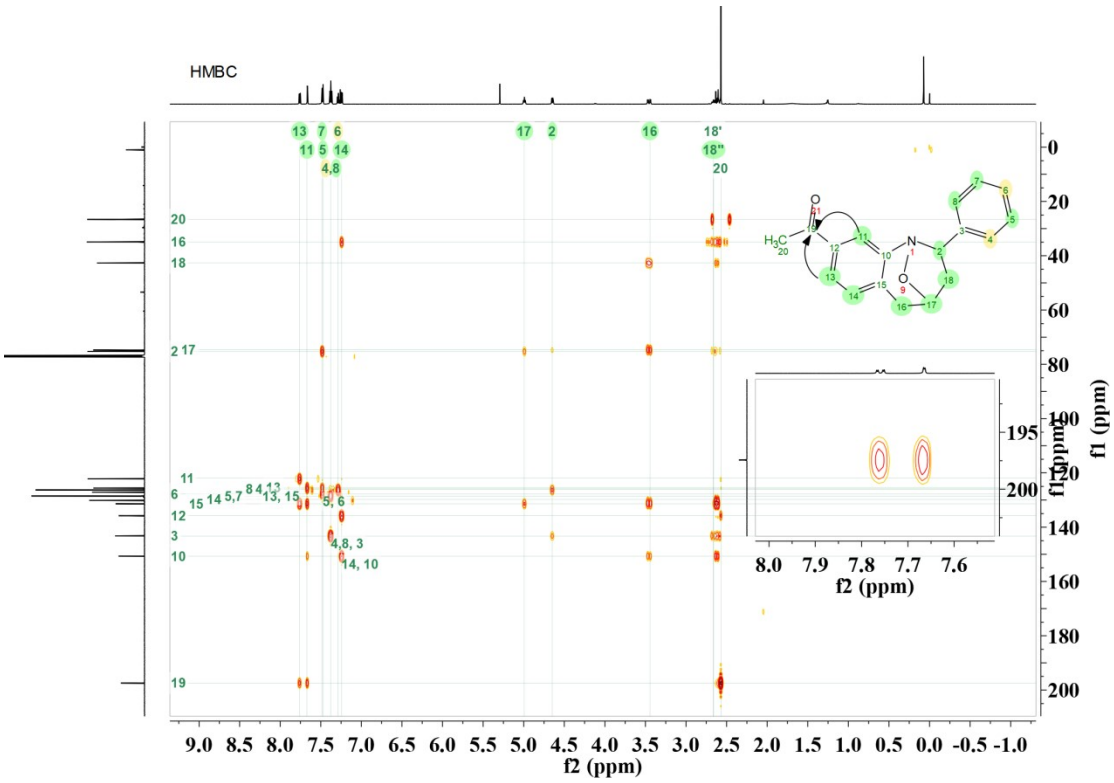
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3ab**



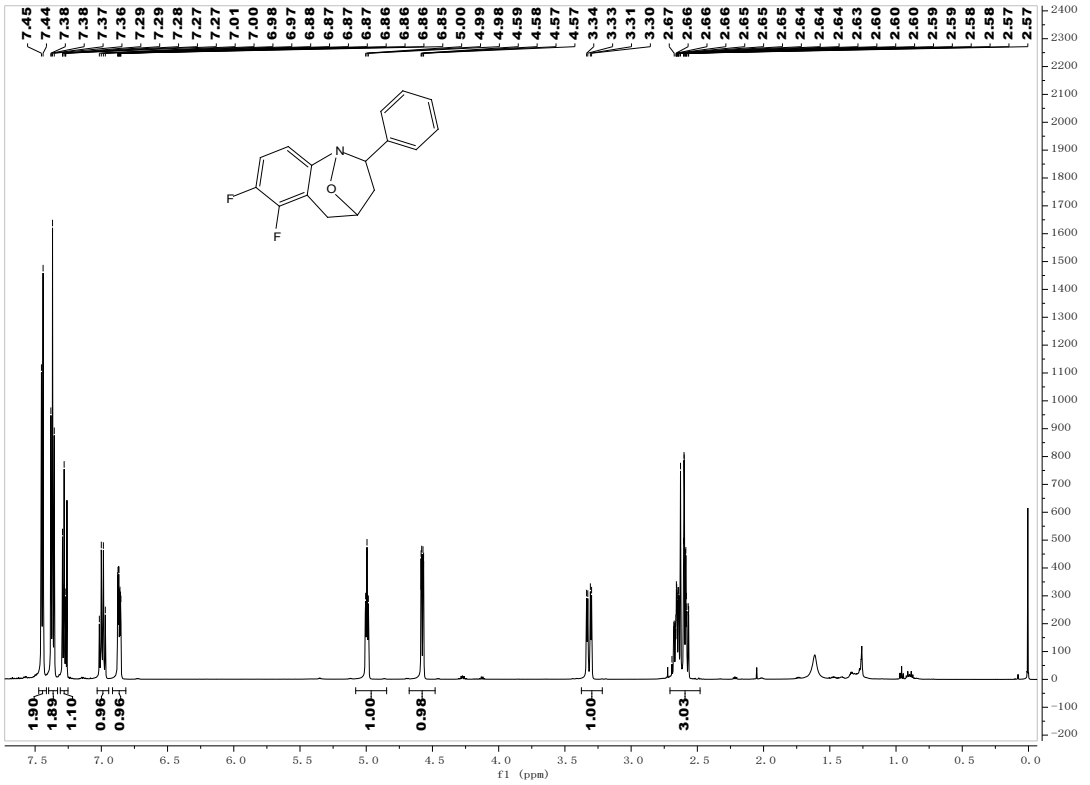
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3ab**



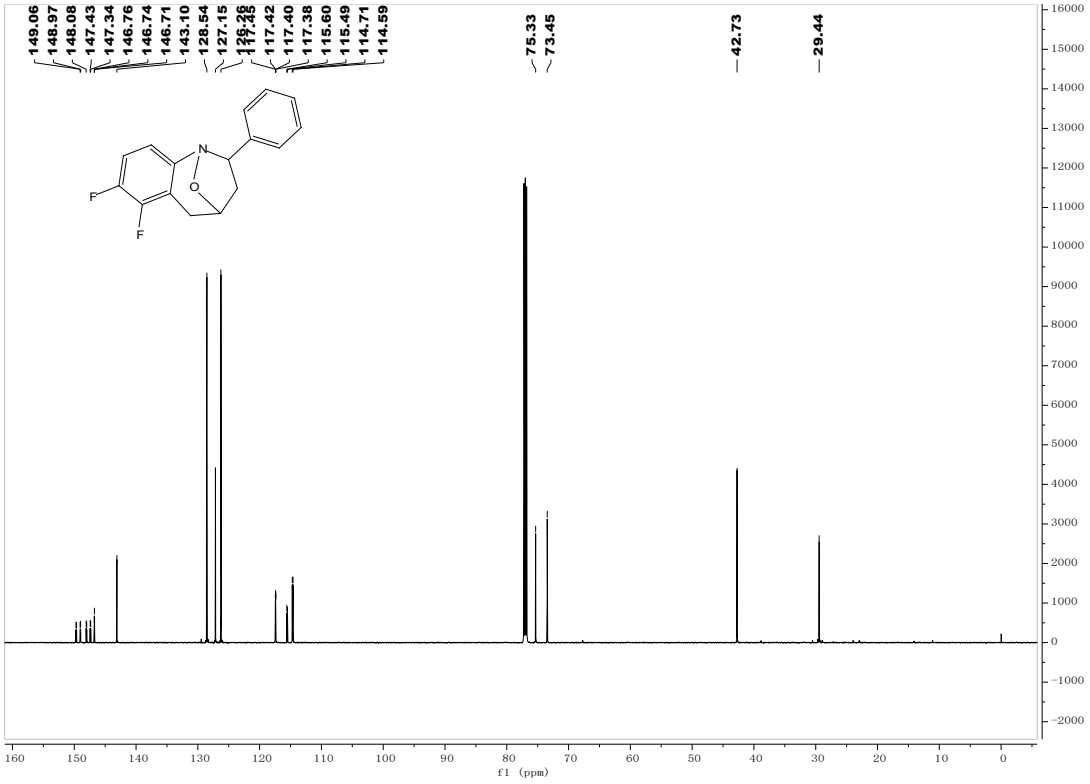

HSQC
f2 (ppm)
f1 (ppm)

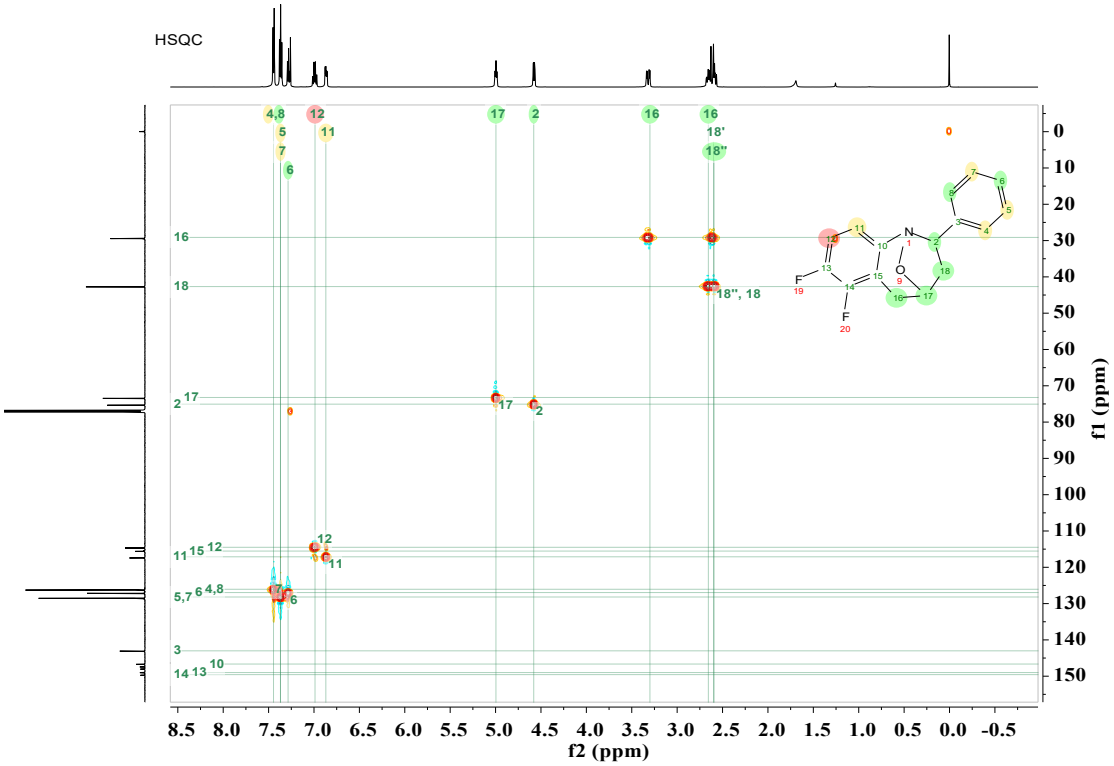

HMBC
f2 (ppm)
f1 (ppm)

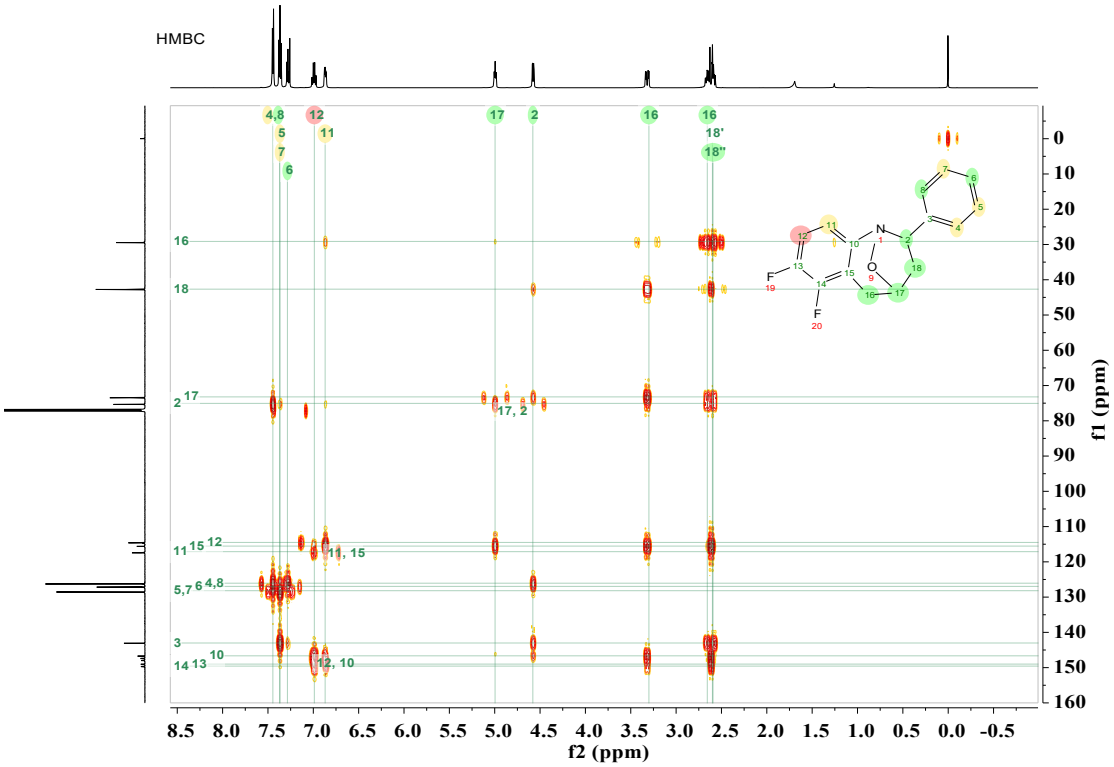
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3ac**



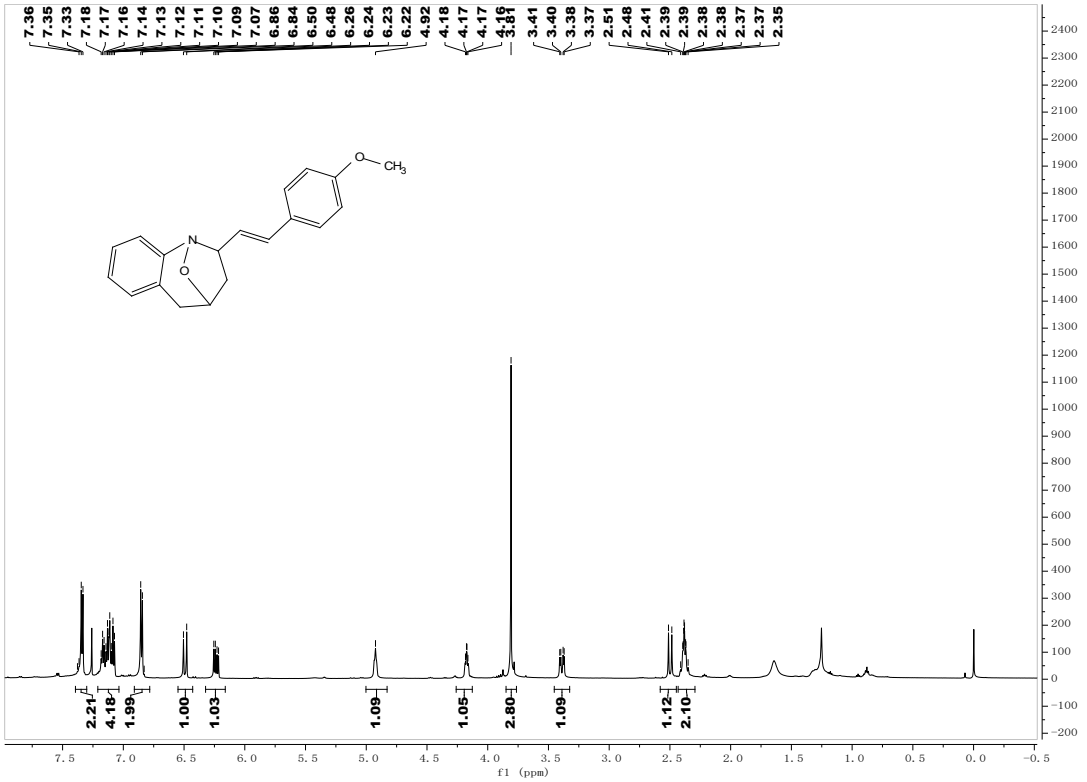
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3ac**



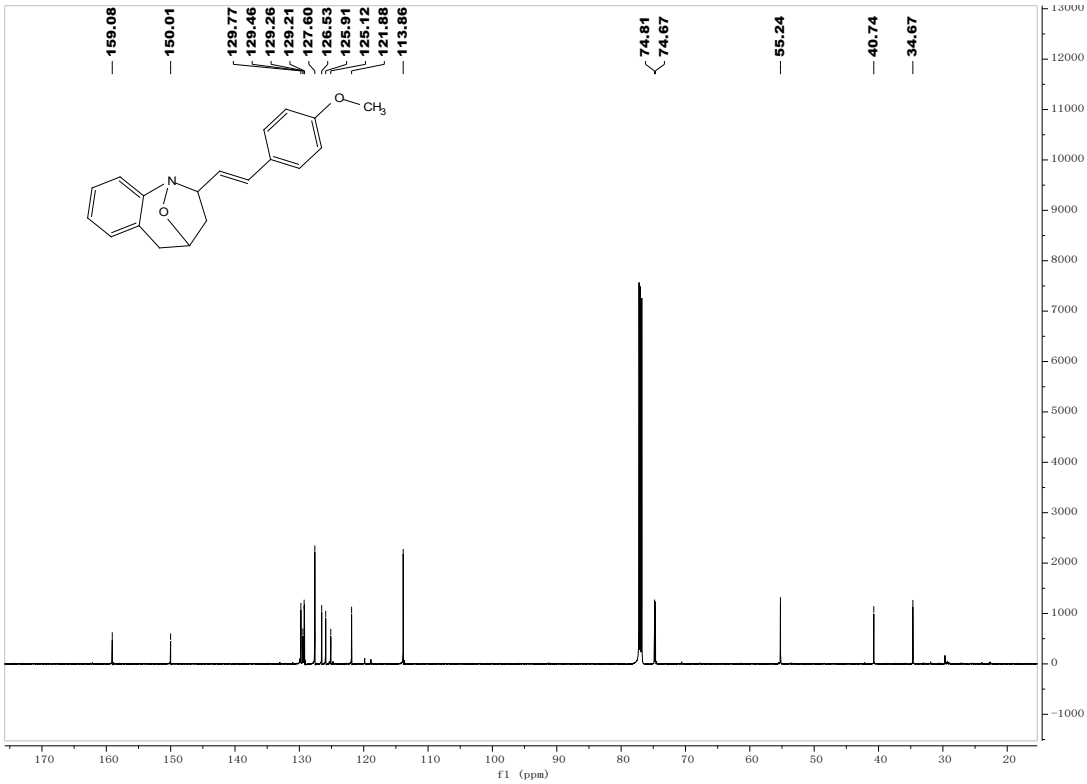

HSQC
f2 (ppm)
f1 (ppm)


HMBC
f2 (ppm)
f1 (ppm)

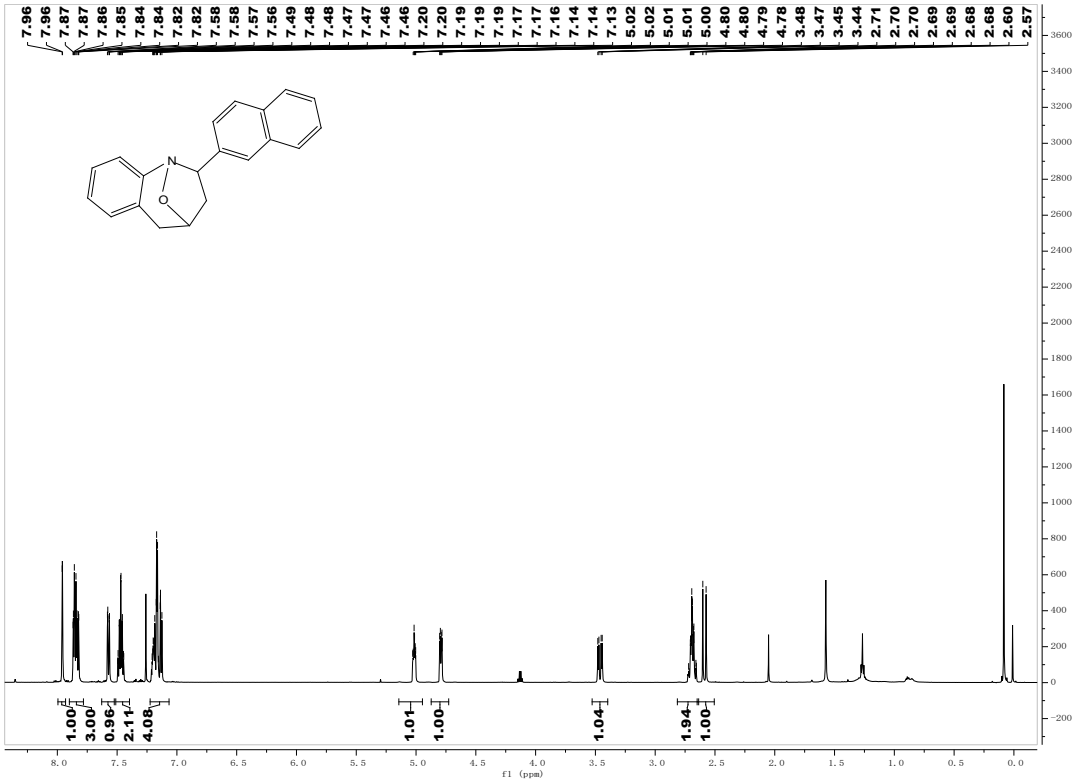
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3ad**



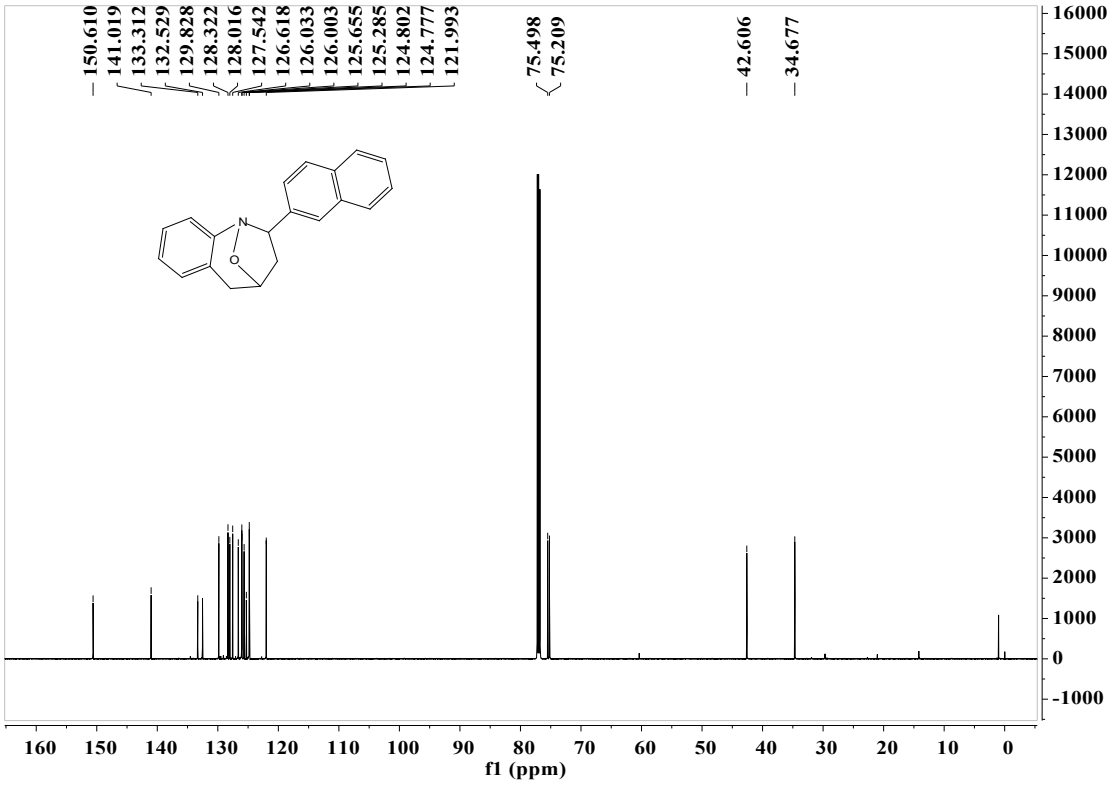
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3ad**



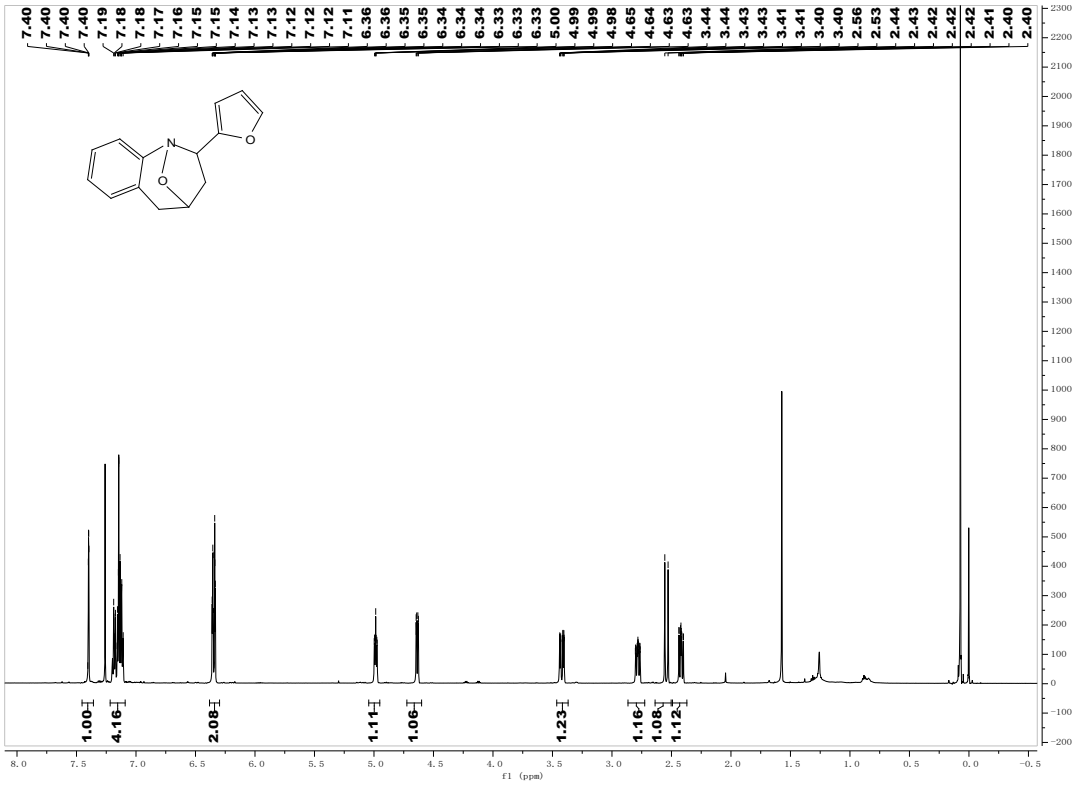
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3ae**



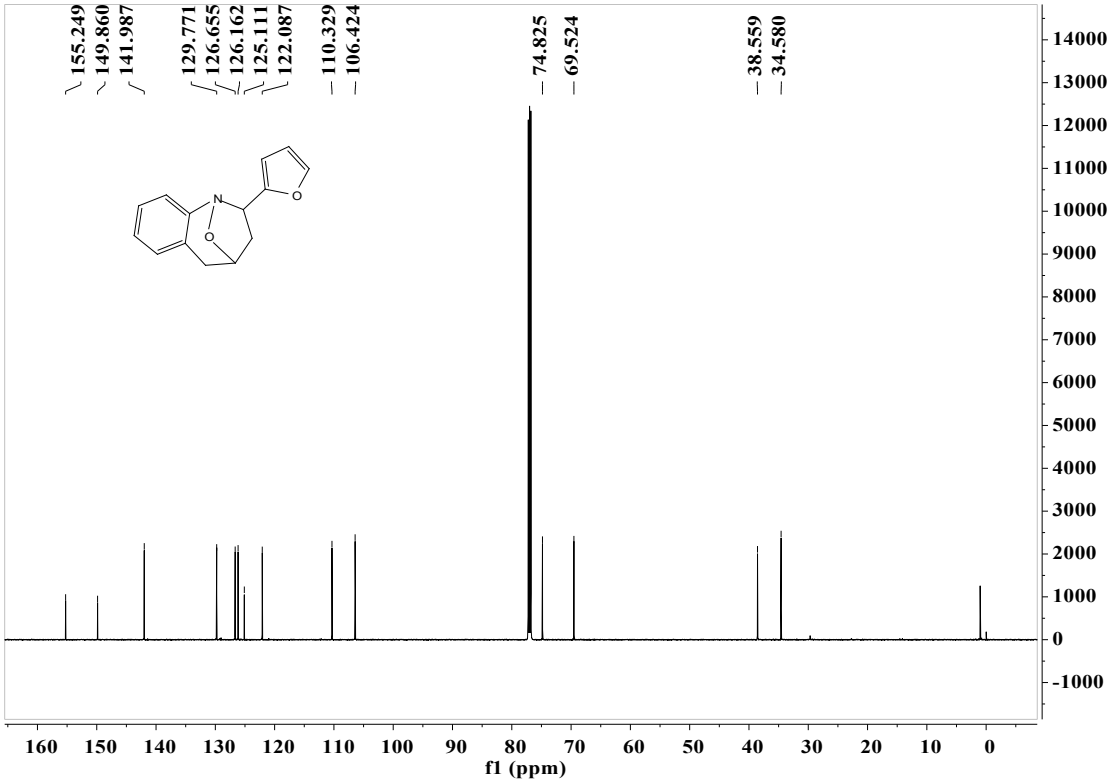
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3ae**



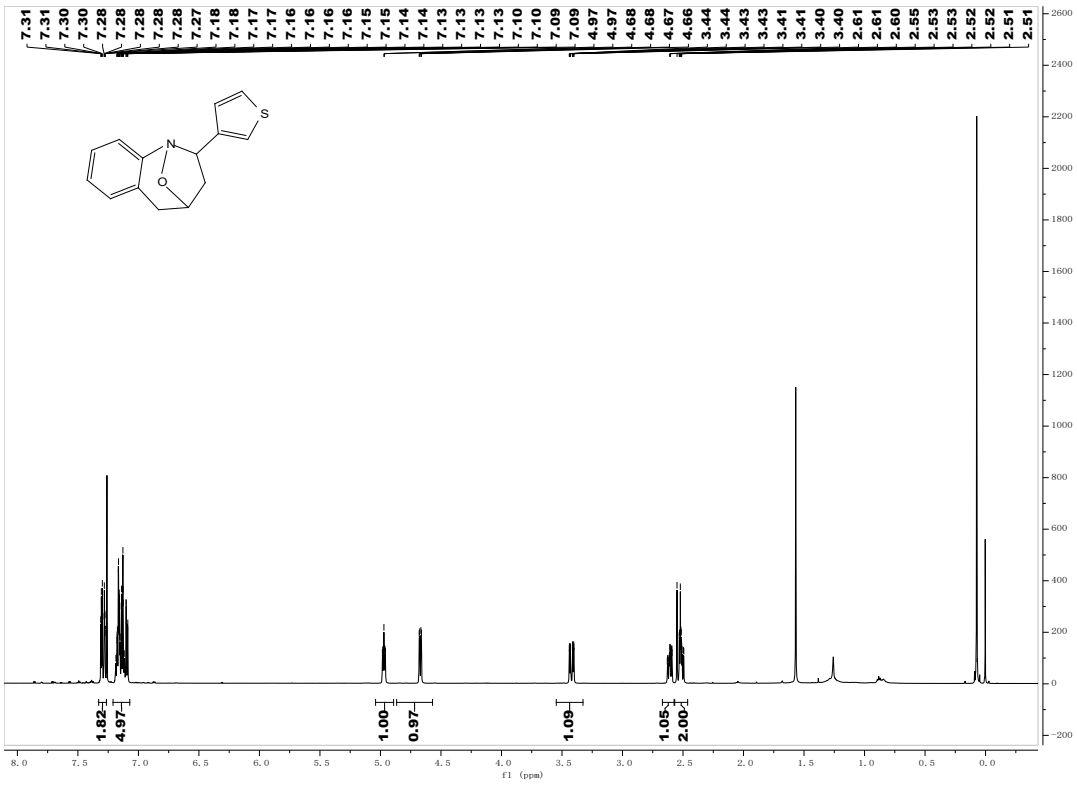
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3af**



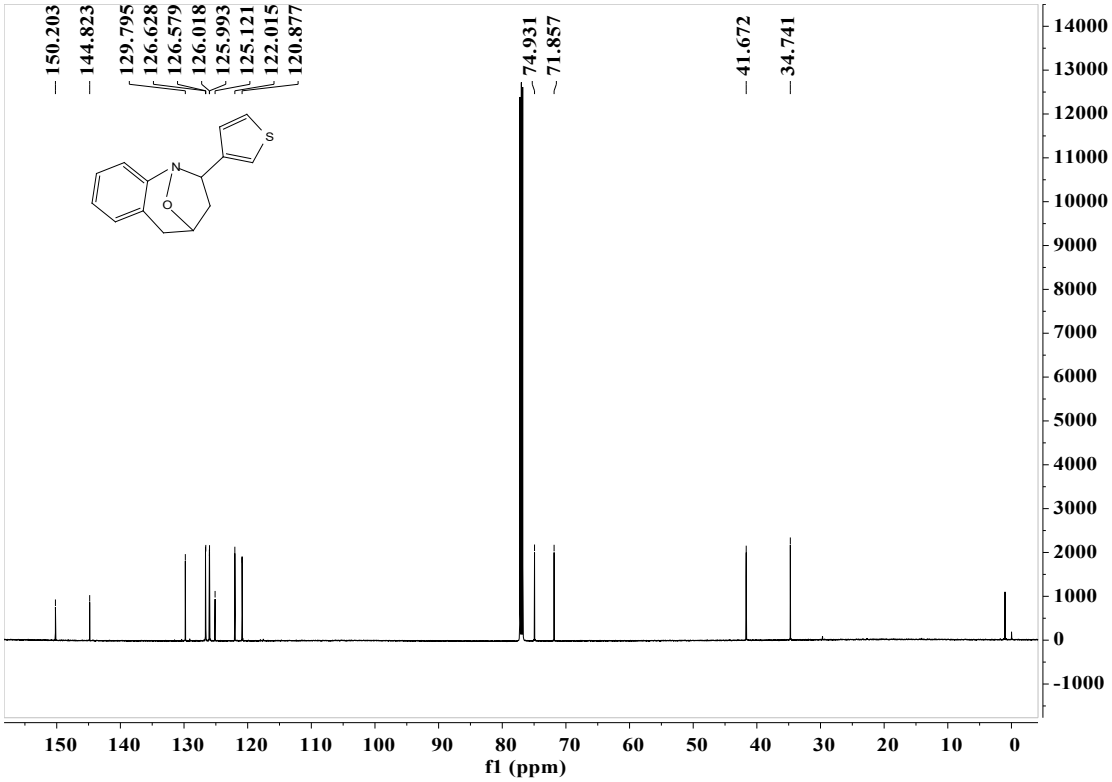
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3af**



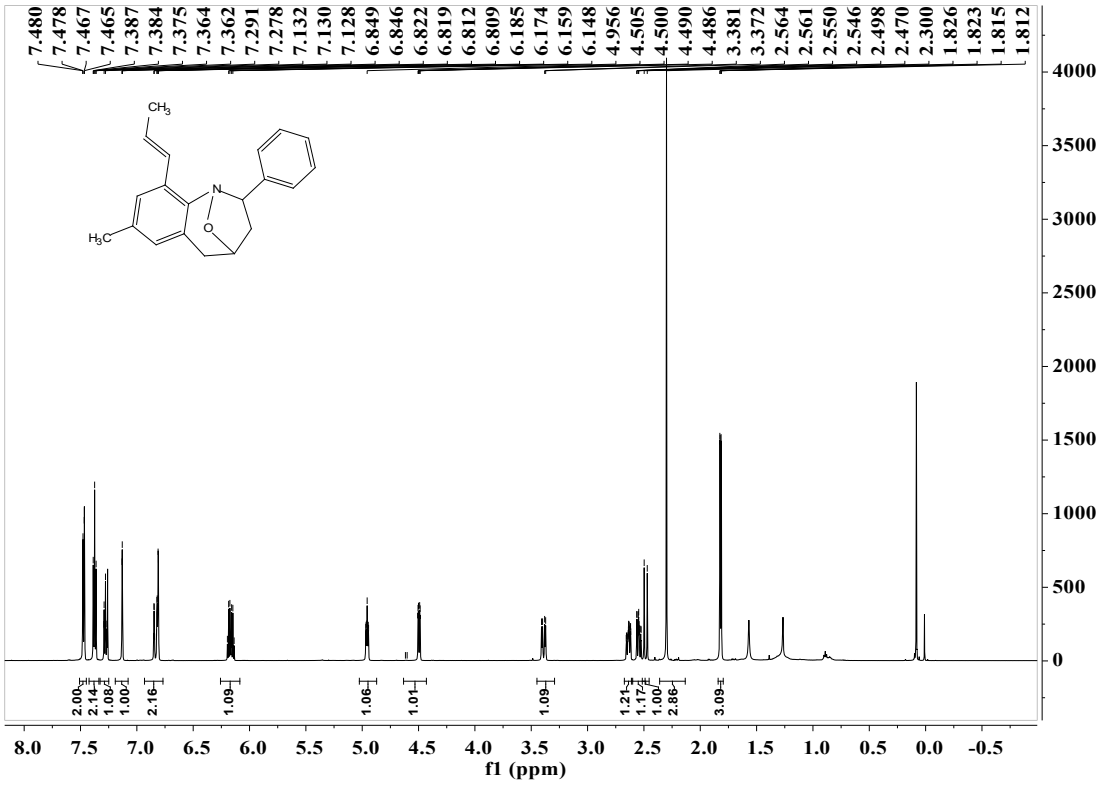
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **3ag**



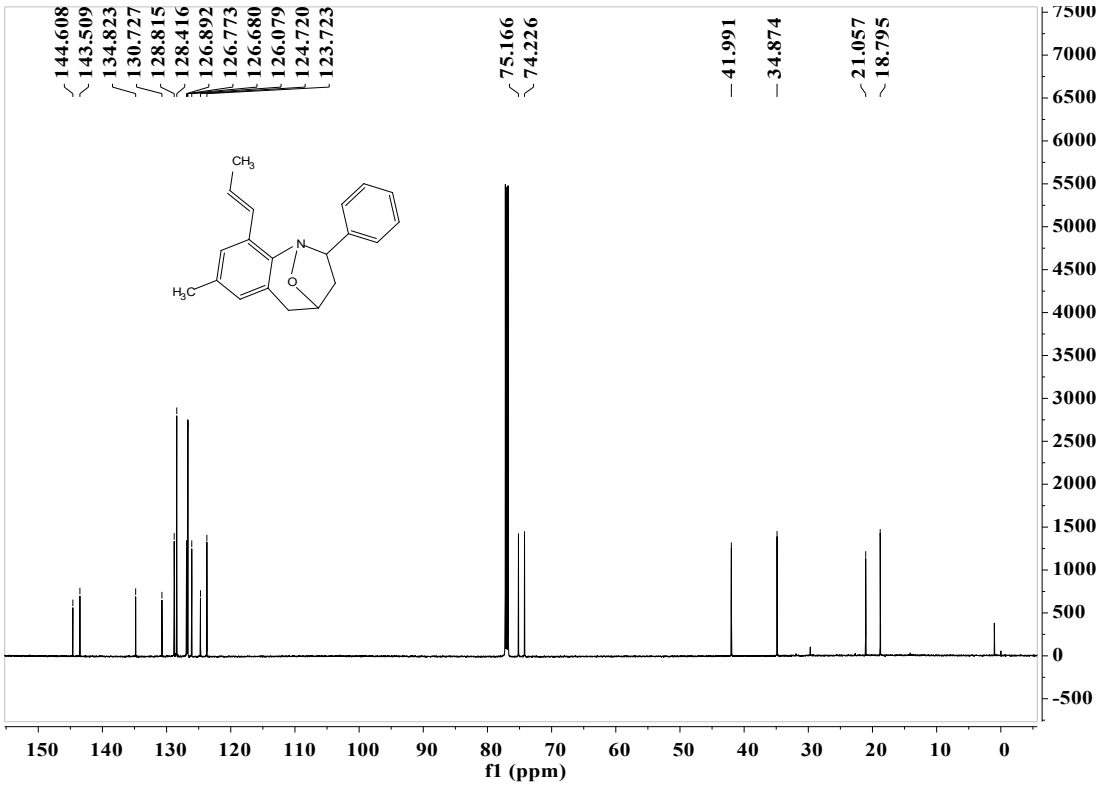
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **3ag**



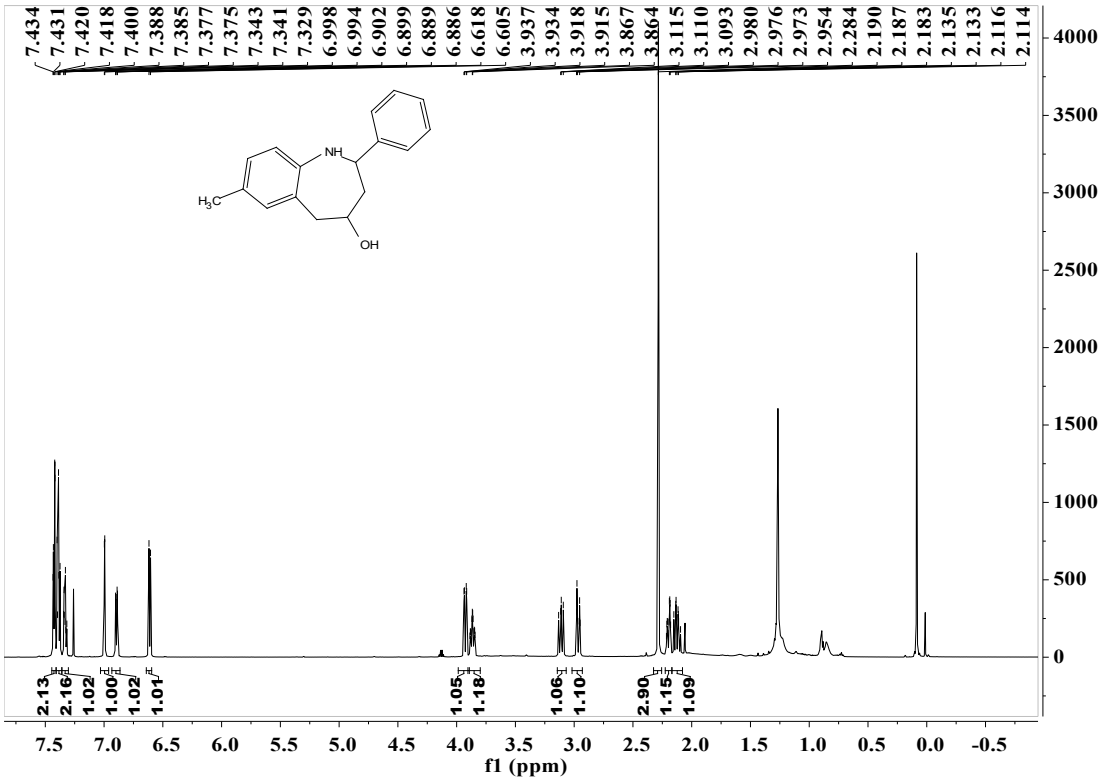
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **5a**



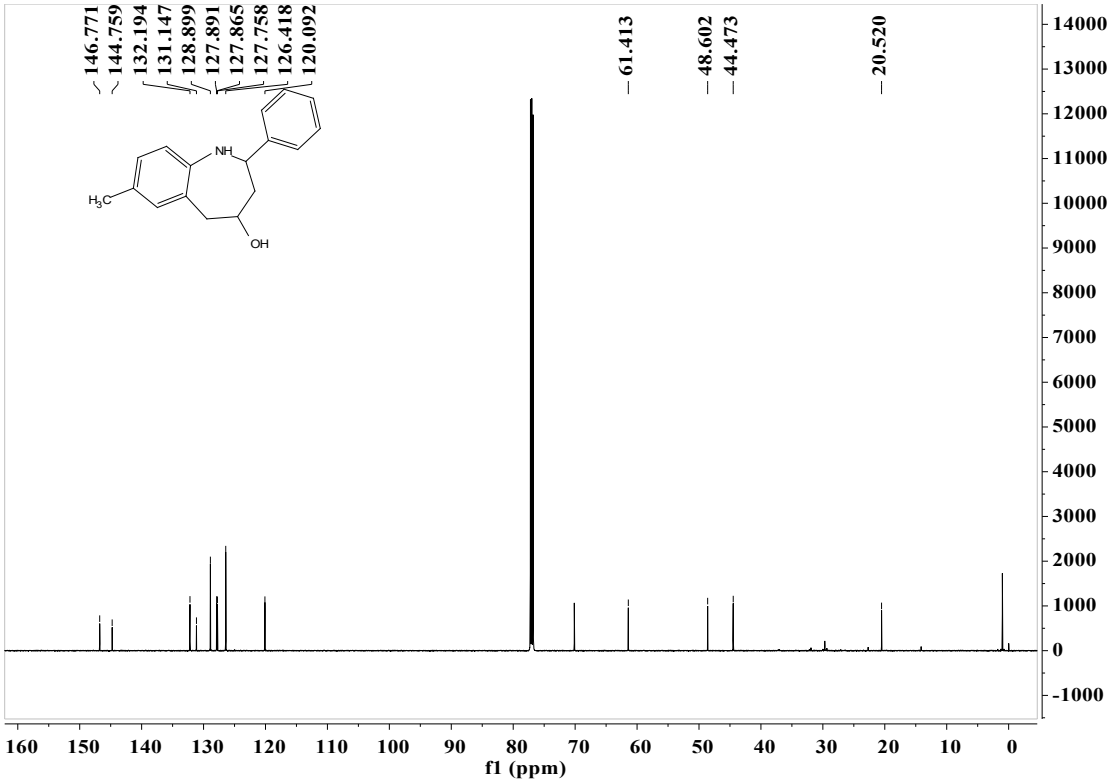
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **5a**



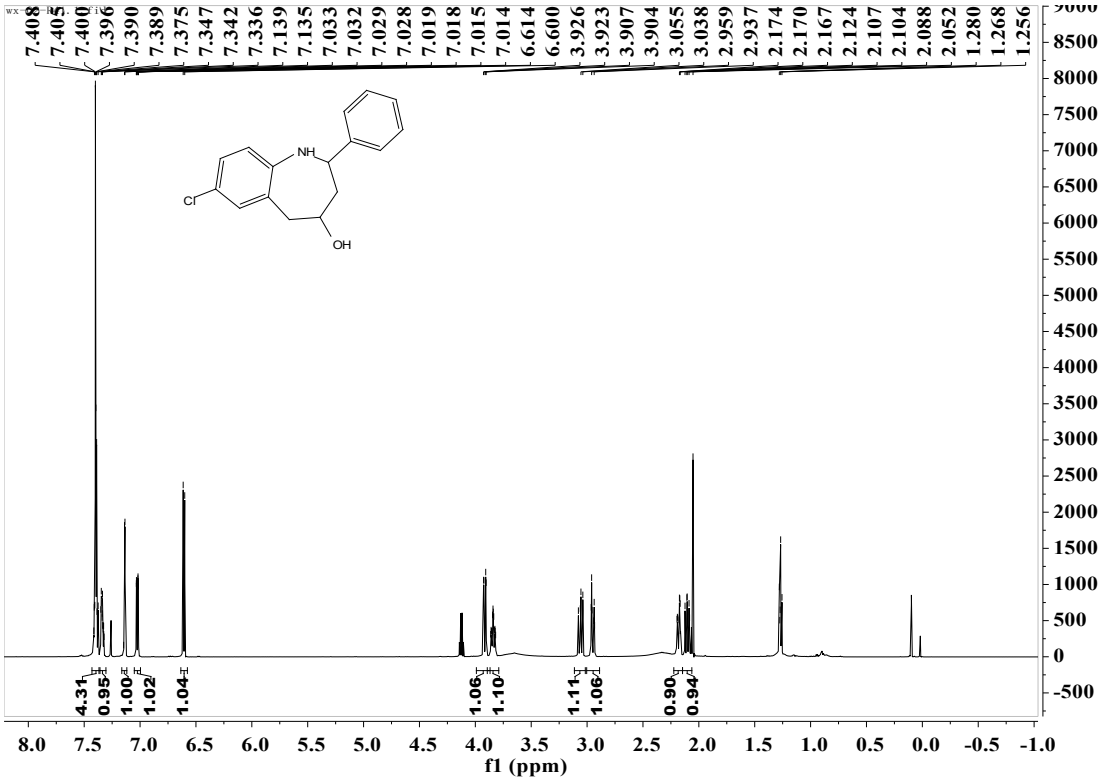
^{1}H NMR (600 MHZ, $CDCl_3$) of compound **4a**



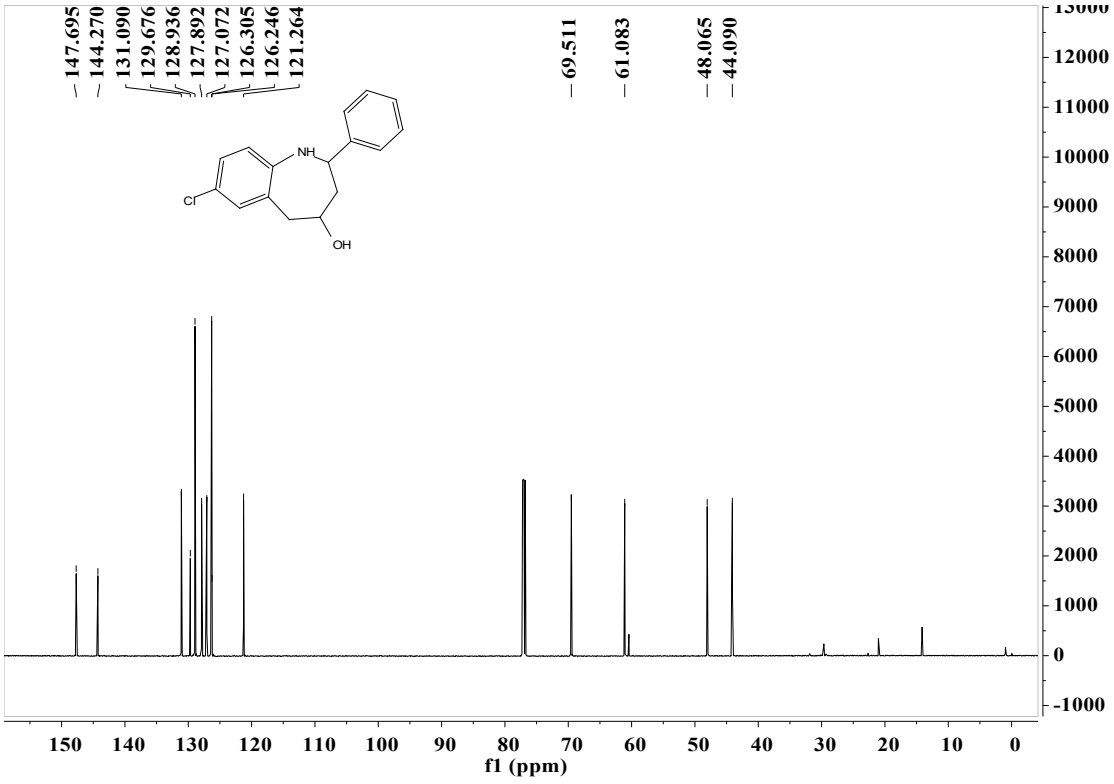
^{13}C NMR (151 MHZ, $CDCl_3$) of compound **4a**



^{1}H NMR (600 MHZ, $CDCl_3$) of compound **4f**



^{13}C NMR (151 MHZ, $CDCl_3$) of compound **4f**



Crystallographic Data

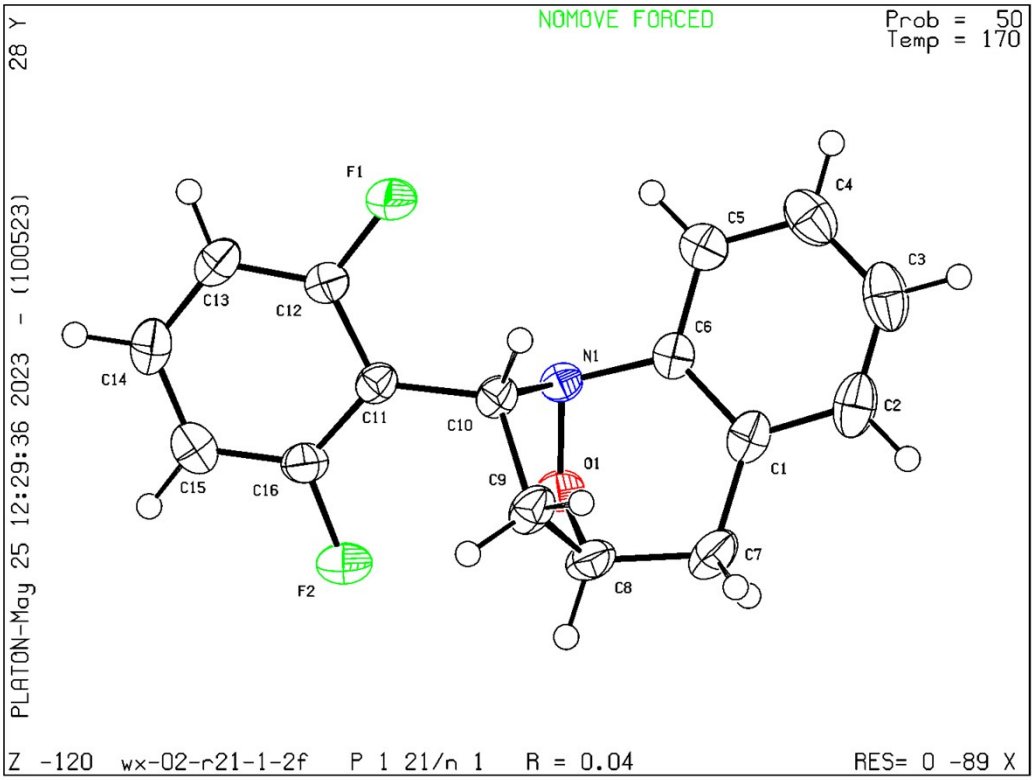


Figure S1. Crystal XRD image of **3w**

Table S2 Crystal data and structure refinement of 3w.

Identification code	3w
Empirical formula	$C_{16}H_{13}F_2NO$
Formula weight	273.27
Temperature/K	170.00(18)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.1690(2)
b/Å	10.8560(2)
c/Å	12.0502(3)
α/°	90
β/°	102.790(2)
γ/°	90
Volume/Å^3	1297.27(5)
Z	4
ρ_{calc}g/cm^3	1.399

μ/mm^{-1}	0.900
F(000)	568.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.32 to 147.42
Index ranges	-12 ≤ h ≤ 12, -8 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	4569
Independent reflections	2541 [R_{int} = 0.0202, R_{sigma} = 0.0245]
Data/restraints/parameters	2541/0/182
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0998
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.1028
Largest diff. peak/hole / e Å^{-3}	0.22/-0.21

Table S3 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3w. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	6018.2(8)	3473.4(9)	6839.5(7)	43.7(3)
F2	1666.8(9)	3950.6(11)	4534.5(8)	52.2(3)
O1	1446.0(9)	3500.1(9)	6869.7(8)	31.3(2)
N1	2848.6(10)	3450.0(10)	7441.4(9)	25.3(3)
C1	2027.7(14)	4707.0(12)	8874.2(12)	32.7(3)
C2	2181.0(17)	5044.8(14)	10006.5(14)	42.9(4)
C3	3218.3(18)	4573.6(16)	10841.6(14)	47.7(4)
C4	4130.5(17)	3756.0(16)	10558.9(13)	42.9(4)
C5	3998.8(14)	3398.2(13)	9435.0(13)	33.3(3)
C6	2951.5(13)	3868.9(11)	8600.6(11)	26.9(3)
C7	905.1(15)	5203.9(14)	7948.1(14)	39.8(4)
C8	1132.3(14)	4807.9(14)	6799.8(13)	35.8(3)
C9	2390.4(14)	5408.2(13)	6530.7(13)	35.6(3)
C10	3452.7(12)	4371.5(12)	6786.2(11)	26.7(3)
C11	3822.0(12)	3785.3(11)	5758.3(11)	26.2(3)
C12	5134.8(13)	3376.9(12)	5820.0(12)	28.7(3)
C13	5600.6(14)	2884.3(13)	4927.9(13)	34.9(3)
C14	4719.9(15)	2789.4(13)	3886.6(13)	37.0(3)
C15	3389.0(16)	3148.5(15)	3760.6(13)	38.4(3)
C16	2984.6(13)	3624.3(13)	4690.6(12)	32.6(3)

Table S4 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3w. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	29.5(4)	59.8(6)	38.3(5)	-5.1(4)	-0.3(4)	10.2(4)
F2	28.9(4)	78.6(7)	45.0(5)	-1.5(5)	-0.9(4)	14.0(4)
O1	24.5(5)	32.2(5)	36.4(5)	1.1(4)	5.1(4)	-0.6(4)
N1	24.0(5)	22.9(5)	29.2(6)	0.8(4)	6.1(4)	0.9(4)
C1	39.6(7)	23.6(7)	39.6(8)	-0.9(5)	18.6(6)	-1.8(5)
C2	57.4(9)	32.3(8)	46.3(9)	-9.0(6)	27.4(8)	-7.6(7)
C3	62.5(10)	48.2(9)	35.2(8)	-11.1(7)	17.1(7)	-21.8(8)
C4	45.4(8)	47.1(9)	33.4(8)	2.1(6)	2.8(6)	-15.0(7)
C5	32.4(7)	32.1(7)	35.0(7)	3.0(6)	6.8(6)	-4.6(5)
C6	30.8(6)	21.5(6)	30.0(7)	-0.3(5)	10.2(5)	-4.1(5)
C7	40.3(8)	34.0(8)	51.4(9)	5.4(6)	23.5(7)	10.9(6)
C8	30.8(7)	35.8(8)	42.8(8)	8.7(6)	12.2(6)	11.4(6)
C9	42.5(8)	26.2(7)	43.1(8)	7.5(6)	20.6(6)	9.4(6)
C10	27.7(6)	23.2(6)	30.7(7)	0.8(5)	9.7(5)	0.6(5)
C11	26.6(6)	22.6(6)	30.6(7)	2.0(5)	9.3(5)	1.5(5)
C12	26.6(6)	28.1(7)	31.6(7)	1.3(5)	6.6(5)	1.5(5)
C13	33.5(7)	32.1(7)	43.4(8)	1.7(6)	17.8(6)	4.4(6)
C14	49.1(8)	31.4(7)	35.8(7)	-1.3(6)	20.8(6)	0.0(6)
C15	45.0(8)	39.6(8)	29.5(7)	0.6(6)	5.4(6)	-2.3(6)
C16	26.7(6)	36.1(7)	34.2(7)	3.3(6)	5.2(5)	4.4(5)

Table S5 Bond Lengths for 3w.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C12	1.3560(15)	C5	C6	1.3900(19)
F2	C16	1.3584(16)	C7	C8	1.515(2)
O1	N1	1.4411(14)	C8	C9	1.5331(19)
O1	C8	1.4535(17)	C9	C10	1.5431(17)
N1	C6	1.4507(17)	C10	C11	1.5120(18)
N1	C10	1.4887(16)	C11	C12	1.3930(18)
C1	C2	1.388(2)	C11	C16	1.3878(19)
C1	C6	1.3986(18)	C12	C13	1.375(2)
C1	C7	1.508(2)	C13	C14	1.375(2)
C2	C3	1.385(3)	C14	C15	1.384(2)
C3	C4	1.380(3)	C15	C16	1.377(2)
C4	C5	1.387(2)			

Table S6 Bond Angles for 3w.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	O1	C8	104.24(9)	C7	C8	C9	112.07(13)
O1	N1	C6	107.53(9)	C8	C9	C10	103.17(11)
O1	N1	C10	101.66(9)	N1	C10	C9	104.07(10)
C6	N1	C10	110.47(10)	N1	C10	C11	110.98(10)
C2	C1	C6	117.94(14)	C11	C10	C9	115.68(11)
C2	C1	C7	122.32(14)	C12	C11	C10	119.94(12)
C6	C1	C7	119.74(13)	C16	C11	C10	126.85(11)
C3	C2	C1	121.23(15)	C16	C11	C12	113.17(12)
C4	C3	C2	120.25(15)	F1	C12	C11	117.30(12)
C3	C4	C5	119.77(15)	F1	C12	C13	117.68(12)
C4	C5	C6	119.76(14)	C13	C12	C11	125.02(13)
C1	C6	N1	121.46(12)	C14	C13	C12	118.37(13)
C5	C6	N1	117.49(12)	C13	C14	C15	120.17(13)
C5	C6	C1	121.05(13)	C16	C15	C14	118.51(14)
C1	C7	C8	109.32(11)	F2	C16	C11	118.66(12)
O1	C8	C7	107.46(11)	F2	C16	C15	116.64(13)
O1	C8	C9	104.16(10)	C15	C16	C11	124.70(13)

Table S7 Torsion Angles for 3w.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C12	C13	C14	-179.50(12)	C7	C1	C6	N1	-0.73(19)
O1	N1	C6	C1	-28.56(15)	C7	C1	C6	C5	179.80(13)
O1	N1	C6	C5	150.93(11)	C7	C8	C9	C10	101.55(13)
O1	N1	C10	C9	38.15(12)	C8	O1	N1	C6	67.32(11)
O1	N1	C10	C11	-86.93(11)	C8	O1	N1	C10	-48.76(11)
O1	C8	C9	C10	-14.32(14)	C8	C9	C10	N1	-14.38(14)
N1	O1	C8	C7	-79.73(12)	C8	C9	C10	C11	107.64(13)
N1	O1	C8	C9	39.33(13)	C9	C10	C11	C12	145.91(12)
N1	C10	C11	C12	-95.83(14)	C9	C10	C11	C16	-31.96(19)
N1	C10	C11	C16	86.29(16)	C10	N1	C6	C1	81.57(14)
C1	C2	C3	C4	0.3(2)	C10	N1	C6	C5	-98.94(13)
C1	C7	C8	O1	47.17(15)	C10	C11	C12	F1	3.24(18)
C1	C7	C8	C9	-66.68(15)	C10	C11	C12	C13	-176.80(13)
C2	C1	C6	N1	178.83(12)	C10	C11	C16	F2	-4.1(2)
C2	C1	C6	C5	-0.6(2)	C10	C11	C16	C15	176.06(13)
C2	C1	C7	C8	171.90(13)	C11	C12	C13	C14	0.5(2)
C2	C3	C4	C5	-0.6(2)	C12	C11	C16	F2	177.87(12)
C3	C4	C5	C6	0.2(2)	C12	C11	C16	C15	-1.9(2)
C4	C5	C6	N1	-179.10(12)	C12	C13	C14	C15	-2.0(2)
C4	C5	C6	C1	0.4(2)	C13	C14	C15	C16	1.5(2)
C6	N1	C10	C9	-75.76(13)	C14	C15	C16	F2	-179.18(13)
C6	N1	C10	C11	159.16(10)	C14	C15	C16	C11	0.6(2)
C6	C1	C2	C3	0.3(2)	C16	C11	C12	F1	-178.61(12)
C6	C1	C7	C8	-8.56(19)	C16	C11	C12	C13	1.3(2)
C7	C1	C2	C3	179.85(14)					

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3w.

Atom	*x*	*y*	*z*	U(eq)
H2	1562.54	5609.93	10212.4	51
H3	3302.38	4814.09	11612.16	57
H4	4846.08	3439.32	11132.29	51
H5	4622.14	2833.39	9235.97	40
H7A	886.27	6114.21	7990.47	48
H7B	27.15	4885.99	8050.43	48
H8	317.36	4977.26	6183.17	43
H9A	2677.09	6133.71	7022.61	43
H9B	2226	5665.72	5723.59	43
H10	4290.55	4708.23	7290.83	32
H13	6508.65	2616.28	5028.76	42
H14	5025.58	2476.54	3251.73	44
H15	2768.42	3068.44	3048.46	46

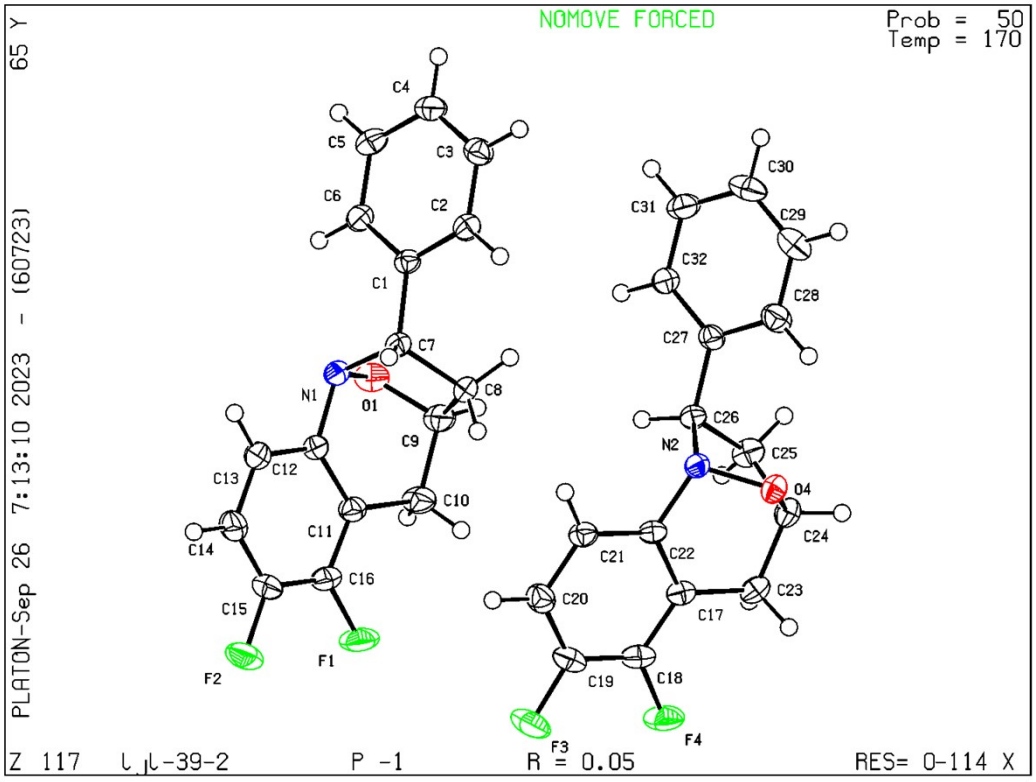


Figure S2. Crystal XRD image of **3ac**

Table S9 Crystal data and structure refinement for 3ac.

Identification code	3ac
Empirical formula	$C_{16}H_{13}F_2NO$
Formula weight	273.27
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.7065(3)
b/Å	11.7198(4)
c/Å	12.0290(4)
α/°	77.710(3)
β/°	89.322(3)
γ/°	71.433(3)
Volume/Å^3	1265.13(8)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.923
F(000)	568.0

Crystal size/mm^3	0.17 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.536 to 147.088
Index ranges	-10 ≤ h ≤ 12, -13 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	8430
Independent reflections	4941 [R_{int} = 0.0289, R_{sigma} = 0.0300]
Data/restraints/parameters	4941/0/361
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0517, wR_2 = 0.1352
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1391
Largest diff. peak/hole / e Å^{-3}	0.30/-0.45

Table S10 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ac. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	11190.3(11)	4985.4(9)	8606.9(10)	44.2(3)
F2	13256.3(11)	4967.1(9)	10075.0(10)	43.1(3)
O1	7001.8(11)	8498.2(10)	8864.5(10)	29.5(3)
N1	8134.3(12)	8929.4(11)	9204.6(10)	22.3(3)
C1	6921.8(14)	11081.1(13)	8162.1(12)	20.9(3)
C2	6718.8(16)	12047.3(13)	7209.7(13)	24.5(3)
C3	5613.5(16)	13158.2(14)	7137.2(13)	28.0(3)
C4	4691.7(16)	13329.3(14)	8019.1(14)	29.3(3)
C5	4882.0(16)	12376.7(15)	8970.2(14)	29.3(3)
C6	5989.0(16)	11258.6(14)	9043.9(13)	25.3(3)
C7	8143.8(14)	9883.6(13)	8185.7(12)	21.4(3)
C8	7991.6(18)	9274.4(14)	7195.2(13)	30.5(3)
C9	7401.1(17)	8237.7(15)	7758.4(15)	31.9(4)
C10	8543.9(17)	6963.7(14)	7972.8(15)	32.5(4)
C11	9678.3(16)	6931.3(13)	8834.5(13)	24.6(3)
C12	9483.2(15)	7909.1(13)	9380.9(12)	22.8(3)
C13	10565.0(17)	7920.0(14)	10115.6(13)	29.1(3)
C14	11852.9(18)	6936.2(15)	10351.7(14)	32.3(4)
C15	12027.8(16)	5950.7(14)	9850.4(14)	29.6(3)
C16	10961.4(17)	5953.4(14)	9102.0(14)	28.2(3)
F3	12598.2(12)	4926.0(9)	5710.0(10)	47.0(3)
F4	10982.8(11)	5046.5(8)	3877.0(10)	41.8(3)
O4	8741.9(11)	9378.1(9)	2250.6(8)	24.6(2)
N2	8813.7(12)	9446.1(11)	3436.5(10)	21.0(3)
C17	9819.7(15)	7186.5(13)	3664.3(13)	24.0(3)
C18	10821.2(17)	6092.6(13)	4242.8(14)	29.5(3)
C19	11648.1(16)	6032.5(14)	5186.4(15)	31.0(3)
C20	11520.4(16)	7070.0(15)	5595.0(14)	29.2(3)
C21	10563.1(15)	8191.9(13)	5013.3(13)	24.6(3)
C22	9734.9(14)	8248.5(13)	4057.2(12)	21.5(3)
C23	8892.9(17)	7241.4(14)	2653.4(13)	28.1(3)
C24	7897.1(16)	8558.3(14)	2223.5(13)	26.2(3)
C25	6667.2(16)	8976.8(14)	3007.7(14)	28.7(3)
C26	7260.8(14)	9684.2(13)	3732.2(12)	21.6(3)
C27	6427.4(14)	11053.8(13)	3490.1(12)	22.7(3)
C28	6420.2(17)	11829.6(15)	2435.1(14)	30.6(3)

Table S10 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ac. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C29	5569.5(18)	13065.4(15)	2217.1(15)	35.4(4)
C30	4708.5(17)	13541.1(14)	3047.1(16)	34.8(4)
C31	4716.0(17)	12784.2(15)	4098.4(15)	33.0(4)
C32	5571.1(16)	11546.1(14)	4318.1(13)	27.1(3)

Table S11 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ac. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	42.4(6)	27.6(5)	60.4(7)	-25.8(5)	-5.7(5)	2.3(4)
F2	31.1(5)	32.5(5)	52.9(7)	-8.3(5)	-8.1(4)	6.9(4)
O1	22.1(5)	28.3(5)	40.5(6)	-9.1(5)	5.9(4)	-10.8(4)
N1	23.0(6)	21.9(6)	22.3(6)	-7.2(5)	2.0(4)	-6.2(5)
C1	19.1(6)	21.0(7)	24.3(7)	-8.5(5)	0.2(5)	-6.5(5)
C2	24.7(7)	25.1(7)	24.6(7)	-6.8(6)	3.6(5)	-8.6(6)
C3	29.0(7)	22.1(7)	31.2(8)	-4.4(6)	-2.5(6)	-6.8(6)
C4	24.0(7)	24.4(7)	38.3(9)	-11.9(6)	-2.1(6)	-2.8(6)
C5	26.0(7)	31.2(8)	33.2(8)	-14.6(6)	8.3(6)	-7.9(6)
C6	27.9(7)	25.2(7)	23.9(7)	-7.8(6)	3.8(6)	-8.7(6)
C7	21.2(6)	21.9(7)	21.5(7)	-6.4(5)	3.8(5)	-6.5(5)
C8	40.3(8)	25.9(7)	19.5(7)	-8.4(6)	-0.5(6)	-0.5(6)
C9	26.6(7)	29.8(8)	40.3(9)	-16.3(7)	-7.9(6)	-4.6(6)
C10	31.3(8)	24.5(8)	44.5(10)	-15.3(7)	-6.0(7)	-7.5(6)
C11	25.6(7)	21.4(7)	26.8(7)	-7.4(5)	0.8(6)	-6.4(6)
C12	25.5(7)	20.6(7)	21.3(7)	-5.5(5)	2.2(5)	-5.4(5)
C13	33.9(8)	25.5(7)	26.9(8)	-9.0(6)	-4.9(6)	-5.9(6)
C14	30.5(8)	32.7(8)	30.8(8)	-7.1(6)	-8.2(6)	-5.7(6)
C15	24.8(7)	24.4(7)	32.6(8)	-3.9(6)	-1.4(6)	0.3(6)
C16	31.0(8)	21.1(7)	32.4(8)	-11.2(6)	3.4(6)	-4.9(6)
F3	41.7(6)	26.5(5)	57.1(7)	1.0(5)	-10.0(5)	4.4(4)
F4	46.2(6)	20.6(5)	58.1(7)	-16.4(4)	2.1(5)	-5.0(4)
O4	28.0(5)	27.1(5)	21.2(5)	-7.0(4)	4.7(4)	-11.5(4)
N2	20.1(6)	21.7(6)	20.9(6)	-6.5(4)	1.6(4)	-5.3(4)
C17	23.5(7)	21.2(7)	27.9(8)	-7.5(6)	5.7(6)	-6.7(5)
C18	28.6(7)	19.4(7)	39.8(9)	-9.5(6)	7.6(6)	-5.3(6)
C19	24.3(7)	22.2(7)	38.8(9)	-1.1(6)	0.3(6)	-0.6(6)
C20	23.3(7)	31.6(8)	29.6(8)	-4.3(6)	-1.3(6)	-5.9(6)
C21	20.9(6)	24.0(7)	28.8(8)	-8.8(6)	2.0(5)	-5.4(5)
C22	17.9(6)	20.0(7)	26.5(7)	-7.1(5)	4.1(5)	-5.0(5)
C23	32.8(8)	26.2(7)	29.9(8)	-13.8(6)	4.3(6)	-10.9(6)
C24	29.4(7)	29.0(8)	24.3(7)	-10.0(6)	0.4(6)	-12.2(6)
C25	24.0(7)	30.6(8)	36.4(8)	-13.1(6)	3.2(6)	-12.0(6)
C26	19.4(6)	22.0(7)	23.0(7)	-5.9(5)	2.7(5)	-5.5(5)
C27	18.0(6)	23.5(7)	25.6(7)	-6.6(5)	-3.4(5)	-4.4(5)
C28	25.9(7)	29.4(8)	31.1(8)	-2.2(6)	1.0(6)	-4.3(6)

Table S11 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ac. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C29	30.9(8)	28.8(8)	40.2(9)	3.5(7)	-4.7(7)	-7.7(7)
C30	27.0(7)	19.7(7)	54.8(11)	-7.9(7)	-9.3(7)	-3.2(6)
C31	28.7(7)	29.4(8)	40.9(9)	-18.0(7)	-1.0(6)	-2.5(6)
C32	25.8(7)	26.9(7)	26.6(8)	-9.3(6)	-1.4(6)	-3.5(6)

Table S12 Bond Lengths for 3ac.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C16	1.3473(17)	F3	C19	1.3540(17)
F2	C15	1.3504(17)	F4	C18	1.3516(18)
O1	N1	1.4435(15)	O4	N2	1.4492(15)
O1	C9	1.449(2)	O4	C24	1.4534(17)
N1	C7	1.4750(17)	N2	C22	1.4482(17)
N1	C12	1.4459(17)	N2	C26	1.4961(17)
C1	C2	1.395(2)	C17	C18	1.384(2)
C1	C6	1.393(2)	C17	C22	1.401(2)
C1	C7	1.5169(18)	C17	C23	1.499(2)
C2	C3	1.385(2)	C18	C19	1.374(2)
C3	C4	1.386(2)	C19	C20	1.376(2)
C4	C5	1.385(2)	C20	C21	1.388(2)
C5	C6	1.391(2)	C21	C22	1.389(2)
C7	C8	1.544(2)	C23	C24	1.518(2)
C8	C9	1.532(2)	C24	C25	1.534(2)
C9	C10	1.521(2)	C25	C26	1.550(2)
C10	C11	1.507(2)	C26	C27	1.5151(19)
C11	C12	1.400(2)	C27	C28	1.394(2)
C11	C16	1.383(2)	C27	C32	1.391(2)
C12	C13	1.385(2)	C28	C29	1.389(2)
C13	C14	1.387(2)	C29	C30	1.388(3)
C14	C15	1.377(2)	C30	C31	1.380(3)
C15	C16	1.379(2)	C31	C32	1.392(2)

Table S13 Bond Angles for 3ac.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	O1	C9	103.89(10)	N2	O4	C24	104.54(10)
O1	N1	C7	101.28(10)	O4	N2	C26	102.20(10)
O1	N1	C12	107.91(10)	C22	N2	O4	106.87(10)
C12	N1	C7	111.42(11)	C22	N2	C26	111.44(10)
C2	C1	C7	118.42(12)	C18	C17	C22	116.59(14)
C6	C1	C2	118.48(13)	C18	C17	C23	121.88(14)
C6	C1	C7	123.10(12)	C22	C17	C23	121.52(13)
C3	C2	C1	120.95(14)	F4	C18	C17	119.08(15)
C2	C3	C4	120.25(14)	F4	C18	C19	118.83(14)
C5	C4	C3	119.37(14)	C19	C18	C17	122.08(14)
C4	C5	C6	120.50(14)	F3	C19	C18	118.56(15)
C5	C6	C1	120.45(14)	F3	C19	C20	120.37(15)
N1	C7	C1	111.48(11)	C18	C19	C20	121.07(14)
N1	C7	C8	102.95(11)	C19	C20	C21	118.47(15)
C1	C7	C8	113.24(12)	C20	C21	C22	120.21(14)
C9	C8	C7	103.30(12)	C17	C22	N2	120.04(13)
O1	C9	C8	103.94(12)	C21	C22	N2	118.43(12)
O1	C9	C10	106.89(13)	C21	C22	C17	121.49(13)
C10	C9	C8	113.29(13)	C17	C23	C24	109.20(12)
C11	C10	C9	107.61(12)	O4	C24	C23	107.95(12)
C12	C11	C10	121.00(13)	O4	C24	C25	103.20(11)
C16	C11	C10	121.71(14)	C23	C24	C25	113.75(13)
C16	C11	C12	117.27(14)	C24	C25	C26	103.81(11)
C11	C12	N1	120.74(13)	N2	C26	C25	104.30(11)
C13	C12	N1	118.13(13)	N2	C26	C27	111.41(11)
C13	C12	C11	121.12(13)	C27	C26	C25	113.28(12)
C12	C13	C14	120.28(14)	C28	C27	C26	122.00(13)
C15	C14	C13	118.81(14)	C32	C27	C26	119.35(13)
F2	C15	C14	120.50(14)	C32	C27	C28	118.53(14)
F2	C15	C16	118.73(14)	C29	C28	C27	120.53(15)
C14	C15	C16	120.77(14)	C30	C29	C28	120.31(15)
F1	C16	C11	119.38(14)	C31	C30	C29	119.68(14)
F1	C16	C15	118.94(14)	C30	C31	C32	120.02(15)
C15	C16	C11	121.67(14)	C27	C32	C31	120.92(15)

Table S14 Torsion Angles for 3ac.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F2	C15	C16	F1	-1.0(2)	F3	C19	C20	C21	178.19(14)
F2	C15	C16	C11	-179.97(14)	F4	C18	C19	F3	0.3(2)
O1	N1	C7	C1	79.92(12)	F4	C18	C19	C20	-179.77(14)
O1	N1	C7	C8	-41.79(12)	O4	N2	C22	C17	-28.88(15)
O1	N1	C12	C11	24.33(16)	O4	N2	C22	C21	148.62(12)
O1	N1	C12	C13	-154.82(13)	O4	N2	C26	C25	33.38(12)
O1	C9	C10	C11	-48.73(16)	O4	N2	C26	C27	-89.16(12)
N1	O1	C9	C8	-38.13(13)	O4	C24	C25	C26	-19.67(14)
N1	O1	C9	C10	81.94(13)	N2	O4	C24	C23	-78.64(13)
N1	C7	C8	C9	18.56(14)	N2	O4	C24	C25	42.08(13)
N1	C12	C13	C14	177.13(14)	N2	C26	C27	C28	52.09(18)
C1	C2	C3	C4	0.4(2)	N2	C26	C27	C32	-131.83(13)
C1	C7	C8	C9	-101.95(13)	C17	C18	C19	F3	179.60(14)
C2	C1	C6	C5	0.0(2)	C17	C18	C19	C20	-0.4(2)
C2	C1	C7	N1	-175.42(12)	C17	C23	C24	O4	41.98(15)
C2	C1	C7	C8	-59.88(17)	C17	C23	C24	C25	-71.89(15)
C2	C3	C4	C5	-0.3(2)	C18	C17	C22	N2	174.30(13)
C3	C4	C5	C6	0.2(2)	C18	C17	C22	C21	-3.1(2)
C4	C5	C6	C1	0.0(2)	C18	C17	C23	C24	179.13(13)
C6	C1	C2	C3	-0.2(2)	C18	C19	C20	C21	-1.8(2)
C6	C1	C7	N1	4.24(19)	C19	C20	C21	C22	1.5(2)
C6	C1	C7	C8	119.78(15)	C20	C21	C22	N2	-176.42(13)
C7	N1	C12	C11	-86.01(15)	C20	C21	C22	C17	1.0(2)
C7	N1	C12	C13	94.84(15)	C22	N2	C26	C25	-80.44(13)
C7	C1	C2	C3	179.48(13)	C22	N2	C26	C27	157.02(12)
C7	C1	C6	C5	-179.64(13)	C22	C17	C18	F4	-177.84(12)
C7	C8	C9	O1	11.23(14)	C22	C17	C18	C19	2.8(2)
C7	C8	C9	C10	-104.42(14)	C22	C17	C23	C24	-2.17(19)
C8	C9	C10	C11	65.15(17)	C23	C17	C18	F4	0.9(2)
C9	O1	N1	C7	50.74(12)	C23	C17	C18	C19	-178.40(14)
C9	O1	N1	C12	-66.37(13)	C23	C17	C22	N2	-4.5(2)
C9	C10	C11	C12	7.1(2)	C23	C17	C22	C21	178.12(13)
C9	C10	C11	C16	-171.57(15)	C23	C24	C25	C26	97.01(14)
C10	C11	C12	N1	5.2(2)	C24	O4	N2	C22	69.38(12)
C10	C11	C12	C13	-175.64(14)	C24	O4	N2	C26	-47.78(12)
C10	C11	C16	F1	-2.0(2)	C24	C25	C26	N2	-8.31(14)
C10	C11	C16	C15	176.93(15)	C24	C25	C26	C27	112.99(13)

Table S14 Torsion Angles for 3ac.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C11	C12	C13	C14	-2.0(2)	C25	C26	C27	C28	-65.12(17)
C12	N1	C7	C1	-165.56(11)	C25	C26	C27	C32	110.95(15)
C12	N1	C7	C8	72.73(13)	C26	N2	C22	C17	81.99(15)
C12	C11	C16	F1	179.27(13)	C26	N2	C22	C21	-100.51(14)
C12	C11	C16	C15	-1.8(2)	C26	C27	C28	C29	175.81(14)
C12	C13	C14	C15	-0.5(2)	C26	C27	C32	C31	-175.76(13)
C13	C14	C15	F2	-178.87(15)	C27	C28	C29	C30	-0.4(2)
C13	C14	C15	C16	1.8(3)	C28	C27	C32	C31	0.5(2)
C14	C15	C16	F1	178.31(14)	C28	C29	C30	C31	0.9(2)
C14	C15	C16	C11	-0.6(3)	C29	C30	C31	C32	-0.8(2)
C16	C11	C12	N1	-176.01(13)	C30	C31	C32	C27	0.1(2)
C16	C11	C12	C13	3.1(2)	C32	C27	C28	C29	-0.3(2)

Table S15 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ac.

Atom	*x*	*y*	*z*	U(eq)
H2	7347.73	11941.97	6601.83	29
H3	5486.78	13805.36	6480.31	34
H4	3936.36	14092.43	7971.94	35
H5	4251.91	12487.87	9576.74	35
H6	6109.37	10611.82	9700.16	30
H7	9101.49	10035.6	8171.45	26
H8A	7303.45	9870.62	6577.44	37
H8B	8945.44	8939.24	6878.65	37
H9	6532.26	8260.53	7304.82	38
H10A	8090.57	6321.48	8268.94	39
H10B	8995.82	6806.52	7254.54	39
H13	10424.2	8604.23	10459.17	35
H14	12600.95	6942.22	10850.4	39
H20	12074.54	7019.91	6259.87	35
H21	10474.25	8923.26	5270.11	29
H23A	8304.06	6686.05	2872.71	34
H23B	9519.44	6965.06	2042.46	34
H24	7492.08	8674.6	1431.61	31
H25A	6469.15	8259.38	3497.08	34
H25B	5761.3	9523.29	2559.03	34
H26	7228.54	9319.52	4559.14	26
H28	7001.53	11510.78	1860.31	37
H29	5577.15	13587.4	1496.61	43
H30	4116.89	14383.54	2892.27	42
H31	4137.57	13107.9	4672.29	40
H32	5569.8	11030.6	5043.51	32