Electronic Supplementary Information

Pd-Catalyzed Sequential Intramolecular Annulation/ Intermolecular [3+2] Cycloaddition of 5-Allenyloxazolidine-2,4-diones with Dipoles: Synthesis of Spiroheterocycles

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General Information

All reactions were performed under Argon atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Visualization on TLC was achieved by use of UV light (254 nm), iodine or basic $KMnO_4$ indicator. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 500 MHz NMR instrument (referenced internally to Me_4Si). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. HRMS analyses were carried out on a Thermo Q-Exactive high resolution mass spectrometer (Thermo Scientific, Waltham, MA, USA) apparatus. The type of mass analyzer used for HRMS measurement is TOF. Data were analyzed using instrument-supplied software Xcalibur Qual Browser. Melting points were determined by an X-4 digital micro melting point apparatus. X-ray crystallographic data were collected using a Bruker D8 venture. In addition, unless noted otherwise, in the reactions that need heating, the heat source is oil bath.

Preparation of Substrates 1, 2, 4 and 6

The nitrile oxides **1**,[1] 5-allenyloxazolidine-2,4-diones **2**,[2] hydrazonyl halides **4**[3] and azomethine imines **6**[4] were synthesized using known literature procedures.

General Procedure for Preparation of Product 3

Under argon atmosphere, an oven-dried 10 mL of Schlenk tube was charged with nitrile oxides **1** (0.1 mmol), 5-allenyloxazolidine-2,4-diones **2** (0.15 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%, 2.6 mg), XantPhos (5 mol%, 2.9 mg) in 1 mL of over-dry $CHCl_3$ at 60 ℃. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **3** (petroleum ether / EtOAc as the eluent).

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(1) (a) Pan, T.; Gao, X.; Yang, S.; Wang, L.; Hu, Y.; Liu, M.; Wang, W.; Wu, Y.; Zheng, B.; Guo, H. *Org. Lett*. **2021**, *23*, 5750–5754. (b) Zhang, L.; Liu, H.; Qiao, G.; Hou, Z.; Liu, Y.; Xiao, Y.; Guo, H. *J. Am. Chem. Soc.* **2015**, *137*, 4316–4319.

(2) Dong, Y.; Liu, J.; Li, K.; Han, S.; Liang, B.; Yang, F.; Yu, S.; Wu, Y.; Zhang, C.; Guo, H. *Org. Lett.* **2023**, *25*, 6328–6333

(3) (a) Bazian, A.; Taheri, M.; Alavi, H. *Russ. J. Gen. Chem.* **2014**, *84*, 586–592. (b) Garve, L. K. B.; Petzold, M.; Jones, P. G.; Werz, D. B. *Org. Lett.* **2016**, 18, 564–567

(4) (a) Wang, T.; Shao, A.; Feng, H.; Yang, S.; Gao, M.; Tian, J.; Lei, A. *Tetrahedron* **2015**, *71*, 4473–4477. (b) Hashimoto, T.; Maeda, Y.; Omote, M.; Nakatsu, H.; Maruoka, K. *J. Am. Chem. Soc*. **2010**, *132*, 4076–4077.

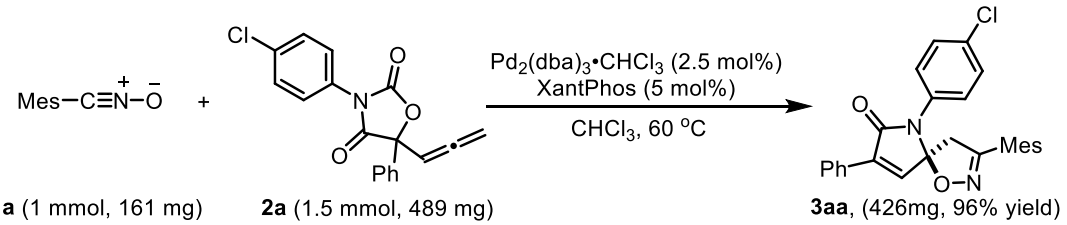
General Procedure for Preparation of Product 5

Under argon atmosphere, an oven-dried 10 mL of Schlenk tube was charged with hydrazonyl halides **4** (0.1 mmol), 5-allenyloxazolidine-2,4-diones **2a** (0.15 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (5 mol%, 5.2 mg), XantPhos (10 mol%, 5.8 mg) and Et_3N in (0.1 mmol) in1 mL of over-dry CH_2Cl_2 at rt. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **5** (petroleum ether / EtOAc as the eluent).

General Procedure for Preparation of Product 7

Under argon atmosphere, an oven-dried 10 mL of Schlenk tube was charged with azomethine imines **6** (0.1 mmol), 5-allenyloxazolidine-2,4-diones **2** (0.15 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%, 2.6 mg), XantPhos (5 mol%, 2.9 mg) in 1 mL of over-dry $CHCl_3$ at rt. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography to afford the product **7** (petroleum ether / EtOAc as the eluent).

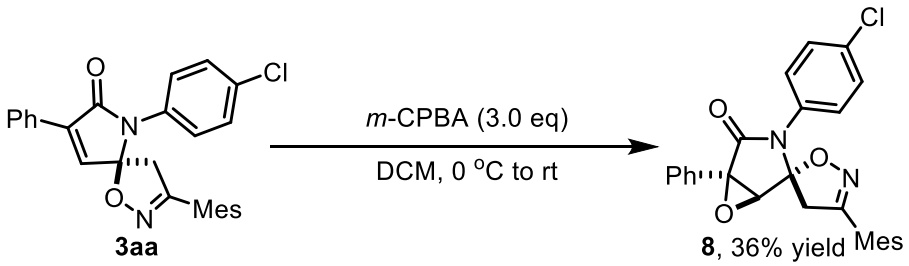
Scale-up Synthesis of the Product 3aa



1a (1 mmol, 161 mg) **2a** (1.5 mmol, 489 mg) **3aa**, (426mg, 96% yield)

Under argon atmosphere, an oven-dried 50 mL of Schlenk tube was charged with nitrile oxide **1a** (1 mmol, 161 mg), 5-allenyloxazolidine-2,4-diones **2a** (1.5 mmol, 489 mg), $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mmol%, 26 mg), XantPhos (5 mmol%, 29 mg) in 10 mL of over-dry $CHCl_3$ at 60 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc : PE = 1:15) to afford the corresponding products **3aa** (426 mg, 96% yield).

Further Transformations of the Product 3aa

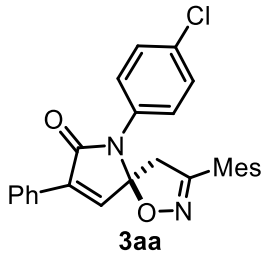


3aa **8**, 36% yield

To a dry tube equipped with a stirring bar added **3aa** (44.3 mg, 0.1 mmol) and anhydrous DCM (1 mL). Dissolved *m*-CPBA (52.0 mg, 0.3 mmol) in 2 mL of DCM and added it drop by drop to the dichloride solution of **3aa** at 0 ℃. The reaction mixture was stirred at 0 ℃ for 30 min, and then transferred it to room temperature for further reaction. Upon completion of the reaction (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column (EtOAc : PE = 1:15) to afford the product **8** (16.4 mg, 36% yield).

Characterization Data of the All Products

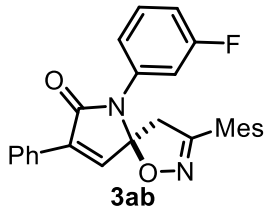
6-(4-chlorophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3aa)



3aa

Prepared according to the general procedure (reaction time: 24 h) as described above in 93% yield (41.2 mg). It was purified by flash chromatography (EtOAc : PE=1:8) to afford a yellow solid. Melting point: 190 – 192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.41 (m, 5H), 7.22 (s, 1H), 6.83 (s, 2H), 3.48 (d, *J* = 18.9 Hz, 1H), 3.21 (d, *J* = 18.9 Hz, 1H), 2.26 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 157.2, 138.4, 136.3, 135.5, 135.4, 133.2, 132.1, 128.79, 128.76, 128.7, 128.6, 127.65, 127.64, 126.7, 123.6, 98.5, 42.5, 20.0, 18.3; IR (film) ν_{max} 2922, 1713, 1493, 1378, 1332, 1263, 1192, 1089, 1017, 886, 791, 734, 694, 648, 512 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}ClN_2O_2^+$ $[M+H]^+$ 443.1521, found 443.1519.

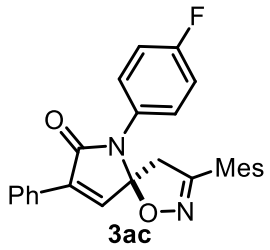
6-(3-fluorophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ab)



3ab

Prepared according to the general procedure (reaction time: 24 h) as described above in 95% yield (40.6 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 186 – 188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.48 – 7.29 (m, 6H), 7.21 (s, 1H), 7.08 (tdd, *J* = 8.3, 2.6, 1.1 Hz, 1H), 6.83 (s, 2H), 3.46 (d, *J* = 19.0 Hz, 1H), 3.23 (d, *J* = 19.0 Hz, 1H), 2.25 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 162.05 (d, *J* = 247.8 Hz), 157.3, 138.4, 136.4, 135.4, 135.2, 135.1, 135.0, 129.7, 129.6, 128.74, 128.72, 127.7, 127.6, 126.7, 123.6, 122.65 (d, *J* = 3.3 Hz), 114.26 (dd, *J* = 31.7, 22.0 Hz), 98.6, 42.4, 20.0, 18.3; IR (film) ν_{max} 2923, 1717, 1610, 1593, 1492, 1451, 1377, 1333, 1248, 1202, 854, 834, 787, 750, 691 cm^{-1};HRMS (ESI) calcd for $C_{27}H_{24}FN_2O_2^+$ $[M+H]^+$ 427.1816, found 427.1814.

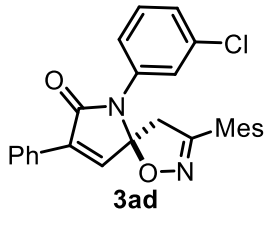
6-(4-fluorophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ac)



3ac

Prepared according to the general procedure (reaction time: 24 h) as described above in 85% yield (36.2 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 192 – 194 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.55 – 7.47 (m, 2H), 7.46 – 7.38 (m, 3H), 7.21 (s, 1H), 7.19 – 7.10 (m, 2H), 6.81 (s, 2H), 3.48 (d, *J* = 18.9 Hz, 1H), 3.20 (d, *J* = 19.0 Hz, 1H), 2.24 (s, 3H), 1.87 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 161.37 (d, *J* = 248.6 Hz), 157.1, 138.4, 136.3, 135.4, 129.6, 129.5, 129.4, 129.3, 128.9, 128.7, 127.63, 127.61, 126.7, 123.6, 115.51 (d, *J* = 22.6 Hz), 98.4, 42.5, 20.0, 18.2; IR (film) ν_{max} 2922, 1754, 1715, 1510, 1493, 1450, 1383, 1333, 1229, 1196, 888, 819, 788, 694, 521, 422 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}FN_2O_2^+$ $[M+H]^+$ 427.1816, found 427.1814.

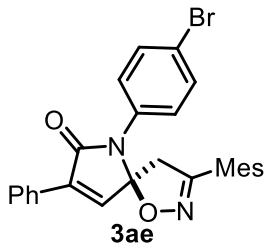
6-(3-chlorophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ad)



3ad

Prepared according to the general procedure (reaction time: 24 h) as described above in 89% yield (39.5 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a light yellow solid. Melting point: 193 – 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.58 (t, *J* = 1.9 Hz, 1H), 7.49 – 7.31 (m, 6H), 7.21 (s, 1H), 6.82 (s, 2H), 3.47 (d, *J* = 18.9 Hz, 1H), 3.21 (d, *J* = 19.0 Hz, 1H), 2.25 (s, 3H), 1.93 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 157.3, 138.4, 136.4, 135.5, 135.2, 134.8, 134.1, 129.5, 128.7, 128.7, 127.7, 127.6, 127.3, 127.2, 126.7, 125.3, 123.6, 98.5, 42.4, 20.0, 18.3; IR (film) ν_{max} 2923, 1717, 1593, 1480, 1375, 1332, 1194, 1133, 1044, 887, 851, 809, 788, 742, 694 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}ClN_2O_2^+$ $[M+H]^+$ 443.1521, found 443.1519.

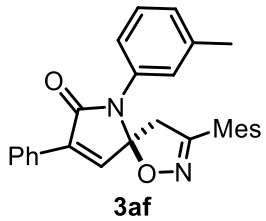
6-(4-bromophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ae)



3ae

Prepared according to the general procedure (reaction time: 24 h) as described above in 90% yield (44.1 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a orange solid. Melting point: 196 – 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.61 – 7.54 (m, 2H), 7.47 – 7.38 (m, 5H), 7.21 (s, 1H), 6.82 (s, 2H), 3.47 (d, *J* = 19.0 Hz, 1H), 3.19 (d, *J* = 19.0 Hz, 1H), 2.25 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 157.2, 138.4, 136.3, 135.4, 135.3, 132.6, 131.7, 128.9, 128.8, 128.7, 127.64, 127.63, 126.7, 123.6, 121.2, 98.4, 42.5, 20.0, 18.2; IR (film) ν_{max} 2923, 1715, 1491, 1449, 1378, 1333, 1195, 1099, 1070, 1014, 886, 851, 792 , 694, 648 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{24}BrN_2O_2^+$ $[M+H]^+$ 487.1016, found 487.1013.

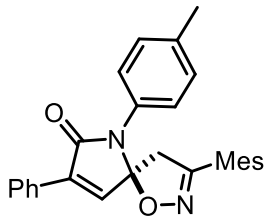
3-mesityl-8-phenyl-6-(*m*-tolyl)-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3af)



3af

Prepared according to the general procedure (reaction time: 24 h) as described above in 91% yield (38.3 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 193 – 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.47 – 7.37 (m, 3H), 7.36 – 7.27 (m, 3H), 7.20 (s, 1H), 7.19 – 7.16 (m, 1H), 6.80 (s, 2H), 3.45 (d, *J* = 18.9 Hz, 1H), 3.24 (d, *J* = 18.9 Hz, 1H), 2.36 (s, 3H), 2.24 (s, 3H), 1.86 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 156.9, 138.6, 138.2, 136.3, 135.5, 135.4, 133.3, 129.0, 128.5, 128.4, 128.1, 128.0, 127.6, 127.5, 126.7, 124.6, 123.8, 98.5, 42.3, 20.3, 20.0, 18.2; IR (film) ν_{max} 2962, 2921, 1713, 1492, 1378, 1204, 1091, 1019, 888, 854, 790, 695, 420 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_2^+$ $[M+H]^+$ 423.2067, found 423.2065.

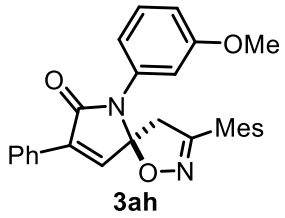
3-mesityl-8-phenyl-6-(*p*-tolyl)-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ag)



3ag

Prepared according to the general procedure (reaction time: 24 h) as described above in 99% yield (42.0 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a brown solid. Melting point: 160 – 162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.44 – 7.36 (m, 5H), 7.25 (d, *J* = 3.1 Hz, 2H), 7.20 (s, 1H), 6.79 (s, 2H), 3.45 (d, *J* = 18.9 Hz, 1H), 3.23 (d, *J* = 18.9 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 156.9, 138.2, 137.4, 136.2, 135.6, 135.5, 130.7, 129.2, 129.1, 128.5, 127.6, 127.5, 127.4, 126.7, 123.8, 98.5, 42.3, 20.1, 20.0, 18.1; IR (film) ν_{max} 2961, 1709, 1513, 1382, 1262, 1196, 1130, 1102, 1031, 887, 850, 803, 786, 734, 695, 514 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_2^+$ $[M+H]^+$ 423.2067, found 423.2065.

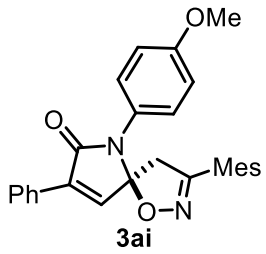
3-mesityl-6-(3-methoxyphenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ah)



3ah

Prepared according to the general procedure (reaction time: 24 h) as described above in 86% yield (37.9 mg). It was purified by flash chromatography (EtOAc : PE = 1:6) to afford a light yellow solid. Melting point: 193 – 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.46 – 7.38 (m, 3H), 7.37 – 7.31 (m, 1H), 7.20 (s, 1H), 7.12 – 7.06 (m, 2H), 6.96 – 6.89 (m, 1H), 6.81 (s, 2H), 3.80 (s, 3H), 3.45 (d, *J* = 18.9 Hz, 1H), 3.27 (d, *J* = 18.9 Hz, 1H), 2.24 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 159.5, 157.1, 138.3, 136.3, 135.6, 135.4, 134.5, 129.2, 129.0, 128.6, 127.6, 127.5, 126.7, 123.8, 119.6, 113.6, 112.6, 98.6, 54.4, 42.3, 20.0, 18.2; IR (film) ν_{max} 2924, 1712, 1603, 1492, 1453, 1379, 1332, 1286, 1254, 1209, 1043, 888,854, 828, 786, 693 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3^+$ $[M+H]^+$ 439.2016, found 439.2016.

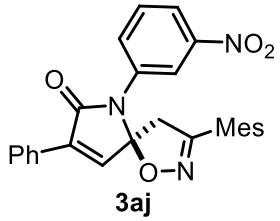
3-mesityl-6-(4-methoxyphenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ai)



3ai

Prepared according to the general procedure (reaction time: 24 h) as described above in 98% yield (42.9 mg). It was purified by flash chromatography (EtOAc : PE = 1:6) to afford a yellow solid. Melting point: 218 – 220 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.47 – 7.36 (m, 5H), 7.20 (s, 1H), 7.00 – 6.93 (m, 2H), 6.80 (s, 2H), 3.82 (s, 3H), 3.47 (d, *J* = 18.9 Hz, 1H), 3.24 (d, *J* = 18.9 Hz, 1H), 2.24 (s, 3H), 1.86 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 158.6, 156.8, 138.2, 136.1, 135.6, 135.5, 129.11, 129.09, 128.5, 127.6, 127.5, 126.7, 125.8, 123.8, 113.9, 98.4, 54.6, 42.4, 20.0, 18.2; IR (film) ν_{max} 2923, 1710, 1512, 1385, 1250, 1098, 1029, 887, 850, 804, 788, 696 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3^+$ $[M+H]^+$ 439.2016, found 439.2015.

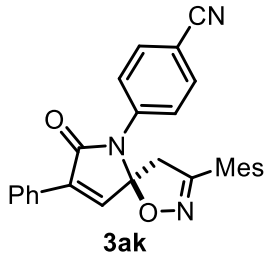
3-mesityl-6-(3-nitrophenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3aj)



3aj

Prepared according to the general procedure (reaction time: 18 h) as described above in 98% yield (40.5 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 179 – 181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (t, *J* = 2.2 Hz, 1H), 8.23 (ddd, *J* = 8.4, 2.3, 1.0 Hz, 1H), 8.05 – 7.91 (m, 3H), 7.65 (t, *J* = 8.2 Hz, 1H), 7.53 – 7.38 (m, 3H), 7.26 (d, *J* = 1.9 Hz, 1H), 6.82 (s, 2H), 3.52 (d, *J* = 19.1 Hz, 1H), 3.22 (d, *J* = 19.1 Hz, 1H), 2.24 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 157.6, 147.8, 138.6, 136.6, 135.2, 135.1, 135.0, 132.7, 129.4, 128.9, 128.4, 127.7, 126.7, 123.4, 121.9, 121.7, 98.6, 42.7, 20.0, 18.4; HRMS (ESI) calcd for $C_{27}H_{24}N_3O_4^+$ $[M+H]^+$ 454.1761, found 454.1752.

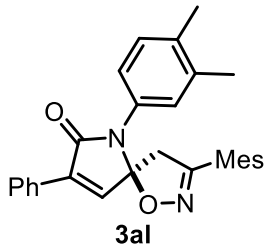
4-(3-mesityl-7-oxo-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-6-yl)benzonitrile (3ak)



3ak

Prepared according to the general procedure (reaction time: 18h) as described above in 78% yield (33.9 mg). It was purified by flash chromatography (EtOAc : PE = 1:7) to afford a white solid. Melting point: 181 – 183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.80 – 7.67 (m, 4H), 7.51 – 7.39 (m, 3H), 7.24 (s, 1H), 6.85 (s, 2H), 3.47 (d, *J* = 19.1 Hz, 1H), 3.21 (d, *J* = 19.1 Hz, 1H), 2.27 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 157.8, 138.7, 138.3, 136.7, 135.3, 135.1, 132.3, 128.9, 128.4, 127.8, 127.7, 126.7, 126.6, 123.4, 117.2, 110.2, 98.6, 42.7, 20.0, 18.5; HRMS (ESI) calcd for $C_{28}H_{24}N_3O_2^+$ $[M+H]^+$ 434.1863, found 434.1854.

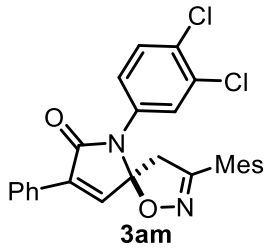
6-(3,4-dimethylphenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3al)



3al

Prepared according to the general procedure (reaction time: 24 h) as described above in 93% yield (40.6 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 186 – 188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.46 – 7.35 (m, 3H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.80 (s, 2H), 3.45 (d, *J* = 18.9 Hz, 1H), 3.24 (d, *J* = 18.9 Hz, 1H), 2.26 (d, *J* = 5.0 Hz, 6H), 2.24 (s, 3H), 1.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 156.8, 138.2, 137.0, 136.1, 136.0, 135.6, 135.5, 130.8, 129.7, 129.1, 128.52, 128.49, 127.6, 127.5, 126.7, 125.0, 123.9, 98.5, 42.2, 20.0, 18.7, 18.4, 18.1; IR (film) ν_{max} 2922, 1710, 1503, 1450, 1378, 1261, 1093, 1020, 890, 837, 787, 735, 695, 652 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_2O_2^+$ $[M+H]^+$ 437.2224, found 437.2221.

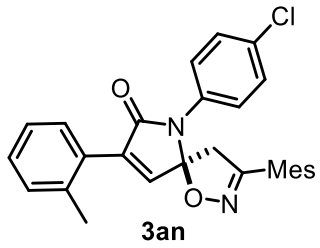
6-(3,4-dichlorophenyl)-3-mesityl-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3am)



3am

Prepared according to the general procedure (reaction time: 48 h) as described above in 65% yield (31.2 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a orange solid. Melting point: 236 – 238 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.21 (s, 1H), 6.84 (s, 2H), 3.48 (d, *J* = 19.0 Hz, 1H), 3.20 (d, *J* = 19.0 Hz, 1H), 2.26 (s, 3H), 1.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 157.4, 138.5, 136.5, 135.4, 135.2, 133.1, 132.5, 131.3, 130.1, 128.8, 128.6, 128.5, 127.7, 126.7, 126.2, 123.5, 98.5, 42.5, 20.0, 18.3; IR (film) ν_{max} 2923, 1715, 1476, 1372, 1332, 1262, 1192, 1134 , 1032, 887, 852, 814, 787, 747, 695 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}Cl_2N_2O_2^+$ $[M+H]^+$ 477.1131, found 477.1130.

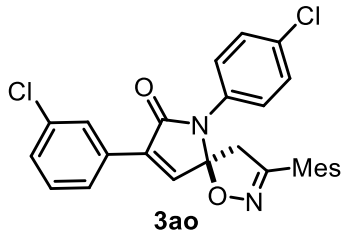
6-(4-chlorophenyl)-3-mesityl-8-(*o*-tolyl)-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3an)



3an

Prepared according to the general procedure (reaction time: 24 h) as described above in 97% yield (44.5 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a yellow solid. Melting point: 196 – 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.47 – 7.40 (m, 3H), 7.34 – 7.25 (m, 3H), 7.02 (s, 1H), 6.83 (s, 2H), 3.47 (d, *J* = 18.9 Hz, 1H), 3.23 (d, *J* = 18.9 Hz, 1H), 2.43 (s, 3H), 2.25 (s, 3H), 1.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 157.3, 139.8, 138.4, 137.4, 135.9, 135.4, 133.0, 132.2, 129.6, 128.9, 128.7, 128.5, 128.2, 127.6, 124.8, 123.6, 98.8, 42.5, 20.0, 19.7, 18.3; IR (film) ν_{max} 2958, 2924, 1715, 1493, 1377, 1261, 1090, 1017, 850, 815, 788, 734 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_2O_2^+$ $[M+H]^+$ 457.1677, found 457.1675.

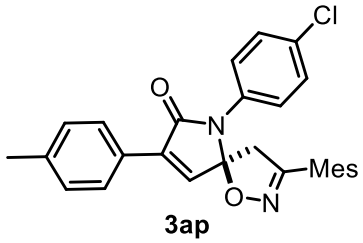
8-(3-chlorophenyl)-6-(4-chlorophenyl)-3-mesityl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ao)



3ao

Prepared according to the general procedure (reaction time: 24 h) as described above in 99% yield (47.1 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a white solid. Melting point: 194 – 196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.84 (dt, *J* = 6.9, 1.8 Hz, 1H), 7.48 – 7.42 (m, 4H), 7.40 – 7.33 (m, 2H), 7.24 (s, 1H), 6.82 (s, 2H), 3.48 (d, *J* = 19.0 Hz, 1H), 3.20 (d, *J* = 18.9 Hz, 1H), 2.25 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 157.2, 138.5, 137.3, 135.4, 134.1, 133.6, 133.3, 131.8, 130.4, 128.9, 128.8, 128.7, 128.6, 127.6, 126.7, 124.8, 123.4, 98.3, 42.5, 20.0, 18.2; IR (film) ν_{max} 2922, 1712, 1493, 1379, 1331, 1194, 1090, 885, 854, 821, 792, 735, 719 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}Cl_2N_2O_2^+$ $[M+H]^+$ 477.1131, found 477.1127.

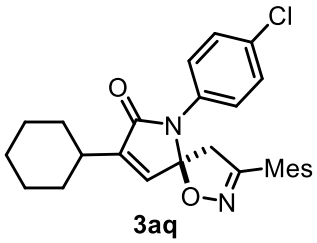
6-(4-chlorophenyl)-3-mesityl-8-(*p*-tolyl)-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ap)



3ap

Prepared according to the general procedure (reaction time: 24 h) as described above in 91% yield (41.1 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a orange solid. Melting point: 180 – 182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) 1H NMR (500 MHz, Chloroform-d) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 7.25 (d, *J* = 1.6 Hz, 2H), 7.16 (s, 1H), 6.82 (s, 2H), 3.45 (d, *J* = 19.0 Hz, 1H), 3.18 (d, *J* = 19.0 Hz, 1H), 2.39 (s, 3H), 2.25 (s, 3H), 1.89 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 157.2, 138.9, 138.4, 135.4, 135.3, 135.2, 133.1, 132.1, 128.71, 128.66, 128.4, 127.6, 126.6, 126.0, 123.6, 98.5, 42.5, 20.4, 20.0, 18.2; IR (film) ν_{max} 2922, 1714, 1493, 1378, 1332, 1262, 1184, 1091, 1018, 886, 848, 818, 762, 734 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClN_2O_2^+$ $[M+H]^+$ 457.1677, found 457.1675.

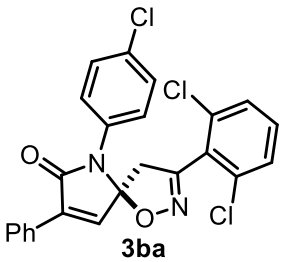
6-(4-chlorophenyl)-8-cyclohexyl-3-mesityl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3aq)



3aq

Prepared according to the general procedure (reaction time: 48 h) as described above in 56% yield (25.2 mg). It was purified by flash chromatography (EtOAc : PE = 1:12) to afford a oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 4H), 6.81 (s, 2H), 6.63 (d, *J* = 1.4 Hz, 1H), 3.34 (d, *J* = 18.9 Hz, 1H), 3.11 (d, *J* = 18.9 Hz, 1H), 2.48 (ttd, *J* = 11.6, 3.4, 1.4 Hz, 1H), 2.24 (s, 3H), 2.07 – 1.99 (m, 2H), 1.88 (s, 6H), 1.82 (dt, *J* = 12.8, 3.5 Hz, 2H), 1.40 (qt, *J* = 12.8, 3.4 Hz, 2H), 1.26 (dddt, *J* = 19.9, 12.8, 10.1, 3.3 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 157.2, 144.3, 138.3, 135.4, 135.3, 132.8, 132.3, 128.6, 128.3, 127.6, 123.8, 99.2, 42.3, 33.7, 30.6, 30.5, 25.1, 25.0, 20.0, 18.3; HRMS (ESI) calcd for $C_{27}H_{30}ClN_2O_2^+$ $[M+H]^+$ 449.1990, found 449.1989.

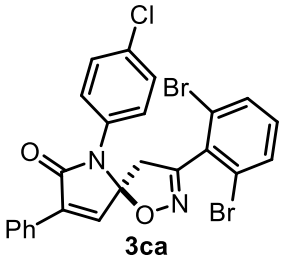
6-(4-chlorophenyl)-3-(2,6-dichlorophenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ba)



3ba

Prepared according to the general procedure (reaction time: 48 h) as described above in 77% yield (36.1 mg). It was purified by flash chromatography (EtOAc : PE=1:8) to afford a brown solid. Melting point: 199 – 201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.88 (m, 2H), 7.52 – 7.46 (m, 2H), 7.46 – 7.39 (m, 5H), 7.33 – 7.23 (m, 4H), 3.58 (d, *J* = 18.7 Hz, 1H), 3.34 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 153.6, 136.0, 135.4, 133.9, 132.8, 132.0, 130.5, 128.8, 128.7, 128.6, 128.3, 127.7, 127.2, 126.8, 126.3, 99.5, 40.5; IR (film) ν_{max} 2923, 1715, 1493, 1377, 1330, 1264, 1194, 1089, 895, 785, 732, 701, 647 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}Cl_3N_2O_2^+$ $[M+H]^+$ 469.0272, found 469.0268.

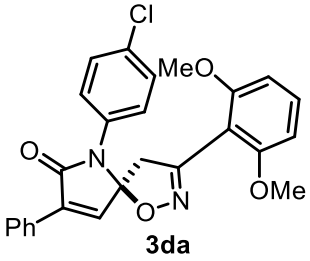
6-(4-chlorophenyl)-3-(2,6-dibromophenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ca)



3ca

Prepared according to the general procedure (reaction time: 48 h) as described above in 90% yield (50.0 mg). It was purified by flash chromatography (EtOAc : PE=1:8) to afford a brown solid. Melting point: 205 – 207 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.56 – 7.49 (m, 4H), 7.47 – 7.38 (m, 5H), 7.26 (s, 1H), 7.13 (t, *J* = 8.1 Hz, 1H), 3.54 (d, *J* = 18.6 Hz, 1H), 3.39 (d, *J* = 18.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 156.5, 136.2, 135.1, 132.8, 132.0, 131.2, 130.9, 129.9, 128.8, 128.7, 128.6, 127.7, 126.8, 122.7, 99.7, 40.0; IR (film) ν_{max} 2924, 1717, 1493, 1381, 1260, 1091, 1016, 794, 729, 695 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}Br_2ClN_2O_2^+$ $[M+H]^+$ 556.9262, found 556.9260.

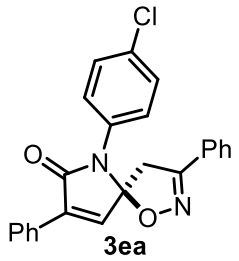
6-(4-chlorophenyl)-3-(2,6-dimethoxyphenyl)-8-phenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3da)



3da

Prepared according to the general procedure (reaction time: 48 h) as described above in 78% yield (36.0 mg). It was purified by flash chromatography (EtOAc : PE = 1:5) to afford a white solid. Melting point: 202 – 204 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 – 7.35 (m, 5H), 7.28 – 7.22 (m, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 3.67 (s, 6H), 3.63 (s, 1H), 3.28 (d, *J* = 18.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 157.5, 152.6, 136.9, 135.3, 132.5, 132.0, 130.5, 129.1, 128.5, 128.2, 127.7, 127.6, 126.7, 105.0, 102.8, 98.4, 54.8, 42.0; IR (film) ν_{max} 2932, 1712, 1593, 1493, 1473, 1376, 1256, 1112, 1017, 788, 734 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{22}ClN_2O_4^+$ $[M+H]^+$ 461.1262, found 461.1260.

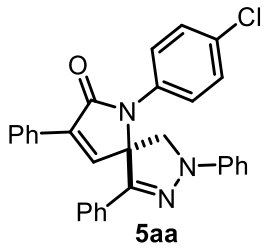
6-(4-chlorophenyl)-3,8-diphenyl-1-oxa-2,6-diazaspiro[4.4]nona-2,8-dien-7-one (3ea)



3ea

Prepared according to the general procedure (reaction time: 48 h) as described above in 79% yield (31.5 mg). It was purified by flash chromatography (EtOAc : PE = 1:5) to afford a yellow solid. Melting point: 170 – 172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.57 – 7.49 (m, 2H), 7.48 – 7.31 (m, 10H), 7.20 (s, 1H), 3.66 (d, *J* = 18.0 Hz, 1H), 3.37 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 156.5, 136.1, 135.6, 132.5, 132.1, 129.8, 128.8, 128.74, 128.6, 127.9, 127.7, 127.3, 127.2, 126.7, 125.6, 99.2, 38.8; HRMS (ESI) calcd for $C_{24}H_{18}ClN_2O_2^+$ $[M+H]^+$ 401.1051, found 401.1046.

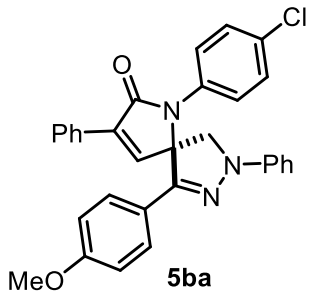
1-(4-chlorophenyl)-3,6,8-triphenyl-1,7,8-triazaspiro[4.4]nona-3,6-dien-2-one (5aa)



5aa

Prepared according to the general procedure (reaction time: 12 h) as described above in 75% yield (35.9 mg). It was purified by flash chromatography (EtOAc : PE = 1:15) to afford a yellow solid. Melting point: 58 – 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.57 – 7.51 (m, 2H), 7.40 – 7.34 (m, 3H), 7.34 – 7.25 (m, 5H), 7.22 – 7.16 (m, 6H), 7.12 (s, 1H), 6.89 (tt, *J* = 6.9, 1.6 Hz, 1H), 3.64 (d, *J* = 18.0 Hz, 1H), 3.42 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 146.2, 142.3, 139.3, 135.7, 132.8, 131.9, 130.5, 128.9, 128.6, 128.5, 128.31, 128.26, 127.70, 127.67, 126.59, 126.55, 124.6, 120.9, 114.8, 86.2, 41.4; IR (film) ν_{max} 1706, 1493, 1275, 1260, 764, 750, 713, 691, 417 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{23}ClN_3O^+$ $[M+H]^+$ 476.1524, found 476.1518.

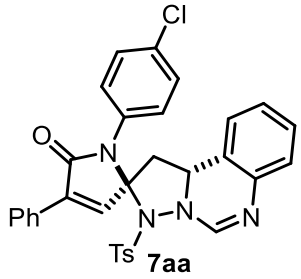
1-(4-chlorophenyl)-6-(4-methoxyphenyl)-3,8-diphenyl-1,7,8-triazaspiro[4.4]nona-3,6-dien-2-one (5ba)



5ba

Prepared according to the general procedure (reaction time: 12 h) as described above in 92% yield (46.4 mg). It was purified by flash chromatography (EtOAc : PE = 1:8) to afford a yellow solid. Melting point: 70 – 72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.6, 2.2 Hz, 2H), 7.53 (dd, *J* = 8.9, 2.2 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.35 – 7.29 (m, 2H), 7.26 – 7.19 (m, 6H), 7.15 (d, *J* = 2.1 Hz, 1H), 6.94 – 6.86 (m, 3H), 3.81 (s, 3H), 3.64 (dd, *J* = 18.0, 2.2 Hz, 1H), 3.43 (dd, *J* = 18.0, 2.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 159.6, 146.2, 142.5, 139.5, 135.6, 132.9, 131.8, 129.0, 128.54, 128.47, 128.2, 127.7, 126.6, 126.5, 126.1, 123.2, 120.6, 114.7, 113.1, 86.1, 54.3, 41.6; IR (film) ν_{max} 2171, 1978, 1275, 1261, 764, 749, 696, 529, 422, 411 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{27}ClN_3O^+$ $[M+H]^+$ 506.1630, found 581.1625.

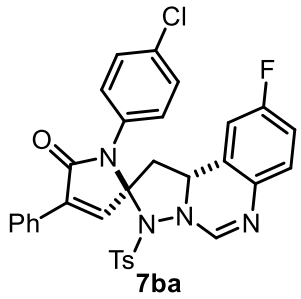
1'-(4-chlorophenyl)-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro[pyrazolo[1,5-*c*]quina-zoline-2,2'-pyrrol]-5'(1'*H*)-one (7aa)



7aa

Prepared according to the general procedure (reaction time: 24 h) as described above in 93% yield (54.0 mg). It was purified by flash chromatography (EtOAc : PE = 1:3) to afford a red-brown solid. Melting point: 146 – 148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.94 (m, 2H), 7.85 – 7.78 (m, 2H), 7.54 – 7.42 (m, 5H), 7.38 – 7.32 (m, 5H), 7.27 (td, *J* = 7.6, 1.4 Hz, 1H), 7.18 – 7.07 (m, 2H), 6.93 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.31 (s, 1H), 4.73 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.87 (t, *J* = 12.5 Hz, 1H), 2.47 (s, 3H), 2.44 (dd, *J* = 12.7, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$)δ 168.5, 151.6, 145.8, 137.6, 136.3, 135.7, 135.3, 134.5, 132.4, 131.5, 130.1, 130.0, 129.9, 129.8, 129.7, 128.9, 128.7, 127.6, 127.0, 126.8, 126.2, 122.2, 84.2, 58.0, 43.6, 21.8; IR (film) ν_{max} 2923, 1711, 1493, 1378, 1260, 1163, 1121, 1090, 1032, 1009, 788, 736, 683, 567 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{26}ClN_4O_3S^+$ $[M+H]^+$ 581.1409, found 581.1405.

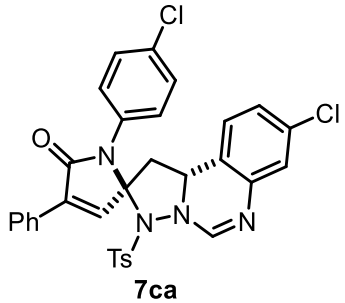
1'-(4-chlorophenyl)-9-fluoro-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro [pyrazolo[1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ba)



7ba

Prepared according to the general procedure (reaction time: 30 h) as described above in 98% yield (59.0 mg). It was purified by flash chromatography (EtOAc : PE = 1:3) to afford an orange solid**.** Melting point: 193 – 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.82 – 7.78 (m, 2H), 7.52 – 7.40 (m, 5H), 7.34 (ddd, *J* = 8.9, 4.5, 2.0 Hz, 5H), 7.10 (dd, *J* = 8.7, 5.2 Hz, 1H), 6.94 (td, *J* = 8.4, 2.8 Hz, 1H), 6.65 (dd, *J* = 8.1, 2.8 Hz, 1H), 6.26 (s, 1H), 4.69 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.85 (t, *J* = 12.5 Hz, 1H), 2.47 (s, 3H), 2.44 (t, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 160.8, 158.8, 149.77, 149.75, 144.9, 135.3, 134.5, 134.3, 133.3, 133.0, 132.9, 131.3, 130.5, 129.1, 129.0, 128.8, 128.7, 127.8, 127.7, 127.6, 127.5, 126.6, 123.0, 122.9, 115.5, 115.3, 112.2, 112.0, 83.1, 56.8, 42.3, 20.8; IR (film) ν_{max} 2924, 1687, 1494, 1378, 1165, 1122, 1091, 1033, 1010, 815 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{25}ClFN_4O_3S^+$ $[M+H]^+$ 599.1314, found 599.1310.

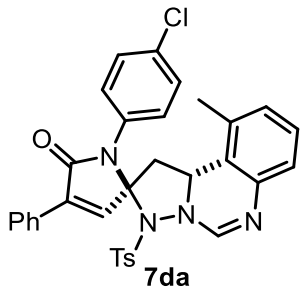
8-chloro-1'-(4-chlorophenyl)-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro[pyrazolo[1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ca)



7ca

Prepared according to the general procedure (reaction time: 24 h) as described above in 96% yield (59.0 mg). It was purified by flash chromatography (EtOAc : PE = 1:3) to afford an orange solid. Melting point: 158 – 160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.84 – 7.74 (m, 2H), 7.49 – 7.41 (m, 5H), 7.37 – 7.30 (m, 5H), 7.16 – 7.02 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.28 (s, 1H), 4.73 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.82 (t, *J* = 12.5 Hz, 1H), 2.46 (s, 3H), 2.44 (t, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 151.3, 145.0, 135.3, 134.5, 134.3, 134.3, 133.1, 131.3, 130.4, 129.2, 129.1, 128.8, 128.7, 127.8, 127.7, 126.6, 126.2, 125.9, 119.5, 83.13, 56.6, 42.6, 20.8; IR (film) ν_{max} 2923, 1701, 1644, 1492, 1163, 1121, 1089, 1032, 1010, 812, 683, 566 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{25}Cl_2N_4O_3S^+$ $[M+H]^+$ 615.1019, found 615.1016.

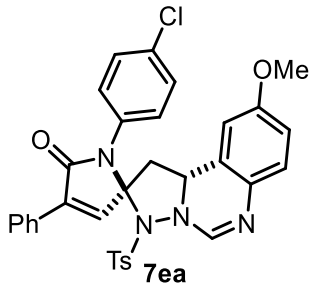
1'-(4-chlorophenyl)-10-methyl-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro[pyrazolo [1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7da)



7da

Prepared according to the general procedure (reaction time: 48 h) as described above in 58% yield (34.6 mg). It was purified by flash chromatography (EtOAc : PE = 1:3) to afford a brown solid. Melting point: 180 – 182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.86 – 7.77 (m, 2H), 7.53 – 7.41 (m, 5H), 7.36 – 7.31 (m, 5H), 7.05 (q, *J* = 8.9, 8.0 Hz, 2H), 6.75 (s, 1H), 6.29 (s, 1H), 4.73 – 4.64 (m, 1H), 2.84 (t, *J* = 12.6 Hz, 1H), 2.47 (s, 3H), 2.42 (dd, *J* = 12.8, 4.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 150.8, 145.8, 137.1, 136.3, 135.7, 135.3, 134.5, 132.4, 131.5, 130.4, 130.1, 130.0, 130.0, 129.7, 128.9, 128.7, 127.6, 126.8, 84.3, 58.1, 43.6, 21.8, 21.1; IR (film) ν_{max} 2924, 1688, 1493, 1379, 1166, 1122, 1090, 1033, 1011, 814, 790, 683, 568 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}ClN_4O_3S^+$ $[M+H]^+$ 595.1565, found 595.1561.

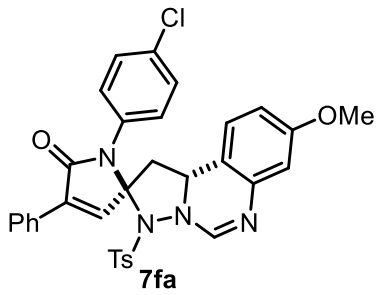
1'-(4-chlorophenyl)-9-methoxy-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro[pyrazolo [1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ea)



7ea

Prepared according to the general procedure (reaction time: 24 h) as described above in 80% yield (48.8 mg). It was purified by flash chromatography (EtOAc : PE = 1:2) to afford an orange solid. Melting point: 168 – 170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.84 – 7.76 (m, 2H), 7.49 – 7.39 (m, 5H), 7.34 (ddd, *J* = 8.1, 4.4, 2.4 Hz, 5H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.46 (d, J = 2.7 Hz, 1H), 6.23 (s, 1H), 4.66 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.76 (s, 3H), 2.82 (t, *J* = 12.5 Hz, 1H), 2.46 (s, 3H), 2.43 (dd, *J* = 12.7, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 157.3, 148.6, 144.7, 135.2, 134.8, 134.2, 133.5, 131.4, 130.5, 130.0, 129.03, 129.00, 128.9, 128.7, 127.8, 127.7, 127.0, 126.6, 122. 5, 113.1, 111.0, 83.4, 57.2, 54.5, 42.4, 20.8; IR (film) ν_{max} 2924, 1686, 1493, 1378, 1260, 1216, 1165, 1121, 1090, 1033, 1011, 813, 567 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{28}ClN_4O_4S^+$ $[M+H]^+$ 611.1514, found 611.1512.

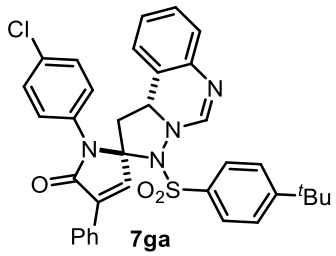
1'-(4-chlorophenyl)-8-methoxy-4'-phenyl-3-tosyl-1,10b-dihydro-3*H*-spiro[pyrazolo [1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7fa)



7fa

Prepared according to the general procedure (reaction time: 48 h) as described above in 50% yield (30.7 mg). It was purified by flash chromatography (EtOAc : PE = 1:2) to afford a yellow solid. Melting point: 140 – 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.83 – 7.78 (m, 2H), 7.50 – 7.41 (m, 5H), 7.34 (dd, *J* = 8.6, 2.3 Hz, 4H), 7.30 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.71 – 6.63 (m, 2H), 6.34 (s, 1H), 4.67 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.76 (s, 3H), 2.80 (t, *J* = 12.5 Hz, 1H), 2.47 (s, 3H), 2.39 (dd, *J* = 12.7, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 159.7, 151.0, 144.7, 137.7, 135.2, 134.7, 134.2, 133.5, 131.4, 130.5, 129.1, 129.0, 128.9, 128.7, 127.8, 127.7, 126.6, 125.9, 113.1, 112.2, 110.5, 83.3, 56.8, 54.4, 42.6, 20.8; IR (film) ν_{max} 2925, 1698, 1614, 1494, 1451, 1379, 1293, 1213, 1167, 1123, 1090, 1033, 1011, 815 cm^{-1}; HRMS (ESI) $C_{33}H_{28}ClN_4O_4S^+$ $[M+H]^+$ 611.1514, found 611.1512.

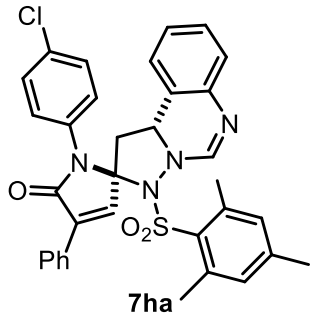
3-((4-(*tert*-butyl)phenyl)sulfonyl)-1'-(4-chlorophenyl)-4'-phenyl-1,10b-dihydro-3*H*-spiro[pyrazolo[1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ga)



7ga

Prepared according to the general procedure (reaction time: 24 h) as described above in 86% yield (53.5 mg). It was purified by flash chromatography (EtOAc : PE = 1:5) to afford a yellow solid. Melting point: 190 – 192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.88 – 7.81 (m, 2H), 7.58 – 7.52 (m, 2H), 7.49 – 7.41 (m, 5H), 7.38 – 7.32 (m, 3H), 7.28 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.13 (dd, *J* = 8.0, 6.9 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.38 (s, 1H), 4.78 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.87 (t, *J* = 12.6 Hz, 1H), 2.45 (dd, *J* = 12.8, 4.7 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 157.7, 150.6, 135.1, 134.8, 134.2, 133.4, 131.4, 130.5, 129.1, 128.9, 128.8, 128.7, 127.7, 126.6, 126.0, 125.6, 125.5, 125.2, 121.2, 83.2, 57.1, 42.5, 34.4, 30.0; IR (film) ν_{max} 2960, 2924, 1695, 1494, 1377, 1261, 1169, 1092, 1017, 797, 755, 421 cm^{-1}; HRMS (ESI) $C_{35}H_{32}ClN_4O_3S^+$ $[M+H]^+$ 623.1878, found 623.1874.

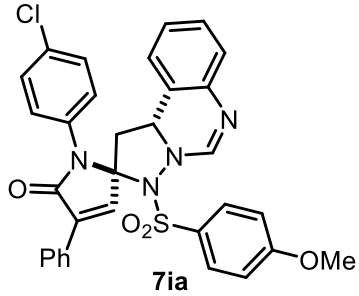
1'-(4-chlorophenyl)-3-(mesitylsulfonyl)-4'-phenyl-1,10b-dihydro-3*H*-spiro[pyrazolo [1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ha)



7ha

Prepared according to the general procedure (reaction time: 42 h) as described above in 99% yield (60.2 mg). It was purified by flash chromatography (EtOAc : PE = 1:3) to afford a yellow solid. Melting point: 178 – 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.91 (s, 1H), 7.48 – 7.38 (m, 3H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.01 – 6.95 (m, 3H), 5.88 (s, 1H), 5.33 (dd, *J* = 11.4, 5.8 Hz, 1H), 2.92 (dd, *J* = 13.0, 11.4 Hz, 1H), 2.74 (dd, *J* = 13.0, 5.9 Hz, 1H), 2.63 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 148.3, 143.7, 136.7, 136.5, 133.9, 133.5, 132.1, 131.4, 129.3, 129.1, 129.0, 128.9, 128.5, 128.4, 127.6, 126.8, 125.9, 125.7, 125.3, 121.4, 84.3, 57.1, 44.0, 22.2, 20.1; IR (film) ν_{max} 2922, 1732, 1696, 1523, 1496, 1454, 1262, 1089, 750, 451 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{30}ClN_4O_3S^+$ $[M+H]^+$ 609.1722, found 609.1719.

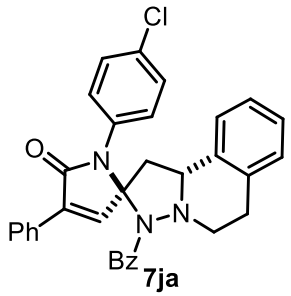
1'-(4-chlorophenyl)-3-((4-methoxyphenyl)sulfonyl)-4'-phenyl-1,10b-dihydro-3*H*-spiro[pyrazolo[1,5-*c*]quinazoline-2,2'-pyrrol]-5'(1'*H*)-one (7ia)



7ia

Prepared according to the general procedure (reaction time: 48 h) as described above in 99% yield (58.9 mg). It was purified by flash chromatography (EtOAc : PE=1:2) to afford a brown solid. Melting point: 151 – 153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.87 – 7.80 (m, 2H), 7.48 – 7.39 (m, 5H), 7.37 – 7.29 (m, 3H), 7.27 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.01 – 6.95 (m, 2H), 6.93 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.44 (s, 1H), 4.79 (dd, *J* = 12.3, 4.8 Hz, 1H), 3.88 (s, 3H), 2.85 (t, *J* = 12.5 Hz, 1H), 2.48 (dd, *J* = 12.8, 4.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 163.3, 150.6, 136.6, 135.2, 134.9, 134.2, 131.4, 130.5, 130.1, 129.0, 128.9, 128.8, 128.7, 127.7, 127.6, 126.6, 126.0, 125.7, 125.2, 121.2, 113.6, 83.1, 57.0, 54.8, 42.5; IR (film) ν_{max} 2960, 2924, 1696, 1593, 1495, 1260, 1160, 1091, 1024, 799, 421 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{26}ClN_4O_4S^+$ $[M+H]^+$ 597.1358, found 597.1354.

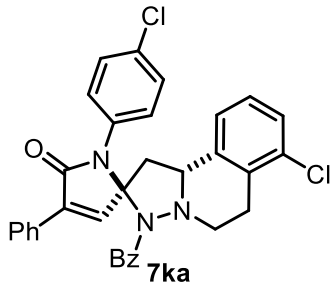
3-benzoyl-1'-(4-chlorophenyl)-4'-phenyl-1,5,6,10b-tetrahydro-3*H*-spiro[pyrazolo[5,1-*a*]isoquinoline-2,2'-pyrrol]-5'(1'*H*)-one (7ja)



7ja

Prepared according to the general procedure (reaction time: 6 h) as described above in 95% yield (50.6 mg). It was purified by flash chromatography (EtOAc : PE=1:5) to afford a yellow solid. Melting point: 218 – 220 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.81 – 7.74 (m, 2H), 7.50 – 7.29 (m, 10H), 7.21 – 7.13 (m, 3H), 7.08 – 7.02 (m, 1H), 6.96 – 6.90 (m, 1H), 4.13 (dd, *J* = 11.9, 6.0 Hz, 1H), 2.98 (ddd, *J* = 12.7, 9.9, 3.1 Hz, 1H), 2.93 – 2.85 (m, 2H), 2.83 – 2.76 (m, 1H), 2.76 – 2.69 (m, 1H), 2.54 (dt, *J* = 16.4, 2.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 165.6, 140.9, 135.0, 133.9, 133.8, 133.2, 132.6, 131.5, 130.1, 129.9, 129.6, 129.0, 128.0, 127.8, 127.6, 127.5, 126.7, 126.6, 126.3, 125.9, 125.5, 82.8, 58.5, 48.4, 41.9, 28.1; IR (film) ν_{max} 2960, 2925, 1702, 1644, 1493, 1383, 1261, 1089, 1016, 788, 765, 735, 695 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{27}ClN_3O_2^+$ $[M+H]^+$ 532.1786, found 532.1789.

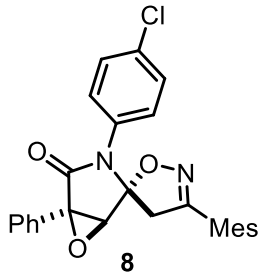
3-benzoyl-7-chloro-1'-(4-chlorophenyl)-4'-phenyl-1,5,6,10b-tetrahydro-3H-spiro[pyrazolo [5,1-a]isoquinoline-2,2'-pyrrol]-5'(1'H)-one (7ka)



7ka

Prepared according to the general procedure (reaction time: 6 h) as described above in 63% yield (35.5 mg). It was purified by flash chromatography (EtOAc : PE=1:5) to afford a yellow solid. Melting point: 220 – 222 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.79 – 7.73 (m, 2H), 7.50 – 7.29 (m, 10H), 7.25 – 7.22 (m, 1H), 7.19 – 7.10 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.10 (dd, *J* = 11.9, 6.1 Hz, 1H), 2.98 – 2.74 (m, 5H), 2.53 (dt, *J* = 17.5, 9.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 165.6, 140.7, 135.1, 134.7, 133.82, 133.79, 133.11, 133.07, 130.1, 130.01, 129.96, 129.6, 129.0, 128.0, 127.7, 127.5, 127.0, 126.8, 126.6, 124.4, 82.7, 58.3, 47.9, 41.7, 26.2; IR (film) ν_{max} 2924, 1703, 1646, 1493, 1447, 1384, 1261, 1090, 1017, 787, 734, 695 cm^{-1}; HRMS (ESI) calcd for $C_{33}H_{26}Cl_2N_3O_2^+$ $[M+H]^+$ 588.1216, found 588.1214.

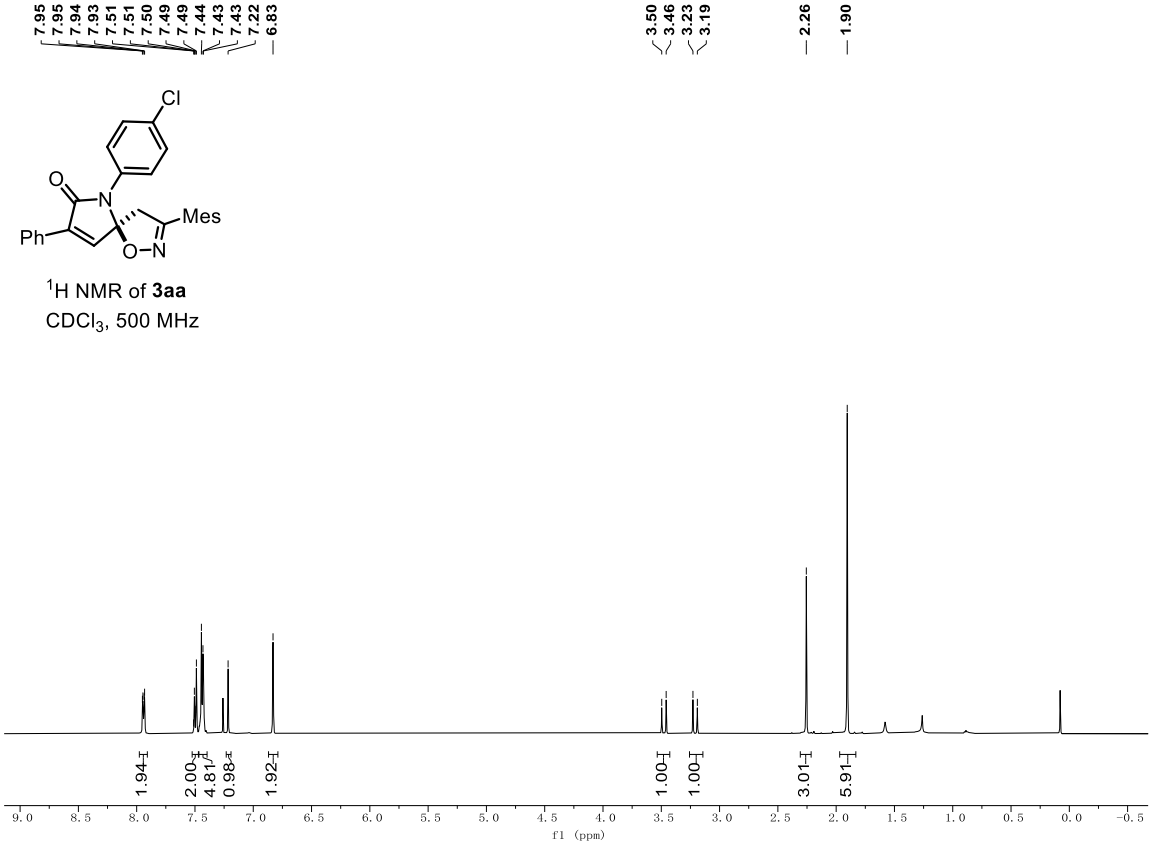
3-(4-chlorophenyl)-3'-mesityl-5-phenyl-4'*H*-6-oxa-3-azaspiro[bicyclo[3.1.0]hexane-2,5'-isoxazol]-4-one (8)



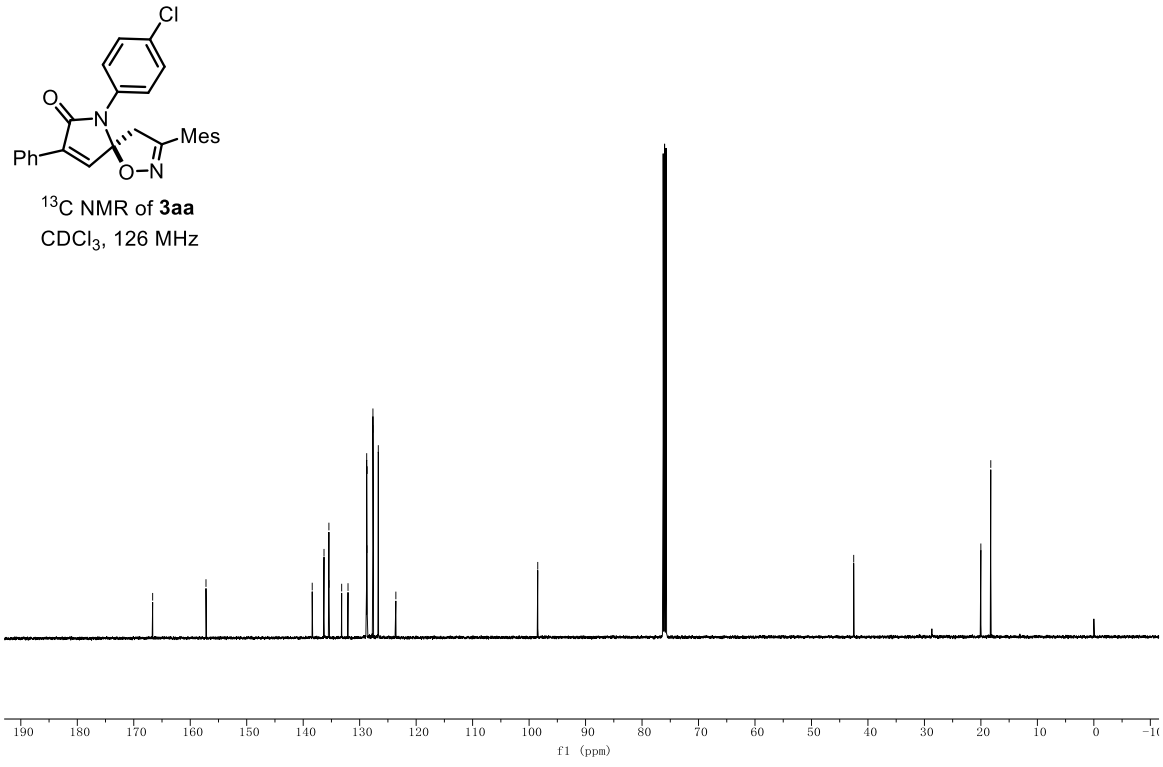
8

Prepared according to the general procedure (reaction time: 24 h) as described above in 36% yield (16.4 mg). It was isolated by simple filtration and dried to afford a white solid. Melting point: 134 – 136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 2H), 7.49 – 7.37 (m, 7H), 6.84 (s, 2H), 4.36 (s, 1H), 3.51 (d, J = 19.3 Hz, 1H), 3.14 (d, J = 19.3 Hz, 1H), 2.26 (s, 3H), 1.98 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 157.9, 138.5, 135.2, 133.7, 131.5, 128.9, 128.5, 128.4, 127.64, 127.58, 127.5, 126.4, 123.4, 97.5, 63.4, 60.1, 41.6, 20.0, 18.4; IR (film) ν_{max} 3737, 3725, 3615, 1732, 1494, 1379, 843, 755, 510, 490, 471, 440, 422 cm^{-1}; HRMS (ESI) calculated for $C_{27}H_{24}ClN_2O_3$ $[M+H]^+$ 459.1397, found 459.1408.

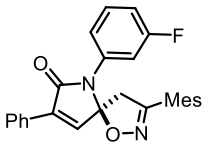
^{1}H and ^{13}C NMR Spectra of All Products



^{1}H NMR of **3aa**
$CDCl_3$, 500 MHz

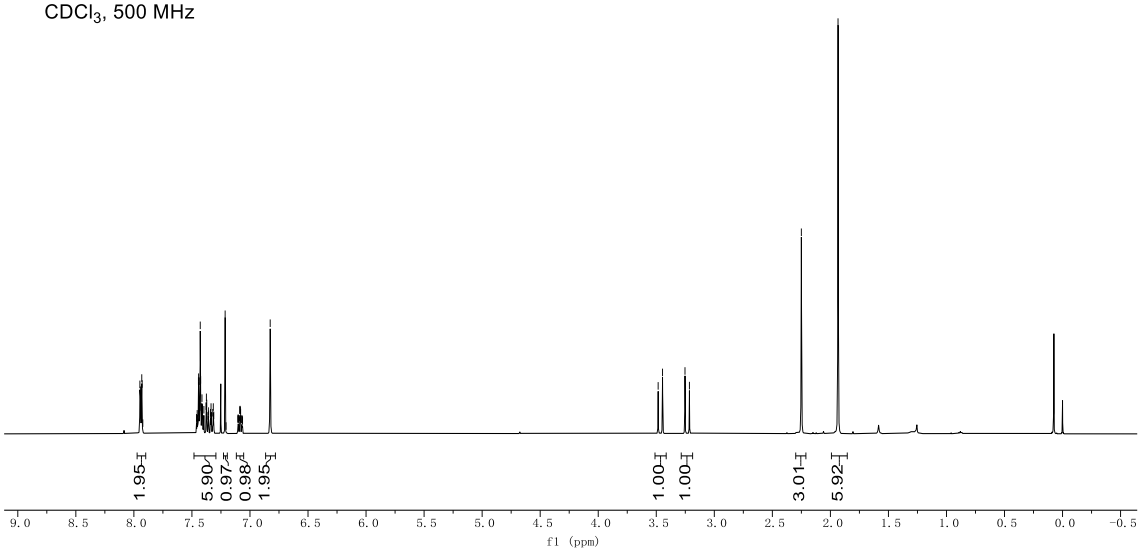


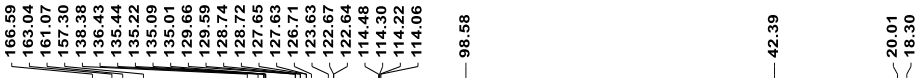
^{13}C NMR of **3aa**
$CDCl_3$, 126 MHz

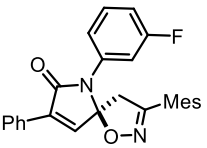


^{1}H NMR of **3ab**

$CDCl_3$, 500 MHz

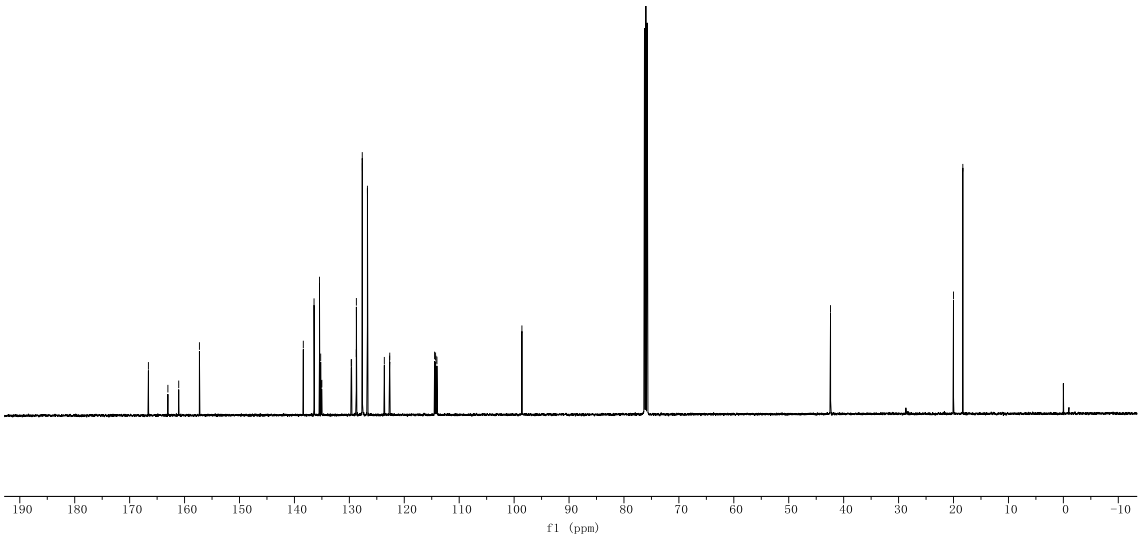


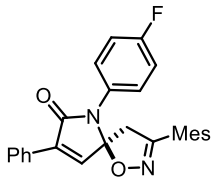




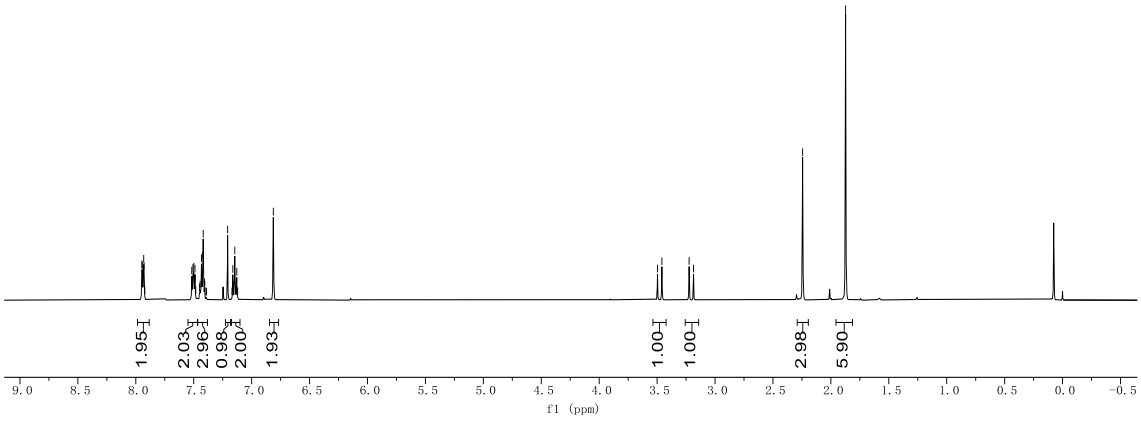
^{13}C NMR of **3ab**

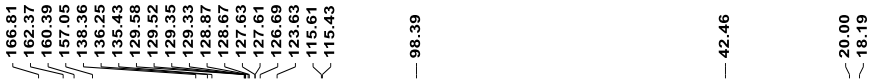
$CDCl_3$, 126 MHz

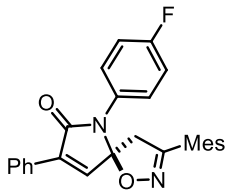




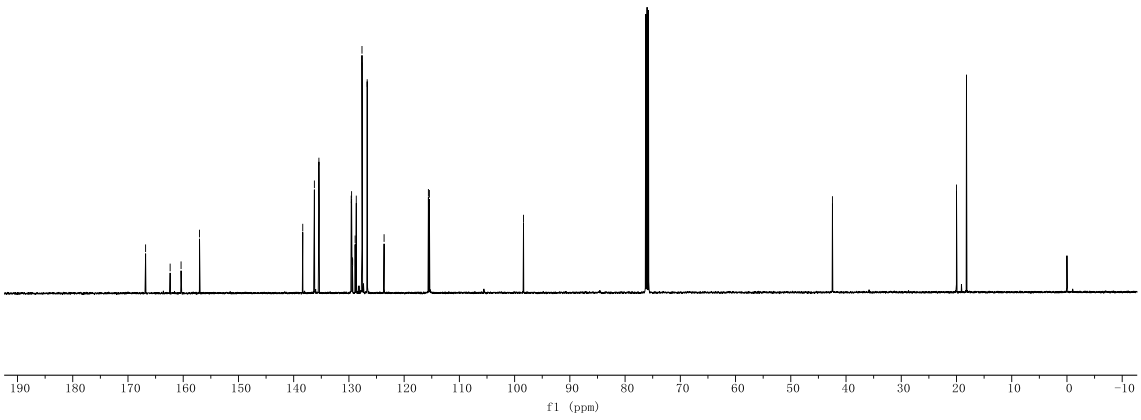
^{1}H NMR of **3ac**
$CDCl_3$, 500 MHz

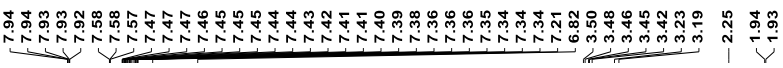


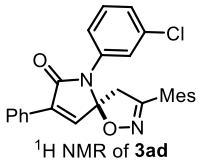




^{13}C NMR of **3ac**
$CDCl_3$, 126 MHz

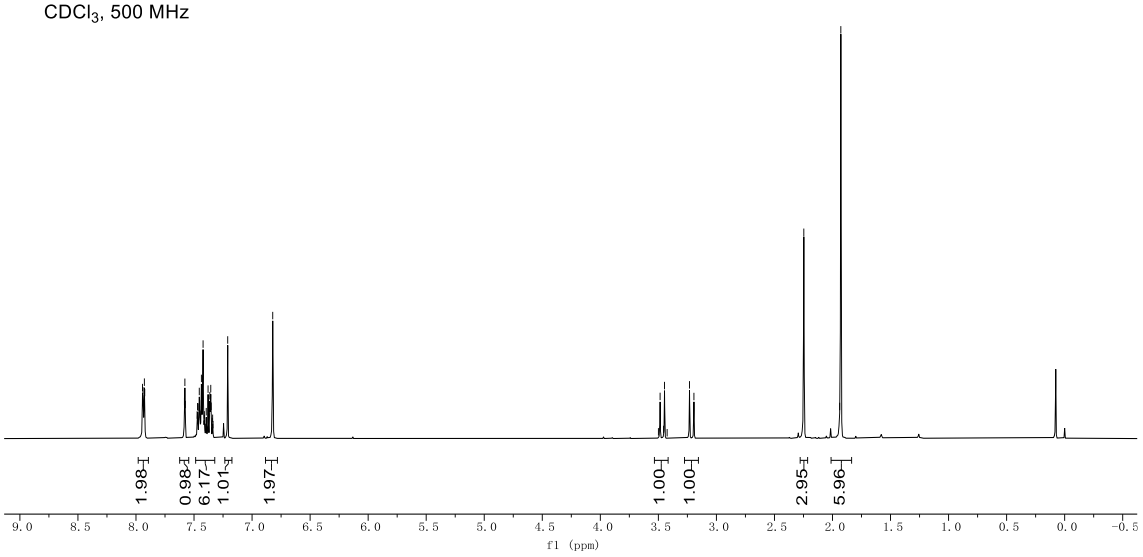


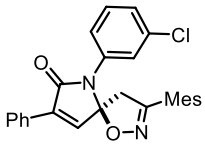




^{1}H NMR of **3ad**

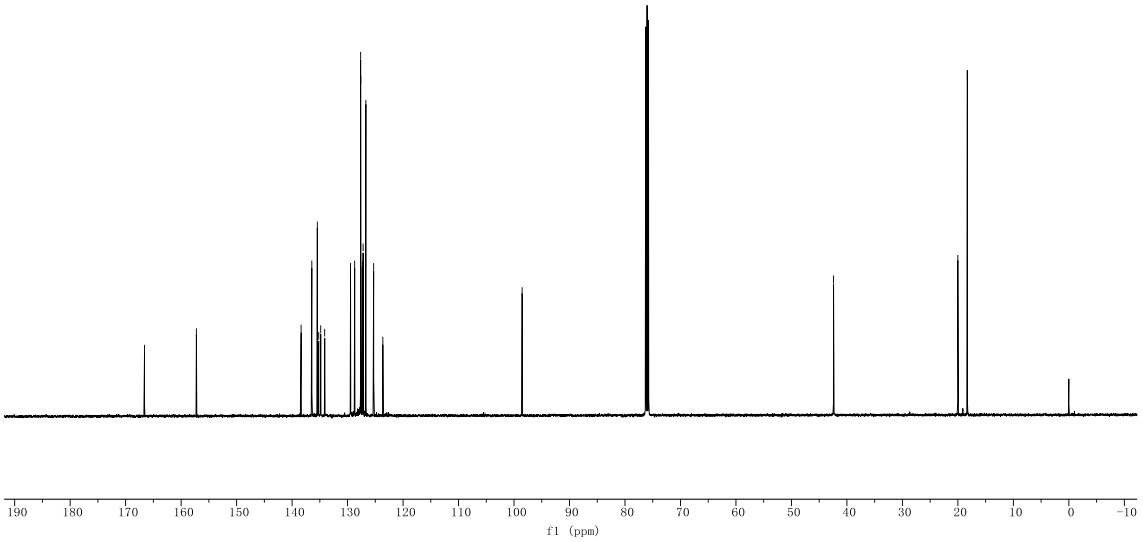
$CDCl_3$, 500 MHz

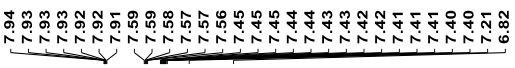


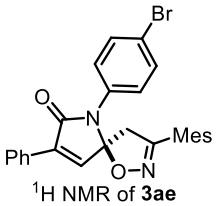


^{13}C NMR of **3ad**

$CDCl_3$, 126 MHz

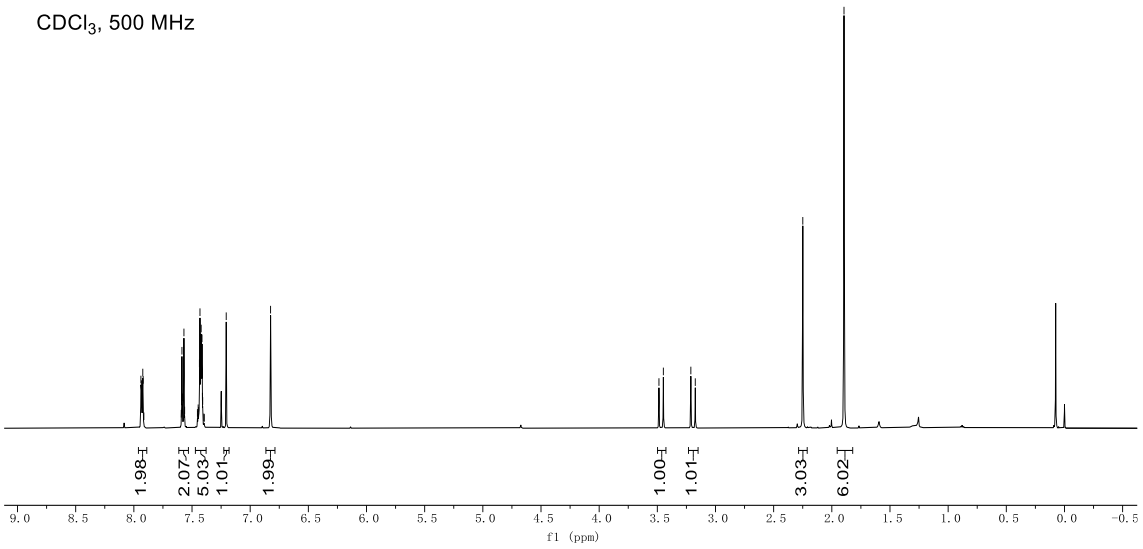


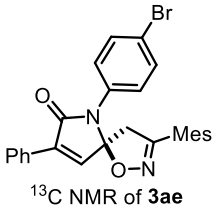




^{1}H NMR of **3ae**

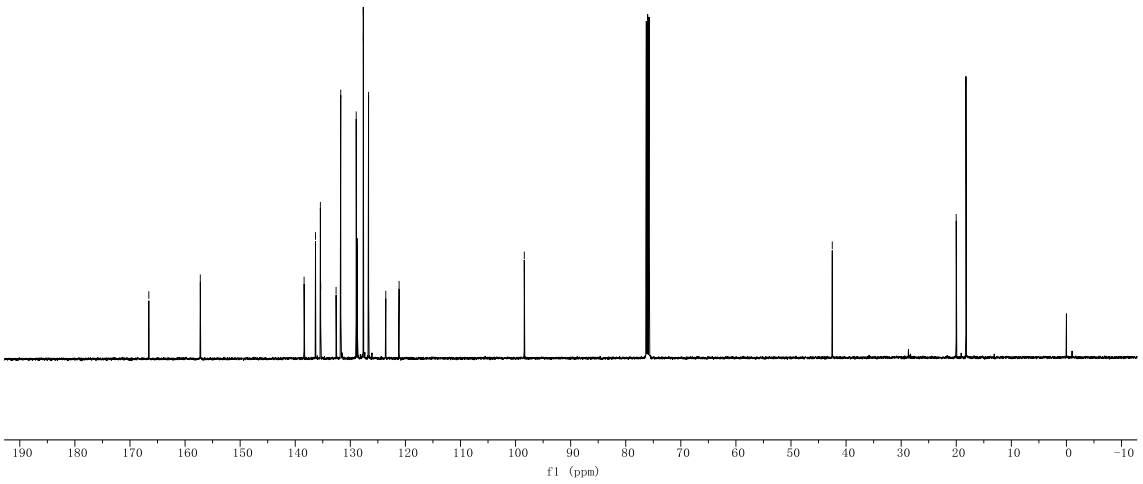
$CDCl_3$, 500 MHz

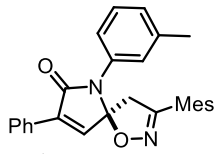




^{13}C NMR of **3ae**

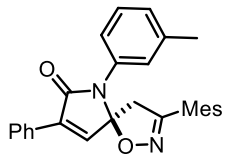
$CDCl_3$, 126 MHz





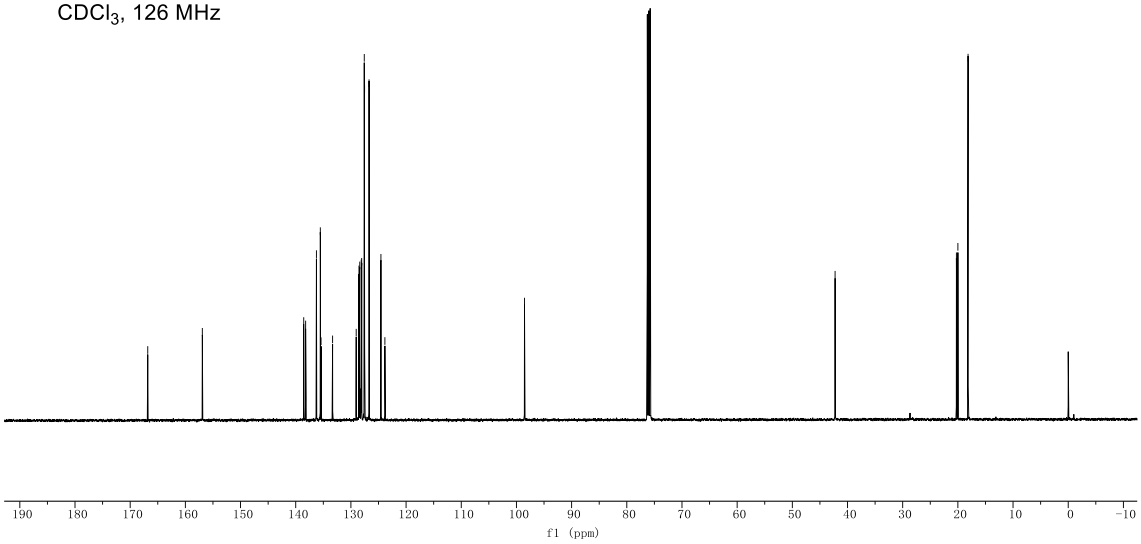
^{1}H NMR of **3af**

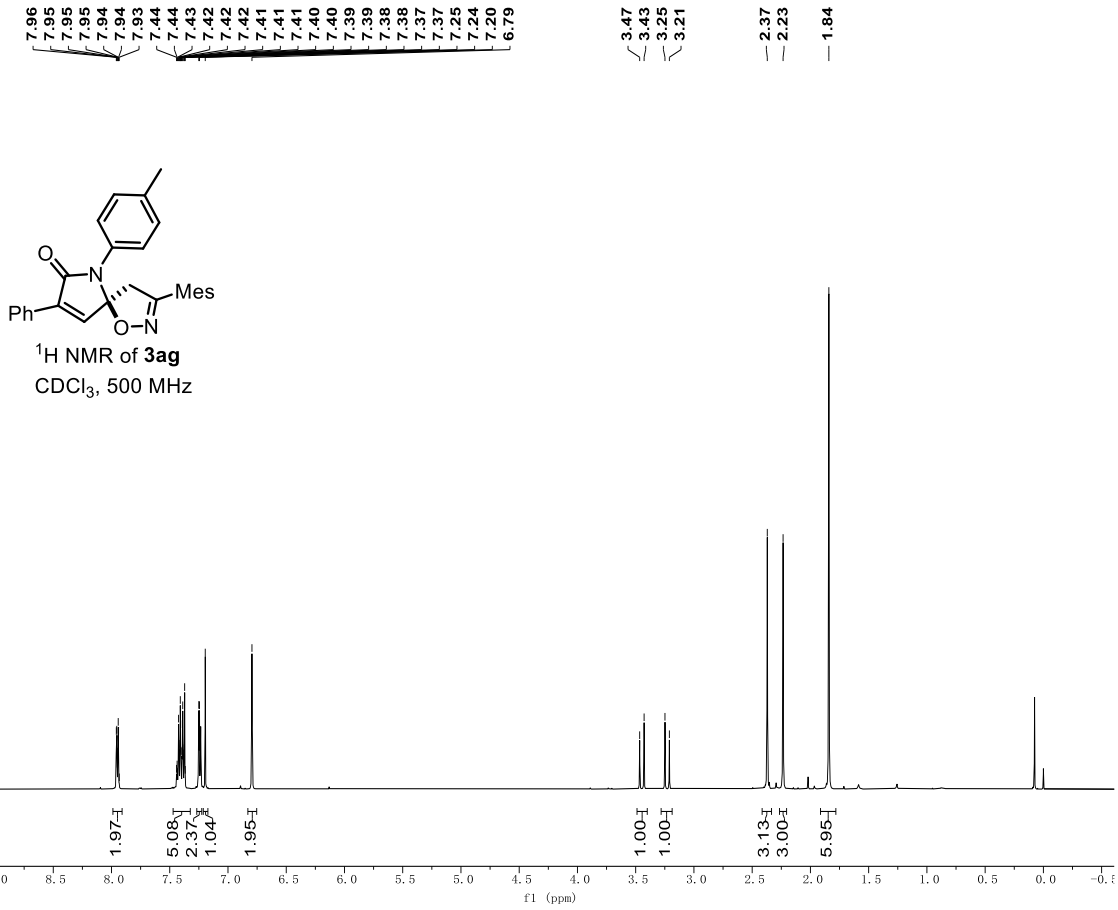
$CDCl_3$, 500 MHz

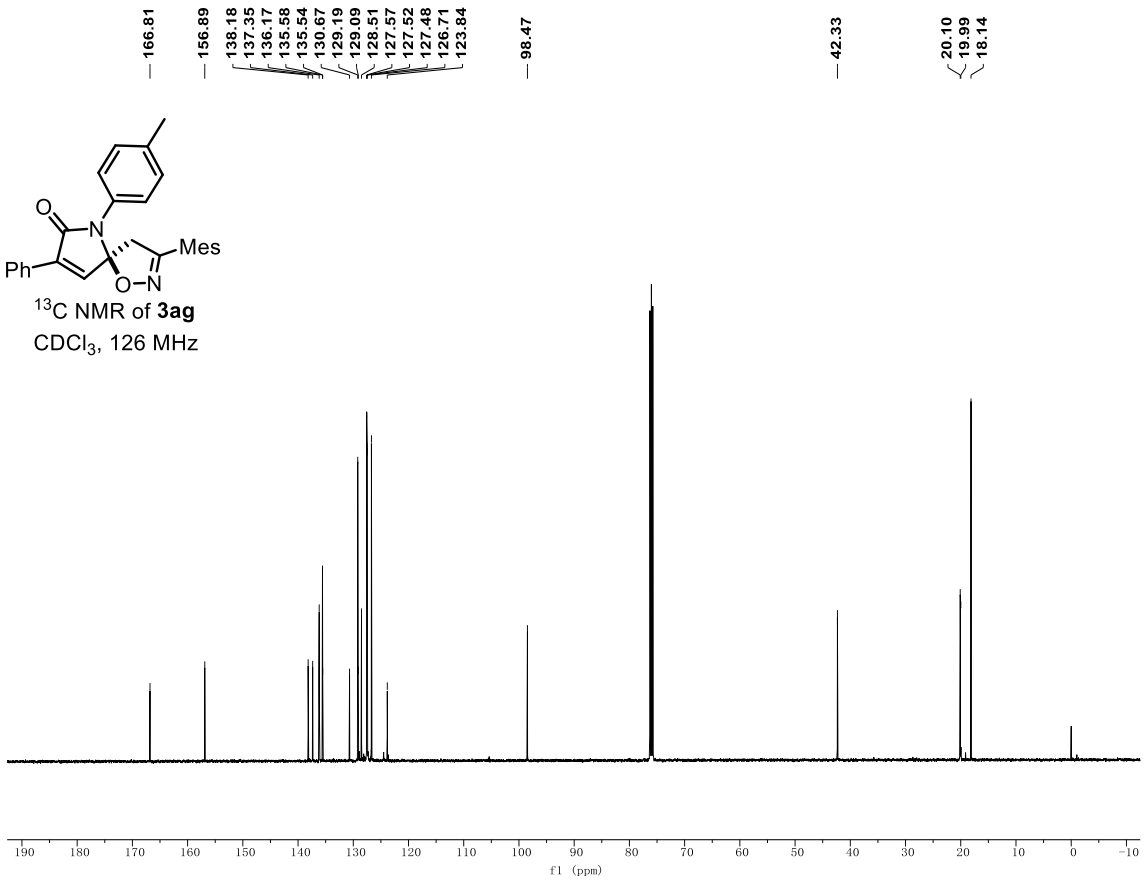


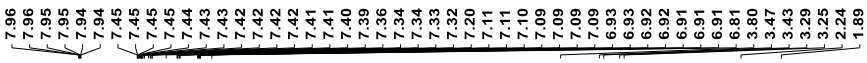
^{13}C NMR of **3af**

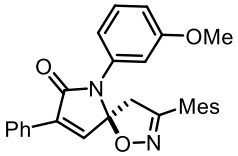
$CDCl_3$, 126 MHz




7.96
7.95
7.95
7.95
7.94
7.94
7.93
7.44
7.44
7.43
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.25
7.24
7.20
6.79
3.47
3.43
3.25
3.21
2.37
2.23
1.84
O
N
Mes
Ph
O–N
1H NMR of 3ag
CDCl3, 500 MHz
1.97
5.08
2.37
1.04
1.95
1.00
1.00
3.13
3.00
5.95
f1 (ppm)

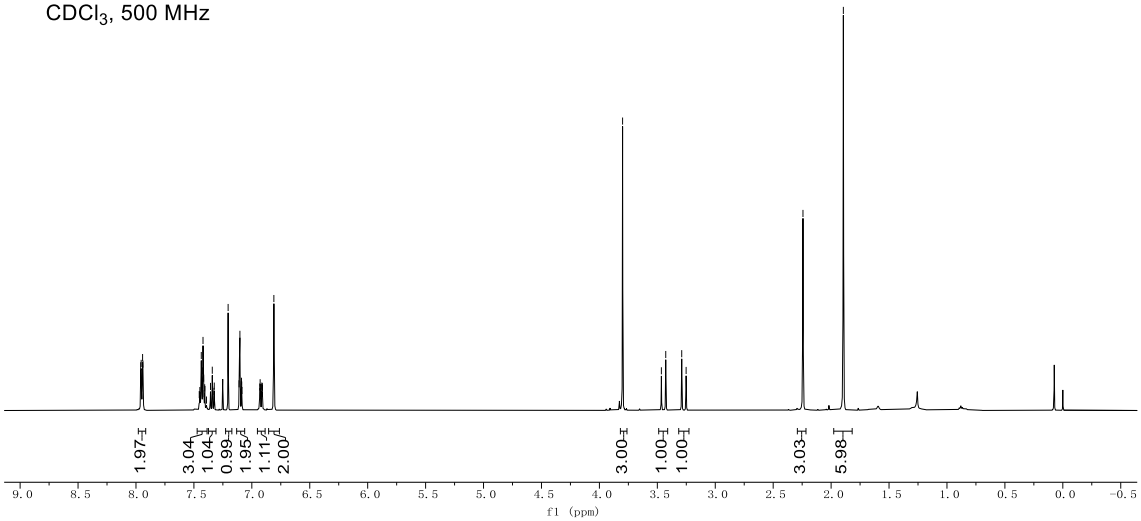

166.81
156.89
138.18
137.35
136.17
135.58
135.54
130.67
129.19
129.09
128.51
127.57
127.52
127.48
126.71
123.84
98.47
42.33
20.10
19.99
18.14
O
N
Mes
Ph
O–N
13C NMR of 3ag
CDCl3, 126 MHz
f1 (ppm)

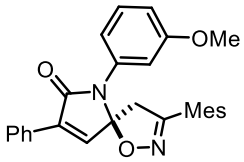




^{1}H NMR of **3ah**

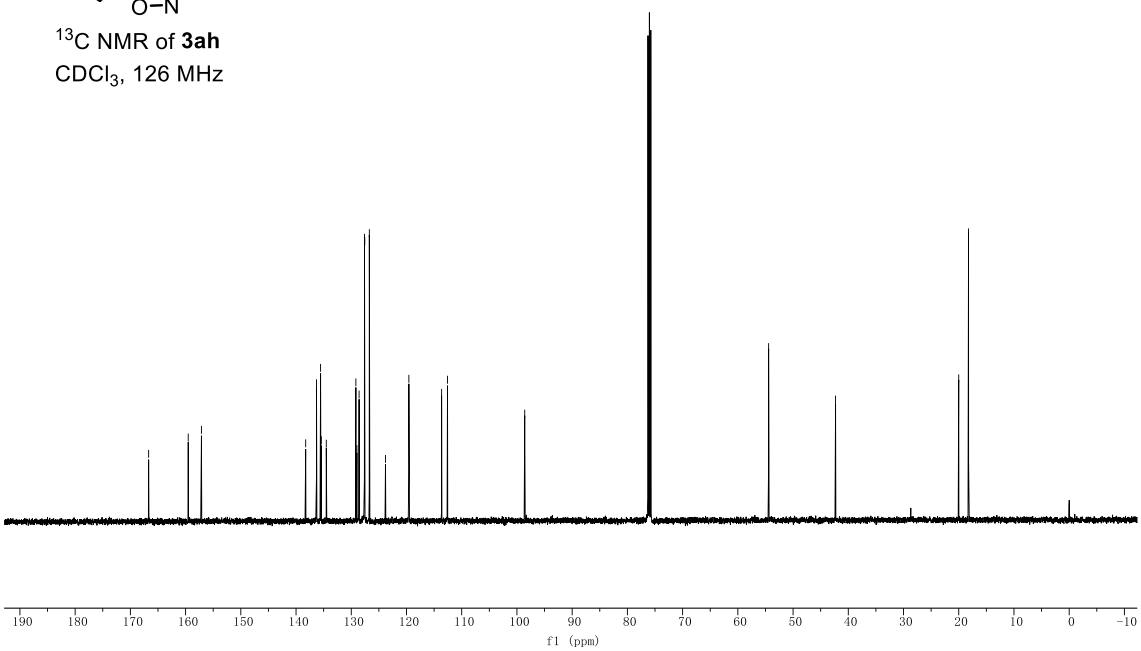
$CDCl_3$, 500 MHz

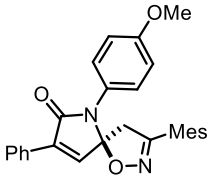




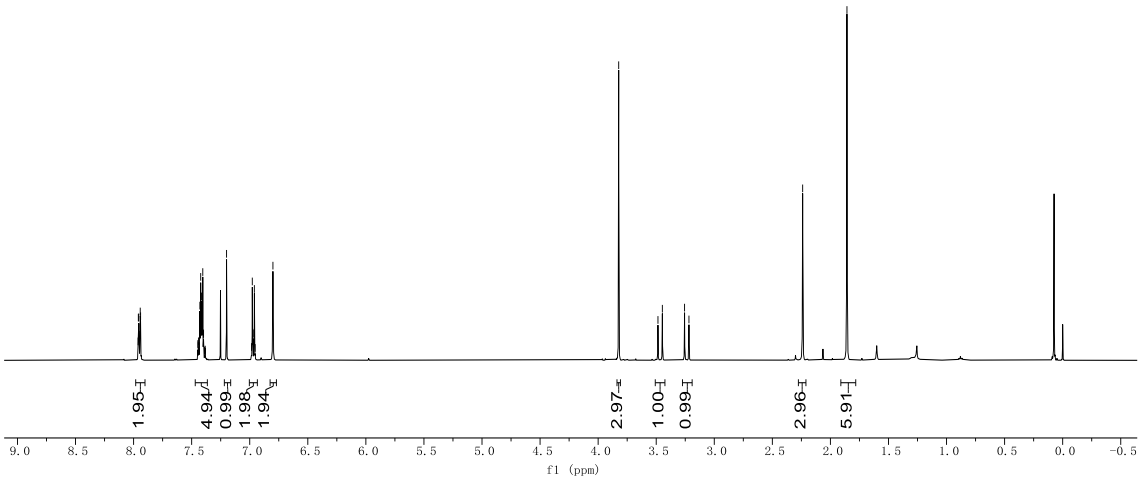
^{13}C NMR of **3ah**

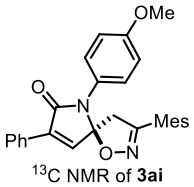
$CDCl_3$, 126 MHz



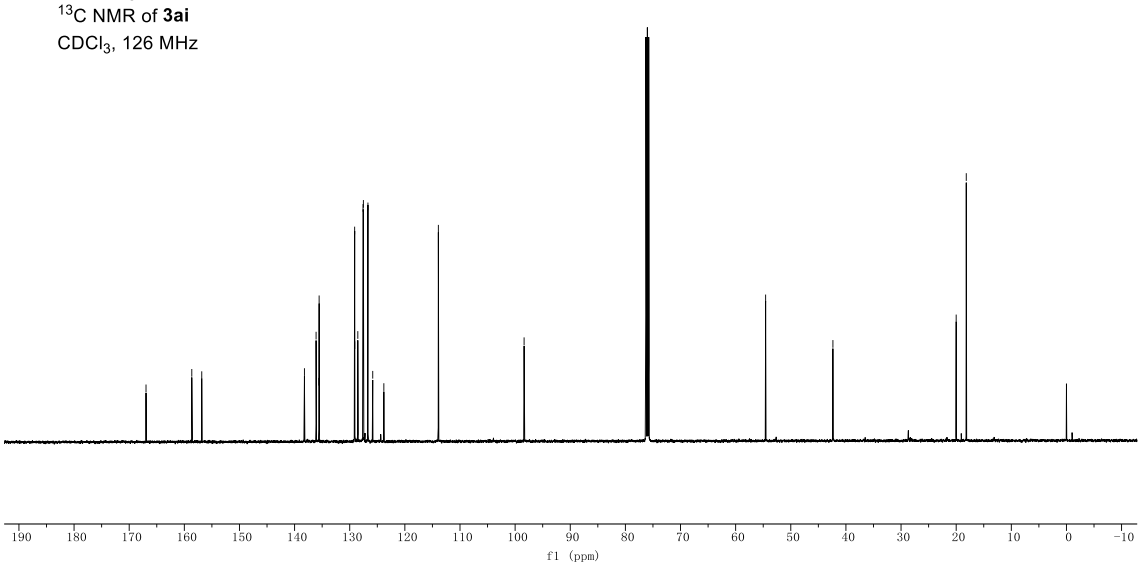


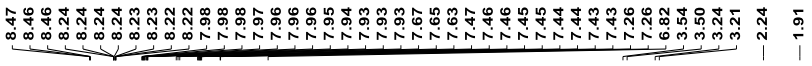
^{1}H NMR of **3ai**
$CDCl_3$, 500 MHz

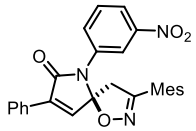




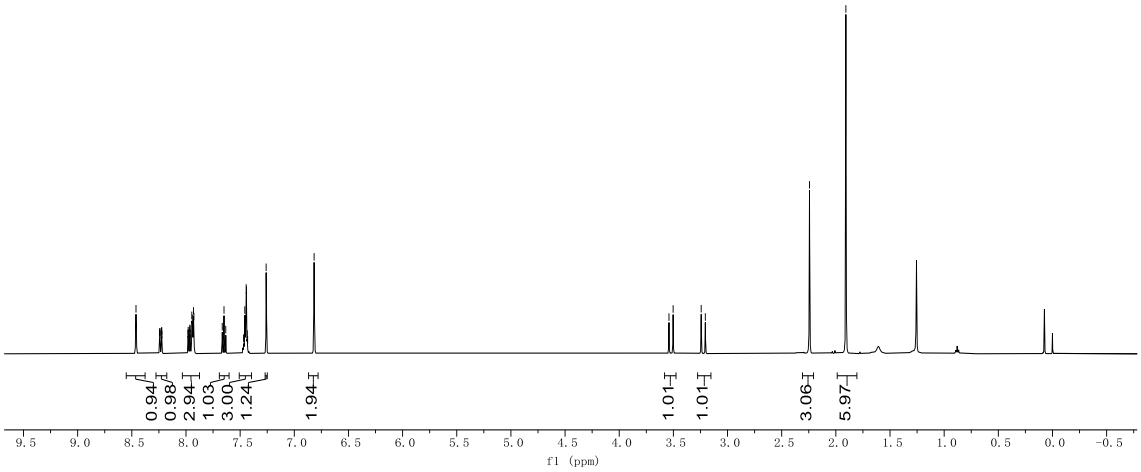
^{13}C NMR of **3ai**
$CDCl_3$, 126 MHz

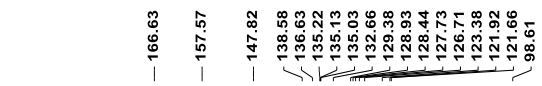


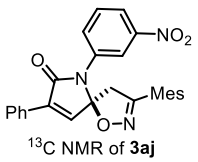




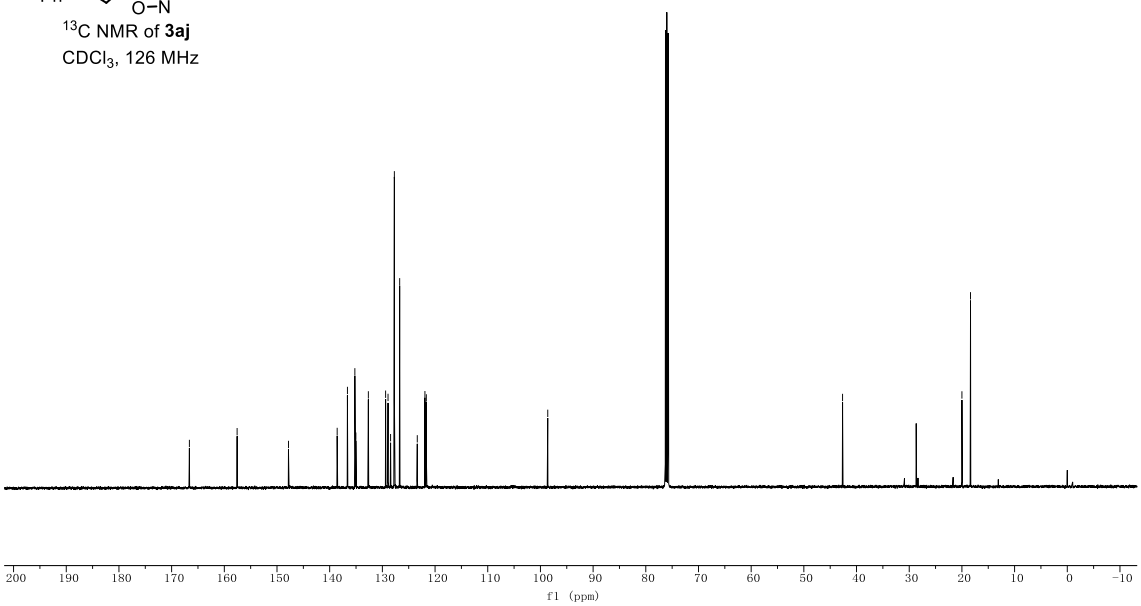
^{1}H NMR of **3aj**
$CDCl_3$, 500 MHz

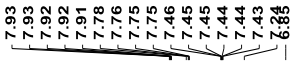


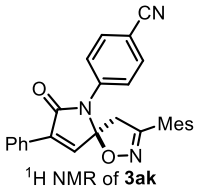




^{13}C NMR of **3aj**
$CDCl_3$, 126 MHz

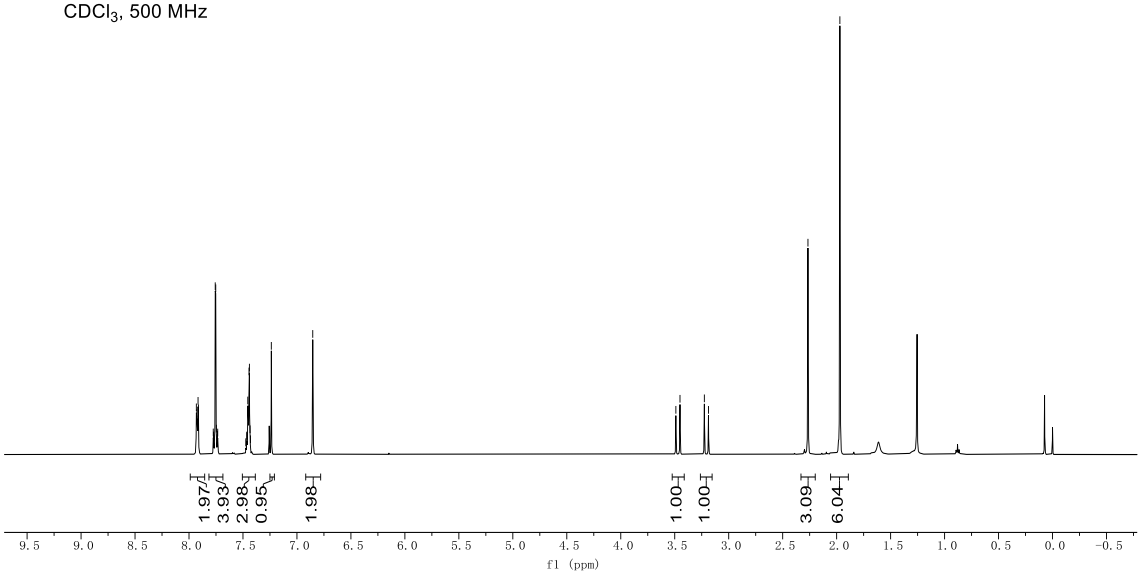


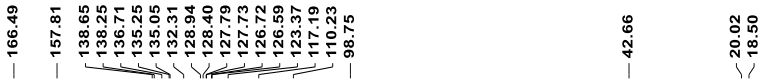


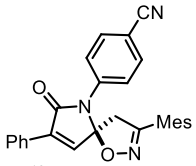


^{1}H NMR of **3ak**

$CDCl_3$, 500 MHz

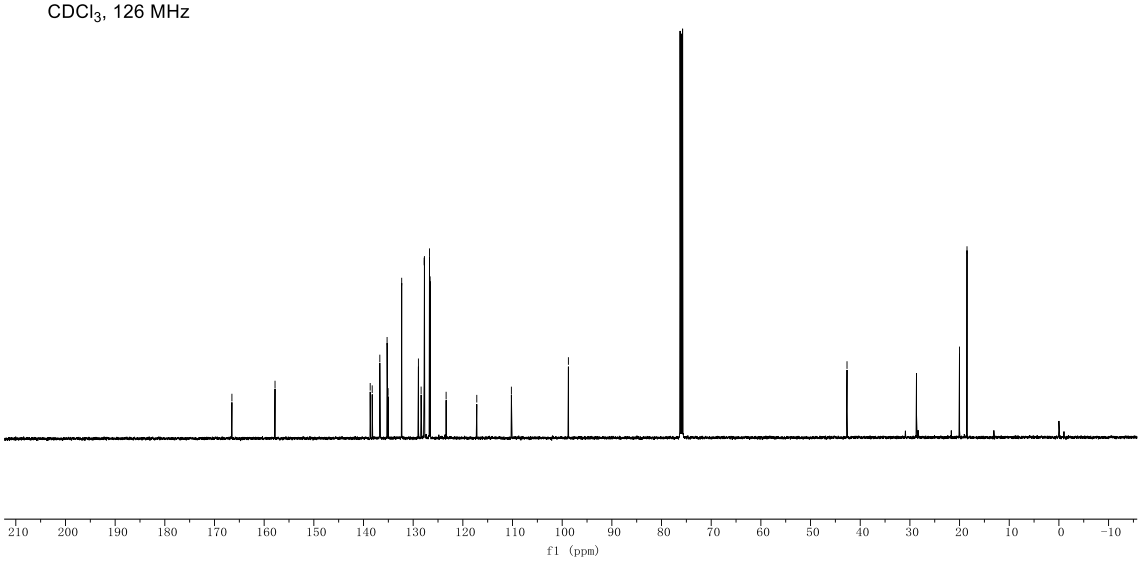


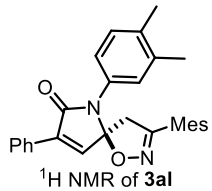




^{13}C NMR of **3ak**

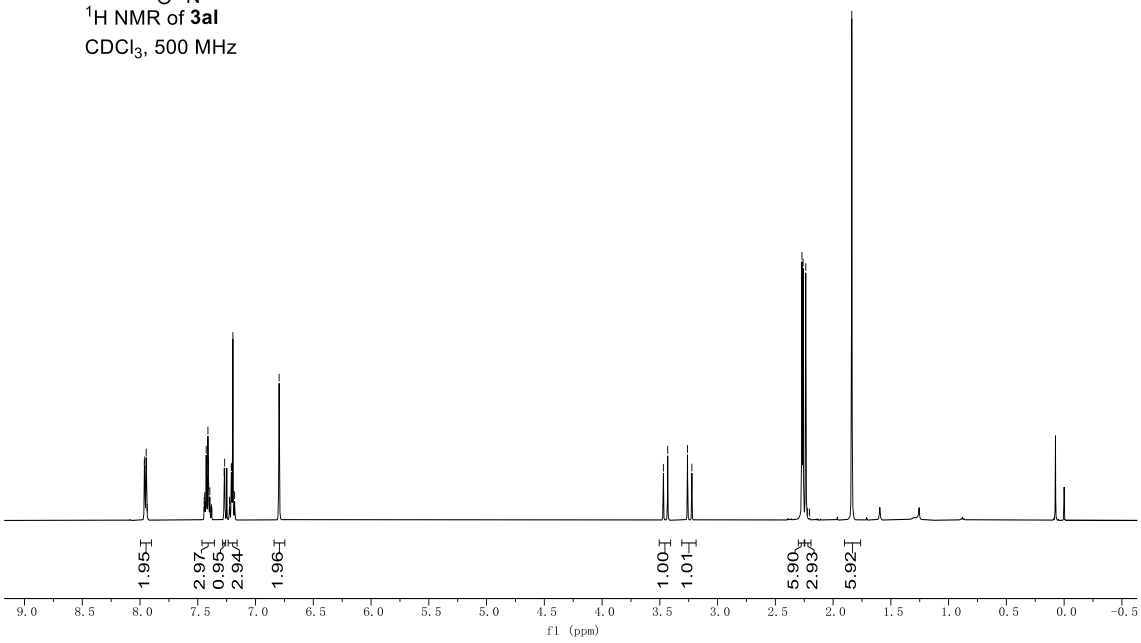
$CDCl_3$, 126 MHz

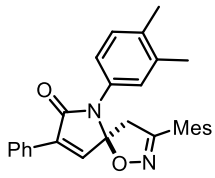




^{1}H NMR of **3al**

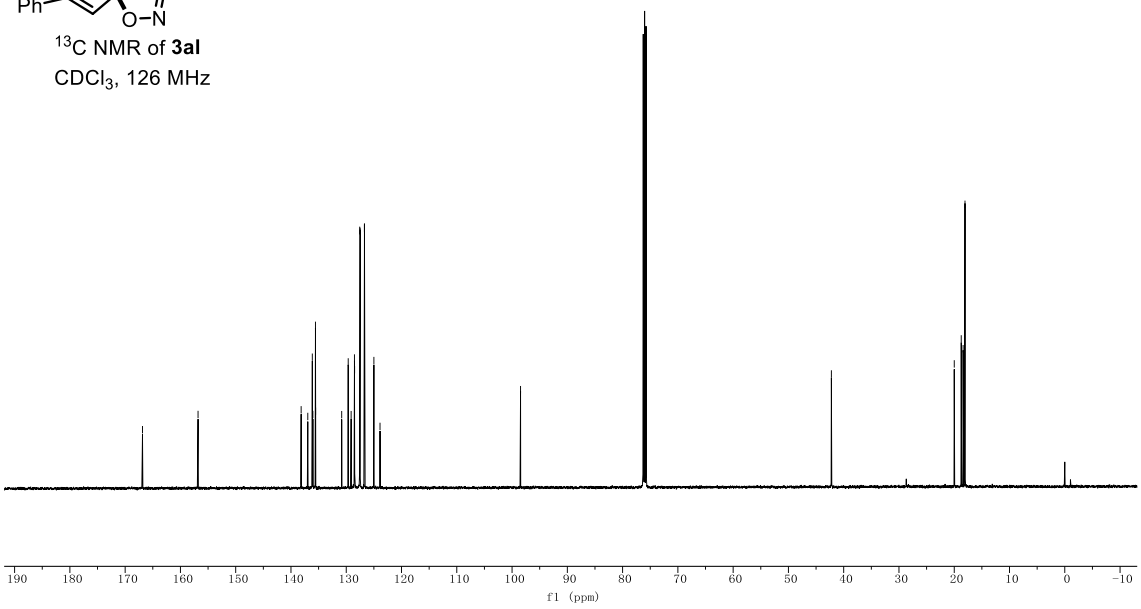
$CDCl_3$, 500 MHz

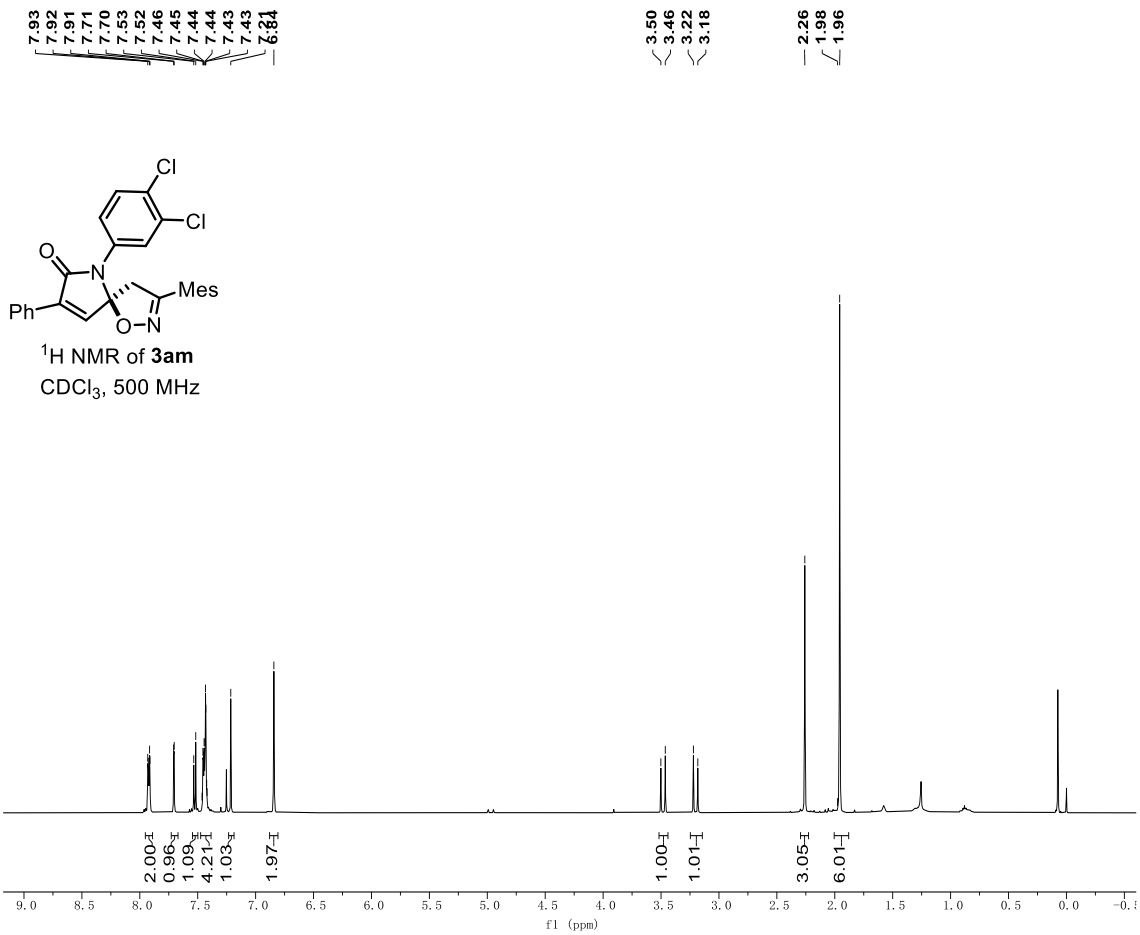




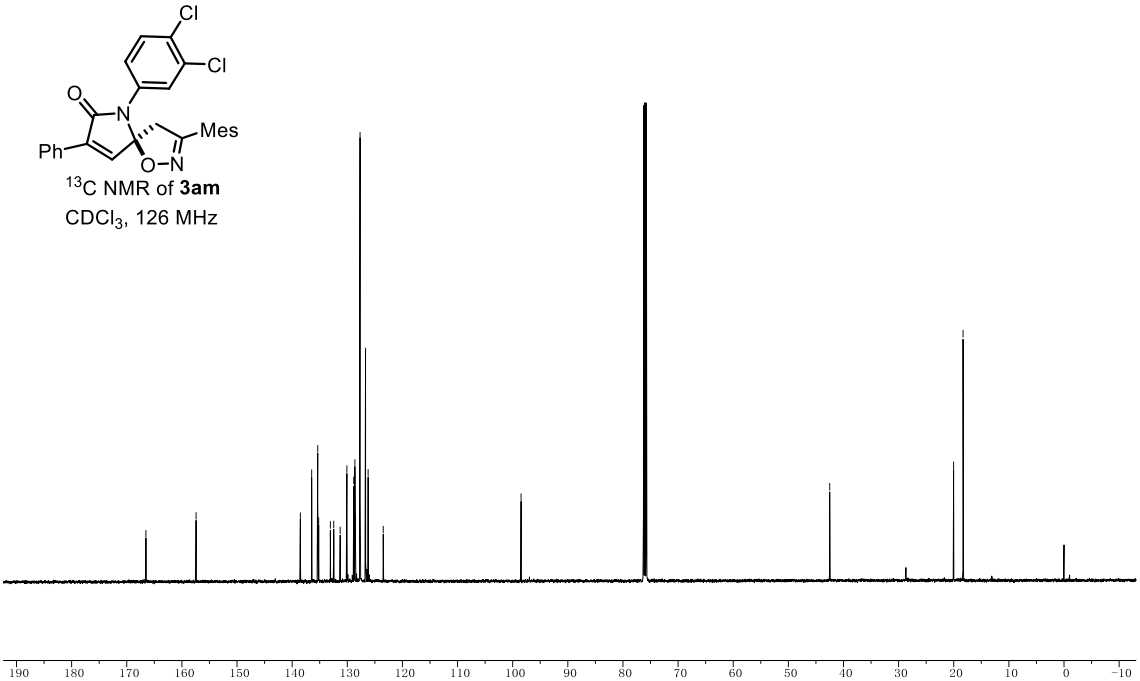
^{13}C NMR of **3al**

$CDCl_3$, 126 MHz

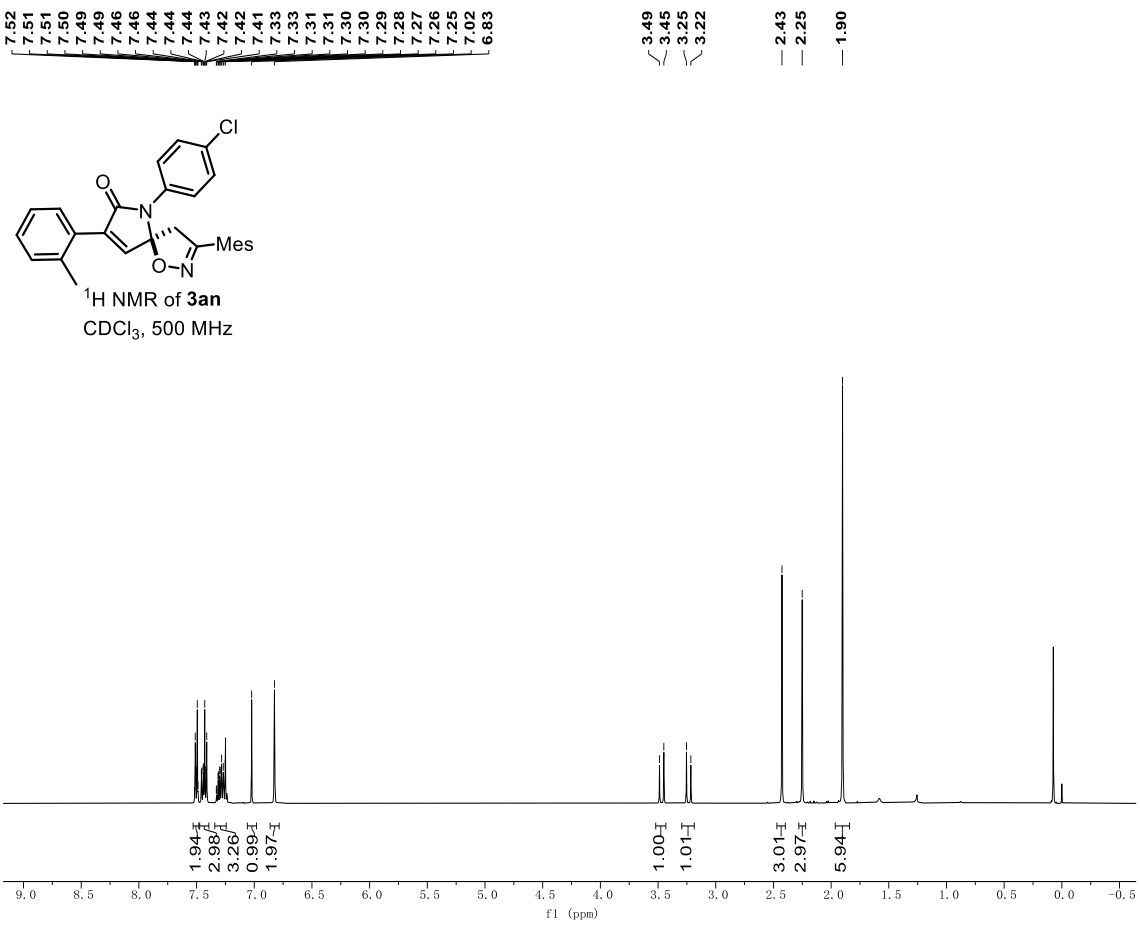




^{1}H NMR of **3am**
$CDCl_3$, 500 MHz



^{13}C NMR of **3am**
$CDCl_3$, 126 MHz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7.51
7.51
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7.46
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7.43
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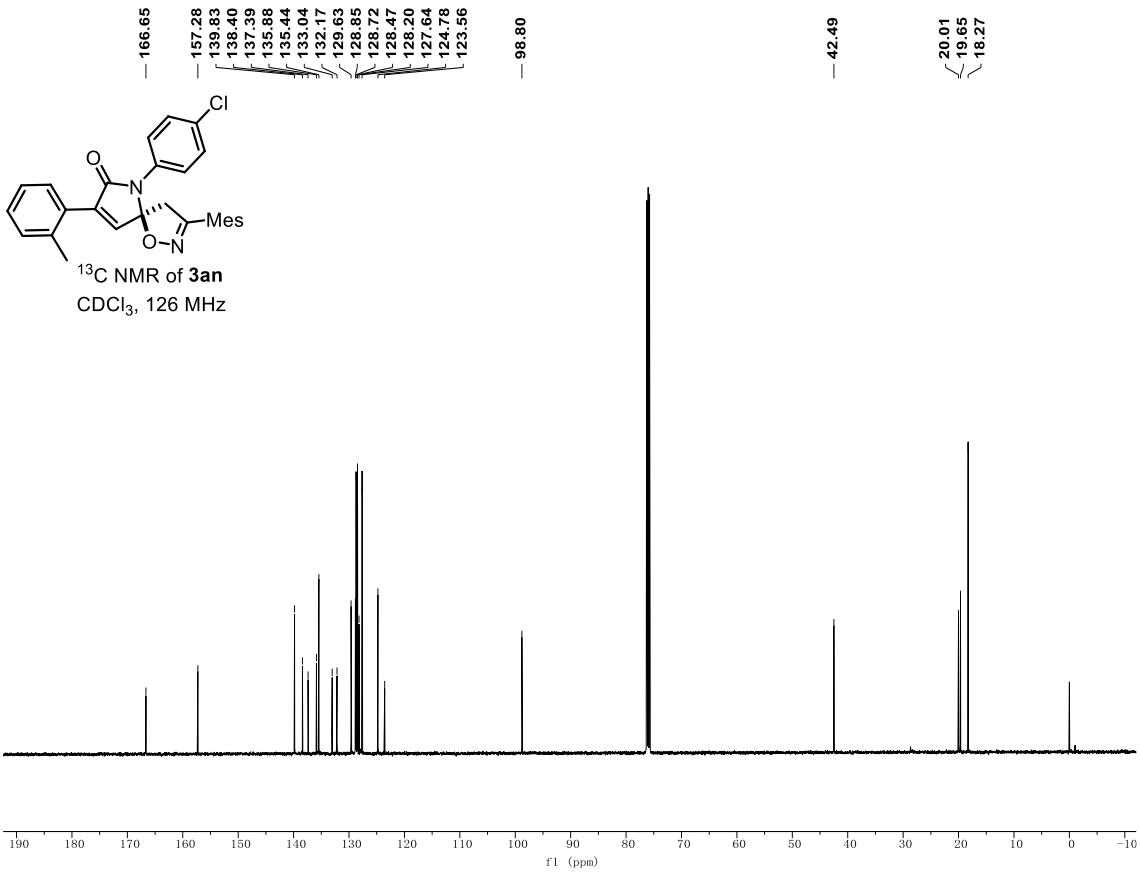
7.42
7.41
7.33
7.33
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.25
7.02
6.83
3.49
3.45
3.25
3.22
2.43
2.25
1.90
Cl
O
N
Mes
O
N
1H NMR of 3an
CDCl3, 500 MHz
1.94
2.98
3.26
0.99
1.97
1.00
1.01
3.01
2.97
5.94
f1 (ppm)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157.28
139.83
138.40
137.39
135.88
135.44
133.04
132.17
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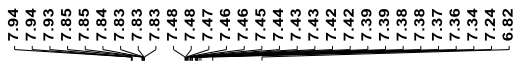
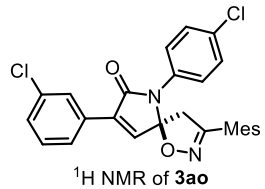
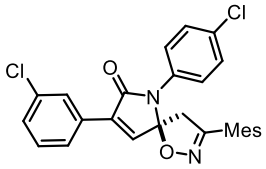
128.85
128.72
128.47
128.20
127.64
124.78
123.56
98.80
42.49
20.01
19.65
18.27
Cl
O
N
Mes
O
N
13C NMR of 3an
CDCl3, 126 MHz
f1 (ppm)

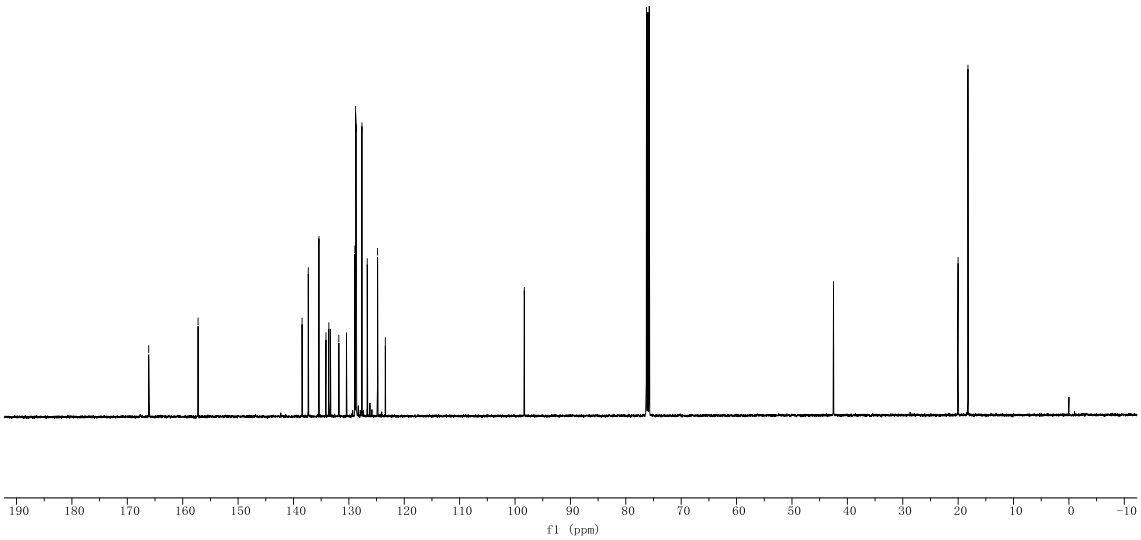


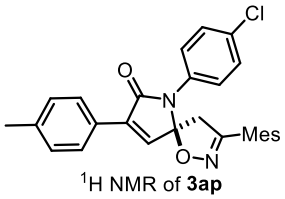


^{1}H NMR of **3ao**
$CDCl_3$, 500 MHz



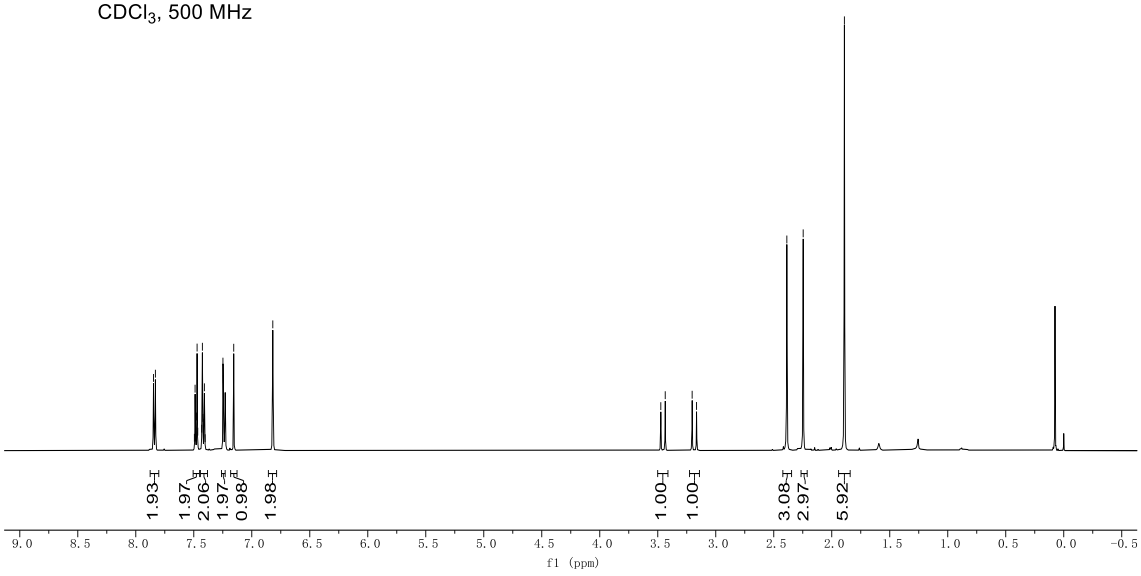
^{13}C NMR of **3ao**
$CDCl_3$, 126 MHz

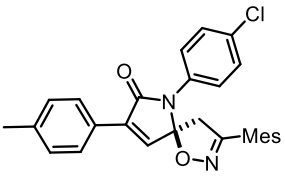




^{1}H NMR of **3ap**

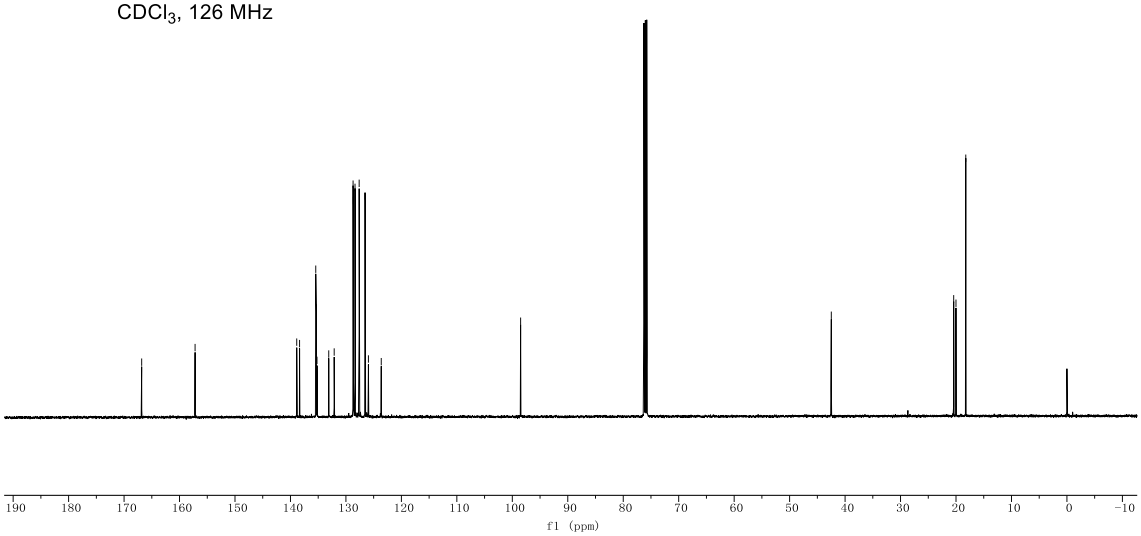
$CDCl_3$, 500 MHz

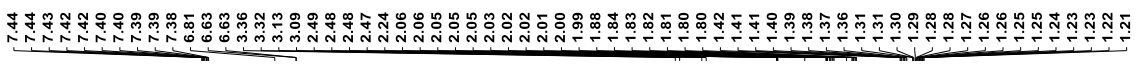


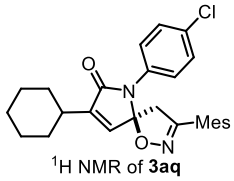


^{13}C NMR of **3ap**

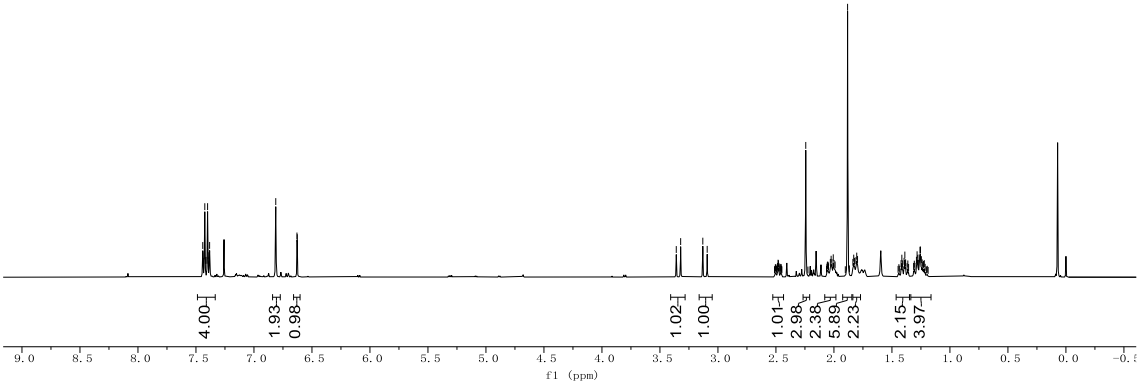
$CDCl_3$, 126 MHz

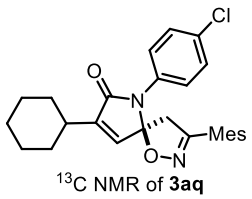




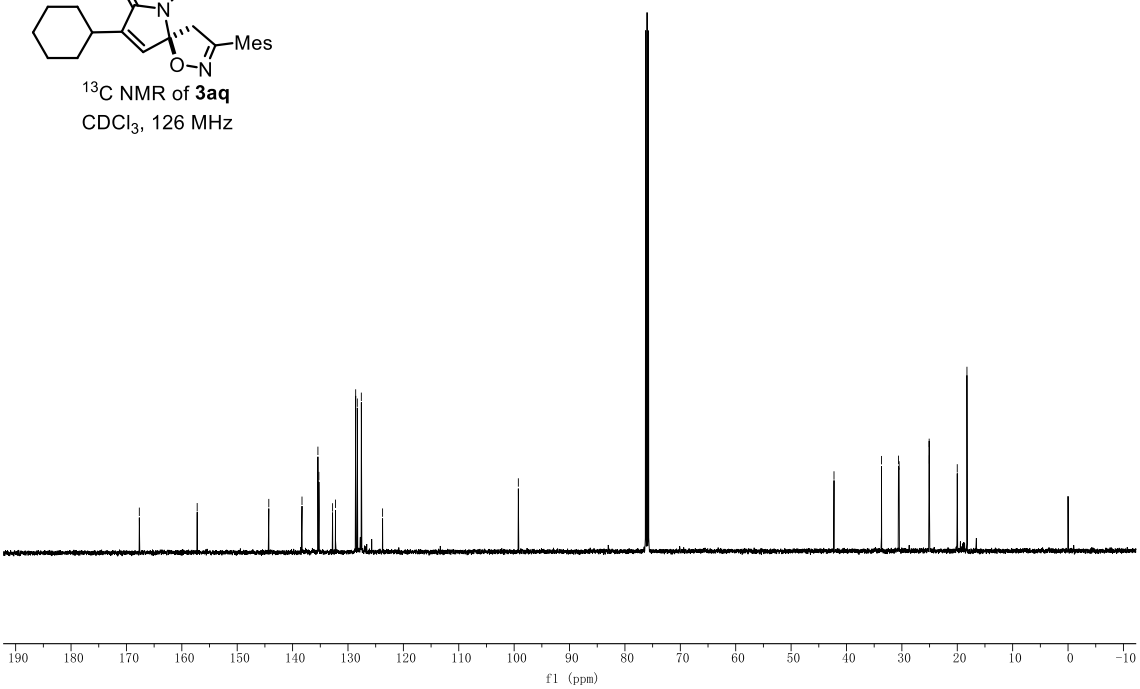


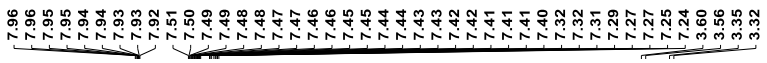
^{1}H NMR of **3aq**
$CDCl_3$, 500 MHz

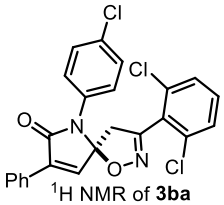




^{13}C NMR of **3aq**
$CDCl_3$, 126 MHz

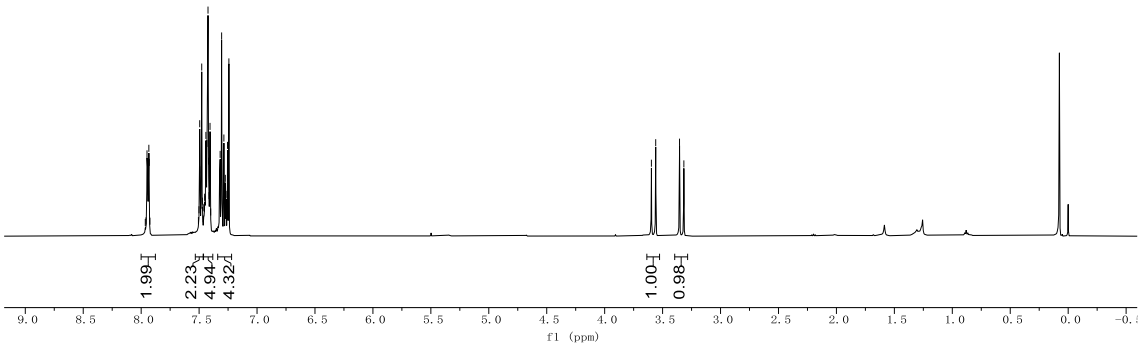


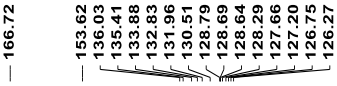


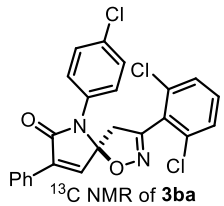


^{1}H NMR of **3ba**

$CDCl_3$, 500 MHz

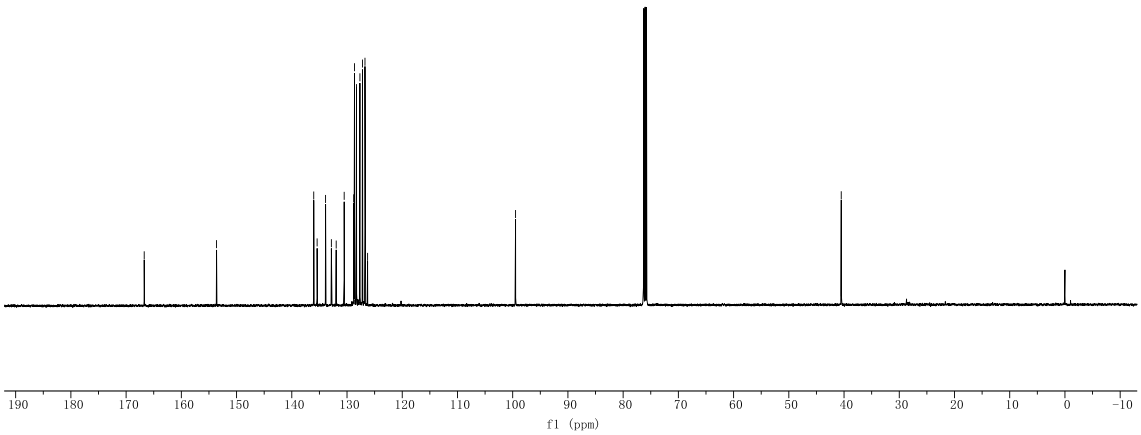


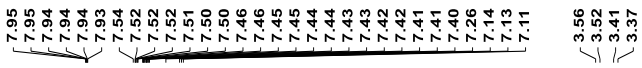


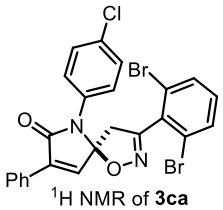


^{13}C NMR of **3ba**

$CDCl_3$, 126 MHz

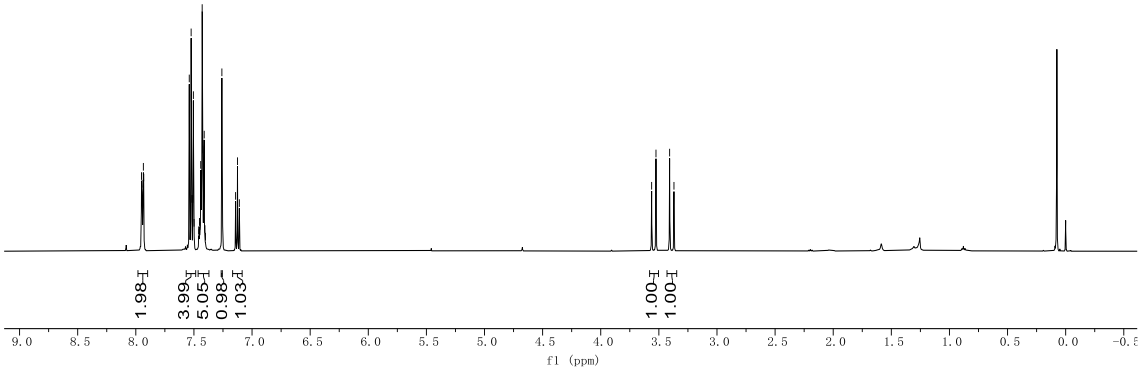


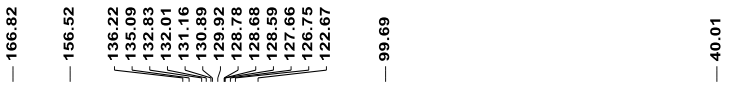


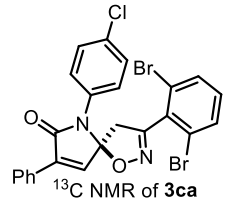


^{1}H NMR of **3ca**

$CDCl_3$, 500 MHz

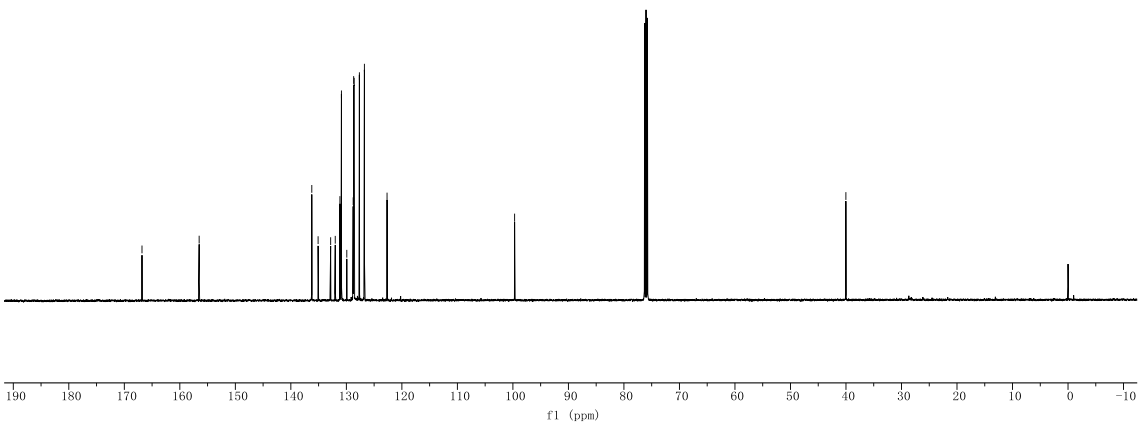


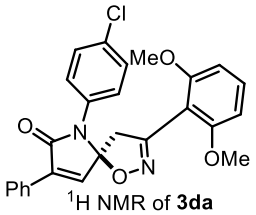




^{13}C NMR of **3ca**

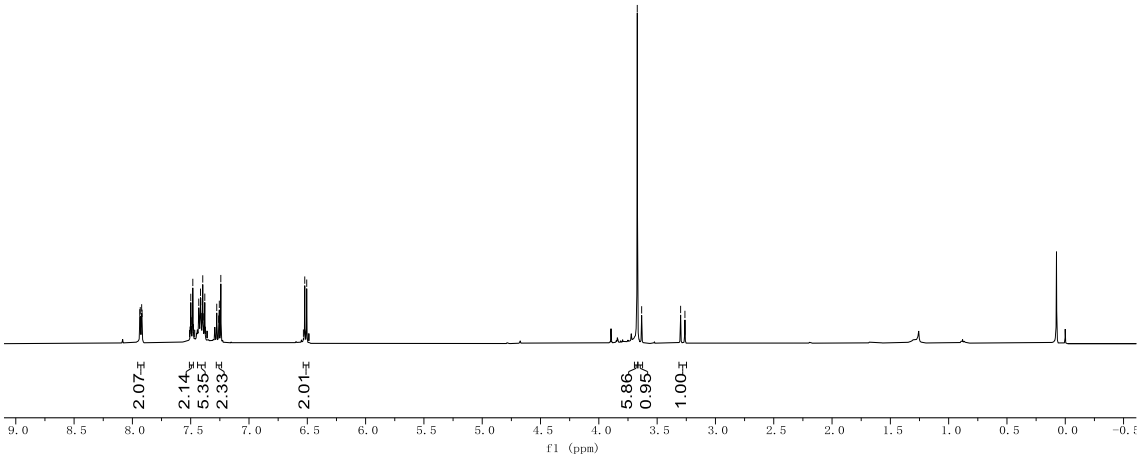
$CDCl_3$, 126 MHz

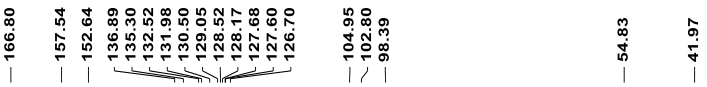


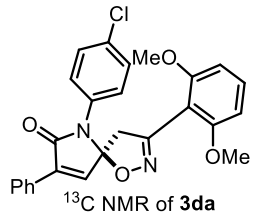


^{1}H NMR of **3da**

$CDCl_3$, 500 MHz

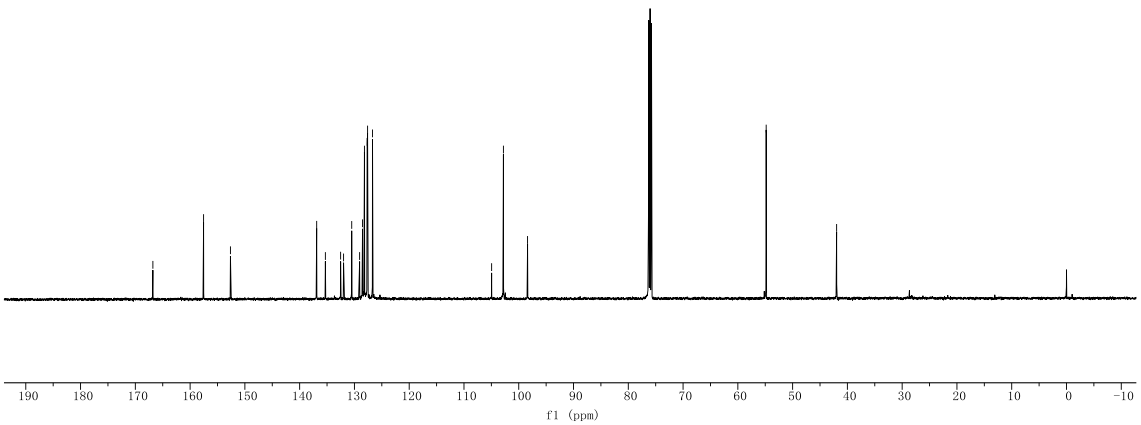


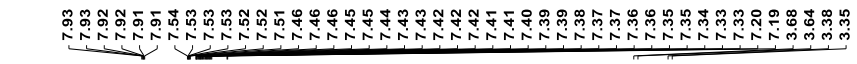


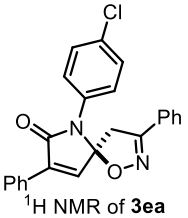


^{13}C NMR of **3da**

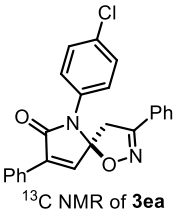
$CDCl_3$, 126 MHz



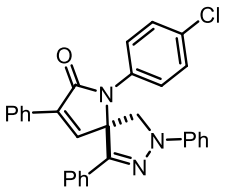




^{1}H NMR of **3ea**
$CDCl_3$, 500 MHz

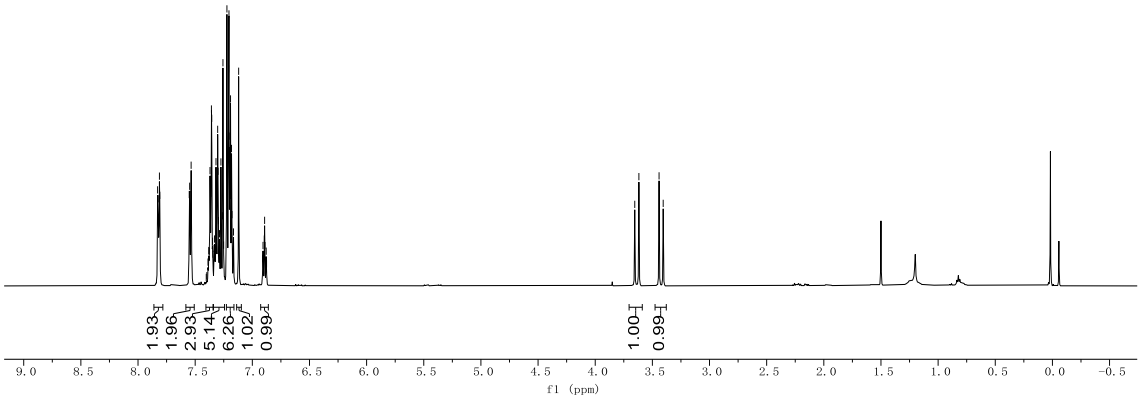


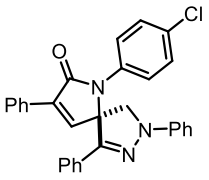
^{13}C NMR of **3ea**
$CDCl_3$, 126 MHz



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

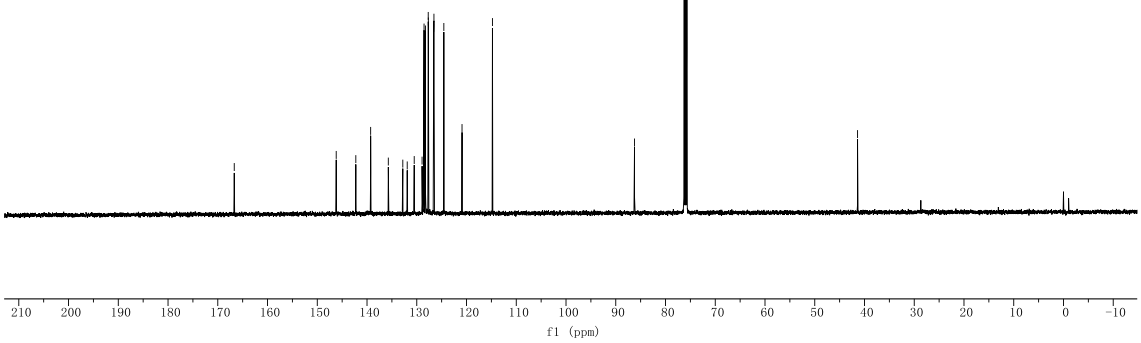
$CDCl_3$, 500 MHz

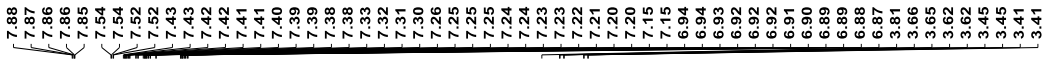


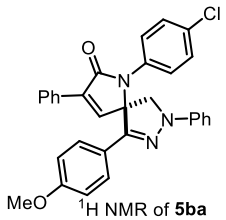


^{13}C NMR of **5aa**

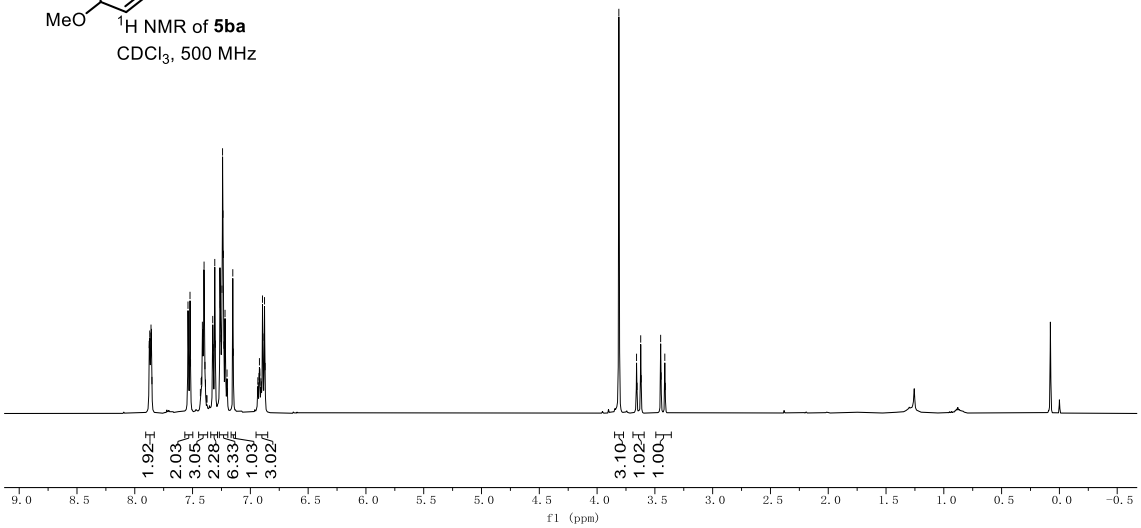
$CDCl_3$, 126 MHz

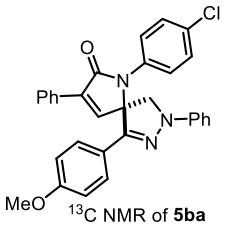




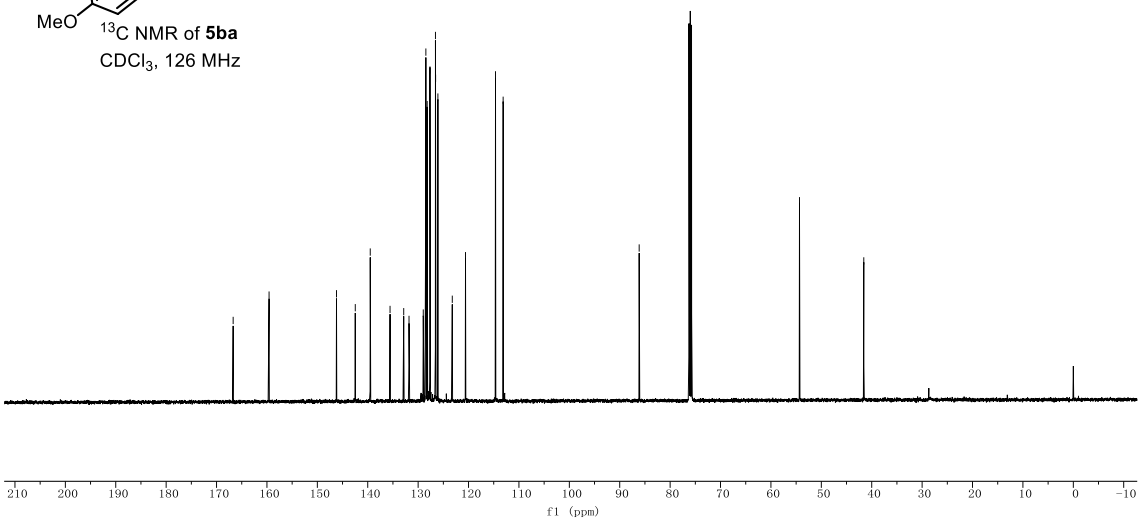


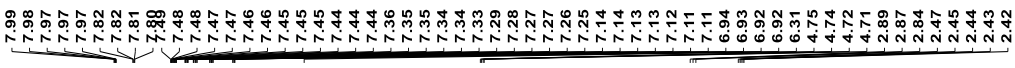
^{1}H NMR of **5ba**
$CDCl_3$, 500 MHz

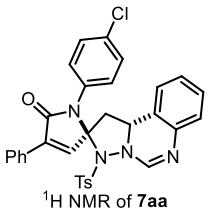




^{13}C NMR of **5ba**
$CDCl_3$, 126 MHz

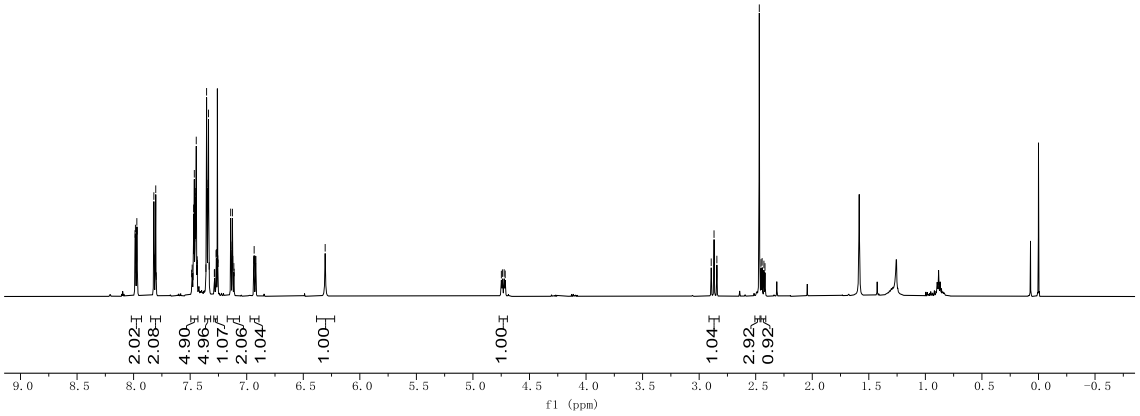


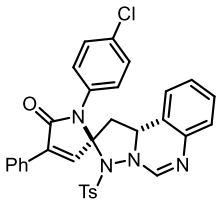




^{1}H NMR of **7aa**

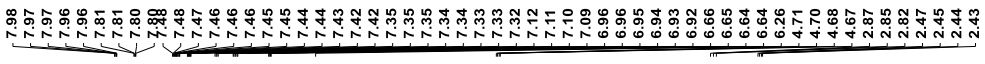
$CDCl_3$, 500 MHz

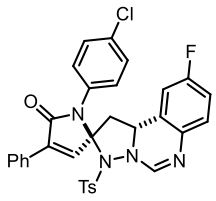




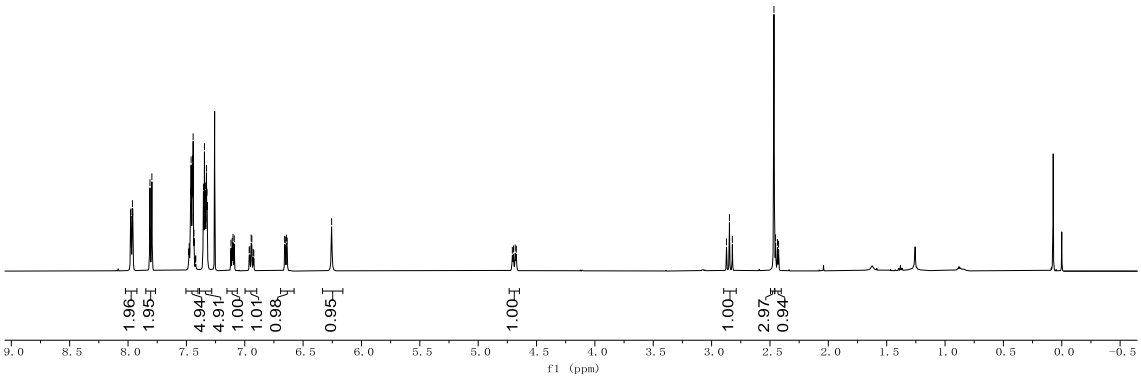
^{13}C NMR of **7aa**

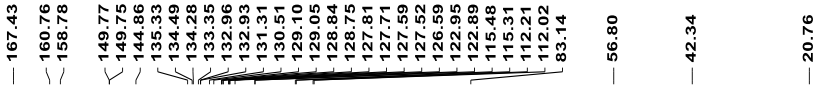
$CDCl_3$, 126 MHz

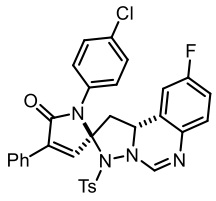




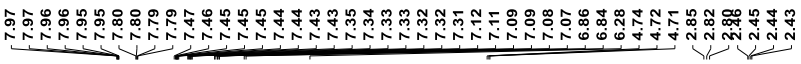
^{1}H NMR of **7ba**
$CDCl_3$, 500 MHz

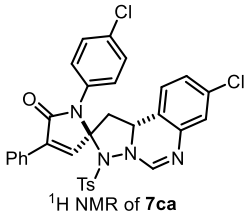






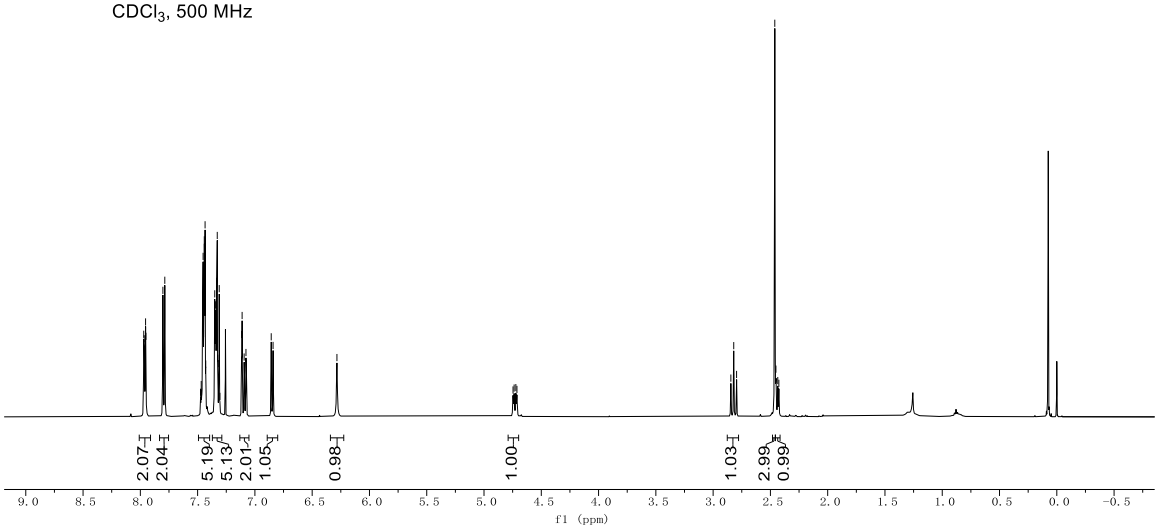
^{13}C NMR of **7ba**
$CDCl_3$, 126 MHz

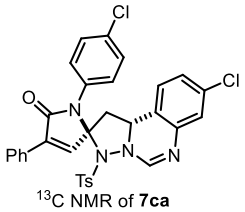




^{1}H NMR of **7ca**

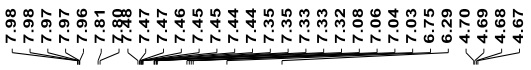
$CDCl_3$, 500 MHz

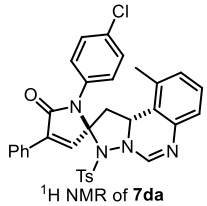




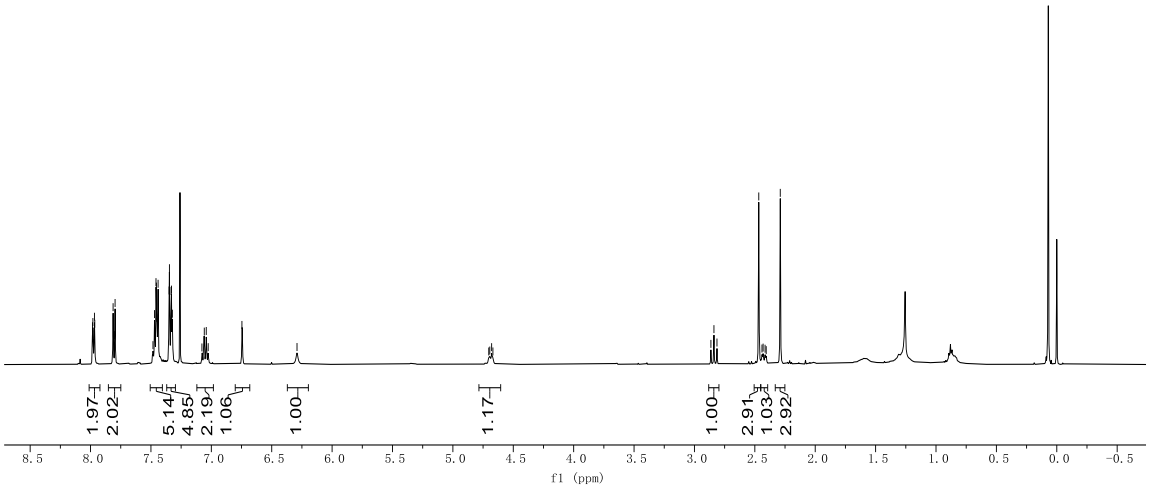
^{13}C NMR of **7ca**

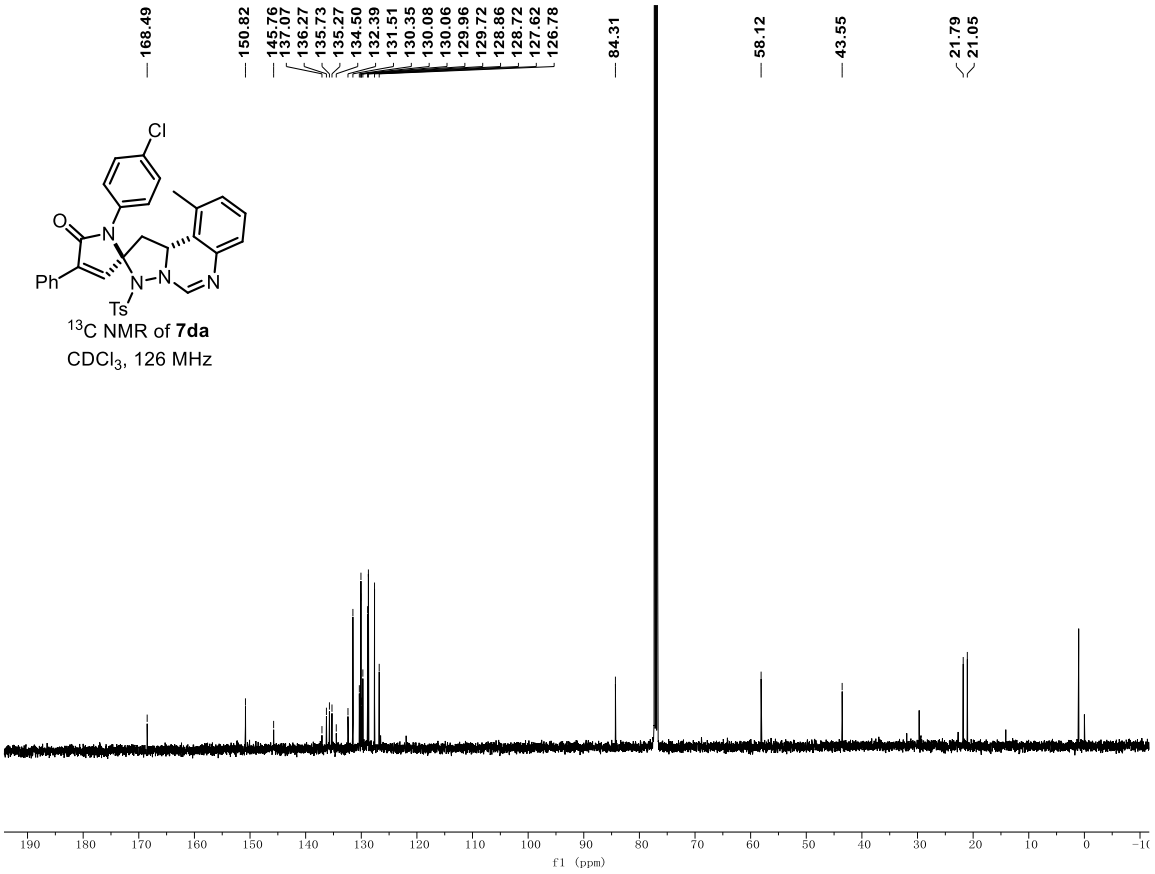
$CDCl_3$, 126 MHz



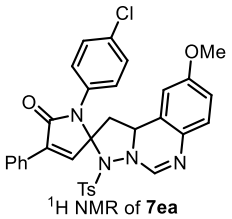


^{1}H NMR of **7da**
$CDCl_3$, 500 MHz



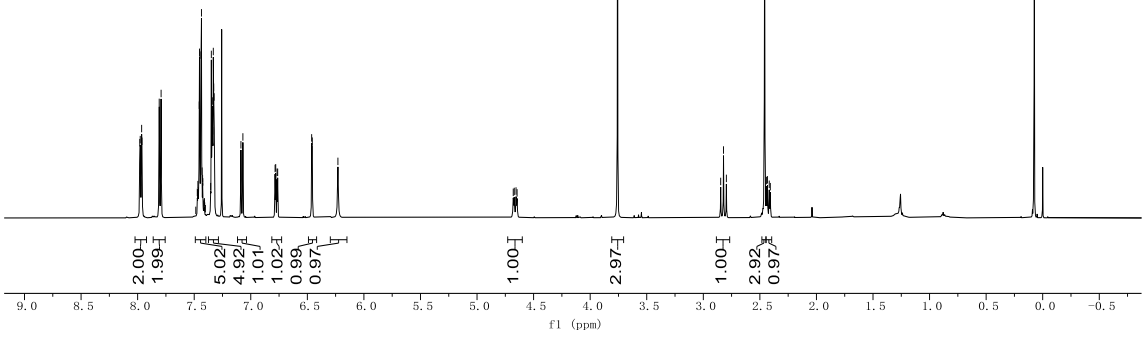


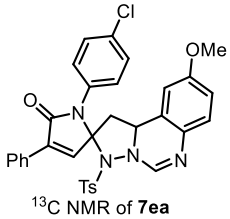
^{13}C NMR of **7da**
$CDCl_3$, 126 MHz



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

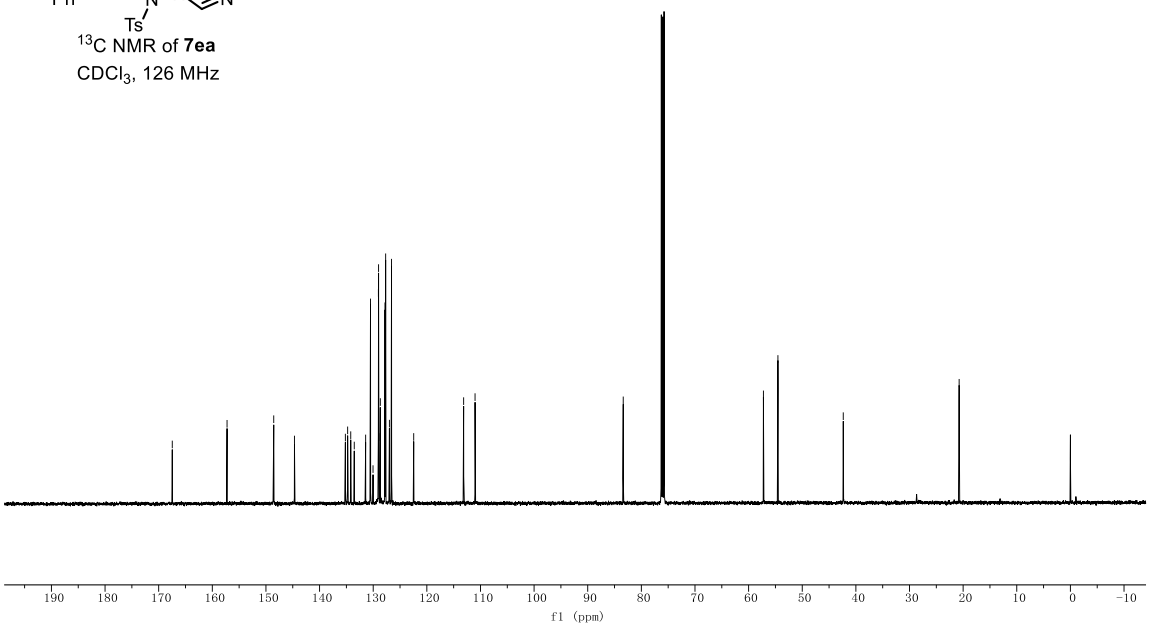
$CDCl_3$, 500 MHz

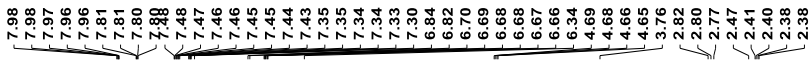


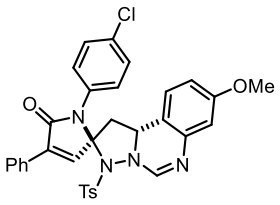


^{13}C NMR of **7ea**

$CDCl_3$, 126 MHz

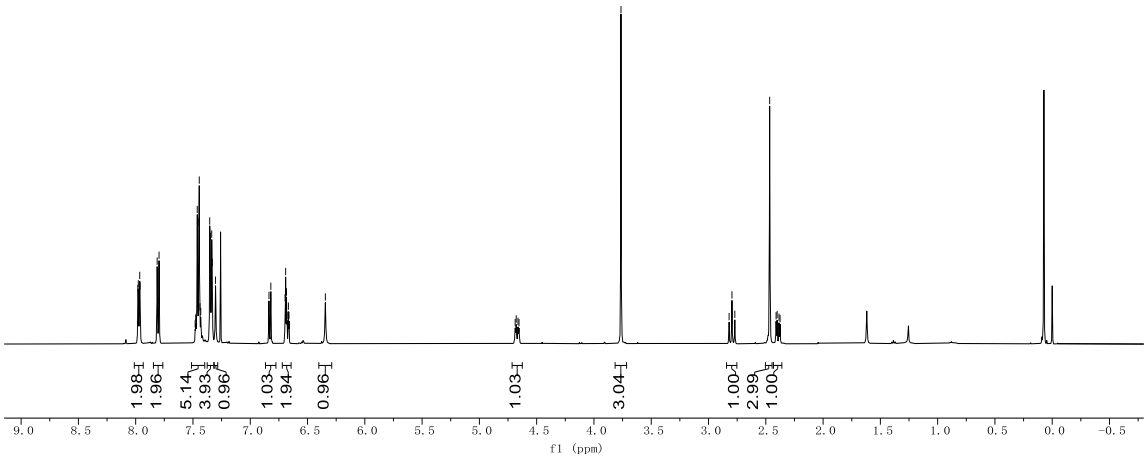


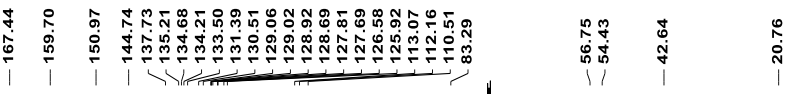


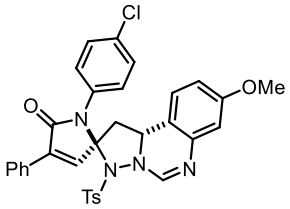


^{1}H NMR of **7fa**

$CDCl_3$, 500 MHz

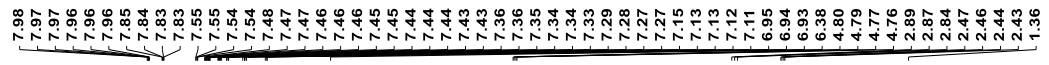


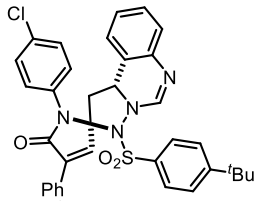




^{13}C NMR of **7fa**

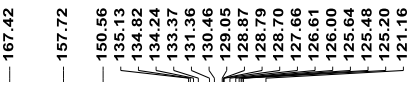
$CDCl_3$, 126 MHz

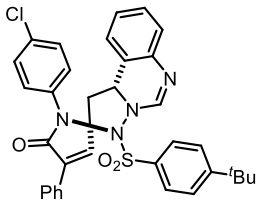




^{1}H NMR of **7ga**

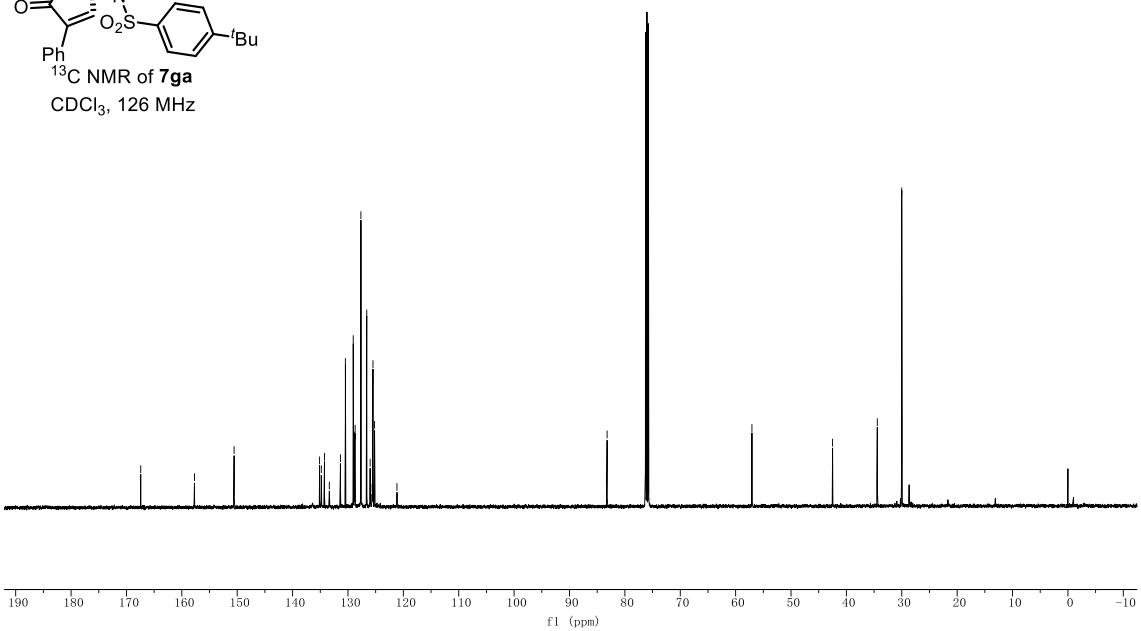
$CDCl_3$, 500 MHz

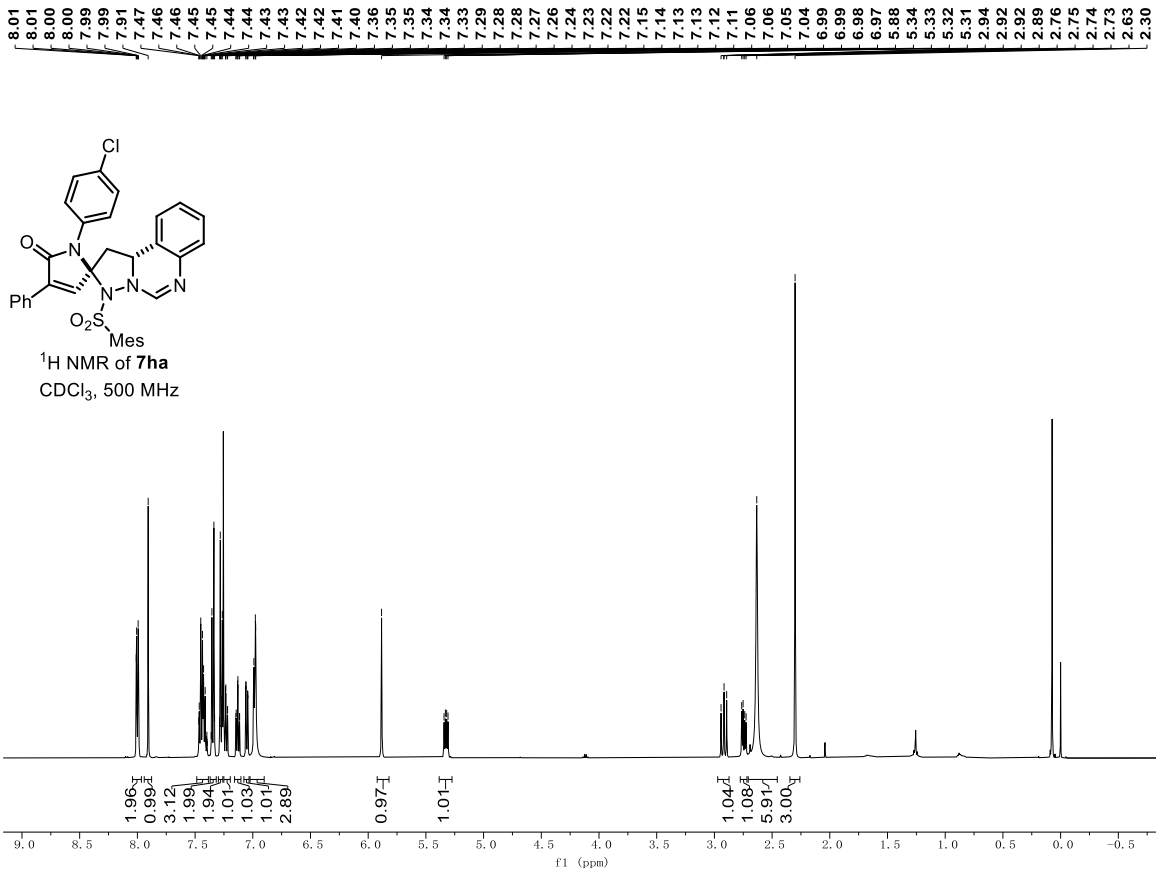


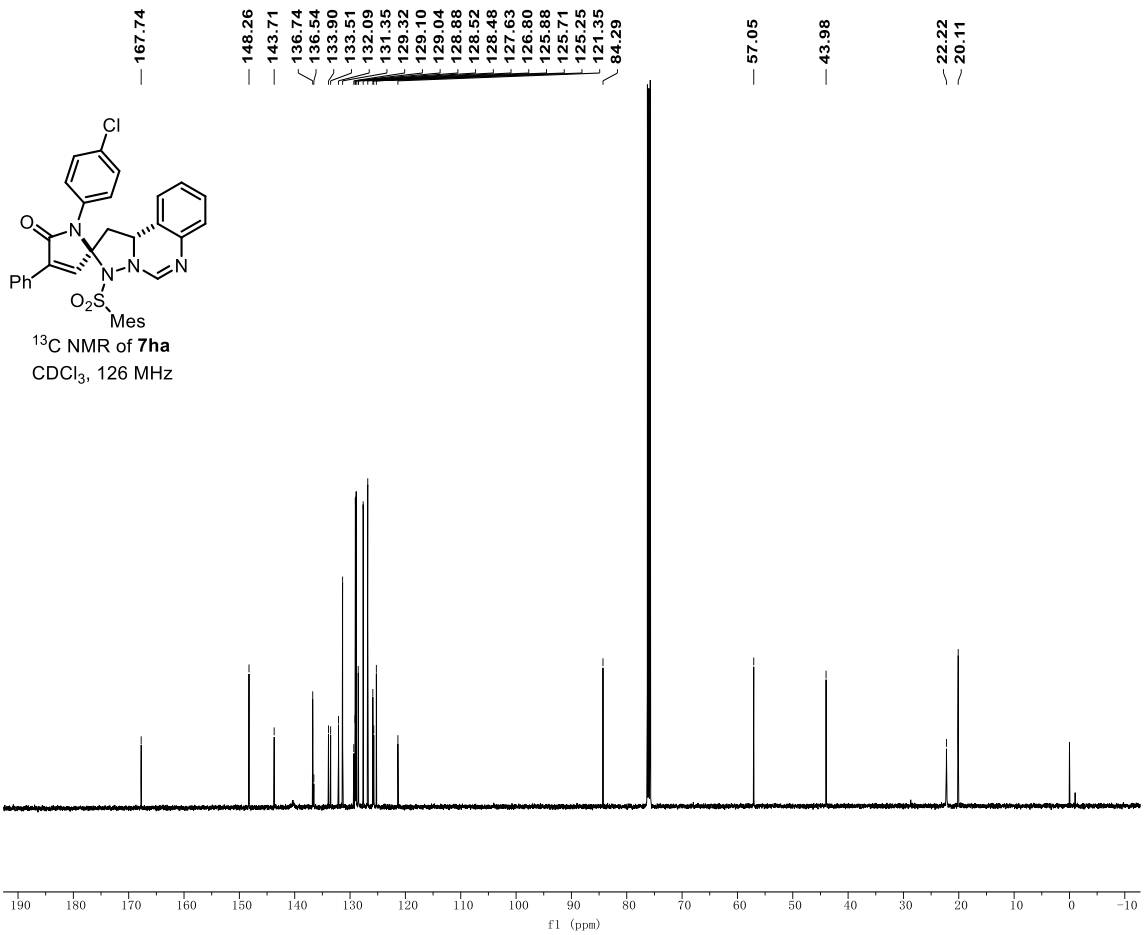


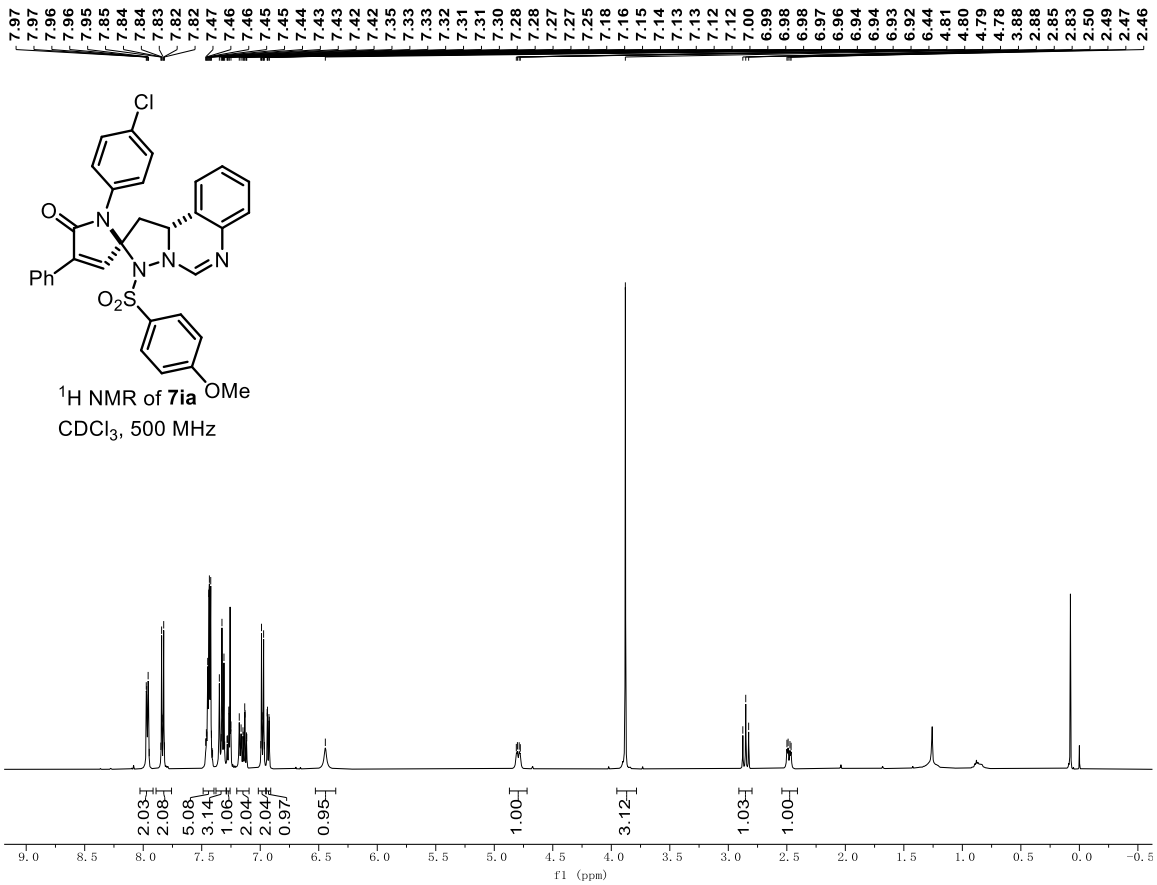
^{13}C NMR of **7ga**

$CDCl_3$, 126 MHz

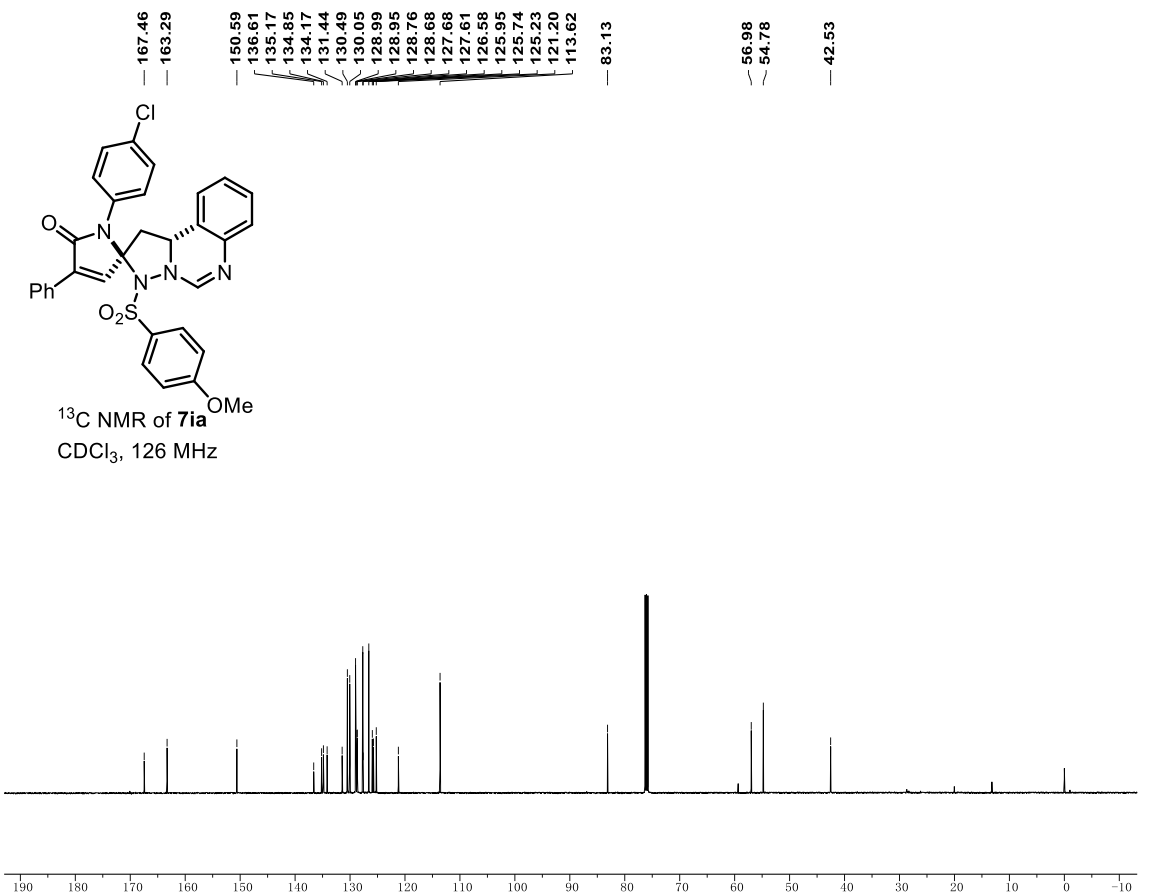



Cl
O
N
Ph
N
N
N
O2S
Mes
1H NMR of 7ha
CDCl3, 500 MHz
f1 (ppm)

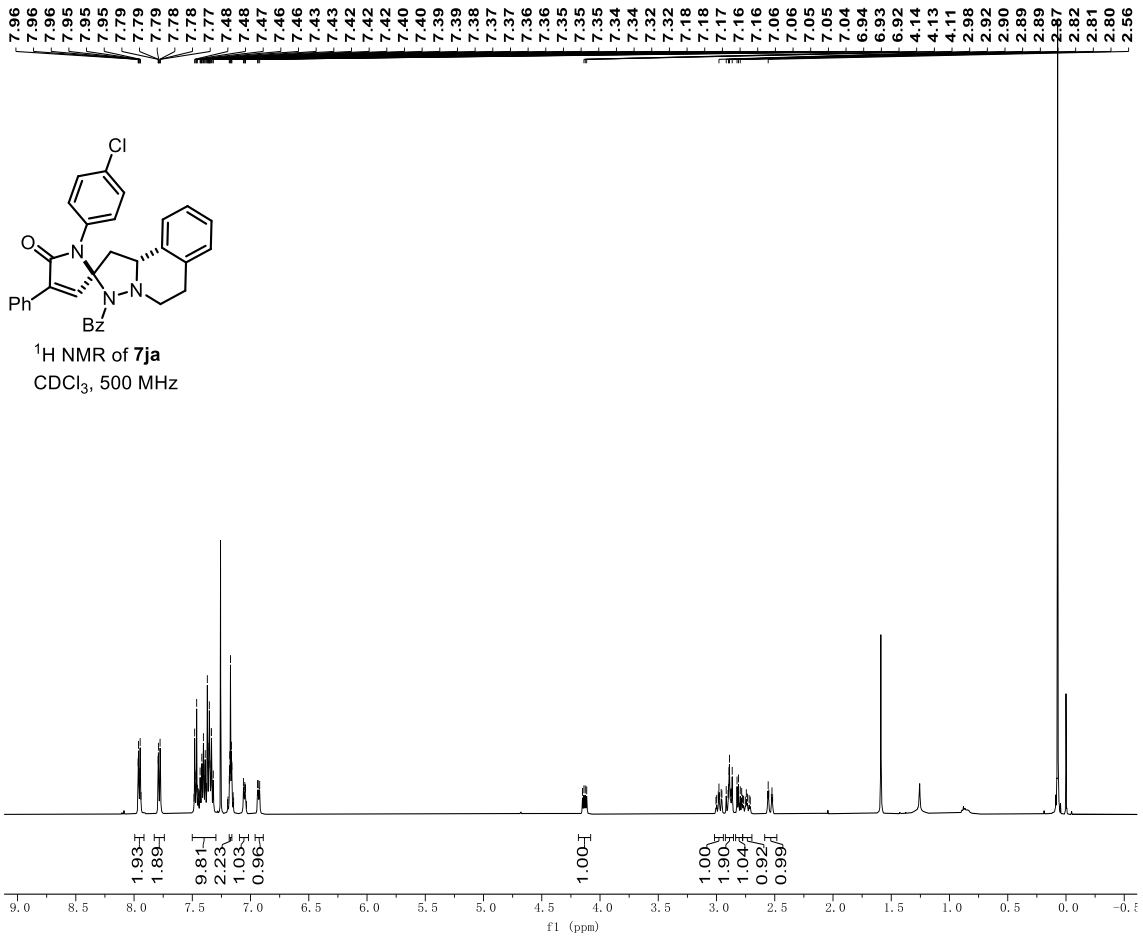

Cl
O
N
Ph
N
N
N
O2S
Mes
13C NMR of 7ha
CDCl3, 126 MHz
f1 (ppm)



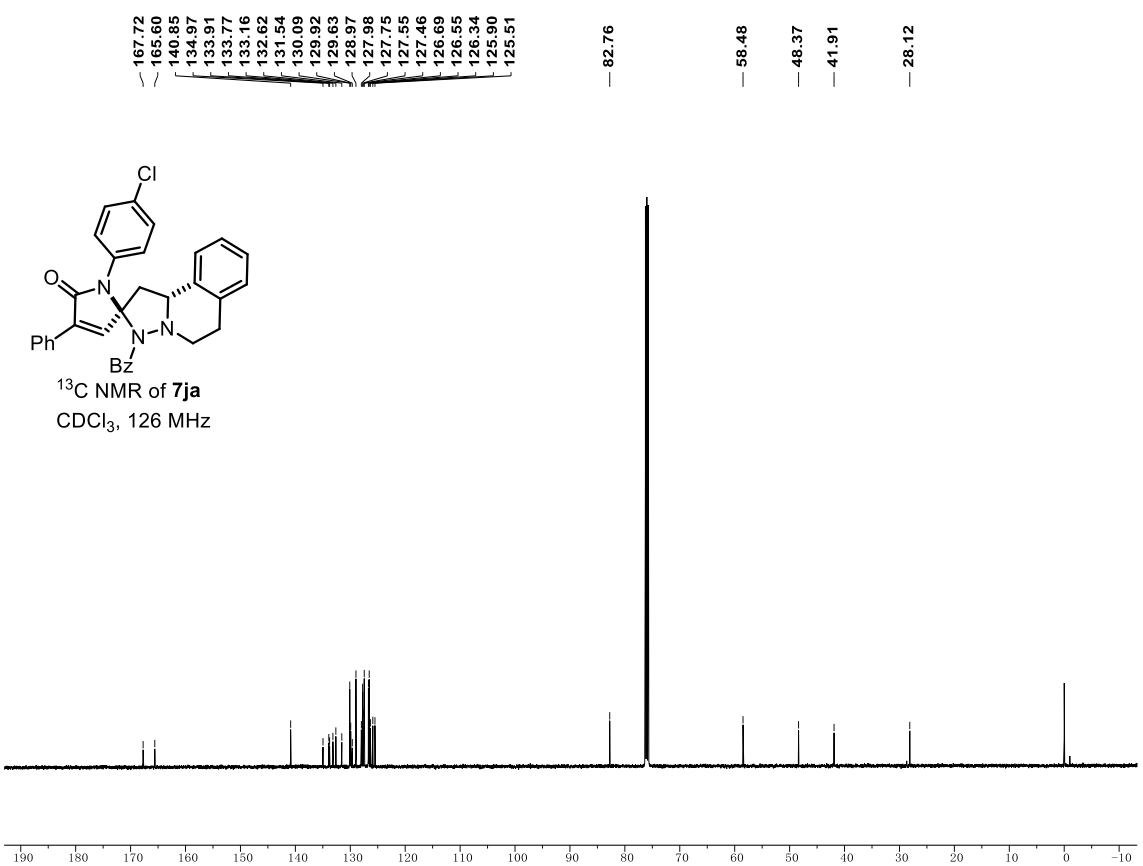
^{1}H NMR of **7ia**
$CDCl_3$, 500 MHz



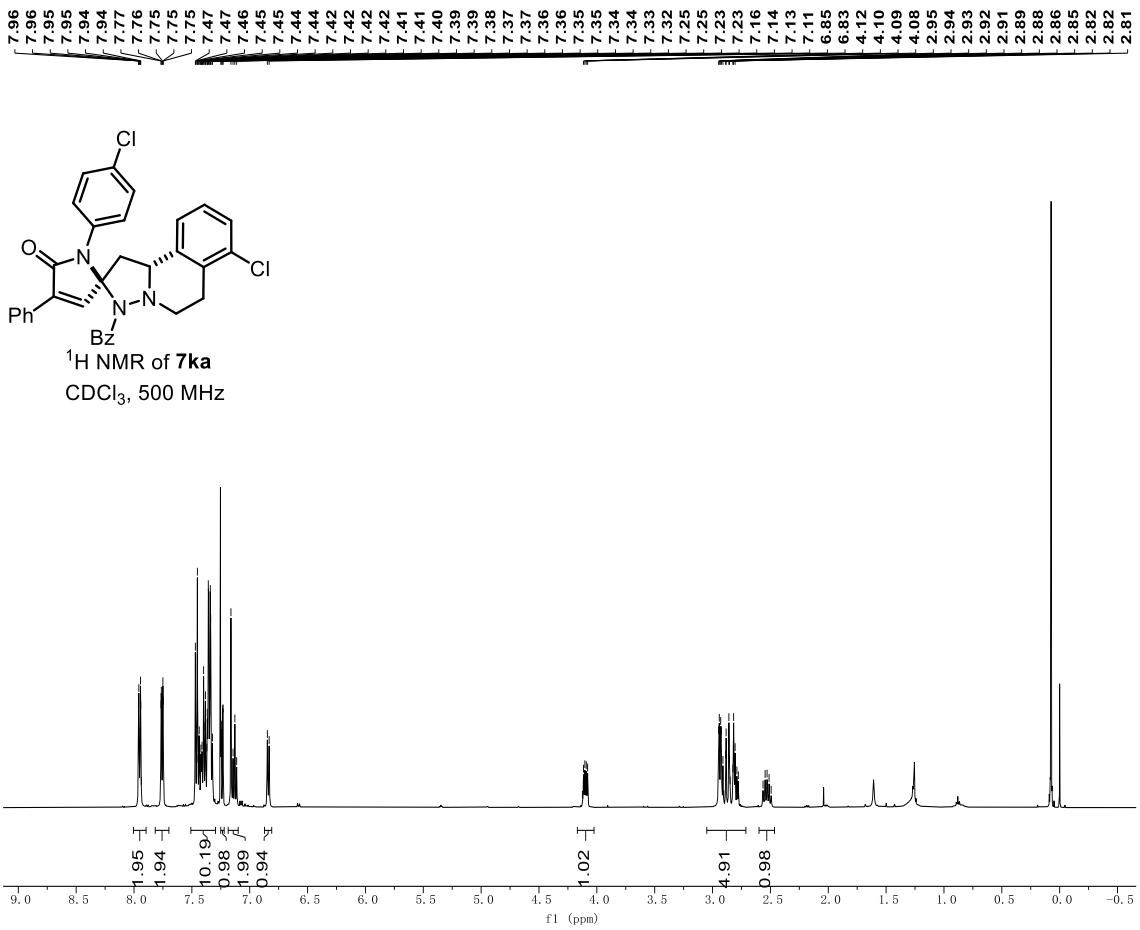
^{13}C NMR of **7ia**
$CDCl_3$, 126 MHz

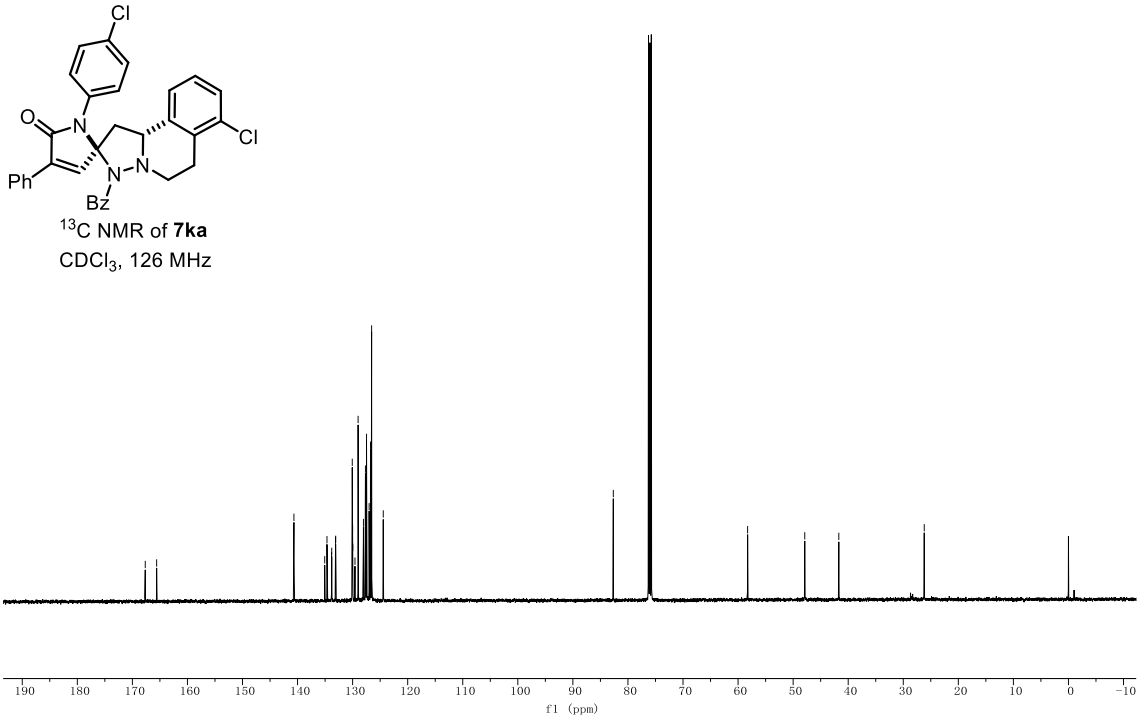


^{1}H NMR of **7ja**
$CDCl_3$, 500 MHz



^{13}C NMR of **7ja**
$CDCl_3$, 126 MHz


Cl
O
N
Cl
Ph
N
N
Bz
1H NMR of 7ka
CDCl3, 500 MHz
1.95
1.94
10.19
0.98
1.99
0.94
1.02
4.91
0.98
f1 (ppm)


Cl
O
N
Cl
Ph
N
N
Bz
13C NMR of 7ka
CDCl3, 126 MHz
167.66
165.59
140.66
135.07
134.66
133.82
133.79
133.11
133.07
130.07
130.01
129.96
129.57
129.01
128.04
127.67
127.47
127.00
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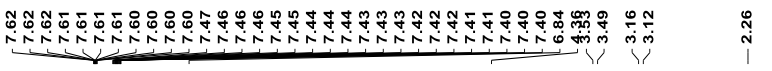
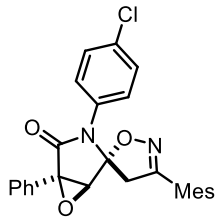
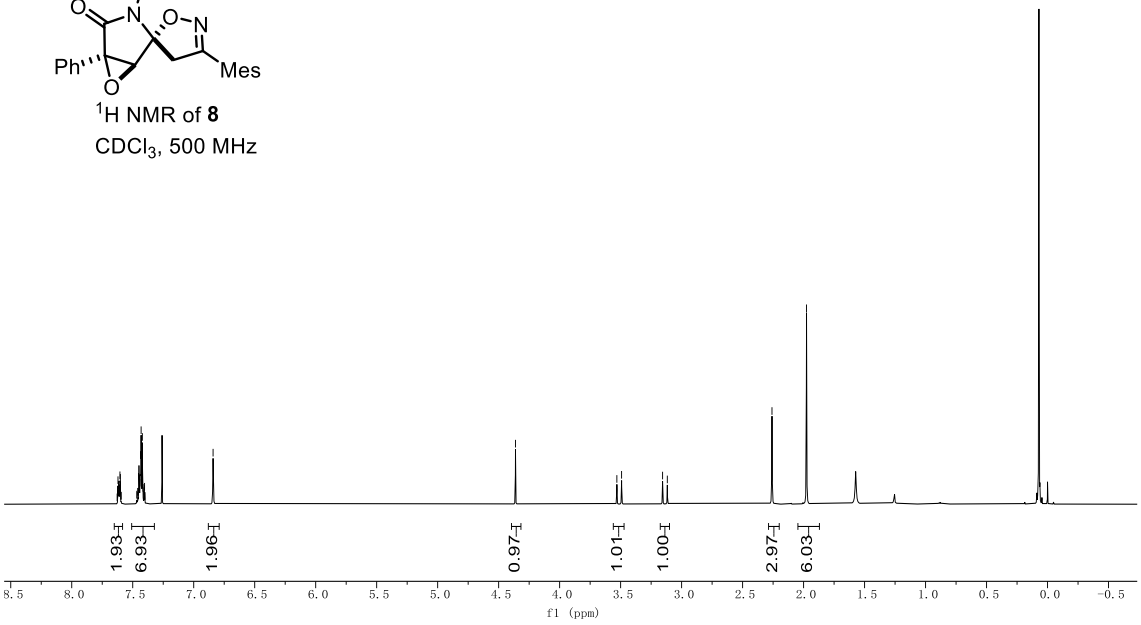
58.27
47.89
41.70
26.19
f1 (ppm)

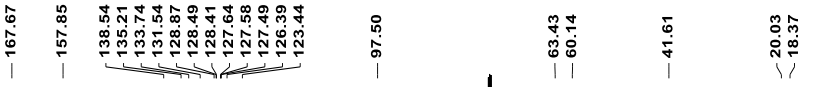


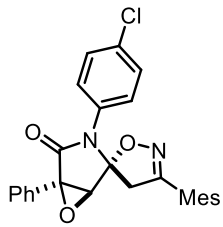


^{1}H NMR of **8**

$CDCl_3$, 500 MHz







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

$CDCl_3$, 126 MHz

X-Ray Crystallographic Data of 3aa, 7ja and 8

Crystallographic data for **3aa**, **7ja** and **8** have been deposited with the Cambridge Crystallographic Data Centre as deposition number 2293891, 2293893 and 2293898, respectively. These data can be obtained free of charge via www.ccdc.cam. ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of **3aa** were obtained by slow evaporation of a solution containing **3aa** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **3aa** are listed in the Table S1.

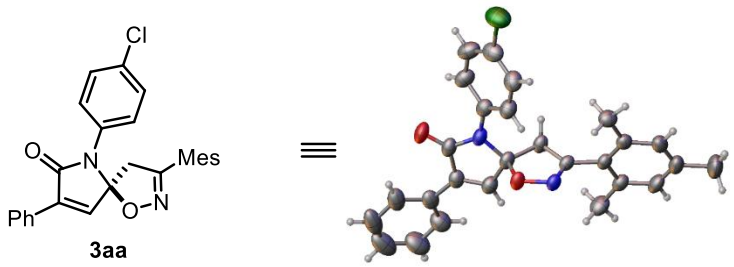


Figure S1. ORTEP view of the compound **3aa** with thermal ellipsoids drawn at the 50% probability level

Table S1. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**
Empirical formula	$C_{27}H_{23}ClN_2O_2$
Formula weight	442.92
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8079(5)
b/Å	20.5558(11)
c/Å	22.6273(12)
α/°	90
β/°	94.844(2)
γ/°	90
Volume/ $Å^3$	4545.6(4)

Z	8
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.195
F(000)	1856.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.682 to 52.754
Index ranges	-12 ≤ h ≤ 9, -18 ≤ k ≤ 25, -28 ≤ l ≤ 27
Reflections collected	42097
Independent reflections	9237 [R_{int} = 0.0611, R_{sigma} = 0.0433]
Data/restraints/parameters	9237/0/583
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1301
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1423
Largest diff. peak/hole / e Å^{-3}	0.20/-0.36

Single crystals of **7ja** were obtained by slow evaporation of a solution containing **7ja** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **7ja** are listed in the Table S2.

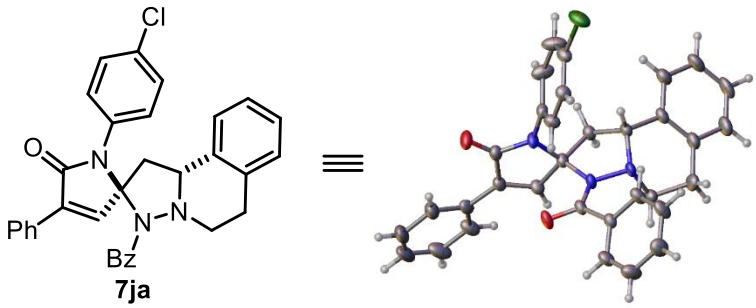


Figure S2. ORTEP view of the compound **7ja** with thermal ellipsoids drawn at the 50% probability level

Table S2. Crystal data and structure refinement for **7ja**.

Identification code	**7ja**
Empirical formula	$C_{33}H_{26}ClN_3O_2$

Formula weight	532.046
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1281(2)
b/Å	17.8377(2)
c/Å	13.6750(2)
α/°	90
β/°	102.387(1)
γ/°	90
Volume/ $Å^3$	2651.29(7)
Z	4
$\rho_{calc}g/cm^3$	1.333
μ/mm^{-1}	1.562
F(000)	1116.7
Crystal size/mm^3	0.3 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.14 to 151.64
Index ranges	$-13 \leq h \leq 13$, $-21 \leq k \leq 22$, $-11 \leq l \leq 17$
Reflections collected	18334
Independent reflections	5394 [R_{int} = 0.0397, R_{sigma} = 0.0293]
Data/restraints/parameters	5394/0/352
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0410, wR_2 = 0.0916
Final R indexes [all data]	R_1 = 0.0455, wR_2 = 0.0951
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.49

Single crystals of **8** were obtained by slow evaporation of a solution containing **8** in the mixture of petroleum ether and ethyl acetate at room temperature. A suitable crystal was selected and the crystal data and structure refinement results for compound **8** are listed in the Table S3.

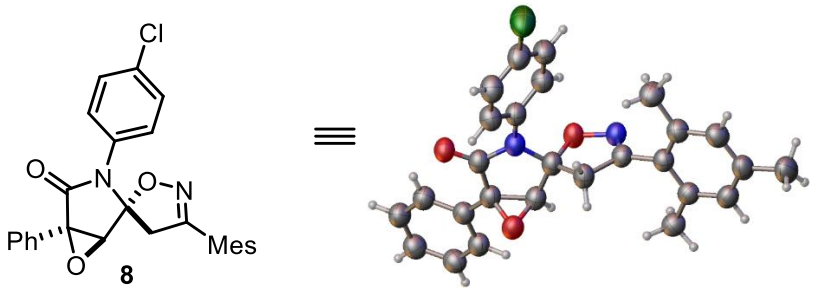


Figure S3. ORTEP view of the compound **8** with thermal ellipsoids drawn at the 50% probability level

Table S3. Crystal data and structure refinement for **8**

Identification code	**8**
Empirical formula	$C_{27}H_{23.5}ClN_2O_{3.25}$
Formula weight	463.43
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.2073(3)
b/Å	14.4300(5)
c/Å	18.0454(5)
α/°	76.612(2)
β/°	83.712(2)
γ/°	82.660(2)
Volume/Å^3	2305.32(13)
Z	4
ρ_{calc}g/cm^3	1.335
μ/mm-1	1.738
F(000)	970.0
Crystal size/mm^3	0.15 × 0.12 × 0.1

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.052 to 149.788
Index ranges	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$
Reflections collected	29955
Independent reflections	9422 [R_{int} = 0.0381, R_{sigma} = 0.0454]
Data/restraints/parameters	9422/0/609
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0781, wR_2 = 0.2103
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.2210
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.71