Supporting Information

Diastereoselective construction of bridged piperidines through an interrupted dearomative reduction

Huabin Han, Lele Wang, Xinyue Niu, Chaoyang Li, Yuanqing Xu,* and Qilin Wang*

College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

E-mail: wangqilin@henu.edu.cn, xuyuanqing@henu.edu.cn

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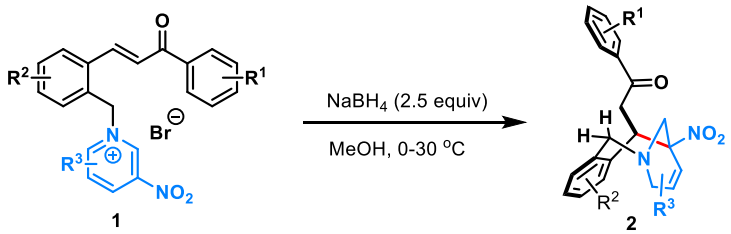
1. General methods

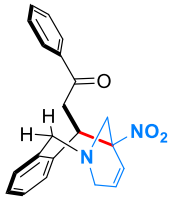
NMR spectra were recorded with tetramethylsilane as the internal standard. For compound **4**, ^{1}H NMR spectra were recorded at 400 MHz (Bruker Avance) and ^{13}C NMR spectra were recorded at 125 MHz (Bruker Avance). For compound **10**, ^{1}H NMR spectra were recorded at 300 MHz (Bruker Avance) and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). For compound **11**, ^{1}H NMR spectra were recorded at 300 MHz (Bruker Avance), and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). For other products, ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). For compounds **2f**, **2l**, **2m** and **2n**, ^{19}F NMR spectra were recorded at 376 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

2. Experimental data for the formation of 2-7



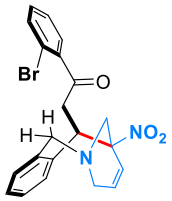
General procedure: A solution of pyridinium salts **1** (0.2 mmol) in 1.0 mL of MeOH was cooled to 0 °C, and then $NaBH_4$ (18.9 mg, 0.50 mmol) was added successively. The reaction mixture was warmed to 30 °C until the complete consumption of **1** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **2**. It was of note that when R^1 was

3,4-dimethoxyl group, **2h** was produced in 57% yield together with the formation of un-cyclized product **3** in 16% yield.



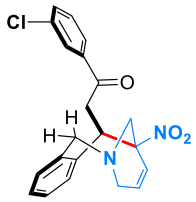
2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one (**2a**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 54.8 mg, 79% yield; dr > 20:1; reaction time = 12 h; mp 136.4-137.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 16.0 Hz, 3H), 5.97 (d, *J* = 16.0 Hz, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 3.93 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.58 (d, *J* = 20.0 Hz, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 3.39 (d, *J* = 12.0 Hz, 1H), 2.98 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 138.3, 136.6, 133.2, 132.4, 131.6, 131.0, 128.6, 127.9, 127.7, 127.0, 126.4, 85.2, 61.0, 53.7, 49.8, 48.5, 39.0, one carbon missing in the aromatic region. IR (KBr) ν 3426, 2920, 1689, 1534, 759 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{21}N_2O_3$ $[M+H]^+$: 349.1547, found: 349.1546.



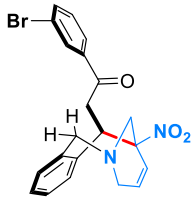
1-(2-bromophenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2b**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 3:1); 40.4 mg, 47% yield; dr > 20:1; reaction time = 24 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.28-7.20 (m, 3H), 7.17-7.11 (m, 2H), 7.08-7.04 (m, 2H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.62 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 8.0 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 4.00-3.88 (m, 2H), 3.72 (d, *J* = 16.0 Hz, 1H), 3.63-3.53 (m, 2H), 3.26 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.96 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 141.1, 138.5, 137.8, 133.4, 132.3, 131.6, 131.6, 130.8, 128.2, 127.7, 127.3, 127.1, 126.1, 118.2, 84.9, 60.8, 53.6, 49.7, 48.4, 42.8. IR (KBr) ν 3415, 2921, 1703, 762 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}BrN_2O_3$ $[M+H]^+$: 427.0652, found: 427.0659.



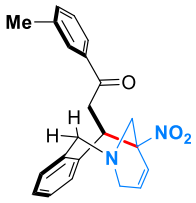
1-(3-chlorophenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2c**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 47.1 mg, 62% yield; dr > 20:1; reaction time = 12 h; mp 151.8-152.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.34 (s, 1H), 7.25 (s, 1H), 7.09 (d, *J* = 16.0 Hz, 3H), 5.96 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 12.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.77 (d, *J* = 12.0 Hz, 1H), 3.61-3.36 (m, 3H), 2.98 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 138.3, 138.2, 138.0, 134.9, 133.1, 132.3, 131.7, 131.1, 129.9, 128.0, 127.7, 127.1, 126.2, 126.0, 85.1, 61.0, 53.8, 49.5, 48.5, 39.1. IR (KBr) ν 3420, 2867, 1692, 1638, 801 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}ClN_2O_3$ $[M+H]^+$: 383.1157, found: 383.1156.



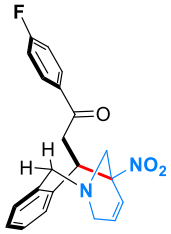
1-(3-bromophenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2d**)

Red solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1); 43.4 mg, 51% yield; dr > 20:1; reaction time = 16 h; mp 144.5-145.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.13 (d, *J* = 4.0 Hz, 2H), 7.07 (s, 1H), 5.97 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.61-3.36 (m, 3H), 2.99 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 138.3, 138.2, 138.2, 136.1, 132.4, 131.7, 131.1, 131.0, 130.2, 127.8, 127.2, 126.5, 126.3, 123.0, 85.1, 61.0, 53.8, 49.5, 48.5, 39.1. IR (KBr) ν 3427, 2922, 1632, 796 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}BrN_2O_3$ $[M+H]^+$: 427.0652, found: 427.0651.



2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-(*m*-tolyl)ethan-1-one (**2e**)

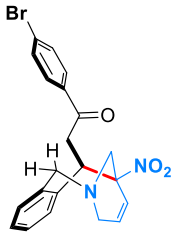
Yellow solid obtained by column chromatography (dichloromethane as the eluent); 46.8 mg, 65% yield; dr > 20:1; reaction time = 7 h; mp 154.9-155.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.34-7.24 (m, 3H), 7.11-7.06 (m, 3H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.10 (d, *J* = 12.0 Hz, 1H), 3.93 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 12.0 Hz, 1H), 3.60-3.48 (m, 2H), 3.38 (d, *J* = 16.0 Hz, 1H), 2.98 (d, *J* = 20.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 138.4, 138.4, 136.6, 134.0, 132.4, 131.6, 131.0, 128.5, 128.4, 127.7, 127.0, 126.4, 125.1, 85.2, 61.0, 53.7, 49.8, 48.5, 39.0, 21.3, one carbon missing in the aromatic region. IR (KBr) ν 3425, 2917, 1685, 1527, 772 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1703.



1-(4-fluorophenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2f**)

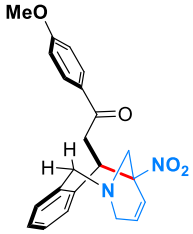
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 32.9 mg, 45% yield; dr > 20:1; reaction time = 7 h; mp 156.3-157.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (q, *J* = 4.0 Hz, 2H), 7.24-7.22 (m, 1H), 7.15-7.05 (m, 5H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.64 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.79 (d, *J* = 16.0 Hz, 1H), 3.63-3.57 (m, 1H), 3.49 (dd, J_1 = 20.0 Hz, J_2 = 12.0 Hz, 1H), 3.37 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 2.99 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 165.7 (d, *J* = 254.0 Hz, 1C), 138.3, 138.2, 132.9 (d, *J* = 3.0 Hz, 1C), 132.4, 131.7, 131.1, 130.7 (d, *J* = 10.0 Hz, 1C), 127.8, 127.1, 126.3, 115.7 (d, *J* = 22.0 Hz, 1C), 85.2, 61.0, 53.7, 49.8, 48.5, 38.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.6. IR (KBr) ν 3575, 3064, 1686, 1537, 1230, 762 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}FN_2O_3$ $[M+H]^+$: 367.1458, found:

367.1461.



1-(4-bromophenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2g**)

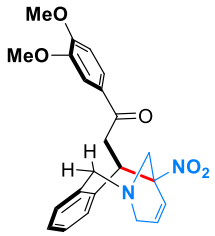
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 41.2 mg, 48% yield; dr > 20:1; reaction time = 12 h; mp 147.4-147.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.13-7.05 (m, 3H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 16.0 Hz, 1H), 4.08 (d, *J* = 16.0 Hz, 1H), 3.93 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.58 (d, *J* = 20.0 Hz, 1H), 3.48 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 3.37 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.98 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 138.4, 138.1, 135.2, 132.3, 131.9, 131.7, 131.1, 129.5, 128.4, 127.8, 127.2, 126.3, 85.2, 61.0, 53.7, 49.8, 48.5, 39.0. IR (KBr) ν 3422, 2971, 1685, 1533, 765 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}BrN_2O_3$ $[M+H]^+$: 427.0652, found: 427.0649.



1-(4-methoxyphenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2h**)

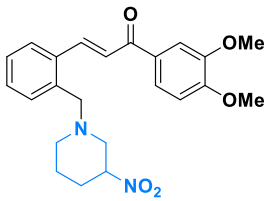
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 62.3 mg, 82% yield; dr > 20:1; reaction time = 12 h; mp 122.4-123.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.24-7.22 (m, 1H), 7.12-7.04 (m, 3H), 6.89 (d, *J* = 12.0 Hz, 2H), 5.98 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 3.93 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 3.79 (d, *J* = 12.0 Hz, 1H), 3.59 (d, *J* = 20.0 Hz, 1H), 3.48 (dd, J_1 = 16.0 Hz, J_2 = 12.0 Hz, 1H), 3.34 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.99 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 163.5, 138.4,

138.3, 132.3, 131.6, 160.9, 130.2, 129.5, 127.6, 126.9, 126.4, 113.6, 85.2, 60.9, 55.3, 53.6, 49.9, 48.5, 38.5. IR (KBr) ν 3417, 2923, 1674, 1602, 1532, 1255, 764 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1652, found: 379.1653.



1-(3,4-dimethoxyphenyl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)ethan-1-one (**2i**)

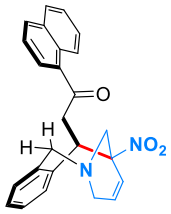
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 2:1); 45.7 mg, 57% yield; dr > 20:1; reaction time = 21 h; mp 128.6-129.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 1H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.06 (d, *J* = 12.0 Hz, 3H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.95 (d, *J* = 12.0 Hz, 1H), 5.61 (d, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.77 (d, *J* = 16.0 Hz, 1H), 3.57 (d, *J* = 16.0 Hz, 1H), 3.46 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 3.33 (d, *J* = 12.0 Hz, 1H), 2.98 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 153.3, 149.0, 138.3, 138.2, 132.3, 131.7, 131.0, 129.7, 127.6, 127.0, 126.4, 122.5, 110.1, 109.9, 85.3, 61.0, 56.0, 55.9, 53.5, 50.3, 48.5, 38.4. IR (KBr) ν 3419, 2923, 1673, 1525, 765 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{25}N_2O_5$ $[M+H]^+$: 409.1758, found: 409.1758.



(*E*)-1-(3,4-dimethoxyphenyl)-3-(2-((3-nitropiperidin-1-yl)methyl)phenyl)prop-2-en-1-one (**3**)

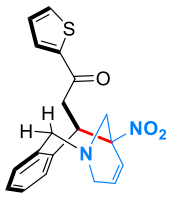
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 13.4 mg, 16% yield; reaction time = 21 h; mp 136.4-137.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 16.0 Hz, 1H), 7.73 (d, *J* = 4.0 Hz, 1H), 7.70 (d, *J* = 12.0 Hz, 1H), 7.64 (s, 1H), 7.43 (d, *J* = 16.0 Hz, 1H), 7.37-7.31 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.44-4.39 (m, 1H), 3.98 (s, 6H), 3.69 (q, *J* = 16.0 Hz, 2H), 3.12 (d, *J* = 4.0 Hz, 1H), 2.74-2.63 (m, 2H), 2.28-2.17 (m, 2H), 1.97-1.89 (m, 1H), 1.86-1.81 (m, 1H), 1.65-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 153.2, 149.3, 141.9,

137.2, 135.2, 131.3, 130.7, 129.7, 128.0, 126.9, 123.1, 123.0, 110.8, 109.9, 81.2, 60.4, 56.1, 56.0, 55.3, 52.8, 28.5, 23.1. IR (KBr) ν 3422, 2924, 2381, 1597, 1265, 763 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{27}N_2O_5$ $[M+H]^+$: 411.1914, found: 411.1914.



1-(naphthalen-1-yl)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[c]azonin-7-yl)ethan-1-one (**2j**)

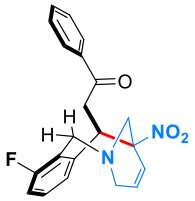
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 16.7 mg, 21% yield; dr > 20:1; reaction time = 24 h; mp 55.8-56.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.13 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.84-7.83 (m, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51-7.41 (m, 3H), 7.21-7.19 (m, 1H), 7.16-7.08 (m, 3H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.64 (d, *J* = 12.0 Hz, 1H), 4.55 (t, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.62-3.55 (m, 2H), 3.47 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.99 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 138.2, 138.2, 135.8, 133.8, 132.6, 132.3, 131.6, 131.1, 129.9, 128.3, 127.9, 127.8, 127.2, 126.9, 126.5, 126.3, 125.5, 124.3, 85.2, 61.0, 53.6, 50.4, 48.5, 42.5. IR (KBr) ν 3409, 2924, 1684, 1535, 769 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{23}N_2O_3$ $[M+H]^+$: 399.1709, found: 399.1714.



2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-(thiophen-2-yl)ethan-1-one (**2k**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 2:1); 37.9 mg, 54% yield; dr > 20:1; reaction time = 15 h; mp 160.6-161.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 8.0 Hz, 2H), 7.22-7.19 (m, 1H), 7.14-7.05 (m, 4H), 5.96 (d, *J* = 8.0 Hz, 1H), 5.64-5.61 (m, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.62-3.56 (m, 1H), 3.47 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 3.30 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.99 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (100

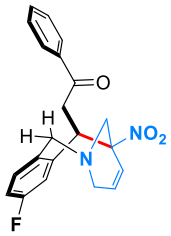
MHz, $CDCl_3$) δ 188.9, 143.6, 138.2, 137.9, 133.9, 132.4, 131.8, 131.7, 131.0, 128.1, 127.8, 127.1, 126.3, 85.2, 61.0, 53.5, 50.2, 48.5, 39.6. IR (KBr) ν 3093, 3021, 1661, 1535, 1301, 764 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{19}N_2O_3S$ $[M+H]^+$: 355.1116, found: 355.1122.



2-(11-fluoro-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one

(**2l**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 34.7 mg, 47% yield; dr > 20:1; reaction time = 7 h; mp 166.6-167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 4.0 Hz, 2H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.07 (s, 2H), 6.87 (s, 1H), 5.98 (d, *J* = 12.0 Hz, 1H), 5.67 (d, *J* = 12.0 Hz, 1H), 4.59 (t, *J* = 12.0 Hz, 2H), 4.08 (d, *J* = 16.0 Hz, 1H), 3.81 (dd, J_1 = 20.0 Hz, J_2 = 16.0 Hz, 2H), 3.63-3.50 (m, 2H), 3.41 (d, *J* = 16.0 Hz, 1H), 2.96 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 161.3 (d, *J* = 243.0 Hz, 1C), 141.0, 136.4, 133.3, 131.7, 128.7, 128.6, 128.5, 127.9, 126.0, 125.2 (d, *J* = 13.0 Hz, 1C), 114.3 (d, *J* = 24.0 Hz, 1C), 84.8, 53.8, 49.6, 49.5, 48.8, 38.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.4. IR (KBr) ν 3423, 2926, 1689, 1535, 765 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}FN_2O_3$ $[M+H]^+$: 367.1452, found: 367.1445.

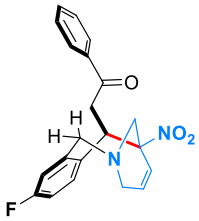


2-(9-fluoro-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one

(**2m**)

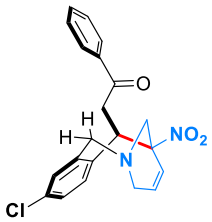
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 6:1); 35.3 mg, 48% yield; dr > 20:1; reaction time = 24 h; mp 151.9-152.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.06-6.99 (m, 2H), 6.81-6.76 (m, 1H), 5.97 (d, *J* = 12.0 Hz, 1H), 5.65 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.92 (d, *J* = 16.0 Hz, 1H),

3.77 (d, J = 12.0 Hz, 1H), 3.62-3.50 (m, 2H), 3.40 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.97 (d, J = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 161.7 (d, J = 248.0 Hz, 1C), 140.5 (d, J = 7.0 Hz, 1C), 136.4, 134.2 (d, J = 3.0 Hz, 1C), 133.4, 132.4 (d, J = 8.0 Hz, 1C), 131.9, 128.7, 127.9, 126.2, 119.6 (d, J = 22.0 Hz, 1C), 113.4 (d, J = 20.0 Hz, 1C), 85.0, 60.2, 53.7, 49.3, 48.5, 38.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8. IR (KBr) ν 3425, 2925, 1688, 1536, 775 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}FN_2O_3$ $[M+H]^+$: 367.1452, found: 367.1451.



2-(10-fluoro-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one (**2n**)

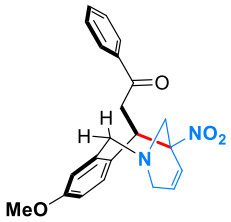
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 6:1); 38.1 mg, 52% yield; dr > 20:1; reaction time = 24 h; mp 134.6-135.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 4.0 Hz, 2H), 7.53 (s, 1H), 7.42 (s, 2H), 7.24 (d, J = 4.0 Hz, 1H), 6.78 (s, 2H), 5.96 (d, J = 8.0 Hz, 1H), 5.66 (d, J = 8.0 Hz, 1H), 4.51 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 16.0 Hz, 1H), 4.08 (d, J = 12.0 Hz, 1H), 3.82 (dd, J_1 = 16.0 Hz, J_2 = 12.0 Hz, 2H), 3.54 (dd, J_1 = 20.0 Hz, J_2 = 8.0 Hz, 2H), 3.36 (d, J = 16.0 Hz, 1H), 2.99 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 161.3 (d, J = 246.0 Hz, 1C), 141.0 (d, J = 6.0 Hz, 1C), 136.4, 134.2 (d, J = 8.0 Hz, 1C), 134.0 (d, J = 3.0 Hz, 1C), 133.4, 131.7, 128.6, 127.9, 126.3, 117.8 (d, J = 21.0 Hz, 1C), 114.0 (d, J = 20.0 Hz, 1C), 85.1, 60.6, 53.6, 48.9, 48.6, 38.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9. IR (KBr) ν 3424, 3010, 1655, 1608, 768 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}FN_2O_3$ $[M+H]^+$: 367.1452, found: 367.1453.



2-(10-chloro-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one (**2o**)

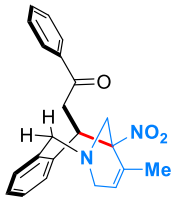
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 8:1 to 6:1);

38.5 mg, 50% yield; dr > 20:1; reaction time = 24 h; mp 129.1-130.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 5.96 (d, *J* = 8.0 Hz, 1H), 5.67 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.87 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.59 (d, *J* = 20.0 Hz, 1H), 3.51 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 3.37 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.99 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 140.5, 136.9, 136.4, 133.9, 133.4, 132.7, 131.8, 130.7, 128.7, 127.9, 127.5, 126.3, 85.0, 60.5, 53.6, 49.0, 48.6, 38.8. IR (KBr) ν 3422, 2927, 1683, 1537, 773 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}ClN_2O_3$ $[M+H]^+$: 383.1157, found: 383.1159.



2-(10-methoxy-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one (**2p**)

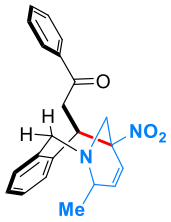
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1 to 3:1); 36.7 mg, 49% yield; dr > 20:1; reaction time = 14 h; mp 146.1-146.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.64-6.61 (m, 2H), 5.98 (d, *J* = 12.0 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.29 (d, *J* = 16.0 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.89 (d, *J* = 12.0 Hz, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 3.62-3.48 (m, 2H), 3.34 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 3.02 (d, *J* = 20.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 158.2, 139.7, 136.6, 133.6, 133.2, 131.6, 130.2, 128.6, 128.0, 126.4, 117.6, 111.4, 85.5, 61.1, 55.1, 53.6, 49.1, 48.5, 39.2. IR (KBr) ν 3647, 3055, 2926, 1686, 1535, 1244, 765 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1658, found: 379.1663.



2-(5-methyl-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one

(**2q**)

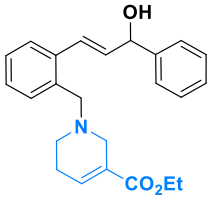
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 6:1); 33.7 mg, 47% yield; dr > 20:1; reaction time = 24 h; mp 135.9-136.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 4.0 Hz, 2H), 7.54-7.43 (m, 4H), 7.09 (d, *J* = 20.0 Hz, 3H), 5.32 (s, 1H), 4.88 (s, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 4.02-3.89 (m, 3H), 3.72 (d, *J* = 16.0 Hz, 1H), 3.53 (s, 2H), 2.97 (d, *J* = 16.0 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 138.3, 138.2, 136.8, 133.2, 131.6, 130.8, 128.6, 128.4, 128.0, 128.0, 127.7, 127.0, 89.9, 60.7, 56.3, 49.2, 45.1, 39.8, 17.3. IR (KBr) ν 3422, 2927, 1687, 1530, 758 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1701.



2-(3-methyl-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one

(**2r**)

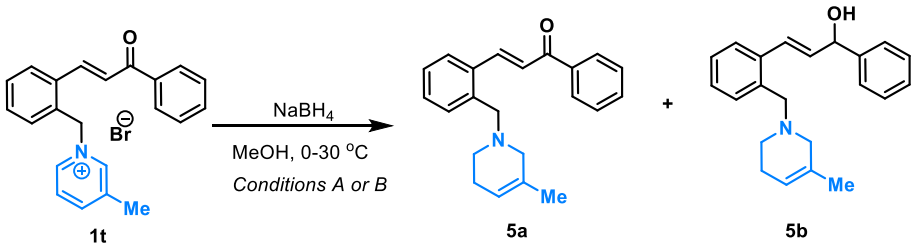
Red oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1 to 3:1); 26.0 mg, 36% yield; dr > 20:1; reaction time = 7 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 2H), 6.96 (s, 1H), 5.85 (d, *J* = 12.0 Hz, 1H), 5.53 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 3.91-3.75 (m, 3H), 3.44 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 3.30 (d, *J* = 16.0 Hz, 1H), 2.99 (s, 1H), 1.08 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 138.2, 138.1, 136.7, 136.5, 133.2, 132.3, 131.0, 128.6, 127.9, 127.6, 127.0, 125.7, 85.2, 61.1, 52.2, 49.7, 49.5, 39.0, 19.3. IR (KBr) ν 3427, 2922, 1689, 1530, 768 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}N_2O_3$ $[M+H]^+$: 363.1703, found: 363.1702.



ethyl

(*E*)-1-(2-(3-hydroxy-3-phenylprop-1-en-1-yl)benzyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4**)

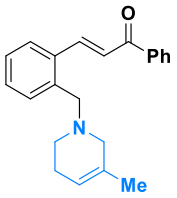
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 3:1); 11.0 mg, 15% yield; reaction time = 72 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.30-7.26 (m, 3H), 7.24-7.18 (m, 2H), 7.08 (d, *J* = 16.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.28 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 5.39 (d, *J* = 4.0 Hz, 1H), 4.19 (q, *J* = 8.0 Hz, 2H), 3.67 (s, 2H), 3.22 (s, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 2.27 (s, 2H), 1.28 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 142.8, 137.6, 136.8, 133.3, 130.5, 129.9, 129.1, 128.6, 128.6, 128.5, 127.6, 127.4, 126.4, 126.3, 75.2, 60.4, 60.0, 51.5, 48.1, 26.4, 14.3. IR (KBr) ν 3449, 1704, 1627, 1266, 755 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{28}NO_3$ $[M+H]^+$: 378.2069, found: 378.2075.



1t 5a 5b

Condition A: $NaBH_4$ (2.5 equiv), 11 h, 31% (**5a**), 41% (**5b**)
Condition B: $NaBH_4$ (4.0 equiv), 1.5 h, 0% (**5a**), 76% (**5b**)

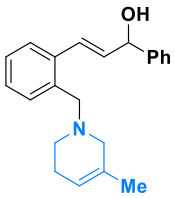
General procedure： A solution of pyridinium salts **1t** (0.2 mmol) in 1.0 mL of MeOH was cooled to 0 °C, and then $NaBH_4$ (18.9 mg, 0.50 mmol) was added successively. The reaction mixture was warmed to 30 °C until the complete consumption of **1t** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **5a** and **5b** in 31% and 41% yields, respectively. When 4.0 equivalents of $NaBH_4$ were used, **5b** was afforded in 76% yield without the formation of **5a**.



(*E*)-3-(2-((5-methyl-3,6-dihydropyridin-1(2*H*)-yl)methyl)phenyl)-1-phenylprop-2-en-1-one (**5a**)

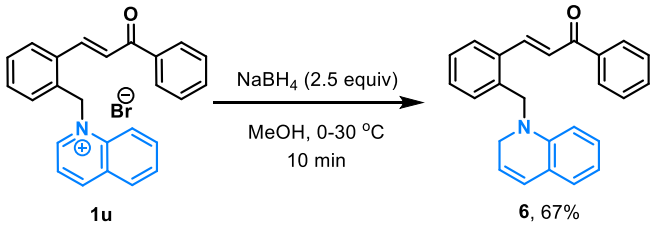
Yellow solid obtained by column chromatography (dichloromethane as the eluent); 19.7 mg, 31% yield; reaction time = 11 h; mp 127.4-128.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 16.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 4.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* =

8.0 Hz, 2H), 7.28 (d, *J* = 16.0 Hz, 4H), 5.33 (s, 1H), 3.57 (s, 2H), 2.73 (s, 2H), 2.42 (s, 2H), 1.98 (s, 2H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 143.3, 138.3, 138.2, 134.9, 132.5, 132.0, 130.8, 129.7, 128.6, 128.4, 127.5, 126.9, 124.0, 119.5, 60.3, 56.8, 49.3, 25.9, 20.9. IR (KBr) ν 3424, 2919, 1637, 805 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1852, found: 318.1855.

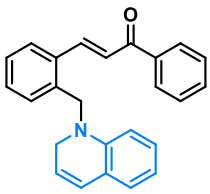


(*E*)-3-(2-((5-methyl-3,6-dihydropyridin-1(2*H*)-yl)methyl)phenyl)-1-phenylprop-2-en-1-ol (**5b**)

White solid obtained by column chromatography (dichloromethane as the eluent); 26.4 mg, 41% yield; reaction time = 11 h; mp 142.1-142.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 3H), 7.22-7.17 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 5.28 (d, *J* = 32.0 Hz, 2H), 3.47 (s, 2H), 3.33 (br, 1H), 2.69 (s, 2H), 2.37 (s, 2H), 1.97 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 136.7, 135.4, 133.3, 132.1, 130.4, 128.3, 128.2, 127.4, 127.3, 127.1, 126.3, 126.1, 119.3, 74.9, 60.2, 56.7, 49.4, 25.7, 20.9. IR (KBr) ν 3418, 2919, 1261, 753 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}NO$ $[M+H]^+$: 320.2009, found: 320.2015.

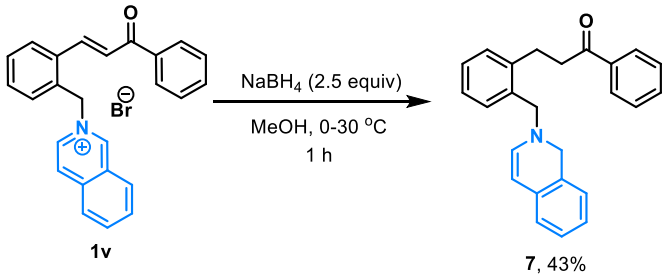


General procedure： A solution of pyridinium salts **1u** (0.2 mmol) in 1.0 mL of MeOH was cooled to 0 °C, and then $NaBH_4$ (18.9 mg, 0.50 mmol) was added successively. The reaction mixture was warmed to 30 °C until the complete consumption of **1u** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **6** in 67% yield.

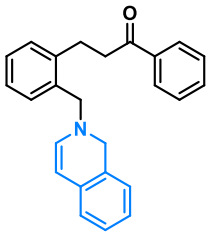


(*E*)-1-phenyl-3-(2-(quinolin-1(2H)-ylmethyl)phenyl)prop-2-en-1-one (**6**)

Yellow solid obtained by filtration of the precipitate; 46.8 mg, 67% yield; reaction time = 10 min; mp 162.1-162.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.57-7.44 (m, 4H), 7.36 (t, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.61 (t, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 2H), 5.66-5.64 (m, 1H), 4.50 (s, 2H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 144.9, 141.2, 137.9, 136.4, 134.0, 132.7, 130.3, 129.1, 128.6, 128.5, 127.9, 127.5, 127.5, 127.0, 126.4, 124.4, 121.9, 121.9, 117.2, 110.0, 51.7, 50.3. IR (KBr) ν 3418, 2922, 1689, 1530, 768 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{22}NO$ $[M+H]^+$: 352.1696, found: 352.1692.



General procedure: A solution of pyridinium salts **1v** (0.2 mmol) in 1.0 mL of MeOH was cooled to 0 °C, and then $NaBH_4$ (18.9 mg, 0.50 mmol) was added successively. The reaction mixture was warmed to 30 °C until the complete consumption of **1v** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **6** in 43% yield.



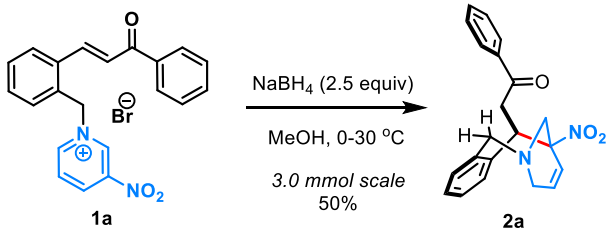
3-(2-(Isoquinolin-2(1*H*)-ylmethyl)phenyl)-1-phenylpropan-1-one (**7**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 30.1 mg, 43% yield; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 1H), 7.41-7.35 (m, 3H),

7.27 (d, J = 4.0 Hz, 4H), 7.20-7.13 (m, 4H), 6.99 (d, J = 4.0 Hz, 1H), 6.29 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 5.33 (d, J = 4.0 Hz, 1H), 3.71 (s, 2H), 3.64 (s, 2H), 2.88 (t, J = 4.0 Hz, 2H), 2.75 (t, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.8, 135.4, 134.8, 134.4, 133.1, 130.5, 128.6, 128.4, 127.5, 127.2, 126.6, 126.3, 126.2, 126.0, 125.5, 75.0, 60.5, 55.9, 50.4, 29.1, two carbons missing in the aromatic region. IR (KBr) ν 3427, 2922, 1685, 1528, 765 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{24}NO$ $[M+H]^+$: 354.1852, found: 354.1852.

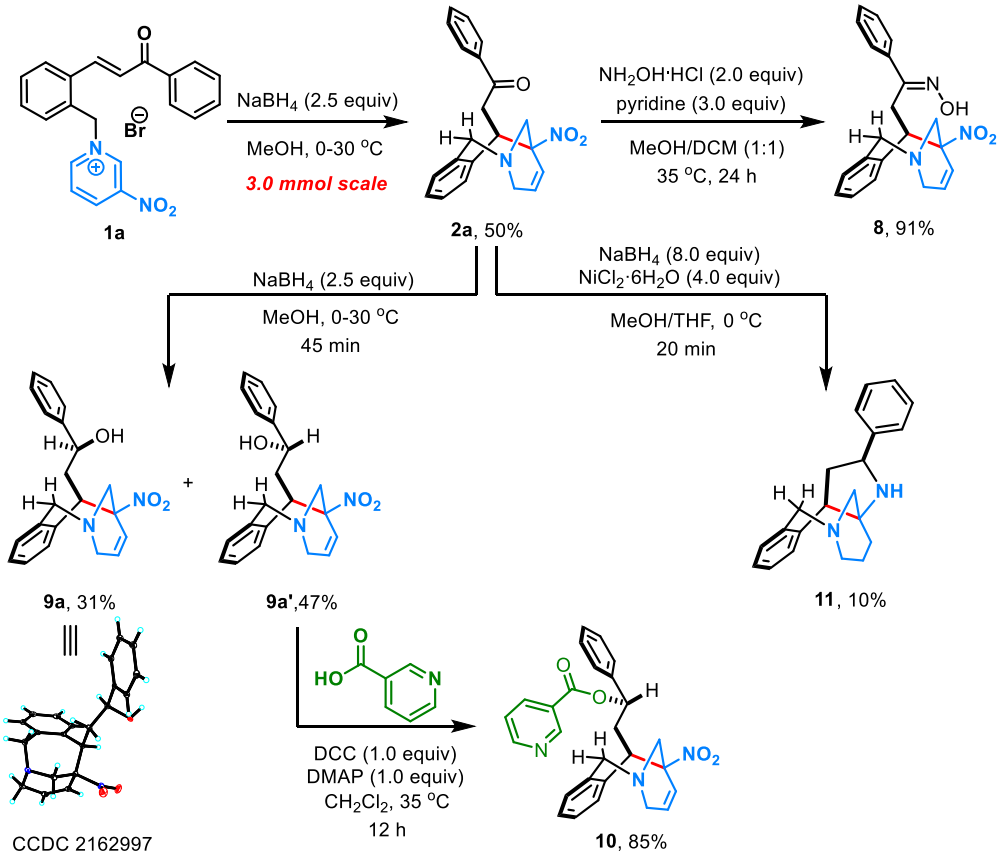
3. Synthetic application

3.1 Scalable preparation of 2a

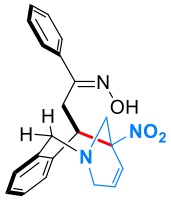


General procedure: A solution of pyridinium salts **1a** (1.28 g, 3.0 mmol) in 15.0 mL of MeOH was cooled to 0 °C, and then $NaBH_4$ (0.28 mg, 7.5 mmol) was added successively. The reaction mixture was warmed to 30 °C until the complete consumption of **1a** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **2a** in 50% yield (0.50 g).

3.2 Chemical conversions of 2a



General procedure for the synthesis of 8: To a 5.0 mL vial were successively added **2a** (69.7 mg, 0.20 mmol), hydroxylamine hydrochloride (27.8 mg, 0.40 mmol) and 1.0 mL MeOH and 1.0 mL of CH_2Cl_2. Then, pyridine (0.60 mmol) was added by syringe. The resulting mixture was stirred at 35 ^oC for 24 h until almost full consumption of **2a** as monitored by thin layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 4:1) to afford the corresponding oxime **8** in 91% yield.

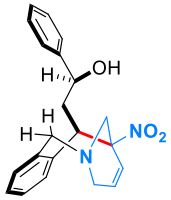


(*E*)-2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-one oxime (**8**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 33.1 mg, 91% yield; dr > 20:1; reaction time = 24 h; mp 218.7-219.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.35 (s, 1H), 7.31-7.29 (m, 1H), 7.25-7.15 (m, 4H), 7.13-7.07 (m, 2H), 6.72-6.70 (m, 1H), 5.96

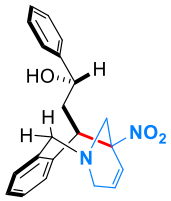
(d, J = 12.0 Hz, 1H), 5.69 (d, J = 8.0 Hz, 1H), 4.85 (d, J = 16.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.39 (d, J = 12.0 Hz, 1H), 4.12-4.02 (m, 2H), 3.85 (d, J = 16.0 Hz, 1H), 3.60 (d, J = 12.0 Hz, 2H), 3.38 (d, J = 20.0 Hz, 1H), 2.90 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6, 137.1, 135.7, 132.7, 131.5, 129.1, 128.5, 128.1, 127.6, 127.1, 126.9, 125.6, 125.3, 85.7, 57.2, 51.1, 48.0, 46.9, 24.8. IR (KBr) ν 3416, 2922, 2378, 1543, 765 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{22}N_3O_3$ $[M+H]^+$: 364.1656, found: 364.1654.

General procedure for the formation of 9a/9a'： A solution of **2a** (139.4 mg, 0.40 mmol) in 2.0 mL of MeOH and 2.0 mL of DCM was cooled to 0 ^{o}C, and then $NaBH_4$ (37.8 mg, 1.0 mmol) was added successively. The reaction mixture was stirred at 0 ^{o}C for 45 min until the complete consumption of **2a** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **9a** and **9a'** in 31% and 47% yields, respectively.



2-(-6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-ol (**9a**)

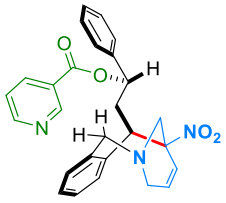
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 43.7 mg, 31% yield; dr > 20:1; reaction time = 45 min; mp 159.1-159.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 8.0 Hz, 3H), 7.25-7.22 (m, 2H), 7.21-7.18 (m, 3H), 7.11 (d, J = 8.0 Hz, 1H), 5.96 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 5.61-5.57 (m, 1H), 4.34 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.17 (d, J = 8.0 Hz, 1H), 4.14 (s, 1H), 3.93 (d, J = 12.0 Hz, 1H), 3.84 (d, J = 16.0 Hz, 1H), 3.69 (d, J = 12.0 Hz, 1H), 3.57-3.51 (m, 1H), 2.95 (d, J = 20.0 Hz, 1H), 2.10-1.91 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 138.7, 138.1, 132.3, 131.4, 131.3, 128.6, 127.8, 127.6, 127.2, 127.0, 125.6, 85.8, 71.1, 60.8, 52.5, 52.0, 48.6, 38.9. IR (KBr) ν 3415, 2925, 1626, 1532, 767 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1703, found: 351.1708.



2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethan-1-ol (**9a'**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 66.2 mg, 47% yield; dr > 20:1; reaction time = 45 min; mp 182.3-182.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21-7.15 (m, 2H), 7.09-7.06 (m, 1H), 6.97-6.95 (m, 1H), 5.73 (d, *J* = 12.0 Hz, 1H), 5.51-5.48 (m, 1H), 4.43 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 3.96 (d, *J* = 12.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.61 (d, *J* = 12.0 Hz, 1H), 3.44 (d, *J* = 20.0 Hz, 1H), 3.38 (d, *J* = 8.0 Hz, 1H), 2.86 (d, *J* = 20.0 Hz, 1H), 2.40 (s, 1H), 2.39-2.31 (m, 1H), 2.18-2.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.7, 138.6, 131.6, 131.5, 131.4, 128.9, 128.4, 127.6, 127.1, 126.7, 85.4, 73.4, 60.4, 52.4, 52.3, 48.4, 37.9, one carbon missing in the aromatic region. IR (KBr) ν 3415, 2925, 1624, 1536, 767 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1703, found: 351.1703.

General procedure for the synthesis of 10： To a 5.0 mL vial were successively added **9a'** (70.1 mg, 0.20 mmol), nicotinic acid (27.1 mg, 0.22 mmol), DCC (41.3 mg, 0.20 mmol), DMAP (34.4 mg, 0.20 mmol) and 1.0 mL of CH_2Cl_2. The resulting mixture was stirred at 35 ^{o}C for 12 h until almost full consumption of **9a'** as monitored by thin layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 1:1) to afford the corresponding oxime **10** in 85% yield.

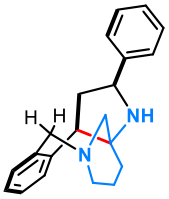


2-(6-nitro-1,3,6,7-tetrahydro-2,6-methanobenzo[*c*]azonin-7-yl)-1-phenylethyl nicotinate (**10**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1); 77.6 mg, 85% yield; dr > 20:1; reaction time = 12 h; mp 165.8-166.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.67 (d, *J* = 3.0 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.47-7.34 (m, 5H), 7.26 (d, *J* = 12.0 Hz, 1H), 7.06-7.02 (m, 3H), 6.92-6.89 (m, 1H), 5.83-5.72 (m, 2H), 5.54-5.50 (m, 1H), 4.37 (d, *J* = 18.0 Hz, 1H), 4.06 (d, *J* = 15.0 Hz, 1H), 3.89 (d, *J* = 15.0 Hz, 1H), 3.72 (d, *J* = 15.0 Hz, 1H), 3.55 (s, 1H), 3.49 (d, *J* = 9.0 Hz, 1H), 2.91 (d, *J* = 18.0 Hz, 1H), 2.77-2.66 (m, 1H), 2.37-2.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 153.3, 150.8, 138.7, 138.2, 137.8, 136.9, 131.8, 131.7, 131.5, 129.0, 128.9, 127.7, 127.3, 127.2, 126.5, 125.8, 123.0, 85.5, 76.4, 60.6, 52.7, 52.6, 48.6,

35.1. IR (KBr) ν 3415, 2921, 2376, 1725, 1535, 1273, 753 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{26}N_3O_4$ $[M+H]^+$: 456.1918, found: 456.1919.

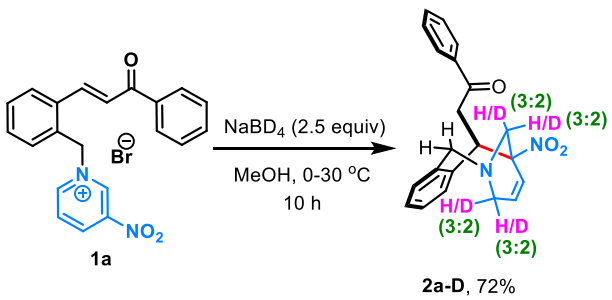
General procedure for the synthesis of 11： A solution of **2a** (174.2 mg, 0.50 mmol) and $NiCl_2{\cdot}6H_2O$ (475.4 mg, 2.0 mmol) in the combined solvents of MeOH and THF (4.0 mL, v/v = 1:1) was cooled to 0 °C, and then $NaBH_4$ (151.3 mg, 4.0 mmol) was added successively. The reaction mixture was stirred at 0 °C for 20 min until the complete consumption of **2a** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (petroleum ether/ ethyl acetate = 5:1) to afford the corresponding product **11** in 10% yield.



2-Phenyl-2,3,5,6,8,12b-hexahydro-1*H*,4*H*-3a,7-methanobenzo[*c*]pyrrolo[3,2-*e*]azonine (**11**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 14.7 mg, 10% yield; dr > 20:1; reaction time = 20 min; mp 212.6-213.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, J_1 = 3.0 Hz, J_2 = 9.0 Hz, 2H), 7.50-7.43 (m, 4H), 7.33-7.28 (m, 2H), 7.07 (d, J = 6.0 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 3.98 (d, J = 12.0 Hz, 1H), 3.83 (d, J = 9.0 Hz, 1H), 3.76 (d, J = 18.0 Hz, 1H), 3.41-3.15 (m, 3H), 3.05 (d, J = 12.0 Hz, 1H), 2.49 (d, J = 12.0 Hz, 2H), 1.97-1.78 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 137.6, 133.7, 132.7, 131.5, 131.1, 129.5, 128.6, 127.7, 127.2, 123.3, 73.9, 60.3, 58.6, 57.7, 43.8, 35.8, 30.9, 18.7. IR (KBr) ν 3413, 2376, 1397, 690 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{25}N_2$ $[M+H]^+$: 305.2012, found: 305.2016.

4. Mechanistic studies



Scheme S1 Control experiment

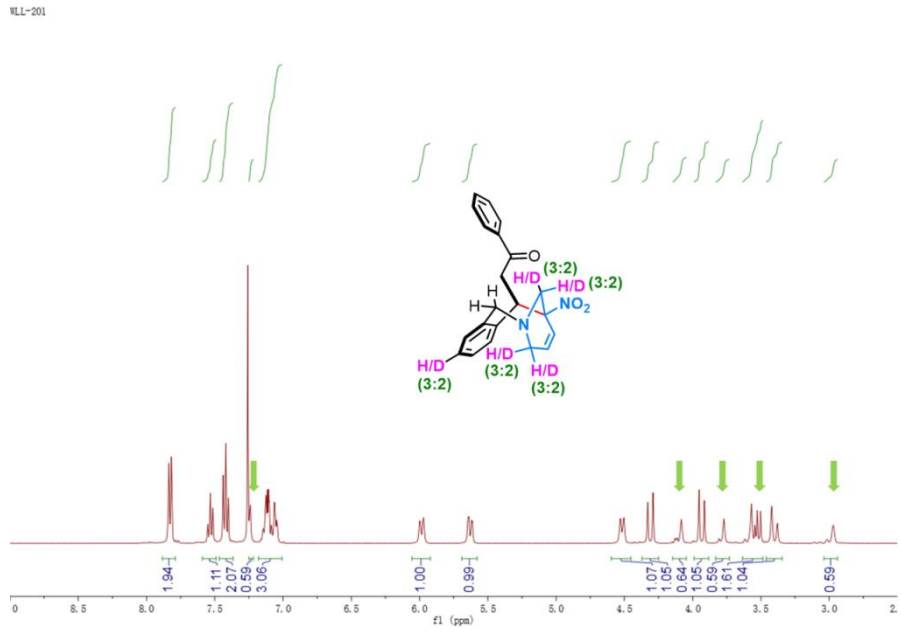
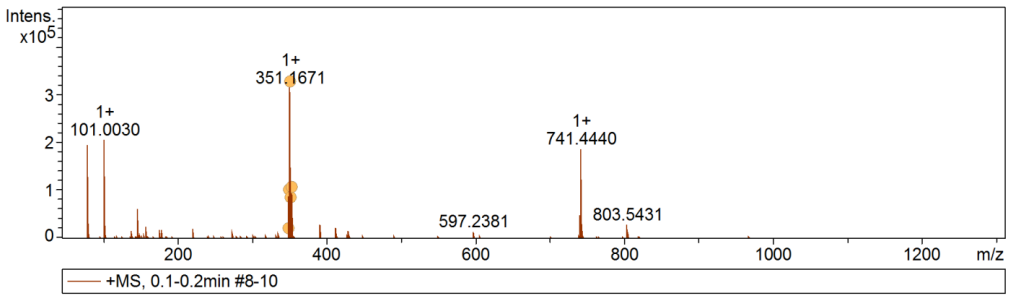
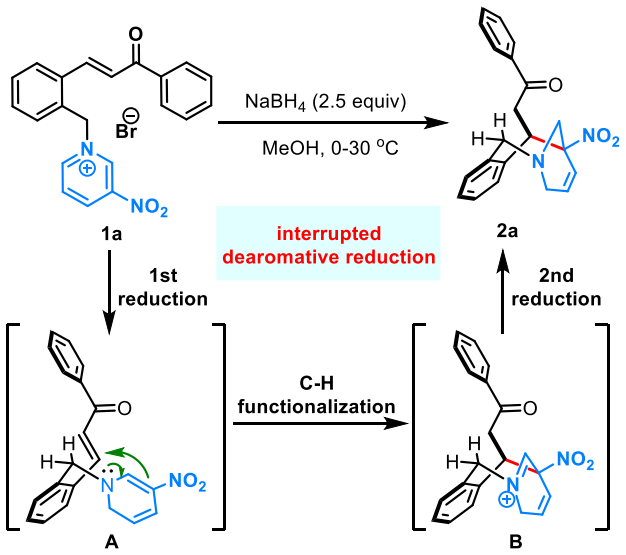


Figure S1. ^{1}H NMR spectrum of **2a-D**



Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
349.1546	1	C21H21N2O3	C21H20N2O3	349.1547	M+H	0.3	1+	792.9	100.00	13.0	ok	even
350.1608	1	C21H20DN2O3	C21H19DN2O3	350.1609	M+H	0.3	1+	614.6	100.00	13.0	ok	even
351.1671	1	C21H19D2N2O3	C21H18D2N2O3	351.1672	M+H	0.3	1+	19.5	100.00	13.0	ok	even
352.1703	1	C21H14D5N2O3	C21H13D5N2O3	352.1704	M+H	0.3	1+	n.a.	100.00	14.0	ok	even

Figure S2. HRMS spectrum of **2a-D**



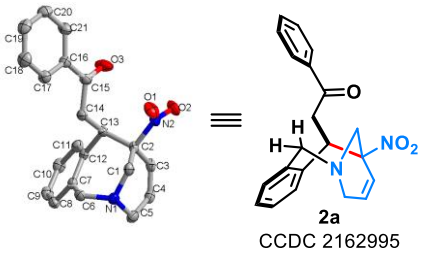
Scheme S2 Proposed mechanism

To understand the reaction pathway in depth, a control experiment was conducted by using $NaBD_4$ as the reductant to reduce **1a** (Scheme S1). And the result revealed that deuterium incorporation was observed at both the C2 and C6 positions of pyridinium ring, while was not at the C4 position. This phenomenon clearly indicated that the first reduction proceeded at the C6 position with complete regioselectivity to generate bienamine intermediate **A** (Scheme S2). Followed by a nucleophilic addition to the chalcone moiety by harnessing the nucleophilicity of bienamine, intermediate **B** bearing an imine ion was produced. In the end, the second reduction occurred to deliver the desired bridged piperidine **2a**.

5. Crystal structures

5.1 Crystal structure of 2a

Preparation of the single crystals of **2a**: About 10.0 mg of pure compound **2a** was dissolved in the combined solvents of dichloromethane and methanol (3 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about five days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **2a**. The data were collected by a Rigaku Gemini E at 293.0 K.



2a

CCDC 2162995

Table S1. Crystal data and structure refinement for **2a**.

Bond precision:	C-C = 0.0048 A		Wavelength=1.54184
Cell:	a = 22.6978(5)	b = 7.32067(11)	c = 12.3466(3)
	alpha = 90	beta = 121.241(3)	gamma = 90
Temperature:	293 K		
	Calculated		Reported
Volume	1754.06(8)		1754.07(8)

Space group	C c	C 1 c 1
Hall group	C -2yc	C -2yc
Moiety formula	$C_{21}H_{20}N_2O_3$	$C_{21}H_{20}N_2O_3$
Sum formula	$C_{21}H_{20}N_2O_3$	$C_{21}H_{20}N_2O_3$
Mr	348.39	348.39
Dx,g cm-3	1.319	1.319
Z	4	4
Mu (mm-1)	0.720	0.720
F000	736.0	736.0
F000'	738.24	
h,k,lmax	26,8,14	26,8,14
Nref	3130[1567]	2357
Tmin,Tmax	0.925,0.965	0.851,1.000
Tmin'	0.898	

Correction method= # Reported T Limits: Tmin=0.851 Tmax=1.000 AbsCorr = MULTI-SCAN

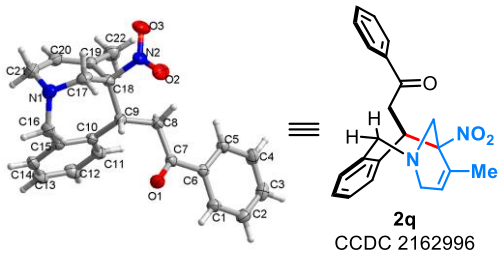
Data completeness= 1.50/0.75 Theta(max)= 67.059

R(reflections)= 0.0338(2272) wR2(reflections)= 0.0911(2357)

S = 1.061 Npar= 235

5.2 Crystal structure of 2q

Preparation of the single crystals of **2q**: About 10.0 mg of pure compound **2q** was dissolved in the combined solvents of dichloromethane and methanol (3 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about five days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **2q**. The data were collected by a Rigaku Gemini E at 293.0 K.



2q

CCDC 2162996

Table S2. Crystal data and structure refinement for **2q**.

Bond precision: C-C = 0.0025 A Wavelength = 1.54184

Cell: a = 12.3385(5) b = 7.6142(3) c = 19.6850(8)

alpha = 90 beta = 99.363(4) gamma = 90

Temperature: 293 K

	Calculated	Reported
Volume	1824.73(13)	1824.71(13)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{22}H_{22}N_2O_3$	$C_{22}H_{22}N_2O_3$
Sum formula	$C_{22}H_{22}N_2O_3$	$C_{22}H_{22}N_2O_3$
Mr	362.42	362.41
Dx,g cm-3	1.319	1.319
Z	4	4
Mu (mm-1)	0.712	0.712
F000	768.0	768.0
F000'	770.31	
h,k,lmax	14,9,23	14,9,23
Nref	3259	3260
Tmin,Tmax	0.926,0.945	0.880,1.000
Tmin'	0.905	

Correction method= # Reported T Limits: Tmin=0.880 Tmax=1.000 AbsCorr = MULTI-SCAN

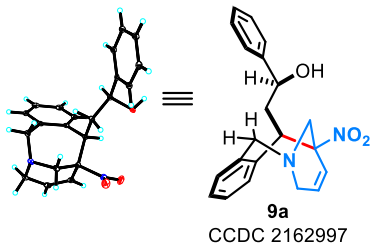
Data completeness= 1.000 Theta(max)= 67.078

R(reflections)= 0.0429(2641) wR2(reflections)= 0.1198(3260)

S = 1.017 Npar= 245

5.3 Crystal structure of 9a

Preparation of the single crystals of **9a**: About 15.0 mg of pure compound **9a** was dissolved in the combined solvents of chroloform, petroleum ether and ethyl acetate (3 mL, v/v/v = 2:1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at 0 ^{o}C. After about four days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure of **9a**. The data were collected by a Bruker D8 QUEST PHOTON II diffractometer at 273.0 K.



Displacement ellipsoids are drawn at the 30% probability level

Table S3. Crystal data and structure refinement for **9a**.

Bond precision: C-C = 0.0025 A Wavelength=1.54178

Cell: a = 10.3484(2) b = 10.5112(2) c = 16.0533(3)

alpha = 90 beta = 90 gamma = 90

Temperature: 100 K

	Calculated	Reported
Volume	1746.18(6)	1746.18(6)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{21}H_{22}N_2O_3$	$C_{21}H_{22}N_2O_3$
Sum formula	$C_{21}H_{22}N_2O_3$	$C_{21}H_{22}N_2O_3$

Mr	350.41	350.40
Dx,g cm-3	1.333	1.333
Z	4	4
Mu (mm-1)	0.724	0.724
F000	744.0	744.0
F000'	746.24	
h,k,lmax	12,12,19	12,12,19
Nref	3437[1971]	3392
Tmin,Tmax	0.840,0.917	0.760,0.920
Tmin'	0.696	

Correction method= # Reported T Limits: Tmin=0.760 Tmax=0.920 AbsCorr = MULTI-SCAN

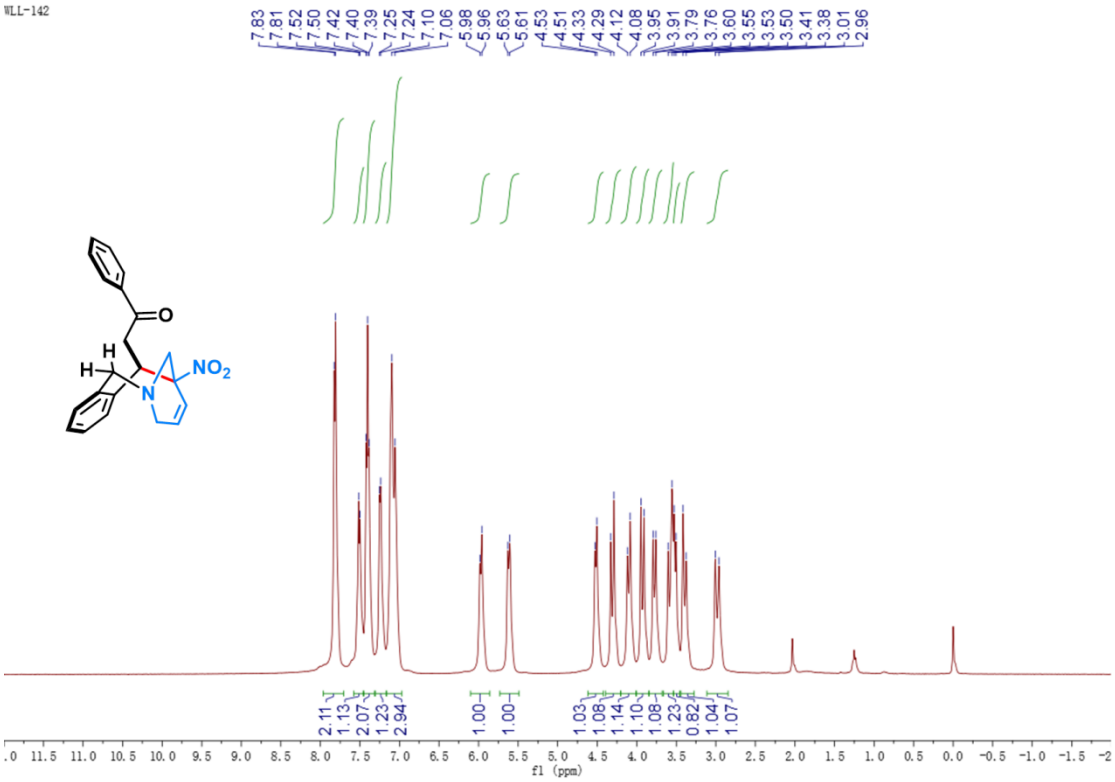
Data completeness= 1.72/0.99 Theta(max)= 72.140

R(reflections)= 0.0312(3292) wR2(reflections)= 0.0989(3392)

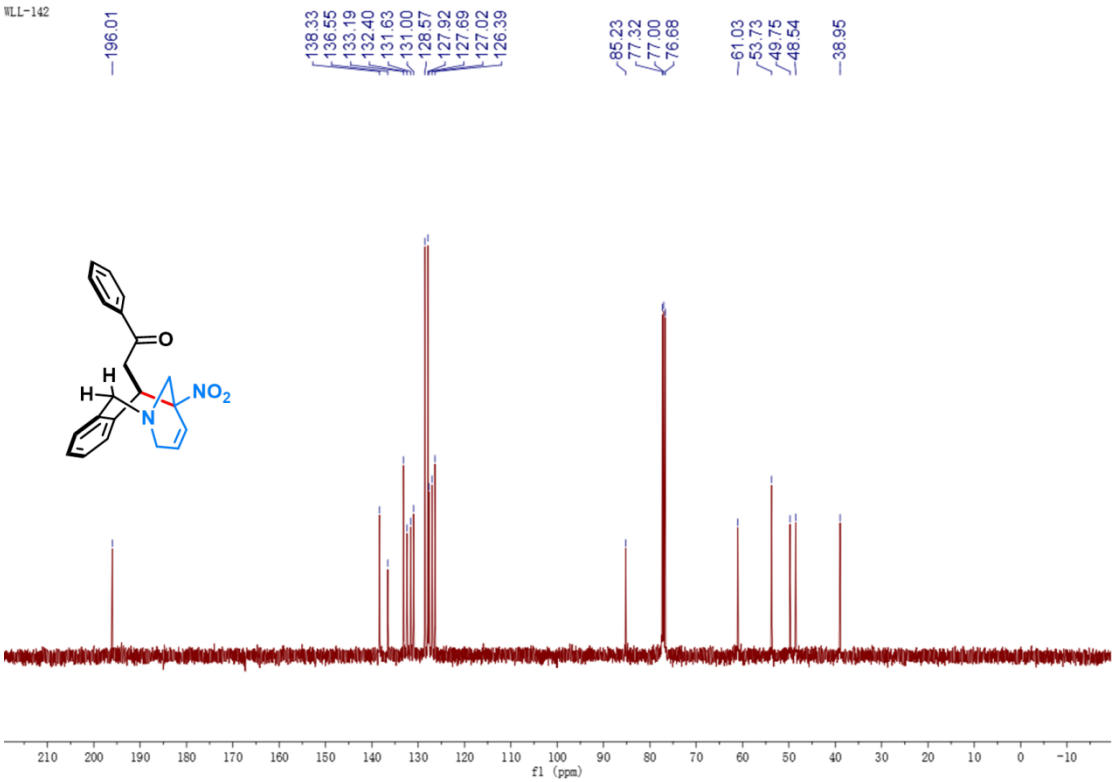
S = 0.862 Npar= 236

6. NMR spectra

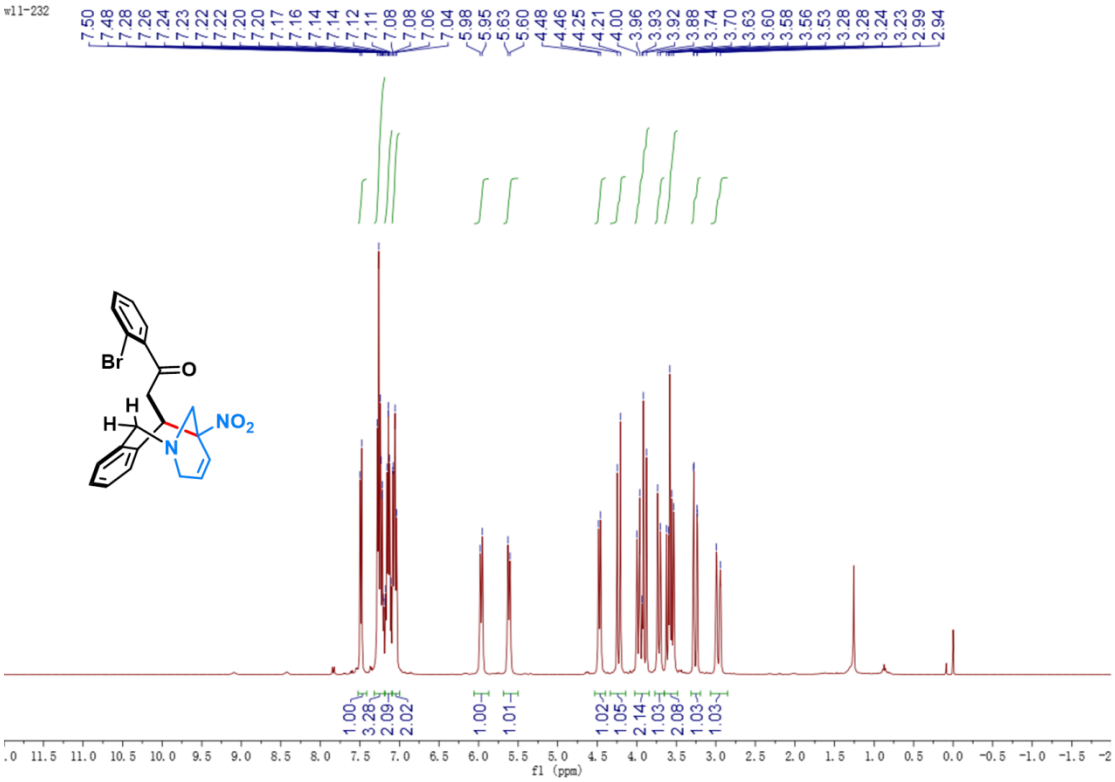
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



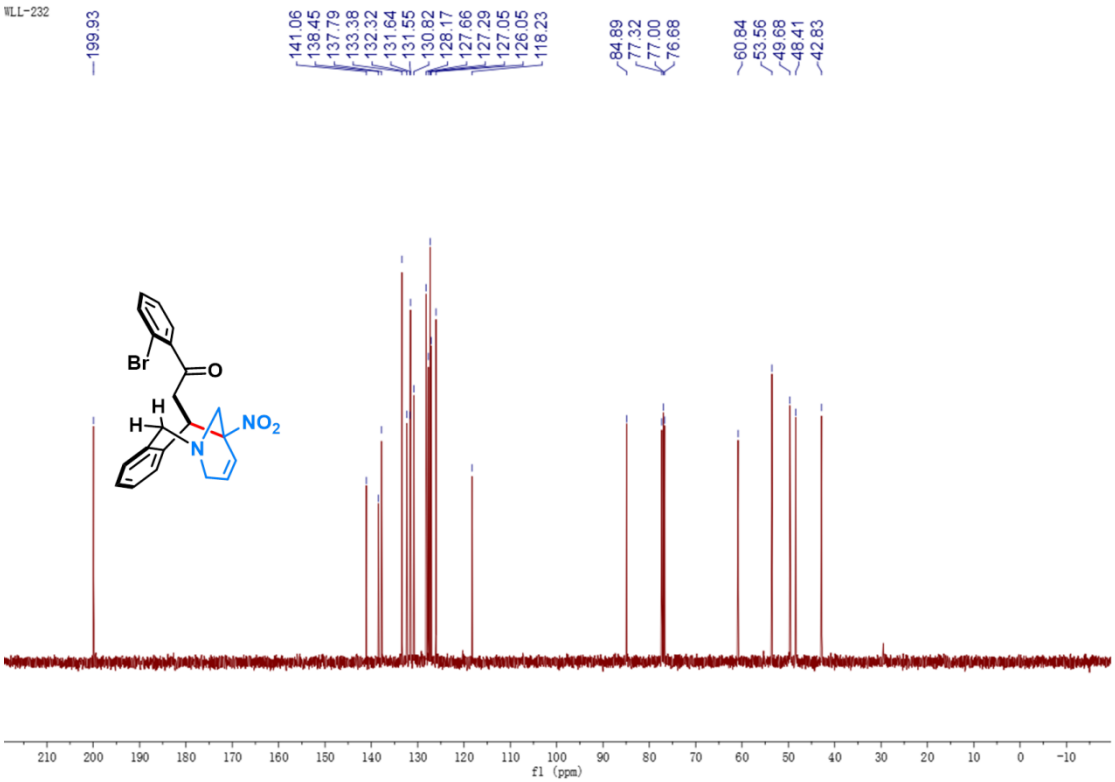
^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)



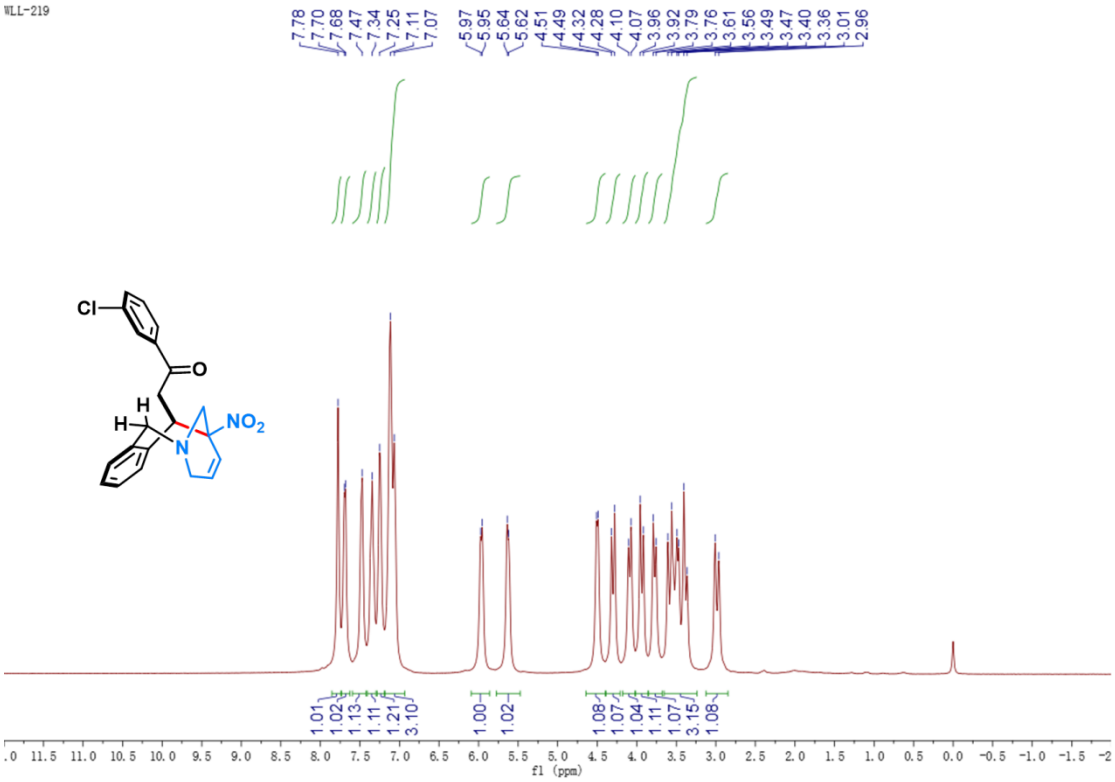
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



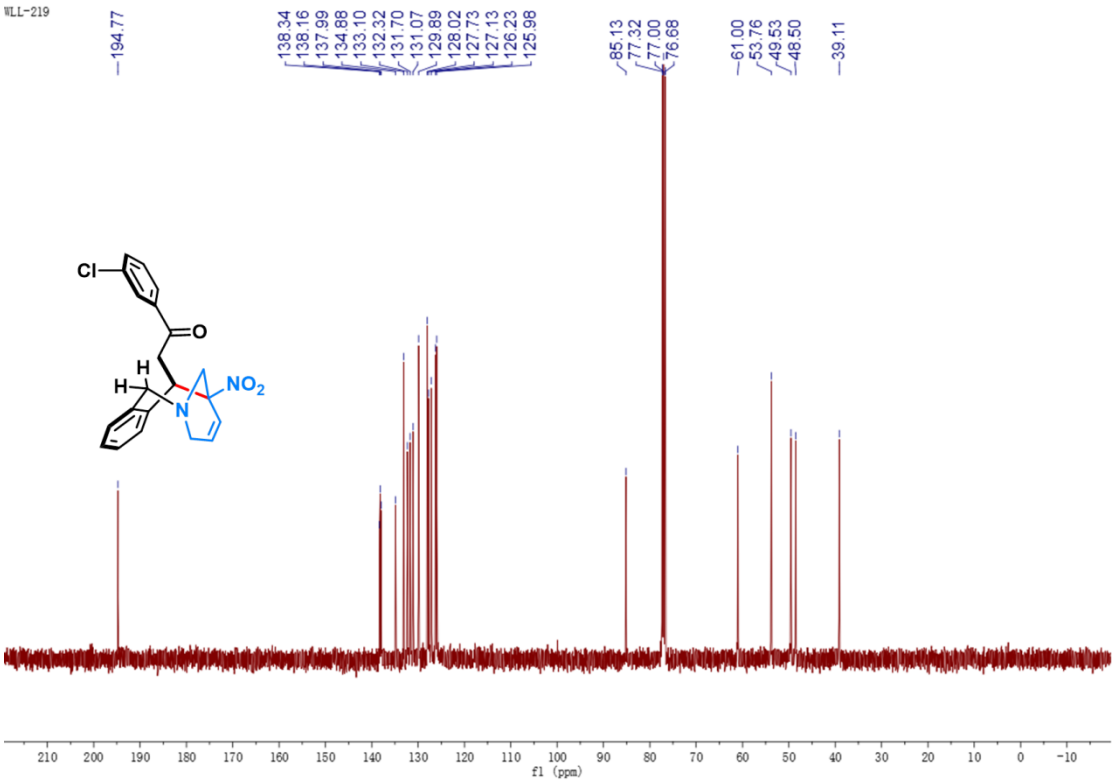
^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)



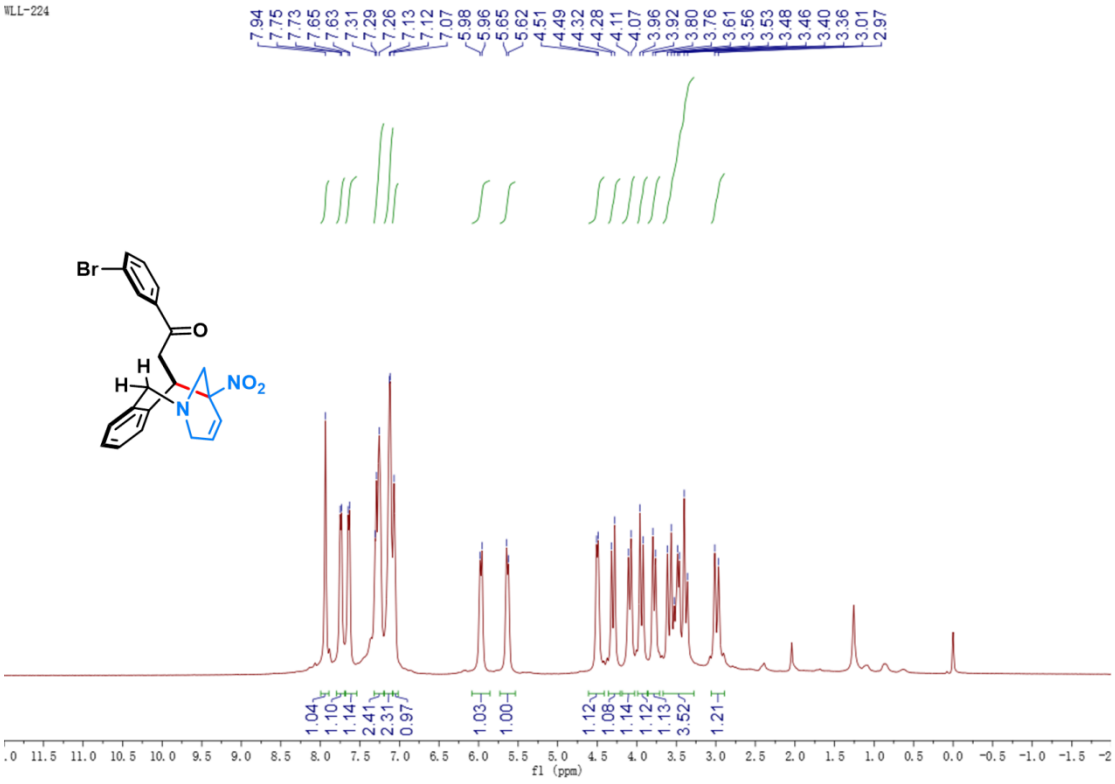
^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)



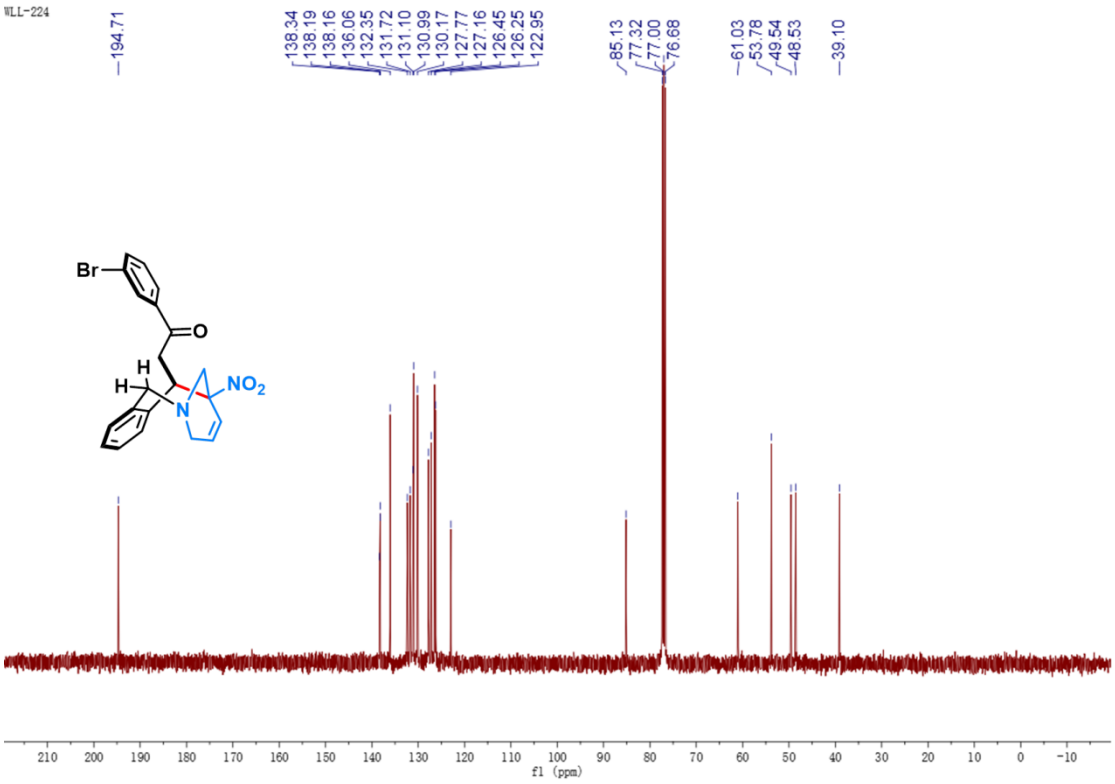
^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)



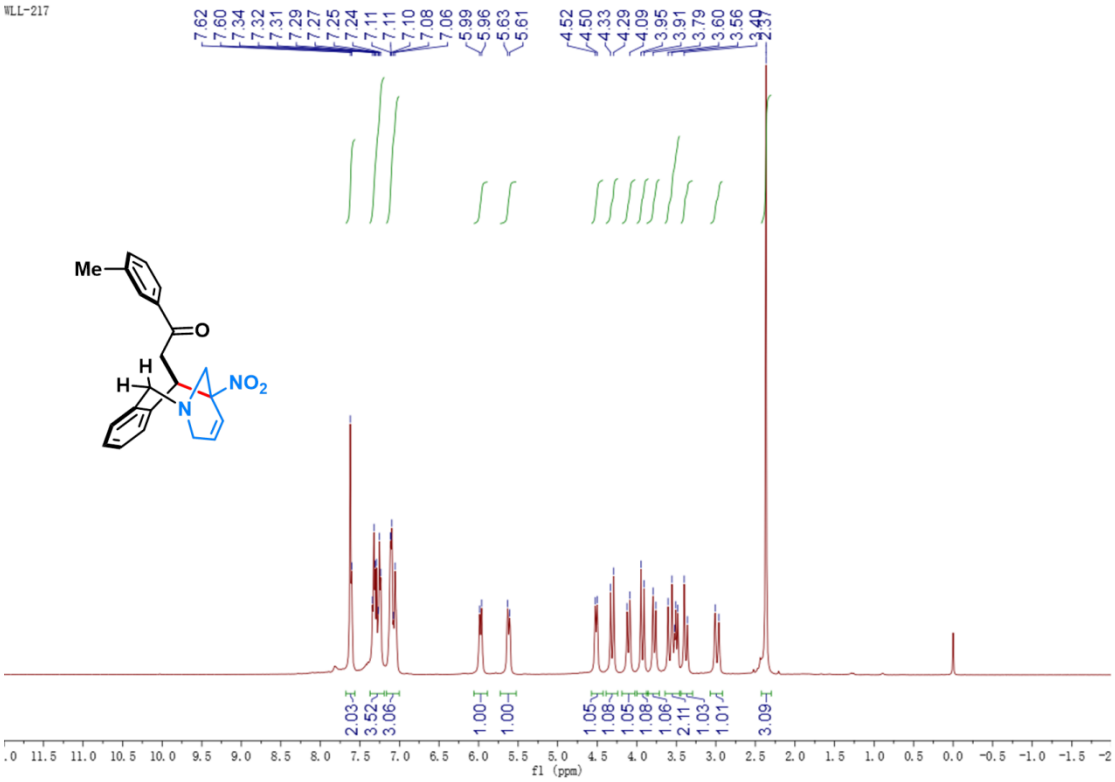
^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)



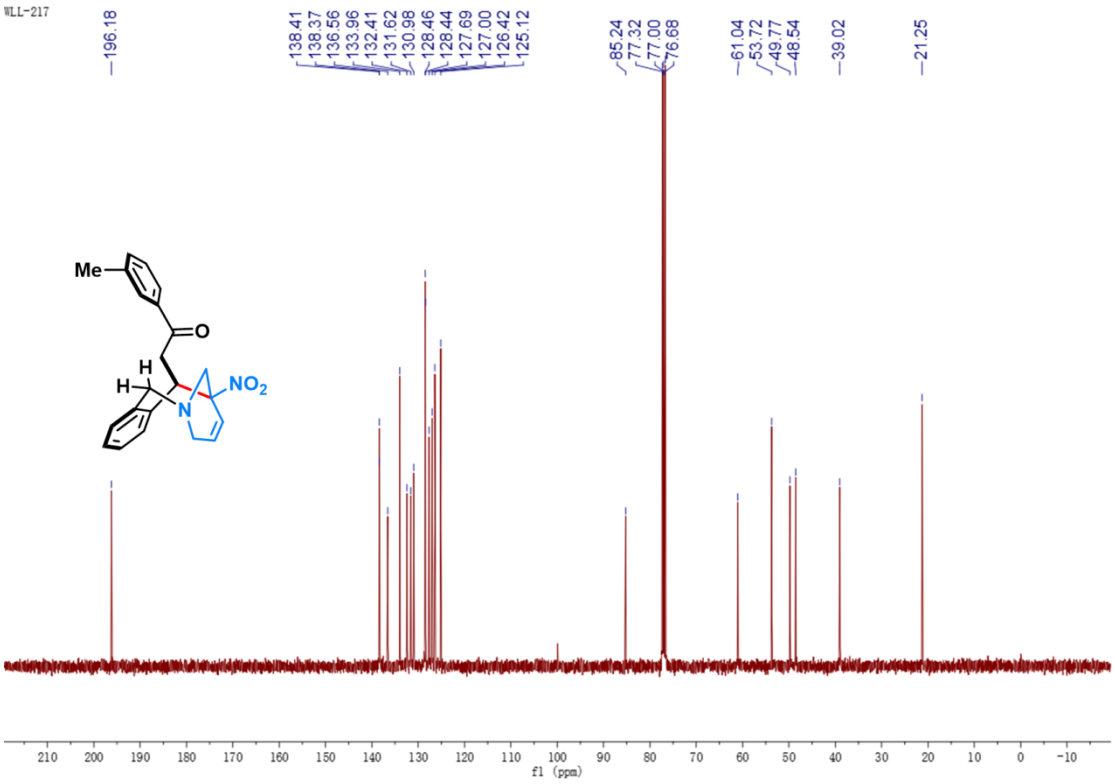
^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)



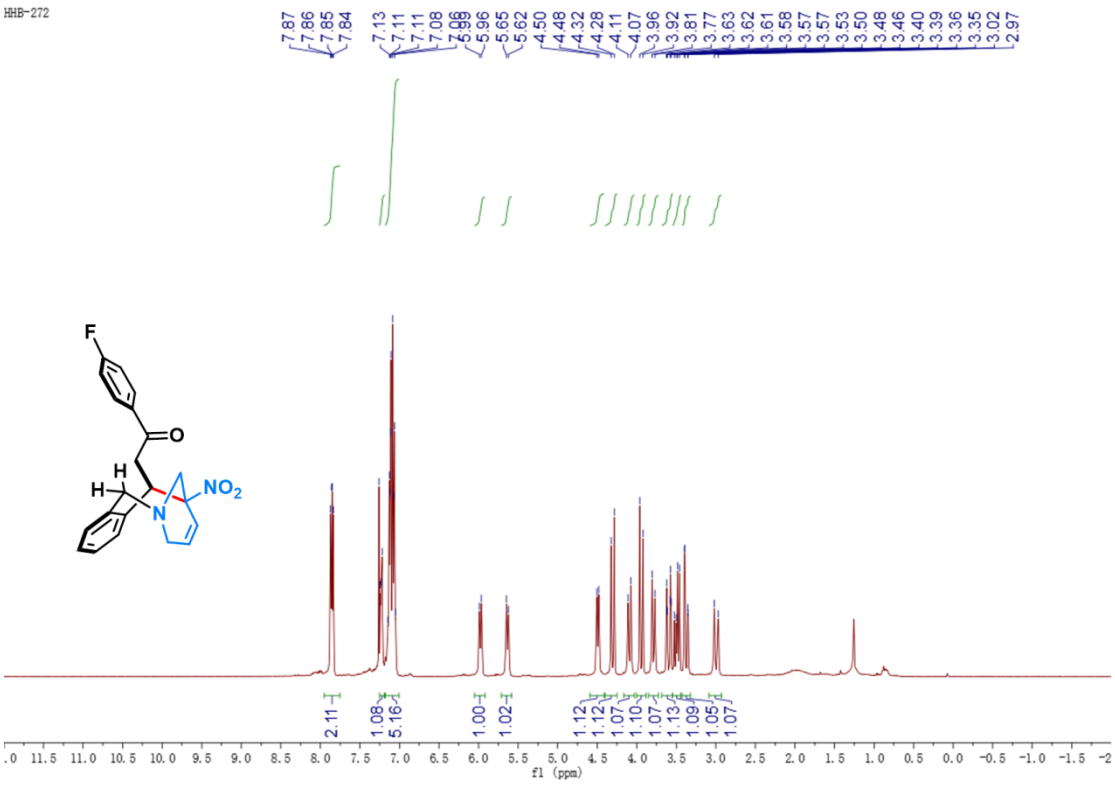
^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)



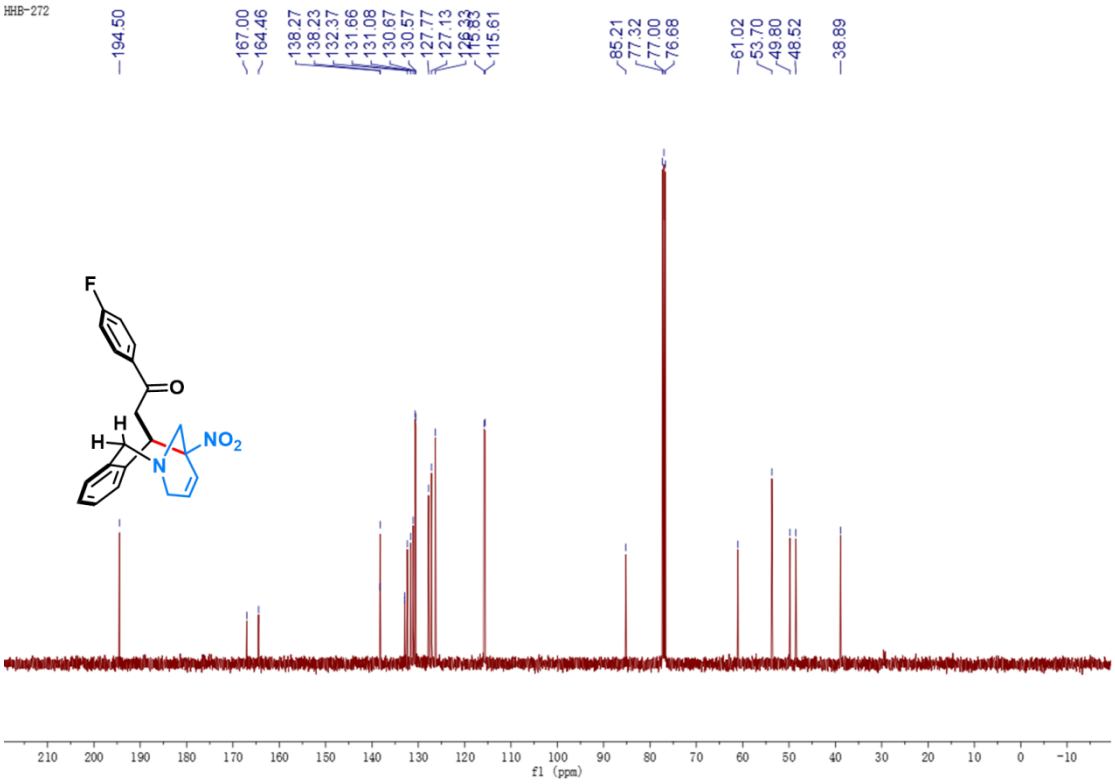
^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)



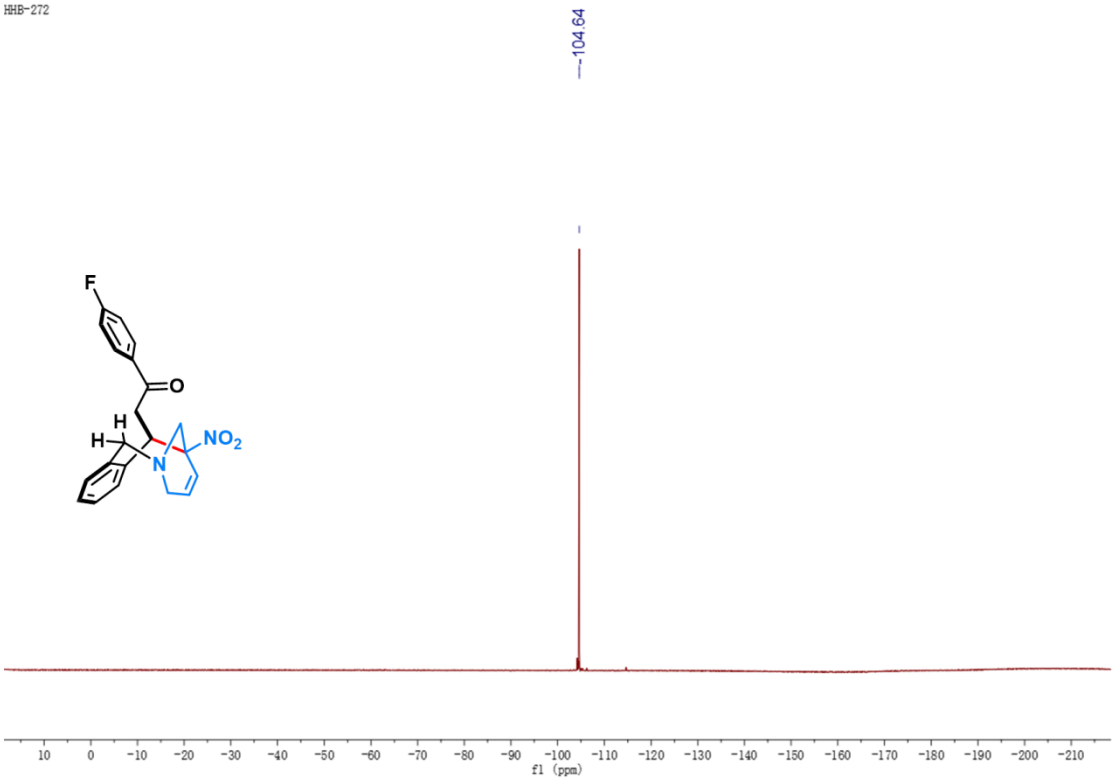
^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)



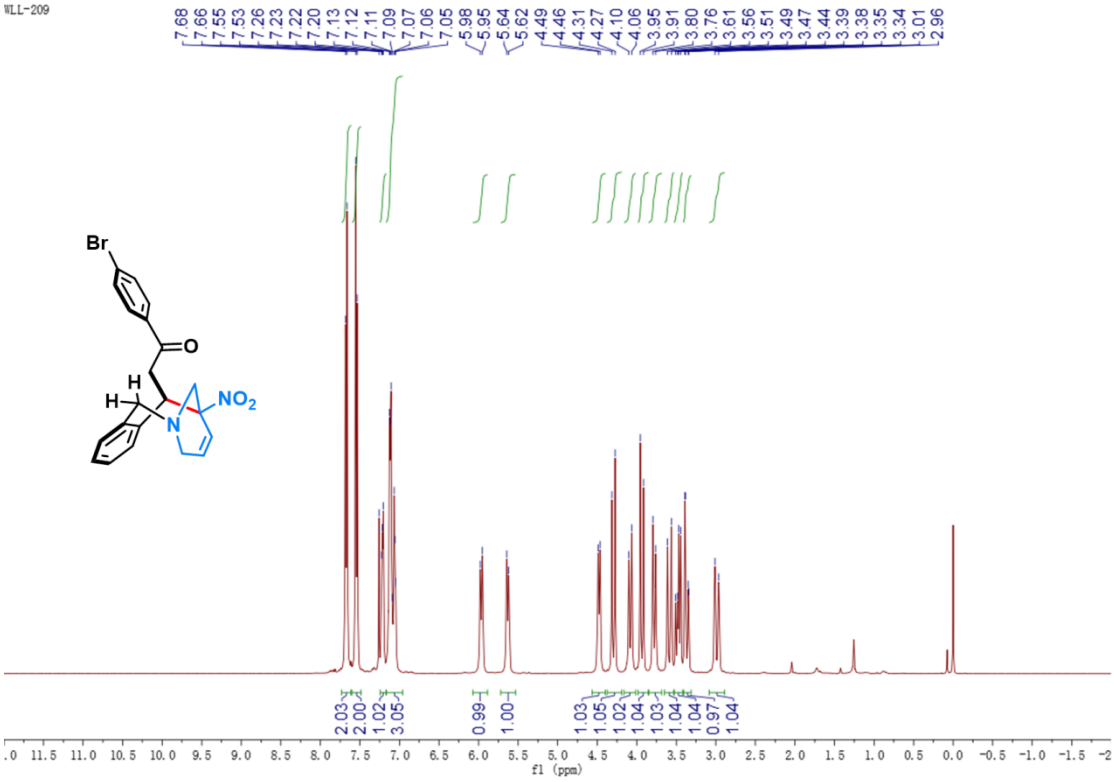
^{13}C NMR spectrum of **2f** (100 MHz, $CDCl_3$)



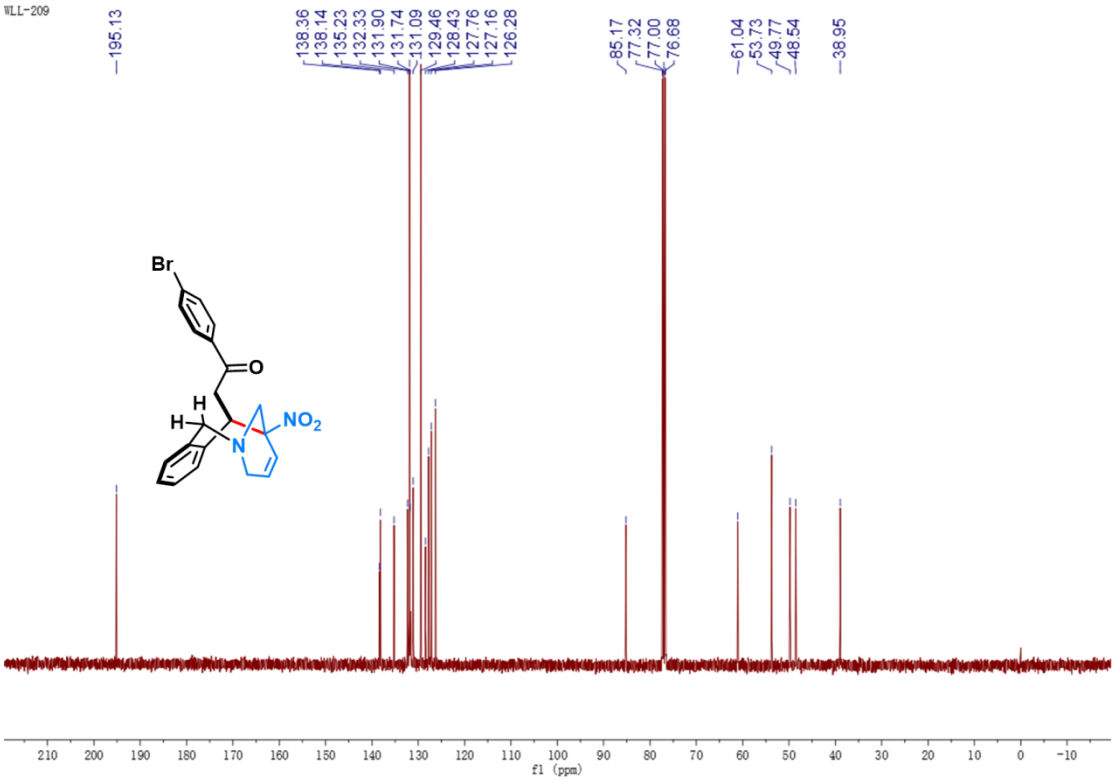
^{19}F NMR spectrum of **2f** (376 MHz, $CDCl_3$)



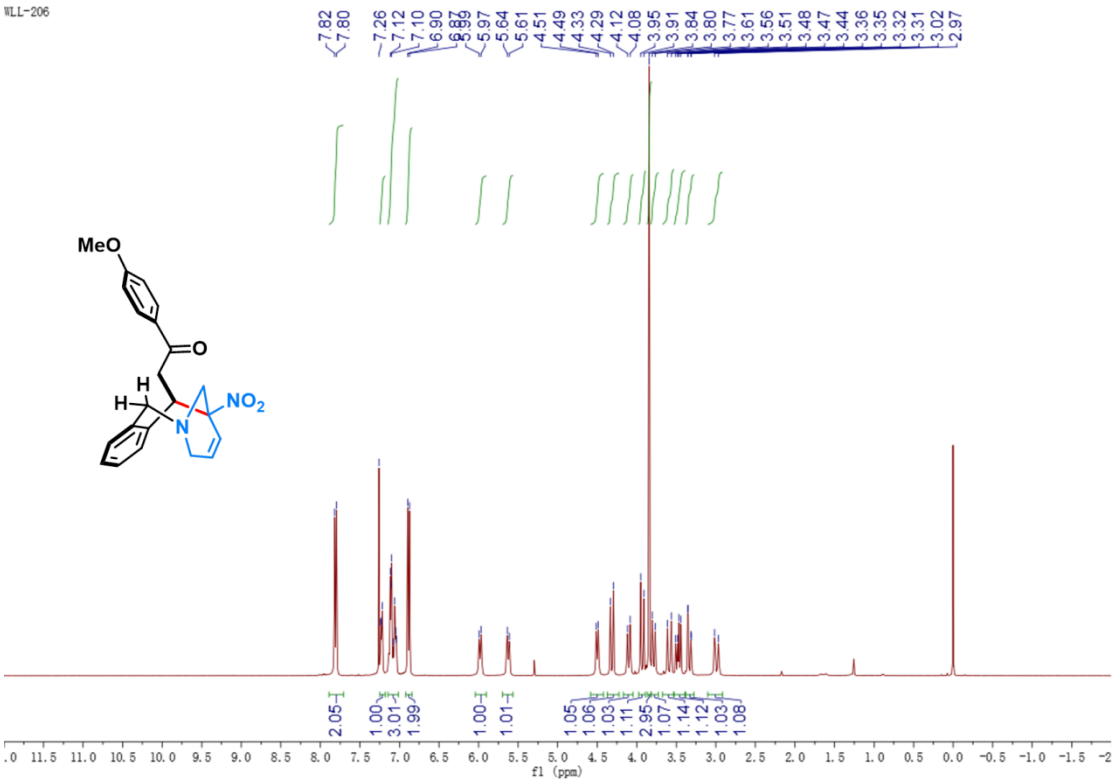
^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)



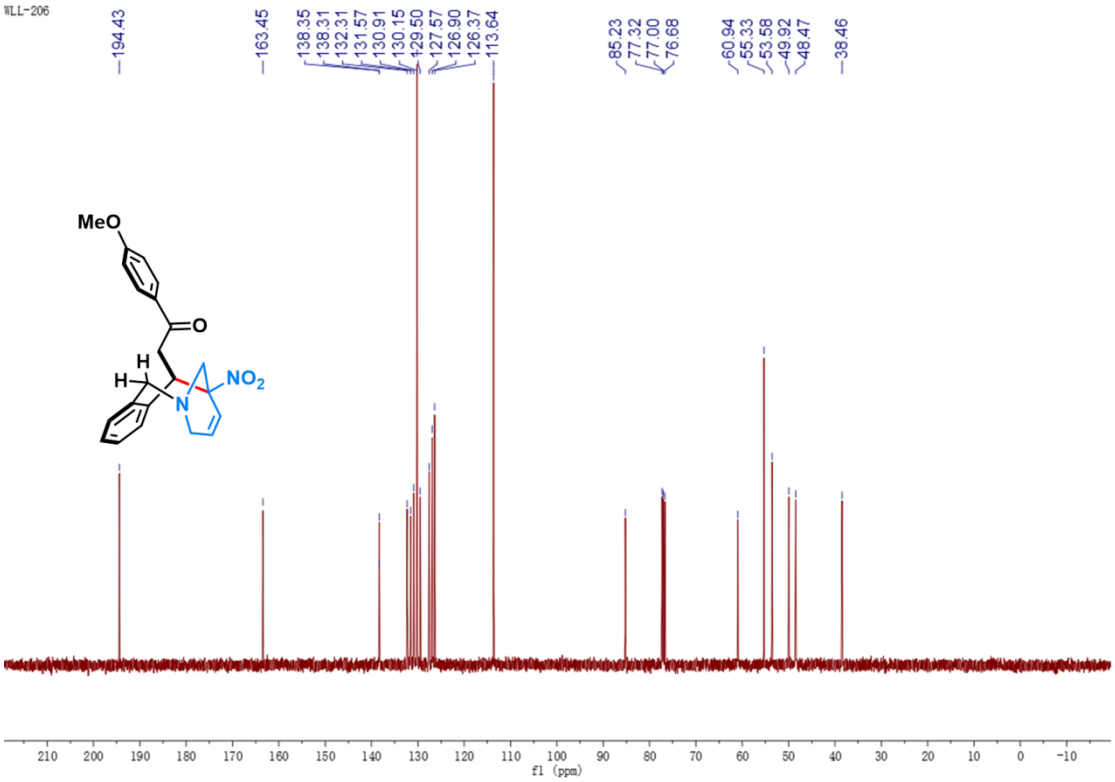
^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)



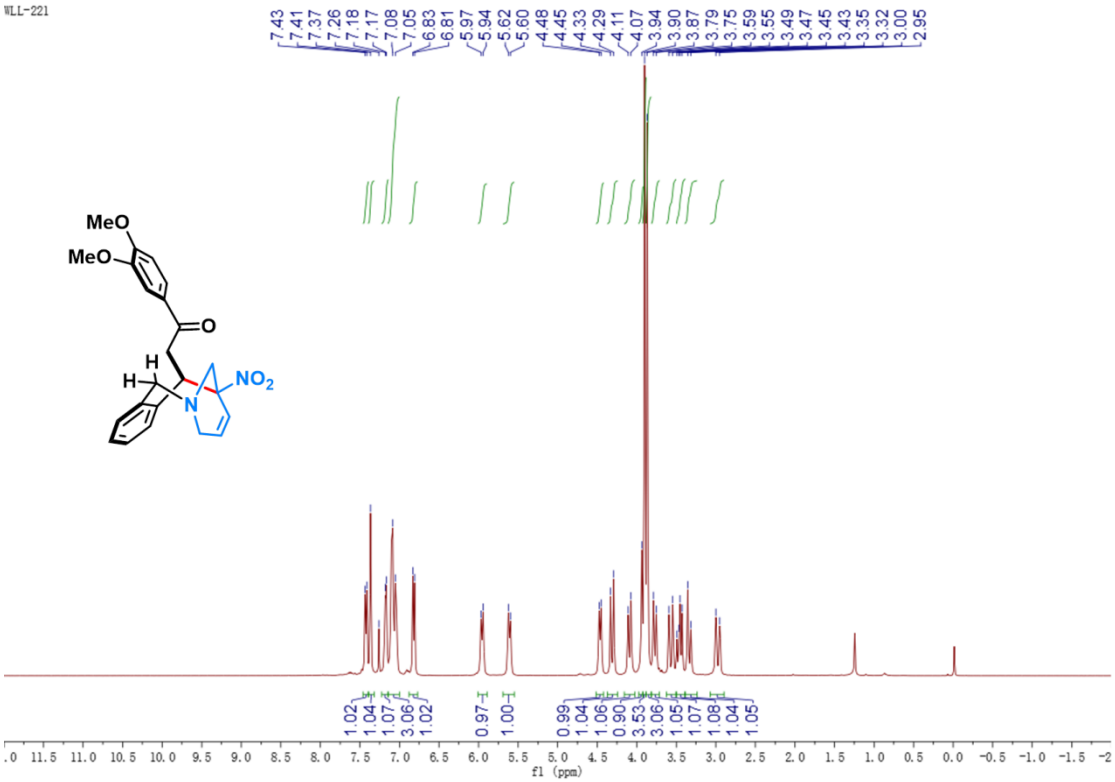
^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)



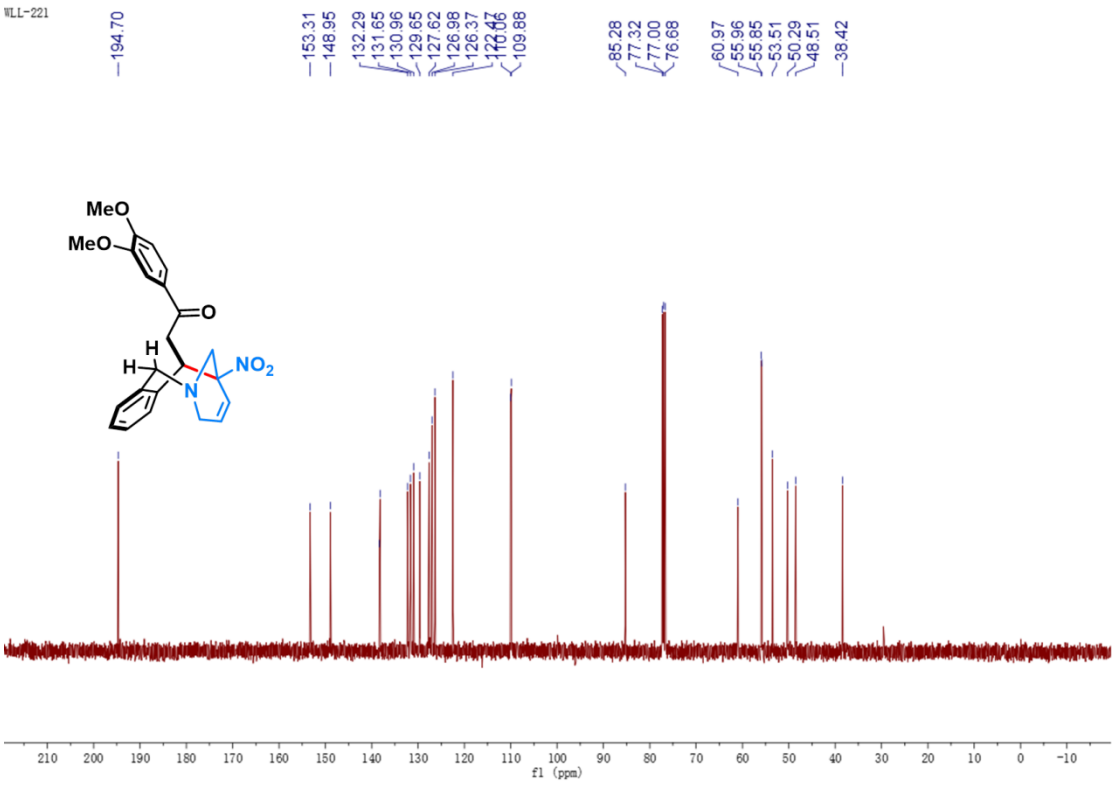
^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)



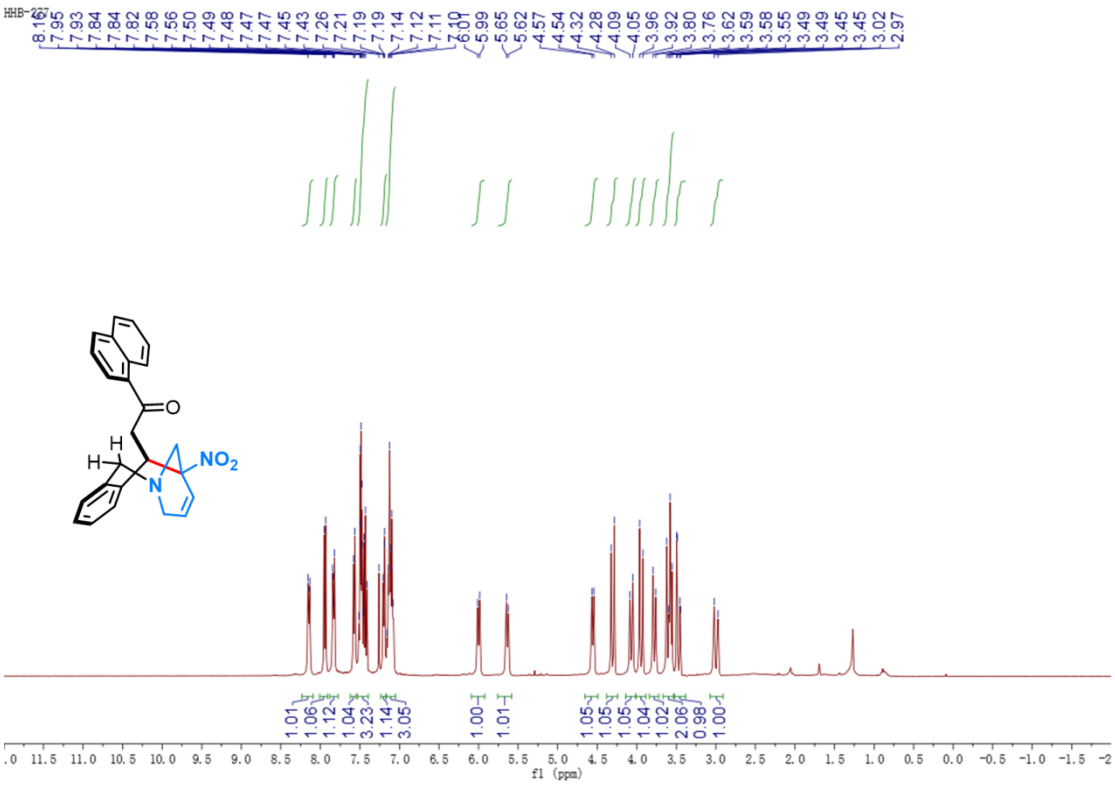
^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)



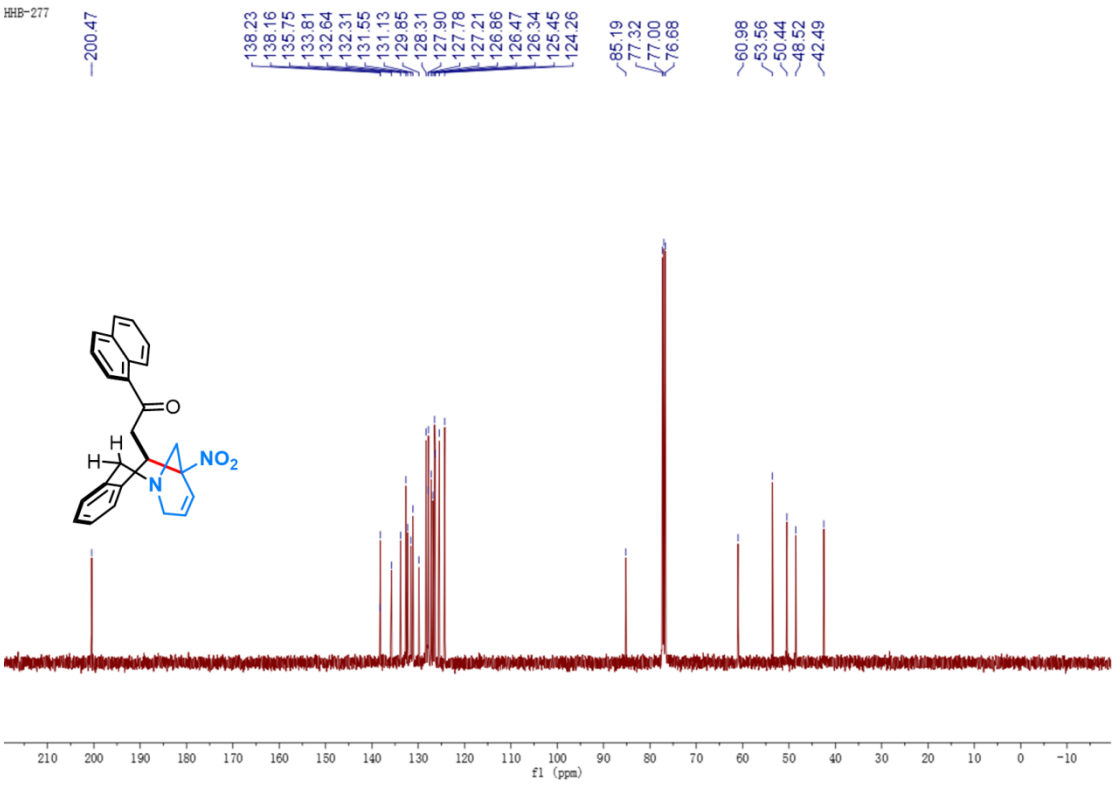
^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)



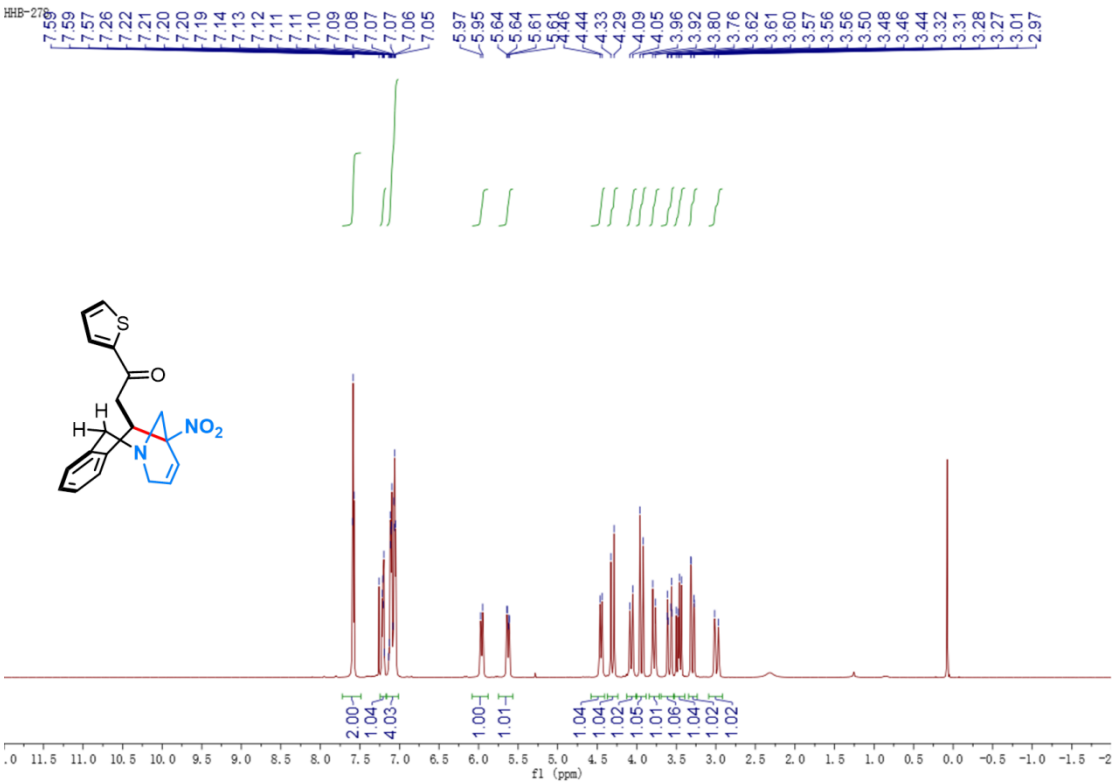
^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)



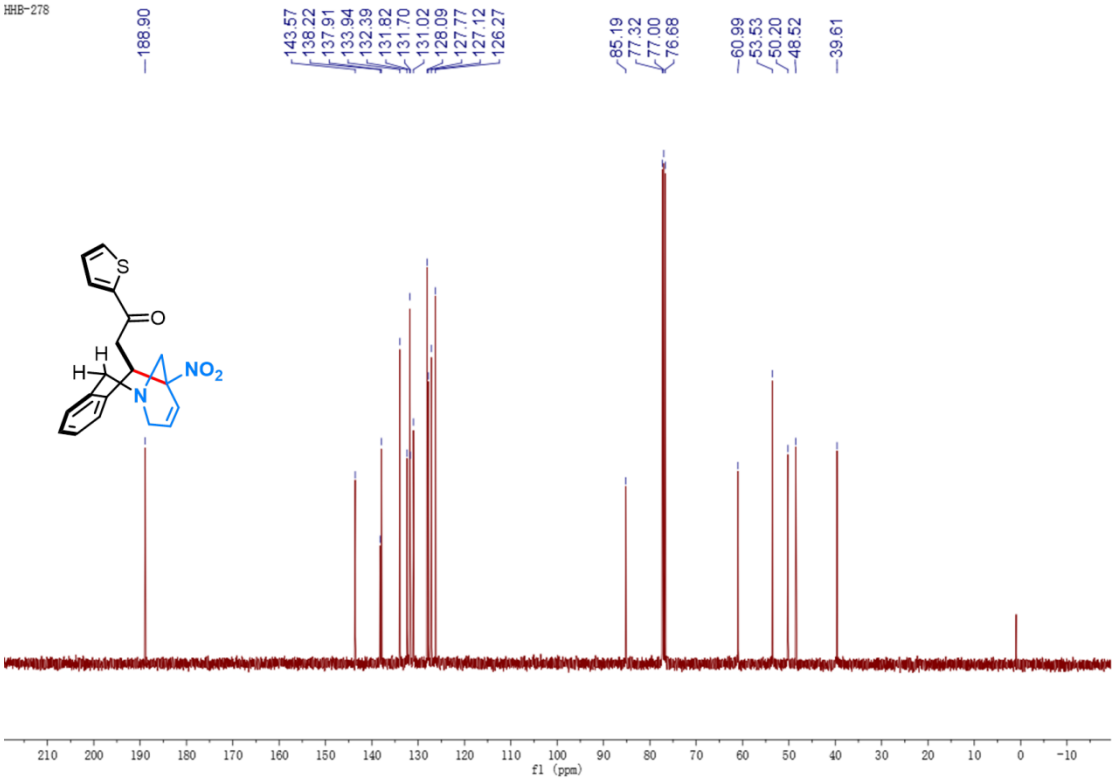
^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$)



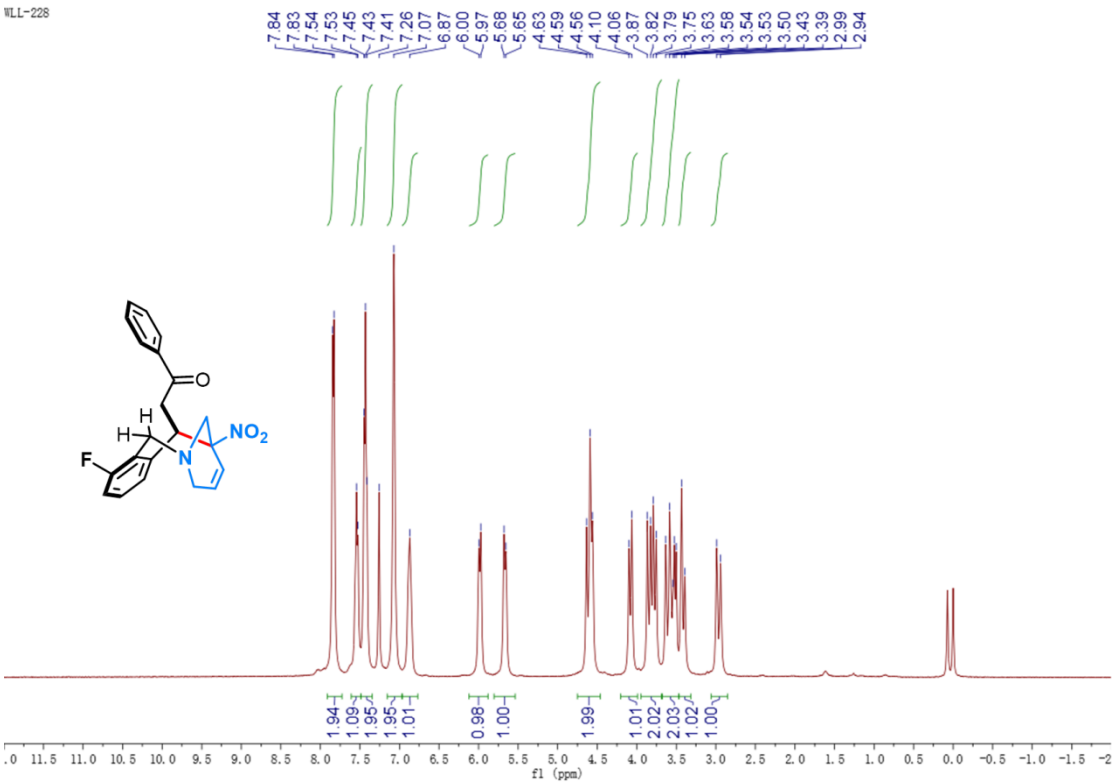
^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)



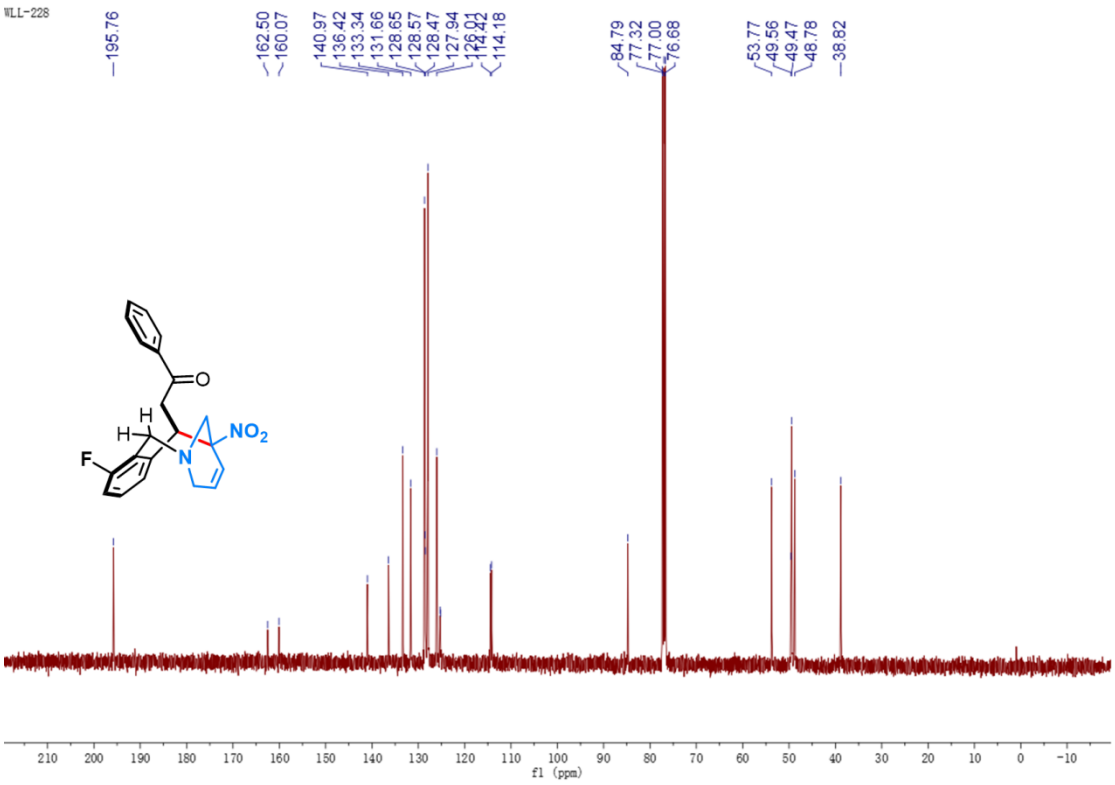
^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)



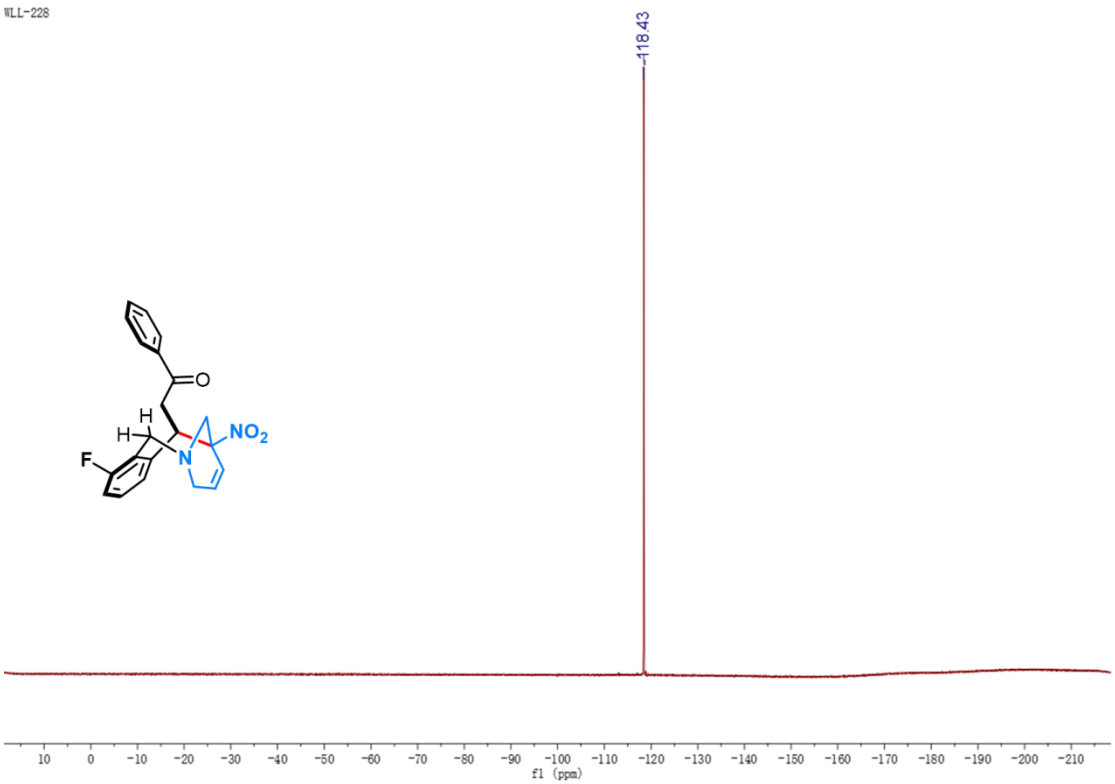
^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$)



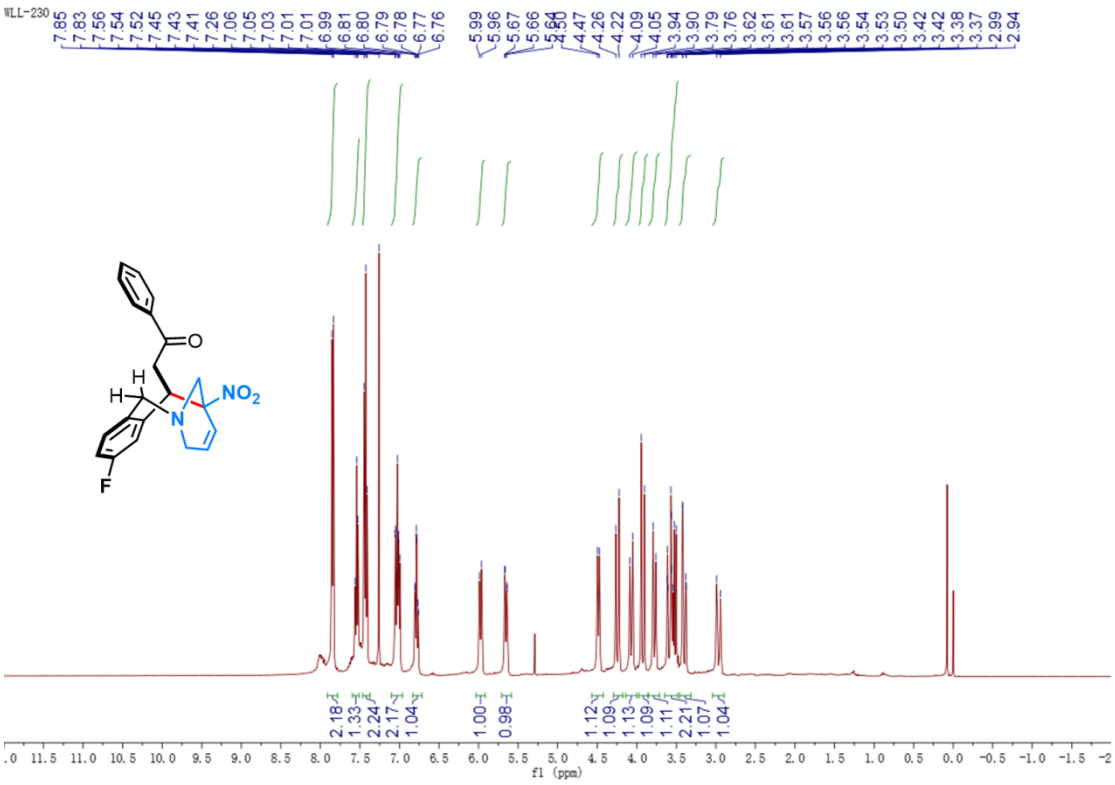
^{13}C NMR spectrum of **2l** (100 MHz, $CDCl_3$)



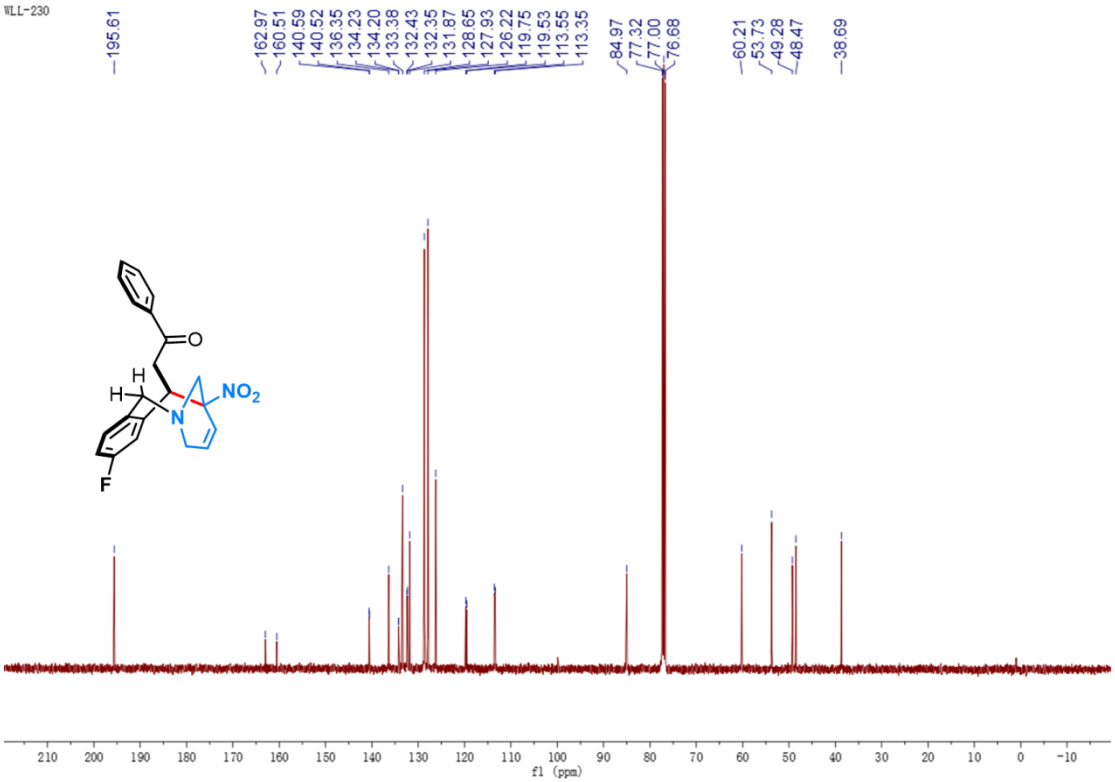
^{19}F NMR spectrum of **2l** (376 MHz, $CDCl_3$)



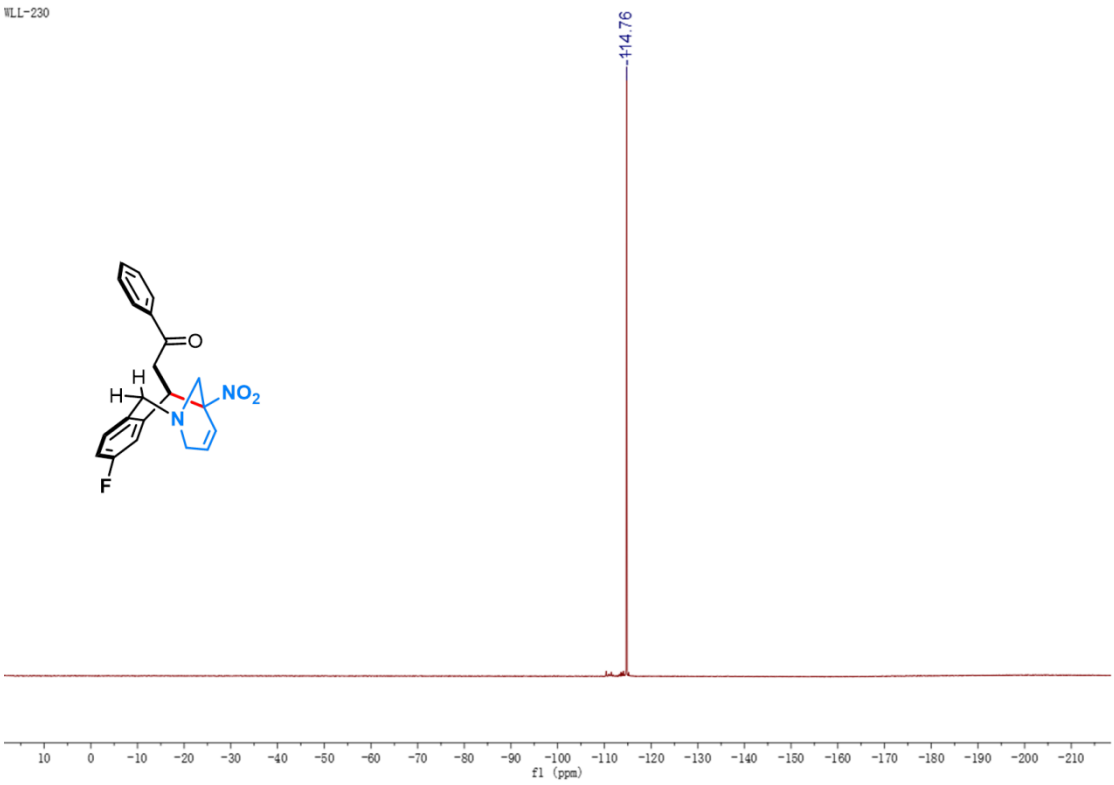
^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$)



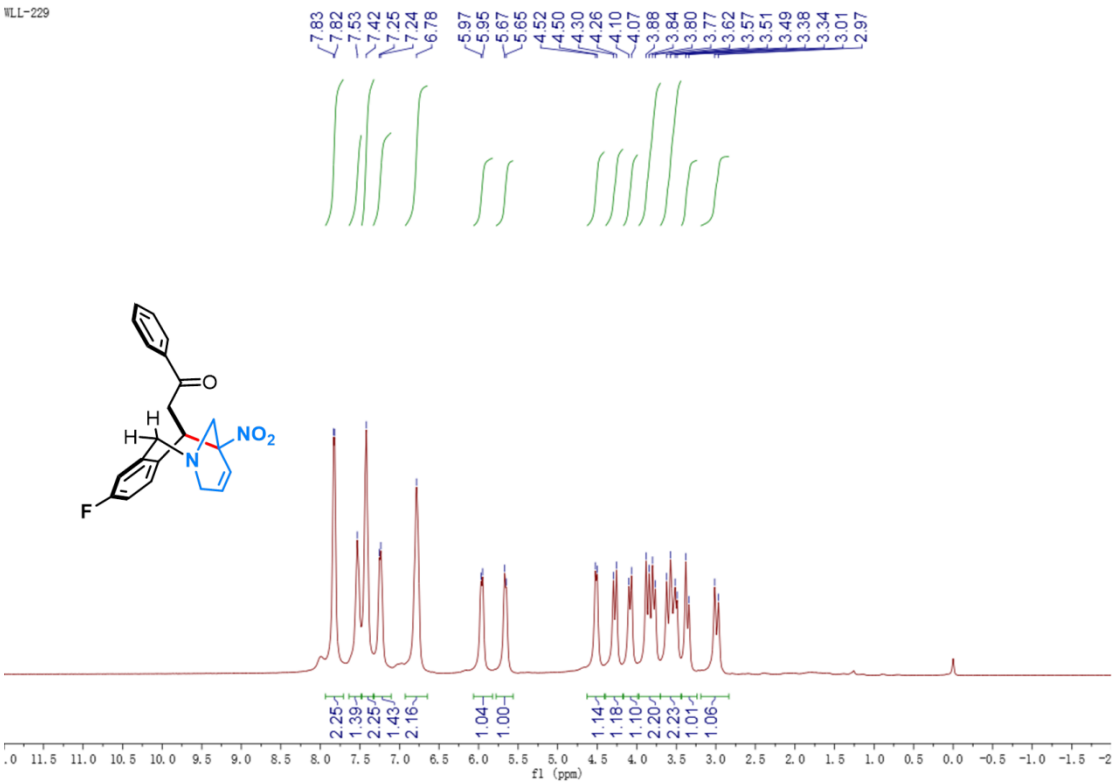
^{13}C NMR spectrum of **2m** (100 MHz, $CDCl_3$)



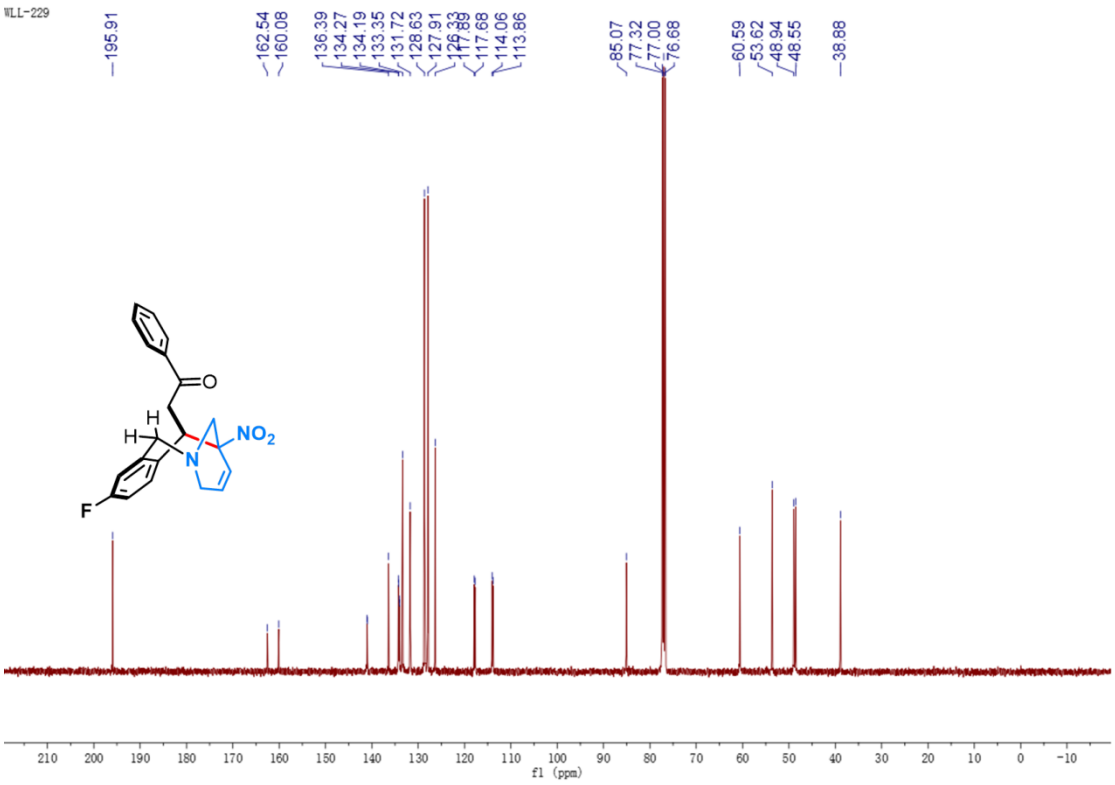
^{19}F NMR spectrum of **2m** (376 MHz, $CDCl_3$)



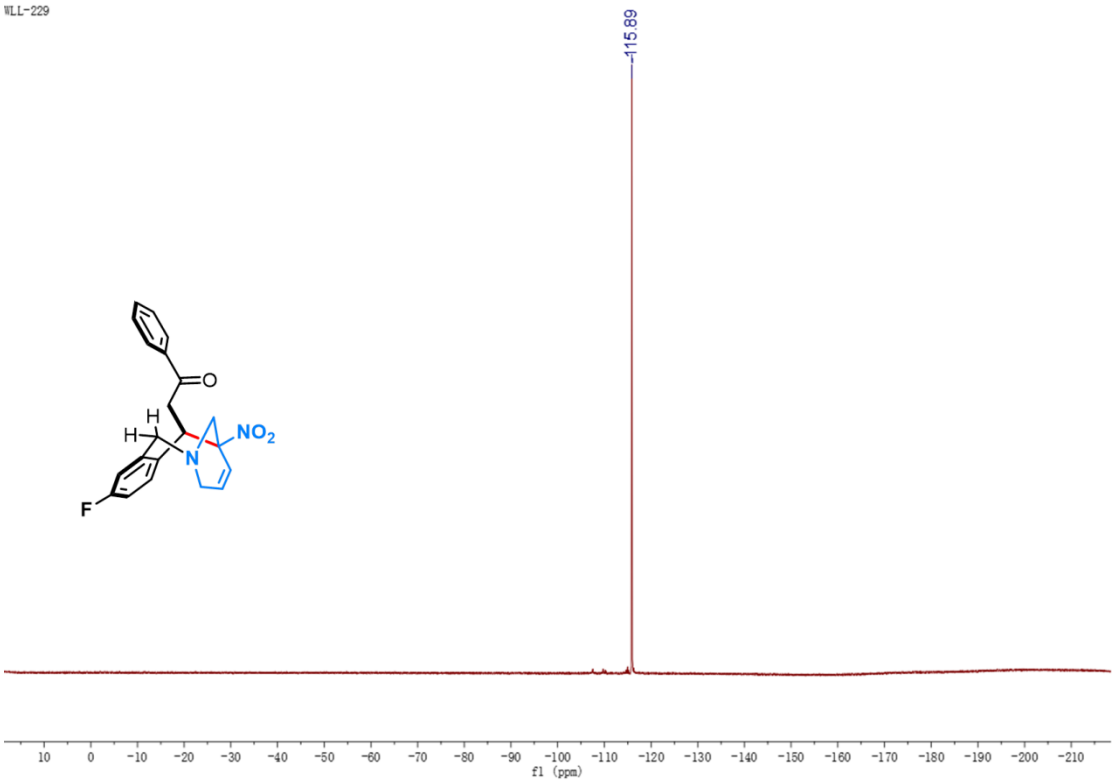
^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)



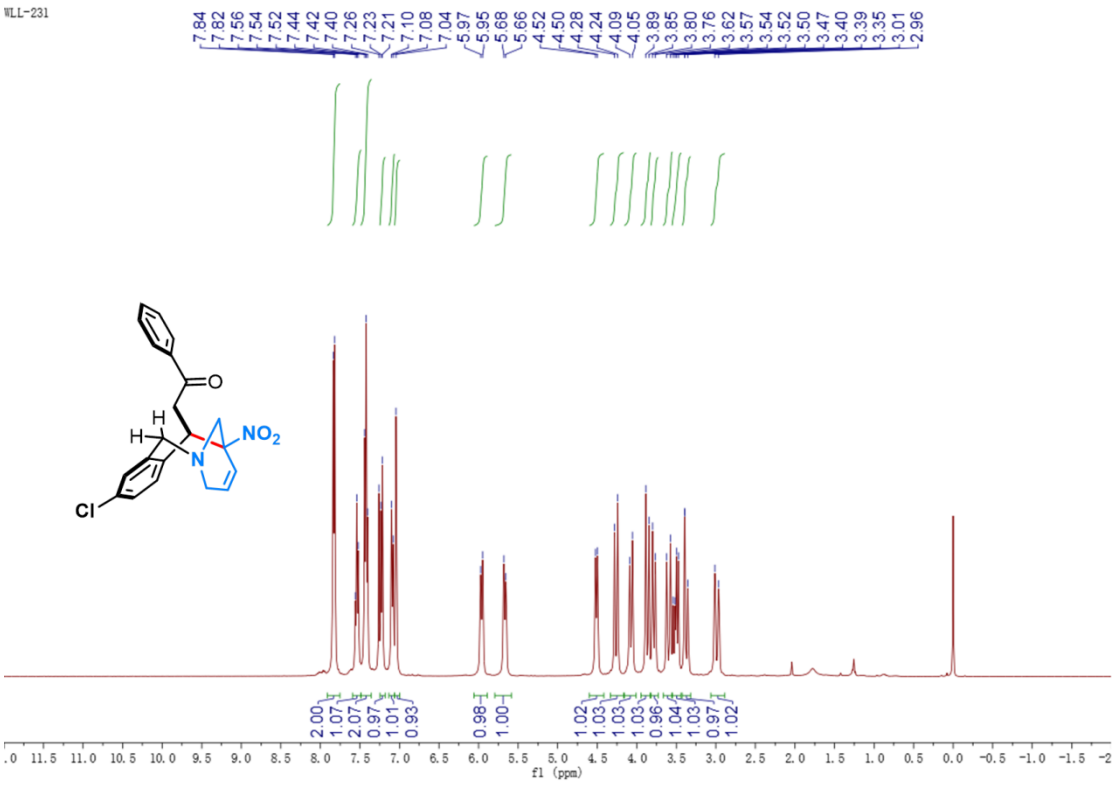
^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)



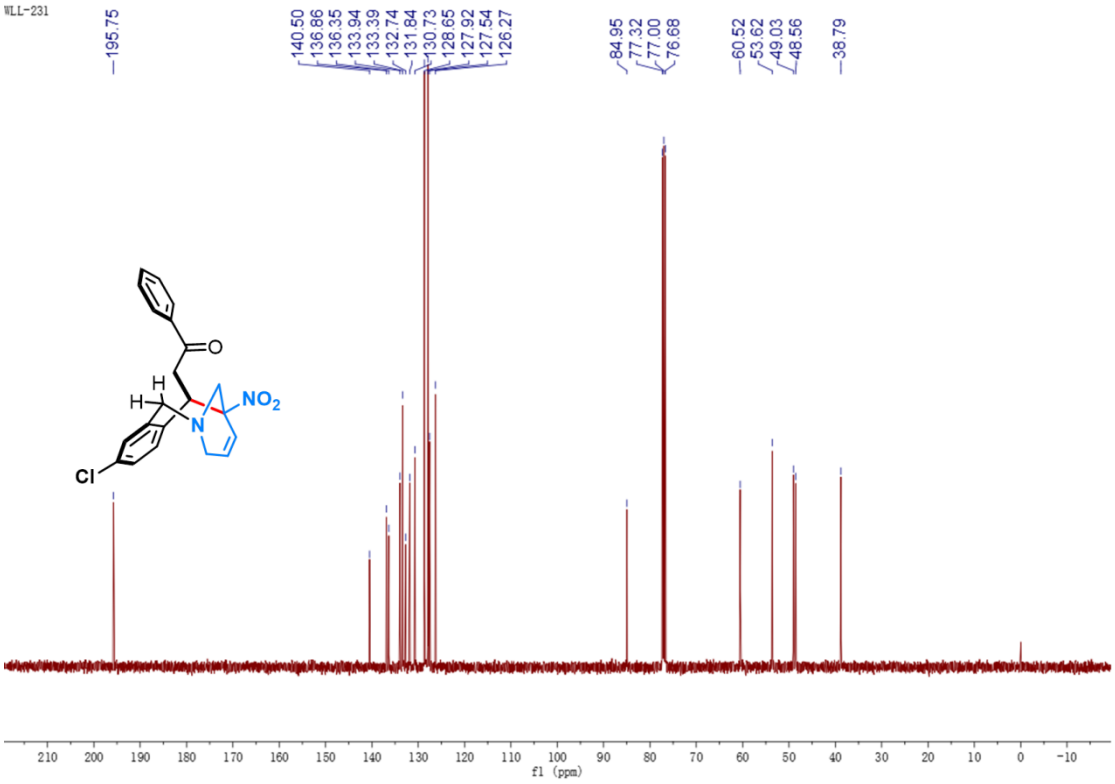
^{19}F NMR spectrum of **2n** (376 MHz, $CDCl_3$)



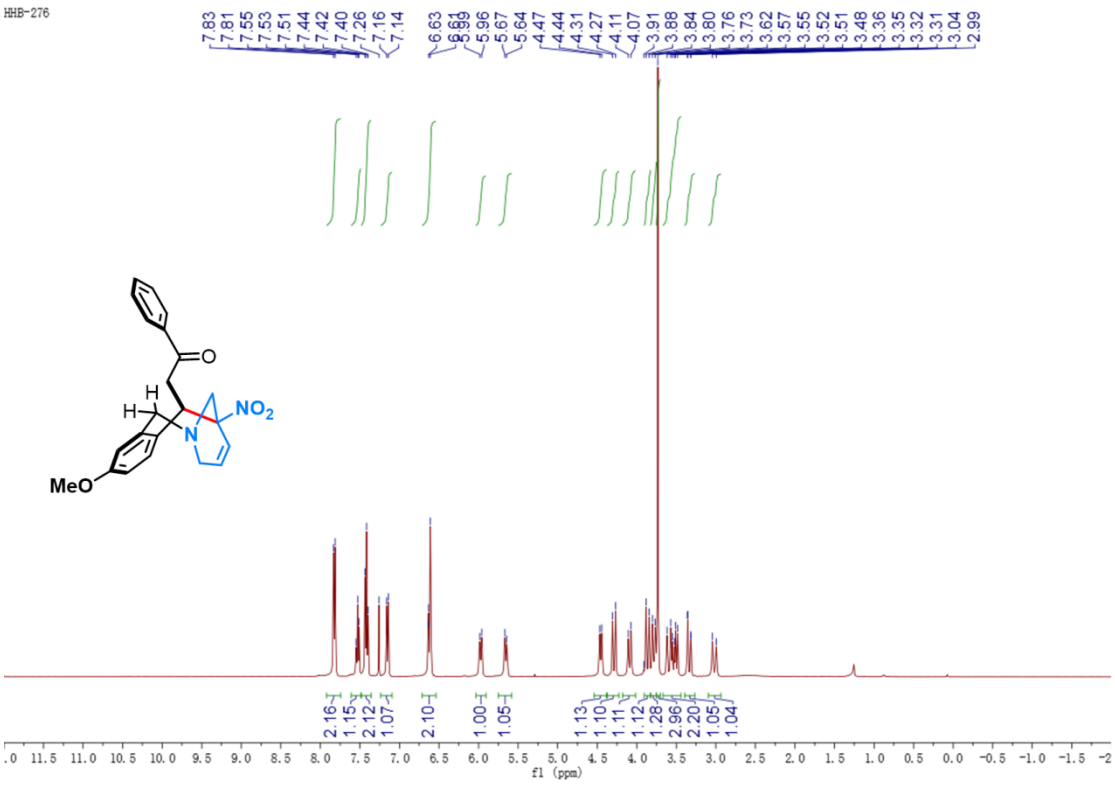
^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)



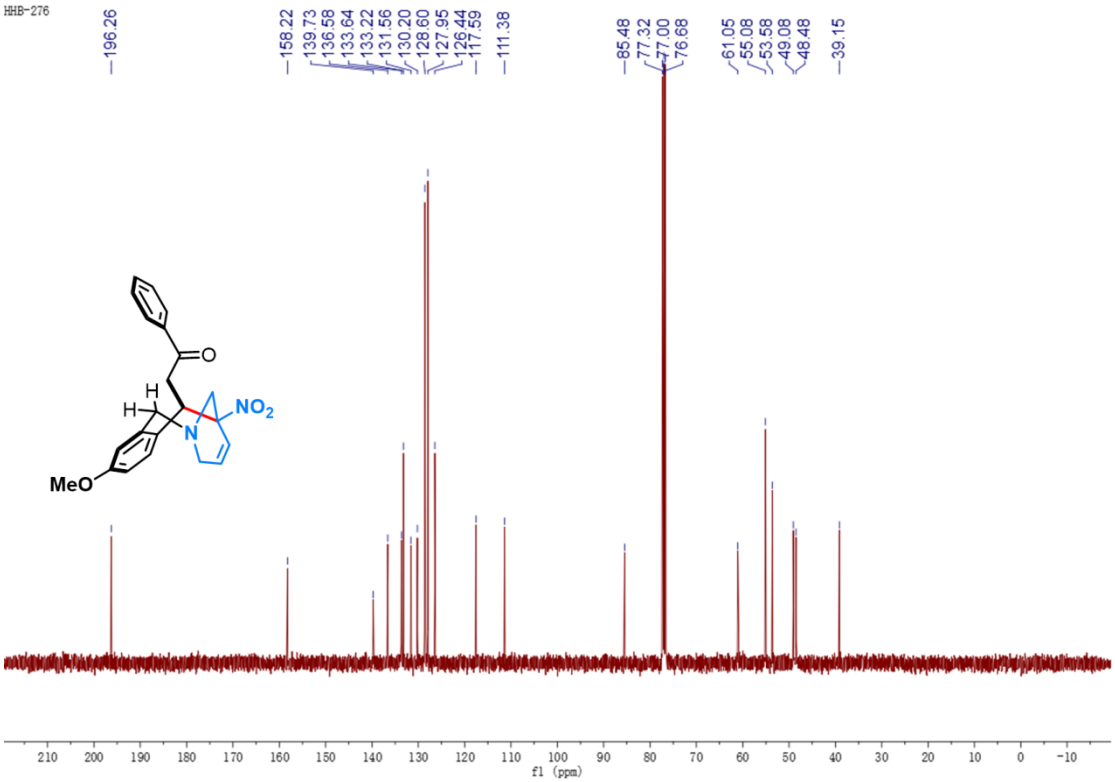
^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)



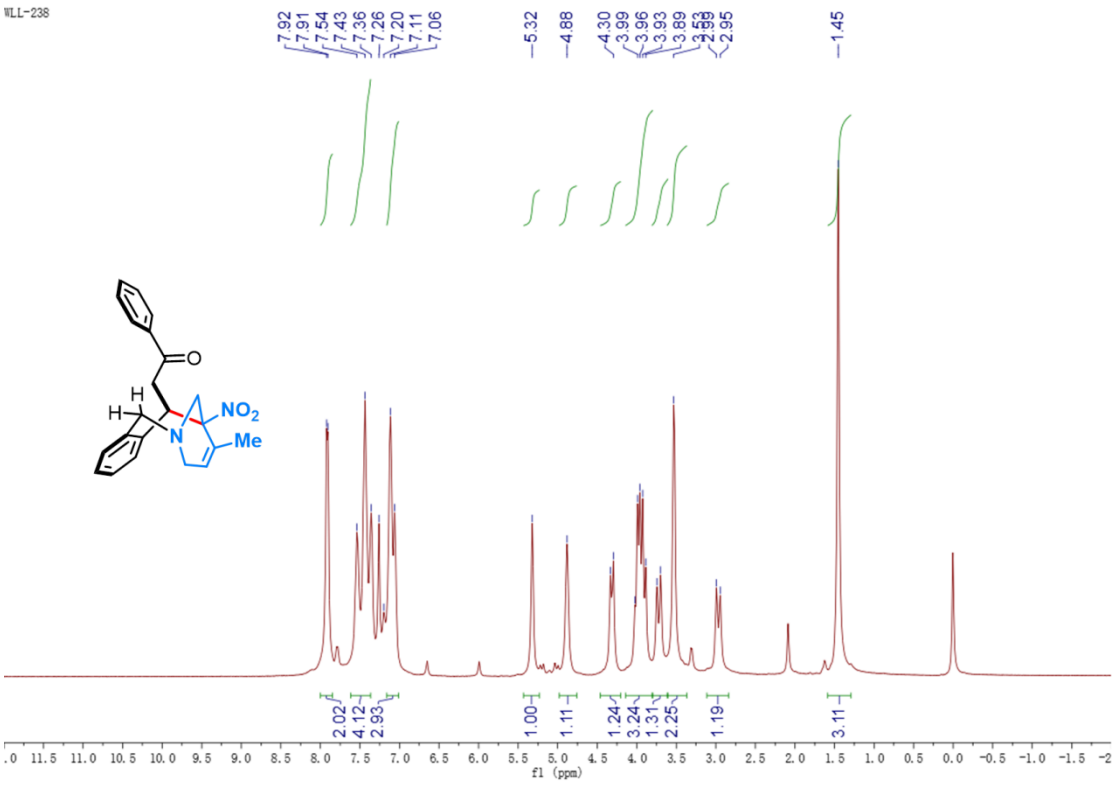
^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)



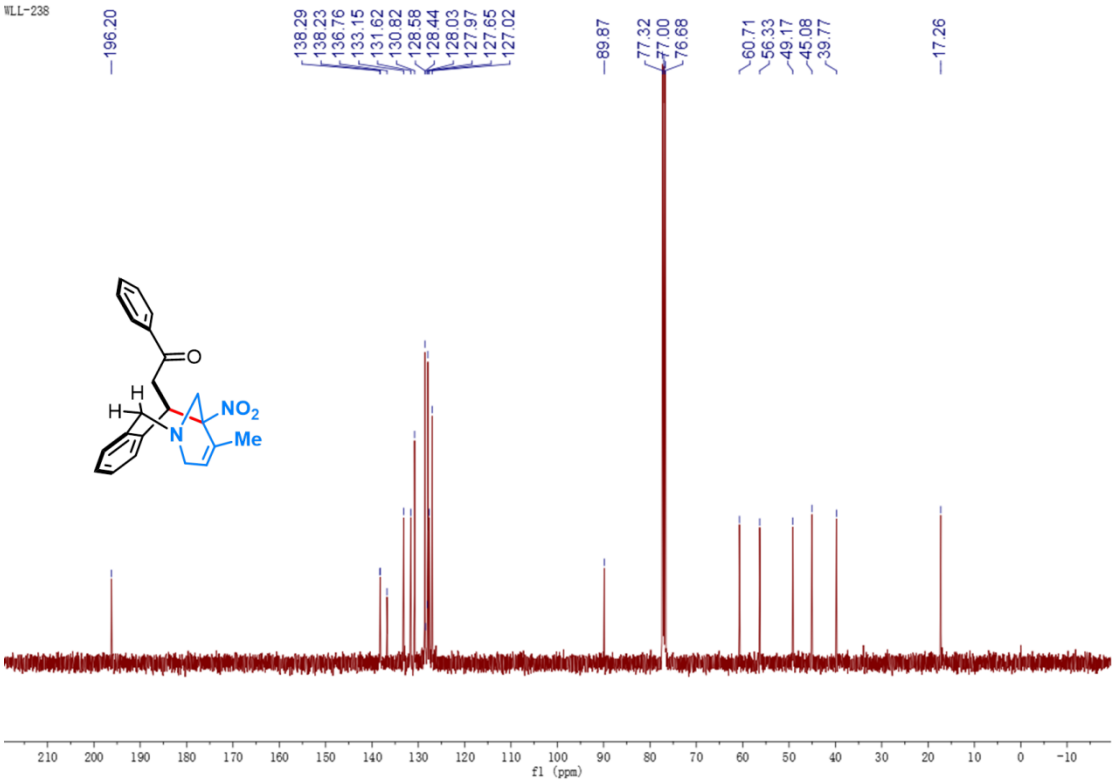
^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)



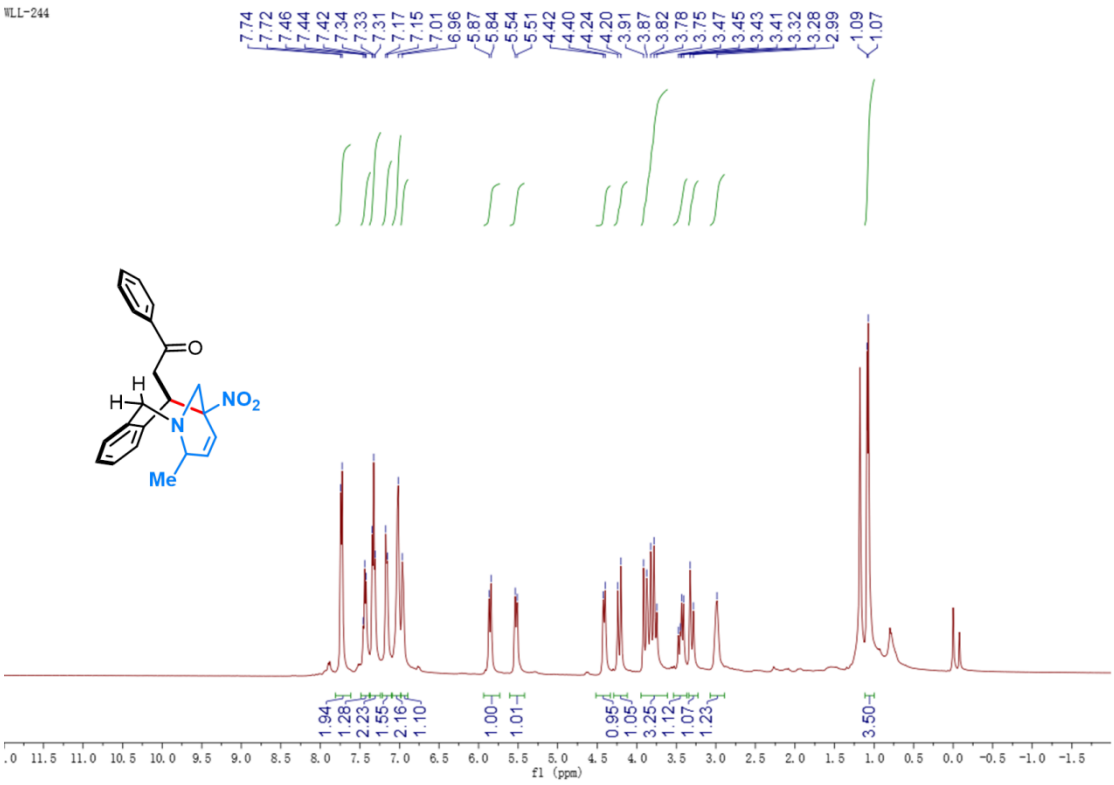
^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)



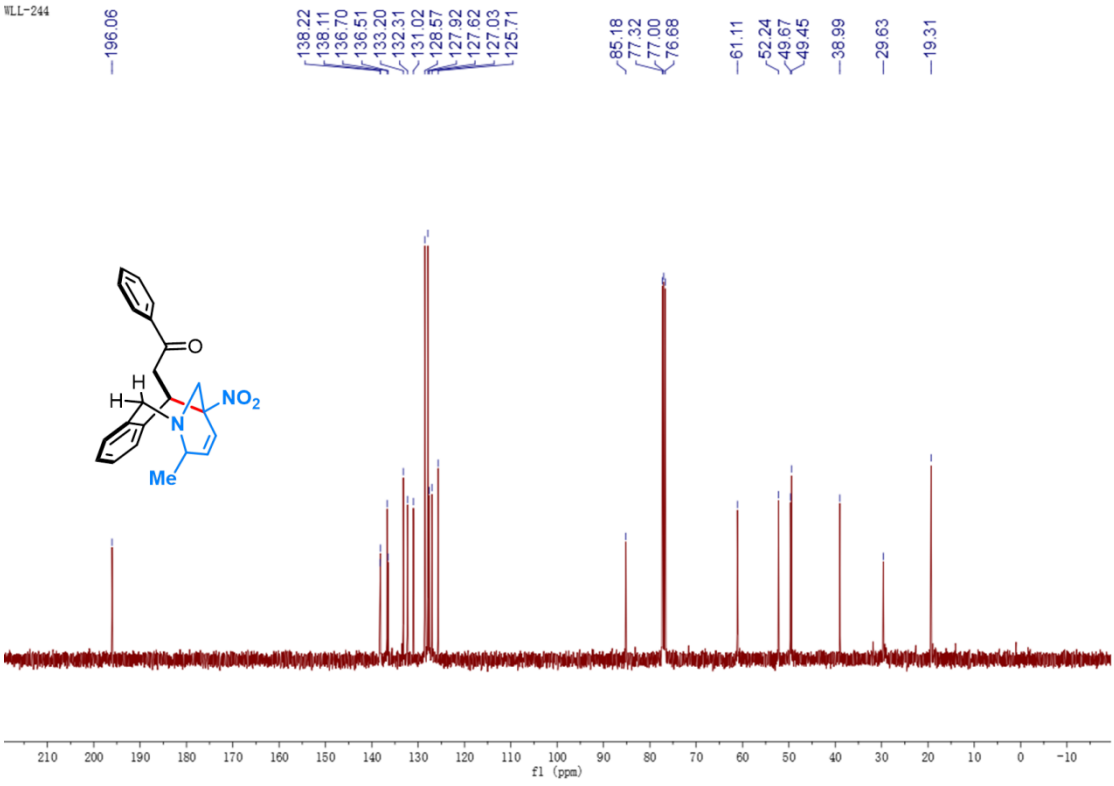
^{13}C NMR spectrum of **2q** (100 MHz, $CDCl_3$)



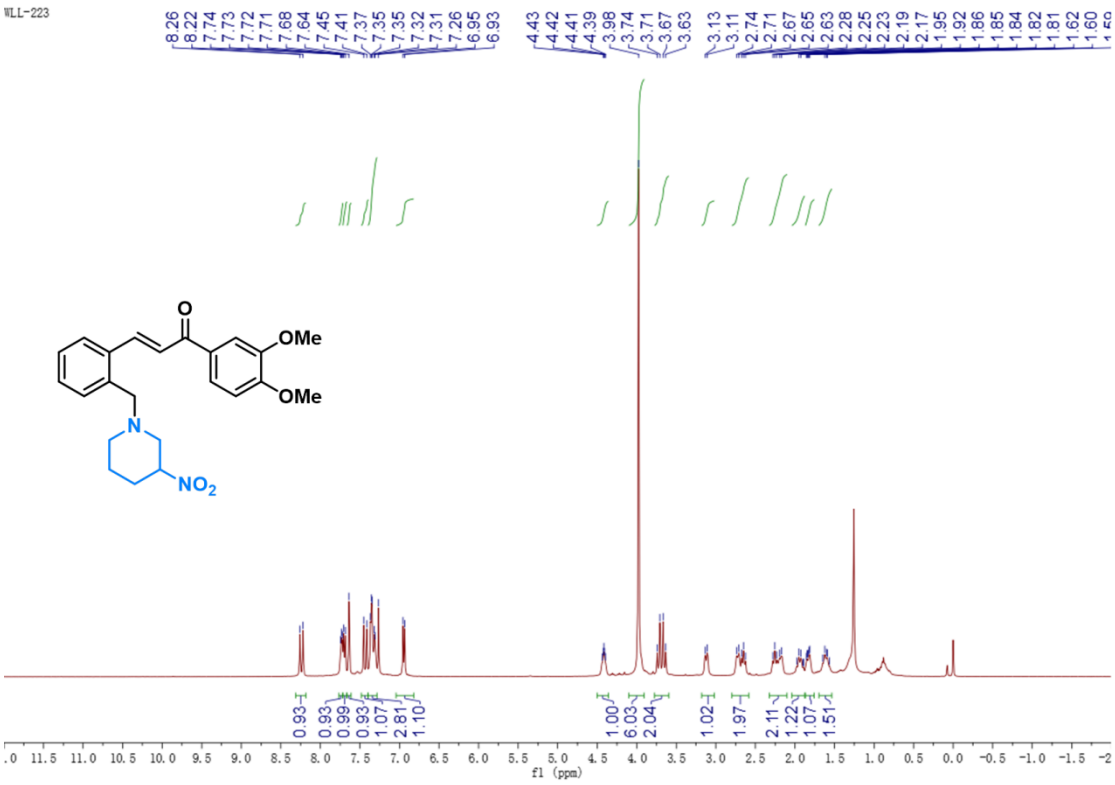
^{1}H NMR spectrum of **2r** (400 MHz, $CDCl_3$)



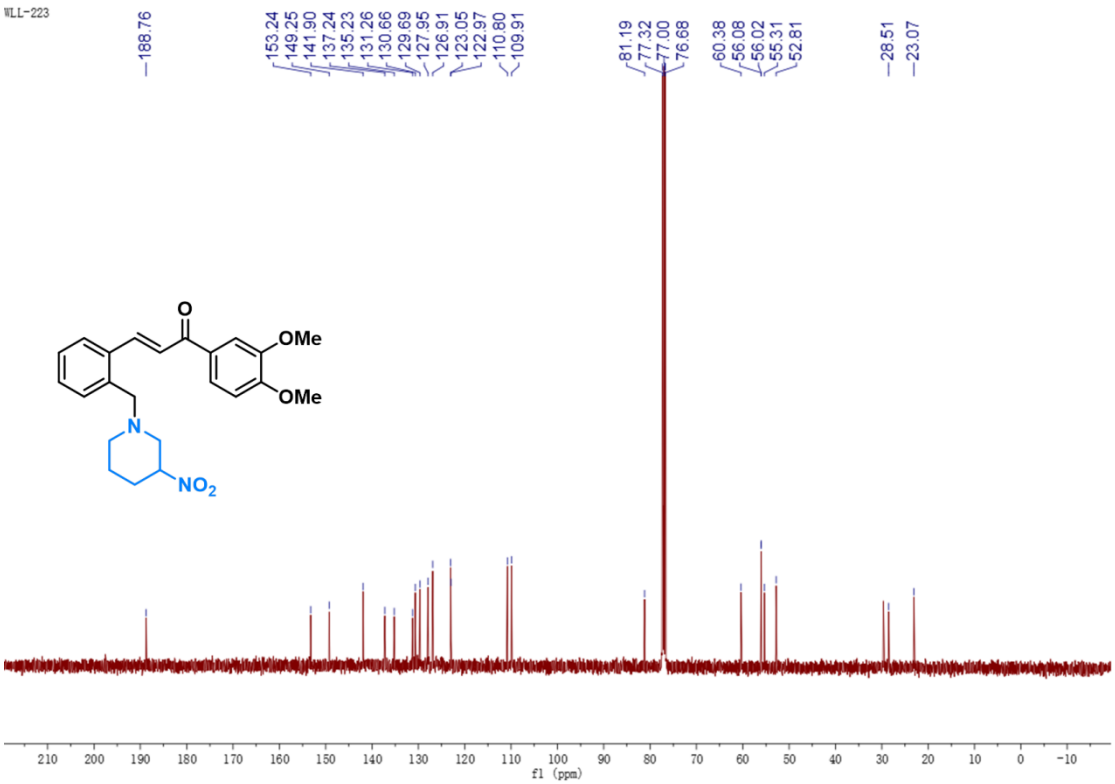
^{13}C NMR spectrum of **2r** (100 MHz, $CDCl_3$)



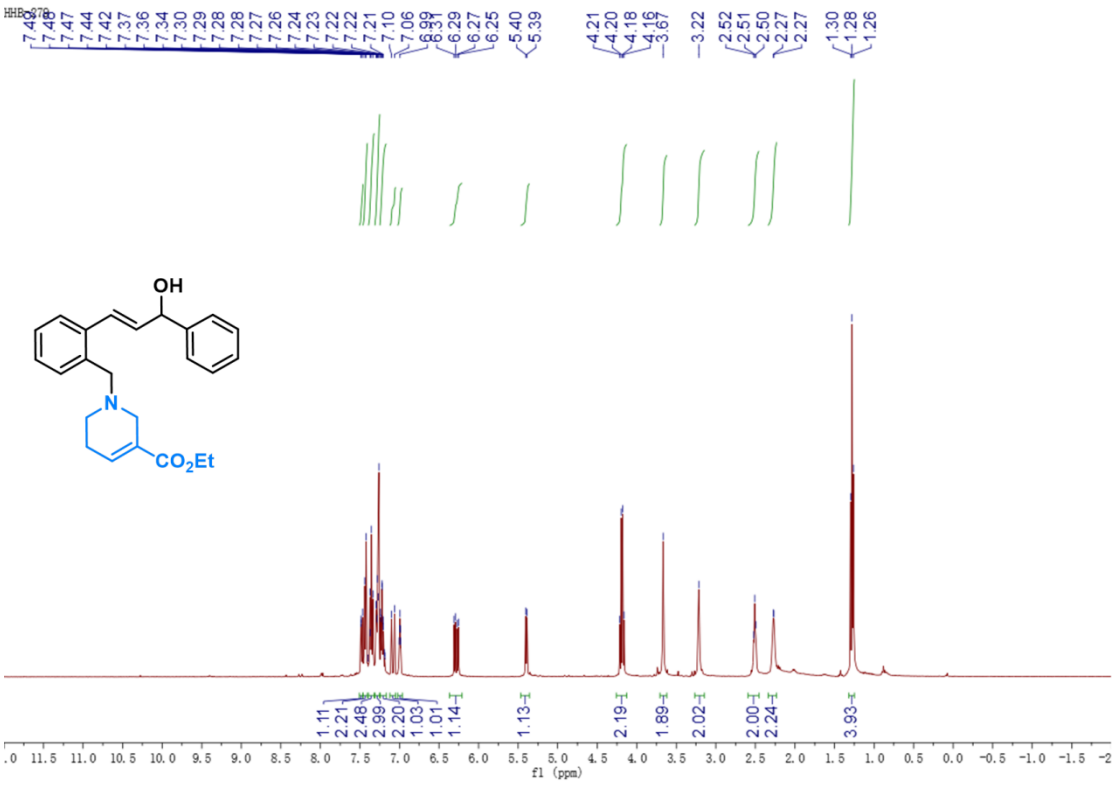
^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$)



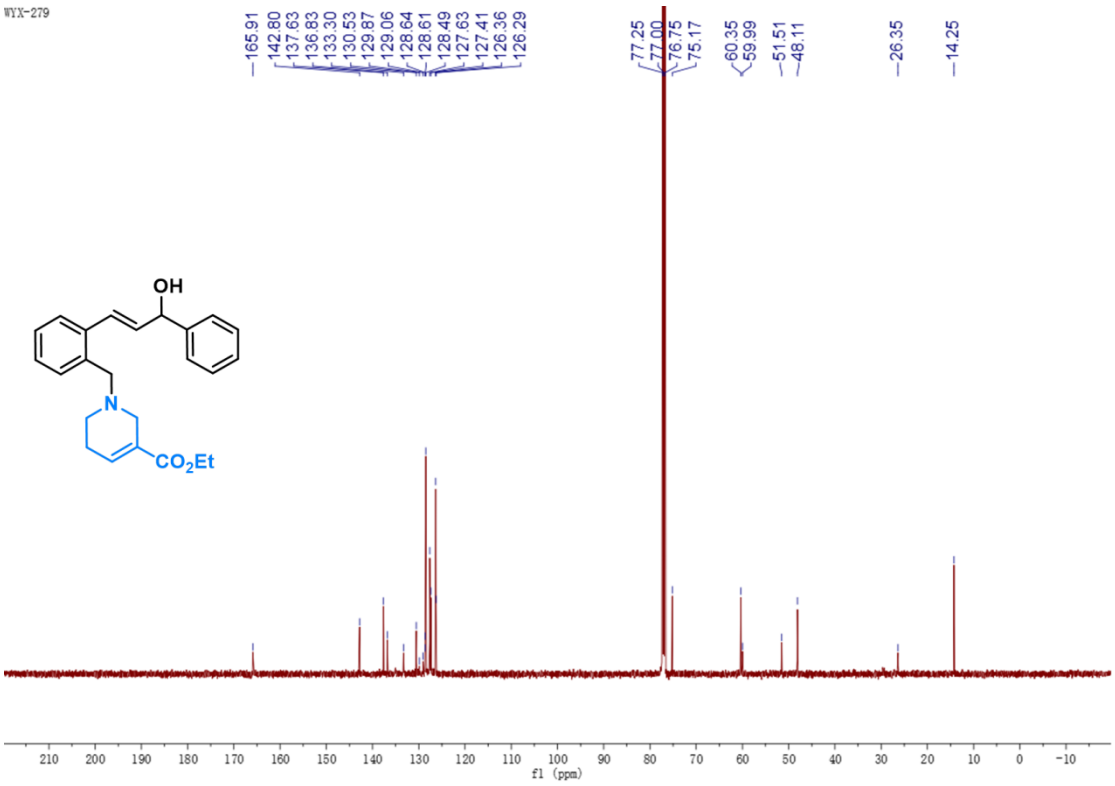
^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$)



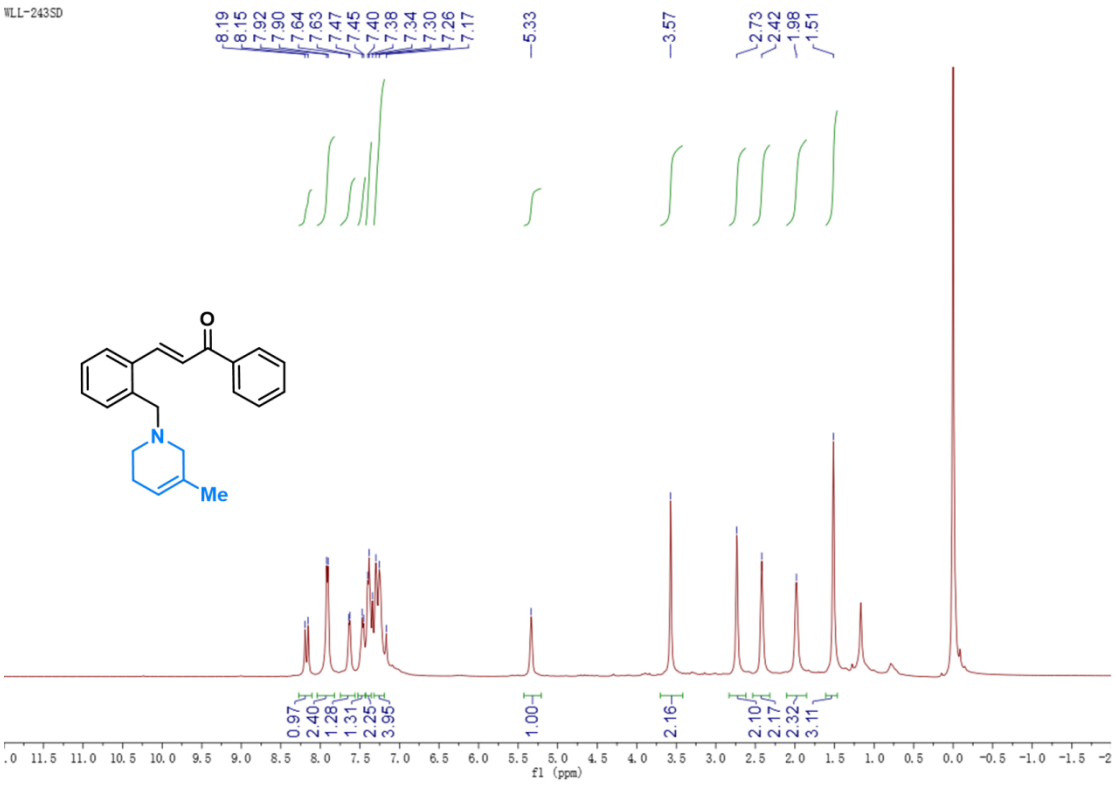
^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$)



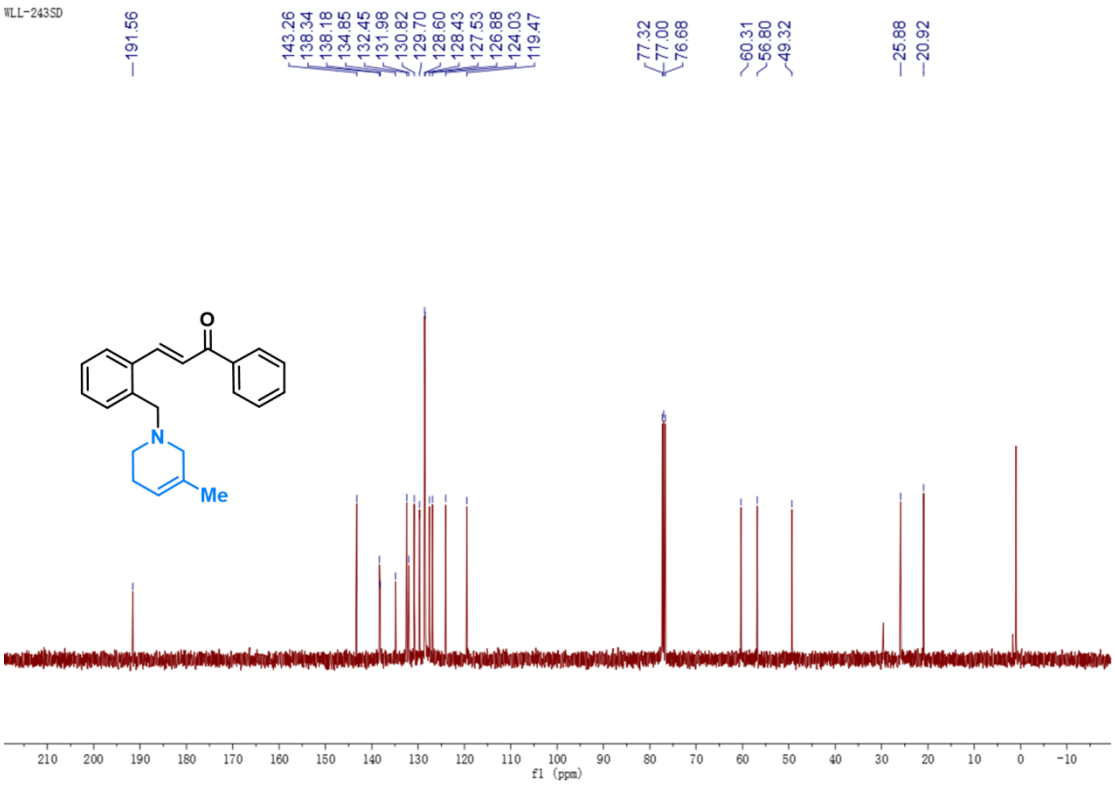
^{13}C NMR spectrum of **4** (125 MHz, $CDCl_3$)



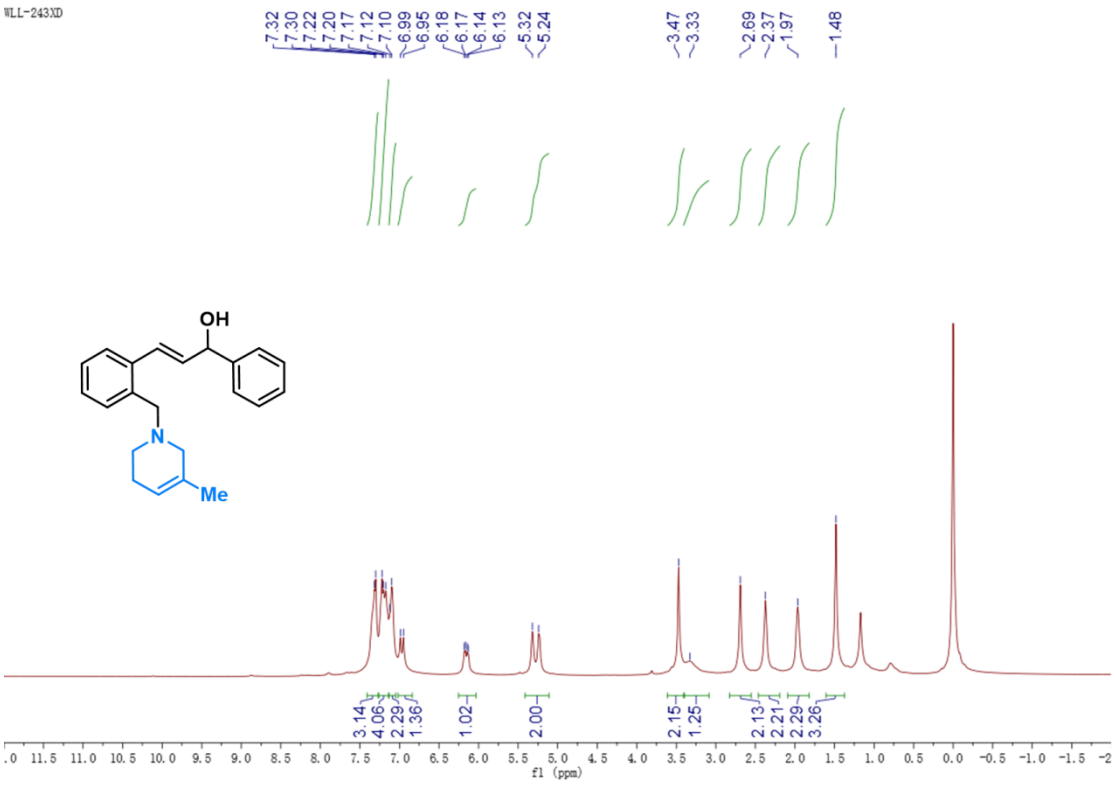
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



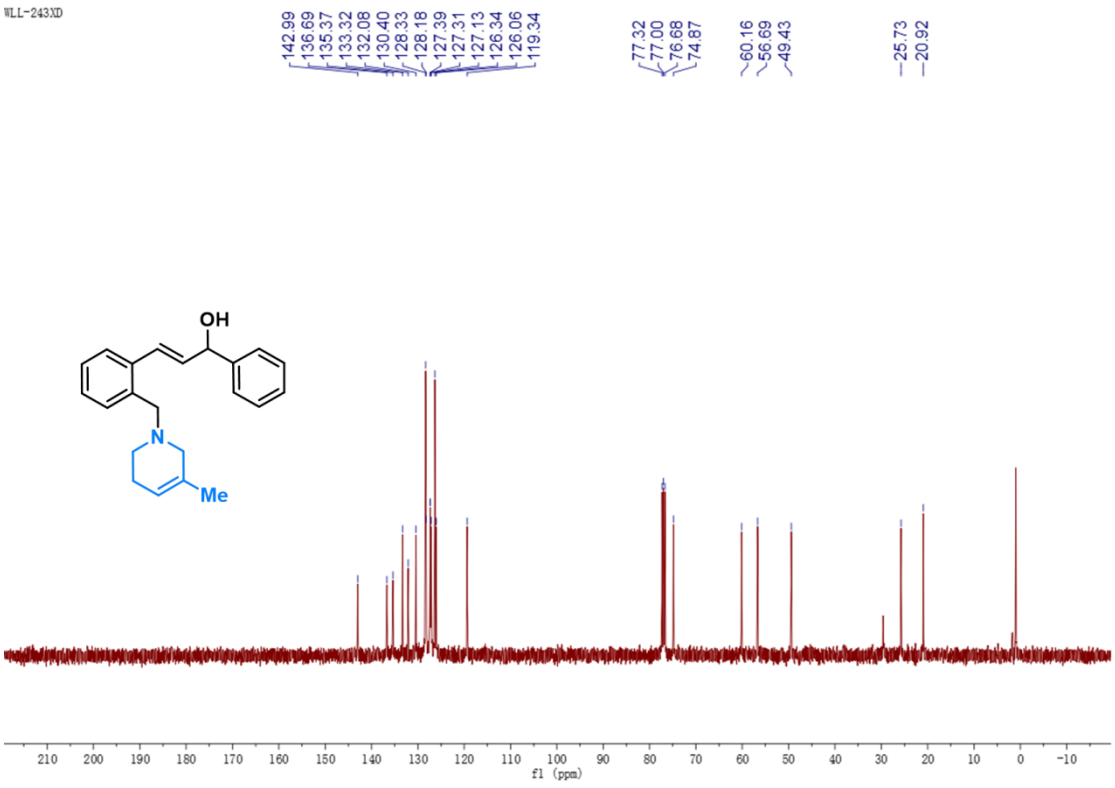
^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)



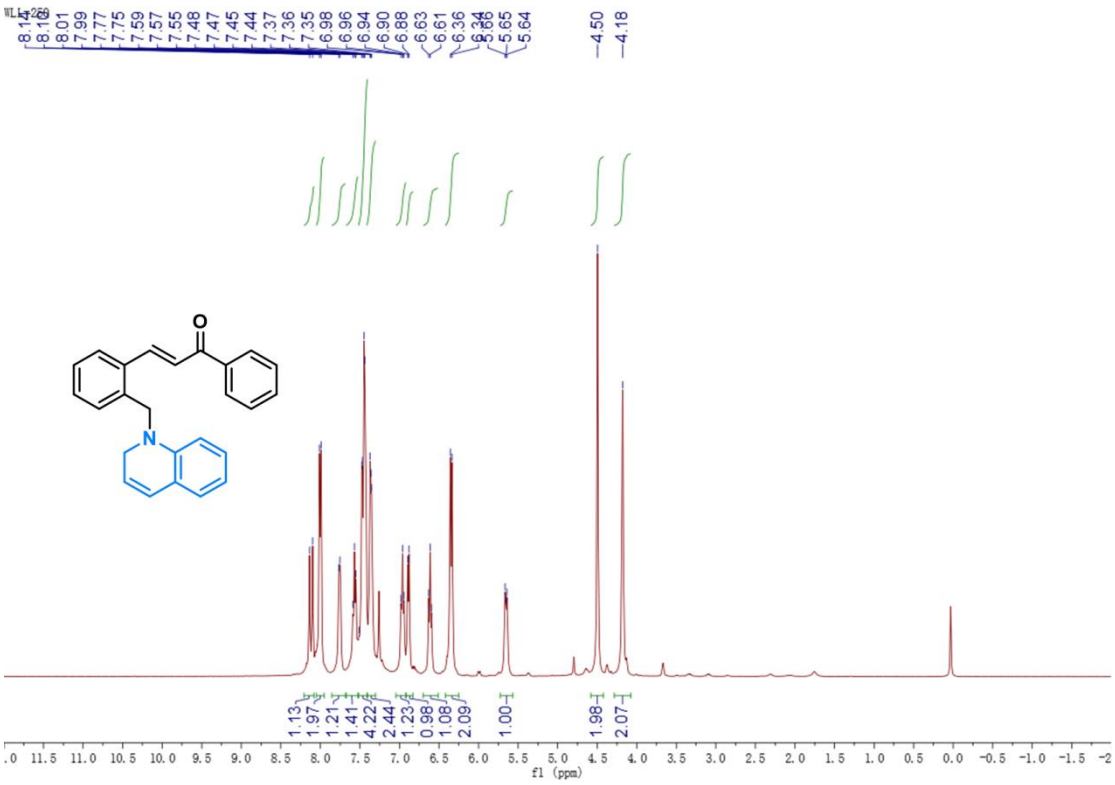
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



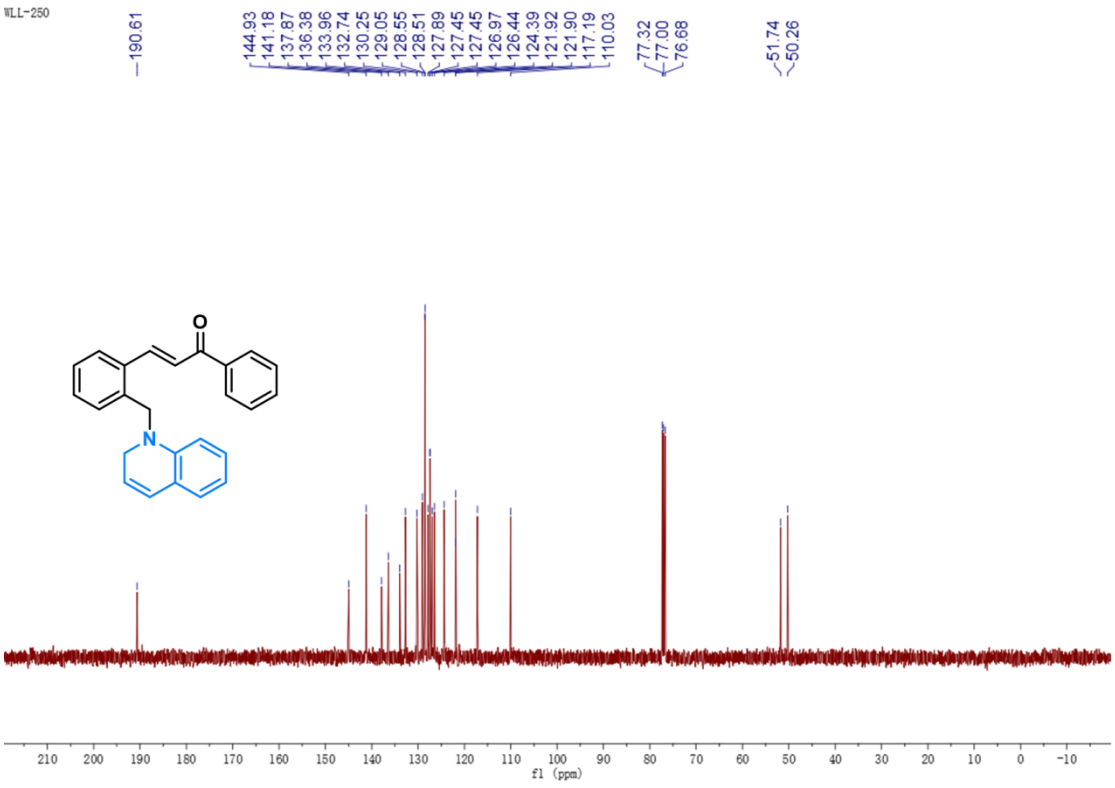
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



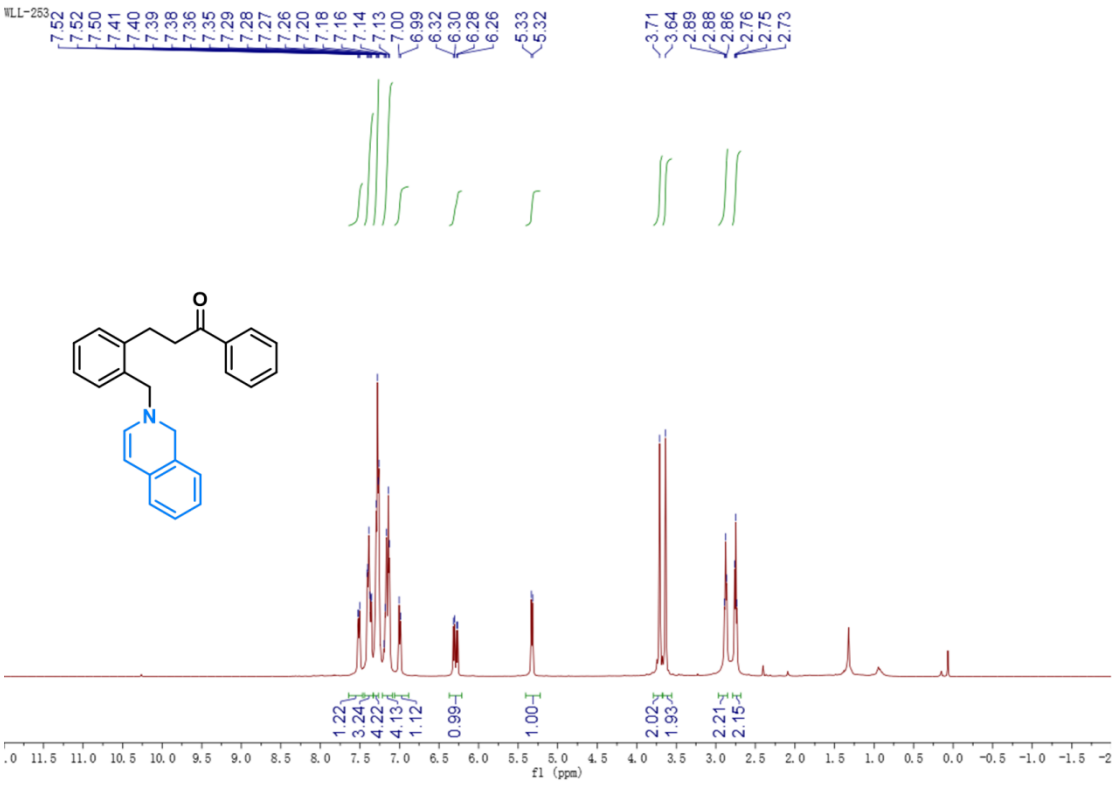
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



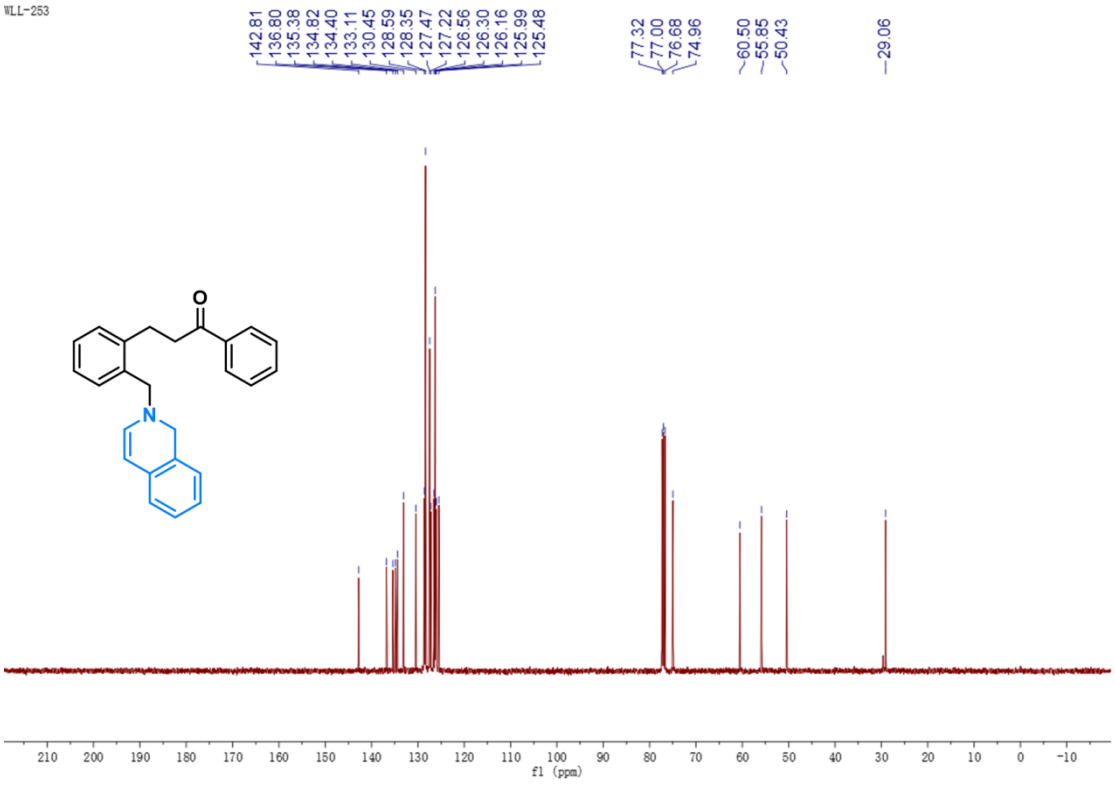
^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)



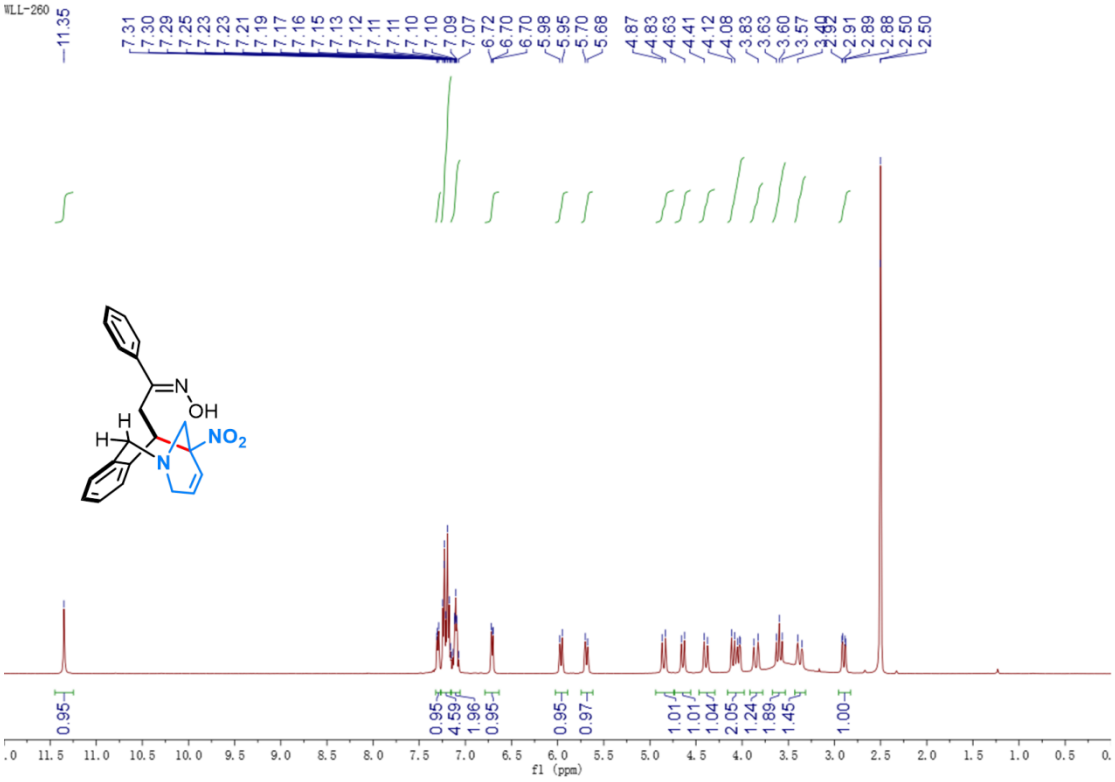
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



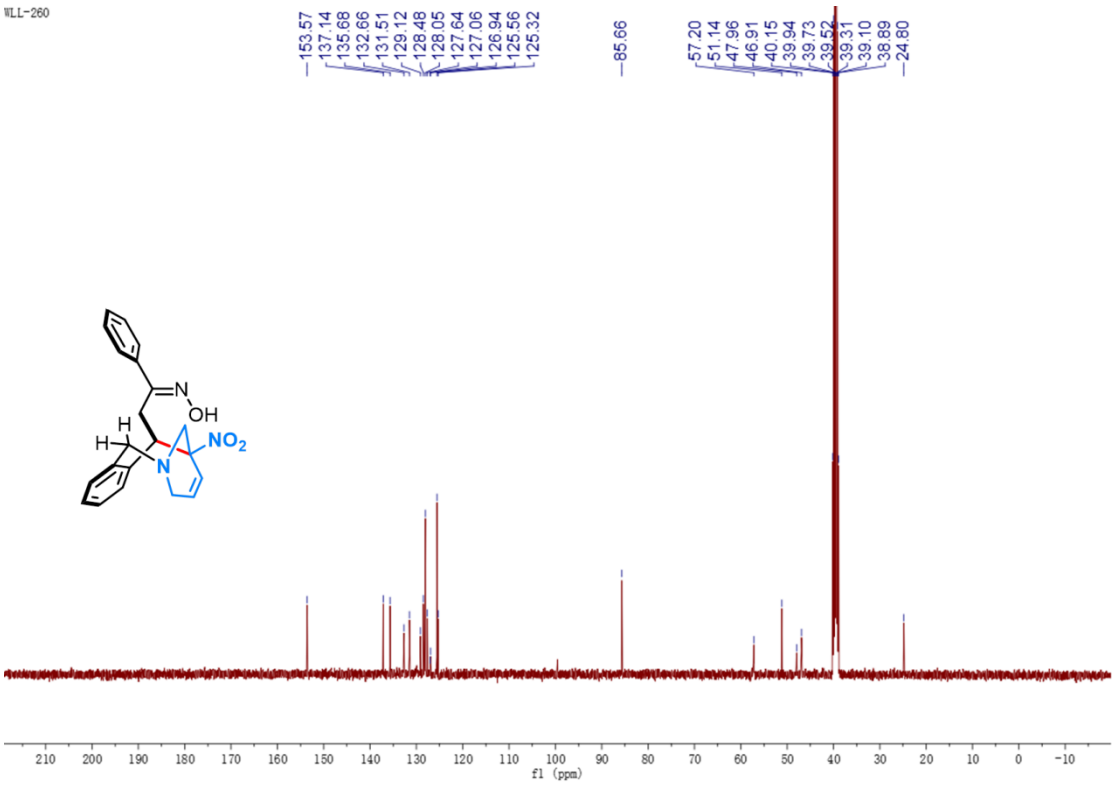
^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$)



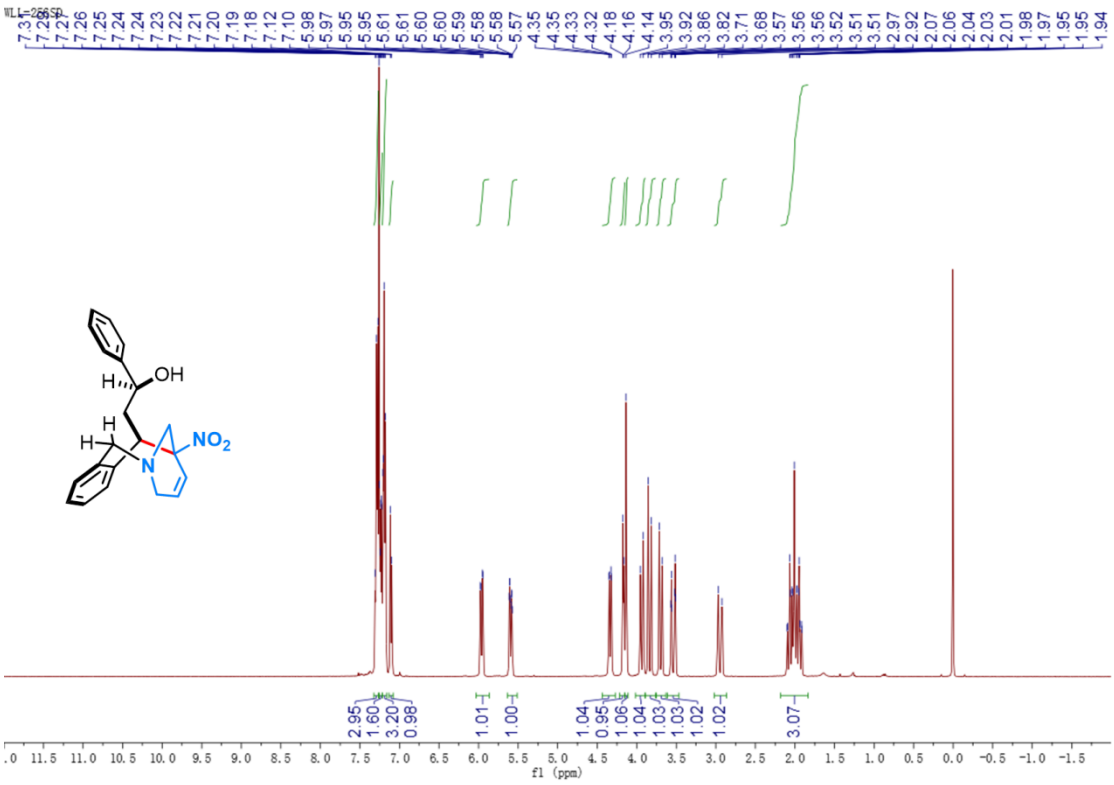
^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$)



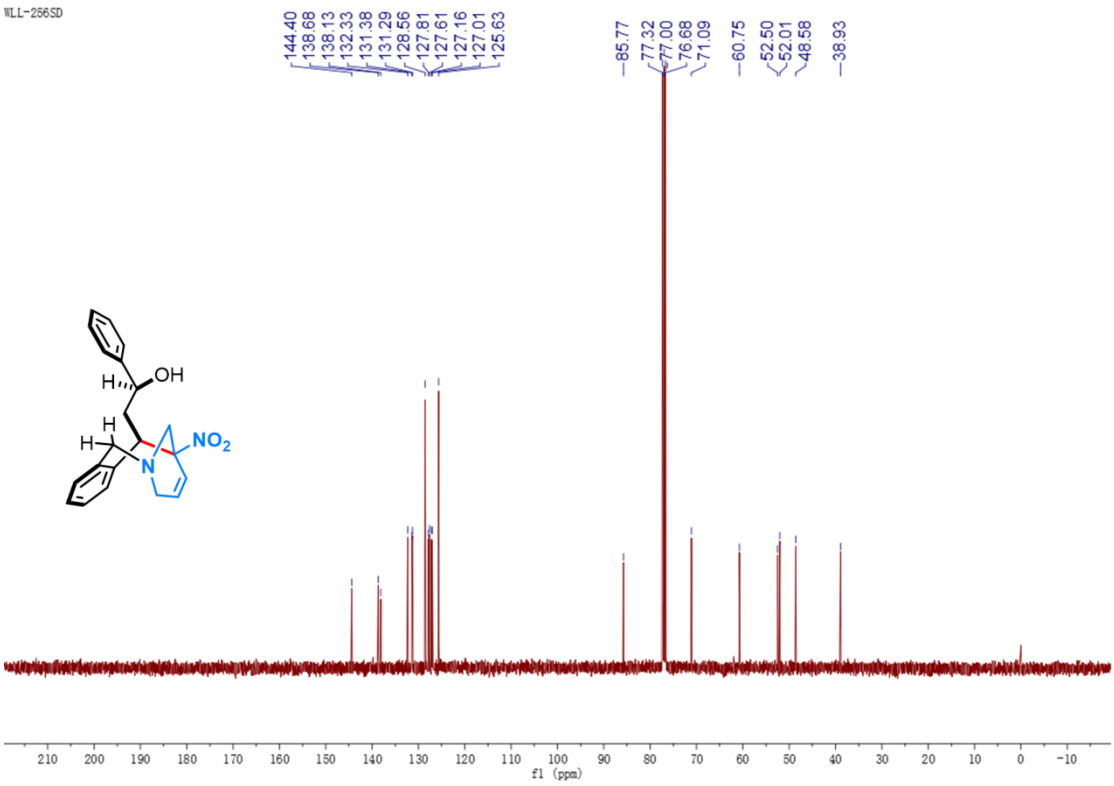
^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$)



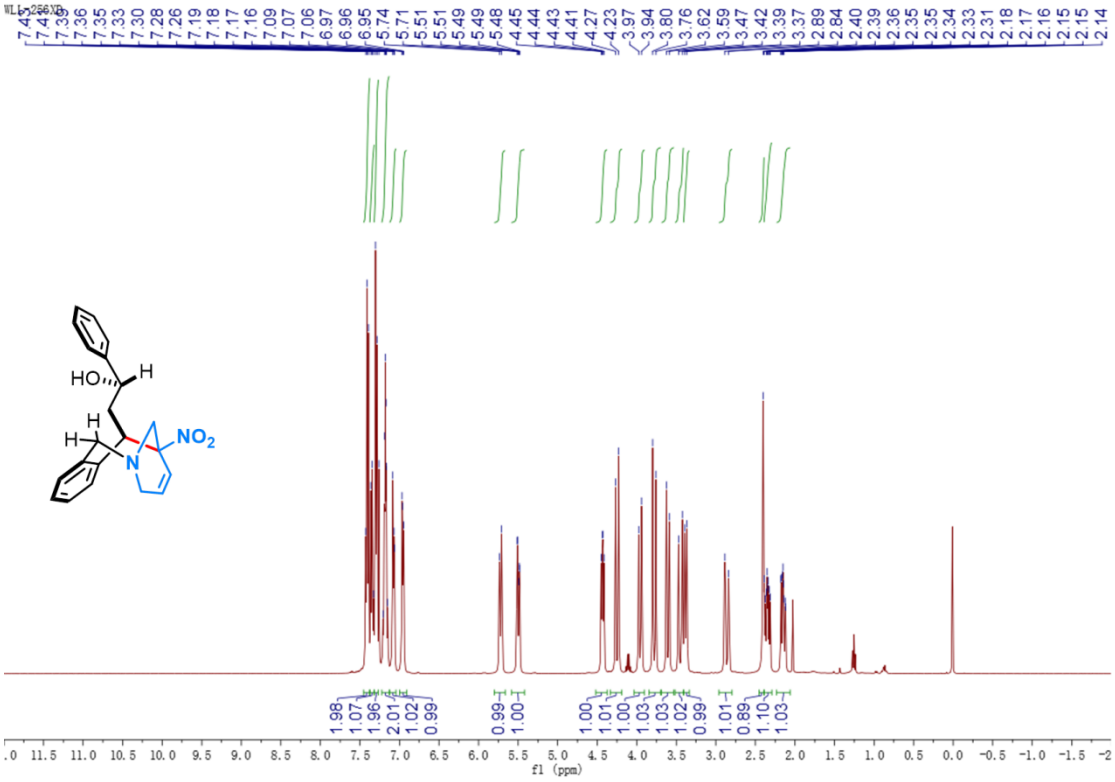
^{1}H NMR spectrum of **9a** (400 MHz, $CDCl_3$)



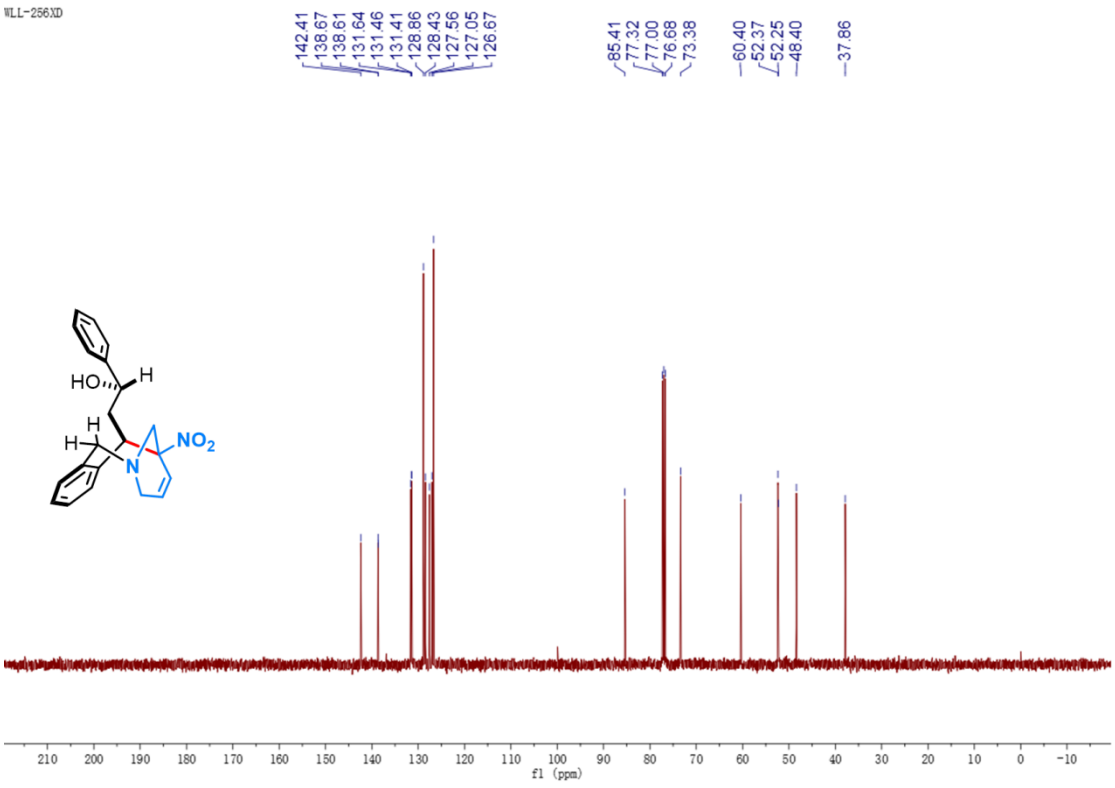
^{13}C NMR spectrum of **9a** (100 MHz, $CDCl_3$)



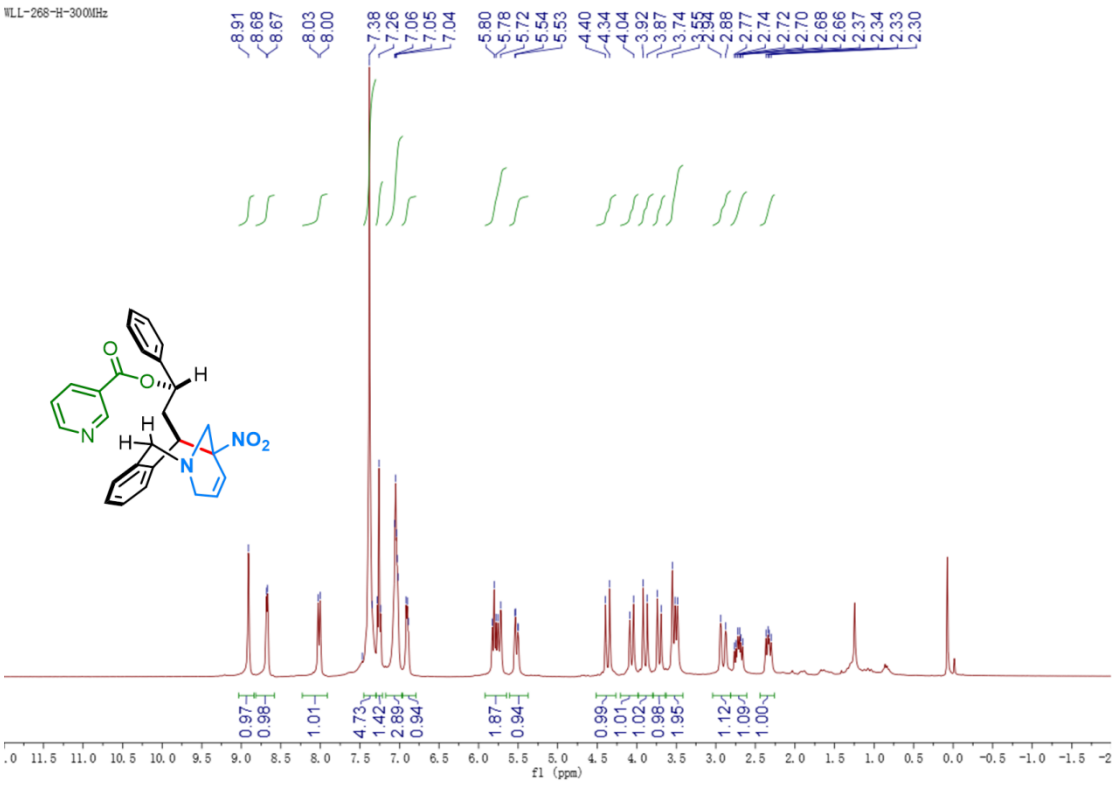
^{1}H NMR spectrum of **9a'** (400 MHz, $CDCl_3$)



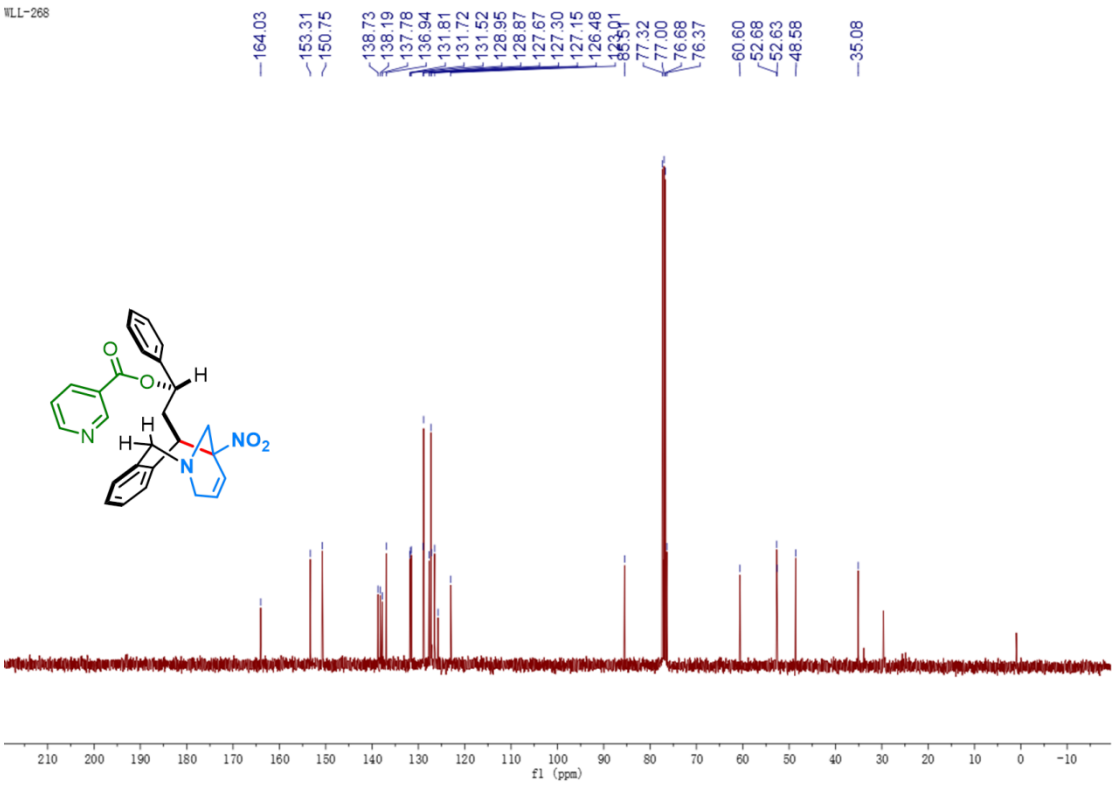
^{13}C NMR spectrum of **9a'** (100 MHz, $CDCl_3$)



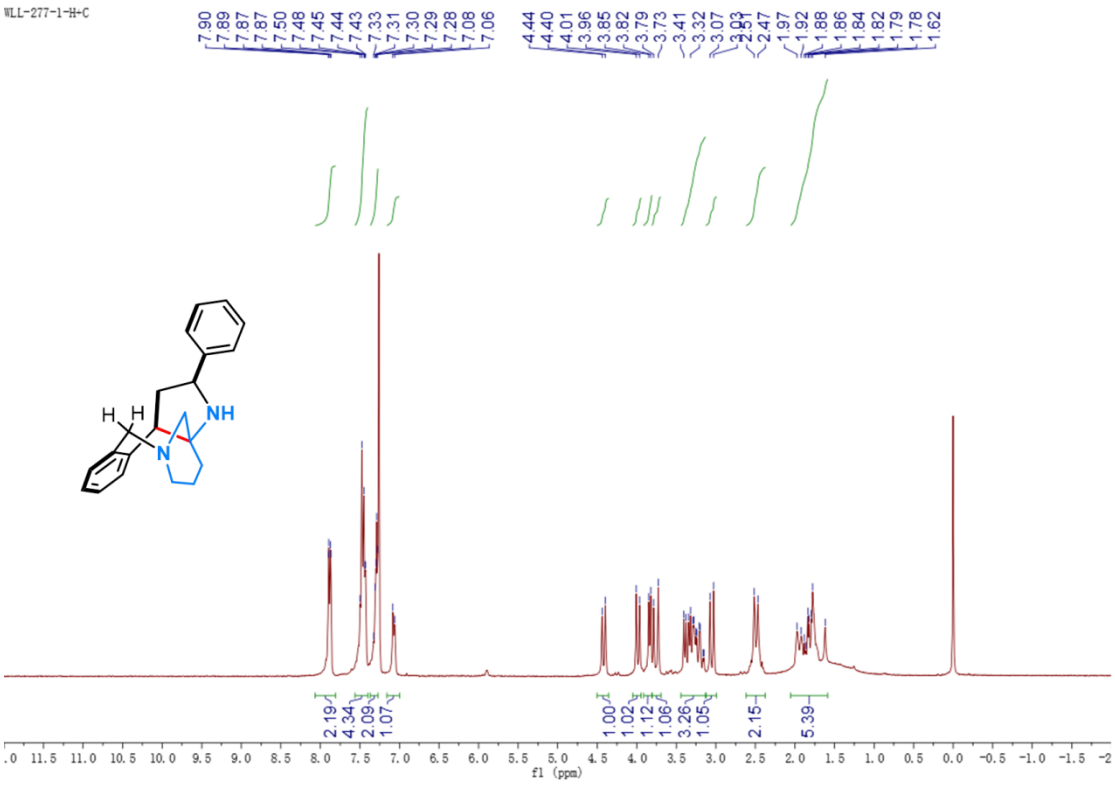
^{1}H NMR spectrum of **10** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **11** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of **11** (75 MHz, $CDCl_3$)