Supporting Information

Chalcone-based pyridinium salts and their diastereoselective dearomatization to access bi-bridged benzoazepines

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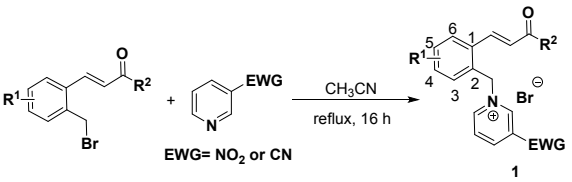
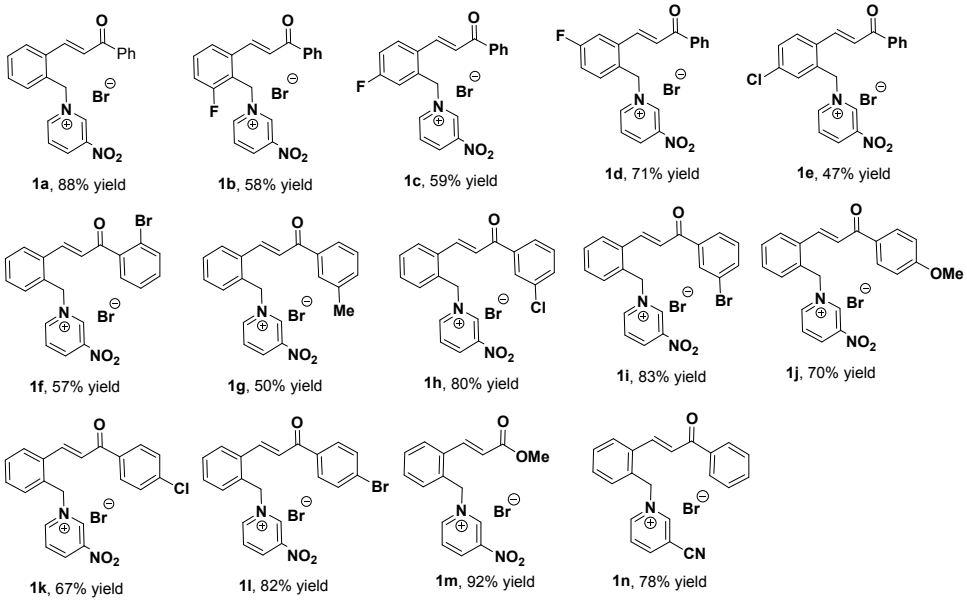
1. General methods

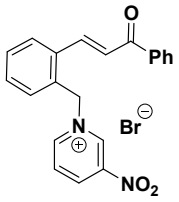
NMR spectra were recorded with tetramethylsilane as the internal standard. For most of the samples, ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). For others, ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 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 novel chalcone-based pyridinium salts 1



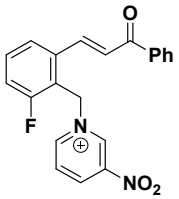


General procedure： A solution of *ortho*-bromomethyl chalcones (1.5 equiv.) and 3-nitro or 3-cyanopyridine (1.0 equiv.) in CH_3CN was placed in a Dean-Stark apparatus and the mixture was heated to reflux in oil bath for 16 h. During the reaction process, much precipitate was generated. To purify them, a simple filtration was needed, affording chalcone-based pyridinium salts **1** in 47-92% yields.



(*E*)-3-nitro-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)pyridin-1-ium bromide (**1a**)

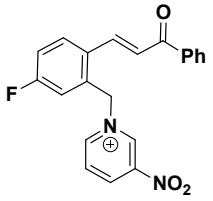
According to the general procedure, **1a** was prepared on a scale of 8.0 mmol. Yellow solids, 3.00 g, 88% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 210.5-211.4°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 9.41 (d, J = 8.0 Hz, 1H), 9.37 (d, J = 8.0 Hz, 1H), 8.47 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 8.17-8.14 (m, 3H), 8.08 (d, J = 16.0 Hz, 1H), 7.88 (d, J = 16.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.61-7.50 (m, 4H), 7.22 (d, J = 8.0 Hz, 1H), 6.43 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.0, 149.7, 146.6, 142.9, 140.6, 139.1, 137.1, 134.0, 133.5, 133.0, 130.8, 129.7, 129.2, 129.1, 128.9, 128.7, 128.2, 126.0, 61.4. IR (KBr) v 3421, 3021, 1655, 1599, 1547, 1348, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}N_2O_3$ [M-Br]$^+$: 345.1234, found: 345.1232.



(*E*)-1-(2-fluoro-6-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium (**1b**)

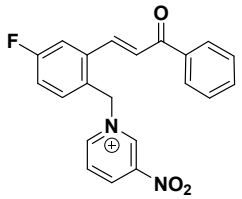
According to the general procedure, **1b** was prepared on a scale of 3.10 mmol. Yellow solids, 0.80 g, 58% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 164.5-165.3°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 9.36 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 9.23 (d, J = 8.0 Hz, 1H), 8.39 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 8.17-8.12 (m, 3H), 8.05 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 16.0 Hz, 1H), 7.72-7.68 (m, 2H), 7.59 (t, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 1H), 6.40 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9, 161.6 (d, $^1J_{C\text{-}F}$ = 247.0 Hz, 1C),

149.1, 146.2, 142.2, 140.7, 138.2, 137.8, 137.0, 133.6, 132.6 (d, J = 10.0 Hz, 1C), 129.2, 128.9, 128.7, 127.9, 124.5, 118.8 (d, $^2J_{C\text{-}F}$ = 14.0 Hz, 1C), 117.4 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, 1C), 55.3. IR (KBr) ν 3443, 3019, 1654, 1597, 1549, 1243, 707 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}FN_2O_3$ [M-Br]$^+$: 363.1139, found: 363.1137.



(*E*)-1-(5-fluoro-2-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium (**1c**)

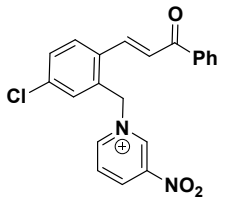
According to the general procedure, **1c** was prepared on a scale of 2.50 mmol. Yellow solids, 0.65 g, 59% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 171.3-172.1°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 9.44-9.39 (m, 2H), 8.48 (dd, J_1 = J_2 = 8.0 Hz, 1H), 8.25 (dd, J_1 = J_2 = 4.0 Hz, 1H), 8.17 (dd, J_1 = J_2 = 4.0 Hz, 2H), 8.02 (d, J = 12.0 Hz, 1H), 7.89 (d, J = 12.0 Hz, 1H), 7.72-7.68 (m, 1H), 7.59 (t, J = 8.0 Hz, 2H), 7.45-7.41 (m, 1H), 7.08 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.44 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9, 163.2 (d, $^1J_{C\text{-}F}$ = 248.0 Hz, 1C), 149.8, 146.7, 143.2, 140.7, 138.0, 137.1, 135.7 (d, $^3J_{C\text{-}F}$ = 7.0 Hz, 1C), 133.5, 130.8 (d, $^3J_{C\text{-}F}$ = 7.0 Hz, 1C), 130.3 (d, $^3J_{C\text{-}F}$ = 7.0 Hz, 1C), 129.3, 128.9, 128.7, 125.7, 116.6 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, 1C), 115.9 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, 1C), 60.9. IR (KBr) ν 3441, 3067, 2943, 1653, 1594, 1550, 1220, 718 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}FN_2O_3$ [M-Br]$^+$: 363.1139, found: 363.1138.



(*E*)-1-(4-fluoro-2-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium (**1d**)

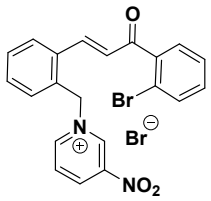
According to the general procedure, **1d** was prepared on a scale of 2.50 mmol. Yellow solids, 0.79 g, 71% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 174.2-174.8°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 9.40-9.35 (m, 2H), 8.47-8.43 (m, 1H), 8.18 (t, J = 4.0 Hz, 2H), 8.10 (dd, J_1 = J_2 = 4.0 Hz, 1H), 8.02 (d, J = 16.0 Hz, 1H),7.96 (d, J = 16.0 Hz, 1H),7.70 (t, J = 8.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 2H), 7.48-7.38 (m, 2H), 6.41 (d, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9, 162.7 (d, $^1J_{C\text{-}F}$ = 246.0 Hz, 1C), 149.5, 146.5,

142.7, 140.6, 137.7, 137.0, 136.9, 133.6, 132.4 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz, 1C), 129.2, 128.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz, 1C), 128.9, 128.7, 127.2, 117.5 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz, 1C), 114.7 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz, 1C), 60.8. IR (KBr) *v* 3442, 2998, 1655, 1605, 1544, 1351, 1214, 726 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}FN_2O_3$ $[M\text{-}Br]^+$: 363.1139, found: 363.1137.



(*E*)-1-(5-chloro-2-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium (**1e**)

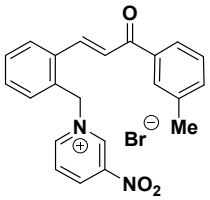
According to the general procedure, **1e** was prepared on a scale of 2.88 mmol. Yellow solids, 0.61g, 47% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 157.7-158.6°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H), 9.41 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 8.47 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 8.18 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 8.02 (d, *J* = 16.0 Hz, 1H),7.91 (d, *J* = 16.0 Hz, 1H),7.70 (t, *J* = 8.0 Hz, 1H), 7.65-7.57 (m, 3H), 7.37 (d, *J* = 4.0 Hz, 1H), 6.44 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9, 149.7, 146.6, 143.2, 140.7, 137.9, 137.0, 135.3, 134.9, 133.5, 133.0, 130.0, 129.7, 129.2, 128.9, 128.7, 126.5, 60.8, one carbon missing in the aromatic region. IR (KBr) *v* 3448, 2929, 1648, 1601, 776 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}ClN_2O_3$ $[M\text{-}Br]^+$: 379.0844, found: 379.0848.



(*E*)-1-(2-(3-(2-bromophenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1f**)

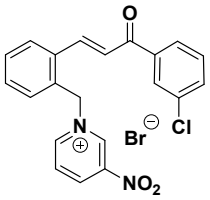
According to the general procedure, **1f** was prepared on a scale of 2.59 mmol. Yellow solids, 0.74 g, 57% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 131.2-133.4°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 9.44 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 9.32 (d, *J* = 4.0 Hz, 1H), 8.48 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 7.99 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.80 (d, *J*= 16.0 Hz, 1H), 7.75 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.61-7.47 (m, 5H), 7.25 (d, *J* = 16.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.34 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.0, 149.7, 146.6, 142.8, 140.7, 140.6, 140.2, 133.4, 133.0, 132.4, 131.1, 129.8, 129.6, 129.4, 129.3, 129.0, 128.1, 128.0, 118.8, 61.3, one carbon missing in the aromatic region. IR (KBr) *v* 3440, 3010, 1615, 1545,

1356, 746 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}BrN_2O_3$ $[M\text{-}Br]^+$: 423.0339, found: 423.0340.



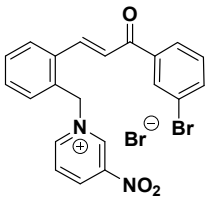
(*E*)-3-nitro-1-(2-(3-oxo-3-(*m*-tolyl)prop-1-en-1-yl)benzyl)pyridin-1-ium bromide (**1g**)

According to the general procedure, **1g** was prepared on a scale of 2.60 mmol. Yellow solids, 0.57 g, 50% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 190.2-191.0°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 9.43-9.38 (m, 2H), 8.49 (dd, J_1 = J_2 = 4.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 16.0 Hz, 1H), 7.99 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.59-7.45 (m, 4H), 7.24 (d, J = 8.0 Hz, 1H), 6.45 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.0, 149.7, 146.6, 142.8, 140.6, 138.9, 138.3, 137.2, 134.1, 134.0, 132.9, 130.8, 129.7, 129.3, 129.2, 129.1, 128.8, 128.2, 126.1, 125.9, 61.4, 20.9. IR (KBr) v 3441, 1648, 1354, 765 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{19}N_2O_3$ $[M\text{-}Br]^+$: 359.1390, found: 359.1390.



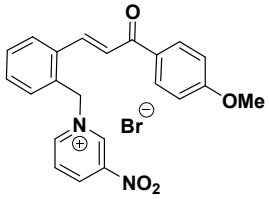
(*E*)-1-(2-(3-(3-chlorophenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1h**)

According to the general procedure, **1h** was prepared on a scale of 2.80 mmol. Yellow solids, 1.03g, 80% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 171.3-171.8°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 9.43-9.37 (m, 2H), 8.47 (dd, J_1 = J_2 = 4.0 Hz, 1H), 8.20-8.18 (m, 2H), 8.14-8.09 (m, 2H), 7.90 (d, J = 16.0 Hz, 1H),7.76 (dd, J_1 = J_2 = 4.0 Hz, 1H),7.64-7.51 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H), 6.44 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.8, 149.7, 146.6, 142.8, 140.6, 139.8, 139.0, 133.9, 133.8, 133.2, 133.0, 131.0, 130.9, 129.7, 129.2, 129.2, 128.3, 128.2, 127.3, 125.5, 61.4. IR (KBr) v 3440, 3010, 1653, 1602, 1552, 1354, 764 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}ClN_2O_3$ $[M\text{-}Br]^+$: 379.0844, found: 379.0843.



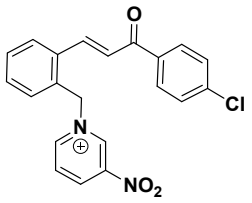
(*E*)-1-(2-(3-(3-bromophenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1i**)

According to the general procedure, **1i** was prepared on a scale of 3.00 mmol. Yellow solids, 1.24 g, 83% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 169.3-170.2°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 9.41 (d, J = 8.0 Hz, 1H), 9.37 (d, J = 8.0 Hz, 1H), 8.47 (dd, J_1 = J_2 = 8.0 Hz, 1H), 8.32 (s, 1H), 8.18 (t, J = 8.0 Hz, 2H), 8.11 (d, J = 12.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H),7.88 (s, 1H), 7.58-7.53 (m, 3H), 7.24 (d, J = 8.0 Hz, 1H), 6.44 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.8, 149.7, 146.6, 142.9, 140.6, 139.8, 139.2, 136.1, 133.8, 133.1, 131.1, 131.1, 131.0, 129.7, 129.2, 129.1, 128.3, 127.7, 125.5, 122.4, 61.4. IR (KBr) v 3445, 3012, 1653, 1615, 1549, 768 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}BrN_2O_3$ [M-Br]$^+$: 423.0339, found: 423.0334.



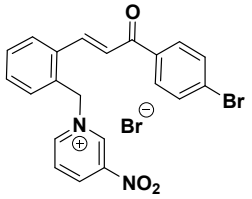
(*E*)-1-(2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1j**)

According to the general procedure, **1j** was prepared on a scale of 2.40 mmol. Yellow solids, 0.76 g, 70% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 172.8-173.4°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 9.43-9.37 (m, 2H), 8.47 (dd, J_1 = J_2 = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 16.0 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.58-7.48 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 12.0 Hz, 2H), 6.44 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.2, 163.4, 149.7, 146.5, 142.9, 140.6, 138.2, 134.2, 132.8, 131.1, 130.6, 130.0, 129.7, 129.2, 129.1, 128.2, 126.0, 114.1, 61.5, 55.7. IR (KBr) v 3444, 2922, 1648, 1598, 1220, 1178, 765 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{19}N_2O_4$ [M-Br]$^+$: 375.1339, found: 375.1346.



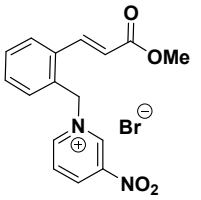
(*E*)-1-(2-(3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1k**)

According to the general procedure, **1k** was prepared on a scale of 3.0 mmol. Yellow solids, 0.92 g, 67% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 144.9-145.4°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 9.41-9.40 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 9.37 (d, J = 4.0 Hz, 1H), 8.47 (t, J = 8.0 Hz, 1H), 8.21-8.15 (m, 3H), 8.09 (d, J = 16.0 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.66 (d, J = 12.0 Hz, 2H), 7.59-7.50 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 6.43 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.0, 149.7, 146.6, 142.9, 140.6, 139.5, 138.4, 135.8, 133.9, 133.0, 130.9, 130.6, 129.7, 129.2, 129.1, 129.0, 128.2, 125.7, 61.4. IR (KBr) v 3442, 3001, 1649, 1595, 1555, 748 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}ClN_2O_3$ [M-Br]$^+$: 379.0844, found: 379.0840.



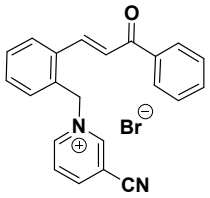
(*E*)-1-(2-(3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1l**)

According to the general procedure, **1l** was prepared on a scale of 3.0 mmol. Yellow solids, 1.23 g, 82% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 176.2-177.1°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 9.42-9.40 (m, 1H), 9.38-9.36 (m, 1H), 8.47 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 8.16-8.07 (m, 4H), 7.86 (d, J = 16.0 Hz, 1H), 7.79 (d, J = 12.0 Hz, 2H), 7.59-7.50 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 6.43 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.2, 149.7, 146.6, 142.9, 140.6, 139.5, 136.1, 133.9, 133.0, 131.9, 130.9, 130.7, 129.7, 129.2, 129.1, 128.2, 127.7, 125.6, 61.4. IR (KBr) v 3433, 2999, 2938, 1650, 1593, 1349, 1217, 745 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{16}BrN_2O_3$ [M-Br]$^+$: 423.0339, found: 423.0334.



(*E*)-1-(2-(3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-3-nitropyridin-1-ium bromide (**1m**)

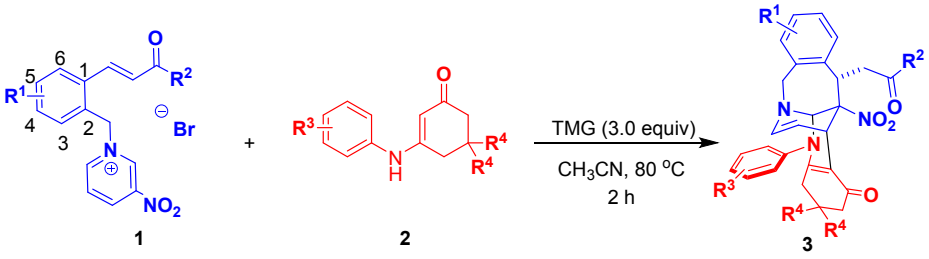
According to the general procedure, **1m** was prepared on a scale of 6.0 mmol. Yellow solids, 2.09 g, 92% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 165.0-165.9 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.26 (s, 1H), 9.41 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 8.50 (t, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 18.0$ Hz, 1H), 7.86 (d, $J = 12.0$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 2H), 7.25 (t, $J = 12.0$ Hz, 1H), 7.57 (d, $J = 15.0$ Hz, 1H), 6.43 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 149.7, 146.5, 142.9, 140.7, 140.1, 133.4, 132.6, 130.8, 129.8, 129.3, 129.1, 127.9, 121.9, 61.2, 51.8. IR (KBr) v 3432, 3028, 1718, 1548, 1221, 771 cm^{-1}. HRMS (ESI) calcd. for $C_{16}H_{15}N_2O_4$ [M-Br]$^+$: 299.1026, found: 299.1025.



(*E*)-3-cyano-1-(2-(3-oxo-3-phenylprop-1-en-1-yl)benzyl)pyridin-1-ium bromide (**1n**)

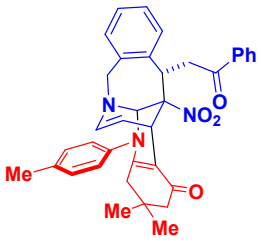
According to the general procedure, **1n** was prepared on a scale of 4.0 mmol. Yellow solids, 1.25 g, 78% isolated yield obtained by filtration of the precipitate; Reaction time = 16 h; m. p. 178.6-179.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 9.30 (d, $J = 8.0$ Hz, 1H), 9.17 (d, $J = 8.0$ Hz, 1H), 8.40 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 8.17-8.13 (m, 3H), 8.04 (d, $J = 16.0$ Hz, 1H), 7.85 (d, $J = 16.0$ Hz, 1H), 7.69 (t, $J = 8.0$ Hz, 1H), 7.60-7.51 (m, 4H), 7.33 (d, $J = 8.0$ Hz, 1H), 6.30 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 189.0, 149.4, 149.3, 148.5, 139.2, 137.1, 134.2, 133.5, 132.5, 130.8, 129.8, 129.8, 128.9, 128.7, 128.3, 125.9, 113.8, 113.1, 61.3, one carbon missing in the aromatic region. IR (KBr) v 3457,2909, 1659, 1590, 1218, 763 cm^{-1}. HRMS (ESI) calcd. for $C_{22}H_{17}N_2O$ [M-Br]$^+$: 325.1335, found: 325.1338.

3. Experimental data for bi-bridged benzoazepines 3



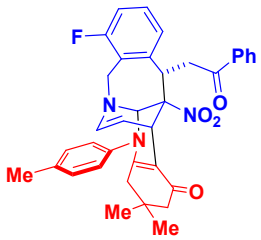
General procedure：To a 5.0 mL vial were successively added chalcone-based pyridinium salts **1** (0.15 mmol), enaminones **2** (0.375 mmol), TMG (0.45 mmol) and 1.0 mL CH_3CN. The resulting mixture was stirred at 80 °C in oil bath for 2 h, and then the reaction mixture was directly

subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding bi-bridged benzoazepines **3**.



3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3a**)

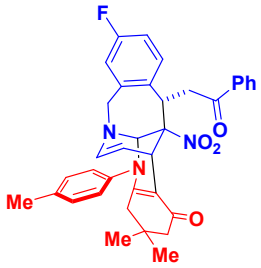
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 65.6 mg, 76% yield; dr > 20:1; reaction time = 2 h; mp 208.8-209.7°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.17-7.05 (m, 4H), 6.92 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.16 (d, J = 8.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.06 (s, 1H), 4.53 (d, J = 4.0 Hz, 1H), 4.44-4.31 (m, 3H), 3.72-3.58 (m, 2H), 2.36 (s, 3H), 2.14 (d, J = 4.0 Hz, 2H), 1.91 (d, J = 20.0 Hz, 1H), 1.72 (d, J = 20.0 Hz, 1H), 0.87 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 192.4, 156.4, 139.2, 138.0, 137.5, 136.3, 135.1, 133.7, 133.5, 129.9, 128.7, 128.1, 128.0, 127.6, 127.4, 125.8, 108.0, 107.1, 88.9, 74.0, 58.5, 49.3, 40.7, 38.5, 35.3, 32.7, 29.3, 28.5, 27.5, 21.1. IR (KBr) ν 3421, 2950, 1627, 1578, 1391, 757 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_4$ $[M+H]^+$ 574.2700, found 574.2698.



8-fluoro-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3b**)

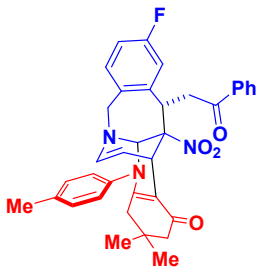
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 40.7 mg, 46% yield; dr > 20:1; reaction time = 2 h; mp 228.6-229.3°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.93 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 4.0 Hz, 2H), 7.01-6.85 (m, 4H), 6.68 (d, J = 8.0 Hz, 1H), 6.17 (d, J = 4.0 Hz, 1H), 5.21 (t, J = 8.0 Hz, 1H), 5.08 (s, 1H), 4.69 (d, J = 16.0 Hz, 1H), 4.53 (d, J = 4.0 Hz, 1H), 4.42 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.15

(d, J = 16.0 Hz, 1H), 3.69-3.55 (m, 2H), 2.35 (s, 3H), 2.14 (t, J = 16.0 Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.75 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 192.2, 161.2, 158.7, 156.0, 139.1, 138.1, 137.6, 136.1, 133.6, 133.5, 128.6, 128.1 (d, $^3J_{C\text{-}F}$ = 9.0 Hz, 1C), 127.9, 125.4 (d, $^3J_{C\text{-}F}$ = 13.0 Hz, 1C), 121.7, 114.6 (d, $^2J_{C\text{-}F}$ = 23.0 Hz, 1C), 107.5, 107.2, 88.7, 73.8, 50.4, 49.3, 40.6, 38.5, 35.7, 32.6, 29.3, 28.4, 27.5, 21.0. IR (KBr) v 3449, 2956, 1624, 1572, 1397, 1240, 758cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}FN_3O_4$ $[M+H]^+$ 592.2606, found 592.2619.



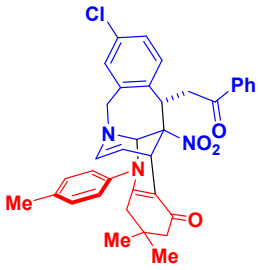
9-fluoro-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3c**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 48.6 mg, 55% yield; dr > 20:1; reaction time = 2 h; mp 197.5-198.3°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.94 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.99-6.82 (m, 3H), 6.77-6.68 (m, 2H), 6.15 (d, J = 8.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.02 (s, 1H), 4.53 (d, J = 4.0 Hz, 1H), 4.40 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 8.0 Hz, 2H), 3.61 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 2.14 (t, J = 16.0 Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.73 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 192.3, 163.0, 160.5, 156.2, 139.8 (d, $^3J_{C\text{-}F}$ = 6.0 Hz, 1C), 139.1, 138.1, 136.2, 133.6, 133.5, 130.9, 128.7, 128.0, 127.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, 1C), 115.1 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, 1C), 114.9 (d, $^2J_{C\text{-}F}$ = 20.0 Hz, 1C), 108.2, 107.0, 88.8, 74.0, 58.2, 49.3, 40.6, 38.0, 35.4, 32.6, 29.2, 28.5, 27.5, 21.1. IR (KBr) v 3444, 2936, 1626, 1580, 1390, 736 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}FN_3O_4$ $[M+H]^+$ 592.2606, found 592.2620.



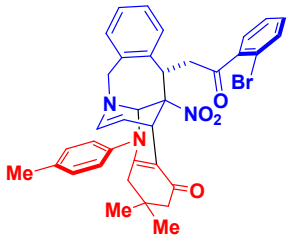
10-fluoro-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3d**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 51.3 mg, 58% yield; dr > 20:1; reaction time = 2 h; mp 216.9-217.1°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 4.0 Hz, 2H), 6.96-6.82 (m, 4H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.23 (t, *J* = 8.0 Hz, 1H), 5.04 (s, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.36-4.31 (m, 3H), 3.67-3.52 (m, 2H), 2.37 (s, 3H), 2.14 (t, *J* = 16.0 Hz, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 1.72 (d, *J* = 16.0 Hz, 1H), 0.87 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 192.3, 163.3, 160.8, 156.2, 139.2, 138.1, 137.9 (d, $^3J_{C\text{-}F}$ = 7.0 Hz, 1C), 136.1, 133.7, 133.1 (d, $^4J_{C\text{-}F}$ = 3.0 Hz, 1C), 129.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, 1C), 128.8, 128.0, 127.5, 114.4 (d, $^2J_{C\text{-}F}$ = 21.0 Hz, 1C), 113.4 (d, $^2J_{C\text{-}F}$ = 23.0 Hz, 1C), 108.1, 107.0, 88.6, 74.0, 57.9, 49.4, 40.7, 38.4, 35.4, 32.7, 29.3, 28.6, 27.5, 21.1. IR (KBr) *v* 3387, 2975, 2892, 1639, 1387, 1088, 1049, 881cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}FN_3O_4$ $[M+H]^+$ 592.2606, found 592.2594.



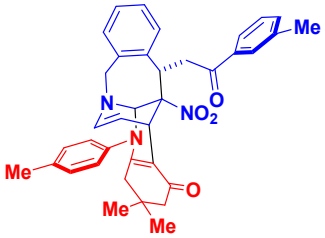
9-chloro-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3e**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 62.4 mg, 68% yield; dr > 20:1; reaction time = 2 h; mp 230.6-231.2°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.98-6.80 (m, 4H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.24 (t, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 4.52 (d, *J* = 4.0 Hz, 1H), 4.43-4.28 (m, 3H), 3.62 (d, *J* = 4.0 Hz, 2H), 2.39 (s, 3H), 2.15 (t, *J* = 16.0 Hz, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 1.74 (d, *J* = 16.0 Hz, 1H), 0.87 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 192.4, 156.2, 139.5, 139.2, 138.2, 136.2, 133.9, 133.7, 133.6, 133.4, 130.8, 129.9, 128.8, 128.1, 127.4, 127.2, 108.3, 107.0, 88.7, 74.0, 58.1, 49.4, 40.7, 38.2, 35.4, 32.7, 29.3, 28.6, 27.6, 21.2. IR (KBr) *v* 3429, 2953, 1688, 1628, 1580, 1391, 1138, 759cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}ClN_3O_4$ $[M+H]^+$ 608.2311, found 608.2322.



12-(2-(2-bromophenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1*(2H)*-one (**3f**)

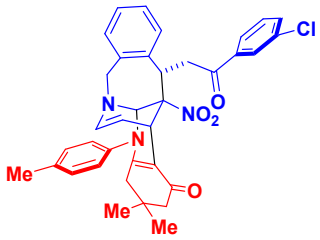
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 52.6 mg, 54% yield; dr > 20:1; reaction time = 2 h; mp 214.6-215.5°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.59 (d, J = 8.0 Hz, 1H), 7.35-7.27 (m, 3H), 7.17-7.12 (m, 4H), 6.97 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.11 (d, J = 8.0 Hz, 1H), 5.25 (t, J = 8.0 Hz, 1H), 5.01 (s, 1H), 4.54 (d, J = 4.0 Hz, 1H), 4.29 (s, 2H), 4.24 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.71(d, J = 16.0 Hz, 1H), 3.45 (dd, $J_1 = J_2$ = 12.0 Hz, 1H), 2.35 (s, 3H), 2.13 (t, J = 16.0 Hz, 2H), 1.90 (d, J = 16.0 Hz, 1H), 1.70 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 192.2, 156.2, 140.4, 139.2, 138.0, 137.6, 134.7, 133.9, 133.6, 132.0, 129.8, 128.9, 128.0, 127.8, 127.4, 127.3, 126.5, 118.8, 108.1, 107.1, 88.6, 73.9, 58.5, 49.4, 40.7, 39.5, 39.2, 32.7, 29.2, 28.6, 27.5, 21.1. IR (KBr) *v* 3424, 2955, 2871, 1624, 1578, 1393, 732 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}BrN_3O_4$ $[M+H]^+$ 652.1805, found 652.1796.



3,3-dimethyl-12a-nitro-12-(2-oxo-2-(*m*-tolyl)ethyl)-5-(p-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3g**)

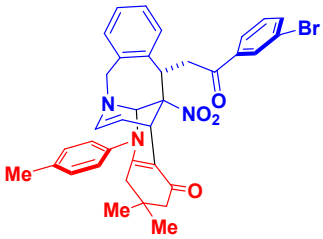
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 44.5 mg, 51% yield; dr > 20:1; reaction time = 2 h; mp 232.4-233.2°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.76 (d, J = 8.0 Hz, 2H), 7.40-7.32 (m, 2H), 7.14 (t, J = 8.0 Hz, 2H), 7.10 (d, J = 4.0 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.92 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.15 (d, J = 4.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.06 (s, 1H), 4.54 (d, J = 4.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.71-3.57 (m, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 2.15 (t, J = 16.0 Hz, 2H), 1.92 (d, J = 16.0 Hz, 1H), 1.73 (d, J = 16.0 Hz, 1H), 0.87 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 192.2, 156.3, 139.2, 138.4, 138.0, 137.4, 136.3, 135.1, 134.2, 133.7, 130.5, 129.8, 128.5, 128.0, 127.6, 127.3, 125.7, 125.2, 108.0, 107.1,

88.8, 74.0, 58.5, 49.3, 40.7, 38.5, 35.3, 32.6, 29.2, 28.5, 27.5, 21.2, 21.1. IR (KBr) *v* 3467, 2954, 1684, 1622, 1572, 1394, 1138, 731 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_3O_4$ $[M+H]^+$ 588.2857, found 588.2854.



12-(2-(3-chlorophenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3h**)

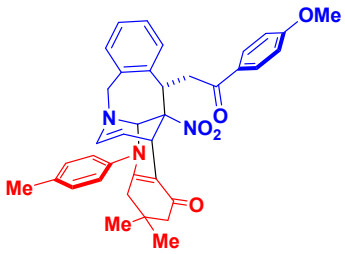
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 40.2 mg, 44% yield; dr > 20:1; reaction time = 2 h; mp 223.7-224.5°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.89 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.14-7.05 (m, 4H), 6.91 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.15 (d, *J* = 4.0 Hz, 1H), 5.22 (t, *J* = 8.0 Hz, 1H), 5.04 (s, 1H), 4.53 (d, *J* = 4.0 Hz, 1H), 4.42-4.31 (m, 3H), 3.60 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.13 (t, *J* = 16.0 Hz, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 1.72 (d, *J* = 16.0 Hz, 1H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 192.2, 156.3, 139.1, 138.0, 137.8, 137.5, 135.0, 134.8, 133.7, 133.4, 130.4, 130.0, 128.1, 128.0, 127.7, 127.4, 126.1, 125.6, 107.9, 107.0, 88.8, 73.9, 58.4, 49.3, 40.6, 38.4, 35.5, 32.6, 29.3, 28.5, 27.5, 21.0. IR (KBr) *v* 3464, 2955, 1622, 1566, 1397, 738 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}ClN_3O_4$ $[M+H]^+$ 608.2311, found 608.2302.



12-(2-(3-bromophenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3i**)

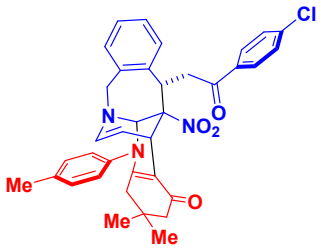
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 45.9 mg, 47% yield; dr > 20:1; reaction time = 2 h; mp 223.3-224.1°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.05 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.37-7.32 (m, 1H), 7.15-7.08 (m, 4H), 6.92 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.15 (d, *J* = 4.0 Hz, 1H), 5.22 (t, *J* = 8.0 Hz, 1H), 5.05 (s, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.61 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.17 (t, *J* = 16.0

Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 192.3, 156.3, 139.2, 138.0, 137.9, 137.5, 136.3, 134.8, 133.7, 131.0, 130.3, 129.8, 128.1, 127.7, 127.4, 126.5, 125.6, 123.1, 107.9, 107.0, 88.8, 73.9, 58.5, 49.3, 40.7, 38.4, 35.5, 32.6, 29.3, 28.5, 27.5, 21.1. IR (KBr) v 3465, 2955, 1691, 1621, 1565, 1397, 741 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}BrN_3O_4$ $[M+H]^+$ 652.1805, found 652.1791.



12-(2-(4-methoxyphenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3j**)

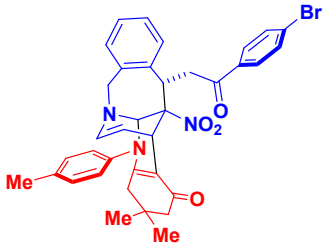
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 81.0 mg, 89% yield; dr > 20:1; reaction time = 2 h; mp 237.7-238.0°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.93 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.99-6.88 (m, 6H), 6.14 (d, J = 4.0 Hz, 1H), 5.22 (t, J = 8.0 Hz, 1H), 5.05 (s, 1H), 4.52 (dd, J_1 = J_2= 4.0 Hz, 1H), 4.42-4.30 (m, 3H), 3.84 (s, 3H), 3.66-3.51 (m, 2H), 2.35 (s, 3H), 2.13 (t, J = 16.0 Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 192.2, 163.7, 156.2, 139.2, 137.9, 137.4, 135.2, 133.7, 130.3, 129.4, 128.0, 127.5, 127.3, 126.8, 125.7, 113.7, 108.0, 107.1, 88.9, 74.0, 58.5, 55.4, 49.3, 40.6, 38.5, 34.8, 32.6, 29.2, 28.5, 27.5, 21.0. IR (KBr) v 3438, 2952, 1585, 1391, 1261, 1176, 838 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_3O_5$ $[M+H]^+$ 604.2806, found 604.2817.



12-(2-(4-chlorophenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3k**)

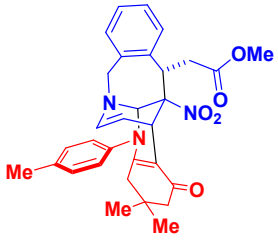
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 55.6 mg, 61% yield; dr > 20:1; reaction time = 2 h; mp 238.2-238.8°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ

7.90(d, J = 8.0 Hz, 2H), 7.44 (d, J = 12.0 Hz, 2H), 7.14 (q, J = 8.0 Hz, 3H), 7.07 (t, J = 8.0 Hz, 1H), 6.91 (dd, J_1 = J_2 = 8.0 Hz, 4H), 6.15 (d, J = 4.0 Hz, 1H), 5.22 (t, J = 8.0 Hz, 1H), 5.04 (s, 1H), 4.51 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.67-3.55 (m, 2H), 2.36 (s, 3H), 2.14 (t, J = 16.0 Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 192.3, 156.3, 140.0, 139.2, 138.0, 137.5, 134.9, 134.6, 133.7, 129.8, 129.4, 129.0, 128.1, 127.7, 127.4, 125.6, 108.0, 107.0, 88.8, 73.9, 58.5, 49.3, 40.7, 38.4, 35.3, 32.7, 29.3, 28.5, 27.5, 21.1. IR (KBr) v 3443, 2958, 1686, 1627, 1579, 1392, 741 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}ClN_3O_4$ $[M+H]^+$ 608.2311, found 608.2290.



12-(2-(4-bromophenyl)-2-oxoethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3l**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 54.3 mg, 56% yield; dr > 20:1; reaction time = 2 h; mp 236.1-236.7°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82(d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.16-7.11 (m, 3H), 7.07 (t, J = 8.0 Hz, 1H), 6.90 (dd, J_1 = J_2 = 8.0 Hz, 4H), 6.15 (d, J = 4.0 Hz, 1H), 5.22 (t, J = 8.0 Hz, 1H), 5.04 (s, 1H), 4.51 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.66-3.55 (m, 2H), 2.36 (s, 3H), 2.14 (t, J = 16.0 Hz, 2H), 1.91 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 192.3, 156.3, 139.2, 138.0, 137.5, 135.0, 134.9, 133.7, 132.0, 130.3, 129.5, 128.7, 128.1, 127.7, 127.4, 125.6, 108.0, 107.0, 88.8, 73.9, 58.5, 49.3, 40.7, 38.4, 35.3, 32.7, 29.3, 28.5, 27.5, 21.1. IR (KBr) v 3442, 2955, 1628, 1579, 1389, 738 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{35}BrN_3O_4$ $[M+H]^+$ 652.1805, found 652.1820.

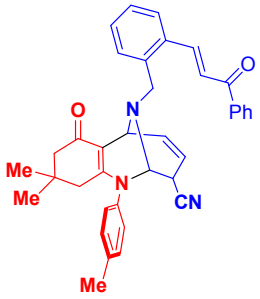


methyl

2-(3,3-dimethyl-12a-nitro-1-oxo-5-(*p*-tolyl)-1,2,3,4,5,5a,7,12,12a,13-decahydro-6,13-ethenobenzo

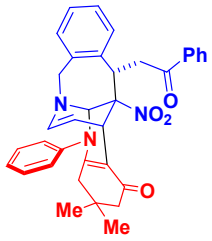
[5,6]azepino[2,3-*b*]quinolin-12-yl)acetate(**3m**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 3:1); 22.3mg, 28% yield; dr > 20:1; reaction time = 2 h; mp 223.9-224.7 °C; ^{1}H NMR (300 MHz, DMSO-d_6), δ 7.21-6.91 (m, 8H), 6.29 (s, 1H), 5.00 (d, J = 24.0 Hz, 2H), 4.34 (d, J = 21.0 Hz, 3H),3.99 (s, 1H), 3.52 (s, 3H), 3.08 (s, 1H), 2.74 (s, 1H), 2.30 (s, 3H), 2.09-1.94 (m, 3H), 1.63 (d, J = 18.0 Hz, 1H), 0.79 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 190.7, 171.1, 154.9, 139.1, 137.9, 137.6, 134.7, 134.1, 130.6, 130.4, 128.1, 127.9, 127.4, 126.0, 107.2, 106.7, 88.3, 79.2, 73.6, 57.9, 51.9, 48.9, 32.6, 31.1, 31.0, 28.6, 26.6, 20.7. IR (KBr) v 3430, 2947, 1747, 1580, 1390, 1169, 758 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{34}N_3O_5$ $[M+H]^+$ 528.2493, found 528.2492.



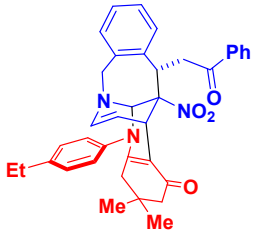
9,9-dimethyl-7-oxo-11-(2-((*E*)-3-oxo-3-phenylprop-1-en-1-yl)benzyl)-1-(*p*-tolyl)-1,2,3,6,7,8,9,10-octahydro-2,6-epiminobenzo[*b*]azocine-3-carbonitrile (**3n**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 21.1mg, 25% yield; dr >20:1; reaction time = 0.5 h; mp 197.3-197.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.16 (d, J = 15.0 Hz, 1H), 7.96 (t, J = 6.0 Hz, 2H), 7.70 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.49 (t, J = 9.0 Hz, 2H), 7.36-7.27 (m, 3H), 7.25-7.18 (m, 4H), 6.90 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.63 (s, 1H), 3.96 (d, J = 3.0 Hz, 1H),3.80 (q, J = 12.0 Hz, 2H),2.59-2.50 (m, 1H), 2.44 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.38 (s, 3H), 2.29 (d, J = 15.0 Hz, 1H), 2.22 (m, 2H), 2.07 (d, J = 18.0 Hz, 1H), 1.71 (s, 1H), 1.04 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 190.8, 153.6, 147.5, 142.5, 139.4, 138.1, 137.7, 136.0, 135.0, 132.8, 130.4, 130.3, 130.0, 128.6, 128.5, 128.3, 127.2, 124.0, 117.8, 110.8, 107.1, 73.2, 54.2, 50.3, 47.0, 41.1, 34.2, 32.9, 29.7, 28.0, 21.0. IR (KBr) v 3429, 2927, 1621, 1568, 1401, 1257, 756 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_3O_2$ $[M+H]^+$ 554.2802, found 554.2801.



3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-phenyl-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3o**)

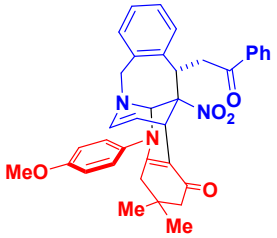
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 67.0 mg, 80% yield; dr > 20:1; reaction time = 2 h; mp 153.1-153.9°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 3H), 7.11 (tt, J_1= J_2=8.0 Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 5.25 (t, *J* = 8.0 Hz, 1H), 5.10 (s, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.45-4.31 (m, 3H), 3.73-3.59 (m, 2H), 2.16 (t, *J* = 16.0 Hz, 2H), 1.92 (d, *J* = 16.0 Hz, 1H), 1.72 (d, *J* = 16.0 Hz, 1H), 0.88 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 192.4, 156.1, 141.9, 137.5, 136.4, 135.2, 133.8, 133.5, 128.7, 128.1, 128.1, 127.7, 127.5, 125.8, 108.1, 107.4, 88.9, 74.1, 58.6, 49.4, 40.8, 38.5, 35.4, 32.8, 29.3, 28.6, 27.6, two carbons missing in the aromatic region. IR (KBr) *v* 3441, 2955, 1628, 1576, 1390, 738 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{34}N_3O_4$ $[M+H]^+$ 560.2544, found 560.2550.



5-(4-ethylphenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3p**)

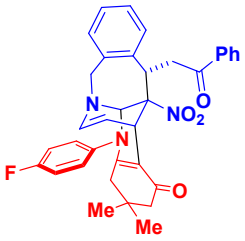
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 38.3 mg, 43% yield; dr > 20:1; reaction time = 2 h; mp 158.1-158.9°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.95 (d, *J* = 4.0 Hz, 2H), 7.57 (t, *J* = 4.0 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 2H), 7.17-6.89 (m, 8H), 6.15 (s, 1H), 5.23 (s, 1H), 5.07 (s, 1H), 4.54 (s, 1H), 4.37 (q, *J* = 16.0 Hz, 3H), 3.72-3.58 (m, 2H), 2.66 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 2H), 1.92 (d, *J* = 16.0 Hz, 1H), 1.73 (d, *J* = 16.0 Hz, 1H), 1.25 (t, *J* = 8.0 Hz, 3H), 0.87 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.2, 156.3, 144.1, 139.4, 137.5, 136.3, 135.1, 133.7, 133.5, 128.9, 128.6, 128.0, 128.0, 127.6, 127.3, 125.7, 108.0,

107.1, 88.9, 74.0, 58.5, 49.4, 40.7, 38.5, 35.3, 32.7, 29.3, 28.5, 28.3, 27.5, 15.1. IR (KBr) *v* 3437, 2958, 1626, 1578, 1392, 1237, 738 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_3O_4$ $[M+H]^+$ 588.2857, found 588.2865.



5-(4-methoxyphenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3q**)

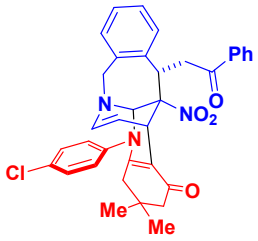
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 60.1 mg, 68% yield; dr > 20:1; reaction time = 2 h; mp 214.2-214.9°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 4H), 6.16 (d, *J* = 4.0 Hz, 1H), 5.23 (t, *J* = 8.0 Hz, 1H), 5.01 (s, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.45-4.33 (m, 3H), 3.82 (s, 3H), 3.72-3.58 (m, 2H), 2.14 (t, *J* = 16.0 Hz, 2H), 1.89 (d, *J* = 16.0 Hz, 1H), 1.74 (d, *J* = 16.0 Hz, 1H), 0.87 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 192.3, 159.0, 156.6, 137.5, 136.3, 135.1, 134.6, 133.7, 133.5, 128.7, 128.1, 128.0, 127.7, 127.4, 125.8, 125.8, 108.1, 107.0, 88.9, 74.2, 58.6, 55.4, 49.4, 40.7, 38.5, 35.3, 32.6, 29.3, 28.5, 27.7. IR (KBr) *v* 3441, 2951, 1623, 1577, 1392, 1240, 734 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_5$ $[M+H]^+$ 590.2649, found 590.2651.



5-(4-fluorophenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3r**)

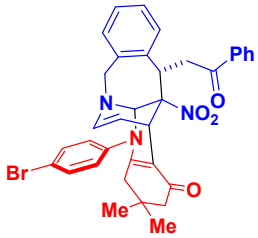
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 63.5 mg, 73% yield; dr > 20:1; reaction time = 2 h; mp 223.1-223.6°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.95 (d, *J* = 4.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.16-6.97 (m, 7H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 4.0 Hz, 1H), 5.24 (t, *J* = 8.0 Hz, 1H), 5.01 (s, 1H), 4.53 (d, *J* = 4.0 Hz,

1H), 4.45-4.31 (m, 3H), 3.72-3.57 (m, 2H), 2.14 (t, J = 16.0 Hz, 2H), 1.87 (d, J = 16.0 Hz, 1H), 1.71 (d, J = 16.0 Hz, 1H), 0.87 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.4, 161.9 (d, J = 247.0 Hz, 1C), 155.8, 133.8, 133.8, 137.3, 136.3, 135.0, 133.7, 133.5, 128.7, 128.1, 128.0, 127.7, 127.5, 125.7, 108.2, 107.5, 88.8, 74.1, 58.5, 49.3, 40.7, 38.4, 35.2, 32.6, 29.2, 28.5, 27.6. IR (KBr) v 3445, 2954, 1626, 1581, 1391, 1222, 732 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{33}FN_3O_4$ $[M+H]^+$ 578.2450, found 578.2447.



5-(4-chlorophenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3s**)

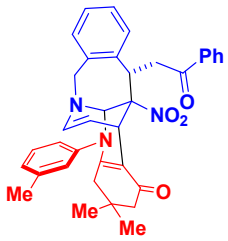
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 66.9 mg, 75% yield; dr > 20:1; reaction time = 2 h; mp 215.6-216.1°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, J = 4.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 4.0 Hz, 2H), 7.16-6.88 (m, 6H), 6.15 (d, J = 4.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.03 (s, 1H), 4.54-4.32 (m, 4H), 3.72-3.46 (m, 2H), 2.15 (t, J = 16.0 Hz, 2H), 1.90 (d, J = 16.0 Hz, 1H), 1.70 (d, J = 16.0 Hz, 1H), 0.88 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 192.4, 155.5, 140.3, 137.3, 136.2, 135.0, 133.9, 133.7, 133.5, 129.6, 128.7, 128.1, 128.0, 127.7, 127.5, 125.7, 108.2, 107.8, 88.8, 74.0, 58.5, 49.3, 40.7, 38.4, 35.2, 32.7, 29.2, 28.5, 27.5. IR (KBr) v 3437, 2926, 1631, 1585, 1390, 758 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{33}ClN_3O_4$ $[M+H]^+$ 594.2154, found 594.2149.



5-(4-bromophenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3t**)

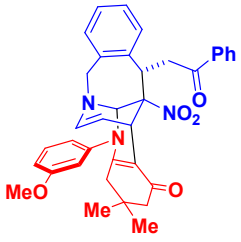
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 62.8 mg, 66% yield; dr > 20:1; reaction time = 2 h; mp 150.4-151.2°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.48 (dd, J_1 = J_2 =8.0 Hz, 4H), 7.15 (t, J = 8.0 Hz,

1H), 7.08 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 4.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.15 (d, J = 4.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.04 (s, 1H), 4.53 (d, J = 8.0 Hz, 1H), 3.38 (dd, J_1 = J_2 = 16.0 Hz, 3H), 3.72-3.57 (m, 2H), 2.15 (t, J = 16.0 Hz, 2H), 1.90 (d, J = 16.0 Hz, 1H), 1.70 (d, J = 16.0 Hz, 1H), 0.88 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 192.5, 155.4, 140.9, 137.3, 136.3, 135.0, 133.7, 133.6, 133.1, 128.7, 128.1, 128.0, 127.8, 127.5, 125.7, 122.0, 108.2, 107.8, 88.8, 74.0, 58.5, 49.3, 40.8, 38.5, 35.2, 32.8, 29.2, 28.6, 27.5. IR (KBr) v 3441, 2954, 1629, 1582, 1389, 737 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{33}BrN_3O_4$ $[M+H]^+$ 638.1649, found 638.1646.



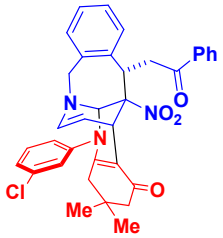
3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*m*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3u**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 60.1 mg, 70% yield; dr > 20:1; reaction time = 2 h; mp 237.3-237.8°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.95 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.24 (s, 1H), 7.12 (dd, J_1 =8.0 Hz, J_2 = 4.0 Hz, 2H), 7.05 (t, J = 8.0 Hz, 1H), 6.92 (dd, J_1 =J_2 = 8.0 Hz, 4H), 6.16 (d, J = 4.0 Hz, 1H), 5.23 (t, J = 8.0 Hz, 1H), 5.08 (s, 1H), 4.54 (d, J = 4.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.73-3.58 (m, 2H), 2.34 (d, J = 8.0 Hz, 3H), 2.14 (t, J = 16.0 Hz, 2H), 1.92 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.87 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.2, 156.1, 141.7, 137.5, 136.3, 135.0, 133.7, 133.4, 129.6, 129.3, 128.9, 128.6, 128.0, 127.9, 127.6, 127.4, 127.3, 125.7, 107.9, 107.1, 88.8, 73.9, 58.5, 49.3, 40.7, 38.4, 35.3, 32.6, 29.2, 28.5, 27.4, 21.2. IR (KBr) v 3444, 2954, 1627, 1578, 1390, 732 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_4$ $[M+H]^+$ 574.2700, found 574.2707.



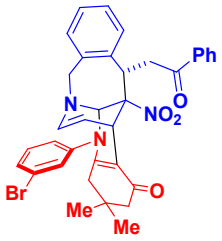
5-(3-methoxyphenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3v**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 60.2 mg, 68% yield; dr > 20:1; reaction time = 2 h; mp 260.2-261.1°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.77 (d, *J* = 4.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 6.94-6.86 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 8.0 Hz, 2H), 6.46 (br, 2H), 5.98 (d, *J* = 4.0 Hz, 1H), 5.06 (t, *J* = 4.0 Hz, 1H), 4.93 (s, 1H), 4.36 (d, *J* = 4.0 Hz, 1H), 4.25-4.20 (m, 3H), 3.59-3.40 (m, 5H), 1.97 (t, *J* = 16.0 Hz, 2H), 1.79 (d, *J* = 16.0 Hz, 1H), 1.59 (d, *J* = 16.0 Hz, 1H), 0.70 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 192.2, 160.0, 155.8, 142.9, 137.4, 136.2, 135.0, 133.6, 133.4, 130.2, 128.6, 128.0, 127.9, 127.6, 127.3, 125.7, 119.0, 113.2, 107.9, 107.3, 88.7, 73.8, 58.4, 55.3, 49.3, 40.5, 38.4, 35.2, 32.6, 29.2, 28.4, 27.4. IR (KBr) *v* 3440, 2952, 1625, 1575, 1391, 731 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_5$ $[M+H]^+$ 590.2649, found 590.2664.



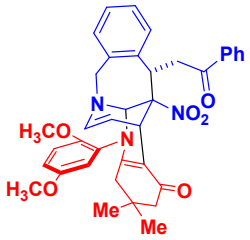
5-(3-chlorophenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3w**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 67.3 mg, 76% yield; dr > 20:1; reaction time = 2 h; mp 229.1-229.8°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.31 (s, 2H), 7.12-6.88 (m, 6H), 6.15 (d, *J* = 4.0 Hz, 1H), 5.23 (t, *J* = 4.0 Hz, 1H), 5.05 (s, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.43-4.31 (m, 3H), 3.72-3.56 (m, 2H), 2.14 (t, *J* = 16.0 Hz, 2H), 1.90 (d, *J* = 16.0 Hz, 1H), 1.70 (d, *J* = 16.0 Hz, 1H), 0.87 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 192.3, 155.1, 142.9, 137.2, 136.2, 134.9, 134.8, 133.6, 133.4, 130.7, 130.5, 128.6, 128.4, 128.0, 127.9, 127.7, 127.4, 125.7, 108.0, 107.9, 88.7, 73.9, 58.4, 49.2, 40.6, 38.4, 35.1, 32.7, 29.1, 28.5, 27.4. IR (KBr) *v* 3455, 2954, 1630, 1577, 1387, 759 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{33}ClN_3O_4$ $[M+H]^+$ 594.2154, found 594.2158.



5-(3-bromophenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3x**)

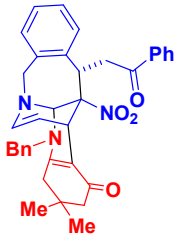
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 71.3 mg, 74% yield; dr > 20:1; reaction time = 2 h; mp 251.3-252.1°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.89(d, *J* = 4.0 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.42 (q, *J* = 8.0 Hz, 3H), 7.21-7.92 (m, 6H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 4.0 Hz, 1H), 6.17 (t, *J* = 8.0 Hz, 1H), 4.99 (t, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.33 (dd, J_1= J_2= 16.0 Hz, 3H), 3.66-3.50 (m, 2H), 2.09 (t, *J* = 16.0 Hz, 2H), 1.84 (d, *J* = 16.0 Hz, 1H), 1.64 (d, *J* = 16.0 Hz, 1H), 0.82 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.5, 155.3, 143.2, 137.3, 136.3, 135.0, 133.7, 133.6, 131.5, 131.0, 130.9, 128.7, 128.2, 128.0, 127.8, 127.6, 125.8, 122.8, 108.2, 108.1, 88.8, 74.0, 58.6, 49.4, 40.8, 38.5, 35.3, 32.8, 29.3, 28.6, 27.5. IR (KBr) *v* 3443, 2953, 1629, 1572, 1388, 692 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{33}BrN_3O_4$ $[M+H]^+$ 638.1649, found 638.1663.



5-(2,5-dimethoxyphenyl)-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3y**)

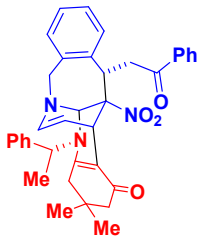
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 49.0 mg, 53% yield; dr = 3:1 (inseperable isomers); reaction time = 2 h; mp 223.8-224.8°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.13-7.00 (m, 2H), 6.94-6.81 (m, 3H), 6.78 (d, *J* = 12.0 Hz, 1H), 6.73 (d, *J* = 4.0 Hz, 1H), 6.12 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 5.21 (t, *J* = 8.0 Hz, 1H), 4.89 (s, 1H), 4.52-4.46 (m, 1H), 4.39-4.25 (m, 3H), 3.77 (s, 3H), 3.65-3.58 (m, 2H), 3.51 (s, 3H), 2.20-2.07 (m, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 1.75 (d, *J* = 16.0 Hz, 1H), 0.86 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.4, 156.6, 153.2, 149.5, 137.4, 136.3, 135.5, 135.2, 130.0, 128.6, 127.9, 127.8, 127.2,

127.1, 126.1, 117.1, 113.9, 112.7, 108.2, 107.4, 88.4, 72.6, 58.4, 55.7, 55.7, 49.5, 39.7, 38.7, 35.2, 32.6, 28.9, 28.6, 27.5. IR (KBr) *v* 3422, 2952, 1688, 1626, 1582, 1388, 1037, 732 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_3O_6$ $[M+H]^+$ 620.2755, found 620.2749.



5-benzyl-3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3z**)

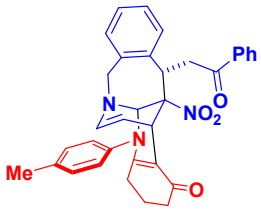
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1 to 3:1); 6.9mg, 8% yield; dr > 20:1; reaction time = 2 h; mp 147.5-148.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.23-7.19 (m, 4H), 7.07-6.95 (m, 5H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.05 (d, *J* = 8.0 Hz, 1H), 5.13 (t, *J* = 8.0 Hz, 1H), 4.62 (s, 1H), 4.52-4.31 (m, 4H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.60-3.45 (m, 2H), 2.16-2.01 (m, 4H), 0.83 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 192.0, 156.8, 137.0, 136.5, 136.2, 135.2, 133.7, 133.5, 128.7, 128.0, 127.6, 127.5, 127.5, 126.5, 125.7, 107.8, 106.7, 88.5, 71.5, 58.6, 52.1, 49.1, 39.6, 38.5, 35.1, 32.7, 29.0, 27.4, two carbons missing in the aromatic region. IR (KBr) *v* 3295, 2926, 1660, 1623, 1566, 739 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_4$ $[M+H]^+$ 574.2700, found 574.2698.



3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-((R)-1-phenylethyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3za**)

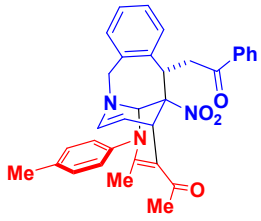
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 8.6mg, 10% yield; dr =1.4:1; reaction time = 2 h; mp 116.5-117.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.58 (t, *J* = 6.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 6.0 Hz, 1H), 7.30-7.18 (m, 5H), 7.18-7.02 (m, 2H), 6.98-6.80 (m, 2H), 6.23 (d, *J* = 6.0 Hz, 1H), 5.23 (t, *J* = 6.0 Hz, 1H),5.07-4.86 (m, 1H), 4.83-4.59 (m, 1H), 4.54-4.24 (m, 3H), 4.19-3.96 (m, 1H), 3.65-3.41

(m, 2H), 2.40-2.13 (m, 3H), 1.65 (d, J = 6.0 Hz, 3H), 0.90 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 191.9, 156.9, 139.9, 137.3, 136.2, 135.3, 133.4, 128.6, 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 127.0, 125.3, 108.2, 107.1, 88.8, 58.0, 57.2, 49.0, 40.1, 38.3, 35.1, 32.2, 29.6, 28.9, 28.3, 27.5, 17.5. IR (KBr) v 3429, 2924, 1624, 1568, 1390, 743 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_3O_4$ $[M+H]^+$ 588.2857, found 588.2856.



12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**3zb**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 42.0 mg, 51% yield; dr > 20:1; reaction time = 2 h; mp 215.2-215.9°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.96 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.14-6.88 (m, 8H), 6.16 (d, J = 4.0 Hz, 1H), 5.24 (s, 1H), 5.02 (s, 1H), 4.55 (s, 1H), 4.45-4.35 (m, 3H), 3.72-3.56 (m, 2H), 2.35 (s, 3H), 2.25 (d, J = 4.0 Hz, 2H), 2.04 (d, J = 16.0 Hz, 1H), 1.89 (d, J = 16.0 Hz, 1H), 1.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 192.7, 157.7, 139.3, 138.1, 137.5, 136.3, 135.1, 133.7, 133.5, 130.4, 130.2, 129.9, 128.7, 128.1, 128.0, 127.6, 127.4, 125.7, 108.3, 88.9, 73.8, 58.5, 38.5, 35.6, 35.3, 29.3, 27.2, 21.4, 21.1. IR (KBr) v 3430, 2948, 1624, 1571, 1387, 1130, 746 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{32}N_3O_4$ $[M+H]^+$ 546.2387, found 546.2381.

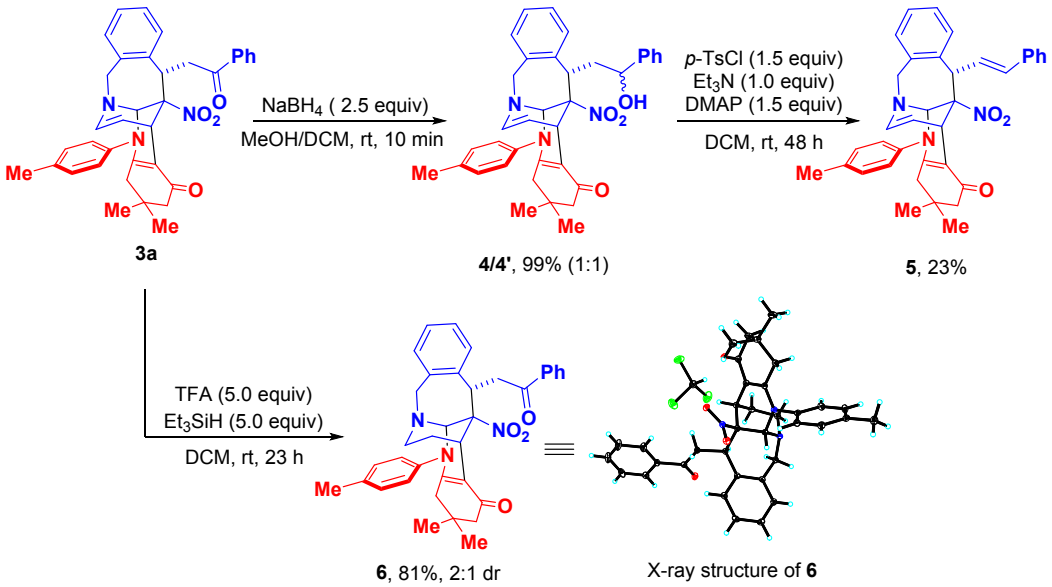


2-(3-acetyl-2-methyl-4a-nitro-1-(*p*-tolyl)-1,4,4a,5,10,11a-hexahydro-4,11-ethenobenzo[*e*]pyrido[2,3-b]azepin-5-yl)-1-phenylethan-1-one (**3zc**)

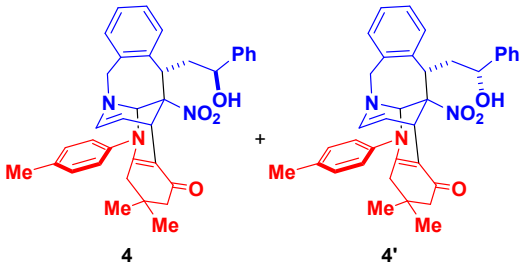
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 25.6mg, 32% yield; dr > 20:1; reaction time = 2 h; mp 127.4-128.3°C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.00 (d, J = 6.0 Hz, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.15-7.06 (m, 4H), 6.94 (dd, $J_1 = J_2$ = 6.0 Hz, 4H), 6.21 (d, J = 8.0 Hz, 1H), 5.20 (t, J = 8.0 Hz, 1H),5.02 (s, 1H), 4.47-4.22 (m,

4H), 3.71 (dd, $J_1 = J_2 = 12.0$ Hz, 1H),3.51 (d, $J = 18.0$ Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 194.1, 153.3, 140.1, 137.7, 137.5, 136.4, 135.2, 133.6, 133.4, 130.4, 129.7, 129.5, 128.8, 128.1, 127.8, 127.4, 125.7, 107.9, 107.5, 89.4, 73.3, 57.9, 38.6, 35.4, 34.4, 30.0, 21.1, 19.0. IR (KBr) ν 3434, 2923, 1631, 1547, 1138, 754 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{32}N_3O_4$ $[M+H]^+$ 534.2387, found 534.2388.

4. Chemical transformations of 3a



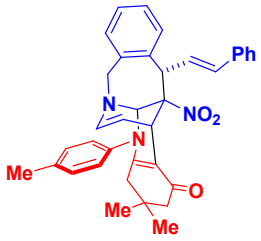
General procedure for the formation of 4/4': A solution of **3a** (229.5 mg, 0.40 mmol) in 40 mL MeOH and 2.0 mL DCM was cooled to 0 °C, and then $NaBH_4$ (37.8 mg,1.0 mmol) was added successively. The reaction mixture was stirred at 0°C for 10min until the complete consumption of **3a** as monitored 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 **4/4'** in 99% yield with 1:1 dr.



12-(2-hydroxy-2-phenylethyl)-3,3-dimethyl-12a-nitro-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**4/4'**)

White solid obtained by silica gel column chromatography (petroleum ether/ethylacetate = 4:1 to 1:1), 227.5mg, 99% yield; Reaction time = 10 min; dr = 1:1 (**4**/**4'**, separable isomers); m. p. 231.8-232.4°C (**4**), 233.1-233.7 °C (**4'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **4**, δ 7.34-7.18 (m, 7H), 7.08 (q, *J* = 8.0 Hz, 4H), 6.93 (d, *J* = 4.0 Hz, 1H), 6.84 (br, 2H), 5.59 (d, *J* = 8.0 Hz, 1H), 4.79 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 1H), 4.43 (d, *J* = 4.0 Hz, 1H), 4.15 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 12.0 Hz, 1H), 3.11-2.97 (m, 2H), 2.45-2.22 (m, 6H), 1.83 (d, *J* = 16.0 Hz, 1H), 1.63 (d, *J* = 16.0 Hz, 1H), 0.80 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **4** δ 192.3, 156.3, 143.3, 139.3, 139.3, 137.8, 137.6, 135.0, 132.9, 128.5, 127.8, 127.7, 127.6, 127.5, 127.4, 126.1, 108.0, 107.1, 88.3, 74.0, 72.5, 58.5, 49.3, 40.7, 39.8, 34.8, 32.6, 28.7, 28.6, 27.4, 21.1. ^{1}H NMR (400 MHz, $CDCl_3$) for **4'**, δ 7.37-7.29 (m, 5H), 7.24-7.14 (m, 5H), 7.03-6.92 (m, 3H), 6.13 (d, *J* = 4.0 Hz, 1H), 5.31 (t, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 4.0 Hz, 1H), 4.78 (d, *J* = 4.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.34 (q, *J* = 16.0 Hz, 2H), 4.13 (d, *J* = 12.0 Hz, 1H), 3.44 (s, 1H), 2.56 (t, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 2.05 (t, *J* = 12.0 Hz, 3H), 1.89 (d, *J* = 16.0 Hz, 1H), 1.67 (d, *J* = 16.0 Hz, 1H), 0.82 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **4'**δ 192.6, 156.6, 144.8, 139.3, 138.5, 137.9, 134.9, 133.4, 129.8, 128.5, 128.2, 127.6, 127.5, 127.3, 127.0, 125.7, .108.7, 107.4, 89.0, 74.5, 71.0, 58.6, 49.1, 40.8, 39.7, 34.8, 32.6, 28.8, 28.7, 27.3, 21.1 IR (KBr) for **4***v* 3402, 2955, 1620, 1569, 1391, 762cm^{-1}. IR (KBr) for **4'***v* 3437, 2948, 1624, 1570, 1395, 752cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{38}N_3O_4$ $[M+H]^+$ 576.2857, found 576.2845.

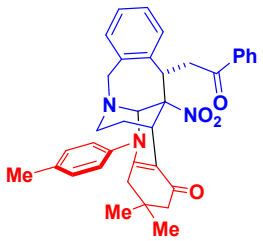
General procedure for the formation of 5: To a solution of **4/4'** (221.1 mg, 0.38 mmol) in 2.0 mL DCM, *p*-TsCl (109.8 mg, 0.58mmol), DMAP (46.9 mg, 0.38 mmol) and Et_3N (58.3 mg, 0.58 mmol) were successively added. The resulting mixture was stirred at room temperature for 48 h, then diluted with Et_2O, washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1 to 1:1) to afford **5** as a yellow solid in 23% yield.



3,3-dimethyl-12a-nitro-12-((*E*)-styryl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethenobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**5**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1 to 1:1); 50.1 mg, 23% yield; dr > 20:1; reaction time = 48 h; mp 147.2-147.9°C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.31 (d, J = 4.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 2H), 7.18-7.15 (m, 3H), 7.12-7.07 (m, 4H), 6.92 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 6.15 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 5.94 (d, J = 8.0 Hz, 1H), 5.18 (t, J = 8.0 Hz, 1H), 5.15 (d, J = 4.0 Hz, 1H), 4.36 (d, J = 4.0 Hz, 1H), 4.29 (d, J = 8.0 Hz, 1H), 4.23 (d, J = 4.0 Hz, 1H), 2.30 (s, 3H), 2.03 (t, J = 16.0 Hz, 2H), 1.83 (d, J = 16.0 Hz, 1H), 1.65 (d, J = 16.0 Hz, 1H), 0.78 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 155.9, 139.4, 138.0, 137.4, 136.9, 136.3, 136.0, 133.4, 130.4, 128.9, 128.5, 128.0, 127.8, 127.5, 127.4, 126.8, 122.5, 109.2, 107.9, 89.0, 74.6, 58.3, 49.4, 48.9, 40.8, 32.6, 29.6, 28.7, 27.4, 21.1. IR (KBr) ν 3437, 2926, 2862, 1627, 1573, 1390, 807cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_3O_3$ $[M+H]^+$ 558.2751, found 558.2758.

General procedure for the formation of 6： A solution of **3a** (229.5 mg, 0.40 mmol) in 2.0 mL DCM was cooled to 0 °C, and then Et_3SiH (232.6 mg, 2.0 mmol) and TFA (46.9 mg, 2.0 mmol) was added successively. The reaction mixture was stirred at room temperature for 23 h until the complete consumption of **3a** as monitored by thin layer chromatography. After completion of the reaction, the reaction mixture was concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 4:1) to afford **6** as a yellow solid in 81% yield with 2:1 dr.

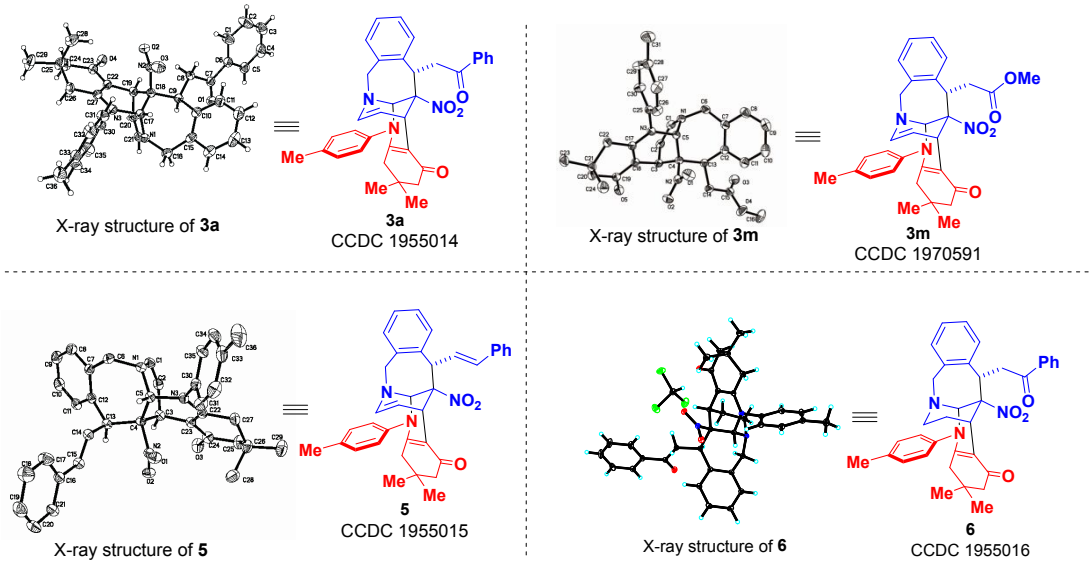


3,3-dimethyl-12a-nitro-12-(2-oxo-2-phenylethyl)-5-(*p*-tolyl)-3,4,5,5a,7,12,12a,13-octahydro-6,13-ethanobenzo[5,6]azepino[2,3-*b*]quinolin-1(2*H*)-one (**6**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 186.3 mg, 81% yield; dr = 2:1 (inseperable isomers); reaction time = 23 h; mp 176.3-177.1°C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 7.99 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 3H), 7.29 (d, J = 4.0 Hz, 1H), 7.19-7.16 (m, 4H), 5.56 (d, J = 4.0 Hz, 1H), 4.59 (d, J = 16.0 Hz, 1H), 4.40 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.23-4.15 (m, 1H), 3.86 (s, 1H), 3.76 (t, J = 8.0 Hz, 1H), 3.09 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.88-2.82 (m, 1H), 2.48-2.44 (m, 1H), 2.39 (s,

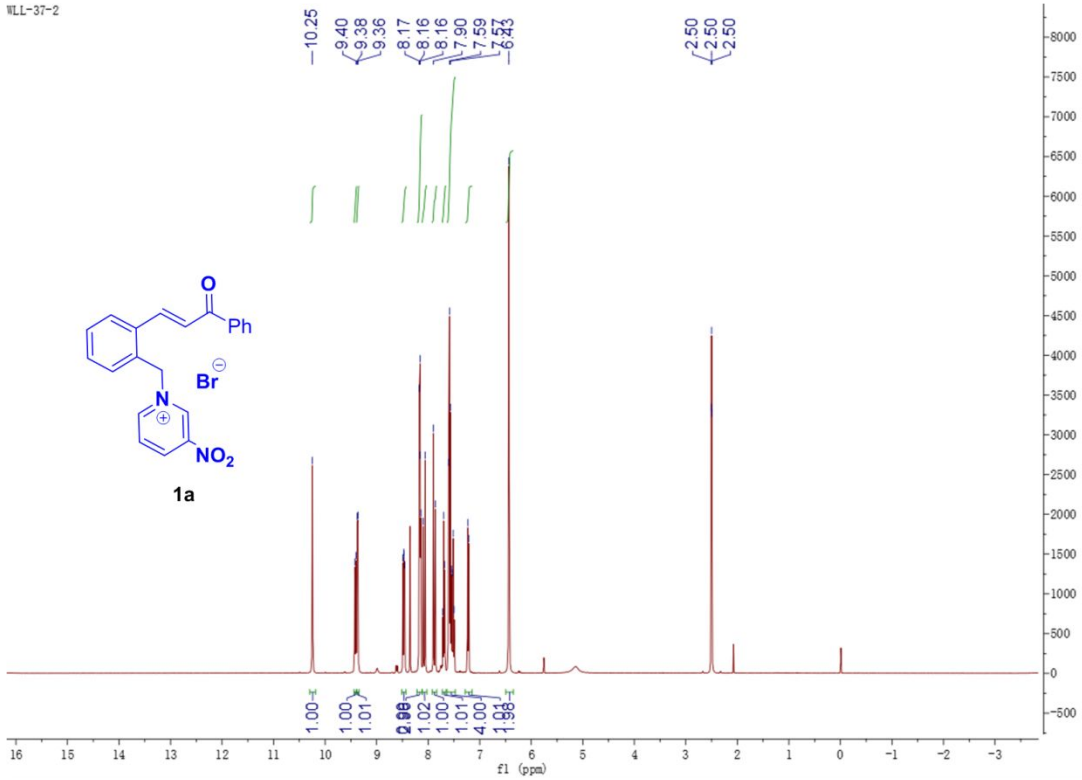
3H), 2.26 (s, 1H), 2.15 (t, J = 16.0 Hz, 2H), 2.04 (d, J = 16.0 Hz, 1H), 1.92 (d, J = 16.0 Hz, 1H), 1.72 (d, J = 16.0 Hz, 1H), 0.82 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.1, 190.7, 156.1, 140.2, 139.8, 138.8, 137.3, 136.0, 133.5, 130.9, 130.4, 128.7, 128.5, 128.1, 127.8, 127.6, 107.3, 90.5, 76.3, 56.6, 54.9, 49.0, 48.3, 40.5, 36.1, 35.4, 32.4, 28.9, 28.8, 26.5, 20.7. IR (KBr) v 3443, 2967, 1687, 1581, 1409, 1260, 751cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{38}N_3O_4$ $[M+H]^+$576.2857, found 576.2859.

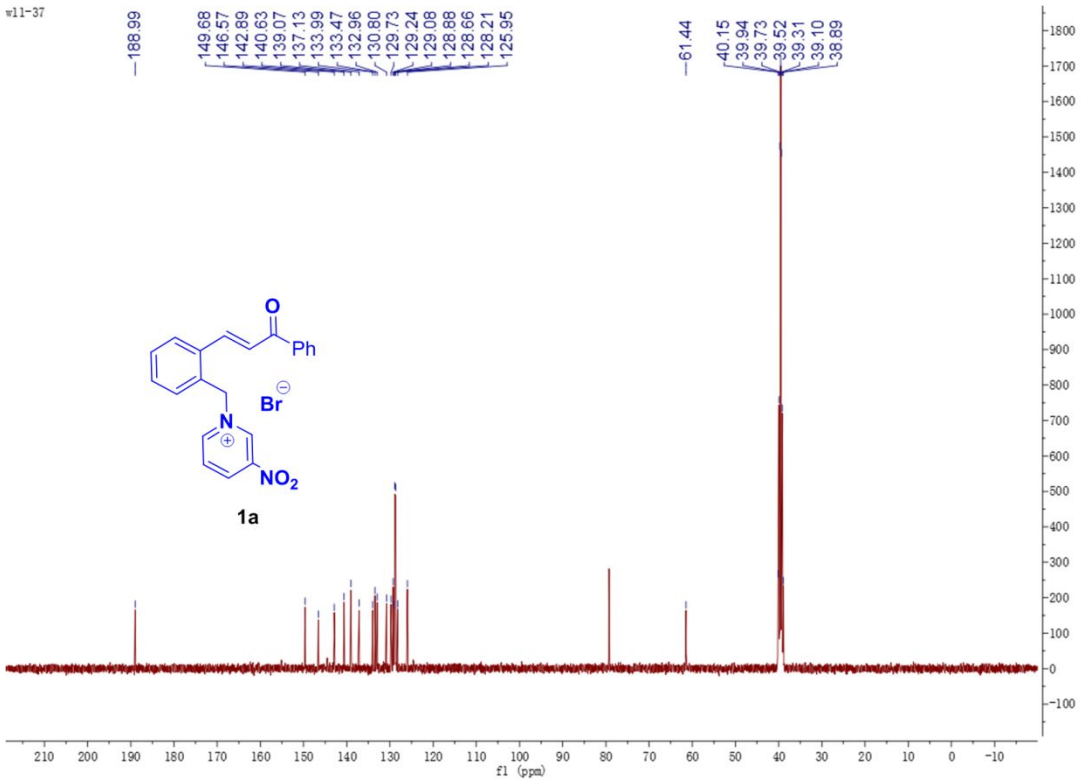
5. Crystal data for 3a, 3m, 5 and 6



Displacement ellipsoids are drawn at the 30% probability level.

6. ^{1}H NMR and ^{13}C NMR spectra

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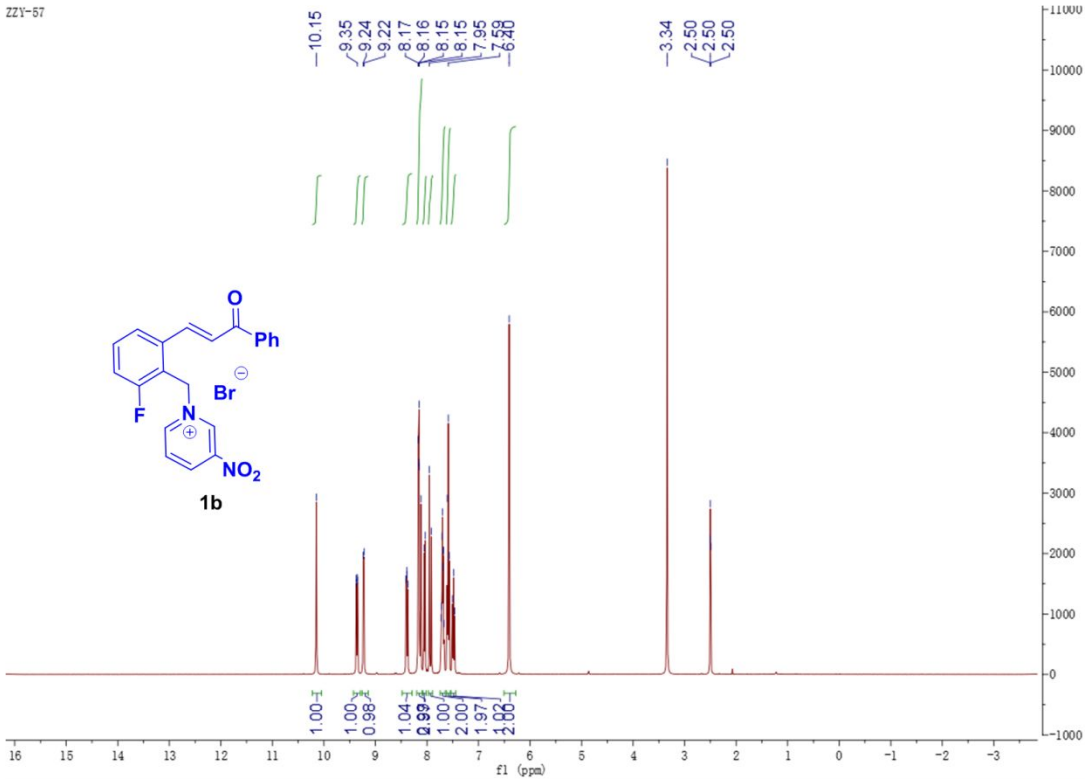
140.63
139.07
137.13
133.99
133.47
132.96
130.80
129.73
129.24
129.08
128.88
128.66
128.21
125.95
61.44
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Ph
Br
N
NO2
1a
f1 (ppm)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8.15
8.15
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3.34
2.50
2.50
2.50
O
Ph
Br
F
N
NO2
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1.00
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1.00
2.00
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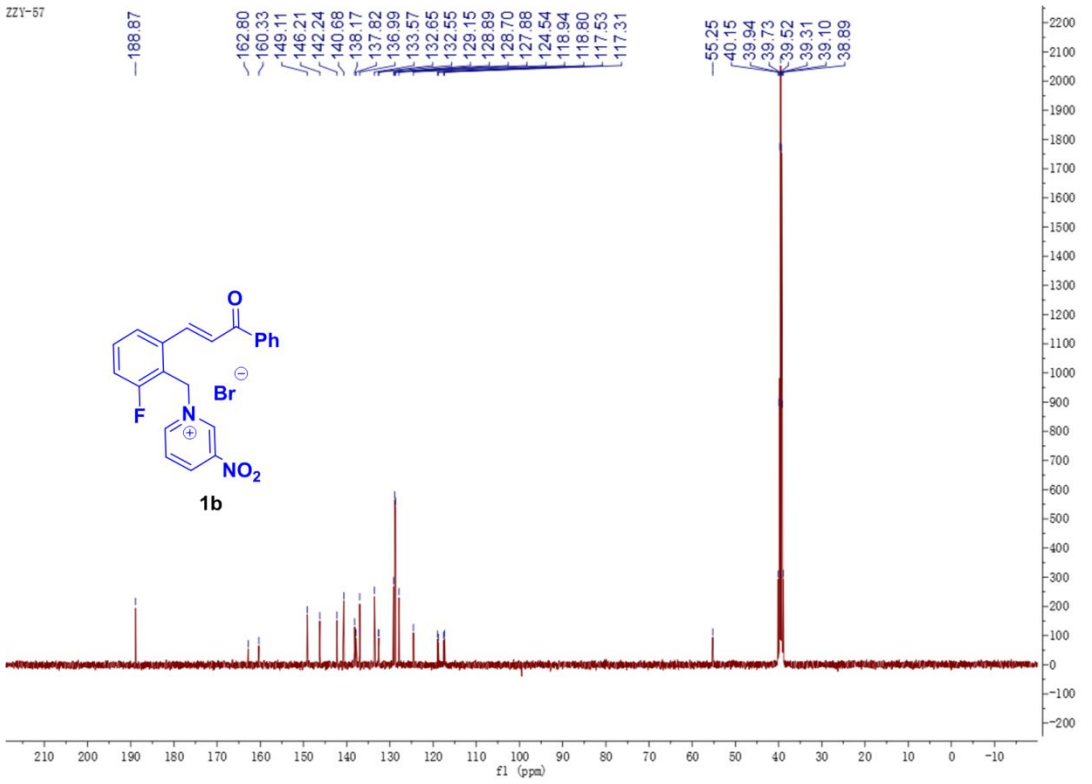
2.00
f1 (ppm)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132.55
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128.89
128.70
127.88
124.54
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118.80
117.53
117.31
55.25
40.15
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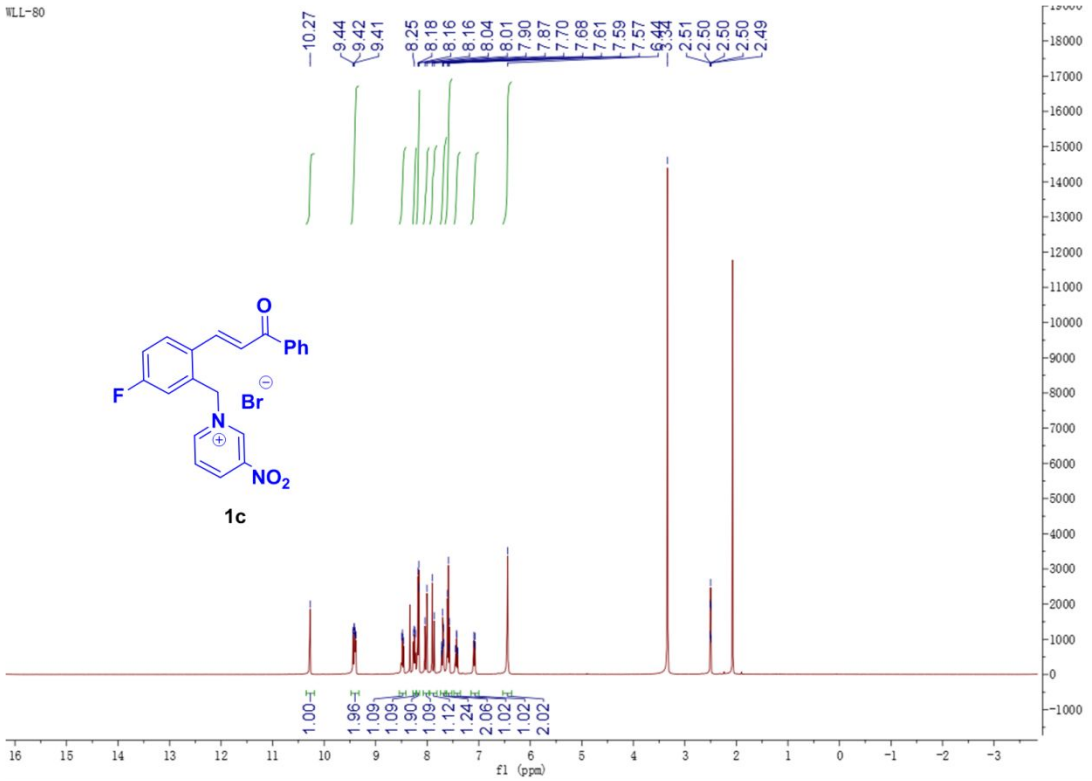
O
Ph
Br
F
N
NO2
1b
f1 (ppm)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8.01
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7.59
7.57
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2.50
2.50
2.50
2.49
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1.09
1.09
1.90
1.09
1.12
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1.02
1.02
2.02
O
Ph
Br
F
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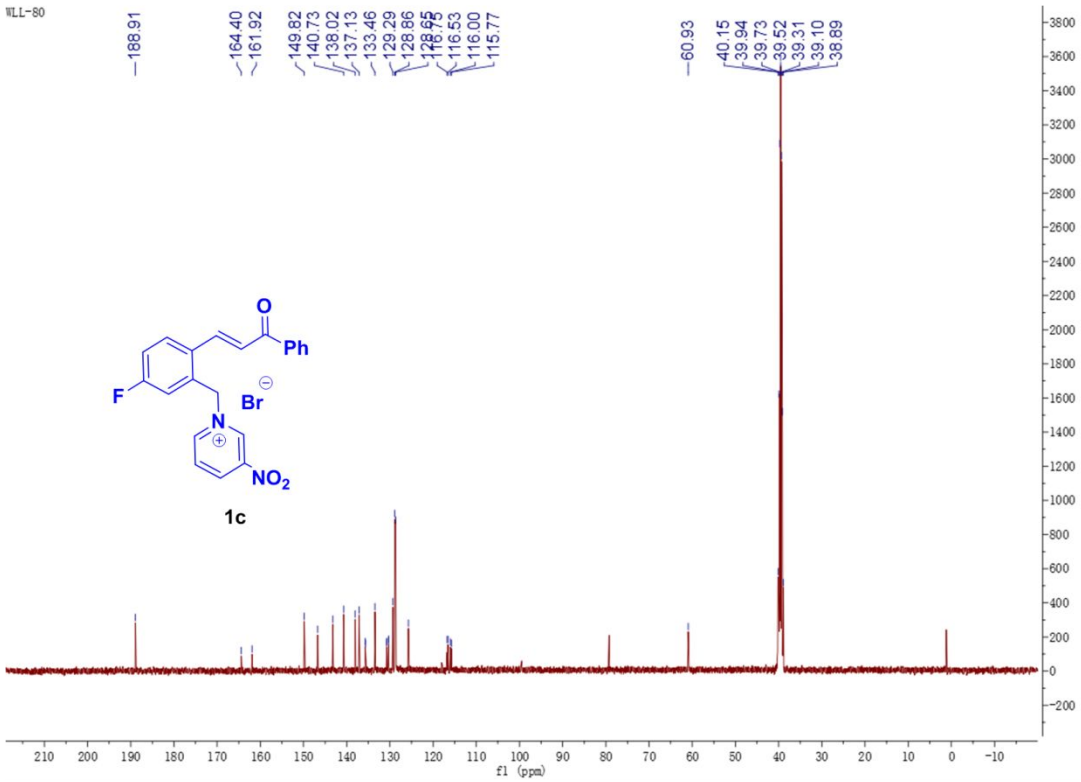
NO2
1c
f1 (ppm)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140.73
138.02
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129.29
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116.00
115.77
60.93
40.15
39.94
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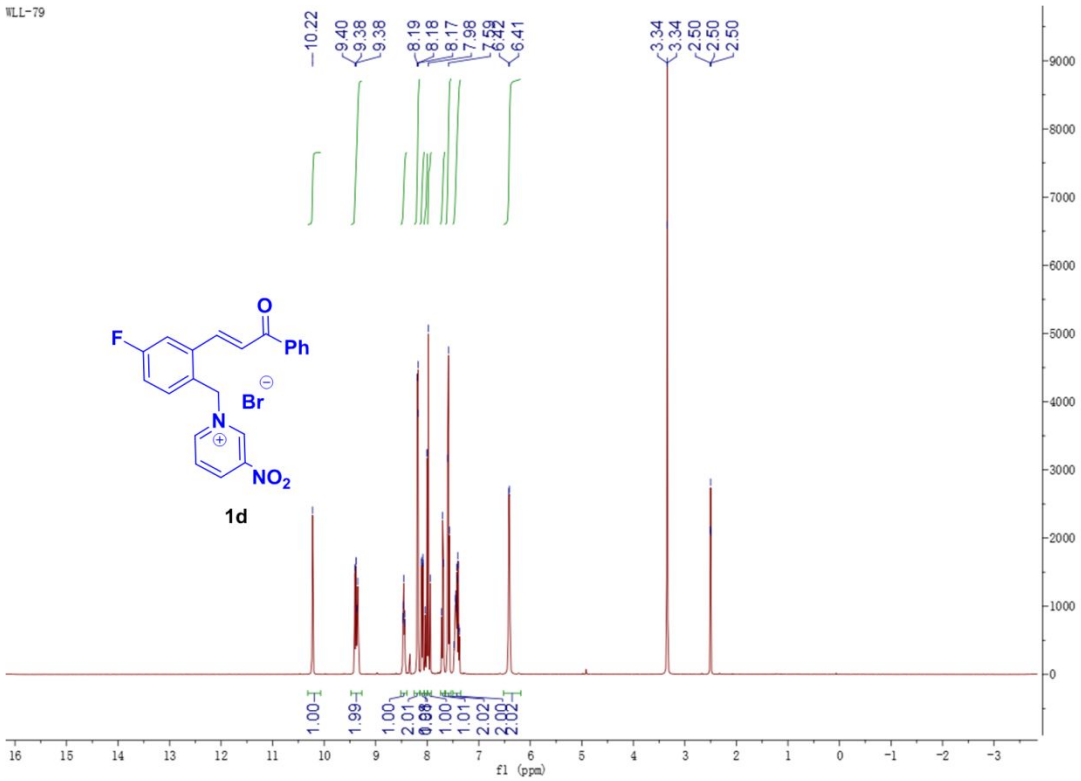
39.52
39.31
39.10
38.89
O
Ph
F
Br
N
NO2
1c
f1 (ppm)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6.41
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3.34
2.50
2.50
2.50
O
Ph
F
Br
N
NO2
1d
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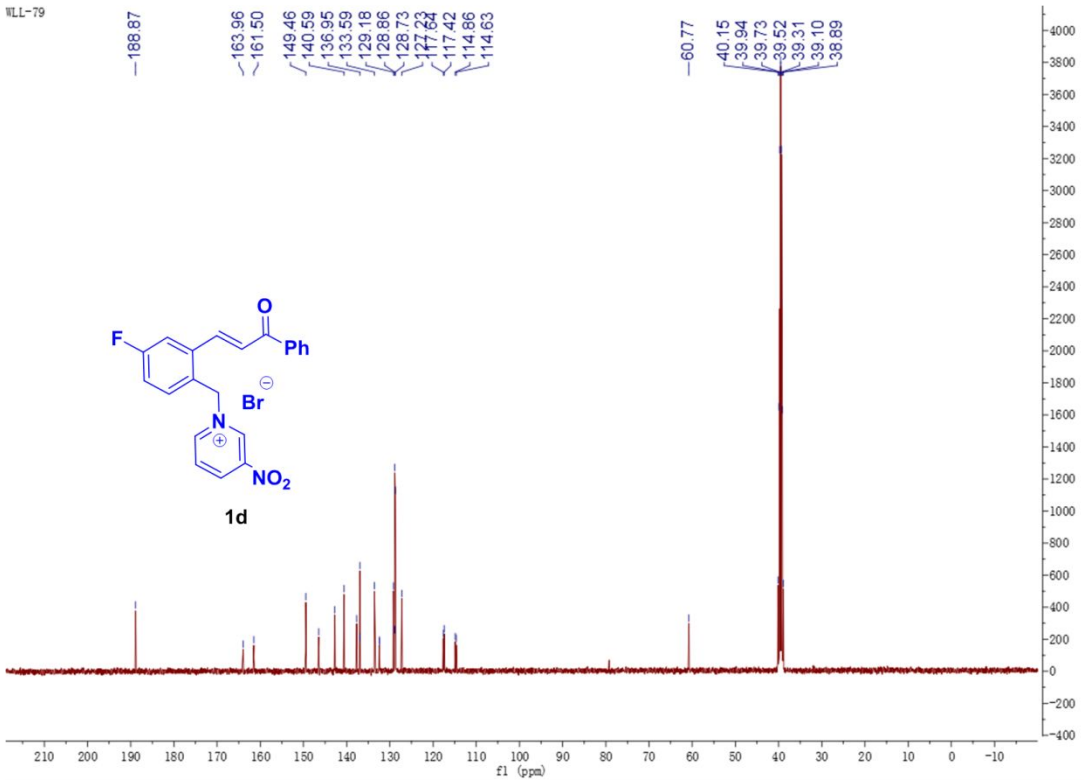
1.99
1.00
2.01
1.00
1.01
2.02
2.00
2.02
f1 (ppm)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128.86
128.73
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117.42
114.86
114.63
60.77
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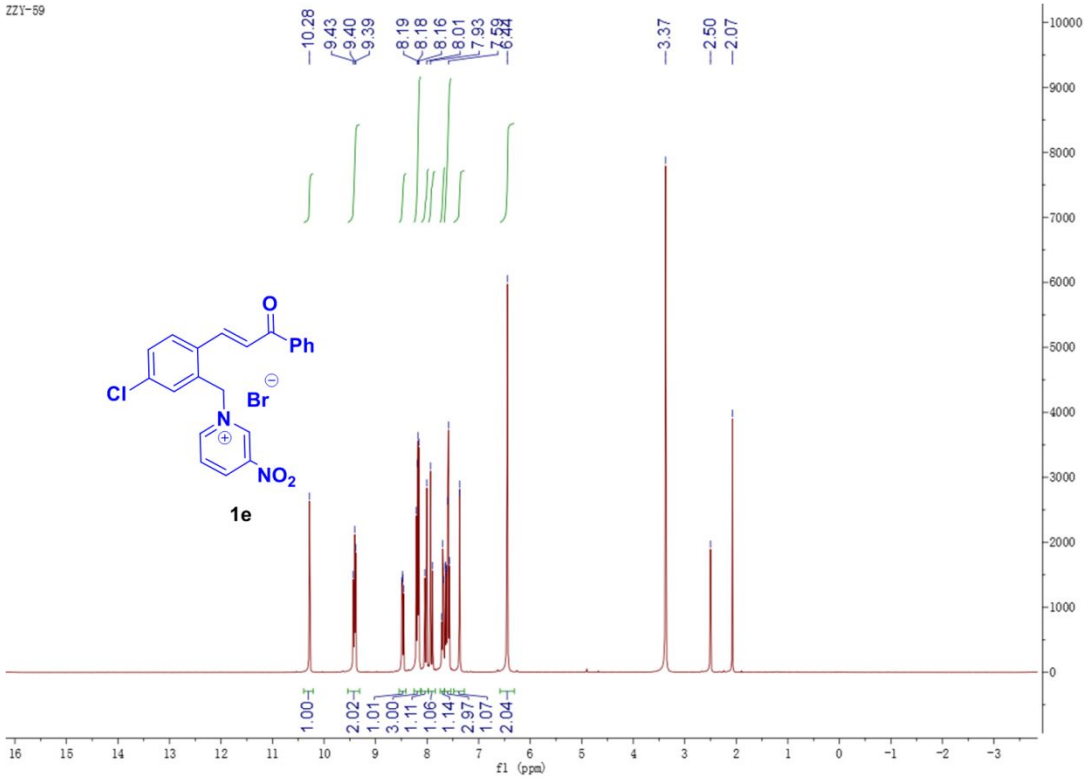
F
O
Ph
Br
N
NO2
1d
f1 (ppm)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8.19
8.18
8.16
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7.59
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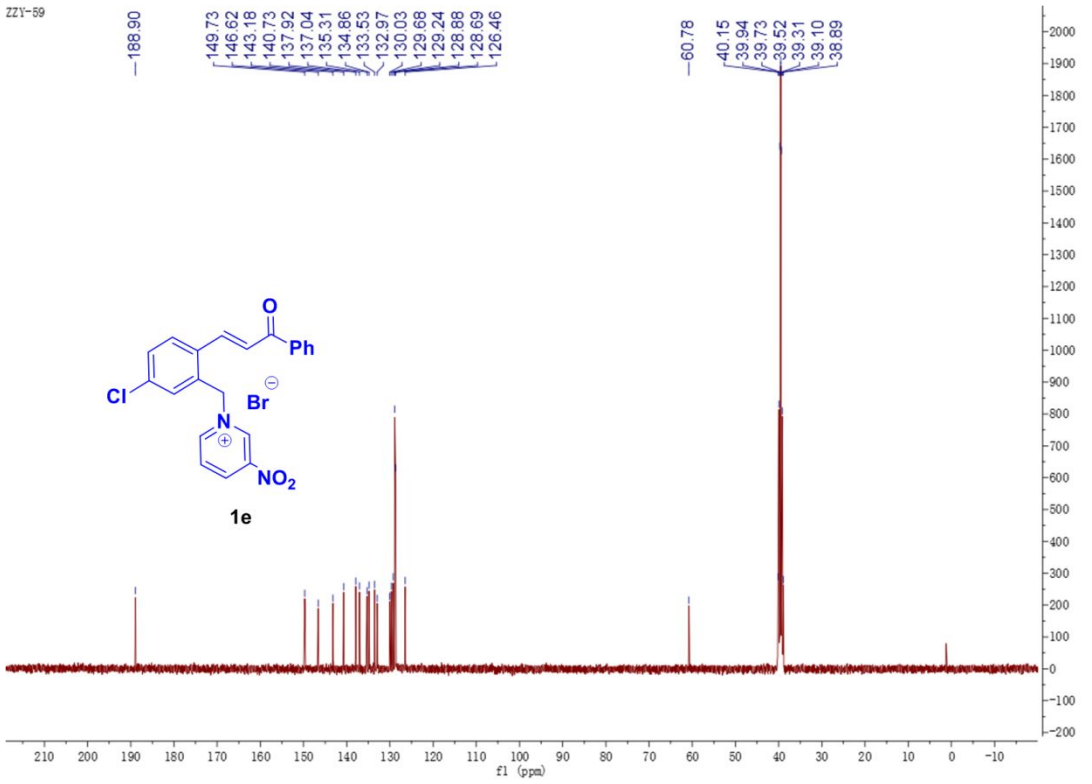
1.00
2.02
1.01
3.00
1.11
1.06
1.14
2.97
1.07
2.04
Cl
O
Ph
Br
N
NO2
1e
f1 (ppm)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143.18
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133.53
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129.68
129.24
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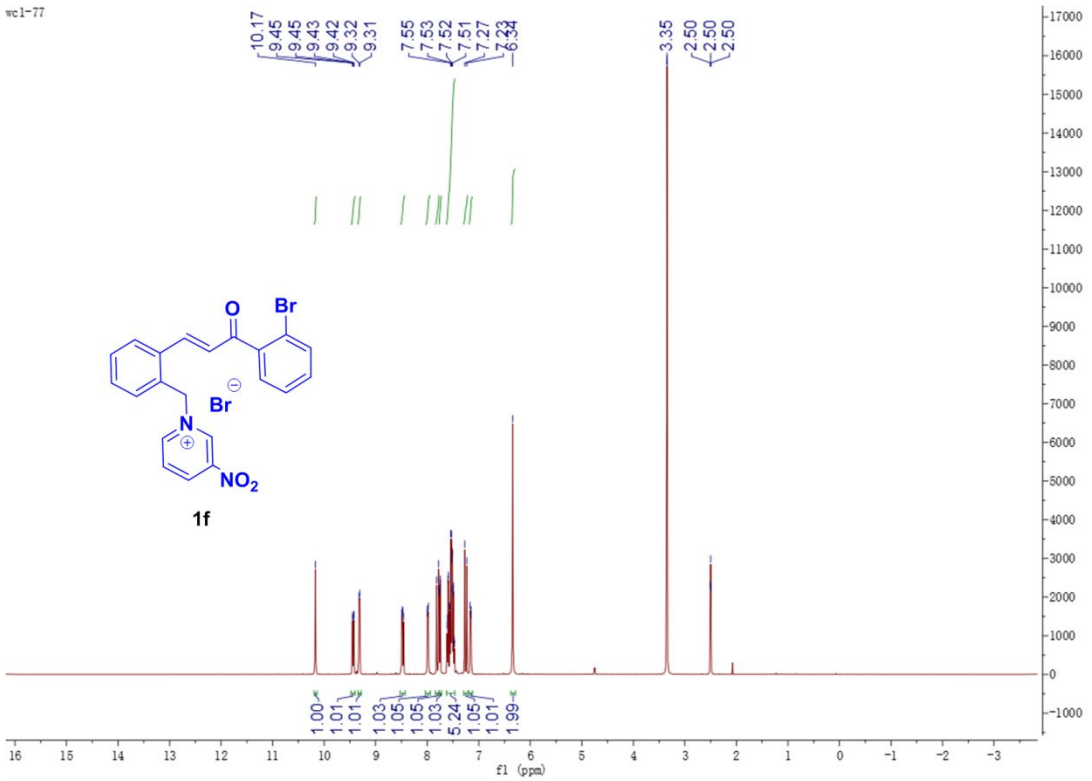
O
Ph
Cl
Br
N
NO2
1e
f1 (ppm)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7.52
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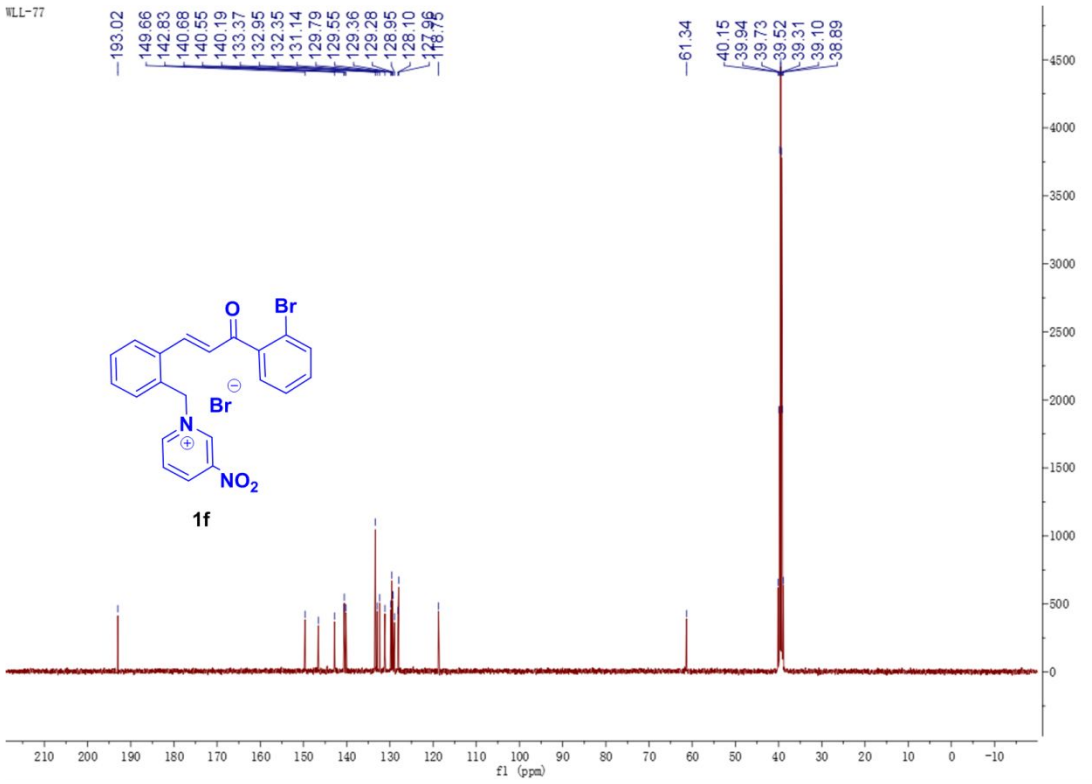
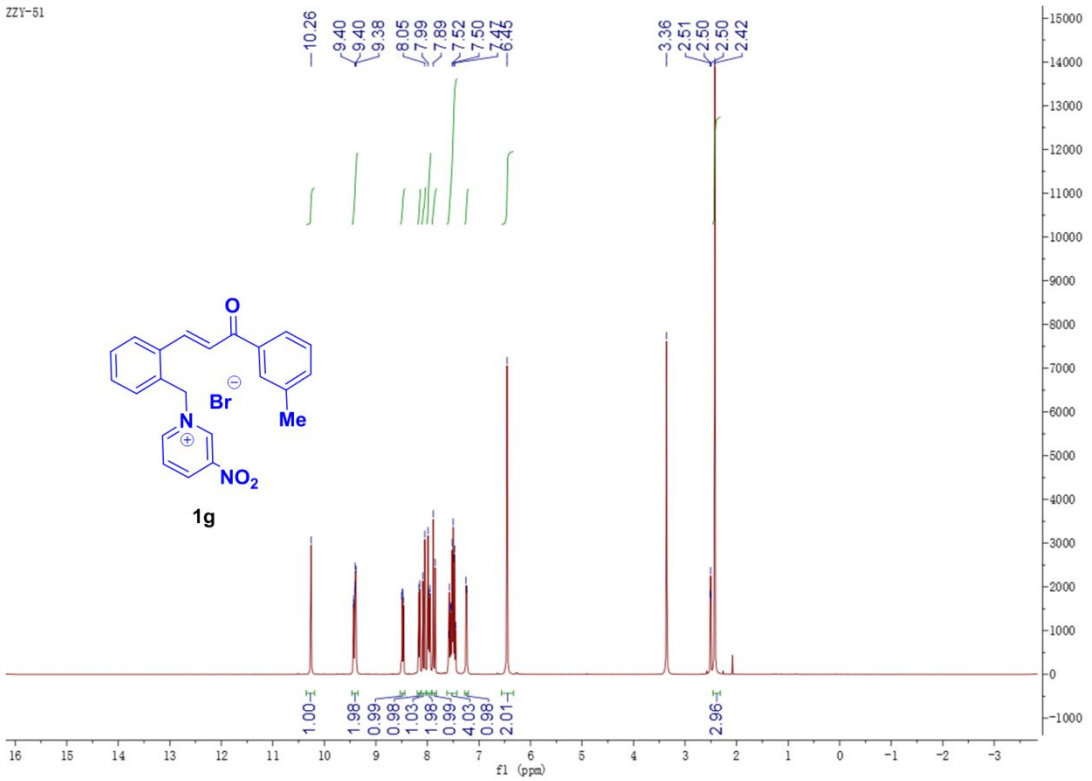
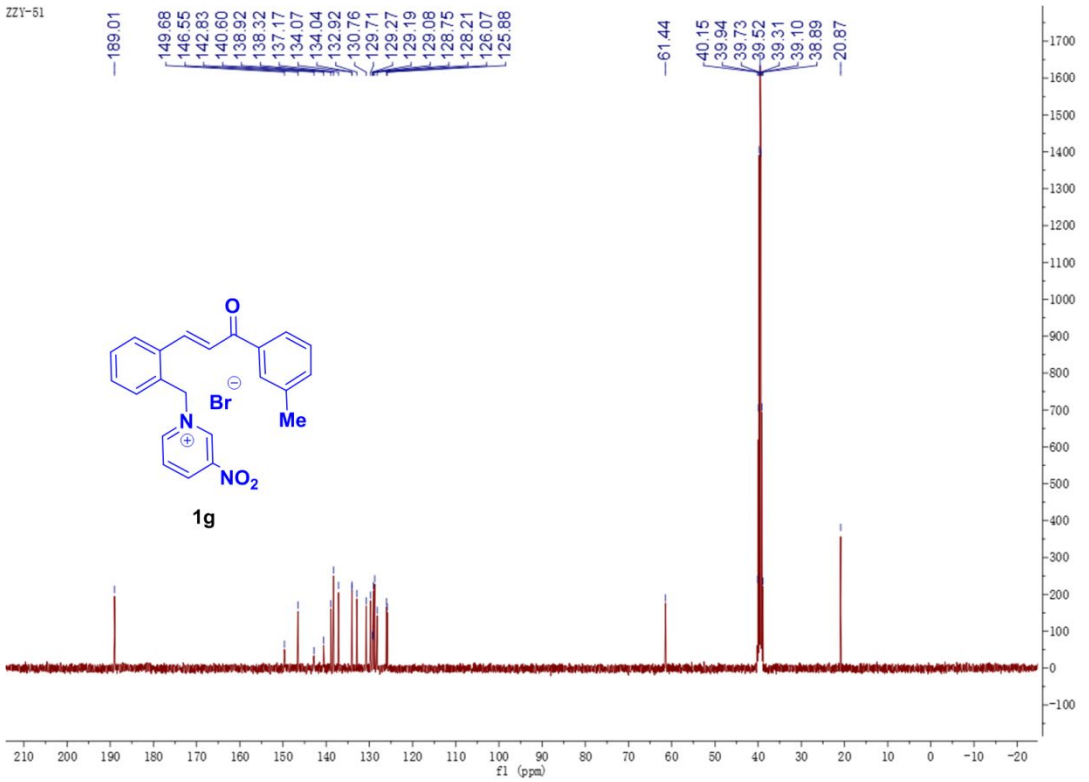
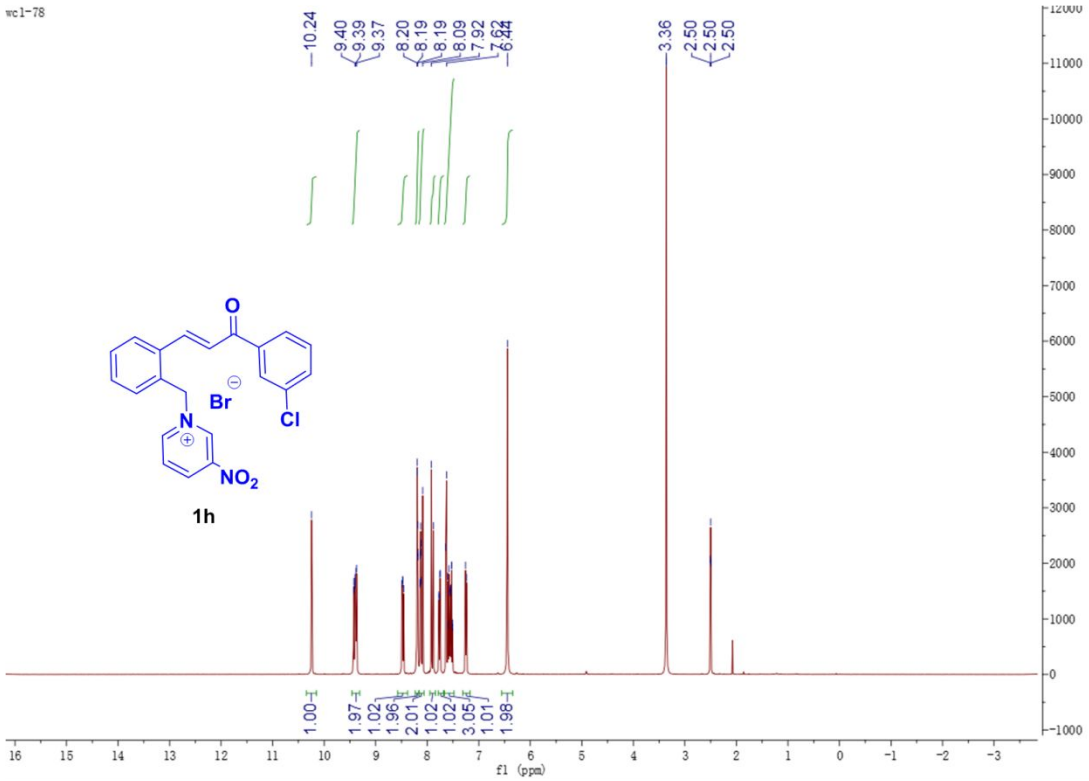
7.27
7.23
6.34
3.35
2.50
2.50
2.50
O
Br
Br
N
NO2
1f
1.00
1.01
1.01
1.03
1.05
1.05
1.03
5.24
1.05
1.01
1.99
f1 (ppm)


WLL-77
193.02
149.66
142.83
140.68
140.55
140.19
133.37
132.95
132.35
131.14
129.79
129.55
129.36
129.28
128.95
128.10
127.96
118.75
61.34
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Br
Br
N
NO2
1f
f1 (ppm)

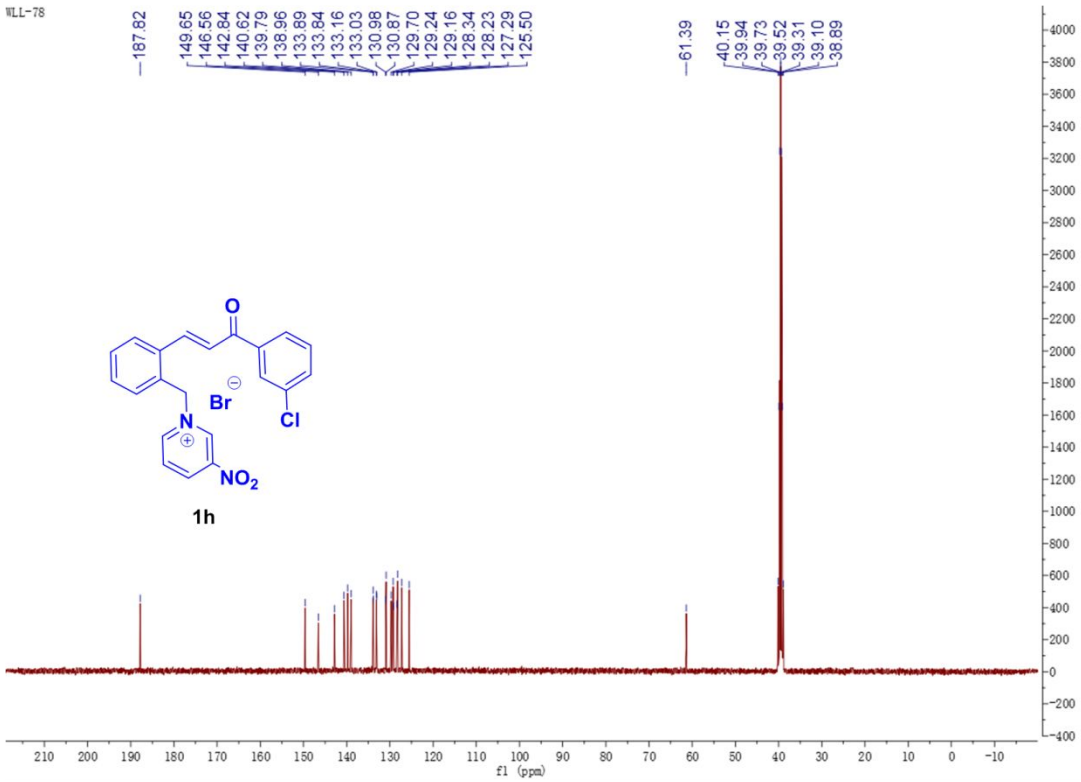

ZZY-51
10.26
9.40
9.40
9.38
8.05
7.99
7.89
7.52
7.50
7.47
6.45
3.36
2.51
2.50
2.50
2.42
O
Br
Me
N
NO2
1g
1.00
1.98
0.99
0.98
1.03
1.98
0.99
4.03
0.98
2.01
2.96
f1 (ppm)

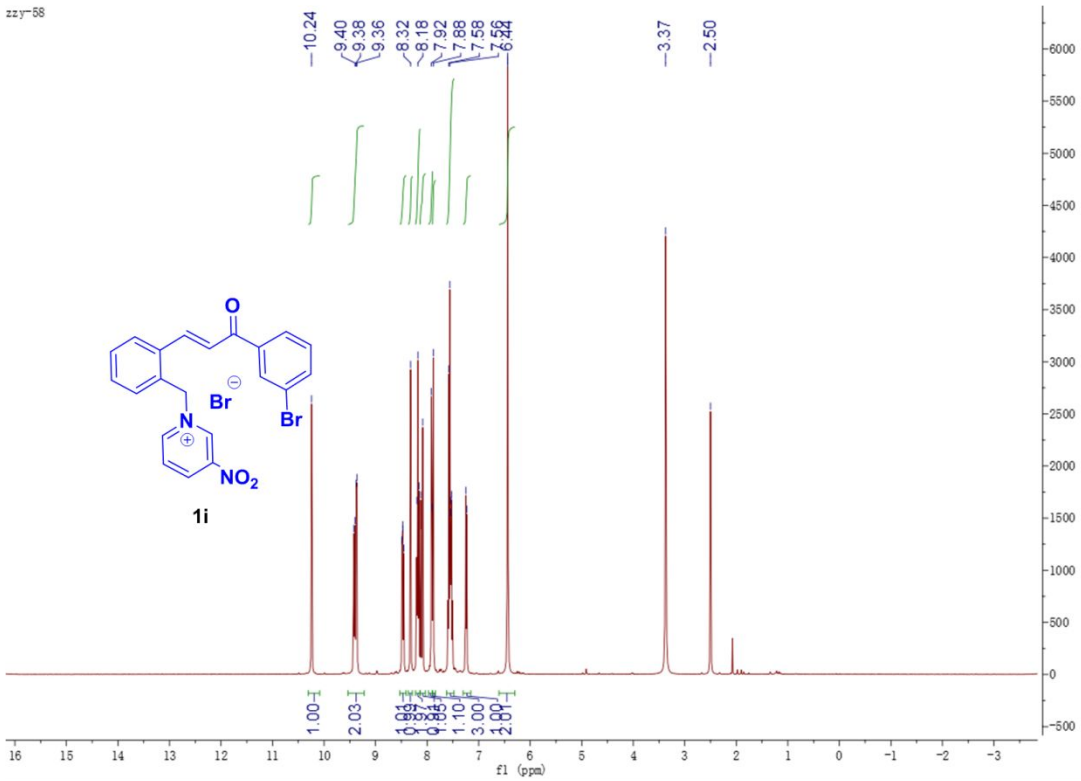

ZZY-51
189.01
149.68
146.55
142.83
140.60
138.92
138.32
137.17
134.07
134.04
132.92
130.76
129.71
129.27
129.19
129.08
128.75
128.21
126.07
125.88
61.44
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.87
O
Br
N
Me
NO2
f1 (ppm)

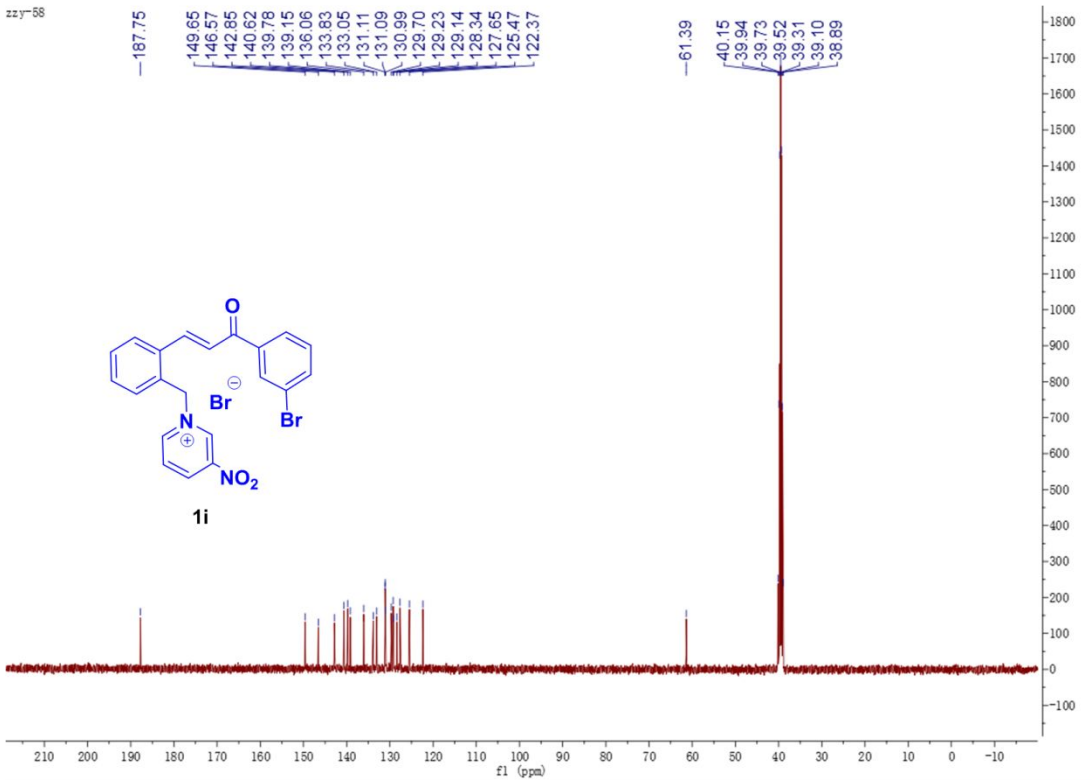
1g


wc1-78
10.24
9.40
9.39
9.37
8.20
8.19
8.19
8.09
7.92
7.62
7.44
3.36
2.50
2.50
2.50
1.00
1.97
1.02
1.96
2.01
1.02
1.02
3.05
1.01
1.98
O
Br
N
Cl
NO2
f1 (ppm)

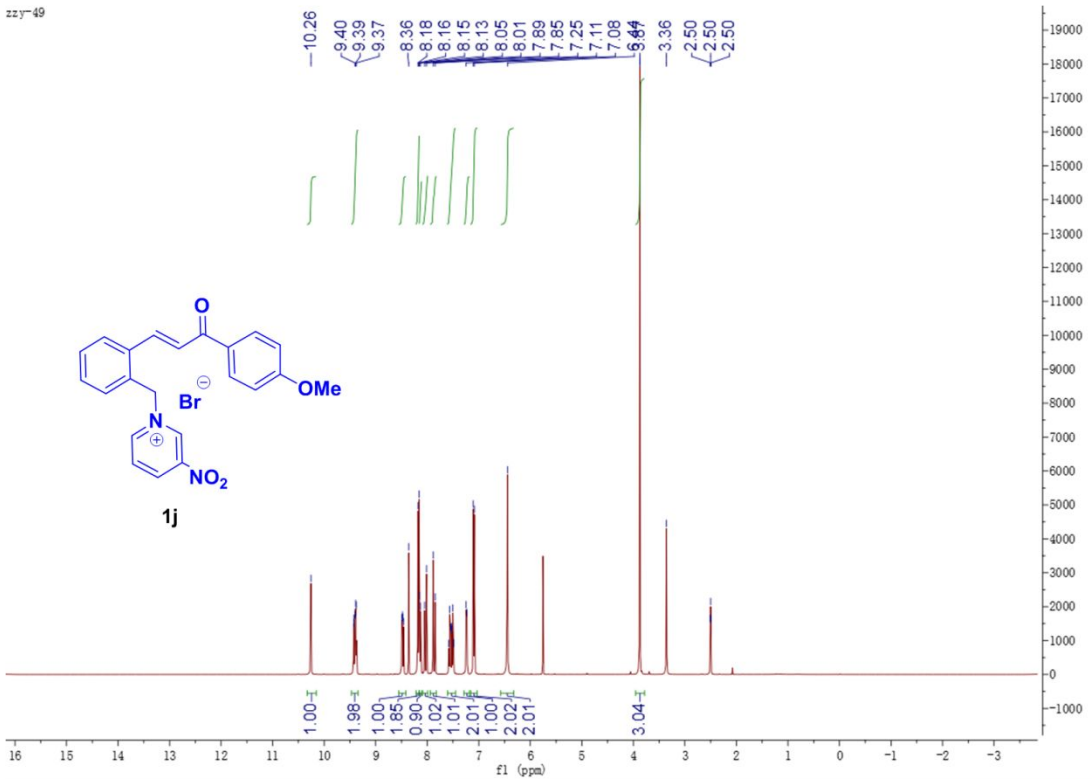
1h


WLL-78
187.82
149.65
146.56
142.84
140.62
139.79
138.96
133.89
133.84
133.16
133.03
130.98
130.87
129.70
129.24
129.16
128.34
128.23
127.29
125.50
61.39
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Br
Cl
N
NO2
1h
f1 (ppm)

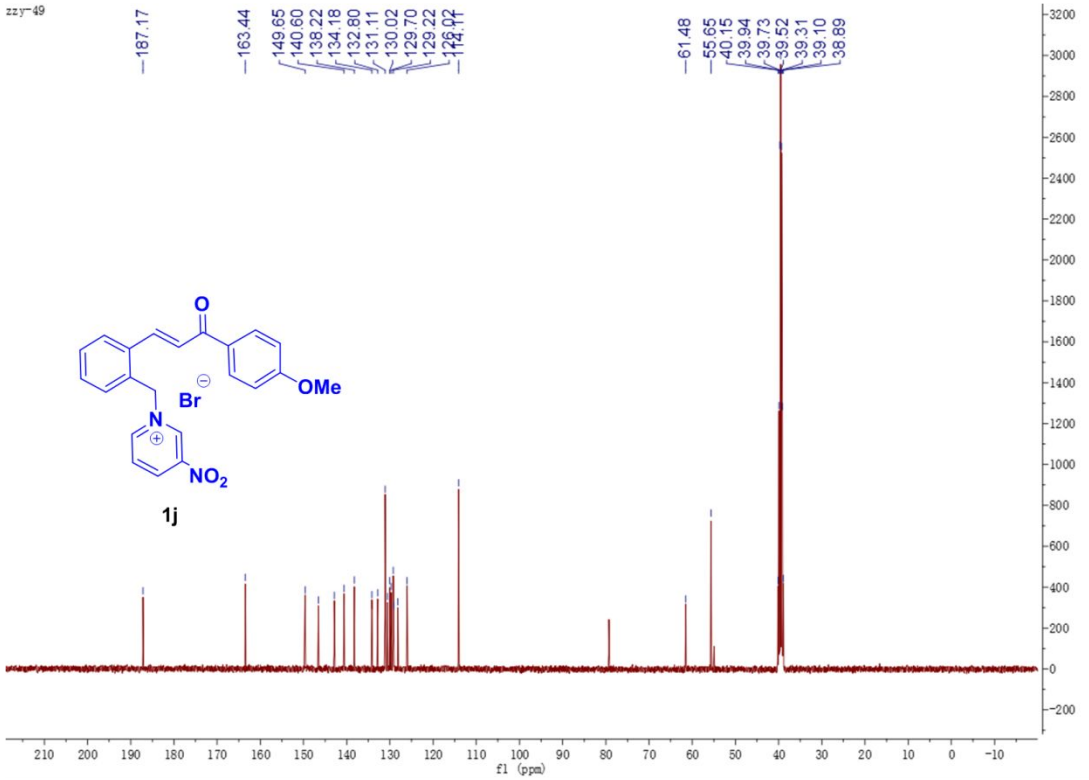

zzy-58
10.24
9.40
9.38
9.36
8.32
8.18
7.92
7.88
7.58
7.56
6.44
3.37
2.50
O
Br
Br
N
NO2
1i
1.00
2.03
1.01
0.99
0.97
0.85
1.10
3.00
1.00
2.01
f1 (ppm)

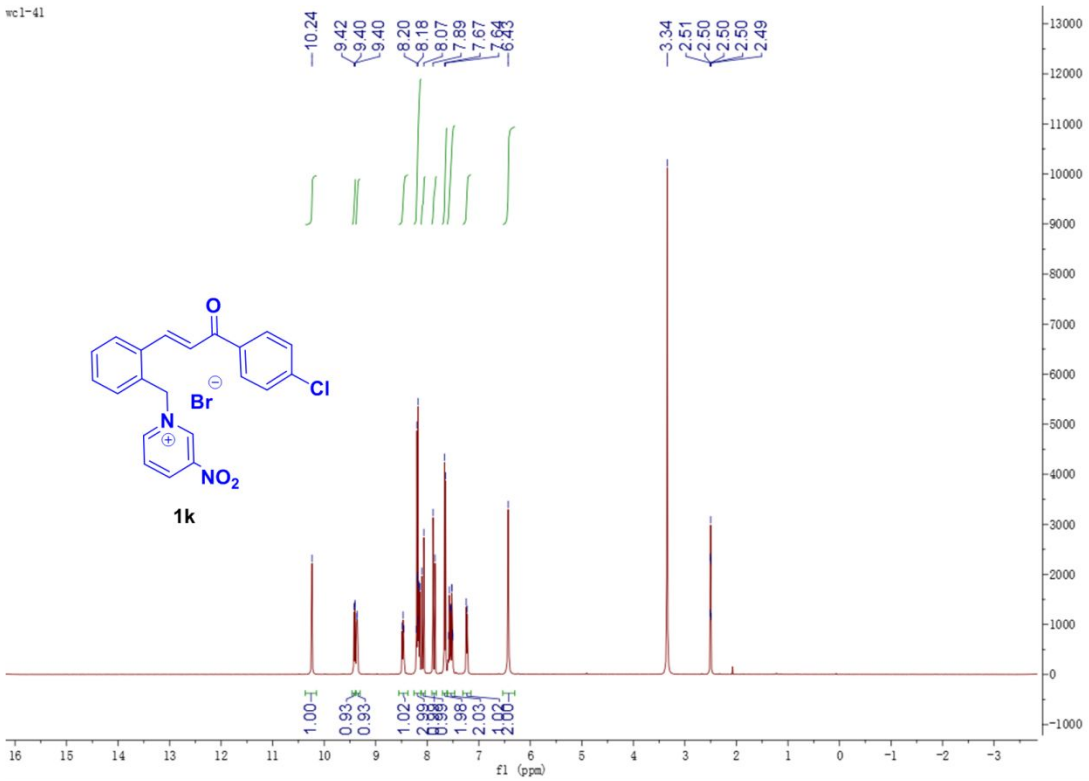

zzy-58
187.75
149.65
146.57
142.85
140.62
139.78
139.15
136.06
133.83
133.05
131.11
131.09
130.99
129.70
129.23
129.14
128.34
127.65
125.47
122.37
61.39
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Br
Br
N
NO2
f1 (ppm)

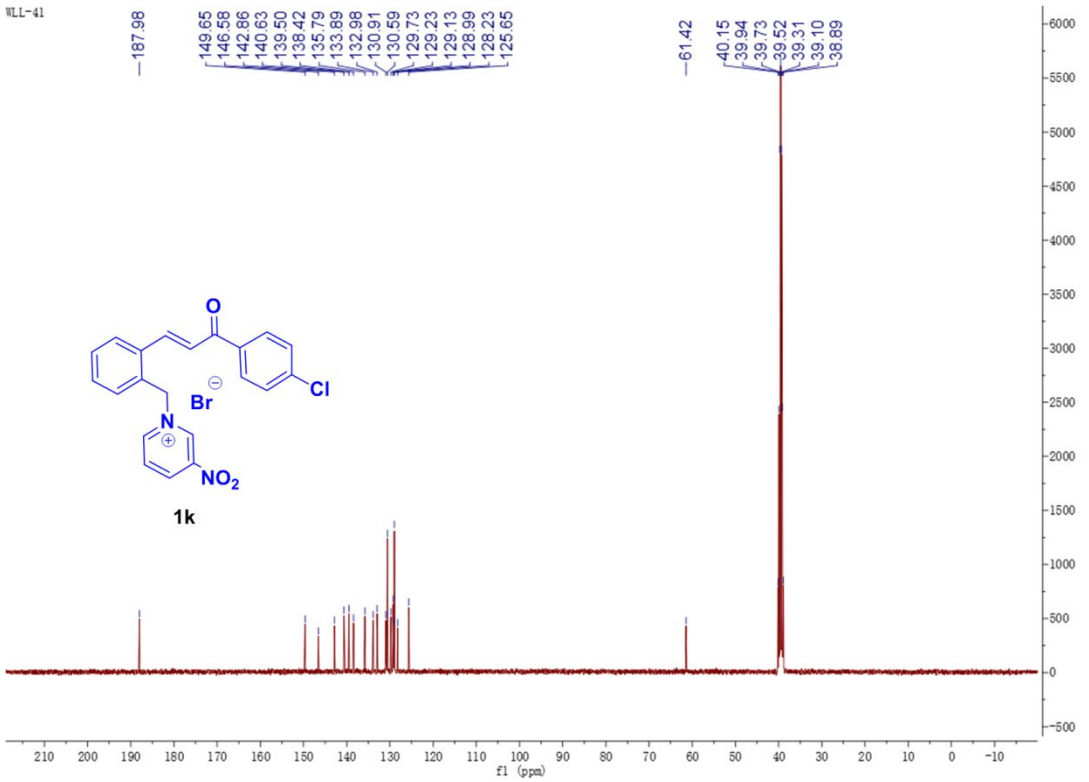
1i

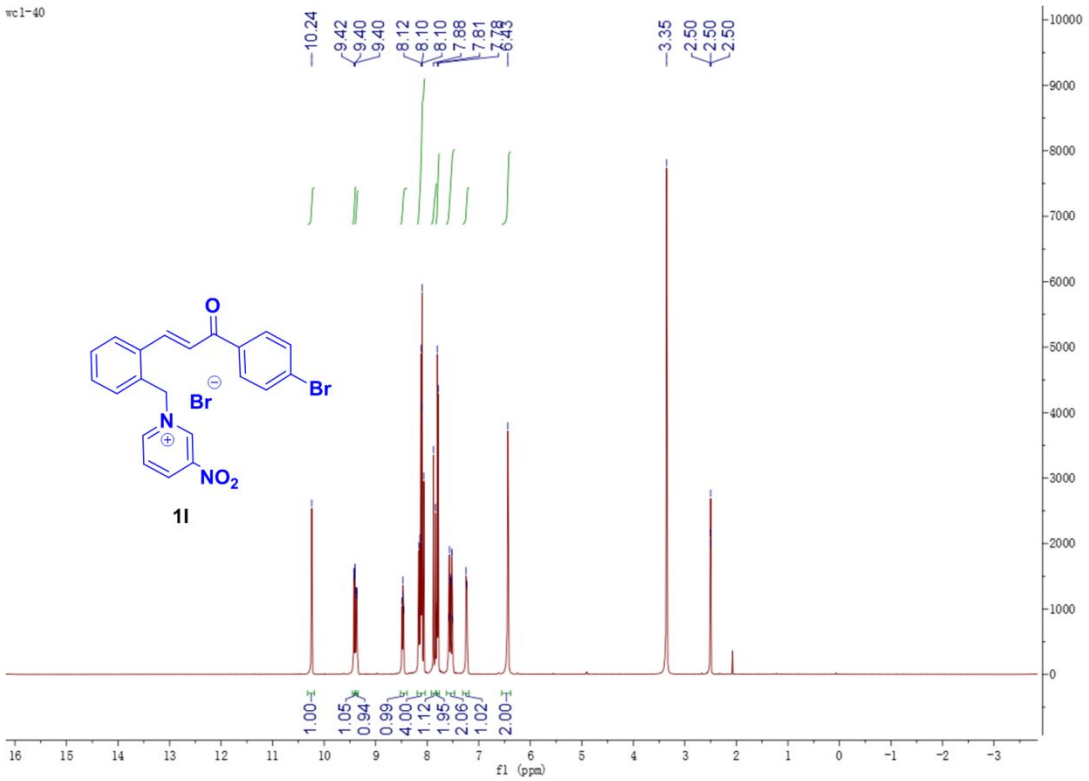

zzy-49
10.26
9.40
9.39
9.37
8.36
8.18
8.16
8.15
8.13
8.05
8.01
7.89
7.85
7.25
7.11
7.08
3.36
2.50
2.50
2.50
O
OMe
Br
N
NO2
1.00
1.98
1.00
1.85
0.90
1.02
1.01
2.01
1.00
2.02
2.01
3.04
f1 (ppm)

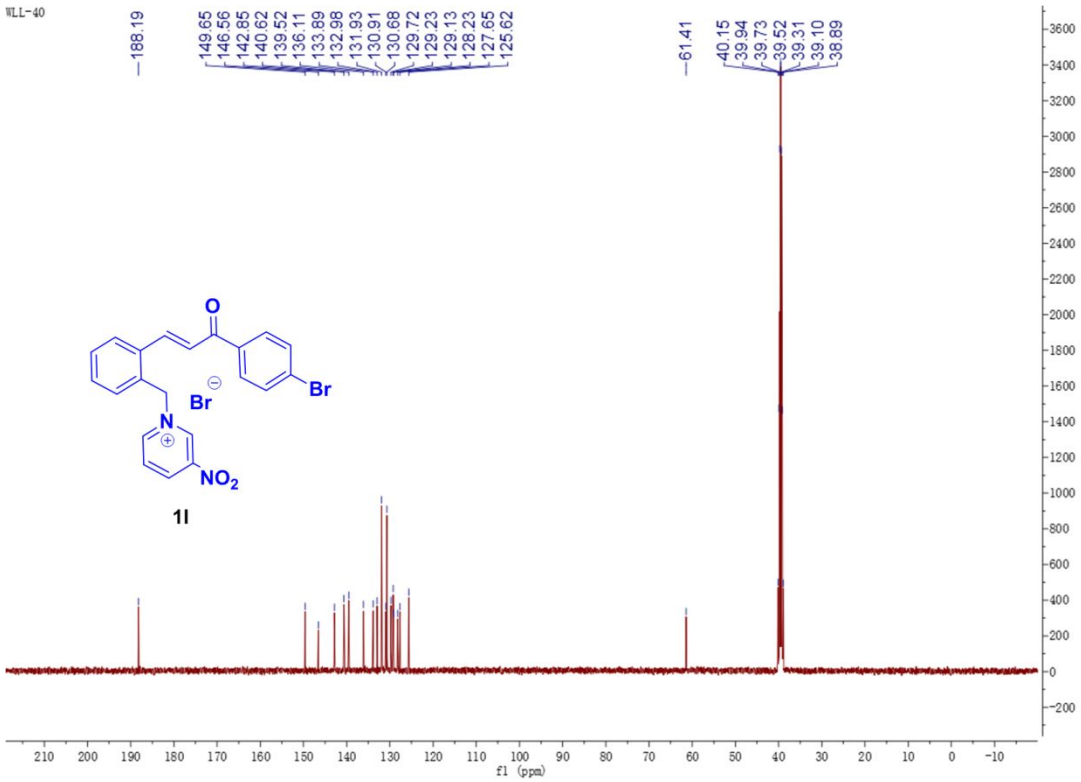
1j

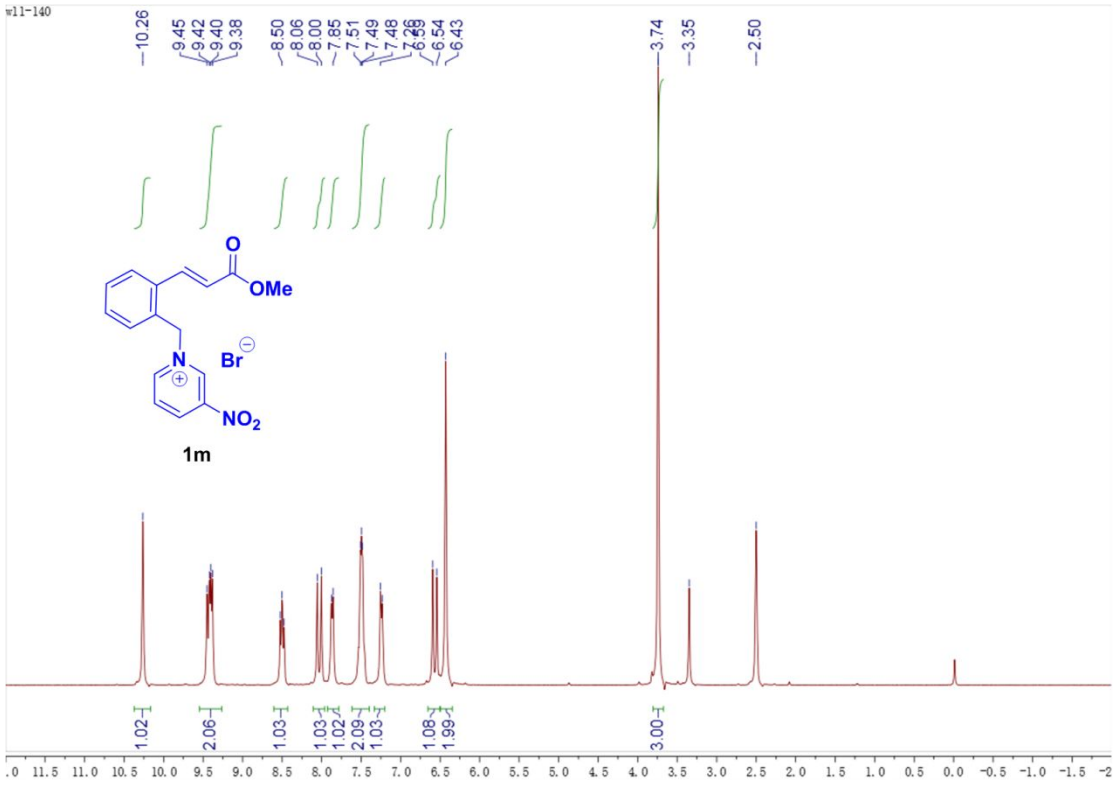

zzy-49
187.17
163.44
149.65
140.60
138.22
134.18
132.80
131.11
130.02
129.70
129.22
61.48
55.65
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
OMe
Br
N
NO2
1j
f1 (ppm)

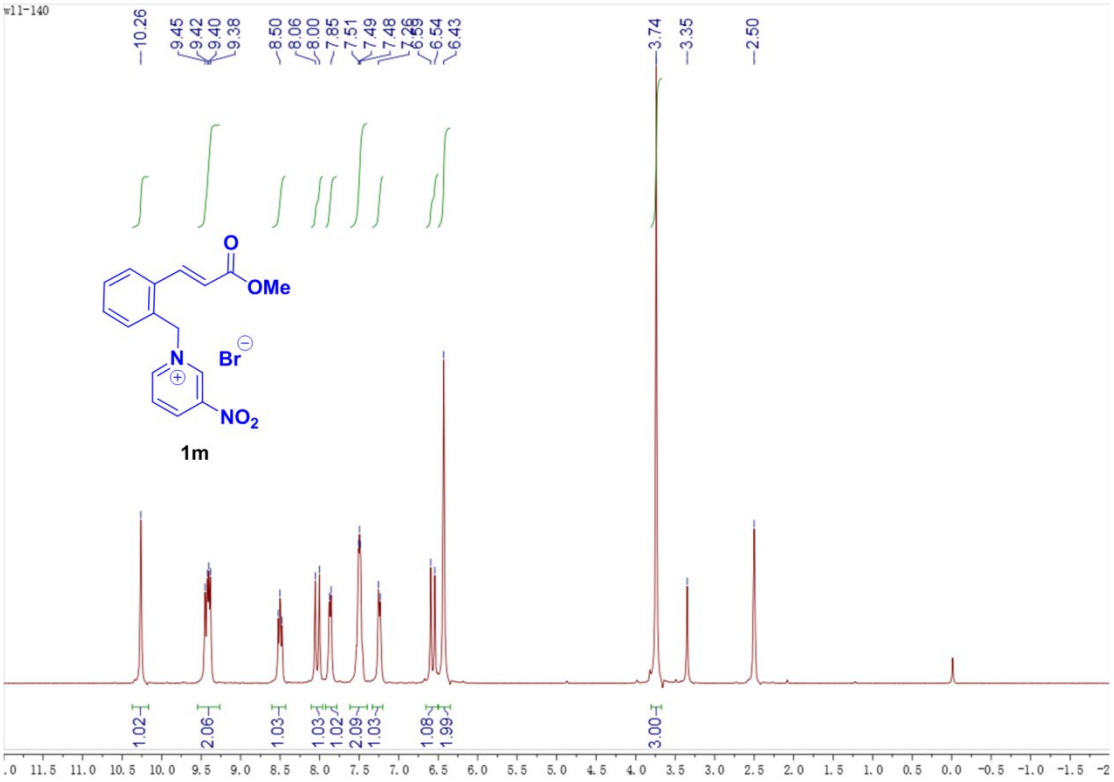

wc1-41
10.24
9.42
9.40
9.40
8.20
8.18
8.07
7.89
7.67
7.64
6.43
3.34
2.51
2.50
2.50
2.50
2.49
1.00
0.93
0.93
1.02
1.98
2.03
2.00
O
Cl
Br
N
NO2
1k
f1 (ppm)

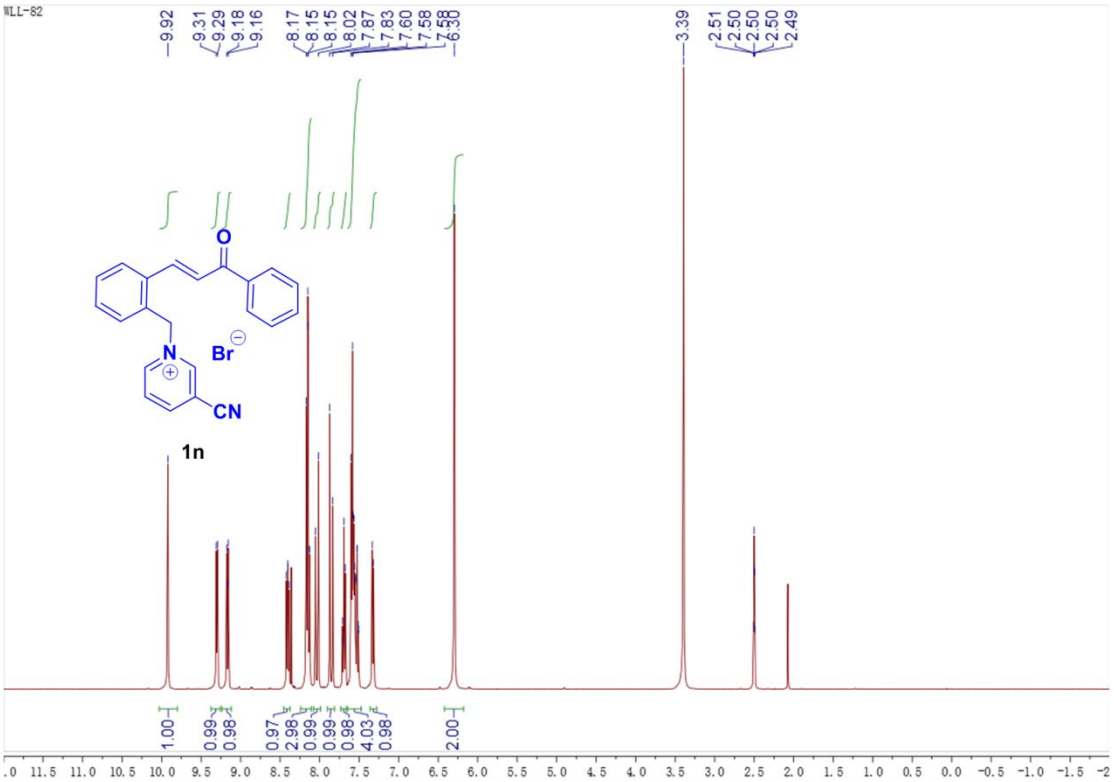

WLL-41
187.98
149.65
146.58
142.86
140.63
139.50
138.42
135.79
133.89
132.98
130.91
130.59
129.73
129.23
129.13
128.99
128.23
125.65
61.42
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Cl
Br
N
NO2
1k
f1 (ppm)

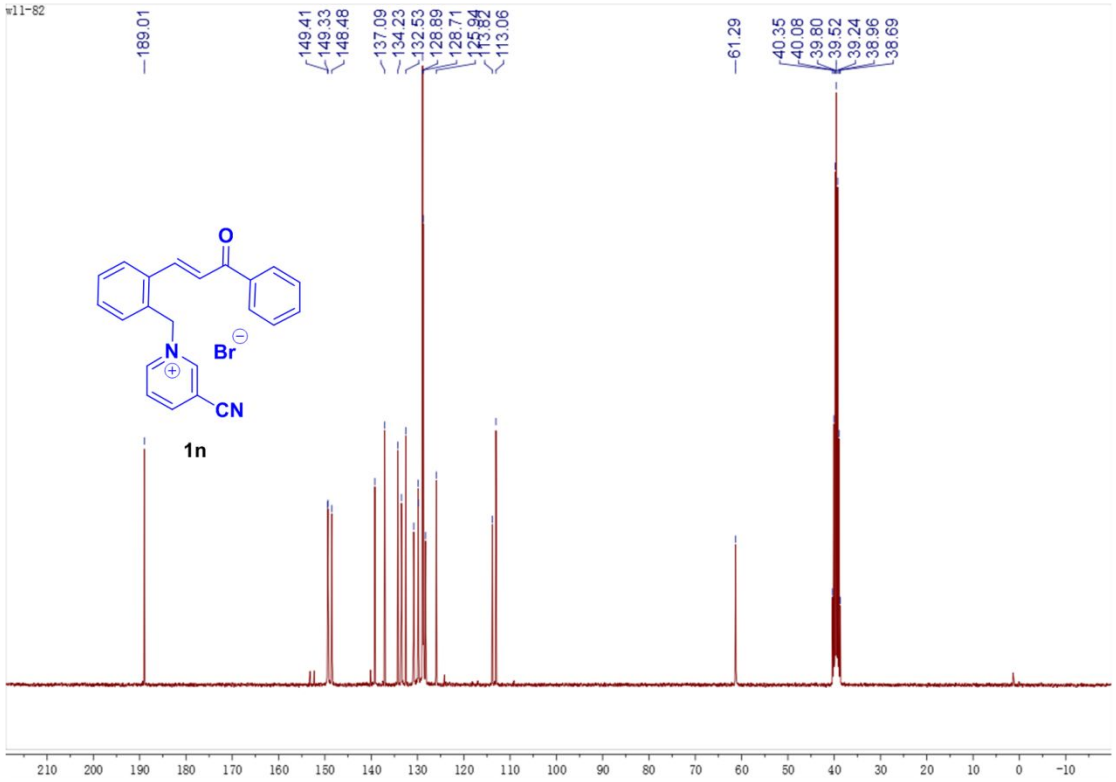

wc1-40
10.24
9.42
9.40
9.40
8.12
8.10
8.10
7.88
7.81
7.78
6.43
3.35
2.50
2.50
2.50
1.00
1.05
0.94
0.99
4.00
1.12
1.95
2.06
1.02
2.00
O
Br
Br
N
NO2
1l
f1 (ppm)

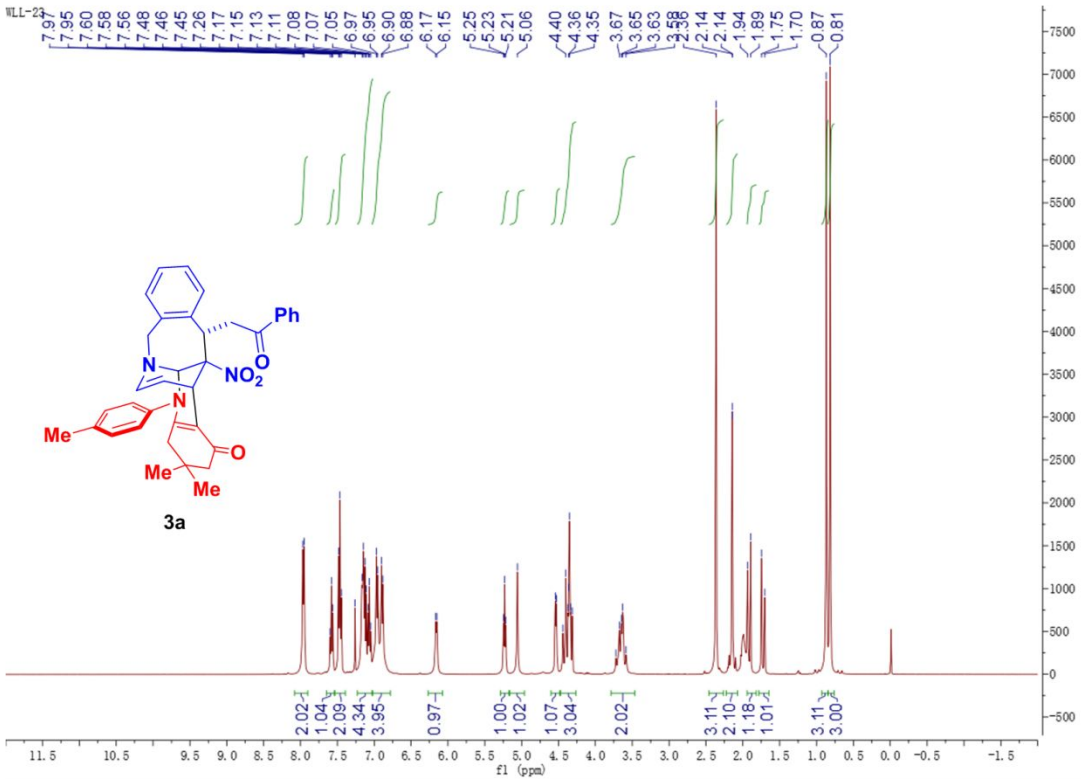

WLL-40
188.19
149.65
146.56
142.85
140.62
139.52
136.11
133.89
132.98
131.93
130.91
130.68
129.72
129.23
129.13
128.23
127.65
125.62
61.41
40.15
39.94
39.73
39.52
39.31
39.10
38.89
O
Br
Br
N
NO2
1l
f1 (ppm)

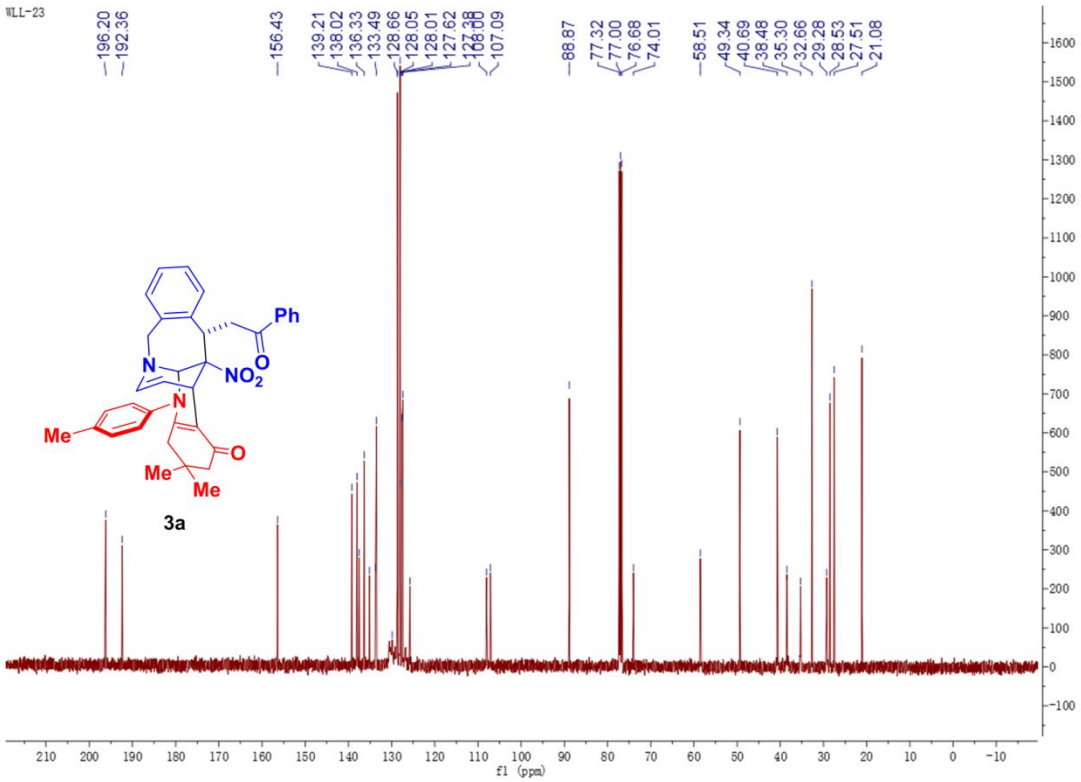

w11-140
10.26
9.45
9.42
9.40
9.38
8.50
8.06
8.00
7.85
7.51
7.49
7.48
6.59
6.54
6.43
3.74
3.35
2.50
O
OMe
N
Br
NO2
1m
1.02
2.06
1.03
1.03
1.02
2.09
1.03
1.08
1.99
3.00


w11-140
10.26
9.45
9.42
9.40
9.38
8.50
8.06
8.00
7.85
7.51
7.49
7.48
6.54
6.43
3.74
3.35
2.50
O
OMe
N
Br
NO2
1m
1.02
2.06
1.03
1.03
1.02
2.09
1.03
1.08
1.99
3.00

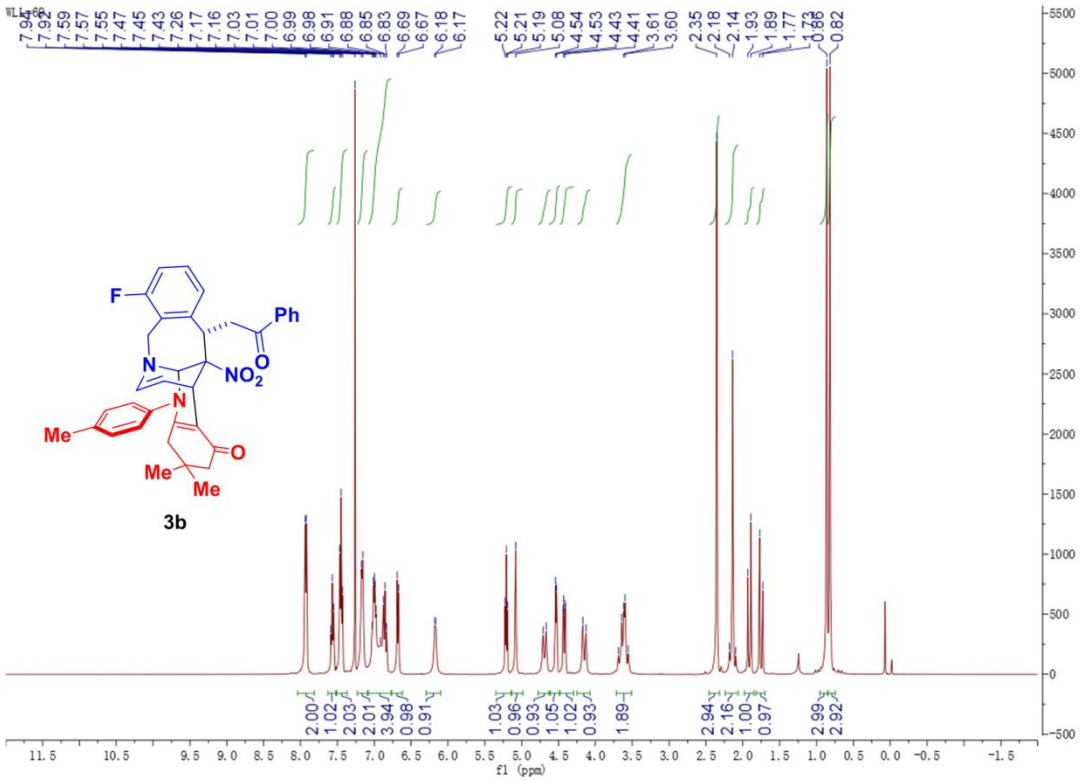

WLL-82
9.92
9.31
9.29
9.18
9.16
8.17
8.15
8.15
8.02
7.87
7.83
7.60
7.58
7.58
6.38
3.39
2.51
2.50
2.50
2.50
2.49
O
N
Br
CN
1n
1.00
0.99
0.98
0.97
2.98
0.99
0.99
0.98
4.03
0.98
2.00


w11-82
189.01
149.41
149.33
148.48
137.09
134.23
132.53
128.89
128.71
125.94
113.82
113.06
61.29
40.35
40.08
39.80
39.52
39.24
38.96
38.69
O
N
Br
CN
1n

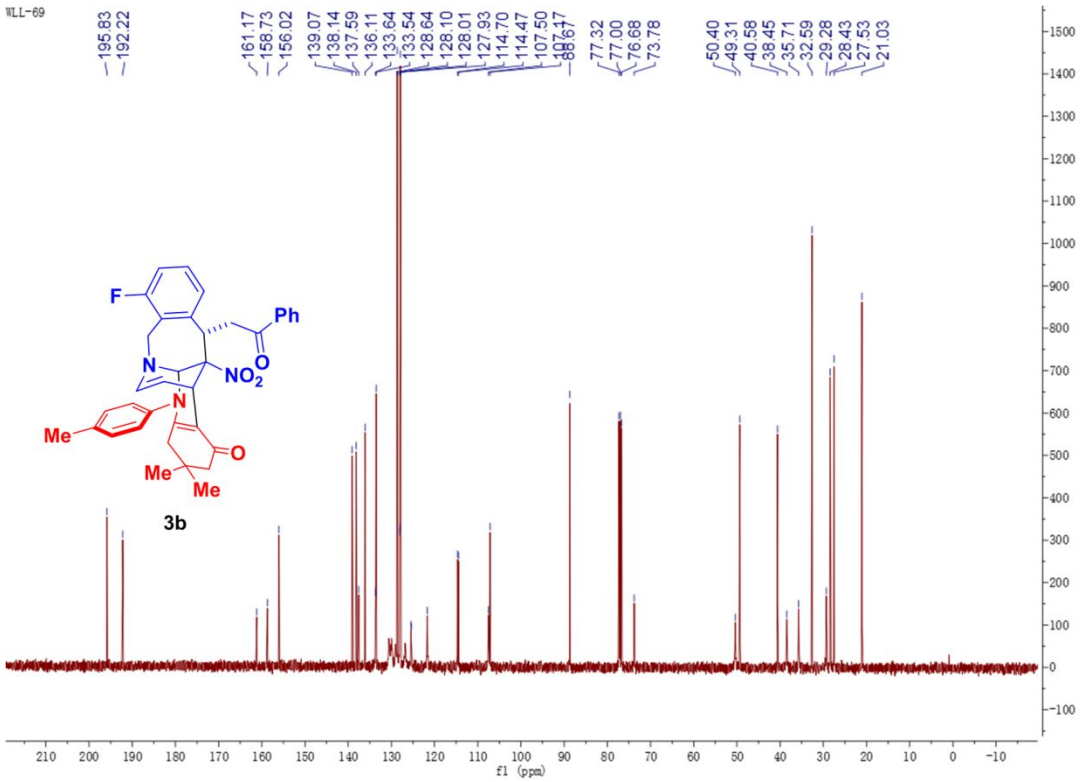

WLL-23
7.97
7.95
7.60
7.58
7.56
7.48
7.46
7.45
7.26
7.17
7.15
7.13
7.11
7.08
7.07
7.05
6.97
6.95
6.90
6.88
6.17
6.15
5.25
5.23
5.21
5.06
4.40
4.36
4.35
3.67
3.65
3.63
2.58
2.30
2.14
2.14
1.94
1.89
1.75
1.70
0.87
0.81
Ph
O
N
NO2
N
Me
O
Me
Me
3a
2.02
1.04
2.09
4.34
3.95
0.97
1.00
1.02
1.07
3.04
2.02
3.11
2.10
1.18
1.01
3.11
3.00
f1 (ppm)

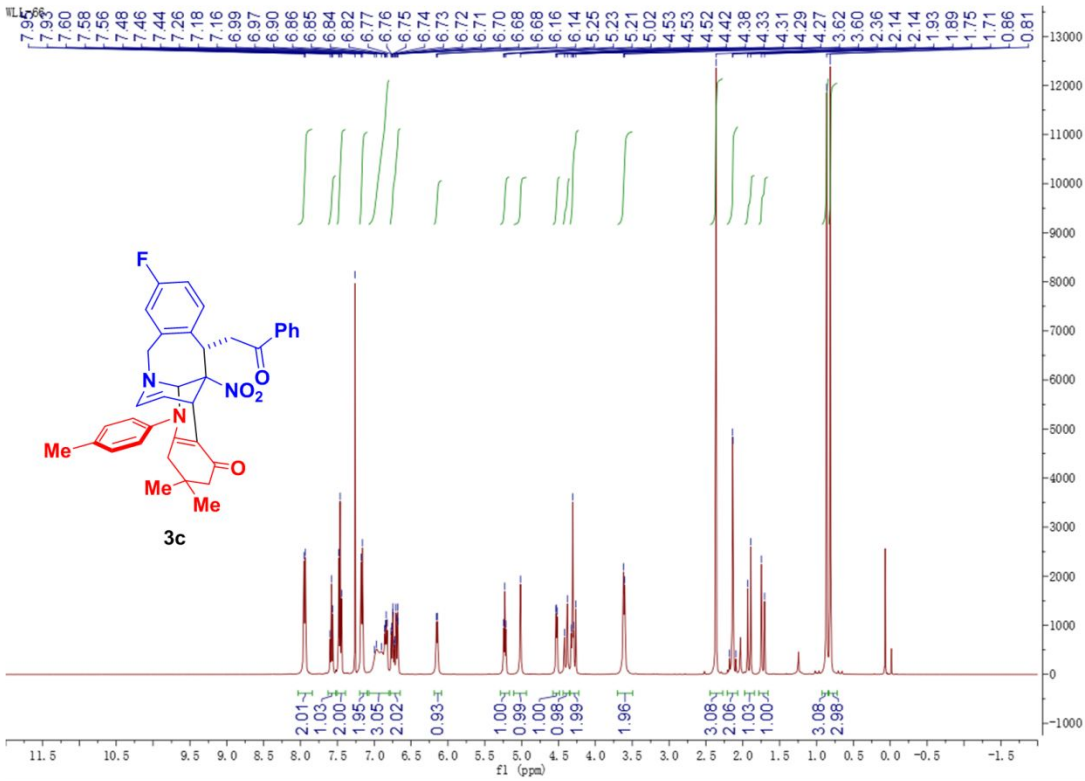

WLL-23
196.20
192.36
156.43
139.21
138.02
136.33
133.49
128.66
128.05
128.01
127.62
88.87
77.32
77.00
76.68
74.01
58.51
49.34
40.69
38.48
35.30
32.66
29.28
28.53
27.51
21.08
Ph
O
NO2
N
Me
Me
Me
O
f1 (ppm)

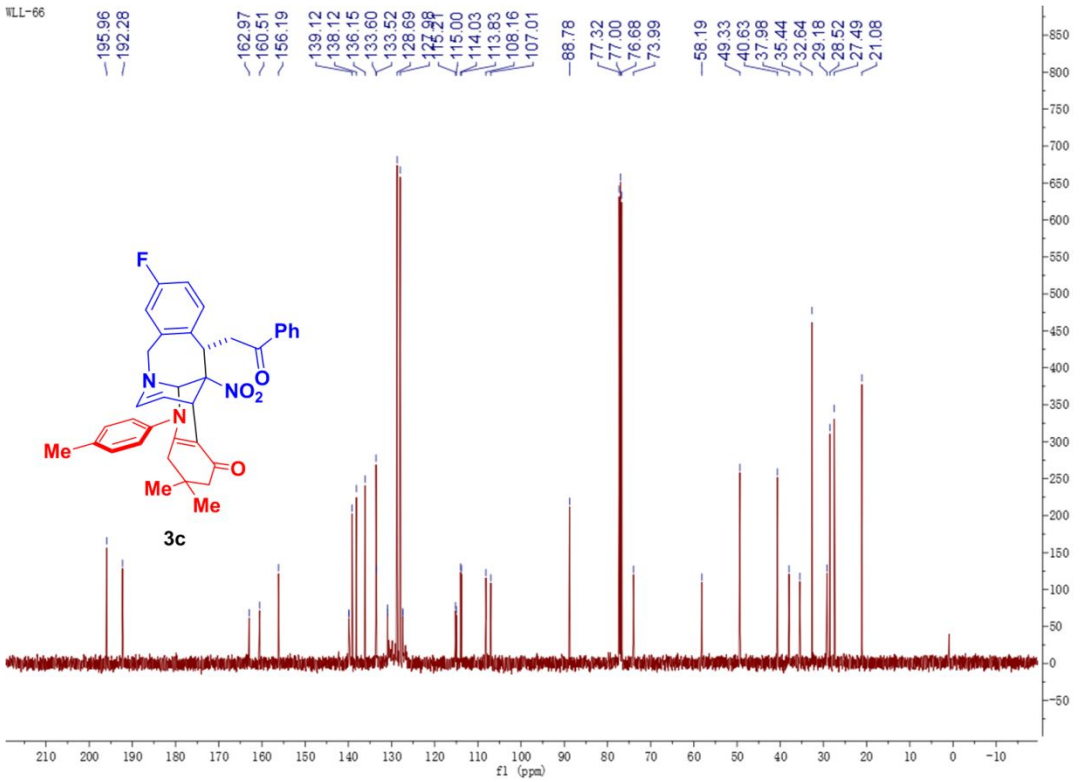
3a

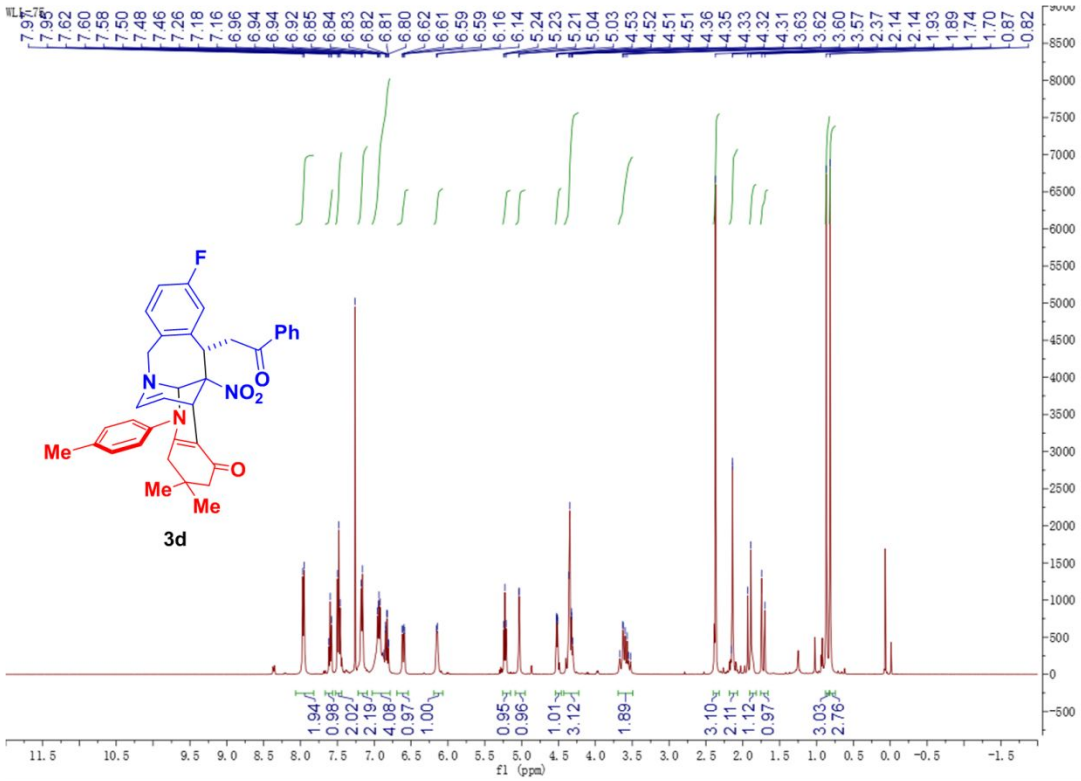

7.94
7.92
7.59
7.57
7.55
7.47
7.45
7.43
7.26
7.17
7.16
7.03
7.01
7.00
6.99
6.98
6.91
6.88
6.85
6.83
6.69
6.67
6.18
6.17
5.22
5.21
5.19
5.08
4.54
4.53
4.43
4.41
3.61
3.60
2.35
2.18
2.14
1.93
1.89
1.77
1.73
0.86
0.82
F
Ph
O
NO2
N
Me
Me
Me
O
2.00
1.02
2.03
2.01
3.94
0.98
0.91
1.03
0.96
0.93
1.05
1.02
0.93
1.89
2.94
2.16
1.00
0.97
2.99
2.92
f1 (ppm)

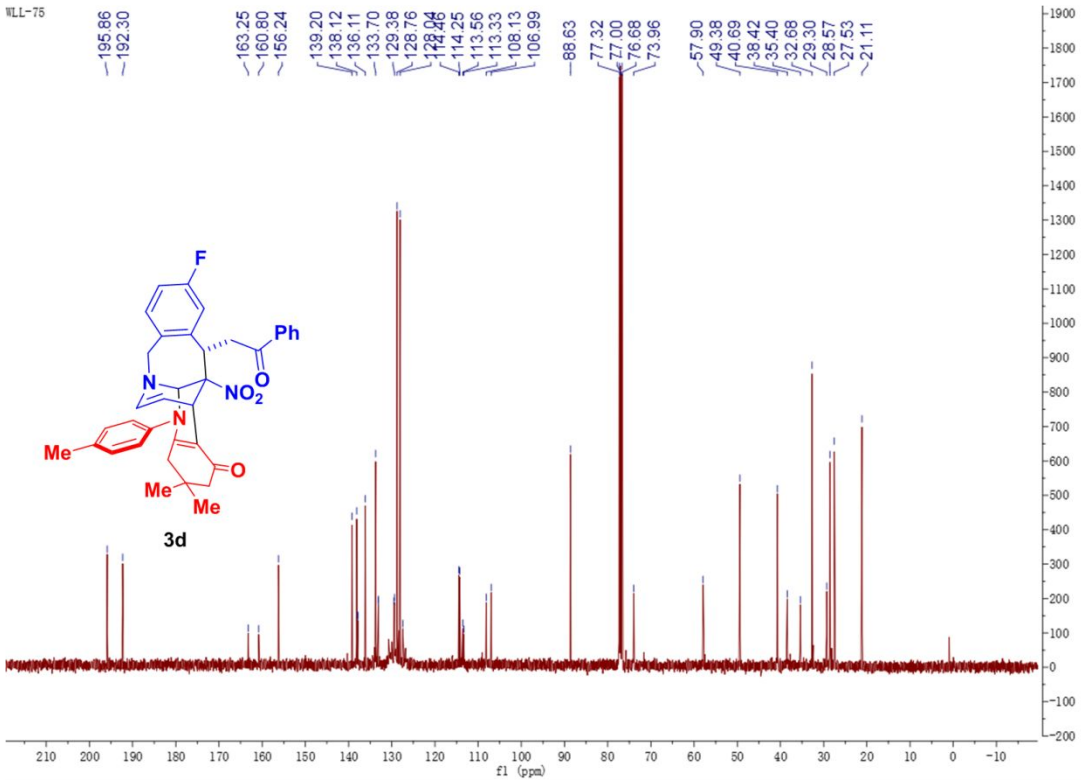
3b


WLL-69
195.83
192.22
161.17
158.73
156.02
139.07
138.14
137.59
136.11
133.64
133.54
128.64
128.10
128.01
127.93
114.70
114.47
107.50
107.17
88.67
77.32
77.00
76.68
73.78
50.40
49.31
40.58
38.45
35.71
32.59
29.28
28.43
27.53
21.03
F
Ph
N
NO2
O
N
Me
O
Me
Me
3b
f1 (ppm)

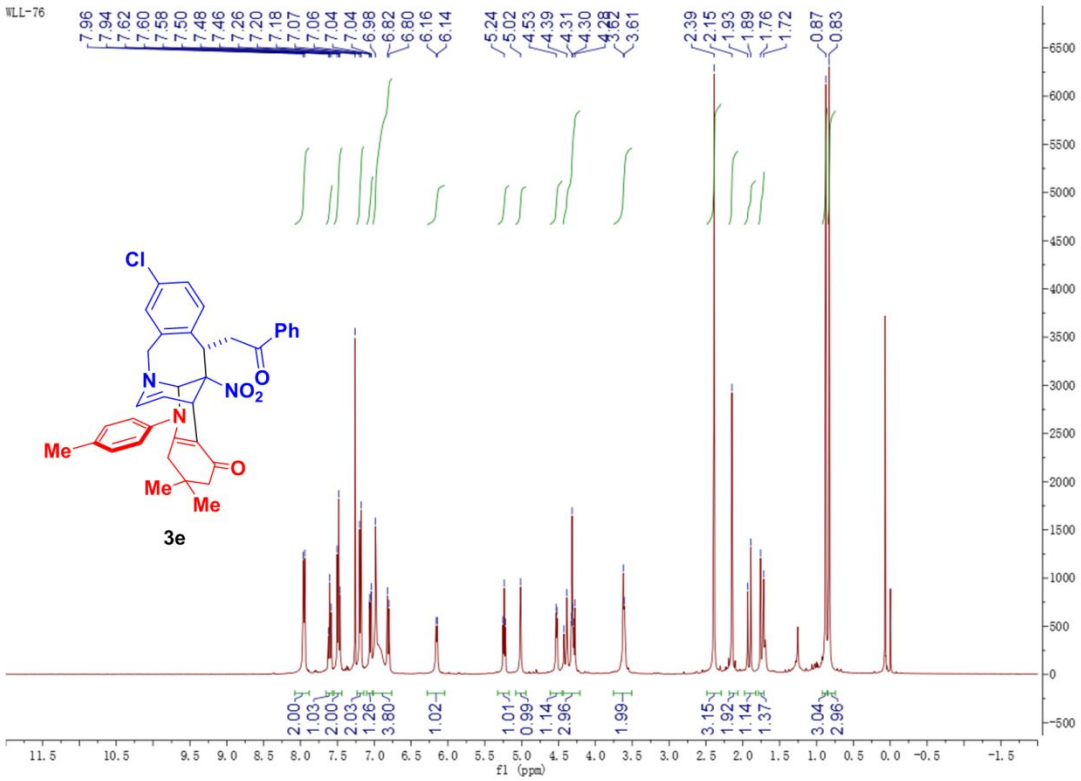

F
Ph
N
NO2
O
N
Me
O
Me
Me
3c
f1 (ppm)


WLL-66
195.96
192.28
162.97
160.51
156.19
139.12
138.12
136.15
133.60
133.52
128.69
127.98
127.21
115.00
114.03
113.83
108.16
107.01
88.78
77.32
77.00
76.68
73.99
58.19
49.33
40.63
37.98
35.44
32.64
29.18
28.52
27.49
21.08
F
Ph
N
O
NO2
N
Me
O
Me
Me
3c
f1 (ppm)

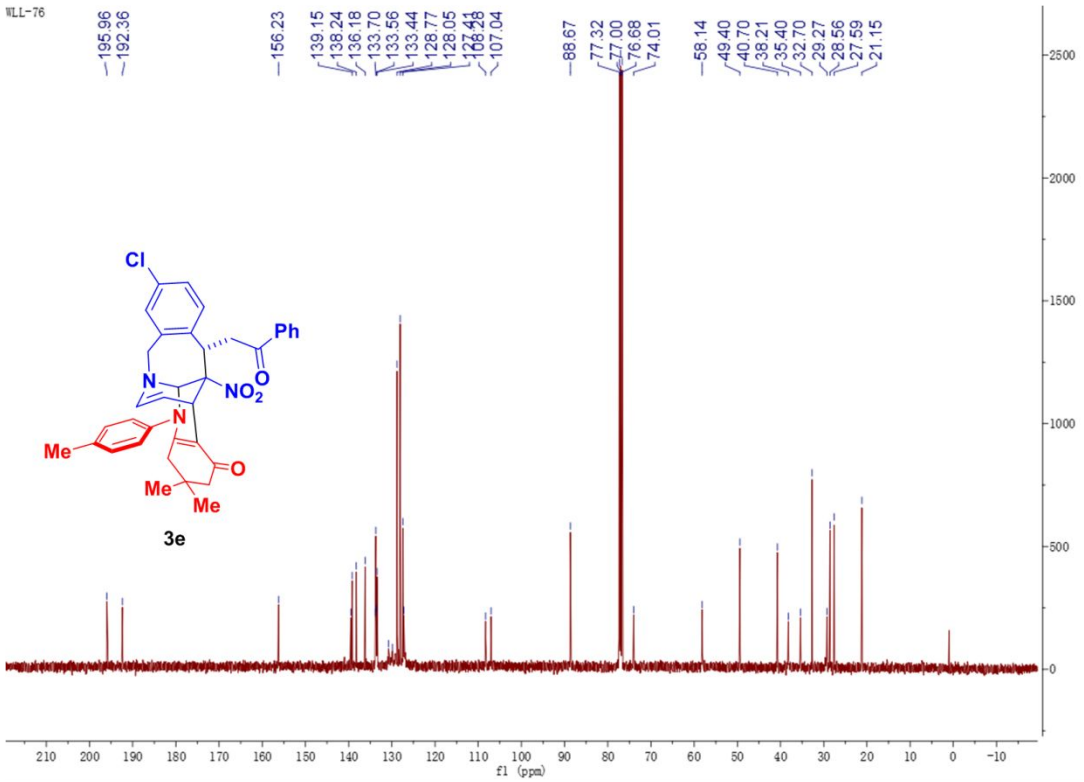

7.95
7.62
7.60
7.58
7.50
7.48
7.46
7.26
7.18
7.16
6.96
6.94
6.92
6.85
6.84
6.83
6.82
6.81
6.80
6.62
6.61
6.59
6.59
6.16
6.14
5.24
5.23
5.21
5.04
5.03
4.53
4.52
4.51
4.51
4.36
4.35
4.33
4.32
4.31
3.63
3.62
3.60
3.57
2.37
2.14
2.14
1.93
1.89
1.74
1.70
0.87
0.82
F
Ph
N
O
NO2
N
Me
O
Me
Me
3d
1.94
0.98
2.02
2.19
4.08
0.97
1.00
0.95
0.96
1.01
3.12
1.89
3.10
2.11
1.12
0.97
3.03
2.76
f1 (ppm)


WLL-75
195.86
192.30
163.25
160.80
156.24
139.20
138.12
136.11
133.70
129.38
128.76
114.25
113.56
113.33
108.13
106.99
88.63
77.32
77.00
76.68
73.96
57.90
49.38
40.69
38.42
35.40
32.68
29.30
28.57
27.53
21.11
F
Ph
O
N
NO2
N
Me
O
Me
Me
f1 (ppm)

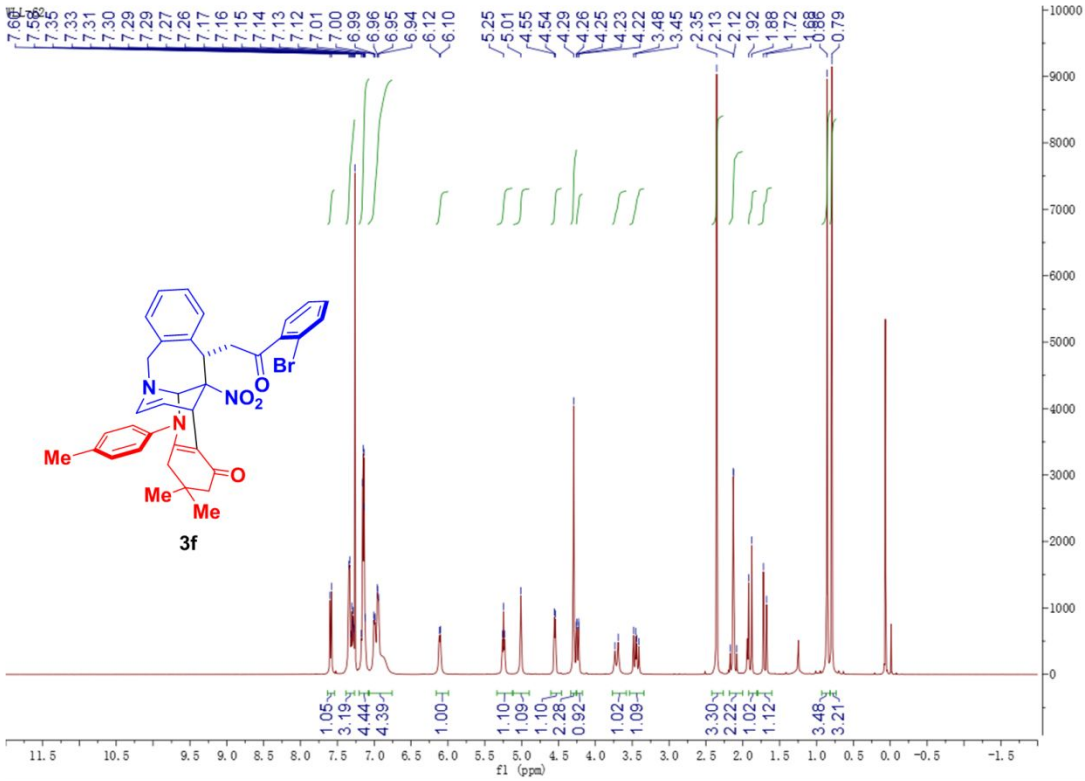
3d


WLL-76
7.96
7.94
7.62
7.60
7.58
7.50
7.48
7.46
7.26
7.20
7.18
7.07
7.06
7.04
7.04
6.98
6.82
6.80
6.16
6.14
5.24
5.02
4.53
4.39
4.31
4.30
3.62
3.61
2.39
2.15
1.93
1.89
1.76
1.72
0.87
0.83
Cl
Ph
O
N
NO2
N
Me
O
Me
Me
2.00
1.03
2.00
2.03
1.26
3.80
1.02
1.01
0.99
1.14
2.96
1.99
3.15
1.92
1.14
1.37
3.04
2.96
f1 (ppm)

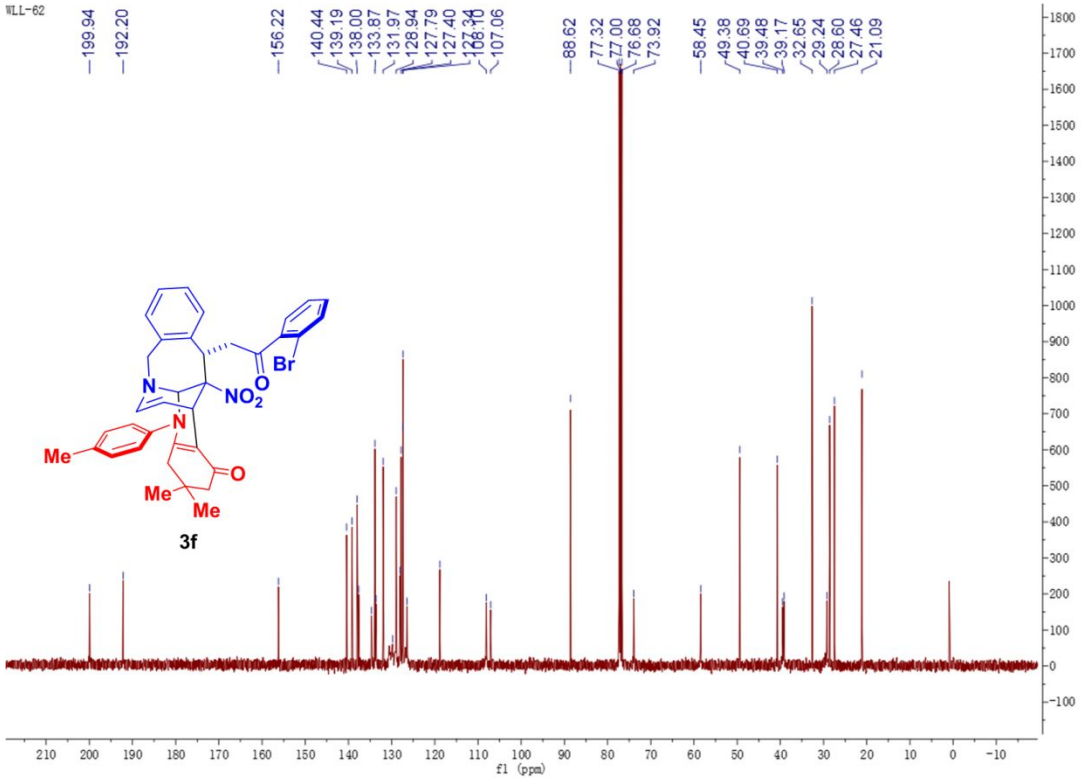
3e

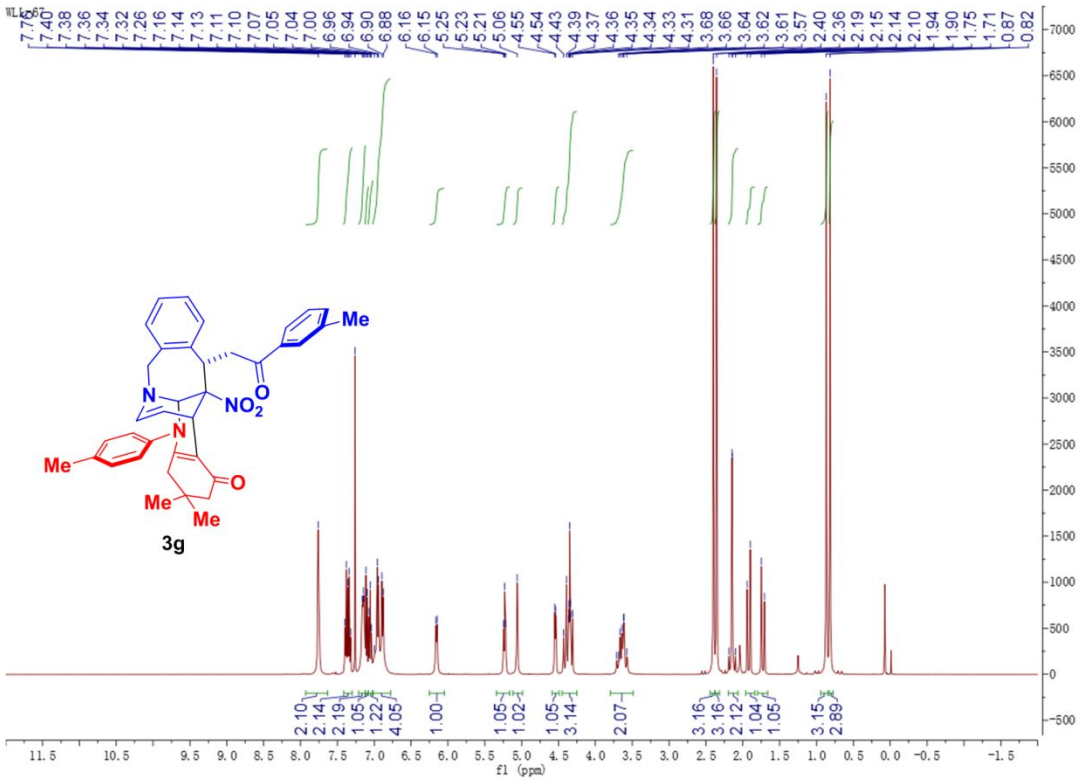

WLL-76
195.96
192.36
156.23
139.15
138.24
136.18
133.70
133.56
133.44
128.77
128.05
88.67
77.32
77.00
76.68
74.01
58.14
49.40
40.70
38.21
35.40
32.70
29.27
28.56
27.59
21.15
Cl
Ph
O
N
NO2
N
Me
O
Me
Me
f1 (ppm)

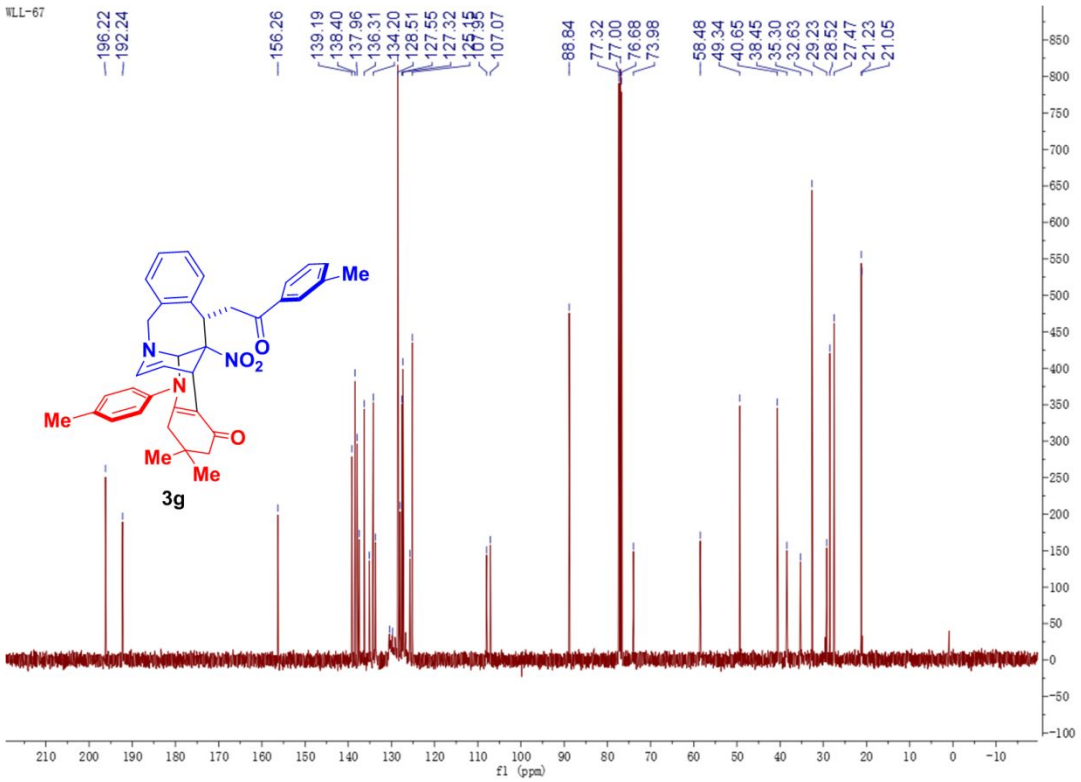
3e

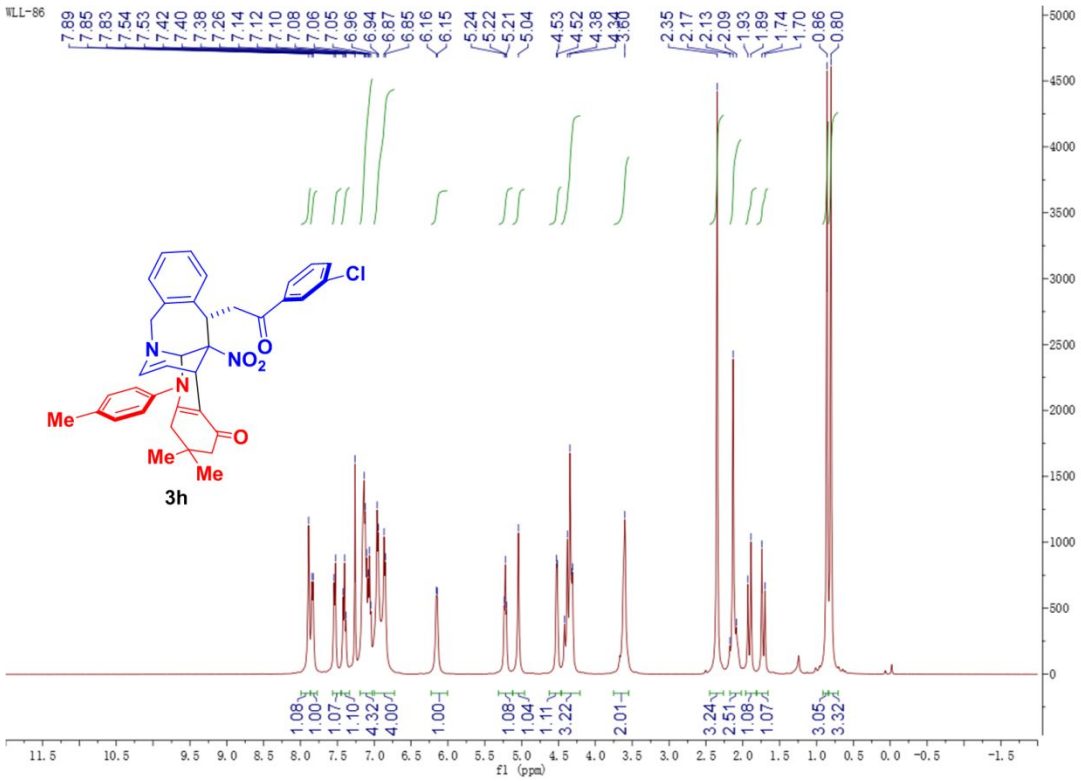

7.66
7.58
7.35
7.33
7.31
7.30
7.29
7.29
7.27
7.26
7.17
7.16
7.15
7.14
7.13
7.12
7.01
7.00
6.99
6.96
6.95
6.94
6.12
6.10
5.25
5.01
4.55
4.54
4.29
4.26
4.25
4.23
4.22
3.48
3.45
2.35
2.13
2.12
1.92
1.88
1.72
1.68
0.88
0.79
Br
O
N
NO2
N
Me
O
Me
Me
1.05
3.19
4.44
4.39
1.00
1.10
1.09
1.10
2.28
0.92
1.02
1.09
3.30
2.22
1.02
1.12
3.48
3.21
f1 (ppm)

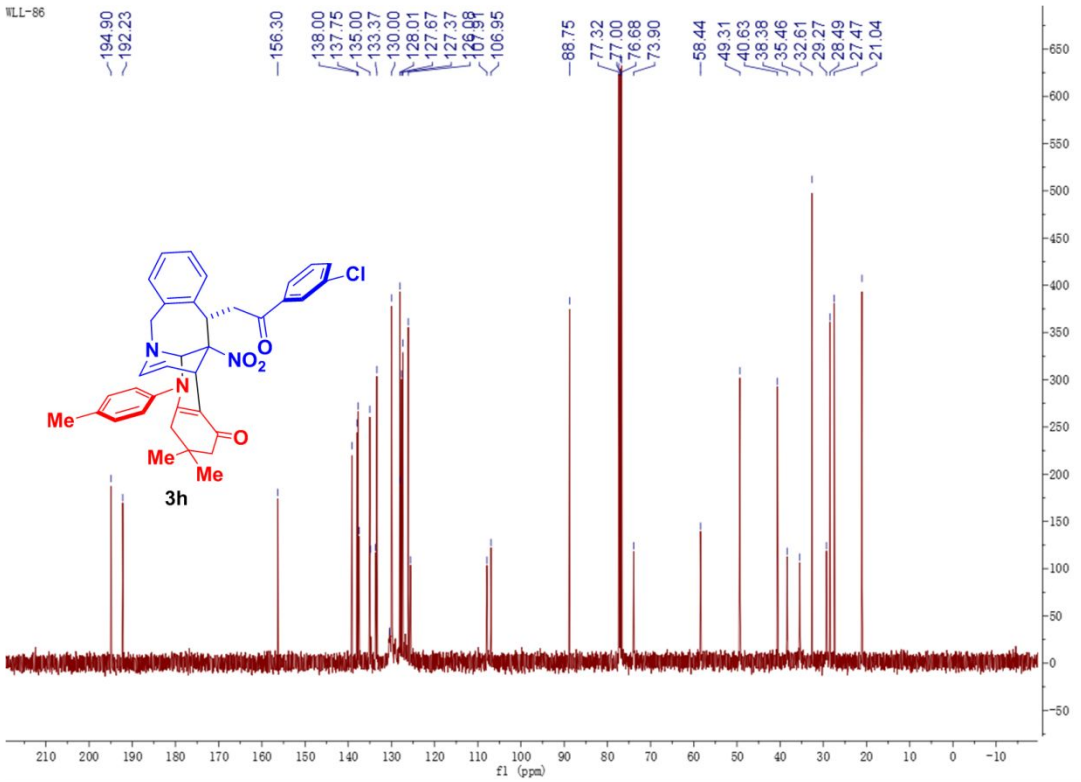
3f

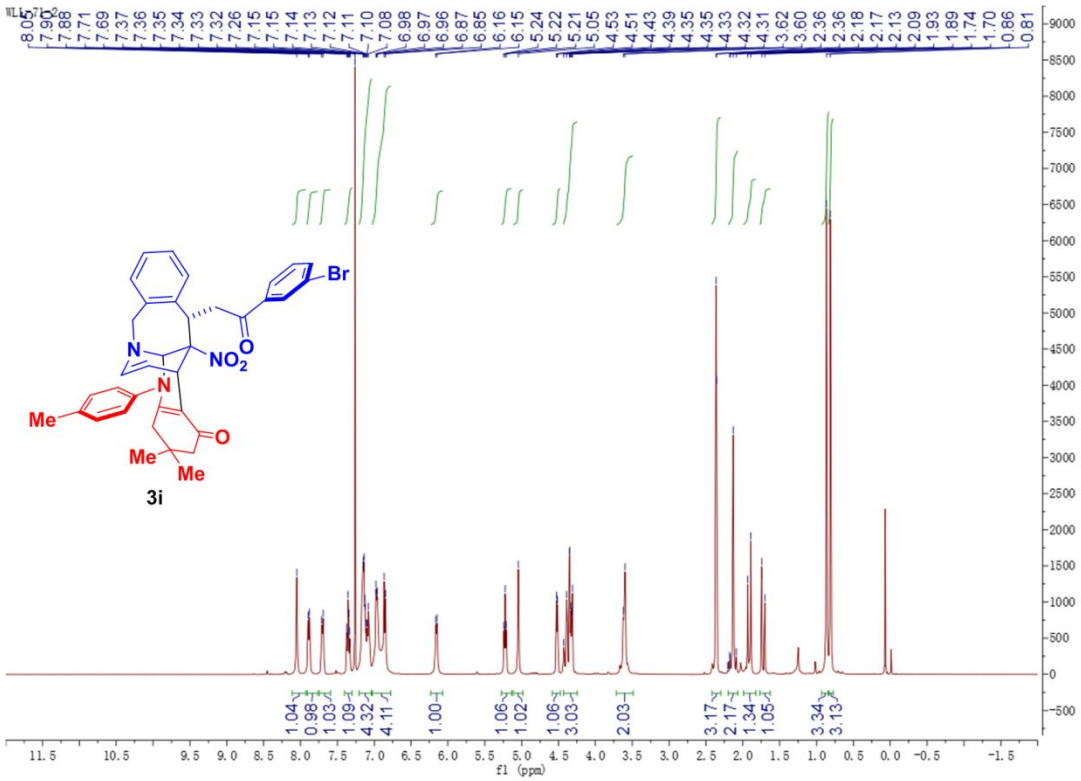

WLL-62
199.94
192.20
156.22
140.44
139.19
138.00
133.87
131.97
128.94
127.79
127.40
88.62
77.32
77.00
76.68
73.92
58.45
49.38
40.69
39.48
39.17
32.65
29.24
28.60
27.46
21.09
Br
O
NO2
N
N
Me
O
Me
Me
3f
f1 (ppm)

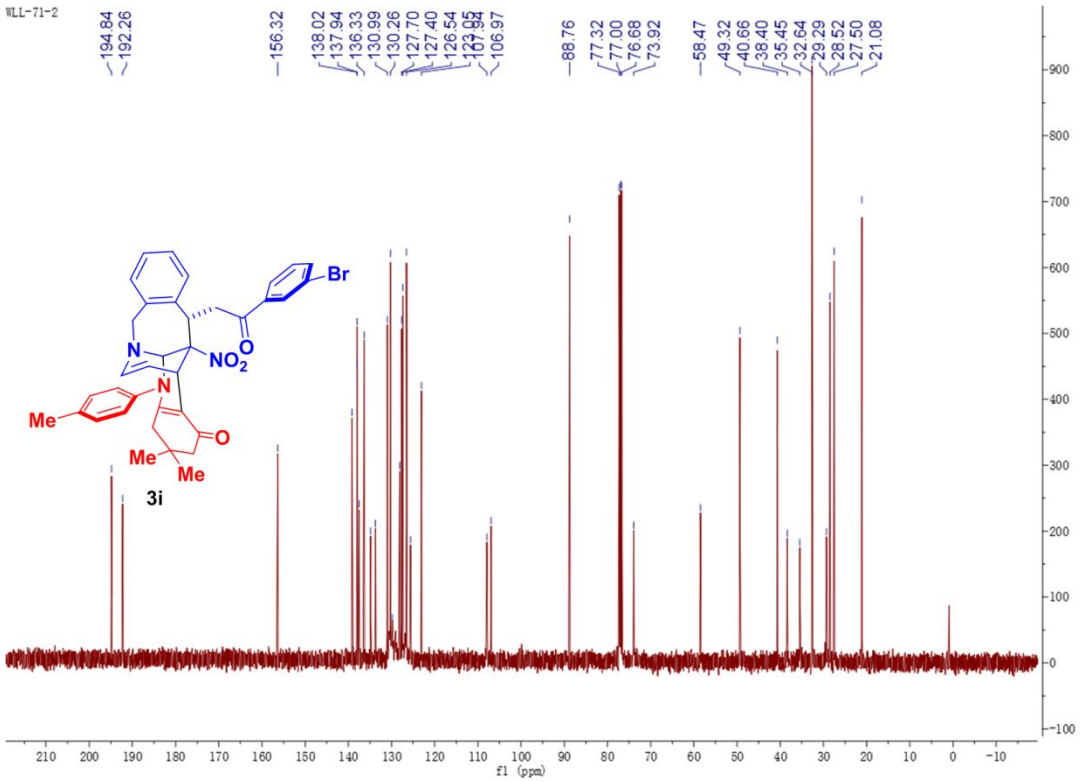

7.76
7.40
7.38
7.36
7.34
7.32
7.26
7.16
7.14
7.13
7.11
7.10
7.07
7.05
7.04
7.00
6.96
6.94
6.90
6.88
6.16
6.15
5.25
5.23
5.21
5.06
4.55
4.54
4.43
4.39
4.37
4.36
4.35
4.34
4.33
4.31
3.68
3.66
3.64
3.62
3.61
3.57
2.40
2.36
2.19
2.15
2.14
2.10
1.94
1.90
1.75
1.71
0.87
0.82
Me
O
NO2
N
N
Me
O
Me
Me
3g
2.10
2.14
2.19
1.05
1.22
4.05
1.00
1.05
1.02
1.05
3.14
2.07
3.16
3.16
2.12
1.04
1.05
3.15
2.89
f1 (ppm)

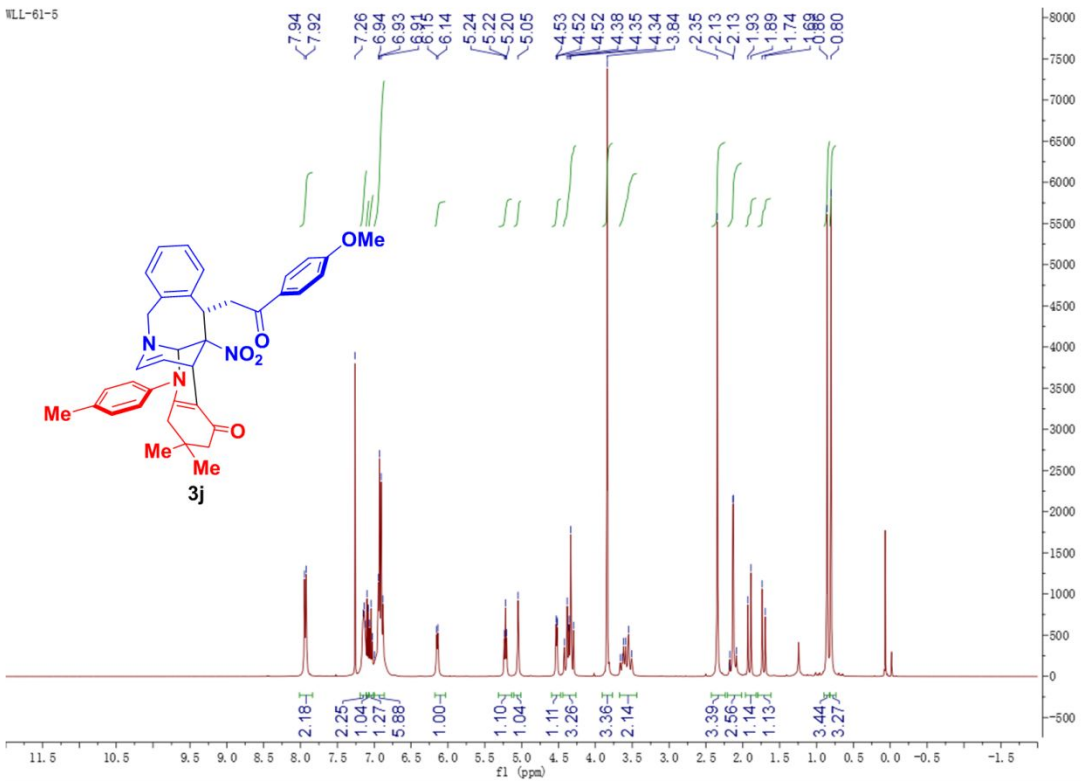

WLL-67
196.22
192.24
156.26
139.19
138.40
137.96
136.31
134.20
128.51
127.55
127.32
125.15
107.95
107.07
88.84
77.32
77.00
76.68
73.98
58.48
49.34
40.65
38.45
35.30
32.63
29.23
28.52
27.47
21.23
21.05
Me
N
NO2
O
N
Me
O
Me
Me
3g
f1 (ppm)

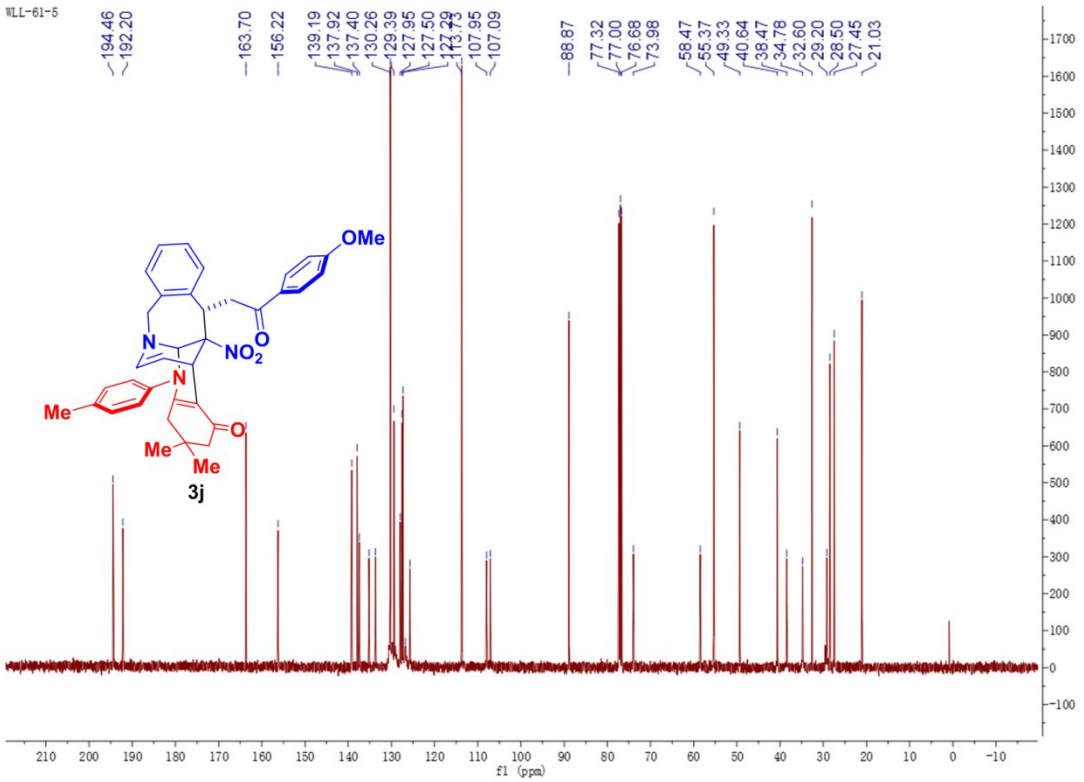

WLL-86
7.89
7.85
7.83
7.54
7.53
7.42
7.40
7.38
7.26
7.14
7.12
7.10
7.08
7.06
7.05
6.96
6.94
6.87
6.85
6.16
6.15
5.24
5.22
5.21
5.04
4.53
4.52
4.38
4.34
3.60
2.35
2.17
2.13
2.09
1.93
1.89
1.74
1.70
0.86
0.80
Cl
N
NO2
O
N
Me
O
Me
Me
3h
1.08
1.00
1.07
1.10
4.32
4.00
1.00
1.08
1.04
1.11
3.22
2.01
3.24
2.51
1.08
1.07
3.05
3.32
f1 (ppm)

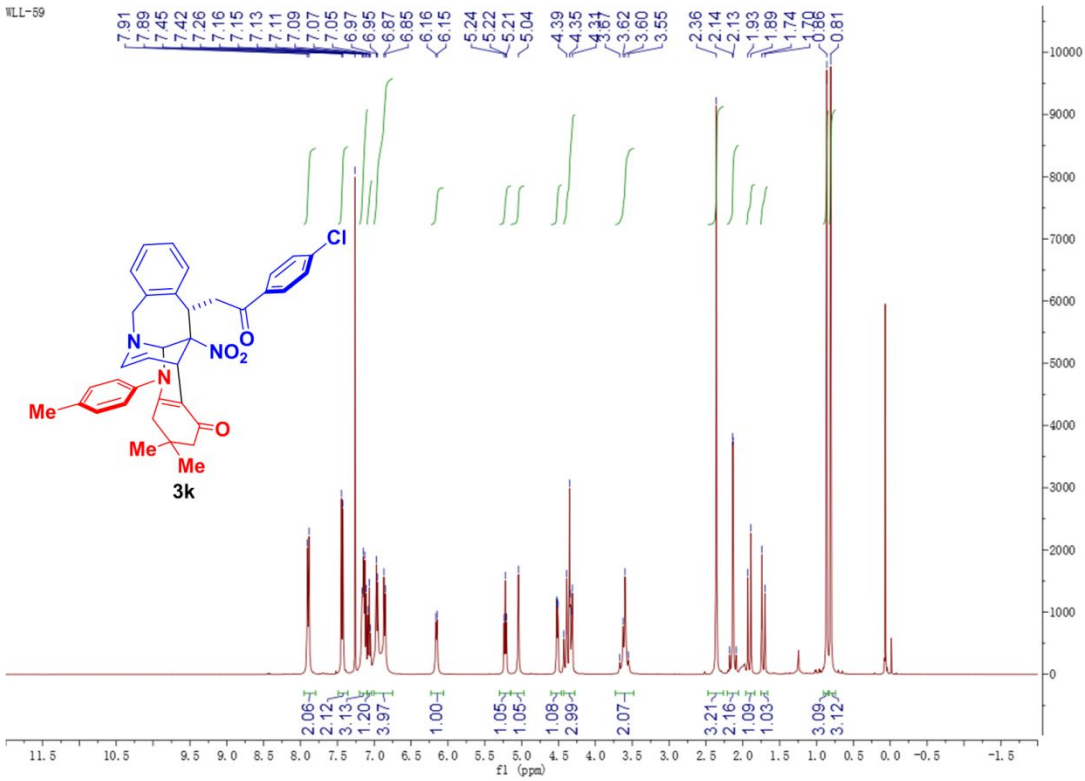

WLL-86
194.90
192.23
156.30
138.00
137.75
135.00
133.37
130.00
128.01
127.67
127.37
126.08
107.91
106.95
88.75
77.32
77.00
76.68
73.90
58.44
49.31
40.63
38.38
35.46
32.61
29.27
28.49
27.47
21.04
Cl
O
NO2
N
N
Me
O
Me
Me
3h
f1 (ppm)

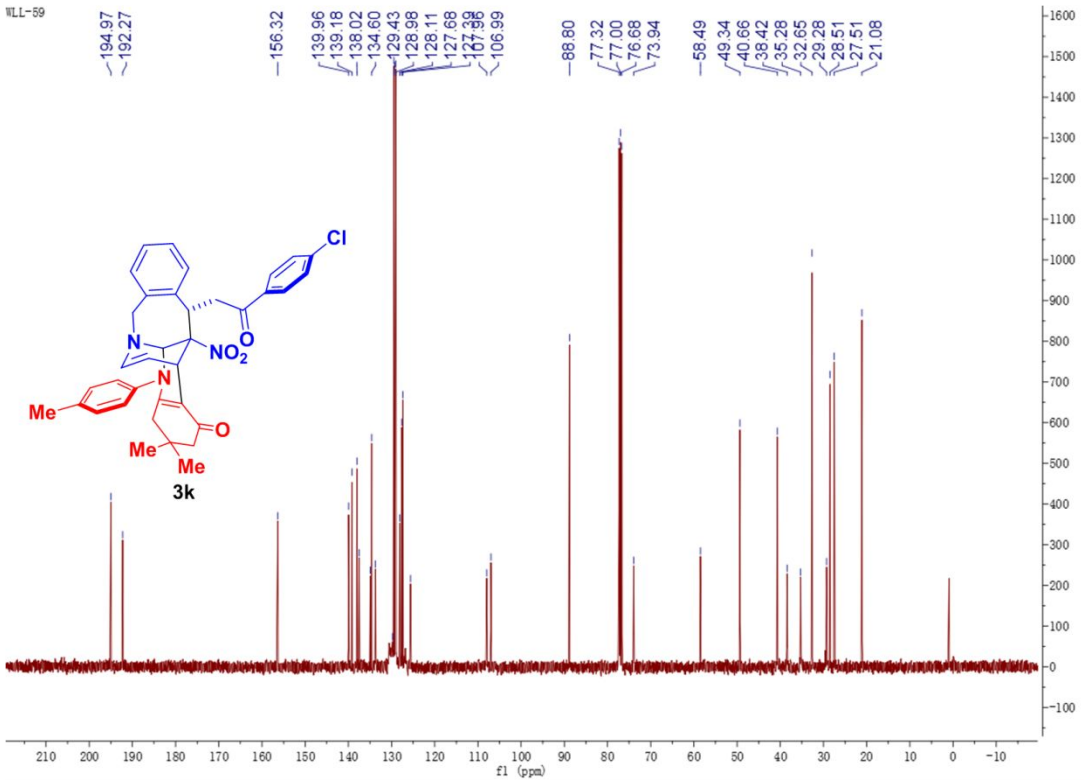

WLL-Th2
8.05
7.90
7.88
7.71
7.69
7.37
7.36
7.35
7.34
7.33
7.32
7.26
7.15
7.14
7.13
7.12
7.11
7.10
7.08
6.98
6.97
6.96
6.87
6.85
6.16
6.15
5.24
5.22
5.21
5.05
4.53
4.51
4.43
4.39
4.35
4.35
4.33
4.32
4.31
3.62
3.60
2.36
2.36
2.18
2.17
2.13
2.09
1.93
1.89
1.74
1.70
0.86
0.81
Br
O
NO2
N
N
Me
O
Me
Me
3i
1.04
0.98
1.03
1.09
4.32
4.11
1.00
1.06
1.02
1.06
3.03
2.03
3.17
2.17
1.34
1.05
3.34
3.13
f1 (ppm)

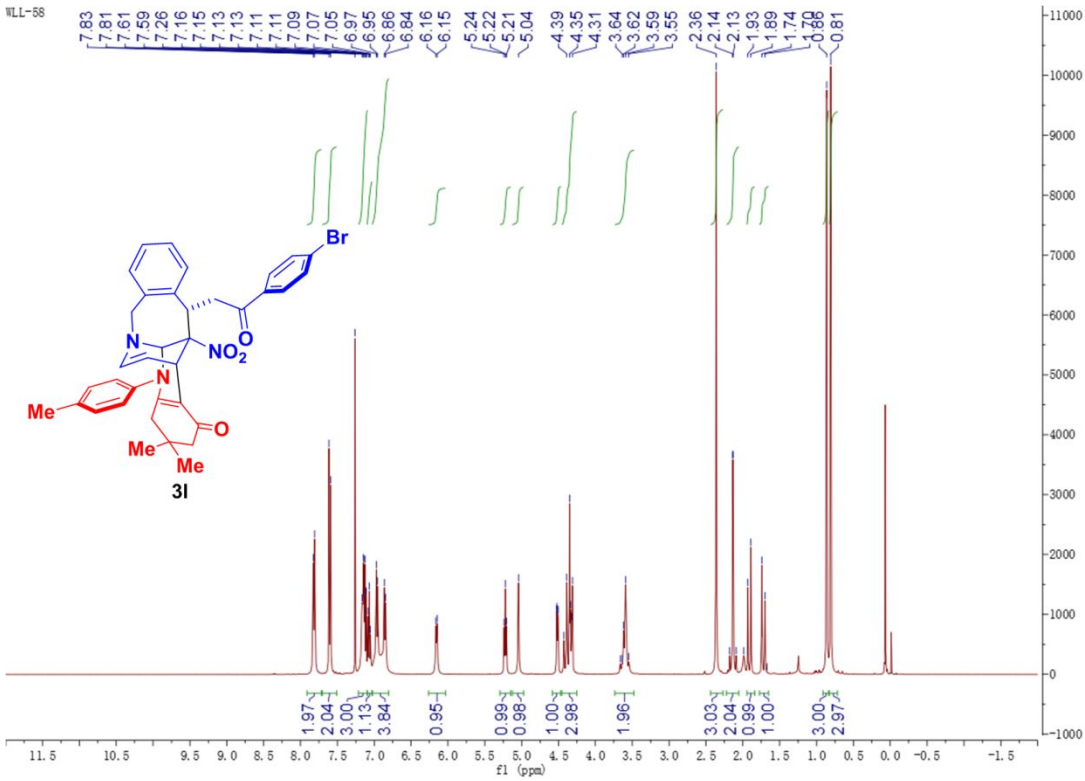

WLL-71-2
194.84
192.26
156.32
138.02
137.94
136.33
130.99
130.26
127.70
127.40
126.54
88.76
77.32
77.00
76.68
73.92
58.47
49.32
40.66
38.40
35.45
32.64
29.29
28.52
27.50
21.08
Br
O
NO2
N
N
Me
O
Me
Me
3i
f1 (ppm)

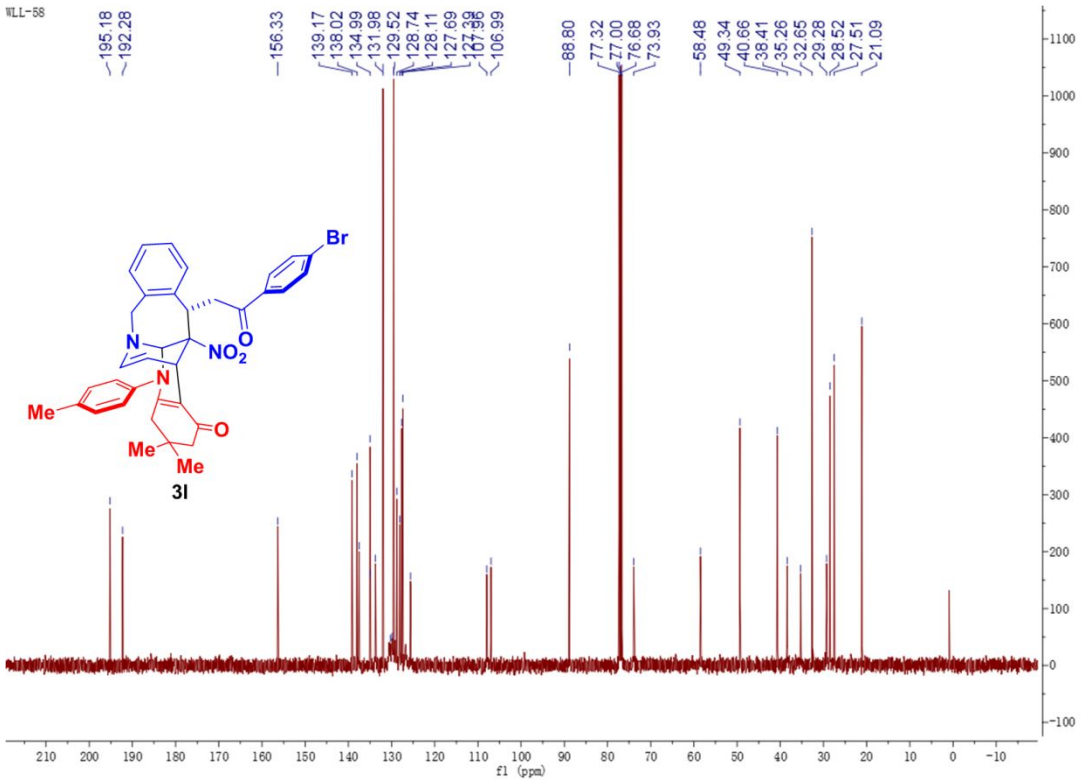

WLL-61-5
7.94
7.92
7.26
6.94
6.93
6.91
6.15
6.14
5.24
5.22
5.20
5.05
4.53
4.52
4.52
4.38
4.35
4.34
3.84
2.35
2.13
2.13
1.93
1.89
1.74
1.69
0.86
0.80
OMe
O
NO2
N
N
Me
O
Me
Me
3j
2.18
2.25
1.04
1.27
5.88
1.00
1.10
1.04
1.11
3.26
3.36
2.14
3.39
2.56
1.14
1.13
3.44
3.27
f1 (ppm)

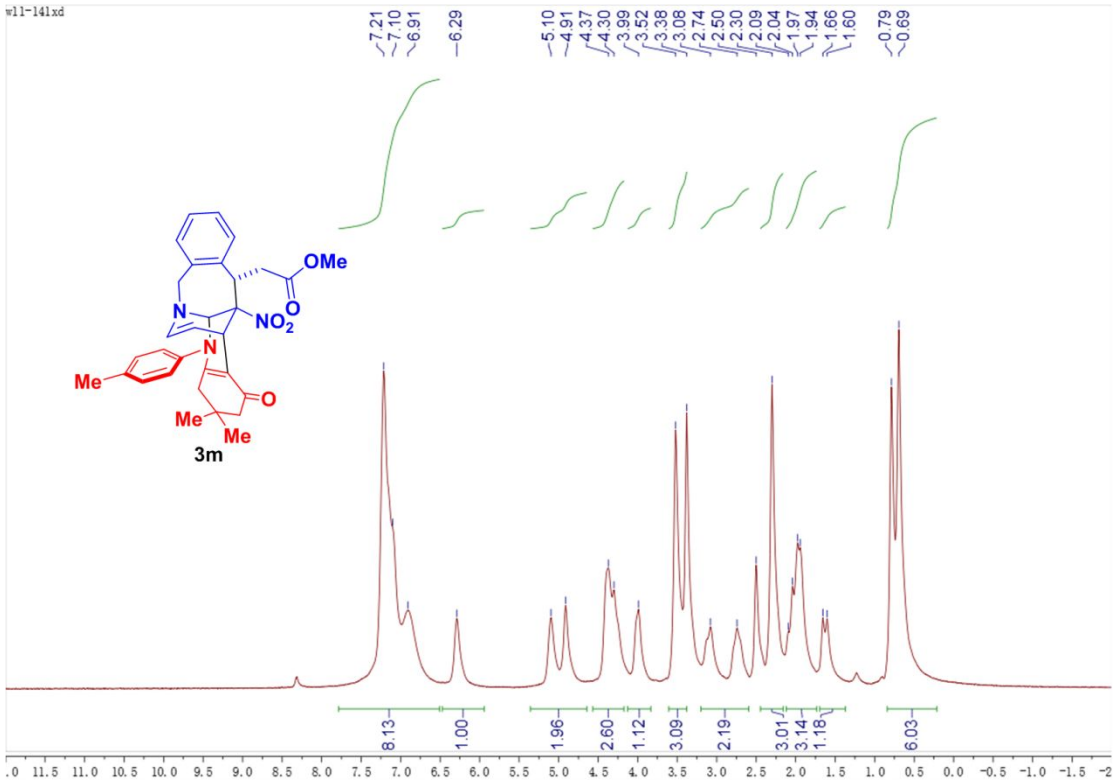

WLL-61-5
194.46
192.20
163.70
156.22
139.19
137.92
137.40
130.26
129.39
127.95
127.50
127.29
113.43
107.95
107.09
88.87
77.32
77.00
76.68
73.98
58.47
55.37
49.33
40.64
38.47
34.78
32.60
29.20
28.50
27.45
21.03
OMe
O
NO2
N
N
Me
O
Me
Me
3j
f1 (ppm)

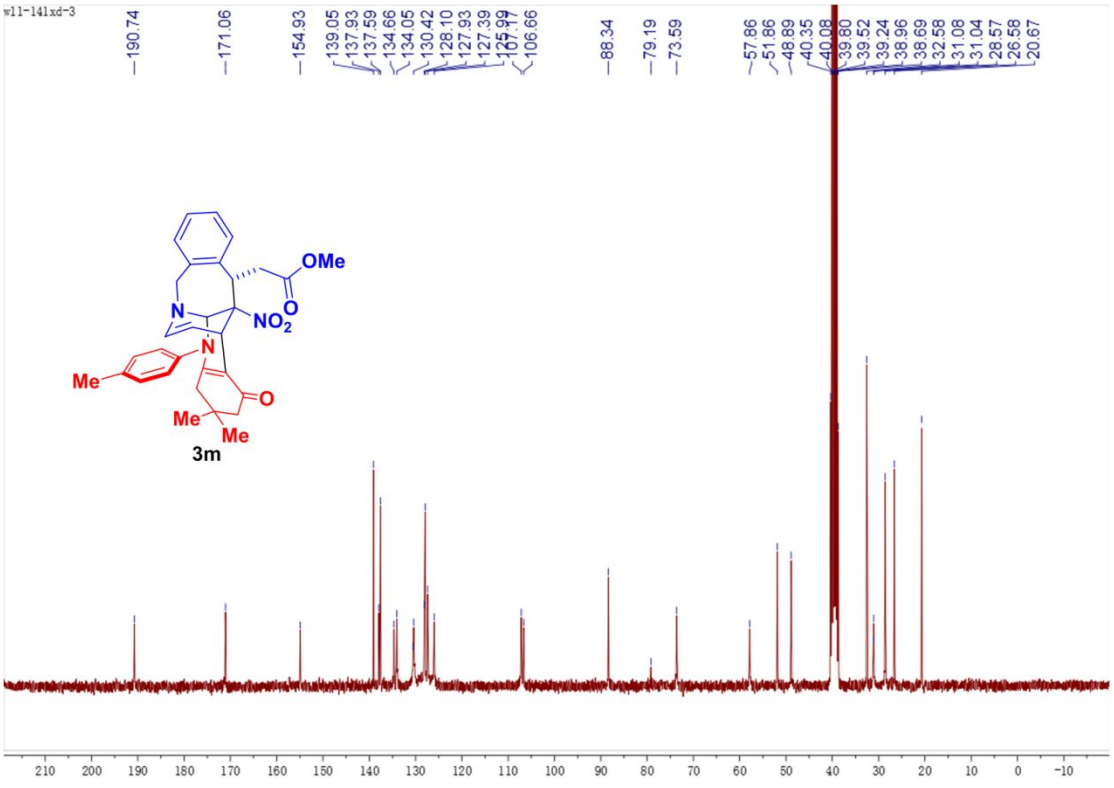

WLL-59
7.91
7.89
7.45
7.42
7.26
7.16
7.15
7.13
7.11
7.09
7.07
7.05
6.97
6.95
6.87
6.85
6.16
6.15
5.24
5.22
5.21
5.04
4.39
4.35
3.67
3.62
3.60
3.55
2.36
2.14
2.13
1.93
1.89
1.74
1.70
0.86
0.81
Cl
O
NO2
N
N
Me
O
Me
Me
3k
2.06
2.12
3.13
1.20
3.97
1.00
1.05
1.05
1.08
2.99
2.07
3.21
2.16
1.09
1.03
3.09
3.12
f1 (ppm)

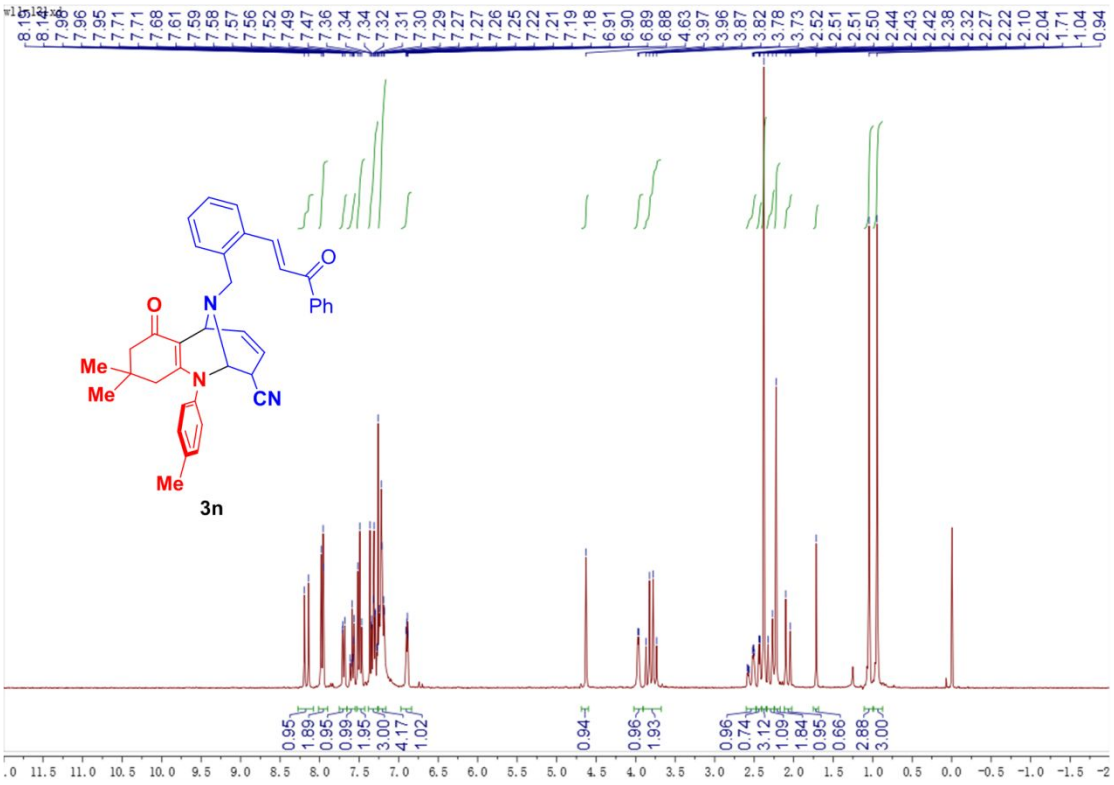

WLL-59
194.97
192.27
156.32
139.96
139.18
138.02
134.60
129.43
128.98
128.11
127.68
127.39
107.96
106.99
88.80
77.32
77.00
76.68
73.94
58.49
49.34
40.66
38.42
35.28
32.65
29.28
28.51
27.51
21.08
Cl
N
NO2
O
N
Me
O
Me
Me
3k
f1 (ppm)

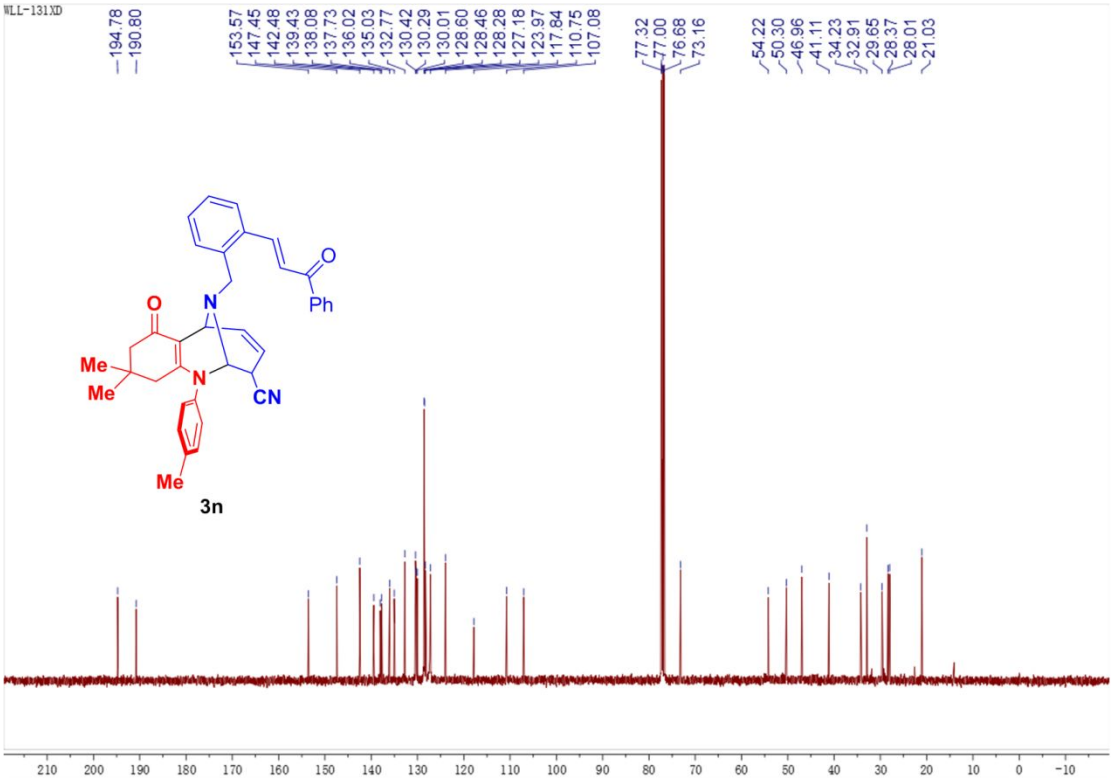

WLL-58
7.83
7.81
7.61
7.59
7.26
7.16
7.15
7.13
7.13
7.11
7.11
7.09
7.07
7.05
6.97
6.95
6.86
6.84
6.16
6.15
5.24
5.22
5.21
5.04
4.39
4.35
4.31
3.64
3.62
3.59
3.55
2.36
2.14
2.13
1.93
1.89
1.74
1.70
0.86
0.81
Br
N
NO2
O
N
Me
O
Me
Me
3l
1.97
2.04
3.00
1.13
3.84
0.95
0.99
0.98
1.00
2.98
1.96
3.03
2.04
0.99
1.00
3.00
2.97
f1 (ppm)

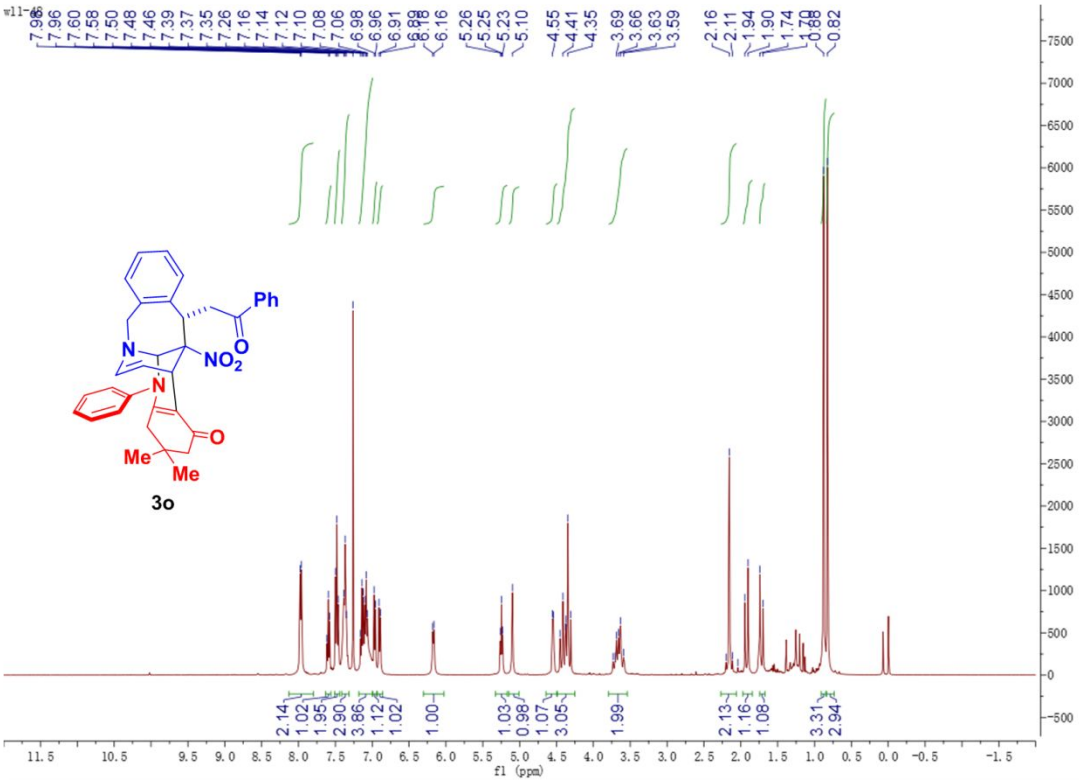

WLL-58
195.18
192.28
156.33
139.17
138.02
134.99
131.98
129.52
128.74
128.11
127.69
88.80
77.32
77.00
76.68
73.93
58.48
49.34
40.66
38.41
35.26
32.65
29.28
28.52
27.51
21.09
Br
O
NO2
N
N
Me
O
Me
Me
3l
f1 (ppm)


w11-141xd
7.21
7.10
6.91
6.29
5.10
4.91
4.37
4.30
3.99
3.52
3.38
3.08
2.74
2.50
2.30
2.09
2.04
1.97
1.94
1.66
1.60
0.79
0.69
OMe
O
NO2
N
N
Me
O
Me
Me
3m
8.13
1.00
1.96
2.60
1.12
3.09
2.19
3.01
3.14
1.18
6.03


w11-141xd-3
190.74
171.06
154.93
139.05
137.93
137.59
134.66
134.05
130.42
128.10
127.93
127.39
125.99
125.77
106.66
88.34
79.19
73.59
57.86
51.86
48.89
40.35
40.08
39.80
39.52
39.24
38.96
38.69
32.58
31.08
31.04
28.57
26.58
20.67
OMe
O
N
NO2
N
Me
O
Me
Me
3m


8.15
8.14
7.98
7.96
7.95
7.71
7.71
7.68
7.61
7.59
7.58
7.57
7.56
7.52
7.49
7.47
7.36
7.34
7.34
7.32
7.31
7.30
7.29
7.27
7.27
7.26
7.25
7.22
7.21
7.19
7.18
6.91
6.90
6.89
6.88
4.63
3.97
3.96
3.87
3.82
3.78
3.73
2.52
2.51
2.50
2.44
2.43
2.42
2.38
2.32
2.27
2.22
2.10
2.04
1.71
1.04
0.94
O
Ph
N
O
Me
Me
N
CN
Me
3n
0.95
1.89
0.95
0.99
1.95
3.00
4.17
1.02
0.94
0.96
1.93
0.96
0.74
3.12
1.09
1.84
0.95
0.66
2.88
3.00


WLL-131XD
194.78
190.80
153.57
147.45
142.48
139.43
138.08
137.73
136.02
135.03
132.77
130.42
130.29
130.01
128.60
128.46
128.28
127.18
123.97
117.84
110.75
107.08
77.32
77.00
76.68
73.16
54.22
50.30
46.96
41.11
34.23
32.91
29.65
28.37
28.01
21.03
O
Ph
O
N
Me
Me
N
CN
Me
3n


w11-46
7.96
7.96
7.60
7.58
7.50
7.48
7.46
7.39
7.37
7.35
7.26
7.16
7.14
7.12
7.10
7.08
7.06
6.98
6.96
6.91
6.89
6.18
6.16
5.26
5.25
5.23
5.10
4.55
4.41
4.35
3.69
3.66
3.63
3.59
2.16
2.11
1.94
1.90
1.74
1.70
0.88
0.82
Ph
O
N
NO2
N
O
Me
Me
3o
2.14
1.02
1.95
2.90
3.86
1.12
1.02
1.00
1.03
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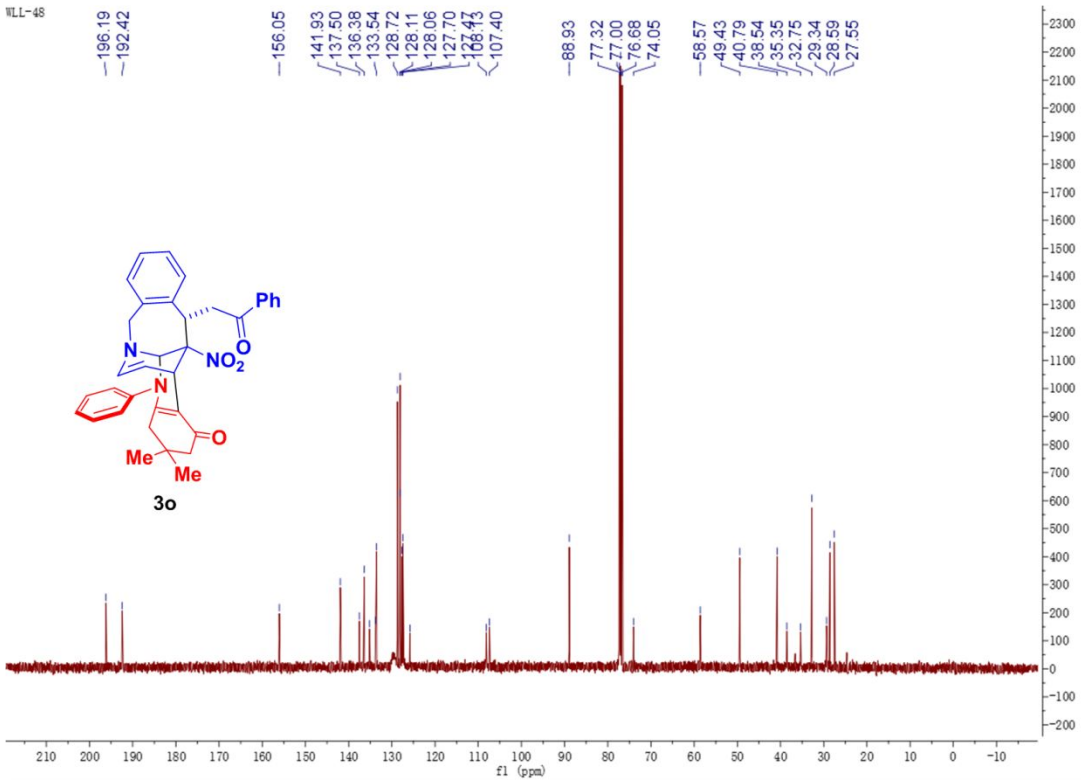
1.07
3.05
1.99
2.13
1.16
1.08
3.31
2.94
f1 (ppm)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192.42
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137.50
136.38
133.54
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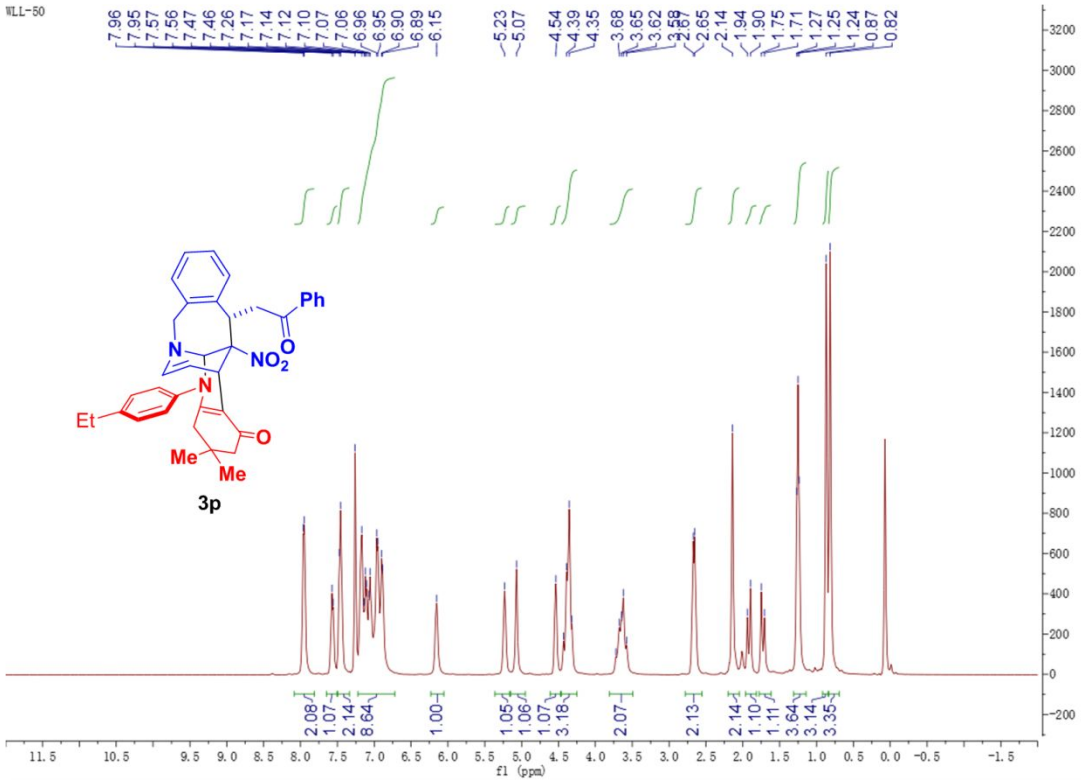
128.11
128.06
127.70
88.93
77.32
77.00
76.68
74.05
58.57
49.43
40.79
38.54
35.35
32.75
29.34
28.59
27.55
Ph
O
NO2
N
N
O
Me
Me
3o
f1 (ppm)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7.26
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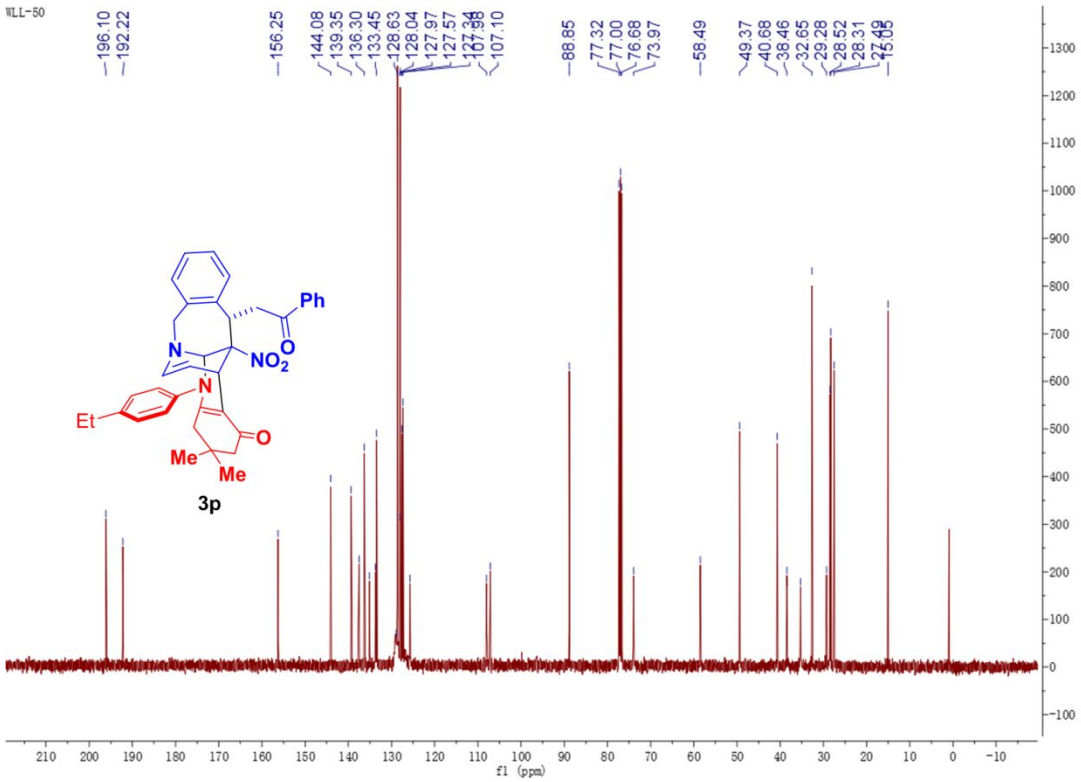
7.14
7.12
7.10
7.07
7.06
6.96
6.95
6.90
6.89
6.15
5.23
5.07
4.54
4.39
4.35
3.68
3.65
3.62
2.65
2.14
1.94
1.90
1.75
1.71
1.27
1.25
1.24
0.87
0.82
Ph
O
NO2
N
N
Et
O
Me
Me
3p
2.08
1.07
2.14
8.64
1.00
1.05
1.06
1.07
3.18
2.07
2.13
2.14
1.10
1.11
3.64
3.14
3.35
f1 (ppm)


WLL-50
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133.45
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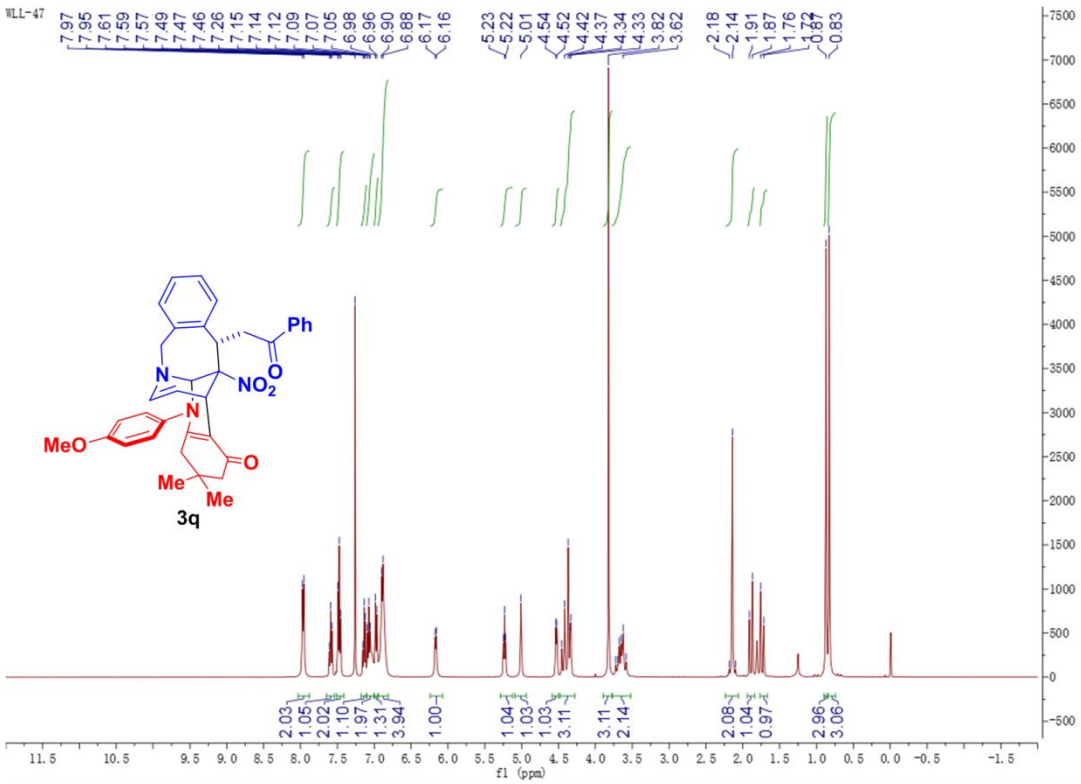
128.04
127.97
127.57
107.10
88.85
77.32
77.00
76.68
73.97
58.49
49.37
40.68
38.46
32.65
29.28
28.52
28.31
15.05
Ph
O
NO2
N
N
Et
O
Me
Me
3p
f1 (ppm)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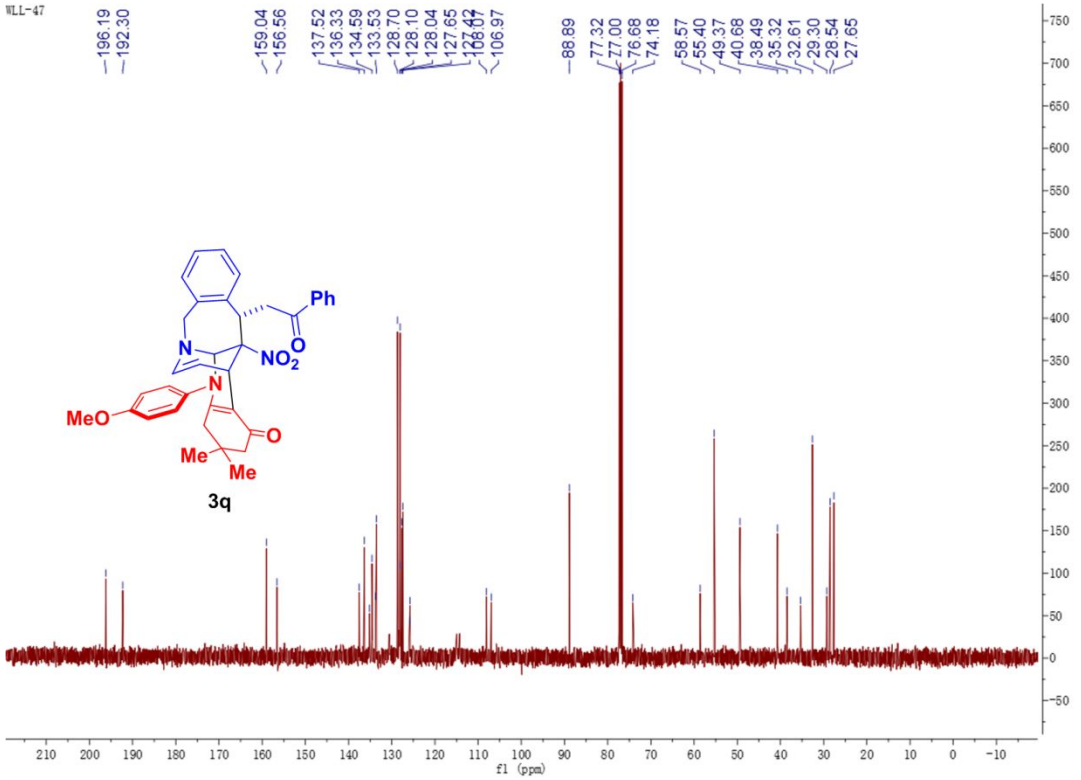
7.47
7.46
7.26
7.15
7.14
7.12
7.09
7.07
7.05
6.98
6.96
6.90
6.88
6.17
6.16
5.23
5.22
5.01
4.54
4.52
4.42
4.37
4.34
4.33
3.82
3.62
2.18
2.14
1.91
1.87
1.76
1.72
0.87
0.83
Ph
O
NO2
N
N
MeO
O
Me
Me
3q
2.03
1.05
2.02
1.10
1.97
1.31
3.94
1.00
1.04
1.03
1.03
3.11
3.11
2.14
2.08
1.04
0.97
2.96
3.06
f1 (ppm)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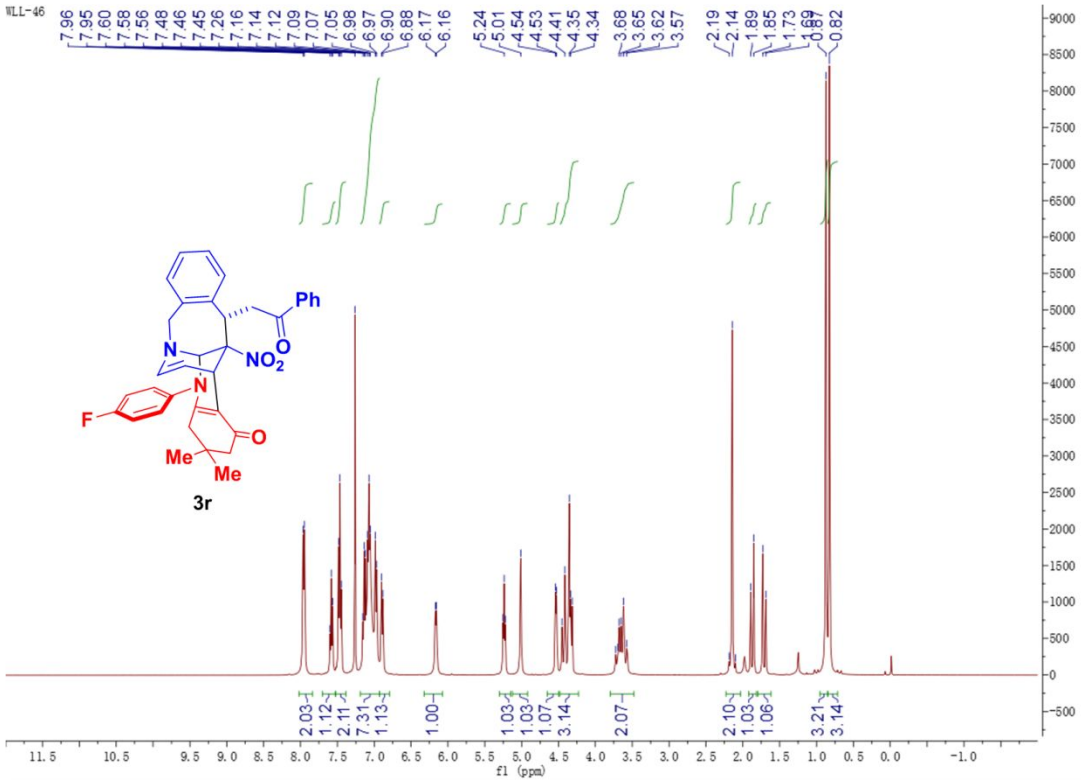
136.33
134.59
133.53
128.70
128.10
128.04
127.65
106.97
88.89
77.32
77.00
76.68
74.18
58.57
55.40
49.37
40.68
38.49
35.32
32.61
29.30
28.54
27.65
Ph
O
NO2
N
N
MeO
O
Me
Me
f1 (ppm)

3q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7.95
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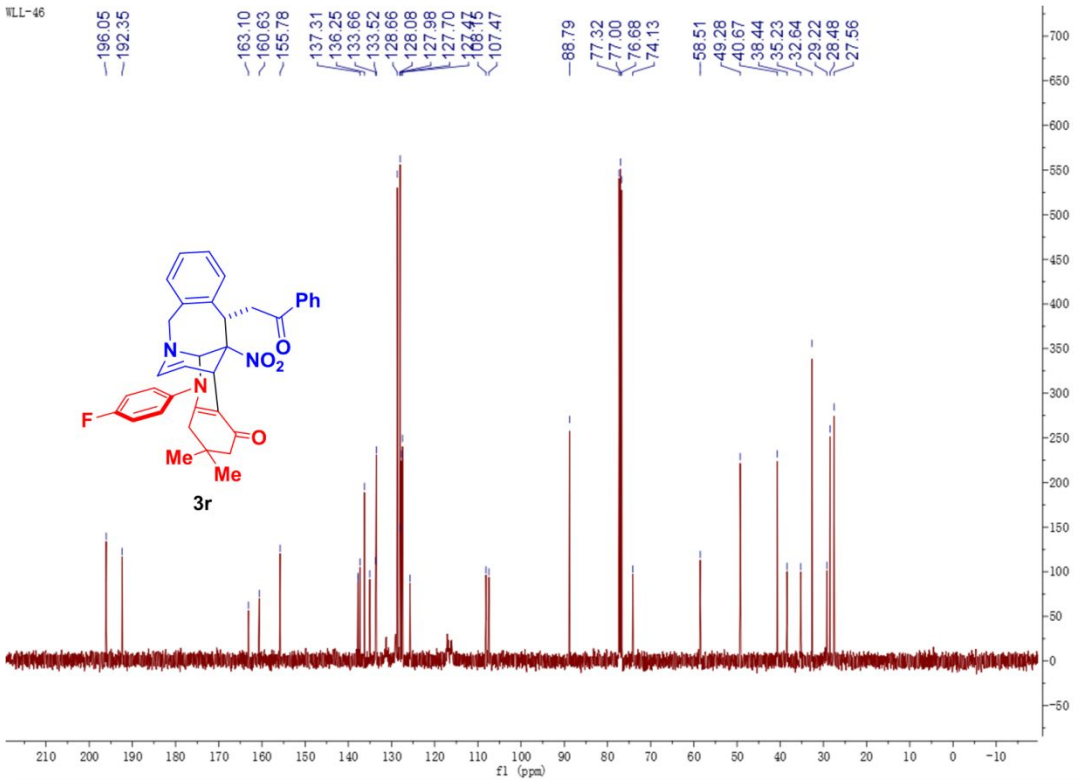
7.56
7.48
7.46
7.45
7.26
7.16
7.14
7.12
7.09
7.07
7.05
6.98
6.97
6.90
6.88
6.17
6.16
5.24
5.01
4.54
4.53
4.41
4.35
4.34
3.68
3.65
3.62
3.57
2.19
2.14
1.89
1.85
1.73
1.69
0.87
0.82
Ph
O
NO2
N
N
F
O
Me
Me
2.03
1.12
2.11
7.31
1.13
1.00
1.03
1.03
1.07
3.14
2.07
2.10
1.03
1.06
3.21
3.14
f1 (ppm)

3r


WLL-46
196.05
192.35
163.10
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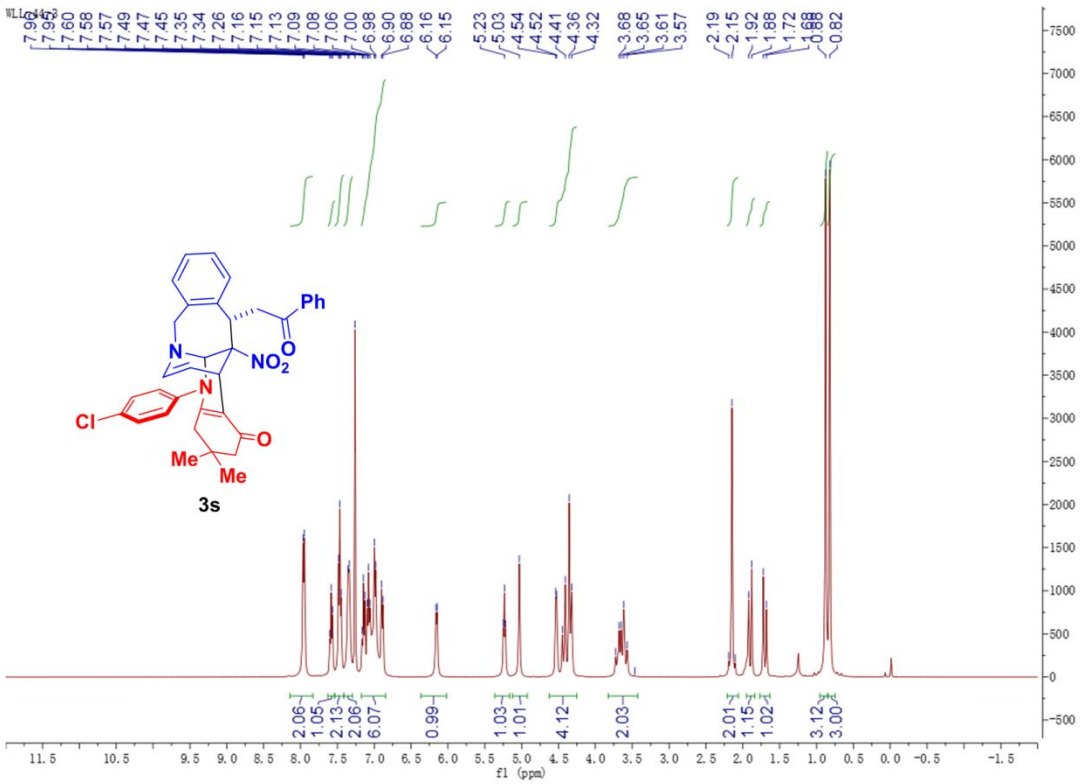
137.31
136.25
133.66
133.52
128.66
128.08
127.98
127.70
88.79
77.32
77.00
76.68
74.13
58.51
49.28
40.67
38.44
35.23
32.64
29.22
28.48
27.56
Ph
O
N
NO2
N
F
O
Me
Me
f1 (ppm)

3r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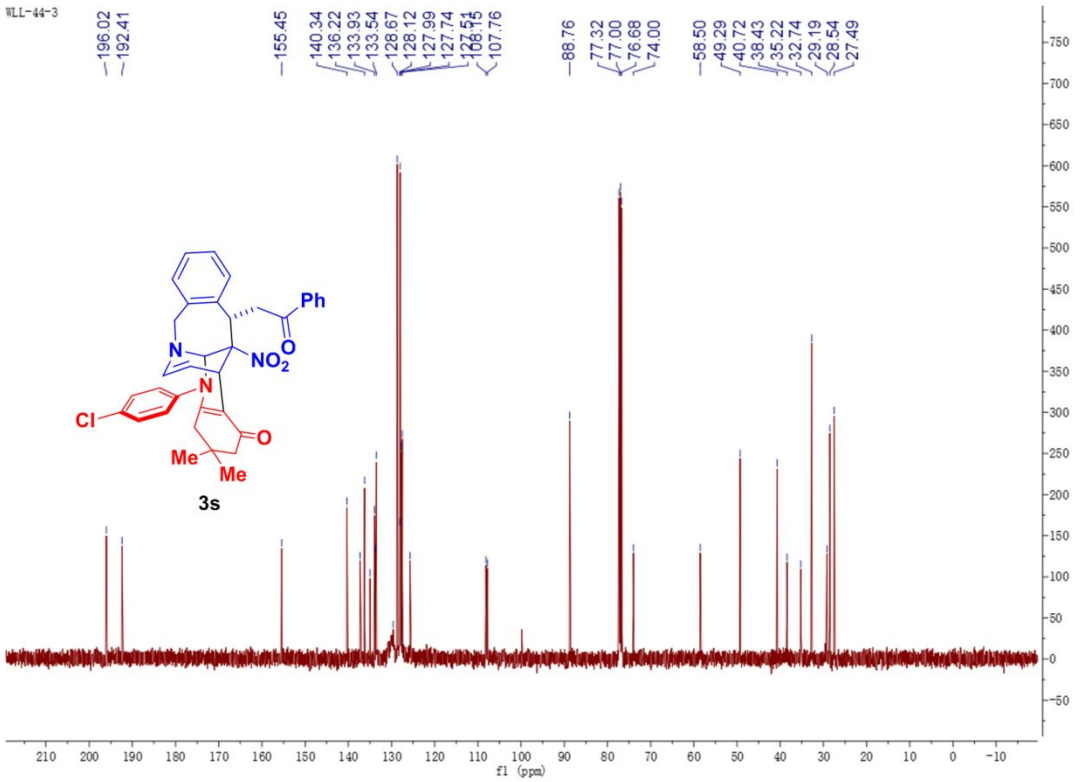
7.95
7.60
7.58
7.57
7.49
7.47
7.45
7.35
7.34
7.26
7.16
7.15
7.13
7.09
7.08
7.06
7.00
6.98
6.90
6.88
6.16
6.15
5.23
5.03
4.54
4.52
4.41
4.36
4.32
3.68
3.65
3.61
3.57
2.19
2.15
1.92
1.88
1.72
1.68
0.88
0.82
Ph
O
N
NO2
N
Cl
O
Me
Me
2.06
1.05
2.13
2.06
6.07
0.99
1.03
1.01
4.12
2.03
2.01
1.15
1.02
3.12
3.00
f1 (ppm)

3s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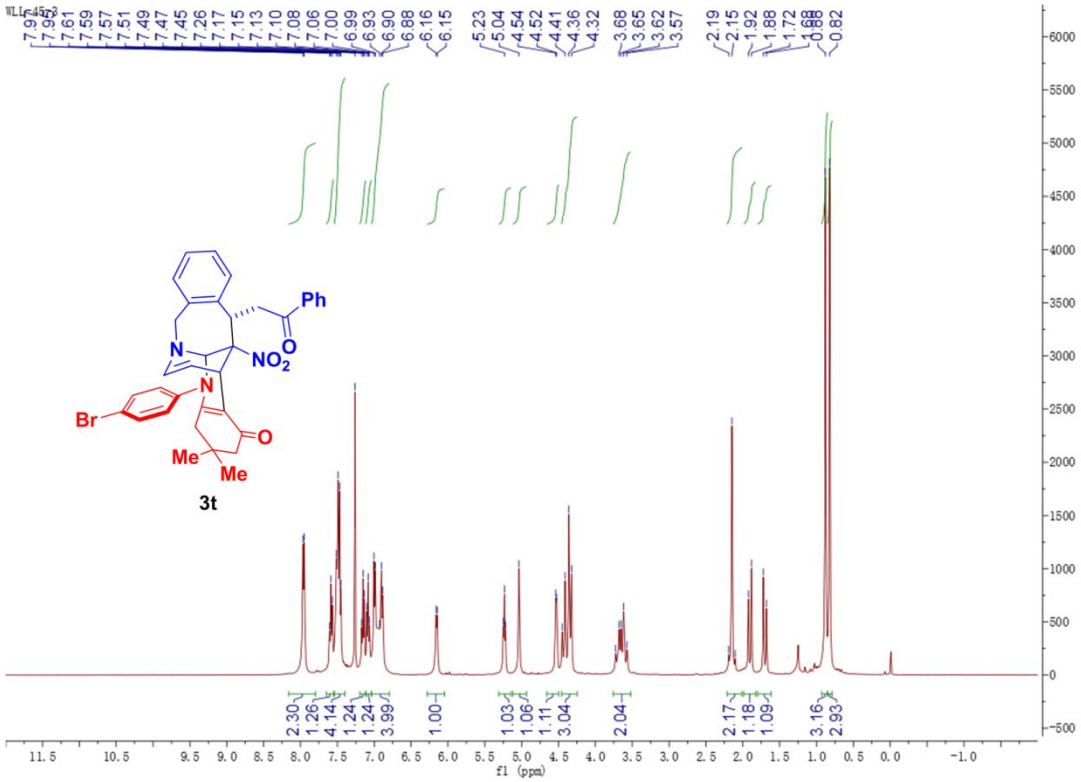
192.41
155.45
140.34
136.22
133.93
133.54
128.67
128.12
127.99
127.74
88.76
77.32
77.00
76.68
74.00
58.50
49.29
40.72
38.43
35.22
32.74
29.19
28.54
27.49
Ph
O
NO2
N
N
Cl
O
Me
Me
3s
f1 (ppm)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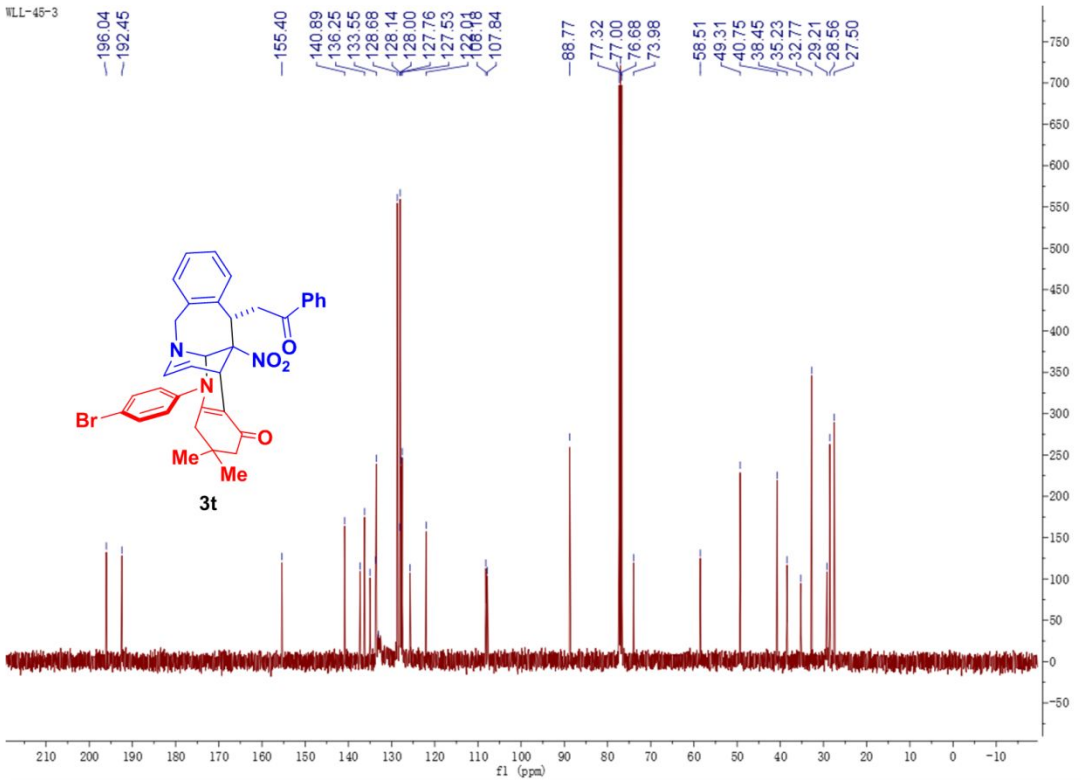
7.61
7.59
7.57
7.51
7.49
7.47
7.45
7.26
7.17
7.15
7.13
7.10
7.08
7.06
7.00
6.99
6.93
6.90
6.88
6.16
6.15
5.23
5.04
4.54
4.52
4.41
4.36
4.32
3.68
3.65
3.62
3.57
2.19
2.15
1.92
1.88
1.72
0.88
0.82
Ph
O
NO2
N
N
Br
O
Me
Me
3t
2.30
1.26
4.14
1.24
1.24
3.99
1.00
1.03
1.06
1.11
3.04
2.04
2.17
1.18
1.09
3.16
2.93
f1 (ppm)


WLL-45-3
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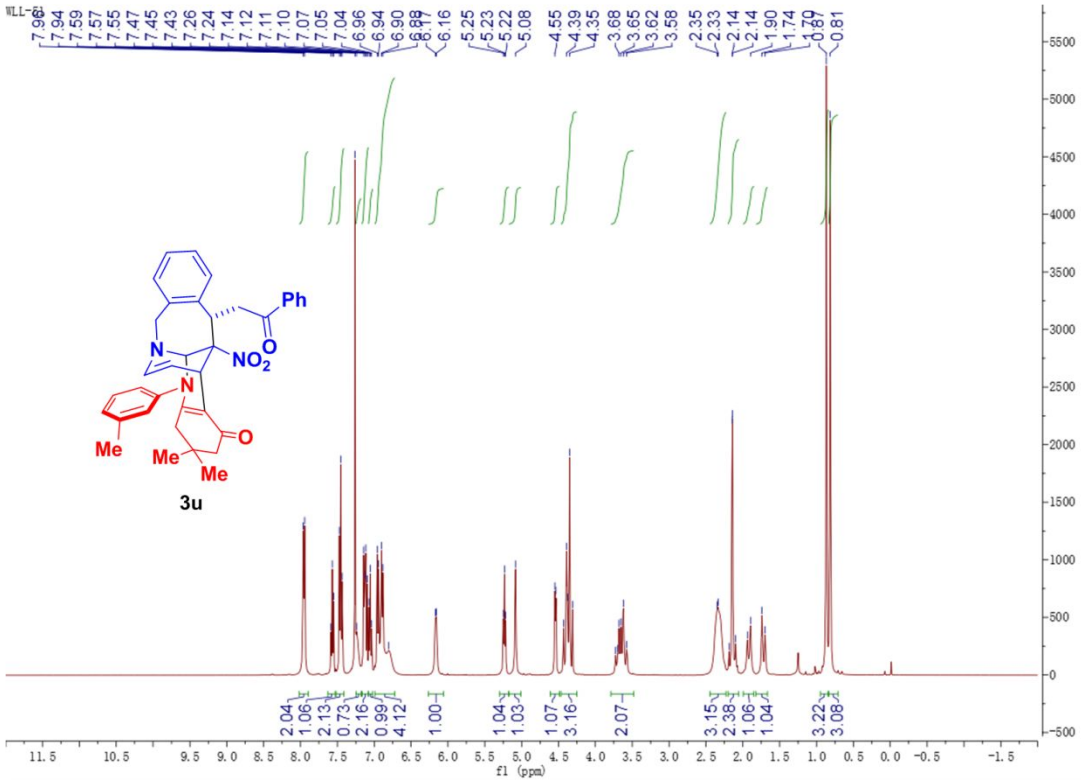
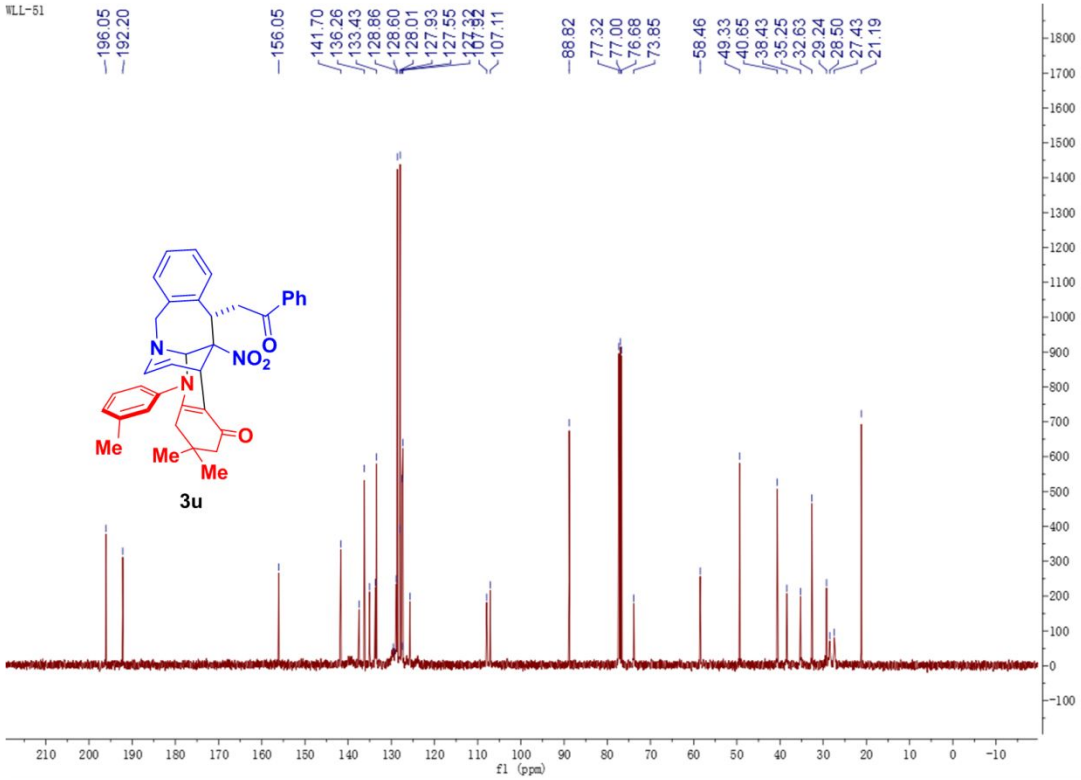
192.45
155.40
140.89
136.25
133.55
128.68
128.14
128.00
127.76
127.53
122.01
108.18
107.84
88.77
77.32
77.00
76.68
73.98
58.51
49.31
40.75
38.45
35.23
32.77
29.21
28.56
27.50
Ph
O
NO2
N
N
Br
O
Me
Me
3t
f1 (ppm)


7.96
7.94
7.59
7.57
7.55
7.47
7.45
7.43
7.26
7.24
7.14
7.12
7.11
7.10
7.07
7.05
7.04
6.96
6.94
6.90
6.88
6.17
6.16
5.25
5.23
5.22
5.08
4.55
4.39
4.35
3.68
3.65
3.62
3.58
2.35
2.33
2.14
2.14
1.90
1.74
1.70
0.87
0.81
Ph
O
NO2
N
N
Me
O
Me
Me
3u
2.04
1.06
2.13
0.73
2.16
0.99
4.12
1.00
1.04
1.03
1.07
3.16
2.07
3.15
2.38
1.06
1.04
3.22
3.08
f1 (ppm)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192.20
156.05
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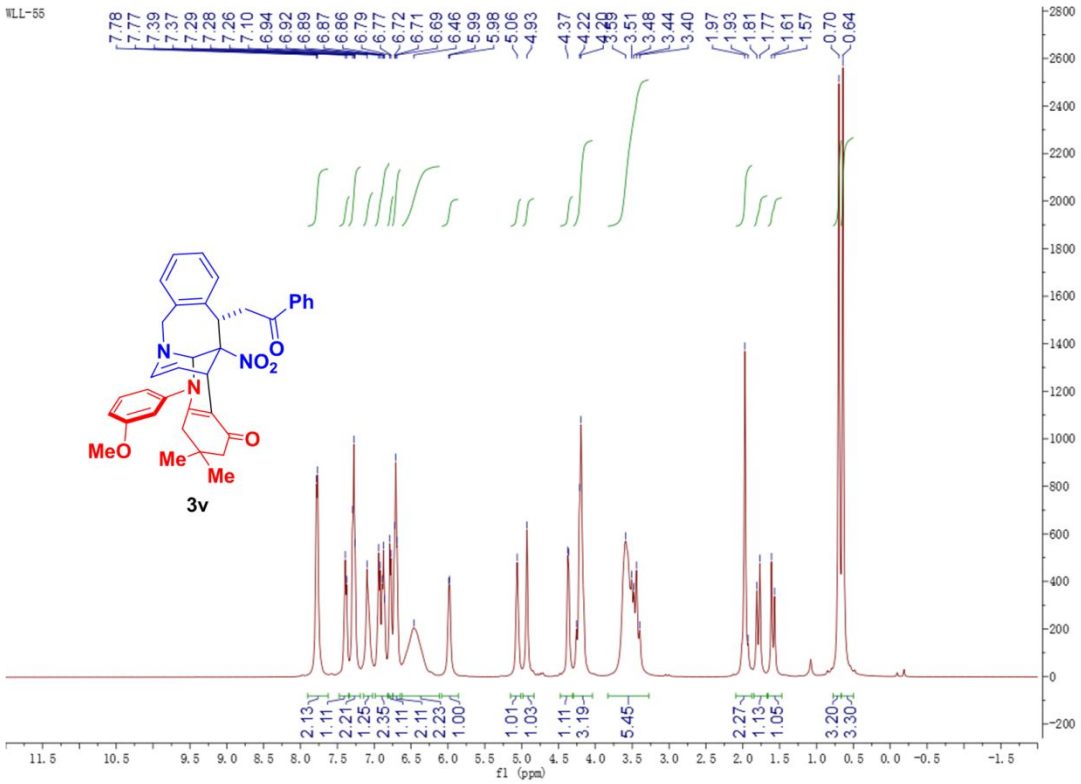
128.60
128.01
127.93
127.55
88.82
77.32
77.00
76.68
73.85
58.46
49.33
40.65
38.43
35.25
32.63
29.24
28.50
27.43
21.19
Ph
O
NO2
N
N
O
Me
Me
Me
3u
f1 (ppm)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7.39
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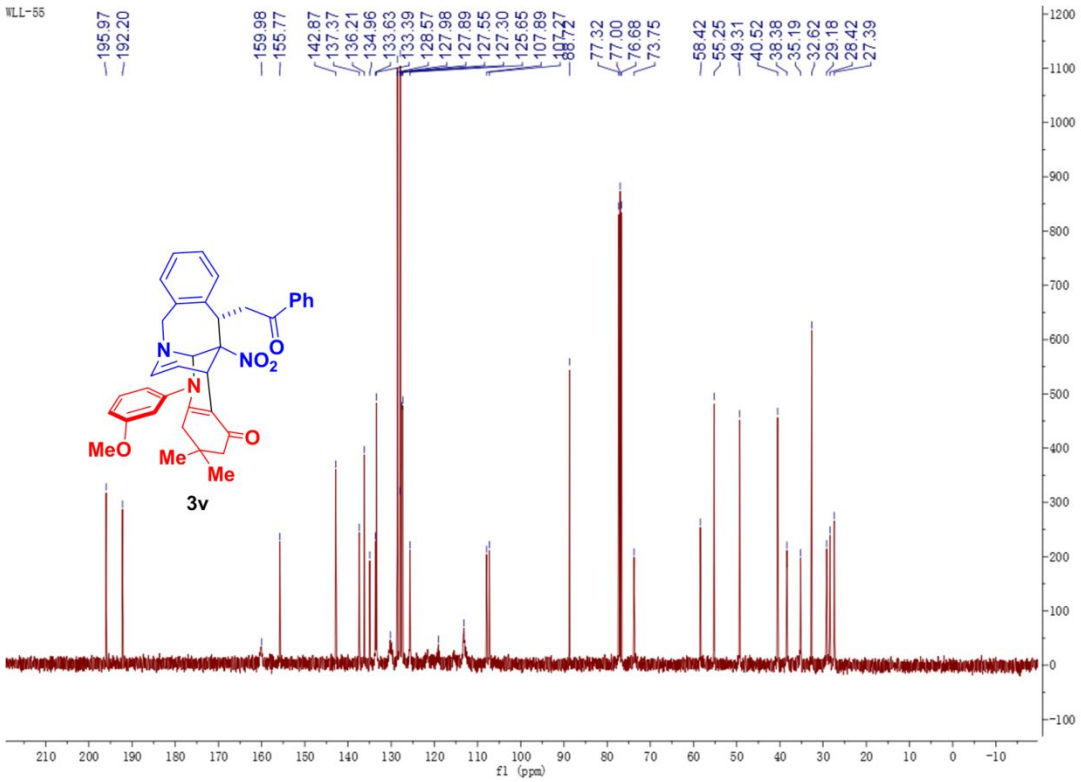
7.26
7.10
6.94
6.92
6.89
6.87
6.86
6.79
6.77
6.72
6.71
6.69
6.46
5.99
5.98
5.06
4.93
4.37
4.22
3.51
3.48
3.44
3.40
1.97
1.93
1.81
1.77
1.61
1.57
0.70
0.64
Ph
O
NO2
N
N
O
MeO
Me
Me
3v
2.13
1.11
2.21
1.25
2.35
1.11
2.11
2.23
1.00
1.01
1.03
1.11
3.19
5.45
2.27
1.13
1.05
3.20
3.30
f1 (ppm)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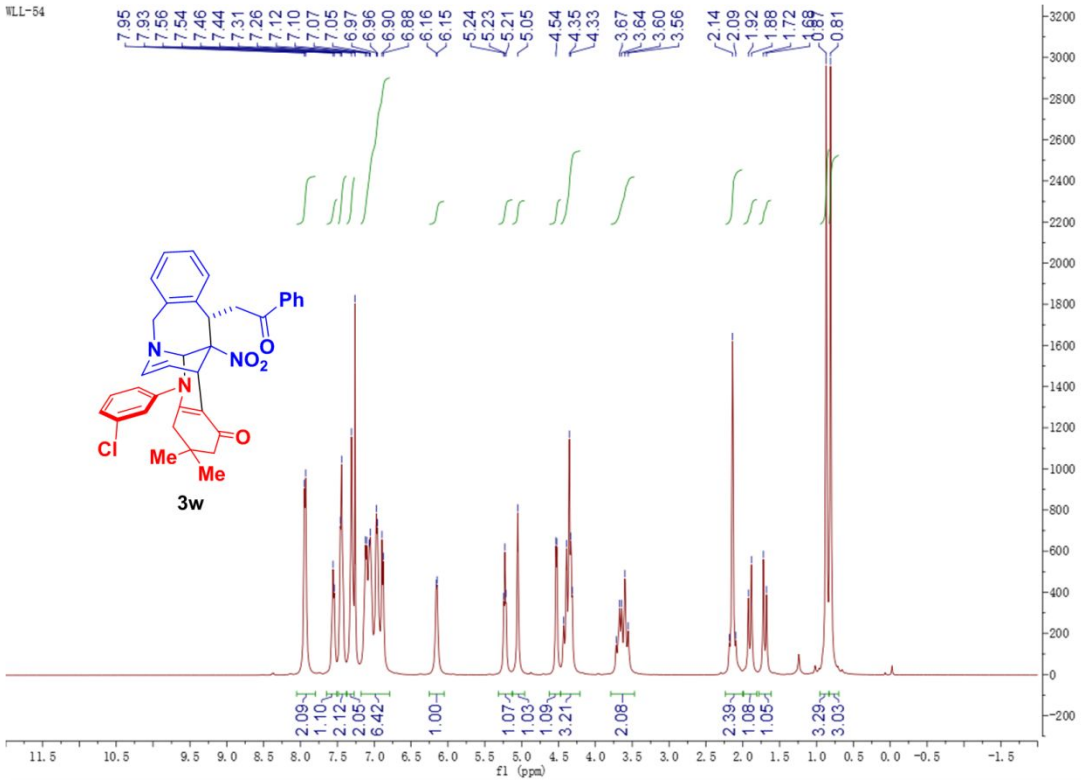
133.63
133.39
128.57
127.98
127.89
127.55
127.30
125.65
107.89
88.72
77.32
77.00
76.68
73.75
58.42
55.25
49.31
40.52
38.38
35.19
32.62
29.18
28.42
27.39
Ph
NO2
O
N
N
MeO
Me
Me
O
3v
f1 (ppm)


WLL-54
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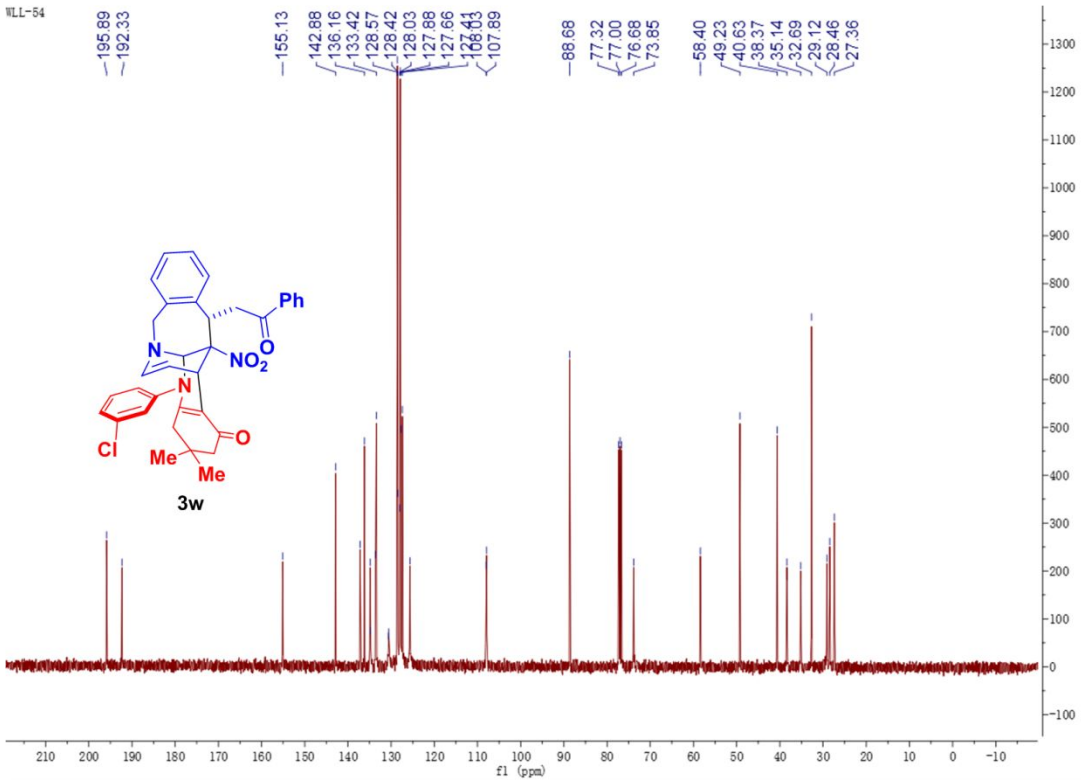
7.12
7.10
7.07
7.05
6.97
6.96
6.90
6.88
6.16
6.15
5.24
5.23
5.21
5.05
4.54
4.35
4.33
3.67
3.64
3.60
3.56
2.14
2.09
1.92
1.88
1.72
1.68
0.87
0.81
Ph
NO2
O
N
N
Cl
Me
Me
O
3w
2.09
1.10
2.12
2.05
6.42
1.00
1.07
1.03
1.09
3.21
2.08
2.39
1.08
1.05
3.29
3.03
f1 (ppm)


WLL-54
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128.57
128.42
128.03
127.88
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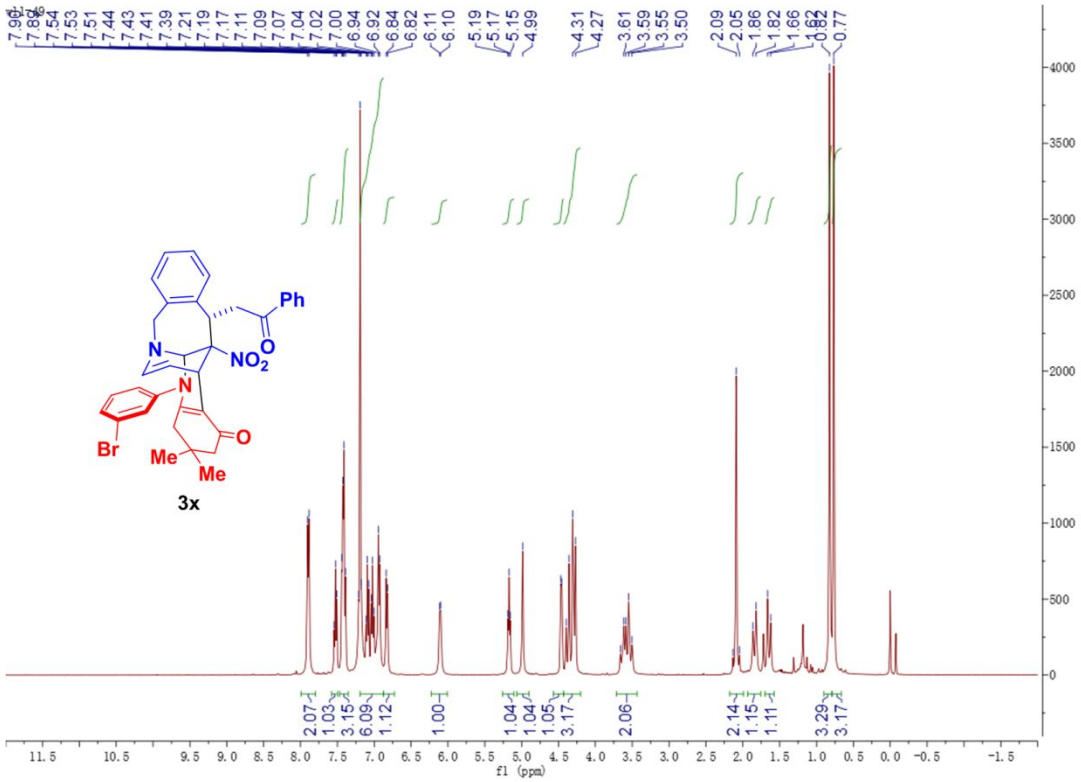
77.32
77.00
76.68
73.85
58.40
49.23
40.63
38.37
35.14
32.69
29.12
28.46
27.36
Ph
O
NO2
N
N
Cl
O
Me
Me
f1 (ppm)

3w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7.41
7.39
7.21
7.19
7.17
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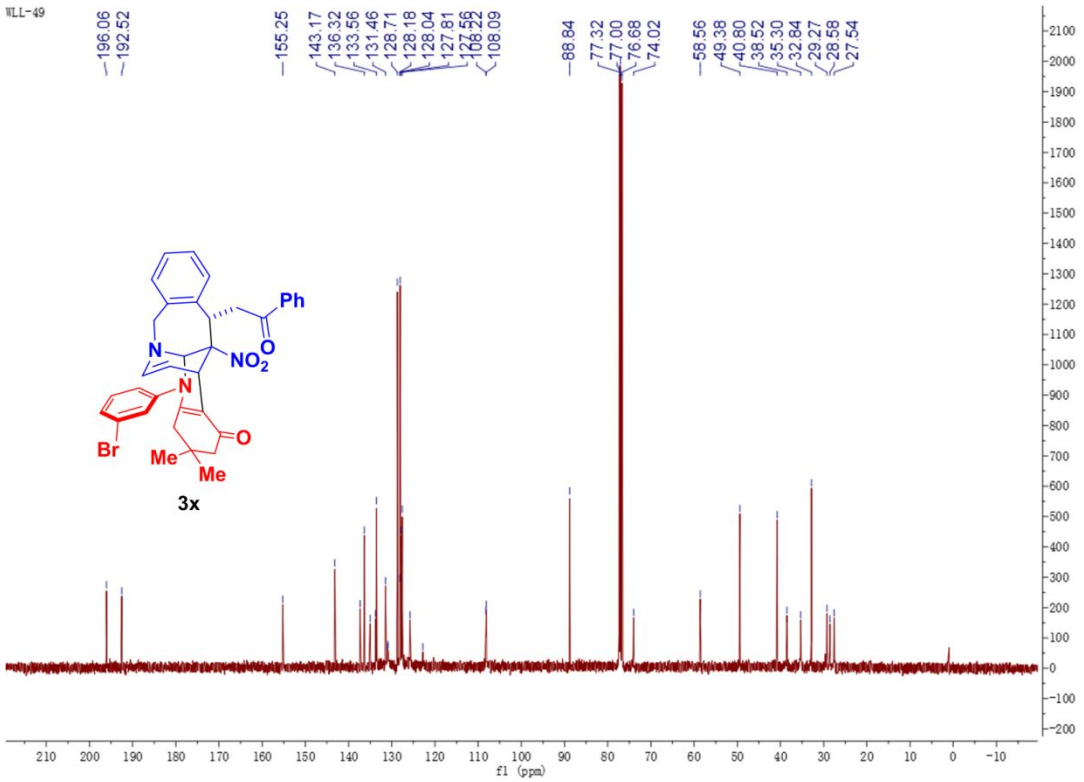
7.09
7.07
7.04
7.02
7.00
6.94
6.92
6.84
6.82
6.11
6.10
5.19
5.17
5.15
4.99
4.31
4.27
3.61
3.59
3.55
3.50
2.09
2.05
1.86
1.82
1.66
1.62
0.82
0.77
Ph
O
NO2
N
N
Br
O
Me
Me
2.07
1.03
3.15
6.09
1.12
1.00
1.04
1.04
1.05
3.17
2.06
2.14
1.15
1.11
3.29
3.17
f1 (ppm)

3x


WLL-49
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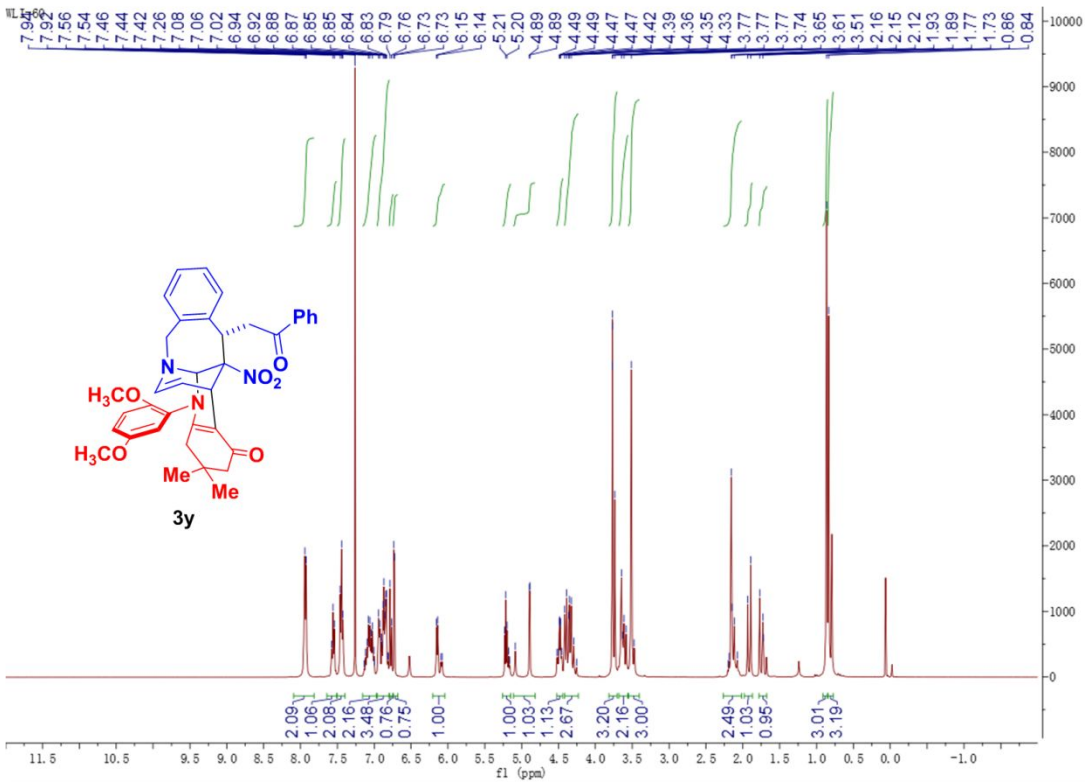
192.52
155.25
143.17
136.32
133.56
131.46
128.71
128.18
128.04
127.81
108.22
108.09
88.84
77.32
77.00
76.68
74.02
58.56
49.38
40.80
38.52
35.30
32.84
29.27
28.58
27.54
Ph
O
NO2
N
N
Br
Me
Me
O
3x
f1 (ppm)


7.94
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7.46
7.44
7.42
7.26
7.08
7.06
7.02
6.94
6.92
6.88
6.87
6.85
6.85
6.84
6.83
6.79
6.76
6.73
6.73
6.15
6.14
5.21
5.20
4.89
4.89
4.49
4.49
4.47
4.47
4.42
4.39
4.36
4.35
4.33
3.77
3.77
3.77
3.74
3.65
3.61
3.51
2.16
2.15
2.12
1.93
1.89
1.77
1.73
0.86
0.84
Ph
O
NO2
N
N
H3CO
H3CO
Me
Me
O
3y
2.09
1.06
2.08
2.16
3.48
0.76
0.75
1.00
1.00
1.03
1.13
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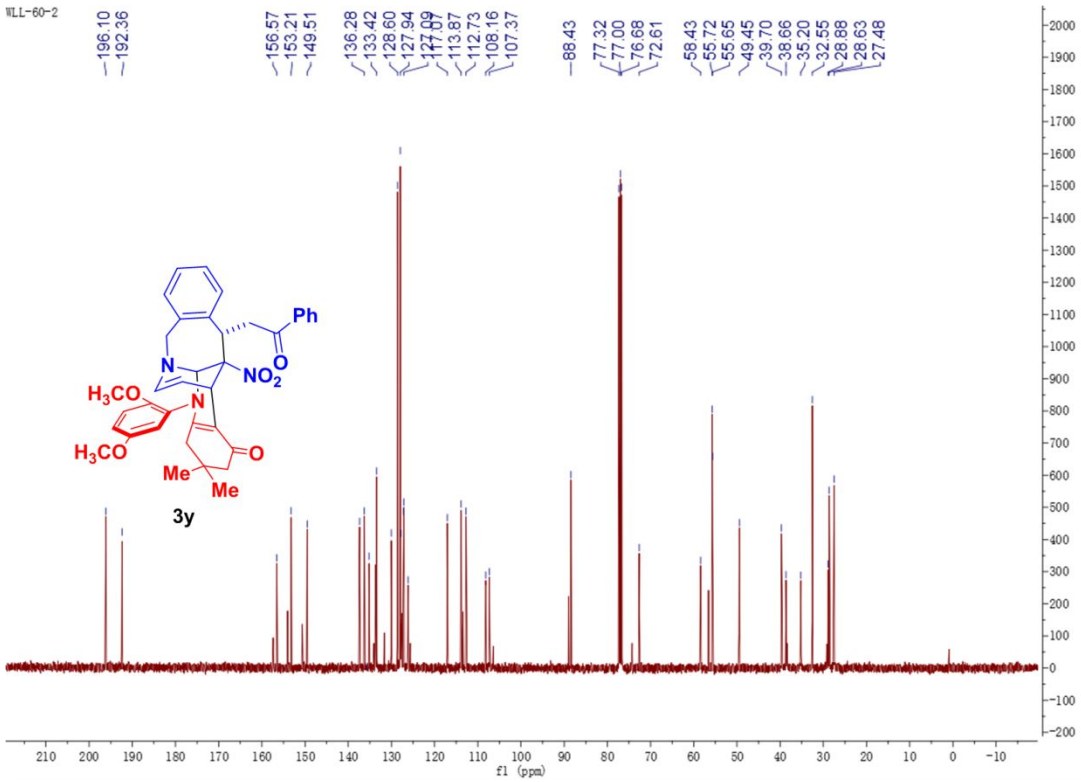
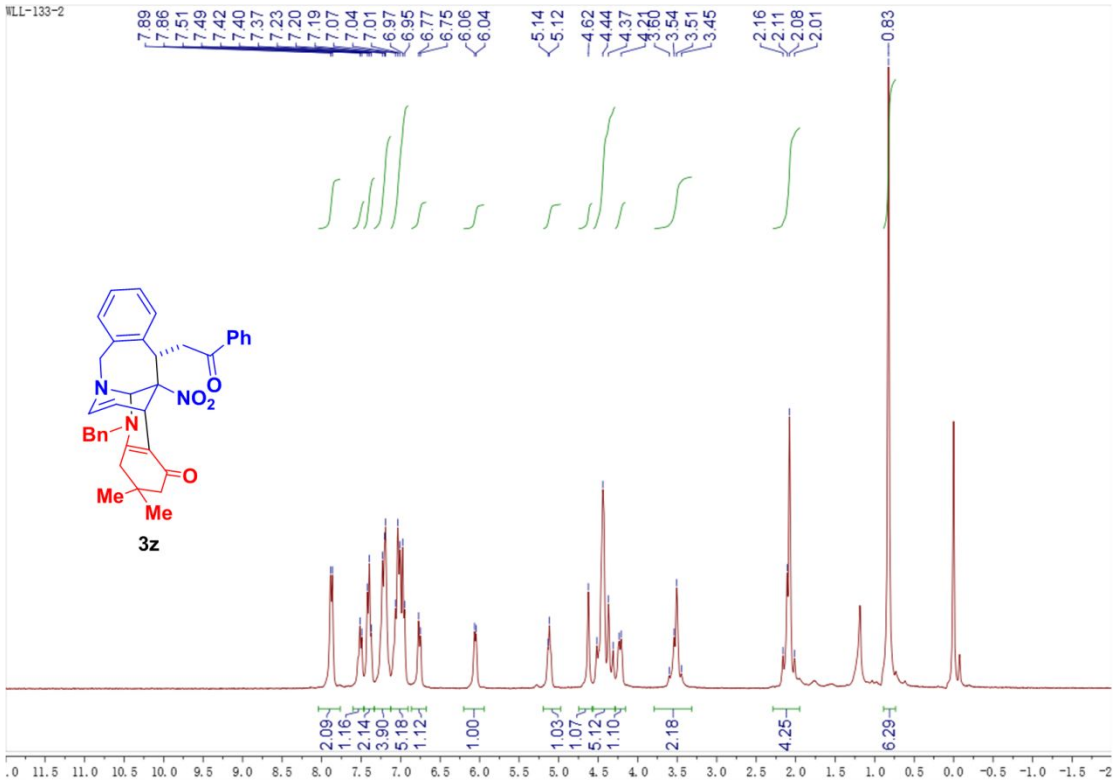
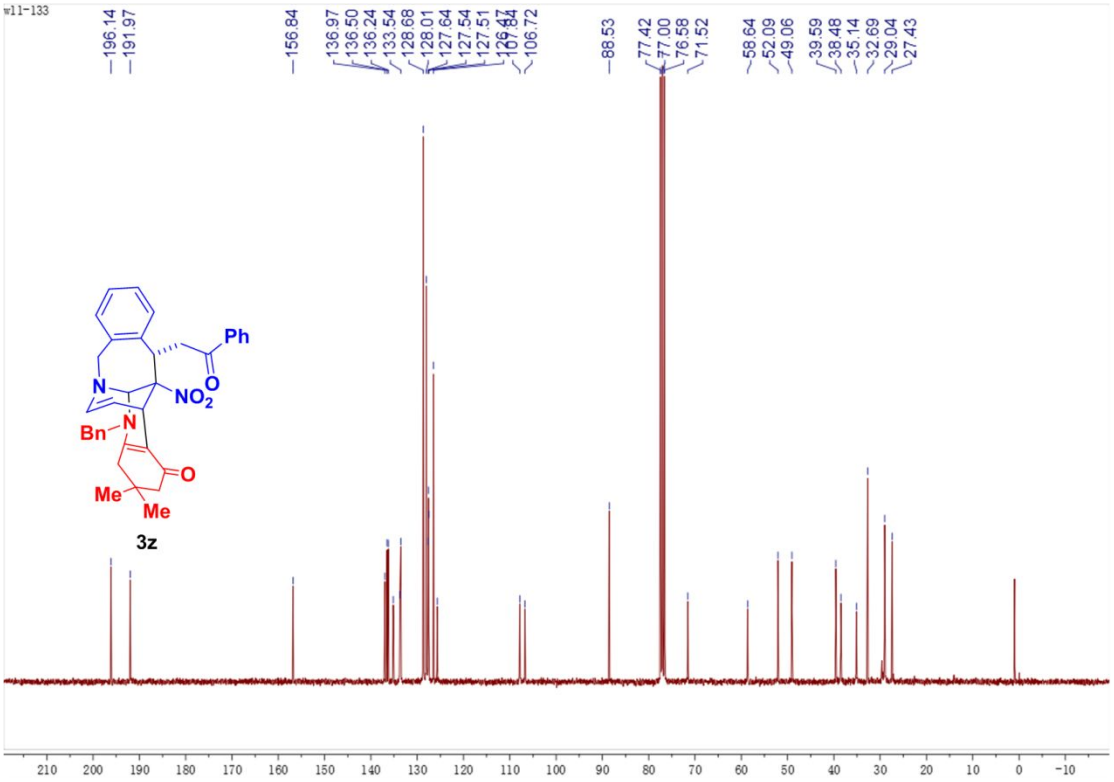
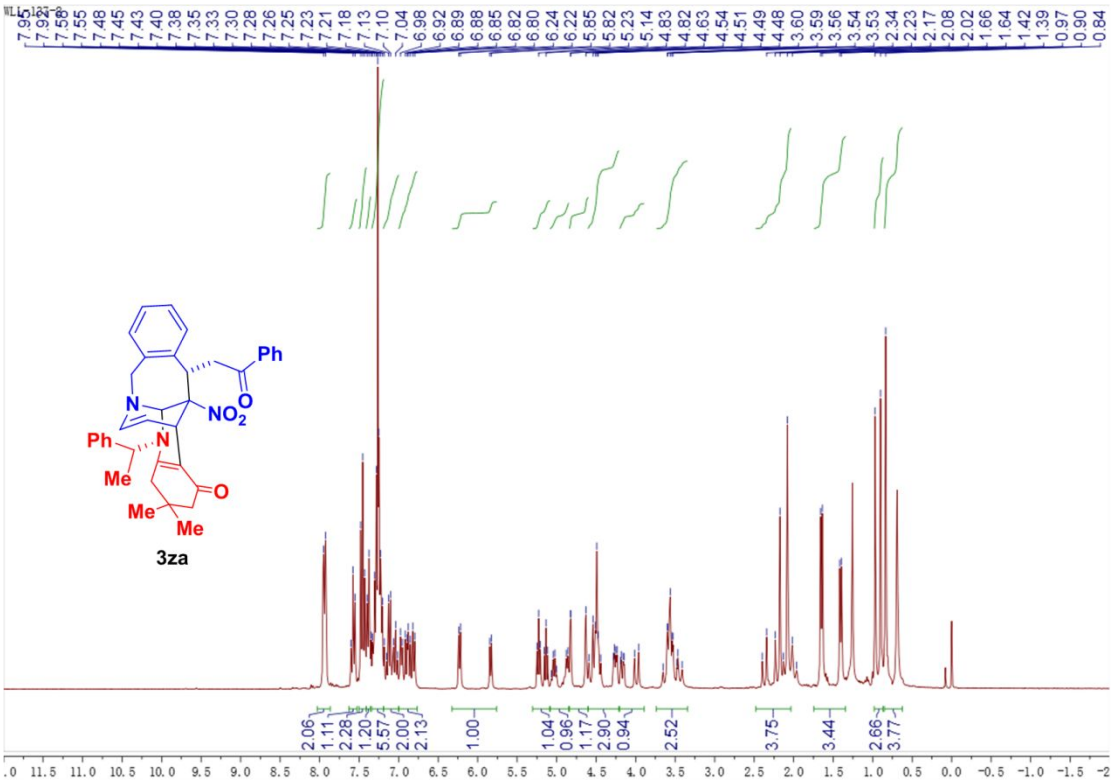
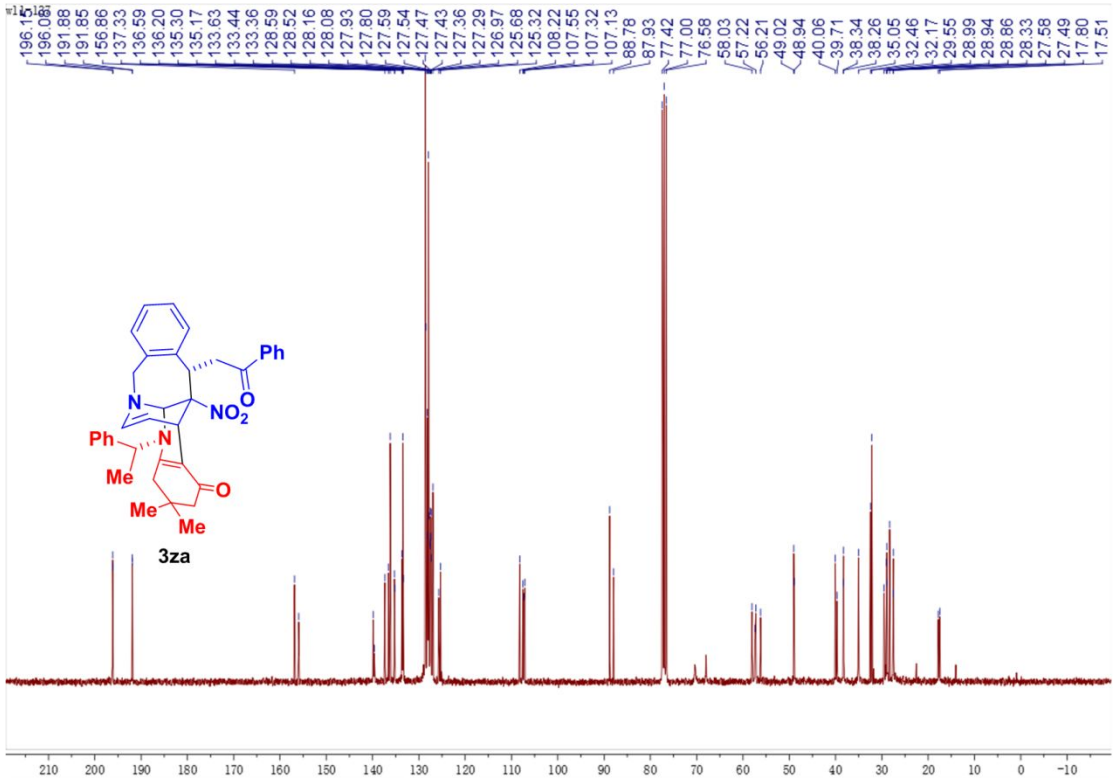
3.20
2.16
3.00
2.49
1.03
0.95
3.01
3.19
f1 (ppm)

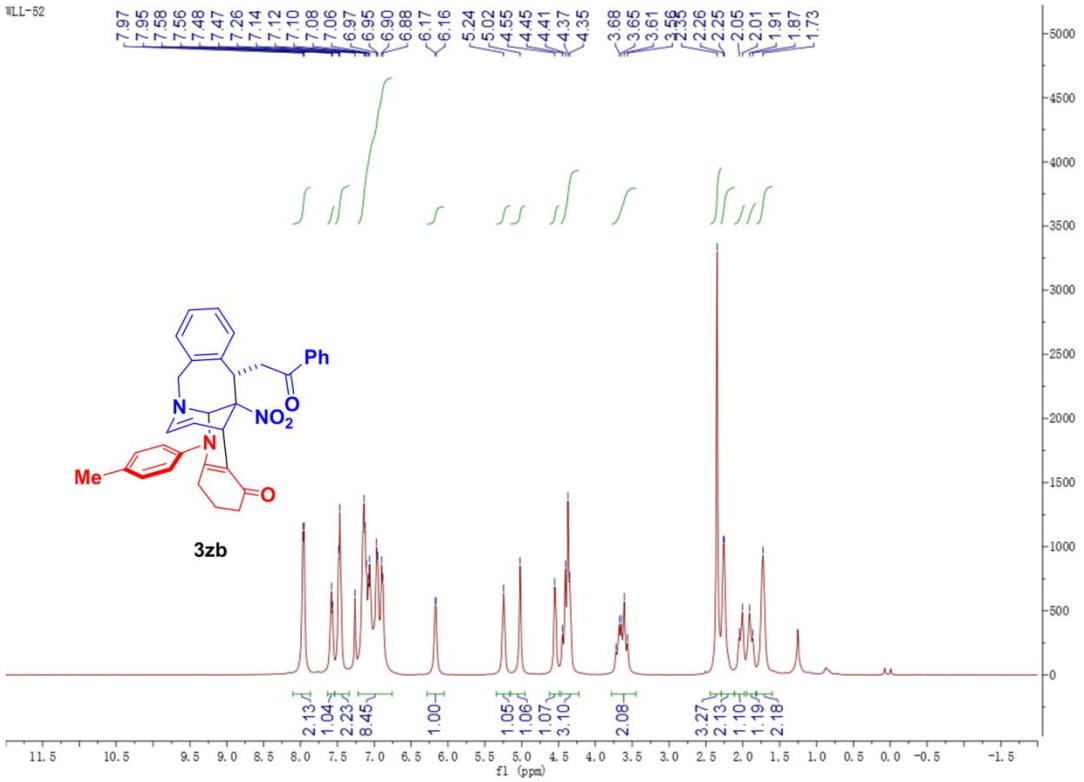

WLL-60-2
196.10
192.36
156.57
153.21
149.51
136.28
133.42
128.60
127.94
127.09
117.07
113.87
112.73
108.16
107.37
88.43
77.32
77.00
76.68
72.61
58.43
55.72
55.65
49.45
39.70
38.66
35.20
32.55
28.88
28.63
27.48
Ph
O
N
NO2
H3CO
N
H3CO
O
Me
Me
3y
f1 (ppm)

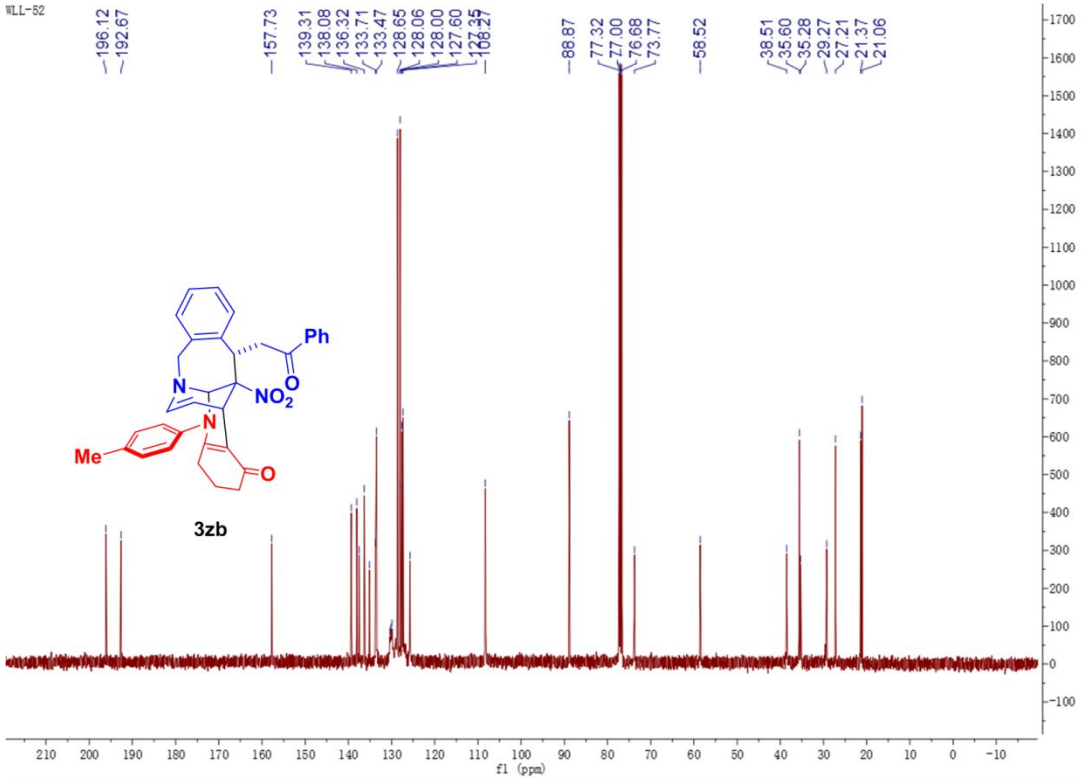

WLL-133-2
7.89
7.86
7.51
7.49
7.42
7.40
7.37
7.23
7.20
7.19
7.07
7.04
7.01
6.97
6.95
6.77
6.75
6.06
6.04
5.14
5.12
4.62
4.44
4.37
4.21
4.20
3.54
3.51
3.45
2.16
2.11
2.08
2.01
0.83
Ph
O
N
NO2
Bn
N
O
Me
Me
3z
2.09
1.16
2.14
3.90
5.18
1.12
1.00
1.03
1.07
5.12
1.10
2.18
4.25
6.29

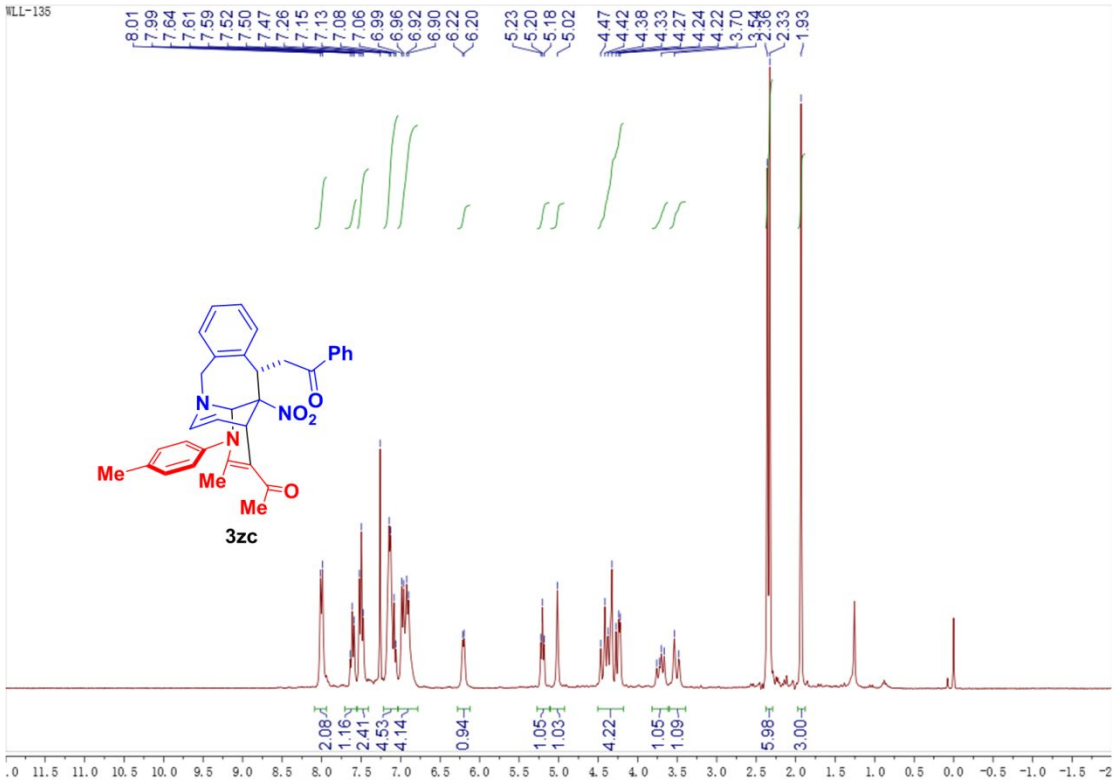

w11-133
196.14
191.97
156.84
136.97
136.50
136.24
133.54
128.68
128.01
127.64
127.54
127.51
106.72
88.53
77.42
77.00
76.58
71.52
58.64
52.09
49.06
39.59
38.48
35.14
32.69
29.04
27.43
Ph
O
NO2
N
Bn
N
O
Me
Me
3z

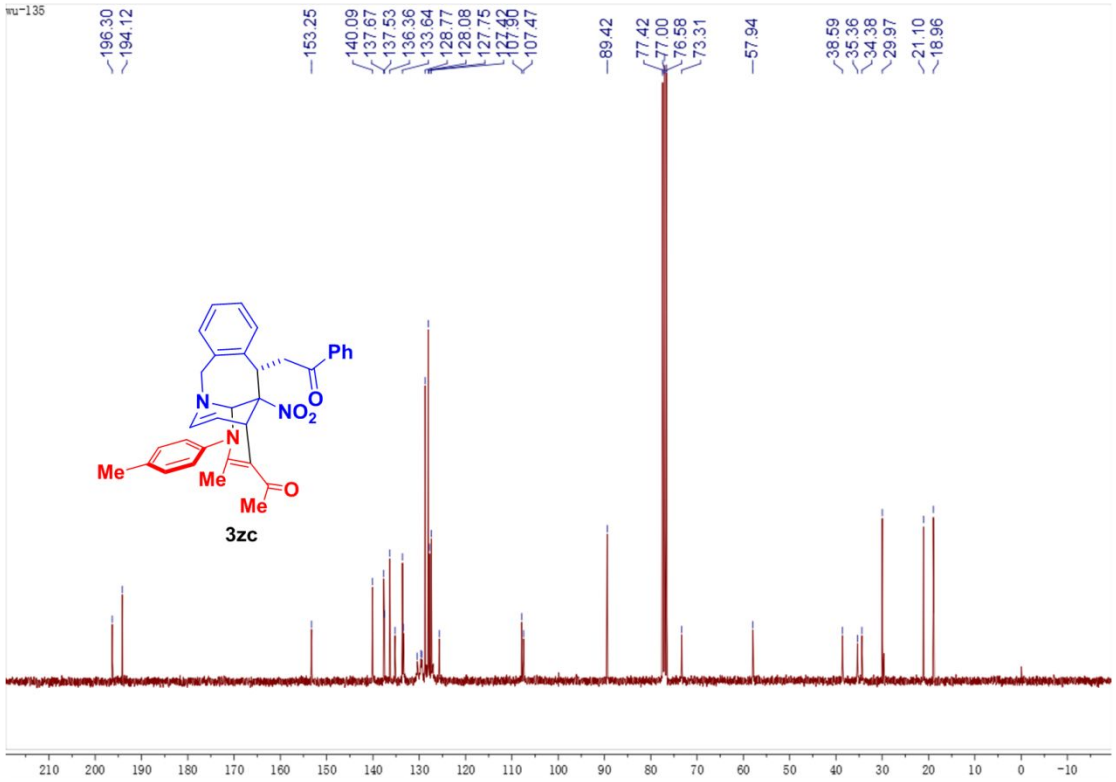

Ph
O
NO2
N
Ph
N
Me
O
Me
Me
3za

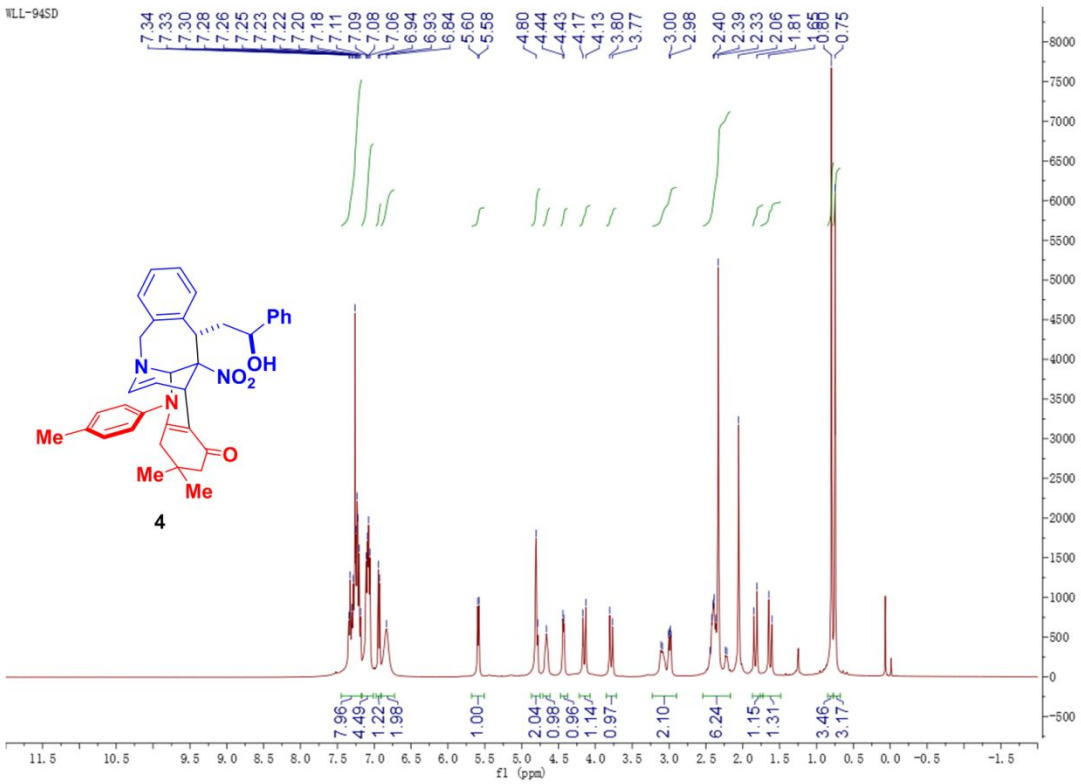

196.15
196.08
191.88
191.85
156.86
137.33
136.59
136.20
135.30
135.17
133.63
133.44
133.36
128.59
128.52
128.16
128.08
127.93
127.80
127.59
127.54
127.47
127.43
127.36
127.29
126.97
125.68
125.32
108.22
107.55
107.32
107.13
88.78
87.93
77.42
77.00
76.58
58.03
57.22
56.21
49.02
48.94
40.06
39.71
38.34
38.26
35.05
32.46
32.17
29.55
28.99
28.94
28.86
28.33
27.58
27.49
17.80
17.51
Ph
O
NO2
N
Ph
N
Me
O
Me
Me
3za

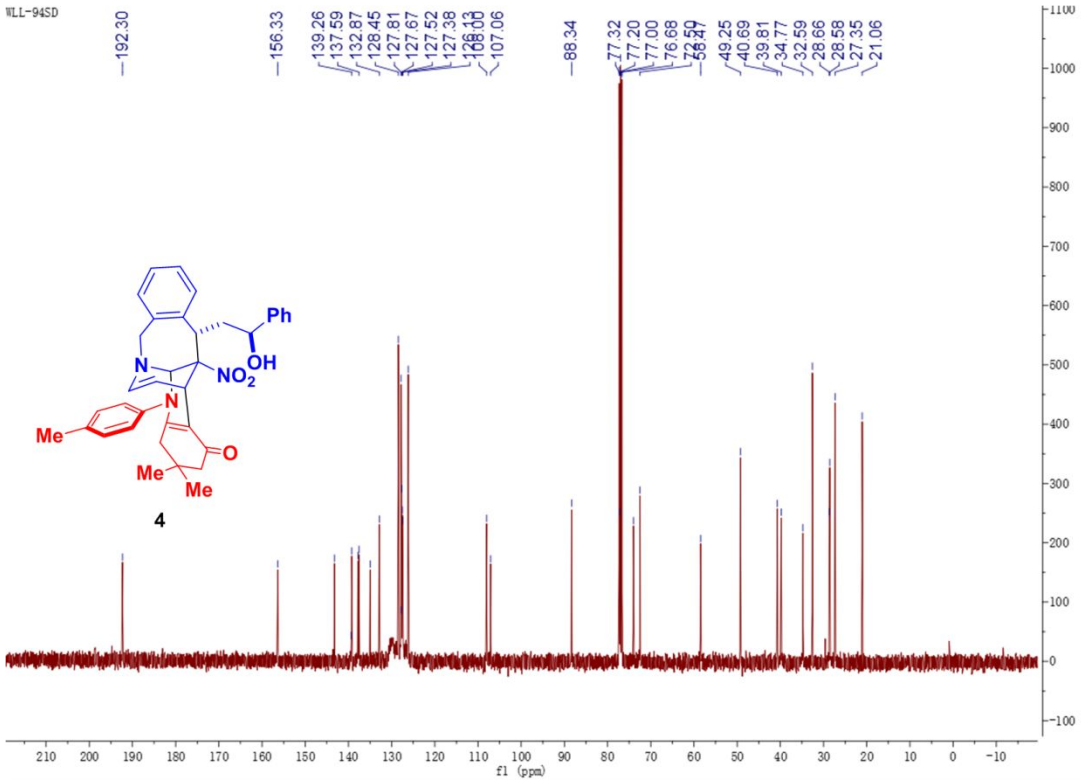

WLL-52
7.97
7.95
7.58
7.56
7.48
7.47
7.26
7.14
7.12
7.10
7.08
7.06
6.97
6.95
6.90
6.88
6.17
6.16
5.24
5.02
4.55
4.45
4.41
4.37
4.35
3.68
3.65
3.61
2.26
2.25
2.05
2.01
1.91
1.87
1.73
Ph
O
NO2
N
N
Me
O
3zb
2.13
1.04
2.23
8.45
1.00
1.05
1.06
1.07
3.10
2.08
3.27
2.13
1.10
1.19
2.18
f1 (ppm)


WLL-52
196.12
192.67
157.73
139.31
138.08
136.32
133.71
133.47
128.65
128.06
128.00
127.60
88.87
77.32
77.00
76.68
73.77
58.52
38.51
35.60
35.28
29.27
27.21
21.37
21.06
Ph
O
N
NO2
N
Me
O
3zb
f1 (ppm)

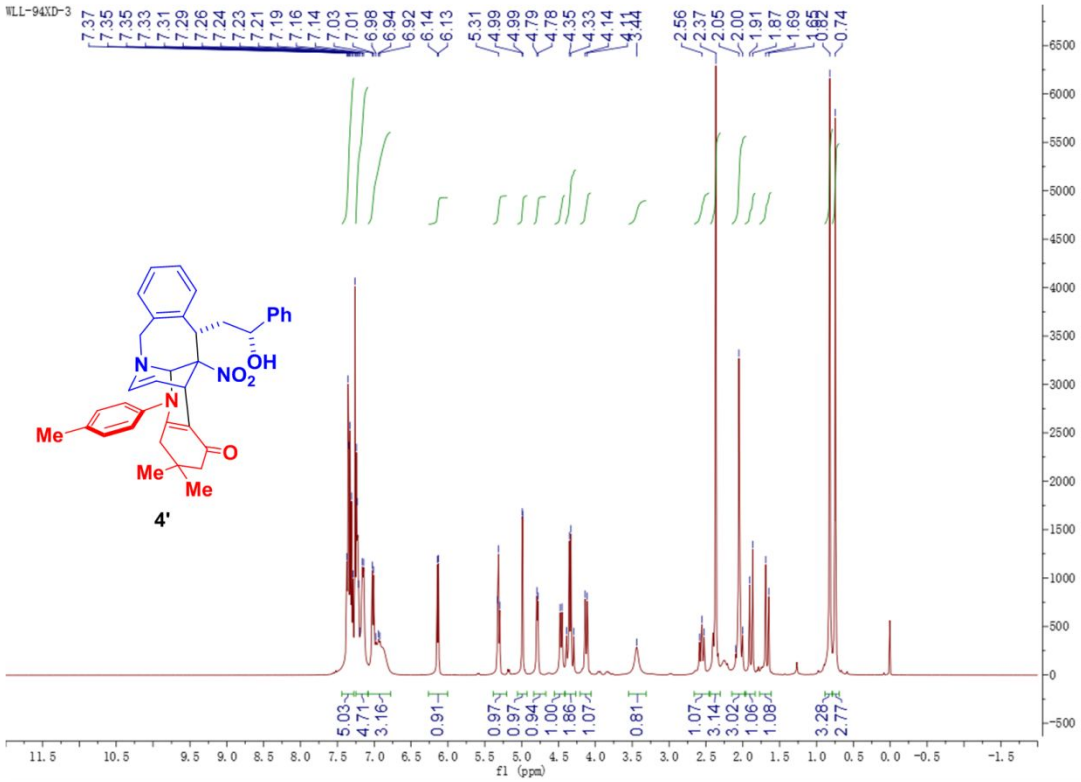

WLL-135
8.01
7.99
7.64
7.61
7.59
7.52
7.50
7.47
7.26
7.15
7.13
7.08
7.06
6.99
6.96
6.92
6.90
6.22
6.20
5.23
5.20
5.18
5.02
4.47
4.42
4.38
4.33
4.27
4.24
4.22
3.70
2.33
1.93
Ph
O
N
NO2
N
Me
Me
Me
O
3zc
2.08
1.16
2.41
4.53
4.14
0.94
1.05
1.03
4.22
1.05
1.09
5.98
3.00


wu-135
196.30
194.12
153.25
140.09
137.67
137.53
136.36
133.64
128.77
128.08
127.75
127.42
107.96
107.47
89.42
77.42
77.00
76.58
73.31
57.94
38.59
35.36
34.38
29.97
21.10
18.96
Ph
O
NO2
N
N
Me
Me
Me
O
3zc

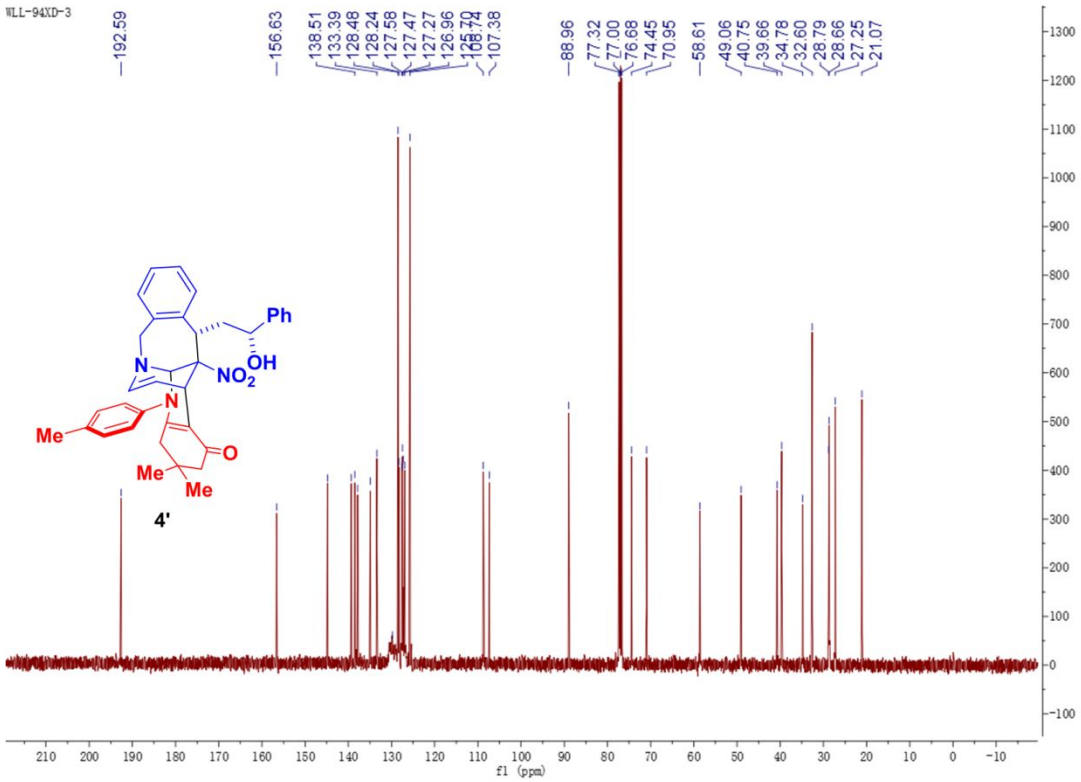

WLL-94SD
7.34
7.33
7.30
7.28
7.26
7.25
7.23
7.22
7.20
7.18
7.11
7.09
7.08
7.06
6.94
6.93
6.84
5.60
5.58
4.80
4.44
4.43
4.17
4.13
3.80
3.77
3.00
2.98
2.40
2.39
2.33
2.06
1.81
0.75
Ph
OH
NO2
N
N
Me
Me
Me
O
4
7.96
4.49
1.22
1.98
1.00
2.04
0.98
0.96
1.14
0.97
2.10
6.24
1.15
1.31
3.46
3.17
f1 (ppm)


WLL-94SD
192.30
156.33
139.26
137.59
132.87
128.45
127.81
127.67
127.52
127.38
107.06
88.34
77.32
77.20
77.00
76.68
49.25
40.69
39.81
34.77
32.59
28.66
28.58
27.35
21.06
Ph
OH
NO2
N
Me
O
Me
Me
f1 (ppm)

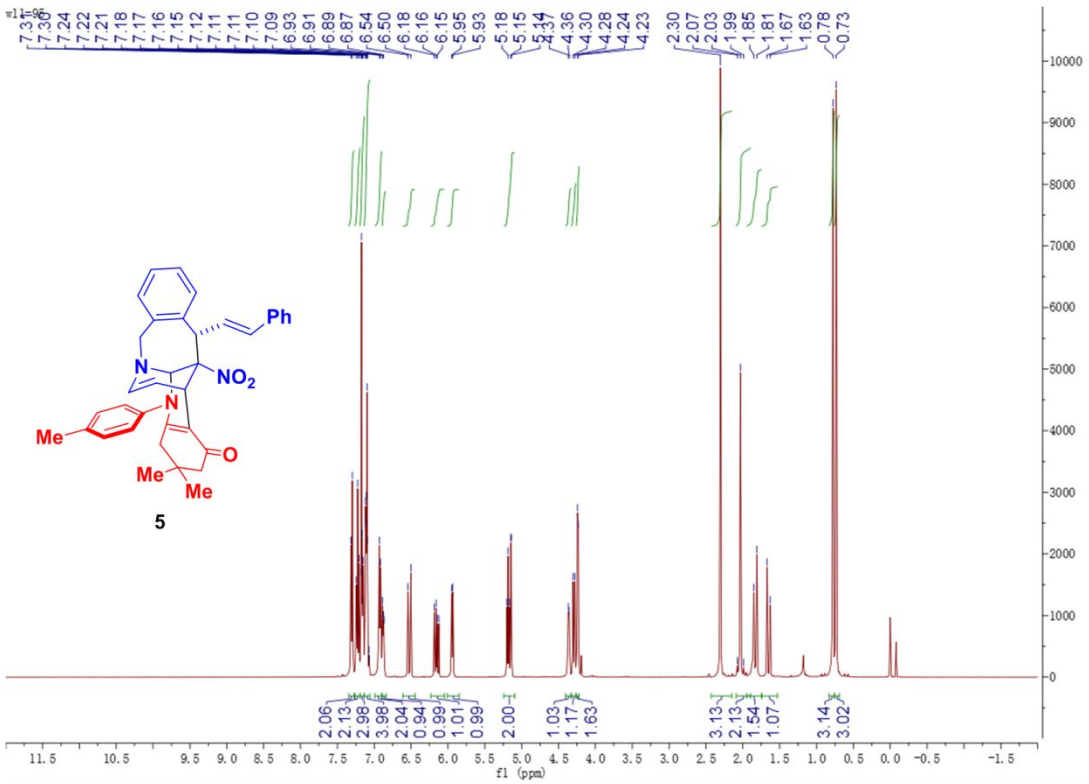
4


WLL-94XD-3
7.37
7.35
7.35
7.33
7.31
7.29
7.26
7.24
7.23
7.21
7.19
7.16
7.14
7.03
7.01
6.98
6.94
6.92
6.14
6.13
5.31
4.99
4.99
4.79
4.78
4.35
4.33
4.14
4.11
3.44
2.56
2.37
2.05
2.00
1.91
1.87
1.69
0.82
0.74
5.03
4.71
3.16
0.91
0.97
0.97
0.94
1.00
1.86
1.07
0.81
1.07
3.14
3.02
1.06
1.08
3.28
2.77
Ph
OH
NO2
N
Me
O
Me
Me
f1 (ppm)

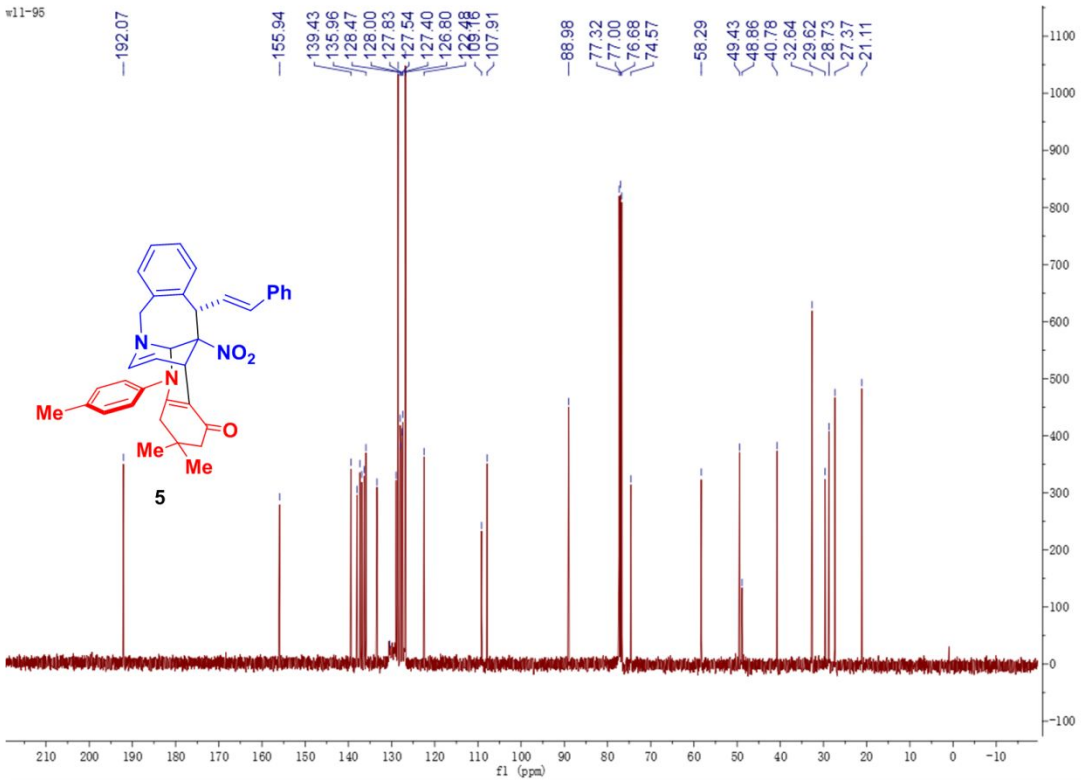
4'


WLL-94XD-3
192.59
156.63
138.51
133.39
128.48
128.24
127.58
127.47
127.27
126.96
125.70
108.74
107.38
88.96
77.32
77.00
76.68
74.45
70.95
58.61
49.06
40.75
39.66
34.78
32.60
28.79
28.66
27.25
21.07
Ph
OH
NO2
N
N
Me
O
Me
Me
f1 (ppm)

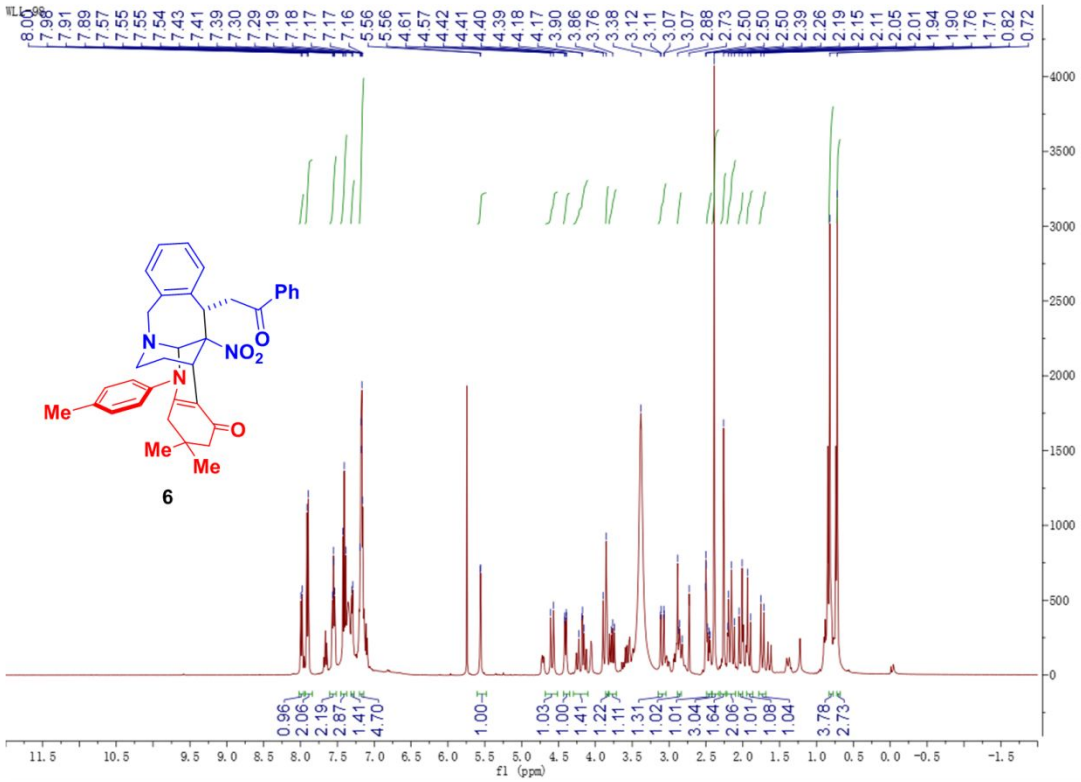
4'


wll-96
7.37
7.36
7.24
7.22
7.21
7.18
7.17
7.16
7.15
7.12
7.11
7.11
7.10
7.09
6.93
6.91
6.89
6.87
6.54
6.50
6.18
6.16
6.15
5.95
5.93
5.18
5.15
5.14
4.37
4.36
4.30
4.28
4.24
4.23
2.30
2.07
2.03
1.99
1.85
1.81
1.67
1.63
0.78
0.73
Ph
NO2
N
N
Me
O
Me
Me
2.06
2.13
2.98
3.98
2.04
0.94
0.99
1.01
0.99
2.00
1.03
1.17
1.63
3.13
2.13
1.54
1.07
3.14
3.02
f1 (ppm)

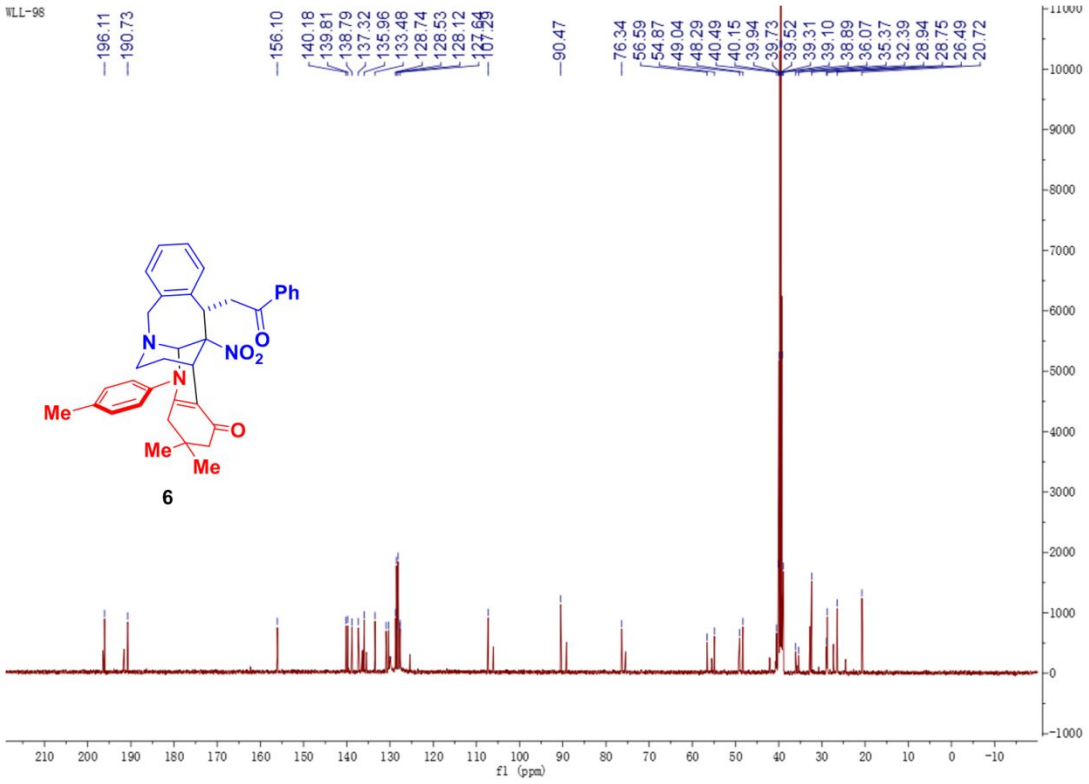
5


w11-95
192.07
155.94
139.43
135.96
128.47
128.00
127.83
127.54
127.40
126.80
107.91
88.98
77.32
77.00
76.68
74.57
58.29
49.43
48.86
40.78
32.64
29.62
28.73
27.37
21.11
Ph
NO2
N
N
Me
O
Me
Me
f1 (ppm)

5


WLL-98
8.00
7.98
7.91
7.89
7.57
7.55
7.55
7.54
7.43
7.41
7.39
7.30
7.29
7.19
7.18
7.17
7.17
7.16
5.56
5.56
4.61
4.57
4.42
4.41
4.40
4.39
4.18
4.17
3.90
3.86
3.76
3.38
3.12
3.11
3.07
3.07
2.88
2.73
2.50
2.50
2.50
2.39
2.26
2.19
2.15
2.11
2.05
2.01
1.94
1.90
1.76
1.71
0.82
0.72
Ph
O
NO2
N
N
Me
O
Me
Me
0.96
2.06
2.19
2.87
1.41
4.70
1.00
1.03
1.00
1.41
1.22
1.11
1.31
1.02
1.01
3.04
1.64
2.06
1.01
1.08
1.04
3.78
2.73
f1 (ppm)

6


WLL-98
196.11
190.73
156.10
140.18
139.81
138.79
137.32
135.96
133.48
128.74
128.53
128.12
90.47
76.34
56.59
54.87
49.04
48.29
40.49
40.15
39.94
39.73
39.52
39.31
39.10
38.89
36.07
35.37
32.39
28.94
28.75
26.49
20.72
Ph
O
N
NO2
N
Me
O
Me
Me
f1 (ppm)

6