Supporting Information

Regioselective and Diastereoselective Dearomative Multifunctionalization of In-Situ-Activated Azaarenes: An Access to Bridged Azaheterocycles

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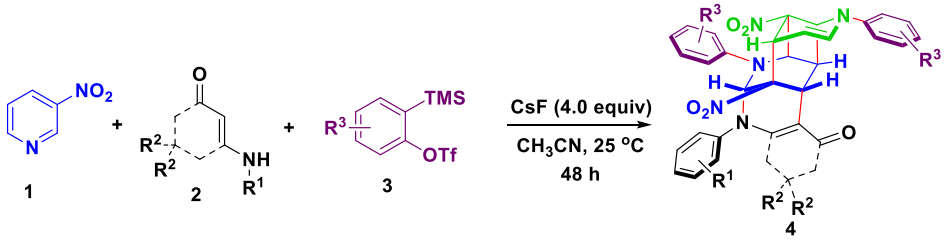
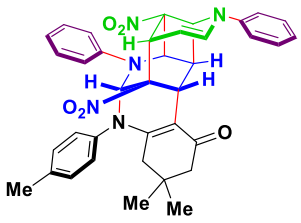
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz and some at 300 MHz, and ^{13}C NMR spectra were recorded at 100 MHz and some 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 the formation of 4

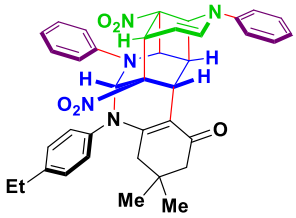


General procedure: To a 5.0 mL vial were successively added 3-nitropyridine **1** (0.30 mmol), enaminones **2** (0.15mmol), aryne precursors **3** (0.60 mmol), CsF (0.60 mmol) and 1.0 mL of CH_3CN. The resulting mixture was stirred at 25 °C for 48 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **4**. For some cases, such as **4a-c** and **4e-h**, the products precipitated out from the reaction systems and only a filtration was needed to purify them.



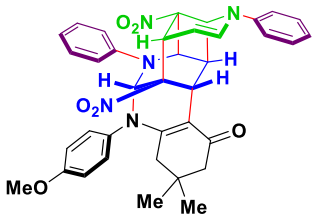
3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4a**)

Yellow solid obtained by filtration of the precipitate; 80.3 mg, 85% yield; dr > 20:1; reaction time = 48 h; mp 218.2-218.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 4H), 7.00 (q, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 5H), 6.37 (br, 2H), 5.96 (s, 1H), 4.45 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.27 (t, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.99 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.95 (s, 1H), 3.19 (t, *J* = 8.0 Hz, 1H), 2.23-2.13 (m, 5H), 1.87 (t, *J* = 16.0 Hz, 2H), 0.87 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.6, 145.5, 145.1, 139.6, 137.8, 134.0, 130.0, 129.9, 129.6, 129.6, 124.7, 123.6, 123.5, 118.7, 107.4, 87.4, 85.6, 84.4, 59.7, 52.5, 50.0, 48.5, 41.5, 38.5, 32.8, 29.1, 26.7, 25.3, 20.9. IR (KBr) *v* 3431, 2957, 1587, 1542, 1266, 756 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_5$ $[M+H]^+$ 630.2711, found 630.2702.



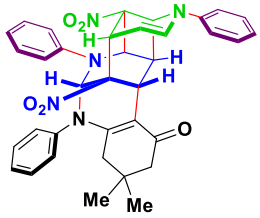
5-(4-ethylphenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4b**)

Yellow solid obtained by filtration of the precipitate; 72.1 mg, 75% yield; dr > 20:1; reaction time = 48 h; mp 219.9-220.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 4H), 7.05-6.86 (m, 7H), 6.40 (br, 2H), 5.97 (s, 1H), 4.46 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.29 (t, *J* = 8.0 Hz, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.99 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.96 (s, 1H), 3.19 (t, *J* = 8.0 Hz, 1H), 2.52 (q, *J* = 16.0 Hz, 2H), 2.24-2.14 (m, 2H), 1.90 (s, 2H), 1.13 (t, *J* = 8.0 Hz, 3H), 0.89 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 153.7, 145.6, 145.2, 144.1, 139.8, 134.1, 129.7, 129.6, 128.7, 124.8, 124.2, 123.6, 123.5, 118.8, 107.5, 87.5, 85.7, 84.5, 59.8, 52.6, 50.1, 48.6, 41.6, 38.6, 32.9, 29.1, 28.3, 26.8, 25.4, 15.3, one carbon missing in the aromatic region. IR (KBr) *v* 3439, 2960, 1633, 1582, 1541, 1501, 1358, 1294, 751 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{38}N_5O_5$ $[M+H]^+$ 644.2867, found 644.2870.



5-(4-methoxyphenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4c**)

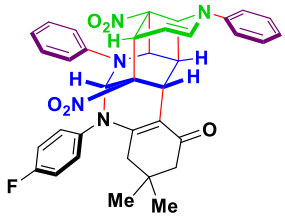
Yellow solid obtained by filtration of the precipitate; 70.1 mg, 72% yield; dr > 20:1; reaction time = 48 h; mp 233.1-233.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 4H), 7.12-7.04 (m, 2H), 6.98-6.93 (m, 3H), 6.67 (br, 4H), 6.05 (s, 1H), 4.52 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 4.22 (d, *J* = 8.0 Hz, 1H), 4.06 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.04 (s, 1H), 3.75 (s, 3H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.30-2.20 (m, 2H), 1.93 (q, *J* = 16.0 Hz, 2H), 0.95 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.8, 153.8, 145.5, 145.2, 135.0, 134.0, 129.6, 129.6, 124.6, 123.6, 123.2, 118.8, 114.3, 107.0, 87.5, 85.6, 84.4, 59.6, 55.4, 52.6, 50.0, 48.6, 41.5, 38.5, 32.7, 29.2, 26.7, 25.3, one carbon missing in the aromatic region. IR (KBr) *v* 3430, 2955, 1579, 1502, 1297, 1235, 745 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_6$ $[M+H]^+$ 646.2660, found 646.2647.



3,3-dimethyl-7b,13-dinitro-5,7,11-triphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4d**)

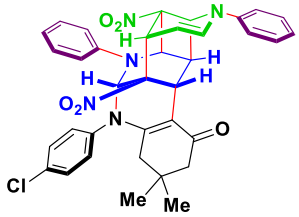
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 76.2 mg, 83% yield; dr > 20:1; reaction time = 48 h; mp 178.2-178.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.26-7.20 (m, 6H), 7.13-7.06 (m, 2H), 6.96 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.59 (br, 2H), 6.07 (s, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 4.21 (d, *J* = 8.0 Hz, 1H),4.07 (d, *J* = 4.0 Hz, 1H), 4.05 (s, 1H), 3.27 (t, *J* = 8.0 Hz, 1H), 2.27 (t, *J* = 16.0 Hz, 2H), 2.00-1.92 (m, 3H), 0.97 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 153.3, 145.5, 145.2, 142.3, 134.1, 129.7, 129.6, 129.4, 129.4, 127.8, 124.9, 123.7, 123.6, 118.8, 107.7, 87.5,

85.6, 84.5, 59.8, 52.6, 50.1, 48.6, 41.7, 38.6, 33.0, 29.2, 26.8, 25.4. IR (KBr) *v* 3441, 2954, 1588, 1544, 756 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{34}N_5O_5$ $[M+H]^+$ 616.2554, found 616.2540.



5-(4-fluorophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4e**)

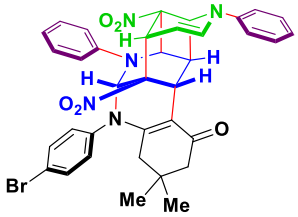
Yellow solid obtained by filtration of the precipitate; 69.7 mg, 73% yield; dr > 20:1; reaction time = 48 h; mp 143.7-144.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 4H), 7.11 (t, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 8.0 Hz, 5H), 6.57 (br, 2H), 6.05 (s, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 4.19 (d, *J* = 8.0 Hz, 1H), 4.07 (d, *J* = 8.0 Hz, 1H), 4.04 (s, 1H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.27 (t, *J* = 16.0 Hz, 2H), 2.00-1.85 (m, 2H), 0.97 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 161.6 (d, *J* = 247.0 Hz, 1C), 153.1, 145.5, 145.2, 138.3, 134.2, 129.7, 129.7, 125.1, 123.7, 123.7, 118.9, 107.8, 87.5, 85.5, 84.4, 59.9, 52.6, 50.0, 48.6, 41.6, 38.6, 32.9, 29.2, 26.7, 25.4, two carbons missing in the aromatic region. IR (KBr) *v* 3441, 1544, 1501, 1593, 1223, 747 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}FN_5O_5$ $[M+H]^+$ 634.2460, found 634.2451.



5-(4-chlorophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4f**)

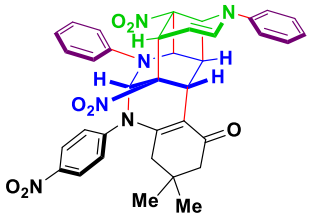
Yellow solid obtained by filtration of the precipitate; 78.5 mg, 81% yield; dr > 20:1; reaction time = 48 h; mp171.6-172.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 8.0 Hz, 3H), 6.98 (t, *J* = 8.0 Hz, 3H), 6.49 (br, 2H), 6.03 (s, 1H), 4.52 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 8.0 Hz, 1H),

4.07 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.04 (s, 1H), 3.26 (t, J = 8.0 Hz, 1H), 2.27 (t, J = 16.0 Hz, 2H), 1.94 (s, 2H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 152.7, 145.4, 145.2, 140.8, 134.2, 133.7, 129.8, 129.7, 129.6, 128.9, 125.3, 124.0, 123.7, 118.8, 108.3, 87.4, 85.5, 84.4, 59.9, 52.5, 50.0, 48.6, 41.7, 38.6, 33.1, 29.0, 26.9, 25.4. IR (KBr) v 3433, 1588, 1539, 1229, 746 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}ClN_5O_5$ $[M+H]^+$ 650.2165, found 650.2171.



5-(4-bromophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4g**)

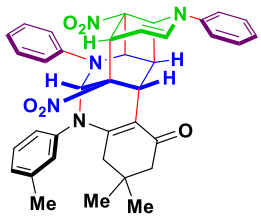
Yellow solid obtained by filtration of the precipitate; 84.6 mg, 81% yield; dr > 20:1; reaction time = 48 h; mp 177.9-178.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 8.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 4H), 7.21 (d, J = 8.0 Hz, 2H), 7.13 (q, J = 8.0 Hz, 2H), 6.98 (t, J = 8.0 Hz, 3H), 6.42 (br, 2H), 6.02 (s, 1H), 4.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.36 (t, J = 8.0 Hz, 1H), 4.17 (d, J = 8.0 Hz, 1H), 4.07 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.03 (s, 1H), 3.26 (t, J = 8.0 Hz, 1H), 2.27 (t, J = 16.0 Hz, 2H), 1.94 (s, 2H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 152.6, 145.4, 145.2, 141.3, 134.2, 132.6, 129.8, 129.7, 129.3, 125.4, 124.1, 123.7, 121.7, 118.9, 108.4, 87.4, 85.5, 84.5, 60.0, 52.5, 50.1, 48.6, 41.7, 38.6, 33.1, 29.0, 26.9, 25.4. IR (KBr) v 3431, 1588, 1536, 1263, 750 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}BrN_5O_5$ $[M+H]^+$ 694.1660, found 694.1661.



3,3-dimethyl-7b,13-dinitro-5-(4-nitrophenyl)-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4h**)

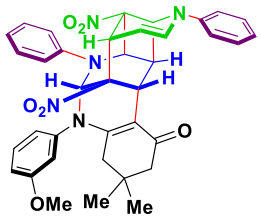
Yellow solid obtained by filtration of the precipitate; 69.2 mg, 70% yield; dr > 20:1; reaction time = 48 h; mp 182.3-183.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.41 (t, J =

8.0 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H),7.21 (t, *J* = 8.0 Hz, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 4.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 4.13-4.09 (m, 2H), 4.04 (s, 1H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.34 (t, *J* = 16.0 Hz, 2H), 2.16 (d, *J* = 16.0 Hz, 1H), 1.95 (d, *J* = 16.0 Hz, 1H), 1.02 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 151.2, 147.8, 145.9, 145.2, 145.1, 134.3, 130.1, 129.7, 127.2, 126.3, 125.3, 125.0, 123.9, 118.9, 111.4, 87.3, 85.3, 84.6, 60.3, 52.3, 50.3, 48.4, 42.0, 38.8, 33.6, 28.4, 27.4, 25.7. IR (KBr) *v* 3437, 1637, 1586, 1345, 737 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}N_6O_7$ $[M+H]^+$ 661.2405, found 661.2387.



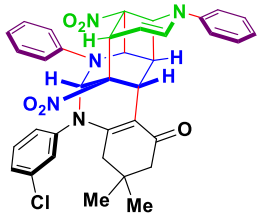
3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-5-(*m*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4i**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 71.2 mg, 75% yield; dr > 20:1; reaction time = 48 h; mp157.9-158.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.23 (q, *J* = 8.0 Hz, 5H), 7.09 (q, *J* = 8.0 Hz, 2H), 7.02-6.95 (m, 4H), 6.45 (br, 2H), 6.06 (s, 1H), 4.54 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 4.08 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.04 (s, 1H), 3.27 (t, *J* = 8.0 Hz, 1H), 2.31-1.92 (m, 7H), 0.97 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.4, 145.6, 145.2, 142.1, 134.1, 129.7, 129.7, 129.5, 128.5, 124.9, 123.9, 123.8, 123.6, 118.8, 107.4, 87.4, 85.6, 84.5, 59.9, 52.6, 50.1, 48.7, 41.6, 38.6, 33.0, 29.1, 26.8, 25.4, 21.1, two carbons missing in the aromatic region. IR (KBr) *v* 3443, 2954, 1587, 1543, 746 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_5$ $[M+H]^+$ 630.2711, found 630.2699.



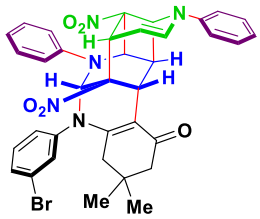
5-(3-methoxyphenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4j**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 74.1 mg, 77% yield; dr > 20:1; reaction time = 48 h; mp 165.1-165.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 2H), 7.27-7.19 (m, 4H), 7.10 (t, *J* = 8.0 Hz, 3H), 6.99 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.76 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.21 (br, 2H), 6.06 (s, 1H), 4.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 4.08 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.03 (s, 1H), 3.53 (br, 3H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.32-2.23 (m, 2H), 2.07-1.97 (m, 2H), 0.98 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 160.2, 153.3, 145.6, 145.2, 143.2, 134.0, 130.0, 129.7, 129.6, 125.1, 125.1, 124.1, 123.6, 118.8, 114.3, 112.5, 107.9, 87.4, 85.6, 84.5, 60.0, 55.1, 52.5, 50.1, 48.5, 41.5, 38.6, 33.0, 29.0, 26.9, 25.4. IR (KBr) *v* 3445, 2953, 1591, 1493, 754 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_6$ $[M+H]^+$ 646.2660, found 646.2663.



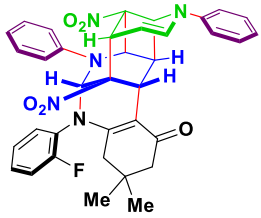
5-(3-chlorophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4k**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 69.3 mg, 71% yield; dr > 20:1; reaction time = 48 h; mp 168.2-169.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (t, *J* = 6.0 Hz, 2H), 7.28-7.17 (m, 5H), 7.11 (q, *J* = 6.0 Hz, 3H), 6.98 (d, *J* = 6.0 Hz, 3H), 6.51 (br, 2H), 6.05 (s, 1H), 4.53 (d, *J* = 3.0 Hz, 1H), 4.34 (t, *J* = 6.0 Hz, 1H), 4.17 (d, *J* = 6.0 Hz, 1H), 4.07 (d, *J* = 3.0 Hz, 1H), 4.04 (s, 1H), 3.26 (t, *J* = 6.0 Hz, 1H), 2.28 (s, 2H), 1.96 (s, 2H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 152.5, 145.2, 145.1, 143.2, 134.7, 134.1, 130.2, 129.8, 129.7, 129.6, 128.0, 127.9, 125.4, 124.1, 123.6, 118.7, 108.4, 87.3, 85.4, 84.4, 59.9, 52.4, 50.0, 48.5, 41.6, 38.6, 33.0, 28.9, 26.8, 25.4. IR (KBr) *v* 3438, 2954, 1587, 1545, 747 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}ClN_5O_5$ $[M+H]^+$ 650.2165, found 650.2152.



5-(3-bromophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4l**)

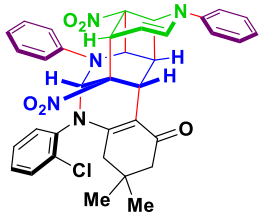
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 79.6 mg, 76% yield; dr > 20:1; reaction time = 48 h; mp 176.3-176.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.90 (d, *J* = 8.0 Hz, 3H), 6.50 (br, 2H), 5.96 (s, 1H), 4.45 (d, *J* = 4.0 Hz, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 4.08 (d, *J* = 8.0 Hz, 1H), 3.99 (d,*J* = 4.0 Hz, 1H), 3.95 (s, 1H), 3.17 (t, *J* = 8.0 Hz, 1H), 2.20 (t, *J* = 16.0 Hz, 2H), 1.88 (s, 2H), 0.90 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 152.5, 145.2, 145.1, 143.4, 134.1, 130.9, 130.5, 129.8, 129.6, 125.4, 124.2, 123.6, 122.6, 118.8, 108.4, 87.3, 85.4, 84.4, 59.9, 52.4, 50.0, 48.6, 41.6, 38.6, 33.1, 28.9, 26.9, 25.4, two carbons missing in the aromatic region. IR (KBr) *v* 3443, 2957, 1590, 1544, 744 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}BrN_5O_5$ $[M+H]^+$ 694.1660, found 694.1662.



5-(2-fluorophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4m**)

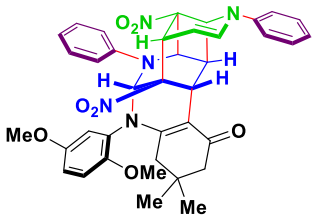
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 67.3 mg, 71% yield; dr =1.4:1; reaction time = 48 h; mp 173.8-174.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 4H), 7.13-6.97 (m, 5H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.76(t, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 4.57 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.40-4.33 (m, 2H), 4.10-4.02 (m, 2H), 3.27 (q, *J* = 8.0 Hz, 1H), 2.30 (t, *J* = 16.0 Hz, 2H), 2.08 (dd, J_1 = J_2 = 16.0 Hz, 1H), 1.82 (dd, J_1 = J_2 = 16.0 Hz, 1H), 0.98 (d, *J* = 8.0 Hz, 3H), 0.91 (d, *J* = 32.0

Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 159.5 (d, *J* = 66.0 Hz, 1C), 153.5, 145.7, 145.2, 134.4, 130.3, 130.0, 129.7, 129.2, 126.0, 125.5, 123.8, 123.2, 119.9, 119.0, 116.6 (d, *J* = 20.0 Hz, 1C), 106.4, 88.0, 85.4, 84.1, 58.8, 52.9, 49.9, 48.5, 39.6, 38.4, 32.7, 30.2, 25.7, 25.0. IR (KBr) *v* 3439, 2954, 1592, 1543, 756 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}FN_5O_5$ $[M+H]^+$ 634.2460, found 634.2445.



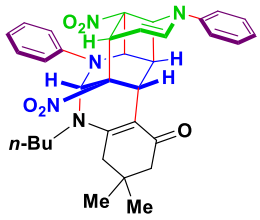
5-(2-chlorophenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4n**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 68.5 mg, 70% yield; dr =1.2:1; reaction time = 48 h; mp 166.8-167.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.20-7.10 (m, 4H), 7.06-6.95 (m, 4H), 6.91 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.81(t, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 8.0 Hz, 2H), 6.18 (d, *J* = 4.0 Hz, 1H), 4.49 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.33-4.26 (m, 2H), 4.04-3.94 (m, 2H), 3.19 (t, *J* = 8.0 Hz, 1H), 2.22 (t, *J* = 20.0 Hz, 2H), 2.14-1.89 (m, 1H), 1.75 (dd, J_1 = J_2 = 16.0 Hz, 1H), 0.91 (d, *J* = 4.0 Hz, 3H), 0.84 (d, *J* = 32.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 153.4, 145.7, 145.2, 134.4, 130.3, 130.0, 129.7, 129.1, 125.5, 124.6, 123.8, 123.1, 119.9, 119.0, 116.5, 116.3, 106.4, 88.0, 85.4, 84.1, 58.8, 52.9, 49.9, 48.5, 40.9, 38.4, 32.6, 30.1, 25.7, 25.0. IR (KBr) *v* 3441, 2956, 1593, 1498, 756 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{33}ClN_5O_5$ $[M+H]^+$ 650.2165, found 650.2163.



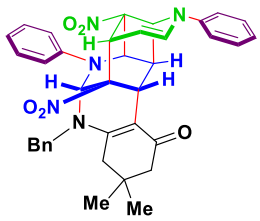
5-(2,5-dimethoxyphenyl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4o**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 60.7 mg, 61% yield; dr =1.8:1; reaction time = 48 h; mp 222.4-223.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 3H), 7.18-6.87 (m, 7H), 6.75-6.39 (m, 4H), 5.81 (s, 1H),4.48-4.41 (m, 1H), 4.28-4.22 (m, 1H), 3.97 (dd, J_1 = J_2 = 8.0 Hz, 2H), 3.58 (s, 3H), 3.24-3.16 (m, 2H), 3.15 (s, 3H), 2.19 (s, 2H), 1.84 (s, 2H), 0.89 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 155.0, 153.0, 149.2, 146.2, 145.2, 133.9, 130.7, 130.0, 129.6, 125.5, 123.5, 118.8, 118.7, 115.8, 114.2, 112.2, 106.5, 86.8, 85.8, 84.5, 60.7, 55.3, 55.2, 52.5, 50.2, 48.6, 40.7, 38.9, 32.6, 29.2, 26.9, 24.9. IR (KBr) *v* 3447, 2959, 1588, 1502, 1225, 1036, 750 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{38}N_5O_7$ $[M+H]^+$ 676.2766, found 676.2772.



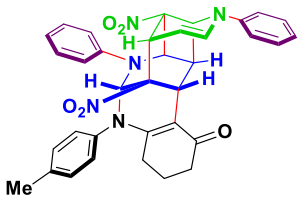
5-butyl-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4p**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 34.1 mg, 38% yield; dr >20:1; reaction time = 48 h; mp 199.1-199.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4H), 7.19-7.04 (m, 6H), 6.95 (d, J = 8.0 Hz, 1H), 5.68 (s, 1H), 4.49 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, J = 8.0 Hz, 1H), 4.11 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.04 (d, J = 8.0 Hz, 1H), 3.91 (s, 1H), 3.27-3.17 (m, 2H), 3.00-2.93 (m, 1H), 2.29-2.14 (m, 4H), 1.34-1.28 (m, 1H), 1.15-1.11 (m, 3H), 1.06 (s, 3H), 1.01 (s, 3H), 0.82 (t, J = 8.0 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 154.2, 146.2, 145.2, 133.9, 129.7, 129.6, 125.2, 124.1, 123.6, 118.7, 106.4, 87.4, 85.7, 84.6, 59.9, 52.6, 51.2, 49.6, 48.9, 39.6, 38.5, 32.5, 31.4, 29.5, 27.0, 25.3, 19.7, 13.6. IR (KBr) *v* 3453, 2959, 1632, 1577, 1225, 752 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{38}N_5O_5$ $[M+H]^+$ 596.2857, found 596.2870.



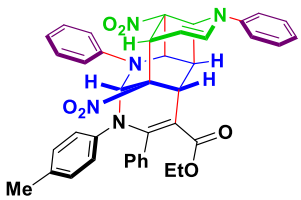
5-benzyl-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4q**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 39.7 mg, 42% yield; dr > 20:1; reaction time = 48 h; mp 214.6-215.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.27-7.25 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 3H), 7.10 (q, *J* = 8.0 Hz, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.83 (dd, J_1 = J_2 = 4.0 Hz, 2H), 5.76 (s, 1H), 4.48 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.44 (s, 1H), 4.29 (t, *J* = 8.0 Hz, 1H), 4.11 (d, *J* = 16.0 Hz, 1H), 4.06-4.03 (m, 2H), 3.97 (s, 1H), 3.20 (t, *J* = 8.0 Hz, 1H), 2.31-2.22 (m, 4H), 1.03 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 154.5, 146.4, 145.2, 135.8, 134.1, 129.9, 129.7, 128.8, 127.9, 126.4, 125.5, 124.5, 123.6, 118.8, 106.9, 87.0, 85.6, 84.4, 60.5, 53.9, 52.6, 49.6, 49.0, 40.2, 38.5, 32.7, 29.6, 26.8, 25.2. IR (KBr) *v* 3440, 2945, 1633, 1588, 1543, 750 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_5$ $[M+H]^+$ 630.2711, found 630.2713.



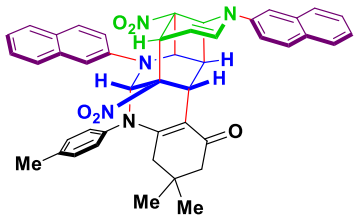
7b,13-dinitro-7,11-diphenyl-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4r**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 61.2 mg, 68% yield; dr > 20:1; reaction time = 48 h; mp 165.4-166.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 4H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.94 (dd, J_1 = J_2 = 8.0 Hz, 4H), 6.50 (br, 2H), 6.07 (s, 1H), 4.53 (d, *J* = 4.0 Hz, 1H), 4.33 (t, *J* = 8.0 Hz, 1H), 4.24 (d, *J* = 4.0 Hz, 1H), 4.04 (s, 2H), 3.28 (t, *J* = 8.0 Hz, 1H), 2.43-2.30 (m, 3H), 2.27 (s, 3H), 2.07 (t, *J* = 8.0 Hz, 2H), 1.87-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 155.3, 145.4, 145.1, 139.6, 137.9, 133.9, 129.8, 129.6, 129.4, 127.5, 124.4, 123.5, 122.8, 118.7, 108.0, 87.5, 85.6, 84.2, 76.0, 59.3, 52.6, 48.5, 38.5, 36.3, 28.1, 25.3, 21.5, 20.9. IR (KBr) *v* 3438, 1572, 1502, 739 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{32}N_5O_5$ $[M+H]^+$ 602.2398, found 602.2386.



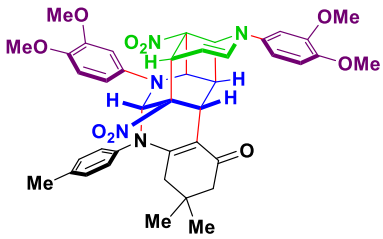
ethyl 10a,11-dinitro-1,4,7-triphenyl-3-(*p*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epi methanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine-5-carboxylate (**4s**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 57.5 mg, 56% yield; dr > 20:1; reaction time = 48 h; mp 232.6-233.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 3H), 7.12-7.00 (m, 7H), 6.93 (br, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 4.66 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.46 (t, *J* = 8.0 Hz, 1H), 4.19 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.16 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 1H), 3.95-3.82 (m, 2H), 3.24 (t, *J* = 8.0 Hz, 1H), 2.07 (s, 3H), 0.80 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 150.5, 145.5, 144.7, 141.4, 136.3, 135.6, 133.2, 129.9, 129.7, 129.2, 127.9, 127.3, 126.9, 126.2, 126.1, 123.1, 117.6, 103.1, 87.2, 87.0, 85.1, 78.0, 60.1, 59.7, 51.7, 48.6, 38.6, 28.7, 20.7, 13.8, one carbon missing in the aromatic region. IR (KBr) *v* 3450, 2922, 1681, 1594, 1544, 1233, 1121, 744 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{36}N_5O_6$ $[M+H]^+$ 682.2660, found 682.2660.



3,3-dimethyl-7,11-di(naphthalen-2-yl)-7b,13-dinitro-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4t**)

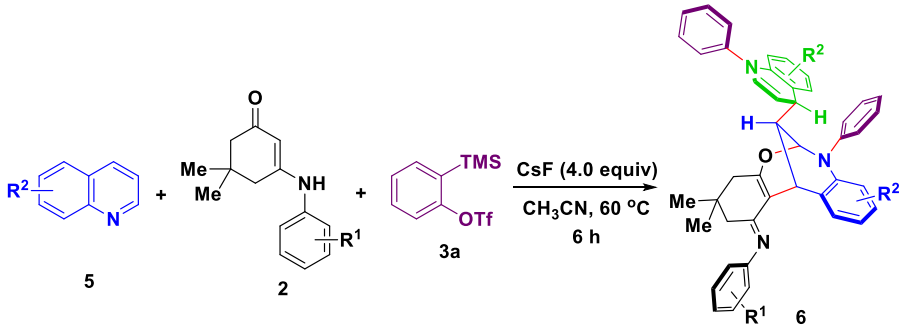
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 77.3 mg, 71% yield; dr > 20:1; reaction time = 48 h; mp 246.2-246.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.63 (m, 5H), 7.52 (s, 1H), 7.42-7.35 (m, 5H), 7.18-7.05 (m, 4H), 6.85 (br, 2H), 6.44 (br, 2H), 6.17 (s, 1H), 4.61 (s, 1H), 4.38 (s, 2H), 4.08 (s, 2H), 3.35 (s, 1H), 2.26-2.19 (m, 5H), 1.90 (q, *J* = 16.0 Hz, 2H), 0.89 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 153.7, 142.9, 142.8, 139.8, 138.0, 134.4, 134.1, 133.9, 130.4, 130.4, 130.0, 130.0, 129.8, 129.6, 127.6, 127.5, 127.5, 127.2, 126.7, 126.7, 125.3, 124.9, 121.7, 119.3, 119.2, 115.5, 107.3, 87.6, 86.2, 84.3, 59.3, 53.0, 50.1, 48.5, 41.7, 38.6, 32.9, 29.4, 26.6, 25.5, 20.9. IR (KBr) *v* 3440, 2957, 1631, 1590, 1541, 743 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{40}N_5O_5$ $[M+H]^+$ 730.3024, found 730.3024.



7,11-bis(3,4-dimethoxyphenyl)-3,3-dimethyl-7b,13-dinitro-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**4u**)

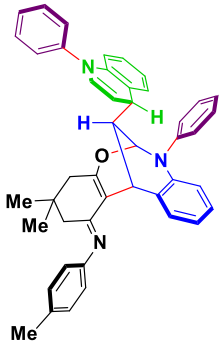
Yellowoil obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 87.5 mg, 78% yield; dr > 20:1; reaction time = 48 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, J_1 = J_2 = 8.0 Hz, 1H), 6.95 (br, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.82 (dd, J_1 = J_2 = 4.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.56 (dd, J_1 = J_2 = 4.0 Hz, 2H), 6.42 (br, 2H), 5.81 (s, 1H), 4.39 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.21 (t, J = 8.0 Hz, 1H), 4.07 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.00 (s, 1H), 3.97 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 3.87-3.81 (m, 5H), 3.71 (s, 3H), 3.17 (t, J = 8.0 Hz, 1H), 2.25 (s, 5H), 2.17-1.90 (m, 3H), 0.96 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 153.4, 149.6, 149.6, 147.1, 146.2, 139.7, 139.5, 139.0, 137.5, 135.4, 129.9, 123.8, 117.7, 112.7, 111.9, 111.5, 109.4, 108.0, 105.3, 87.4, 84.5, 83.8, 78.3, 60.7, 56.1, 56.0, 55.7, 52.8, 50.1, 48.5, 41.6, 38.6, 33.0, 28.7, 27.1, 25.4, 20.1. IR (KBr) v 3443, 2950, 1586, 1514, 1238, 1024, 769 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{44}N_5O_9$ $[M+H]^+$ 750.3134, found 750.3147.

3. Experimental data for the formation of 6



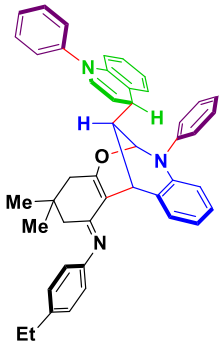
General procedure：To a 5.0 mL vial were successively added quinolines **5** (0.30 mmol), enaminones **2** (0.15 mmol), benzyne precursor **3a** (0.60 mmol), CsF (0.60 mmol) and 1.0 mL of CH_3CN. The resulting mixture was stirred at 60 °C in oil bath for 6 h. Upon completion of the reaction (monitoring by TLC), the products **6** were precipitated from the reaction mixtures and only a filtration was needed to purify them. (Note: The products were sensitive to acidic

conditions, which could not be purified by silica gel column chromatography. They were liable to lose one molecule of quinoline to afford mono-quinoline bridged cyclic compounds **7**.)



3,3-dimethyl-7-phenyl-13-(1-phenyl-1,4-dihydroquinolin-4-yl)-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6a**)

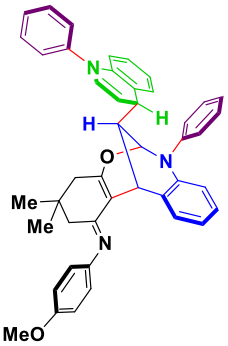
White solid obtained by filtration of the precipitate; 68.9 mg, 72% yield; dr > 20:1; reaction time = 6 h; mp 195.5-196.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 6H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02-6.92 (m, 3H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.66-6.59 (m, 5H), 5.44 (s, 1H), 4.96 (t, *J* = 8.0 Hz, 1H), 4.65 (s, 1H), 3.21 (q, *J* = 8.0 Hz, 1H), 2.32 (s, 3H), 2.29 (d, *J* = 16.0 Hz, 1H), 2.12 (d, *J* = 16.0 Hz, 1H), 1.99 (s, 2H), 1.89 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.1, 150.0, 145.1, 143.7, 142.1, 141.9, 131.9, 131.3, 129.9, 129.8, 129.7, 129.4, 129.3, 127.8, 126.6, 126.6, 126.2, 126.2, 126.1, 122.7, 121.4, 119.8, 118.8, 114.4, 114.1, 113.4, 100.2, 84.5, 41.6, 41.6, 41.1, 36.1, 31.3, 29.0, 28.2, 27.5, 20.8. IR (KBr) *v* 3435, 2952, 1604, 1494, 1379, 753 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{42}N_3O$ $[M+H]^+$ 640.3322, found 640.3310.



N-(4-ethylphenyl)-3,3-dimethyl-7-phenyl-13-(1-phenyl-1,4-dihydroquinolin-4-yl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6b**)

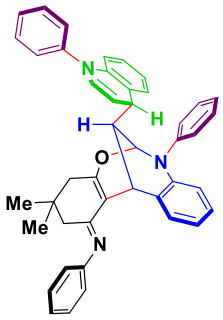
White solid obtained by filtration of the precipitate; 78.8 mg, 80% yield; dr > 20:1; reaction time = 6 h; mp 201.9-202.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, J_1 = J_2 = 3.0 Hz, 1H), 7.50-7.41

(m, 5H), 7.33-7.29 (m, 6H), 7.18 (d, J = 3.0 Hz, 1H), 7.12 (d, J = 9.0 Hz, 2H), 7.04-6.91 (m, 3H), 6.77 (t, J = 6.0 Hz, 1H), 6.66-6.61 (m, 4H), 5.44 (t, J = 3.0 Hz, 1H), 4.96 (t, J = 6.0 Hz, 1H), 4.65 (s, 1H), 3.21 (q, J = 6.0 Hz, 1H), 2.63 (q, J = 6.0 Hz, 2H), 2.28 (tt, J_1 = J_2 = 3.0 Hz, 1H), 2.14 (d, J = 15.0 Hz, 1H), 2.04 (s, 2H), 1.90 (d, J = 18.0 Hz, 1H), 1.25 (t, J = 6.0 Hz, 3H), 0.93 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 158.0, 150.2, 145.1, 143.7, 142.1, 141.9, 137.9, 131.9, 129.9, 129.8, 129.7, 129.4, 128.1, 127.8, 126.6, 126.6, 126.2, 126.1, 126.1, 122.7, 121.4, 119.8, 118.8, 114.4, 114.1, 113.4, 100.2, 84.5, 41.6, 41.5, 41.2, 36.1, 31.3, 29.0, 28.3, 28.2, 27.5, 15.8. IR (KBr) v 3439, 2959, 2314, 1607, 1493, 1380, 754 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{44}N_3O$ $[M+H]^+$ 654.3479, found 654.3485.



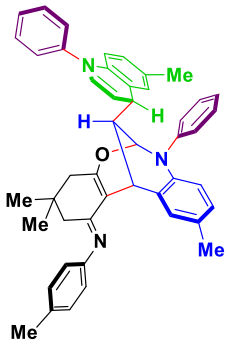
N-(4-methoxyphenyl)-3,3-dimethyl-7-phenyl-13-(1-phenyl-1,4-dihydroquinolin-4-yl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6c**)

White solid obtained by filtration of the precipitate; 68.4 mg, 70% yield; dr > 20:1; reaction time = 6 h; mp 221.2-221.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.45 (q, J = 8.0 Hz, 6H), 7.29 (t, J = 8.0 Hz, 4H), 7.17 (d, J = 8.0 Hz, 1H), 7.02-6.92 (m, 3H), 6.85 (d, J = 8.0 Hz, 2H), 6.77 (t, J = 8.0 Hz, 1H), 6.66-6.60 (m, 5H), 5.44 (s, 1H), 4.96 (t, J = 8.0 Hz, 1H), 4.66 (s, 1H), 3.78 (s, 3H), 3.22 (q, J = 8.0 Hz, 1H), 2.29 (d, J = 8.0 Hz, 1H), 2.13 (d, J = 16.0 Hz, 1H), 2.04 (s, 2H), 1.89 (d, J = 16.0 Hz, 1H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 158.0, 155.2, 145.9, 145.1, 143.7, 142.1, 141.9, 131.9, 129.8, 129.8, 129.7, 129.4, 127.7, 126.6, 126.6, 126.2, 126.1, 126.1, 122.7, 121.4, 120.9, 118.8, 114.4, 114.1, 114.1, 113.4, 100.2, 84.5, 55.5, 41.6, 41.6, 41.2, 36.1, 31.3, 28.9, 28.2, 27.5. IR (KBr) v 3448, 2955, 1644, 1605, 1495, 1230, 753 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{42}N_3O_2$ $[M+H]^+$ 656.3272, found 656.3290.



3,3-dimethyl-*N*,7-diphenyl-13-(1-phenyl-1,4-dihydroquinolin-4-yl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6d**)

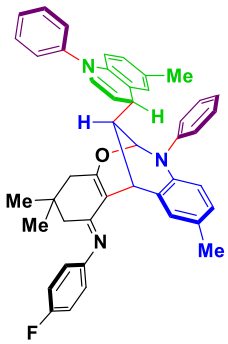
White solid obtained by filtration of the precipitate; 56.4 mg, 60% yield; dr > 20:1; reaction time = 6 h; mp 198.7-199.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.48-7.41 (m, 6H), 7.27 (q, *J* = 8.0 Hz, 6H),7.17 (d, *J* = 4.0 Hz, 1H), 7.03-6.92 (m, 4H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.70-6.61 (m, 5H), 5.44 (s, 1H), 4.96 (t, *J* = 8.0 Hz, 1H), 4.65 (s, 1H), 3.22 (q, *J* = 8.0 Hz, 1H), 2.29 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 2.04 (s, 2H), 1.88 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.4, 152.7, 145.1, 143.7, 142.1, 141.9, 132.0, 129.8, 129.8, 129.7, 129.4, 128.7, 127.8, 126.7, 126.6, 126.2, 126.2, 126.1, 122.7, 122.1, 121.4, 119.9, 118.8, 114.3, 114.1, 113.4, 100.2, 84.6, 41.6, 41.6, 41.2, 36.1, 31.3, 28.9, 28.2, 27.5. IR (KBr) *v* 3453, 2953, 1610, 1569, 1498, 1261, 1034, 755 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{40}N_3O$ $[M+H]^+$ 626.3166, found 626.3159.



3,3,10-trimethyl-13-(6-methyl-1-phenyl-1,4-dihydroquinolin-4-yl)-7-phenyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6e**)

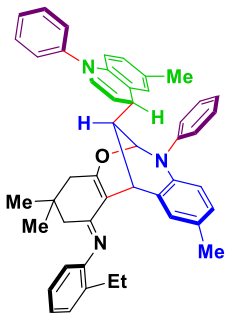
White solid obtained by filtration of the precipitate; 70.3 mg, 70% yield; dr > 20:1; reaction time = 6 h; mp 223.9-224.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.39 (m, 7H), 7.33-7.22 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.67-6.54 (m, 5H), 5.43 (s, 1H), 4.99-4.95 (m, 1H), 4.62 (s, 1H), 3.21-3.18 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.25-2.22 (m, 1H),

2.19 (s, 3H), 2.12 (d, *J* = 16.0 Hz, 1H), 2.03 (s, 2H), 1.86 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.3, 150.1, 145.4, 143.9, 139.5, 139.4, 131.9, 131.2, 130.5, 130.4, 129.9, 129.7, 129.5, 129.3, 127.9, 127.2, 126.6, 126.3, 126.2, 125.9, 125.7, 122.6, 119.7, 114.4, 113.9, 113.2, 99.9, 84.9, 41.6, 41.6, 41.1, 36.2, 31.3, 29.0, 28.1, 27.5, 20.8, 20.5, 20.3. IR (KBr) *v* 3442, 3253, 1610, 1499, 1271, 1033, 760 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{46}N_3O$ $[M+H]^+$ 668.3635, found 668.3661.



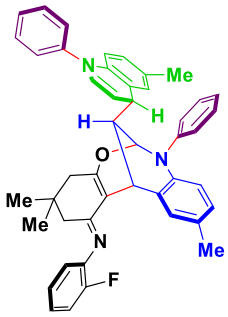
N-(4-fluorophenyl)-3,3,10-trimethyl-13-(6-methyl-1-phenyl-1,4-dihydroquinolin-4-yl)-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6f**)

White solid obtained by filtration of the precipitate; 63.4 mg, 63% yield; dr > 20:1;reaction time = 6 h; mp 233.4-233.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J_1 = J_2 = 4.0 Hz, 7H), 7.29-7.22 (m, 4H), 7.00-6.94 (m, 3H), 6.81 (t, *J* = 4.0 Hz,1H), 6.79 (t, *J* = 4.0 Hz,1H), 6.67-6.60 (m, 4H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.44 (t, *J* = 4.0 Hz, 1H), 4.97 (t, *J* = 8.0 Hz,1H), 4.59 (s, 1H), 3.20 (q, *J* = 8.0 Hz, 1H), 2.27 (s, 3H), 2.22 (tt, J_1 = J_2 = 4.0 Hz, 1H), 2.19 (s, 3H), 2.09 (d, *J* = 16.0 Hz, 1H), 2.04 (s, 2H), 1.84 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.8, 158.8 (d, *J* = 238.0 Hz, 1C), 148.8 (d, *J* = 3.0 Hz, 1C), 145.3, 143.9, 139.4 (d, *J* = 16.0 Hz, 1C), 131.9, 130.6, 130.3, 129.9, 129.7, 129.6, 127.9, 127.2, 126.7, 126.3, 126.0, 125.9, 125.8, 122.6, 120.9 (d, *J* = 8.0 Hz, 1C), 115.5, 115.3, 114.4, 114.0, 113.3, 99.9, 85.0, 41.6, 41.5, 41.2, 36.2, 31.3, 29.0, 28.1, 27.5, 20.5, 20.3. IR (KBr) *v* 3439, 2956, 1607, 1497, 1212, 760 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}FN_3O$ $[M+H]^+$ 672.3385, found 672.3392.



N-(2-ethylphenyl)-3,3,10-trimethyl-13-(6-methyl-1-phenyl-1,4-dihydroquinolin-4-yl)-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6g**)

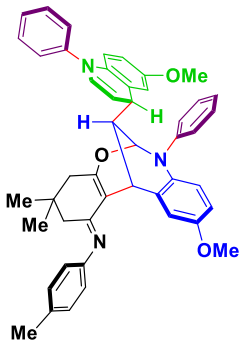
White solid obtained by filtration of the precipitate; 69.8 mg, 68% yield; dr > 20:1; reaction time = 6 h; mp 239.4-239.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 3.0 Hz, 6H), 7.08-6.99 (m, 6H), 6.87 (t, *J* = 6.0 Hz, 1H), 6.75 (t, *J* = 6.0 Hz, 2H), 6.57 (d, *J* = 6.0 Hz, 2H), 6.43 (d, *J* = 6.0 Hz, 1H), 6.38-6.29 (m, 3H), 5.19 (s, 1H), 4.74 (t, *J* = 3.0 Hz, 1H), 4.40 (s, 1H), 2.96-2.93 (m, 1H), 2.27-2.24 (m, 2H), 1.99 (d, *J* = 15.0 Hz, 7H), 1.84 (d, *J* = 18.0 Hz, 3H), 1.58 (d, *J* = 18.0 Hz, 1H), 0.87 (t, *J* = 6.0 Hz, 3H), 0.68 (s, 3H), 0.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 158.6, 150.9, 145.4, 143.9, 139.5, 139.3, 133.7, 131.8, 130.6, 130.5, 130.0, 129.8, 129.7, 129.6, 129.5, 128.0, 127.9, 127.2, 126.8, 126.3, 126.0, 125.8, 125.7, 122.7, 122.4, 119.3, 114.5, 114.0, 113.3, 100.0, 84.8, 41.8, 41.7, 36.2, 31.4, 28.4, 28.2, 24.2, 20.3, 14.0, three carbons missing in the aliphatic region. IR (KBr) *v* 3441, 2958, 1604, 1496, 1270, 763 cm^{-1}. HRMS (ESI) calcd for $C_{48}H_{48}N_3O$ $[M+H]^+$ 682.3792, found 682.3811.



N-(2-fluorophenyl)-3,3,10-trimethyl-13-(6-methyl-1-phenyl-1,4-dihydroquinolin-4-yl)-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6h**)

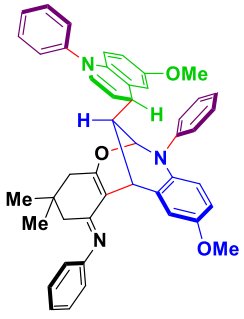
White solid obtained by filtration of the precipitate; 66.2 mg, 66% yield; dr > 20:1; reaction time = 6 h; mp 221.2-221.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.41 (m, 7H), 7.31-7.23 (m, 4H), 7.09-6.94 (m, 4H), 6.81-6.74 (m, 3H), 6.67-6.54 (m, 3H), 5.43 (s, 1H), 4.97 (t, *J* = 6.0 Hz, 1H), 4.62 (s, 1H), 3.21 (t, *J* = 6.0 Hz, 1H), 2.28-2.10 (m, 7H), 1.86 (d, *J* = 9.0 Hz, 1H), 2.06 (s, 3H),

0.94 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 159.6, 152.6 (d, *J* = 241.5 Hz, 1C), 145.4, 143.9, 140.1 (d, *J* = 10.5 Hz, 1C), 139.4 (d, *J* = 28.5 Hz, 1C), 132.0, 130.6, 129.9, 129.7, 129.6, 128.1, 127.2, 126.7, 126.4, 125.9, 125.8, 124.1, 123.2, 123.1, 123.1, 122.6, 122.6, 122.6, 115.9, 115.6, 114.6, 113.9, 113.2, 99.8, 85.2, 41.7, 41.5, 41.4, 36.2, 31.4, 28.8, 28.0, 27.6, 20.4, 20.3. IR (KBr) *v* 3444, 2952, 1623, 1495, 1265, 1033, 759 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}FN_3O$ $[M+H]^+$ 672.3385, found 672.3362.



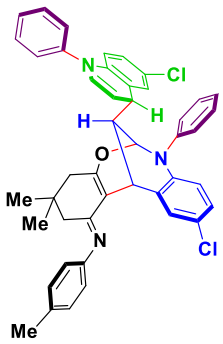
10-methoxy-13-(6-methoxy-1-phenyl-1,4-dihydroquinolin-4-yl)-3,3-dimethyl-7-phenyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6i**)

White solid obtained by filtration of the precipitate; 61.2 mg, 58% yield; dr > 20:1; reaction time = 6 h; mp 218.1-218.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.0 Hz, 6H), 7.23-7.15 (m, 5H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.63-6.49 (m, 8H), 5.44 (s, 1H), 4.84 (t, *J* = 8.0 Hz,1H), 4.55 (s, 1H), 3.67 (s, 3H), 3.46 (s, 3H), 3.16 (q, *J* = 8.0 Hz,1H), 2.24 (s, 3H), 2.17 (d, *J* = 8.0 Hz, 1H), 2.02 (d, *J* = 16.0 Hz, 1H), 1.97 (s, 2H), 1.81 (d, *J* = 16.0 Hz, 1H), 0.84 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 158.7, 154.8, 152.6, 150.2, 145.6, 144.0, 135.8, 135.4, 132.0, 131.3, 129.7, 129.7, 129.4, 127.3, 127.0, 126.0, 125.7, 125.6, 124.1, 119.7, 115.3, 114.3, 114.2, 113.8, 113.1, 112.8, 99.1, 85.1, 55.7, 55.6, 41.6, 41.6, 41.2, 36.7, 31.3, 28.8, 28.4, 27.7, 20.8. IR (KBr) *v* 3446, 2948, 1606, 1496, 1219, 760 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{46}N_3O_3$ $[M+H]^+$ 700.3534, found 700.3512.



10-methoxy-13-(6-methoxy-1-phenyl-1,4-dihydroquinolin-4-yl)-3,3-dimethyl-*N*,7-diphenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6j**)

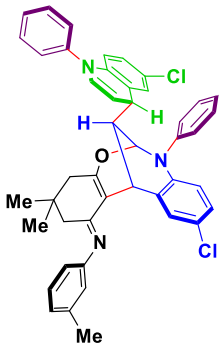
White solid obtained by filtration of the precipitate; 62.9 mg, 62% yield; dr > 20:1; reaction time = 6 h; mp 196.3-196.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.37 (m, 10H), 7.28 (t, *J* = 8.0 Hz,4H), 6.93 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.56 (dd, J_1 = J_2 = 4.0 Hz, 3H), 5.43 (t, *J* = 4.0 Hz, 1H), 4.96 (t, *J* = 8.0 Hz,1H), 4.55 (s, 1H), 3.18 (q, *J* = 8.0 Hz, 1H), 2.26 (s, 3H), 2.22 (t, *J* = 4.0 Hz,1H), 2.20 (s, 3H), 2.06 (d, *J* = 16.0 Hz, 1H), 2.04 (s, 2H), 1.84 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.2, 151.8, 145.3, 143.9, 139.5, 139.4, 131.9, 131.7, 130.7, 130.3, 129.9, 129.7, 129.6, 128.0, 127.2, 126.8, 126.3, 126.0, 125.9, 125.8, 122.6, 121.7, 114.8, 114.3, 114.0, 113.3, 99.9, 85.0, 41.6, 41.5, 41.3, 36.1, 31.4, 29.0, 28.1, 27.5, 20.5, 20.3. IR (KBr) *v* 3443, 2954, 1607, 1493, 1379, 1219, 761 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{44}N_3O_3$ $[M+H]^+$ 686.3377, found 686.3351.



10-chloro-13-(6-chloro-1-phenyl-1,4-dihydroquinolin-4-yl)-3,3-dimethyl-7-phenyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6k**)

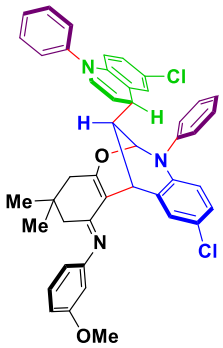
White solid obtained by filtration of the precipitate; 67.2 mg, 63% yield; dr > 20:1; reaction time = 6 h; mp 253.2-253.7 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 4.0 Hz, 1H), 7.47 (q, *J* = 8.0 Hz, 4H),7.38 (d, *J* = 4.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.17 (d, *J* = 4.0 Hz, 1H),7.11 (d, *J* = 8.0 Hz, 2H), 6.97 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.93 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.62-6.54 (m, 5H), 5.37 (s, 1H), 4.96 (t, *J* = 8.0 Hz, 1H), 4.58 (s, 1H), 3.15 (q, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.26 (tt, J_1 = J_2 = 4.0 Hz, 1H), 2.14 (d, *J* = 16.0 Hz, 1H), 2.04 (s, 2H), 1.90 (d, *J* = 16.0 Hz, 1H), 0.93 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 158.3, 149.7, 144.6, 143.3, 140.9, 140.6, 132.2, 131.6, 130.0, 129.4, 129.3, 128.9, 127.7, 126.7, 126.7, 126.6, 126.6, 126.2, 126.0, 125.0, 123.7, 123.6, 119.7, 115.3, 114.8, 113.8, 99.6, 84.1, 41.5, 41.4, 41.0, 36.1, 31.3, 28.7, 28.1, 27.7, 20.8. IR

(KBr) *v* 3441, 2955, 1610, 1490, 1266, 1173, 1033, 758 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{40}Cl_2N_3O$ $[M+H]^+$ 708.2543, found 708.2531.



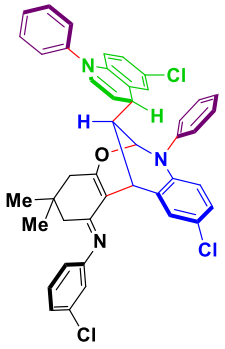
10-chloro-13-(6-chloro-1-phenyl-1,4-dihydroquinolin-4-yl)-3,3-dimethyl-7-phenyl-*N*-(*m*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6l**)

White solid obtained by filtration of the precipitate; 63.1 mg, 59% yield; dr > 20:1; reaction time = 6 h; mp 247.0-247.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.0 Hz, 1H), 7.42-7.35 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 4H), 7.12-7.09 (m, 2H), 6.90-6.84 (m, 2H), 6.76 (d, *J* = 8.0 Hz,1H), 6.52-6.46 (m, 4H), 6.42 (d, *J* = 8.0 Hz,1H), 5.30 (t, *J* = 4.0 Hz, 1H), 4.87 (t, *J* = 8.0 Hz,1H), 4.50 (s, 1H), 3.09 (q, *J* = 8.0 Hz, 1H), 2.25 (s, 3H), 2.18 (tt, J_1 = J_2 = 4.0 Hz, 1H), 2.06 (d, *J* = 16.0 Hz, 1H), 1.96 (s, 2H), 1.82 (d, *J* = 16.0 Hz, 1H), 0.86 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 158.4, 152.3, 144.5, 143.3, 140.8, 140.6, 138.6, 132.2, 130.0, 129.3, 128.9, 128.7, 127.6, 126.7, 126.6, 126.6, 126.2, 126.0, 123.7, 123.6, 123.1, 120.5, 116.7, 115.3, 114.8, 113.7, 99.6, 84.2, 41.5, 41.3, 41.1, 36.1, 31.3, 28.7, 28.1, 27.7, 21.5, two carbons missing in the aromatic region. IR (KBr) *v* 3443, 2956, 1622, 1485, 1378, 753 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{39}Cl_2N_3NaO$ $[M+Na]^+$ 730.2362, found 730.2349.



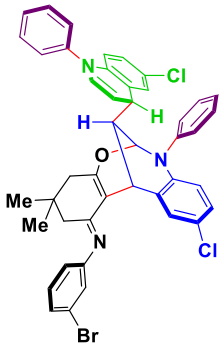
10-chloro-13-(6-chloro-1-phenyl-1,4-dihydroquinolin-4-yl)-*N*-(3-methoxyphenyl)-3,3-dimethyl-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6m**)

White solid obtained by filtration of the precipitate; 68.9 mg, 63% yield; dr > 20:1; reaction time = 6 h; mp 249.9-250.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 4.0 Hz, 1H), 7.42-7.36 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 4H), 7.14-7.09 (m, 2H), 6.90-6.84 (m, 2H), 6.52-6.46 (m,4H), 6.21 (d, *J* = 8.0 Hz,2H), 5.30 (t, *J* = 4.0 Hz, 1H), 4.87 (t, *J* = 8.0 Hz,1H), 4.49 (s, 1H), 3.72 (s, 3H), 3.09 (q, *J* = 8.0 Hz, 1H), 2.19 (tt, J_1 = J_2 = 4.0 Hz, 1H), 2.08 (d, *J* = 16.0 Hz, 1H), 1.97 (s, 2H), 1.83 (d, *J* = 16.0 Hz, 1H), 0.87 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.3, 158.7, 153.8, 144.5, 143.3, 140.8, 140.5, 132.2, 130.0, 129.6, 129.3, 128.8, 127.6, 127.6, 126.7, 126.6, 126.2, 126.0, 123.7, 123.6, 115.3, 114.8, 113.7, 112.1, 108.4, 105.1, 99.6, 84.2, 55.2, 41.5, 41.3, 41.0, 36.1, 31.3, 28.7, 28.1, 27.7, two carbons missing in the aromatic region. IR (KBr) *v* 3441, 2954, 1593, 1485, 1379, 1289, 1146, 768 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{40}Cl_2N_3O_2$ $[M+H]^+$724.2492, found 724.2484.



10-chloro-13-(6-chloro-1-phenyl-1,4-dihydroquinolin-4-yl)-*N*-(3-chlorophenyl)-3,3-dimethyl-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6n**)

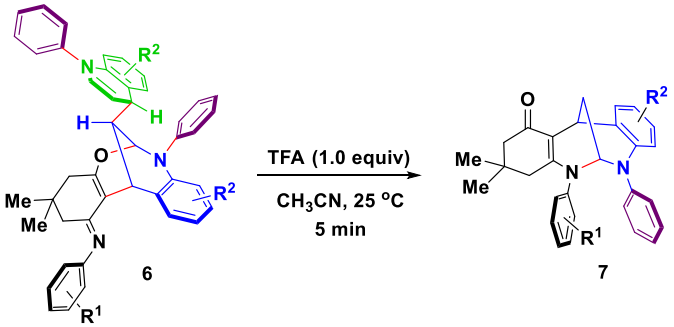
White solid obtained by filtration of the precipitate; 66.0 mg, 60% yield; dr > 20:1; reaction time = 6 h; mp 244.7-245.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.50-7.44 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.34-7.27 (m, 4H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 4.0 Hz, 1H), 7.00-6.93 (m, 3H), 6.72 (t, *J* = 4.0 Hz, 1H), 6.60-6.54 (m, 4H), 5.39 (t, *J* = 4.0 Hz, 1H), 4.94 (t, *J* = 8.0 Hz, 1H), 4.53 (s, 1H), 3.15 (q, *J* = 8.0 Hz, 1H), 2.25 (tt,J_1 = J_2 = 4.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 2.06 (s, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 0.94 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 159.4, 153.7, 144.4, 143.3, 140.8, 140.6, 134.4, 132.3, 130.0, 130.0, 129.9, 129.2, 128.8, 127.6, 127.4, 126.7, 126.7, 126.6, 126.3, 126.0, 123.7, 123.6, 122.3, 119.9, 118.2, 115.3, 114.9, 113.6, 99.4, 84.3, 41.5, 41.3, 36.1, 31.4, 28.6, 28.1, 27.7, one carbon missing in the aliphatic region. IR (KBr) *v* 3438, 2956, 1618, 1588, 1486, 754 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{36}Cl_3N_3NaO$ $[M+Na]^+$ 750.1816, found 750.1795.



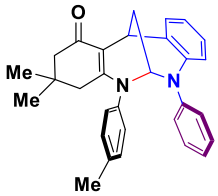
N-(3-bromophenyl)-10-chloro-13-(6-chloro-1-phenyl-1,4-dihydroquinolin-4-yl)-3,3-dimethyl-7-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**6o**)

White solid obtained by filtration of the precipitate; 66.8 mg, 58% yield; dr > 20:1; reaction time = 6 h; mp 241.8-242.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 4.0 Hz, 1H), 7.48 (q, *J* = 8.0 Hz, 4H), 7.39-7.27 (m, 6H), 7.15 (d, *J* = 4.0 Hz, 3H), 6.99-6.93 (m, 2H), 6.88 (s, 1H), 6.63-6.54 (m, 4H), 5.39 (s, 1H), 4.94 (t, *J* = 8.0 Hz, 1H), 4.52 (s, 1H), 3.15 (q, *J* = 8.0 Hz, 1H), 2.25 (d, *J* = 8.0 Hz, 1H), 2.10 (d, *J* = 16.0 Hz, 1H), 2.06 (s, 2H), 1.91 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.5, 153.8, 144.4, 143.3, 140.8, 140.5, 132.3, 130.2, 130.0, 130.0, 129.2, 128.8, 127.6, 127.4, 126.7, 126.7, 126.6, 126.3, 126.0, 125.2, 123.7, 123.6, 122.8, 122.6, 118.6, 115.3, 114.9, 113.6, 99.4, 84.3, 41.5, 41.3, 36.1, 31.4, 28.6, 28.1, 27.7, one carbon missing in the aliphatic region. IR (KBr) *v* 3442, 2957, 1615, 1589, 1486, 1380, 754 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{36}BrCl_2N_3NaO$ $[M+Na]^+$ 794.1311, found 794.1283.

4. Experimental data for the formation of 7

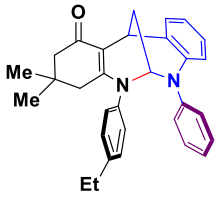


General procedure： To a 5.0 mL vial were successively added the above-obtained bridged products **6** (0.10 mmol) with 1.0 equivalent of TFA in 1.0 mL of CH_3CN. The resulting mixture was stirred at room temperature for 5 min. Upon completion of the reaction (monitoring by TLC), the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **7**.



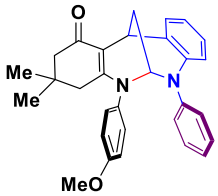
3,3-dimethyl-7-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g]*[1,3]diazocin-1(2*H*)-one (**7a**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 40.1 mg, 92% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 12.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 3H), 7.03 (t, *J* = 8.0 Hz, 3H), 6.82 (d, *J* = 12.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 12.0 Hz, 2H), 5.21 (s, 1H), 4.42 (s, 1H), 2.28 (s, 3H), 2.16 (tt,J_1 = J_2 = 4.0 Hz, 1H), 2.10 (s, 2H), 1.94 (tt, J_1 = J_2 = 4.0 Hz, 1H), 1.87 (s, 2H), 0.87 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 155.6, 147.0, 141.0, 140.8, 137.2, 130.0, 129.8, 129.6, 128.9, 126.8, 125.9, 125.0, 119.2, 116.3, 113.9, 75.8, 50.1, 41.8, 32.8, 28.6, 27.8, 26.8, 25.4, 21.0. IR (KBr) *v* 3442, 2954, 1765, 1498, 1196, 757 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{31}N_2O$ $[M+H]^+$ 435.2431, found 435.2421.



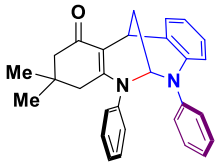
5-(4-ethylphenyl)-3,3-dimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**7b**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 41.8 mg, 93% yield; dr > 20:1; reaction time = 5 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 4.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 4H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 8.0 Hz, 3H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.37 (s, 1H), 4.54 (s, 1H), 2.68 (q, *J* = 8.0 Hz, 2H), 2.43-2.26 (m, 3H), 2.10-1.98 (m, 3H), 1.26 (t, *J* = 8.0 Hz, 3H), 0.97 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 161.1, 146.6, 144.5, 140.2, 140.1, 129.6, 129.1, 129.0, 128.9, 126.4, 126.3, 125.2, 119.7, 116.7, 112.8, 76.4, 47.5, 41.8, 32.8, 28.4, 28.4, 27.5, 26.5, 25.3, 15.4. IR (KBr) *v* 3442, 2960, 1573, 1497, 1378, 1194, 754 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{33}N_2O$ $[M+H]^+$ 449.2587, found 449.2576.



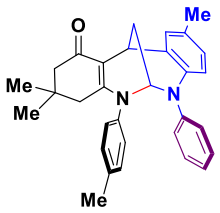
5-(4-methoxyphenyl)-3,3-dimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7c**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 43.4 mg, 96% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.15 (dd, J_1 =J_2 = 8.0 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.77 (dd, J_1 =J_2 = 8.0 Hz, 6H), 6.64 (t, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 2H), 5.19 (s, 1H), 4.42 (s, 1H), 3.73 (s, 3H), 2.15 (tt, J_1 =J_2 = 4.0 Hz, 1H), 2.12 (s, 2H), 1.93 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.86 (s, 2H), 0.86 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 158.6, 156.6, 147.0, 140.6, 136.2, 129.7, 129.5, 128.9, 126.4, 125.9, 124.9, 119.3, 116.5, 114.5, 113.4, 76.0, 55.4, 49.6, 41.7, 32.6, 28.5, 27.7, 26.6, 25.4. IR (KBr) *v* 3442, 2954, 1619, 1567, 1499, 755 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{31}N_2O_2$ $[M+H]^+$ 451.2380, found 451.2382.



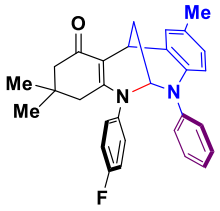
3,3-dimethyl-5,7-diphenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7d**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 38.3 mg, 91% yield; dr > 20:1;reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J_1 =J_2 = 4.0 Hz, 1H), 7.29-7.21 (m, 6H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.89 (tt, J_1 =J_2 = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.74 (tt, J_1 =J_2 = 8.0 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.50 (s, 1H), 2.26 (tt, J_1 =J_2 = 4.0 Hz, 1H), 2.19 (s, 2H), 2.04 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.96 (d, *J* = 8.0 Hz, 2H), 0.95 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 155.2, 147.0, 143.7, 140.8, 129.6, 129.6, 129.4, 129.0, 127.3, 126.9, 126.0, 125.1, 119.2, 116.2, 114.2, 75.9, 50.2, 41.9, 32.9, 28.6, 27.8, 26.8, 25.5. IR (KBr) *v* 3441, 2948, 1580, 1489, 1374, 758 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{29}N_2O$ $[M+H]^+$ 421.2274, found 421.2279.



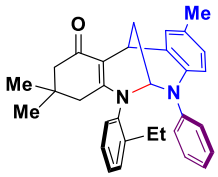
3,3,10-trimethyl-7-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7e**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 43.5 mg, 97% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 4.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 4H), 6.97 (t, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 3H), 6.48 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 1H), 4.42 (s, 1H), 2.31 (s, 3H), 2.23 (d, *J* = 4.0 Hz, 2H), 2.21-2.17 (m, 1H), 2.16 (s, 3H), 1.96-1.83 (m, 3H), 0.88 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 159.4, 147.3, 140.3, 138.0, 137.7, 130.2, 129.5, 129.5, 129.1, 127.0, 125.9, 124.7, 117.3, 113.0, 76.5, 48.3, 41.8, 32.8, 28.7, 27.5, 26.4, 25.3, 21.1, 20.5. IR (KBr) *v* 3440, 2962, 1678, 1529, 1199, 811 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{33}N_2O$ $[M+H]^+$ 449.2587, found 449.2585.



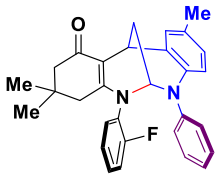
5-(4-fluorophenyl)-3,3,10-trimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7f**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 43.9 mg, 97% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.11 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 4H),6.70 (d, *J* = 8.0 Hz, 3H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.18 (s, 1H), 4.38 (s, 1H), 2.17-2.11 (m, 6H), 1.92-1.76 (m, 3H), 0.87 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 161.4 (d, *J* = 246.0 Hz, 1C), 155.4, 147.3, 139.5, 137.9, 129.8, 129.5, 129.4, 128.8, 126.8, 126.1, 124.7, 116.8, 116.2 (d, *J* = 22.0 Hz, 1C), 113.9, 76.0, 49.8, 41.7, 32.7, 28.8, 27.5, 26.5, 25.4, 20.4. IR (KBr) *v* 3442, 2953, 1567, 1498, 1374, 1204, 735 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}FN_2O$ $[M+H]^+$ 453.2337, found 453.2334.



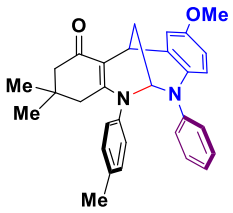
5-(2-ethylphenyl)-3,3,10-trimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7g**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 41.7 mg, 90% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (td, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 7.36 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.97 (s, 1H), 4.58 (s, 1H), 2.58 (q, *J* = 8.0 Hz, 2H), 2.32-2.26 (m, 6H), 2.03 (d, *J* = 16.0 Hz, 2H), 1.72 (d, *J* = 16.0 Hz, 1H), 1.29 (t, *J* = 8.0 Hz, 3H), 0.99 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 158.1, 148.0, 141.0, 140.3, 137.2, 130.9, 130.4, 129.6, 129.3, 128.8, 126.9, 126.9, 124.7, 124.0, 118.6, 112.5, 75.7, 48.9, 41.3, 32.8, 29.4, 27.1, 26.1, 24.6, 23.2, 21.5, 14.2, one carbon missing in the aromatic region. IR (KBr) *v* 3440, 2957, 1562, 1491, 1377, 771 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{35}N_2O$ $[M+H]^+$ 463.2744, found 463.2741.



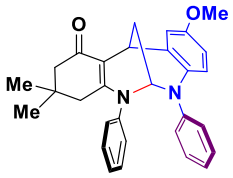
5-(2-fluorophenyl)-3,3,10-trimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7h**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 40.4 mg, 89% yield; dr = 3:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 5H), 7.10-6.93 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.70 (dd, J_1 =J_2 = 8.0 Hz, 1H),6.56 (t, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 4.47 (s, 1H), 2.29-2.18 (m, 6H), 2.12-2.07 (m, 1H), 1.99 (d, *J* = 16.0 Hz, 1H), 1.80 (d, *J* = 16.0 Hz, 1H), 0.96 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 158.6 (d, *J* = 247.0 Hz, 1C), 155.6, 147.2, 138.0, 131.8, 129.8, 129.5, 129.5, 128.9 (d, *J* = 38.0 Hz, 1C), 126.8, 126.2, 125.5, 124.7, 124.5 (d, *J* = 4.0 Hz, 1C), 116.7, 116.4 (d, *J* = 20.0 Hz, 1C), 113.6, 75.1, 49.8, 41.2, 32.7, 29.1, 27.4, 26.5, 25.3, 20.4. IR (KBr) *v* 3443, 2951, 1578, 1497, 1378, 761 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}FN_2O$ $[M+H]^+$ 453.2337, found 453.2333.



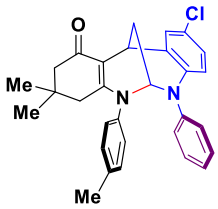
10-methoxy-3,3-dimethyl-7-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7i**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 44.9 mg, 97% yield; dr > 20:1;reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.09 (m, 5H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 12.0 Hz, 3H), 6.61 (d, *J* = 12.0 Hz, 1H), 6.52 (dd, J_1=J_2 = 4.0 Hz, 1H), 5.23 (s, 1H), 4.48 (s, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 2.26 (d, *J* = 16.0 Hz, 2H), 2.18 (s, 1H), 2.02-1.86 (m, 3H), 0.95 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.1, 153.3, 147.9, 140.7, 137.4, 133.8, 131.5, 130.1, 129.3, 125.4, 124.0, 119.1, 113.2, 112.8, 76.3, 55.6, 49.9, 41.6, 32.8, 28.7, 27.7, 26.8, 25.1, 21.1. IR (KBr) *v*3442, 2950, 1567, 1498, 1378, 1203, 764 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{33}N_2O_2$ $[M+H]^+$ 465.2537, found 465.2540.



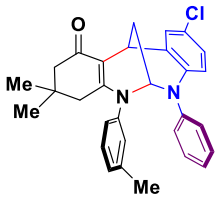
10-methoxy-3,3-dimethyl-5,7-diphenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7j**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 40.9 mg, 91% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.0 Hz, 3H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 4.0 Hz, 1H),7.01 (t, *J* = 8.0 Hz, 3H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.52 (dd, J_1=J_2 = 4.0 Hz, 1H), 5.26 (s, 1H), 4.49 (s, 1H), 3.76 (s, 3H), 2.27 (tt, J_1=J_2 = 4.0 Hz, 1H), 2.19 (d, *J* = 4.0 Hz, 2H), 2.02-1.95 (m, 2H), 1.89 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 155.7, 153.3, 147.8, 143.4, 133.8, 131.4, 129.5, 129.4, 127.5, 125.5, 124.1, 119.0, 113.5, 113.2, 112.9, 76.3, 55.6, 49.9, 41.7, 32.8, 28.8, 27.6, 26.9, 25.2. IR (KBr) *v*3441, 2953, 1561, 1491, 1203, 1048, 761 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{31}N_2O_2$ $[M+H]^+$ 451.2380, found 451.2378.



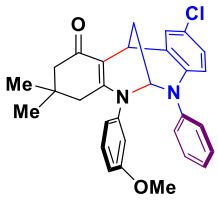
10-chloro-3,3-dimethyl-7-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7k**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 45.1 mg, 96% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 3H), 7.04 (t, *J* = 8.0 Hz, 3H), 6.75-6.72 (m, 3H), 6.42 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 1H), 4.37 (s, 1H), 2.28 (s, 3H), 2.15 (s, 2H), 2.12 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.94 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.88 (d, *J* = 4.0 Hz, 2H), 0.87 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 157.0, 146.5, 140.6, 139.5, 137.6, 131.1, 130.1, 129.7, 128.4, 126.6, 126.0, 125.4, 123.9, 117.4, 112.9, 75.7, 49.4, 41.8, 32.8, 28.5, 27.7, 26.7, 25.2, 21.0. IR (KBr) *v* 3440, 2953, 1575, 1481, 1417, 1378, 1189, 763 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}ClN_2O$ $[M+H]^+$469.2041, found 469.2048.



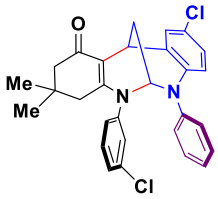
10-chloro-3,3-dimethyl-7-phenyl-5-(*m*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7l**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 42.1 mg, 90% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 4H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.76 (dd, J_1 =J_2 = 4.0 Hz, 4H), 6.43 (d, *J* = 12.0 Hz, 1H), 5.26 (s, 1H), 4.37 (s, 1H), 2.20-2.11 (m, 6H), 1.97 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.91 (s, 2H), 0.88 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 157.7, 146.3, 143.0, 139.7, 139.4, 130.8, 129.8, 129.3, 128.5, 128.4, 126.8, 126.2, 125.6, 123.8, 117.1, 116.9, 112.7, 75.6, 49.0, 41.9, 32.8, 28.5, 27.7, 26.7, 25.3, 21.2. IR (KBr) *v* 3442, 2955, 1567, 1486, 1378, 731 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}ClN_2O$ $[M+H]^+$ 469.2041, found 469.2046.



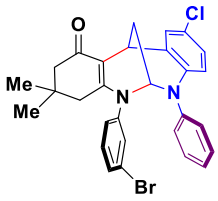
10-chloro-5-(3-methoxyphenyl)-3,3-dimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7m**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 41.9 mg, 86% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.0 Hz, 1H), 7.21 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 7.14-7.07 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.77-6.73 (m, 2H), 6.38 (d, *J* = 8.0 Hz, 3H), 5.24 (s, 1H), 4.35 (s, 1H), 3.60 (s, 3H), 2.13-2.10 (m, 3H), 1.97-1.92 (m, 3H), 0.89 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 160.4, 155.2, 146.4, 144.7, 139.8, 130.9, 130.0, 129.9, 128.4, 127.2, 126.0, 125.6, 123.7, 116.8, 116.8, 113.9, 113.5, 75.4, 55.4, 50.2, 41.9, 32.9, 28.5, 27.9, 26.9, 25.3. IR (KBr) *v* 3443, 2952, 1627, 1572, 1486, 1378, 775 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}ClN_2O_2$ $[M+H]^+$ 485.1990, found 485.1997.



10-chloro-5-(3-chlorophenyl)-3,3-dimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7n**)

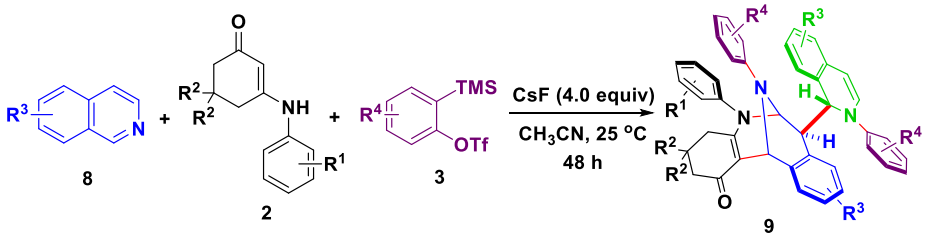
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 41.2 mg, 84% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.25-7.12 (m,6H), 6.84 (d, *J* =8.0 Hz,2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.40 (d, *J* =8.0 Hz,1H), 5.25 (s, 1H), 4.33 (s, 1H), 2.12 (d, *J* =12.0 Hz, 3H), 1.96 (d, *J* =12.0 Hz, 1H), 1.89 (s, 2H), 0.89 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 154.5, 146.1, 144.7, 139.7, 134.9, 130.6, 130.3, 129.9, 128.4, 128.3, 127.5, 127.2, 126.1, 126.0, 123.7, 116.6, 114.3, 75.4, 50.0, 42.0, 32.9, 28.5, 27.8, 26.8, 25.4. IR (KBr) *v* 3441, 2955, 1629, 1571, 1483, 1377, 807 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{27}Cl_2N_2O$ $[M+H]^+$ 489.1495, found 489.1476.



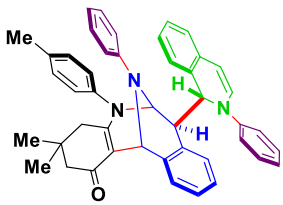
5-(3-bromophenyl)-10-chloro-3,3-dimethyl-7-phenyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**7o**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 46.0 mg, 86% yield; dr > 20:1; reaction time = 5 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.0 Hz, 2H), 7.33 (d, *J* =8.0 Hz,1H), 7.24 (t, *J* =8.0 Hz,2H), 7.11 (q, *J* = 8.0 Hz, 2H), 6.84 (d, *J* =8.0 Hz, 2H), 6.77 (dd, J_1 =J_2 = 4.0 Hz, 2H), 6.42 (d, *J* =8.0 Hz,1H), 5.27 (s, 1H), 4.34 (s, 1H), 2.20 (s, 2H), 2.14 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.98 (tt, J_1 =J_2 = 4.0 Hz, 1H), 1.90 (s, 2H), 0.89 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 156.5, 146.0, 144.5, 139.5, 130.8, 130.6, 130.4, 130.0, 128.3, 127.1, 126.3, 126.1, 123.9, 122.9, 116.8, 113.8, 75.6, 49.1, 42.0, 33.0, 28.4, 27.8, 26.8, 25.5, one carbon missing in the aromatic region. IR (KBr) *v* 3443, 2954, 1628, 1568, 1483, 1378, 733 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{27}BrClN_2O$ $[M+H]^+$ 533.0990, found 533.0994.

5. Experimental data for the formation of 9

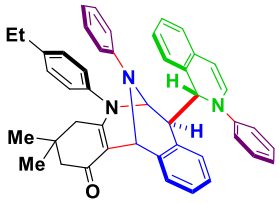


General procedure: To a 5.0 mL vial were successively added isoquinolines **8** (0.30 mmol), enaminones **2** (0.15 mmol), aryne precursors **3** (0.60 mmol), CsF (0.60 mmol) and 1.0 mL of CH_3CN. The resulting mixture was stirred at 60 °C in oil bath. Upon completion of the reaction (monitoring by TLC), the products **9** were precipitated from the reaction mixtures and only a filtration was needed to purify them.



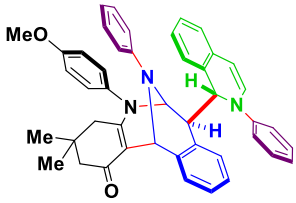
3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9a**)

White solid obtained by filtration of the precipitate; 82.2 mg, 86% yield; dr > 20:1; reaction time = 6 h; mp 243.2-243.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.14 (q, *J* = 8.0 Hz, 2H), 7.07-6.88 (m, 9H), 6.75 (q, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.52 (br, 2H), 6.34 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.64 (s, 1H), 5.23 (d, *J* = 12.0 Hz, 1H), 3.26 (d, *J* = 12.0 Hz, 1H), 2.32 (s, 3H), 2.07-1.93 (m, 3H), 1.51 (d,*J* = 16.0 Hz, 1H), 0.70 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 155.3, 148.3, 145.3, 138.8, 137.8, 136.7, 131.3, 130.5, 130.1, 130.0, 129.4, 129.2, 128.9, 128.5, 127.7, 127.3, 127.2, 126.9, 126.0, 125.0, 123.6, 121.3, 121.0, 117.9, 117.0, 109.7, 105.9, 71.9, 63.2, 52.4, 49.5, 43.3, 41.1, 33.4, 29.8, 26.2, 21.0. IR (KBr) *v* 3447, 2953, 1610, 1564, 1501, 1259, 761 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{42}N_3O$ $[M+H]^+$ 640.3322, found 640.3323.



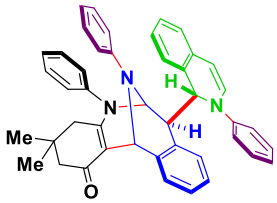
5-(4-ethylphenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9b**)

White solid obtained by filtration of the precipitate;85.6 mg, 87% yield; dr > 20:1;reaction time = 2 h; mp 255.9-256.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.06 (q, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 2H), 6.95-6.88 (m, 6H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.68 (t, *J* = 8.0 Hz, 2H), 6.51 (dd, J_1 = J_2 = 4.0 Hz, 3H), 6.27 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 5.75 (d, *J* = 4.0 Hz, 1H), 5.57 (s, 1H), 5.14 (d, *J* = 8.0 Hz, 1H), 3.17 (d, *J* = 8.0 Hz, 1H), 2.54 (q, *J* = 8.0 Hz, 2H), 1.92 (q, *J* = 16.0 Hz, 2H), 1.46 (d, *J* = 16.0 Hz, 1H), 1.17 (t,*J* = 8.0 Hz, 3H), 0.63 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 155.3, 148.4, 145.3, 143.1, 138.9, 138.0, 131.3, 130.6, 129.4, 129.3, 128.9, 128.9, 128.5, 127.7, 127.4, 127.2, 126.9, 126.1, 126.0, 125.0, 123.6, 121.4, 121.1, 117.9, 117.1, 109.6, 105.9, 72.1, 63.2, 52.4, 49.5, 42.3, 41.2, 33.5, 29.8, 28.4, 26.3, 15.6. IR (KBr) *v* 3442, 2956, 1607, 1559, 1498, 1390, 1257, 761 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}N_3NaO$ $[M+Na]^+$676.3298, found 676.3305.



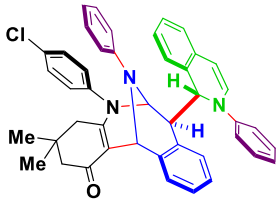
5-(4-methoxyphenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9c**)

White solid obtained by filtration of the precipitate; 88.7 mg, 90% yield; dr> 20:1; reaction time = 2 h; mp 238.1-238.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 4.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95-6.82 (m, 6H), 6.70-6.61 (m, 5H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.45 (br, 1H), 6.27 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 5.79 (d, *J* = 8.0 Hz, 1H), 5.50 (s, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 3.72 (s, 3H), 3.22 (d, *J* = 8.0 Hz, 1H), 1.98-1.86 (m, 3H), 1.43 (d,*J* = 16.0 Hz, 1H), 0.62 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 158.3, 155.6, 148.4, 145.3, 138.8, 133.2, 131.3, 130.5, 129.5, 129.3, 129.2, 128.9, 128.5, 127.7, 127.4, 127.3, 126.9, 126.1, 126.0, 125.0, 123.6, 121.3, 121.1, 117.8, 117.1, 109.4, 105.9, 72.2, 63.3, 55.5, 52.3, 49.4, 42.4, 41.0, 33.3, 29.7, 26.4. IR (KBr) *v* 3443, 2953, 1560, 1501, 1251, 760 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{41}N_3NaO_2$ $[M+Na]^+$ 678.3091, found 678.3094.



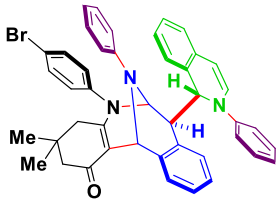
3,3-dimethyl-5,13-diphenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9d**)

White solid obtained by filtration of the precipitate; 71.9 mg, 77% yield; dr > 20:1; reaction time = 2 h; mp 183.7-184.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.25-7.12 (m, 7H), 7.06-6.88 (m, 7H), 6.77 (q, *J* = 8.0 Hz, 2H), 6.64 (br, 2H), 6.59 (d, *J* = 4.0 Hz, 1H), 6.33 (s, 1H), 6.30 (d, *J* = 4.0 Hz, 2H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.67 (s, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 3.23 (d, *J* = 12.0 Hz, 1H), 2.06 (dd, J_1 =J_2 = 4.0 Hz, 2H), 1.96 (d,*J* = 16.0 Hz, 1H), 1.51 (d,*J* = 16.0 Hz, 1H), 0.71 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 155.1, 148.4, 145.3, 140.6, 138.7, 131.3, 130.7, 129.6, 129.4, 129.3, 128.9, 128.6, 127.7, 127.4, 127.3, 127.0, 126.8, 126.1, 126.1, 125.1, 123.7, 121.5, 121.1, 117.9, 117.1, 110.1, 106.0, 72.0, 63.3, 52.5, 49.5, 42.2, 41.3, 33.6, 29.8, 26.2. IR (KBr) *v* 3451, 2954, 1603, 1558, 1493, 1390, 735 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{40}N_3O$ $[M+H]^+$ 626.3166, found 626.3189.



5-(4-chlorophenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9e**)

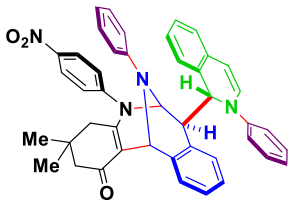
White solid obtained by filtration of the precipitate; 91.1 mg, 92% yield; dr > 20:1; reaction time = 2 h; mp 236.2-236.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.19-7.11 (m, 6H), 7.05-6.96 (m, 6H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.76 (q, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.65 (s, 1H), 5.23 (d, *J* = 8.0 Hz, 1H), 3.21 (d, *J* = 8.0 Hz, 1H), 2.07-1.94 (m, 3H), 1.48 (d,*J* = 16.0 Hz, 1H), 0.72 (s, 3H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 154.4, 148.2, 145.2, 139.1, 138.5, 132.3, 131.4, 130.6, 129.6, 129.3, 129.2, 128.9, 128.6, 127.6, 127.5, 127.4, 127.0, 126.2, 126.0, 125.1, 123.7, 121.6, 121.2, 117.9, 117.0, 110.7, 105.9, 72.0, 63.2, 52.4, 49.5, 42.3, 41.3, 33.6, 29.9, 26.1. IR (KBr) *v* 3444, 2954, 1597, 1561, 1492, 759 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}ClN_3NaO$ $[M+Na]^+$ 682.2596, found 682.2603.



5-(4-bromophenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9f**)

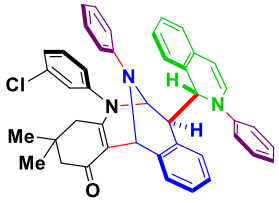
White solid obtained by filtration of the precipitate; 99.8 mg, 94% yield; dr > 20:1; reaction time = 2 h; mp 244.0-244.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.28-7.20 (m, 4H), 7.13-7.04 (m, 4H), 6.98-6.88 (m, 6H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.72-6.65 (m, 2H), 6.54 (dd, J_1 =J_2 = 4.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 8.0 Hz, 2H), 6.19 (s, 1H), 5.81 (d, *J* = 8.0 Hz, 1H), 5.59 (s, 1H), 5.16 (d, *J* = 8.0 Hz, 1H), 3.13 (d, *J* = 12.0 Hz, 1H), 2.00-1.87 (m, 3H), 1.41 (d,*J* = 16.0 Hz, 1H), 0.65 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 154.3, 148.2, 145.2, 139.6, 138.5, 132.6, 131.4, 130.6, 129.3, 129.2, 128.9, 128.6, 127.5, 127.5, 127.4, 127.0, 126.2, 126.0, 125.1, 123.7, 121.6, 121.2, 120.2, 117.9, 117.1, 110.8, 105.9, 72.0, 63.2, 52.4,

49.5, 42.3, 41.3, 33.6, 29.9, 26.1. IR (KBr) *v* 3448, 2954, 1593, 1561, 1491, 1387, 759 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}BrN_3NaO$ $[M+Na]^+$ 726.2090, found 726.2096.



3,3-dimethyl-5-(4-nitrophenyl)-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9g**)

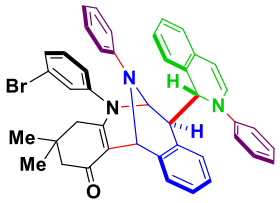
White solid obtained by filtration of the precipitate; 93.6 mg, 93% yield; dr > 20:1; reaction time = 2 h; mp 226.7-227.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.10-7.07 (m, 3H), 7.05-6.99 (m, 1H), 6.92 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 4H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.70 (dd, J_1 =J_2 = 4.0 Hz, 2H), 6.55 (t, *J* = 8.0 Hz, 3H), 6.24 (s, 2H), 5.81 (d, *J* = 4.0 Hz, 2H), 5.15 (d, *J* = 8.0 Hz, 1H), 3.02 (d, *J* = 8.0 Hz, 1H), 2.35-1.89 (m, 5H), 1.44 (d,*J* = 16.0 Hz, 1H), 0.72 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 152.7, 147.9, 146.5, 145.1, 144.7, 137.7, 131.5, 130.8, 129.5, 128.9, 128.8, 128.6, 127.7, 127.5, 127.5, 127.1, 126.5, 126.0, 125.3, 124.8, 123.9, 122.2, 121.3, 120.8, 118.0, 116.9, 113.9, 71.5, 63.1, 52.9, 49.6, 42.3, 42.0, 34.2, 30.2, 25.6. IR (KBr) *v* 3448, 2948, 1569, 1496, 1268, 759 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}N_4NaO_3$ $[M+Na]^+$ 693.2836, found 693.2841.



5-(3-chlorophenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9h**)

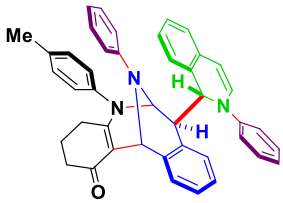
White solid obtained by filtration of the precipitate; 82.5 mg, 83% yield; dr > 20:1; reaction time = 6 h; mp 191.5-192.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.24-6.89 (m, 13H), 6.76 (t, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 4.0 Hz, 2H), 6.49 (br, 1H), 6.33 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.66 (s, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 3.20 (d, *J* = 8.0 Hz, 1H), 2.14-1.95 (m, 3H), 1.49 (d, *J* = 16.0 Hz, 1H), 0.74 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.1, 148.2, 145.2, 141.8, 138.4, 131.3, 131.2, 130.7, 129.4,

129.3, 129.1, 128.8, 128.8, 128.5, 127.5, 127.4, 126.9, 126.8, 126.2, 126.0, 125.1, 125.1, 123.7, 121.7, 121.1, 117.9, 117.0, 111.2, 106.0, 71.9, 63.2, 52.5, 49.5, 42.2, 41.4, 33.7, 30.0, 26.0. IR (KBr) *v* 3441, 2948, 1563, 1489, 1230, 759 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}ClN_3NaO$ $[M+Na]^+$ 682.2596, found 682.2587.



5-(3-bromophenyl)-3,3-dimethyl-13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9i**)

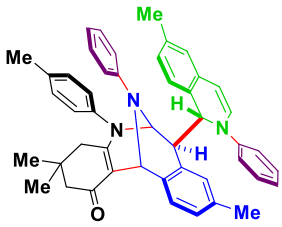
White solid obtained by filtration of the precipitate; 92.1 mg, 87% yield; dr > 20:1; reaction time = 6 h; mp 221.4-222.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.37-7.30 (m, 3H), 7.22-7.12 (m, 4H), 7.06-6.97 (m, 7H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.79-6.74 (m, 3H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.53 (br, 1H), 6.34 (d, *J* = 8.0 Hz, 2H), 6.28 (s, 1H), 5.89 (d, *J* = 4.0 Hz, 1H), 5.65 (s, 1H), 5.22 (d, *J* = 8.0 Hz, 1H), 3.20 (d, *J* = 8.0 Hz, 1H), 2.13-1.95 (m, 3H), 1.49 (d, *J* = 16.0 Hz, 1H), 0.75 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 154.1, 148.2, 145.2, 142.0, 138.4, 130.7, 130.3, 129.8, 129.7, 129.4, 129.2, 128.8, 128.6, 128.0, 127.5, 127.4, 126.9, 126.6, 126.2, 126.0, 125.1, 123.8, 123.7, 121.7, 121.2, 117.9, 117.0, 111.2, 106.0, 72.0, 63.2, 52.5, 49.5, 42.3, 41.4, 33.8, 30.0, 26.0. IR (KBr) *v* 3451, 2954, 1605, 1561, 1489, 1387, 760 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}BrN_3NaO$ $[M+Na]^+$ 726.2090, found 726.2098.



13-phenyl-7-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9j**)

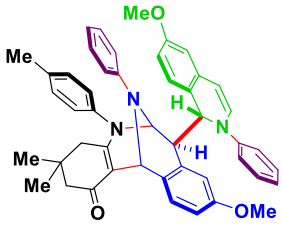
White solid obtained by filtration of the precipitate; 80.9 mg, 88% yield; dr > 20:1; reaction time = 6 h; mp 238.3-239.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.15-7.09 (m, 2H), 7.02-6.89 (m, 8H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.61-6.56 (m, 3H), 6.36 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 5.84 (d, *J* = 8.0 Hz, 1H), 5.60 (s, 1H), 5.24 (d, *J* = 8.0 Hz, 1H), 3.30 (d, *J* = 12.0 Hz, 1H), 2.32 (s, 3H), 2.19-2.05

(m, 3H), 1.78-1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 157.1, 148.5, 145.3, 139.0, 137.9, 137.0, 131.3, 130.5, 130.0, 129.6, 129.2, 129.0, 128.6, 127.6, 127.4, 127.2, 126.9, 126.2, 126.0, 125.0, 123.6, 121.4, 121.1, 118.1, 117.1, 110.2, 105.8, 72.2, 63.3, 52.3, 42.9, 36.0, 27.4, 22.2, 21.0. IR (KBr) *v* 3448, 2936, 1607, 1556, 1500, 758 cm^{-1}. HRMS (ESI) calcd for $C_{43}H_{38}N_3O$ $[M+H]^+$ 612.3009, found 612.3013.



3,3,9-trimethyl-7-(6-methyl-2-phenyl-1,2-dihydroisoquinolin-1-yl)-13-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9k**)

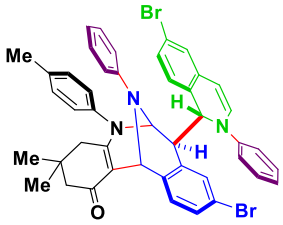
White solid obtained by filtration of the precipitate; 72.8 mg, 73% yield; dr > 20:1; reaction time = 6 h; mp 232.8-233.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.91-6.84 (m, 6H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 8.0 Hz, 2H), 6.53 (t, *J* = 8.0 Hz, 4H), 6.28 (d, *J* = 4.0 Hz, 2H), 6.12 (s, 1H), 5.69 (d, *J* = 4.0 Hz, 1H), 5.59 (s, 1H), 5.12 (d, *J* = 8.0 Hz, 1H), 3.14 (d, *J* = 8.0 Hz, 1H), 2.24 (d, *J* = 16.0 Hz, 6H), 1.98-1.85 (m, 6H), 1.43 (d, *J* = 16.0 Hz, 1H), 0.63 (s, 3H), 0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 155.1, 148.5, 145.3, 138.0, 136.8, 126.7, 136.0, 135.3, 131.3, 131.1, 129.9, 129.3, 129.2, 129.0, 128.5, 127.8, 126.7, 125.8, 125.7, 125.3, 124.1, 121.2, 120.8, 117.9, 116.7, 109.8, 105.6, 72.1, 62.8, 52.0, 49.5, 42.7, 41.2, 33.5, 30.0, 26.2, 21.1, 21.0, 20.9. IR (KBr) *v* 3434, 2956, 1607, 1554, 750 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{45}N_3NaO$ $[M+Na]^+$ 690.3455, found 690.3454.



9-methoxy-7-(6-methoxy-2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-13-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9l**)

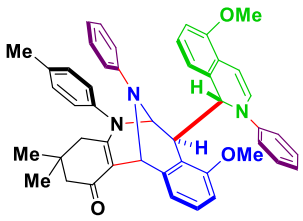
White solid obtained by filtration of the precipitate; 75.5 mg, 72% yield; dr > 20:1; reaction time = 6 h; mp 241.2-241.9 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.02-6.95 (m, 5H), 6.71 (t, *J* = 8.0 Hz, 1H), 6.67-6.59 (m, 7H),

6.45 (d, *J* = 4.0 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 5.79 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 5.21 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.45 (s, 3H), 3.23 (d, *J* = 8.0 Hz, 1H), 2.34 (s, 3H), 2.06-1.97 (m, 3H), 1.52 (d, *J* = 16.0 Hz, 1H), 0.71 (s, 3H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 159.1, 157.7, 155.1, 148.4, 145.1, 137.9, 136.8, 132.5, 131.7, 130.9, 130.0, 129.2, 129.1, 128.6, 127.8, 127.0, 121.3, 121.1, 120.7, 117.8, 116.7, 115.7, 113.7, 111.2, 109.8, 108.1, 105.7, 71.9, 62.6, 55.3, 55.3, 51.7, 49.5, 42.9, 41.1, 33.4, 29.7, 26.3, 21.0. IR (KBr) *v* 3449, 2942, 1605, 1561, 1498, 1235, 754 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{45}N_3NaO_3$ $[M+Na]^+$ 722.3353, found 722.3343.



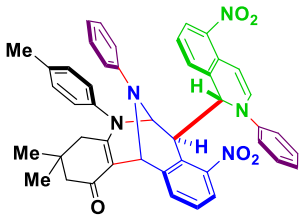
9-bromo-7-(6-bromo-2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-13-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9m**)

White solid obtained by filtration of the precipitate; 92.8 mg, 78% yield; dr > 20:1; reaction time = 6 h; mp 246.7-247.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, J_1 = J_2 = 8.0 Hz, 4H), 7.07-6.99 (m, 6H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 8.0 Hz, 2H), 6.15 (s, 1H), 5.72 (d, *J* = 4.0 Hz, 1H), 5.60 (s, 1H), 5.19 (d, *J* = 8.0 Hz, 1H), 3.18 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.06-1.94 (m, 3H), 1.56 (d, *J* = 16.0 Hz, 1H), 0.73 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 155.3, 148.1, 144.7, 138.1, 137.5, 137.4, 133.5, 133.3, 133.3, 131.6, 130.4, 130.3, 130.1, 129.4, 128.8, 128.0, 127.8, 127.5, 126.1, 125.9, 121.9, 121.4, 119.6, 118.1, 117.1, 108.8, 104.1, 71.7, 62.7, 52.2, 49.4, 42.8, 41.1, 33.4, 29.7, 26.4, 21.0. IR (KBr) *v* 3449, 2955, 2230, 1553, 1499, 724 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{39}Br_2N_3NaO$ $[M+Na]^+$ 818.1352, found 818.1356.



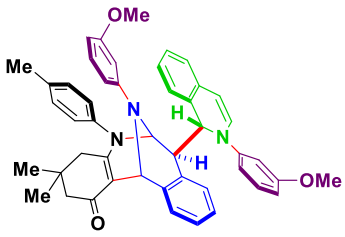
8-methoxy-7-(5-methoxy-2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-13-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9n**)

White solid obtained by filtration of the precipitate; 80.2 mg, 76% yield; dr > 20:1;reaction time = 6 h; mp 181.2-181.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.11 (m, 7H), 7.06 (br, 2H), 6.88 (dd, $J_1 = J_2$ = 8.0 Hz, 7H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.60 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.20 (s, 1H), 5.78 (d, *J* = 4.0 Hz, 1H), 5.66 (d, *J* = 8.0 Hz, 2H), 5.48 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.71 (d, *J* = 4.0 Hz, 1H), 3.50 (s, 3H), 2.31 (s, 3H), 1.98 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 1.89 (d, *J* = 16.0 Hz, 1H), 1.54 (d, *J* = 16.0 Hz, 1H), 0.68 (s, 3H), 0.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 157.6, 155.2, 152.6, 147.9, 145.7, 141.6, 138.6, 137.1, 130.2, 129.3, 128.8, 128.6, 128.4, 127.9, 125.0, 121.3, 120.9, 120.6, 119.2, 119.1, 118.6, 118.3, 117.8, 108.9, 108.8, 107.7, 98.1, 72.1, 60.4, 55.2, 55.1, 51.5, 49.5, 44.4, 41.1, 33.3, 29.7, 26.5, 21.0. IR (KBr) *v* 3441, 2950, 1683, 1558, 1502, 1264, 765 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{45}N_3NaO_3$ $[M+Na]^+$ 722.3353, found 722.3360.



3,3-dimethyl-8-nitro-7-(5-nitro-2-phenyl-1,2-dihydroisoquinolin-1-yl)-13-phenyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9o**)

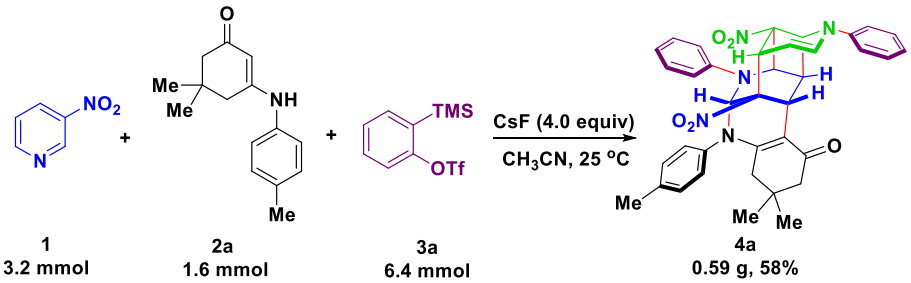
White solid obtained by filtration of the precipitate; 93.4 mg, 85% yield; dr > 20:1; reaction time = 6 h; mp 237.9-238.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.93 (q, *J* = 8.0 Hz, 3H), 6.81 (t, *J* = 8.0 Hz, 3H), 6.78-6.68 (m, 3H), 6.51 (t, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 5.77 (s, 1H), 5.58 (d, *J* = 4.0 Hz, 1H), 4.44 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.35 (s, 3H), 1.90 (s, 2H), 1.86 (d, *J* = 16.0 Hz, 1H), 1.47 (d, *J* = 16.0 Hz, 1H), 0.59 (s, 3H), 0.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 156.0, 150.5, 147.2, 145.3, 142.4, 141.5, 138.1, 127.4, 126.3, 131.8, 129.5, 129.4, 129.1, 129.0, 128.1, 128.0, 126.0, 124.9, 124.8, 124.3, 123.7, 123.1, 121.9, 120.3, 117.7, 107.7, 97.7, 72.5, 63.3, 51.6, 49.3, 45.6, 40.7, 33.2, 29.4, 26.5, 21.2. IR (KBr) *v* 3444, 2950, 1560, 1514, 1266, 752 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{39}N_5NaO_5$ $[M+Na]^+$ 752.2843, found 752.2856.



13-(3-methoxyphenyl)-7-(2-(3-methoxyphenyl)-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b*,*e*]azocin-1(2*H*)-one (**9p**)

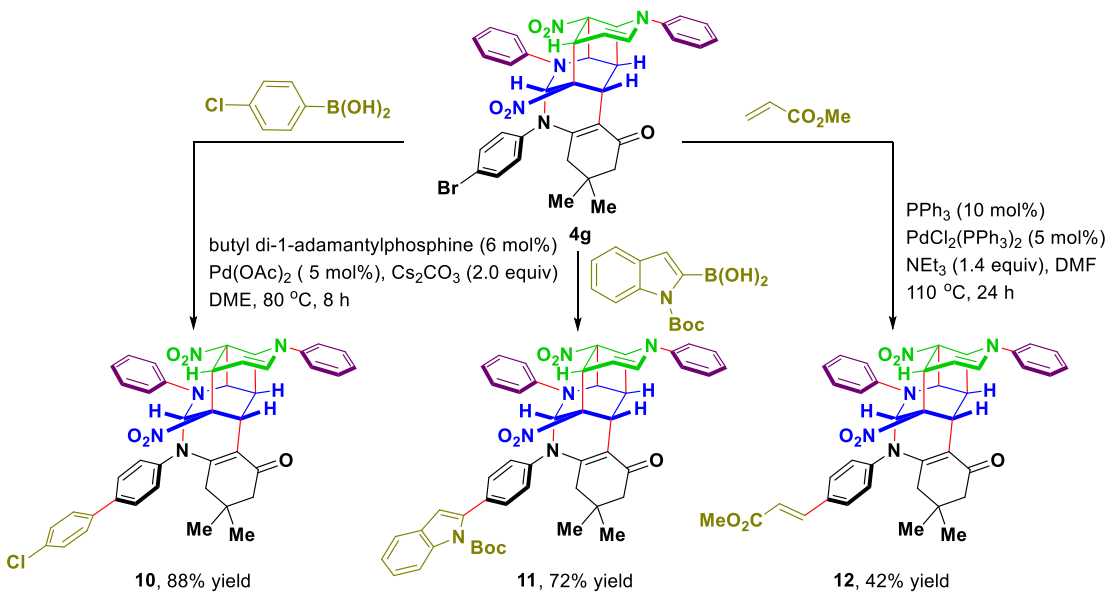
White solid obtained by filtration of the precipitate; 79.7 mg, 76% yield; dr > 20:1; reaction time = 6 h; mp 237.3-238.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.16 (q, *J* = 8.0 Hz, 1H), 7.11-7.04 (m, 2H), 6.98 (q, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 8.0 Hz, 3H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 6.52-6.46 (m, 4H), 6.25 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.17 (s, 1H), 5.92 (d, *J* = 8.0 Hz, 1H), 5.78 (t, *J* = 8.0 Hz, 2H), 5.53 (s, 1H), 5.12 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.50 (s, 3H),3.15 (d, *J* = 4.0 Hz, 1H), 2.26 (s, 3H), 1.99-1.86 (m, 4H), 1.46 (d, *J* = 16.0 Hz, 1H), 0.63 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 160.6, 159.9, 155.3, 149.9, 146.7, 138.7, 137.7, 136.8, 131.3, 130.7, 130.0, 129.8, 129.4, 129.1, 128.9, 127.8, 127.4, 127.3, 127.0, 126.1, 126.0, 125.1, 123.6, 110.6, 109.8, 109.7, 107.5, 107.1, 106.1, 104.2, 102.2, 72.1, 63.2, 55.3, 55.0, 52.7, 49.5, 42.3, 41.1, 33.5, 29.7, 26.3, 20.9. IR (KBr) *v* 3420, 2953, 1598, 1558, 1264, 766 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{45}N_3NaO_3$ $[M+Na]^+$ 722.3353, found 722.3356.

6. Experimental data for the scalable preparation of 4a

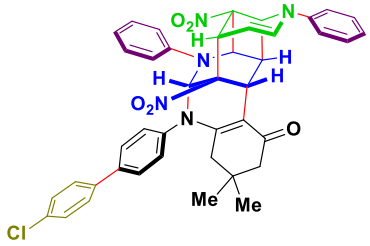


General procedure: To a 25.0 mL round-bottom flask were successively added 3-nitropyridine **1** (0.40 g, 3.2 mmol), enaminone **2a** (0.37 g, 1.6 mmol), aryne precursors **3a** (1.6 mL, 6.4 mmol), CsF (1.00 g, 6.4 mmol) and 5.0 mL of CH_3CN. The resulting mixture was stirred at 25 °C for 48 h. During the reaction process, a large amount of precipitate occurred, and only a simple filtration was required to purify them once the reaction went completion. The desired product **4a** was obtained as yellow solid in 58% yield (0.59 g).

7. Experimental data for derivations of 4g



General procedure for the formation of 10: Under nitrogen atmosphere, compound **4g** (111.1 mg, 0.16mmol), 4-chlorophenyl boronic acid (37.5 mg, 0.24mmol, 1.5 equiv), Cs_2CO_3 (104.3 mg, 0.32 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by addition of 2.0 mL DME. The resulting mixture was stirred at 80 °C in oil bath for 8 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **10** as a yellow solid in 88% yield.

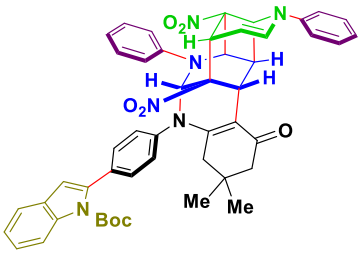


5-(4'-chloro-[1,1'-biphenyl]-4-yl)-3,3-dimethyl-7b,13-dinitro-7,11-diphenyl-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one(**10**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 102.6 mg, 88% yield; dr> 20:1; reaction time = 8 h; mp 223.7-224.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8.0 Hz, 3H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.23 (dd, J_1 = J_2 = 8.0 Hz, 5H), 7.10 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 3H), 6.63 (br, 2H), 6.09 (s, 1H), 4.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 4.08 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.06 (s, 1H), 3.28 (t, *J* = 8.0 Hz, 1H), 2.29 (t, *J* = 16.0 Hz, 2H), 2.04 (t, *J* = 16.0 Hz, 2H), 0.99 (s, 3H), 0.95 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.0, 145.4, 145.1, 141.6, 139.2, 138.0, 134.0, 133.8, 129.6, 129.6, 129.0, 128.1, 127.9, 127.7, 125.1, 124.0, 123.6, 118.7, 108.2, 87.4, 85.5, 84.4, 59.8, 52.4, 50.1, 48.5, 41.7, 38.6, 33.0, 28.9, 26.9, 25.4. IR (KBr) *v* 3431, 2954, 1590, 1544, 1490, 1381, 754 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{37}ClN_5O_5$ $[M+H]^+$ 726.2478, found 726.2481.

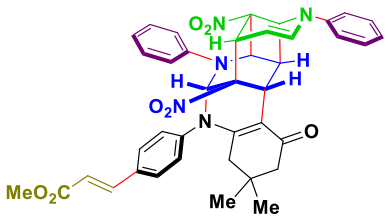
General procedure for the formation of 11: Under nitrogen atmosphere, compound **4g** (111.1 mg, 0.16mmol), 2-indolylboronic acid (62.7 mg, 0.24mmol, 1.5 equiv), Cs_2CO_3 (104.3 mg, 0.32 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by addition of 2.0 mL DME. The resulting mixture was stirred at 80 °C in oil bath for 8 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **11** as a yellow liquid in 72% yield.



tert-butyl 2-(4-(3,3-dimethyl-7b,13-dinitro-1-oxo-7,11-diphenyl-2,3,4,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-5(1*H*)-yl)phenyl)-1*H*-indole-1-carboxylate (**11**)

Yellow liquid obtained by column chromatography (petroleum ether/ethyl acetate = 7:1 to 3:1); 95.8 mg, 72% yield; dr > 20:1; reaction time = 8 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.30-7.20 (m, 8H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.52 (br, 2H), 6.06 (s, 1H), 4.53 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.37 (t, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 8.0 Hz, 1H), 4.09 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.06 (s, 1H), 3.28 (t, *J* = 8.0 Hz, 1H), 2.30 (t, *J* = 16.0 Hz, 2H), 2.06 (q, *J* = 16.0 Hz, 2H), 1.35 (s, 9H), 0.99 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 153.0, 149.9, 145.5, 145.2, 141.5, 138.8, 137.6, 134.5, 134.1, 129.8, 129.7, 129.6, 128.9, 126.9, 125.4, 124.7, 124.4, 123.7, 123.1, 120.5, 118.8, 115.2, 110.7, 108.3, 87.4, 85.5, 84.5, 83.6, 60.0, 52.5, 50.1, 48.6, 41.8, 38.7, 33.1, 28.8, 27.7, 27.1, 25.5. IR (KBr) *v* 3433, 2931, 1734, 1594, 1326, 743 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{47}N_6O_7$ $[M+H]^+$ 831.3501, found 831.3505.

General procedure for the formation of 12: Under nitrogen atmosphere, compound **4g** (69.5 mg, 0.10mmol), methyl acrylate (10.8 uL, 0.12mmol, 1.2equiv), Et_3N (1.4equiv), $PdCl_2(PPh_3)_2$ (0.05 equiv) and triphenylphosphine (0.1equiv) were successively added to a 15 mL dried tube, followed by addition of 2.0 mL DMF. The resulting mixture was stirred at 110 °C in oil bath for 24 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **12** as a yellow liquid in 42% yield.



methyl (*E*)-3-(4-(3,3-dimethyl-7b,13-dinitro-1-oxo-7,11-diphenyl-2,3,4,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-5(1*H*)-yl)phenyl)acrylate (**12**)

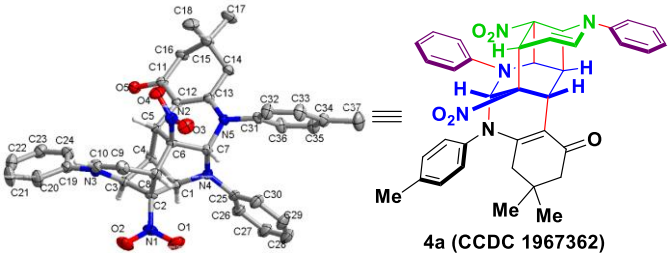
Yellow liquid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 3:1); 29.1 mg, 42% yield; dr > 20:1; reaction time = 24 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.23 (dd, J_1 = J_2 = 8.0 Hz, 4H), 7.12 (q, J = 8.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 3H), 6.58 (br, 2H), 6.37 (d, J = 16.0 Hz, 1H), 6.04 (s, 1H), 4.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.35 (t, J = 8.0 Hz, 1H), 4.17 (d, J = 8.0 Hz, 1H), 4.08 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.04 (s, 1H), 3.80 (s, 3H), 3.26 (t, J = 8.0 Hz, 1H), 2.29 (t, J = 16.0 Hz, 2H), 2.02 (t, J = 16.0 Hz, 2H), 0.99 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 167.0, 152.0, 145.4, 145.2, 143.7, 143.1, 134.1, 133.6, 129.8, 129.7, 129.0, 127.7, 125.4, 124.3, 123.7, 118.9, 118.8, 109.0, 87.4, 85.5, 84.5, 60.0, 52.5, 51.8, 50.1, 48.5, 41.8, 38.6, 33.2, 28.8, 27.0, 25.5. IR (KBr) ν 34427, 2951, 1594, 1546, 1502, 1175, 745 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{38}N_5O_7$ $[M+H]^+$ 700.2766, found 700.2766.

8. Crystal structures of 4a, 6a, 7a and 9a

8.1 Crystal structure of 4a

Preparation of the single crystals of **4a**: 15.0 mg of pure compound **4a** was dissolved in the combined solvents of $CHCl_3$ and EtOH (6 mL, v/v = 1:1) at room

temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about one week, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **4a**. The data were collected by a Rigaku Gemini E at 293.0 K.



Displacement ellipsoids are drawn at the 30% probability level.

Bond precision: C-C = 0.0074 A Wavelength=1.54184

Cell: a=18.48959(17) b=13.61717(13) c=27.3852(2)
alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	6894.93(10)	6894.95(11)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	2(C_{37} $H_{35}N_5O_5$), $CHCl_3$	2($C_{37}H_{35}N_5O_5$), $CHCl_3$
Sum formula	$C_{75}H_{71}Cl_3N_{10}O_{10}$	$C_{75}H_{71}Cl_3N_{10}O_{10}$
Mr	1378.77	1378.76
Dx,g cm-3	1.328	1.328
Z	4	4
Mu (mm-1)	1.757	1.757
F000	2888.0	2888.0
F000'	2900.55	
h,k,lmax	22,16,33	22,16,33
Nref	13311[6804]	11754
Tmin,Tmax	0.744,0.839	0.789,1.000
Tmin'	0.716	

Correction method= # Reported T Limits: Tmin=0.789 Tmax=1.000 AbsCorr = MULTI-SCAN

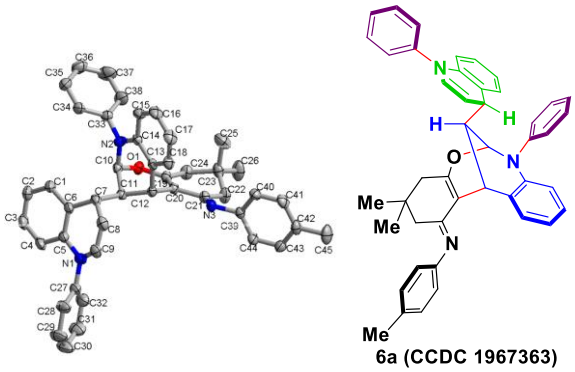
Data completeness= 1.73/0.88 Theta(max)= 70.835

R(reflections)= 0.0610(10516) wR2(reflections)= 0.1778(11754)

S = 1.019 Npar= 889

8.2 Crystal structure of 6a

Preparation of the single crystals of **6a**: 15.0 mg of pure compound **6a** was dissolved in the combined solvents of CH_2Cl_2 and EtOH (6 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about one week, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **6a**. The data were collected by a Rigaku Gemini E at 293.0 K.



Displacement ellipsoids are drawn at the 30% probability level.

Bond precision: C-C = 0.0033 A Wavelength=1.54184

Cell: a=16.5693(2) b=10.74988(15) c=20.4362(2)
alpha=90 beta=93.2630(11) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3634.15(8)	3634.17(8)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{45}H_{41}N_3O$	$C_{45}H_{41}N_3O$
Sum formula	$C_{45}H_{41}N_3O$	$C_{45}H_{41}N_3O$
Mr	639.81	639.81
Dx,g cm-3	1.169	1.169
Z	4	4
Mu (mm-1)	0.539	0.539
F000	1360.0	1360.0
F000'	1363.61	
h,k,lmax	19,12,24	19,12,24

Nref	6495	6495
Tmin,Tmax	0.919,0.948	
Tmin'	0.903	

Correction method= Not given

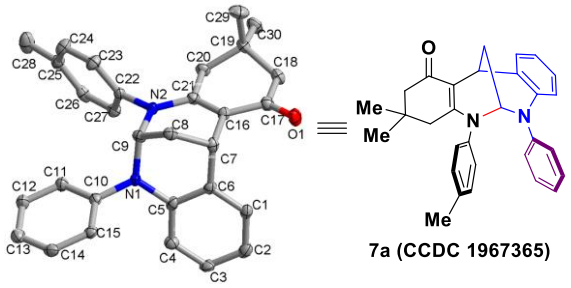
Data completeness= 1.000 Theta(max)= 67.073

R(reflections)= 0.0584(5323) wR2(reflections)= 0.1754(6495)

S = 1.036 Npar= 445

8.3 Crystal structure of 7a

Preparation of the single crystals of **7a**: 10.0 mg of pure compound **7a** was dissolved in the combined solvents of petroleum and ethyl acetate (6 mL, v/v = 5:1) at 0 °C. The bottle was sealed by a piece of plastic film with one tiny hole, thus allowing slow evaporation of the solvents at 0 °C. After about four weeks, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **7a**. The data were collected by a Bruker D8 VENTURE PHOTON II CCD diffractometer at 273.0 K.



Displacement ellipsoids are drawn at the 30% probability level.

Bond precision: C-C = 0.0071 A Wavelength=0.71073

Cell: a=13.7699(16) b=17.9992(18) c=19.133(3)

alpha=90 beta=90 gamma=90

Temperature: 273 K

	Calculated	Reported
Volume	4742.1(10)	4742.1(10)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	$C_{30}H_{30}N_2O$	$C_{30}H_{30}N_2O$
Sum formula	$C_{30}H_{30}N_2O$	$C_{30}H_{30}N_2O$
Mr	434.56	434.56
Dx,g cm-3	1.217	1.217
Z	8	8

Mu (mm-1)	0.073	0.073
F000	1856.0	1856.0
F000'	1856.68	
h,k,lmax	16,21,22	16,21,22
Nref	4238	4237
Tmin,Tmax	0.989,0.993	0.531,0.746
Tmin'	0.986	

Correction method= # Reported T Limits: Tmin=0.531 Tmax=0.746 AbsCorr = MULTI-SCAN

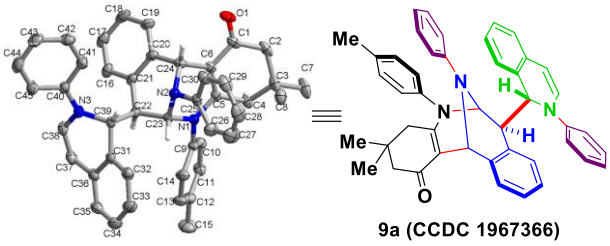
Data completeness= 1.000 Theta(max)= 25.122

R(reflections)= 0.0768(1715) wR2(reflections)= 0.2023(4237)

S = 1.016 Npar= 301

8.4 Crystal structure of 9a

Preparation of the single crystals of **9a**: 15.0 mg of pure compound **9a** was dissolved in the combined solvents of CH_2Cl_2 and EtOH (6 mL, v/v = 1:1) at room temperature. The bottle was sealed by a piece of plastic film with three tiny holes, thus allowing slow evaporation of the solvents at room temperature. After about one week, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **9a**. The data were collected by a Rigaku Gemini E at 293.0 K.



Displacement ellipsoids are drawn at the 30% probability level.

Bond precision: C-C = 0.0030 A Wavelength=1.54184

Cell: a=9.5513(2) b=22.5642(6) c=16.2921(5)

alpha=90 beta=101.061(3) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3446.01(16)	3446.01(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc

Moiety formula	$C_{45}H_{41}N_3O$	$C_{45}H_{41}N_3O$
Sum formula	$C_{45}H_{41}N_3O$	$C_{45}H_{41}N_3O$
Mr	639.81	639.81
Dx,g cm-3	1.233	1.233
Z	4	4
Mu (mm-1)	0.568	0.568
F000	1360.0	1360.0
F000'	1363.61	
h,k,lmax	11,26,19	11,26,19
Nref	6168	6167
Tmin,Tmax	0.903,0.939	0.915,1.000
Tmin'	0.898	

Correction method= # Reported T Limits: Tmin=0.915 Tmax=1.000 AbsCorr = MULTI-SCAN

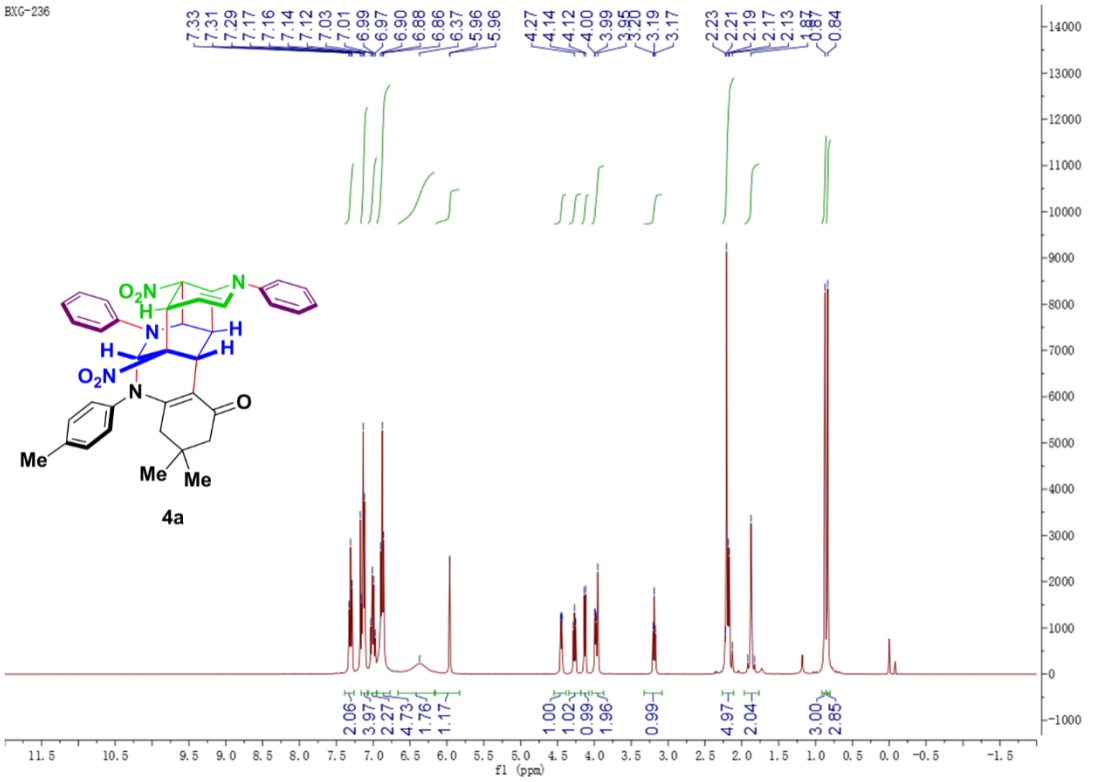
Data completeness= 1.000 Theta(max)= 67.074

R(reflections)= 0.0486(4904) wR2(reflections)= 0.1448(6167)

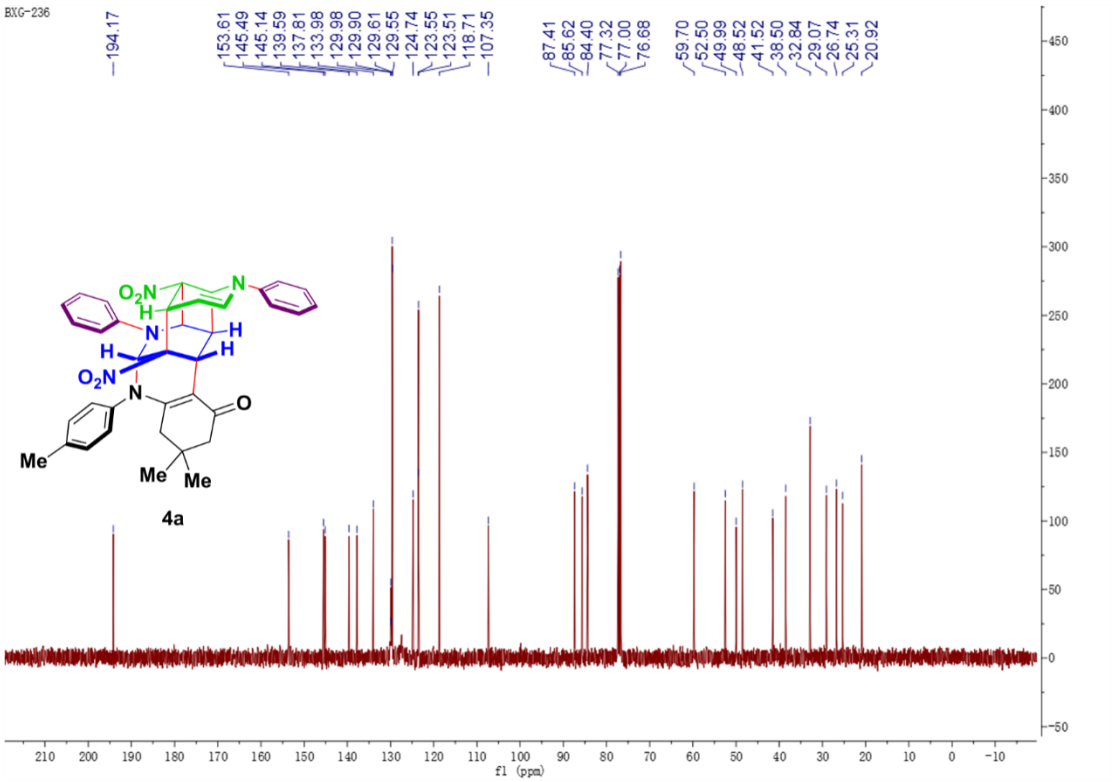
S = 1.029 Npar= 445

9. ^{1}H NMR and ^{13}C NMR spectra

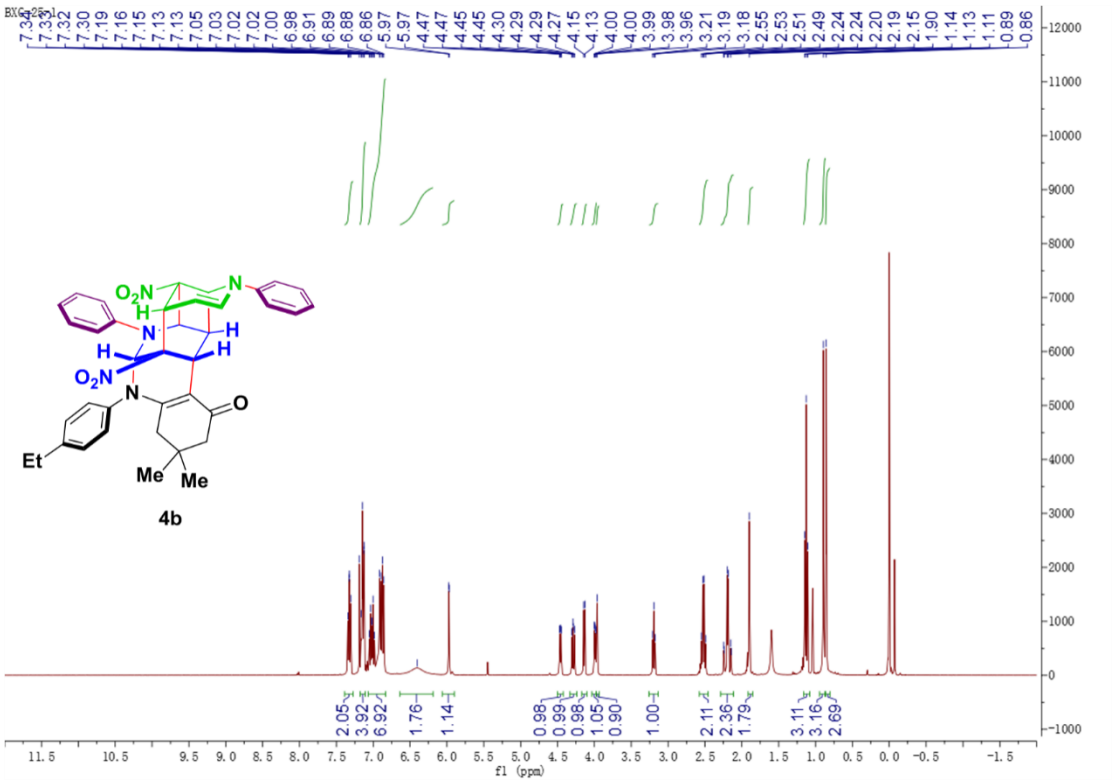
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



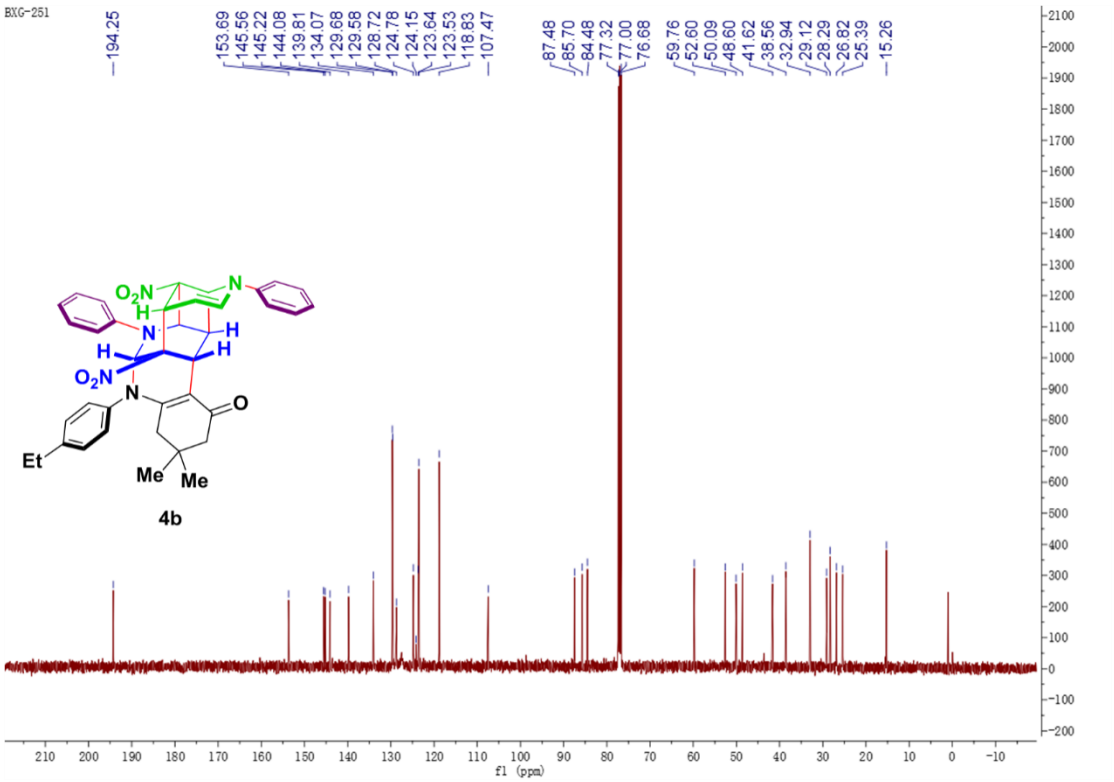
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



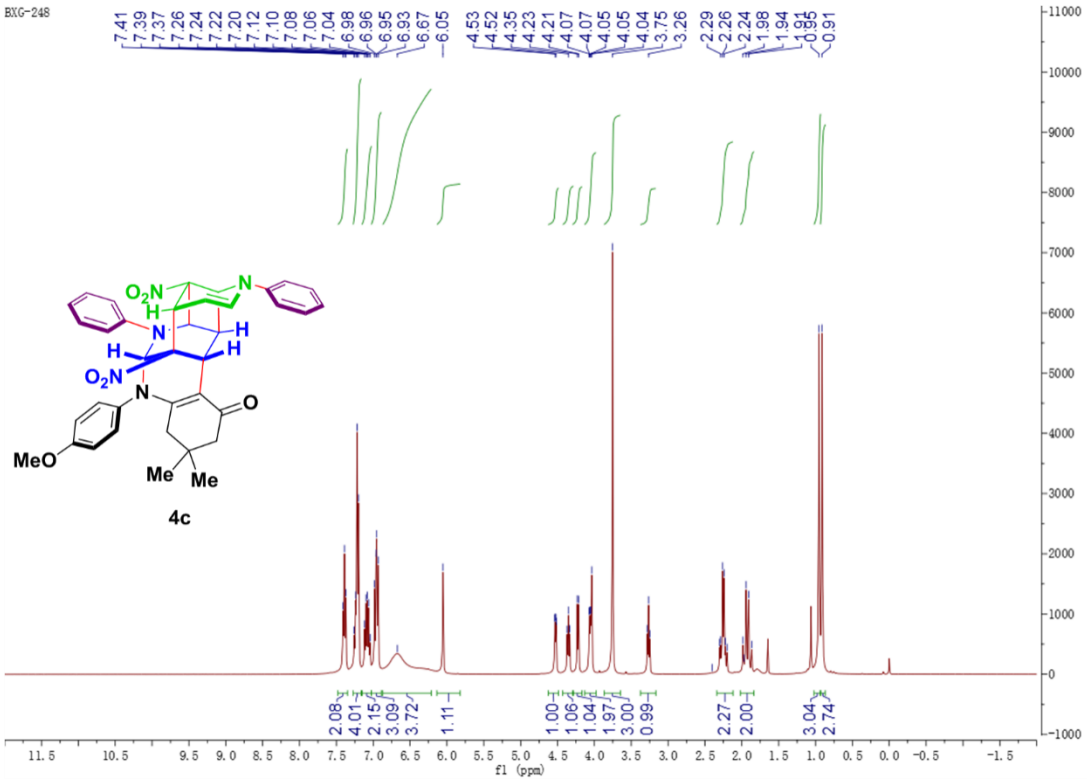
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



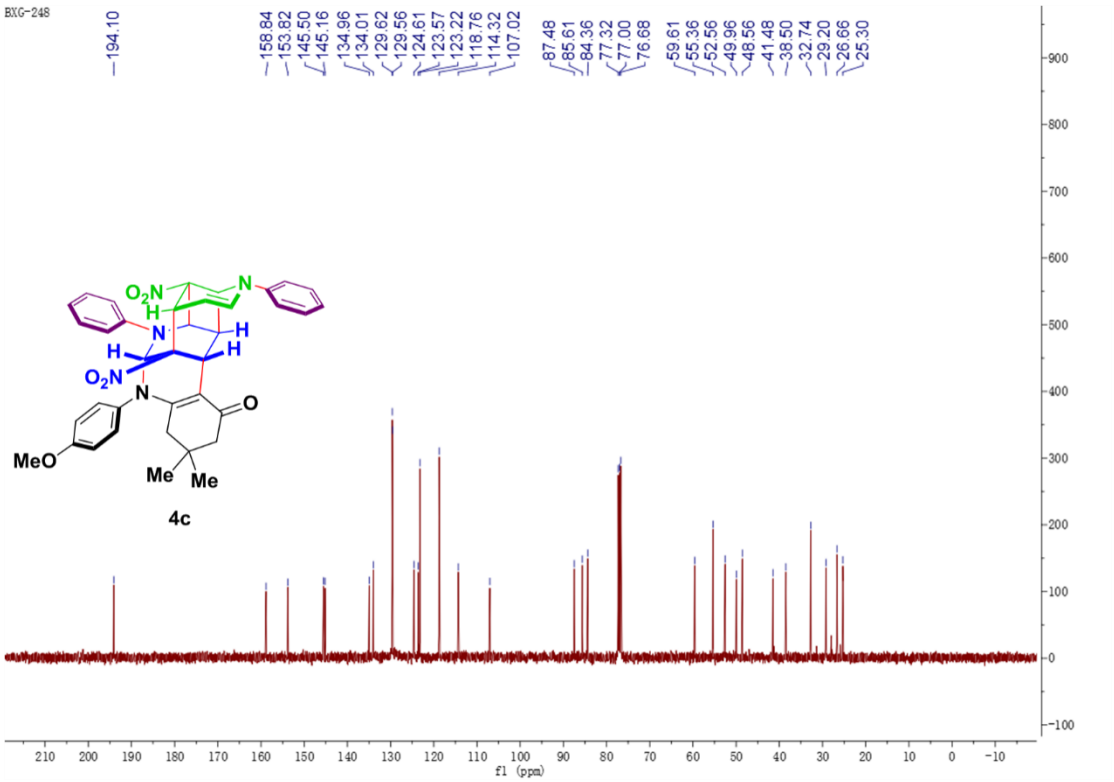
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



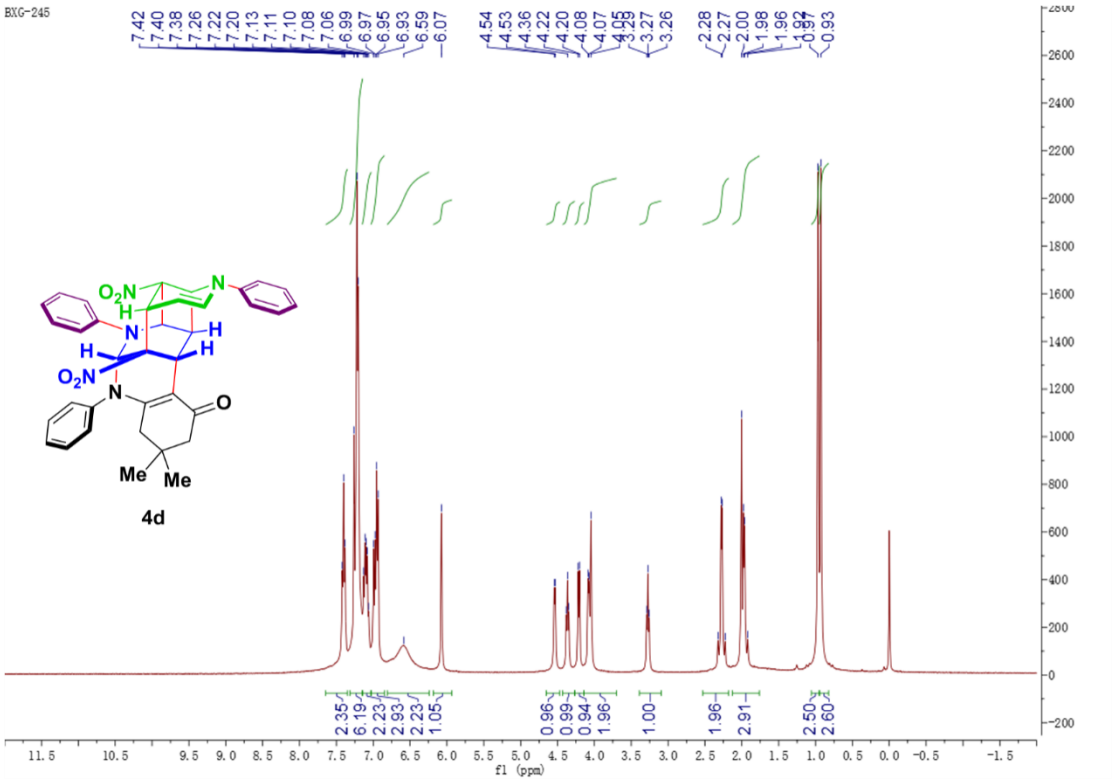
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



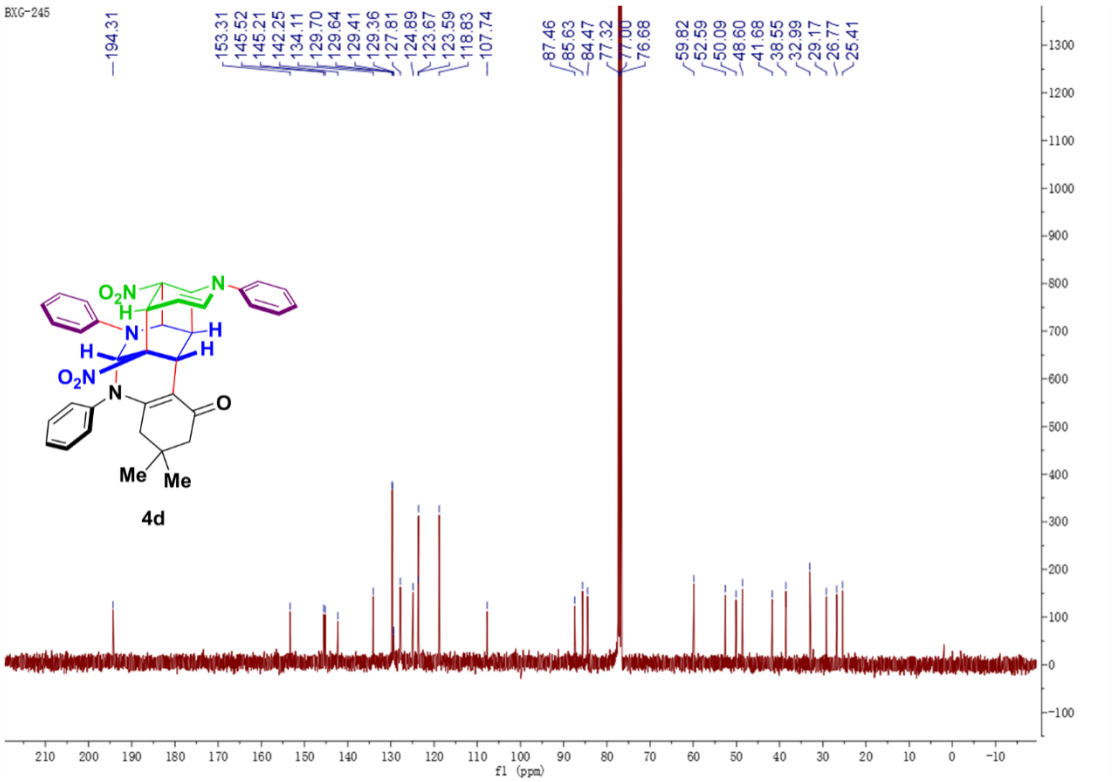
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



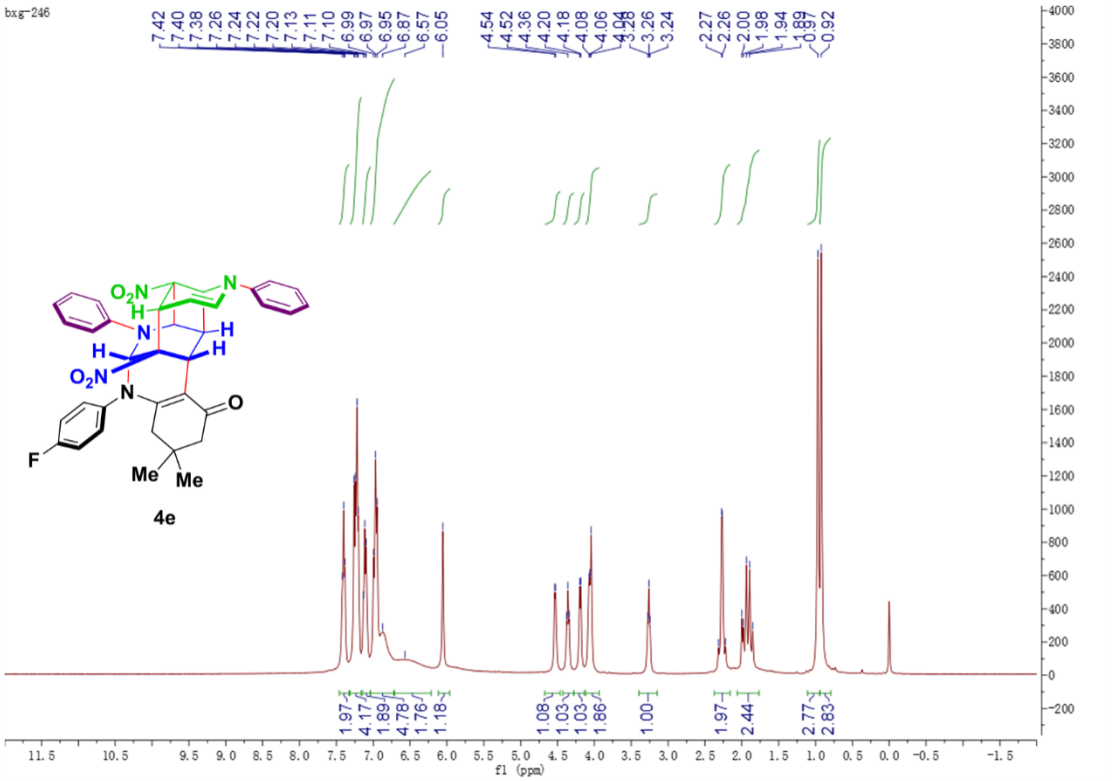
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



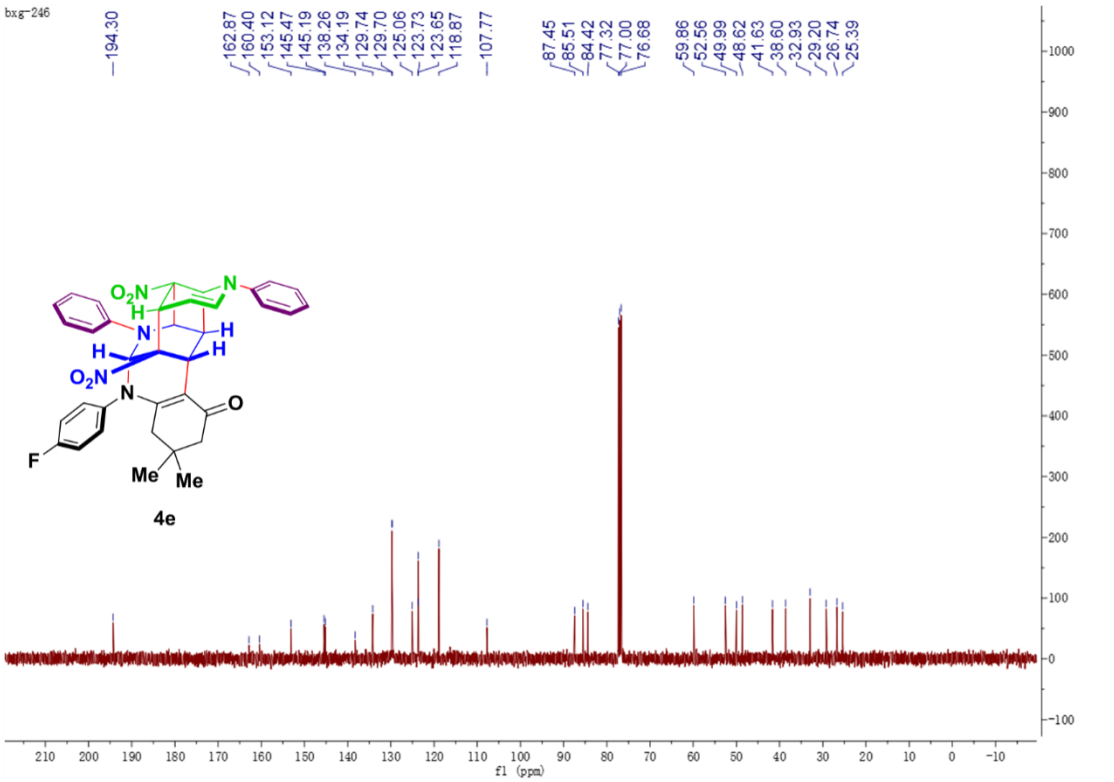
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



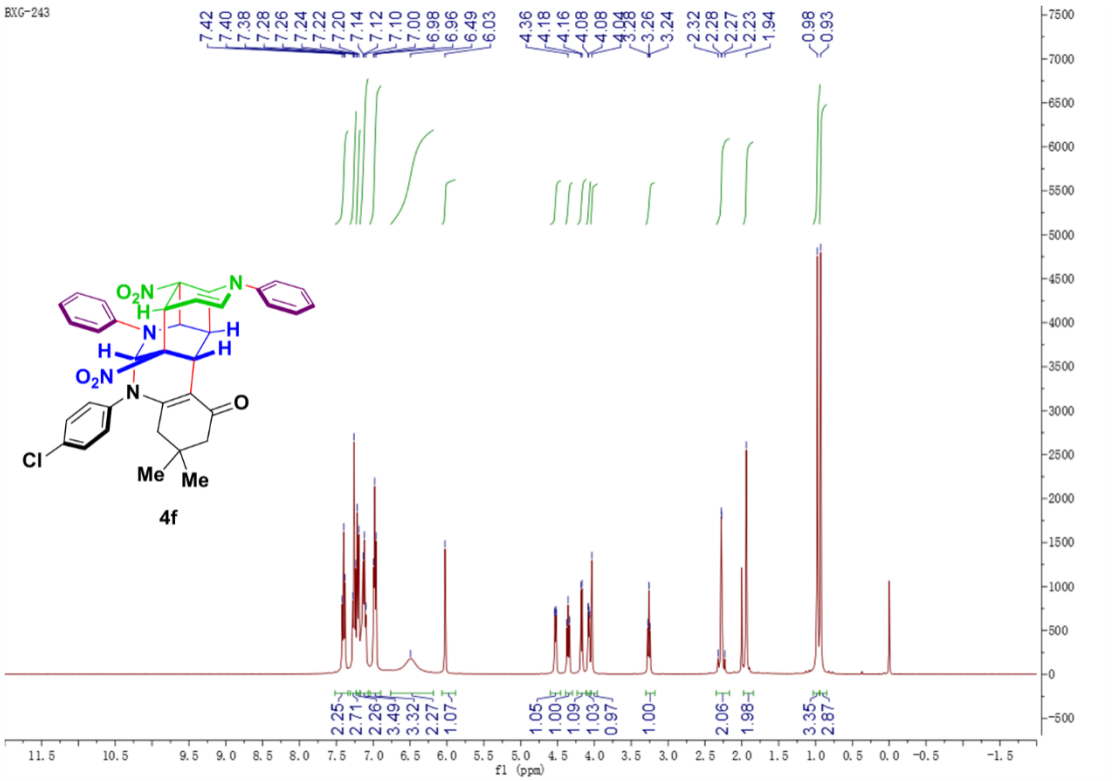
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



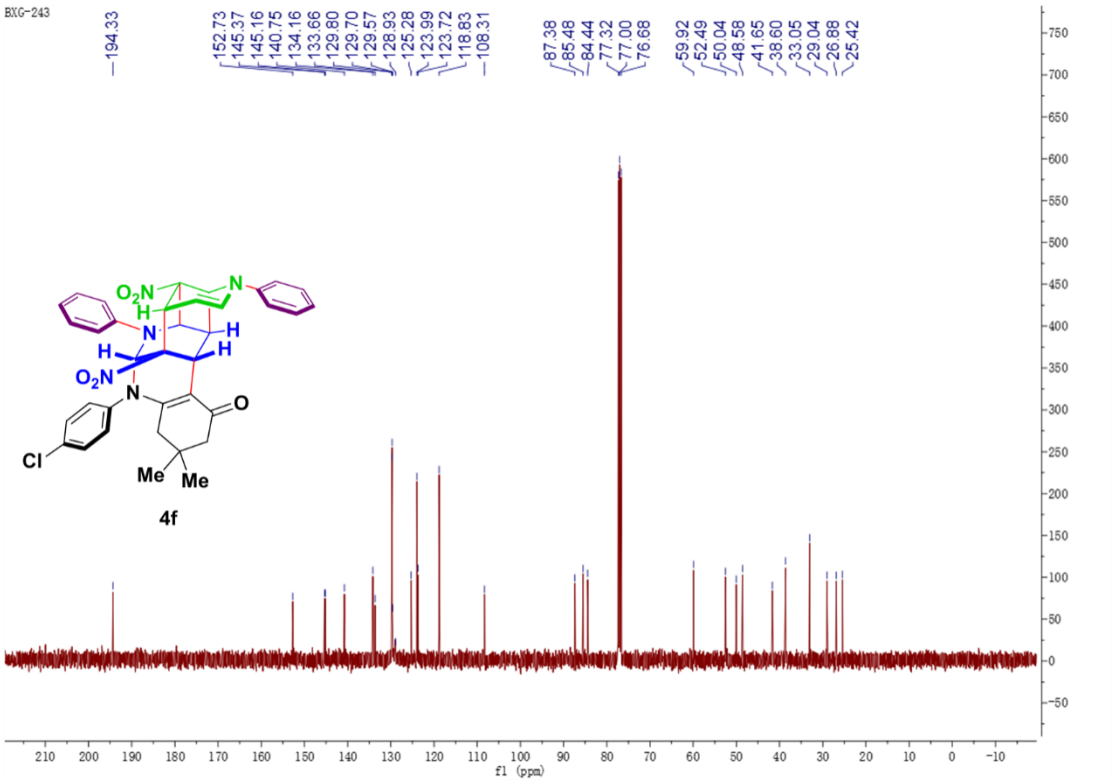
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



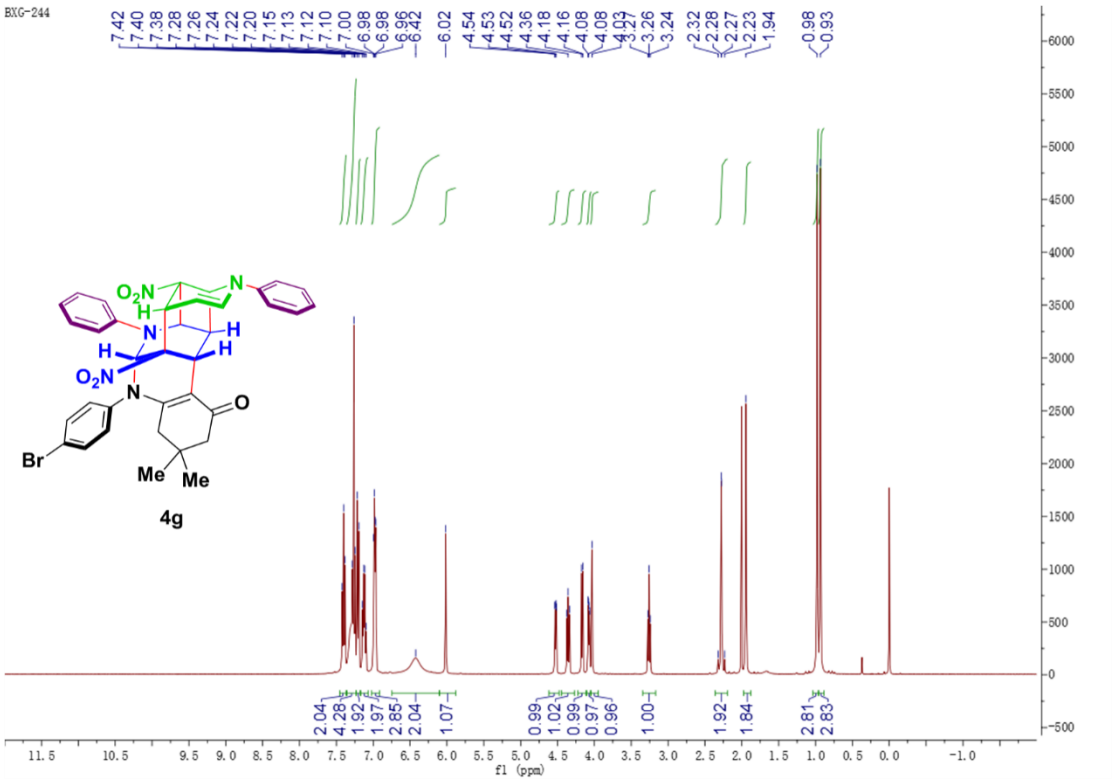
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



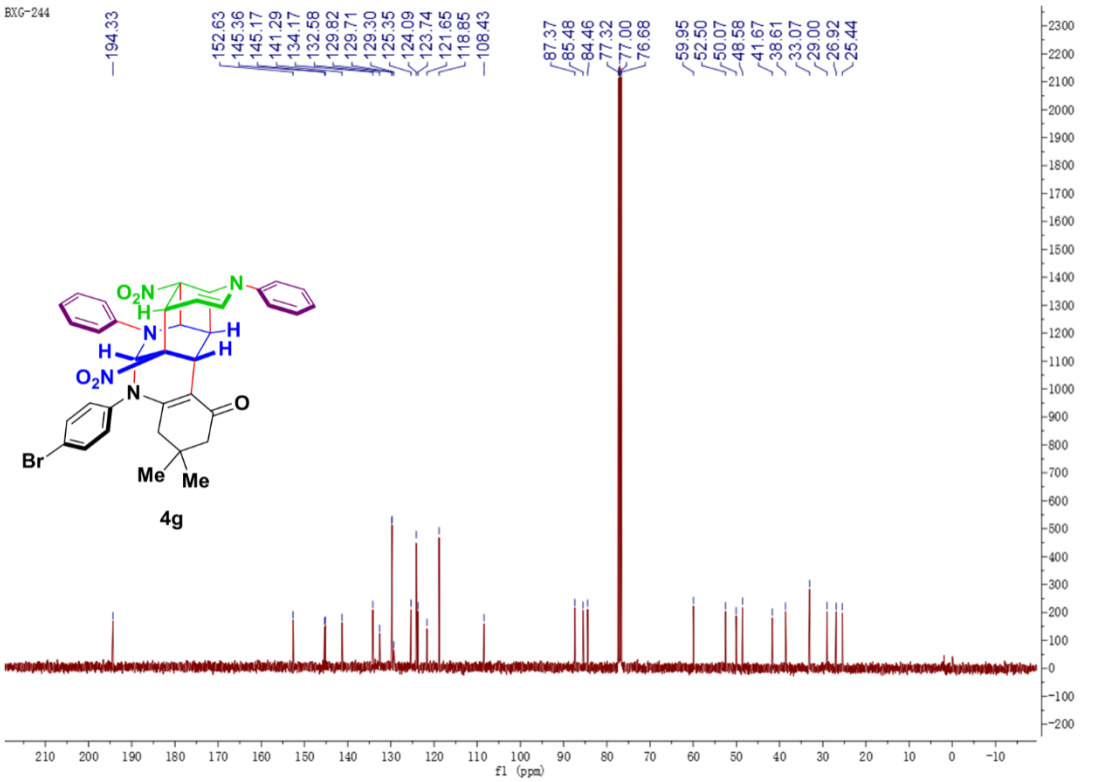
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



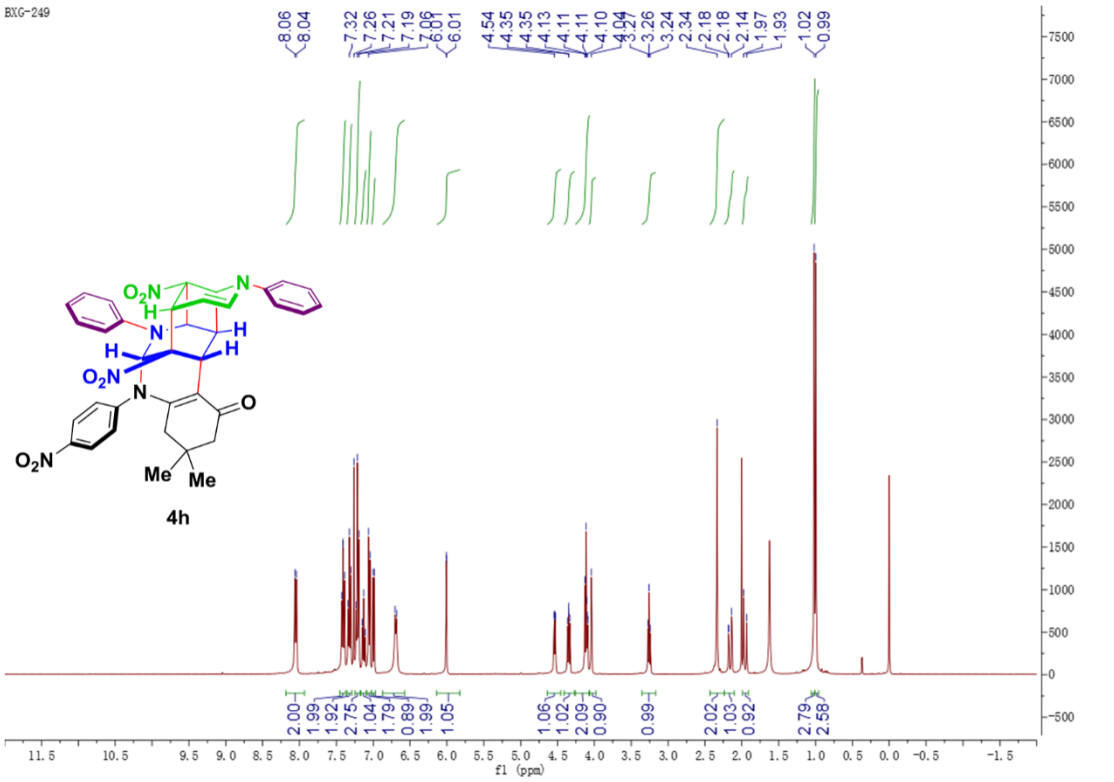
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



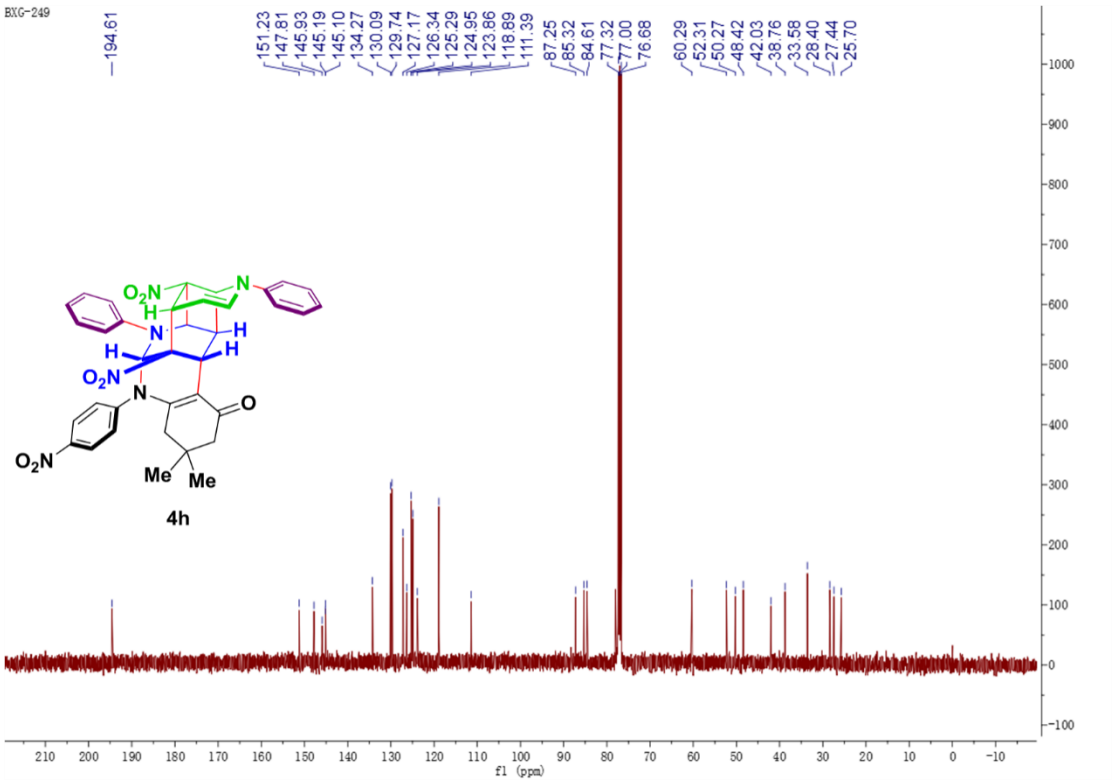
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



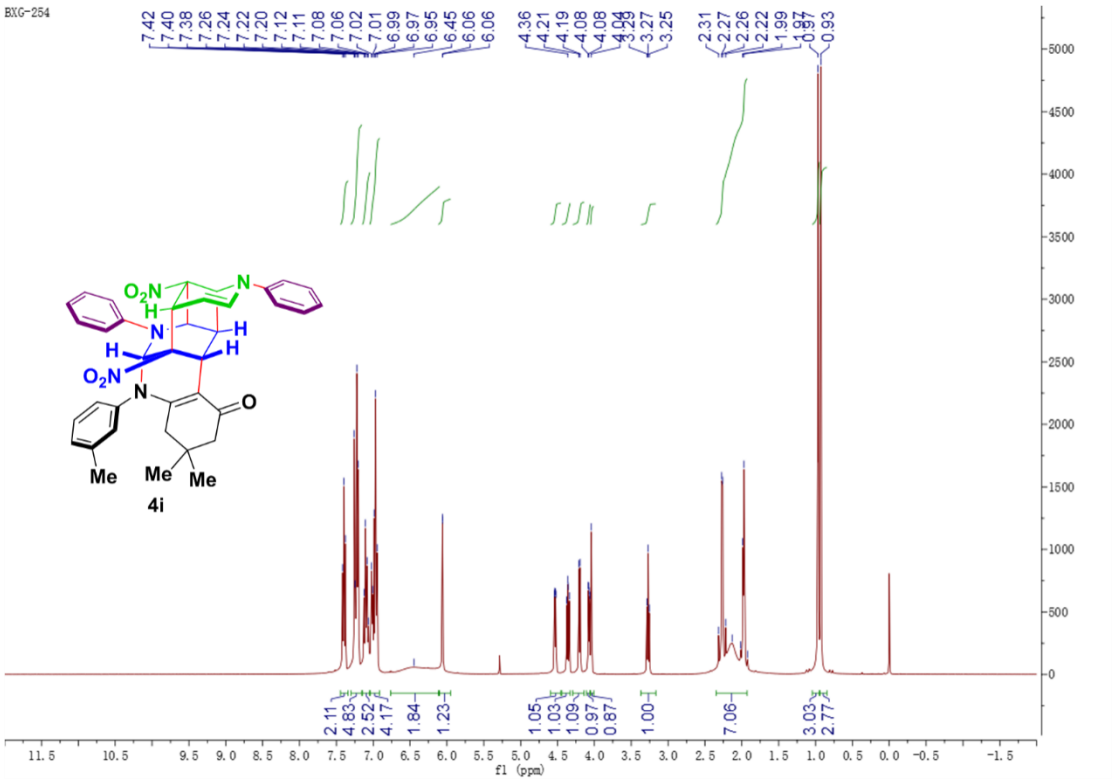
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



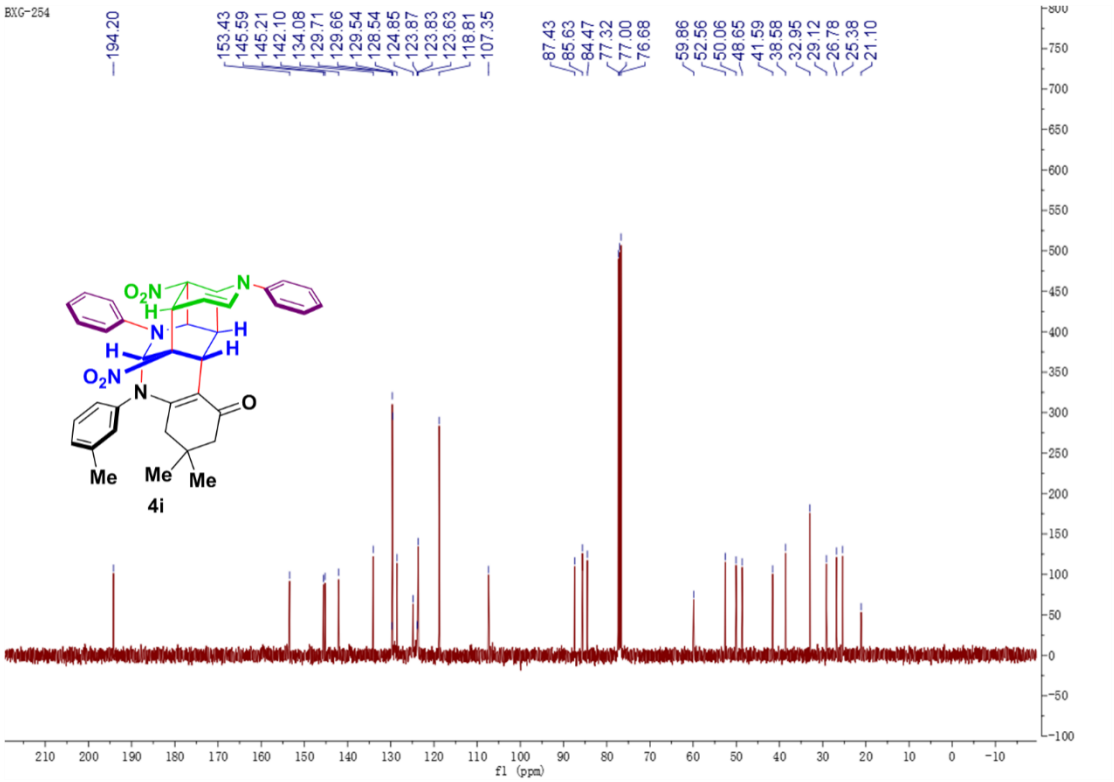
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



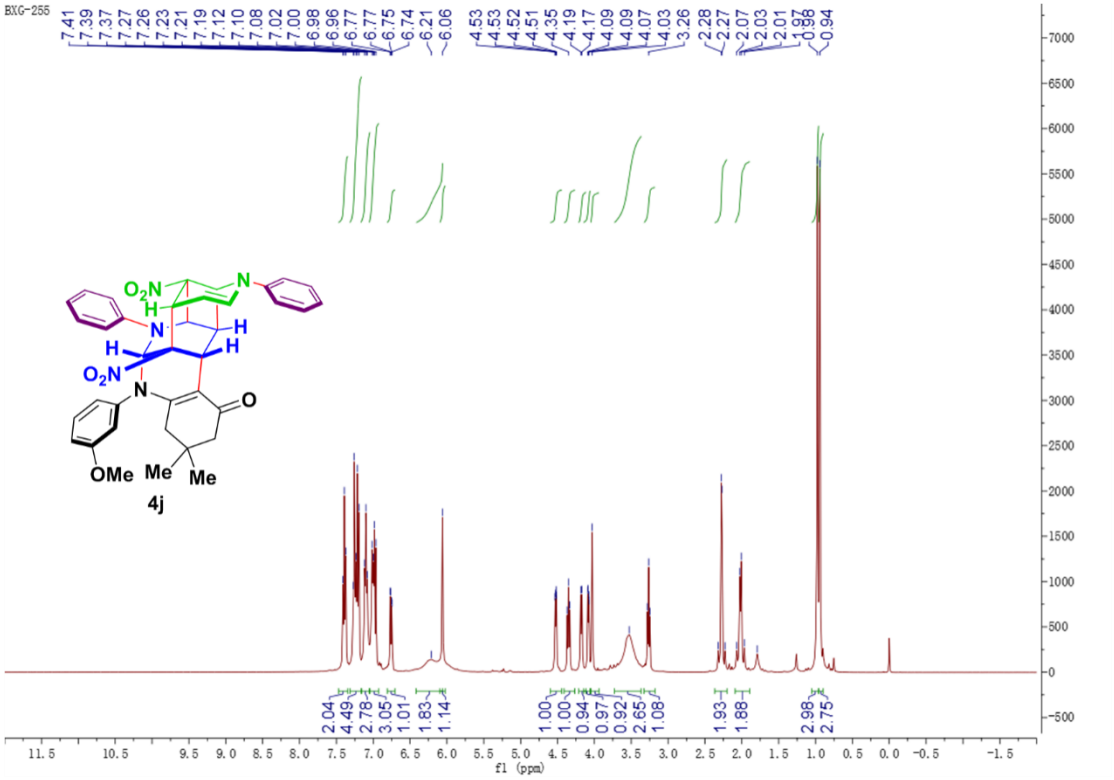
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



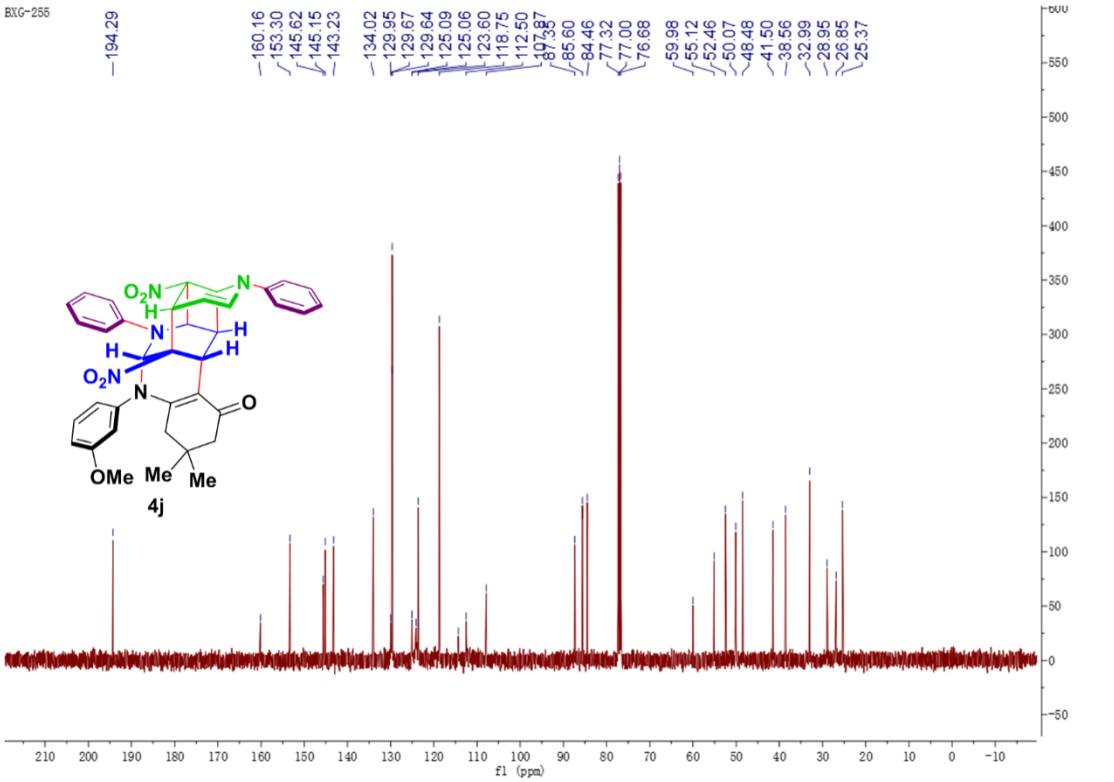
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



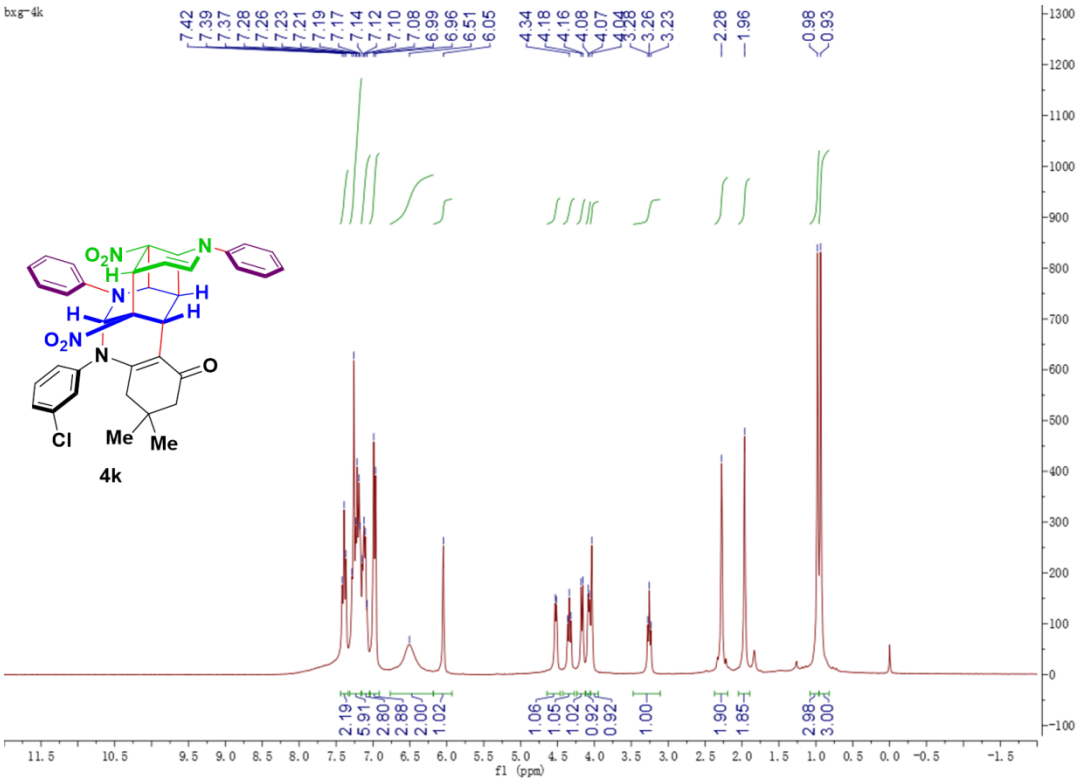
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



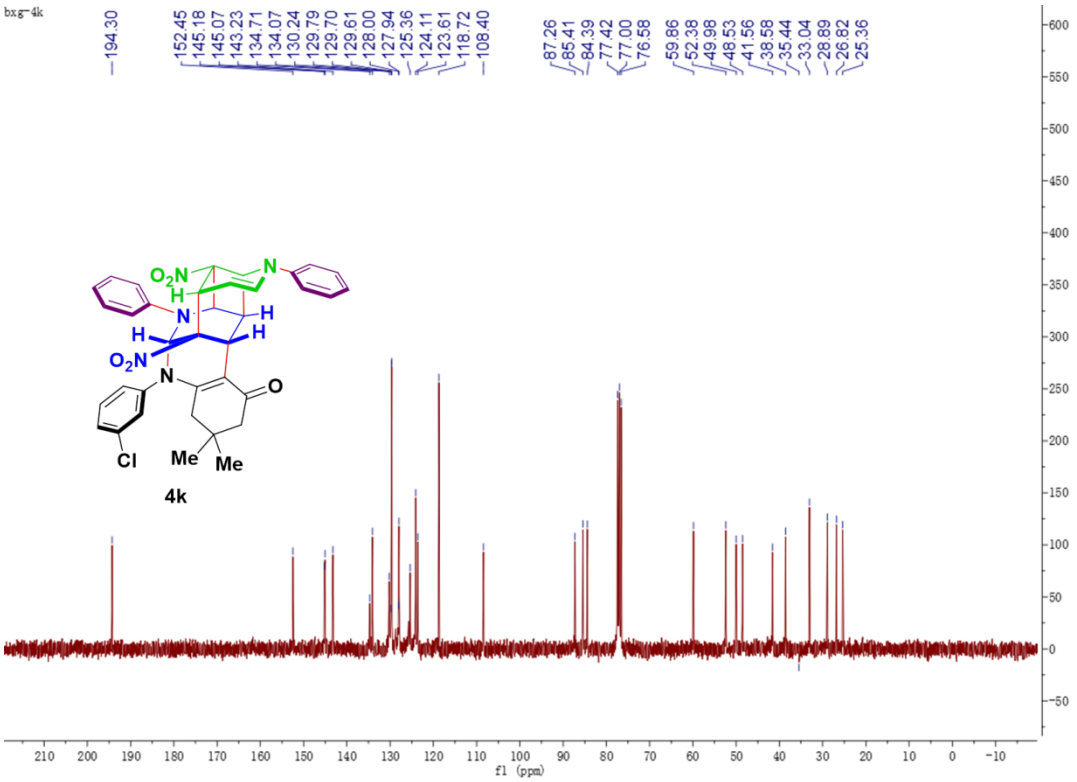
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



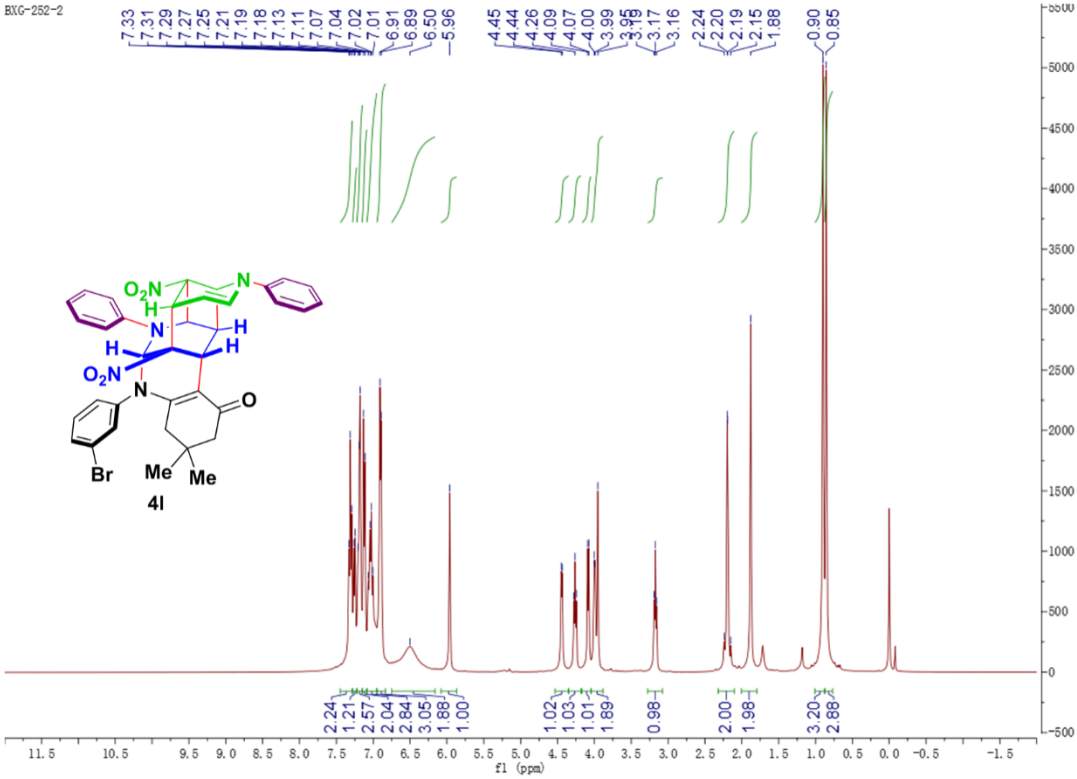
^{1}H NMR spectrum of **4k** (300 MHz, $CDCl_3$)



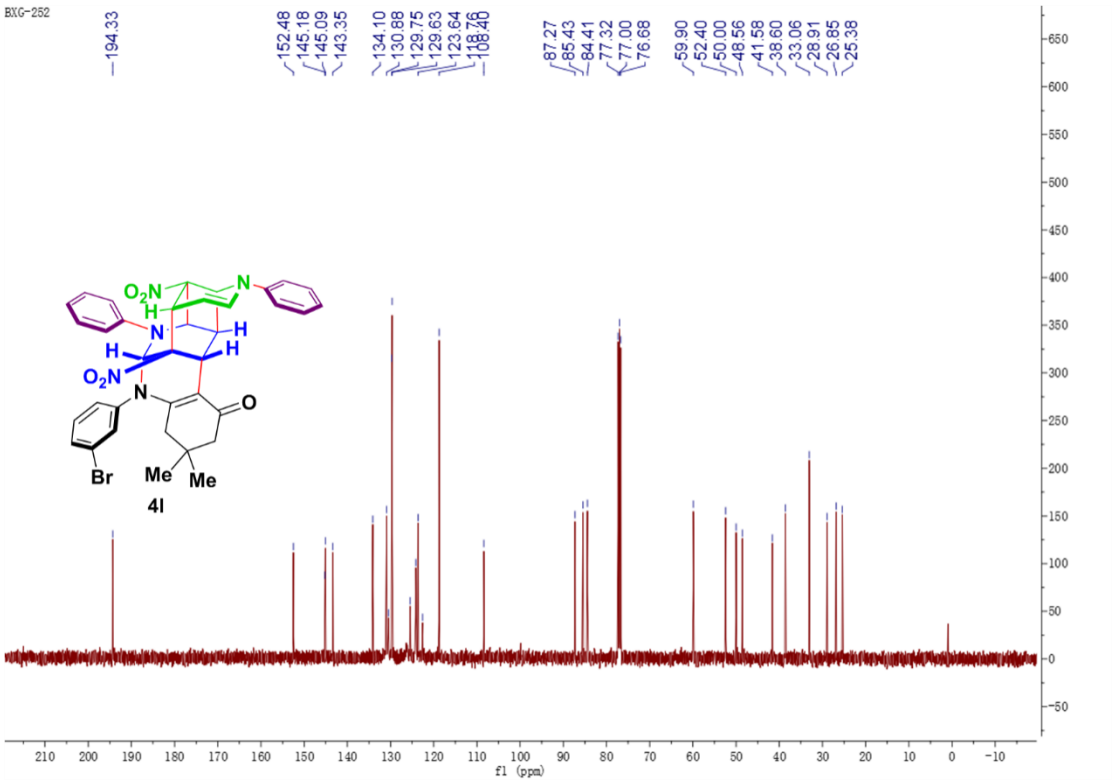
^{13}C NMR spectrum of **4k** (75 MHz, $CDCl_3$)



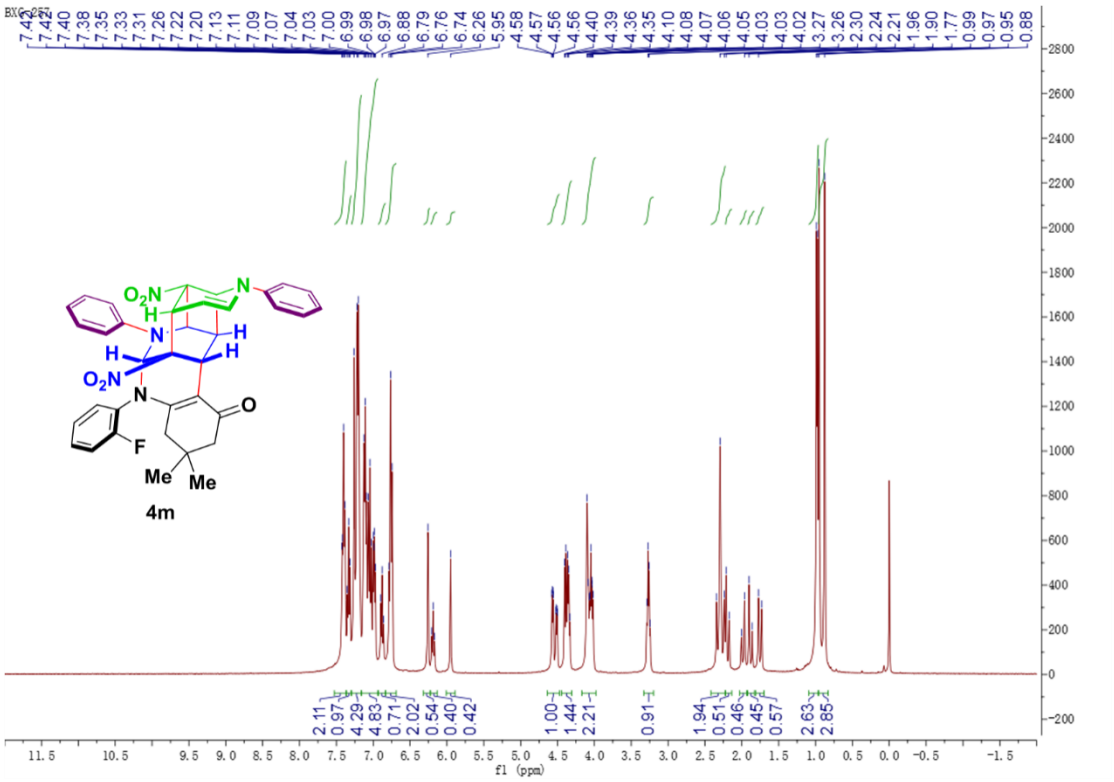
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



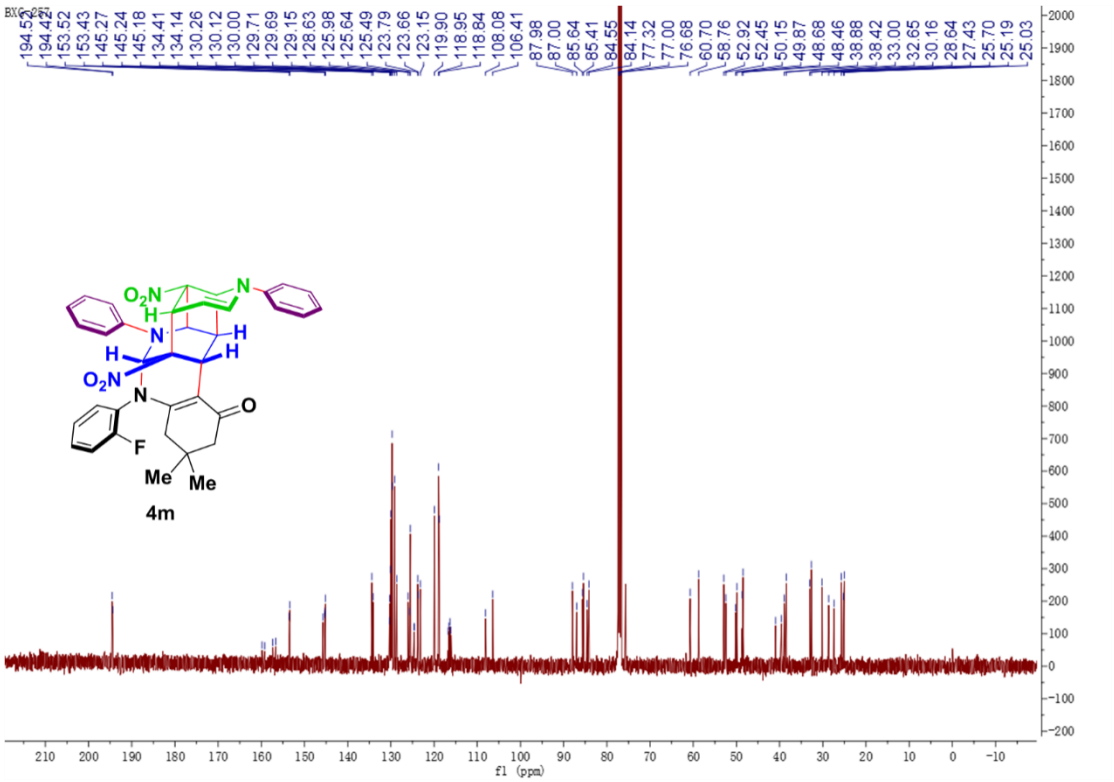
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



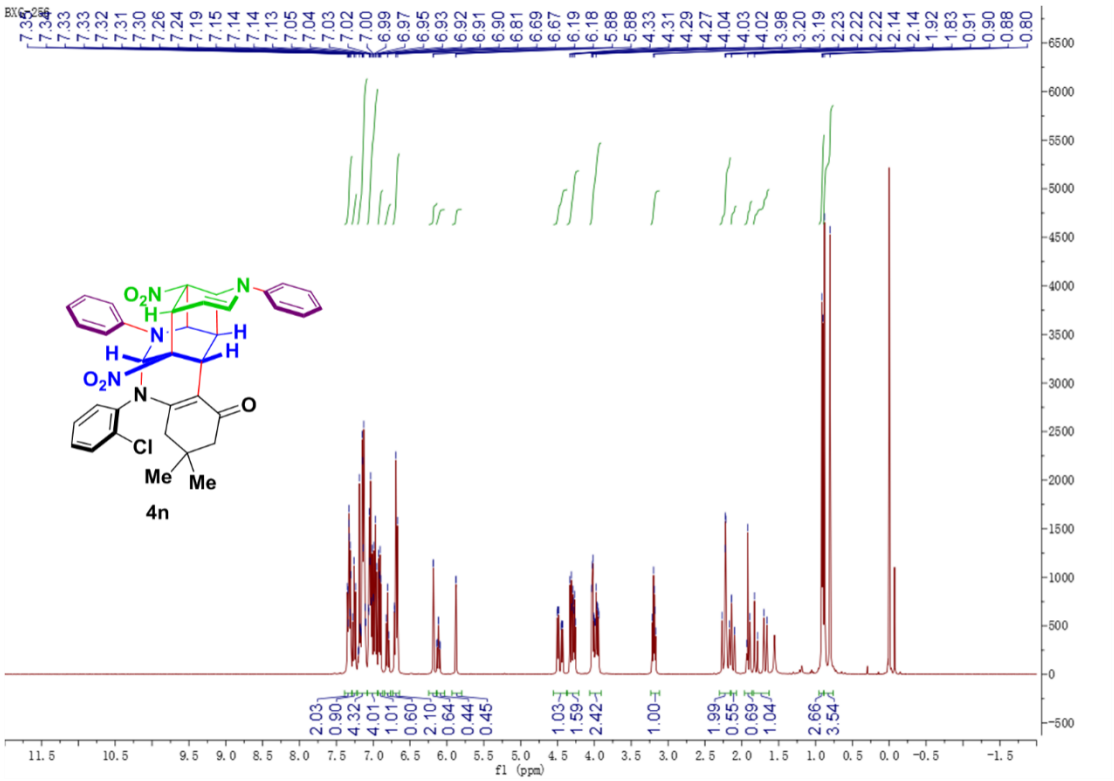
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$)



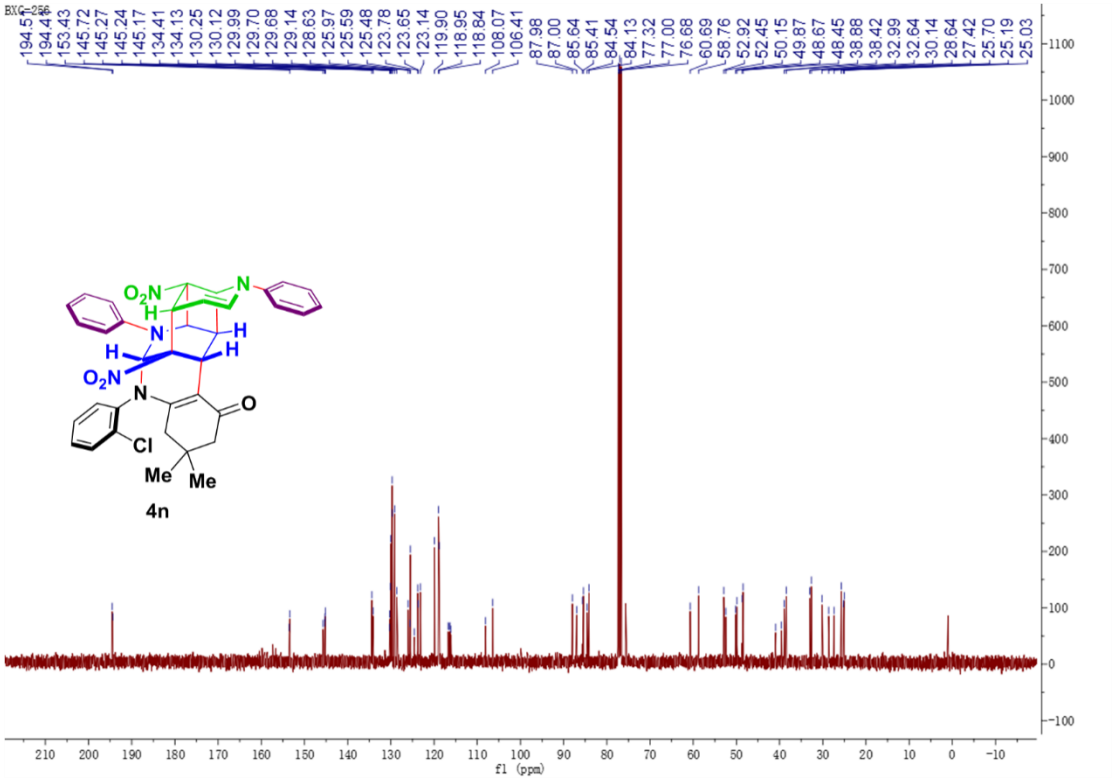
^{13}C NMR spectrum of **4m** (100 MHz, $CDCl_3$)



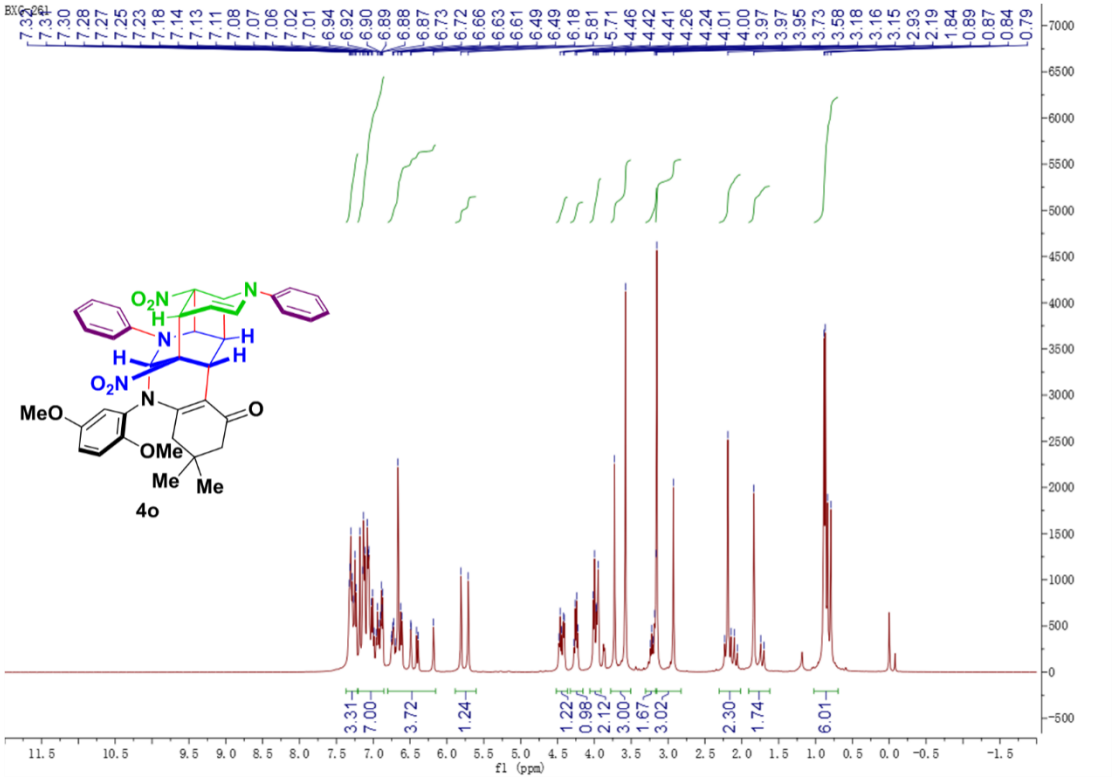
^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$)



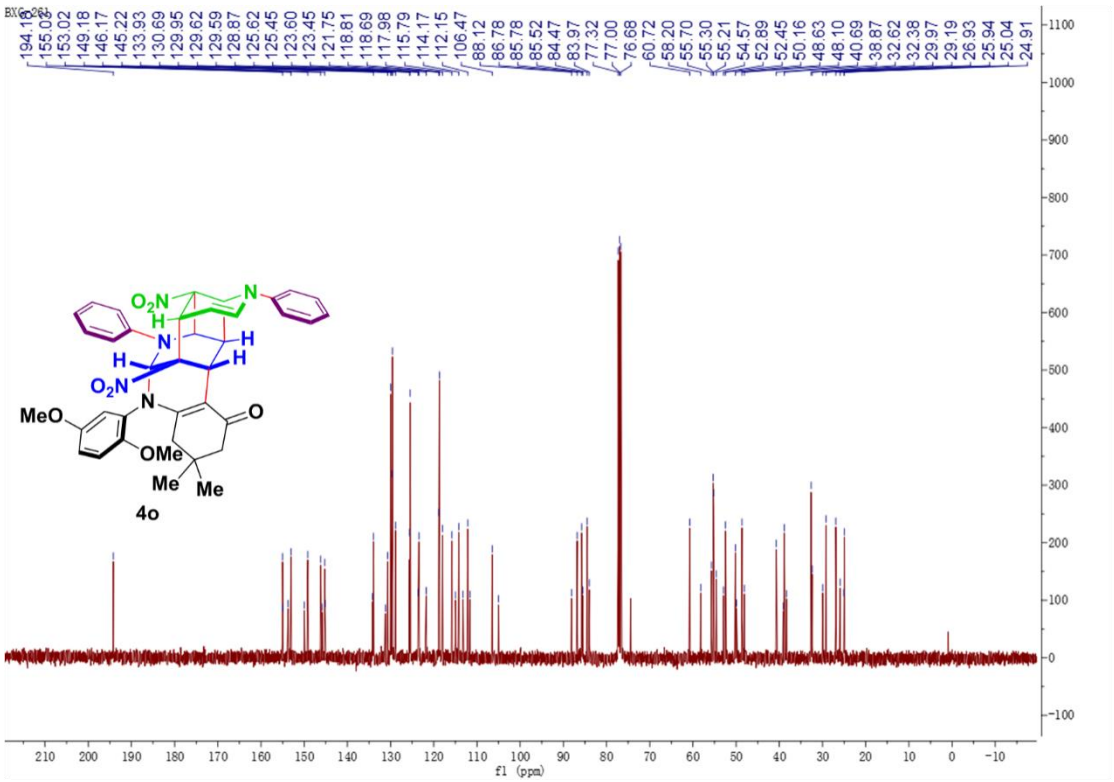
^{13}C NMR spectrum of **4n** (100 MHz, $CDCl_3$)



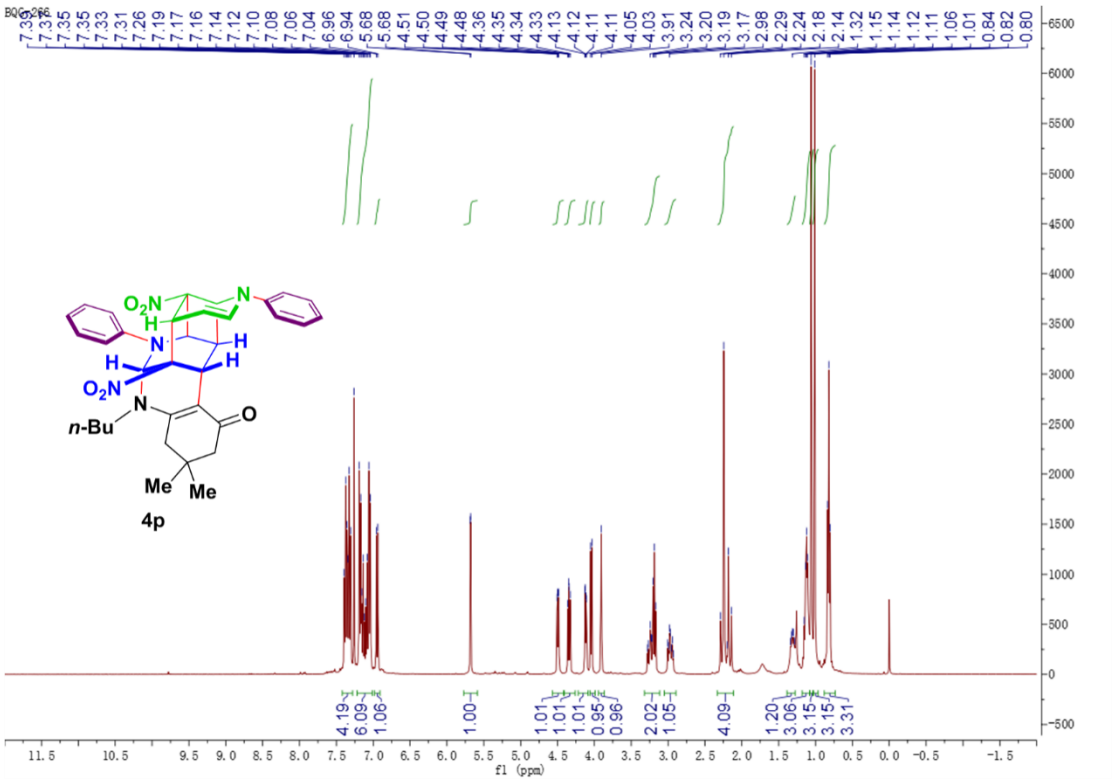
^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$)



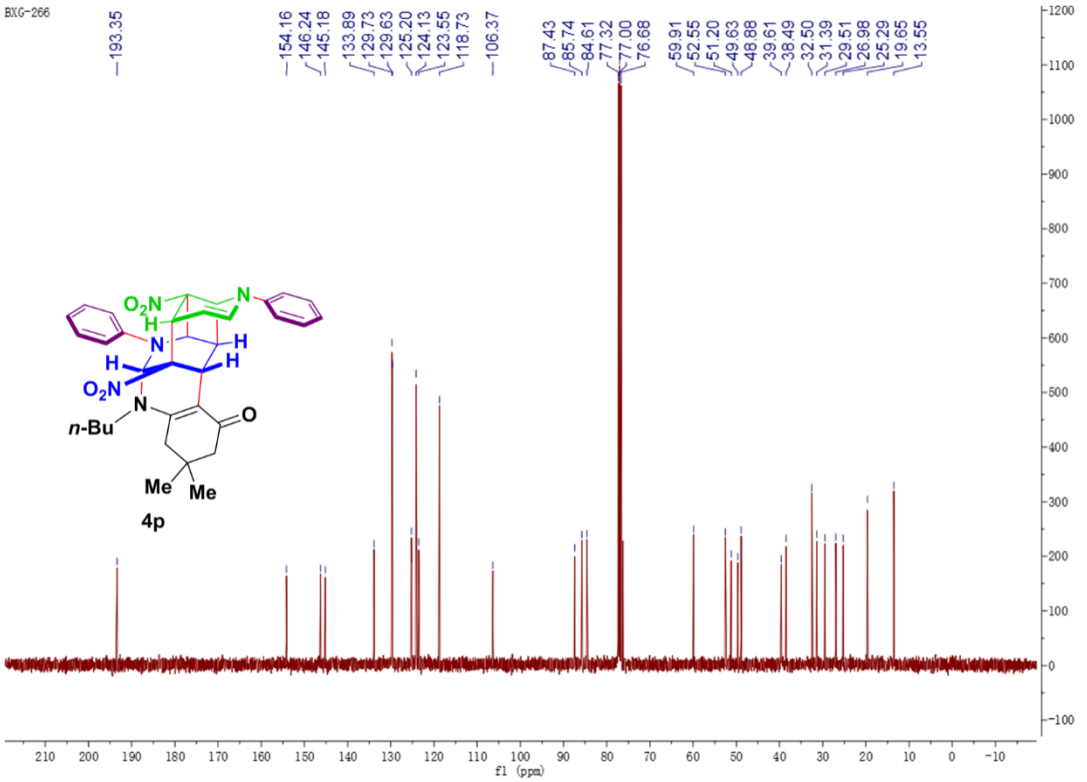
^{13}C NMR spectrum of **4o** (100 MHz, $CDCl_3$)



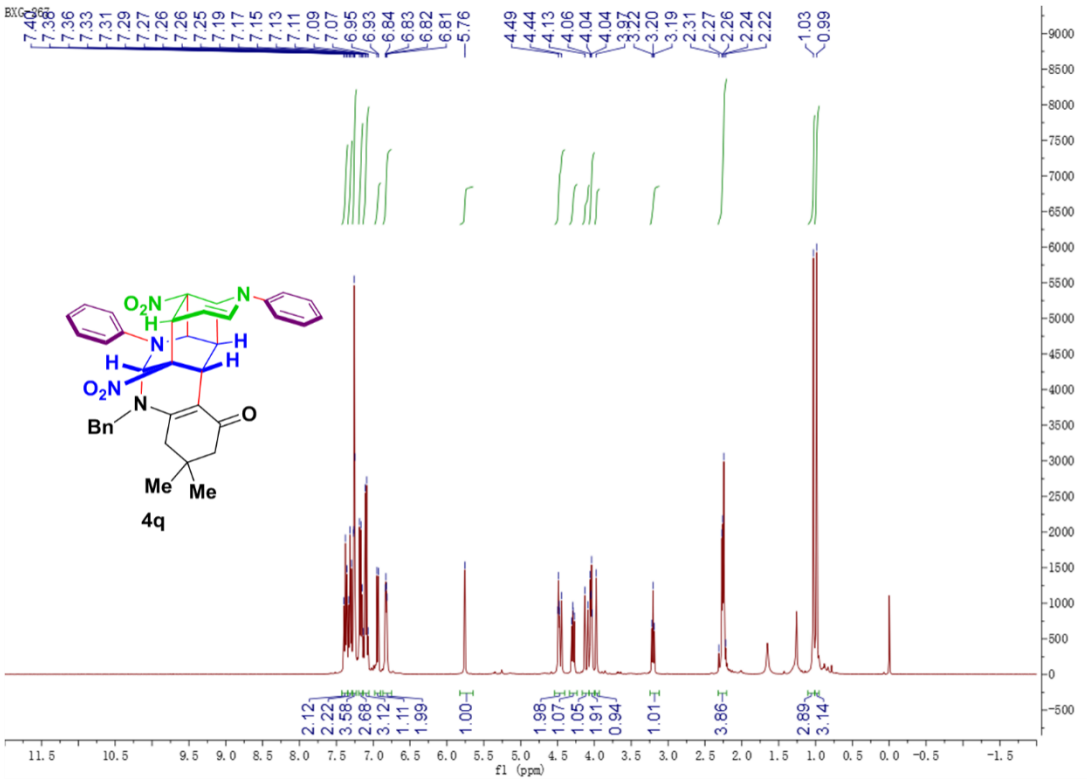
^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$)



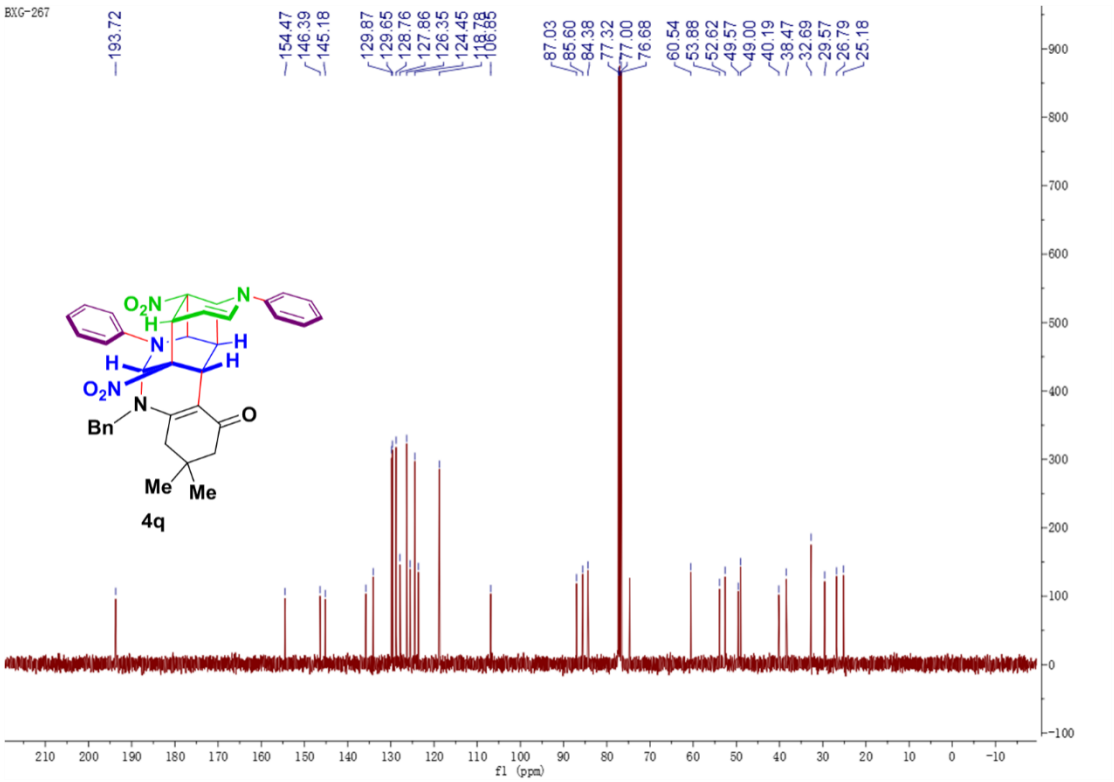
^{13}C NMR spectrum of **4p** (100 MHz, $CDCl_3$)



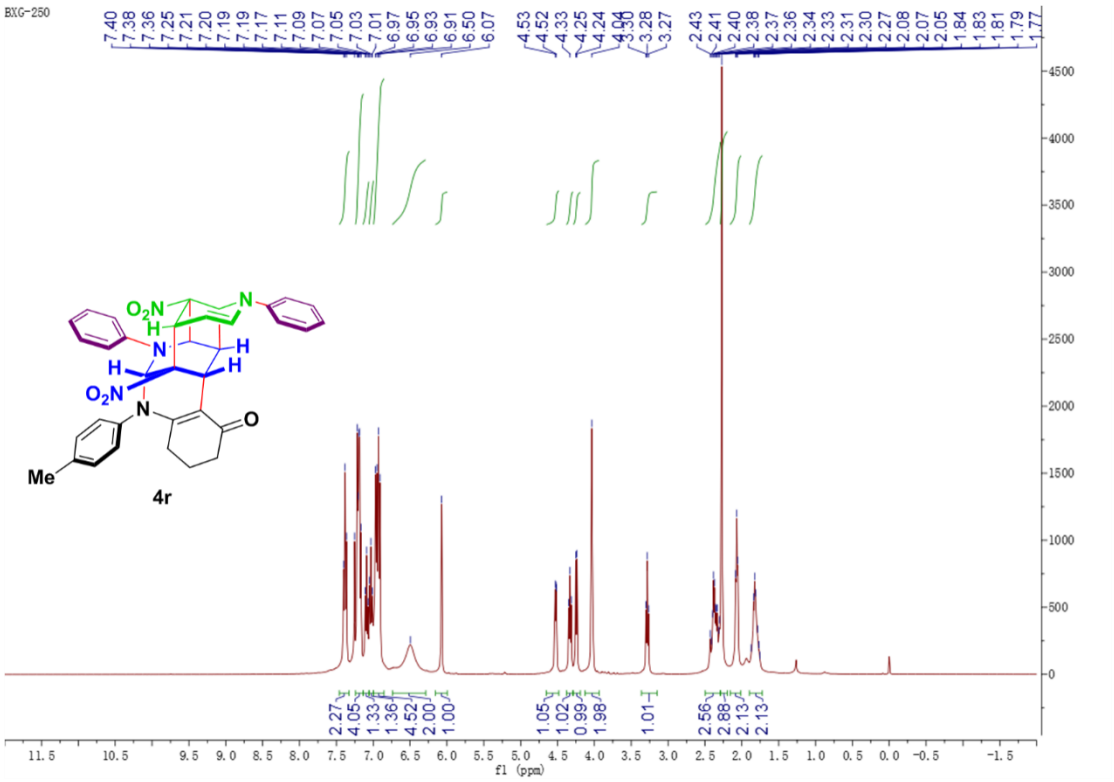
^{1}H NMR spectrum of **4q** (400 MHz, $CDCl_3$)



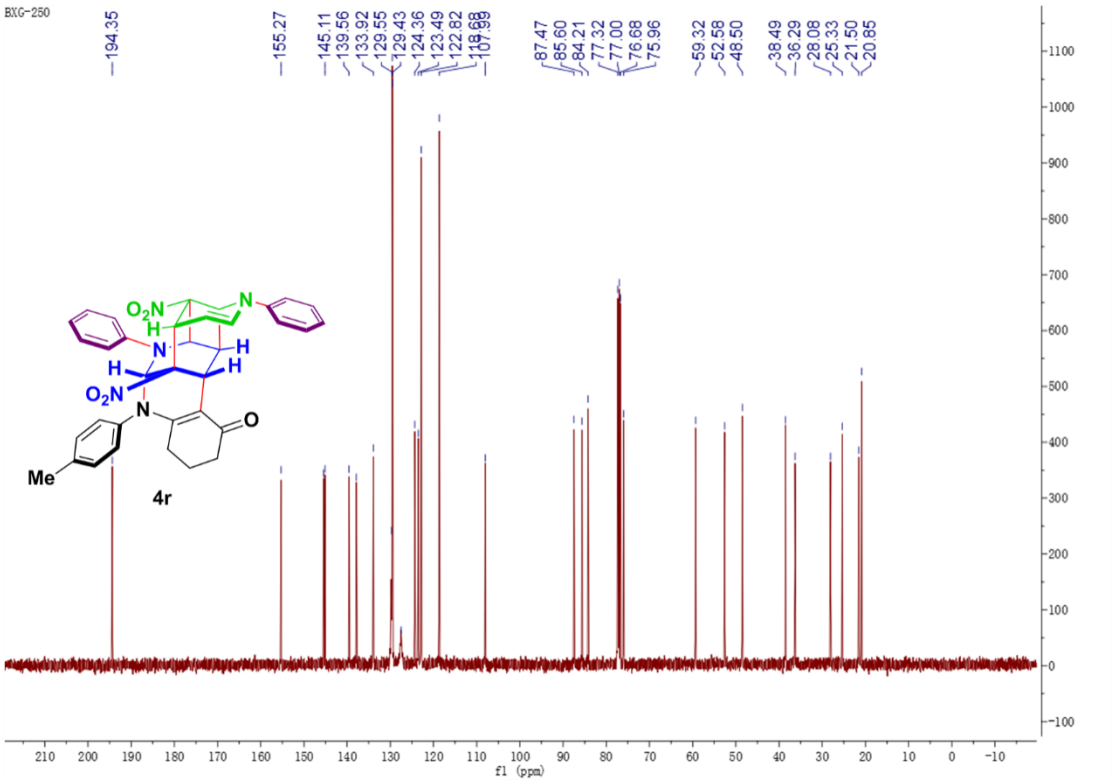
^{13}C NMR spectrum of **4q** (100 MHz, $CDCl_3$)



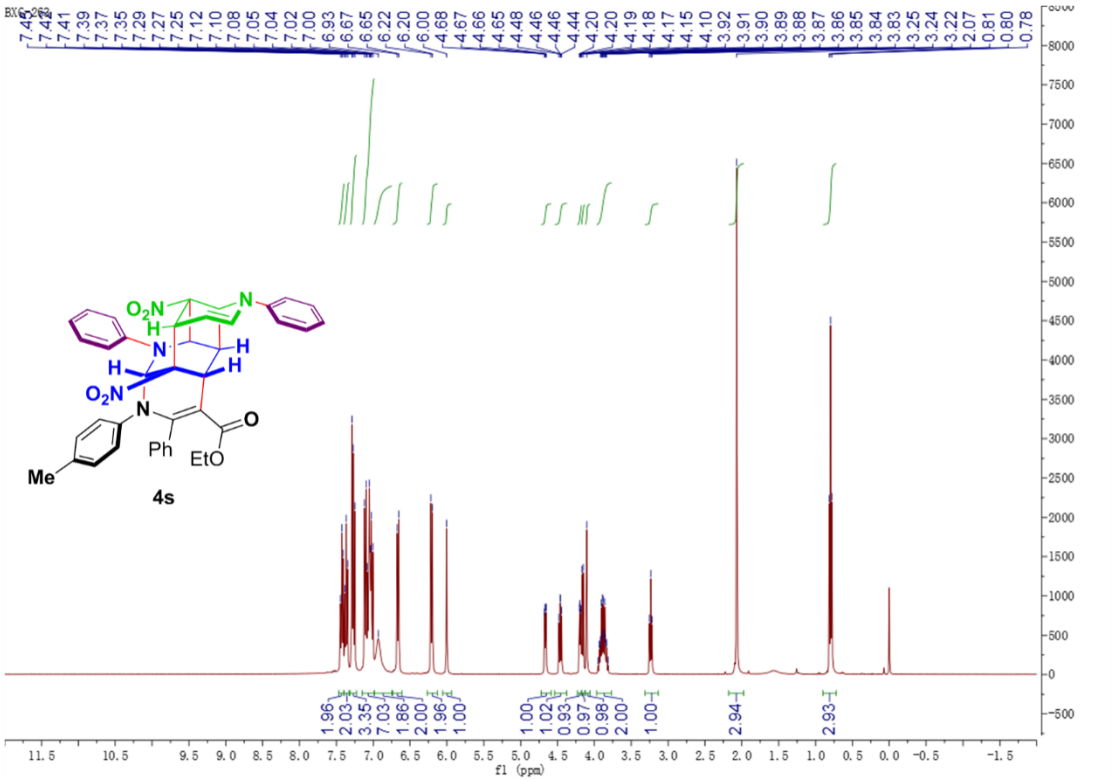
^{1}H NMR spectrum of **4r** (400 MHz, $CDCl_3$)



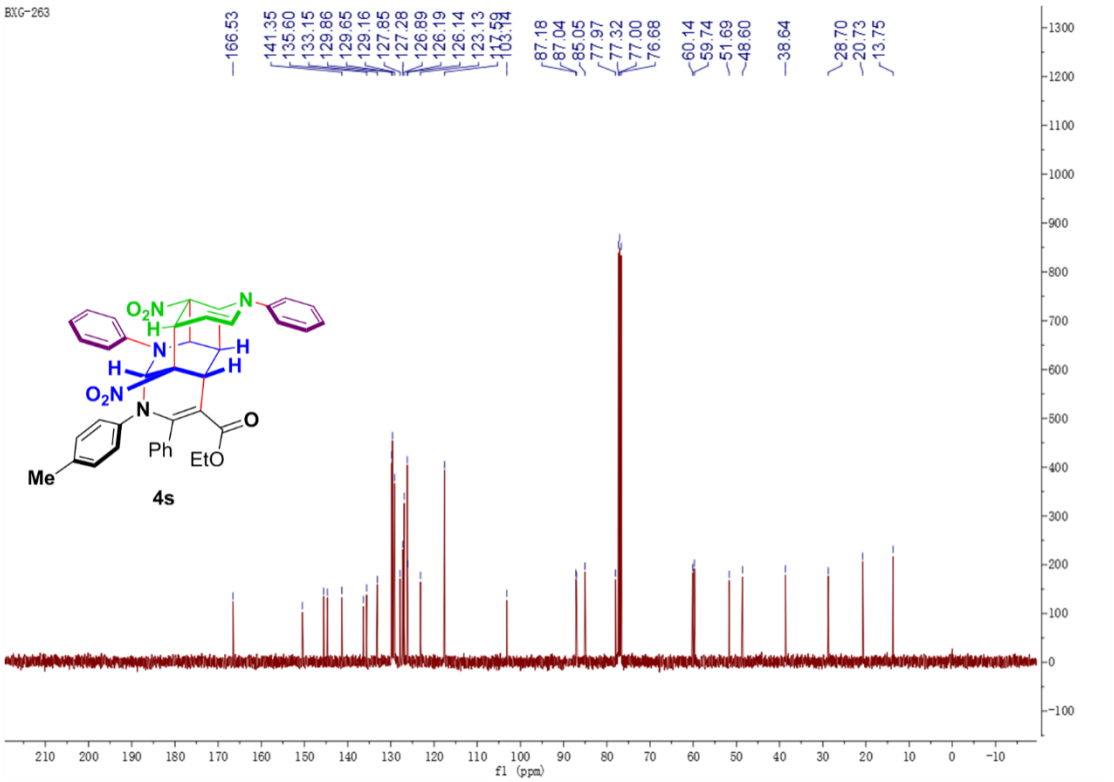
^{13}C NMR spectrum of **4r** (100 MHz, $CDCl_3$)



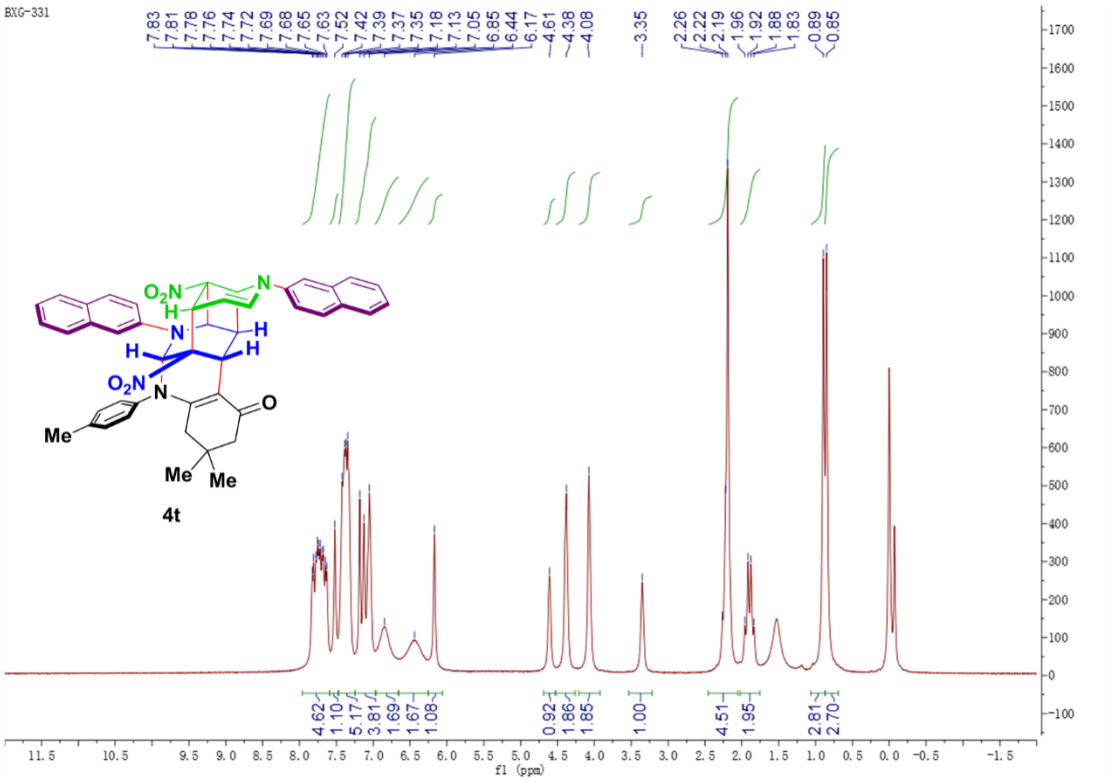
^{1}H NMR spectrum of **4s** (400 MHz, $CDCl_3$)



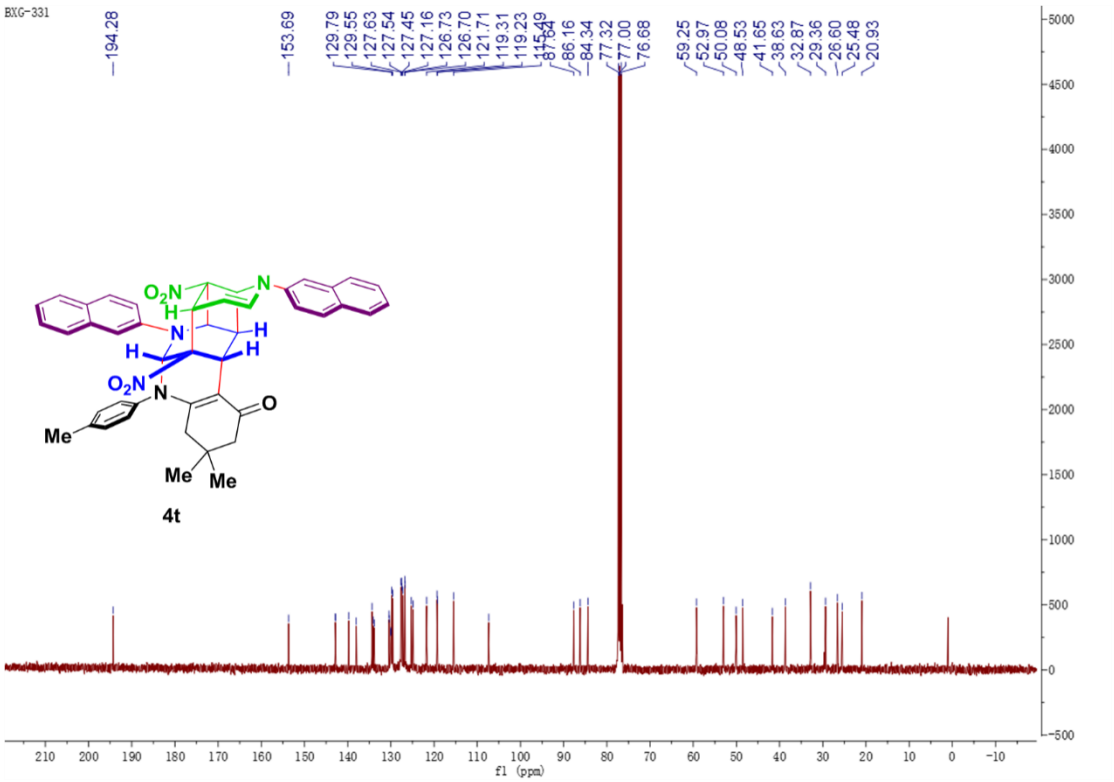
^{13}C NMR spectrum of **4s** (100 MHz, $CDCl_3$)



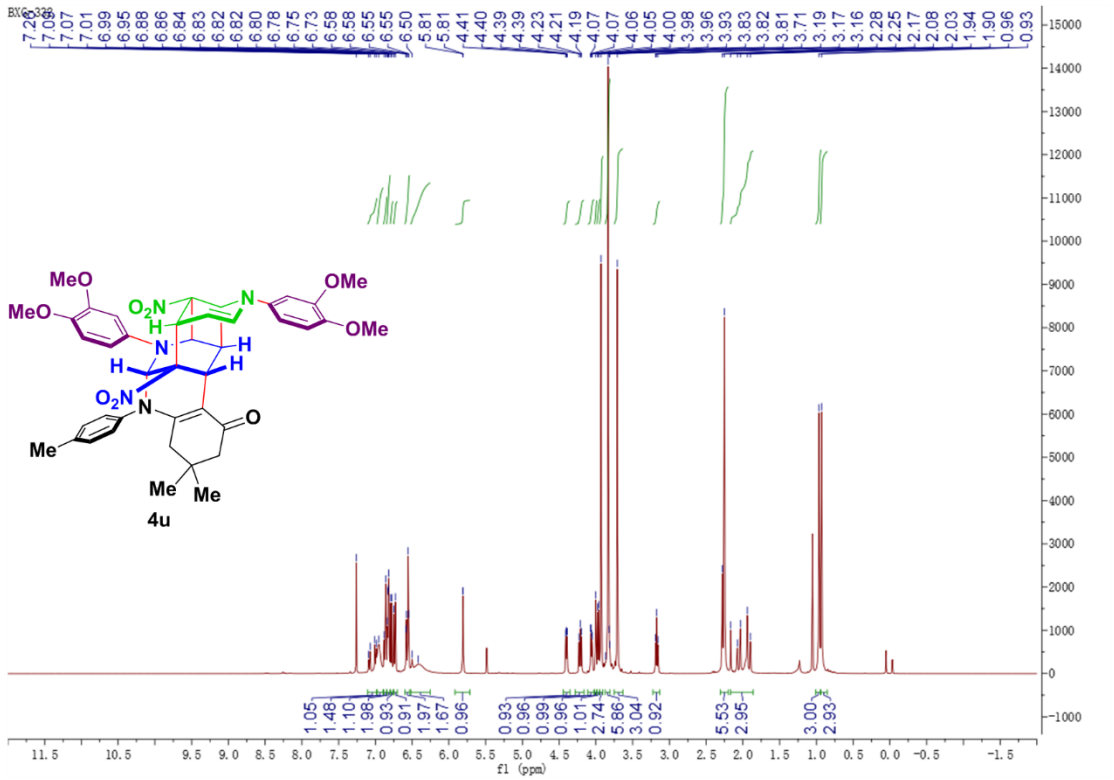
^{1}H NMR spectrum of **4t** (400 MHz, $CDCl_3$)



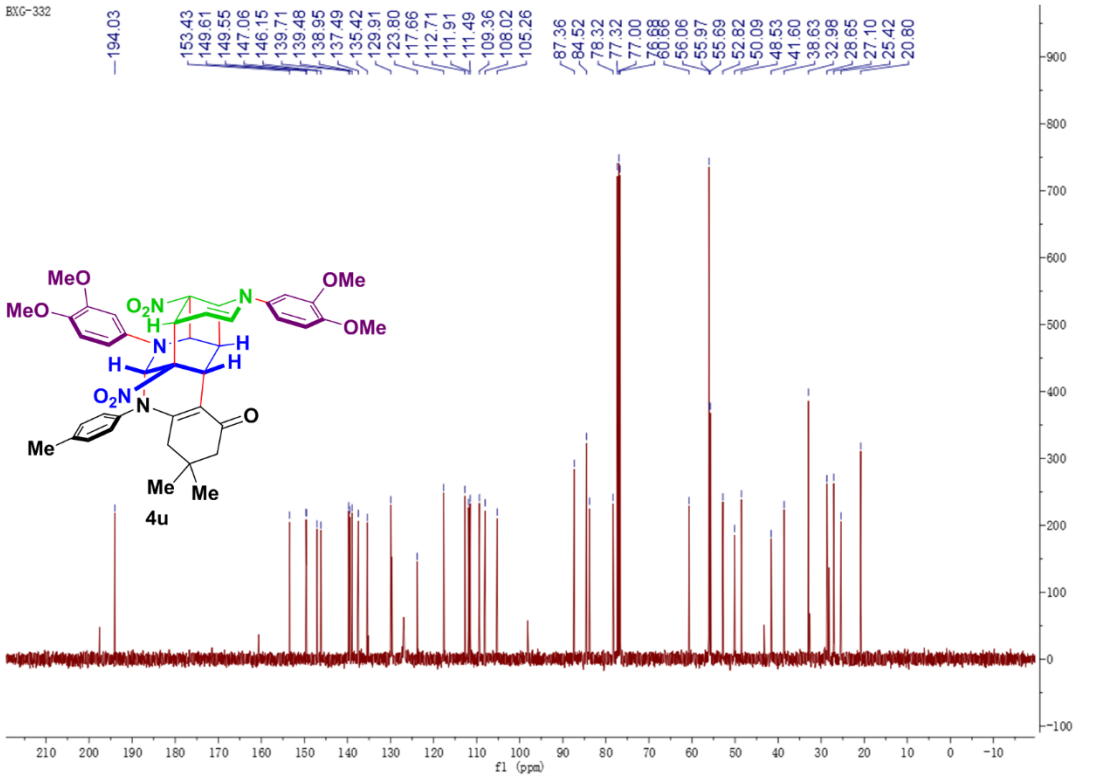
^{13}C NMR spectrum of **4t** (100 MHz, $CDCl_3$)



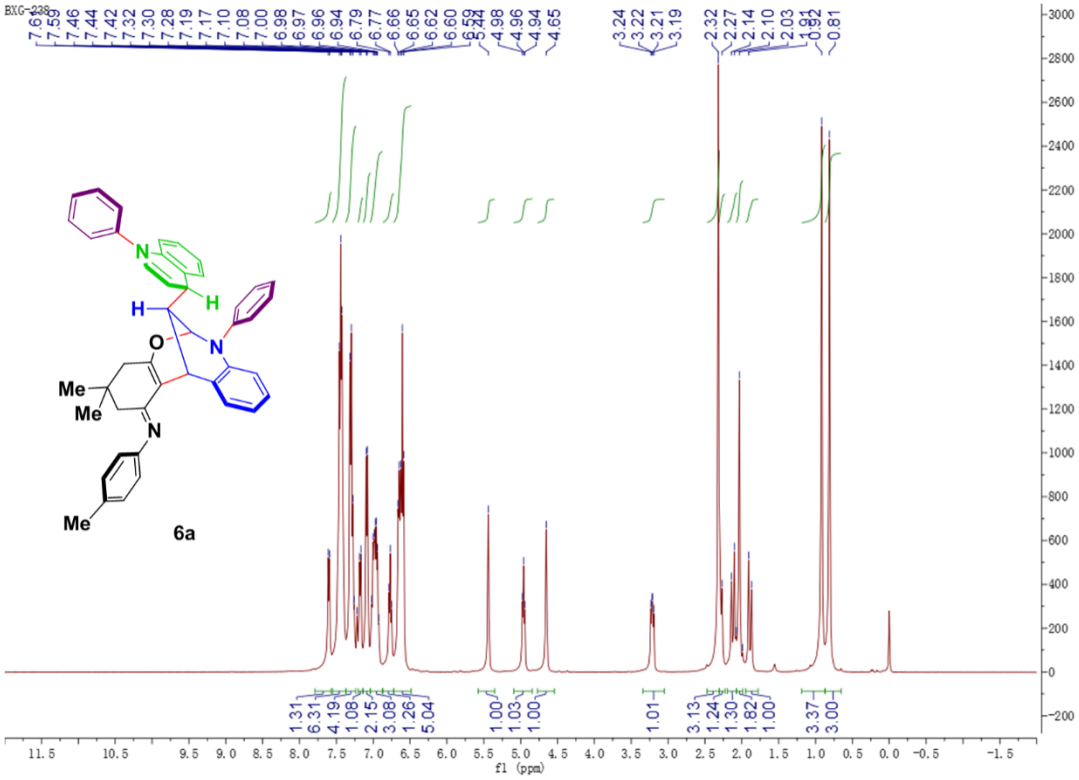
^{1}H NMR spectrum of **4u** (400 MHz, $CDCl_3$)



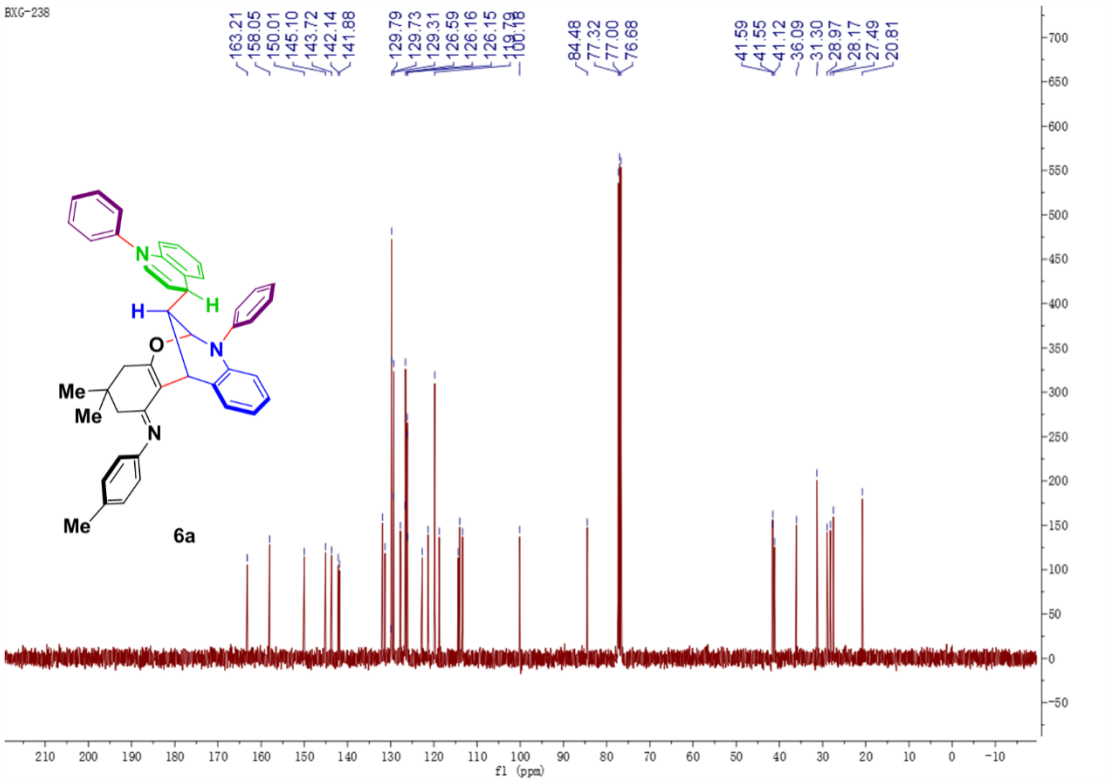
^{13}C NMR spectrum of **4u** (100 MHz, $CDCl_3$)



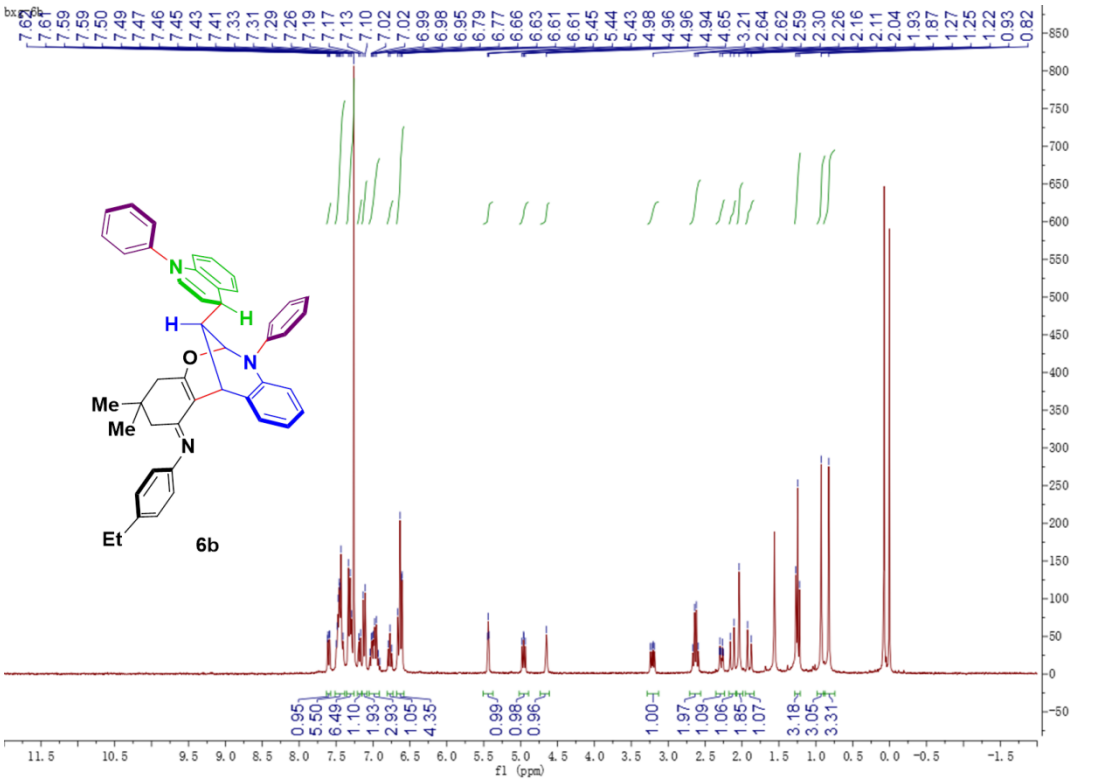
^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



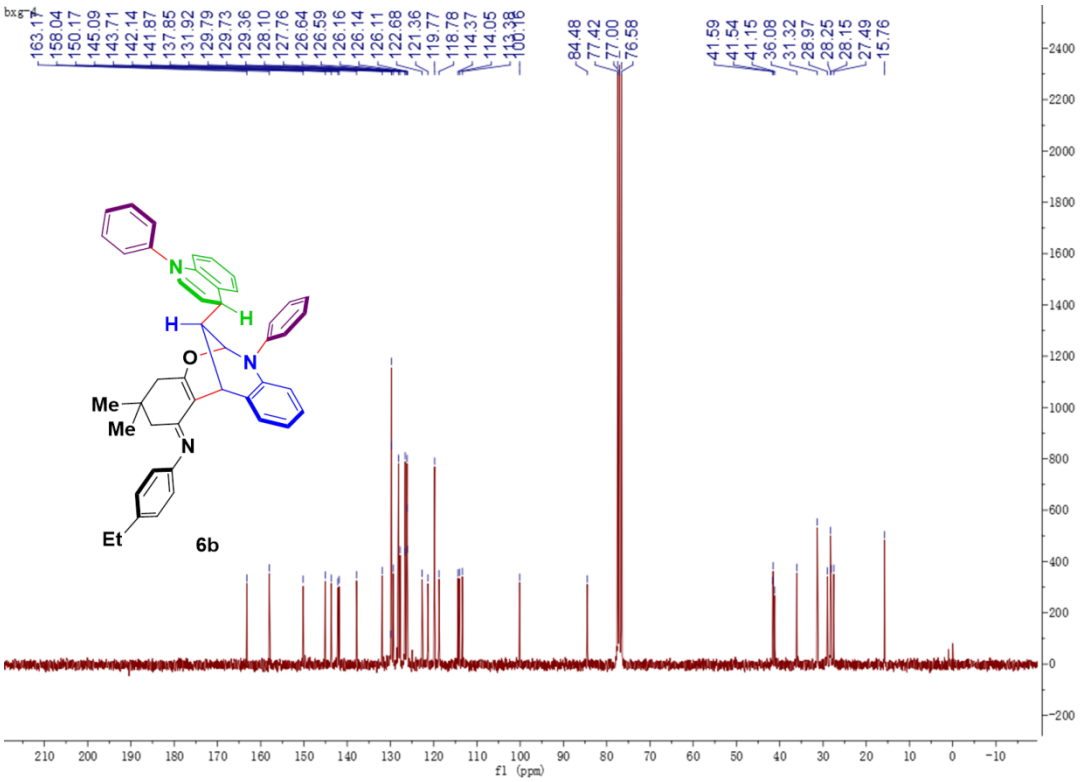
^{13}C NMR spectrum of **6a** (100 MHz, $CDCl_3$)



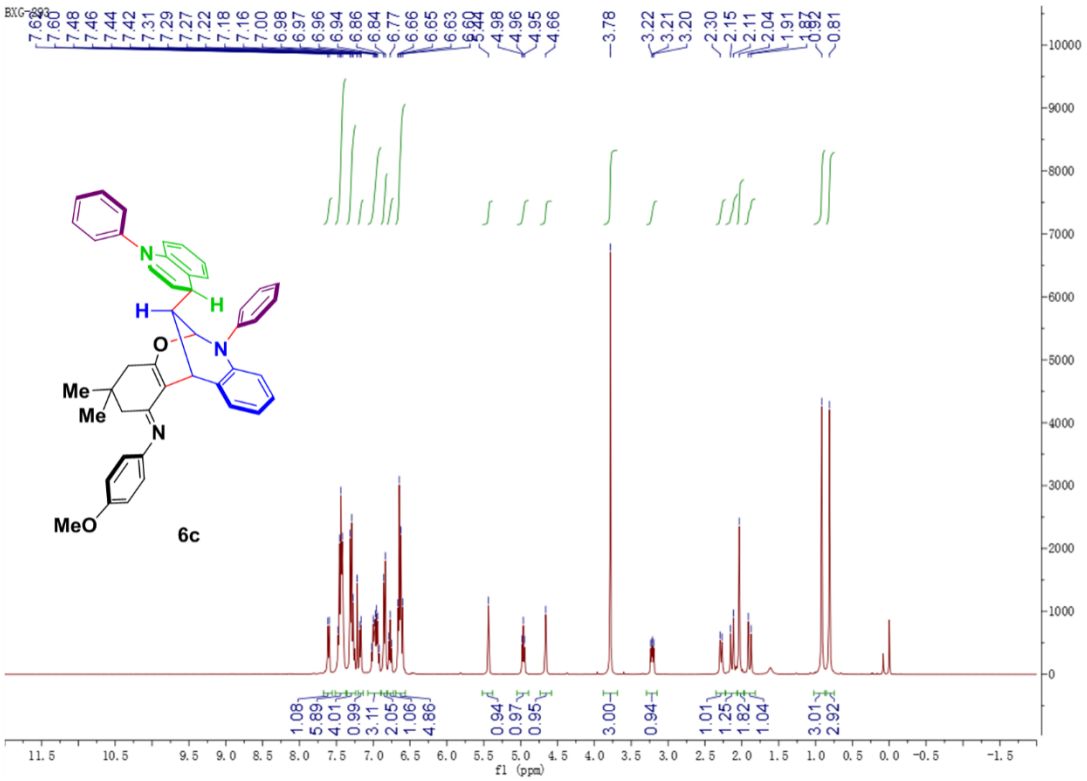
^{1}H NMR spectrum of **6b** (300 MHz, $CDCl_3$)



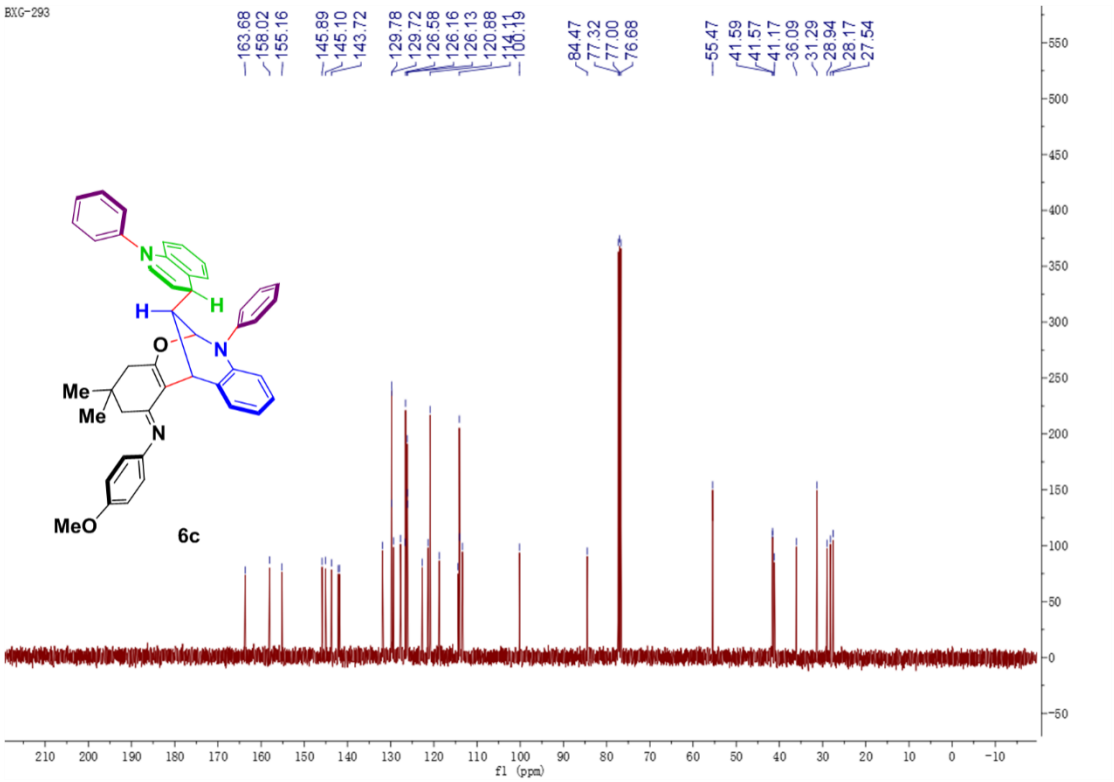
^{13}C NMR spectrum of **6b** (75 MHz, $CDCl_3$)



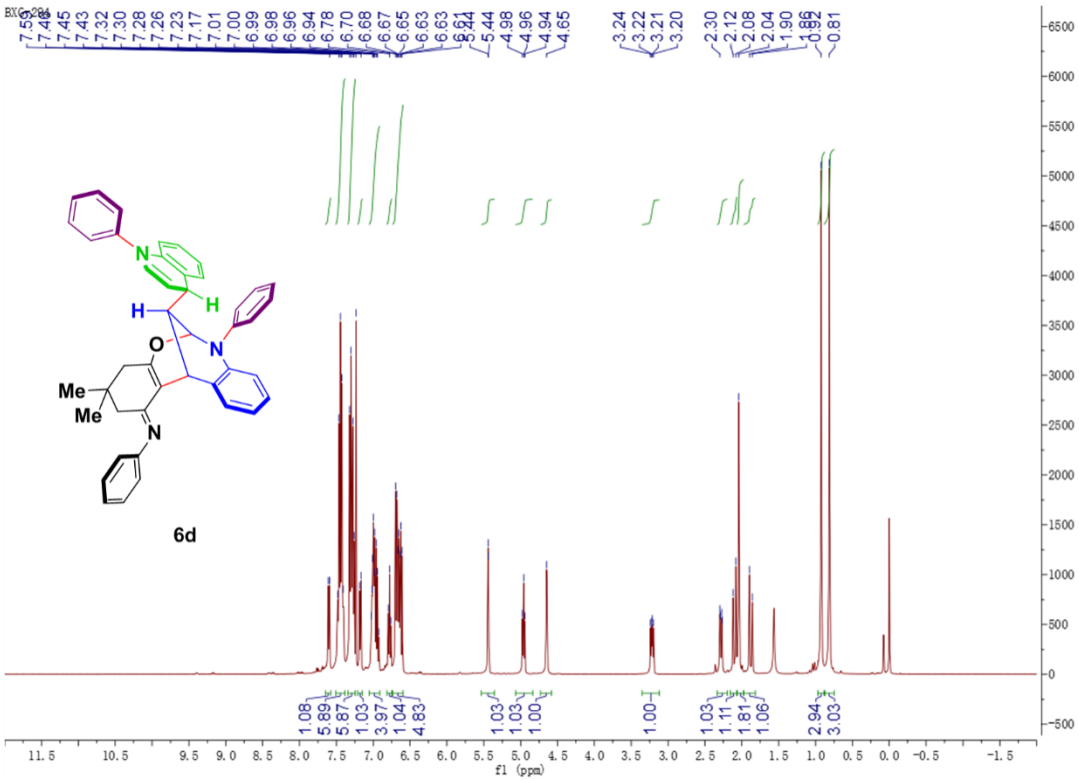
^{1}H NMR spectrum of **6c** (400 MHz, $CDCl_3$)



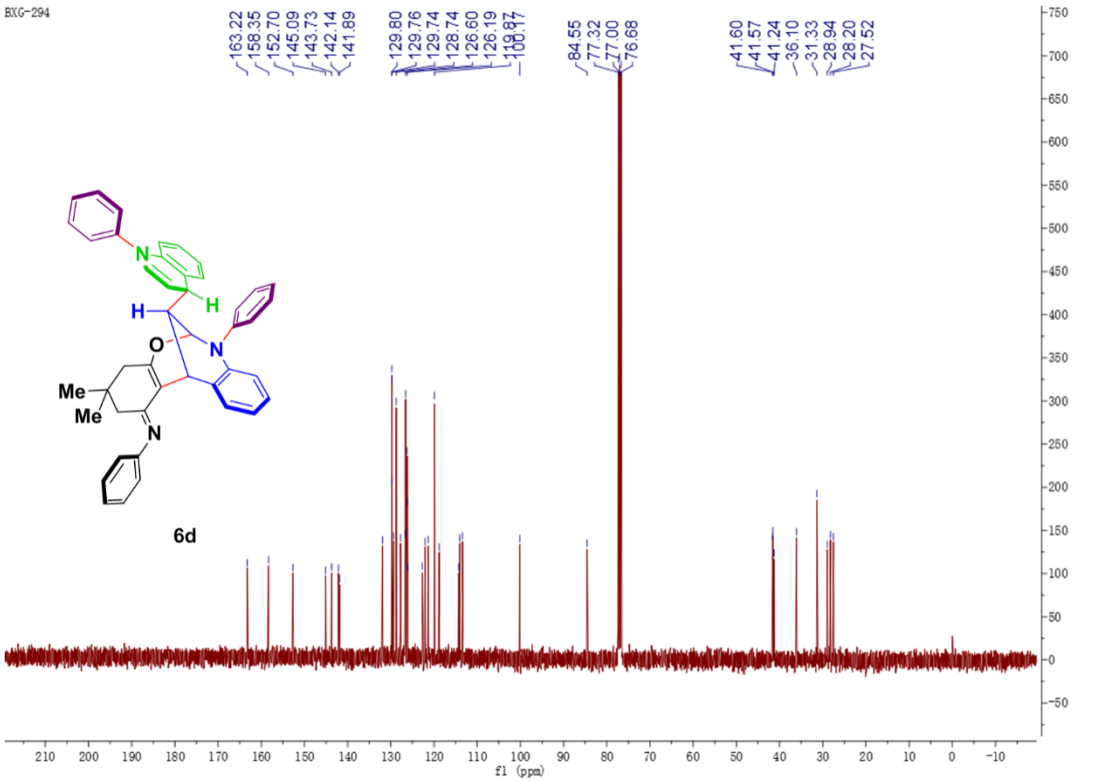
^{13}C NMR spectrum of **6c** (100 MHz, $CDCl_3$)



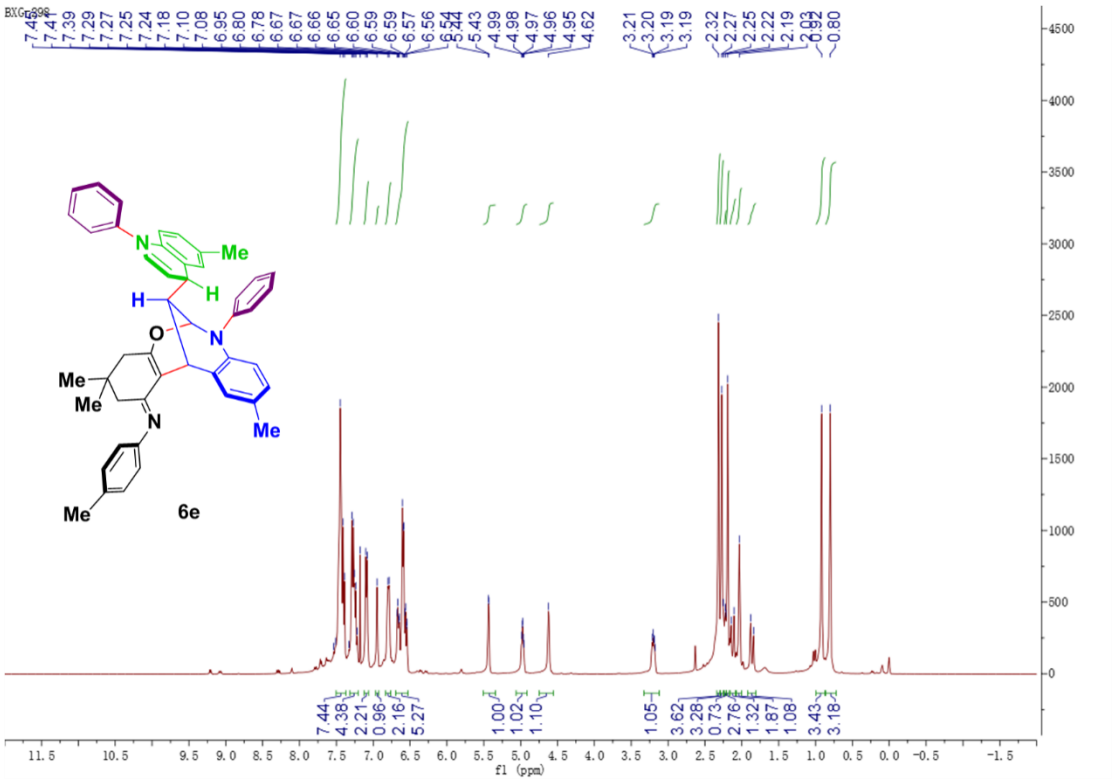
^{1}H NMR spectrum of **6d** (400 MHz, $CDCl_3$)



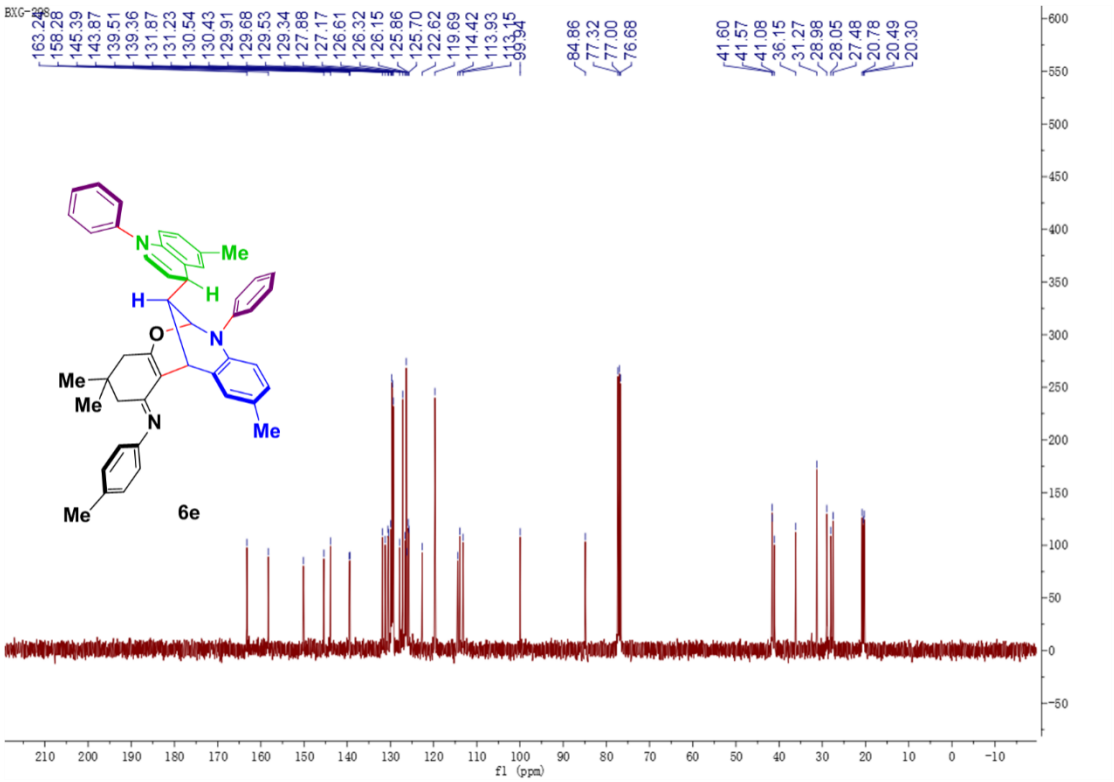
^{13}C NMR spectrum of **6d** (100 MHz, $CDCl_3$)



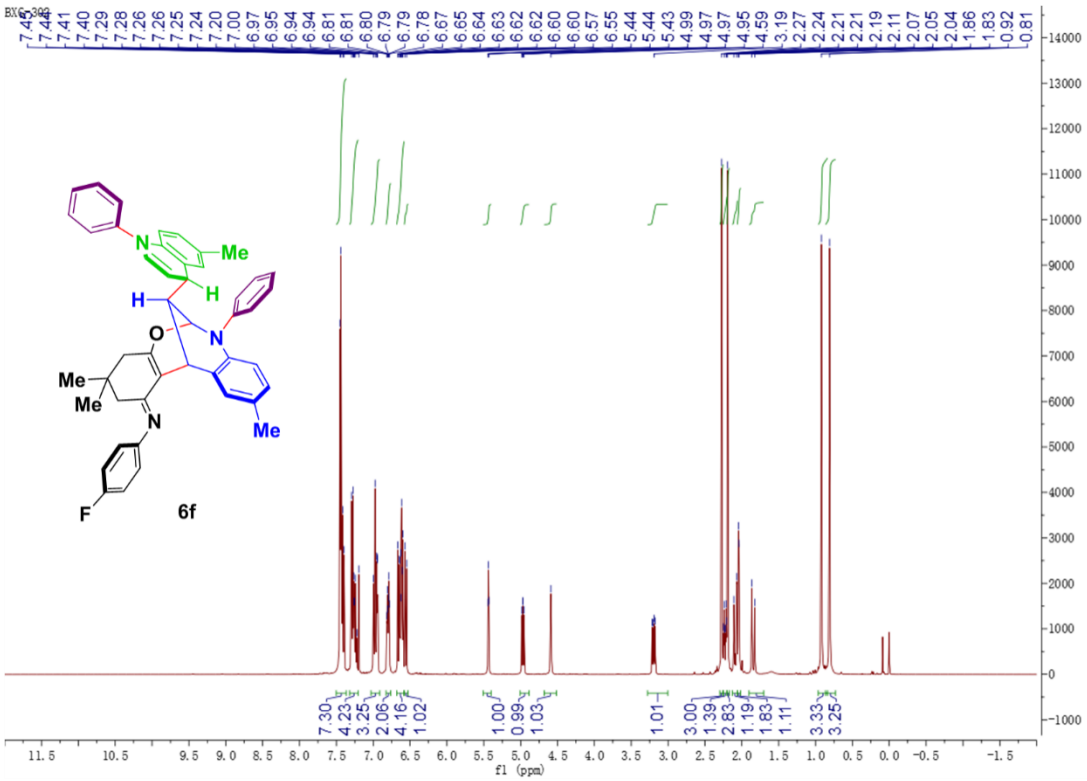
^{1}H NMR spectrum of **6e** (400 MHz, $CDCl_3$)



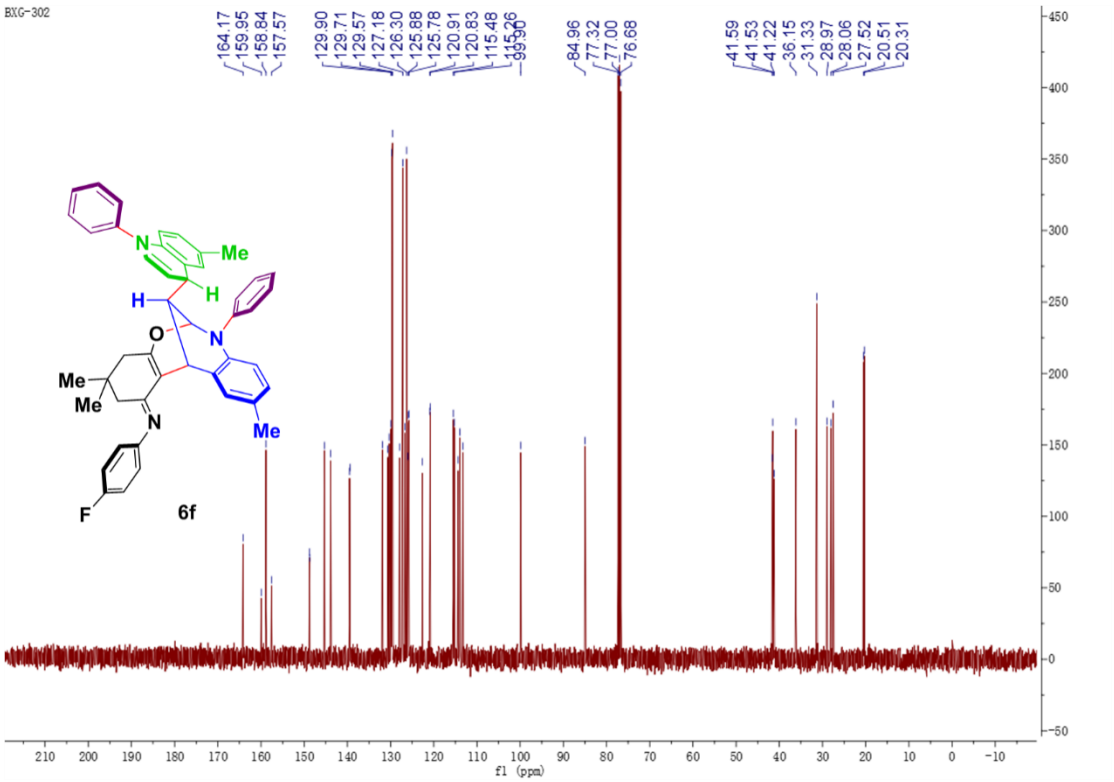
^{13}C NMR spectrum of **6e** (100 MHz, $CDCl_3$)



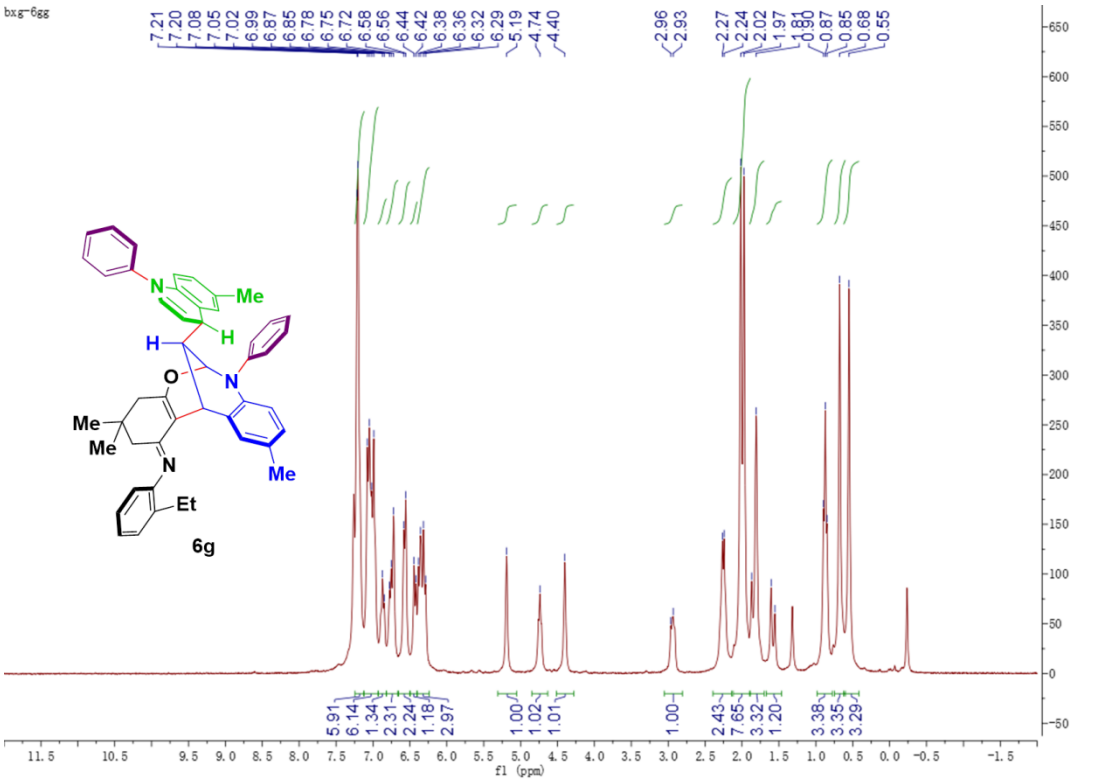
^{1}H NMR spectrum of **6f** (400 MHz, $CDCl_3$)



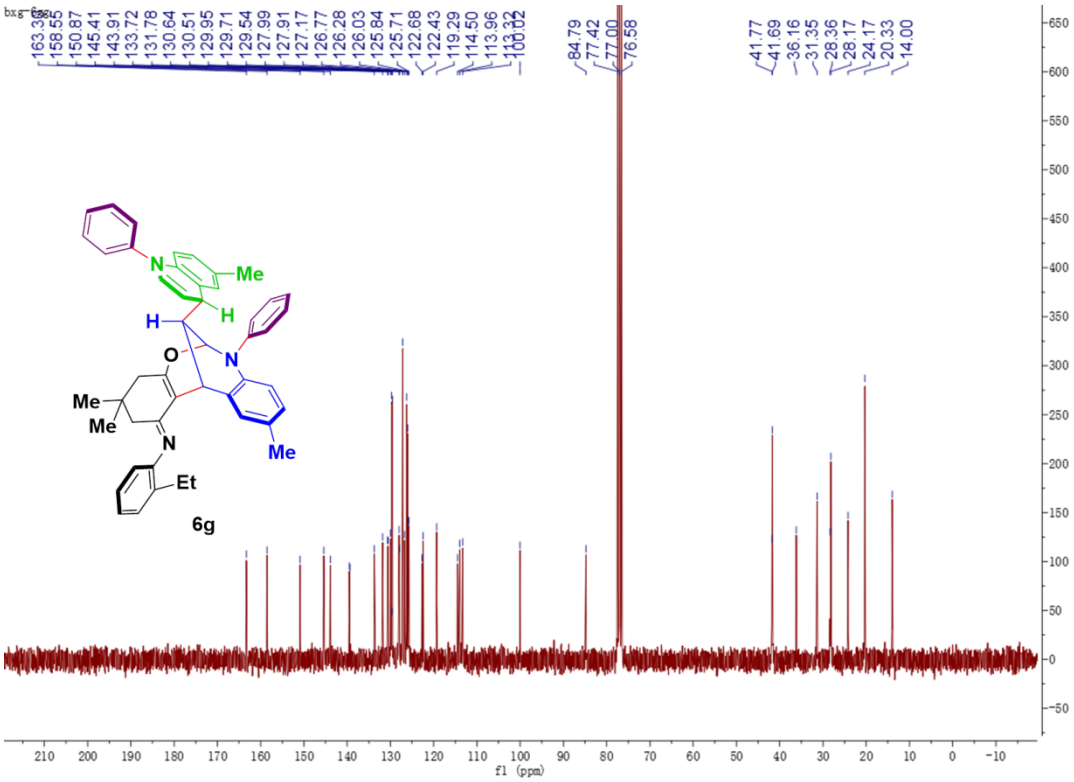
^{13}C NMR spectrum of **6f** (100 MHz, $CDCl_3$)



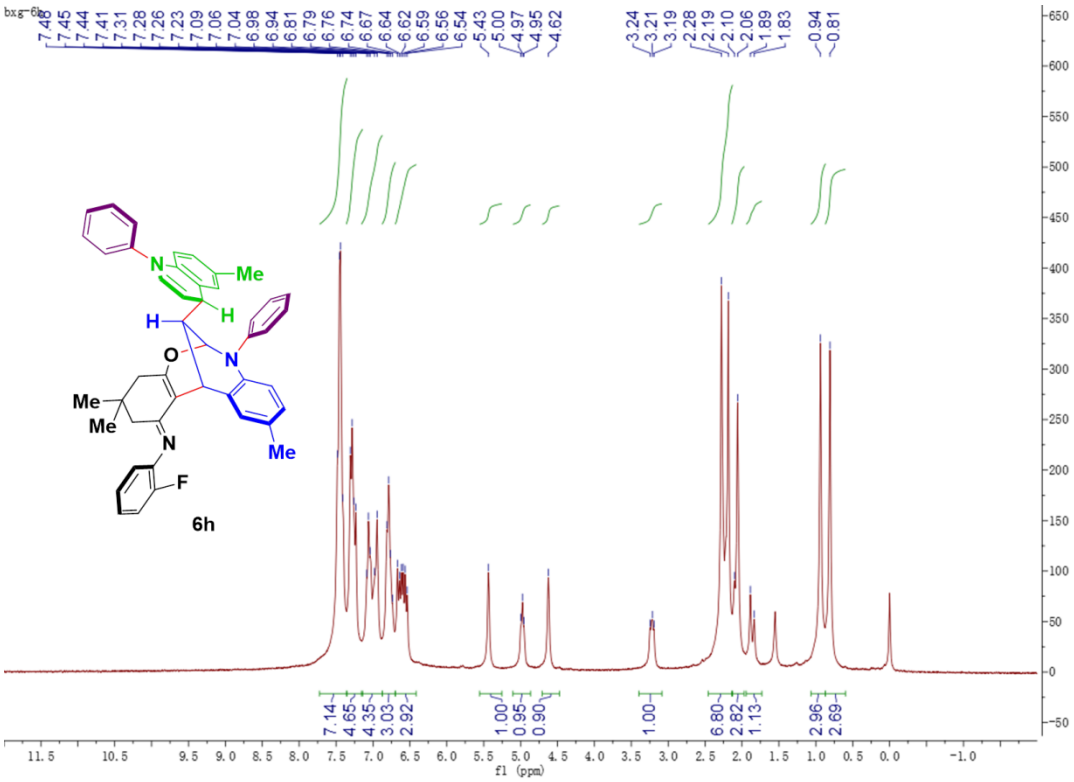
^{1}H NMR spectrum of **6g** (300 MHz, $CDCl_3$)



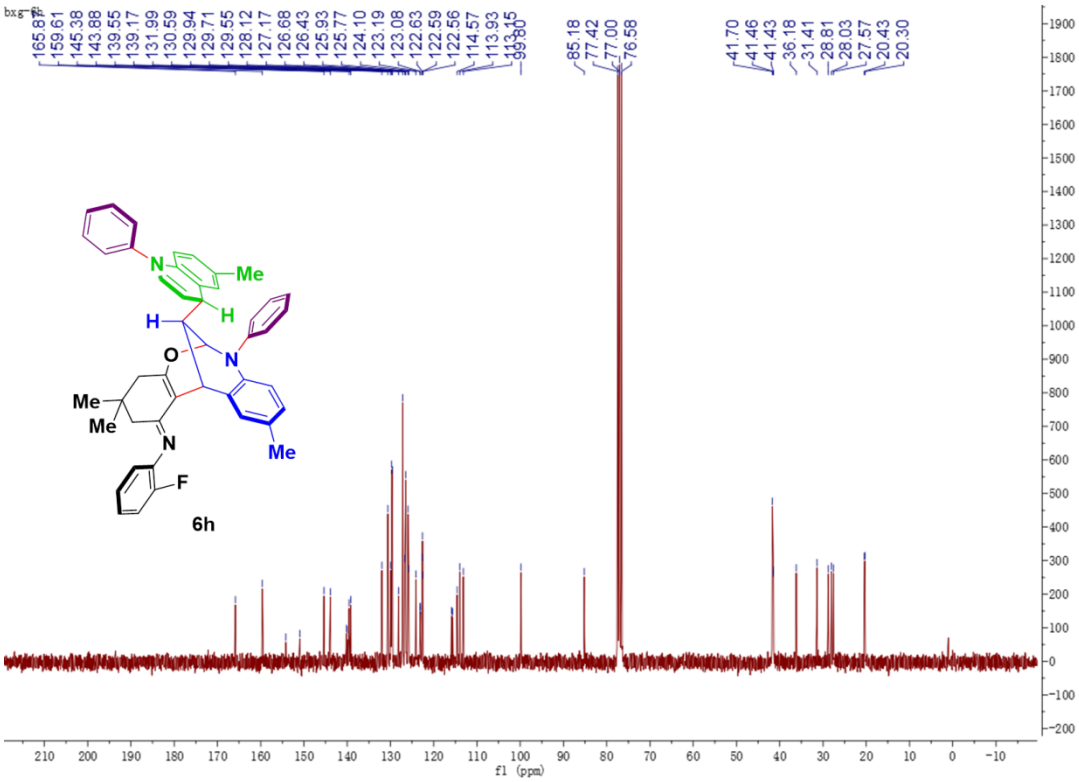
^{13}C NMR spectrum of **6g** (75 MHz, $CDCl_3$)



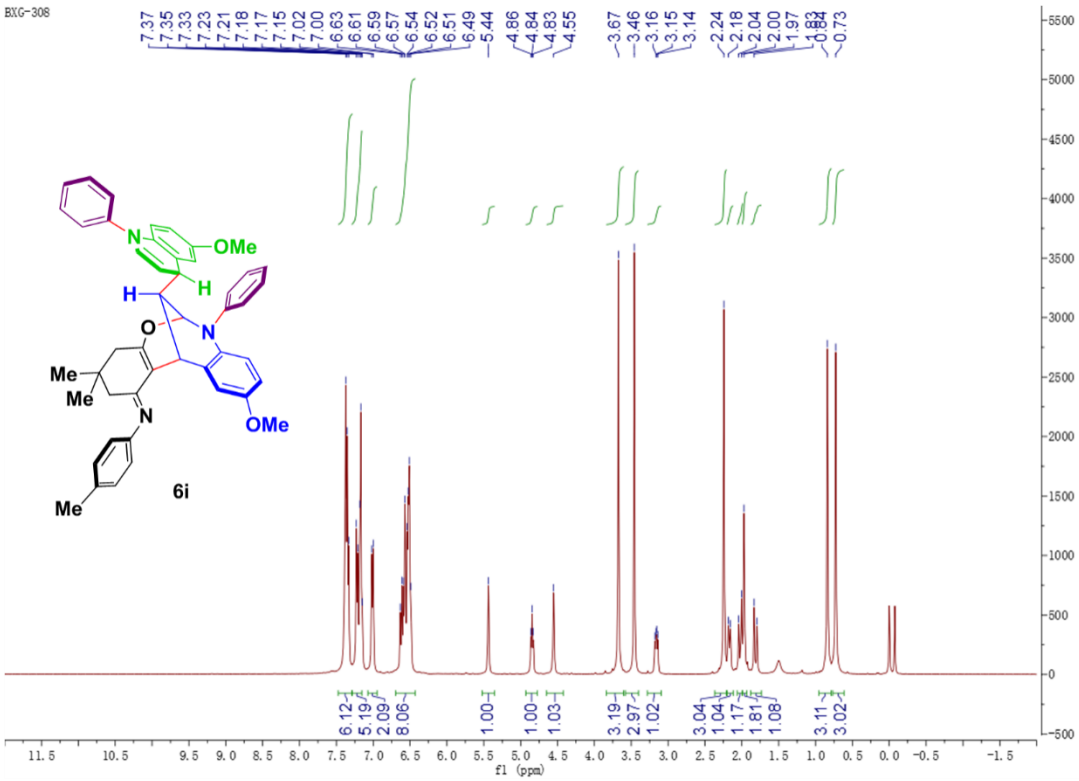
^{1}H NMR spectrum of **6h** (300 MHz, $CDCl_3$)



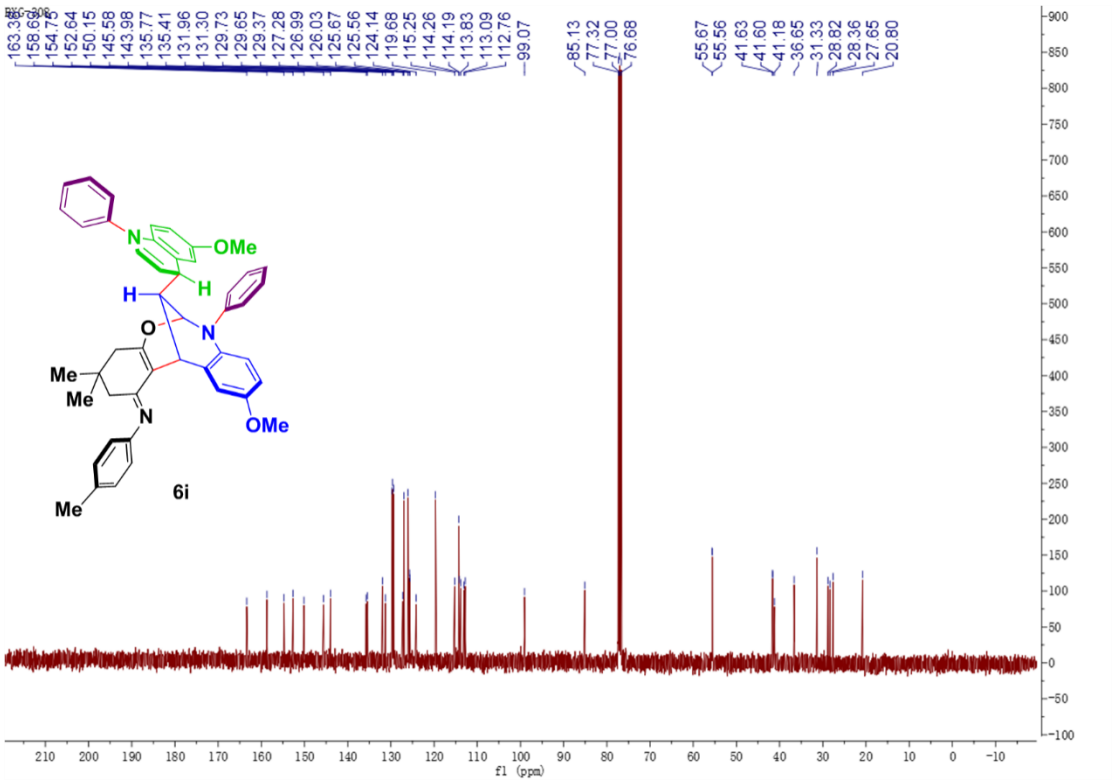
^{13}C NMR spectrum of **6h** (75 MHz, $CDCl_3$)



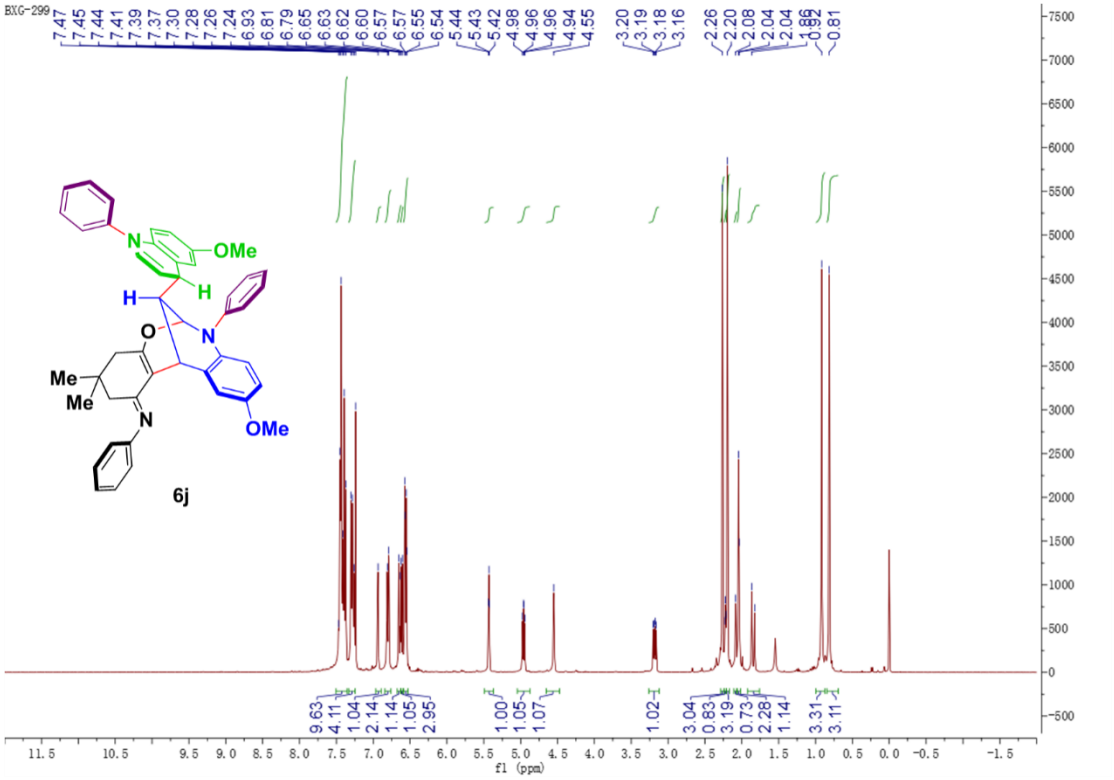
^{1}H NMR spectrum of **6i** (400 MHz, $CDCl_3$)



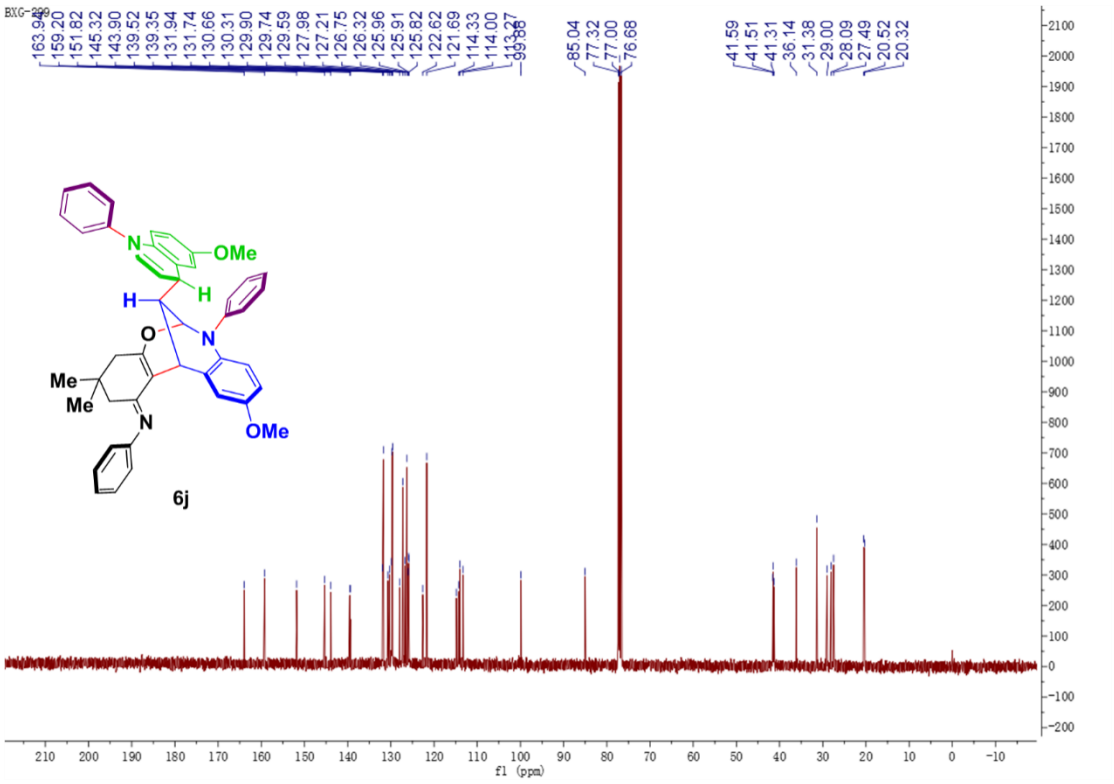
^{13}C NMR spectrum of **6i** (100 MHz, $CDCl_3$)



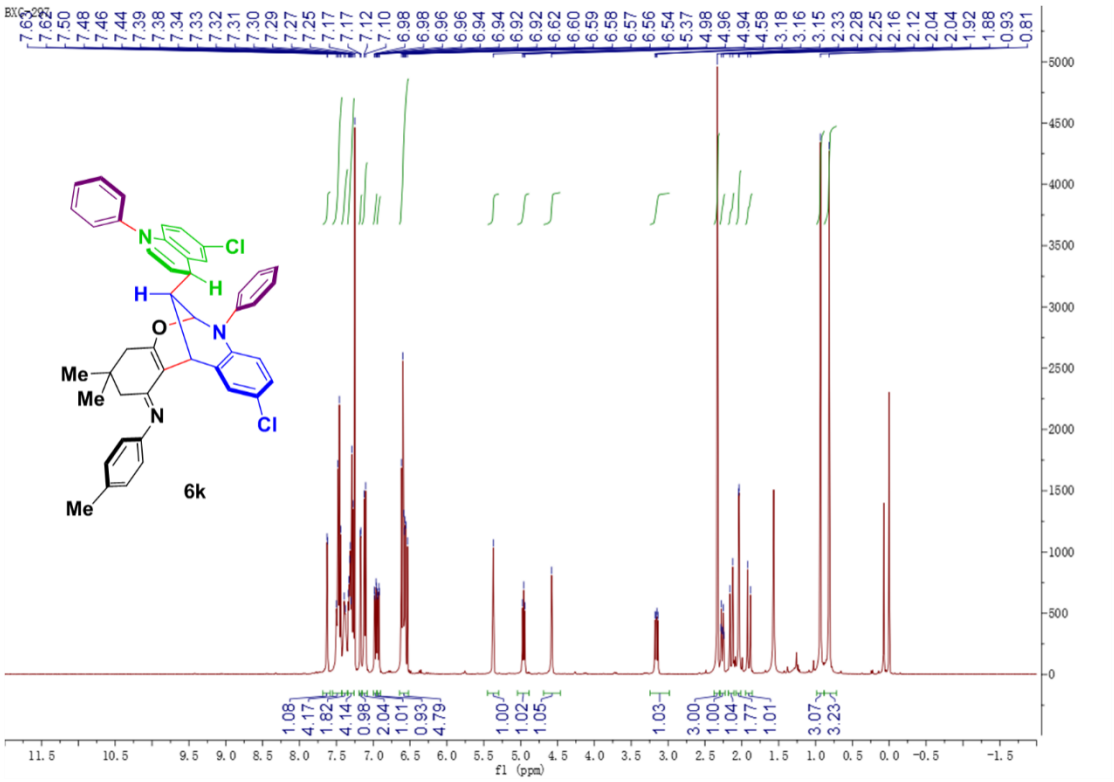
^{1}H NMR spectrum of **6j** (400 MHz, $CDCl_3$)



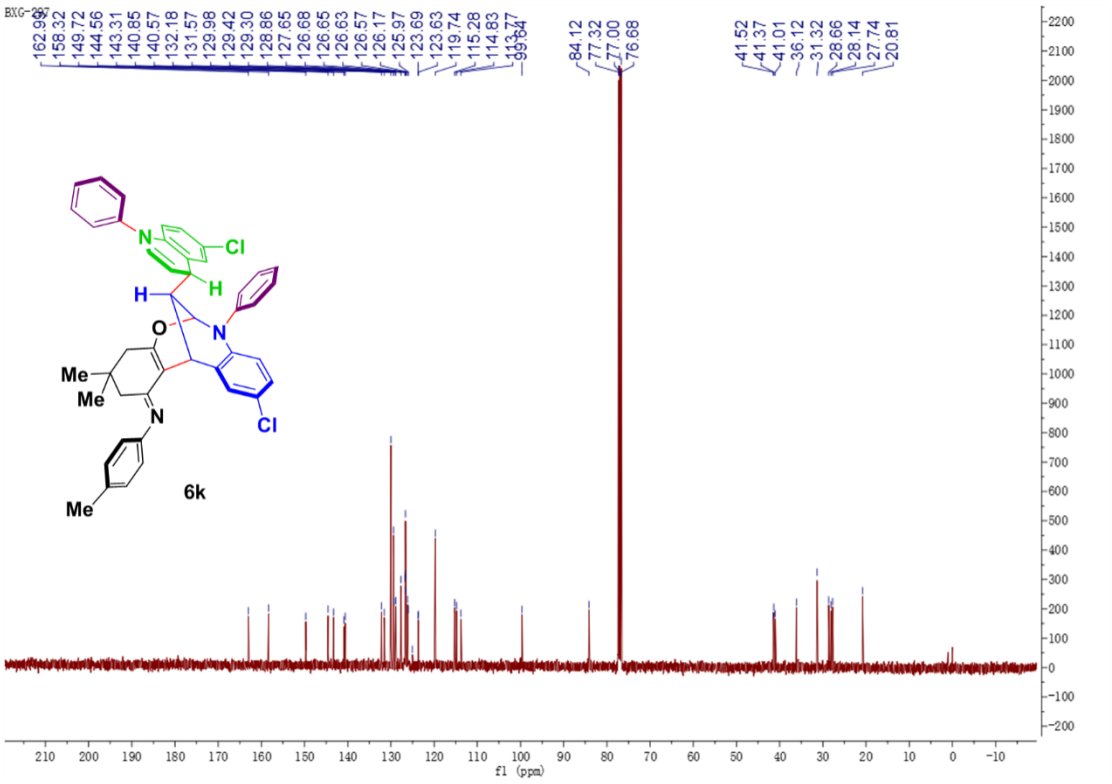
^{13}C NMR spectrum of **6j** (100 MHz, $CDCl_3$)



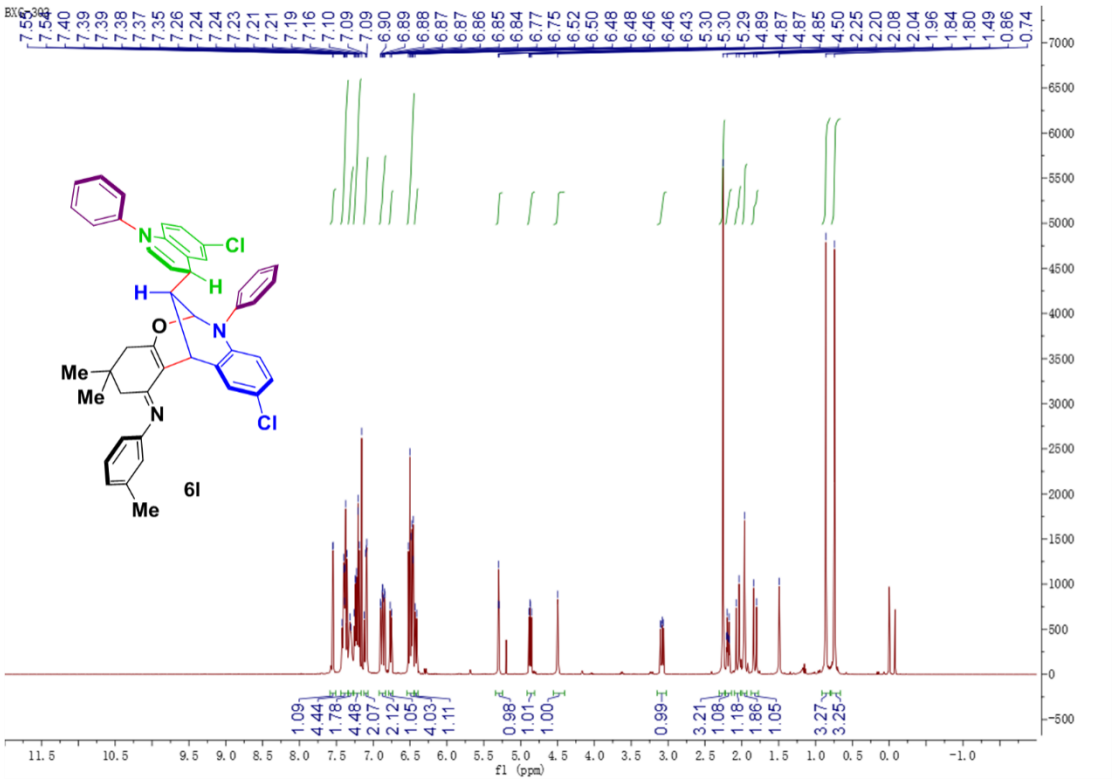
^{1}H NMR spectrum of **6k** (400 MHz, $CDCl_3$)



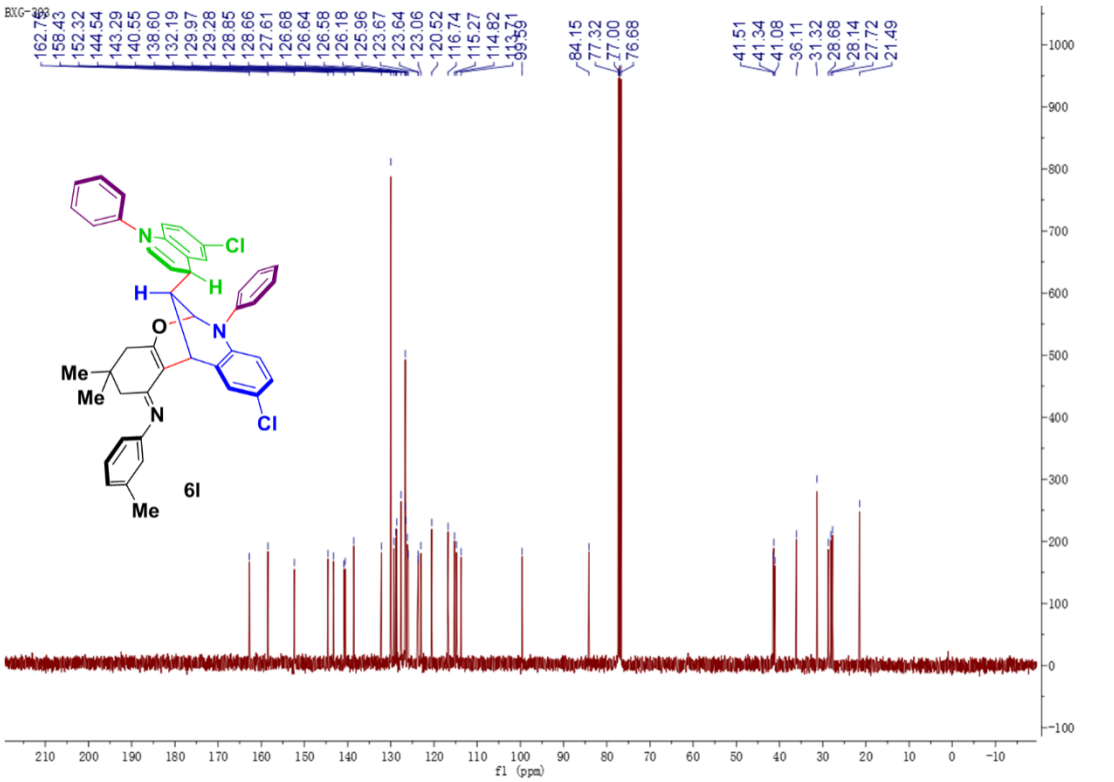
^{13}C NMR spectrum of **6k** (100 MHz, $CDCl_3$)



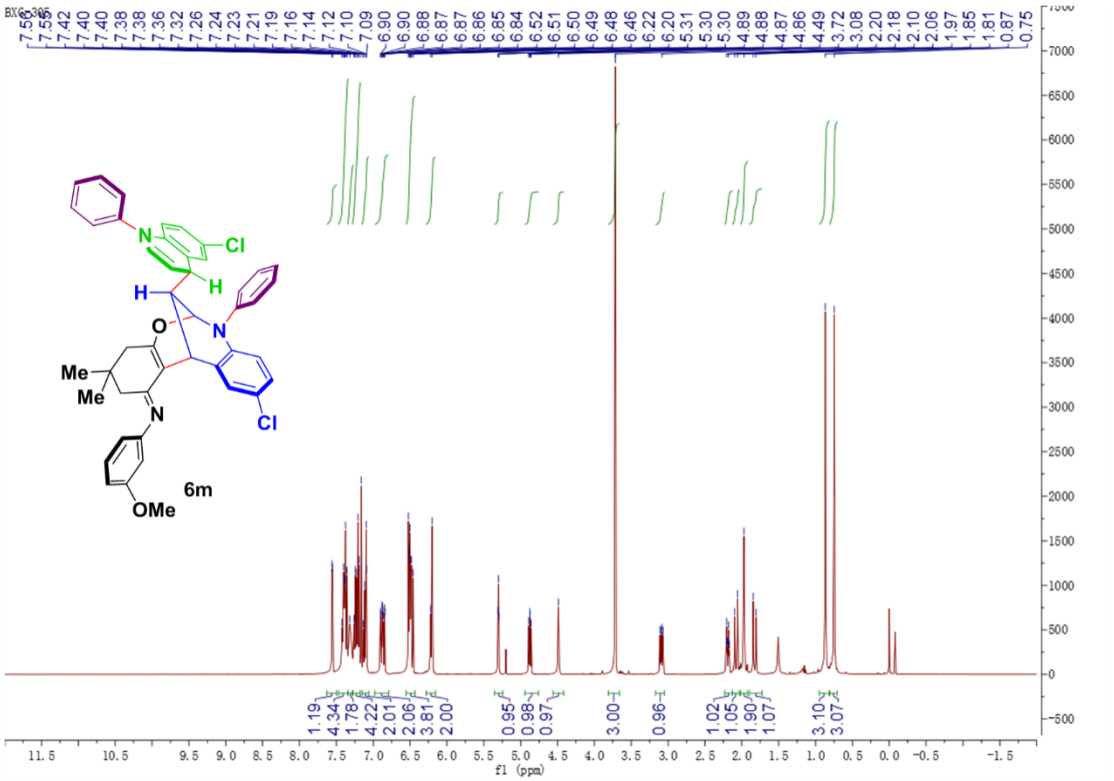
^{1}H NMR spectrum of **6l** (400 MHz, $CDCl_3$)



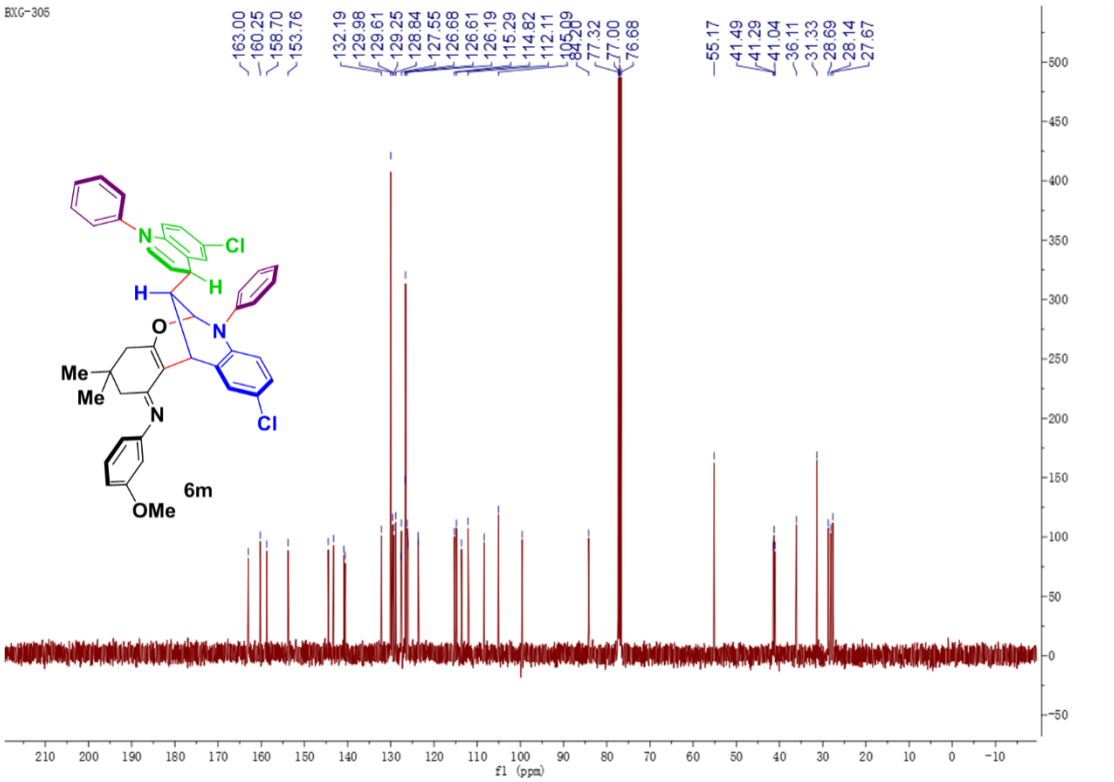
^{13}C NMR spectrum of **6l** (100 MHz, $CDCl_3$)



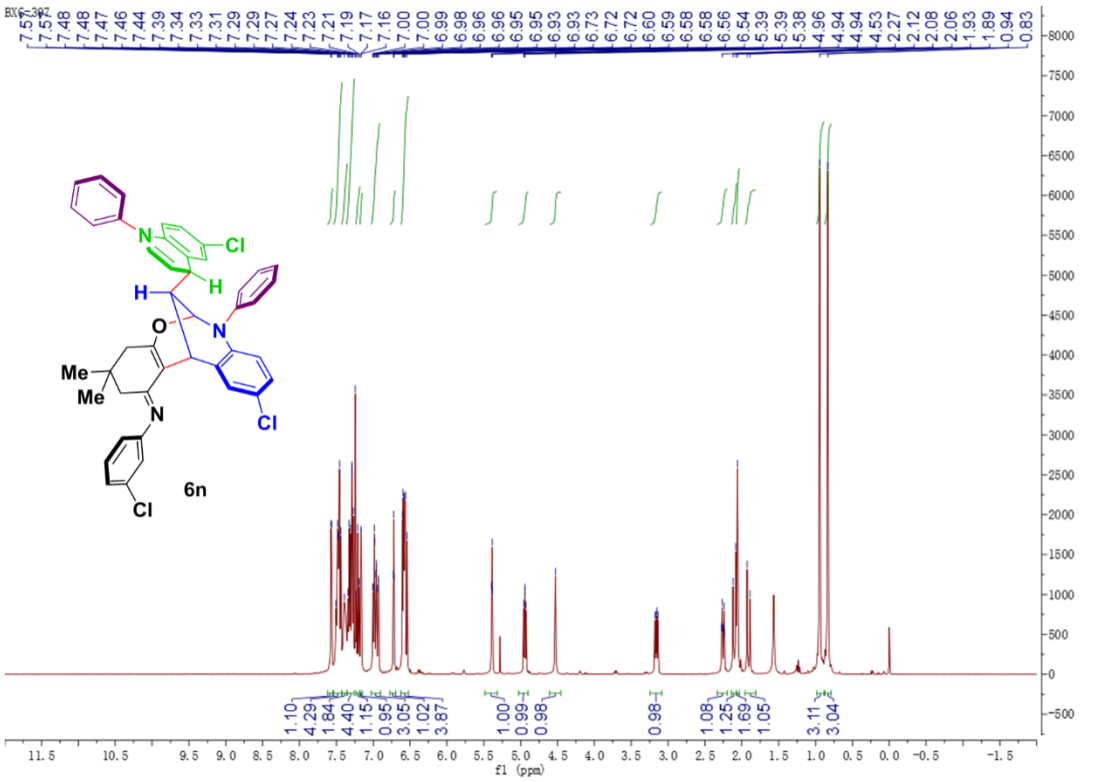
^{1}H NMR spectrum of **6m** (400 MHz, $CDCl_3$)



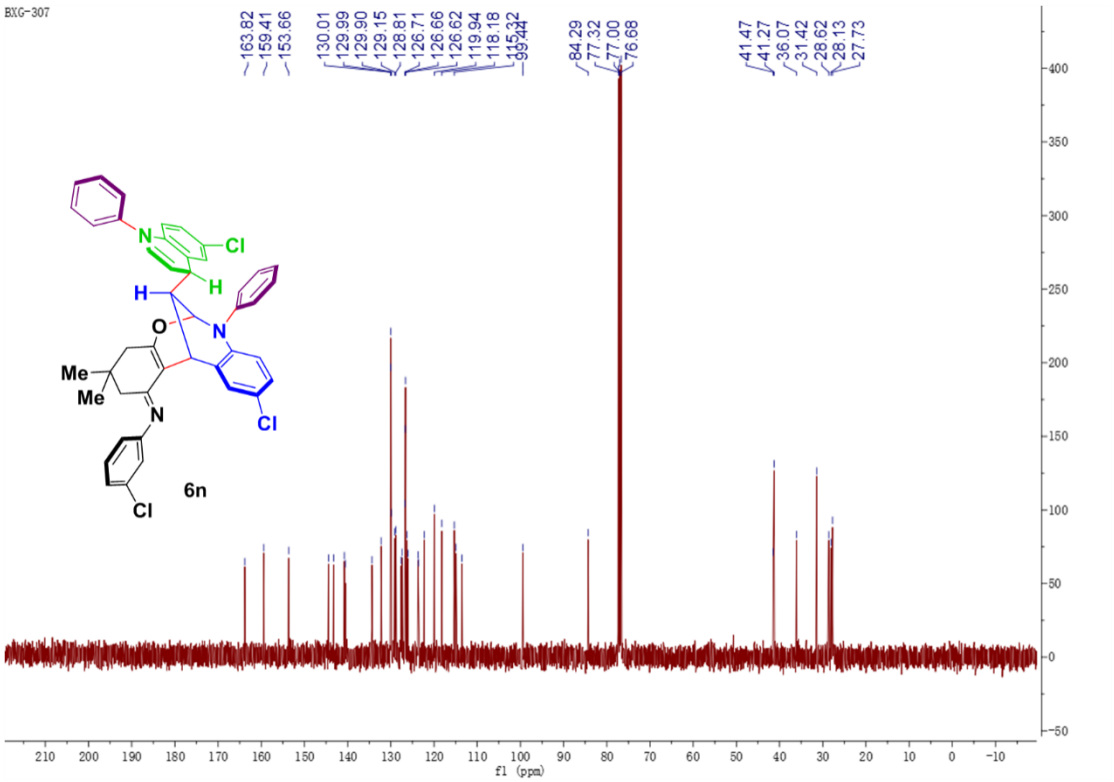
^{13}C NMR spectrum of **6m** (100 MHz, $CDCl_3$)



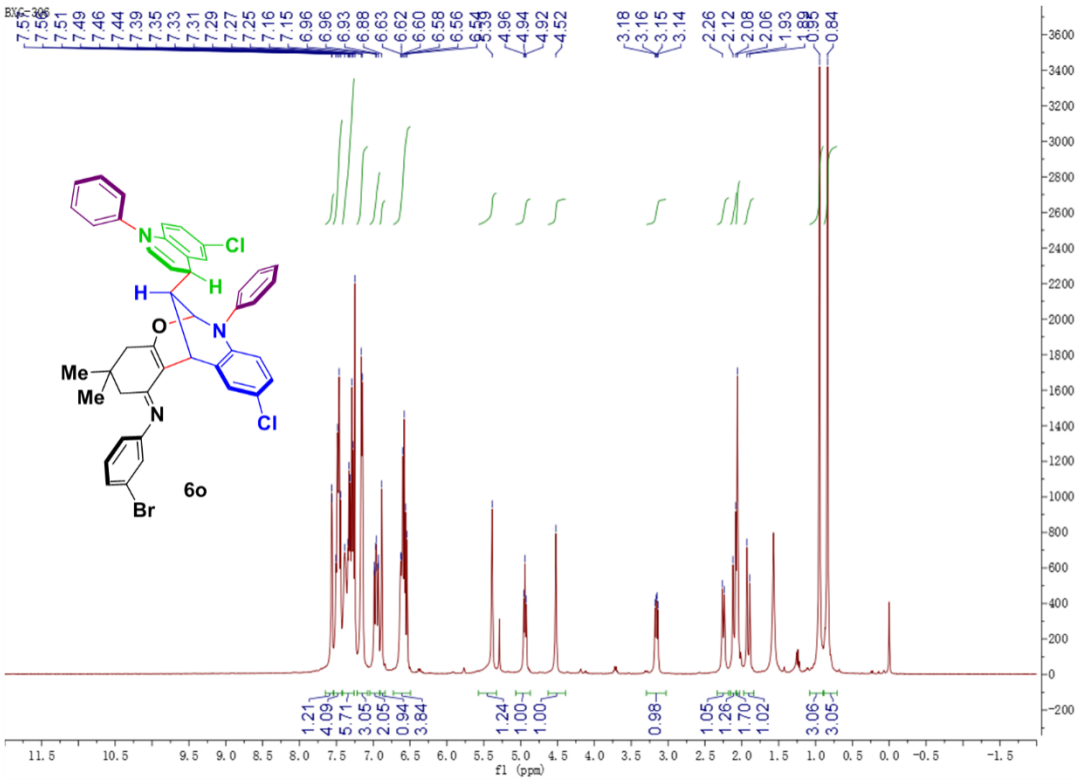
^{1}H NMR spectrum of **6n** (400 MHz, $CDCl_3$)



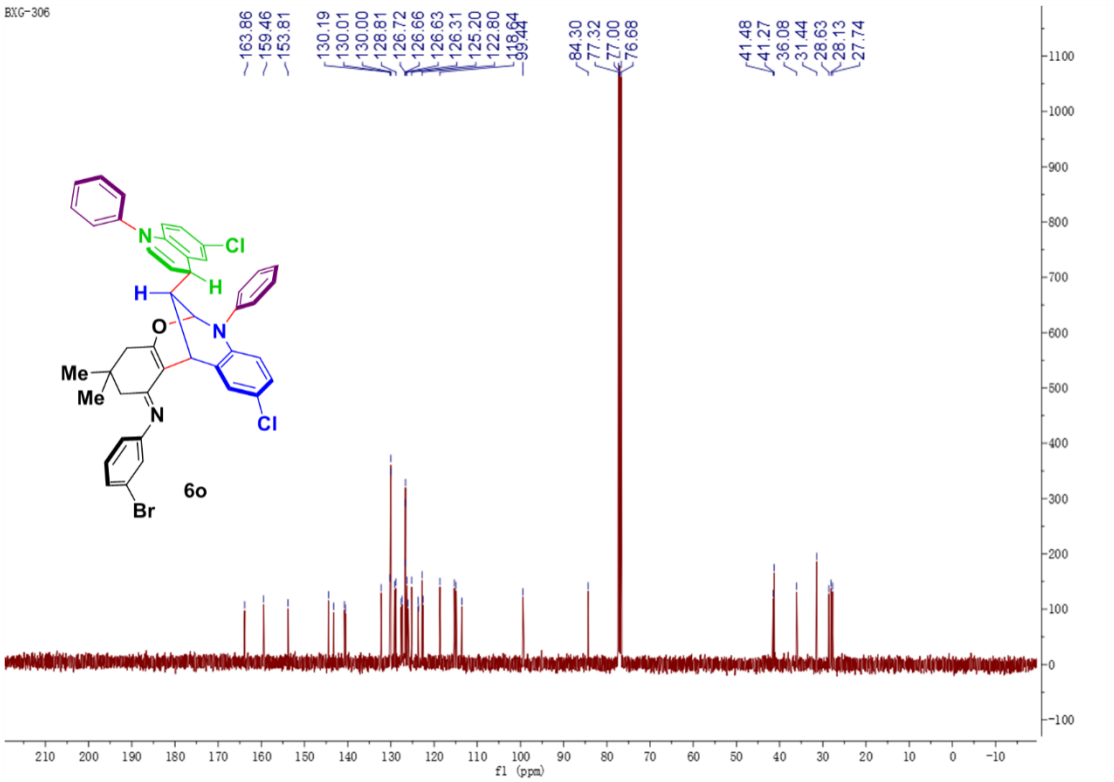
^{13}C NMR spectrum of **6n** (100 MHz, $CDCl_3$)



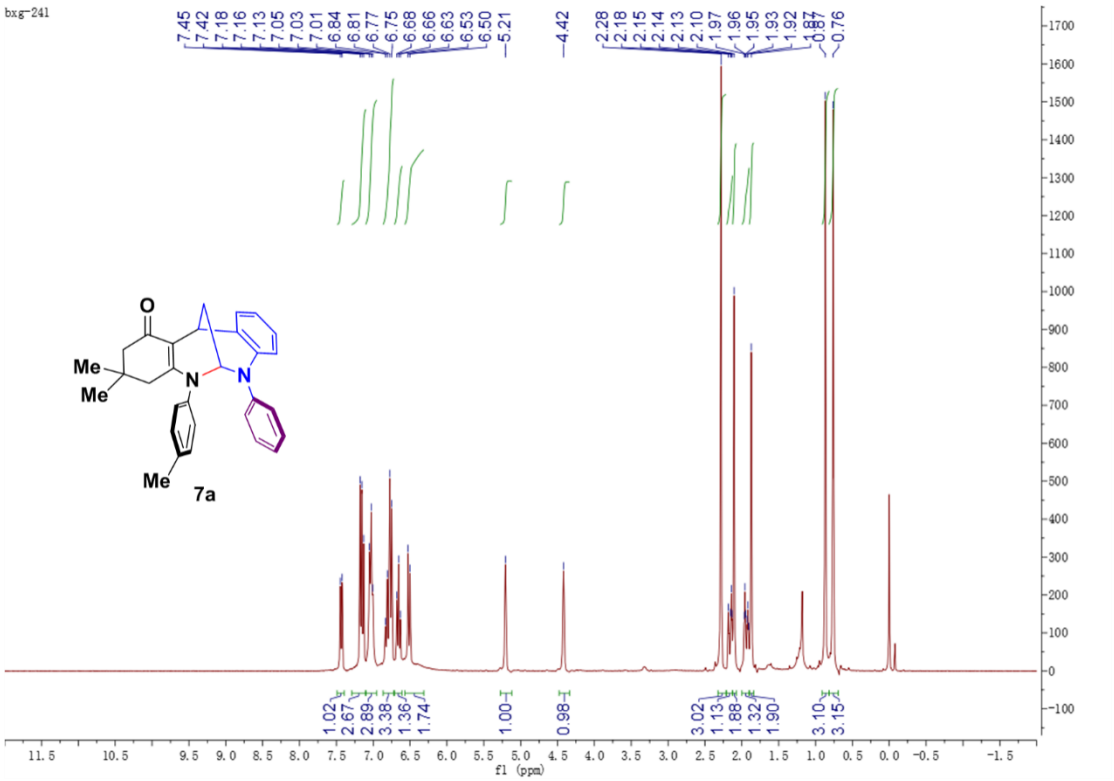
^{1}H NMR spectrum of **6o** (400 MHz, $CDCl_3$)



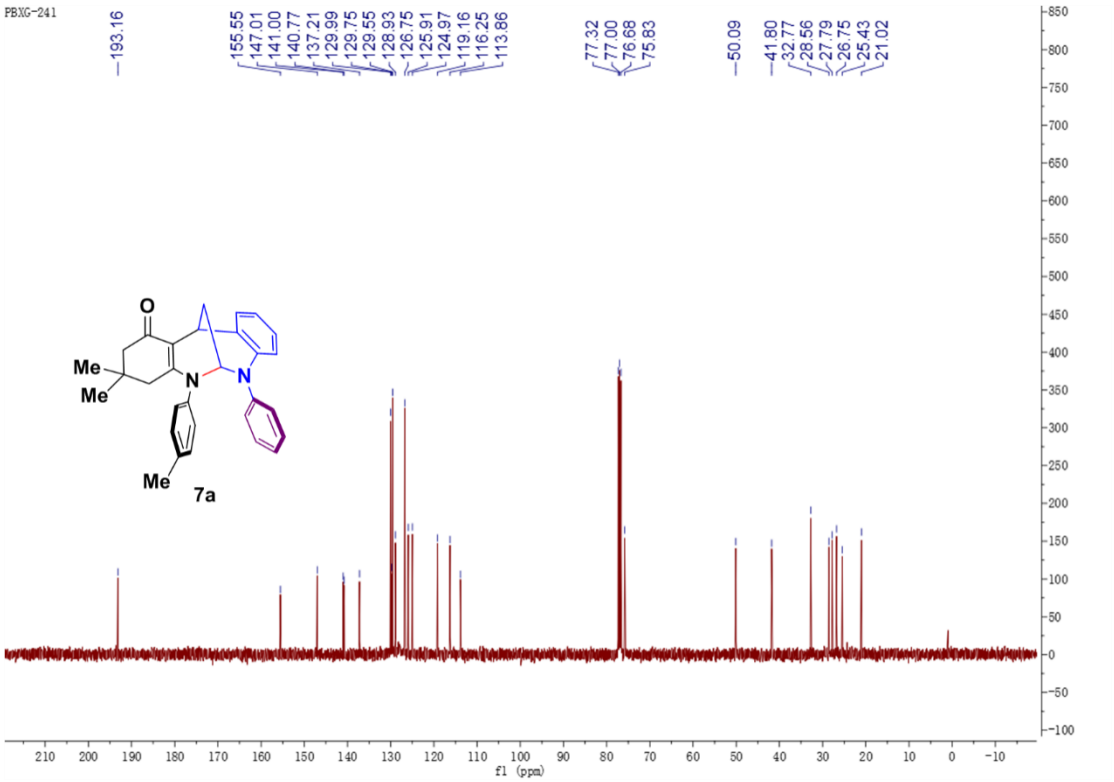
^{13}C NMR spectrum of **6o** (100 MHz, $CDCl_3$)



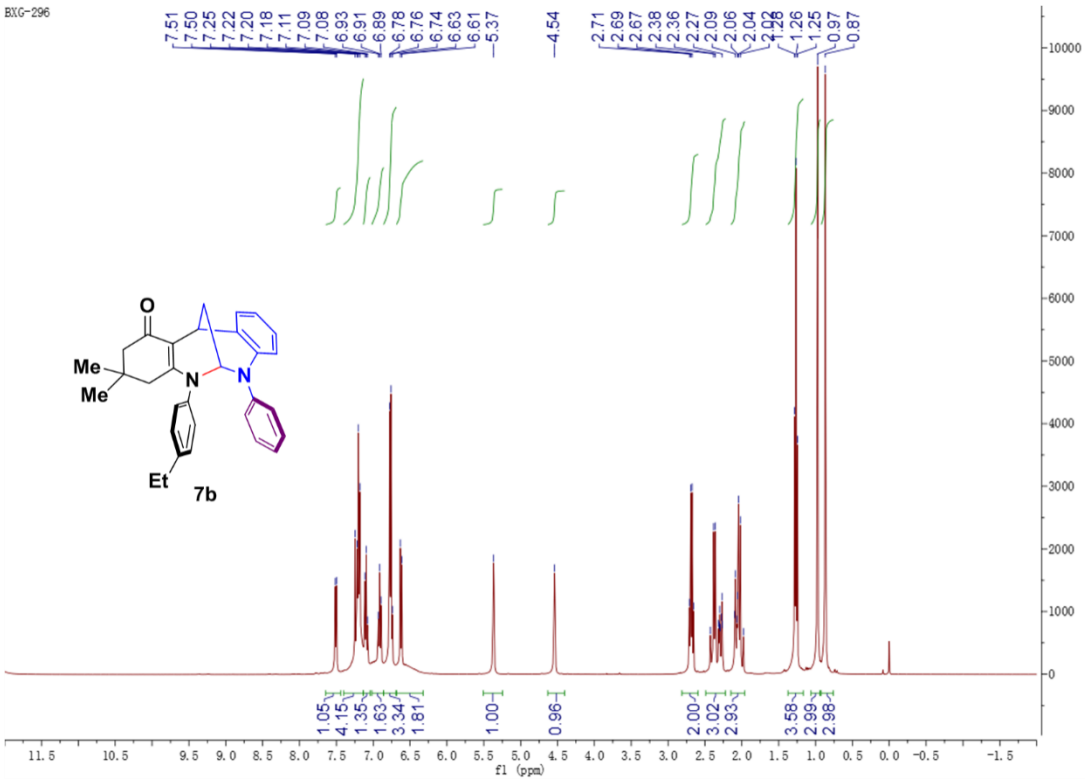
^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$)



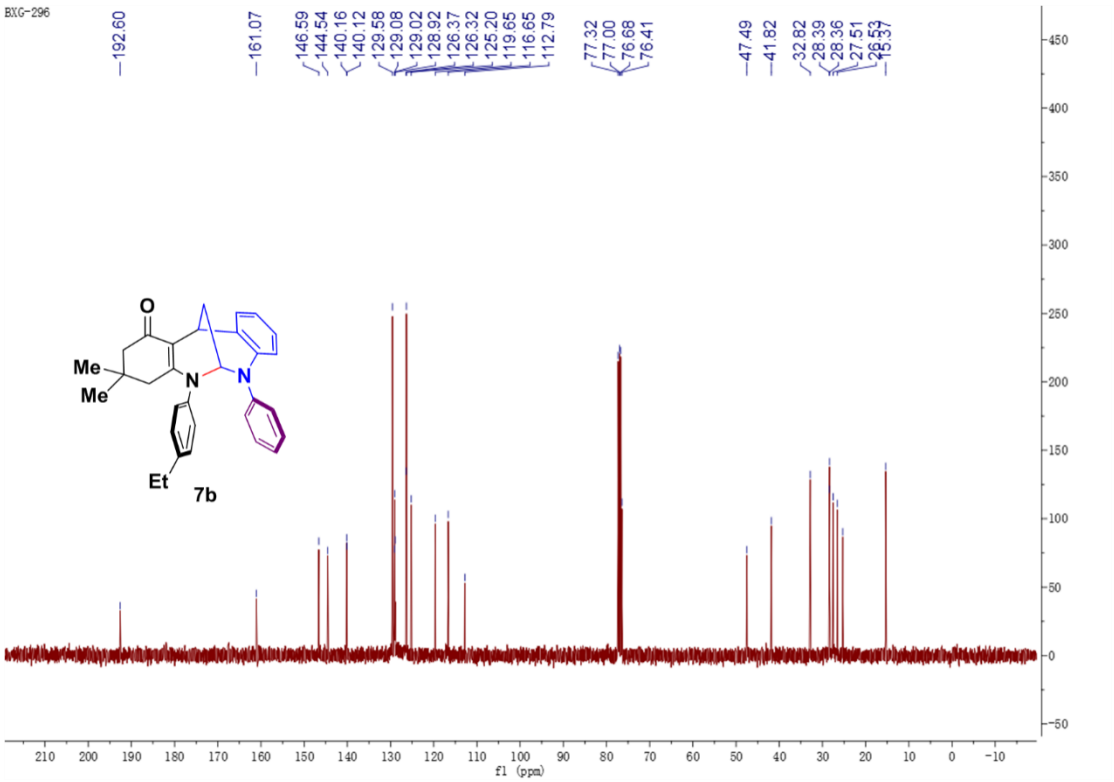
^{13}C NMR spectrum of **7a** (100 MHz, $CDCl_3$)



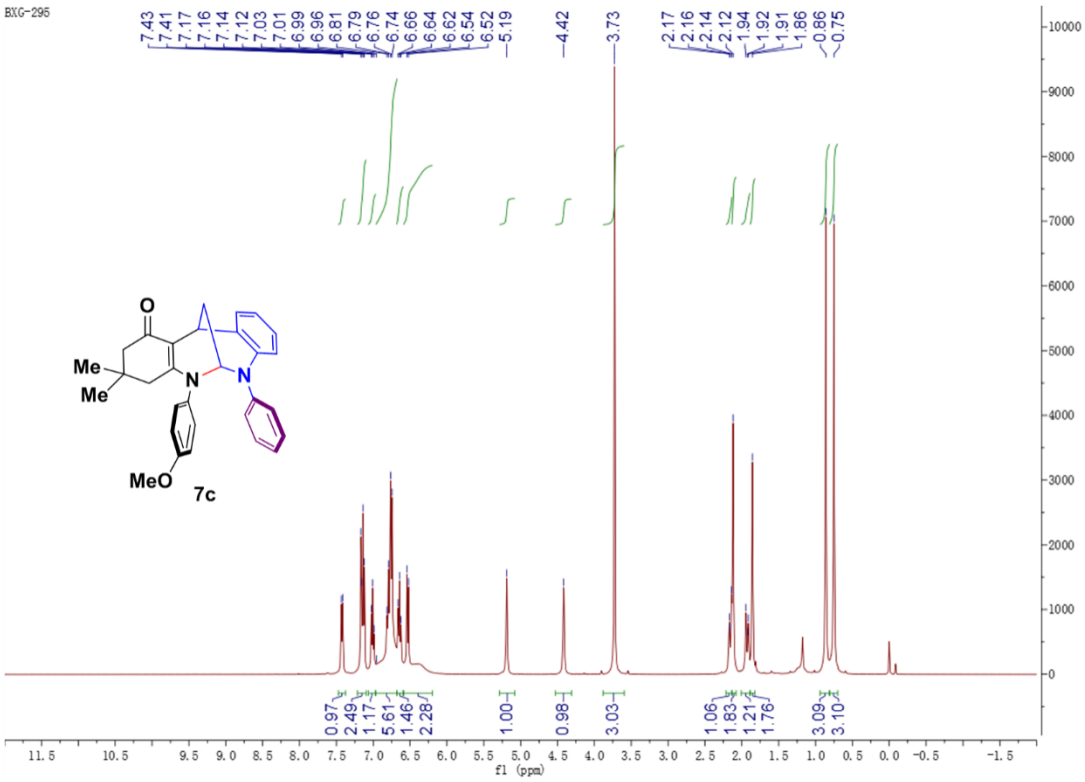
^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$)



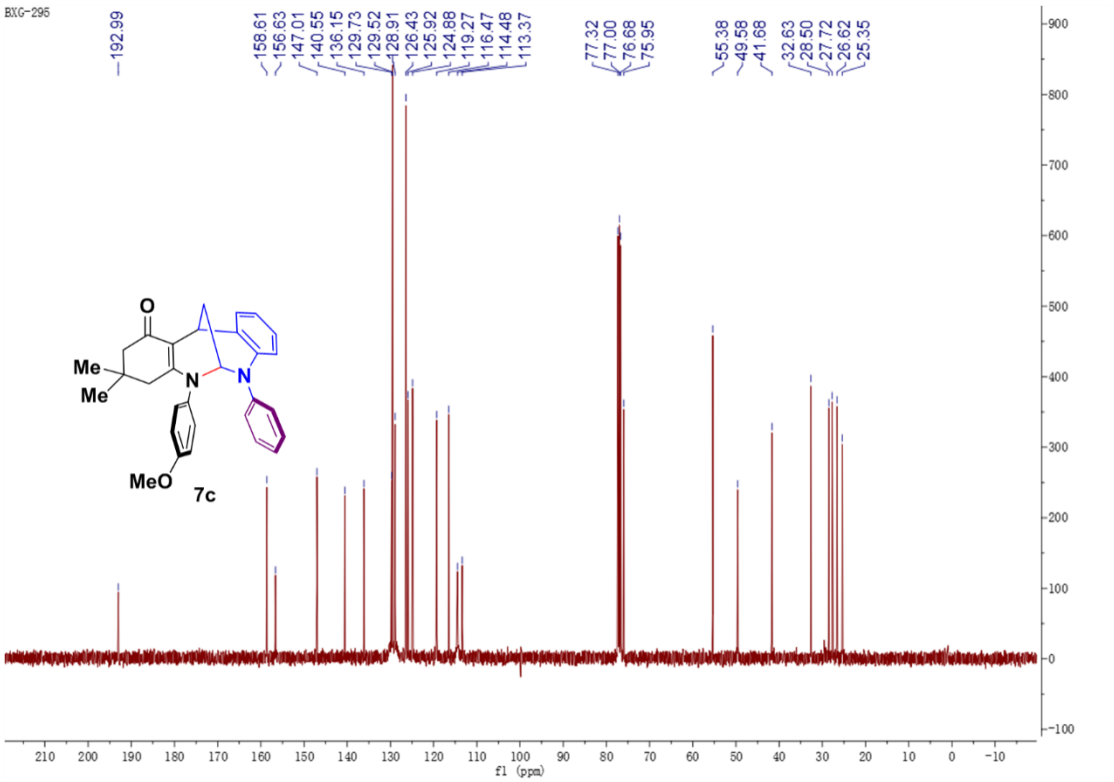
^{13}C NMR spectrum of **7b** (100 MHz, $CDCl_3$)



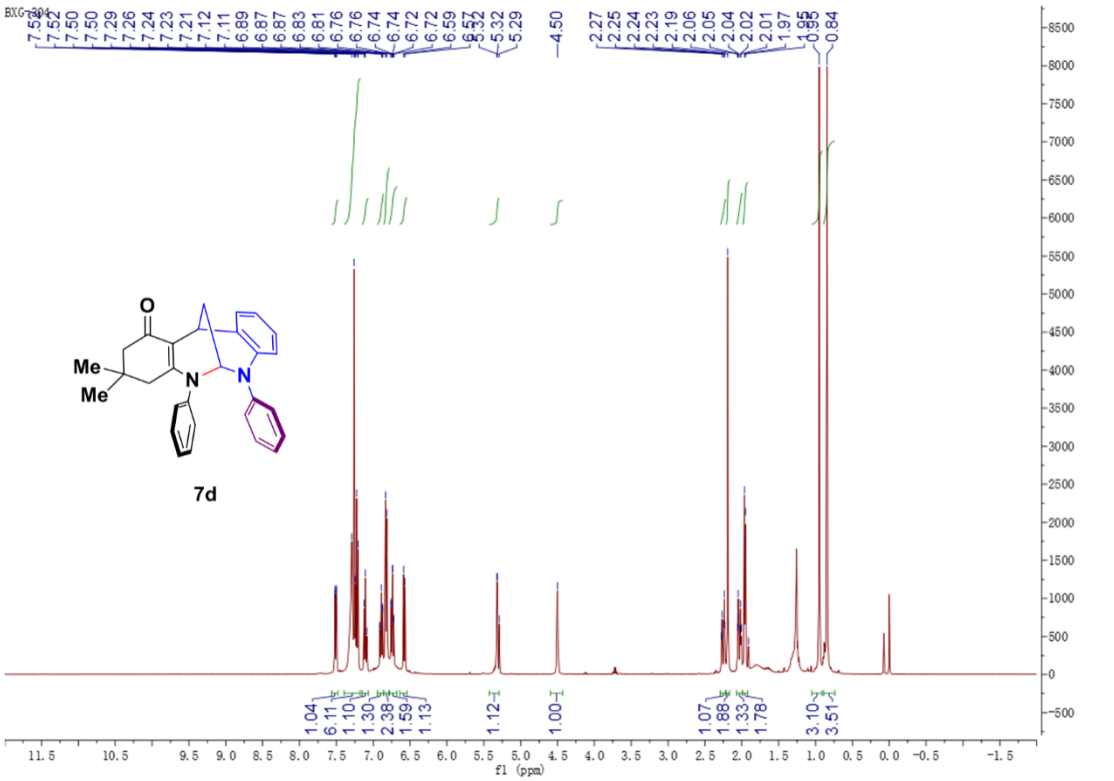
^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$)



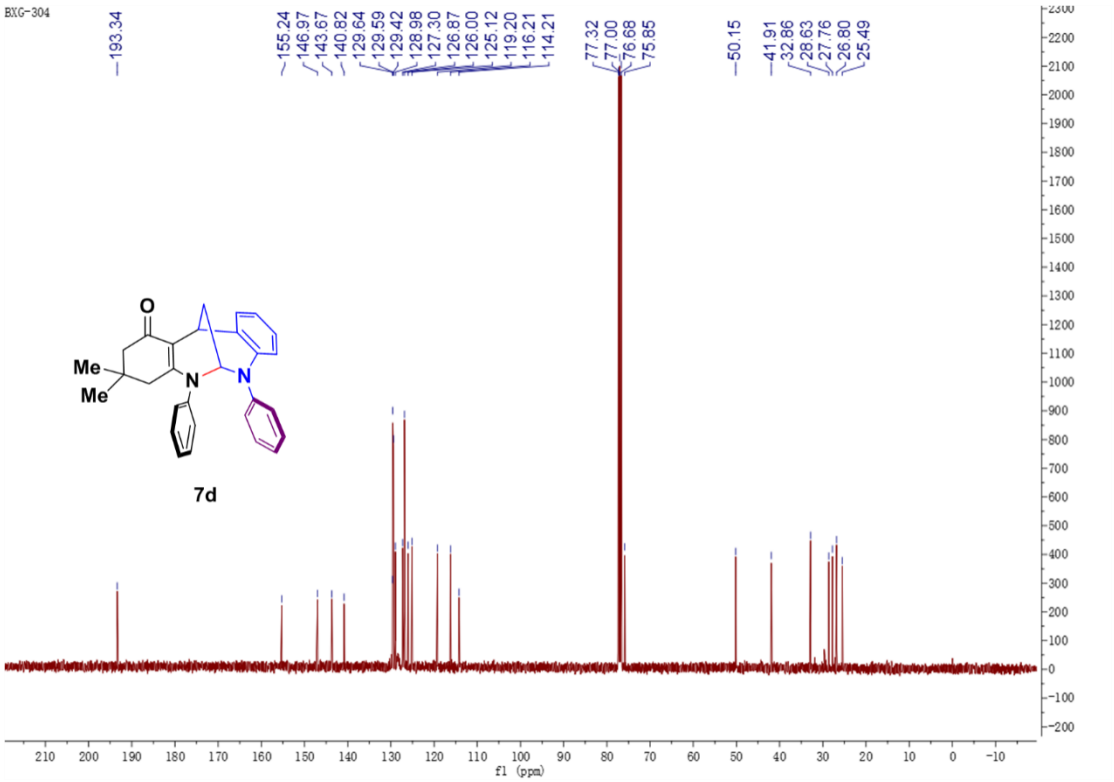
^{13}C NMR spectrum of **7c** (100 MHz, $CDCl_3$)



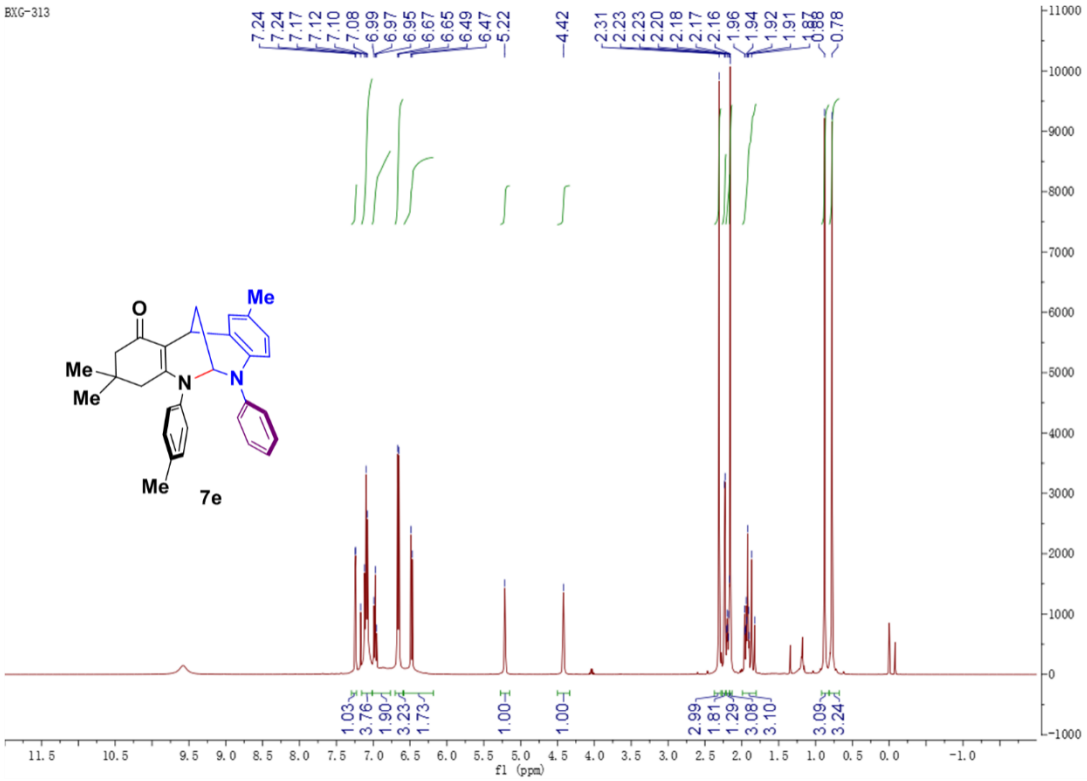
^{1}H NMR spectrum of **7d** (400 MHz, $CDCl_3$)



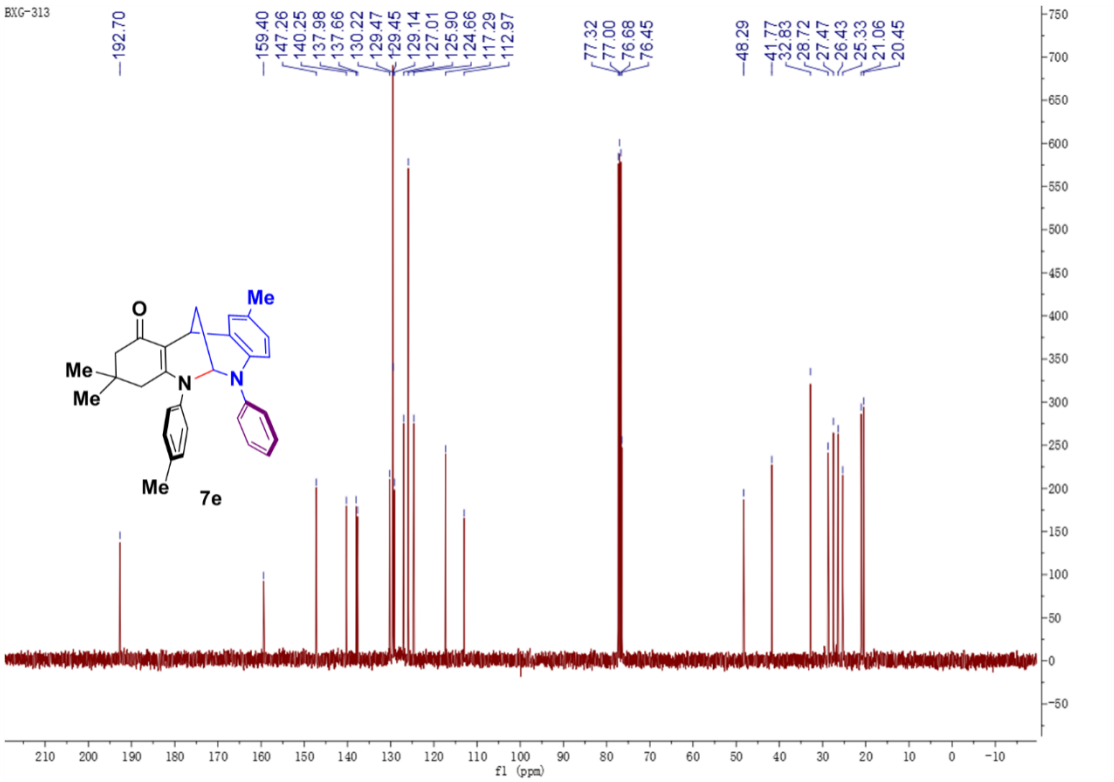
^{13}C NMR spectrum of **7d** (100 MHz, $CDCl_3$)



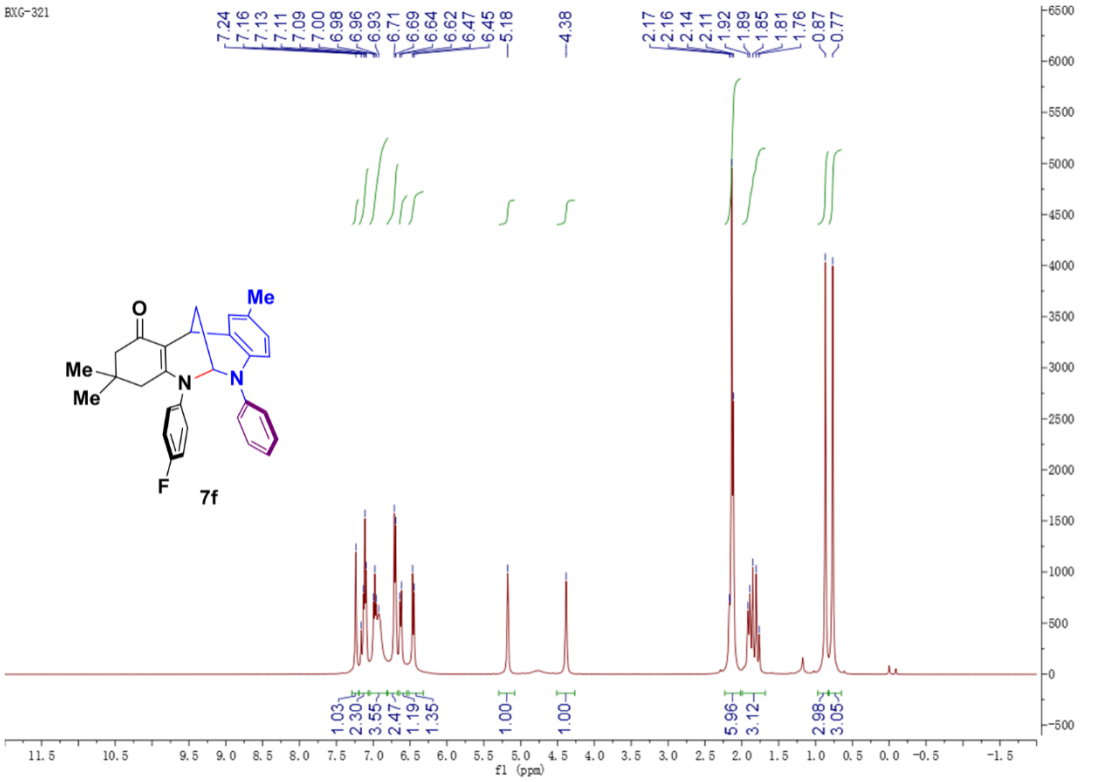
^{1}H NMR spectrum of **7e** (400 MHz, $CDCl_3$)



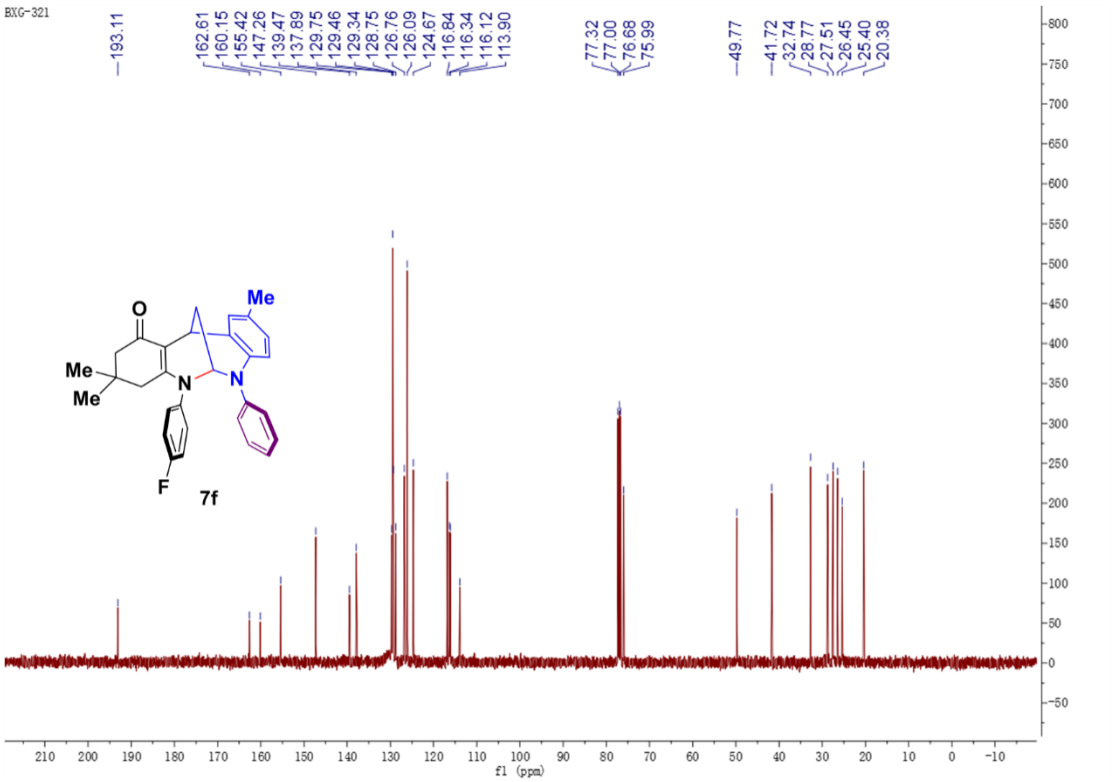
^{13}C NMR spectrum of **7e** (100 MHz, $CDCl_3$)



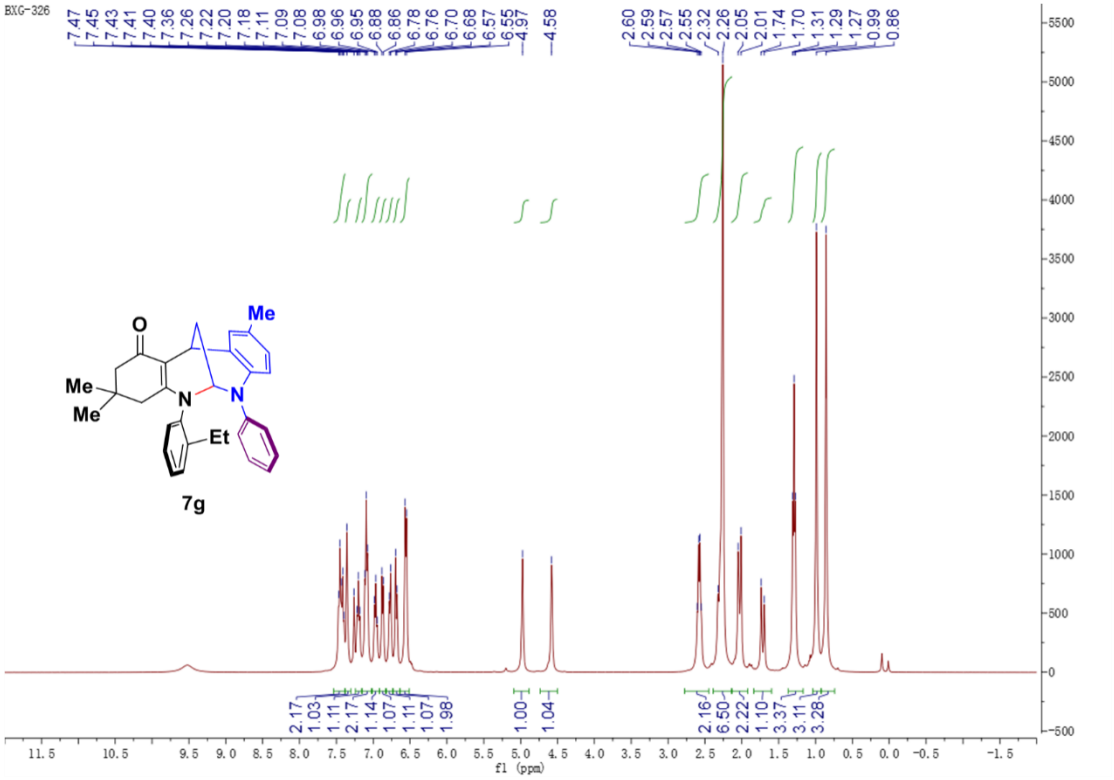
^{1}H NMR spectrum of **7f** (400 MHz, $CDCl_3$)



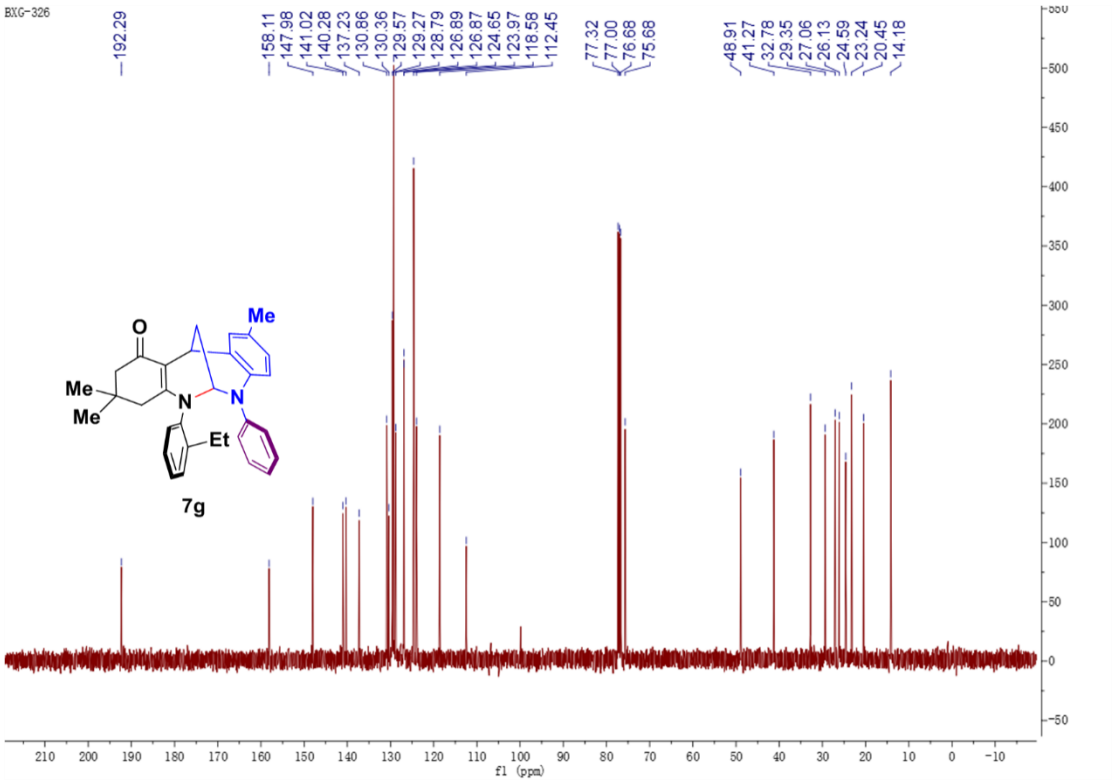
^{13}C NMR spectrum of **7f** (100 MHz, $CDCl_3$)



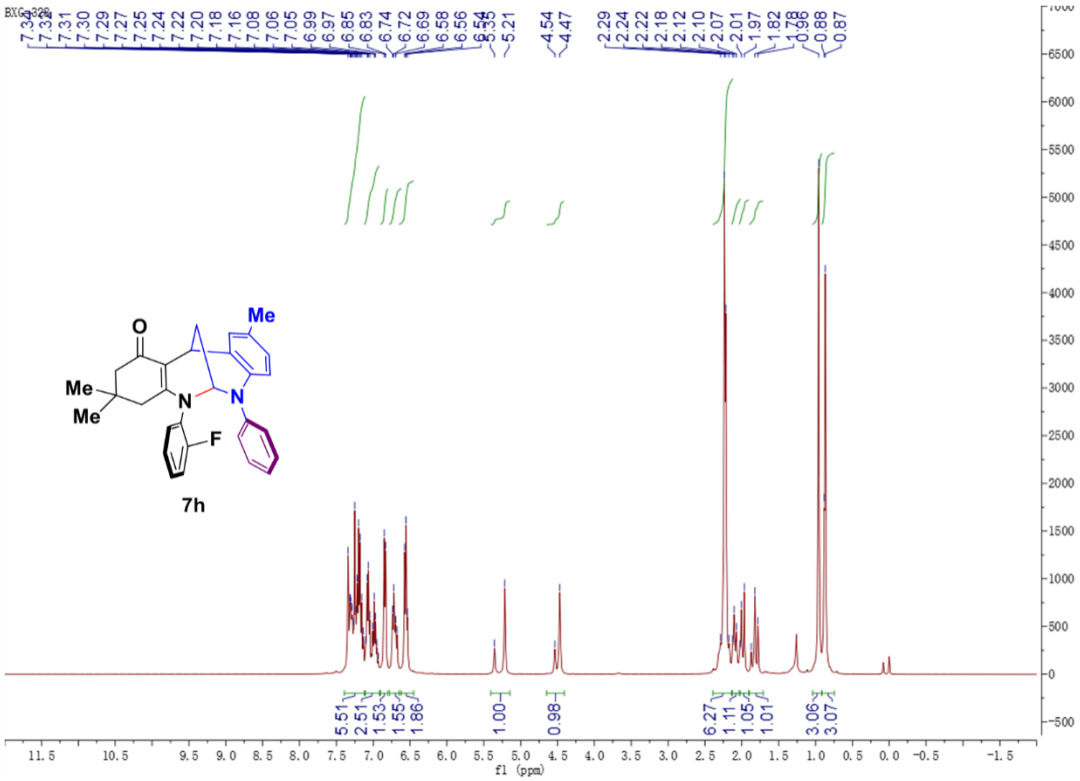
^{1}H NMR spectrum of **7g** (400 MHz, $CDCl_3$)



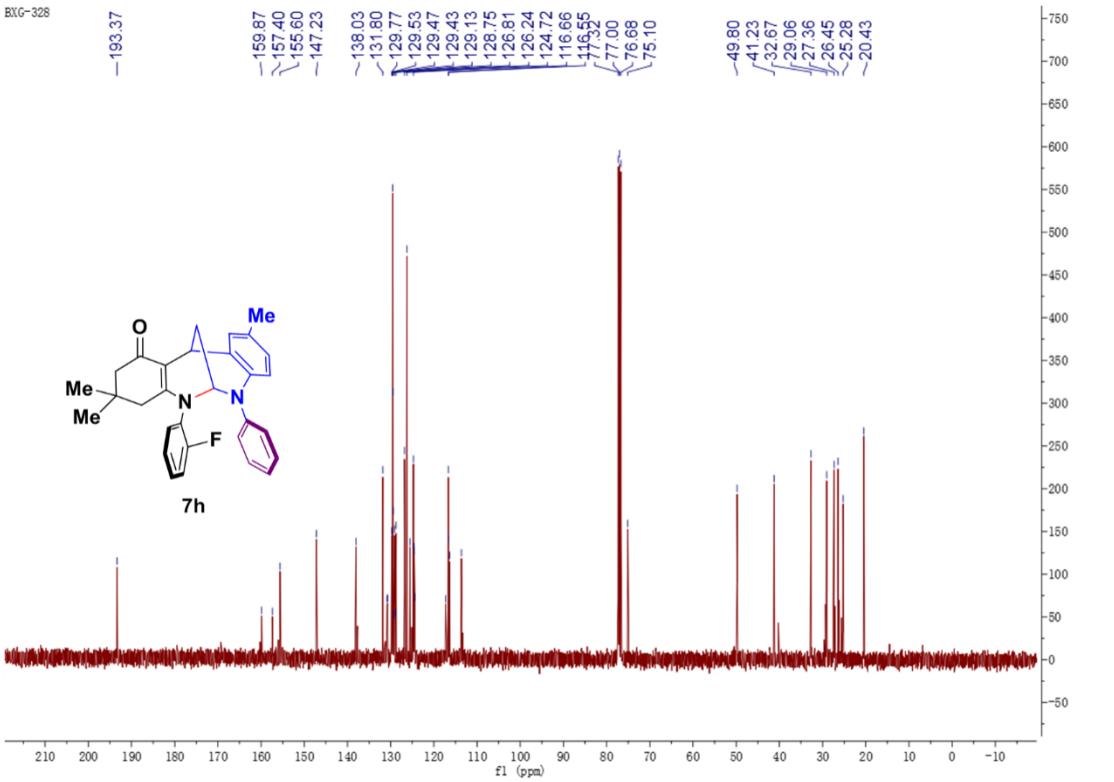
^{13}C NMR spectrum of **7g** (100 MHz, $CDCl_3$)



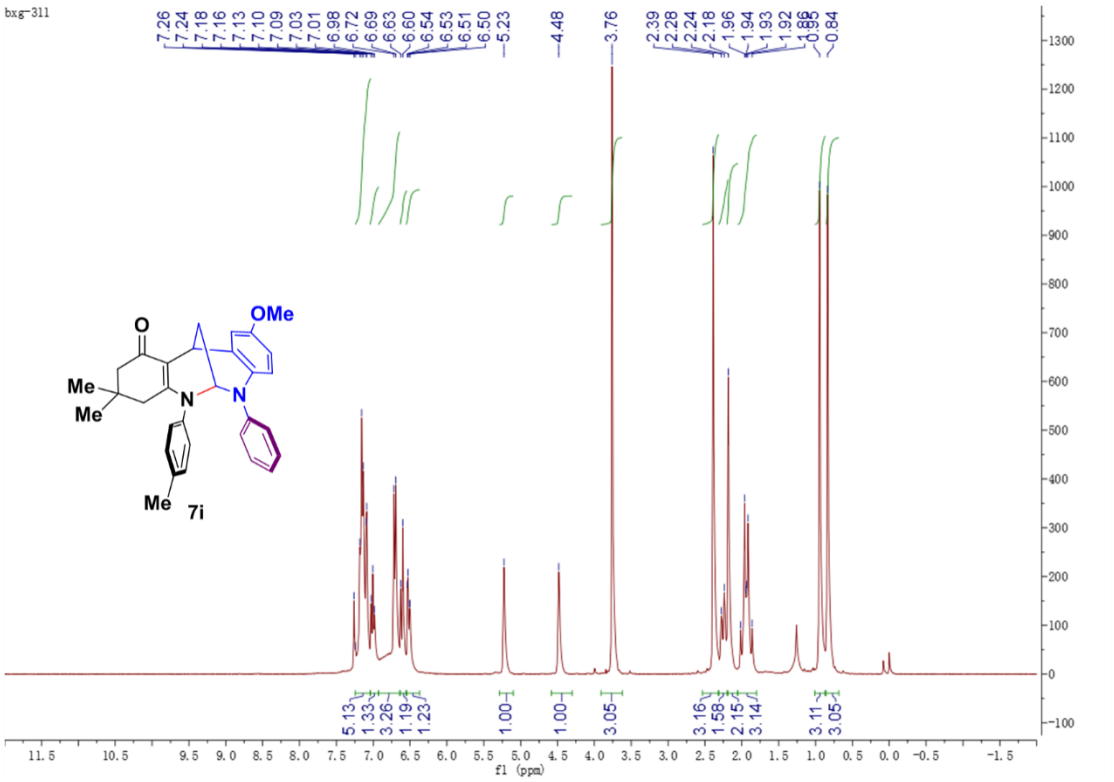
^{1}H NMR spectrum of **7h** (400 MHz, $CDCl_3$)



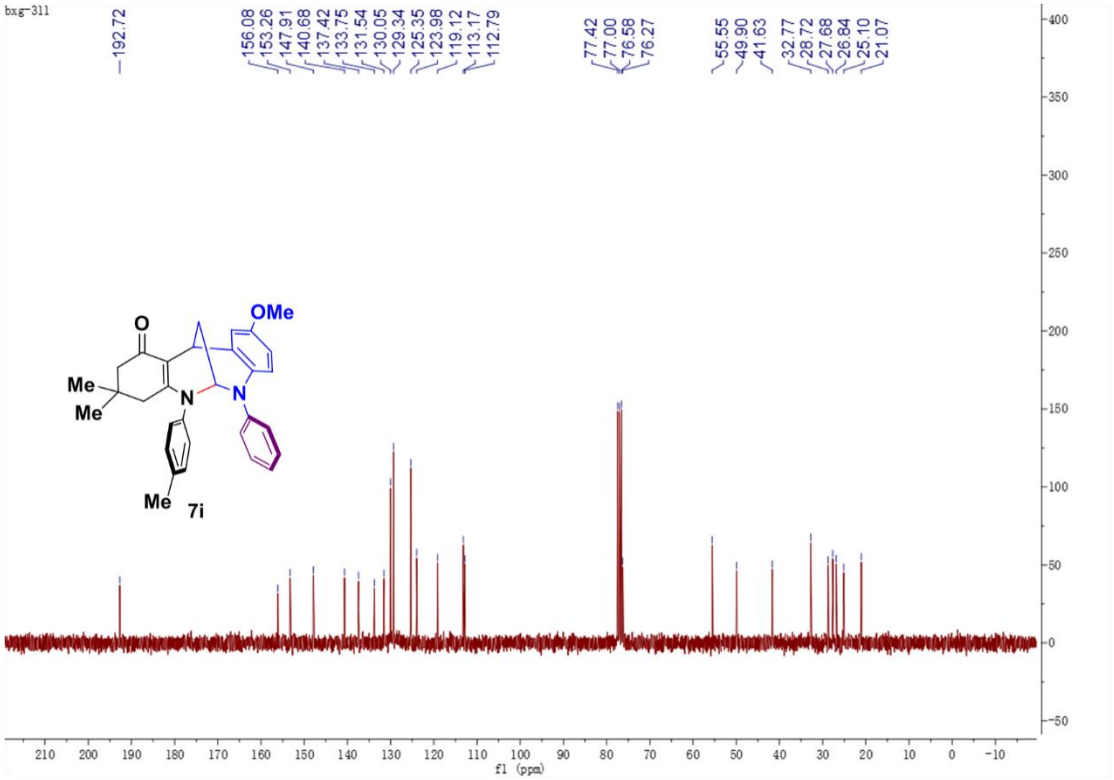
^{13}C NMR spectrum of **7h** (100 MHz, $CDCl_3$)



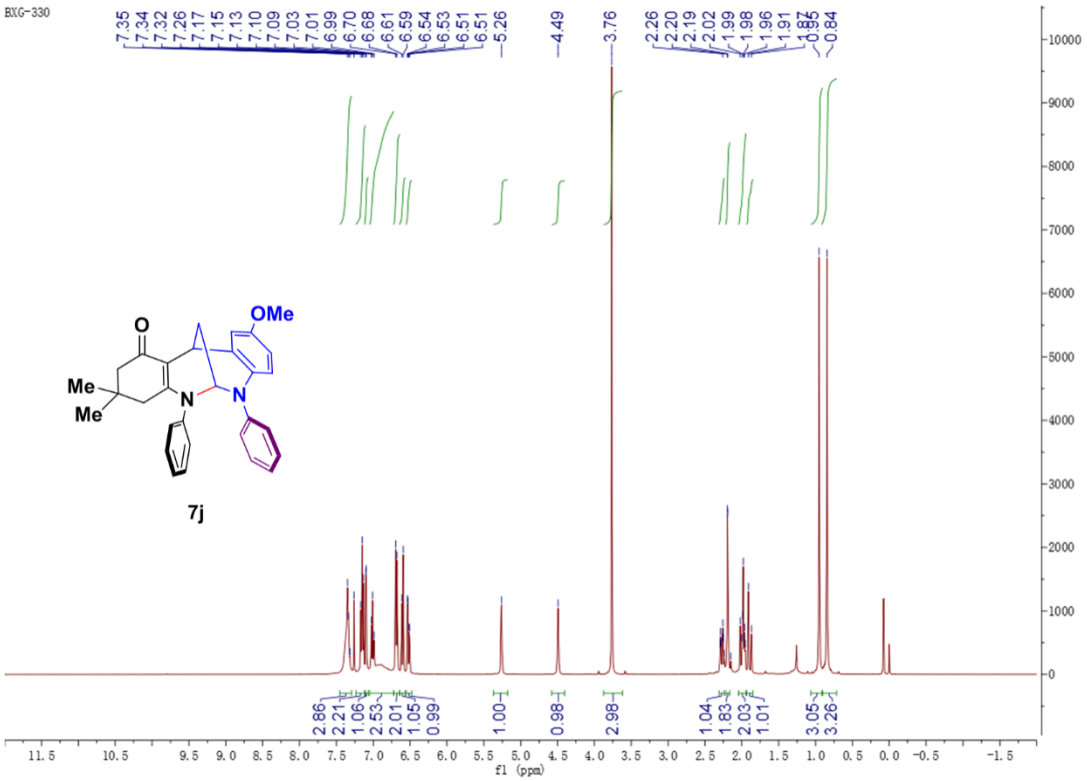
^{1}H NMR spectrum of **7i** (400 MHz, $CDCl_3$)



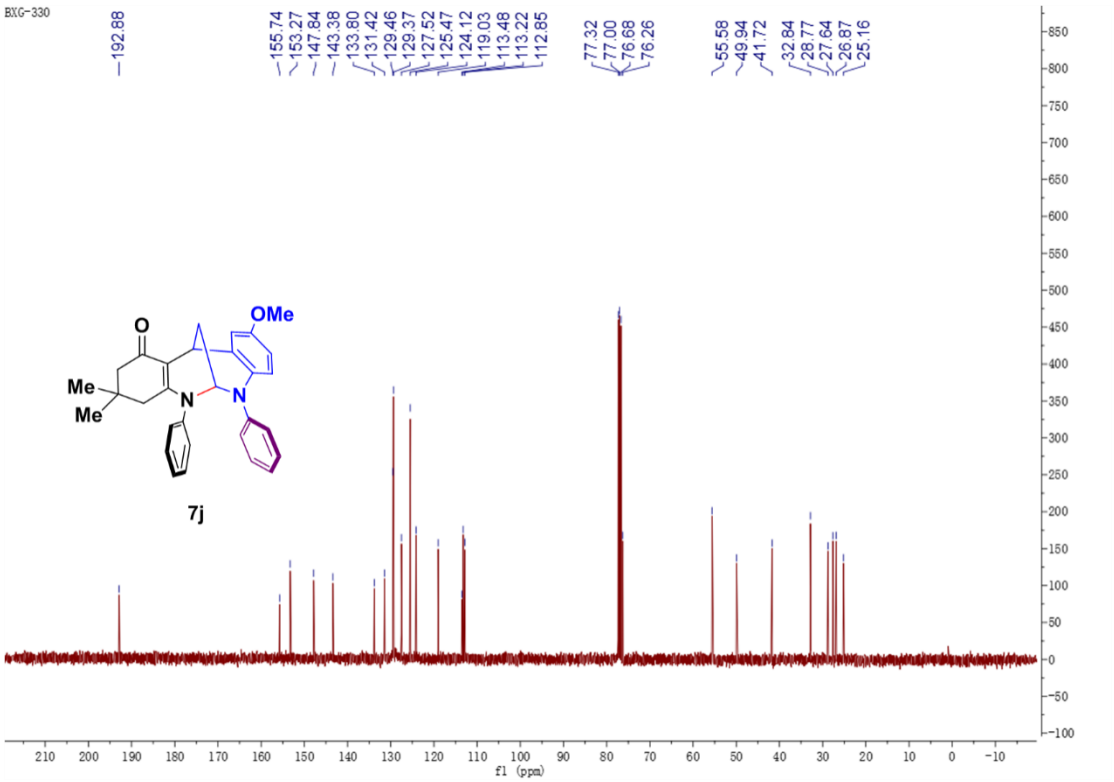
^{13}C NMR spectrum of **7i** (100 MHz, $CDCl_3$)



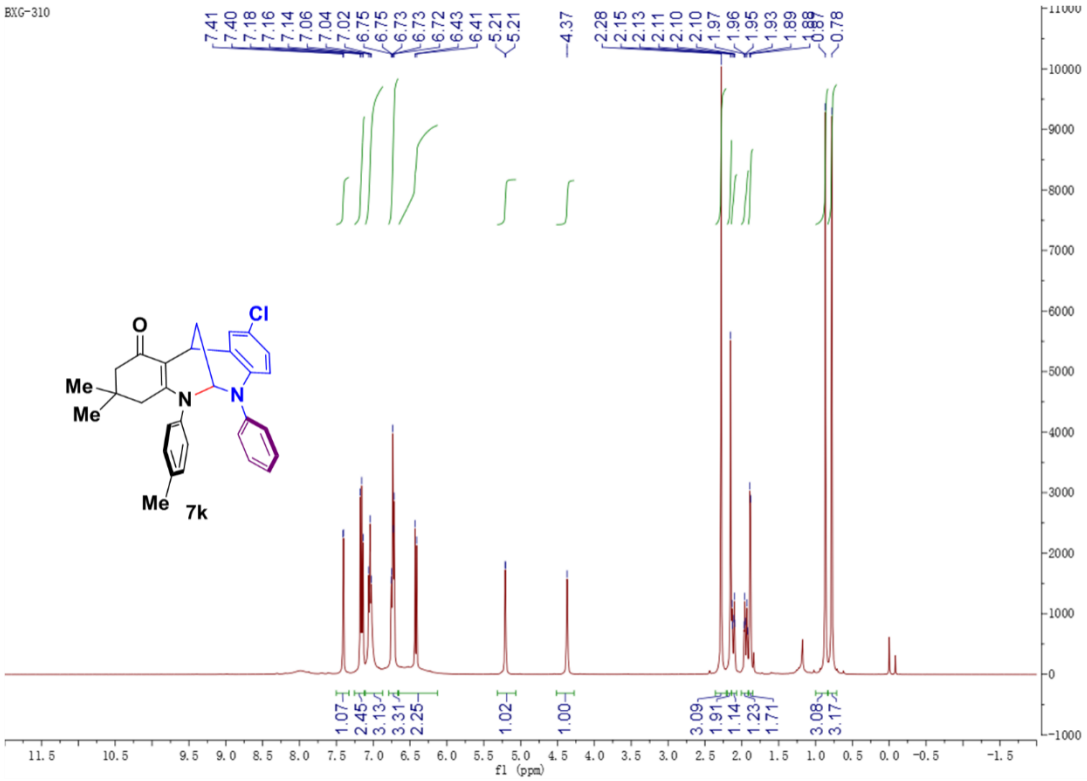
^{1}H NMR spectrum of **7j** (400 MHz, $CDCl_3$)



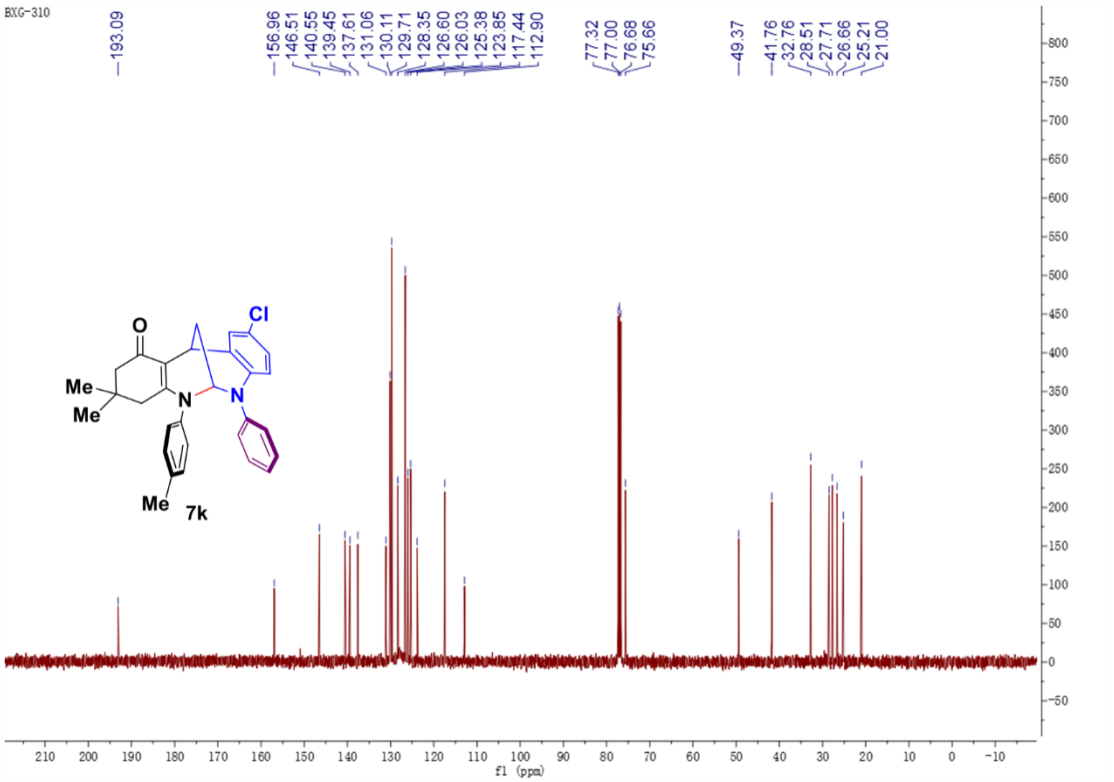
^{13}C NMR spectrum of **7j** (100 MHz, $CDCl_3$)



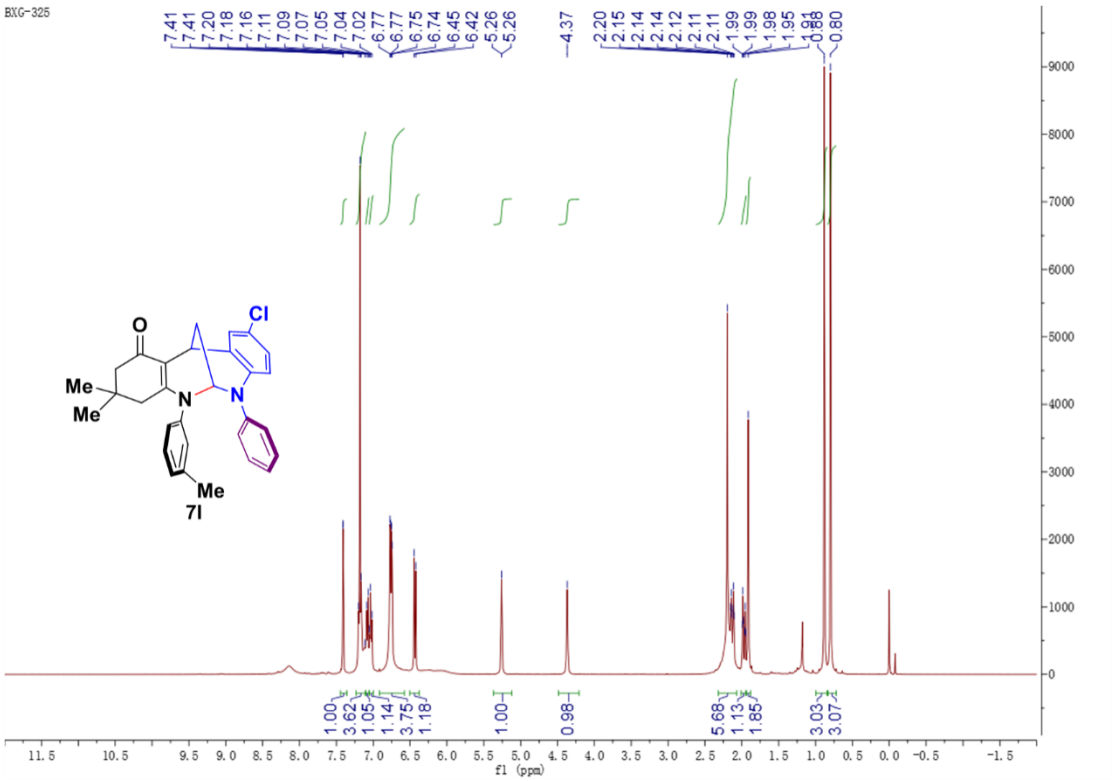
^{1}H NMR spectrum of **7k** (400 MHz, $CDCl_3$)



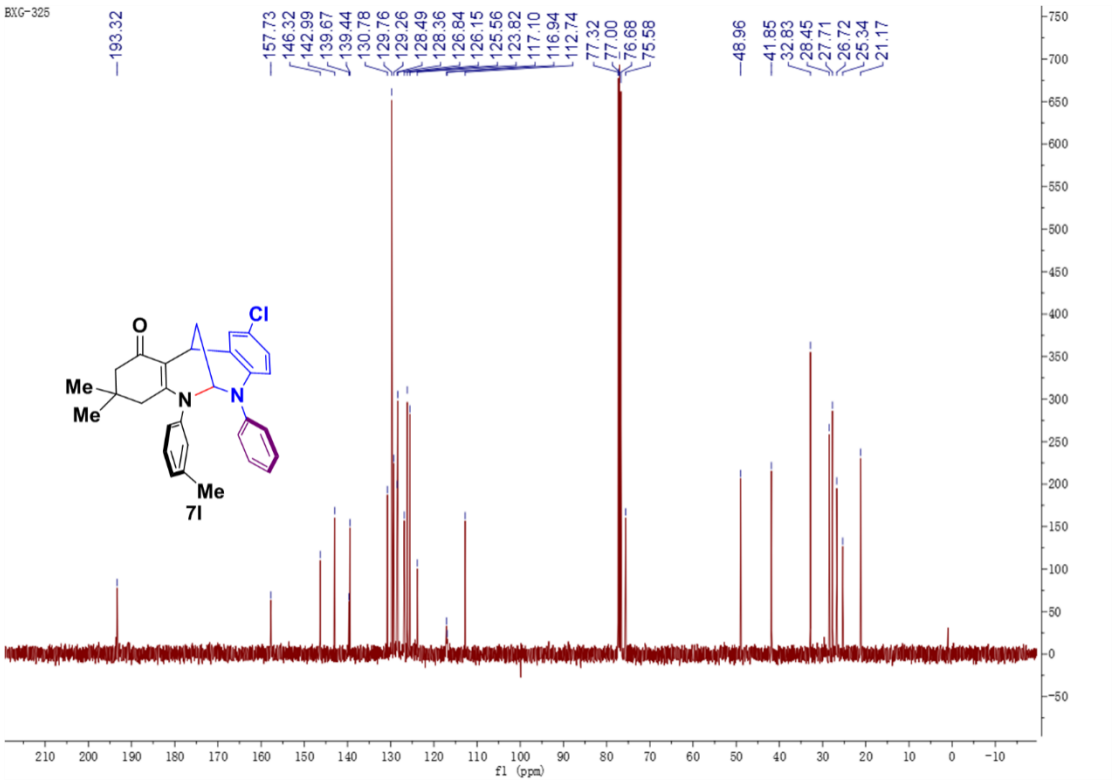
^{13}C NMR spectrum of **7k** (100 MHz, $CDCl_3$)



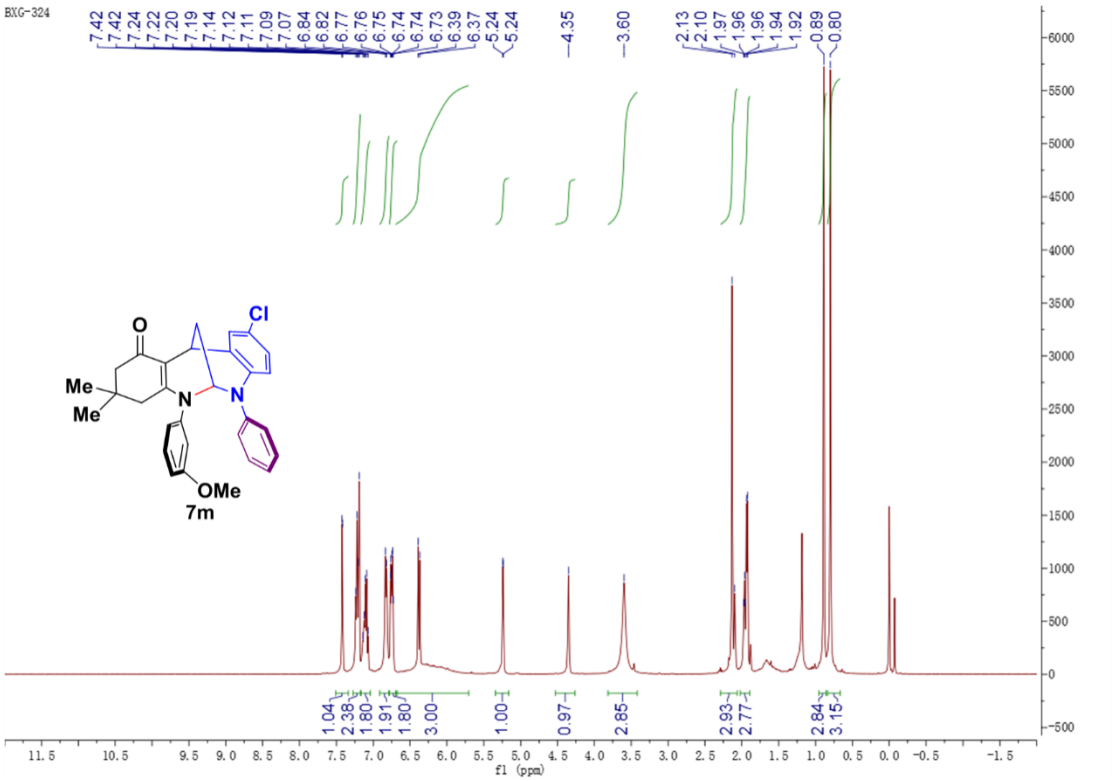
^{1}H NMR spectrum of **7l** (400 MHz, $CDCl_3$)



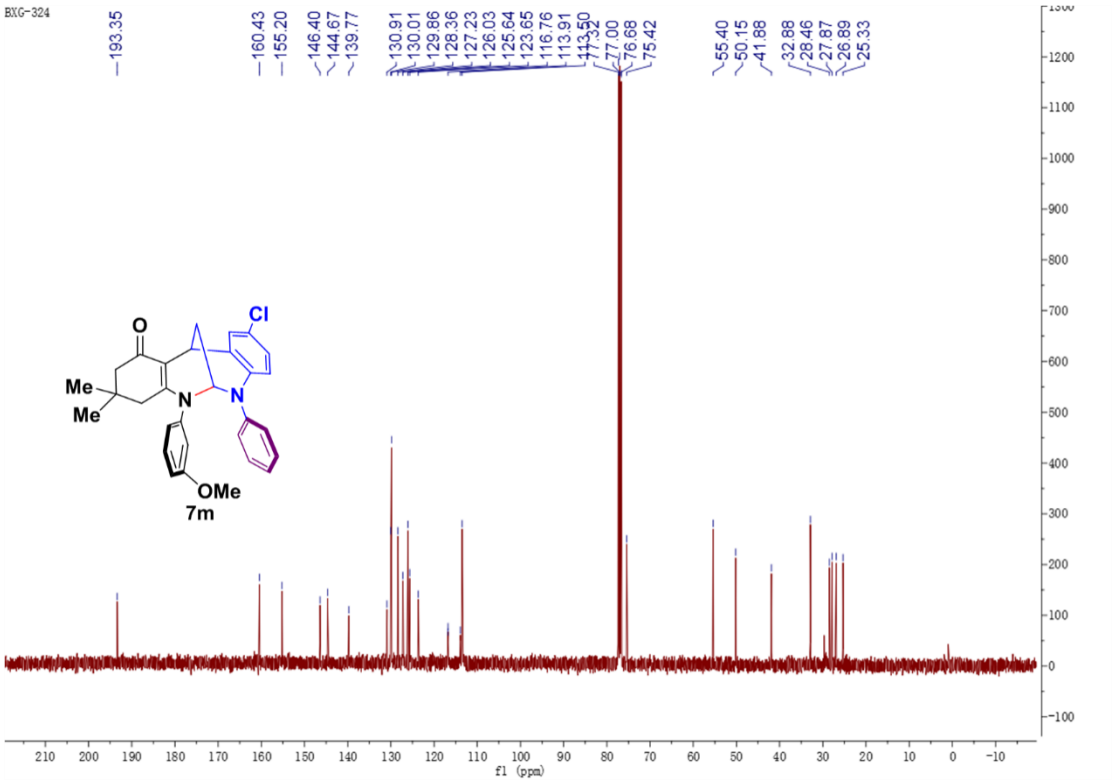
^{13}C NMR spectrum of **7l** (100 MHz, $CDCl_3$)



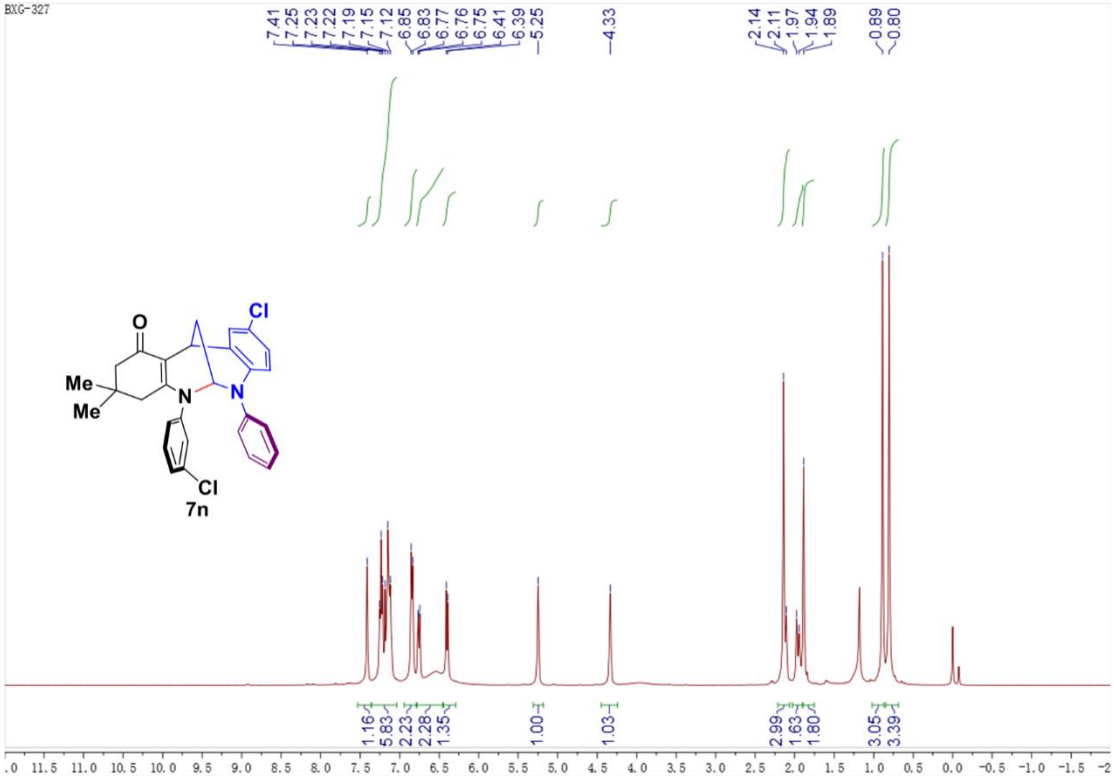
^{1}H NMR spectrum of **7m** (400 MHz, $CDCl_3$)



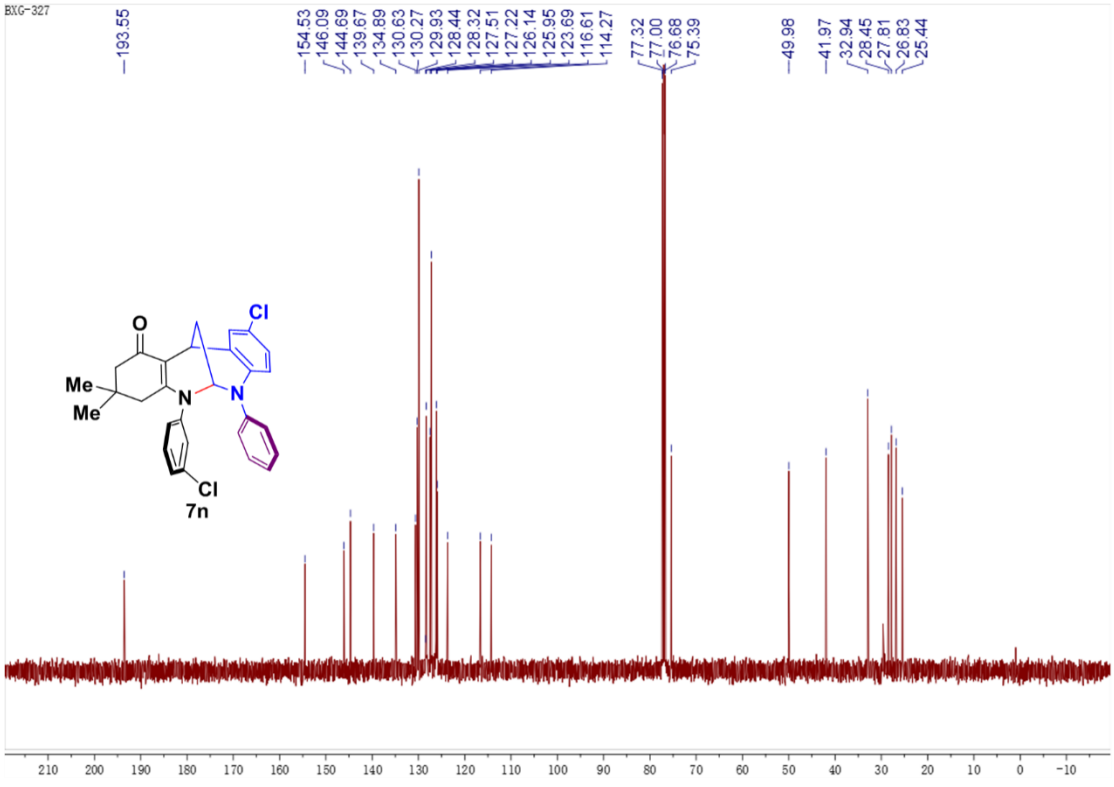
^{13}C NMR spectrum of **7m** (100 MHz, $CDCl_3$)



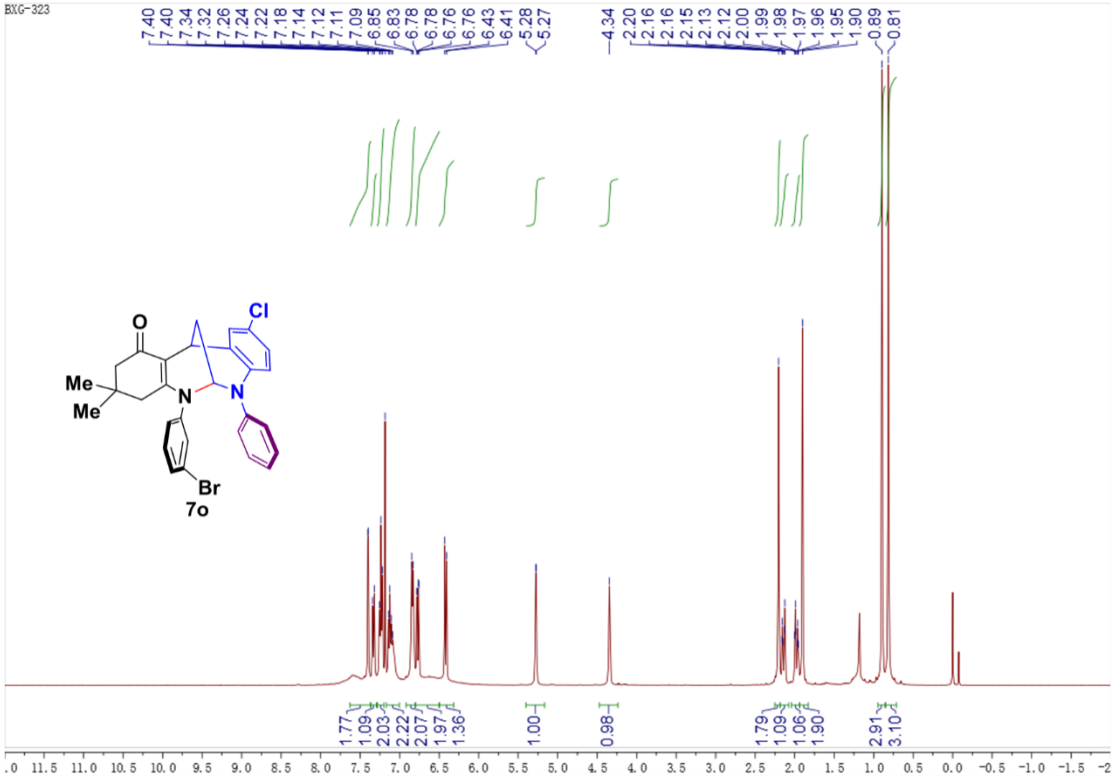
^{1}H NMR spectrum of **7n** (400 MHz, $CDCl_3$)



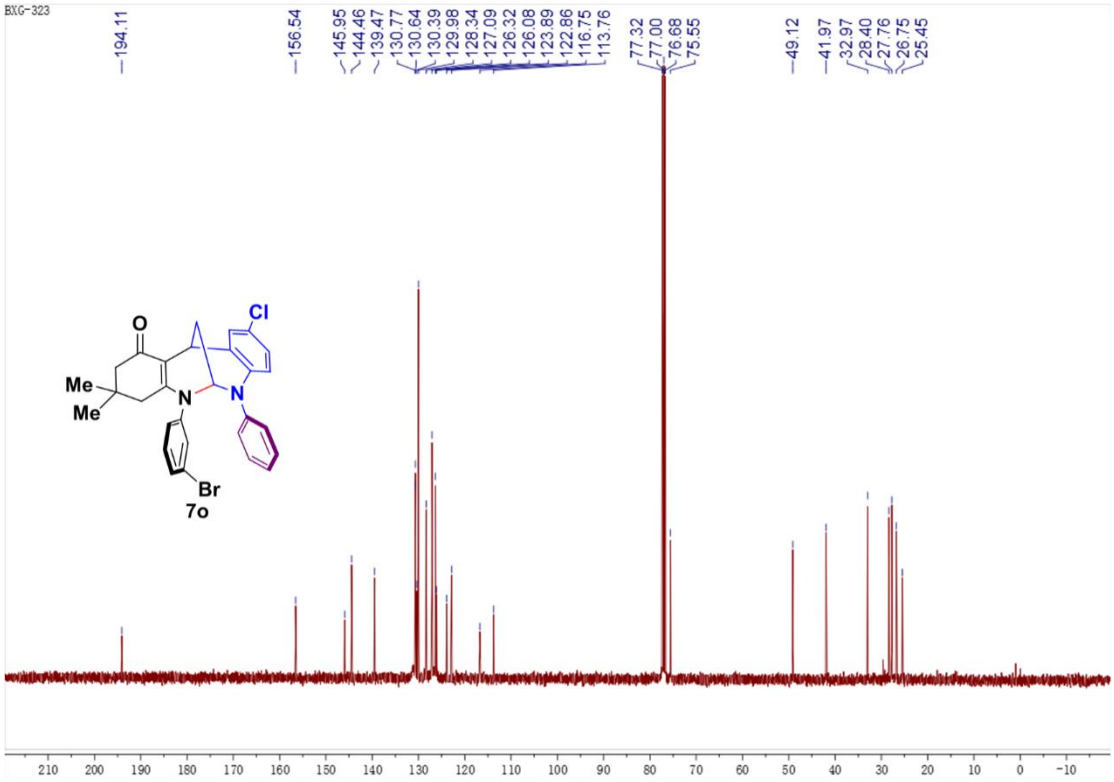
^{13}C NMR spectrum of **7n** (100 MHz, $CDCl_3$)



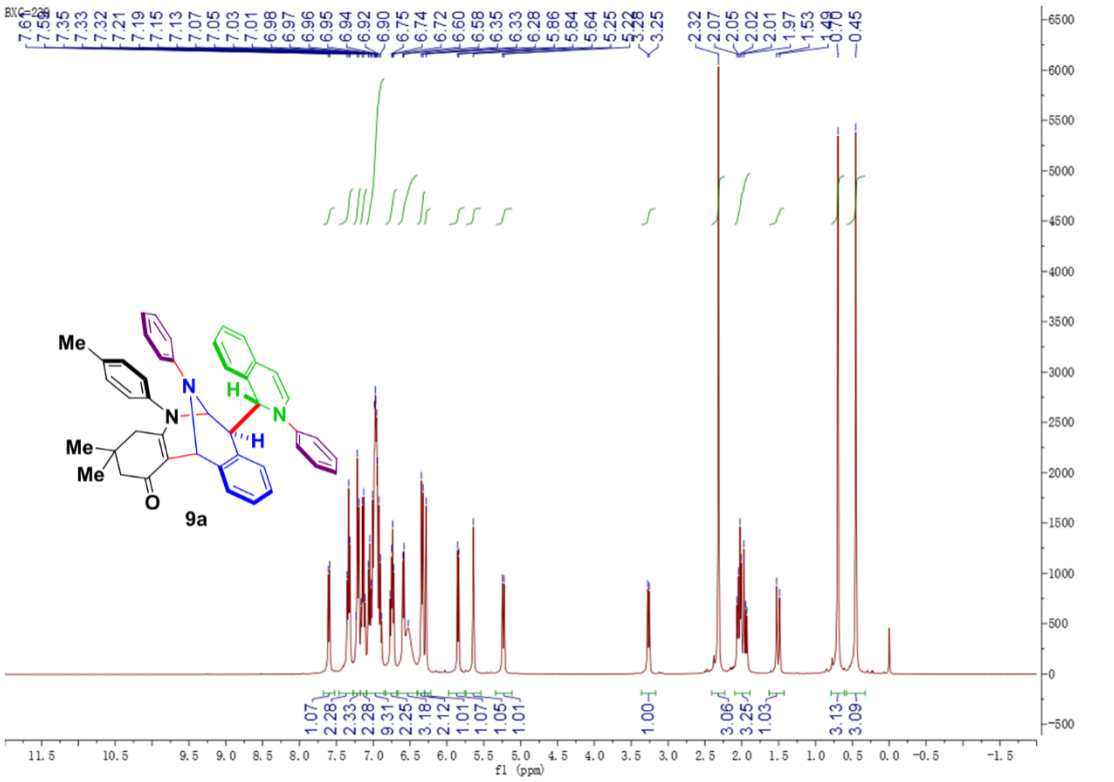
^{1}H NMR spectrum of **7o** (400 MHz, $CDCl_3$)



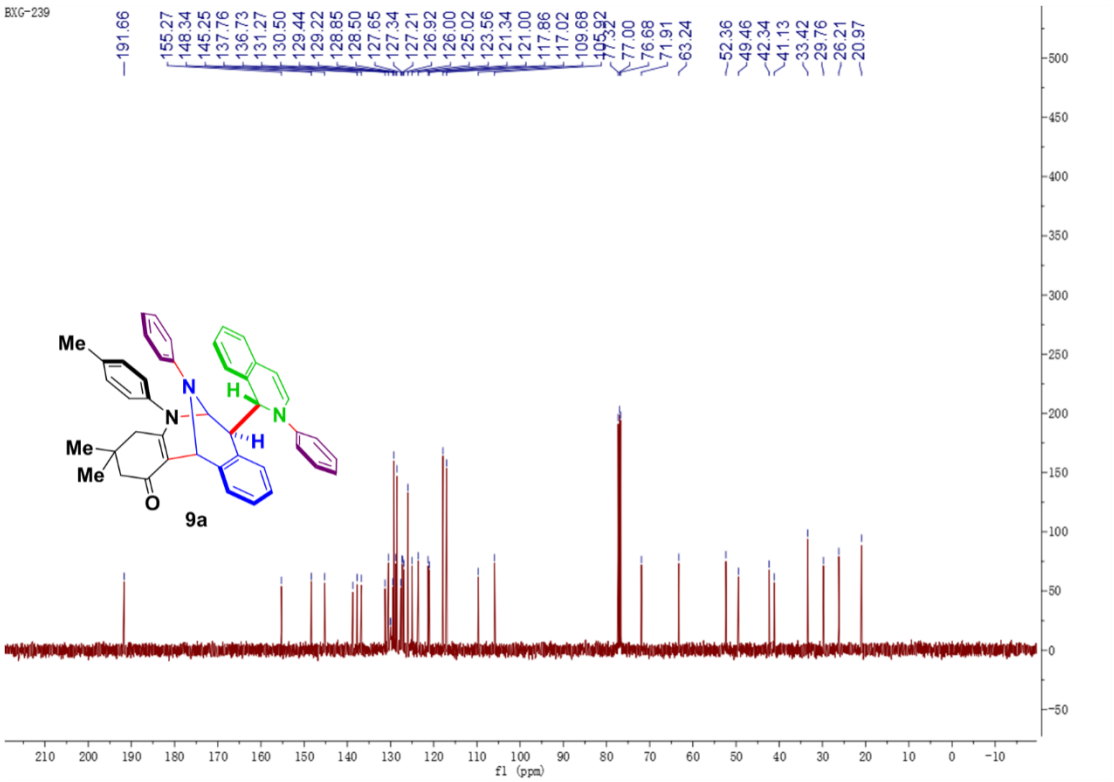
^{13}C NMR spectrum of **7o** (100 MHz, $CDCl_3$)



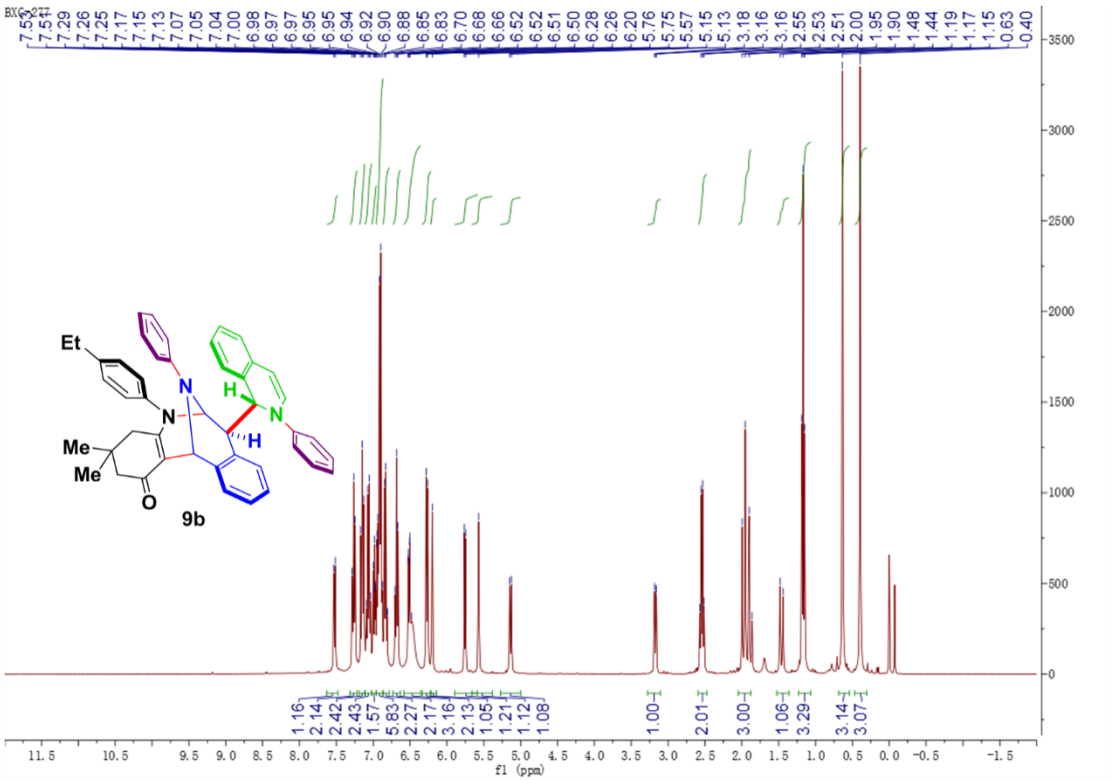
^{1}H NMR spectrum of **9a** (400 MHz, $CDCl_3$)



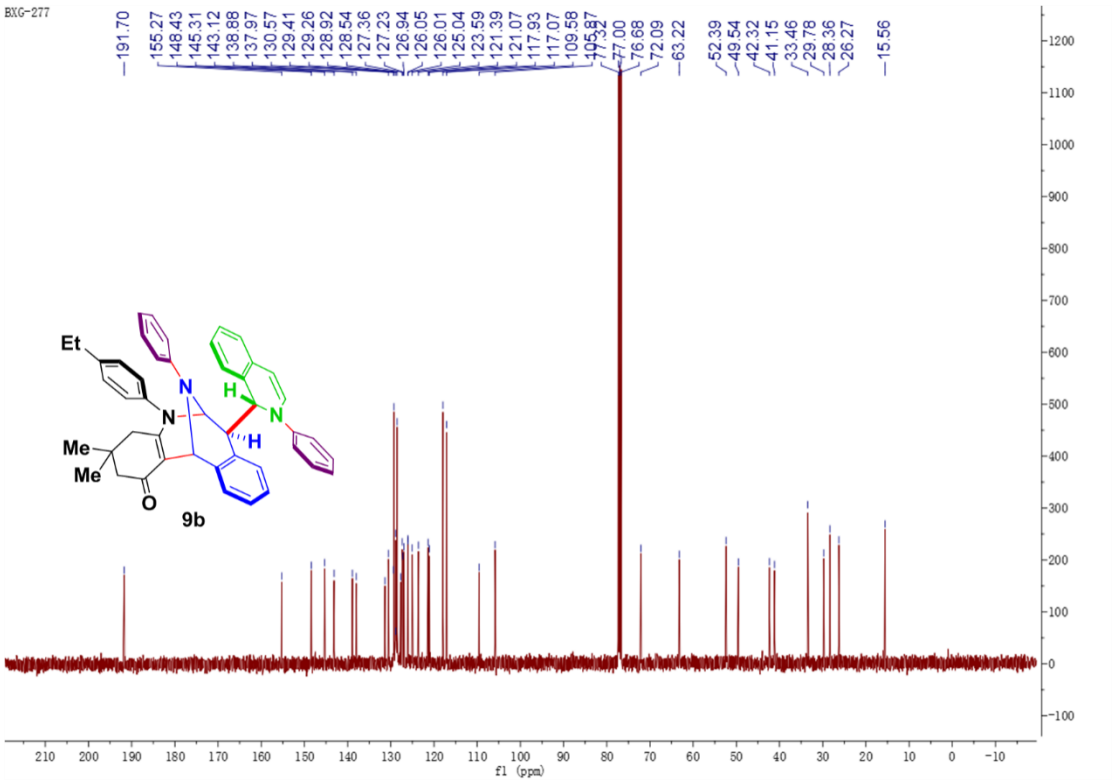
^{13}C NMR spectrum of **9a** (100 MHz, $CDCl_3$)



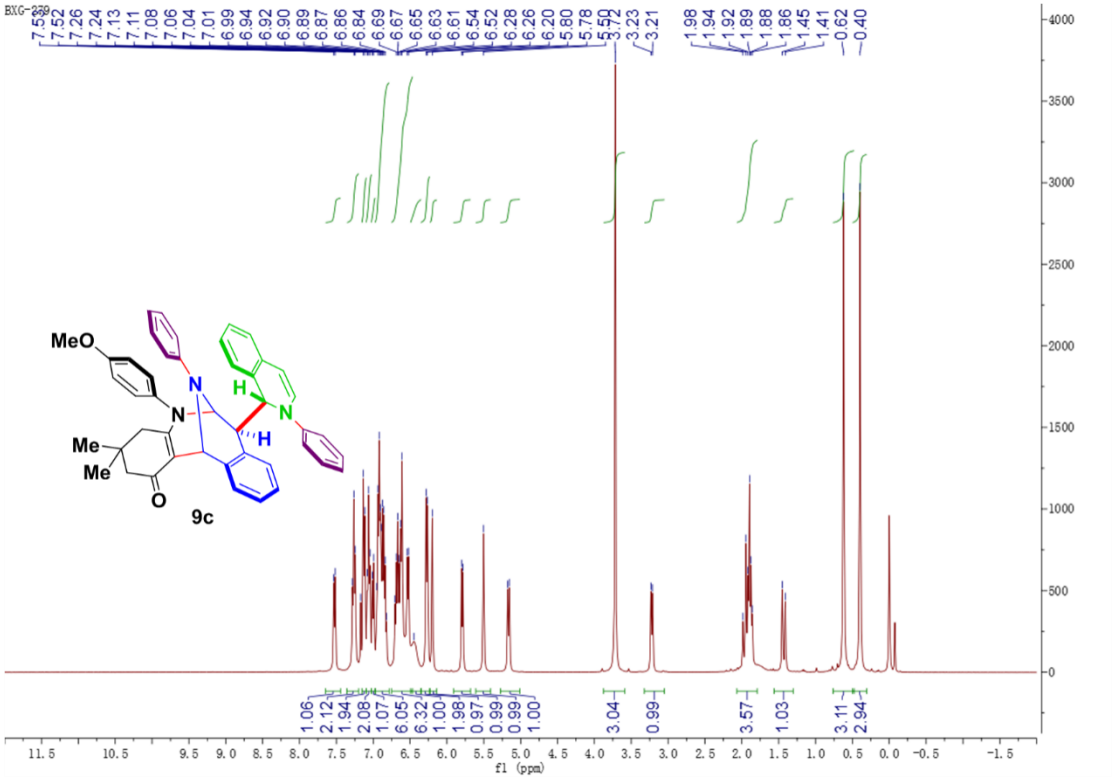
^{1}H NMR spectrum of **9b** (400 MHz, $CDCl_3$)



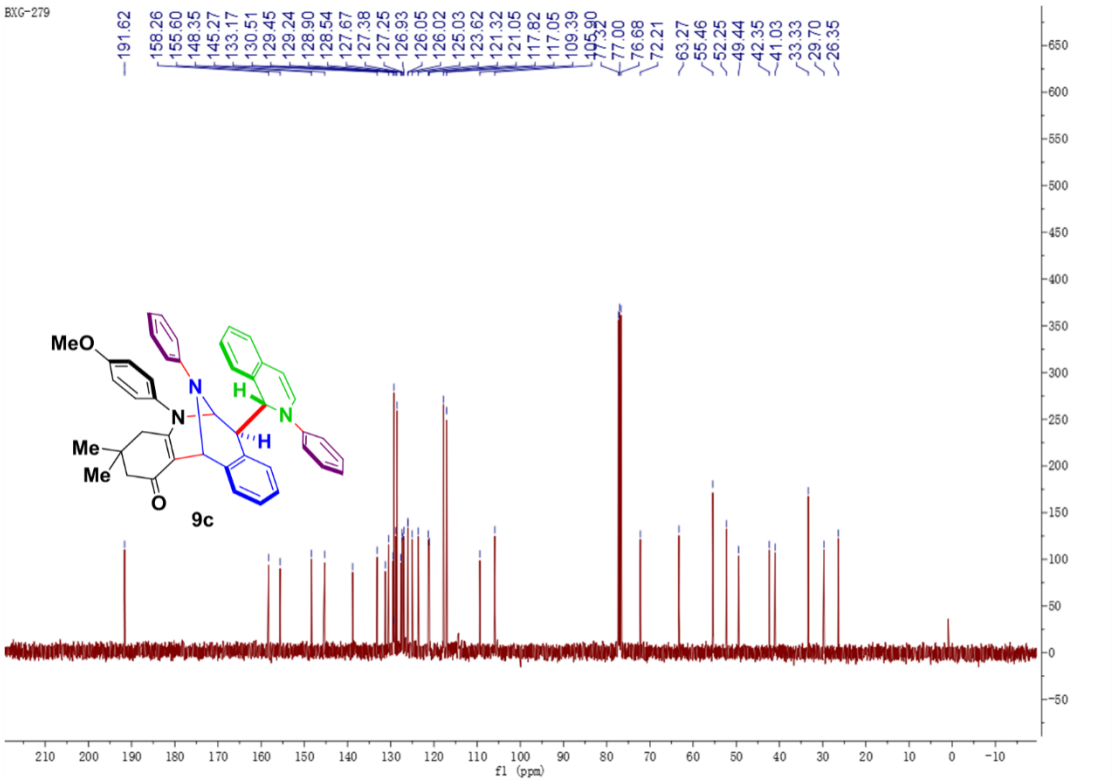
^{13}C NMR spectrum of **9b** (100 MHz, $CDCl_3$)



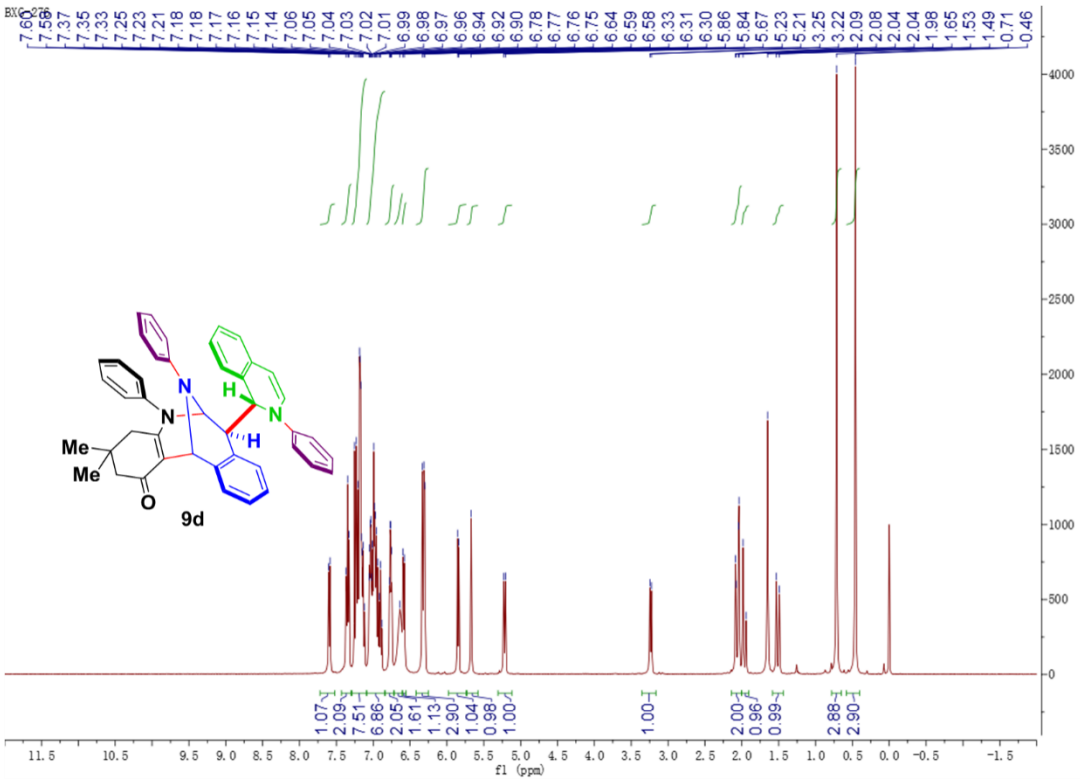
^{1}H NMR spectrum of **9c** (400 MHz, $CDCl_3$)



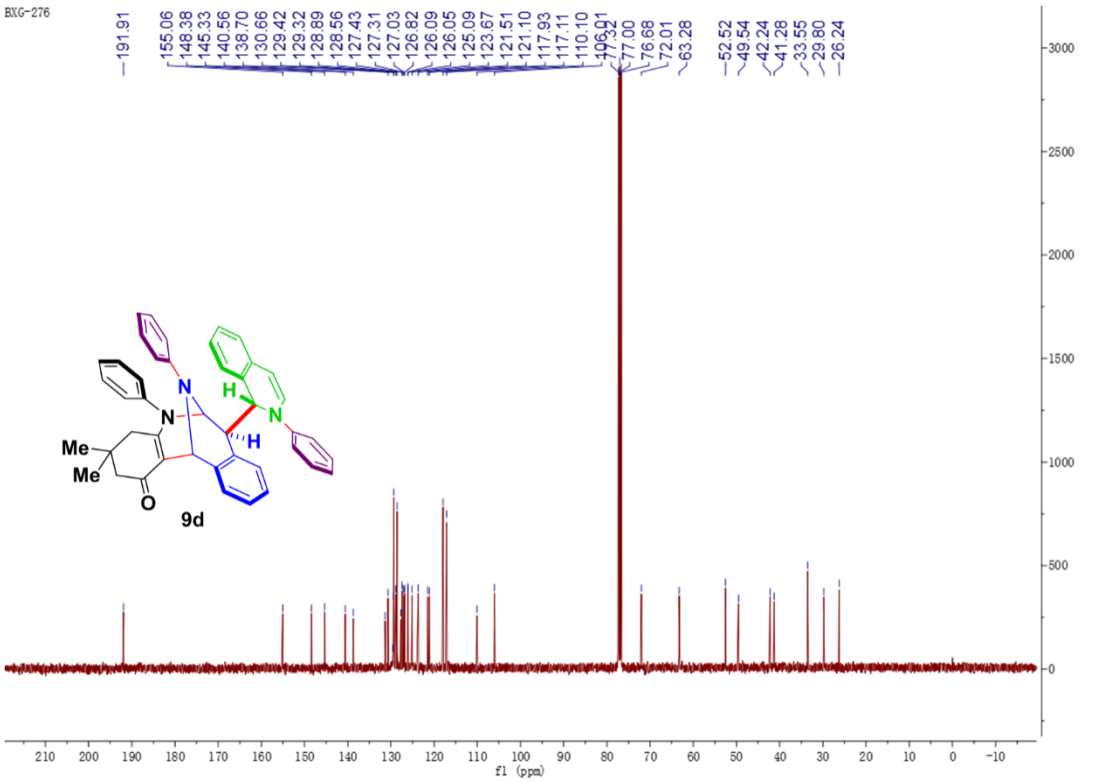
^{13}C NMR spectrum of **9c** (100 MHz, $CDCl_3$)



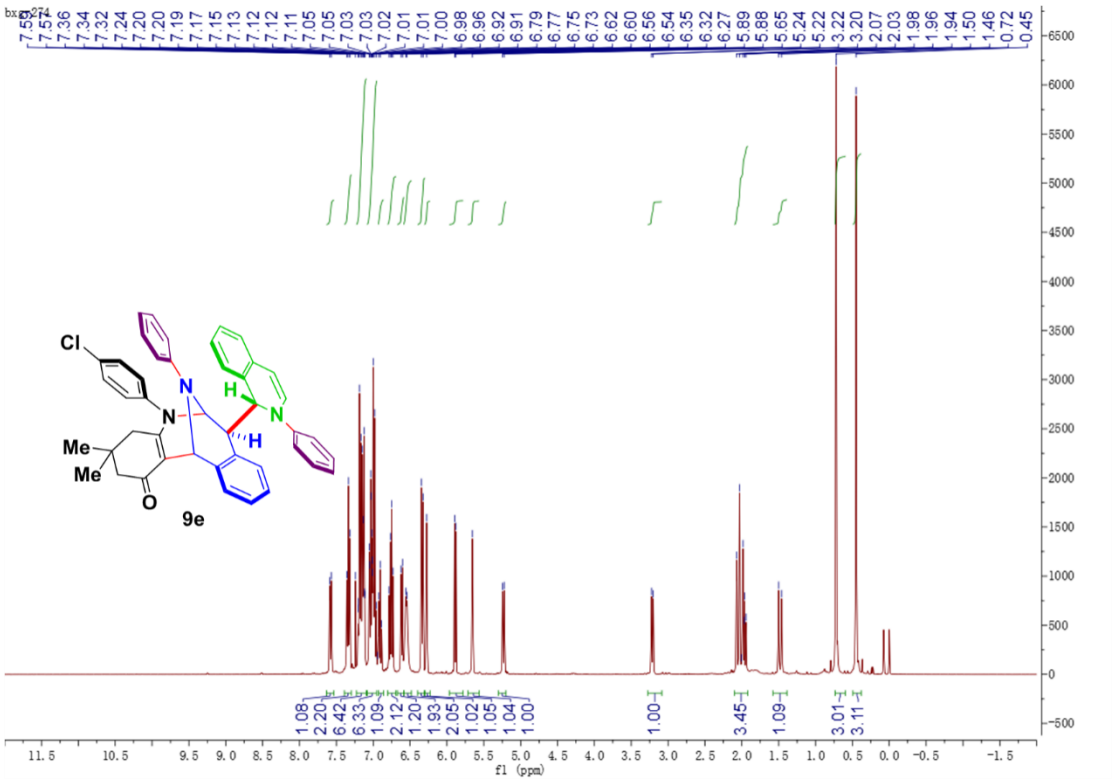
^{1}H NMR spectrum of **9d** (400 MHz, $CDCl_3$)



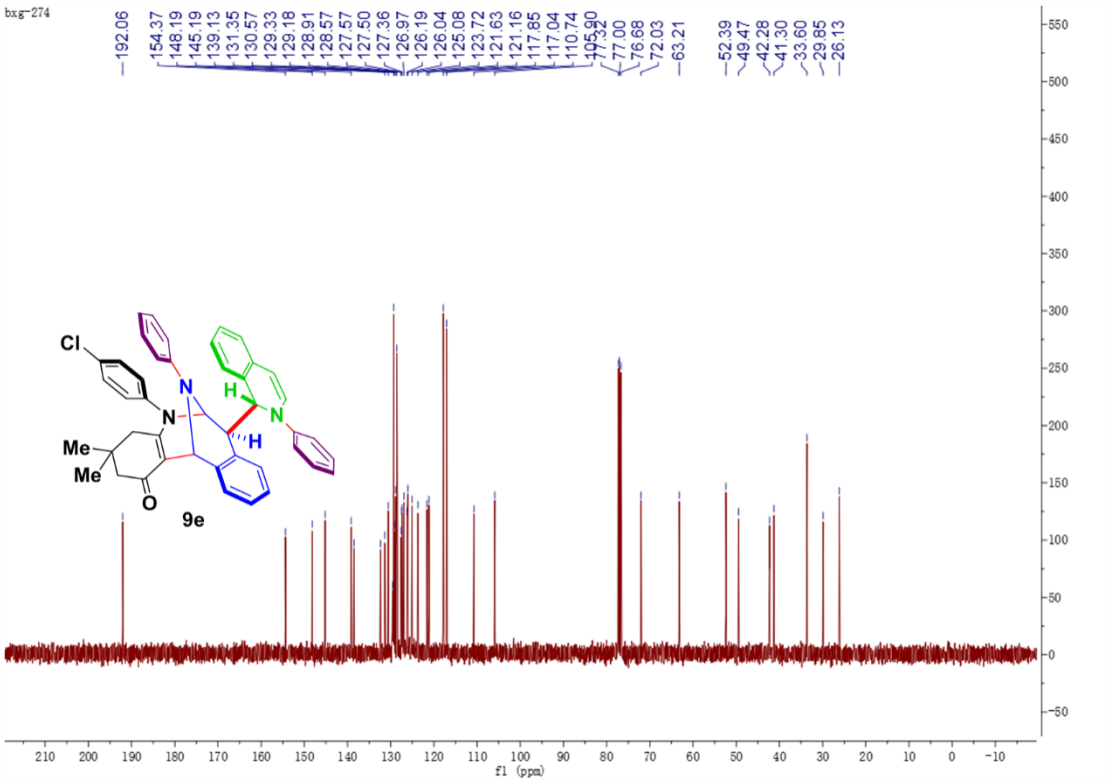
^{13}C NMR spectrum of **9d** (100 MHz, $CDCl_3$)



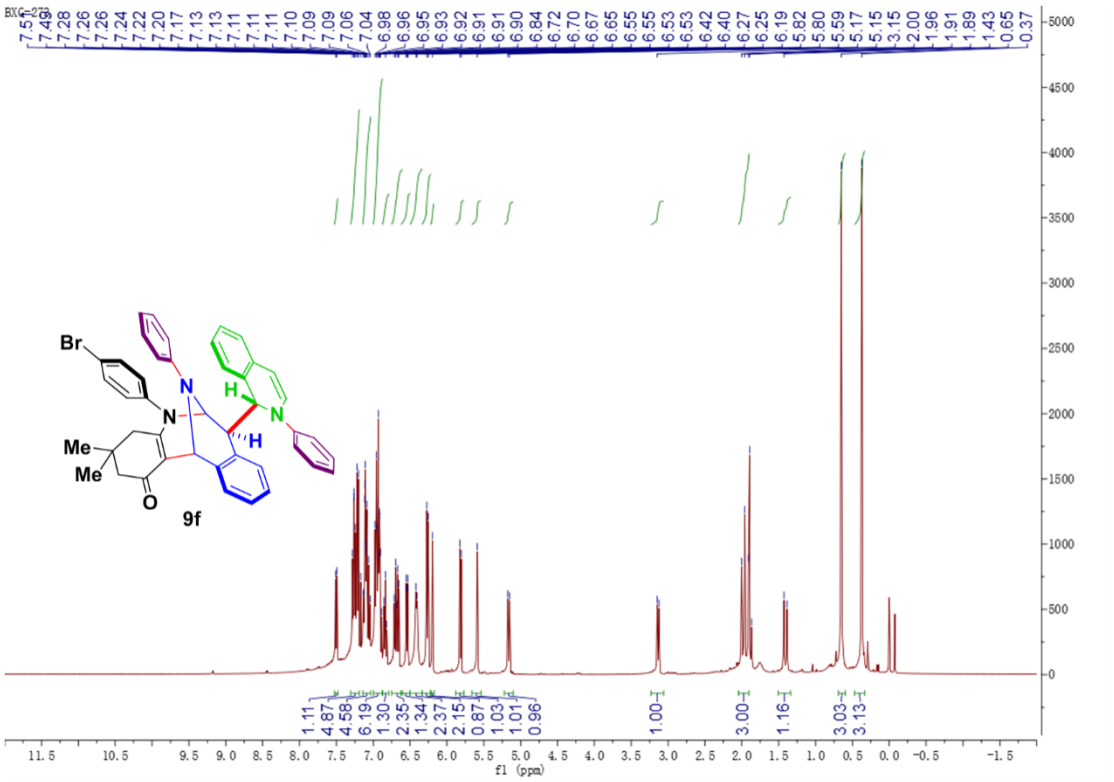
^{1}H NMR spectrum of **9e** (400 MHz, $CDCl_3$)



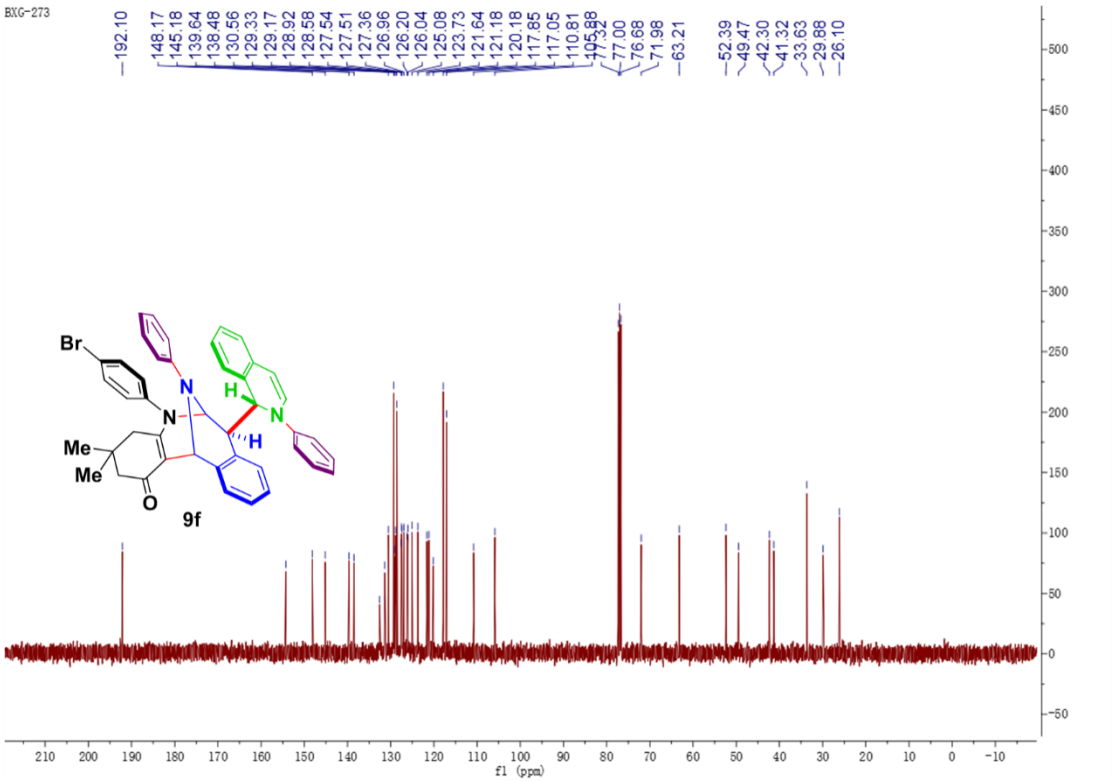
^{13}C NMR spectrum of **9e** (100 MHz, $CDCl_3$)



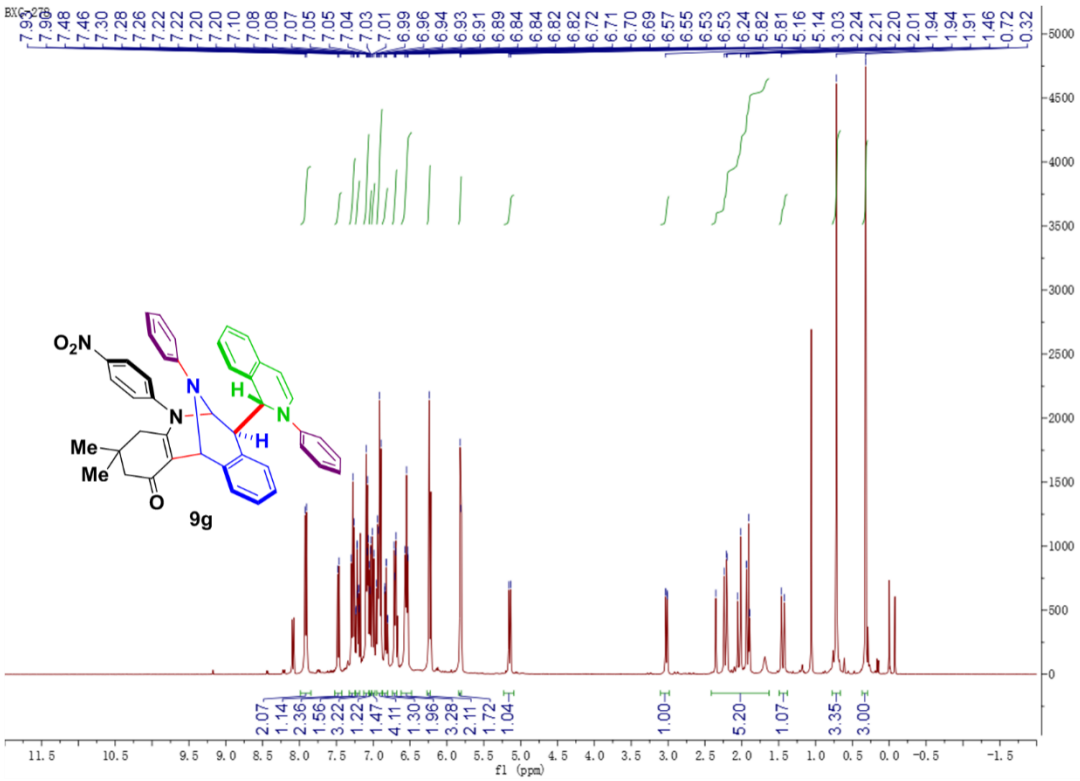
^{1}H NMR spectrum of **9f** (400 MHz, $CDCl_3$)



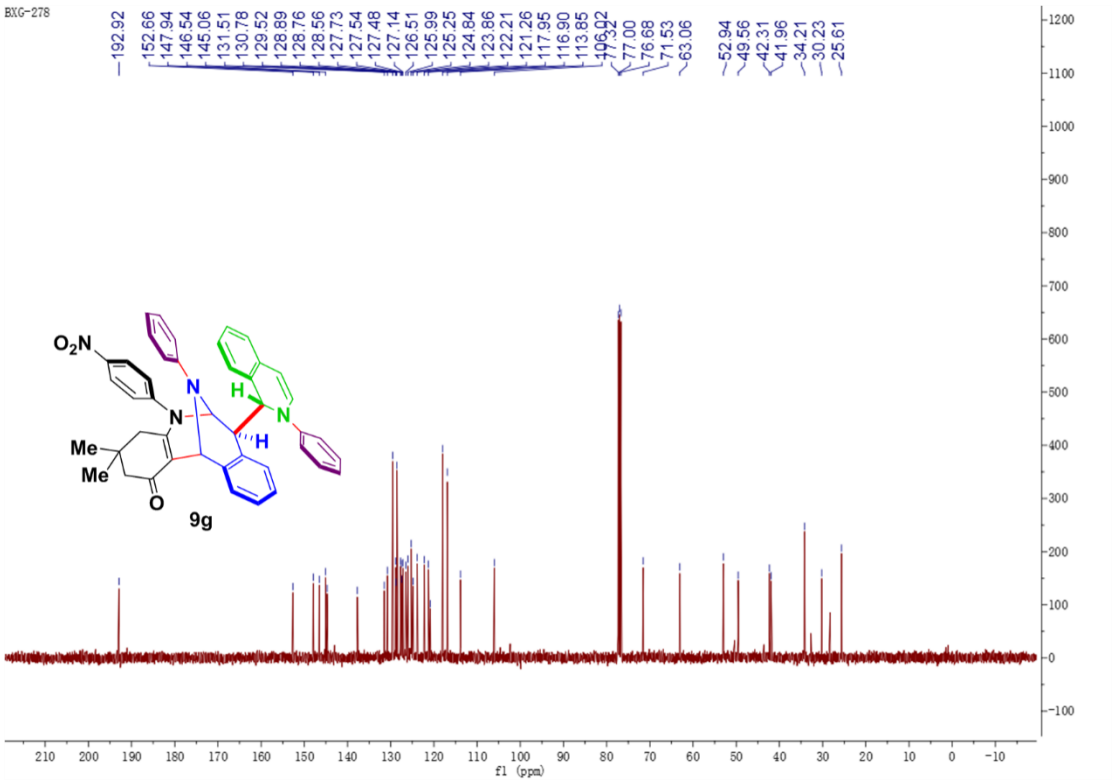
^{13}C NMR spectrum of **9f** (100 MHz, $CDCl_3$)



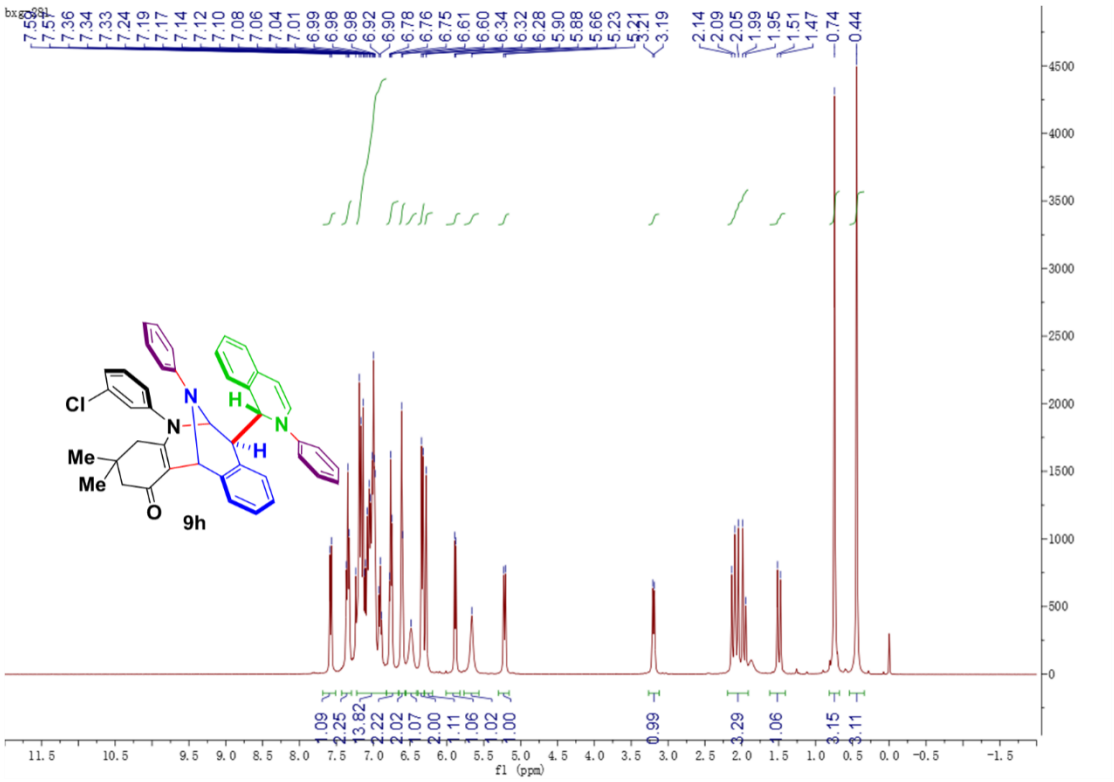
^{1}H NMR spectrum of **9g** (400 MHz, $CDCl_3$)



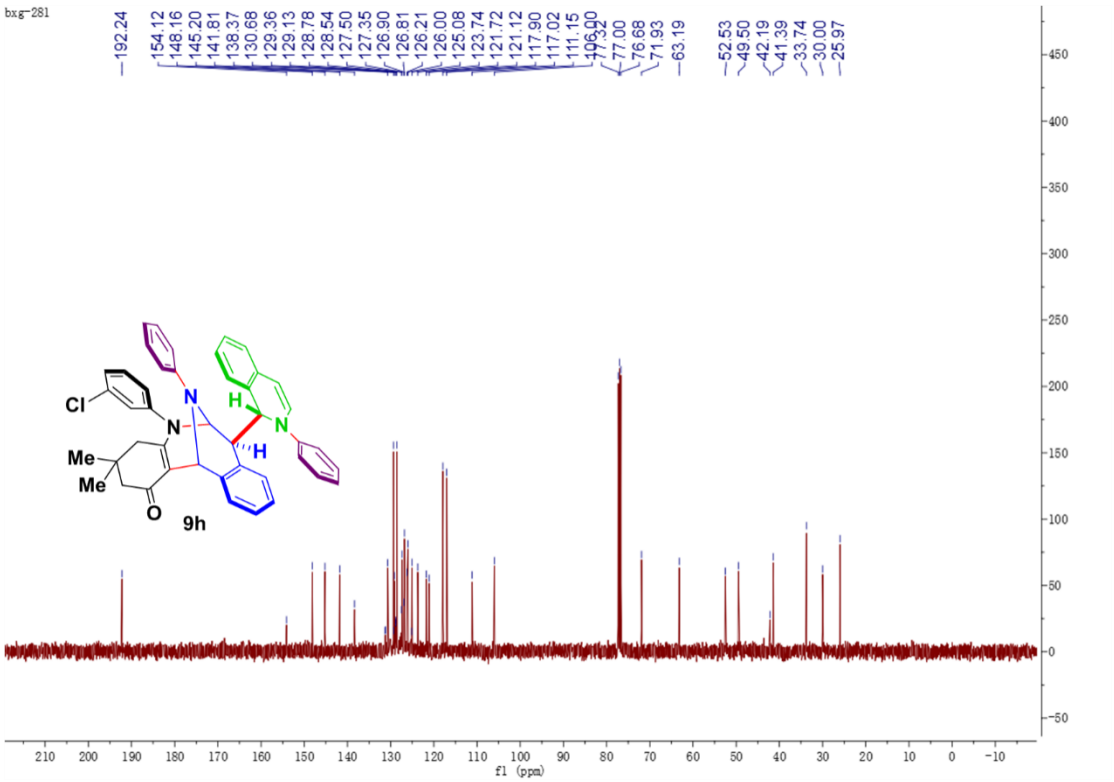
^{13}C NMR spectrum of **9g** (100 MHz, $CDCl_3$)



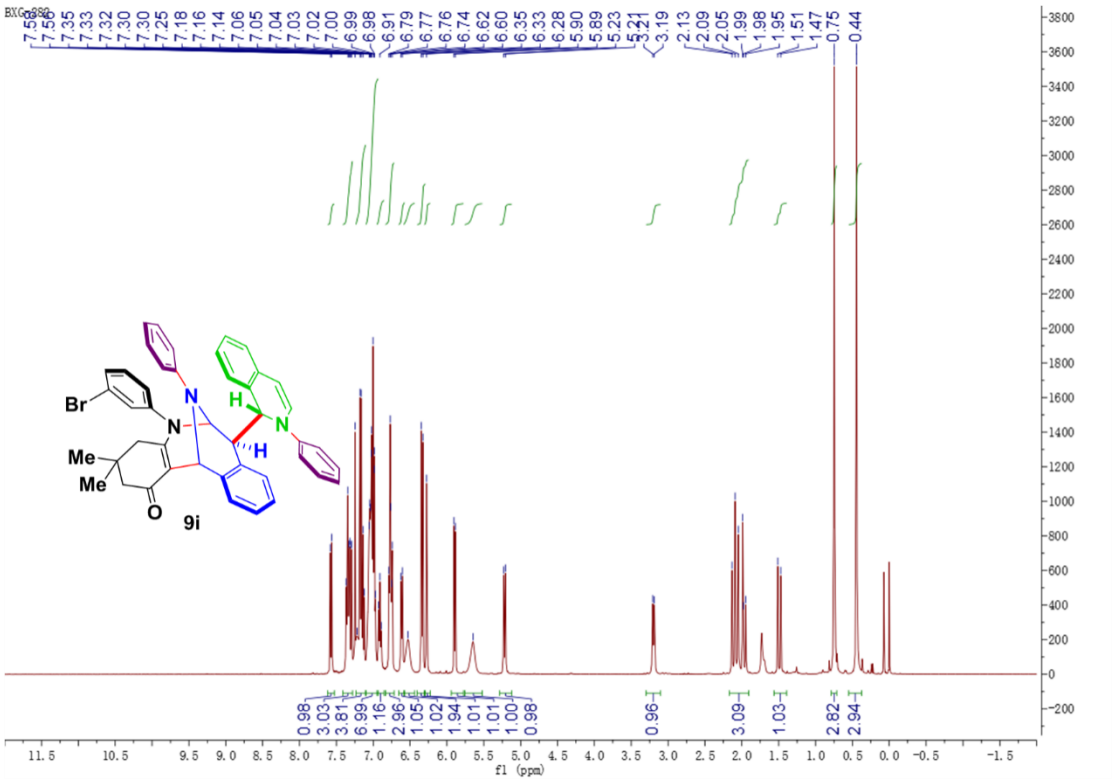
^{1}H NMR spectrum of **9h** (400 MHz, $CDCl_3$)



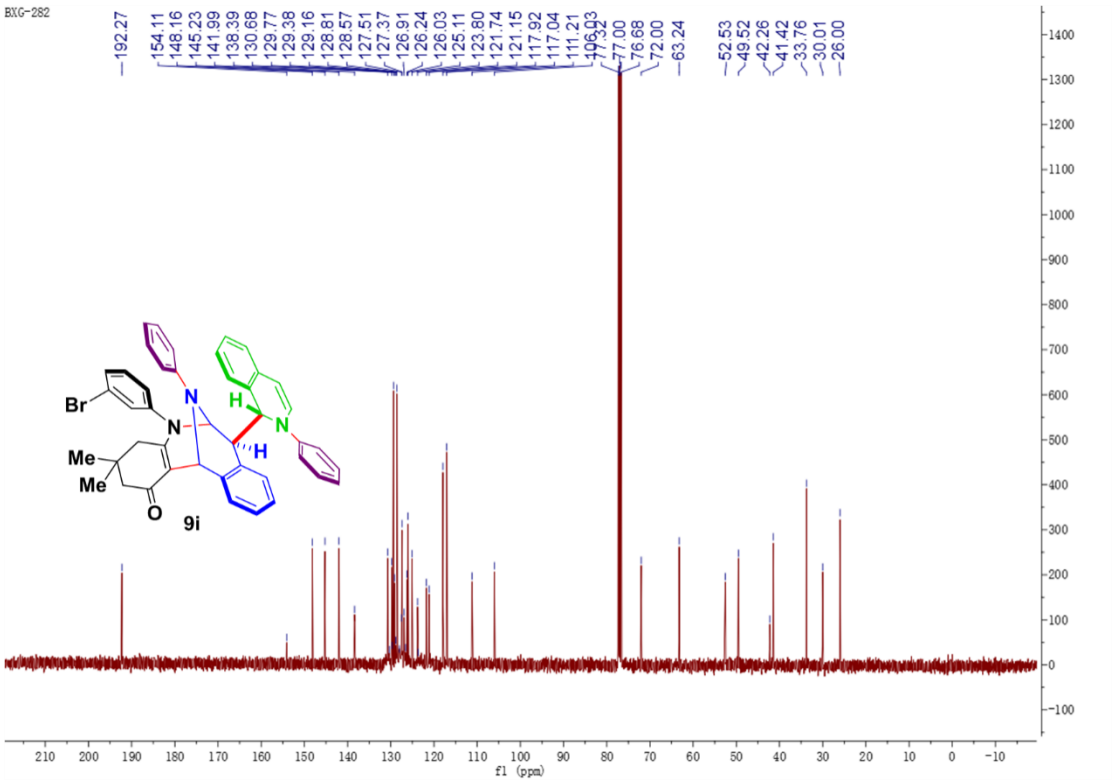
^{13}C NMR spectrum of **9h** (100 MHz, $CDCl_3$)



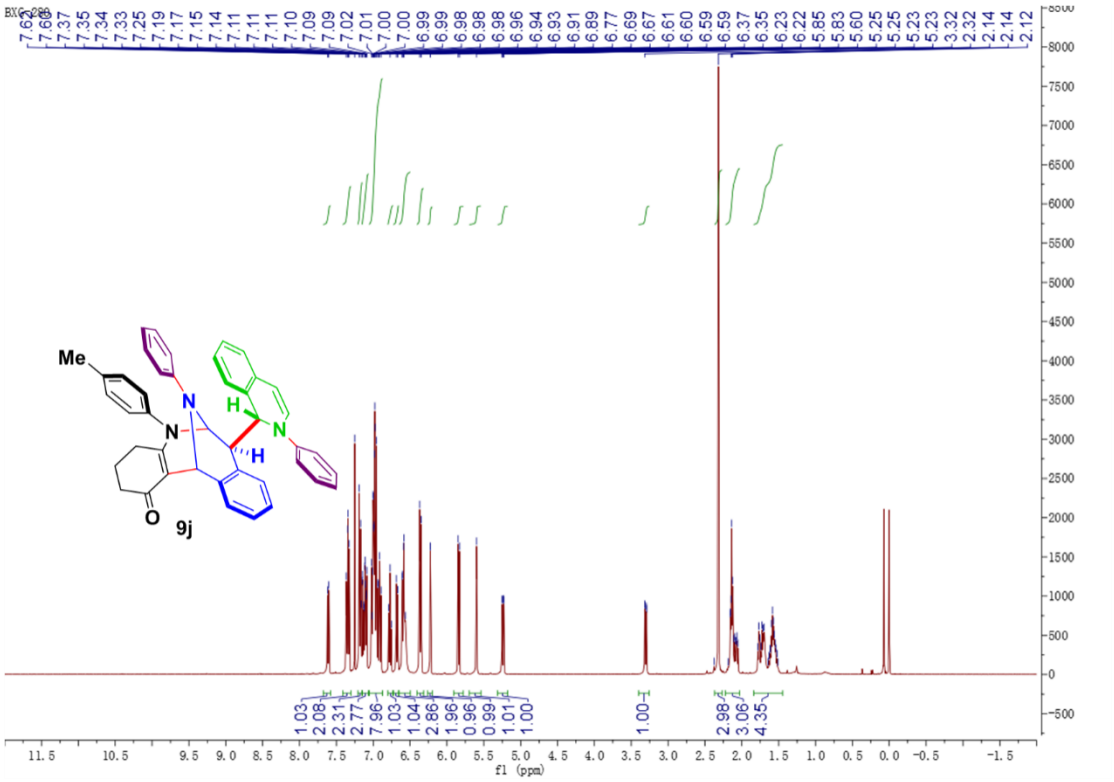
^{1}H NMR spectrum of **9i** (400 MHz, $CDCl_3$)



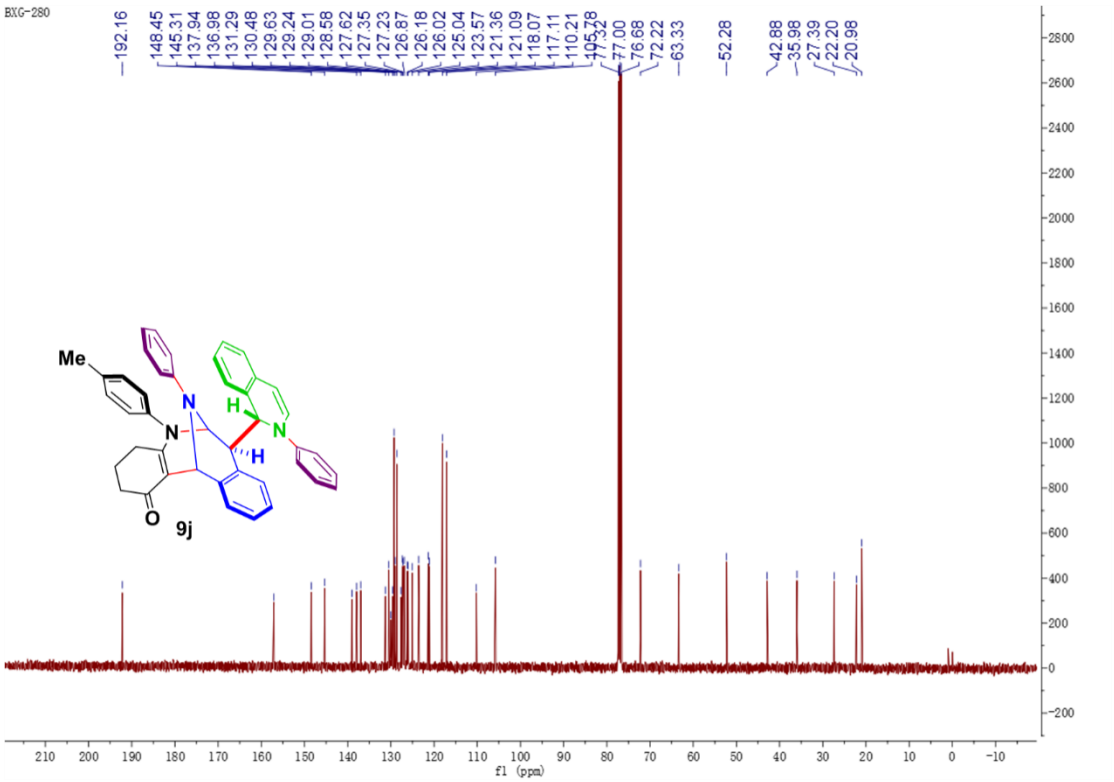
^{13}C NMR spectrum of **9i** (100 MHz, $CDCl_3$)



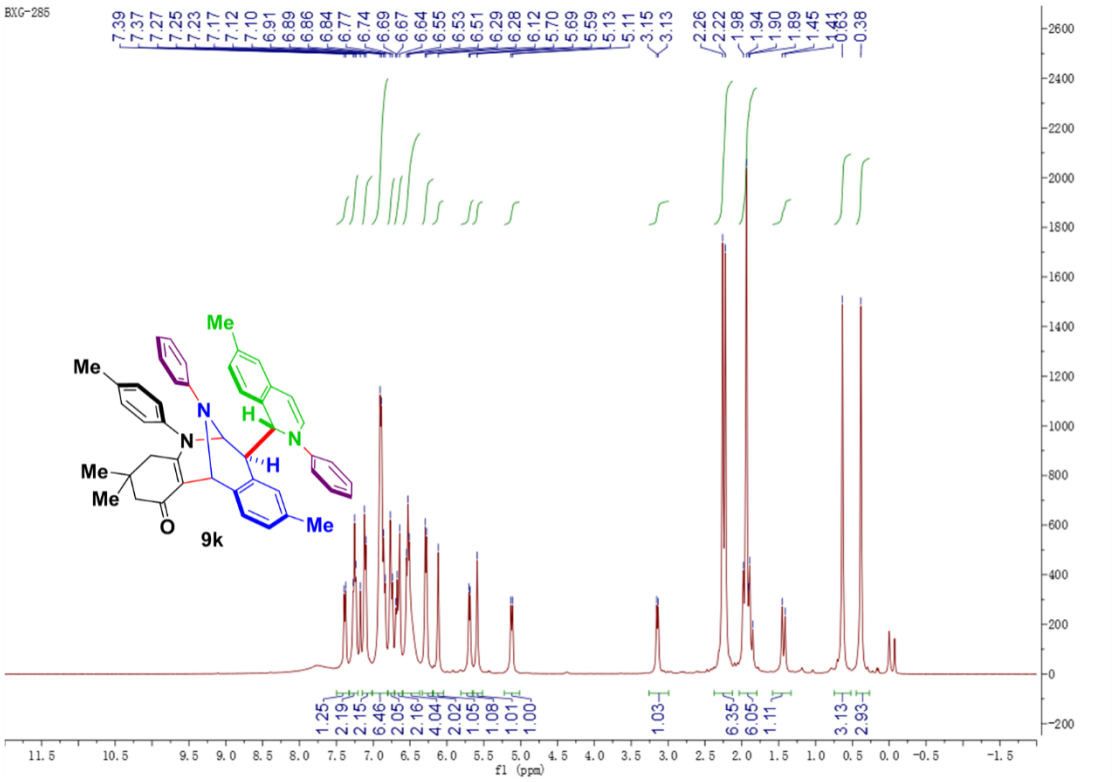
^{1}H NMR spectrum of **9j** (400 MHz, $CDCl_3$)



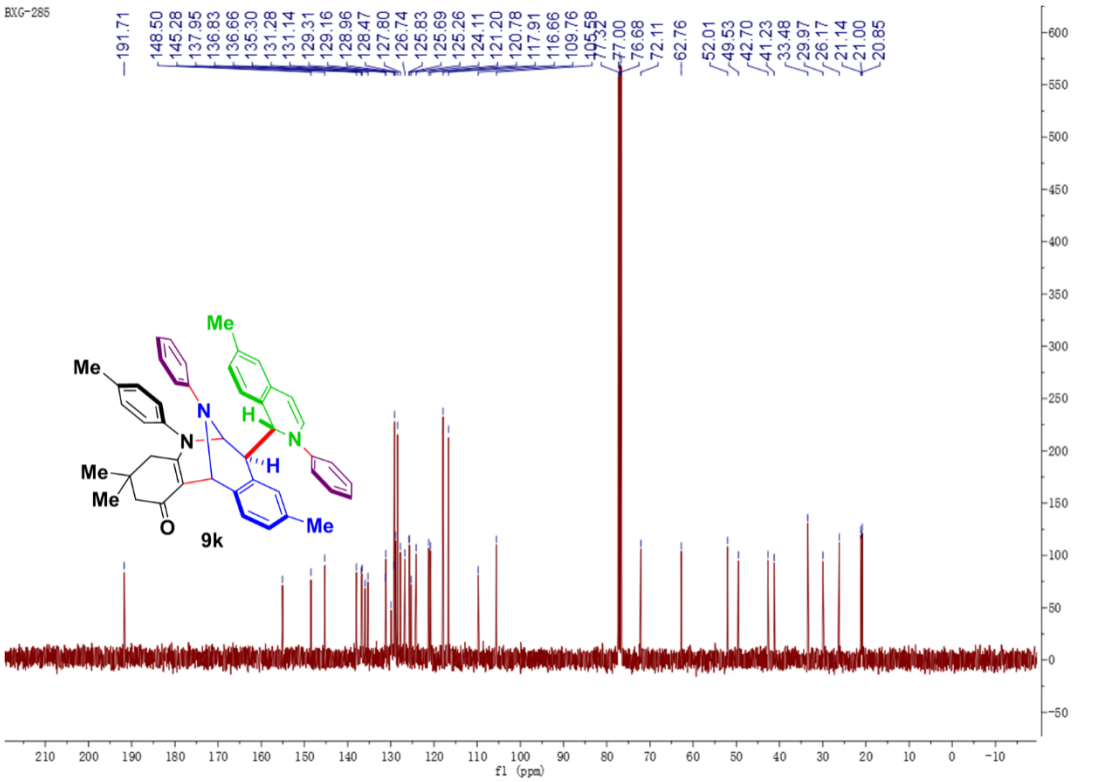
^{13}C NMR spectrum of **9j** (100 MHz, $CDCl_3$)



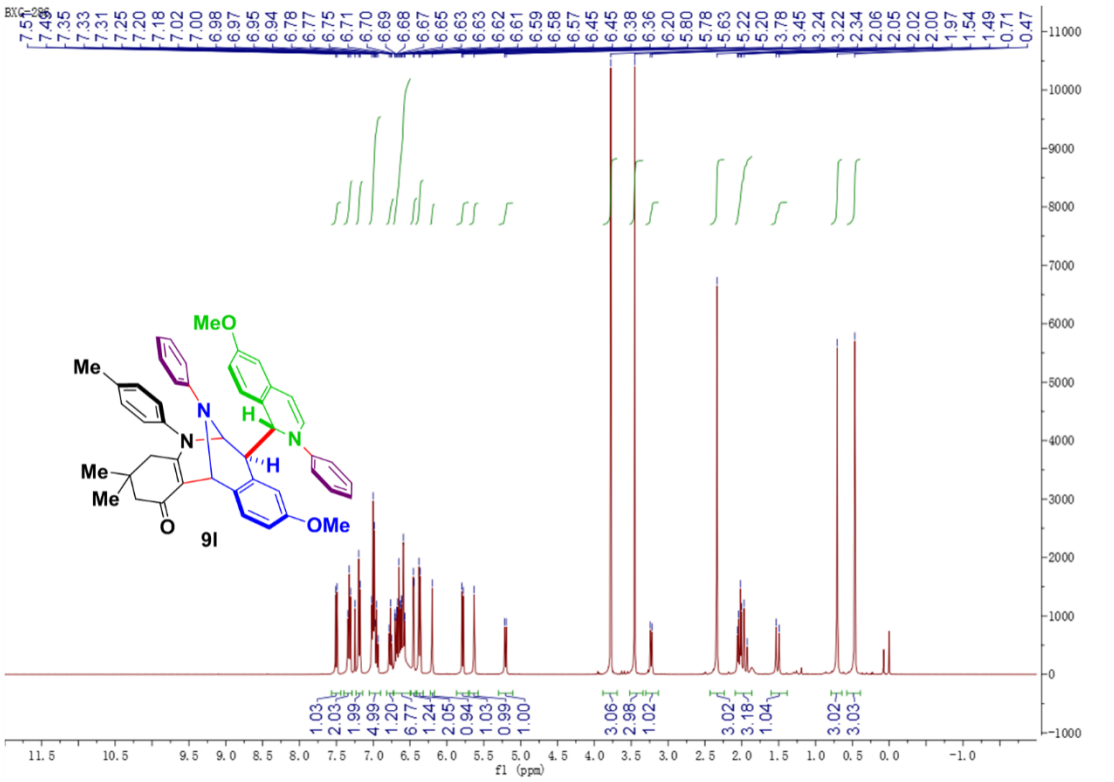
^{1}H NMR spectrum of **9k** (400 MHz, $CDCl_3$)



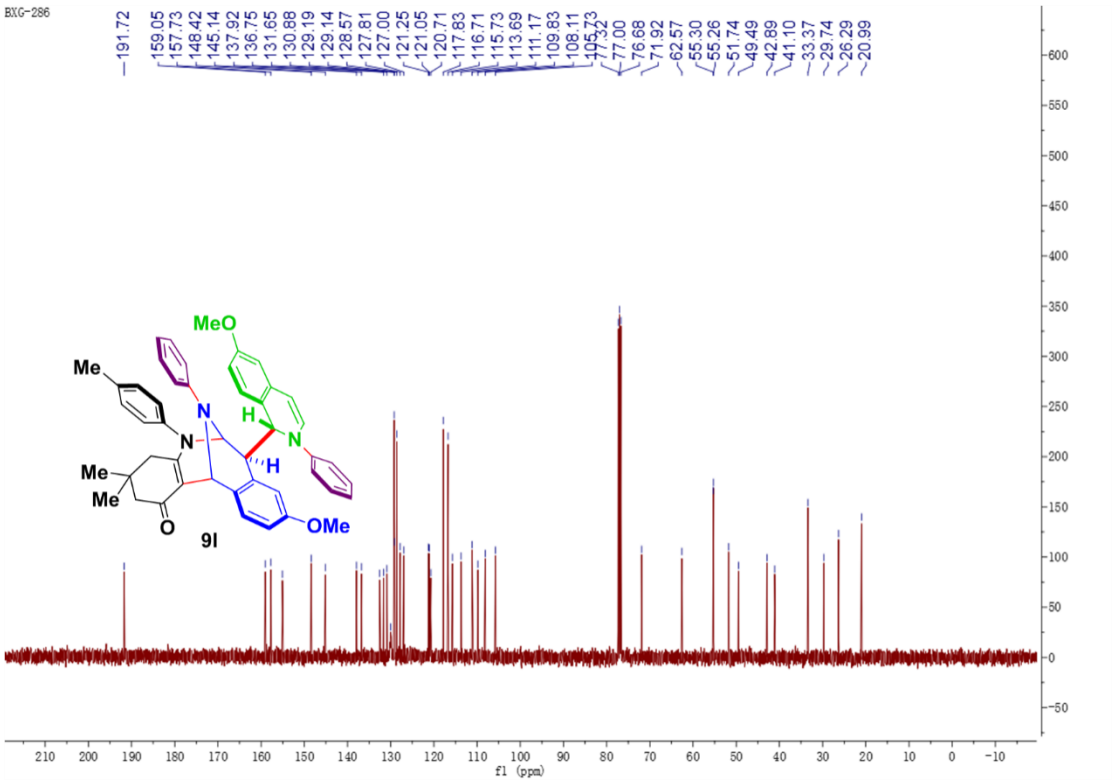
^{13}C NMR spectrum of **9k** (100 MHz, $CDCl_3$)



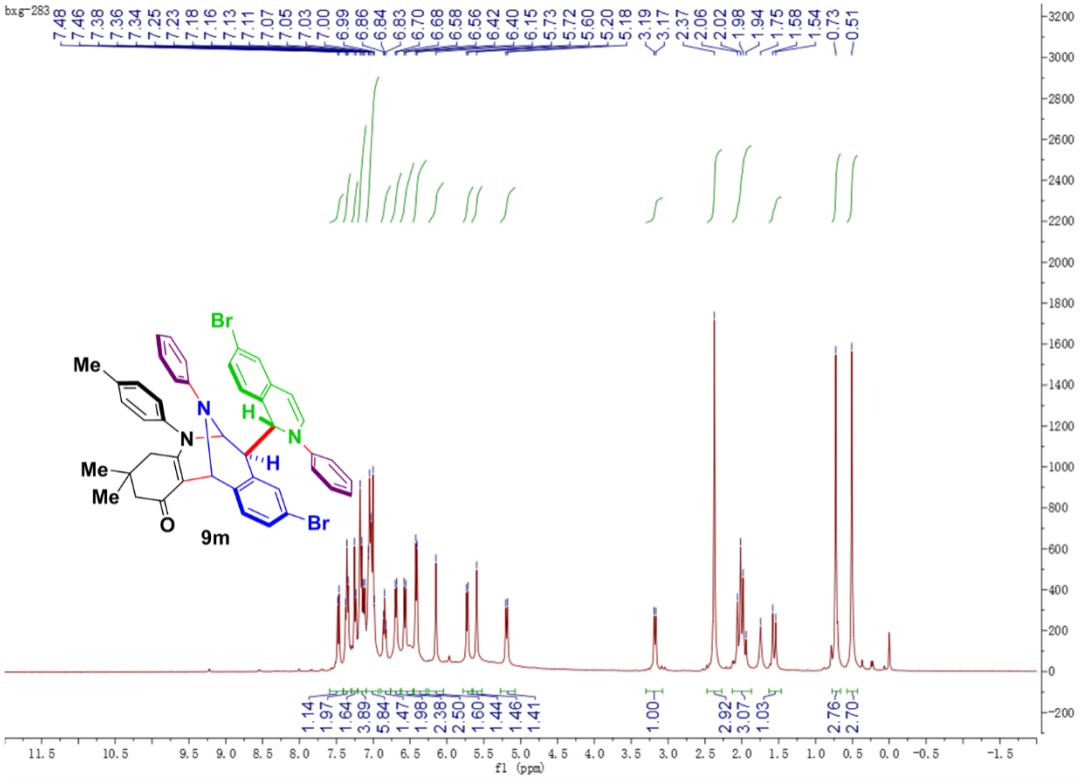
^{1}H NMR spectrum of **9l** (400 MHz, $CDCl_3$)



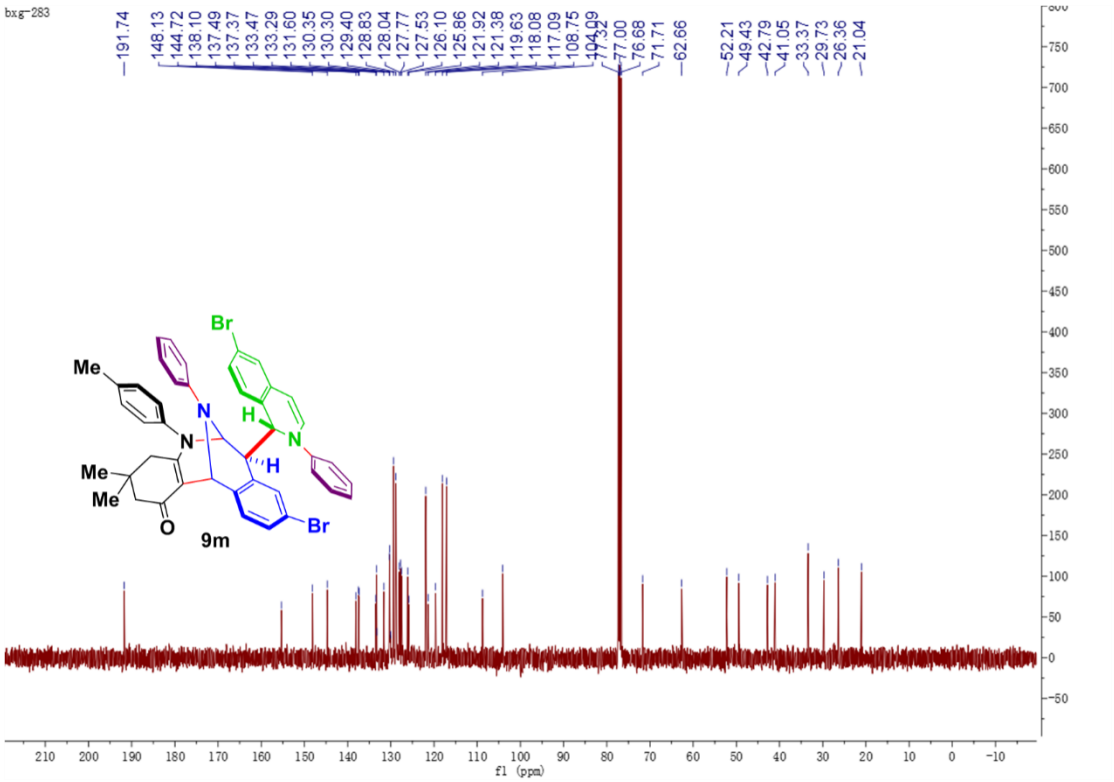
^{13}C NMR spectrum of **9l** (100 MHz, $CDCl_3$)



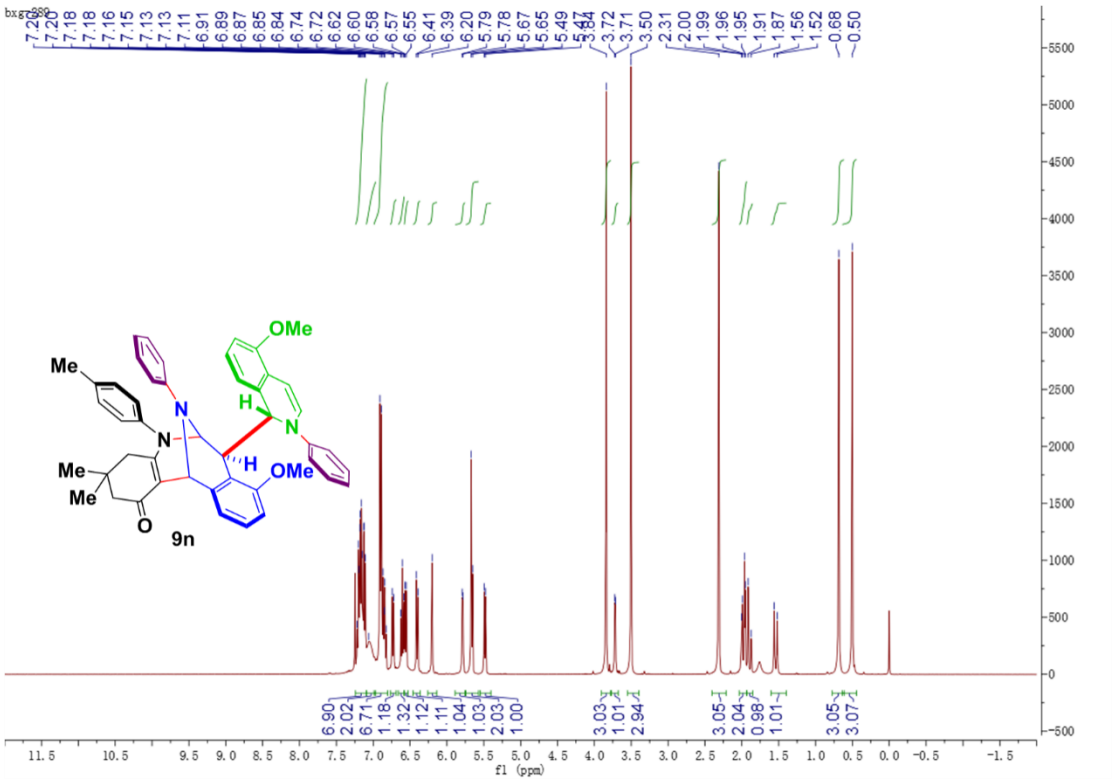
^{1}H NMR spectrum of **9m** (400 MHz, $CDCl_3$)



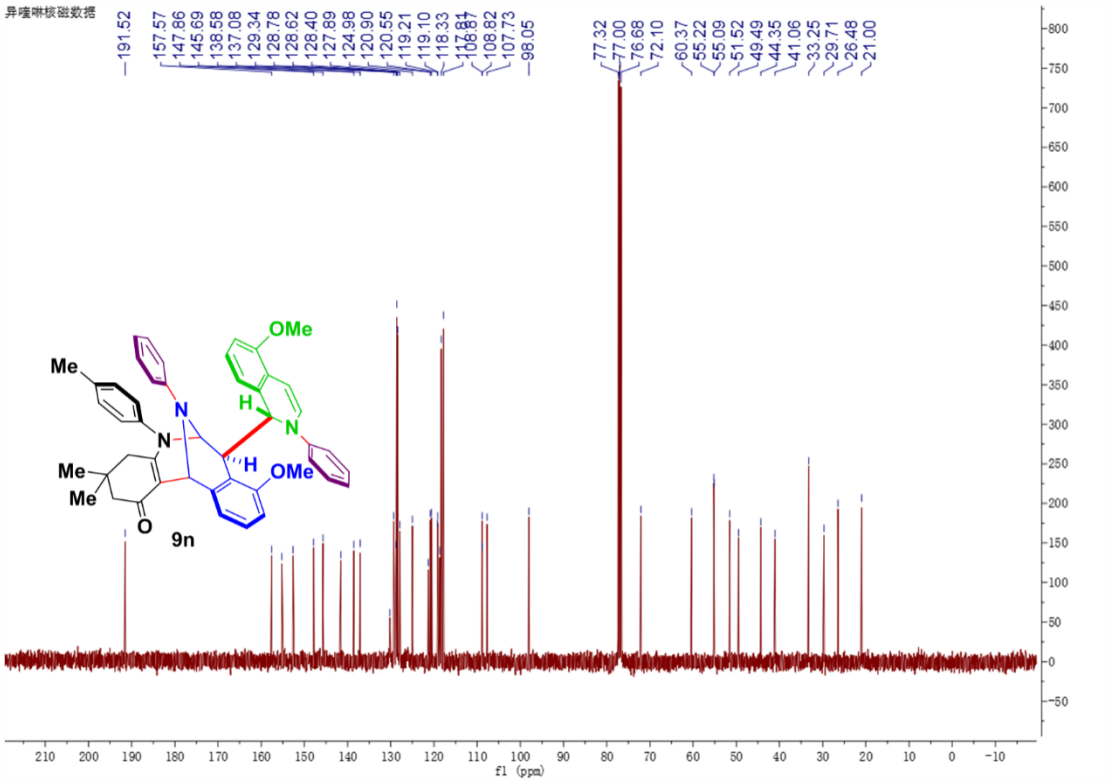
^{13}C NMR spectrum of **9m** (100 MHz, $CDCl_3$)



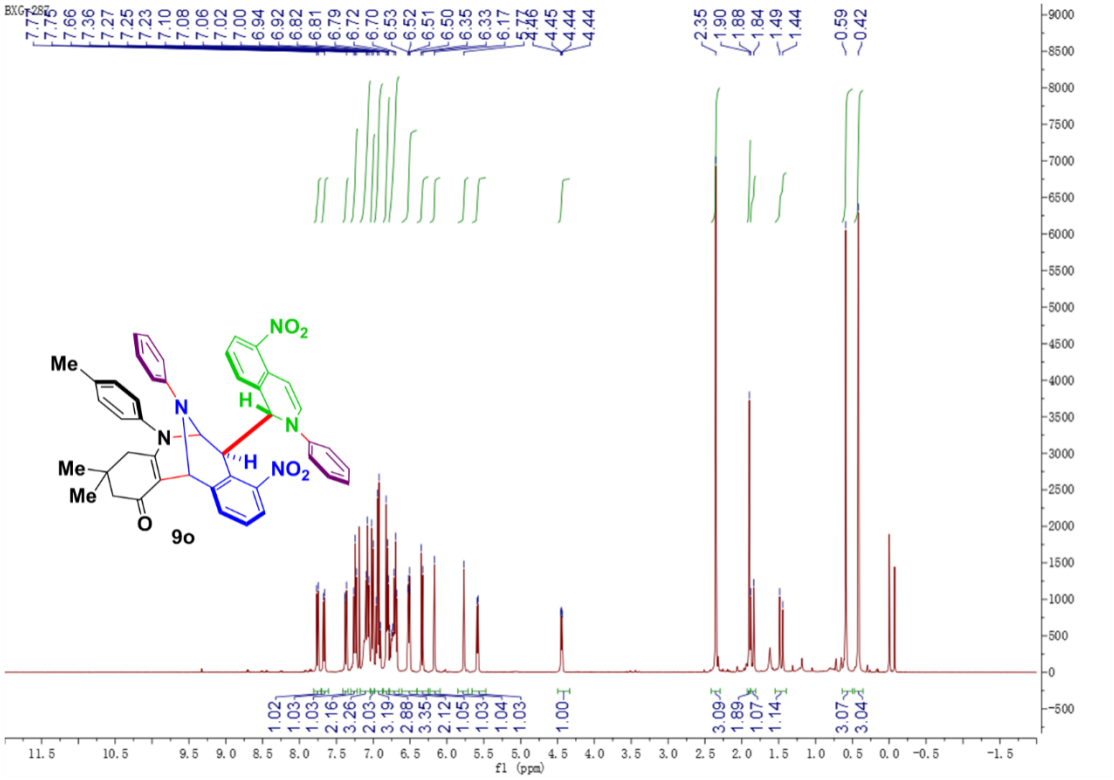
^{1}H NMR spectrum of **9n** (400 MHz, $CDCl_3$)



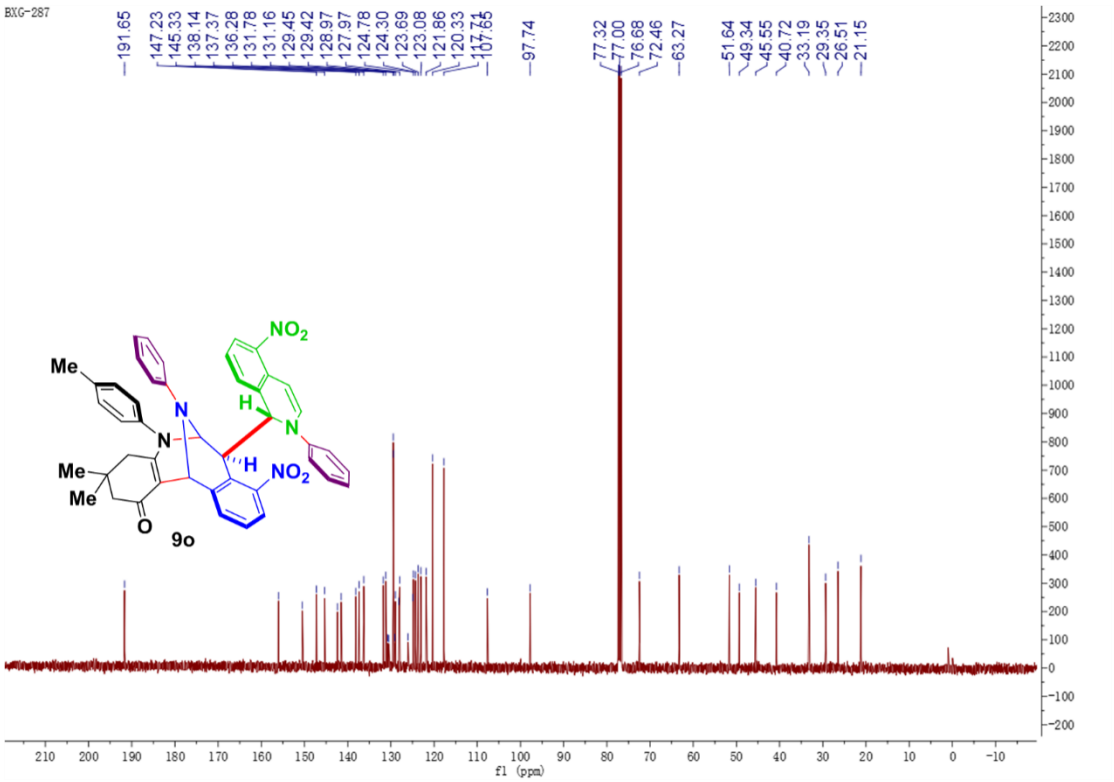
^{13}C NMR spectrum of **9n** (100 MHz, $CDCl_3$)



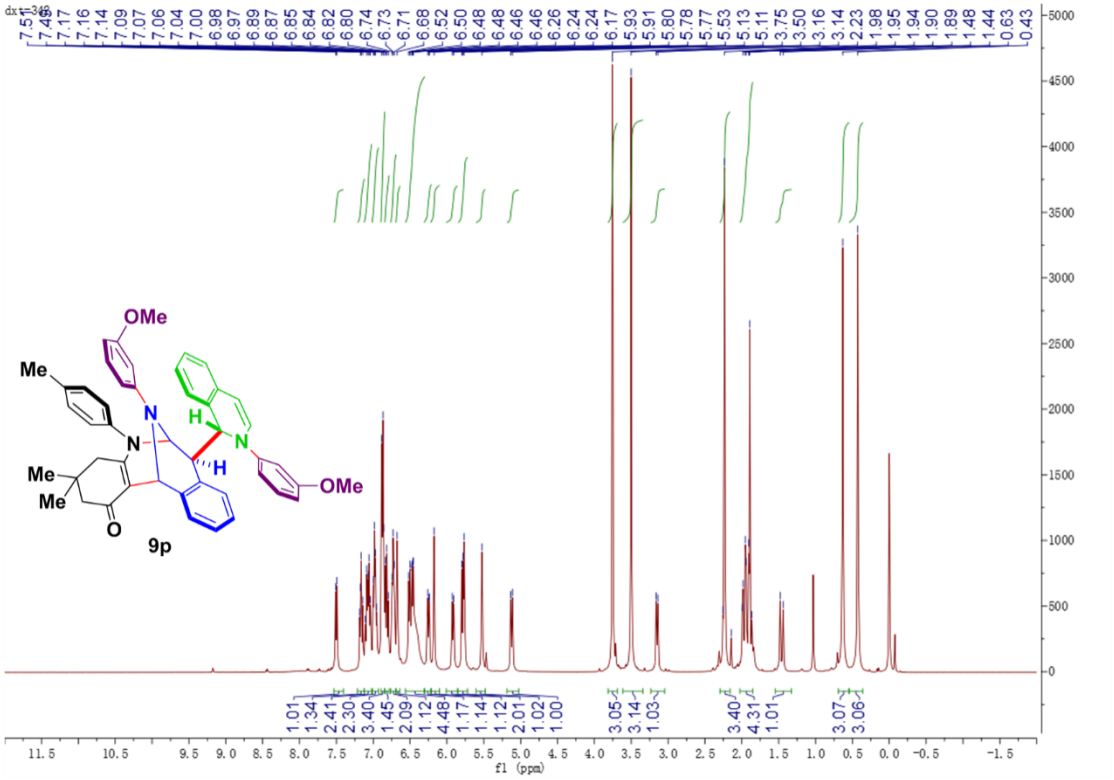
^{1}H NMR spectrum of **9o** (400 MHz, $CDCl_3$)



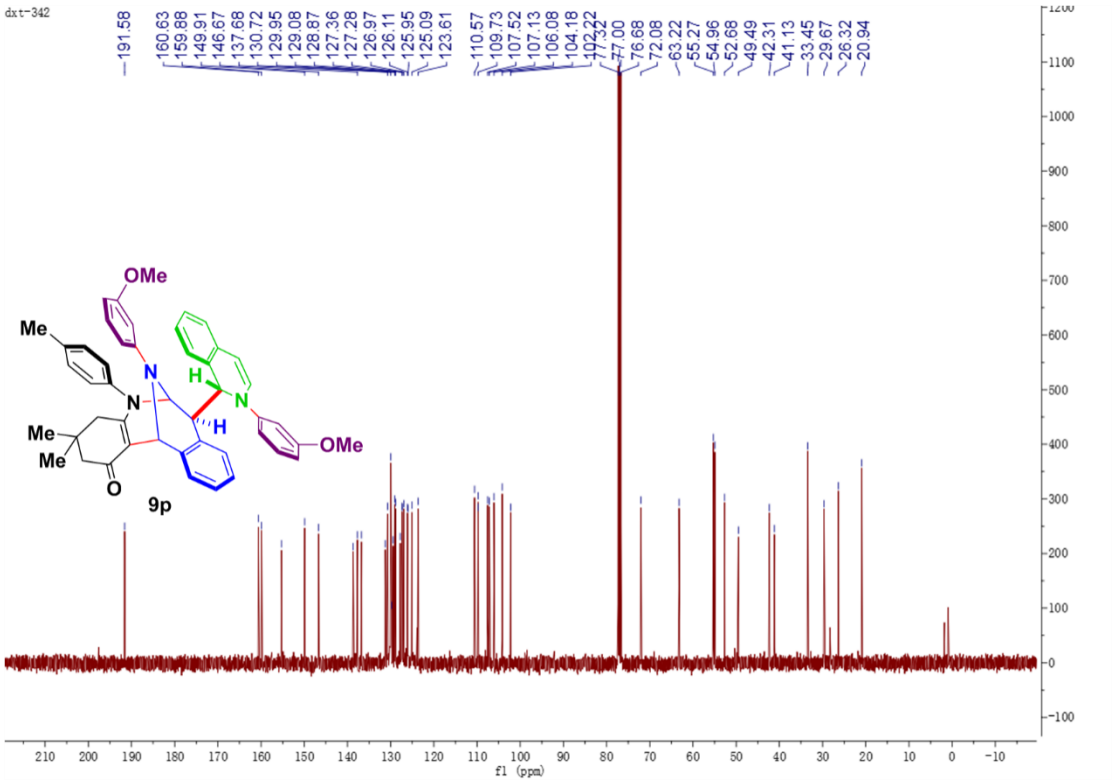
^{13}C NMR spectrum of **9o** (100 MHz, $CDCl_3$)



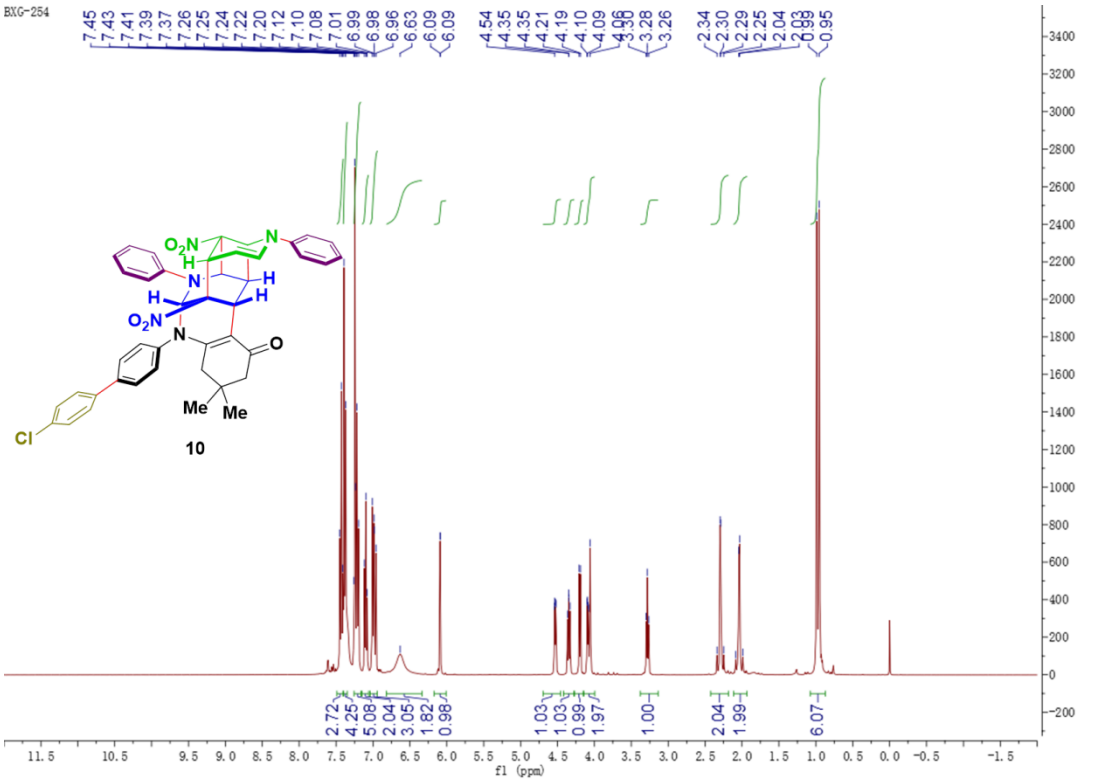
^{1}H NMR spectrum of **9p** (400 MHz, $CDCl_3$)



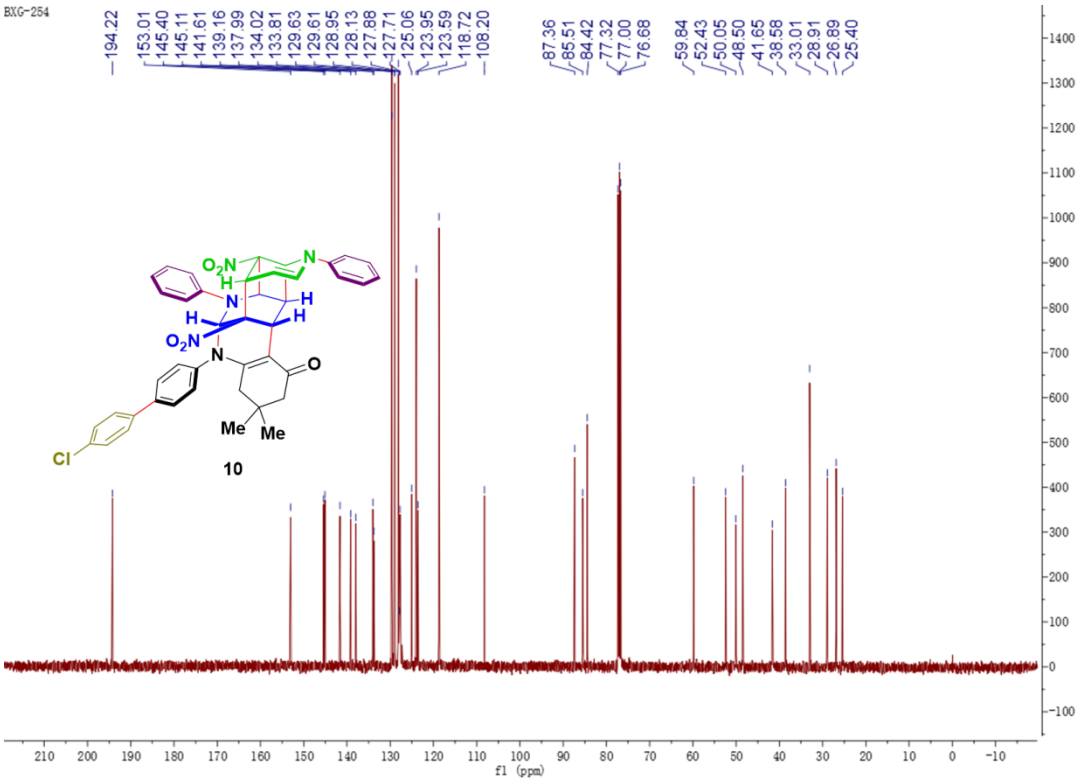
^{13}C NMR spectrum of **9p** (100 MHz, $CDCl_3$)



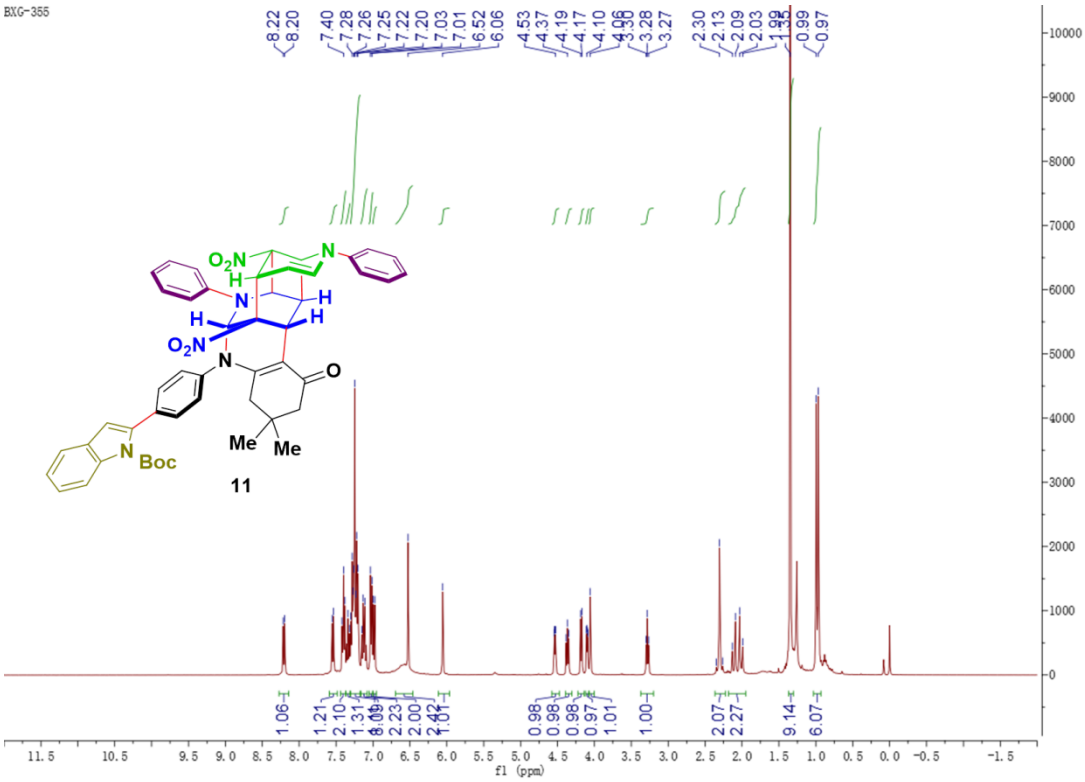
^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$)



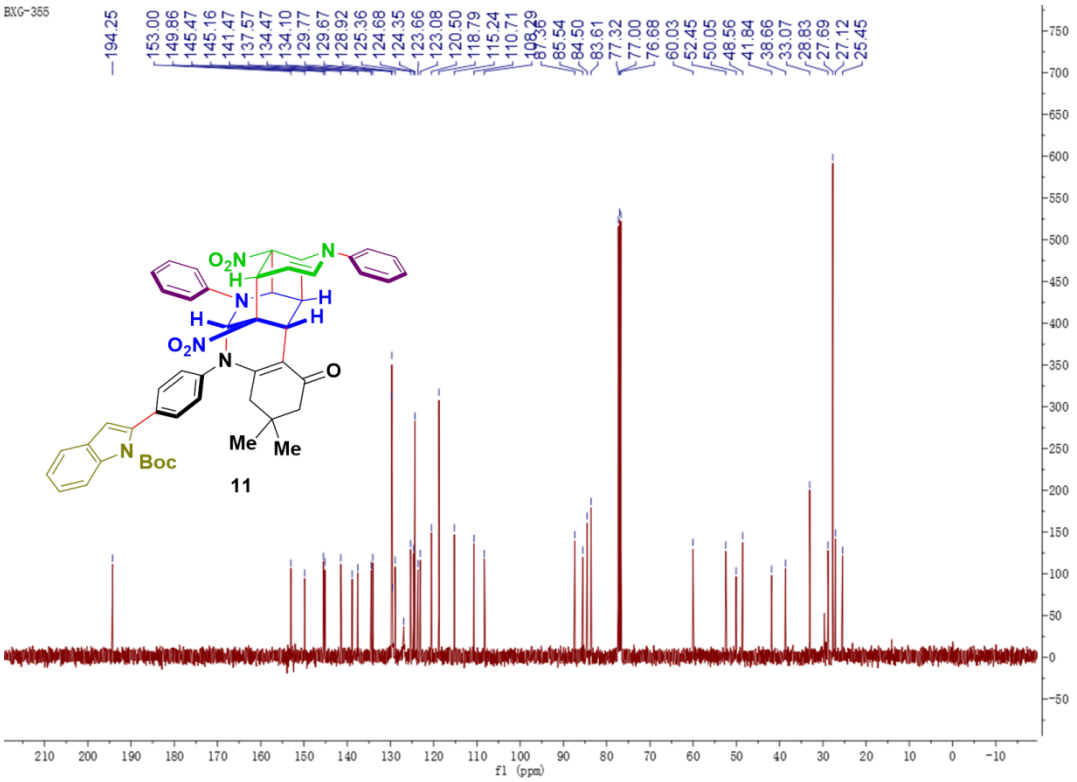
^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$)



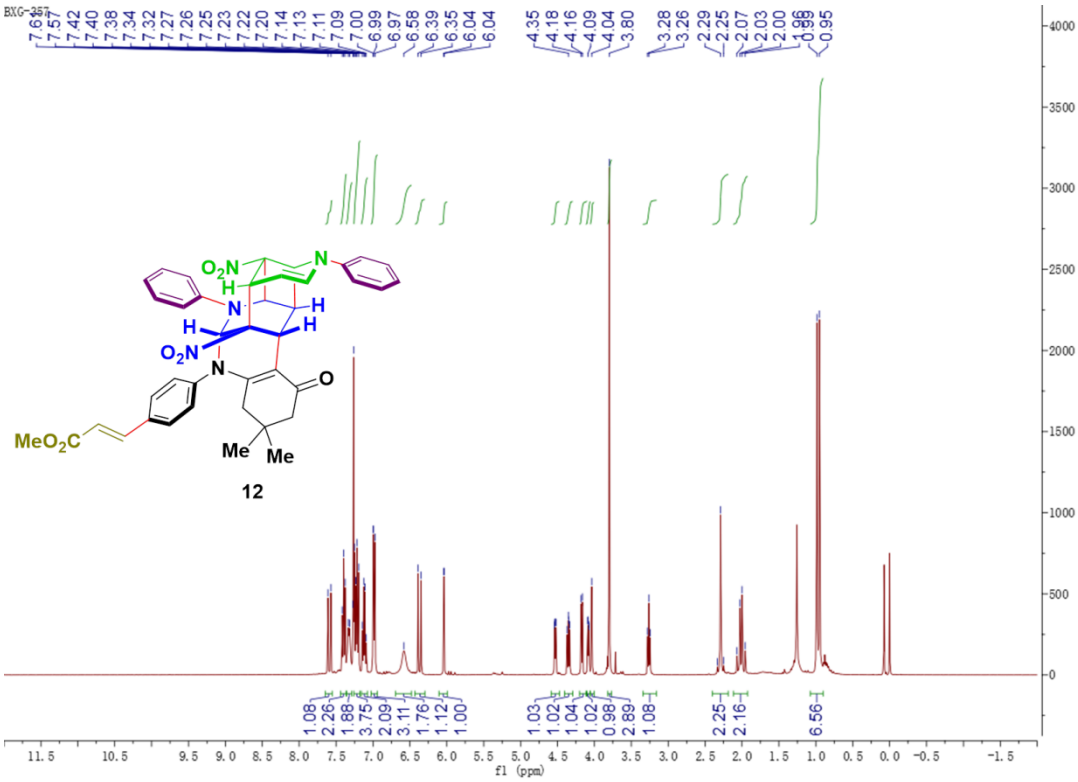
^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$)



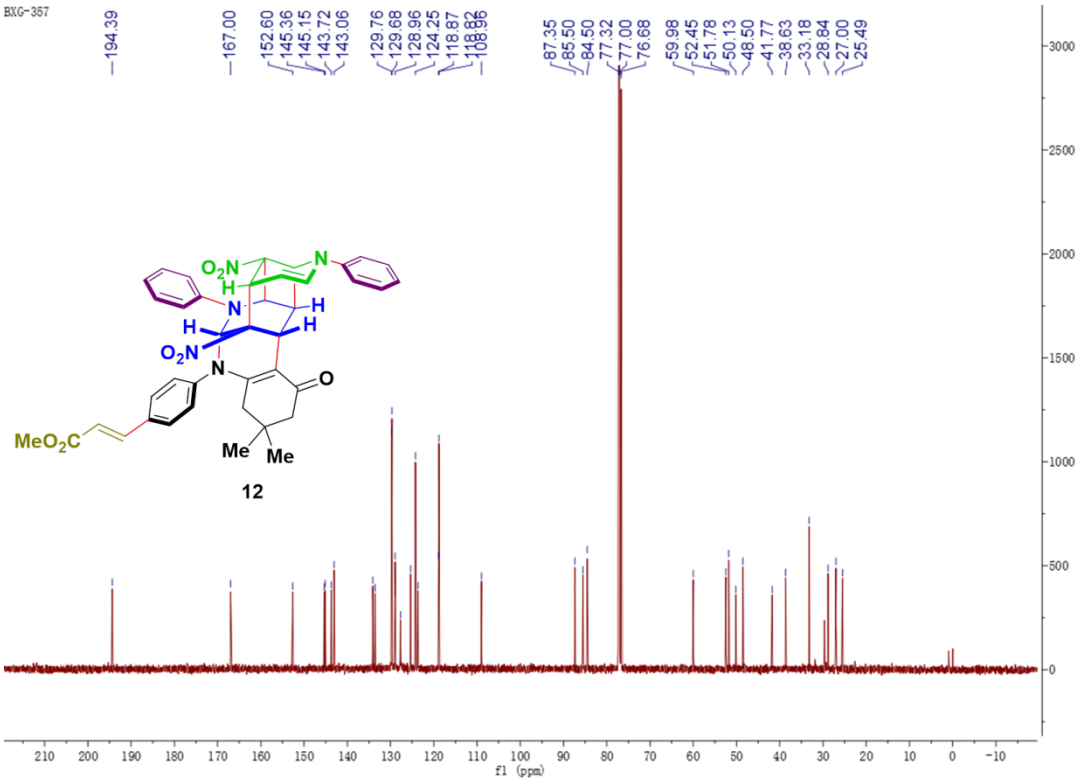
^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **12** (100 MHz, $CDCl_3$)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129.68
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87.35
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84.50
77.32
77.00
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50.13
48.50
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O2N
H
N
H
H
O2N
N
O
MeO2C
Me
Me
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2500
2000
1500
1000
500
0
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200
190
180
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150
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120
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100
90
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70
60
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40
30
20
10
0
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f1 (ppm)