Supporting Information

Diastereoselective construction of cage-like and bridged azahetereocycles through dearomative maximization of the reactive sites of azaarenes

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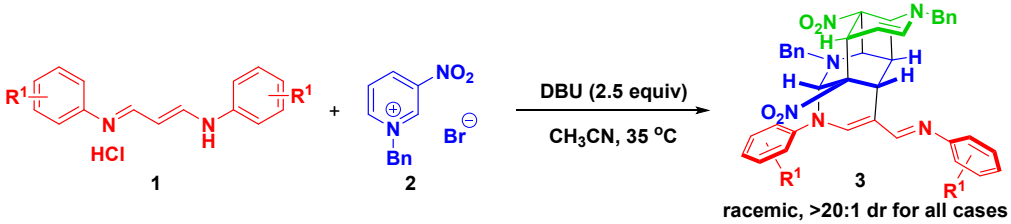
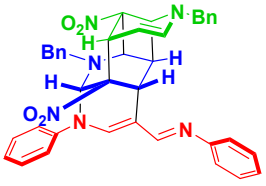
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 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 3



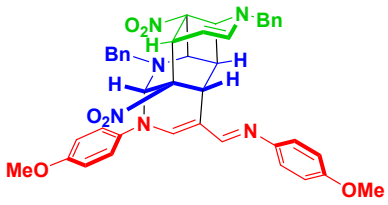
General procedure: To a 5.0 mL vial were successively added 1,5-diazapentadienium salts **1** (0.10 mmol), *N*-benyl 3-nitropyridinium salt **2** (0.22 mmol) and 0.8 mL of CH_3CN. And then, DBU (38.1 mg, 0.25 mmol) was added by syringe. The resulting mixture was stirred at 35 °C for 2 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3**. For **3a** and **3j**, the products were precipitated from the homogeneous reaction systems and only a filtration was needed to purify them.



1-(1,7-dibenzyl-10a,11-dinitro-3-phenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-

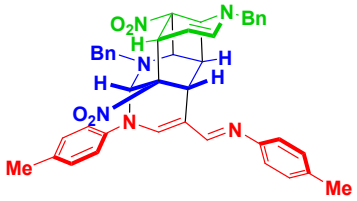
(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-phenylmethanimine (**3a**)

Yellow solid obtained by filtration of the precipitate; 48.9 mg, 75% yield; dr > 20:1; reaction time = 2 h; mp 193.8-194.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.46 (q, *J* = 4.0 Hz, 2H), 7.38 (q, *J* = 16.0 Hz, 4H), 7.23-7.16 (m, 12H), 7.05 (s, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.20 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 3.98 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.79-3.75 (m, 2H), 3.34 (d, *J* = 8.0 Hz, 1H), 2.76 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 152.8, 144.7, 139.2, 139.2, 136.8, 136.5, 130.0, 129.0, 128.7, 128.6, 128.3, 128.2, 127.8, 127.8, 125.4, 124.7, 121.5, 120.9, 113.7, 88.1, 83.2, 78.1, 58.5, 58.2, 56.2, 51.8, 45.7, 39.8, 26.0, one carbon missing in the aromatic region. IR (KBr) *v* 3444, 2862, 1634, 1582, 1233, 761 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_6O_4$ $[M+H]^+$ 651.2714, found 651.2726.



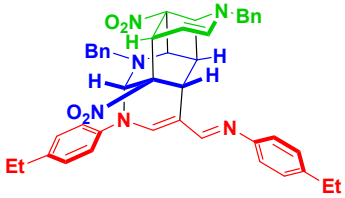
1-(1,7-dibenzyl-3-(4-methoxyphenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(4-methoxyphenyl)methanimine (**3b**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 55.4 mg, 78% yield; dr > 20:1; reaction time = 2 h; mp 169.7-170.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.46 (q, *J* = 4.0 Hz, 2H), 7.23-7.18 (m, 8H), 7.11-7.04 (m, 4H), 6.94-6.86 (m, 5H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.59 (s, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.21-4.14 (m, 3H), 3.94 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.77-3.71 (m, 2H), 3.30 (d, *J* = 8.0 Hz, 1H), 2.72 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 157.1, 156.0, 146.0, 139.4, 139.2, 138.2, 136.9, 136.6, 128.7, 128.6, 128.3, 128.2, 127.8, 127.7, 123.7, 121.8, 115.0, 114.3, 88.3, 83.3, 78.6, 58.7, 58.1, 56.1, 55.5, 51.8, 45.8, 39.8, 25.8, one carbon in the aromatic region and two carbons in the aliphatic region are missing. IR (KBr) *v* 3417, 2843, 1622, 1503, 1239, 737 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{39}N_6O_6$ $[M+H]^+$ 711.2926, found 711.2921.



1-(1,7-dibenzyl-10a,11-dinitro-3-(*p*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(*p*-tolyl)methanimine (**3c**)

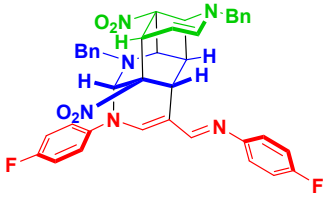
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 50.7 mg, 75% yield; dr > 20:1; reaction time = 2 h; mp 153.7-154.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.46 (q, *J* = 4.0 Hz, 2H), 7.25-7.11 (m, 12H), 7.07-7.03 (m, 4H), 6.99 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.68 (s, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 4.21-4.14 (m, 3H), 3.95 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.76-3.73 (m, 2H), 3.30 (d, *J* = 8.0 Hz, 1H), 2.73 (t, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.3, 142.4, 139.3, 139.3, 136.9, 136.6, 135.3, 134.3, 130.5, 129.7, 128.8, 128.6, 128.4, 128.3, 127.8, 127.8, 121.7, 120.8, 113.3, 88.2, 83.4, 83.3, 78.2, 58.6, 58.1, 56.1, 51.8, 45.8, 39.9, 26.0, 21.0, 20.9. IR (KBr) *v* 3418, 2857, 1633, 1584, 1228, 733 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{39}N_6O_4$ $[M+H]^+$ 679.3027, found 679.3036.



1-(1,7-dibenzyl-3-(4-ethylphenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(4-ethylphenyl)methanimine (**3d**)

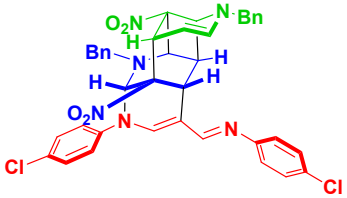
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 50.4 mg, 71% yield; dr > 20:1; reaction time = 2 h; mp 184.8-185.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.47 (q, *J* = 4.0 Hz, 2H), 7.25-7.15 (m, 12H), 7.10-7.05 (m, 4H), 7.01 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.23-4.16 (m, 3H), 3.97 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.80-3.77 (m, 2H), 3.32 (d, *J* = 4.0 Hz, 1H), 2.76 (t, *J* = 8.0 Hz, 1H), 2.72-2.61 (m, 4H), 1.29 (t, *J* = 8.0 Hz, 3H), 1.24 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 150.5, 142.5, 141.5, 140.7, 139.2, 139.2, 136.9, 136.6, 129.2, 128.7, 128.6, 128.4, 128.3, 128.2, 127.7, 127.7, 121.6, 120.8, 113.3, 88.1, 83.3, 83.2, 78.1, 58.5, 58.0, 56.1, 51.7, 45.7,

39.8, 28.4, 28.2, 25.9, 15.7, 15.4. IR (KBr) *v* 3428, 2862, 1633, 1542, 1232, 737 cm^{-1}. HRMS (ESI) calcd for $C_{43}H_{43}N_6O_4$ $[M+H]^+$ 707.3340, found 707.3336.



1-(1,7-dibenzyl-3-(4-fluorophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(4-fluorophenyl)methanimine (**3e**)

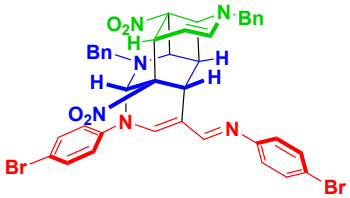
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 56.9 mg, 83% yield; dr > 20:1; reaction time = 2 h; mp 181.2-182.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.46 (q, *J* = 4.0 Hz, 2H), 7.23-7.15 (m, 8H), 7.12-7.02 (m, 8H), 6.95 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 1H), 4.46 (d, *J* = 16.0 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 4.24-4.15 (m, 3H), 3.95 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.79-3.72 (m, 2H), 3.34 (d, *J* = 4.0 Hz, 1H), 2.73 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, *J* = 241.0 Hz, 1C), 160.3 (d, *J* = 245.0 Hz, 1C), 157.3, 148.8 (d, *J* = 5.0 Hz, 1C), 140.9, 140.9, 139.5, 139.3, 136.7, 136.5, 128.7, 128.6, 128.2, 128.1, 127.8, 123.7 (d, *J* = 9.0 Hz, 1C), 122.1 (d, *J* = 8.0 Hz, 1C), 116.7 (d, *J* = 23.0 Hz, 1C), 115.7 (d, *J* = 22.0 Hz, 1C), 113.5, 88.1, 83.2, 83.1, 78.6, 58.8, 58.3, 56.2, 51.9, 45.8, 39.8, 25.8. ^{19}F NMR (375 MHz, $CDCl_3$) δ -116.0, -118.9. IR (KBr) *v* 3430, 2864, 1628, 1503, 1228, 734 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}F_2N_6O_4$ $[M+H]^+$ 687.2526, found 687.2528.



N-(4-chlorophenyl)-1-(1,7-dibenzyl-3-(4-chlorophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**3f**)

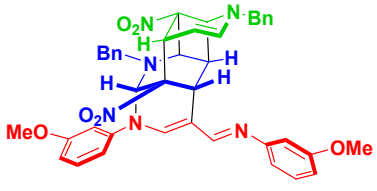
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 58.1 mg, 81% yield; dr > 20:1; reaction time = 2 h; mp 180.1-181.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.45 (q, *J* = 4.0 Hz, 2H), 7.35-7.29 (m, 4H), 7.22-7.11 (m, 8H), 7.07-6.98 (m, 5H), 6.52 (d, *J* = 8.0 Hz, 1H), 5.68 (s, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.34 (d, *J* = 16.0 Hz, 1H), 4.23-4.13 (m,

3H), 3.94 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.78-3.73 (m, 2H), 3.34 (d, $J = 4.0$ Hz, 1H), 2.71 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 151.2, 143.0, 139.3, 139.2, 136.6, 136.4, 130.9, 130.1, 130.0, 129.1, 128.7, 128.7, 128.2, 127.8, 122.7, 122.2, 114.0, 88.0, 83.2, 83.0, 78.2, 58.8, 58.3, 56.3, 51.9, 45.7, 39.8, 25.9, two carbons missing in the aromatic region. IR (KBr) *v* 3428, 64, 1628, 1503, 1229, 740 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}Cl_2N_6O_4$ $[M+H]^+$ 719.1935, found 719.1932.



N-(4-bromophenyl)-1-(1,7-dibenzyl-3-(4-bromophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**3g**)

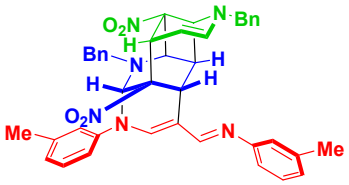
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 63.3 mg, 78% yield; dr > 20:1; reaction time = 2 h; mp 164.9-166.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.45 (q, $J = 4.0$ Hz, 2H), 7.35-7.30 (m, 4H), 7.22-7.18 (m, 6H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.06-6.98 (m, 5H), 6.52 (d, $J = 8.0$ Hz, 1H), 5.68 (s, 1H), 4.45 (d, $J = 16.0$ Hz, 1H), 4.34 (d, $J = 16.0$ Hz, 1H), 4.23-4.14 (m, 3H), 3.94 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.78-3.74 (m, 2H), 3.34 (d, $J = 4.0$ Hz, 1H), 2.71 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 151.6, 143.5, 139.3, 139.1, 136.6, 136.4, 133.0, 132.0, 128.7, 128.7, 128.2, 127.9, 122.9, 122.6, 118.6, 117.9, 114.1, 88.0, 83.2, 83.0, 78.1, 58.8, 58.3, 56.3, 51.9, 45.7, 39.8, 25.9, two carbons missing in the aromatic region. IR (KBr) *v* 3432, 2857, 1633, 1486, 1227, 732 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}Br_2N_6O_4$ $[M+H]^+$ 807.0925, found 807.0926.



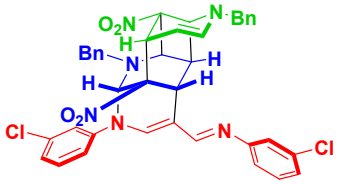
1-(1,7-dibenzyl-3-(3-methoxyphenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(3-methoxyphenyl)methanimine (**3h**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 53.5 mg,

75% yield; dr > 20:1; reaction time = 2 h; mp 182.0-183.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.41 (q, *J* = 4.0 Hz, 2H), 7.24-7.14 (m, 8H), 7.04-6.99 (m, 3H), 6.77-6.62 (m, 6H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.18-4.10 (m, 3H), 3.91 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.80 (s, 3H), 3.77-3.71 (m, 5H), 3.29 (d, *J* = 8.0 Hz, 1H), 2.69 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.3, 157.7, 154.3, 145.8, 139.3, 136.8, 136.5, 130.7, 129.7, 128.7, 128.6, 128.3, 128.2, 127.8, 127.7, 113.6, 113.6, 113.3, 110.6, 110.6, 107.9, 107.5, 106.5, 88.1, 83.2, 83.2, 77.9, 58.5, 58.2, 56.2, 55.3, 55.3, 51.8, 45.7, 39.8, 26.0. IR (KBr) *v* 3439, 2843, 1633, 1581, 1150, 735 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{39}N_6O_6$ $[M+H]^+$ 711.2926, found 711.2926.



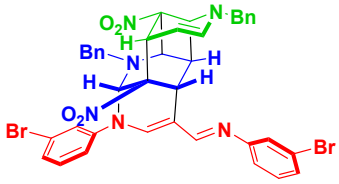
1-(1,7-dibenzyl-10a,11-dinitro-3-(*m*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(*m*-tolyl)methanimine (**3i**)
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 51.9 mg, 77% yield; dr > 20:1; reaction time = 2 h; mp 169.1-170.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.43 (q, *J* = 4.0 Hz, 2H), 7.22-7.17 (m, 8H), 7.02-6.91 (m, 9H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.43 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.19-4.12 (m, 3H), 3.94 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.75-3.71 (m, 2H), 3.30 (d, *J* = 8.0 Hz, 1H), 2.72 (t, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 152.9, 144.6, 139.9, 139.2, 139.2, 138.7, 136.9, 136.6, 129.7, 128.8, 128.7, 128.5, 128.3, 128.2, 127.7, 127.7, 126.2, 125.4, 122.1, 121.6, 118.5, 118.0, 113.5, 88.1, 83.3, 78.0, 58.5, 58.1, 56.3, 51.8, 45.7, 39.8, 26.0, 21.4, two carbons missing in the aliphatic region. IR (KBr) *v* 3435, 2857, 1635, 1578, 1224, 740 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{39}N_6O_4$ $[M+H]^+$ 679.3027, found 679.3023.



N-(3-chlorophenyl)-1-(1,7-dibenzyl-3-(3-chlorophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-

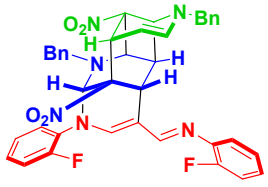
d][1,3]diazocin-5-yl)methanimine (**3j**)

Yellow solid obtained by filtration of the precipitate; 47.0 mg, 65% yield; dr > 20:1; reaction time = 2 h; mp 185.4-186.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.42 (q, *J* = 4.0 Hz, 2H), 7.30-6.99 (m, 17H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.42 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.22-4.10 (m, 3H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.78-3.75 (m, 2H), 3.35 (d, *J* = 8.0 Hz, 1H), 2.70 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.0, 145.4, 139.3, 139.1, 136.5, 136.4, 135.6, 134.6, 130.9, 130.0, 128.7, 128.6, 128.1, 127.8, 125.4, 124.7, 121.4, 120.9, 119.5, 119.1, 114.3, 87.9, 83.2, 83.0, 78.0, 58.8, 58.3, 56.5, 51.8, 45.6, 39.8, 25.9, two carbons missing in the aromatic region. IR (KBr) *v* 3417, 2857, 1636, 1576, 1226, 753 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}Cl_2N_6O_4$ $[M+H]^+$ 719.1935, found 719.1929.



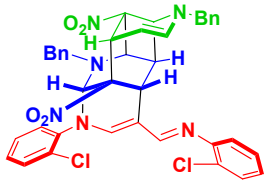
N-(3-bromophenyl)-1-(1,7-dibenzyl-3-(3-bromophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**3k**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1) 68.3 mg, 85% yield; dr > 20:1; reaction time = 2 h; mp 188.3-189.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.42 (q, *J* = 4.0 Hz, 2H), 7.33-7.16 (m, 12H), 7.13-7.10 (m, 1H), 7.06-7.03 (m, 1H), 7.00-6.98 (m, 3H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.69 (s, 1H), 4.42 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.21-4.10 (m, 3H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.78-3.74 (m, 2H), 3.35 (d, *J* = 8.0 Hz, 1H), 2.69 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.1, 145.5, 139.3, 139.2, 136.5, 136.4, 131.1, 130.3, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.9, 127.6, 124.3, 123.7, 123.5, 122.7, 120.1, 119.6, 114.3, 87.9, 83.2, 83.0, 78.0, 58.9, 58.3, 56.5, 51.9, 45.6, 39.7, 25.9. IR (KBr) *v* 3434, 2857, 1636, 1573, 1225, 749 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}Br_2N_6O_4$ $[M+H]^+$ 807.0925, found 807.0926.



1-(1,7-dibenzyl-3-(2-fluorophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(2-fluorophenyl)methanimine (**3l**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 40.6 mg, 59% yield; dr > 20:1; reaction time = 2 h; mp 173.7-174.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.40 (q, J = 4.0 Hz, 2H), 7.21-7.06 (m, 16H), 6.91 (s, 1H), 6.50 (d, J = 8.0 Hz, 1H), 5.55 (s, 1H), 4.46 (d, J = 16.0 Hz, 1H), 4.34 (d, J = 16.0 Hz, 1H), 4.19 (d, J = 8.0 Hz, 1H), 4.12 (t, J = 8.0 Hz, 2H), 3.94 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.77 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.70 (d, J = 8.0 Hz, 1H), 3.32 (d, J = 8.0 Hz, 1H), 2.81 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 156.4 (d, J = 248.0 Hz, 1C), 155.7 (d, J = 247.0 Hz, 1C), 141.3, 141.2, 140.7, 140.6, 139.4, 136.5 (d, J = 15.0 Hz, 1C), 132.2 (d, J = 11.0 Hz, 1C), 128.6, 128.6, 128.5, 128.2, 127.9 (d, J = 8.0 Hz, 1C), 127.7 (d, J = 10.0 Hz, 1C), 126.0, 125.4 (d, J = 4.0 Hz, 1C), 125.4, 124.4 (d, J = 4.0 Hz, 1C), 121.4 (d, J = 2.0 Hz, 1C), 117.1 (d, J = 20.0 Hz, 1C), 116.0 (d, J = 20.0 Hz, 1C), 113.3, 87.9, 83.6, 82.4, 78.5, 59.0, 57.4, 55.9, 51.2, 45.5, 39.6, 25.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -123.1, -126.7. IR (KBr) v 3416, 2860, 1631, 1584, 1236, 750 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}F_2N_6O_4$ $[M+H]^+$ 687.2526, found 687.2519.

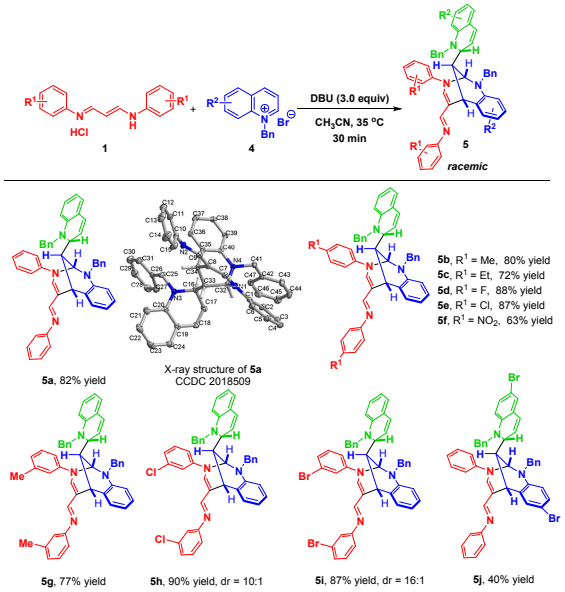


N-(2-chlorophenyl)-1-(1,7-dibenzyl-3-(2-chlorophenyl)-10a,11-dinitro-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**3m**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 40.5 mg, 56% yield; dr > 20:1; reaction time = 2 h; mp 180.1-180.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.46-7.40 (m, 2H), 7.33-7.19 (m, 12H), 7.11-7.05 (m, 3H), 7.00 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.90 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 5.50 (s, 1H), 4.48 (d, J = 16.0 Hz, 1H), 4.35 (d, J = 16.0 Hz, 1H), 4.14 (d, J = 8.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 2H), 3.98 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.88 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.65 (d, J = 8.0 Hz, 1H), 3.36 (d, J = 8.0 Hz, 1H), 2.97 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 150.2, 141.8, 141.5, 139.3, 136.8, 136.0, 131.2, 130.0, 129.7,

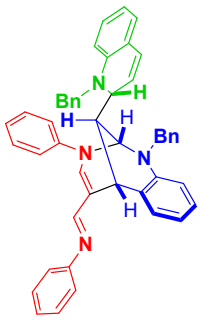
128.7, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.6, 125.2, 119.9, 112.6, 88.1, 83.7, 81.8, 78.3, 59.3, 56.9, 55.5, 51.2, 45.7, 39.3, 25.7. IR (KBr) *v* 3451, 2857, 1635, 1542, 1228, 749 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{33}Cl_2N_6O_4$ $[M+H]^+$ 719.1935, found 719.1934.

3. Experimental data for the formation of 5



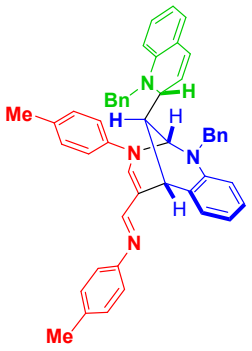
Scheme S1 Diastereoselective dearomatization of quinolinium salts.

General procedure： To a 5.0 mL vial were successively added 1,5-diazapentadienium salts **1** (0.20 mmol), *N*-benyl quinilinium salts **4** (0.44 mmol) and 0.8 mL of CH_3CN. And then, DBU (91.4 mg, 0.60 mmol) was added by syringe. The resulting mixture was stirred at 35 °C for 30 min. During the reaction process, a large amount of precipitate is generated. So, only a simple filtration was needed to obtain the pure products **5**. The filtrate contained a small amount of products, which can be purified by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1). (*Note: compounds **5** were not very stable in solution, but they were very stable in solid state.*)



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-phenyl-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-phenylmethanimine (**5a**)

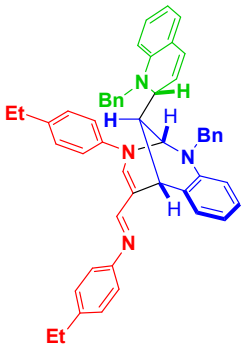
White solid obtained by filtration of the precipitate; 108.2 mg, 82% yield; dr > 20:1; reaction time = 30 min; mp 188.4-188.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.30 (q, J = 8.0 Hz, 4H), 7.20-6.91 (m, 20H), 6.77 (t, J = 8.0 Hz, 2H), 6.64-6.59 (m, 2H), 6.47 (d, J = 8.0 Hz, 1H), 5.45 (s, 1H), 5.26 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.07 (d, J = 16.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 2H), 4.29 (d, J = 16.0 Hz, 1H), 4.14 (d, J = 16.0 Hz, 1H), 3.79 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.39 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 153.9, 146.2, 143.1, 142.4, 141.6, 138.9, 138.4, 130.0, 129.8, 128.9, 128.8, 128.7, 128.2, 127.3, 127.2, 127.1, 126.7, 126.5, 124.6, 124.3, 124.0, 123.1, 121.3, 120.9, 120.7, 119.7, 117.9, 116.9, 114.7, 110.4, 68.7, 56.1, 56.0, 52.7, 40.7, 30.9, two carbons missing in the aromatic region. IR (KBr) ν 3443, 3029, 1611, 1582, 1491, 1165, 741 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{41}N_4$ $[M+H]^+$ 661.3326, found 661.3345.



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(*p*-tolyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(*p*-tolyl)methanimine (**5b**)

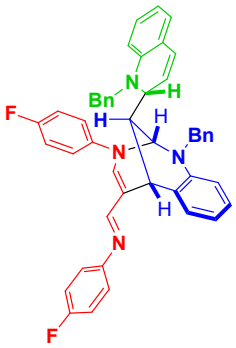
Light yellow solid obtained by filtration of the precipitate; 109.8 mg, 80% yield; dr > 20:1; reaction time = 30 min; mp 177.6-178.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 4.0 Hz, 1H), 7.19-6.99 (m, 15H), 6.92 (t, J = 4.0 Hz, 6H), 6.85-6.74 (m, 3H), 6.63-6.58 (m, 2H), 6.45 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.38 (s, 1H), 5.24 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.07 (d, J = 16.0 Hz, 1H), 4.55 (d, J = 12.0 Hz, 2H), 4.28 (d, J = 16.0 Hz, 1H), 4.15 (d, J = 16.0 Hz, 1H), 3.79 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.38-2.31 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 151.4, 143.9, 143.2, 142.4, 141.7, 139.0, 138.5, 134.0, 133.4, 130.3, 130.0, 129.5, 128.8, 128.6, 128.2, 127.2, 127.1, 126.7, 126.6, 126.5, 124.7, 123.1, 121.3, 120.9, 120.7, 120.4, 120.4, 119.3, 117.8, 116.8, 114.7, 110.4, 68.9, 56.1, 55.9, 52.8, 40.8, 30.8, 20.9, 20.8. IR (KBr) ν 3439, 3025, 2860, 1613, 1580, 1502, 1161, 740 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{45}N_4$ $[M+H]^+$ 689.3639,

found 689.3624.



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(4-ethylphenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(4-ethylphenyl)methanimine (**5c**)

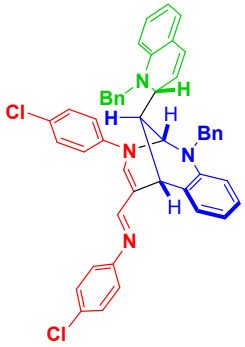
Light yellow solid obtained by filtration of the precipitate; 103.3 mg, 72% yield; dr > 20:1; reaction time = 30 min; mp 161.6-162.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 4.0 Hz, 1H), 7.77 (s, 1H), 7.23-7.11 (m, 10H), 7.06-6.87 (m, 12H), 6.76 (q, J = 8.0 Hz, 2H), 6.61 (q, J = 8.0 Hz, 2H), 6.46 (d, J = 12.0 Hz, 1H), 5.39 (s, 1H), 5.25 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.08 (d, J = 16.0 Hz, 1H), 4.56 (d, J = 16.0 Hz, 2H), 4.29 (d, J = 16.0 Hz, 1H), 4.16 (d, J = 16.0 Hz, 1H), 3.79 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.66-2.59 (m, 4H), 2.38 (d, J = 8.0 Hz, 1H), 1.25-1.21 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 151.6, 144.0, 143.2, 142.4, 141.7, 140.4, 139.9, 139.0, 138.5, 130.0, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.2, 127.1, 126.7, 126.6, 126.5, 124.8, 123.1, 121.4, 121.0, 120.9, 120.7, 119.3, 117.8, 116.8, 114.7, 110.5, 68.9, 56.1, 56.0, 52.8, 40.8, 30.8, 28.4, 28.2, 15.8, 15.6. IR (KBr) v 3441, 2962, 1613, 1583, 1501, 1165, 743 cm^{-1}. HRMS (ESI) calcd for $C_{51}H_{49}N_4$ $[M+H]^+$ 717.3952, found 717.3972.



1-(1-benzyl-11-(-1-benzyl-1,2-dihydroquinolin-2-yl)-3-(4-fluorophenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(4-fluorophenyl)methanimine (**5d**)

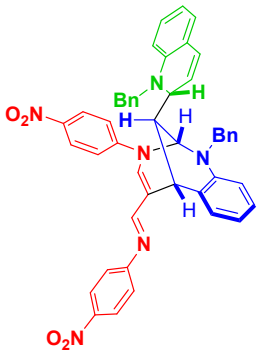
White solid obtained by filtration of the precipitate; 123.0 mg, 88% yield; dr > 20:1; reaction time

= 30 min; mp 181.8-183.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.72 (s, 1H), 7.21-7.12 (m, 6H), 7.07-6.90 (m, 15H), 6.78 (t, *J* = 8.0 Hz, 3H), 6.62 (q, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.33 (s, 1H), 5.24 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.54 (t, *J* = 16.0 Hz, 2H), 4.27 (d, *J* = 16.0 Hz, 1H), 4.14 (d, *J* = 16.0 Hz, 1H), 3.79 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.37 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, *J* = 241.0 Hz, 1C), 159.7 (d, *J* = 244.0 Hz, 1C), 158.3, 149.9 (d, *J* = 3.0 Hz, 1C), 143.1, 142.5 (d, *J* = 3.0 Hz, 1C), 142.2, 141.9, 138.8, 138.2, 129.9, 128.8, 128.7, 128.2, 127.3 (d, *J* = 3.0 Hz, 1C), 127.2 (d, *J* = 4.0 Hz, 1C), 127.1, 126.8, 126.4, 124.5, 123.1, 123.0, 122.9, 122.0, 121.9, 121.2, 119.5, 118.0, 116.9, 116.5 (d, *J* = 23.0 Hz, 1C), 115.4 (d, *J* = 22.0 Hz, 1C), 114.7, 110.6, 69.7, 56.1, 55.8, 53.0, 40.7, 30.7. IR (KBr) *v* 3440, 2948, 1612, 1499, 1161, 744 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}F_2N_4$ $[M+H]^+$ 697.3137, found 697.3125.



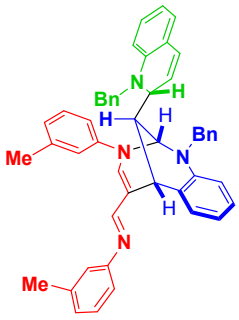
1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(4-chlorophenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(4-chlorophenyl)methanimine (**5e**)

Light yellow solid obtained by filtration of the precipitate; 127.5 mg, 87% yield; dr > 20:1; reaction time = 30 min; mp 187.4-188.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.25-7.13 (m, 9H), 7.03-6.78 (m, 15H), 6.92 (s, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 1H), 5.25 (s, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.55 (d, *J* = 16.0 Hz, 2H), 4.26 (d, *J* = 16.0 Hz, 1H), 4.18 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 1H), 2.35 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 152.2, 144.5, 143.1, 142.2, 141.4, 141.1, 138.8, 138.1, 129.9, 129.8, 129.6, 129.4, 128.9, 128.7, 128.4, 128.2, 127.3, 127.1, 126.8, 126.6, 126.4, 124.2, 123.1, 122.1, 121.8, 121.4, 121.0, 120.2, 118.0, 117.0, 114.8, 110.6, 69.2, 56.1, 55.8, 53.0, 40.6, 30.8. IR (KBr) *v* 3446, 3033, 1609, 1570, 1490, 1165, 741 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Cl_2N_4$ $[M+H]^+$ 729.2546, found 729.2539.



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(4-nitrophenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(4-nitrophenyl)methanimine (**5f**)

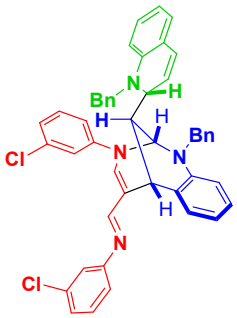
Yellow solid obtained by filtration of the precipitate; 94.9 mg, 63% yield; dr > 20:1; reaction time = 30 min; mp 153.7-154.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.84 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.24-7.02 (m, 14H), 6.93 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 4H), 6.84 (q, J = 8.0 Hz, 2H), 6.67 (t, J = 8.0 Hz, 2H), 6.55 (d, J = 8.0 Hz, 1H), 5.62 (s, 1H), 5.35 (dd, J_1 = J_2 = 8.0 Hz, 1H), 5.05 (d, J = 16.0 Hz, 1H), 4.58 (t, J = 16.0 Hz, 2H), 4.34 (d, J = 16.0 Hz, 1H), 4.26 (d, J = 16.0 Hz, 1H), 3.79 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.38 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.0, 149.9, 144.5, 143.0, 142.9, 142.0, 140.5, 138.5, 137.6, 129.9, 129.0, 128.9, 128.3, 127.9, 127.7, 127.6, 127.5, 127.0, 127.0, 126.3, 125.8, 125.0, 124.9, 123.1, 122.9, 121.3, 120.5, 118.5, 118.3, 117.3, 114.9, 110.7, 68.8, 56.3, 55.7, 53.0, 40.4, 31.0. IR (KBr) v 3442, 3030, 1563, 1500, 1334, 1166, 744 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}N_6O_4$ $[M+H]^+$ 773.2847, found 773.2844.



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(*m*-tolyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(*m*-tolyl)methanimine (**5g**)

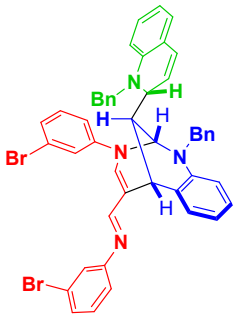
White solid obtained by filtration of the precipitate; 105.8 mg, 77% yield; dr > 20:1; reaction time = 30 min; mp 174.7-175.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 4.0 Hz, 1H), 7.78 (s, 1H), 7.22-7.13 (m, 8H), 7.06-6.89 (m, 12H), 6.85-6.75 (m, 4H), 6.64-6.60 (m, 2H), 6.47 (d, J =

8.0 Hz, 1H), 5.42 (s, 1H), 5.26 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 5.07 (d, $J = 16.0$ Hz, 1H), 4.56 (d, $J = 8.0$ Hz, 2H), 4.28 (d, $J = 16.0$ Hz, 1H), 4.18 (d, $J = 16.0$ Hz, 1H), 3.79 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.39-2.34 (m, 4H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.0, 146.1, 143.2, 142.4, 141.6, 1397, 138.9, 138.6, 138.5, 130.0, 129.5, 128.8, 128.7, 128.6, 128.2, 127.2, 127.1, 127.1, 126.7, 126.6, 125.0, 124.7, 124.6, 123.1, 121.7, 121.4, 121.3, 119.6, 117.8, 117.8, 117.6, 116.8, 114.7, 110.4, 68.7, 56.1, 56.0, 52.8, 40.7, 30.9, 21.5, 21.4, two carbons missing in the aromatic region. IR (KBr) ν 3442, 3033, 1580, 1491, 1157, 741 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{45}N_4$ $[M+H]^+$ 689.3639, found 689.3643.



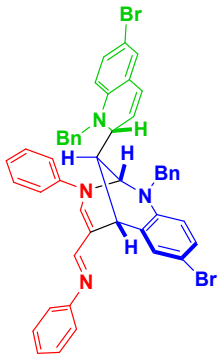
1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(3-chlorophenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(3-chlorophenyl)methanimine (**5h**)

Light yellow solid obtained by filtration of the precipitate; 131.8 mg, 90% yield; dr = 10:1; reaction time = 30 min; mp 173.1-174.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.0$ Hz, 2H), 7.23-7.18 (m, 5H), 7.15-7.14 (m, 3H), 7.10-6.88 (m, 14H), 6.80 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 2H), 6.65 (dd, $J_1 = J_2 = 4.0$ Hz, 2H), 6.50 (d, $J = 8.0$ Hz, 1H), 5.41 (s, 1H), 5.26 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 5.05 (d, $J = 16.0$ Hz, 1H), 4.56 (t, $J = 16.0$ Hz, 2H), 4.26 (d, $J = 16.0$ Hz, 1H), 4.20 (d, $J = 16.0$ Hz, 1H), 3.77 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.35 (tt, $J_1 = J_2 = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.9, 146.9, 143.1, 142.2, 141.2, 138.8, 138.1, 135.5, 134.4, 130.7, 130.0, 129.9, 128.9, 128.7, 128.5, 128.4, 128.3, 127.4, 127.4, 127.4, 127.1, 126.8, 126.7, 126.5, 124.2, 124.1, 123.1, 121.2, 121.0, 120.6, 119.2, 118.3, 118.1, 117.0, 114.8, 110.6, 68.9, 56.2, 55.9, 52.9, 40.6, 30.8. IR (KBr) ν 3430, 3029, 1575, 1483, 1452, 1177, 738 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Cl_2N_4$ $[M+H]^+$ 729.2546, found 729.2548.



1-(1-benzyl-11-(1-benzyl-1,2-dihydroquinolin-2-yl)-3-(3-bromophenyl)-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-(3-bromophenyl)methanimine (**5i**)

Light yellow solid obtained by filtration of the precipitate; 142.8 mg, 87% yield; dr = 16:1; reaction time = 30 min; mp 193.2-194.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.18-7.14 (m, 6H), 7.12-7.06 (m, 6H), 7.00-6.92 (m, 4H), 6.88-6.82 (m, 6H), 6.72 (dd, $J_1 = J_2$ = 8.0 Hz, 2H), 6.58-6.55 (m, 2H), 6.42 (d, J = 8.0 Hz, 1H), 5.32 (s, 1H), 5.17 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 4.97 (d, J = 16.0 Hz, 1H), 4.48 (t, J = 20.0 Hz, 2H), 4.16 (dd, $J_1 = J_2$ = 16.0 Hz, 2H), 3.68 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.26 (tt, $J_1 = J_2$ = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 155.1, 147.0, 143.1, 142.2, 141.2, 138.8, 138.1, 130.9, 130.2, 130.0, 128.9, 128.7, 128.7, 128.5, 128.4, 128.2, 127.4, 127.4, 127.1, 127.1, 127.0, 126.8, 126.6, 124.0, 124.0, 123.5, 123.1, 122.6, 121.0, 120.6, 119.7, 118.7, 118.1, 117.0, 114.8, 110.5, 68.9, 56.2, 55.8, 52.9, 40.6, 30.8. IR (KBr) *v* 3439, 3054, 1612, 1572, 1482, 1176, 739 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Br_2N_4$ $[M+H]^+$ 817.1536, found 817.1548.

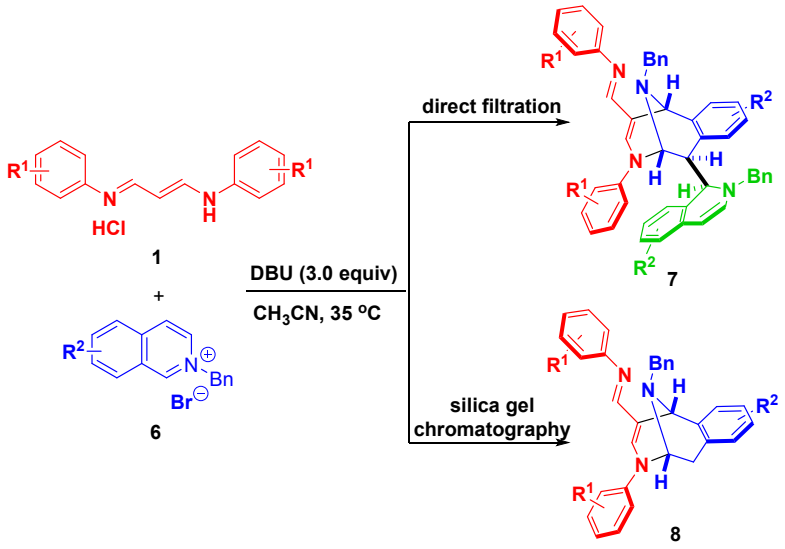


1-(1-benzyl-11-(1-benzyl-6-bromo-1,2-dihydroquinolin-2-yl)-8-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-methanobenzo[*d*][1,3]diazocin-5-yl)-*N*-phenylmethanimine (**5j**)

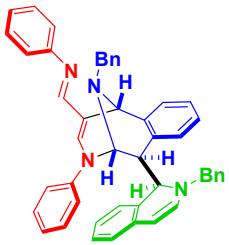
White solid obtained by filtration of the precipitate; 66.1 mg, 40% yield; dr > 20:1; reaction time = 30 min; mp 188.6-189.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.28-7.13 (m, 11H), 7.11-6.99 (m, 12H), 6.94 (s, 1H), 6.46 (q, J = 8.0 Hz, 1H), 6.15 (d, J = 8.0 Hz,

1H), 5.54 (s, 1H), 4.69-4.50 (m, 3H), 4.42 (t, J = 8.0 Hz, 1H), 4.25 (d, J = 20.0 Hz, 1H), 4.08 (s, 1H), 3.15 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 1.99 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.1, 146.0, 142.0, 141.0, 139.6, 138.1, 137.1, 133.7, 132.7, 132.2, 129.9, 129.8, 129.6, 128.9, 128.8, 128.8, 127.3, 127.3, 126.5, 126.4, 126.3, 124.4, 124.3, 124.2, 120.9, 120.4, 119.7, 113.8, 113.1, 111.8, 109.5, 98.1, 69.7, 53.4, 53.1, 41.5, 35.9, 31.0. IR (KBr) ν 3448, 3066, 1616, 1578, 1498, 1210, 748 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Br_2N_4$ $[M+H]^+$ 817.1536, found 817.1533.

4. Experimental data for the formation of 7 and 8

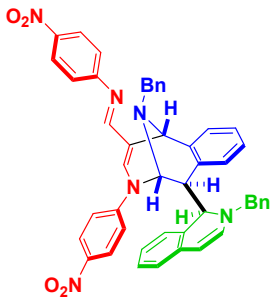


General procedure: To a 5.0 mL vial were successively added 1,5-diazapentadienium salts **1** (0.20 mmol), *N*-benyl quinilinium salts **4** (0.44 mmol) and 0.8 mL of CH_3CN. And then, DBU (91.4 mg, 0.60 mmol) was added by syringe. The resulting mixture was stirred at 35 °C and the reaction went completion after 1 h. During the reaction process, a large amount of precipitate was generated. The reaction was quite dependent on the workup procedures. By a simple filtration, the trifunctionalized products **7** were obtained. And we got bifunctionalized products **8** as the sole products by directly subjecting the reaction mixture to silica gel column chromatography with petroleum ether and ethyl acetate as eluents. (*Note: compounds 7 were not very stable in solution, but they were very stable in solid state.*)



1-(11-benzyl-1-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**7a**)

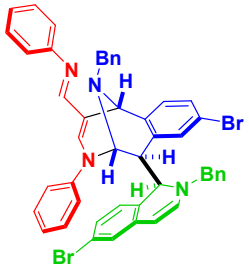
White solid obtained by filtration of the precipitate; 106.6 mg, 81% yield; dr > 20:1; reaction time = 1 h; mp 163.8-164.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 2H), 7.35-7.27 (m, 5H), 7.19-7.03 (m, 11H), 6.99 (q, *J* = 8.0 Hz, 2H), 6.90 (q, *J* = 8.0 Hz, 2H), 6.82-6.79 (m, 3H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 8.0 Hz, 1H), 5.77 (s, 1H), 5.27 (t, *J* = 8.0 Hz, 2H), 4.99 (d, *J* = 4.0 Hz, 1H), 3.94 (d, *J* = 16.0 Hz, 1H), 3.89 (d, *J* = 16.0 Hz, 1H), 3.77 (d, *J* = 16.0 Hz, 1H), 3.57 (d, *J* = 16.0 Hz, 1H), 2.98 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.6, 143.1, 139.8, 138.2, 138.1, 137.9, 137.2, 134.3, 132.3, 129.8, 129.5, 129.2, 128.9, 128.4, 128.2, 127.9, 127.6, 127.5, 127.5, 127.1, 126.5, 126.2, 125.8, 124.8, 124.0, 122.8, 122.5, 120.8, 117.7, 112.8, 95.7, 72.4, 65.5, 58.6, 57.6, 54.4, 50.7, one carbon missing in the aromatic region. IR (KBr) *v* 3441, 3027, 1617, 1574, 1488, 1228, 758 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{41}N_4$ $[M+H]^+$ 661.3326, found 661.3331.



1-(11-benzyl-1-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3-(4-nitrophenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(4-nitrophenyl)methanimine (**7b**)

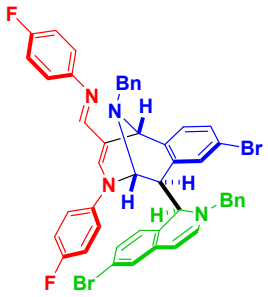
Red solid obtained by filtration of the precipitate; 76.4 mg, 51% yield; dr > 20:1; reaction time = 1 h; mp 177.9-178.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 12.0 Hz, 2H), 7.93 (s, 1H), 7.79 (d, *J* = 12.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.40-7.16 (m, 15H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 4.0 Hz, 2H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.51 (s, 1H), 5.29 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 4.38 (d, *J* = 8.0 Hz,

1H), 3.86 (s, 1H), 3.82 (d, J = 4.0 Hz, 1H), 3.50 (d, J = 16.0 Hz, 1H), 3.19 (d, J = 16.0 Hz, 1H), 3.03 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 158.5, 146.6, 144.5, 142.0, 138.3, 138.1, 136.9, 136.8, 136.6, 133.7, 132.4, 130.2, 129.0, 128.9, 128.4, 128.1, 127.4, 127.3, 127.2, 127.1, 126.2, 125.9, 125.8, 125.5, 125.3, 125.0, 124.4, 122.9, 121.3, 117.6, 115.0, 97.4, 70.0, 61.7, 59.1, 57.3, 54.2, 44.2. IR (KBr) v 3435, 3028, 1556, 1499, 1330, 1175, 761 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{38}N_6NaO_4$ $[M+Na]^+$ 773.2847, found 773.2842.



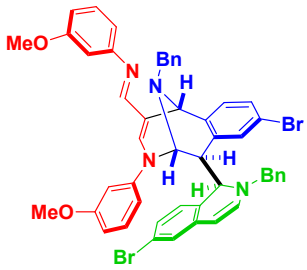
1-(11-benzyl-1-(2-benzyl-6-bromo-1,2-dihydroisoquinolin-1-yl)-9-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**7c**)

Light yellow solid obtained by filtration of the precipitate; 96.5 mg, 59% yield; dr > 20:1; reaction time = 1 h; mp 153.7-154.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.40-7.29 (m, 7H), 7.21-7.07 (m, 11H), 7.01 (t, J = 8.0 Hz, 1H), 6.90 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.77 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 6.65 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 8.0 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 5.65 (s, 1H), 5.26 (s, 1H), 5.18 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 4.0 Hz, 1H), 3.96 (d, J = 16.0 Hz, 1H), 3.82 (q, J = 12.0 Hz, 2H), 3.54 (d, J = 16.0 Hz, 1H), 2.87 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 153.3, 142.9, 138.7, 138.6, 137.6, 137.3, 136.1, 134.1, 132.1, 129.7, 129.6, 129.5, 129.4, 129.0, 128.9, 128.5, 128.4, 128.1, 127.7, 127.4, 127.3, 125.7, 124.8, 124.2, 123.6, 121.7, 120.8, 120.8, 119.5, 118.6, 112.3, 95.1, 71.7, 64.2, 58.8, 57.5, 53.2, 50.8. IR (KBr) v 3424, 3029, 1618, 1574, 1488, 1179, 762 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Br_2N_4$ $[M+H]^+$ 817.1536, found 817.1521.



1-(11-benzyl-1-(2-benzyl-6-bromo-1,2-dihydroisoquinolin-1-yl)-9-bromo-3-(4-fluorophenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(4-fluorophenyl)methanimine (**7d**)

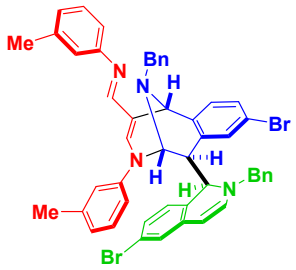
Light yellow solid obtained by filtration of the precipitate; 142.1 mg, 83% yield; dr > 20:1; reaction time = 1 h; mp 187.4-188.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.32-7.23 (m, 5H), 7.18-7.11 (m, 4H), 7.02 (s, 1H), 6.94-6.86 (m, 5H), 6.85 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 8.0 Hz, 2H), 6.70 (t, J = 8.0 Hz, 3H), 6.51 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 6.32 (d, J = 8.0 Hz, 1H), 6.14 (d, J = 8.0 Hz, 1H), 5.50 (s, 1H), 5.14 (s, 1H), 5.07 (d, J = 8.0 Hz, 1H), 4.74 (d, J = 4.0 Hz, 1H), 3.87 (d, J = 16.0 Hz, 1H), 3.75 (q, J = 12.0 Hz, 2H), 3.46 (d, J = 16.0 Hz, 1H), 2.74 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, J = 241.0 Hz, 1C), 159.2 (d, J = 243.0 Hz, 1C), 157.6, 149.4 (d, J = 3.0 Hz, 1C), 139.4 (d, J = 3.0 Hz, 1C), 138.9, 138.7, 138.0, 137.5, 137.2, 136.2, 134.1, 132.0, 129.7, 129.5, 128.9, 128.6, 128.5, 128.2, 127.8, 127.5, 127.5, 125.8, 124.9, 121.9, 121.8, 120.9, 120.8, 119.7, 116.3 (d, J = 23.0 Hz, 1C), 115.5 (d, J = 23.0 Hz, 1C), 112.0, 94.7, 72.3, 64.1, 58.8, 57.6, 53.6, 50.7. IR (KBr) ν 3429, 3029, 1614, 1580, 1497, 1227, 1176, 719 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{37}Br_2F_2N_4$ $[M+H]^+$ 853.1348, found 853.1335.



1-(11-benzyl-1-(2-benzyl-6-bromo-1,2-dihydroisoquinolin-1-yl)-9-bromo-3-(3-methoxyphenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(3-methoxyphenyl)methanimine (**7e**)

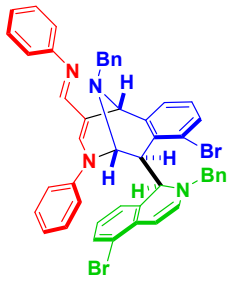
Yellow solid obtained by filtration of the precipitate; 139.1 mg, 79% yield; dr > 20:1; reaction time = 1 h; mp 157.2-158.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.24-7.20 (m, 1H), 7.16-7.07 (m, 5H), 7.02 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 4.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.83 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.68 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 6.61 (d, J = 4.0 Hz, 1H), 6.58 (d, J = 4.0 Hz, 1H), 6.56 (t, J = 4.0 Hz, 1H), 6.52-6.49 (m, 2H), 6.30 (t, J = 4.0 Hz, 1H), 6.25 (d, J = 8.0 Hz, 1H), 6.14 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 5.50 (s, 1H), 5.17 (d, J = 4.0 Hz, 1H), 5.15 (s, 1H), 4.68 (d, J = 4.0 Hz, 1H), 3.90 (d, J = 16.0 Hz, 1H), 3.73 (s, 5H), 3.70 (s, 3H), 3.43 (d, J = 16.0 Hz, 1H), 2.84 (d, J = 4.0 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 160.3, 157.9, 154.8, 144.2, 138.6, 138.2, 137.8, 137.6, 135.9, 133.8, 132.5, 130.4, 129.9, 129.6, 129.4, 129.0, 128.5, 128.4, 127.9, 127.8, 127.4, 127.3, 127.3, 127.2, 125.6, 124.9, 121.8, 119.4, 113.1, 112.3, 111.0, 110.0, 108.3, 106.5, 105.8, 96.0, 71.7, 64.3, 58.8, 57.5, 55.4, 55.2, 52.3, 51.2. IR (KBr) *v* 3438, 2928, 1611, 1572, 1482, 1139, 767 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{43}Br_2N_4O_2$ $[M+H]^+$ 877.1747, found 877.1743.



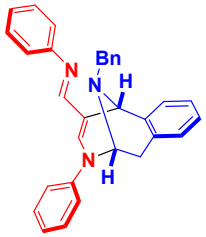
1-(11-benzyl-1-(2-benzyl-6-bromo-1,2-dihydroisoquinolin-1-yl)-9-bromo-3-(*m*-tolyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(*m*-tolyl)methanimine (**7f**)

White solid obtained by filtration of the precipitate; 93.5 mg, 55% yield; dr > 20:1; reaction time = 1 h; mp 177.6-178.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33-7.21 (m, 5H), 7.13-7.08 (m, 5H), 7.01-6.94 (m, 3H), 6.82-6.76 (m, 5H), 6.67 (s, 2H), 6.53 (d, *J* = 12.0 Hz, 2H), 6.36 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 6.14 (d, *J* = 4.0 Hz, 1H), 5.51 (s, 1H), 5.19 (s, 1H), 5.15 (d, *J* = 8.0 Hz, 1H), 4.69 (d, *J* = 4.0 Hz, 1H), 3.88 (d, *J* = 16.0 Hz, 1H), 3.74 (q, *J* = 12.0 Hz, 2H), 3.45 (d, *J* = 16.0 Hz, 1H), 2.84 (d, *J* = 4.0 Hz, 1H), 2.27 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 153.4, 143.1, 139.5, 138.7, 138.7, 138.3, 137.8, 137.6, 137.5, 136.0, 133.9, 132.4, 129.9, 129.4, 129.0, 128.8, 128.5, 128.4, 127.9, 127.7, 127.4, 127.4, 127.2, 125.7, 124.9, 124.8, 124.6, 124.5, 121.7, 121.6, 119.7, 119.3, 117.8, 115.8, 112.2, 95.9, 71.6, 64.3, 58.9, 57.5, 52.5, 51.1, 21.7, 21.4. IR (KBr) *v* 3441, 2850, 1624, 1574, 1234, 695 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{43}Br_2N_4$ $[M+H]^+$ 845.1849, found 845.1847.



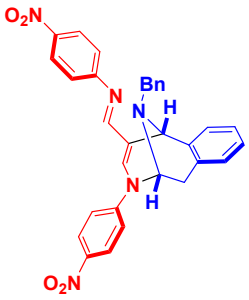
1-(11-benzyl-1-(2-benzyl-5-bromo-1,2-dihydroisoquinolin-1-yl)-10-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**7g**)

Yellow solid obtained by filtration of the precipitate; 90.7 mg, 56% yield; dr > 20:1; reaction time = 1 h; mp 174.5-175.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41-7.29 (m, 8H), 7.20 (d, *J* = 8.0 Hz, 4H), 7.11-7.03 (m, 7H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.84 (s, 2H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 5.67 (s, 1H), 5.53 (d, *J* = 4.0 Hz, 1H), 5.27 (s, 1H), 4.06 (d, *J* = 12.0 Hz, 1H), 3.97 (d, *J* = 16.0 Hz, 1H), 3.71 (d, *J* = 16.0 Hz, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 3.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 153.5, 142.7, 141.6, 137.6, 137.3, 137.1, 134.2, 132.0, 131.7, 131.6, 131.5, 131.5, 129.9, 129.6, 128.9, 128.5, 128.4, 128.4, 127.8, 127.6, 127.5, 126.5, 125.8, 125.5, 124.8, 124.1, 123.2, 120.8, 118.0, 117.8, 111.7, 92.1, 72.6, 60.2, 58.8, 57.4, 56.4, 49.8. IR (KBr) *v* 3438, 2925, 1619, 1589, 1501, 1220, 737 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{39}Br_2N_4$ $[M+H]^+$ 817.1536, found 817.1519.



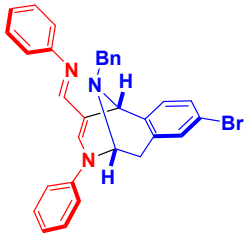
1-(11-benzyl-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**8a**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 75.8 mg, 86% yield; dr > 20:1; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 4.0 Hz, 1H), 7.72-7.70 (m, 1H), 7.34-7.27 (m, 9H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.15-7.07 (m, 7H), 7.00-6.98 (m, 2H), 5.28 (d, *J* = 4.0 Hz, 1H), 5.05 (s, 1H), 3.88 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.65 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.32 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.96 (dd, $J_1 = J_2$ = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 153.5, 143.9, 139.8, 137.7, 137.6, 130.0, 129.8, 129.4, 128.9, 128.5, 128.4, 127.4, 126.6, 126.1, 125.7, 124.1, 123.6, 120.9, 118.7, 113.3, 69.3, 56.9, 53.0, 35.8. IR (KBr) *v* 3419, 3030, 1619, 1571, 1491, 1247, 754 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{28}N_3$ $[M+H]^+$ 442.2278, found 442.2277.



1-(11-benzyl-3-(4-nitrophenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(4-nitrophenyl)methanimine (**8b**)

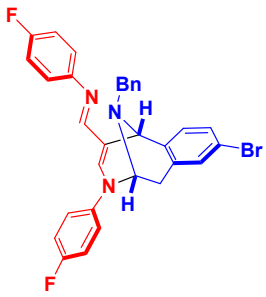
Red oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 56.4 mg, 53% yield; dr > 20:1; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 4H), 7.99 (s, 1H), 7.61 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.45 (s, 1H), 7.31 (s, 5H), 7.21-7.09 (m, 7H), 5.27 (s, 1H), 5.20 (d, J = 8.0 Hz, 1H), 3.92 (d, J = 16.0 Hz, 1H), 3.66 (d, J = 16.0 Hz, 1H), 3.49 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.02 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 158.6, 147.7, 144.5, 142.5, 138.4, 136.7, 129.5, 129.2, 128.6, 128.6, 127.8, 126.7, 126.4, 126.0, 125.9, 125.0, 121.2, 117.1, 116.0, 69.6, 57.0, 52.6, 35.4, one carbon missing in the aromatic region. IR (KBr) *v* 3387, 3029, 1558, 1501, 1330, 1176, 1105, 736 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{26}N_5O_4$ $[M+H]^+$ 532.1979, found 532.1977.



1-(11-benzyl-9-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**8c**)

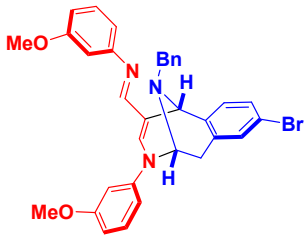
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 84.4 mg, 81% yield; dr > 20:1; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.35-7.27 (m, 9H), 7.21-7.19 (m, 2H), 7.17 (s, 1H), 7.13-7.07 (m, 4H), 6.98 (d, J = 8.0 Hz, 2H), 5.24 (s, 1H), 5.02 (d, J = 4.0 Hz, 1H), 3.85 (d, J = 16.0 Hz, 1H), 3.65 (d, J = 16.0 Hz, 1H), 3.28 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.92 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.2, 143.7, 138.8, 137.7, 137.5, 132.6, 131.2, 129.8, 129.3, 129.0, 128.8, 128.4, 128.2, 127.5, 124.2, 123.9, 120.8, 119.6, 118.9, 112.9, 69.0, 56.8, 52.5, 35.6. IR (KBr) *v* 3450, 3054,

1621, 1571, 1488, 1242, 755 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{26}BrN_3$ $[M+H]^+$ 520.1383, found 520.1377.



1-(11-benzyl-9-bromo-3-(4-fluorophenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(4-fluorophenyl)methanimine (**8d**)

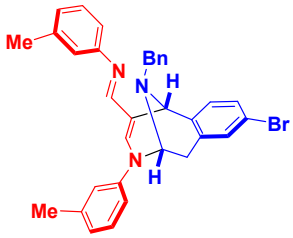
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 92.6 mg, 83% yield; dr > 20:1; reaction time = 1 h; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.25-7.22 (m, 5H), 7.16-7.14 (m, 2H), 7.01-6.91 (m, 7H), 6.89-6.85 (m, 2H), 5.14 (s, 1H), 4.85 (d, J = 4.0 Hz, 1H), 3.81 (d, J = 16.0 Hz, 1H), 3.58 (d, J = 16.0 Hz, 1H), 3.18 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.82 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, J = 67.0 Hz, 1C), 158.6 (d, J = 69.0 Hz, 1C), 157.8, 149.3 (d, J = 3.0 Hz, 1C), 140.3 (d, J = 3.0 Hz, 1C), 138.8, 138.3, 137.4, 132.5, 131.3, 129.3, 128.9, 128.5, 128.2, 127.6, 121.8 (d, J = 8.0 Hz, 1C), 121.4 (d, J = 8.0 Hz, 1C), 119.7, 116.6 (d, J = 23.0 Hz, 1C), 115.5 (d, J = 23.0 Hz, 1C), 112.6, 69.6, 56.9, 52.5, 35.5. IR (KBr) ν 3445, 1620, 1590, 1500, 1217, 736 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{25}BrFN_3$ $[M+H]^+$ 556.1194, found 556.1192.



1-(11-benzyl-9-bromo-3-(3-methoxyphenyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(3-methoxyphenyl)methanimine (**8e**)

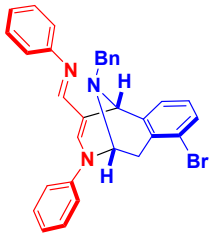
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 106.7 mg, 92% yield; dr > 20:1; reaction time = 1 h; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 4.0 Hz, 1H), 7.65-7.62 (m, 1H), 7.41-7.33 (m, 5H), 7.31-7.27 (m, 4H), 7.23 (s, 1H), 6.79-6.69 (m, 4H), 6.64 (d, J = 8.0 Hz, 1H), 6.58 (d, J = 4.0 Hz, 1H), 5.29 (s, 1H), 5.07 (d, J = 4.0 Hz, 1H), 3.92 (d, J = 16.0

Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (d, J = 16.0 Hz, 1H), 3.33 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.99 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.3, 158.2, 154.7, 144.9, 138.8, 137.8, 137.5, 132.6, 131.3, 130.6, 129.6, 129.3, 128.8, 128.4, 128.2, 127.6, 119.7, 113.1, 112.8, 111.3, 110.1, 108.9, 106.5, 105.4, 69.0, 56.9, 55.4, 55.2, 52.6, 35.6. IR (KBr) v 3421, 1566, 1485, 1244, 1137, 773 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{31}BrN_3O_2$ $[M+H]^+$ 580.1594, found 580.1589.



1-(11-benzyl-9-bromo-3-(*m*-tolyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(*m*-tolyl)methanimine (**8f**)

Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 95.9 mg, 88% yield; dr > 20:1; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 4.0 Hz, 1H), 7.58 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.37-7.30 (m, 5H), 7.23-7.21 (m, 4H), 7.16 (s, 1H), 6.95-6.93 (m, 4H), 6.80 (d, J = 8.0 Hz, 2H), 5.23 (s, 1H), 5.02 (d, J = 4.0 Hz, 1H), 3.87 (d, J = 12.0 Hz, 1H), 3.67 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.29 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.94 (d, J = 16.0 Hz, 1H), 2.35 (dd, $J_1 = J_2$ = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 153.3, 143.8, 139.8, 138.9, 138.7, 137.9, 137.6, 132.7, 131.3, 129.6, 129.4, 128.8, 128.8, 128.4, 128.3, 127.5, 125.0, 124.8, 121.7, 119.9, 119.6, 117.8, 116.2, 112.7, 69.0, 56.9, 52.3, 35.7, 21.6, 21.4. IR (KBr) v 3451, 2919, 1614, 1570, 1486, 693 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{31}BrN_3$ $[M+H]^+$ 548.1696, found 548.1690.

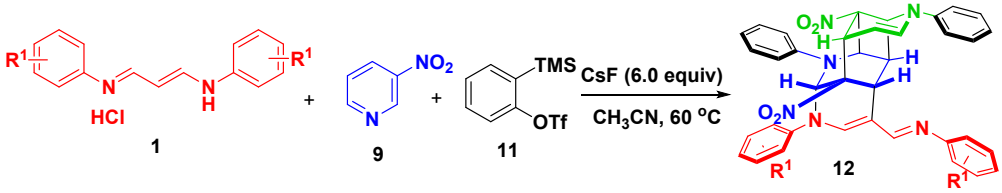


1-(11-benzyl-10-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-N-phenylmethanimine (**8g**)

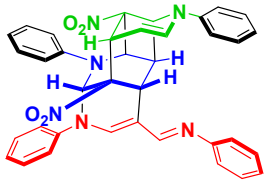
Yellow oil obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 95.7 mg, 92% yield; dr > 20:1; reaction time = 1 h; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.38-7.29 (m, 10H), 7.22 (d, J = 4.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 4H), 7.03 (t, J = 8.0

Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 5.28 (s, 1H), 5.08 (d, J = 4.0 Hz, 1H), 3.89 (d, J = 16.0 Hz, 1H), 3.67 (d, J = 16.0 Hz, 1H), 3.23 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.97 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.3, 143.8, 142.1, 137.7, 137.4, 130.5, 130.0, 129.9, 129.4, 129.0, 128.5, 127.6, 127.3, 125.8, 124.8, 124.3, 123.9, 120.9, 118.8, 112.5, 69.3, 56.6, 53.0, 38.0. IR (KBr) v 3423, 3032, 1619, 1571, 1491, 1179, 756 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{26}BrN_3$ $[M+H]^+$ 520.1383, found 520.1380.

5. Experimental data for the formation of 12



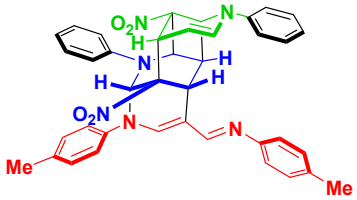
General procedure: To a 5.0 mL vial were successively added 1,5-diazapentadienium salts **1** (0.23 mmol), 3-nitropyridine **9** (0.30 mmol), CsF (0.90 mmol) and 1.0 mL of CH_3CN. And then, benzyne precursor **11** (0.68 mmol) was added by syringe. The resulting mixture was stirred at 60 °C in oil bath. 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 **12**.



1-(10a,11-dinitro-1,3,7-triphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-phenylmethanimine (**12a**)

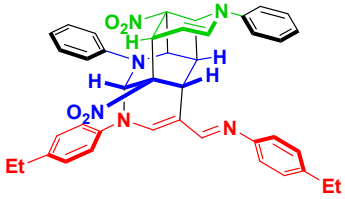
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 68.4 mg, 73% yield; dr > 20:1; reaction time = 4 h; mp 213.7-214.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40-7.20 (m, 8H), 7.17-7.06 (m, 7H), 7.02-6.99 (m, 3H), 6.87 (d, J = 12.0 Hz, 2H), 6.79 (d, J = 12.0 Hz, 2H), 6.29 (s, 1H), 4.63 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.41 (t, J = 8.0 Hz, 1H), 4.31 (d, J = 8.0 Hz, 1H), 4.21 (s, 1H), 4.19 (d, J = 4.0 Hz, 1H), 3.59 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 151.8, 145.5, 145.2, 144.7, 138.6, 134.2, 129.7, 129.6, 129.5, 129.0, 125.1, 125.0, 124.5, 123.7, 123.1, 121.0, 120.9, 119.2, 113.8, 87.5, 85.8, 84.9, 75.7, 59.2, 52.7, 48.3, 38.7, 26.6. IR (KBr) v 3449, 2311, 1637, 1591, 757 cm^{-1}. HRMS (ESI) calcd for

$C_{37}H_{31}N_6O_4$ $[M+H]^+$ 623.2401, found 623.2399.



1-(10a,11-dinitro-1,7-diphenyl-3-(*p*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(*p*-tolyl)methanimine (**12b**)

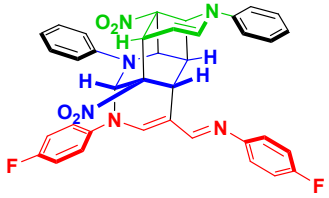
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 64.5 mg, 66% yield; dr > 20:1; reaction time = 4 h; mp 221.7-222.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.20-7.13 (m, 5H), 7.02 (dd, $J_1 = J_2$ = 8.0 Hz, 7H), 6.91 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 4.64 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.42 (t, J = 8.0 Hz, 1H), 4.33 (d, J = 8.0 Hz, 1H), 4.22 (s, 1H), 4.20 (s, 1H), 3.59 (t, J = 8.0 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 149.2, 145.5, 145.2, 142.3, 138.4, 134.8, 134.6, 134.1, 130.1, 129.6, 129.5, 129.4, 124.3, 123.6, 122.9, 120.8, 120.8, 119.1, 113.4, 87.5, 85.8, 84.8, 75.8, 59.1, 52.6, 48.3, 38.7, 26.5, 20.9, 20.7. IR (KBr) v 3447, 2922, 1634, 1586, 1503, 1295, 1204, 750 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_6O_4$ $[M+H]^+$ 651.2714, found 651.2715.



N-(4-ethylphenyl)-1-(3-(4-ethylphenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12c**)

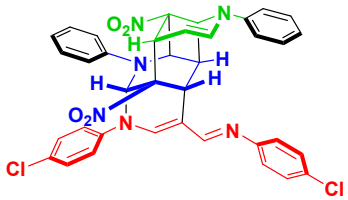
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 65.9 mg, 65% yield; dr > 20:1; reaction time = 4 h; mp 192.3-192.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.42 (s, 2H), 7.33 (s, 2H), 7.19-7.01 (m, 12H), 6.92 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 4.65 (s, 1H), 4.44 (s, 1H), 4.35 (d, J = 4.0 Hz, 1H), 4.24 (s, 2H), 3.60 (s, 1H), 2.69 (d, J = 8.0 Hz, 2H), 2.62 (d, J = 8.0 Hz, 2H), 1.26 (d, J = 24.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 149.4, 145.5, 145.2, 142.4, 141.2, 141.1, 138.4, 134.1, 129.5,

129.4, 128.9, 128.3, 124.3, 123.6, 122.9, 120.9, 120.8, 119.1, 113.4, 87.5, 85.8, 84.8, 75.8, 59.0, 52.6, 48.3, 38.7, 28.3, 28.1, 26.5, 15.6, 15.5. IR (KBr) *v* 3444, 2964, 1635, 1504, 1292, 1206, 755 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{39}N_6O_4$ $[M+H]^+$ 679.3027, found 679.3030.



N-(4-fluorophenyl)-1-(3-(4-fluorophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12d**)

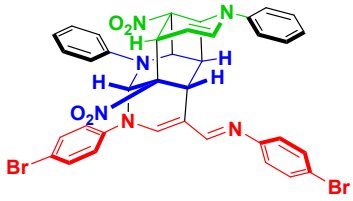
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 69.2 mg, 70% yield; dr > 20:1; reaction time = 4 h; mp 189.6-190.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 6H), 6.87 (dd, $J_1 = J_2$ = 8.0 Hz, 5H), 6.72 (s, 2H), 6.24 (s, 2H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 2H), 3.53 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 53.0 Hz, 1C), 159.1 (d, *J* = 53.0 Hz, 1C), 155.9, 147.6, 145.2, 145.0, 141.0 (d, *J* = 3.0 Hz, 1C), 138.7, 134.0, 129.5, 129.5, 124.5, 123.6, 123.1 (d, *J* = 8.0 Hz, 1C), 122.9, 122.1 (d, *J* = 8.0 Hz, 1C), 118.8, 116.3 (d, *J* = 23.0 Hz, 1C), 115.6 (d, *J* = 23.0 Hz, 1C), 113.3, 87.4, 85.8, 84.7, 75.8, 59.1, 52.4, 48.3, 38.7, 26.3. IR (KBr) *v* 3449, 3067, 1635, 1595, 1502, 1222, 754 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}F_2N_6O_4$ $[M+H]^+$ 659.2213, found 659.2212.



N-(4-chlorophenyl)-1-(3-(4-chlorophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12e**)

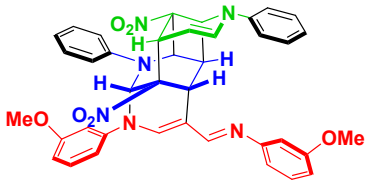
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 77.9 mg, 75% yield; dr > 20:1; reaction time = 4 h; mp 216.5-217.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 4H), 7.19-7.09 (m, 5H), 7.04 (t, *J* =

8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 3H), 6.94 (s, 1H), 6.88 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 8.0 Hz, 2H), 6.24 (s, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.38 (t, J = 8.0 Hz, 1H), 4.25 (d, J = 8.0 Hz, 1H), 4.17 (d, J = 8.0 Hz, 2H), 3.52 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.0, 145.1, 144.9, 143.0, 138.3, 134.1, 130.5, 130.4, 129.6, 129.6, 129.5, 129.0, 125.0, 123.6, 123.5, 122.2, 122.0, 118.8, 114.1, 87.3, 85.7, 84.8, 75.7, 59.3, 52.3, 48.1, 38.7, 26.4. IR (KBr) v 3449, 3067, 1635, 1595, 1502, 1222, 754 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}Cl_2N_6O_4$ $[M+H]^+$ 691.1622, found 691.1623.



N-(4-bromophenyl)-1-(3-(4-bromophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12f**)

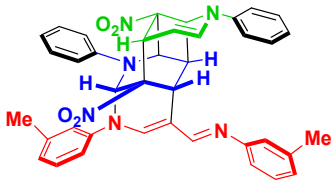
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 98.9 mg, 85% yield; dr > 20:1; reaction time = 4 h; mp 239.2-240.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 4.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.91 (dd, J_1 = J_2 = 8.0 Hz, 5H), 6.60 (d, J = 8.0 Hz, 2H), 6.23 (s, 1H), 4.61 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.37 (t, J = 8.0 Hz, 1H), 4.24 (d, J = 8.0 Hz, 1H), 4.17 (d, J = 8.0 Hz, 2H), 3.51 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.4, 145.1, 144.9, 143.4, 138.2, 134.1, 132.6, 131.9, 129.6, 129.5, 125.0, 123.6, 122.6, 122.2, 118.8, 118.2, 118.1, 114.3, 87.3, 85.7, 84.8, 75.7, 59.3, 52.3, 48.1, 38.7, 26.4, one carbon missing in the aromatic region. IR (KBr) v 3444, 3055, 1636, 1597, 1490, 1287, 1201, 755 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}Br_2N_6O_4$ $[M+H]^+$ 779.0612, found 779.0607.



N-(3-methoxyphenyl)-1-(3-(3-methoxyphenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-

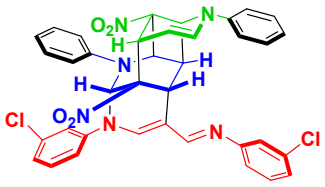
d][1,3]diazocin-5-yl)methanimine (**12g**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 65.2 mg, 64% yield; dr > 20:1; reaction time = 4 h; mp 188.8-189.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.13-7.10 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 8.0 Hz, 1H), 6.25 (s, 2H), 4.60 (d, *J* = 4.0 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 4.0 Hz, 1H), 4.19 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 3.61 (s, 3H), 3.56 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 160.3, 156.6, 153.1, 145.7, 145.5, 145.1, 138.5, 134.1, 130.4, 129.6, 129.5, 129.5, 124.8, 123.6, 119.0, 113.7, 113.0, 112.9, 111.1, 106.7, 106.2, 87.4, 85.8, 84.8, 75.8, 59.3, 55.2, 55.2, 52.5, 48.2, 38.7, 26.5, two carbons missing in the aromatic region. IR (KBr) *v* 3449, 3068, 1635, 1584, 1493, 1208, 765 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_6O_6$ $[M+H]^+$ 683.2613, found 683.2612.



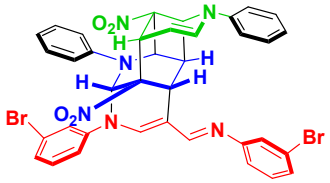
1-(10a,11-dinitro-1,7-diphenyl-3-(*m*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)-*N*-(*m*-tolyl)methanimine (**12h**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 62.4 mg, 64% yield; dr > 20:1; reaction time = 4 h; mp 185.6-185.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15-7.09 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.93-6.79 (m, 8H), 6.50 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.45 (s, 1H), 6.17 (s, 1H), 4.54 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.31 (t, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 4.0 Hz, 1H), 4.11 (s, 1H), 3.48 (t, *J* = 8.0 Hz, 1H), 2.27 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 151.6, 145.5, 145.1, 144.5, 139.6, 138.7, 138.4, 134.1, 129.5, 129.4, 129.4, 128.7, 125.8, 124.6, 123.6, 123.4, 122.2, 121.5, 119.1, 117.8, 117.6, 113.6, 87.5, 85.8, 84.9, 75.8, 59.2, 52.5, 48.3, 38.7, 26.5, 21.4, 21.3, one carbon missing in the aromatic region. IR (KBr) *v* 3449, 3049, 1636, 1586, 1494, 1209, 758 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{35}N_6O_4$ $[M+H]^+$ 651.2714, found 651.2714.



N-(3-chlorophenyl)-1-(3-(3-chlorophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12i**)

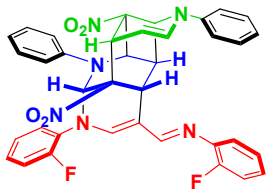
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 52.9 mg, 51% yield; dr > 20:1; reaction time = 4 h; mp 203.2-203.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.17-7.07 (m, 6H), 7.04 (d, J = 4.0 Hz, 1H), 6.99 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.94 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 4.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.27 (s, 1H), 4.65 (dd, J_1 = J_2 = 8.0 Hz, 1H), 4.42 (t, J = 8.0 Hz, 1H), 4.25 (d, J = 4.0 Hz, 1H), 4.22 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.18 (s, 1H), 3.54 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 152.7, 145.5, 145.1, 145.0, 138.3, 135.3, 134.6, 134.2, 130.6, 130.0, 129.7, 129.6, 125.4, 125.2, 125.1, 124.1, 123.8, 121.6, 121.0, 119.0, 119.0, 118.7, 114.5, 87.3, 85.8, 85.0, 75.9, 59.5, 52.4, 48.3, 38.7, 26.5. IR (KBr) ν 3446, 3068, 1634, 1580, 1489, 1204, 757 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}Cl_2N_6O_4$ $[M+H]^+$ 691.1622, found 691.1618.



N-(3-bromophenyl)-1-(3-(3-bromophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12j**)

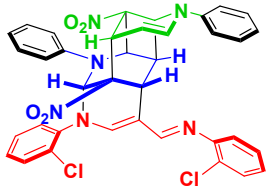
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 55.4 mg, 47% yield; dr > 20:1; reaction time = 4 h; mp 208.4-209.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.28-7.25 (m, 5H), 7.20 (dd, J_1 = J_2 = 8.0 Hz, 3H), 7.16 (d, J = 8.0 Hz, 1H), 7.14-7.07 (m, 2H), 7.05-6.99 (m, 3H), 6.93 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 6.70 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.26 (s, 1H), 4.65 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.41 (t, J = 8.0 Hz, 1H), 4.24 (d, J = 8.0 Hz, 1H), 4.22 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.17 (s, 1H), 3.53 (t, J = 8.0 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 152.8, 145.6, 145.1, 144.9, 138.3, 134.3, 130.9, 130.3, 129.7, 129.7, 128.1, 128.0, 125.4, 124.5, 124.2, 124.0, 123.9, 123.2, 122.7, 119.4, 119.2, 118.9, 114.5, 87.3, 85.8, 85.0, 75.9, 59.6, 52.3, 48.3, 38.7, 26.5. IR (KBr) *v* 3448, 3065, 1636, 1572, 1488, 1202, 755 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}Br_2N_6O_4$ $[M+H]^+$ 779.0612, found 779.0606.



N-(2-fluorophenyl)-1-(3-(2-fluorophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12k**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 56.0 mg, 57% yield; dr > 20:1; reaction time = 4 h; mp 201.9-202.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.39-7.29 (m, 6H), 7.27-7.08 (m, 7H), 7.03 (t, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 4.98 (d, *J* = 4.0 Hz, 1H), 4.73 (d, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 4.17 (d, *J* = 4.0 Hz, 1H), 3.90 (s, 1H), 3.49 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.5, 156.6 (d, *J* = 70.0 Hz, 1C), 154.1 (d, *J* = 68.0 Hz, 1C), 144.9 (d, *J* = 40.0 Hz, 1C), 142.7, 140.1 (d, *J* = 10.0 Hz, 1C), 133.5, 132.2 (d, *J* = 10.0 Hz, 1C), 129.4, 128.8, 128.1 (d, *J* = 8.0 Hz, 1C), 125.5 (d, *J* = 8.0 Hz, 1C), 125.2, 125.2, 125.1, 124.7 (d, *J* = 4.0 Hz, 1C), 122.7, 122.0, 121.6, 119.5, 117.4, 116.6 (d, *J* = 20.0 Hz, 1C), 115.8 (d, *J* = 20.0 Hz, 1C), 111.8, 87.8, 85.9, 83.6, 79.2, 72.6, 56.6, 51.9, 47.1, 25.7. IR (KBr) *v* 3451, 1636, 1592, 1499, 754 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}F_2N_6O_4$ $[M+H]^+$ 659.2213, found 659.2208.

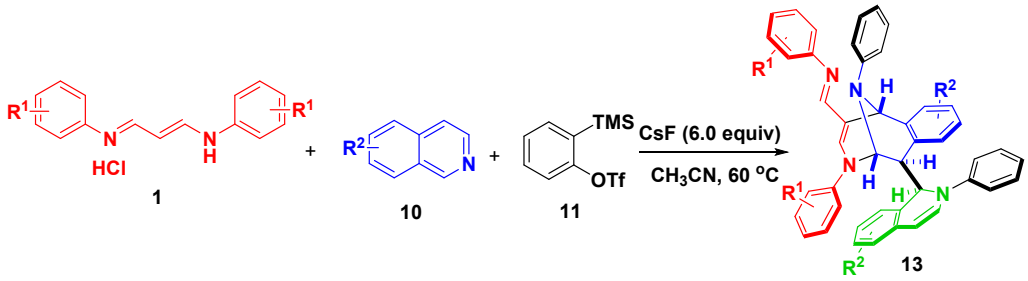


N-(2-chlorophenyl)-1-(3-(2-chlorophenyl)-10a,11-dinitro-1,7-diphenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)methanimine (**12l**)

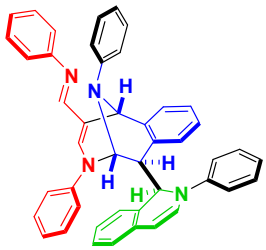
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 70:1 to 30:1); 56.2 mg, 54% yield; dr > 20:1; reaction time = 4 h; mp 212.2-213.1 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.80 (s, 1H), 7.39-7.29 (m, 5H), 7.24 (s, 1H), 7.19-7.12 (m, 3H), 7.08-6.97 (m, 6H), 6.85 (t, *J* = 8.0 Hz, 3H), 6.73 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 4.64 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 4.0 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 1H), 4.19 (s, 1H), 4.13 (d, *J* = 4.0 Hz, 1H), 3.76 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 150.6, 145.3, 142.1, 141.5, 134.3, 130.8, 130.5, 129.6, 129.5, 129.3, 128.2, 128.0, 127.6, 126.8, 125.1, 123.7, 122.8, 120.4, 119.5, 119.4, 111.1, 87.9, 85.5, 83.8, 74.3, 58.1, 53.3, 48.4, 38.6, 26.1, two carbons missing in the aromatic region. IR (KBr) *v* 3447, 3059, 1634, 1597, 1488, 1212, 753 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}Cl_2N_6O_4$ $[M+H]^+$ 691.1622, found 691.1618.

6. Experimental data for the formation of 13



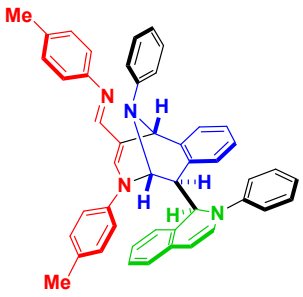
General procedure: To a 5.0 mL vial were successively added 1,5-diazapentadienium salts **1** (0.23 mmol), isoquinolines **10** (0.30 mmol), CsF (0.90 mmol) and 1.0 mL of CH_3CN. And then, benzyne precursor **11** (0.68 mmol) was added by syringe. The resulting mixture was stirred at 60 °C in oil bath. During the reaction process, a large amount of precipitate is generated. So, only a simple filtration was needed to obtain the pure products **13**. (*Note: compounds **13** were not very stable in solution, but they were very stable in solid state.*)



1-(3,11-diphenyl-1-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**13a**)

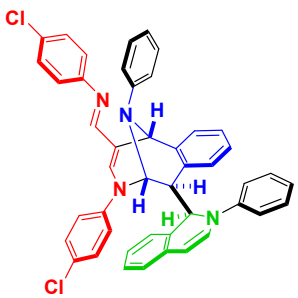
Yellow solid obtained by filtration of the precipitate; 80.2 mg, 85% yield; dr > 20:1; reaction time = 4 h; mp 220.2-221.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.37-7.22 (m, 6H), 7.16-7.03 (m, 10H), 6.98 (q, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.87 (q, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 4.0 Hz, 1H), 6.50 (s, 1H), 6.36 (d, *J* = 8.0 Hz,

2H), 6.30 (d, J = 8.0 Hz, 2H), 6.09 (d, J = 8.0 Hz, 1H), 5.98 (s, 1H), 5.35 (d, J = 8.0 Hz, 1H), 3.45 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 153.2, 148.5, 145.3, 141.6, 137.7, 136.4, 132.2, 131.4, 129.6, 129.5, 129.4, 129.2, 128.9, 128.5, 127.8, 127.8, 127.5, 127.2, 126.2, 125.6, 124.3, 123.7, 122.6, 121.9, 121.1, 120.9, 118.5, 116.9, 116.7, 115.9, 106.6, 66.8, 63.3, 54.5, 42.8, one carbon missing in the aromatic region. IR (KBr) v 3443, 3065, 1565, 1528, 1244, 752 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{37}N_4$ $[M+H]^+$ 633.2941, found 633.2938.



1-(11-phenyl-1-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3-(*p*-tolyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(*p*-tolyl)methanimine (**13b**)

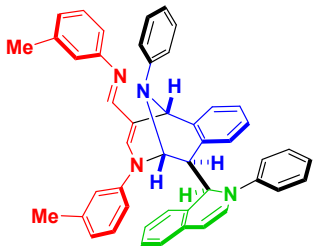
Yellow solid obtained by filtration of the precipitate; 84.2 mg, 85% yield; dr > 20:1; reaction time = 4 h; mp 225.3-226.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.31-7.24 (m, 3H), 7.16-7.08 (m, 6H), 7.04-6.94 (m, 7H), 6.85 (t, J = 8.0 Hz, 4H), 6.76 (t, J = 8.0 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.49 (s, 1H), 6.35 (d, J = 8.0 Hz, 2H), 6.20 (d, J = 8.0 Hz, 2H), 6.11 (d, J = 8.0 Hz, 1H), 5.93 (s, 1H), 5.35 (d, J = 8.0 Hz, 1H), 3.45 (d, J = 8.0 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 150.7, 148.6, 145.3, 139.3, 137.8, 136.1, 133.7, 132.2, 132.0, 131.3, 130.1, 129.5, 129.5, 129.3, 129.2, 128.5, 127.8, 127.8, 127.5, 127.1, 126.1, 125.6, 125.5, 123.7, 121.8, 121.1, 120.7, 118.5, 116.8, 116.2, 115.7, 106.6, 66.8, 63.2, 54.6, 42.8, 20.9, 20.4. IR (KBr) v 3442, 3028, 1609, 1569, 1504, 1237, 1225, 747 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{41}N_4$ $[M+H]^+$ 661.3326, found 661.3326.



N-(4-chlorophenyl)-1-(3-(4-chlorophenyl)-11-phenyl-1-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-

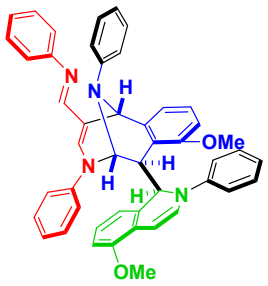
1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)methanimine (**13c**)

Yellow solid obtained by filtration of the precipitate; 91.2 mg, 87% yield; dr > 20:1; reaction time = 6 h; mp 207.1-207.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 3H), 7.31-7.28 (m, 1H), 7.20-7.02 (m, 13H), 6.95 (s, 1H), 6.90 (q, *J* = 8.0 Hz, 2H), 6.82-6.76 (m, 2H), 6.46 (s, 1H), 6.36 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 1H), 5.35 (d, *J* = 8.0 Hz, 1H), 3.43 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 151.5, 148.3, 145.3, 140.1, 137.5, 136.2, 132.2, 131.5, 129.7, 129.6, 129.6, 129.5, 129.4, 129.3, 129.0, 128.9, 128.6, 128.0, 127.8, 127.6, 127.5, 127.3, 126.4, 125.6, 125.5, 123.8, 122.2, 121.2, 118.5, 117.2, 116.9, 106.5, 67.1, 63.2, 54.5, 42.6. IR (KBr) *v* 3450, 3066, 1610, 1564, 1493, 1242, 752 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{35}Cl_2N_4$ $[M+H]^+$ 701.2233, found 701.2231.



1-(11-phenyl-1-(2-phenyl-1,2-dihydroisoquinolin-1-yl)-3-(*m*-tolyl)-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-(*m*-tolyl)methanimine (**13d**)

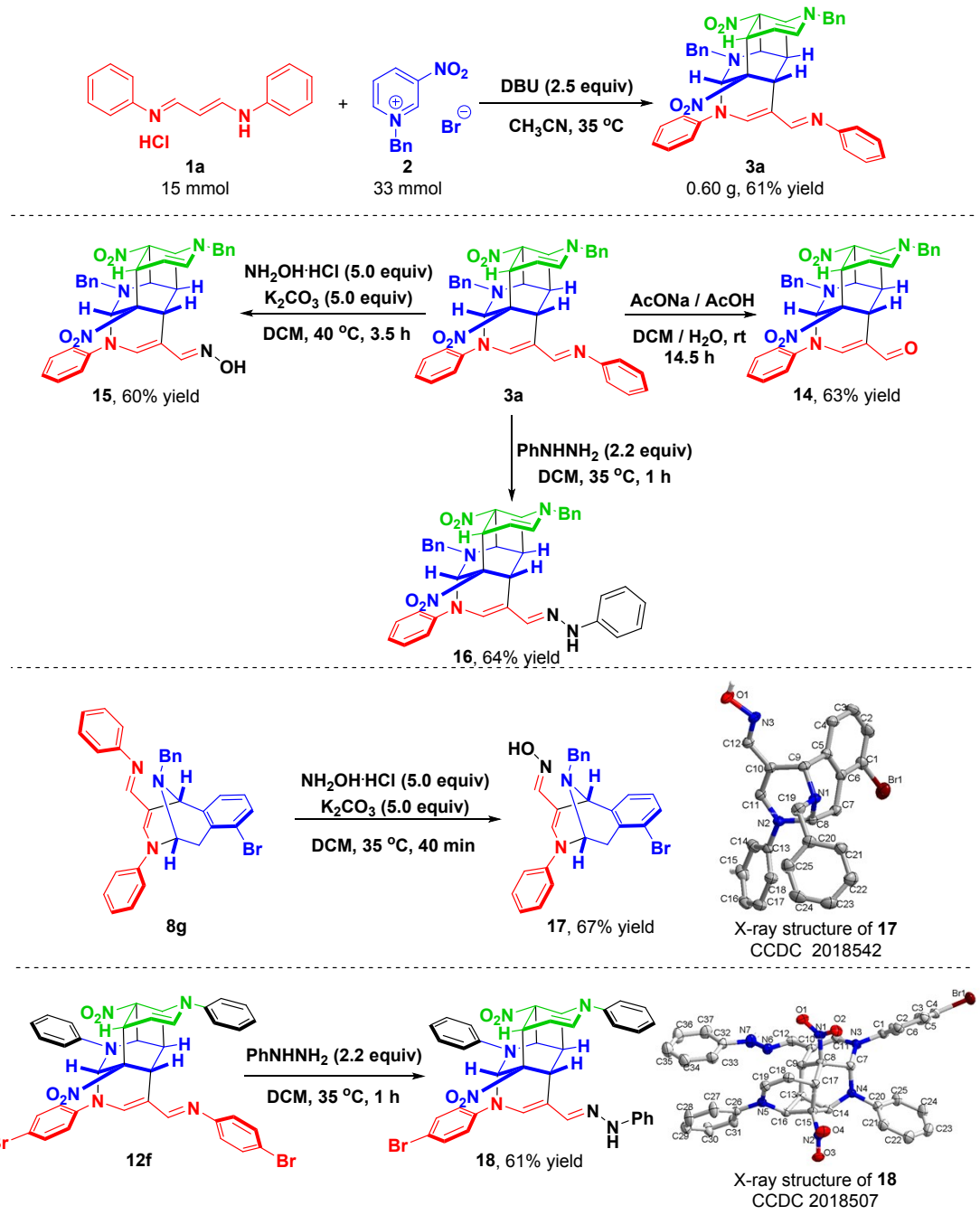
Yellow solid obtained by filtration of the precipitate; 77.7 mg, 78% yield; dr > 20:1; reaction time = 6 h; mp 212.6-213.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.40-7.33 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.19-7.15 (m, 4H), 7.09-6.99 (m, 6H), 6.93 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.83-6.75 (m, 3H), 6.52 (s, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 6.26 (s, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 6.02 (s, 1H), 5.41 (d, *J* = 8.0 Hz, 1H), 3.53 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 153.2, 148.6, 145.4, 141.8, 139.7, 138.6, 137.7, 136.6, 132.0, 131.4, 129.6, 129.4, 129.3, 129.2, 128.7, 128.5, 128.0, 127.9, 127.5, 127.2, 126.2, 125.6, 125.5, 125.0, 123.9, 123.5, 121.9, 121.7, 121.0, 118.6, 117.9, 116.8, 116.7, 116.6, 113.4, 106.8, 66.8, 63.4, 54.6, 43.1, 21.6, 21.4. IR (KBr) *v* 3439, 2104, 1636, 1551, 1530, 1267, 752 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{41}N_4$ $[M+H]^+$ 661.3326, found 661.3329.



1-(10-methoxy-1-(5-methoxy-2-phenyl-1,2-dihydroisoquinolin-1-yl)-3,11-diphenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocin-5-yl)-*N*-phenylmethanimine (**13e**)

Yellow solid obtained by filtration of the precipitate; 82.8 mg, 80% yield; dr > 20:1; reaction time = 6 h; mp 219.6-220.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.20-7.09 (m, 7H), 7.05-6.99 (m, 4H), 6.96-6.82 (m, 8H), 6.78 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.57 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.43-6.40 (m, 2H), 5.72 (d, J = 4.0 Hz, 1H), 5.71 (s, 1H), 5.64 (d, J = 8.0 Hz, 1H), 5.42 (d, J = 8.0 Hz, 1H), 3.96 (d, J = 4.0 Hz, 1H), 3.76 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.4, 153.2, 152.8, 148.0, 145.9, 142.2, 140.5, 136.2, 129.7, 129.3, 129.1, 128.8, 128.5, 128.0, 127.9, 125.1, 124.1, 122.5, 121.4, 121.2, 120.8, 120.7, 119.2, 119.1, 118.8, 116.4, 116.0, 116.0, 108.5, 107.9, 101.0, 66.9, 60.7, 55.1, 54.1, 45.4, one carbon in the aromatic region and one carbon in the aliphatic region were missing. IR (KBr) v 3447, 3055, 1574, 1493, 1256, 754 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{41}N_4O_2$ $[M+H]^+$ 693.3224, found 693.3221.

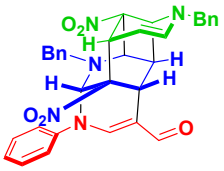
7. Scalable preparation of 3a and chemical conversions of 3a, 8g and 12f



Scheme S2 Scale-up preparation of **3a** and chemical conversions of **3a**, **8g** and **12f**.

General procedure for the scale-up preparation of 3a: To a 25.0 mL round-bottom flask were successively added 1,5-diazapentadienium salt **1a** (0.39 g, 15.0 mmol), *N*-benyl 3-nitropyridinium salt **2a** (0.97 g, 33.0 mmol), DBU (0.57 g, 37.5 mmol) and 10.0 mL of CH_3CN. The resulting mixture was stirred at 35 °C for 2 h. Then, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 15:1) to afford the desired product **3a** as a yellow solid in 61% yield (0.60 g).

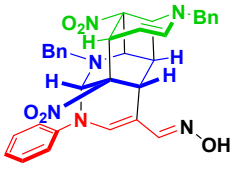
General procedure for the formation of 14: A 0.5 mL of sodium acetate/acetic acid aqueous solution (pH = 5) was added to a solution of **3a** (65.1 mg, 0.10 mmol) in 1.0 mL of CH_2Cl_2. The reaction mixture was stirred at 35 °C for 14.5 h until the complete consumption of **3a** as monitored by thin layer chromatography. Then, the mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **14** in 63% yield as a yellow solid.



1,7-dibenzyl-10a,11-dinitro-3-phenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine-5-carbaldehyde (**14**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 36.5 mg, 63% yield; dr > 20:1; reaction time = 14.5 h; mp 167.2-168.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.42-7.37 (m, 6H), 7.31-7.27 (m, 2H), 7.24-7.16 (m, 6H), 6.99-6.95 (m, 2H), 6.51 (d, J = 8.0 Hz, 1H), 5.73 (s, 1H), 4.37 (q, J = 16.0 Hz, 2H), 4.17 (d, J = 12.0 Hz, 1H), 4.11 (t, J = 8.0 Hz, 1H), 3.91 (dd, J_1 = J_2 = 4.0 Hz, 2H), 3.89 (d, J = 4.0 Hz, 1H), 3.77 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.68 (d, J = 16.0 Hz, 1H), 3.28 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.2, 147.7, 144.0, 139.2, 136.5, 136.4, 130.2, 128.9, 128.7, 128.2, 128.2, 128.0, 127.9, 126.7, 122.2, 115.5, 87.9, 82.8, 82.4, 78.5, 58.7, 58.5, 55.2, 52.0, 46.1, 39.5, 24.5. IR (KBr) ν 3399, 2921, 1624, 1460, 1187, 734 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{30}N_5O_5$ $[M+H]^+$ 576.2241, found 576.2238.

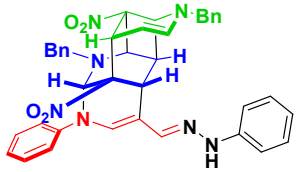
General procedure for the formation of 15: To a 10.0 mL vial were successively added **3a** (130.1 mg, 0.20 mmol), hydroxylamine hyrdochcloride (69.5 mg, 1.00 mmol), anhydrous potassium carbonate (138.2 mg, 1.00 mmol) and 2.0 mL of CH_2Cl_2. The resulting mixture was stirred at 40 °C for 3.5 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to afford the corresponding product **15** as a yellow solid in 60% yield.



1,7-dibenzyl-10a,11-dinitro-3-phenyl-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine-5-carbaldehyde oxime (**15**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 70.6 mg, 60% yield; dr > 20:1; reaction time = 3.5 h; mp 186.5-187.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.34-7.25 (m, 8H), 7.20 (t, J = 4.0 Hz, 3H), 7.10 (q, J = 8.0 Hz, 3H), 6.99 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 6.71 (s, 1H), 6.46 (d, J = 8.0 Hz, 1H), 5.65 (s, 1H), 4.32 (d, J = 4.0 Hz, 2H), 4.15-4.07 (m, 2H), 3.90 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.78 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.73 (d, J = 16.0 Hz, 2H), 3.31 (d, J = 8.0 Hz, 1H), 2.66 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 144.7, 138.9, 136.9, 136.9, 134.2, 129.9, 129.3, 128.6, 128.6, 128.2, 128.1, 127.8, 125.0, 121.1, 118.6, 115.1, 107.3, 88.0, 83.0, 82.9, 58.2, 56.3, 52.0, 45.5, 39.7, 26.2. IR (KBr) ν 3417, 3062, 1638, 1541, 1495, 938, 750 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{31}N_6O_5$ $[M+H]^+$ 591.2350, found 591.2352.

General procedure for the formation of 16: Phenylhyrdrazine (47.5 mg, 0.44 mmol) was successively added to a solution of **3a** (130.1 mg, 0.20 mmol) in 2.0 mL of CH_2Cl_2 by syringe. The resulting mixture was stirred at 35 °C for 1 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 6:1) to afford the corresponding product **16** as a yellow solid in 64% yield.

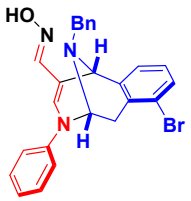


1,7-dibenzyl-10a,11-dinitro-3-phenyl-5-(2-phenylhydrazono)methyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine (**16**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 6:1); 85.0 mg, 64% yield; dr > 20:1; reaction time = 1 h; mp 151.7-152.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 2H), 7.28-7.25 (m, 7H), 7.24-7.16 (m, 5H), 7.07-7.00 (m, 7H), 6.81 (br, 1H), 6.65 (br, 1H), 6.49 (d, J = 8.0 Hz, 1H), 5.67 (s, 1H), 4.46 (d, J = 16.0 Hz, 2H), 4.13 (d, J = 12.0 Hz, 1H), 4.09 (d, J = 8.0 Hz, 1H), 3.93 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 3.85 (br, 1H), 3.76 (d, J = 12.0 Hz, 1H), 3.35 (d, J = 8.0 Hz, 1H), 2.84 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.6, 137.0, 136.7, 136.7, 131.6, 129.8, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.7,

127.5, 124.4, 120.7, 112.5, 88.1, 83.6, 82.3, 58.1, 56.8, 56.6, 51.2, 45.3, 39.8, 26.5, one carbon missing in the aromatic region. IR (KBr) *v* 3443, 2925, 1630, 1543, 750 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{36}N_7O_4$ $[M+H]^+$ 666.2667, found 664.2671.

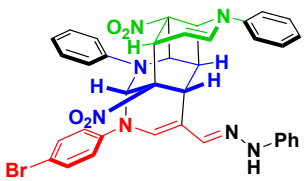
General procedure for the formation of 17: To a 10.0 mL vial were successively added **8g** (77.9 mg, 0.15 mmol), hydroxylamine hyrdochcloride (52.1 mg, 0.75 mmol), anhydrous potassium carbonate (103.7 mg, 0.75 mmol) and 2.0 mL of CH_2Cl_2. The resulting mixture was stirred at 35 °C for 40 min, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 10:1 to 6:1) to afford the corresponding product **17** as a yellow solid in 67% yield.



11-benzyl-10-bromo-3-phenyl-1,2,3,6-tetrahydro-2,6-epiminobenzo[*d*]azocine-5-carbaldehyde oxime (**17**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 6:1); 46.4 mg, 67% yield; dr > 20:1; reaction time = 40 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.37-7.29 (m, 9H), 7.07 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 2H), 6.92 (s, 1H), 6.81 (br, 1H), 5.03 (d, J = 8.0 Hz, 1H), 4.80 (s, 1H), 3.81 (d, J = 16.0 Hz, 1H), 3.67 (d, J = 16.0 Hz, 1H), 3.25 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.96 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 143.9, 141.5, 137.3, 132.3, 130.8, 130.1, 129.8, 129.3, 128.4, 127.5, 127.2, 125.4, 124.9, 123.1, 117.9, 105.9, 68.4, 56.6, 53.0, 38.1. IR (KBr) *v* 3441, 2920, 1622, 1588, 1184, 928, 752 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{23}BrN_3O$ $[M+H]^+$ 460.1019, found 460.1017.

General procedure for the formation of 18: Phenylhyrdrazine (32.4 mg, 0.30 mmol) was successively added to a solution of **12f** (117.1 mg, 0.15 mmol) in 2.0 mL of CH_2Cl_2 by syringe. The resulting mixture was stirred at 35 °C for 1 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 30:1 to 10:1) to afford the corresponding product **18** as a yellow solid in 61% yield.



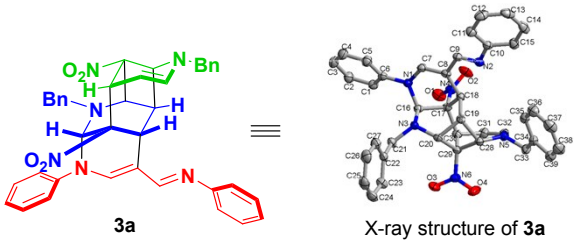
3-(4-bromophenyl)-10a,11-dinitro-1,7-diphenyl-5-((2-phenylhydrazono)methyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine (**18**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 10:1); 65.5 mg, 61% yield; dr > 20:1; reaction time = 1 h; mp 228.9-229.7 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 7.55 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 4H), 7.32 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 3H), 7.03 (d, J = 4.0 Hz, 3H), 6.98 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 8.0 Hz, 1H), 6.81 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.55 (t, J = 8.0 Hz, 3H), 4.98 (d, J = 8.0 Hz, 1H), 4.88 (d, J = 8.0 Hz, 1H), 4.42 (t, J = 8.0 Hz, 1H), 4.25 (d, J = 4.0 Hz, 1H), 3.76 (s, 1H), 3.40 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.5, 145.3, 143.7, 143.7, 137.6, 132.0, 131.8, 129.7, 129.5, 128.9, 128.8, 122.5, 121.7, 121.0, 120.0, 117.4, 115.0, 114.5, 112.7, 111.3, 87.7, 87.3, 84.0, 71.4, 57.6, 50.7, 45.8, 38.4, 26.4. IR (KBr) v 3452, 1637, 1597, 1493, 751 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}BrN_7O_4$ $[M+H]^+$ 716.1615, found 716.1605.

8. Crystal structures of 3a, 5a, 7a, 8e, 12a, 13a, 17 and 18

8.1 Crystal structure of 3a

Preparation of the single crystals of **3a**: 30.0 mg of pure compound **3a** was dissolved in the combined solvents of petroleum ether and ethyl acetate (6 mL, v/v = 5:1) 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 **3a**. The data were collected by a Rigaku Gemini E at 293.0 K.



3a

X-ray structure of **3a**
CCDC 2018508

Bond precision: C-C = 0.0036 A Wavelength=1.54184

Cell: a=41.271(2) b=10.95781(13) c=23.7743(13)
alpha=90 beta=142.144(12) gamma=90

Temperature: 293 K

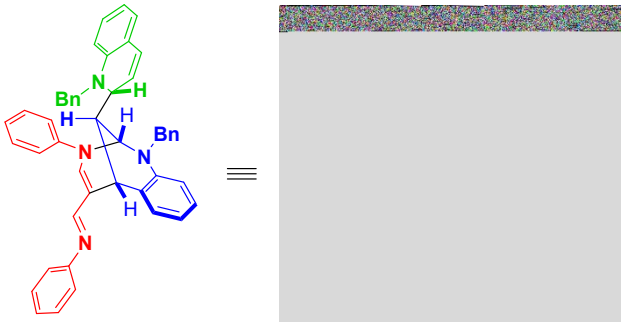
	Calculated	Reported
Volume	6598.1(18)	6598.2(12)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	$C_{39}H_{34}N_6O_4$	$C_{39}H_{34}N_6O_4$
Sum formula	$C_{39}H_{34}N_6O_4$	$C_{39}H_{34}N_6O_4$
Mr	650.72	650.72
Dx,g cm-3	1.310	1.310
Z	8	8
Mu (mm-1)	0.701	0.701
F000	2736.0	2736.0
F000'	2744.18	
h,k,lmax	49,13,28	49,13,28
Nref	5891	5889
Tmin,Tmax	0.881,0.926	0.729,1.000
Tmin'	0.875	

Correction method= # Reported T Limits: Tmin=0.729 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 1.000 Theta(max)= 67.076
R(reflections)= 0.0449(4897) wR2(reflections)= 0.1271(5889)
S = 1.042 Npar= 442

8.2 Crystal structure of 5a

Preparation of the single crystals of **5a**: about 30.0 mg of pure compound **5a** was dissolved in the combined solvents of petroleum ether and ethyl acetate (6 mL, v/v = 5:1) at room temperature. To prevent the decomposition of **5a**, a drop of NEt_3 was added to this solution. 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 **5a**. The data were collected by a Rigaku Gemini E at 293.0 K.



5a ≡ X-ray structure of **5a**
CCDC 2018509

Bond precision: C-C = 0.0036 A Wavelength=0.71073

Cell: a=11.4180(7) b=11.7859(7) c=13.6713(9)
alpha=102.345(2) beta=99.707(2) gamma=97.839(2)

Temperature: 150 K

	Calculated	Reported
Volume	1742.86(19)	1742.86(19)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{47}H_{40}N_4$	$C_{47}H_{40}N_4$
Sum formula	$C_{47}H_{40}N_4$	$C_{47}H_{40}N_4$
Mr	660.83	660.83
Dx,g cm-3	1.259	1.259
Z	2	2
Mu (mm-1)	0.074	0.074
F000	700.0	700.0
F000'	700.24	
h,k,lmax	13,14,16	13,14,16
Nref	6229	6206
Tmin,Tmax	0.988,0.999	0.660,0.746
Tmin'	0.988	

Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.123

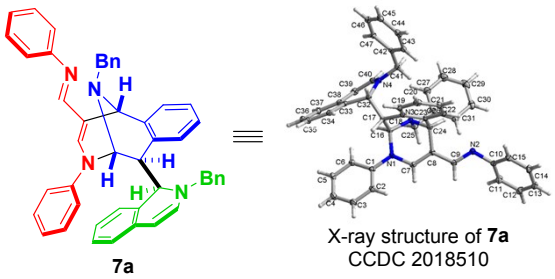
R(reflections)= 0.0556(3834) wR2(reflections)= 0.1329(6206)

S = 1.023 Npar= 461

8.3 Crystal structure of 7a

Preparation of the single crystals of **7a**: about 30.0 mg of pure compound **7a** was dissolved in the combined solvents of petroleum ether and ethyl acetate (6 mL, v/v = 5:1) at room temperature. To prevent the decomposition of **7a**, a drop of NEt_3 was added to

this solution. 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 **7a**. The data were collected by a Rigaku Gemini E at 293.0 K.



Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=10.9944(6) b=12.7289(6) c=13.2362(6)

alpha=73.126(2) beta=89.213(2) gamma=79.311(2)

Temperature: 150 K

	Calculated	Reported
Volume	1740.27(15)	1740.27(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{47}H_{40}N_4$	$C_{47}H_{40}N_4$
Sum formula	$C_{47}H_{40}N_4$	$C_{47}H_{40}N_4$
Mr	660.83	660.83
Dx,g cm-3	1.261	1.261
Z	2	2
Mu (mm-1)	0.074	0.074
F000	700.0	700.0
F000'	700.24	
h,k,lmax	13,15,15	13,15,15
Nref	6204	6187
Tmin,Tmax	0.984,0.988	0.570,0.746
Tmin'	0.982	

Correction method= # Reported T Limits: Tmin=0.570 Tmax=0.746

AbsCorr = MULTI-SCAN

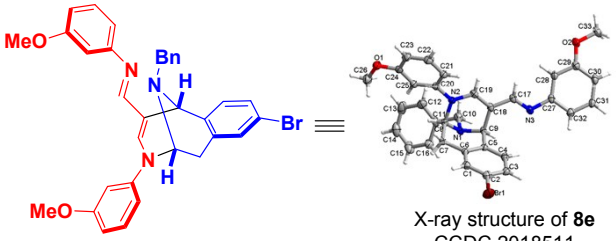
Data completeness= 0.997 Theta(max)= 25.123

R(reflections)= 0.0527(4136) wR2(reflections)= 0.1263(6187)

S = 1.036 Npar= 461

8.4 Crystal structure of 8e

Preparation of the single crystals of **8e**: about 15.0 mg of pure compound **8a** was dissolved in $CDCl_3$ 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 one month, 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 **8e**. The data were collected by a Bruker D8 VENTURE PHOTON II CCD diffractometer at 273.0 K.



8e

X-ray structure of **8e**
CCDC 2018511

Bond precision: C-C = 0.0065 A Wavelength=0.71073

Cell: a=14.509(3) b=18.909(4) c=10.234(2)
alpha=90 beta=103.567(5) gamma=90

Temperature: 285 K

	Calculated	Reported
Volume	2729.4(10)	2729.2(10)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{33}H_{30}BrN_3O_2$	$C_{33}H_{30}BrN_3O_2$
Sum formula	$C_{33}H_{30}BrN_3O_2$	$C_{33}H_{30}BrN_3O_2$
Mr	580.50	580.51
Dx,g cm-3	1.413	1.413
Z	4	4
Mu (mm-1)	1.542	1.542
F000	1200.0	1200.0
F000'	1199.27	
h,k,lmax	18,23,12	18,23,12
Nref	5588	5580
Tmin,Tmax	0.831,0.884	0.641,0.746
Tmin'	0.831	

Correction method= # Reported T Limits: Tmin=0.641 Tmax=0.746 AbsCorr = MULTI-SCAN

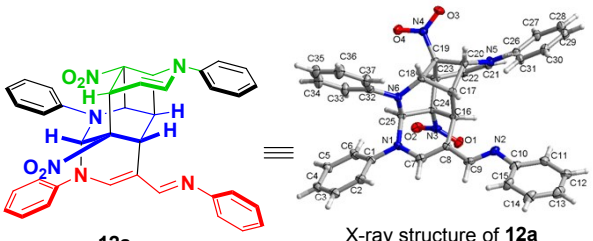
Data completeness= 0.999 Theta(max)= 26.372

R(reflections)= 0.0556(2611) wR2(reflections)= 0.1363(5580)

S = 1.000 Npar= 355

8.5 Crystal structure of 12a

Preparation of the single crystals of **12a**: about 15.0 mg of pure compound **12a** was dissolved in the combined solvents of dichloromethane and ethanol (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 three days, several small particles were observed at the bottom of the bottle. The crystals were chosen and subjected to the single crystal X-ray diffraction analysis for the determination of the structure and relative configuration of **12a**. The data were collected by a Bruker D8 VENTURE PHOTON II CCD diffractometer at 273.0 K.



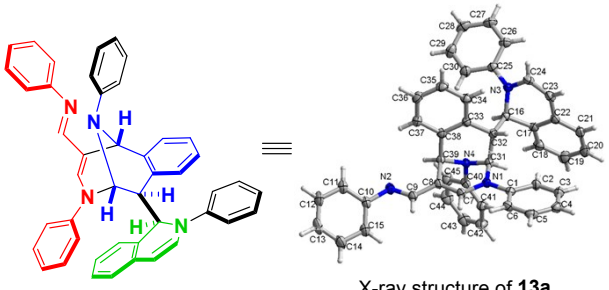
Bond precision:	C-C = 0.0075 A		Wavelength=0.71073
Cell:	a=27.936(2)	b=8.2416(4)	c=27.402(2)
	alpha=90	beta=103.792(2)	gamma=90
Temperature: 150 K			
	Calculated		Reported
Volume	6127.1(7)		6127.1(7)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	$C_{37}H_{30}N_6O_4$		$C_{37}H_{30}N_6O_4$
Sum formula	$C_{37}H_{30}N_6O_4$		$C_{37}H_{30}N_6O_4$
Mr	622.67		622.67
Dx,g cm-3	1.350		1.350
Z	8		8
Mu (mm-1)	0.090		0.090
F000	2608.0		2608.0
F000'	2609.08		
h,k,lmax	33,9,32		33,9,32
Nref	10938		10931
Tmin,Tmax	0.986,0.991		0.658,0.739
Tmin'	0.977		

Correction method= # Reported T Limits: Tmin=0.658 Tmax=0.739
AbsCorr = MULTI-SCAN
Data completeness= 0.999 Theta(max)= 25.123
R(reflections)= 0.0819(5108) wR2(reflections)= 0.2397(10931)

S = 1.000 Npar= 847

8.6 Crystal structure of 13a

Preparation of the single crystals of **13a**: about 15.0 mg of pure compound **13a** was dissolved in the combined solvents of dichloromethane and ethanol (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 **13a**. The data were collected by a Bruker D8 VENTURE PHOTON II CCD diffractometer at 273.0 K.



13a X-ray structure of **13a** CCDC 2018505

Bond precision: C-C = 0.0047 A Wavelength=0.71073

Cell: a=9.6677(17) b=14.679(3) c=15.095(3)

alpha=88.518(6) beta=72.204(6) gamma=87.368(6)

Temperature: 266 K

	Calculated	Reported
Volume	2037.4(7)	2037.3(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{45}H_{36}N_4$, $2(CH_2Cl_2)$	$C_{45}H_{36}N_4$, $2(CH_2Cl_2)$
Sum formula	$C_{47}H_{40}Cl_4\ N_4$	$C_{47}H_{40}Cl_4N_4$
Mr	802.63	802.63
Dx,g cm-3	1.308	1.308
Z	2	2
Mu (mm-1)	0.329	0.329
F000	836.0	836.0
F000'	837.43	
h,k,lmax	12,18,18	12,18,18
Nref	8326	8306
Tmin,Tmax	0.950,0.968	0.698,0.746
Tmin'	0.949	

Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.746 AbsCorr = MULTI-SCAN

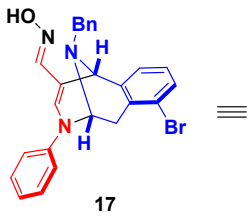
Data completeness= 0.998 Theta(max)= 26.372

R(reflections)= 0.0685(4731) wR2(reflections)= 0.2159(8306)

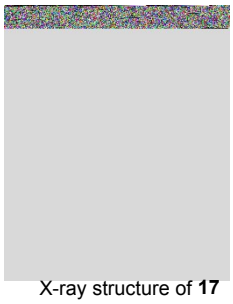
S = 1.030 Npar= 497

8.7 Crystal structure of 17

Preparation of the single crystals of **17**: about 30.0 mg of pure compound **17** was dissolved in the combined solvents of dichloromethane and methanol (6 mL, v/v = 1:1) at 0 °C. 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 **17**. The data were collected by a Rigaku Gemini E at 293.0 K.



17



X-ray structure of **17**
CCDC 2018542

Bond precision: C-C = 0.0048 A Wavelength=1.54184

Cell: a=11.1382(4) b=8.5927(3) c=22.4191(6)

alpha=90 beta=96.700(3) gamma=90

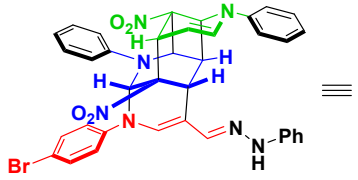
Temperature: 293 K

	Calculated	Reported
Volume	2131.02(12)	2131.01(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{25}H_{22}BrN_3O$	$C_{25}H_{22}BrN_3O$
Sum formula	$C_{25}H_{22}BrN_3O$	$C_{25}H_{22}BrN_3O$
Mr	460.36	460.36
Dx,g cm-3	1.435	1.435
Z	4	4
Mu (mm-1)	2.794	2.794
F000	944.0	944.0
F000'	943.52	
h,k,lmax	13,10,26	13,10,26
Nref	3813	3807
Tmin,Tmax	0.710,0.756	0.847,1.000
Tmin'	0.644	

Correction method= # Reported T Limits: Tmin=0.847 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 67.075
R(reflections)= 0.0465(3089) wR2(reflections)= 0.1302(3807)
S = 1.028 Npar= 275

8.8 Crystal structure of 18

Preparation of the single crystals of **18**: 8.0 mg of pure compound **18** was dissolved in the combined solvents of chloroform and ethanol (6 mL, v/v = 2:1) 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 day, 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 **18**. The data were collected by a Rigaku Gemini E at 293.0 K.



18

X-ray structure of **18**
CCDC 2018507

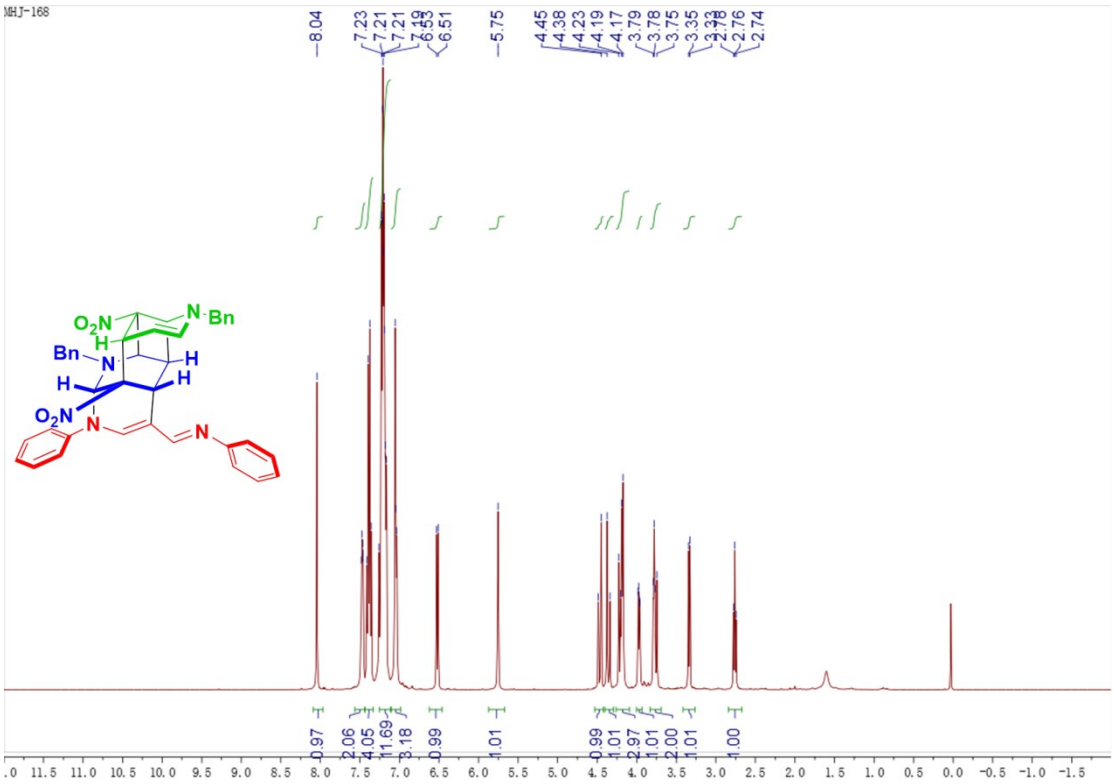
Bond precision: C-C = 0.0078 A Wavelength=1.54184
Cell: a=10.61266(19) b=19.0807(5) c=28.5794(7)
alpha=73.853(2) beta=82.1239(17) gamma=87.0339(19)
Temperature: 293 K

	Calculated	Reported
Volume	5505.9(2)	5506.0(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{37}H_{30}BrN_7O_4$ [+ solvent]	$C_{37}H_{30}BrN_7O_4$
Sum formula	$C_{37}H_{30}BrN_7O_4$ [+ solvent]	$C_{37}H_{30}BrN_7O_4$
Mr	716.58	716.59
Dx,g cm-3	1.297	1.297
Z	6	6
Mu (mm-1)	1.915	1.915
F000	2208.0	2208.0
F000'	2210.01	
h,k,lmax	12,22,34	12,22,34
Nref	19673	19619
Tmin,Tmax	0.813,0.875	0.870,1.000

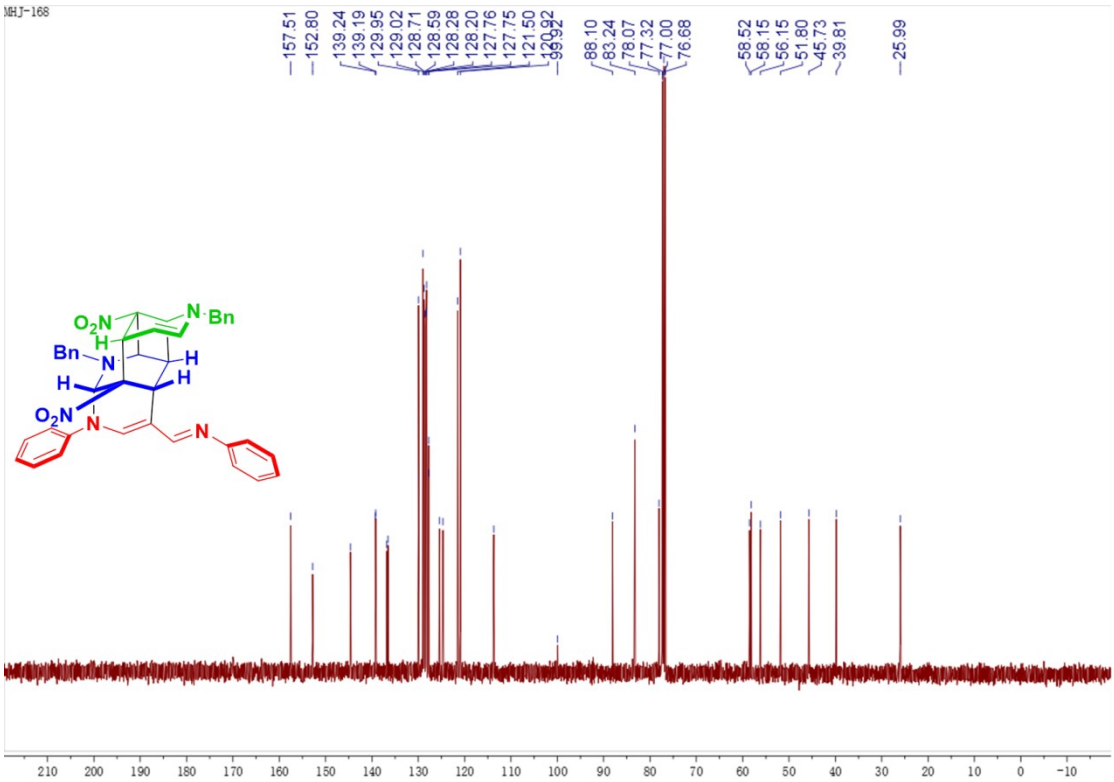
Tmin' 0.810
Correction method= # Reported T Limits: Tmin=0.870 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.997 Theta(max)= 67.077
R(reflections)= 0.0668(12122) wR2(reflections)= 0.2084(19619)
S = 1.044 Npar= 1331

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

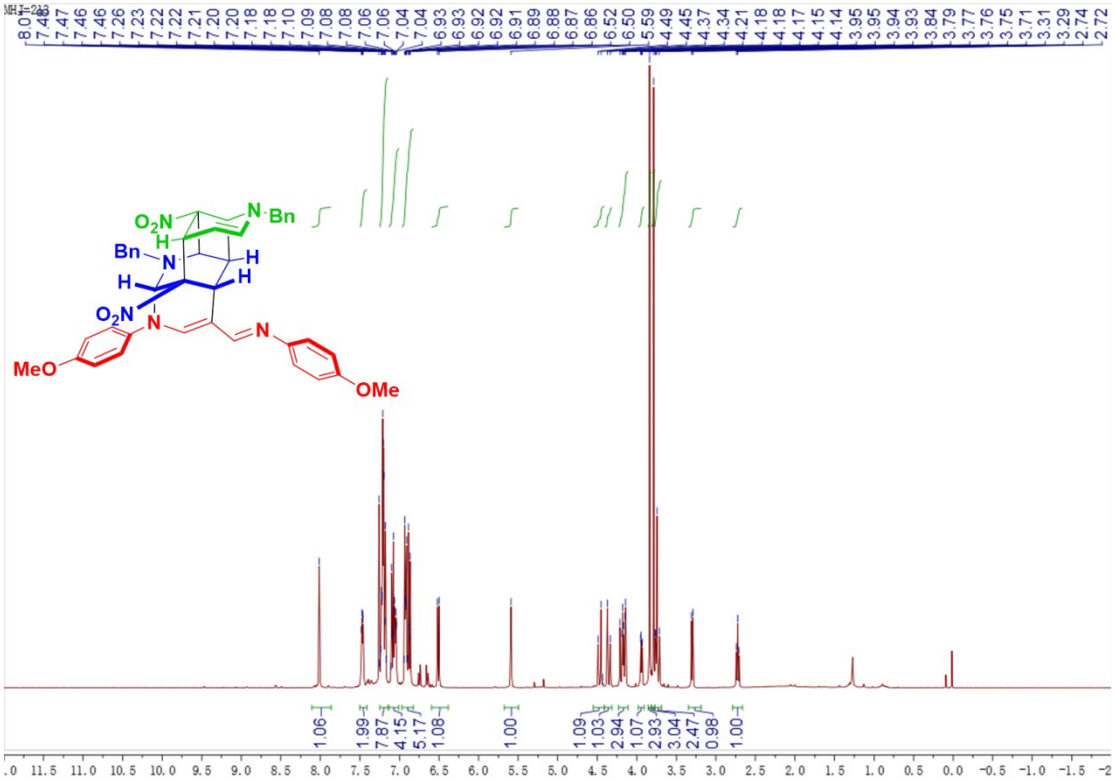
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



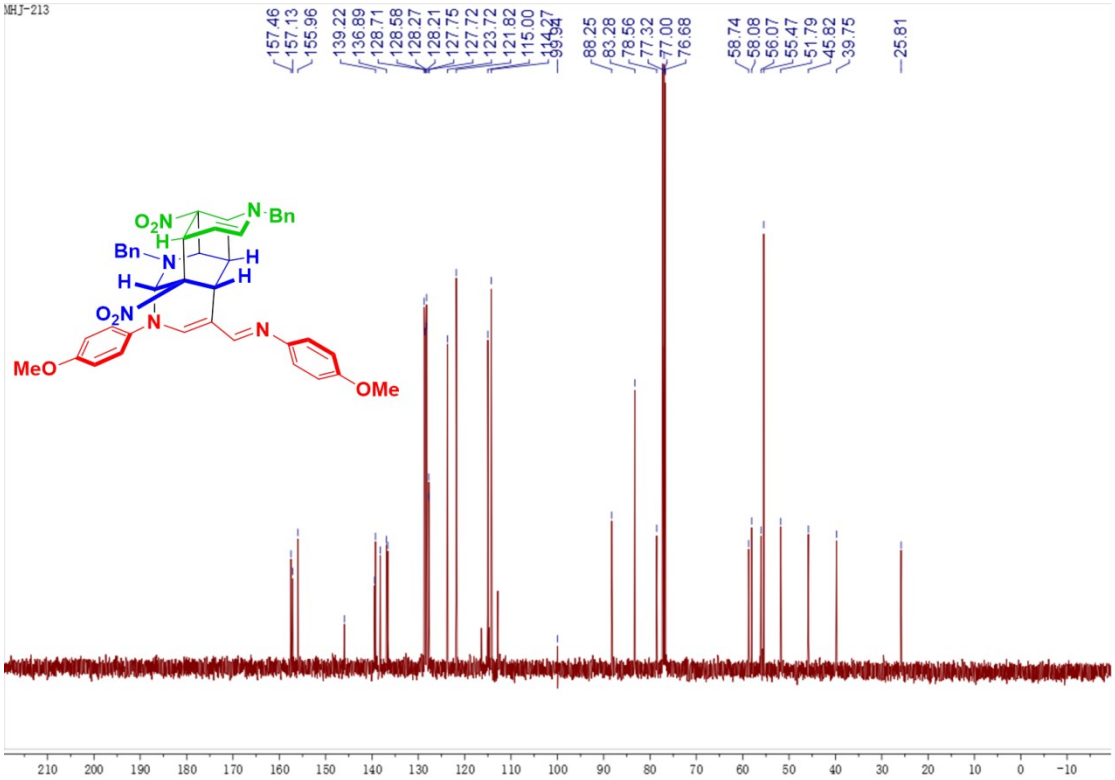
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



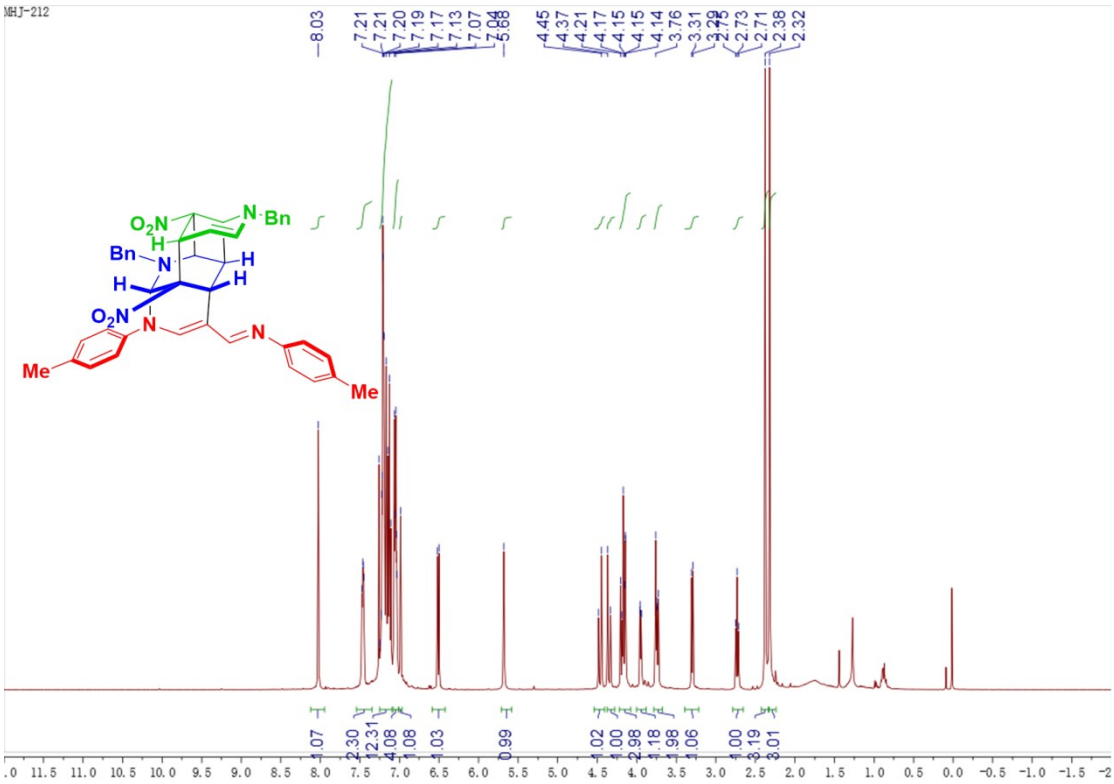
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



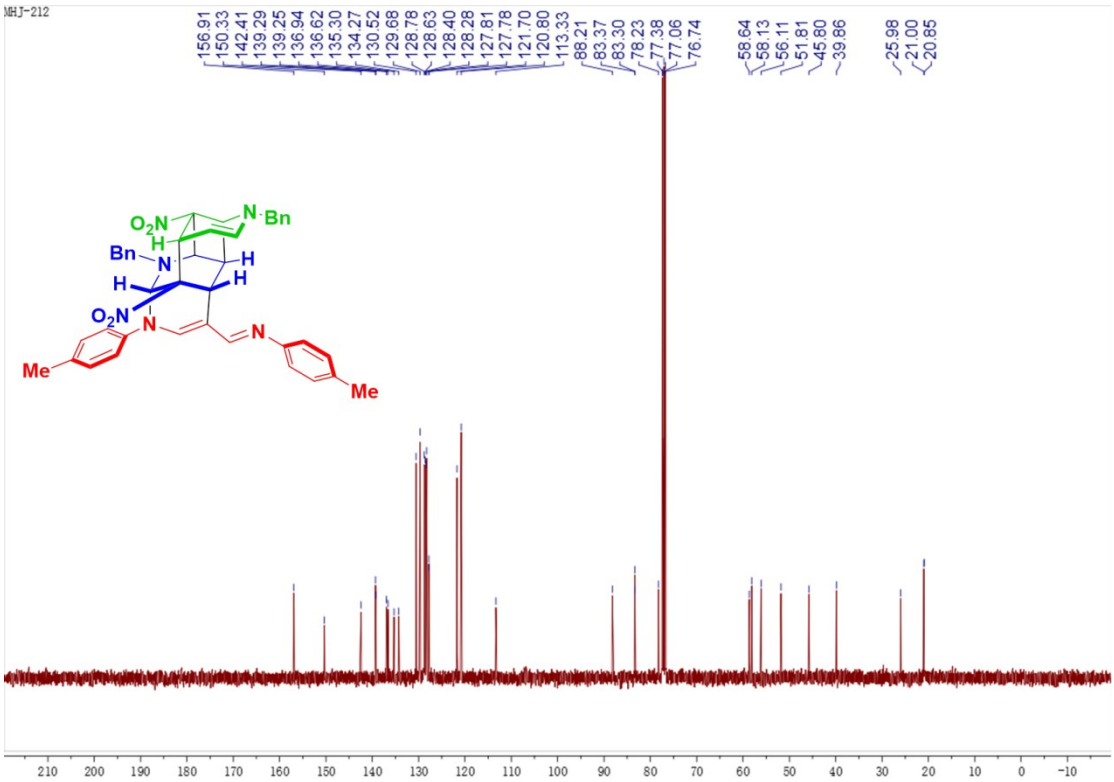
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



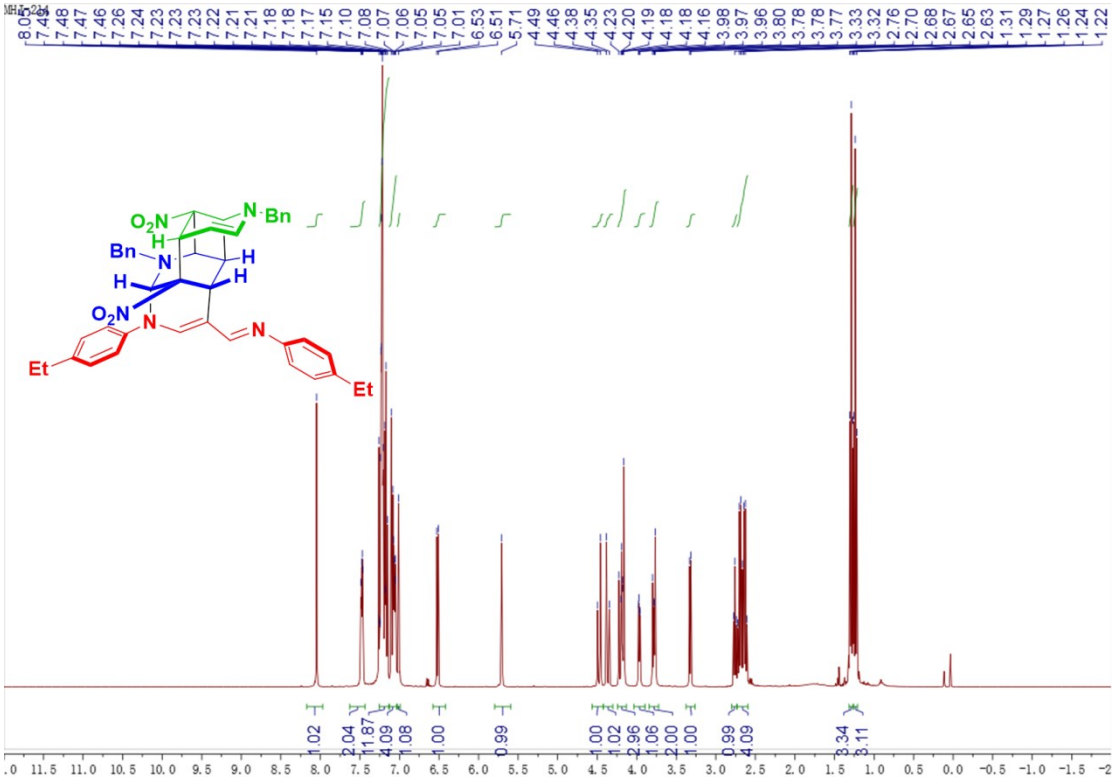
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



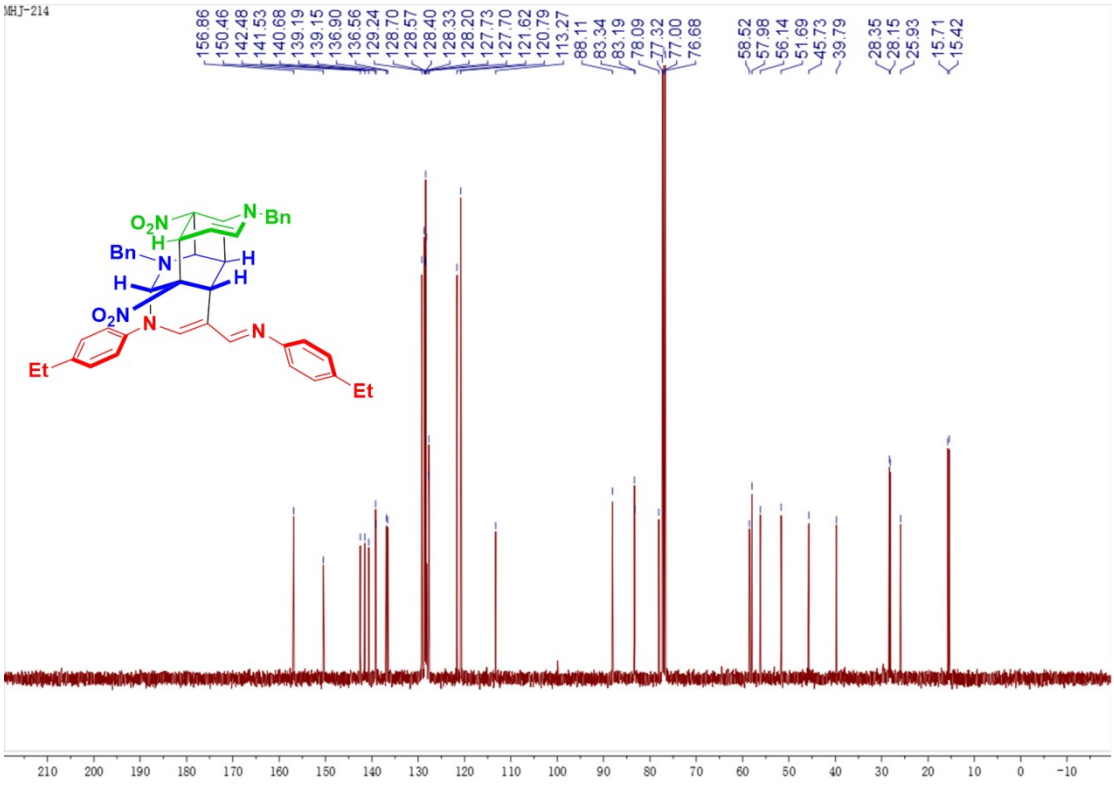
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



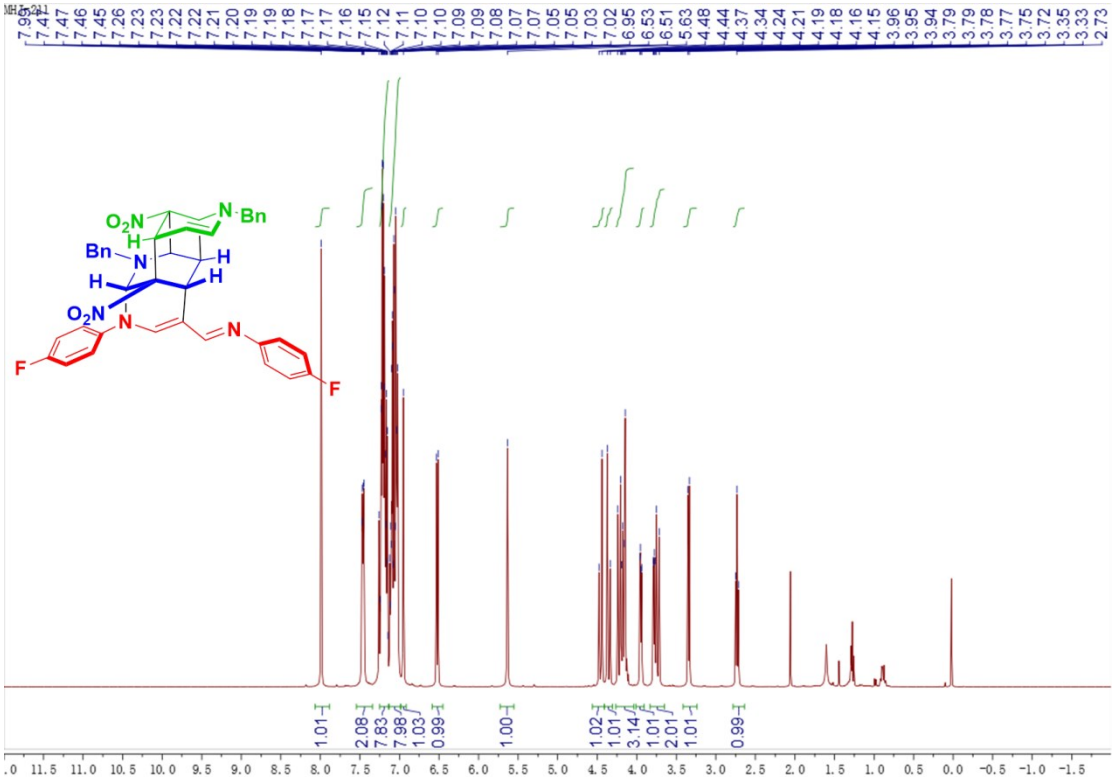
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



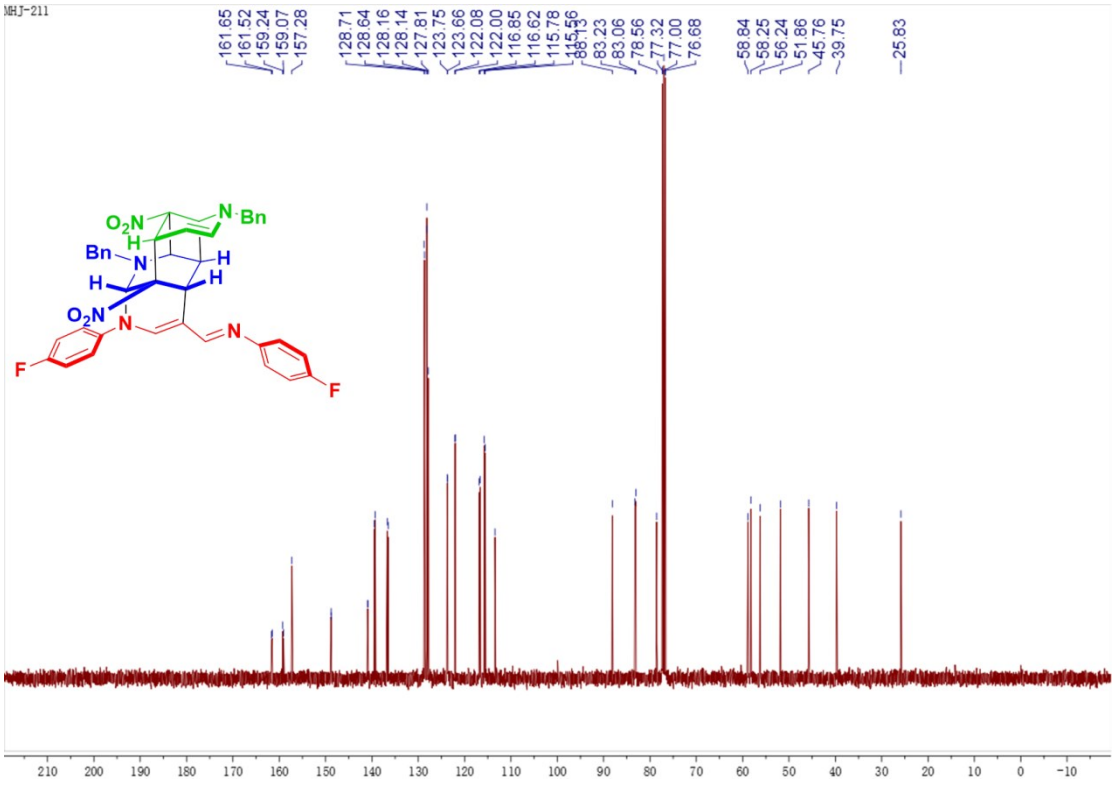
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



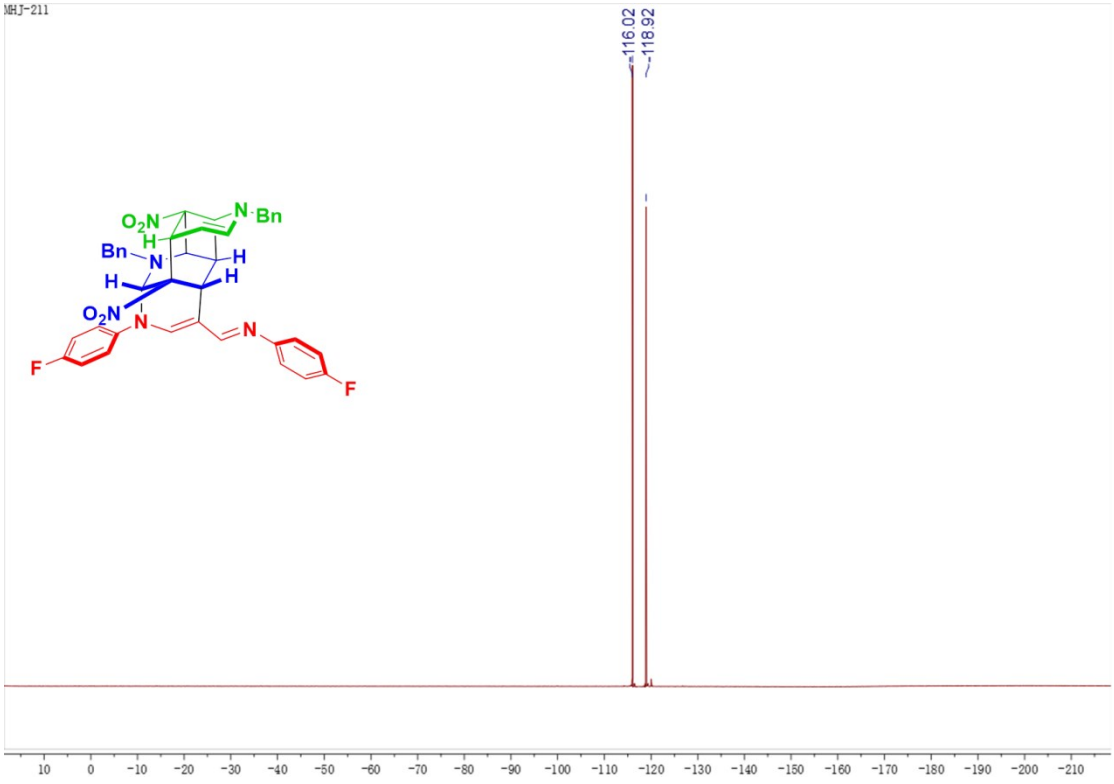
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



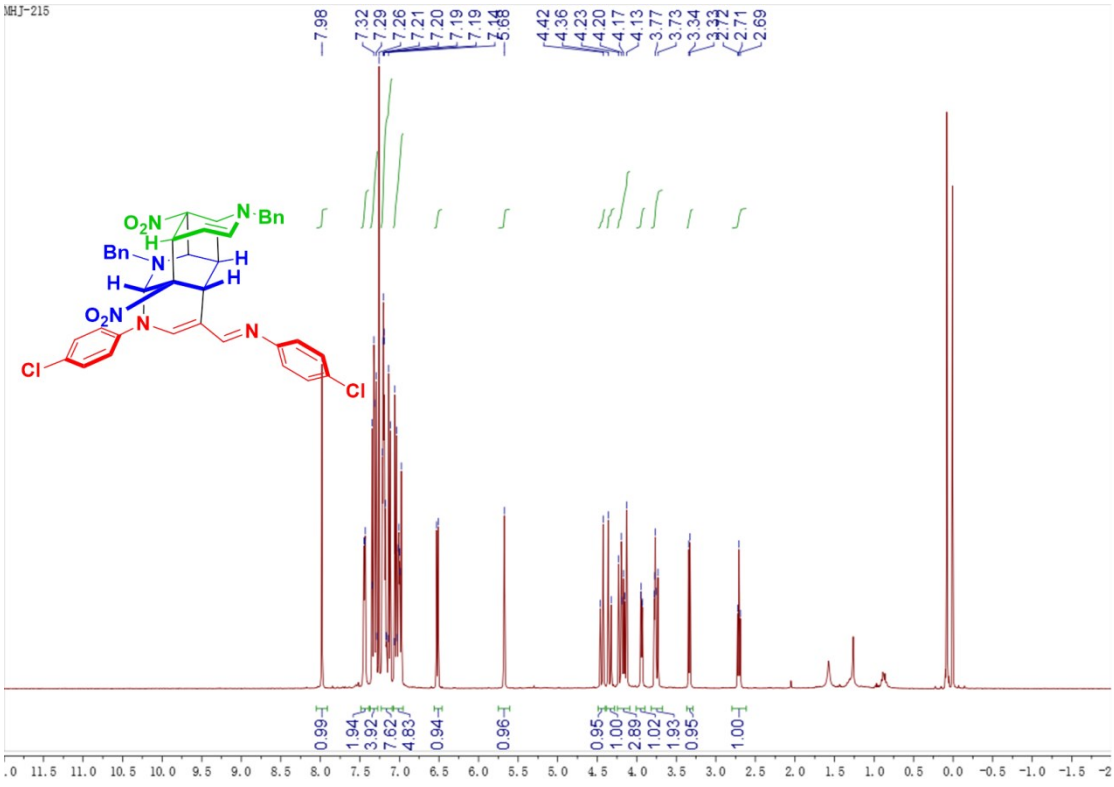
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



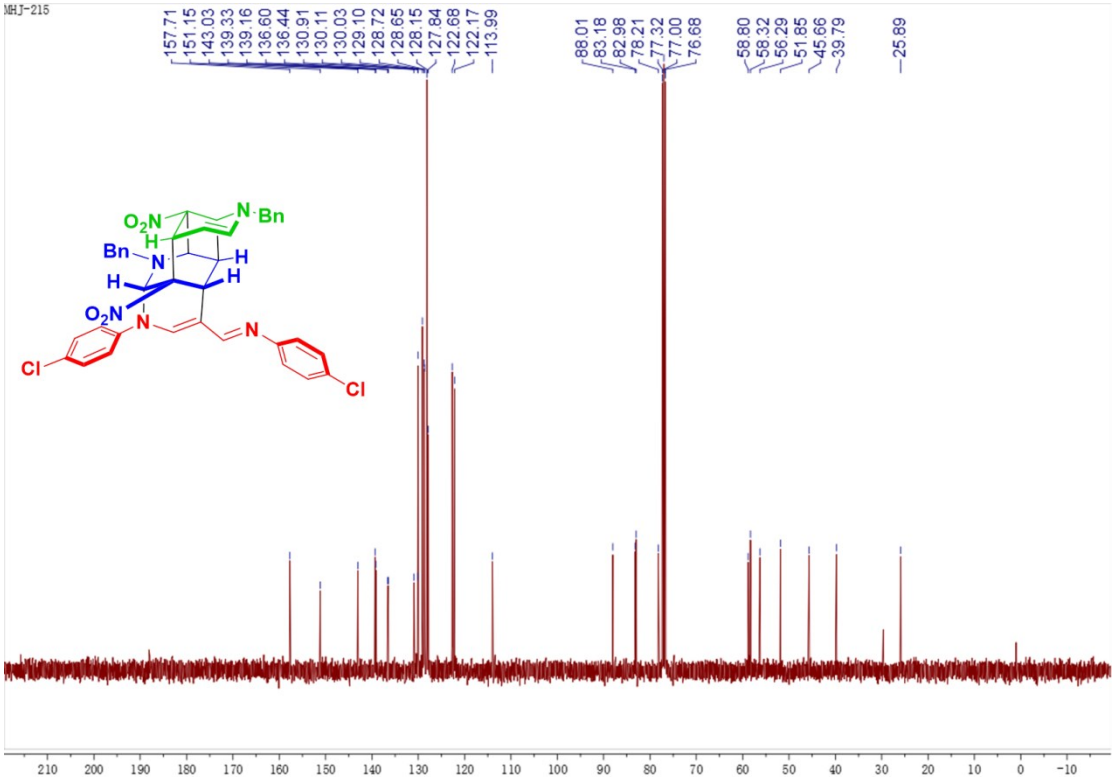
^{19}F NMR spectrum of **3e** (375 MHz, $CDCl_3$)



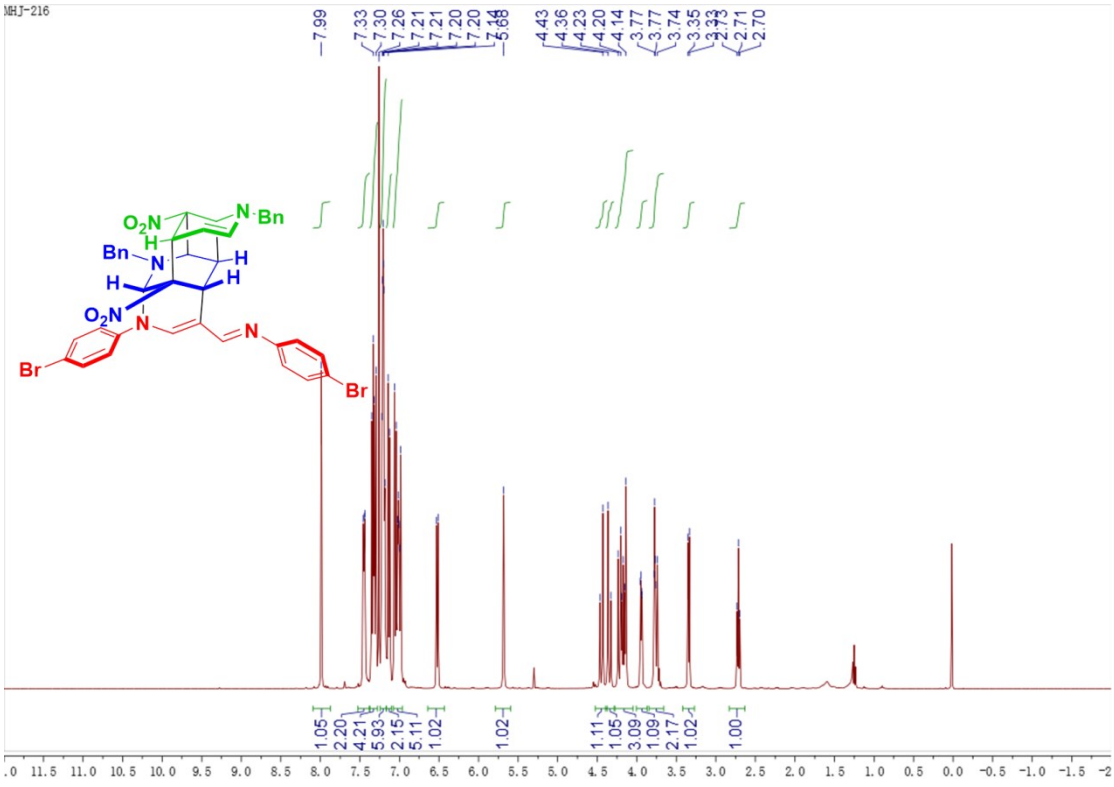
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



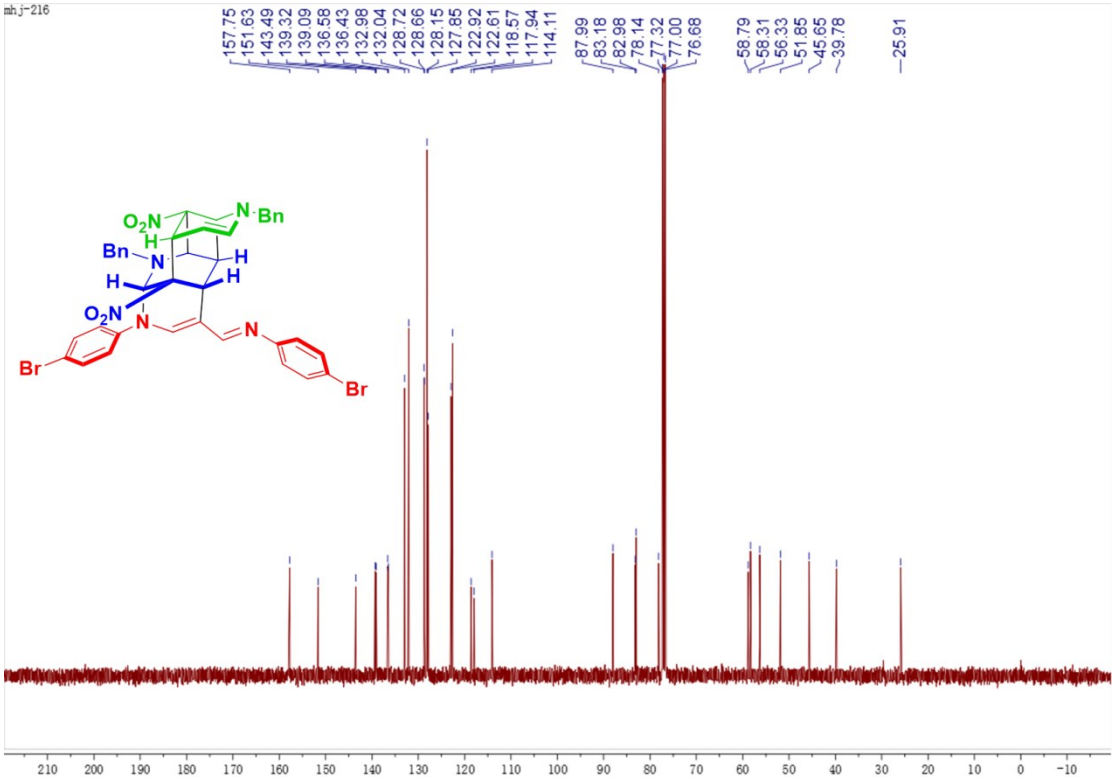
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



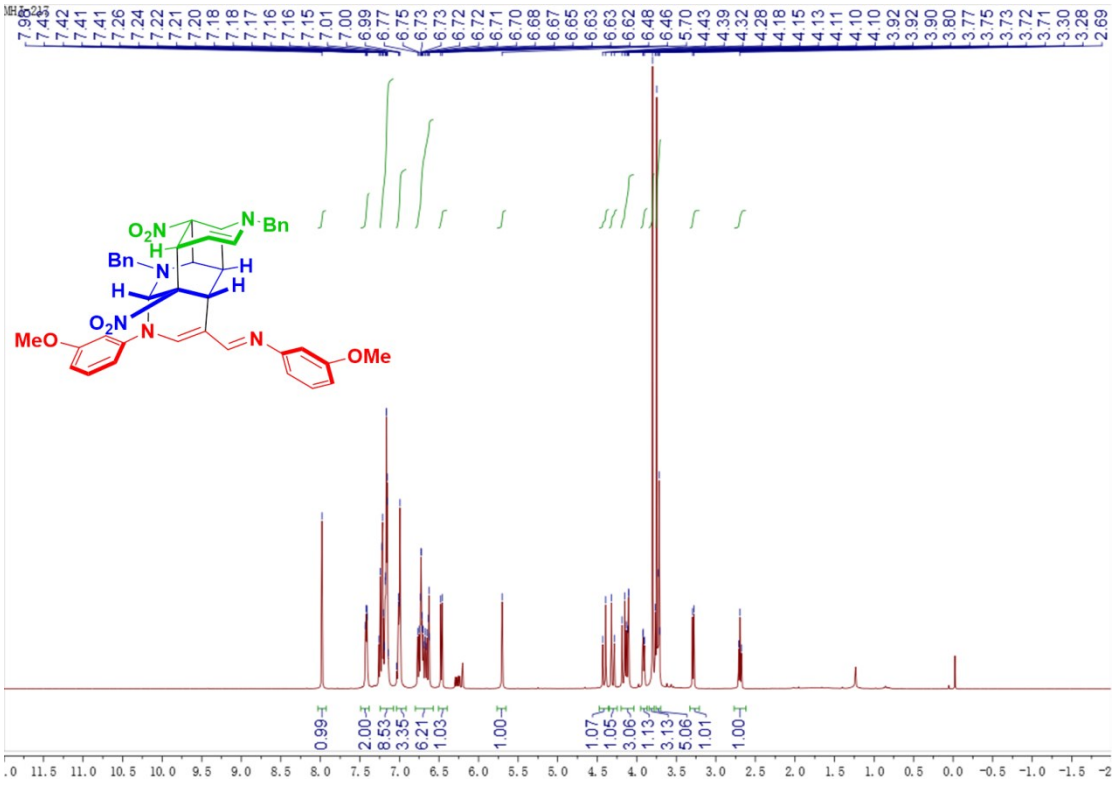
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



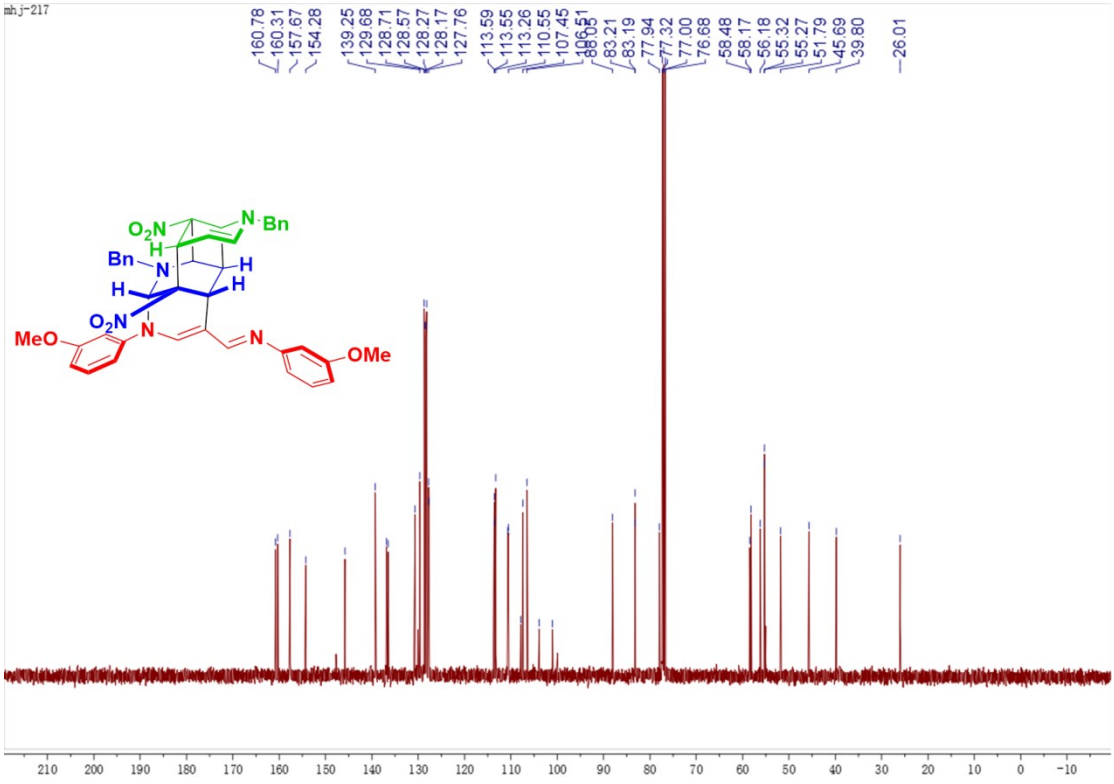
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



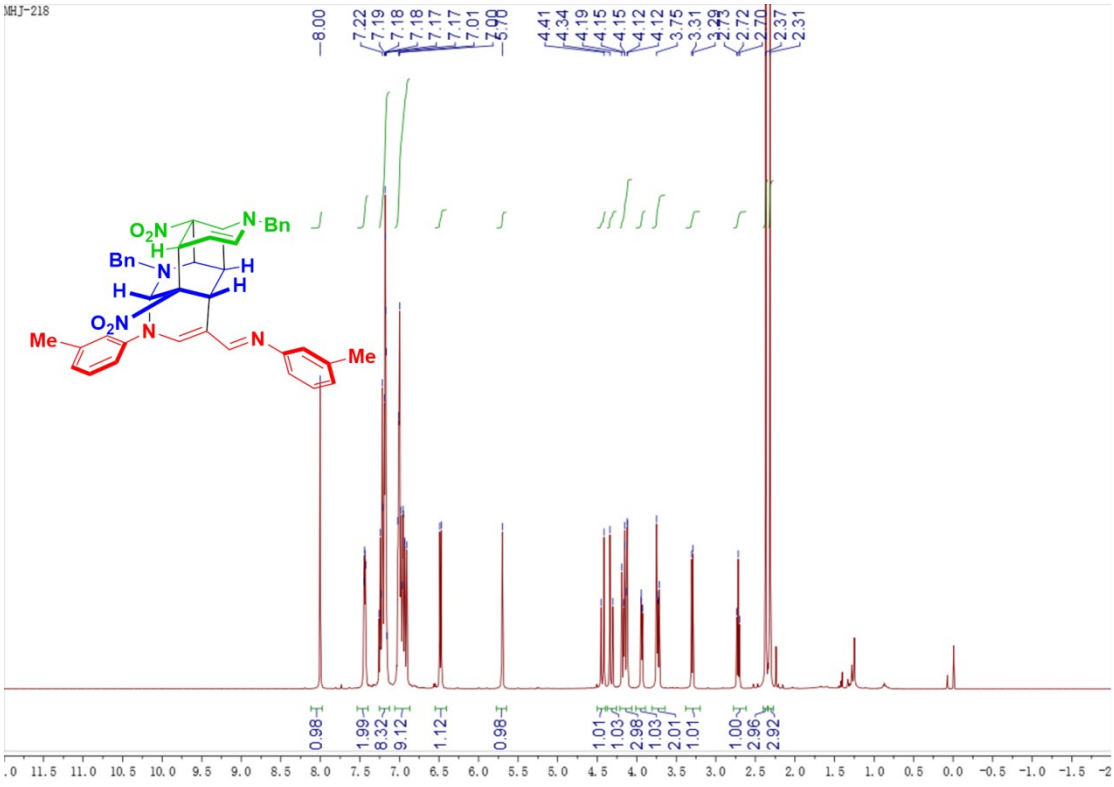
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



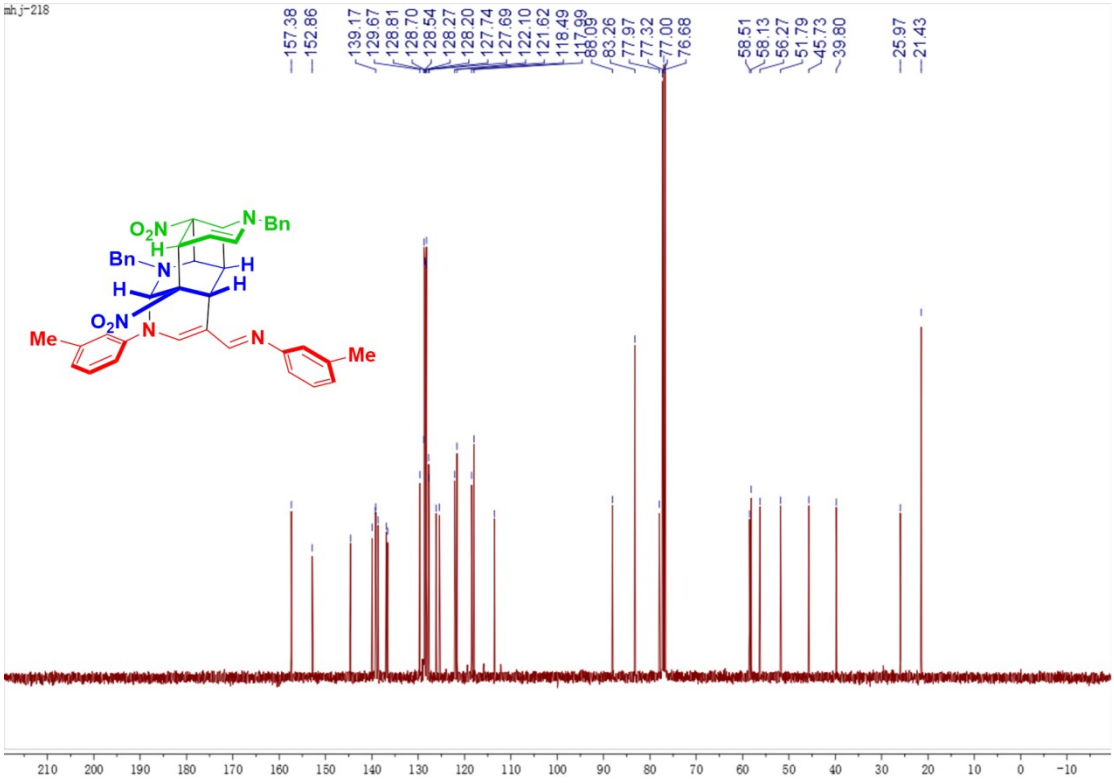
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



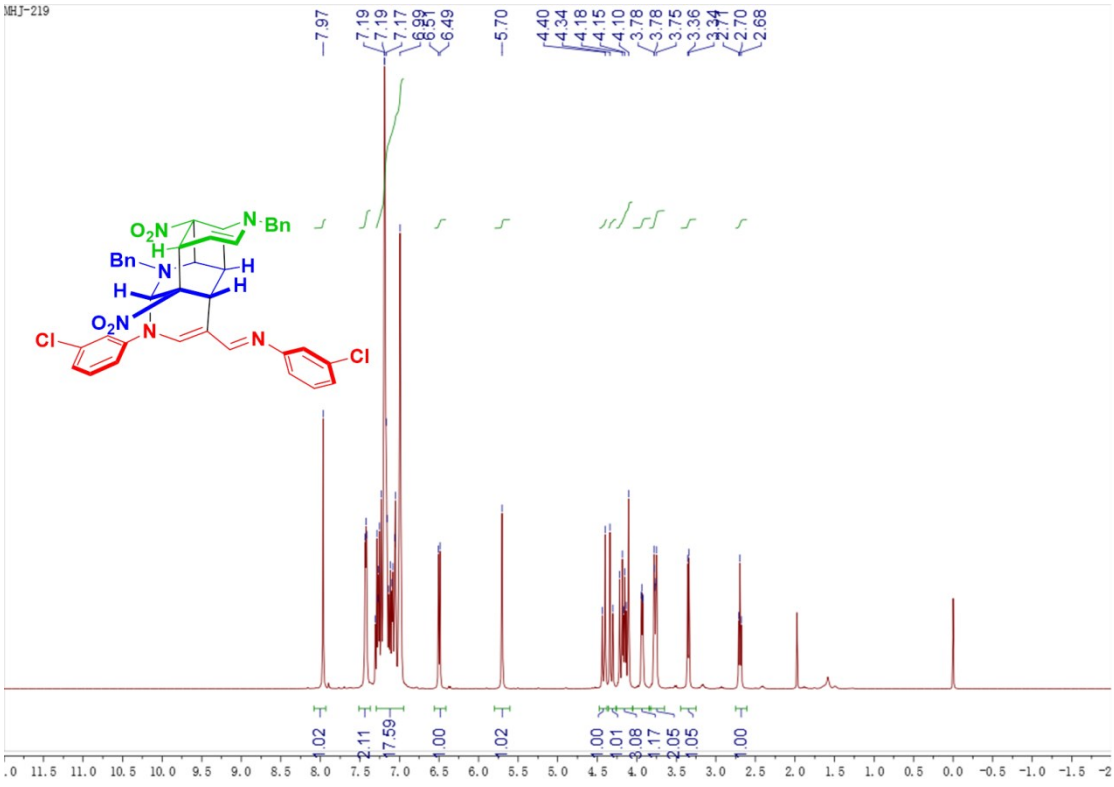
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



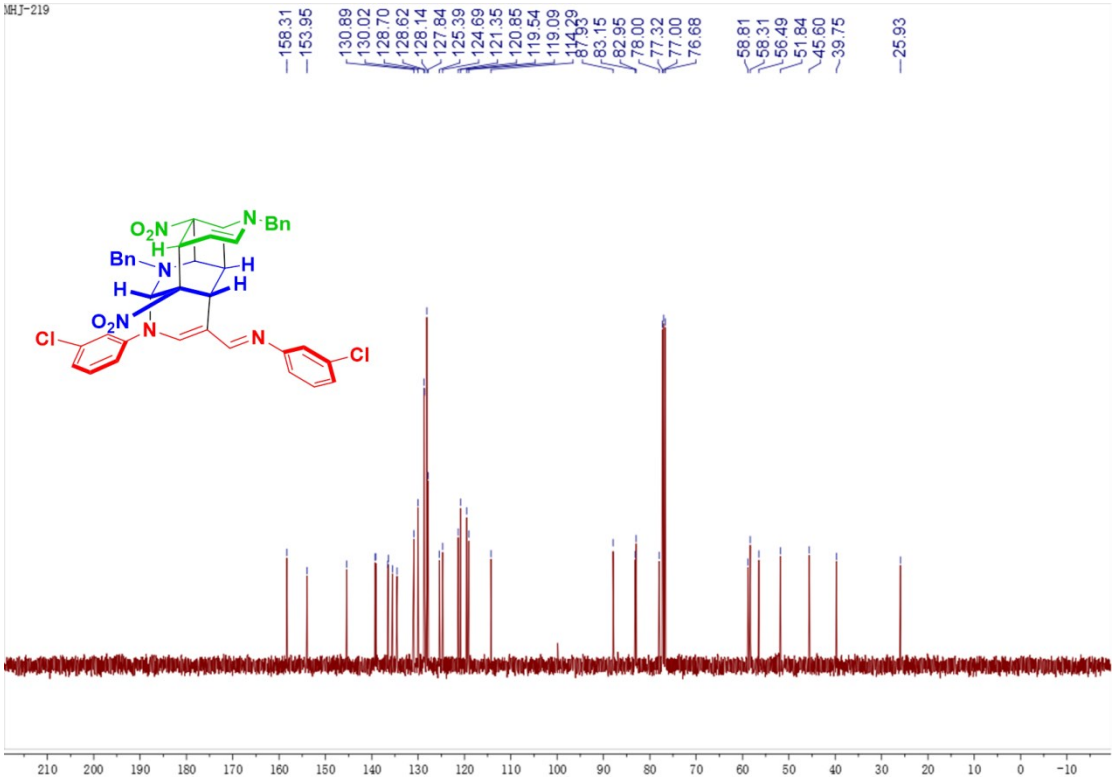
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



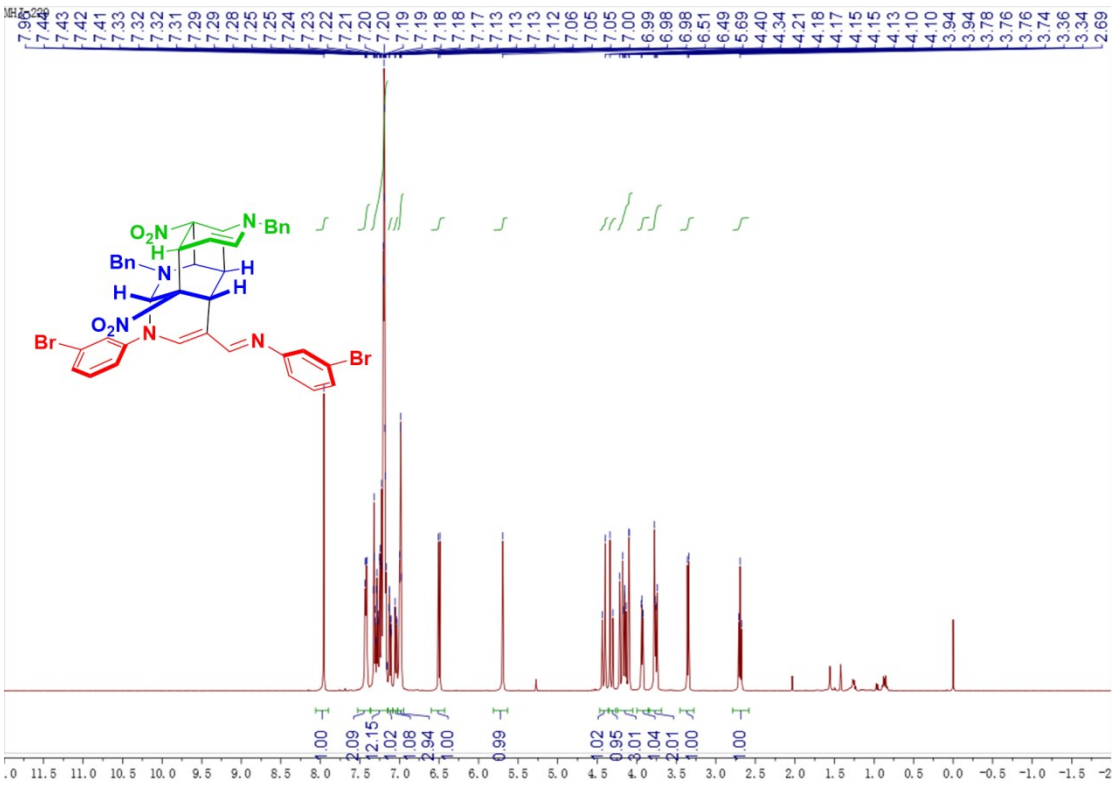
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



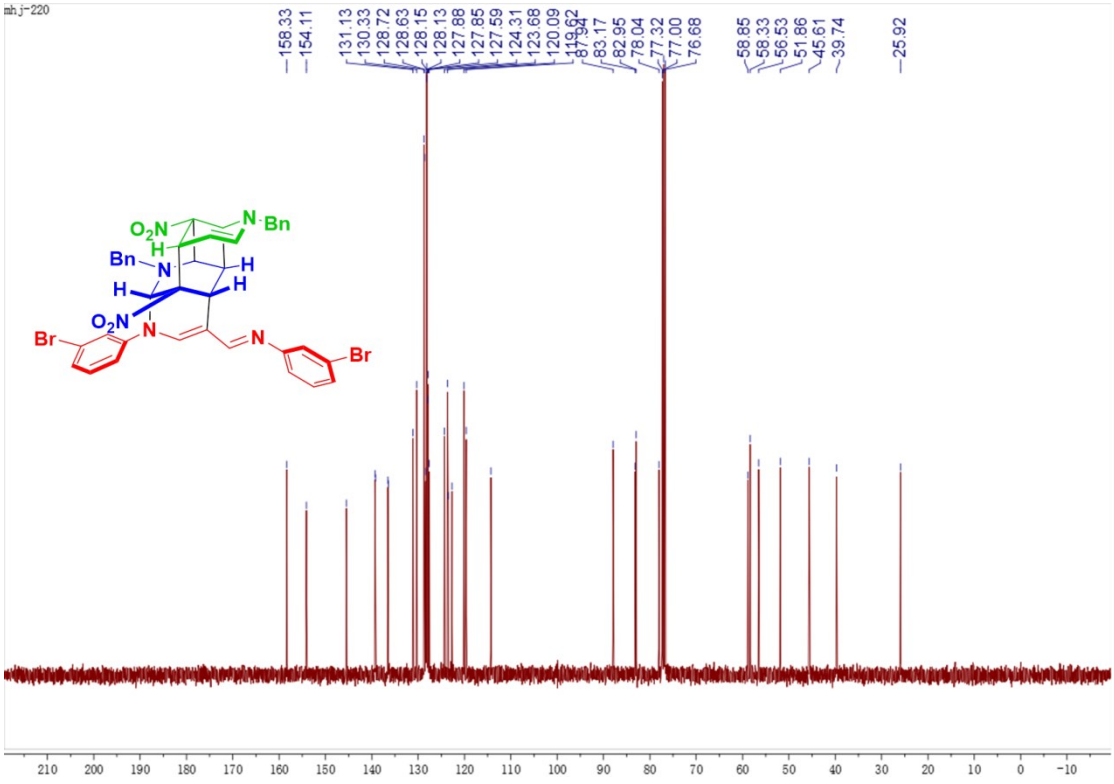
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



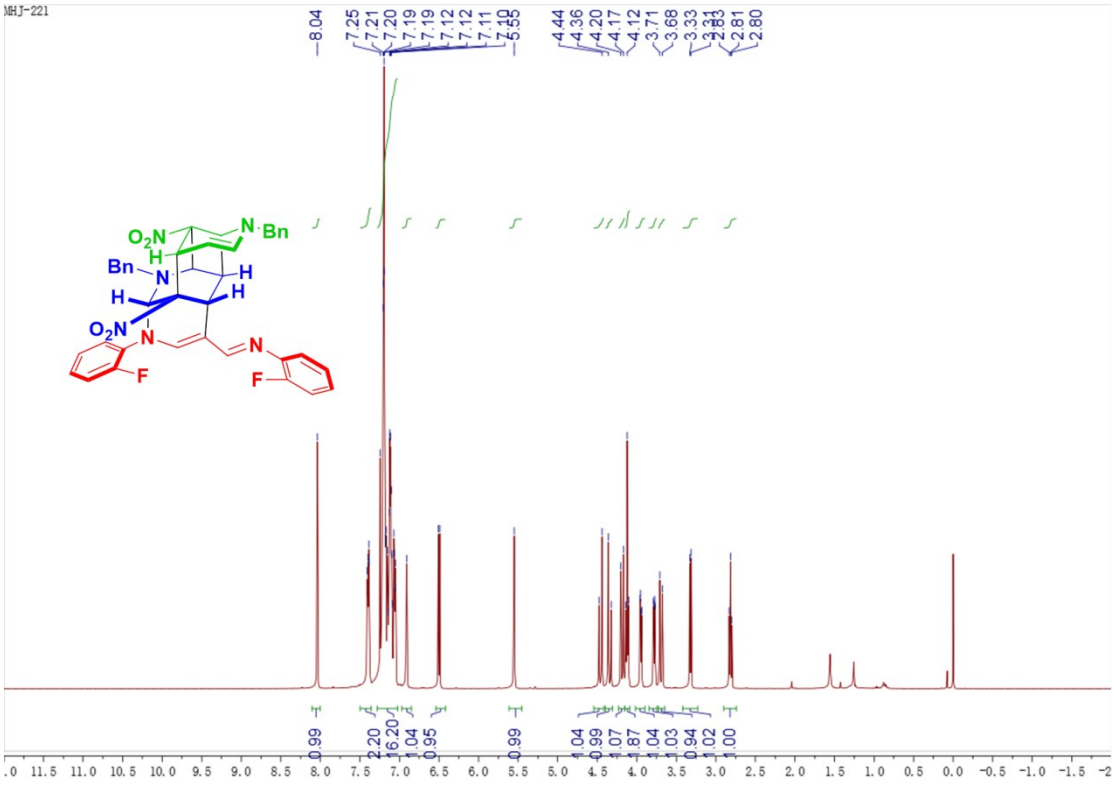
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



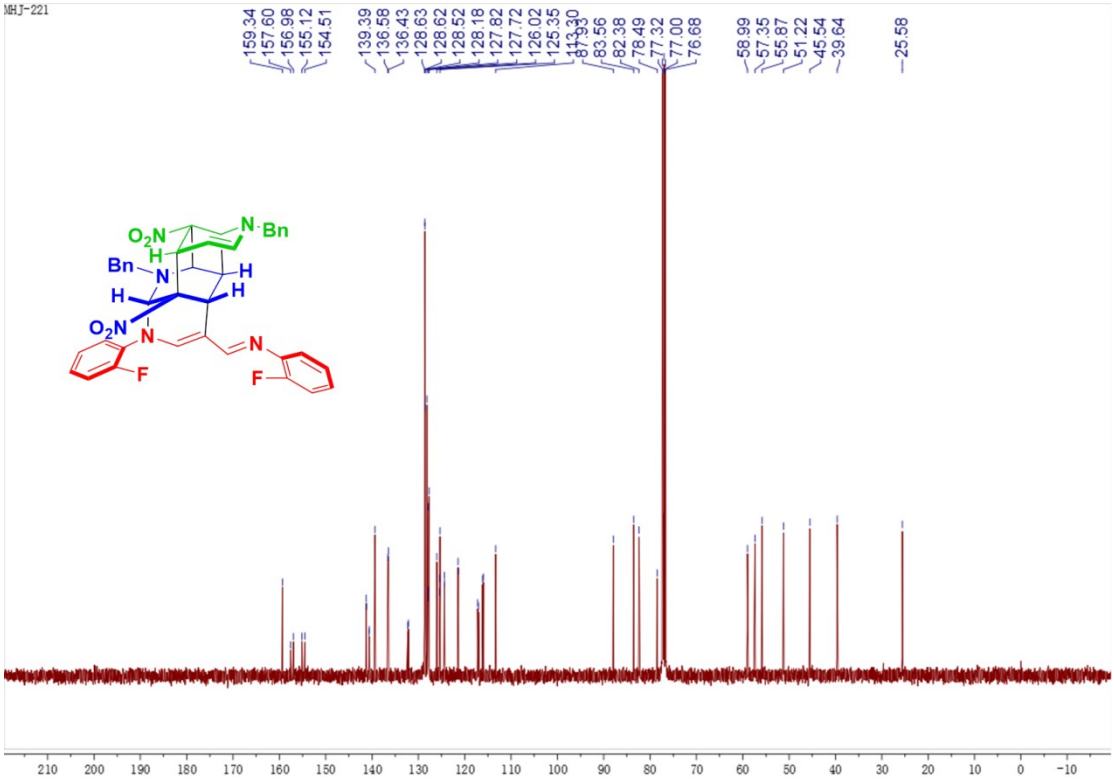
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



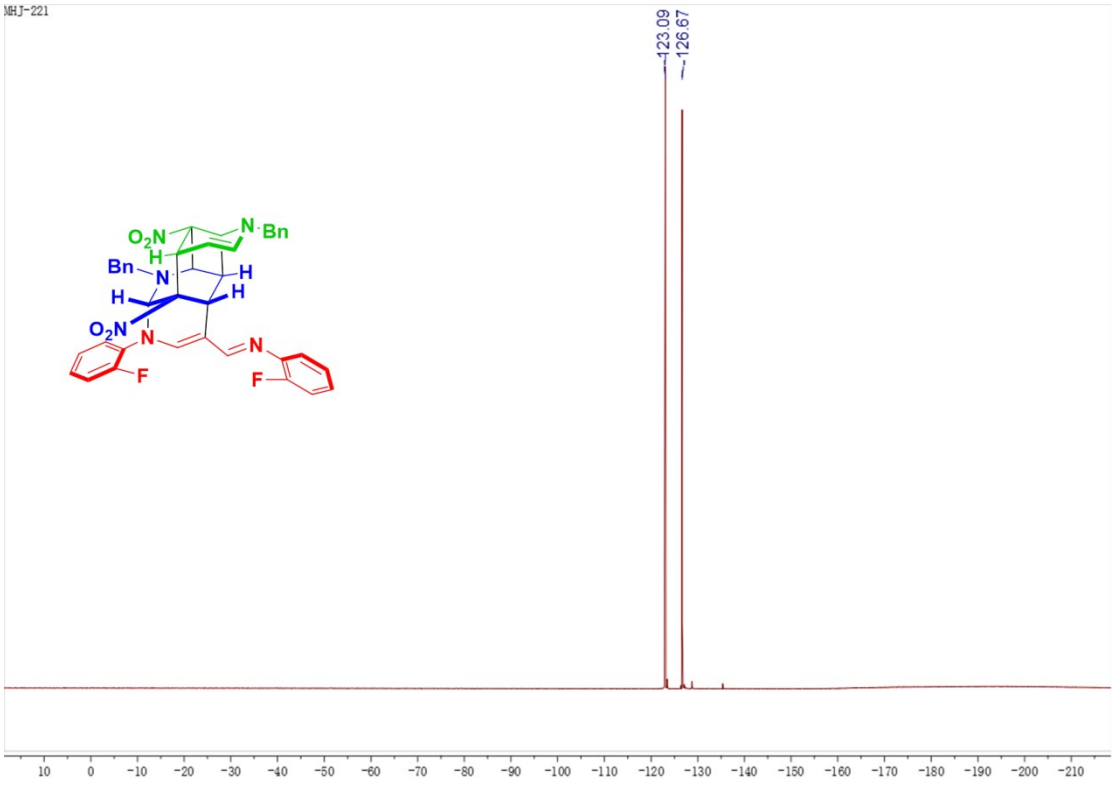
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



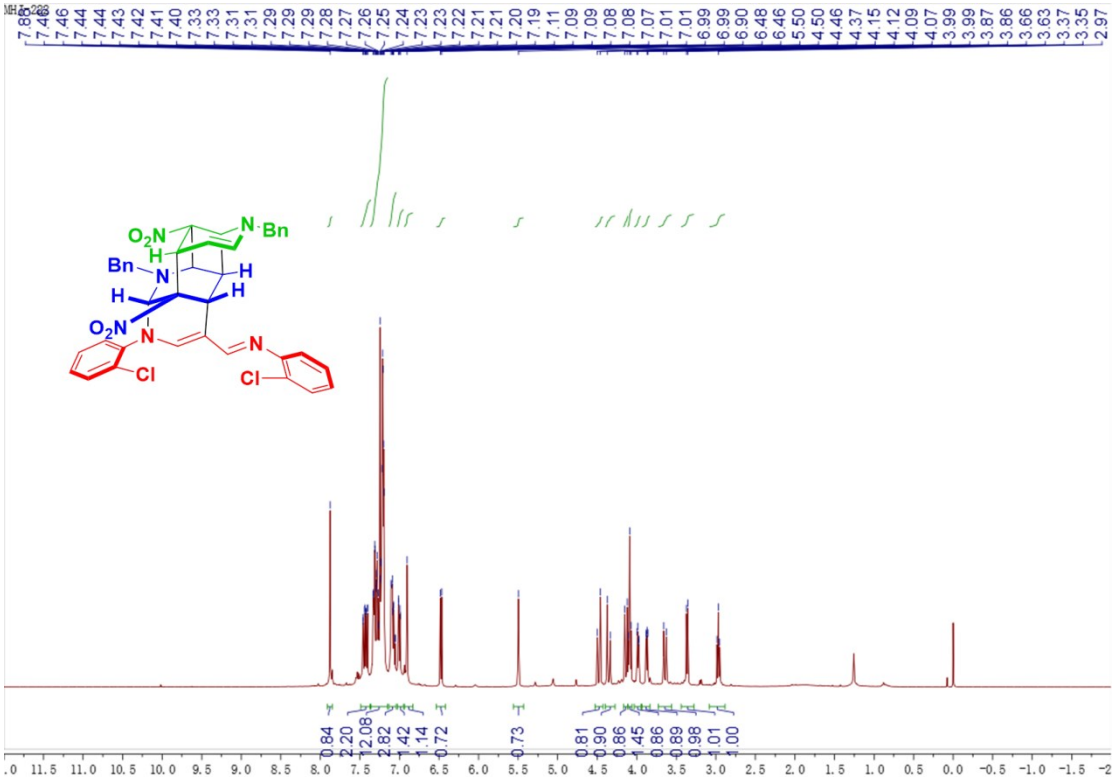
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



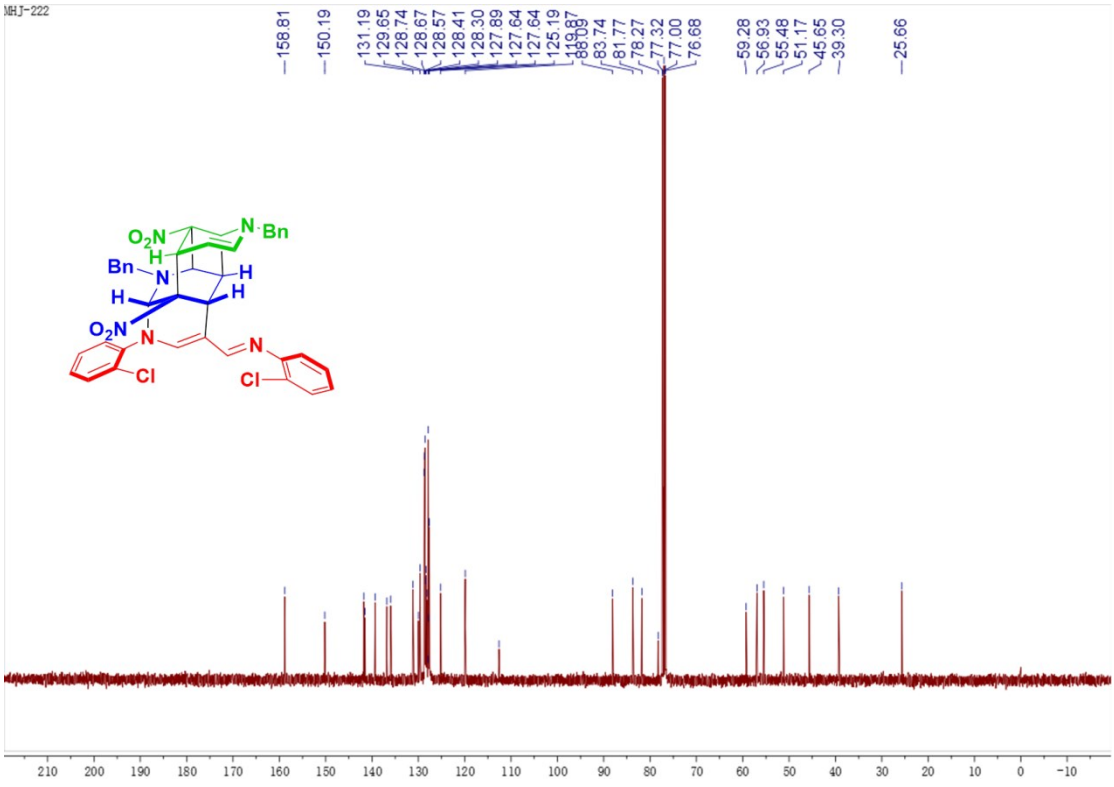
^{19}F NMR spectrum of **3l** (375 MHz, $CDCl_3$)



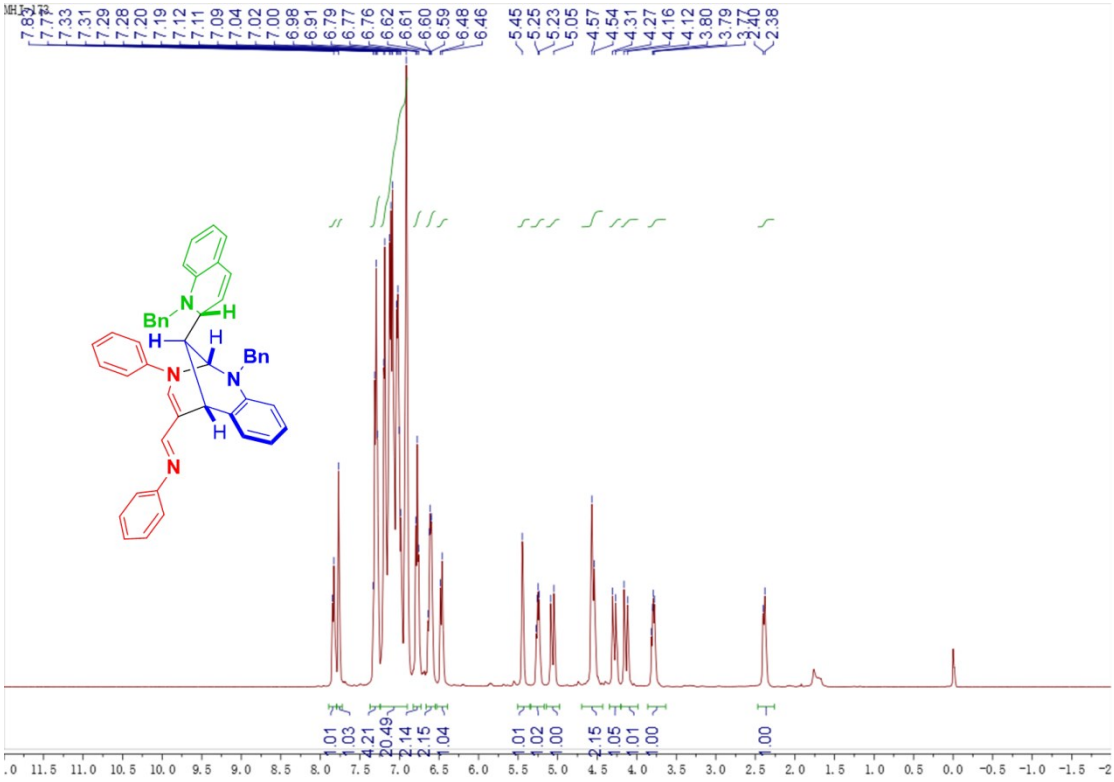
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



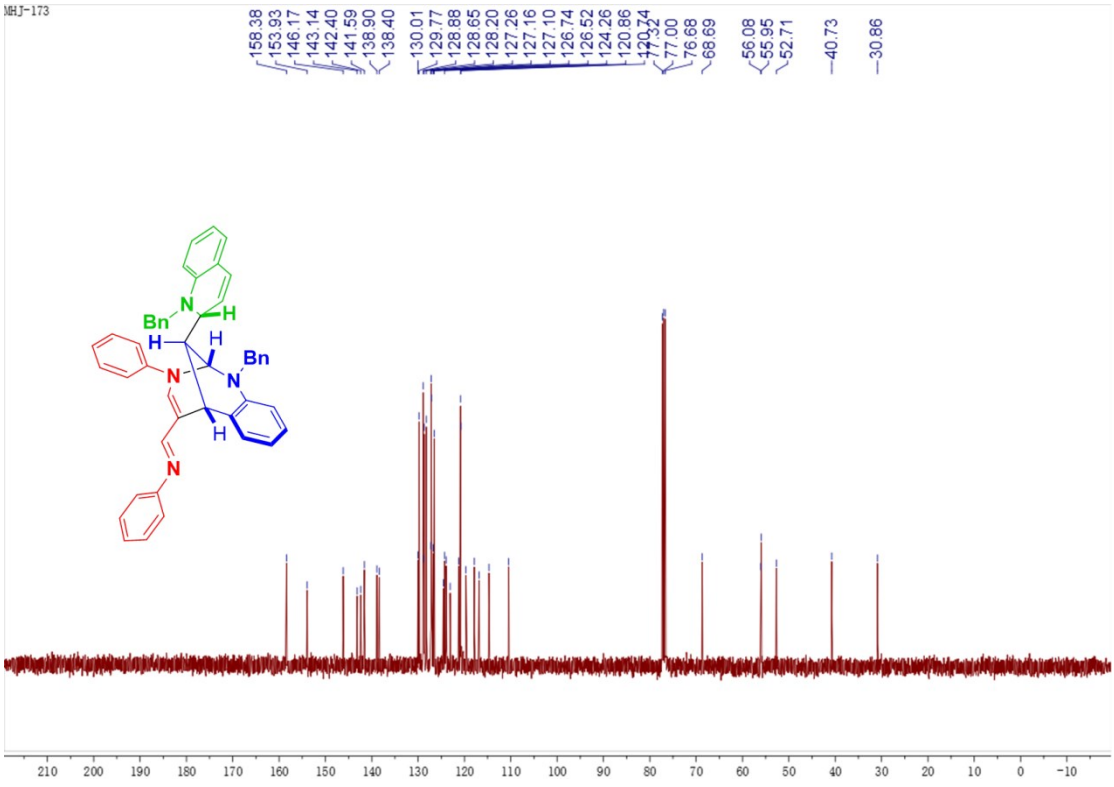
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



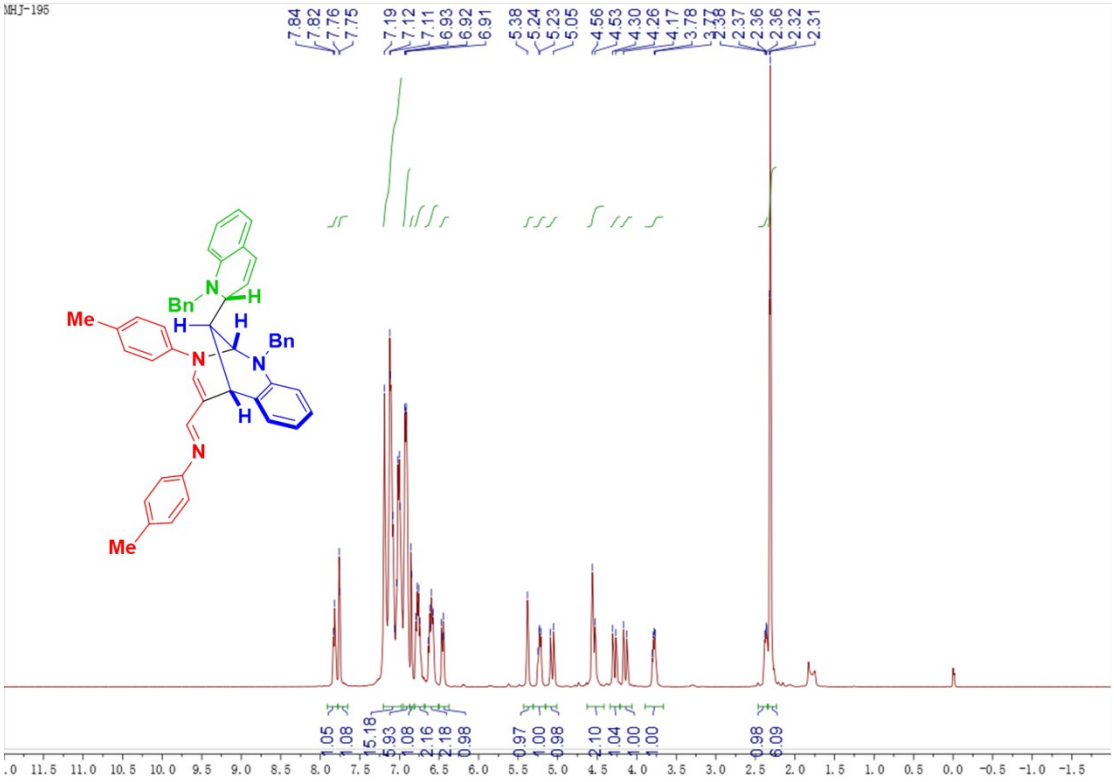
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



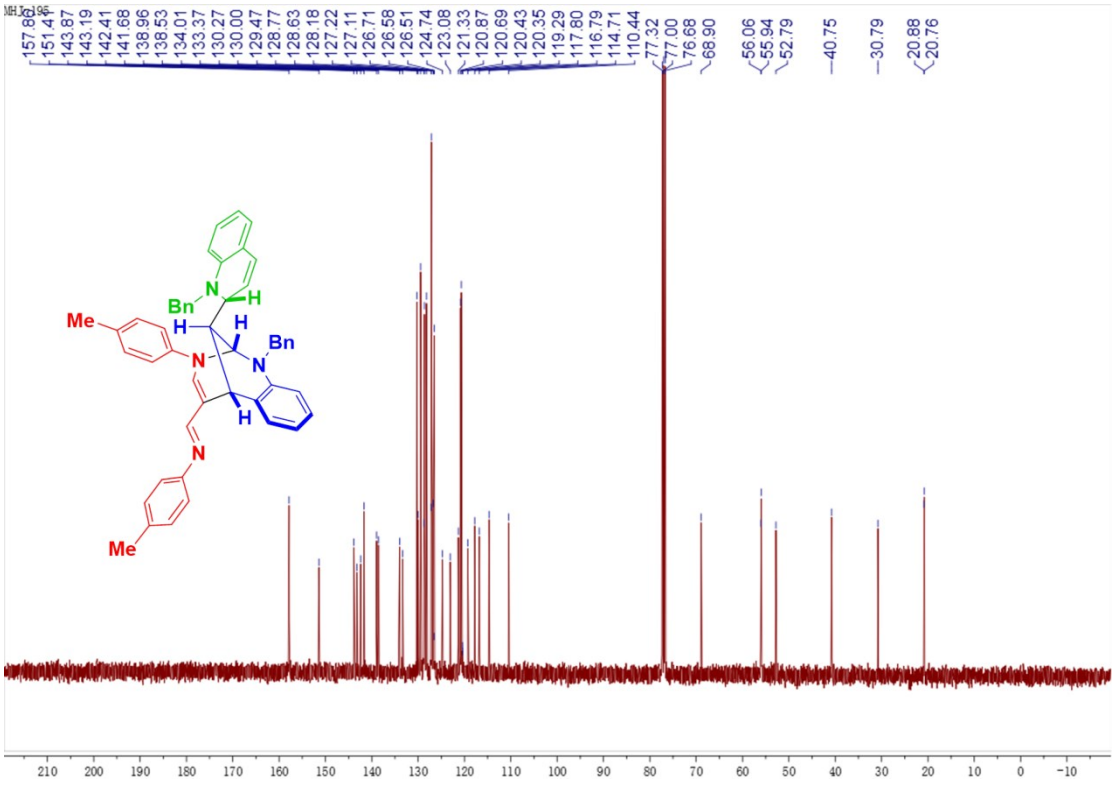
^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)



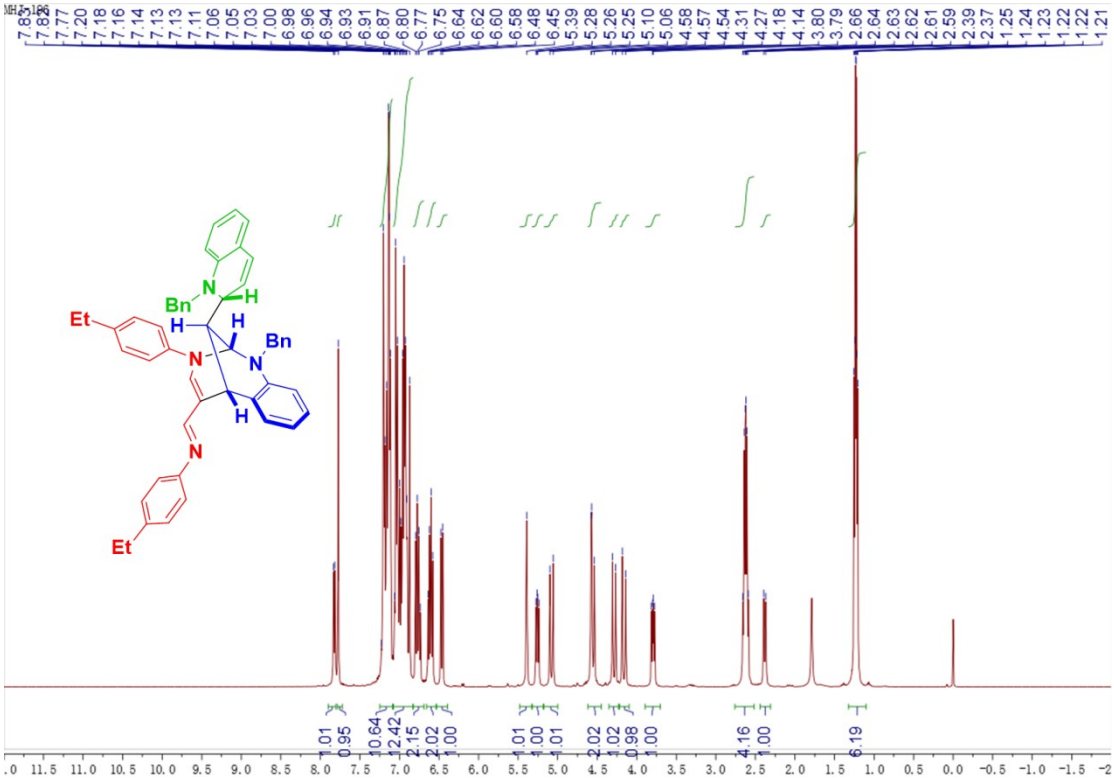
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



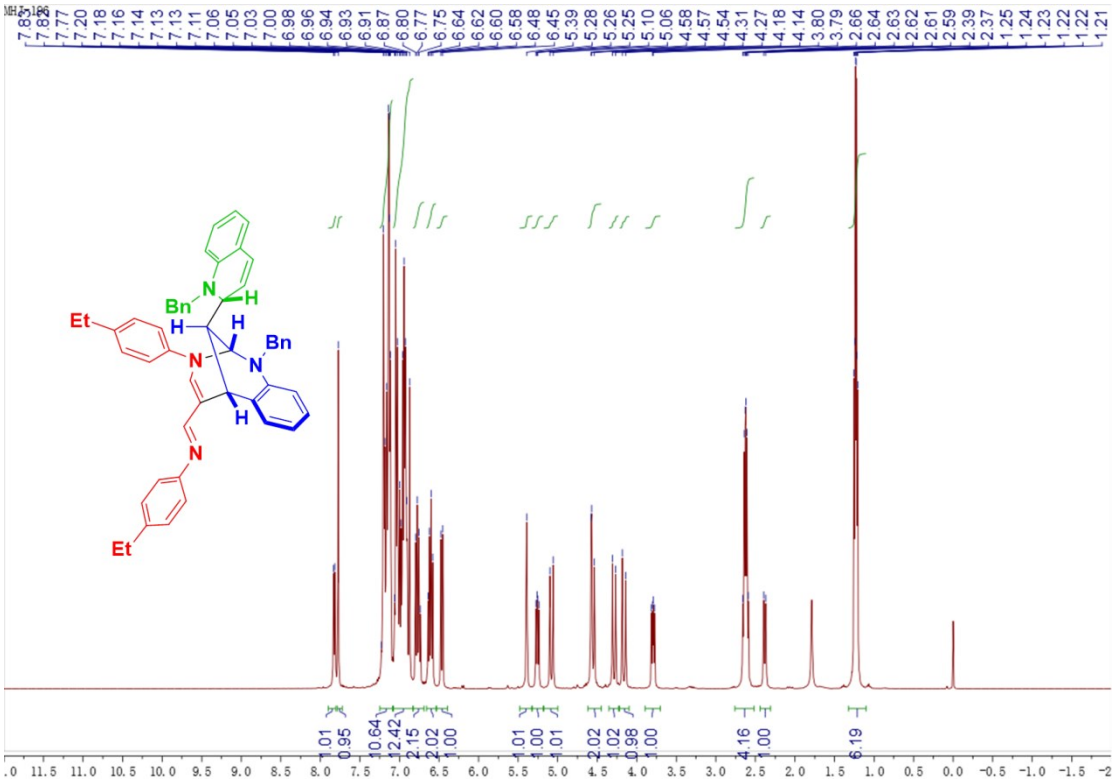
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



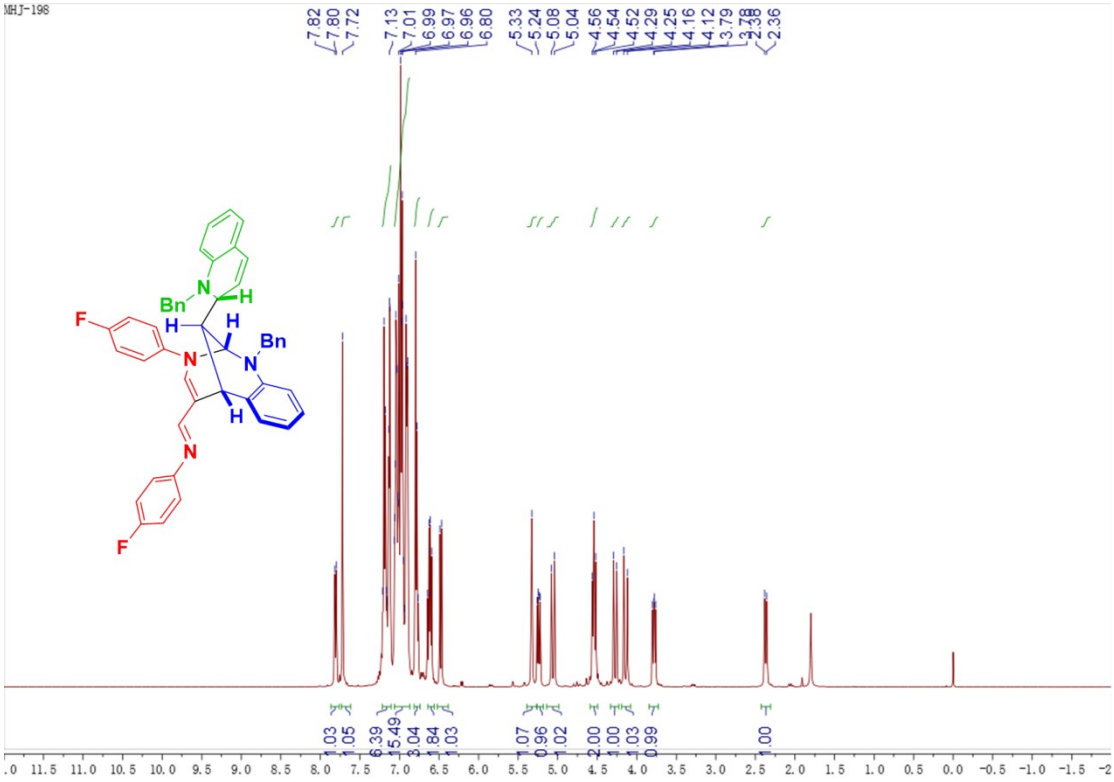
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



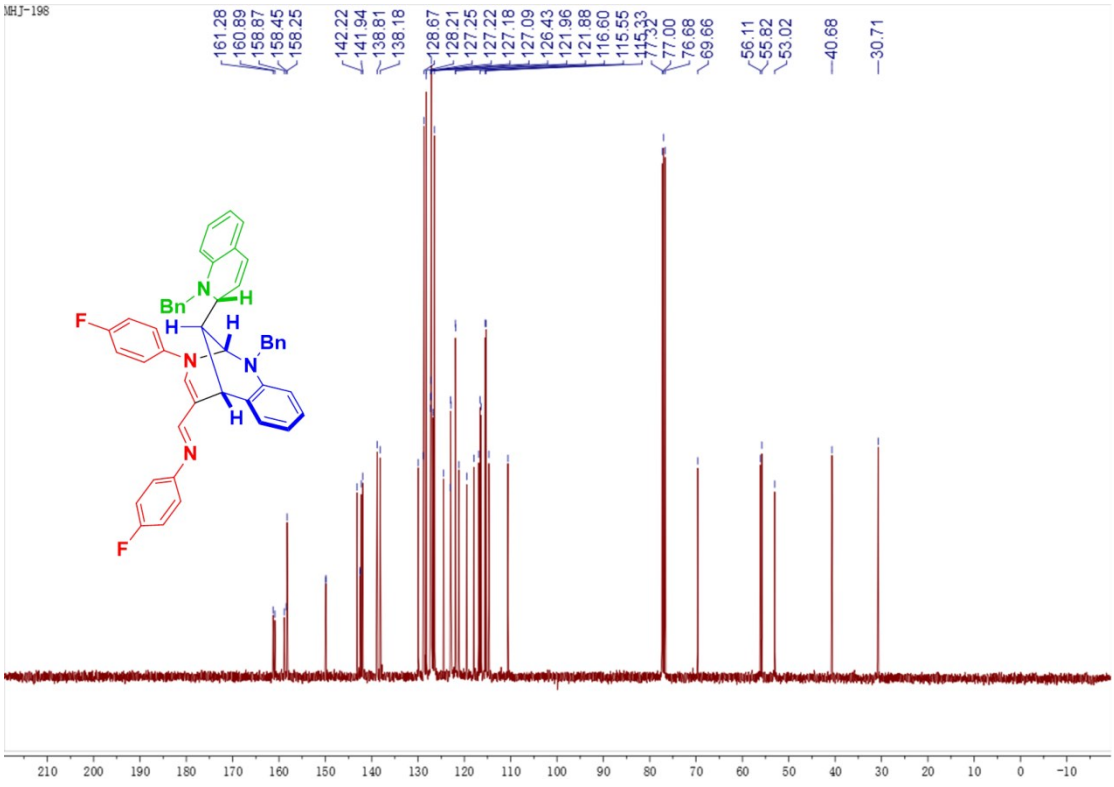
^{13}C NMR spectrum of **5c** (100 MHz, $CDCl_3$)



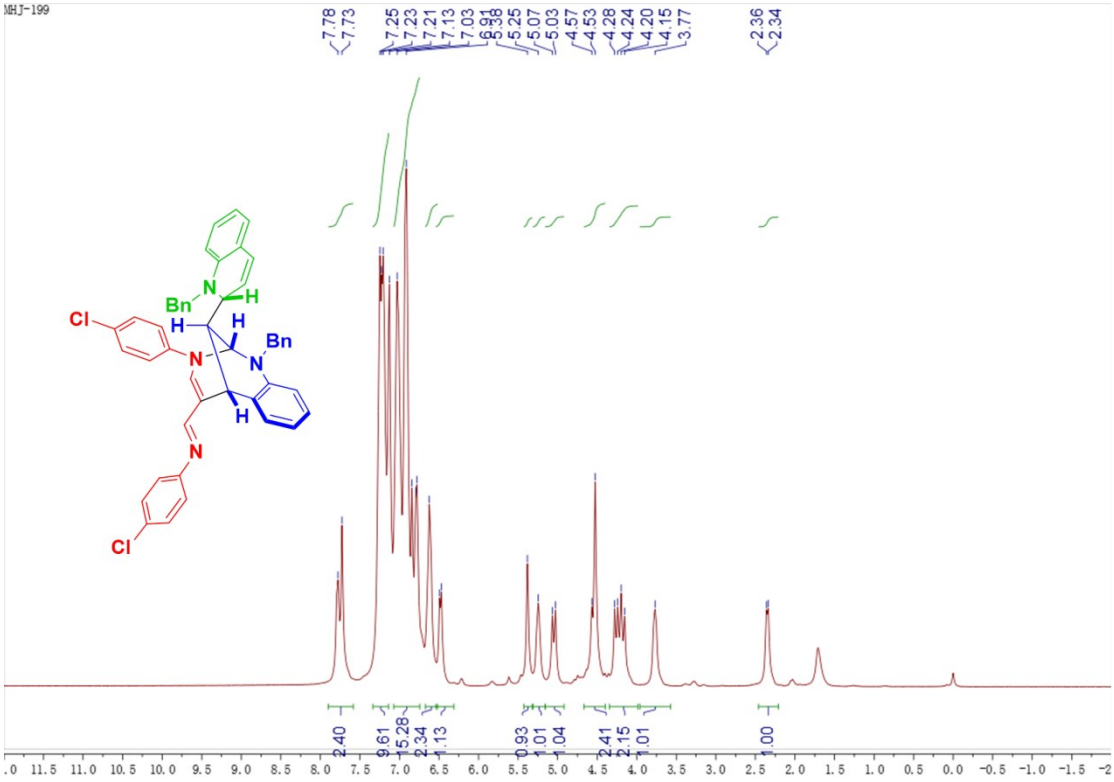
^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



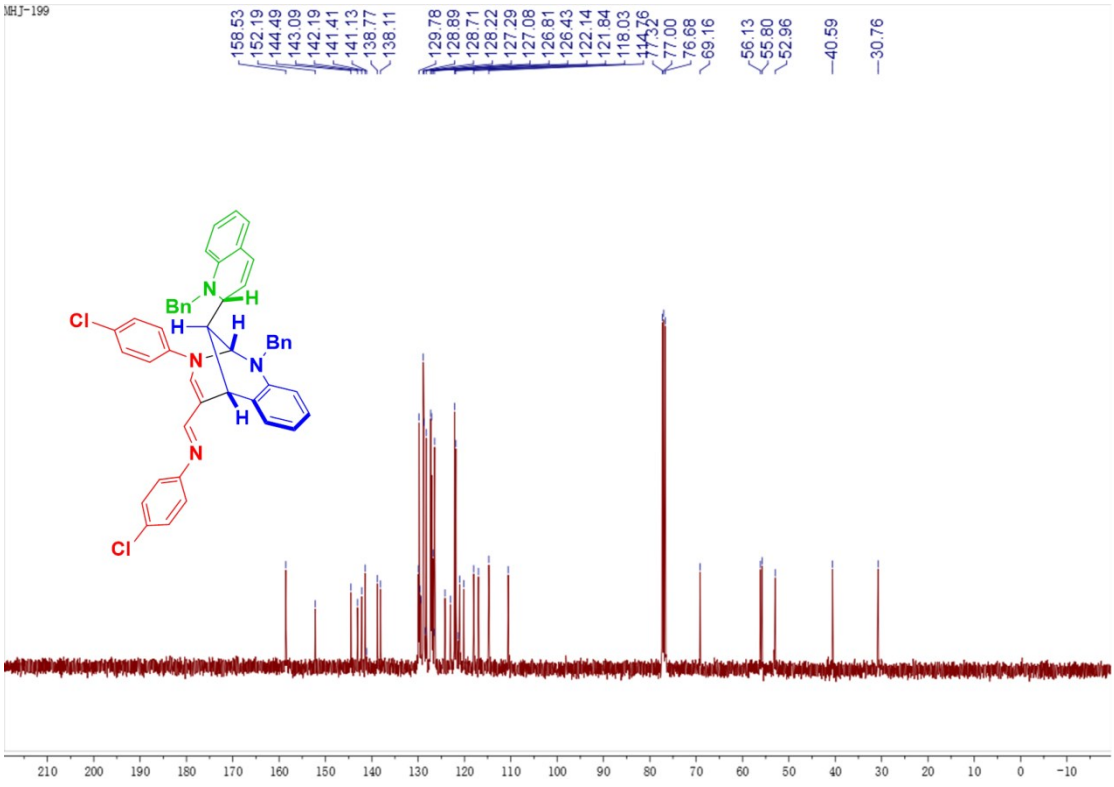
^{13}C NMR spectrum of **5d** (100 MHz, $CDCl_3$)



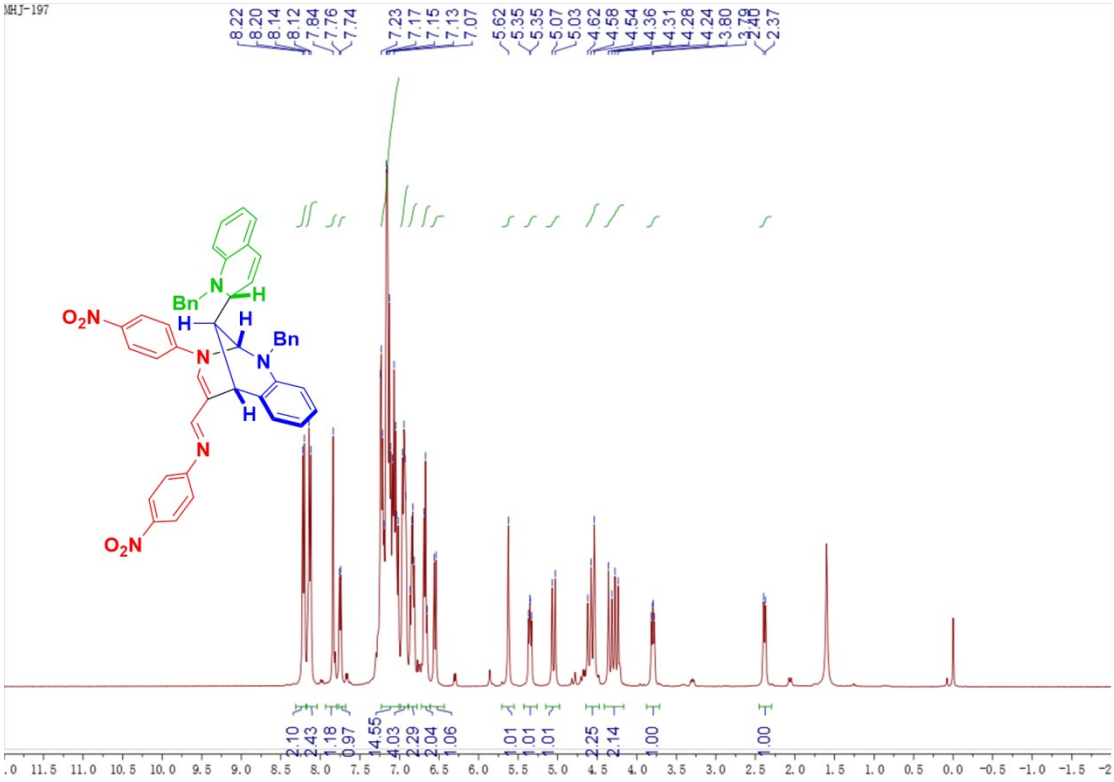
^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)



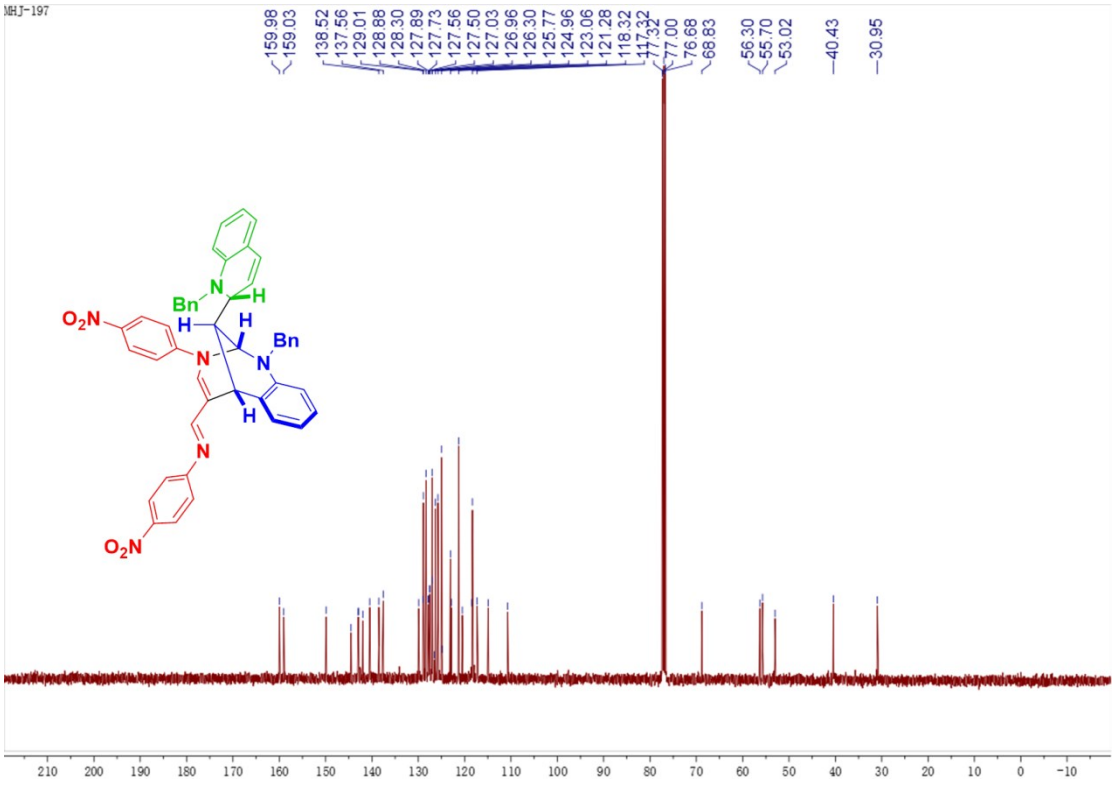
^{13}C NMR spectrum of **5e** (100 MHz, $CDCl_3$)



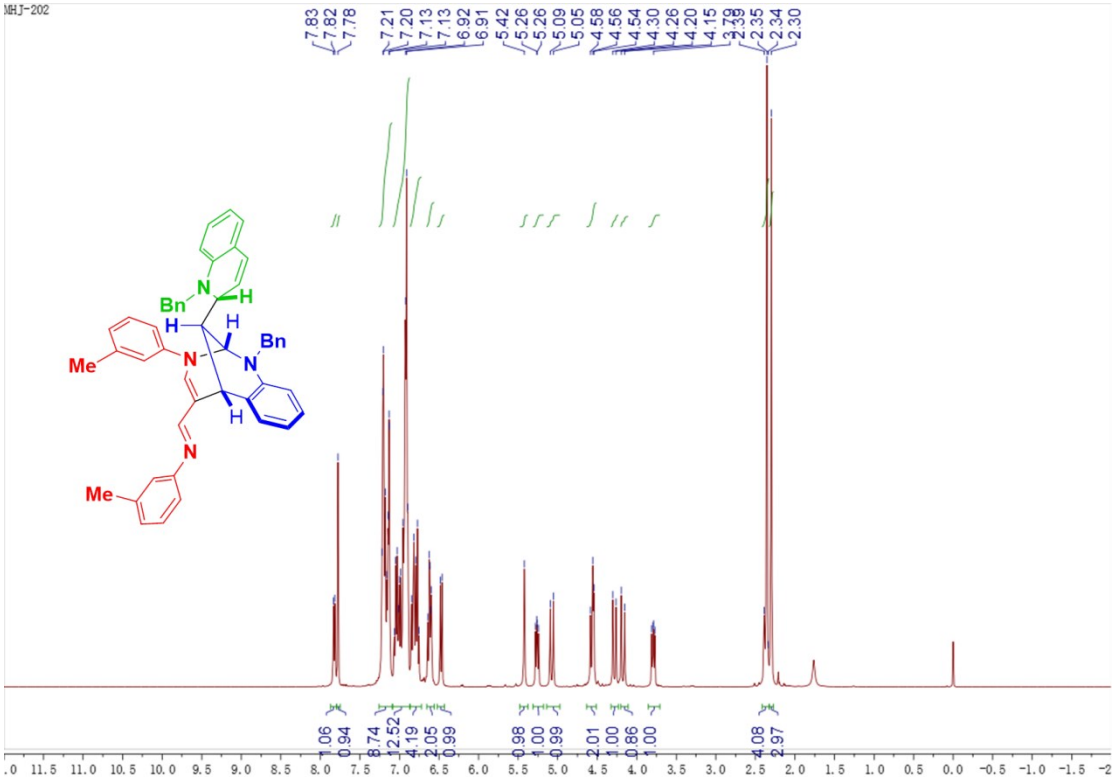
^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)



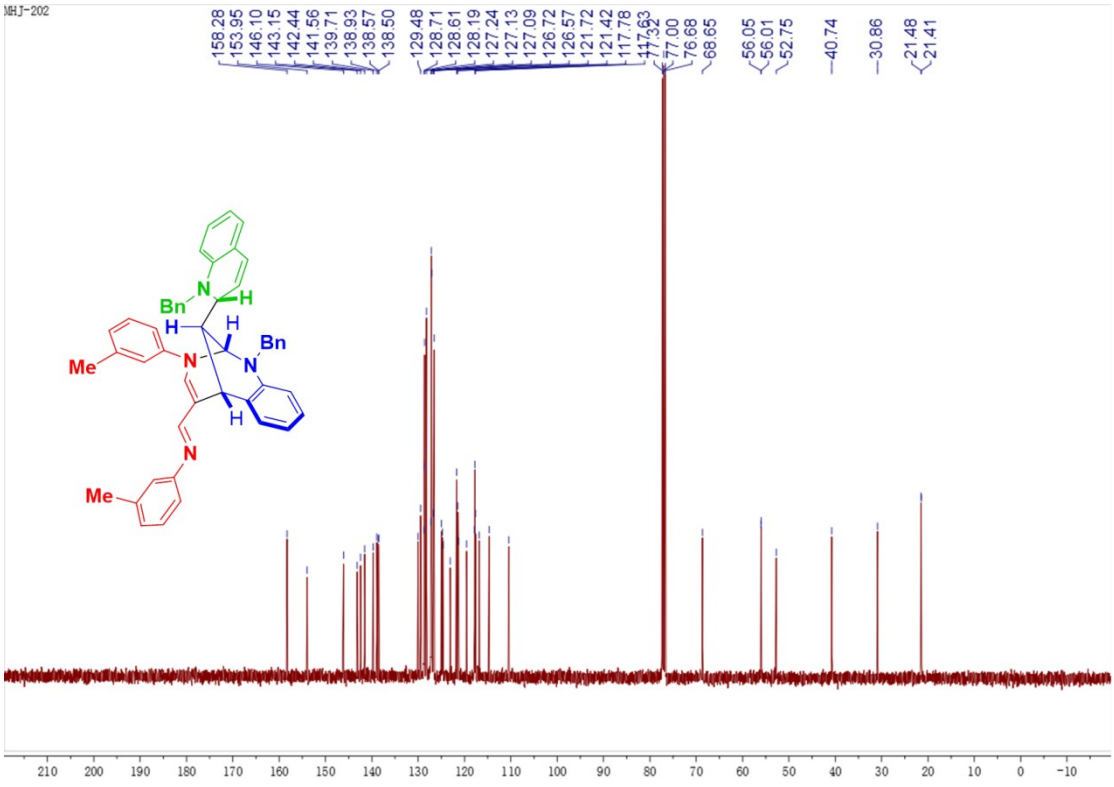
^{13}C NMR spectrum of **5f** (100 MHz, $CDCl_3$)



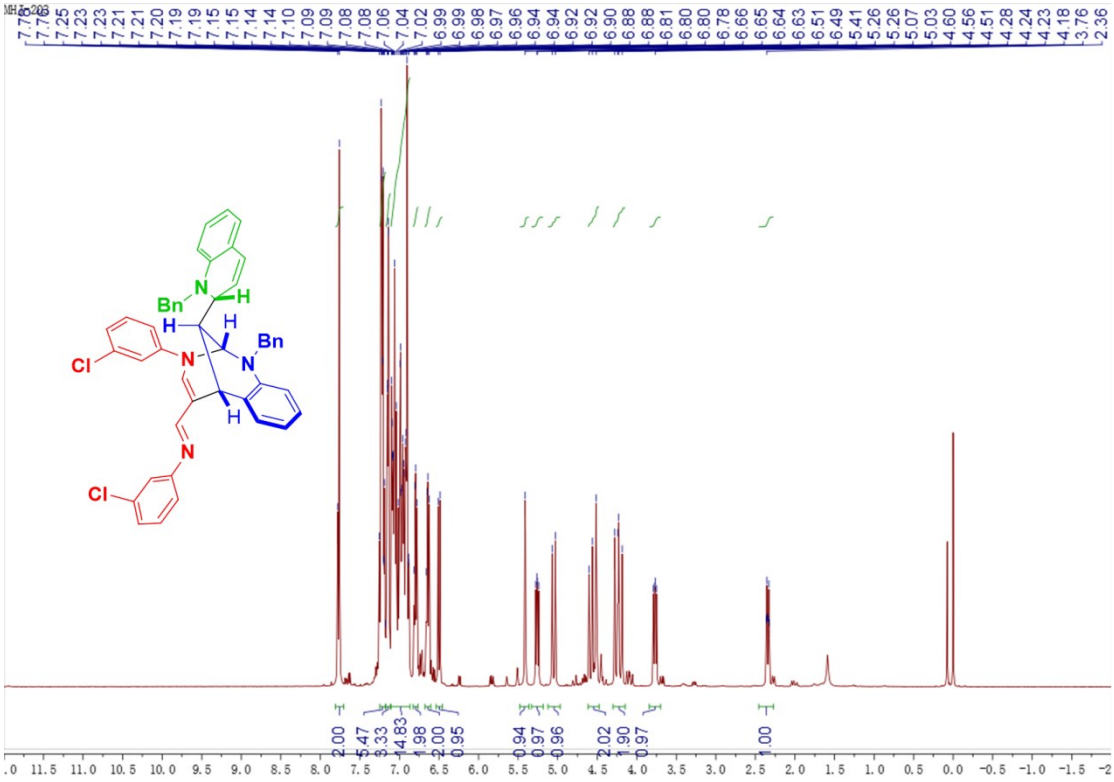
^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)



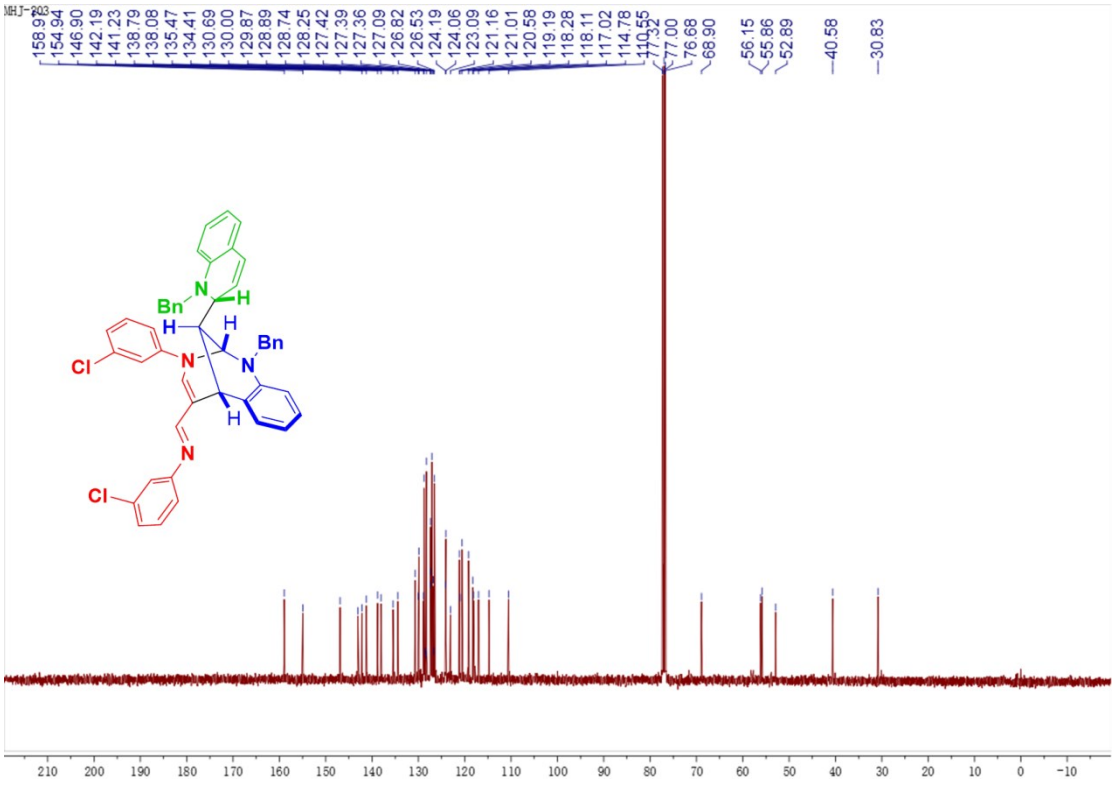
^{13}C NMR spectrum of **5g** (100 MHz, $CDCl_3$)



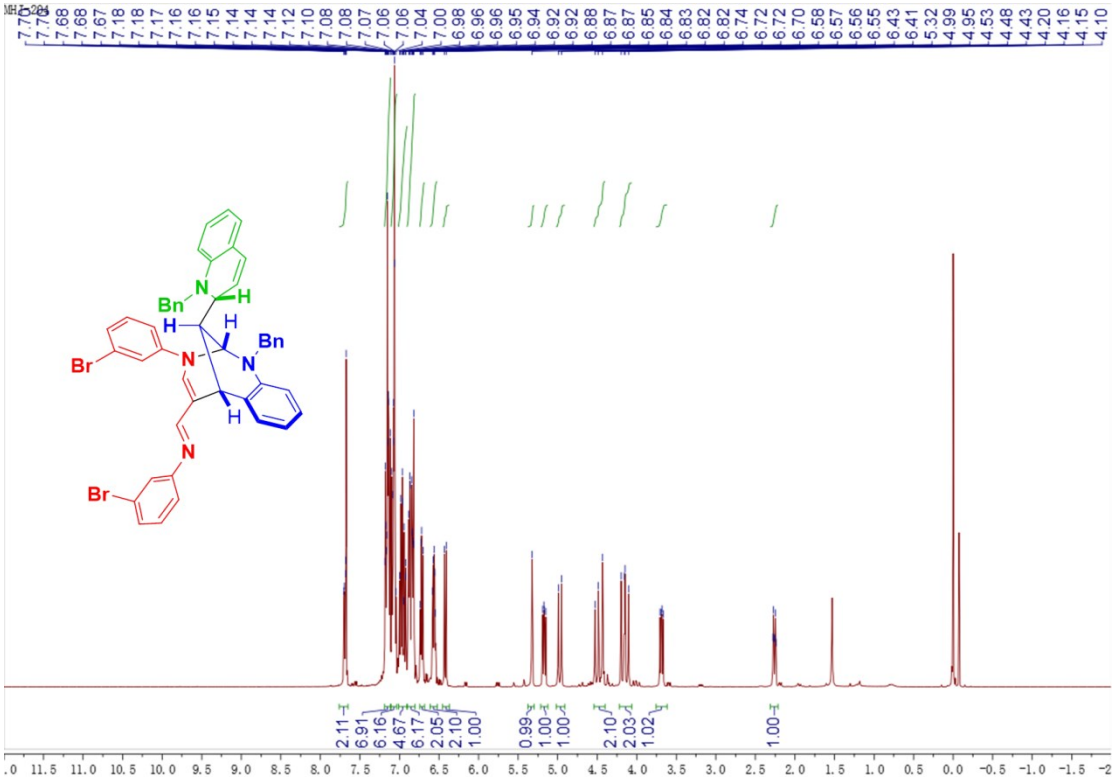
^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)



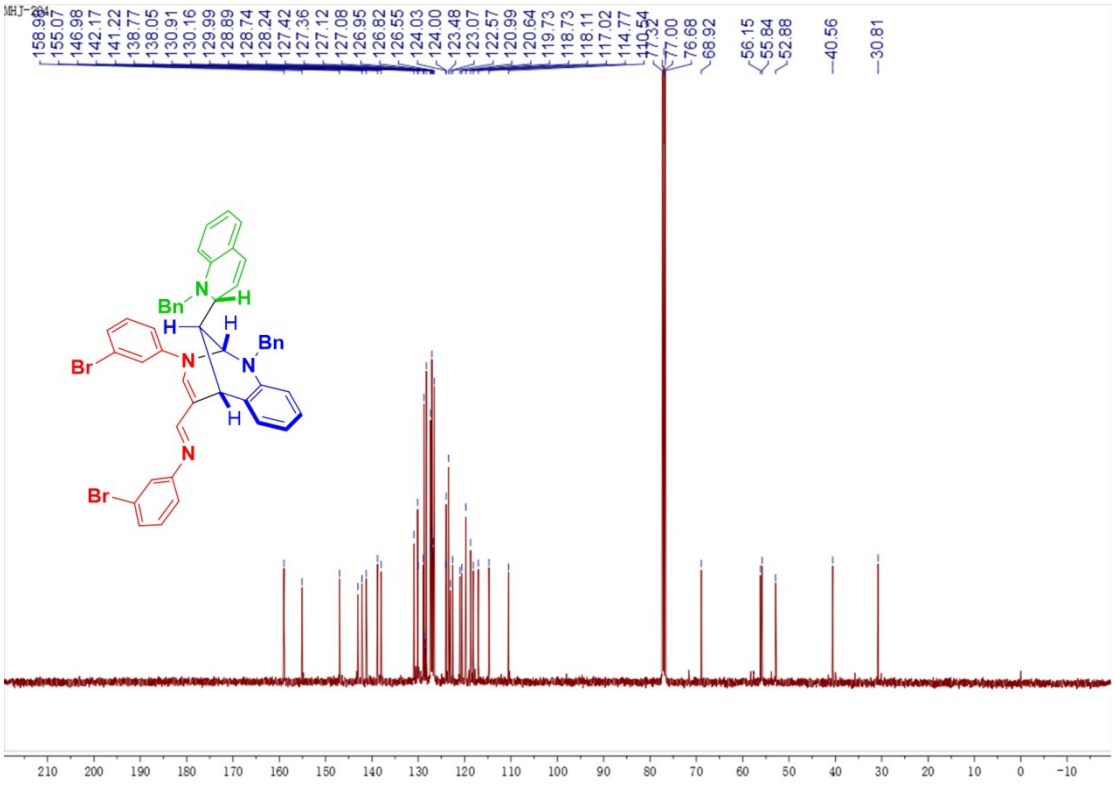
^{13}C NMR spectrum of **5h** (100 MHz, $CDCl_3$)



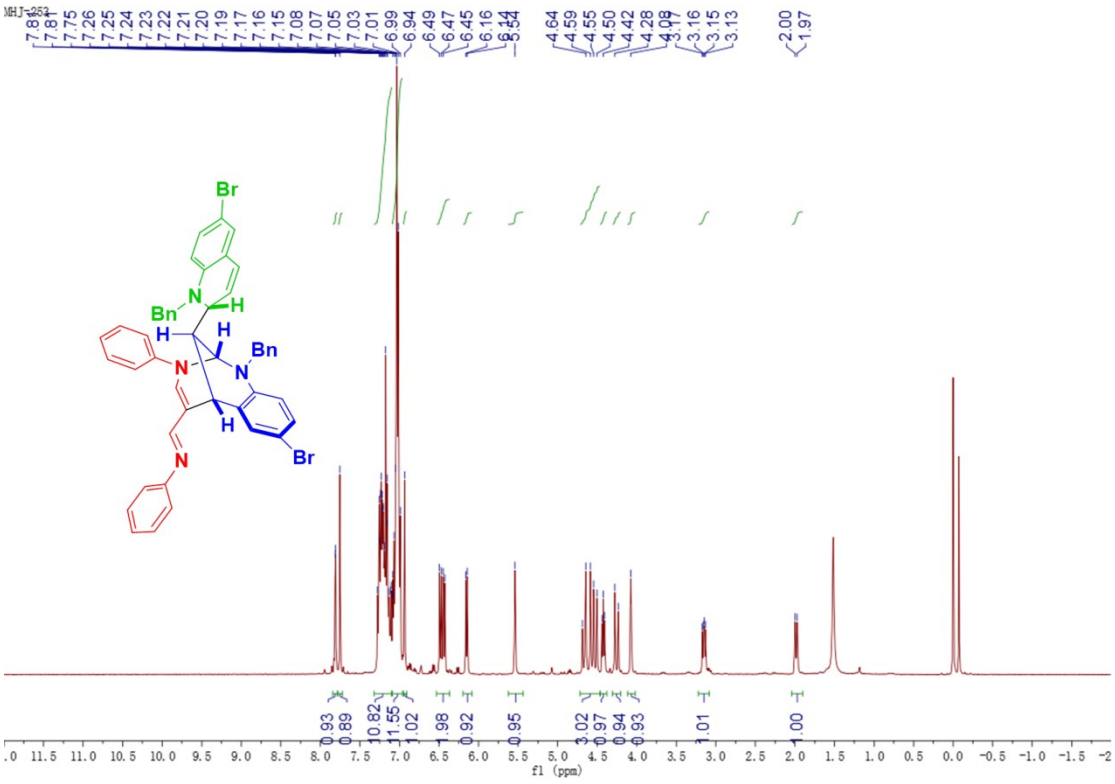
^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)



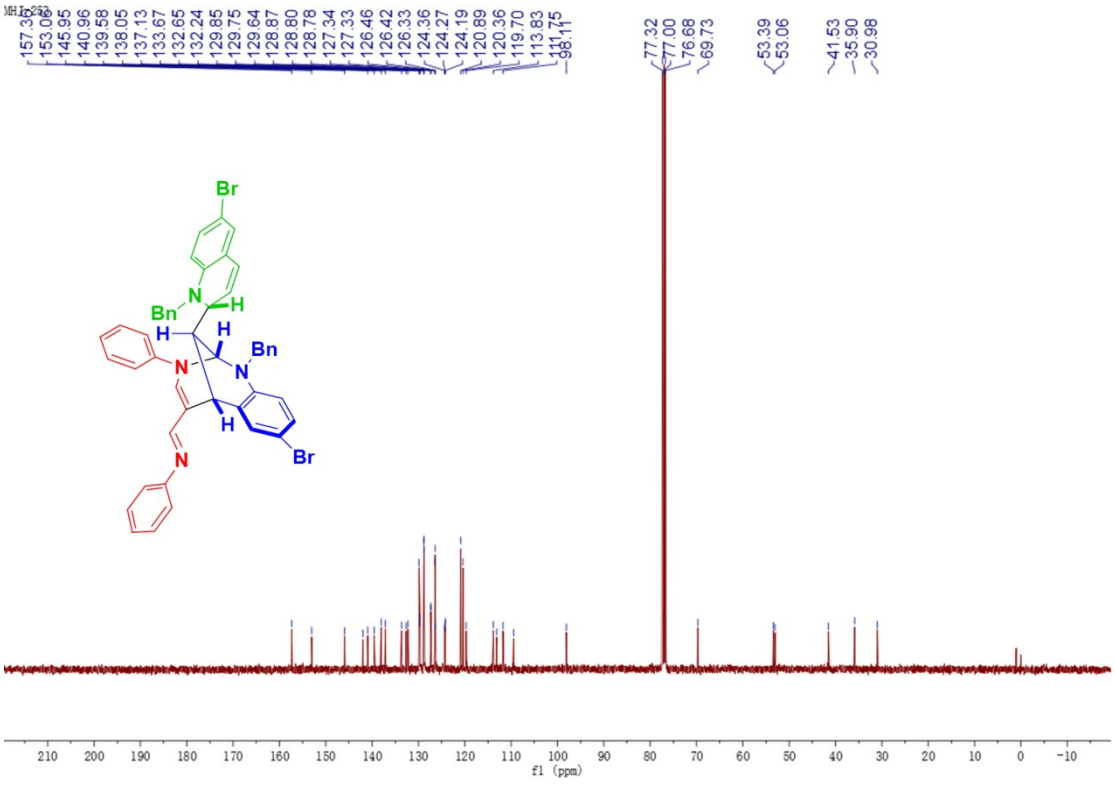
^{13}C NMR spectrum of **5i** (100 MHz, $CDCl_3$)



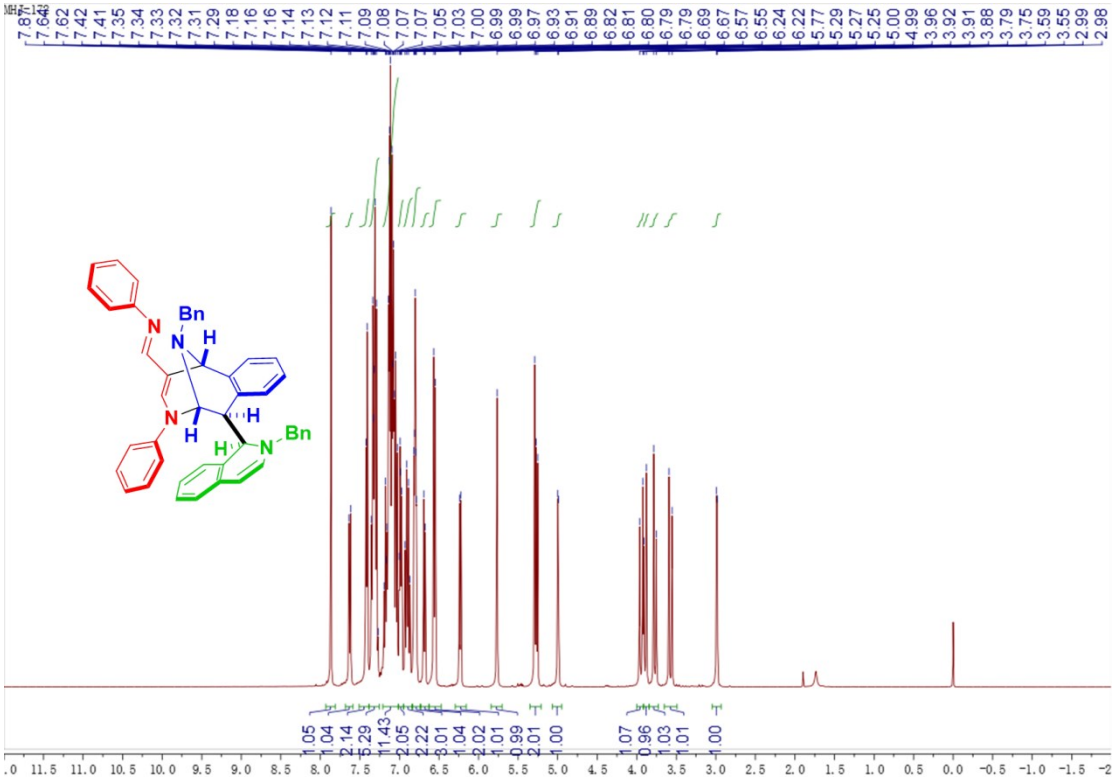
^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)



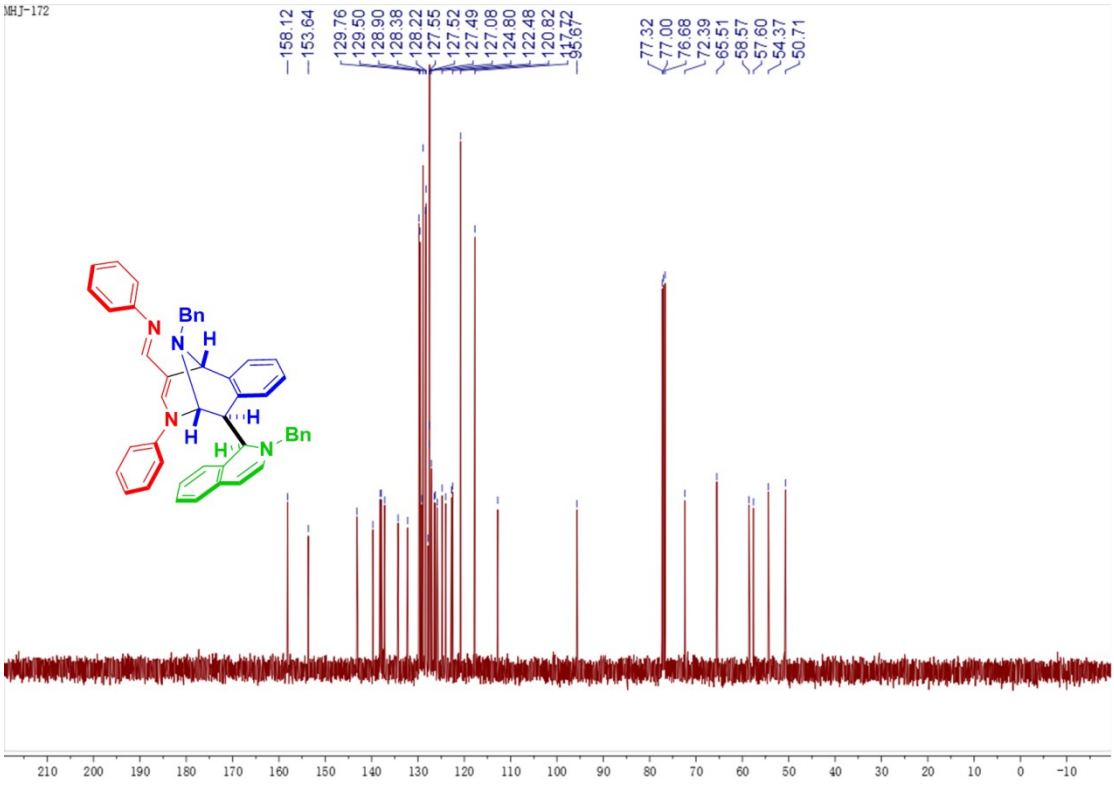
^{13}C NMR spectrum of **5j** (100 MHz, $CDCl_3$)



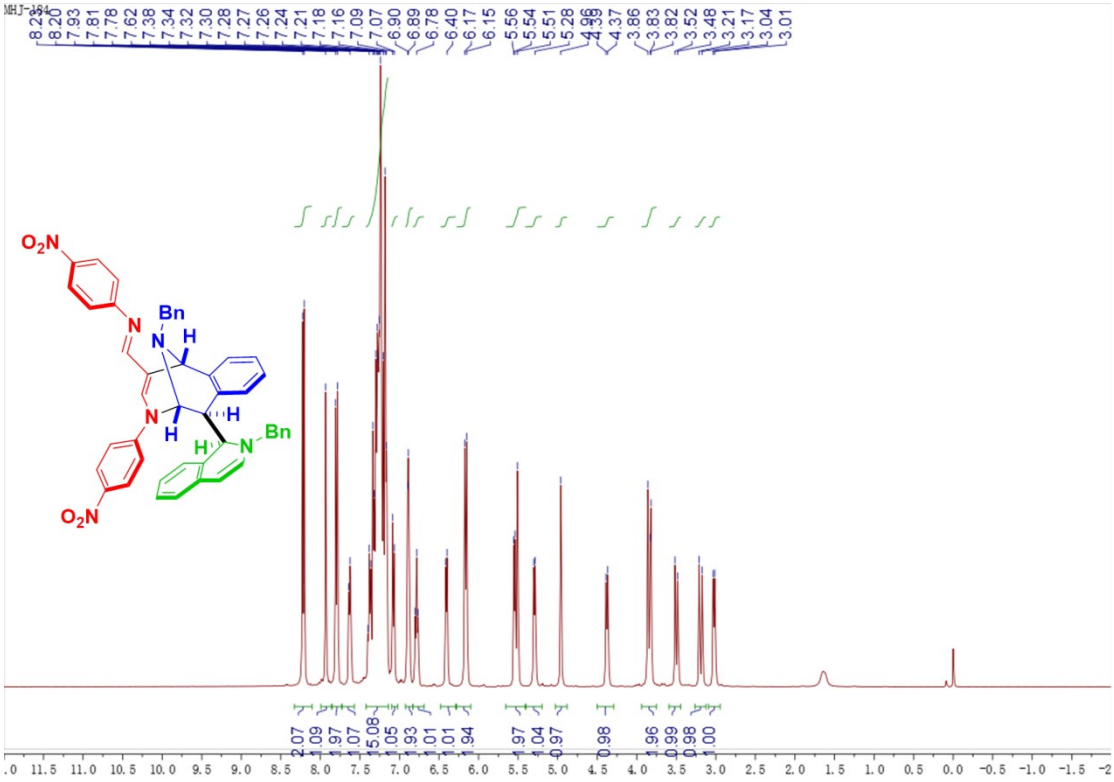
^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$)



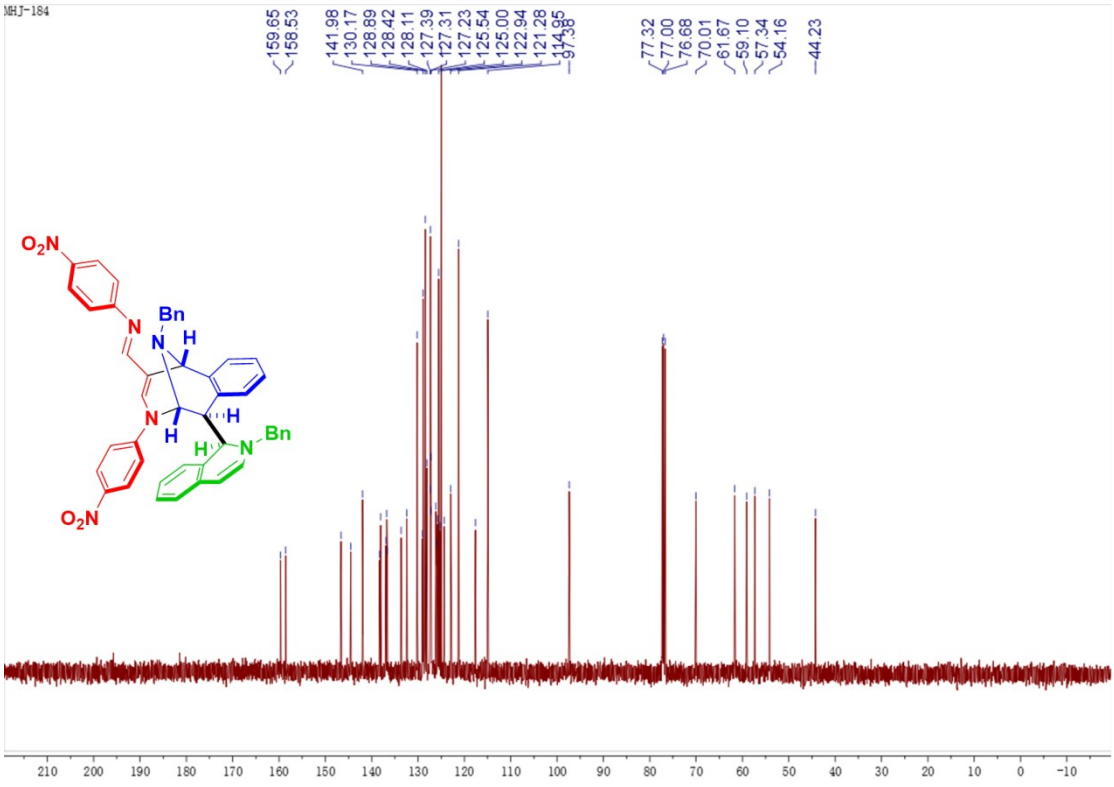
^{13}C NMR spectrum of **7a** (100 MHz, $CDCl_3$)



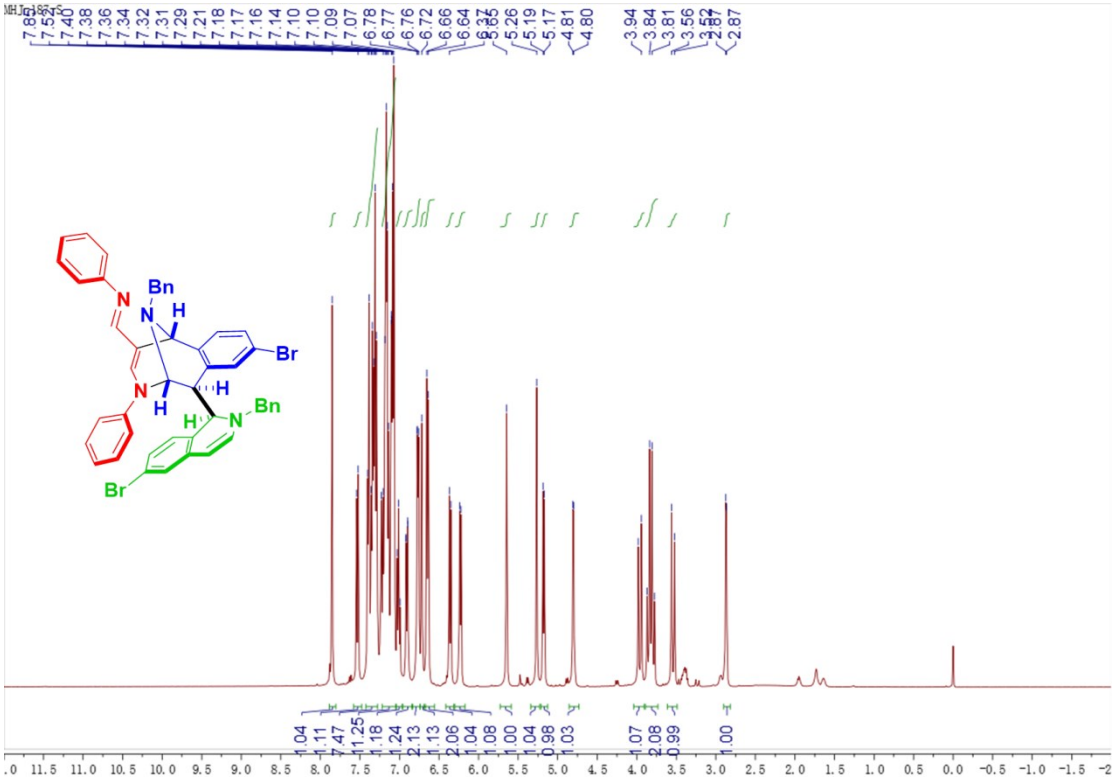
^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$)



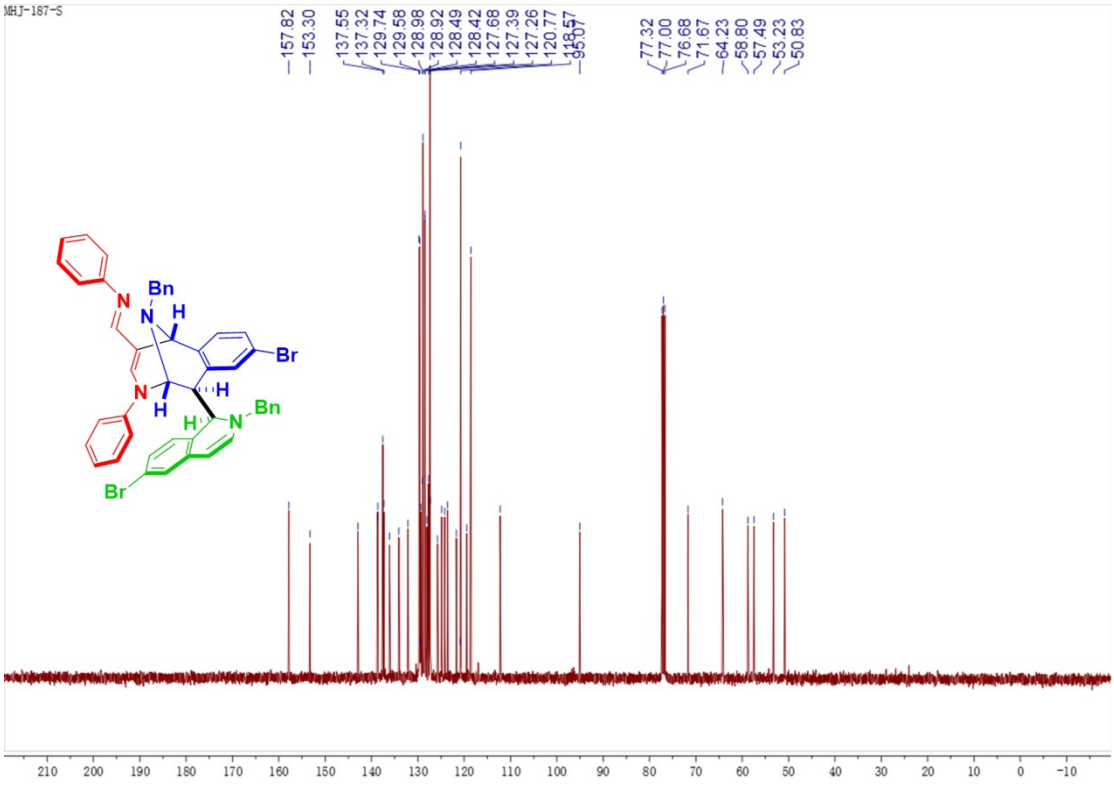
^{13}C NMR spectrum of **7b** (100 MHz, $CDCl_3$)



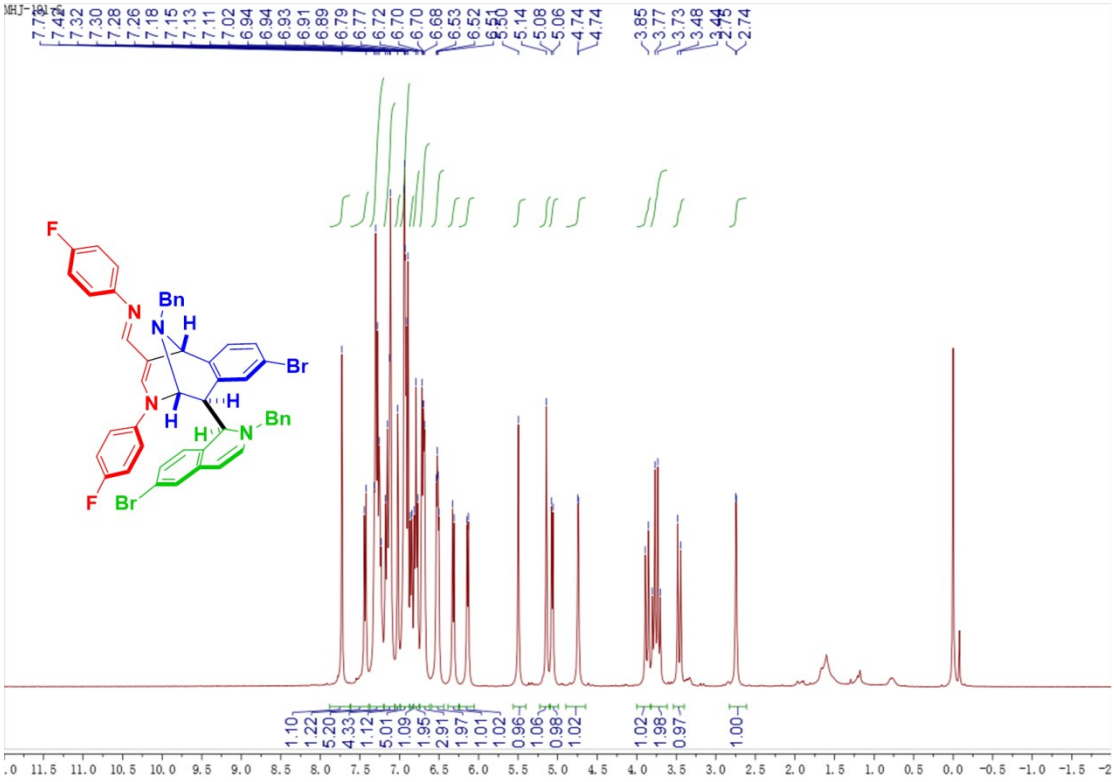
^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$)



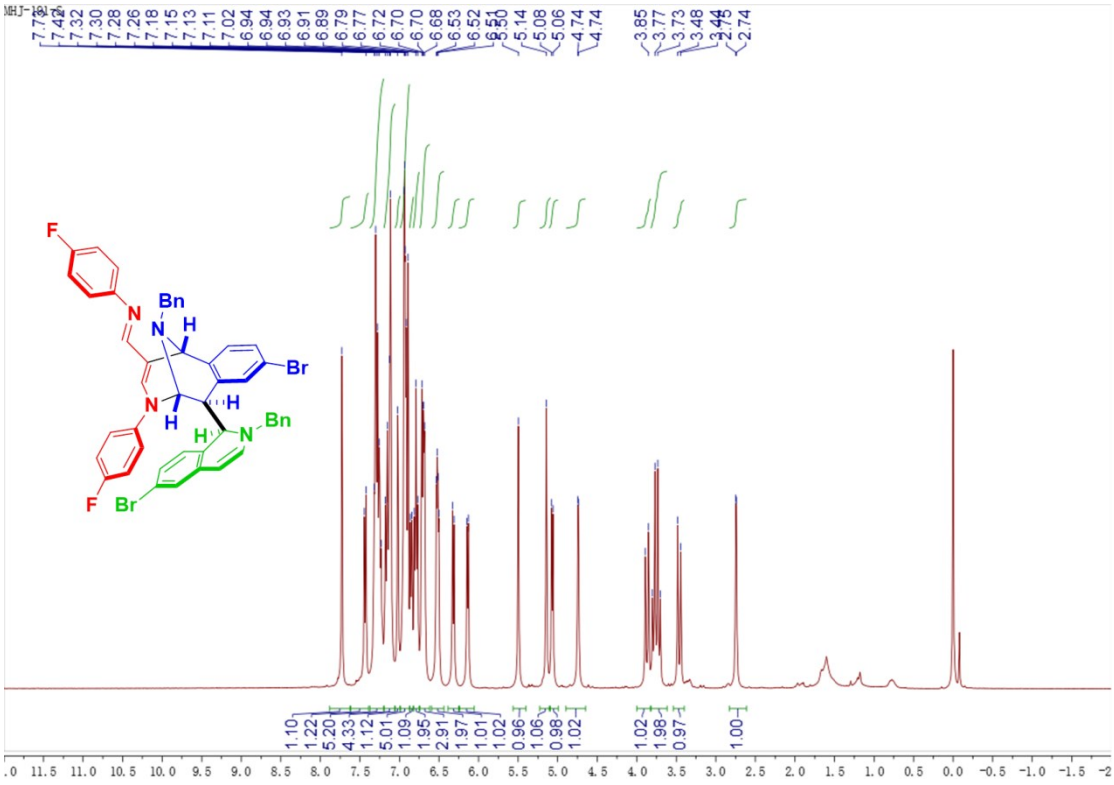
^{13}C NMR spectrum of **7c** (100 MHz, $CDCl_3$)



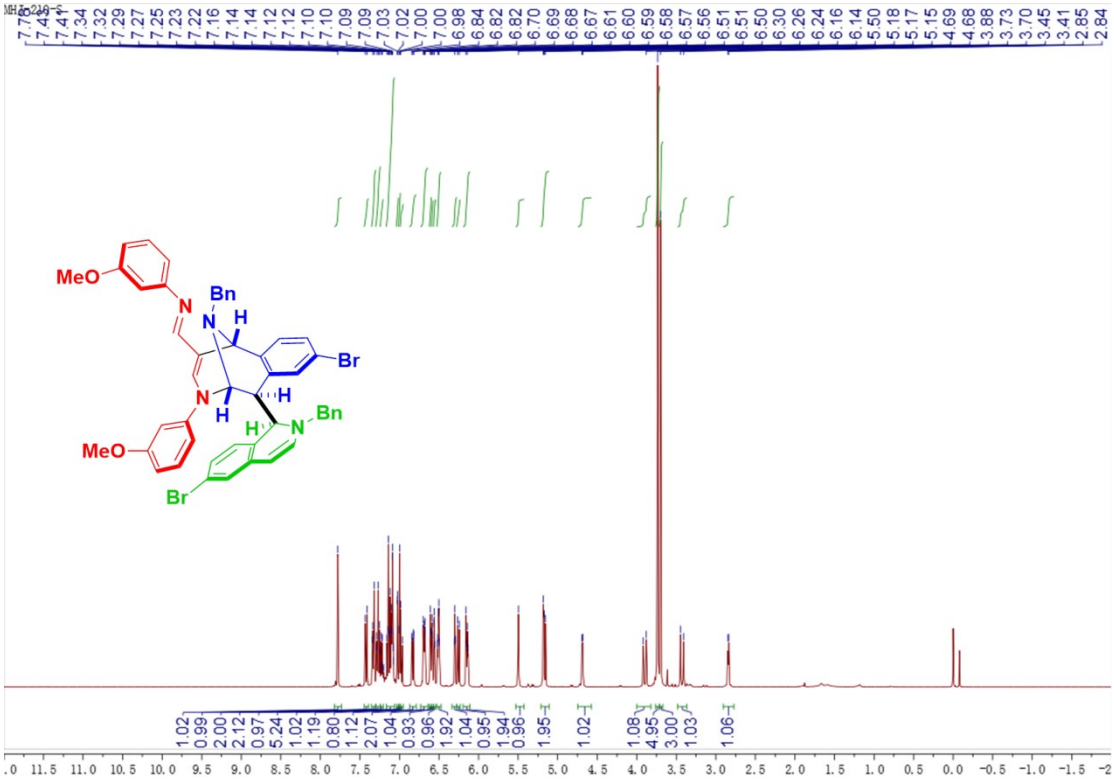
^{1}H NMR spectrum of **7d** (400 MHz, $CDCl_3$)



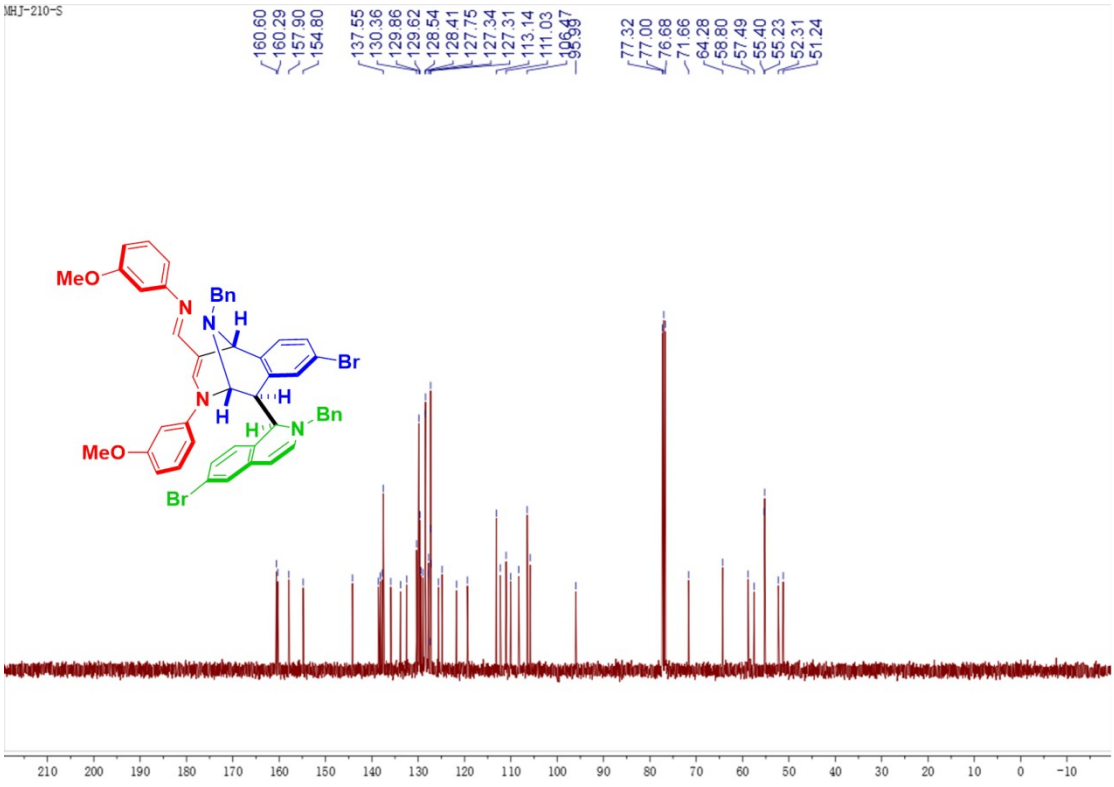
^{13}C NMR spectrum of **7d** (100 MHz, $CDCl_3$)



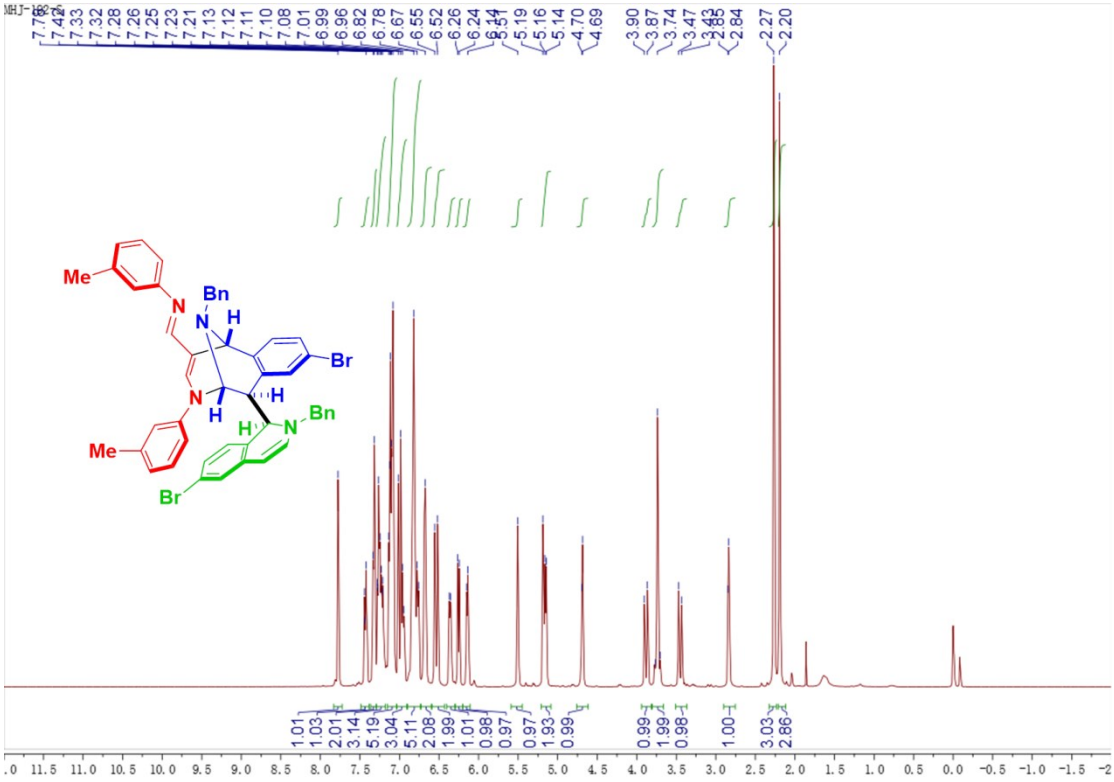
^{1}H NMR spectrum of **7e** (400 MHz, $CDCl_3$)



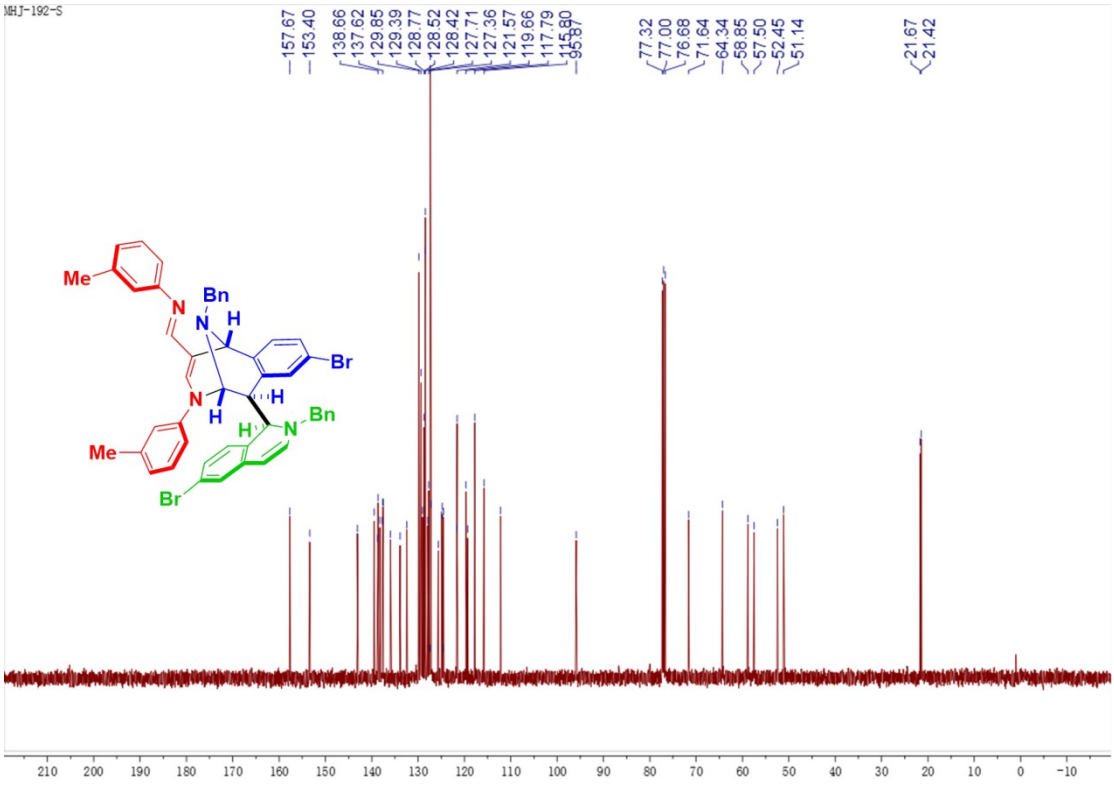
^{13}C NMR spectrum of **7e** (100 MHz, $CDCl_3$)



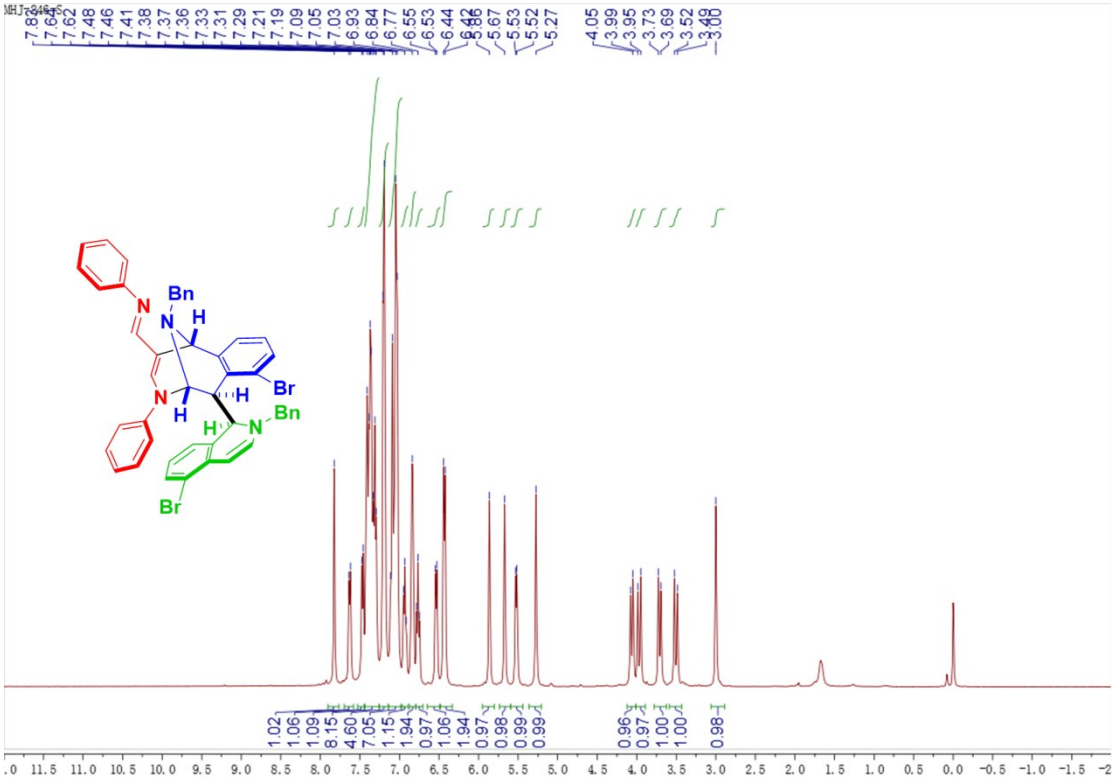
^{1}H NMR spectrum of **7f** (400 MHz, $CDCl_3$)



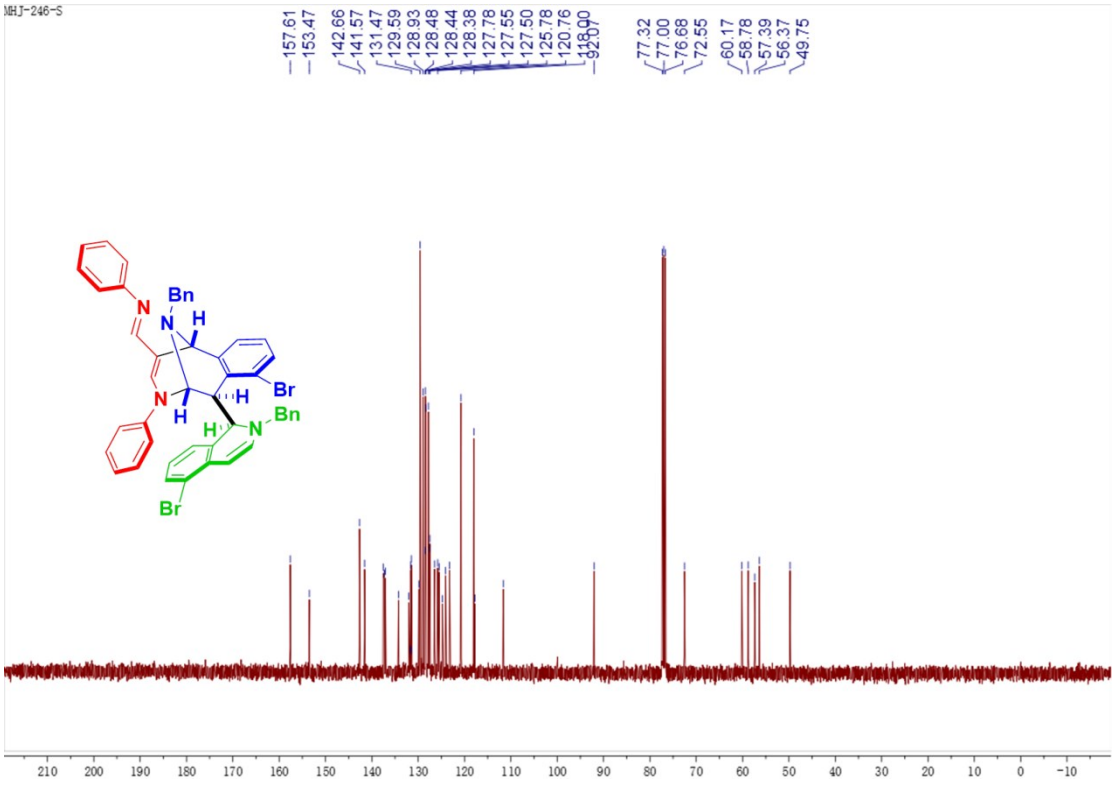
^{13}C NMR spectrum of **7f** (100 MHz, $CDCl_3$)



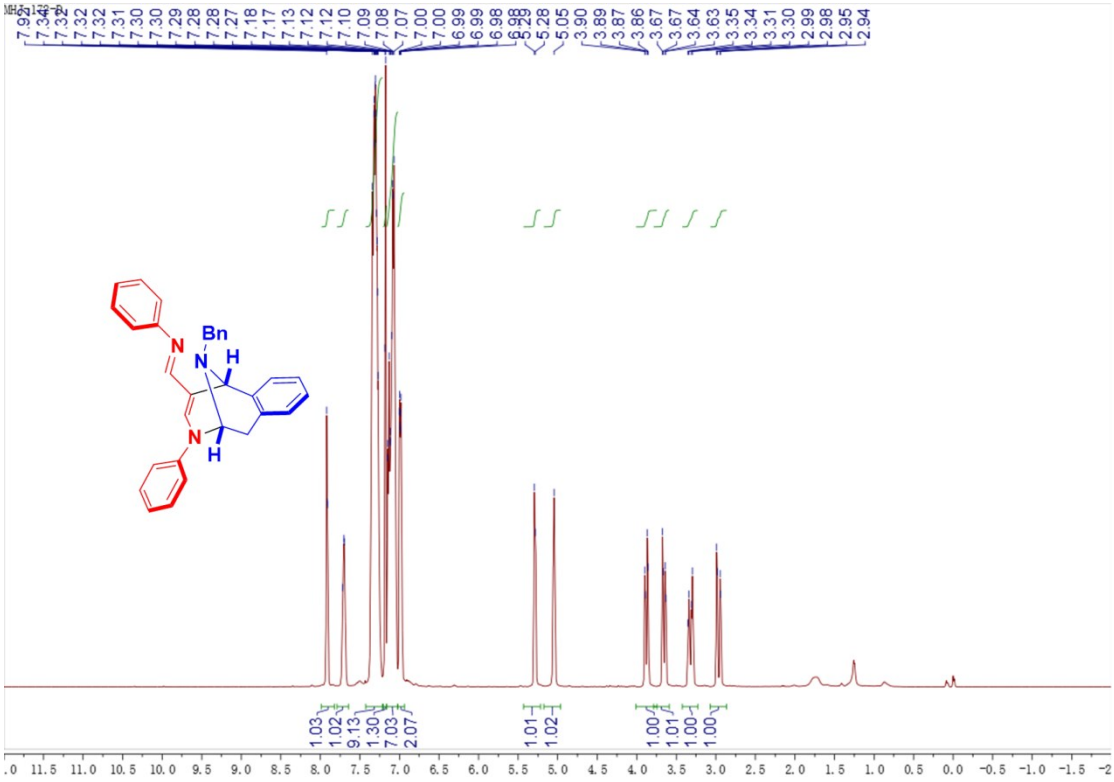
^{1}H NMR spectrum of **7g** (400 MHz, $CDCl_3$)



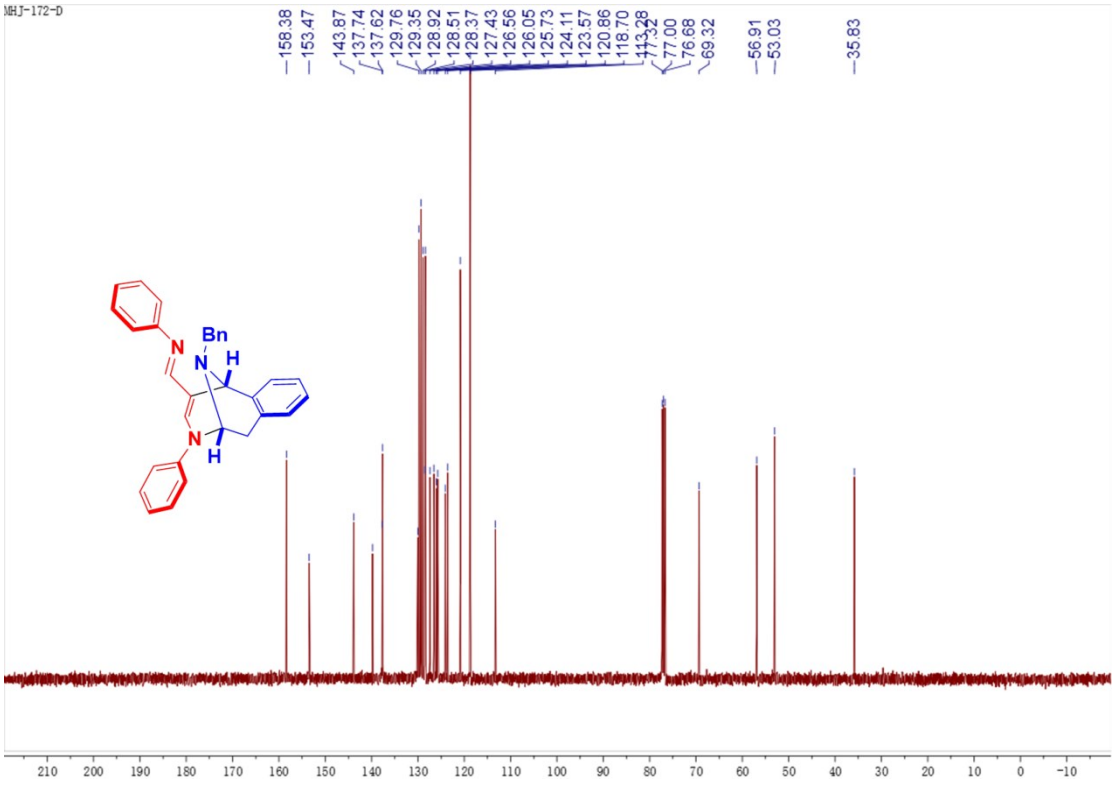
^{13}C NMR spectrum of **7g** (100 MHz, $CDCl_3$)



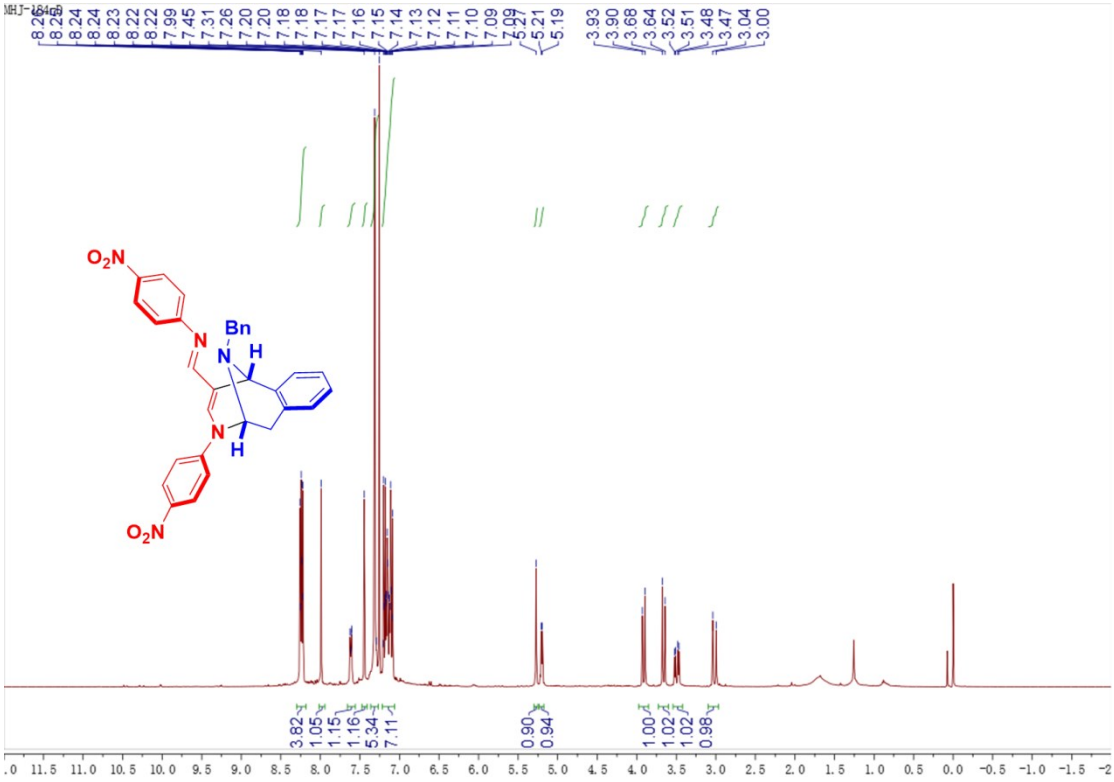
^{1}H NMR spectrum of **8a** (400 MHz, $CDCl_3$)



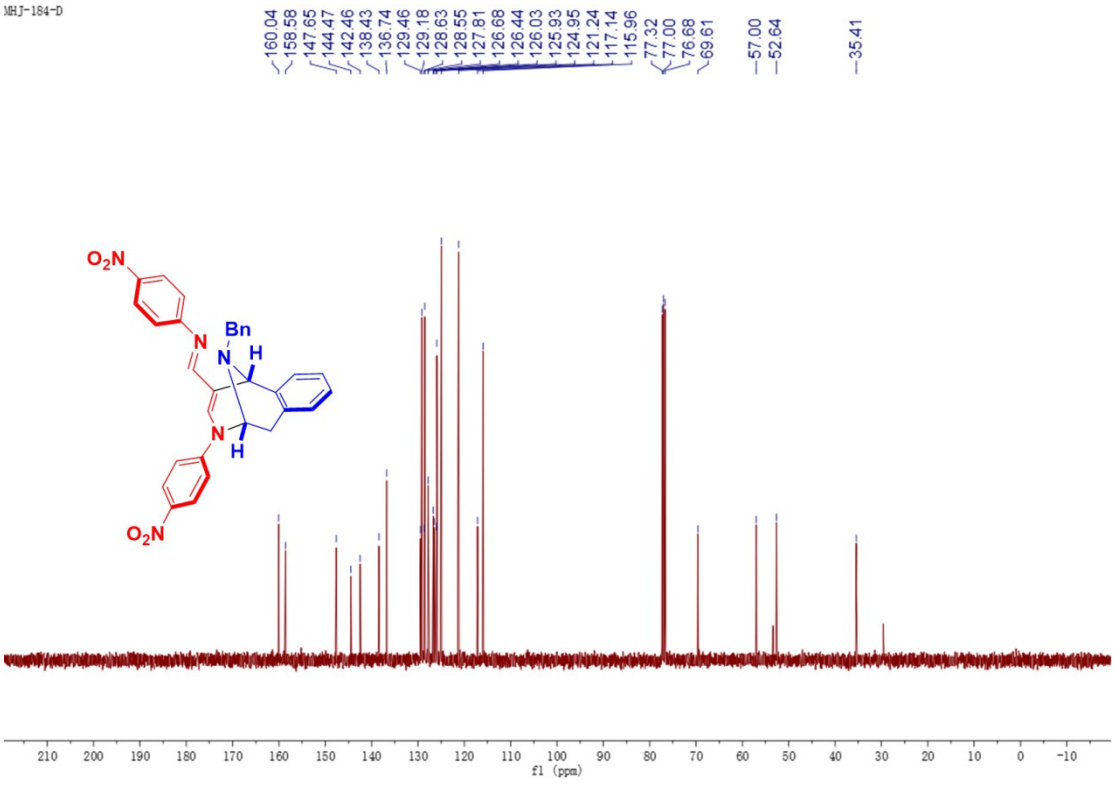
^{13}C NMR spectrum of **8a** (100 MHz, $CDCl_3$)



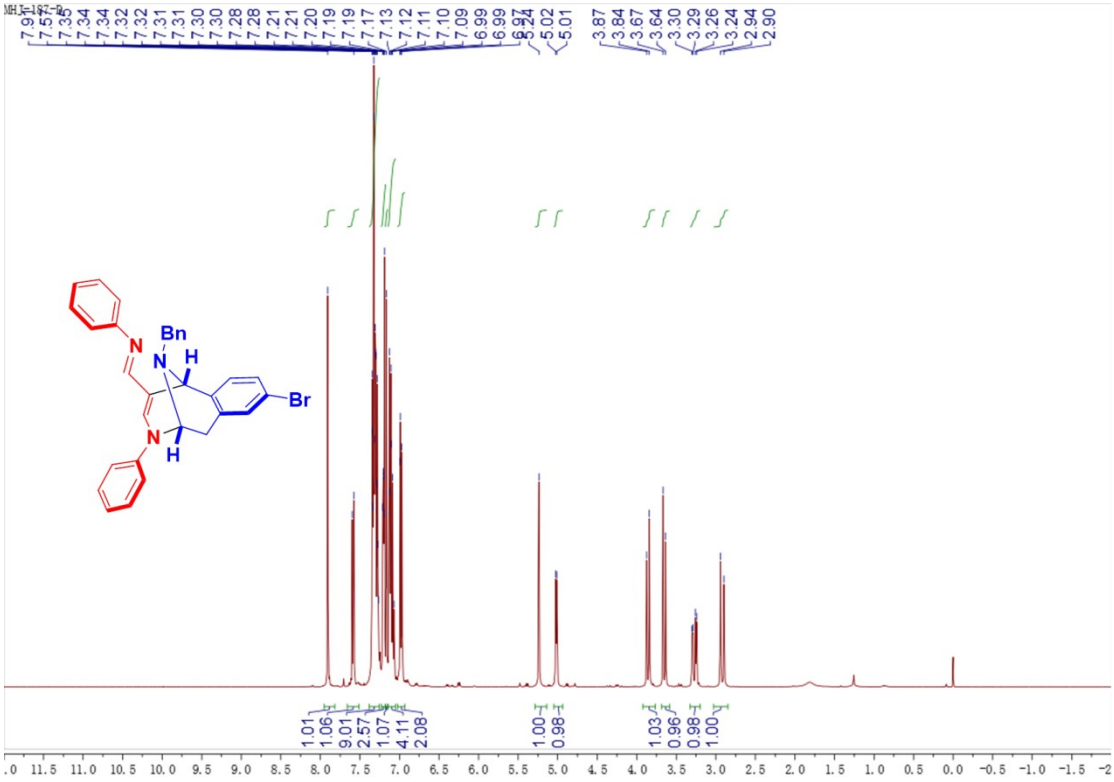
^{1}H NMR spectrum of **8b** (400 MHz, $CDCl_3$)



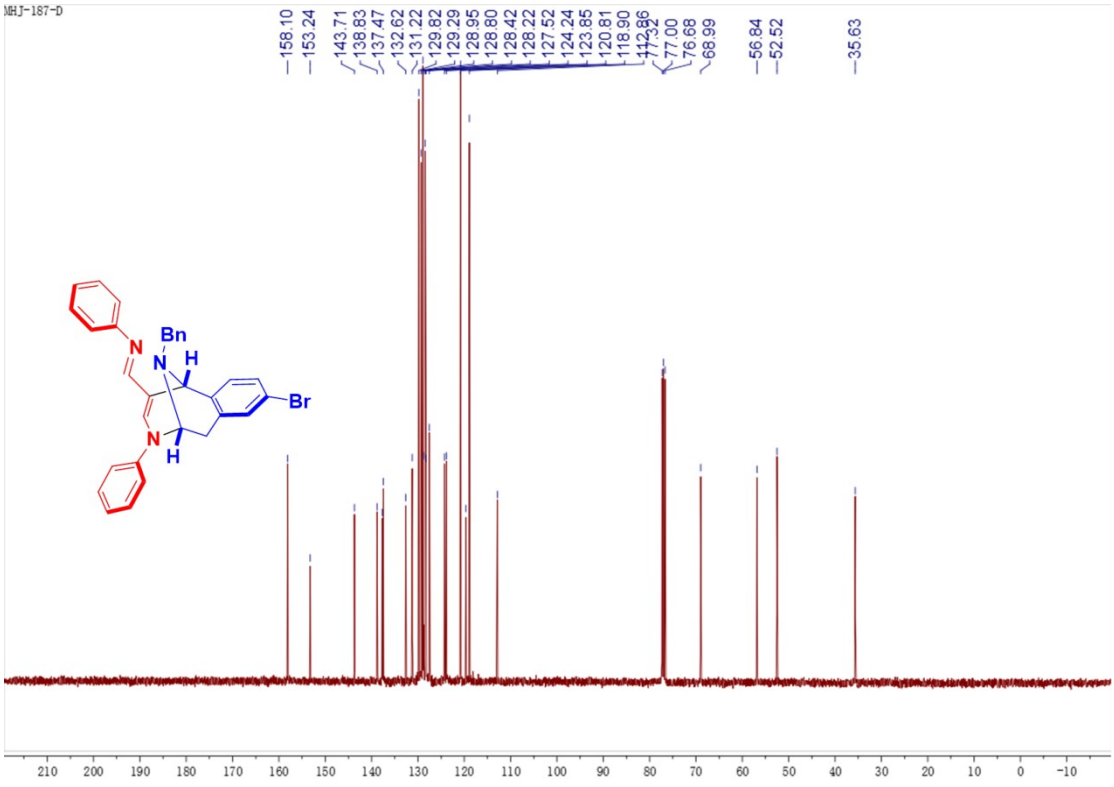
^{13}C NMR spectrum of **8b** (100 MHz, $CDCl_3$)



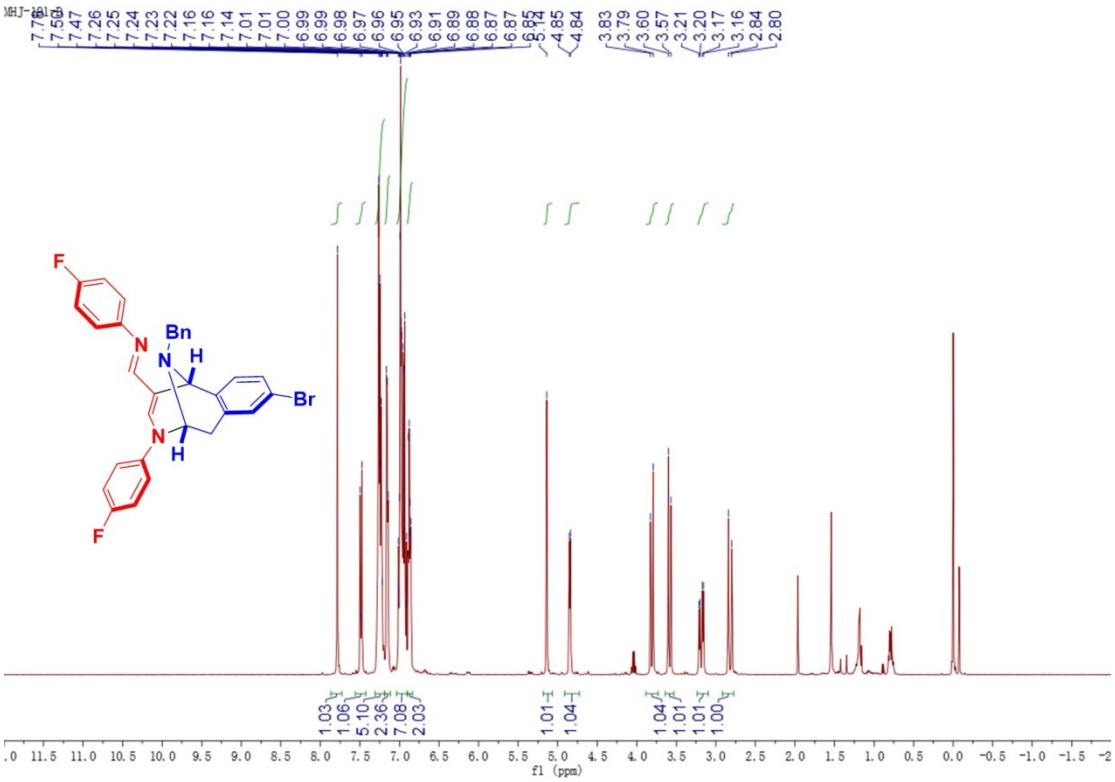
^{1}H NMR spectrum of **8c** (400 MHz, $CDCl_3$)



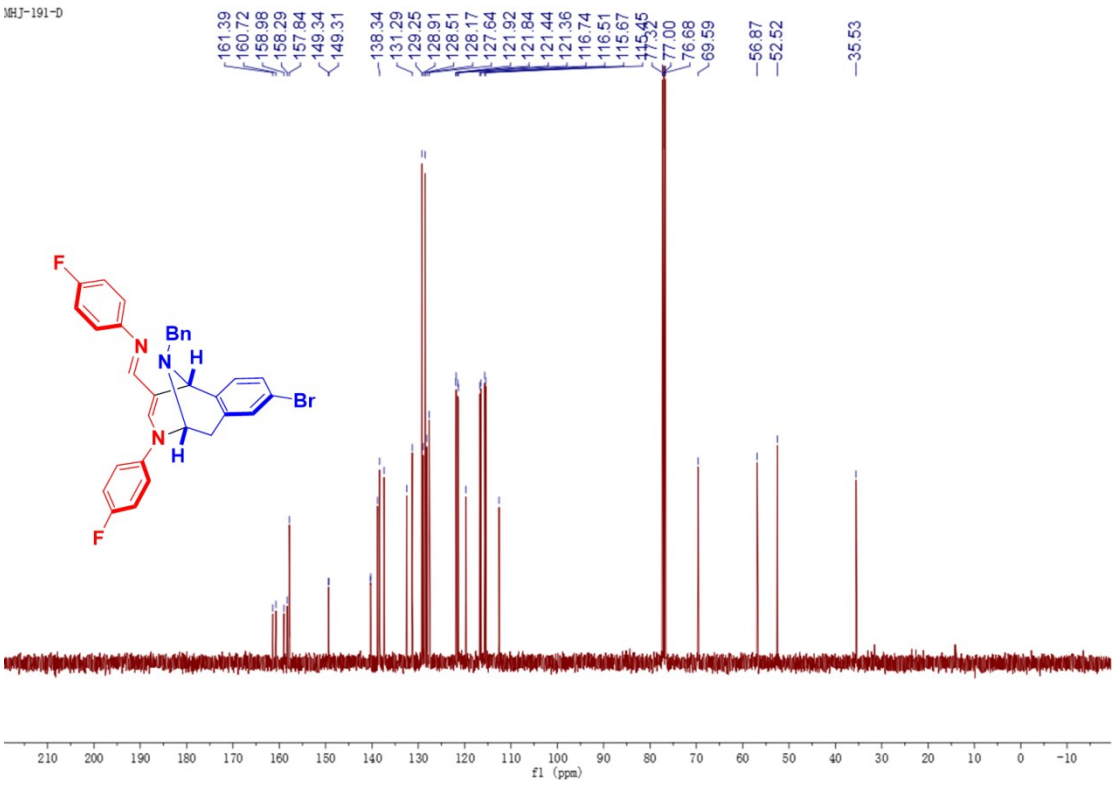
^{13}C NMR spectrum of **8c** (100 MHz, $CDCl_3$)



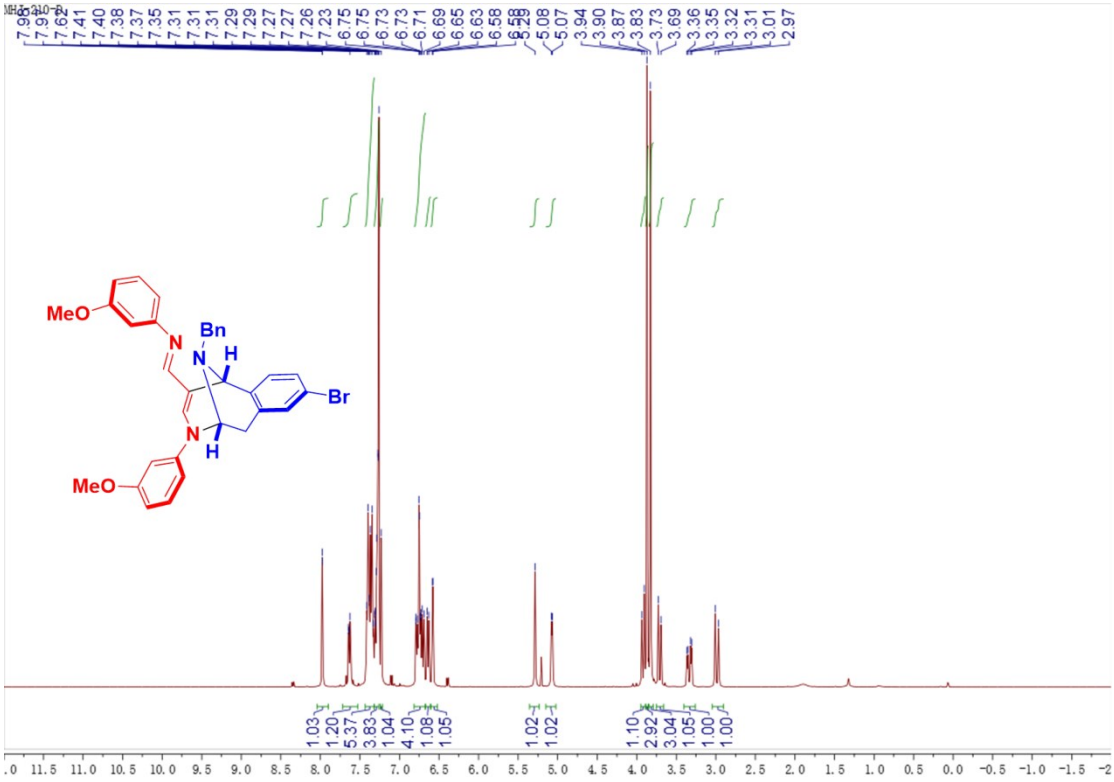
^{1}H NMR spectrum of **8d** (400 MHz, $CDCl_3$)



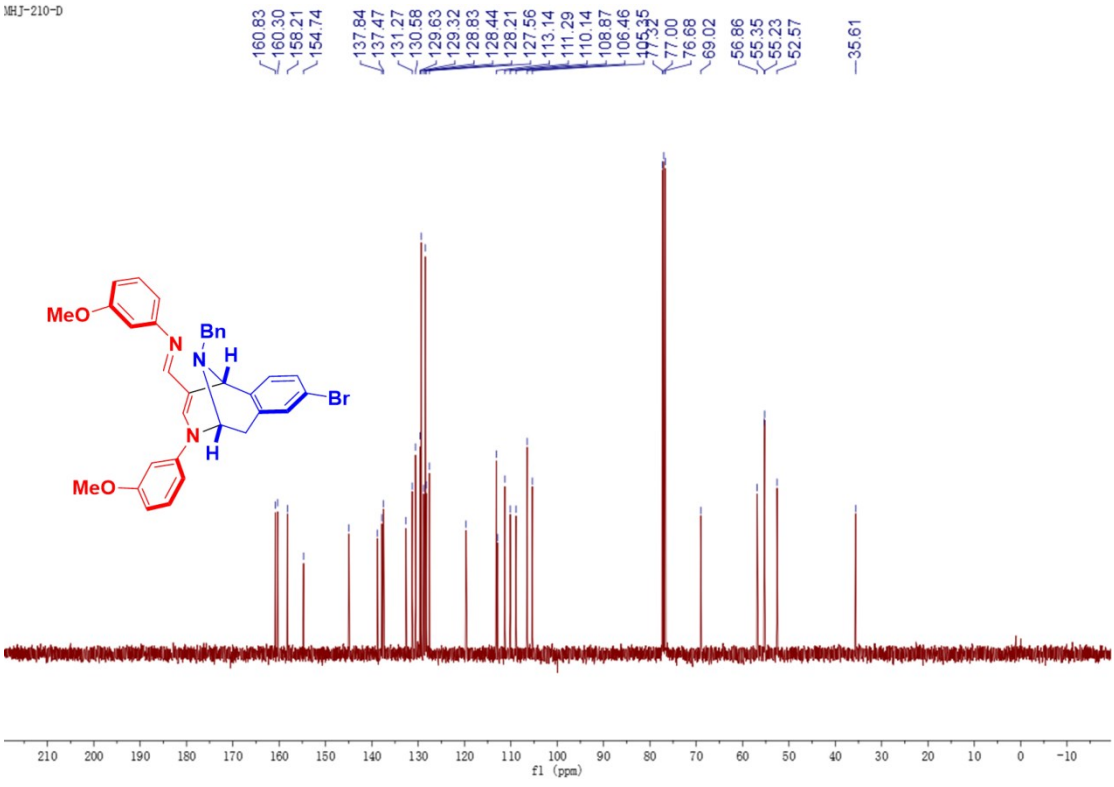
^{13}C NMR spectrum of **8d** (100 MHz, $CDCl_3$)



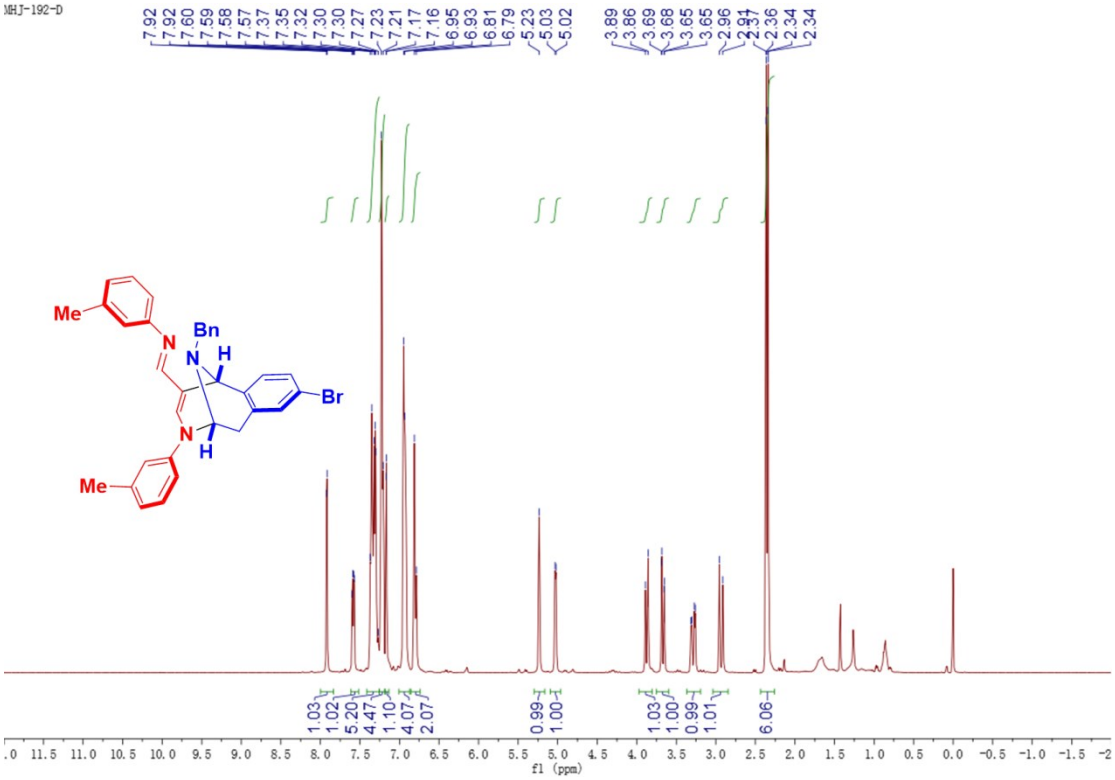
^{1}H NMR spectrum of **8e** (400 MHz, $CDCl_3$)



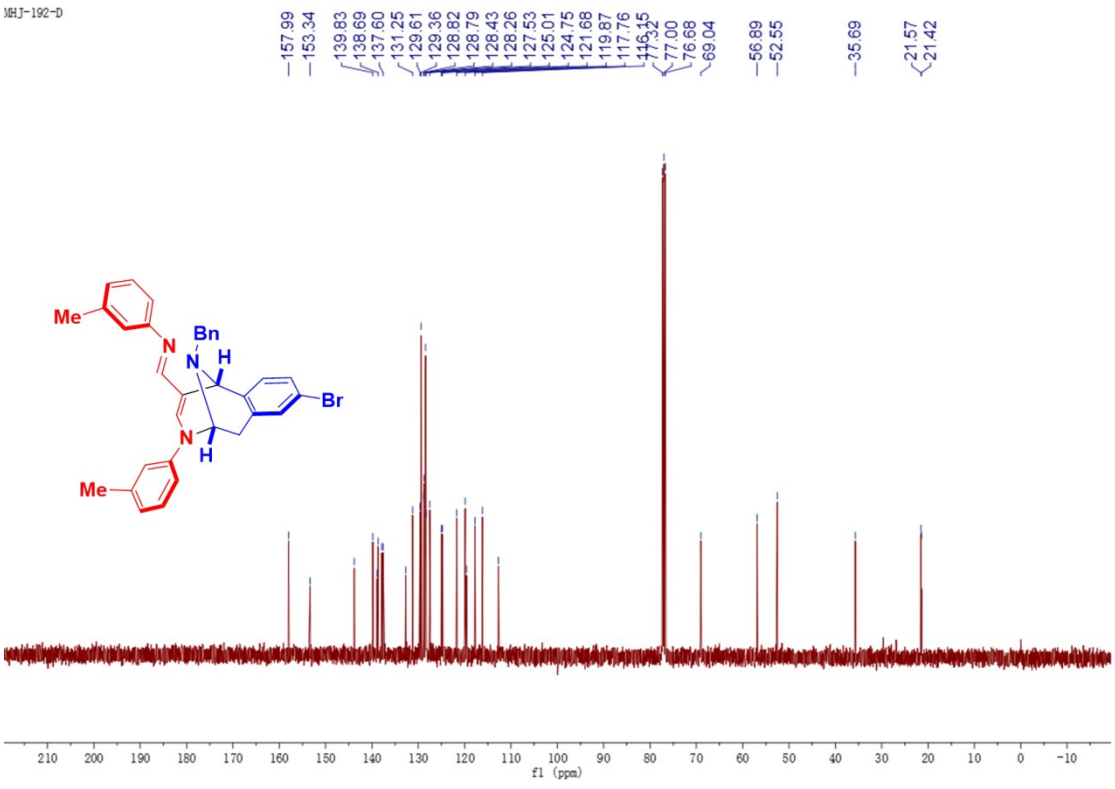
^{13}C NMR spectrum of **8e** (100 MHz, $CDCl_3$)



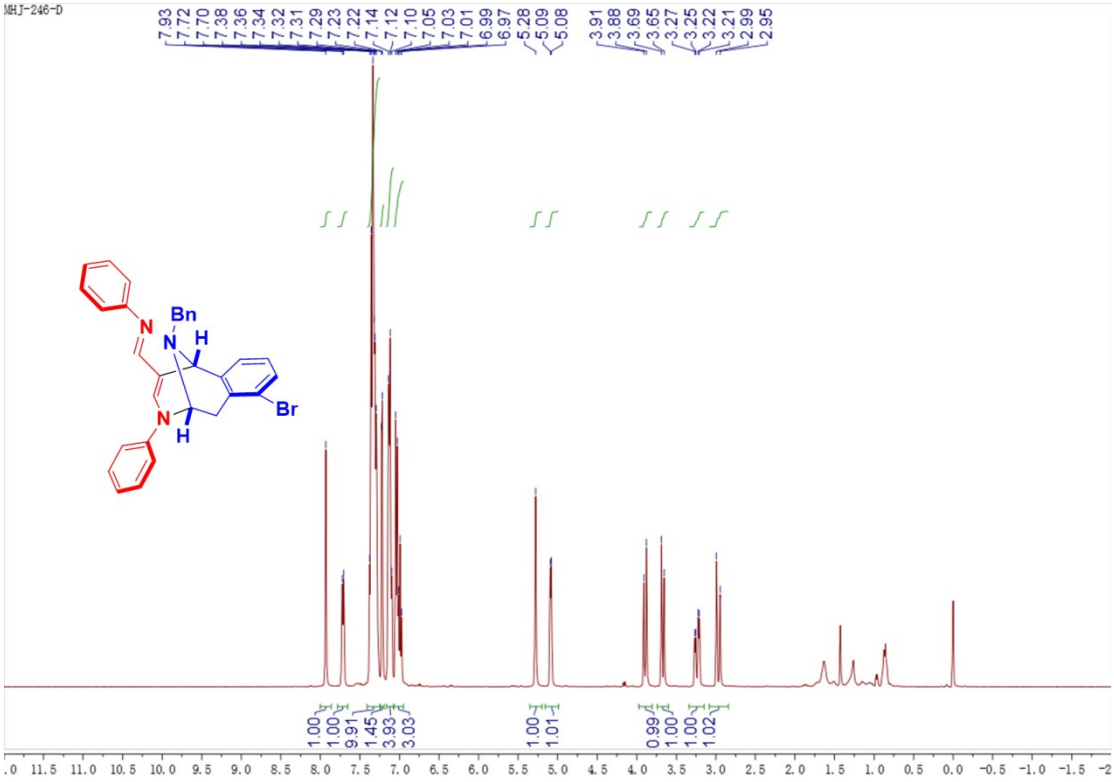
^{1}H NMR spectrum of **8f** (400 MHz, $CDCl_3$)



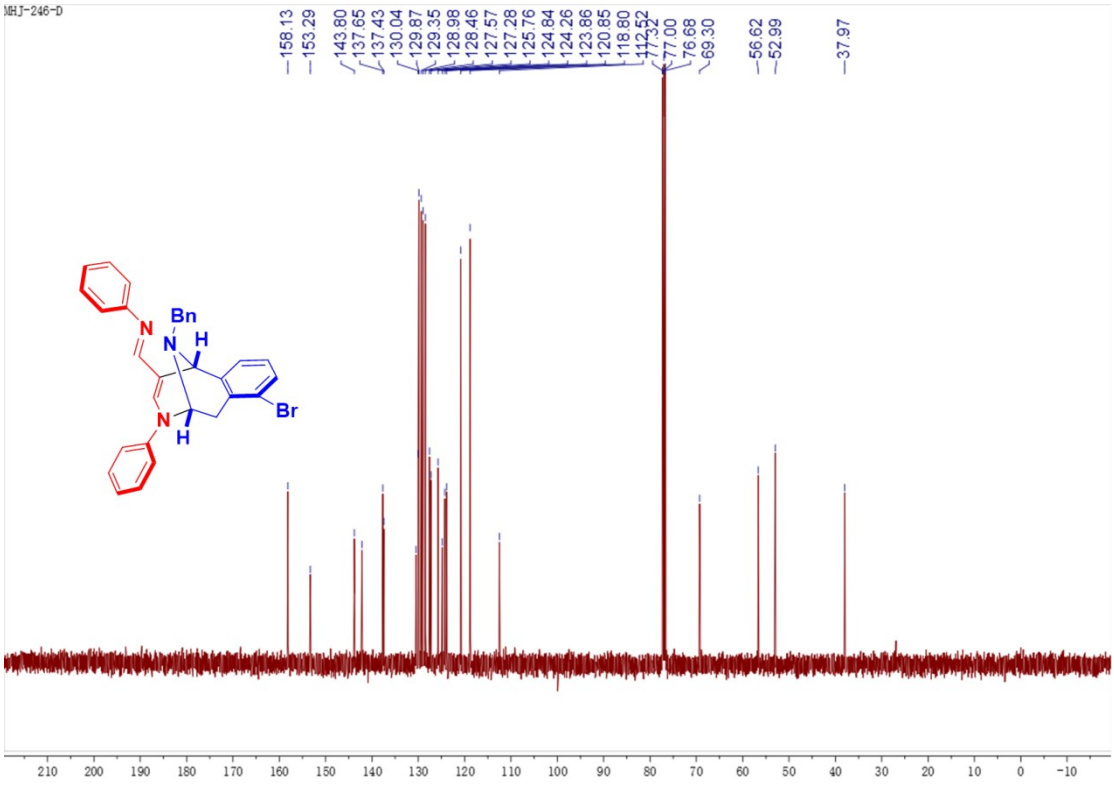
^{13}C NMR spectrum of **8f** (100 MHz, $CDCl_3$)



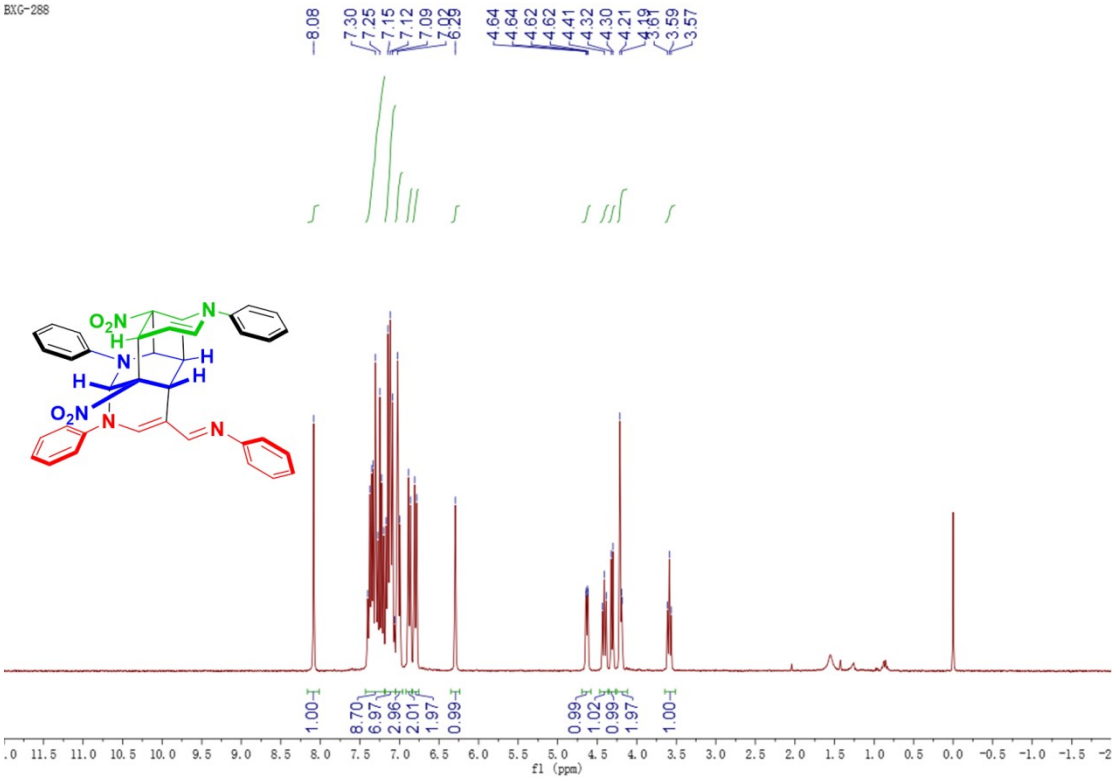
^{1}H NMR spectrum of **8g** (400 MHz, $CDCl_3$)



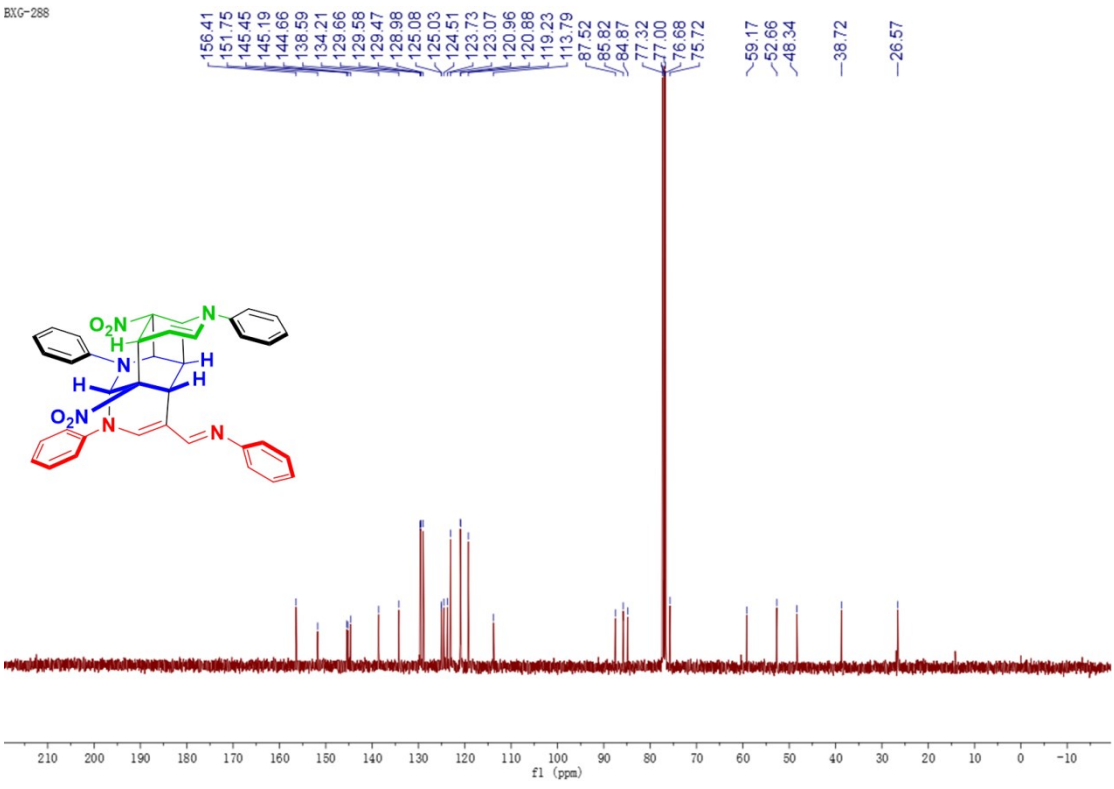
^{13}C NMR spectrum of **8g** (100 MHz, $CDCl_3$)



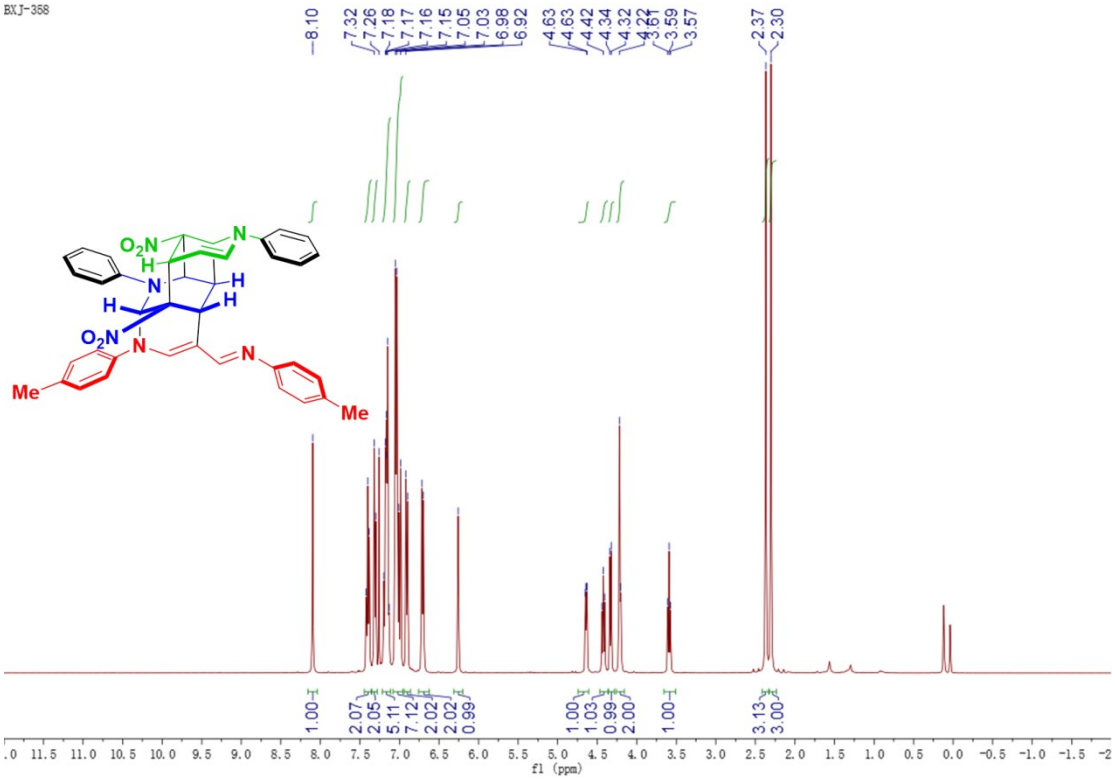
^{1}H NMR spectrum of **12a** (400 MHz, $CDCl_3$)



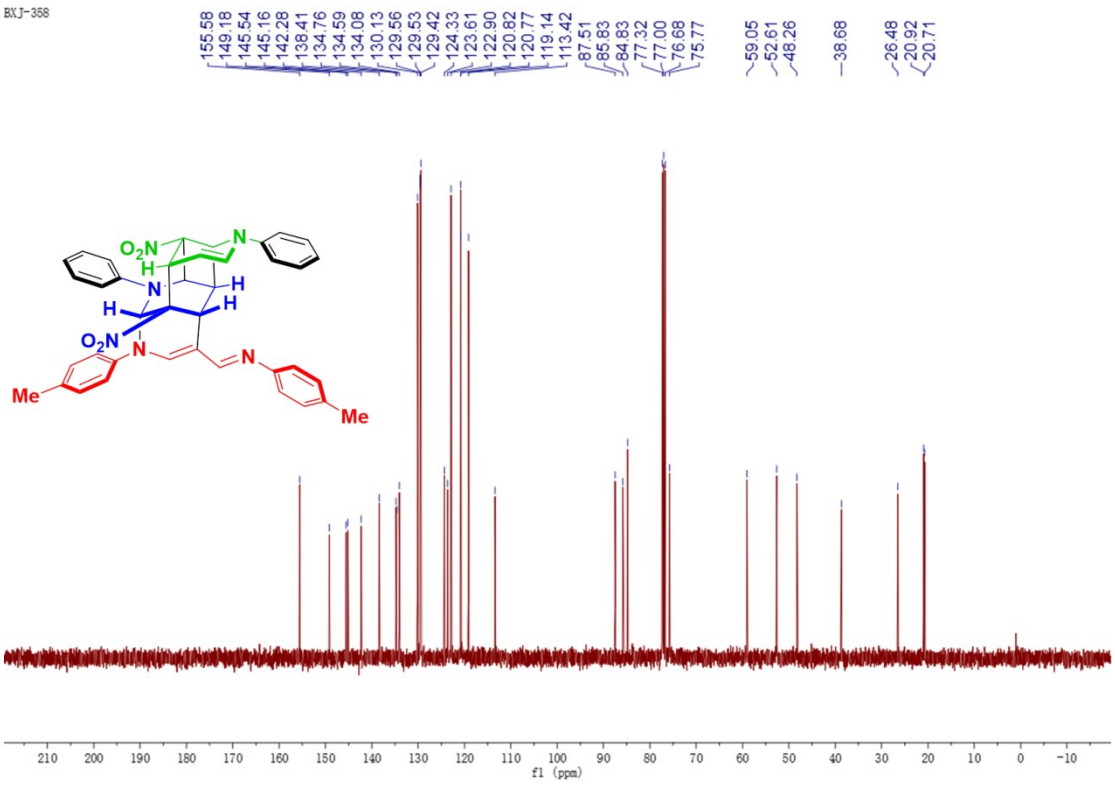
^{13}C NMR spectrum of **12a** (100 MHz, $CDCl_3$)



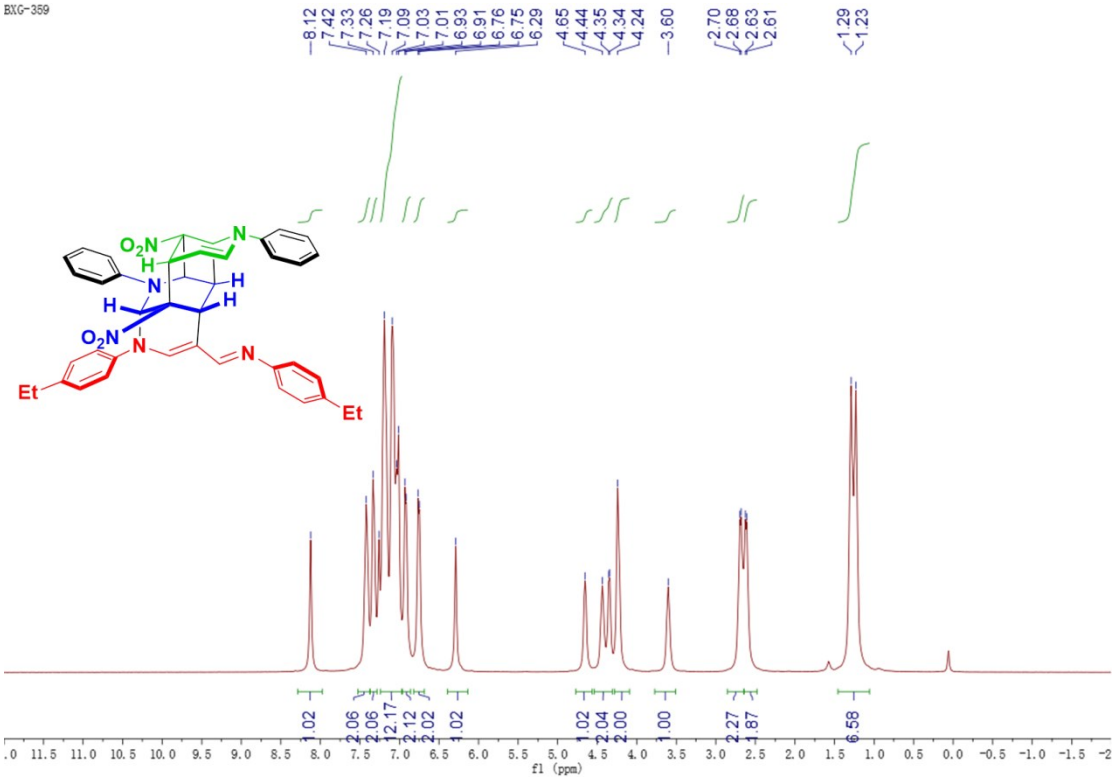
^{1}H NMR spectrum of **12b** (400 MHz, $CDCl_3$)



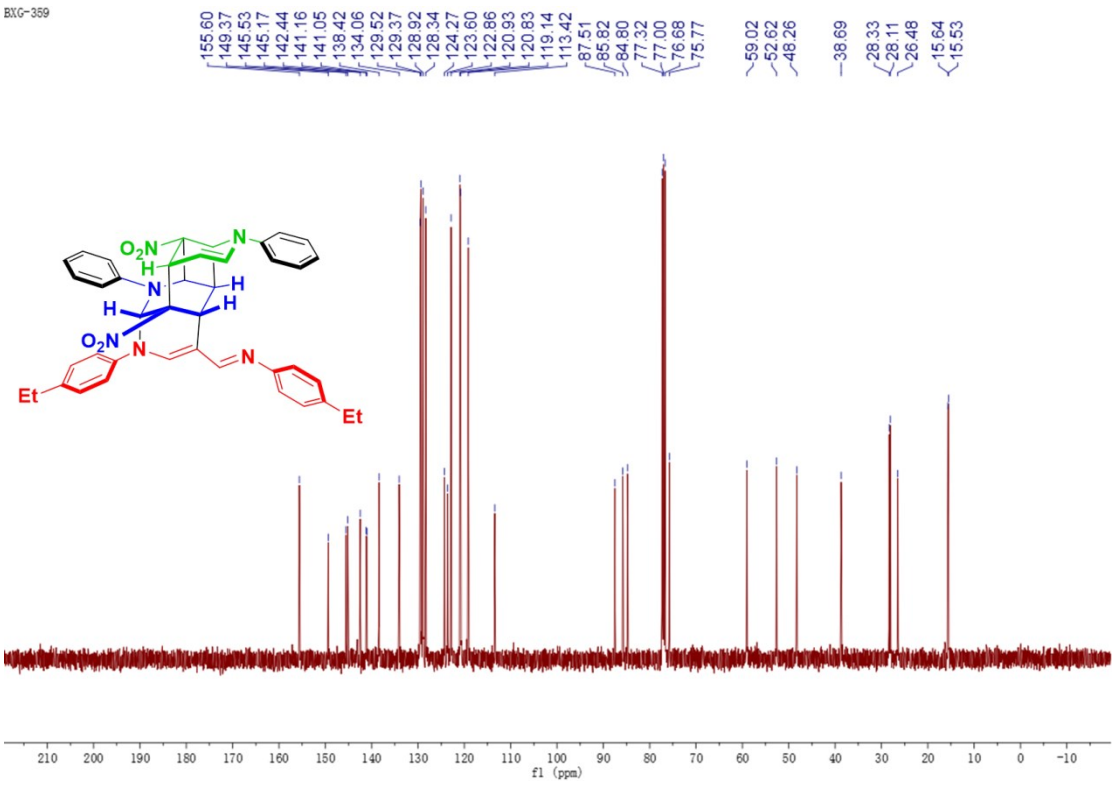
^{13}C NMR spectrum of **12b** (100 MHz, $CDCl_3$)



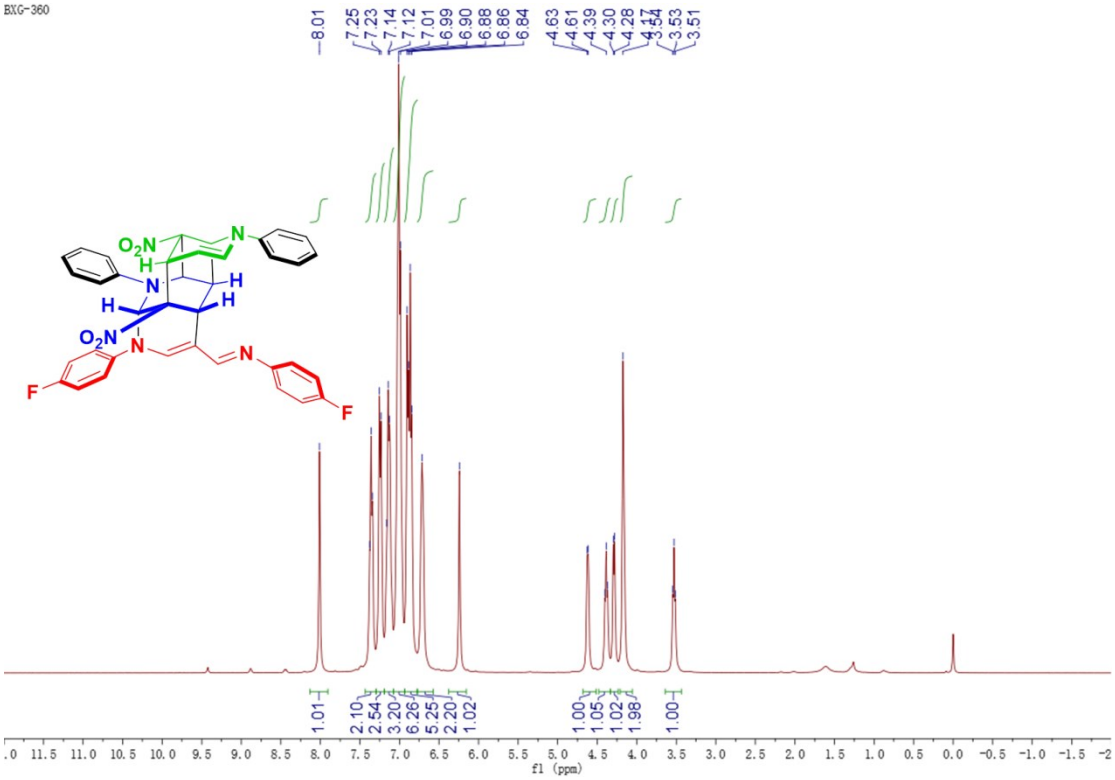
^{1}H NMR spectrum of **12c** (400 MHz, $CDCl_3$)



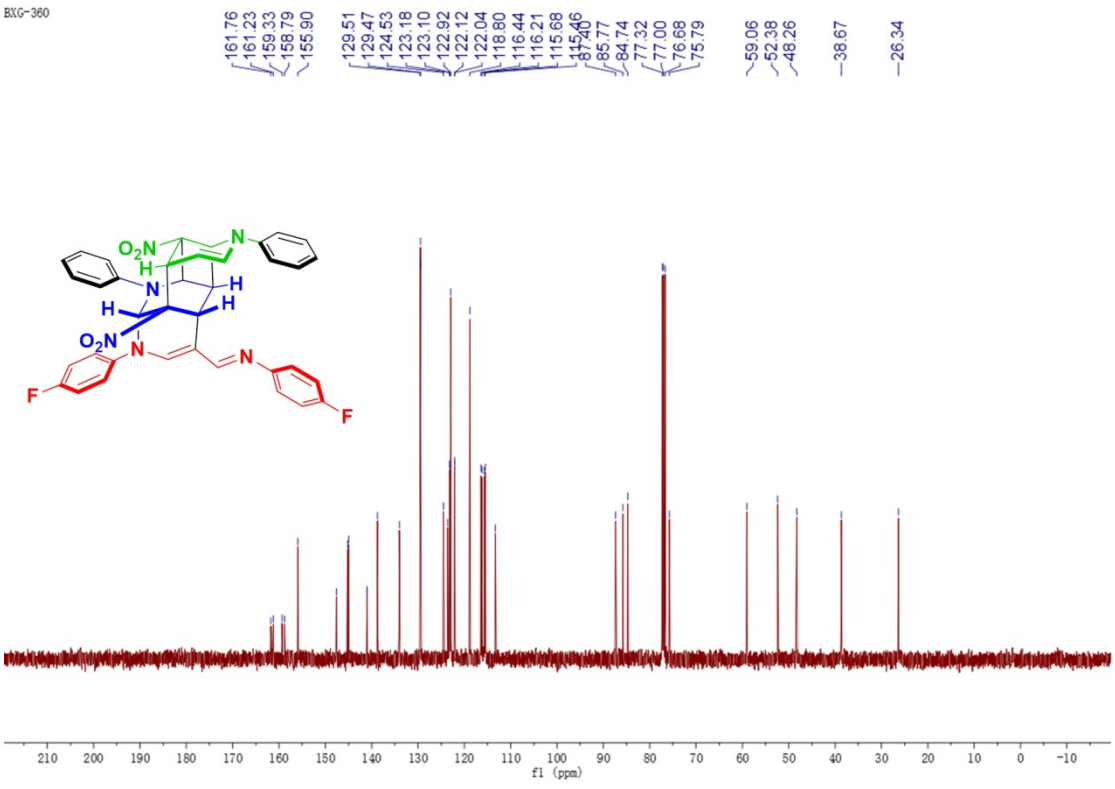
^{13}C NMR spectrum of **12c** (100 MHz, $CDCl_3$)



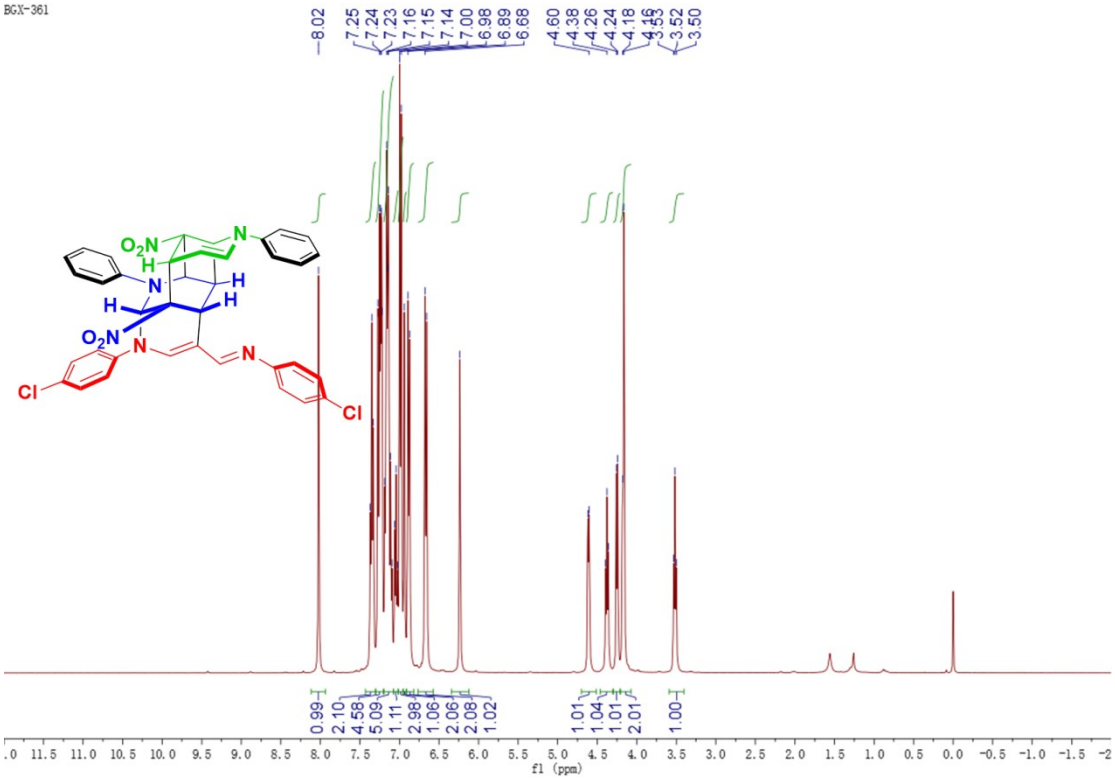
^{1}H NMR spectrum of **12d** (400 MHz, $CDCl_3$)



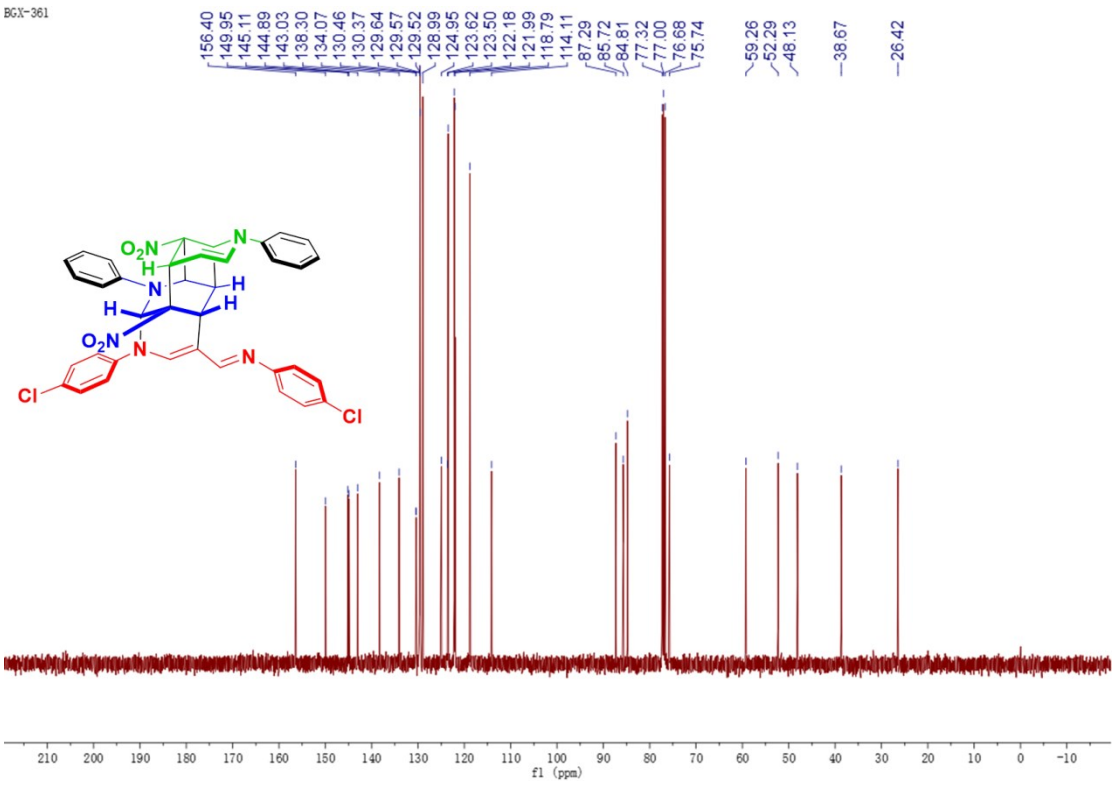
^{13}C NMR spectrum of **12d** (100 MHz, $CDCl_3$)



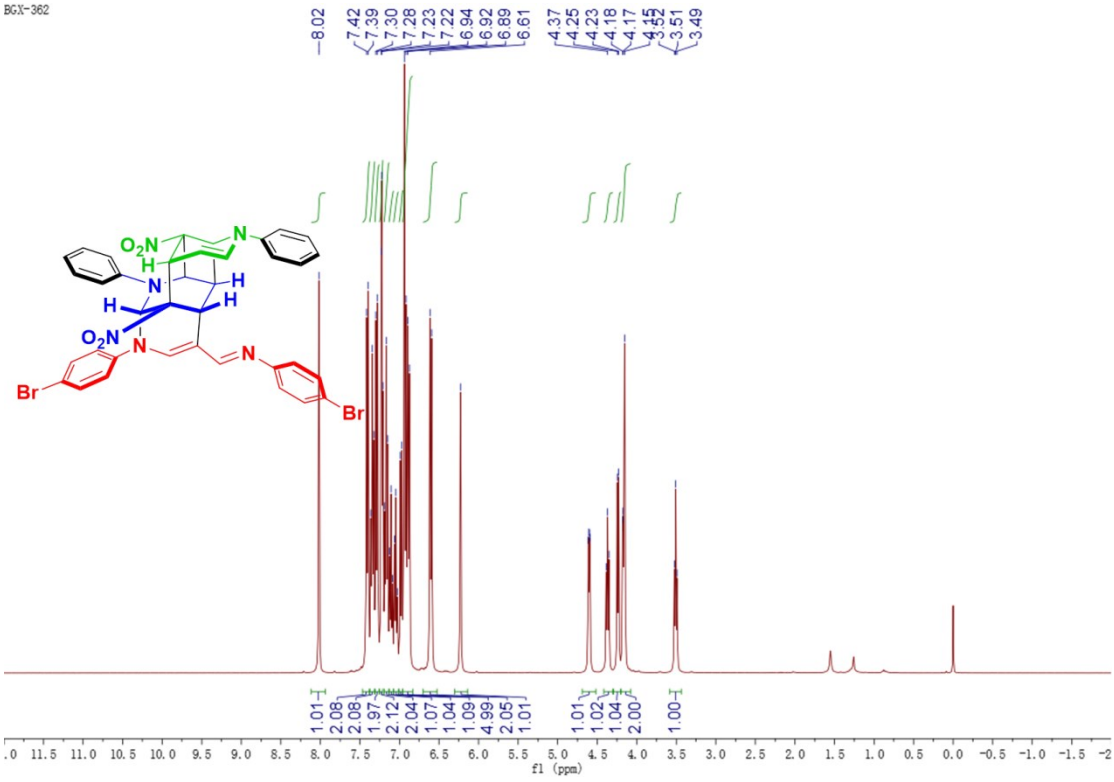
^{1}H NMR spectrum of **12e** (400 MHz, $CDCl_3$)



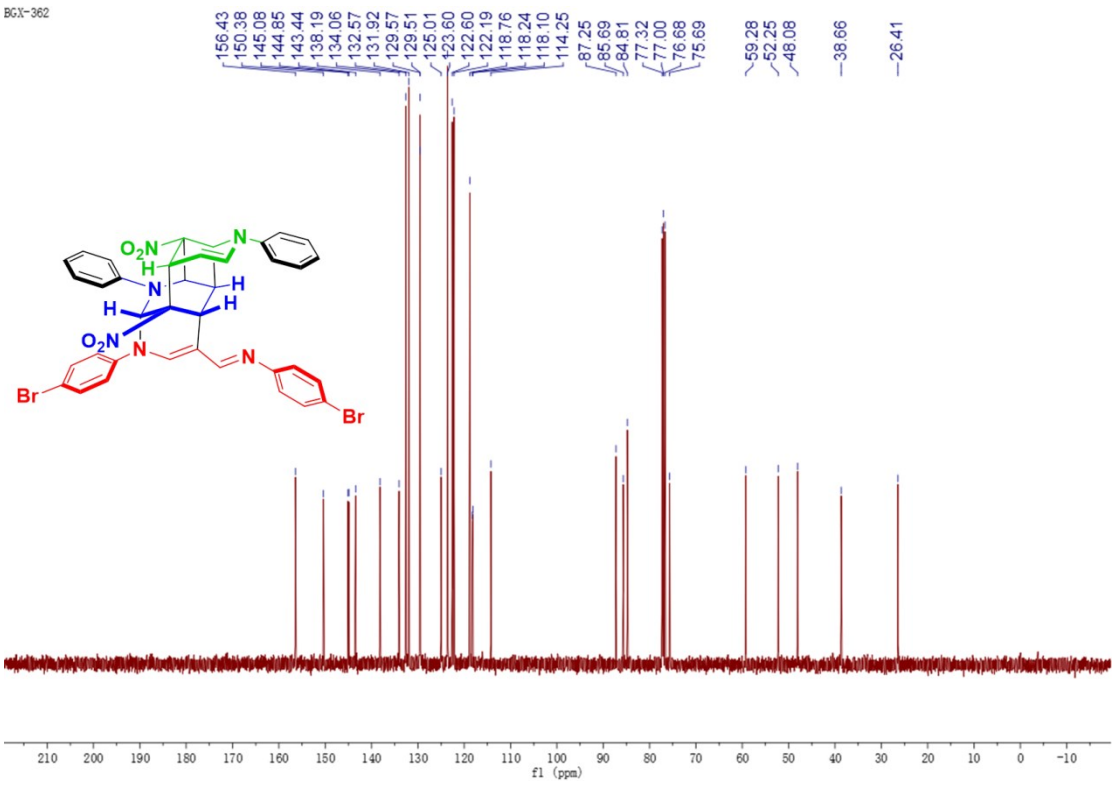
^{13}C NMR spectrum of **12e** (100 MHz, $CDCl_3$)



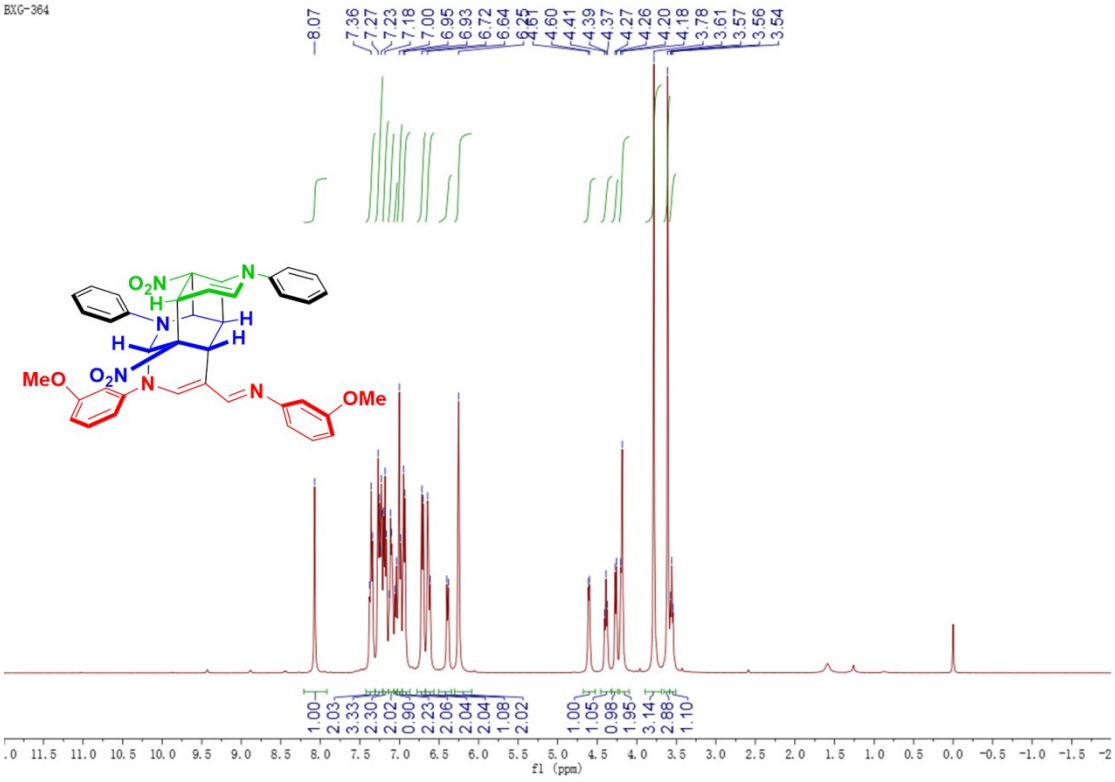
^{1}H NMR spectrum of **12f** (400 MHz, $CDCl_3$)



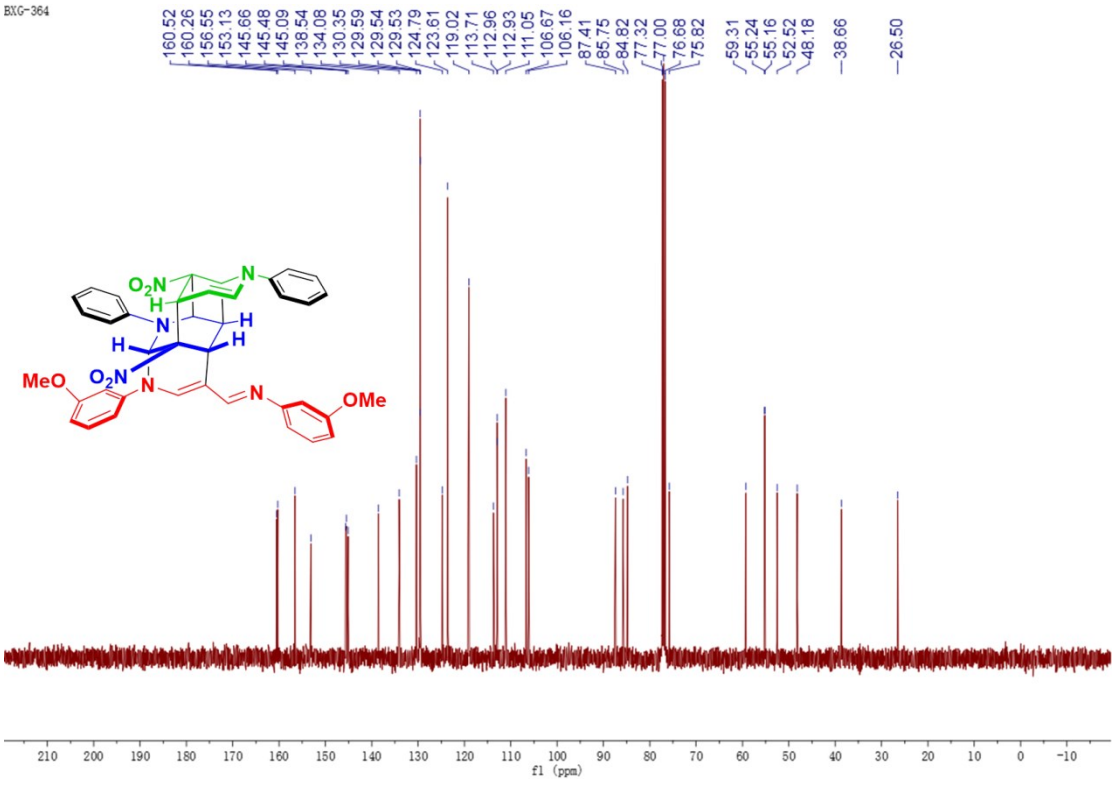
^{13}C NMR spectrum of **12f** (100 MHz, $CDCl_3$)



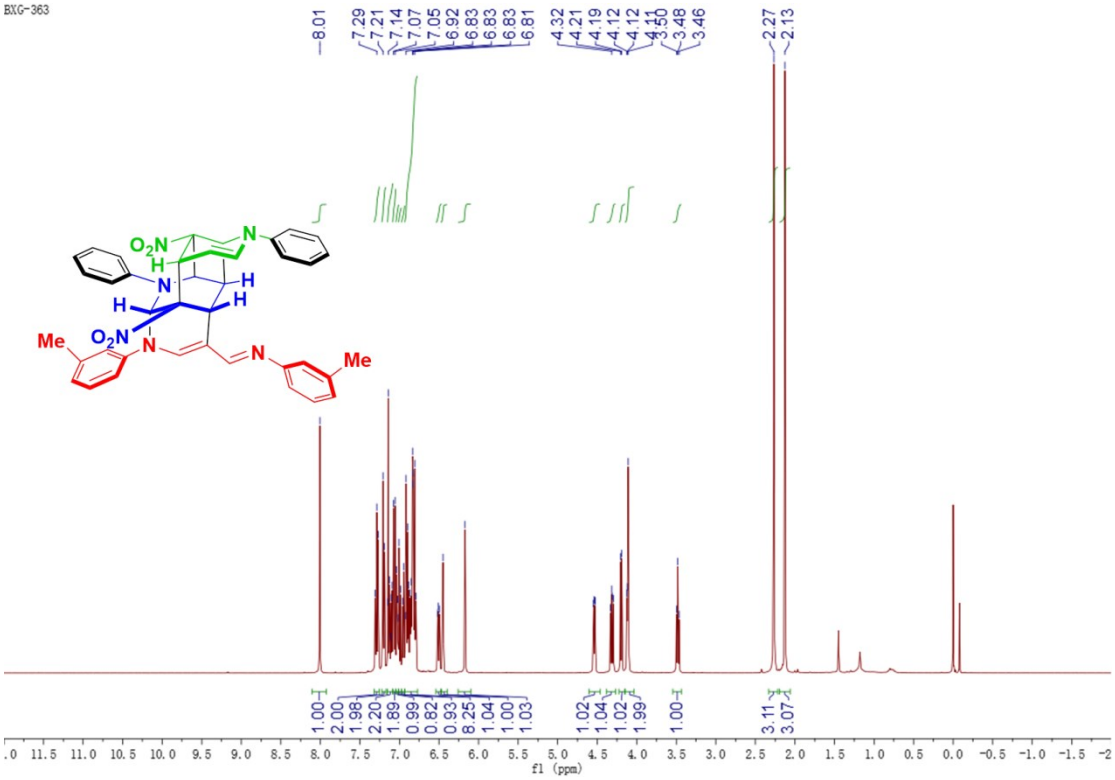
^{1}H NMR spectrum of **12g** (400 MHz, $CDCl_3$)



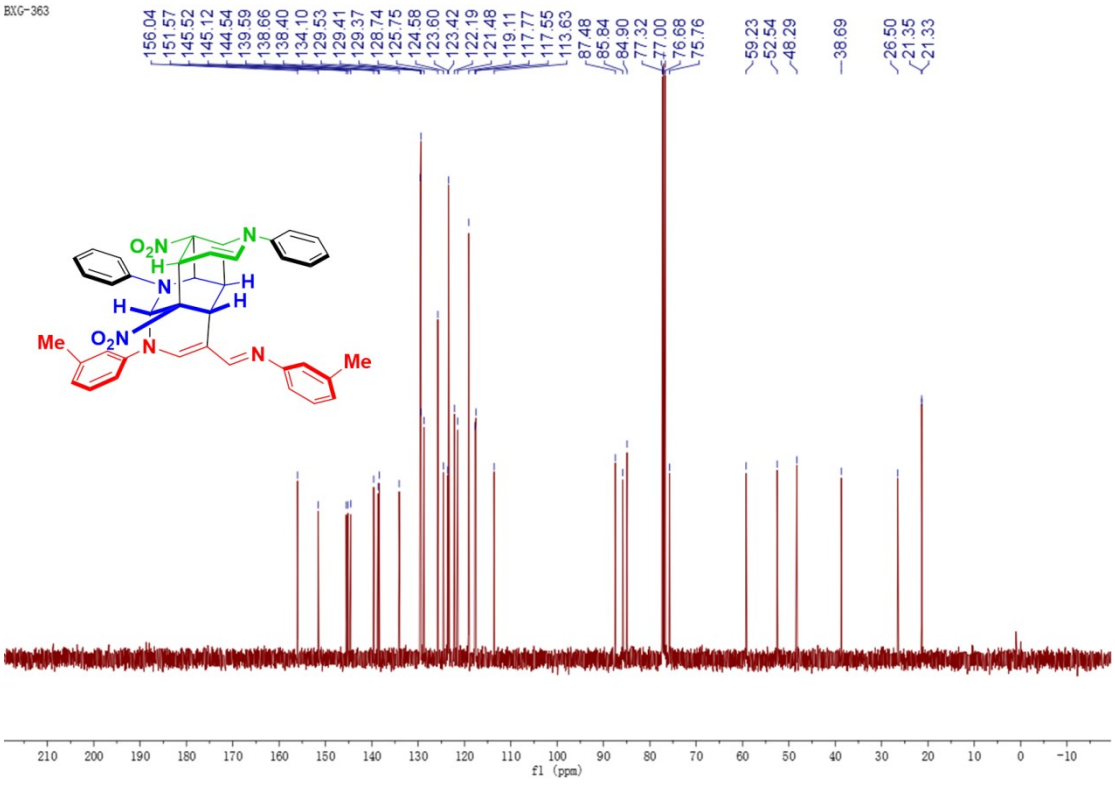
^{13}C NMR spectrum of **12g** (100 MHz, $CDCl_3$)



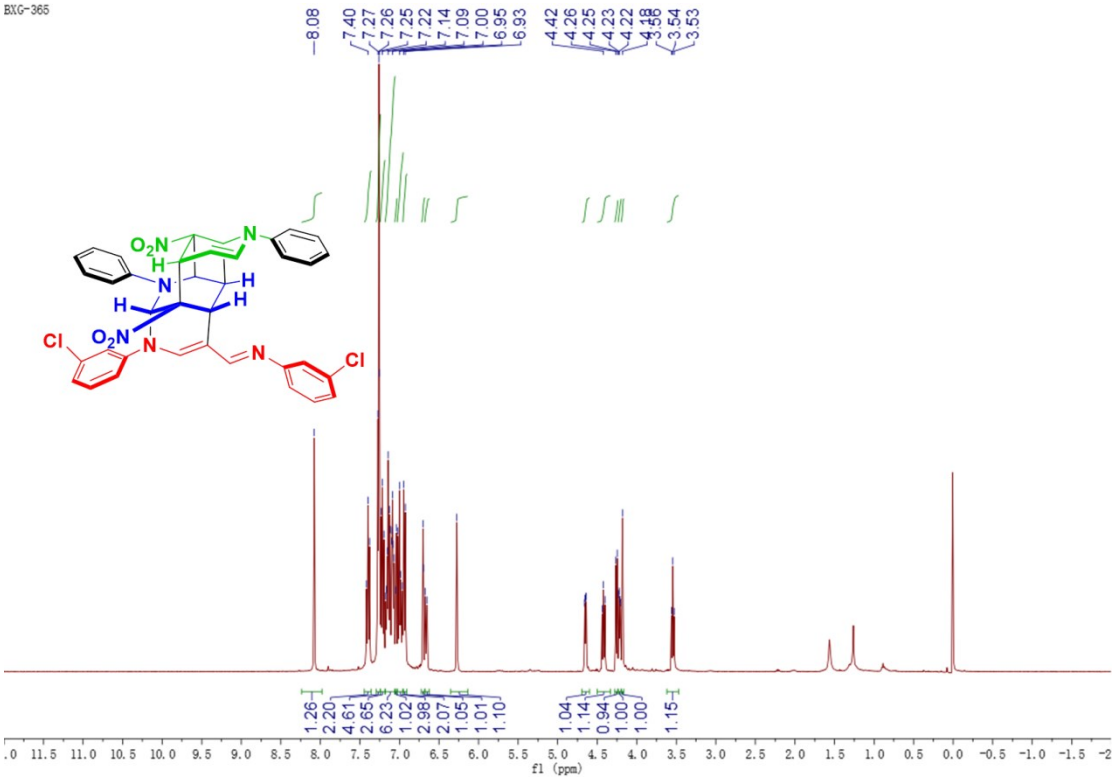
^{1}H NMR spectrum of **12h** (400 MHz, $CDCl_3$)



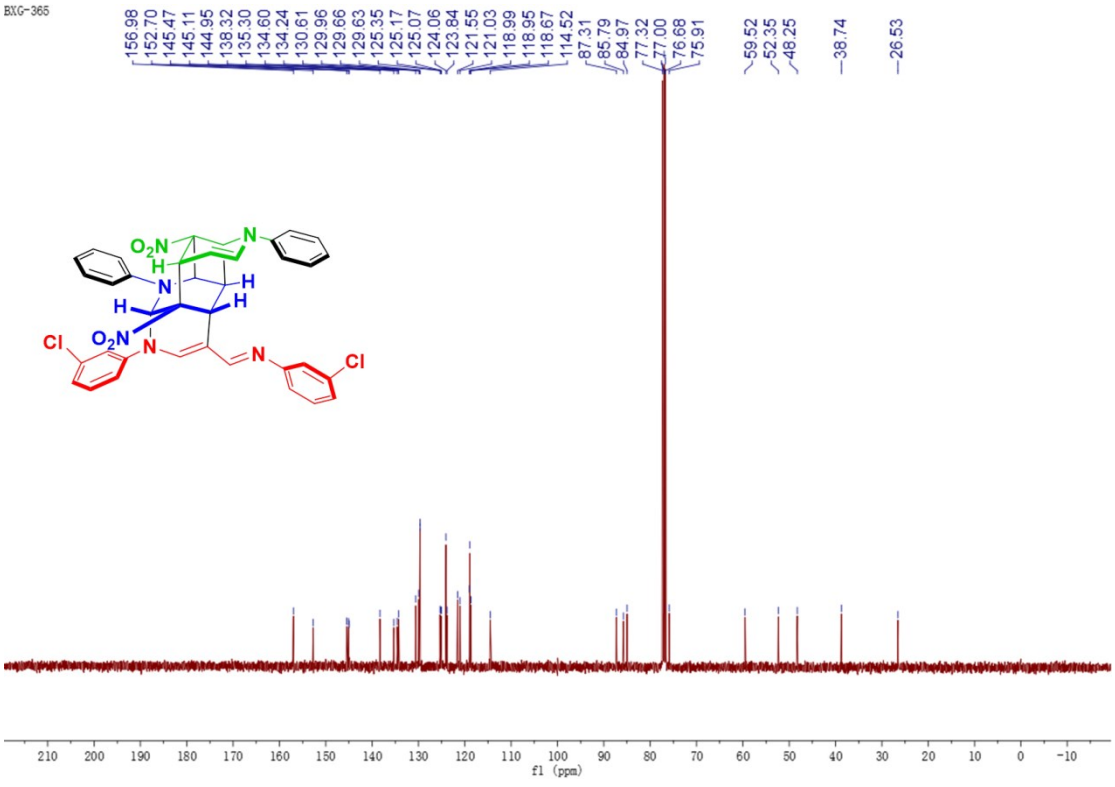
^{13}C NMR spectrum of **12h** (100 MHz, $CDCl_3$)



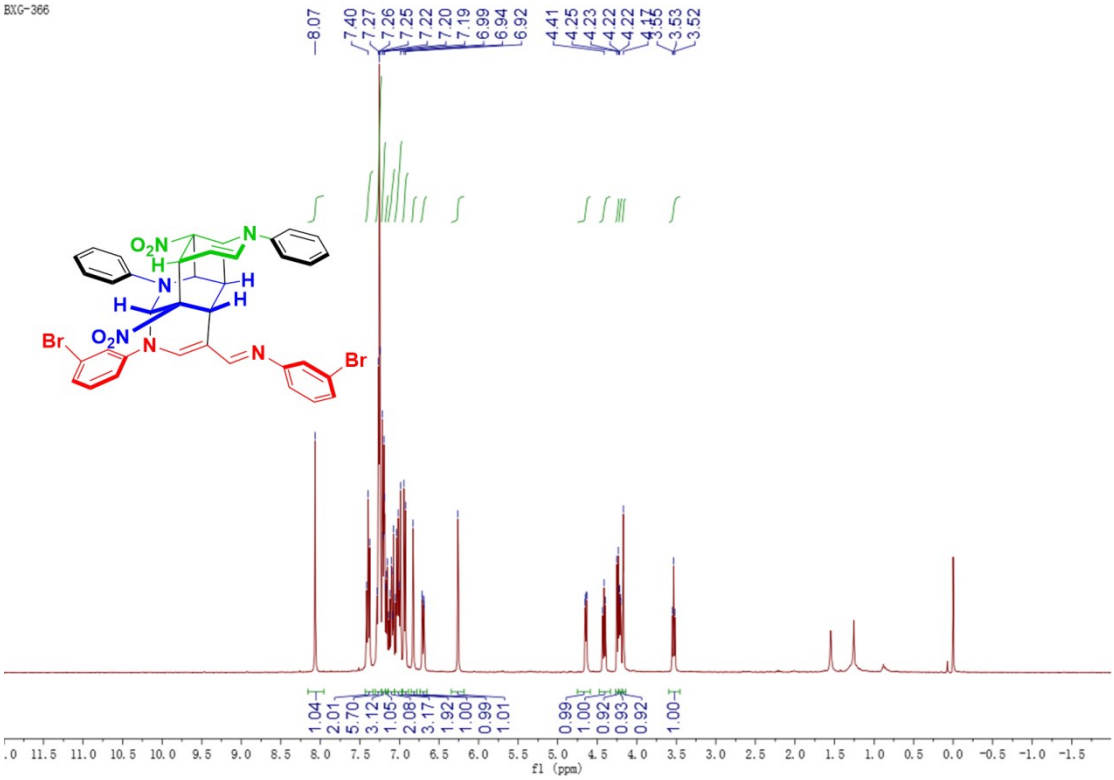
^{1}H NMR spectrum of **12i** (400 MHz, $CDCl_3$)



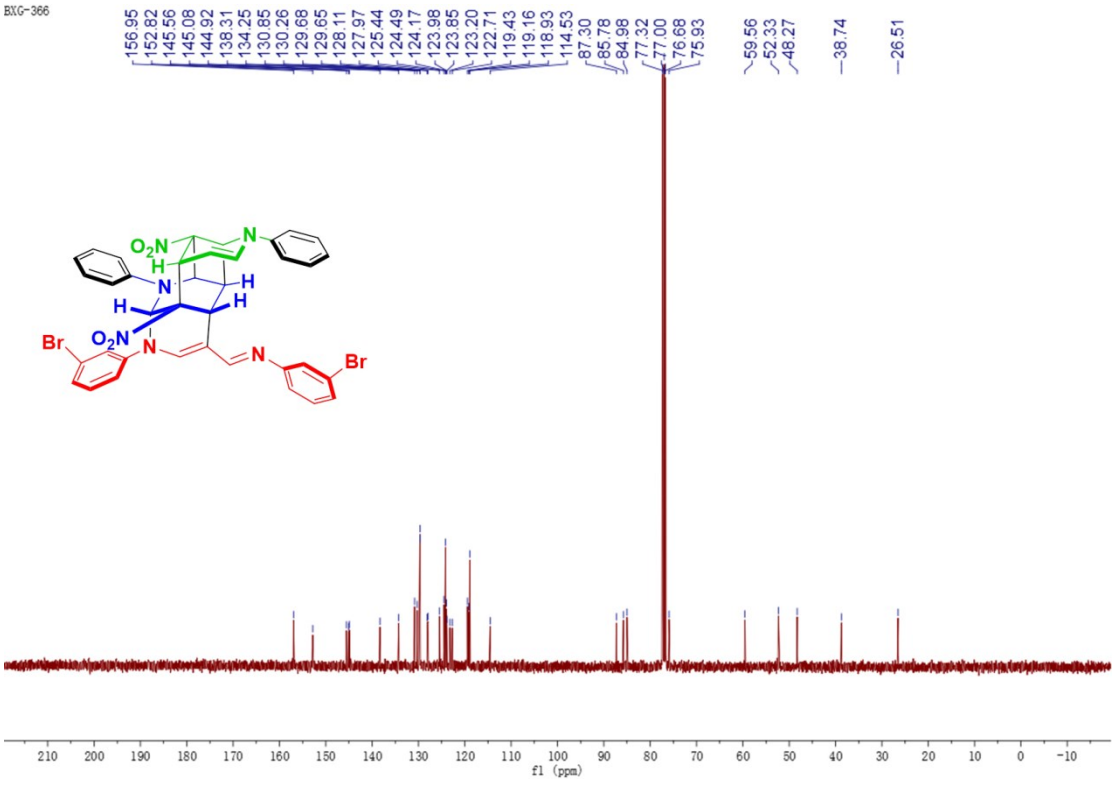
^{13}C NMR spectrum of **12i** (100 MHz, $CDCl_3$)



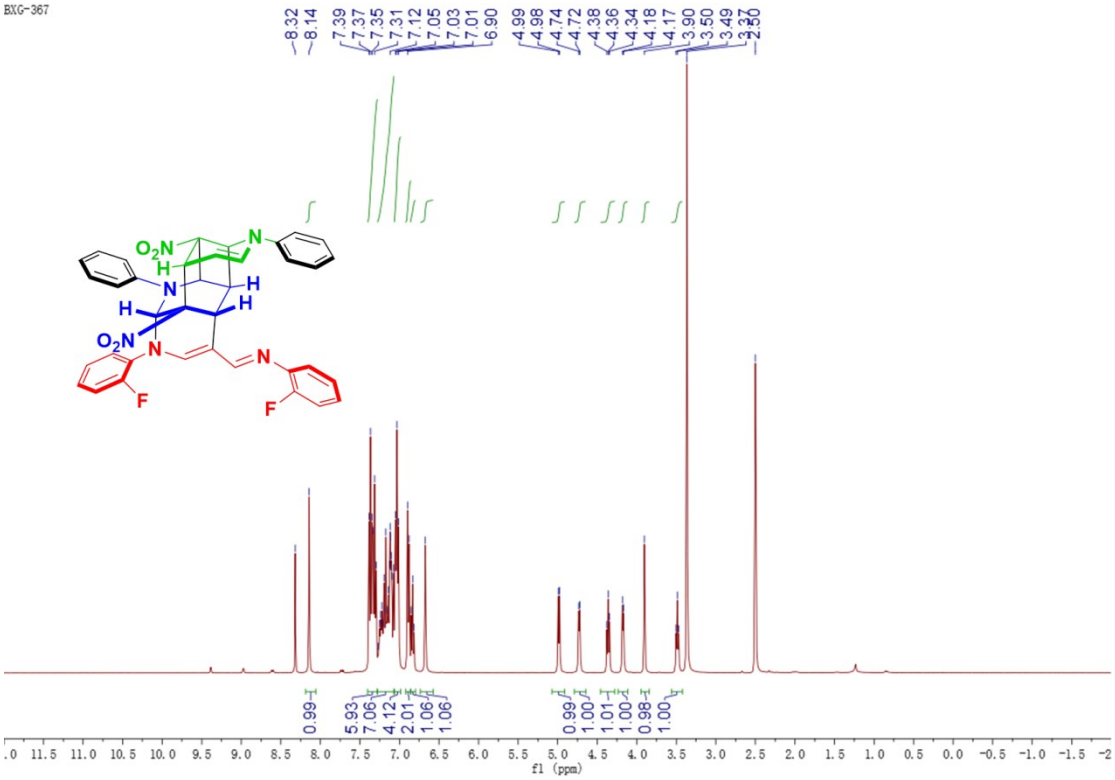
^{1}H NMR spectrum of **12j** (400 MHz, $CDCl_3$)



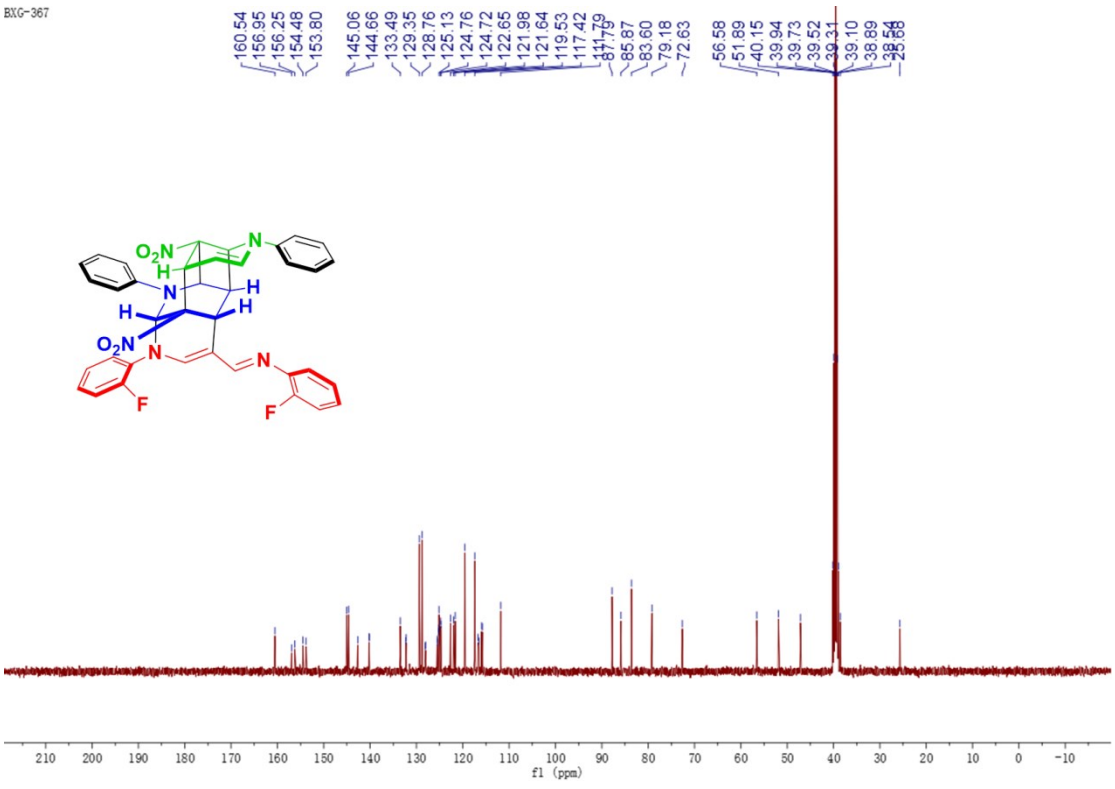
^{13}C NMR spectrum of **12j** (100 MHz, $CDCl_3$)



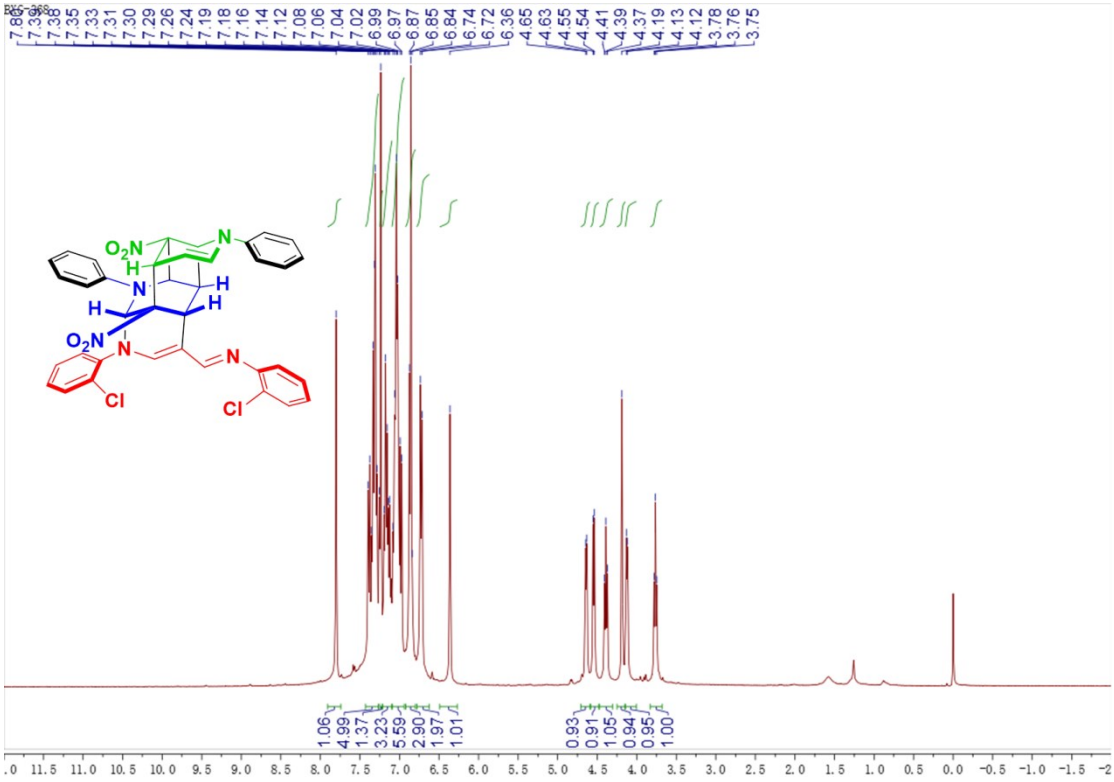
^{1}H NMR spectrum of **12k** (400 MHz, $CDCl_3$)



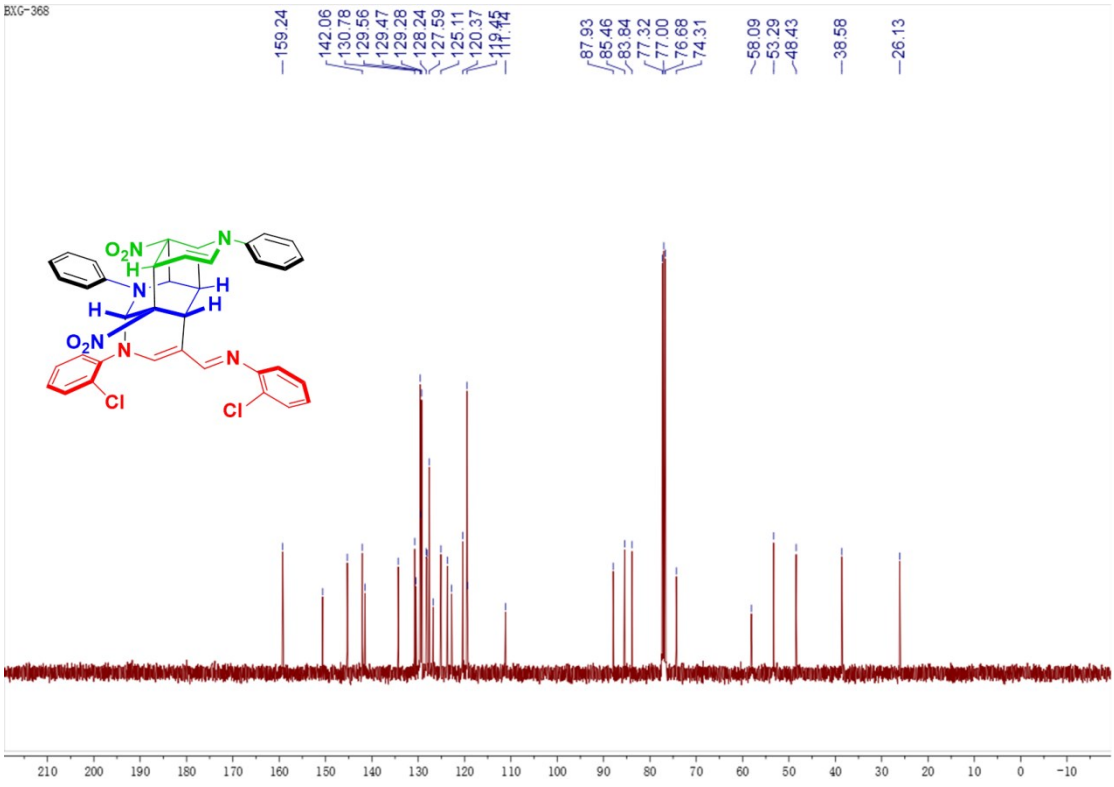
^{13}C NMR spectrum of **12k** (100 MHz, $CDCl_3$)



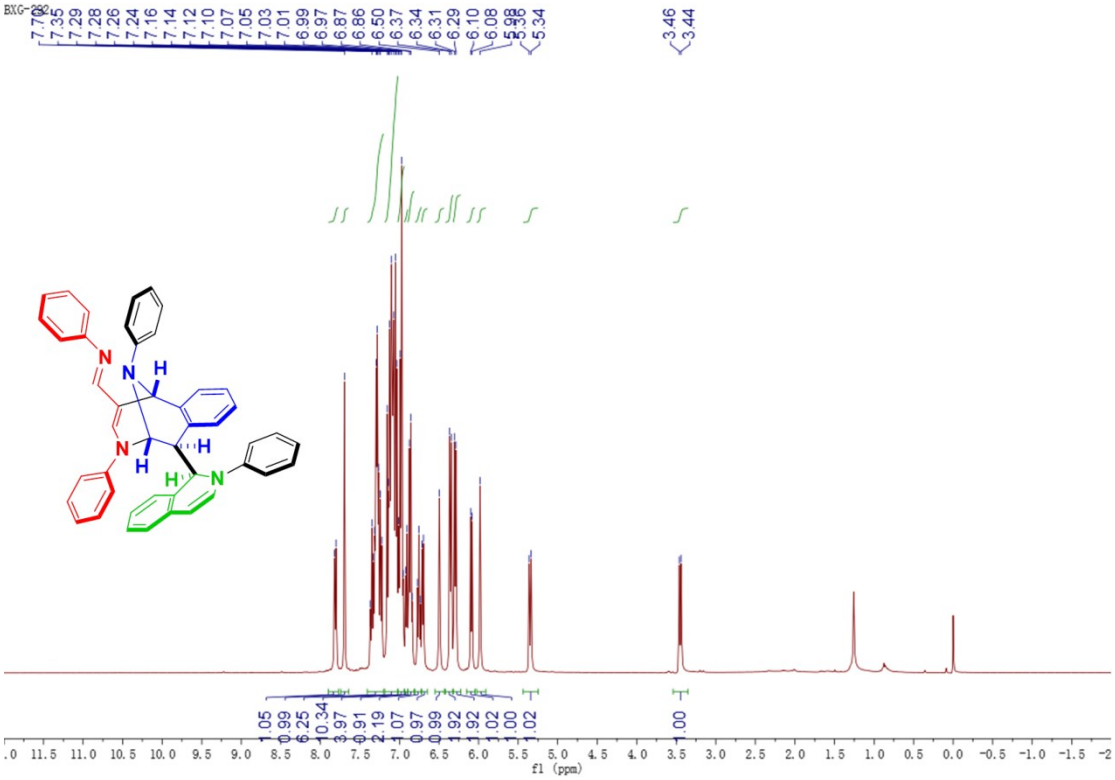
^{1}H NMR spectrum of **12l** (400 MHz, $CDCl_3$)



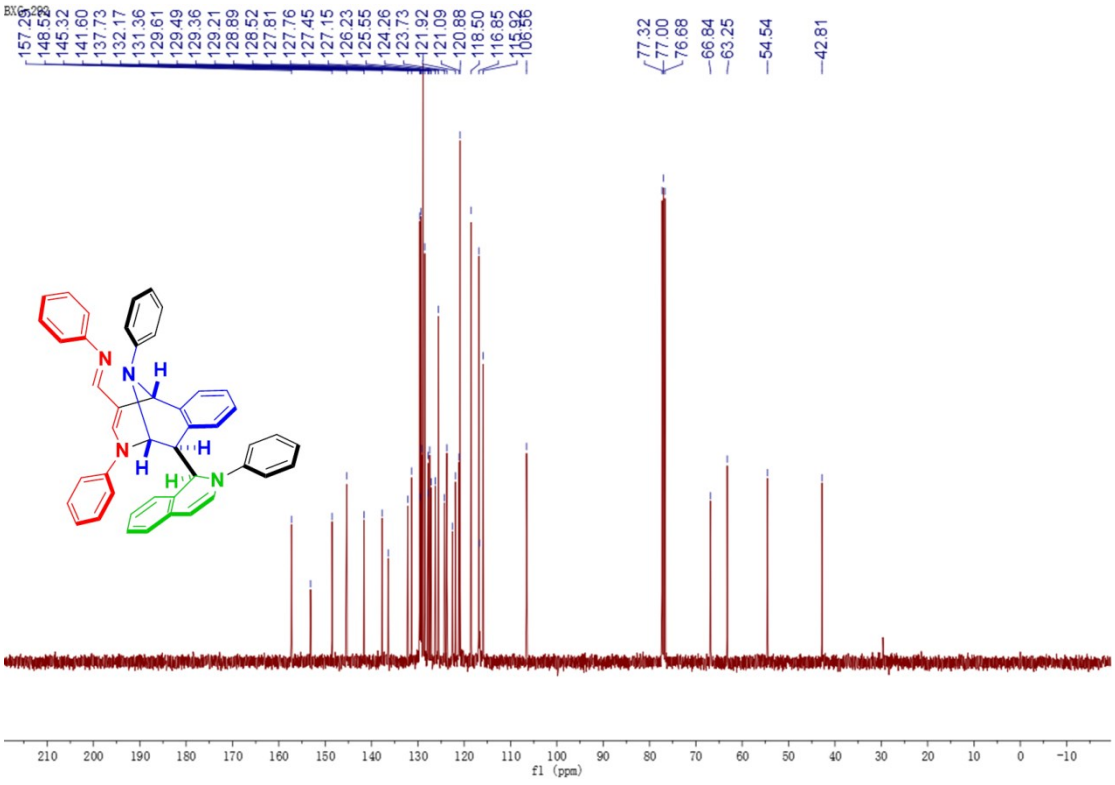
^{13}C NMR spectrum of **12l** (100 MHz, $CDCl_3$)



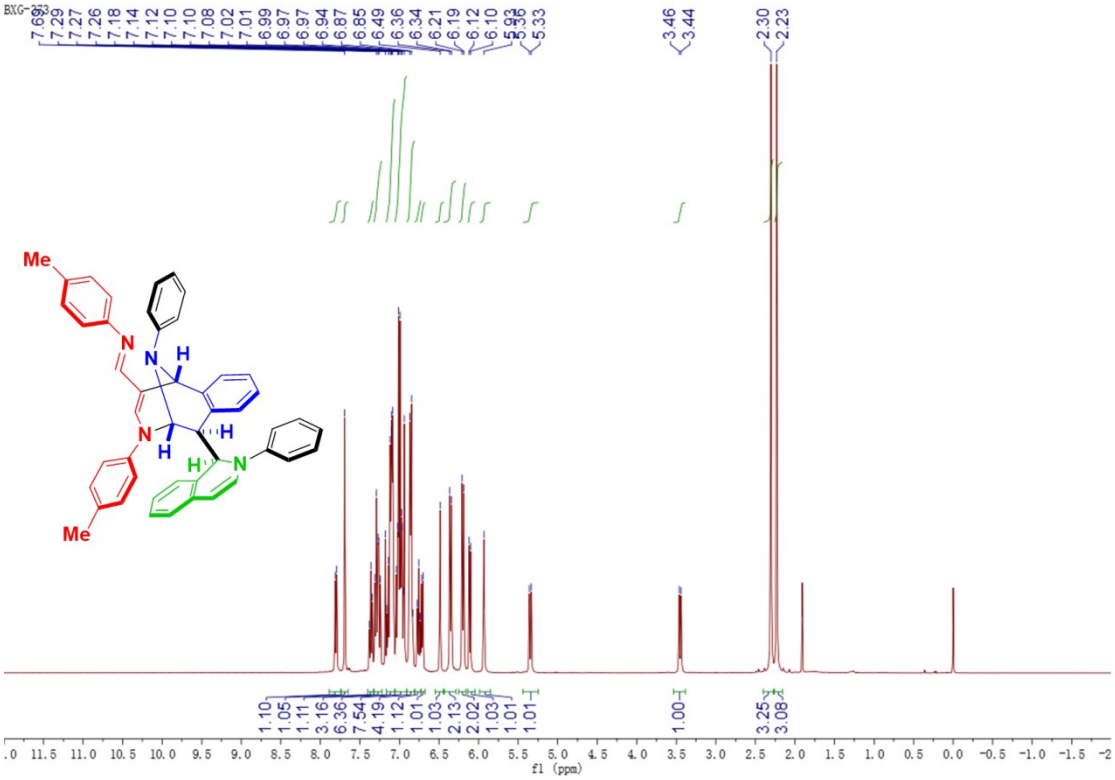
^{1}H NMR spectrum of **13a** (400 MHz, $CDCl_3$)



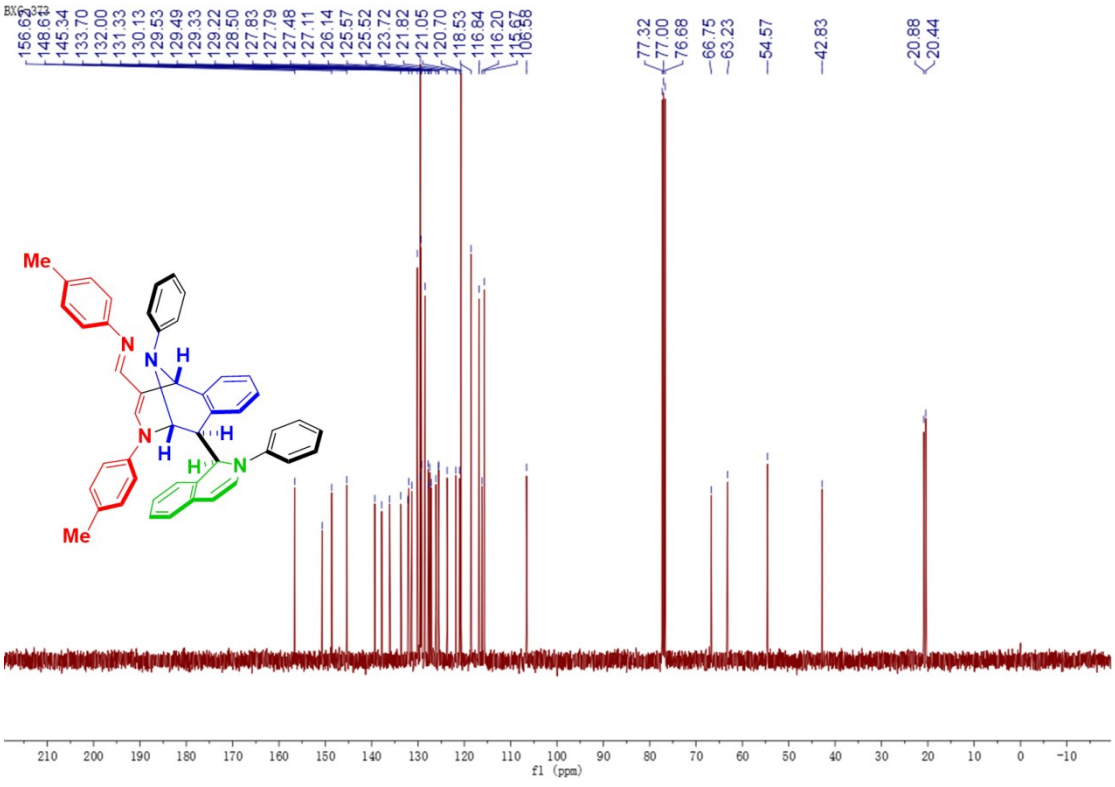
^{13}C NMR spectrum of **13a** (100 MHz, $CDCl_3$)



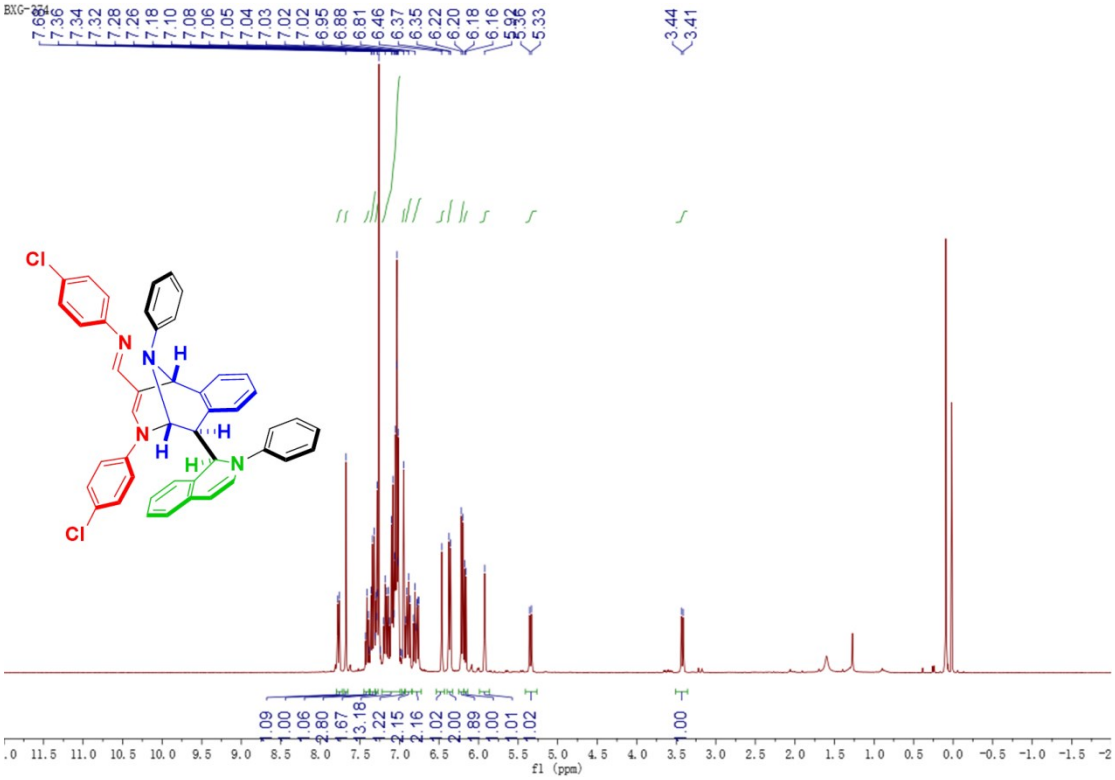
^{1}H NMR spectrum of **13b** (400 MHz, $CDCl_3$)



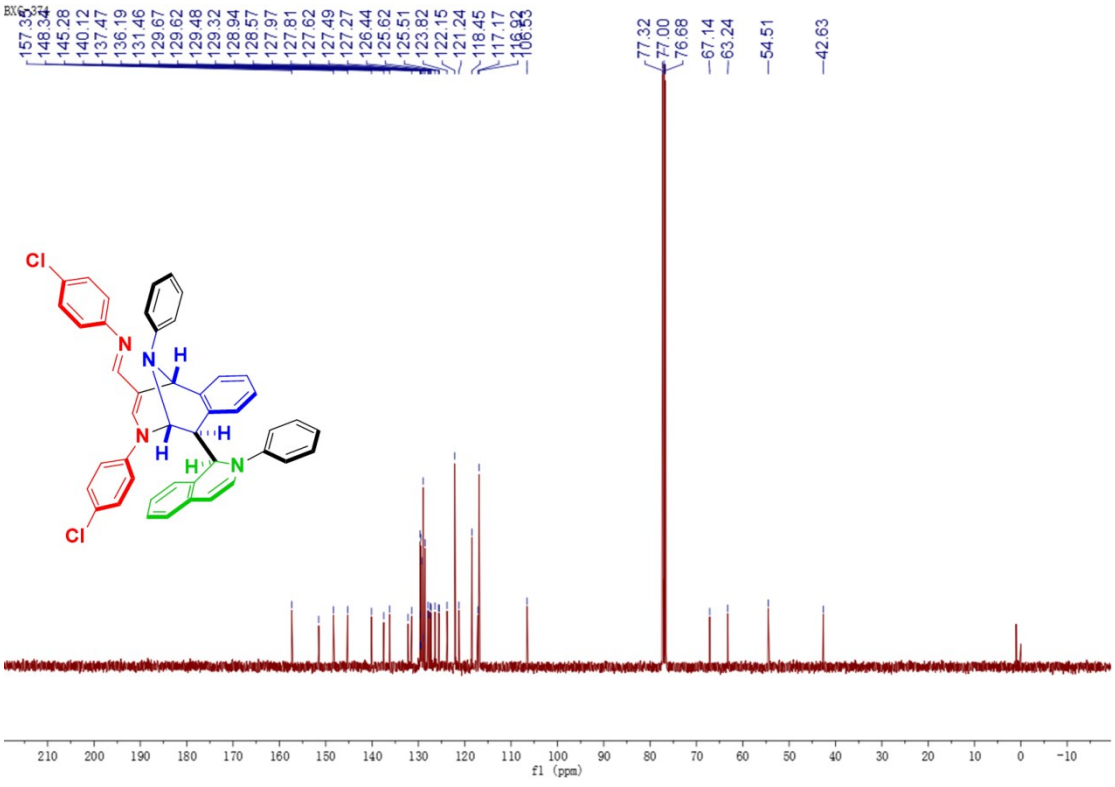
^{13}C NMR spectrum of **13b** (100 MHz, $CDCl_3$)



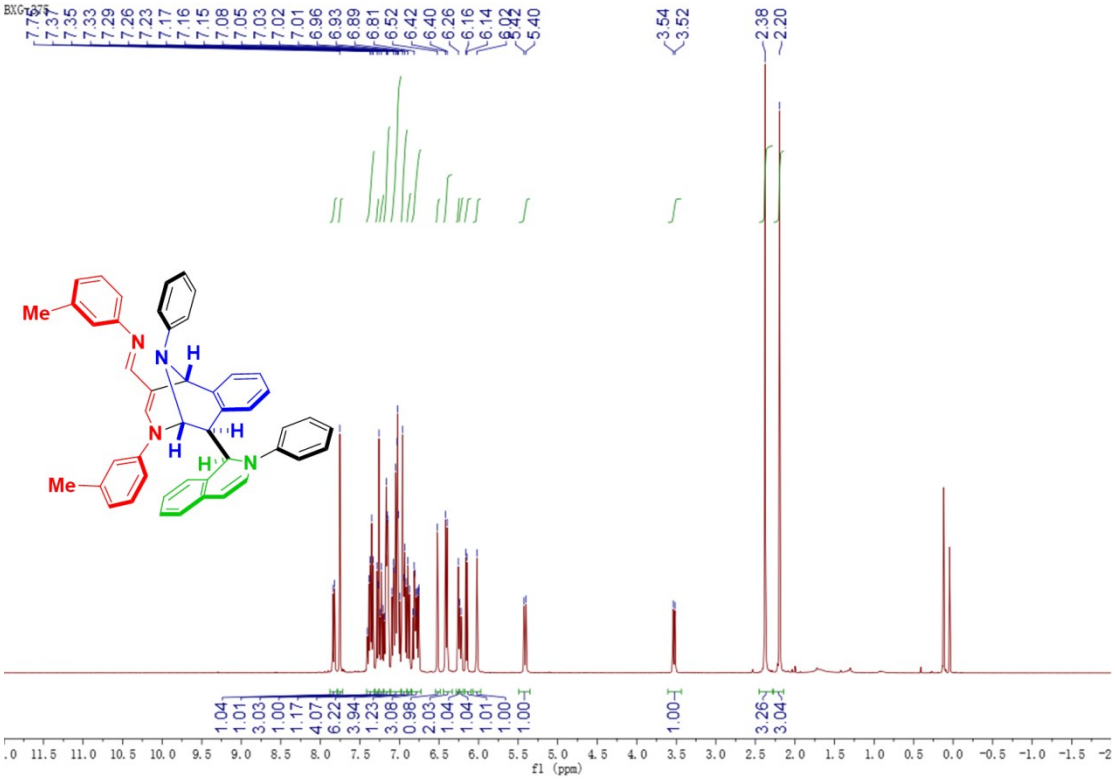
^{1}H NMR spectrum of **13c** (400 MHz, $CDCl_3$)



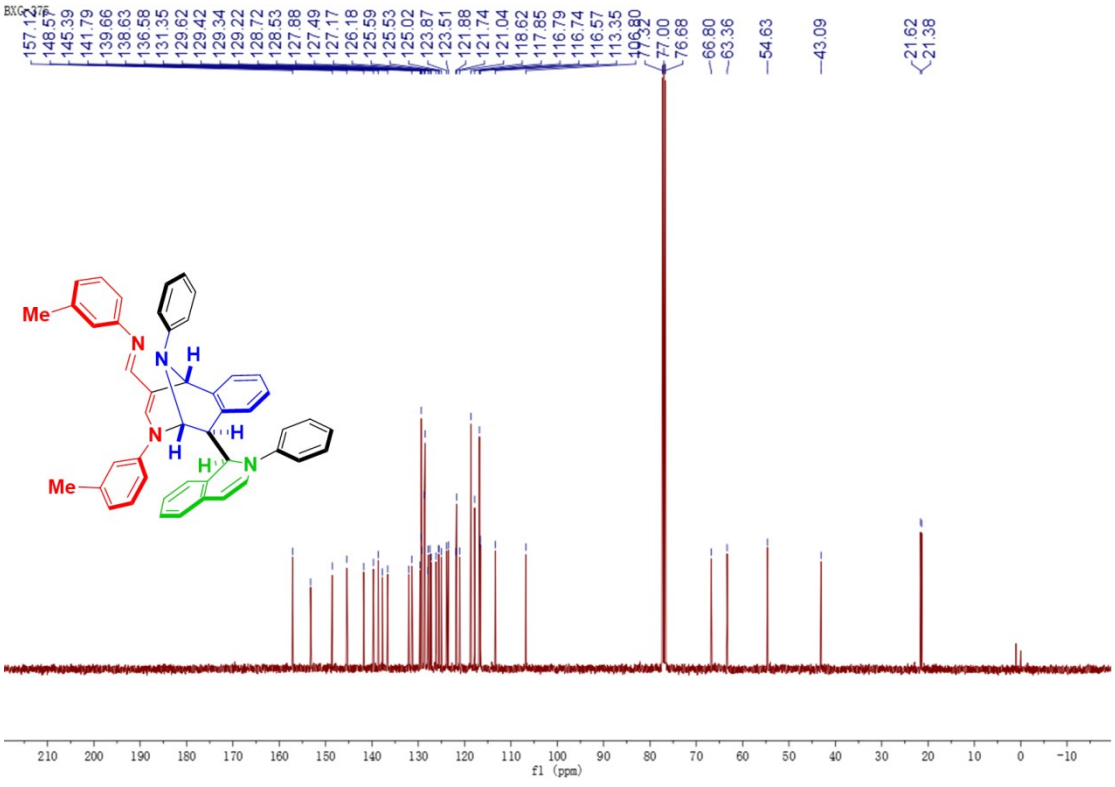
^{13}C NMR spectrum of **13c** (100 MHz, $CDCl_3$)



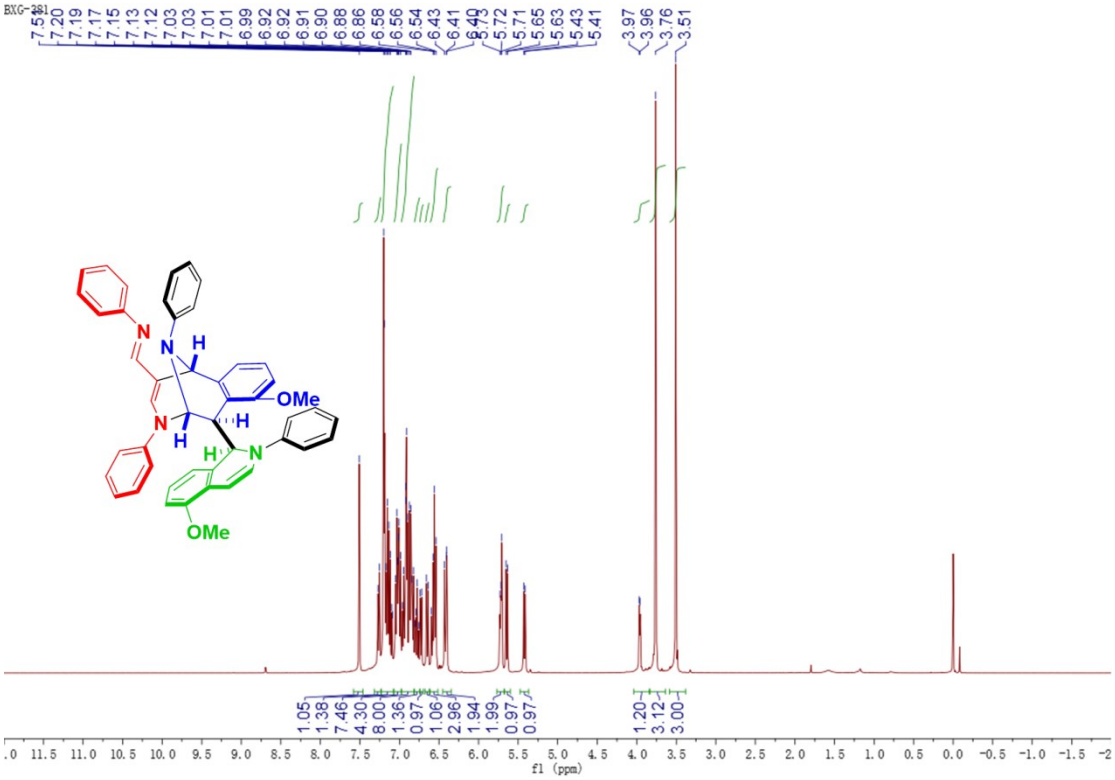
^{1}H NMR spectrum of **13d** (400 MHz, $CDCl_3$)



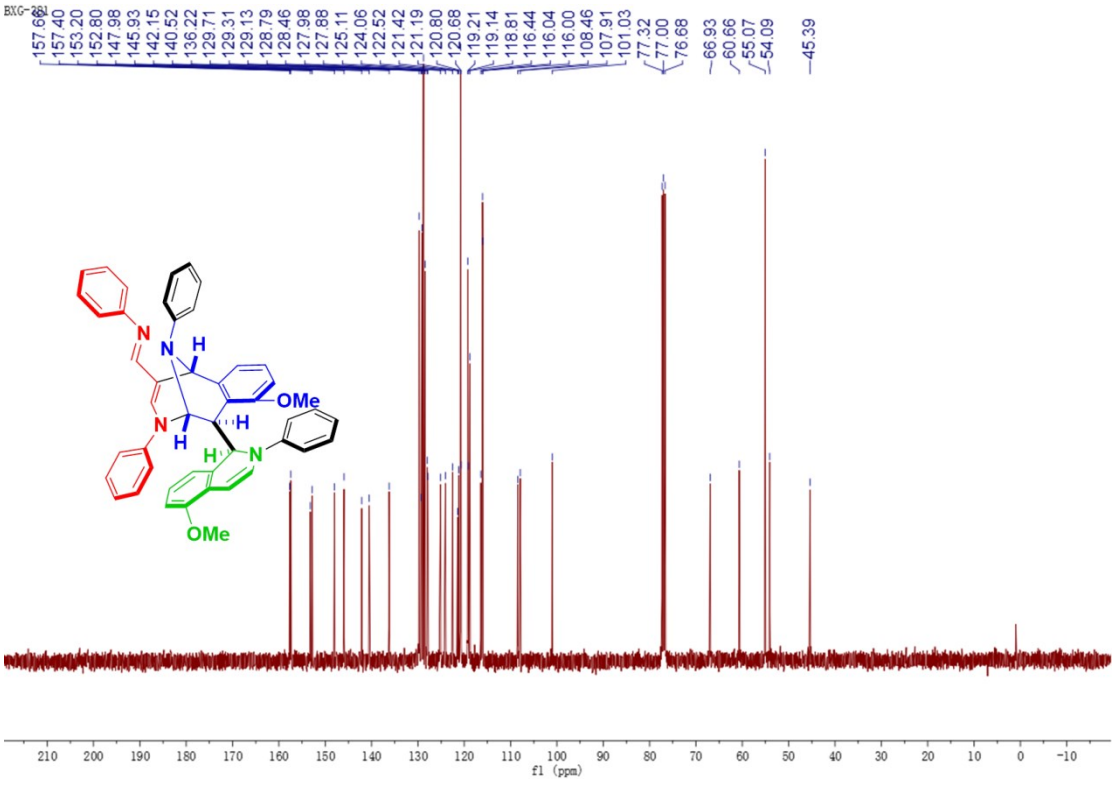
^{13}C NMR spectrum of **13d** (100 MHz, $CDCl_3$)



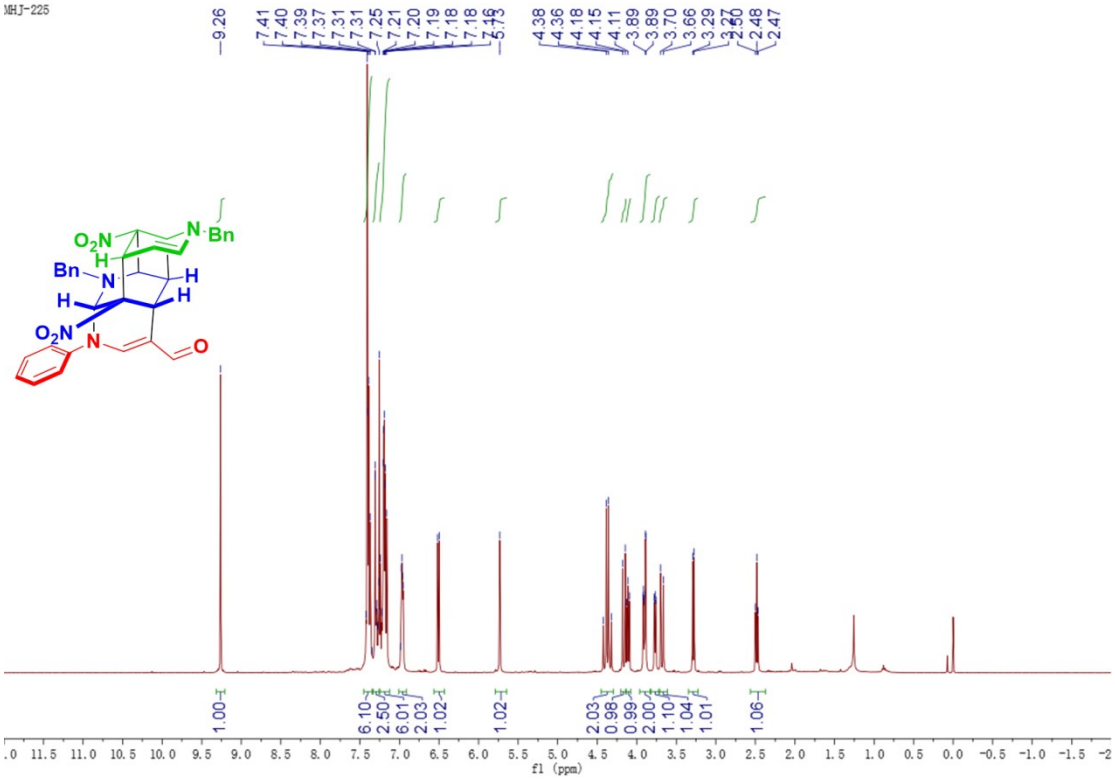
^{1}H NMR spectrum of **13e** (400 MHz, $CDCl_3$)



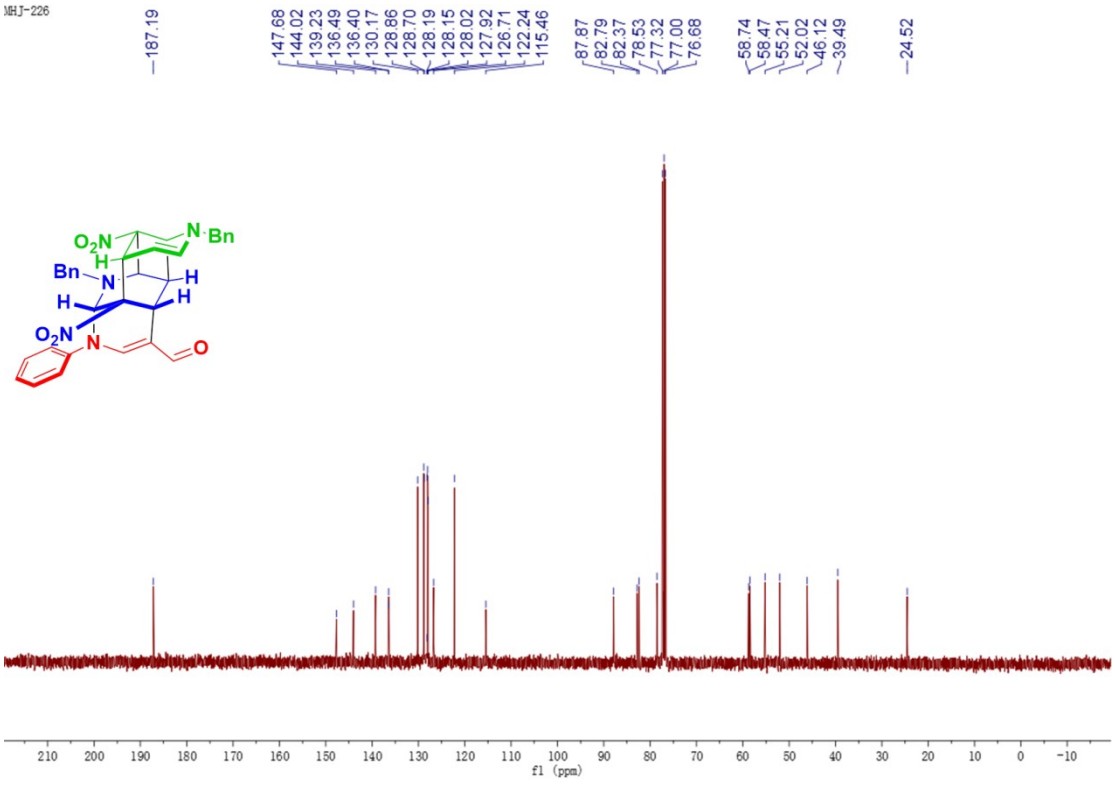
^{13}C NMR spectrum of **13e** (100 MHz, $CDCl_3$)



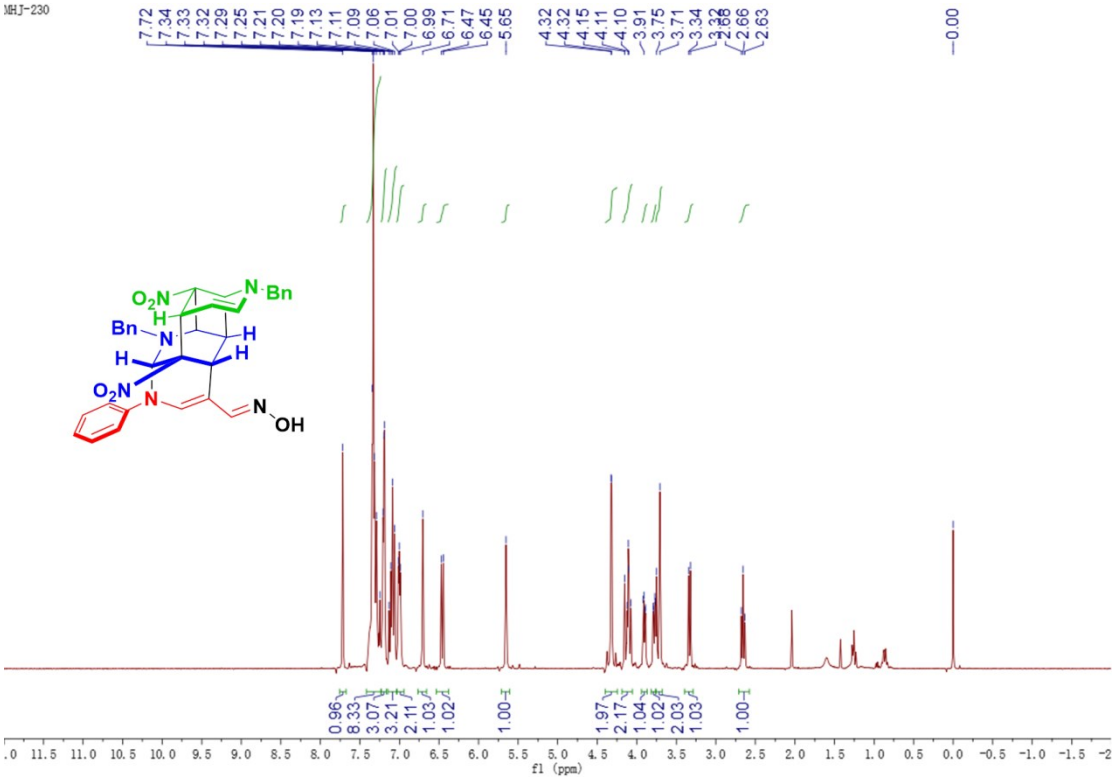
^{1}H NMR spectrum of **14** (400 MHz, $CDCl_3$)



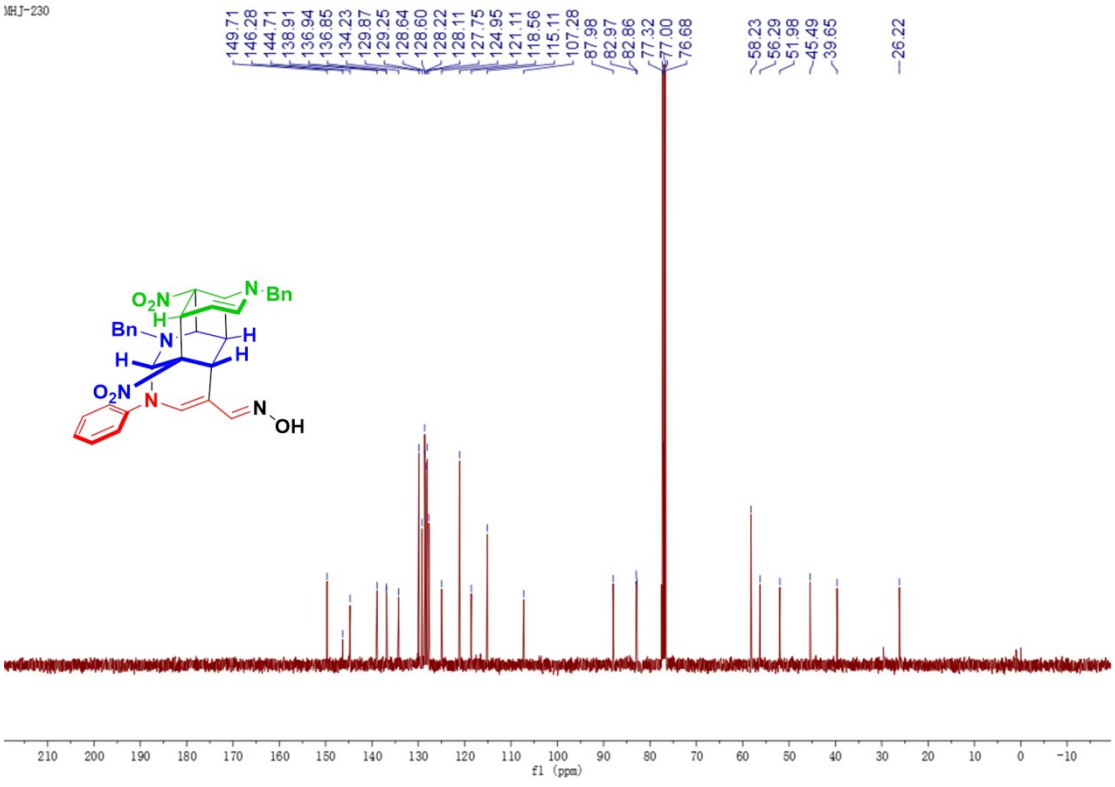
^{13}C NMR spectrum of **14** (100 MHz, $CDCl_3$)



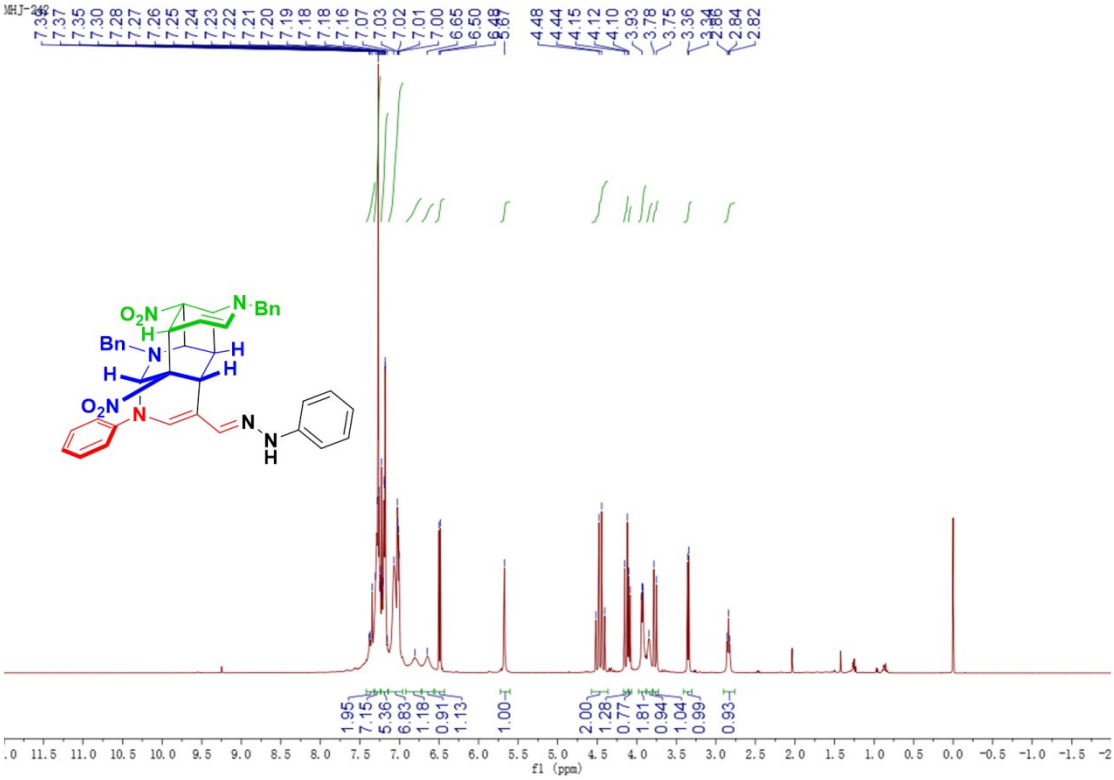
^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$)



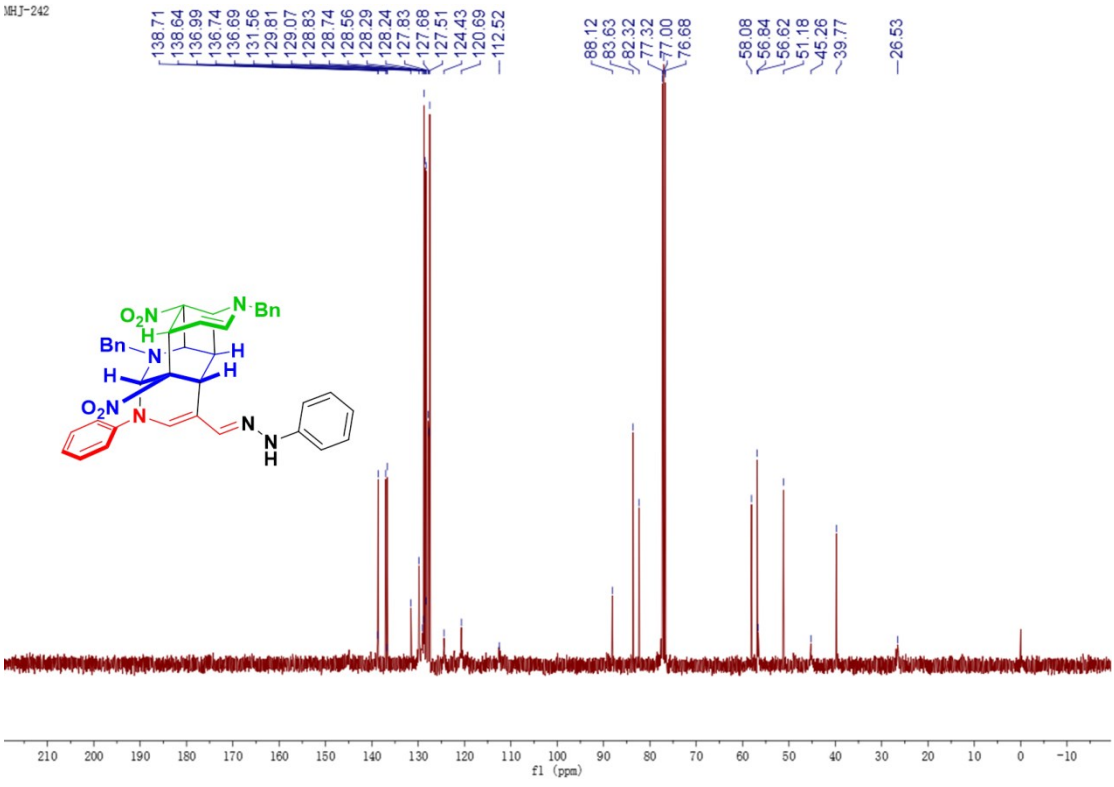
^{13}C NMR spectrum of **15** (100 MHz, $CDCl_3$)



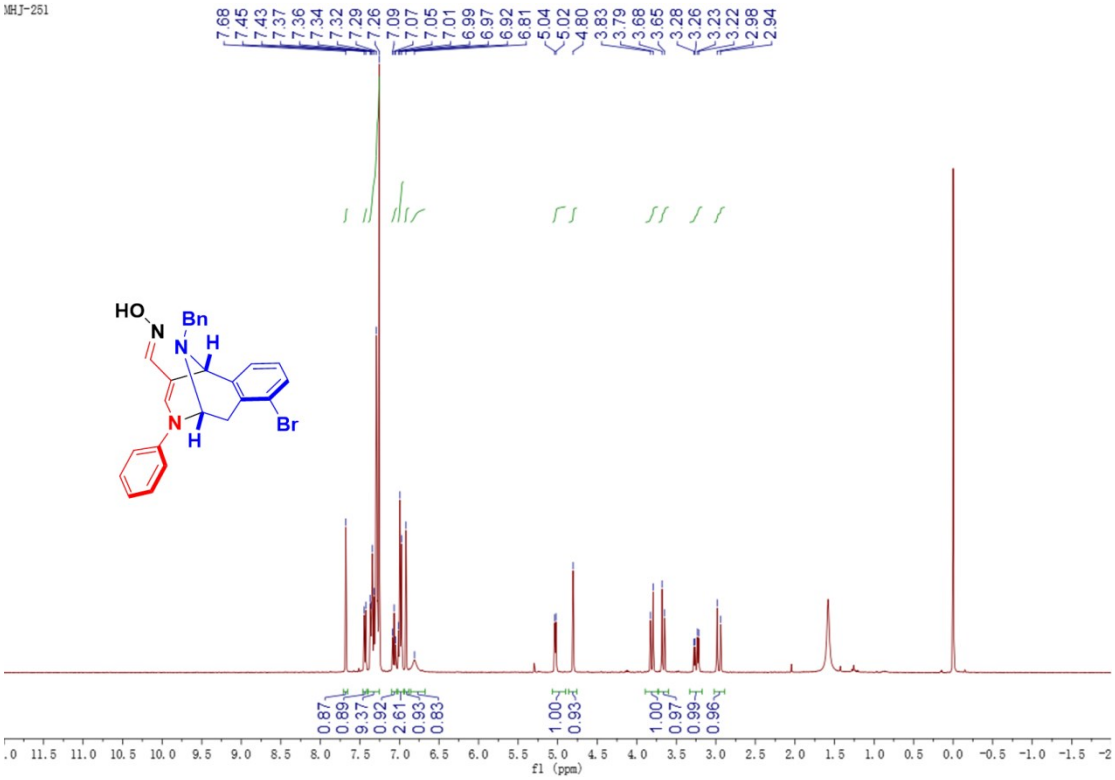
^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$)



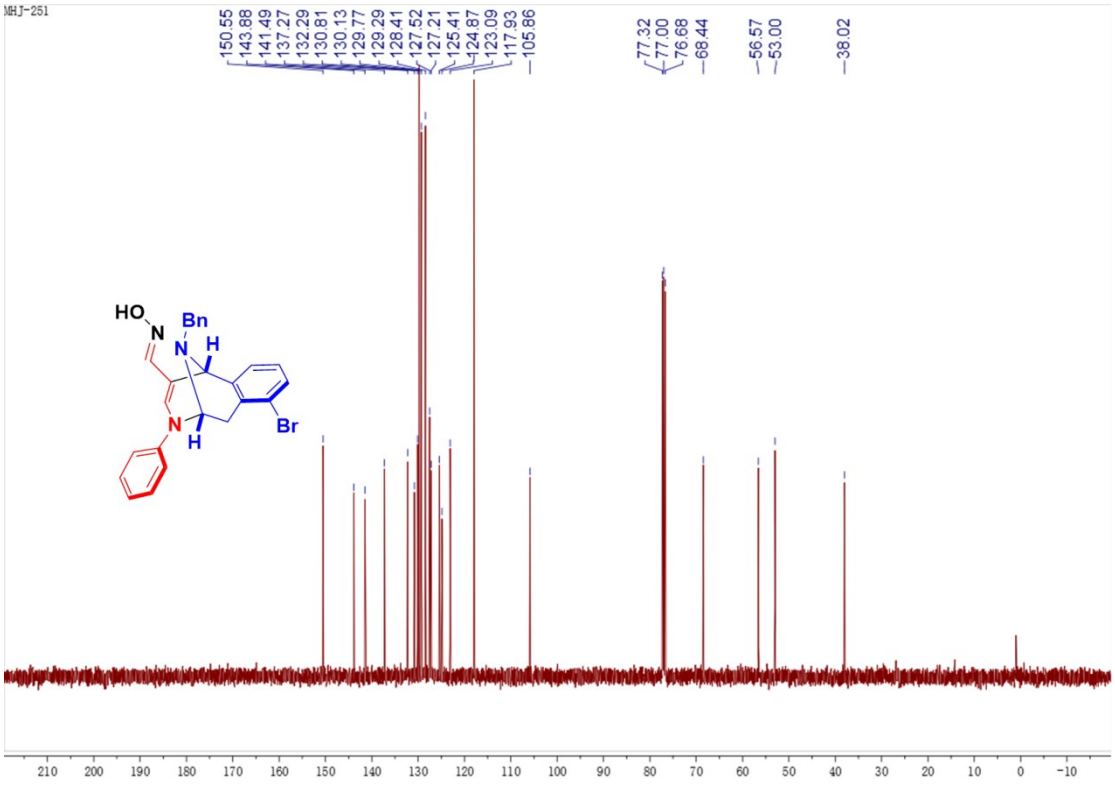
^{13}C NMR spectrum of **16** (100 MHz, $CDCl_3$)



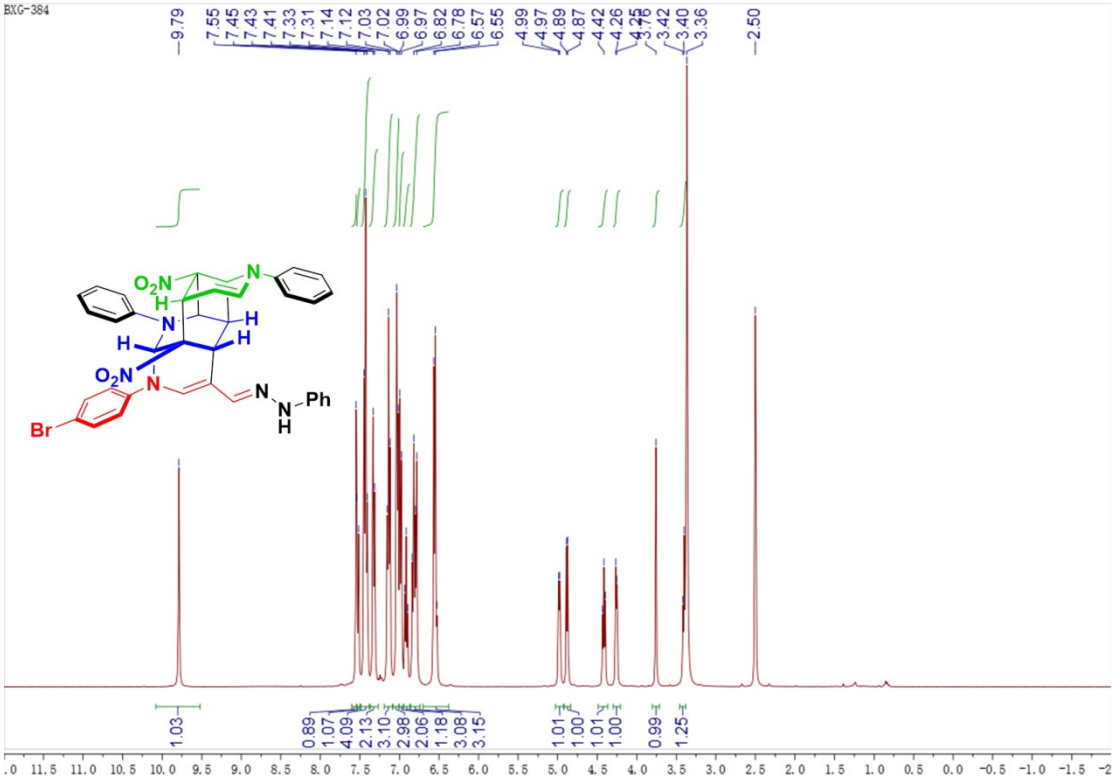
^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **17** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **18** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **18** (100 MHz, DMSO-d_6)