Supporting Information

Regio- and Diastereoselective Dearomatizations of *N*-Alkyl Activated Azaarenes: the Maximization of the Reactive Sites

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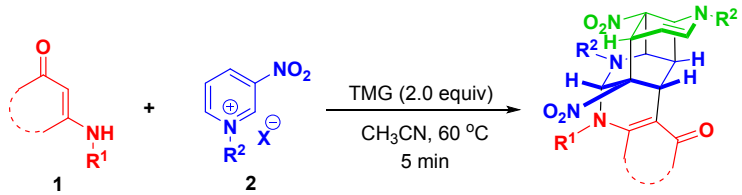
1. General methods

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. Enantiomeric excess was determined by HPLC analysis on chiralpak IA column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm.

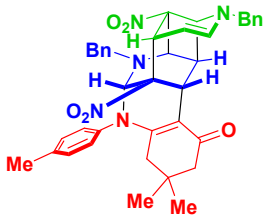
2. Experimental data for the formation of 3



1 + 2 → 3

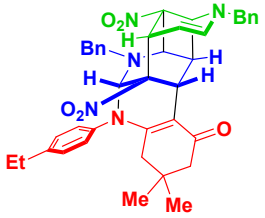
2a, R^2 = Bn, X= Br; **2b**, R^2 = Me, X= I
2c, R^2 = Et, X= I; **2d**, R^2 = Allyl, X= Br
2e, R^2 = *n*-Pr, X= I; **2f**, R^2 = *n*-Bu, X= I

General procedure: To a 5.0 mL vial were successively added enaminones **1** (0.15 mmol), *N*-alkyl 3-nitropyridinium salts **2** (0.33 mmol) and 0.8 mL of CH_3CN. And then, TMG (34.6 mg, 0.30 mmol) was added by syringe. The resulting mixture was stirred at 60 °C for 5 min, 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 some cases, such as **3a-b**, **3d-h**, **3k**, **3n** and **3z**, the products were precipitated from the homogeneous reaction systems and only a filtration was needed to purify them.



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

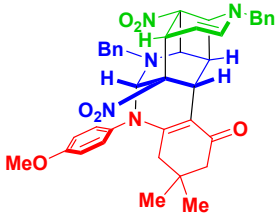
Yellow solid obtained by filtration of the precipitate; 93.8 mg, 95% yield; dr > 20:1; reaction time = 5 min; mp 222.4-223.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.34 (m, 4H), 7.28-7.11 (m, 8H), 6.98 (s, 2H), 6.46 (d, J = 8.0 Hz, 1H), 5.27 (s, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.20 (d, J = 16.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.95 (s, 1H), 3.84 (d, J = 16.0 Hz, 2H), 3.74 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 2.55 (t, J = 8.0 Hz, 1H), 2.35 (s, 3H), 2.24 (q, J = 16.0 Hz, 3H), 1.87 (d, J = 16.0 Hz, 1H), 1.00 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.6, 140.0, 139.2, 138.3, 136.8, 136.6, 128.7, 128.0 (2C), 127.8, 127.7, 107.0, 87.9, 83.3, 82.5, 80.0, 59.0, 57.6, 55.4, 51.5, 50.1, 45.8, 41.8, 39.1, 32.9, 29.9, 26.2, 24.8, 21.1, two carbons missing in the aromatic region. IR (KBr) ν 3030, 2956, 2870, 1586, 1393, 748 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}N_5O_5$ $[M+H]^+$ 658.3024, found 658.3023.



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

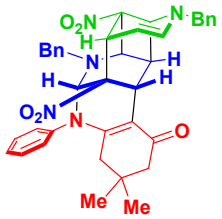
Yellow solid obtained by filtration of the precipitate; 82.2 mg, 82% yield; dr > 20:1; reaction time = 5 min; mp 200.3-201.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.35 (m, 4H), 7.28-7.11 (m, 8H), 7.00 (s, 2H), 6.46 (d, J = 8.0 Hz, 1H), 5.28 (s, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.21 (d, J = 16.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.87 (dd, J_1 = J_2 = 4.0 Hz, 2H), 3.75 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 2.66 (q, J = 8.0 Hz, 2H), 2.56 (t, J = 8.0 Hz, 1H), 2.34-2.17 (m, 3H), 1.88 (d, J = 16.0 Hz, 1H), 1.24 (t, J = 8.0 Hz, 3H), 1.01 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 194.1, 153.6, 144.5, 140.2, 139.2, 136.9, 136.6, 128.7, 128.1, 128.0, 127.8, 127.7, 107.0, 87.9, 83.3, 82.6, 80.0, 59.0, 57.7, 55.5, 51.6, 50.2, 45.8, 41.8, 39.2, 33.0, 29.8, 28.4, 26.2, 24.9, 15.2, two carbons missing in the aromatic region. IR (KBr) *v* 3031, 2960, 2869, 1587, 1386, 741 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{42}N_5O_5$ $[M+H]^+$ 672.3181, found 672.3178.



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

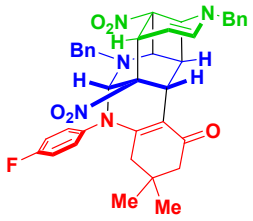
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 80.7 mg, 80% yield; dr > 20:1; reaction time = 5 min; mp 206.8-208.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.34 (m, 4H), 7.29-7.25 (m, 5H), 7.12 (t, J = 8.0 Hz, 2H), 6.99 (s, 2H), 6.87 (s, 2H), 6.46 (d, J = 12.0 Hz, 1H), 5.26 (d, J = 4.0 Hz, 1H), 4.39 (q, J = 20.0 Hz, 2H), 4.23 (d, J = 20.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.95 (s, 1H), 3.88 (t, J = 4.0 Hz, 1H), 3.81 (s, 3H), 3.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 2.55 (t, J = 8.0 Hz, 1H), 2.35-2.15 (m, 3H), 1.86 (d, J = 20.0 Hz, 1H), 1.01 (3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 159.0, 153.8, 139.1, 136.8, 136.5, 135.2, 128.7, 128.6, 127.9, 127.7, 127.6, 114.7, 106.8, 87.9, 83.1, 82.4, 80.0, 58.9, 57.5, 55.4, 51.5, 50.0, 45.7, 41.7, 39.0, 32.8, 29.8, 26.1, 24.7, three carbons missing in the aromatic region. IR (KBr) *v* 3022, 2960, 1636, 1585, 1538, 1389, 1241, 735 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}N_5O_6$ $[M+H]^+$ 674.2973, found 674.2974.



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

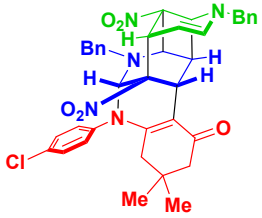
Yellow solid obtained by filtration of the precipitate; 88.1 mg, 91% yield; dr > 20:1; reaction time = 5 min; mp 221.4-222.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.35 (m, 7H), 7.28-7.24 (m, 4H),

7.11 (d, J = 4.0 Hz, 4H), 6.46 (d, J = 8.0 Hz, 1H), 5.31 (d, J = 4.0 Hz, 1H), 4.38 (q, J = 12.0 Hz, 2H), 4.20 (d, J = 12.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.88-3.81 (m, 2H), 3.75 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.27 (d, J = 8.0 Hz, 1H), 2.56 (t, J = 8.0 Hz, 1H), 2.35-2.19 (m, 3H), 1.87 (d, J = 16.0 Hz, 1H), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.3, 142.6, 139.2, 136.8, 136.6, 128.7, 128.2, 128.0 (2C), 127.8, 127.7, 107.4, 87.9, 83.2, 82.5, 80.0, 58.9, 57.6, 55.5, 51.5, 50.1, 45.8, 41.9, 39.1, 33.0, 29.8, 26.2, 24.8, two carbons missing in the aromatic region. IR (KBr) v 3033, 2950, 2869, 1582, 1539, 1392, 745 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{38}N_5O_5$ $[M+H]^+$ 644.2868, found 644.2864.



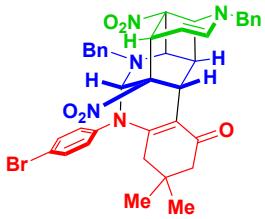
7,11-dibenzyl-5-(4-fluorophenyl)-3,3-dimethyl-7b,13-dinitro-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3e**)

Yellow solid obtained by filtration of the precipitate; 85.7 mg, 86% yield; dr > 20:1; reaction time = 5 min; mp 223.2-224.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.35 (m, 4H), 7.29-7.26 (m, 4H), 7.11-7.05 (m, 6H), 6.47 (d, J = 8.0 Hz, 1H), 5.26 (s, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.25 (d, J = 16.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.87-3.82 (m, 2H), 3.75 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.28 (d, J = 8.0 Hz, 1H), 2.56 (t, J = 8.0 Hz, 1H), 2.28 (q, J = 16.0 Hz, 2H), 2.16 (d, J = 16.0 Hz, 1H), 1.83 (d, J = 16.0 Hz, 1H), 1.01 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 161.9 (d, J = 248.0 Hz, 1C), 153.1, 139.2, 138.6 (d, J = 4.0 Hz, 1C), 136.6 (d, J = 20.0 Hz, 1C), 128.8, 128.7, 128.0, 127.9, 127.8 (2C), 107.6, 87.9, 83.2, 82.4, 80.2, 59.1, 57.7, 55.6, 51.6, 50.1, 45.8, 41.9, 39.2, 33.0, 29.8, 26.2, 24.8, two carbons missing in the aromatic region. IR (KBr) v 3030, 2956, 2871, 1591, 1540, 1392, 749 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}FN_5O_5$ $[M+H]^+$ 6462.2773, found 662.2772.



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

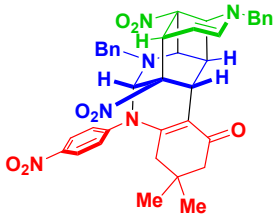
Yellow solid obtained by filtration of the precipitate; 81.8 mg, 80% yield; dr > 20:1; reaction time = 5 min; mp 217.6-218.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.33 (m, 6H), 7.29-7.25 (m, 4H), 7.10-7.08 (m, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.47 (d, J = 8.0 Hz, 1H), 5.26 (d, J = 4.0 Hz, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.24 (d, J = 16.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.95 (s, 1H), 3.87-3.81 (m, 2H), 3.75 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.28 (d, J = 4.0 Hz, 1H), 2.56 (t, J = 8.0 Hz, 1H), 2.29 (q, J = 16.0 Hz, 2H), 2.17 (d, J = 16.0 Hz, 1H), 1.84 (d, J = 16.0 Hz, 1H), 1.02 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 152.7, 141.1, 139.2, 136.7, 136.5, 134.1, 128.8 (2C), 128.0, 127.9 (2C), 127.8, 108.0, 87.9, 83.2, 82.4, 80.2, 59.1, 57.7, 55.7, 51.6, 50.1, 45.8, 41.9, 39.2, 33.1, 29.8, 26.2, 24.9, one carbon missing in the aromatic region. IR (KBr) ν 3031, 2952, 2870, 1592, 1540, 1390, 742 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}ClN_5O_5$ $[M+H]^+$ 678.2478, found 678.2469.



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

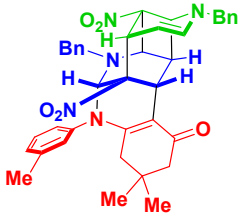
Yellow solid obtained by filtration of the precipitate; 87.1 mg, 80% yield; dr > 20:1; reaction time = 5 min; mp 220.8-222.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.49 (d, J = 8.0 Hz, 2H), 7.42-7.35 (m, 4H), 7.25 (s, 4H), 7.10 (s, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.47 (d, J = 8.0 Hz, 1H), 5.26 (s, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.24 (d, J = 16.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.95 (s, 1H), 3.84-3.74 (m, 3H), 3.28 (d, J = 4.0 Hz, 1H), 2.55 (t, J = 8.0 Hz, 1H), 2.28 (q, J = 16.0 Hz, 2H), 2.16 (d, J = 16.0 Hz, 1H), 1.85 (d, J = 16.0 Hz, 1H), 1.02 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 152.6, 141.6, 139.2, 136.7, 136.5, 133.1, 128.8, 128.7, 128.0, 127.9 (2C), 127.8, 122.0, 108.1, 87.9, 83.1, 82.4, 80.2, 59.1, 57.7, 55.7, 51.6, 50.1, 45.7, 41.9, 39.2, 33.0, 29.8, 26.2, 24.9. IR (KBr) ν 3030, 2955, 2870, 1593, 1540, 1390, 737 cm^{-1}. HRMS (ESI) calcd for

$C_{38}H_{37}BrN_5O_5$ $[M+H]^+$ 722.1973, found 722.1976.



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

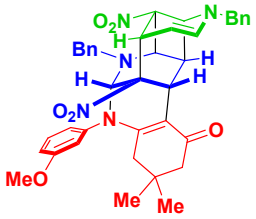
Yellow solid obtained by filtration of the precipitate; 75.6 mg, 73% yield; dr > 20:1; reaction time = 5 min; mp 204.5-205.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.20 (d, J = 12.0 Hz, 2H), 7.43-7.36 (m, 4H), 7.29-7.25 (m, 4H), 7.14-7.08 (m, 4H), 6.49 (d, J = 8.0 Hz, 1H), 5.35 (s, 1H), 4.40 (q, J = 16.0 Hz, 2H), 4.29 (d, J = 12.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.85 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 2H), 3.77 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.35 (d, J = 8.0 Hz, 1H), 2.58 (t, J = 8.0 Hz, 1H), 2.34 (t, J = 16.0 Hz, 2H), 2.16 (d, J = 16.0 Hz, 1H), 1.99 (d, J = 16.0 Hz, 1H), 1.04 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 151.3, 148.1, 146.3, 139.3, 136.5, 136.4, 128.9, 128.8, 128.1, 128.0, 127.8 (2C), 125.3, 110.7, 87.7, 83.0, 82.2, 80.7, 59.1, 57.8, 56.2, 51.5, 50.3, 45.6, 42.2, 39.4, 33.4, 29.4, 26.5, 25.1. IR (KBr) v 3029, 2952, 2867, 1590, 1537, 1345, 745 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}N_6O_7$ $[M+H]^+$ 689.2718, found 689.2718.



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

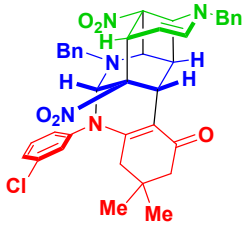
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 85.7 mg, 87% yield; dr > 20:1; reaction time = 5 min; mp 193.1-194.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.43-7.34 (m, 4H), 7.29-7.25 (m, 6H), 7.12 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 3H), 6.88 (s, 2H), 6.47 (d, J = 8.0 Hz, 1H), 5.30 (s, 1H), 4.39 (q, J = 20.0 Hz, 2H), 4.20 (d, J = 16.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.88 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.75 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.27 (d,

J = 8.0 Hz, 1H), 2.56 (t, *J* = 8.0 Hz, 1H), 2.36-2.19 (m, 6H), 1.86 (d, *J* = 24.0 Hz, 1H), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.5, 142.4, 139.2, 136.8, 136.6, 129.0, 128.7 (2C), 128.0, 127.8, 127.7, 107.1, 87.9, 83.3, 82.5, 79.9, 59.0, 57.6, 55.5, 51.5, 50.1, 45.8, 41.8, 39.1, 33.0, 29.9, 26.1, 24.8, 21.3, five carbons missing in the aromatic region. IR (KBr) *v* 3432, 2952, 2870, 1631, 1584, 1541, 1392, 747 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}N_5O_5$ $[M+H]^+$ 658.3024, found 658.3032.



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

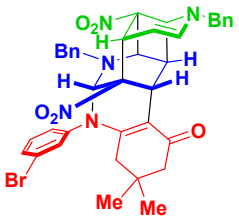
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 97.5 mg, 97% yield; dr > 20:1; reaction time = 5 min; mp 196.8-197.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.33-7.25 (m, 3H), 7.19-7.14 (m, 6H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.60-6.52 (m, 2H), 6.36 (d, *J* = 8.0 Hz, 1H), 5.25 (d, *J* = 4.0 Hz, 1H), 4.29 (q, *J* = 16.0 Hz, 2H), 4.15 (d, *J* = 12.0 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.87 (s, 1H), 3.80-3.76 (m, 2H), 3.66-3.62 (m, 4H), 3.18 (d, *J* = 4.0 Hz, 1H), 2.47 (t, *J* = 8.0 Hz, 1H), 2.26-2.13 (m, 3H), 1.83 (d, *J* = 16.0 Hz, 1H), 0.93 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.2, 143.6, 139.1, 136.9, 136.5, 129.2, 128.7, 128.5, 127.9, 127.8, 127.7, 127.6, 114.0, 107.2, 87.8, 83.2, 82.4, 79.9, 58.9, 57.6, 55.5, 55.2, 51.5, 50.1, 45.8, 41.6, 39.1, 32.9, 29.7, 26.1, 24.8, two carbons missing in the aromatic region. IR (KBr) *v* 3030, 2954, 2873, 1582, 1540, 1389, 738 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}N_5O_6$ $[M+H]^+$ 674.2973, found 674.2974.



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

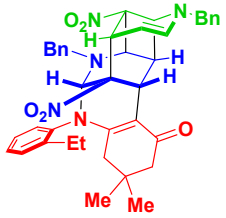
1(2*H*)-one (**3k**)

Yellow solid obtained by filtration of the precipitate; 85.5 mg, 84% yield; dr > 20:1; reaction time = 5 min; mp 200.6-201.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42-7.25 (m, 10H), 7.11-7.08 (m, 3H), 6.98 (d, J = 4.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 5.28 (d, J = 4.0 Hz, 1H), 4.39 (q, J = 16.0 Hz, 2H), 4.22 (d, J = 16.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.87 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.76 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 2H), 3.29 (d, J = 8.0 Hz, 1H), 2.55 (t, J = 8.0 Hz, 1H), 2.29 (q, J = 16.0 Hz, 2H), 2.20 (d, J = 16.0 Hz, 1H), 1.85 (d, J = 16.0 Hz, 1H), 1.02 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 152.6, 143.6, 139.2, 136.6, 136.5, 130.8, 128.8, 128.7, 128.5, 128.0, 127.9, 127.8, 126.1, 108.3, 87.8, 83.2, 82.4, 80.2, 59.2, 57.7, 55.7, 51.6, 50.1, 45.7, 41.9, 39.1, 33.1, 29.8, 26.1, 24.8, two carbons missing in the aromatic region. IR (KBr) v 3033, 2951, 2869, 1581, 1539, 1391, 747 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}ClN_5O_5$ $[M+H]^+$ 678.2478, found 678.2482.



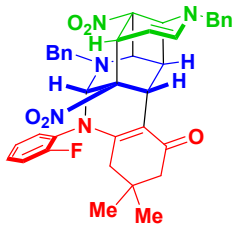
7,11-dibenzyl-5-(3-bromophenyl)-3,3-dimethyl-7b,13-dinitro-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3l**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 85.4 mg, 79% yield; dr > 20:1; reaction time = 5 min; mp 185.2-185.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (d, J = 8.0 Hz, 1H), 7.39 (q, J = 8.0 Hz, 4H), 7.30-7.26 (m, 7H), 7.11-7.02 (m, 3H), 6.47 (d, J = 12.0 Hz, 1H), 5.28 (s, 1H), 4.39 (q, J = 20.0 Hz, 2H), 4.22 (d, J = 20.0 Hz, 1H), 4.08 (t, J = 8.0 Hz, 1H), 3.96 (s, 1H), 3.88 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.77 (dd, J_1 = J_2 = 8.0 Hz, 2H), 3.29 (d, J = 8.0 Hz, 1H), 2.54 (t, J = 8.0 Hz, 1H), 2.30 (d, J = 12.0 Hz, 1H), 2.20 (d, J = 20.0 Hz, 1H), 1.85 (d, J = 20.0 Hz, 1H), 1.02 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 152.6, 143.7, 139.3, 136.5 (2C), 131.4, 131.0, 128.8, 128.7, 128.0 (3C), 127.8, 126.6, 108.3, 87.8, 83.2, 82.4, 80.2, 59.2, 57.7, 55.6, 51.6, 50.1, 45.7, 41.9, 39.1, 33.2, 29.9, 26.1, 24.8, one carbon missing in the aromatic region. IR (KBr) v 3433, 2955, 2872, 1642, 1586, 1541, 1379, 1161, 743 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}BrN_5O_5$ $[M+H]^+$ 722.1973, found 722.1974.



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

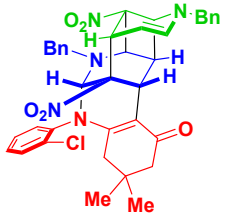
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 77.8 mg, 77% yield; dr = 7:1 (inseparable diastereoisomers); reaction time = 5 min; mp 205.9-207.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.31-7.14 (m, 11H), 7.06 (dd, $J_1 = J_2 = 8.0$ Hz, 3H), 6.35 (d, $J = 4.0$ Hz, 1H), 4.88 (s, 1H), 4.28 (q, $J = 16.0$ Hz, 2H), 4.03-3.88 (m, 4H), 3.70 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.49 (d, $J = 12.0$ Hz, 1H), 3.20 (d, $J = 8.0$ Hz, 1H), 2.45-2.37 (m, 3H), 2.25-2.09 (m, 3H), 1.51 (d, $J = 16.0$ Hz, 1H), 1.13 (t, $J = 8.0$ Hz, 3H), 0.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 154.8, 141.9, 139.5, 136.5, 135.9, 130.8, 130.1, 129.1, 128.7, 128.6, 128.1, 127.9, 127.8, 127.7, 126.4, 107.8, 87.6, 83.2, 82.5, 78.1, 60.2, 57.5, 54.8, 51.6, 50.0, 46.1, 42.1, 38.4, 33.2, 30.4, 25.6, 24.2, 23.2, 14.3. IR (KBr) *v* 3032, 2960, 2874, 1596, 1542, 1396, 735 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{42}N_5O_6$ $[M+H]^+$ 672.3181, found 672.3184.



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

Yellow solid obtained by filtration of the precipitate; 86.9 mg, 88% yield; dr = 3:1 (inseparable diastereoisomers); reaction time = 5 min; mp 215.2-216.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.41-7.34 (m, 5H), 7.28-7.23 (m, 5H), 7.19-7.10 (m, 4H), 6.46 (d, $J = 8.0$ Hz, 1H), 5.21 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 4.38 (q, $J = 16.0$ Hz, 2H), 4.15-3.70 (m, 6H), 3.27 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz, 1H), 2.57-2.50 (m, 1H), 2.38-2.07 (m, 3H), 1.86 (t, $J = 16.0$ Hz, 1H), 1.00 (d, $J = 4.0$ Hz, 4H), 0.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 158.5 (d, $J = 248.0$ Hz, 1C), 153.4, 139.2,

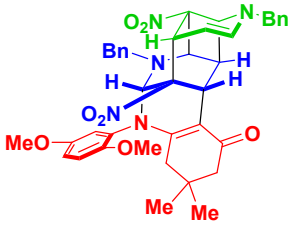
136.4 (d, J = 32.0 Hz, 1C), 130.4, 129.6, 128.8, 128.7, 128.6, 128.0, 127.7, 126.0 (d, J = 4.0 Hz, 1C), 124.8 (d, J = 5.0 Hz, 1C), 116.8, 116., 107.2, 88.3, 83.2, 82.4, 80.4, 59.1, 57.7, 54.8, 51.5, 50.1, 45.6, 39.9, 39.1, 32.8, 29.9, 26.0, 24.8. IR (KBr) v 3440, 3032, 2952, 2870, 1587, 1542, 1393, 752 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}FN_5O_5$ $[M+H]^+$ 662.2773, found 662.2775.



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

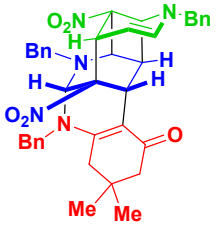
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 76.6 mg, 75% yield; dr = 1.7:1 (separable diastereoisomers); reaction time = 5 min; mp 186.1-186.9 °C (major isomer), 190.2-191.4 °C (minor isomer); ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 7.47 (dd, J_1 = J_2 = 8.0 Hz, 1H), 7.42-7.33 (m, 6H), 7.28-7.17 (m, 6H), 7.08 (dd, J_1 = J_2 = 8.0 Hz, 1H), 6.46 (d, J = 12.0 Hz, 1H), 5.20 (d, J = 4.0 Hz, 1H), 4.39 (q, J = 20.0 Hz, 2H), 4.15 (d, J = 20.0 Hz, 1H), 4.06 (q, J = 8.0 Hz, 2H), 3.97 (s, 1H), 3.90 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.73 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.29 (d, J = 12.0 Hz, 1H), 2.58 (t, J = 8.0 Hz, 1H), 2.42 (dd, J_1 = J_2 = 24.0 Hz, 2H), 2.24 (d, J = 20.0 Hz, 1H), 1.76 (d, J = 24.0 Hz, 1H), 1.01 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 194.5, 153.4, 140.6, 139.3, 136.5, 135.9, 133.7, 130.8, 130.0 (2C), 129.1, 128.7, 128.6 (2C), 128.0, 127.8, 127.7, 106.5, 88.3, 83.2, 82.4, 80.9, 59.5, 57.6, 54.6, 51.4, 50.1, 45.5, 39.6, 38.8, 32.7, 29.9, 26.1, 24.6. ^{1}H NMR (400 MHz, $CDCl_3$) for minor isomer δ 7.53 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.43-7.33 (m, 6H), 7.31-7.24 (m, 6H), 7.15 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.47 (d, J = 12.0 Hz, 1H), 5.05 (d, J = 4.0 Hz, 1H), 4.38 (q, J = 20.0 Hz, 2H), 4.19 (d, J = 20.0 Hz, 1H), 4.12 (t, J = 12.0 Hz, 1H), 4.01 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.96 (s, 1H), 3.78 (dd, J_1 = 4.0 Hz, J_2 = 20.0 Hz, 2H), 3.30 (d, J = 8.0 Hz, 1H), 2.53 (t, J = 8.0 Hz, 1H), 2.30 (s, 2H), 2.09 (d, J = 24.0 Hz, 1H), 1.65 (d, J = 24.0 Hz, 1H), 1.02 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for minor isomer δ 194.3, 153.5, 139.5, 138.8, 136.6, 136.1, 133.8, 131.7, 131.1, 130.2, 128.9, 128.7, 128.0 (2C), 127.9, 127.8, 127.5, 107.8, 87.1, 83.1, 82.8, 77.9, 60.1, 57.6, 54.9, 51.7, 50.0, 46.3, 41.7, 38.5, 33.1, 30.1, 26.0, 24.2. IR (KBr) for major isomer v 3029, 2956, 2869, 1587,

1538, 1386, 739 cm^{-1}. IR (KBr) for minor isomer *v* 3032, 2954, 2869, 1600, 1543, 1391, 741 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{37}ClN_5O_5$ $[M+H]^+$ 678.2478, found 678.2479.



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

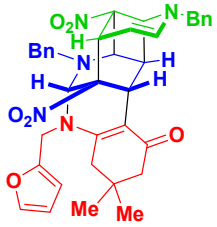
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 54.1 mg, 51% yield; dr = 1.2:1 (inseparable diastereoisomers); reaction time = 5 min; mp 187.4-189.1 °C; ^1H NMR (400 MHz, $CDCl_3$), δ 7.41 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.30-7.16 (m, 6H), 6.89-6.80 (m, 2H), 6.61 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.44 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 5.15 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.44-4.33 (m, 2H), 4.18-4.05 (m, 2H), 3.93-3.88 (m, 2H), 3.84-3.68 (m, 4H), 3.54 (d, J = 28.0 Hz, 3H), 3.26 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 2.57 (t, J = 8.0 Hz, 1H), 2.37-2.08 (m, 3H), 1.87 (q, J = 16.0 Hz, 2H), 1.01 (s, 3H), 0.96 (d, J = 16.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 154.4, 153.2, 149.5, 139.2, 137.2, 136.7, 131.0, 128.7, 128.4, 128.0, 127.7, 127.5, 115.4, 114.9, 112.8, 106.6, 87.0, 83.2, 82.8, 79.0, 59.2, 57.5, 55.7, 55.5, 55.1, 51.6, 50.2, 46.3, 41.2, 39.1, 32.8, 29.7, 26.6, 24.4. IR (KBr) *v* 3029, 2954, 2872, 1582, 1541, 1392, 733 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{42}N_5O_7$ $[M+H]^+$ 704.3079, found 704.3073.



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

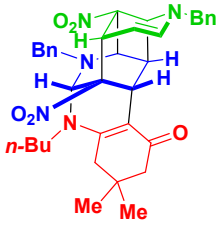
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 30.3 mg, 31% yield; dr > 20:1; reaction time = 5 min; mp 187.3-188.5 °C; ^1H NMR (400 MHz, $CDCl_3$), δ 7.41-7.35 (m, 4H), 7.30-7.24 (m, 8H), 7.11 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.43 (d, J = 4.0 Hz, 1H), 4.93 (d, J = 4.0 Hz, 1H), 4.43-4.27 (m, 4H), 4.16 (d, J = 16.0 Hz, 1H),

4.02 (t, J = 8.0 Hz, 1H), 3.87 (s, 1H), 3.83-3.79 (m, 2H), 3.73 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.30 (d, J = 8.0 Hz, 1H), 2.58 (t, J = 8.0 Hz, 1H), 2.28-2.21 (m, 3H), 1.08 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 154.7, 139.0, 137.3, 136.6 (2C), 128.9, 128.7 (2C), 128.0, 127.9 (2C), 127.8, 127.7, 126.5, 107.3, 87.7, 83.2, 82.4, 78.6, 59.2, 57.6, 56.9, 54.0, 51.4, 49.8, 45.9, 40.3, 39.2, 32.8, 28.9, 27.6, 24.9. IR (KBr) v 3031, 2954, 2867, 1633, 1578, 1539, 1354, 735 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}N_5O_5$ $[M+H]^+$ 658.3024, found 658.3023.



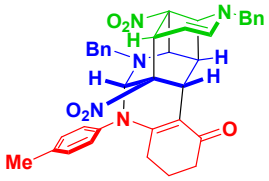
7,11-dibenzyl-5-(furan-2-ylmethyl)-3,3-dimethyl-7b,13-dinitro-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3r**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 39.4 mg, 41% yield; dr > 20:1; reaction time = 5 min; mp 197.4-198.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.41-7.35 (m, 4H), 7.29-7.23 (m, 6H), 7.08 (t, J = 4.0 Hz, 2H), 6.42 (d, J = 8.0 Hz, 1H), 6.27 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.18 (d, J = 4.0 Hz, 1H), 4.99 (d, J = 4.0 Hz, 1H), 4.37 (q, J = 16.0 Hz, 2H), 4.11 (s, 2H), 4.02 (t, J = 8.0 Hz, 1H), 3.81 (dd, J_1 = J_2 = 4.0 Hz, 2H), 3.71 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 2H), 3.27 (d, J = 8.0 Hz, 1H), 2.54 (t, J = 8.0 Hz, 1H), 2.46 (d, J = 16.0 Hz, 1H), 2.33 (d, J = 16.0 Hz, 1H), 2.28 (s, 2H), 1.11 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 154.2, 149.7, 142.9, 138.9, 137.7, 136.7, 128.7, 128.6, 128.1, 128.0, 127.7 (2C), 110.6, 108.6, 107.4, 87.5, 83.3, 82.4, 78.3, 58.5, 57.6, 57.2, 51.3, 49.8, 47.1, 45.8, 40.1, 39.4, 32.8, 28.5, 28.1, 25.0. IR (KBr) v 3438, 2951, 2874, 1629, 1572, 1538, 1356, 737 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{38}N_5O_6$ $[M+H]^+$ 648.2817, found 648.2814.



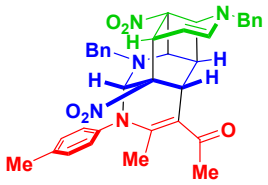
7,11-dibenzyl-5-butyl-3,3-dimethyl-7b,13-dinitro-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3s**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 22.4 mg, 24% yield; dr > 20:1; reaction time = 5 min; mp 173.6-175.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.39 (q, *J* = 8.0 Hz, 4H), 7.30-7.27 (m, 5H), 7.14 (t, *J* = 4.0 Hz, 2H), 6.43 (d, *J* = 12.0 Hz, 1H), 4.93 (d, *J* = 4.0 Hz, 1H), 4.39-4.29 (m, 3H), 4.13 (d, *J* = 20.0 Hz, 1H), 4.05 (t, *J* = 8.0 Hz, 1H), 3.85 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.80 (s, 1H), 3.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.33 (d, *J* = 8.0 Hz, 1H), 3.12-3.01 (m, 1H), 2.74-2.64 (m, 1H), 2.58 (t, *J* = 8.0 Hz, 1H), 2.26-2.16 (m, 5H), 1.41-1.33 (m, 1H), 1.28-1.22 (m, 1H), 1.10 (s, 3H), 1.03 (s, 3H), 0.85 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 154.4, 139.0, 137.8, 136.7, 128.7 (2C), 128.0, 127.9, 127.8, 127.7, 106.4, 87.8, 83.4, 82.5, 78.7, 59.6, 58.0, 57.5, 51.3, 50.2, 49.8, 46.1, 39.7, 39.4, 32.5, 31.4, 29.5, 27.1, 24.9, 19.7, 13.5. IR (KBr) *v* 3431, 3031, 2958, 2868, 1628, 1575, 1539, 1361, 739 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{42}N_5O_5$ $[M+H]^+$ 624.3181, found 624.3184.



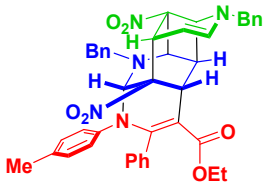
7,11-dibenzyl-7b,13-dinitro-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3t**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 87.7 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 223.7-225.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.28-7.23 (m, 5H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 4.0 Hz, 1H), 5.27 (d, *J* = 4.0 Hz, 1H), 4.38 (q, *J* = 12.0 Hz, 2H), 4.19 (d, *J* = 12.0 Hz, 1H), 4.06 (t, *J* = 8.0 Hz, 1H), 3.95 (s, 1H), 3.86-3.82 (m, 2H), 3.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.26 (d, *J* = 8.0 Hz, 1H), 2.59 (t, *J* = 8.0 Hz, 1H), 2.43-2.37 (m, 2H), 2.34 (s, 3H), 2.28-2.24 (m, 1H), 1.90-1.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 155.3, 139.9, 139.1, 138.3, 136.8, 136.6, 130.3, 128.7 (2C), 128.0, 127.9, 127.8, 127.7, 107.9, 88.0, 83.2, 82.5, 79.4, 58.9, 57.6, 55.5, 51.5, 45.8, 39.1, 36.5, 28.4, 24.9, 21.8, 21.0, one carbon missing in the aromatic region. IR (KBr) *v* 3056, 2929, 2863, 1633, 1584, 1536, 1370, 1165, 735 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{36}N_5O_5$ $[M+H]^+$ 630.2711, found 630.2714.



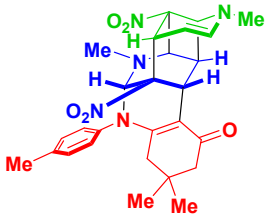
1-(1,7-dibenzyl-4-methyl-10a,11-dinitro-3-(*p*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocin-5-yl)ethan-1-one (**3u**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 39.1 mg, 42% yield; dr > 20:1; reaction time = 5 min; mp 185.5-187.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.34-7.27 (m, 8H), 7.13-7.10 (m, 4H), 6.98 (br, 2H), 6.50 (d, J = 8.0 Hz, 1H), 5.27 (d, J = 4.0 Hz, 1H), 4.30 (s, 2H), 4.12 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 2H), 3.88-3.78 (m, 4H), 3.27 (d, J = 12.0 Hz, 1H), 2.40 (t, J = 8.0 Hz, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 150.1, 141.0, 139.0, 137.9, 136.7 (2C), 129.3, 128.8, 128.7, 128.6, 128.2, 128.1, 128.0, 127.8, 109.1, 87.5, 83.2, 82.8, 78.9, 58.9, 58.4, 54.8, 52.3, 46.9, 38.9, 30.6, 28.3, 21.0, 20.6. IR (KBr) v 3425, 2925, 1639, 1544, 1355, 746 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{36}N_5O_5$ $[M+H]^+$ 618.2711, found 618.2714.



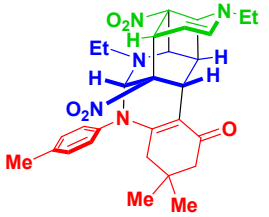
ethyl 1,7-dibenzyl-10a,11-dinitro-4-phenyl-3-(*p*-tolyl)-1,2,3,6,6a,6b,7,10,10a,10b-decahydro-2,6,10-(epimethanetriyl)pyrido[2',3':3,4]cyclobuta[1,2-*d*][1,3]diazocine-5-carboxylate (**3v**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 45.5 mg, 43% yield; dr > 20:1; reaction time = 5 min; mp 169.8-170.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.35-7.25 (m, 10H), 7.07 (d, J = 12.0 Hz, 5H), 6.81 (d, J = 12.0 Hz, 2H), 6.63 (d, J = 12.0 Hz, 2H), 6.46 (d, J = 12.0 Hz, 1H), 5.36 (s, 1H), 4.36 (q, J = 8.0 Hz, 4H), 4.12 (t, J = 8.0 Hz, 1H), 4.03 (s, 1H), 3.96-3.88 (m, 3H), 3.78 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.39 (d, J = 12.0 Hz, 1H), 2.61 (t, J = 8.0 Hz, 1H), 2.13 (s, 3H), 0.85 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 150.2, 141.7, 138.6, 137.5, 136.8, 136.7, 135.9, 129.7, 129.5, 128.8, 128.7, 128.0, 127.9, 127.8, 127.7, 127.4, 127.2, 115.5, 103.3, 87.6, 83.2, 83.0, 80.0, 59.6, 57.8, 57.7, 56.0, 51.6, 46.4, 39.4, 28.6, 20.8, 13.8. IR (KBr) v 3429, 3032, 2978, 1668, 1539, 1370, 1230, 1117, 746 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{40}N_5O_6$ $[M+H]^+$ 710.2973, found 710.2975.



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

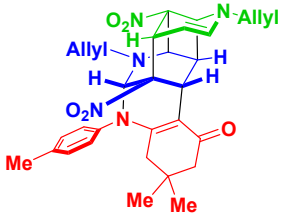
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 53.5 mg, 71% yield; dr > 20:1; reaction time = 5 min; mp 209.8-211.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 6.90 (s, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 4.96 (d, *J* = 4.0 Hz, 1H), 3.96-3.91 (m, 2H), 3.76-3.73 (m, 2H), 3.44 (d, *J* = 8.0 Hz, 1H), 3.02 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 1H), 2.63 (s, 3H), 2.38 (s, 3H), 2.26-2.13 (m, 3H), 1.77 (d, *J* = 16.0 Hz, 1H), 0.93 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.9, 140.1, 139.2, 138.3, 106.7, 87.6, 83.6, 81.2, 81.0, 60.3, 53.2, 50.0, 45.6, 44.0, 41.6, 40.7, 38.5, 32.8, 30.2, 25.7, 24.0, 21.1, three carbons missing in the aromatic region. IR (KBr) *v* 3035, 2951, 2871, 1631, 1582, 1539, 1394, 752 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{32}N_5O_5$ $[M+H]^+$ 506.2398, found 506.2401.



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

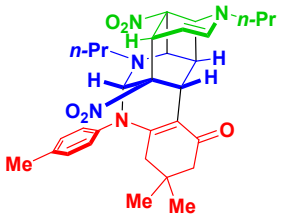
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 58.9 mg, 74% yield; dr > 20:1; reaction time = 5 min; mp 213.5-214.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.93 (s, 2H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 4.0 Hz, 1H), 4.02 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.94 (t, *J* = 8.0 Hz, 1H), 3.80 (s, 1H), 3.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.64 (d, *J* = 8.0 Hz, 1H), 3.26-3.16 (m, 2H), 3.05-2.94 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 1H), 2.61-2.53 (m, 1H), 2.37 (s, 3H), 2.24 (d, *J* = 16.0 Hz, 1H), 2.15 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 1.76 (d, *J* = 20.0 Hz, 1H), 1.30 (t, *J* = 8.0 Hz, 3H), 0.92-0.87 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.6, 140.0, 138.1, 137.9, 130.3, 128.0, 107.0, 88.3, 83.7, 81.0, 79.6, 56.7, 52.9, 50.0, 49.4, 49.2, 47.2, 41.8, 38.2, 32.8, 30.2, 25.7, 24.8, 21.1, 14.9, 13.4, one carbon missing in the aromatic region. IR

(KBr) *v* 3435, 2964, 2873, 1632, 1583, 1539, 1393, 748 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{36}N_5O_5$ $[M+H]^+$ 534.2711, found 534.2716.



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

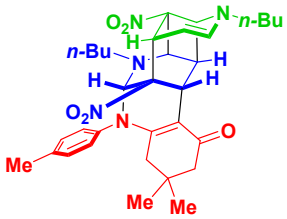
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 66.5 mg, 80% yield; dr > 20:1; reaction time = 5 min; mp 179.6-180.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.19 (d, J = 8.0 Hz, 2H), 6.95 (br, 2H), 6.31 (d, J = 8.0 Hz, 1H), 6.08-5.96 (m, 1H), 5.65-5.55 (m, 1H), 5.27 (dd, J_1 = 16.0 Hz, J_2 = 12.0 Hz, 2H), 5.10 (d, J = 8.0 Hz, 2H), 4.95 (d, J = 16.0 Hz, 1H), 3.98 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 2H), 3.84-3.72 (m, 4H), 3.61 (d, J = 8.0 Hz, 1H), 3.54 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.16 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.70 (t, J = 8.0 Hz, 1H), 2.37 (s, 3H), 2.25 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.0 Hz, 2H), 1.77 (d, J = 16.0 Hz, 1H), 0.94 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.7, 139.9, 138.4, 138.2, 134.3, 133.3, 130.4, 127.9, 127.4, 119.7, 118.3, 106.9, 88.2, 83.6, 81.9, 79.0, 57.9, 57.0, 56.9, 52.3, 50.0, 46.5, 41.7, 38.5, 32.8, 30.1, 25.8, 24.9, 21.1. IR (KBr) *v* 3082, 2955, 2930, 2870, 2214, 1635, 1580, 1393, 729 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{36}N_5O_5$ $[M+H]^+$ 558.2711, found 558.2713.



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

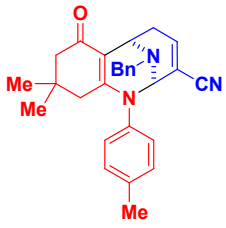
Yellow solid obtained by filtration of the precipitate; 74.1 mg, 88% yield; dr > 20:1; reaction time = 5 min; mp 194.2-195.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.19 (d, J = 8.0 Hz, 2H), 6.93 (s, 2H), 6.30 (d, J = 8.0 Hz, 1H), 5.04 (d, J = 4.0 Hz, 1H), 4.00 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.92 (t, J = 8.0 Hz, 1H), 3.79 (s, 1H), 3.75 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.62 (d, J = 8.0 Hz, 1H), 3.17-3.05 (m, 2H),

3.01-2.95 (m, 1H), 2.74 (t, J = 8.0 Hz, 1H), 2.50-2.42 (m, 1H), 2.38 (s, 3H), 2.18 (t, J = 16.0 Hz, 2H), 1.80 (d, J = 20.0 Hz, 1H), 1.76-1.63 (m, 2H), 1.48-1.32 (m, 1H), 1.31-1.18 (m, 2H), 0.98 (t, J = 8.0 Hz, 3H), 0.93 (s, 3H), 0.88 (s, 3H), 0.74 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 153.7, 140.0, 138.5, 138.1, 130.2, 127.6, 107.3, 88.3, 83.5, 80.6, 80.1, 57.0, 56.9, 56.8, 53.1, 50.1, 47.2, 41.8, 38.3, 32.8, 29.9, 26.0, 24.9, 22.8, 21.3, 21.1, 11.3, 11.2, one carbon missing in the aromatic region. IR (KBr) v 3439, 3037, 2964, 2934, 2873, 1634, 1591, 1539, 1392, 749 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{40}N_5O_5$ $[M+H]^+$ 562.3024, found 562.3028.



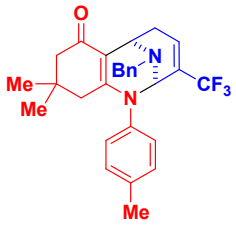
7,11-dibutyl-3,3-dimethyl-7b,13-dinitro-5-(*p*-tolyl)-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**3za**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 75.4 mg, 85% yield; dr > 20:1; reaction time = 5 min; mp 200.6-201.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.17 (d, J = 8.0 Hz, 2H), 6.92 (s, 2H), 6.27 (d, J = 4.0 Hz, 1H), 5.02 (d, J = 4.0 Hz, 1H), 4.00 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.91 (t, J = 8.0 Hz, 1H), 3.77-3.73 (m, 2H), 3.61 (d, J = 8.0 Hz, 1H), 3.19-3.09 (m, 2H), 3.01-2.94 (m, 1H), 2.73 (t, J = 8.0 Hz, 1H), 2.53-2.46 (m, 1H), 2.36 (s, 3H), 2.21-2.10 (m, 3H), 1.79 (d, J = 16.0 Hz, 1H), 1.69-1.60 (m, 2H), 1.41-1.33 (m, 3H), 1.20-1.09 (m, 3H), 0.95 (t, J = 8.0 Hz, 3H), 0.91 (s, 3H), 0.87 (s, 3H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 153.5, 140.0, 138.4, 138.0, 130.2, 127.6, 107.2, 88.2, 83.5, 80.7, 80.1, 56.8, 54.9, 54.4, 52.9, 50.0, 46.9, 41.8, 38.3, 32.8, 31.3, 30.2, 29.9, 25.9, 24.8, 21.0, 19.9, 19.8, 13.7 (2C), one carbon missing in the aromatic region. IR (KBr) v 3392, 2959, 2866, 1632, 1581, 1394, 733 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{44}N_5O_5$ $[M+H]^+$ 590.3337, found 590.3336.



3-benzyl-9,9-dimethyl-7-oxo-1-(*p*-tolyl)-1,2,3,6,7,8,9,10-octahydro-2,6-methanobenzo[*d*][1,3]diazocine-5-carbonitrile (**3zb**)

White solid obtained by filtration of the precipitate; 31.6 mg, 50% yield; dr > 20:1; reaction time = 5 min; mp 180.4-182.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.28 (d, J = 8.0 Hz, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.89 (s, 3H), 4.91 (s, 1H), 4.14 (d, J = 20.0 Hz, 1H), 4.05 (s, 1H), 3.73 (d, J = 20.0 Hz, 1H), 2.45 (s, 3H), 2.30-2.12 (m, 3H), 1.88-1.68 (m, 3H), 0.96 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 155.0, 144.7, 140.7, 137.9, 136.1, 130.5, 128.8, 128.0, 127.3, 121.3, 113.7, 84.1, 69.3, 58.3, 49.6, 41.2, 32.7, 29.2, 27.1, 25.9, 22.1, 21.1. IR (KBr) ν 3433, 2955, 2872, 1642, 1586, 1541, 1379, 1161, 743 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{30}N_3O$ $[M+H]^+$ 424.2383, found 424.2380.

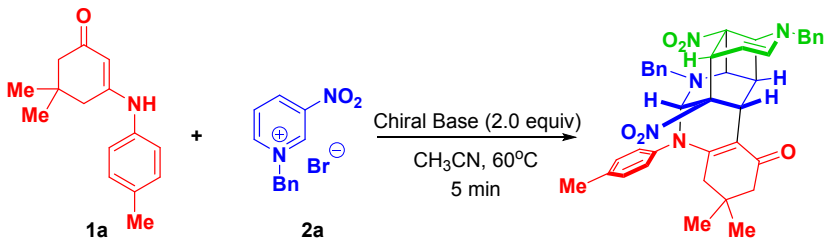


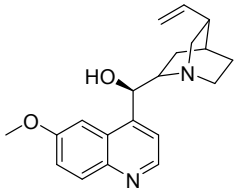
3-benzyl-9,9-dimethyl-1-(*p*-tolyl)-11-(trifluoromethyl)-2,3,6,8,9,10-hexahydro-2,6-methanobenzo[*d*][1,3]diazocin-7(1*H*)-one (**3zc**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 28.9 mg, 41% yield; dr > 20:1; reaction time = 5 min; mp 186.4-187.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.39-7.32 (m, 4H), 7.29 (d, J = 8.0 Hz, 1H), 7.22 (br, 2H), 6.88 (br, 2H), 6.43-6.40 (m, 1H), 5.65 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.68 (s, 1H), 4.53 (d, J = 8.0 Hz, 1H), 3.81 (d, J = 16.0 Hz, 1H), 3.60 (d, J = 16.0 Hz, 1H), 2.91-2.84 (m, 1H), 2.37 (s, 3H), 2.24-2.20 (m, 3H), 1.88 (d, J = 16.0 Hz, 1H), 1.08 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 154.9, 138.1 (d, J = 22.0 Hz, 1C), 136.8 (d, J = 14.0 Hz, 1C), 131.3, 130.3, 129.0, 128.4, 127.6, 127.3, 123.0, 114.1, 103.4, 73.6 (d, J = 3.0 Hz, 1C), 57.0, 49.0 (d, J = 131.0 Hz, 1C), 45.3, 45.0, 44.8, 41.0, 33.0, 28.6 (d, J = 173.0 Hz, 1C), 21.0. IR (KBr) ν 3439, 2958, 2929, 1616, 1559, 1508, 1391, 1272, 1119, 742 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{30}F_3N_2O$ $[M+H]^+$ 467.2305, found 467.2302.

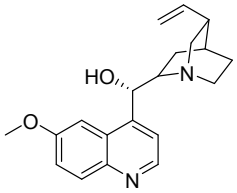
3. Screening chiral bases for asymmetric synthesis of 3a

Table S1 Screening chiral bases[a]

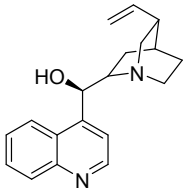




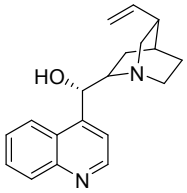
C1



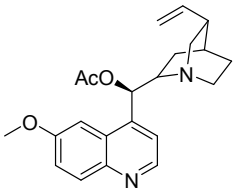
C2



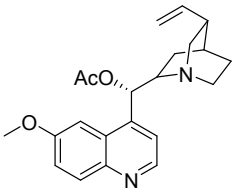
C3



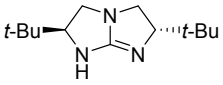
C4



C5



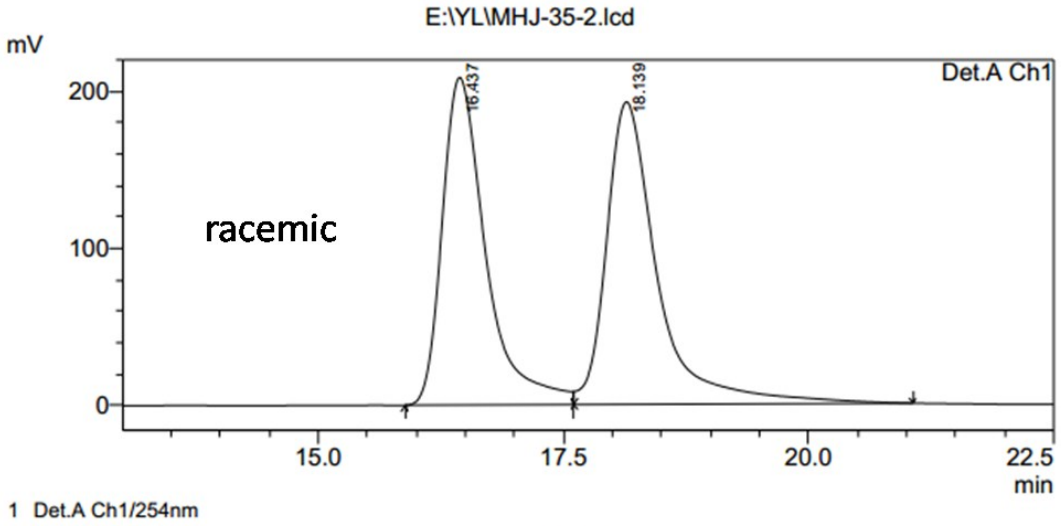
C6



C7

entry	chiral bases	yield (%)[b]	ee (%)[c]
1	C1	12	-6
2	C2	6	-5
3	C3	trace	N.D.
4	C4	9	-4
5	C5	17	-5
6	C6	18	-1
7	C7	55	10

[a] Unless otherwise noted, the reactions were conducted with 0.15 mmol **1a** with 2.2 equivalents of **2a** in the presence of 2.0 equivalents of base in 0.8 mL of CH_3CN at 60 °C. [b] Isolated yields obtained by column chromatography. [c] The enantiomeric excess (ee) was determined by chiral HPLC.

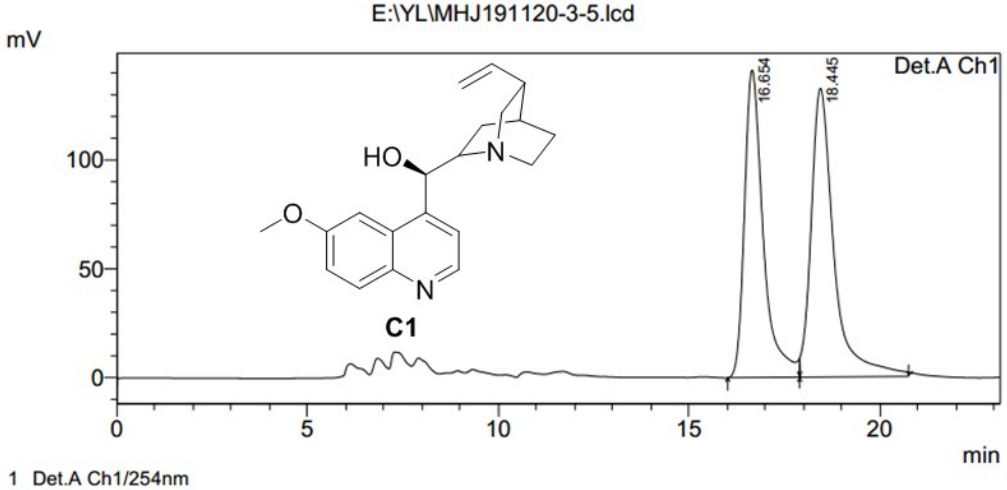


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.437	6466038	208988	48.095
2	18.139	6978225	192888	51.905
Total		13444263		100.000

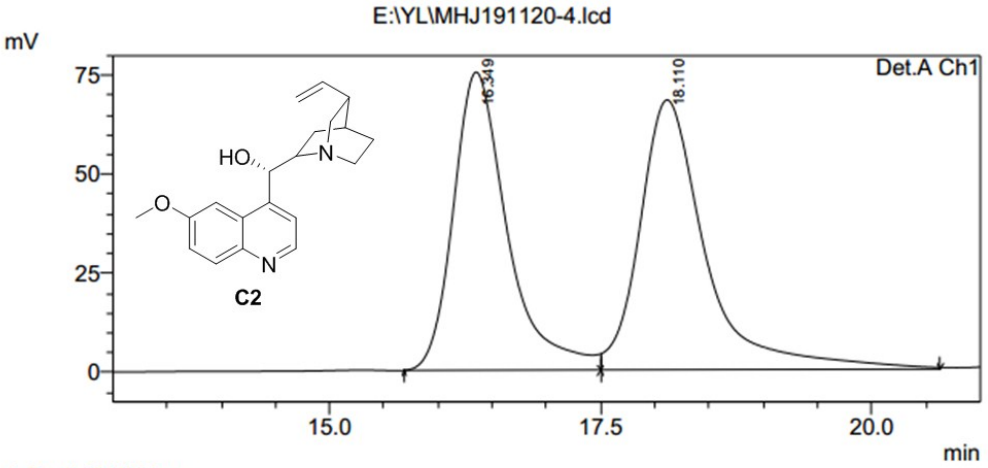


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.654	4835060	140908	46.844
2	18.445	5486588	132287	53.156
Total		10321648		100.000

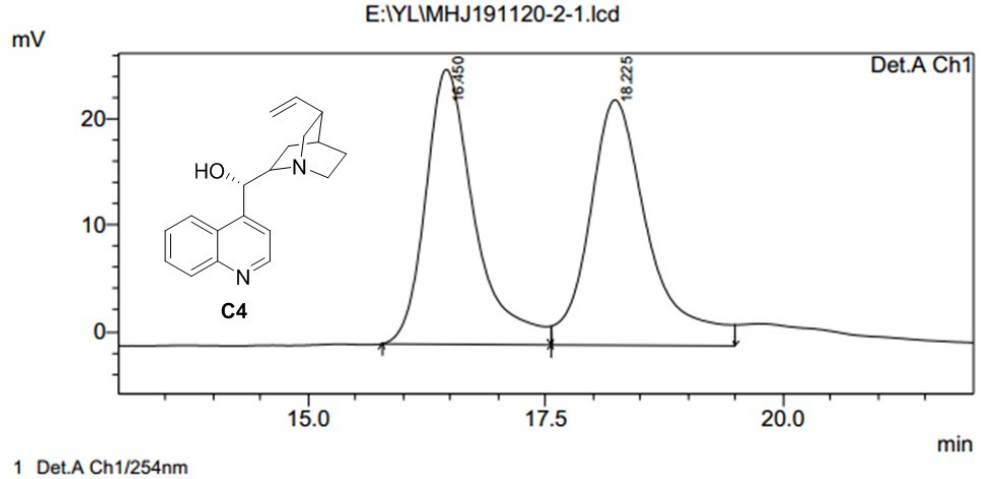


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.349	2602879	75237	47.399
2	18.110	2888502	68123	52.601
Total		5491382		100.000

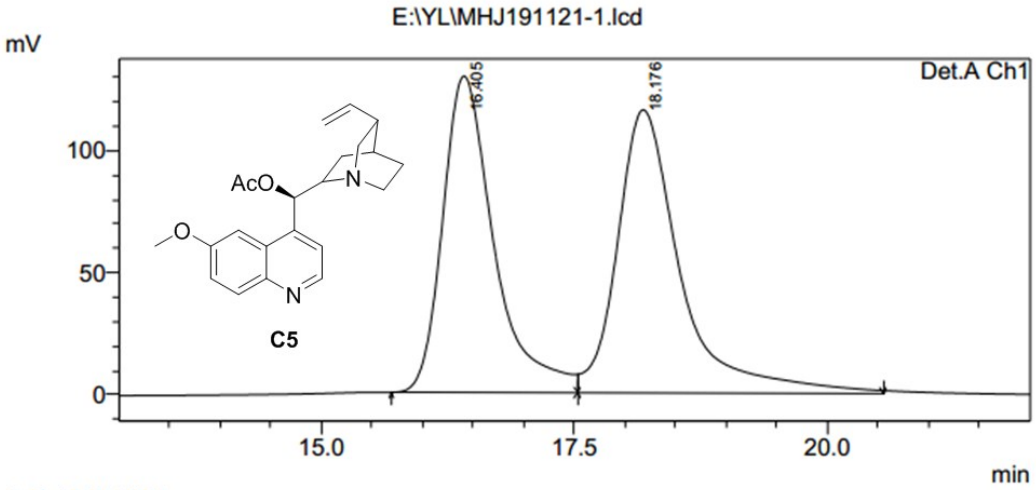


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.450	926463	25805	48.081
2	18.225	1000412	23033	51.919
Total		1926876		100.000

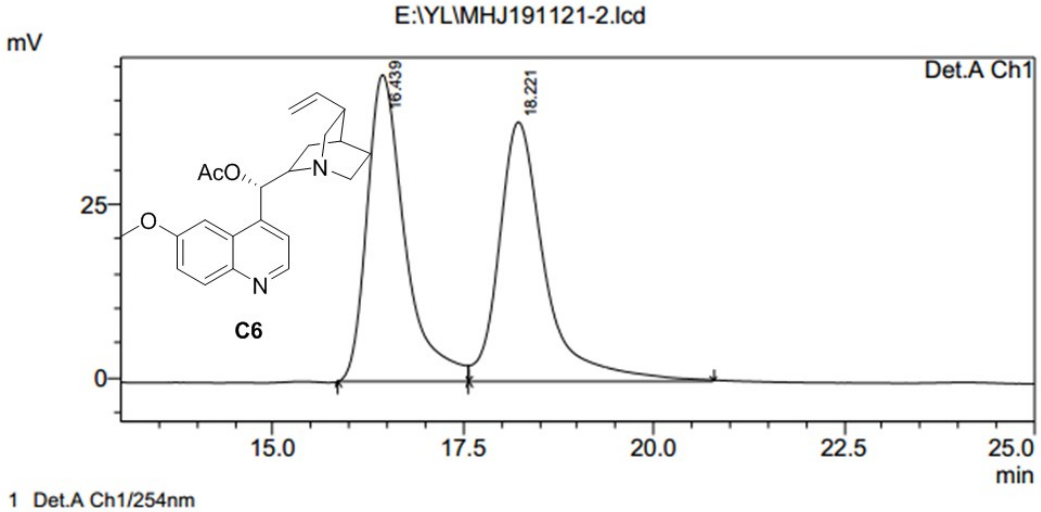


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.405	4576647	129686	47.647
2	18.176	5028612	116027	52.353
Total		9605259		100.000



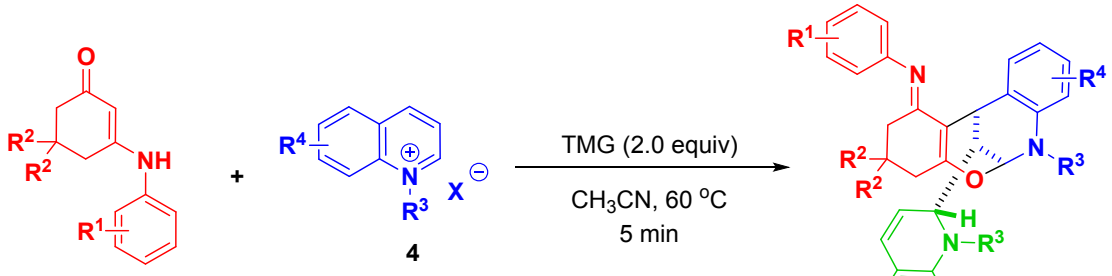
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.439	1535675	44301	49.395
2	18.221	1573281	37464	50.605
Total		3108956		100.000

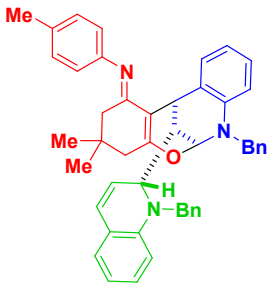
4. Experimental data for the formation of 5



1 4 5

4a, R^3 = Bn, R^4 = H, X = Br; **4b**, R^3 = Bn, R^4 = Cl, X = Br
4c, R^3 = Et, R^4 = H, X = I; **4d**, R^3 = Allyl, R^4 = H, X = Br
4e, R^3 = Bn, R^4 = 6-Me, X = Br; **4f**, R^3 = Bn, R^4 = 6-Br, X = Br
4g, R^3 = Bn, R^4 = 6-NO_2, X = Br; **4h**, R^3 = Bn, R^4 = 7-Me, X = Br

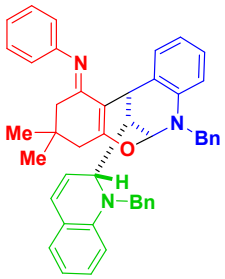
General procedure: To a 5.0 mL vial were successively added enaminones **1** (0.15 mmol), *N*-alkyl quinolinium salts **4** (0.33 mmol) and 0.8 mL of CH_3CN. And then, TMG (34.6 mg, 0.30 mmol) was added by syringe. The resulting mixture was stirred at 60 °C for 5 min. Upon completion of the reaction (monitoring by TLC), the products **5** were precipitated from the reaction mixtures and only a filtration was needed to purify them. (Note: The products were sensitive to acidic conditions, which could not be purified by silica gel column chromatography. They were liable to lose one molecule of quinoline to afford mono-quinoline bridged cyclic compounds **6**.) For substrates **4k** and **4j**, only mono-quinoline bridged cyclic compounds **7** and **8** were generated, which were purified by column chromatography.



7-benzyl-13-(1-benzyl-1,2-dihydroquinolin-2-yl)-3,3-dimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5a**)

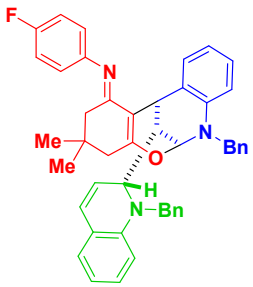
White solid obtained by filtration of the precipitate; 97.7 mg, 98% yield; dr > 20:1; reaction time = 5 min; mp 189.5-190.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.29-7.21 (m, 5H), 7.10 (d, *J* = 4.0 Hz, 5H), 7.03-6.96 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.61 (t, *J* = 8.0 Hz, 4H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 2H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.78 (d, *J* = 16.0 Hz, 1H), 4.68 (d, *J* = 16.0 Hz, 1H), 4.50 (s, 1H), 4.21 (d, *J* = 16.0

Hz, 1H), 3.73 (t, J = 8.0 Hz, 1H), 2.44 (d, J = 8.0 Hz, 1H), 2.33 (s, 3H), 2.10-2.03 (m, 3H), 1.83 (d, J = 16.0 Hz, 1H), 0.90 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.0, 150.1, 142.9, 141.6, 138.8, 138.5, 131.3, 129.8, 129.4, 128.7, 128.2, 127.3, 127.1, 127.1, 126.8, 126.8, 126.6, 126.5, 125.3, 123.0, 121.2, 119.7, 118.3, 116.7, 114.5, 114.0, 110.7, 82.9, 56.6, 55.7, 53.2, 41.5, 41.0, 40.6, 31.2, 29.0, 28.9, 27.7, 20.8. IR (KBr) v 3421, 3029, 2951, 1597, 1494, 1222, 747 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{46}N_3O$ $[M+H]^+$ 668.3635, found 668.3617.



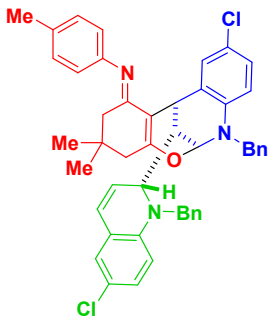
7-benzyl-13-(1-benzyl-1,2-dihydroquinolin-2-yl)-3,3-dimethyl-*N*-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5b**)

White solid obtained by filtration of the precipitate; 81.9 mg, 84% yield; dr = 2.7:1; reaction time = 5 min; mp 185.6-186.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.67 (d, J = 8.0 Hz, 1H), 7.35-6.91 (m, 15H), 6.78-6.54 (m, 7H), 6.44 (d, J = 12.0 Hz, 1H), 5.78-5.35 (m, 2H), 5.01 (d, J = 16.0 Hz, 1H), 4.80-4.43 (m, 3H), 4.21 (d, J = 16.0 Hz, 1H), 3.74 (q, J = 8.0 Hz, 1H), 2.45 (d, J = 12.0 Hz, 1H), 2.03 (t, J = 12.0 Hz, 3H), 1.81 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H), 0.90 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.3, 152.8, 142.9, 141.6, 138.7, 138.5, 129.8, 128.8, 128.6, 128.5, 128.3, 128.2, 127.3, 127.1, 127.1, 126.9, 126.7, 126.5, 125.2, 122.9, 122.1, 121.2, 119.8, 118.3, 116.7, 114.5, 113.9, 110.7, 82.9, 56.6, 55.6, 53.1, 41.5, 41.0, 40.6, 31.2, 28.9, 27.6. IR (KBr) v 3434, 2953, 1594, 1492, 1381, 746 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{44}N_3O$ $[M+H]^+$ 654.3479, found 654.3461.



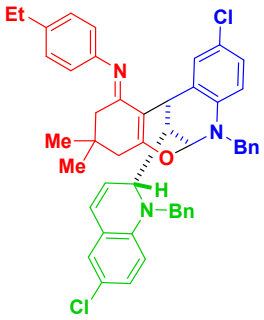
7-benzyl-13-(1-benzyl-1,2-dihydroquinolin-2-yl)-*N*-(4-fluorophenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5c**)

White solid obtained by filtration of the precipitate; 82.8 mg, 83% yield; dr > 20:1; reaction time = 5 min; mp 184.1-185.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 7.24-7.14 (m, 5H), 7.03-6.95 (m, 8H), 6.72-6.55 (m, 8H), 5.76 (t, *J* = 8.0 Hz, 1H), 5.44 (s, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 4.58 (t, *J* = 16.0 Hz, 2H), 4.38 (s, 1H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.60 (t, *J* = 8.0 Hz, 1H), 2.37 (d, *J* = 8.0 Hz, 1H), 2.07-2.00 (m, 3H), 1.78 (d, *J* = 16.0 Hz, 1H), 0.89 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 158.2, 148.5, 142.8, 141.1, 138.4, 138.3, 129.3, 128.5, 128.5, 128.4, 127.3, 127.2, 127.1, 126.9, 126.9, 126.8, 126.6, 124.5 (d, *J* = 73.0 Hz, 1C), 122.5, 121.0, 120.9, 117.9 (d, *J* = 33.0 Hz, 1C), 115.5, 115.4, 115.3, 114.0, 110.8, 85.2, 57.9, 56.8, 54.0, 41.5, 41.1, 40.0, 31.2, 29.2, 27.8, 27.4. IR (KBr) *v* 3437, 3033, 2954, 1599, 1494, 1215, 750 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}FN_3O$ $[M+H]^+$ 672.3385, found 672.3361.



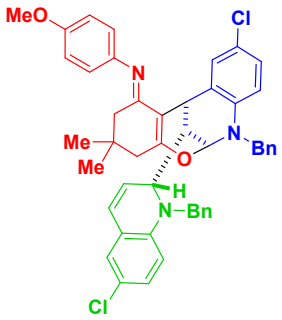
7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-3,3-dimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**5d**)

White solid obtained by filtration of the precipitate; 114.2 mg, 99% yield; dr > 20:1; reaction time = 5 min; mp 194.8-196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.67 (d, *J* = 4.0 Hz, 1H), 7.32-7.27 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 7H), 6.99-6.93 (m, 5H), 6.61 (d, *J* = 8.0 Hz, 3H), 6.51 (d, *J* = 12.0 Hz, 1H), 6.40 (d, *J* = 12.0 Hz, 1H), 5.42 (t, *J* = 8.0 Hz, 1H), 5.31 (s, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.76 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 16.0 Hz, 1H), 4.40 (s, 1H), 4.19 (d, *J* = 20.0 Hz, 1H), 3.69(t, *J* = 8.0 Hz, 1H), 2.39 (t, *J* = 4.0 Hz, 1H), 2.35 (s, 3H), 2.13-2.03 (m, 3H), 1.85 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 158.2, 149.8, 141.4, 140.1, 138.0 (2C), 131.6, 129.5, 129.4, 128.8, 128.4 (2C), 127.3, 127.0, 126.8, 126.7, 126.6, 126.5, 126.4, 124.4, 123.0, 122.5, 121.9, 119.7, 115.9, 113.4, 111.9, 82.8, 56.5, 56.2, 53.4, 41.4, 40.9, 40.3, 31.2, 28.9, 28.6, 27.9, 20.8. IR (KBr) *v* 3419, 2955, 1603, 1493, 1218, 878 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Cl_2N_3O$ $[M+H]^+$ 736.2856, found 736.2847.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(4-ethylphenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5e**)

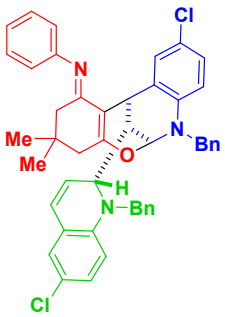
White solid obtained by filtration of the precipitate; 104.3 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 177.6-178.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.74 (d, J = 4.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 3H), 7.19 (d, J = 4.0 Hz, 7H), 7.00 (s, 5H), 6.66 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 6.55 (d, J = 8.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 5.47 (t, J = 8.0 Hz, 1H), 5.36 (s, 1H), 4.98 (d, J = 20.0 Hz, 1H), 4.80 (d, J = 20.0 Hz, 1H), 4.68 (d, J = 16.0 Hz, 1H), 4.45 (s, 1H), 4.24 (d, J = 16.0 Hz, 1H), 3.73 (t, J = 8.0 Hz, 1H), 2.70 (t, J = 8.0 Hz, 2H), 2.42 (d, J = 12.0 Hz, 1H), 2.11 (dd, $J_1 = J_2$ = 16.0 Hz, 3H), 1.90 (d, J = 16.0 Hz, 1H), 1.31 (t, J = 8.0 Hz, 3H), 0.97 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 158.2, 150.0, 141.3, 140.1, 138.1, 138.0 (2C), 129.4, 128.8, 128.4 (2C), 128.3, 127.3, 127.0, 126.8, 126.7, 126.6, 126.4 (2C), 124.3, 123.0, 122.5, 121.9, 119.7, 115.9, 113.4, 111.9, 82.8, 56.5, 56.1, 53.4, 41.4, 40.9, 40.3, 31.2, 28.9, 28.6, 28.3, 27.9, 15.8. IR (KBr) v 3442, 2958, 1603, 1492, 1220, 860 cm^{-1}. HRMS (ESI) calcd for $C_{48}H_{46}Cl_2N_3O$ $[M+H]^+$ 750.3012, found 750.3000.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(4-methoxyphenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5f**)

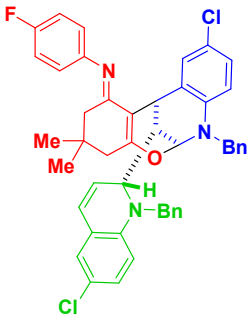
White solid obtained by filtration of the precipitate; 96.8 mg, 86% yield; dr > 20:1; reaction time = 5 min; mp 163.4-164.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.73 (s, 1H), 7.33 (d, J = 8.0 Hz, 3H), 7.19 (d, J = 8.0 Hz, 5H), 7.02-6.93 (m, 7H), 6.70-6.64 (m, 3H), 6.54 (d, J = 8.0 Hz, 1H), 6.44 (d, J

= 8.0 Hz, 1H), 5.46 (t, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 4.99 (d, *J* = 16.0 Hz, 1H), 4.80 (d, *J* = 20.0 Hz, 1H), 4.68 (d, *J* = 20.0 Hz, 1H), 4.45 (s, 1H), 4.24 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.73 (t, *J* = 8.0 Hz, 1H), 2.41 (d, *J* = 8.0 Hz, 1H), 2.24-2.00 (m, 3H), 1.90 (d, *J* = 16.0 Hz, 1H), 0.96 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 158.2, 155.3, 145.7, 141.4, 140.1, 138.0, 137.9, 129.4, 128.8, 128.4 (2C), 127.3, 127.0, 126.8, 126.7, 126.6, 126.4 (2C), 124.3, 123.0, 122.5, 121.9, 120.8, 115.9, 114.3, 113.5, 111.9, 82.8, 56.4, 56.2, 55.5, 53.4, 41.4, 40.9, 40.3, 31.2, 28.9, 28.6, 28.0. IR (KBr) *v* 3424, 2953, 1602, 1494, 1228, 879 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Cl_2N_3O_2$ $[M+H]^+$ 752.2805, found 752.2807.



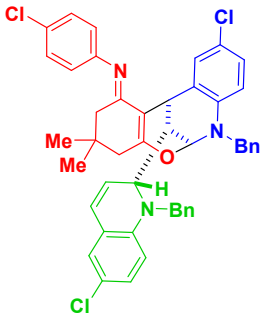
7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-3,3-dimethyl-*N*-phenyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5g**)

White solid obtained by filtration of the precipitate; 77.0 mg, 71% yield; dr = 3.5:1; reaction time = 5 min; mp 169.9-170.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.70 (s, 1H), 7.32-6.94 (m, 16H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.43 (d, *J* = 8.0 Hz, 1H), 5.33 (s, 1H), 4.94 (d, *J* = 20.0 Hz, 1H), 4.78-4.59 (m, 2H), 4.55-4.36 (m, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 2.39 (d, *J* = 8.0 Hz, 1H), 2.11-2.01 (m, 3H), 1.83 (d, *J* = 16.0 Hz, 1H), 0.91 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 158.5, 152.4, 141.3, 140.1, 137.9, 137.9, 129.2, 128.9, 128.7, 128.4, 128.3, 127.3, 127.1, 127.0, 126.8, 126.7, 126.6, 126.4, 124.3, 123.0, 122.4, 122.3, 121.8, 119.7, 115.9, 113.3, 111.9, 82.7, 56.4, 56.1, 53.3, 41.4, 40.9, 40.2, 31.1, 28.9, 28.6, 27.8. IR (KBr) *v* 3426, 2955, 1596, 1489, 1377, 1220, 703 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{42}Cl_2N_3O$ $[M+H]^+$ 722.2699, found 722.2705.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(4-fluorophenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5h**)

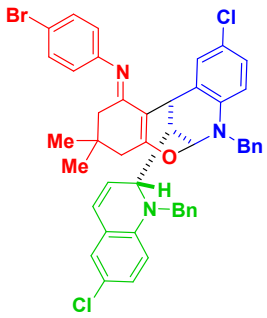
White solid obtained by filtration of the precipitate; 91.9 mg, 83% yield; dr = 5.0:1; reaction time = 5 min; mp 185.7-186.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.66 (s, 1H), 7.28-6.95 (m, 14H), 6.62 (d, *J* = 8.0 Hz, 3H), 6.51 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.42 (d, *J* = 8.0 Hz, 1H), 5.33 (s, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.78-4.48 (m, 2H), 4.39 (s, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 2.38 (d, *J* = 8.0 Hz, 1H), 2.08-2.01 (m, 3H), 1.82 (d, *J* = 16.0 Hz, 1H), 0.91 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 158.8, 148.4, 140.7 (d, *J* = 127.0 Hz, 1C), 137.9, 137.8, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 127.3, 127.0, 126.9, 126.7, 126.6, 126.4, 124.3, 122.7 (d, *J* = 53.0 Hz, 1C), 121.9, 120.9, 120.8, 115.9, 115.6, 115.4, 113.3, 111.9, 82.8, 56.3, 56.2, 53.3, 41.4, 40.9, 40.2, 31.2, 28.9, 28.6, 27.9. IR (KBr) *v* 3440, 2955, 1600, 1493, 1213, 725 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{41}Cl_2FN_3O$ $[M+H]^+$ 740.2605, found 740.2609.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(4-chlorophenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5i**)

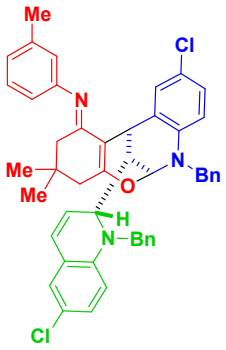
White solid obtained by filtration of the precipitate; 103.3 mg, 91% yield; dr > 20:1; reaction time = 5 min; mp 182.7-183.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.63 (d, *J* = 4.0 Hz, 1H), 7.31-7.28 (m, 5H), 7.16 (s, 5H), 7.01-6.95 (m, 5H), 6.64 (d, *J* = 8.0 Hz, 3H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.42 (t, *J* = 8.0 Hz, 1H), 5.33 (s, 1H), 4.95 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 16.0 Hz, 1H), 4.36 (s, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.69 (t, *J* = 8.0 Hz,

1H), 2.37 (d, J = 12.0 Hz, 1H), 2.11-2.05 (m, 3H), 1.84 (d, J = 16.0 Hz, 1H), 0.93 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.1, 151.0, 141.4, 140.1, 137.9, 137.8, 129.2, 128.9, 128.8, 128.4 (2C), 127.5, 127.3, 127.0, 126.8, 126.7 (2C), 126.6, 126.4, 124.4, 123.0, 122.4, 122.0, 121.2, 116.0, 113.3, 112.0, 82.9, 56.3 (2C), 53.4, 41.4, 41.0, 40.2, 31.2, 28.9, 28.6, 27.9. IR (KBr) v 3442, 1634, 1487, 725 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{41}Cl_3N_3O$ $[M+H]^+$ 756.2310, found 756.2314.



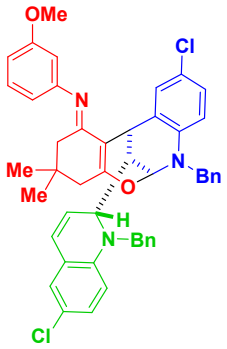
7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-*N*-(4-bromophenyl)-10-chloro-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5j**)

White solid obtained by filtration of the precipitate; 90.7 mg, 76% yield; dr > 20:1; reaction time = 5 min; mp 192.5-193.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.61 (s, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.28 (s, 4H), 7.15 (s, 5H), 6.96 (s, 5H), 6.64-6.50 (m, 5H), 6.40 (d, J = 8.0 Hz, 1H), 5.41 (t, J = 8.0 Hz, 1H), 5.32 (s, 1H), 4.93 (d, J = 16.0 Hz, 1H), 4.75 (d, J = 16.0 Hz, 1H), 4.64 (d, J = 16.0 Hz, 1H), 4.35 (s, 1H), 4.19 (d, J = 16.0 Hz, 1H), 3.67 (t, J = 8.0 Hz, 1H), 2.36 (d, J = 8.0 Hz, 1H), 2.05 (s, 2H), 1.82 (d, J = 16.0 Hz, 1H), 0.92 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 159.1, 151.4, 141.4, 140.1, 138.0, 137.9, 131.8, 129.2, 128.8, 128.6, 128.5, 128.4, 127.4, 127.0, 126.9, 126.7, 126.6, 126.4, 124.4, 123.0, 122.4, 122.0, 121.7, 116.0, 115.1, 113.3, 112.0, 82.9, 56.3, 53.4, 41.4, 41.1, 41.0, 40.2, 31.3, 28.9, 28.6, 27.9. IR (KBr) v 3420, 2955, 1601, 1487, 1382, 1219, 725 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{41}BrCl_2N_3O$ $[M+H]^+$ 800.1657, found 800.1659.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-3,3-dimethyl-*N*-(*m*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**5k**)

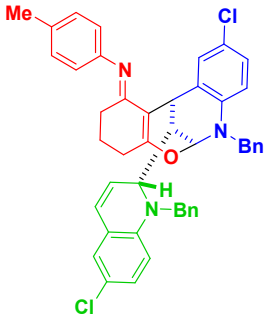
White solid obtained by filtration of the precipitate; 105.8 mg, 96% yield; dr = 6.6:1; reaction time = 5 min; mp 194.9-196.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.70 (s, 1H), 7.29-6.84 (m, 15H), 6.61-6.49 (s, 4H), 6.39 (d, *J* = 12.0 Hz, 1H), 5.42 (t, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.94 (d, *J* = 16.0 Hz, 1H), 4.78-4.61 (m, 2H), 4.41 (s, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.69 (t, *J* = 8.0 Hz, 1H), 2.35 (t, *J* = 20.0 Hz, 4H), 2.06 (q, *J* = 20.0 Hz, 3H), 1.83 (d, *J* = 16.0 Hz, 1H), 0.92 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 158.3, 152.4, 141.3, 140.1, 138.6, 137.9, 137.9, 129.3, 128.7, 128.5, 128.5, 128.4, 128.3, 127.3, 127.0, 126.8, 126.7, 126.6, 126.6, 126.4, 124.3, 123.1, 123.0, 122.5, 121.9, 120.4, 116.7, 115.9, 113.3, 111.9, 82.8, 56.4, 56.1, 53.4, 41.4, 40.9, 40.2, 31.2, 28.6, 27.8, 21.5. IR (KBr) *v* 3439, 2953, 1596, 1490, 1376, 879 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Cl_2N_3O$ $[M+H]^+$ 736.2856, found 736.2861.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(3-methoxyphenyl)-3,3-dimethyl-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d*,*g*][1,3]oxazocin-1-imine (**5l**)

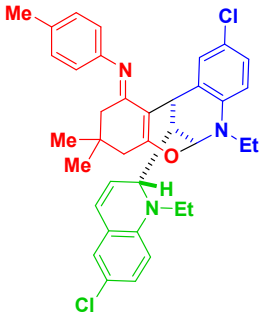
White solid obtained by filtration of the precipitate; 86.4 mg, 77% yield; dr > 20:1; reaction time = 5 min; mp 189.2-190.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.70 (s, 1H), 7.28-7.14 (m, 9H), 6.94 (d, *J* = 4.0 Hz, 5H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 2H), 5.41 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.95 (d, *J* = 16.0 Hz, 1H), 4.78-4.59 (m, 2H), 4.39 (s, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.69 (d, *J* = 8.0 Hz, 1H), 2.38 (d, *J* = 12.0 Hz, 1H), 2.10 (t, *J* = 16.0 Hz, 3H), 1.84 (d, *J* = 16.0 Hz, 1H), 0.93 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.3, 158.6, 153.8, 141.3, 140.1, 138.0, 137.9, 129.7, 129.3, 128.8, 128.4, 128.3, 127.3, 127.3, 127.0, 126.8, 126.7, 126.7, 126.6, 126.4, 124.3, 123.0, 122.4, 121.9, 115.9, 113.3, 112.0, 111.9, 108.3, 105.0, 82.8, 56.4, 56.2, 55.2, 53.4, 41.4, 40.9, 40.2, 31.2, 28.7, 27.8. IR (KBr) *v* 3433, 2953, 1593, 1488, 1149, 876 cm^{-1}. HRMS (ESI) calcd for

$C_{47}H_{44}Cl_2N_3O_2$ $[M+H]^+$ 752.2805, found 752.2805.



7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5m**)

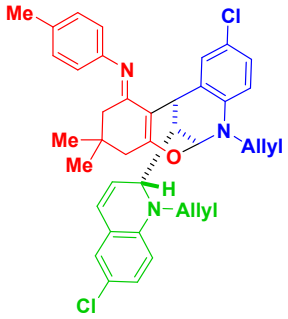
White solid obtained by filtration of the precipitate; 91.1 mg, 86% yield; dr > 20:1; reaction time = 5 min; mp 159.7-160.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.72 (s, 1H), 7.28-7.14 (m, 10H), 6.95 (s, 5H), 6.64 (d, *J* = 8.0 Hz, 3H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.42 (t, *J* = 8.0 Hz, 1H), 5.30 (s, 1H), 4.95 (d, *J* = 24.0 Hz, 1H), 4.79-4.62 (m, 2H), 4.43 (s, 1H), 4.20 (d, *J* = 20.0 Hz, 1H), 3.66 (t, *J* = 8.0 Hz, 1H), 2.33 (s, 5H), 2.18 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 159.9, 149.7, 141.3, 140.2, 137.9, 131.6, 129.5, 129.4, 128.8, 128.4, 128.3, 127.3, 127.0, 126.8, 126.7, 126.6, 126.4, 126.3, 124.4, 123.0, 122.7, 121.9, 119.8, 115.9, 114.5, 111.8, two carbons missing in the aromatic region, 82.5, 56.2, 56.1, 53.2, 40.1, 28.8, 27.5, 27.3, 20.8, 20.8. IR (KBr) *v* 3432, 2947, 1601, 1493, 1383, 803 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{40}Cl_2N_3O$ $[M+H]^+$ 708.2543, found 708.2533.



10-chloro-13-(6-chloro-1-ethyl-1,2-dihydroquinolin-2-yl)-7-ethyl-3,3-dimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5n**)

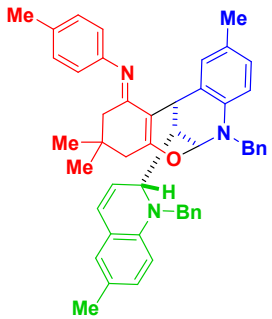
White solid obtained by filtration of the precipitate; 67.2 mg, 73% yield; dr > 20:1; reaction time = 5 min; mp 185.4-186.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.52 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 4H), 6.79-6.50 (m, 5H), 6.19 (d, *J* = 4.0 Hz, 1H), 5.47 (s, 1H), 4.61 (s, 1H), 4.02 (s, 1H), 3.77 (d, *J* = 8.0 Hz, 1H), 3.52-3.46 (m, 3H), 2.94 (s, 1H), 2.30 (s, 3H), 2.06-1.95 (m, 4H), 1.74 (d, *J* = 16.0 Hz,

1H), 1.24 (d, J = 24.0 Hz, 6H), 0.87 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 158.2, 149.9, 139.7, 138.8, 132.5, 131.2, 129.7, 129.3, 129.2, 127.1, 126.6, 126.2, 125.1, 123.8, 122.0, 119.7, 113.5, 112.3, 110.4, 97.4, 84.3, 44.4, 44.3, 41.7, 40.8, 40.5, 35.8, 31.1, 29.0, 27.2, 20.8, 13.3, 12.7. IR (KBr) v 3437, 2961, 1604, 1492, 1380, 1219, 806 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{40}Cl_2N_3O$ $[M+H]^+$ 612.2543, found 612.2529.



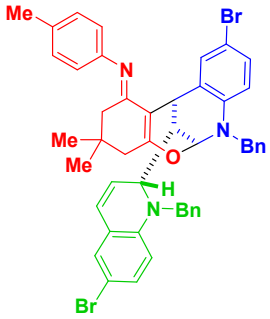
7-allyl-13-(1-allyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-3,3-dimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5o**)

White solid obtained by filtration of the precipitate; 65.2 mg, 68% yield; dr = 16:1; reaction time = 5 min; mp 170.9-172.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.58 (s, 1H), 7.12-7.08 (m, 4H), 6.84 (d, J = 4.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.58 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 3H), 6.25 (d, J = 8.0 Hz, 1H), 5.98-5.84 (m, 2H), 5.52 (s, 1H), 5.31-5.13 (m, 4H), 4.71 (t, J = 8.0 Hz, 1H), 4.29 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 4.12 (d, J = 8.0 Hz, 4H), 3.05 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 2.35 (s, 3H), 2.13-1.99 (m, 4H), 1.78 (d, J = 16.0 Hz, 1H), 0.93 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.0, 149.8, 140.2, 139.1, 133.8, 133.0, 132.7, 131.2, 129.5, 129.2, 126.8, 126.6, 126.2, 125.5, 123.6, 122.5, 119.7, 117.2, 116.6, 113.5, 113.0, 111.2, 97.6, 83.8, 52.2, 52.1, 41.6, 40.7, 40.6, 35.7, 31.1, 29.2, 28.9, 27.1, 20.7. IR (KBr) v 3420, 2955, 1608, 1491, 1376, 1218, 929, 805 cm^{-1}. HRMS (ESI) calcd for $C_{39}H_{40}Cl_2N_3O$ $[M+H]^+$ 636.2543, found 636.2518.



7-benzyl-13-(1-benzyl-6-methyl-1,2-dihydroquinolin-2-yl)-3,3,10-trimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5p**)

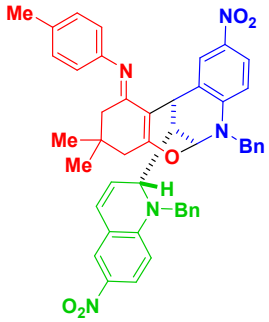
White solid obtained by filtration of the precipitate; 63.7 mg, 61% yield; dr > 20:1; reaction time = 5 min; mp 180.6-181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (s, 1H), 7.34-7.20 (m, 5H), 7.12 (d, *J* = 4.0 Hz, 5H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 2H), 6.58 (d, *J* = 8.0 Hz, 3H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.40 (t, *J* = 8.0 Hz, 1H), 5.34 (s, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 4.64 (d, *J* = 16.0 Hz, 1H), 4.45 (s, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.72 (t, *J* = 8.0 Hz, 1H), 2.43 (d, *J* = 12.0 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H), 2.10-2.01 (m, 3H), 1.82 (d, *J* = 16.0 Hz, 1H), 0.91 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 158.1, 150.3, 140.7, 139.3, 139.1, 138.8, 131.3, 130.5, 129.4, 129.3, 128.6, 128.2, 127.7, 127.2 (2C), 127.0 (2C), 126.8, 126.6, 125.7, 125.4, 123.0, 121.6, 119.6, 114.5, 114.0, 110.6, 83.3, 56.8, 55.8, 53.3, 41.6, 41.0, 40.5, 31.2, 29.1, 28.9, 27.7, 20.8, 20.5, 20.3. IR (KBr) *v* 3434, 2954, 1603, 1500, 1380, 1220, 804 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{50}N_3O$ $[M+H]^+$ 696.3948, found 696.3925.



7-benzyl-13-(1-benzyl-6-bromo-1,2-dihydroquinolin-2-yl)-10-bromo-3,3-dimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5q**)

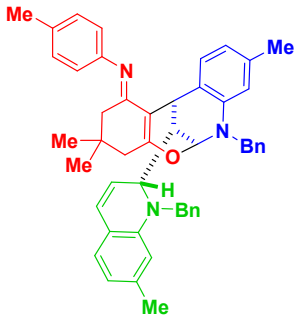
White solid obtained by filtration of the precipitate; 100.7 mg, 81% yield; dr > 20:1; reaction time = 5 min; mp 191.7-192.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.83 (s, 1H), 7.28-7.07 (m, 13H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 12.0 Hz, 2H), 6.57 (d, *J* = 12.0 Hz, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 6.39 (d, *J* = 12.0 Hz, 1H), 5.40 (t, *J* = 8.0 Hz, 1H), 5.30 (s, 1H), 4.95 (d, *J* = 20.0 Hz, 1H), 4.78-4.60 (m, 2H), 4.39 (s, 1H), 4.20 (d, *J* = 20.0 Hz, 1H), 3.68 (t, *J* = 12.0 Hz, 1H), 2.39 (s, 1H), 2.35 (s, 3H), 2.09 (t, *J* = 20.0 Hz, 3H), 1.84 (d, *J* = 20.0 Hz, 1H), 0.93 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 158.2, 149.7, 141.7, 140.5, 137.8, 137.8, 132.1, 131.5, 131.2, 129.5, 129.5, 128.7, 128.5, 128.3, 127.3, 127.1, 127.0, 126.8, 126.4, 126.3, 124.8, 122.4, 119.6, 116.3, 113.3, 112.3, 110.2, 109.0, 82.6, 56.3, 56.0, 53.3, 41.3, 40.7, 40.2, 31.1, 28.7, 27.8, 20.8. IR (KBr) *v* 3426, 2954, 1601, 1490, 1221, 800 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Br_2N_3O$ $[M+H]^+$

824.1846, found 824.1824.



7-benzyl-13-(1-benzyl-6-nitro-1,2-dihydroquinolin-2-yl)-3,3-dimethyl-10-nitro-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5r**)

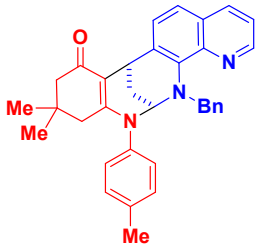
White solid obtained by filtration of the precipitate; 87.0 mg, 77% yield; dr > 20:1; reaction time = 5 min; mp 203.1-204.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.68 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 (s, 2H), 7.33 (s, 3H), 7.16 (s, 7H), 6.91 (s, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 3H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.39 (t, *J* = 8.0 Hz, 2H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.84 (s, 2H), 4.55 (s, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 3.77 (t, *J* = 12.0 Hz, 1H), 2.45 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.21-2.02 (m, 3H), 1.87 (d, *J* = 16.0 Hz, 1H), 0.94 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 157.8, 149.0, 147.9, 147.0, 139.2, 138.2, 136.4, 136.1, 132.0, 129.5, 129.4, 129.0, 128.7, 127.9, 127.6, 126.8, 126.5, 125.3, 125.2, 124.7, 123.9, 123.4, 122.2, 121.7, 119.8, 113.4, 112.9, 110.2, 81.7, 57.1, 56.1, 53.6, 41.1, 40.8, 40.6, 31.2, 29.0, 27.9, 20.8. IR (KBr) *v* 3430, 2954, 1601, 1501, 1322, 1099, 738 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}N_5O_5$ $[M+H]^+$ 758.3337, found 758.3315.



7-benzyl-13-(1-benzyl-7-methyl-1,2-dihydroquinolin-2-yl)-3,3,9-trimethyl-*N*-(*p*-tolyl)-2,3,4,6,7,12-hexahydro-1*H*-6,12-methanodibenzo[*d,g*][1,3]oxazocin-1-imine (**5s**)

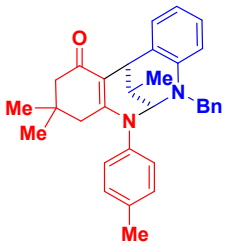
White solid obtained by filtration of the precipitate; 96.8 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 179.2-180.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.53 (d, *J* = 4.0 Hz, 1H), 7.10 (s, 9H), 6.89 (d, *J* = 24.0 Hz, 3H), 6.59-6.38 (m, 8H), 5.29 (d, *J* = 16.0 Hz, 2H), 5.00 (d, *J* = 16.0 Hz, 1H),

4.71 (q, J = 16.0 Hz, 2H), 4.46 (s, 1H), 4.20 (d, J = 16.0 Hz, 1H), 3.69 (s, 1H), 2.40-2.01 (m, 13H), 1.83 (d, J = 16.0 Hz, 1H), 0.91 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 157.9, 150.2, 143.0, 141.6, 139.0, 138.7, 138.5, 136.4, 131.3, 129.6, 129.4, 128.6, 128.1, 127.1, 127.0, 126.9, 126.8, 126.6, 126.5, 122.6, 120.4, 120.1, 119.7, 119.1, 117.6, 115.0, 114.1, 111.3, 82.8, 56.5, 55.5, 52.9, 41.5, 41.0, 40.7, 31.2, 29.1, 28.5, 27.7, 21.9, 20.8. IR (KBr) v 3417, 2655, 1607, 1500, 1220, 708 cm^{-1}. HRMS (ESI) calcd for $C_{49}H_{50}N_3O$ $[M+H]^+$ 696.3948, found 696.3932.



7-benzyl-11,11-dimethyl-9-(*p*-tolyl)-8,9,10,11,12,14-hexahydro-8,14-methanobenzo[7,8][1,3]diazocino[5,4-*h*]quinolin-13(7*H*)-one (**7**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 64.8 mg, 87% yield; dr > 20:1; reaction time = 5 min; mp 217.2-218.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.90 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 8.16 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.41-7.36 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 4H), 6.67 (d, J = 12.0 Hz, 2H), 5.17 (d, J = 12.0 Hz, 1H), 4.92 (s, 1H), 4.74 (s, 1H), 4.05 (d, J = 12.0 Hz, 1H), 2.39 (s, 3H), 2.32-2.19 (m, 3H), 1.93-1.79 (m, 3H), 0.89 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 161.1, 146.9, 141.1, 138.8, 138.2, 138.1, 137.8, 137.7, 132.4, 129.9, 129.8, 128.9, 128.6, 128.3, 127.7, 126.6, 121.4, 120.1, 111.4, 72.0, 57.4, 47.7, 41.2, 32.6, 28.3, 27.4, 21.7, 21.0. IR (KBr) v 3435, 2953, 1556, 1453, 1192, 1140, 797 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{34}N_3O$ $[M+H]^+$ 500.2696, found 500.2686.

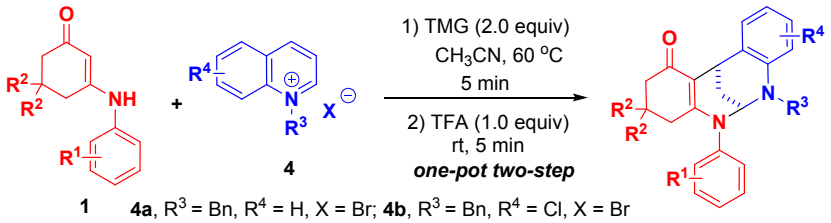


7-benzyl-3,3,13-trimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d*,*g*][1,3]diazocin-1(2*H*)-one (**8**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 38.0 mg, 51% yield; dr > 20:1; reaction time = 5 min; mp 147.8-148.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ

7.48 (d, J = 8.0 Hz, 1H), 7.28-7.20 (m, 5H), 6.99 (d, J = 8.0 Hz, 5H), 6.72 (t, J = 8.0 Hz, 1H), 6.56 (d, J = 12.0 Hz, 1H), 4.93 (s, 1H), 4.48 (d, J = 24.0 Hz, 1H), 4.24 (s, 1H), 3.96 (d, J = 20.0 Hz, 1H), 2.50-2.34 (m, 5H), 2.26 (d, J = 8.0 Hz, 1H), 2.15 (d, J = 20.0 Hz, 1H), 1.85 (d, J = 20.0 Hz, 1H), 1.06 (d, J = 8.0 Hz, 3H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 163.6, 140.4, 139.8, 139.0, 137.8, 130.7, 130.3, 128.5, 127.2, 127.1, 126.8, 124.5, 118.5, 113.8, 111.2, 79.6, 54.5, 46.1, 41.7, 32.9 (2C), 29.7, 29.3, 26.6, 21.1, 15.5. IR (KBr) v 3451, 2959, 1612, 1504, 1188, 1150, 744 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{35}N_2O$ $[M+H]^+$ 463.2744, found 463.2750.

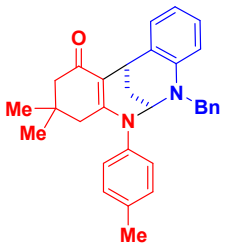
5. Experimental data for the formation of 6



1 4 6

4a, R^3 = Bn, R^4 = H, X = Br; **4b**, R^3 = Bn, R^4 = Cl, X = Br
4c, R^3 = Et, R^4 = H, X = I; **4d**, R^3 = Allyl, R^4 = H, X = Br
4e, R^3 = Bn, R^4 = 6-Me, X = Br; **4f**, R^3 = Bn, R^4 = 6-Br, X = Br
4g, R^3 = Bn, R^4 = 6-NO_2, X = Br; **4h**, R^3 = Bn, R^4 = 7-Me, X = Br

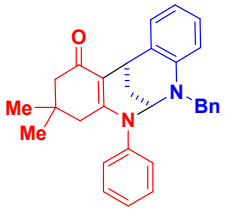
General procedure：To a 5.0 mL vial were successively added enaminones **1** (0.15 mmol), *N*-alkyl quinolinium salts **4** (0.33 mmol) and 0.8 mL of CH_3CN. And then, TMG (34.6 mg, 0.30 mmol) was added by syringe. The resulting mixture was stirred at 60 °C for 5 min. Upon completion of the reaction (monitoring by TLC), 0.15 mmol of TFA was added with continuing stirring at room temperature for another 5 min. And then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **6**.



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

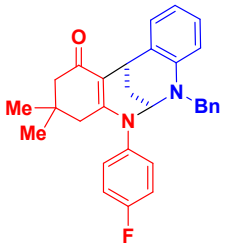
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 78.5 mg, 99% yield; dr > 20:1; reaction time = 5 min; mp 201.3-202.5; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.52

(d, J = 8.0 Hz, 1H), 7.21-7.14 (m, 5H), 6.90 (dd, J_1 = J_2 = 8.0 Hz, 4H), 6.89 (t, J = 8.0 Hz, 1H), 6.63 (t, J = 8.0 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.15 (s, 1H), 4.49 (d, J = 16.0 Hz, 2H), 4.10 (d, J = 20.0 Hz, 1H), 2.40 (s, 3H), 2.25-2.05 (m, 5H), 1.81 (d, J = 16.0 Hz, 1H), 0.94 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 155.4, 141.6, 140.6, 138.2, 137.4, 130.2, 128.8, 128.5, 127.8, 126.8, 126.5, 126.0, 117.1, 113.7, 110.8, 73.9, 54.0, 50.0, 41.6, 32.7, 29.6, 26.9 (2C), 16.3, 21.0. IR (KBr) v 3419, 2949, 1566, 1501, 1389, 739 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{33}N_2O$ $[M+H]^+$ 449.2587, found 449.2589.



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

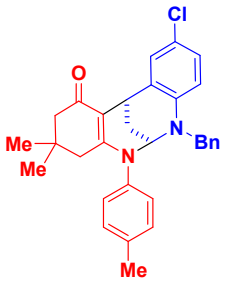
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 61.1 mg, 94% yield; dr > 20:1; reaction time = 5 min; mp 196.2-197.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.44 (d, J = 8.0 Hz, 1H), 7.35-7.27 (m, 3H), 7.12 (dd, J_1 = J_2 = 8.0 Hz, 3H), 7.01 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 12.0 Hz, 2H), 6.83 (t, J = 8.0 Hz, 1H), 6.56 (t, J = 8.0 Hz, 1H), 6.34 (d, J = 12.0 Hz, 1H), 5.10 (s, 1H), 4.41 (d, J = 24.0 Hz, 2H), 3.97 (d, J = 20.0 Hz, 1H), 2.16-1.98 (m, 5H), 1.72 (d, J = 24.0 Hz, 1H), 0.86 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 155.1, 144.3, 140.7, 138.2, 129.7, 128.9, 128.5, 127.8, 127.5, 126.9, 126.6, 126.1, 117.3, 114.1, 110.8, 74.0, 54.0, 50.1, 41.7, 32.8, 29.6, 27.0, 26.9, 26.4. IR (KBr) v 3433, 2951, 1568, 1391, 1064, 736 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{31}N_2O$ $[M+H]^+$ 435.2431, found 435.2435.



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

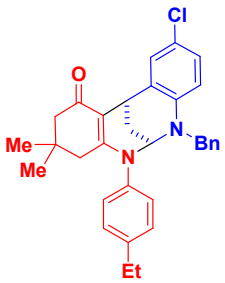
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 58.7 mg, 87% yield; dr > 20:1; reaction time = 5 min; mp 199.6-200.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ

7.42 (d, J = 4.0 Hz, 1H), 7.16-7.09 (m, 3H), 7.03-6.93 (m, 6H), 6.84 (t, J = 8.0 Hz, 1H), 6.56 (t, J = 8.0 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 5.03 (s, 1H), 4.42 (t, J = 8.0 Hz, 2H), 4.01 (d, J = 20.0 Hz, 1H), 2.17-1.95 (m, 5H), 1.69 (d, J = 16.0 Hz, 1H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 161.5 (d, J = 247.0 Hz, 1C), 154.9, 140.6, 140.2 (d, J = 4.0 Hz, 1C), 138.0, 128.9, 128.5, 127.7, 126.9, 126.6, 126.1, 117.4, 116.6 (d, J = 18.0 Hz, 1C), 114.3, 111.0, 74.1, 54.2, 50.0, 41.7, 32.7, 29.6, 26.9, 26.8, 26.2. IR (KBr) ν 3396, 2942, 1568, 1497, 1391, 1211, 735 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}FN_2O$ $[M+H]^+$ 453.2337, found 453.2340.



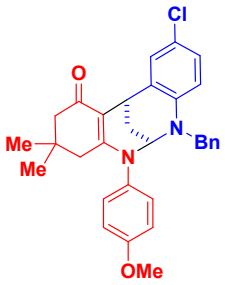
7-benzyl-10-chloro-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6d**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 67.2 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 170.2-171.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.41 (d, J = 4.0 Hz, 1H), 7.17-7.09 (m, 5H), 6.89 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.21 (d, J = 8.0 Hz, 1H), 5.06 (s, 1H), 4.36 (d, J = 16.0 Hz, 2H), 4.02 (d, J = 16.0 Hz, 1H), 2.32 (s, 3H), 2.15-2.10 (m, 3H), 2.05-1.98 (m, 2H), 1.73 (d, J = 20.0 Hz, 1H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 155.8, 141.3, 139.3, 137.7, 130.4, 129.4, 128.6, 128.3, 127.8, 127.0, 126.3, 126.0, 121.9, 113.0, 111.9, 73.9, 54.3, 49.8, 41.5, 32.7, 29.5, 26.9 (2C), 26.1, 21.0. IR (KBr) ν 3434, 2950, 1567, 1491, 1393, 698 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2O$ $[M+H]^+$ 483.2198, found 483.2201.



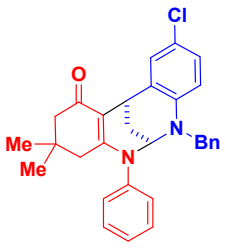
7-benzyl-10-chloro-5-(4-ethylphenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6e**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 69.2 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 182.3-184.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.41 (d, J = 4.0 Hz, 1H), 7.16-7.09 (m, 5H), 6.90 (d, J = 8.0 Hz, 4H), 6.74 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.22 (d, J = 8.0 Hz, 1H), 5.06 (s, 1H), 4.36 (d, J = 16.0 Hz, 2H), 4.02 (d, J = 16.0 Hz, 1H), 2.62 (q, J = 8.0 Hz, 2H), 2.17-1.98 (m, 5H), 1.76 (d, J = 20.0 Hz, 1H), 1.20 (t, J = 8.0 Hz, 3H), 0.86 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 156.3, 144.0, 141.4, 139.3, 137.7, 129.3, 129.2, 128.6, 128.3, 127.0, 126.3, 126.0, 121.9, 113.0, 112.0, 74.0, 54.3, 49.6, 41.6, 32.7, 29.4, 28.3, 26.9 (2C), 26.1, 15.3. IR (KBr) v 3422, 2957, 1565, 1498, 1389, 729 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{34}ClN_2O$ $[M+H]^+$ 497.2354, found 493.2356.



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

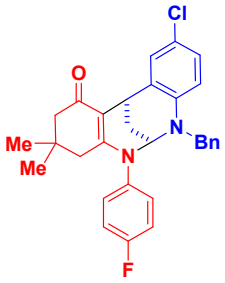
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 72.8 mg, 97% yield; dr > 20:1; reaction time = 5 min; mp 175.6-177.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (d, J = 4.0 Hz, 1H), 7.25-7.18 (m, 3H), 7.00 (d, J = 8.0 Hz, 4H), 6.92 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 8.0 Hz, 1H), 5.11 (s, 1H), 4.46 (t, J = 8.0 Hz, 2H), 4.11 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H), 2.22-2.06 (m, 5H), 1.82 (d, J = 16.0 Hz, 1H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 158.8, 156.4, 139.2, 137.7, 136.5, 129.4, 128.6, 128.3, 127.0, 126.3, 126.0, 121.9, 114.9, 112.9, 112.0, 74.1, 55.5, 54.4, 49.6, 41.5, 32.6, 29.5, 27.0, 26.8, 26.1. IR (KBr) v 3417, 2948, 1567, 1501, 1391, 1250, 732 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2O_2$ $[M+H]^+$ 499.2147, found 499.2145.



7-benzyl-10-chloro-3,3-dimethyl-5-phenyl-3,4,5,6,7,12-hexahydro-6,12-

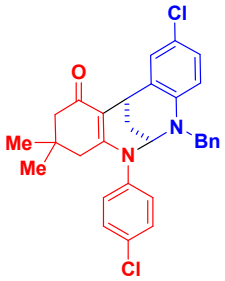
methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6g**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 60.7 mg, 86% yield; dr > 20:1; reaction time = 5 min; mp 161.2-162.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.49 (d, *J* = 4.0 Hz, 1H), 7.43-7.35 (m, 3H), 7.24-7.16 (m, 3H), 7.08 (d, *J* = 4.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.83 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 5.17 (s, 1H), 4.44 (d, *J* = 16.0 Hz, 2H), 4.06 (d, *J* = 16.0 Hz, 1H), 2.24-2.07 (m, 5H), 1.82 (d, *J* = 20.0 Hz, 1H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 155.4, 144.0, 139.3, 137.6, 129.8, 129.3, 128.6, 128.3, 127.7, 127.0, 126.3, 126.0, 122.0, 113.4, 112.0, 73.9, 54.2, 49.9, 41.6, 32.8, 29.5, 26.9 (2C), 26.1. IR (KBr) *v* 3434, 2950, 1567, 1491, 1393, 698 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{30}ClN_2O$ $[M+H]^+$ 469.2041, found 469.2046.



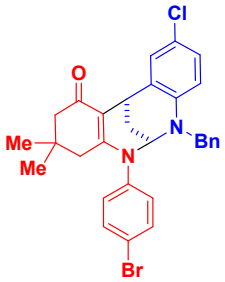
7-benzyl-10-chloro-5-(4-fluorophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6h**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 73.6 mg, 99% yield; dr > 20:1; reaction time = 5 min; mp 195.2-196.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.24-7.19 (m, 3H), 7.12-7.05 (m, 4H), 7.00 (d, *J* = 4.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.10 (s, 1H), 4.46 (t, *J* = 8.0 Hz, 2H), 4.10 (d, *J* = 20.0 Hz, 1H), 2.23-2.04 (m, 5H), 1.78 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 161.6 (d, *J* = 248.0 Hz, 1C), 155.1, 139.9 (d, *J* = 4.0 Hz, 1C), 139.2, 137.5, 129.3, 128.7, 128.4, 127.1, 126.4, 126.0, 122.2, 116.7 (d, *J* = 17.0 Hz, 1C), 113.7, 112.2, 74.1, 54.5, 49.9, 41.7, 32.8, 29.5, 27.0, 26.8, 26.1. IR (KBr) *v* 3435, 2946, 1569, 1498, 1392, 736 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}ClFN_2O$ $[M+H]^+$ 487.1947, found 487.1948.



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

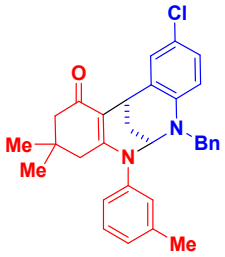
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 69.9 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 188.6-189.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.47 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.22 (dd, $J_1 = J_2$ = 8.0 Hz, 3H), 7.00 (d, J = 8.0 Hz, 4H), 6.84 (d, J = 8.0 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 5.12 (s, 1H), 4.45 (d, J = 16.0 Hz, 2H), 4.12 (d, J = 20.0 Hz, 1H), 2.23-2.04 (m, 5H), 1.79 (d, J = 16.0 Hz, 1H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 154.6, 142.5, 139.2, 137.5, 133.4, 129.9, 129.3, 128.6, 128.4, 127.1, 126.4, 126.0, 122.2, 114.0, 112.2, 74.0, 54.5, 49.9, 41.7, 32.8, 29.5, 26.9, 26.8, 26.0. IR (KBr) v 3441, 2945, 1569, 1490, 1391, 735 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}Cl_2N_2O$ $[M+H]^+$ 503.1652, found 503.1655.



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

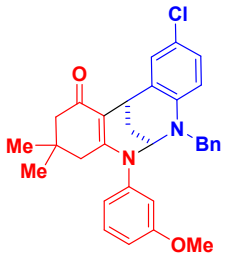
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 75.4 mg, 92% yield; dr > 20:1; reaction time = 5 min; mp 205.7-207.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.52 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 4.0 Hz, 1H), 7.25-7.19 (m, 3H), 6.99 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 5.12 (s, 1H), 4.45 (t, J = 8.0 Hz, 2H), 4.12 (d, J = 16.0 Hz, 1H), 2.21-2.04 (m, 5H), 1.19 (d, J = 16.0 Hz, 1H), 0.94 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 154.8, 142.9, 139.2, 137.4, 132.9, 129.2, 128.7, 128.4, 127.1, 126.4, 126.1, 122.2, 121.4, 114.0, 112.3, 74.0, 54.5, 49.8, 41.7, 32.8, 29.5,

26.9, 26.8, 25.9. IR (KBr) *v* 3429, 2950, 1618, 1562, 1486, 1385, 1067, 730 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}BrClN_2O$ $[M+H]^+$ 547.1146, found 547.1150.



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

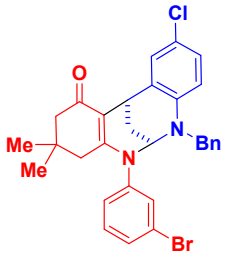
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 68.9 mg, 95% yield; dr > 20:1; reaction time = 5 min; mp 187.6-188.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.46 (d, *J* = 4.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.28-7.18 (m, 4H), 6.96-6.88 (m, 5H), 6.38 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 4.49 (t, *J* = 8.0 Hz, 2H), 4.07 (d, *J* = 20.0 Hz, 1H), 2.50-2.39 (m, 5H), 2.27 (d, *J* = 12.0 Hz, 1H), 2.17 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 1.92 (d, *J* = 16.0 Hz, 1H), 0.98 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 163.2, 160.2, 159.8, 142.6, 138.6, 137.0, 129.7, 128.7, 128.6, 128.3, 127.3, 127.0, 126.1, 122.7, 117.0, 114.2, 112.8, 111.9, 74.9, 54.7, 46.4, 41.7, 32.8, 29.1, 26.8, 26.0, 21.2. IR (KBr) *v* 3432, 2960, 1496, 1207, 1148, 802 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2O$ $[M+H]^+$ 483.2198, found 483.2185.



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

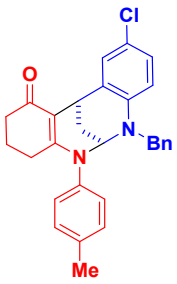
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 59.2 mg, 79% yield; dr > 20:1; reaction time = 5 min; mp 179.6-180.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.48 (d, *J* = 4.0 Hz, 1H), 7.33-7.18 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.84 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.67 (d, *J* = 12.0 Hz, 1H), 6.59 (s, 1H), 6.30 (d, *J* = 12.0 Hz, 1H), 5.17 (s, 1H), 4.47 (d, *J* = 20.0 Hz, 2H), 4.17 (d, *J* = 24.0 Hz, 1H), 3.76 (s, 3H), 2.21-2.04 (m, 5H),

1.87 (d, J = 20.0 Hz, 1H), 0.95 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 160.6, 155.5, 145.1, 139.3, 137.7, 130.4, 129.3, 128.6, 128.4, 127.0, 126.4, 126.0, 122.0, 120.4, 113.9, 113.4, 113.2, 112.0, 73.9, 55.4, 54.3, 49.8, 41.6, 32.8, 29.4, 27.0, 26.1. IR (KBr) v 3419, 2949, 1605, 1562, 1489, 1392, 698 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}ClN_2O_2$ $[M+H]^+$ 499.2147, found 499.2149.



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

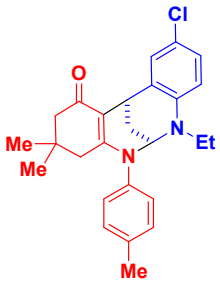
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 81.9 mg, 99% yield; dr > 20:1; reaction time = 5 min; mp 200.0-200.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.51 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 4.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.24-7.19 (m, 4H), 7.01 (dd, J_1 = J_2 = 8.0 Hz, 3H), 6.83 (dd, J_1 = J_2 = 4.0 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 5.17 (s, 1H), 4.46 (d, J = 20.0 Hz, 2H), 4.13 (d, J = 16.0 Hz, 1H), 2.23-2.06 (m, 5H), 1.84 (d, J = 16.0 Hz, 1H), 0.96 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 156.3, 144.8, 139.0, 137.1, 131.0, 128.8, 128.6, 128.2, 127.1, 126.8, 126.8, 126.4, 126.0, 123.1, 122.1, 113.6, 112.3, one carbon missing in the aromatic region, 74.1, 54.4, 49.0, 41.5, 32.8, 29.3, 26.8, 25.8. IR (KBr) v 3434, 2953, 1565, 1485, 1387, 1158, 732 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{29}BrClN_2O$ $[M+H]^+$ 547.1146, found 547.1146.



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

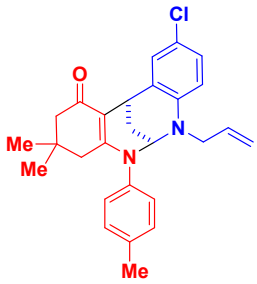
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 60.5 mg,

89% yield; dr > 20:1; reaction time = 5 min; mp 174.7-175.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.52 (d, J = 4.0 Hz, 1H), 7.23-7.17 (m, 5H), 6.99 (d, J = 8.0 Hz, 4H), 6.83 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 6.30 (d, J = 8.0 Hz, 1H), 5.14 (s, 1H), 4.45 (t, J = 8.0 Hz, 2H), 4.12 (d, J = 16.0 Hz, 1H), 2.39 (s, 3H), 2.32-2.27 (m, 2H), 2.24-2.17 (m, 2H), 2.10-2.07 (m, 1H), 1.98 (tt, $J_1 = J_2$ = 4.0 Hz, 1H), 1.80 (q, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 157.3, 141.4, 139.4, 137.7, 137.7, 130.3, 129.5, 128.6, 128.5, 126.9, 126.2, 125.9, 121.8, 114.1, 111.8, one carbon missing in the aromatic region, 73.6, 54.2, 36.3, 28.0, 27.0, 26.1, 22.0, 21.0. IR (KBr) ν 3422, 2948, 1554, 1496, 1385, 723 cm^{-1}. HRMS (ESI) calcd for $C_{29}H_{27}ClN_2O$ $[M+H]^+$ 455.1885, found 455.1881.



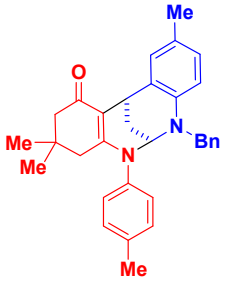
10-chloro-7-ethyl-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6o**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 55.7 mg, 88% yield; dr > 20:1; reaction time = 5 min; mp 190.9-192.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.43 (d, J = 4.0 Hz, 1H), 7.23 (d, J = 12.0 Hz, 2H), 7.00-6.94 (m, 3H), 6.49 (d, J = 12.0 Hz, 1H), 5.03 (s, 1H), 4.38 (s, 1H), 3.42-3.30 (m, 1H), 2.83-2.71 (m, 1H), 2.40 (s, 3H), 2.20 (s, 2H), 2.09-1.91 (m, 3H), 1.80 (d, J= 20.0 Hz, 1H), 0.94 (t, J= 8.0 Hz, 6H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 157.4, 140.8, 138.7, 137.9, 130.4, 129.4, 128.5, 126.4, 121.3, 112.5, 111.4, 73.6, 49.0, 45.4, 41.5, 32.7, 29.5, 26.8 (2C), 26.1, 21.1, 12.2. IR (KBr) ν 3422, 2967, 1498, 1191, 1149, 799 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{30}ClN_2O$ $[M+H]^+$ 421.2041, found 421.2044.



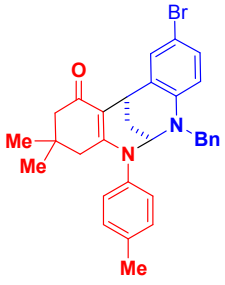
7-allyl-10-chloro-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6p**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 56.9 mg, 88% yield; dr > 20:1; reaction time = 5 min; mp 180.5-181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.43 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 3H), 6.48 (d, J = 8.0 Hz, 1H), 5.63-5.53 (m, 1H), 5.16 (s, 1H), 5.04 (d, J = 12.0 Hz, 1H), 4.91 (d, J = 16.0 Hz, 1H), 4.45 (s, 1H), 3.92 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.38 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.49-2.36 (m, 5H), 2.15 (d, J = 20.0 Hz, 3H), 1.91 (d, J = 16.0 Hz, 1H), 0.97 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 163.6, 139.9, 139.2, 138.4, 132.4, 130.8, 128.5, 128.1, 126.9, 122.4, 116.5, 112.6, 111.7, 74.5, 74.5, 53.3, 46.3, 46.2, 41.6, 32.8, 29.1, 26.7, 25.9, 21.1. IR (KBr) v 3433, 2966, 1766, 1500, 1193, 1148, 801 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{30}ClN_2O$ $[M+H]^+$ 433.2041, found 433.2042.



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

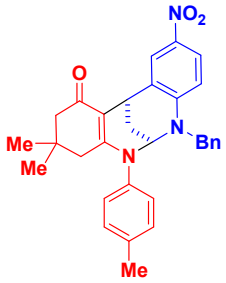
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 69.3 mg, 99% yield; dr > 20:1; reaction time = 5 min; mp 177.0-177.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.13 (t, J = 8.0 Hz, 6H), 6.90 (t, J = 12.0 Hz, 4H), 6.66 (t, J = 12.0 Hz, 1H), 6.25 (t, J = 12.0 Hz, 1H), 5.08 (s, 1H), 4.40 (t, J = 8.0 Hz, 2H), 3.95 (d, J = 20.0 Hz, 1H), 2.32 (s, 3H), 2.19-1.96 (m, 8H), 1.72 (d, J = 20.0 Hz, 1H), 0.86 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 157.5, 141.3, 138.3, 138.1, 137.8, 130.4, 129.6, 128.5, 127.6, 127.2, 126.8, 126.5, 126.1, 113.3, 111.1, 74.3, 54.3, 49.1, 41.7, 32.8, 29.7, 26.8, 26.7, 26.5, 21.1, 20.2. IR (KBr) v 3431, 2949, 1565, 1505, 1390, 731 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{35}N_2O$ $[M+H]^+$ 463.2744, found 463.2743.



7-benzyl-10-bromo-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-

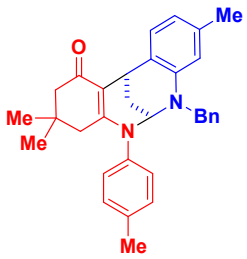
methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6r**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 70.3 mg, 89% yield; dr > 20:1; reaction time = 5 min; mp 184.0-185.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.59 (d, J = 4.0 Hz, 1H), 7.28-7.20 (m, 5H), 7.04-6.95 (m, 5H), 6.31 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 4.48 (t, J = 12.0 Hz, 2H), 4.04 (d, J = 16.0 Hz, 1H), 2.49-2.36 (m, 5H), 2.26 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.17-2.13 (m, 2H), 1.88 (d, J = 20.0 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 162.8, 140.2, 139.1, 139.1, 137.1, 131.4, 129.9, 128.8, 128.8, 127.3, 126.0, 113.2, 112.1, 110.1, 74.9, 54.7, 46.6, 41.7, 32.9, 29.2, 26.8, 26.6, 26.1, 21.2. IR (KBr) *v* 3429, 2958, 1496, 1189, 1135, 795 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}BrN_2O$ $[M+H]^+$ 527.1693, found 527.1692.



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

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 66.0 mg, 89% yield; dr > 20:1; reaction time = 5 min; mp 197.7-198.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.36 (d, J = 4.0 Hz, 1H), 7.78 ($J_1 = J_2$ = 4.0 Hz, 1H), 7.29-7.22 (m, 5H), 7.00 (dd, $J_1 = J_2$ = 4.0 Hz, 4H), 6.39 (d, J = 8.0 Hz, 1H), 5.22 (s, 1H), 4.63 (d, J = 20.0 Hz, 1H), 4.54 (s, 1H), 4.27 (d, J = 20.0 Hz, 1H), 2.42 (s, 3H), 2.19-2.04 (m, 5H), 1.87 (d, J = 16.0 Hz, 1H), 0.95 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 155.3, 146.6, 140.9, 138.1, 138.1, 136.3, 130.6, 128.8, 127.7, 127.4, 125.8, 124.3, 123.5, 112.6, 109.9, one carbon missing in the aromatic region, 73.8, 54.4, 49.7, 41.4, 32.6, 29.4, 27.0, 25.7, 21.0. IR (KBr) *v* 3434, 2958, 1574, 1498, 1320, 719 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}N_3O_3$ $[M+H]^+$ 494.2438, found 494.2430.

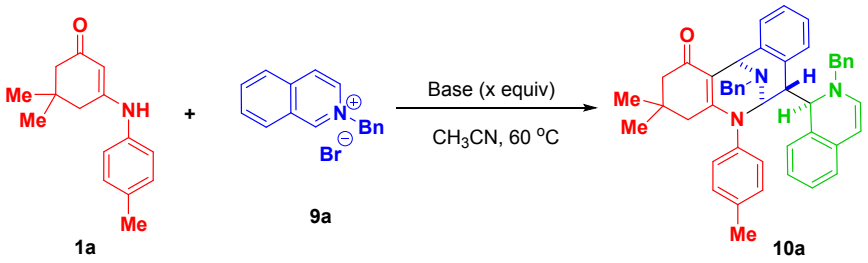


7-benzyl-3,3,9-trimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[*d,g*][1,3]diazocin-1(2*H*)-one (**6t**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 66.3 mg, 96% yield; dr > 20:1; reaction time = 5 min; mp 188.1-189.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.24-7.18 (m, 5H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.33 (s, 1H), 5.21 (s, 1H), 4.53 (d, *J* = 16.0 Hz, 2H), 4.00 (d, *J* = 20.0 Hz, 1H), 2.43 (t, *J* = 12.0 Hz, 4H), 2.36 (d, *J* = 20.0 Hz, 1H), 2.26 (tt, J_1 = J_2 = 4.0 Hz, 1H), 2.15 (s, 3H), 2.13-2.08 (m, 2H), 1.86 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 162.4, 140.5, 140.0, 138.8, 137.8, 136.8, 130.7, 130.7, 129.0, 128.6, 127.0, 126.2, 124.1, 118.8, 112.9, 112.1, 74.8, 54.2, 46.7, 41.7, 32.8, 29.4, 26.7, 26.3, 21.6, 21.1. IR (KBr) *v* 3424, 2955, 1569, 1509, 1189, 1144, 726 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{35}N_2O$ $[M+H]^+$ 463.2744, found 463.2743.

6. Optimization of reaction conditions for the formation of 10a

Table S2. Optimization of conditions for the formation of **10a**[a]



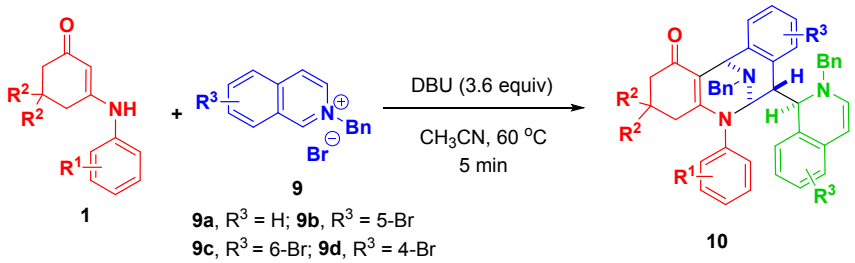
1a + **9a** → **10a**

entry	base	x	Time (min)	Yield (%)[b]
1	TMG	2.0	10	36
2	DBU	2.0	10	57[c]
3	DABCO·6H_2O	2.0	10	27
4	DBU	1.0	10	48
5	DBU	2.6	5	79[c]
6	DBU	3.0	5	83[c]

7	DBU	3.6	5	94[c]

[a] Unless otherwise noted, the reactions were conducted with 0.15 mmol enaminone **1a**, 2.2 equivalent of isoquinolinium salt **9a** in 0.8 mL of CH_3CN at 60 °C. Only one diastereoisomer was obtained for all cases. [b] Isolated yields obtained by column chromatography. [c] Isolated yields obtained by filtration of the precipitate.

7. Experimental data for the formation of 10



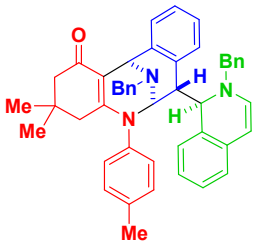
1

9

9a, R^3 = H; **9b**, R^3 = 5-Br
9c, R^3 = 6-Br; **9d**, R^3 = 4-Br

10

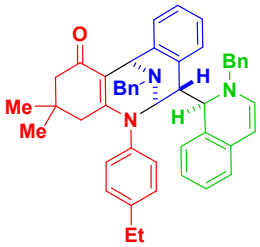
General procedure: To a 5.0 mL vial were successively added enaminones **1** (0.15 mmol), *N*-alkyl isoquinolinium salts **9** (0.33 mmol) and 0.8 mL of CH_3CN. And then, DBU (82.2 mg, 0.54 mmol) was added by syringe. The resulting mixture was stirred at 60 °C for 5 min. Upon completion of the reaction (monitoring by TLC), most of the products **10** were precipitated from the reaction mixtures and only a filtration was needed to purify them. For products **10d**, **10l**, **10n** and **10o**, they could not be precipitated from the reaction systems, which were purified by silica gel column chromatography. When 4-bromosubstituted isoquinolinium salt **9d** was employed as substrate, only mono-isoquinoline functionalized bridged cyclic compound **10p** was afforded in 54% yield.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10a**)

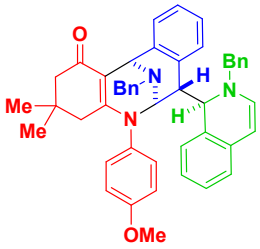
White solid obtained by filtration of the precipitate; 93.9 mg, 94% yield; dr > 20:1; reaction time = 5 min; mp 175.2-175.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.50 (d, *J* = 4.0 Hz, 1H), 7.21-7.12 (m, 12H), 6.95-6.86 (m, 5H), 6.70-6.49 (m, 4H), 6.18 (d, *J* = 4.0 Hz, 1H), 5.25 (t, *J* = 8.0 Hz, 3H), 4.66 (s, 1H), 4.30 (d, *J* = 8.0 Hz, 1H), 3.81 (d, *J* = 16.0 Hz, 1H), 3.67 (d, *J* = 16.0 Hz, 1H), 3.55 (d,

J = 12.0 Hz, 1H), 3.33 (d, *J* = 16.0 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.26 (s, 3H), 2.12 (d, *J* = 12.0 Hz, 2H), 1.77 (d, *J* = 16.0 Hz, 1H), 1.02 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 154.5, 141.0, 138.3, 138.2, 137.8, 136.7, 136.6, 132.5, 131.1, 129.7, 129.4, 128.4, 128.3, 127.5, 127.3, 127.1, 126.8, 126.7, 126.5, 126.0, 125.4, 125.3, 123.5, 122.2, 105.8, 99.8, 96.4, 74.9, 61.5, 58.0, 57.2, 52.2, 49.8, 45.7, 41.0, 33.1, 29.6, 27.4, 20.9. IR (KBr) *v* 3441, 1611, 1565, 1391, 756 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{46}N_3O$ $[M+H]^+$ 668.3635, found 668.3635.



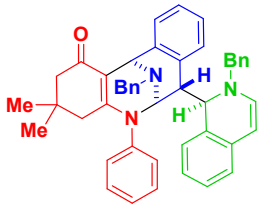
13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-ethylphenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10b**)

White solid obtained by filtration of the precipitate; 94.3 mg, 92% yield; dr > 20:1; reaction time = 5 min; mp 173.6-174.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.24-7.13 (m, 11H), 6.97-6.84 (m, 5H), 6.68-6.48 (m, 4H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.25 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 8.0 Hz, 1H), 4.64 (s, 1H), 4.26 (d, *J* = 8.0 Hz, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.67 (d, *J* = 16.0 Hz, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 16.0 Hz, 1H), 2.90 (d, *J* = 8.0 Hz, 1H), 2.55 (q, *J* = 8.0 Hz, 2H), 2.13 (d, *J* = 12.0 Hz, 3H), 1.79 (d, *J* = 16.0 Hz, 1H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.03 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 154.5, 142.9, 141.0, 138.3 (2C), 137.9, 136.7, 132.5, 131.2, 129.8, 129.4, 128.4 (2C), 127.5, 127.3, 127.1, 126.8, 126.6, 126.5, 126.0, 125.4, 125.3, 123.5, 122.2, 105.7, 96.4, 74.8, 61.5, 58.1, 57.2, 52.3, 49.9, 45.6, 41.0, 33.1, 29.6, 28.3, 27.4, 15.6, one carbon missing in the aromatic region. IR (KBr) *v* 3445, 2953, 1616, 1558, 1389, 760 cm^{-1}. HRMS (ESI) calcd for $C_{48}H_{48}N_3O$ $[M+H]^+$ 682.3792, found 682.3786.



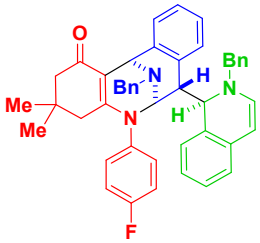
13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-methoxyphenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10c**)

White solid obtained by filtration of the precipitate; 99.8 mg, 97% yield; dr > 20:1; reaction time = 5 min; mp 183.6-184.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.51 (d, J = 8.0 Hz, 1H), 7.24-7.13 (m, 11H), 6.92-6.86 (m, 3H), 6.68 (dd, $J_1 = J_2$ = 8.0 Hz, 4H), 6.50 (t, J = 8.0 Hz, 2H), 6.21 (d, J = 8.0 Hz, 1H), 5.28 (d, J = 8.0 Hz, 1H), 5.25 (s, 1H), 5.20 (d, J = 8.0 Hz, 1H), 4.59 (s, 1H), 4.28 (d, J = 8.0 Hz, 1H), 3.81 (d, J = 12.0 Hz, 1H), 3.73 (s, 3H), 3.70 (d, J = 16.0 Hz, 1H), 3.55 (d, J = 12.0 Hz, 1H), 3.33 (d, J = 16.0 Hz, 1H), 2.93 (d, J = 8.0 Hz, 1H), 2.14 (s, 2H), 2.07 (d, J = 16.0 Hz, 1H), 1.77 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 158.0, 154.7, 141.0, 138.3, 137.8, 136.7, 133.5, 132.5, 131.2, 129.7, 129.4, 128.5, 128.3, 127.5, 127.3, 127.1, 126.8, 126.7, 126.5, 125.9, 125.3 (2C), 123.5, 122.3, 105.7, 96.5, 74.8, 61.5, 58.1, 57.2, 55.4, 52.4, 49.8, 45.6, 40.9, 33.0, 29.5, 27.5, one carbon missing in the aromatic region. IR (KBr) v 3442, 2951, 1611, 1563, 1504, 1247, 756 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{45}N_3NaO_2$ $[M+Na]^+$ 706.3404, found 706.3410.



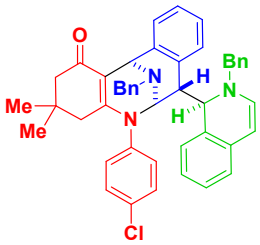
13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-5-phenyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10d**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 94.7 mg, 97% yield; dr > 20:1; reaction time = 5 min; mp 166.8-168.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.50 (d, J = 4.0 Hz, 1H), 7.24-7.13 (m, 14H), 6.92-6.86 (m, 3H), 6.68 (d, J = 8.0 Hz, 3H), 6.51 (t, J = 8.0 Hz, 1H), 6.19 (d, J = 8.0 Hz, 1H), 5.24 (q, J = 8.0 Hz, 3H), 4.71 (s, 1H), 4.30 (d, J = 8.0 Hz, 1H), 3.82 (d, J = 16.0 Hz, 1H), 3.67 (d, J = 16.0 Hz, 1H), 3.57 (d, J = 16.0 Hz, 1H), 3.31 (d, J = 16.0 Hz, 1H), 2.91 (d, J = 8.0 Hz, 1H), 2.15 (s, 2H), 1.90 (s, 1H), 1.76 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.2, 140.8 (2C), 138.2, 137.7, 136.6, 132.5, 131.1, 129.7, 129.6, 129.3, 128.4, 128.3, 127.5, 127.3, 127.0, 126.7, 126.6 (2C), 126.5, 125.9, 125.3 (2C), 123.5, 122.2, 106.0, 96.4, 74.8, 61.4, 58.0, 57.2, 52.2, 49.8, 45.6, 41.0, 33.1, 29.5, 27.3. IR (KBr) v 3438, 2949, 1615, 1557, 1387, 759 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{44}N_3O$ $[M+H]^+$ 654.3479, found 654.3488.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-fluorophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10e**)

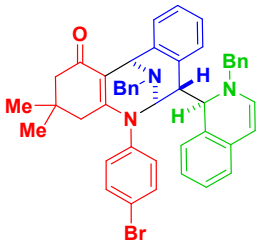
White solid obtained by filtration of the precipitate; 95.3 mg, 95% yield; dr > 20:1; reaction time = 5 min; mp 167.5-168.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.51 (d, J = 8.0 Hz, 1H), 7.29-7.16 (m, 11H), 6.90 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 3H), 6.81 (t, J = 8.0 Hz, 2H), 6.72-6.48 (m, 4H), 6.23 (d, J = 8.0 Hz, 1H), 5.30 (d, J = 8.0 Hz, 2H), 5.15 (d, J = 8.0 Hz, 1H), 4.55 (s, 1H), 4.23 (d, J = 8.0 Hz, 1H), 3.83 (d, J = 12.0 Hz, 1H), 3.73 (d, J = 16.0 Hz, 1H), 3.53 (d, J = 12.0 Hz, 1H), 3.30 (d, J = 16.0 Hz, 1H), 2.85 (d, J = 8.0 Hz, 1H), 2.29-2.05 (m, 3H), 1.73 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 160.8 (d, J = 246.0 Hz, 1C), 154.1, 140.7, 138.2, 137.7, 136.9, 136.8, 136.7, 132.5, 131.4, 129.8, 129.1, 128.6, 128.4, 127.7, 127.3, 127.1, 126.8, 126.7, 126.6, 125.9, 125.4, 125.3, 123.5, 122.2, 106.4, 96.6, 74.7, 61.3, 58.4, 57.3, 52.6, 49.8, 45.2, 41.0, 33.1, 29.5, 27.5. IR (KBr) ν 3440, 2953, 1611, 1566, 1502, 1220, 757 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{42}FN_3NaO$ $[M+Na]^+$ 694.3204, found 694.3190.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-chlorophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10f**)

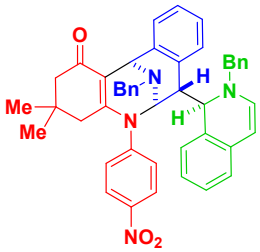
White solid obtained by filtration of the precipitate; 98.3 mg, 95% yield; dr > 20:1; reaction time = 5 min; mp 168.3-169.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.50 (d, J = 8.0 Hz, 1H), 7.25-7.17 (m, 11H), 7.08 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 8.0 Hz, 3H), 6.73 (d, J = 8.0 Hz, 1H), 6.53 (q, J = 8.0 Hz, 3H), 6.23 (d, J = 8.0 Hz, 1H), 5.29 (t, J = 8.0 Hz, 2H), 5.16 (d, J = 8.0 Hz, 1H), 4.60 (s, 1H), 4.23 (d, J = 8.0 Hz, 1H), 3.82 (d, J = 12.0 Hz, 1H), 3.72 (d, J = 12.0 Hz, 1H), 3.52 (d, J = 12.0 Hz, 1H), 3.31 (d, J = 16.0 Hz, 1H), 2.83 (d, J = 8.0 Hz, 1H), 2.28-2.09 (m, 3H), 1.73 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 153.7, 140.6, 139.4, 138.2,

137.7, 136.6, 132.6, 132.2, 131.4, 129.8, 129.3, 129.1, 128.6, 128.3, 127.7, 127.3, 127.1, 126.8, 126.6 (2C), 125.9, 125.4, 125.3, 123.5, 122.4, 106.9, 96.6, 74.6, 61.4, 58.4, 57.2, 52.5, 49.8, 45.2, 41.1, 33.2, 29.6, 27.4. IR (KBr) *v* 3440, 2929, 1614, 1564, 1387, 762 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}ClN_3O$ $[M+H]^+$ 688.3089, found 688.3077.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-bromophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10g**)

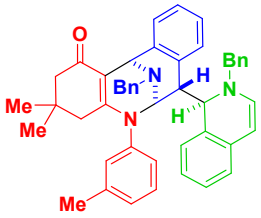
White solid obtained by filtration of the precipitate; 97.5 mg, 89% yield; dr > 20:1; reaction time = 5 min; mp 151.2-151.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.23-7.07 (m, 13H), 6.87-6.81 (m, 3H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.45 (t, *J* = 8.0 Hz, 3H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.22 (t, *J* = 8.0 Hz, 2H), 5.08 (d, *J* = 8.0 Hz, 1H), 4.53 (s, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.75 (d, *J* = 12.0 Hz, 1H), 3.65 (d, *J* = 16.0 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 2.74 (d, *J* = 8.0 Hz, 1H), 2.05 (d, *J* = 8.0 Hz, 3H), 1.66 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 153.6, 140.6, 140.0, 138.2, 137.7, 136.6, 132.6, 132.3, 131.4, 129.8, 129.1, 128.6, 128.4, 127.7, 127.3, 127.1, 126.8, 126.6, 125.9, 125.4, 125.3, 123.5, 122.4, 120.1, 106.9, 96.7, 74.6, 61.4, 58.4, 57.3, 52.5, 49.8, 45.2, 41.1, 33.3, 29.7, 27.4, one carbon missing in the aromatic region. IR (KBr) *v* 3426, 2950, 1615, 1563, 1387, 762 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}BrN_3O$ $[M+H]^+$ 732.2584, found 732.2587.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-5-(4-nitrophenyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10h**)

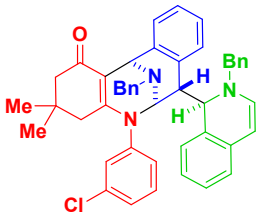
Yellow solid obtained by filtration of the precipitate; 99.7 mg, 95% yield; dr > 20:1; reaction time = 5 min; mp 158.7-159.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* =

8.0 Hz, 1H), 7.34-7.20 (m, 11H), 6.96 (t, J = 8.0 Hz, 1H), 6.86 (s, 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.61 (q, J = 8.0 Hz, 3H), 6.26 (d, J = 8.0 Hz, 1H), 5.37 (s, 1H), 5.28 (d, J = 4.0 Hz, 1H), 5.11 (d, J = 8.0 Hz, 1H), 4.77 (s, 1H), 4.17 (d, J = 8.0 Hz, 1H), 3.86 (d, J = 12.0 Hz, 1H), 3.76 (d, J = 12.0 Hz, 1H), 3.54 (d, J = 12.0 Hz, 1H), 3.25 (d, J = 16.0 Hz, 1H), 2.67 (d, J = 8.0 Hz, 1H), 2.30 (d, J = 16.0 Hz, 1H), 2.21 (s, 2H), 1.75 (d, J = 16.0 Hz, 1H), 1.05 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 152.3, 147.0, 144.6, 139.9, 138.0, 137.4, 136.5, 132.7, 131.6, 129.8, 128.7, 128.6, 128.3, 127.9, 127.2, 127.1, 127.0, 126.8, 126.4, 125.7, 125.6, 125.3, 124.4, 123.5, 122.4, 109.5, 96.7, 74.2, 61.1, 58.6, 57.3, 52.9, 49.9, 44.9, 41.6, 33.7, 29.8, 27.0. IR (KBr) v 3421, 2930, 1618, 1556, 1340, 760 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{42}N_4NaO_3$ $[M+Na]^+$ 721.3149, found 721.3165.



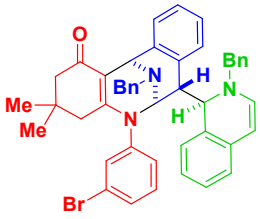
13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-3,3-dimethyl-5-(*m*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10i**)

White solid obtained by filtration of the precipitate; 90.3 mg, 90% yield; dr > 20:1; reaction time = 5 min; mp 174.3-175.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.51 (d, J = 8.0 Hz, 1H), 7.21-7.12 (m, 12H), 7.01 (t, J = 8.0 Hz, 1H), 6.89 (t, J = 8.0 Hz, 4H), 6.70 (d, J = 8.0 Hz, 1H), 6.42 (q, J = 8.0 Hz, 3H), 6.19 (d, J = 12.0 Hz, 1H), 5.24 (q, J = 8.0 Hz, 3H), 4.68 (s, 1H), 4.29 (d, J = 8.0 Hz, 1H), 3.83 (d, J = 16.0 Hz, 1H), 3.68 (d, J = 24.0 Hz, 1H), 3.56 (d, J = 16.0 Hz, 1H), 3.28 (d, J = 20.0 Hz, 1H), 2.90 (dd, J_1 = J_2 = 8.0 Hz, 1H), 2.20 (s, 3H), 2.15 (s, 2H), 1.77 (d, J = 12.0 Hz, 1H), 1.04 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.3, 140.9, 140.7, 139.5, 138.3, 137.8, 136.7, 132.6, 131.3, 129.8, 129.3, 128.8, 128.5, 128.4, 127.6, 127.5, 127.3, 127.1, 126.8, 126.7, 126.5, 126.0, 125.5, 125.3, 123.5, 123.2, 122.3, 106.1, 96.4, 74.6, 61.4, 58.2, 57.2, 52.4, 49.9, 45.4, 41.1, 33.2, 29.7, 27.3, 21.2. IR (KBr) v 3438, 2952, 1609, 1562, 1396, 753 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{46}N_3O$ $[M+H]^+$ 668.3635, found 668.3635.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(3-chlorophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10j**)

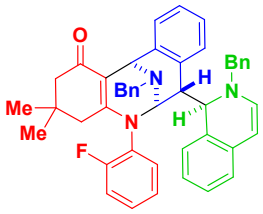
White solid obtained by filtration of the precipitate; 100.2 mg, 97% yield; dr > 20:1; reaction time = 5 min; mp 188.2-189.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.29-7.13 (m, 11H), 7.04 (q, *J* = 12.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 3H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 2H), 6.23 (d, *J* = 8.0 Hz, 1H), 5.28 (t, *J* = 8.0 Hz, 2H), 5.20 (d, *J* = 12.0 Hz, 1H), 4.67 (s, 1H), 4.25 (d, *J* = 8.0 Hz, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.72 (d, *J* = 20.0 Hz, 1H), 3.53 (d, *J* = 16.0 Hz, 1H), 3.31 (d, *J* = 20.0 Hz, 1H), 2.83 (d, *J* = 12.0 Hz, 1H), 2.16 (d, *J* = 12.0 Hz, 3H), 1.73 (d, *J* = 12.0 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 153.4, 142.1, 140.5 (2C), 138.2, 137.5, 136.6, 132.4, 131.3, 129.7, 129.0, 128.6, 128.3, 127.7, 127.3, 127.2, 127.1, 126.9, 126.8, 126.7, 126.6, 126.5, 125.9, 125.4, 125.3, 123.5, 122.3, 107.0, 96.6, 74.7, 61.3, 58.2, 57.2, 52.3, 49.8, 45.6, 41.1, 33.3, 29.8, 27.2. IR (KBr) *v* 3427, 2952, 1611, 1564, 1394, 759 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{42}ClN_3NaO$ $[M+Na]^+$ 710.2909, found 710.2905.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(3-bromophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10k**)

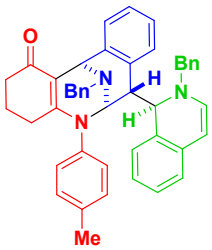
White solid obtained by filtration of the precipitate; 101.8 mg, 93% yield; dr > 20:1; reaction time = 5 min; mp 168.7-169.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.49 (d, *J* = 12.0 Hz, 1H), 7.22-7.15 (m, 12H), 7.01-6.82 (m, 5H), 6.73 (d, *J* = 12.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 2H), 6.23 (d, *J* = 8.0 Hz, 1H), 5.30 (d, *J* = 8.0 Hz, 1H), 5.25 (s, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 4.67 (s, 1H), 4.26 (s, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.72 (d, *J* = 20.0 Hz, 1H), 3.53 (d, *J* = 16.0 Hz, 1H), 3.30 (d, *J* = 20.0 Hz, 1H), 2.84 (s, 1H), 2.16 (d, *J* = 12.0 Hz, 3H), 1.71 (t, *J* = 20.0 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 153.3, 142.3, 142.2, 140.5, 138.1, 137.5, 136.6,

131.3, 130.1, 130.0, 129.7, 129.6, 129.1, 128.5, 128.3, 127.7, 127.3, 127.1, 126.8, 126.5, 125.9, 125.4, 125.3, 123.6, 123.5, 122.3 (2C), 106.8, 96.6, 74.8, 61.3, 58.2, 57.2, 52.2, 49.8, 45.7, 41.1, 33.3, 29.8, 27.2. IR (KBr) ν 3444, 2952, 1612, 1562, 1395, 759 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{42}BrN_3NaO$ $[M+Na]^+$ 754.2403, found 754.2398.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(2-fluorophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10l**)

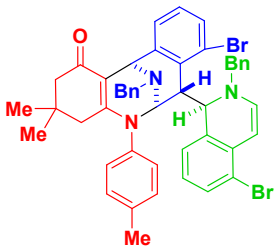
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 91.0 mg, 90% yield; dr = 1.6:1; reaction time = 5 min; mp 140.3-141.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.49 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 7.25-7.14 (m, 12H), 6.96-6.84 (m, 5H), 6.68 (t, J = 8.0 Hz, 2H), 6.49 (t, J = 8.0 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H), 5.33-5.20 (m, 3H), 4.52 (s, 1H), 4.27 (d, J = 8.0 Hz, 1H), 3.86-3.54 (m, 3H), 3.34 (t, J = 16.0 Hz, 1H), 2.95 (d, J = 8.0 Hz, 1H), 2.21-1.96 (m, 3H), 1.77 (dd, $J_1 = J_2$ = 16.0 Hz, 1H), 1.04 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 159.1, 156.6, 154.6, 140.8, 138.4, 138.1, 136.7, 132.4, 131.3 (d, J = 36.0 Hz, 1C), 129.9, 129.4, 129.3, 128.6, 128.5, 128.3, 127.6, 127.3, 127.3, 127.1, 126.8, 126.6, 126.5, 125.9, 125.4, 125.3, 125.1, 122.8 (d, J = 144.0 Hz, 1C), 116.7 (d, J = 20.0 Hz, 1C), 106.8, 96.6, 73.9, 61.4, 58.4, 56.9, 52.5, 49.8, 45.9, 40.6, 32.9, 29.2. IR (KBr) ν 3430, 1620, 1562, 1390, 757 cm^{-1}. HRMS (ESI) calcd for $C_{46}H_{43}FN_3O$ $[M+H]^+$ 672.3385, found 672.3366.



13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10m**)

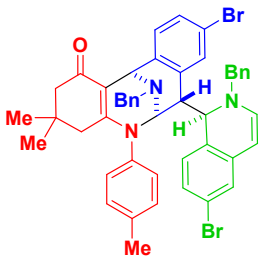
White solid obtained by filtration of the precipitate; 85.7 mg, 89% yield; dr > 20:1; reaction time = 5 min; mp 181.7-182.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.53 (d, J = 8.0 Hz, 1H), 7.25-7.12 (m, 11H), 6.94-6.5 (m, 5H), 6.69-6.47 (m, 4H), 6.19 (d, J = 8.0 Hz, 1H), 5.27 (d, J = 12.0 Hz, 2H),

5.18 (d, J = 8.0 Hz, 1H), 4.63 (s, 1H), 4.28 (d, J = 8.0 Hz, 1H), 3.79 (d, J = 12.0 Hz, 1H), 3.67 (d, J = 16.0 Hz, 1H), 3.53 (d, J = 12.0 Hz, 1H), 3.32 (d, J = 16.0 Hz, 1H), 2.93 (d, J = 4.0 Hz, 1H), 2.34-2.15 (m, 6H), 1.97 (d, J = 16.0 Hz, 1H), 1.83-1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 156.3, 141.0, 138.3, 138.2, 137.9, 136.7, 136.6, 132.5, 131.2, 130.8, 129.7, 129.5, 128.4, 128.3, 128.1, 127.4, 127.3, 127.0, 126.8, 126.6, 126.4, 126.1, 125.3, 125.3, 123.5, 122.2, 106.6, 96.4, 74.6, 61.4, 58.0, 57.0, 52.3, 45.9, 36.3, 27.3, 22.4, 20.8. IR (KBr) v 3436, 2932, 1612, 1558, 1446, 751 cm^{-1}. HRMS (ESI) calcd for $C_{45}H_{42}N_3O$ $[M+H]^+$ 640.3322, found 640.3323.



13-benzyl-7-(2-benzyl-5-bromo-1,2-dihydroisoquinolin-1-yl)-8-bromo-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10n**)

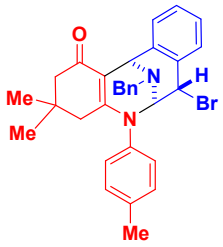
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 109.3 mg, 88% yield; dr > 20:1; reaction time = 5 min; mp 175.3-176.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.37 (dd, J_1 = J_2 = 8.0 Hz, 3H), 7.25-7.20 (m, 9H), 7.03 (d, J = 4.0 Hz, 2H), 6.97 (t, J = 8.0 Hz, 2H), 6.83 (t, J = 4.0 Hz, 2H), 6.40 (t, J = 8.0 Hz, 1H), 6.13 (d, J = 4.0 Hz, 1H), 5.51 (dd, J_1 = J_2 = 4.0 Hz, 3H), 5.43 (d, J = 4.0 Hz, 1H), 4.62 (s, 1H), 4.01 (d, J = 16.0 Hz, 1H), 3.79 (d, J = 12.0 Hz, 1H), 3.71 (d, J = 4.0 Hz, 1H), 3.59 (d, J = 4.0 Hz, 1H), 3.56 (s, 1H), 2.50 (s, 3H), 2.14 (d, J = 16.0 Hz, 1H), 2.04 (s, 2H), 1.77 (d, J = 20.0 Hz, 1H), 1.03 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 154.1, 144.3, 139.3, 138.4, 137.7, 137.6, 136.3, 133.0, 131.0, 131.0, 130.4, 130.2, 129.4, 129.1, 128.7, 128.7, 128.6, 128.0, 127.5, 127.4, 127.1, 126.3, 125.7, 124.8, 124.0, 118.9, 104.3, 95.1, 78.0, 60.5, 56.7, 55.1, 49.8, 48.7, 48.2, 40.8, 32.9, 27.5, 21.2. IR (KBr) v 3440, 2925, 1630, 794 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Br_2N_3O$ $[M+H]^+$ 824.1846, found 824.1834.



13-benzyl-7-(2-benzyl-6-bromo-1,2-dihydroisoquinolin-1-yl)-9-bromo-3,3-dimethyl-5-(*p*-tolyl)-

3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10o**)

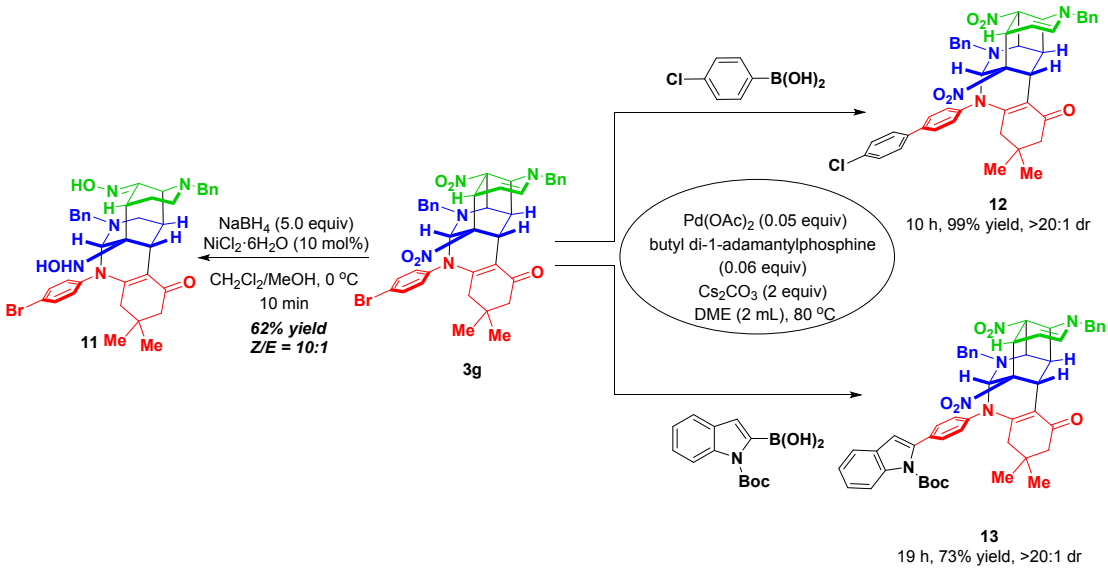
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 4:1); 101.2 mg, 82% yield; dr > 20:1; reaction time = 5 min; mp 194.9-196.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.44 (d, J = 8.0 Hz, 1H), 7.34-7.23 (m, 8H), 7.19 (d, J = 8.0 Hz, 2H), 6.98 (s, 2H), 6.90 (d, J = 4.0 Hz, 2H), 6.78 (d, J = 4.0 Hz, 1H), 6.56 (dd, J_1 = J_2 = 4.0 Hz, 2H), 6.49 (s, 1H), 6.30 (d, J = 8.0 Hz, 1H), 5.24 (t, J = 8.0 Hz, 2H), 4.78 (d, J = 8.0 Hz, 1H), 4.43 (s, 1H), 4.07 (d, J = 8.0 Hz, 1H), 3.82 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 2H), 3.51 (d, J = 12.0 Hz, 1H), 3.35 (d, J = 16.0 Hz, 1H), 2.76 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H), 2.13 (d, J = 16.0 Hz, 3H), 1.80 (d, J = 20.0 Hz, 1H), 1.02 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.6, 140.1, 137.7, 137.7, 137.6, 137.4, 137.2, 134.7, 134.1, 131.6, 130.3, 129.9, 129.8, 128.7, 128.5, 127.8, 127.7, 127.4, 127.3, 126.8, 126.1, 124.9, 124.6, 123.0, 120.7, 119.0, 105.2, 95.9, 73.4, 61.0, 58.6, 57.1, 52.6, 49.8, 44.3, 40.9, 33.1, 29.6, 20.9. IR (KBr) ν 3437, 2924, 1614, 1566, 1393, 723 cm^{-1}. HRMS (ESI) calcd for $C_{47}H_{44}Br_2N_3O$ $[M+H]^+$ 824.1846, found 824.1854.



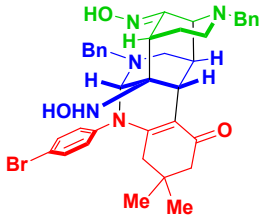
13-benzyl-7-bromo-3,3-dimethyl-5-(*p*-tolyl)-3,4,5,6,7,12-hexahydro-6,12-epiminodibenzo[*b,e*]azocin-1(2*H*)-one (**10p**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1); 43.0 mg, 54% yield; dr > 20:1; reaction time = 5 min; mp 171.0-172.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.54 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.37 (q, J = 8.0 Hz, 3H), 7.31 (d, J = 8.0 Hz, 1H), 7.22-7.15 (m, 4H), 6.86 (s, 2H), 5.27 (d, J = 8.0 Hz, 2H), 4.79 (s, 1H), 3.99 (d, J = 16.0 Hz, 1H), 3.71 (t, J = 4.0 Hz, 1H), 2.38 (s, 3H), 2.17 (q, J = 16.0 Hz, 2H), 2.06 (d, J = 16.0 Hz, 1H), 1.79 (d, J = 16.0 Hz, 1H), 1.07 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 153.5, 138.6, 138.4, 138.2, 136.7, 130.8, 130.0, 129.4, 129.0, 128.9, 128.4, 127.7, 126.6, 126.5, 105.8, 79.6, 57.0, 51.3, 49.8, 47.1, 40.7, 33.0, 29.5, 27.5, 21.1. IR (KBr) ν 3431, 2956, 1567, 1391, 747 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{32}BrN_2O$ $[M+H]^+$ 527.1693, found 527.1689.

8. Experimental data for the derivations of 3g



General procedure for the formation of 11: A solution of **3g** (144.5 mg, 0.20 mmol) and $NiCl_2·6H_2O$ (4.8 mg, 0.02 mmol) in 1.0 mL MeOH and 1.0 mL DCM was cooled to 0 °C, and then $NaBH_4$ (37.8 mg, 1.0 mmol) was added successively. The reaction mixture was stirred at 0 °C for 10 min until the complete consumption of **3g** as monitored by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **11** in 62% yield with 10:1 Z/E.

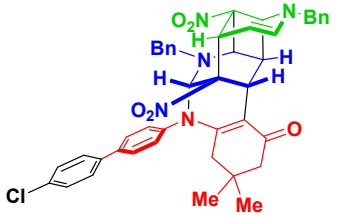


3,13-dibenzyl-8-(4-bromophenyl)-6a-(hydroxyamino)-15-(hydroxyimino)-10,10-dimethyl-2,3,4,5,6,6a,7,8,9,10,11,12b-dodecahydro-7,1-(epiminomethano)-2,6-methanoazocino[5,4-*c*]quinolin-12(1*H*)-one (**11**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 1:1); 86.3 mg, 62% yield; Z/E = 10:1; reaction time = 10 min; mp 224.7-225.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6), δ 10.09 (s, 1H), 7.57-7.19 (m, 10H), 7.08-6.86 (m, 5H), 5.02 (s, 1H), 4.64 (s, 1H), 3.90 (s, 1H), 3.78-3.70 (m, 2H), 3.62 (d, J = 12.0 Hz, 1H), 3.48 (s, 2H), 3.07 (s, 1H), 2.69-2.51 (m, 3H), 2.32-2.14 (m, 4H), 2.05-1.88 (m, 3H), 1.71 (s, 1H), 1.00 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4, 157.2, 157.1, 144.7, 139.7, 136.5, 128.9, 128.0, 127.5, 126.8, 126.5, 119.1,

104.8, 78.3, 63.6, 61.5, 59.8, 58.7, 57.5, 49.7, 47.5, 45.8, 40.9, 32.0, 30.8, 29.3, 26.8, 26.7, 24.5, 20.8, 14.1. IR (KBr) *v* 3280, 2953, 1554, 1409, 1245, 739 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{43}BrN_5O_3$ $[M+H]^+$ 696.2544, found 696.2549.

General procedure for the formation of 12： Under nitrogen atmosphere, compound **3g** (72.3 mg, 0.10 mmol), 4-chlorophenyl boronic acid (23.5 mg, 0.15 mmol, 1.5 equiv), Cs_2CO_3 (2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by adding 2.0 mL DME. The resulting mixture was stirred at 80 °C for 10 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **12** as a yellow solid in 99% yield.

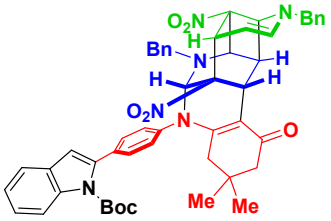


7,11-dibenzyl-5-(4'-chloro-[1,1'-biphenyl]-4-yl)-3,3-dimethyl-7b,13-dinitro-3,4,5,6,7,7a,7b,8,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[*d*]pyrido[3',2':3,4]cyclobuta[1,2-*g*][1,3]diazocin-1(2*H*)-one (**12**)

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 5:1); 82.7 mg, 99% yield; dr > 20:1; reaction time = 10 h; mp 179.4-180.5 °C; ^1H NMR (400 MHz, $CDCl_3$), δ 7.64 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42-7.39 (m, 6H), 7.29-7.25 (m, 3H), 7.13 (q, J = 4.0 Hz, 4H), 6.46 (d, J = 8.0 Hz, 1H), 5.33 (d, J = 4.0 Hz, 1H), 4.38 (q, J = 16.0 Hz, 2H), 4.25 (d, J = 12.0 Hz, 1H), 4.09 (t, J = 8.0 Hz, 1H), 3.98 (s, 1H), 3.88 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.75 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.29 (d, J = 8.0 Hz, 1H), 2.57 (t, J = 8.0 Hz, 1H), 2.33-2.22 (m, 3H), 1.98 (dd, J_1 = 4.0 Hz, J_2 = 16.0 Hz, 2H), 1.03 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.2, 141.9, 139.7, 139.2, 137.9, 136.6, 134.0, 129.1, 129.0, 128.7 (2C), 128.2 (2C), 128.0, 127.9 (2C), 127.7, 127.4 (2C), 107.7, 87.9, 83.2, 82.4, 80.1, 59.0, 57.7, 51.5, 50.1, 45.7, 41.9, 39.2, 33.0, 26.2, 24.9. IR (KBr) *v* 3436, 3033, 2953, 1635, 1585, 1542, 1390, 740 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{41}ClN_5O_5$ $[M+H]^+$ 754.27917, found 754.2797.

General procedure for the formation of 13： Under nitrogen atmosphere, compound **3g** (72.3 mg, 0.10 mmol), 2-indolyl boronic acid (39.2 mg, 0.15 mmol, 1.5 equiv), Cs_2CO_3 (2.0 equiv),

$Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by adding 2.0 mL DME. The resulting mixture was stirred at 80 °C for 19 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **13** as a yellow solid in 73% yield.



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

Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 7:1); 63.7 mg, 73% yield; dr > 20:1; reaction time = 19 h; mp 179.9-181.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.21 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.45-7.32 (m, 6H), 7.30-7.25 (m, 6H), 7.15-7.10 (m, 4H), 6.58 (s, 1H), 6.48 (d, J = 8.0 Hz, 1H), 5.33 (d, J = 4.0 Hz, 1H), 4.40 (q, J = 16.0 Hz, 2H), 4.26 (d, J = 12.0 Hz, 1H), 4.10 (t, J = 8.0 Hz, 1H), 3.97 (d, J = 8.0 Hz, 1H), 3.88 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.76 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.30 (d, J = 4.0 Hz, 1H), 2.58 (t, J = 8.0 Hz, 1H), 2.37-2.23 (m, 3H), 1.99 (d, J = 12.0 Hz, 1H), 1.69 (s, 1H), 1.34 (s, 9H), 1.03 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 153.0, 149.9, 141.8, 139.2, 138.7, 137.7, 136.8, 136.6, 135.0, 130.0, 129.0, 128.8 (2C), 128.0, 127.9 (2C), 127.8, 127.2, 124.8, 123.1, 120.6, 115.3, 111.0, 107.9, 87.9, 83.7, 83.2, 82.5, 80.3, 59.0, 57.7, 55.7, 51.6, 50.1, 45.8, 42.1, 39.3, 33.1, 29.7, 26.4, 25.0. IR (KBr) ν 3445, 3034, 2956, 2870, 1734, 1637, 1589, 1542, 1327, 743 cm^{-1}. HRMS (ESI) calcd for $C_{51}H_{51}N_6O_7$ $[M+H]^+$ 859.3814, found 859.3818.

9. Crystal structures of 3a, 3zb, 5m, 6n, 10g, 10p and 11

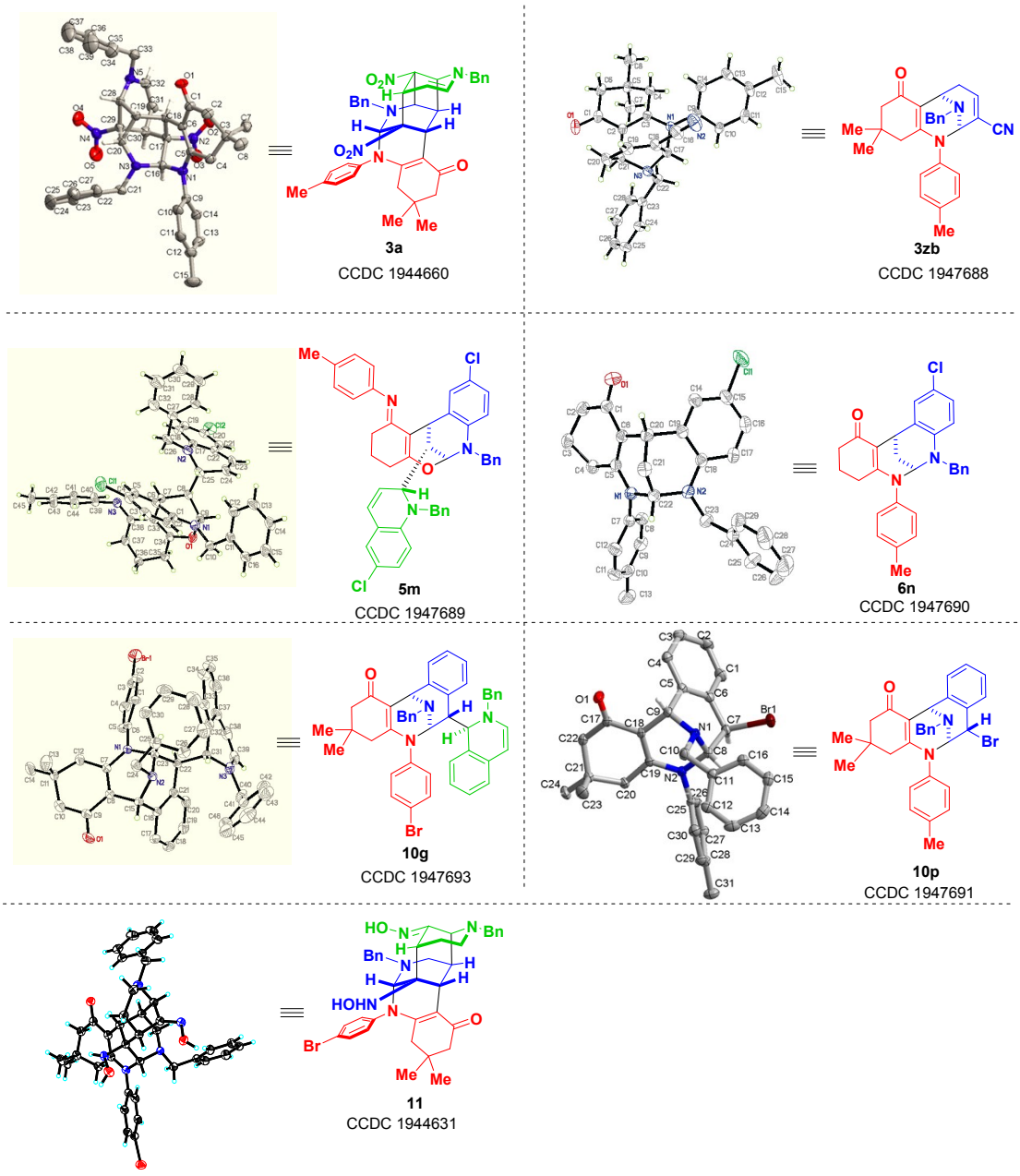
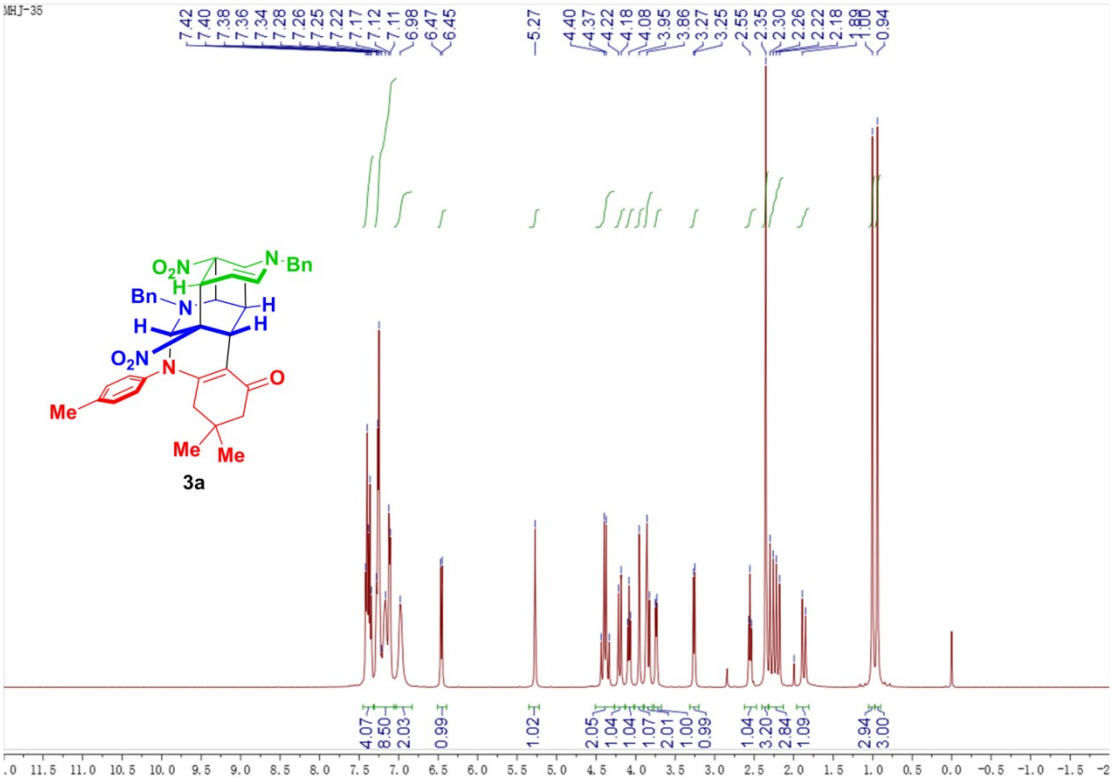


Figure S1. X-ray structures of **3a**, **3zb**, **5m**, **6n**, **10g**, **10p** and **11**. Displacement ellipsoids are drawn at the 30% probability level.

10. ^{1}H NMR and ^{13}C NMR spectra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7.22
7.17
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6.98
6.47
6.45
5.27
4.40
4.37
4.22
4.18
4.08
3.95
3.86
3.27
3.25
2.55
2.35
2.30
2.26
2.22
2.18
1.89
1.80
0.94
4.07
8.50
2.03
0.99
1.02
2.05
1.04
1.04
1.07
2.01
1.00
0.99
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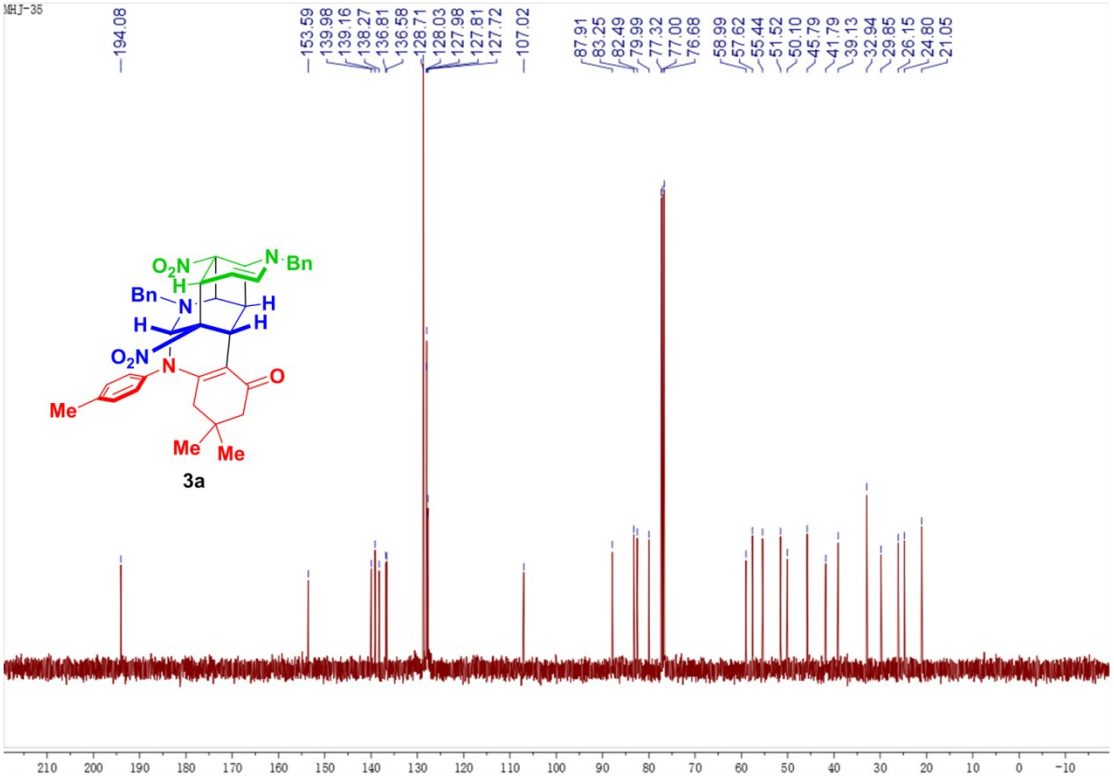
3.20
2.84
1.09
2.94
3.00
3a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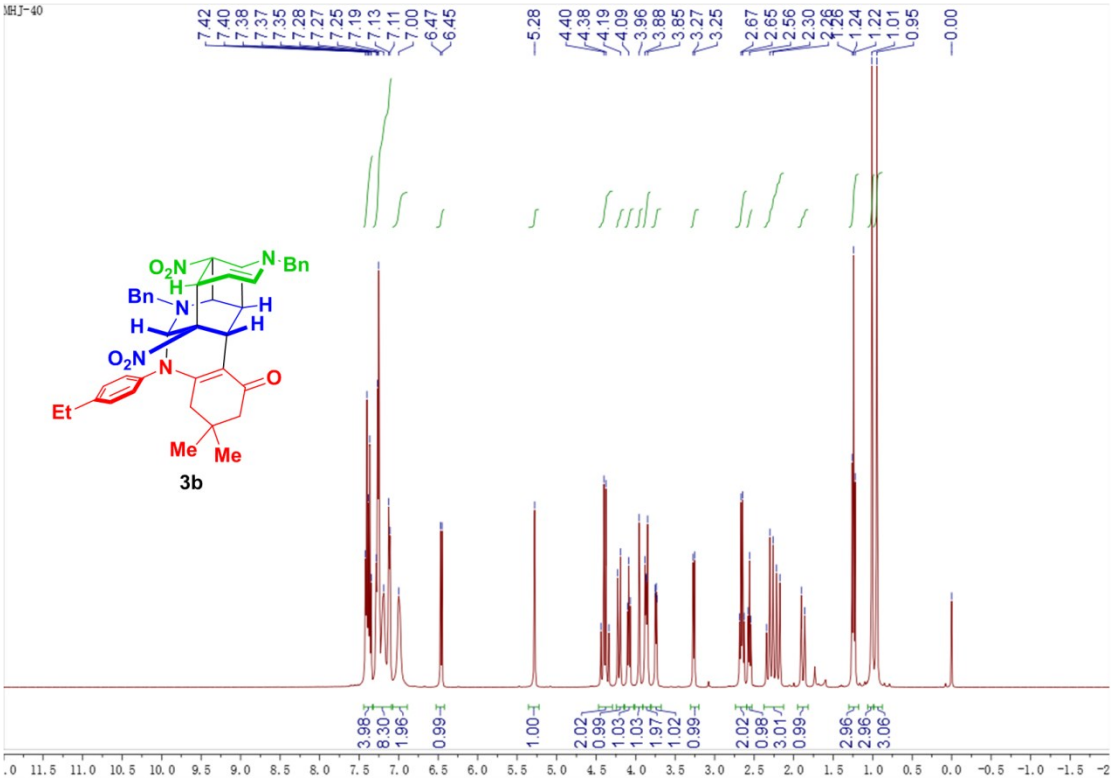
77.32
77.00
76.68
58.99
57.62
55.44
51.52
50.10
45.79
41.79
39.13
32.94
29.85
26.15
24.80
21.05
3a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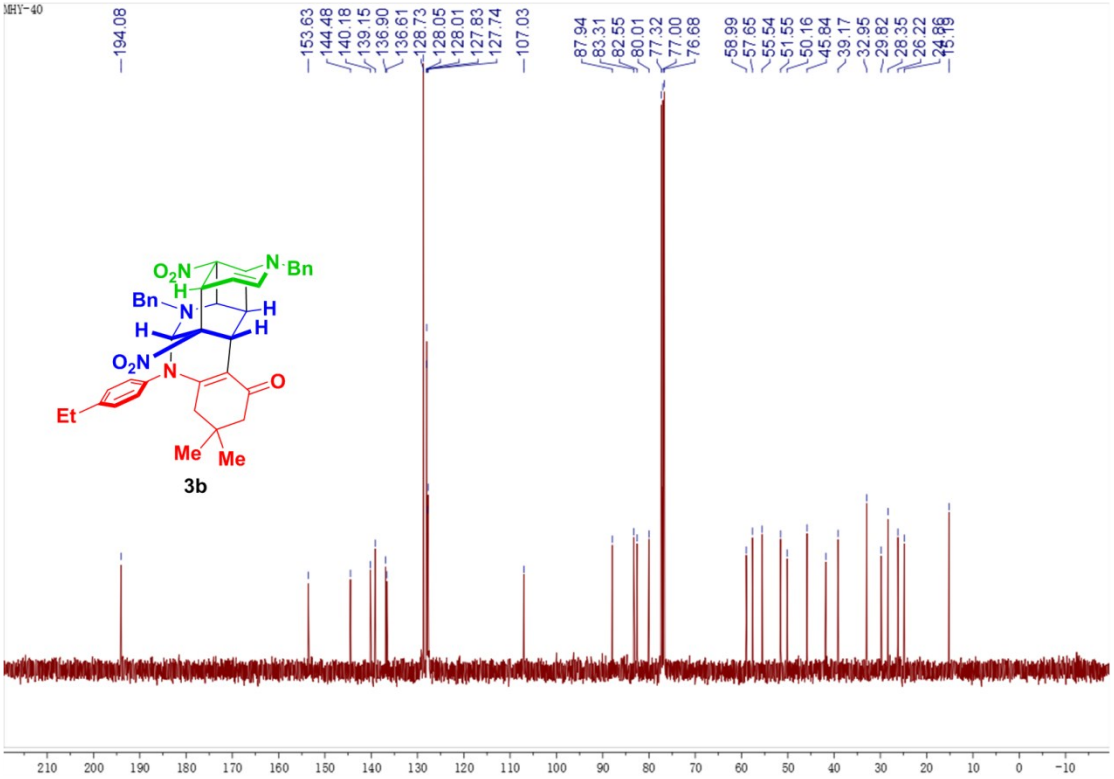
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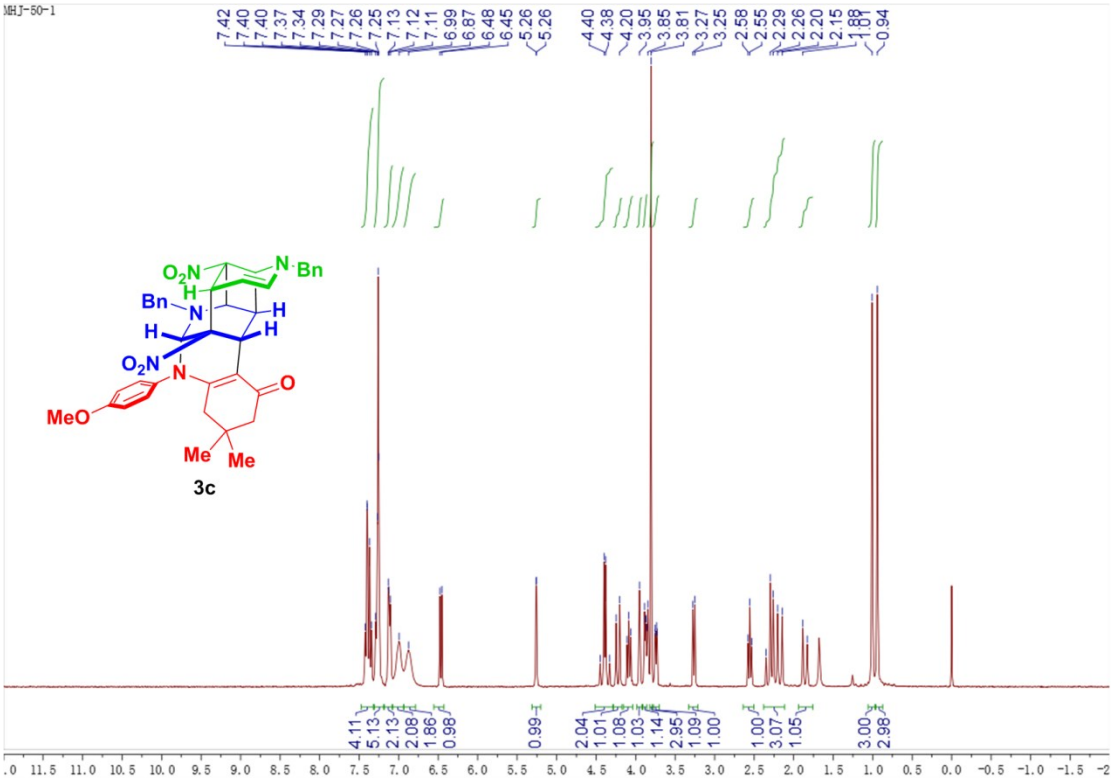
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2.26
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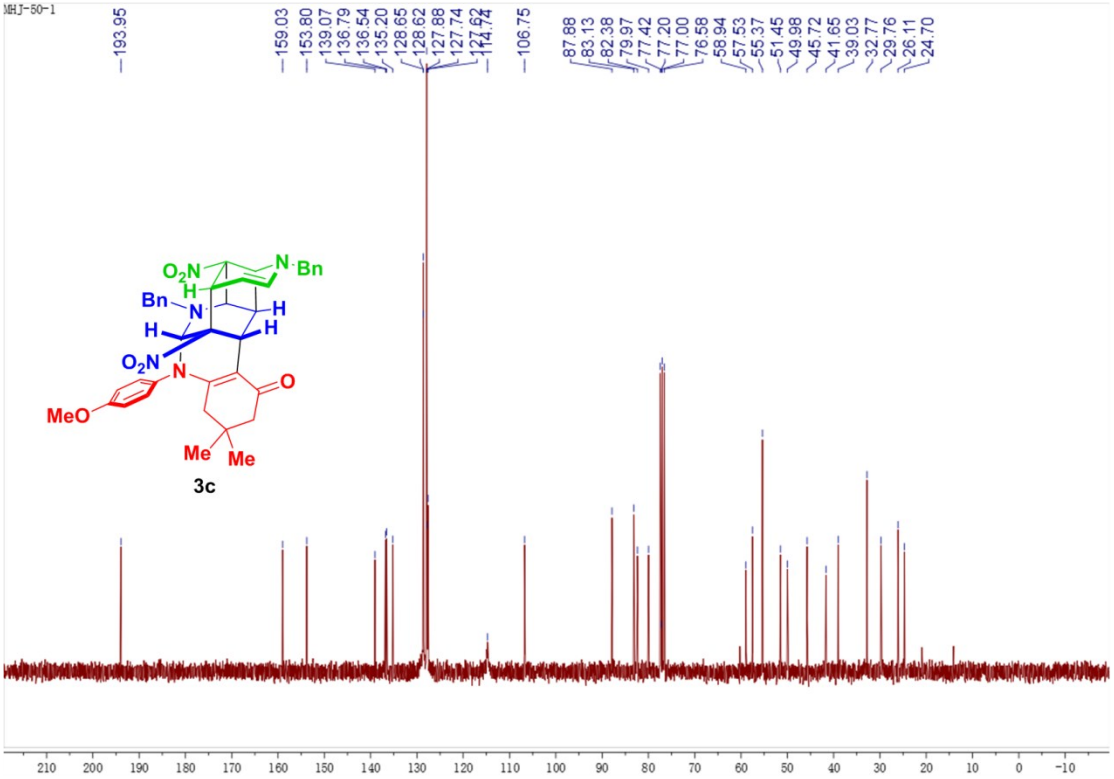
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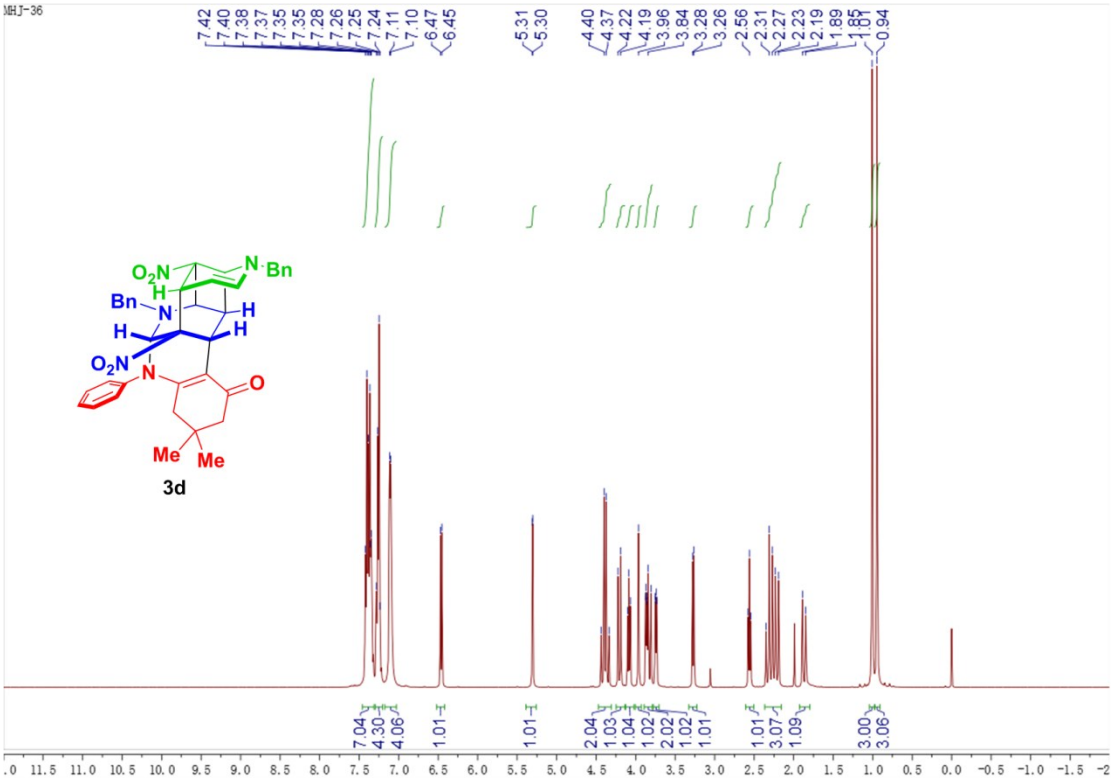
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3.28
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1.85
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2.04
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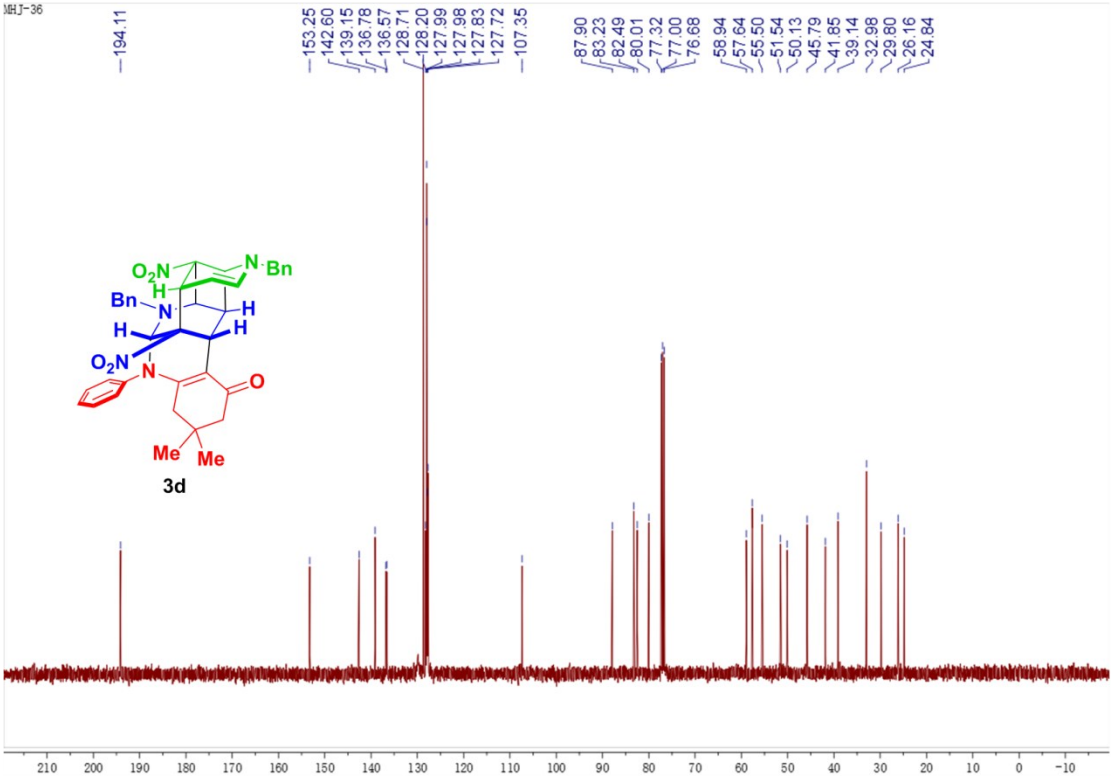
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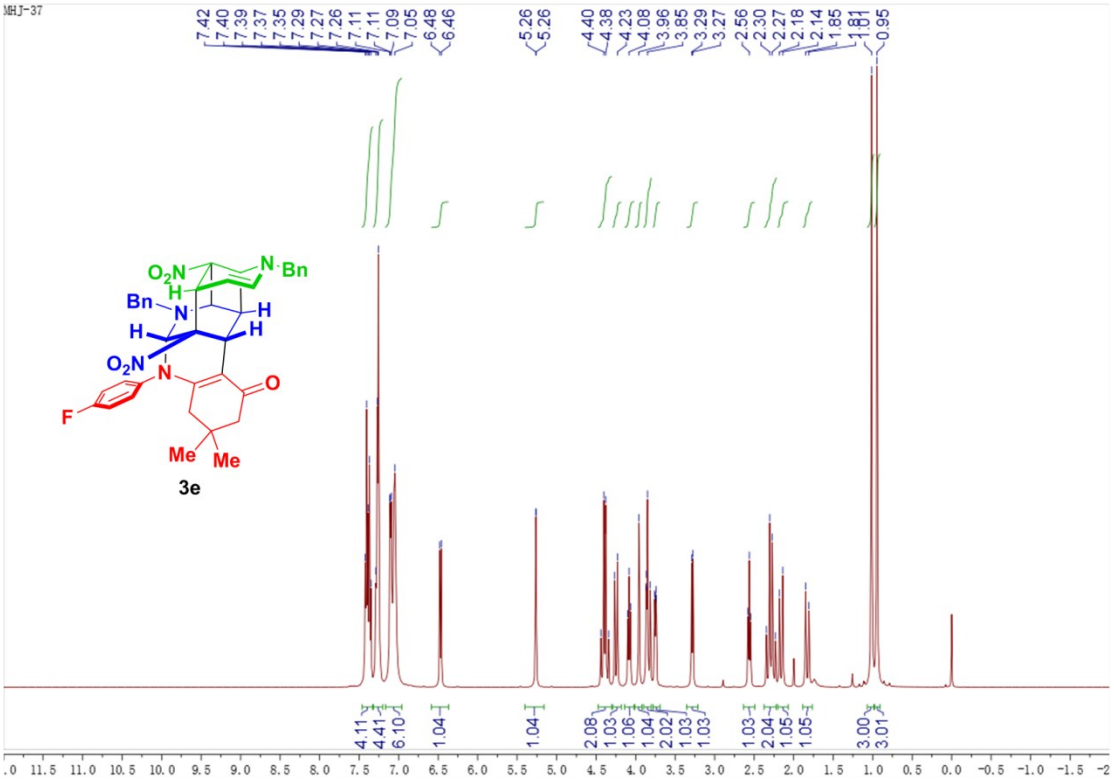
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7.05
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4.40
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2.08
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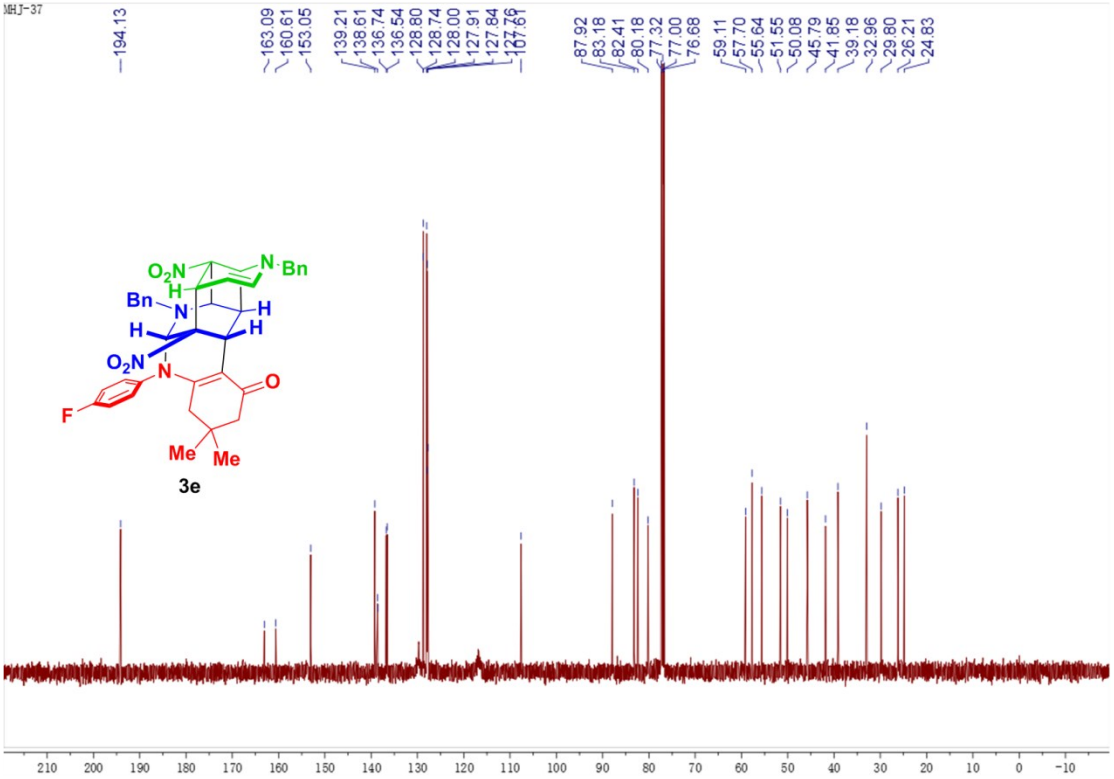
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77.00
76.68
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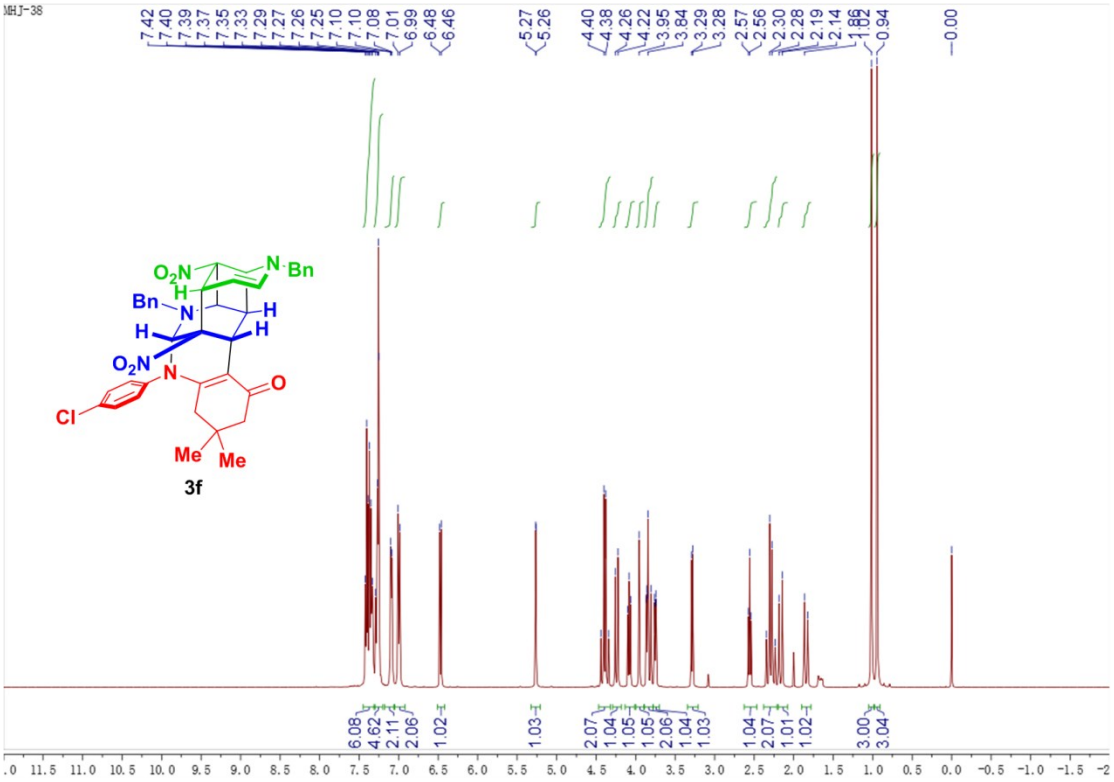
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3.04
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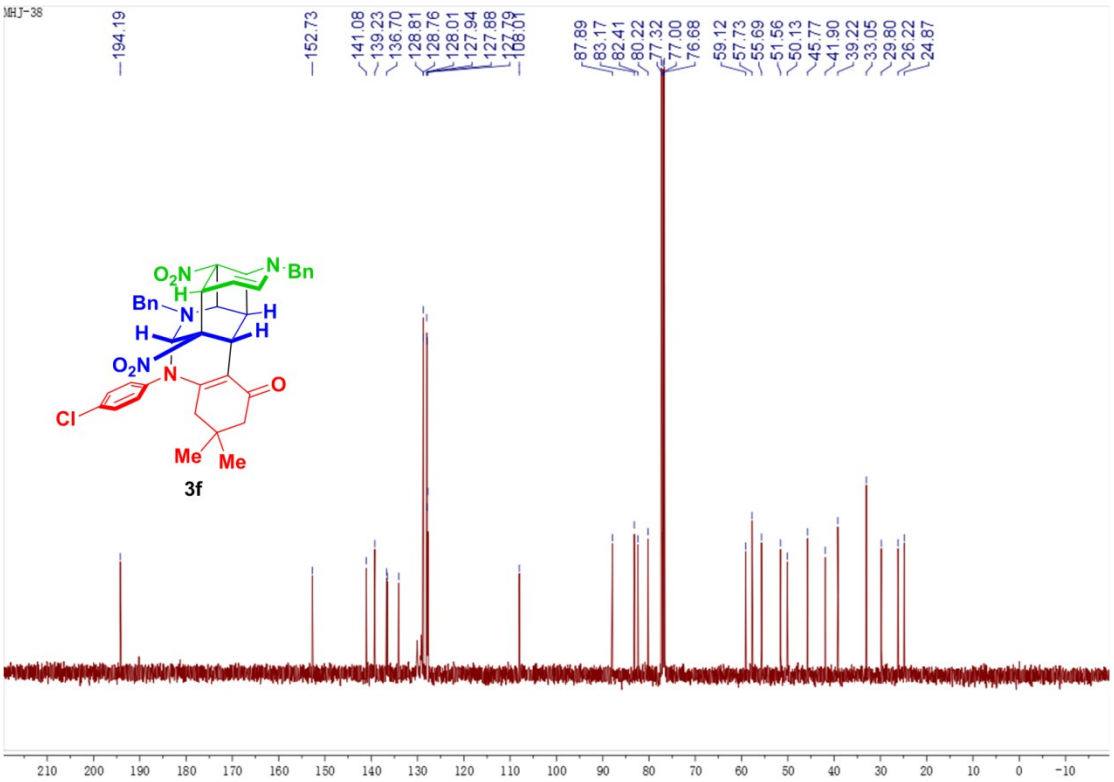
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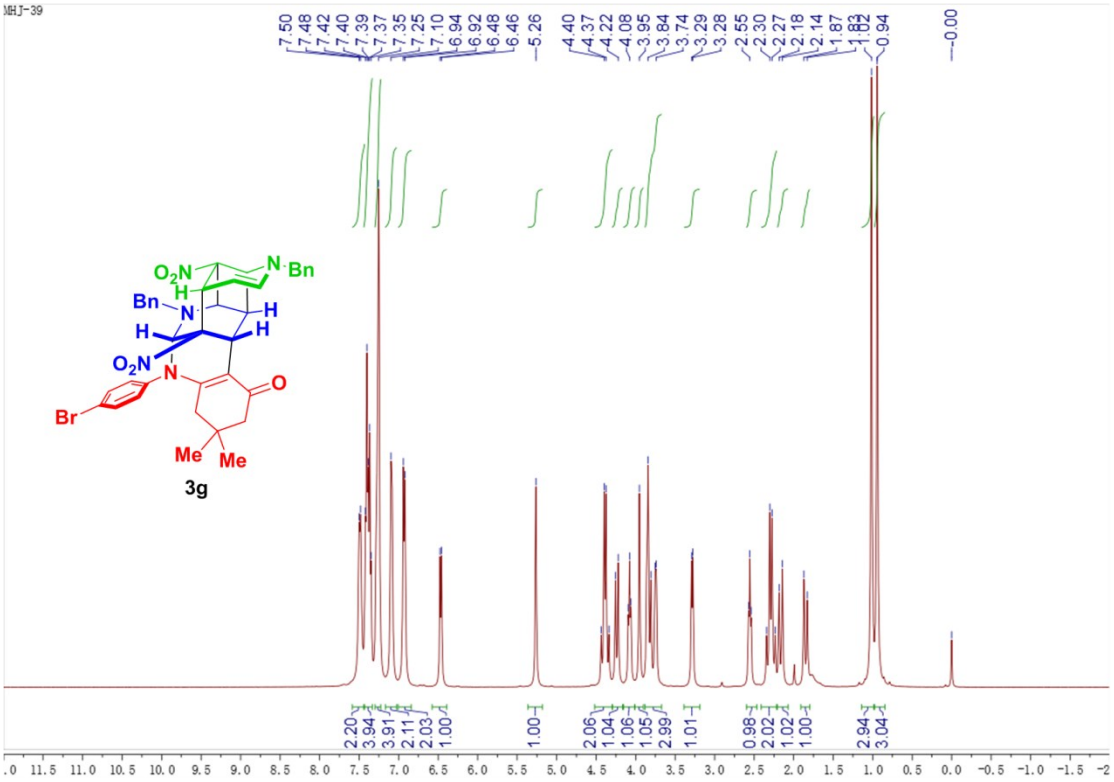
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7.10
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6.46
5.26
4.40
4.37
4.22
4.08
3.95
3.84
3.74
3.29
3.28
2.55
2.30
2.27
2.18
2.14
1.87
1.82
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0.00
2.20
3.94
3.91
2.11
2.03
1.00
1.00
2.06
1.04
1.06
1.05
2.99
1.01
0.98
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1.02
1.00
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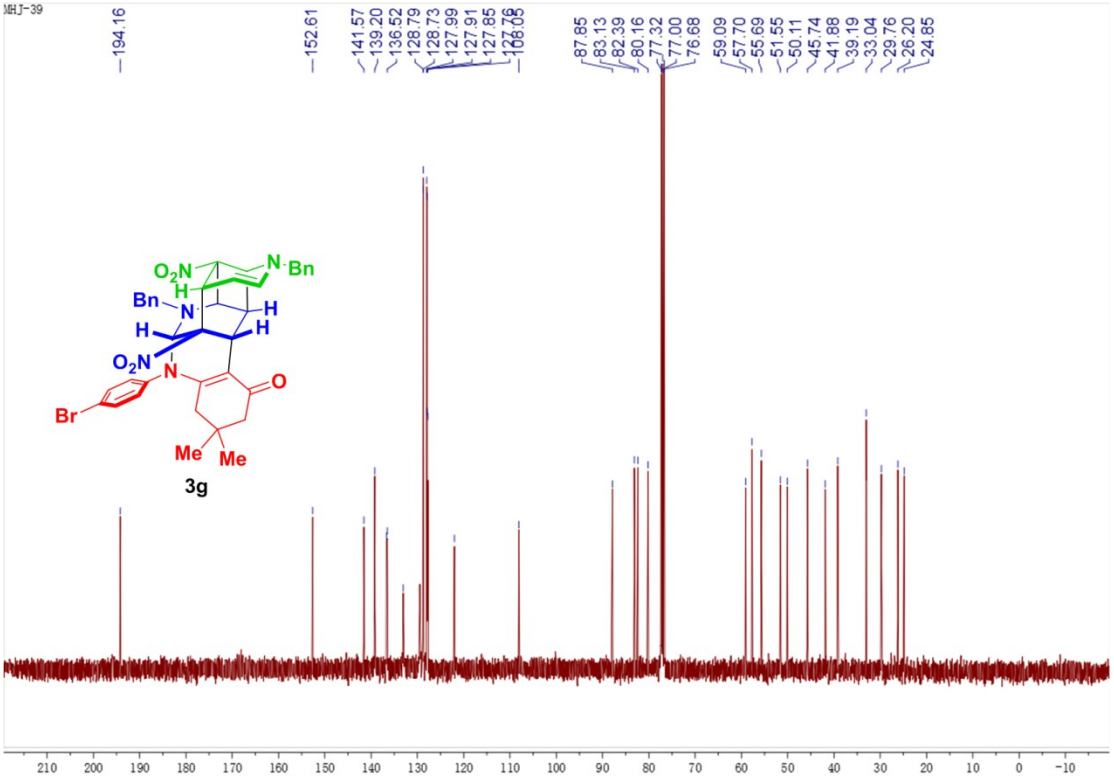
H
Bn
N
H
H
O2N
N
O
Br
Me
Me
3g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127.85
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80.16
77.32
77.00
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59.09
57.70
55.69
51.55
50.11
45.74
41.88
39.19
33.04
29.76
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H
Bn
N
H
H
O2N
N
O
Br
Me
Me
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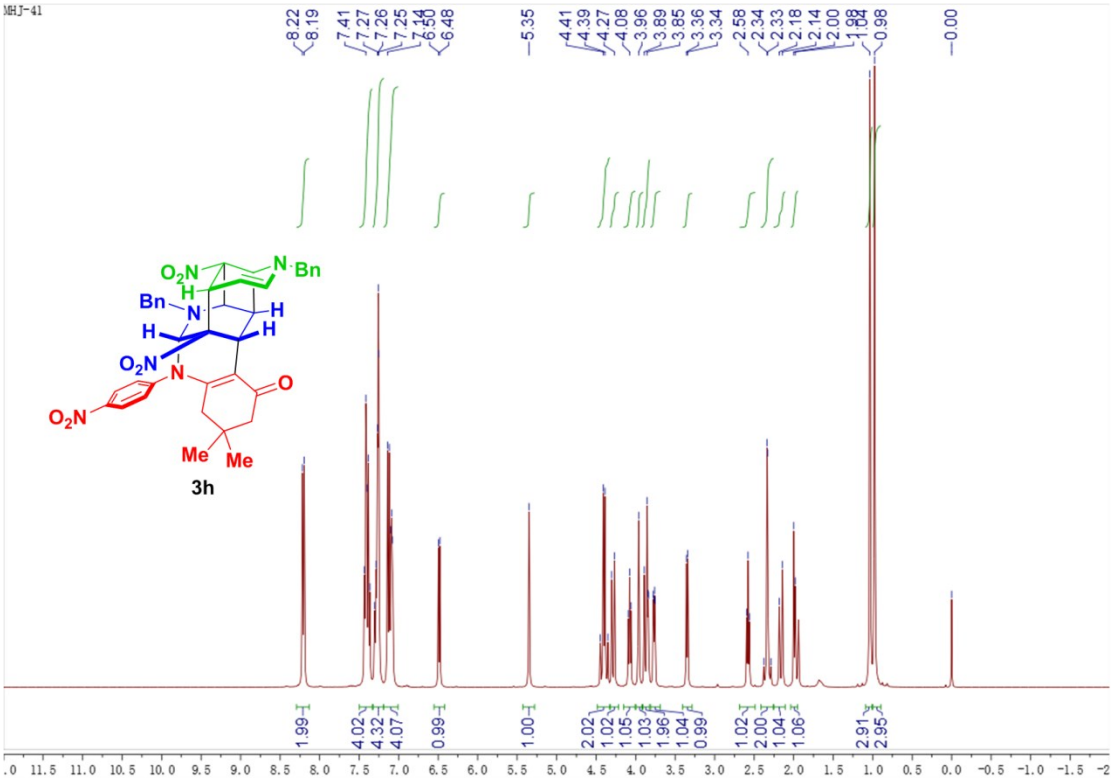
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1.99
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4.07
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2.02
1.02
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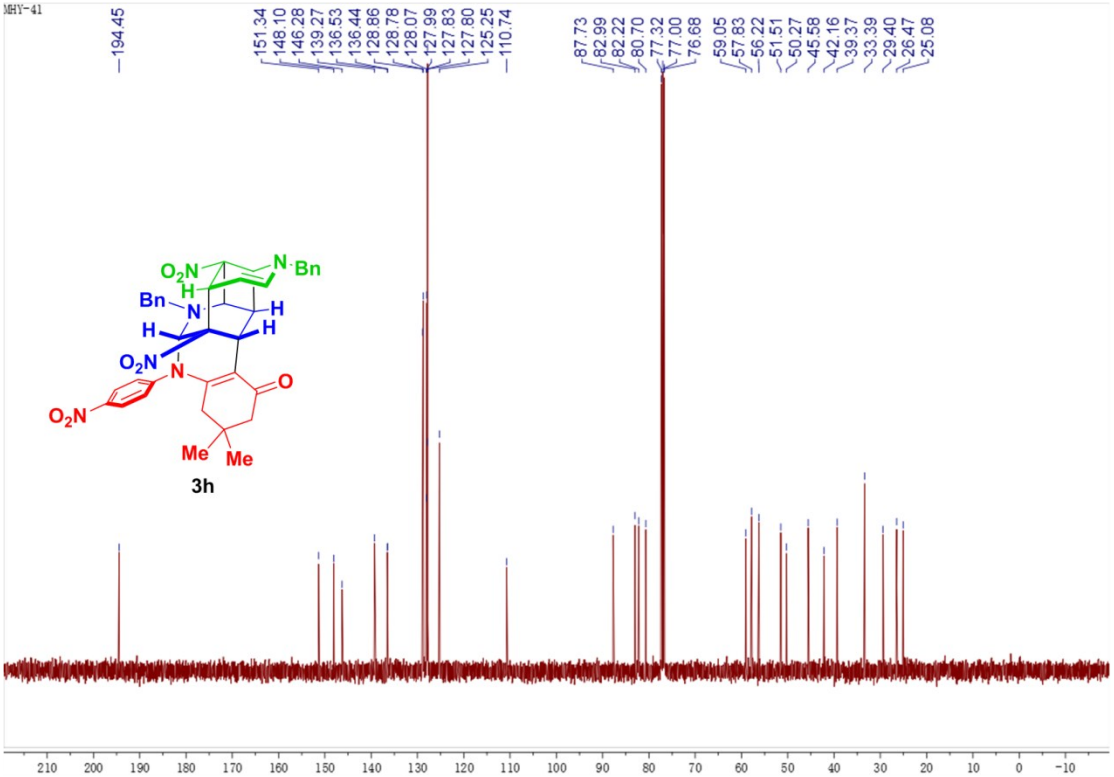
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77.00
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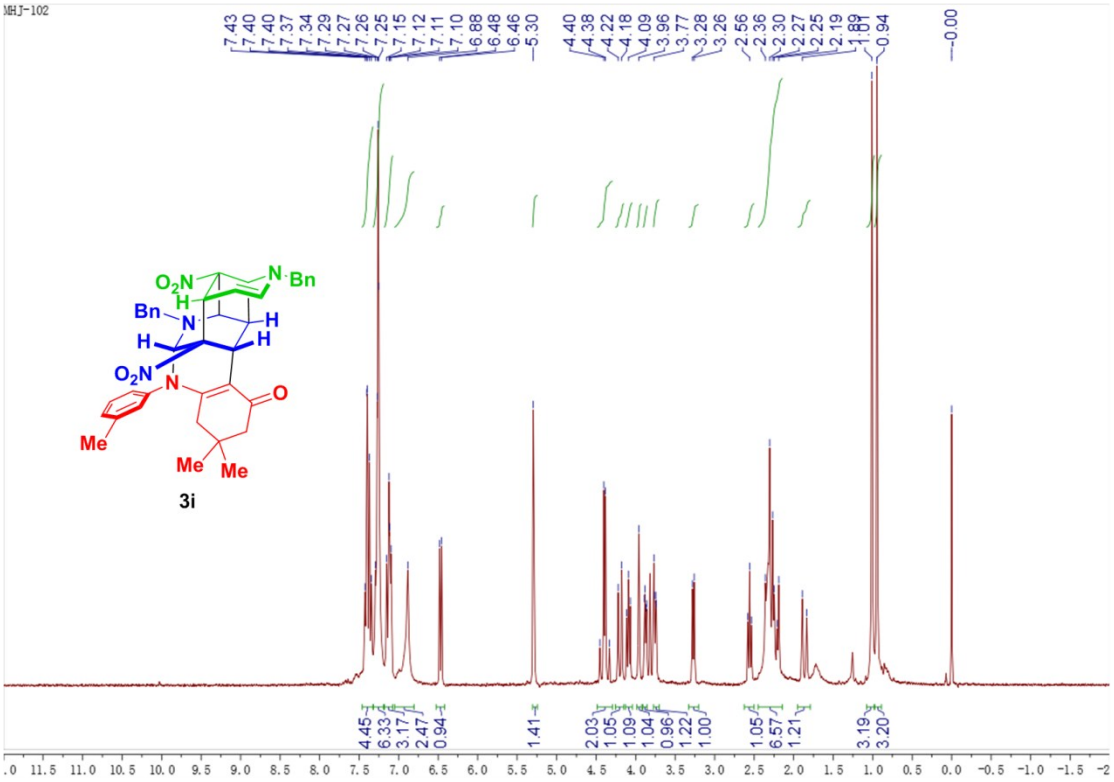
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2.03
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1.04
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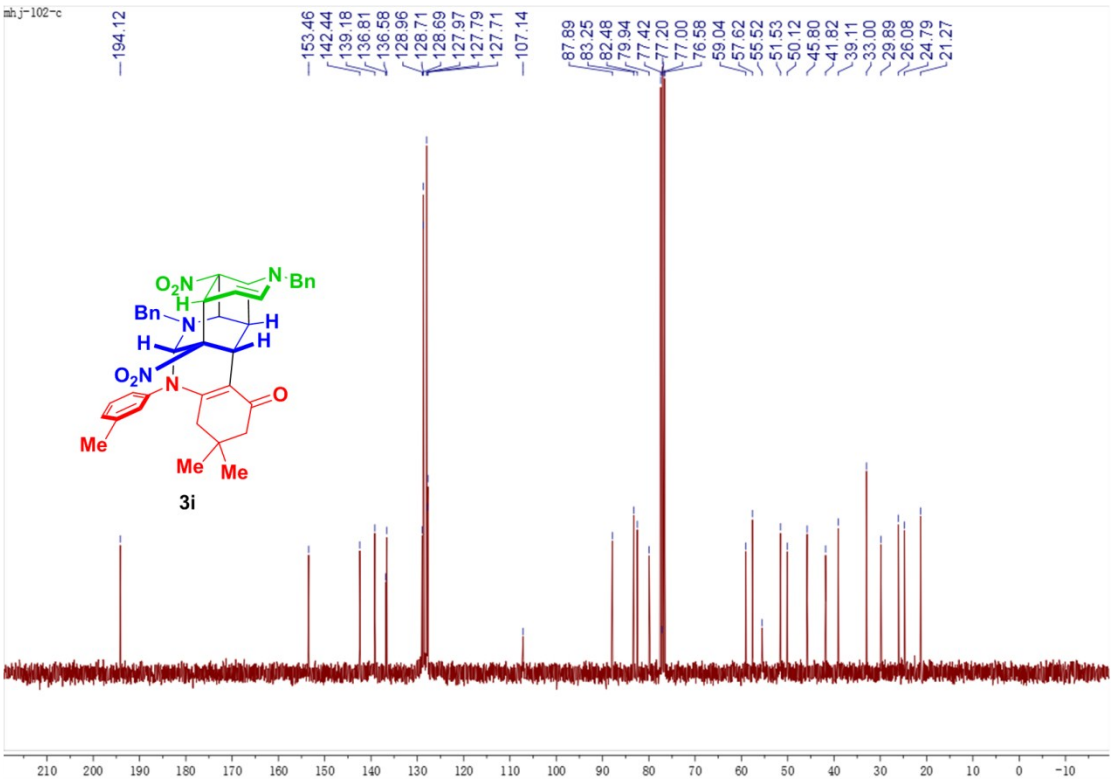
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127.71
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79.94
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77.20
77.00
76.58
59.04
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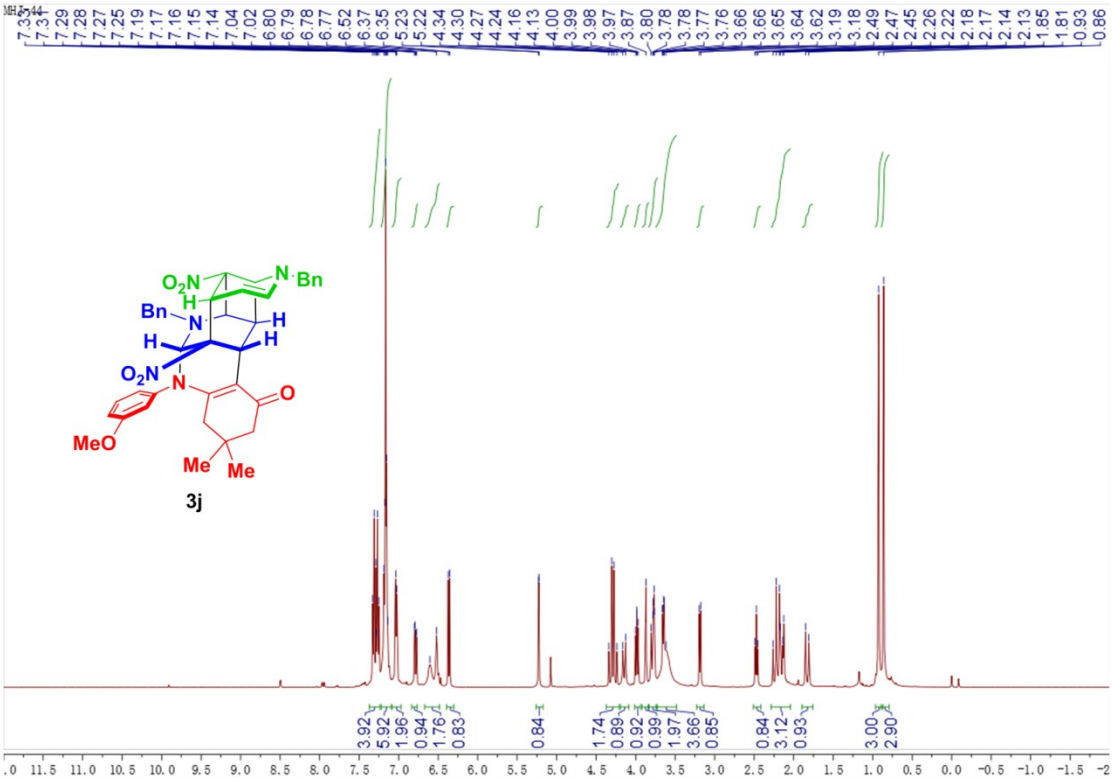
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3.97
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2.18
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2.13
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0.86
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0.94
1.76
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0.84
1.74
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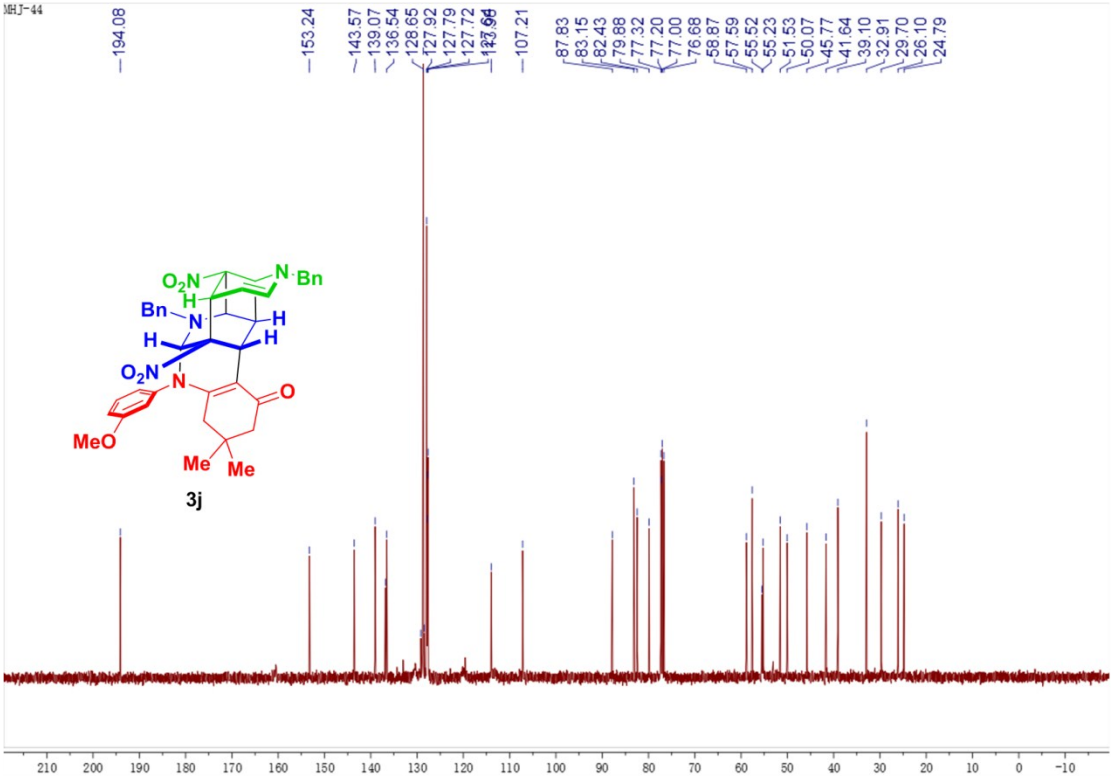
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24.79
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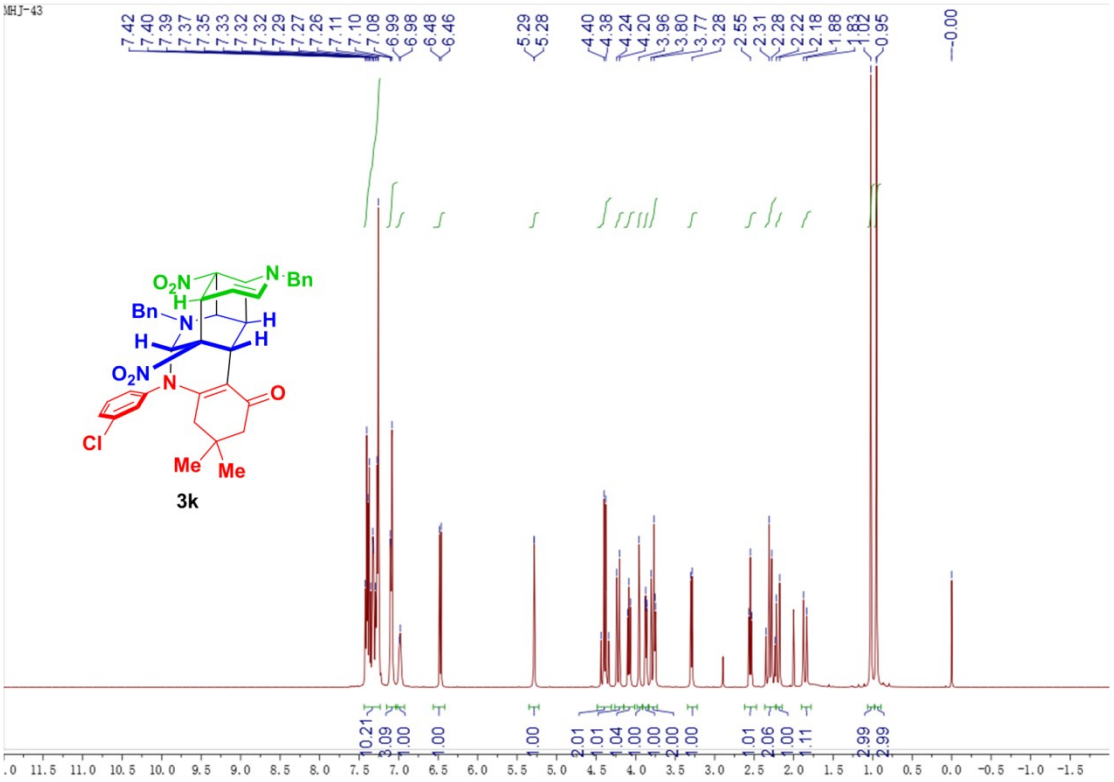
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7.08
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5.29
5.28
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4.24
4.20
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3.80
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2.28
2.22
2.18
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1.83
1.82
1.05
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0.00
10.21
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1.00
1.00
1.00
2.01
1.01
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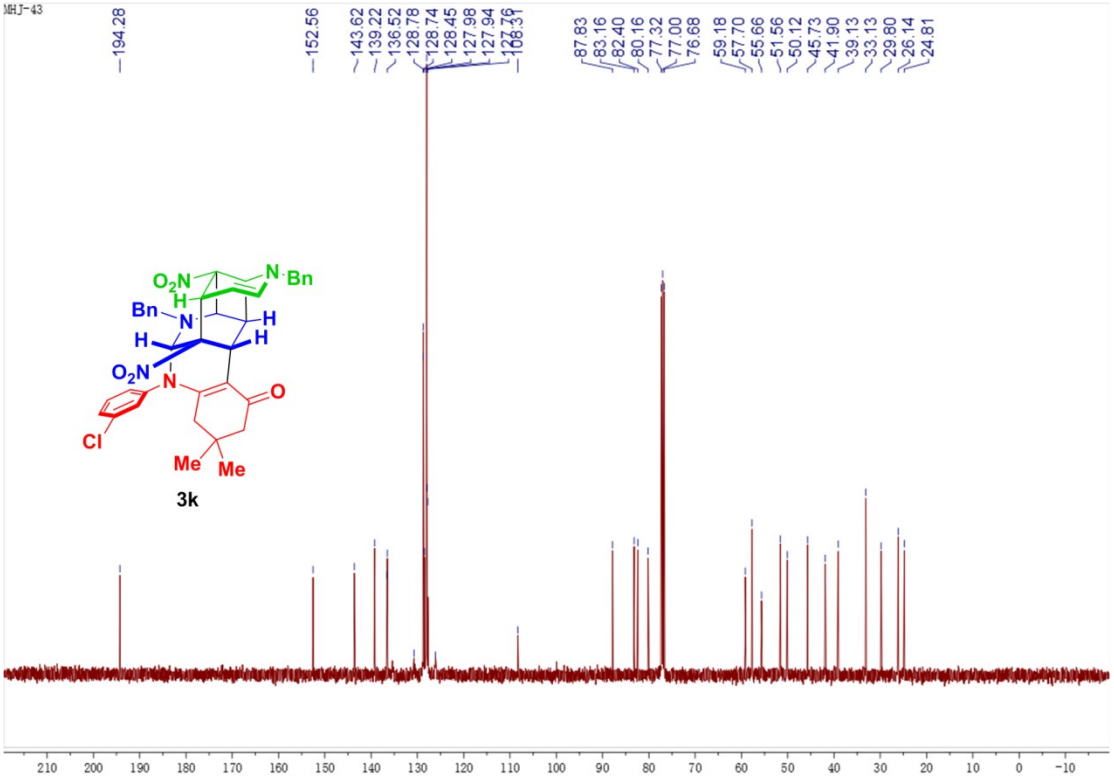
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127.94
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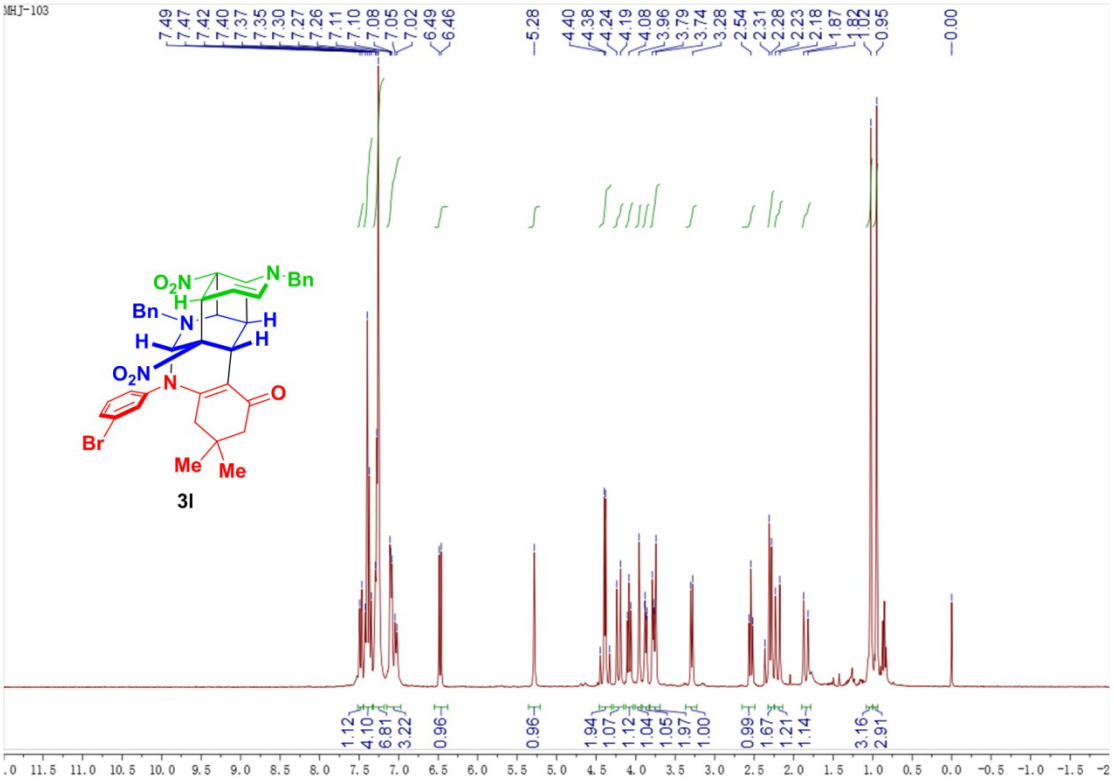
3k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7.10
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7.02
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6.46
5.28
4.40
4.38
4.24
4.19
4.08
3.96
3.79
3.74
3.28
2.54
2.31
2.28
2.23
2.18
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1.82
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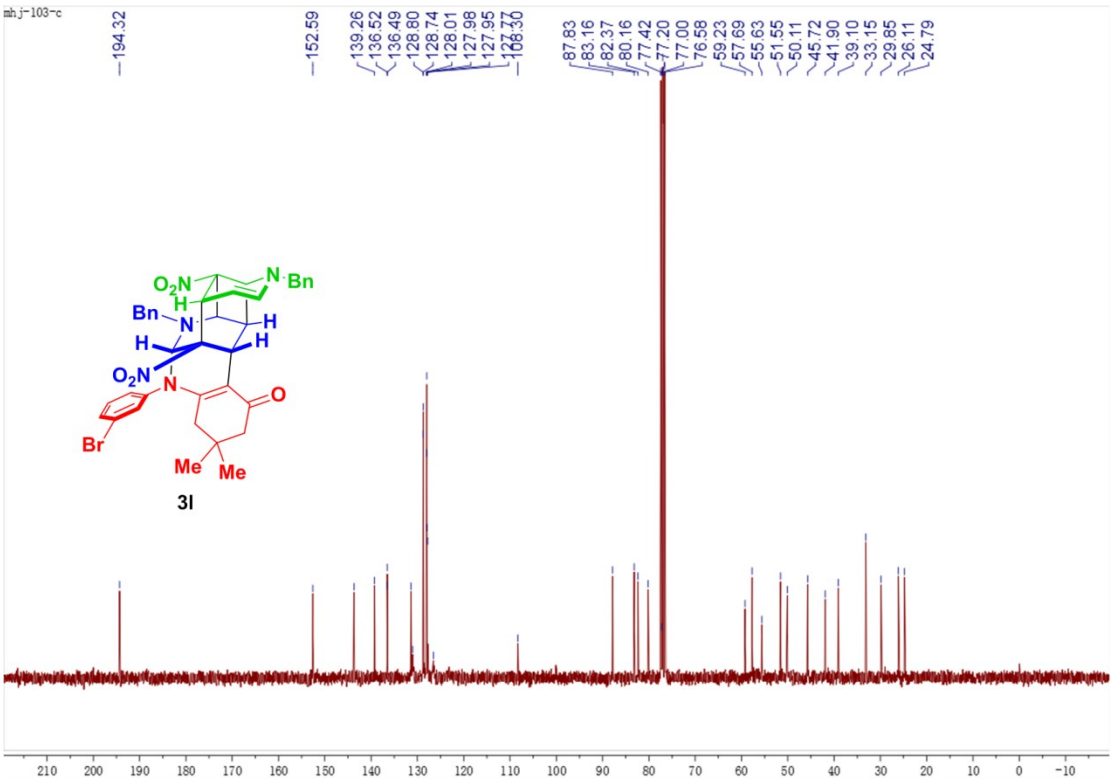
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26.11
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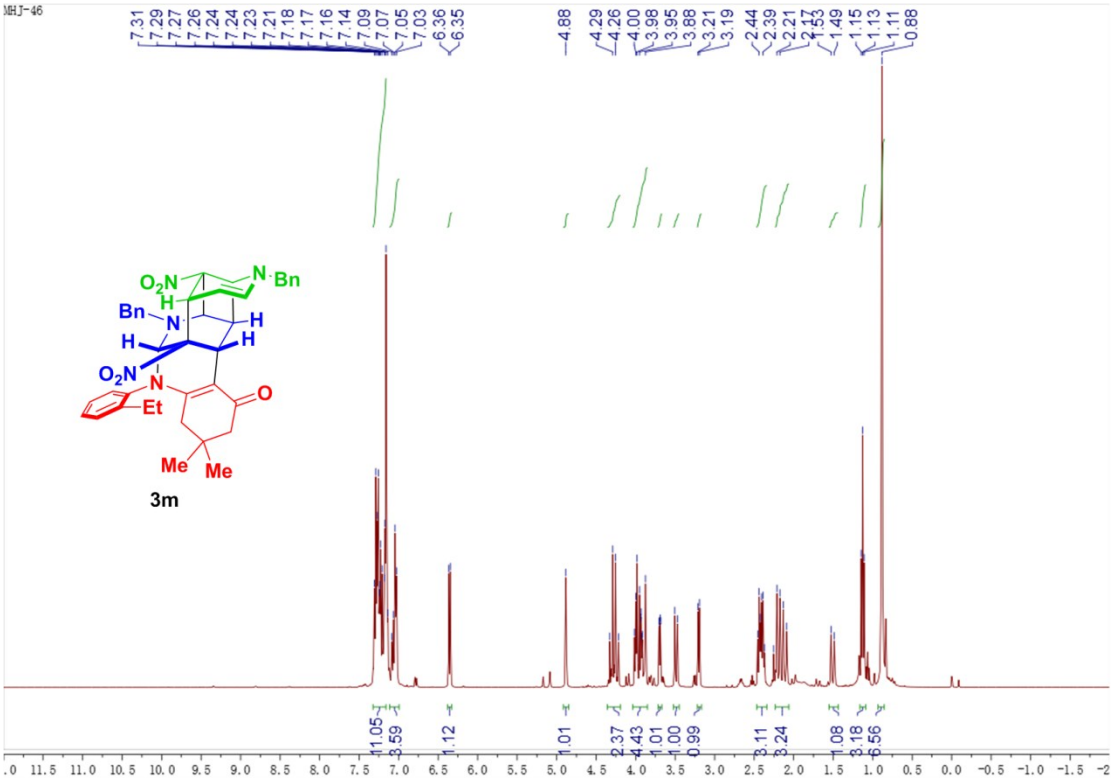
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7.07
7.05
7.03
6.36
6.35
4.88
4.29
4.26
4.00
3.98
3.95
3.88
3.21
3.19
2.44
2.39
2.21
2.17
1.53
1.49
1.15
1.13
1.11
0.88
11.05
8.59
1.12
1.01
2.37
4.43
1.01
1.00
0.99
3.11
3.24
1.08
8.18
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Bn
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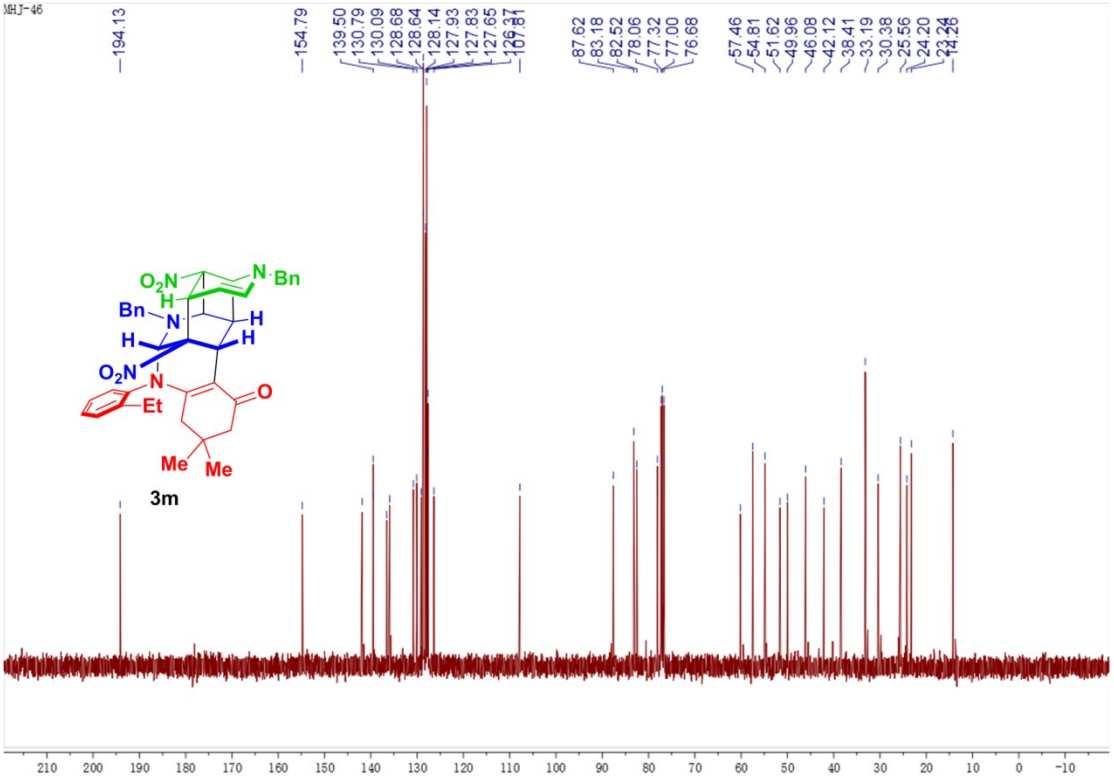
Et
O
Me
Me
3m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127.65
87.62
83.18
82.52
78.06
77.32
77.00
76.68
57.46
54.81
51.62
49.96
46.08
42.12
38.41
33.19
30.38
25.56
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H
Bn
N
H
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O2N
N
Et
O
Me
Me
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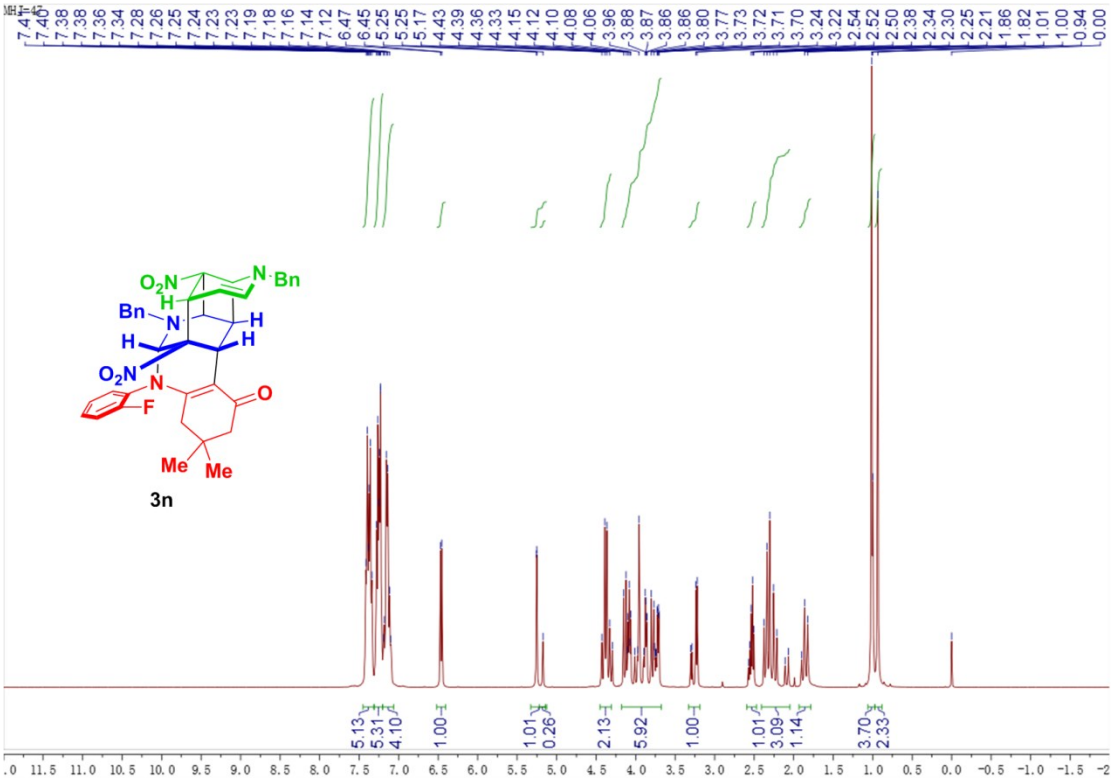
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7.23
7.19
7.18
7.16
7.14
7.12
6.47
6.45
5.25
5.25
5.17
4.43
4.39
4.36
4.33
4.15
4.12
4.10
4.08
4.06
3.96
3.88
3.87
3.86
3.86
3.80
3.77
3.73
3.72
3.71
3.70
3.24
3.22
2.54
2.52
2.50
2.38
2.34
2.30
2.25
2.21
1.86
1.82
1.01
1.00
0.94
0.00
5.13
5.31
4.10
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0.26
2.13
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1.00
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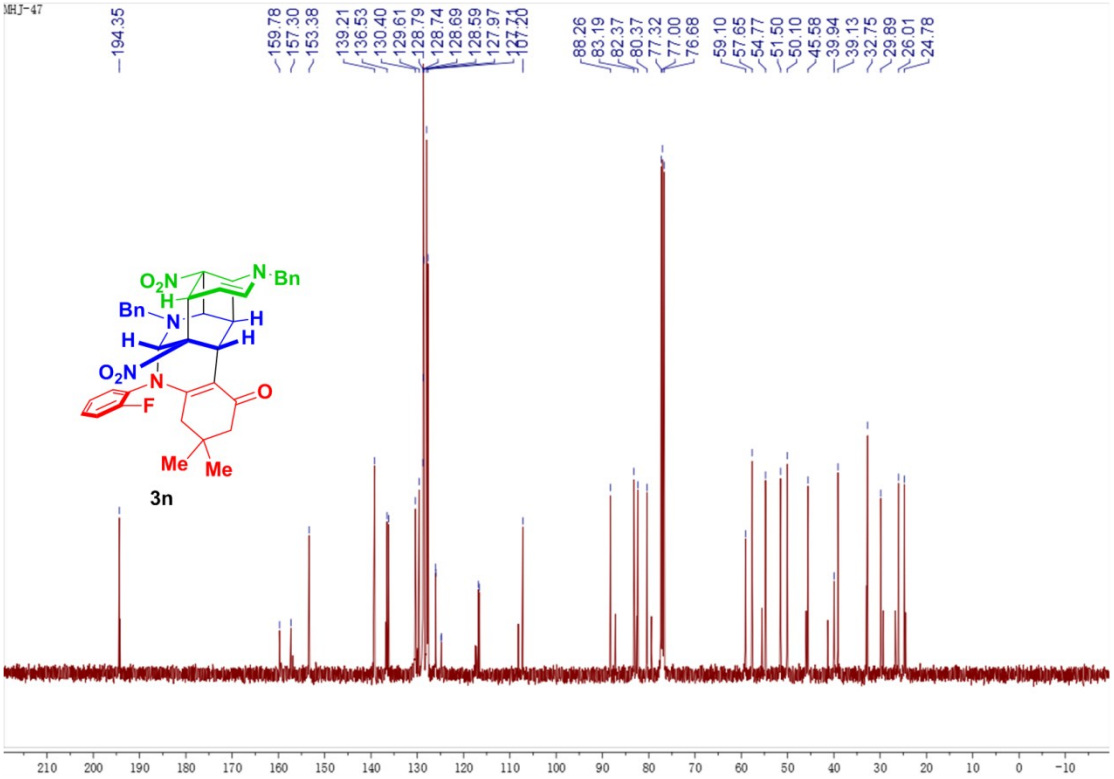
3.70
2.33
3n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130.40
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128.59
127.97
127.71
127.20
88.26
83.19
82.37
80.37
77.32
77.00
76.68
59.10
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51.50
50.10
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32.75
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26.01
24.78
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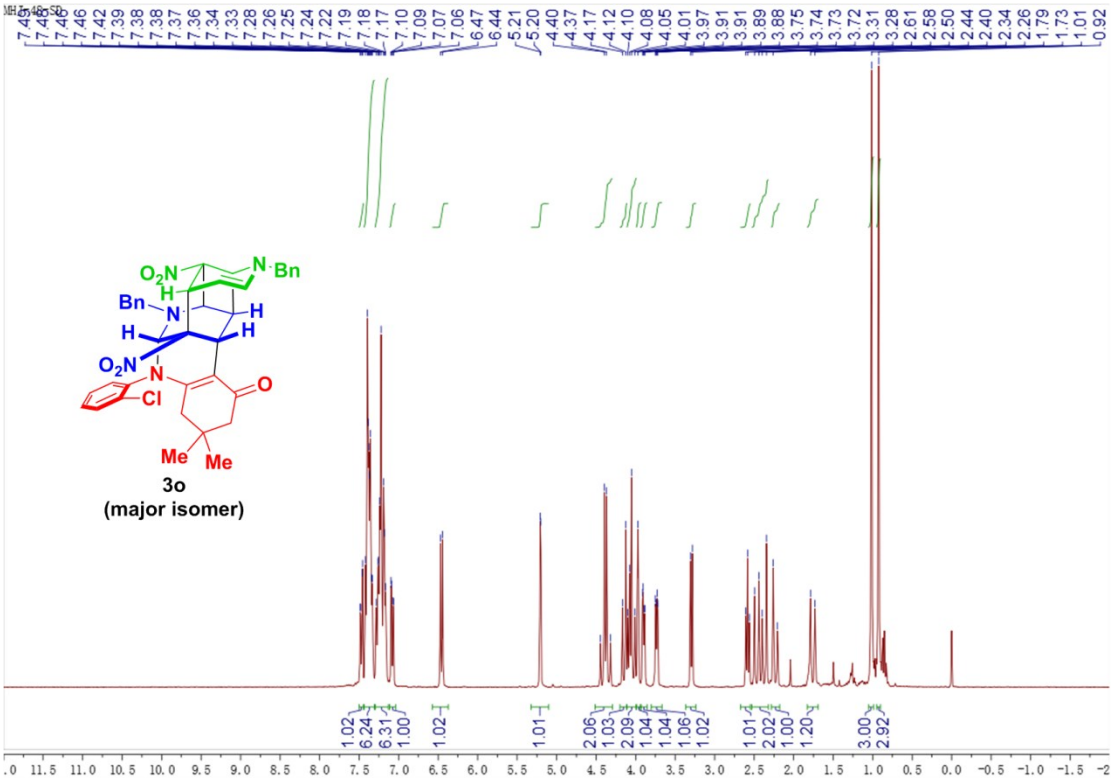
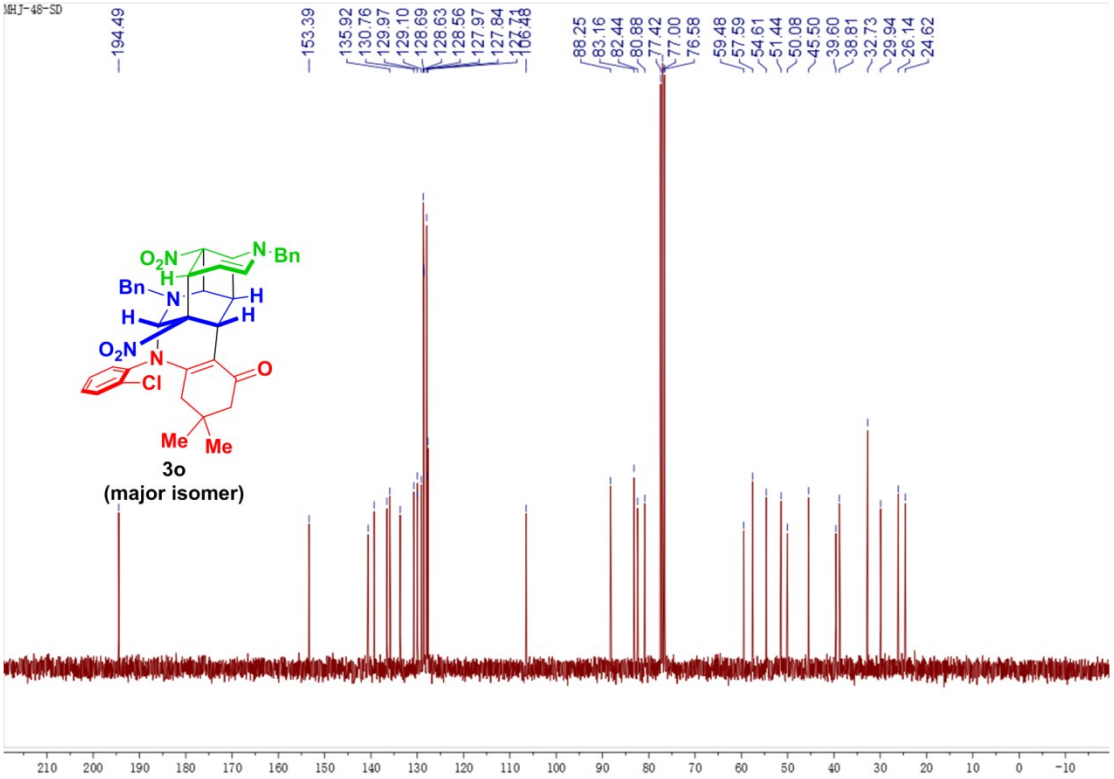
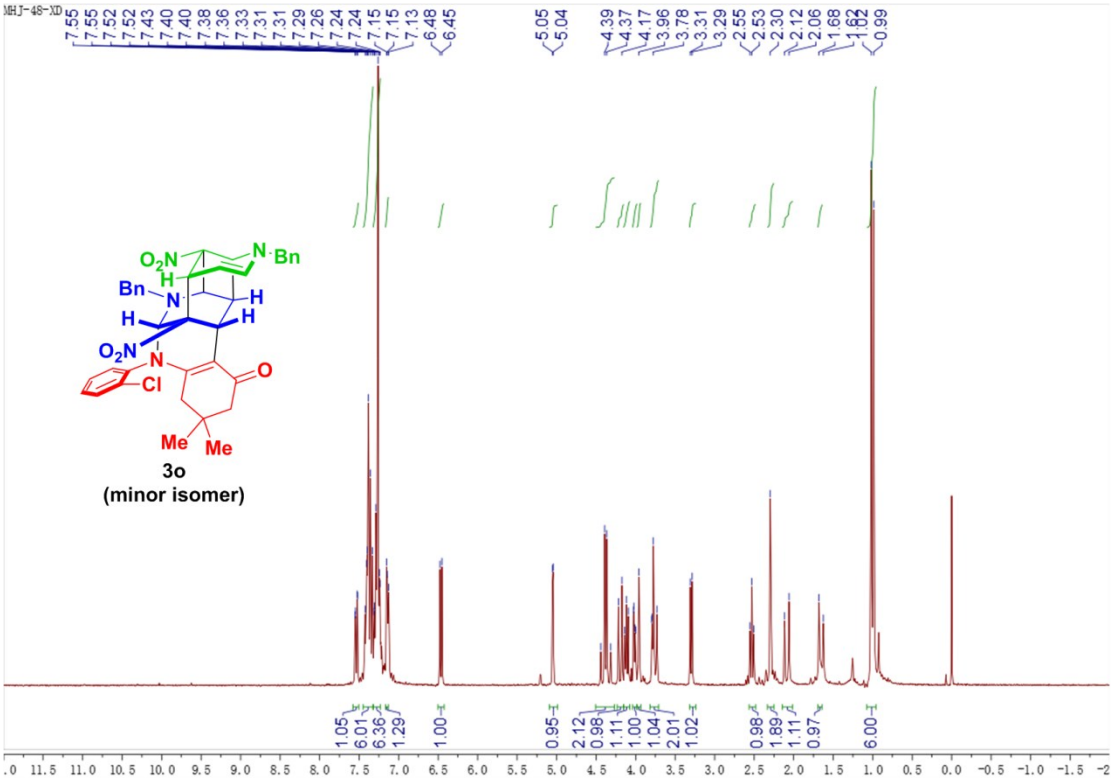

3o
(major isomer)


3o
(major isomer)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7.55
7.52
7.52
7.43
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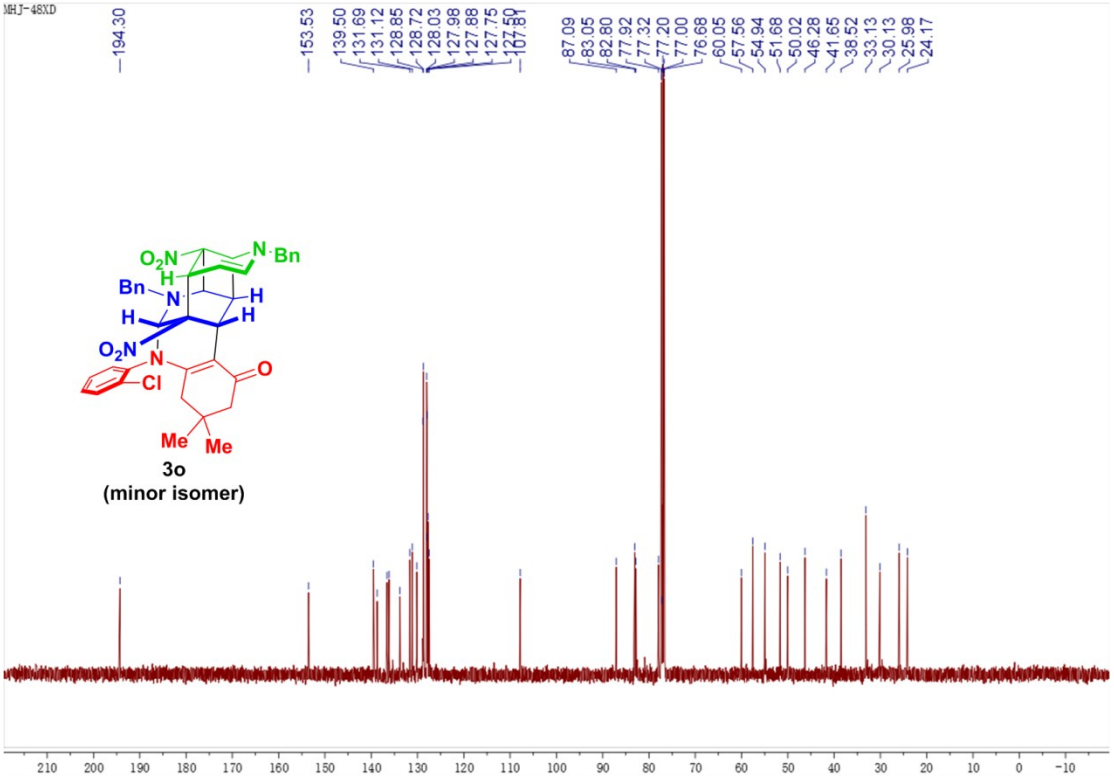
7.36
7.33
7.31
7.31
7.29
7.26
7.24
7.24
7.15
7.15
7.13
6.48
6.45
5.05
5.04
4.39
4.37
4.17
3.96
3.78
3.31
3.29
2.55
2.53
2.30
2.12
2.06
1.68
1.62
0.99
1.05
6.01
6.36
1.29
1.00
0.95
2.12
0.98
1.11
1.00
1.04
2.01
1.02
0.98
1.89
1.11
0.97
6.00
O2N
N·Bn
H
Bn
N
H
H
H
O2N
N
Cl
O
Me
Me
3o
(minor isomer)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139.50
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131.12
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128.72
128.03
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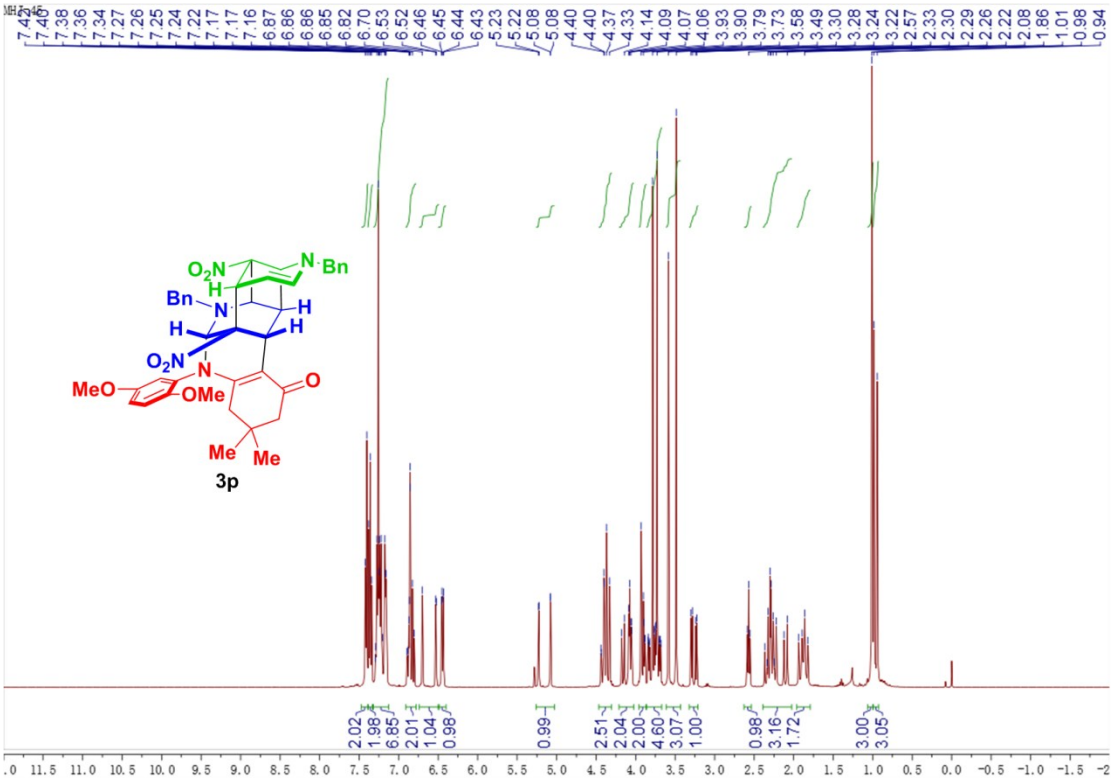
127.88
127.75
87.09
83.05
82.80
77.92
77.32
77.20
77.00
76.68
60.05
57.56
54.94
51.68
50.02
46.28
41.65
38.52
33.13
30.13
25.98
24.17
O2N
N·Bn
H
Bn
N
H
H
H
O2N
N
Cl
O
Me
Me
3o
(minor isomer)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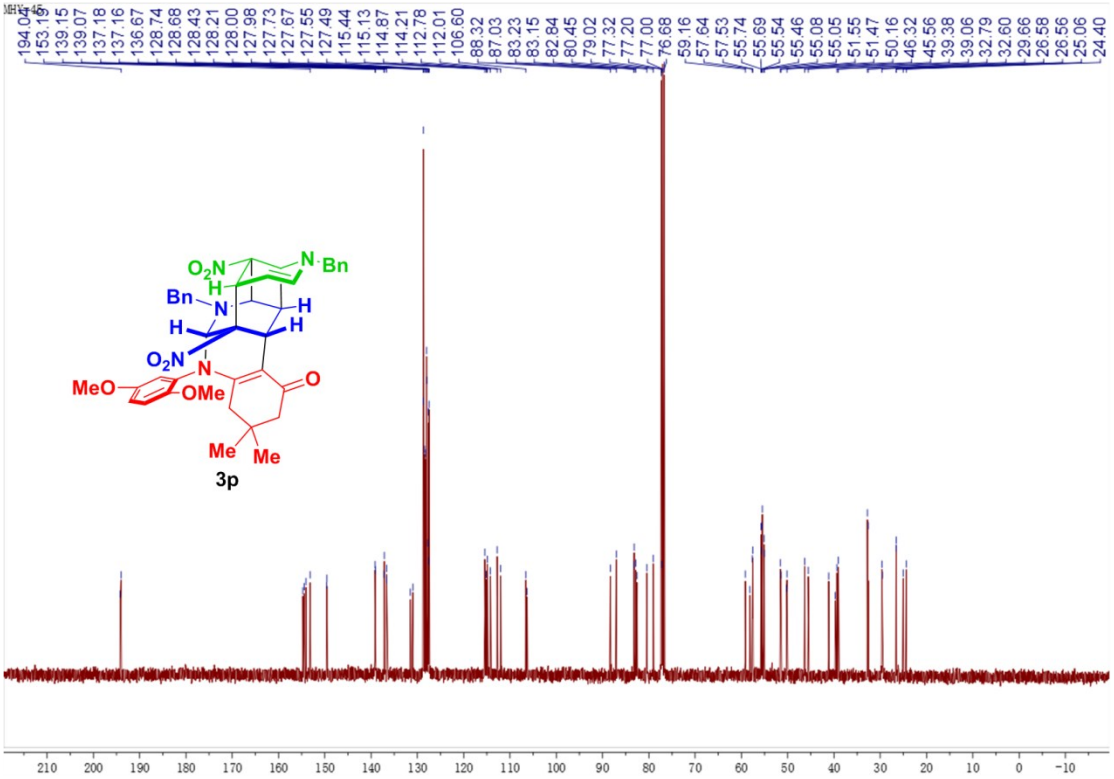
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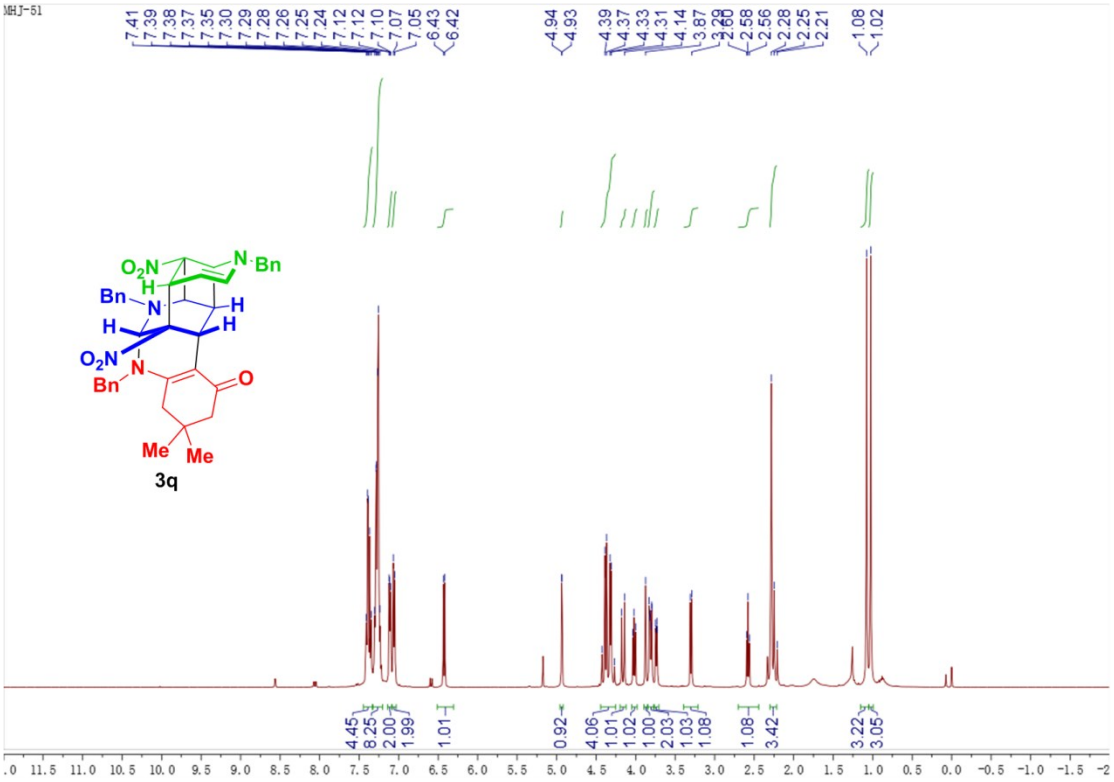
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7.39
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7.24
7.12
7.12
7.10
7.07
7.05
6.43
6.42
4.94
4.93
4.39
4.37
4.33
4.31
4.14
3.87
3.29
3.60
2.58
2.56
2.28
2.25
2.21
1.08
1.02
3q
4.45
8.25
2.00
1.99
1.01
0.92
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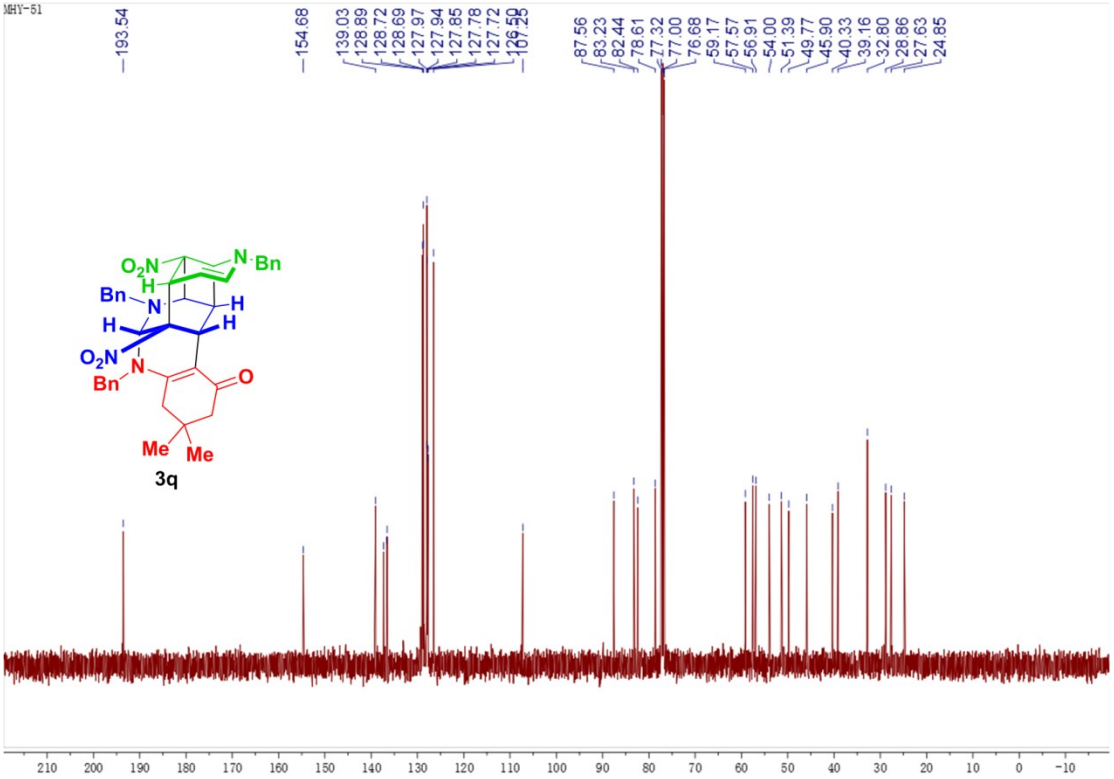
1.01
1.02
1.00
2.03
1.03
1.08
1.08
3.42
3.22
3.05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127.97
127.94
127.85
127.78
127.72
126.59
87.56
83.23
82.44
78.61
77.32
77.00
76.68
59.17
57.57
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51.39
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32.80
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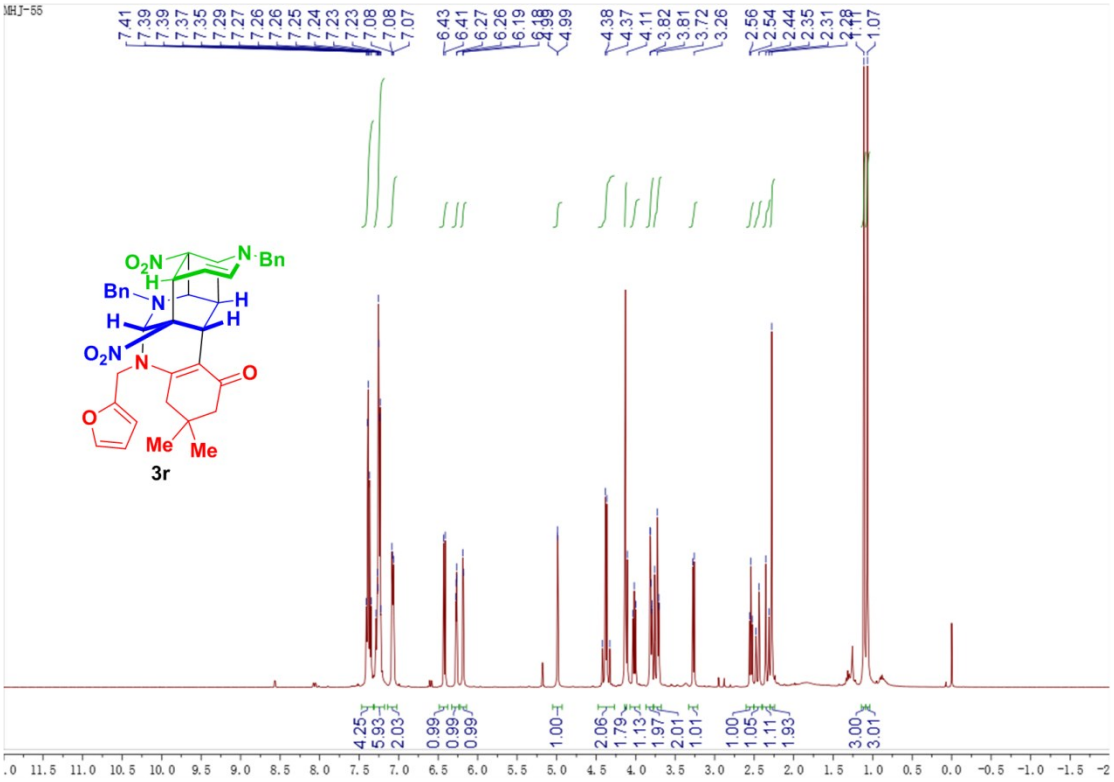
27.63
24.85
3q


MHJ-55
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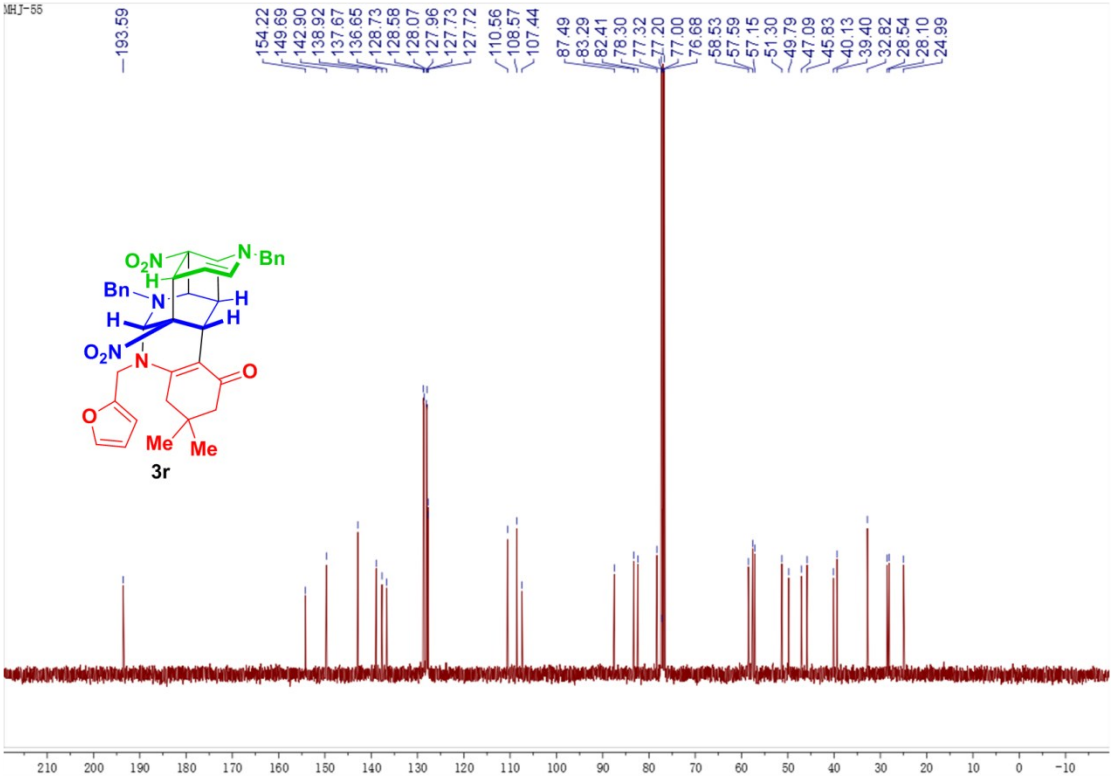
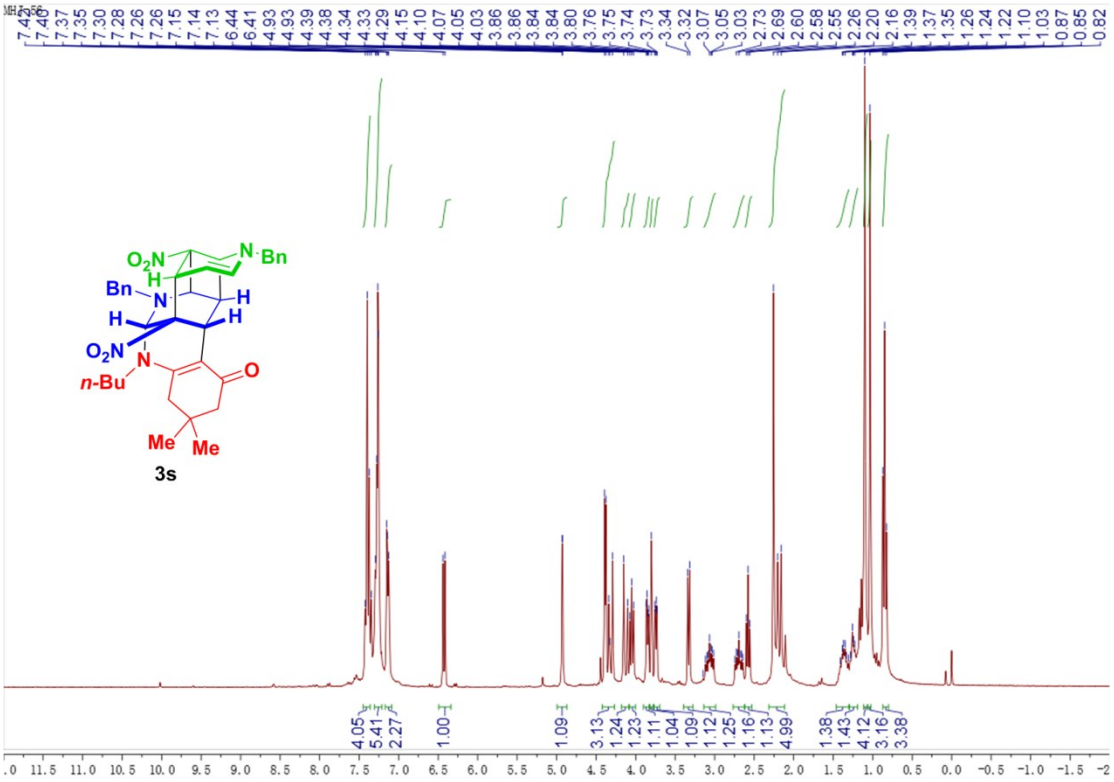

MHJ-55
3r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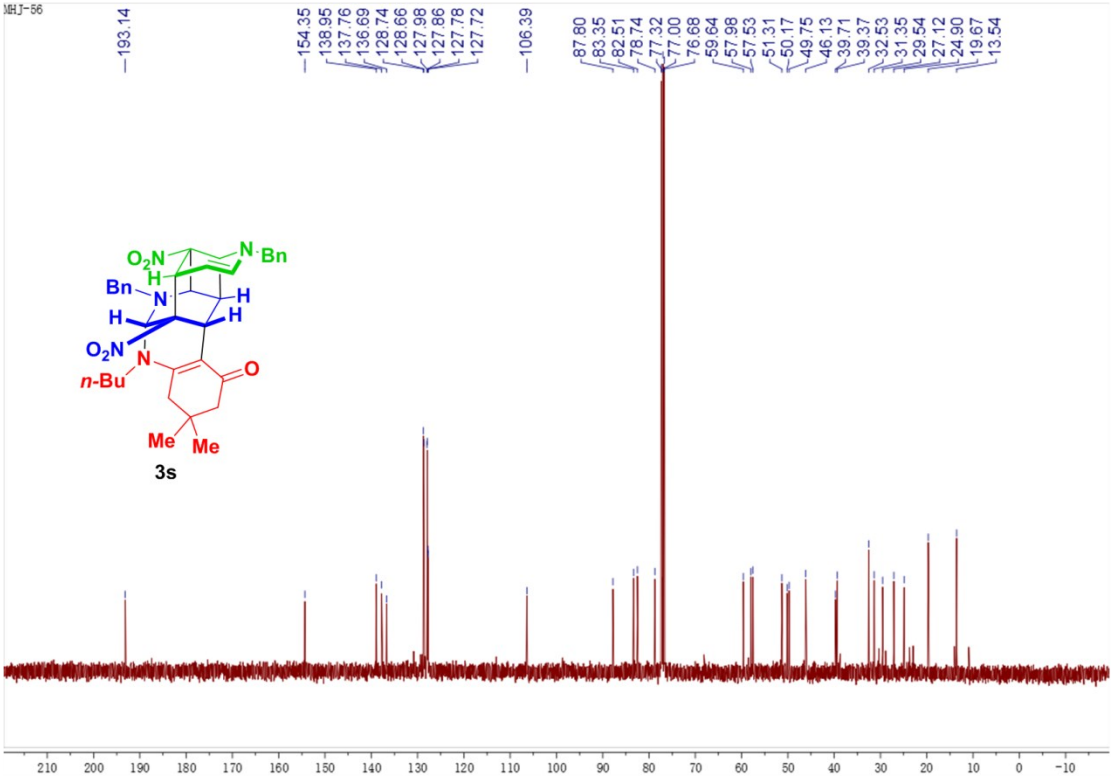
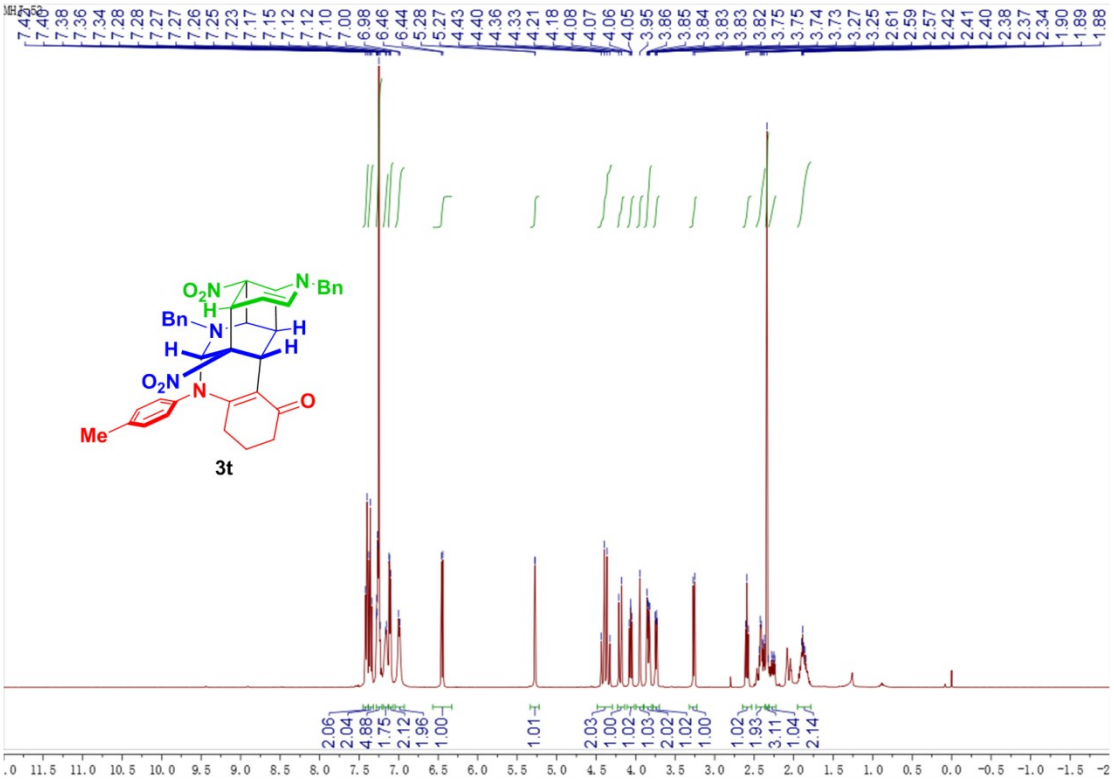

3s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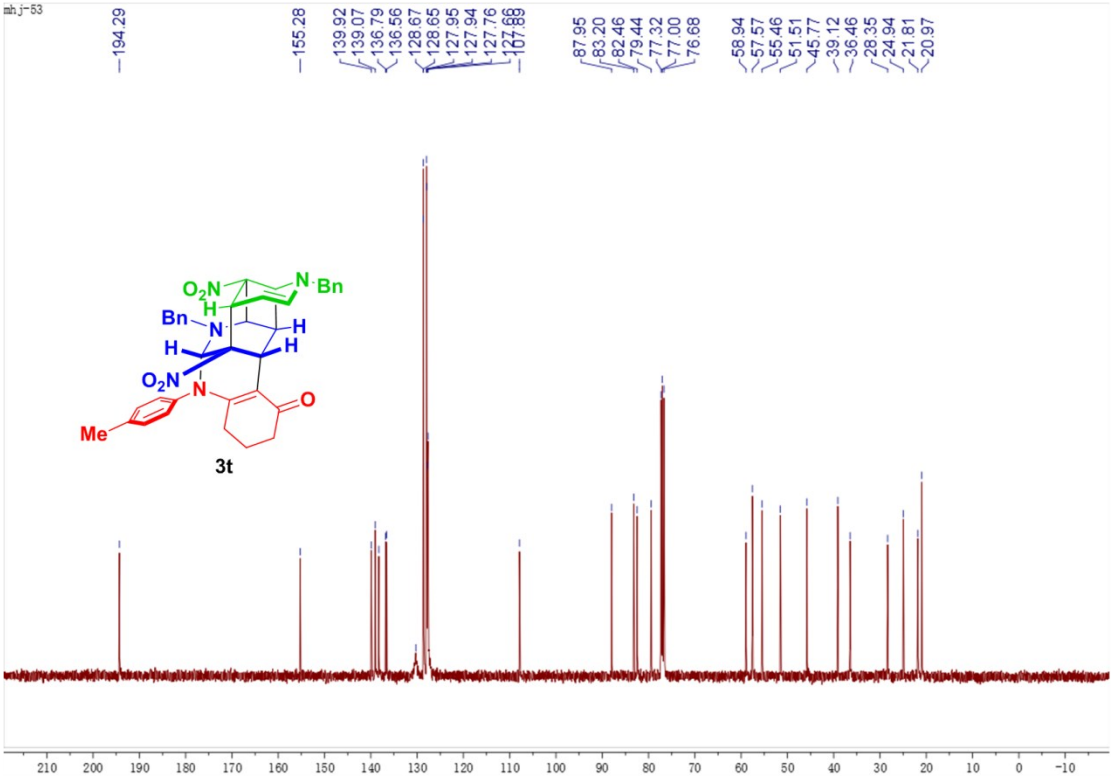
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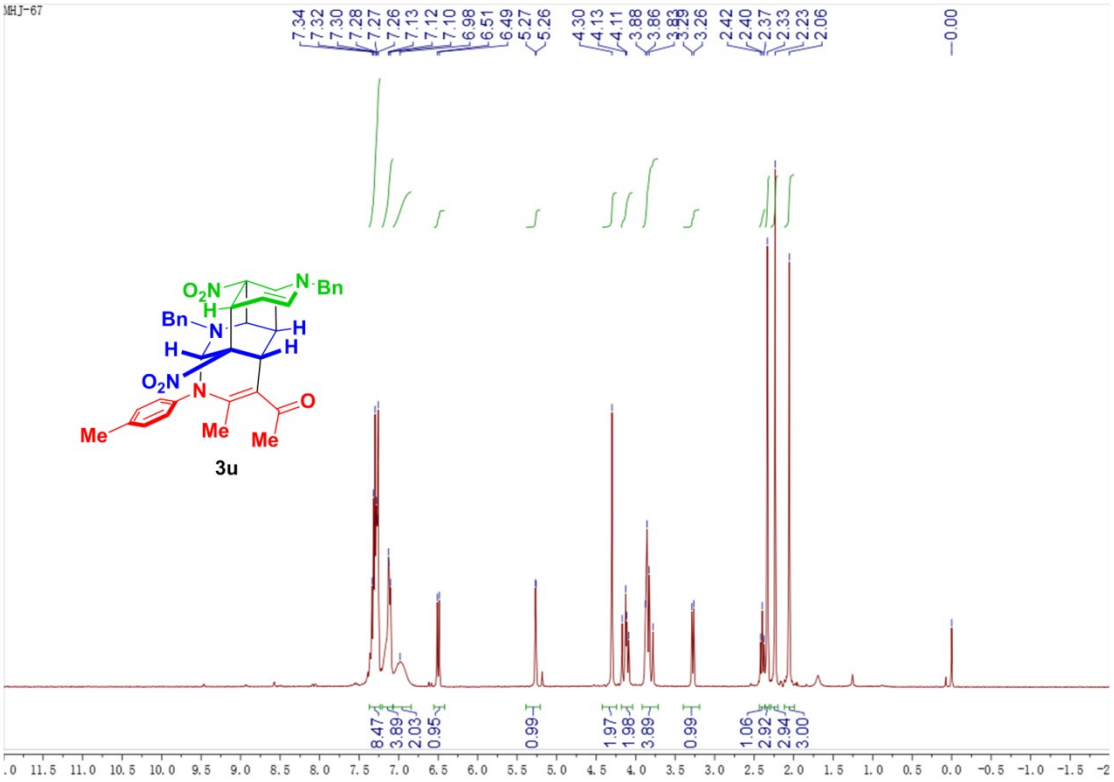
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7.13
7.12
7.10
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6.51
6.49
5.27
5.26
4.30
4.13
4.11
3.88
3.86
3.26
2.42
2.40
2.37
2.33
2.23
2.06
0.00
8.47
3.89
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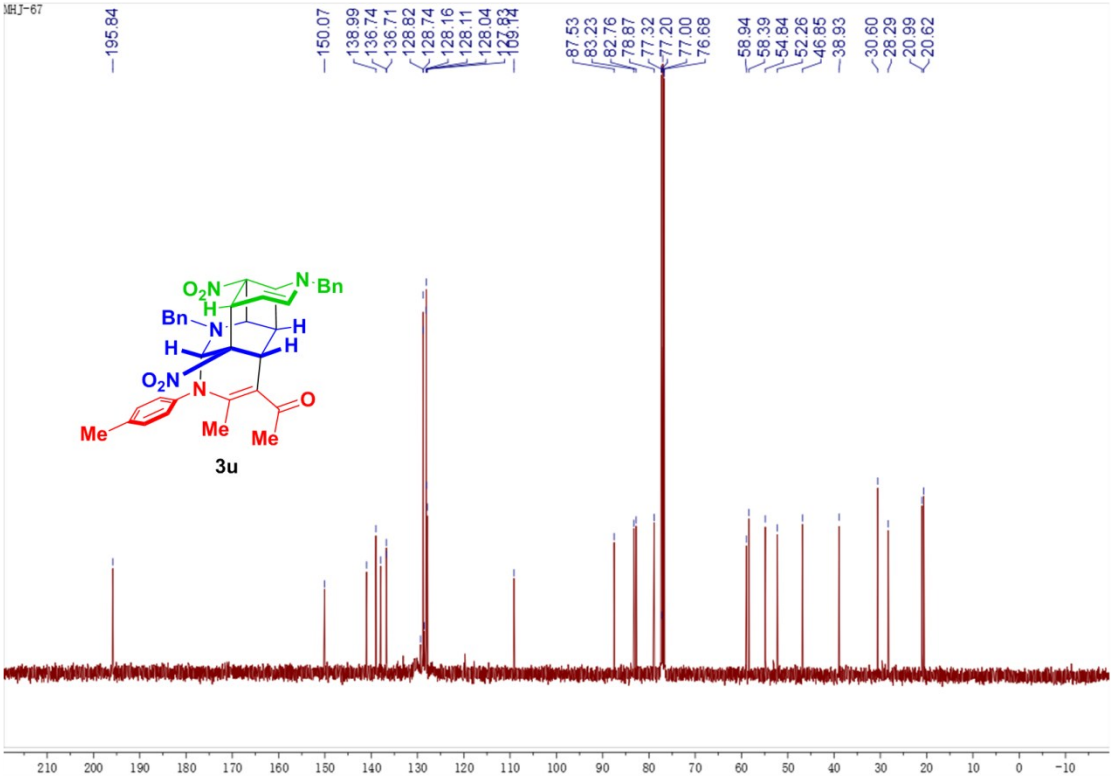
0.99
1.97
1.98
3.89
0.99
1.06
2.92
2.94
3.00
3u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136.71
128.82
128.74
128.16
128.11
128.04
87.53
83.23
82.76
78.87
77.32
77.20
77.00
76.68
58.94
58.39
54.84
52.26
46.85
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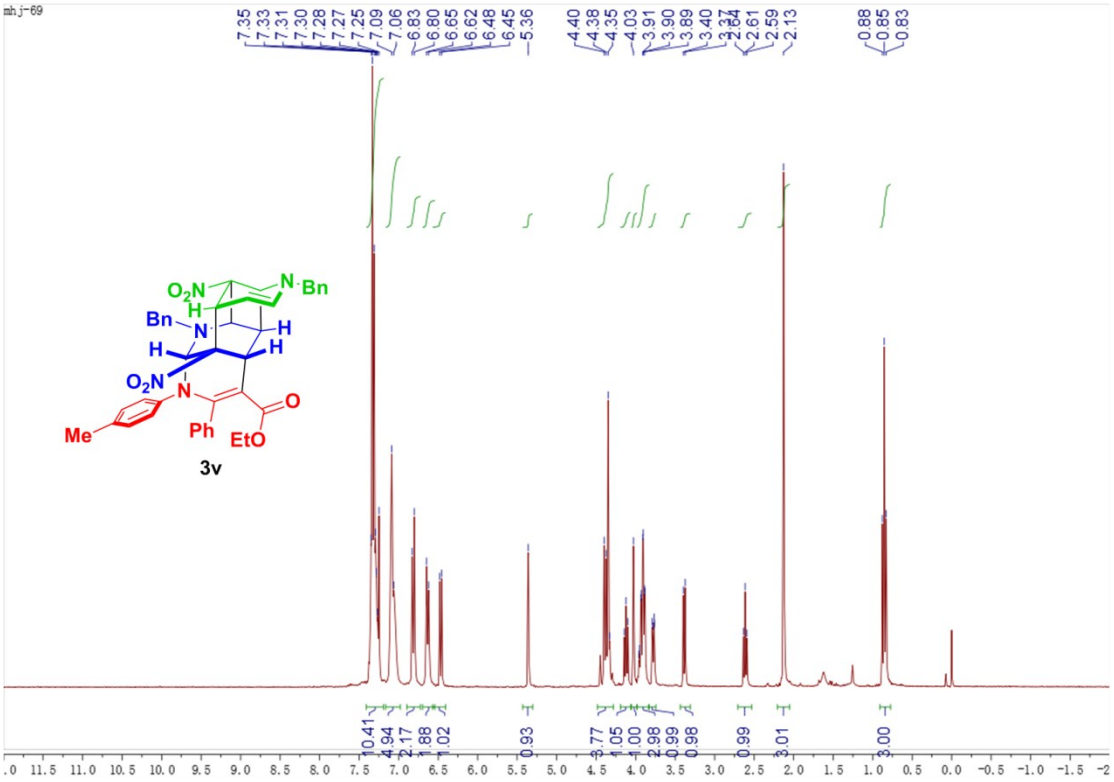
30.60
28.29
20.99
20.62
3u


mhj-69
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7.25
7.09
7.06
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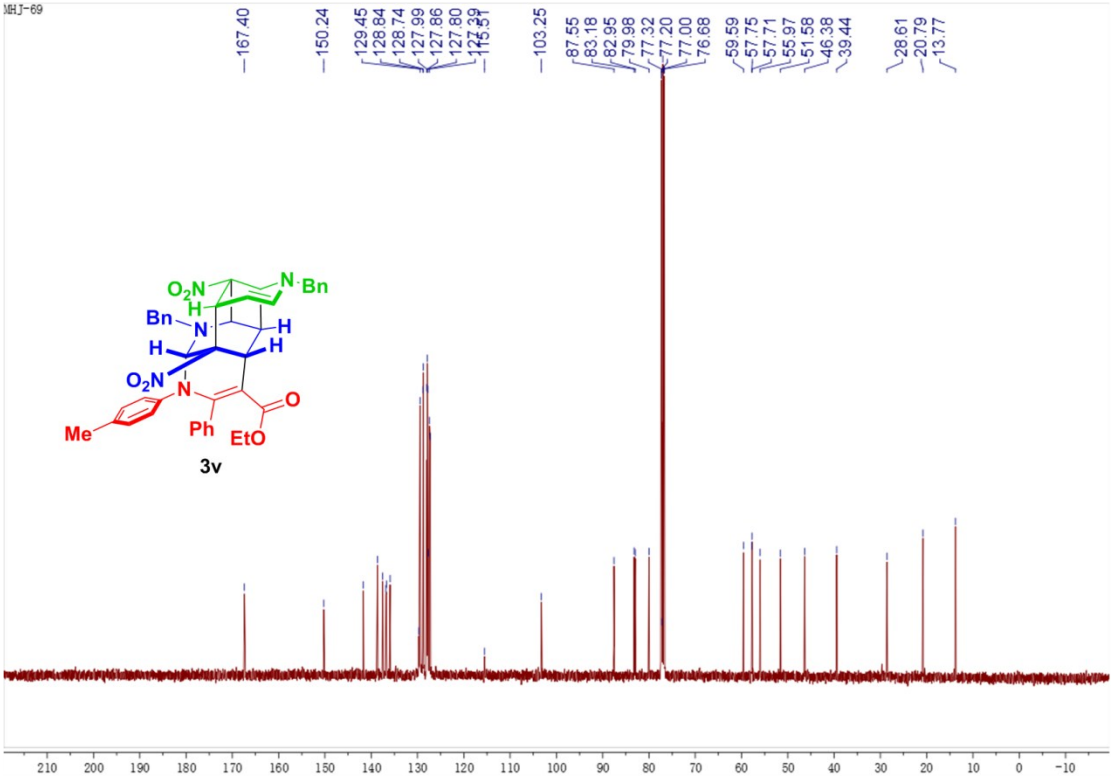
6.80
6.65
6.62
6.48
6.45
5.36
4.40
4.38
4.35
4.03
3.91
3.90
3.89
3.40
2.64
2.61
2.59
2.13
0.88
0.85
0.83
10.41
4.94
2.17
1.88
1.02
0.93
3.77
1.05
1.00
2.98
0.99
0.98
0.99
3.01
3.00
O2N
N·Bn
H
Bn
N
H
H
H
O2N
N
O
Me
Ph
EtO
3v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127.80
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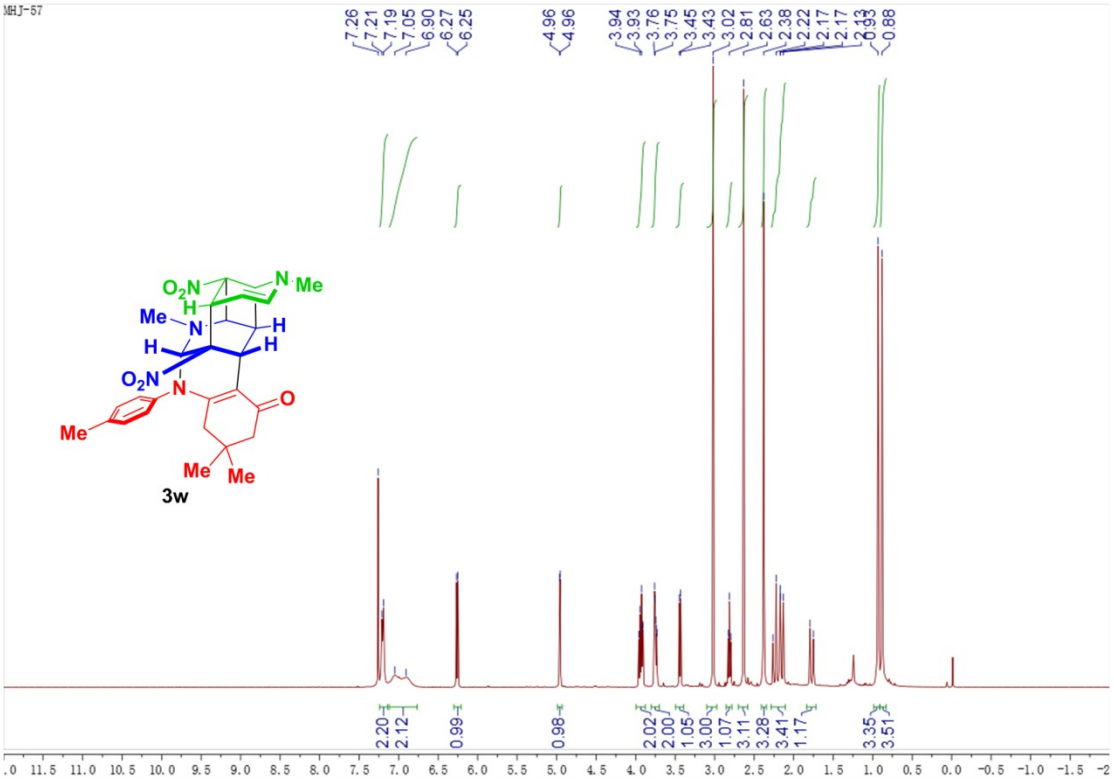
82.95
79.98
77.32
77.20
77.00
76.68
59.59
57.75
57.71
55.97
51.58
46.38
39.44
28.61
20.79
13.77
O2N
N·Bn
H
Bn
N
H
H
H
O2N
N
O
Me
Ph
EtO
3v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6.25
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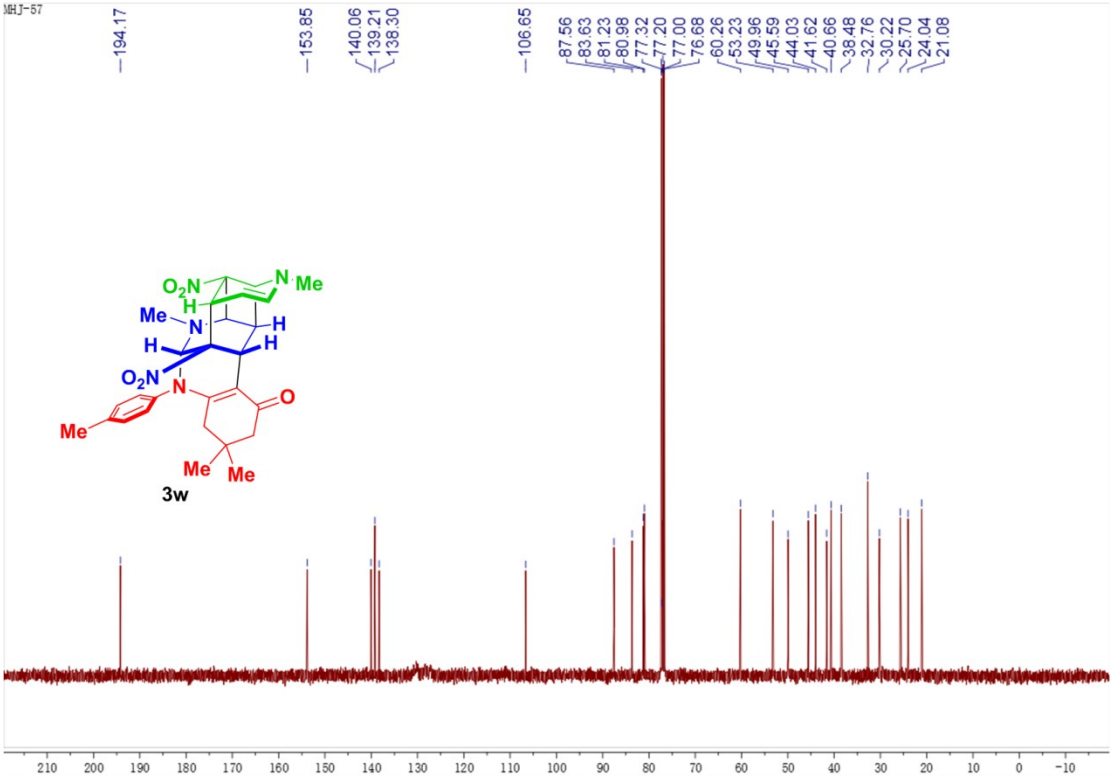
4.96
3.94
3.93
3.76
3.75
3.45
3.43
3.02
2.81
2.63
2.38
2.22
2.17
2.17
2.13
0.93
0.88
3w
2.20
2.12
0.99
0.98
2.02
2.00
1.05
3.00
1.07
3.11
3.28
3.41
1.17
3.35
3.51


MHJ-57
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83.63
81.23
80.98
77.32
77.20
77.00
76.68
60.26
53.23
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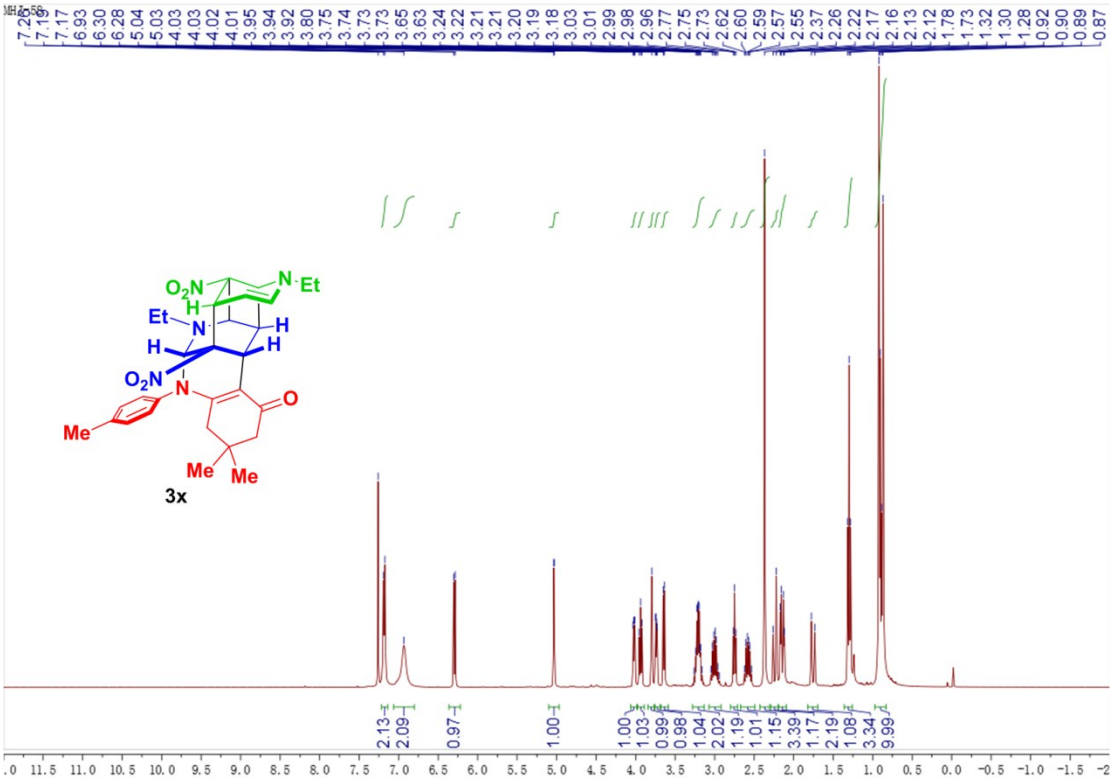
44.03
41.62
40.66
38.48
32.76
30.22
25.70
24.04
21.08
3w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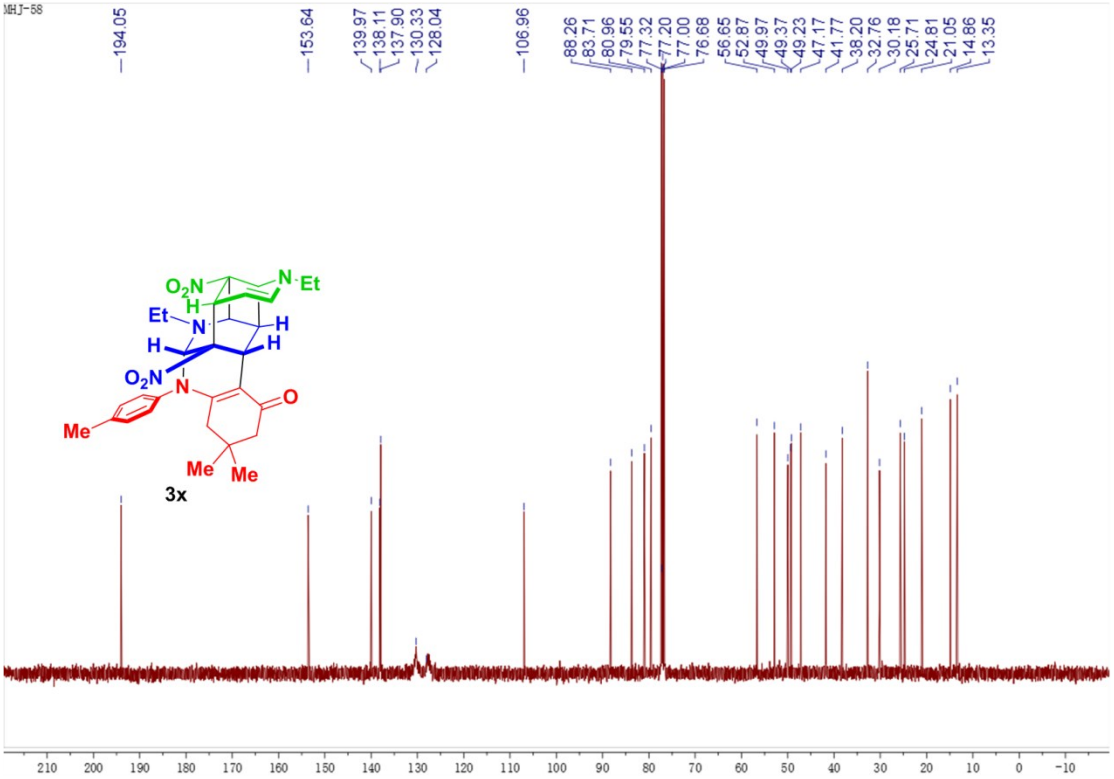
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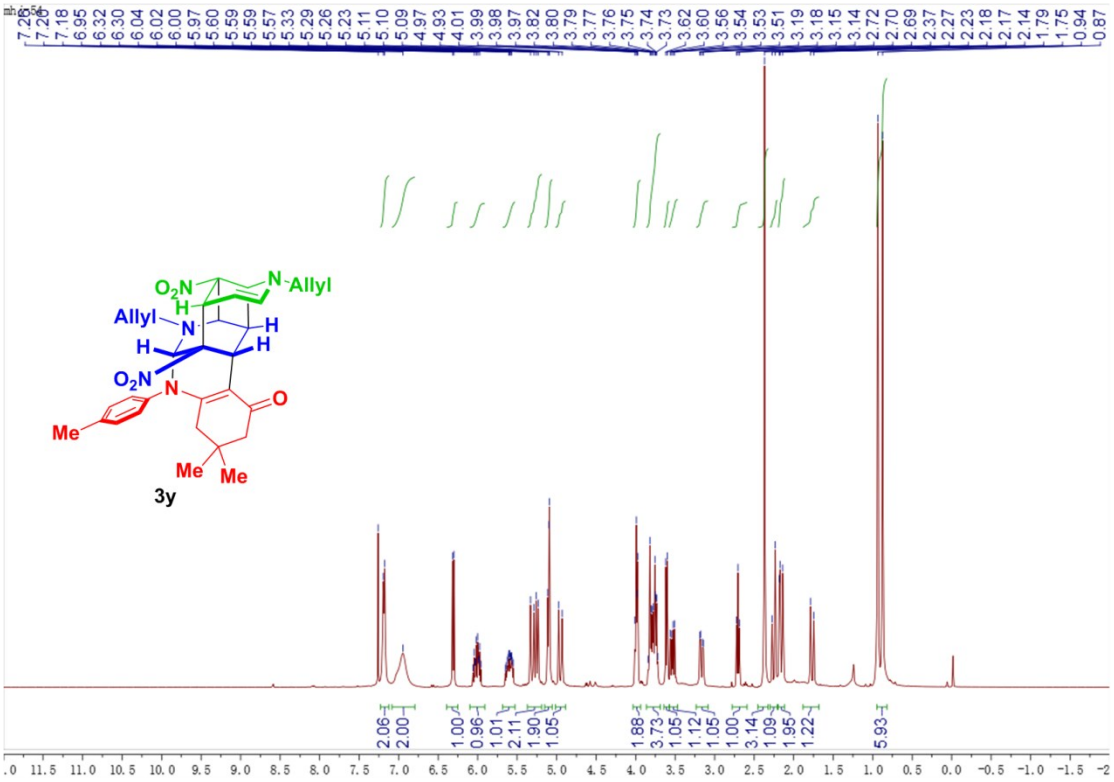
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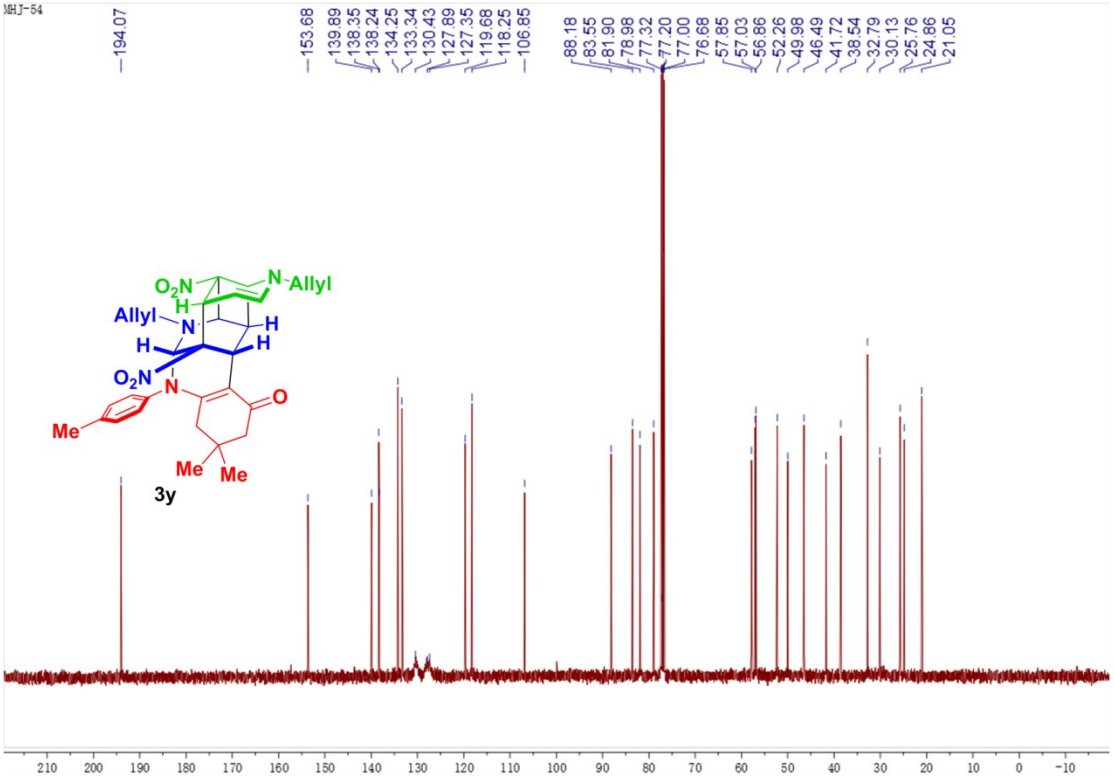
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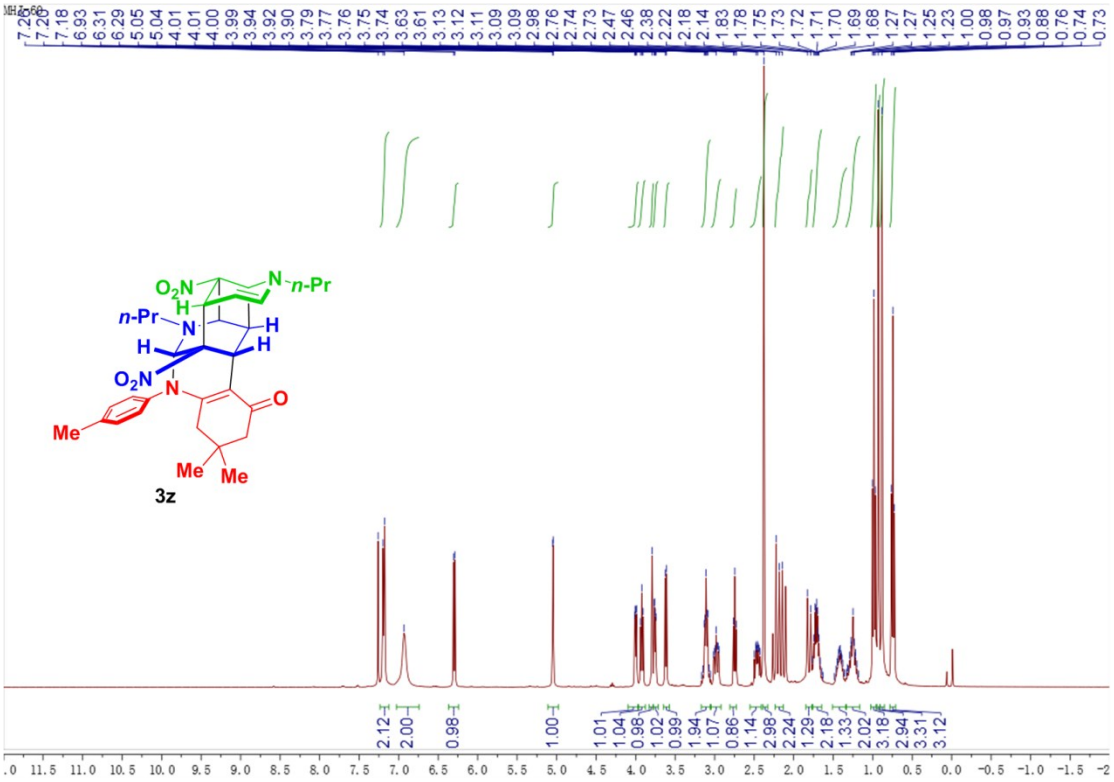
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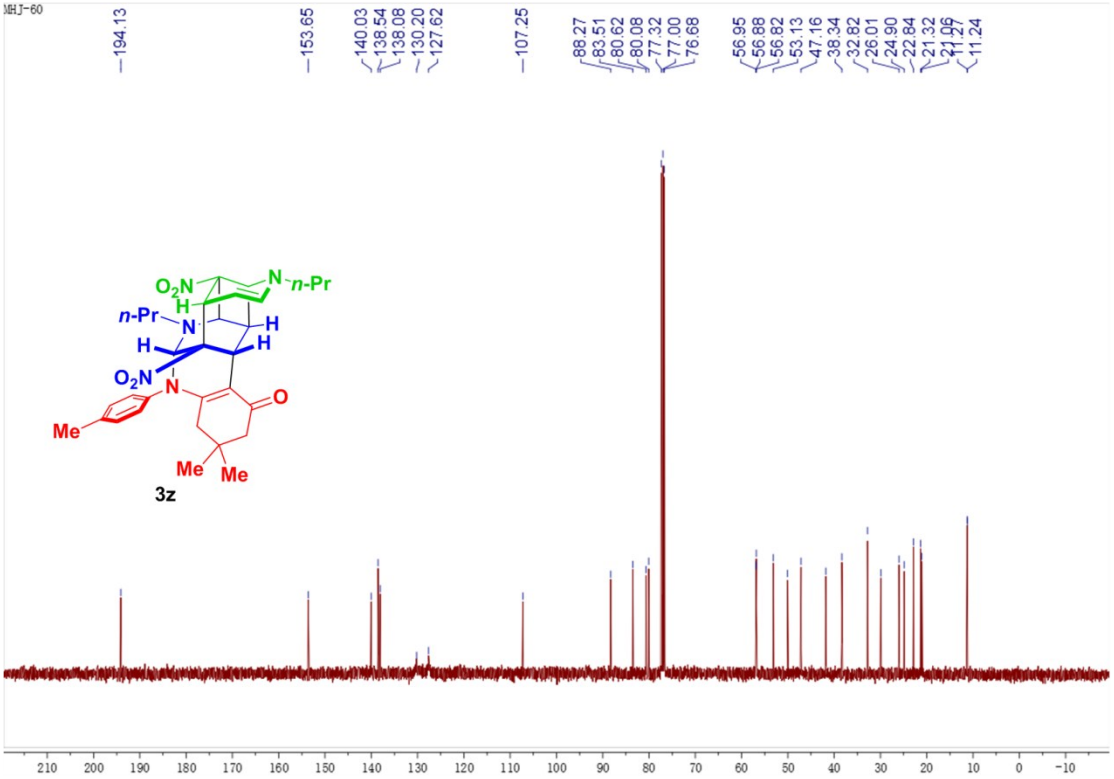
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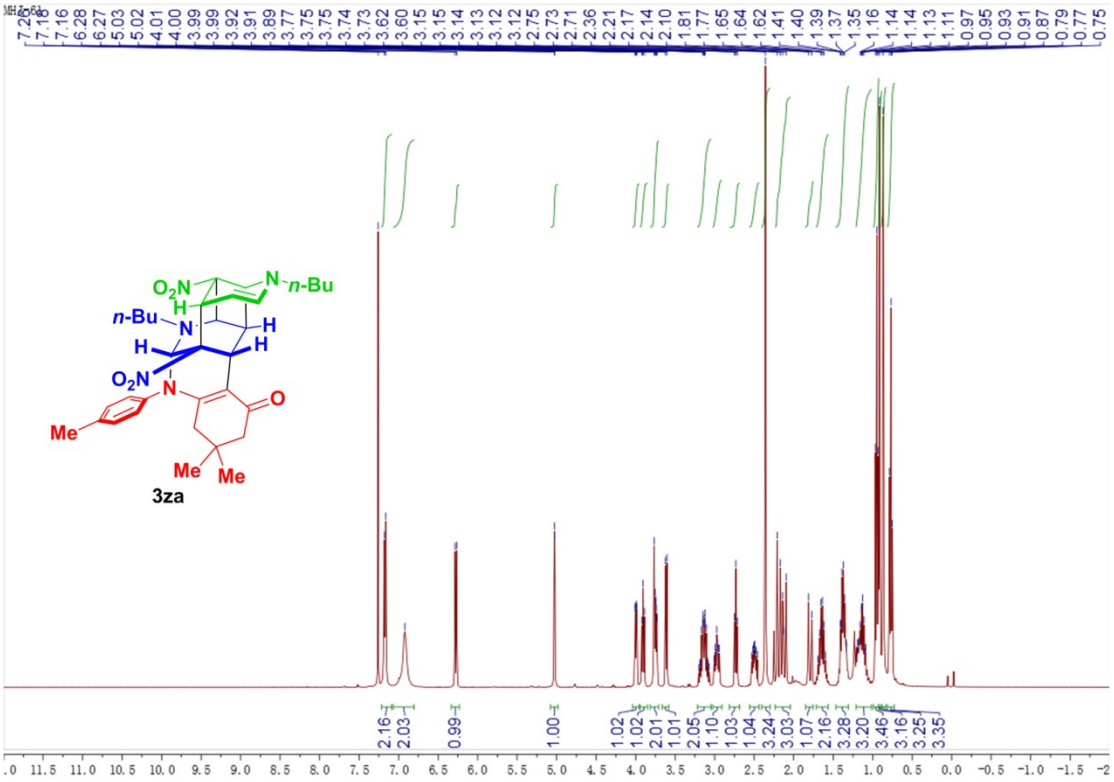
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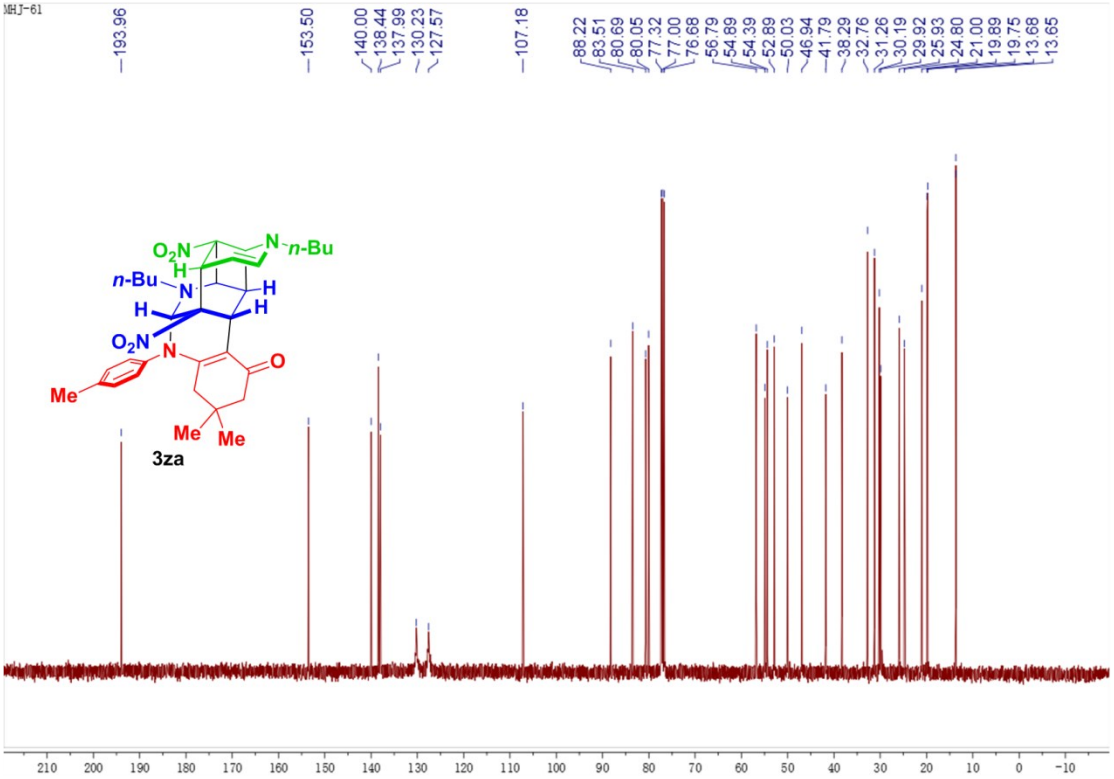
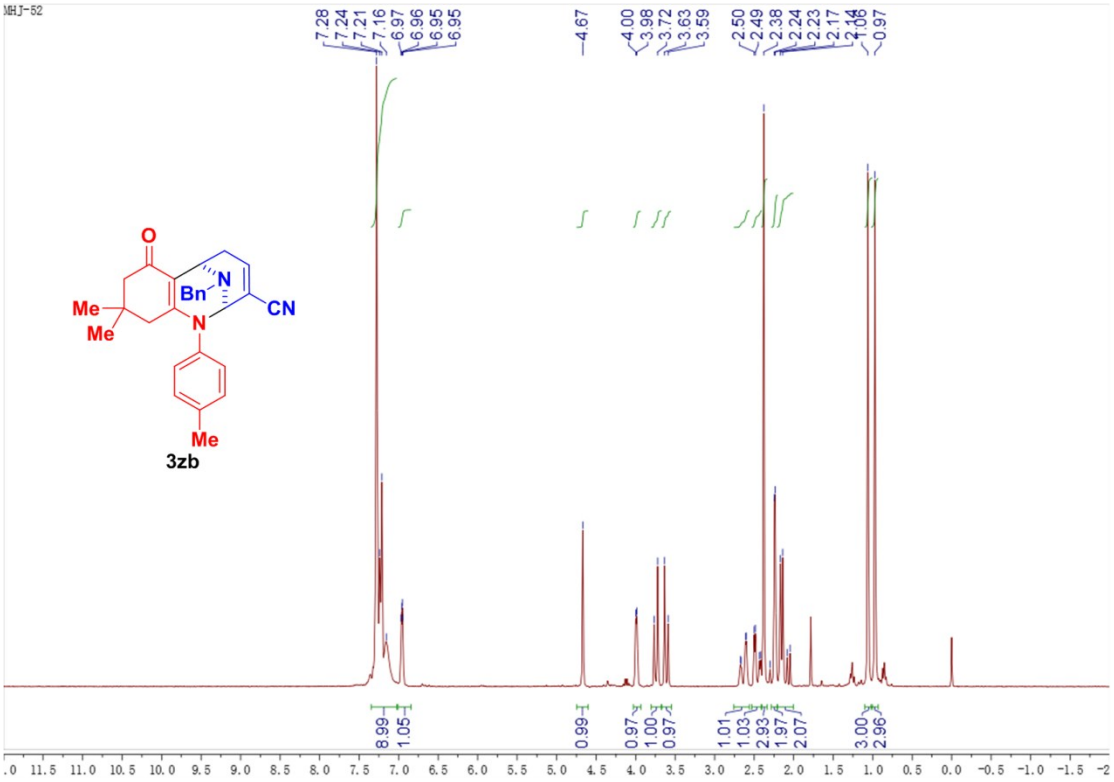

3za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4.00
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3.72
3.63
3.59
2.50
2.49
2.38
2.24
2.23
2.17
1.08
0.97
O
Bn
N
CN
Me
Me
N
Me
3zb
8.99
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1.00
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1.01
1.03
2.93
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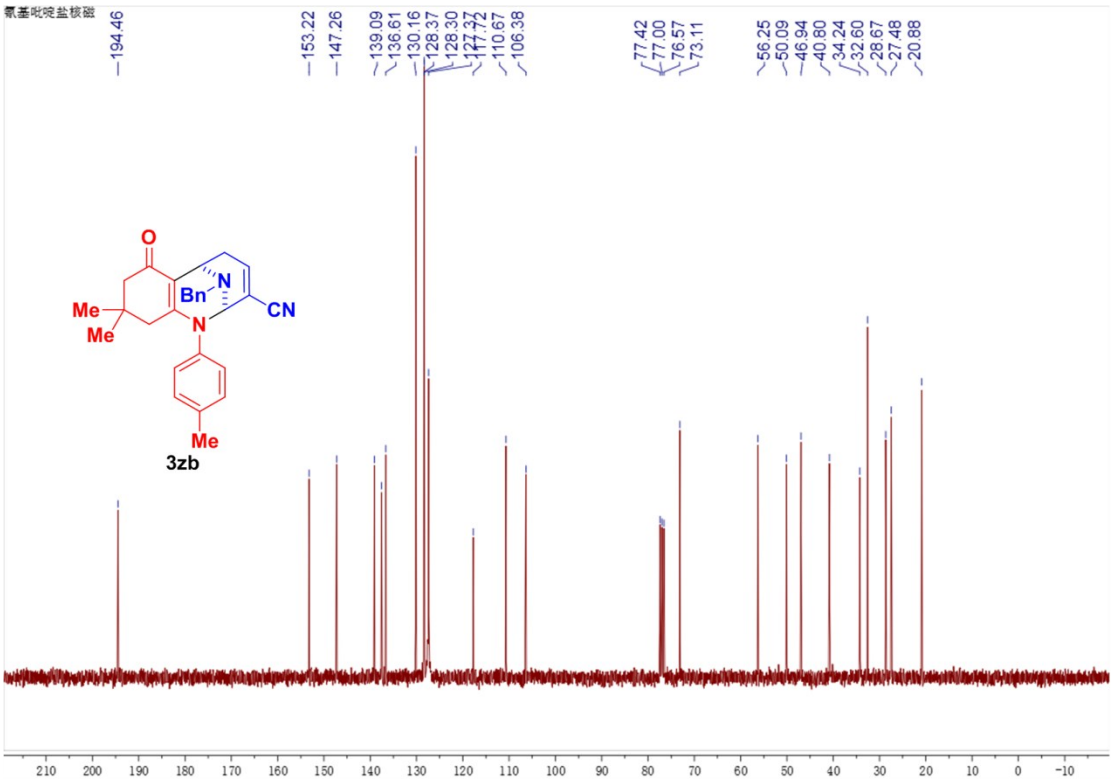
2.96


氰基吡啶盐核磁
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147.26
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136.61
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128.30
127.37
127.32
110.67
106.38
77.42
77.00
76.57
73.11
56.25
50.09
46.94
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32.60
28.67
27.48
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Bn
N
CN
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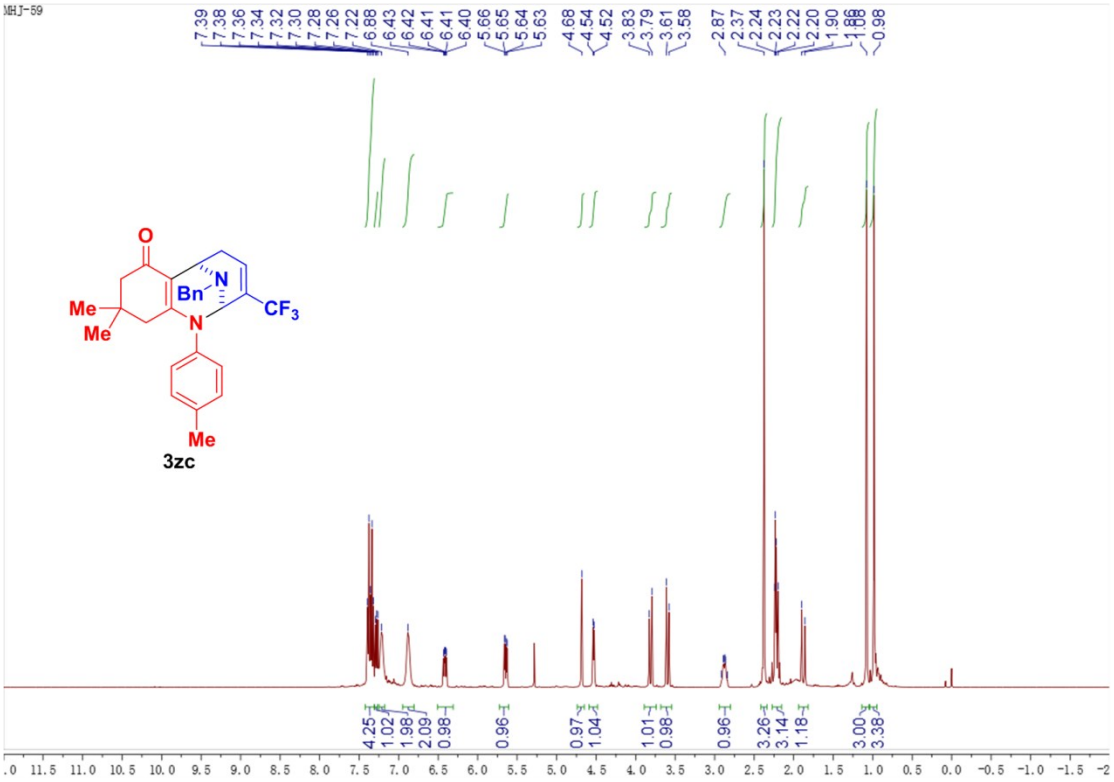
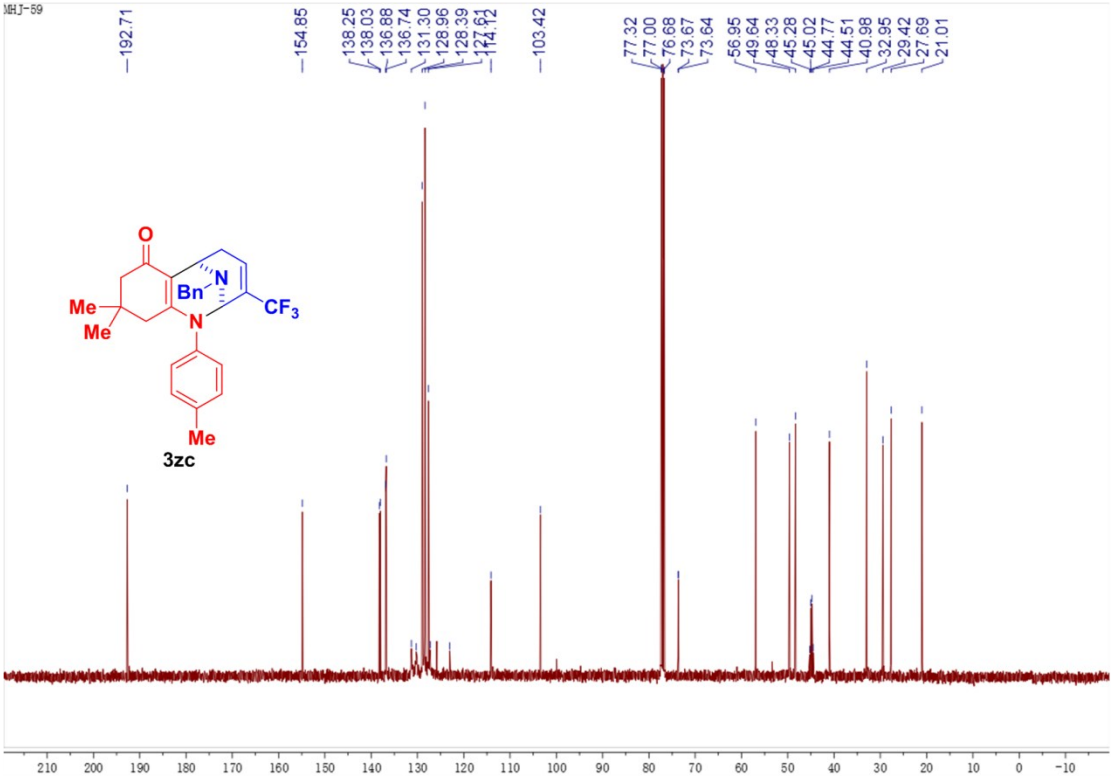
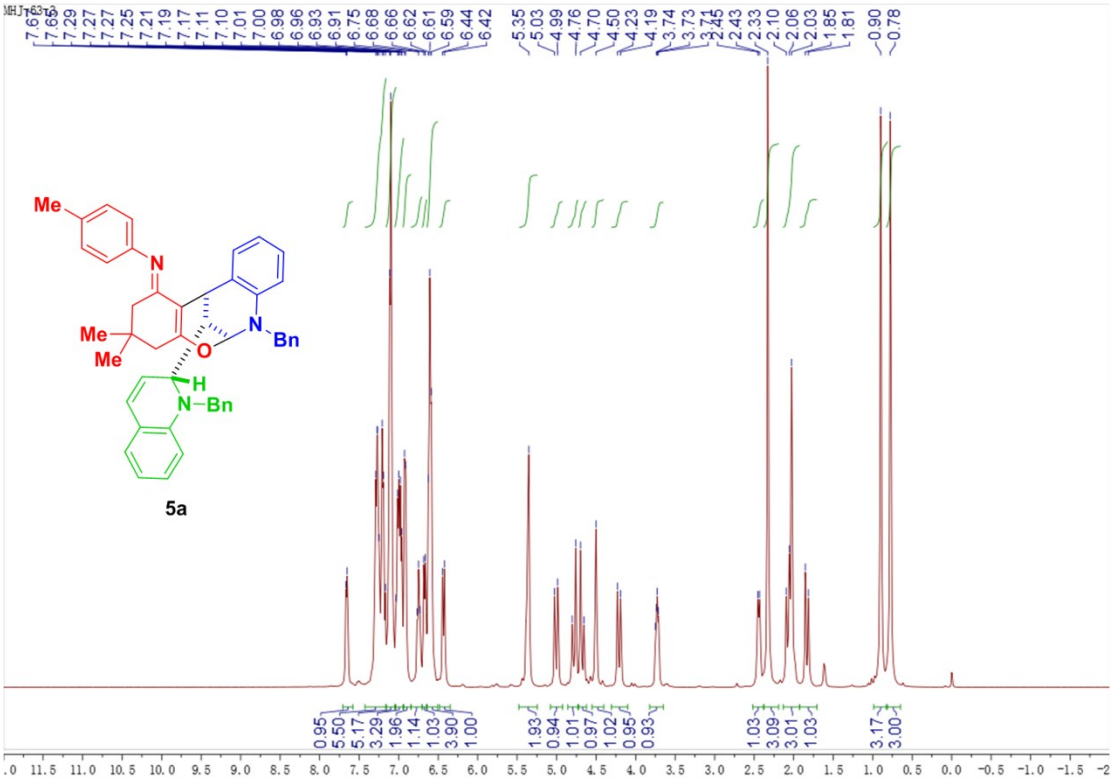
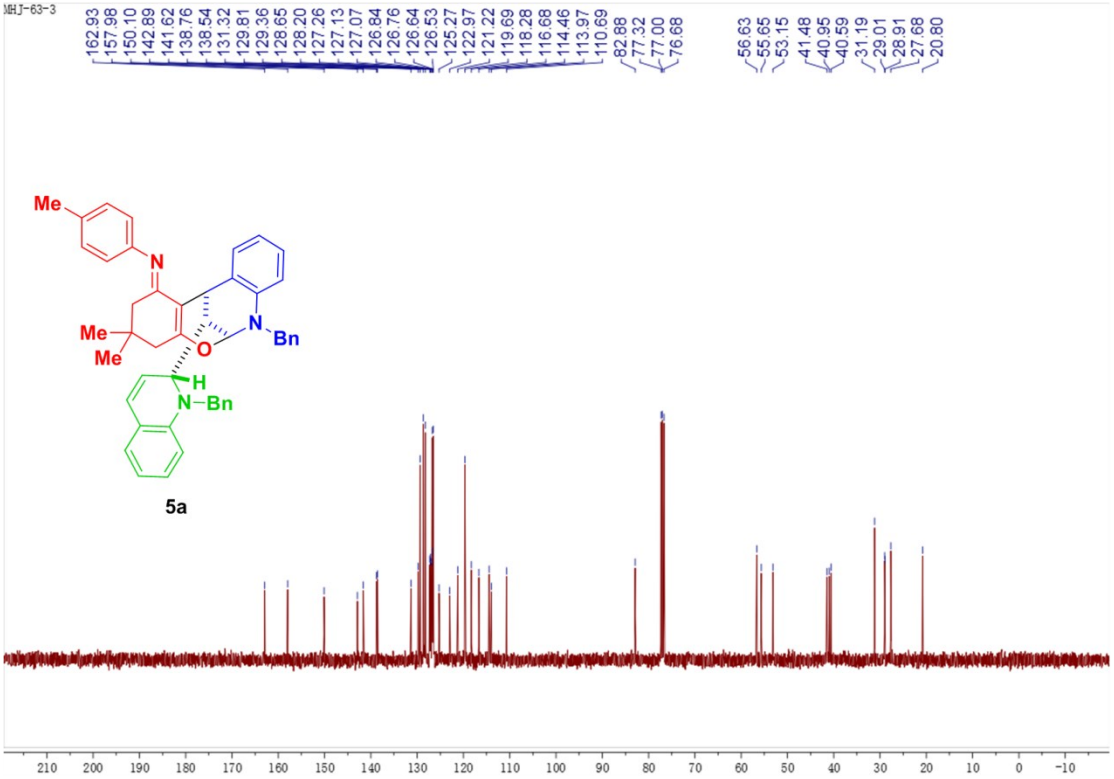
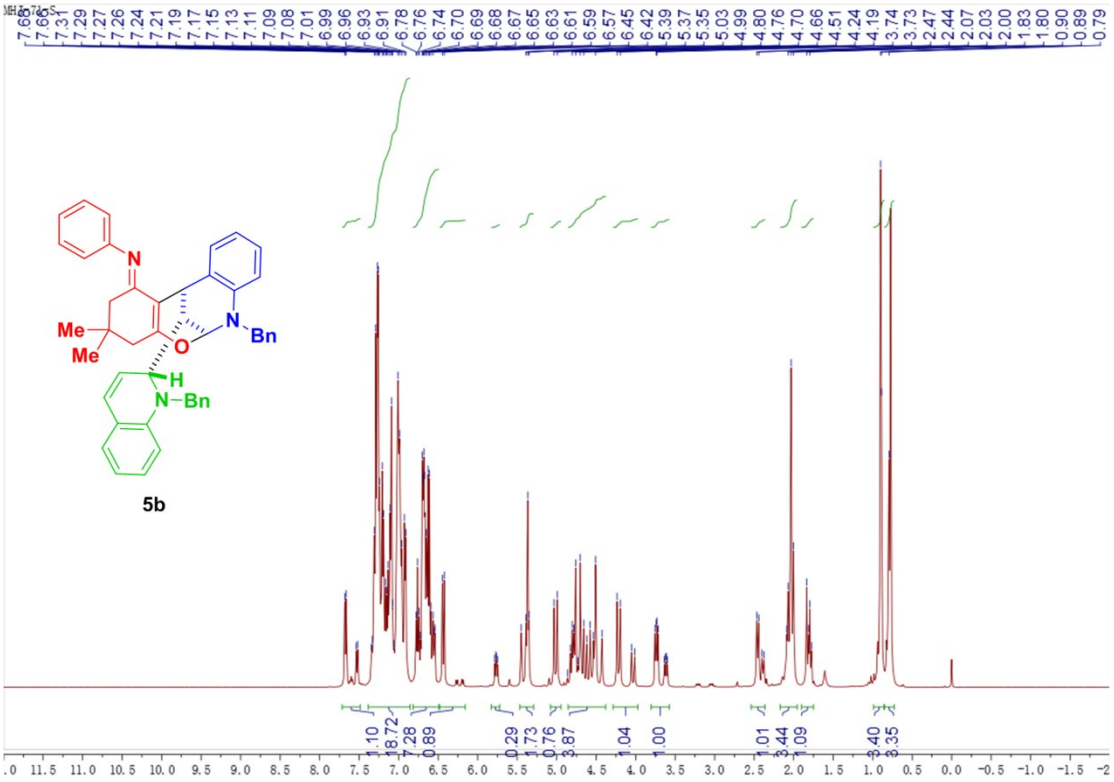
Me
N
Me
3zb

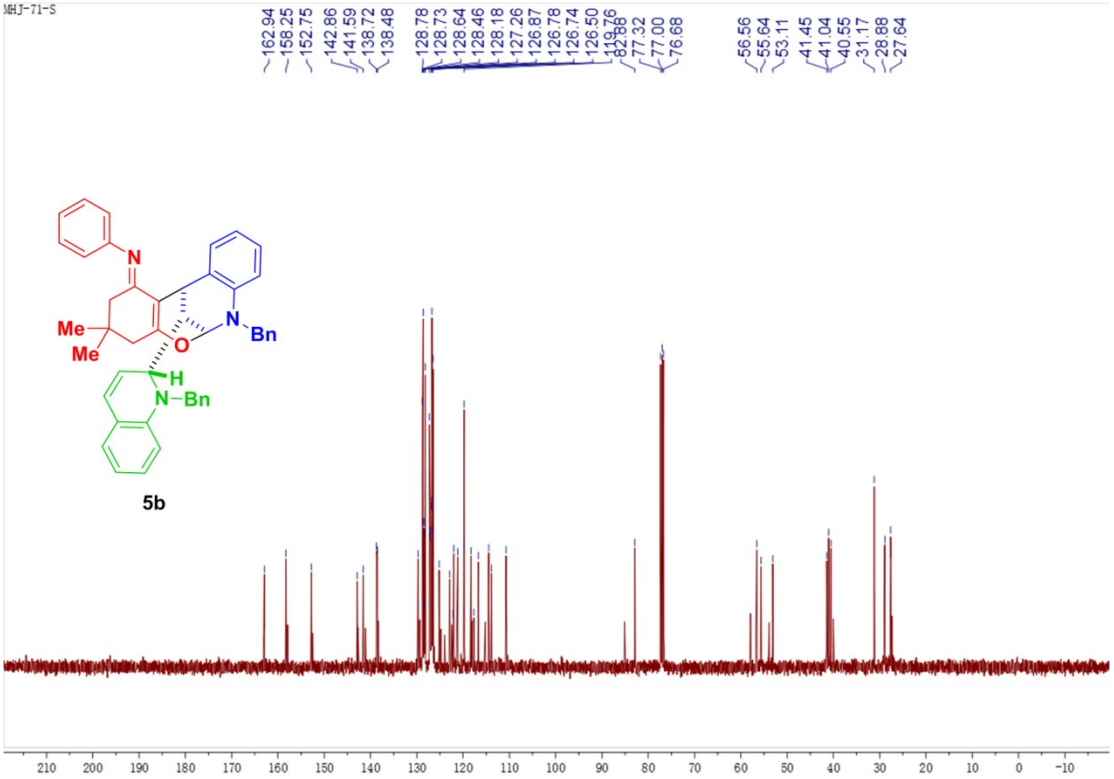

MHJ-59
7.39
7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.22
6.88
6.43
6.42
6.41
6.41
6.40
5.66
5.65
5.64
5.63
4.68
4.54
4.52
3.83
3.79
3.61
3.58
2.87
2.37
2.24
2.23
2.22
2.20
1.90
0.98
O
Bn
N
CF3
Me
Me
N
Me
3zc
4.25
1.02
1.98
2.09
0.98
0.96
0.97
1.04
1.01
0.98
0.96
3.26
3.14
1.18
3.00
3.38

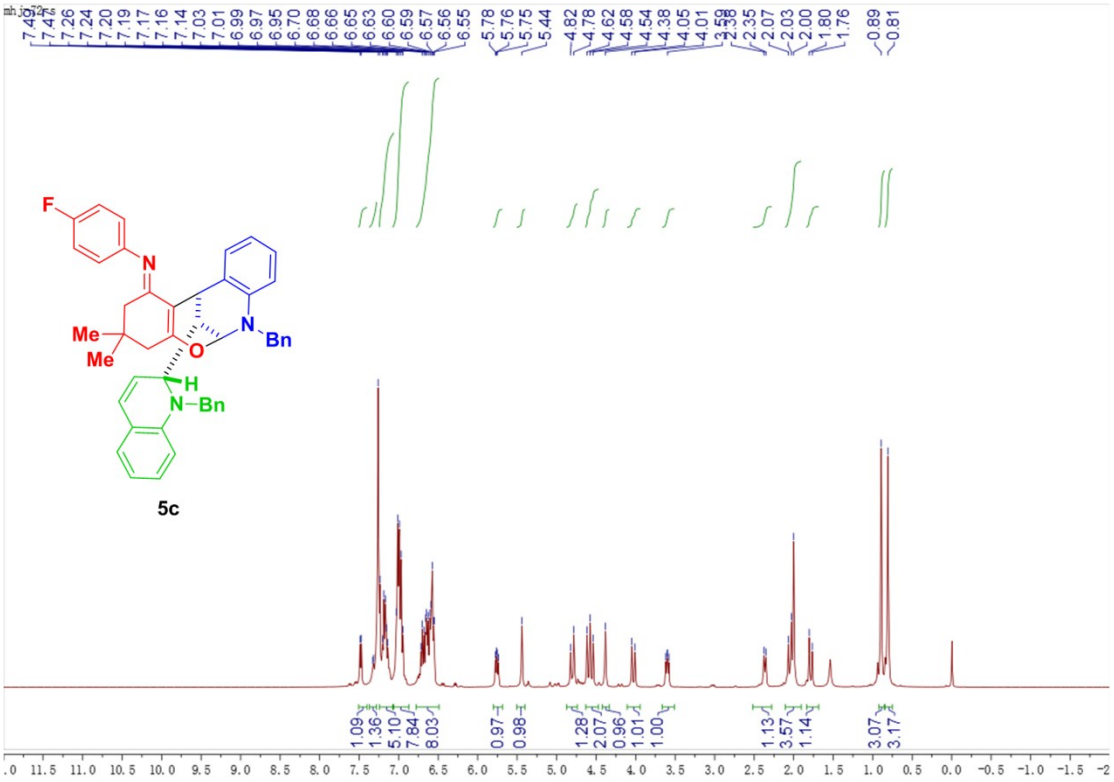

MHJ-59
192.71
154.85
138.25
138.03
136.88
136.74
131.30
128.96
128.39
103.42
77.32
77.00
76.68
73.67
73.64
56.95
49.64
48.33
45.28
45.02
44.77
44.51
40.98
32.95
29.42
27.69
21.01
O
Bn
N
CF3
Me
Me
N
Me
3zc

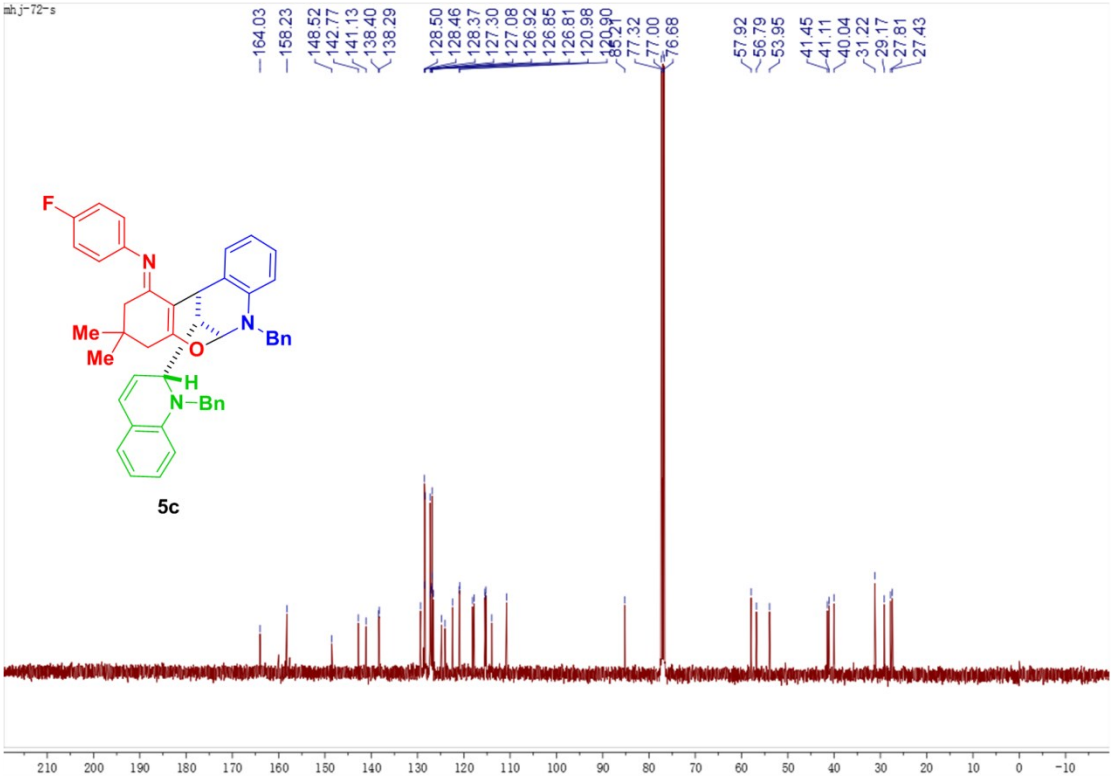

Me
N
Me
Me
O
N
Bn
H
N–Bn
5a

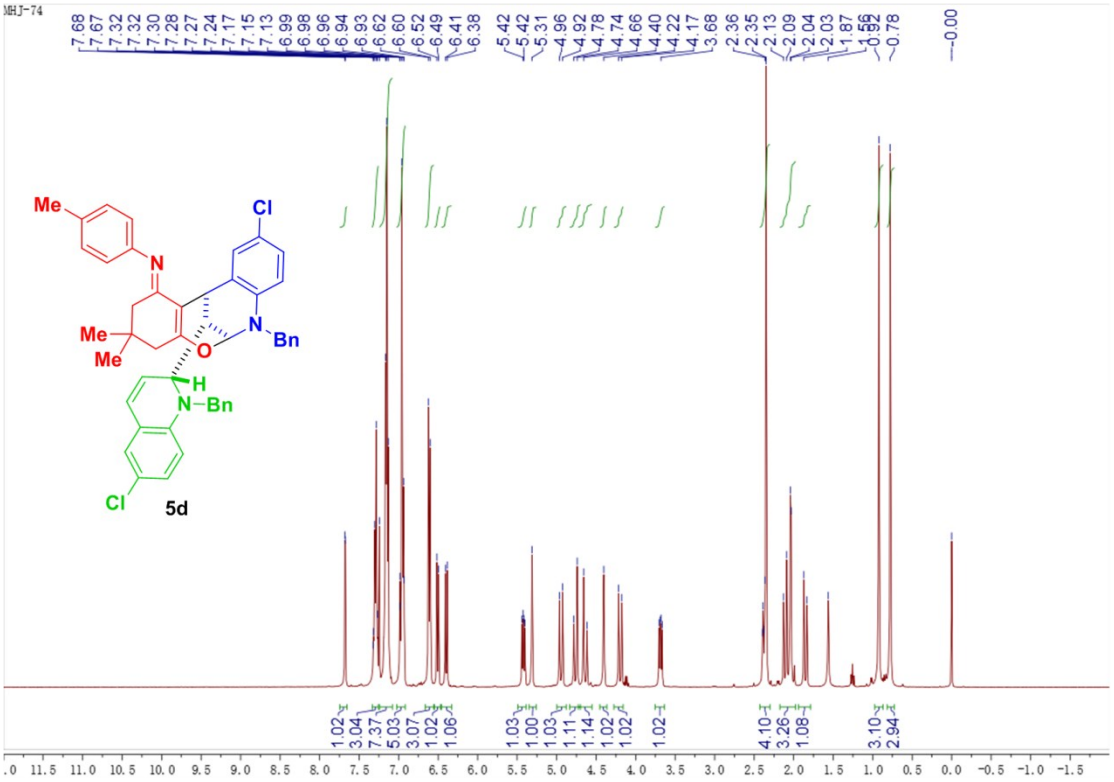

Me
N
Me
Me
O
N
Bn
H
N–Bn
5a

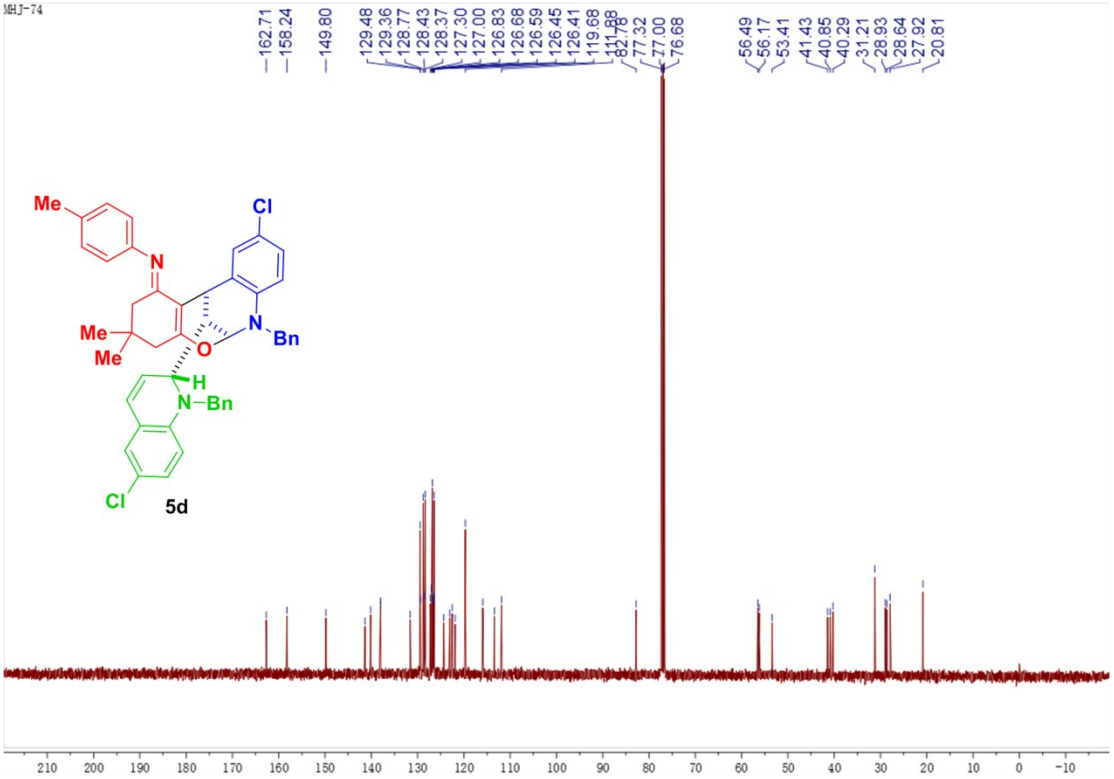

Me
Me
O
N
Bn
H
N–Bn
5b

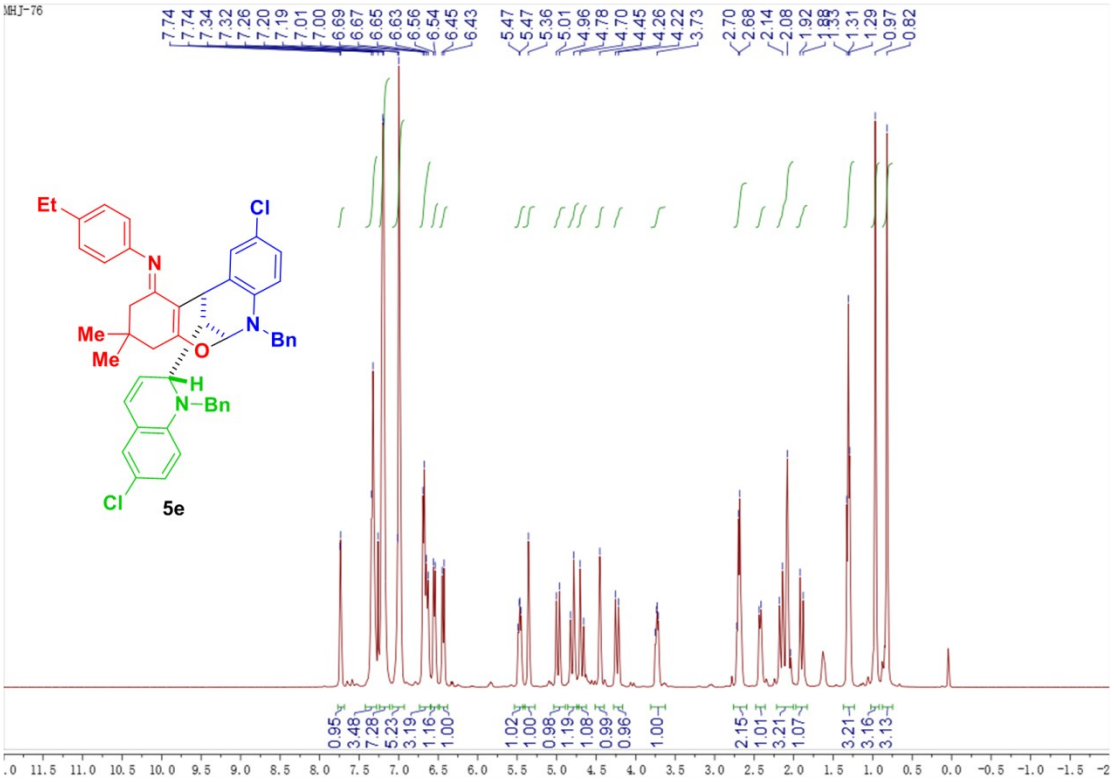

MHJ-71-S
Me
Me
O
N
Bn
H
N–Bn
5b

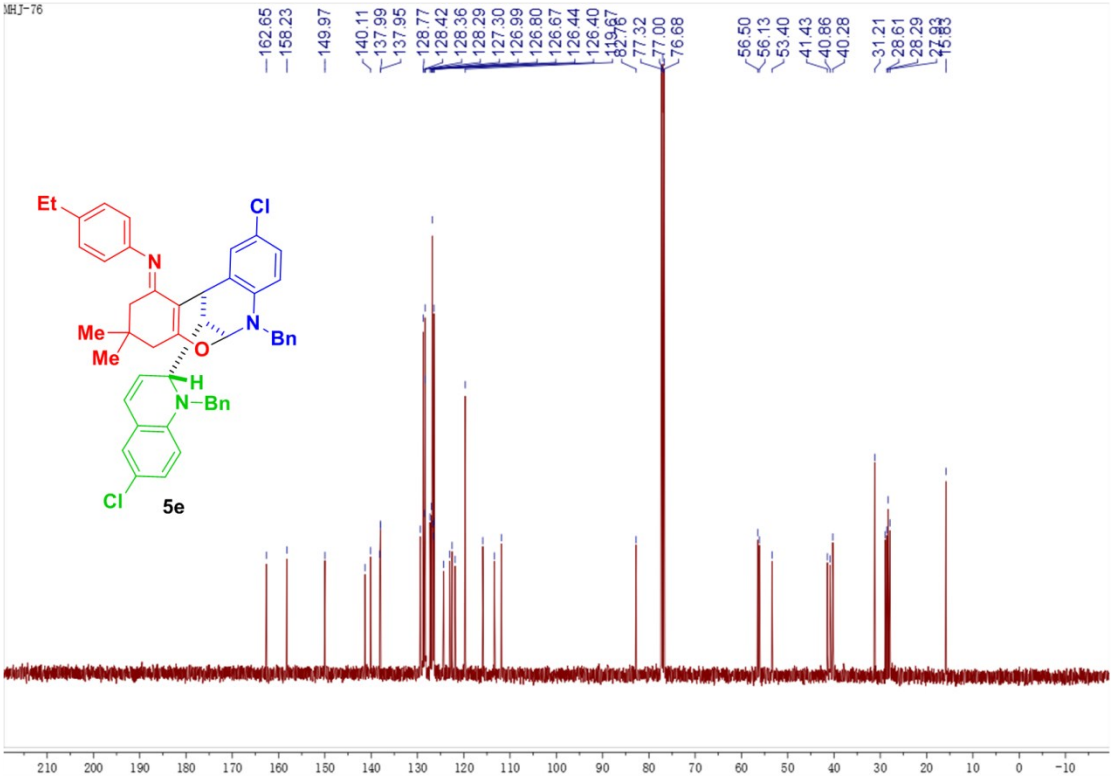

F
N
Me
Me
O
N
Bn
H
N–Bn
5c

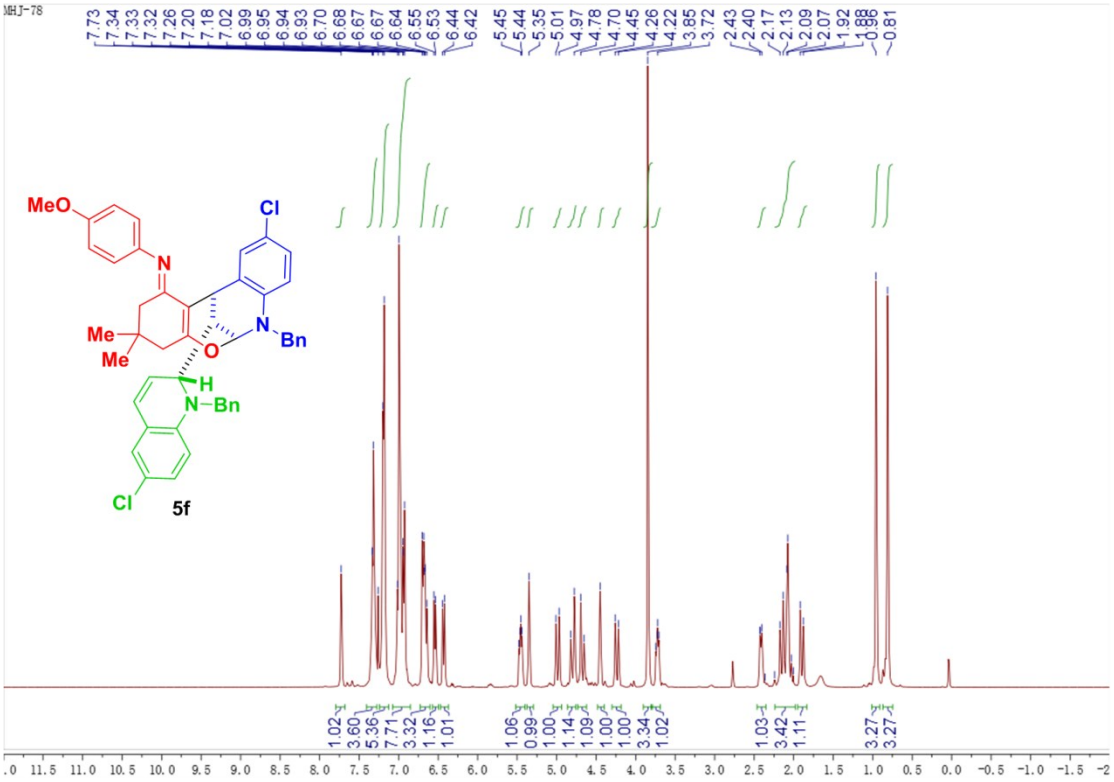

F
N
Me
Me
O
N
Bn
H
N–Bn
5c

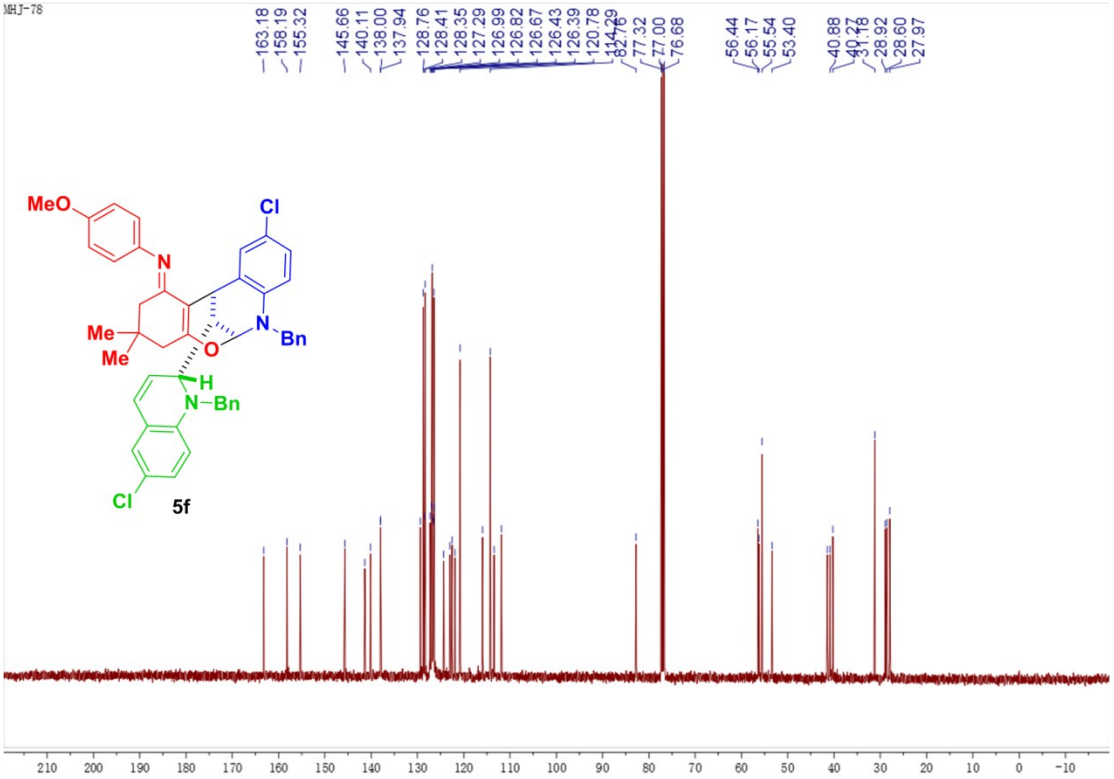

MHJ-74
Me
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5d

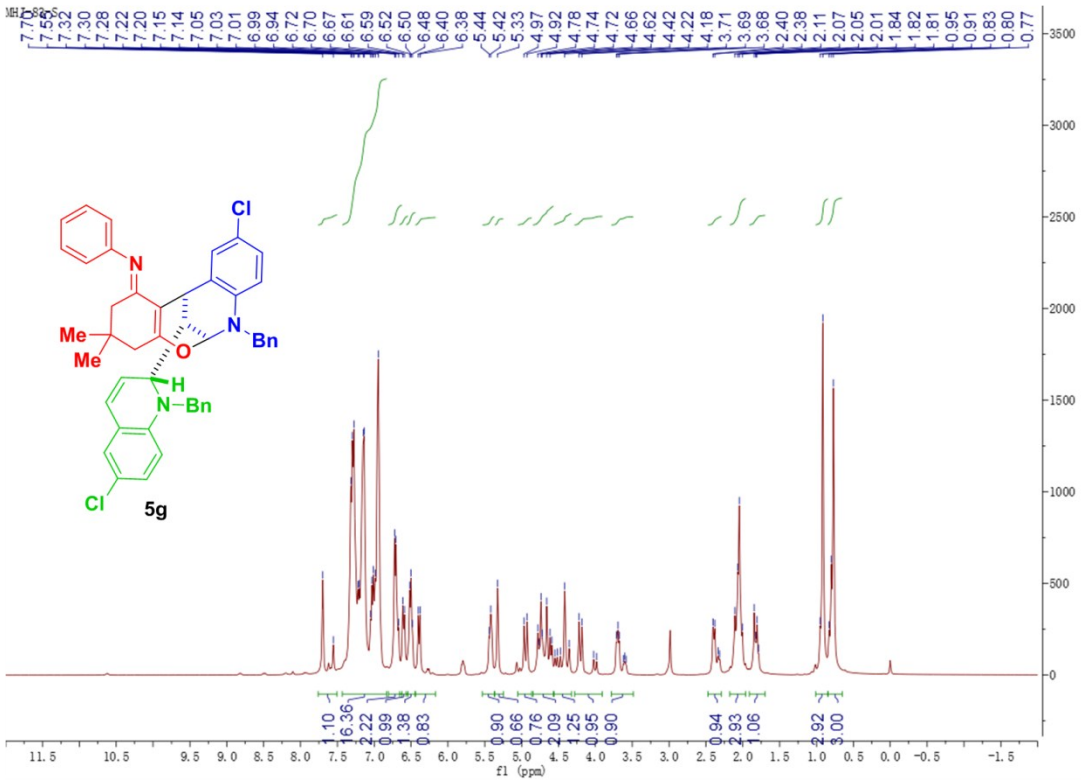

MHJ-74
Me
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5d

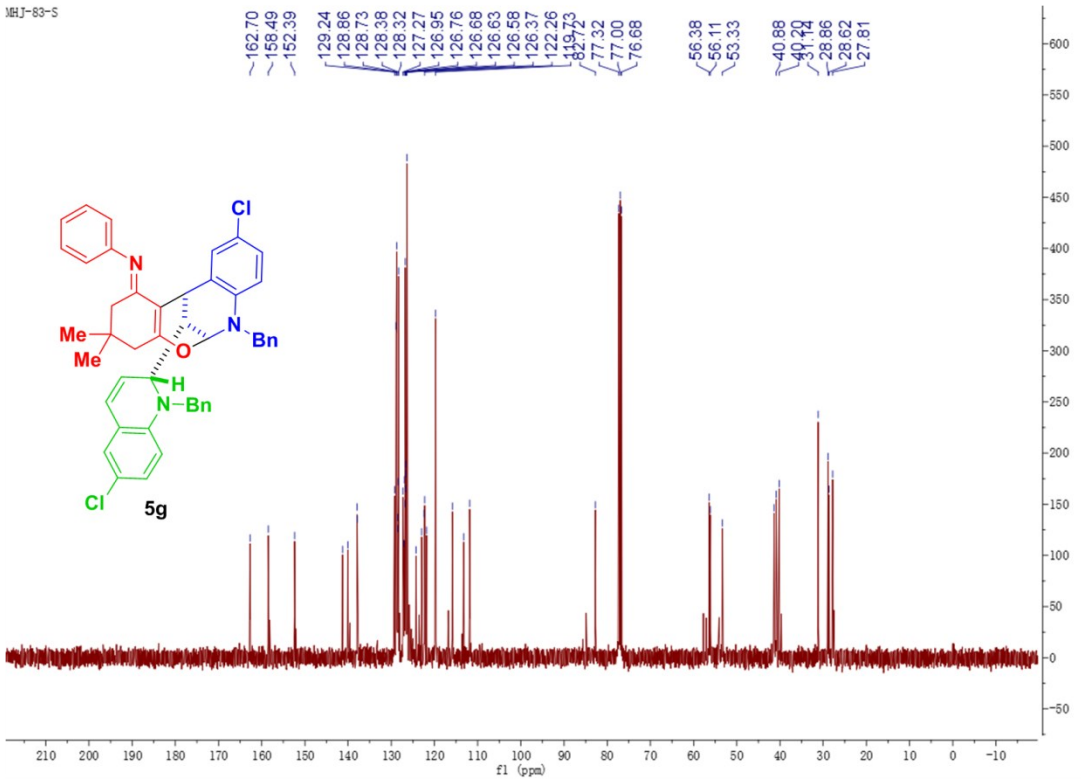

MHJ-76
Et
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5e

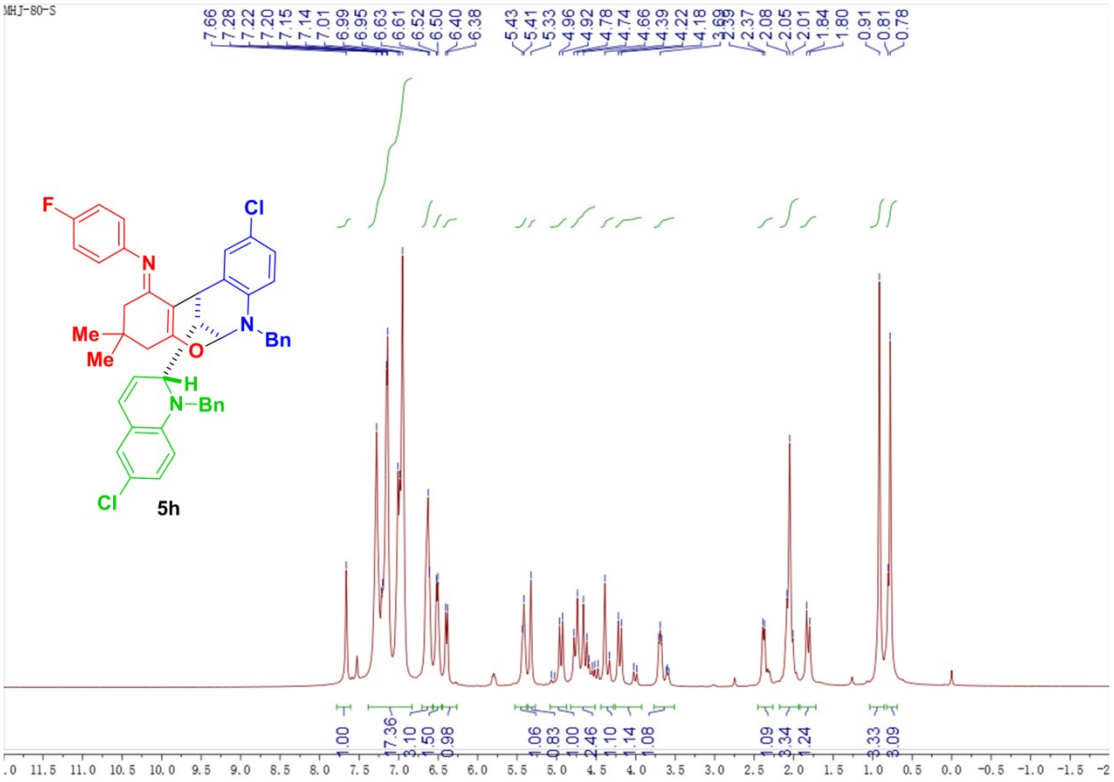

MHJ-76
Et
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5e

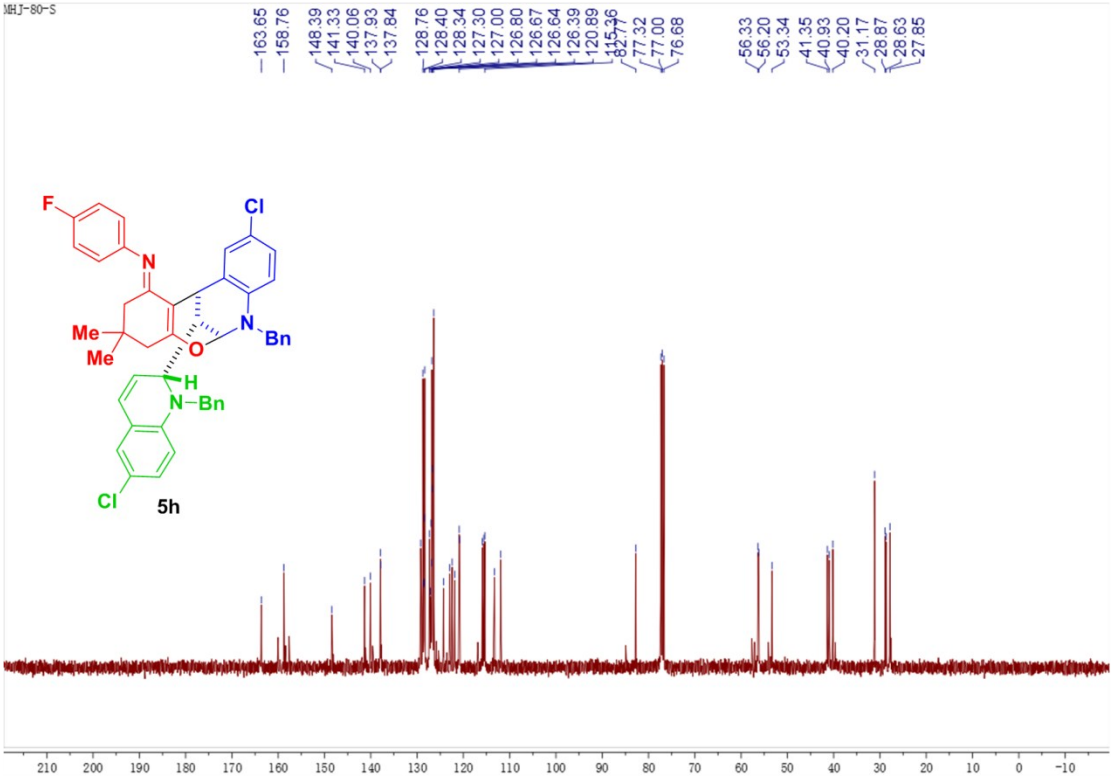

MeO
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5f

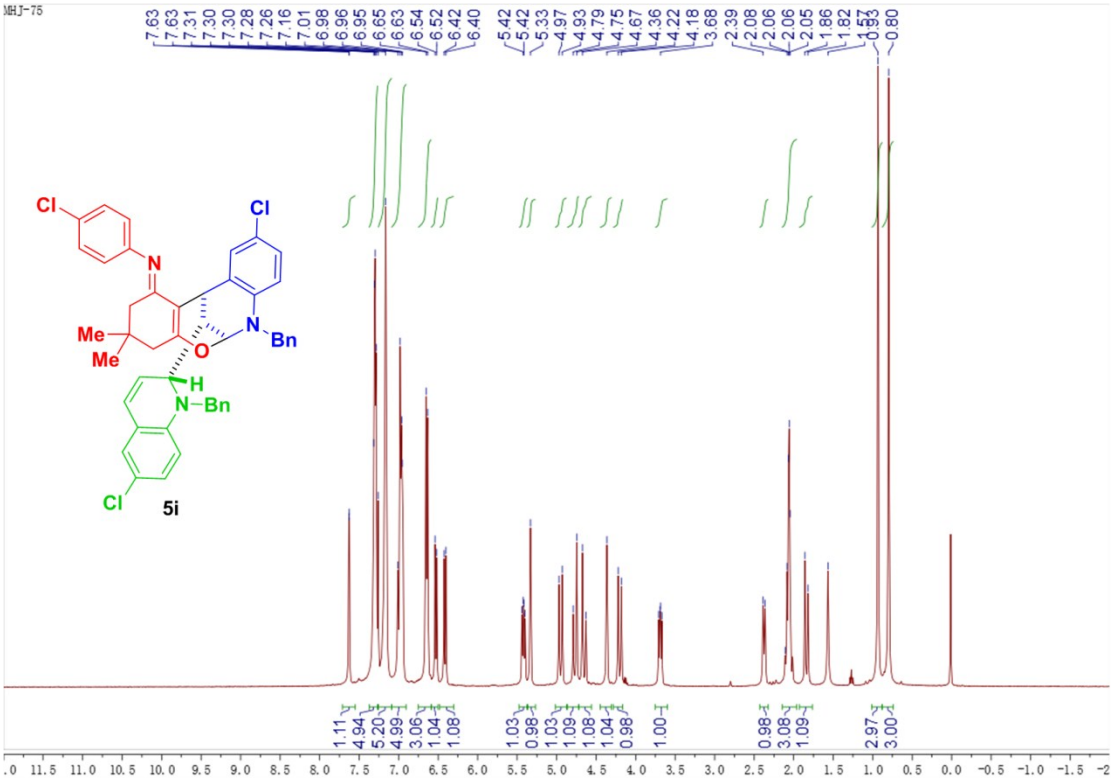

MeO
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5f

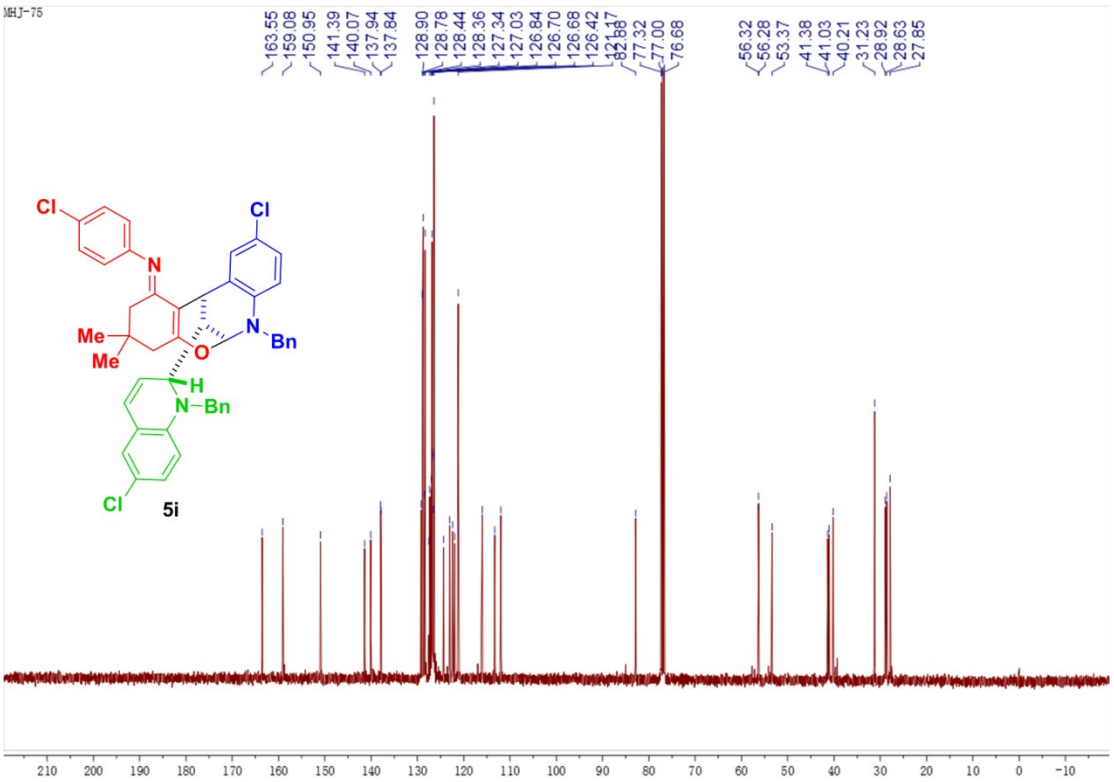

Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5g
f1 (ppm)

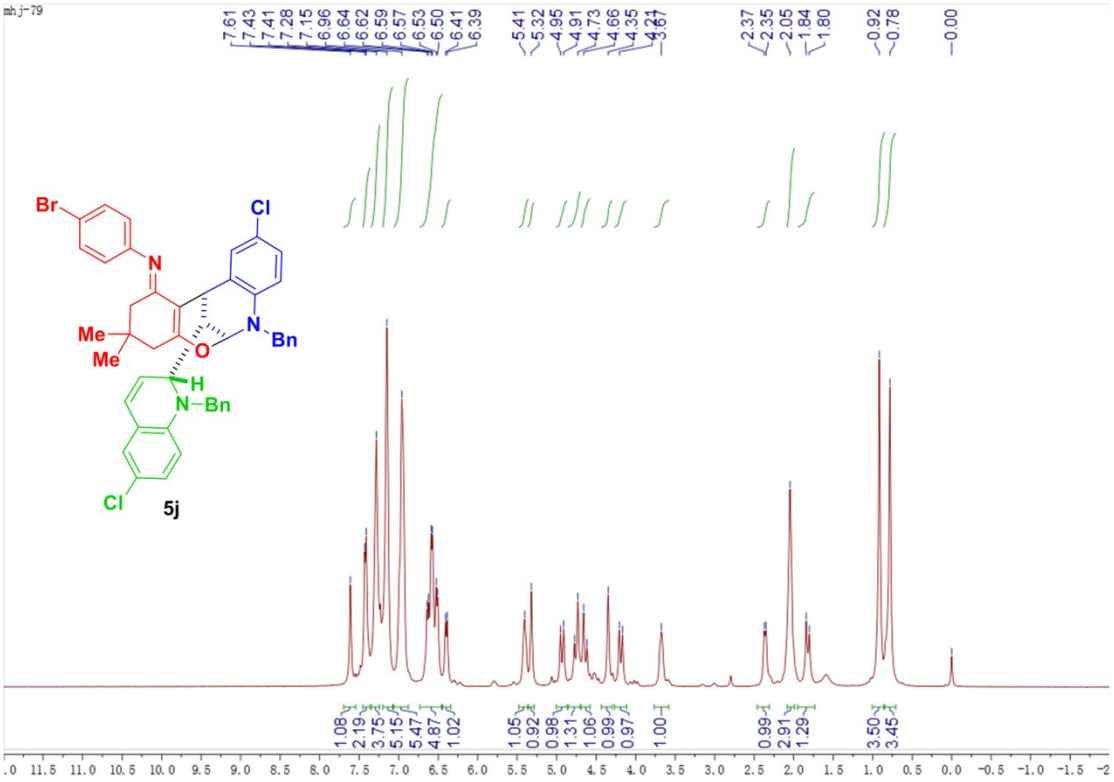

MHJ-83-S
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5g
f1 (ppm)

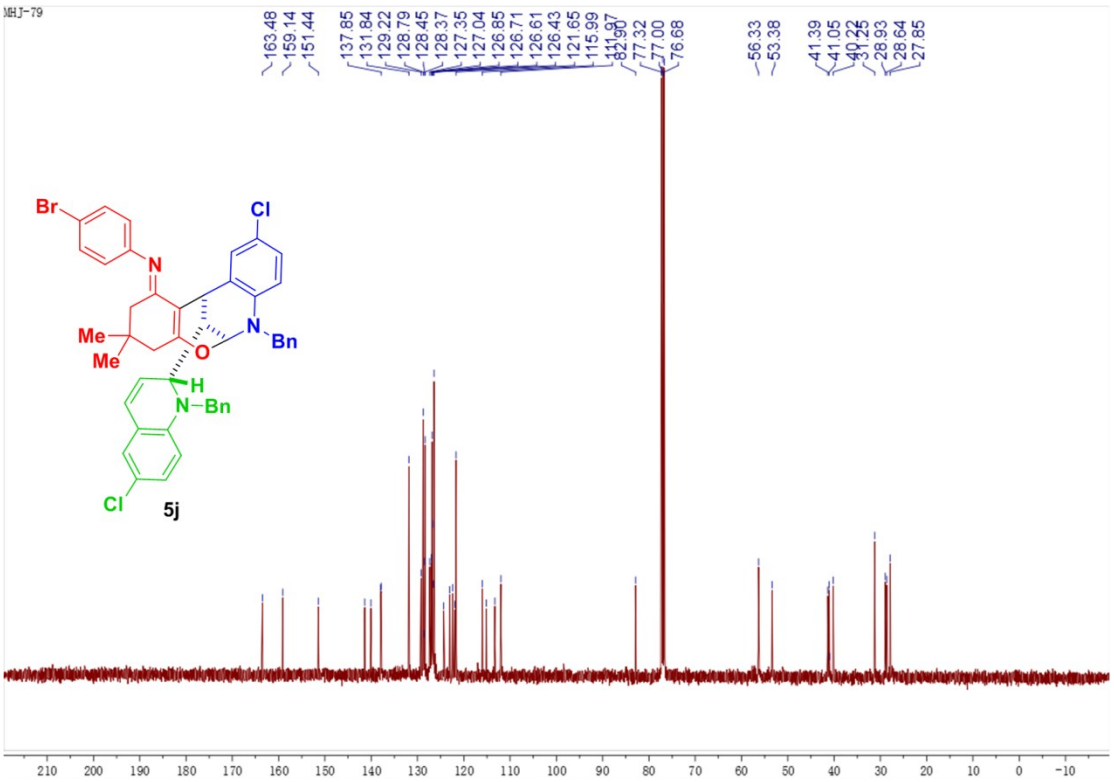

MHJ-80-S
7.66
7.28
7.22
7.20
7.15
7.14
7.01
6.99
6.95
6.63
6.61
6.52
6.50
6.40
6.38
5.43
5.41
5.33
4.96
4.92
4.78
4.74
4.66
4.39
4.22
4.18
3.69
3.39
2.37
2.08
2.05
2.01
1.84
1.80
0.91
0.81
0.78
F
Cl
N
Me
Me
O
N
Bn
H
N
Bn
Cl
5h
1.00
17.36
3.10
1.50
0.98
1.06
0.83
1.00
2.46
1.10
1.14
1.08
1.09
3.34
1.24
3.33
3.09

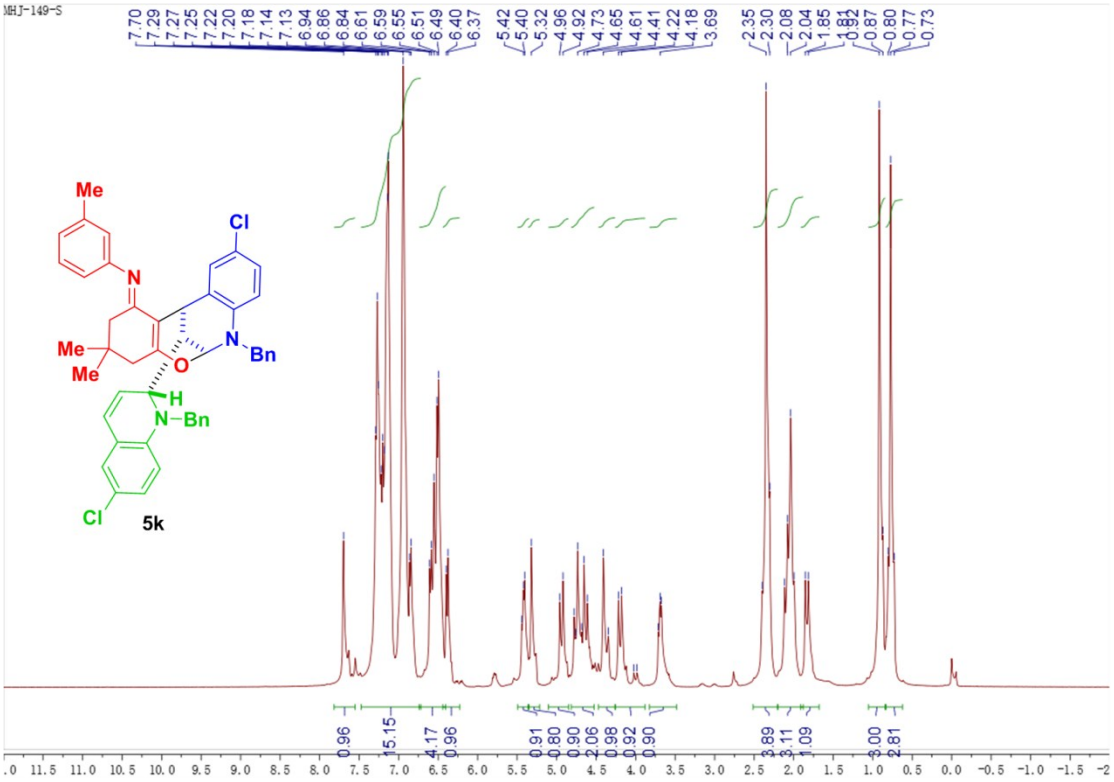

MHJ-80-S
163.65
158.76
148.39
141.33
140.06
137.93
137.84
128.76
128.40
128.34
127.30
127.00
126.80
126.67
126.64
126.39
120.89
115.36
82.77
77.32
77.00
76.68
56.33
56.20
53.34
41.35
40.93
40.20
31.17
28.87
28.63
27.85
F
Cl
N
Me
Me
O
N
Bn
H
N
Bn
Cl
5h

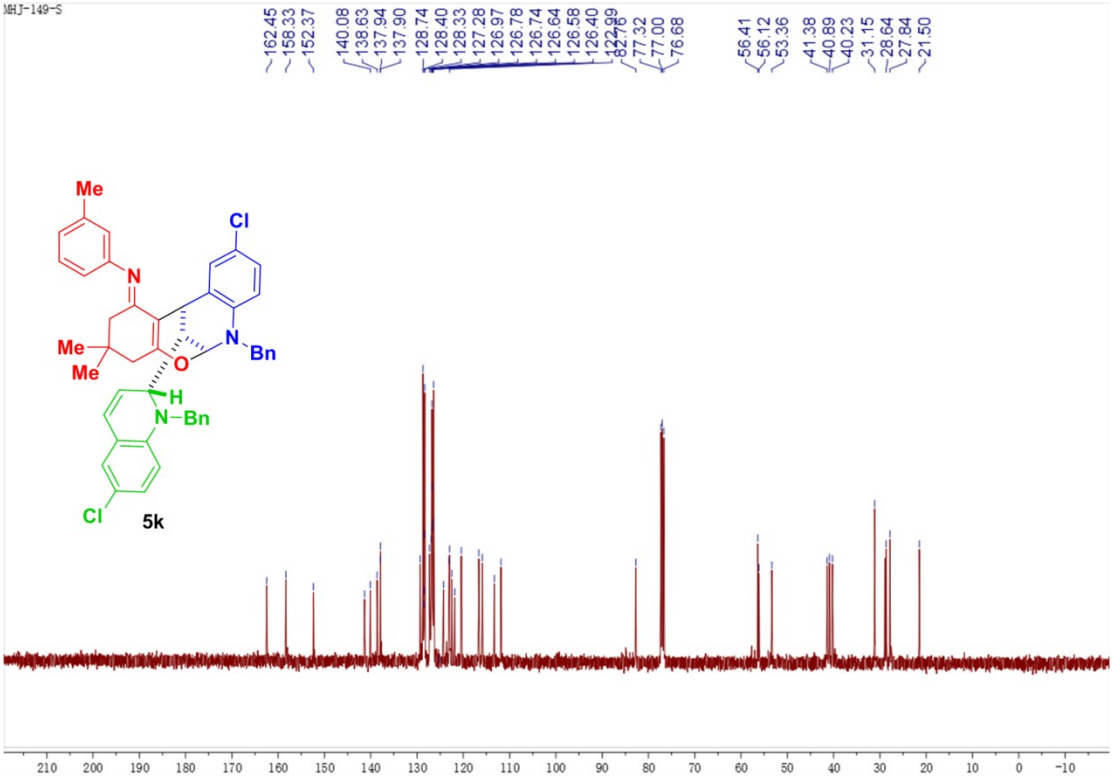

MHJ-75
7.63
7.63
7.31
7.30
7.30
7.28
7.26
7.16
7.01
6.98
6.96
6.95
6.65
6.63
6.54
6.52
6.42
6.40
5.42
5.42
5.33
4.97
4.93
4.79
4.75
4.67
4.36
4.22
4.18
3.68
2.39
2.08
2.06
2.06
2.05
1.86
1.82
1.57
0.93
0.80
Cl
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5i
1.11
4.94
5.20
4.99
3.06
1.04
1.08
1.03
0.98
1.03
1.09
1.08
1.04
0.98
1.00
0.98
3.08
1.09
2.97
3.00

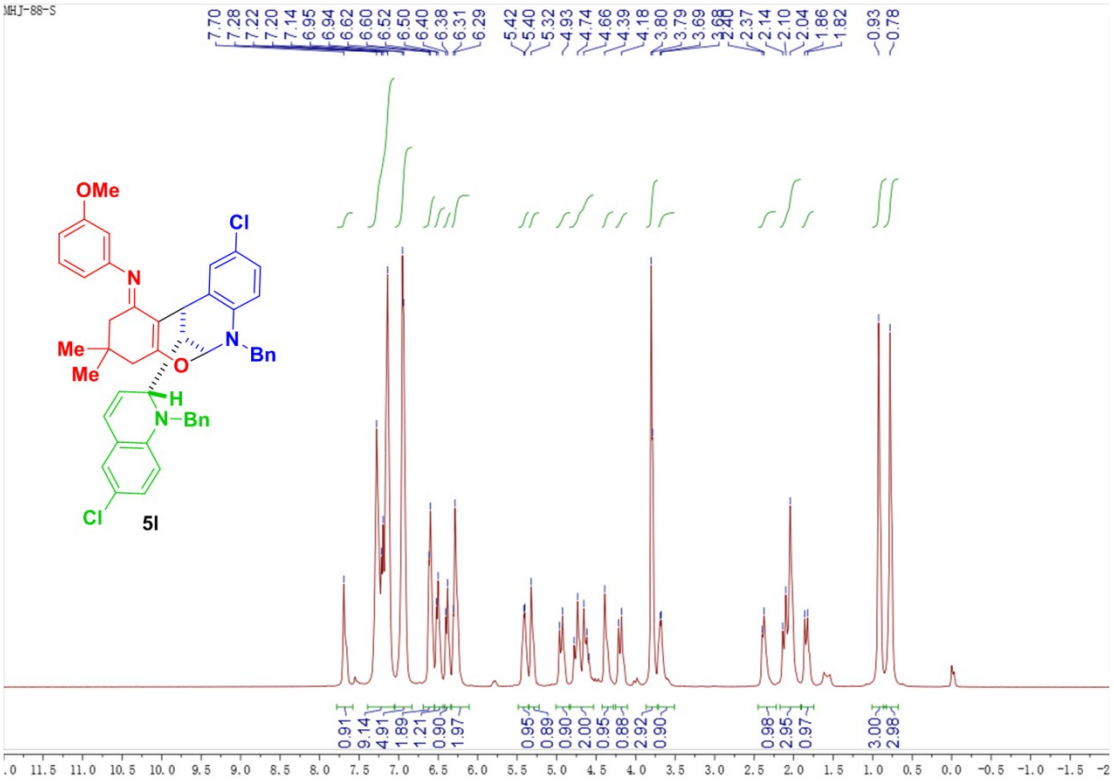

MHJ-75
163.55
159.08
150.95
141.39
140.07
137.94
137.84
128.90
128.78
128.44
128.36
127.34
127.03
126.84
126.70
126.68
126.42
121.17
82.88
77.32
77.00
76.68
56.32
56.28
53.37
41.38
41.03
40.21
31.23
28.92
28.63
27.85
Cl
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5i

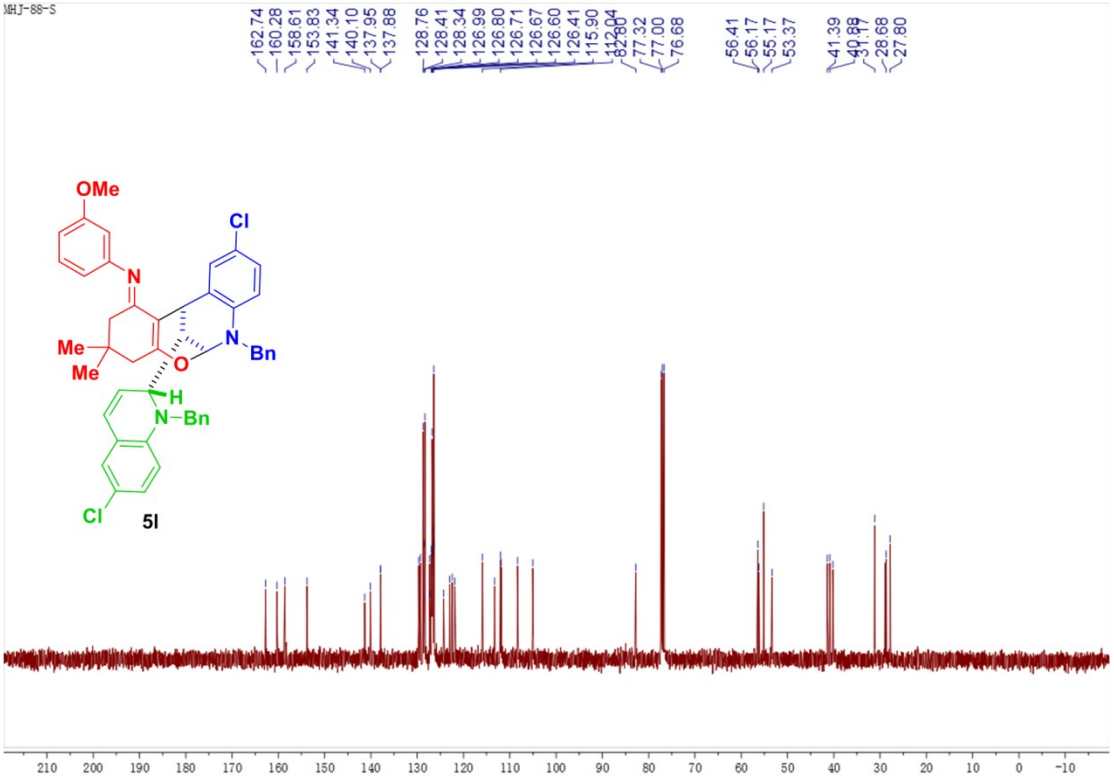

mhj-79
7.61
7.43
7.41
7.28
7.15
6.96
6.64
6.62
6.59
6.57
6.53
6.50
6.41
6.39
5.41
5.32
4.95
4.91
4.73
4.66
4.35
4.21
3.67
2.37
2.35
2.05
1.84
1.80
0.92
0.78
0.00
Br
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5j
1.08
2.19
3.75
5.15
5.47
4.87
1.02
1.05
0.92
0.98
1.31
1.06
0.99
0.97
1.00
0.99
2.91
1.29
3.50
3.45

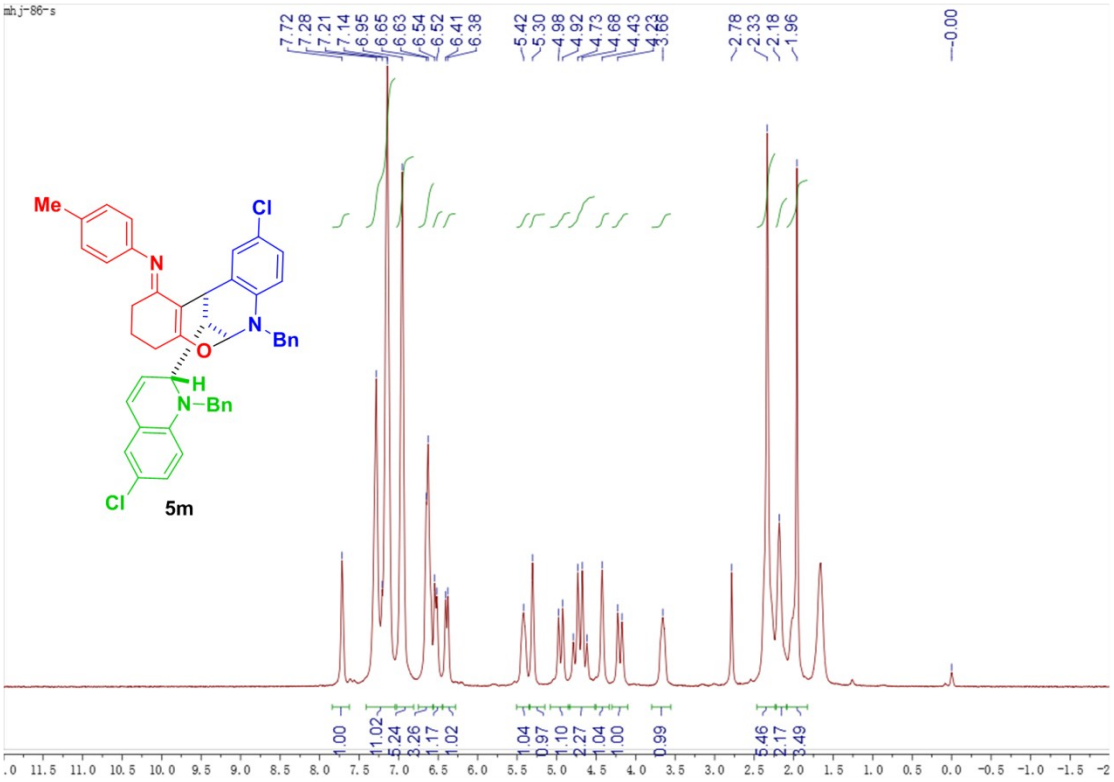

MHJ-79
163.48
159.14
151.44
137.85
131.84
129.22
128.79
128.45
128.37
127.35
127.04
126.85
126.71
126.61
126.43
121.65
115.99
111.97
82.90
77.32
77.00
76.68
56.33
53.38
41.39
41.05
40.22
31.25
28.93
28.64
27.85
Br
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5j

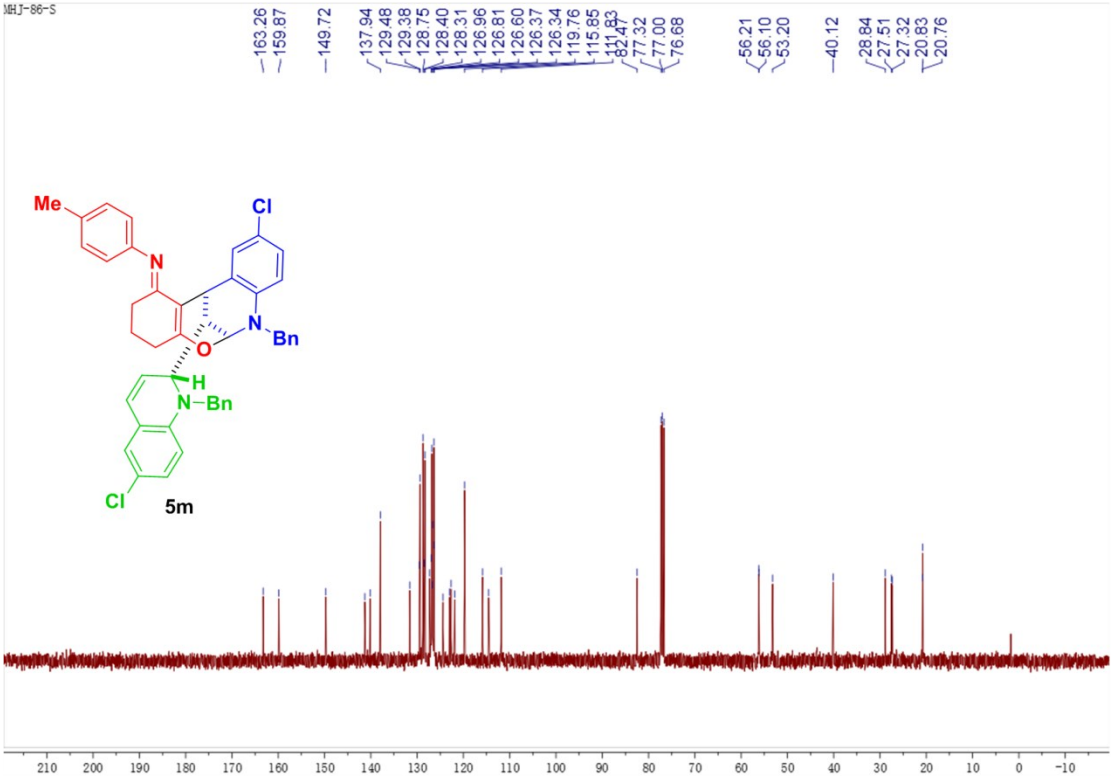

MHJ-149-S
Me
Cl
N
Me
Me
O
N
Bn
H
N
Bn
Cl
5k

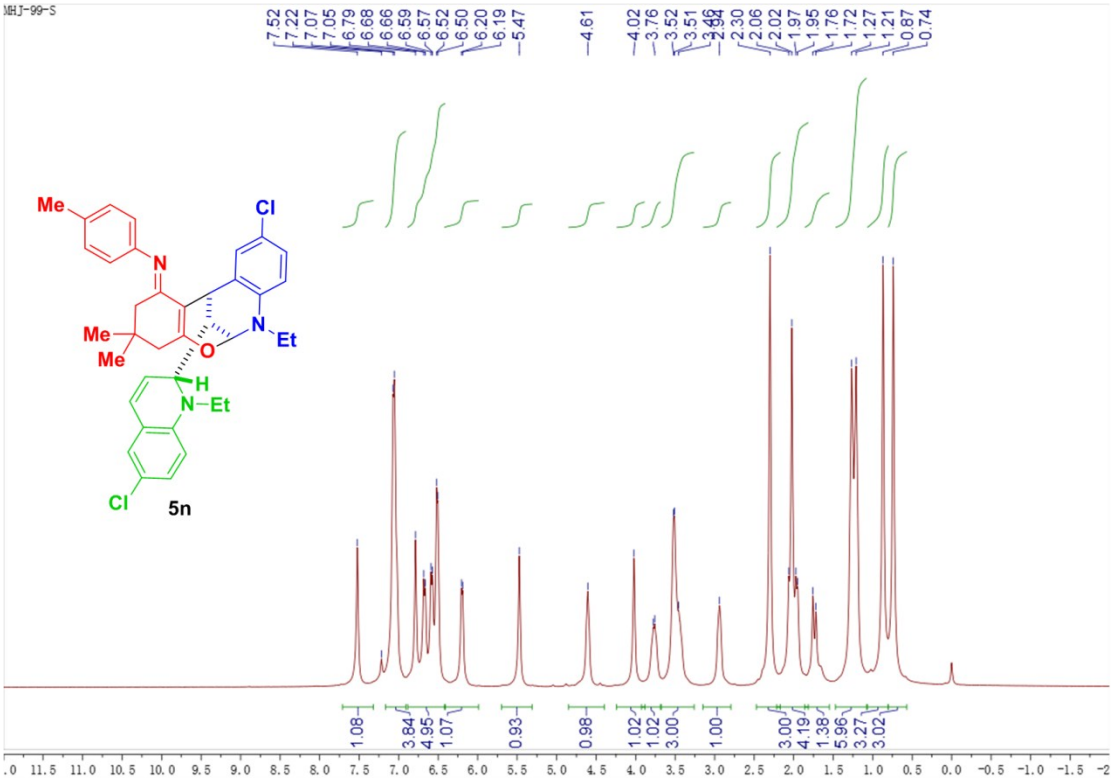

MHJ-149-S
Me
Cl
N
Me
Me
O
N
Bn
H
N
Bn
Cl
5k

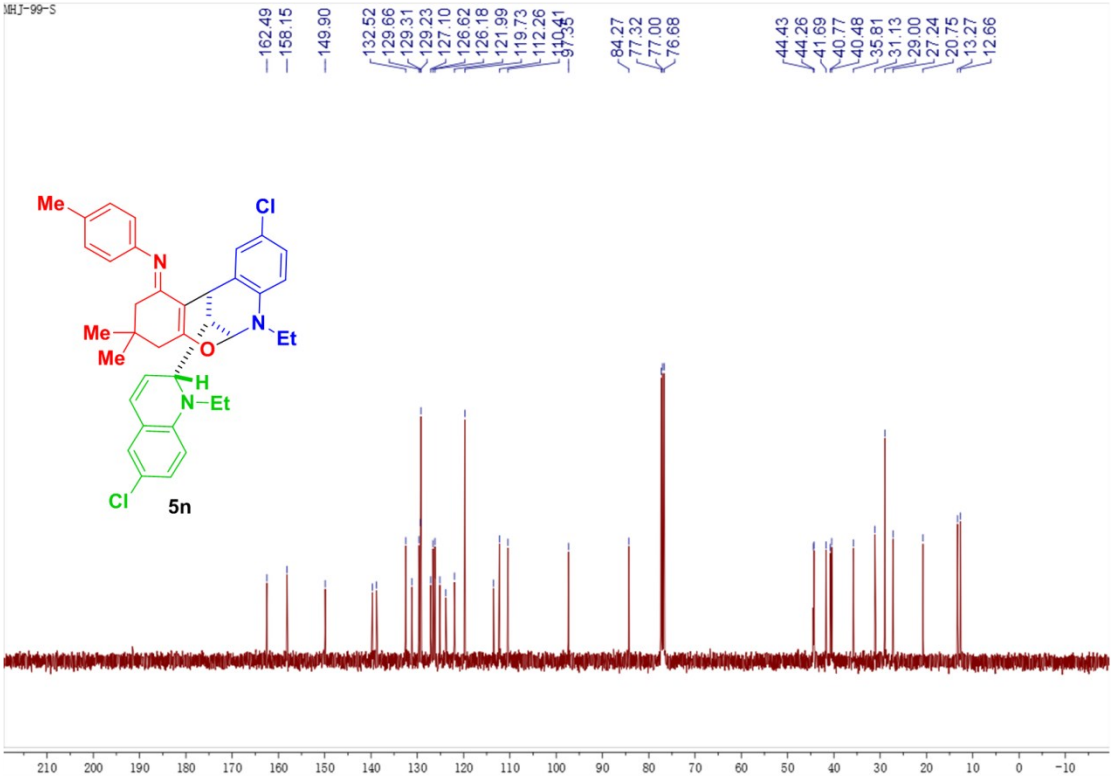

MHJ-88-S
OMe
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5l

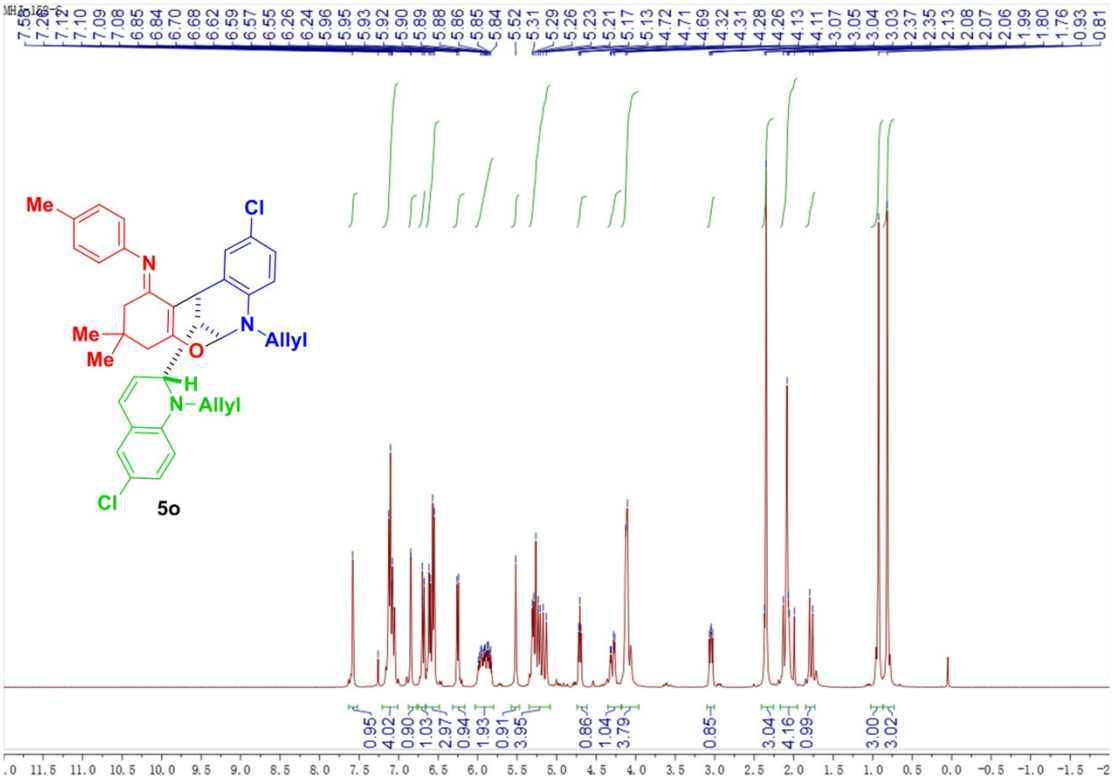

MHJ-88-S
OMe
Cl
N
Me
Me
O
N
Bn
H
N–Bn
Cl
5l

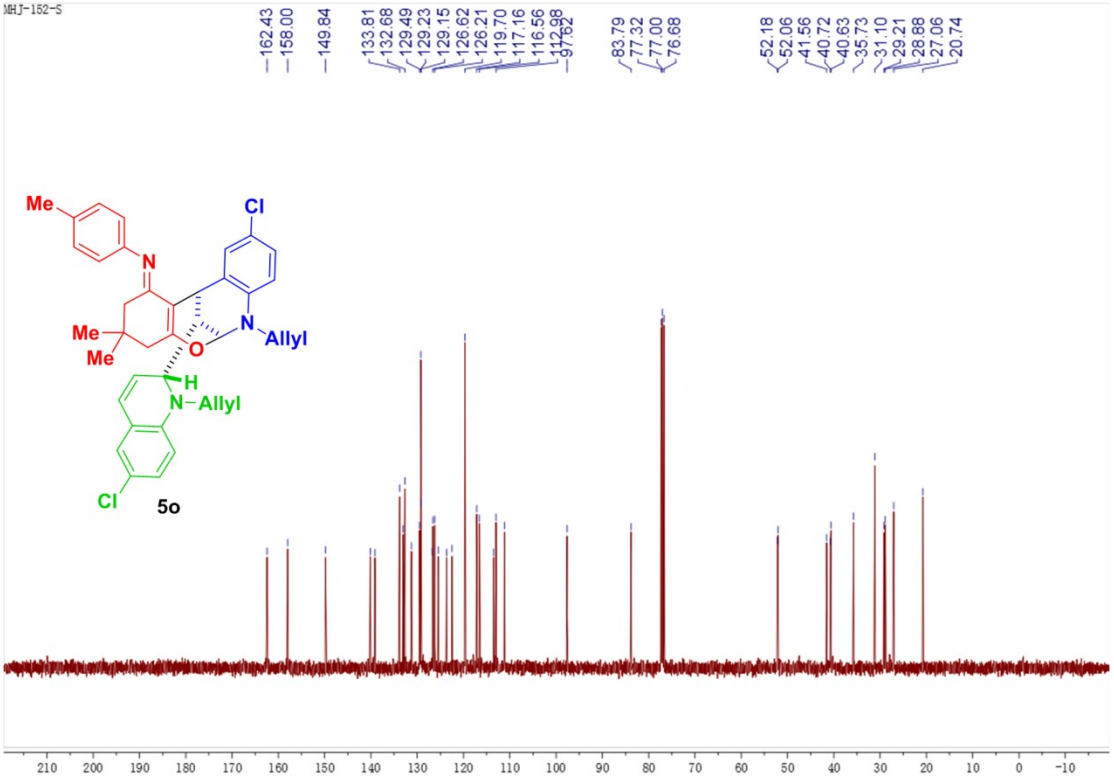

mhj-86-s
7.72
7.28
7.21
7.14
6.95
6.65
6.63
6.54
6.52
6.41
6.38
5.42
5.30
4.98
4.92
4.73
4.68
4.43
4.23
3.66
2.78
2.33
2.18
1.96
0.00
Me
Cl
N
N
Bn
O
H
N
Bn
Cl
5m
1.00
11.02
5.24
3.26
3.17
1.02
1.04
0.97
1.10
2.27
1.04
1.00
0.99
5.46
2.17
3.49

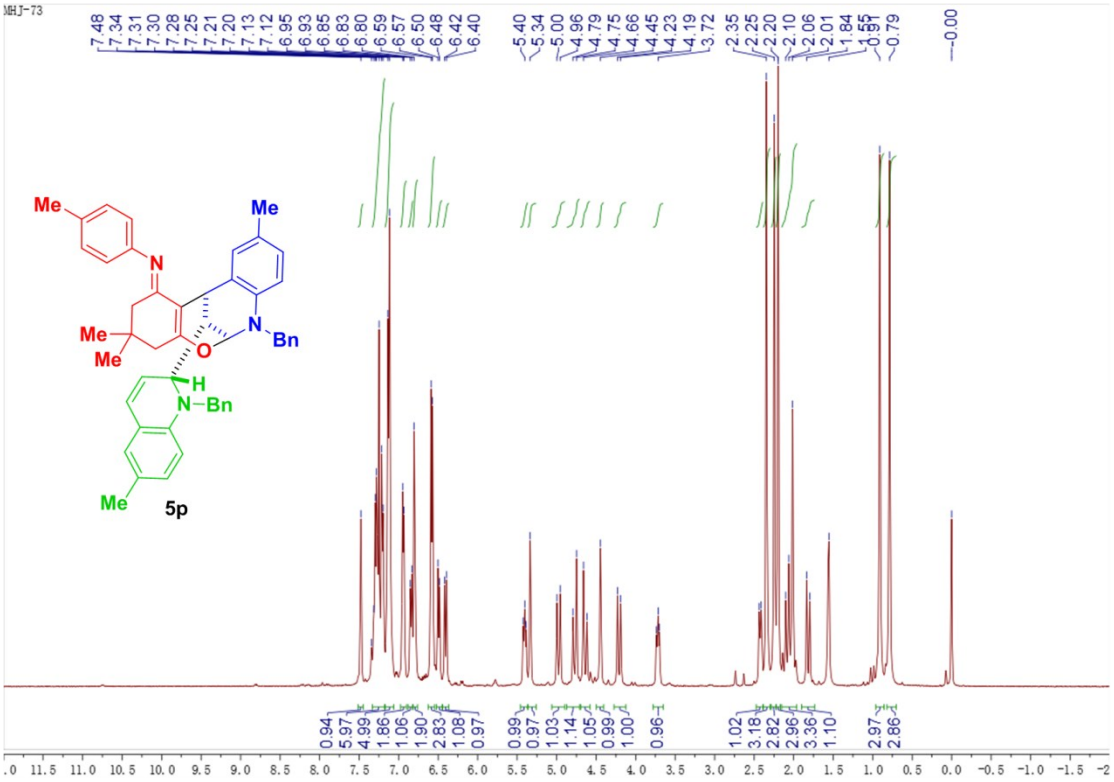

MHJ-86-S
163.26
159.87
149.72
137.94
129.48
129.38
128.75
128.40
128.31
126.96
126.81
126.60
126.37
126.34
119.76
115.85
111.83
82.47
77.32
77.00
76.68
56.21
56.10
53.20
40.12
28.84
27.51
27.32
20.83
20.76
Me
Cl
N
N
Bn
O
H
N
Bn
Cl
5m

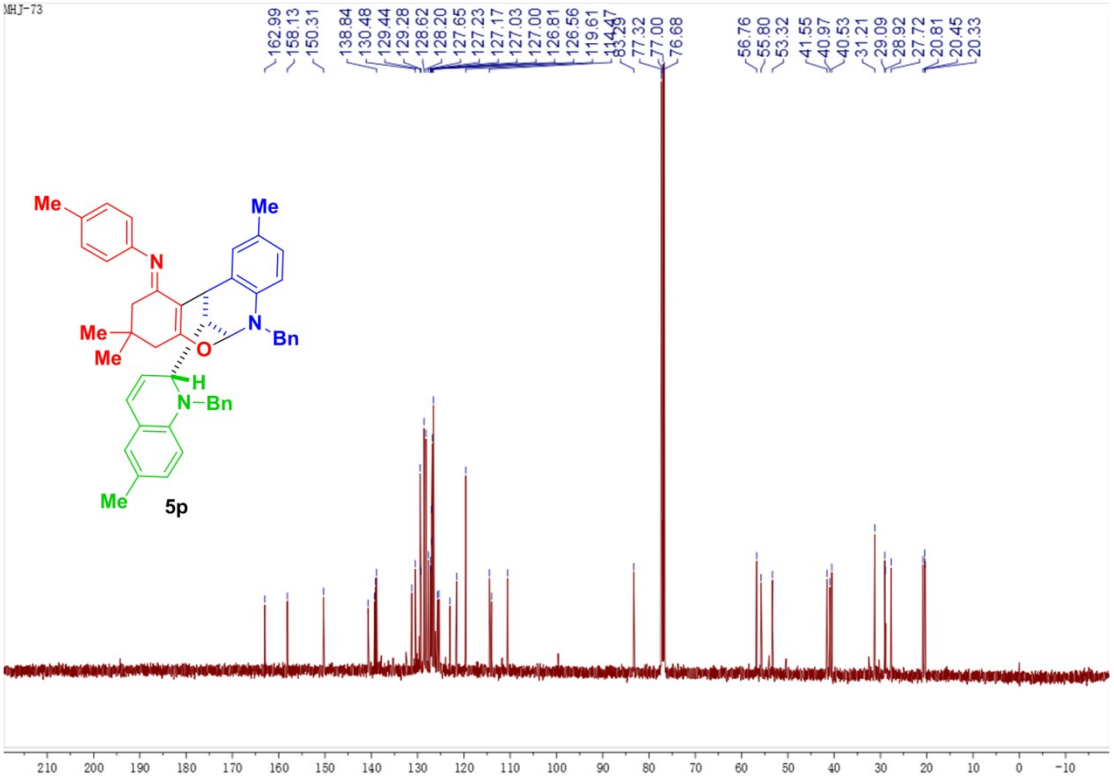

MHJ-99-S
Me
Cl
N
Me
Me
O
N
Et
H
N–Et
Cl
5n

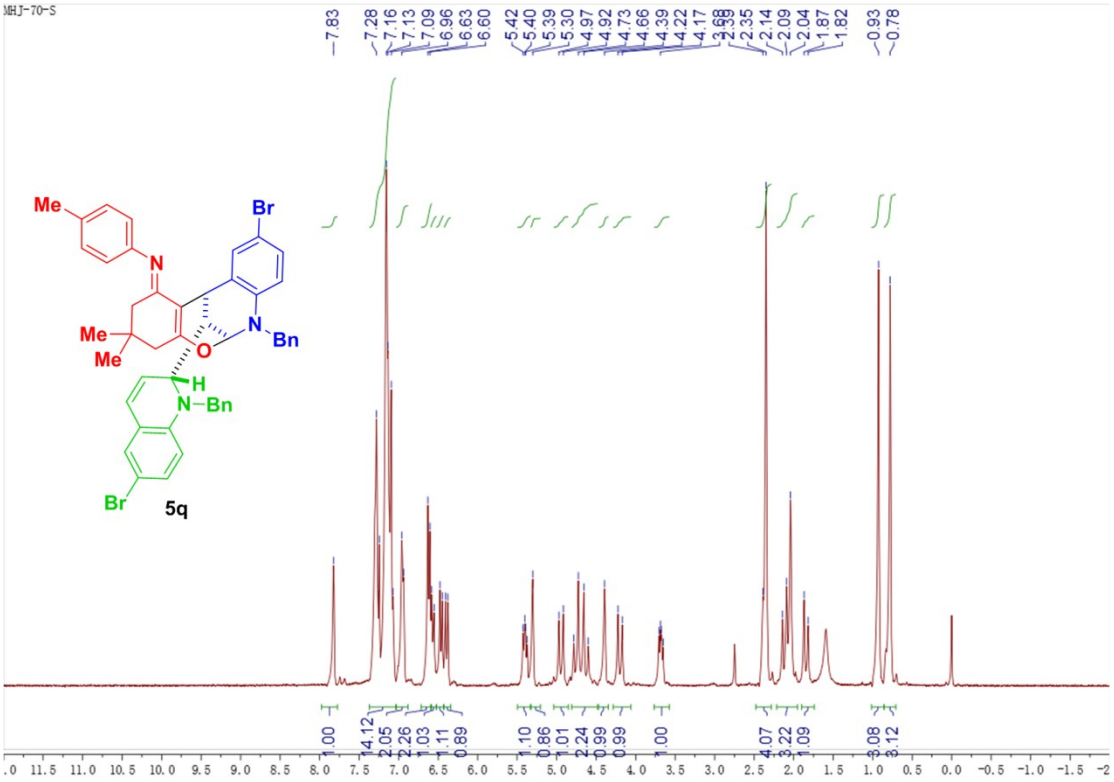

MHJ-99-S
Me
Cl
N
Me
Me
O
N
Et
H
N–Et
Cl
5n


Me
Cl
N
Me
Me
O
N
Allyl
H
N–Allyl
Cl
5o


Me
Cl
N
Me
Me
O
N
Allyl
H
N–Allyl
Cl
5o


MHJ-73
Me
Me
N
Me
Me
O
N
Bn
H
N–Bn
Me
5p


MHJ-73
Me
Me
N
Me
Me
O
N
Bn
H
N–Bn
Me
5p


MHJ-70-S
7.83
7.28
7.16
7.13
7.09
6.96
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4.22
4.17
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2.09
2.04
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Me
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Bn
H
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Br
5q
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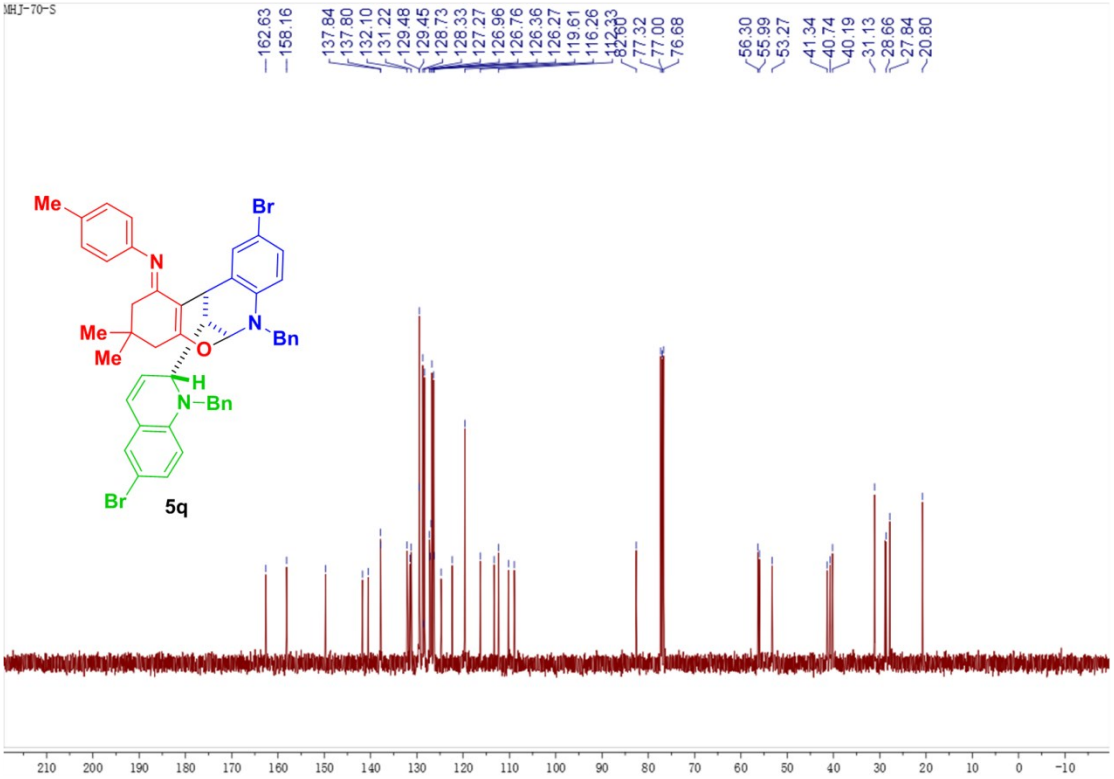
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Br
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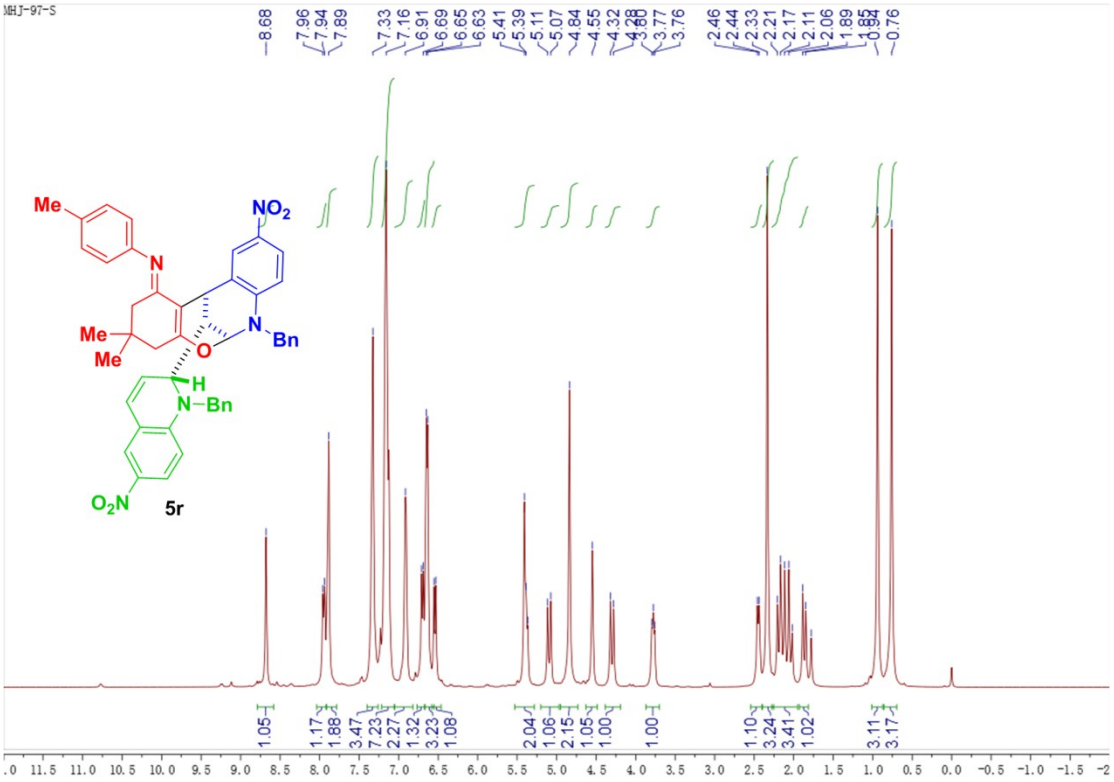
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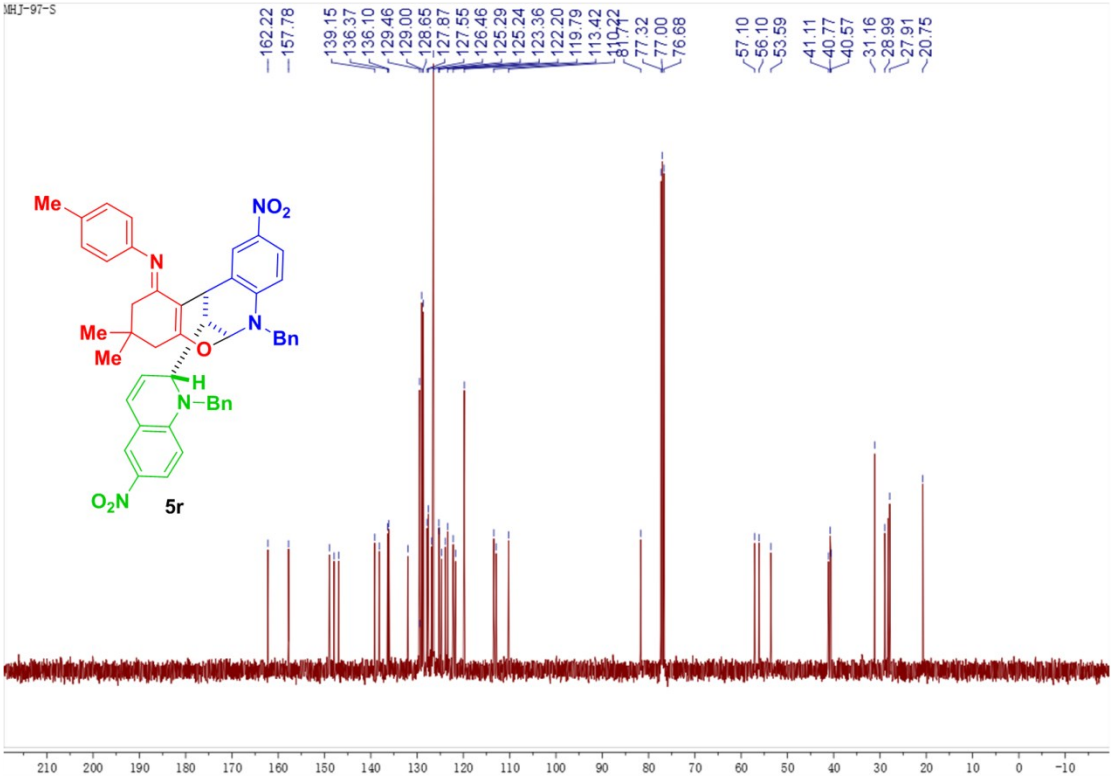
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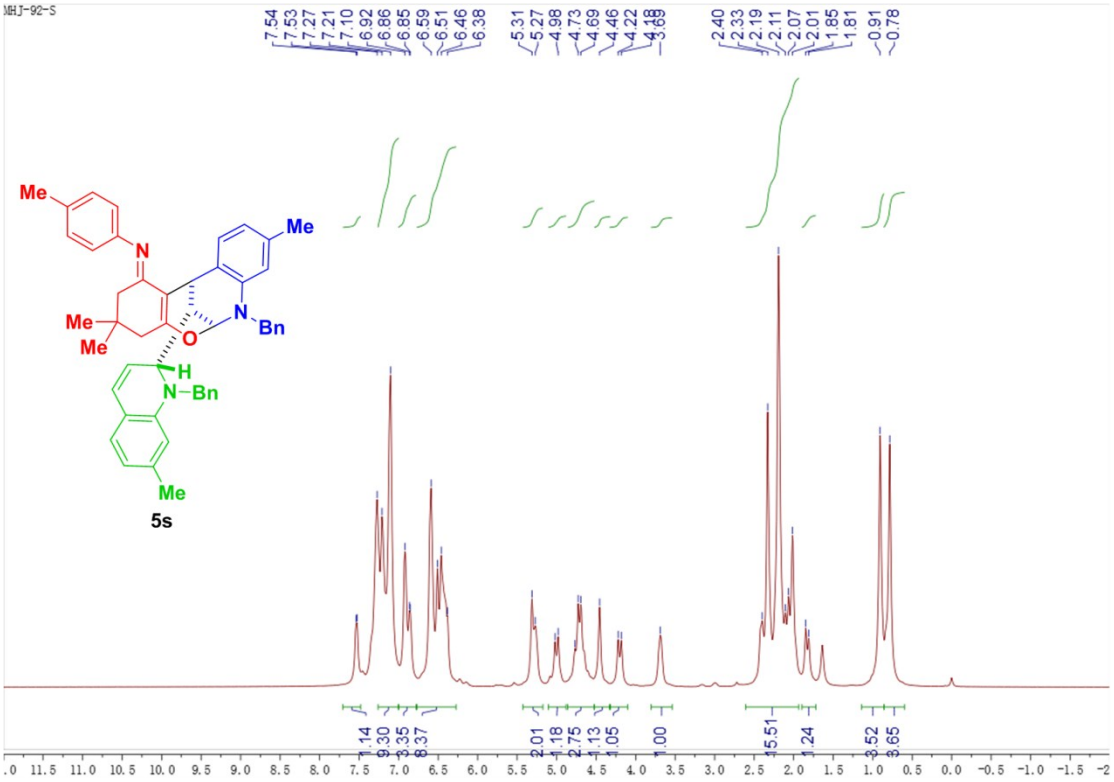
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2.33
2.19
2.11
2.07
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0.78
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Me
N
Bn
O
H
N
Bn
Me
5s
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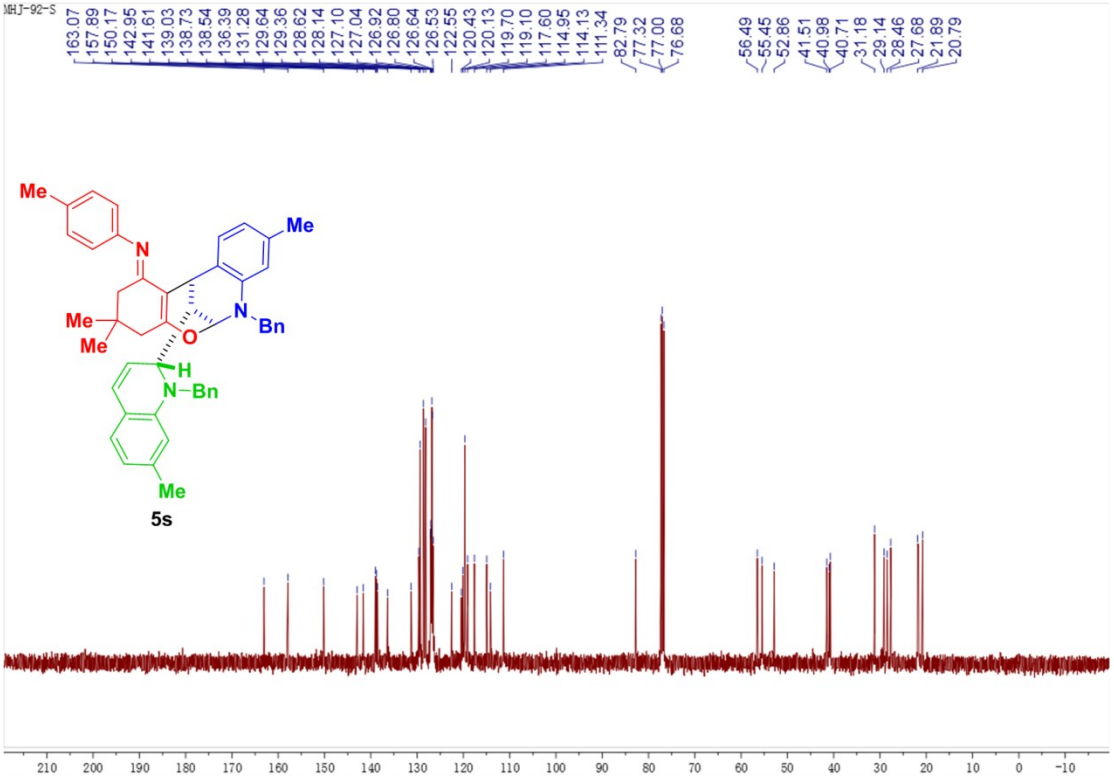
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111.34
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29.14
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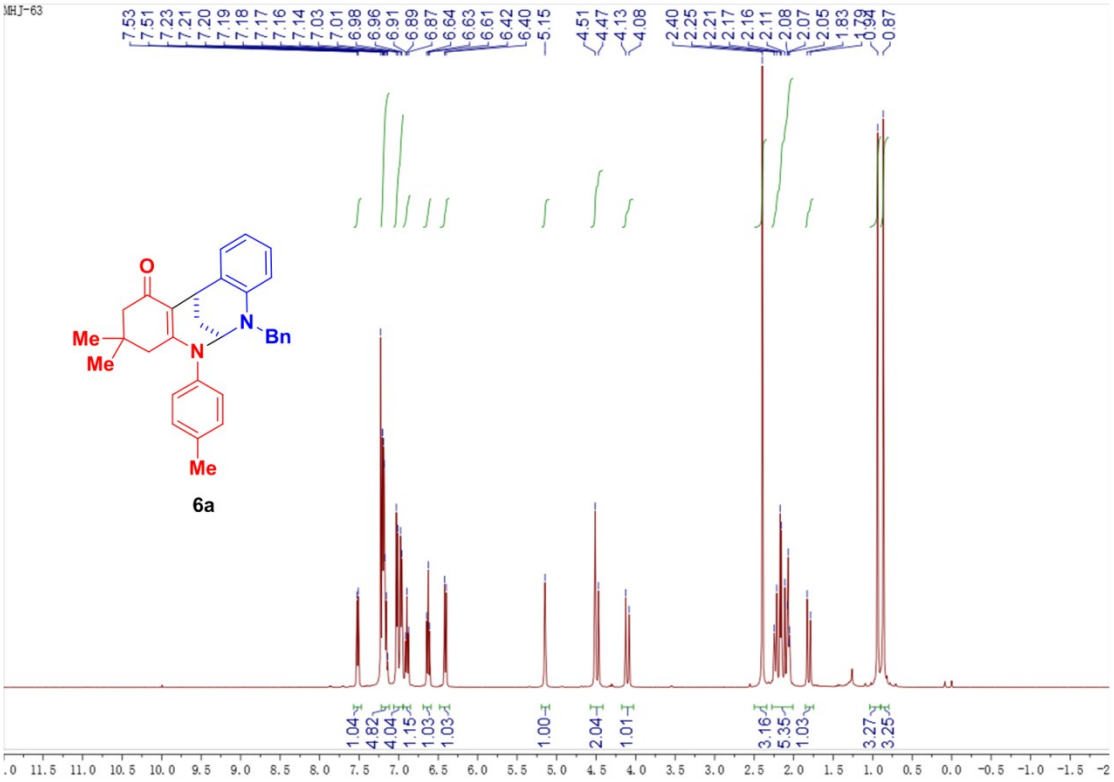
Bn
Me
5s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2.08
2.07
2.05
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Bn
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Me
N
Me
6a
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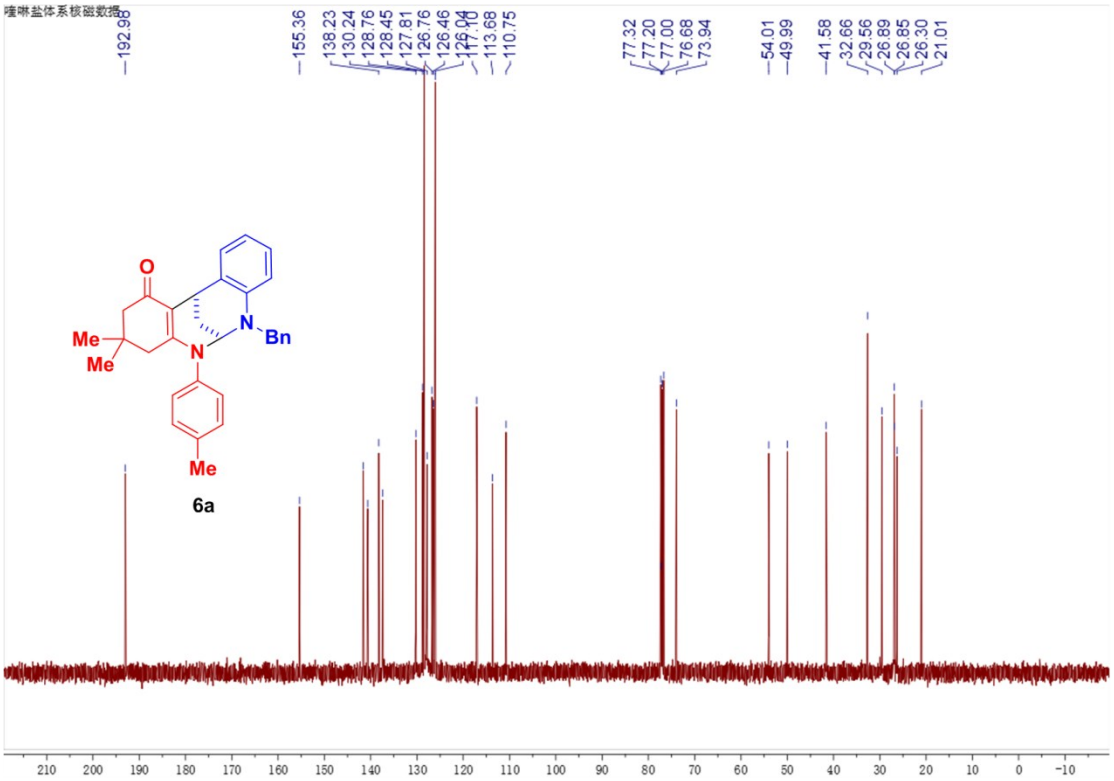
喹啉盐体系核磁数据
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77.00
76.68
73.94
54.01
49.99
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21.01
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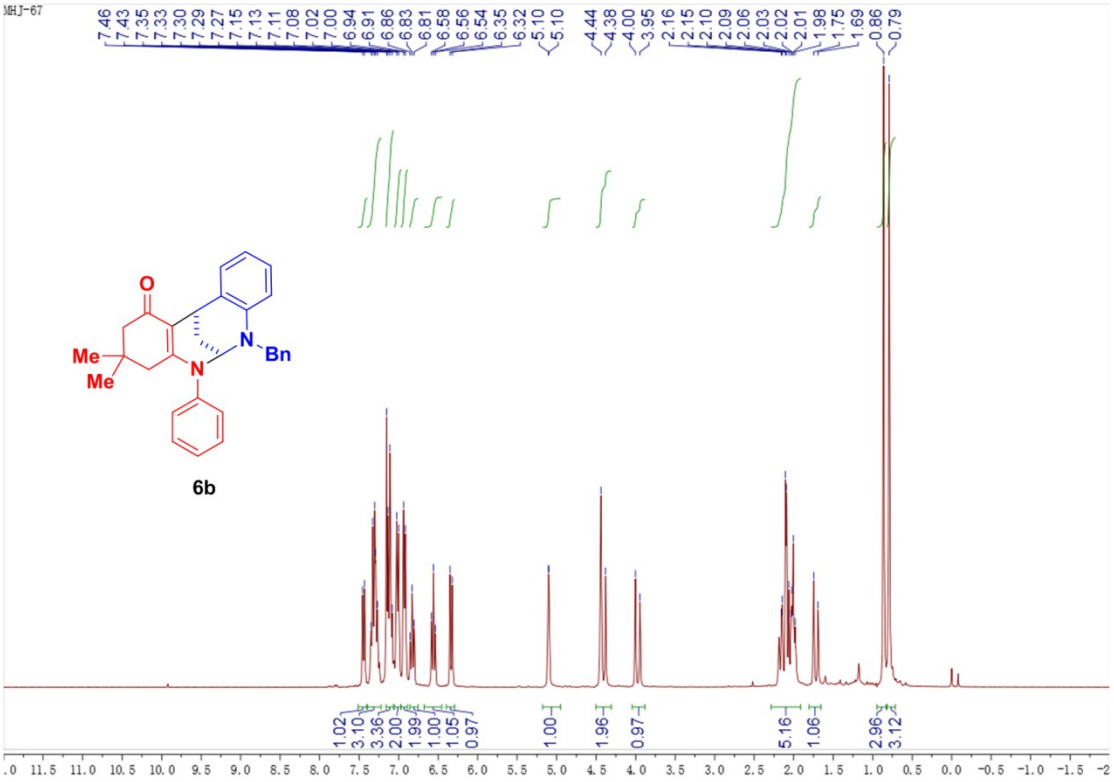
Me
N
Me
6a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6.56
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5.10
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2.10
2.09
2.06
2.03
2.02
2.01
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1.69
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0.79
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6b
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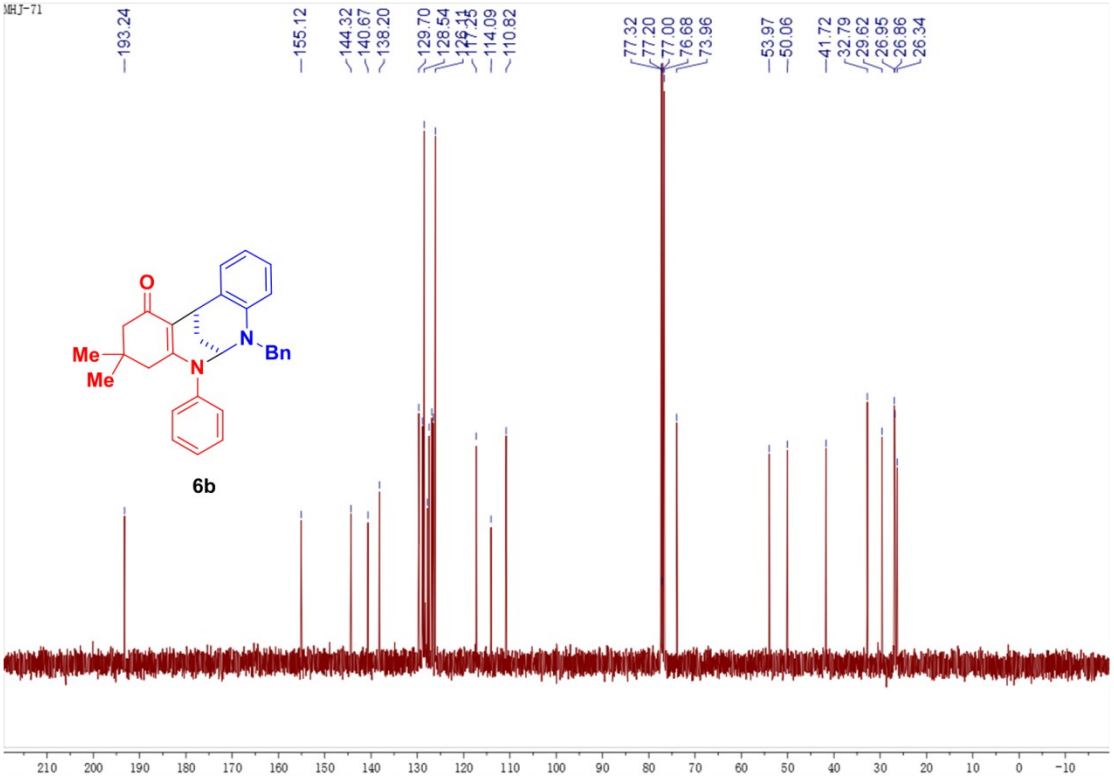
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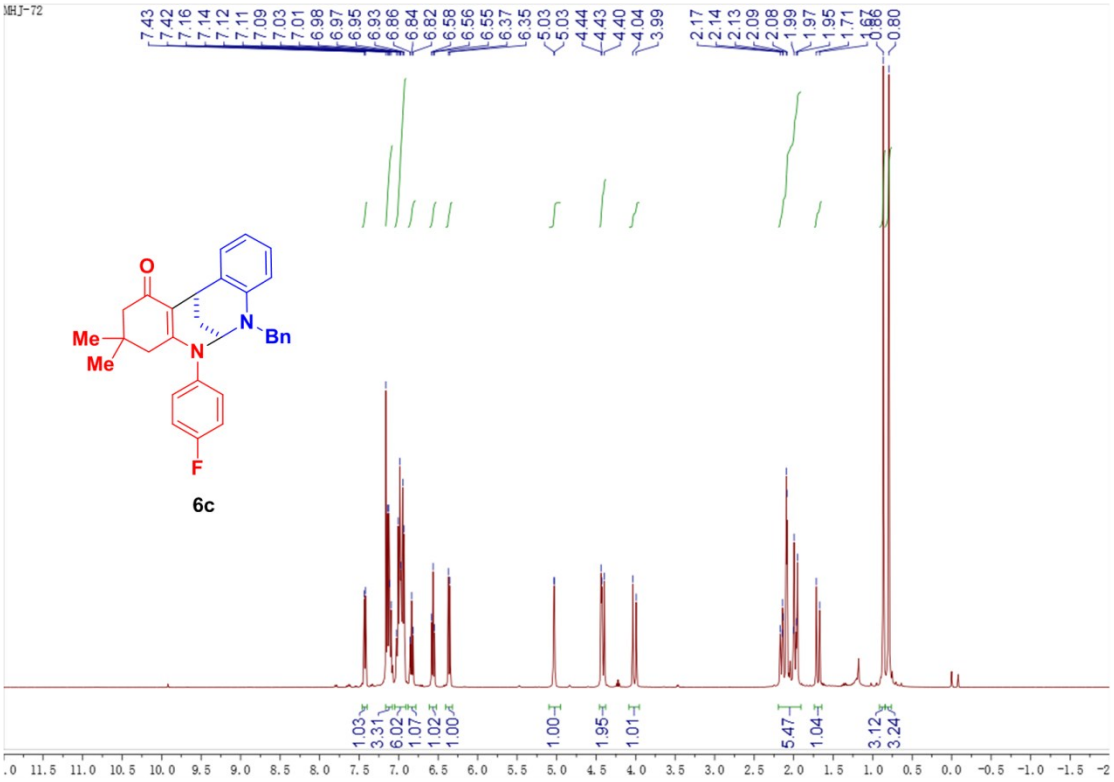
N
Bn
6b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6.86
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6.82
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6.55
6.37
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4.40
4.04
3.99
2.17
2.14
2.13
2.09
2.08
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1.95
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1.67
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Me
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N
Bn
F
6c
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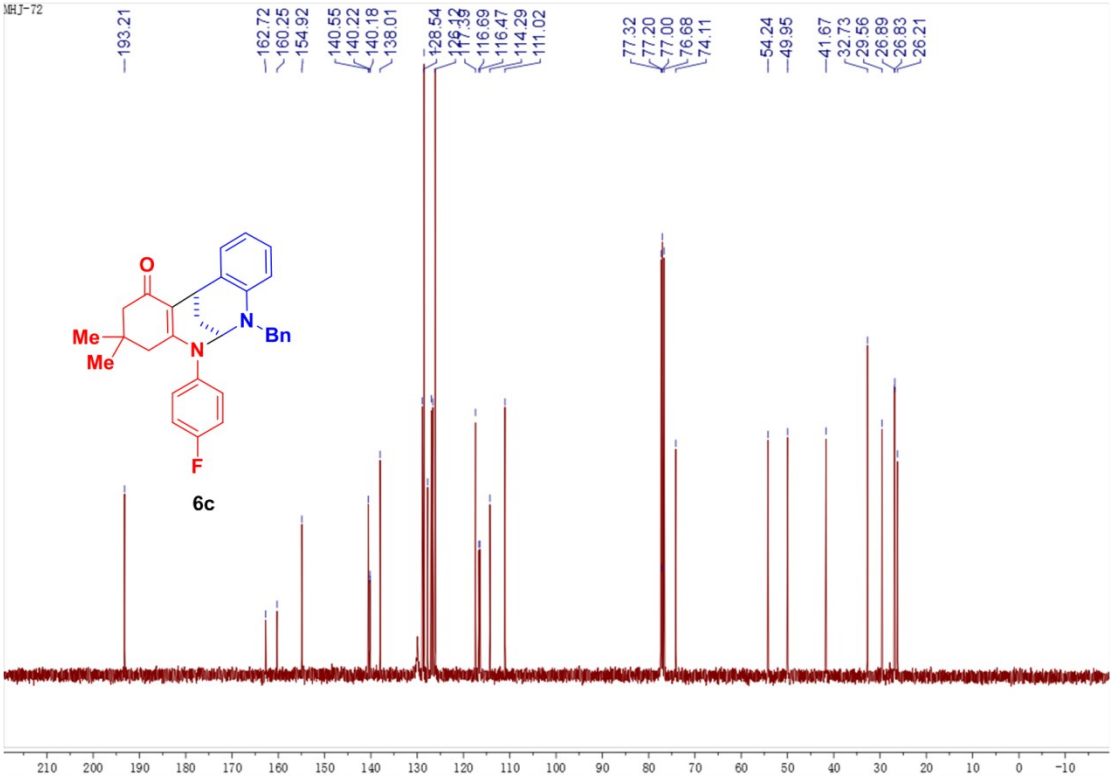
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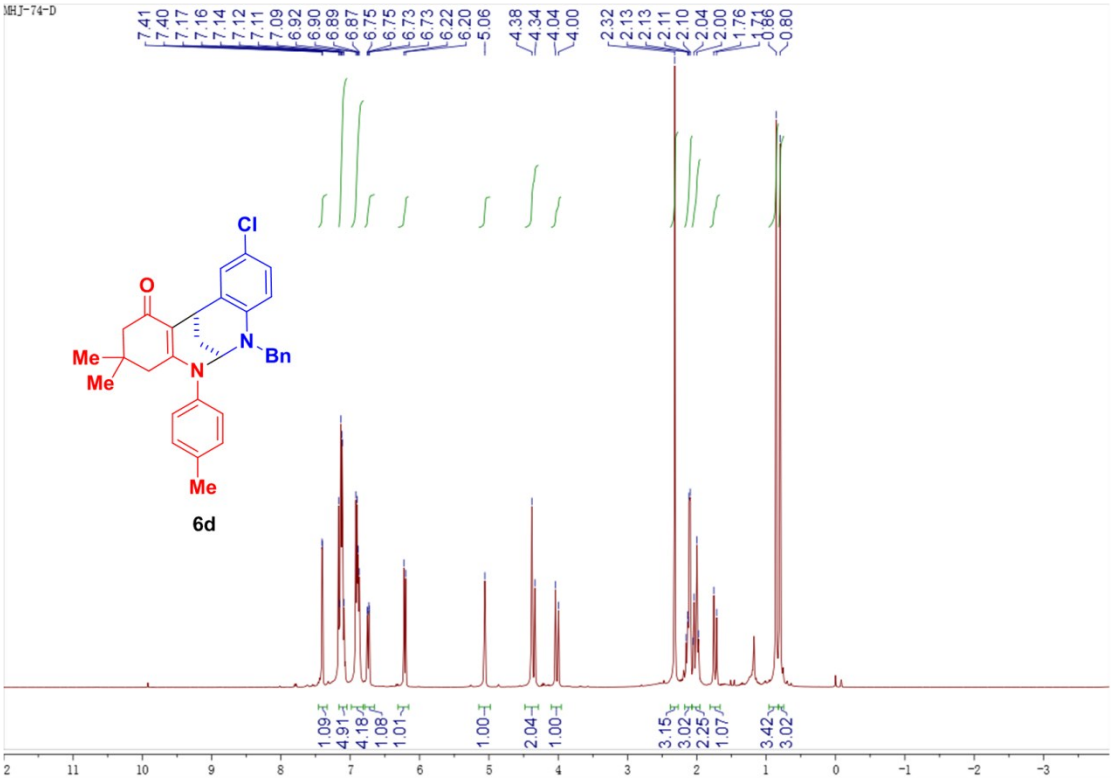
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2.13
2.13
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2.10
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Bn
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6d
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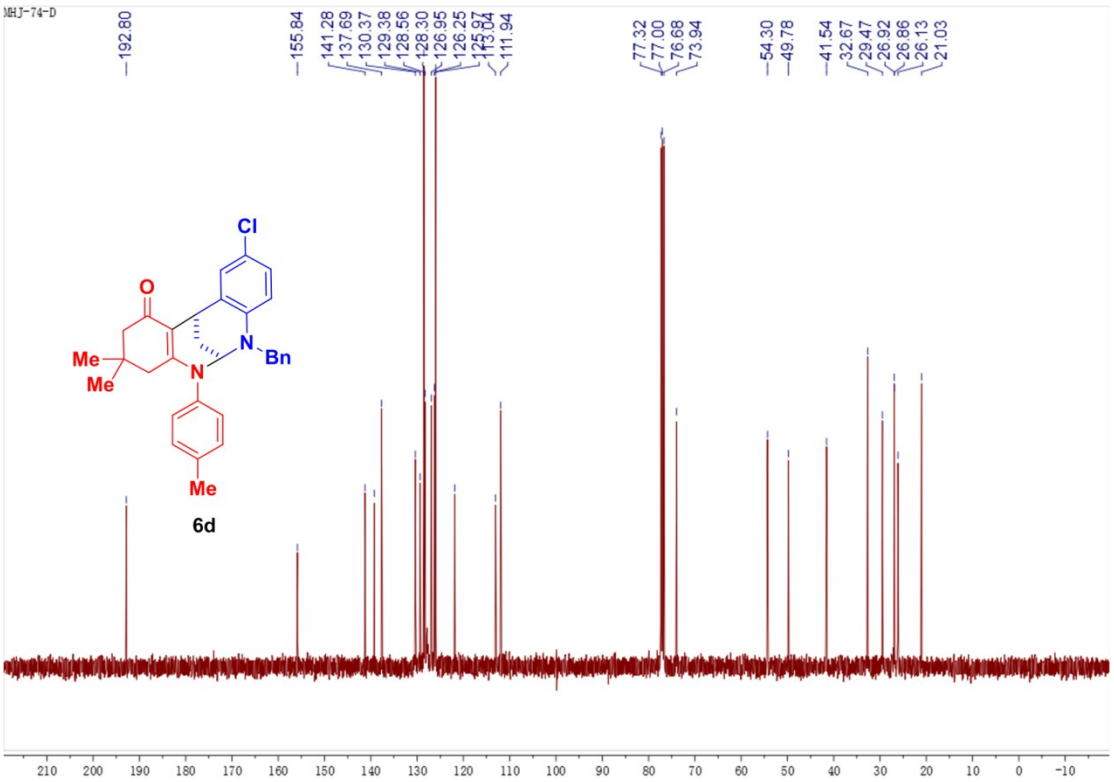
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41.54
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26.13
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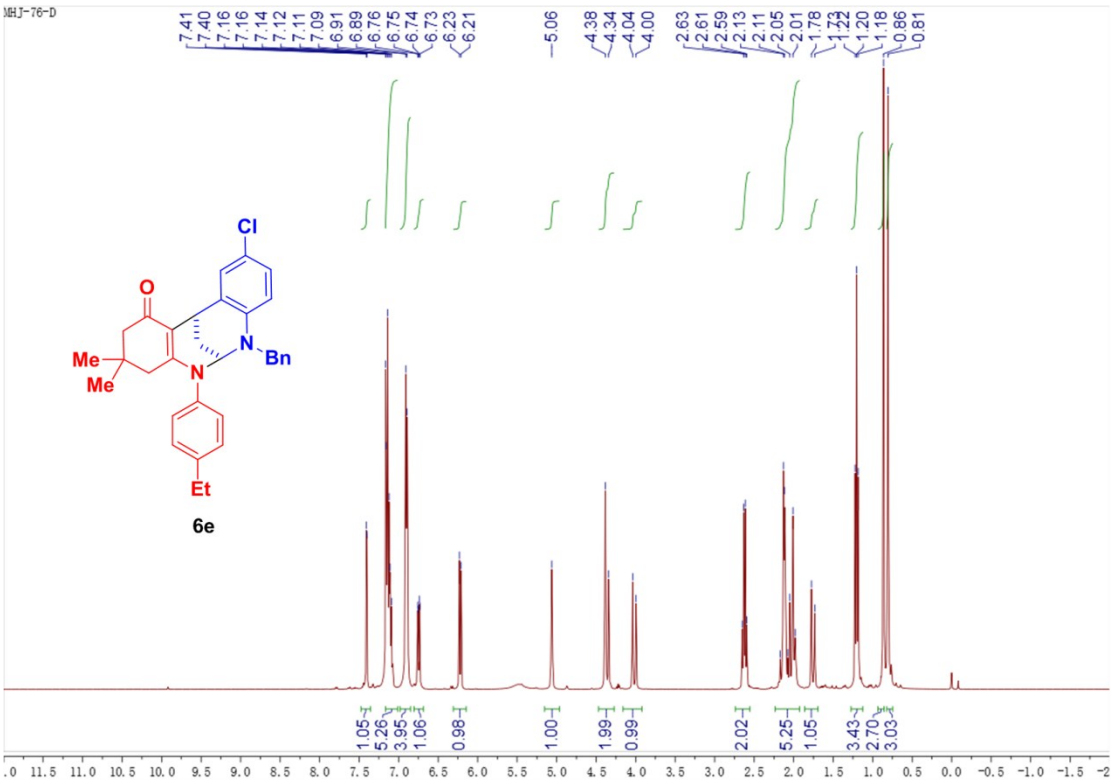
Me
6d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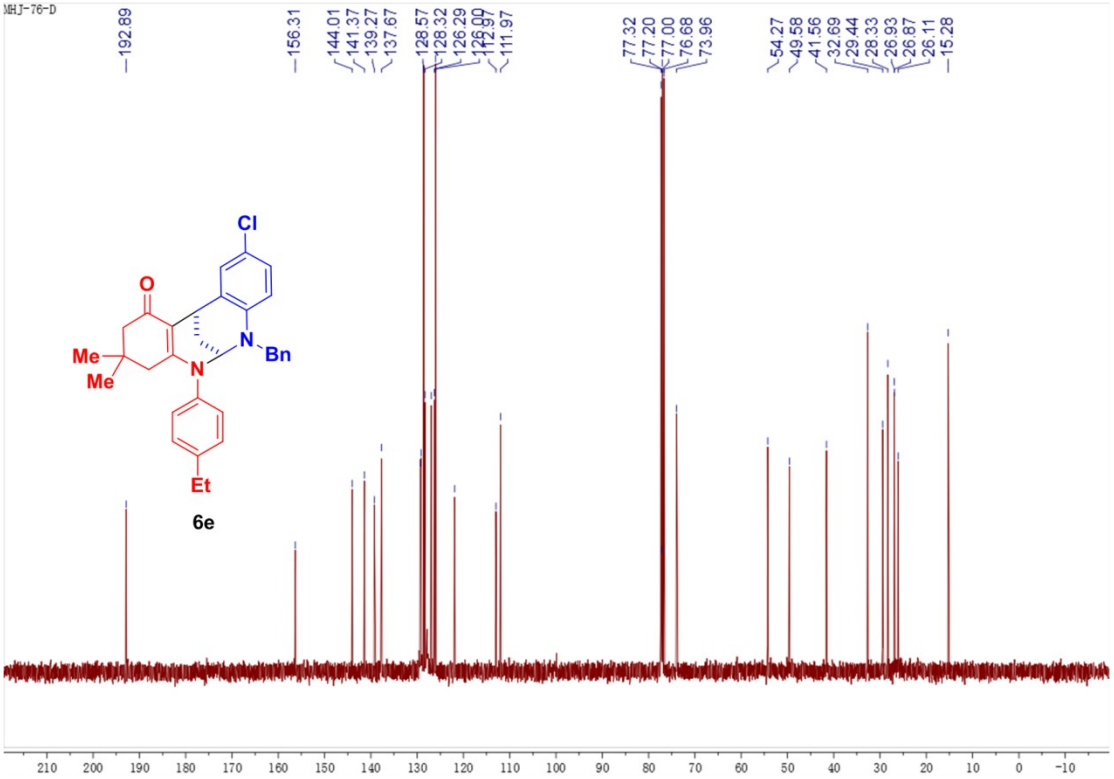
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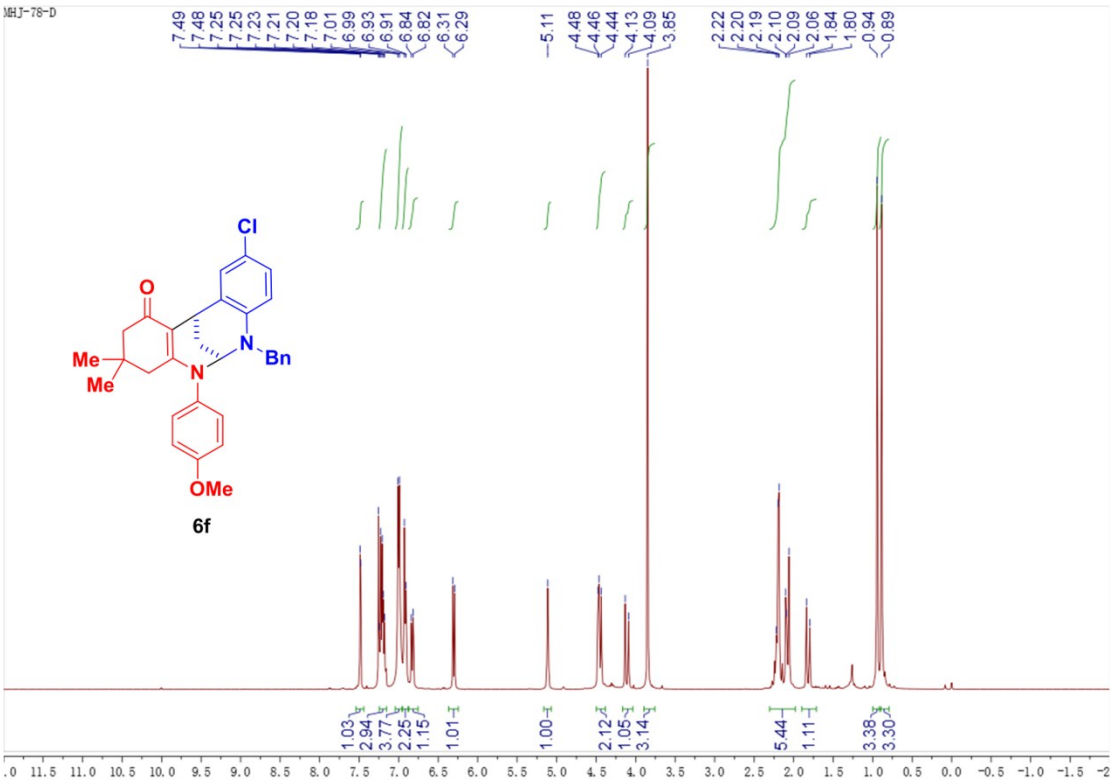
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2.06
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0.89
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Me
N
Bn
N
OMe
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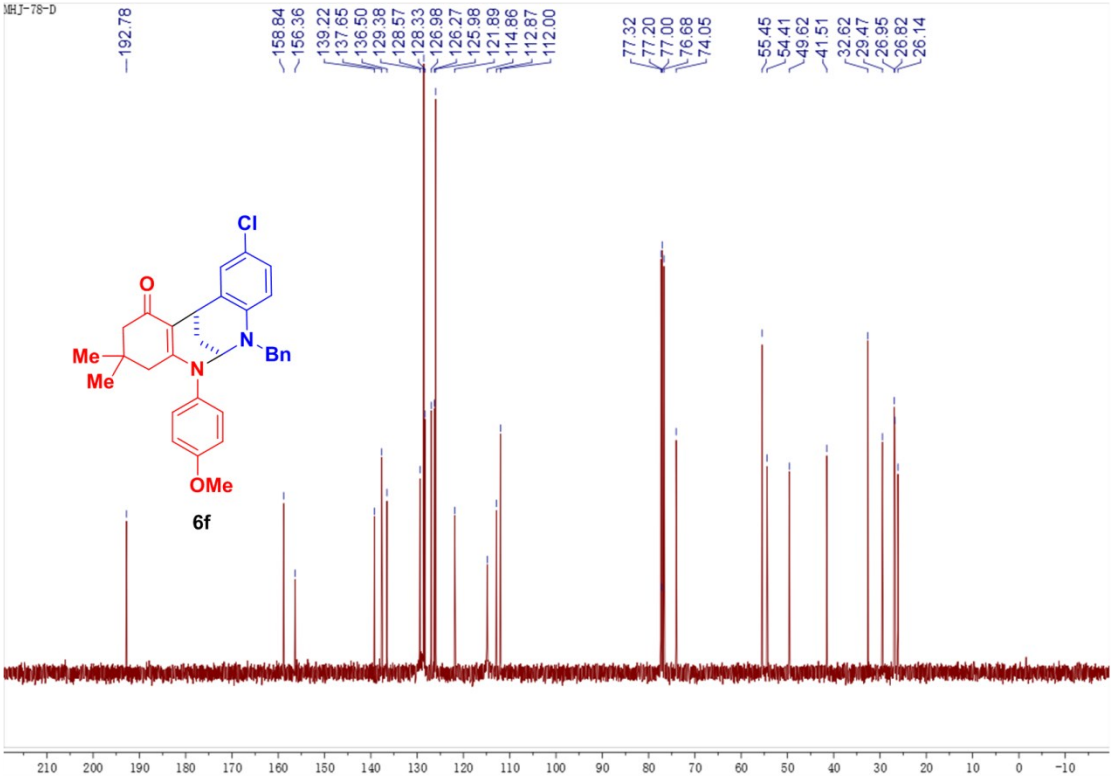
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OMe
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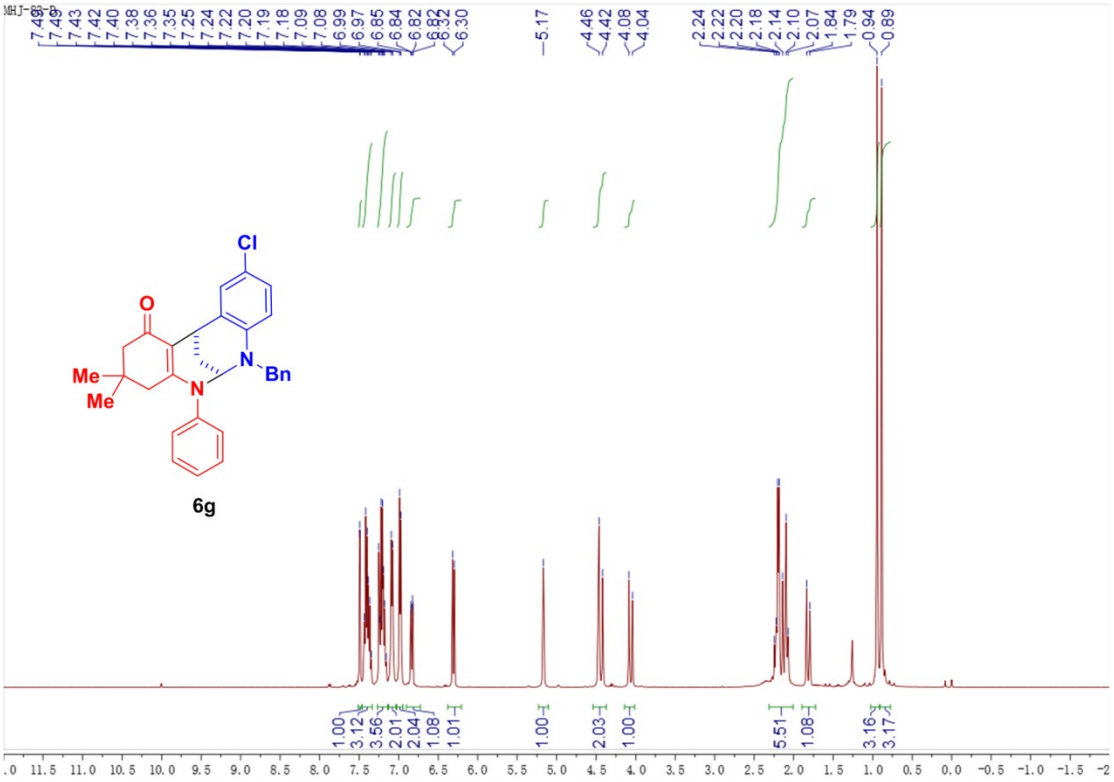
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6.97
6.85
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6.32
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4.08
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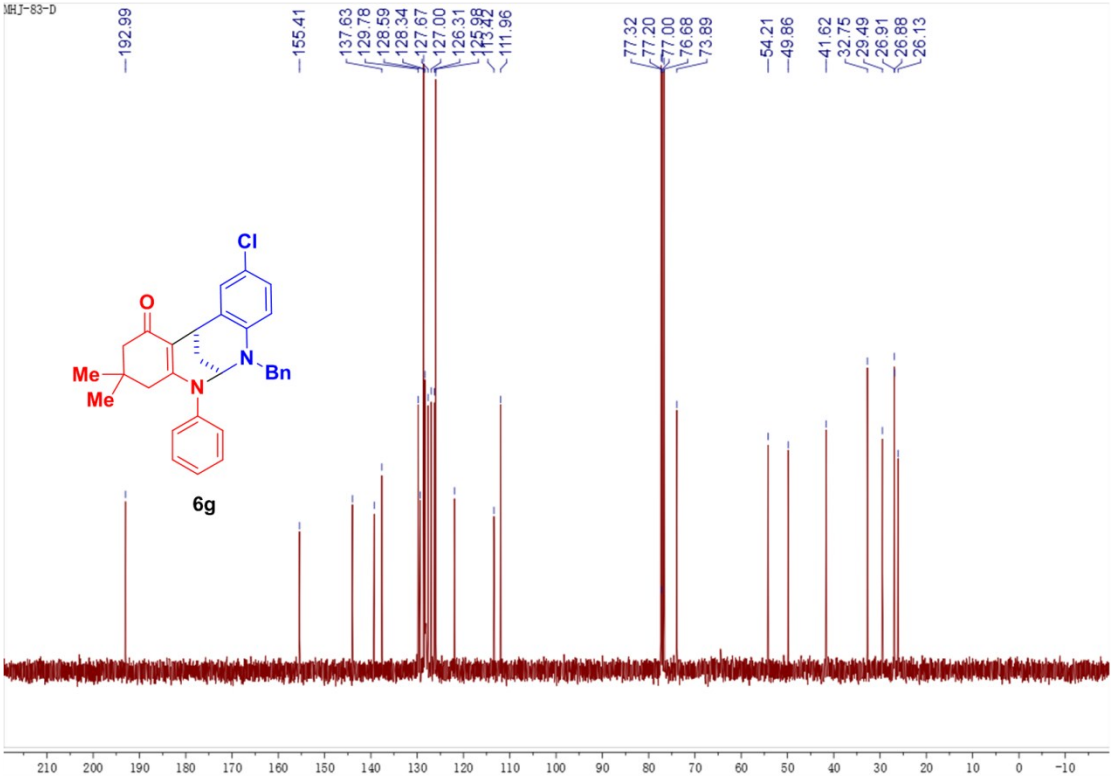
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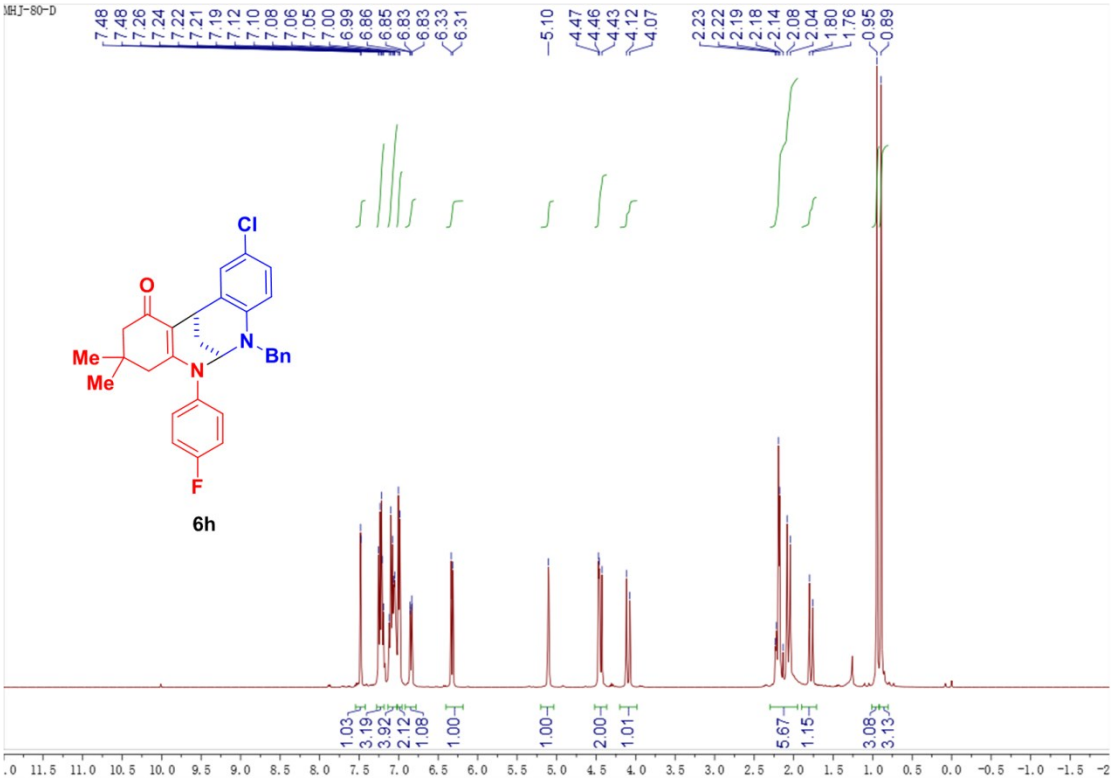
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6.86
6.85
6.83
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6.31
5.10
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4.43
4.12
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2.22
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2.18
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2.08
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N
Bn
F
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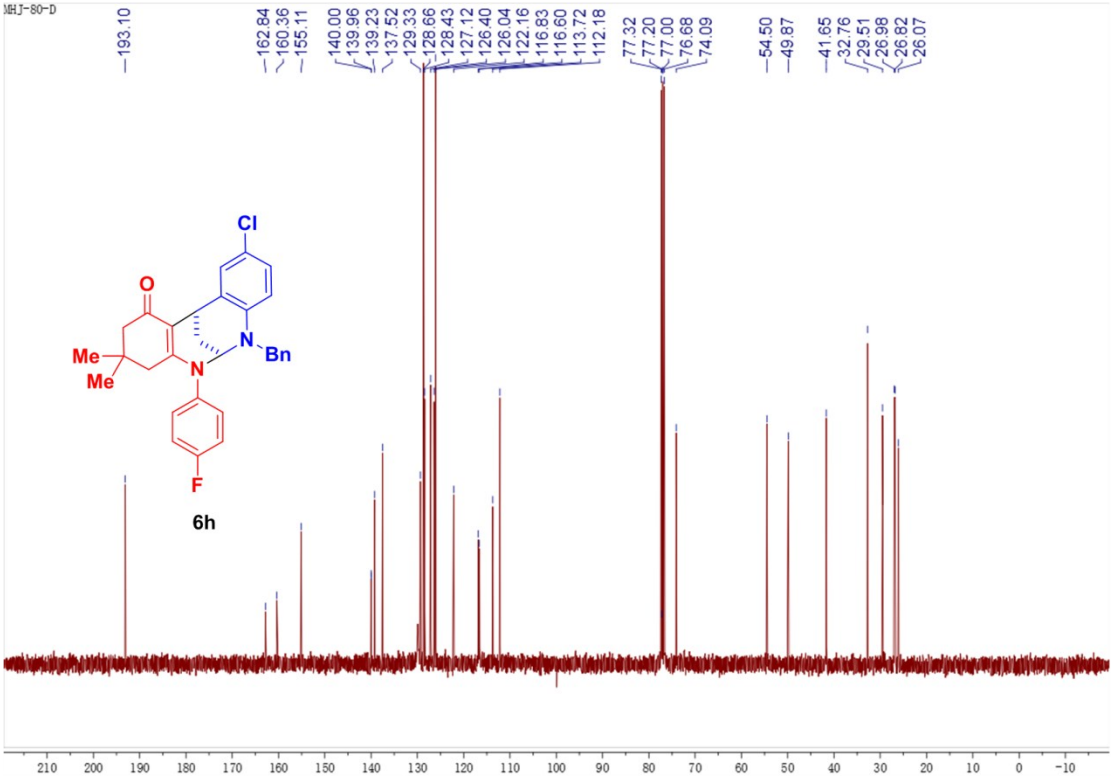
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Bn
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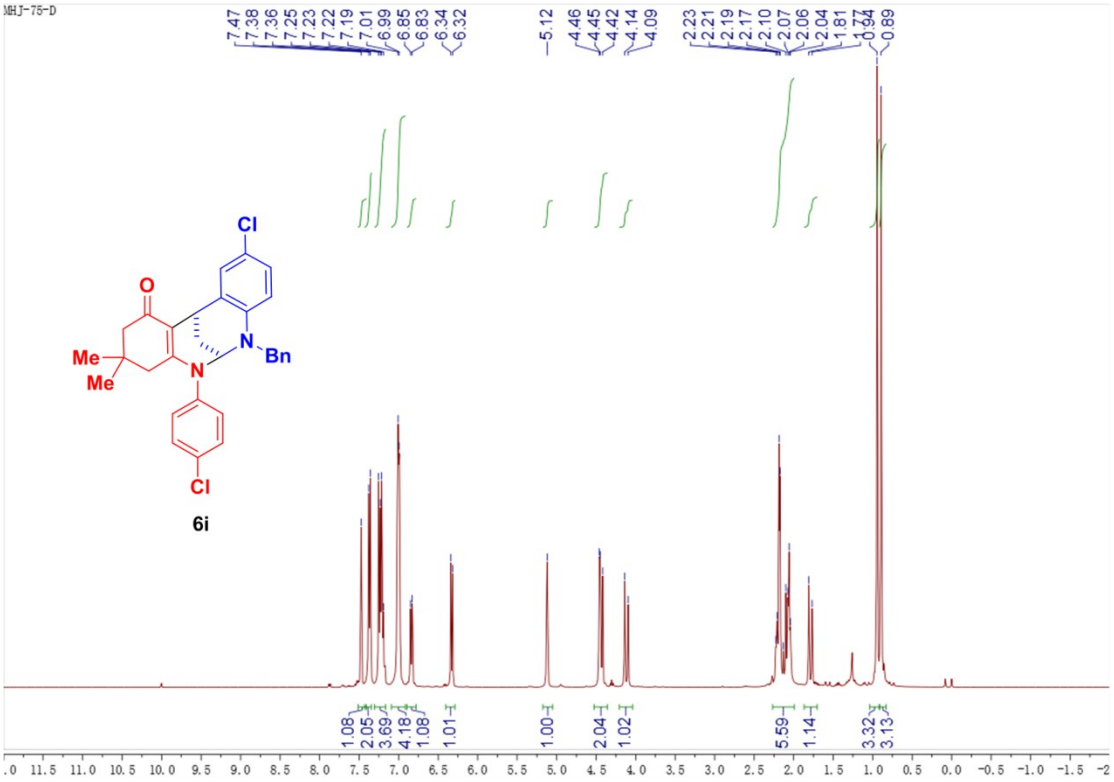
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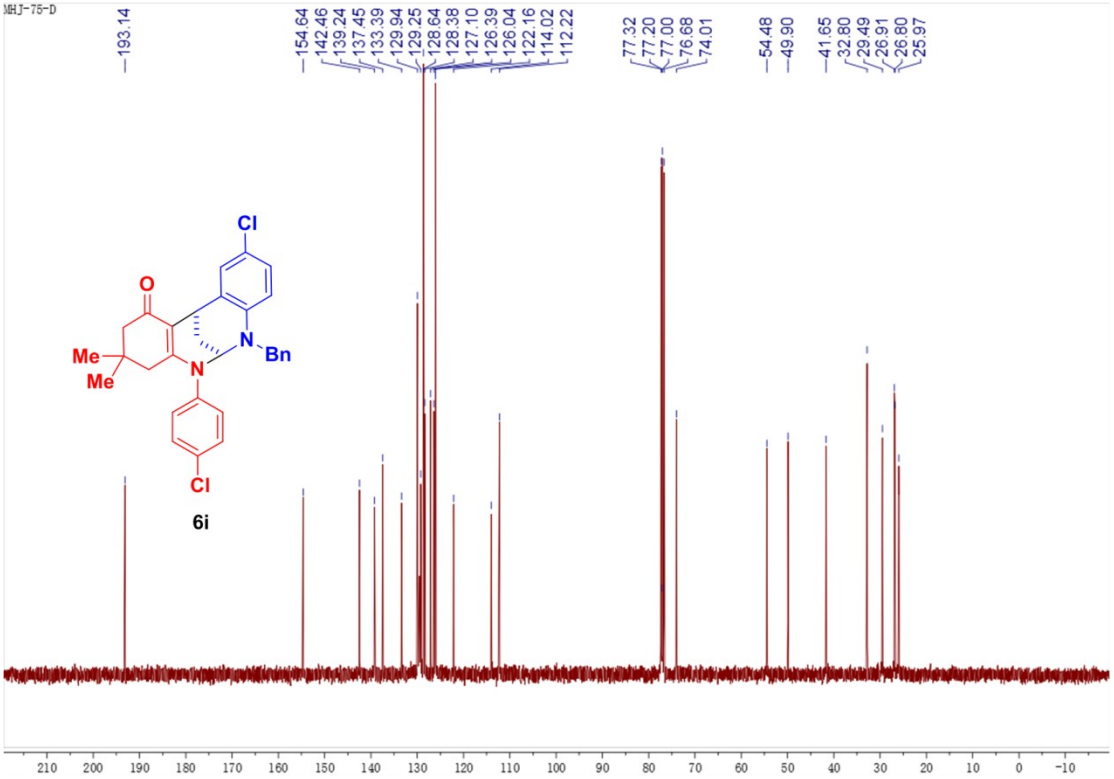
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74.01
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49.90
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Cl
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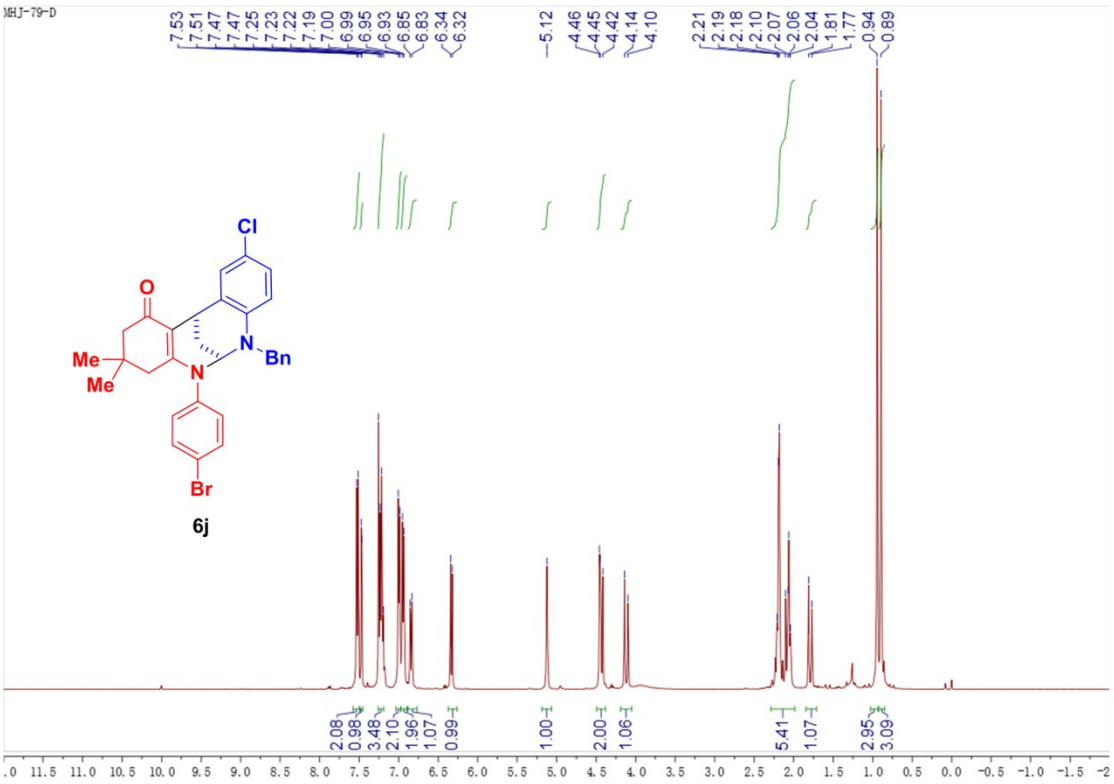
MHJ-79-D
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7.51
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6.93
6.85
6.83
6.34
6.32
5.12
4.46
4.45
4.42
4.14
4.10
2.21
2.19
2.18
2.10
2.07
2.06
2.04
1.81
1.77
0.94
0.89
Cl
O
Me
Me
N
N
Bn
Br
6j
2.08
0.98
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1.06
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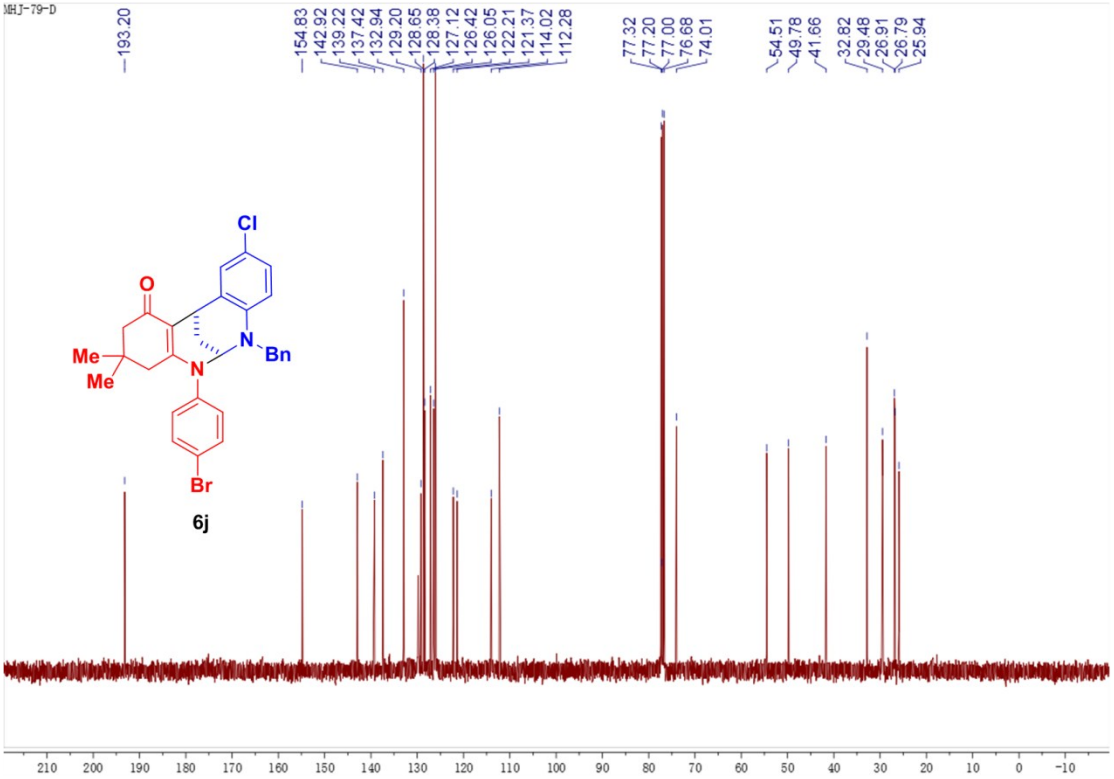
2.95
3.09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128.65
128.38
127.12
126.42
126.05
122.21
121.37
114.02
112.28
77.32
77.20
77.00
76.68
74.01
54.51
49.78
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29.48
26.91
26.79
25.94
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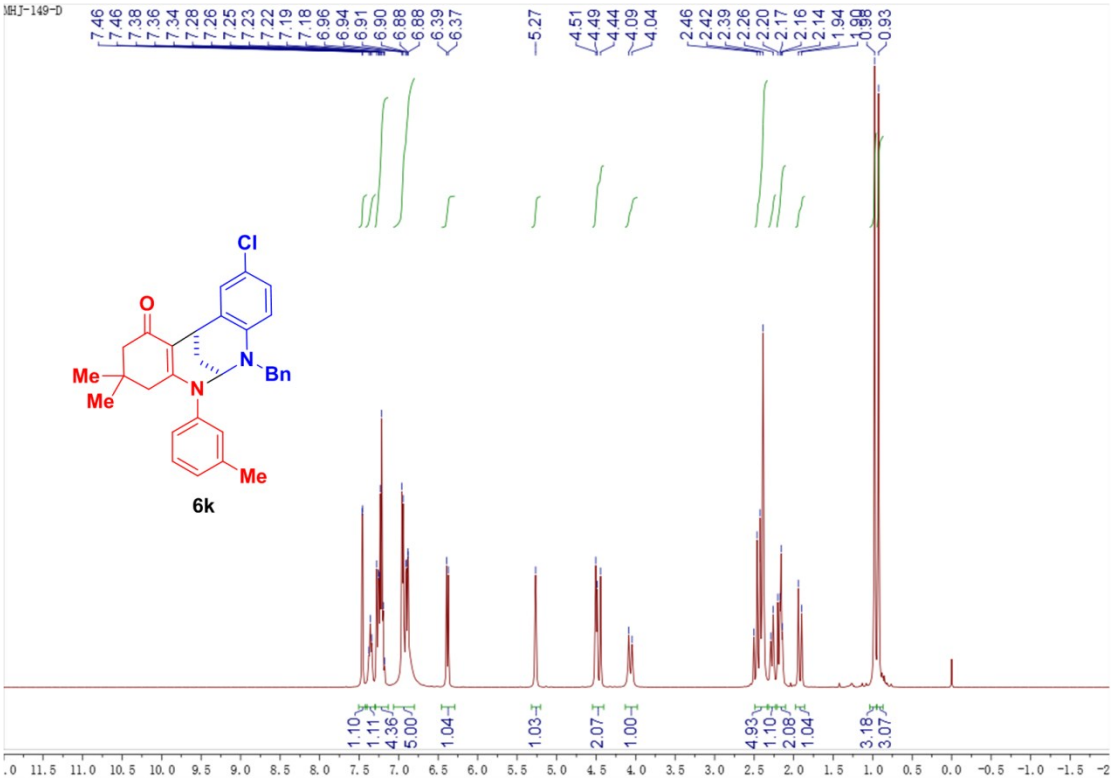
O
Me
Me
N
N
Bn
Br
6j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7.23
7.22
7.19
7.18
6.96
6.94
6.91
6.90
6.88
6.88
6.39
6.37
5.27
4.51
4.49
4.44
4.09
4.04
2.46
2.42
2.39
2.26
2.20
2.17
2.16
2.14
1.94
0.98
0.93
Cl
O
N
Bn
Me
Me
N
Me
6k
1.10
1.11
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1.04
1.03
2.07
1.00
4.93
1.10
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1.04
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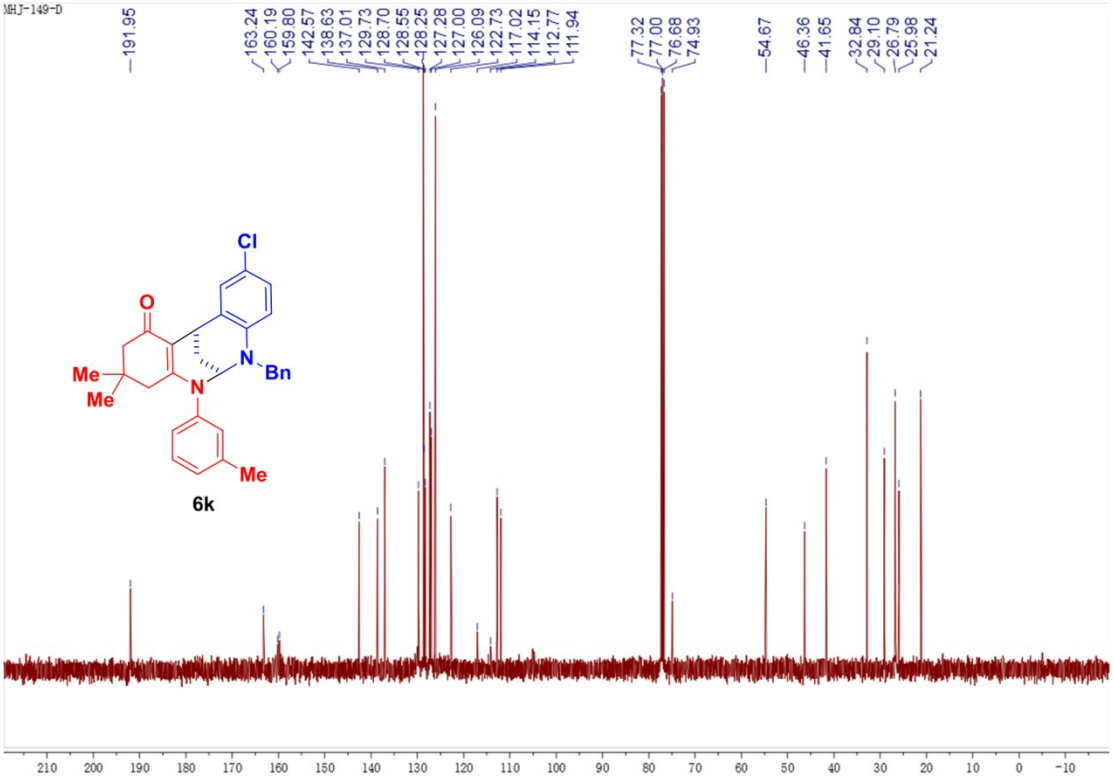
3.07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127.00
126.09
122.73
117.02
114.15
112.77
111.94
77.32
77.00
76.68
74.93
54.67
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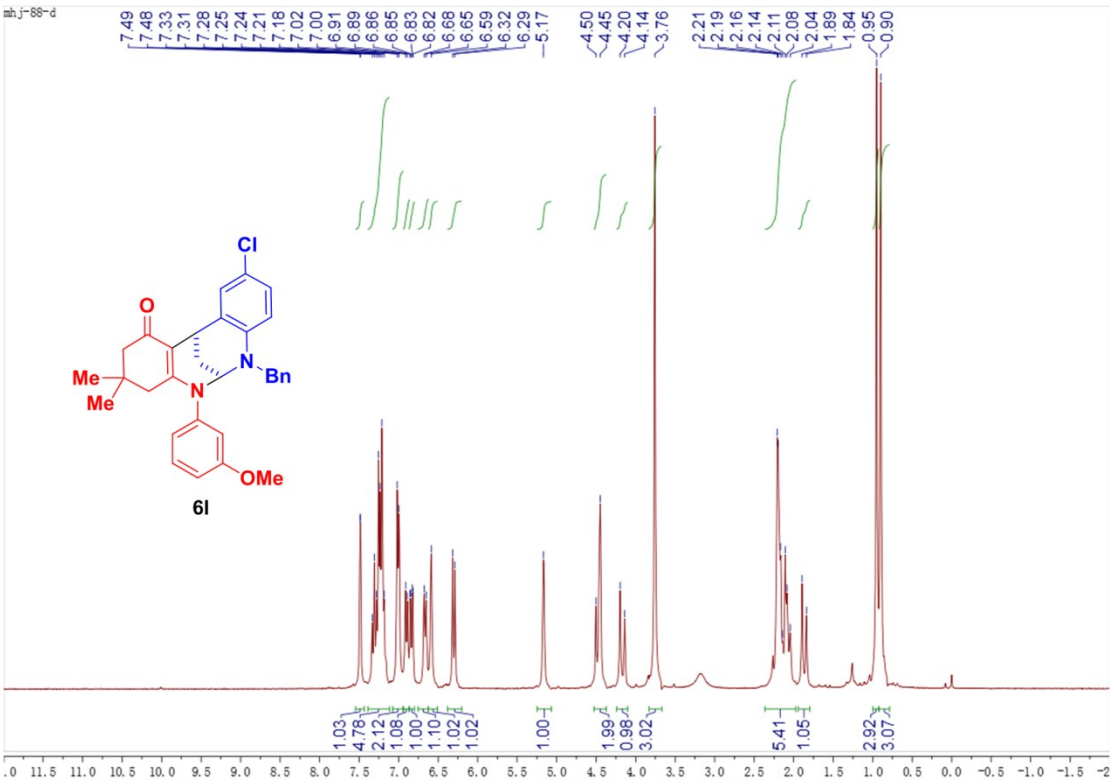
Me
6k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7.18
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6.86
6.85
6.83
6.82
6.68
6.65
6.59
6.32
6.29
5.17
4.50
4.45
4.20
4.14
3.76
2.21
2.19
2.16
2.14
2.11
2.08
2.04
1.89
1.84
0.95
0.90
Cl
O
N
Bn
Me
Me
N
OMe
6l
1.03
4.78
2.12
1.08
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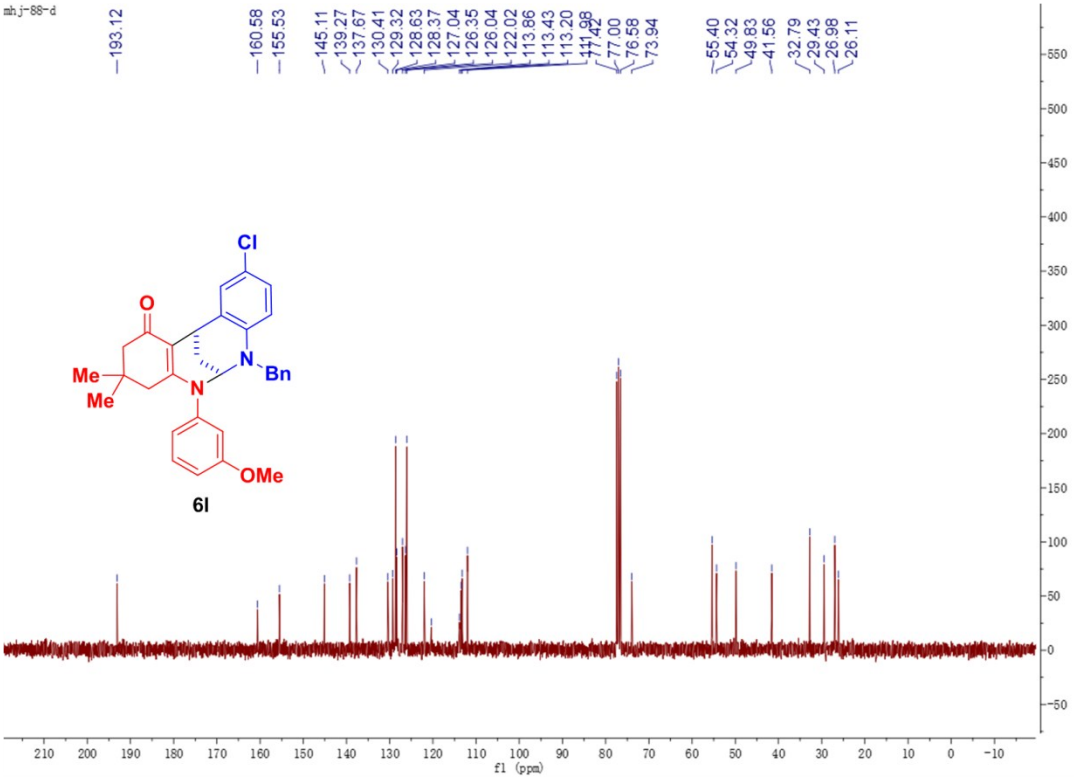
3.07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127.04
126.35
126.04
122.02
113.86
113.43
113.20
111.98
77.42
77.00
76.58
73.94
55.40
54.32
49.83
41.56
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26.11
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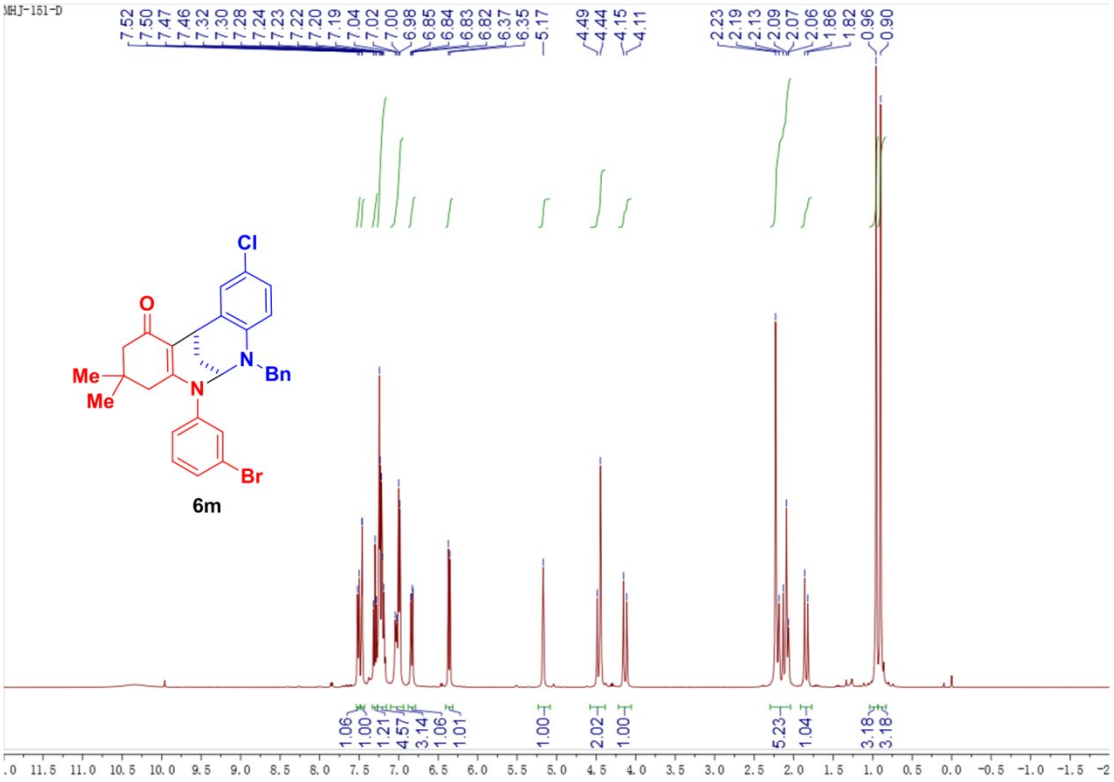
Bn
Me
Me
N
OMe
6l
f1 (ppm)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7.28
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7.23
7.22
7.20
7.19
7.04
7.02
7.00
6.98
6.85
6.84
6.83
6.82
6.37
6.35
5.17
4.49
4.44
4.15
4.11
2.23
2.19
2.13
2.09
2.07
2.06
1.86
1.82
0.96
0.90
Cl
O
N
Bn
Me
Me
N
Br
6m
1.06
1.00
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1.06
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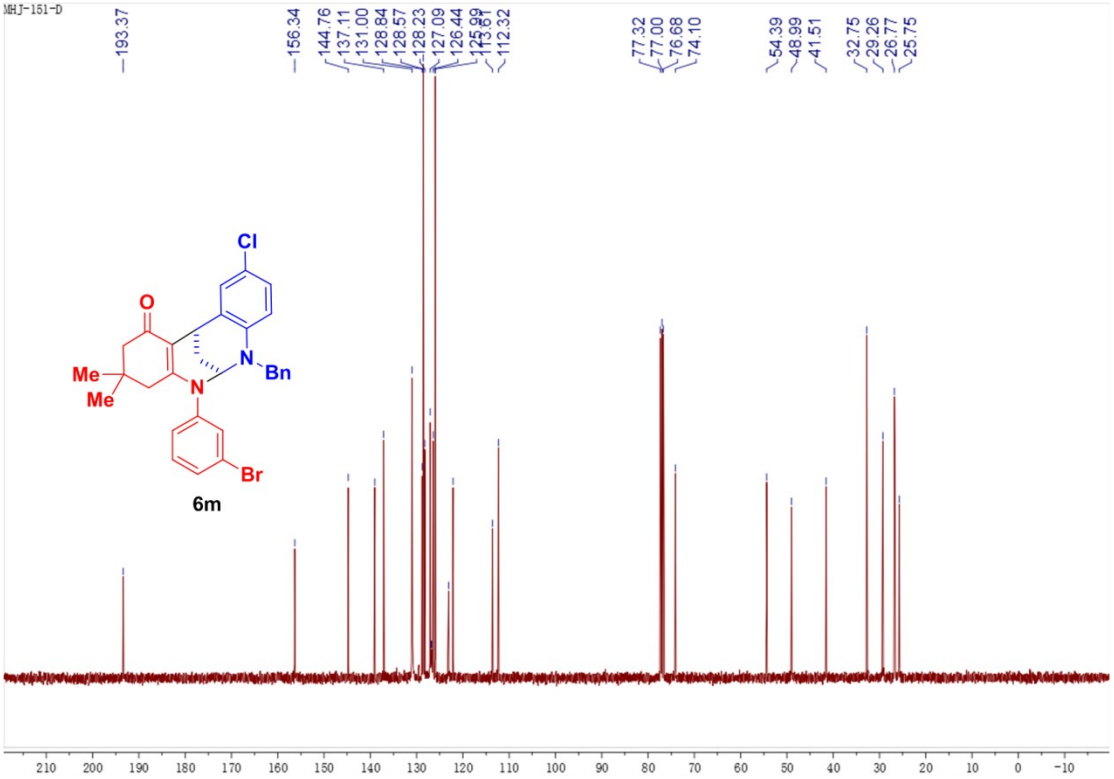
1.00
2.02
1.00
5.23
1.04
3.18
3.18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77.32
77.00
76.68
74.10
54.39
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32.75
29.26
26.77
25.75
Cl
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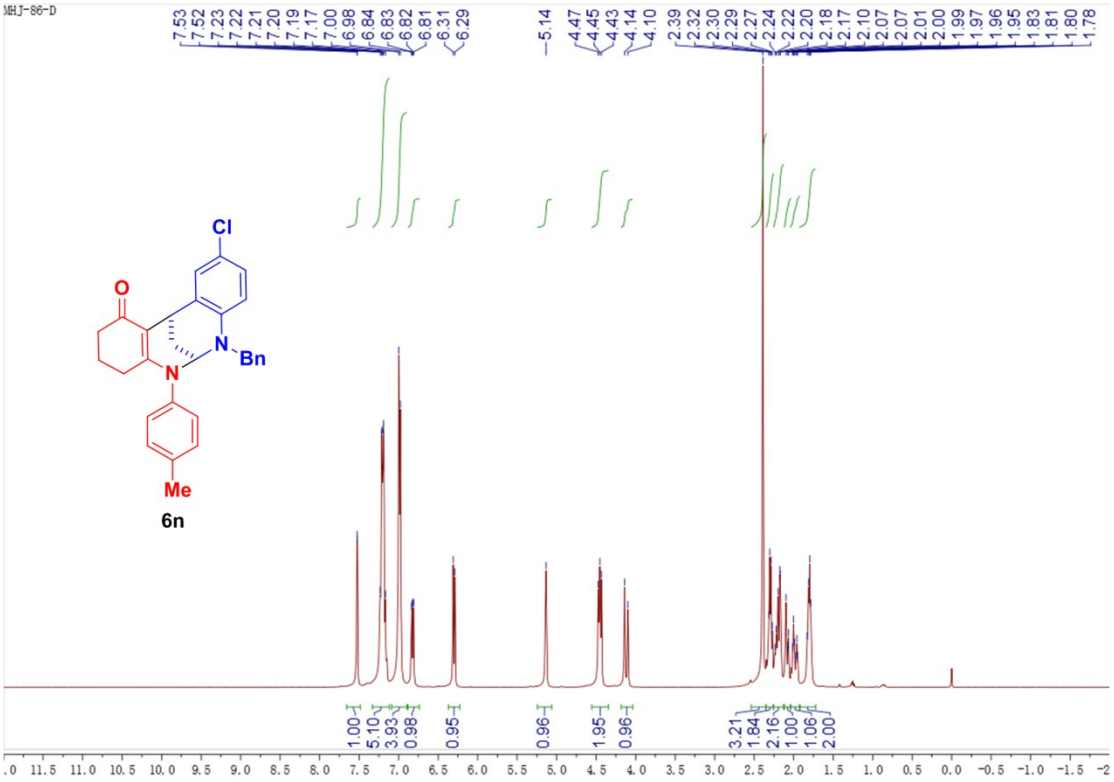
N
Bn
Me
Me
N
Br
6m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7.53 7.52 7.23 7.22 7.21 7.20 7.19 7.17 7.00 6.98 6.84 6.83 6.82 6.81 6.31 6.29
5.14
4.47 4.45 4.43 4.14 4.10
2.39 2.32 2.30 2.29 2.27 2.24 2.22 2.20 2.18 2.17 2.10 2.07 2.07 2.01 2.00 1.99 1.97 1.96 1.95 1.83 1.81 1.80 1.78
Cl
O
N
Bn
N
Me
6n
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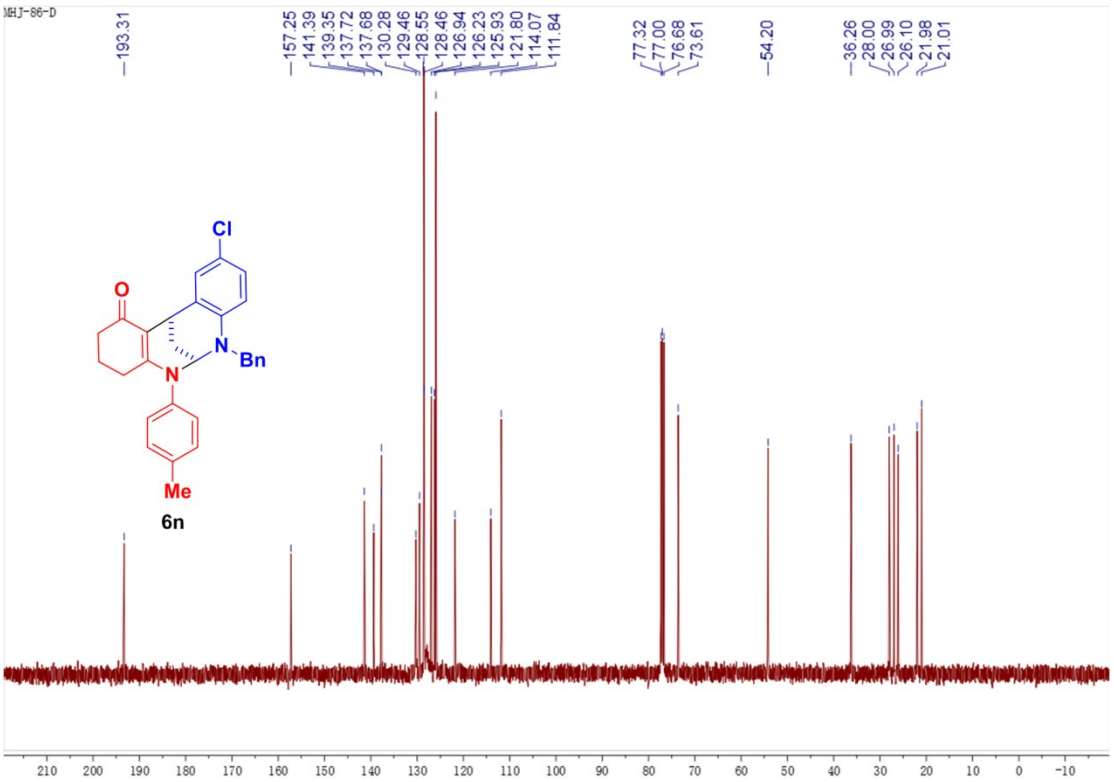
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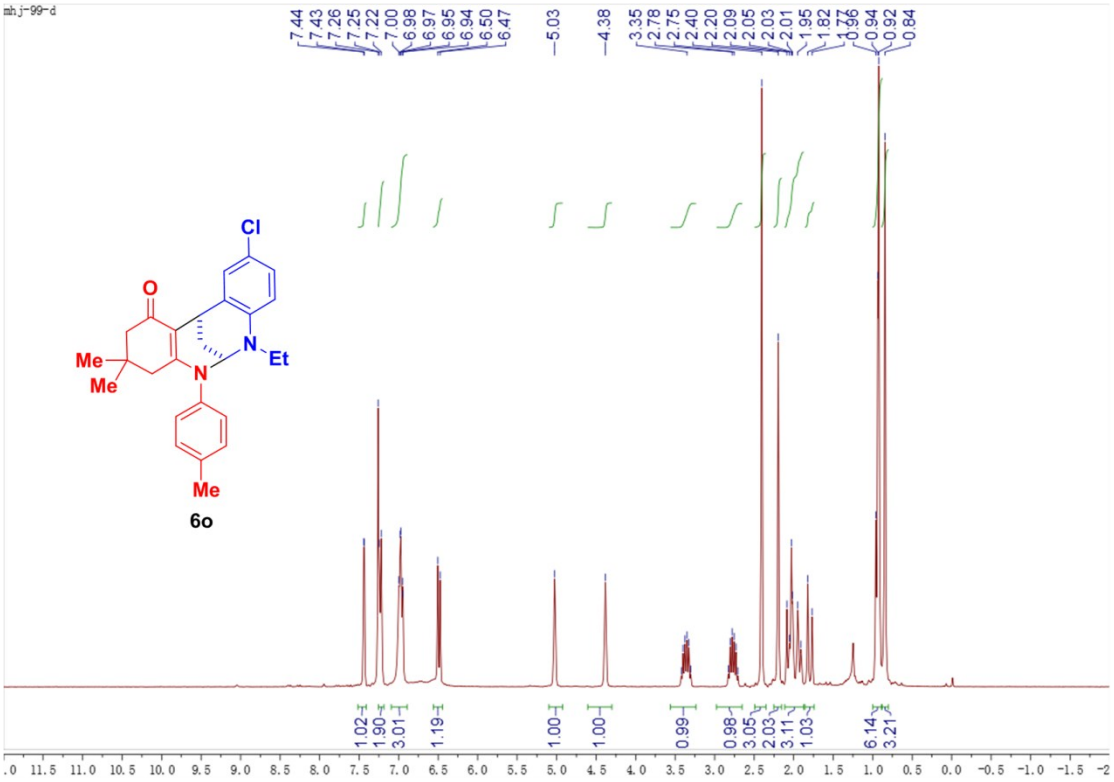
77.32 77.00 76.68 73.61
54.20
36.26 28.00 26.99 26.10 21.98 21.01
Cl
O
N
Bn
N
Me
6n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6.97
6.95
6.94
6.50
6.47
5.03
4.38
3.35
2.78
2.75
2.40
2.20
2.09
2.05
2.03
2.01
1.95
1.82
1.77
0.96
0.94
0.92
0.84
Cl
O
Me
Me
N
Et
N
Me
6o
1.02
1.90
3.01
1.19
1.00
1.00
0.99
0.98
3.05
2.03
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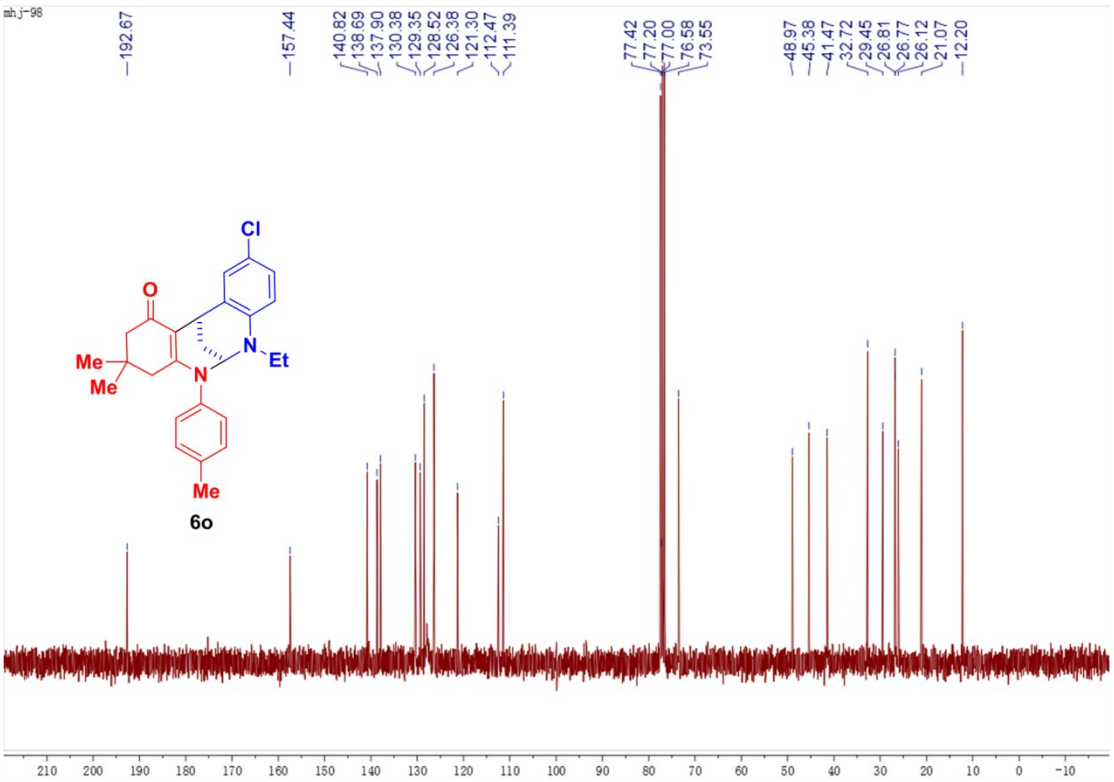
1.03
6.14
3.21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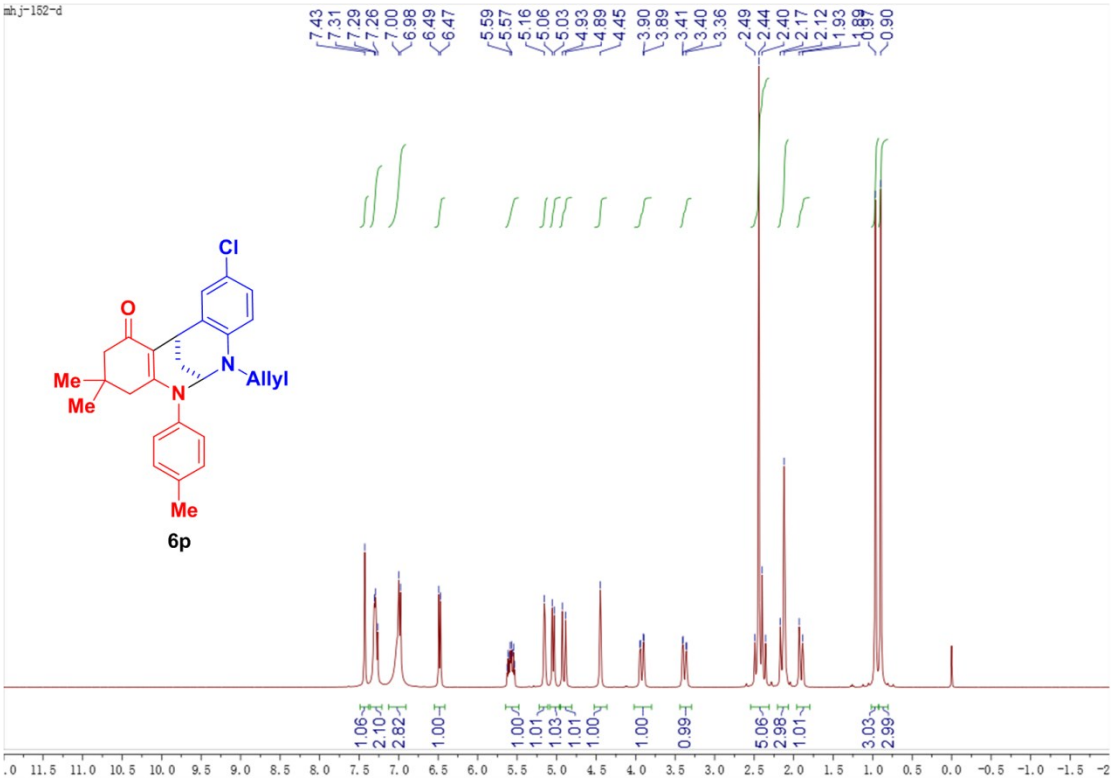
129.35
128.52
126.38
121.30
112.47
111.39
77.42
77.20
77.00
76.58
73.55
48.97
45.38
41.47
32.72
29.45
26.81
26.77
26.12
21.07
12.20
Cl
O
Me
Me
N
Et
N
Me
6o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6.49
6.47
5.59
5.57
5.16
5.06
5.03
4.93
4.89
4.45
3.90
3.89
3.41
3.40
3.36
2.49
2.44
2.40
2.17
2.12
1.93
0.97
0.90
Cl
O
N
Allyl
Me
Me
N
Me
6p
1.06
2.10
2.82
1.00
1.00
1.01
1.03
1.01
1.00
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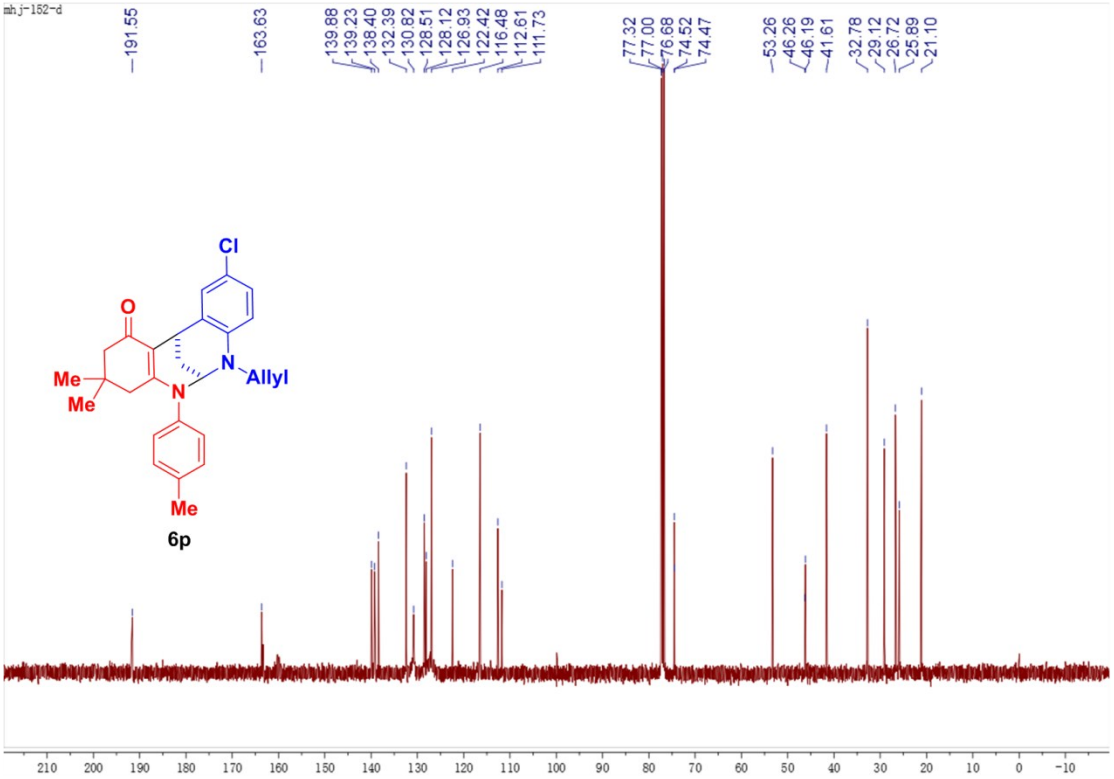
5.06
2.98
1.01
3.03
2.99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116.48
112.61
111.73
77.32
77.00
76.68
74.52
74.47
53.26
46.26
46.19
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26.72
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21.10
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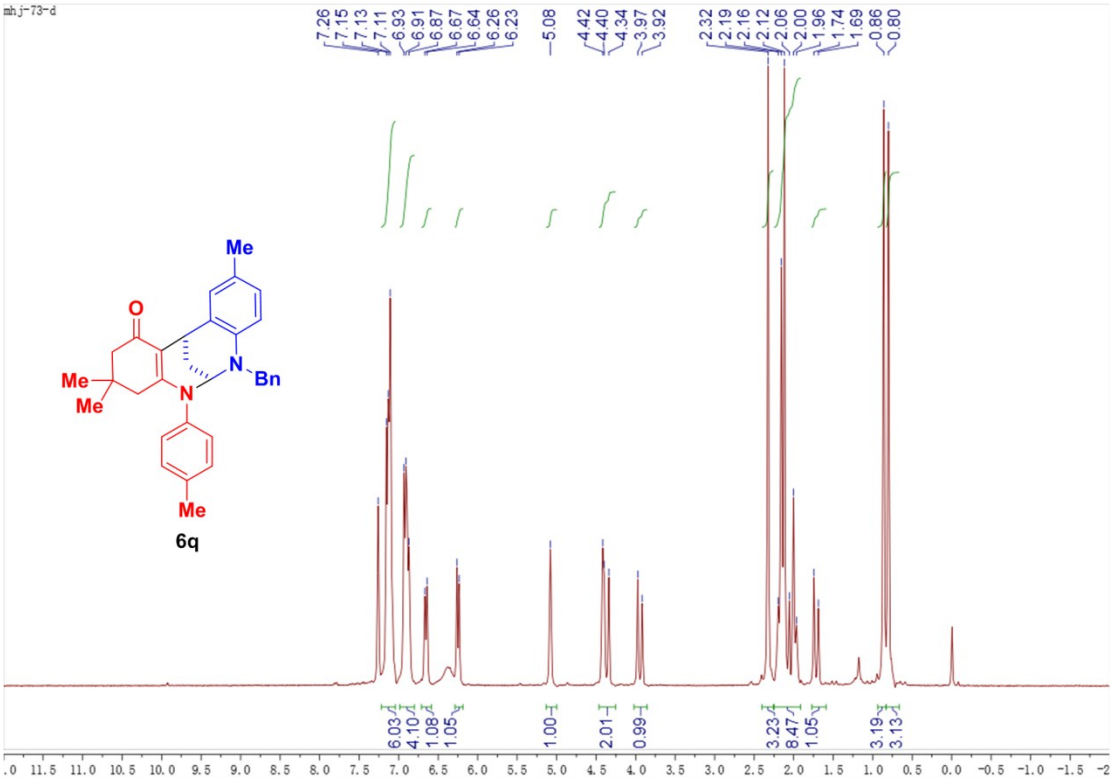
N
Allyl
Me
Me
N
Me
6p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6.23
5.08
4.42
4.40
4.34
3.97
3.92
2.32
2.19
2.16
2.12
2.06
2.00
1.96
1.74
1.69
0.86
0.80
Me
O
N
Bn
Me
Me
N
Me
6q
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1.05
1.00
2.01
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3.23
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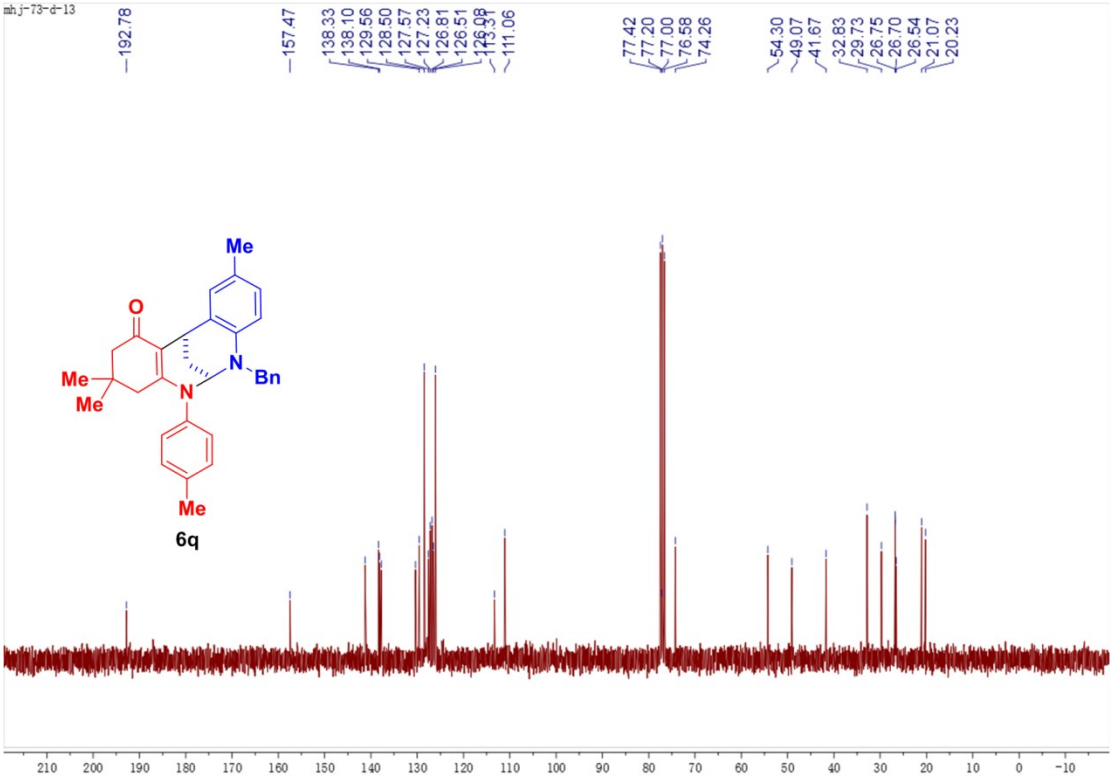
3.13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127.23
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126.51
111.06
77.42
77.20
77.00
76.58
74.26
54.30
49.07
41.67
32.83
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26.70
26.54
21.07
20.23
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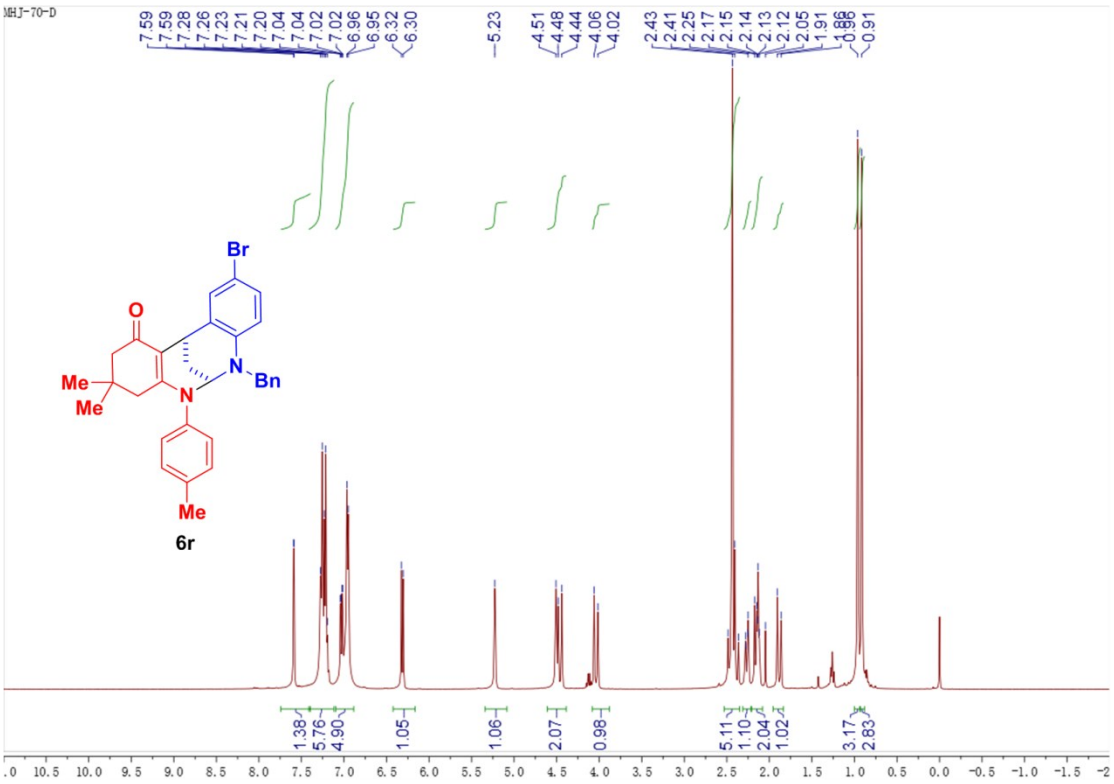
O
N
Bn
Me
Me
N
Me
6q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7.04
7.02
7.02
6.96
6.95
6.32
6.30
5.23
4.51
4.48
4.44
4.06
4.02
2.43
2.41
2.25
2.17
2.15
2.14
2.13
2.12
2.05
1.91
0.91
Br
O
N
Bn
Me
Me
N
Me
6r
1.38
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1.06
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1.10
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1.02
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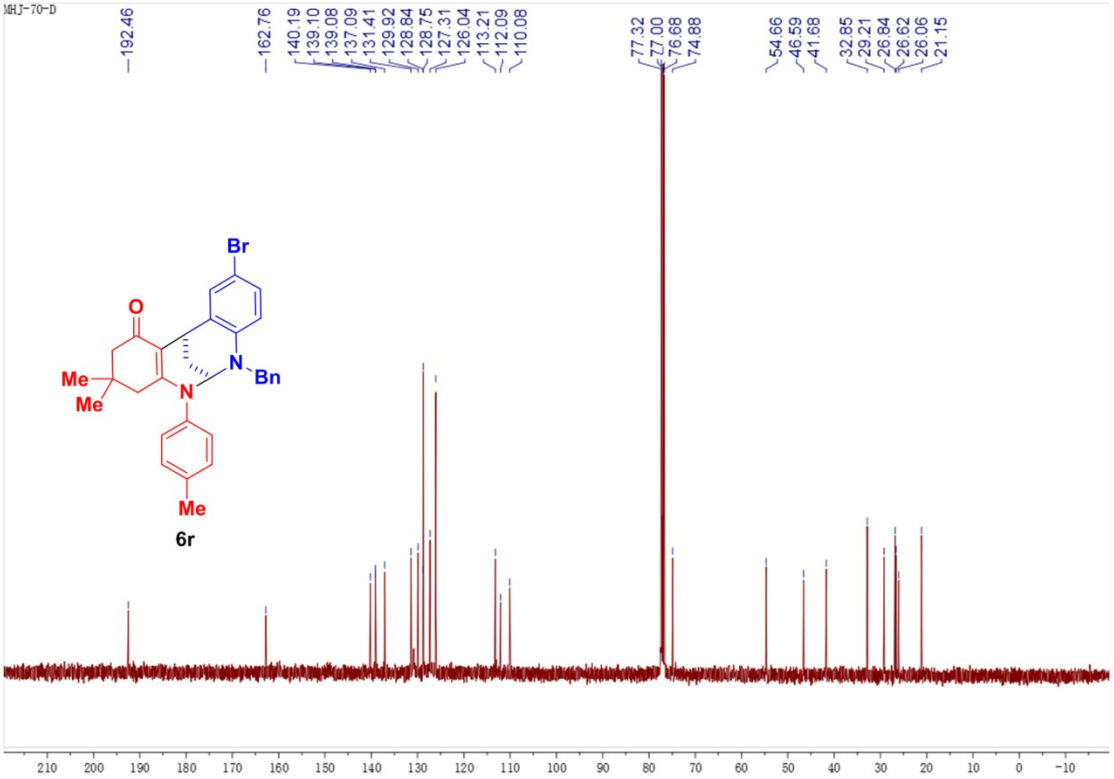
2.83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128.84
128.75
127.31
126.04
113.21
112.09
110.08
77.32
77.00
76.68
74.88
54.66
46.59
41.68
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26.84
26.62
26.06
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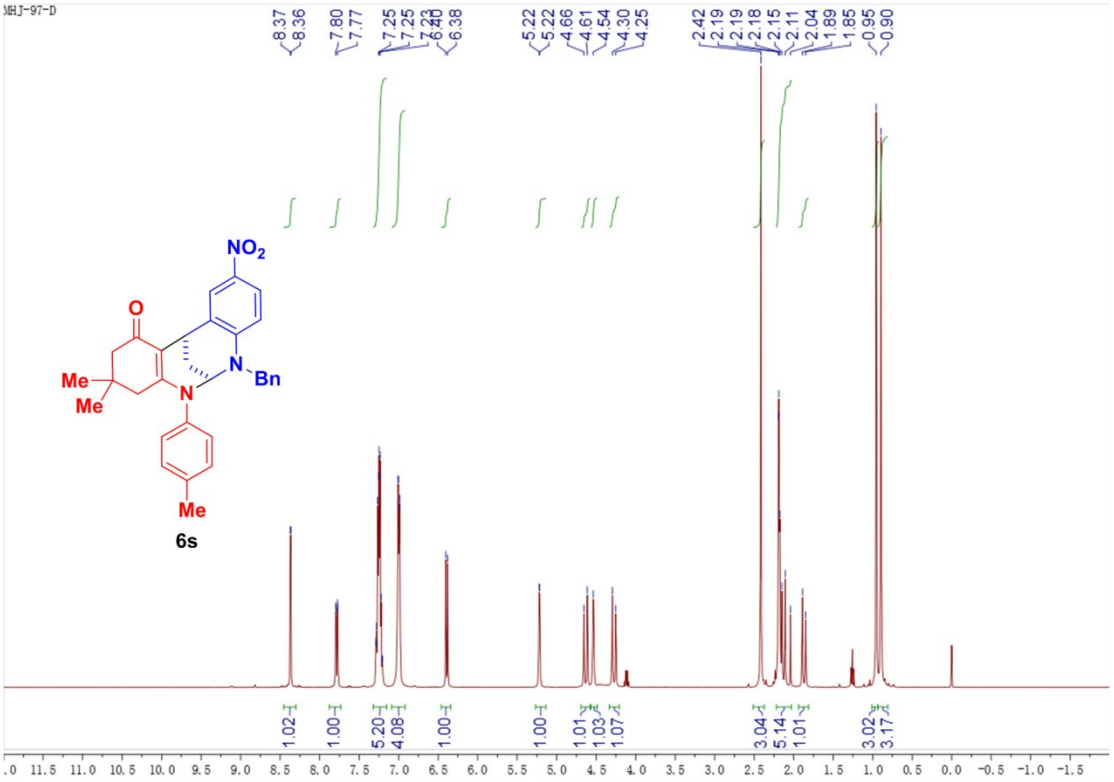
O
N
Bn
Me
Me
N
Me
6r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7.23
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5.22
5.22
4.66
4.61
4.54
4.30
4.25
2.42
2.19
2.19
2.18
2.15
2.11
2.04
1.89
1.85
0.95
0.90
1.02
1.00
5.20
4.08
1.00
1.00
1.01
1.03
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5.14
1.01
3.02
3.17
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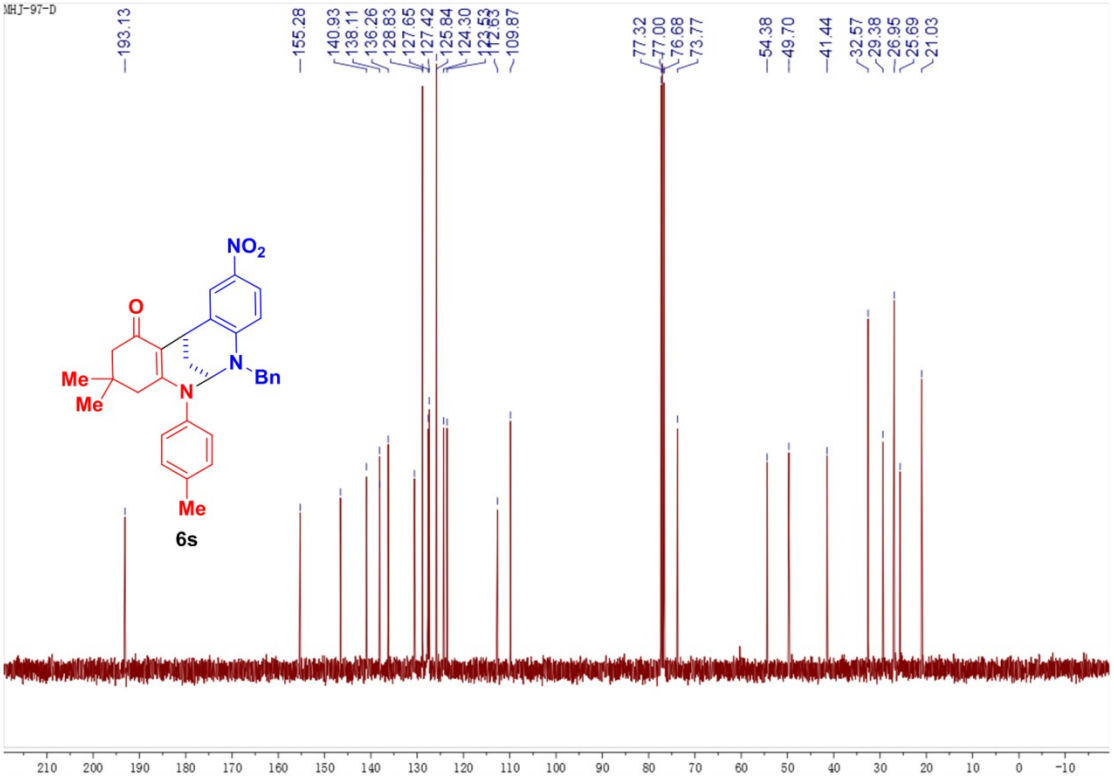
Me
Me
N
N
Bn
Me
6s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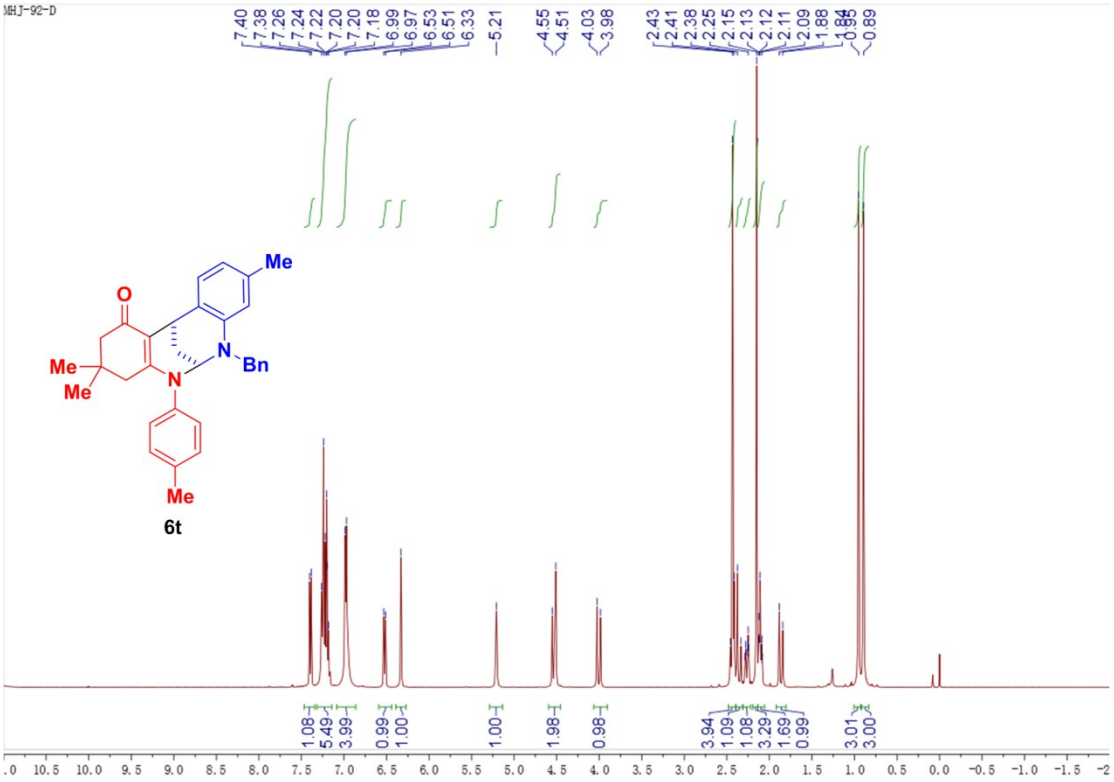
127.65
127.42
125.84
124.30
123.53
112.63
109.87
77.32
77.00
76.68
73.77
54.38
49.70
41.44
32.57
29.38
26.95
25.69
21.03
NO2
O
Me
Me
N
N
Bn
Me
6s


MHJ-92-D
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6.51
6.33
5.21
4.55
4.51
4.03
3.98
2.43
2.41
2.38
2.25
2.15
2.13
2.12
2.11
2.09
1.88
0.95
0.89
Me
O
N
Bn
Me
Me
N
Me
6t
1.08
5.49
3.99
0.99
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1.00
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0.98
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1.09
1.08
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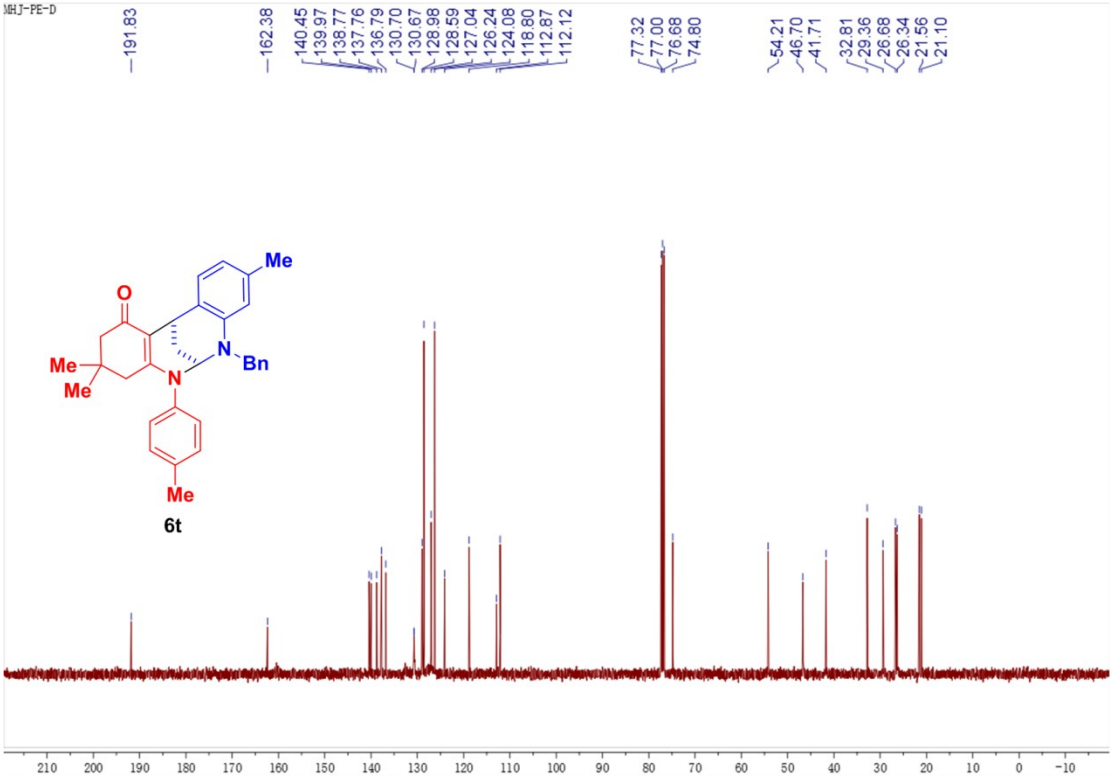
0.99
3.01
3.00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130.67
128.98
128.59
127.04
126.24
124.08
118.80
112.87
112.12
77.32
77.00
76.68
74.80
54.21
46.70
41.71
32.81
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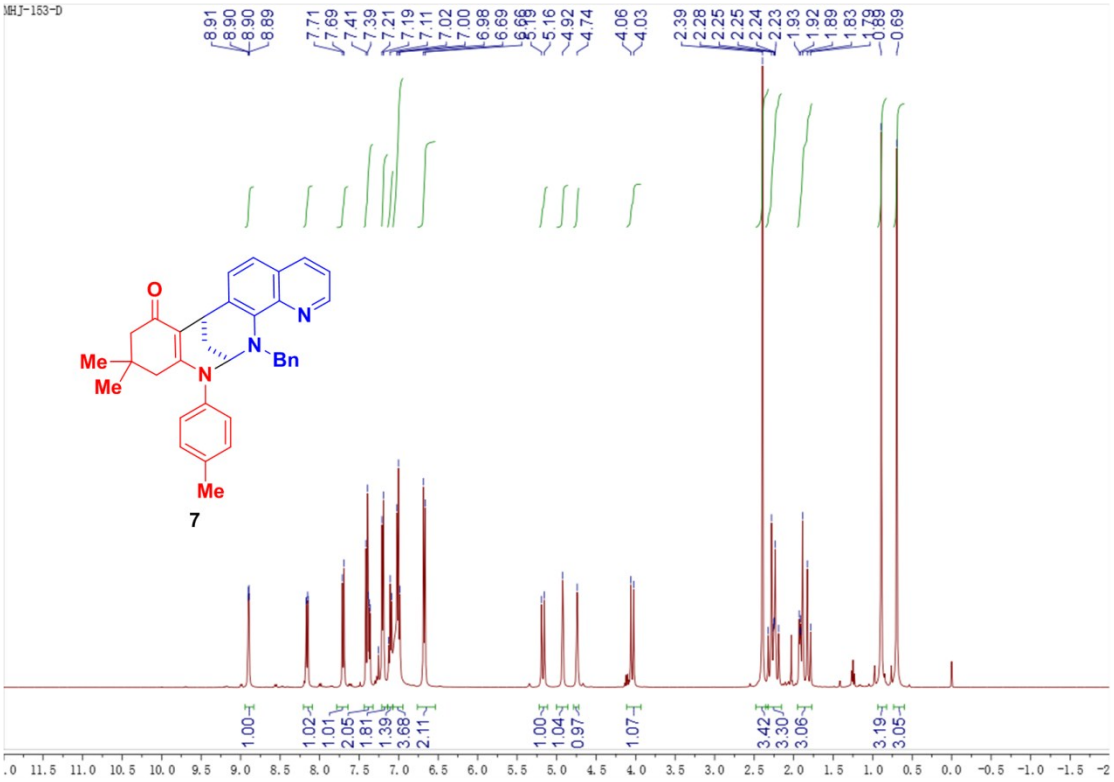
26.68
26.34
21.56
21.10
Me
O
N
Bn
Me
Me
N
Me
6t


MHJ-153-D
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6.98
6.69
6.66
5.19
5.16
4.92
4.74
4.06
4.03
2.39
2.28
2.25
2.25
2.24
2.23
1.93
1.92
1.89
1.83
0.89
0.69
O
N
N
Bn
N
Me
Me
Me
7
1.00
1.02
1.01
2.05
1.81
1.39
3.68
2.11
1.00
1.04
0.97
1.07
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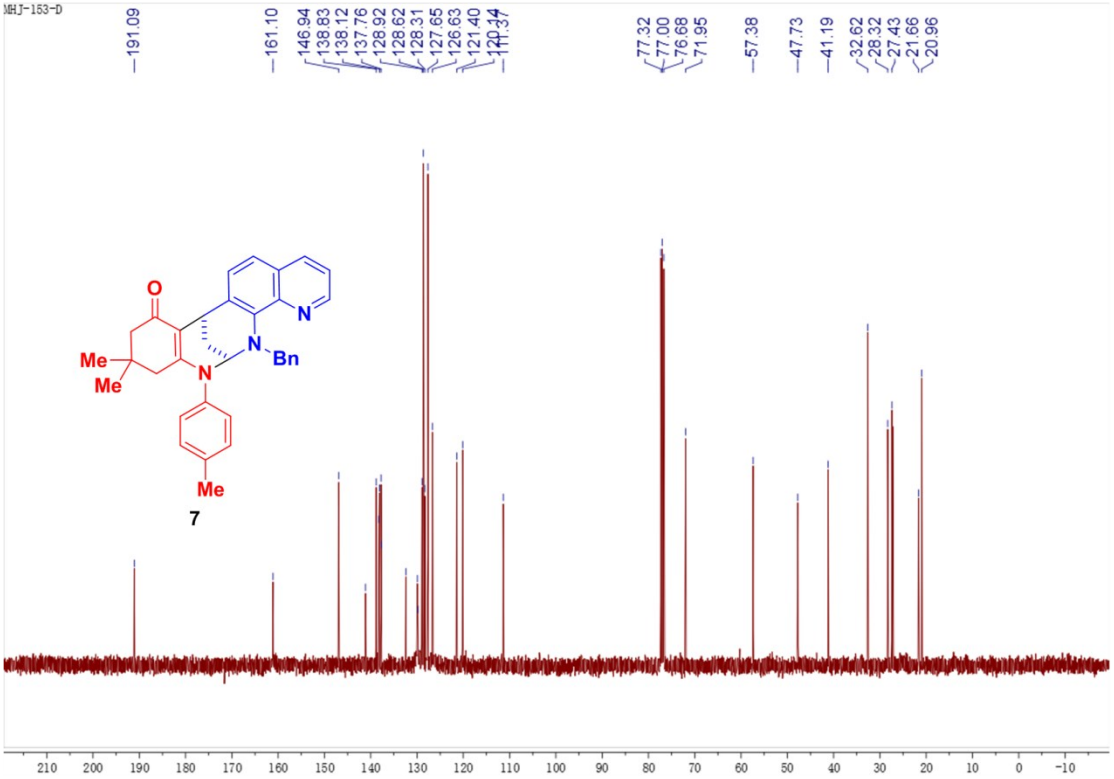
3.05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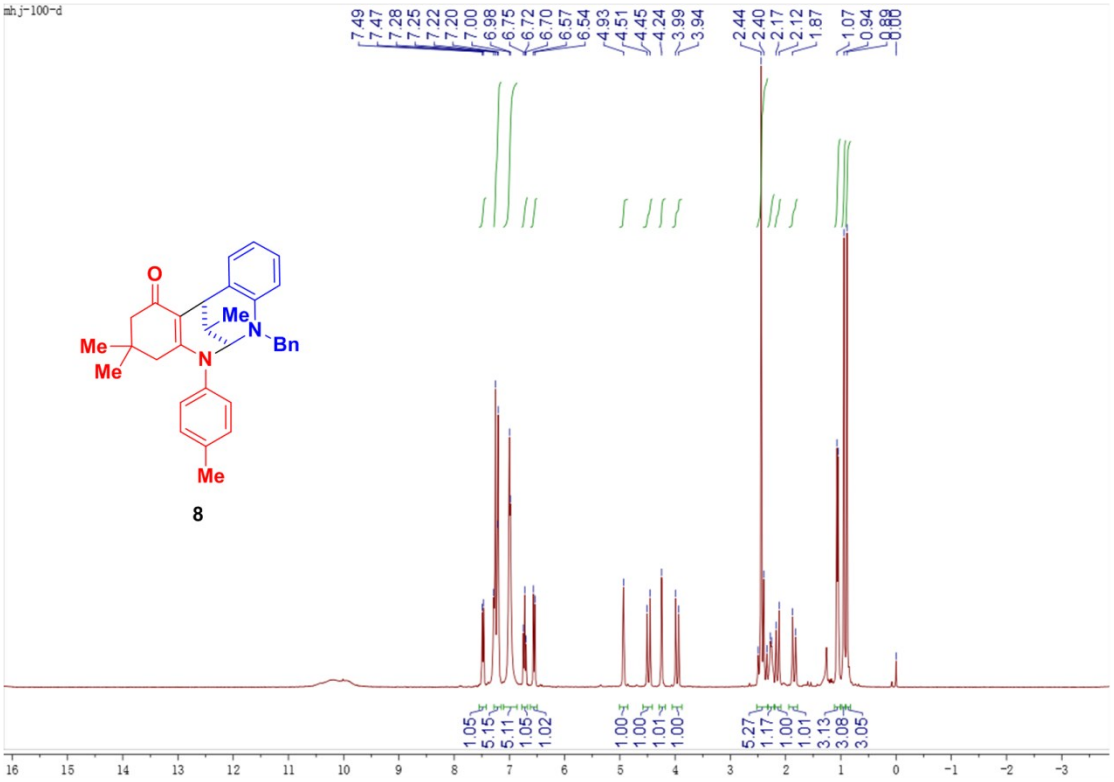
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0.88
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Me
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Me
N
Me
8
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1.01
1.00
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1.00
1.01
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3.08
3.05
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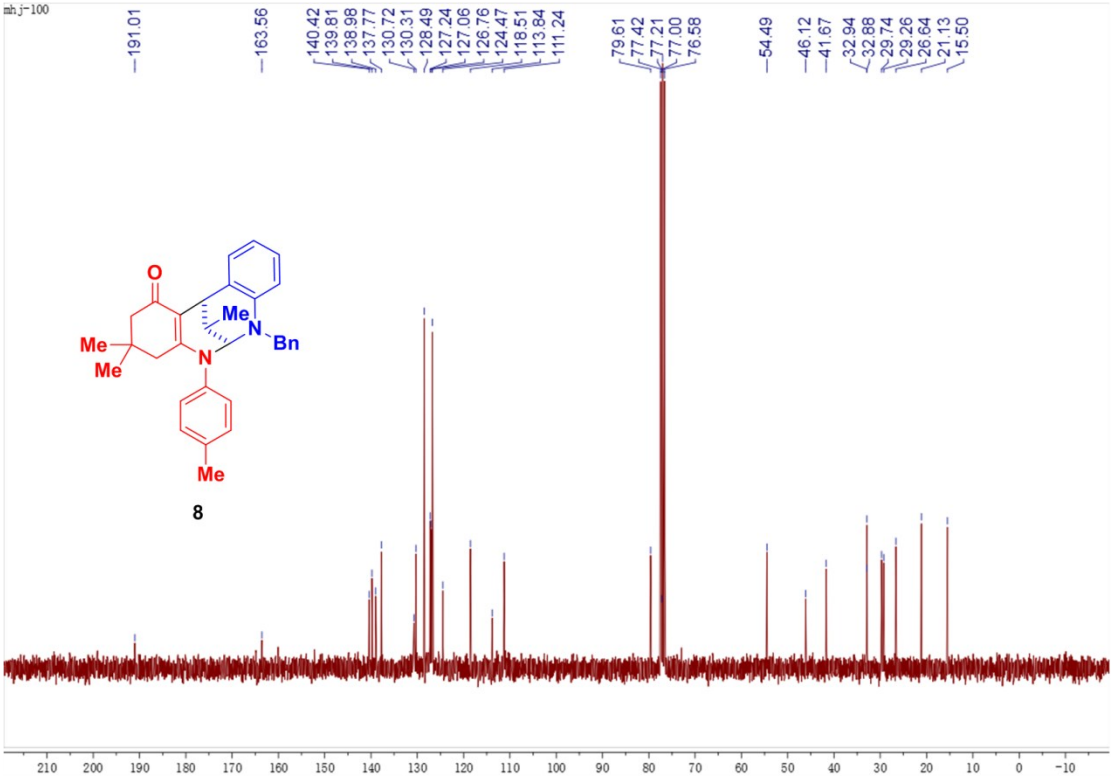
-3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29.74
29.26
26.64
21.13
15.50
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Me
N
Bn
Me
Me
N
Me
8
210
200
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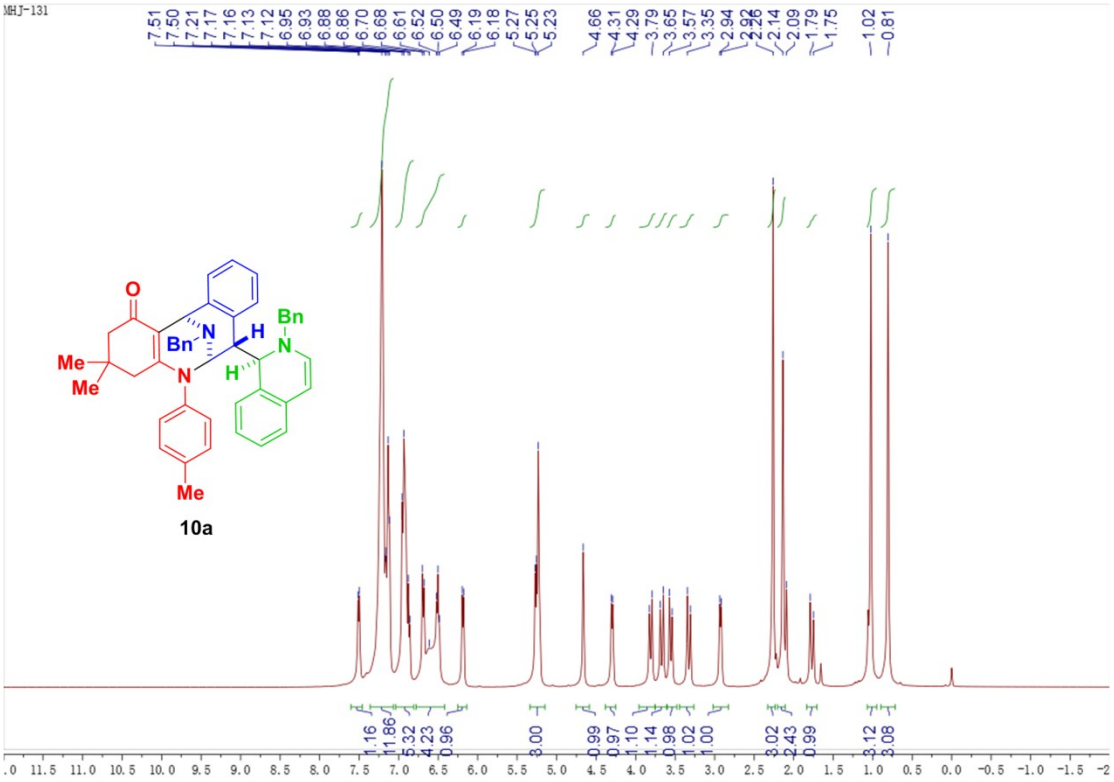
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6.61
6.52
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6.19
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5.27
5.25
5.23
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3.79
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3.35
2.94
2.92
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2.14
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1.75
1.02
0.81
1.16
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0.97
1.10
1.14
0.98
1.02
1.00
8.02
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Me
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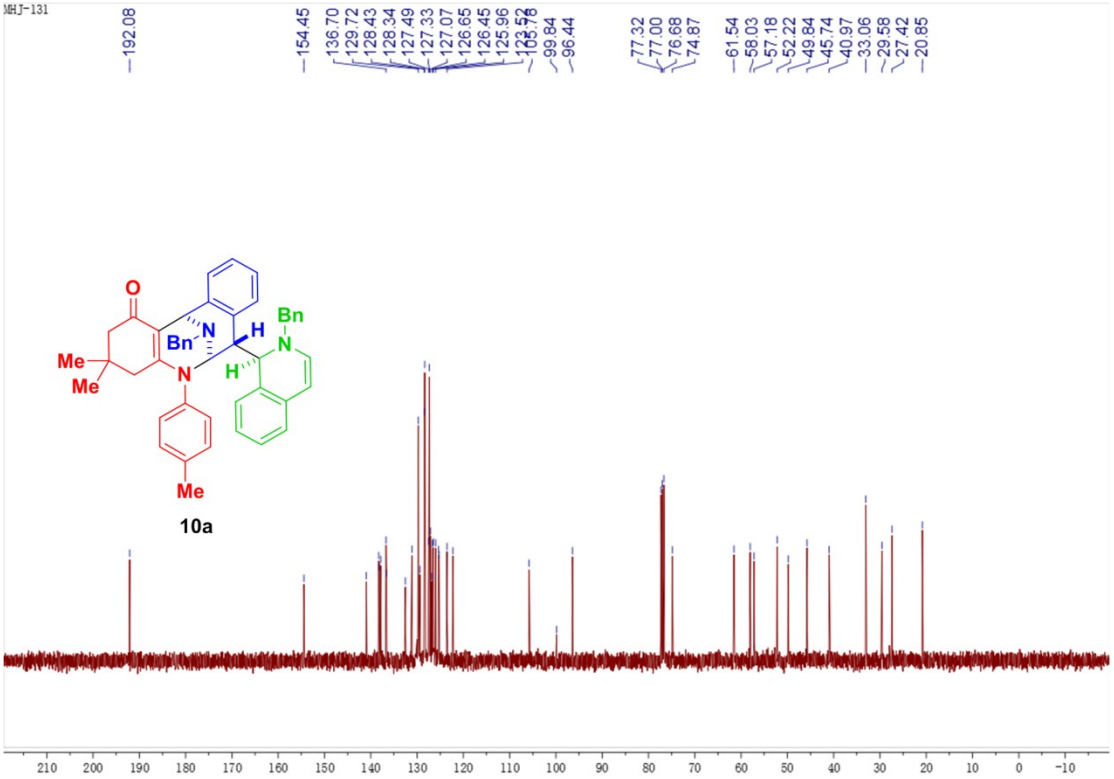
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76.68
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57.18
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45.74
40.97
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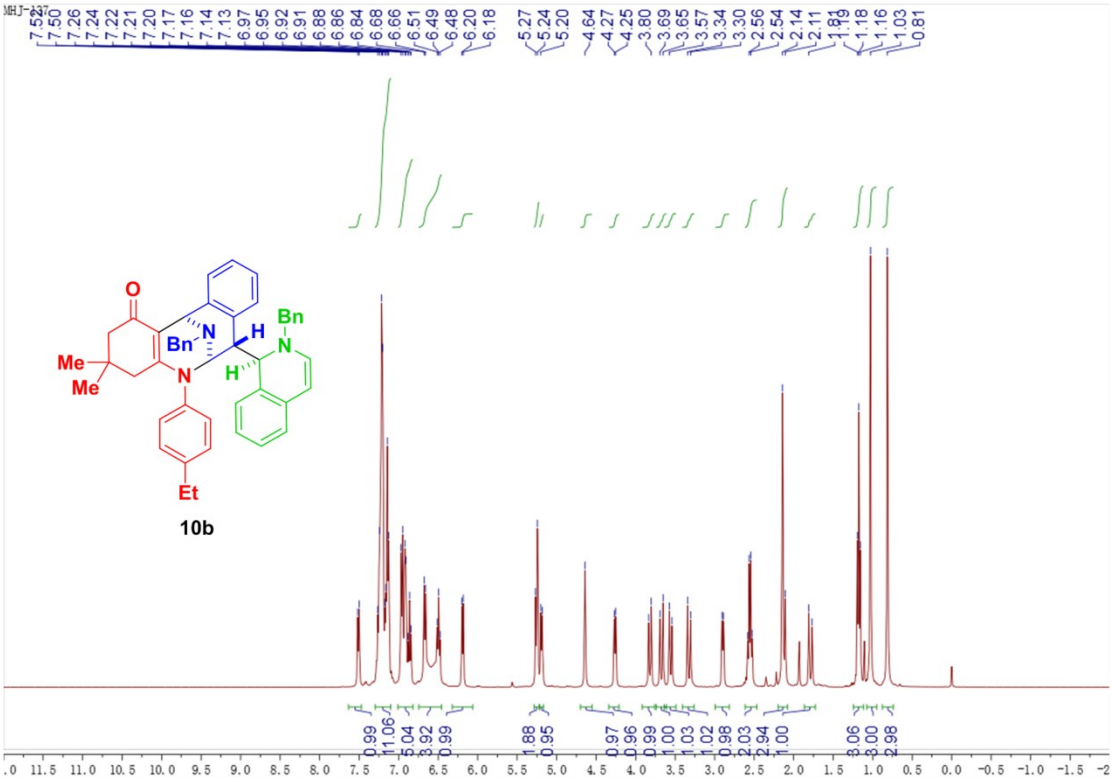
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6.92
6.91
6.88
6.86
6.84
6.68
6.66
6.51
6.49
6.48
6.20
6.18
5.27
5.24
5.20
4.64
4.27
4.25
3.80
3.69
3.65
3.57
3.34
3.30
2.56
2.54
2.14
2.11
1.81
1.19
1.18
1.16
1.03
0.81
O
Bn
N
H
Me
Me
N
H
Bn
N
Et
10b
0.99
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1.88
0.95
0.97
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1.03
1.02
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2.03
2.94
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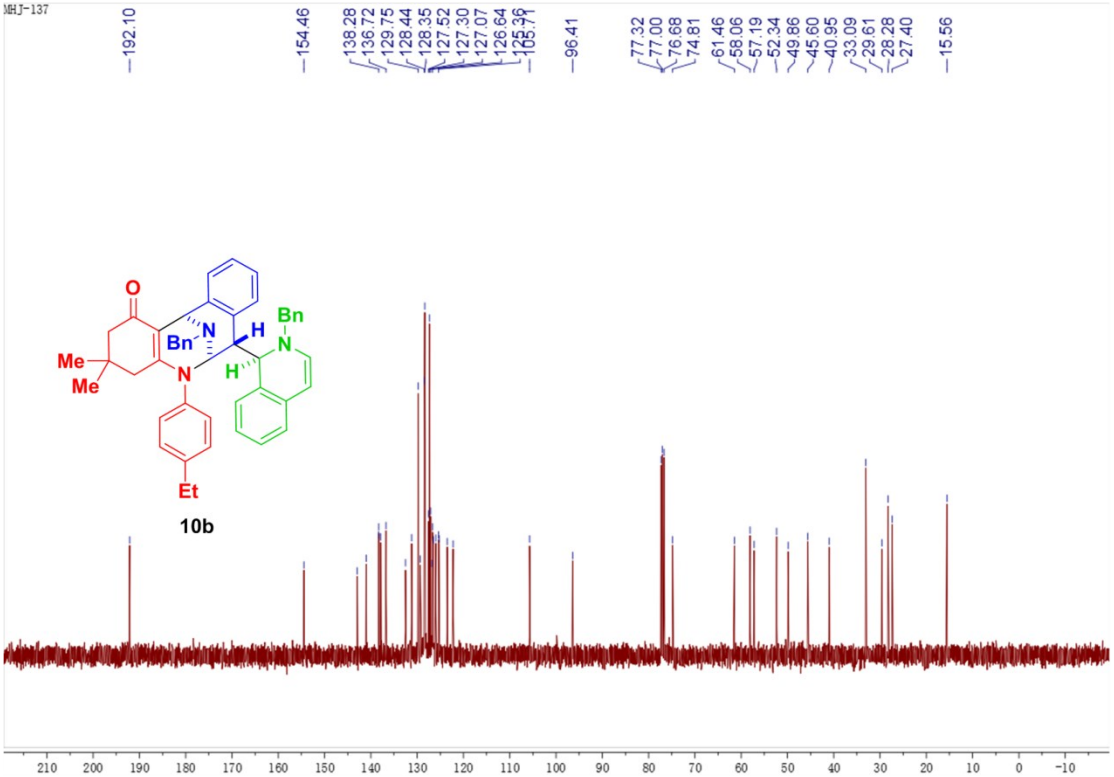
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77.00
76.68
74.81
61.46
58.06
57.19
52.34
49.86
45.60
40.95
33.09
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Bn
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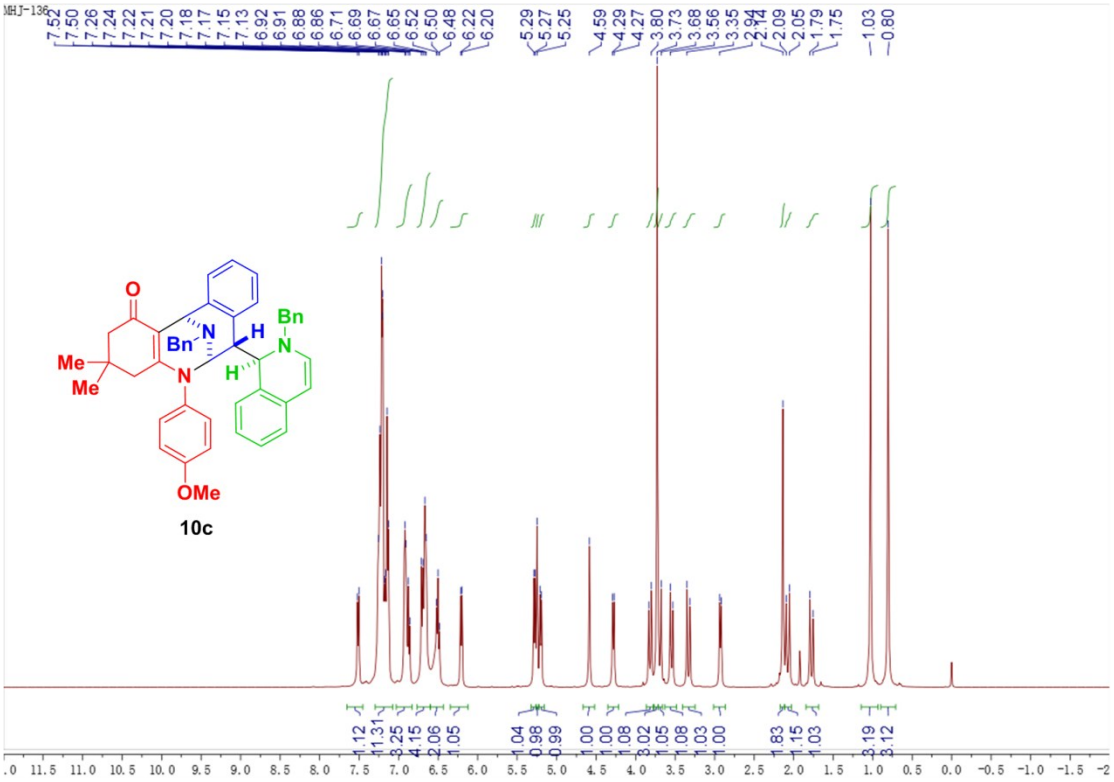
Et
10b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6.69
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5.27
5.25
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3.35
2.94
2.14
2.09
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1.03
0.80
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Bn
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Me
Me
N
H
Bn
N
OMe
10c
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1.31
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1.04
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0.99
1.00
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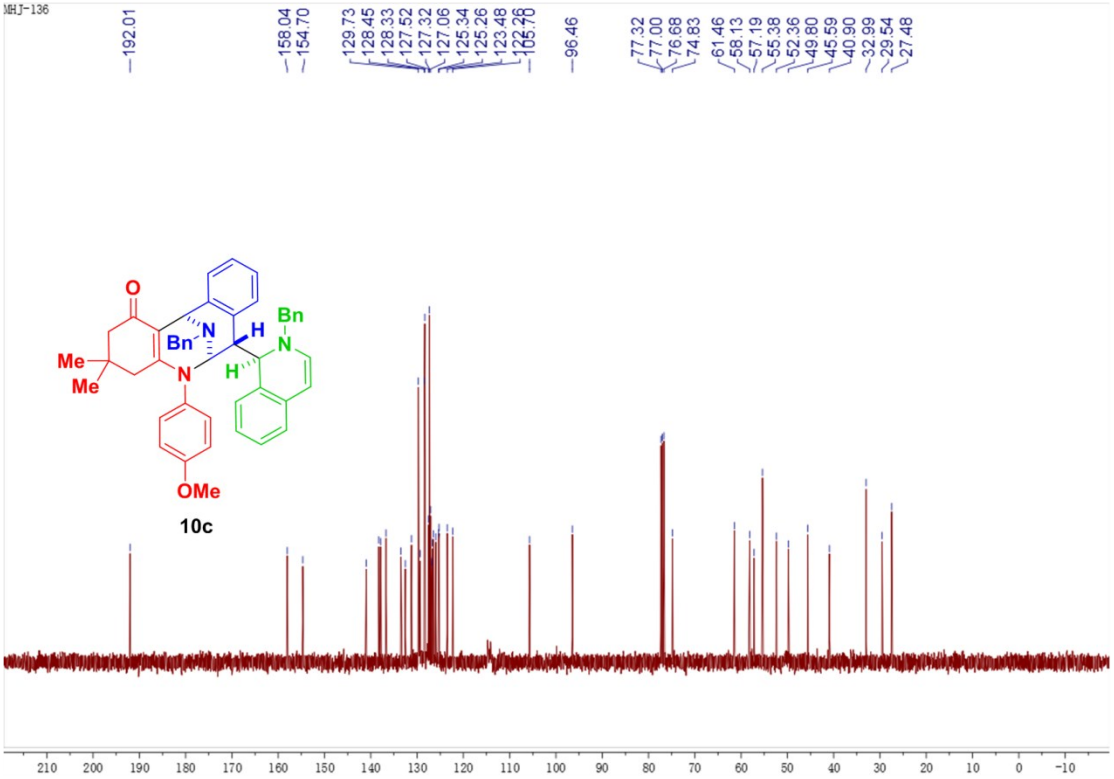
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77.00
76.68
74.83
61.46
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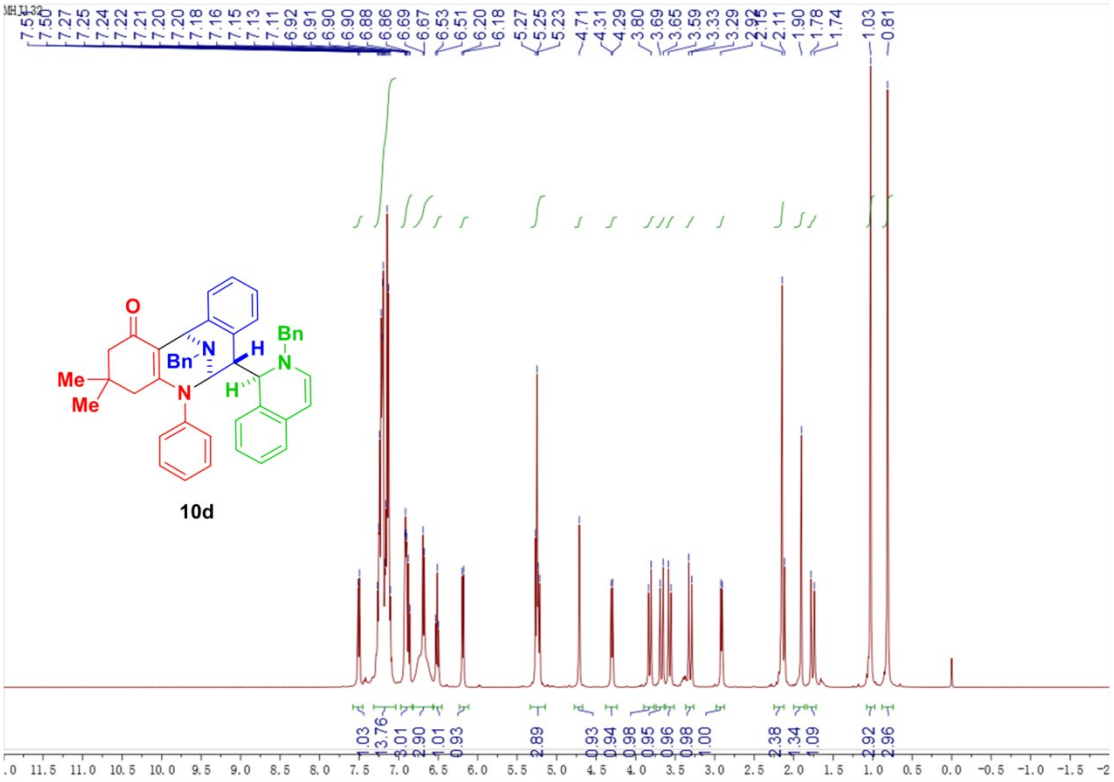
N
OMe
10c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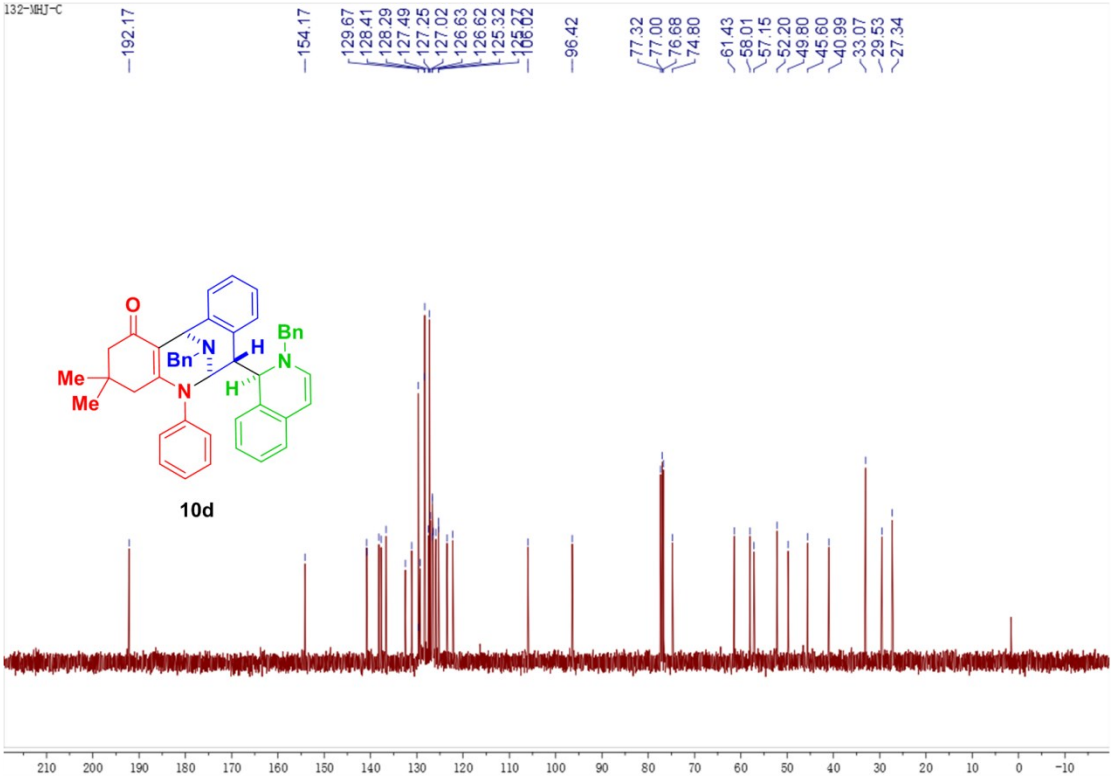
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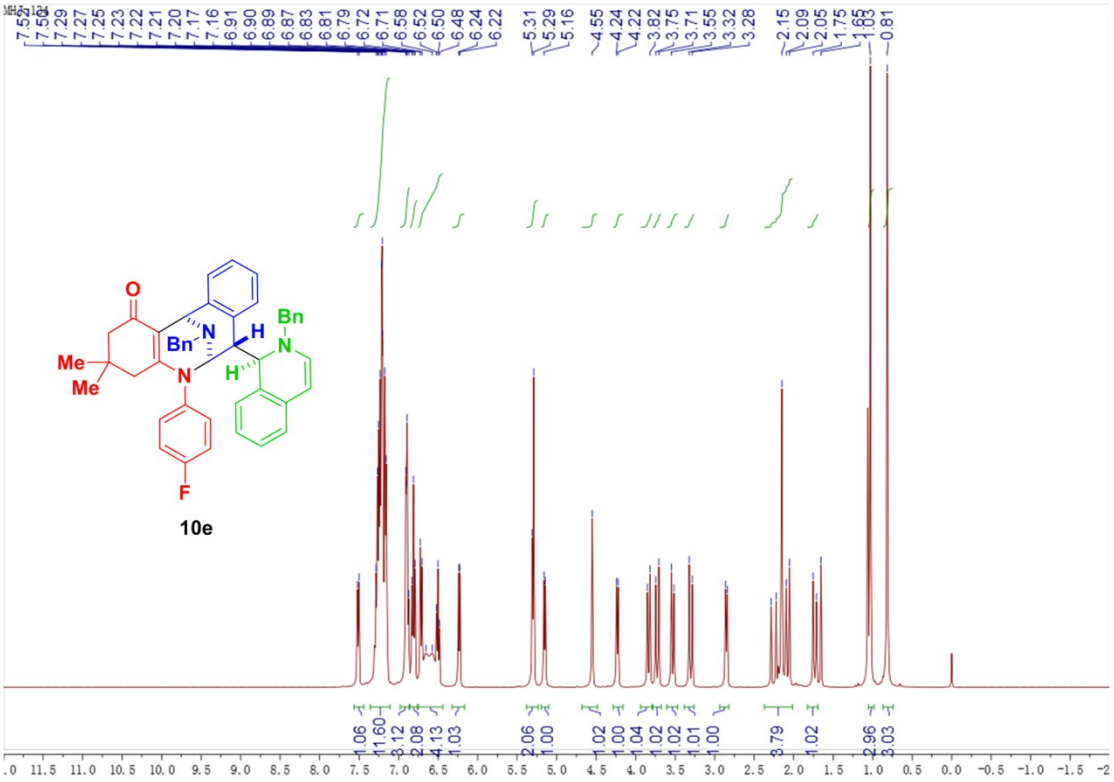
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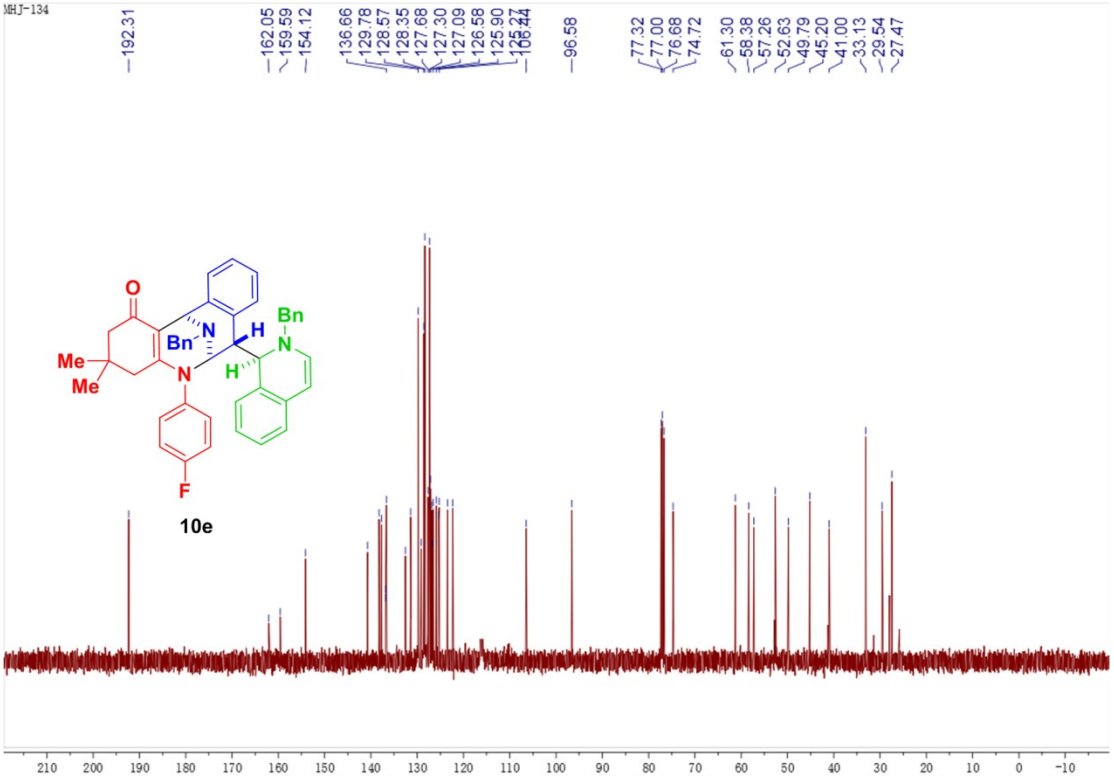
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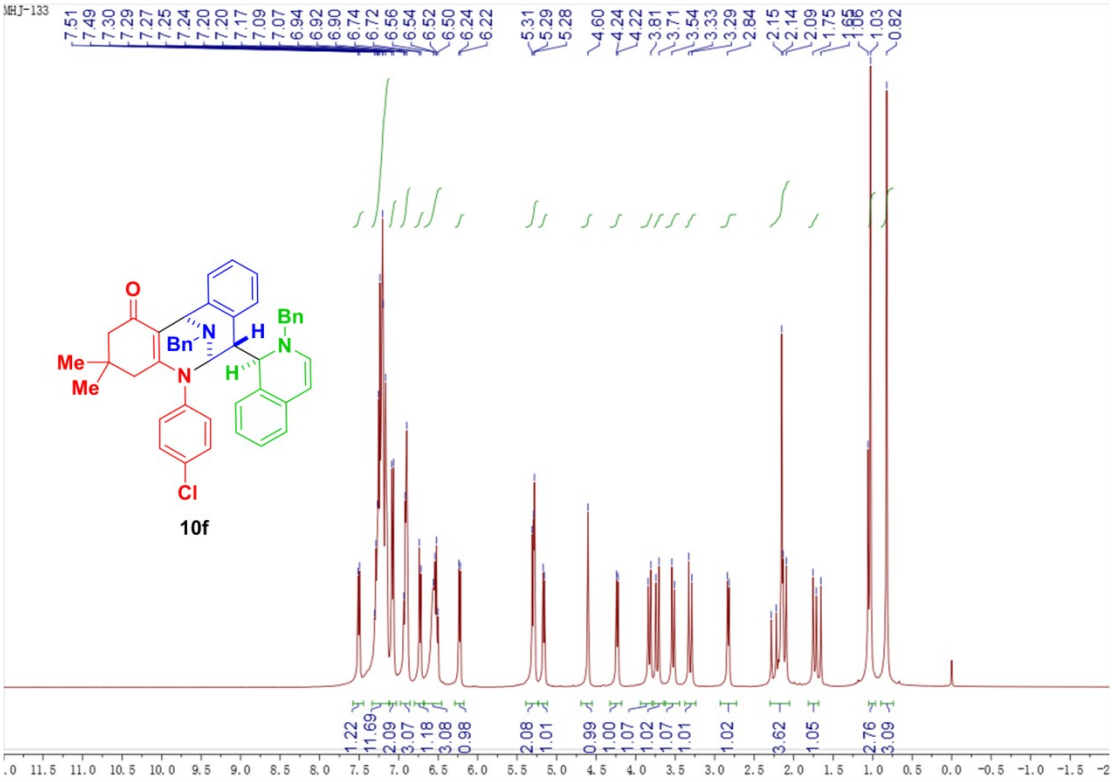
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7.07
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6.90
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5.29
5.28
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3.29
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2.15
2.14
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2.09
3.07
1.18
3.08
0.98
2.08
1.01
0.99
1.00
1.07
1.02
1.07
1.01
1.02
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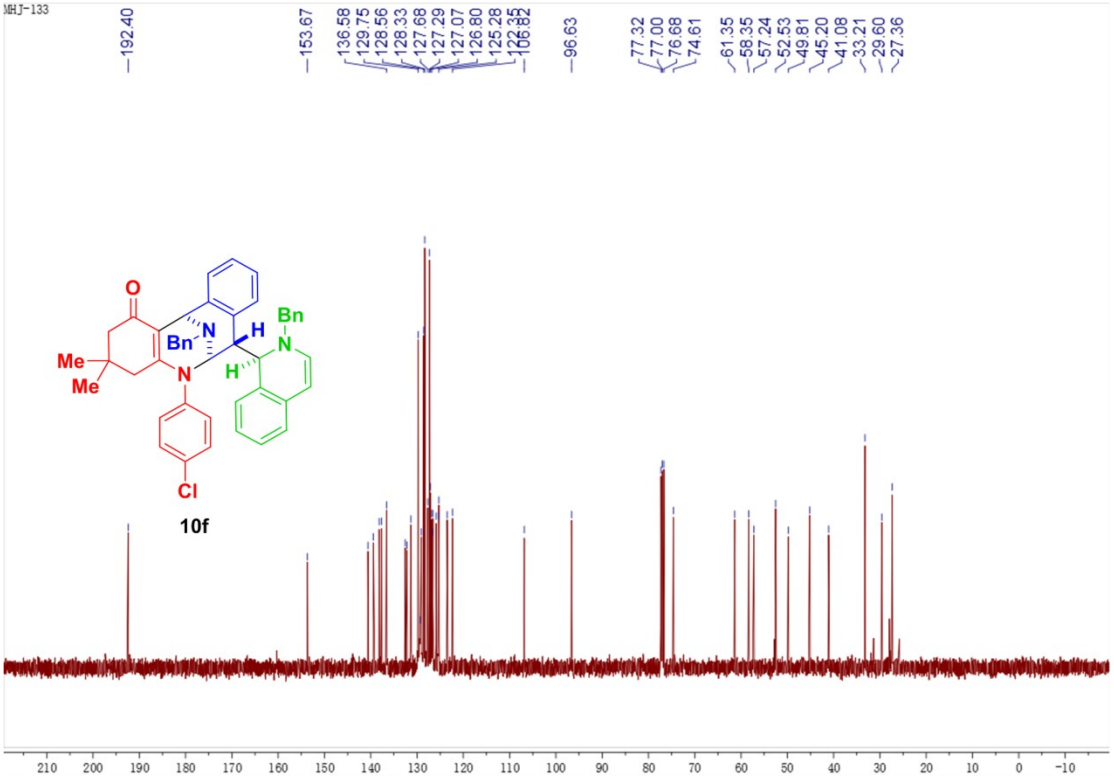
Bn
N
Cl
10f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57.24
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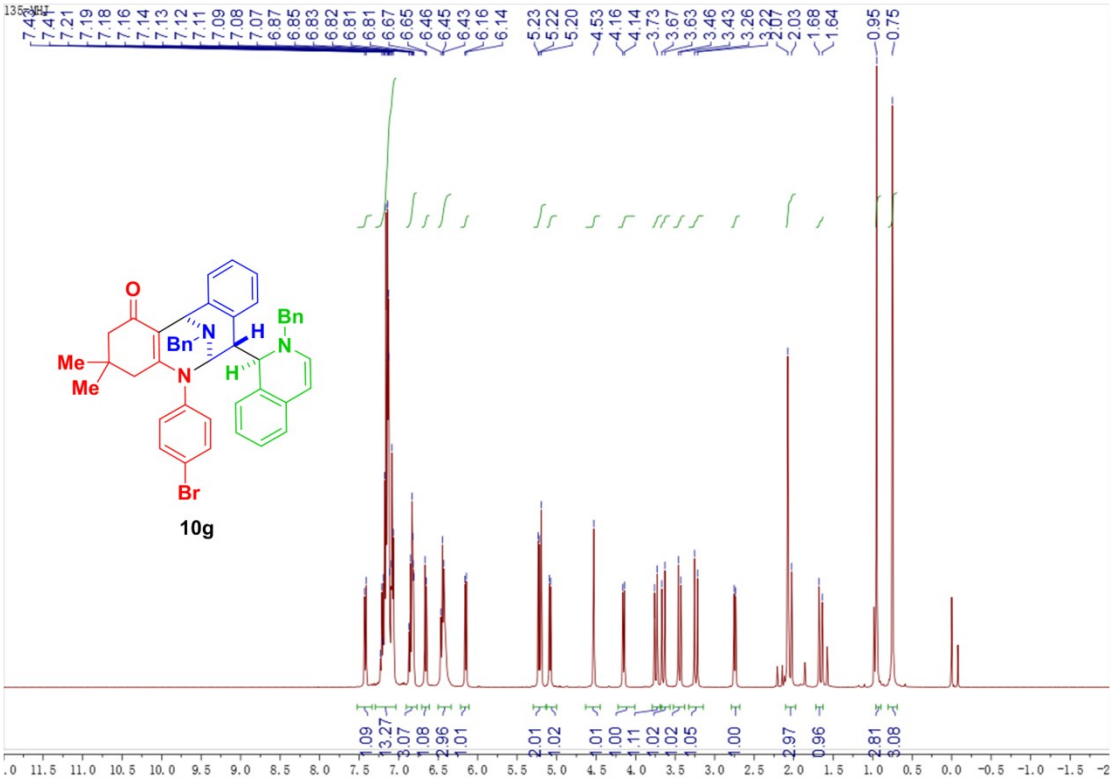
Cl
10f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6.81
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2.03
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3.07
1.08
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2.01
1.02
1.01
1.00
1.11
1.02
1.02
1.05
1.00
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Me
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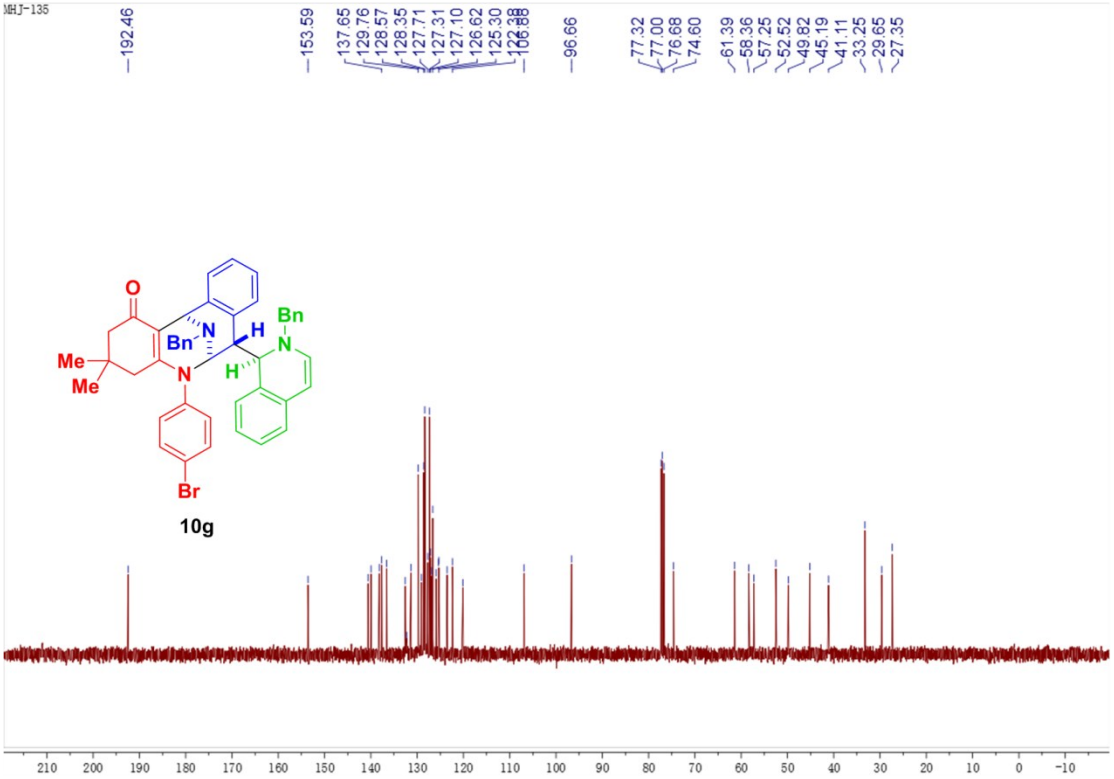
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74.60
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57.25
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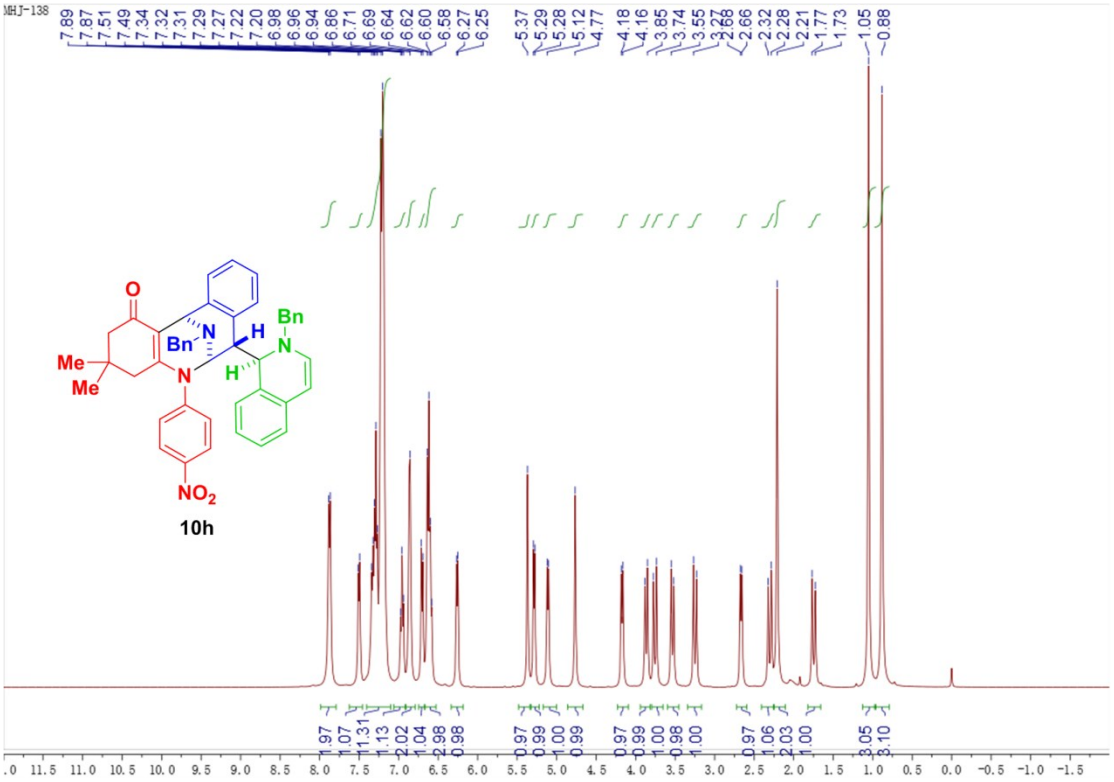
10g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6.25
5.37
5.29
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1.07
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0.98
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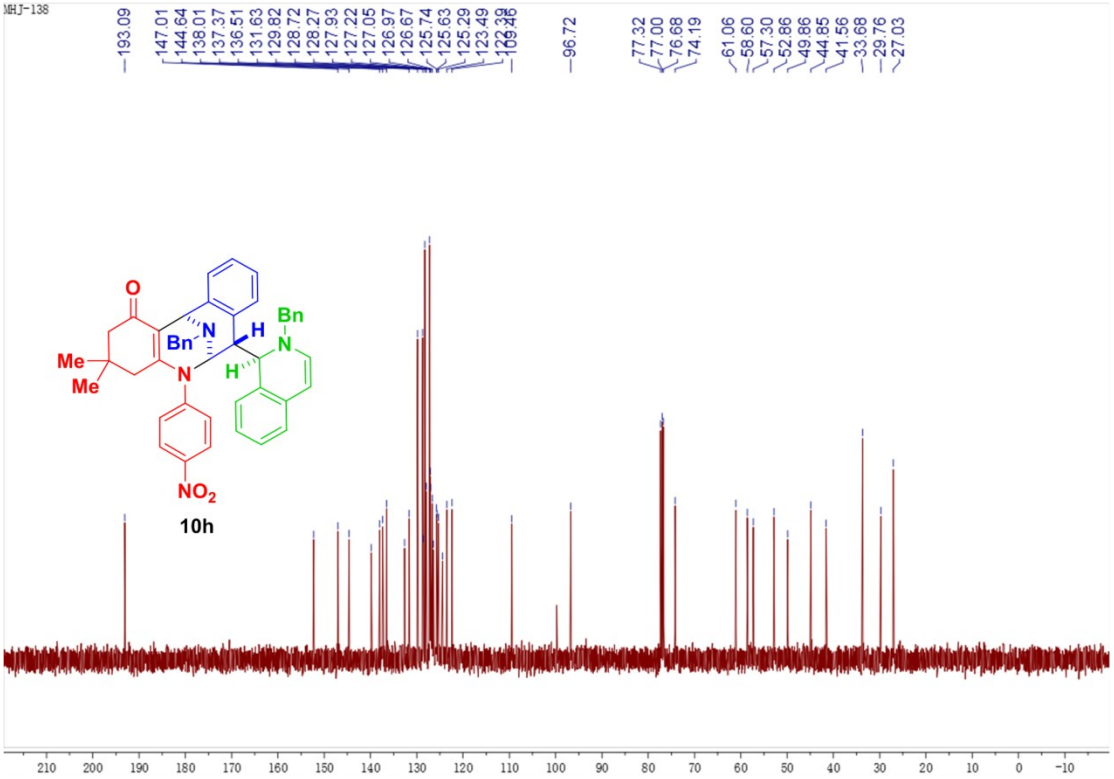
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49.86
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Bn
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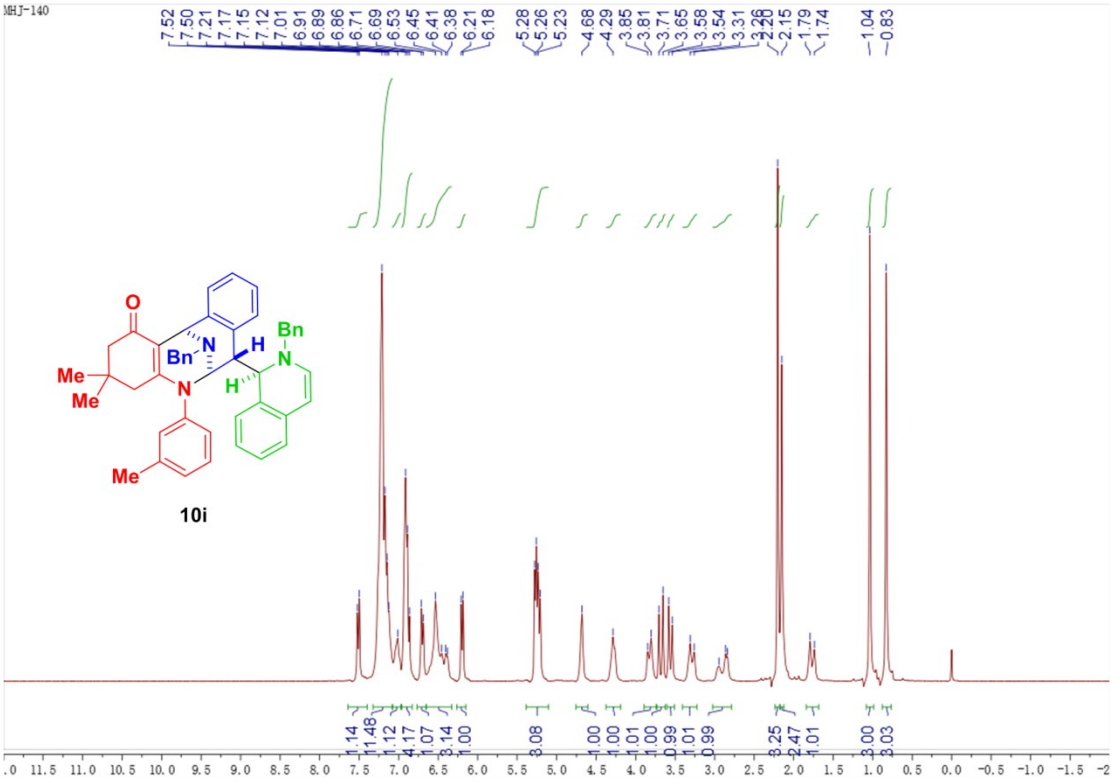
NO2
10h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6.18
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5.23
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3.71
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3.58
3.54
3.31
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1.04
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Bn
N
H
Me
Me
N
Bn
N
H
Me
10i
1.14
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1.07
3.14
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8.08
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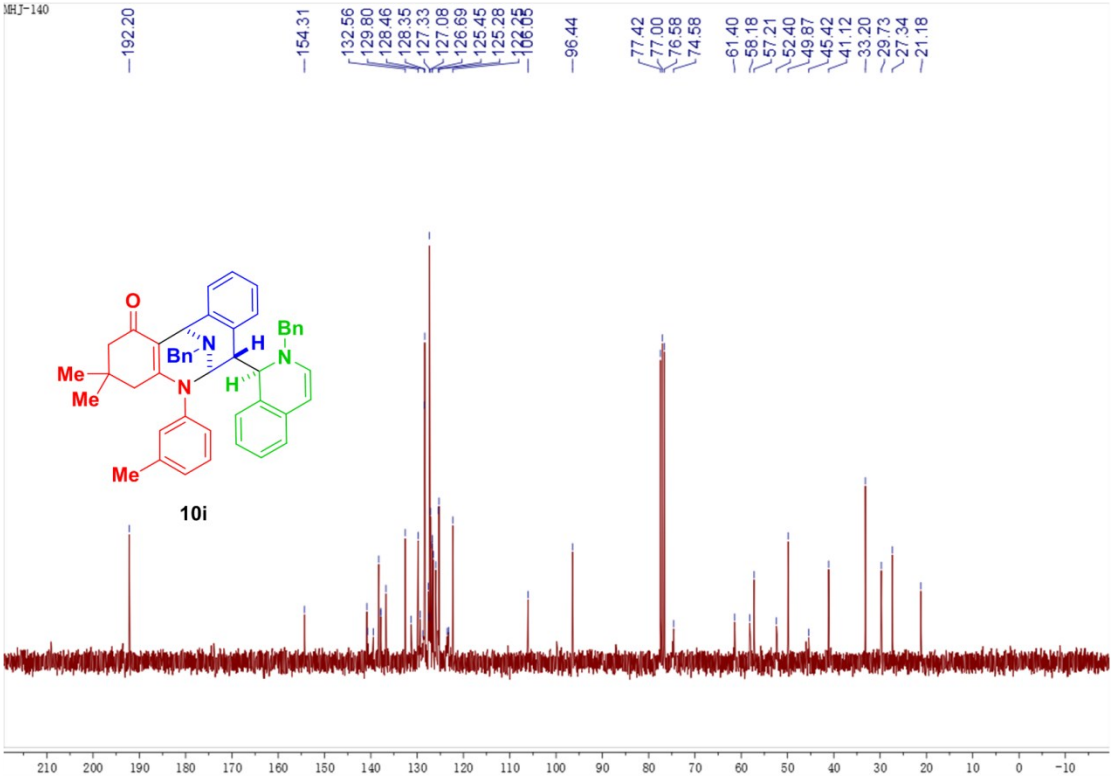
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58.18
57.21
52.40
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45.42
41.12
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27.34
21.18
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Me
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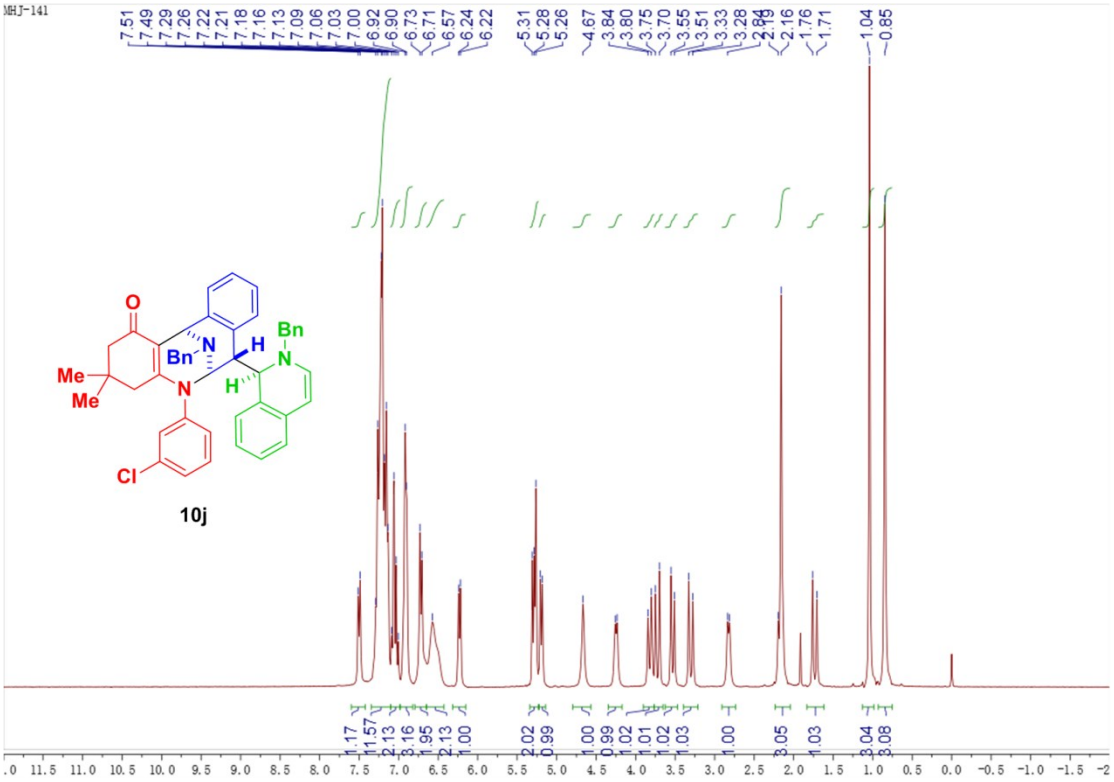
Bn
N
H
Me
10i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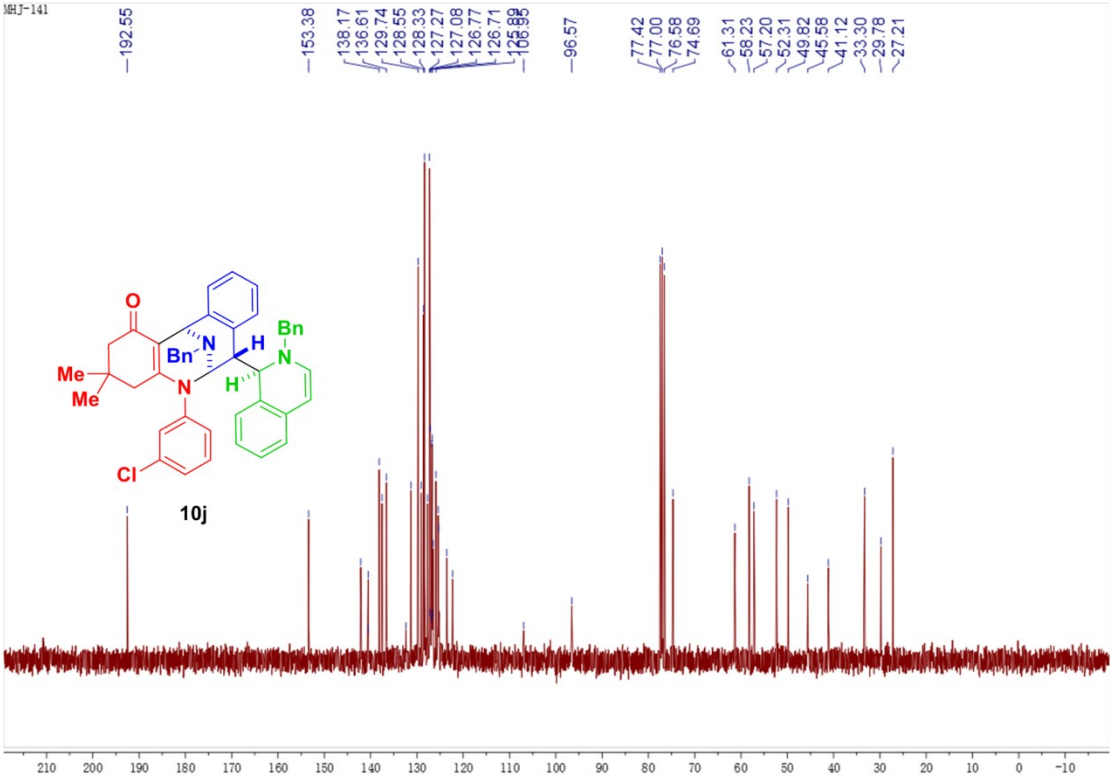
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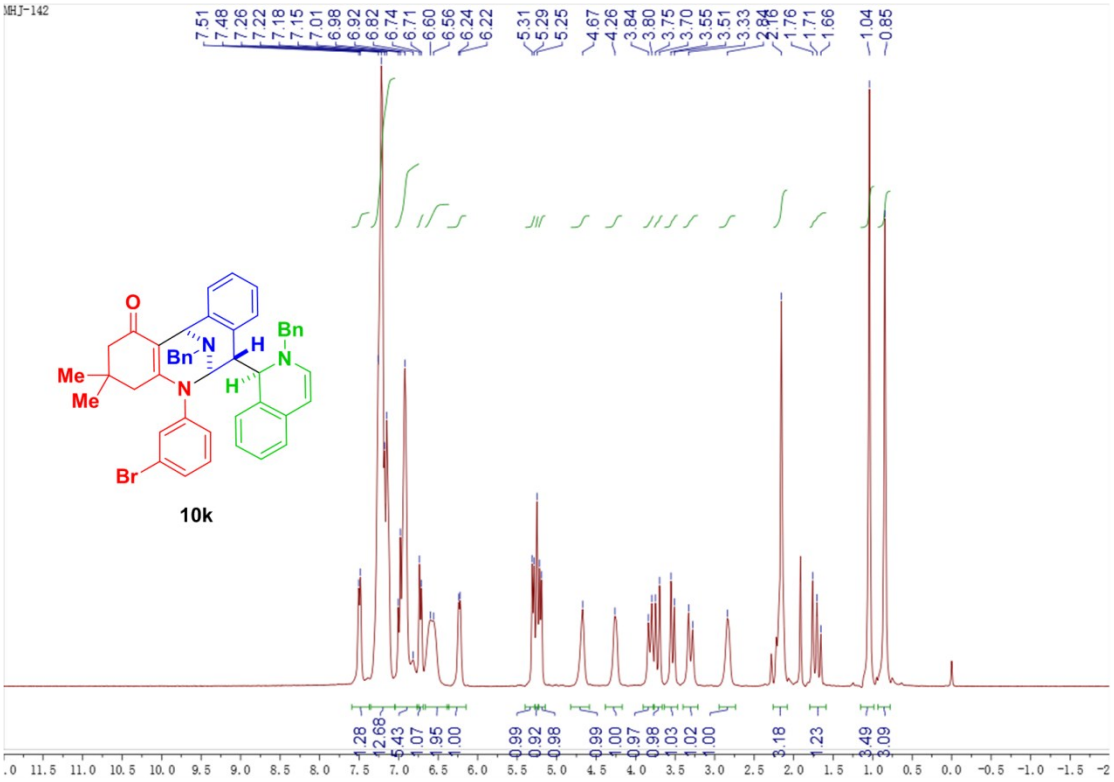
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6.22
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5.25
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3.51
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1.28
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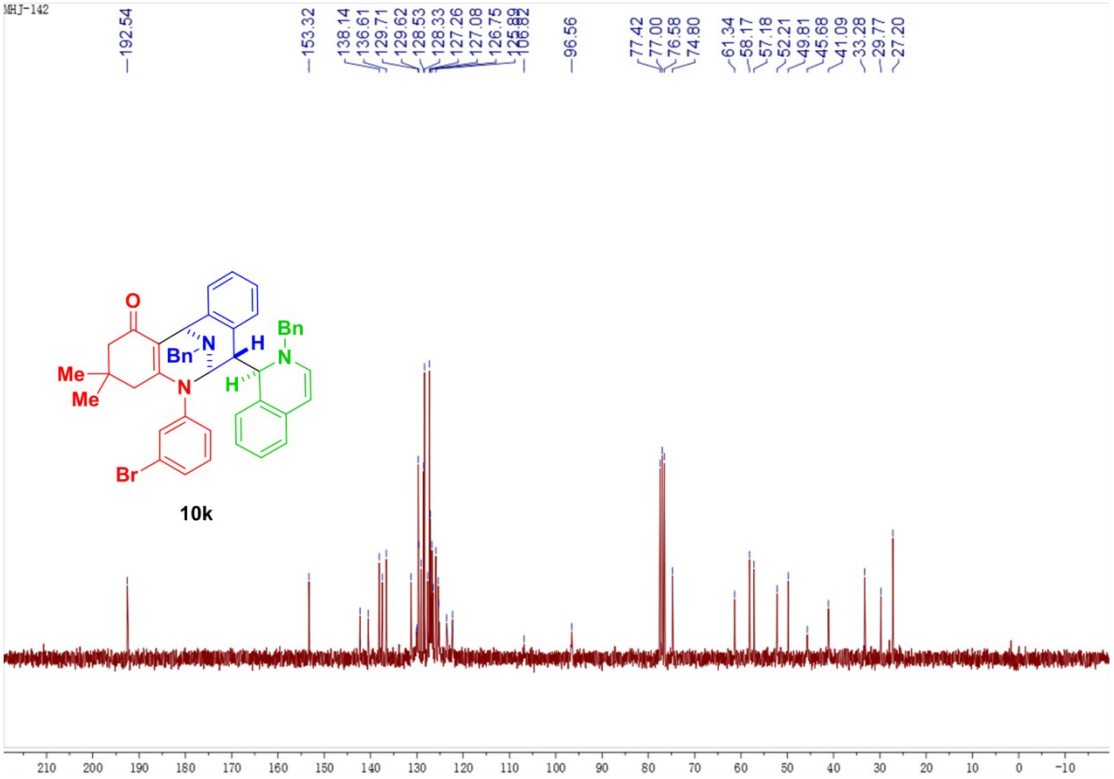
0.99
0.92
0.98
0.99
1.00
0.97
0.98
1.03
1.02
1.00
3.18
1.23
3.49
3.09
O
Bn
N
H
Me
Me
N
H
Bn
N
Br
10k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128.33
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126.75
125.89
125.82
96.56
77.42
77.00
76.58
74.80
61.34
58.17
57.18
52.21
49.81
45.68
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29.77
27.20
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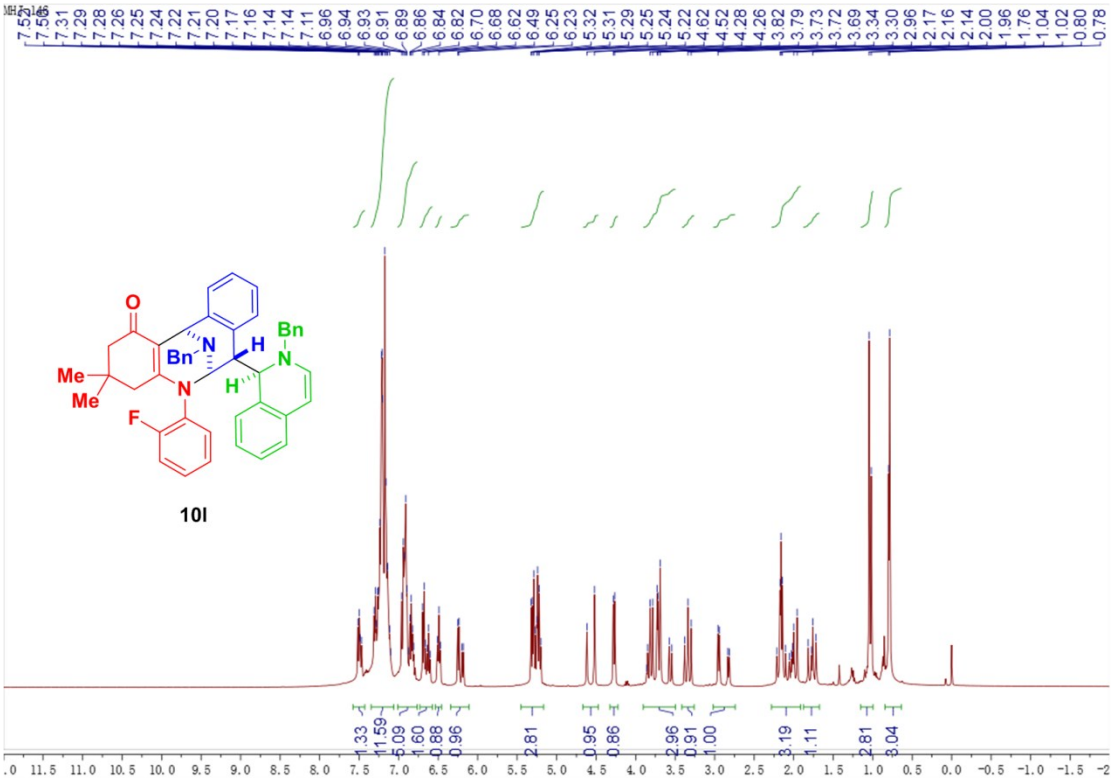
Me
Me
N
H
Bn
N
Br
10k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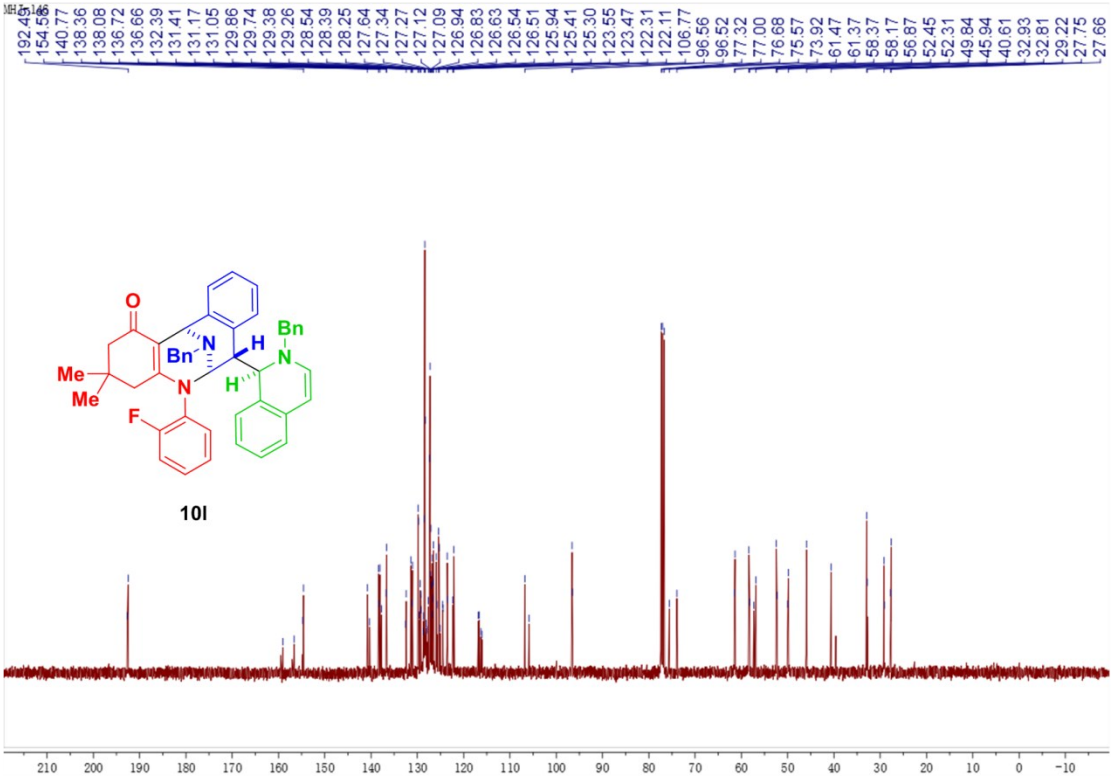
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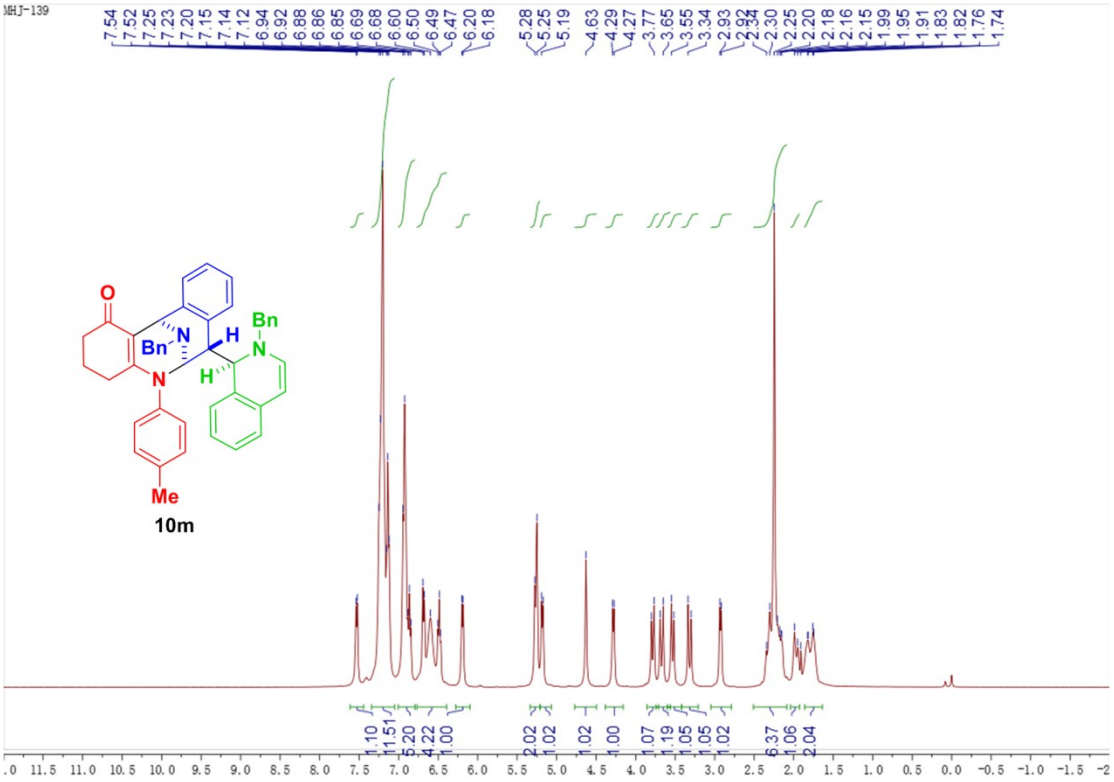
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7.15
7.14
7.12
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6.92
6.88
6.86
6.85
6.69
6.68
6.60
6.50
6.49
6.47
6.20
6.18
5.28
5.25
5.19
4.63
4.29
4.27
3.77
3.65
3.55
3.34
2.93
2.30
2.25
2.20
2.18
2.16
2.15
1.99
1.95
1.91
1.83
1.82
1.76
1.74
1.10
11.51
5.20
4.22
1.00
2.02
1.02
1.02
1.00
1.07
1.19
1.05
1.05
1.02
6.37
1.06
2.04
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Bn
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H
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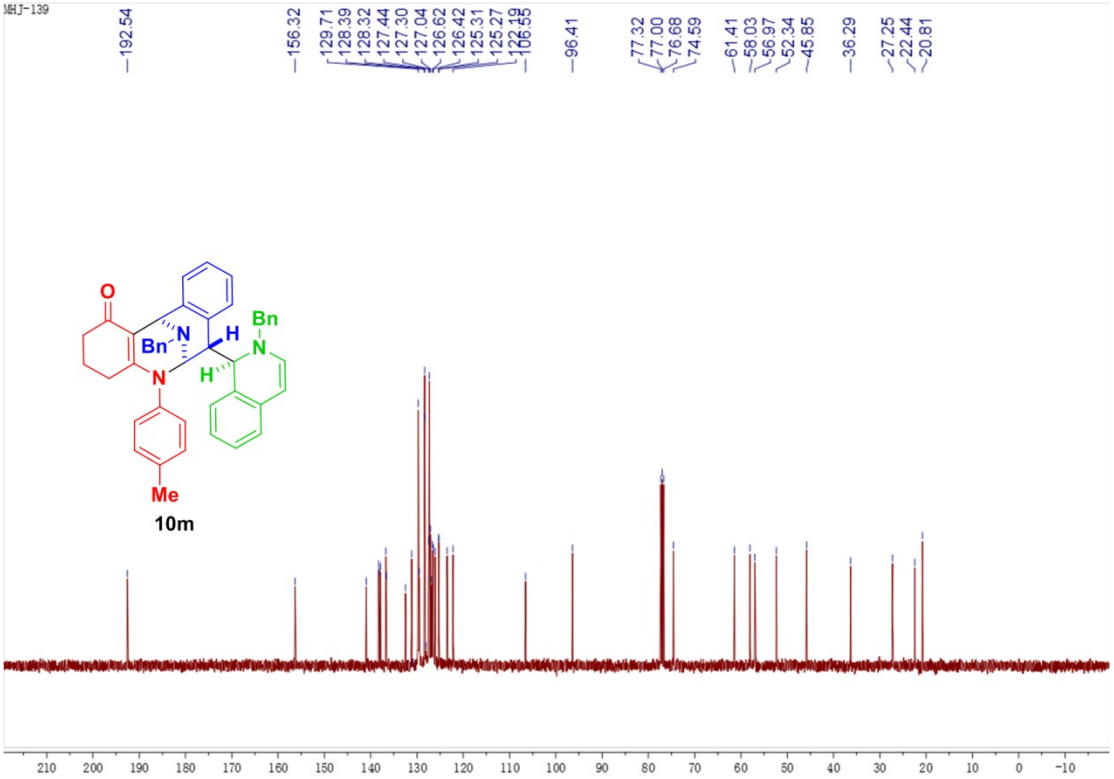
Bn
H
N
Me
10m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96.41
77.32
77.00
76.68
74.59
61.41
58.03
56.97
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22.44
20.81
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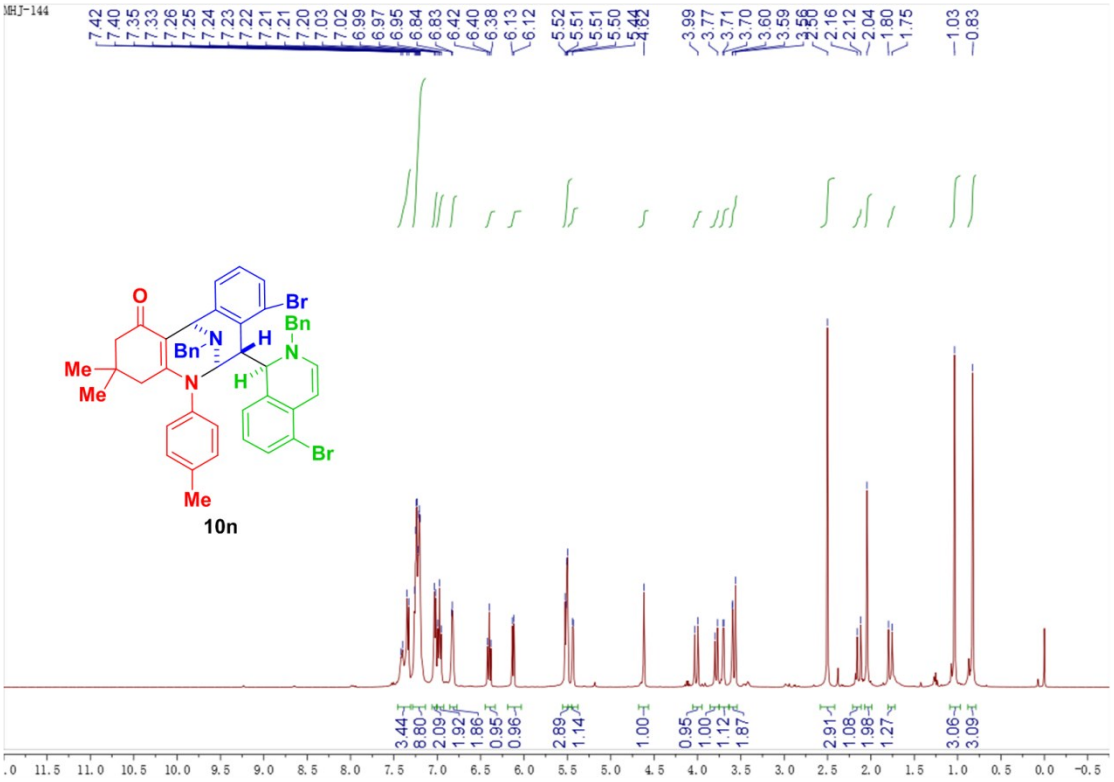
Bn
N
H
N
Bn
H
N
Me
10m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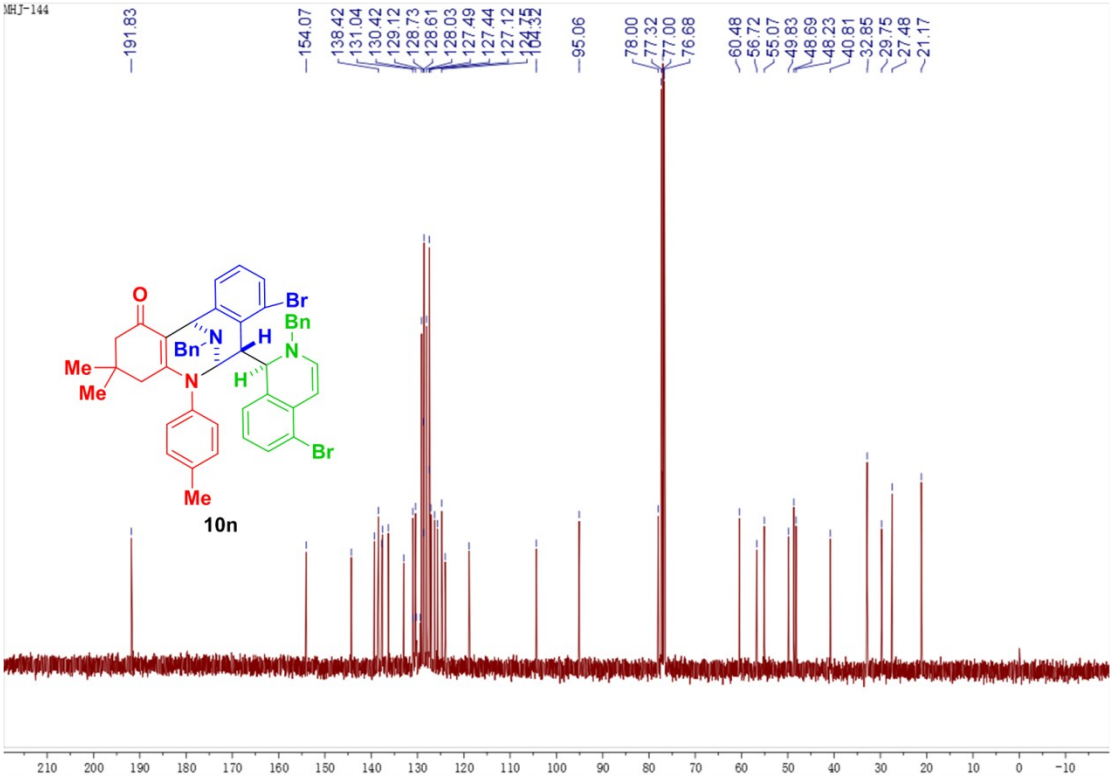
MHJ-144
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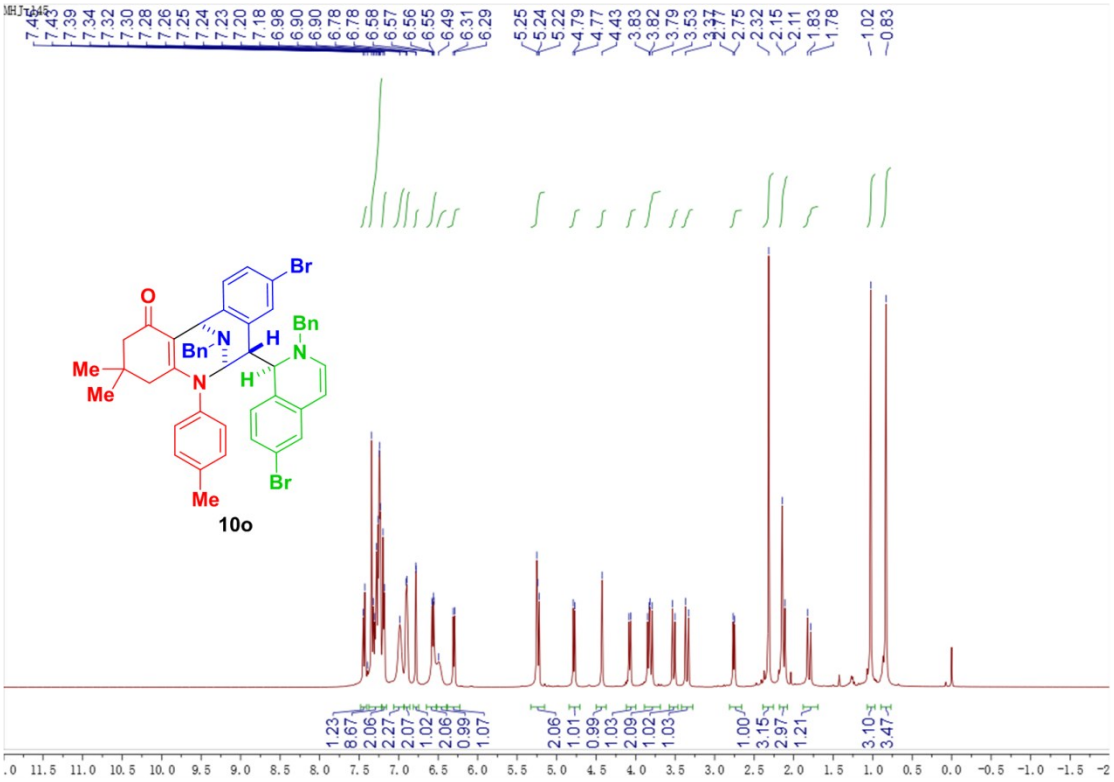
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7.20
7.18
6.98
6.90
6.90
6.78
6.78
6.58
6.57
6.56
6.55
6.49
6.31
6.29
5.25
5.24
5.22
4.79
4.77
4.43
3.83
3.82
3.79
3.53
3.37
3.17
2.75
2.32
2.15
2.11
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1.78
1.02
0.83
Br
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Bn
N
H
Bn
N
H
Me
Me
N
Me
Br
10o
1.23
8.67
2.06
2.27
2.07
1.02
2.06
0.99
1.07
2.06
1.01
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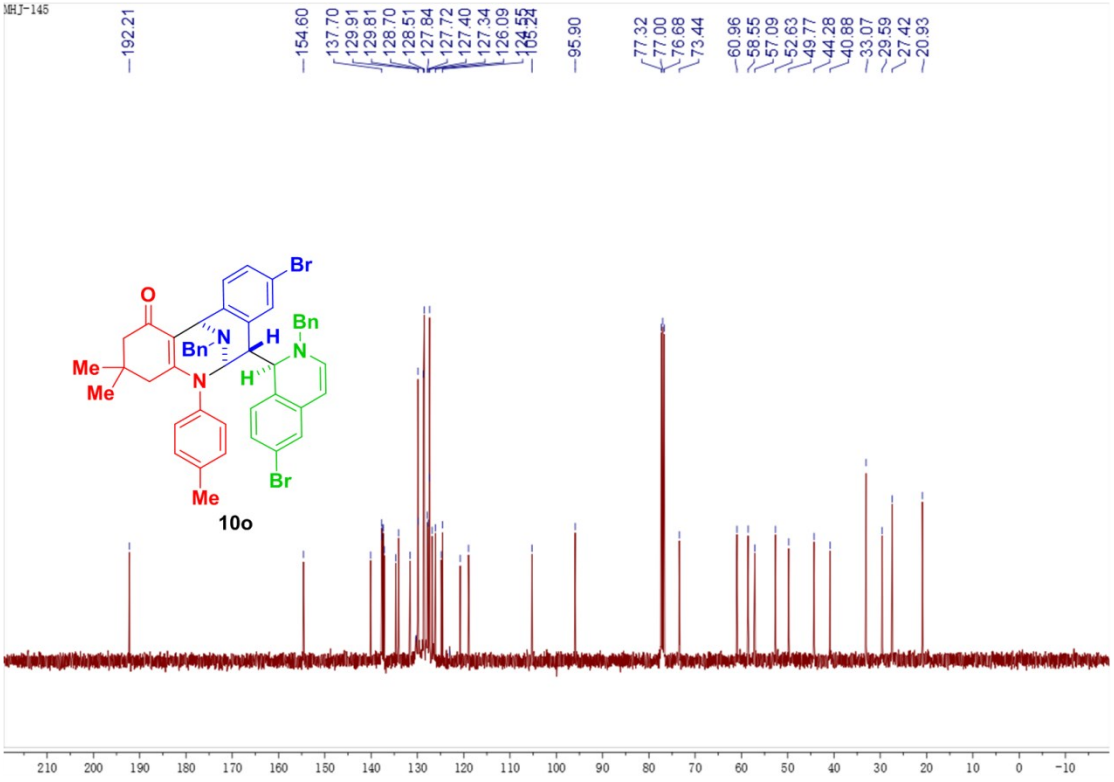
1.03
2.09
1.02
1.03
1.00
3.15
2.97
1.21
3.10
3.47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127.34
126.09
95.90
77.32
77.00
76.68
73.44
60.96
58.55
57.09
52.63
49.77
44.28
40.88
33.07
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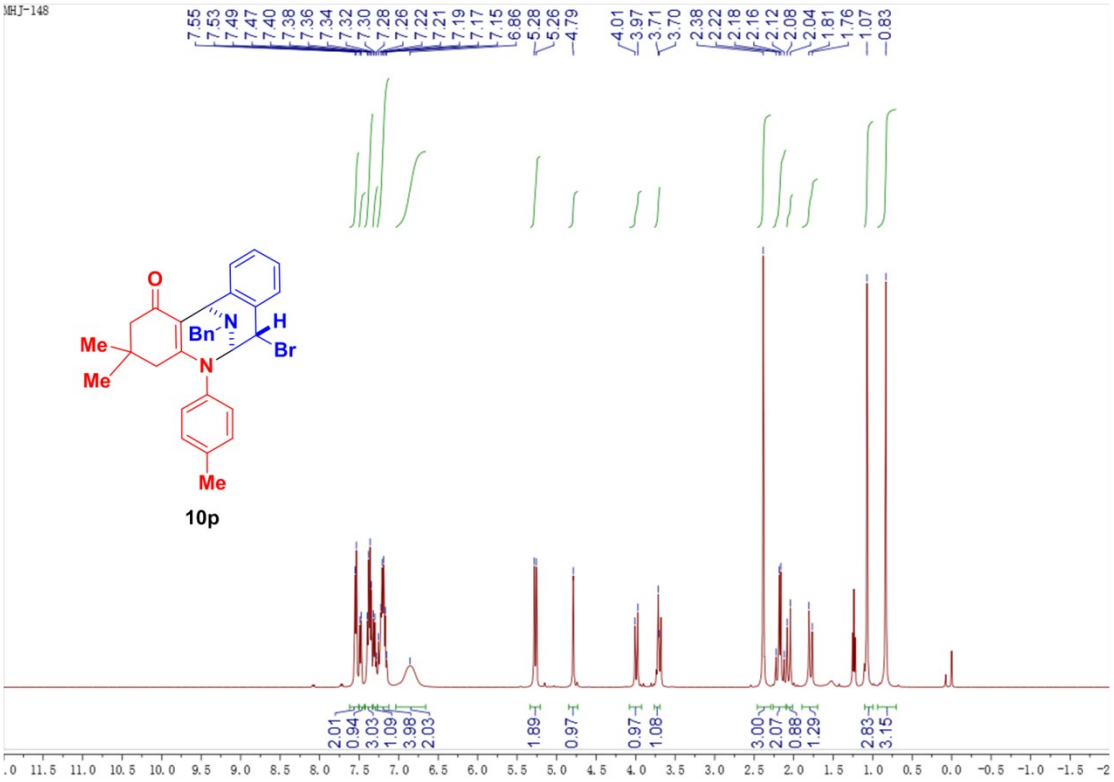
Me
Br
10o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7.26
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7.21
7.19
7.17
7.15
6.86
5.28
5.26
4.79
4.01
3.97
3.71
3.70
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2.22
2.18
2.16
2.12
2.08
2.04
1.81
1.76
1.07
0.83
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Bn
N
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Me
Me
N
Me
10p
2.01
0.94
3.03
1.09
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1.08
3.00
2.07
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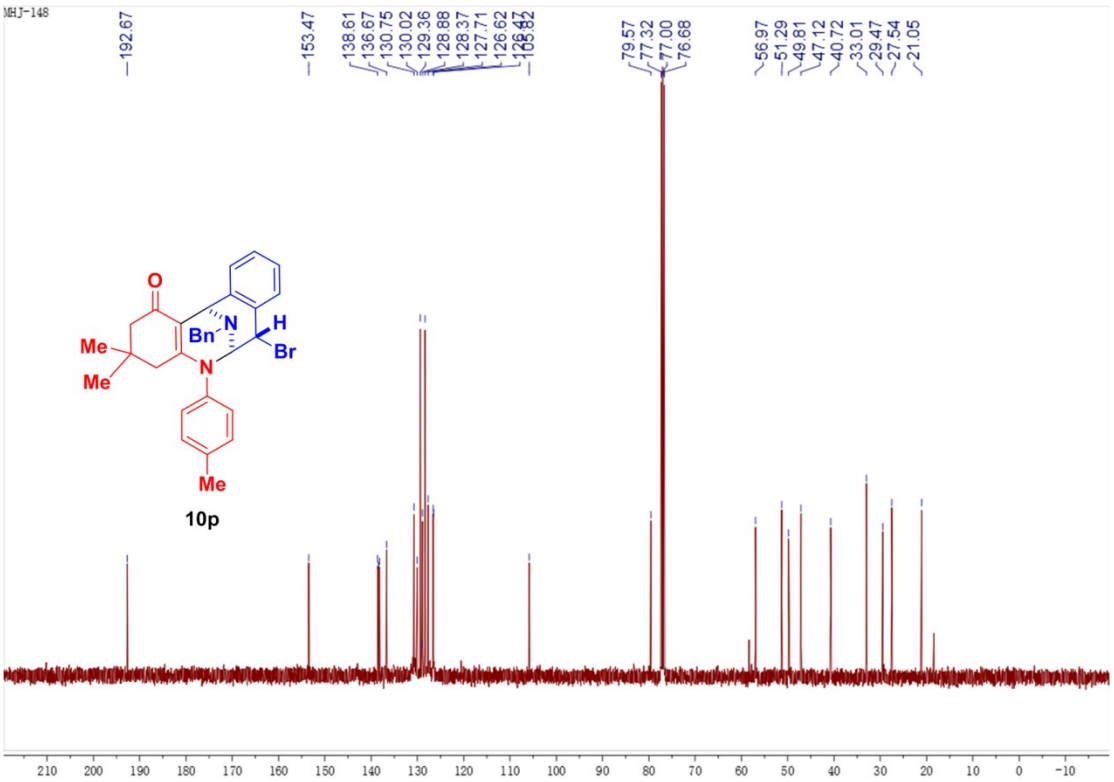
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129.36
128.88
128.37
127.71
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77.00
76.68
56.97
51.29
49.81
47.12
40.72
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29.47
27.54
21.05
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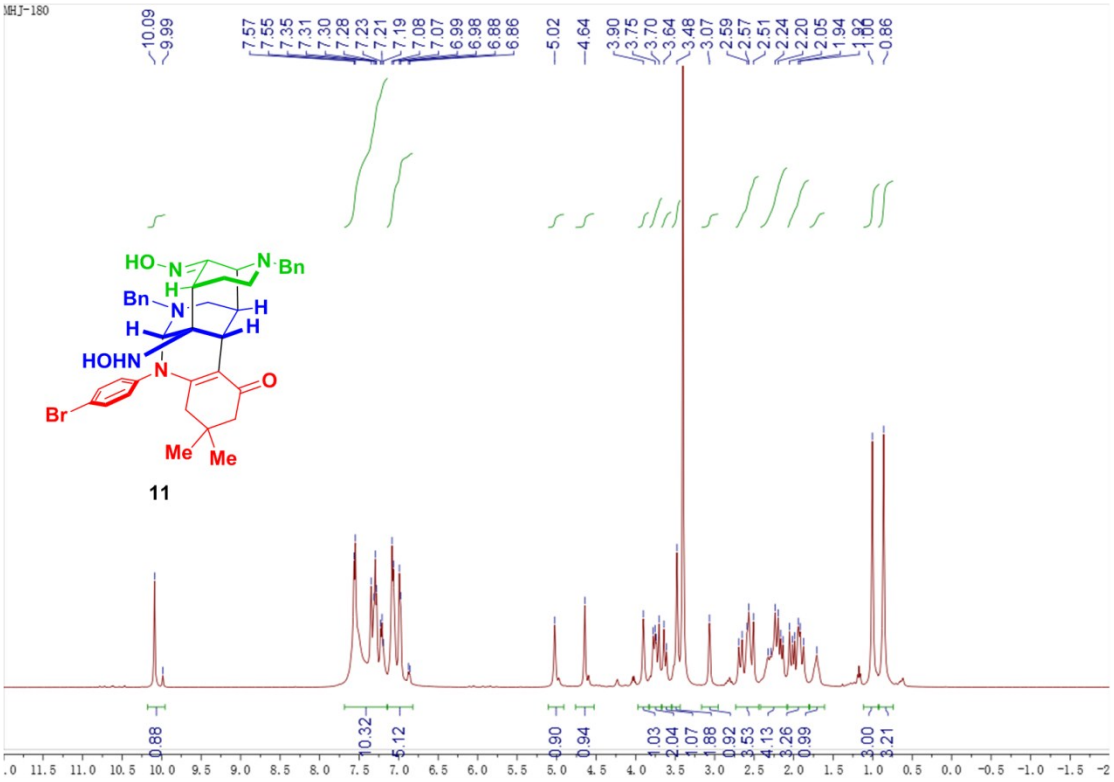
Me
10p


MHJ-180
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Bn
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H
H
HOHN
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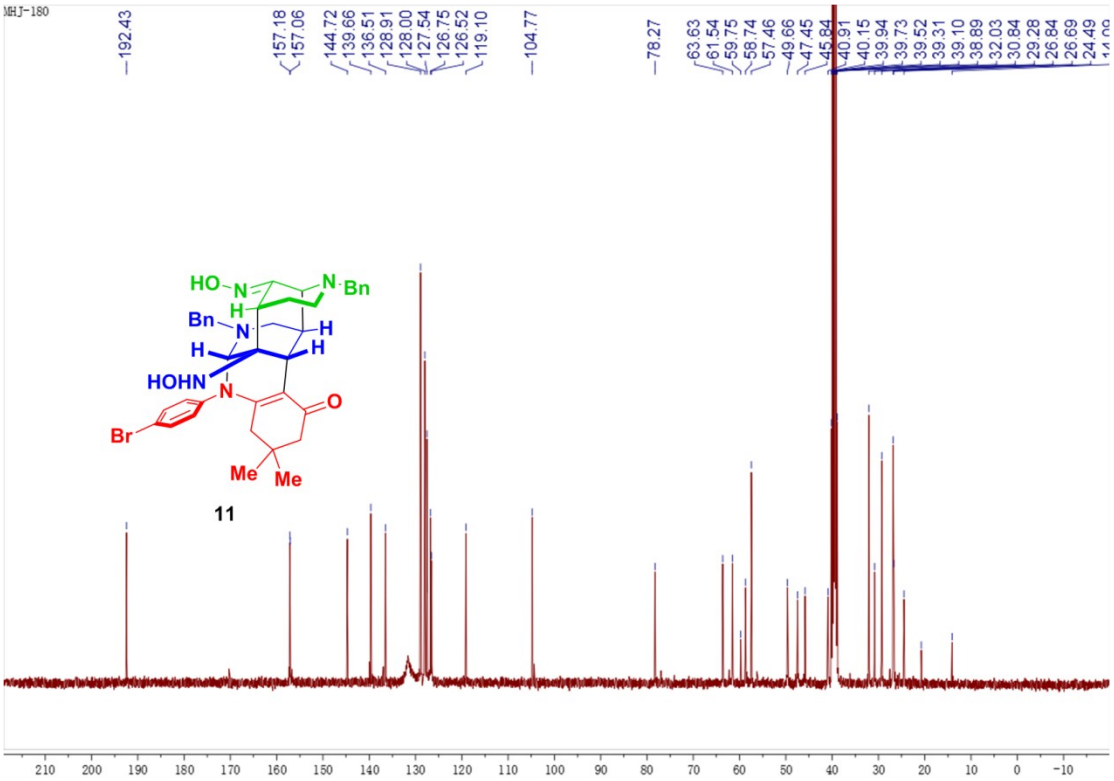
Br
Me
Me
11


MHJ-180
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H
HOHN
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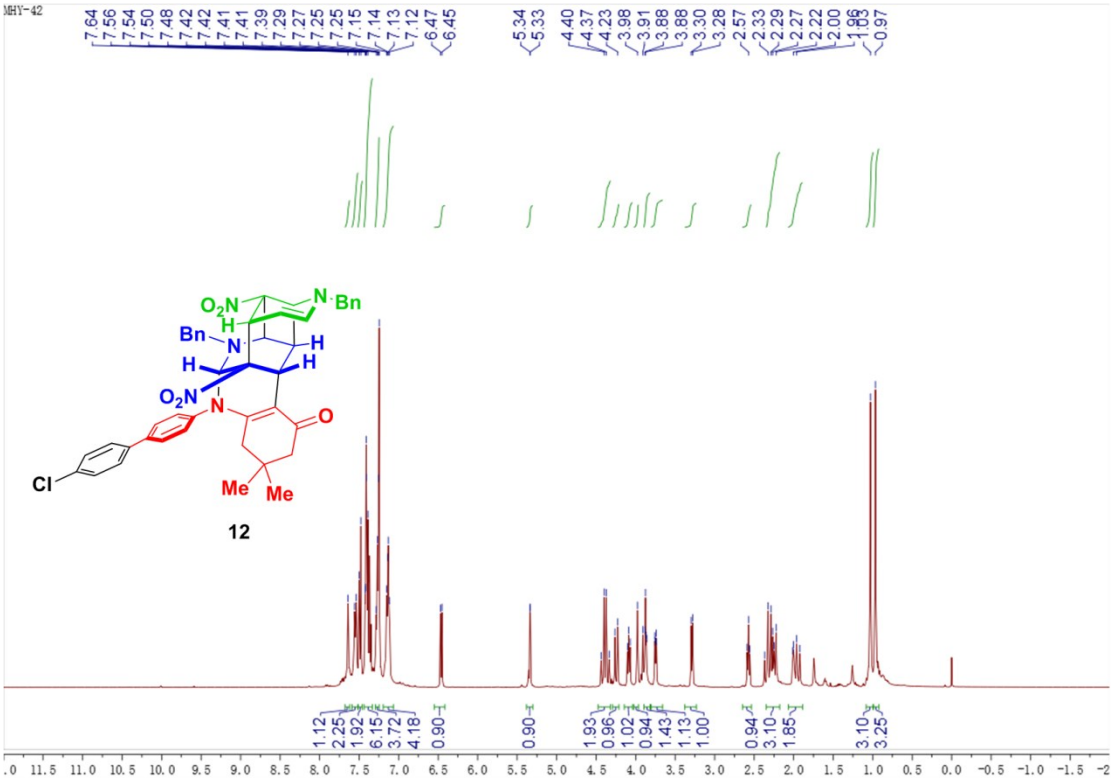
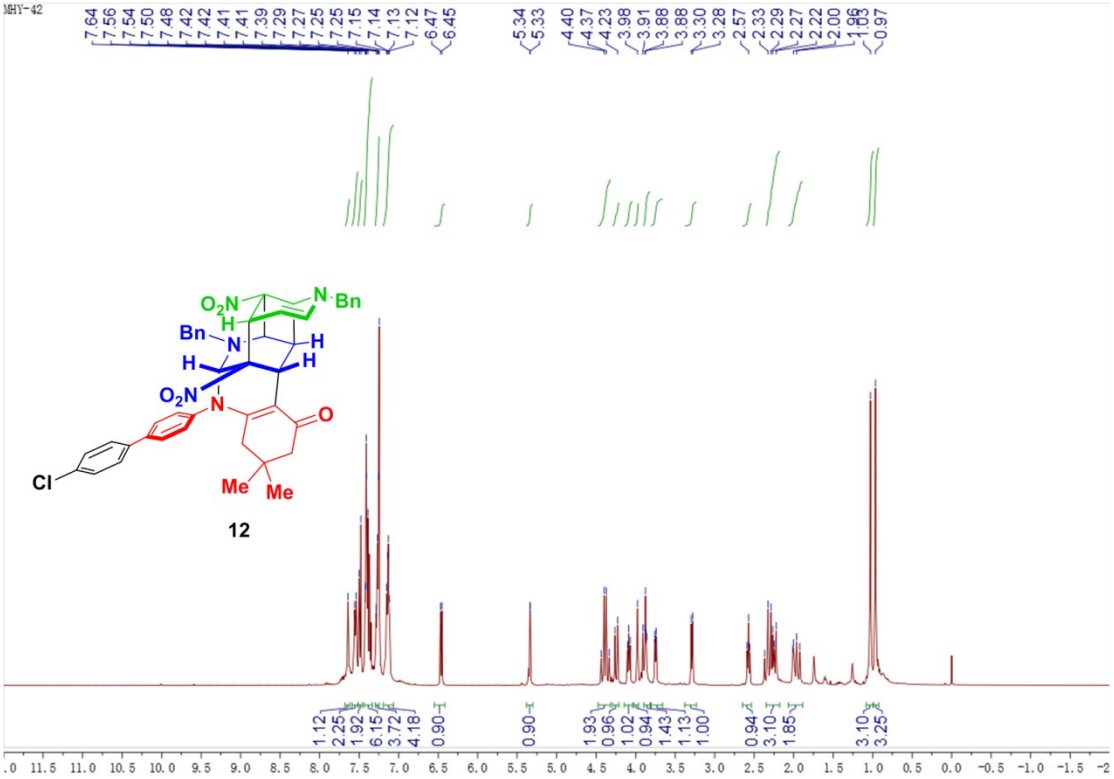
Me
Me
11


MHY-42
12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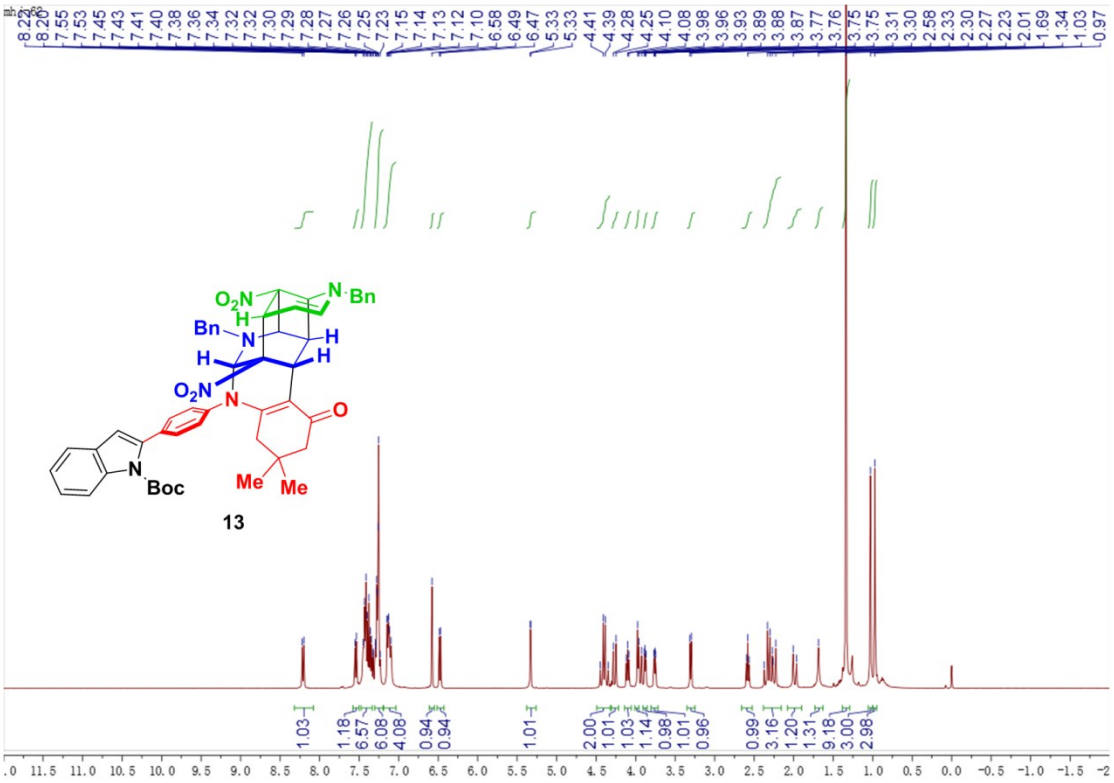
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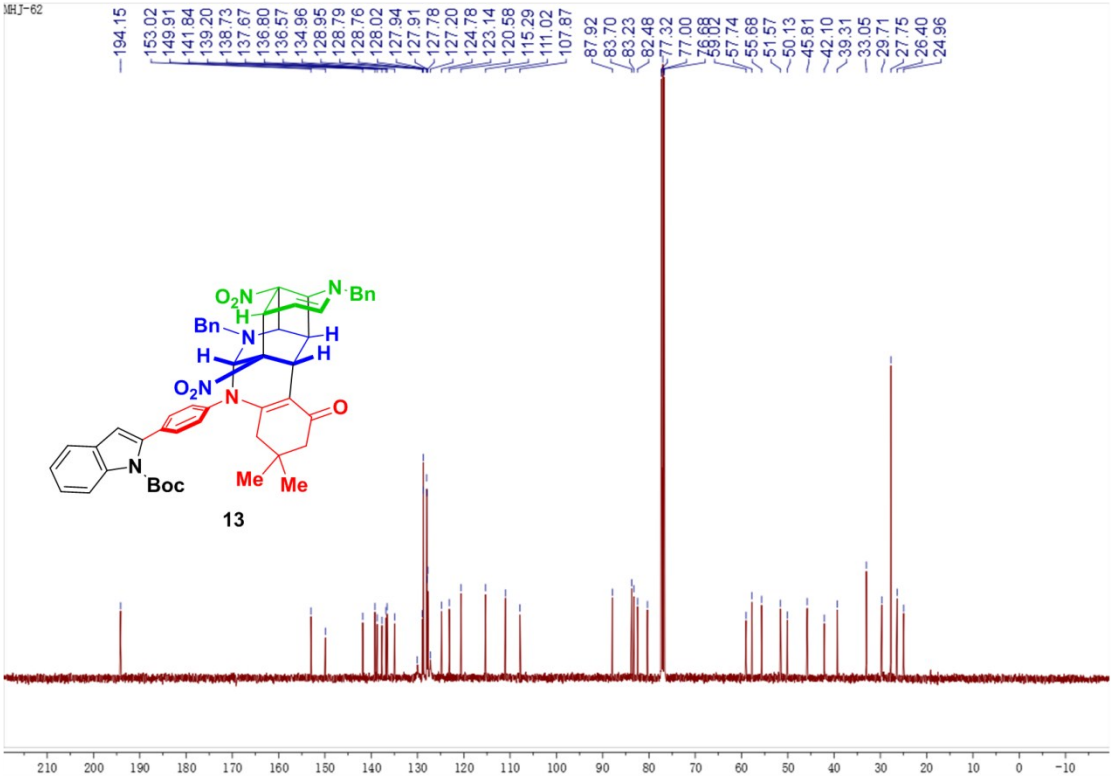
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