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$_3$)$_2$SO 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$_3$)$_2$SO 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

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$_3$CN. 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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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
C₃₉H₄₀N₅O₅ [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 4.0 Hz, 2H), 3.75 (dd, J₁ = J₂ = 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); 13C NMR (100
MHz, CDCl$_3$ $\delta$ 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) $\nu$ 3031, 2960, 2869, 1587, 1386, 741 cm$^{-1}$. HRMS (ESI) calcd for C$_{40}$H$_{42}$N$_5$O$_5$ [M+H]$^+$ 672.3181, found 672.3178.

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$_3$), $\delta$ 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$_3$) $\delta$ 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) $\nu$ 3022, 2960, 1636, 1585, 1538, 1389, 1241, 735 cm$^{-1}$. HRMS (ESI) calcd for C$_{39}$H$_{40}$N$_5$O$_5$ [M+H]$^+$ 674.2973, found 674.2974.

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$_3$), $\delta$ 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, J1 = J2 = 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); 13C NMR (100 MHz, CDCl3) 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) ν 3033, 2950, 2869, 1582, 1539, 1392, 745 cm⁻¹. HRMS (ESI) calcd for C38H38N5O5 [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(2H)-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; 1H NMR (400 MHz, CDCl3), 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, J1 = J2 = 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); 13C NMR (100 MHz, CDCl3) 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) ν 3030, 2956, 2871, 1591, 1540, 1392, 749 cm⁻¹. HRMS (ESI) calcd for C38H38FN5O5 [M+H]+ 646.2773, 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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₈H₃₉ClN₅O₅ [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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), 3.32 (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); ¹³C NMR (100 MHz,
CDCl₃) 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, 742 cm⁻¹. HRMS (ESI) calcd for C₃₈H₃₉ClN₅O₅ [M+H]^+ 678.2478,
found 678.2469.
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\(_3\)), \(\delta\) 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, \(J_1 = J_2 = 4.0\) Hz, 1H), 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\(_3\)) \(\delta\) 194.5, 151.3, 148.1, 146.3, 139.3, 136.5, 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) \(\nu\) 3029, 2952, 2867, 1590, 1537, 1345, 745 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{38}\)H\(_{37}\)N\(_6\)O\(_7\) [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(2H)-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\(_3\)), \(\delta\) 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$_3$) $\delta$ 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) $\nu$ 3432, 2952, 2870, 1631, 1584, 1541, 1392, 747 cm$^{-1}$. HRMS (ESI) calcd for C$_{39}$H$_{40}$N$_5$O$_6$ [M+H]$^+$ 658.3024, found 658.3032.

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 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ 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), 3.80-3.66 (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$_3$) $\delta$ 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) $\nu$ 3030, 2954, 2873, 1582, 1540, 1389, 738 cm$^{-1}$. HRMS (ESI) calcd for C$_{39}$H$_{40}$N$_5$O$_6$ [M+H]$^+$ 674.2973, found 674.2974.
1(2H)-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; 1H 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); 13C 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, 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) ν 3033, 2951, 2869, 1581, 1539, 1391, 747 cm$^{-1}$. HRMS (ESI) calcd for C$_{38}$H$_{37}$ClN$_5$O$_5$ [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(2H)-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; 1H 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); 13C 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) ν 3433, 2951, 2869, 1581, 1539, 1391, 747 cm$^{-1}$. HRMS (ESI) calcd for C$_{38}$H$_{37}$BrN$_5$O$_5$ [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(2H)-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; 1H NMR (400 MHz, CDCl₃), δ 7.31-7.14 (m, 11H), 7.06 (dd, J₁ = J₂ = 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3032, 2960, 2874, 1596, 1542, 1396, 735 cm⁻¹. HRMS (ESI) calcd for C₄₀H₄₂N₅O₆ [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 4.0 Hz, 1H), 4.38 (q, J = 16.0 Hz, 2H), 4.15-3.70 (m, 6H), 3.27 (dd, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) \(\nu = 3440, 3032, 2952, 2870, 1587, 1542, 1393, 752 \text{ cm}^{-1}\). HRMS (ESI) calcd for \(C_{38}H_{37}FN_5O_5\) [\(M+H\)]\(^+\) 662.2773, found 662.2775.

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 \(\delta\) 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), 3.29 (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 \(\delta\) 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 \(\delta\) 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, \(J_1 = J_2 = 4.0\) 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 \(\delta\) 194.3, 153.5, 139.5, 138.8, 136.8, 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 \(\nu = 3029, 2956, 2869, 1587, 1542, 1393, 752 \text{ cm}^{-1}\).
1538, 1386, 739 cm\(^{-1}\). IR (KBr) for minor isomer \(\nu\) 3032, 2954, 2869, 1600, 1543, 1391, 741 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{38}\)H\(_{37}\)ClN\(_{5}\)O\(_{5}\) [M+H]\(^+\) 678.2478, found 678.2479.

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; \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) \(\nu\) 3029, 2954, 2872, 1582, 1541, 1392, 733 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{40}\)H\(_{42}\)N\(_5\)O\(_7\) [M+H]\(^+\) 704.3079, found 704.3073.

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; \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) 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), 3.98 (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$_3$) $\delta$ 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) $\nu$ 3031, 2954, 2867, 1633, 1578, 1539, 1354, 735 cm$^{-1}$. HRMS (ESI) calcd for C$_{39}$H$_{40}$N$_5$O$_5$ [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(2H)-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$_3$), $\delta$ 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$_3$) $\delta$ 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) $\nu$ 3438, 2951, 2874, 1629, 1572, 1538, 1356, 737 cm$^{-1}$. HRMS (ESI) calcd for C$_{37}$H$_{38}$N$_5$O$_6$ [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(2H)-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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) \(\nu\) 3431, 3031, 2958, 2868, 1628, 1575, 1539, 1361, 739 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{36}\)H\(_{42}\)N\(_5\)O\(_5\) [M+H]\(^+\) 624.3181, found 624.3184.

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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) \(\nu\) 3056, 2929, 2863, 1633, 1584, 1536, 1370, 1165, 735 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{36}\)H\(_{42}\)N\(_5\)O\(_5\) [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; \(^1H\) 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); \(^13C\) 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) ν 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; \(^1H\) 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 (s, \(J = 8.0\) Hz, 3H); \(^13C\) 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, 128.5, 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) ν 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.
3,7,11-tetramethyl-7b,13-dinitro-5-(p-tolyl)-3,4,5,6,7,7a,7b,8,9,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[d]pyrido[3′,2′:3,4]cyclobuta[1,2-g][1,3]diazocin-1(2H)-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; 1H NMR (400 MHz, CDCl3), 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); 13C NMR (100 MHz, CDCl3) 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) ν 3035, 2951, 2871, 1631, 1582, 1539, 1394, 752 cm⁻¹. HRMS (ESI) calcd for C27H32N5O5 [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,8,9,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[d]pyrido[3′,2′:3,4]cyclobuta[1,2-g][1,3]diazocin-1(2H)-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; 1H NMR (400 MHz, CDCl3), 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, J₁ = J₂ = 4.0 Hz, 1H), 3.94 (t, J = 8.0 Hz, 1H), 3.80 (s, 1H), 3.74 (dd, J₁ = J₂ = 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl3) 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
\( \nu \) 3435, 2964, 2873, 1632, 1583, 1539, 1393, 748 cm\(^{-1}\). HRMS (ESI) calcd for \( \text{C}_{29}\text{H}_{36}\text{N}_{5}\text{O}_{5} \) \([\text{M+H}]^+\) 534.2711, found 534.2716.

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\(_3\)), \( \delta \) 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\(_3\)) \( \delta \) 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) \( \nu \) 3082, 2955, 2930, 2870, 2214, 1635, 1580, 1393, 729 cm\(^{-1}\). HRMS (ESI) calcd for \( \text{C}_{31}\text{H}_{36}\text{N}_{5}\text{O}_{5} \) \([\text{M+H}]^+\) 558.2711, found 558.2713.

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\(_3\)), \( \delta \) 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), 3.05-2.93 (m, 2H), 2.85 (d, \( J = 8.0 \) Hz, 1H), 2.26-2.16 (m, 2H), 1.98-1.88 (m, 2H), 1.88-1.78 (m, 2H), 1.67 (d, \( J = 16.0 \) Hz, 1H), 1.52 (d, \( J = 16.0 \) Hz, 2H), 1.31 (s, 3H), 1.27 (s, 3H), 1.10 (s, 3H), 1.08 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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) \( \nu \) 3082, 2955, 2930, 2870, 2214, 1635, 1580, 1393, 729 cm\(^{-1}\). HRMS (ESI) calcd for \( \text{C}_{31}\text{H}_{36}\text{N}_{5}\text{O}_{5} \) \([\text{M+H}]^+\) 558.2711, found 558.2713.
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\(_3\)) \(\delta\) 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) \(\nu\) 3439, 3037, 2964, 2934, 2873, 1634, 1591, 1539, 1392, 749 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{31}\)H\(_{40}\)N\(_5\)O\(_5\) [M+H]\(^{+}\) 562.3024, found 562.3028.

N\(_n\)-Bu H H O 2 N H Me Me O H n-Bu O 2 N Me 7,11-dibutyl-3,3-dimethyl-7b,13-dinitro-5-(p-tolyl)-3,4,5,6,7,7a,8,9,11,11a,11b,12-dodecahydro-6,8,12-(epimethanetriyl)benzo[d]pyrido[3',2':3,4]cyclobuta[1,2-\text{g}][1,3]diazocin-1(2\text{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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) \(\nu\) 3392, 2959, 2866, 1632, 1581, 1394, 733 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{33}\)H\(_{44}\)N\(_5\)O\(_5\) [M+H]\(^{+}\) 590.3337, found 590.3336.

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

S18
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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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 C₂₈H₃₀F₃N₃O [M+H]+ 424.2383, found 424.2380.

3. Screening chiral bases for asymmetric synthesis of 3a

Table S1 Screening chiral bases
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$_3$CN at 60 °C. b Isolated yields obtained by column chromatography. c The enantiomeric excess (ee) was determined by chiral HPLC.
racemic
4. Experimental data for the formation of 5

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$_3$CN. 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.

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), 4.03 (d, $J$ = 16.0 Hz, 1H), 3.95 (d, $J$ = 16.0 Hz, 1H), 3.72 (s, 3H).
7-benzyl-13-(1-benzyl-1,2-dihydroquinolin-2-yl)-3,3-dimethyl-N-phenyl-2,3,4,6,7,12-hexahydro-1H-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 °C; 1H NMR (400 MHz, CDCl₃), 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, J₁ = 8.0 Hz, J₂ = 12.0 Hz, 1H), 0.90 (s, 3H), 0.79 (s, 3H);

13C NMR (100 MHz, CDCl₃), 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) ν 3434, 2953, 1594, 1492, 1381, 746 cm⁻¹. HRMS (ESI) calcd for C_{47}H_{46}N₃O [M+H]^+ 668.3635, found 668.3617.

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

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 °C; 1H NMR (400 MHz, CDCl₃), 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, J₁ = 8.0 Hz, J₂ = 12.0 Hz, 1H), 0.90 (s, 3H), 0.79 (s, 3H);

13C NMR (100 MHz, CDCl₃), 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) ν 3434, 2953, 1594, 1492, 1381, 746 cm⁻¹. HRMS (ESI) calcd for C_{46}H_{44}FNO [M+H]^+ 654.3479, found 654.3461.
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; 1H NMR (400 MHz, CDCl₃), δ 7.48 (d, J = 8.0 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); 13C NMR (100 MHz, CDCl₃) δ 160.4, 158.2, 148.5, 142.8, 141.1, 138.4, 138.3, 129.3, 128.5, 128.4, 127.3, 127.1, 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) ν 3437, 3033, 2954, 1599, 1494, 1215, 750 cm⁻¹. HRMS (ESI) calcd for C₄₆H₄₃FN₃O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3419, 2955, 1603, 1493, 1218, 878 cm⁻¹. HRMS (ESI) calcd for C₄₆H₄₃Cl₂N₃O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3442, 2958, 1603, 1492, 1220, 860 cm⁻¹. HRMS (ESI) calcd for C₄₈H₄₆Cl₂N₃O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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
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-1H-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; 1H NMR (400 MHz, CDCl3), 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); 13C NMR (100 MHz, CDCl3) 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) ν 3426, 2955, 1596, 1489, 1377,
1220, 703 cm⁻¹. HRMS (ESI) calcd for C46H42Cl2N3O [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-1H-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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) \(\nu\) 3440, 2955, 1600, 1493, 1213, 725 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{46}\)H\(_{41}\)Cl\(_2\)FN\(_3\)O [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-1H-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\(_3\)), \(\delta\) 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,
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-1H-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3420, 2955, 1601, 1487, 1382, 1219, 725 cm⁻¹. HRMS (ESI) calcd for C₄₆H₄₄BrCl₂N₃O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) δ 162.5, 158.3, 152.4, 141.3, 140.1, 138.6, 137.9, 137.9, 129.3, 128.7, 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) ν 3439, 2953, 1596, 1490, 1376, 879 cm⁻¹. HRMS (ESI) calcd for C₄₇H₄₂Cl₂N₃O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3433, 2953, 1593, 1488, 1149, 876 cm⁻¹. HRMS (ESI) calcd for C₄₇H₄₂Cl₂N₃O [M+H]^+ 736.2856, found 736.2861.
7-benzyl-13-(1-benzyl-6-chloro-1,2-dihydroquinolin-2-yl)-10-chloro-N-(p-tolyl)-2,3,4,6,7,12-hexahydro-1H-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3432, 2947, 1601, 1493, 1383, 803 cm⁻¹. HRMS (ESI) calcd for C₄₅H₄₅Cl₂N₆O [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-1H-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; 1H NMR (400 MHz, CDCl₃), 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, 8H), 1.49 (d, J = 6.0 Hz, 3H).
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-1H-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; 1H NMR (400 MHz, CDCl3), 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, J1 = 12.0 Hz, J2 = 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, J1 = 4.0 Hz, J2 = 8.0 Hz, 1H), 4.12 (d, J = 8.0 Hz, 4H), 3.05 (dd, J1 = 8.0 Hz, J2 = 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); 13C NMR (100 MHz, CDCl3) 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) ν 3420, 2955, 1608, 1491, 1376, 1218, 929, 805 cm⁻¹. HRMS (ESI) calcd for C39H40Cl2N3O [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-1H-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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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, 55.8, 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) ν 3434, 2954, 1603, 1500, 1380, 1220, 804 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{49}\)H\(_{50}\)N\(_3\)O \([\text{M+H}]^+\) 696.3948, found 696.3925.

![Chemical structure](image)

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-1H-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\(_3\)), \(\delta\) 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\(_3\)) \(\delta\) 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) ν 3426, 2954, 1601, 1490, 1221, 804 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{49}\)H\(_{44}\)Br\(_2\)N\(_3\)O \([\text{M+H}]^+\)
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-1H-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; 1H NMR (400 MHz, CDCl3), 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); 13C NMR (100 MHz, CDCl3) 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) ν 3430, 2954, 1601, 1501, 1322, 1099, 738 cm⁻¹. HRMS (ESI) calced for C₄₇H₄₄N₅O₅ [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-1H-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; 1H NMR (400 MHz, CDCl3), 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$_3$) $\delta$ 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) $\nu$ 3417, 2655, 1607, 1500, 1220, 708 cm$^{-1}$. HRMS (ESI) calcd for C$_{49}$H$_{50}$N$_3$O [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(7H)-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$_3$), $\delta$ 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$_3$) $\delta$ 191.1, 161.1, 146.9, 141.1, 138.8, 138.2, 138.1, 137.8, 137.7, 137.3, 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) $\nu$ 3435, 2953, 1556, 1453, 1192, 1140, 797 cm$^{-1}$. HRMS (ESI) calcd for C$_{34}$H$_{34}$N$_3$O [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(2H)-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$_3$), $\delta$
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\(_3\)) \(\delta\) 191.1, 163.6, 140.4, 139.8, 139.0, 137.8, 130.7, 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) \(\nu\) 3451, 2959, 1612, 1504, 1188, 1150, 744 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{32}\)H\(_{35}\)N\(_2\)O \([M+H]^+\) 463.2744, found 463.2750.

5. Experimental data for the formation of 6

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\(_3\)CN. And then, TMG (34.6 mg, 0.30 mmol) was added by syringe. The resulting mixture was stirred at 60 \(^{\circ}\)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.

![Diagram](image)

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\(_3\)), \(\delta\) 7.52
(d, J = 8.0 Hz, 1H), 7.21-7.14 (m, 5H), 6.90 (dd, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3419, 2949, 1566, 1501, 1389, 739 cm⁻¹. HRMS (ESI) calcd for C₃₁H₃₃N₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), δ 7.44 (d, J = 8.0 Hz, 1H), 7.35-7.27 (m, 3H), 7.12 (dd, J₁ = J₂ = 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); ¹³C NMR (100 MHz, CDCl₃) 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) ν 3433, 2951, 1568, 1391, 1064, 736 cm⁻¹. HRMS (ESI) calcd for C₃₀H₃₁N₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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$_2$O [M+H]$^+$ 453.2337, found 453.2340.

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$_2$O [M+H]$^+$ 483.2198, found 483.2201.

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(2H)-one (6d)

7-benzyl-10-chloro-3,3-dimethyl-5-(4-ethylphenyl)-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[d,g][1,3]diazocin-1(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) δ 192.9, 156.3, 144.0, 141.4, 139.3, 137.7, 129.3, 129.2, 128.6, 128.3, 127.0, 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) ν 3422, 2957, 1565, 1498, 1389, 729 cm⁻¹. HRMS (ESI) calcd for C₃₂H₃₄ClN₂O [M+H]⁺ 497.2354, found 493.2356.

`\[
\begin{align*}
\text{7-benzyl-10-chloro-5-(4-methoxyphenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-6,12-methanodibenzo[d,g][1,3]diazocin-1(2H)-one (6f)}
\end{align*}
\]

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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3417, 2948, 1567, 1501, 1391, 1250, 732 cm⁻¹. HRMS (ESI) calcd for C₃₁H₃₂ClN₂O₂ [M+H]⁺ 499.2147, found 499.2145.

`\[
\begin{align*}
\text{7-benzyl-10-chloro-3,3-dimethyl-5-phenyl-3,4,5,6,7,12-hexahydro-6,12-}
\end{align*}
\]

S40
methanodibenzo[d,g][1,3]diazocin-1(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3434, 2950, 1567, 1491, 1393, 698 cm⁻¹. HRMS (ESI) calcd for C₃₀H₃₀ClN₂O [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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 (d, 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3435, 2946, 1569, 1498, 1392, 736 cm⁻¹. HRMS (ESI) calcd for C₃₀H₂₉ClF₂N₂O [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(2H)-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; 1H 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); 13C 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) ν 3441, 2945, 1569, 1490, 1391, 735 cm$^{-1}$. HRMS (ESI) calcd for C$_{30}$H$_{29}$Cl$_2$N$_2$O [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(2H)-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; 1H 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); 13C 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) ν 3429, 2950, 1618, 1562, 1486, 1385, 1067, 730 cm⁻¹. HRMS (ESI) calcd for C₃₀H₂₉BrClN₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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, J₁ = 12.0 Hz, J₂ = 8.0 Hz, 2H), 1.92 (d, J = 16.0 Hz, 1H), 0.98 (s, 3H), 0.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 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) ν 3432, 2960, 1496, 1207, 1148, 802 cm⁻¹. HRMS (ESI) calcd for C₃₁H₃₂ClN₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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) ν 3419, 2949, 1605, 1562, 1489, 1392, 698 cm$^{-1}$. HRMS (ESI) calcd for C$_{31}$H$_{32}$ClN$_2$O$_2$ [M+H]$^+$ 499.2147, found 499.2149.

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) ν 3434, 2953, 1565, 1485, 1387, 1158, 732 cm$^{-1}$. HRMS (ESI) calcd for C$_{30}$H$_{29}$BrClN$_2$O [M+H]$^+$ 547.1146, found 547.1146.

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

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; 1H NMR (400 MHz, CDCl3), 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, J1 = J2 = 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, J1 = J2 = 4.0 Hz, 1H), 1.80 (q, J = 8.0 Hz, 2H); 13C NMR (100 MHz, CDCl3) 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 C29H27ClN2O [M+H]+ 455.1885, found 455.1881.

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; 1H NMR (400 MHz, CDCl3), 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); 13C NMR (100 MHz, CDCl3) 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 C26H30ClN2O [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 4.0 Hz, 1H), 3.38 (dd, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3433, 2966, 1766, 1500, 1193, 1148, 801 cm⁻¹. HRMS (ESI) calcd for C₂₇H₃₀ClN₂O [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3431, 2949, 1565, 1505, 1390, 731 cm⁻¹. HRMS (ESI) calcd for C₃₂H₃₅N₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), 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, J₁ = J₂ = 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₃₁H₃₂BrN₂O [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(2H)-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; ¹H NMR (400 MHz, CDCl₃), δ 8.36 (d, J = 4.0 Hz, 1H), 7.78 (J₁ = J₂ = 4.0 Hz, 1H), 7.29-7.22 (m, 5H), 7.00 (dd, J₁ = J₂ = 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); ¹³C NMR (100 MHz, CDCl₃) δ 193.1, 155.3, 146.6, 140.9, 138.1, 138.1, 136.1, 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 C₃₁H₃₂N₃O₃ [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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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 (tt, J = 12.0 Hz, 4H); 2.36 (d, J = 20.0 Hz, 1H); 2.26 (tt, J₁ = J₂ = 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); 13C NMR (100 MHz, CDCl₃) 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) ν 3424, 2955, 1569, 1509, 1189, 1144 cm⁻¹. HRMS (ESI) calcd for C₃₂H₃₅N₂O [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

| entry | base       | x   | Time (min) | Yield (%)³ |
|-------|------------|-----|------------|------------|
| 1     | TMG        | 2.0 | 10         | 36         |
| 2     | DBU        | 2.0 | 10         | 57³        |
| 3     | DABCO·6H₂O | 2.0 | 10         | 27         |
| 4     | DBU        | 1.0 | 10         | 48         |
| 5     | DBU        | 2.6 | 5          | 79³        |
| 6     | DBU        | 3.0 | 5          | 83³        |
Unless otherwise noted, the reactions were conducted with 0.15 mmol enaminoe 1a, 2.2 equivalent of isoquinolinium salt 9a in 0.8 mL of CH$_3$CN at 60 °C. Only one diastereoisomer was obtained for all cases. Isolated yields obtained by column chromatography. Isolated yields obtained by filtration of the precipitate.

### 7. Experimental data for the formation of 10

#### General procedure:
To a 5.0 mL vial were successively added enaminoes 1 (0.15 mmol), N-alkyl isoquinolinium salts 9 (0.33 mmol) and 0.8 mL of CH$_3$CN. 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.

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, 3.39 (d, 3.20 (d), 3.08 (d), 2.95 (d), 2.82 (d), 2.69 (d), 2.56 (d), 2.43 (d), 2.30 (d), 2.17 (d), 2.04 (d), 1.81 (d), 1.68 (d), 1.55 (d), 1.42 (d), 1.29 (d), 1.16 (d), 0.93 (d), 0.80 (d), 0.67 (d), 0.54 (d), 0.41 (d), 0.28 (d), 0.15 (d), 0.02 (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$_3$) $\delta$ 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, 127.1, 126.8, 126.7, 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) $\nu$ 3441, 1611, 1565, 1391, 756 cm$^{-1}$. HRMS (ESI) calcd for C$_{47}$H$_{46}$N$_3$O $[\text{M+H}]^+$ 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 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ 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$_3$) $\delta$ 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) $\nu$ 3445, 2953, 1616, 1558, 1389, 760 cm$^{-1}$. HRMS (ESI) calcd for C$_{48}$H$_{46}$N$_3$O $[\text{M+H}]^+$ 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)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.1, 154.5, 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) $\nu$ 3445, 2953, 1616, 1558, 1389, 760 cm$^{-1}$. HRMS (ESI) calcd for C$_{48}$H$_{46}$N$_3$O $[\text{M+H}]^+$ 682.3792, found 682.3786.
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; ¹H NMR (400 MHz, CDCl₃), δ 7.51 (d, J = 8.0 Hz, 1H), 7.24-7.13 (m, 11H), 6.92-6.86 (m, 3H), 6.68 (dd, J₁ = J₂ = 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), 1.77 (d, J = 16.0 Hz, 1H), 1.03 (s, 3H), 0.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 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) ν 3442, 2951, 1611, 1563, 1504, 1247, 756 cm⁻¹. HRMS (ESI) calcd for C₄₇H₄₅N₅NaO₂ [M+Na]⁺ 706.3404, found 706.3410.

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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(2H)-one (10d)
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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; ¹H NMR (400 MHz, CDCl₃), 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); ¹³C NMR (100 MHz, CDCl₃) 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) ν 3438, 2949, 1615, 1557, 1387, 759 cm⁻¹. HRMS (ESI) calcd for C₄₇H₄₅N₅O [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(2H)-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\(_3\)), \(\delta\) 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, 1H), 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, \(J = 8.0\) Hz, 1H), 3.53 (d, \(J = 8.0\) 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), 0.82 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 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) \(\nu\) 3440, 2953, 1611, 1566, 1502, 1220, 757 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{46}\)H\(_{42}\)FN\(_3\)NaO [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(2H)-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\(_3\)), \(\delta\) 7.50 (d, \(J = 8.0\) Hz, 1H), 7.08 (d, \(J = 8.0\) Hz, 1H), 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\(_3\)) \(\delta\) 192.4, 153.7, 140.6, 139.4, 138.2,
13.7, 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) \( \nu \) 3440, 2929, 1614, 1564, 1387, 762 cm\(^{-1}\). HRMS (ESI) calcd for \( \text{C}_{45}\text{H}_{42}\text{ClN}_3\text{O} \ [\text{M+H}]^+ \) 688.3089, found 688.3077.

[Diagram of compound 10g]

13-benzyl-7-(2-benzyl-1,2-dihydroisoquinolin-1-yl)-5-(4-bromophenyl)-3,3-dimethyl-3,4,5,6,7,12-hexahydro-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\(_3\)), \( \delta \) 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), 3.35 (d, \( J = 16.0 \) Hz, 1H), 3.24 (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\(_3\)), \( \delta \) 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) \( \nu \) 3426, 2950, 1615, 1563, 1387, 762 cm\(^{-1}\). HRMS (ESI) calcd for \( \text{C}_{46}\text{H}_{43}\text{BrN}_3\text{O} \ [\text{M+H}]^+ \) 732.2584, found 732.2587.

[Diagram of compound 10h]

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\(_3\)), \( \delta \) 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, \( J = 8.0 \) 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\(_3\)) \( \delta 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) \( \nu \) 3421, 2930, 1618, 1556, 1340, 760 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{46}\)H\(_{42}\)N\(_4\)O\(_3\) [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(2H)-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\(_3\)), \( \delta 7.51 (d, J = 8.0 \) 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\(_3\)) \( \delta 192.2, 154.3, 140.9, 140.7, 139.5, 138.3, 137.8, 136.7, 132.6, 131.3, 129.8, 129.3, 128.9, 128.5, 128.4, 127.6, 127.5, 127.3, 127.1, 126.8, 126.7, 126.5, 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) \( \nu \) 3438, 2952, 1609, 1562, 1396, 753 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{46}\)H\(_{42}\)N\(_3\)O \([\text{M+H}]^{+}\) 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[\textit{b,e}]azocin-1(2\textit{H})-one (\textit{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; \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}), δ 7.50 (d, \textit{J} = 8.0 Hz, 1H), 7.29-7.13 (m, 11H), 7.04 (q, \textit{J} = 12.0 Hz, 2H), 6.91 (d, \textit{J} = 8.0 Hz, 3H), 6.72 (d, \textit{J} = 8.0 Hz, 2H), 6.57 (s, 2H), 6.23 (d, \textit{J} = 8.0 Hz, 1H), 5.28 (t, \textit{J} = 8.0 Hz, 2H), 5.20 (d, \textit{J} = 12.0 Hz, 1H), 4.67 (s, 1H), 4.25 (d, \textit{J} = 8.0 Hz, 1H), 3.82 (d, \textit{J} = 16.0 Hz, 1H), 3.72 (d, \textit{J} = 20.0 Hz, 1H), 3.53 (d, \textit{J} = 16.0 Hz, 1H), 3.31 (d, \textit{J} = 20.0 Hz, 1H), 2.83 (d, \textit{J} = 12.0 Hz, 1H), 2.16 (d, \textit{J} = 12.0 Hz, 3H), 1.73 (d, \textit{J} = 12.0 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H); \textit{13}C NMR (100 MHz, CDCl\textsubscript{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, 126.5, 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) ν 3427, 2952, 1611, 1564, 1394, 759 cm\textsuperscript{-1}. HRMS (ESI) calcd for C\textsubscript{46}H\textsubscript{42}ClN\textsubscript{3}NaO [M+Na]\textsuperscript{+} 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[\textit{b,e}]azocin-1(2\textit{H})-one (\textit{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; \textit{1}H NMR (400 MHz, CDCl\textsubscript{3}), δ 7.49 (d, \textit{J} = 12.0 Hz, 1H), 7.22-7.15 (m, 12H), 7.01-6.82 (m, 5H), 6.73 (d, \textit{J} = 12.0 Hz, 1H), 6.58 (d, \textit{J} = 16.0 Hz, 2H), 6.23 (d, \textit{J} = 8.0 Hz, 1H), 5.30 (d, \textit{J} = 8.0 Hz, 1H), 5.25 (s, 1H), 5.21 (d, \textit{J} = 12.0 Hz, 1H), 4.67 (s, 1H), 4.26 (s, 1H), 3.82 (d, \textit{J} = 16.0 Hz, 1H), 3.72 (d, \textit{J} = 20.0 Hz, 1H), 3.53 (d, \textit{J} = 16.0 Hz, 1H), 3.30 (d, \textit{J} = 20.0 Hz, 1H), 2.84 (s, 1H), 2.16 (d, \textit{J} = 12.0 Hz, 3H), 1.71 (t, \textit{J} = 20.0 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H); \textit{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 192.5, 153.3, 142.3, 142.2, 140.5, 138.1, 137.5, 136.6,
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(2H)-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; 1H NMR (400 MHz, CDCl₃), δ 7.49 (dd, J₁ = J₂ = 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, J₁ = J₂ = 16.0 Hz, 1H), 1.04 (s, 3H), 0.80 (s, 3H); 13C NMR (100 MHz, CDCl₃) 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 C₄₆H₄₃BrN₃O [M+Na]⁺ 754.2403, found 754.2398.

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(2H)-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; 1H NMR (400 MHz, CDCl₃), 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, \( J = 8.0 \text{ Hz}, 1H \)), 4.63 (s, 1H), 4.28 (d, \( J = 8.0 \text{ Hz}, 1H \)), 3.79 (d, \( J = 12.0 \text{ Hz}, 1H \)), 3.67 (d, \( J = 16.0 \text{ Hz}, 1H \)), 3.53 (d, \( J = 12.0 \text{ Hz}, 1H \)), 3.32 (d, \( J = 16.0 \text{ Hz}, 1H \)), 2.93 (d, \( J = 4.0 \text{ Hz}, 1H \)), 2.34-2.15 (m, 6H), 1.97 (d, \( J = 16.0 \text{ Hz}, 1H \)), 1.83-1.74 (m, 2H); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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, 129.4, 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) \( \nu \) 3436, 2932, 1612, 1558, 1446, 751 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{45}\)H\(_{42}\)N\(_3\)O [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-epiminodibenz[b,e]azocin-1(2H)-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\(_3\)), \( \delta \) 7.37 (dd, \( J_1 = J_2 = 8.0 \text{ Hz}, 3H \)), 7.25-7.20 (m, 9H), 7.03 (d, \( J = 4.0 \text{ Hz}, 2H \)), 6.97 (t, \( J = 8.0 \text{ Hz}, 2H \)), 6.40 (t, \( J = 8.0 \text{ Hz}, 1H \)), 6.13 (d, \( J = 4.0 \text{ Hz}, 1H \)), 5.51 (dd, \( J_1 = J_2 = 4.0 \text{ Hz}, 3H \)), 5.62 (s, 1H), 5.41 (d, \( J = 4.0 \text{ Hz}, 1H \)), 4.62 (s, 1H), 4.01 (d, \( J = 16.0 \text{ Hz}, 1H \)), 3.79 (d, \( J = 12.0 \text{ Hz}, 1H \)), 3.71 (d, \( J = 4.0 \text{ Hz}, 1H \)), 3.59 (d, \( J = 4.0 \text{ Hz}, 1H \)), 3.56 (s, 1H), 2.50 (s, 3H), 2.14 (d, \( J = 16.0 \text{ Hz}, 1H \)), 2.04 (s, 2H), 1.77 (d, \( J = 20.0 \text{ Hz}, 1H \)), 1.03 (s, 3H), 0.83 (s, 3H); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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) \( \nu \) 3440, 2925, 1630, 794 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{47}\)H\(_{44}\)Br\(_2\)N\(_3\)O [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(2H)-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; 1H NMR (400 MHz, CDCl3), 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, J1 = J2 = 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, J1 = J2 = 8.0 Hz, 2H), 3.51 (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); 13C NMR (100 MHz, CDCl3) δ 192.2, 154.6, 140.1, 137.7, 137.7, 137.6, 137.4, 137.2, 134.7, 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 C47H44Br2N3O [M+H]⁺ 824.1846, found 824.1854.

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; 1H NMR (400 MHz, CDCl3), 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); 13C NMR (100 MHz, CDCl3) 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, 1614, 1566, 1393, 723 cm⁻¹. HRMS (ESI) calcd for C31H32BrN2O [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 NiCl₂·6H₂O (4.8 mg, 0.02 mmol) in 1.0 mL MeOH and 1.0 mL DCM was cooled to 0 °C, and then NaBH₄ (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. NH₄Cl solution was added. The mixture was extracted with CH₂Cl₂. The combined organic phase was dried over MgSO₄, 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(1H)-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; ¹H NMR (400 MHz, DMSO-d₆), 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); ¹³C NMR (100 MHz, DMSO-d₆) 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) \( \nu \) 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.

![Chemical structure of 12](image)

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; \(^1\)H NMR (400 MHz, CDCl\(_3\)), \( \delta \) 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\(_3\)) \( \delta \) 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) \( \nu \) 3436, 3033, 2953, 2935, 2855, 1585, 1542, 1390 cm\(^{-1}\). HRMS (ESI) calcd for \( C_{44}H_{41}ClN_5O_5 \)[M+H]\(^+\) 754.2797, 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.

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$_3$), $\delta$ 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$_3$) $\delta$ 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) $\nu$ 3445, 3034, 2956, 2870, 1734, 1637, 1589, 1542, 1327, 743 cm$^{-1}$. HRMS (ESI) calex for C$_{51}$H$_{51}$N$_6$O$_7$ [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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