Supporting Information

Synthesis of Fused Indoline Heterocycles via Dearomatization of Indoles with α-Bromohydrzones: A Systematic Study on the Substrates

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Table of Contents

General information.................................................................page S2
General procedure for assembly of indoline derivatives.............................page S2
Optimization of the reaction conditions........................................ page S3
Analytical and spectral data for compounds.......................................page S4
The 1H and 13C spectra of compounds........................................page S18
Experimental Section:

General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without need of precautions to exclude air and moisture unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. $^1$H, $^{13}$C NMR spectra were recorded in CDCl$_3$ on 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for $^1$H NMR and $^{13}$C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

General procedure for assembly of indoline derivatives

\[
\begin{align*}
\text{NH}_2 & \quad \text{Br} & \quad \text{O} \\
1a & & 2a \\
\text{Cs}_2\text{CO}_3 & \quad \text{CH}_2\text{Cl}_2, 24h \quad 3aa
\end{align*}
\]

$\alpha$-bromohydrazone 1a (0.5 mmol), 1,3-dimethyliodoole 2a (0.7 mmol), Cs$_2$CO$_3$ (0.5 mmol) was stirred at room temperature under air atmosphere in 3 mL of dichloromethane. Upon completion of the reaction (indicated by TLC), solvent was removed in vacuum and the residue was purified by flash silica gel column chromatography using petroleum ether/ethyl acetate as eluent, affording pure product 3aa.
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<th>Yield b (%)</th>
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aReaction conditions: 1a (0.3mmol), 2a (0.5mmol), Cs₂CO₃ (1.0equiv) and CH₂Cl₂ (3mL).

bLC yields. The yields were determined by LC analysis using biphenyl as the internal standard.

cIsolated yields.
Analytical and spectral data of products:

((4aR,9aR)-4a,9-dimethyl-3-phenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3aa): Yield = 81% (154mg). White solid. M.p. 105.7-107.2 °C. IR (KBr) $\nu$ = 2984, 2928, 1667, 1322, 1112, 923, 743, 722, 684 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.88–7.71 (m, 2H), 7.58–7.41 (m, 5H), 7.31–7.23 (m, 3H), 7.22–7.09 (m, 2H), 6.86–6.74 (m, 1H), 6.58 (d, $J$ = 7.8 Hz, 1H), 5.73 (s, 1H), 2.88 (s, 3H), 2.62 (d, $J$ = 2.7 Hz, 2H), 1.41 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 172.1, 150.1, 149.0, 136.1, 135.2, 134.9, 130.1, 129.4, 129.1, 128.1, 128.0, 127.0, 125.2, 120.5, 118.5, 108.0, 76.7, 38.1, 33.3, 33.3, 21.2 ppm. HRMS m/z: calcd for C$_{25}$H$_{24}$N$_3$O [M+H]$^+$ 382.1919, found: 382.1920.

((4aS,9aR)-9-methyl-3,4a-diphenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ab): Yield = 44% (97mg). White solid. M.p. 145.7-146.8 °C. IR (KBr) $\nu$ = 2921, 1656, 1395, 1342, 1020, 939, 751, 702, 689, 650 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62–7.52 (m, 4H), 7.40–7.26 (m, 4H), 7.25–7.21 (m, 6H), 7.14 (dd, $J$ = 16.5, 8.7 Hz, 2H), 6.91 (d, $J$ = 7.2 Hz, 1H), 6.73 (t, $J$ = 7.4 Hz, 1H), 6.59 (d, $J$ = 7.8 Hz, 1H), 5.96 (s, 1H), 3.25 (d, $J$ = 17.7 Hz, 1H), 2.85 (s, 3H), 2.79 (d, $J$ = 17.7 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 171.8, 149.9, 149.1, 140.8, 135.7, 135.0, 134.7, 130.1, 129.3, 129.2, 128.3, 128.2, 128.1, 127.1, 127.0, 126.9, 125.3, 122.4, 119.0, 108.6, 78.0, 46.4, 33.4, 31.7 ppm. HRMS m/z: calcd for C$_{30}$H$_{26}$N$_3$O [M+H]$^+$ 444.2076, found: 444.2081.
((4aR,9aR)-9-methyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ac): Yield = 71% (130mg). White solid. M.p. 124.7-125.1 °C. IR (KBr) ν = 3051, 2956, 1642, 1389, 1338, 737, 712, 688, 644 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.83–7.72 (m, 2H), 7.54–7.41 (m, 5H), 7.33–7.25 (m, 3H), 7.16 (dd, J = 17.7, 7.5 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.51 (d, J = 7.8 Hz, 1H), 6.23 (d, J = 7.6 Hz, 1H), 3.59–3.48 (m, 1H), 3.01–2.80 (m, 4H), 2.62 (dd, J = 16.9, 7.6 Hz, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 171.6, 152.5, 149.8, 135.9, 134.9, 130.5, 130.1, 129.3, 129.2, 128.3, 128.0, 127.0, 125.3, 122.6, 118.2, 107.4, 70.6, 35.0, 33.0, 26.2 ppm. HRMS m/z: calcd for C₂₄H₂₂N₃O [M+H]+ 368.1763, found: 368.1760.

((4aR,9aR)-9-ethyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ad): Yield = 58% (110mg). White solid. M.p. 114.5-115.4 °C. IR (KBr) ν = 2966, 1638, 1488, 1389, 1064, 909, 786, 747, 694 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.85–7.67 (m, 2H), 7.51 (dd, J = 8.0, 1.5 Hz, 2H), 7.49–7.39 (m, 3H), 7.34–7.25 (m, 3H), 7.16 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.47 (dd, J = 14.3, 8.0 Hz, 2H), 3.66 (dd, J = 14.7, 7.3 Hz, 1H), 3.56–3.43 (m, 1H), 3.36–3.20 (m, 1H), 2.84 (dd, J = 16.6, 7.3 Hz, 1H), 2.69 (dd, J = 16.6, 6.6 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 171.5, 154.2, 148.4, 135.8, 135.0, 130.4, 130.1, 129.2, 129.2, 128.2, 128.0, 127.0, 125.4, 122.7, 117.4, 107.0, 68.0, 38.8, 36.1, 26.6, 9.8 ppm. HRMS m/z: calcd for C₂₅H₂₄N₃O [M+H]+ 382.1919, found: 382.1927.

((4aR,9aR)-9-allyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ae): Yield = 64% (114mg). White solid. M.p. 95.5-97.2 °C. IR (KBr) ν = 2922, 1642, 1386, 1343, 928, 737, 718, 690, 643 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.76–7.66 (m, 2H), 7.53 (dd, J = 8.1, 1.5 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.34–7.26 (m,
3H), 7.15 (s, 1H), 7.07 (t, J = 7.7 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.55 (d, J = 8.5 Hz, 1H), 6.43 (d, J = 7.8 Hz, 1H), 5.98–5.85 (m, 1H), 5.25 (dd, J = 17.2, 1.7 Hz, 1H), 5.12 (dd, J = 10.3, 1.6 Hz, 1H), 4.15 (dd, J = 16.9, 5.3 Hz, 1H), 3.98–3.76 (m, 2H), 2.84 (d, J = 6.6 Hz, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 171.8, 155.9, 149.8, 143.6, 136.2, 135.4, 133.6, 130.5, 130.2, 129.8, 129.7, 128.6, 128.5, 127.4, 125.9, 123.1, 118.1, 116.4, 107.6, 70.2, 48.8, 37.6, 27.1 ppm. HRMS m/z: calcd for C$_{26}$H$_{24}$N$_3$O [M+H]$^+$ 394.1919, found: 394.1926.

((4aR,9aR)-3,9-diphenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3af): Yield = 53% (114mg). White solid. M.p. 155.9-157.6 °C. IR (KBr) v = 3061, 1651, 1499, 1503, 1495, 1436, 1264, 1053, 743, 695, 650 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.57–7.50 (m, 2H), 7.47–7.26 (m, 12H), 7.24 (d, J = 8.1 Hz, 2H), 7.11–6.95 (m, 2H), 6.74 (t, J = 7.1 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 4.03 (dd, J = 12.9, 7.9 Hz, 1H), 2.96 (dd, J = 16.1, 5.0 Hz, 1H), 2.84 (dd, J = 16.1, 7.5 Hz, 1H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 170.1, 148.5, 140.7, 135.8, 134.7, 130.0, 129.7, 129.4, 128.9, 128.7, 128.0, 126.8, 126.4, 125.8, 125.5, 123.1, 118.4, 107.8, 70.4, 38.2, 27.4 ppm. HRMS m/z: calcd for C$_{29}$H$_{24}$N$_3$O [M+H]$^+$ 430.1919, found: 430.1926.

((4aR,9aR)-9-benzyl-3-phenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ag): Yield = 58% (128mg). White solid. M.p. 144.9-145.6 °C. IR (KBr) v = 3057, 2928, 1628, 1395, 905, 745, 708, 689, 647 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.54 (dd, J = 8.0, 1.5 Hz, 2H), 7.42–7.37 (m, 3H), 7.36–7.28 (m, 6H), 7.26–7.12 (m, 5H), 7.01 (t, J = 7.7 Hz, 1H), 6.69 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.32 (d, J = 7.8 Hz, 1H), 4.78 (d, J = 16.5 Hz, 1H), 4.45 (d, J = 16.5 Hz, 1H), 3.85 (dd, J = 14.5, 6.9 Hz, 1H), 2.94–2.81 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 171.4, 149.8, 138.7, 135.8, 134.8, 129.8, 129.7, 129.4, 128.9, 128.2, 128.0,
128.0, 126.8, 126.4, 126.2, 125.4, 122.7, 117.9, 106.8, 70.5, 50.5, 37.2, 30.5, 26.5 ppm. HRMS m/z: calcd for C_{30}H_{26}N_{3}O [M+H]^+ 444.2076, found: 444.2079.

((4aR,9aR)-6,9-dimethyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ah): Yield = 69% (131mg). White solid. M.p. 131.8-133.2 °C. IR (KBr) ν = 2930, 1650, 1339, 1272, 924, 815, 761, 708, 693, 643 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 7.84–7.72 (m, 2H), 7.54 (dd, J = 7.8, 1.7 Hz, 2H), 7.49–7.41 (m, 3H), 7.35–7.26 (m, 3H), 7.06–6.93 (m, 2H), 6.46 (d, J = 7.9 Hz, 1H), 6.11 (d, J = 7.2 Hz, 1H), 3.44–3.30 (m, 1H), 3.01–2.76 (m, 4H), 2.52 (dd, J = 17.2, 8.3 Hz, 1H), 2.29 (s, 3H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) δ = 171.7, 150.9, 147.4, 136.0, 134.9, 131.1, 130.0, 129.3, 129.0, 128.4, 127.9, 127.8, 127.0, 125.2, 123.4, 107.8, 70.6, 34.1, 33.7, 26.0, 20.4 ppm. HRMS m/z: calcd for C_{25}H_{24}N_{3}O [M+H]^+ 382.1919, found: 382.1930.

((4aR,9aR)-6-methoxy-9-methyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ai): Yield = 76% (151mg). White solid. M.p. 140.1-141.7 °C. IR (KBr) ν = 3264, 1638, 1515, 1493, 1226, 778, 727, 695 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 7.86–7.78 (m, 2H), 7.56 (dd, J = 7.8, 1.8 Hz, 2H), 7.53–7.41 (m, 4H), 7.34–7.26 (m, 3H), 7.24 (dd, J = 7.5, 5.1 Hz, 1H), 6.72 (d, J = 7.7 Hz, 1H), 6.10 (d, J = 6.8 Hz, 1H), 3.99–3.86 (m, 4H), 3.23 (dd, J = 17.8, 7.6 Hz, 1H), 2.87 (s, 3H), 2.34 (dd, J = 17.8, 9.1 Hz, 1H) ppm. \(^13\)C NMR (101 MHz, CDCl\(_3\)) δ = 171.7, 150.9, 147.4, 136.0, 134.9, 131.1, 130.0, 129.3, 129.0, 128.4, 127.9, 127.8, 127.0, 125.2, 123.4, 107.8, 70.6, 34.1, 33.7, 26.0, 20.4 ppm. HRMS m/z: calcd for C_{25}H_{24}N_{3}O [M+H]^+ 398.1869, found: 398.1878.
((4aR,9aR)-6-bromo-9-methyl-3-phenyl-4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3aj): Yield = 76% (169mg). White solid. M.p. 136.5-137.6 °C. IR (KBr) \( \nu = 2930, 1652, 1386, 1334, 1261, 796, 761, 712, 695, 649 \) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.77 \) (dd, \( J = 8.2, 1.4 \) Hz, 2H), 7.56–7.41 (m, 5H), 7.37–7.26 (m, 4H), 7.23 (dd, \( J = 8.3, 2.0 \) Hz, 1H), 6.37 (d, \( J = 8.3 \) Hz, 1H), 6.24 (d, \( J = 7.6 \) Hz, 1H), 3.57–3.49 (m, 1H), 2.95–2.78 (m, 4H), 2.60 (dd, \( J = 16.9, 7.5 \) Hz, 1H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 171.5, 152.2, 148.8, 135.7, 134.6, 132.6, 130.9, 130.2, 129.3, 129.3, 128.0, 127.0, 125.6, 125.2, 109.6, 108.7, 70.4, 34.8, 32.8, 26.0 ppm. HRMS m/z: calcd for C\(_{24}\)H\(_{21}\)BrN\(_3\)O \([\text{M}^+\text{H}]^+\) 446.0868, found: 446.0862.

(4aR,9aR)-1-benzoyl-9-methyl-3-phenyl-4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indole-5-carbonitrile (3ak): Yield = 61% (120mg). White solid. M.p. 154.9-156.4 °C. IR (KBr) \( \nu = 2965, 1649, 1398, 1265, 922, 786, 761, 722, 694, 639 \) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.81–7.70 \) (m, 2H), 7.60–7.41 (m, 5H), 7.37–7.27 (m, 3H), 7.18 (t, \( J = 7.9 \) Hz, 1H), 6.93 (d, \( J = 7.6 \) Hz, 1H), 6.60 (d, \( J = 8.0 \) Hz, 1H), 6.45 (d, \( J = 8.2 \) Hz, 1H), 3.98 (dd, \( J = 14.9, 7.0 \) Hz, 1H), 2.97 (dd, \( J = 6.9, 3.8 \) Hz, 2H), 2.93 (s, 3H) ppm. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 171.5, 154.5, 150.6, 135.2, 134.4, 133.6, 130.4, 129.7, 129.3, 129.2, 128.1, 127.1, 125.4, 120.4, 116.9, 110.3, 107.0, 70.3, 36.3, 32.2, 24.6 ppm. HRMS m/z: calcd for C\(_{25}\)H\(_{21}\)N\(_3\)O \([\text{M}^+\text{H}]^+\) 393.1715, found: 393.1720.

Methyl(4aR,9aR)-1-benzoyl-9-methyl-3-phenyl-4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indole-5-carboxylate (3al): Yield = 52% (111mg). White solid. M.p. 150.3-151.1 °C. IR (KBr) \( \nu = 2963, 1711, 1656, 1408, 1269, 1114, 920, 746, 695, 631 \) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta =\)
7.86–7.78 (m, 2H), 7.56 (dd, J = 7.8, 1.8 Hz, 2H), 7.53–7.41 (m, 4H), 7.34–7.26 (m, 3H), 7.24 (dd, J = 7.5, 5.1 Hz, 1H), 6.72 (d, J = 7.7 Hz, 1H), 6.10 (d, J = 6.8 Hz, 1H), 3.99–3.86 (m, 4H), 3.23 (dd, J = 17.8, 7.6 Hz, 1H), 2.87 (s, 3H), 2.34 (dd, J = 17.8, 9.1 Hz, 1H) ppm.

13C NMR (101 MHz, CDCl3) δ = 172.0, 166.3, 150.1, 150.0, 136.1, 134.8, 133.8, 130.1, 129.4, 129.0, 128.2, 127.9, 127.0, 125.2, 124.7, 119.7, 111.8, 70.0, 51.5, 33.5, 33.3, 24.2 ppm. HRMS m/z: calcd for C26H24N3O3 [M+H]+ 426.1818, found: 426.1810.

((4aS,9aR)-9-isopropyl-3,4a-diphenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3am): Yield = 21% (49mg). White solid. M.p. 119.6–121.1 °C. IR (KBr) ν = 2924, 1661, 1474, 1387, 1330, 1232, 1021, 791, 755, 692 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ = 7.55 (t, J = 8.5 Hz, 4H), 7.41–7.28 (m, 4H), 7.27 (s, 2H), 7.25–7.13 (m, 5H), 7.06 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 7.2 Hz, 1H), 6.74–6.62 (m, 2H), 6.21 (s, 1H), 3.82–3.71 (m, 1H), 3.18 (d, J = 17.3 Hz, 1H), 2.92 (d, J = 17.3 Hz, 1H), 1.34 (dd, J = 12.1, 6.9 Hz, 6H) ppm. 13C NMR (101 MHz, CDCl3) δ = 171.1, 152.7, 147.0, 141.3, 135.6, 135.1, 135.0, 130.0, 129.3, 129.1, 128.3, 128.1, 127.8, 127.0, 126.8, 125.4, 122.7, 117.9, 109.8, 75.3, 47.6, 46.5, 32.2, 29.2, 19.1, 16.8 ppm. HRMS m/z: calcd for C32H30N3O [M+H]+ 472.2389, found: 472.2395.

((2Z,6Z)-3,7-diphenyl-1,2,5,6-tetrazocine-1,5(4H,8H)-diyl)bis(phenylmethanone) (3an‘): Yield = 16% (23mg). Yellow solid. M.p. 94.7-96.5 °C. IR (KBr) ν = 2962, 2925, 1725, 1491, 1260, 1018, 794, 688 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ = 8.17–8.08 (m, 4H), 7.90 (dd, J = 6.5, 3.1 Hz, 4H), 7.55–7.44 (m, 12H), 5.00 (s, 4H). 13C NMR (101 MHz, CDCl3) δ = 154.2, 153.2, 132.6, 131.6, 130.7, 129.2, 128.5, 128.0, 127.6, 125.9, 58.9. HRMS m/z: calcd for C30H35N4O2 [M+Na]+ 495.1797, found:495.1803.
((4aR,9aR)-4a-methyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ao): Yield = 45% (83mg). White solid. M.p. 119.7-121.1 °C. IR (KBr) ν = 2925, 1661, 1386, 1325, 1231, 737, 713, 691 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.81 (d, J = 7.5 Hz, 2H), 7.62–7.57 (m, 2H), 7.51–7.41 (m, 3H), 7.33 (d, J = 6.3 Hz, 3H), 7.12 (dd, J = 13.7, 7.3 Hz, 2H), 6.82 (t, J = 7.4 Hz, 1H), 6.72 (d, J = 7.7 Hz, 1H), 5.67 (s, 1H), 5.34 (s, 1H), 2.72 (s, 2H), 1.44 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 171.8, 148.6, 146.8, 136.2, 134.2, 133.0, 130.2, 129.7, 129.0, 128.0, 127.0, 125.2, 121.2, 119.2, 109.9, 74.1, 39.9, 31.8, 22.8 ppm. HRMS m/z: calcd for C₂₄H₂₀N₃O [M+H]+ 368.1763, found: 368.1757.

((4aR,9aR)-4a,9a-dimethyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ap): Yield = 46% (88mg). White solid. M.p. 146.2-147.7 °C. IR (KBr) ν = 3363, 1635, 1610, 1344, 1099, 749, 713, 690 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (dd, J = 7.6, 1.9 Hz, 2H), 7.44–7.34 (m, 3H), 7.33–7.25 (m, 5H), 7.08–6.99 (m, 1H), 6.95 (d, J = 7.2 Hz, 1H), 6.71 (dd, J = 15.7, 7.7 Hz, 2H), 6.61 (s, 1H), 3.32 (d, J = 17.7 Hz, 1H), 2.64 (d, J = 17.7 Hz, 1H), 1.94 (s, 3H), 1.39 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 171.8, 146.9, 144.0, 136.5, 136.2, 133.8, 129.4, 128.8, 128.8, 128.0, 127.7, 126.7, 124.8, 120.6, 119.2, 109.7, 84.8, 45.4, 28.3, 24.4, 17.3 ppm. HRMS m/z: calcd for C₂₅H₂₄N₄O [M+H]+ 382.1919, found: 382.1923.

methyl(4aR,9aR)-1-benzoyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indole-5-carboxylate (3aq): Yield = 25% (51mg). White solid. M.p. 115.6-116.9 °C. IR (KBr) ν = 3334, 1713, 1658, 1408, 1267, 1016, 914, 752, 687, 664, 625 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.84 (d, J
= 7.4 Hz, 2H), 7.64 (d, J = 3.8 Hz, 2H), 7.54–7.41 (m, 4H), 7.33 (d, J = 4.5 Hz, 3H), 7.19 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 6.03 (d, J = 3.9 Hz, 1H), 5.48 (s, 1H), 4.02–3.79 (m, 4H), 3.44 (dd, J = 16.5, 6.0 Hz, 1H), 2.22 (dd, J = 16.4, 11.2 Hz, 1H) ppm. 13C NMR (101 MHz, CDCl3) δ = 171.9, 166.2, 149.1, 148.3, 136.1, 134.1, 132.5, 130.3, 129.7, 129.0, 128.2, 128.0, 127.0, 125.7, 125.4, 120.7, 114.0, 68.1, 51.6, 35.0, 23.3 ppm. HRMS m/z: calcd for C25H22N3O3 [M+H]+ 412.1661, found: 412.1660.

((4aR,9aR)-4a,9-dimethyl-3-(p-tolyl)-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ba): Yield = 89% (176mg). White solid. M.p. 121.3–122.6 °C. IR (KBr) ν = 2954, 2873, 1667, 1331, 936, 718, 657 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ = 7.87–7.72 (m, 2H), 7.56–7.35 (m, 5H), 7.23–7.03 (m, 4H), 6.80 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.8 Hz, 1H), 5.73 (s, 1H), 2.88 (s, 3H), 2.67–2.54 (m, 2H), 2.31 (s, 3H), 1.41 (s, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ = 172.4, 151.0, 149.5, 139.7, 135.6, 135.4, 133.8, 130.5, 129.8, 129.1, 128.5, 127.4, 125.6, 120.9, 118.9, 108.4, 77.2, 38.8, 33.7, 33.7, 21.9, 21.3 ppm. HRMS m/z: calcd for C26H22N3O3 [M+H]+ 396.2076, found: 396.2088.

((4aR,9aR)-3-(4-methoxyphenyl)-4a,9-dimethyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ca): Yield = 76% (152mg). Brown solid. M.p. 128.8–130.2 °C. IR (KBr) ν = 2964, 1664, 1396, 1330, 1254, 1175, 1113, 1028, 928, 831, 720, 658 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ = 7.84–7.74 (m, 2H), 7.51–41 (m, 5H), 7.20–7.09 (m, 2H), 6.79 (dd, J = 8.0, 4.1 Hz, 3H), 6.55 (d, J = 7.8 Hz, 1H), 5.75 (s, 1H), 3.77 (s, 3H), 2.89 (s, 3H), 2.68–2.52 (m, 2H), 1.42 (s, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ = 171.8, 160.3, 150.6, 149.1, 135.1, 135.0, 130.0, 129.3, 128.7, 128.0, 127.0, 126.7, 120.5, 118.4, 113.3, 107.8, 76.8, 54.8, 38.7, 33.3, 33.2, 21.6 ppm. HRMS m/z: calcd for C26H26N3O2 [M+H]+ 412.2025, found: 412.2027.
((4aR,9aR)-3-(4-bromophenyl)-4a,9-dimethyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3da): Yield = 46% (106mg). White solid. M.p. 158.8-159.6 °C. IR (KBr) ν = 2964, 2878, 1671, 1334, 930, 763, 712, 693, 692 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.84–7.72 (m, 2H), 7.57–7.33 (m, 7H), 7.23–7.10 (m, 2H), 6.83 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 7.8 Hz, 1H), 5.70 (s, 1H), 2.87 (s, 3H), 2.57 (s, 2H), 1.40 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 172.6, 149.3, 149.1, 135.5, 135.5, 135.2, 131.6, 130.7, 129.7, 128.6, 127.5, 127.2, 123.9, 120.9, 119.1, 108.7, 77.2, 38.2, 33.8, 33.5, 21.5 ppm. HRMS m/z: calcd for C₂₅H₂₃BrN₃O [M+H]⁺ 460.1024, found: 460.1019.

((4aR,9aR)-3-(4-chlorophenyl)-4a,9-dimethyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ea): Yield = 54% (112mg). White solid. M.p. 145.5-146.1 °C. IR (KBr) ν = 2923, 2883, 1658, 1331, 932, 744, 719, 707, 654 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.83–7.74 (m, 2H), 7.53–7.42 (m, 5H), 7.26 (s, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.21–7.11 (m, 2H), 6.82 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 5.70 (s, 1H), 2.87 (s, 3H), 2.57 (s, 2H), 1.40 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 172.1, 148.9, 148.7, 135.1, 135.1, 134.8, 134.6, 130.2, 129.3, 128.2, 128.1, 127.1, 126.4, 120.4, 118.7, 108.2, 76.8, 37.8, 33.4, 33.1, 21.1 ppm. HRMS m/z: calcd for C₂₅H₂₂ClN₃O [M+H]⁺ 416.1530, found: 416.4541.

((4aR,9aR)-3-(4-fluorophenyl)-4a,9-dimethyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3fa): Yield = 76% (152mg). White solid. M.p. 98.2-99.3 °C. IR (KBr) ν = 2966, 1667, 1332, 1230, 1113, 934, 824, 745, 720 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ =
7.82–7.74 (m, 2H), 7.53–7.42 (m, 5H), 7.21–7.11 (m, 2H), 6.96 (t, J = 8.7 Hz, 2H), 6.82 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 7.8 Hz, 1H), 5.72 (s, 1H), 2.88 (s, 3H), 2.64–2.53 (m, 2H), 1.41 (s, 3H) ppm.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 172.0, 163.1 (d, $J$ = 252 Hz), 148.9, 135.0 (d, $J$ = 22 Hz), 132.3, 132.3, 130.2, 129.2, 128.1, 127.2, 127.1, 120.4, 118.6, 115.0 (d, J = 22 Hz), 108.1, 38.1, 33.3, 21.2 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -111.34 ppm.

HRMS m/z: calcd for C$_{25}$H$_{23}$FN$_3$O$_3$ [M+H]$^+$ 400.1825, found: 400.1834.

((4aR,9aR)-4a,9-dimethyl-3-(4-nitrophenyl)-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3ga): Yield = 92% (196mg). Yellow solid. M.p. 142.6–143.2 °C. IR (KBr) $\nu$ = 2864, 1672, 1518, 1346, 1326, 1113, 762, 722, 688, 653 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.13 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.57–7.45 (m, 3H), 7.24–7.14 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 5.68 (s, 1H), 2.87 (s, 3H), 2.69–2.54 (m, 2H), 1.41 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 172.3, 148.6, 147.6, 146.5, 142.0, 135.0, 134.4, 130.5, 129.2, 128.3, 127.2, 125.8, 123.2, 120.4, 119.0, 108.6, 76.4, 37.1, 33.6, 33.0, 20.6 ppm. HRMS m/z: calcd for C$_{25}$H$_{23}$FN$_3$O$_3$ [M+H]$^+$ 427.1770, found: 427.1764.

((4aR,9aR)-4a,9-dimethyl-3-(4-hydroxyphenyl)-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(4-hydroxyphenyl)methanone (3ha): Yield = 84% (167mg). White solid. M.p. 93.5–94.1 °C. IR (KBr) $\nu$ = 2956, 1607, 1399, 1344, 1240, 1169, 800, 761, 651 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.75 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 5.1 Hz, 2H), 7.31 (s, 3H), 7.15 (dd, J = 12.5, 6.8 Hz, 2H), 6.90–6.76 (m, 3H), 6.55 (d, J = 7.5 Hz, 1H), 5.76 (s, 1H), 2.87 (s, 3H), 2.64 (dd, J = 35.4, 16.8 Hz, 2H), 1.42 (s, 4H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 171.9, 158.3, 151.3, 149.0, 136.0, 135.0, 132.0, 129.2, 128.1, 128.0, 126.0, 125.3, 120.5, 118.4, 114.1, 107.9, 77.0, 38.8, 33.5, 33.2, 21.6 ppm. HRMS m/z: calcd for C$_{25}$H$_{24}$N$_2$O$_2$ [M+H]$^+$ 398.1869, found: 398.1871.
\((4aR,9aR)-4a,9\text{-dimethyl-3-phenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl}(4\text{-methoxyphenyl})methanone\) \((3ia)\): Yield = 84\% (173mg). White solid. M.p. 139.6-140.3 °C. IR (KBr) \(\nu = 2862, 1655, 1322, 1250, 745, 686 \text{ cm}^{-1}\). \(^1\text{H} \text{NMR (400 MHz, CDCl}_3) \delta = 7.87 (d, J = 8.9 \text{ Hz, } 2\text{H}), 7.66-7.53 (m, 2\text{H}), 7.31 (dd, J = 5.2, 1.9 \text{ Hz, } 3\text{H}), 7.16 (dd, J = 14.6, 7.1 \text{ Hz, } 2\text{H}), 6.96 (d, J = 8.9 \text{ Hz, } 2\text{H}), 6.81 (t, J = 7.4 \text{ Hz, } 1\text{H}), 6.57 (d, J = 7.8 \text{ Hz, } 1\text{H}), 5.73 (s, 1\text{H}), 3.89 (s, 3\text{H}), 2.86 (s, 3\text{H}), 2.69-2.57 (m, 2\text{H}), 1.40 (s, 3\text{H}) \text{ ppm}. \(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3) \delta = 171.7, 161.6, 150.3, 149.5, 136.8, 135.7, 132.4, 129.4, 128.5, 128.4, 127.2, 125.7, 120.9, 118.9, 112.8, 108.5, 77.2, 55.4, 38.6, 33.8, 33.8, 21.7 \text{ ppm. HRMS m/z: calcd for C}_{26}\text{H}_{36}\text{N}_3\text{O}_2 \text{ [M+H]}^+ 412.2025, \text{found: 412.2034}.\)

\((4aR,9aR)-4a,9\text{-dimethyl-3-phenyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl}(4\text{-nitrophenyl})methanone\) \((3ja)\): Yield = 94\% (200mg). Yellow solid. M.p. 198.2-199.4 °C. IR (KBr) \(\nu = 2958, 1667, 1522, 1338, 1110, 860, 760, 746, 729, 688 \text{ cm}^{-1}\). \(^1\text{H} \text{NMR (400 MHz, CDCl}_3) \delta = 8.29 (d, J = 8.7 \text{ Hz, } 2\text{H}), 7.92 (d, J = 8.6 \text{ Hz, } 2\text{H}), 7.47 (d, J = 6.9 \text{ Hz, } 2\text{H}), 7.35-7.26 (m, 3\text{H}), 7.18 (dd, J = 14.9, 7.4 \text{ Hz, } 2\text{H}), 6.83 (t, J = 7.4 \text{ Hz, } 1\text{H}), 6.60 (d, J = 7.8 \text{ Hz, } 1\text{H}), 5.69 (s, 1\text{H}), 2.90 (s, 3\text{H}), 2.66 (s, 2\text{H}), 1.43 (s, 3\text{H}) \text{ ppm}. \(^{13}\text{C} \text{NMR (101 MHz, CDCl}_3) \delta = 170.2, 151.6, 148.8, 148.2, 141.3, 135.6, 134.8, 130.0, 129.5, 128.2, 128.1, 125.2, 122.3, 120.6, 118.9, 108.2, 76.8, 38.1, 33.5, 33.3, 21.3 \text{ ppm. HRMS m/z: calcd for C}_{25}\text{H}_{22}\text{N}_4\text{O}_3 \text{ [M+H]}^+ 427.1770, \text{found: 427.1776}.\)
1-((4aR,9aR)-4a,9-dimethyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)ethan-1-one (3ka): Yield = 87% (139mg). Colorless oil. IR (KBr) ν = 2958, 2871, 1683, 1393, 1315, 927, 742, 692 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.75–7.66 (m, 2H), 7.35 (d, J = 3.7 Hz, 3H), 7.18–7.07 (m, 2H), 6.79 (t, J = 6.7 Hz, 1H), 6.55 (d, J = 6.7 Hz, 1H), 5.46 (s, 1H), 2.75 (d, J = 2.8 Hz, 3H), 2.57 (d, J = 3.1 Hz, 3H), 2.50 (t, J = 12.3 Hz, 2H), 1.28 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 174.2, 149.0, 148.8, 136.5, 135.4, 129.1, 128.0, 125.2, 120.4, 118.6, 108.3, 75.6, 36.9, 33.4, 33.0, 22.1, 20.5 ppm. HRMS m/z: calcd for C₂₀H₂₂N₃O⁺ 320.1763, found: 320.1751.

Methyl(4aR,9aR)-4a,9-dimethyl-3-phenyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indole-1-carboxylate (3la): Yield = 85% (142mg). White solid. M.p. 45.2–46.7 °C. IR (KBr) ν = 2955, 1704, 1440, 1321, 1193, 1131, 991, 759, 692 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.69 (dd, J = 6.4, 2.9 Hz, 2H), 7.40–7.30 (m, 3H), 7.19–7.03 (m, 2H), 6.76 (t, J = 7.4 Hz, 1H), 6.52 (d, J = 7.8 Hz, 1H), 5.33 (s, 1H), 3.96 (s, 3H), 2.81 (s, 3H), 2.57 (dd, J = 38.7, 16.8 Hz, 2H), 1.38 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 148.9, 136.5, 134.8, 129.1, 128.0, 125.4, 120.5, 118.3, 107.6, 79.0, 53.4, 38.9, 33.7, 32.6, 26.4, 21.6 ppm. HRMS m/z: calcd for C₂₀H₂₂N₃O₂ [M+H]⁺ 336.1712, found:336.1724.

(4aR,9aR)-4a,9-dimethyl-3-phenyl-1-tosyl-4,4a,9,9a-tetrahydro-1H-pyridazino[3,4-b]indole (3ma): Yield = 88% (190mg). White solid. M.p. 154.4–155.2 °C. IR (KBr) ν = 2857, 1647, 1482, 1357, 1169, 1089, 816, 755, 670, 607 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.91 (d, J = 8.3 Hz, 2H), 7.66 (dd, J = 6.7, 3.0 Hz, 2H), 7.39–7.32 (m, 3H), 7.29 (d, J = 8.1 Hz, 2H), 7.21–7.13 (m, 1H), 7.08–6.99 (m, 1H), 6.84–6.75 (m, 1H), 6.61 (d, J = 7.8 Hz, 1H), 4.97 (s, 1H), 2.96 (s, 3H), 2.50–2.30 (m, 5H), 0.77 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 149.9, 148.9, 144.2, 136.7, 136.7, 135.4, 129.1, 128.0, 125.4, 120.5, 118.3, 107.6, 79.0, 53.4, 38.9, 33.7, 32.6, 26.4, 21.6 ppm. HRMS m/z: calcd for C₂₀H₂₂N₃O₂ [M+H]⁺ 336.1712, found:336.1724.
135.5, 135.1, 129.5, 129.4, 128.5, 128.4, 128.3, 125.6, 120.9, 119.1, 108.8, 81.2, 36.3, 32.8, 32.4, 21.6, 19.5 ppm. HRMS m/z: calcd for C_{25}H_{26}N_{5}O_{2}S [M+H]^+ 432.1746, found: 432.1755.

(4aR,9aR)-1-(2,4-dinitrophenyl)-4a,9-dimethyl-3-phenyl-4,4a,9a-tetrahydro-1H-pyridazino [3,4-b]indole (3na): Yield = 90% (199mg). Red solid. M.p. 177.7-178.6 °C. IR (KBr) ν = 2955, 1704, 1441, 1131, 759, 692 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 8.60 (d, \(J = 2.3\) Hz, 1H), 8.31 (dd, \(J = 9.3, 2.3\) Hz, 1H), 7.58 (dd, \(J = 24.3, 6.2\) Hz, 3H), 7.34 (d, \(J = 2.9\) Hz, 1H), 7.16 (d, \(J = 5.5\) Hz, 2H), 6.83 (t, \(J = 7.4\) Hz, 1H), 6.52 (d, \(J = 8.0\) Hz, 1H), 5.14 (s, 1H), 2.74 (s, 3H), 2.73 – 2.50 (m, 2H), 1.51 (s, 3H) ppm. 13C NMR (101 MHz, CDCl\(_3\)) δ = 154.5, 148.1, 145.6, 139.9, 139.6, 135.4, 134.6, 129.5, 128.3, 128.1, 126.5, 125.2, 122.2, 120.7, 119.0, 117.8, 107.8, 83.0, 40.9, 34.0, 33.1, 21.7 ppm. HRMS m/z: calcd for C_{25}H_{22}N_{5}O_{2}S [M+H]^+ 444.1672, found: 444.1683.

((4aR,9aR)-3-(7-bromo-9,9-difluoro-9H-fluoren-2-yl)-4a,9-dimethyl-4,4a,9a-tetrahydro-1H-pyridazino[3,4-b]indol-1-yl)(phenyl)methanone (3pa): Yield = 84% (245mg). White solid. M.p. 196.4-197.3 °C. IR (KBr) ν = 2959, 1679, 1391, 1330, 1202, 1048, 817, 762, 726, 701, 654 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 7.88 – 7.75 (m, 3H), 7.70 (s, 1H), 7.63 (d, \(J = 7.4\) Hz, 1H), 7.51 (dd, \(J = 22.3, 6.9\) Hz, 4H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.35 (d, \(J = 7.6\) Hz, 1H), 7.25 – 7.14 (m, 2H), 6.84 (t, \(J = 6.9\) Hz, 1H), 6.61 (d, \(J = 7.4\) Hz, 1H), 5.70 (s, 1H), 2.88 (s, 3H), 2.62 (s, 2H), 1.41 (s, 3H) ppm. 13C NMR (101 MHz, CDCl\(_3\)) δ = 172.1, 148.8, 148.0, 139.4 (d, \(J = 25\) Hz), 138.8, 137.3 (d, \(J = 15\) Hz), 137.2 (d, \(J = 5\) Hz) 135.1, 134.7, 134.6, 130.3, 129.4, 129.1, 128.2, 127.1, 126.9, 124.0, 122.4, 121.5, 120.7, 120.5, 120.0, 118.8, 108.4, 76.5, 37.5, 33.4, 33.1, 20.8 ppm. 19F NMR (376 MHz, CDCl\(_3\)) δ = -111.25. HRMS m/z: calcd for C_{32}H_{25}BrF_{2}N_{3}O [M+H]^+ 584.1149, found:584.1142.
(R)-4a,9-dimethyl-3-phenyl-4a,9-dihydro-4H-pyridazino[3,4-b]indole (4aa): Yield = 66%.

White solid. M.p. 96.4-97.3 °C. ¹H NMR (400 MHz, CDCl₃) δ = 7.95 (d, J = 7.8 Hz, 2H), 7.44 (d, J = 7.4 Hz, 3H), 7.29 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 3.36 (s, 3H), 3.29 (d, J = 16.6 Hz, 1H), 2.64 (d, J = 16.6 Hz, 1H), 1.26 (s, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 166.6, 151.5, 145.5, 137.1, 133.9, 129.2, 128.2, 128.1, 126.0, 121.9, 121.0, 107.5, 37.3, 30.6, 27.6, 21.3 ppm. HRMS m/z: calcd for C₁₈H₁₇N₅ [M+H]+ 276.1501, found: 276.1509.
The $^1$H, $^{13}$C spectra of compounds: