Supporting Information for

A novel approach to 5H-pyrazino[2,3-b]indoles via annihilation of 3-diazoinindolin-2-imines with 2H-azirines or 5-alkoxyisoxazoles under Rh(II) catalysis

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General Information

Melting points were determined on a Stuart Melting Point Apparatus SMP30 and are uncorrected. $^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a Bruker AVANCE 400 spectrometer in solvents indicated below. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane. High-resolution mass spectra were recorded on a Bruker MaXis mass spectrometer, electrospray ionization, positive mode. IR spectrum was recorded on a FTIR-8400S Shimadzu spectrometer using KBr disc method. Thin-layer chromatography (TLC) was conducted on aluminum sheets precoated with SiO$_2$ ALUGRAM SIL G/UV254. Column chromatography was performed on silica gel 60 M (0.04–0.063 mm). All solvents were distilled and dried over sodium metal. 1,2-Dichloroethane was washed with concentrated H$_2$SO$_4$ and water, distilled from P$_2$O$_5$, and stored over anhydrous K$_2$CO$_3$. Acetonitrile was distilled from P$_2$O$_5$ and redistilled from K$_2$CO$_3$. DMSO was refluxed over CaH$_2$ and distilled in vacuo. The catalysts Rh$_2$(Oct)$_4$$^1$, Rh$_2$(Piv)$_4$$^2$, and Rh$_2$(esp)$_2$$^3$ were prepared by the reported procedures and gave satisfactory elemental analyses. Isoxazoles 1a,b,d–f, 4c,g, 5 3-diazoindolin-2-imines 2a–g,k–m$^6$ and azirines 3e, 7 3f,g, 8 3h, 9 3i,j, 10 3k$^5$ were prepared by the reported procedures.

Synthesis of 3-diazoindolin-2-imines 2

General procedure for the synthesis of 3-diazoindolin-2-imines 2

3-Diazoindolin-2-imines 2 were prepared similarly to the reported procedure.$^6$ To an oven-dried round-bottom flask equipped with a magnetic stirring bar were added corresponding indole (10 mmol), sulfonyl azide (20 mmol), and anhydrous DMSO (20 mL). The reaction mixture was stirred at 50 °C for 18 h, then quenched with water (200 mL) and extracted with CH$_2$Cl$_2$ (3 × 200 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent petroleum ether–EtOAc, 3:1).

Note that low conversion of indoles with electron-withdrawing substituents was observed (about 5–20%).

3-Diazoindolin-2-imines 2a–g,k–m are known compounds and have full characterization data.$^6$

$N$-(3-Diazo-1-methyl-7-nitroindolin-2-ylidene)-4-methylbenzenesulfonamide (2h)

Orange solid (185 mg, yield 5%); mp 180–182 °C (dec.); $R_f$ = 0.59 (hexane–EtOAc, 1:1); $^1$H NMR (CDCl$_3$) δ 7.91 (d, $J$ = 8.2 Hz, 2H), 7.70 (d, $J$ = 8.2 Hz, 1H), 7.44 (d, $J$ = 7.7 Hz, 1H), 7.34 (d, $J$ = 8.2 Hz, 2H), 7.31–7.26 (m, 1H), 3.46 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (CDCl$_3$) δ 156.0, 143.1, 139.2, 136.4, 129.5, 126.9, 126.5, 122.7, 122.3, 121.8, 120.2, 32.8, 21.5; HRMS–ESI [M + H]$^+$ calcd for C$_{16}$H$_{14}$N$_3$O$_4$S$^+$ 372.0761; found 372.0774.
**N-(6-Chloro-3-diazo-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (2i)**

Orange solid (432 mg, yield 12%); mp 192–194 °C; \( R_f = 0.32 \) (hexane–EtOAc, 3:1); IR (KBr), ν/cm\(^{-1}\): 2145 (C=\(\overset{\text{N+}}{\text{N}}\)); \(^1\)H NMR (CDCl\(_3\)) δ 7.90 (d, \( J = 8.2 \) Hz, 2H), 7.32 (d, \( J = 8.2 \) Hz, 2H), 7.22–7.14 (m, 2H), 7.10 (d, \( J = 1.4 \) Hz, 1H), 3.44 (s, 3H), 2.45 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) δ 155.5, 142.6, 139.8, 135.0, 131.8, 129.4, 126.3, 123.0, 117.5, 117.2, 110.2, 64.3, 29.1, 21.5; HRMS–ESI [M + H]\(^+\) calcd for C\(_{16}\)H\(_{14}\)ClN\(_{4}\)O\(_2\)S\(^+\) 361.0521; found 361.0530.

**N-(6-Bromo-3-diazo-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (2j)**

Orange solid (525 mg, yield 13%); mp 168–170 °C (dec.); \( R_f = 0.33 \) (hexane–EtOAc, 3:1); \(^1\)H NMR (CDCl\(_3\)) δ 7.90 (d, \( J = 8.2 \) Hz, 2H), 7.35–7.29 (m, 3H), 7.23 (s, 1H), 7.10 (d, \( J = 8.1 \) Hz, 1H), 3.43 (s, 3H), 2.44 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) δ 155.3, 142.7, 139.8, 135.3, 129.4, 126.4, 125.8, 119.1, 117.9, 117.8, 113.0, 64.3, 29.1, 21.5; HRMS–ESI [M + H]\(^+\) calcd for C\(_{16}\)H\(_{14}\)BrN\(_{4}\)O\(_2\)S\(^+\) 405.0015; found 405.0028.

**N-(4-Bromo-3-diazo-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (2n)**

Orange solid (242 mg, yield 6%); mp 197–198 °C (dec.); \( R_f = 0.41 \) (hexane–EtOAc, 3:1); \(^1\)H NMR (CDCl\(_3\)) δ 7.92 (d, \( J = 8.2 \) Hz, 2H), 7.32 (d, \( J = 8.2 \) Hz, 2H), 7.29–7.26 (m, 1H), 7.13 (t, \( J = 8.0 \) Hz, 1H), 7.03 (d, \( J = 8.0 \) Hz, 1H), 3.44 (s, 3H), 2.45 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) δ 155.9, 142.6, 140.1, 135.4, 129.3, 126.9, 126.7, 126.3, 116.7, 113.0, 108.6, 29.1, 21.5; HRMS–ESI [M + H]\(^+\) calcd for C\(_{16}\)H\(_{14}\)BrN\(_{4}\)O\(_2\)S\(^+\) 405.0015; found 405.0022.

**N-(3-diazo-1-methyl-1,3-dihydro-2H-pyrrrolo[2,3-b]pyridin-2-ylidene)-4-methylbenzenesulfonamide (2o)**

Orange solid (229 mg, yield 7%); mp 173–174 °C (dec.); \( R_f = 0.35 \) (hexane–EtOAc, 1:1); \(^1\)H NMR (CDCl\(_3\)) δ 8.24 (dd, \( J = 5.1, 1.4 \) Hz, 1H), 7.95–7.88 (m, 2H), 7.53 (dd, \( J = 7.6, 1.4 \) Hz, 1H), 7.32 (d, \( J = 8.2 \) Hz, 2H), 7.12 (dd, \( J = 7.6, 5.1 \) Hz, 1H), 3.54 (s, 3H), 2.45 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) δ 155.3, 146.6, 145.4, 142.8, 139.6, 129.4, 126.4, 124.0, 118.3, 113.5, 27.9, 21.5; HRMS–ESI [M + H]\(^+\) calcd for C\(_{15}\)H\(_{14}\)N\(_3\)O\(_2\)S\(^+\) 328.0863; found 328.0877.
Synthesis of 2H-azirines 3

General procedure for the synthesis of azirine-2-carboxylates 3a–d and azirine-2-carboxamide 3l
To a solution of isoxazole (0.6 mmol) in degassed acetonitrile (5 mL) was added iron(II) chloride tetrahydrate (12 mg, 0.06 mmol) under a stream of argon and the mixture was stirred at room temperature for 24 h. Then the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent petroleum ether–EtOAc).

Azirine-2-carboxylates 3a, 5 3b, 12 3c13 are known compounds and have full characterization data.

Methyl 3-(4-nitrophenyl)-2H-azirine-2-carboxylate (3d)

Obtained from 5-methoxy-3-(4-nitrophenyl)isoxazole.14 Yellow solid (120 mg, yield 91%); mp 96–98 °C; $R_f = 0.39$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) δ 8.49–8.44 (m, 2H), 8.14–8.10 (m, 2H), 3.80 (s, 3H), 3.01 (s, 1H); $^{13}$C NMR (CDCl$_3$) δ 171.2, 158.5, 150.8, 131.3, 127.9, 124.5, 52.6, 30.3; HRMS–ESI [M + Na]$^+$ calcd for C$_{10}$H$_8$N$_2$NaO$_4$ 243.0376; found 243.0382.

N-Benzyl-N-methyl-3-phenyl-2H-azirine-2-carboxamide (3l)

Obtained from N-benzyl-N-methyl-3-phenylisoxazol-5-amine.5 Yellow oil (123 mg, yield 78%); $R_f = 0.39$ (hexane–EtOAc, 1:1); $^1$H NMR (CDCl$_3$) δ (rotameric mixture ~ 1:1) 7.93 (d, $J = 7.1$ Hz, 1H), 7.81 (d, $J = 7.1$ Hz, 1H), 7.67–7.50 (m, 3H), 7.48–7.41 (m, 1H), 7.41–7.28 (m, 5H), 5.00 and 4.88 (AB-q, $J = 16.8$ Hz, 1H), 4.78 and 4.56 (AB-q, $J = 14.6$ Hz, 1H), 3.29 (s, 1.5H), 3.16 (s, 0.5H), 3.09 (s, 0.5H), 3.08 (s, 1.5H); $^{13}$C NMR (CDCl$_3$) δ (rotameric mixture ~ 1:1) 170.8, 170.5, 159.3, 159.0, 137.0, 136.8, 133.43, 133.37, 130.29, 130.26, 129.14, 129.06, 129.0, 128.6, 128.2, 127.8, 127.4, 126.5, 123.1, 123.0, 53.3, 51.5, 34.9, 34.6, 29.1, 29.0; HRMS–ESI [M + H]$^+$ calcd for C$_{17}$H$_{17}$N$_2$O$^+$ 265.1335; found 265.1343.
Synthesis of 5H-pyrazino[2,3-b]indoles 4

**General Procedure A (for 4a−d,i−m)**
Azirine 3 (0.2 mmol), 3-diazoindolin-2-imine 2a (0.4−0.8 mmol), Rh₂(OAc)₄ (4.4 mg, 0.01 mmol), and toluene (1 mL) were placed into a screw cap glass tube and heated at 140 °C (oil bath temperature) under stirring for 1 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (eluent hexane−EtOAc, 3:1) to give the desired products.

**General Procedure B (for 4e−h,t−z,aa−af)**
Azirine 3 (0.2 mmol), 3-diazoindolin-2-imine 2 (0.4−0.6 mmol), Rh₂(OAc)₄ (4.4 mg, 0.01 mmol), and toluene (1 mL) were placed into a screw cap glass tube and heated at 140 °C (oil bath temperature) under stirring until nitrogen evolution had ceased (about 2−5 min). Then, for elimination of p-toluenesulfinic acid, to the reaction mixture was added p-toluenesulfonic acid (14 mg, 0.08 mmol). The resulting mixture was stirred at 140 °C for 1 h and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent hexane−EtOAc, 3:1) to give the desired products.

**General Procedure C (for 4a,n−s)**
5-Alkoxyisoxazole 1 (0.2 mmol), Rh₂(OAc)₄ (4.4 mg, 0.01 mmol), and toluene (1 mL) were placed into a screw cap glass tube and heated at 140 °C (oil bath temperature) under stirring for 3 h until full consumption of isoxazole was detected (control by TLC, eluent hexane−Et₂O, 3:1). Then 3-diazoindolin-2-imine 2a (0.6 mmol) was added to the reaction mixture. The resulting mixture was stirred at 140 °C for 1 h and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent hexane−EtOAc, 3:1) to give the desired products.
Characterization data for 5H-pyrazino[2,3-b]indoles 4

Methyl 5-methyl-2-phenyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4a)

Obtained from azirine 3a and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A (55 mg, yield 87%). Also obtained from isoxazole 1a and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure C (47 mg, yield 75%). White solid; mp 143–145 °C; Rf = 0.37 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.46 (d, J = 7.8 Hz, 1H), 7.76–7.69 (m, 3H), 7.58–7.40 (m, 5H), 4.04 (s, 3H), 3.84 (s, 3H); 13C NMR (CDCl3) δ 168.1, 145.8, 143.3, 143.0, 139.2, 138.9, 136.8, 130.1, 128.8, 128.39, 128.38, 122.4, 121.2, 119.2, 109.6, 52.7, 27.8; HRMS−ESI [M + Na]+ calcd for C19H15N3NaO2 340.1056; found 340.1070.

Methyl 2-(4-methoxyphenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4b)

Obtained from azirine 3b and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A as a white solid (58 mg, yield 84%); mp 151–153 °C; Rf = 0.20 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.44 (d, J = 7.8 Hz, 1H), 7.73–7.65 (m, 3H), 7.53 (d, J = 8.3 Hz, 1H), 7.44–7.38 (m, 1H), 7.08–7.03 (m, 2H), 4.02 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H); 13C NMR (CDCl3) δ 168.4, 160.0, 145.5, 143.3, 142.9, 138.9, 136.8, 131.4, 130.1 (2C), 122.4, 121.1, 119.3, 114.0, 109.6, 55.3, 52.8, 27.8; HRMS−ESI [M + H]+ calcd for C20H18N3O3 348.1343; found 348.1335.

Methyl 2-(4-bromophenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4c)

Obtained from azirine 3c and 3-diazoindolin-2-imine 2a (0.4 mmol) according to the general procedure A as a white solid (51 mg, yield 65%); mp 167–169 °C; Rf = 0.48 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.44 (d, J = 7.8 Hz, 1H), 7.76–7.70 (m, 1H), 7.68–7.57 (m, 4H), 7.55 (d, J = 8.3 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 4.03 (s, 3H), 3.87 (s, 3H); 13C NMR (CDCl3) δ 167.8, 144.7, 143.5, 143.2, 138.9, 138.0, 137.0, 131.6, 130.5, 130.4, 122.9, 122.5, 121.4, 119.1,
109.7, 52.9, 27.9; HRMS–ESI [M + Na]⁺ calcd for C₁₉H₁₄²⁵BrN₃NaO₂⁺ 418.0162; found 418.0169.

**Methyl 5-methyl-2-(4-nitrophenyl)-5H-pyrazino[2,3-b]indole-3-carboxylate (4d)**

![Chemical structure of 4d](image)

Obtained from azirine 3d and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A as a white solid (40 mg, yield 55%); mp 224–225 °C; Rₐ = 0.49 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 8.46 (d, J = 7.8 Hz, 1H), 8.41–8.35 (m, 2H), 7.92–7.85 (m, 2H), 7.81–7.75 (m, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.50–7.44 (m, 1H), 4.07 (s, 3H), 3.89 (s, 3H); ¹³C NMR (CDCl₃) δ 167.3, 147.7, 145.6, 143.7 (2C), 143.4, 138.9, 137.2, 130.8, 129.9, 123.5, 122.6, 121.7, 119.0, 109.9, 53.0, 28.0; HRMS–ESI [M + H]⁺ calcd for C₁₉H₁₅N₃O₂⁺ 363.1088; found 363.1090.

**5-Methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4e)**

![Chemical structure of 4e](image)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2a (0.4 mmol) according to the general procedure B (62 mg, yield 93%). Also obtained from azirine 3e and 3-diazoindolin-2-imine 2b (0.4 mmol) according to the general procedure B (40 mg, yield 60%). White solid; mp 202–203 °C; Rₐ = 0.47 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 8.47 (d, J = 7.8 Hz, 1H), 7.70–7.64 (m, 1H), 7.55–7.49 (m, 5H), 7.43–7.35 (m, 4H), 7.34–7.29 (m, 2H), 4.02 (s, 3H); ¹³C NMR (CDCl₃) δ 148.3, 145.5, 144.3, 142.4, 140.3, 140.0, 134.1, 130.27, 130.26, 128.8, 128.1, 128.0 (2C), 127.5, 121.9, 120.7, 119.8, 109.3, 27.6; HRMS–ESI [M + H]⁺ calcd for C₂₃H₁₈N₃⁺ 336.1495; found 336.1507.

**3-(4-Chlorophenyl)-5-methyl-2-phenyl-5H-pyrazino[2,3-b]indole (4f)**

![Chemical structure of 4f](image)

Obtained from azirine 3f and 3-diazoindolin-2-imine 2a (0.4 mmol) according to the general procedure B as a white solid (73 mg, yield 99%); mp 198–200 °C; Rₐ = 0.40 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 8.46 (d, J = 7.8 Hz, 1H), 7.71–7.64 (m, 1H), 7.60–7.51 (m, 5H), 7.43–7.35 (m, 4H), 7.34–7.29 (m, 2H), 4.02 (s, 3H); ¹³C NMR (CDCl₃) δ 146.9, 145.3, 144.3, 142.5, 140.1, 138.5, 134.4, 134.2, 131.6, 130.2, 129.0, 128.31, 128.28, 127.7, 122.0, 120.9, 119.7, 109.4, 27.6; HRMS–ESI [M + H]⁺ calcd for C₂₃H₁₇³⁵ClN₃⁺ 370.1106; found 370.1119.
2-(4-Chlorophenyl)-5-methyl-3-phenyl-5H-pyrazino[2,3-b]indole (4g)

Obtained from azirine 3g and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure B as a white solid (51 mg, yield 69%); mp 220–222 °C; $R_f = 0.65$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.44 (d, $J = 7.8$ Hz, 1H), 7.70–7.64 (m, 1H), 7.57–7.51 (m, 3H), 7.50–7.45 (m, 2H), 7.43–7.35 (m, 4H), 7.34–7.29 (m, 2H), 4.02 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 148.3, 144.4, 144.1, 142.4, 139.8, 138.8, 134.2, 133.6, 131.6, 130.2, 129.0, 128.33, 128.25 (2C), 121.9, 120.9, 119.7, 109.4, 27.6; HRMS–ESI [M + H]$^+$ calcd for C$_{23}$H$_{17}$ClN$_3$ $^+$ 370.1106; found 370.1119.

3,5-Dimethyl-2-phenyl-5H-pyrazino[2,3-b]indole (4h)

Obtained from azirine 3h and 3-diazoindolin-2-imine 2a (0.4 mmol) according to the general procedure B as a white solid (40 mg, yield 73%); mp 150–151 °C; $R_f = 0.41$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.40 (d, $J = 7.8$ Hz, 1H), 7.69–7.66 (m, 2H), 7.65–7.60 (m, 1H), 7.56–7.48 (m, 3H), 7.48–7.43 (m, 1H), 7.40–7.34 (m, 1H), 3.99 (s, 3H), 2.77 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 147.1, 146.2, 144.4, 141.6, 140.3, 133.3, 129.5, 128.30, 128.29, 128.27, 127.8, 121.5, 120.6, 119.9, 109.2, 27.4, 23.8; HRMS–ESI [M + H]$^+$ calcd for C$_{18}$H$_{16}$N$_3$ $^+$ 274.1339; found 274.1352.

5-Methyl-2-(4-methylphenyl)-5H-pyrazino[2,3-b]indole (4i)

Azirine 3i (0.2 mmol), 3-diazoindolin-2-imine 2a (0.24 mmol), Rh$_2$(OAc)$_4$ (4.4 mg, 0.01 mmol), and 1,2-dichloroethane (1 mL) were placed into a screw cap glass tube and heated at 115 °C (oil bath temperature) under stirring for 1 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (eluent hexane–EtOAc, 3:1) to give 4i as a white solid (20 mg, yield 37%): mp 140–142 °C; $R_f = 0.40$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.85 (s, 1H), 8.46 (d, $J = 7.8$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 2H), 7.68–7.63 (m, 1H), 7.50 (d, $J = 8.2$ Hz, 1H), 7.43–7.34 (m, 3H), 3.98 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 145.4, 144.5, 141.9, 138.3, 137.2, 135.4, 135.3, 129.6, 128.9, 126.7, 121.9, 120.7, 119.9, 109.3, 27.5, 21.2; HRMS–ESI [M + H]$^+$ calcd for C$_{18}$H$_{16}$N$_3$ $^+$ 274.1339; found 274.1346.
2-(4-Methoxyphenyl)-5-methyl-5H-pyrazino[2,3-b]indole (4j)

Obtained from azirine 3j and 3-diazoindolin-2-imine 2a as described above for the synthesis of 4i. White solid (30 mg, yield 52%); mp 112–114 °C; $R_f = 0.30$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.83 (s, 1H), 8.46 (d, $J = 7.8$ Hz, 1H), 8.12–8.06 (m, 2H), 7.69–7.63 (m, 1H), 7.52 (d, $J = 8.2$ Hz, 1H), 7.43–7.37 (m, 1H), 7.12–7.06 (m, 2H), 4.00 (s, 3H), 3.92 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 160.0, 145.2, 144.3, 141.9, 136.8, 135.3, 130.8, 128.8, 128.0, 121.8, 120.6, 119.8, 114.3, 109.3, 55.4, 27.5; HRMS–ESI $[M + H]^+$ calcd for C$_{18}$H$_{16}$N$_3$O $290.1288$; found 290.1299.

tert-Butyl 5-methyl-2-phenyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4k)

Obtained from azirine 3k and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A as a white solid (50 mg, yield 70%); mp 165–166 °C; $R_f = 0.37$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.44 (d, $J = 7.8$ Hz, 1H), 7.73–7.67 (m, 3H), 7.56–7.45 (m, 4H), 7.43–7.37 (m, 1H), 4.04 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 166.6, 145.7, 143.3, 143.1, 140.9, 139.6, 136.2, 129.8, 129.2, 128.3, 128.2, 122.4, 121.0, 119.3, 109.5, 82.8, 27.8, 27.6; HRMS–ESI $[M + H]^+$ calcd for C$_{22}$H$_{22}$N$_3$O$_2$ $360.1707$; found 360.1723.

N-Benzyl-N,5-dimethyl-2-phenyl-5H-pyrazino[2,3-b]indole-3-carboxamide (4l)

Obtained from azirine 3l and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A as a yellow oil (64 mg, yield 79%); $R_f = 0.51$ (hexane–EtOAc, 1:1); $^1$H NMR (CDCl$_3$) $\delta$ (rotameric mixture ~ 1:1.5) 8.48–8.41 (m, 1H), 7.94 (d, $J = 6.8$ Hz, 0.8H), 7.89–7.82 (m, 1.2H), 7.74–7.65 (m, 1H), 7.58–7.46 (m, 4H), 7.45–7.38 (m, 1H), 7.33–7.25 (m, 2H), 7.25–7.21 (m, 1H), 7.13–7.09 (m, 1.2H), 7.07–7.03 (m, 0.8H), 4.73 (s, 1.2H), 4.08 (s, 0.8H), 4.03 (s, 1.8H), 3.97 (s, 1.2H), 2.95 (s, 1.2H), 2.52 (s, 1.8H); $^{13}$C NMR (CDCl$_3$) $\delta$ (rotameric mixture ~ 1:1.3) 169.4, 169.0, 143.6, 143.5, 143.3, 143.09, 143.07, 142.70, 142.69, 137.97, 137.95, 136.06, 136.05, 135.9, 135.6, 129.63, 129.62, 129.2, 128.65, 128.63, 128.61, 128.52, 128.50, 128.46, 128.3, 127.6, 127.43, 127.38, 122.1, 121.10, 121.09, 119.5, 109.6, 109.5, 54.1, 50.3, 35.1, 32.2, 27.8, 27.7; HRMS–ESI $[M + H]^+$ calcd for C$_{26}$H$_{25}$N$_4$O$^+$ 407.1866; found 407.1867.
[3-(4-Bromophenyl)-1H-pyrazol-1-yl)(5-methyl-2-phenyl-5H-pyrazino[2,3-b]indol-3-yl)methanone (4m)

Obtained from azirine 3m and 3-diazoindolin-2-imine 2a (0.8 mmol) according to the general procedure A (reaction time: 5 min) as a white solid (82 mg, yield 81%); mp 171–172 °C; Rf = 0.47 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.53 (d, J = 7.8 Hz, 1H), 8.33 (d, J = 2.9 Hz, 1H), 7.78–7.70 (m, 3H), 7.58 (d, J = 8.3 Hz, 1H), 7.50–7.45 (m, 5H), 7.28–7.24 (m, 1H), 6.65 (d, J = 2.9 Hz, 1H), 4.03 (s, 3H); 13C NMR (CDCl3) δ 166.4, 155.0, 145.8, 143.3, 143.2, 140.5, 138.3, 136.9, 131.7, 130.5, 130.3, 128.7, 128.42, 128.40, 127.9, 123.4, 122.5, 121.3, 119.4, 109.7, 107.8, 27.9; HRMS–ESI [M + H]+ calcd for C27H19BrN5O+ 508.0767; found 508.0791.

Methyl 2-(2,4-dimethylphenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4n)

Obtained from isoxazole 1b and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (65 mg, yield 94%); mp 181–182 °C; Rf = 0.29 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.44 (d, J = 7.8 Hz, 1H), 7.76–7.68 (m, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.22–7.08 (m, 3H), 4.06 (s, 3H), 3.80 (s, 3H), 2.42 (s, 3H), 2.21 (s, 3H); 13C NMR (CDCl3) δ 167.0, 147.3, 143.5, 143.1, 138.8, 138.0, 136.9, 136.1, 135.9, 131.0, 130.3, 129.1, 126.3, 122.6, 121.2, 119.1, 109.6, 52.6, 27.8, 21.3, 19.8; HRMS–ESI [M + H]+ calcd for C21H20N3O2+ 346.1550; found 346.1563.

Methyl 2-(2,5-dimethylphenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4o)

Obtained from isoxazole 1c and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (53 mg, yield 77%); mp 124–126 °C; Rf = 0.29 (hexane–EtOAc, 3:1); 1H NMR (CDCl3) δ 8.46 (d, J = 7.8 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.25–7.17 (m, 2H), 7.13 (s, 1H), 4.07 (s, 3H), 3.79 (s, 3H), 2.39 (s, 3H), 2.17 (s, 3H); 13C NMR (CDCl3) δ 166.9, 147.4, 143.5, 143.2, 138.7, 138.6, 136.9, 134.9, 133.2, 130.3, 130.0, 129.8, 129.2, 122.6, 121.2, 119.1, 109.6, 52.6, 27.8, 20.9, 19.3; HRMS–ESI [M + H]+ calcd for C21H20N3O2+ 346.1550; found 346.1558.
Methyl 2-(4-chlorophenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4p)

Obtained from isoxazole 1d and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (52 mg, yield 74%); mp 153−155 °C; R_f = 0.45 (hexane−EtOAc, 3:1); ^1H NMR (CDCl_3) δ 8.45 (d, J = 7.8 Hz, 1H), 7.78−7.71 (m, 1H), 7.68−7.63 (m, 2H), 7.57 (d, J = 8.3 Hz, 1H), 7.52−7.47 (m, 2H), 7.44 (t, J = 7.5 Hz, 1H), 4.05 (s, 3H), 3.87 (s, 3H); ^13C NMR (CDCl_3) δ 167.9, 144.7, 143.5, 143.1, 138.9, 137.5, 136.9, 134.7, 130.4, 130.2, 128.6, 122.5, 121.4, 119.1, 109.7, 52.9, 27.9; HRMS−ESI [M + H]^+ calcd for C_{19}H_{15}ClN_3O_2^+ 352.0847; found 352.0860.

Methyl 2-(4-cyanophenyl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4q)

Obtained from isoxazole 1e and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (36 mg, yield 53%); mp 205−206 °C; R_f = 0.30 (hexane−EtOAc, 3:1); ^1H NMR (CDCl_3) δ 8.43 (d, J = 7.8 Hz, 1H), 7.84−7.78 (m, 4H), 7.75 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 4.04 (s, 3H), 3.88 (s, 3H); ^13C NMR (CDCl_3) δ 167.9, 144.7, 143.5, 143.1, 138.9, 137.5, 136.9, 134.7, 130.4, 130.2, 128.6, 122.5, 121.4, 119.1, 109.7, 52.9, 27.9; HRMS−ESI [M + H]^+ calcd for C_{20}H_{15}N_4O_2^+ 343.1190; found 343.1193.

Methyl 2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4r)

Obtained from isoxazole 1f and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (62 mg, yield 83%); mp 180−182 °C; R_f = 0.30 (hexane−EtOAc, 3:1); ^1H NMR (CDCl_3) δ 8.43 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.3, 2.0 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 4.34 (s, 4H), 4.01 (s, 3H), 3.90 (s, 3H); ^13C NMR (CDCl_3) δ 168.2, 145.1, 144.1, 143.6, 143.3, 142.9, 139.0, 136.7, 132.2, 130.1, 122.4, 122.0, 121.2, 119.2, 117.9, 117.2, 109.6, 64.5, 64.3, 52.8, 27.8; HRMS−ESI [M + H]^+ calcd for C_{21}H_{18}N_3O_4^+ 376.1292 found 376.1298.
Hexyl 5-methyl-2-phenyl-5H-pyrazino[2,3-b]indole-3-carboxylate (4s)

Obtained from isoxazole 1g and 3-diazoindolin-2-imine 2a according to the general procedure C as a white solid (61 mg, yield 79%); $R_f = 0.57$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.45 (d, $J = 7.9$ Hz, 1H), 7.75–7.68 (m, 3H), 7.56–7.39 (m, 5H), 4.22 (t, $J = 6.6$ Hz, 2H), 4.03 (s, 3H), 1.51–1.42 (m, 2H), 1.34–1.07 (m, 6H), 0.89 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 168.0, 145.7, 143.25, 143.15, 139.8, 139.1, 136.6, 130.0, 128.9, 128.40, 128.35, 122.4, 121.2, 119.3, 109.6, 66.2, 31.3, 28.1, 27.8, 25.3, 22.4, 13.9; HRMS–ESI [M + H]$^+$ calcd for C$_{24}$H$_{26}$N$_3$O$_2$+ 388.2020; found 388.2027.

5-Benzyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4t)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2c (0.4 mmol) according to the general procedure B as a white solid (59 mg, yield 72%); mp 205–206 °C; $R_f = 0.49$ (hexane–EtOAc, 3:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.48 (d, $J = 7.8$ Hz, 1H), 7.60–7.54 (m, 5H), 7.45 (d, $J = 8.2$ Hz, 1H), 7.41–7.27 (m, 12H), 5.77 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 148.4, 145.9, 144.3, 141.6, 140.4, 139.9, 136.8, 134.0, 130.34, 130.25, 128.8, 128.7, 128.2, 128.05, 127.98, 127.61, 127.60, 127.3, 122.0, 120.9, 120.1, 110.3, 45.1; HRMS–ESI [M + H]$^+$ calcd for C$_{29}$H$_{22}$N$_3$+ 412.1808; found 412.1825.

5-Isopropyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4u)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2d (0.4 mmol) according to the general procedure B as a white solid (52 mg, yield 72%); mp 141–143 °C; $R_f = 0.63$ (hexane–EtOAc, 9:1); $^1$H NMR (CDCl$_3$) $\delta$ 8.48 (d, $J = 7.8$ Hz, 1H), 7.69–7.61 (m, 2H), 7.58–7.50 (m, 4H), 7.40–7.30 (m, 7H), 5.43 (sept, $J = 7.0$ Hz, 1H), 1.82 (d, $J = 7.0$ Hz, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 147.9, 145.2, 143.9, 140.9, 140.5, 140.2, 134.0, 130.35, 130.25, 128.5, 128.1, 128.0, 127.9, 127.5, 122.1, 120.25, 120.21, 110.8, 46.0, 20.9; HRMS–ESI [M + H]$^+$ calcd for C$_{25}$H$_{22}$N$_3$+ 364.1808; found 364.1817.
5-Allyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4v)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2e (0.4 mmol) according to the general procedure B as a white solid (71 mg, yield 98%); mp 164–165 °C; $R_f = 0.57$ (hexane–EtOAc, 9:1); $^1$H NMR (CDCl$_3$) δ 8.46 (d, $J = 7.8$ Hz, 1H), 7.63 (t, $J = 7.7$ Hz, 1H), 7.57–7.50 (m, 5H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.37–7.31 (m, 6H), 6.15–6.04 (m, 1H), 5.30–5.16 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 148.3, 145.8, 143.9, 141.7, 140.3, 140.0, 134.0, 132.4, 130.3, 130.2, 128.7, 128.1, 128.02, 127.99, 127.6, 122.0, 120.8, 119.9, 117.4, 110.2, 43.7; HRMS–ESI [M + H]$^+$ calcd for C$_{25}$H$_{20}$N$_3$ 362.1652; found 362.1660.

2,3-Diphenyl-5H-pyrazino[2,3-b]indole (4w)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2f (0.4 mmol) according to the general procedure B as a white solid (29 mg, yield 45%); mp 279–281 °C; $R_f = 0.49$ (hexane–EtOAc, 3:1); $^1$H NMR (DMSO-d$_6$) δ 12.21 (s, 1H), 8.25 (d, $J = 7.8$ Hz, 1H), 7.65–7.58 (m, 2H), 7.46–7.39 (m, 4H), 7.37–7.28 (m, 7H); $^{13}$C NMR (DMSO-d$_6$) δ 147.9, 144.8, 144.1, 141.1, 140.1, 139.7, 133.3, 130.0, 129.9, 129.0, 127.94, 127.93, 127.91, 127.4, 121.1, 120.6, 119.3, 112.2; HRMS–ESI [M + H]$^+$ calcd for C$_{22}$H$_{16}$N$_3$ 322.1339; found 322.1351.

6-Bromo-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4x)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2g (0.4 mmol) according to the general procedure B as a white solid (72 mg, yield 87%); mp 239–241 °C; $R_f = 0.64$ (hexane–EtOAc, 9:1); $^1$H NMR (CDCl$_3$) δ 8.40 (d, $J = 7.7$ Hz, 1H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.59–7.51 (m, 4H), 7.39–7.32 (m, 6H), 7.20 (t, $J = 7.8$ Hz, 1H), 4.43 (s, 3H); $^{13}$C NMR (CDCl$_3$) δ 149.3, 146.5, 144.8, 140.0, 139.7, 138.9, 133.8, 133.2, 130.3, 130.2, 128.25, 128.16, 128.1, 127.7, 123.0, 121.7, 120.9, 103.9, 30.7; HRMS–ESI [M + H]$^+$ calcd for C$_{23}$H$_{17}$BrN$_3$ 414.0600; found 414.0619.
5-Methyl-6-nitro-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4y)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2h (0.4 mmol) according to the general procedure B as a white solid (50 mg, yield 66%); mp 244–245 °C; \( R_f = 0.49 \) (hexane–EtOAc, 3:1); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 8.71 (dd, \( J = 7.7, 2.0 \) Hz, 1H), 8.17 (dd, \( J = 8.0, 2.0 \) Hz, 1H), 7.59–7.51 (m, 4H), 7.44 (t, \( J = 7.9 \) Hz, 1H), 7.40–7.33 (m, 6H), 4.11 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 150.4, 147.8, 145.6, 139.6, 139.3, 136.5, 133.7, 132.5, 130.2, 130.1, 128.6, 128.2, 128.1, 126.8, 125.3, 124.3, 119.9, 31.4; HRMS–ESI \([M + H]^+\) calcd for C\(_{23}\)H\(_{17}\)N\(_4\)O\(_2\)\(^+\) 381.1346; found 381.1352.

7-Chloro-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4z)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2i (0.4 mmol) according to the general procedure B as a white solid (50 mg, yield 68%); mp 232–234 °C; \( R_f = 0.57 \) (hexane–EtOAc, 9:1); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 8.35 (d, \( J = 8.3 \) Hz, 1H), 7.58–7.49 (m, 5H), 7.38–7.31 (m, 6H), 4.00 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 148.7, 146.1, 144.6, 142.8, 140.1, 139.8, 134.7, 133.5, 130.23, 130.18, 128.19, 128.16, 128.1, 127.7, 122.8, 121.4, 118.3, 109.7, 27.7; HRMS–ESI \([M + H]^+\) calcd for C\(_{23}\)H\(_{17}\)\(^{35}\)ClN\(_3\)\(^+\) 370.1106; found 370.1105.

7-Bromo-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4aa)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2j (0.4 mmol) according to the general procedure B as a white solid (53 mg, yield 64%); mp 250–252 °C; \( R_f = 0.59 \) (hexane–EtOAc, 9:1); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 8.29 (d, \( J = 8.3 \) Hz, 1H), 7.69 (s, 1H), 7.58–7.48 (m, 5H), 7.38–7.31 (m, 6H), 4.00 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 148.8, 146.2, 144.4, 142.9, 140.1, 139.8, 133.5, 130.23, 130.19, 128.21, 128.17, 128.1, 127.7, 124.1, 123.0, 122.7, 118.7, 112.7, 27.7; HRMS–ESI \([M + H]^+\) calcd for C\(_{23}\)H\(_{17}\)\(^{79}\)BrN\(_3\)\(^+\) 414.0600; found 414.0594.
5,8-Dimethyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4ab)

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Me
N=N
N
Ph
N
Ph
Me
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Obtained from azirine 3e and 3-diazoindolin-2-imine 2k (0.4 mmol) according to the general procedure B as a white solid (67 mg, yield 96%); mp 231–232 °C; Rf = 0.52 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 8.27 (s, 1H), 7.59–7.51 (m, 4H), 7.48 (dd, J = 8.4, 1.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.38–7.31 (m, 6H), 4.01 (s, 3H), 2.59 (s, 3H); ¹³C NMR (CDCl₃) δ 148.1, 145.2, 144.5, 140.7, 140.4, 140.1, 134.0, 130.3, 130.24, 130.23, 130.17, 128.1, 128.02, 127.97, 127.4, 121.7, 119.8, 109.0, 27.6, 21.3; HRMS–ESI [M + H⁺] calcd for C₂₄H₂₀N₃⁺ 350.1652; found 315.1660.

8-Methoxy-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4ac)

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MeO
N=N
N
Ph
N
Ph
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Obtained from azirine 3e and 3-diazoindolin-2-imine 2l (0.4 mmol) according to the general procedure B as a white solid (62 mg, yield 85%); mp 199–200 °C; Rf = 0.43 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 7.94 (d, J = 2.4 Hz, 1H), 7.59–7.50 (m, 4H), 7.44 (d, J = 7.9 Hz, 1H), 7.38–7.28 (m, 7H), 4.01 (s, 3H), 3.97 (s, 3H); ¹³C NMR (CDCl₃) δ 154.8, 148.3, 145.1, 144.6, 140.4, 140.0, 137.2, 133.9, 130.3, 130.2, 128.1, 128.02, 128.01, 127.5, 119.9, 118.9, 110.3, 103.5, 56.0, 27.6; HRMS–ESI [M + H⁺] calcd for C₂₄H₂₀N₃O⁺ 366.1601; found 366.1613.

8-Bromo-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4ad)

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Br
N=N
N
Ph
N
Ph
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Obtained from azirine 3e and 3-diazoindolin-2-imine 2m (0.4 mmol) according to the general procedure B as a white solid (82 mg, yield 99%); mp 228–229 °C; Rf = 0.63 (hexane–EtOAc, 3:1); ¹H NMR (CDCl₃) δ 8.58 (d, J = 1.9 Hz, 1H), 7.73 (dd, J = 8.7, 1.9 Hz, 1H), 7.58–7.49 (m, 4H), 7.40 (d, J = 8.7 Hz, 1H), 7.37–7.34 (m, 6H), 4.01 (s, 3H); ¹³C NMR (CDCl₃) δ 149.2, 146.1, 144.4, 140.8, 140.0, 139.7, 132.8, 131.4, 130.24, 130.16, 128.3, 128.2, 128.1, 127.7, 124.6, 121.3, 113.7, 110.9, 27.7; HRMS–ESI [M + H⁺] calcd for C₂₅H₁₇⁷⁹BrN₃⁺ 414.0600; found 414.0614.
9-Bromo-5-methyl-2,3-diphenyl-5H-pyrazino[2,3-b]indole (4ae)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2n (0.6 mmol) according to the general procedure B as a white solid (69 mg, yield 84%); mp 235–236 °C; \( R_f = 0.59 \) (hexane–EtOAc, 3:1); \( ^1H \) NMR (CDCl\(_3\)) \( \delta 7.66–7.54 \) (m, 5H), 7.52–7.46 (m, 2H), 7.41–7.30 (m, 6H), 4.04 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\)) \( \delta 148.7, 145.6, 144.0, 143.2, 140.05, 130.4, 130.2, 128.9, 128.3, 128.2, 128.0, 127.6, 124.9, 118.7, 117.1, 108.2, 27.7; HRMS–ESI [M + H]+ calcd for C\(_{23}\)H\(_{17}\)BrN\(_3\)+ 414.0600; found 414.0617.

5-Methyl-2,3-diphenyl-5H-pyrido[3',2':4,5]pyrrolo[2,3-b]pyrazine (4af)

Obtained from azirine 3e and 3-diazoindolin-2-imine 2o (0.5 mmol) according to the general procedure B as a white solid (59 mg, yield 88%); mp 203–204 °C; \( R_f = 0.20 \) (hexane–EtOAc, 3:1); \( ^1H \) NMR (CDCl\(_3\)) \( \delta 8.72–8.66 \) (m, 2H), 7.60–7.48 (m, 4H), 7.39–7.31 (m, 7H), \( \delta 4.13 \) (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\)) \( \delta 152.9, 149.5, 148.8, 146.7, 144.2, 140.0, 139.6, 132.0, 130.3, 130.12, 130.07, 128.3, 128.2, 128.1, 127.8, 116.8, 113.5, 26.5; HRMS–ESI [M + H]+ calcd for C\(_{22}\)H\(_{17}\)N\(_3\)+ 337.1448; found 337.1463.

Methyl 5-methyl-4-(4-phenylsulfonyl)-2-phenyl-4,5-dihydro-3H-pyrazino[2,3-b]indole-3-carboxylate (5a)

Obtained from azirine 3a and 3-diazoindolin-2-imine 2a (0.6 mmol) according to the general procedure A (temperature: 110 °C, reaction time: 2 min) as a white solid (53 mg, yield 56%); mp 100–103 °C; \( R_f = 0.47 \) (hexane–EtOAc, 3:1); \( ^1H \) NMR (CDCl\(_3\)) \( \delta 7.82 \) (d, \( J = 7.8 \) Hz, 1H), 7.74–7.69 (m, 2H), 7.45 (d, \( J = 8.2 \) Hz, 1H), 7.43–7.34 (m, 4H), 7.28–7.23 (m, 1H), \( \delta 7.11 \) (d, \( J = 8.2 \) Hz, 2H), 6.77 (d, \( J = 8.2 \) Hz, 2H), 6.03 (s, 1H), 4.04 (s, 3H), 3.60 (s, 3H), 2.22 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\)) \( \delta 166.8, 147.5, 145.0, 136.6, 135.7, 132.8, 129.7, 129.2, 128.1, 127.0, 126.8, 124.6, 123.0, 122.1, 120.9, 120.0, 118.4, 110.1, 58.1, 53.2, 31.2, 21.5; HRMS–ESI [M + H]+ calcd for C\(_{26}\)H\(_{24}\)N\(_3\)O\(_4\)S\(_2\)+ 474.1482; found 474.1499.
References

$^1$H and $^{13}$C NMR spectra of 3-diazooindolin-2-imines 2h–j, n, o

$^1$H and $^{13}$C NMR spectra of compound 2h
$^1$H and $^{13}$C NMR spectra of compound 2i
$^1$H and $^{13}$C NMR spectra of compound 2j
$^1$H and $^{13}$C NMR spectra of compound 2n
$^1$H and $^{13}$C NMR spectra of azirines 3d, l

$^1$H and $^{13}$C NMR spectra of compound 3d

![NMR Spectra of Compound 3d](image-url)
$^1$H and $^{13}$C NMR spectra of compound 3l (rotameric mixture ~ 1:1)
$^1$H and $^{13}$C NMR spectra of 5H-pyrazino[2,3-b]indoles 4

$^1$H and $^{13}$C NMR spectra of compound 4a
$^1$H and $^{13}$C NMR spectra of compound 4b
$^1$H and $^{13}$C NMR spectra of compound 4c
$^1$H and $^{13}$C NMR spectra of compound 4d
$^1$H and $^{13}$C NMR spectra of compound 4e
$^{1}H$ and $^{13}C$ NMR spectra of compound 4f
$^1$H and $^{13}$C NMR spectra of compound 4g
\(^1\)H and \(^{13}\)C NMR spectra of compound 4h
$^1$H and $^{13}$C NMR spectra of compound 4i
$^1$H and $^{13}$C NMR spectra of compound 4j
$^1$H and $^{13}$C NMR spectra of compound 4k
$^1$H and $^{13}$C NMR spectra of compound 4l (rotameric mixture $\sim 1$:1.5)
$^1$H and $^{13}$C NMR spectra of compound 4m
$^1$H and $^{13}$C NMR spectra of compound 4n
$^1$H and $^{13}$C NMR spectra of compound 40
$^1$H and $^{13}$C NMR spectra of compound 4p
$^1$H and $^{13}$C NMR spectra of compound 4q
$^1$H and $^{13}$C NMR spectra of compound 4r
$^1$H and $^{13}$C NMR spectra of compound 4s
$^1$H and $^{13}$C NMR spectra of compound 4t
$^1$H and $^{13}$C NMR spectra of compound 4u
$^1$H and $^{13}$C NMR spectra of compound 4v
$^1$H and $^{13}$C NMR spectra of compound 4w
$^1$H and $^{13}$C NMR spectra of compound 4x
$^1$H and $^{13}$C NMR spectra of compound 4y
$^1$H and $^{13}$C NMR spectra of compound 4z
$^1$H and $^{13}$C NMR spectra of compound \textbf{4aa}
$^1$H and $^{13}$C NMR spectra of compound 4ab
$^1$H and $^{13}$C NMR spectra of compound 4ac
$^1$H and $^{13}$C NMR spectra of compound 4ad
$^1$H and $^{13}$C NMR spectra of compound 4ae
$^1$H and $^{13}$C NMR spectra of compound 4af
$^1$H and $^{13}$C NMR spectra of compound 5a
X-Ray crystal structure of compound 4j