Supporting Information

Halogenations of 3-aryl-1H-pyrazol-5-amines

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1. General materials and instruments

Unless otherwise noted, all synthetic steps were performed under the air atmosphere using sealed tube. The materials obtained from commercial sources were used without further purification. $^1$H NMR, $^{13}$C NMR spectra were recorded on a Brucker Advance III HD 400 MHz spectrometer in CDCl$_3$ solution. All chemical shifts were reported in ppm ($\delta$) relative to the internal standard TMS (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (APCI) mode using a TOF mass analyzer.

2. Characterization data of the products

4-bromo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (3a)

Yield: 99%; Yellow solid; M.p. = 95.5-96.3 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J=8.4$ Hz, 2H), 7.82 (dd, $J=6.7$, 3.0 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.33 (d, $J=8.0$ Hz, 2H), 5.13 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.6, 146.8, 145.9, 134.1, 130.9, 130.8, 130.0, 129.3, 128.3, 128.0, 127.97, 76.2, 21.8; HRMS(APCI): m/z calcd for C$_{16}$H$_{15}$N$_3$O$_2$SBr [M+H]$^+$ 392.0068, found 392.0070.

4-bromo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (3b)

Yield: 95%; Yellow solid; M.p. = 133.3-134.7 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J=8.4$ Hz, 2H), 7.72 (d, $J=8.2$ Hz, 2H), 7.30 (d, $J=7.9$ Hz, 2H), 7.20 (d, $J=7.7$ Hz, 2H), 5.14 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.8, 146.9, 146.0, 139.5, 134.2, 130.1, 129.0, 128.0, 127.97, 76.3, 21.8, 21.5; HRMS(APCI): m/z calcd for C$_{17}$H$_{17}$N$_3$O$_2$SBr [M+H]$^+$ 406.0225, found 406.0230.

4-bromo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (3c)

Yield: 90%; Yellow solid; M.p. = 117.1-123.2 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (d, $J=8.4$ Hz, 2H), 7.62 (d, $J=9.1$ Hz, 2H), 7.31 (d, $J=8.2$ Hz, 2H), 7.27 (d, $J=7.4$ Hz, 1H), 7.23 – 7.17 (m, 1H), 5.14 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.9, 146.9, 146.0, 138.1, 134.2, 130.8, 130.2, 130.1, 128.7, 128.2, 128.1, 125.2, 76.4,
4-bromo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (3d)

Yield: 93%; Yellow solid; M.p. = 95.3-97.6 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 8.4\) Hz, 2H), 7.25 (d, \(J = 8.1\) Hz, 2H), 7.19 (d, \(J = 8.2\) Hz, 1H), 7.13 (q, \(J = 6.7, 5.4\) Hz, 3H), 5.06 (s, 2H), 2.35 (s, 3H), 2.05 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 155.1, 146.5, 146.0, 137.3, 134.2, 130.4, 130.3, 130.1, 129.3, 128.1, 125.5, 76.8, 21.9, 20.0; HRMS(APCI): m/z calcd for C\(_{17}\)H\(_{17}\)N\(_3\)O\(_2\)SBr [M+H]\(^+\) 406.0225, found 406.0224.

4-bromo-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (3e)

Yield: 100%; Yellow solid; M.p. = 143.1-147.6 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.4\) Hz, 2H), 7.77 (d, \(J = 8.6\) Hz, 2H), 7.36 (d, \(J = 8.6\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 5.15 (s, 2H), 2.42 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.5, 147.0, 146.2, 135.5, 134.1, 130.2, 129.43, 129.35, 128.7, 128.1, 76.0, 21.9; HRMS(APCI): m/z calcd for C\(_{16}\)H\(_{14}\)N\(_3\)O\(_2\)SBr [M+H]\(^+\) 425.9679, found 425.9678.

4-bromo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (3f)

Yield: 92%; Yellow solid; M.p. = 154.5-159.3 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.4\) Hz, 2H), 7.78 (d, \(J = 8.8\) Hz, 2H), 7.31 (d, \(J = 8.1\) Hz, 2H), 6.91 (d, \(J = 8.9\) Hz, 2H), 5.13 (s, 2H), 3.82 (s, 3H), 2.40 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.6, 152.5, 146.9, 146.0, 134.2, 130.1, 129.4, 128.1, 123.5, 113.8, 76.2, 55.4, 21.8; HRMS(APCI): m/z calcd for C\(_{17}\)H\(_{17}\)N\(_3\)O\(_3\)SBr [M+H]\(^+\) 422.0169, found 422.0165.

4-bromo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (3g)

Yield: 93%; Yellow solid; M.p. = 123.8-124.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (dd, \(J = 8.5, 1.3\) Hz, 2H), 7.86 – 7.78 (m, 2H), 7.63 (t, \(J = 7.5\) Hz, 1H), 7.53 (t, \(J = 7.7\) Hz, 2H), 7.43 – 7.36 (m, 3H), 5.18 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.9, 147.1, 137.1, 134.7, 130.8, 129.5, 128.4, 128.03, 127.98, 76.3; HRMS(APCI): m/z calcd for C\(_{19}\)H\(_{13}\)N\(_3\)O\(_2\)SBr [M+H]\(^+\) 377.9912, found 377.9915.
4-bromo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (3h)

Yield: 92%; Yellow solid; M.p. = 113.2-116.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 7.2\) Hz, 2H), 7.73 (d, \(J = 8.2\) Hz, 2H), 7.62 (d, \(J = 7.5\) Hz, 1H), 7.52 (t, \(J = 7.7\) Hz, 2H), 7.20 (d, \(J = 7.6\) Hz, 2H), 5.16 (s, 2H), 2.37 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 153.0, 147.0, 139.5, 137.1, 134.6, 129.4, 129.1, 128.0, 127.95, 127.92, 76.4, 21.5; HRMS(APCI): \(m/\zeta\) calcd for C\(_{16}\)H\(_{15}\)N\(_3\)O\(_2\)SBr [M+H\(^+\)] 392.0068, found 392.0067.

4-bromo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (3i)

Yield: 95%; Yellow solid; M.p. = 90.9-92.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.7\) Hz, 2H), 7.66 – 7.59 (m, 3H), 7.54 (t, \(J = 7.8\) Hz, 2H), 7.28 (t, \(J = 7.6\) Hz, 1H), 7.20 (d, \(J = 7.6\) Hz, 1H), 5.15 (s, 2H), 2.38 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 147.0, 138.1, 137.2, 134.7, 130.7, 130.3, 129.5, 128.7, 128.2, 128.0, 125.2, 76.6, 21.5; HRMS(APCI): \(m/\zeta\) calcd for C\(_{16}\)H\(_{15}\)N\(_3\)O\(_2\)SBr [M+H\(^+\)] 392.0068, found 392.0068.

4-bromo-1-(phenylsulfonyl)-3-(4-chlorophenyl)-1H-pyrazol-5-amine (3j)

Yield: 98%; Yellow solid; M.p. = 169.3-170.1 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (dd, \(J = 8.5, 1.2\) Hz, 2H), 7.77 (d, \(J = 8.7\) Hz, 2H), 7.66 (t, \(J = 7.5\) Hz, 1H), 7.55 (t, \(J = 7.8\) Hz, 2H), 7.36 (d, \(J = 8.7\) Hz, 2H), 5.17 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.8, 147.1, 137.1, 135.6, 134.9, 129.6, 129.3, 128.7, 128.1, 76.1; HRMS(APCI): \(m/\zeta\) calcd for C\(_{15}\)H\(_{12}\)N\(_3\)O\(_2\)SClBr [M+H\(^+\)] 411.9522, found 411.9525.

4-bromo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (3k)

Yield: 78%; Yellow solid; M.p. = 112.5-113.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (dd, \(J = 8.5, 1.2\) Hz, 2H), 7.77 (d, \(J = 8.7\) Hz, 2H), 7.66 (t, \(J = 7.5\) Hz, 1H), 7.55 (t, \(J = 7.8\) Hz, 2H), 7.36 (d, \(J = 8.7\) Hz, 2H), 5.17 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 153.0, 147.0, 135.7, 133.9, 132.0, 130.8, 130.1, 129.93, 129.92, 129.8, 129.5, 128.3, 128.1, 128.0, 122.4, 76.4; HRMS(APCI): \(m/\zeta\) calcd for C\(_{19}\)H\(_{15}\)N\(_3\)O\(_2\)SBr [M+H\(^+\)] 428.0068, found 428.0065.

4-bromo-1-((4-(tert-butyl)phenyl)sulfonyl)-3-phenyl-1H-pyrazol-5-amine (3l)
Yield: 60%; Yellow solid; M.p. = 217.6-222.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.39 (dd, J = 5.1, 2.0 Hz, 3H), 5.14 (s, 2H), 1.32 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 152.6, 146.9, 134.2, 131.0, 129.5, 128.4, 128.1, 128.0, 126.6, 76.3, 35.5, 31.1; HRMS(APCI): m/z calcd for C₁₉H₂₁N₃O₂SBr [M+H]+ 434.0538, found 434.0541.

4-bromo-3-phenyl-1H-pyrazol-5-amine (3m)

Yield: 70%; Yellow solid; M.p. = 107.6-109.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 8.1, 1.5 Hz, 2H), 7.46 – 7.36 (m, 3H), 3.75 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 141.8, 129.2, 129.1, 129.0, 127.2, 80.2. HRMS(APCI): m/z calcd for C₉H₉N₃Br [M+H]+ 237.9980, found 237.9985.
methyl 5-amino-4-bromo-3-phenyl-1H-pyrazole-1-carboxylate (3n)

Yield: 80%; Yellow solid; M.p. = 127.6-129.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.80 (m, 2H), 7.50 – 7.34 (m, 3H), 5.52 (s, 2H), 4.07 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 152.1, 151.9, 148.2, 131.1, 129.5, 128.5, 128.2, 75.5, 54.9; HRMS(APCI): m/z calcd for C₁₄H₁₄N₃O₂Br [M+H]+ 296.0029, found 296.0023.

4-iodo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (4a)

Yield: 100%; Red solid; M.p. = 124.1-126.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.4 Hz, 2H), 7.82 – 7.67 (m, 2H), 7.42 – 7.35 (m, 3H), 7.31 (d, J = 8.2 Hz, 2H), 5.24 (s, 2H), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 149.6, 146.0, 134.1, 131.6, 130.1, 129.3, 128.4, 128.2, 128.1, 43.0, 21.8; HRMS(APCI): m/z calcd for C₁₆H₁₅N₃O₂SI [M+H]+ 439.9930, found 439.9934.

4-iodo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (4b)

Yield: 98%; Red solid; M.p. = 143.4-144.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 5.22 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.1, 149.6, 149.6, 145.9, 139.4, 134.2, 130.1, 129.0, 128.8, 128.3, 128.1, 43.1, 21.8, 21.5; HRMS(APCI): m/z
calcd for C₁₇H₁₇N₃O₂SI [M+H]⁺ 454.0086, found 454.0092.

4-iodo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (4c)

Yield: 91%; Red solid; M.p. = 139.0-140.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.9 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 5.13 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 155.2, 149.6, 146.0, 138.0, 134.2, 131.5, 130.12, 130.09, 129.0, 128.1, 128.0, 125.6, 77.5, 77.2, 76.8, 43.2, 21.8, 21.5; HRMS(APCI): m/z calcd for C₁₇H₁₇N₃O₂SI [M+H]⁺ 454.0086, found 454.0086.

4-iodo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (4d)

Yield: 95%; Red solid; M.p. = 137.6-138.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.77 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.18 (dd, J = 5.5, 2.6 Hz, 1H), 7.10 (d, J = 7.8 Hz, 3H), 5.13 (s, 2H), 2.34 (s, 3H), 1.99 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 149.4, 146.0, 137.2, 134.3, 131.4, 130.3, 130.09, 129.3, 128.1, 125.4, 46.3, 21.9, 20.0; HRMS(APCI): m/z calcd for C₁₇H₁₇N₃O₂SI [M+H]⁺ 454.0086, found 454.0084.

3-(4-chlorophenyl)-4-iodo-1-tosyl-1H-pyrazol-5-amine (4e)

Yield: 99%; Red solid; M.p. = 138.7-141.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.23 (s, 2H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 153.9, 149.74, 149.72, 146.2, 135.4, 134.1, 130.19, 130.17, 129.7, 128.6, 128.1, 42.7, 21.9; HRMS(APCI): m/z calcd for C₁₆H₁₄N₃O₂SClI [M+H]⁺ 473.9540, found 473.9537.

4-iodo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (4f)

Yield: 98%; Red solid; M.p. = 139.6-143.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 5.21 (s, 2H), 3.81 (s, 3H), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.5, 154.7, 149.6, 145.9, 134.2, 130.1, 129.8, 128.1, 124.2, 113.7, 55.4, 43.0, 21.8; HRMS(APCI): m/z calcd for C₁₇H₁₇N₃O₃SI [M+H]⁺ 470.0035, found 470.0034.
4-iodo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (4g)

Yield: 92%; Red solid; M.p. = 130.5-132.7 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.13 – 7.94 (m, 2H), 7.75 (dd, $J$ = 6.6, 3.1 Hz, 2H), 7.64 (t, $J$ = 7.5 Hz, 1H), 7.53 (t, $J$ = 7.8 Hz, 2H), 7.44 – 7.35 (m, 3H), 5.25 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.2, 149.7, 137.1, 134.7, 131.6, 129.5, 129.4, 128.4, 128.3, 128.0, 43.2; HRMS(APCI): $m/z$ calcd for C$_{17}$H$_{17}$N$_3$O$_3$SI [M+H]$^+$ 425.9773, found 425.9773.

4-iodo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (4h)

Yield: 95%; Red solid; M.p. = 129.4-131.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (dd, $J$ = 8.5, 1.2 Hz, 2H), 7.66 (d, $J$ = 8.2 Hz, 2H), 7.62 (d, $J$ = 7.5 Hz, 1H), 7.52 (t, $J$ = 7.8 Hz, 2H), 7.20 (d, $J$ = 7.8 Hz, 2H) 5.24 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.2, 149.7, 139.4, 137.1, 134.6, 129.4, 129.0, 128.7, 128.3, 128.0, 43.2, 21.5; HRMS(APCI): $m/z$ calcd for C$_{16}$H$_{15}$N$_3$O$_2$SI [M+H]$^+$ 439.9930, found 439.9931.

4-iodo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (4i)

Yield: 99%; Red solid; M.p. = 98.7-99.8 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J$ = 8.7 Hz, 2H), 7.54 (t, $J$ = 7.5 Hz, 1H), 7.44 (dd, $J$ = 14.3, 6.4 Hz, 4H), 7.19 (t, $J$ = 8.3 Hz, 1H), 7.11 (d, $J$ = 7.5 Hz, 1H), 5.15 (s, 2H), 2.28 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.4, 149.7, 138.0, 137.1, 134.7, 131.4, 130.2, 129.5, 129.0, 128.1, 128.0, 125.6, 43.4, 21.5; HRMS(APCI): $m/z$ calcd for C$_{16}$H$_{15}$N$_3$O$_2$SI [M+H]$^+$ 439.9930, found 439.9938.

3-(4-chlorophenyl)-4-iodo-1-(phenylsulfonyl)-1H-pyrazol-5-amine (4j)

Yield: 99%; Red solid; M.p. = 160.3-165.1 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 – 7.98 (m, 2H), 7.70 (d, $J$ = 8.5 Hz, 2H), 7.65 (t, $J$ = 7.5 Hz, 1H), 7.54 (t, $J$ = 7.8 Hz, 2H), 7.35 (d, $J$ = 8.5 Hz, 2H), 5.26 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.0, 149.8, 137.0, 135.5, 134.8, 130.0, 129.7, 129.5, 128.5, 128.0, 42.8; HRMS(APCI): $m/z$ calcd for C$_{15}$H$_{12}$N$_3$O$_2$SCI [M+H]$^+$ 459.9385, found 459.9396.

4-iodo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (4k)
Yield: 79%; Red solid; M.p. = 60.5-65.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 8.02 – 7.93 (m, 3H), 7.89 (d, J = 8.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 6.8 Hz, 1H), 7.40 – 7.35 (m, 3H), 5.29 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 155.3, 149.7, 135.7, 134.0, 132.0, 131.6, 130.2, 129.93, 129.91, 129.8, 129.4, 128.5, 128.3, 128.1, 128.0, 122.4, 43.3.; HRMS(APCI): m/z calcd for C₁₉H₁₅N₃O₂SI [M+H]+ 475.9930, found 475.9935.

1-((4-(tert-butyl)phenyl)sulfonyl)-4-iodo-3-phenyl-1H-pyrazol-5-amine (4l)

Yield: 62%; Red solid; M.p. = 191.7-197.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.8 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.40 (dd, J = 5.1, 1.8 Hz, 3H), 5.23 (s, 2H), 1.32 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 154.9, 149.6, 134.2, 131.7, 129.4, 128.5, 128.3, 128.0, 126.6, 43.1, 35.5, 31.1; HRMS(APCI): m/z calcd for C₁₉H₂₁N₃O₂SI [M+H]+ 482.0399, found 482.0405.

4-iodo-3-phenyl-1H-pyrazol-5-amine (4m)

Yield: 80%; Brown solid; M.p. = 120.7-123.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 8.0, 1.5 Hz, 2H), 7.50 – 7.38 (m, 3H), 5.46 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 155.6, 145.1, 129.9, 129.3, 129.0, 127.7, 47.2; HRMS(APCI): m/z calcd for C₉H₉N₃I [M+H]+ 285.9836, found 285.9831.

methyl 5-amino-4-iodo-3-phenyl-1H-pyrazole-1-carboxylate (4n)

Yield: 82%; Brown solid; M.p. = 132.5-136.9, ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.74 (m, 2H), 7.41 (dd, J = 5.0, 2.2 Hz, 3H), 5.62 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 154.4, 151.7, 151.1, 131.8, 129.3, 128.5, 128.3, 54.9, 42.0; HRMS(APCI): m/z calcd for C₁₁H₁₁N₃O₂I [M+H]+ 343.9890, found 343.9885.

4-chloro-3-phenyl-1-tosyl-1H-pyrazol-5-amine (5a)

Yield: 69%; Pale yellow solid; M.p. = 121.3-123.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.5 Hz, 2H), 7.88 – 7.81 (m, 2H), 7.39 (dd, J = 5.1, 2.0 Hz, 3H), 7.32 (d, J = 8.1 Hz, 2H), 5.09 (s, 2H), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 151.7, 146.1, 145.6, 134.2,
4-chloro-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (5b)

Yield: 60%; Pale yellow solid; M.p. = 145.3-151.0 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.4\) Hz, 2H), 7.74 (d, \(J = 8.2\) Hz, 2H), 7.31 (d, \(J = 8.2\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 2H), 5.06 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.8, 146.0, 145.6, 139.5, 134.2, 130.1, 129.1, 128.1, 127.7, 91.1, 21.9, 21.5; HRMS(APCI): \(m/z\) calcd for C\(_{16}\)H\(_{15}\)N\(_3\)O\(_2\)SCl \([M+H]^+\) 348.0574, found 348.0580.

4-chloro-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (5c)

Yield: 55%; Pale yellow solid; M.p. = 152.1-155.4 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 8.4\) Hz, 2H), 7.60 (d, \(J = 12.0\) Hz, 2H), 7.27 (d, \(J = 10.3\) Hz, 2H), 7.23 (d, \(J = 8.9\) Hz, 1H), 7.15 (d, \(J = 7.6\) Hz, 1H), 5.03 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.9, 146.0, 145.6, 138.2, 134.2, 130.4, 130.3, 130.1, 128.4, 128.3, 128.1, 125.0, 91.2, 21.9, 21.5; HRMS(APCI): \(m/z\) calcd for C\(_{17}\)H\(_{17}\)N\(_3\)O\(_2\)SCl \([M+H]^+\) 362.0730, found 362.0729.

4-chloro-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (5d)

Yield: 72%; Pale yellow solid; M.p. = 120.6-123.7 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.4\) Hz, 2H), 7.80 (d, \(J = 8.9\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 6.91 (d, \(J = 8.9\) Hz, 2H), 5.06 (s, 2H), 3.81 (s, 3H), 2.39 (s, 3H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.6, 151.5, 145.9, 145.6, 134.2, 130.1, 129.2, 128.0, 123.1, 113.8, 90.8, 55.4, 21.8; HRMS(APCI): \(m/z\) calcd for C\(_{17}\)H\(_{17}\)N\(_3\)O\(_3\)SCl \([M+H]^+\) 378.0679, found 378.0681.

4-chloro-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (5e)

Yield: 59%; Pale yellow solid; M.p. = 157.2-160.1 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.4\) Hz, 2H), 7.80 (d, \(J = 8.6\) Hz, 2H), 7.36 (d, \(J = 8.6\) Hz, 2H), 7.33 (d, \(J = 8.3\) Hz, 2H), 5.09 (s, 2H), 2.41 (s, 3H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.5, 146.2, 145.7, 135.5, 134.1, 130.2, 129.1, 128.7, 128.1, 90.8, 21.9; HRMS(APCI): \(m/z\) calcd for C\(_{16}\)H\(_{16}\)N\(_3\)O\(_2\)SCl\(_2\)
4-chloro-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (5f)

Yield: 60%; Pale yellow solid; M.p. = 150.6-152.6 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (dd, \(J = 8.4, 1.1\) Hz, 2H), 7.89 – 7.77 (m, 2H), 7.65 (t, \(J = 7.5\) Hz, 1H), 7.54 (t, \(J = 7.8\) Hz, 2H), 7.39 (dd, \(J = 5.1, 1.8\) Hz, 3H), 5.09 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.9, 145.7, 137.2, 134.7, 130.5, 129.6, 129.5, 128.5, 128.0, 127.8, 91.2; HRMS(APCI): \(m/z\) calcd for C\(_{15}\)H\(_{13}\)N\(_3\)O\(_2\)SCl [M+H]\(^+\) 334.0417, found 334.0416.

4-chloro-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (5g)

Yield: 48%; Pale yellow solid; M.p. = 146.4-148.6 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.3\) Hz, 2H), 7.80 (d, \(J = 8.7\) Hz, 2H), 7.65 (d, \(J = 8.7\) Hz, 1H), 7.55 (t, \(J = 7.8\) Hz, 2H), 7.36 (d, \(J = 8.7\) Hz, 2H), 5.10 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.7, 145.8, 137.1, 135.6, 134.9, 129.6, 129.1, 129.0, 128.7, 128.1, 91.0; HRMS(APCI): \(m/z\) calcd for C\(_{15}\)H\(_{12}\)N\(_3\)O\(_2\)SCl\(_2\) [M+H]\(^+\) 368.0027, found 368.0032.

4-chloro-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (5h)

Yield: 32%; Pale yellow solid; M.p. = 102.4-104.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.63 (s, 1H), 8.00 (d, \(J = 7.8\) Hz, 1H), 7.97 (d, \(J = 1.7\) Hz, 2H), 7.89 (d, \(J = 7.9\) Hz, 1H), 7.82 (dd, \(J = 6.7, 3.1\) Hz, 2H), 7.72 – 7.59 (m, 2H), 7.39 – 7.34 (m, 3H), 5.14 (s, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.9, 145.7, 135.8, 134.0, 132.0, 130.5, 130.2, 130.0, 129.9, 129.8, 129.5, 128.4, 128.1, 128.0, 127.9, 122.4; HRMS(APCI): \(m/z\) calcd for C\(_{19}\)H\(_{15}\)N\(_3\)O\(_2\)SCl [M+H]\(^+\) 384.0574, found 384.0574.

1-phenyl-3H-pyrazolo[3,4-e]pyrrolo[1,2-a]pyrazine (4aa)

Yield: 36%; White solid; M.p. = 102.4-104.8 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 12.85 (s, 1H), 8.73 (s, 1H), 7.78 (d, \(J = 6.8\) Hz, 2H), 7.72 (d, \(J = 2.6\) Hz, 1H), 7.57 (t, \(J = 7.3\) Hz, 2H), 7.51 (d, \(J = 7.3\) Hz, 1H), 7.03 (dd, \(J = 4.2, 1.2\) Hz, 1H), 6.78 (dd, \(J = 4.2, 2.5\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.2, 132.5, 129.12, 129.05, 128.9, 127.2, 116.7, 113.7, 110.8, 108.4; HRMS(APCI): \(m/z\) calcd for C\(_{14}\)H\(_{14}\)N\(_4\) [M+H]\(^+\) 235.0978, found 235.0976.
3. $^1$H NMR, $^{13}$C NMR spectra of the products

4-bromo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (3a)
4-bromo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (3b)
4-bromo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (3c)
4-bromo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (3d)
4-bromo-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (3e)
4-bromo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (3f)
4-bromo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (3g)
4-bromo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (3h)
4-bromo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (3i)
4-bromo-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (3j)
4-bromo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (3k)
4-bromo-1-((4-(tert-butyl)phenyl)sulfonyl)-3-phenyl-1H-pyrazol-5-amine (31)
4-bromo-3-phenyl-1H-pyrazol-5-amine (3m)
methyl 5-amino-4-bromo-3-phenyl-1H-pyrazole-1-carboxylate (3n)
4-iodo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (4a)
4-iodo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (4b)
4-iodo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (4c)
4-iodo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (4d)
3-(4-chlorophenyl)-4-iodo-1-tosyl-1H-pyrazol-5-amine (4e)
4-iodo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (4f)
4-ido-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (4g)
4-ido-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (4h)
4-iodo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (4i)
3-(4-chlorophenyl)-4-iodo-1-(phenylsulfonyl)-1H-pyrazol-5-amine (4j)
4-iodo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (4k)
1-((4-(tert-butyl)phenyl)sulfonyl)-4-iodo-3-phenyl-1H-pyrazol-5-amine (41)
4-bromo-3-phenyl-1H-pyrazol-5-amine (4m)
methyl 5-amino-4-iodo-3-phenyl-1H-pyrazole-1-carboxylate (4n)
4-chloro-3-phenyl-1-tosyl-1H-pyrazol-5-amine (5a)
4-chloro-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (5b)
4-chloro-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (5c)
4-chloro-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (5d)
4-chloro-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (5e)
4-chloro-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (5f)
4-chloro-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (5g)
4-chloro-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (5h)
1-phenyl-3H-pyrrozolo[3,4-e]pyrrolo[1,2-a]pyrazine (4aa)