Electronic Supporting Information for:


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3 Catalysis:

3.1 General information:

Thin-layer chromatography (TLC) was performed on Merck 1.055 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by Merck silica gel 60 (0.063–0.200 mm). $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were taken in CDCl$_3$ or DMSO-d$_6$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

3.2 Typical procedure for $N$-alkylation of (hetero)aromatic amines with alcohols

In a 25 mL round bottomed flask were placed 0.5 mol % of ruthenium(II) catalyst, 2 mmol of alcohol, 2 mmol of amine and 50 mol % of KOH and 2 mL of toluene. The reaction flask was heated at 100 °C for 12 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H$_2$O (3 mL) was added and the organic layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was purified by column chromatography (ethyl acetate/hexane). Reported isolated yields are an average of two runs.

3.3 Typical procedure for $N_1$, $C_5$-dialkylation of amines with alcohols

In a 25 mL round bottomed flask were placed 1 mol % of ruthenium(II) catalyst, 4 mmol of benzyl alcohol, 2 mmol of 4-phenylthiazol-2-amine and 50 mol % of KOH and 2.0 mL of toluene. The reaction flask was heated at 120 °C for 24 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H$_2$O (3 mL) was added and the organic layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and
concentrated. The crude product was purified by column chromatography (ethyl acetate/dichloromethane). Reported isolated yields are an average of two runs.

3.4 Typical procedure for N-alkylation of sulfonamides with alcohols

In a 25 mL round bottomed flask were placed 0.5 mol % of ruthenium(II) catalyst, 2 mmol of benzyl alcohol, 2 mmol of sulfonamide, 50 mol % of KOH and 2 mL of toluene. The reaction flask was heated at 120 °C for 12 h in an oil bath. Upon completion (as monitored by TLC), the reaction mixture was cooled at ambient temperature, H$_2$O (3 mL) was added and the organic layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were dried with magnesium sulfate and concentrated. The crude product was purified by column chromatography (ethylacetate/hexane). Reported isolated yields are an average of two runs.
Table S1 Alkylation of various amines with aliphatic alcohols

\[ R'\text{OH} + R''\text{NH}_2 \rightarrow R'-R''\text{N} \text{OH} \]

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</tr>
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\(^a\)Reaction conditions: 2.00 mmol of heterocyclic amines, 2.00 mmol of alcohol, KOH (50 mol%), catalyst 1 (0.5 mol %) in 2 mL of toluene at 100 °C. \(^b\)Isolated yields
3.5 Characterization data of compounds

*N-(4-Methoxybenzyl)benzo[d]thiazol-2-amine*¹ (Table 5, entry 1)

Following the general experimental procedure with 2-aminobenzothiazole (2 mmol), 4-methoxybenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/ethyl acetate, 80:20) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 3.82 (s, 3H), 4.58 (s, 2H), 5.86 (bs, 1H), 6.96–6.87 (m, 2H), 7.05 (t, J = 8 Hz, 1H), 7.31–7.27 (m, 3H), 7.53 (d, J =8 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 48.8, 55.2, 114.3, 118.7, 120.6, 126.1, 129.3, 129.9, 130.5, 152.5, 159.4, 167.5.

*N-Benzylbenzo[d]thiazol-2-amine*² (Table 5, entry 2)

Following the general experimental procedure with 2-aminobenzothiazole (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 4.56 (s, 2H), 7.16–7.11 (m, 1H), 7.32–7.24 (m, 1H), 7.4–7.34 (m, 5H), 7.53 (d, J = 7.9, 2H), 7.60 (d, J = 7.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 49.4, 119.4, 121.6, 122.6, 126.2, 128.1, 128.6, 129.6, 130.7, 137.6, 152.8, 167.7.

*N-(4-Methylbenzyl)benzo[d]thiazol-2-amine*³ (Table 5, entry 3)

Following the general experimental procedure with 2-aminobenzothiazole (2 mmol), 4-methylbenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 2.32 (s, 2H), 4.56 (s, 2H), 6.36 (bs, 1H), 7.06 (t, J = 7.9, 1H), 7.15 (d, J = 8 Hz, 2H), 7.29–7.26 (m, 4H), 7.43
(d, $J = 7.9$ Hz, 1H), 7.53 (d, $J = 8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.4, 119.3, 121.1, 121.6, 122.2, 123.4, 126.9, 130.6, 134.8, 137.3, 152.4, 167.4.$

$N$-(4-Chlorobenzyl)benzo[$d$]thiazol-2-amine$^3$ (Table 5, entry 4)

Following the general experimental procedure with 2-aminobenzothiazole (2 mmol), 4-chlorobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 80:20) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.56$ (d, $J = 7.8$ Hz, 2H), 7.07 (t, $J = 7.9$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.41–7.36 (m, 5H), 7.63 (d, $J = 7.8$ Hz, 1H), 8.57 (t, $J = 6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 47.9, 118.6, 121.5, 125.6, 128.2, 129.2, 130.5, 131.5, 138.1, 153.4, 166.2.$

$N$-(4-Bromobenzyl)benzo[$d$]thiazol-2-amine$^4$ (Table 5, entry 5)

Following the general experimental procedure with 2-aminobenzothiazole (2 mmol), 4-bromobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 80:20) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.57$ (s, 2H), 7.06 (t, $J = 7.8$ Hz, 1H), 7.25 (t, $J = 7.9$ Hz, 1H), 7.39–7.32 (m, 3H), 7.53 (d, $J = 7.9$ Hz, 2H), 7.67 (d, $J = 7.8$ Hz, 1H), 8.56 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 46.4, 117.2, 120.1, 120.9, 121.1, 125.2, 129.5, 130.5, 131.2, 138.3, 152.4, 166.0.$

$N$-Benzylpyrimidin-2-amine (Table 5, entry 6)

Following the general experimental procedure with 2-aminopyrimidine (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 90:10) yields a colorless solid. $^1$H NMR
(400MHz, CDCl₃): δ = 4.69 (s, 2H), 5.24 (bs, 1H), 6.61 (m, 2H), 7.21 (d, J = 7.9 Hz, 1H), 7.41–7.32 (m, 2H), 7.48 (m, 1H), 8.22–8.10 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 46.9, 107.8, 110.4, 113.7, 127.6, 127.9, 128.9, 158.9, 162.9, 167.6.

**N-(4-Methylbenzyl)pyrimidin-2-amine (Table 5, entry 7)**

Following the general experimental procedure with 2-aminopyrimidine (2 mmol), 4-methylbenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 90:10) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 2.24 (s, 3H), 4.61 (s, 2H), 5.32 (bs, 1H), 6.22 (d, J = 7.9 Hz, 1H), 6.43-6.31 (m, 1H), 7.27–7.11 (m, 1H), 7.43–7.31 (m, 2H), 8.32–8.10 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 24.5, 45.4, 124.2, 124.6, 127.6, 129.2, 130.3, 133.2, 138.5, 158.4, 162.9, 168.0.

**N-(4-Methoxybenzyl)pyrimidin-2-amine (Table 5, entry 8)**

Following the general experimental procedure with 2-aminopyrimidine (2 mmol), 4-methoxybenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 90:10) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 2.24 (s, 3H), 4.61 (s, 2H), 5.32 (bs, 1H), 6.41-6.32 (m, 1H), 6.91-6.93 (m, 1H), 7.26–7.14 (m, 1H), 7.45–7.34 (m, 2H), 8.34–8.26 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 22.5, 45.6, 110.6, 112.7, 113.6, 119.6, 130.9, 143.1, 159.1, 162.3, 167.5.

**N-(4-Chlorobenzyl)pyrimidin-2-amine (Table 5, entry 9)**

Following the general experimental procedure with 2-aminopyrimidine (2 mmol), 4-chlorobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 90:10) yields a colorless
solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.71$ (s, 2H), 5.53 (bs, 1H), 6.34 (m, 1H), 6.67–6.59 (m, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 7.31–7.22 (m, 1H), 7.45–7.30 (m, 1H), 8.34–8.12 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 45.6, 110.4, 124.2, 124.8, 127.6, 130.1, 133.3, 139.1, 162.3, 167.8$.

$N$-(4-Bromobenzyl)pyrimidin-2-amine (Table 5, entry 10)

Following the general experimental procedure with 2-aminopyrimidine (2 mmol), 4-bromobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 90:10) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.71$ (s, 2H), 5.53 (bs, 1H), 6.34 (m, 1H), 6.67–6.59 (m, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 7.31–7.22 (m, 1H), 7.45–7.30 (m, 1H), 8.34–8.12 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 45.8, 110.6, 124.6, 127.8, 129.0, 130.5, 133.0, 139.2, 162.3, 167.6$.

$N$-Benzylpyridin-2-amine$^5$ (Table 5, entry 11)

Following the general experimental procedure with 2-aminopyridine (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 80:20) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.43$ (d, $J = 5.8$ Hz, 2H), 4.78 (bs, 1H), 6.37 (d, $J = 8.4$ Hz, 1H), 6.57 (t, $J = 5.9$ Hz, 1H), 7.44–7.24 (m, 6H), 8.08 (d, $J = 5.1$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 46.7, 107.2, 113.4, 127.4, 127.5, 128.6, 137.6, 148.6, 158.7$.

$N$-(4-Methylbenzyl)pyridin-2-amine$^6$ (Table 5, entry 12)

Following the general experimental procedure with 2-aminopyridine (2 mmol), 4-methylbenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 60:40) yields a colorless
solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 2.34$ (s, 3H), 4.43, (d, $J = 5.2$ Hz, 2H), 4.84 (bs, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 6.57 (t, $J = 6.4$ Hz, 1H), 7.17 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 5.9$ Hz, 2H), 7.39 (t, $J = 7.9$ Hz, 1H), 8.07 (d, $J = 5.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.3, 46.4, 107.0, 113.4, 127.5, 129.5, 136.3, 137.2, 148.4, 158.8.

$N$-(4-Methoxybenzyl)pyridin-2-amine$^6$ (Table 5, entry 13)

Following the general experimental procedure with 2-aminopyridine (2 mmol), 4-methoxybenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 60:40) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 3.85$ (s, 3H), 4.47 (d, $J = 6.3$ Hz 2H), 4.94 (bs, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 6.54 (t, $J = 6.1$Hz, 1H), 6.87 (t, $J = 6.1$ Hz, 1H), 7.23 (t, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 8$ Hz, 1H), 8.08 (d, $J = 5.5$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 55.6, 106.8, 110.3, 113.1, 120.6, 127.4, 129.6, 128.9, 137.5, 148.2, 157.9, 159.2.

$N$-(4-Chlorobenzyl)pyridin-2-amine$^6$ (Table 5, entry 14)

Following the general experimental procedure with 2-aminopyridine (2 mmol), 4-chlorobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 50:50) yields a colorless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 4.45$ (d, $J = 4.1$ Hz 2H), 4.86 (s, 1H), 6.32 (d, $J = 8.4$ Hz, 1H), 6.57 (d, $J = 7.1$ Hz, 1H), 7.41–7.24 (m, 5H), 8.09 (d, $J = 4.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 45.8, 107.0, 113.3, 128.8, 129.0, 133.0, 137.6, 138.1, 148.7, 158.5.

$N$-(4-Bromobenzyl)pyridin-2-amine$^6$ (Table 5, entry 15)
Following the general experimental procedure with 2-aminopyridine (2 mmol), 4-bromobenzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 50:50) yields a colorless solid. ¹H NMR (400MHz, CDCl₃): δ = 4.55 (d, J = 4.4 Hz, 2H), 4.72 (bs, 1H), 6.38 (d, J = 8.4 Hz, 1H), 6.57 (d, J = 7.3 Hz, 1H), 7.40–7.26 (m, 5H), 8.10 (d, J = 4.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 46.9, 107.8, 113.1, 111.7, 128.5, 129.4, 133.9, 137.9, 138.1, 148.4, 157.1.

**N-(Phenyl)aminomethylferrocene** (Table 5, entry 16)

Following the general experimental procedure with aniline (2 mmol), ferrocenemethanol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 70:30) yields a yellow solid. ¹H NMR (400MHz, CDCl₃): δ = 3.91 (s, 1H), 3.98 (s, 2H), 4.18 (t, J = 1.9 Hz, 2H), 4.22 (s, 5H), 4.26 (t, J = 1.9 Hz, 2H), 6.73-6.64 (m, 2H), 6.78 (m, 1H), 7.26-7.22 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 43.7, 66.9, 68.3, 68.5, 86.4, 112.7, 116.9, 129.5, 148.5.

**N-(4-Methylphenyl)aminomethylferrocene** (Table 5, entry 17)

Following the general experimental procedure with 4-methoxyaniline (2 mmol), ferrocenemethanol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.24 (s, 3H), 3.81 (br s, 1H), 3.96 (s, 2H), 4.12 (t, J = 1.7 Hz, 2H), 4.19 (s, 5H), 4.30 (t, J = 1.7 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.0, 43.6, 67.9, 86.3, 86.7, 113.1, 126.5, 129.7, 146.3.

**N-(4-Chlorobenzyl)aminomethylferrocene** (Table 5, entry 18)
Following the general experimental procedure with 4-chloroaniline (2 mmol), ferrocenemethanol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a yellow solid. \(^1\)H NMR (400 MHz, CDCl₃): δ = 3.87 (br s, 1H), 3.94 (s, 2H), 4.17 (t, \(J = 1.8\) Hz, 2H), 4.21 (s, 5H), 4.27 (t, \(J = 1.8\) Hz, 2H), 6.61 (d, \(J = 8.9\) Hz, 2H), 7.16 (d, \(J = 8.6\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃): δ = 43.7, 68.0, 68.3, 86.4, 113.9, 122.3, 126.5, 129.4, 146.9.

\(\text{N-(4-Bromobenzyl)aminomethylferrocene}^7\) (Table 5, entry 19)

Following the general experimental procedure with 4-bromoaniline (2 mmol), ferrocenemethanol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a yellow solid. \(^1\)H NMR (400 MHz, CDCl₃): δ = 3.87 (br s, 1H), 3.94 (s, 2H), 4.16 (t, \(J = 1.7\) Hz, 2H), 4.22 (s, 5H), 4.28 (t, \(J = 1.8\) Hz, 2H), 6.61 (d, \(J = 8.9\) Hz, 2H), 7.18 (d, \(J = 8.9\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl₃): δ = 43.5, 68.1, 68.3, 86.1, 113.9, 122.1, 129.4, 146.7.

\(\text{N,N’-Bis(4-methylbenzyl)pyridine-2,6-diamine}^8\) (Table 5, entry 20)

Following the general experimental procedure with 2,6-diaminopyridine (2 mmol), benzyl alcohol (4 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; hexane/EtOAc, 80:20) yields a colourless solid. \(^1\)H NMR (400MHz, CDCl₃): δ = 2.38 ppm (s, 6H), 4.43 (d, \(J = 5.9\) Hz, 4H), 4.65 (t, \(J = 5.4\) Hz, 2H), 5.69 (t, \(J = 8.05\) Hz, 2H), 7.12 (d, \(J = 7.6\) Hz, 4 H), 7.22 (t, \(J = 7.8\) Hz, 1H), 7.31 (s, 4H). \(^{13}\)C NMR (100 MHz, CDCl₃): δ = 20.9, 46.3, 127.9, 95.3, 129.8, 135.4, 136.0, 139.1, 158.9.

\(\text{N,N’-Bis(4-chlorobenzyl)pyridine-2,6-diamine}^8\) (Table 5, entry 21)
Following the general experimental procedure with 2,6-diaminopyridine (2 mmol), 4-chlorobenzyl alcohol (4 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 60:40) yields a colourless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 4.45 (d, $J$ = 5.7 Hz, 4H), 4.65 (t, $J$ = 5.6 Hz, 2H), 5.72 (d, $J$ = 7.6 Hz, 2H), 7.19 (t, $J$ = 8.4 Hz, 1H), 7.32 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 45.2, 95.6, 128.6, 129.8, 138.3, 139.5, 157.7.

$N,N'$-Bis(4-bromobenzyl)pyridine-2,6-diamine$^8$ (Table 5, entry 22)

Following the general experimental procedure with 2,6-diaminopyridine (2 mmol), 4-bromobenzyl alcohol (4 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 100 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; hexane/EtOAc, 60:40) yields a colourless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 4.43 (d, $J$ = 5.6 Hz, 4H), 4.63 (t, $J$ = 5.4 Hz, 2H), 5.70 (d, $J$ = 7.5 Hz, 2H), 7.16 (t, $J$ = 8.5 Hz, 1H), 7.31 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.2, 46.2, 123.9, 95.0, 128.3, 128.6, 138.5, 139.1, 139.6, 158.0.

$N,5$-Dibenzyl-4-phenylthiazol-2-amine (Scheme 6)

Following the general experimental procedure with 2-amino-4-phenylthiazole (2 mmol), benzyl alcohol (4 mmol), Ru (1 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 24 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$/EtOAc, 60:40) yields a colourless solid. $^1$H NMR (400 MHz, DMSO) ppm: $\delta$ = 4.19 (s, 2H), 4.42 (d, $J$ = 5.5 Hz, 2H), 7.16−7.25 (m, 4H), 7.27−7.34 (m, 5H), 7.38 (t, $J$ = 7.6 Hz, 4H), 7.53 (d, $J$ = 7.5 Hz, 2H), 8.02 (t, $J$ = 5.5 Hz, 1H); $^{13}$C NMR (100 MHz, DMSO): $\delta$ 32.7, 47.8, 119.3, 126.8, 127.4, 127.6, 127.8, 128.4, 128.7, 129.0, 135.8, 139.6, 140.9, 146.2, 168.0.
N,5-Bis(4-methoxybenzyl)-4-phenylthiazol-2-amine (Scheme 6)

Following the general experimental procedure with 2-amino-4-phenylthiazole (2 mmol), benzyl alcohol (4 mmol), Ru (1 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 24 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; CH₂Cl₂/EtOAc, 80:20) yields a colourless solid. ¹H NMR (400 MHz, DMSO) : δ 3.70 (s, 3H), 3.71 (s, 3H), 4.02 (s, 2H), 4.35 (d, J = 6 Hz, 2H), 6.85–6.90 (m, 4H), 7.09 (d, J = 7.5 Hz, 2H), 7.28–7.31 (m, 3H), 7.37 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 7 Hz, 2H) 7.89 (t, J = 6 Hz, 1H); ¹³C NMR (100 MHz, DMSO) : δ 31.8, 47.4, 55.4, 114.1, 114.3, 120.0, 127.6, 128.3, 128.7, 129.3, 129.7, 131.6, 132.8, 135.8, 146.1, 158.3, 158.8, 166.1.

N,5-Bis(4-chlorobenzyl)-4-phenylthiazol-2-amine (Scheme 6)

Following the general experimental procedure with 2-amino-4-phenylthiazole (2 mmol), benzyl alcohol (4 mmol), Ru (1 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 24 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂; CH₂Cl₂/EtOAc, 60:40) yields a colourless solid. ¹H NMR (500 MHz, DMSO) : δ 4.12 (s, 2H), 4.41 (d, J = 6 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.35–7.41 (m, 8H), 7.51 (d, J = 7.5 Hz, 2H), 8.03 (t, J = 6 Hz, 1H); ¹³C NMR (100 MHz, DMSO): δ 31.6, 46.2, 118.4, 127.1, 127.7, 128.2, 128.5, 129.2, 129.8, 131.2, 131.3, 131.4, 135.1, 138.3, 140.3, 146.2, 165.9.

N,5-Dibenzyl-4-(4-chlorophenyl)thiazol-2-amine (Scheme 6)

Following the general experimental procedure with 2-amino-4-(4-chlorophenyl)thiazole (2 mmol), benzyl alcohol (4 mmol), Ru (1 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 24 h. After completion of reaction (monitored by TLC), extraction with CH₂Cl₂ and purified by column chromatography (SiO₂;
CH$_2$Cl$_2$/EtOAc, 60:40) yields a colourless solid. $^1$H NMR (400 MHz, DMSO): δ δ 4.07 (s, 2H), 4.42 (d, $J = 6$ Hz, 2H), 7.18–7.26 (m, 4H), 7.29–7.36 (m, 6H), 7.44 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 8.01 (t, $J = 6$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO): δ 30.5, 45.2, 118.5, 127.3, 127.7, 128.5, 128.8, 128.9, 129.3, 129.5, 129.7, 130.4, 131.9, 132.5, 132.9, 134.2, 136.3, 137.7, 145.0, 165.45.

$N,5$-Bis(2-chlorobenzyl)-4-(4-chlorophenyl)thiazol-2-amine (Scheme 6)

Following the general experimental procedure with 2-amino-4-(4-chlorophenyl)thiazole (2 mmol), benzyl alcohol (4 mmol), Ru (1 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 24 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$/EtOAc, 90:10) yields a colourless solid. $^1$H NMR (400 MHz, DMSO): δ δ 4.12 (s, 2H), 4.53 (d, $J = 6$ Hz, 2H), 7.26–7.34 (m, 5H), 7.43–7.49 (m, 5H), 7.55 (d, $J = 8.5$ Hz, 2H), 8.06 (t, $J = 5.5$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO): δ 32.6, 47.8, 120.1, 126.9, 127.4, 127.9, 128.5, 128.7, 129.0, 130.1, 132.1, 134.6, 139.6, 140.6, 145.0, 166.0.

$N$-Benzyl-4-methylenesulfonamide$^9$ (Table 6, entry 1)

Following the general experimental procedure with $p$-toluenesulfonamide (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.44 (s, 3H), 4.11 (d, $J = 5.8$ Hz, 2H), 4.92 (br, 1H), 7.31–7.16 (m, 7H)

$^{13}$C NMR (100 MHz, CDCl$_3$): δ = 21.4, 47.9, 127.3, 127.7, 127.8, 128.8, 129.7, 136.1, 136.8, 143.5.
\textbf{N-(2-Chlorobenzyl)-4-methybenzenesulfonamide}^10 (Table 6, entry 2)

Following the general experimental procedure with \textit{p}-toluenesulfonamide (2 mmol), 4-chlorobenzyl alcohol (2 mmol), Ru (0.5 mol\%) and KOH (50 mol\%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 2.46 (s, 3H), 4.26 (d, $J$ = 5.9 Hz, 2H), 4.75 (t, $J$ = 5.9 Hz, 1H), 7.15–7.35 (m, 6H), 7.78 (d, $J$ = 7.9 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.2, 45.5, 126.8, 127.1, 129.2, 129.5, 129.7, 133.6, 134.2, 136.8, 143.2.

\textbf{N-(2-Bromobenzyl)-4-methybenzenesulfonamide}^11 (Table 6, entry 3)

Following the general experimental procedure with \textit{p}-toluenesulfonamide (2 mmol), 4-bromobenzyl alcohol (2 mmol), Ru (1 mol\%) and KOH (50 mol\%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 2.43 (s, 3H), 4.26 (d, $J$ = 5.9 Hz, 2H), 4.69 (t, $J$ = 5.9 Hz, 1H), 7.16–7.33 (m, 6H), 7.76 (d, $J$ = 7.9 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.3, 47.5, 123.4, 127.2, 127.1, 129.2, 129.5, 130.3, 132.6, 135.4, 137.0, 143.8.

\textbf{N-Benzyl-4-chlorobenzenesulfonamide}^12 (Table 6, entry 4)

Following the general experimental procedure with \textit{p}-chlorobenzenesulfonamide (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol\%) and KOH (50 mol\%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 4.16 (d, $J$ = 6.1 Hz, 2H), 4.68 (b, 1H), 7.19–7.18 (m, 2H), 7.29–7.27
(m, 3H), 7.48-7.47 (m, 2H), 7.80-7.78 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 47.4$, 127.9, 128.1, 128.6, 128.8, 129.4, 138.6, 139.3.

**N-Benzylbenzenesulfonamide** (Table 6, entry 5)

Following the general experimental procedure with benzenesulfonamide (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.16$ (d, $J = 6.1$ Hz, 2H), 4.68 (b, 1H), 7.19-7.18 (m, 2H), 7.29-7.27 (m, 4H), 7.48-7.47 (m, 2H), 7.80-7.78 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 47.7$, 126.4, 128.3, 128.6, 128.9, 129.7, 135.9, 137.2, 139.4.

**N-Cyclohexyl-4-methylenesulfonamide** (Table 6, entry 6)

Following the general experimental procedure with p-toluenesulfonamide (2 mmol), cyclohexanol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.2$–1.8 (m, 11H), 2.39 (s, 3H), 4.92 (br, 1H), 7.15–7.35 (m, 2H), 7.78 (d, $J = 7.9$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 21.2$, 24.82, 25.03, 31.76, 52.49, 127.7, 127.8, 128.8, 136.8, 143.5.

**N-Benzylmethanesulfonamide** (Table 6, entry 7)

Following the general experimental procedure with methanesulfonamide (2 mmol), benzyl alcohol (2 mmol), Ru (0.5 mol%) and KOH (50 mol%) in 2 mL toluene at 120 °C for 12 h. After completion of reaction (monitored by TLC), extraction with CH$_2$Cl$_2$ and purified by column chromatography (SiO$_2$; n-hexane/EtOAc, 80:20) yields a colourless solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 2.81$ (s, 3H), 4.28 (d, $J = 6.2$ Hz, 2H), 5.10 (b, 1H), 7.37-7.28 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 41.0$, 47.1, 127.9, 128.1, 128.9, 136.8.
3.6 References