Electronic Supplementary Information (ESI)

Direct N-Alkylation of Amino-azoles with Alcohols Catalyzed by an Iridium Complex/Base System

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General Experimental Details

Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-Tof MS(Micro) spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion [M+H]⁺. Melting points were measured on a X-6 micro-melting apparatus (Beijing Tech Instrument Co., Ltd). Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 500 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for CDCl₃ and 2.50 ppm for DMSO-d₆. Coupling constants J values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded at 125 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for CDCl₃ and 39.5 ppm for DMSO-d₆. ¹³C NMR spectra were routinely run with broadband decoupling.

[Cp*IrCl₂]₂ (Cp* = pentamethylcyclopentadienyl) and [Ir(cod)Cl]₂ (cod = 1,5-cyclooctadiene) were prepared according to literature methods.¹² Commercially unavailable amino-azoles were synthesized according to the previously reported procedures.³⁴ Reactions tubes were purchased from Beijing Synthware Glass Inc. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates.

General Procedure for direct N-alkylation of amino-azoles with alcohols catalyzed by an iridium complex/base system

To an oven-dried, nitrogen purged 20 ml Schlenk tube were added amino-azole (1mmol), [Cp*IrCl₂]₂ (0.002 mmol, 0.2 mol%), base (0.2 mmol, 20 mol%) and alcohol (5 mmol, 500 mol%). The resulting mixture was heated at 150 °C for 12h, followed by the mixture of the reaction was allowed to cool to ambient temperature. The mixture of the reaction was concentrated in vacuo and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product.
N-butylbenzo[d]thiazol-2-amine (3aa)

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mp 69.6-70.6 °C (lit. 68 °C); 1H NMR (500 MHz, CDCl3) δ 7.58 (d, J = 7.9 Hz, 1H, ArH), 7.52 (d, J = 8.1 Hz, 1H, ArH), 7.29 (t, J = 7.6 Hz, 1H, ArH), 7.07 (t, J = 7.6 Hz, 1H, ArH), 5.49 (br s, 1H, NH), 3.42 (t, J = 7.1 Hz, 2H, CH2N), 1.68 (quint, J = 7.3 Hz, 2H, CH2), 1.45 (sext, J = 7.4 Hz, 2H, CH2), 0.97 (t, J = 7.4 Hz, 3H, CH3); 13C NMR (125MHz, CDCl3) δ 168.0, 152.4, 130.2, 125.9, 121.2, 120.7, 118.5, 45.4, 31.6, 20.0, 13.7.
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N-hexylbenzo[d]thiazol-2-amine (3ab)

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mp 58.5-59.4 °C (lit. 53.2-55.4 °C); 1H NMR (500 MHz, CDCl3) δ 7.58 (d, J = 7.9 Hz, 1H, ArH), 7.53 (d, J = 8.1 Hz, 1H, ArH), 7.29 (t, J = 7.7 Hz, 1H, ArH), 7.10 (t, J = 7.5 Hz, 1H, ArH), 5.39 (br s, 1H, NH), 3.41 (t, J = 7.1Hz, 2H, CH2N), 1.68 (quint, J = 7.3 Hz, 2H, CH2), 1.41 (quint, J = 7.2 Hz, 2H, CH2), 1.34-1.30 (m, 4H, 2xCH2), 0.90 (t, J = 7.1Hz, 3H, CH3); 13C NMR (125MHz, CDCl3) δ 168.0, 152.5, 130.2, 125.8, 121.2, 120.7, 118.5, 45.7, 31.4, 29.5, 26.5, 22.5, 13.9.
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N-octylbenzo[d]thiazol-2-amine (3ac)

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mp 43.0-44.3 °C; 1H NMR (500 MHz, CDCl3) δ 7.58 (d, J = 7.7 Hz, 1H, ArH), 7.50 (d, J = 8.1 Hz, 1H, ArH) 7.28 (t, J = 7.8 Hz, 1H, ArH), 7.06 (t, J = 7.6 Hz, 1H, ArH), 6.29 (br s, 1H, NH), 3.38 (t, J = 7.1 Hz, 2H, CH2N), 1.67 (quint, J = 7.3 Hz, 2H, CH2), 1.38 (quint, J = 7.3 Hz, 2H, CH2), 1.33-1.23 (m, 8H, 4xCH2), 0.87 (t, J = 7.0 Hz, 3H, CH3); 13C NMR (125MHz, CDCl3) δ 168.0, 152.5, 130.2, 125.8, 121.2, 120.7, 118.5, 45.7, 31.4, 29.5, 29.2, 29.1, 26.8, 22.6, 14.0; FTIR (net, cm⁻¹) 3196, 2915, 1606, 1557, 1468, 1125; HRMS-EI (70 eV) m/z calcd for C15H23N2S [M+H]+ 263.1582, found 263.1585.
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N-isopentylbenzo[d]thiazol-2-amine (3ad)

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mp 76.8-77.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 8.0\) Hz, 1H, ArH), 7.53 (d, \(J = 8.0\) Hz, 1H, ArH), 7.29 (t, \(J = 7.7\) Hz, 1H, ArH), 7.07 (t, \(J = 7.6\) Hz, 1H, ArH), 5.45 (brs, 1H, NH), 3.43 (t, \(J = 7.4\) Hz, 2H, CH\(_2\)N), 1.72 (m, 1H, CH), 1.58 (quart, \(J = 7.2\) Hz, 2H, CH\(_2\)), 0.96 (d, \(J = 6.6\) Hz, 6H, 2xCH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 168.0, 152.5, 130.2, 125.8, 121.2, 120.7, 118.5, 44.0, 38.4, 25.7, 22.4; FTIR (net, cm\(^{-1}\)) 3194, 2954, 1609, 1557, 1446, 1125; HRMS-EI (70 eV) m/z calcd for C\(_{12}\)H\(_{17}\)N\(_2\)S [M+H]\(^+\) 221.1112, found 221.1107.

N-(2-ethylhexyl)benzo[d]thiazol-2-amine (3ae)

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\begin{array}{c}
\text{N} \end{array}
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mp 80.2-81.2 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 7.8\) Hz, 1H, ArH), 7.51 (d, \(J = 8.2\) Hz, 1H, ArH), 7.29 (t, \(J = 7.3\) Hz, 1H, ArH), 7.07 (t, \(J = 7.1\) Hz, 1H, ArH) 5.50 (br s, 1H, NH), 3.32 (d, \(J = 6.2\) Hz, 2H, CH\(_2\)N), 1.61 (sept, \(J = 6.1\) Hz, 1H, CH), 1.41 (quint, \(J = 7.2\) Hz, 2H, CH\(_2\)), 1.37-1.26 (m, 6H, 3xCH\(_2\)), 0.94-0.90 (m, 6H, 2xCH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 168.3, 152.5, 130.3, 125.9, 121.2, 120.7, 118.6, 48.9, 39.5, 30.9, 28.8, 24.2, 22.9, 14.0, 10.9; FTIR (net, cm\(^{-1}\)) 3196, 2950, 1623, 1575, 1467, 1146, 1124; HRMS-EI (70 eV) m/z calcd for C\(_{15}\)H\(_{23}\)N\(_2\)S [M+H]\(^+\) 263.1582, found 263.1583.

N-(2-methoxyethyl)benzo[d]thiazol-2-amine (3af)

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\begin{array}{c}
\text{N} \end{array}
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Oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.56-7.54 (m, 2H, ArH), 7.28 (t, \(J = 8.1\) Hz, 1H, ArH), 7.07 (t, \(J = 7.6\) Hz, 1H, ArH), 6.13 (br s, 1H, NH), 3.65-3.60 (m, 4H, CH\(_2\)N, CH\(_2\)O), 3.37 (d, \(J = 3.8\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 167.2, 152.4, 130.4, 125.8, 121.5, 120.7, 118.8, 70.7, 58.7, 44.7; FTIR (net, cm\(^{-1}\)) 3218, 2921, 1681, 1597, 1443, 1119; HRMS-EI (70 eV) m/z calcd for C\(_{10}\)H\(_{13}\)N\(_2\)OS [M+H]\(^+\) 209.0749, found 209.0751.

N-(2-(phenylthio)ethyl)benzo[d]thiazol-2-amine (3ag)

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\begin{array}{c}
\text{N} \end{array}
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mp 147.5-148.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.57 (d, \(J = 7.7\) Hz, 1H, ArH), 7.54 (d, \(J = 8.1\) Hz, 1H, ArH), 7.42 (d, \(J = 7.6\) Hz, 2H, ArH), 7.32-7.28 (m, 3H, ArH), 7.23 (t, \(J = 7.4\) Hz, 1H, ArH), 7.09 (t, \(J = 7.6\) Hz, 1H, ArH), 5.61 (br s, 1H, NH), 3.67 (t, \(J = 6.4\) Hz, 2H, CH\(_2\)N), 3.24 (t, \(J = 6.4\) Hz, 2H, CH\(_2\)S); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 166.7, 152.3, 134.5, 130.5, 130.2, 129.1, 126.8, 126.0, 121.8,
120.8, 119.0, 43.9, 33.6; FTIR (net, cm\(^{-1}\)) 3188, 2903, 1614, 1574, 1436; HRMS-EI (70 eV) m/z calcd for C\(_{15}H_{15}N_2S_2\) [M+H]\(^+\) 287.0677, found 287.0679.

\(N\)-phenethylbenzo[d]thiazol-2-amine (3ah)

![Image of 3ah]

mp 143.6-144.4 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 7.9\) Hz, 1H, ArH), 7.53 (d, \(J = 8.1\) Hz, 1H, ArH), 7.34-7.28 (m, 3H, ArH), 7.27-7.23 (m, 4H, ArH), 7.09 (t, \(J = 7.6\) Hz, 1H, ArH), 5.42 (br s, 1H, NH), 3.70 (t, \(J = 6.9\) Hz, 2H, CH\(_2\)N), 3.01 (t, \(J = 6.9\) Hz, 2H, CH\(_2\)Ph); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 167.4, 152.4, 138.3, 130.3, 128.8, 128.7, 126.7, 126.0, 121.5, 120.8, 118.8, 46.6, 35.5; FTIR (net, cm\(^{-1}\)) 3199, 2910, 1620, 1573, 1446, 1186; HRMS-EI (70 eV) m/z calcd for C\(_{15}H_{15}N_2S_2\) [M+H]\(^+\) 255.0956, found 255.0959.

\(N\)-(3-phenylpropyl)benzo[d]thiazol-2-amine (3ai)\(^7\)

![Image of 3ai]

mp 101.2-102.0 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 7.9\) Hz, 1H, ArH), 7.53 (d, \(J = 8.0\) Hz, 1H, ArH), 7.31-7.28 (m, 3H, ArH), 7.23-7.19 (m, 3H, ArH), 7.09 (t, \(J = 7.6\) Hz, 1H, ArH), 5.54 (br s, 1H, NH), 3.45 (t, \(J = 7.0\) Hz, 2H, CH\(_2\)N), 2.75 (t, \(J = 7.6\) Hz, 2H, CH\(_2\)Ph), 2.04 (quint, \(J = 7.3\) Hz, 2H, CH\(_2\)), \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 167.9, 152.4, 141.0, 130.2, 128.5, 127.0, 126.0, 125.9, 121.3, 120.8, 118.6, 45.1, 33.0, 31.0.

\(N\)-benzylbenzo[d]thiazol-2-amine (3aj)\(^8\)

![Image of 3aj]

\(^1\)H NMR (500 MHz, DMSO-d\(_6\)) \(\delta\) 8.50 (t, \(J = 5.6\) Hz, 1H, NH), 7.67 (d, \(J = 7.8\) Hz, 1H, ArH), 7.39-7.33 (m, 5H, ArH), 7.26 (t, \(J = 7.1\)Hz, 1H, ArH), 7.22 (t, \(J = 7.7\) Hz, 1H, ArH), 7.02 (t, \(J = 7.5\) Hz, 1H, ArH), 4.60 (br s, 2H, CH\(_2\)N); \(^{13}\)C NMR (125MHz, DMSO-d\(_6\)) \(\delta\) 166.2, 152.4, 138.9, 130.4, 128.3, 127.3, 127.0, 125.5, 120.95, 120.89, 118.1, 47.2.

\(N\)-(4-methoxybenzyl)benzo[d]thiazol-2-amine (3ak)\(^8\)

![Image of 3ak]
1H NMR (500 MHz, DMSO-d6) \( \delta \) 8.42 (t, \( J = 5.6 \) Hz, 1H, NH), 7.66 (d, \( J = 7.5 \) Hz, 1H, ArH), 7.38 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.31 (d, \( J = 8.5 \) Hz, 2H, ArH), 7.21 (t, \( J = 7.6 \) Hz, 1H, ArH), 7.01 (t, \( J = 7.5 \) Hz, 1H, ArH), 6.90 (d, \( J = 8.5 \), 2H, ArH), 4.51 (d, \( J = 5.7 \) Hz, 2H, CH\(_2\)N), 3.73 (s, 3H, OCH\(_3\)); 13C NMR (125 MHz, DMSO-d6) \( \delta \) 166.1, 158.4, 152.5, 130.7, 130.4, 128.8, 125.5, 120.9, 118.0, 113.7, 55.0, 46.7.

\[ \textit{N-(2-chlorobenzyl)benzo[d]thiazol-2-amine (3a)} \]

1H NMR (500 MHz, DMSO-d6) \( \delta \) 8.54 (br s, 1H, NH), 7.69 (d, \( J = 7.8 \) Hz, 1H, ArH), 7.48 (d, \( J = 6.7 \) Hz, 2H, ArH), 7.40 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.35-7.30 (m, 2H, ArH), 7.22 (t, \( J = 7.6 \) Hz, 1H, ArH), 7.04(t, \( J = 7.6 \) Hz, 1H, ArH), 4.68 (br s, 2H, CH\(_2\)N); 13C NMR (125 MHz, DMSO-d6) \( \delta \) 166.0, 152.3, 135.9, 132.3, 130.5, 129.3, 129.1, 128.9, 127.2, 125.6, 121.1, 121.0, 118.2, 45.0.

\[ \textit{N-(1,2,3,4-tetrahydronaphthalen-1-yl)benzo[d]thiazol-2-amine (3am)} \]

mp 131.7-132.3 °C; 1H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.56 (d, \( J = 7.5 \), 1H, ArH), 7.42 (d, \( J = 7.8 \) Hz, 1H, ArH), 7.37 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.24 (t, \( J = 7.6 \) Hz, 1H, ArH), 7.20-7.13 (m, 2H, ArH), 7.10 (d, \( J = 7.5 \) Hz, 1H, ArH), 7.06 (t, \( J = 7.6 \) Hz, 1H, ArH), 6.04 (br s, 1H, NH), 5.01 (t, \( J = 5.5 \) Hz, 1H, CHN), 2.85-2.73 (m, 2H, CH\(_2\)), 2.19-2.13 (m, 1H, CH), 2.07-2.01 (m, 1H, CH), 1.94-1.81 (m, 2H, CH\(_2\)); 13C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 166.6, 152.4, 137.5, 136.1, 130.2, 129.2, 128.9, 127.6, 126.3, 125.9, 121.5, 120.7, 118.8, 53.9, 29.9, 29.1, 19.9; FTIR (net, cm\(^{-1}\)) 3213, 2937, 1722, 1567, 1447, 1155; HRMS-EI (70 eV) m/z calcd for C\(_{17}\)H\(_{17}\)N\(_2\)S [M+H]\(^+\) 281.1112, found 281.1113.

\[ \textit{N-butyl-6-methylbenzo[d]thiazol-2-amine (3ba)} \]
mp 90.7-91.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 8.2\) Hz, 1H, ArH), 7.38 (s, 1H, ArH), 7.09 (d, \(J = 8.2\) Hz, 2H, ArH), 5.47 (br s, 1H, NH), 3.39 (t, \(J = 7.0\) Hz, 2H, CH\(_2\)N), 2.39 (s, 3H, CH\(_3\)Ar), 1.66 (quint, \(J = 7.3\) Hz, 2H), 1.43 (sext, \(J = 7.5\) Hz, 2H), 0.96 (t, \(J = 7.4\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 167.4, 150.2, 130.9, 130.3, 127.0, 120.8, 118.1, 45.4, 31.6, 21.1, 20.0, 13.7.

\(N\)-butyl-6-phenoxybenzo[d]thiazol-2-amine (3ca)

\[\text{PhO} \]

mp 116.0-116.7 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.48 (d, \(J = 8.8\) Hz, 1H, ArH), 7.31 (t, \(J = 8.0\) Hz, 2H, ArH), 7.25 (s, 1H, ArH), 7.06 (t, \(J = 7.4\) Hz, 1H, ArH), 7.00 (dd, \(J = 8.3\) Hz and 2.5 Hz, 1H, ArH), 6.98 (d, \(J = 7.9\) Hz, 1H, ArH), 5.23 (br s, 1H, NH), 3.41 (t, \(J = 7.1\) Hz, 2H, CH\(_2\)N), 1.67 (quint, \(J = 7.4\) Hz, 2H, CH\(_2\)), 1.45 (sext, \(J = 7.4\) Hz, 2H, CH\(_2\)), 0.97 (t, \(J = 7.4\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 167.2, 158.3, 151.4, 148.9, 131.3, 129.6, 122.6, 119.2, 118.3, 117.9, 112.0, 45.3, 31.6, 20.0, 13.7; FTIR (net, cm\(^{-1}\)) 3165, 2956, 1611, 1593, 1455, 1149. HRMS-EI (70 eV) m/z calcd for C\(_{17}\)H\(_{19}\)N\(_2\)OS [M+H]\(^+\) 299.1218, found 299.1223.

\(N\)-butyl-4,6-dimethylbenzo[d]thiazol-2-amine (3da)

\[\text{Me} \]

mp 46.0-47.2 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.24 (s, 1H, ArH), 6.93 (s, 1H, ArH), 5.29 (br s, 1H, NH), 3.34 (quart, \(J = 5.8\) Hz, 2H, CH\(_2\)N), 2.51 (s, 3H, CH\(_3\)Ar), 2.35 (s, 3H, CH\(_3\)Ar), 1.65 (quint, \(J = 5.8\) Hz, 2H, CH\(_2\)), 1.44 (sext, \(J = 7.4\) Hz, 2H, CH\(_2\)), 0.96 (t, \(J = 7.4\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \(\delta\) 166.7, 149.2, 130.8, 130.1, 128.0, 127.9, 118.3, 45.6, 31.6, 21.1, 19.9, 18.3, 13.7; FTIR (net, cm\(^{-1}\)) 3242, 2959, 1606, 1557, 1447, 1145; HRMS-EI (70 eV) m/z calcd for C\(_{13}\)H\(_{19}\)N\(_2\)S [M+H]\(^+\) 235.1269, found 235.1271.

\(N\)-butyl-6-fluorobenzo[d]thiazol-2-amine (3ea)

\[\text{F} \]

mp 95.8-96.6 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.43 (dd, \(J = 8.7\) Hz and 4.8 Hz, 1H, ArH), 7.29 (dd, \(J = 8.2\) Hz and 2.5 Hz, 1H, ArH), 7.00 (td, \(J = 8.9\) Hz and 2.6 Hz, 1H, ArH), 5.40 (br s, 1H, NH), 3.40 (t,
\[ J = 7.1 \text{ Hz, } 2\text{H, } \text{CH}_2N \], 1.67 (quint, \( J = 7.3 \text{ Hz, } 2\text{H, } \text{CH}_2 \)), 1.44 (sext, \( J = 7.5 \text{ Hz, } 2\text{H, } \text{CH}_2 \)), 0.96 (t, \( J = 7.4 \text{ Hz, } 3\text{H, } \text{CH}_3 \)); \( ^{13} \text{C NMR (125MHz, CDCl}_3 \) \( \delta \) 167.4, 158.1 (d, \( J_{\text{C-F}} = 238.3 \text{ Hz} \)), 148.9, 131.0 (d, \( J_{\text{C-F}} = 10.7 \text{ Hz} \)), 118.9, 113.5 (d, \( J_{\text{C-F}} = 23.6 \text{ Hz} \)), 107.5 (d, \( J_{\text{C-F}} = 26.2 \)), 45.4, 31.6, 20.0, 13.7; FTIR (net, cm\(^{-1}\)) 3214, 2972, 1621, 1569, 1461, 1137; HRMS-EI (70 eV) m/z calcd for C\(_{11}\)H\(_{14}\)N\(_2\)FS [M+H]\(^+\) 225.0862, found 225.0863

N-butyl-6-chlorobenzo[d]thiazol-2-amine (3fa)\(^{10}\)
3094, 1619, 1574, 1455, 1143; HRMS-EI (70 eV) m/z calcd for \( \text{C}_{12}\text{H}_{14}\text{N}_{2}\text{O}_{3}\text{S} [\text{M+H}]^+ \) 291.0779, found 291.0775.

**N-butyl-5-methyl-4-phenthiazol-2-amine (3ia)**

![Structural formula of 3ia]

mp 55.4-56.8 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.57 (d, \( J = 7.8 \) Hz, 2H, ArH), 7.38 (t, \( J = 7.7 \) Hz, 2H, ArH), 7.28 (t, \( J = 7.4 \) Hz, 1H, ArH), 5.26 (br s, 1H, NH), 3.20 (quart, \( J = 6.0 \) Hz, 2H, CH\(_2\)N), 3.40 (s, 3H, CH\(_3\)), 1.59 (quint, \( J = 7.3 \) Hz, 2H, CH\(_2\)), 1.39 (sext, \( J = 7.4 \) Hz, 2H, CH\(_2\)), 0.94 (t, \( J = 7.4 \) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \( \delta \) 166.2, 146.3, 135.4, 128.4, 128.2, 127.1, 115.3, 45.9, 31.6, 20.0, 13.7, 12.4.

**N-butyl-4,5-diphenthiazol-2-amine (3ja)**

![Structural formula of 3ja]

mp 116.2-117.0 (lit.\(^{12}\) mp 117-118 °C); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.47 (dd, \( J = 7.9 \) Hz and 2.2 Hz, 2H, ArH), 7.27-7.17 (m, 8H, ArH), 6.15 (br s 1H, NH), 3.14 (quart, \( J = 6.2 \) Hz, 2H, CH\(_2\)N), 1.51 (quint, \( J = 7.4 \) Hz, 2H, CH\(_2\)) 1.33 (sext, \( J = 7.4 \) Hz, 2H, CH\(_2\)), 0.90 (t, \( J = 7.3 \) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \( \delta \) 168.0, 146.1, 135.6, 133.0, 129.2, 129.0, 128.4, 128.2, 127.1, 119.9, 46.0, 31.3, 20.0, 13.7.

**N-butyl-4,5-dihydronaphtho[1,2-d]thiazol-2-amine (3ka)**

![Structural formula of 3ka]

mp 89.8-90.6 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.70 (d, \( J = 7.6 \) Hz, 1H, ArH), 7.23 (t, \( J = 7.3 \) Hz, 1H, ArH), 7.17-7.11 (m, 3H, ArH), 5.1 (br s, 1H, NH), 3.27 (quart, \( J = 6.5 \) Hz, 2H, CH\(_2\)N), 3.02 (t, \( J = 7.8 \) Hz, 2H, CH\(_2\)), 2.85 (t, \( J = 7.8 \) Hz, 2H, CH\(_2\)), 1.65 (quint, \( J = 7.3 \) Hz, 2H, CH\(_2\)), 1.43 (sext, \( J = 7.5 \) Hz, 2H, CH\(_2\)), 0.96 (t, \( J = 7.3 \) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (125MHz, CDCl\(_3\)) \( \delta \) 168.3, 145.4, 134.4, 131.8, 127.5, 126.8, 126.5, 122.7, 117.7, 45.8, 31.5, 29.2, 21.8, 20.0, 13.7; FTIR (net, cm\(^{-1}\)) 3201, 2958, 1600, 1553, 1435, 1138; HRMS-EI (70 eV) m/z calcd for \( \text{C}_{15}\text{H}_{19}\text{N}_{2}\text{S} [\text{M+H}]^+ \) 259.1269, found 259.1274.

**N-butyl-5-chlorobenzo[d]oxazol-2-amine (3la)**

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mp 109.5-110.6 °C; 1H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 (s, 1H, ArH), 7.13 (d, $J = 8.3$ Hz, 1H, ArH), 6.98 (d, $J = 8.1$ Hz, 1H, ArH), 5.18 (br s, 1H, NH), 3.48 (quart, $J = 6.4$ Hz, 2H, CH$_2$N), 1.67 (quint, $J = 7.2$ Hz, 2H, CH$_2$), 1.44 (sext, $J = 7.5$ Hz, 2H, CH$_2$), 0.97 (t, $J = 7.4$ Hz, 3H, CH$_3$); 13C NMR (125MHz, CDCl$_3$) $\delta$ 163.2, 147.1, 144.4, 129.2, 120.4, 116.2, 109.1, 42.8, 31.8, 19.9, 13.7.

$N$-butyl-5-phenylbenzo[d]oxazol-2-amine (3ma)

mp 132.3-133.6 °C; 1H NMR (500 MHz, CDCl$_3$) $\delta$ 7.59-7.58 (m, 3H, ArH), 7.43 (t, $J = 7.7$ Hz, 2H, ArH), 7.33 (t, $J = 7.4$, 1H, ArH), 7.29-7.26 (m, 2H, ArH), 5.10 (br s, 1H, NH), 3.51 (t, $J = 6.6$ Hz, 2H, CH$_2$N), 1.68 (quint, $J = 7.4$ Hz, 2H, CH$_2$), 1.45 (sext, $J = 7.5$ Hz, 2H, CH$_2$), 0.97 (t, $J = 7.4$ Hz, 3H, CH$_3$); 13C NMR (125MHz, CDCl$_3$) $\delta$ 162.7, 148.1, 143.6, 141.6, 137.7, 128.7, 127.3, 126.9, 120.1, 114.8, 108.6, 42.9, 31.8, 19.9, 13.7; FTIR (net, cm$^{-1}$) 3157, 2953, 1690, 1592, 1467, 1181; HRMS-EI (70 eV) m/z calcd for C$_{17}$H$_{19}$N$_2$O [M+H]$^+$ 267.1497, found 267.1499.

Procedure for the condensation of 4,5-diphenylthiazol-2-amine with benzaldehyde

To an oven-dried, nitrogen purged 20 ml Schlenk tube were added 4,5-diphenylthiazol-2-amine (1 mmol), base (0.2 mmol, 20 mol%) and benzaldehyde (5 mmol, 500 mol%). The resulting mixture was heated at 150 °C for 12h, followed by the mixture of the reaction was allowed to cool to ambient temperature. The mixture of the reaction was concentrated in vacuo and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product.

(E)-$N$-benzylidene-4,5-diphenylthiazol-2-amine

mp 109.4-110.2 °C; 1H NMR (500 MHz, CDCl$_3$) $\delta$ 9.09 (s, 1H, CH=N), 8.01 (d, $J = 7.1$ Hz, 2H, ArH), 7.58-7.56 (m, 2H, ArH), 7.54 (d, $J = 7.1$ Hz, 1H, ArH), 7.50 (t, $J = 7.3$ Hz, 2H, ArH), 7.39-7.37 (m, 2H, ArH), 7.34-7.32 (m, 3H, ArH), 7.30-7.29 (m, 3H, ArH); 13C NMR (125MHz, CDCl$_3$) $\delta$ 169.8, 163.1, 148.5, 135.1, 134.8, 132.6, 132.2, 132.1, 129.9, 129.6, 129.2, 128.9, 128.7, 128.24, 128.17, 127.9.

Procedure for the reaction of (E)-$N$-benzylidene-4,5-diphenylthiazol-2-amine with benzyl alcohol
To an oven-dried, nitrogen purged 20 ml Schlenk tube were added (E)-N-benzylidene-4,5-diphenylthiazol-2-amine (1mmol), [Cp*IrCl₂]₂ (0.002 mmol, 0.2 mol%), NaOH (0.2 mmol, 20 mol%) and benzyl alcohol (5 mmol, 500 mol%). The resulting mixture was heated at 150 °C for 12h, followed by the mixture of the reaction was allowed to cool to ambient temperature. The mixture of the reaction was concentrated in vacuo and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product. The yield of N-benzyl-4,5-diphenylthiazol-2-amine is isolated yield, and the yield of benzaldehyde is determined by the ¹H NMR integration.

\textit{N-benzyl-4,5-diphenylthiazol-2-amine}¹¹

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{structure.png}
\end{figure}

mp 142.1-143.2 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.47 (m, 2H, ArH), 7.38-7.33 (m, 4H, ArH), 7.31-7.28 (m, 1H, ArH), 7.25-7.19 (m, 8H, ArH), 6.13 (br s, 1H, NH), 4.42 (s, 2H, CH₂); ¹³C NMR (125MHz, CDCl₃) δ 167.3, 146.0, 137.7, 135.5, 132.8, 129.3, 129.0, 128.7, 128.5, 128.1, 127.7, 127.6, 127.5, 127.0, 120.8, 49.8
References


N-butylbenzo[d]thiazol-2-amine
Proton CDCl3
N-butylnbenzo[d]thiazol-2-amine
C13CPD CDC13
N-hexylbenzo[d]thiazol-2-amine
Proton CDCl3
N-hexylbenzo[d]thiazol-2-amine
C13CPD CDCl3
N-octylbenzo[d]thiazol-2-amine
Proton CDCl3
N-octylbenzo[d]thiazol-2-amine
C13CPD CDCl3
N-isopentylbenzo[d]thiazol-2-amine
Proton CDCl3
N-isopentylbenzothiazol-2-amine
C13CPD CDCl3
N-(2-ethylhexyl)benzo[d]thiazol-2-amine
Proton CDCl3

Bruker
N-(2-ethylhexyl)benzo[d]thiazol-2-amine
C13CPD CDCl3
N-(2-methoxyethyl)benzo[d]thiazol-2-amine
Proton CDCl3
N-(2-methoxyethyl)benzo[d]thiazol-2-amine

C13CPD CDC13

167.181
152.358
130.405
125.811
121.498
120.668
118.804
77.000
70.701
58.724
44.667
N-(2-phenylthio)ethyl 10benzo[d]thiazol-2-amine
Proton CDCl3
N-((2-(phenylthio)ethyl)benzo[d]thiazol-2-amine

C13CPD CDCl3
N-phenethylbenzo[d]thiazol-2-amine
Proton CDCl₃
N-phenethylbenzo[d]thiazol-2-amine
C13CPD CDC13

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N-(3-phenylpropyl)benzo[d]thiazol-2-amine

Proton CDCl3
N-(3-phenylpropyl)benzo[d]thiazol-2-amine

C13CPD CDCl3
N-benzylbenzo[d]thiazol-2-amine
Proton DMSO-d6
N-benzylbenzo[d]thiazol-2-amine
Proton DMSO-d6
N-(4-methoxybenzyl)benzo[d]thiazol-2-amine
Proton DMSO-d6
N-(4-methoxybenzyl)benzo[d]thiazol-2-amine
C13CPD DMSO-d6
N-(2-chlorobenzyl)benzo[d]thiazol-2-amine
Proton DMSO-d6
N-(2-chlorobenzyl)benzo[d]thiazol-2-amine

C13CPD DMSO-d6
N-(1,2,3,4-tetrahydronaphthalen-1-yl)benzo[d]thiazol-2-amine

Proton CDCl3

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Supplementary Material (ESI) for Chemical Communications
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N-(1,2,3,4-tetrahydronaphthalen-1-yl)benzo[d]thiazol-2-amine
C\textsubscript{13}CPD CDCl\textsubscript{3}
N-butyl-6-methylbenzo[d]thiazol-2-amine
Proton CDCl$_3$
N-butyl-6-methylbenzo[d]thiazol-2-amine
C13CPD CDC13
N-butyl-6-phenoxybenzo[d]thiazol-2-amine
Proton CDCl3
N-butyl-6-phenoxybenzo[d]thiazol-2-amine

C13CPD CDCl3
N-butyl-4,6-dimethylbenzo[d]thiazol-2-amine
Proton CDCl3
N-butyl-4,6-dimethylbenzo[d]thiazol-2-amine
C13CPD CDCl3

|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|

![N-butyl-4,6-dimethylbenzo[d]thiazol-2-amine](image)
N-butyl-6-fluorobenzo[d]thiazol-2-amine
Proton CDCl3
N-butyl-6-fluorobenzo[d]thiazol-2-amine
C13CPD CDCl3
N-butyl-6-chlorobenzo[d]thiazol-2-amine
Proton CDCl3
N-butyl-6-chlorobenzothiazol-2-amine
C13CPD CDCl3
N-butyl-6-chloro-4-methylbenzo[d]thiazol-2-amine
Proton CDCl$_3$
N-butyl-6-chloro-4-methylbenzo[d]thiazol-2-amine
C13CPD CDCl3
N-butyl-6-(trifluoromethoxy)benzo[d]thiazol-2-amine
Proton CDCl3
N-butyl-6-(trifluoromethoxy)benzo[d]thiazol-2-amine
C13CPD CDCl3
N-butyl-5-methyl-4-phenylthiazol-2-amine
Proton CDC13
N-butyl-5-methyl-4-phenylthiazol-2-amine
C13CPD CDCl3
N-butyl-4,5-diphenylthiazol-2-amine
Proton CDCl3
N-butyl-4,5-diphenylthiazol-2-amine
C13CPD CDCl3
N-butyl-4,5-dihydropyridinopyrrolo[1,2-d][1,3]thiazol-2-amine

Proton CDCl3
N-butyl-4,5-dihydronaphtho[1,2-d]thiazol-2-amine

C13CPD CDCl3
N-butyl-5-chlorobenzo[d]oxazol-2-amine
Proton CDCl3
N-butyl-5-chlorobenzo[d]oxazol-2-amine
C13CPD CDC13
N-butyl-5-phenylbenzo[d]oxazol-2-amine

Proton CDCl3
N-butyl-5-phenylbenzo[d]oxazol-2-amine
C13CPD CDC13
(E)-N-benzylidene-4,5-diphenylthiazol-2-amine
Proton CDCl₃
(E)-N-benzylidene-4,5-diphenylthiazol-2-amine
C13CPD CDC13
N-benzyl-4,5-diphenylthiazol-2-amine
Proton CDCl3
N-benzyl-4,5-diphenylthiazol-2-amine
C13CPD CDC13