A Metal-free Oxidative Amination of Benzoxazoles with Primary Amines and Ammonia

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Supporting Information

I. General Methods

$^1$H NMR spectra were recorded on an Avance 400 MHz instrument in deuterated chloroform CDCl$_3$. Chemical shifts ($\delta$) are given in parts per million (ppm). $^1$H NMR spectra were referenced to the residual hydrogen signal in CDCl$_3$ at $\delta = 7.26$ ppm or to residual hydrogen singulet signal at $\delta = 4.84$ ppm when measured in methanol-$d_4$. $^{13}$C NMR spectra were recorded on 100 MHz and were fully decoupled by broad band decoupling. $^{13}$C spectra were referenced to the CDCl$_3$ triplet signal at $\delta = 77.0$ ppm or to septet signal at $\delta = 49.05$ ppm in methanol-$d_4$. The following abbreviations were used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplet, m = multiplet. Coupling constants $J$ are given in Hz. Mass spectra were recorded on a Finnigan MAT95 by using EI or FAB method. HRMS was measured on a APEX II Bruker DALTONICS ESI FT-ICR-MS. Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV$_{254}$) and visualization was achieved by UV light (254 nm). Gas chromatography was measured on a Hewlett Packard 5890 (chiral column: 977 TBDMS-diacetyl-beta-CD). Flash chromatography was performed on silica gel (0.040 – 0.063 mm). Unless otherwise stated all reactions were carried out under air. For air or moisture sensitive reactions standard Schlenk-techniques were applied under an argon atmosphere. Schlenk-glassware was heated in vacuo and flushed with argon several times before they were used. Reagents and solvents were added by syringe/septum techniques. IR spectra were recorded on JASCO FT/IR-4100. A selection of
signals is given in reciprocal centimeters (cm$^{-1}$). Optical rotary power was recorded on a JASCO P-1020 in MeOH with a concentration of C=1.

**Solvents and reagents**

For all conversions HPLC grade acetonitrile was used. Solvents for flash chromatography (hexane, ethyl acetate, dichloromethane) were distilled before use. Morpholine was distilled before use. Benzoxazole derivatives were synthesized and purified according to a literature procedure from their ortho-aminophenol derivatives (S. H. Cho, J. Y. Kim, S. Y. Lee, S. Chang *Angew. Chem. Int. Ed.* 2009, 48, 9127 supporting information). The tetrabutylammonium iodide catalyst was prepared according to a literature procedure by precipitation from an aqueous solution of tetrabutylammonium bromide with sodium iodide and dried in vacuo without further purification (H. Usui, H. Nakayama *Bull. Chem. Soc. Jpn.* 1986, 59, 833). The catalytic activity for the observed conversions of tetrabutylammonium bromide and chloride was tested but they did not reveal any catalytic activity. Unless stated, all other commercially available substances and reagents were used as received from their suppliers (Acros, Alfa Aesar, Sigma Aldrich) without further purification.

II. General Experimental procedure

a) 2-Amination of benzoxazole with n-butylamine

A reaction vessel was charged with acetic acid (0.061 g, 1.010 mmol, 3 equiv.) and tert-butyl-hydroperoxide (70 % in water, 0.065 g, 0.504 mmol, 1.5 equiv) in acetonitrile (0.2 mL). After the addition of tetra-butylammonium iodide (0.006 g, 0.017 mmol, 5 mol%), butylamin (0.029 g, 0.403 mmol, 1.2 equiv) and benzoxazole (0.040 g, 0.336 mmol, 1 equiv) in acetonitrile (0.2 mL) were added. The reaction mixture was stirred until TLC showed full conversion of benzoxazole. The reaction was quenched by addition of an aqueous solution of sodium disulfite (2 mL) and a saturated solution of sodium hydrogen carbonate (5 mL). The mixture was extracted with dichloromethane (5 × 5 mL), combined organic phases were dried over Na$_2$SO$_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, hexane : ethyl acetate v/v 20:1) to yield 3a (0.065 g, 0.272 mmol, 81%) as a white amorphous solid.
**N-butylbenzo[d]oxazol-2-amine (3a):** white amorphous solid (44 mg, 69%); eluent: hexane : ethyl acetate v/v 20:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, 1H, \(J = 7.8\) Hz), 7.23 (d, 1H, \(J = 7.9\) Hz), 7.15 (dt, 1H, \(J = 7.8\) and 1.2 Hz), 7.01 (dt, 1H, \(J = 7.8\) and 1.2 Hz), 5.84 (bs, 1H), 3.48 (t, 2H, \(J = 7.2\) Hz), 1.70-1.63 (m, 2H), 1.48-1.40 (m, 2H), 0.95 (t, 3H, \(J = 7.6\) Hz); \(^{13}\)C\({^1}\)H NMR (CDCl\(_3\), 100 MHz) \(\delta\): 162.3, 148.4, 143.0, 123.8, 120.5, 115.0, 108.6, 42.8, 31.8, 19.9, 13.7 (cm\(^{-1}\)); IR (neat): 2951, 2926, 2868, 1689, 1583, 1461, 1245, 944, 733, 726 (cm\(^{-1}\)); HRMS (ESI) m/z calcld for C\(_{11}\)H\(_{15}\)N\(_2\)O \([M+H]^+:\) 191.11789, found: 190.11776 \[^1\]

**N-isopropylbenzo[d]oxazol-2-amine (3b):** white amorphous solid (43 mg, 72%); eluent: hexane : ethyl acetate v/v 10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 (d, 1H, \(J = 7.8\) Hz), 7.24 (d, 1H, \(J = 7.9\) Hz), 7.15 (dt, 1H, \(J = 7.6\) and 0.8 Hz), 7.01 (dt, 1H, \(J = 7.6\) and 1.2 Hz), 5.65 (bs, 1H), 4.11-4.06 (m, 1H), 1.34-1.33 (d, 6H, \(J = 6.5\) Hz); \(^{13}\)C\({^1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\): 161.6, 148.3, 143.0, 123.8, 120.5, 116.0, 108.6, 45.3, 23.1 (cm\(^{-1}\)); IR (neat): 2971, 1745, 1647, 1585, 1458, 1365, 1242, 737, 725 (cm\(^{-1}\)); MS (EI) m/z: 177.1 ([M+H]\(^+)\)

**N-isobutylbenzo[d]oxazol-2-amine (3c):** white amorphous solid (49 mg, 76%); eluent: hexane : ethyl acetate v/v 10:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (d, 1H, \(J = 7.6\) Hz), 7.24 (d, 1H, \(J = 8.0\) Hz), 7.17-7.13 (m, 1H), 7.03-6.88 (m, 1H), 5.84 (bs, 1H), 3.32-3.30 (m, 2H), 2.02-1.92 (m, 1H), 1.00 (d, 6H, \(J = 6.7\) Hz); \(^{13}\)C\({^1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\): 162.5, 148.4, 143.0, 123.8, 120.5, 116.0, 108.6, 50.5, 28.6, 20.0; IR (neat): 2961, 2955, 1639, 1582, 1459, 1242, 1076, 938, 733 (cm\(^{-1}\)); MS (EI) m/z: 190.1 ([M]\(^+)\)

**N-tert-butylbenzo[d]oxazol-2-amine (3d):** white amorphous solid (29 mg, 46%); eluent: hexane : ethyl acetate v/v 20:1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.37 (d, 1H, \(J = 7.6\) Hz), 7.24 (d, 1H, \(J = 8.0\) Hz), 7.15 (dt, 1H, \(J = 7.6\) and 0.8 Hz), 7.02 (dt, 1H, \(J = 7.6\) and 1.2 Hz), 5.30 (bs, 1H), 1.50 (s, 9H); \(^{13}\)C\({^1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\): 160.8, 148.1, 143.1, 123.7, 120.6, 116.3, 108.5,
N-benzylbenzo[d]oxazol-2-amine (3e): brown amorphous solid (44 mg, 59%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.27 (m, 5H), 7.25-7.20 (m, 2H), 7.14-7.10 (m, 1H), 7.02-6.98 (m, 1H), 6.31 (bs, 1H), 4.64 (s, 2H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 148.4, 142.7, 137.7, 128.7, 127.7, 127.5, 123.9, 120.8, 116.2, 108.7, 46.9; IR (neat): 3027, 2970, 1658, 1648, 1580, 1458, 1366, 1241, 949, 728 (cm$^{-1}$); MS (EI) m/z: 224.1 ([M]$^+$)

N-(1-phenylethyl)benzo[d]oxazol-2-amine (3f): white amorphous solid (61 mg, 81%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.41 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.20 (m, 3H), 7.12 (t, 1H, $J$ = 7.7 Hz), 6.99 (t, 1H, $J$ = 7.7 Hz), 6.88 (bs, 1H), 5.11 (q, 1H, $J$ = 6.8 Hz), 1.66 (d, 3H, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 161.6, 148.4, 143.4, 142.7, 128.7, 127.4, 125.9, 123.8, 120.6, 116.0, 108.8, 52.8, 23.1; IR (neat): 2970, 1658, 1580, 1458, 1366, 1217, 698 (cm$^{-1}$); HRMS (EI) m/z calcd for C$_{12}$H$_{14}$N$_2$O$_2$ [M]$^+$: 238.1106, found: 238.1095. Optical rotary power of (R)-N-(1-phenylethyl)benzooxazol-2-amine ((R)-3f): [$\alpha$]$_{D}^{22}$ = +113.6 $^\circ$(c=1 in MeOH).

N-cyclopentylbenzo[d]oxazol-2-amine (3g): white amorphous solid (49 mg, 73%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, 1H, $J$ = 7.6 Hz), 7.03-6.99 (m, 1H), 5.70 (bs, 1H), 4.24-4.23 (m, 1H), 2.16-2.08 (m, 2H), 1.77-1.58 (m, 6H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 161.9, 148.4, 143.0, 123.3, 120.5, 116.0, 108.6, 54.8, 33.4, 23.5; IR (neat): 2970, 2927, 1746, 1658, 1648, 1458, 1351, 1241, 949, 728 (cm$^{-1}$); HRMS (ESI) m/z calcd for C$_{12}$H$_{15}$N$_2$O$_2$ [M+H]$^+$: 203.11789, found: 203.11781.

N-cyclohexylbenzo[d]oxazol-2-amine (3h): white amorphous solid (43 mg, 59%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.27 (m, 5H), 7.25-7.20 (m, 2H), 7.14-7.10 (m, 1H), 7.02-6.98 (m, 1H), 6.31 (bs, 1H), 4.64 (s, 2H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 148.4, 142.7, 137.7, 128.7, 127.7, 127.5, 123.9, 120.8, 116.2, 108.7, 46.9; IR (neat): 3027, 2970, 1658, 1648, 1580, 1458, 1366, 1217, 698 (cm$^{-1}$); MS (EI) m/z: 224.1 ([M]$^+$)
NMR (400 MHz, CDCl₃) δ 7.35 (d, 1H, J = 7.8 Hz), 7.23 (d, 1H, J = 7.9 Hz), 7.15 (dt, 1H, J = 8 and 0.8 Hz), 7.00 (dt, J = 8.0 and 1.2 Hz), 5.40 (s, 1H), 3.76-3.75 (m, 1H), 2.15-2.11 (m, 2H), 1.80-1.75 (m, 2H), 1.68-1.62 (m, 1H), 1.49-1.38 (m, 2H), 1.35-1.17 (m, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.5, 148.3, 143.0, 123.8, 120.5, 116.0, 108.6, 52.0, 33.4, 25.5, 24.7; IR (neat): 2926, 1748, 1646, 1581, 1458, 1234, 737 (cm⁻¹); MS (EI) m/z: 216.1 ([M]+)

**N-(bicyclo[2.2.1]heptan-2-yl)benzo[d]oxazol-2-amine (3i):**
white amorphous solid (62 mg, 80%); eluent: hexane : ethyl acetate v/v 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, 1H, J = 7.7 Hz), 7.27 (d, 1H, J = 7.8 Hz), 7.19-7.15 (m, 1H), 7.05-7.00 (m, 1H), 6.42 (bs, 1H), 3.78- (s, 1H), 2.45-2.37 (m, 2H), 1.96-1.90 (m, 1H), 1.64-1.43 (m, 4H), 1.37-1.18 (m, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.7, 148.4, 143.0, 123.8, 120.3, 115.8, 108.6, 56.2, 42.4, 40.3, 35.7, 35.3, 28.3, 26.2; IR (neat): 2954, 1745, 1658, 1648, 1581, 1460, 1352, 1217, 735, 725 (cm⁻¹); MS (EI) m/z: 228.1 ([M]+)

**N-allyl-benzo[d]oxazol-2-amine (3j):** yellow amorphous solid (16 mg, 28%); eluent: hexane : ethyl acetate v/v 8:1; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, 1H, J = 7.1 Hz), 7.25 (d, 1H, J = 7.1 Hz), 7.17 (dt, 1H, J = 8.0 and 1.2 Hz), 7.04 (dt, 1H, J = 8.0 and 0.8 Hz), 6.05-5.95 (m, 1H), 5.47 (bs, 1H), 5.33 (dd, 1H, J = 17.2 and 1.3 Hz), 5.22 (dd, 1H, J = 10.2 and 1.3 Hz), 4.13-4.12 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.9, 148.5, 142.7, 133.7, 123.9, 120.9, 116.9, 116.4, 108.8, 45.4; IR (neat): 2916, 1739, 1658, 1586, 1458, 1374, 1241, 913, 749 (cm⁻¹); MS (EI) m/z: 174.1 ([M]+)

**N-(1-ethynylcyclohexy)benzo[d]oxazol-2-amine (3k):** yellow amorphous solid (53 mg, 66%); eluent: hexane : ethyl acetate v/v 15:1; ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.42 (m, 1H), 7.30-7.28 (m, 1H), 7.17 (dt, 1H, J = 7.6 and 1.1 Hz), 7.05 (dt, 1H, J = 7.8 and 1.2 Hz), 5.76 (bs, 1H), 2.42 (s, 1H), 2.34-2.31 (m, 2H), 1.92-1.86 (m, 2H), 1.75-1.69 (m, 5H), 1.38-1.26 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.3, 148.3, 142.7, 123.8, 121.0, 116.8, 108.8, 85.4,
b) Amination of benzoxazole derivatives (1a-1g) with 1-phenylethylamine (2f)

The amination of benzoxazole derivatives (0.336 mmol, 1 equiv) with 1-phenylethylamine (0.049 g, 0.403 mmol, 1.2 equiv) was performed analogously to the procedure described in II a). Unless otherwise stated work-up was performed under the same conditions as described in II a) and conditions for the chromatographic purification are given with the corresponding substrate.

**5-Methyl-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3l):** brown amorphous solid (73 mg, 86%); eluent: hexane : ethyl acetate v/v 15:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.43 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.27 (m, 1H), 7.12-7.09 (m, 2H), 6.84-6.81 (m, 1H), 6.46 (bs, 1H), 5.12 (q, 1H, $J$ = 6.8 Hz), 2.38 (d, 3H, $J$ = 6.8 Hz), 1.69-1.67 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.7, 146.6, 143.4, 142.9, 133.5, 128.7, 127.4, 125.9, 121.3, 116.6, 108.1, 52.8, 22.9, 21.4; IR (neat): 1649, 1585, 1361, 1254, 1184, 917, 798, 697 (cm$^{-1}$); MS (EI) m/z: 252.2 ([M$^+$])

**6-Methyl-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3m):** yellow amorphous solid (76 mg, 90%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.33 (m, 2H), 7.27-7.24 (m, 2H), 7.20-7.16 (m, 1H), 7.00-6.99 (m, 2H), 6.73-6.70 (m, 1H), 6.36 (bs, 1H), 5.02 (q, 1H, $J$ = 6.8 Hz), 2.28 (s, 3H), 1.58 (d, 3H, $J$ = 6.9 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.7, 146.6, 143.4, 142.8, 133.5, 128.7, 127.4, 125.9, 121.3, 116.5, 108.1, 52.8, 23.0, 21.4; IR (neat): 1749, 1683, 1456, 1363, 1306, 1135, 916, 753 (cm$^{-1}$); MS (EI) m/z: 252.2 ([M$^+$])

**5-tert-Butyl-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3n):** brown amorphous solid (76 mg, 77%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34-7.31 (m, 2H), 7.29-7.28 (m, 1H), 7.25-7.22 (m, 2H), 7.18-7.14 (m, 1H), 7.05-7.03 (m, 1H), 6.97-6.94 (m, 1H), 6.36 (bs, 1H), 5.02 (q, 1H, $J$ = 6.8 Hz), 1.57 (d, 3H, $J$ = 6.9 Hz), 1.33-1.28 (m, 9H), 1.00 (t, 3H, $J$ = 6.9 Hz); IR (neat): 1657, 1581, 1465, 1358, 1242, 1172, 1038, 917, 798, 698 (cm$^{-1}$); MS (EI) m/z: 310.2 ([M$^+$])
Hz), 1.23 (s, 9H); $^{13}$C$\{^1$H$\}$ NMR (100 MHz, CDCl$_3$) $\delta$ 161.7, 147.3, 146.4, 143.4, 142.6, 128.7, 127.4, 125.9, 117.8, 113.3, 107.8, 52.8, 34.7, 31.8, 22.9; IR (neat): 2967, 2925, 1747, 1648, 1361, 1215, 912, 866, 806, 739, 697 (cm$^{-1}$); MS (EI) m/z: 294.2 ([M$^+$])

**5-Methoxy-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3o):**
yellow amorphous solid (64 mg, 71%); eluent: hexane : ethyl acetate v/v 5:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.40 (m, 2H), 7.37-7.34 (m, 2H), 7.30-7.28 (m, 1H), 7.10-7.08 (m, 1H), 6.90-6.89 (m, 1H), 6.59-6.56 (m, 1H), 5.77 (bs, 1H), 5.09 (q, 1H, $J$ = 7.0 Hz), 3.79 (s, 3H), 1.66 (d, 3H, $J$ = 6.9 Hz); $^{13}$C$\{^1$H$\}$ NMR (100 MHz, CDCl$_3$) $\delta$ 162.1, 156.9, 143.9, 143.1, 143.0, 128.8, 127.6, 125.9, 108.6, 107.3, 101.6, 55.9, 52.8, 22.8; IR (neat): 2924, 1670, 1595, 1439, 1162, 1028, 842, 760, 697 (cm$^{-1}$); MS (EI) m/z: 268 ([M$^+$])

**5-Chloro-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3p):**
yellow amorphous solid (65 mg, 71%); eluent: hexane : ethyl acetate v/v 15:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.40 (m, 2H), 7.38-7.34 (m, 2H), 7.31-7.29 (m, 1H), 7.23-7.22 (m, 1H), 7.16-7.10 (m, 1H), 6.98-6.96 (m, 1H), 6.26 (bs, 1H), 5.08 (q, 1H, $J$ = 6.8 Hz), 1.67 (d, 3H, $J$ = 6.9 Hz); $^{13}$C$\{^1$H$\}$ NMR (100 MHz, CDCl$_3$) $\delta$ 162.2, 147.0, 144.0, 142.8, 129.3, 128.8, 127.7, 125.9, 120.6, 116.3, 109.3, 52.9, 22.8; IR (neat): 1669, 1576, 1460, 1351, 1247, 1180, 904, 806, 697 (cm$^{-1}$); MS (EI) m/z: 272.0, 274.0, 273.0 ([M$^+$])

**5-Fluoro-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3q):**
red amorphous solid (48 mg, 56%); eluent: hexane : ethyl acetate v/v 6:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.41 (m, 2H), 7.36 (dt, 2H, $J$ = 6.2 Hz and 1.5 Hz), 7.31-7.27 (m, 1H), 7.11 (q, 1H, $J$ = 4.3 Hz), 6.95 (dd, 1H, $J$ = 8.9 Hz and 2.6 Hz), 6.70 (dt, 1H, $J$ = 8.8 Hz and 2.6 Hz), 6.49 (bs, 1H), 5.08 (q, 1H, $J$ = 7.0 Hz), 1.67 (d, 3H, $J$ = 6.9 Hz); $^{13}$C$\{^1$H$\}$ NMR (100 MHz, CDCl$_3$) $\delta$ 162.7, 160.0 (d, $J$ = 238 Hz), 144.7 (d, $J$ = 1.3 Hz) 143.9 (d, $J$ = 13.4 Hz), 143.0, 128.8, 127.6, 125.9, 108.6 (d, $J$ = 10.4 Hz), 107.1 (d, $J$ = 25.9 Hz), 103.3 (d, $J$ = 26.6 Hz), 25.8, 22.9; IR (neat): 2925, 1659, 1577, 1470, 1443, 1122, 914, 839, 782, 762, 700 (cm$^{-1}$); MS (EI) m/z: 256 ([M$^+$])
6-Nitro-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3r): yellow amorphous solid (17 mg, 18%); eluent: hexane : ethyl acetate v/v 10:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10-8.07 (m, 1H), 8.05-8.04 (m, 1H), 7.36-7.29 (m, 4H), 7.27-7.21 (m, 1H), 7.19-7.18 (m, 1H), 6.20 (bs, 1H), 5.08 (q, 1H, $J = 7.1$ Hz), 1.64 (d, 3H, $J = 6.9$ Hz); $^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$) δ 164.2, 149.5, 147.6, 142.1, 141.7, 129.0, 128.0, 125.9, 121.3, 115.1, 105.2, 53.2, 22.6; IR (neat): 2919, 1670, 1590, 1509, 1328, 1276, 1232, 1056, 909, 870, 820, 727, 696; MS (EI) m/z: 283.1 ([M$^+$])

N-(1-phenylethyl)naphto[2,1-d]benzooxazol-2-amine (3s): brown oil (40 mg, 41%); eluent: hexane : ethyl acetate v/v 15:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11-8.09 (m, 1H), 7.67-7.65 (m, 1H), 7.32-7.31 (m, 2H), 7.29-7.28 (m, 4H), 7.24-7.21 (m, 2H), 7.14-7.11 (m, 1H), 5.64 (bs, 1H), 5.09 (m, 1H), 1.58 (d, 3H, $J = 6.9$ Hz); $^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$) δ 161.3, 144.6, 143.3, 137.7, 131.0, 128.7, 128.3, 127.5, 125.9, 125.7, 125.0, 124.5, 122.1, 121.0, 109.8, 52.9, 22.9; IR (neat): 1645, 1613, 1573, 1396, 999, 795, 697 (cm$^{-1}$); MS (EI) m/z: 289.1 ([M+H$^+$])

c) Amination of benzoxazole derivatives with ammonia

The amination of benzoxazole derivatives (0.336 mmol, 1 equiv) with ammonia (0.027 g, 0.403 mmol, 1.2 equiv) was performed analogously to the procedure described in II a). An aqueous solution of ammonia (25%) was used for the reaction. Unless otherwise stated work-up was performed under the same conditions as described in II a) and conditions for the chromatographic purification are given with the corresponding substrate.

Benzo[d]oxazol-2-amine (3t): brown amorphous solid (33 mg, 73%); eluent: DCM : methanol v/v 20:1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35-7.33 (m, 1H), 7.28-7.26 (m, 1H), 7.18 (dt, 1H, $J = 7.7$ and 1 Hz), 7.07 (dt, 1H, $J = 7.7$ and 1 Hz), 5.76 (bs, 2H); $^{13}$C{${^1}$H} NMR (100 MHz, CDCl$_3$) δ 161.8, 148.5, 142.5, 124.0, 121.3, 116.4, 109.0; IR (neat): 3334, 3142, 1658, 1567, 1459, 1399, 1246, 960, 755 (cm$^{-1}$); MS (EI) m/z:134.2 ([M$^+$])

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5-Methylbenzo[d]oxazol-2-amine (3u): yellow amorphous solid (19 mg, 46%); eluent: DCM : methanol v/v 20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.15-7.13 (m, 2H), 6.88-6.86 (m, 1H), 5.48 (bs, 2H), 2.40 (s, 3H); $^{13}$C$^1$H] NMR (100 MHz, CDCl$_3$) $\delta$ 161.8, 146.8, 142.6, 133.7, 122.0, 116.9, 108.3, 21.4; IR (neat): 3017, 1649, 1556, 1379, 1258, 1184, 960, 864, 791, 770, 748, 701 (cm$^{-1}$); MS (EI) m/z: 148.2 ([M]$^+$)

6-Methylbenzo[d]oxazol-2-amine (3v): yellow amorphous solid (23 mg, 54%); eluent: DCM : methanol v/v 20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.15-7.13 (m, 2H), 6.88-6.86 (m, 1H), 5.61 (bs, 2H), 2.40 (s, 3H); $^{13}$C$^1$H] NMR (100 MHz, CDCl$_3$) $\delta$ 161.9, 146.7, 142.7, 133.7, 122.0, 116.8, 108.3, 21.4; IR (neat): 3031, 2222, 1746, 1600, 1342, 1288, 1214, 1050, 882, 774, 693 (cm$^{-1}$); MS (EI) m/z: 148.2 ([M]$^+$)

5-tert-Butylbenzo[d]oxazol-2-amine (3w): red amorphous solid (21 mg, 33%); eluent: DCM : methanol v/v 20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (m, 1H), 7.20-7.17 (m, 1H), 7.12-7.10 (m, 1H), 5.66 (bs, 2H), 1.35 (s, 9H); $^{13}$C$^1$H] NMR (100 MHz, CDCl$_3$) $\delta$ 162.0, 147.5, 146.5, 142.3, 118.5, 113.5, 108.0, 34.8, 31.8; IR (neat): 2951, 2926, 2868, 1689, 1583, 1461, 1353, 1245, 944, 751, 733, 698 (cm$^{-1}$); MS (EI) m/z: 190.2 ([M]$^+$)

5-Chlorobenzo[d]oxazol-2-amine (3x): brown amorphous solid (2 mg, 35%); eluent: DCM : methanol v/v 20:1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (m, 1H), 7.19-7.17 (m, 1H) 7.06-7.03 (m, 1H), 5.53 (bs, 2H); $^{13}$C$^1$H] NMR (100 MHz, CDCl$_3$) $\delta$ 162.5, 147.2, 143.8, 129.5, 121.5, 116.7, 109.6; IR (neat): 3471, 3025, 1688, 1557, 1426, 1381, 1252, 957, 849, 782, 711 (cm$^{-1}$); MS (EI) m/z: 168.0, 170.0, 169.0 ([M]$^+$)
1H and 13C NMR Spectra
**N-butylbenzooxazol-2-amine (3a):**

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**Diagram:**

[Image of the NMR spectrum of N-butylbenzooxazol-2-amine (3a)]
N-iso-propylbenzooxazol-2-amine (3b)
*N-iso*-butylbenzooxazol-2-amine (3c)
\textbf{N-tert-butylnbenzoxazol-2-amine (3d)}

\begin{center}
\includegraphics[width=\textwidth]{image}
\end{center}

\begin{center}
\textbf{ppm (f1)}
\end{center}
N-benzylbenzoxazol-2-amine (3e)
N-(1-phenylethyl)benzooxazol-2-amine (3f)
N-pentylbenzoxazol-2-amine (3g)
N-cyclohexylbenzooxazol-2-amine (3h)
$N$-(bicyclo[2.2.1]heptan-2-yl)benzo[$d$]oxazol-2-amine (3i)
$N$-allylbenzooxazol-2-amine (3j)
$N$-(1-ethynlycyclohexy)benzooxazol-2-amine (3k)
5-methyl-N-(1-phenylethyl)benzooxazol-2-amine (3l)
6-methyl-N-(1-phenylethyl)benzooxazol-2-amine (3m)
5-tert-butyl-N-(1-phenylethyl)benzooxazol-2-amine (3n)
5-Methoxy-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3o)
5-chloro-N-(1-phenylethyl)benzooxazol-2-amine (3p)
5-Fluoro-N-(1-phenylethyl)benzo[d]oxazol-2-amine (3q)
6-Nitro-N-(1-phenylethyl)benzooxazol-2-amine (3r)
$N$-(1-phenylethyl)naphto[2,1-$d$]benzooxazol-2-amine (3s)
Benzooxazol-2-amine (3t)
5-Methylbenzooxazol-2-amine (3u)
6-Methylbenzoxazol-2-amine (3v)
6-Methylbenzoxazol-2-amine (3w)

The diagram shows the chemical structure of 6-Methylbenzoxazol-2-amine (3w) with various ppm values for different chemical shifts.
5-Chlorobenzooxazol-2-amine (3x)
Acquire: 10.06.201 14:03:22
Created: 10.06.201 14:03:23
Project: ROHDATEN
Amount: 0
ISTD Amount: 0
Sample D: 977 TBMDS-diacetyl-beta-CD
Calibrant: 977 TBMDS-diacetyl-beta-CD
Mobile phase: H2
Flow Rate: 
Note: 
Autotag: 60,00, min
Detector: Signal 1
Subtraction chromatogram: (None)
External Start: Start - Restart, Down
Range 1: Bipolar, 1250 mV, 10 Samp per Sec.
Matching: No Change

Result Table (UXRF - nachtsheim 10-Jun-2011 212)

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<th>Height [mV]</th>
<th>Area [mV]</th>
<th>W05 [min]</th>
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<td>10,691</td>
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<td>Total</td>
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<td>78,221</td>
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Acquire: 10.06.2011 10:57:23
Created: 10.06.2011 10:57:24
Project: ROHDATEN
Amount: 0
ISTD Amount: 0
Sample D: 977 TBDMS-diacyetyl-beta-CD
Calibration:

Column: 977 TBDMS-diacyetyl-beta-CD
Mobile Phase: H2
Flow Rate: 1
Pressure: 90 kPa

Autostop: 60.00, min
Detector: Signal 1
Subtraction chromatogram: (None)

Detection: FID
Temperature: 180
Pressure: 90 kPa

External Start: Start - Restart, Down
Range 1: Bipolar, 1250 mV, 10 Samp. per Sec.
Matching: No Change

Result Table (Uncal - E:\DATA\Arbeitskreise\Nachtsheimnachtsheim 10-Jun-2011 209

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<thead>
<tr>
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<th>W05 [min]</th>
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