Supporting Information

Mechanistic Pathways in Amide Activation: Flexible Synthesis of Oxazoles and Imidazoles

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1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. Triflic anhydride was distilled over P$_4$O$_{10}$ prior to use. All other reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F$_{254}$ with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infrared spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ($\nu_{\text{max}}$) are reported in cm$^{-1}$. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker AV-400 or AV-600 spectrometer at 300K. Chemical shifts were given in parts per million (ppm, $\delta$), referenced to the solvent peak of CDCl$_3$, defined at $\delta = 7.26$ ppm ($^1$H NMR) and $\delta = 77.16$ ($^{13}$C NMR). Coupling constants are quoted in Hz ($J$). $^1$H NMR and $^{13}$C splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), sextet (sext), septet (sept). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).
## 2. Optimization

### 2.1. Oxazole

![Chemical Structure](image)

| Entry | Solvent         | Nitrile [equiv.] | T     | t   | Yield<sup>a</sup> |
|-------|-----------------|------------------|-------|-----|-------------------|
| 1     | MeCN (0.02M)    | solvent          | 110°C | 2h  | 63%               |
| 2     | MeCN (0.02M)    | solvent          | rt    | 12h | 27%               |
| 3     | DCM (0.02M)     | 20               | rt    | 12h | 14%               |
| 4     | DCM (0.1M)      | 20               | 40°C  | 2h  | 14%               |
| 5     | DCM (0.1M)      | 40               | 40°C  | 2h  | 26%               |
| 6     | MeCN (0.1M)     | solvent          | 80°C  | 2h  | 64% (59%<sup>b</sup>) |

Reaction conditions: 1a (0.2 mmol), base (2 equiv.), MS 3Å, solvent, triflic anhydride (1.0 equiv.) for 15 min at 0 °C, then lutidine-N-oxide (1.05 equiv.) added and stirred at 80 °C for 2 h. <sup>a</sup>NMR yield using 1,3,5-trimethoxybenzene as internal standard. <sup>b</sup>Isolated yield.
2.2. Imidazole

| Entry | Base      | T          | Solvent  | Yielda |
|-------|-----------|------------|----------|--------|
| 1b    | 2-I-pyr   | 0 to 80 °C | MeCN (0.02M) | 12%    |
| 2     | 2-I-pyr   | 0 to 23 °C | MeCN (0.05M) | 14%    |
| 3     | 2-Cl-pyr  | 0 to 23 °C | MeCN (0.05M) | 23%    |
| 4     | 2-F-pyr   | 0 to 23 °C | MeCN (0.05M) | 37%    |
| 5     | 2-NO₂-pyr | 0 to 23 °C | MeCN (0.05M) | 44%    |
| 6     | 2-NO₂-pyr | –20 to 23 °C | MeCN (0.05M) | 22%    |
| 7     | 2-NO₂-pyr | 0 to 40 °C | MeCN (0.05M) | 27%    |
| 8     | 2-NO₂-pyr | 0 to 23 °C | DCM (0.2M)d | 37%    |
| 9     | 2-NO₂-pyr | 0 to 23 °C | DCE (0.2M)d | 30%    |
| 10    | 2-NO₂-pyr | 0 to 23 °C | PhMe (0.05M)d | 22%    |

Reaction conditions: 1j (0.2 mmol), base (2 equiv.), MS 3Å, solvent, triflic anhydride (2 equiv.) for 2 h. aNMR yield using 1,3,5-trimethoxybenzene as internal standard. bWith 2,6-lutidine N-oxide (1.05 equiv.). cReaction time 14 h. dWith 20 equiv. of nitrile. 2-I-pyr = 2-iodopyridine; 2-Cl-pyr = 2-chloropyridine; 2-F-pyr = 2-fluoropyridine; 2-NO₂-pyr = 2-nitropyridine.
3. Substrates

3.1. General Procedure A (1a–d)

To a solution of the amine (1.00 equiv.), triethylamine (1.00 equiv.), hydroxybenzotriazole (HOBt, 1.00 equiv.) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI*HCl, 1.00 equiv.) in dichloromethane (0.1 M), the corresponding carboxylic acid was added and the resulting solution was stirred at ambient temperature overnight (14 h). After this time, the organic solution was extracted sequentially with 0.5 M aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride. The washed solution was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired compound.

3.2. General Procedure B (1j–m)

To a solution of N-Boc-sarcosine (1.00 equiv.) in anhydrous DCM (0.1M), 1-hydroxybenzotriazole hydrate (HOBt, 1.00 equiv.), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI*HCl, 1.00 equiv.) and triethylamine (1.00 equiv.) were added and stirred until complete dissolution. After this, the secondary amine was added and the solution was stirred for 12 h at 23 °C. The reaction was worked up by the addition of an aqueous solution of HCl (0.5M) in a ratio 4:1 with respect to the solvent. The organic phase was then washed with a saturated aqueous solution of NaHCO₃ in a 4:1 ratio with respect to the solvent and then with brine. The washed solution was dried over anhydrous Na₂SO₄, filtered and the filtrate was concentrated under reduced pressure. The crude residue was dissolved in DCM (0.1M) and trifluoroacetic acid (36.0 equiv.) was added. The resulting solution was stirred for 3 h at 23 °C. After this time, the acid was quenched by the dropwise addition of a saturated aqueous solution of NaHCO₃. The organic phase was then separated and washed with brine, dried over anhydrous Na₂SO₄, filtered and the filtrate was concentrated under reduced pressure. The crude residue was used in the next steps without further purification.
To a solution of the amide (1.00 equiv.) in DCM (0.1M), triethylamine (4.00 equiv.) was added, followed by the corresponding sulfonyl chloride (R₂SO₂Cl) (3.00 equiv.). The mixture was stirred until complete dissolution and then stirred for 3 h at 23 °C. Excess sulfonyl chloride was quenched by the addition of a saturated aqueous solution of NaHCO₃ in a 4:1 ratio with respect to the solvent. The organic phase was separated and subsequently washed with brine. The organic phase was then dried over anhydrous Na₂SO₄, filtered and the filtrate was concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired product.
3.3. Characterization of Substrates

1-(Indolin-1-yl)-2-phenylethan-1-one (1a)

[化合物结构图]

Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.\(^1\)

\(^1\)H-NMR included below.

\(\text{N,N-Diethyl-2-phenylacetamide (1b)}\)

[化合物结构图]

Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.\(^2\)

\(^1\)H-NMR included below.

\(\text{N,N-Dimethyl-2-(4-(trifluoromethyl)phenyl)acetamide (1c)}\)

[化合物结构图]

Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.\(^3\)

\(^1\)H-NMR included below.

\(\text{2-Phenyl-1-(pyrrolidin-1-yl)ethan-1-one (1d)}\)

[化合物结构图]

Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.\(^4\)

\(^1\)H-NMR included below.
**N,N-Dibenzyl-2-((N,4-dimethylphenyl)sulfonamido)acetamide (1j)**

Synthesized following general procedure B; colorless solid; 862 mg (69% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.68–7.64 (m, 2H), 7.42–7.28 (m, 8H), 7.21–7.16 (m, 2H), 4.58 (app d, \(J = 3.6\) Hz, 4H), 3.97 (s, 2H), 2.85 (s, 3H), 2.43 (s, 3H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): δ 167.8, 143.9, 136.9, 136.2, 134.1, 129.8 (2C), 129.2 (2C), 128.8 (2C), 128.4 (2C), 128.0, 127.9 (2C), 127.8, 127.8 (2C), 52.4, 49.8, 48.8, 35.8, 21.7; IR (neat) \(\nu_{\text{max}}\): 3030, 1664, 1599, 1495, 1451, 1423, 1340, 1307, 1216, 1163, 1121, 1089 700; HRMS (ESI\(^+\)): exact mass calculated for \([M+Na]^+\) (C\(_{24}\)H\(_{26}\)N\(_2\)O\(_3\)SNa) requires \(m/z\) 445.1556, found \(m/z\) 445.1556.

**2-((N,4-Dimethylphenyl)sulfonamido)-N,N-diisobutylacetamide (1k)**

Synthesized following general procedure B; light-yellow oil, 348 mg (33% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.69–7.65 (m, 2H), 7.33–7.29 (m, 2H), 3.89 (s, 2H), 3.25 (d, \(J = 7.6\) Hz, 2H), 3.16 (d, \(J = 7.6\) Hz, 2H), 2.79 (s, 3H), 2.42 (s, 3H), 2.02–1.90 (m, 2H), 0.96 (d, \(J = 6.7\) Hz, 6H), 0.86 (d, \(J = 6.7\) Hz, 6H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)): δ 167.5, 143.8, 134.0, 129.8 (2C), 127.8 (2C), 54.7, 53.1, 52.7, 35.6, 27.8, 26.4, 21.7, 20.3, 20.1; IR (neat) \(\nu_{\text{max}}\): 2959, 2930, 1647, 1454, 1338, 1162, 1021, 921, 759, 690; HRMS (ESI\(^+\)): exact mass calculated for \([M+Na]^+\) (C\(_{18}\)H\(_{30}\)N\(_2\)O\(_3\)SNa) requires \(m/z\) 377.1869, found \(m/z\) 377.1861.

**N,N-Dibenzyl-2-((N-methylmethylsulfonamido)acetamide (1l)**

Synthesized following general procedure B; colorless oil, 576 mg (64% yield). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.41–7.30 (m, 6H), 7.21–7.13 (m, 4H), 4.61 (s, 2H), 4.40 (s, 2H), 4.23 (s, 2H), 3.08 (s, 3H), 3.02 (s, 3H); \(^1^3\)C-NMR (150 MHz, CDCl\(_3\)): δ 169.3, 137.3, 136.4, 130.1 (2C), 129.7 (2C), 129.1 (2C), 128.9, 128.6, 127.1 (2C), 52.4, 50.2, 49.8, 39.4, 36.4; IR (neat) \(\nu_{\text{max}}\): 2923, 1657, 1495, 1468, 1324, 1218, 1156, 1139, 1002, 786, 736, 700; HRMS (ESI\(^+\)): exact mass calculated for \([M+Na]^+\) (C\(_{18}\)H\(_{26}\)N\(_2\)O\(_3\)SNa) requires \(m/z\) 369.1243, found \(m/z\) 369.1249.
$N,N$-Dibenzyl-2-((N-methyl-3-nitrophenyl)sulfonamido)acetamide (1m)

![Chemical Structure](image)

Synthesized following general procedure B; yellow solid, 112 mg (44% yield). $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.13–8.08 (m, 1H), 7.70–7.65 (m, 2H), 7.62–7.58 (m, 1H), 7.41–7.29 (m, 6H), 7.18–7.16 (m, 4H), 4.56 (s, 2H), 4.44 (s, 2H), 4.28 (s, 2H), 3.08 (s, 3H); $^{13}$C-NMR (150 MHz, CDCl$_3$): δ 168.5, 143.3, 137.5, 136.6, 134.2, 133.6, 132.5, 131.9, 130.0, 129.5, 129.2, 128.8, 128.5, 127.3, 124.9, 52.4, 50.2, 49.8, 37.1; IR (neat) $\nu_{\text{max}}$: 3359, 3193, 2956, 2921, 2850, 1659, 1632, 1543, 1352; HRMS (ESI$^+$): exact mass calculated for [M+Na]$^+$ ($C_{23}H_{23}N_3O_5SNa$) requires $m/z$ 476.1251, found $m/z$ 476.1248.
4. Products
4.1. Oxazoles

To a stirred solution of amide 1 (1.00 equiv., 0.200 mmol) and 2-iodopyridine (2.00 equiv., 0.400 mmol, 42.5 µl) in the corresponding nitrile (2 mL, 0.1M) was added triflic anhydride (1.00 equiv., 0.200 mmol, 34 µl) at 0°C under an atmosphere of argon. After 15 min, lutidine-N-oxide (1.05 equiv., 0.210 mmol, 23.5 µl) was added and the reaction mixture was heated at 80°C for another 2 h. After cooling to room temperature, the reaction mixture was quenched by the addition of saturated aqueous solution of NaHCO₃ (10 mL), extracted with DCM (2 × 10 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using (heptane/ethyl acetate) to afford the desired products 2.

5-(Indolin-1-yl)-2-methyl-4-phenyloxazole (2a)

Reddish solid, 23 mg (59% yield); ¹H-NMR (400 MHz, CDCl₃): δ 7.74–7.71 (m, 2H), 7.26 (t, J = 7.7 Hz, 2H), 7.18–7.10 (m, 2H), 6.93 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.27 (d, J = 7.8 Hz, 1H), 3.84 (t, J = 8.6 Hz, 2H), 3.15 (t, J = 8.7 Hz, 2H), 2.07 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 157.7, 147.8, 143.3, 131.2, 129.4, 128.4 (2C), 127.5, 127.2, 126.1 (2C), 125.0, 120.1 (2C), 109.2, 52.2, 28.7, 14.4; IR (neat) νₘₐₓ: 3055, 2984, 1733, 1648, 1484, 1374, 1265, 1046, 736, 705, 631; HRMS (ESI⁺): exact mass calculated for [M+H]⁺ (C₁₈H₁₆N₂O) requires m/z 277.1341, found m/z 277.1329.

N,N-Diethyl-2-methyl-4-phenyloxazol-5-amine (2b)

Yellowish oil, 21 mg (44% yield); ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.2 Hz, 1H), 2.99 (q, J = 7.2 Hz, 4H), 2.34 (s, 3H), 0.98 (t, J = 7.2 Hz, 6H); ¹³C-NMR (100 MHz, CDCl₃): δ 156.8, 149.7, 143.3, 132.2, 128.2 (2C), 126.6, 125.8 (2C), 47.6 (2C), 41.5, 13.0 (2C); IR (neat) νₘₐₓ: 2972, 1705, 1634, 1589, 1447, 1344, 1257, 1219, 1147, 1043, 957, 715, 694; HRMS (ESI⁺): exact mass calculated for [M+H]⁺ (C₁₄H₁₈N₂O) requires m/z 231.1497, found m/z 231.1485.
**N,N,2-Trimethyl-4-(4-(trifluoromethyl)phenyl)oxazol-5-amine (2c)**

Colorless oil, 21 mg (39% yield); $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 2.82 (s, 6H), 2.44 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 155.6, 153.5, 136.0, 125.7 (4C), 125.2 (2C), 121.3, 42.3 (2C), 14.2; $^{19}$F-NMR (700 MHz, CDCl$_3$): δ –62.32; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{13}$H$_{13}$N$_2$OF$_3$) requires m/z 271.1058, found m/z 271.1045.

**N,N-Diethyl-4-phenyl-2-propyloxazol-5-amine (2d)**

Yellowish oil, 17 mg (33% yield); $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.28 (t, $J = 7.9$ Hz, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 3.00 (q, $J = 7.2$ Hz, 4H), 1.31 (s, 9H), 0.97 (t, $J = 7.2$ Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 160.3, 149.3, 132.4, 128.1 (2C), 127.3, 126.6, 125.8 (2C), 47.6 (2C), 30.7, 20.7, 13.7, 13.0 (2C); IR (neat) ν$_{\text{max}}$: 3057, 2969, 2873, 1737, 1603, 1497, 1342, 1290, 1181, 1090, 1046, 982, 738, 698; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{16}$H$_{22}$N$_2$O) requires m/z 259.1810, found m/z 259.1800.

**2-(tert-Butyl)-N,N-diethyl-4-phenyloxazol-5-amine (2e)**

Colorless oil, 31 mg (57% yield); $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.27 (t, $J = 7.9$ Hz, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 3.00 (q, $J = 7.2$ Hz, 4H), 1.31 (s, 9H), 0.97 (t, $J = 7.2$ Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 166.1, 149.3, 132.7, 131.3, 128.1 (2C), 126.4, 125.9 (2C), 47.5 (2C), 33.9, 28.3 (3C), 13.0 (2C); IR (neat) ν$_{\text{max}}$: 2972, 2932, 1640, 1604, 1449, 1378, 1087, 978; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{17}$H$_{23}$N$_2$O) requires m/z 273.1967, found m/z 273.1963.
2,4-Diphenyl-5-(pyrrolidin-1-yl)oxazole (2f)

Yellowish oil, 35 mg (60% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J = 7.9\) Hz, 2H), 7.66 (d, \(J = 8.2\) Hz, 2H), 7.37–7.25 (m, 5H), 7.15 (t, \(J = 7.2\) Hz, 1H), 3.31–3.25 (m, 4H), 1.94–1.88 (m, 4H); \(^13\)C-NMR (175 MHz, CDCl\(_3\)): \(\delta\) 153.0, 150.6, 133.0, 129.0, 128.6 (2C), 128.1 (2C), 127.0 (2C), 126.0, 125.3 (2C), 119.7, 50.1 (2C), 25.4 (2C); IR (neat) \(\nu_{\text{max}}\): 2967, 2932, 2872, 1638, 1583, 1497, 1378, 1341, 1289, 1150, 1068, 1043, 1023, 981, 958, 716, 695; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) (C\(_{19}\)H\(_{18}\)N\(_2\)O) requires \(m/z\) 291.1497, found \(m/z\) 291.1491.

4-Phenyl-5-(pyrrolidin-1-yl)-2-(o-tolyl)oxazole (2g)

colorless oil, 27 mg (44% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98–7.92 (m, 1H), 7.79–7.74 (m, 2H), 7.43–7.36 (m, 2H), 7.28–7.26 (m, 2H), 7.26–7.19 (m, 2H), 3.39–3.32 (m, 4H), 2.74 (s, 3H), 2.02–1.95 (m, 4H); \(^13\)C-NMR (175 MHz, CDCl\(_3\)): \(\delta\) 153.7, 150.5, 136.7, 133.4, 131.6, 128.9, 128.2 (2C), 128.0, 127.1, 126.9 (2C), 126.1, 125.9, 119.7, 50.4 (2C), 25.6 (2C), 22.2; IR (neat) \(\nu_{\text{max}}\): 2968, 2925, 2872, 1613, 1498, 1447, 1420, 1039, 768, 724, 700; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) (C\(_{20}\)H\(_{21}\)N\(_2\)O) requires \(m/z\) 305.1648, found \(m/z\) 305.1643.

2-(4-Fluorophenyl)-4-phenyl-5-(pyrrolidin-1-yl)oxazole (2h)

orange oil, 33.1 mg (53% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.01–7.94 (m, 2H), 7.75–7.69 (m, 2H), 7.42–7.36 (m, 2H), 7.26–7.21 (m, 1H), 7.15–7.08 (m, 2H), 3.38–3.3 (m, 4H), 2.02–1.95 (m, 4H); \(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.4 (d, \(J = 249.5\) Hz), 152.5, 150.8, 133.1, 128.3 (2C), 127.4 (d, \(J = 8.4\) Hz, 2C), 127.1 (2C), 126.3, 124.6 (d, \(J = 3.2\) Hz), 119.8, 115.8 (d, \(J = 22.2\) Hz, 2C), 50.3 (2C), 25.6 (2C); \(^19\)F-NMR (659 MHz, CDCl\(_3\)): –111.64; IR (neat) \(\nu_{\text{max}}\): 2954, 2924, 2872, 2853, 1611, 1501, 1446, 1412, 1231, 1155; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) (C\(_{19}\)H\(_{16}\)FN\(_2\)O) requires \(m/z\) 309.1398, found \(m/z\) 309.1389.
To a stirred solution of amide $1b$ (1.0 equiv., 1.5 mmol, 287 mg) and 2-iodopyridine (2.0 equiv., 3.0 mmol, 319 µl) in acetonitrile (15 mL, 0.1M) was added triflic anhydride (1.0 equiv., 1.65 mmol, 466 µl) at 0°C under an atmosphere of argon. After 15 min, lutidine-$N$-oxide (1.05 equiv., 1.58 mmol, 194 µl) was added and the reaction mixture was heated at 80 °C for another 2 h. After cooling to room temperature, the reaction mixture was quenched by the addition of saturated aqueous solution of NaHCO$_3$ (10 mL), extracted with DCM (2 × 10 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using (heptane/ethyl acetate: 10/1) to afford the desired products $2b$ as yellowish oil in 41% yield (141 mg).
4.3. **Imidazoles**

To a cooled (0 °C) solution of the corresponding amide (1.00 equiv.) and 2-nitropyridine (2.00 equiv.) in the appropriate nitrile (0.05M) over activated molecular sieves (3Å), triflic anhydride (2.00 equiv.) was added. The resulting mixture was allowed to stir at 0 °C for 15 min, after which the cooling bath was removed and the reaction mixture was stirred at 23 °C for 2 h. After this time, the mixture was filtered over celite and the molecular sieves were washed with DCM. The resulting filtrate was washed with a saturated aqueous solution of NaHCO$_3$ (4:1 with respect to the solvent) and then with brine. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired compound.

For nitriles solid at 0 °C, DCM was added to the reaction mixture. The corresponding ratios are given below.

**N,N-Dibenzyl-1,2-dimethyl-5-tosyl-1H-imidazol-4-amine (3j)**

![Chemical structure](image)

colorless solid, 39.1 mg (44% yield); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.61–7.57 (m, 2H), 7.30–7.19 (m, 10H), 7.18–7.14 (m, 2H), 4.48 (s, 4H), 3.55 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.5, 147.2, 143.5, 140.7, 139.1 (2C), 129.7 (2C), 128.7 (4C), 128.3 (4C), 126.9 (2C), 126.5 (2C), 111.5, 56.6 (2C), 32.8, 21.6, 13.8; IR (neat) $\nu_{\text{max}}$: 3027, 1597, 1520, 1452, 1406, 1365, 1318, 1152, 1134, 1078, 832, 699; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{26}$H$_{28}$N$_3$O$_2$S) requires m/z 446.1897, found m/z 446.1901.
**N,N-Dibenzyl-1-methyl-2-propyl-5-tosyl-1H-imidazol-4-amine (3k)**

Light-yellow oil, 41.5 mg (44% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56–7.54 (m, 2H), 7.31–7.15 (m, 12H), 4.48 (s, 4H), 3.54 (s, 3H), 2.55 (t, \(J = 7.4\) Hz, 2H), 2.38 (s, 3H), 1.67 (app sext, \(J = 7.6\) Hz, 2H), 0.89 (t, \(J = 7.4\) Hz, 3H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.7, 150.7, 143.4, 140.7, 139.2 (2C), 129.7 (2C), 128.8 (4C), 128.2 (4C), 126.9 (2C), 126.5 (2C), 111.4, 56.8 (2C), 32.4, 29.1, 21.6, 21.1, 13.7; IR (neat) \(\nu_{\text{max}}\): 3358, 3062, 3029, 2959, 2926, 2855, 1721, 1658, 1607, 1524, 1494, 1452, 1395; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) \((C_{28}H_{32}N_3O_2S)\) requires \(m/z\) 474.2210, found \(m/z\) 474.2217.

**N,N-dibenzyl-2-cyclohexyl-1-methyl-5-tosyl-1H-imidazol-4-amine (3l)**

10% v/v DCM were added to the reaction mixture; yellow oil, 39.3 mg (38% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52–7.47 (m, 2H), 7.36–7.32 (m, 4H), 7.29–7.25 (m, 3H), 7.25–7.18 (m, 3H), 7.15–7.11 (m, 2H), 4.48 (s, 4H), 3.52 (s, 3H), 2.52 (tt, \(J = 11.4, 3.6\) Hz, 1H), 2.38 (s, 3H), 1.89–1.80 (m, 2H), 1.80–1.70 (m, 3H), 1.69–1.57 (m, 2H), 1.37–1.28 (m, 3H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.8, 154.1, 143.2, 140.8, 139.4 (2C), 129.7 (2C), 129.1 (4C), 128.1 (4C), 126.8 (2C), 126.4 (2C), 110.9, 56.9 (2C), 36.1, 31.9, 31.0 (2C), 26.1 (2C), 25.8, 21.6; IR (neat) \(\nu_{\text{max}}\): 3511, 3452, 3359, 2923, 2851, 1657, 1632, 1522, 1494, 1467, 1451, 1421, 1373; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) \((C_{31}H_{38}N_3O_2S)\) requires \(m/z\) 514.2523, found \(m/z\) 514.2524.
\textit{N,N-Dibenzyl-1-methyl-2-phenyl-5-tosyl-\textit{IH}-imidazol-4-amine (3m)}

yellow solid, 64.2 mg (63\% yield); \textit{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\textit{): }\delta 7.65–7.61 (m, 2H), 7.53–7.48 (m, 2H), 7.48–7.43 (m, 3H), 7.36–7.32 (m, 4H), 7.31–7.27 (m, 3H), 7.27–7.20 (m, 3H), 7.20–7.16 (m, 2H), 4.54 (s, 4H), 3.66 (s, 3H), 2.39 (s, 3H); \textit{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\textit{): }\delta 156.9, 149.3, 143.7, 140.5, 139.1 (2C), 130.0, 129.8 (2C), 129.7 (2C), 129.4, 128.9 (4C), 128.8 (2C), 128.3 (4C), 127.0 (2C), 126.7 (2C), 113.3, 56.7 (2C), 34.7, 21.7; \textit{IR (neat) }\nu_{\text{max}}\textit{: }3367, 3061, 3030, 2924, 2851, 1745, 1712, 1684, 1615, 1493, 1032, 1011; \textit{HRMS (ESI\textsuperscript{+}): }exact mass calculated for [M+H]\textsuperscript{+} (C\textsubscript{31}H\textsubscript{30}N\textsubscript{3}O\textsubscript{2}S) requires \(m/z\) 508.2053, found \(m/z\) 508.2060.

\textit{N,N-dibenzyl-2-(4-fluorophenyl)-1-methyl-5-tosyl-\textit{IH}-imidazol-4-amine (3n)}

55\% v/v DCM were added to the reaction mixture; yellow oil, 53.5 mg (51\% yield); \textit{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\textit{): }\delta 7.65–7.60 (m, 2H), 7.51–7.46 (m, 2H), 7.34–7.29 (m, 4H), 7.29–7.25 (m, 3H), 7.25–7.10 (m, 7H), 4.51 (s, 4H), 3.63 (s, 3H), 2.38 (s, 3H); \textit{\textsuperscript{13}C-NMR (100 MHz, CDCl}_3\textit{): }\delta 163.7 (d, \textit{J} = 250 Hz), 156.8, 148.3, 143.8, 140.5, 139.0 (2C), 131.7 (d, \textit{J} = 8.7 Hz, 2C), 129.9 (2C), 128.9 (4C), 128.3 (4C), 127.0 (2C), 126.7 (2C), 125.5 (d, \textit{J} = 3.5 Hz), 116.0 (d, \textit{J} = 11.0 Hz, 2C), 113.4, 56.7 (2C), 34.7, 21.7; \textit{IR (neat) }\nu_{\text{max}}\textit{: }3362, 3198, 2921, 2851, 1658, 1632, 1467, 736, 703; \textit{HRMS (ESI\textsuperscript{+}): }exact mass calculated for [M+H]\textsuperscript{+} (C\textsubscript{31}H\textsubscript{29}FN\textsubscript{3}O\textsubscript{2}S) requires \(m/z\) 526.1959, found \(m/z\) 526.1957.
**N,N-dibenzyl-1-methyl-5-tosyl-2-(4-(trifluoromethyl)phenyl)-1H-imidazol-4-amine (3o)**

70% v/v DCM were added to the reaction mixture; yellow oil, 25.1 mg (22% yield); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.75–7.70 (m, 2H), 7.67–7.63 (m, 4H), 7.36–7.18 (m, 12H), 4.53 (s, 4H), 3.69 (s, 3H), 2.30 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.7, 147.5, 143.9, 140.3, 139.0 (2C), 134.0 (q, $J = 5.7$ Hz), 132.9, 130.1, 129.9, 128.9 (4C), 128.7 (q, $J = 38.1$ Hz, 2C), 128.3 (4C), 127.1 (2C), 126.7 (2C), 125.7 (q, $J = 3.7$ Hz, 2C), 121.2 (q, $J = 262.2$ Hz), 114.2, 56.8 (2C), 34.8, 21.7; $^{19}$F-NMR (659 MHz, CDCl$_3$): $\delta$ –62.90; IR (neat) $\nu_{\text{max}}$: 3361, 2921, 2851, 1658, 1632, 1614, 1520, 1452, 1365, 1158, 700, 683; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{32}$H$_{32}$F$_3$N$_3$O$_2$S) requires $m/z$ 576.1927, found $m/z$ 576.1922.

**N,N-Dibenzyl-1-methyl-2-(p-tolyl)-5-tosyl-1H-imidazol-4-amine (3p)**

70% v/v DCM were added to the reaction mixture; light-yellow oil, 60.5 mg (58% yield); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.64–7.59 (m, 2H), 7.41–7.37 (m, 2H), 7.35–7.31 (m, 4H), 7.29–7.14 (m, 10H), 4.53 (s, 4H), 3.63 (s, 3H), 2.38 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.9, 149.5, 143.6, 140.6, 140.1, 139.1 (2C), 129.8 (2C), 129.5 (2C), 129.4 (2C), 128.9 (4C), 128.2 (4C), 126.9 (2C), 126.6 (2C), 126.4, 113.0, 56.7 (2C), 34.7, 21.7, 21.5; IR (neat) $\nu_{\text{max}}$: 3360, 2921, 2851, 1658, 1632, 1614, 1452, 1365, 1158, 700, 683; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{32}$H$_{32}$N$_3$O$_2$S) requires $m/z$ 522.2210, found $m/z$ 522.2208.
N,N-Dibenzyl-2-(4-(tert-butyl)phenyl)-1-methyl-5-tosyl-1H-imidazol-4-amine (3q)

10% v/v DCM were added to the reaction mixture; yellow oil, 49.5 mg (44% yield); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.65–7.60 (m, 2H), 7.47–7.44 (m, 3H), 7.35–7.31 (m, 4H), 7.30–7.21 (m, 7H), 7.19–7.16 (m, 2H), 4.54 (s, 4H), 3.66 (s, 3H), 2.39 (s, 3H), 1.33 (s, 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 157.0, 153.3, 149.5, 143.6, 140.7, 139.2 (2C), 129.8 (2C), 129.4 (2C), 128.9 (4C), 128.2 (4C), 126.9 (2C), 126.6 (2C), 126.5, 125.8 (2C), 112.9, 56.7 (2C), 35.0, 34.7, 31.3 (3C), 21.9; IR (neat) $\nu_{max}$: 3359, 2922, 2852, 1659, 1632, 1467, 1422, 1265, 736, 703; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{35}$H$_{38}$N$_3$O$_2$S) requires m/z 564.2679, found m/z 564.2673.

N,N-Diisobutyl-1-methyl-2-phenyl-5-tosyl-1H-imidazol-4-amine (3r)

colorless oil, 44.8 mg (51% yield); $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.76–7.72 (m, 2H), 7.55–7.51 (m, 2H), 7.46–7.42 (m, 4H), 7.29–7.26 (m, 2H), 3.67 (s, 3H), 3.27 (d, $J = 7.3$ Hz, 4H), 2.41 (s, 3H), 1.91 (sept, $J = 6.7$ Hz, 2H), 0.81 (d, $J = 6.7$ Hz, 12H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.6, 150.1, 143.3, 141.5, 132.9, 129.9, 129.8 (2C), 129.7 (2C), 128.7 (2C), 125.3 (2C), 108.8, 59.8 (2C), 35.0, 27.0 (2C), 21.6, 20.4 (4C); IR (neat) $\nu_{max}$: 3360, 2959, 1649, 1460, 1263, 1164, 918, 747; HRMS (ESI$^+$): exact mass calculated for [M+H]$^+$ (C$_{25}$H$_{34}$N$_3$O$_2$S) requires m/z 440.2366, found m/z 440.2374.
**N,N-Dibenzyl-1,2-dimethyl-5-(methylsulfonyl)-1H-imidazol-4-amine (3s)**

![Chemical Structure](image)

Colorless oil, 36.8 mg (47% yield); **^1H-NMR (400 MHz, CDCl₃):** δ 7.29–7.22 (m, 8H), 7.22–7.16 (m, 2H), 4.37 (s, 4H), 3.66 (s, 3H), 2.86 (s, 3H), 2.35 (s, 3H); **^13C-NMR (150 MHz, CDCl₃):** δ 154.9, 146.9, 138.8 (2C), 128.8 (4C), 128.4 (4C), 127.1 (2C), 113.8, 56.5 (2C), 44.9, 33.0, 13.8; **IR (neat):** νₓ max: 2921, 2851, 1520, 1494, 1452, 1406, 1362, 1305, 1149, 1121, 950, 760, 741, 699; **HRMS (ESI⁺):** exact mass calculated for [M+H]^+ (C₂₀H₂₃N₃O₂SNa) requires m/z 392.1403, found m/z 392.1408.

**N,N-Dibenzyl-1-methyl-5-(methylsulfonyl)-2-phenyl-1H-imidazol-4-amine (3t)**

![Chemical Structure](image)

Yellow oil, 39.7 mg (46% yield); **^1H-NMR (400 MHz, CDCl₃):** δ 7.59–7.55 (m, 2H), 7.53–7.47 (m, 3H), 7.36–7.19 (m, 10H), 4.46 (s, 4H), 3.80 (s, 3H), 2.99 (s, 3H); **^13C-NMR (100 MHz, CDCl₃):** δ 155.3, 149.2, 138.9 (2C), 130.0, 129.7 (2C), 129.3, 129.0 (4C), 128.9 (2C), 128.4 (4C), 127.2 (2C), 115.6, 56.7 (2C), 44.9, 34.9; **IR (neat):** νₓ max: 2956, 2923, 2853, 1520, 1494, 1467, 1453, 1398, 1365, 1312, 1266, 1155, 951, 735, 700; **HRMS (ESI⁺):** exact mass calculated for [M+H]^+ (C₂₅H₂₆N₃O₂S) requires m/z 432.1740, found m/z 432.1740.
yellow oil, 47.2 mg (50% yield); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.60–7.53 (m, 2H), 7.35–7.17 (m, 12H), 4.45 (s, 4H), 3.78 (s, 3H), 3.00 (s, 3H); \(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.8 (d, \(J = 250.0\) Hz), 155.2, 148.2, 138.8 (2C), 131.8 (d, \(J = 8.2\) Hz, 2C), 129.0 (4C), 128.4 (4C), 127.2 (2C), 125.5 (d, \(J = 3.5\) Hz), 116.1 (d, \(J = 21.9\) Hz, 2C), 115.5, 56.6 (2C), 45.0, 34.9; IR (neat) \(\nu_{\text{max}}\): 2920, 2851, 1526, 1458, 1376, 1314, 1263, 1230, 1156, 1121, 952, 844, 742, 702; HRMS (ESI\(^+\)): exact mass calculated for [M+H]\(^+\) (C\(_{25}\)H\(_{20}\)FN\(_3\)O\(_2\)Na) requires m/z 472.1465, found m/z 472.1471.
5. NMR Spectra

5.1. Substrates
5.2. Products – Oxazoles

![Chemical Structure](image)

![Chemical Structure](image)
5.3. Products – Imidazoles
6. Computational Details

All structures were optimized at the B3LYP-D3/6-31+G(d,p) level of theory.\textsuperscript{[5–7]} The nature of all stationary points (minima and transition states) was verified through computation of the vibrational frequencies. The thermal corrections to the Gibbs free energy were combined with single point energies calculated at the RI-MP2/def2-TZVP//B3LYP-D3/6-31+G(d,p) level\textsuperscript{[8]} to yield Gibbs free energies ($G_{298}$) at 298.15 K (all energies are reported in kcal mol$^{-1}$). The density-based solvation model SMD\textsuperscript{[9]} (for geometry optimization) and Conductor-like screening model COSMO\textsuperscript{[10]} (for RI-MP2 single-point calculations) were applied to consider solvent effects. The DFT calculations have been performed with the Gaussian09 program package,\textsuperscript{[11]} whereas for the RI-MP2 single point calculations the Turbomole V7.0 program package\textsuperscript{[12]} was used. Computed structures were visualized using the Chemcraft software.\textsuperscript{[13]}

Cartesian coordinates (the most stable ($\Delta G_{298,MeCN}$) conformations as computed at the RI-MP2-COSMO/def2-TZVP//B3LYP-D3-SMD/6-31+G(d,p) level of theory

|   |  |  |  |
|---|---|---|---|
| A | -1.968644 | -1.135411 | -0.990484 |
| S | -1.910880 | -2.599398 | -1.130261 |
| O | -1.697321 | -0.271881 | -2.150752 |
| N | -0.761738 | -0.726827 | 0.184677  |
| C | 1.548718  | 0.256933  | -2.129401 |
| C | -0.617514 | 0.662157  | 0.430442  |
| N | -0.907537 | 0.808489  | -1.349576 |
| O | 0.201349  | 2.825481  | -0.412198 |
| C | -0.713754 | 3.535589  | 0.480558  |
| C | 1.511252  | 3.471630  | -0.579213 |
| N | 0.907537  | 0.808489  | -1.349576 |
| N | 2.086429  | 2.986162  | -1.369642 |
| H | -1.158826 | 1.093721  | 1.266404  |
| C | 0.957373  | 0.808489  | -1.349576 |
| N | 0.201349  | 2.825481  | -0.412198 |
| C | 0.713754  | 3.535589  | 0.480558  |
| C | 1.511252  | 3.471630  | -0.579213 |
| H | 2.086429  | 2.986162  | -1.369642 |
| H | 1.345404  | 4.511173  | -0.868278 |
| H | 2.091302  | 3.446183  | 0.354103  |
| H | -1.729805 | 3.152089  | 0.354772  |
| H | -0.422536 | 3.439529  | 1.536896  |
| H | -0.699689 | 4.592770  | 0.208890  |
| C | 2.327948  | -0.442520 | -3.112215 |
| H | 3.291010  | -0.729477 | -2.677552 |

S50
C -2.410167  1.207371  1.590613  H  -3.668208  -0.740084  3.143254
C  -3.323353  0.081382  1.399061  H  -3.068725  -2.812892  0.240225
C  -3.001595  2.546222  1.575493  H  -1.347206  -3.091975  0.633241
H  -2.229382  3.306096  1.676624  H  -2.622579  -3.650276  1.750681
H  -3.531386  2.696683  0.629159  C  1.118306  -2.076683  3.754195
H  -3.715343  2.645942  2.400315  H  0.170613  -1.869921  4.250919
H  -3.040213  -0.503495  0.516538  H  1.387235  -3.127826  3.903827
H  -3.324956  -0.574490  2.276620  H  1.909742  -1.460472  4.189389
H  -4.329206  0.473234  1.251450  C  2.071354  0.169323  0.070825
C  1.783171  3.362964  1.789939  C  2.894232  1.016222  0.819089
H  1.413367  3.979008  2.610081  C  0.943617  0.649041  -0.600356
H  2.746219  2.916763  2.063234  C  2.556731  2.366282  0.917239
H  1.948412  3.980801  0.900805  H  3.771960  0.634317  1.333899
C  1.387192  -0.601993  -1.136088  C  0.626639  2.000165  -0.493912
C  0.142975  -0.287581  -1.705241  H  0.323041  -0.029445  -1.175963
C  2.242900  -1.562661  -1.697828  C  1.420141  2.876248  0.269937
C  -0.220873  -0.932721  -2.884855  H  3.179982  3.029203  1.510454
H  -0.508146  0.453946  -1.259247  H  -0.255360  2.383553  -1.000166
C  1.852672  -2.182612  -2.879219  C  1.043835  4.330287  0.385802
H  3.191265  -1.807364  -1.231094  H  1.162210  4.839878  -0.578277
H  0.620311  -1.882516  -3.489318  C  -0.006429  4.438372  0.679136
H  -1.174060  -0.690152  -3.345272  H  1.664253  4.849142  1.121570
H  2.513062  -2.913859  -3.336214  C  -0.052762  2.152933  3.706351
C  0.229182  -2.552098  -4.778785  H  -1.051569  2.590321  3.838558
H  0.724618  -2.059661  -5.625552  H  0.436385  2.047604  4.681715
H  0.539723  -3.601629  -4.787849  H  0.572171  2.828537  3.111598
H  -0.850041  -2.500073  -4.947099
C  1.277712  -1.755664  2.449244
H  2.367176  -1.814171  2.417559
H  0.955887  -1.825030  3.490950
H  0.836373  -2.579224  1.876888

C
S  2.541951  -1.561668  -0.052237
O  2.204849  -2.029880  1.669661
O  1.574111  -2.227458  -0.972954
N  -0.055904  0.857345  3.057084
C  1.031797  -1.808856  2.282224
C  -1.169673  0.355246  2.706916
C  -1.170214  -0.978454  2.033763
H  -2.128377  0.853322  2.863984
N  -0.006378  -1.490796  1.602768
N  -2.307712  -1.575555  1.740199
C  -2.330200  -2.868448  1.043077
C  -3.628312  -1.012274  2.087964
H  -3.846415  -0.143080  1.462454
H  -4.374734  -1.782399  1.901066

TSC-D
S  5.246464  5.614071  -3.648532
O  6.215379  6.543697  -2.413440
O  3.986627  6.386167  -3.862885
N  7.355237  4.325876  -1.046927
C  6.137983  6.087881  -1.164925
C  6.548731  3.580568  -0.418470
C  5.189843  4.199149  -0.245836
H  6.806003  2.599261  -0.025929
N  5.052945  5.389743  -0.790036
N  4.186028  3.589702  0.379234
C  2.906854  4.297212  0.499427
C  4.173098  2.175314  0.763853
H  5.160913  1.727008  0.697047
H  3.819677  2.094958  1.794597
H  3.489275  1.627083  0.106999
H  3.074118  5.323676  0.831168
H  2.392332  4.315564  -0.468322
H  2.287979  3.773663  1.228057
C  6.937822  6.918871  -0.201635

S52
C  4.283448  -0.456497  0.548108  H  -1.565238  -2.217794  -1.969382
H  4.757944  -1.785077  -1.085719  H  0.078272  -1.183280  1.767844
H  3.465277   0.822149   2.083471  H  -0.313397  -2.883195  1.438204
C  5.722536  -0.257694  0.953599  H  1.028933  -2.098622  0.569003
H  5.801998   0.330278   1.874225  C  -4.385815   1.515734  -1.183314
H  6.221772  -1.219697   1.178200  H  -5.178615   1.610893  -0.431847
H  6.280519   0.265133   0.169080  H  -4.171673   2.520763  -1.562022
C  -3.775675  -1.436568  -0.253541  H  -4.730520   0.875867  -1.995226
H  -3.164222  -2.333911  -0.141774  C  1.543450   0.685249  -0.103980
H  -4.573156  -1.435832   0.492441  C  2.380082   0.576136  1.011221
H  -4.189336  -1.374205  -1.258316  C  1.765091  -0.054474  -1.270875
      C  3.462911  -0.297505   0.947245
      H  2.192447   1.163571   1.903700
      C  2.853740  -0.922069  -1.310089
      O  0.403638   2.845999   0.959640
      O  -0.280271   2.121560  -1.397635
      C  -2.504362   1.549519   0.429411
      H  -3.171872   0.935878  -0.563235
      C  -1.328625   0.778379   0.722634
      C  -1.603662  -0.467295  -0.092516
      H  -1.113834   0.670937   1.785674
      H  -2.663580  -0.261211  -0.902749
      N  -0.907148  -1.581510  -0.070490
      C  0.035424  -1.945961   0.994316
      C  -1.193901  -2.648181  -1.040996
      H  -0.264906  -3.189900  -1.226617
      H  -1.939747  -3.333509  -0.625616
7. X-Ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture diffractometer equipped with multilayer monochromators, Cu Kα INCOATEC micro focus sealed tube and Kryoflex II cooling device. The structures were solved by *direct methods* and refined by *full-matrix least-squares techniques*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with a riding model respectively as rotating groups. The following software was used: *Bruker SAINT software package*\(^{14}\) using a narrow-frame algorithm for frame integration, *SADABS*\(^{15}\) for absorption correction, *OLEX2*\(^{16}\) for structure solution, refinement, molecular diagrams and graphical user-interface, *Shelxle*\(^{17}\) for refinement and graphical user-interface *SHELXS-2013*\(^{18}\) for structure solution, *SHELXL-2013*\(^{19}\) for refinement, *Platon*\(^{20}\) for symmetry check. Experimental data and CCDC-Codes can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2, 3, 4 and 5. Molecular structures in “Ortep View” are displayed in Figure 1 and 2.

**Table 1** Experimental parameter and CCDC-Code.

| Sample | Machine | Source | Temp. | Detector Distance | Time/Frame | #Frames | Frame width | CCDC  |
|--------|---------|--------|-------|-------------------|------------|---------|-------------|-------|
| 2a     | D8      | Cu     | 100   | 40                | 50         | 1672    | 0.7         | 1537944 |
| 3j     | D8      | Cu     | 100   | 40                | 2          | 2910    | 0.8         | 1553624 |
5-(Indolin-1-yl)-2-methyl-4-phenyloxazole [2a] for “Organic letters”.

Figure 1 Crystal structure of [2a], drawn with 50% displacement ellipsoids. Bond precision: C-C = 0.0020Å.

Table 2 Data collection and structure refinement of [2a].

| Index ranges          | Theta range for data collection [°] | Data / restraints / parameters | Final R indices | Theta range for data collection [°] |
|-----------------------|-------------------------------------|--------------------------------|-----------------|-------------------------------------|
| Reflections number    | -14 ≤ h ≤ 14, -8 ≤ k ≤ 8, -19 ≤ l ≤ 19 | 10676                          | 2670/0/191      | 11.164 to 144.136                   |
| Refinement method     | Least squares                       | Data / restraints / parameters | Final R indices | R1 = 0.0515, wR2 = 0.0923           |
| Function minimized    | Σ w(Fo² - Fc²)²                      |                               | R1 = 0.0385, wR2 = 0.0870 |
| Goodness-of-fit on F² | 1.024                               |                               | R1 = 0.0385, wR2 = 0.0870 |
| Largest diff. peak and hole [e Å⁻³] | 0.19/-0.20                          |                               | R1 = 0.0385, wR2 = 0.0870 |

where P = (Fo² + 2Fc²)/3
Table 3 Sample and crystal data of [2a].

| Chemical formula | C18H16N2O | Crystal system | monoclinic |
|------------------|------------|----------------|------------|
| Formula weight [g/mol] | 276.33 | Space group | P21/c |
| Temperature [K] | 100 | Z | 4 |
| Measurement method | f and w scans | Volume [Å³] | 1371.97(9) |
| Radiation (Wavelength [Å]) | CuKα (λ = 1.54178) | Unit cell dimensions [Å] and [°] | 12.1454(5) | 90 |
| Crystal size / [mm³] | 0.332 × 0.042 × 0.019 | 7.1266(2) | 97.206(3) |
| Crystal habit | clear colourless needle | 15.9769(6) | 90 |
| Density (calculated) / [g/cm³] | 1.338 | Absorption coefficient / [mm⁻¹] | 0.664 |
| Abs. correction Tmin | 0.6614 | Abs. correction Tmax | 0.7536 |
| Abs. correction type | multi-scan | F(000) [e⁻] | 584 |
$N,N$-Dibenzyl-1,2-dimethyl-5-tosyl-$1H$-imidazol-4-amine [3j] for “Organic letters”.

Figure 2  Crystal structure of [3j], drawn with 50% displacement ellipsoids. Bond precision: C-C=0.0020Å.
Table 4 Sample and crystal data of [3j].

| Chemical formula | C26H27N3O2S | Crystal system | triclinic |
|------------------|--------------|----------------|-----------|
| Formula weight [g/mol] | 445.56 | Space group | P-1 |
| Temperature [K] | 100 | Z | 2 |
| Measurement method | γf and γw scans | Volume [Å³] | 1117.35(19) |
| Radiation (Wavelength [Å]) | CuKα (λ = 1.54178) | Unit cell dimensions [Å] and [°] | 9.3234(9) | 78.305(3) |
| Crystal size / [mm³] | 0.816 × 0.561 × 0.404 | | 9.9427(10) | 78.596(3) |
| Crystal habit | clear brown block | | 13.0102(13) | 73.067(3) |
| Density (calculated) / [g/cm³] | 1.324 | Absorption coefficient / [mm⁻¹] | 1.513 |
| Abs. correction Tmin | 0.5616 | Abs. correction Tmax | 0.7536 |
| Abs. correction type | multi-scan | F(000) [e⁻] | 472 |

Table 5 Data collection and structure refinement of [3g].

| Index ranges | -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16 | Theta range for data collection [°] | 10.028 to 145.794 |
|--------------|------------------------------------------|---------------------------------|-------------------|
| Reflections number | 17436 | Data / restraints / parameters | 4389/0/292 |
| Refinement method | Least squares | Final R indices | all data | R1 = 0.0375, wR2 = 0.0947 |
| Function minimized | Σ w(Fo² - Fc²)² | | I>2σ(I) | R1 = 0.0365, wR2 = 0.0939 |
| Goodness-of-fit on F² | 1.069 | Weighting scheme | w=1/[σ²(Fo²)+(0.0466P)²+0.5788P] |
| Largest diff. peak and hole [e Å⁻³] | 0.45/-0.47 | | where P=(Fo²+2Fc²)/3 |
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