Supplementary Information for

Atom economical synthesis of N-alkylbenzamides via iron(III)
sulfate catalyzed rearrangement of 2-alkyl-3-aryloxaziridines in
water and in the presence of surfactant

Jamil Kraiem\textsuperscript{a,b,*} and Thierry Ollevier\textsuperscript{a,*}

\textsuperscript{a} Département de chimie, Université Laval, 1045 avenue de la Médecine, Québec (QC), G1V 0A6, Canada.

\textsuperscript{b} Laboratoire de Développement Chimique, Galénique et Pharmacologique des Médicament, Faculté de Pharmacie de Monastir, Université de Monastir, Rue Avicenne, 5000 Monastir, Tunisia.

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General methods

NMR spectra were acquired using CDCl$_3$ as solvent, running at 300 and 400 MHz for $^1$H, and at 75 and 100 MHz for $^{13}$C. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CHCl$_3$, 7.28 ppm and H$_2$O 1.61 ppm for $^1$H NMR; CDCl$_3$, 76.5 ppm for $^{13}$C NMR). In all $^1$H NMR spectra, multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constant values (in Hertz) and number of protons for each signal are also indicated. The IR spectra were recorded on Perkin-Elmer FT-IR spectrometer. Melting points were determined on a Büchi SMP-20 capillary apparatus and are uncorrected. TLC was carried out on Merck 60F-254 precoated silica gel plates (0.25 mm). Dimethyl carbonate (Reagent plus®, 99%), hydrogen peroxide (30 % wt in water), were purchased from Sigma-Aldrich. All starting materials purchased from commercial suppliers were used without further purification, except alkyamines and aromatic aldehydes which were distilled or recrystallized (solid reagents) before use.

Synthesis of N-alkyloxaziridines

$N$-Alkyloxaziridines were prepared according to the green method developed by our group.$^1$ General procedure: To a solution of the aldehyde (1 mmol) in DMC (1 mL) was added the $N$-alkylamine (1.5 mmol). The mixture was stirred for 10 mn. A 5 mmol of hydrogen peroxide solution (30 % wt) was then added over a period of 5 mn. The mixture was stirred at room temperature until disappearance of aldehyde (15 h, reaction monitored by TLC). Then, the mixture was washed with 3 mL of aqueous saturated solution of sodium sulfite, centrifuged (5 mn, 4000 rpm, Figure 1) to separate the organic and the aqueous phases, and further extracted with 2×1 mL of DMC (we extracted the oxaziridine with 2 mL of DMC instead of 11 mL of ethyl acetate$^1$). The combined organic phases were concentrated under reduced pressure to yield pure oxaziridine.

$N$-tert-Butyloxaziridines 1a-f were obtained in the trans-isomer form (100%)$^1$. Oxaziridines with smaller substituents (1g-q) were obtained as mixtures of trans and cis-isomers (trans/cis ratio: from 92:8 to 88:12). Oxaziridines 1a,$^1$ 1b,$^2$ 1c,$^3$ 1d,$^1$ 1e,$^4$ 1f,$^3$ 1g,$^1$ 1h,$^5$ 1i,$^5$ 1j,$^6$ 1k,$^1$ 1l,$^1$ 1m,$^7$ 1n,$^8$ 1o,$^4$ 1p,$^9$ and 1q$^1$ are known compounds.
Synthesis of \( N \)-alkylbenzamides

General procedure: A mixture of \( H_2O \) (1 mL), \( Fe_2(SO_4)3.5H_2O \) (2.5 mol%), SDS (15 mol%) was stirred for 5 mn at room temperature. After that, oxaziridine (0.5 mmol) was added and the reaction was stirred in a 5 mL sealed vial at 70 °C until disappearance of the oxaziridine (TLC). After completion of the reaction, the mixture was extracted with 3×1 mL portions of ethyl acetate, filtered through a short pad of silica gel and concentrated under reduced pressure to yield pure \( N \)-alkylbenzamide.

\( N \)-Alkylbenzamides \( 2a, 10 \), \( 2b, 10 \), \( 2c, 10 \), \( 2d, 11 \), \( 2e, 12 \), \( 2f, 11 \), \( 2g, 11 \), \( 2h, 13 \), \( 2i, 13 \), \( 2j, 14 \), \( 2k, 11 \), \( 2l, 15 \), \( 2m, 15 \), \( 2n, 16 \), \( 2o, 17 \), \( 2p, 18 \) and \( 2q, 18 \) are known compounds.

\( N \)-(tert-Butyl)benzamide \( 2a \): According to the general procedure, the product was isolated as white solid (m.p. = 134–135 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 3332 (NH), 1643 (C=O); \( \delta_H \) (400 MHz; CDCl\(_3\)) 7.70 (2 H, m), 7.45–7.37 (3 H, m), 5.97 (1 H, br s), 1.46 (9 H, s); \( \delta_C \) (100 MHz; CDCl\(_3\)) 166.9, 135.8, 131.0, 128.4, 126.6, 51.5, 28.8.

\( N \)-(tert-Butyl)-4-methoxybenzamide \( 2b \): According to the general procedure, the product was isolated as white solid (m.p. = 117–118 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 3330 (NH), 1646 (C=O); \( \delta_H \) (400 MHz; CDCl\(_3\)) 7.67 (2 H, d, \( J = 8.8 \) Hz), 6.88 (2 H, d, \( J = 8.8 \) Hz), 5.89 (1 H, br s), 3.82 (3 H, s), 1.45 (9 H, s); \( \delta_C \) (100 MHz; CDCl\(_3\)) 166.4, 161.8, 128.4, 128.1, 113.5, 55.3, 51.4, 28.9.

4-Bromo-\( N \)-(tert-butyl)benzamide \( 2c \): According to the general procedure, the product was isolated as yellow solid (m.p. = 130–131 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1}\) 3355 (NH), 1652 (C=O); \( \delta_H \) (300 MHz; CDCl\(_3\)) 7.60–7.54 (4H, m), 5.99 (1 H, br s), 1.47 (9 H, s); \( \delta_C \) (75 MHz; CDCl\(_3\)) 165.9, 134.7, 131.6, 128.3, 125.6, 51.7, 28.8.
**N-( tert-Butyl)-4-nitrobenzamide 2d:** According to the general procedure, the product was isolated as yellow solid (m.p. = 157–158 °C); ν_max (KBr)/cm⁻¹ 3330 (NH), 1643 (C=O); δ_H (300 MHz; CDCl₃) 8.22 (2 H, d, J = 8.7 Hz), 7.87 (2 H, d, J = 8.7 Hz), 6.16 (1 H, br s), 1.48 (9 H, s); δ_C (75 MHz; CDCl₃) 164.9, 149.2, 141.5, 127.9, 123.6, 52.2, 28.7.

**N-( tert-Butyl)-2-chlorobenzamide 2e:** According to the general procedure, the product was isolated as yellow solid (m.p. = 109–110 °C); ν_max (KBr)/cm⁻¹ 3385 (NH), 1651 (C=O); δ_H (400 MHz; CDCl₃) 7.58–7.5 (1 H, m), 7.35–7.26 (3 H, m), 5.92 (1 H, br s), 1.46 (9 H, s); δ_C (100 MHz; CDCl₃) 165.8, 136.4, 130.7, 130.3, 130.0, 129.6, 126.9, 52.1, 28.7.

**N-( tert-Butyl)picolinamide 2f:** According to the general procedure, the product was isolated as yellow solid (m.p. = 36–37 °C); ν_max (KBr)/cm⁻¹ 3383 (NH), 1677 (C=O); δ_H (300 MHz; CDCl₃) 8.52–8.49 (1 H, m), 8.19–8.15 (1 H, m), 8.0 (1 H, br), 7.85–7.79 (1 H, m), 7.43–7.36 (1 H, m), 1.49 (9 H, s); δ_C (75 MHz; CDCl₃) 163.3, 150.7, 147.7, 137.3, 125.8, 121.6, 50.8, 28.7.

**N-Cyclohexylbenzamide 2g:** According to the general procedure, the product was isolated as white solid (m.p. = 153–154 °C); ν_max (KBr)/cm⁻¹ 3322 (NH), 1677 (C=O); δ_H (300 MHz; CDCl₃) 7.78–7.77 (2 H, m), 7.49–7.40 (3 H, m), 6.13 (1H, br), 4.03–3.93 (1H, m), 2.05–1.18 (10 H, m); δ_C (75 MHz; CDCl₃) 166.6, 135.0, 131.2, 128.4, 126.8, 48.6, 33.2, 25.5, 24.9.

**N-Cyclohexyl-4-methoxybenzamide 2h:** According to the general procedure, the product was isolated as white solid (m.p. = 160–162 °C); ν_max (KBr)/cm⁻¹ 3315 (NH), 1639 (C=O); δ_H (300 MHz; CDCl₃) 7.73 (2 H, d, J = 8.1 Hz), 6.92 (2 H, d, J = 8.1 Hz), 6.01 (1H, br), 4.10–3.85 (1H, m), 3.85 (3 H, s), 2.05–1.18 (10 H, m); δ_C (75 MHz; CDCl₃) 166.1, 161.9, 128.5, 127.3, 113.6, 55.3, 48.6, 33.2, 25.5, 24.9.

**4-Chloro-N-Cyclohexylbenzamide 2i:** According to the general procedure, the product was isolated as yellow solid (m.p. = 188–190 °C); ν_max (KBr)/cm⁻¹ 3305 (NH), 1631 (C=O); δ_H (300 MHz; CDCl₃) 7.70 (2 H, d, J = 8.4 Hz), 7.38 (2 H, d, J = 8.4 Hz), 6.14 (1H, br), 4.05–3.88 (1H, m), 2.03–1.17 (10 H, m); δ_C (75 MHz; CDCl₃) 165.5, 137.3, 133.4, 128.6, 128.3, 48.8, 33.1, 25.5, 24.9.
\textit{N-Cyclohexyl-2-nitrobenzamide 2j}: According to the general procedure, the product was isolated as yellow solid (m.p. = 156–157 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3411 (NH), 1660 (C=O); \( \delta_{\text{H}} \) (300 MHz; CDCl\(_3\)) 8.06 (2 H, m), 7.69–7.50 (3 H, m), 5.82 (1H, br), 3.99 (1H, m), 2.11–1.22 (10 H, m); \( \delta_{\text{C}} \) (75 MHz; CDCl\(_3\)) 165.6, 146.3, 133.6, 133.3, 130.2, 124.4, 49.0, 32.7, 25.4, 24.8.

\textit{N-Isopropylbenzamide 2k}: According to the general procedure, the product was isolated as white solid (m.p. = 101–103 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 13290 (NH), 1630 (C=O); \( \delta_{\text{H}} \) (400 MHz; CDCl\(_3\)) 7.55–7.53 (2 H, m), 7.45–7.38 (3 H, m), 6.12 (1 H, br s), 4.32–4.20 (1 H, m), 1.23 (6 H, d, \( J = 6.8 \) Hz); \( \delta_{\text{C}} \) (100 MHz; CDCl\(_3\)) 166.7, 134.9, 131.1, 128.4, 126.8, 41.8, 22.7.

\textit{N-Isopropyl-4-methoxybenzamide 2l}: According to the general procedure, the product was isolated as white solid (m.p. = 119–120 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 13290 (NH), 1635 (C=O); \( \delta_{\text{H}} \) (300 MHz; CDCl\(_3\)) 7.73 (2 H, d, \( J = 8.7 \) Hz), 6.90 (2 H, d, \( J = 8.7 \) Hz), 6.01 (1 H, br s), 4.31–4.24 (1 H, m), 3.84 (3 H, s), 1.25 (6 H, d, \( J = 6.6 \) Hz); \( \delta_{\text{C}} \) (75 MHz; CDCl\(_3\)) 166.2, 161.9, 128.5, 127.2, 113.6, 55.3, 41.7, 22.8.

\textit{N-Isopropyl-4-nitrobenzamide 2m}: According to the general procedure, the product was isolated as yellow solid (m.p. = 150–152 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3275 (NH), 1630 (C=O); \( \delta_{\text{H}} \) (300 MHz; CDCl\(_3\)) 8.25 (2 H, d, \( J = 8.4 \) Hz), 7.92 (2 H, d, \( J = 8.7 \) Hz), 6.33 (1 H, br s), 4.34–4.23 (1 H, m), 1.28 (6 H, d, \( J = 6.6 \) Hz); \( \delta_{\text{C}} \) (75 MHz; CDCl\(_3\)) 164.7, 149.3, 140.5, 128.1, 123.6, 42.4, 22.6.

\textit{N-(sec-Butyl)benzamide 2n}: According to the general procedure, the product was isolated as white solid (m.p. = 87–90 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3285 (NH), 1632 (C=O); \( \delta_{\text{H}} \) (300 MHz; CDCl\(_3\)) 7.77 (2 H, m), 7.48–7.40 (3 H, m), 6.14 (1 H, br s), 4.19–4.05 (1 H, m), 1.62–1.53 (2 H, m), 1.22 (3 H, d, \( J = 6.3 \) Hz), 0.96 (3 H, t, \( J = 7.2 \) Hz); \( \delta_{\text{C}} \) (75 MHz; CDCl\(_3\)) 166.9, 135.0, 131.2, 128.4, 126.8, 47.1, 29.7, 20.4, 10.4.

\textit{N-(3-Methylbutan-2yl)benzamide 2o}: According to the general procedure, the product was isolated as white solid (m.p. = 73–75 °C); \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3290 (NH), 1635 (C=O); \( \delta_{\text{H}} \) (300 MHz; CDCl\(_3\)) 7.78–7.75 (2 H, m), 7.49–7.39 (3 H, m), 6.11 (1 H, br s), 4.14–4.02 (1 H, m), 0.98 (3 H, d, \( J = 6.9 \) Hz), 0.96 (3 H, d, \( J = 6.9 \) Hz); \( \delta_{\text{C}} \) (75 MHz; CDCl\(_3\)) 166.8, 135.2, 131.1, 128.4, 126.7, 50.4, 33.1, 18.6, 18.5, 17.6.
**N-(n-Butyl)benzamide 2p:** The product was recrystallized in *n*-hexane and isolated as white solid (m.p. = 39–41 °C); $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3290 (NH), 1635 (C=O); $\delta_{\text{H}}$ (300 MHz; CDCl$_3$) 7.77 (2 H, m), 7.48–7.40 (3 H, m), 6.47 (1 H, br s), 3.47–3.41 (2 H, m), 1.62–1.34 (4 H, m), 0.94 (3 H, t, $J$ = 6.9 Hz); $\delta_{\text{C}}$ (75 MHz; CDCl$_3$) 167.7, 134.7, 131.2, 128.4, 126.8, 39.8, 31.7, 20.1, 13.8.

**N-(n-Propyl)benzamide 2q:** The product was recrystallized in *n*-hexane and isolated as white solid (m.p. = 83–84 °C); $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3270 (NH), 1630 (C=O); $\delta_{\text{H}}$ (300 MHz; CDCl$_3$) 7.78 (2 H, d, $J$ = 7.5 Hz), 7.50–7.41 (3 H, m), 6.31 (1 H, br s), 3.43 (2 H, q, $J$ = 6.6 Hz), 1.65 (2 H, q, $J$ = 7.2 Hz), 1.00 (3 H, t, $J$ = 7.2 Hz); $\delta_{\text{C}}$ (75 MHz; CDCl$_3$) 167.6, 134.8, 131.2, 128.5, 126.8, 41.7, 22.9, 11.4.
(E)-2-(tert-butyl)-3-(2-chlorophenyl)oxaziridine 1e
(E) and (Z)-2-isopropyl-3-(4-nitrophenyl)oxaziridines 1m
(E: 92% and Z: 8%)
\[
(E) = [(R,R,R)+(S,S,S)] + [(R,S,S)+(S,R,R)]
\]
\[
(Z) = [(R,S,R)+(S,S,R)] + [(R,R,S)+(S,S,R)]
\]
N-isopropyl-4-methoxybenzamide 21
References