Supporting Information

Efficient Ring Opening Reaction of Protected and Unprotected Aziridines Promoted by Stable Zinc Selenolate in Ionic Liquid


Experimental Section

General Procedures. $^1$H and $^{13}$C NMR spectra were recorded with tetramethylsilane as internal standard. Column chromatography was performed using Merck Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF$_254$, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. THF was dried over sodium and distilled over benzophenone prior to use. Chloroform was distilled from phosphorus pentoxide. All other solvents were used as purchased unless otherwise noted.

General procedure for the synthesis of 2. In a schlenk flask, under argon atmosphere, PhSeZnBr (0.5 mmol) and aziridine (0.5 mmol) were stirred in (BMIM)BF$_4$ (1 mL) at 90°C for 1 h. After this time, the mixture was cooled to room temperature and the $\beta$-seleno amines were extracted from (BMIM)BF$_4$ with Et$_2$O (3x 10 mL) and dried over MgSO$_4$. The solvent was then removed, yielding the crude products 2a-g, which were purified by column chromatography.

General procedure for recycle of the ionic liquid. After the work-up, the ionic liquid was recovered, dissolved in 5 mL of CH$_2$Cl$_2$ and filtered through a celite pad to remove the inorganic salts. Then, it was subjected to the vacuum for 60 min before using. For the next run, the procedure was identical to that mentioned above.

(S)-tert-butyl 1-phenyl-3-(phenylselenyl)propan-2-ylcarbamate 2a. Yield: 81%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.51-7.48 (m, 2H), 7.29-7.12 (m, 8H), 4.70-4.66 (br, 1H), 4.09-4.06 (m, 1H), 3.04-3.01 (m, 2H), 2.87-2.82 (m, 2H), 1.38 (s, 9H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 154.96, 137.48, 132.74, 129.29, 129.09, 128.68, 128.40, 126.99, 126.44, 80.98, 38.21, 32.77, 28.24, 27.81.

(S)-tert-butyl 3-methyl-1-(phenylselenyl)butan-2-ylcarbamate 2b. Yield: 60%; $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 7.55-7.50 (m, 2H), 7.26-7.23 (m, 3H), 4.60-4.55 (br, 1H), 3.69-3.59 (m, 1H), 3.07 (d, $J$ = 5.6 Hz, 2H), 1.94-1.77 (m, 1H), 1.42 (s, 9H), 0.91-0.87 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.54, 132.93, 129.05, 126.99, 79.10, 55.64, 32.41, 31.69, 28.33, 19.43, 17.97.

(S)-4-methyl-N-(1-phenyl-3-(phenylselenyl)propan-2-yl)benzenesulfonamide 2c. Yield: 99%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.43-7.39 (m, 4H), 7.27-7.09 (m, 9H), 6.93-6.91 (m, 2H), 4.69 (d, $J$ = 7.2 Hz, 1H), 3.55-3.48 (m, 1H), 3.12 (dd, $J^2$ = 12.6 Hz, $J^3$ = 4.4 Hz, 1H), 2.94 (dd, $J^2$ = 13.8 Hz, $J^3$ = 6.4 Hz, 1H), 2.83 (dd, $J^2$ = 12.6 Hz, $J^3$ = 6.8 Hz, 1H), 2.76 (dd, $J^2$ = 14.0 Hz, $J^3$ = 6.8 Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 143.13, 136.79, 136.45, 132.92, 129.51, 129.24, 128.61, 127.29, 126.96, 126.72, 54.49, 40.29, 32.87, 21.47.

(S)-4-methyl-N-(3-methyl-1-(phenylselanyl)butan-2-yl)benzenesulfonamide 2d. Yield: 90%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.62\) (d, \(J = 8.4\) Hz, 2H), 7.37-7.35 (m, 2H), 7.26-7.17 (m, 5H), 4.82 (d, \(J = 6.4\) Hz, 1H), 3.23-3.17 (m, 1H), 3.06 (dd, \(J^2 = 12.8\) Hz, \(J^3 = 4.8\) Hz, 1H), 2.74 (dd, \(J^2 = 12.6\) Hz, \(J^3 = 6.6\) Hz, 1H), 2.38 (s, 3H), 2.01-1.93 (m, 1H), 0.81 (d, \(J = 6.8\) Hz, 3H), 0.76 (d, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 143.19, 137.65, 133.07, 129.54, 129.15, 127.29, 127.05, 58.57, 31.64, 30.68, 21.49, 19.01\).

(S)-4-methyl-N-(4-methyl-1-(phenylselanyl)pentan-2-yl)benzenesulfonamide 2e. Yield: 85%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.60\) (d, \(J = 8.4\) Hz, 2H), 7.42-7.40 (m, 2H), 7.29-7.21 (m, 3H), 7.18 (d, \(J = 8.4\) Hz, 2H), 4.86 (d, \(J = 8.4\) Hz, 1H), 3.46-3.38 (m, 1H), 3.10 (dd, \(J^2 = 12.4\) Hz, \(J^3 = 3.6\) Hz, 1H), 2.73 (dd, \(J^2 = 12.8\) Hz, \(J^3 = 6.8\) Hz, 1H), 2.38 (s, 3H), 1.48-1.36 (m, 2H), 1.29-1.23 (m, 1H), 0.77 (d, \(J = 6.4\) Hz, 3H), 0.59 (d, \(J = 6.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 142.19, 137.65, 133.19, 129.52, 129.08, 127.23, 126.98, 51.54, 43.82, 34.65, 24.30, 22.76, 21.52, 21.43\).

(S)-3-methyl-1-(phenylselanyl)butan-2-amine 2f. Yield: 70%; \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 7.53-7.48\) (m, 2H), 7.25-7.22 (m, 3H), 3.18-3.11 (m, 1H), 2.83-2.64 (m, 2H), 1.77-1.65 (m, 1H), 1.56 (s, 2H), 0.92 (d, \(J = 2.6\) Hz, 3H), 0.89 (d, \(J = 2.6\) Hz, 3H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 132.53, 130.08, 128.95, 126.75, 56.06, 35.04, 33.33, 19.15, 15.62\).

(S)-4-methyl-1-(phenylselanyl)pentan-2-amine 2g. Yield: 52%; \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 7.53-7.48\) (m, 2H), 7.25-7.22 (m, 3H), 3.12-3.02 (m, 1H), 2.98-2.89 (m, 1H), 2.80-2.71 (m, 1H), 1.75-1.65 (m, 1H), 1.60 (s, 2H), 1.28 (t, \(J = 7.0\) Hz, 2H), 0.88-0.82 (m, 6H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 132.62, 130.06, 128.92, 126.76, 48.51, 46.75, 38.07, 24.94, 23.05, 21.98\).

Se-phenyl selenobenzoate 3. Yield: 35%; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.91\) (d, \(J = 7.2\) Hz, 2H), 7.59-7.55 (m, 3H), 7.46-7.39 (m, 5H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 193.18, 138.46, 136.23, 133.78, 129.26, 128.85, 127.23, 125.74\).

Benzyl(phenyl)selane 4. Yield: 94%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.50-7.42\) (m, 2H), 7.28-7.14 (m, 8H), 4.10 (s, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 138.60, 133.53, 130.40, 128.94, 128.82, 128.39, 127.26, 126.82, 32.21\).

Butyl(phenyl)selane 5. Yield: 73%; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.49-7.45\) (m, 2H), 7.26-7.18 (m, 3H), 2.90 (t, \(J = 7.6\) Hz, 2H), 1.71-1.64 (m, 2H), 1.46-1.37 (m, 2H), 0.90 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 132.42, 130.82, 129.02, 126.62, 32.32, 27.66, 23.02, 13.64\).
NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) Spectrum of 2a.

$^1$H NMR (50 MHz, CDCl$_3$) Spectrum of 2a.
$^1$H NMR (200 MHz, CDCl$_3$) Spectrum of 2b.

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectrum of 2b.
$^1$H NMR (400 MHz, CDCl$_3$) Spectrum of 2c.

$^{13}$C NMR (400 MHz, CDCl$_3$) Spectrum of 2c.
\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{)} \text{ Spectrum of 2d.} \]

\[ ^{13}C \text{NMR (400 MHz, CDCl}_3\text{)} \text{ Spectrum of 2d.} \]
$^1$H NMR (400 MHz, CDCl$_3$) Spectrum of 2e.

$^{13}$C NMR (400 MHz, CDCl$_3$) Spectrum of 2e.
$^1$H NMR (200 MHz, CDCl$_3$) Spectrum of 2f.

$^{13}$C NMR (200 MHz, CDCl$_3$) Spectrum of 2f.
$^1$H NMR (200 MHz, CDCl$_3$) Spectrum of 2g.

$^{13}$C NMR (200 MHz, CDCl$_3$) Spectrum of 2g.
$^1$H NMR (400 MHz, CDCl$_3$) Spectrum of 3.

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectrum of 3.
1H NMR (400 MHz, CDCl₃) Spectrum of 4.

13C NMR (100 MHz, CDCl₃) Spectrum of 4.
$^1$H NMR (400 MHz, CDCl$_3$) Spectrum of 5.

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectrum of 5.