Supporting Information

**Na₃PO₄-catalyzed aminochlorination reaction of β-nitrostyrenes in water**

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1. General information

All aminohalogenation reactions were performed in vials at room temperature without protection of inert gases. BocNCl$_2$ was prepared according to the reported methods. The other chemicals were used as obtained from commercial sources without further purification. Flash chromatography was performed using silica gel 60 (200-300 mesh). Thin layer chromatography was carried out on silica gel 60 F-254 TLC plates of 20 cm × 20 cm. Melting points are uncorrected. IR spectra were collected on Bruker Vector 22 in KBr pellets. $^1$H and $^{13}$C NMR (TMS used as internal standard) spectra were recorded with a Bruker ARX 300 spectrometer. High resolution mass spectra for all the new compounds were done by Micromass Q-Tof instrument (ESI).

2. Aminochlorination of β-nitrostyrenes with BocNCl$_2$

Into a reaction vial were taken β-nitrostyrenes (0.5 mmol), Na$_3$PO$_4$·12H$_2$O (0.1 mmol), BocNCl$_2$ (1.25 mmol), MeCN (1.6 mL) and H$_2$O (3.2 mL). The reaction mixture was stirred at room temperature for 12 min, and then the reaction was quenched with saturated Na$_2$SO$_3$ (3.0 mL). The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried with anhydrous Na$_2$SO$_4$, filtered and the solvent was removed to give the crude product, which was purified by TLC plate (hexane/EtOAc, 8:1).

Tert-butyl 2,2-dichloro-2-nitro-1-phenylethylcarbamate (3a): white solid, yield 88%, mp 105-106 °C. $^1$H NMR (CDCl$_3$, 300 MHz): δ = 7.42 (s, 5 H), 5.99 (d, $J$ = 10.5 Hz, 1 H), 5.56 (d, $J$ = 10.5 Hz, 1 H), 1.45 (s, 9 H).
Tert-butyl 2,2-dichloro-1-(2-methoxyphenyl)-2-nitroethylcarbamate (3b): white solid, yield 97%, mp 152-154 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.33$-$7.42$ (m, 2 H), 6.94-7.03 (m, 2 H), 6.28 (d, $J = 10.5$ Hz, 1 H), 6.08 (d, $J = 9.6$ Hz, 1 H), 3.88 (s, 3 H), 1.46 (s, 9 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 157.7$, 154.3, 130.9, 130.6, 120.8, 116.5, 112.8, 111.6, 81.0, 61.0, 55.6, 28.2. IR (KBr): $\nu = 3253$, 3142, 2978, 1697, 1585, 1365, 1249, 1160, 756 cm$^{-1}$. HRMS [M+Na$^+$]: calcd for C$_{14}$H$_{18}$N$_2$O$_5$Cl$_2$Na: 387.0485, found: 387.0490.

Tert-butyl 2,2-dichloro-1-(2-chlorophenyl)-2-nitroethylcarbamate (3c): white solid, yield 98%, mp 168-170 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.48$-$7.51$ (m, 2 H), 7.33-7.40 (m, 2 H), 6.75 (d, $J = 10.2$ Hz, 1 H), 5.58 (d, $J = 10.2$ Hz, 1 H), 1.44 (s, 9 H).

Tert-butyl 2,2-dichloro-1-(3-fluorophenyl)-2-nitroethylcarbamate (3d): white solid, yield 87%, mp 115-117 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 7.35$-$7.43$ (m, 1 H), 7.10-7.24 (m, 3 H), 5.99 (d, $J = 8.7$ Hz, 1 H), 5.55 (s, 1 H), 1.45 (s, 9 H).
**Tert-butyl 2,2-dichloro-1-(3-chlorophenyl)-2-nitroethylcarbamate (3e):**
white solid, yield 73%, mp 136-138 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ = 7.33-7.45 (m, 4 H), 5.97 (d, \(J = 9.3\) Hz, 1 H), 5.58 (s, 1H), 1.45 (s, 9 H).

**Tert-butyl 1-(3-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (3f):**
white solid, yield 86%, mp 152-154 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ = 7.55-7.60 (m, 2 H), 7.39 (d, \(J = 7.2\) Hz, 1 H), 7.31 (d, \(J = 7.8\) Hz, 1 H), 5.96 (d, \(J = 9.0\) Hz, 1 H), 5.57 (d, \(J = 8.7\) Hz, 1 H), 1.45 (s, 9 H).

**Tert-butyl 2,2-dichloro-2-nitro-1-p-tolylethylcarbamate (3g):**
white solid, yield 83%, mp 108-110 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): δ = 7.32 (d, \(J = 7.8\) Hz, 2 H), 7.23 (d, \(J = 8.4\) Hz, 2 H), 5.95 (d, \(J = 9.9\) Hz, 1 H), 5.58 (d, \(J = 9.0\) Hz, 1 H), 2.38 (s, 3 H), 1.45 (s, 9 H).

**Tert-butyl 2,2-dichloro-1-(4-methoxyphenyl)-2-nitroethylcarbamate (3h):**
white solid,
yield 77%, mp 113-114 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta = 7.35 \) (d, \( J = 8.7 \) Hz, 2 H), 6.93 (d, \( J = 9.0 \) Hz, 2 H), 5.93 (d, \( J = 9.3 \) Hz, 1 H), 5.54 (d, \( J = 9.9 \) Hz, 1 H), 3.83 (s, 3 H), 1.45 (s, 9 H).

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\begin{align*}
\text{\textbf{N}} & \text{\textbf{O}} \text{\textbf{2}} \\
\text{\textbf{C}} & \text{\textbf{Cl}} \text{\textbf{Cl}} \\
\text{\textbf{N}} & \text{\textbf{H}} \\
\text{\textbf{O}} & \text{\textbf{O}} \\
\text{\textbf{F}} & \text{\textbf{3}} \\
\end{align*}
\]

\(T\text{ert-butyl 2,2-dichloro-1-(4-fluorophenyl)-2-nitroethylcarbamate (3i): white solid, yield 85\%, mp 109-110 °C.}\) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta = 7.40-7.44 \) (m, 2 H), 7.08-7.13 (m, 2 H), 5.97 (d, \( J = 9.6 \) Hz, 1 H), 5.55 (d, \( J = 9.9 \) Hz, 1 H), 1.44 (s, 9 H).

\[
\begin{align*}
\text{\textbf{N}} & \text{\textbf{O}} \text{\textbf{2}} \\
\text{\textbf{C}} & \text{\textbf{Cl}} \text{\textbf{Cl}} \\
\text{\textbf{N}} & \text{\textbf{H}} \\
\text{\textbf{O}} & \text{\textbf{O}} \\
\text{\textbf{Cl}} & \text{\textbf{Cl}} \\
\end{align*}
\]

\(T\text{ert-butyl 2,2-dichloro-1-(4-chlorophenyl)-2-nitroethylcarbamate (3j): white solid, yield 94\%, mp 101-102 °C.}\) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta = 7.38 \) (s, 4 H), 5.96 (d, \( J = 8.7 \) Hz, 1 H), 5.54 (s, 1 H), 1.44 (s, 9 H).

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\begin{align*}
\text{\textbf{N}} & \text{\textbf{O}} \text{\textbf{2}} \\
\text{\textbf{C}} & \text{\textbf{Cl}} \text{\textbf{Cl}} \\
\text{\textbf{N}} & \text{\textbf{H}} \\
\text{\textbf{O}} & \text{\textbf{O}} \\
\text{\textbf{Br}} & \text{\textbf{Cl}} \\
\end{align*}
\]

\(T\text{ert-butyl 1-(4-bromophenyl)-2,2-dichloro-2-nitroethylcarbamate (3k): white solid, yield 78\%, mp 106-107 °C.}\) \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta = 7.57 \) (d, \( J = 8.4 \) Hz, 2 H), 7.32 (d, \( J = 8.4 \) Hz, 2 H), 5.95 (d, \( J = 9.9 \) Hz, 1 H), 5.52 (s, 1 H), 1.44 (s, 9 H).
Tert-butyl 2,2-dichloro-2-nitro-1-(4-(trifluoromethyl)phenyl)ethylcarbamate (3i): white solid, yield 84%, mp 118-119 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.70\) (d, \(J = 8.4\) Hz, 2 H), 7.60 (d, \(J = 8.1\) Hz, 2 H), 6.06 (d, \(J = 9.0\) Hz, 1 H), 5.60 (d, \(J = 9.3\) Hz, 1 H), 1.44 (s, 9 H).

Tert-butyl 2,2-dichloro-1-(4-cyanophenyl)-2-nitroethylcarbamate (3m): white solid, yield 96%, mp 129-130 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.74\) (d, \(J = 7.5\) Hz, 2 H), 7.60 (d, \(J = 5.7\) Hz, 2 H), 6.04 (d, \(J = 5.1\) Hz, 1 H), 5.63 (d, \(J = 4.8\) Hz, 1 H), 1.43 (s, 9 H).

Tert-butyl 1-(3-bromo-4-methoxyphenyl)-2,2-dichloro-2-nitroethylcarbamate (3n): white solid, yield 90%, mp 169-171 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 7.62\) (s, 1 H), 7.34 (d, \(J = 7.2\) Hz, 1 H), 6.92 (d, \(J = 8.7\) Hz, 1 H), 5.91 (d, \(J = 7.8\) Hz, 1 H), 5.51 (d, \(J = 7.8\) Hz, 1 H), 3.92 (s, 3 H), 1.45 (s, 9 H).

Tert-butyl 2,2-dichloro-1-(naphthalen-1-yl)-2-nitroethylcarbamate (3o): white solid, yield 61%, mp 198-199 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 8.40\) (d, \(J = 6.6\) Hz, 1 H),
7.97 (t, \( J = 8.4 \text{ Hz}, 2 \text{ H} \)), 7.64-7.72 (m, 2 H), 7.52-7.60 (m, 2 H), 7.06 (d, \( J = 8.7 \text{ Hz}, 1 \text{ H} \)), 5.70 (d, \( J = 9.0 \text{ Hz}, 1 \text{ H} \)), 1.42 (s, 9 H).

3. Aminochlorination of β-nitrostyrene with BocNH\(_2\) and NCS

Into a reaction vial were taken β-nitrostyrenes (0.5 mmol), Na\(_3\)PO\(_4\)-12H\(_2\)O (0.1 mmol), BocNH\(_2\) (1.5 mmol), NCS (1.5 mmol), MeCN (1.6 mL) and H\(_2\)O (3.2 mL). The reaction mixture was stirred at room temperature for 48 h, and then the reaction was quenched with saturated Na\(_2\)SO\(_3\) (3.0 mL). The organic layer was taken and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were dried with anhydrous Na\(_2\)SO\(_4\), filtered and the solvent was removed to give the crude product, which was purified by TLC plate (hexane/EtOAc, 8:1).

Reference

4. $^1$H and $^{13}$C NMR spectra for compound 3

$^1$H NMR of 3a
$^1$H NMR of 3b

$^{13}$C NMR of 3b
$^1$H NMR of 3c

$^1$H NMR of 3d
$^1$H NMR of 3e

$^1$H NMR of 3f
$^1$H NMR of 3g

$^1$H NMR of 3h
$^1$H NMR of 3i

$^1$H NMR of 3j
$^1$H NMR of 3k

$^1$H NMR of 3l
$^1$H NMR of 3m

$^1$H NMR of 3n