Spirocyclization of Alkyne-Tethered Aromatics with Silver Nitrate/Silica

**Indoles:**

\[
\begin{align*}
\text{R}^1 & = \text{Ph}, \text{R}^2 = \text{H}, 24 \text{ h, } 94\% \text{ yield} \\
\text{R}^1 & = \alpha-\text{Pr}, \text{R}^2 = \text{H}, 2 \text{ h, r.t., } 98\% \text{ yield} \\
\text{R}^1 & = 4-\text{MeOC}_6\text{H}_4, \text{R}^2 = \text{OMe}, 24 \text{ h, } 40 \text{ °C, } 86\% \text{ yield}
\end{align*}
\]

**Phenols:**

\[
\begin{align*}
\text{R}^1 + \text{Ph}, \text{R}^2 = \text{H}, 24 \text{ h, } 40 \text{ °C, } 94\% \text{ yield} \\
\text{R}^1 = \alpha-\text{Pr}, \text{R}^2 = \text{H}, 2 \text{ h, r.t., } 98\% \text{ yield} \\
\text{R}^1 = 4-\text{MeOC}_6\text{H}_4, \text{R}^2 = \text{OMe}, 24 \text{ h, } 40 \text{ °C, } 86\% \text{ yield}
\end{align*}
\]

**Pyrroles:**

\[
\begin{align*}
\text{R} & = \text{Ph}, 90\% \text{ yield} \\
\text{R} & = 4-\text{MeOC}_6\text{H}_4, 91\% \text{ yield} \\
\text{R} & = 4-\text{FC}_6\text{H}_4, 96\% \text{ yield} \\
\text{R} & = \text{n-Bu}, 91\% \text{ yield}
\end{align*}
\]

**Significance:** Silica-supported silver nitrate (AgNO\(_3\)/SiO\(_2\)) catalyzed the dearomatizing spirocyclization of alkyne-tethered aromatics to give the corresponding spirocycles in 86–100% yield (eqs. 1–4).

**Comment:** The continuous-flow reaction of 1-(1\(H\)-indol-3-yl)-4-phenylbut-3-yn-2-one on a column of AgNO\(_3\)/SiO\(_2\) gave 5-phenyl-3\(H\)-spiro[cyclopent-4-ene-1,3\(H\)·indol]-3-one in quantitative yield (eq. 5).