Synthesis of Thioamides via One-Pot $A^3$-Coupling of Alkynyl Bromides, Amines, and Sodium Sulfide

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A. General method

Melting points were measured with a melting point instrument and were uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker Avance (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. GC-MS was obtained using electron ionization (EI). High-resolution mass spectra were obtained with a LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF$_{254}$) and visualization was effected at 254 nm. All reagents were obtained from commercial suppliers and used without further purification.

B. General procedure for the synthesis of products

\[
\begin{align*}
R^1\text{=C\text{-}}X + HN^R_2 + Na_2S\cdot9H_2O \xrightarrow{80-110^\circ C, 8h, DMF} R^1S-N^R_2
\end{align*}
\]

A mixture of alkynyl halide (1.0 mmol), amine (1.5 mmol), and Na$_2$S·9H$_2$O (1.5 mmol) in DMF (2.5 mL) was placed in a sealed tube (25 mL) equipped with a magnetic stirring bar. The mixture was stirred at 80 °C (or 110 °C) for 8h. After the reaction was completed, the mixture was washed with brine and extracted with ethyl acetate. The organic layer was dried with anhydrous MgSO$_4$, concentrated in vacuo and purified by flash silica gel chromatography using petroleum ether/ethyl acetate 15:1 to give the desired products.
C. NMR Spectra

$^1$H-NMR and $^{13}$C-NMR of 3a
$^1$H-NMR and $^{13}$C-NMR of 3b
$^1$H-NMR and $^{13}$C-NMR of 3c
$^1$H-NMR and $^{13}$C-NMR of 3d
$^1$H-NMR and $^{13}$C-NMR of 3e
$^1$H-NMR and $^{13}$C-NMR of 3f
$^1$H-NMR and $^{13}$C-NMR of 3g
$^1$H-NMR and $^{13}$C-NMR of 3h
$^1$H-NMR and $^{13}$C-NMR of 3i
$^1$H-NMR and $^{13}$C-NMR of 3j
$^1$H-NMR and $^{13}$C-NMR of 3k
$^1$H-NMR and $^{13}$C-NMR of 3l
$^1$H-NMR and $^{13}$C-NMR of 3m
$^1$H-NMR and $^{13}$C-NMR of 4b
$^1$H-NMR and $^{13}$C-NMR of 4c
$^1$H-NMR and $^{13}$C-NMR of 4d
$^1$H-NMR and $^{13}$C-NMR of 4e
$^1$H-NMR and $^{13}$C-NMR of 4f
$^1$H-NMR and $^{13}$C-NMR of 4g
$^1$H-NMR and $^{13}$C-NMR of 4h
$^1$H-NMR and $^{13}$C-NMR of 4i

![NMR Spectra](image)

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$^1$H-NMR and $^{13}$C-NMR of 4j
$^1$H-NMR and $^{13}$C-NMR of 4k
$^{1}H$-NMR and $^{13}C$-NMR of 4l
$^1$H-NMR and $^{13}$C-NMR of 4m
$^1$H-NMR and $^{13}$C-NMR of 4n
$^1$H-NMR and $^{13}$C-NMR of 4o
$^1$H-NMR and $^{13}$C-NMR of 4p
$^1$H-NMR and $^{13}$C-NMR of 5a
$^1$H-NMR and $^{13}$C-NMR of 5b
$^1$H-NMR and $^{13}$C-NMR of 5c
$^1$H-NMR and $^{13}$C-NMR of 5d
$^1$H-NMR and $^{13}$C-NMR of 5e
$^1$H-NMR and $^{13}$C-NMR of 5f
$^1$H-NMR and $^{13}$C-NMR of 5g
$^1$H-NMR and $^{13}$C-NMR of 5h
$^1$H-NMR and $^{13}$C-NMR of 5i
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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$^1$H-NMR and $^{13}$C-NMR of 7

![NMR Spectra](image-url)
$^1$H-NMR and $^{13}$C-NMR of [D]$_n$-3a