Cs$_2$CO$_3$-promoted C(sp$^2$)-N formations of dimethyl thiocarbamate-protected indoles using tetramethylthiuram monosulfide (TMTM)

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Experimental Section

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Yields refer to isolated compounds estimated to be >95% pure as determined by $^1$H NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 NMR instrument in CDCl$_3$ TMS as an internal standard. Chemical shifts are given in ppm and coupling constants ($J$) are given in Hz. All melting points were determined on a RY-1G melting point instrument without correction. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 95Q or Finnigan 90 mass instrument (ESI). TLC was performed using aluminum plates coated with SiO$_2$ (Merck 60, F-254) and visualized with UV light at 254 nm. Column chromatography was performed on silica gel (200-300 mesh) with petroleum ether-EtOAc as eluent.

Typical procedure (TP) for reaction of 1$H$-indoles with tetramethylthiuram monosulfide (TMTM).

1$H$-indoles (0.5 mmol), tetramethylthiuram monosulfide (TMTM, 0.6 mmol), Cs$_2$CO$_3$ (1.0 mmol) and DMSO (2.0 mL) were mixed in a sealed tube and stirred at 100 °C for 2 h. The reaction was checked by TLC until the starting material was finished. The reaction was terminated with sat. NH$_4$Cl solution (4 mL) and then extracted with ethyl acetate. The crude solution was dried over anhydrous Na$_2$SO$_4$ and evaporated under vacuum. The residue was purified by flash column chromatography to afford the desired product 3a.
$^1$H NMR and $^{13}$C NMR Spectra of the products
$N,N$-dimethyl-$1H$-indole-1-carbothioamide (3a)
5-bromo-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3b)
5-methoxy-N,N-dimethyl-1H-indole-1-carbothioamide (3c)
$N,N,5$-trimethyl-$1H$-indole-$1$-carbothioamide (3d)
5-cyano-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3e)
$N,N$-dimethyl-5-nitro-$1H$-indole-1-carbothioamide (3f)
3-acetyl-N,N-dimethyl-1H-indole-1-carbothioamide (3g)
6-bromo-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3h)
6-chloro-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3i)
6-fluoro-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3j)
$N,N,6$-trimethyl-1$H$-indole-1-carbothioamide (3k)
4-bromo-\(N,N\)-dimethyl-1\(H\)-indole-1-carbothioamide (3l)
4-chloro-\(N,N\text{-}\)dimethyl-\(1H\text{-}\)indole-1-carbothioamide (3m)
4-fluoro-N,N-dimethyl-1H-indole-1-carbothioamide (3n)
$N,N,4$-trimethyl-$1H$-indole-$1$-carbothioamide (3o)
$N,N$-dimethyl-$1H$-pyrrolo[2,3-b]pyridine-1-carbothioamide (3p)