**Na₂S mediated thionation: an efficient access to secondary and tertiary α -ketothioamides
via Willgerodt–Kindler reaction of readily available arylglyoxals with amines**

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Representative ¹HNMR and ¹³CNMR and EI and ESI-MS spectra of secondary and tertiary α -ketothioamides

Fig. 1S. ¹HNMR of 2-morpholino-1-phenyl-2-thioxoethanone **2a** (entry 1, Table 1).

Fig. 2S. ¹³CNMR of 2-morpholino-1-phenyl-2-thioxoethanone **2a** (entry 1, Table 1).

Fig. 3S. EI-MS of 2-morpholino-1-phenyl-2-thioxoethanone **2a** (entry 1, Table 1).

Fig. 4S. ¹H NMR of 1-(4-chlorophenyl)-2-morpholino-2-thioxoethanone **2g** (entry 7, Table 1).

Fig. 5S. ¹³CNMR of 1-(4-chlorophenyl)-2-morpholino-2-thioxoethanone **2g** (entry 7, Table 1).

Fig. 6S. ¹H NMR of 1-(4-methoxyphenyl)-2-morpholino-2-thioxoethanone **2m** (entry 13, Table 1).

Fig. 7S. ¹³CNMR of 1-(4-methoxyphenyl)-2-morpholino-2-thioxoethanone **2m** (entry 13, Table 1).

Fig. 8S. ¹H NMR of 1-phenyl-2-(piperidin-1-yl)-2-thioxoethanone **2b** (entry 2, Table 1).

Fig. 9S. ^{13}C NMR of 1-phenyl-2-(piperidin-1-yl)-2-thioxoethanone **2b** (entry 2, Table 1)

Fig. 10S. ¹H NMR of 1-(4-chlorophenyl)-2-(piperidin-1-yl)-2-thioxoethanone **2h** (entry 8, Table 1).

Fig. 11S. ¹H NMR of 1-(4-chlorophenyl)-2-(piperidin-1-yl)-2-thioxoethanone **2h** (entry 8, Table 1).

Fig. 12S. ¹H NMR of 1-(4-methoxyphenyl)-2-(piperidin-1-yl)-2-thioxoethanone **2n** (entry 14, Table 1).

Fig. 13S. ^{13}C NMR of 1-(4-methoxyphenyl)-2-(piperidin-1-yl)-2-thioxoethanone **2n** (entry 14, Table 1).

Fig. 14S. ¹H NMR of 2-oxo-N,2-diphenylethanethioamide **2e** (entry 5, Table 1).

Fig. 15S. ¹³CNMR of 2-oxo-N,2-diphenylethanethioamide **2e** (entry 5, Table 1).

Fig. 16S. EI-MS of 2-oxo-N,2-diphenylethanethioamide **2e** (entry 5, Table 1).

Fig. 17S. ¹H NMR of *N*-benzyl-2-oxo-2-phenylethanethioamide **2d** (entry 4, Table 1)

Fig. 18S. ¹³CNMR of N-benzyl-2-oxo-2-phenylethanethioamide **2d** (entry 4, Table1).

Fig. 19S. EI-MS of N-benzyl-2-oxo-2-phenylethanethioamide **2d** (entry 4, Table1).

Fig. 20S. ¹H NMR of *N*-benzyl-2-(4-methoxyphenyl)-2-oxoethanethioamide **2p** (entry 16, Table 1).

Fig. 21S. ¹³CNMR of *N*-benzyl-2-(4-methoxyphenyl)-2-oxoethanethioamide **2p** (entry 16, Table 1).

Fig. 22S. ESI-MS of 2-(4-methoxyphenyl)-2-oxo-*N*-phenylethanethioamide **2p** (entry 16, Table 1).

Fig. 23S. ¹H NMR of 2-(4-chlorophenyl)-N-(3,5-dimethylphenyl)-2-oxoethanethioamide **2I** (entry 12, Table 1).

Fig. 24S. EI-MS of *N,N*-dimethyl-2-oxo-2-phenylethanethioamide **2c** (entry 3, Table 1).

Fig. 25S. ESI-MS of *N*-(3,5-dimethylphenyl)-2-oxo-2-phenylethanethioamide **2f** (entry 6, Table 1).

Fig. 26S. ESI-MS of *N*-benzyl-2-(4-chlorophenyl)-2-oxoethanethioamide **2j** (entry 10, Table 1).