Pd-catalyzed cross-coupling reactions have been established as essential tools in organic chemistry and are highly important in pharmaceutical and material science [1].

While in the beginning primarily carbon-carbon bond formation has been investigated, nowadays also carbon-heteroatom bond construction plays a significant role. An interesting approach is the activation of Het-CN moieties as it was shown for oxycyanation, aminocyanation and also for the reaction between aryl thiocyanates and alkynes or arynes, respectively [2].

As our group continuously strives for new methods to build up complex and valuable structures or key scaffolds in a single synthetic step, we developed a methodology for the intramolecular cyanosulfenylation of internal alkynes. This transformation leads to novel compounds with a heterocyclic backbone bearing a multi-functionalized tetrasubstituted exocyclic double bond (Scheme 1) [3].

The activation of the sulfur-carbon bond of an aromatic or aliphatic thiocyanate enables the cyanosulfenylation of the terminal substituted triple bond. This transformation includes a thiopalladation and the associated dislocation of the released cyanide as straightforward termination step of the catalytic cycle.

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