$Ti^{(III)}$ reductive electrocyclization of nitrostyrenes

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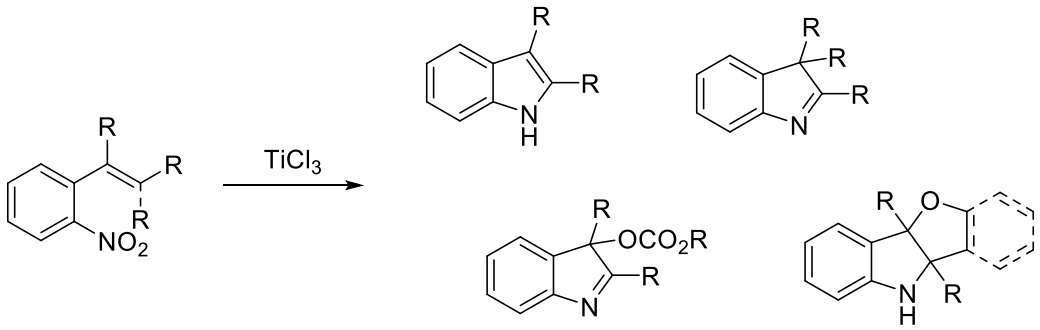
In the presence of $TiCl_3$, the reductive cyclization of tetrasubstituted alkenes bearing a 2-(ortho-nitroaryl) substituent affords indoles, indolenines and furo-indolines in good yields, depending on the alkene substituents.[1-3] This domino process involves the partial reduction of nitro to a nitroso group followed by 5-center-6π-electrocyclization, carbocation trapping, and the further reduction of the resulting nitrone intermediate.



R = alkyl, aryl

This methodology has been used for the total syntheses of several natural products such as (+)-1,2-dehydroaspidospermidine, (+)-condyfoline, and (-)-tubifoline and is currently under investigation for the synthesis of (±)-phalarine.

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[2] Delayre, B.; Piemontesi, C.; Wang, Q.; Zhu, J. *Angew. Chem., Int. Ed.* **2020**, 59, 13990−13997
[3] Boyarskaya, D. V.; Ongaro, A.; Piemontesi, C.; Wang, Q.; Zhu, J. *Org. Lett.* **2022**, 24, 7004−70087007