**Significance:** Herein, the direct and stereospecific amination of various aryl and alkyl pinacol boronates with lithiated methoxyamine is disclosed. The corresponding (un)protected amines are obtained in very good yield and, in case of chiral compounds, with high enantiomeric excess.

**Comment:** Sensitive functional groups such as CN, OMe and CF₃ moieties are well tolerated with this methodology. In addition, this strategy might even be applied to gram-scale reactions without any further drawbacks.

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**Key words**
- boron
- lithium
- direct amination
- pinacol boronates