Direct Difluoroethylation of Heteroaromatics, Michael Acceptors and Thiols

**Significance:** A novel protocol for direct difluoroethylation of a broad range of heterocycles, Michael acceptors and even thiols with sodium difluoroethanesulfinate (DFES-Na) has been described. DFES-Na is shown to be compatible with various sensitive functional groups, reacts site selectively in high conversion and is easy to handle.

**Comment:** Interestingly, performing the reaction with DFES-Na and tert-butylhydroperoxide (TBHP) solely results in only traces of the desired product. Only after addition of stoichiometric amounts of ZnCl₂ and TsOH·H₂O, the product is obtained in high yield.

\[ \text{R}^1 - \text{H} + \text{NaOSO}_2\text{R}^2 \overset{\text{TBHP (5 equiv)}}{\rightarrow} \text{R}^1\text{R}^2 \overset{\text{ZnCl}_2 (1.5 \text{ equiv}), \text{TsOH.H}_2\text{O (1 equiv)}}{\rightarrow} \text{up to 95% yield} \]

\[ \text{CH}_2\text{Cl}_2 - \text{H}_2\text{O (2.5:1), 0-23 °C, up to 24 h} \]

\[ \text{R}^1 = \text{various substituted heteroaromatics, Michael acceptors and thiols} \]
\[ \text{R}^2 = \text{Me, CH}_2\text{-4-BrC}_6\text{H}_4, (\text{CH}_3)_2\text{Cl} \]

**Selected examples:**

- ![Example 1](image1)
  - 92% yield
- ![Example 2](image2)
  - 58% yield
- ![Example 3](image3)
  - 44% yield
- ![Example 4](image4)
  - 67% yield
- ![Example 5](image5)
  - 51% yield
- ![Example 6](image6)
  - 83% yield
- ![Example 7](image7)
  - 66% yield
- ![Example 8](image8)
  - 83% yield
- ![Example 9](image9)
  - 56% yield