An Easy, Efficient and Completely Stereoselective Synthesis of \((E)-\alpha,\beta\)-Unsaturated Esters via Sequential Aldol-Type/Elimination Reactions Promoted by Samarium Diiodide or Chromium Dichloride.

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GENERAL:
Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the higher quality available and were used without further purification. Samarium diiodide was prepared by reaction of \(\text{CH}_2\text{I}_2\) with samarium powder. Flash column chromatography was carried out on silica gel 230-400 mesh. Compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). \(^1\text{H}\) NMR spectra were recorded at 200, 300 or 400 MHz. \(^{13}\text{C}\) NMR spectra and DEPT experiments were determined at 50 or 75 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants \((J)\) are reported in Hz. The diastereomeric excesses were obtained using \(^1\text{H}\)-NMR analysis and GC-MS of crude products. GC-MS and HRMS were measured at 70 eV or using
FAB conditions. When HRMS could not be measured on molecular ion the HRMS of a significant fragment is given. Only the most important IR absorptions (cm$^{-1}$) and the molecular ions and/or base peaks in MS are given.

**General Procedure for the synthesis of α,β-unsaturated esters (2) by using SmI$_2$:** Under nitrogen, a solution of SmI$_2$ (3 mmol) was added to a stirred suspension of ethyl dibromoacetate (0.5 mmol) and the corresponding aldehyde (0.5 mmol) in THF. After stirring at room temperature for two hours, the reaction was quenched with aqueous HCl 0.1 M. The organic layer was then extracted with dichloromethane. The combined extracts were dried over Na$_2$SO$_4$ and the solvent was removed *in vacuo*. Purification by flash chromatography on silica gel (hexane:EtOAc 10:1) afforded products 2.

**Synthesis of SmI$_2$ by Sonication:** Samarium powder (3 mmol) was placed in a Schlenk tube at room temperature and dry THF (30 mL) was added. The Schlenk tube was then partially submerged to the solvent level in a conventional cleaner sonicator (ultrasound laboratory cleaner 230 V, 150 W, 50 Hz) and diidodomethane (3 mmol) was added. After 5 min, a deep blue solution of SmI$_2$ was obtained.

**General Procedure for the synthesis of α,β-unsaturated esters (2) by using CrCl$_2$:** To a stirred suspension of CrCl$_2$ (6 mmol) in THF (10 mL) was added a solution of ethyl dibromoacetate (1 mmol) and the corresponding aldehyde (1 mmol), at 65ºC. After stirring at this temperature for two hours, the reaction was quenched with HCl 0.1M. and extracted with hexane (3 x 10 mL). The combined extracts were dried over Na$_2$SO$_4$ and concentrated. The organic layer was then filtered through a pad of Celite and the solvents were removed *in vacuo*. Purification by column chromatography on silica gel (Hexane/EtOAc 10:1) afforded the α,β-unsaturated esters 2.
2g

2h