

## SUPPORTING INFORMATION FOR:

### Unprecedented Barbier-type reactions catalysed by titanocene(III).

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**General Details.** For all reactions employing titanocene, solvents and additives were thoroughly deoxygenated prior to use. All addition products were isolated as pure samples by flash chromatography and showed NMR data matching those reported.

- *1-Tridecen-4-ol*: T. Ishiyama, T.-a Ahiko, N. Miyaura, *J. Am. Chem. Soc.*, 2002, **124**, 12414.
- *6,10-Dimethyl-1,5,9-undecatrien-4-ol*: Y. Masuyama, R. Hayashi, K. Otake, Y. Kurusu, *J. Chem. Soc., Chem. Commun.*, 1988, 44.
- *1-Phenyl-3-buten-1-ol*: T. Ishiyama, T.-a Ahiko, N. Miyaura, *J. Am. Chem. Soc.*, 2002, **124**, 12414.
- *4-Methyl-1-dodecen-4-ol*: R. Hamasaki, Y. Chounan, H. Horino, Y. Yamamoto, *Tetrahedron Lett.* 2000, **41**, 9883.
- *1-Allyl-4-tert-butylcyclohexanol*: B. M. Trost, M. J. Bogdanowicz, *J. Am. Chem. Soc.*, 1973, **95**, 5321.
- *3-Methyl-1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1,5-hexadien-3-ol*: W. Oroshnik, G. Karmas, R. A. Mallory, *J. Am. Chem. Soc.*, 1954, **76**, 2325.
- *2-Phenyl-4-penten-2-ol*: A. Kasatkin, T. Nakagawa, S. Okamoto, F. Sato, *J. Am. Chem. Soc.*, 1995, **117**, 3881.
- *1-(3',4',5'-Trimethoxyphenyl)-3-buten-1-ol*: H. C. Aspinall, J. S. Bissett, N. Greeves, D. Levin, *Tetrahedron Lett.*, 2002, **43**, 319.
- *1-Phenyl-2-undecanol*: C. K. Reddy, M. Periasamy, *Tetrahedron*, 1993, **39**, 8877.
- *1-Tridecyn-4-ol*: B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.*, 2003, **125**, 7482.
- *4-Methyl-1-dodecyn-4-ol*: B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc.*, 2003, **125**, 7482

**Model procedure for Barbier-type reactions between activated alkyl halides and aromatic or  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds. Reaction between allyl bromide and acetophenone catalysed by titanocene(III).**

Strictly deoxygenated THF (20 mL) was added to a mixture of  $\text{Cp}_2\text{TiCl}_2$  (41 mg, 0.16 mmol) and Mn dust (365 mg, 6.64 mmol) under an Ar atmosphere and the suspension was stirred at room temperature until it turned lime green (after about 15 min). Then, a solution of acetophenone (100 mg, 0.83 mmol), 2,4,6-collidine (703 mg, 5.81 mmol), allyl bromide (251 mg, 2.01 mmol), and  $\text{Me}_3\text{SiCl}$  (358 mg, 3.30 mmol) in THF (3 mL), was added and the mixture was stirred for 16 h. The reaction was then quenched with 2N HCl and extracted with *t*-BuOMe. The organic layer was washed with brine, dried (anhyd  $\text{Na}_2\text{SO}_4$ ) and the solvent removed. The residue was dissolved in MeOH (10 mL) and stirred with KF (481 mg, 8.30 mmol) for 2 h. The mixture was then diluted with *t*-BuOMe, washed with brine, dried (anhyd  $\text{Na}_2\text{SO}_4$ ) and the solvent removed. The residue was chromatographed (hexane: EtOAc, 4:1) to give 2-phenyl-4-penten-2-ol (115 mg, 86 %).

**Enantiomeric excesses (*ee*)** were determined by measuring optical rotation and with the aid of chiral lanthanide NMR shift reagents.<sup>1</sup>

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<sup>1</sup> L. M. Sweeting, D. C. Crans, G. M. Whitesides, *J. Org. Chem.*, 1987, **52**, 2273.