TiCl₄ catalyzed Intermolecular Hydroamination Reactions

Lutz Ackermann

Supporting Information

TiCl₄ catalyzed reactions were carried out on a 5 mmol scale under N₂ using pre-dried glassware. Catalytic reactions in NMR-tubes using **1**, or **2** were set up in a N₂-filled Vacuum Atmosphere inert atmosphere box. NMR-tubes were sealed, and heated in an oil bath. No further special equipment was used. Chemicals were obtained from Aldrich, Fluka, Lancaster, and Acros, and were used without further purification, unless noted otherwise. Liquid amines PhNH₂, ^tBuNH₂, 2,6-Me₂C₆H₃NH₂, and 2,4,6-Me₃C₆H₂NH₂ were distilled under N₂, and stored over molecular sieves (4 Å). Known products were identified by comparison with independently synthesized samples (¹H- and ¹³C-NMR, GC/MS).

(2-Octyl)-(2,4,6-trimethyl-phenyl)-amine (8). Into a Schlenk tube equipped with a magnetic stirring bar was added TiCl₄ (0.06 mL, 0.5 mmol) to a solution of ^tBuNH₂ (0.32 mL, 3.0 mmol) in toluene (5 mL) under N₂ at 25 °C. The orange suspension was stirred for 15 min at 25 °C. Mesitylamine (0.70 mL, 5.0 mmol) and 1-octyne (0.73 mL, 5.0 mmol) were added subsequently and the suspension was stirred at 75 °C for 4 h. The solvent was removed in vacuo, and a solution of ZnBr₂ in THF (6.3 mL, 1.7 M, 10.5 mmol) and NaBH₃CN (314 mg, 5.0 mmol) were added. The brown mixture was stirred at 25 °C for 14 h. Thereafter, aq. HCl (10 mL, 2N) was added, and the mixture was stirred for 2 h at 25 °C. H₂O (50 mL) was added. The mixture was made alkaline using NaOH, and extracted with CH₂Cl₂ (3 x 25 mL).

The combined organic layers were dried (MgSO₄), and concentrated in vacuo. Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 15/1 → 10/1) yielded **8** (767 mg, 62%) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃): δ = 6.82 (s, 2H), 3.21 (m, 1H), 2.67 (brs, 1H), 2.30-2.20 (m, 3H), 2.25 (m, 6H), 1.58 (m, 1H), 1.50-1.35 (m, 3H), 1.30 (s, 6H), 1.06 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 142.5 (C), 130.3 (C), 129.4 (CH), 129.1 (C), 52.7 (CH), 38.4 (CH₂), 31.9 (CH₂), 29.5 (CH₂), 26.5 (CH₂), 22.6 (CH₂), 21.2 (CH₃), 20.5 (CH₃), 18.9 (CH₃), 14.1 (CH₃). IR (KBr): 3369, 2957, 2927, 2856, 1483, 1459, 1374, 1300, 1233, 1156, 1030, 852, 736 cm⁻¹. MS (EI) *m/z* (relative intensity) 247 (15) [M⁺], 232 (7), 163 (11), 162 (100), 134 (5), 91 (3). HR-MS (EI) *m/z* calcd for C₁₇H₂₉N 247.2300, found 247.2298. C₁₇H₂₉N (247.23) Anal. Calcd C, 82.52; H, 11.81; N, 5.66. Found C, 82.34; H, 11.39; N, 5.53.