

Homogeneous catalytic hydrogenation of perfluoro methyl esters

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Supplementary Information

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3. Experimental Section

Instrumentation and starting materials

The reactions were carried out under a nitrogen atmosphere in a 100 mL stainless steel Berghof autoclave (AISI 316 model) with PTFE lining, equipped with a rupture disc at 40 bar. The prepared derivatives were characterised by chromatographic and spectroscopic methods. The NMR spectra were recorded at 298 K using a Varian Gemini XL 300 (^1H , 300.1; ^{13}C , 75.5; ^{19}F , 282.3 MHz) instrument; chemical shifts were referenced internally to residual solvent peaks for ^1H and ^{13}C NMR spectra, and externally to CFCl_3 for ^{19}F NMR spectra; the deuterated solvents used after being appropriately dried and degassed were stored in ampoules under argon on 4Å molecular sieves. GC-MS analysis were performed using an Agilent 5973 instrument inert with column HP 5MS (30 m, 0.25 mm, 0.25 μm); GC analysis were performed using an Hewlett Packard HP-5890 instrument (split/splitless), single FID detector and autosampler with a 10 μL syringe. The yields were determined by GC using decane (Fluka) as internal standard and CH_2Cl_2 (Merck) as diluent. Representative reactions were reproduced to ensure outcome validity.

The perfluoromethyl esters $\text{R}_f\text{C}(\text{O})\text{OMe}$ ($\text{R}_f = \text{C}_3\text{F}_7$, 99%; $\text{R}_f = \text{C}_5\text{F}_{11}$, 90%) were produced inhouse by Miteni S.p.A, via the ECF method;¹ the ruthenium catalysts Ru-MACHOTM (95%) was purchased from Takasago corporation; methanol was bought from Sigma Aldrich with the highest purity and containing molecular sieves; sodium methoxide (reagent grade) was bought from Sigma Aldrich and used as received.

Typical Procedure for Hydrogenation of Methyl Esters in Methanol (Table 1, entry 6). The 100-mL stainless steel autoclave equipped with a Teflon-coated stirring bar and previously filled with nitrogen (three purging cycles) was charged with methanol (7.0 g, 0.22 mol), NaOCH_3 (0.62 g, 0.011 mol), $\text{C}_3\text{F}_7\text{C}(\text{O})\text{OMe}$ (10.0 g, 0.044 mol) and Ru-Macho (0.007 g, 0.011 mmol). The autoclave was closed and purged three times with nitrogen. Successively the vessel was purged three times with hydrogen gas. The mixture was stirred (500 rpm), heated up to 60 °C and

pressurized with hydrogen (10 bar). After stirring for 23 h, the system was cooled to 25 °C, and then the hydrogen gas released. The mixture was analyzed by GC.

GC Conditions for Reactions in Tables 1 and 2. Column: DB-5 (5%-Phenyl-95%-Methyl-Polysiloxane), (l = 60 m, i.d. = 0.25 mm, f.th. = 1.0 μm); carrier gas: helium (0.7 ml/min); injection temp.: 250 °C, split ratio: 72: 1; detector: FID at 250 °C; Oven: 35 °C (15 min) → 120 °C (5 °C/min, 0 min hold) → 240 °C (10 °C/min, 5 min hold).

C₃F₇C(O)OMe. ¹H NMR (300.1 MHz, CDCl₃): δ 3.97 (s, 3H, CH₃); ¹³C NMR (75.5 MHz, CDCl₃): δ 158.9 (t, ²J_{C,F} = 28.8 Hz, C=O), 123.2 ÷ 104.2 (m, C₃F₇), 54.5 (s, CH₃); ¹⁹F NMR (283.5 MHz, CDCl₃): δ -81.4 (m, CF₃), -199.8 (m, CF₂), -127.6 (m, CF₂). Bp: 80-81 °C.

C₅F₁₁C(O)OMe. ¹H NMR (300.1 MHz, CDCl₃): δ 3.98 (s, 3H, CH₃); ¹³C NMR (75.5 MHz, CDCl₃): δ 158.9 (t, ²J_{C,F} = 29.4 Hz, C=O), 123.4 ÷ 104.1 (m, C₅F₁₁), 54.6 (s, CH₃); ¹⁹F NMR (283.5 MHz, CDCl₃): δ -81.3 (m, CF₃), -118.8 (m, CF₂), -123.0 (m, CF₂), -123.2 (m, CF₂), -126.6 (m, CF₂). Bp: 123-130 °C.

C₃F₇CH₂OH. ¹H NMR (300.1 MHz, CDCl₃): δ 4.07 (t, ³J_{H,F} = 14 Hz, 2H, CH₂), 2.39 (bs, 1H, OH); ¹³C NMR (75.5 MHz, CDCl₃): δ 123.0 ÷ 104.1 (m, C₃F₇), 60.3 (t, ²J_{C,F} = 25.7 Hz, CH₂); ¹⁹F NMR (283.5 MHz, CDCl₃): δ -81.2 (m, CF₃), -123.6 (m, CF₂), -128.1 (m, CF₂). Bp: 96-97 °C.

C₅F₁₁CH₂OH. ¹H NMR (300.1 MHz, acetone-d₆): δ 4.08 (td, ³J_{H,F} = 15 Hz, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 5.19 (t, ³J_{H,H} = 7.5 Hz, 1H, OH); ¹³C NMR (75.5 MHz, acetone-d₆): δ 125.1 ÷ 105.8 (m, C₃F₇), 59.5 (t, ²J_{C,F} = 25.7 Hz, CH₂); ¹⁹F NMR (283.5 MHz, acetone-d₆): δ -82.7 (m, CF₃), -123.1 (m, CF₂), -124.1 (m, CF₂), -124.8 (m, CF₂), -127.6 (m, CF₂). bp: 117-119 °C.

References

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