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Supporting Information

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Dihydrogen Reduction of Carboxylic Esters to Alcohols Catalyzed by Homogeneous Ruthenium Complexes: High Efficiency and Unprecedented Chemoselectivity.

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General.

All experiments were carried out under an atmosphere of argon either in an *MBraun* glove box or using standard *Schlenk* line techniques. THF (tetrahydrofuran) was distilled over Na/benzophenone, 1,4-dioxane was distilled over sodium, diglyme (diethylene glycol dimethyl ether) was distilled over sodium under reduced pressure, MeTHF (2-methyltetrahydrofuran), Et_2O, DME (1,2-dimethoxyethane) and PhOMe were distilled over $LiAlH_4$, $PhCF_3$ was distilled over CaH_2. MTBE (methyl *tert*-butyl ether) (SDS synth. grade), *i*PrOH (Carlo Erba, analysis grade), EtOH (Carlo Erba, analysis grade), MeOH (Carlo Erba, analysis grade), PhMe (Carlo Erba, analysis grade) and hexane (SDS, synthesis grade) were degassed by bubbling argon and stored in the glove box.

Ester substrates were distilled over CaH_2 under argon or under vacuum and stored under argon in the glove box. *n*-Tridecane (Acros 99%) was degassed with argon and stored in the glove box.

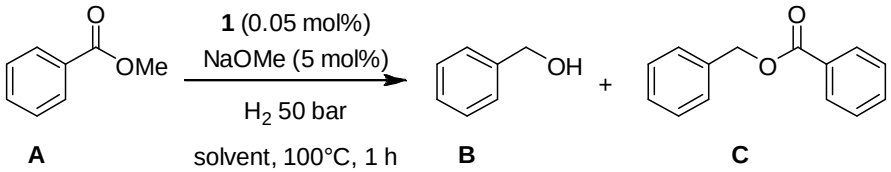
NaOMe (Fluka 95%), KOMe (Fluka 90%), LiOMe (Aldrich 98%), NaOEt (Acros 96%), NaO*t*Bu (Strem 98%), KO*t*Bu (Fluka 97%), $NaN(TMS)_2$ (sodium bis(trimethylsilyl)amide) (Strem 97%), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (Fluka 99%), Et_3N (Acros 99%) were used as received and stored under argon in the glove box. NaO*i*Pr was prepared from *i*PrOH and NaH followed by drying under high vacuum and stored under argon in the glove box.

GC analyses were performed on a 6850 Agilent chromatograph equipped with a FID detector, an Agilent DB-1 (dimethylpolysiloxane, # 127-1012E) capillary column (10 m, ID 0.1 mm, film 0.1 μm) and an automatic liquid injector. GC conditions: 60°C – 0 min – 60°C/min – 300°C – 1 min, with a constant flow of He (0.8 mL/min). Using these conditions, the following retention times were observed: benzyl alcohol (1.11 min), methyl benzoate (1.27 min), *n*-tridecane (1.80 min) and benzyl benzoate (2.69 min). A calibration curve was established by using five different solutions of accurately weight mixtures of benzyl alcohol, methyl benzoate and *n*-tridecane in THF.

General procedure for the H_2 reduction of methyl benzoate to benzyl alcohol.

Under argon in a glove box, a stainless steel 75 mL autoclave, equipped with a magnetic stirring bar, was charged with the ruthenium complex (0.01 mmol), the base (1.0 mmol) and the solvent (6 mL). Then a solution of methyl benzoate (20 mmol) and *n*-tridecane (1 mmol) in the solvent (4 mL) was added. The autoclave was purged by successive pressurization/vent (3 ×) with H_2, pressurized with H_2, closed and placed in a thermostated oil bath. After the desired time, the autoclave was cooled in an ice/water bath and vented. A sample (0.35 mL) of the raction mixture was added to a mixture of MTBE (5 mL) and sat. aq. solution of NH_4Cl (5 mL). After shaking, the organic phase was separated and filtered through a small plug of *Celite 560* in a Pasteur pipette. The filtrate was then analyzed by GC.

Effect of solvent in H_2 reduction of methyl benzoate to benzyl alcohol with complex 1.[a]

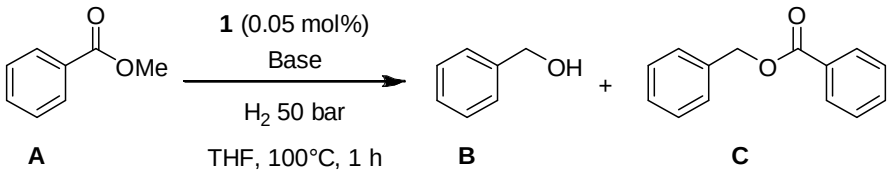


A **B** **C**

Entry	Solvent	**B** yield [%][b]	**B** : **A** : **C**[c]
1	THF	>99	99.8 : 0.2 : 0.0
2	MeTHF	>99	99.6 : 0.4 : 0.0
3	1,4-Dioxane	>99	99.9 : 0.1 : 0.0
4	DME	>99	99.9 : 0.1 : 0.0
5	Diglyme	>99	99.9 : 0.1 : 0.0
6	MTBE	99	97.4 : 2.0 : 0.6
7	Et_2O	97	95.2 : 3.6 : 1.2
8	PhOMe	92	91.1 : 6.5 : 2.4
9	PhMe	83	82.4 : 12.6 : 5.0
10	$PhCF_3$	74	72.5 : 20.1 : 7.4
11	*i*PrOH	95	92.4 : 1.5 : 0.6[d]
12	EtOH	36	34.7 : 8.6 : 0.7[e]
13	MeOH	1	0.7 : 94.2 : 5.1
14	Hexane	68	69.6 : 22.0 : 8.4

[a] Reaction conditions: methyl benzoate (20 mmol), solvent (10 mL). [b] Yield obtained by GC using *n*-tridecane as an internal standard. [c] Ratio of products as observed by GC in the crude reaction mixture. [d] Isopropyl benzoate (5.4%) was also observed in the crude reaction mixture. [e] Ethyl benzoate (57%) was also observed in the crude reaction mixture.

Effect of base in H_2 reduction of methyl benzoate to benzyl alcohol with complex 1.[a]

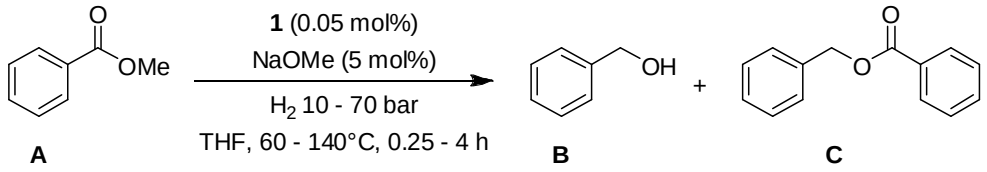


A **B** **C**

Entry	Base ([mol%])	**B** yield [%][b]	**B** : **A** : **C**[c]
1	NaOMe (1)	96	98.7 : 1 : 0.3
2	NaOMe (2.5)	>99	99.7 : 0.3 : 0
3	NaOMe (5)	>99	99.8 : 0.2 : 0
4	NaOMe (10)	>99	99.9 : 0.1 : 0
5	KOMe (5)	>99	99.8 : 0.2 : 0
6	LiOMe (5)	0.6	0.5 : 96 : 3.5
7	NaOEt (5)	>99	99.8 : 0.2 : 0
8	NaO*i*Pr (5)	>99	99.7 : 0.3 : 0
9	NaO*t*Bu (5)	96	99.9 : 0.1 : 0
10	KO*t*Bu (5)	98	99.2 : 0.6 : 0.2
11	Cs_2CO_3 (5)	65	67.1 : 24.4 : 8.5
12	$NaN(TMS)_2$ (5)	20	21.8 : 64.8 : 13.4
13	DBU (5)	0	0 : 100 : 0
14	Et_3N (5)	0	0 : 100 : 0

[a] Reaction conditions: methyl benzoate (20 mmol), THF (10 mL). [b] Yield obtained by GC using *n*-tridecane as an internal standard. [c] Ratio of products as observed by GC in the crude reaction mixture.

Effect of temperature and H_2 pressure in H_2 reduction of methyl benzoate to benzyl alcohol with complex 1.[a]

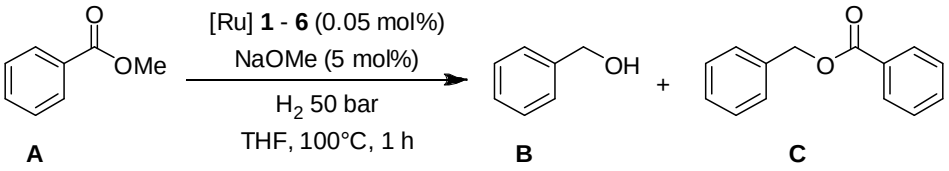


A **B** **C**

Entry	*T* [°C]	H_2 [bar]	*t* [h]	**B** yield [%][b]	**B** : **A** : **C**[c]
1	100	70	1	>99	100 : 0 : 0
2	100	50	0.25	78	78.8 : 16.1 : 5.1
3	100	50	1	>99	99.8 : 0.2 : 0
4	100	30	1	96	95.8 : 3.3 : 0.9
5	100	10	4	47	49.0 : 42.2 : 8.8
6	140	50	1	>99	100 : 0 : 0
7	80	50	1	95	93.5 : 5 : 1.5
8	60	50	1	72	70.8 : 20.8 : 6.4
9	60	50	2	90	89.3 : 8.2 : 2.5

[a] Reaction conditions: methyl benzoate (20 mmol), THF (10 mL). [b] Yield obtained by GC using *n*-tridecane as an internal standard. [c] Ratio of products as observed by GC in the crude reaction mixture.

H_2 reduction of methyl benzoate to benzyl alcohol with complexes 1 - 6.[a]



A **B** **C**

Entry	[Ru]	**B** yield [%][b]	**B** : **A** : **C**[c]
1	**1**	>99	100 : 0 : 0
2	**2**	99	98.6 : 1.1 : 0.3
3	**3**	96	96.2 : 2.9 : 0.9
4	**4**	0	0 : 99 : 1
5	**5**	0.5	0.5 : 97 : 2.5
6	**6**	0	0 : 99.7 : 0.3

[a] Reaction conditions: methyl benzoate (20 mmol), THF (10 mL). [b] Yield obtained by GC using *n*-tridecane as an internal standard. [c] Ratio of products as observed by GC in the crude reaction mixture.