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SUPPORTING INFORMATION

Catalytic (de)hydrogenation promoted by non-precious metals – Fe, Co and Mn: recent advances in an emerging field

Georgy A. Filonenko[a,b,*], Robbert van Putten[a,b], Emiel J. M. Hensen[a] and Evgeny A. Pidko[b,c,*]

[a] Inorganic Materials Chemistry Group, Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands;

[b] Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, the Netherlands

[c] ITMO University, Lomonosova 9, St. Petersburg, 191002, Russia

Corresponding authors: g.a.filonenko@tudelft.nl (G.A.F.); e.a.pidko@tudelft.nl (E.A.P.)

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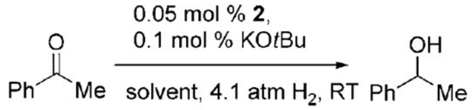
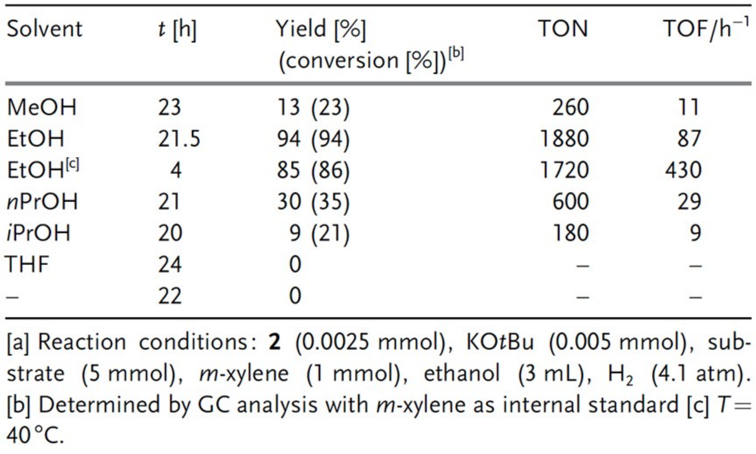
NOTE: All data on catalytic performance reproduced from original publications with full bibliographic citation preceding the used artwork. The Supplementary Material is grouped into subsections according to the main text designations. Catalyst are mentioned in **alphabetical** order according to coding in the main text of the Review. Supplementary Material contains the main substrate scope data while the stoichiometric reactions and optimization studies are omitted and can be found in original works.

3.1.1. – Reduction with molecular hydrogen – Iron Catalysts

A-Fe-1 – Ketones

R. Langer, G. Leitus, Y. Ben-David and D. Milstein, *Angewandte Chemie International Edition*, **2011**, *50*, 2120-2124.



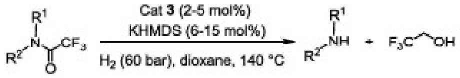


Solvent	*t* [h]	Yield [%] (conversion [%])[b]	TON	TOF/h^{-1}
MeOH	23	13 (23)	260	11
EtOH	21.5	94 (94)	1880	87
EtOH[c]	4	85 (86)	1720	430
*n*PrOH	21	30 (35)	600	29
*i*PrOH	20	9 (21)	180	9
THF	24	0	–	–
–	22	0	–	–

[a] Reaction conditions: **2** (0.0025 mmol), KO*t*Bu (0.005 mmol), substrate (5 mmol), *m*-xylene (1 mmol), ethanol (3 mL), H_2 (4.1 atm). [b] Determined by GC analysis with *m*-xylene as internal standard [c] $T = 40\,°C$.

A-Fe-1 – Amides

J. A. Garg, S. Chakraborty, Y. Ben-David and D. Milstein, *Chemical Communications*, **2016**, *52*, 5285-5288.



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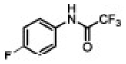
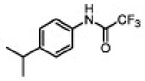
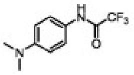
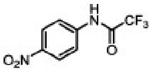
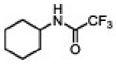
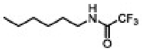
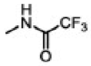
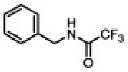
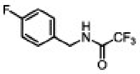
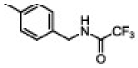
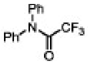
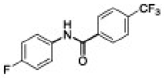
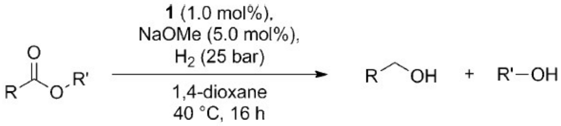
					HO⁀CF₃ (%)	Amine (%)
1		2	12	99	99	*p*-F-aniline (99)
2		2	12	99	99	Isopropylaniline (99)
3		2	12	58	52	*N*,*N*-Dimethylaniline (58)
4		2	24	25	25	*p*-Nitroaniline (25)
5		5	36	35	36	Cyclohexylamine (34)
6		5	36	23	23	Hexylamine (22)
7		5	35	26	26	Methylamine (undetected)
8		5	36	58	44	Benzylamine (58)
9		5	36	62	61	*p*-Fluorobenzylamine (62)
10		5	36	46	42	*p*-Methylbenzylamine (46)
11		5	36	99	99	Diphenylamine (99)
12[c]		5	36	48	45	Fluoroaniline (47)

[a] Unless and otherwise stated, reaction conditions were 2–5 mol% catalyst **3**, 3 equiv. KHMDS relative to catalyst, 60 bar H_2, 140 °C and 1,4-dioxane as solvent. [b] Conversions and amine yields were determined by GC using mesitylene as internal standard and TFE yield is based on ^{19}F NMR. [c] Trifluoromethylbenzylalcohol was obtained and quantified by GC.

A-Fe-2 – Esters

T. Zell, Y. Ben-David and D. Milstein, *Angewandte Chemie International Edition*, **2014**, *53*, 4685-4689.



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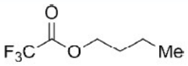
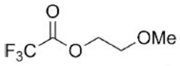
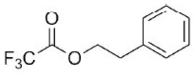
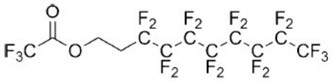
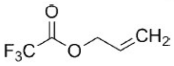
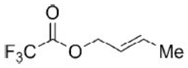
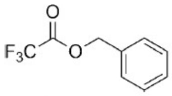
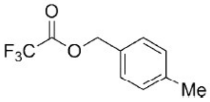
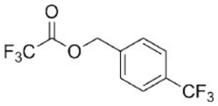
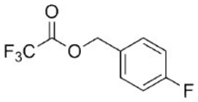
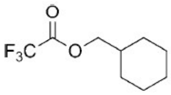
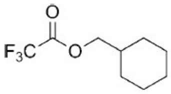
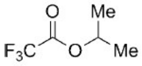
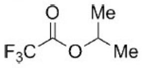
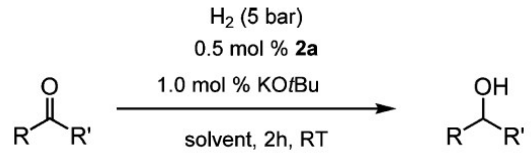
1		77
2		80
3		78
4		>99
5		95
6		84
7		>99
8		>99
9		>99
10		97
11		52
12[b]		95
13		25
14[c]		77

[a] Reaction conditions: H_2 (25 bar), ester (2.0 mmol), **1** (1.0 mol%), NaOMe (5.0 mol%), 1,4-dioxane (2 mL), 16 h, 40°C, performed in an autoclave. Yields based on integration of the $^{19}F\{^1H\}$ NMR spectra of the crude products. [b] 48 h. [c] Ester (0.67 mmol), **1** (3.0 mol%), NaOMe (15.0 mol%), 60 h.

B-Fe-1 – Ketones

N. Gorgas, B. Stöger, L. F. Veiros, E. Pittenauer, G. Allmaier and K. Kirchner, *Organometallics*, **2014**, *33*, 6905-6914.



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	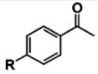	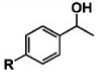		
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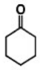
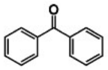
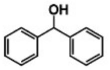
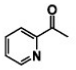
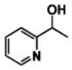
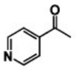
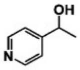
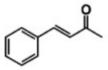
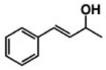
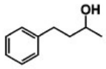
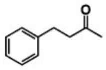
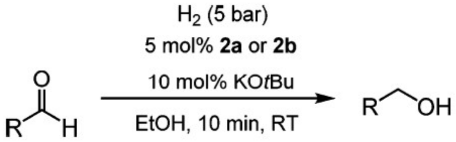
2[b]	R = H		77	770
3	R = Cl		99	100
4	R = Br		99	100
5	R = OMe		34	34
6	R = NO_2		47	47
7	R = NH_2			
8	R = CN			
9			30	30
10			64	64
11[c]			99	200
12				-
13			10	100
			45	
			45	

[a]Reaction conditions: **2a** (0.0125 mmol), KO*t*Bu (0.025 mmol), substrate (2.5 mmol), EtOH (5 mL), H_2 (5 bar), 2 h. [b]Reaction conditions: **2a** (0.0025 mmol), KO*t*Bu (0.005), substrate (2.5 mmol), EtOH (3 mL), 1 h. [c]Reaction time: 1 h. [d]Yields were determined by ^1H NMR.

B-Fe-1 – Aldehydes

N. Gorgas, B. Stöger, L. F. Veiros, E. Pittenauer, G. Allmaier and K. Kirchner, *Organometallics*, **2014**, *33*, 6905-6914.



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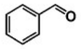
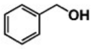
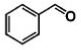
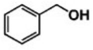
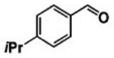
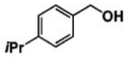
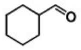
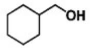
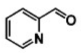
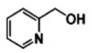
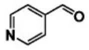
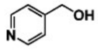
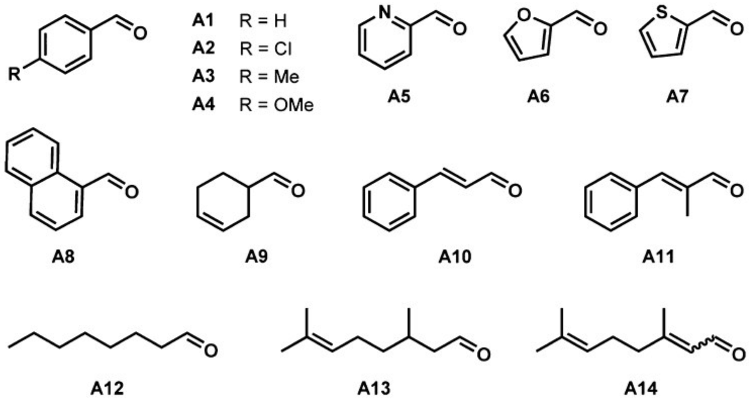
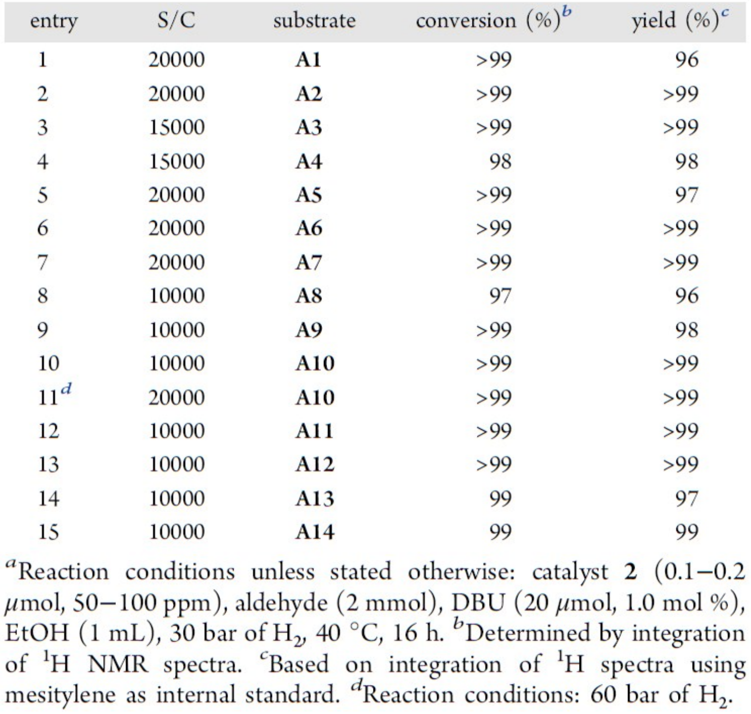
1[b]			23	23
2			99	120
3			99	120
4[c]			99	60
5			99	120
6				

[a] Reaction conditions: **2a** or **2b** (0.125 mmol), KO*t*Bu (0.25 mmol), substrate (2.5 mmol), EtOH (5 mL), H_2 (5 bar), 10 min. [b] Reaction conditions: **2a** (0.0125 mmol), KO*t*Bu (0.025 mmol), substrate (2.5 mmol), EtOH (5 mL), H_2 (5 bar), 2 h. [c] Reaction time: 20 min. [d] Yields were determined by ^{1}H NMR.

B-Fe-1a – Aldehydes

N. Gorgas, B. Stöger, L. F. Veiros and K. Kirchner, *ACS Catalysis*, **2016**, *6*, 2664-2672.



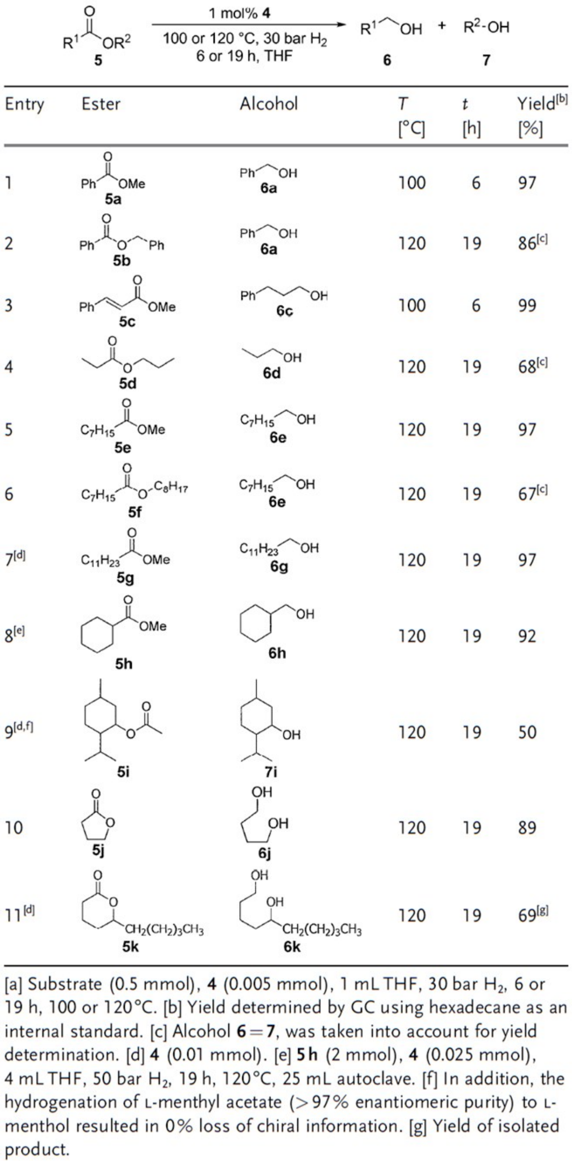


entry	S/C	substrate	conversion (%)[b]	yield (%)[c]
1	20000	**A1**	>99	96
2	20000	**A2**	>99	>99
3	15000	**A3**	>99	>99
4	15000	**A4**	98	98
5	20000	**A5**	>99	97
6	20000	**A6**	>99	>99
7	20000	**A7**	>99	>99
8	10000	**A8**	97	96
9	10000	**A9**	>99	98
10	10000	**A10**	>99	>99
11[d]	20000	**A10**	>99	>99
12	10000	**A11**	>99	>99
13	10000	**A12**	>99	>99
14	10000	**A13**	99	97
15	10000	**A14**	99	99

[a] Reaction conditions unless stated otherwise: catalyst **2** (0.1−0.2 μmol, 50−100 ppm), aldehyde (2 mmol), DBU (20 μmol, 1.0 mol %), EtOH (1 mL), 30 bar of H_2, 40 °C, 16 h. [b] Determined by integration of ^1H NMR spectra. [c] Based on integration of ^1H spectra using mesitylene as internal standard. [d] Reaction conditions: 60 bar of H_2.

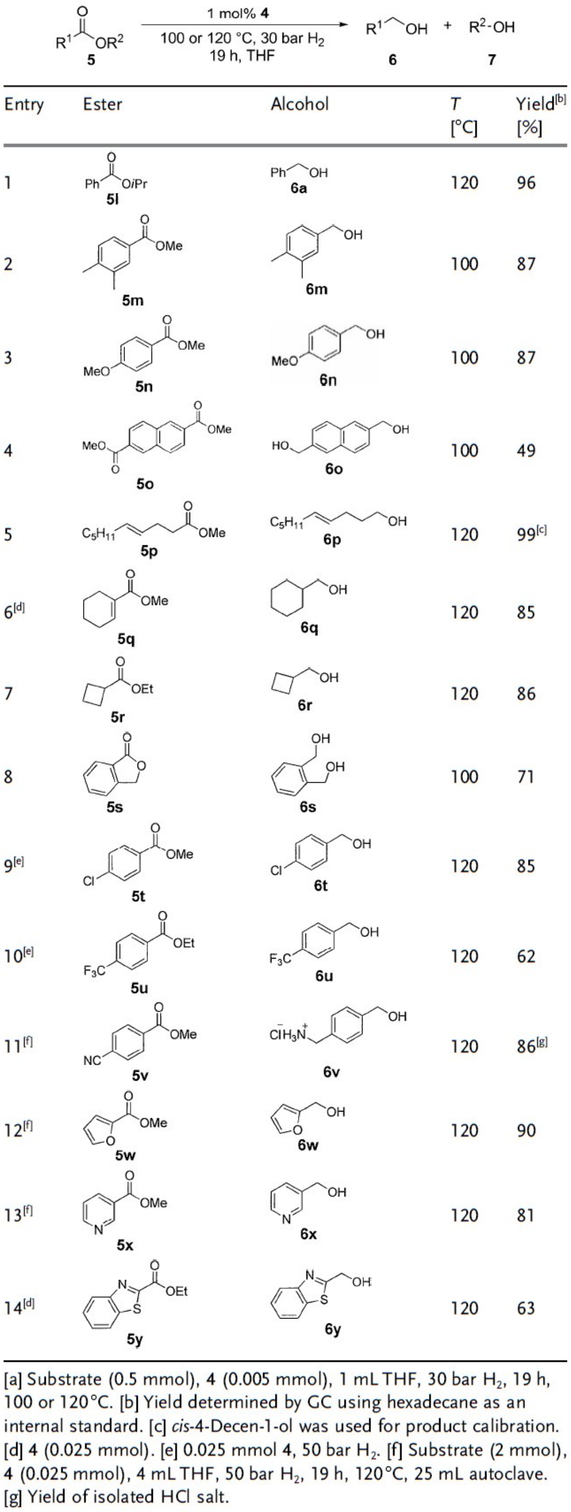
C-Fe-1 – Esters

S. Werkmeister, K. Junge, B. Wendt, E. Alberico, H. Jiao, W. Baumann, H. Junge, F. Gallou and M. Beller, *Angewandte Chemie International Edition*, **2014**, *53*, 8722-8726.



Entry	Ester	Alcohol	T [°C]	t [h]	Yield[b] [%]
1	Ph OMe **5a**	Ph OH **6a**	100	6	97
2	Ph O Ph **5b**	Ph OH **6a**	120	19	86[c]
3	Ph OMe **5c**	Ph OH **6c**	100	6	99
4	**5d**	OH **6d**	120	19	68[c]
5	C_7H_{15} OMe **5e**	C_7H_{15} OH **6e**	120	19	97
6	C_7H_{15} O C_8H_{17} **5f**	C_7H_{15} OH **6e**	120	19	67[c]
7[d]	$C_{11}H_{23}$ OMe **5g**	$C_{11}H_{23}$ OH **6g**	120	19	97
8[e]	OMe **5h**	OH **6h**	120	19	92
9[d,f]	**5i**	OH **7i**	120	19	50
10	**5j**	OH OH **6j**	120	19	89
11[d]	$CH_2(CH_2)_3CH_3$ **5k**	OH OH $CH_2(CH_2)_3CH_3$ **6k**	120	19	69[g]

[a] Substrate (0.5 mmol), **4** (0.005 mmol), 1 mL THF, 30 bar H_2, 6 or 19 h, 100 or 120°C. [b] Yield determined by GC using hexadecane as an internal standard. [c] Alcohol **6** = **7**, was taken into account for yield determination. [d] **4** (0.01 mmol). [e] **5h** (2 mmol), **4** (0.025 mmol), 4 mL THF, 50 bar H_2, 19 h, 120°C, 25 mL autoclave. [f] In addition, the hydrogenation of L-menthyl acetate (>97% enantiomeric purity) to L-menthol resulted in 0% loss of chiral information. [g] Yield of isolated product.

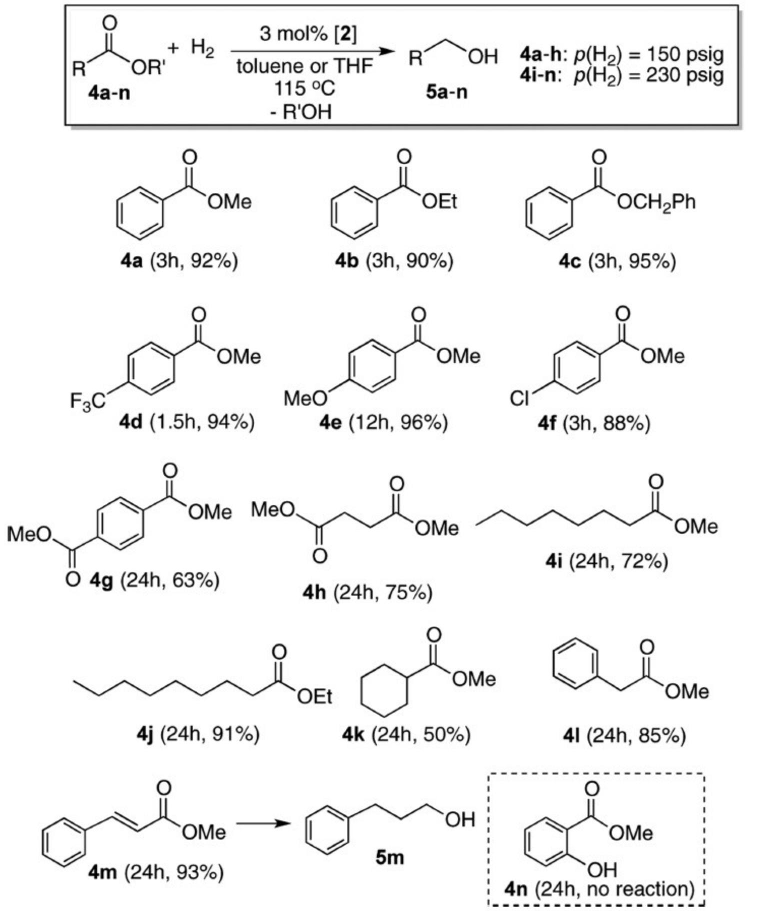


Entry	Ester	Alcohol	T [°C]	Yield[b] [%]
1	Ph O*i*Pr **5l**	Ph OH **6a**	120	96
2	OMe **5m**	OH **6m**	100	87
3	MeO OMe **5n**	MeO OH **6n**	100	87
4	MeO OMe **5o**	HO OH **6o**	100	49
5	C_5H_{11} OMe **5p**	C_5H_{11} OH **6p**	120	99[c]
6[d]	OMe **5q**	OH **6q**	120	85
7	OEt **5r**	OH **6r**	120	86
8	O **5s**	OH OH **6s**	100	71
9[e]	Cl OMe **5t**	Cl OH **6t**	120	85
10[e]	F_3C OEt **5u**	F_3C OH **6u**	120	62
11[f]	NC OMe **5v**	$\bar{Cl}H_3\overset{+}{N}$ OH **6v**	120	86[g]
12[f]	OMe **5w**	OH **6w**	120	90
13[f]	N OMe **5x**	N OH **6x**	120	81
14[d]	N S OEt **5y**	N S OH **6y**	120	63

[a] Substrate (0.5 mmol), **4** (0.005 mmol), 1 mL THF, 30 bar H_2, 19 h, 100 or 120°C. [b] Yield determined by GC using hexadecane as an internal standard. [c] *cis*-4-Decen-1-ol was used for product calibration. [d] **4** (0.025 mmol). [e] 0.025 mmol **4**, 50 bar H_2. [f] Substrate (2 mmol), **4** (0.025 mmol), 4 mL THF, 50 bar H_2, 19 h, 120°C, 25 mL autoclave. [g] Yield of isolated HCl salt.

C-Fe-1 – Esters

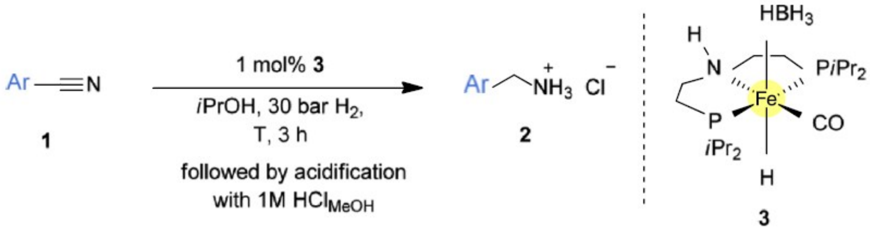
S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause and H. Guan, *Journal of the American Chemical Society*, **2014**, *136*, 7869-7872.

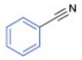
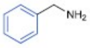
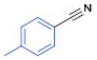
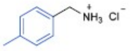
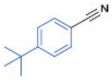
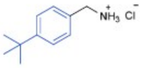
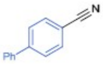
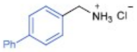
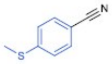
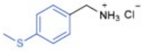
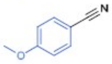
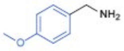
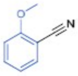
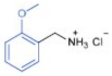
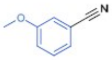
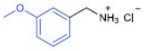
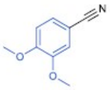
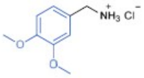
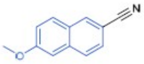
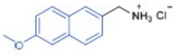
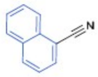
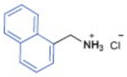
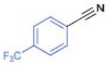
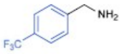
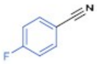
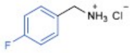
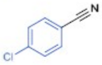
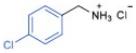
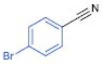
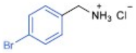
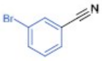
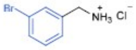


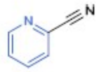
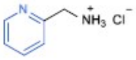
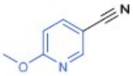
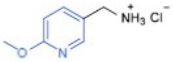
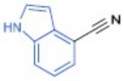
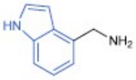
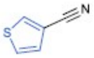
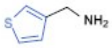
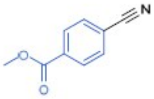
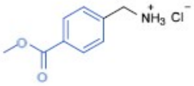
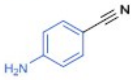
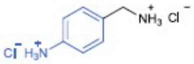
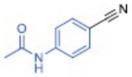
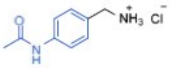
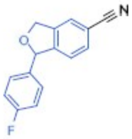
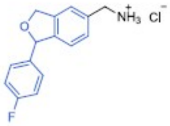
[a]General conditions for hydrogenation: 0.83 mmol of ester, 25 μmol of **2** (3 mol % loading), 0.5 mL of toluene (or THF for **4g**), 115 °C, $p(H_2)$ = 150 or 230 psig. The numbers in the parentheses are reaction time and isolated yield of RCH_2OH.

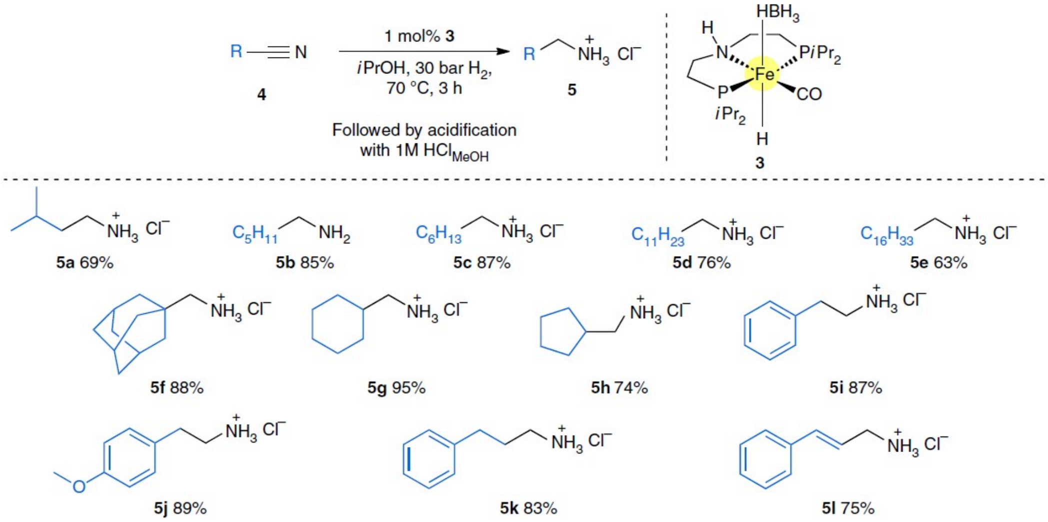
C-Fe-1 – Nitriles

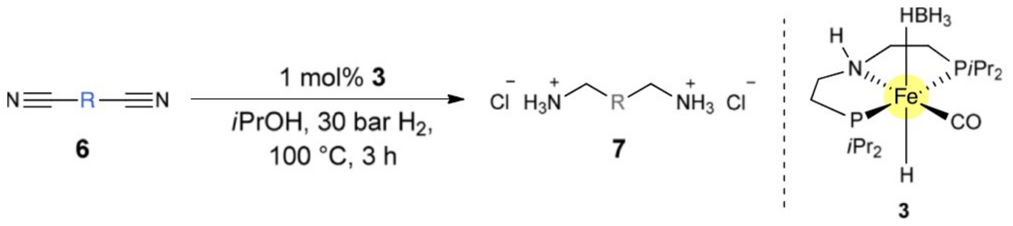
C. Bornschein, S. Werkmeister, B. Wendt, H. Jiao, E. Alberico, W. Baumann, H. Junge, K. Junge and M. Beller, *Nature Communications*, **2014**, *5*.

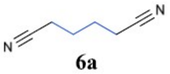
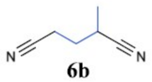
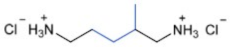
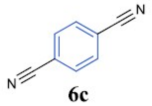
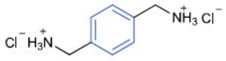


Entry	Aromatic nitrile		Primary amine		T (°C)	Conv. (%)[†]	Yield (%)[‡]
1		**1a**		**2a**	70	>99	97[§]
2		**1b**		**2b**	70	>99	96
3		**1c**		**2c**	70	>99	82
4		**1d**		**2d**	70	>99	99
5		**1e**		**2e**	100	>99	81
6		**1f**		**2f**	100	>99	99[§]
7		**1g**		**2g**	70	>99	84
8		**1h**		**2h**	70	>99	88
9		**1i**		**2i**	70	>99	92
10		**1j**		**2j**	70	>99	98
11		**1k**		**2k**	100	>99	99
12		**1l**		**2l**	100	>99	71
13		**1m**		**2m**	100	>99	81
14		**1n**		**2n**	130	>99	78
15		**1o**		**2o**	100	>99	88
16		**1p**		**2p**	100	>99	92

Entry	Aromatic nitrile		Primary amine		T (°C)	Conv. (%)[†]	Yield (%)[‡]
17		**1q**		**2q**	100	>99	80
18		**1r**		**2r**	130	>99	92
19		**1s**		**2s**	100	>99	40[§]
20		**1t**		**2t**	100	>99	58[§]
21		**1u**		**2u**	130	>99	75[‖]
22		**1v**		**2v**	100	>99	93
23		**1w**		**2w**	100	>99	70
24		**1x**		**2x**	100	>99	93

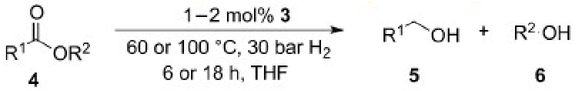


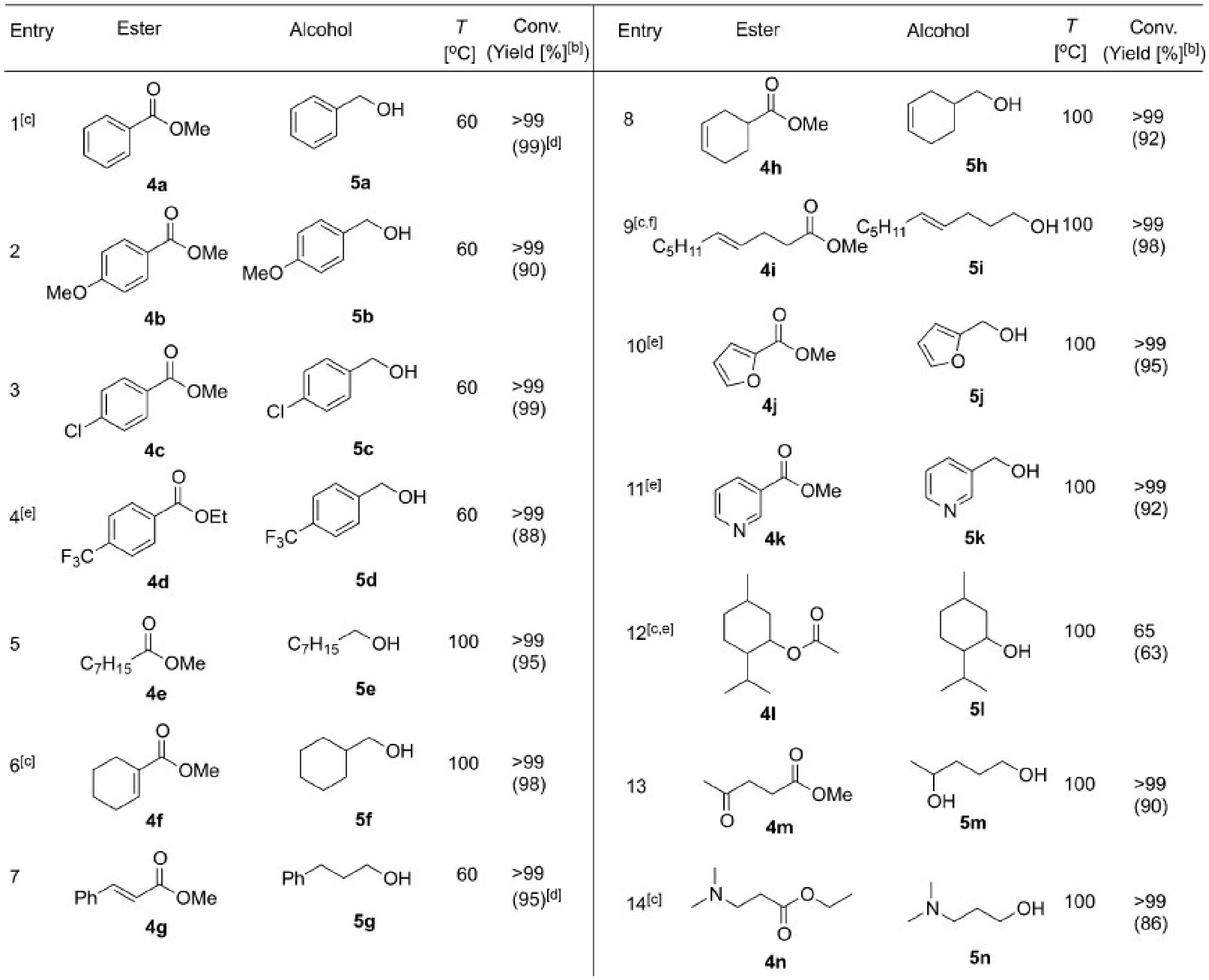


Entry	Dinitrile	Product	*t* (min)	Conv. (%)[†]	Yield (%)[‡]
1	 **6a**	 **7a**	180	>99	95
2	 **6a**	 **7a**	180	>99	87[§]
3	 **6a**	 **7a**	20	>99	83
4	 **6b**	 **7b**	180	>99	41
5	 **6c**	 **7c**	180	>99	85

C-Fe-2 – Esters

S. Elangovan, B. Wendt, C. Topf, S. Bachmann, M. Scalone, A. Spannenberg, H. Jiao, W. Baumann, K. Junge and M. Beller, *Advanced Synthesis & Catalysis*, **2016**, *358*, 820-825.





Entry	Ester	Alcohol	T [°C]	Conv. (Yield [%][b])
1[c]	4a	5a	60	>99 (99)[d]
2	4b	5b	60	>99 (90)
3	4c	5c	60	>99 (99)
4[e]	4d	5d	60	>99 (88)
5	4e	5e	100	>99 (95)
6[c]	4f	5f	100	>99 (98)
7	4g	5g	60	>99 (95)[d]
8	4h	5h	100	>99 (92)
9[c,f]	4i	5i	100	>99 (98)
10[e]	4j	5j	100	>99 (95)
11[e]	4k	5k	100	>99 (92)
12[c,e]	4l	5l	100	65 (63)
13	4m	5m	100	>99 (90)
14[c]	4n	5n	100	>99 (86)

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[a] Substrate (1 mmol), **3** (0.01 mmol), THF (1 mL), 60 or 100 °C, 30 bar H_2, 18 h.

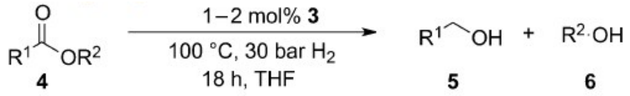
[b] Conversion was determined by GC analysis using hexadecane as an internal standard (isolated yield in parentheses).

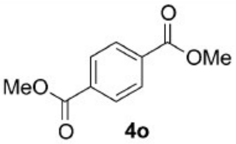
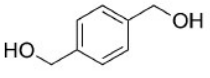
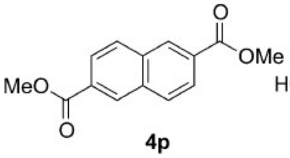
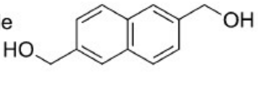
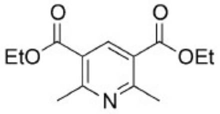
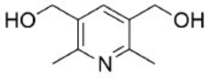
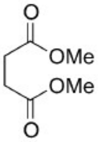
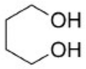
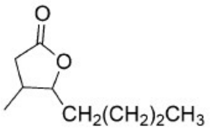
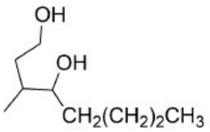
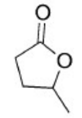
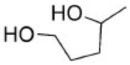
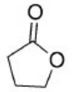
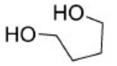
[c] Substrate (0.5 mmol), **3** (0.005 mmol), yield was determined GC analysis using hexadecane as an internal standard.

[d] 6 h reaction time.

[e] 2 mol% **3**.

[f] *cis*-4-Decen-1-ol was used for product calibration.



Entry	Ester	Alcohol	Conv. (Yield [%][b])
1	 **4o**	 **5o**	>99 (96)
2	 **4p**	 **5p**	>99 (89)
3[d]	 **4q**	 **5q**	>99 (91)
4[c]	 **4r**	 **5r**	>99 (97)
5[d]	 **4s**	 **5s**	>99 (97)
6[d]	 **4t**	 **5t**	>99 (98)
7[c,e]	 **4u**	 **5u**	>99 (99)

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[a] Substrate (1 mmol), **3** (0.01 mmol), THF (1 mL), 100 °C, 30 bar H_2, 18 h.

[b] Conversion was determined by GC analysis using hexadecane as an internal standard (isolated yield in parentheses).

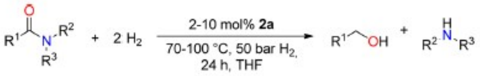
[c] Substrate (0.5 mmol), **3** (0.005 mmol), yield was determined GC analysis using hexadecane as an internal standard.

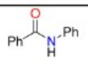
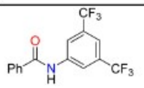
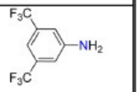
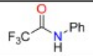
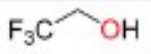
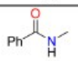
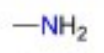
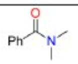
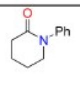
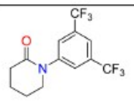
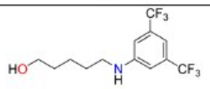
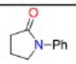
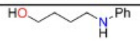
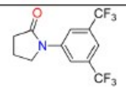
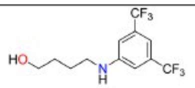
[d] 2 mol% **3**.

[e] 60 °C.

C-Fe-2 – Amides

F. Schneck, M. Assmann, M. Balmer, K. Harms and R. Langer, *Organometallics*, **2016**, *35*, 1931-1943.

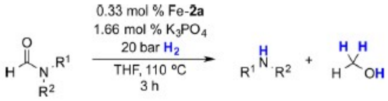


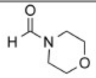
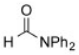
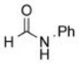
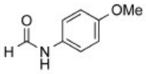
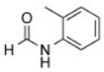
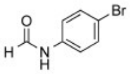
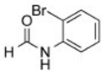
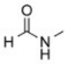
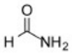
entry	*amide*	*S/C*	*Temperature / °C*	*conversion*[b] */ %*	*alcohol (yield / %)*	*amine (yield / %)*
1						Ph−NH_2
		10/1	70	94	90	93
		50/1	70	57	45	45
		50/1	100	>99	99	99
2						
		10/1	70	>99	82	83
		50/1	70	57	53	53
3		50/1	70	>99	 (n. d.)	Ph−NH_2 99
4						
		10/1	70	0	0	(n. d.)
		10/1	100	14	4	(n. d.)
5						
		10/1	70	36	14	(n. d.)
		10/1	100	53	50	(n. d.)
6						
		10/1	70	0	0	
		10/1	100	0	0	
7						
		10/1	70	0	0	
		10/1	100	0	0	
8						
		10/1	70	0	0	
		10/1	100	49	41[c]	
9						
		10/1	70	84	70[c]	
		10/1	100	>99	92[c]	

[a] Reaction conditions: substrate (1.00 mmol), precatalyst **2a** (0.02–0.10 mmol), and *m*-xylene (1.00 mmol) as internal standard and THF (5 mL).
[b] Conversion and yield were determined by GC analysis using *m*-xylene as an internal standard. [c] Isolated yield.

C-Fe-3 – Formamides

N. M. Rezayee, D. C. Samblanet and M. S. Sanford, *ACS Catalysis*, **2016**, *6*, 6377-6383.

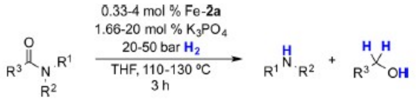


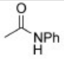
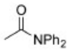
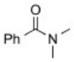
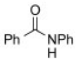
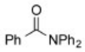
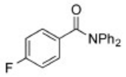
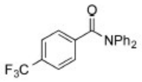
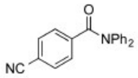
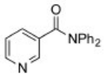
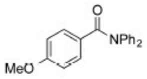
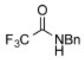
Entry	Substrate	conversion	yield	TON
1		>99%	>99%[b]	300
2		>99%	99%	300
3		>99%	95%	300
4		69%	57%	207
5		>99%	94%	300
6		>99%	96%	300
7		>99%	97%	300
8		12%	12%[b]	36
9		1%	1%[b]	3

[a]Conditions: 3 mmol of amide, 10 μmol of Fe-2a, 50 μmol of K_3PO_4, 2 mL of THF, 20 bar of H_2, 110 °C, 3 h. Yields are isolated yields of the amine product. Conversions (based on DMF) and TONs (based on CH_3OH) were determined by ^1H NMR spectroscopy. [b]Yield determined by ^1H NMR spectroscopy based on CH_3OH.

C-Fe-3 – Amides

N. M. Rezayee, D. C. Samblanet and M. S. Sanford, *ACS Catalysis*, **2016**, *6*, 6377-6383.

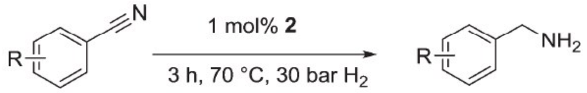


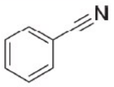
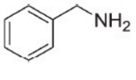
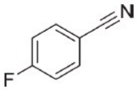
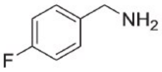
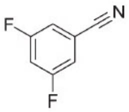
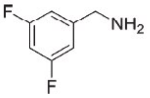
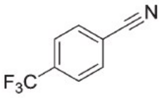
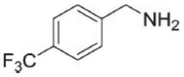
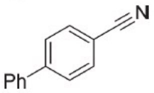
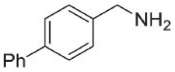
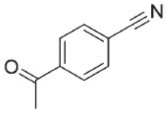
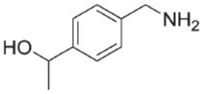
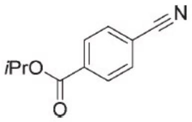
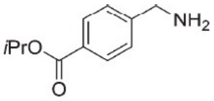
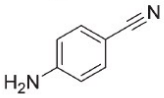
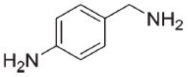
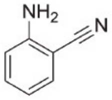
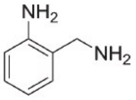
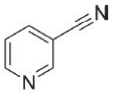
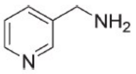
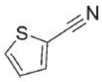
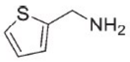
Entry	Substrate	conversion	yield	TON
1[b]		>99%	88%	50
2[b]		>99%	96%	50
3		38%	36%	9
4		>99%	95%	25
5		>99%	99%	25
6		>99%	93%	25
7		>99%	94%	25
8[c]		>99%	94%	25
9		>99%	95%	25
10		<1%	<1%	<1
11[d]		44%[d]	44%[d]	120

[a] Conditions unless specified otherwise: 0.25 mmol of amide, 10 μmol of Fe-2a, 50 μmol of K_3PO_4, 2 mL of THF, 50 bar of H_2, 130 °C, 3 h. Yields are isolated yields of the amine product. Conversions (based on amide substrate) and TONs (based on ROH) were determined by ^{1}H NMR spectroscopy. [b] Conditions: 0.50 mmol of amide, 10 μmol of Fe-2a, 50 μmol of K_3PO_4, 2 mL of THF, 30 bar of H_2, 110 °C, 3 h. [c] The nitrile functional group was also hydrogenated. [d] Conditions: 3 mmol of amide, 10 μmol of Fe-2a, 50 μmol of K_3PO_4, 2 mL of THF, 20 bar of H_2, 110 °C, 3 h. Conversion was determined by ^{19}F NMR spectroscopy and yield by ^{1}H NMR spectroscopy based on 2,2,2-trifluoroethanol.

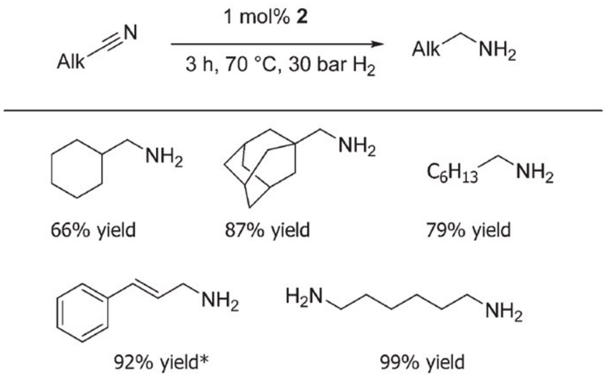
C-Fe-3 – Nitriles

S. Lange, S. Elangovan, C. Cordes, A. Spannenberg, H. Jiao, H. Junge, S. Bachmann, M. Scalone, C. Topf, K. Junge and M. Beller, *Catalysis Science & Technology*, **2016**, *6*, 4768-4772.



Entry	Nitrile	Amine	Yield[b] [%]
1[c]			95
2			84
3			41[d] 44[g]
4[d]			88
5			93
6[d]			63[f]
7[e]			95
8			70[f]
9			94 81[f]
10			41 84[g]
11[d]			90

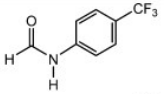
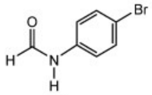
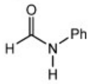
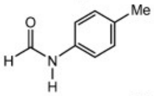
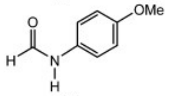
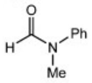
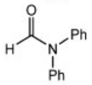
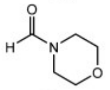
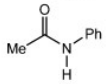
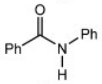
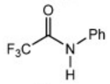
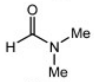
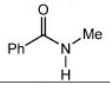
[a] Conditions: 1.0 mmol of nitrile, 1 mol% **2**, 2 mL of iPrOH, 30 bar H_2, 3 h, 70 °C. [b] Determined by GC analysis. [c] 0.5 mol% **2**. [d] 30 bar H_2, 100 °C, 3 h. [e] 1 mol% **3**, 30 bar H_2, 100 °C, 3 h. [f] Isolated yields of ammonium salt. [g] 5 mol% **2**, 30 bar H_2, 100 °C, 3 h.



Scheme 3 Yield of different alkyl amines using **2**. Reaction conditions: 1.0 mmol of nitrile, 1 mol% **2**, 2 mL of iPrOH, 30 bar H_2, 3 h, 70 °C; * 100 °C, *ca.* 8% of C═C hydrogenation.

C-Fe-4 – Formamides

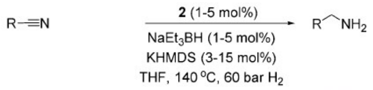
U. Jayarathne, Y. Zhang, N. Hazari and W. H. Bernskoetter, *Organometallics*, **2017**, *36*, 409-416.’

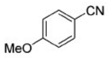
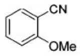
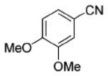
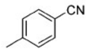
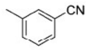
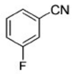
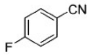
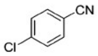
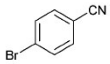
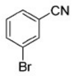
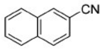
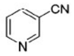
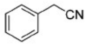
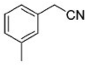
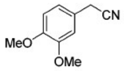
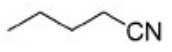
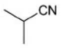
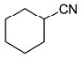
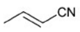
Entry	Substrate	0.070 mol% 1 TON (Conv.)[b]	0.018 mol% 1 TON (Conv.)[b]
1		>1390 (>99%)	4430 (79%)
2		>1390 (>99%)	3360 (60%)
3		>1390 (>99%)	3240 (58%)
4		>1390 (>99%)	2610 (47%)
5		>1390 (>99%)	1920 (34%)
6		60 (4%)	--
7		1190 (85%)	--
8		1360 (97%)	2000
9		50 (<5%)	--
10		130 (9%)	--
11		160 (11%)	--
12		No conversion	--
13		No conversion	--

[a] Reaction conditions: 30 atm H_2 (~450 psi), 5.0−1.25 μmol of 1 (0.07−0.018 mol %), and 7 mmol of amide in 5 mL of THF at 100 °C for 4 h.
[b] Determined by NMR and GC analyses of the product amine or alcohol (in the case of highly volatile product amines) as well as residual starting material. Each entry is the average of two or more trials.

M-Fe-1 – Nitriles

S. Chakraborty, G. Leitus and D. Milstein, *Chemical Communications*, **2016**, *52*, 1812-1815.



Entry[a]	Substrate	Mol% (**2**)	Time (h)	Conv.[b] (%)	Yield[b] (%)
1		1	19	99	99
2		1	36	99	99
3		2	36	92	92
4		1	19	99	99
5		1	16	99	99
6		5	48	99	97
7		5	24	99	98
8		5	48	99	99
9		5	48	99	84
10		5	36	95	63
11		2	36	78	78
12		5	48	68	68
13		1	39	99	99
14		1	48	94	90
15		2	60	99	99
16		5	48	90	90
17		5	48	81	81
18[c]		5	48	83	83
19		5	36	99	99
20[c]		1	36	85	66

[a] Conditions: nitrile (0.4–1 mmol), **2**/$NaHBEt_3$/KHMDS ratio 1 : 1 : 3, H_2 (60 bar), and THF (2 mL), heated in an autoclave at 140 °C bath temperature. [b] Conversions and yields determined by GC-MS or ^1H NMR using *m*-xylene or toluene as internal standard. [c] The reactions were carried out using toluene as solvent.

M-Fe-2 – Esters

P. Gajewski, A. Gonzalez-de-Castro, M. Renom-Carrasco, U. Piarulli, C. Gennari, J. G. de Vries, L. Lefort and L. Pignataro, *ChemCatChem*, **2016**, *8*, 3431-3435.

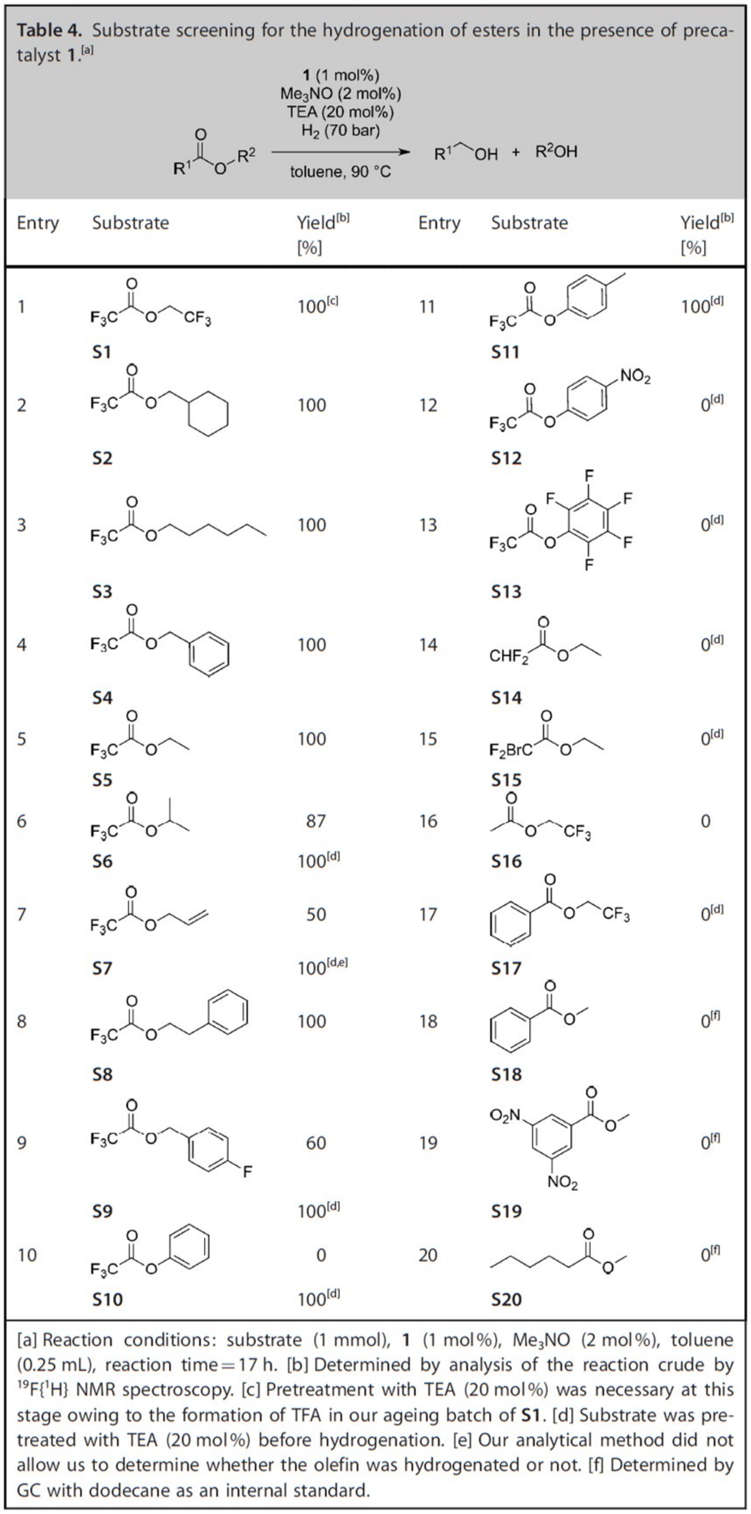


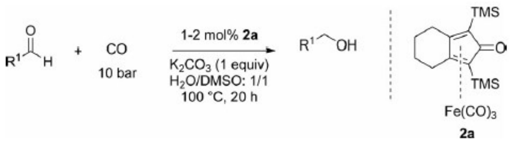
Table 4. Substrate screening for the hydrogenation of esters in the presence of precatalyst **1**.[a]

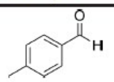
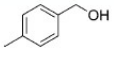
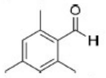
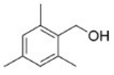
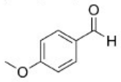
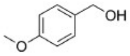
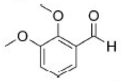
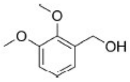
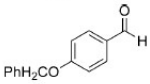
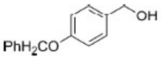
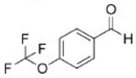
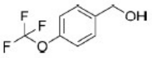
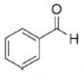
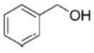
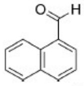
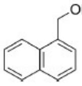
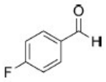
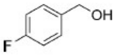
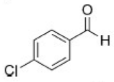
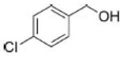
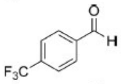
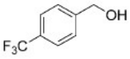
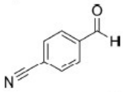
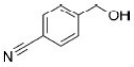
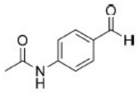
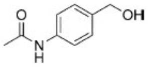
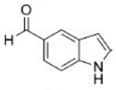
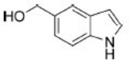
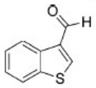
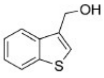
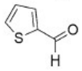
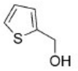
Entry	Substrate	Yield[b] [%]	Entry	Substrate	Yield[b] [%]
1	S1	100[c]	11	S11	100[d]
2	S2	100	12	S12	0[d]
3	S3	100	13	S13	0[d]
4	S4	100	14	S14	0[d]
5	S5	100	15	S15	0[d]
6	S6	87 100[d]	16	S16	0
7	S7	50 100[d,e]	17	S17	0[d]
8	S8	100	18	S18	0[f]
9	S9	60 100[d]	19	S19	0[f]
10	S10	0 100[d]	20	S20	0[f]

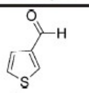
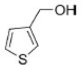
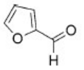
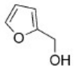
[a] Reaction conditions: substrate (1 mmol), **1** (1 mol%), Me_3NO (2 mol%), toluene (0.25 mL), reaction time = 17 h. [b] Determined by analysis of the reaction crude by $^{19}F\{^1H\}$ NMR spectroscopy. [c] Pretreatment with TEA (20 mol%) was necessary at this stage owing to the formation of TFA in our ageing batch of **S1**. [d] Substrate was pretreated with TEA (20 mol%) before hydrogenation. [e] Our analytical method did not allow us to determine whether the olefin was hydrogenated or not. [f] Determined by GC with dodecane as an internal standard.

M-Fe-2 – Aldehydes

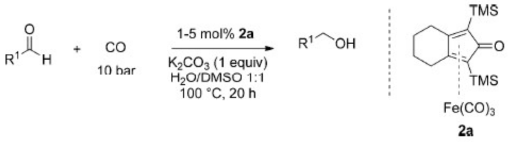
A. Tlili, J. Schranck, H. Neumann and M. Beller, *Chemistry – A European Journal*, **2012**, *18*, 15935-15939.

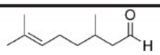
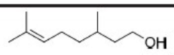
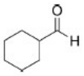
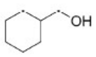
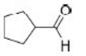
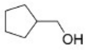
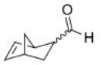
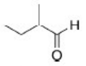
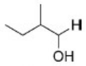
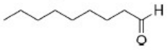
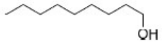


	Aromatic aldehyde	Product	**2a** [mol %]	Yield[b] [%]
1			1	99 (96)
2			1	99
3			1	99
4			1	99
5			1	97 (92)
6			1	99
7			1	99 (95)
8			1	99
9			1	99
10			1	99 (94)
11			1	82
12			2	76
13			1	96
14			1	66 (59)
15			2	78 (76)
16			1	92

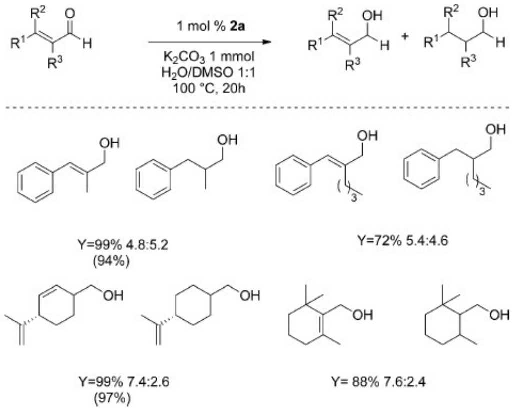
	Aromatic aldehyde	Product	**2a** [mol %]	Yield[b] [%]
17			1	96
18			1	59

[a] Reactions performed with aldehyde (1 mmol), base (1 mmol), **2a** and CO (10 bar). [b] GC yield calculated with hexadecane as internal standard. Yields of the isolated product are in brackets.



	Aliphatic aldehydes	Products	**2a** [mol %]	Yield[b] [%]
1			5	99 (95)
2			1	99
3			1	99
4			1	99 (96)
5			1	92
6			5	62[c]

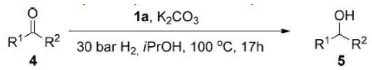
[a] Reactions performed with aldehyde (1 mmol), base(1 mmol), **2a** and CO (10 bar). [b] GC yields calculated with hexadecane as internal standard. Yields of the isolated product are in brackets. [c] Reaction performed with 2 mmol of base. Isolated yields in brackets.



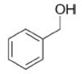
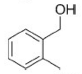
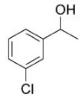
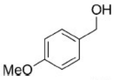
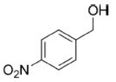
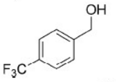
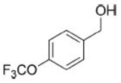
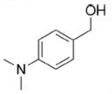
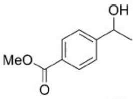
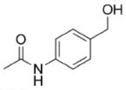
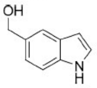
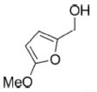
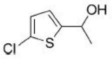
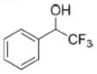
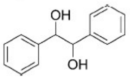
Scheme 3. Iron-catalyzed reduction of α,β-unsaturated aldehydes. Reactions performed with of aldehyde(1 mmol), of base (1 mmol), **2a** (1 mol %) and CO (10 bar). GC yields calculated with hexadecane as the internal standard. Yields of the isolated product are in brackets.

M-Fe-3 – Aldehydes

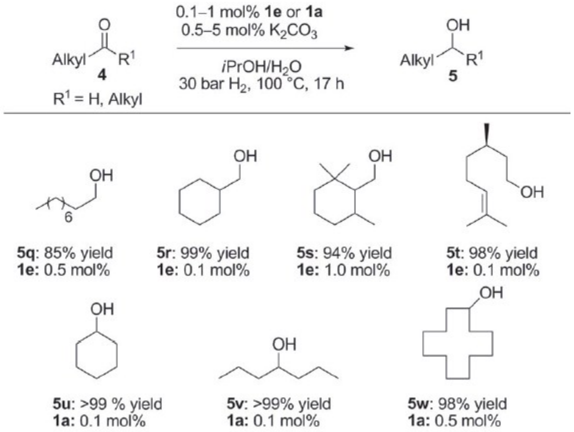
S. Fleischer, S. Zhou, K. Junge and M. Beller, *Angewandte Chemie International Edition*, **2013**, *52*, 5120-5124.



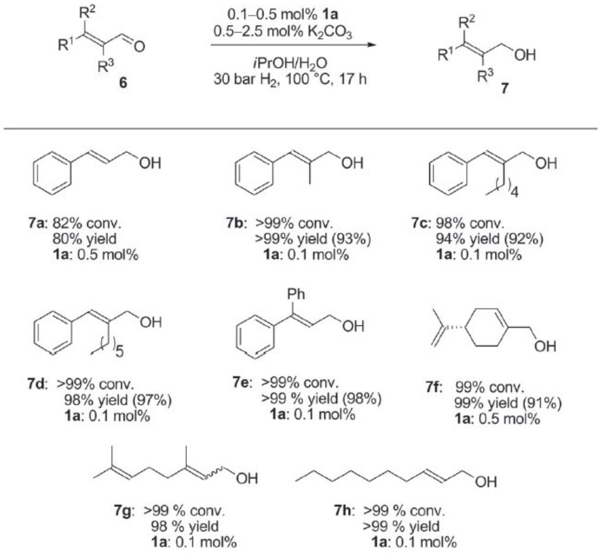
R^1 = aryl, heteroaryl
R^2 = H, alkyl

Entry	Product	1a (mol %)	Yield[c] [%]
1	 **5b**	0.1	94 (89)
2	 **5c**	0.5	99
3	 **5d**	0.1	98
4	 **5e**	0.1	99 (96)
5	 **5f**	0.1	99 (96)
6	 **5g**	1	98
7	 **5h**	1	>99
8	 **5i**	0.1	>99
9	 **5j**	0.5	76
10	 **5k**	0.1	99 (92)
11	 **5l**	0.5	95
12	 **5m**	0.1	>99 (97)
13	 **5n**	0.5	82
14	 **5o**	0.5	>99
15	 **5p**	0.5	>99[c]

[a] General reaction conditions: aldehyde or ketone **4** (1.0 mmol), **1a** (0.01–1 mol %), 5-fold excess K_2CO_3 (0.05–5 mol %), *i*PrOH/H_2O (0.5 mL/0.2 mL), H_2 (10–30 bar) for 17 h. [b] Determined by GC analysis using hexadecane as an internal. Yield of isolated product given within parentheses. [c] *cis*/*trans* ratio 4:1.



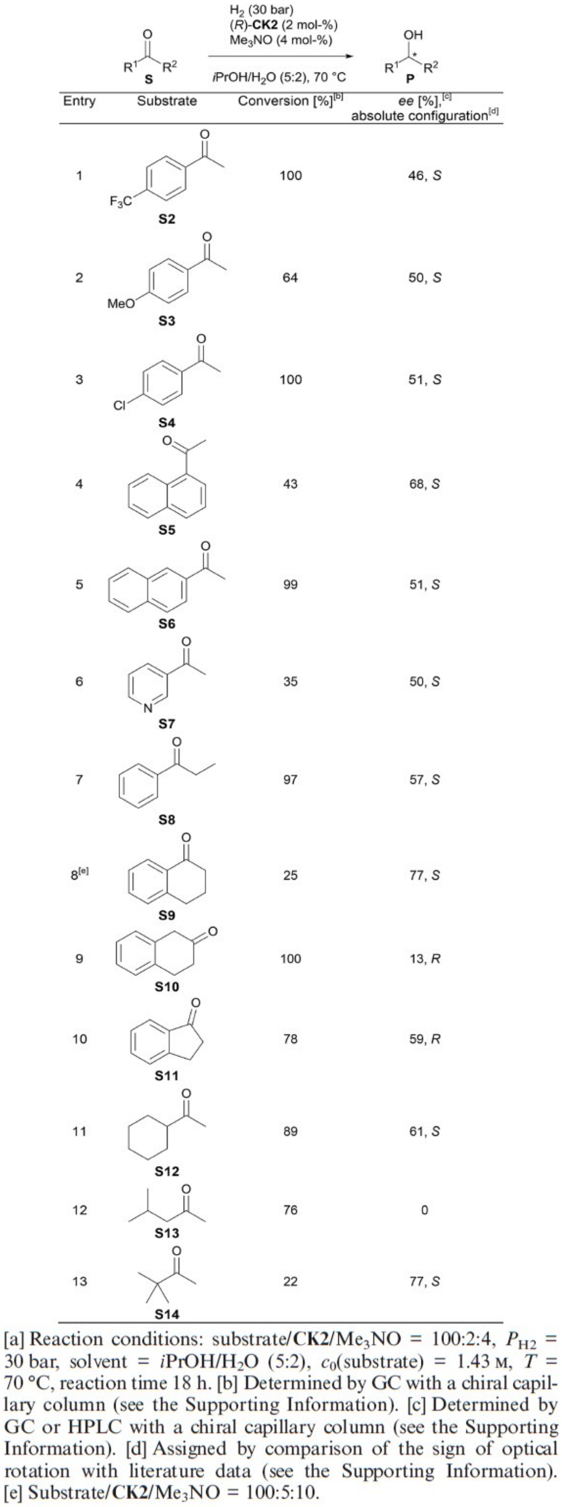
Scheme 2. Iron-catalyzed hydrogenation of aliphatic aldehydes and ketones into allylic and secondary alcohols.



Scheme 3. Iron-catalyzed hydrogenation of α,β-unsaturated aldehydes into allylic alcohols.

M-Fe-4 – Ketones

P. Gajewski, M. Renom-Carrasco, S. V. Facchini, L. Pignataro, L. Lefort, J. G. de Vries, R. Ferraccioli, A. Forni, U. Piarulli and C. Gennari, *European Journal of Organic Chemistry*, **2015**, 1887-1893.



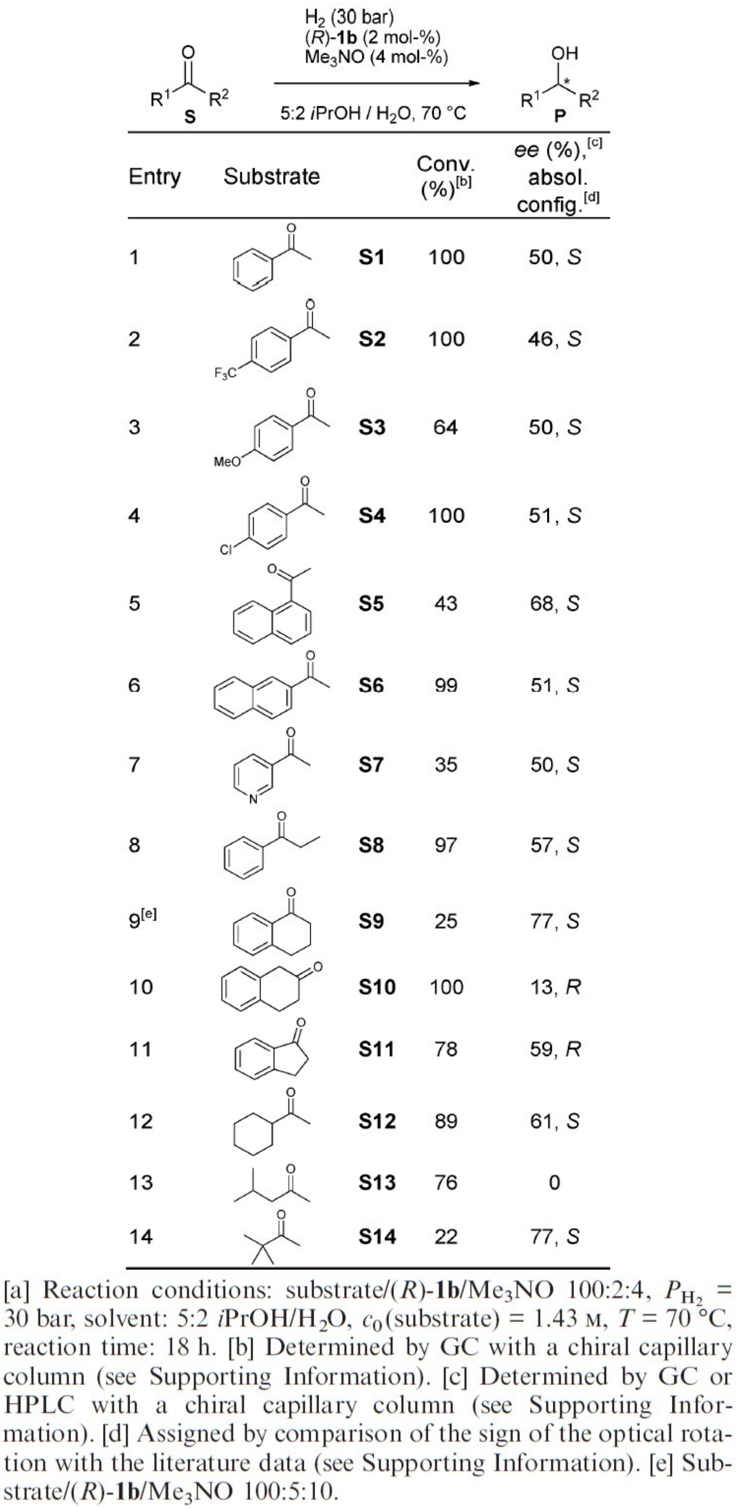
S $\xrightarrow[i\text{PrOH/H}_2\text{O (5:2), 70 °C}]{\text{H}_2\text{ (30 bar), (}R\text{)-}\textbf{CK2}\text{ (2 mol-\%), Me}_3\text{NO (4 mol-\%)}}$ **P**

Entry	Substrate	Conversion [%][b]	*ee* [%],[c] absolute configuration[d]
1	**S2**	100	46, *S*
2	**S3**	64	50, *S*
3	**S4**	100	51, *S*
4	**S5**	43	68, *S*
5	**S6**	99	51, *S*
6	**S7**	35	50, *S*
7	**S8**	97	57, *S*
8[e]	**S9**	25	77, *S*
9	**S10**	100	13, *R*
10	**S11**	78	59, *R*
11	**S12**	89	61, *S*
12	**S13**	76	0
13	**S14**	22	77, *S*

[a] Reaction conditions: substrate/**CK2**/Me_3NO = 100:2:4, P_{H2} = 30 bar, solvent = *i*PrOH/H_2O (5:2), c_0(substrate) = 1.43 м, *T* = 70 °C, reaction time 18 h. [b] Determined by GC with a chiral capillary column (see the Supporting Information). [c] Determined by GC or HPLC with a chiral capillary column (see the Supporting Information). [d] Assigned by comparison of the sign of optical rotation with literature data (see the Supporting Information). [e] Substrate/**CK2**/Me_3NO = 100:5:10.

M-Fe-4 – Ketones

P. Gajewski, M. Renom-Carrasco, S. V. Facchini, L. Pignataro, L. Lefort, J. G. de Vries, R. Ferraccioli, U. Piarulli and C. Gennari, *European Journal of Organic Chemistry*, **2015**, 5526-5536.



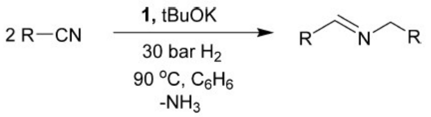
H_2 (30 bar)
(*R*)-**1b** (2 mol-%)
Me_3NO (4 mol-%)
5:2 *i*PrOH / H_2O, 70 °C

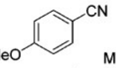
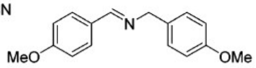
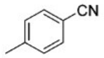
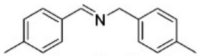
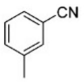
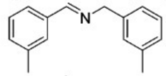
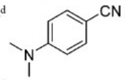
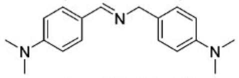
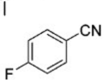
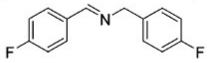
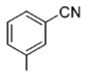
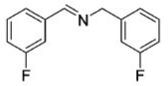
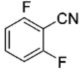
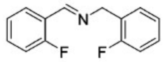
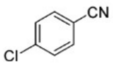
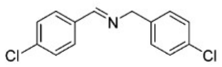
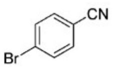
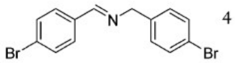
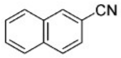
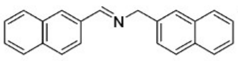
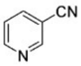
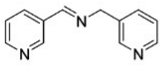
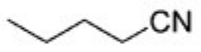
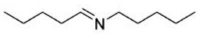
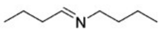
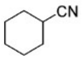
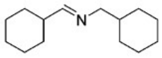
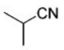
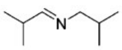
Entry	Substrate	Conv. (%)[b]	*ee* (%),[c] absol. config.[d]
1	**S1**	100	50, *S*
2	**S2**	100	46, *S*
3	**S3**	64	50, *S*
4	**S4**	100	51, *S*
5	**S5**	43	68, *S*
6	**S6**	99	51, *S*
7	**S7**	35	50, *S*
8	**S8**	97	57, *S*
9[e]	**S9**	25	77, *S*
10	**S10**	100	13, *R*
11	**S11**	78	59, *R*
12	**S12**	89	61, *S*
13	**S13**	76	0
14	**S14**	22	77, *S*

[a] Reaction conditions: substrate/(*R*)-**1b**/Me_3NO 100:2:4, P_{H_2} = 30 bar, solvent: 5:2 *i*PrOH/H_2O, c_0(substrate) = 1.43 M, *T* = 70 °C, reaction time: 18 h. [b] Determined by GC with a chiral capillary column (see Supporting Information). [c] Determined by GC or HPLC with a chiral capillary column (see Supporting Information). [d] Assigned by comparison of the sign of the optical rotation with the literature data (see Supporting Information). [e] Substrate/(*R*)-**1b**/Me_3NO 100:5:10.

M-Fe-5 – Nitriles

S. Chakraborty and D. Milstein, *ACS Catalysis*, **2017**, *7*, 3968-3972.



Entry[a]	Substrate	Product	**1** mol%	Time (h)	Conv[b] (%)	Yield[b] (%)
1			1	<36	>99	97
2[c]			2	<36	>99	93
3[c]			1	<36	>99	91
4[d]			2	18	81	52
5[d]			1	24	>99	79
6[d]			4	36	>99	56
7[d]			4	36	59	28
8			4	14	>99	99
9			4	12	>99	99
10[d]			4	16	>99	70
11[d]			4	14	80	61
12			8	36	61	61
13			8	36	32	32
14			8	36	69	69
15			8	36	11	11

[a] Conditions: benzonitrile (1−0.125 mmol), **1** (0.01 mmol), *t*BuOK (1 equiv relative to **1**), and 2 mL of C_6H_6 (1 mL for 4 mol % and 8 mol % cat loading), heated in an autoclave at 90 °C under 30 bar H_2. [b] Yields and conversions determined by GC-MS and ^{1}H NMR analysis using *m*-xylene, or toluene as internal standard. [c] Isolated yield. [d] Differences in conversions of nitriles and yields of secondary imines indicate formation of partially hydrogenated intermediate imines and their trimerized products.

M-Fe-6 – Ketones

A. Zirakzadeh, K. Kirchner, A. Roller, B. Stöger, M. Widhalm and R. H. Morris, *Organometallics*, **2016**, *35*, 3781-3787.

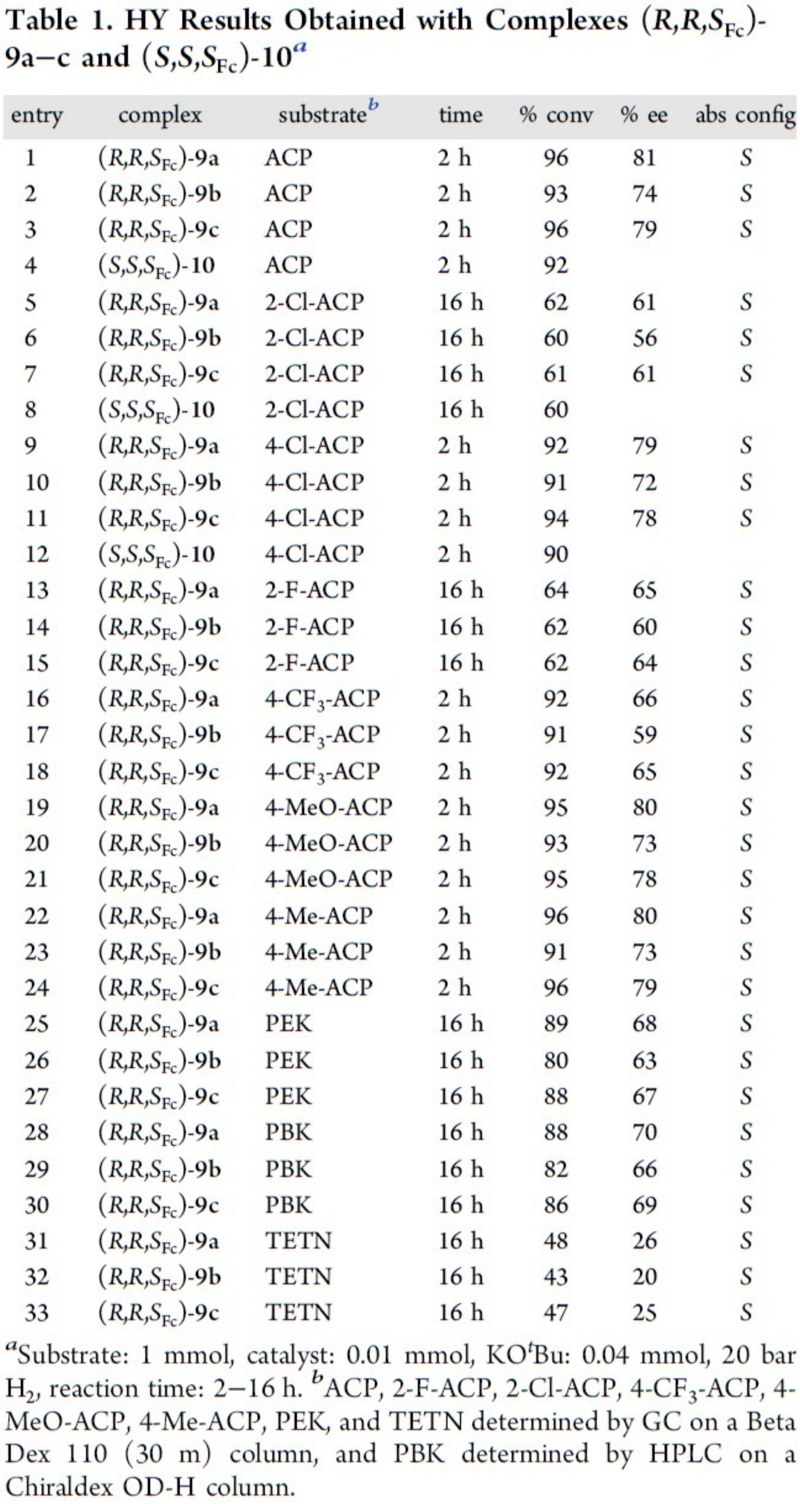


Table 1. HY Results Obtained with Complexes (R,R,S_{Fc})-9a–c and (S,S,S_{Fc})-10[a]

entry	complex	substrate[b]	time	% conv	% ee	abs config
1	(R,R,S_{Fc})-9a	ACP	2 h	96	81	*S*
2	(R,R,S_{Fc})-9b	ACP	2 h	93	74	*S*
3	(R,R,S_{Fc})-9c	ACP	2 h	96	79	*S*
4	(S,S,S_{Fc})-10	ACP	2 h	92		
5	(R,R,S_{Fc})-9a	2-Cl-ACP	16 h	62	61	*S*
6	(R,R,S_{Fc})-9b	2-Cl-ACP	16 h	60	56	*S*
7	(R,R,S_{Fc})-9c	2-Cl-ACP	16 h	61	61	*S*
8	(S,S,S_{Fc})-10	2-Cl-ACP	16 h	60		
9	(R,R,S_{Fc})-9a	4-Cl-ACP	2 h	92	79	*S*
10	(R,R,S_{Fc})-9b	4-Cl-ACP	2 h	91	72	*S*
11	(R,R,S_{Fc})-9c	4-Cl-ACP	2 h	94	78	*S*
12	(S,S,S_{Fc})-10	4-Cl-ACP	2 h	90		
13	(R,R,S_{Fc})-9a	2-F-ACP	16 h	64	65	*S*
14	(R,R,S_{Fc})-9b	2-F-ACP	16 h	62	60	*S*
15	(R,R,S_{Fc})-9c	2-F-ACP	16 h	62	64	*S*
16	(R,R,S_{Fc})-9a	4-CF_3-ACP	2 h	92	66	*S*
17	(R,R,S_{Fc})-9b	4-CF_3-ACP	2 h	91	59	*S*
18	(R,R,S_{Fc})-9c	4-CF_3-ACP	2 h	92	65	*S*
19	(R,R,S_{Fc})-9a	4-MeO-ACP	2 h	95	80	*S*
20	(R,R,S_{Fc})-9b	4-MeO-ACP	2 h	93	73	*S*
21	(R,R,S_{Fc})-9c	4-MeO-ACP	2 h	95	78	*S*
22	(R,R,S_{Fc})-9a	4-Me-ACP	2 h	96	80	*S*
23	(R,R,S_{Fc})-9b	4-Me-ACP	2 h	91	73	*S*
24	(R,R,S_{Fc})-9c	4-Me-ACP	2 h	96	79	*S*
25	(R,R,S_{Fc})-9a	PEK	16 h	89	68	*S*
26	(R,R,S_{Fc})-9b	PEK	16 h	80	63	*S*
27	(R,R,S_{Fc})-9c	PEK	16 h	88	67	*S*
28	(R,R,S_{Fc})-9a	PBK	16 h	88	70	*S*
29	(R,R,S_{Fc})-9b	PBK	16 h	82	66	*S*
30	(R,R,S_{Fc})-9c	PBK	16 h	86	69	*S*
31	(R,R,S_{Fc})-9a	TETN	16 h	48	26	*S*
32	(R,R,S_{Fc})-9b	TETN	16 h	43	20	*S*
33	(R,R,S_{Fc})-9c	TETN	16 h	47	25	*S*

[a] Substrate: 1 mmol, catalyst: 0.01 mmol, KO^{t}Bu: 0.04 mmol, 20 bar H_2, reaction time: 2–16 h. [b] ACP, 2-F-ACP, 2-Cl-ACP, 4-CF_3-ACP, 4-MeO-ACP, 4-Me-ACP, PEK, and TETN determined by GC on a Beta Dex 110 (30 m) column, and PBK determined by HPLC on a Chiraldex OD-H column.

M-Fe-7 – Ketones

S. A. M. Smith, P. O. Lagaditis, A. Lüpke, A. J. Lough and R. H. Morris, *Chemistry – A European Journal*, **2017**, *23*, 7212-7216.

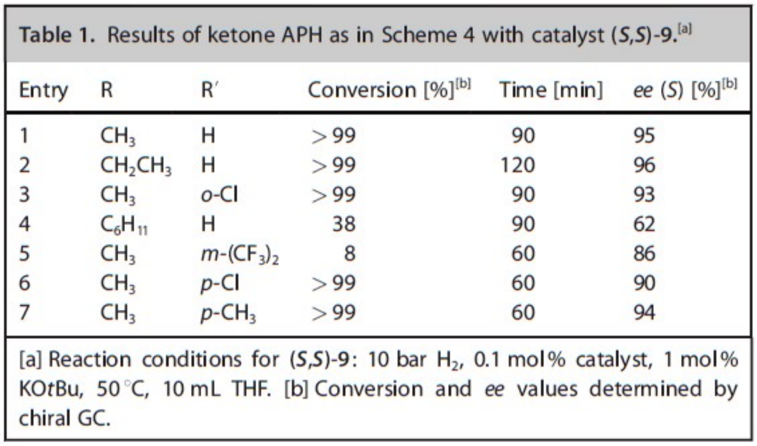
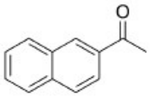


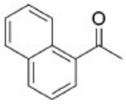
Table 1. Results of ketone APH as in Scheme 4 with catalyst (*S,S*)-**9**.[a]

Entry	R	R′	Conversion [%][b]	Time [min]	*ee* (*S*) [%][b]
1	CH_3	H	>99	90	95
2	CH_2CH_3	H	>99	120	96
3	CH_3	*o*-Cl	>99	90	93
4	C_6H_{11}	H	38	90	62
5	CH_3	*m*-$(CF_3)_2$	8	60	86
6	CH_3	*p*-Cl	>99	60	90
7	CH_3	*p*-CH_3	>99	60	94

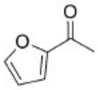
[a] Reaction conditions for (*S,S*)-**9**: 10 bar H_2, 0.1 mol% catalyst, 1 mol% KO*t*Bu, 50 °C, 10 mL THF. [b] Conversion and *ee* values determined by chiral GC.



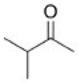
12
99%
90 min
90% (*S*)



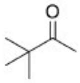
13
61%
90 min
90% (*S*)



14
99%
60 min
95% (*S*)



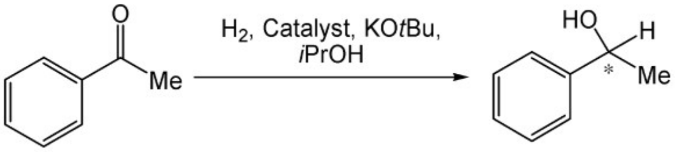
15
99%
60 min
45% (*R*)



16
0%
90 min

M-Fe-0 – Ketones

C. Sui-Seng, F. N. Haque, A. Hadzovic, A.-M. Pütz, V. Reuss, N. Meyer, A. J. Lough, M. Zimmer-De Iuliis and R. H. Morris, *Inorganic Chemistry*, **2009**, *48*, 735-743.



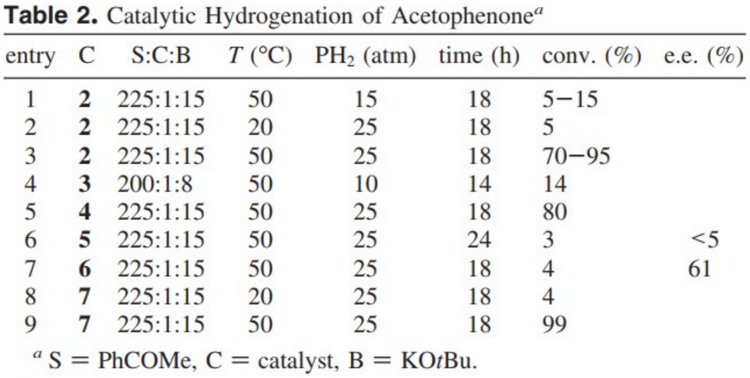


Table 2. Catalytic Hydrogenation of Acetophenone[a]

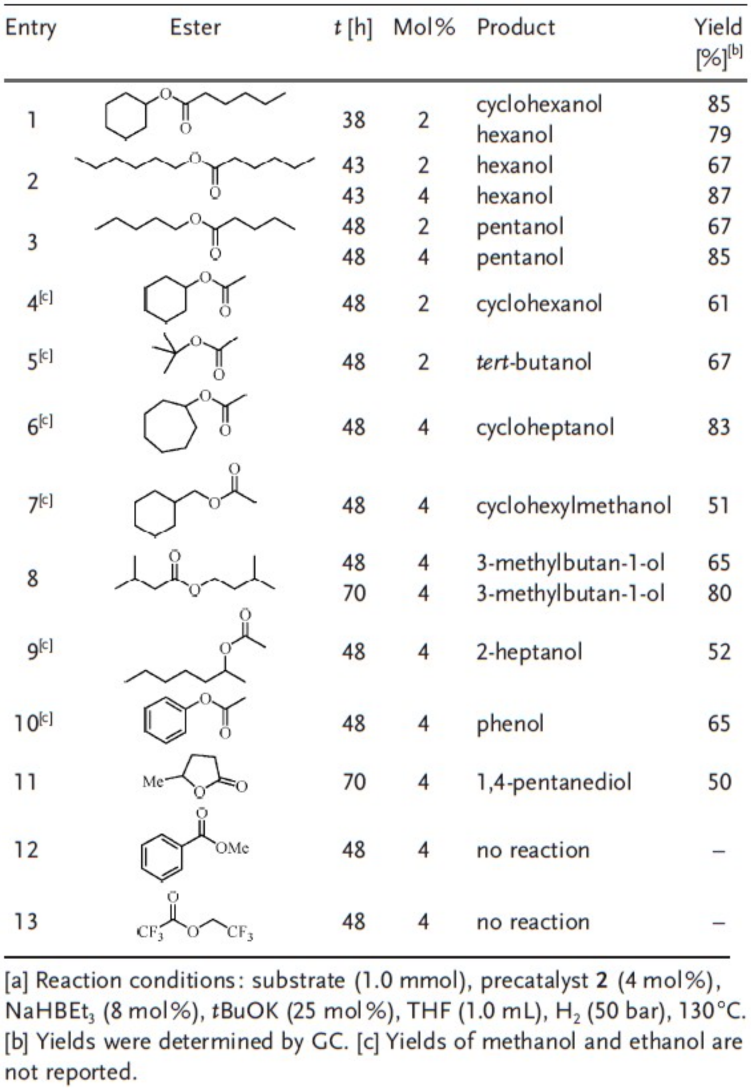
entry	C	S:C:B	*T* (°C)	PH_2 (atm)	time (h)	conv. (%)	e.e. (%)
1	**2**	225:1:15	50	15	18	5−15	
2	**2**	225:1:15	20	25	18	5	
3	**2**	225:1:15	50	25	18	70−95	
4	**3**	200:1:8	50	10	14	14	
5	**4**	225:1:15	50	25	18	80	
6	**5**	225:1:15	50	25	24	3	<5
7	**6**	225:1:15	50	25	18	4	61
8	**7**	225:1:15	20	25	18	4	
9	**7**	225:1:15	50	25	18	99	

[a] S = PhCOMe, C = catalyst, B = KO*t*Bu.

3.1.2. – Reduction with molecular hydrogen – Cobalt Catalysts

A-Co-1 – Esters

D. Srimani, A. Mukherjee, A. F. G. Goldberg, G. Leitus, Y. Diskin-Posner, L. J. W. Shimon, Y. Ben David and D. Milstein, *Angewandte Chemie International Edition*, **2015**, *54*, 12357-12360.

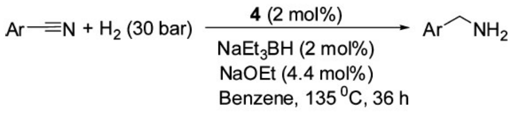


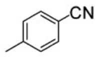
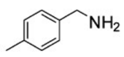
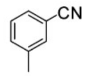
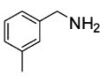
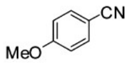
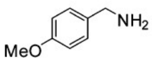
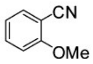
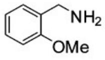
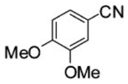
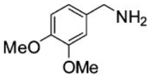
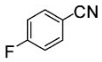
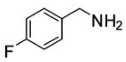
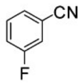
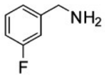
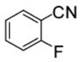
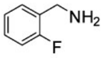
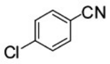
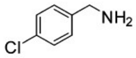
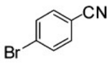
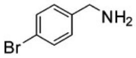
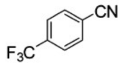
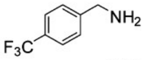
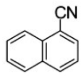
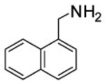
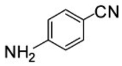
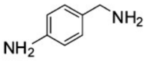
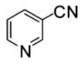
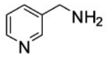
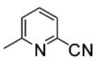
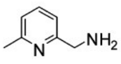
Entry	Ester	*t* [h]	Mol%	Product	Yield [%][b]
1		38	2	cyclohexanol hexanol	85 79
2		43	2	hexanol	67
		43	4	hexanol	87
3		48	2	pentanol	67
		48	4	pentanol	85
4[c]		48	2	cyclohexanol	61
5[c]		48	2	*tert*-butanol	67
6[c]		48	4	cycloheptanol	83
7[c]		48	4	cyclohexylmethanol	51
8		48	4	3-methylbutan-1-ol	65
		70	4	3-methylbutan-1-ol	80
9[c]		48	4	2-heptanol	52
10[c]		48	4	phenol	65
11		70	4	1,4-pentanediol	50
12		48	4	no reaction	–
13		48	4	no reaction	–

[a] Reaction conditions: substrate (1.0 mmol), precatalyst **2** (4 mol%), $NaHBEt_3$ (8 mol%), *t*BuOK (25 mol%), THF (1.0 mL), H_2 (50 bar), 130°C. [b] Yields were determined by GC. [c] Yields of methanol and ethanol are not reported.

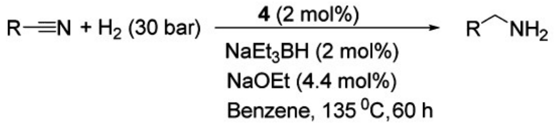
A-Co-1 – Nitriles

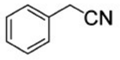
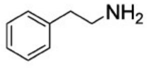
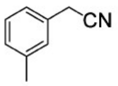
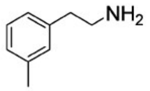
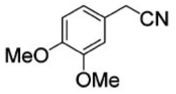
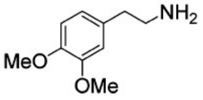
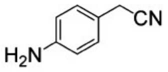
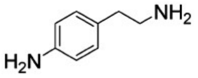
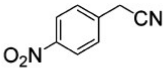
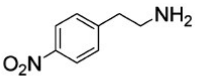
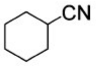
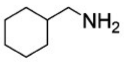
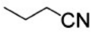
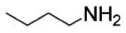
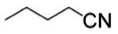
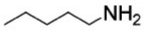
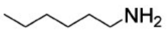
A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David and D. Milstein, *Journal of the American Chemical Society*, **2015**, *137*, 8888-8891.



Entry	Substrate	Product	Conv. (%)[b]	Yield (%)[b]
1			99	99
2			99	99
3			99	99(85)[c]
4			99	99(88)[c]
5			99	99(92)[c]
6			93	83
7			87	78
8			99	99
9			97	93
10			30	6
11			98	57
12			98	98
13			95	86
14			77	71
15			35	30

[a]Conditions: nitrile (1 mmol), **4** (2.0 mol%), $NaEt_3BH$ (2 mol%), NaOEt (4.4 mol%), H_2 (30 bar), and benzene (2 mL), heated in an autoclave at 135 °C bath temperature. [b]Conversions and yields determined by ^1H NMR spectroscopy with respect to toluene or dimethylformamide as an internal standard or by GC analysis. [c]Yields in parentheses refer to isolated product.

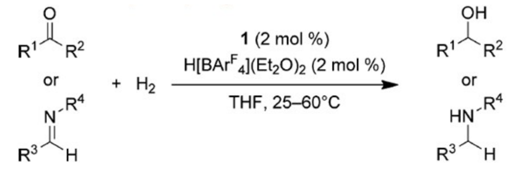


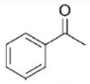
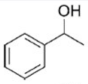
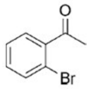
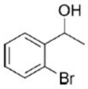
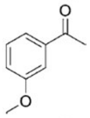
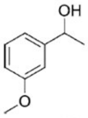
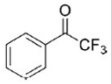
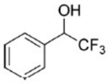
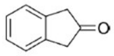
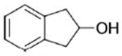
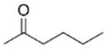
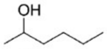
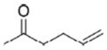
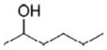
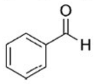
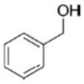
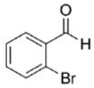
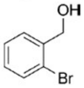
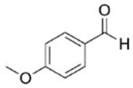
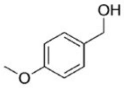
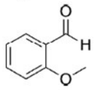
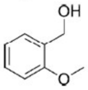
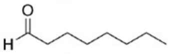
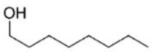
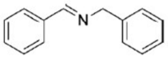
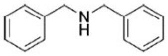
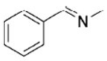
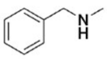
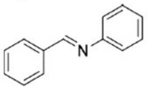
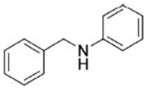
Entry	Substrate	Product	Conv. (%)[b]	Yield (%)
1			85	85
2			99	99
3			86	86
4			85	85
5			-	-
6			90	90
7			67	67
8			70	65[c]
9			99	65[c]

[a] Conditions: nitrile (1 mmol), **4** (2.0 mol%), $NaEt_3BH$ (2 mol%), NaOEt (4.4 mol%), H_2 (30 bar), and benzene (2 mL), heated in an autoclave at 135 °C bath temperature. [b] Conversions and yields determined by ^1H NMR spectroscopy with respect to toluene, dimethylformamide, pyridine, or mesitylene as an internal standard or by GC analysis. [c] Formation of secondary amine was observed.

C-Co-1 – Ketones & Aldehydes

G. Zhang, B. L. Scott and S. K. Hanson, *Angewandte Chemie International Edition*, **2012**, *51*, 12102-12106.

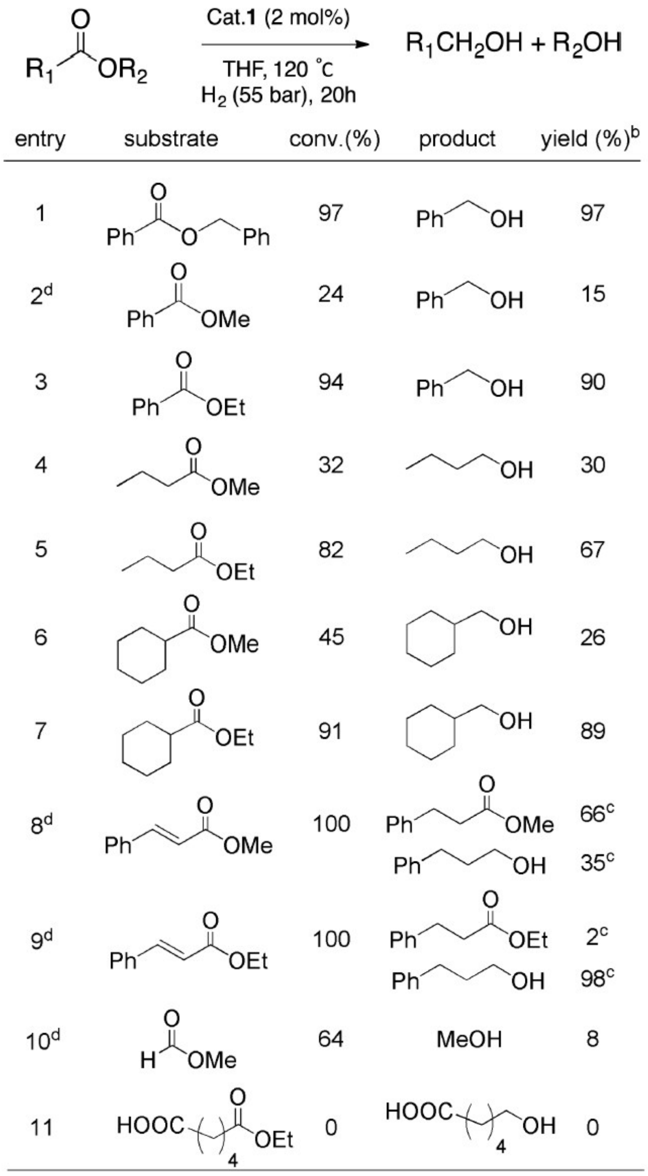


Entry	Substrate	Product	t [h]	Yield[f] [%] (NMR)[g] {GC}[h]
1			24	89 (98)
2[b]			43	86 (94)
3[b]			24	92 (98)
4[b]			48	91 (99)
5[b]			48	97 (99)
6[b]			24	{100}
7[c]			65	{99}
8			24	86 (92)
9			24	96 (100)
10[d]			24	92 (98)
11[d]			24	91 (99)
12[e]			64	92 (100)
13[e]			42	84 (89)
14[e]			72	88 (98)
15[e]			48	65 (70)

[a] Conditions: substrate (0.5 mmol) in THF (2 mL), H_2 (1 atm), 25 °C. [b] Reactions run at 60 °C. [c] Reactions run at 25 °C under 4 atm of H_2. [d] Reactions run at 50 °C. [e] Reactions run at 60 °C under 4 atm of H_2. [f] Yields of isolated products. [g] Yields determined by NMR spectroscopy. [h] Yields determined by GC analysis.

C-Co-2 – Esters

J. Yuwen, S. Chakraborty, W. W. Brennessel and W. D. Jones, *ACS Catalysis*, **2017**, *7*, 3735-3740.



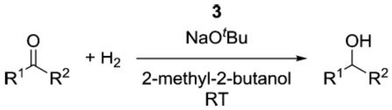
$$R_1C(=O)OR_2 \xrightarrow[\text{THF, 120 °C; } H_2 \text{ (55 bar), 20h}]{\text{Cat.}\mathbf{1}\text{ (2 mol\%)}} R_1CH_2OH + R_2OH$$

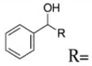
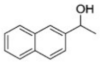
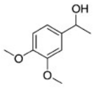
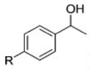
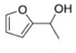
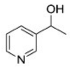
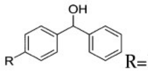
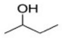
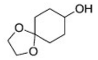
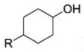
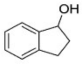
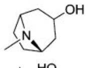
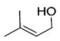
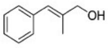
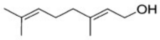
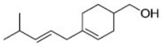
entry	substrate	conv.(%)	product	yield (%)[b]
1	O Ph O Ph	97	Ph OH	97
2[d]	O Ph OMe	24	Ph OH	15
3	O Ph OEt	94	Ph OH	90
4	O OMe	32	OH	30
5	O OEt	82	OH	67
6	O OMe	45	OH	26
7	O OEt	91	OH	89
8[d]	Ph O OMe	100	Ph O OMe Ph OH	66[c] 35[c]
9[d]	Ph O OEt	100	Ph O OEt Ph OH	2[c] 98[c]
10[d]	O H OMe	64	MeOH	8
11	HOOC ( )4 O OEt	0	HOOC ( )4 OH	0

[a]Reaction conditions: substate (0.5 mmol), catalyst **1** (2 mol %), THF (1.0 mL), H_2 (55 bar), 120 °C, 20 h. [b]Yields were determined by GC. [c]Product yields are ratios at 100% conversion. Yields of methanol and ethanol are not reported. [d]Toluene was used as solvent.

M-Co-1 – Ketones & Aldehydes

S. Rösler, J. Obenauf and R. Kempe, *Journal of the American Chemical Society*, **2015**, *137*, 7998-8001.



Entry	Product	Cat. loading [mol%]	Yield[b] [%]
1	 R= CH_3	0.25	>99
2	R= CH_2CH_3	0.5	>99
3	R= $(CH_2)_4CH_3$	0.5	>99
4	R=H	0.5	>99
5		0.5	>99
6		0.25	>99
7	 R=F	1.0	98 (94[c])
8	R=Cl	1.0	>99
9	R=Br	2.0	64
10		3.0	91
11		3.0	95
12	 R=H	0.25	>99
13	R= Me	0.5	>99 (97[c])
14	R= OMe	0.5	97
15		0.5	98
16		0.5	>99
17	 R= H	0.25	>99
18	R= Ph	0.5	>99 (93[c])
19		0.5	>99
20		1.0	>99 (92[c])
21		0.5	>99
22		1.0	>99 (97[c])
23		0.5	>99
24		0.5	>99 (95[c])

[a] Reaction conditions: 3.0 mmol of carbonyl compound, 2.0 mL of 2-methyl-2-butanol, NaO^tBu (2.0 equiv with respect to the precatalyst), 20 °C, 24 h, 20 bar H_2, precatalyst 3. [b] Determined via GC with dodecane as internal standard. [c] Isolated yield.

M-Co-2 – Carboxylic Acids & Esters

T. J. Korstanje, J. Ivar van der Vlugt, C. J. Elsevier and B. de Bruin, *Science*, **2015**, *350*, 298-302.

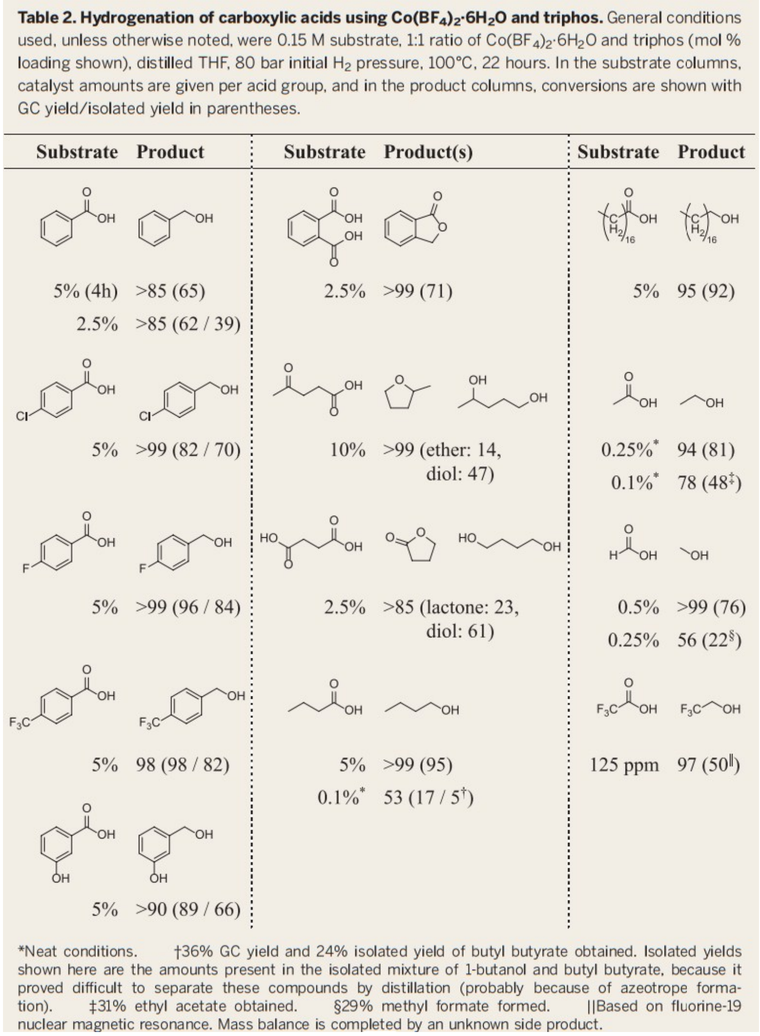
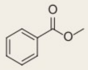
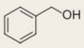
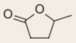
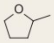
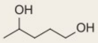
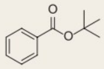
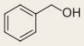
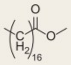
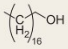
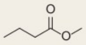
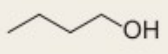
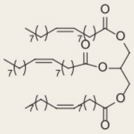
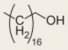
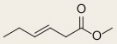


Table 2. Hydrogenation of carboxylic acids using $Co(BF_4)_2 \cdot 6H_2O$ and triphos. General conditions used, unless otherwise noted, were 0.15 M substrate, 1:1 ratio of $Co(BF_4)_2 \cdot 6H_2O$ and triphos (mol % loading shown), distilled THF, 80 bar initial H_2 pressure, 100°C, 22 hours. In the substrate columns, catalyst amounts are given per acid group, and in the product columns, conversions are shown with GC yield/isolated yield in parentheses.

Substrate	Product	Substrate	Product(s)	Substrate	Product
5% (4h) 2.5%	>85 (65) >85 (62 / 39)	2.5%	>99 (71)	5%	95 (92)
5%	>99 (82 / 70)	10%	>99 (ether: 14, diol: 47)	0.25%[*] 0.1%[*]	94 (81) 78 (48[‡])
5%	>99 (96 / 84)	2.5%	>85 (lactone: 23, diol: 61)	0.5% 0.25%	>99 (76) 56 (22[§])
5%	98 (98 / 82)	5% 0.1%[*]	>99 (95) 53 (17 / 5[†])	125 ppm	97 (50[||])
5%	>90 (89 / 66)				

[*] Neat conditions. [†] 36% GC yield and 24% isolated yield of butyl butyrate obtained. Isolated yields shown here are the amounts present in the isolated mixture of 1-butanol and butyl butyrate, because it proved difficult to separate these compounds by distillation (probably because of azeotrope formation). [‡] 31% ethyl acetate obtained. [§] 29% methyl formate formed. [||] Based on fluorine-19 nuclear magnetic resonance. Mass balance is completed by an unknown side product.

Table 1. Hydrogenation of esters using $Co(BF_4)_2 \cdot 6H_2O$ and triphos. General conditions used, unless otherwise noted, were 0.15 M substrate, 1:1 ratio of $Co(BF_4)_2 \cdot 6H_2O$ and triphos (mol % loading shown), distilled MeOH, 80 bar initial H_2 pressure, 100°C, 22 hours. In the substrate columns, catalyst amounts are given per ester group, and in the product columns, conversions are given with gas chromatography (GC) yields in parentheses.

Substrate	Product	Substrate	Product(s)
			 
10% (5h) 5%	98 (95) 99 (79)	10%	98 (ether: 25, diol: 63)
			
10%	>99 (98)	10%	86 (75)
			
5%	50 (47)	10%	>75 (72)
			
10%	>99 (90)		

M-Co-3 – Nitriles

R. Adam, C. B. Bheeter, J. R. Cabrero-Antonino, K. Junge, R. Jackstell and M. Beller, *ChemSusChem*, **2017**, *10*, 842-846.

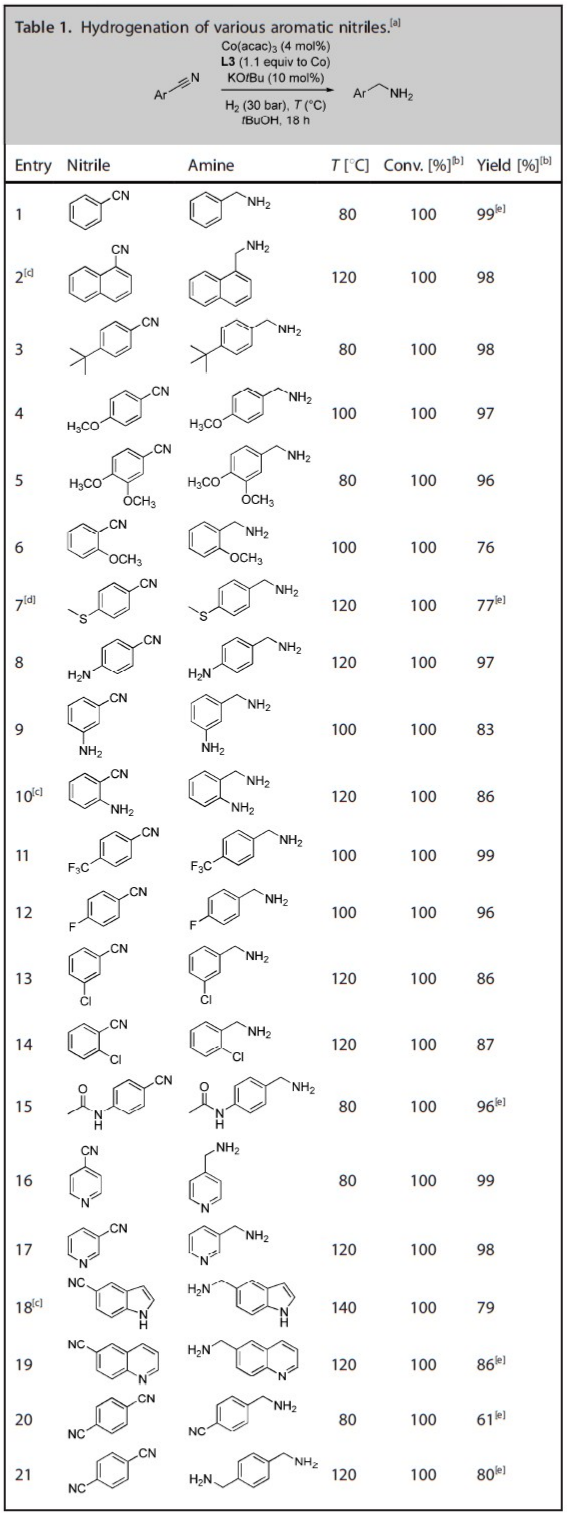
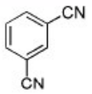
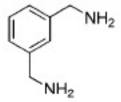


Table 1. Hydrogenation of various aromatic nitriles.[a]

$Co(acac)_3$ (4 mol%)
L3 (1.1 equiv to Co)
KO*t*Bu (10 mol%)
H_2 (30 bar), *T* (°C)
*t*BuOH, 18 h

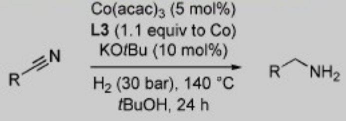
Entry	Nitrile	Amine	*T* [°C]	Conv. [%][b]	Yield [%][b]
1			80	100	99[e]
2[d]			120	100	98
3			80	100	98
4			100	100	97
5			80	100	96
6			100	100	76
7[d]			120	100	77[e]
8			120	100	97
9			100	100	83
10[c]			120	100	86
11			100	100	99
12			100	100	96
13			120	100	86
14			120	100	87
15			80	100	96[e]
16			80	100	99
17			120	100	98
18[c]			140	100	79
19			120	100	86[e]
20			80	100	61[e]
21			120	100	80[e]

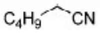
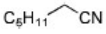
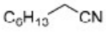
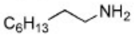
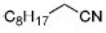
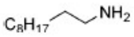
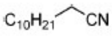
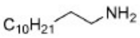
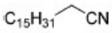
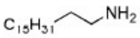
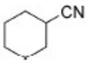
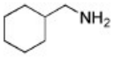
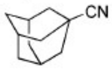
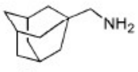
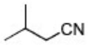
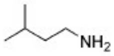
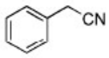
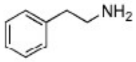
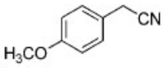
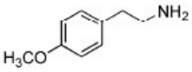
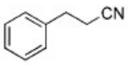
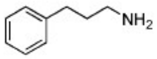
Table 1. (Continued)

Entry	Nitrile	Amine	T [°C]	Conv. [%][b]	Yield [%][b]
22[d]			120	100	79[e]

[a] Standard reaction conditions: nitrile (0.25 mmol), $Co(acac)_3$ (4 mol%), **L3** (4.4 mol%), KO*t*Bu (10 mol%), dry *t*BuOH (2 mL) under 30 bar of H_2, during 18 h. [b] Conversion and yield were calculated by GC using hexadecane as external standard. [c] $Co(acac)_3$ (8 mol%). [d] Run at 48 h. [e] Yield of product isolated as the ammonium salt.

Table 2. Hydrogenation of various aliphatic nitriles.[a]



Entry	Nitrile	Amine	Conv. [%][b]	Yield [%][b]
1			100	83
2			100	99
3			100	91
4[c]			100	99
5[c]			100	98
6[c]			100	70[e]
7			100	99
8			100	90
9[c]			100	92
10[d]			100	71
11[d]			100	87
12			100	89

[a] Standard reaction conditions: nitrile (0.25 mmol), $Co(acac)_3$ (5 mol%), **L3** (5.5 mol%), KO*t*Bu (10 mol%), dry *t*BuOH (2 mL) under 30 bar of H_2 during 24 h. [b] Conversion and yield were calculated by GC using hexadecane as external standard. [c] Run at 48 h. [d] $Co(acac)_3$ (8 mol%). [e] Yield of product isolated as the ammonium salt.

3.1.3. – Reduction with molecular hydrogen – Manganese Catalysts

A-Mn-1 – Esters

N. A. Espinosa-Jalapa, A. Nerush, L. J. W. Shimon, G. Leitus, L. Avram, Y. Ben-David and D. Milstein, *Chemistry – A European Journal*, **2017**, *23*, 5934-5938.

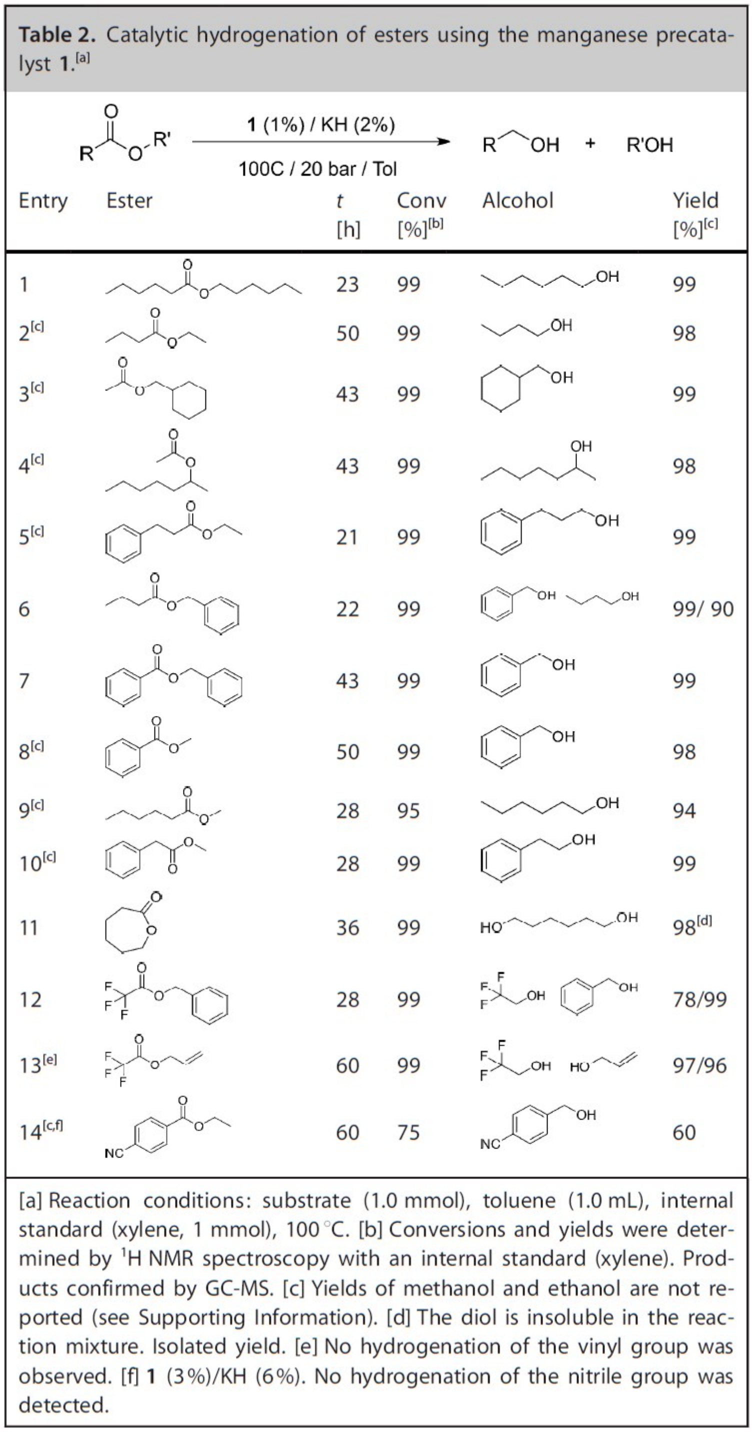


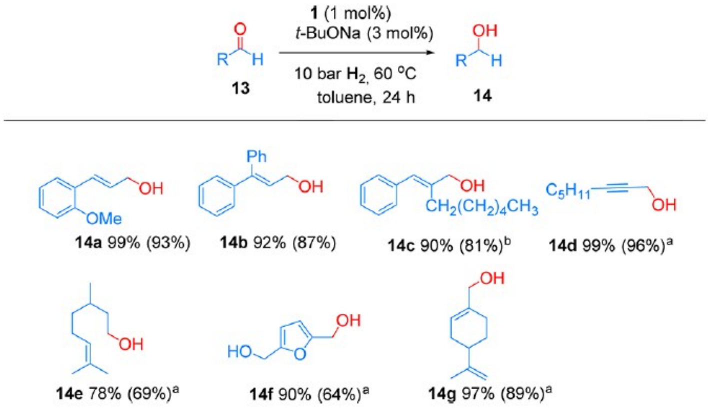
Table 2. Catalytic hydrogenation of esters using the manganese precatalyst **1**.[a]

Entry	Ester	*t* [h]	Conv [%][b]	Alcohol	Yield [%][c]
1		23	99		99
2[c]		50	99		98
3[c]		43	99		99
4[c]		43	99		98
5[c]		21	99		99
6		22	99		99/ 90
7		43	99		99
8[c]		50	99		98
9[c]		28	95		94
10[c]		28	99		99
11		36	99		98[d]
12		28	99		78/99
13[e]		60	99		97/96
14[c,f]		60	75		60

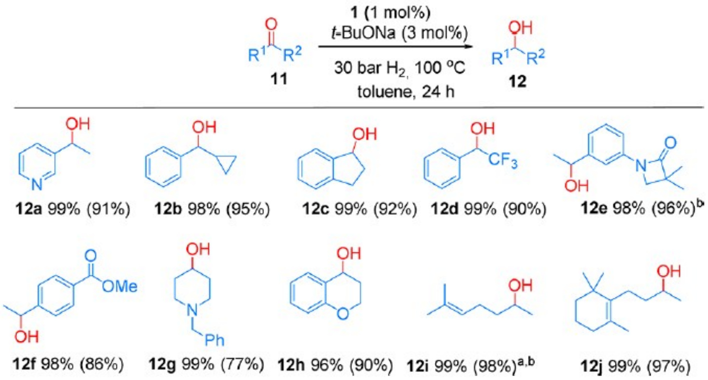
[a] Reaction conditions: substrate (1.0 mmol), toluene (1.0 mL), internal standard (xylene, 1 mmol), 100 °C. [b] Conversions and yields were determined by ^1H NMR spectroscopy with an internal standard (xylene). Products confirmed by GC-MS. [c] Yields of methanol and ethanol are not reported (see Supporting Information). [d] The diol is insoluble in the reaction mixture. Isolated yield. [e] No hydrogenation of the vinyl group was observed. [f] **1** (3%)/KH (6%). No hydrogenation of the nitrile group was detected.

C-Mn-1 – Aldehydes, Ketones & Nitriles

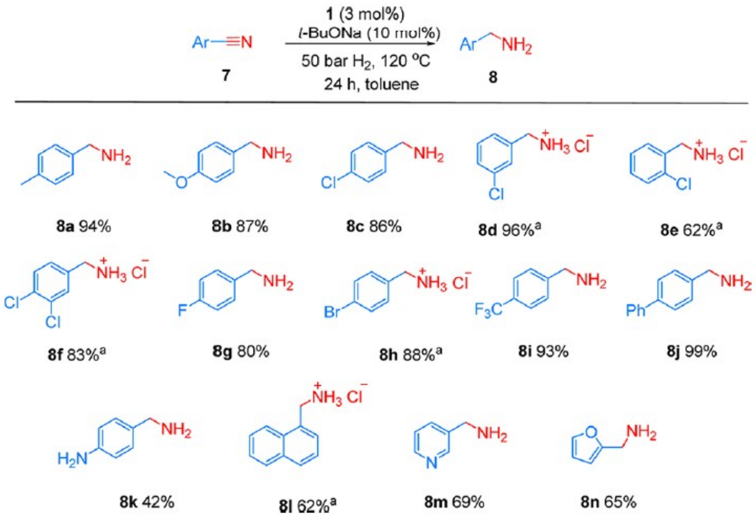
S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge and M. Beller, *Journal of the American Chemical Society*, **2016**, *138*, 8809-8814.



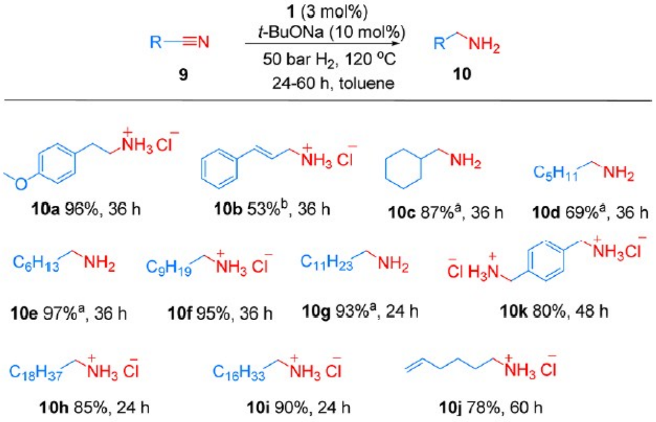
[a]100 °C, 30 bar H_2. [b]3% saturated alcohol observed. Reaction conditions: substrate (1 mmol), **1** (0.01 mmol), *t*-BuONa (0.03 mmol), toluene (1 mL), 24 h, 60 °C, 10 bar H_2. Conversion was determined by GC (isolated yield in parentheses).



[a]GC yield. [b]48 h. Reaction conditions: substrate (1 mmol), **1** (0.01 mmol), *t*-BuONa (0.03 mmol), toluene (1 mL), 24−48 h, 100 °C, 30 bar H_2. Conversion was determined by GC (isolated yield in parentheses).



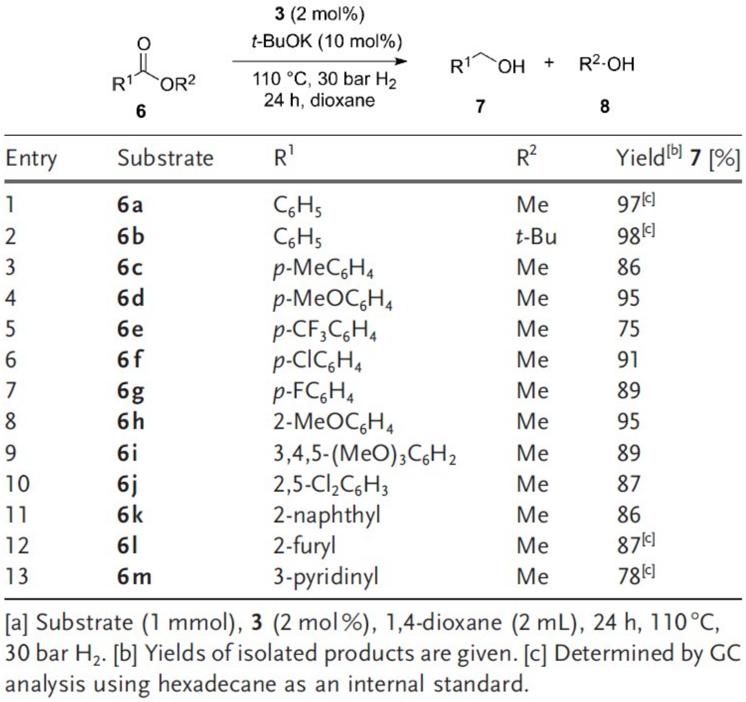
[a]Isolated yield. Reaction conditions: substrate (0.5 mmol), **1** (0.015 mmol), *t*-BuONa (0.05 mmol), toluene (1 mL), 24 h, 120 °C, 50 bar H_2. Conversion (>99%) and yield were determined by GC analysis using hexadecane as an internal standard.



[a]GC yield. [b]25% corresponding saturated amine. Reaction conditions: substrate (0.5 mmol), **1** (0.015 mmol), *t*-BuONa (0.05 mmol), toluene (1 mL), 24–60 h, 100–120 °C, 50 bar H_2. Isolated as a HCl salt. Conversion (>99%) was determined by GC analysis using hexadecane as an internal standard.

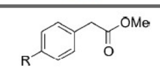
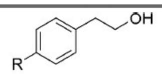
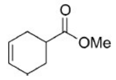
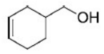
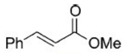
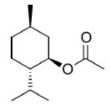
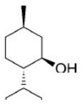
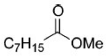
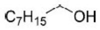
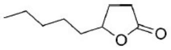
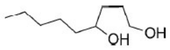
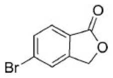
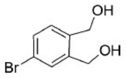
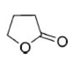
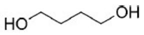
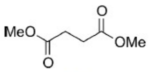
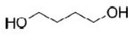
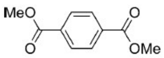
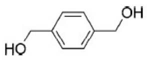
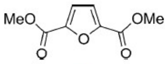
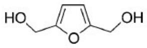
C-Mn-2/3 – Esters

S. Elangovan, M. Garbe, H. Jiao, A. Spannenberg, K. Junge and M. Beller, *Angewandte Chemie International Edition*, **2016**, *55*, 15364-15368.



Entry	Substrate	R^1	R^2	Yield[b] **7** [%]
1	**6a**	C_6H_5	Me	97[c]
2	**6b**	C_6H_5	*t*-Bu	98[c]
3	**6c**	*p*-MeC_6H_4	Me	86
4	**6d**	*p*-$MeOC_6H_4$	Me	95
5	**6e**	*p*-$CF_3C_6H_4$	Me	75
6	**6f**	*p*-ClC_6H_4	Me	91
7	**6g**	*p*-FC_6H_4	Me	89
8	**6h**	2-$MeOC_6H_4$	Me	95
9	**6i**	3,4,5-$(MeO)_3C_6H_2$	Me	89
10	**6j**	2,5-$Cl_2C_6H_3$	Me	87
11	**6k**	2-naphthyl	Me	86
12	**6l**	2-furyl	Me	87[c]
13	**6m**	3-pyridinyl	Me	78[c]

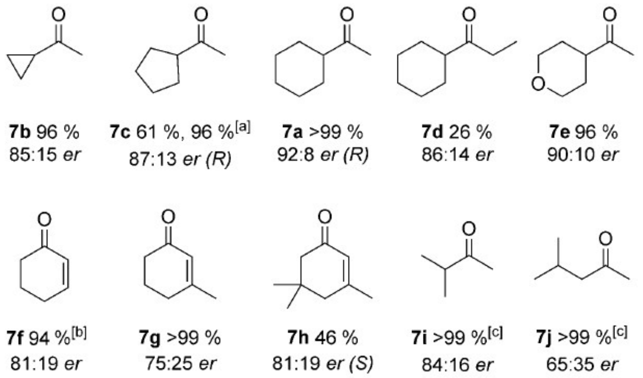
[a] Substrate (1 mmol), **3** (2 mol%), 1,4-dioxane (2 mL), 24 h, 110 °C, 30 bar H_2. [b] Yields of isolated products are given. [c] Determined by GC analysis using hexadecane as an internal standard.

Entry	Ester	Alcohol	Conv. (yield) [%]
			
1	**9a** R=H		>99 (79)
2	**9b** R=Cl		>99 (87)
3	**9c** R=F		>99 (93)
4	**9d** R=*t*-Bu		>99 (95)
5[b,d]	 **9e**		98 (83)
6	 **9f**		>99 (93)
7[c]	 **9g**		97 (88)
8[d]	 **9h**		92 (71)
9	 **9i**		>99 (82)
10	 **9j**		>79 (57)
11[d]	 **9k**		>99 (88)
12[c,d]	 **9l**		>93 (66)
13	 **9m**		>99 (95)
14[c]	 **9n**		>99 (58)

[a] Substrate (1 mmol), **3** (2 mol%), 1,4-dioxane (2 mL), 24 h, 110°C, 30 bar H_2. The conversions were determined by GC using hexadecane as an internal standard. Yields of isolated products are given in parentheses. [b] 48 h. [c] **3** (3 mol%), 48 h, 120°C. [d] The GC yield was determined using hexadecane as an internal standard.

C-Mn-4 – Ketones

M. Garbe, K. Junge, S. Walker, Z. Wei, H. Jiao, A. Spannenberg, S. Bachmann, M. Scalone and M. Beller, *Angewandte Chemie International Edition*, DOI: 10.1002/anie.201705471.



7b 96 % 85:15 *er*

7c 61 %, 96 %[a] 87:13 *er (R)*

7a >99 % 92:8 *er (R)*

7d 26 % 86:14 *er*

7e 96 % 90:10 *er*

7f 94 %[b] 81:19 *er*

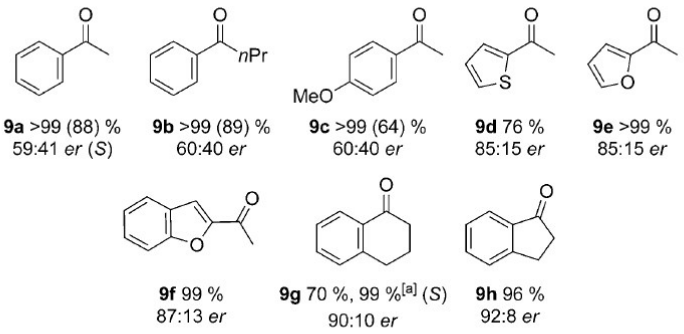
7g >99 % 75:25 *er*

7h 46 % 81:19 *er (S)*

7i >99 %[c] 84:16 *er*

7j >99 %[c] 65:35 *er*

Figure 3. Manganese-catalyzed hydrogenation of aliphatic ketones. General conditions: Substrate (1 mmol), **6** (1 mol%), KO*t*Bu (5 mol%), *tert*-amyl alcohol (2 mL), 4 h, 40°C, 30 bar H_2. Conversion was determined by GC using hexadecane as an internal standard. [a] 4 h, 80°C. [b] **6** (2 mol%), toluene (2 mL), 4 h, 50°C. 6% cyclohexanol. [c] **6** (2 mol%), *tert*-amyl alcohol (2 mL), 4 h, 80°C.



9a >99 (88) % 59:41 *er* (*S*)

9b >99 (89) % 60:40 *er*

9c >99 (64) % 60:40 *er*

9d 76 % 85:15 *er*

9e >99 % 85:15 *er*

9f 99 % 87:13 *er*

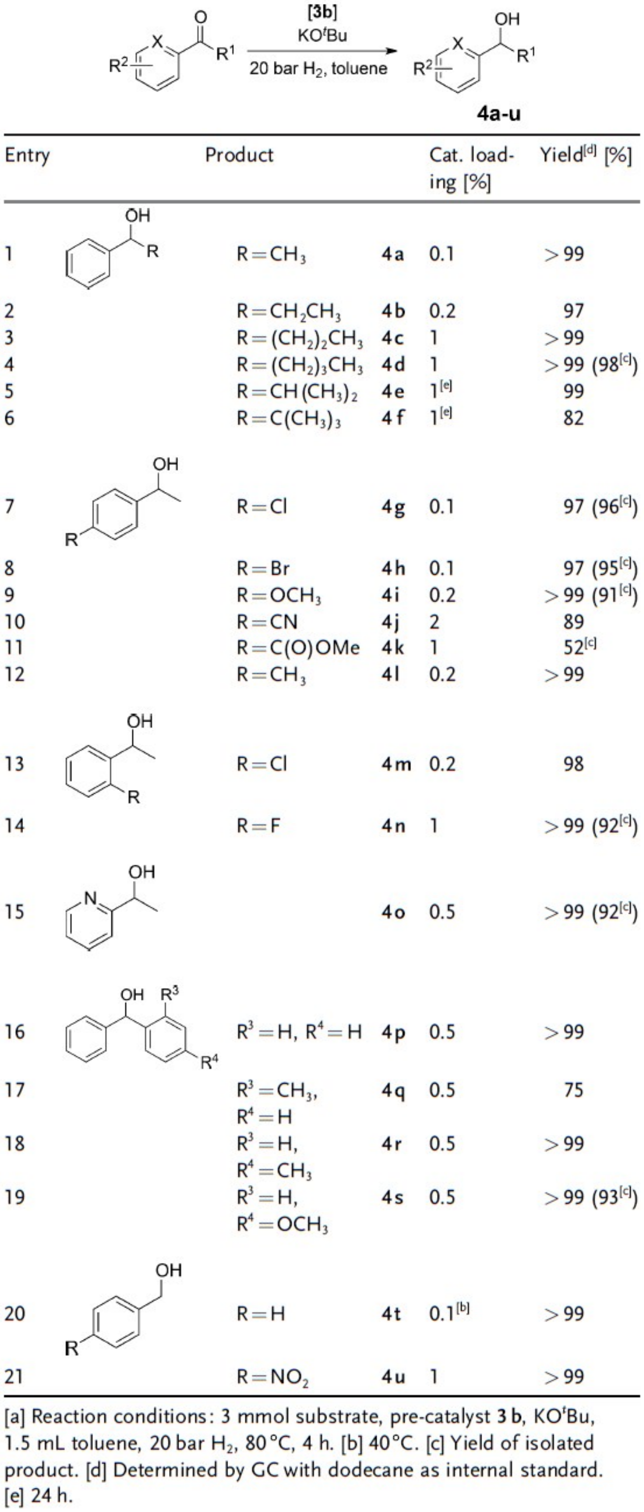
9g 70 %, 99 %[a] (*S*) 90:10 *er*

9h 96 % 92:8 *er*

Figure 4. Manganese-catalyzed asymmetric hydrogenation of aromatic ketones. General conditions: substrate (1 mmol), **6** (1 mol%), KO*t*Bu (5 mol%), 1,4-dioxane (2 mL), 4 h, 30°C, 30 bar H_2. Conversion was determined by GC using hexadecane as an internal standard (Yields of isolated product in parentheses). [a] At 60°C.

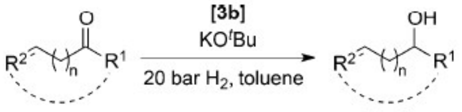
M-Mn-1 – Ketones

F. Kallmeier, T. Irrgang, T. Dietel and R. Kempe, *Angewandte Chemie International Edition*, **2016**, *55*, 11806-11809.

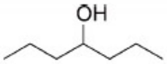
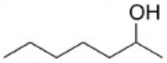
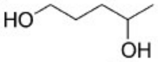
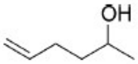
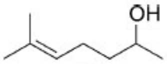
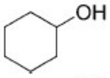
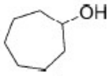
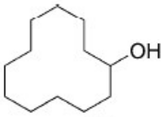
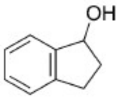


Entry	Product	Cat. loading [%]	Yield[d] [%]
1	R = CH$_3$ **4a**	0.1	>99
2	R = CH$_2$CH$_3$ **4b**	0.2	97
3	R = (CH$_2$)$_2$CH$_3$ **4c**	1	>99
4	R = (CH$_2$)$_3$CH$_3$ **4d**	1	>99 (98[c])
5	R = CH(CH$_3$)$_2$ **4e**	1[e]	99
6	R = C(CH$_3$)$_3$ **4f**	1[e]	82
7	R = Cl **4g**	0.1	97 (96[c])
8	R = Br **4h**	0.1	97 (95[c])
9	R = OCH$_3$ **4i**	0.2	>99 (91[c])
10	R = CN **4j**	2	89
11	R = C(O)OMe **4k**	1	52[c]
12	R = CH$_3$ **4l**	0.2	>99
13	R = Cl **4m**	0.2	98
14	R = F **4n**	1	>99 (92[c])
15	**4o**	0.5	>99 (92[c])
16	R^3 = H, R^4 = H **4p**	0.5	>99
17	R^3 = CH$_3$, R^4 = H **4q**	0.5	75
18	R^3 = H, R^4 = CH$_3$ **4r**	0.5	>99
19	R^3 = H, R^4 = OCH$_3$ **4s**	0.5	>99 (93[c])
20	R = H **4t**	0.1[b]	>99
21	R = NO$_2$ **4u**	1	>99

[a] Reaction conditions: 3 mmol substrate, pre-catalyst **3b**, KO^{t}Bu, 1.5 mL toluene, 20 bar H$_2$, 80 °C, 4 h. [b] 40 °C. [c] Yield of isolated product. [d] Determined by GC with dodecane as internal standard. [e] 24 h.



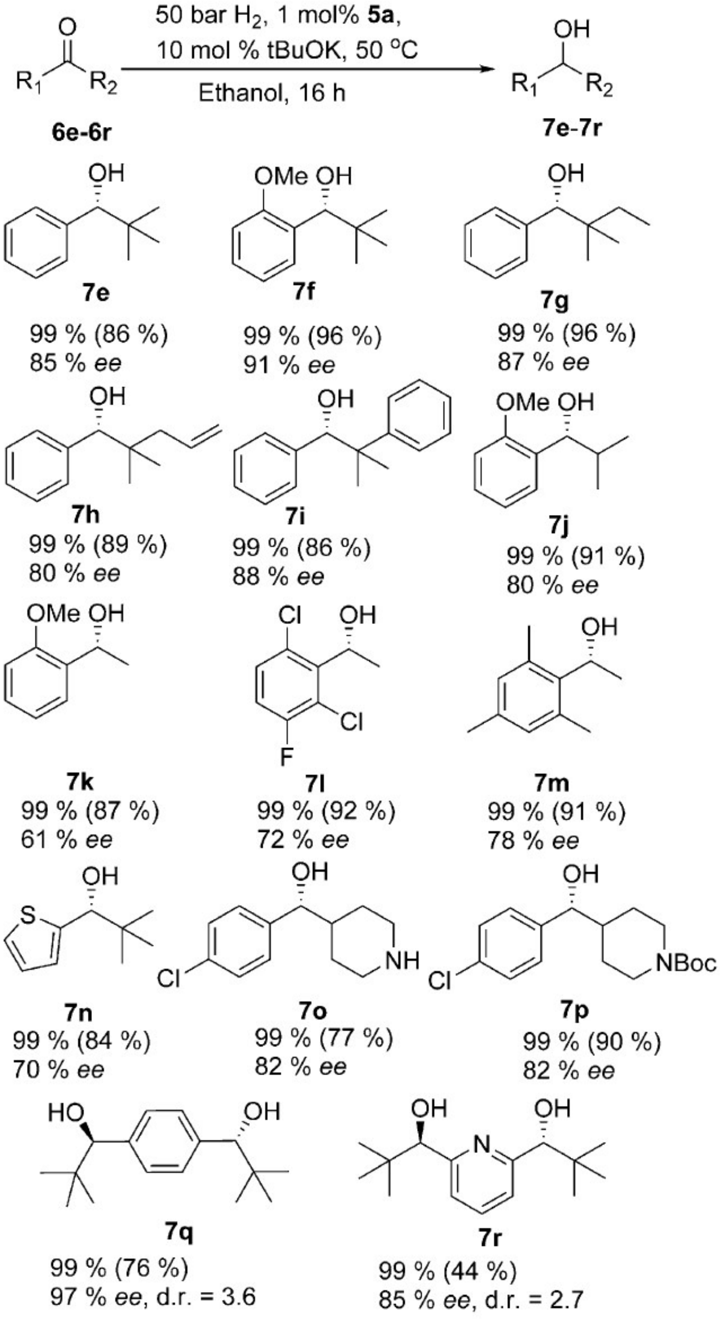
5a-i

Entry	Product	Cat. loading [%]	Yield[b] [%]
1	 **5a**	0.5	> 99
2	 **5b**	0.2	95
3	 **5c**	1	88
4	 **5d**	0.1	> 99 (95[c])
5	 **5e**	0.2	98 (86[c])
6	 **5f**	0.1	98
7	 **5g**	0.2	96
8	 **5h**	1	58
9	 **5i**	1	97

[a] Reaction conditions: 3 mmol substrate, pre-catalyst **3 b**, KO^{t}Bu, 1.5 mL toluene, 20 bar H$_2$, 80 °C, 4 h. [b] Determined by GC with dodecane as internal standard. [c] Yield of isolated product.

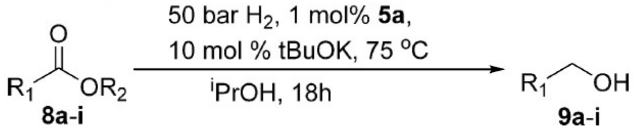
M-Mn-2 – Ketones & Esters

M. B. Widegren, G. J. Harkness, A. M. Z. Slawin, D. B. Cordes and M. L. Clarke, *Angewandte Chemie International Edition*, **2017**, *56*, 5825-5828.



Scheme 1. A range of functionalized ketones hydrogenated in presence of the chiral Mn catalyst **5a**. Typical reaction conditions: 0.34 mmol substrate, 0.003 mmol catalyst, 0.034 mmol base and internal standard (0.06 mmol) in 1.6 mL ethanol (0.2 M) under 50 bar of H_2 at 50 °C for 16 h.

Table 2: Hydrogenation of esters.[a]

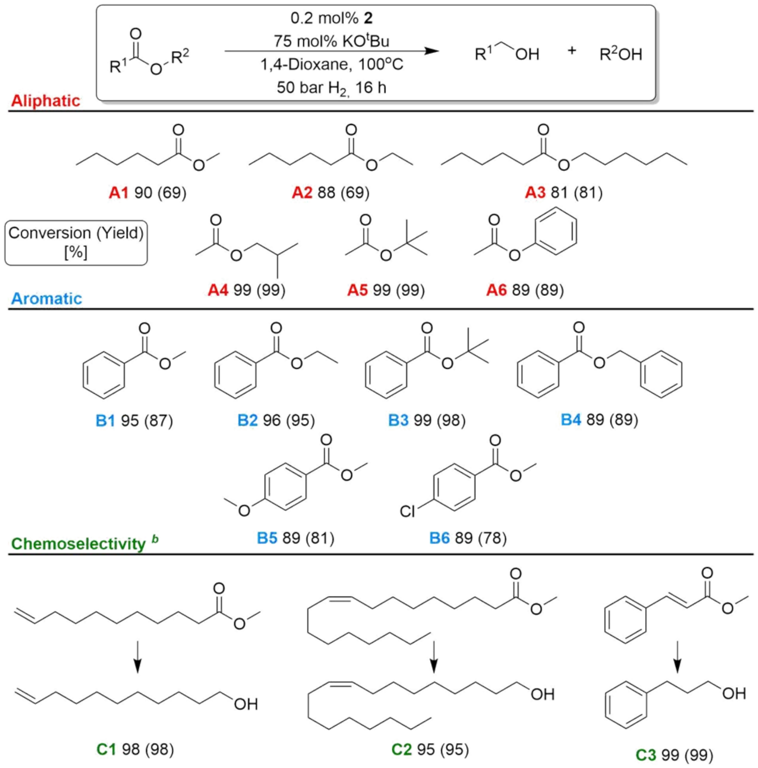


Entry		R_1	R_2	Conversion[b] [%]
1	**8a**	4-F-Ph	CH_3	99 (86)
2	**8b**	2-Br-Ph	CH_3	99 (90)
3	**8c**	$Ph(CH_2)_2$-	CH_2CH_3	99 (84)
4	**8d**	4-H_2N-Ph	CH_3	91 (80)
5	**8e**	4-O_2N-Ph	CH_2CH_3	0
6	**8f**	2-Naphth	CH_3	99 (87)
7	**8g**	4-(Ph-C≡C)-C_6H_4	CH_3	99 (n.d)[c]
8	**8h**	nPr	nBu	82[d]
9	**8i**	 MeO2C CO2Me		99 (86)[e]

[a] Typical reaction conditions: 0.34 mmol substrate, 0.003 mmol catalyst, 0.034 mmol base and internal standard (0.06 mmol) in 1.6 mL isopropanol (0.2 M) under 50 bar of H_2 at 75 °C for 16 h. [b] Conversion was estimated by ^{1}H-NMR using 1-methylnaphthalene as internal standard (8–10 µL). Isolated yield in brackets. [c] ^{1}H-NMR analysis showed the presence of ≈20% alkene. [d] Reaction run neat with 0.1 mol% **5a** and 2 mol% base at 90 °C for 15 h. [e] A 50:50 mixture of *cis* and *trans* isomers.

M-Mn-3 – Esters

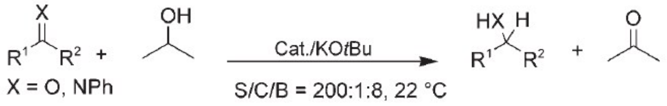
R. van Putten, E. A. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort and E. A. Pidko, *Angewandte Chemie International Edition*, **2017**, *56*, 7531-7534.

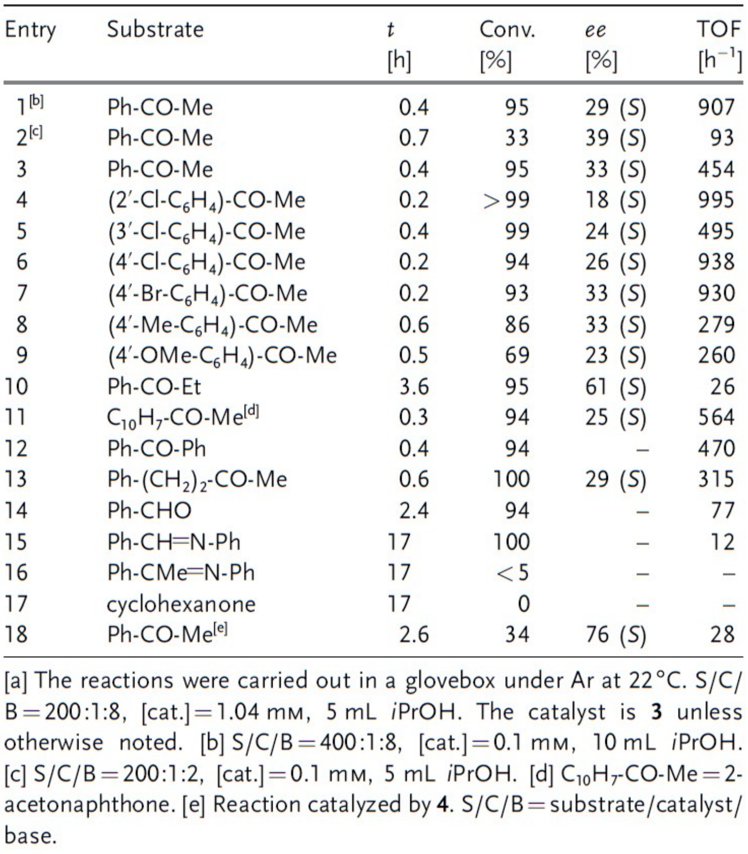


3.2.1. – Transfer Hydrogenation – Iron Catalysts

TH-Fe-1 – Ketones & Imines

C. Sui-Seng, F. Freutel, A. J. Lough and R. H. Morris, *Angewandte Chemie International Edition*, **2008**, *47*, 940-943.



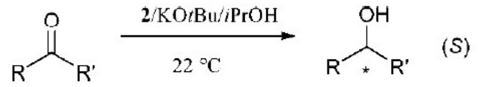


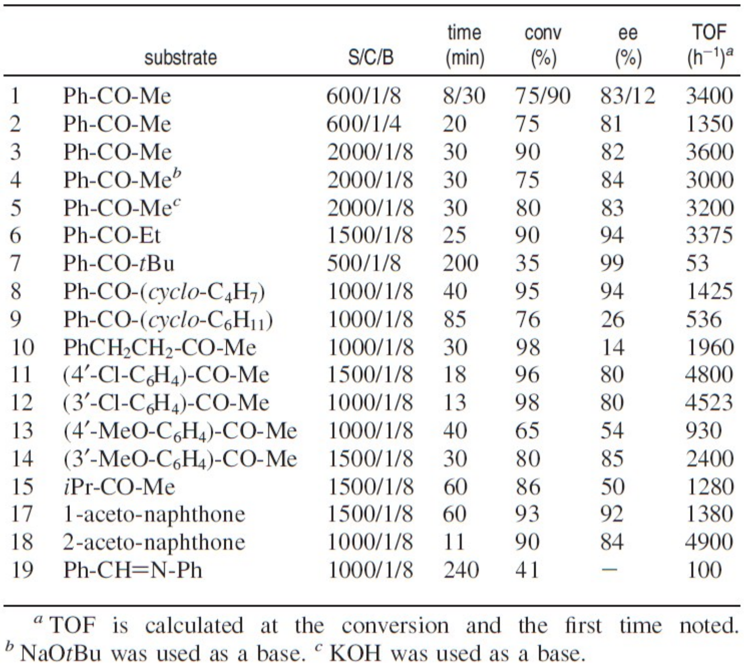
Entry	Substrate	t [h]	Conv. [%]	*ee* [%]	TOF [h^{-1}]
1[b]	Ph-CO-Me	0.4	95	29 (*S*)	907
2[c]	Ph-CO-Me	0.7	33	39 (*S*)	93
3	Ph-CO-Me	0.4	95	33 (*S*)	454
4	(2′-Cl-C_6H_4)-CO-Me	0.2	>99	18 (*S*)	995
5	(3′-Cl-C_6H_4)-CO-Me	0.4	99	24 (*S*)	495
6	(4′-Cl-C_6H_4)-CO-Me	0.2	94	26 (*S*)	938
7	(4′-Br-C_6H_4)-CO-Me	0.2	93	33 (*S*)	930
8	(4′-Me-C_6H_4)-CO-Me	0.6	86	33 (*S*)	279
9	(4′-OMe-C_6H_4)-CO-Me	0.5	69	23 (*S*)	260
10	Ph-CO-Et	3.6	95	61 (*S*)	26
11	$C_{10}H_7$-CO-Me[d]	0.3	94	25 (*S*)	564
12	Ph-CO-Ph	0.4	94	–	470
13	Ph-$(CH_2)_2$-CO-Me	0.6	100	29 (*S*)	315
14	Ph-CHO	2.4	94	–	77
15	Ph-CH=N-Ph	17	100	–	12
16	Ph-CMe=N-Ph	17	<5	–	–
17	cyclohexanone	17	0	–	–
18	Ph-CO-Me[e]	2.6	34	76 (*S*)	28

[a] The reactions were carried out in a glovebox under Ar at 22 °C. S/C/B = 200:1:8, [cat.] = 1.04 mM, 5 mL *i*PrOH. The catalyst is **3** unless otherwise noted. [b] S/C/B = 400:1:8, [cat.] = 0.1 mM, 10 mL *i*PrOH. [c] S/C/B = 200:1:2, [cat.] = 0.1 mM, 5 mL *i*PrOH. [d] $C_{10}H_7$-CO-Me = 2-acetonaphthone. [e] Reaction catalyzed by **4**. S/C/B = substrate/catalyst/base.

TH-Fe-2 – Ketones

A. Mikhailine, A. J. Lough and R. H. Morris, *Journal of the American Chemical Society*, **2009**, *131*, 1394-1395.





	substrate	S/C/B	time (min)	conv (%)	ee (%)	TOF (h^{-1})[a]
1	Ph-CO-Me	600/1/8	8/30	75/90	83/12	3400
2	Ph-CO-Me	600/1/4	20	75	81	1350
3	Ph-CO-Me	2000/1/8	30	90	82	3600
4	Ph-CO-Me[b]	2000/1/8	30	75	84	3000
5	Ph-CO-Me[c]	2000/1/8	30	80	83	3200
6	Ph-CO-Et	1500/1/8	25	90	94	3375
7	Ph-CO-*t*Bu	500/1/8	200	35	99	53
8	Ph-CO-(*cyclo*-C_4H_7)	1000/1/8	40	95	94	1425
9	Ph-CO-(*cyclo*-C_6H_{11})	1000/1/8	85	76	26	536
10	$PhCH_2CH_2$-CO-Me	1000/1/8	30	98	14	1960
11	(4′-Cl-C_6H_4)-CO-Me	1500/1/8	18	96	80	4800
12	(3′-Cl-C_6H_4)-CO-Me	1000/1/8	13	98	80	4523
13	(4′-MeO-C_6H_4)-CO-Me	1000/1/8	40	65	54	930
14	(3′-MeO-C_6H_4)-CO-Me	1500/1/8	30	80	85	2400
15	*i*Pr-CO-Me	1500/1/8	60	86	50	1280
17	1-aceto-naphthone	1500/1/8	60	93	92	1380
18	2-aceto-naphthone	1000/1/8	11	90	84	4900
19	Ph-CH=N-Ph	1000/1/8	240	41	–	100

[a] TOF is calculated at the conversion and the first time noted. [b] NaO*t*Bu was used as a base. [c] KOH was used as a base.

TH-Fe-3 – Ketones

K. Z. Demmans, O. W. K. Ko and R. H. Morris, *RSC Advances*, **2016**, *6*, 88580-88587.

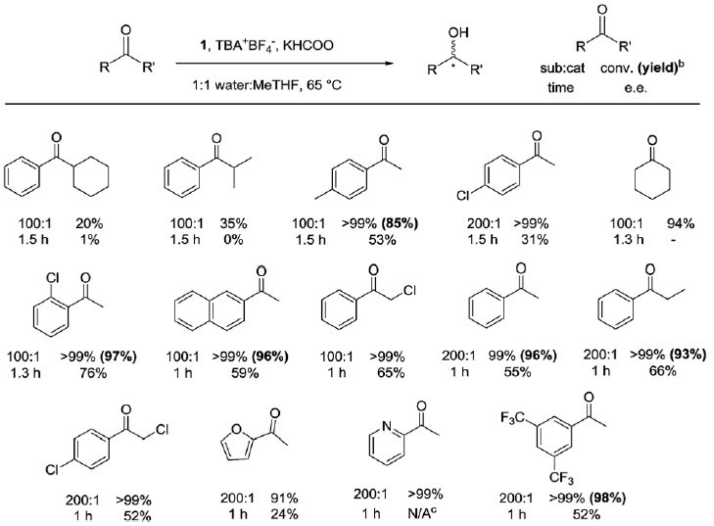
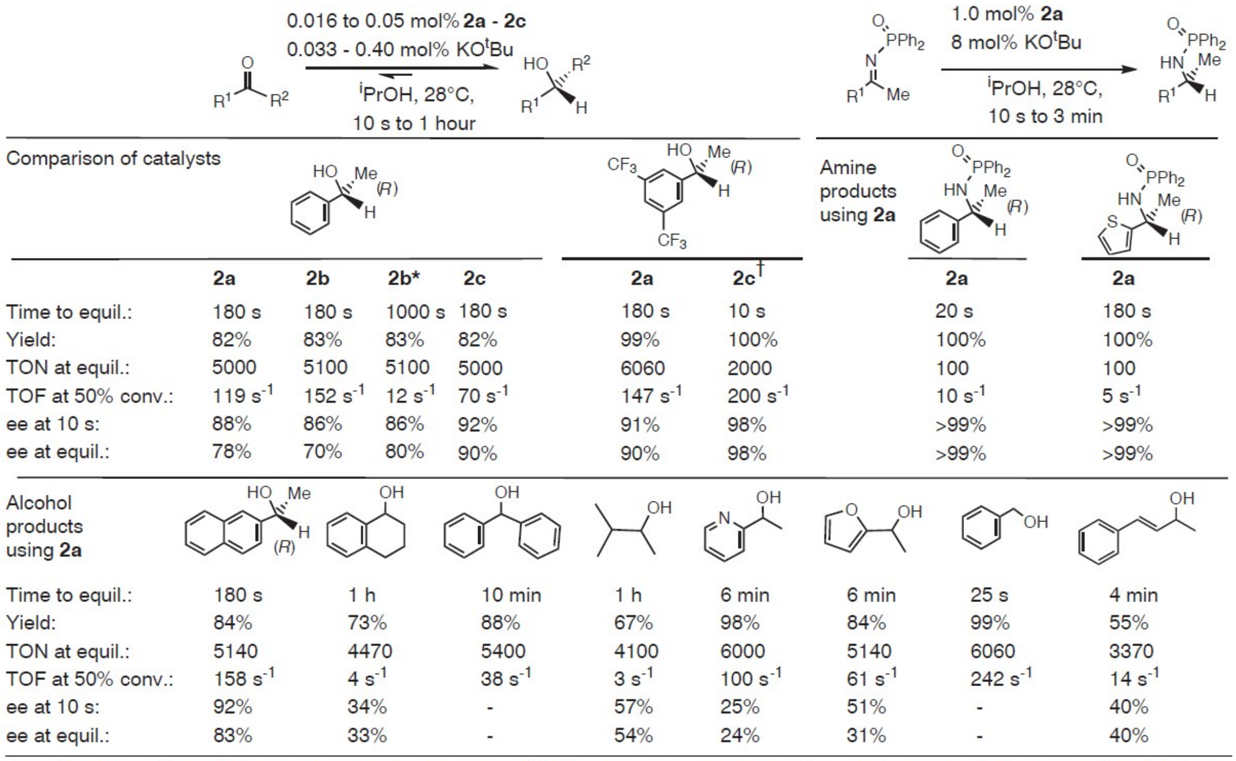


Fig. 4 Substrate scope under optimized conditions[a]. [a] Constant argon flow was used to purge the reaction flask. All values are in equivalents relative to the iron catalyst: 0.006 mmol **1**, 2000 eq. KHCOO, 1 eq. $TBA^+BF_4^-$, 2 mL reaction volume (1 : 1 water : MeTHF), 600 RPM stirring rate. [b] Isolated yield using the specifications found in the ESI.† [c] Gas chromatography could not separate the (*R*) and (*S*) alcohols accurately.

W. Zuo, A. J. Lough, Y. F. Li and R. H. Morris, S*cience,* 2013, **342,** 1080-1083

Table 1. Transfer hydrogenation of ketones and imines catalyzed by complexes 2a to 2c. General conditions for ketones: [Cat] = 6.73×10^{-5} M, [KO^{t}Bu] = 5.45×10^{-4} M, [ketone] = 0.412 M, [^{i}PrOH] = 12.4 M, 28°C; for imines: [Cat, **2a**] = 5.89×10^{-4} M, [KO^{t}Bu] = 4.71×10^{-3} M, [imine] = 5.89×10^{-2} M, [^{i}PrOH] = 12.4 M, 28°C. The absolute configurations were obtained by gas chromatography or high-performance liquid chromatography by comparison to known standards.



	2a	2b	2b*	2c	2a	2c†	2a	2a
Time to equil.:	180 s	180 s	1000 s	180 s	180 s	10 s	20 s	180 s
Yield:	82%	83%	83%	82%	99%	100%	100%	100%
TON at equil.:	5000	5100	5100	5000	6060	2000	100	100
TOF at 50% conv.:	119 s^{-1}	152 s^{-1}	12 s^{-1}	70 s^{-1}	147 s^{-1}	200 s^{-1}	10 s^{-1}	5 s^{-1}
ee at 10 s:	88%	86%	86%	92%	91%	98%	>99%	>99%
ee at equil.:	78%	70%	80%	90%	90%	98%	>99%	>99%

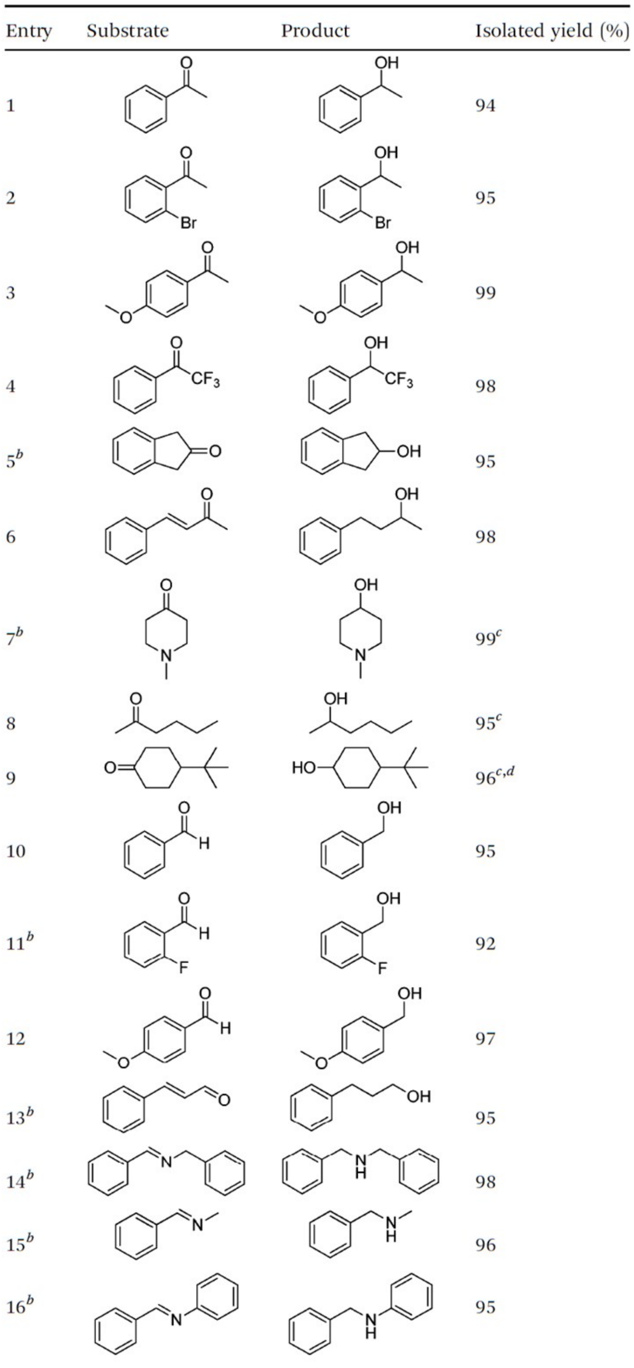
Time to equil.:	180 s	1 h	10 min	1 h	6 min	6 min	25 s	4 min
Yield:	84%	73%	88%	67%	98%	84%	99%	55%
TON at equil.:	5140	4470	5400	4100	6000	5140	6060	3370
TOF at 50% conv.:	158 s^{-1}	4 s^{-1}	38 s^{-1}	3 s^{-1}	100 s^{-1}	61 s^{-1}	242 s^{-1}	14 s^{-1}
ee at 10 s:	92%	34%	-	57%	25%	51%	-	40%
ee at equil.:	83%	33%	-	54%	24%	31%	-	40%

*[Cat, **2b**] = 6.73×10^{-5} M, [KO^{t}Bu] = 1.35×10^{-4} M, [substrate] = 0.412 M, [^{t}PrOH] = 12.4 M, 28°C. †Ketone: Cat ratio = 2000:1 to prevent poisoning by the acidic alcohol product.

3.2.2. – Transfer Hydrogenation – Cobalt Catalysts

C-Co-2 – Ketones, Aldehydes & Imines

G. Zhang and S. K. Hanson, *Chemical Communications*, **2013**, *49*, 10151-10153.

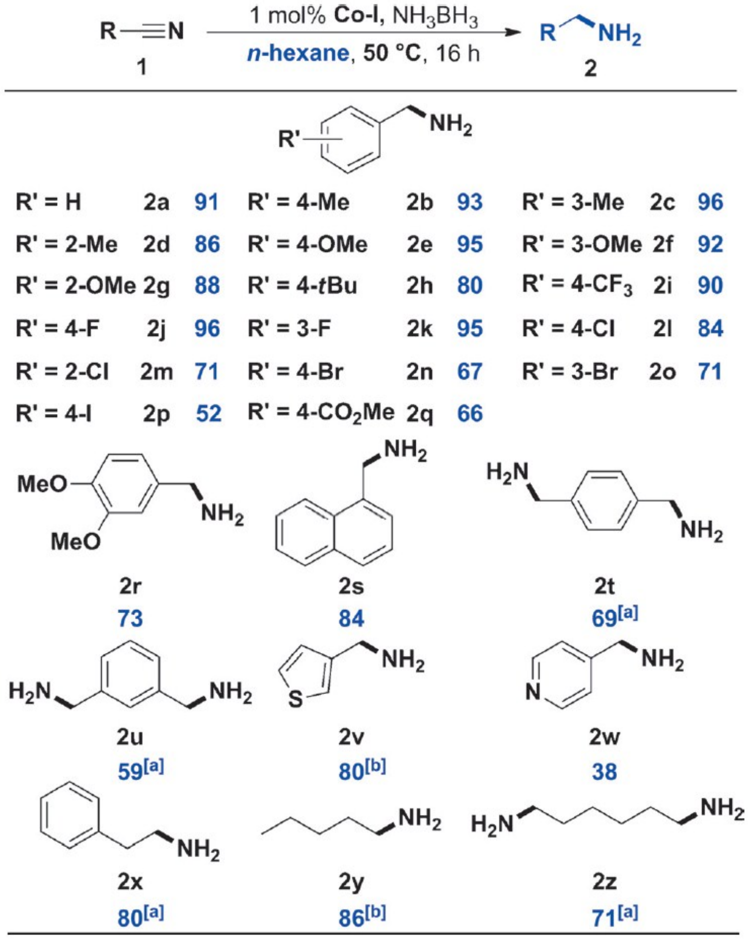


Entry	Substrate	Product	Isolated yield (%)
1			94
2			95
3			99
4			98
5[b]			95
6			98
7[b]			99[c]
8			95[c]
9			96[c,d]
10			95
11[b]			92
12			97
13[b]			95
14[b]			98
15[b]			96
16[b]			95

[a] Conditions: substrate (0.5 mmol) in isopropanol–THF (3 : 1 (v/v), 2 mL), 25 °C, 24 h. [b] Reactions run at 80 °C. [c] GC yield. [d] Ratio of *cis* : *trans* alcohol = 33 : 67.

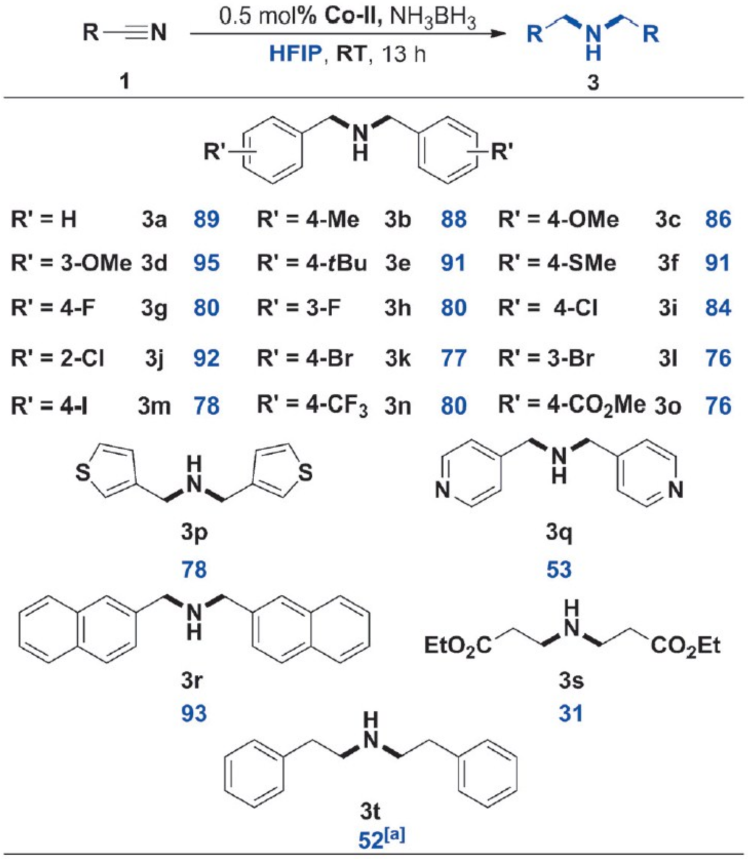
TH-Co-1/2 – Nitriles

Z. Shao, S. Fu, M. Wei, S. Zhou and Q. Liu, *Angewandte Chemie International Edition*, **2016**, *55*, 14653-14657.

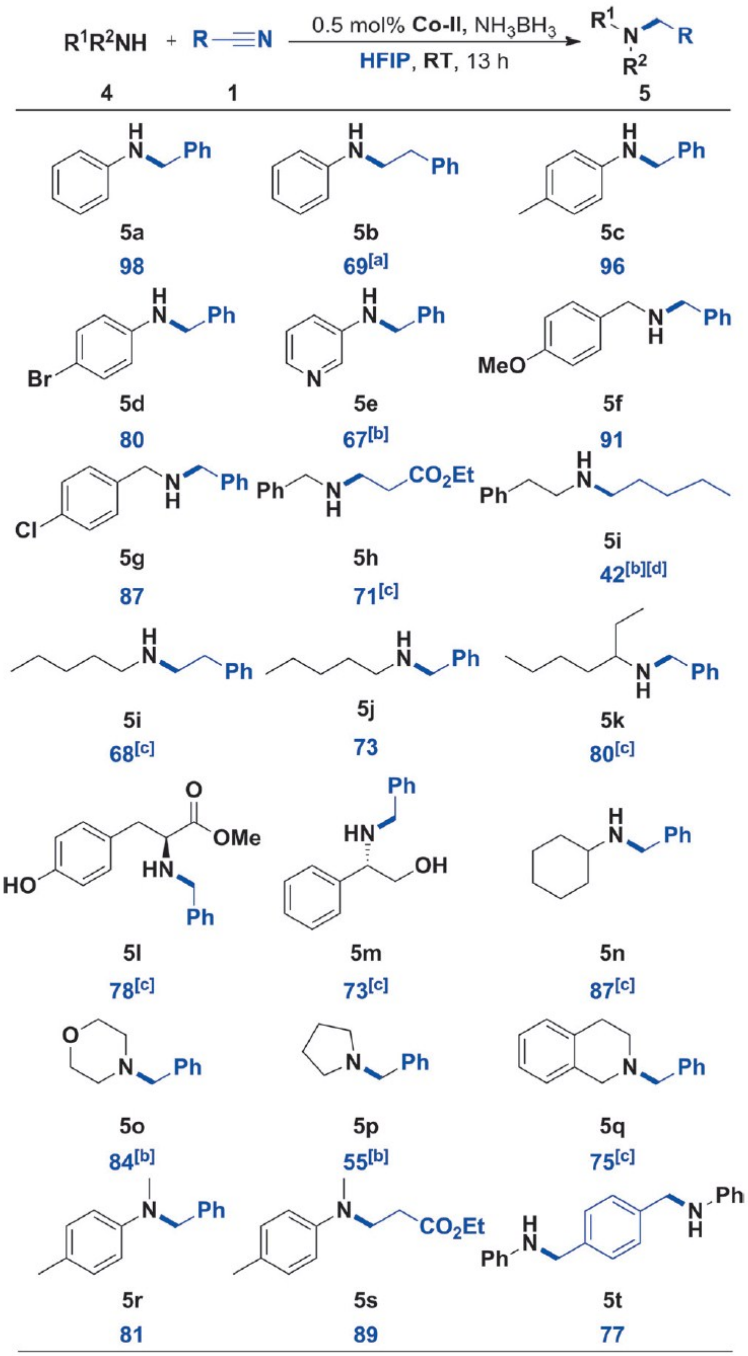


R' = H	2a	91	R' = 4-Me	2b	93	R' = 3-Me	2c	96
R' = 2-Me	2d	86	R' = 4-OMe	2e	95	R' = 3-OMe	2f	92
R' = 2-OMe	2g	88	R' = 4-*t*Bu	2h	80	R' = 4-CF_3	2i	90
R' = 4-F	2j	96	R' = 3-F	2k	95	R' = 4-Cl	2l	84
R' = 2-Cl	2m	71	R' = 4-Br	2n	67	R' = 3-Br	2o	71
R' = 4-I	2p	52	R' = 4-CO_2Me	2q	66			

Scheme 3. Cobalt-catalyzed transfer hydrogenation of nitriles to primary amines. Reaction conditions: **1** (0.5 mmol), AB (0.8 mmol) in 1 mL of *n*-hexane, GC yield (%) were shown using biphenyl as the internal standard. [a] The reaction temperature was 100 °C. [b] The reaction temperature was 120 °C.



Scheme 4. Cobalt-catalyzed transfer hydrogenation of nitriles to symmetric secondary amines. Reaction conditions: **1** (0.5 mmol), AB (0.8 mmol) in 2 mL of HFIP. Isolated yields (%) are shown. [a] The reaction temperature was 50 °C. HFIP = Hexafluoroisopropanol.



Scheme 5. Cobalt-catalyzed reductive amination of nitriles to unsymmetric secondary and tertiary amines. Reaction conditions: **1** (0.6 mmol), **4** (0.5 mmol), AB (0.8 mmol) in 2 mL of HFIP. Isolated yields (%) are shown. [a] **1** (0.5 mmol), **4** (0.6 mmol). [b] **1** (0.5 mmol), **4** (2 mmol). [c] **1** (0.5 mmol), **4** (1 mmol). [d] The reaction was carried out in 2 mL of *n*-hexane at 100 °C.

3.2.3. – Transfer Hydrogenation – Manganese Catalysts

C-Mn-1a/b, C-Mn-2 & TH-Mn-3 – Ketones

M. Perez, S. Elangovan, A. Spannenberg, K. Junge and M. Beller, *ChemSusChem*, **2017**, *10*, 83-86.

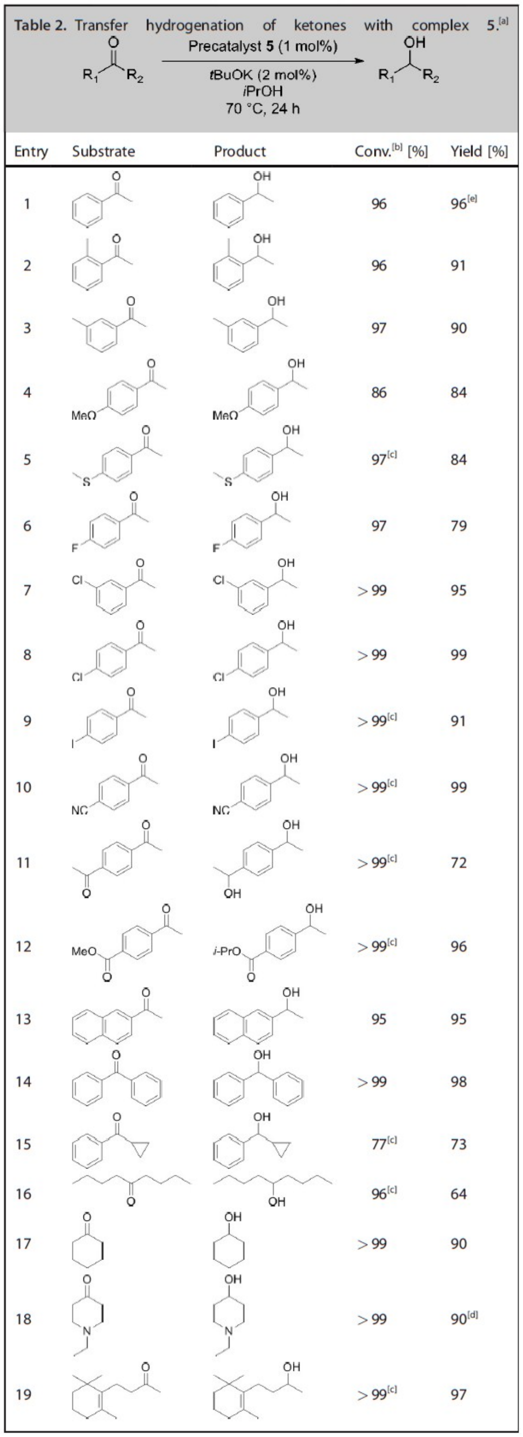
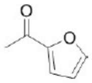
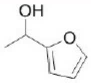
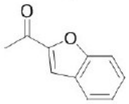
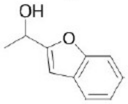
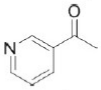
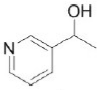
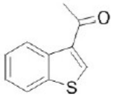
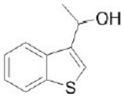


Table 2. Transfer hydrogenation of ketones with complex 5.[a]

Entry	Substrate	Product	Conv.[b] [%]	Yield [%]
1			96	96[e]
2			96	91
3			97	90
4			86	84
5			97[c]	84
6			97	79
7			> 99	95
8			> 99	99
9			> 99[c]	91
10			> 99[c]	99
11			> 99[c]	72
12			> 99[c]	96
13			95	95
14			> 99	98
15			77[c]	73
16			96[c]	64
17			> 99	90
18			> 99	90[d]
19			> 99[c]	97

Table 2. (Continued)

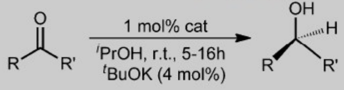
Entry	Substrate	Product	Conv.[b] [%]	Yield [%]
20			97[c]	96[e]
21			> 99[c]	93
22			> 99[c]	97
23			> 99[c]	96

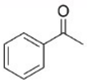
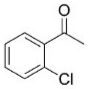
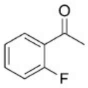
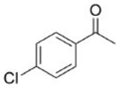
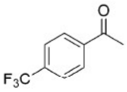
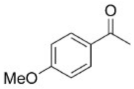
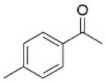
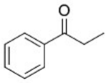
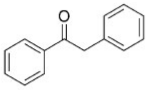
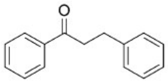
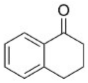
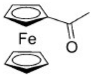
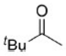
[a] Reaction conditions: substrate (0.5 mmol), complex **5** (0.005 mmol), *t*BuOK (0.01 mmol), *i*PrOH (2.5 mL), 70 °C, 24 h. [b] Conversion was determined by GC. Isolated yield is given. [c] Reaction conditions: substrate (0.50 mmol), complex (0.025 mmol), *t*BuOK (0.030 mmol), *i*PrOH (2.5 mL), 70 °C, 24 h. [d] Isolated as the HCl salt. [e] GC yield.

TH-Mn-1 – Ketones

A. Zirakzadeh, S. R. M. M. de Aguiar, B. Stöger, M. Widhalm and K. Kirchner, *ChemCatChem*, **2017**, *9*, 1744-1748.

Table 2. THY results obtained with complex (R,R,S_{Fc})-**2a**.[a]

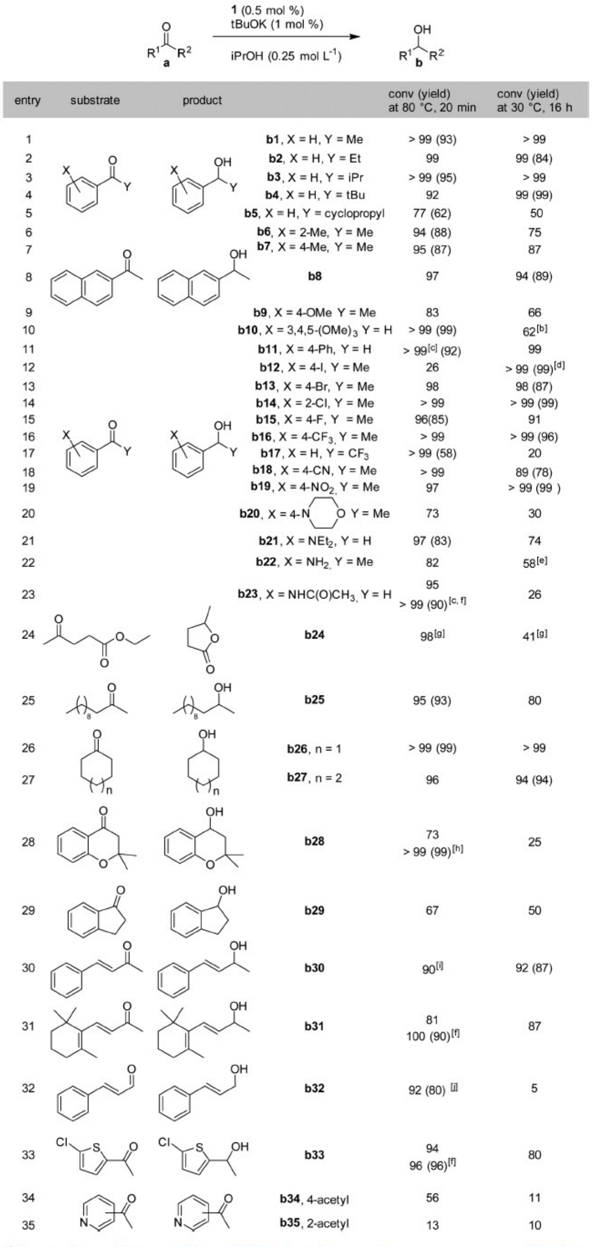


Entry	Substrate	*t* [h]	Conversion [%]	*ee*[b] [%]
1		5	95	85
2		16	73	65
3		16	77	69
4		5	94	83
5		5	90	76
6		5	95	84
7		5	96	85
8		6	93	84
9		6	62	82
10		16	58	79
11		16	60	46
12		16	37	20
13		5	80	74

[a] Reaction conditions: Substrate (1 mmol), catalyst (0.01 mmol), KO*t*Bu (0.04 mmol), *i*PrOH (5 mL), 25 °C. [b] Acetophenone, 2-fluoroacetophenone, 2-chloroacetophenone, 4-trifluoromethylacetophenone, 4-methoxyacetophenone, 4-methylacetophenone, phenyl ethyl ketone, and 1-tetralone determined by GC on a β-Dex 110 (30 m) column and phenyl benzyl ketone and 1,3-diphenylpropan-1-one determined by HPLC on a Chiralcel OD-H column. Acetylferrocene determined by HPLC on a Chiralcel OJ column.[14]

TH-Mn-2 – Ketones

A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J.-B. Sortais, *Organic Letters*, **2017**, *19*, 3656-3659.



entry	substrate	product		conv (yield) at 80 °C, 20 min	conv (yield) at 30 °C, 16 h
1			**b1**, X = H, Y = Me	> 99 (93)	> 99
2			**b2**, X = H, Y = Et	99	99 (84)
3			**b3**, X = H, Y = iPr	> 99 (95)	> 99
4			**b4**, X = H, Y = tBu	92	99 (99)
5			**b5**, X = H, Y = cyclopropyl	77 (62)	50
6			**b6**, X = 2-Me, Y = Me	94 (88)	75
7			**b7**, X = 4-Me, Y = Me	95 (87)	87
8			**b8**	97	94 (89)
9			**b9**, X = 4-OMe Y = Me	83	66
10			**b10**, X = 3,4,5-$(OMe)_3$ Y = H	> 99 (99)	62[b]
11			**b11**, X = 4-Ph, Y = H	> 99[c] (92)	99
12			**b12**, X = 4-I, Y = Me	26	> 99 (99)[d]
13			**b13**, X = 4-Br, Y = Me	98	98 (87)
14			**b14**, X = 2-Cl, Y = Me	> 99	> 99 (99)
15			**b15**, X = 4-F, Y = Me	96(85)	91
16			**b16**, X = 4-CF_3, Y = Me	> 99	> 99 (96)
17			**b17**, X = H, Y = CF_3	> 99 (58)	20
18			**b18**, X = 4-CN, Y = Me	> 99	89 (78)
19			**b19**, X = 4-NO_2, Y = Me	97	> 99 (99)
20			**b20**, X = 4-N O Y = Me	73	30
21			**b21**, X = NEt_2, Y = H	97 (83)	74
22			**b22**, X = NH_2, Y = Me	82	58[e]
23			**b23**, X = $NHC(O)CH_3$, Y = H	95 > 99 (90)[c, f]	26
24			**b24**	98[g]	41[g]
25			**b25**	95 (93)	80
26			**b26**, n = 1	> 99 (99)	> 99
27			**b27**, n = 2	96	94 (94)
28			**b28**	73 > 99 (99)[h]	25
29			**b29**	67	50
30			**b30**	90[i]	92 (87)
31			**b31**	81 100 (90)[f]	87
32			**b32**	92 (80) [j]	5
33			**b33**	94 96 (96)[f]	80
34			**b34**, 4-acetyl	56	11
35			**b35**, 2-acetyl	13	10

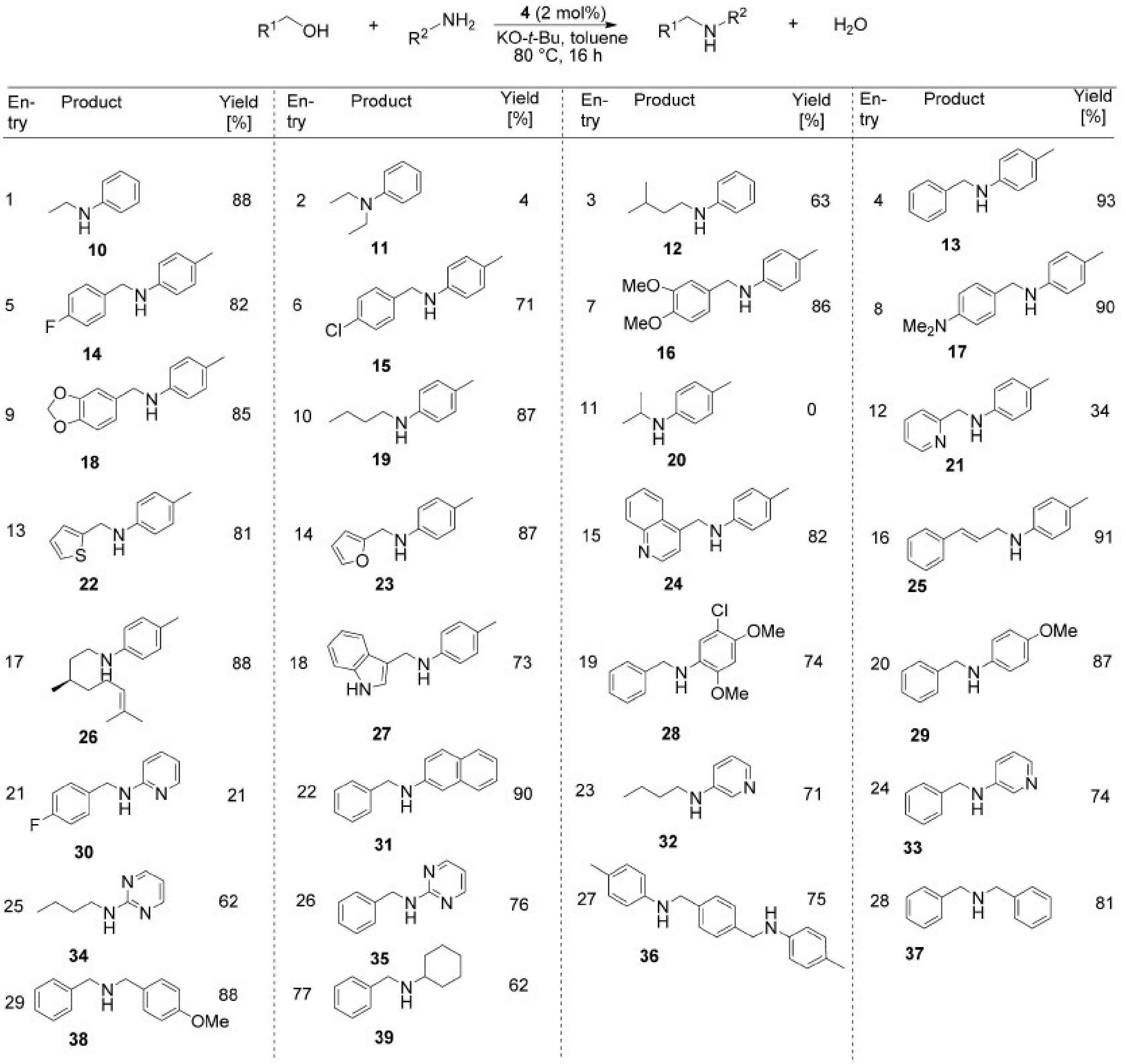
[a] Typical conditions: To a Schlenk tube, under argon, were added in this order: catalyst **1**, iPrOH (0.25 mol L^{-1}), ketone or aldehyde (0.5 or 2 mmol), and tBuOK. The conversion was determined by ^1H NMR on the crude mixture. Isolated yield in parentheses. [b] Selectivity alcohol: aldol byproducts of 67:33. [c] 5% of aldol condensation byproduct was detected in the crude mixture. [d] 1 week, due to low solubility of the starting material. [e] 72 h. [f] 1 h. [g] Selectivity γ-valerolactone/Isopropyl-4-hydroxypentanoate 84/16 at 80 °C and 77/23 at 30 °C. [h] 2 h, iPrOH 4 mL. [i] Enol 95%, 4-phenylbutan-2-ol 5%. [j] 2 h, 7% aldol condensation byproducts were detected in the crude mixture.

3.4.1. – Coupling and Dehydrogenation Reactions – Iron Catalysts

B-Fe-1 – Synthesis of Secondary Amines

M. Mastalir, B. Stöger, E. Pittenauer, M. Puchberger, G. Allmaier and K. Kirchner, *Advanced Synthesis & Catalysis*, **2016**, *358*, 3824-3831.

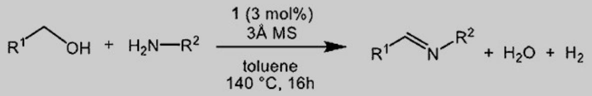
M. Mastalir, M. Glatz, N. Gorgas, B. Stöger, E. Pittenauer, G. Allmaier, L. F. Veiros and K. Kirchner, *Chemistry – A European Journal*, **2016**, *22*, 12316-12320.

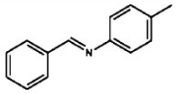
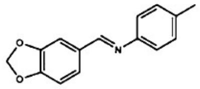
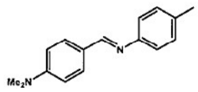
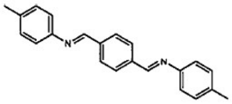
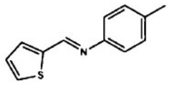
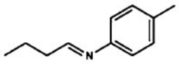
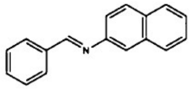
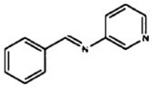
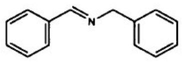
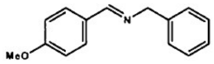
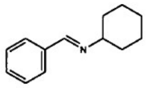
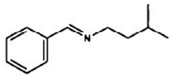


En-try	Product	Yield [%]	En-try	Product	Yield [%]	En-try	Product	Yield [%]	En-try	Product	Yield [%]
1	**10**	88	2	**11**	4	3	**12**	63	4	**13**	93
5	**14**	82	6	**15**	71	7	**16**	86	8	**17**	90
9	**18**	85	10	**19**	87	11	**20**	0	12	**21**	34
13	**22**	81	14	**23**	87	15	**24**	82	16	**25**	91
17	**26**	88	18	**27**	73	19	**28**	74	20	**29**	87
21	**30**	21	22	**31**	90	23	**32**	71	24	**33**	74
25	**34**	62	26	**35**	76	27	**36**	75	28	**37**	81
29	**38**	88	77	**39**	62						

[a] *Reaction conditions:* 1.0 mmol alcohol, 1.2 mmol amine, 1.3 mmol KO-*t*-Bu, 2 mol% catalyst, 4 mL toluene, 80 °C, 16 h.
[b] Isolated yields.
[c] With 4 mol% catalyst.

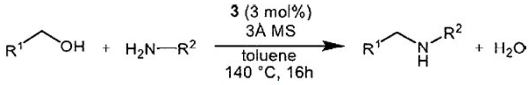
Table 2. Dehydrogenative coupling of alcohols and amines to form imines utilizing catalyst **1**.[a]

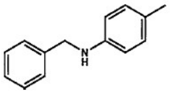
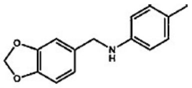
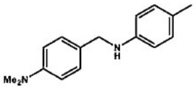
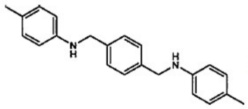
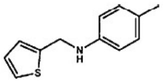
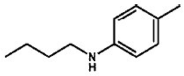
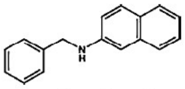
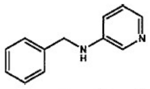
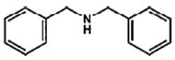
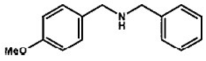
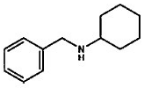
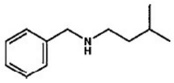


Entry	Product		Entry	Product	
1		90%	2		84%
3		92%	4		71%
5		68%	6		17%
7		90%	8		60%
9		86%	10		92%
11		87%	12		73%

[a] Reaction conditions: 1.0 mmol alcohol, 1.4 mmol amine, 0.3 g 3 Å MS, 3.0 mol% catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields.

Table 3. Coupling of alcohols and amines catalyzed by **3**.[a]

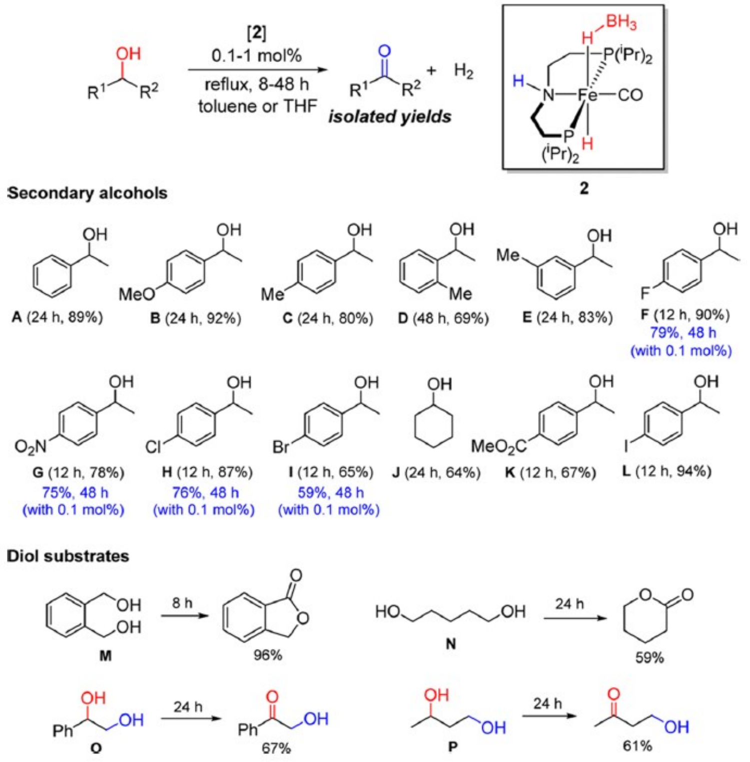


Entry	Product		Entry	Product	
1		91%	2		82%
3		88%	4		67%
5		80%	6		61%
7		93%	8		61%
9		82%	10		89%
11		82%	12		79%

[a] Reaction conditions: 1.0 mmol alcohol, 1.4 mmol amine, 0.3 g 3 Å MS, 3.0 mol% catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields.

C-Fe-1/4 – Synthesis of Ketones

S. Chakraborty, P. O. Lagaditis, M. Förster, E. A. Bielinski, N. Hazari, M. C. Holthausen, W. D. Jones and S. Schneider, *ACS Catalysis*, **2014**, *4*, 3994-4003.



C-Fe-1 – Synthesis of Lactones and Lactams

M. Peña-López, H. Neumann and M. Beller, *ChemCatChem*, **2015**, *7*, 865-871.

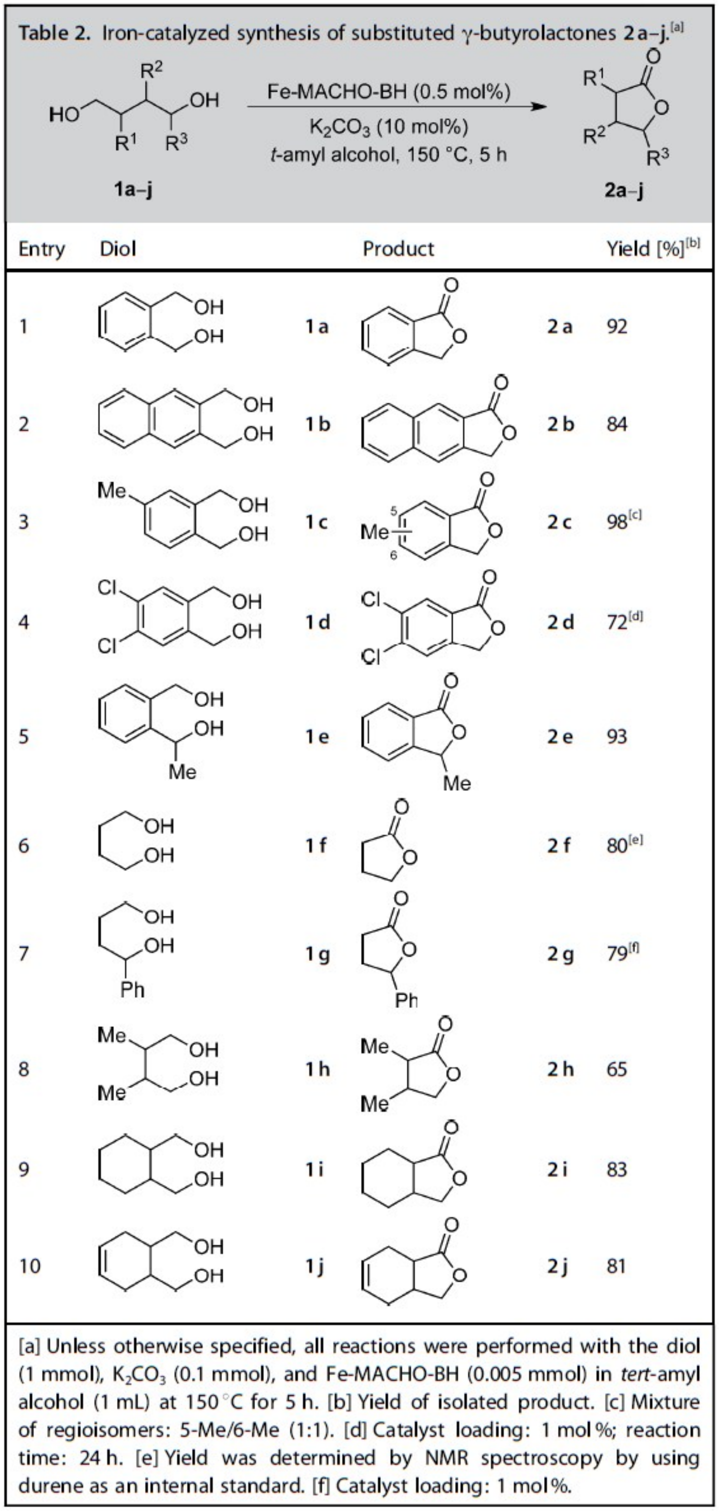
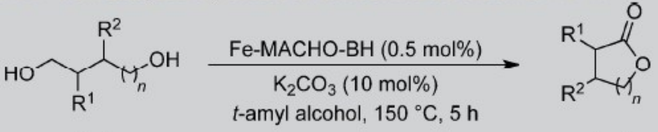


Table 2. Iron-catalyzed synthesis of substituted γ-butyrolactones **2a–j**.[a]

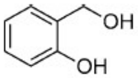
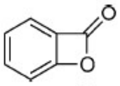
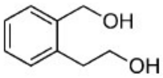
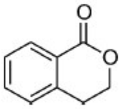
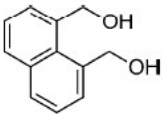
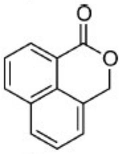
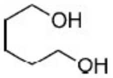
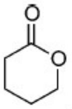
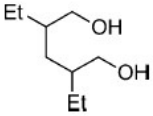
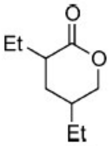
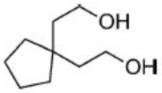
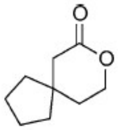
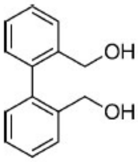
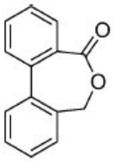
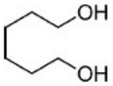
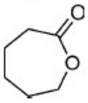
Entry	Diol		Product		Yield [%][b]
1		**1a**		**2a**	92
2		**1b**		**2b**	84
3		**1c**		**2c**	98[c]
4		**1d**		**2d**	72[d]
5		**1e**		**2e**	93
6		**1f**		**2f**	80[e]
7		**1g**		**2g**	79[f]
8		**1h**		**2h**	65
9		**1i**		**2i**	83
10		**1j**		**2j**	81

[a] Unless otherwise specified, all reactions were performed with the diol (1 mmol), K_2CO_3 (0.1 mmol), and Fe-MACHO-BH (0.005 mmol) in *tert*-amyl alcohol (1 mL) at 150 °C for 5 h. [b] Yield of isolated product. [c] Mixture of regioisomers: 5-Me/6-Me (1:1). [d] Catalyst loading: 1 mol %; reaction time: 24 h. [e] Yield was determined by NMR spectroscopy by using durene as an internal standard. [f] Catalyst loading: 1 mol%.

Table 3. Iron-catalyzed synthesis of different-sized lactones **4 a–h**.[a]

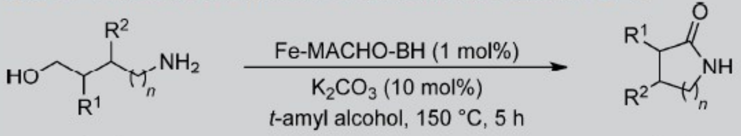


3a–h **4a–h**

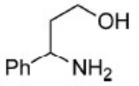
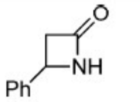
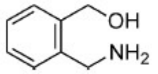
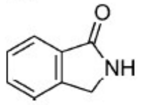
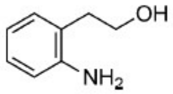
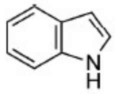
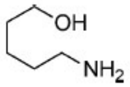
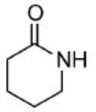
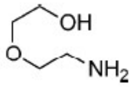
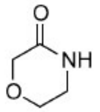
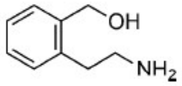
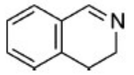
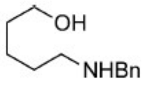
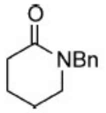
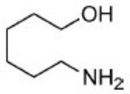
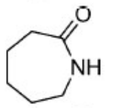
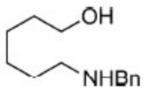
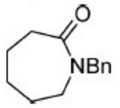
Entry	Diol		Product		Yield [%][b]
1		**3 a**		**4 a**	n.d.[c]
2		**3 b**		**4 b**	81[d]
3		**3 c**		**4 c**	98
4		**3 d**		**4 d**	55[e,f]
5		**3 e**		**4 e**	61
6		**3 f**		**4 f**	82
7		**3 g**		**4 g**	72
8		**3 h**		**4 h**	63[e,f]

[a] Unless otherwise specified, all reactions were performed with the diol (1 mmol), K_2CO_3 (0.1 mmol), and Fe-MACHO-BH (0.005 mmol) in *tert*-amyl alcohol (1 mL) at 150 °C for 5 h. [b] Yield of isolated product. [c] n.d.: not detected. [d] Yield of the mixture of isolated regioisomers: isochroman-1-one/isochroman-3-one (85:15). [e] Yield was determined by NMR spectroscopy by using durene as an internal standard. [f] Reaction was performed in toluene with Fe-MACHO-BH (1 mol%).

Table 4. Iron-catalyzed synthesis of different-sized lactams 6 a–i.[a]



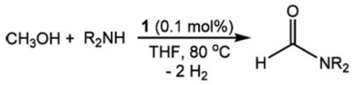
5a–i **6a–i**

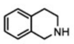
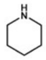
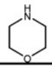
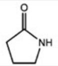
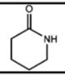
Entry	Amino alcohol		Product		Yield [%][b]
1		5 a		6 a	n.d.[c]
2		5 b		6 b	n.d.[c]
3		5 c		6 c	86 (83)[d]
4		5 d		6 d	75 (64)[d]
5		5 e		6 e	49 (91)[e,f]
6		5 f		6 f	92[g]
7		5 g		6 g	85 (77)[d,e]
8		5 h		6 h	82 (74)[d]
9		5 i		6 i	41 (95)[e,f]

[a] Unless otherwise specified, all reactions were performed with the amino alcohol (1 mmol), K_2CO_3 (0.1 mmol), and Fe-MACHO-BH (0.01 mmol) in *tert*-amyl alcohol (1 mL) at 150 °C for 5 h. [b] Yield was determined by NMR spectroscopy by using durene as an internal standard. [c] n.d.: not detected. [d] Yield of the isolated product is given in parentheses. [e] Catalyst loading: 2 mol%. [f] Yield based on recovered starting material is given in parentheses. [g] Decomposition observed during isolation by chromatography on silica gel.

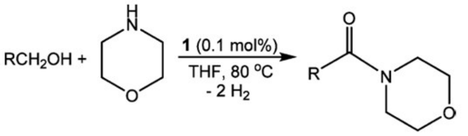
C-Fe-4 – Synthesis of Amides

E. M. Lane, K. B. Uttley, N. Hazari and W. Bernskoetter, *Organometallics*, **2017**, *36*, 2020-2025.



Entry	Amine	TON
1		600[b]
2		564[b]
3		503[b]
4	$(CH_3CH_2)_2NH$	213
5	$(C_6H_5CH_2)_2NH$	126
6	$(C_6H_5)_2NH$	<10
7	$[(CH_3)_2CH]_2NH$	<10
8		0[b]
9		0[b,c]

[a] Reaction conditions: 3 μmol of catalyst (0.1 mol %), 3 mmol of alcohol, and 12 mmol of amine in 5 mL of THF at 80 °C for 8 h. Each entry is an average of two trials, and the TON was determined by GC analysis of amide production unless otherwise indicated. [b] Determined by ^1H NMR spectroscopy. [c] Only one trial.



entry	alcohol	TON
1	CH_3OH	503
2	CH_3CH_2OH	50
3	$CH_3(CH_2)_5OH$	13
4	$C_6H_5(CH_2)_2OH$	10
5	$C_6H_5CH_2OH$	10
6	CF_3CH_2OH	0[b]

[a] Reaction conditions: 3 μmol of catalyst (0.1 mol %), 3 mmol of alcohol, and 12 mmol of amine in 5 mL of THF at 80 °C for 8 h. Each entry is an average of two trials, and the TON was determined by GC analysis of amide production unless otherwise indicated. [b] Determined by ^1H NMR spectroscopy.

M-Fe-2 – Synthesis of Amines

T. Yan, B. L. Feringa and K. Barta, *Nat. Commun.,* 2014, **5,** 5602.

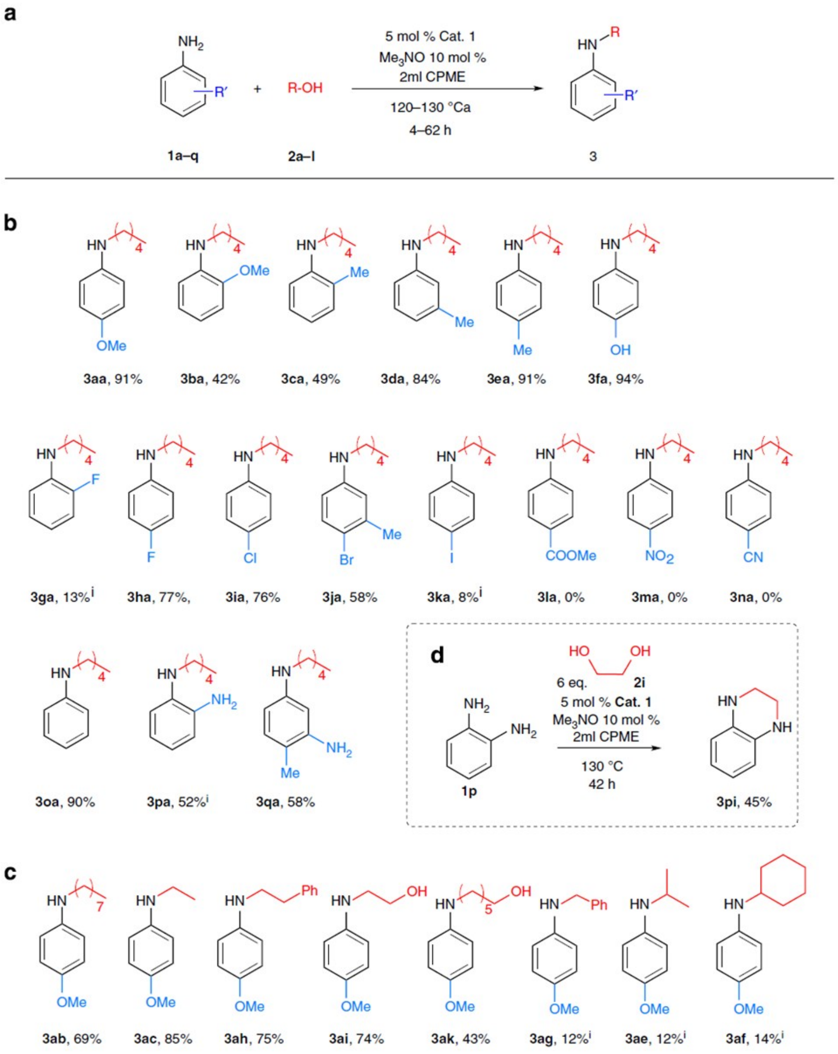


Figure 3 | Selective monoalkylation of functionalized anilines with various alcohols. (**a**) General reaction conditions. The main products are *N*-alkylated aniline derivatives (**3**). Possible side products are imines. No dialkylation is observed. (**b**) *N*-alkylation of various aniline derivatives with pentane-1-ol. Reactivity strongly depends on the substituents on the aromatic ring. Anilines bearing electron-donating groups in the para position were most reactive and **3fa**, **3aa** were obtained in 4 and 7 h, respectively. **3ba**, **3ca**, **3da**, **3ia**, **3ja** were obtained at prolonged reaction times at 120 °C, by addition of molecular sieves. ^{i}GC-FID selectivity is given. (**c**) Reactions of *p*-methoxyaniline with various alcohols. Selective monoalkylation was also observed with ethane-1,2-diol and hexane-1,6-diol (**3ai**, **3ak**). (**d**) Direct 2,3-dihydro-quinoxaline formation from ethylene glycol and *o*-phenylenediamine.

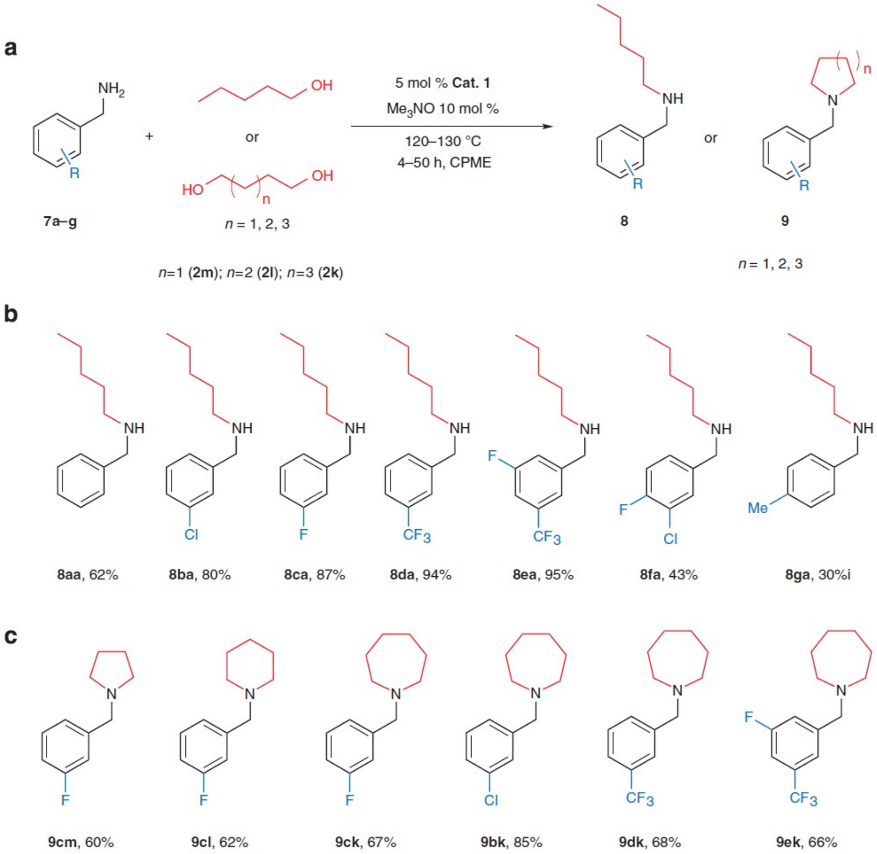
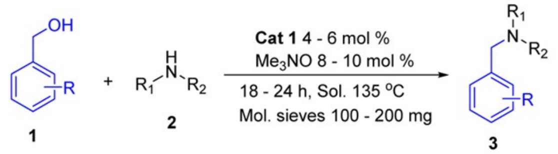
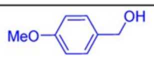
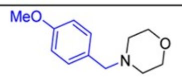
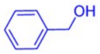
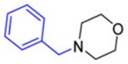
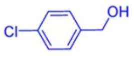
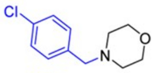
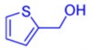
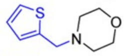
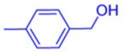
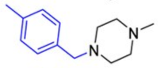
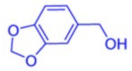
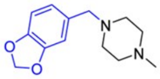
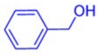
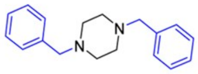
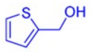
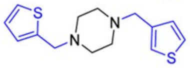
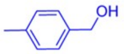
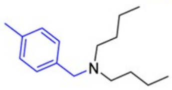
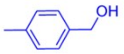
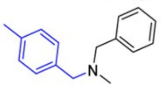
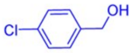
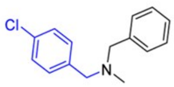
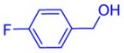
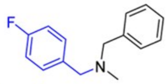
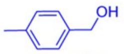
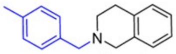
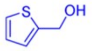
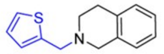
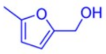
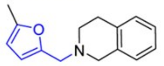


Figure 5 | Reactions of various benzylamines with pentane-1-ol and diols. (**a**) General reaction conditions. (**b**) Reactions of various benzyl-amines with pentanol. Benzyl-amines bearing electron-withdrawing substituents in the meta position were highly reactive, for example, for **8ca**, **8da** and **8ea**, no dialkylated amine or imine were observed. Benzyl amines **7a** and **7g** were less reactive, with these substrates small amounts of dialkylated and imine products were also observed. (**c**) Construction of 5-, 6- or 7-membered *N*-heterocyclic rings using benzylamines **7b**, **7c**, **7d** and **7e** and butane-1,4-diol (**2m**), pentane-1,5-diol (**2l**) or hexane-1,6-diol (**2k**).

T. Yan, B. L. Feringa and K. Barta, *ACS Cat.,* 2016, **6,** 381-388.

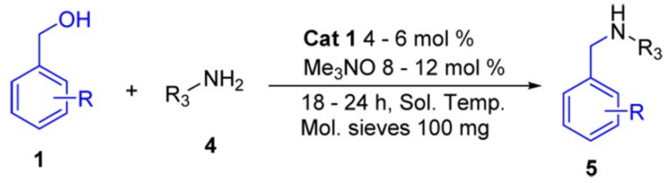
Table 2. Amination of Benzyl Alcohols with Secondary Amines[a]

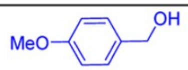
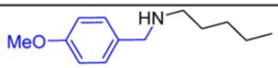
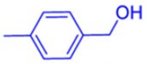
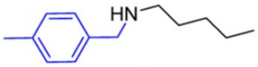
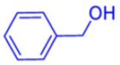
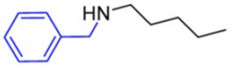
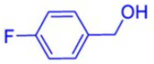
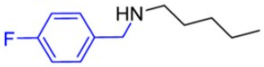
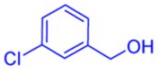
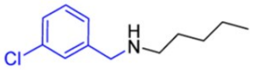
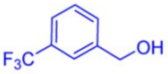
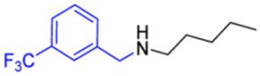
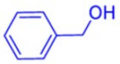
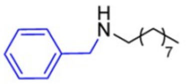
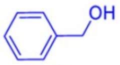
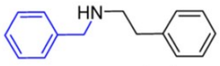
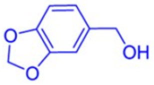
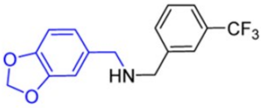
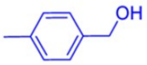
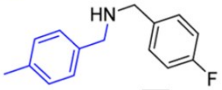
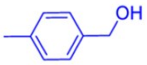
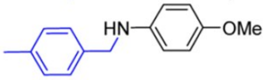
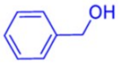
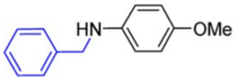


Entry	Substrate **1**		Product **3**		Yield [%][b]
1	**1b**		**3b**		88
2	**1c**		**3c**		60
3	**1d**		**3d**		40
4	**1e**		**3e**		74
5	**1a**		**3f**		78
6	**1f**		**3g**		69
7	**1c**		**3h**		90
8	**1e**		**3i**		80
9	**1a**		**3j**		65
10	**1a**		**3k**		91
11	**1d**		**3l**		63
12	**1g**		**3m**		69
13	**1a**		**3n**		89
14	**1e**		**3o**		79
15	**1h**		**3p**		59

[a] General reaction conditions: general procedure (see page S2 in the Supporting Information), 0.5 mmol of **2**, 2 mmol of **1a**, 0.02−0.03 mmol of **Cat 1**, 0.04−0.06 mmol of Me_3NO, 2 mL of solvent, 18−24 h, 135 °C, 95−105 mg of molecular sieves. For specific conditions see Tables S2a and S2b in the Supporting Information. [b] Isolated yields.

Table 3. Amination of Benzyl Alcohols with Primary Amines[a]



Entry	Substrate **1**		Product **5**		Yield [%][b]
1	**1b**		**5a**		54
2	**1a**		**5b**		61
3	**1c**		**5c**		59
4	**1g**		**5d**		53
5	**1i**		**5e**		42
6	**1j**		**5f**		22
7	**1c**		**5g**		60
8	**1c**		**5h**		61
9	**1f**		**5i**		60
10	**1a**		**5j**		70
11	**1a**		**5k**		66
12	**1c**		**5l**		56

[a] General reaction conditions: general procedure (see page S2 in the Supporting Information), 0.5 mmol of **2**, 2 mmol of **1a**, 0.02−0.03 mmol of **Cat 1**, 0.04−0.06 mmol of Me$_3$NO, 2 mL of solvent, 18−24 h, 135 °C, 95−105 mg of molecular sieves. For specific conditions see Table S3 in the Supporting Information. [b] Isolated yields.

M-Fe-2 – Synthesis of Pyrroles

T. Yan and K. Barta, *ChemSusChem,* 2016, **9,** 2321-2325.

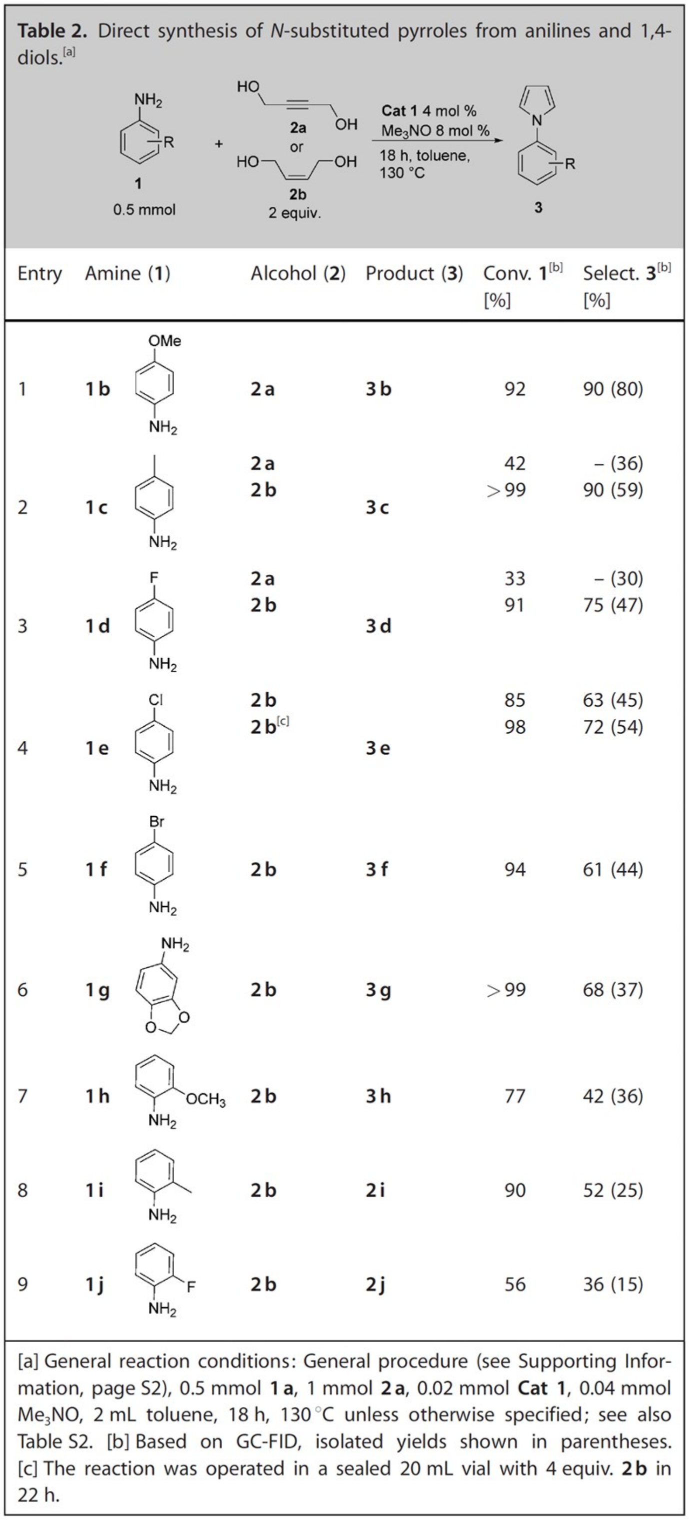
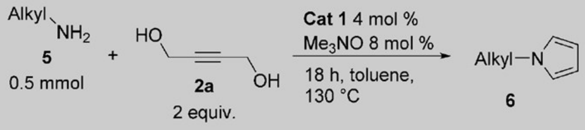


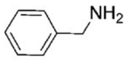
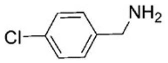
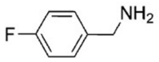
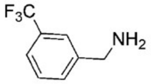
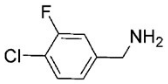
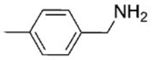
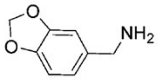
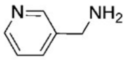
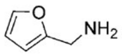
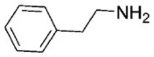
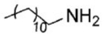
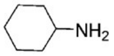
Table 2. Direct synthesis of *N*-substituted pyrroles from anilines and 1,4-diols.[a]

Entry	Amine (**1**)	Alcohol (**2**)	Product (**3**)	Conv. **1**[b] [%]	Select. **3**[b] [%]
1	**1b**	**2a**	**3b**	92	90 (80)
2	**1c**	**2a**	**3c**	42	– (36)
		2b		>99	90 (59)
3	**1d**	**2a**	**3d**	33	– (30)
		2b		91	75 (47)
4	**1e**	**2b**	**3e**	85	63 (45)
		2b[c]		98	72 (54)
5	**1f**	**2b**	**3f**	94	61 (44)
6	**1g**	**2b**	**3g**	>99	68 (37)
7	**1h**	**2b**	**3h**	77	42 (36)
8	**1i**	**2b**	**2i**	90	52 (25)
9	**1j**	**2b**	**2j**	56	36 (15)

[a] General reaction conditions: General procedure (see Supporting Information, page S2), 0.5 mmol **1a**, 1 mmol **2a**, 0.02 mmol **Cat 1**, 0.04 mmol Me$_3$NO, 2 mL toluene, 18 h, 130 °C unless otherwise specified; see also Table S2. [b] Based on GC-FID, isolated yields shown in parentheses. [c] The reaction was operated in a sealed 20 mL vial with 4 equiv. **2b** in 22 h.

Table 3. Direct synthesis of *N*-substituted pyrroles from anilines and 1,4-diols.[a]

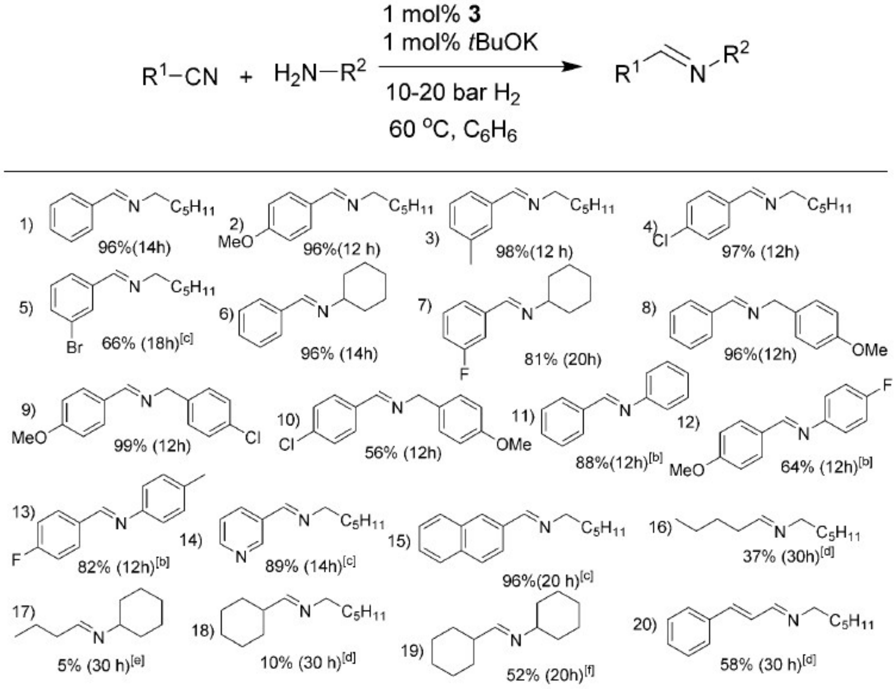


Entry	Amine (5)		Product (6)	Select. 3[b] [%]
1	**5a**		**6a**	90 (61)
2	**5b**		**6b**	85 (57)
3	**5c**		**6c**	73 (52)
4	**5d**		**6d**	88 (55)
5	**5e**		**6e**	87 (65)
6	**5f**		**6f**	87 (65)
7	**5g**		**6g**	83 (55)
8	**5h**		**6h**	92 (76)
9	**5i**		**6i**	71 (43)
10	**5j**		**6j**	– (41)
11	**5k**		**6k**	86 (42)
12	**5l**		**6l**	85 (33)

[a] General reaction conditions: General procedure (see Supporting Information, page S2), 0.5 mmol **5**, 1 mmol **2a**, 0.02 mmol **Cat 1**, 0.04 mmol Me_3NO, 2 mL toluene, 18 h, 130 °C; see also Table S3; in all cases full conversion was obtained. [b] Based on GC-FID, isolated yields shown in parentheses.

M-Fe-5 – Synthesis of Aldimines

S. Chakraborty, G. Leitus and D. Milstein, *Angewandte Chemie International Edition*, **2017**, *56*, 2074-2078.

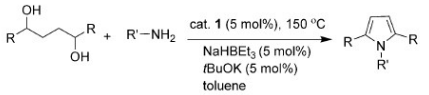


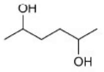
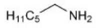
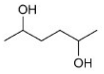
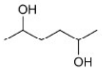
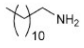
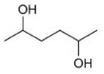
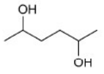
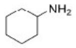
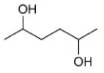
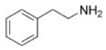
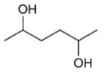
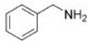
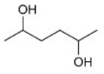
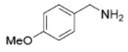
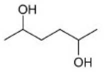
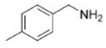
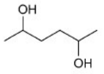
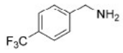
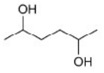
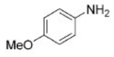
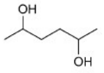
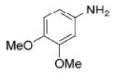
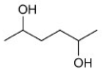
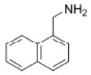
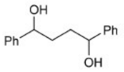
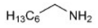
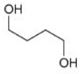
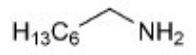
[a] Conditions: benzonitrile (1–0.125 mmol), amine (1–0.125 mmol), **3** (0.01 mmol), tBuOK (1 equiv relative to **3**), 20 bar H_2, and C_6H_6 (2 mL), heated in an autoclave at 60 °C. Yields and conversions determined by GC-MS and NMR analysis using *m*-xylene or toluene as internal standards. [b] 10 bar H_2. [c] 2 mol% catalyst used. [d] 8 mol% catalyst used. [e] 24 mol% *t*BuOK, 30 bar H_2, 90 °C. [f] 8 mol% **3**, 8 mol% tBuOK and 90 °C.

3.4.2. – Coupling and Dehydrogenation Reactions – Cobalt Catalysts

A-Co-4 – Synthesis of 1,2,5-substituted Pyrroles

P. Daw, S. Chakraborty, J. A. Garg, Y. Ben-David and D. Milstein, *Angewandte Chemie International Edition*, **2016**, *55*, 14373-14377.

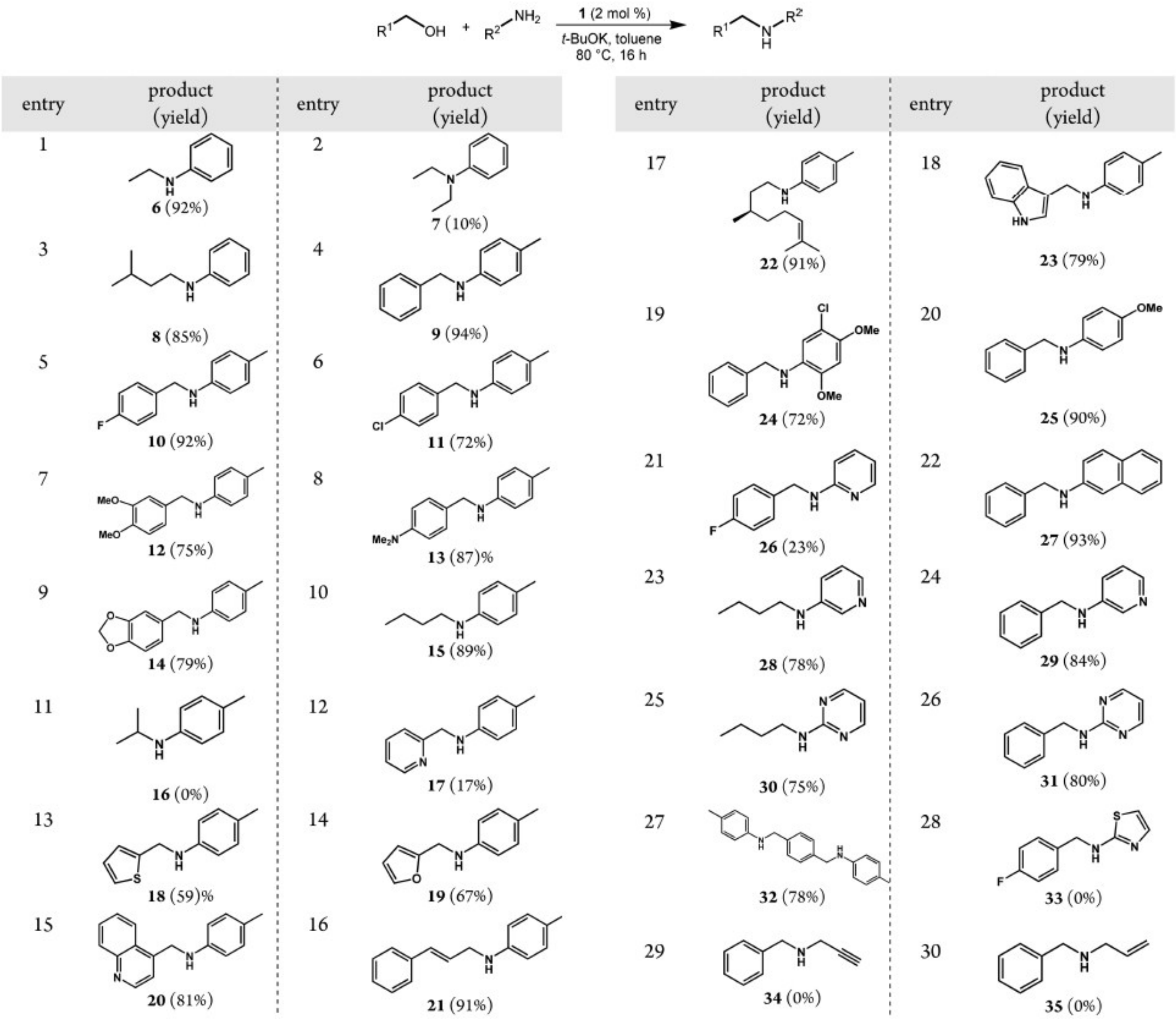


Entry[a]	Diol	Amine (RNH_2)	t [h]	Yield of pyrrole [%]
1			24	88[b]
2			24	93[b]
3			24	86[b]
4			24	90[b]
5			24	70[b]
6			24	62[b]
7			24	89[b]
8			36	68[b]
9			24	87[b]
10			24	60[b]
11			36	25[c]
12			36	22[c]
13			36	78[b]
14			36	56[c]
15			24	58[c]

[a] Conditions: diol (0.5 mmol), amine (0.5 mmol), toluene (2 mL), and 4 Å molecular sieves heated in an closed Schlenk tube for the specified time. [b] Yield of isolated product. [c] Yield determined by GC.

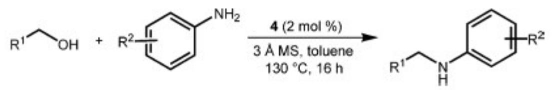
B-Co-1/2 – Synthesis of Secondary Amines

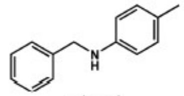
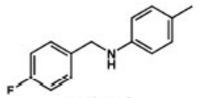
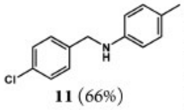
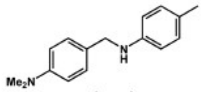
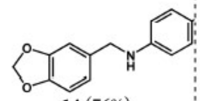
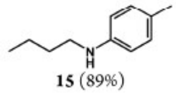
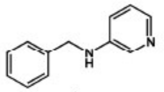
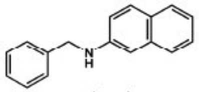
M. Mastalir, G. Tomsu, E. Pittenauer, G. Allmaier and K. Kirchner, *Organic Letters*, **2016**, *18*, 3462-3465.



entry	product (yield)	entry	product (yield)	entry	product (yield)	entry	product (yield)
1	**6** (92%)	2	**7** (10%)	17	**22** (91%)	18	**23** (79%)
3	**8** (85%)	4	**9** (94%)	19	**24** (72%)	20	**25** (90%)
5	**10** (92%)	6	**11** (72%)	21	**26** (23%)	22	**27** (93%)
7	**12** (75%)	8	**13** (87)%	23	**28** (78%)	24	**29** (84%)
9	**14** (79%)	10	**15** (89%)	25	**30** (75%)	26	**31** (80%)
11	**16** (0%)	12	**17** (17%)	27	**32** (78%)	28	**33** (0%)
13	**18** (59)%	14	**19** (67%)	29	**34** (0%)	30	**35** (0%)
15	**20** (81%)	16	**21** (91%)				

^{a}Isolated yields.

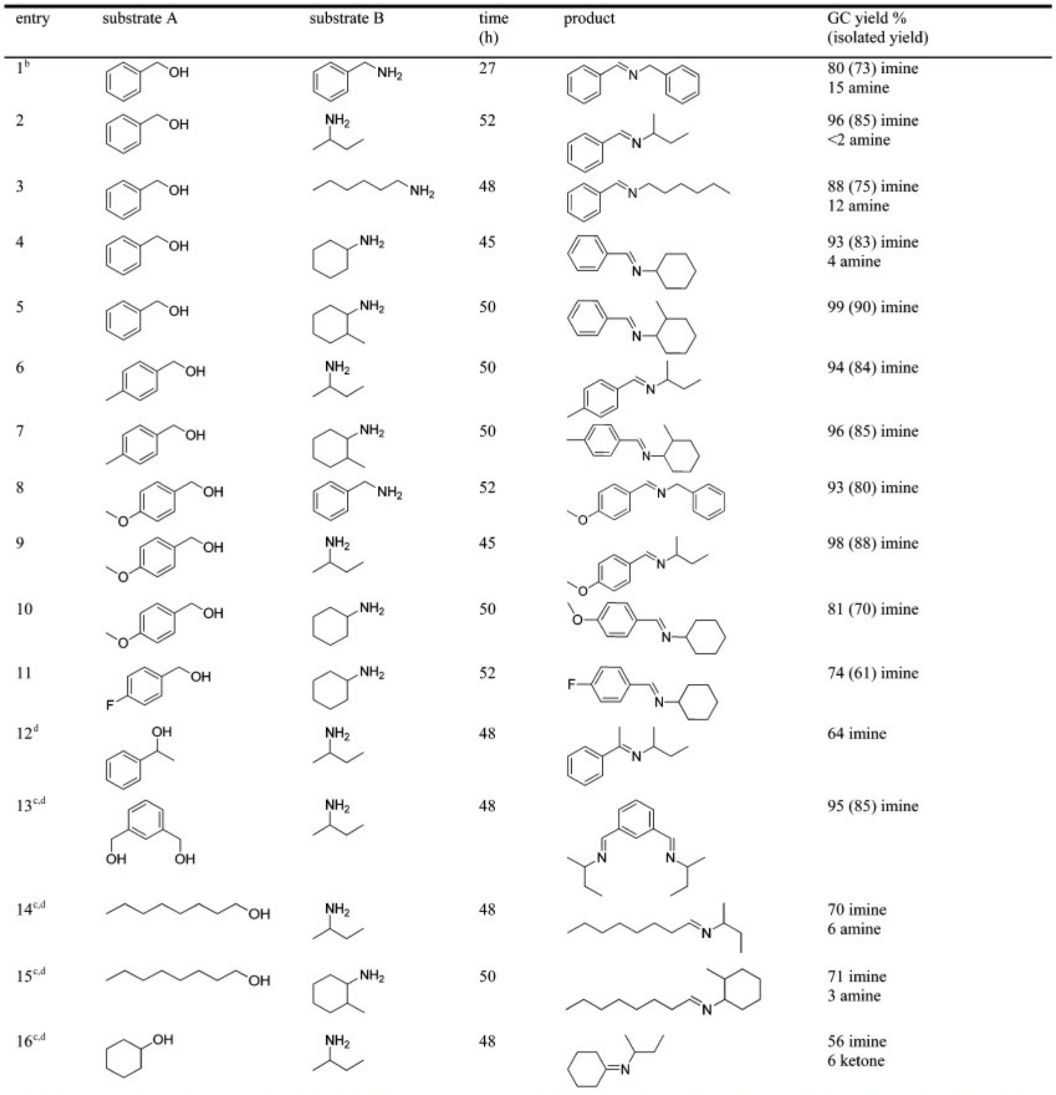


entry	product (yield)	entry	product (yield)
1	 **9** (90%)	2	 **10** (78%)
3	 **11** (66%)	4	 **13** (80%)
5	 **14** (76%)	6	 **15** (89%)
7	 **29** (73)%	8	 **27** (91%)

[a] Isolated yields.

C-Co-1 – Synthesis of Aldimines

G. Zhang and S. K. Hanson, *Organic Letters*, **2013**, *15*, 650-653.

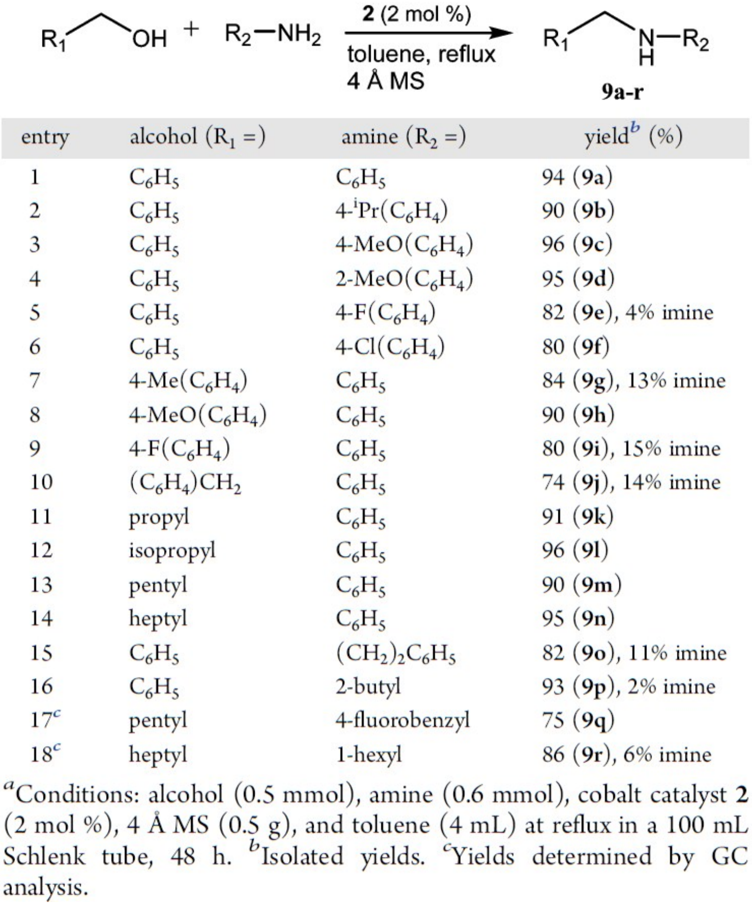


entry	substrate A	substrate B	time (h)	product	GC yield % (isolated yield)
1[b]			27		80 (73) imine 15 amine
2			52		96 (85) imine <2 amine
3			48		88 (75) imine 12 amine
4			45		93 (83) imine 4 amine
5			50		99 (90) imine
6			50		94 (84) imine
7			50		96 (85) imine
8			52		93 (80) imine
9			45		98 (88) imine
10			50		81 (70) imine
11			52		74 (61) imine
12[d]			48		64 imine
13[c,d]			48		95 (85) imine
14[c,d]			48		70 imine 6 amine
15[c,d]			50		71 imine 3 amine
16[c,d]			48		56 imine 6 ketone

[a] Conditions: Substrate A (1.0 mmol), substrate B (1.1 mmol, except for *sec*-butylamine, 5.0 mmol), 1 mol % catalyst (1 mol % complex 1 and 1 mol % $H[BAr^F_4]\cdot(Et_2O)_2$), toluene (2 mL), 120 °C. [b] 0.2 mol % catalyst (0.2 mol % complex 1 and 0.2 mol % $H[BAr^F_4]\cdot(Et_2O)_2$). [c] 2 mol % catalyst was used (2 mol % complex 1 and 2 mol % $H[BAr^F_4]\cdot(Et_2O)_2$). [d] Reactions run in THF (2 mL).

C-Co-2 – Synthesis of Secondary Amines

G. Zhang, Z. Yin and S. Zheng, *Organic Letters*, **2016**, *18*, 300-303.

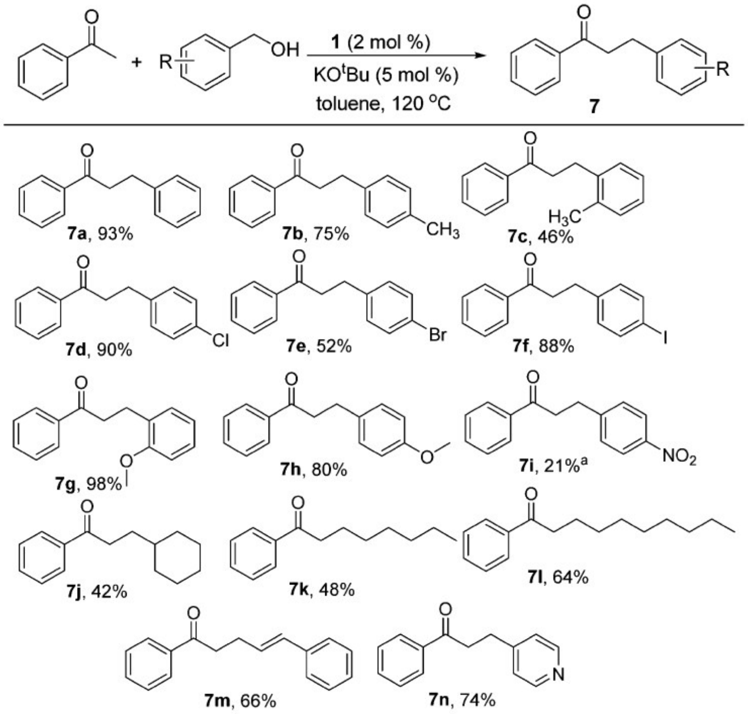


entry	alcohol (R_1 =)	amine (R_2 =)	yield[b] (%)
1	C_6H_5	C_6H_5	94 (**9a**)
2	C_6H_5	4-^{i}Pr(C_6H_4)	90 (**9b**)
3	C_6H_5	4-MeO(C_6H_4)	96 (**9c**)
4	C_6H_5	2-MeO(C_6H_4)	95 (**9d**)
5	C_6H_5	4-F(C_6H_4)	82 (**9e**), 4% imine
6	C_6H_5	4-Cl(C_6H_4)	80 (**9f**)
7	4-Me(C_6H_4)	C_6H_5	84 (**9g**), 13% imine
8	4-MeO(C_6H_4)	C_6H_5	90 (**9h**)
9	4-F(C_6H_4)	C_6H_5	80 (**9i**), 15% imine
10	(C_6H_4)CH_2	C_6H_5	74 (**9j**), 14% imine
11	propyl	C_6H_5	91 (**9k**)
12	isopropyl	C_6H_5	96 (**9l**)
13	pentyl	C_6H_5	90 (**9m**)
14	heptyl	C_6H_5	95 (**9n**)
15	C_6H_5	$(CH_2)_2C_6H_5$	82 (**9o**), 11% imine
16	C_6H_5	2-butyl	93 (**9p**), 2% imine
17[c]	pentyl	4-fluorobenzyl	75 (**9q**)
18[c]	heptyl	1-hexyl	86 (**9r**), 6% imine

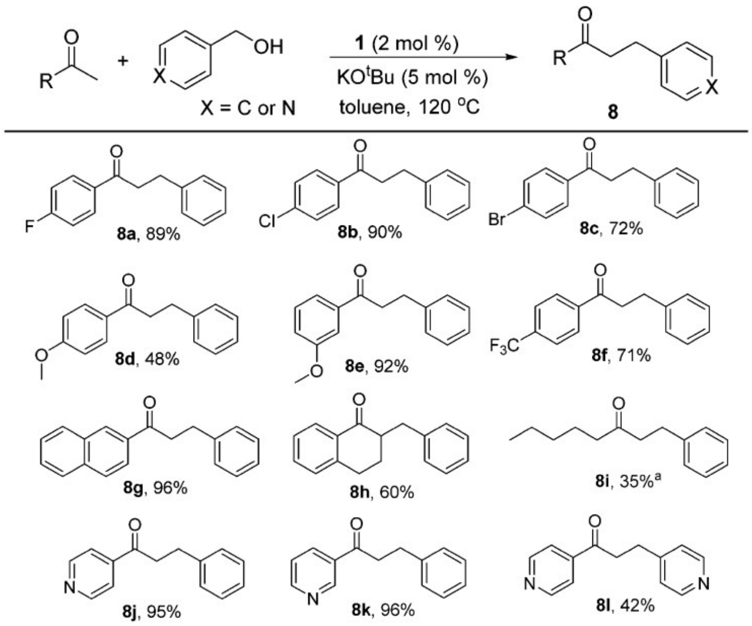
[a] Conditions: alcohol (0.5 mmol), amine (0.6 mmol), cobalt catalyst **2** (2 mol %), 4 Å MS (0.5 g), and toluene (4 mL) at reflux in a 100 mL Schlenk tube, 48 h. [b] Isolated yields. [c] Yields determined by GC analysis.

C-Co-2 – Synthesis of α-Alkylated Ketones

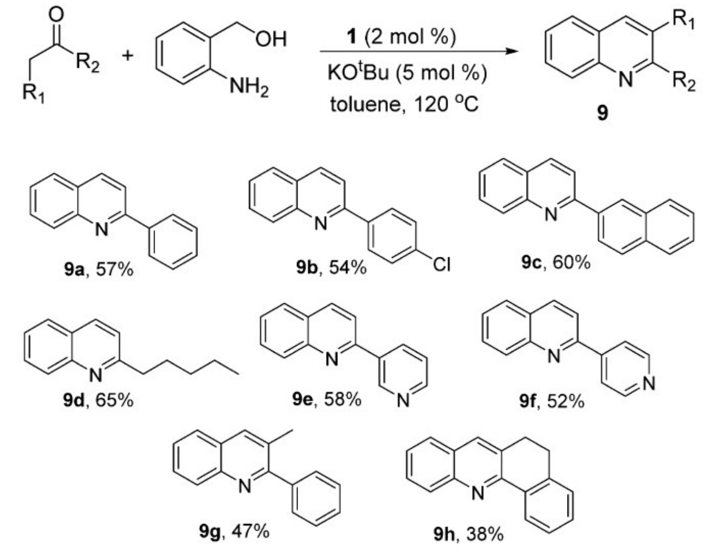
G. Zhang, J. Wu, H. Zeng, S. Zhang, Z. Yin and S. Zheng, *Organic Letters*, **2017**, *19*, 1080-1083.



[a]Conditions: primary alcohol (0.6 mmol), acetophenone (0.5 mmol), cobalt **1** (2 mol %), KOtBu (5 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products. Yield determined by GC analysis.



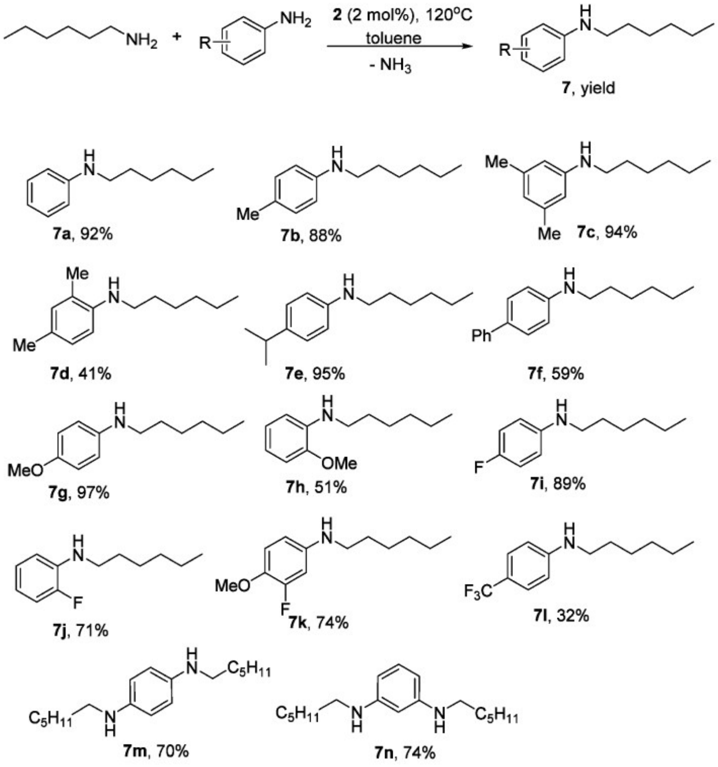
[a]Conditions: benzyl alcohol or 4-pyridinemethanol (0.6 mmol), ketone (0.5 mmol), cobalt **1** (2 mol %), KO^{t}Bu (5 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products. Yield determined by GC analysis.



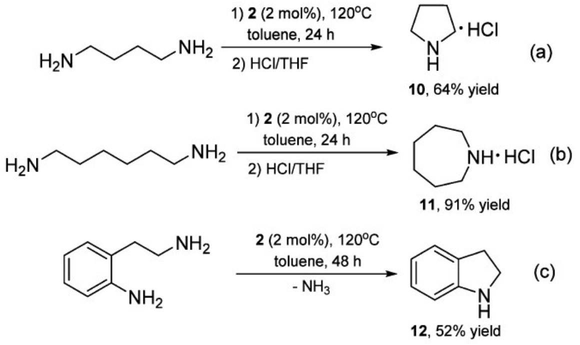
[a]Conditions: 2-aminobenzyl alcohol (0.5 mmol), ketone (0.5 mmol), cobalt **1** (2 mol %), KO^{t}Bu (5 mol %), and toluene (6 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products.

C-Co-2 – Synthesis of Secondary Amines

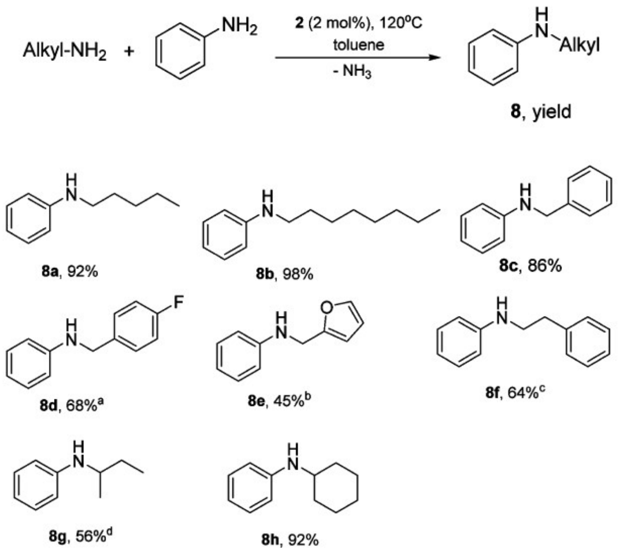
Z. Yin, H. Zeng, J. Wu, S. Zheng and G. Zhang, *ACS Catalysis*, **2016**, *6*, 6546-6550.



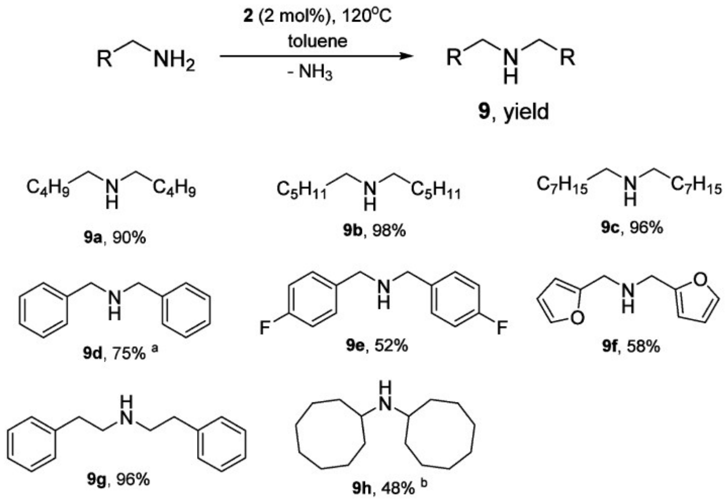
[a]Conditions: 1-hexylamine (0.5 mmol), anilines (0.6 mmol), cobalt **2** (2 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products.



[a]Yields are of isolated products.



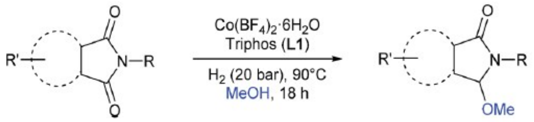
[a]26% homocoupling product observed; [b]28% homocoupling product observed; [c]19% homocoupling product observed; [d]37% imine product observed. [e]Conditions: aliphatic amines (0.5 mmol), aniline (0.6 mmol), cobalt **2** (2 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products.



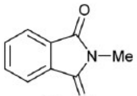
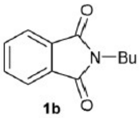
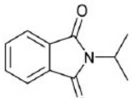
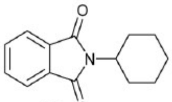
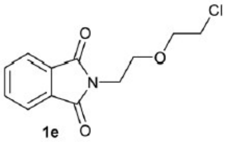
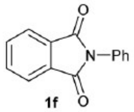
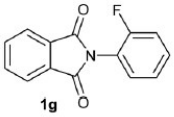
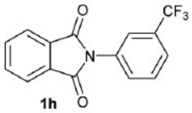
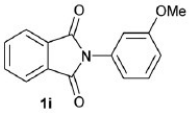
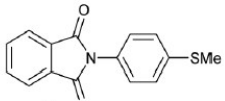
[a]14% imine product observed. [b]Isolated as a HCl salt. [c]Conditions: primary amines (1.0 mmol), cobalt **2** (2 mol % relative to one half amount of amine), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products.

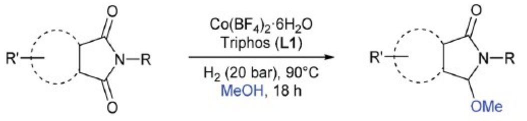
M-Co-2 – Synthesis of C_2-Alkoxylated Products

J. R. Cabrero-Antonino, R. Adam, V. Papa, M. Holsten, K. Junge and M. Beller, *Chemical Science*, **2017**, *8*, 5536-5546.

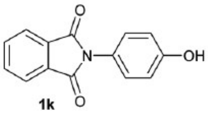
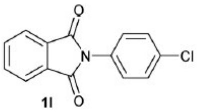
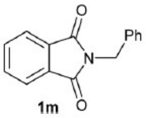
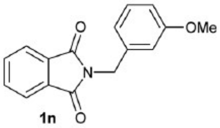
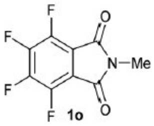
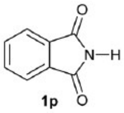
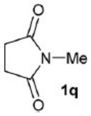
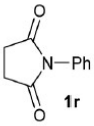
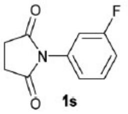
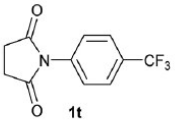


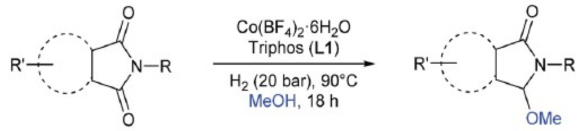
1a-u → **2a-u**

Entry[a]	Cyclic imide 1	[Co] (mol%)	2[b] [%]
1	 **1a**	2.5	**2a** [95]
2	 **1b**	4	**2b** [89]
3	 **1c**	4	**2c** [90]
4	 **1d**	4	**2d** [96]
5	 **1e**	2.5	**2e** [97]
6	 **1f**	2.5	**2f** [93]
7	 **1g**	2.5	**2g** [88]
8	 **1h**	6	**2h** [91]
9	 **1i**	4	**2i** [98]
10[c]	 **1j**	2.5	**2j** [95]

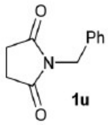


1a-u **2a-u**

Entry[a]	Cyclic imide 1	[Co] (mol%)	2[b] [%]
11	 **1k**	2.5	**2k** [96]
12	 **1l**	2.5	**2l** [94]
13	 **1m**	4	**2m** [99]
14	 **1n**	5	**2n** [99]
15[c]	 **1o**	2.5	**2o** [86]
16	 **1p**	2.5	**2p** [89]
17	 **1q**	2.5	**2q** [81]
18	 **1r**	2.5	**2r** [89]
19	 **1s**	2.5	**2s** [94]
20	 **1t**	2.5	**2t** [85]



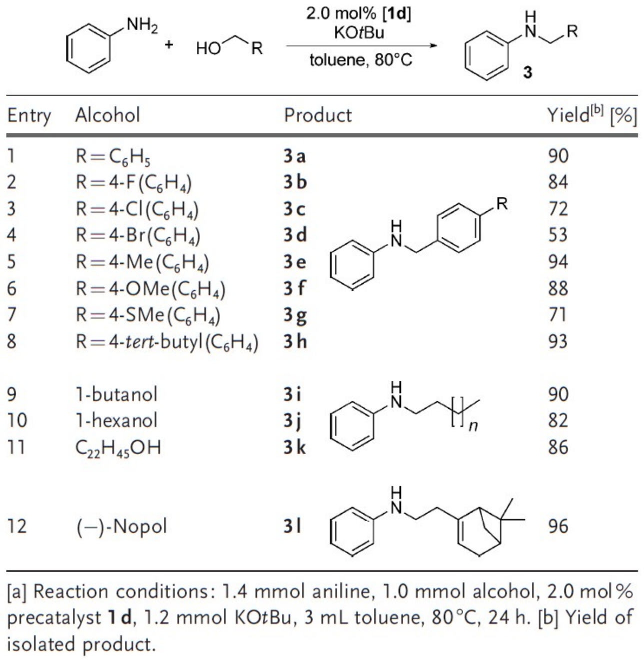
1a-u **2a-u**

Entry[a]	Cyclic imide 1	[Co] (mol%)	2[b] [%]
21	 **1u**	4	**2u** [80]

[a] Standard reaction conditions: cyclic imide (0.5 mmol), $Co(BF_4)_2·6H_2O$ (4.25 mg, 0.0125 mmol, 2.5 mol%), triphos **L1** (15.6 mg, 0.025 mmol, 5 mol%, 2 eq. to Co), H_2 (20 bar), MeOH (2 mL), 90 °C and 18 h. When the reaction was carried out using 4 to 6 mol% of cobalt precatalyst, 1.5 eq. of **L1** respect to the metal was added. [b] Isolated yield of the product after purification by column chromatography on silica are given between brackets. [c] Run at 110 °C.

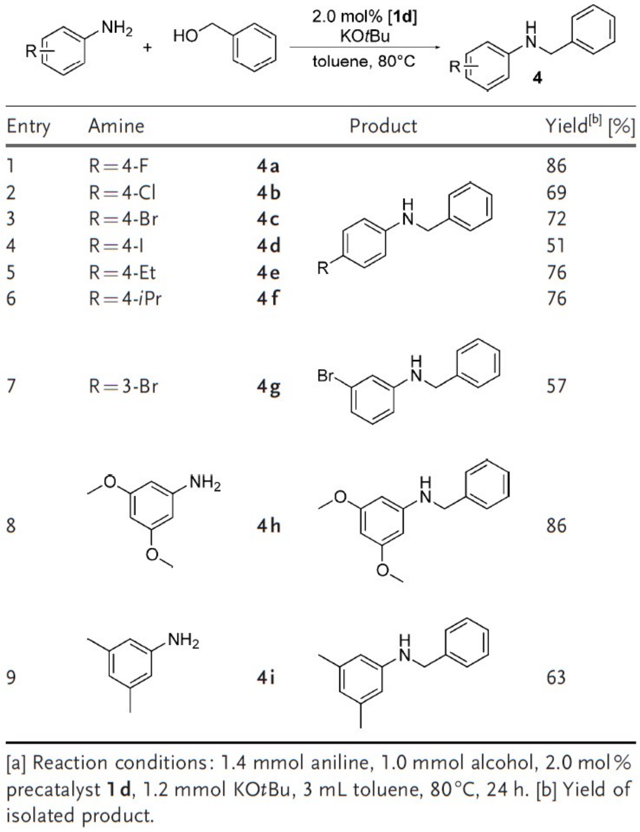
M-Co-10 – Synthesis of Secondary Amines

S. Rösler, M. Ertl, T. Irrgang and R. Kempe, *Angewandte Chemie International Edition*, **2015**, *54*, 15046-15050.



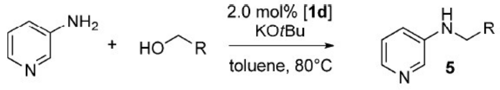
Entry	Alcohol	Product	Yield[b] [%]
1	R = C_6H_5	**3a**	90
2	R = 4-F(C_6H_4)	**3b**	84
3	R = 4-Cl(C_6H_4)	**3c**	72
4	R = 4-Br(C_6H_4)	**3d**	53
5	R = 4-Me(C_6H_4)	**3e**	94
6	R = 4-OMe(C_6H_4)	**3f**	88
7	R = 4-SMe(C_6H_4)	**3g**	71
8	R = 4-*tert*-butyl(C_6H_4)	**3h**	93
9	1-butanol	**3i**	90
10	1-hexanol	**3j**	82
11	$C_{22}H_{45}OH$	**3k**	86
12	(−)-Nopol	**3l**	96

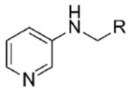
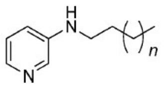
[a] Reaction conditions: 1.4 mmol aniline, 1.0 mmol alcohol, 2.0 mol% precatalyst **1d**, 1.2 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [b] Yield of isolated product.



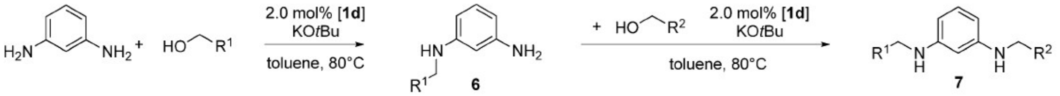
Entry	Amine		Product	Yield[b] [%]
1	R = 4-F	**4a**		86
2	R = 4-Cl	**4b**		69
3	R = 4-Br	**4c**		72
4	R = 4-I	**4d**		51
5	R = 4-Et	**4e**		76
6	R = 4-*i*Pr	**4f**		76
7	R = 3-Br	**4g**		57
8		**4h**		86
9		**4i**		63

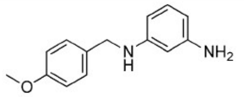
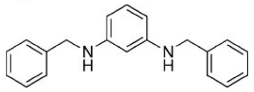
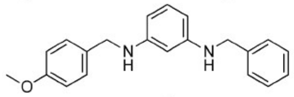
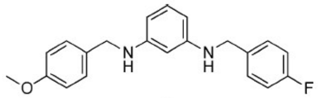
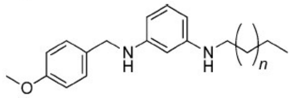
[a] Reaction conditions: 1.4 mmol aniline, 1.0 mmol alcohol, 2.0 mol% precatalyst **1d**, 1.2 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [b] Yield of isolated product.



Entry	Alcohol		Product	Yield[b] [%]
1	R = C_6H_5	**5a**		89
2	R = 4-OMe(C_6H_4)	**5b**		61
3	R = 4-SMe(C_6H_4)	**5c**		76
4	R = 4-Me(C_6H_5)	**5d**		94
5	$C_{22}H_{45}OH$	**5e**		69
6	1-butanol	**5f**		76

[a] Reaction conditions: 1.4 mmol aminopyridine, 1.0 mmol alcohol, 2.0 mol % precatalyst **1 d**, 1.2 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [b] Yield of isolated product.

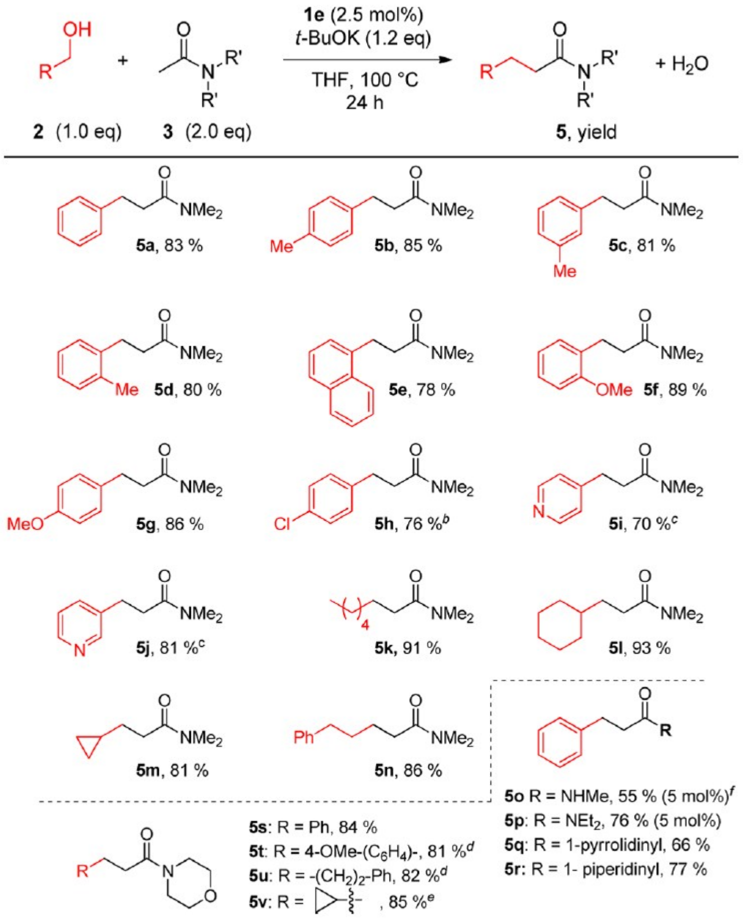


Entry	Alcohol R^1	Alcohol R^2		Product	Yield[d] [%]
1	R^1 = 4-OMe(C_6H_4)	–	**6a**[a]		91
2	R^1 = C_6H_5	R^2 = C_6H_5	**7a**[b]		73
3	R^1 = 4-OMe(C_6H_4)	R^2 = C_6H_5	**7b**[c]		71
4	R^1 = 4-OMe(C_6H_4)	R^2 = 4-F-(C_6H_4)	**7c**[c]		57
5	R^1 = 4-OMe(C_6H_4)	R^2 = propyl	**7d**[c]		76
6	R^1 = 4-OMe(C_6H_4)	R^2 = pentyl	**7e**[c]		79

[a] 3.0 mmol benzenediamine, 1.0 mmol alcohol, 2.0 mol % precatalyst **1 d**, 1.2 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [b] 1.0 mmol benzenediamine, 2.0 mmol alcohol, 4.0 mol % precatalyst **1 d**, 2.4 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [c] 1.0 mmol **6 a**, 1.0 mmol alcohol, 2.0 mol % precatalyst **1 d**, 1.2 mmol KO*t*Bu, 3 mL toluene, 80 °C, 24 h. [d] Yield of isolated product.

M-Co-10 – Synthesis of C-Alkylated Amides

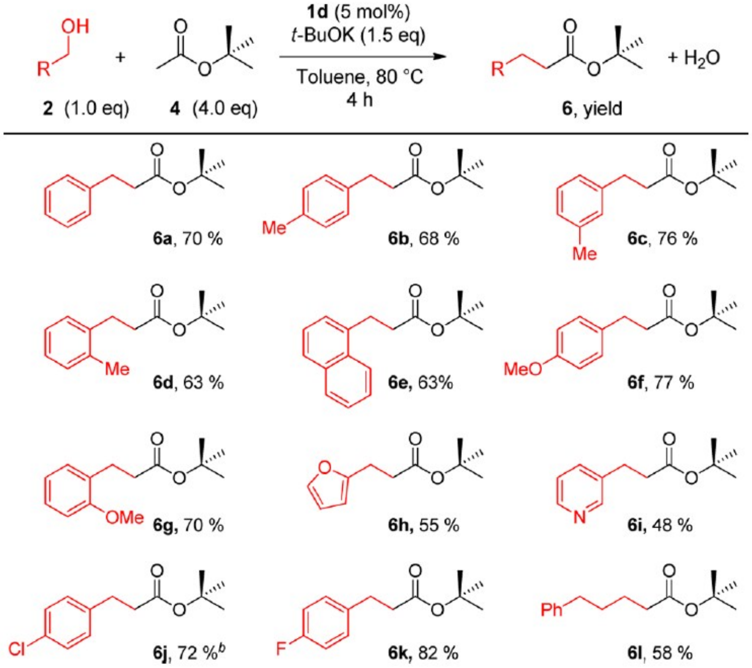
N. Deibl and R. Kempe, *Journal of the American Chemical Society*, **2016**, *138*, 10786-10789.



[a]Alcohol (1 mmol), amide (2 mmol), *t*-BuOK (1.2 mmol), **1e** (0.025 mmol), and THF (4 mL) were heated for 24 h at 100 °C (oil bath) in a closed system. Yields are of isolated products. [b]*t*-BuONa was used as a base. [c]**1f** (5 mol %) was used. [d]10 mmol scale. [e]5 mmol scale. [f]1,4-dioxane, 120 °C, 1.5 equiv *t*-BuOK.

M-Co-11 – Synthesis of C-Alkylated Esters

N. Deibl and R. Kempe, *Journal of the American Chemical Society*, **2016**, *138*, 10786-10789.



[a]Alcohol (1 mmol), *tert*-butyl acetate (4 mmol), *t*-BuOK (1.5 mmol), toluene (1 mL), **1d** (5 mol %), 4 h at 80 °C (oil bath). Yields are of isolated products. [b]*t*-BuONa was used as a base.

M-Co-11 – Synthesis of Alkylated Alcohols

F. Freitag, T. Irrgang and R. Kempe, *Chemistry – A European Journal*, DOI: 10.1002/chem.201701211.

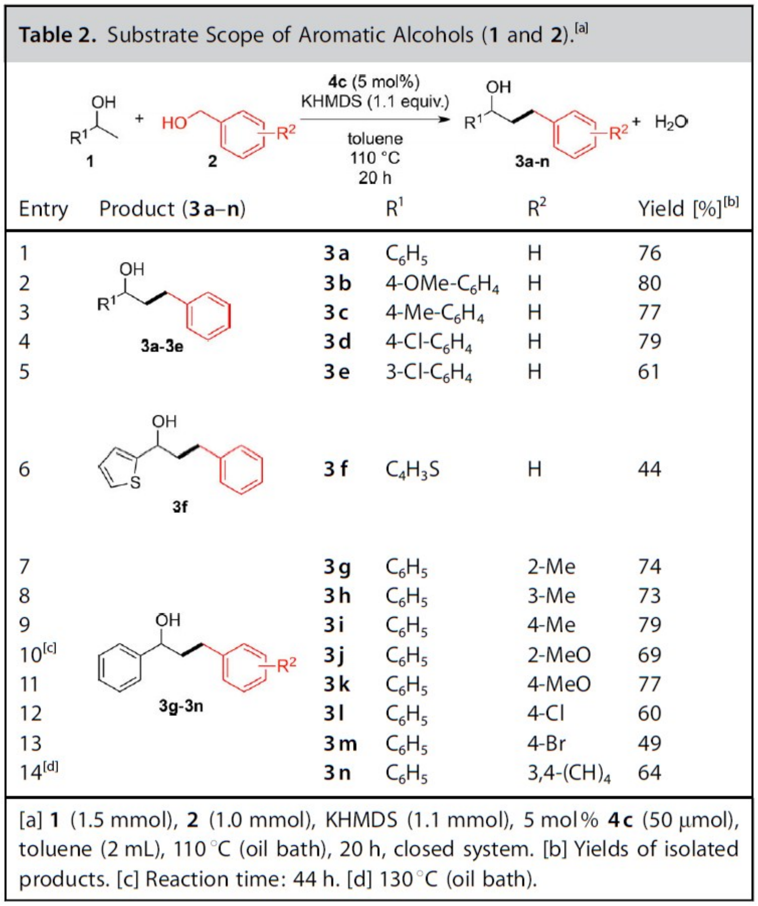


Table 2. Substrate Scope of Aromatic Alcohols (**1** and **2**).[a]

Entry	Product (**3a–n**)		R^1	R^2	Yield [%][b]
1	3a-3e	**3a**	C_6H_5	H	76
2		**3b**	4-OMe-C_6H_4	H	80
3		**3c**	4-Me-C_6H_4	H	77
4		**3d**	4-Cl-C_6H_4	H	79
5		**3e**	3-Cl-C_6H_4	H	61
6	3f	**3f**	C_4H_3S	H	44
7	3g-3n	**3g**	C_6H_5	2-Me	74
8		**3h**	C_6H_5	3-Me	73
9		**3i**	C_6H_5	4-Me	79
10[c]		**3j**	C_6H_5	2-MeO	69
11		**3k**	C_6H_5	4-MeO	77
12		**3l**	C_6H_5	4-Cl	60
13		**3m**	C_6H_5	4-Br	49
14[d]		**3n**	C_6H_5	3,4-$(CH)_4$	64

[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4c** (50 µmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products. [c] Reaction time: 44 h. [d] 130 °C (oil bath).

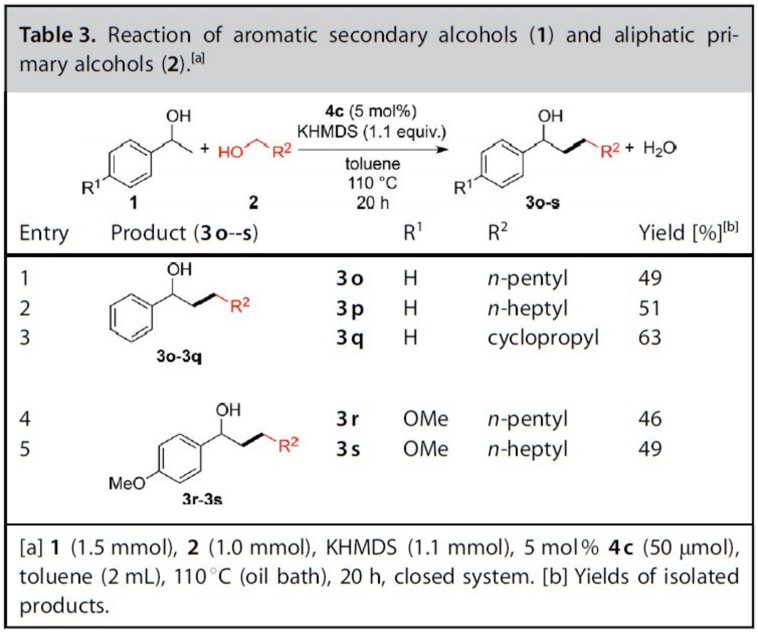
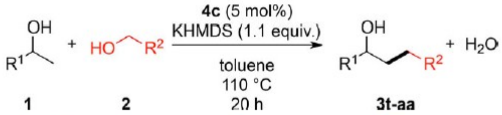


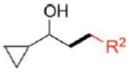
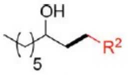
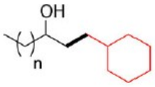
Table 3. Reaction of aromatic secondary alcohols (**1**) and aliphatic primary alcohols (**2**).[a]

Entry	Product (**3o--s**)		R^1	R^2	Yield [%][b]
1	3o-3q	**3o**	H	*n*-pentyl	49
2		**3p**	H	*n*-heptyl	51
3		**3q**	H	cyclopropyl	63
4	3r-3s	**3r**	OMe	*n*-pentyl	46
5		**3s**	OMe	*n*-heptyl	49

[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4c** (50 µmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products.

Table 4. Coupling of aliphatic secondary alcohols (**1**) with primary alcohols (**2**).[a]



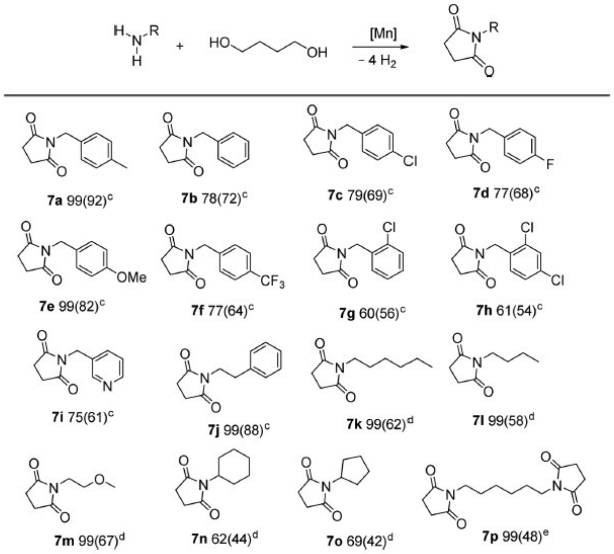
Entry	Product (**3 t**–**aa**)		R1	R2	Yield [%][b]
1	 **3t-3v**	**3 t**	cyclopropyl	C_6H_5	72
2		**3 u**	cyclopropyl	*n*-heptyl	62
3		**3 v**	cyclopropyl	cyclohexyl	54
4	 **3w-3x**	**3 w**	*n*-hexyl	$(CH_2)_3C_6H_5$	40
5		**3 x**	*n*-hexyl	*n*-heptyl	50
6	 **3y**, **3z**, **3aa**	**3 y**	*n*-hexyl (n = 5)	cyclohexyl	70
7		**3 z**	*n*-butyl (n = 3)	cyclohexyl	66
8		**3 aa**	*n*-propyl (n = 2)	cyclohexyl	59

[a] **1** (1.5 mmol), **2** (1.0 mmol), KHMDS (1.1 mmol), 5 mol% **4 c** (50 μmol), toluene (2 mL), 110 °C (oil bath), 20 h, closed system. [b] Yields of isolated products.

3.4.3. – Coupling and Dehydrogenation Reactions – Manganese Catalysts

A-Mn-2 – Synthesis of Cyclic Imides

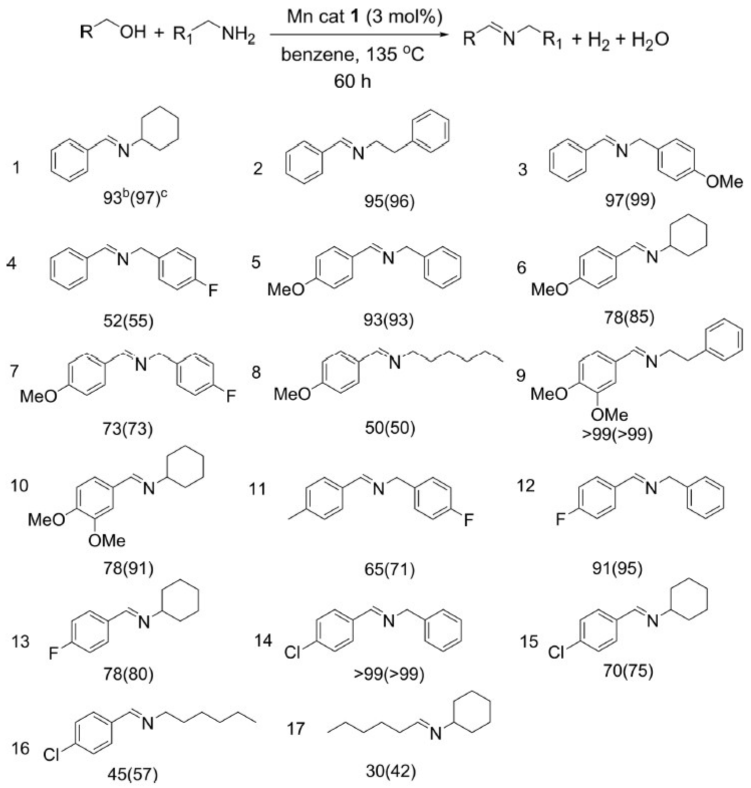
N. A. Espinosa-Jalapa, A. Kumar, G. Leitus, Y. Diskin-Posner and D. Milstein, *Journal of the American Chemical Society*, **2017**, *139*, 11722-11725.



[a]Conversions based on consumption of the amine, determined by ^1H NMR and GC−MS with mesitylene as internal standard. All reactions were performed in open Schlenk tube under argon [b]Yields of isolated product in brackets. [c]Reaction conditions: [Mn] = 1 (5 mol %), KH (10 mol %), toluene (2 mL), 1,4-butanediol (1.0 mmol), amine (1.0 mmol), internal standard (mesitylene, 1 mmol), reflux, 40 h. [d]1,4-Butanediol (0.5 mmol), amine (0.5 mmol), internal standard (mesitylene, 0.5 mmol). [e]1,4-Butanediol (0.5 mmol), amine (0.25 mmol), and internal standard (mesitylene, 0.5 mmol).

A-Mn-3 – Synthesis of Aldimines

A. Mukherjee, A. Nerush, G. Leitus, L. J. W. Shimon, Y. Ben David, N. A. Espinosa Jalapa and D. Milstein, *Journal of the American Chemical Society*, **2016**, *138*, 4298-4301.



[a] Reaction conditions: alcohol (0.5 mmol), amine (0.5 mmol), Mn cat (3 mol %), and benzene (2 mL) at 135 °C (bath temperature) for 60 h in a closed system under N_2 atmosphere. [b] Yields were determined by ^{1}H NMR with respect to toluene or dioxane as an internal standard or by GC analysis. [c] Based on the consumption of alcohol.

B-Mn-1 – Synthesis of Aldimines

M. Mastalir, M. Glatz, N. Gorgas, B. Stöger, E. Pittenauer, G. Allmaier, L. F. Veiros and K. Kirchner, *Chemistry – A European Journal*, **2016**, *22*, 12316-12320.

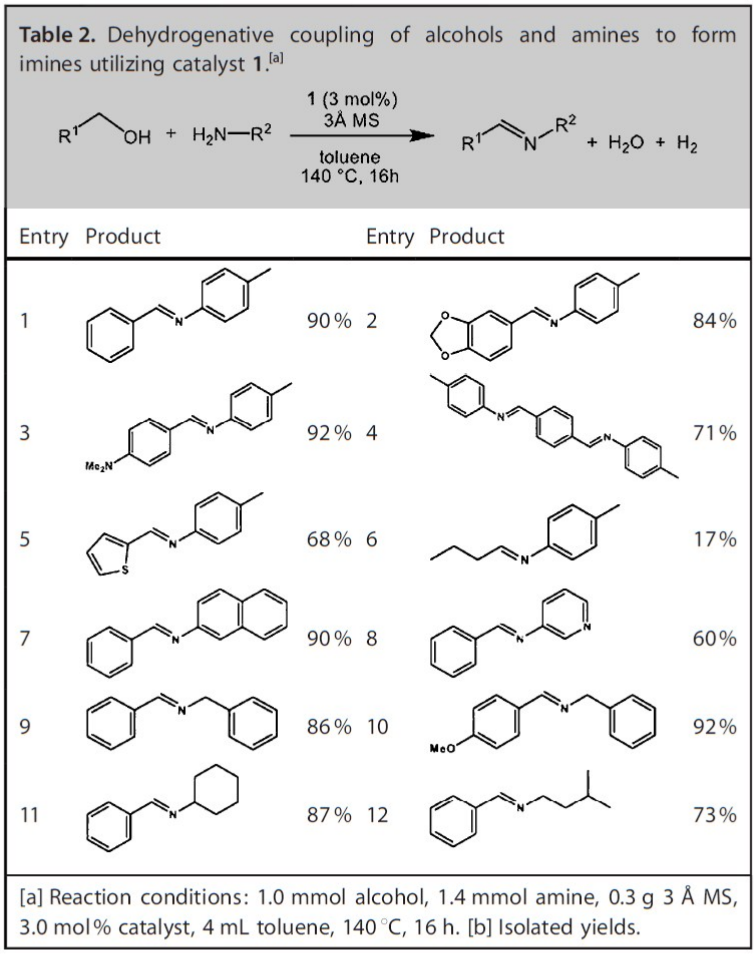


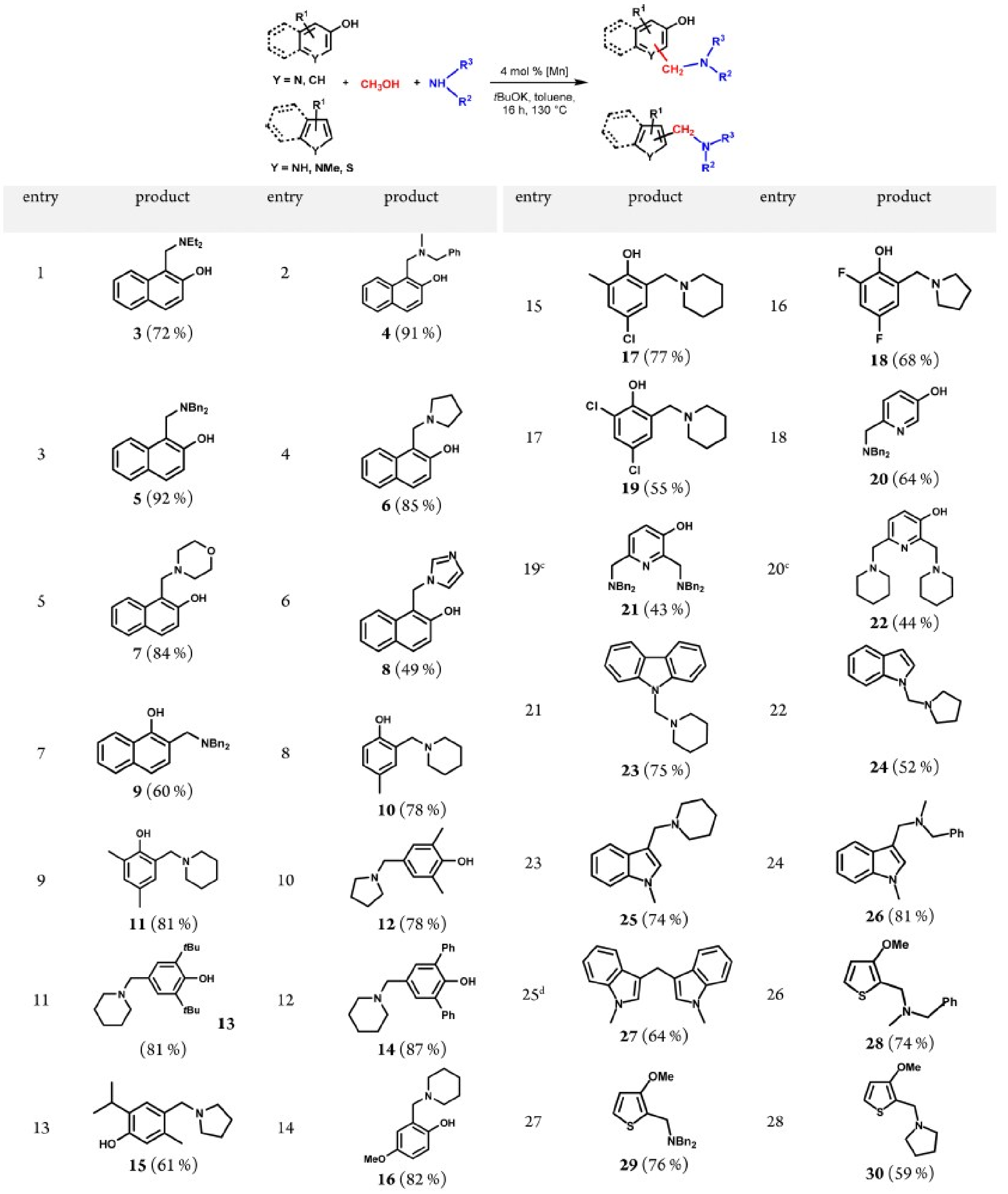
Table 2. Dehydrogenative coupling of alcohols and amines to form imines utilizing catalyst **1**.[a]

Entry	Product		Entry	Product	
1		90%	2		84%
3		92%	4		71%
5		68%	6		17%
7		90%	8		60%
9		86%	10		92%
11		87%	12		73%

[a] Reaction conditions: 1.0 mmol alcohol, 1.4 mmol amine, 0.3 g 3 Å MS, 3.0 mol% catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields.

B-Mn-1 – Synthesis of Aminomethylated Aromatics

M. Mastalir, E. Pittenauer, G. Allmaier and K. Kirchner, *Journal of the American Chemical Society*, **2017**, *139*, 8812-8815.



entry	product	entry	product	entry	product	entry	product
1	**3** (72 %)	2	**4** (91 %)	15	**17** (77 %)	16	**18** (68 %)
3	**5** (92 %)	4	**6** (85 %)	17	**19** (55 %)	18	**20** (64 %)
5	**7** (84 %)	6	**8** (49 %)	19[c]	**21** (43 %)	20[c]	**22** (44 %)
7	**9** (60 %)	8	**10** (78 %)	21	**23** (75 %)	22	**24** (52 %)
9	**11** (81 %)	10	**12** (78 %)	23	**25** (74 %)	24	**26** (81 %)
11	**13** (81 %)	12	**14** (87 %)	25[d]	**27** (64 %)	26	**28** (74 %)
13	**15** (61 %)	14	**16** (82 %)	27	**29** (76 %)	28	**30** (59 %)

[a] Reaction conditions: 1.3 mmol of MeOH, 1.0 mmol of substrate, 1.1 mmol of amine, 1.3 mmol of *t*BuOK, 4 mol % [Mn], 4 mL of toluene, 130 °C. [b] Isolated yields. [c] 2.2 mmol of MeOH, 1.0 mmol of substrate, 2.2 mmol of amine, 2.6 mmol of *t*BuOK, 7 mol % [Mn], 4 mL of toluene. [d] Imidazole as N-nucleophile.

C-Mn-1a/b, C-Mn-2 & TH-Mn-3a – Synthesis of Secondary Amines

S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nature Communications*, **2016**, *7*, 12641.

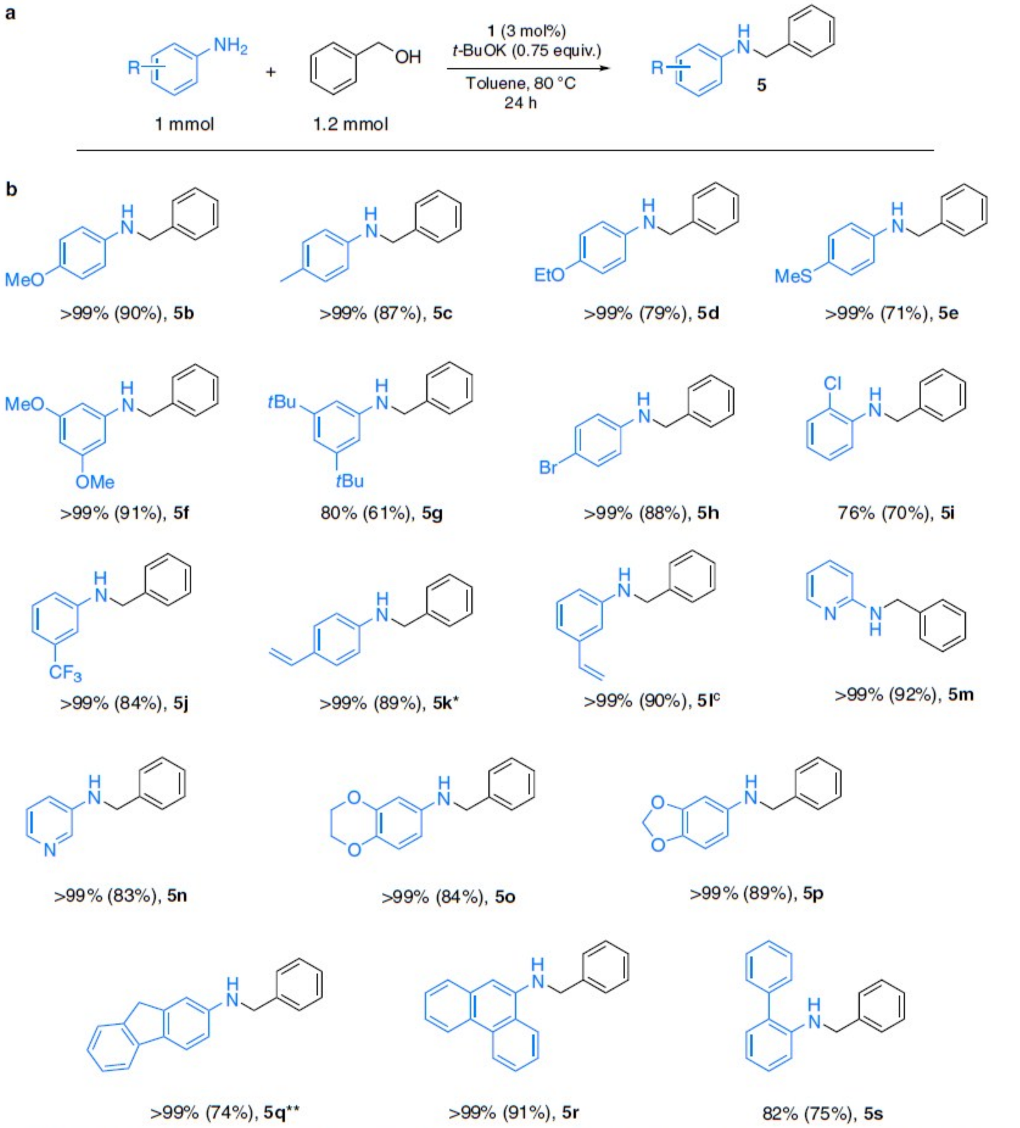


Figure 5 | Selective *N*-alkylation of various aromatic amines with benzyl alcohol. (**a**) General reaction conditions: aniline derivative (1 mmol), benzyl alcohol (1.2 mmol), **1** (3 mol%), *t*-BuOK (0.75 equiv.) and toluene (2 ml), 80 °C, 24 h. (**b**) Reaction of different aniline derivatives with alcohols. Conversion was determined by GC (isolated yield in parentheses). *Traces of reduction (<2%) of double bond were observed. **11% of *N*, 9-dibenzyl-9H-fluoren-2-amine was detected.

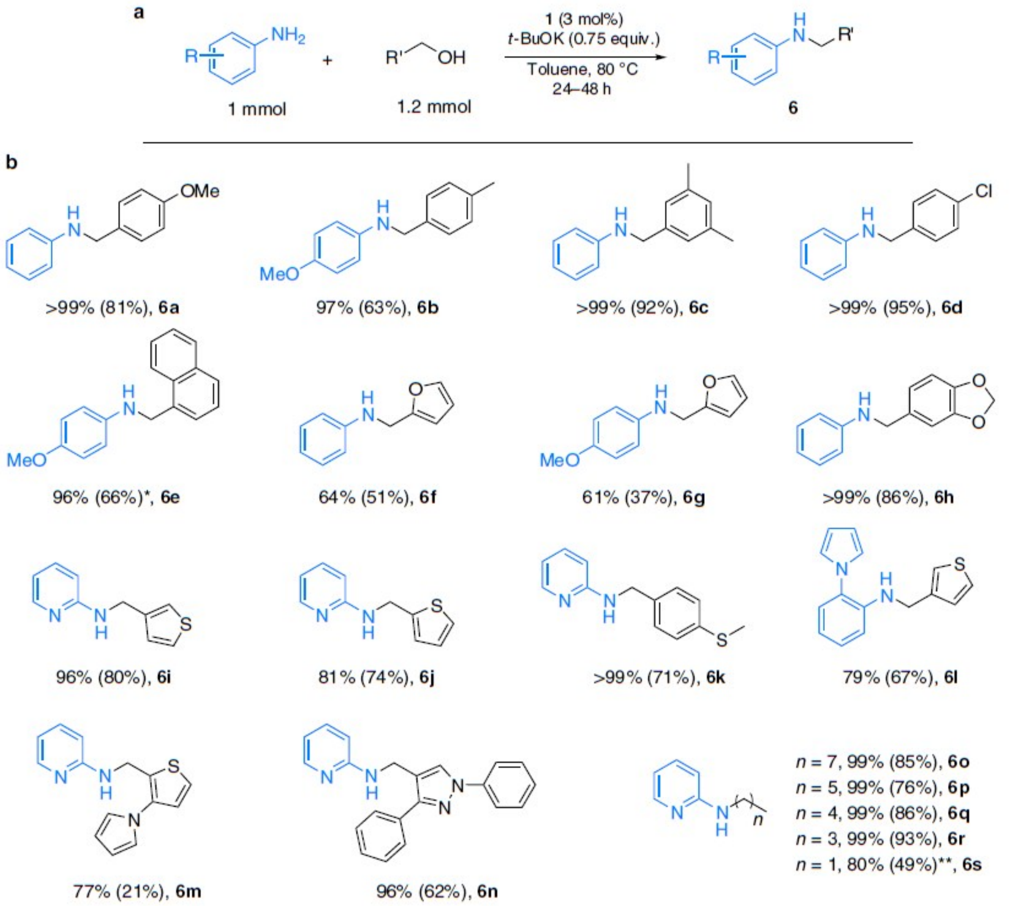
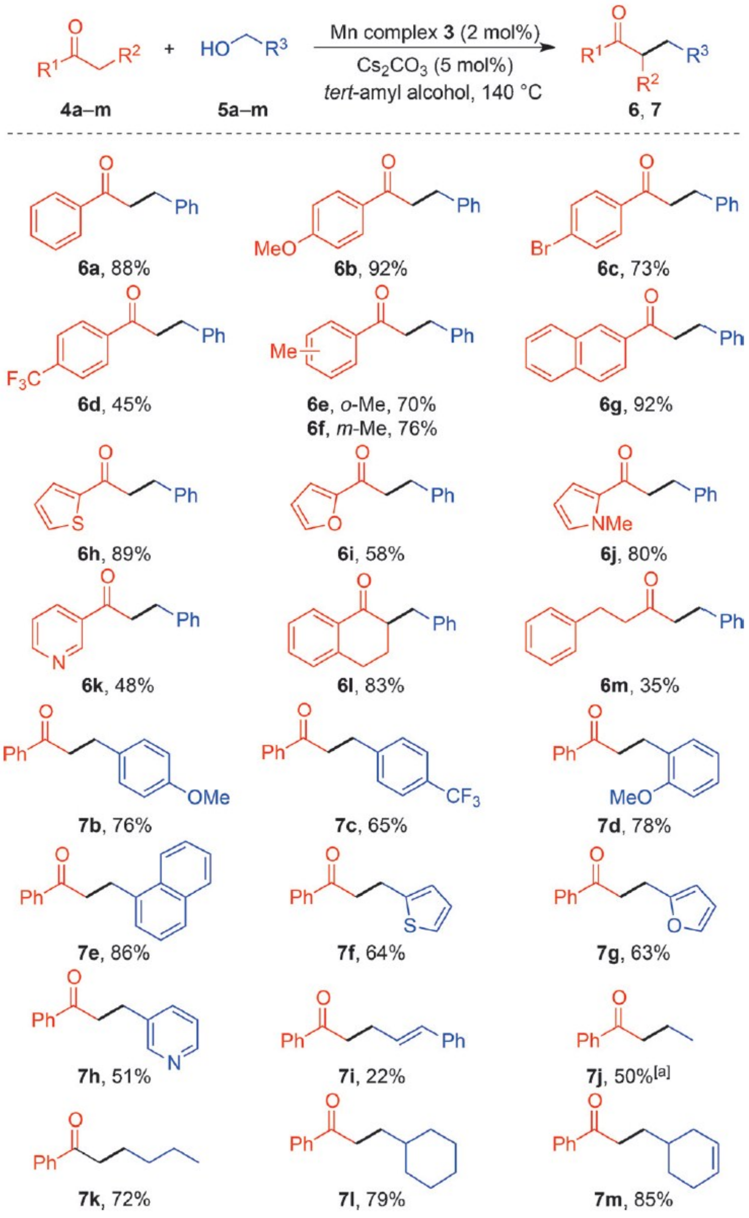


Figure 6 | *N*-alkylation of (hetero)aromatic amines using (hetero)aromatic and aliphatic alcohols. (**a**) General reaction conditions: aniline derivative (1 mmol), benzyl alcohol (1.2 mmol), **1** (3 mol%), *t*-BuOK (0.75 equiv.) and toluene (2 ml), 80 °C, 24 h. (**b**) Conversion was determined by GC (isolated yield in parentheses). **6o–6s** 48 h. *22% of the corresponding imine was observed. **2 equiv. of ethanol was used.

C-Mn-1a/b – Synthesis of α-Alkylated Ketones

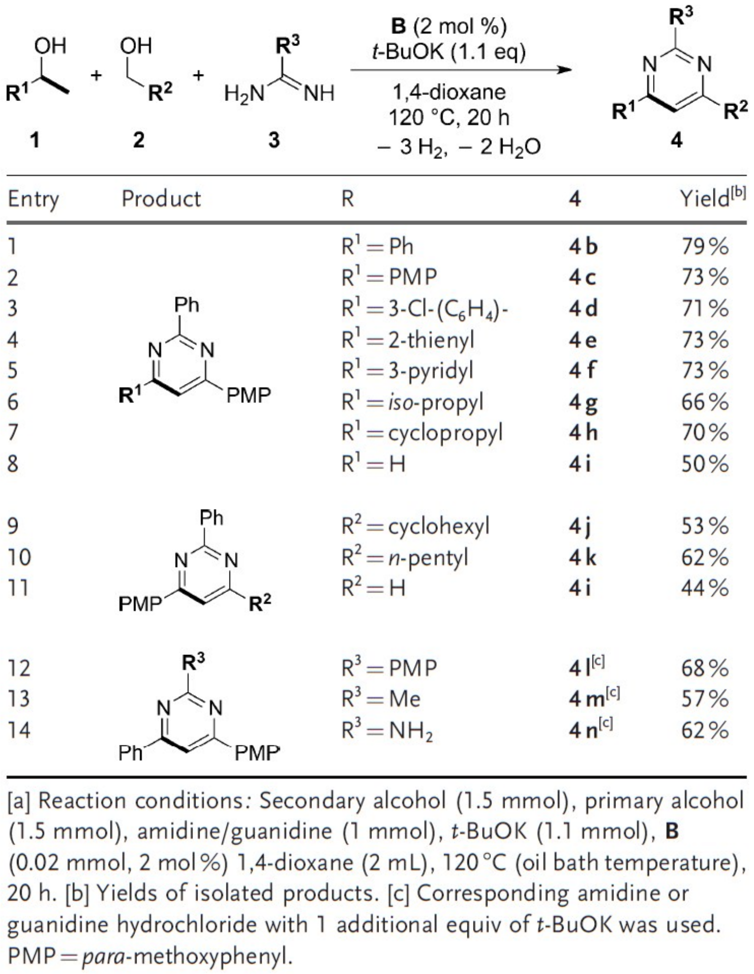
M. Peña-López, P. Piehl, S. Elangovan, H. Neumann and M. Beller, *Angewandte Chemie International Edition*, **2016**, *55*, 14967-14971.



Scheme 2. Manganese-catalyzed reaction of ketones **4** with primary alcohols **5**. Yields are for the isolated product. [a] EtOH (1 mL) was used as the solvent. The yield was determined by GC with hexadecane as an internal standard.

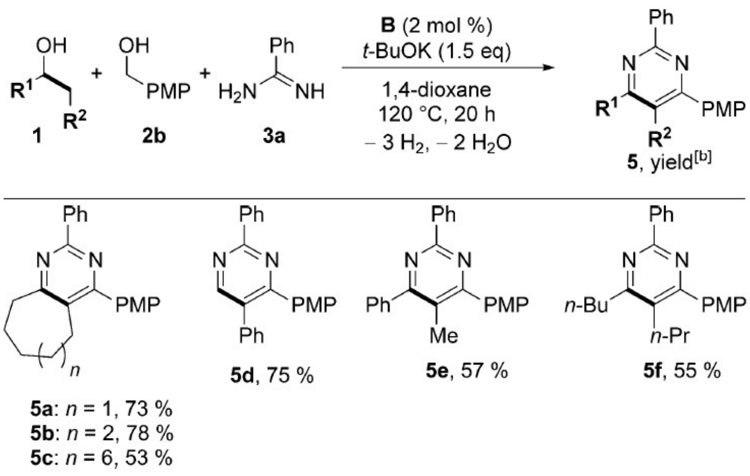
C-Mn-1a – Synthesis of Pyrimidines

N. Deibl and R. Kempe, *Angewandte Chemie International Edition*, **2017**, *56*, 1663-1666.

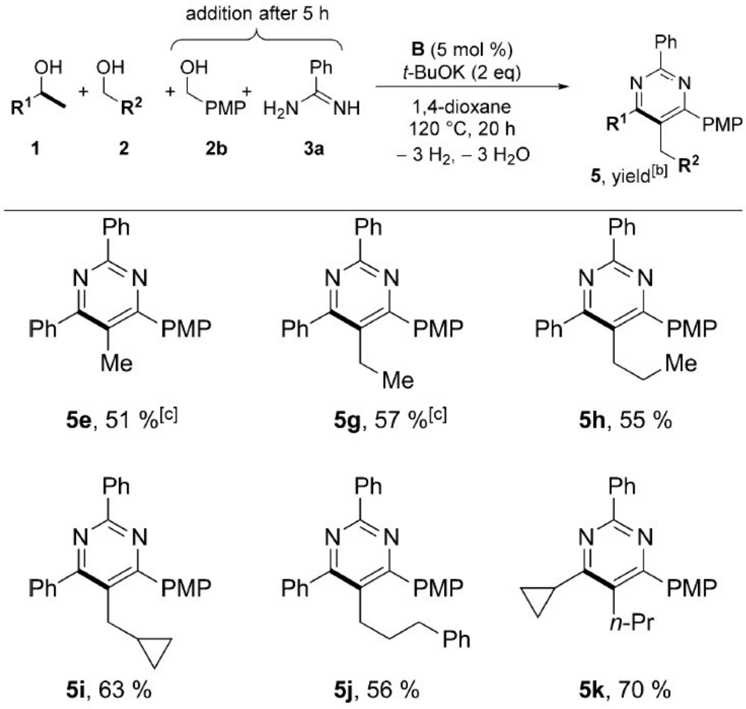


Entry	Product	R	4	Yield[b]
1		$R^1 = Ph$	**4b**	79%
2		$R^1 = PMP$	**4c**	73%
3		$R^1 = 3\text{-Cl-}(C_6H_4)\text{-}$	**4d**	71%
4		R^1 = 2-thienyl	**4e**	73%
5		R^1 = 3-pyridyl	**4f**	73%
6		R^1 = *iso*-propyl	**4g**	66%
7		R^1 = cyclopropyl	**4h**	70%
8		$R^1 = H$	**4i**	50%
9		R^2 = cyclohexyl	**4j**	53%
10		R^2 = *n*-pentyl	**4k**	62%
11		$R^2 = H$	**4i**	44%
12		$R^3 = PMP$	**4l**[c]	68%
13		$R^3 = Me$	**4m**[c]	57%
14		$R^3 = NH_2$	**4n**[c]	62%

[a] Reaction conditions: Secondary alcohol (1.5 mmol), primary alcohol (1.5 mmol), amidine/guanidine (1 mmol), *t*-BuOK (1.1 mmol), **B** (0.02 mmol, 2 mol%) 1,4-dioxane (2 mL), 120 °C (oil bath temperature), 20 h. [b] Yields of isolated products. [c] Corresponding amidine or guanidine hydrochloride with 1 additional equiv of *t*-BuOK was used. PMP = *para*-methoxyphenyl.



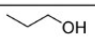
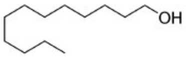
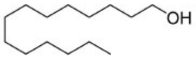
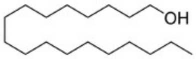
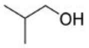
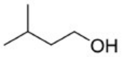
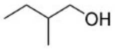
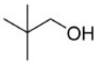
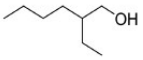
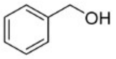
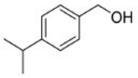
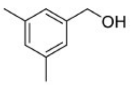
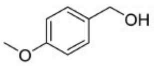
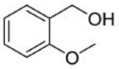
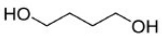
[a] Reaction conditions*:* Secondary alcohol (1.5 mmol), primary alcohol (1.1 mmol), amidine (1.0 mmol), *t*-BuOK (1.5 mmol), **B** (0.02 mmol, 2 mol%) 1,4-dioxane (2 mL), 120°C oil bath, 20 h. [b] Yields of isolated products. PMP=*para*-methoxyphenyl.



[a] Reaction conditions*:* Secondary alcohol (2.0 mmol), primary alcohol (2.2 mmol), *t*-BuOK (2.0 mmol), precatalyst **B** (0.05 mmol, 5 mol%) and 1,4-dioxane (1 mL) were heated for 5 h at 120°C (oil bath temp.). Afterwards, amidine (1.0 mmol) and primary alcohol (1.1 mmol) were added as a solution in 1,4-dioxane (2 mL) and the reaction was heated under reflux for 20 h. [b] Yields of isolated products. [c] The β-alkylation reaction was run in a closed system. PMP=*para*-methoxyphenyl.

C-Mn-5 – Synthesis of Esters

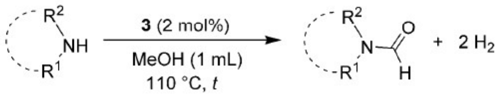
D. H. Nguyen, X. Trivelli, F. Capet, J.-F. Paul, F. Dumeignil and R. M. Gauvin, *ACS Catalysis*, **2017**, *7*, 2022-2032.

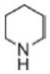
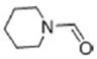
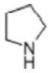
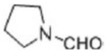
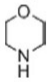
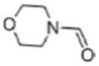
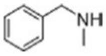
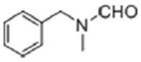
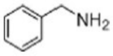
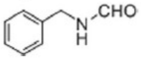
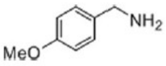
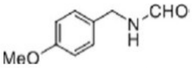
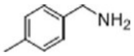
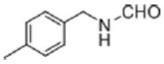
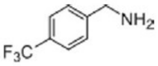
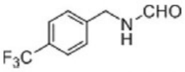
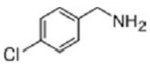
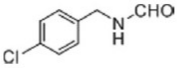
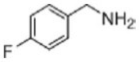
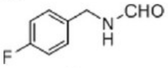
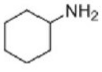
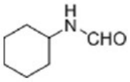
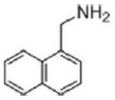
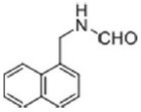
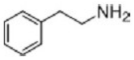
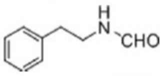
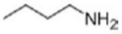
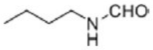
Entry	Substrate	T(°C)	t(h)	Yield (%)[a]	TON
1		110	72	74	123
2		130	72	89	148
3		150	24	84	140
4		150	24	83	138
5		150	24	76	127
6		150	24	82	137
7		150	24	80	133
8		120	72	70	117
9		150	24	74	123
10		150	24	67	112
11		120	72	0	0
12		150	24	37	62
13		150	24	95	158
14		150	24	88	147
15		150	24	82	137
16		150	24	66	110
17		150	24	12	20
18		150	24	95[b]	158

[§]Reaction conditions: Catalyst **1** (0.6 mol %), alcohol (12.04 mmol), argon stream. [a]Ester yield determined by ^{1}H NMR. [b]γ-butyrolactone was formed as the only product.

M-Mn-4 – Synthesis of N-Formylated Amines

S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitus, L. Avram and D. Milstein, *Angewandte Chemie International Edition*, **2017**, *56*, 4229-4233.

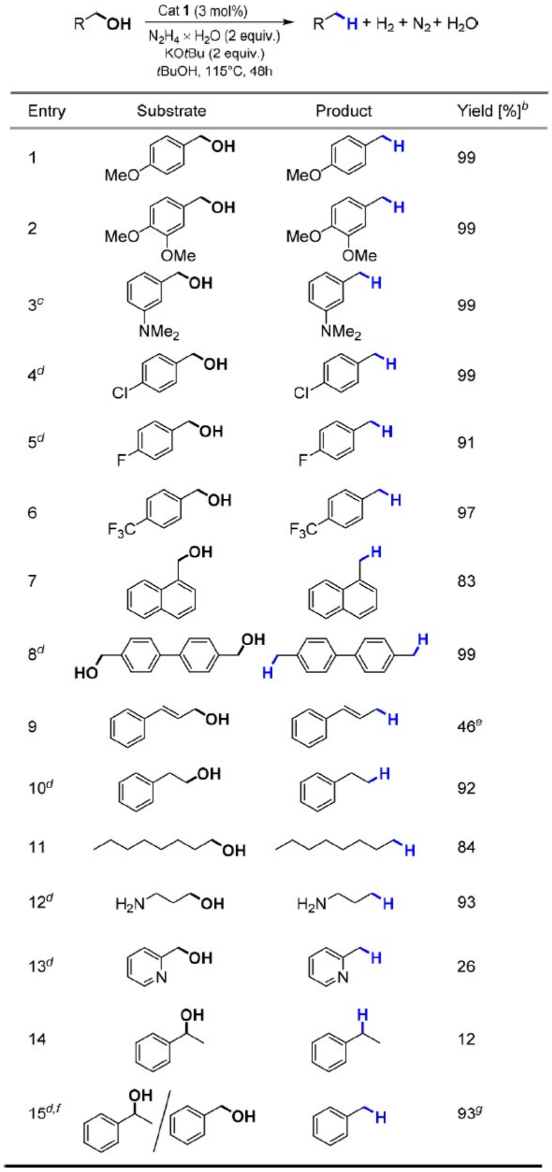


Entry[a]	Amine	Product	*t* [h]	Conv. [%][b]	Yield [%][b]
1			12	99	86
			12	99	72[c]
			12	99	78[d]
2			14	97	61
3			24	99	50
4			15	99	78
5			14	99	70
6			12	99	67
7			18	99	74
8			12	83	71
9			12	99	56
10			14	99	57
11			12	93	66
12			15	99	62
13			24	99	53
14			15	97	64

[a] Reaction conditions: Amine (0.5 mmol), MeOH (1 mL), **3** (0.01 mmol), heated in a 100 mL closed Fischer–Porter tube at 110 °C. [b] Yields and conversions determined by GC or NMR analysis using toluene or *meta*-xylene as the internal standard. The conversions are based on amine consumption. [c] Complex **4** as the catalyst. [d] Complex **5** as the catalyst. Differences in yield and conversion indicate the formation of the N-methylated amine and also an unidentified side product.

M-Mn-4 – Synthesis of Deoxygenated Products from Alcohols

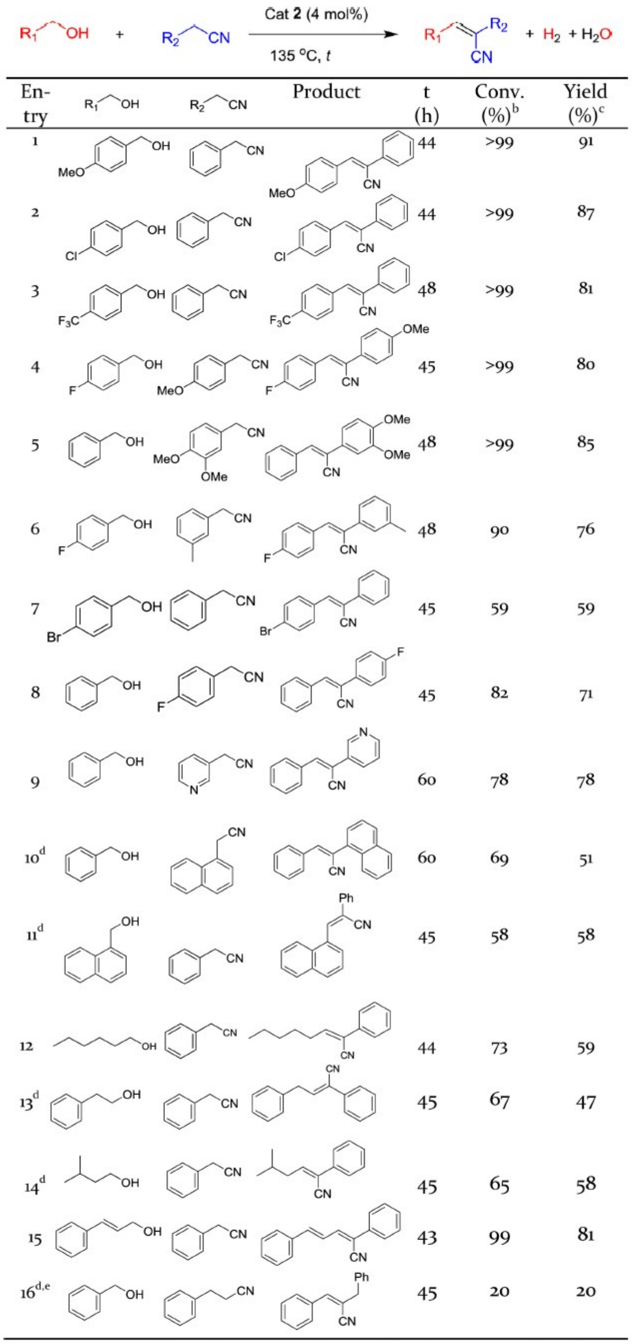
J. O. Bauer, S. Chakraborty and D. Milstein, *ACS Catalysis*, **2017**, *7*, 4462-4466.



[a]Reaction conditions: Mn complex **1** (3 mol %), alcohol (0.5 mmol), hydrazine hydrate (2 equiv, 1.0 mmol), KO*t*Bu (2 equiv, 1.0 mmol), *N,N*-dimethylaniline (internal standard, 0.5 mmol), and *tert*-butanol (1.5 mL) were heated at reflux in a Schlenk flask (oil bath temperature: 115 °C) for 48 h. [b]Yields of products were determined by ^{1}H NMR spectroscopy, using *N,N*-dimethylaniline as an internal standard, supported by GC/MS analysis. [c]1,3,5-Trimethoxybenzene (0.5 mmol) was used as an internal standard. [d]The reaction was carried out in a closed 50 mL Teflon Schlenk tube. [e]Additional formation of 1-phenylpropane (53%) by partial hydrogenation of the C=C double bond. [f]The reaction was carried out using a mixture of benzyl alcohol (0.5 mmol) and 1-phenylethanol (0.5 mmol). [g]Formation of phenylethane (19%) determined by ^{1}H NMR spectroscopy.

M-Mn-4 – Synthesis of α-Olefinated Nitriles

S. Chakraborty, U. K. Das, Y. Ben-David and D. Milstein, *Journal of the American Chemical Society*, **2017**, *139*, 11710-11713.



Entry	R_1CH_2OH	R_2CH_2CN	Product	t (h)	Conv. (%)[b]	Yield (%)[c]
1				44	>99	91
2				44	>99	87
3				48	>99	81
4				45	>99	80
5				48	>99	85
6				48	90	76
7				45	59	59
8				45	82	71
9				60	78	78
10[d]				60	69	51
11[d]				45	58	58
12				44	73	59
13[d]				45	67	47
14[d]				45	65	58
15				43	99	81
16[d,e]				45	20	20

[a] Conditions: alcohol (0.25 mmol), nitrile (0.25 mmol), **2** (0.01 mmol), toluene (1 mL) heated in a 50 mL closed Young Schlenk tube at 135 °C bath temperature. [b] Conversion determined by GC or NMR analysis using *N,N*-dimethylaniline as internal standard. [c] Isolated yields. [d] Yield by GC or NMR analysis using *N,N*-dimethylaniline internal standard. [e] 8 mol % catalyst was used.