Electronic Supplementary Information

Thermoresponsive self-assembled cyclodextrin-end-decorated PNIPAM for aqueous catalysis

Jonathan Potier,[a] Stéphane Menuel,[a] Joël Lyskawa,[b] David Fournier,[b] François Stoffelbach,[c] Eric Monflier,[a] Patrice Woisel,[b] and Frédéric Hapiot*[a]*

a Université d'Artois, Unité de Catalyse et de Chimie du Solide (UCCS, UMR CNRS 8181), Faculté des Sciences Jean Perrin, rue Jean Souvraz, SP18, 62307 Lens Cedex, France

b Université de Lille, Unité des Matériaux Et Transformations (UMET, UMR CNRS 8207), Ingénierie des Systèmes Polymères (ISP) team, 59655 Villeneuve d'Ascq Cedex, France

c Sorbonne Université, UPMC Univ Paris 06, UMR 8232, IPCM, Chimie des Polymères,

F-75005 Paris, France

Materials and methods

All chemicals were purchased from Acros or Aldrich Chemicals in their highest purity. Deionized water was used in all experiments. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ^{1}H nuclei and 75 MHz for ^{13}C nuclei. $CDCl_3$ (99.50% isotopic purity), DMSO-d6 (99.80% isotopic purity), and D_2O (99.92% isotopic purity) were purchased from Eurisotop. Reaction products were analyzed by GC using a VARIAN® 3900 gas chromatograph equipped with a CP Sil 5CB column (15 m×0.25 mm ID, 0.25 µm phase film) and a flame ionization detector (GC:FID). The carrier gas was helium at pressure 0.6 bar and the temperature gradient was programmed from 80 °C (for 5 min) to 250 °C at 15 °C per minute. All hydroformylation experiments were carried out in laboratory reactors from Parr Instrument Company (USA). To prevent oxidation of the catalyst precursors, the reaction mixture was transferred into the reactor using the standard Schlenk technique. Randomly methylated β-CD-NH_2 (RAME-β-CD-NH_2) was obtained as described in the literature.[1]

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[1] J. Potier, S. Menuel, D. Fournier, S. Fourmentin, P. Woisel, F. Hapiot and E. Monflier, *ACS Catal.*, 2012, **2**, 1417.

Representative procedure for the synthesis of RAME-β-CD-Br initiator

RAME-β-CD-NH_2 (1.5 g, 1.2 mmol) was dried under vacuum for 3 h at 70 °C. Freshly distilled pyridine (20 mL) was added and the solution was degassed by three freeze-pump-thaw cycles. At room temperature, α-bromoisobutyryl bromide (309 mg, 1.4 mmol) was added very slowly and the mixture was stirred at 80 °C for 6 h. Pyridine was removed by rotatory evaporation. The solution was then poured into a separatory funnel, diluted with 30 mL $CHCl_3$ and washed with $NaHCO_3$ (aq). After evaporation of the organic solvent, the product was purified by silica gel chromatography using a CH_2Cl_2/MeOH mixture (99/1). The RAME-β-CD-Br initiator was obtained as a white powder in 34% yield (598 mg). Rf = 0.22 with CH_2Cl_2 as eluant). RMN ^1H (300 MHz, 21 °C, D_2O, δ ppm): 5.12 (s, 3.7H) ; 4.92 (s, 3.3H) ; 3.77–3.60 (m, 12.2H) ; 3.59–3.52 (m, 36.6H) ; 3,44 (s, 15.4H) ; 3.42–3.26 (m, 22.1H). MALDI-TOF *m*/*z* (%) = 1431.18 (1.4) (calc. 1442.09 for $[C_{55}H_{94}O_{35}NBr + Na]^+$), 1474.38 (7.2) (calc. 1474.12 for $[C_{58}H_{100}O_{35}NBr + Na]^+$), 1488.41 (63.7) (calc. 1488.13 for $[C_{59}H_{102}O_{35}NBr + Na]^+$), 1502.40 (25.5) (calc. 1502.14 for $[C_{60}H_{104}O_{35}NBr + Na]^+$), 1517.40 (2.2) (calc. 1516.15 for $[C_{61}H_{106}O_{35}NBr + Na]^+$): Molecular weight: 1468 g/mol (Substitution degree: 1.9).

Representative procedure for the polymerization of NIPAM

In a Schlenk tube, CuBr (25 mg, 0.18 mmol) was dried under vacuum and dissolved in degassed Me_6Tren ligand (81 mg, 0.36 mmol). The mixture was vigourously stirred for 5 min. Degassed *t*-BuOH (1.5 mL) was then added and the solution was vigourously stirred for an additional 5 min. Freshly recrystallised NIPAM (2.0 g, 17.7 mmol) was introduced under nitrogen and the mixture was stirred for 10 min. Degassed water (4 mL) was then added and the solution was vigourously stirred for an additional 5 min. A degassed solution of RAME-β-CD-Br initiator (259 mg, 0.18 mmol) in water (1 mL) was introduced and the solution was stirred for 20 min. at room temperature. The solution was dissolved in acetone (15 mL) and the polymer was precipitated upon addition of Et_2O (200 mL). After filtration, the polymer was solubilized in a mixture of water (200 mL) and NH_3 (5 mL) and residual CuBr was removed by silica gel chromatography. The resulting solution was lyophilized to give polymer **1** in 64% yield as a white powder.

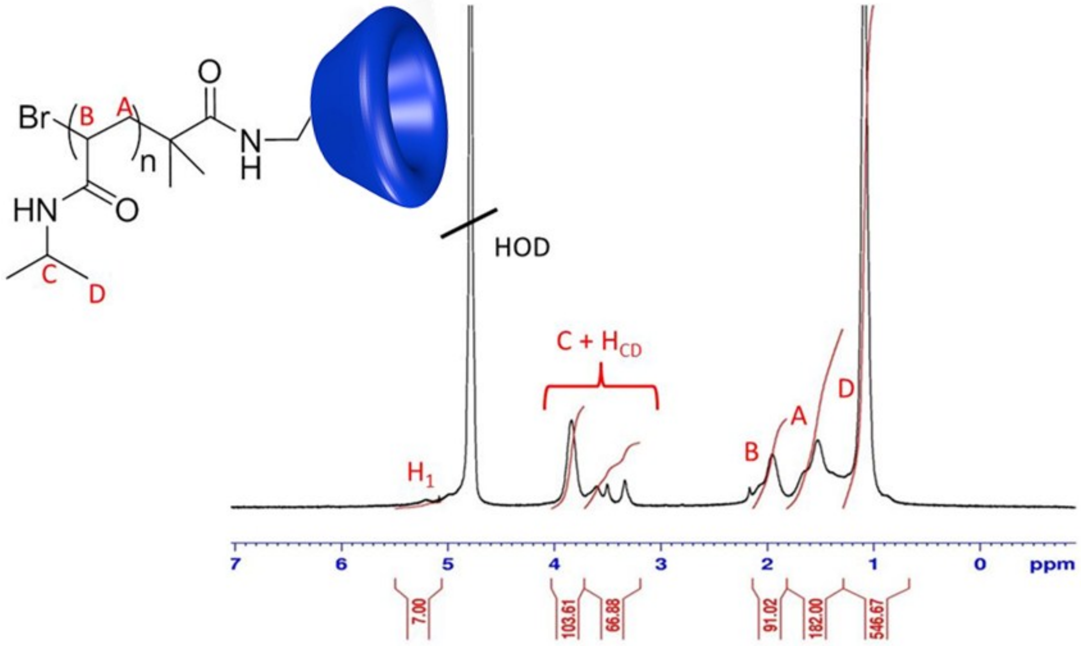


Fig. S1 ^{1}H NMR spectrum of **1** in D_2O at 25 °C.

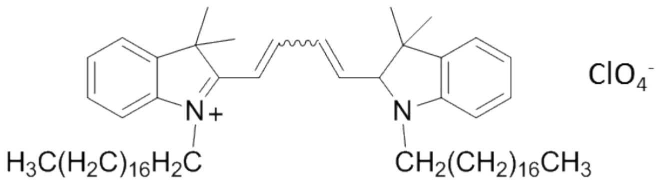
Optical microscopy

The optical microscopy was realized using a Microscope Olympus BH-2 in transmission mode, with the following objectives : x10(MDPlan), X50 (ULWD MSplan), x100 (ULWD MSPlan).The heating of the samples was performed using a furnace Mettler FP90.

Optical fluorescence microscopy

The optical fluorescence microscopy was realized using a Leica DMRD with a photometrics camera CoolSnap and a phase contrast immersion objective (x40). Filters used are N2.1 (exciting zone: 515-560 nm) and I3 (exciting zone: 450-490 nm). The sample heating was performed using a Mettler FP90 furnace.

DiI was used as fluorescent label.



DiI

((2Z)-2-[(E)-3-(3,3-dimethyl-1-octadecylindol-1-ium-2-yl)prop-2-enylidene]-3,3-dimethyl-1-octadecylindole; perchlorate (DiI)

Size-exclusion chromatography (SEC)

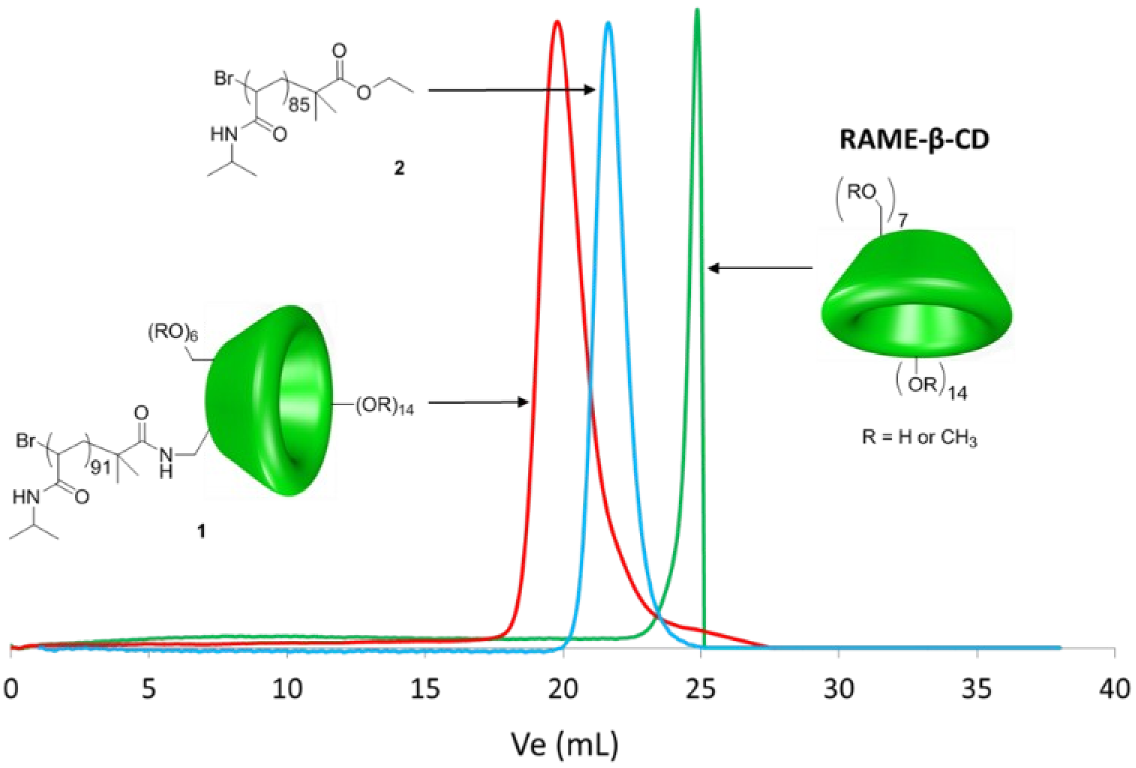


Fig. S2 SEC traces of RAME-β-CD, polymer **1** and polymer **2**.

The polydispersities were determined from SEC. The higher polydispersity measured for **1** (*Đ* = 1.38 vs 1.18 for **2**) might result from a slower rate of bromide transfer between the copper catalyst and the propagating species when RAME-β-CD-Br is used as ATRP initiator compared to ethyl 2-bromoisobutyrate initiator.[2,3,4] As already reported in several studies, the slower rate of ATRP may be due to the coordination between the amide group (of RAME-β-CD-Br initiator) with CuBr. This might lead to a less controlled (but still correct) polymerization and then a higher polydispersity index.

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[2] D. J. Adams and I. Young, *J. Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 6082.

[3] Y. Li, Y. Tang, R. Narain, A. L. Lewis and S. P. Armes, *Langmuir*, 2005, **21**, 9946.

[4] M. Senoo, Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules*, 1999, **32**, 8005.

Dynamic light scattering (DLS)

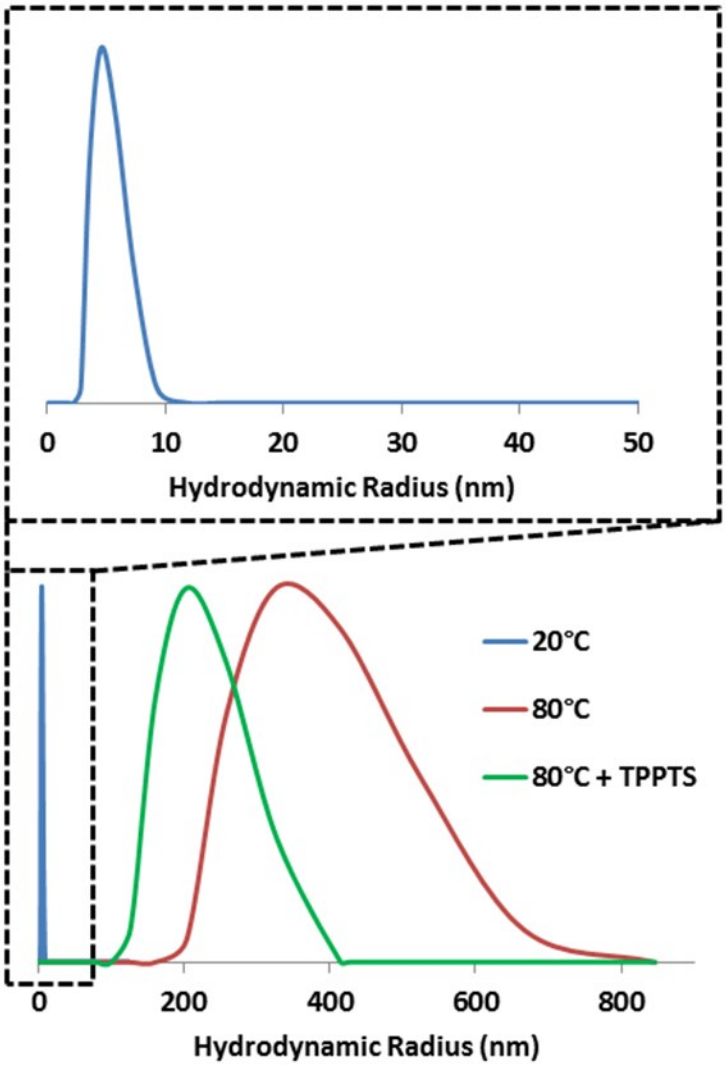

Fig. S3 Size distribution of the average hydrodynamic radius of **1** (3 mg.mL^{-1}) measured by Dynamic Light Scattering (DLS) at 20 °C (blue), 80 °C (red) and 80°C in the presence of TPPTS (0.99 mg.mL^{-1}).

Catalytic experiments

The relative proportions of all the compounds involved in the catalytic process have been chosen according to optimized results stemmed from previous works in the field.[5]

In a Schlenk tube were added $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol, 1 eq), TPPTS (33 mg, 0.058 mmol, 5 eq) and **1** (various amounts dissolved in 6 mL water). Degassed alkene (1.63 mmol, 140 eq) was then cannulated into the Schlenk tube and the resulting mixture was transferred into a N_2-purged autoclave. Once a temperature of 80 °C has been reached, the autoclave was pressurized under CO/H_2 pressure (50 bar) and the solution was vigorously stirred (1500 rpm). When the reaction was over, the apparatus was allowed to cool to room temperature and depressurized. The organic phase was extracted using diethyl ether. After evaporation of diethyl ether under vacuum, the products were analysed by GC, ^1H and ^{13}C NMR experiments. All runs have been performed at least twice in order to ensure reproducibility. ICP-MS measurements realized on organic phases once the reactions were complete showed the Rh amount to be lower than 0.5 ppm. Additionally, no trace of TPPTS could be detected in the organic phase by ^1H and ^{31}P NMR measurements.

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[5] F. Hapiot, L. Leclercq, N. Azaroual, S. Fourmentin, S. Tilloy, E. Monflier, Curr. Org. Synth., 2008, **5**, 162.

Table S1: Effect of varied amount of **1** on the Rh-catalyzed hydroformylation of 1-decene and 1-hexadecene.[a]

Run	**Substrate**	**[1] / [Rh]**[b]	**Conv.** (%)[c]	**Sel.** (%)[c]	**l/b**[d]	**TON**[d]	**TOF** (h^{-1})[e]	**Yield** (%)[f]
1	1-decene	0.30	14	61	2.3	19	6.3	0.08
2	1-decene	0.37	33	66	2.5	45	15.0	0.22
3	1-decene	0.44	54	70	2.3	73	24.3	0.38
4	1-decene	0.55	85	75	2.4	115	38.3	0.64
5	1-decene	0.75	85	84	2.1	115	38.3	0.71
6	1-decene	1.50	85	86	2.4	115	38.3	0.73
7	1-hexadecene	0.30	8	36	3.1	11	3.7	0.03
8	1-hexadecene	0.37	16	41	2.9	22	7.3	0.07
9	1-hexadecene	0.44	27	48	3.0	37	12.7	0.13
10	1-hexadecene	0.55	43	52	2.6	58	19.3	0.22
11	1-hexadecene	0.75	43	59	2.7	58	19.3	0.25
12	1-hexadecene	1.50	43	59	2.9	58	19.3	0.25

[a]Catalytic conditions: substrate (1.63 mmol), $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol), TPPTS (33 mg, 0.058 mmol), 6 mL of H_2O, 80 °C, 3 h, 50 bar CO/H_2. [b]Molar concentrations. [c]Conversion and selectivity were both determined by GC, ^1H and ^{13}C NMR measurements. [d]linear to branched aldehyde ratio. [d]TON = turnover number (number of molecules of substrate converted per catalytic site). [e]TOF = turnover frequency (number of molecules of substrate converted per catalytic site and per hour). [f]Yield = conversion × selectivity.

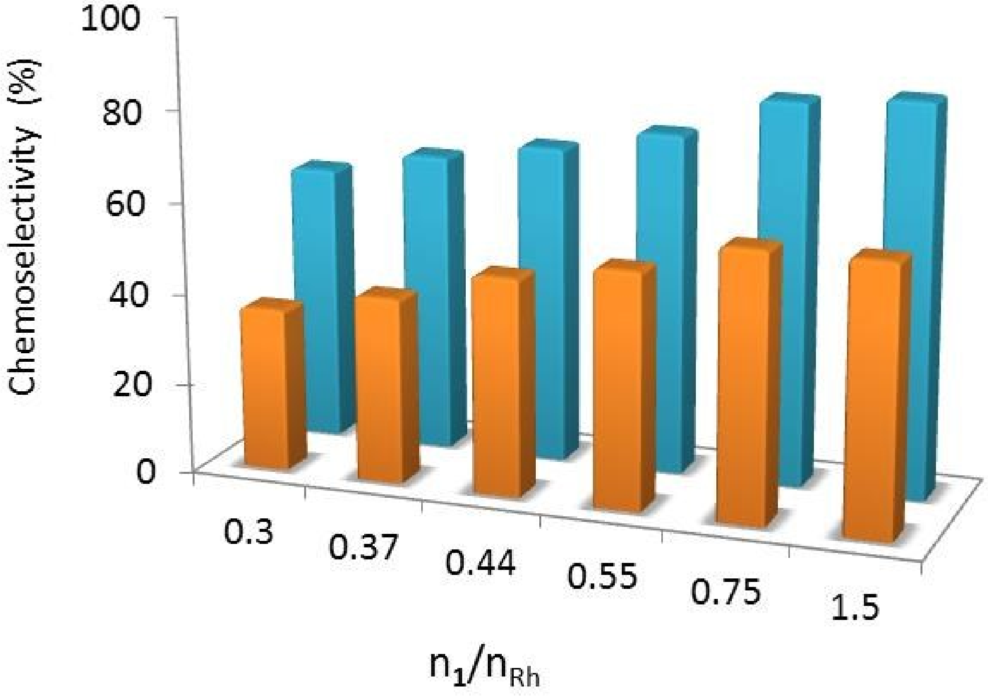

Figure S4. Effect of various amounts of PNIPAM-RAME-β-CD (**1**) on the chemoselectivity of the Rh-catalyzed hydroformylation of 1-decene (blue) and 1-hexadecene (orange). $n_{\mathbf{1}}/n_{Rh}$ = molar ratio of polymer **1** and Rh-catalyst. Conditions: Rh/TPPTS/substrate (1:5:140), 80 °C, 50 bar CO/H_2.

Table S2: Catalytic performance of **1** in the Rh-catalyzed hydroformylation of 1-decene and 1-hexadecene.[a]

Run	**Substrate**	**Time**	**Conv.** (%)[b]	**Sel.** (%)[b]	**l/b**[c]	**TON**[d]	**TOF** (h^{-1})[e]	**Yield** (%)[f]
13	1-decene	1	31	86	2.2	42	42.0	0.27
14	1-decene	2	59	82	2.4	80	40.0	0.48
15	1-decene	4	85	85	2.3	115	28.7	0.72
16	1-decene	5	84	87	2.1	114	38.0	0.73
17	1-hexadecene	1	13	63	2.5	18	18.0	0.08
18	1-hexadecene	2	31	59	2.4	42	21.0	0.18
20	1-hexadecene	4	43	60	2.7	58	14.6	0.26
21	1-hexadecene	5	43	58	2.6	58	11.6	0.25
22[g]	1-hexadecene	5	41	60	2.7	56	11.2	0.25
23[h]	1-hexadecene	5	42	59	2.7	57	11.4	0.25

[a]Catalytic conditions: substrate (1.63 mmol), $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol), TPPTS (33 mg, 0.058 mmol), **1** (100 mg, 0.009 mmol), 6 mL of H_2O, 80 °C, 50 bar CO/H_2. [b]Conversion and selectivity were both determined by GC, ^{1}H and ^{13}C NMR measurements. [c]linear to branched aldehyde ratio. [d]TON = turnover number (number of molecules of substrate converted per catalytic site). [e]TOF = turnover frequency (number of molecules of substrate converted per catalytic site and per hour). [f]Yield = conversion × selectivity. [g]Performed using the aqueous catalytic phase recovered from run 21. [h]Performed using the aqueous catalytic phase recovered from run 22.

Table S3: Catalytic performance of **1**, **2**, RAME-β-CD and the 1:1 physical mixture of **2** and RAME-β-CD in the Rh-catalyzed hydroformylation of 1-decene and 1-hexadecene.[a]

Run	**Substrate**	**Additive**	**Conv. (%)**[b]	**Sel.(%)**[b]	**l/b**[c]	**TON**[d]	**TOF** (h^{-1})[e]	**Yield** (%)[e]
24	1-decene	**1**	85	84	2.1	115	38.3	0.71
25	1-decene	**2**	32	68	2.7	43	14.3	0.22
26	1-decene	RAME-β-CD	43	91	2.1	58	19.3	0.39
27	1-decene	Physical mixture	46	67	2.1	62	20.6	0.31
28	1-hexadecene	**1**	43	59	2.9	58	19.0	0.25
29	1-hexadecene	**2**	6	52	2.7	8	2.7	0.03
30	1-hexadecene	RAME-β-CD	11	56	2.4	15	5.0	0.06
31	1-hexadecene	Physical mixture	9	54	2.9	73	24.4	0.05

[a] Catalytic conditions: substrate (1.63 mmol), $Rh(CO)_2(acac)$ (3 mg, 0.012 mmol), TPPTS (33 mg, 0.058 mmol), Additive (0.009 mmol), 6 mL of H_2O, 80 °C, 50 bar CO/H_2, 3 h. [b] Conversion and selectivity were both determined by GC, ^1H and ^{13}C NMR measurements. [c] Linear to branched aldehyde ratio. [d] TON = turnover number (number of molecules of substrate converted per catalytic site). [e] TOF = turnover frequency (number of molecules of substrate converted per catalytic site and per hour). [f] Yield = conversion × selectivity.