Bio-Related Polymers

Poly(vinyl alcohol)-*Graft*-Poly(ethylene glycol)-Supported Hydroxyproline Catalysis of Stereoselective Aldol Reactions

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Summary: The good swelling and high loading of poly(vinyl alcohol)-*graft*-poly-(ethylene glycol) (PVA-*g*-PEG) resins proved to be effective for performing supported proline-catalyzed aldol reactions stereoselectively in a wide range of polar non-protic, protic and non-polar solvents as well as in neat substrate. The catalysts could be recovered by filtration and recycled, without significant loss of activity. The use of poly(vinyl alcohol)-*graft*-poly(ethylene glycol) matrix improved the solubility of the proline-derived catalysts and expanded the scope of permissible solvents for performing selective aldol chemistry.

Keywords: catalysis; enantioselective synthesis; green chemistry; poly(vinyl alcohol)-*graft*-poly(ethylene glycol); polymer supports

Introduction

The proline–catalyzed aldol reaction has been examined for enantioselective carbon-carbon bond formation on a wide range of substrates.[1–2] Enantioselectivity has been contingent on solvent and restricted due to the preferred solubility of proline in polar solvents, such as DMSO or DMF. For example, the proline-catalyzed aldol reaction of cyclohexanone with *p*-nitrobenzaldehyde proceeded smoothly in DMSO with high diastereo- and enantio-selectivity, yet failed in water.[3] Although proline analogs with hydrophobic groups have been used to form emulsions that may favor aldol condensation,[4] immobilization of proline on solid support may be the most effective method for surmounting issues of catalyst solubility, product separation and catalyst recovery for recycle and reuse.[5] For example, hydroxyproline immobilized on a variety of supports, including silica gel, mesoporous siliceous materials, soluble poly(ethylene glycol) and polystyrene-based resins, has been used for enantioselective aldol condensations in modest to excellent selectivities (59-98% ee) contingent on support, substrate and solvent.[6] For example, polystyrene-supported proline catalyzed aldol condensations with high stereoselectivity in water, yet less effectively in pure DMF or DMSO and in the absence of a solvent.[7]

Poly(vinyl alcohol)-*graft*-poly(ethylene glycol) (PVA-*g*-PEG) resins have been shown to be effective for solid-phase synthesis, supported TEMPO catalysis and on-bead HR-MAS ^{1}H NMR spectral analysis.[8–10] In contrast to most resins, the PVA-*g*-PEG matrix has high loading, and high swelling in both organic and aqueous solvents. Considering that the solvent and conditions for enantioselective aldol chemistry are contingent on substrate, we have explored the attributes of the PVA-PEG resin in supported catalysis using hydroxyproline and its 1,1-diphenyl-leucinol amide. In the pursuit of green chemistry, it is also interesting to test the use of the catalysts in the absence of solvents.

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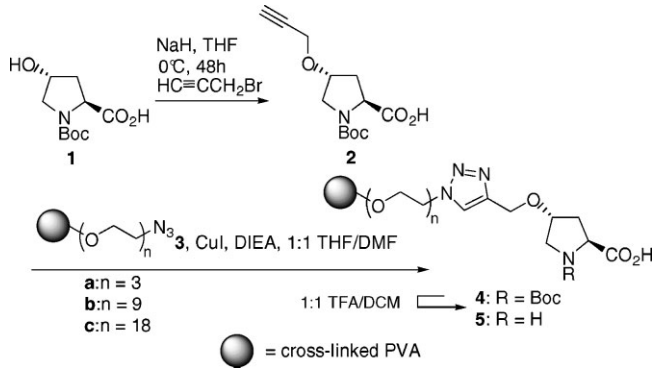
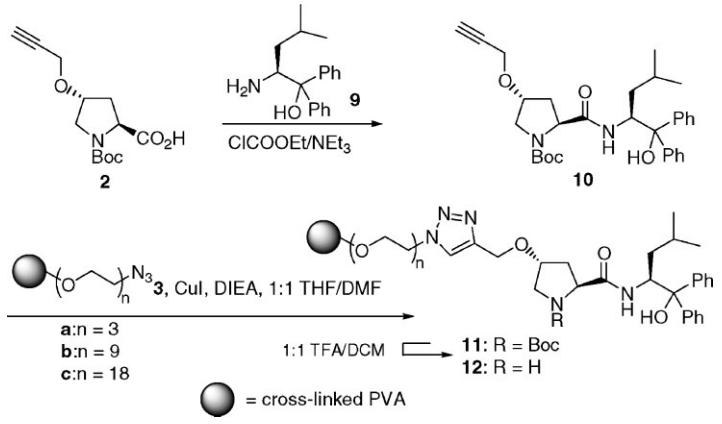
Results and Discussion

Supported hydroxyproline catalysts **5a-c** were prepared by the Cu(I)-catalyzed [2 + 3]-dipolar cycloaddition of *O*-propargyl-*N*-Boc-hydroxyproline **2** onto azide resins **3a-c** with 3-, 9- and 18-unit PEG-chains, respectively,[11] followed by Boc group removal with 50% TFA in CH_2Cl_2 (Scheme 1). The progress of the cycloaddition and solvolysis steps was monitored by IR spectroscopy of the resin samples withdrawn from the reaction vessel at different time periods, following the disappearances of the azide and Boc-carbonyl stretching bands: 2100, 1704 and 1407 cm^{-1}. PVA-*g*-PEG-supported hydroxyproline catalysts **5a-c** with 3, 9 and 18 PEG units had loadings of 1.98, 1.55 and 1.10 mmol/g, respectively, on the basis of nitrogen elemental analyses.

The catalytic activity of **5a-c** was tested in various solvents and without solvent in the aldol reaction of *p*-nitrobenzaldehyde (**6**) and cyclohexanone (**7**, Table 1). In all cases, catalyst **5a**, possessing a 3-unit PEG spacer, gave the lowest conversion after 24 h, at best 78% in DMSO, the poorest diastereoselectivity and similar if not lower enantioselectivity relative to those with longer PEG spacers. Resins **5b** and **5c**, with respectively 9- and 18-unit PEG spacers, both behaved reasonably well in the Lewis basic polar aprotic solvents DMF and DMSO demonstrating >98% conversion, ≥97:3 diasteroselectivity and 70-73%

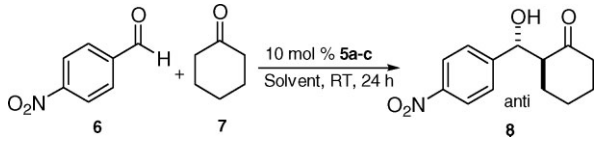


Scheme 1.
Synthesis of catalysts **5a-c**.



Scheme 2.
Synthesis of catalysts **12a-c**.

Table 1.
Solvent effects on the aldol reaction of **6** and **7** catalyzed by resins **5a-c**[a].



6 7 8

entry	solvent	resin	conv[b] (%)	yield (%)	*anti*:*syn*[b]	ee[c] (%)
1	DMF	**5a**	15	14	71:29	72
2		**5b**	98	81	97:3	72
3		**5c**	100	60	99:1	70
4	DMSO	**5a**	78	50	86:14	70
5		**5b**	99	97	99:1	72
6		**5c**	100	73	99:1	73
7	$CHCl_3$	**5a**	<5	4	53:47	59
8		**5b**	18	17	70:30	82
9		**5c**	96	77	95:5	78
10	H_2O	**5a**[d]	<5	–	–	–
11		**5b**[d]	<5	–	–	–
12		**5c**[d]	<5	–	–	–
13	EtOH	**5a**[d]	21	20	69:31	68
14		**5b**[d]	91	54	96:4	82
15		**5c**[d]	99	57	98:2	87
16	Toluene	**5a**[d]	<5	–	–	–
17		**5b**[d]	88	66	96:4	75
18		**5c**[d]	87	50	91:9	86
19	neat	**5a**[d]	<5	–	–	–
20		**5b**[d]	98	60	95:5	81
21		**5c**[d]	99	83	99:1	82

[a]*Reaction conditions*: Aldehyde **6** (0.4 mmol), cyclohexanone **7** (2 mmol), catalyst **5a-c** (0.04 mmol), solvent (150 μl).[b]Determined by ^{1}H NMR of the crude product.[c]Determined by chiral-phase SFC analysis for **8**.[d]Catalyst sample was recycled.

ee values (Table 1, entries 2, 3, 5 and 6). In the polar aprotic solvent chloroform, the 18-unit resin **5c** proved superior to the 9-unit counterpart **5b**, with respect to conversion, yield and diastereoselectivity, yet gave similarly high enantiomeric selectivity (78-82% *ee*, Table 1, entries 7 and 8). In the polar protic solvents, the reaction proceeded sluggishly and gave <5% conversion after 24 h at room temperature in H_2O (Table 1, entries 10-12). On the other hand, in EtOH, catalysts **5b** and **5c** performed well giving ≥91% conversion, ≥96:4 dr and 82-87% *ee* (Table 1, entries 14 and 15) with best results from **5c** with a PEG length of 18 units. In the nonpolar solvent toluene, supported catalysts **5b** and **5c** proved again to be effective with ≥87% conversion, ≥91:9 dr and 75-86% *ee* for the major *anti* diastereoisomer **8** (Table 1, entries 17 and 18); catalyst **5c** with a longer PEG chain gave higher enantiomeric selectivity. The performance of PVA-*g*-PEG catalysts **5b** and **5c** in non-polar solvents is notable in light of the lack of solubility and activity of L-proline in toluene.

In the absence of a solvent, resins **5b** and **5c** exhibited some of their best catalytic activity achieving ≥98% conversion, ≥95:5 dr and 81-82% *ee* (Table 1, entries 20-21). Catalyst **5c** was again more stereoselective than its shorter PEG chain counterpart. To the best of our knowledge, this example represents the first stereoselective aldol reaction to be performed using a supported-proline in neat substrate, and opens up opportunity for economical proline catalysis without solvents. Residual water was shown not to play a role in this reaction with

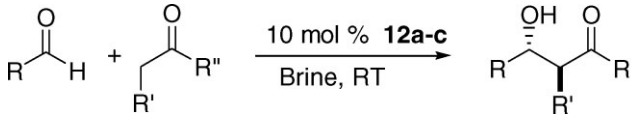
no solvent, because adding catalytic amounts (0.5 mol%) of water to the resin **5**, as well as to resin in toluene caused decreased conversions (39% and 7%, respectively) and lower diastereoselectivities (dr 84:16 and 66:34, respectively).

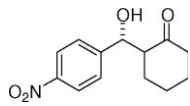
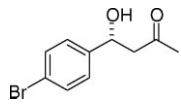
To achieve aldol chemistry in aqueous media, PEG-*g*-PVA-supported proline catalysts **12** were prepared by linking *O*-propargyl hydroxyproline 1,1-diphenyl leucinol amide to the azide resins **3**. The parent 1,1-diphenyl leucinol proline amide has been used in the condensation of cyclohexanone and 4-nitrobenzaldehyde in brine at –10 °C to give β-hydroxy ketone **8** in 69-85% yield, 87:13 diastereoselectivity and 91% enantioselectivity.[12] *O*-Propargyl-*N*-Boc-hydroxyproline amide **10** was synthesized by coupling proline **2** to 1,1-diphenyl leucinol **9**[13–15] by way of the mixed anhydride formed with ethyl chloroformate in DCM at 0 °C in 44% yield.[16] Supported prolinamide catalysts **12a-c** with PEG-chains of respectively 3, 9 and 18 units were prepared similarly to their proline counterparts by the Cu(I)-catalyzed [2 + 3]-dipolar cycloaddition of propargyl ether **10** onto azide resins **3** (PVA-*g*-PEG_n-N_3, n = 3, 9, 18) in a 1/1 THF/DMF solution at 35 °C, followed by Boc group removal using 50% TFA in CH_2Cl_2 for 1 h.[11]

The catalytic activity of **12b** (10 mol %) in the aldol reaction of **6** and **7** at room temperature was similar to its proline amide counterpart in solution at 0 °C. PVA-*g*-PEG supported proline amide **12b** performed stereoselective chemistry in brine to give β-hydroxy ketone **8** in ≥ 99% conversion, ≥99:1 dr and 90% *ee*. In other solvents and in the absence of a solvent, supported proline amide **12b** exhibited reduced selectivity. Catalysts possessing 3 and 18 units of PEG (**12a** and **12c**) gave poorer results. Moreover, PVA-*g*-PEG supported proline amide **12b** catalyzed aldol condensations of aldehyde **6** with acetone, giving product of 80% enantiomeric purity, albeit in lower conversion, likely because of the solubility of acetone in water (Table 2, entries 4-6).

PVA-*g*-PEG resins **5** and **12** were recycled and reused multiple times. After filtration, washing with EtOAc and acetone, and drying under vacuum over desiccant, the PVA-*g*-PEG resin **5b** could be repeatedly used for at least three times without loss of selectivity, but with somewhat lower yield (97%, 78%, 77% and 74% for first through fourth uses, respectively). Similar treatment of resin **12c** allowed the same sample to be used four times with no effect on the levels of conversion, *anti/syn* ratio and *ee* values.

Table 2.
Influence of the PEG chain length on the aldol reaction in brine.



entry	resin	product	time (h)	conv[b] (%)	yield (%)	anti:syn[b]	ee[c] (%)
1	**12a**		22	47	27	73:7	93
2	**12b**		22	99	70	99:1	90
3	**12c**		22	99	67	99:1	86
4	**12a**		72	<5	–	–	–
5	**12b**		68	28	20	–	80
6	**12c**		68	27	10	–	57

[b]Determined by ^{1}H NMR of the crude product.[c]Determined by chiral-phase SFC analysis.

Conclusion

Two classes of supported proline catalysts were linked to PVA-*g*-PEG resins with PEG chains of 3, 9 and 18 repeating units. Proline and proline amide catalysts linked to PVA-*g*-PEG resins with relatively longer PEG chains (9 and 18 units) (**5** and **12**) performed better in aldol reactions than those linked to resins with shorter PEG chains. In comparison with other supported hydroxyprolines,[7] catalysts **5b** and **5c** exhibited broader solvent compatibility. In contrast to polystyrene-supported hydroxyproline,[6] which functioned best in aqueous medium and less effectively in other solvents and in the neat, resins **5** failed in water, yet performed stereoselective reactions in DMF, DMSO, $CHCl_3$, EtOH, toluene and in the absence of a solvent. In toluene and in neat substrate, catalysts **5b** and **5c** performed better than L-hydroxyproline anchored to the monomethyl ether of PEG5000 via a succinate spacer, without need for recovery by precipitation.[17] In brine, the PVA-*g*-PEG supported catalyst **12b** performed with similarly high selectivity as its proline amide counterpart. In general, the PVA-*g*-PEG support either enhanced or maintained the activity and selectivity of the native proline catalyst. PVA-*g*-PEG-supported proline catalysts **5** and **12** make thus a complimentary pair for effectively performing aldol chemistry in a broad spectrum of solvent conditions and merit further investigation in other proline-catalyzed chemistry. It also demonstrates that the derivatized PVA-*g*-PEG resins are candidates of desirable support materials for synthesis and catalysis in the development of green chemistry.

Experimental Part

Trans-(2*S*, 4*R*)-*O*-Propargyl-*N*-Boc-Hydroxyproline (2)

A solution of *trans*-(2*S*, 4*R*)-*N*-Boc-hydroxyproline **1** (1 g, 4.329 mmol, prepared as described in ref [18]) in THF (10 mL) was added to a suspension of sodium hydride (0.240 g, 10 mmol) in THF (15 mL) at 0 °C under argon, stirred for 10 min, and treated drop-wise with propargyl bromide (4 mL, 36.53 mmol). After stirring for 1 h at 0 °C, the mixture was allowed to reach room temperature, and stirred for an additional 48 h then evaporated to a residue that was partitioned between H_2O (20 mL) and EtOAc (20 mL). The aqueous phase was acidified with 0.1 M HCl to pH 4 and extracted with EtOAc (5×20 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to afford propargyl ether **2** (0.61 g, 52%) as a yellow solid: ^{1}H NMR ($CDCl_3$, 400 MHz) showed a 1:1 mixture of carbamate isomer: 1.42 (s, 9H), [1.48 (s, 9H)], 2.16-2.17 (m, 1H), 2.32-2.35 (m, 1H), 2.36-2.47 (m, 1H), 3.56-3.61 (m, 1H), 3.62-3.66 (m, 1H), 4.15-4.17 (m, 2H), 4.33-4.59 (m, 2H), 11.04 (br, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): 27.8, (27.9), 34.1, (36.1), 50.7, (51.4), 56.0, (56.1), 57.4, 74.6, 75.3, (75.7), 78.8, 80.4, (81.1), 153.4, (155.5), 175.4, (178.3); $[\alpha]_D^{20\,°C} = -60.5$ ($c = 1$ in CH_2Cl_2); m.p. 92-94 °C. HRMS (ESI): m/z: 292.1155 [M + Na]; calcd for $C_{13}H_{18}NNaO_5$: 292.1157.

PVA-*g*-PEG-Linked *N*-Boc-Hydroxyproline Resin (4)

Azido PVA-*g*-PEG resin **3** (0.1 g,) was swollen in DMF/THF 1/1 (5 mL) treated with *O*-propargyl-*N*-Boc-hydroxyproline **2** (1.2 equiv), DIEA (1.2 equiv), and CuI (10 mol%) and agitated in a *Radleys*™ carousel at 35 °C for 24 h. The resin was collected by filtration, rinsed successively with water (3×20 mL), DMF (3×20 mL), THF (3×20 mL), THF/MeOH 1/1 (3×20 mL), MeOH (3×20 mL) and THF (3×20 mL), and dried under vacuum for 24 h to yield a brown resin **4**.

PVA-*g*-PEG-Linked Hydroxyproline Resin (5)

Trifluoroacetic acid (2.3 mL) was added to a suspension of resin **4** (0.1 g) swollen in CH_2Cl_2 (2.3 mL) in a 12 mL polypropylene tube equipped with a polyethylene frit and

stopper. The mixture was shaken for 1 h at room temperature and the removal of the Boc group was monitored by FT-IR spectroscopy on resin samples withdrawn from the reaction vessel following the disappearance of the carbonyl stretches at 1704 and 1407 cm^{-1}. The resin was collected by filtration and rinsed successively with a 2% solution of Et_3N in THF (3 × 5 mL), water (3 × 5 mL), THF (3 × 5 mL), THF/MeOH 1/1 (3 × 5 mL), MeOH (3 × 5 mL) and THF (3 × 5 mL), and dried under vacuum for 24 h to yield a brown solid **5**. The degree of functionalization *f* (mmol of functional fragment/g of resin) was calculated from the results of elemental analysis using the formula $f = (0.714/n) \times N\%$ where *n* is the number of nitrogen atoms in the functional unit and N% is the percent of nitrogen provided by the elemental analysis. Loadings of resins **5a-c** with PEG chains of 3, 9 and 18 units, respectively, were determined to be 1.98, 1.55 and 1.1 mmol/g by nitrogen elemental analysis. Elemental analysis (%) **5a** = N 11.09, C 44.01, H 5.63, **5b** = N 8.69, C 45.75, H 6.05, **5c** = N 6.15, C 54.06, H 8.21

Trans-(2*S*, 4*R*, 2'*S*)-*O*-Propargyl-*N*-Boc-Hydroxyprolinyl-1,1-Diphenyl-Leucinol Amide (10)

A solution of *O*-propargyl-*N*-Boc-hydroxyproline **2** (0.3 g, 1.11 mmol) in DCM (15 mL) at 0 °C, was treated slowly with triethylamine (0.112 g, 1.11 mmol) followed by dropwise addition of ethyl chloroformate (0.342 g, 3.13 mmol), stirred at 0 °C for 15 min, treated with 1,1-diphenyl-leucinol **9** (0.3 g, 1.11 mmol, prepared according to ref 16) and stirred for 5 h. The reaction mixture was diluted with DCM, filtered and the volatiles were removed under reduced pressure to a give residue, that was purified by re-crystallization with ethyl acetate to provide amide **10** as a white solid (0.25 g, 44%). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.87 (m, 3H), 0.97 (d, $J = 4.8$ Hz, 3H), 1.21 (t, $J = 12$Hz, 1H), 1.40 (s, 9H), 1.47-1.93 (m, 5H), 2.44 (t, $J = 2.2$Hz, 1H), 3.44 (m, 2H), 4.1-4.35 (m, 5H), 4.9 (br, 1H), 7.16-7.33 (m, 6H), 7.52-7.55 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 24.0, 24.8, 28.2, 33.7, 38.9, 51.5, 54.6, 55.4, 56.5, 58.7, 74.6, 75.6, 76.7, 79.4, 80.6, 81.1, 125.5, 126.6, 126,8, 127,9, 128.4, 144.9, 145.9, 171.6. $[\alpha]_D^{20\,°C} = -39$ ($c = 0.6$ in MeOH). m.p. 187-189 °C. HRMS (ESI): m/z: 521.3012 [M + Na]; calcd for $C_{31}H_{41}N_2O_5$: 521.3010.

PVA-*g*-PEG-Linked *N*-(Boc)Hydroxyproline Amide Resin (11)

Resin **11** was synthesized according to a modification of the procedure for making the Boc-hydroxyproline resin **4** above with *O*-propargyl-*N*-Boc-hydroxyprolinamide **10** (4 equiv), DIEA (4 equiv), and CuI (10 mol%) in DMF/THF 1/1 (5 mL) at 35 °C for 72 h.

PVA-*g*-PEG-Linked Hydroxyproline Amide Resin (12)

Resin **12** was synthesized according to a modification of the procedure for making the hydroxyproline resin **5** above by shaking resin **11** (0.2 g) in a 1/1 mixture TFA/CH_2Cl_2 (8 mL) for 1 h at room temperature. Loadings of resins **12a-c** with PEG chains of 3, 9 and 18 units, respectively, were determined to be 1.27, 1.20 and 1.10 mmol/g by nitrogen elemental analysis. Elemental analysis (%) **12a** = N 8.91, C 56.88, H 6.04, **12b** = N 8.43, C 59.82, H 6.76, **12c** = N 7.71, C 60.32, H 7.05. IR (KBr) = 2919 (C-H), 1647 (C = O), 757 (C = C) cm^{-1}.

Representative Procedure for the Aldol Condensation: Synthesis of 2-[Hydroxy-(4-Nitro-phenyl)-Methyl]-Cyclohexanone (8)

PVA-*g*-PEG-linked hydroxproline **5b** (0.025 g, 10 mol%) was added to a suspension of 4-nitrobenzaldehyde (0.061 g, 0.4 mmol) and cyclohexanone (0.207 mL, 2 mmol) in dry DMSO (0.15 mL). The mixture was stirred at room temperature for 24 h and then poured in EtOAc. Filtration and evaporation, followed by chromatography (EtOAc/hexane: 1/9 up to EtOAc/hexane: 3/7) gave [hydroxy-(4-nitrophenyl)-methyl]-cyclohexanone **8** (0.097 g, 97%) as a yellow solid. The diastereoisomeric ratio *anti*/*syn* = 99:1 was determined

by ^{1}H NMR spectroscopy of the crude mixture and the 72% ee by SFC on a Chiralcel AS-H 25-cm column, 210 nm, iPrOH/CO_2Sc 10/90, 2.0 mL/min; r*t* 7.2 min (major), r*t* 19.4 min (minor).

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[1] *Modern Aldol Reactions*, Vols. *1 & 2* (Ed.: R. Mahrwald,), Wiley-VCH, Weinheim **2004**.
[2] (a) B. List, R. A. Lerner, C. F. Barbas, III *J. Am. Chem. Soc.* **2000**, *122*, 2395. Reviews on proline catalyzed reactions; (b) B. List, *Tetrahedron* **2002**, *58*, 5573. E. R. Jarvo, S. J. Miller, *Tetrahedron* **2002**, *58*, 2481; (c) W. Notz, F. Tanaka, C. F. Barbas, III *Acc. Chem. Res.* **2004**, *37*, 580.
[3] N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas, *J. Am. Chem. Soc.* **2006**, *128*, 734.
[4] Y. Hayashi, *Angew. Chem. Int. Ed.* **2006**, *45*, 8103.
[5] (a) F. Cozzi, *Adv. Syn. Catal.* **2006**, *348*, 1367; (b) M. Benaglia, A. Puglisi, F. Cozzi, *Chem. Rev.* **2003**, *103*, 3401; (c) A. Corma, H. Garcia, *Adv. Syn. Catal.* **2006**, *348*, 1391.
[6] G. Guillena, C. Najera, D. J. Ramon, *Tetrahedron: Asymmetry* **2007**, *18*, 2249.
[7] (a) D. Font, S. Salayero, A. Bastero, C. Jimeno, M. A. Pericàs, *Org. Lett.* **2008**, *10*, 337; (b) M. Gruttadauria, F. Giacalone, A. M. Marculescu, P. Lo Meo, S. Riela, R. Noto, *Eur. J. Org.* **2007**, *28*, 4688.
[8] J. Luo, C. Pardin, X. X. Zhu, W. D. Lubell, *J. Comb. Chem.* **2007**, *9*, 582.
[9] J. Luo, C. Pardin, W. D. Lubell, X. X. Zhu, *Chem. Commun.* **2007**, *21*, 2136.
[10] X. X. Zhu, J. Luo, W. A. Lubell, C. Pardin, T. Kassem, *PCT Int. Appl.* **2007**, WO2007143848.
[11] D. Font, C. Jimeno, M. A. Pericàs, *Org. Lett.* **2006**, *8*, 4653.
[12] V. Maya, M. Raj, V. K. Singh, *Org. Lett.* **2007**, *9*, 2593.
[13] N. Elders, R. F. Schmitz, F. J. J. de Kanter, E. Ruijter, M. B. Groen, R. V. A. Orru, *J. Org. Chem.* **2007**, *72*, 6135.
[14] J. Bach, R. Berenguer, J. Garcia, T. Loscertales, J. Vilarrasa, *J. Org. Chem.* **1996**, *61*, 9021.
[15] Y. J. Wu, H. Y. Yun, Y. S. Wu, K. L. Ding, Y. Zhou, *Tetrahedron: Asymmetry* **2000**, *11*, 3543.
[16] M. Raj, V. S. K. Ginotra, V. K. Singh, *Org. Lett.* **2006**, *8*, 4097.
[17] M. Benaglia, M. Cinquini, F. Cozzi, A. Puglisi, G. Celentano, *Adv. Syn. Catal.* **2002**, *344*, 533.
[18] M. Biel, P. Deck, A. Giannis, H. Waldmann, *Chem. Eur. J.* **2006**, *12*, 4121.

