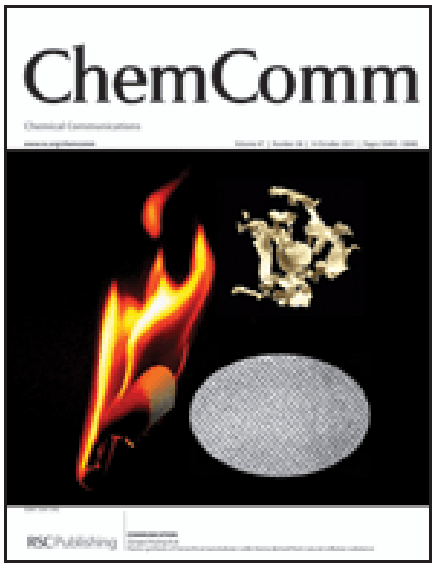
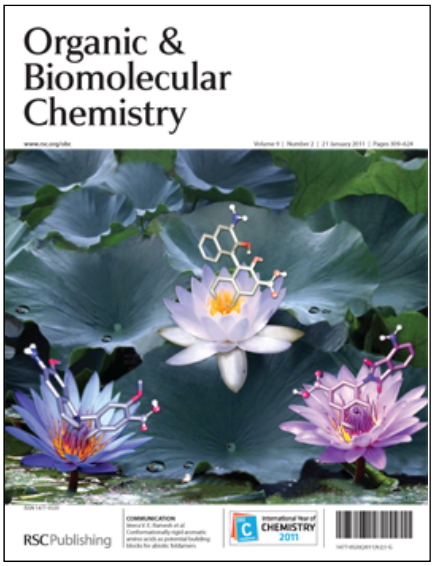




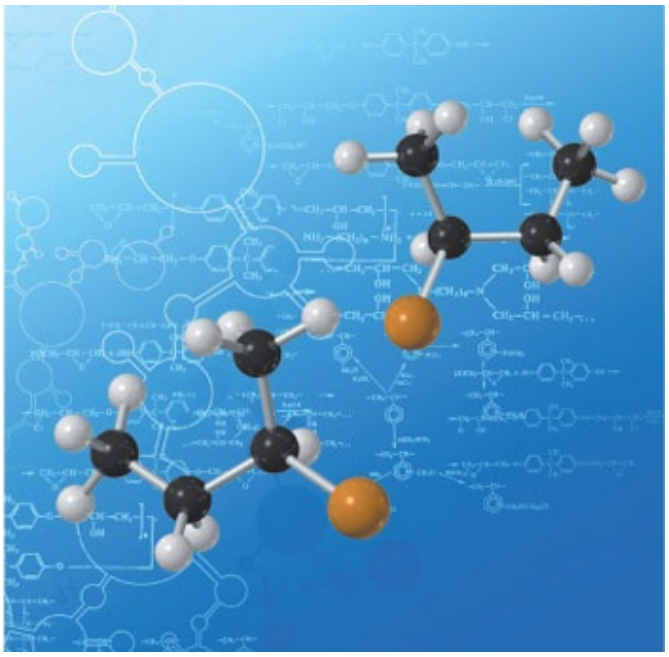
This article is part of the

Organocatalysis

web themed issue

Guest editors: Professors Keiji Maruoka, Hisashi Yamamoto, Liu-Zhu Gong and Benjamin List

All articles in this issue will be gathered together online at www.rsc.org/organocatalysis



Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 2209

www.rsc.org/obc

COMMUNICATION

Highly efficient asymmetric aldol reaction in brine using a fluorous sulfonamide organocatalyst†‡

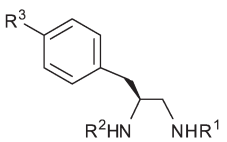
Tsuyoshi Miura,*[a] Hikaru Kasuga,[a] Kie Imai,[a] Mariko Ina,[a] Norihiro Tada,[a] Nobuyuki Imai[b] and Akichika Itoh[a]

Received 22nd November 2011, Accepted 6th January 2012
DOI: 10.1039/c2ob06955e

A fluorous organocatalyst promotes direct asymmetric aldol reactions of aromatic aldehydes with ketones in brine to afford the corresponding *anti*-aldol products in high yield with up to 96% ee. Fluorous organocatalyst can be readily recovered by solid phase extraction using fluorous silica gel and reused without purification.

Formation of new carbon–carbon bonds is one of the most important transformations in organic chemistry. In particular, direct asymmetric aldol reactions using organocatalysts have attracted considerable attention in recent years. Proline and its derivatives with cyclic secondary amino groups are good organocatalysts for direct aldol reactions.[1] Moreover, many chiral primary amines have been reported as excellent organocatalysts.[2,3] In addition, the use of water as a reaction solvent plays an important role in the field of green chemistry.[4] Organocatalysts that can promote aldol reactions in water have recently been reported by several research groups.[2,5] Most of the organocatalysts used in water bear hydrophobic units such as alkyl chain groups or aromatic groups that function as a reaction field in water. In addition, fluorous chain groups such as perfluoroalkyl groups can be utilized as hydrophobic reaction fields; however, asymmetric reactions in water using organocatalysts bearing a fluorous tag have rarely been reported.[5m,6,7] Fluorous compounds with high fluorine content can be easily separated from non-fluorous compounds by fluorous solid phase extraction (FSPE) using fluorous silica gel or fluorous organic solvent extraction.[8] There are many reports of asymmetric reactions in which fluorous organocatalysts are recyclable.[9]

We have recently reported a direct aldol reaction in water using the fluorous sulfonamide organocatalyst **1b**,[7] the Michael addition reaction using a fluorous thiourea organocatalyst,[10] and the oxidation reaction using fluorous IBX.[11] In addition, we have reported a method for the synthesis of both enantiomeric aldol products in brine using organocatalysts **1a**[12] and **2**,[13] which are easily prepared from L-phenylalanine, a commercially available, inexpensive natural amino acid (Scheme 1). The asymmetric synthesis of both enantiomeric products using two different organocatalysts, which are prepared from a common chiral source, has not been extensively reported, although Maruoka and co-worker elaborated the concept for the first time.[14] Furthermore, we successively developed the recyclable fluorous organocatalyst **1b**,[7] which can provide the *anti*-aldol product **6a**, by appending a fluorous tag to β-aminosulfonamide **1a**. However, direct aldol reactions using organocatalyst **2**,[13] which afford the opposite absolute configuration product **7a**, require high catalyst loading (0.2 equiv). In addition, a protocol for recovery and reuse of **2** has not yet been developed. Therefore, to improve the catalytic activity of **2** and enable catalyst recovery, we attempted to develop a novel organocatalyst **4** bearing a fluorous tag that can effectively promote asymmetric aldol reactions in water. Herein, we report highly efficient direct asymmetric aldol reactions using **4**.



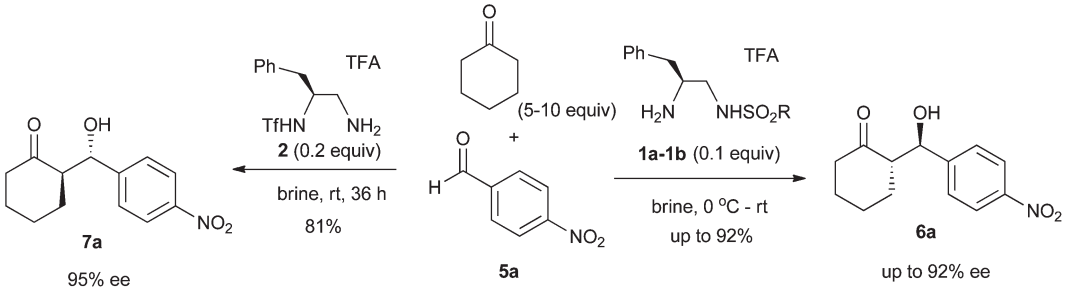
1a: $R^1 = SO_2CF_3$, R^2 = H, R^3 = H
1b: $R^1 = SO_2C_8F_{17}$, R^2 = H, R^3 = H
2 : R^1 = H, $R^2 = SO_2CF_3$, R^3 = H
3 : R^1 = Ts, R^2 = Ms, $R^3 = O(CH_2)_3C_8F_{17}$
4 : R^1 = H, $R^2 = SO_2CF_3$, $R^3 = O(CH_2)_3C_8F_{17}$

The preparation of **4** bearing a fluorous tag is shown in Scheme 2. Treatment of **8**, which is an intermediate in the synthesis of chiral ligand **3**,[15] with methanesulfonyl chloride (MsCl) in the presence of triethylamine in THF afforded **9** in 98% yield. Azide **10** was then obtained in 85% yield *via* the reaction of **9** with sodium azide in DMF. Next, the Boc group of **10** was removed by treatment with hydrogen chloride in ethyl acetate, followed by reaction with trifluoromethanesulfonic anhydride (Tf_2O) in the presence of triethylamine in CH_2Cl_2 to give

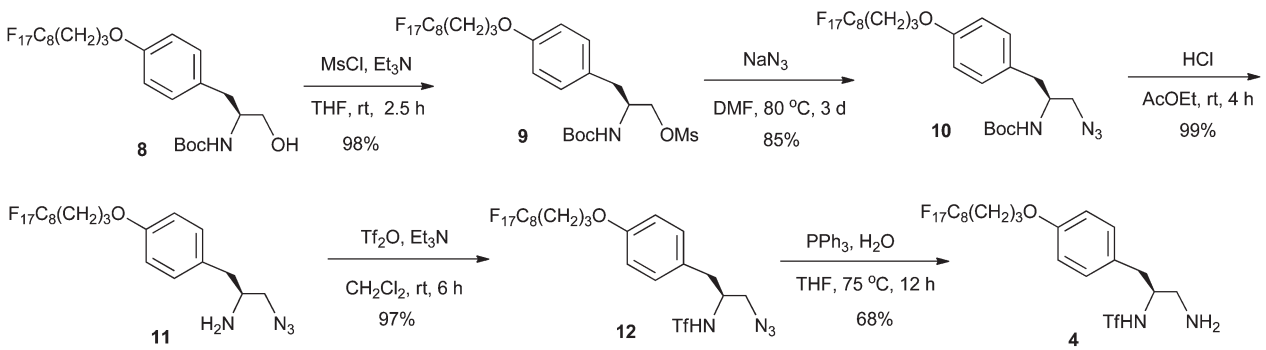
[a]*Gifu Pharmaceutical University 1-25-4, Daigaku-nishi, Gifu 501-1196, Japan. E-mail: miura@gifu-pu.ac.jp*
[b]*Faculty of Pharmacy, Chiba Institute of Science, 15-8 Shiomi-cho, Choshi, Chiba 288-0025, Japan*

†Electronic supplementary information (ESI) available: Experimental procedure and spectral data for compound **4**, **7a–7n** and **9–12**. See DOI: 10.1039/c2ob06955e

‡This article is part of the joint *ChemComm–Organic & Biomolecular Chemistry* 'Organocatalysis' web themed issue.

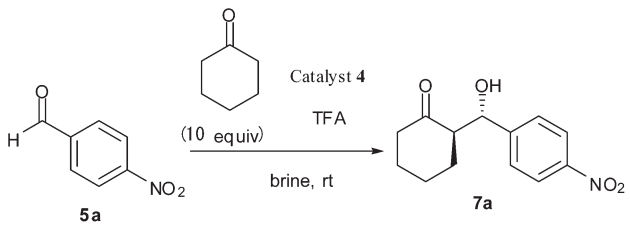


Scheme 1 Our previous work.



Scheme 2 Preparation of organocatalyst.

Table 1 Optimization of reaction conditions



Entry	**4** (equiv)	TFA (equiv)	Cyclohexanone (equiv)	Time (h)	Yield (%)[a]	*anti* : *syn*[b]	%ee[c]
1	0.1	0.1	10	72	58	87 : 13	88
2	0.1	0.05	10	72	93	92 : 8	92
3	0.1	0.025	10	72	79	89 : 11	94
4	0.1	0.025	5	48	98	88 : 12	86
5	0.05	0.0125	5	48	90	94 : 6	94
6	0.05	0.0125	3	48	98	92 : 8	86
7	0.05	—	5	48	98	85 : 15	87

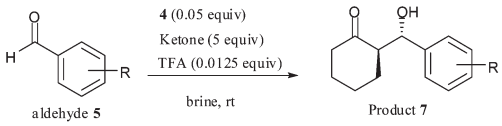
[a] ^{1}H NMR yield. [b] Determined by ^{1}H NMR. [c] Determined by HPLC analysis using Chiralcel AS-H.

the corresponding sulfonamide **12** in excellent yield. Finally, the azide group of **12** was reduced by triphenylphosphine in THF–H_2O to afford **4**.

Optimized conditions for enantioselective direct aldol reactions using **4** are shown in Table 1. Aldol reactions were carried out with *p*-nitrobenzaldehyde (**5a**) and cyclohexanone as test reactants in the presence of a catalytic amount of **4** and trifluoroacetic acid (TFA) in brine. Finally, the most suitable conditions were found when the reaction was performed in the presence of TFA (0.0125 equiv) and **4** (0.05 equiv) at room temperature (entry 5). When no TFA was added, a slight reduction in enantioselectivity was observed (entry 7). Fluorous organocatalyst **4** is an excellent catalyst and provides high yield and excellent stereoselectivity even at low catalyst loading (0.05 equiv) and with reasonable amount of cyclohexanone (5 equiv) as compared to **2**, which requires high catalyst loading (0.2 equiv) and large amount of cyclohexanone (10 equiv).

Considering the optimized reaction conditions, the scope and limitation of the direct asymmetric aldol reactions between various aldehydes and ketones were examined (Table 2). We

Table 2 Direct asymmetric aldol reactions using organocatalyst **4**



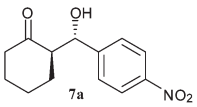
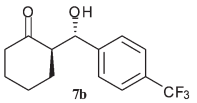
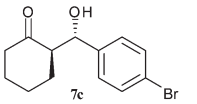
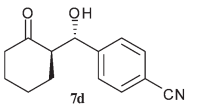
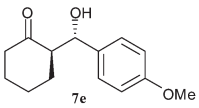
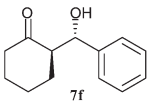
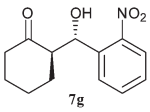
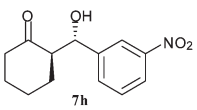
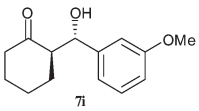
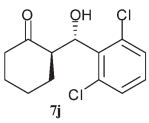
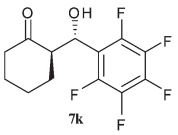
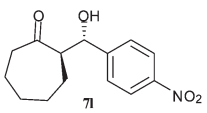
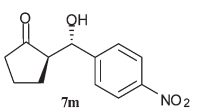
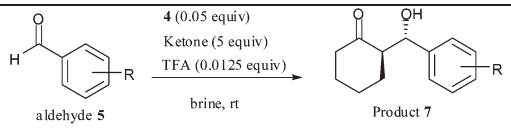
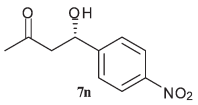
Entry	Product	Time (h)	Yield (%)[a]	*anti* : *syn*[b]	% ee[c]
1		48	90	94 : 6	94
2		72	96	91 : 9	94
3		120	54	88 : 12	95
4		120	93	78 : 22	91
5		120	11	92 : 8	91
6		120	34	93 : 7	94
7		120	69	95 : 5	96
8[d]		120	79	79 : 21	91
9		120	21	93 : 7	94
10		120	86	94 : 6	94
11		120	81	88 : 12	84
12		120	79	68 : 32	73
13		96	70	70 : 30	88

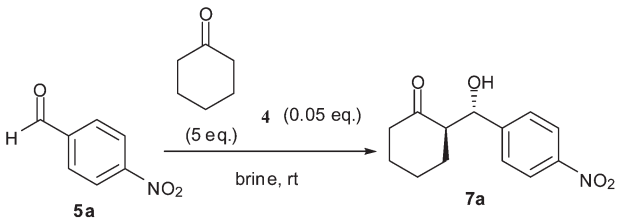
Table 2 *(Contd.)*



Entry	Product	Time (h)	Yield (%)[a]	*anti* : *syn*[b]	% ee[c]
14[e,f]		120	40	—	70

[a] ^{1}H NMR yields. [b] Determined by ^{1}H NMR. [c] Determined by HPLC analysis. [d] Catalyst **4** (0.1 equiv) and TFA (0.025 equiv) were used. [e] The reaction was carried at 0 °C. [f] The reaction was carried out with 30 equiv of acetone in brine.

Table 3 Recycling and reuse of the fluorous catalyst by FSPE



Entry	Time (h)	Yield (%)[a]	*anti* : *syn*[b]	%ee[c]	Cat. recovery (%)
Initial	48	82	89 : 11	88	100
1st reuse	72	82	90 : 10	77	77
2nd reuse	168	70	87 : 13	91	83

[a] Isolated yield. [b] Determined by ^{1}H NMR. [c] Determined by HPLC analysis using Chiralcel AS-H.

selected methoxy substituents as the representative electron-donating group and nitro, trifluoromethyl, and halogen substituents as the electron-withdrawing groups on the benzene ring of benzaldehyde. The reactions between aromatic aldehydes with electron-withdrawing groups and cyclohexanone smoothly resulted in the corresponding *anti*-aldol products in good to excellent yield with 84–96% ee (entries 1–4, 7, 8, and 10 and 11). On the other hand, the reactions between aldehydes with electron-donating groups and cyclohexanone provided the *anti*-aldol products in low yield; however, high enantioselectivity was obtained (entries 5 and 9). Moreover, we examined the reactions between other types of ketones and *p*-nitrobenzaldehyde (**5a**). The aldol reactions of cycloheptanone and cyclopentanone with **4a** resulted in the expected aldol products **7l** and **7m** in high yield with 73 and 88% ee, respectively (entries 12 and 13). The reaction of acetone as an acyclic ketone with **5a** afforded **7n** in moderate yield with 70% ee (entry 14). The stereochemistry of the *anti*-aldol products obtained using **4** was determined by comparison with reported chiral-phase HPLC retention times, optical rotation data, and NMR spectroscopy.

Next, the recyclability of the catalyst was evaluated. After use in the aldol reaction between cyclohexanone and **5a** under the similar conditions, **4** was readily recovered by FSPE using fluorous silica gel.[8] Moreover, the recovered **4** can be reused, and it retained its catalytic activity and enantioselectivity without further purification although longer reaction times were necessary for the second reuse (Table 3).

Conclusions

In conclusion, the novel fluorous organocatalyst **4** can be easily prepared from L-tyrosine, an inexpensive and commercially available amino acid. Fluorous organocatalyst **4**, which is a simple β-aminosulfonamide with only one chiral center, efficiently catalyzes the direct aldol reactions of various aromatic aldehydes with ketones in brine to afford the corresponding *anti*-aldol products with high enantioselectivity. Fluorous organocatalyst **4** is a better catalyst than the original organocatalyst **2**[13] and can efficiently catalyze aldol reactions even under mild reaction conditions, at only low catalyst loading (0.05 equiv) and with reasonable amount of cyclohexanone (5 equiv). The excellent performance is probably due to the ability of the fluorous tag ($-C_8F_{17}$) on **4** to function as a preferable hydrophobic reaction field in brine. Fluorous organocatalyst **4** was readily recovered by simple solid phase extraction using fluorous silica gel and was immediately reusable without purification. Further application of this catalyst in the synthesis of bioactive compounds is currently under progress in our laboratory.

Notes and references

1 For selected reviews on organocatalysts, see: (*a*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138; (*b*) H. Pellisier, *Tetrahedron*, 2007, **63**, 9267; (*c*) S. Mukherjee, J. W. Yang, S. Hoffmann and B. List, *Chem. Rev.*, 2007, **107**, 5471; (*d*) A. Dondoni and A. Massi, *Angew. Chem., Int. Ed.*, 2008, **47**, 4638; (*e*) A. Lattanzi, *Chem. Commun.*, 2009, 1452; (*f*) X. Liu, L. Lin and X. Feng, *Chem. Commun.*, 2009, 6145; (*g*) X.-H. Chen, J. Yu and L.-Z. Gong, *Chem. Commun.*, 2010, **46**, 6437; (*h*) M. Bhanushali and C.-G. Zhao, *Synthesis*, 2011, 1815.

2 For examples of organocatalyzed aldol reactions in water using organocatalysts with primary amino group, see: (*a*) Z. Jiang, Z. Liang, X. Wu and Y. Lu, *Chem. Commun.*, 2006, 2801; (*b*) X. Wu, Z. Jiang, H.-M. Shen and Y. Lu, *Adv. Synth. Catal.*, 2007, **349**, 812; (*c*) M.-K. Zhu, X.-Y. Xu and L.-Z. Gong, *Adv. Synth. Catal.*, 2008, **350**, 1390; (*d*) S. S. V. Ramasastry, K. Albertshofer, N. Utsumi and C. F. Barbas, *Org. Lett.*, 2008, **10**, 1621; (*e*) Y.-C. Tea and P. P. Lee, *Synth. Commun.*, 2009, **39**, 3081; (*f*) F.-Z. Peng, Z.-H. Shao, X.-W. Pu and H.-B. Zhang, *Adv. Synth. Catal.*, 2008, **350**, 2199; (*g*) X. Ma, C.-S. Da, L. Yi, Y.-N. Jia, Q.-P. Guo, L.-P. Che, F.-C. Wu, J.-R. Wang and W.-P. Li, *Tetrahedron: Asymmetry*, 2009, **20**, 1419; (*h*) H. Zhou, Y. Xie, L. Ren and K. Wang, *Adv. Synth. Catal.*, 2009, **351**, 1284; (*i*) J. Li, N. Fu, X. Li, S. Luo and J.-P. Cheng, *J. Org. Chem.*, 2010, **75**, 4501; (*j*) A. Ricci, L. Bernardi, C. Gioia, S. Vierucci, M. Robitzer and F. Quignard, *Chem. Commun.*, 2010, **46**, 6288.

3 For examples of organocatalyzed aldol reactions in organic solvents using organocatalysts with primary amino groups, see: (*a*) A. Córdova, W. Zou, I. Ibrahem, E. Reyes, M. Engqvist and W.-W. Liao, *Chem. Commun.*, 2005, 3586; (*b*) W. Zou, I. Ibrahem, P. Dziedzic, H. Sundén and A. Córdova, *Chem. Commun.*, 2005, 4946; (*c*) P. Dziedzic, W. Zou, J. Háfren and A. Córdova, *Org. Biomol. Chem.*, 2006, **4**, 38; (*d*) A. Córdova, W. Zou, P. Dziedzic, I. Ibrahem, E. Reyes and Y. Xu, *Chem.–Eur. J.*, 2006, **12**, 5383; (*e*) S. S. V. Ramasastry, H. Zhang, F. Tanaka and C. F. Barbas, *J. Am. Chem. Soc.*, 2007, **129**, 288; (*f*) S. Luo, H. Xu, J. Li, L. Zhang and J.-P. Cheng, *J. Am. Chem. Soc.*, 2007, **129**, 3074; (*g*) N. Utsumi, M. Imai, F. Tanaka, S. S. V. Ramasastry and C. F. Barbas, *Org. Lett.*, 2007, **9**, 3445; (*h*) X.-Y. Xu, Y.-Z. Wang and L.-Z. Gong, *Org. Lett.*, 2007, **9**, 4247; (*i*) S. Luo, H. Xu, L. Zhang, J. Li and J.-P. Cheng, *Org. Lett.*, 2008, **10**, 653; (*j*) S. Luo, J. Li, L. Zhang, H. Xu and J.-P. Cheng, *Chem.–Eur. J.*, 2008, **14**, 1273; (*k*) S. Luo, H. Xu, L. Chen and J.-P. Cheng, *Org. Lett.*, 2008, **10**, 1775; (*l*) X. Wu, Z. Ma, Z. Ye, S. Qian and G. Zhao, *Adv. Synth. Catal.*, 2009, **351**, 158; (*m*) J. Li, S. Luo and J.-P. Cheng, *J. Org. Chem.*, 2009, **74**, 1747; (*n*) S. Luo, Y. Qiao, L. Zhang, J. Li, X. Li and J.-P. Cheng, *J. Org. Chem.*, 2009, **74**, 9521; (*o*) S. Luo, P. Zhou, J. Li and J.-P. Cheng, *Chem.–Eur. J.*, 2010, **16**, 4457; (*p*) J. Li, N. Fu, X. Li, S. Luo and J.-P. Cheng, *J. Org. Chem.*, 2010, **75**, 4501; (*q*) P. Zhou, S. Luo and J.-P. Cheng, *Org. Biomol. Chem.*, 2011, **9**, 1784.

4 For reviews on organic synthesis in water, see: (*a*) *Organic Synthesis in Water*, ed. P. A. Grieco, Blackie A & P, London, 1998; (*b*) S. Kobayashi and K. Manabe, *Acc. Chem. Res.*, 2002, **35**, 209; (*c*) U. M. Lindstrom, *Chem. Rev.*, 2002, **102**, 2751; (*d*) C. J. Li, *Chem. Rev.*, 2005, **105**, 3095; (*e*) M. Raj and V. K. Singh, *Chem. Commun.*, 2009, 6687; (*f*) J. Paradowska, M. Stodulski and J. Mlynarski, *Angew. Chem., Int. Ed.*, 2009, **48**, 4288; (*g*) M. Gruttadauria, F. Giacalone and R. Noto, *Adv. Synth. Catal.*, 2009, **351**, 33; (*h*) N. Mase and C. F. Barbas, *Org. Biomol. Chem.*, 2010, **8**, 4043.

5 For examples of organocatalyzed aldol reactions in water without any organic solvent using pyrrolidine derivatives, see: (*a*) S. S. Chimni, D. Mahajan and V. V. S. Babu, *Tetrahedron Lett.*, 2005, **46**, 5617; (*b*) N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka and C. F. Barbas, *J. Am. Chem. Soc.*, 2006, **128**, 734; (*c*) Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima and M. Shoji, *Angew. Chem., Int. Ed.*, 2006, **45**, 958; (*d*) Y. Hayashi, S. Aratake, T. Okano, J. Takahashi, T. Sumiya and M. Shoji, *Angew. Chem., Int. Ed.*, 2006, **45**, 5527; (*e*) D. Font, C. Jimeno and M. A. Pericàs, *Org. Lett.*, 2006, **8**, 4653; (*f*) Y. Wu, Y. Zhang, M. Yu, G. Zhao and S. Wang, *Org. Lett.*, 2006, **8**, 4417; (*g*) W.-P. Huang, J.-R. Chen, X.-Y. Li, Y.-J. Cao and W.-J. Xiao, *Can. J. Chem.*, 2007, **85**, 208; (*h*) F. Giacalone, M. Gruttadauria, A. M. Marculescu and R. Noto, *Tetrahedron Lett.*, 2007, **48**, 255; (*i*) S. Aratake, T. Itoh, T. Okano, T. Usui, M. Shoji and Y. Hayashi, *Chem. Commun.*, 2007, 2524; (*j*) V. Maya, M. Raj and V. K. Singh, *Org. Lett.*, 2007, **9**, 2593; (*k*) M. Gruttadauria, F. Giacalone, A. M. Marculescu, P. L. Meo, S. Riela and R. Noto, *Eur. J. Org. Chem.*, 2007, 4688; (*l*) D. Font, S. Sayalero, A. Bastero, C. Jimeno and M. A. Pericàs, *Org. Lett.*, 2008, **10**, 337; (*m*) L. Zu, H. Xie, H. Li, J. Wang and W. Wang, *Org. Lett.*, 2008, **10**, 1211; (*n*) M. Lombardo, F. Pasi, S. Easwar and C. Trombini, *Synlett*, 2008, 2471; (*o*) S. S. Chimni, S. Singh and D. Mahajan, *Tetrahedron: Asymmetry*, 2008, **19**, 2276; (*p*) S. S. Chimni, S. Singh and A. Kumar, *Tetrahedron: Asymmetry*, 2009, **20**, 1722; (*q*) S.-P. Zhang, X.-K. Fu and S.-D. Fu, *Tetrahedron Lett.*, 2009, **50**, 1173; (*r*) S.-D. Fu, X.-K. Fu, S.-P. Zhang, X.-C. Zou and X.-J. Wu, *Tetrahedron: Asymmetry*, 2009, **20**, 2390; (*s*) M. D. Nisco, S. Pedatella, H. Ullah, J. H. Zaidi, D. Naviglio, O. Ozdamar and R. Caputo, *J. Org. Chem.*, 2009, **74**, 9562; (*t*) M. R. Vishnumaya and V. K. Singh, *J. Org. Chem.*, 2009, **74**, 4289; (*u*) N. Mase, N. Noshiro, A. Mokuya and K. Takabe, *Adv. Synth. Catal.*, 2009, **351**, 2791; (*v*) Y.-N. Jia, F.-C. Wu, X. Ma, G.-J. Zhu and C.-S. Da, *Tetrahedron Lett.*, 2009, **50**, 3059; (*w*) Y.-J. An, Y.-X. Zhang, Y. Wu, Z.-M. Liu, C. Pi and J.-C. Tao, *Tetrahedron: Asymmetry*, 2010, **21**, 688; (*x*) R. Pedrosa, J. M. Andrés, R. Manzano, D. Román and S. Téllez, *Org. Biomol. Chem.*, 2011, **9**, 935.

6 L. Zu, J. Wang, H. Li and W. Wang, *Org. Lett.*, 2006, **8**, 3077.

7 (*a*) T. Miura, K. Imai, M. Ina, N. Tada, N. Imai and A. Itoh, *Org. Lett.*, 2010, **12**, 1620; (*b*) T. Miura, K. Imai, H. Kasuga, M. Ina, N. Tada, N. Imai and A. Itoh, *Tetrahedron*, 2011, **67**, 6340.

8 For a review on fluorous tag techniques, see (*a*) D. P. Curran, *Synlett*, 2001, 1488; (*b*) D. P. Curran, in *The Handbook of Fluorous Chemistry*, ed. J. A. Gladysz, I. T. Horváth, D. P. Curran, Wiley-VCH, Weinheim, 2004; (*c*) W. Thang and D. P. Curran, *Tetrahedron*, 2006, **62**, 11837.

9 For a review on fluorous organocatalysts, see: W. Zhang and C. Cai, *Chem. Commun.*, 2008, 5686; For examples of fluorous organocatalysts, see: (*a*) F. Fache and O. Piva, *Tetrahedron Lett.*, 2001, **42**, 5655; (*b*) F. Fache and O. Piva, *Tetrahedron: Asymmetry*, 2003, **14**, 139; (*c*) Z. Dalicsek, F. Pollreisz, A. Gomory and T. Soós, *Org. Lett.*, 2005, **7**, 3243; (*d*) L. Zu, J. Wang, H. Li and W. Wang, *Org. Lett.*, 2006, **8**, 3077; (*e*) L. Zu, J. Wang, H. Li, X.-H. Yu and W. Wang, *Tetrahedron Lett.*, 2006, **47**, 5131; (*f*) Q. Chu, W. Zhang and D. P. Curran, *Tetrahedron Lett.*, 2006, **47**, 9287; (*g*) A. V. Malkov, M. Figlus, S. Stončius and P. Kočovský, *J. Org. Chem.*, 2007, **72**, 1315; (*h*) S. Goushi, K. Funabiki, M. Ohta, K. Hatano and M. Matsui, *Tetrahedron*, 2007, **63**, 4061;

(*i*) H. Cui, Y. Li, C. Zheng, G. Zhao and S. Zhu, *J. Fluorine Chem.*, 2008, **129**, 45; (*j*) Q. Chu, M. S. Yu and D. P. Curran, *Org. Lett.*, 2008, **10**, 749; (*k*) F. O. Seidel and J. A. Gladysz, *Adv. Synth. Catal.*, 2008, **350**, 2443; (*l*) A. Gheorghe, T. Chinnusamy, E. C. Yanez, P. Hilgers and O. Reiser, *Org. Lett.*, 2008, **10**, 4171; (*m*) D. Vuluga, J. Legros, B. Crousse and D. B. Delpon, *Chem.–Eur. J.*, 2010, **16**, 1776; (*n*) L. Wang, C. Cai, D. P. Curran and W. Zhang, *Synlett*, 2010, 433; (*o*) S. Dordonne, B. Crousse, D. B. Delpon and J. Legros, *Chem. Commun.*, 2011, **47**, 5855.

10 T. Miura, S. Nishida, A. Masuda, N. Tada and A. Itoh, *Tetrahedron Lett.*, 2011, **52**, 4158.

11 T. Miura, K. Nakashima, N. Tada and A. Itoh, *Chem. Commun.*, 2011, **47**, 1875.

12 (*a*) T. Miura, Y. Yasaku, N. Koyata, Y. Murakami and N. Imai, *Tetrahedron Lett.*, 2009, **50**, 2632; (*b*) T. Miura, M. Ina, K. Imai, K. Nakashima, Y. Yasaku, N. Koyata, Y. Murakami, N. Imai, N. Tada and A. Itoh, *Tetrahedron: Asymmetry*, 2011, **22**, 1028.

13 T. Miura, M. Ina, K. Imai, K. Nakashima, A. Masuda, N. Imai, N. Tada and A. Itoh, *Synlett*, 2011, 410.

14 The first example of the synthesis of both enantiomeric products using two different organocatalysts that were prepared from common chiral source: K. Nakayama and K. Maruoka, *J. Am. Chem. Soc.*, 2008, **130**, 17666.

15 We have reported fluorous chiral ligand **3** for enantioselective Simmons–Smith cyclopropanation: T. Miura, K. Itoh, Y. Yasaku, N. Koyata, Y. Murakami and N. Imai, *TetrahedronLett.*, 2008, **49**, 5813.