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Fluorinated β-nitro amines by a selective $ZrCl_4$-catalyzed aza-Henry reaction of (*E*)-trifluoromethyl aldimines†

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$ZrCl_4$ was found to be an ideal catalyst to promote aza-Henry reactions between trifluoromethyl aldimines and some nitro alkanes giving new fluorinated β-nitro amines. The reaction is strongly influenced by the CF_3 group, the yield by the alkyl chain of the nitro compound, while the stereochemical outcome seems to be unaffected, the *anti* isomer being always the major product.

Fluorine-containing amino compounds are of particular interest among the relevant fluorinated molecules.[1] In fact, it has been well demonstrated that a selective substitution of hydrogen by fluorine induces deep modifications in chemical, physical, and biological properties of organic compounds.[2] These modifications are due to the fluorine atoms nature, which produces profound stereo-electronic effects on the neighboring groups, leading to special performances of these compounds in different fields, from the organic, to the pharmaceutical ones.[3] In particular, a trifluoromethyl group usually increases the lipophilicity[4] of a parent molecule and can often avoid undesired metabolic transformations observed for analogous unfluorinated compounds.

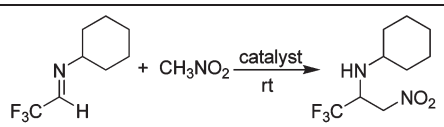
Unfortunately, most of the approaches to synthesize CF_3-containing organic compounds[5] suffer from serious drawbacks, above all, the choice of the starting materials. Thus, the most common methods involve the use of small trifluoromethyl molecules as scaffolds.[6] Recently, we reported[7] the stereoselective synthesis of different (*E*)-trifluoromethyl aldimines,[8] obtained by a solvent-free condensation reaction between trifluoroacetaldehyde ethyl hemiacetal[9] and various amines, and the successive transformation in their corresponding trifluoromethyl diaziridines or oxaziridines by an aza- or an oxa-anion nucleophilic attack.[10]

Continuing our studies on the reactivity of trifluoromethyl compounds, an aza-Henry[11] reaction between different (*E*)-trifluoromethyl aldimines (Schiff bases) and some nitro alkanes was considered to obtain trifluoromethyl β-nitro amines,[12] as interesting starting materials to synthesize differently substituted trifluoromethyl amino compounds.[13]

The aza-Henry condensation was tested between (*E*)-*N*-(2,2,2-trifluoroethylidene)cyclohexanamine (**1a**) and nitromethane by using different reaction conditions, as reported in Table 1.

At first, the aza-Henry reaction was attempted without a solvent and an added base, to test if the same imine could generate *in situ* the nitronate,[14] but no reaction was observed and both reagents were quantitatively recovered (entry 1). Then, different inorganic or organic bases in polar protic[15] (entries 2 and 3) or aprotic solvents (entries 5 and 6) were added to the reaction mixture to promote the formation of nucleophilic species, but both aldimine **1a** and nitromethane were quantitatively recovered under all conditions. Therefore, the aza-Henry condensation was tested under acid catalysis conditions with the aim of increasing the electrophilicity of **1a**. Oxalic acid was tested as an organic protic catalyst (entry 8) but no reaction occurred and the

Table 1 Aza-Henry under different reaction conditions



1a **2a** **3a**

Entry	Catalyst	Solvent	Molar ratios **1a** : **2a** : catalyst	Time (h)	Yield[a] (%)
1	—	—	1 : 5 : 0	24	—
2	KF	i-PrOH	1 : 5 : 0.4	24	—
3	KF[b]	i-PrOH	1 : 5 : 0.4	24	—
4	KF	—	1 : 5 : 0.4	24	—
5	Et_3N	THF	1 : 5 : 1	24	—
6	Et_3N[b]	THF	1 : 5 : 1	24	—
7	Et_3N	—	1 : 5 : 1	24	—
8	$(CO_2H)_2$	—	1 : 5 : 0.5	24	—
9	$ZrCl_4$	—	1 : 5 : 1	2	65[c]
10	$ZrCl_4$	—	1 : 5 : 1.3	2	Trace
11	$ZrCl_4$	—	1 : 5 : 0.5	2	87[c]
12	$ZrCl_4$	—	1 : 2.5 : 0.5	2	50
13	$ZrCl_4$	—	1 : 5 : 0.25	2	20
14	$ZrCl_4$	—	1 : 5 : 0.25	18	20

[a] By ^1H NMR spectra on the crude mixtures. [b] Performed at 70 °C. [c] After purification on silica gel.

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reactants were quantitatively recovered. Thus, inspired by our recent results,[16] $ZrCl_4$ was chosen as a suitable Lewis acid catalyst and the expected *N*-(1,1,1-trifluoro-3-nitropropan-2-yl)cyclohexanamine (**3a**) was finally obtained under solvent-free reaction conditions (entries 9 and 10).[17] In order to optimize the $ZrCl_4$-catalyzed aza-Henry reaction, different molar ratios between the catalyst and reagents were considered, the best reaction conditions being those of entry 11. To test the specific role of $ZrCl_4$, other different Lewis acids were used as catalysts in the optimal molar ratios (**1a** : **2a** : catalyst = 1 : 5 : 0.5). However, after 24 h neither the use of classical $AlCl_3$, $BF_3{\cdot}Et_2O$, nor the use of Cu(I), Cu(II), and Ti(IV), employed in similar condensation reactions,[18] led to the expected product, except in traces (only for $TiCl_4$).

Therefore, the $ZrCl_4$-catalyzed aza-Henry reaction has been extended to different (*E*)-trifluoromethyl aldimines and nitro alkanes. As detected by ^1H NMR spectra performed on the crude mixtures, quantitative conversions were found in all cases and then the obtained β-nitro α-trifluoromethyl amines were purified on silica gel. The results are reported in Table 2.

As shown in Table 2, the aza-Henry reaction outcome seems to be independent of the cyclic or linear nature of the R groups,[19] while it was deeply influenced by the nature of the used nitro compound, showing to suffer from steric hindrance. In fact, moving from nitromethane (entries 1, 4, 7, and 9) to nitroethane (entries 2, 5, 8, and 10) and 1-nitropropane (entries 3 and 6) the reactions needed more time to occur and the corresponding β-nitro α-trifluoromethyl amines were obtained in lower yields. Moreover, when the reaction was performed with 2-nitropropane no condensation was observed and both reagents were quantitatively recovered. In contrast, the stereochemical reaction outcome is not influenced by the used nitro alkane, the major product being the *anti* isomer[20] in all cases. The *syn*/*anti* diastereomeric ratios were determined by ^1H NMR analysis on the crude mixture. In order to improve the diastereoselectivity, the aza-Henry reaction was performed on **1a** by changing the reaction temperature (−20 °C, 0 °C and 70 °C), but in all cases no changes in diastereomeric ratios were observed. Except for **3c** and **3f**, the *syn*/*anti* isomers were obtained as pure compounds after separation by flash chromatography on silica gel. Moreover, **3b** was converted by a selective reduction reaction of the nitro group in the corresponding diamine **4b** (Scheme 1). This last compound can be further deprotected by a classical Pd catalyzed hydrogenolysis of the benzylic residue.

The collected data show a strong influence of the fluorine on the imine reactivity in the aza-Henry reaction. Contrary to what one might expect, the inductive electron-withdrawing effect of the CF_3 group seems to be strong enough to decrease both carbon electrophilicity and nitrogen basicity of the C=N double bond.

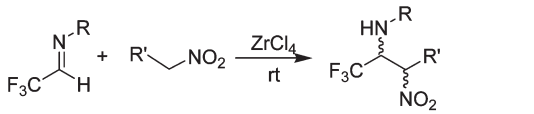
In order to confirm our hypothesis, the reactivity of unfluorinated imines (*E*)-**5a–e**[21] was tested in the aza-Henry condensations with nitro alkanes **2a,b**. While the use of $ZrCl_4$ as a catalyst led to exothermic reactions with probable complete polymerizations of the starting materials, the condensation performed without the catalyst and solvent gave the expected unfluorinated β-nitro amines **6a–d** in good yields, under solvent-free conditions. The results are reported in Table 3.

Working with unfluorinated substrates, while no differences on the stereochemical outcome were observed, the reaction pathway is completely different and still interesting. Probably, the same imines act as both substrates and bases, generating *in situ* the nitronate and activating itself by self-protonation, thus confirming the effect of the trifluoromethyl group on the reactivity of compounds in which it is present.

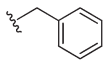
Starting from these data, a catalytic cycle to explain the $ZrCl_4$-catalyzed aza-Henry reaction pathway performed on (*E*)-trifluoromethyl aldimines can be proposed (Scheme 2).

Zr(IV) coordinates both the imino nitrogen and the nitro alkane oxygen,[22] determining an increase of acidity of the nitro

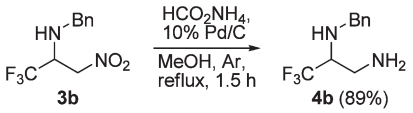
Table 2 Synthesis of β-nitro α-trifluoromethyl amines



1a-d **2a-c** **3a-j** (*syn*/*anti* = 30:70, for R' ≠ H)

Entry	1	R	2[a]	R′	3	Time (h)	Yield[b] (%)
1	**a**		**a**	H	**a**	2	87
2			**b**	Me	**b**	18	82
3			**c**	Et	**c**	24	79
4	**b**		**a**	H	**d**	2	84
5			**b**	Me	**e**	18	80
6			**c**	Et	**f**	24	75
7	**c**		**a**	H	**g**	2	86
8			**b**	Me	**h**	18	77
9	**d**		**a**	H	**i**	2	83
10			**b**	Me	**j**	18	78

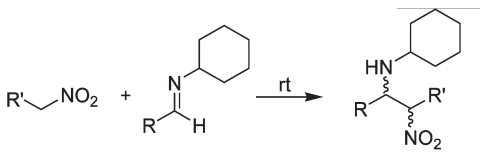
[a] Molar ratios **1** : **2** : $ZrCl_4$ = 1 : 5 : 0.5. [b] After purification on silica gel.



3b **4b** (89%)

Scheme 1 Synthesis of **4b**.

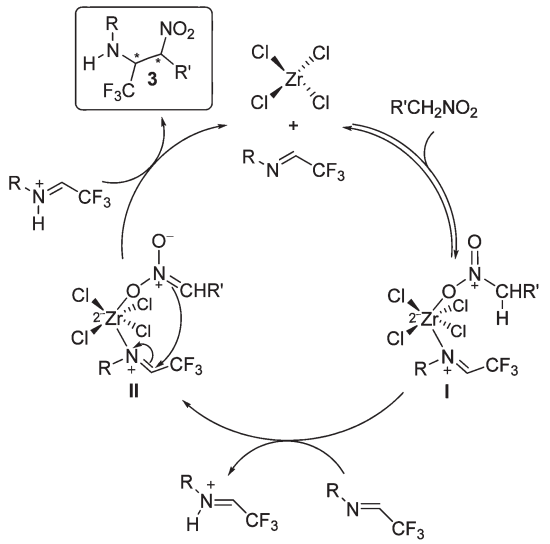
Table 3 Synthesis of β-nitro amines



2a-b **5a-b** **6a-d** (*syn*/*anti* = 30:70, for R' ≠ H)

Entry	2	R′	5[a]	R	6	Time (h)	Yield[b] (%)
1	**a**	H	**a**	Me	**a**	3	95
2	**b**	Me	**a**	Me	**b**	18	90
3	**a**	H	**b**	i-Bu	**c**	3	90
4	**b**	Me	**b**	i-Bu	**d**	18	89

[a] Molar ratios **2** : **5** = 5 : 1. [b] After fast filtration through a plug filled with silica gel.



Scheme 2 Proposed catalytic cycle of the new aza-Henry reaction of trifluoromethyl aldimines.

compound, that can be then deprotonated by a second molecule of the trifluoromethyl aldimine. Finally, a favored intramolecular nucleophilic attack followed by protonation leads to the formation of fluorinated β-nitro amines **3**.

In conclusion in this paper a zirconium tetrachloride catalyzed aza-Henry reaction of (*E*)-trifluoromethyl aldimines is reported. The new methodology here presented is strongly dependent on the presence in the imines of the CF_3 moiety that induces deep modifications in the substrate reactivity. Recently, an elegant work reported $ZrCl_4$ as a suitable and efficient catalyst, compatible with the CF_3 group.[23] The obtained trifluoromethyl β-nitro amines are useful synthetic building blocks, due to the known chemical versatility of the nitro group often called *synthetic chameleon*,[24] that easily undergoes reduction reactions,[25] giving the corresponding fluorinated 1,2-diamines,[26] or Nef reaction,[27] that lead to valuable trifluoromethyl α-amino acids[28] or ketones.[29]

N-(1,1,1-Trifluoro-3-nitropropan-2-yl)cyclohexanamine (3a)

To a mixture of (*E*)-trifluoromethyl aldimine **1a** (1 mmol) and nitro compound **2a** (5 mmol), $ZrCl_4$ (0.5 mmol) was added. The reaction was performed under solvent-free conditions and stirred at room temperature (2–24 h). Then, after addition of water (5 mL), the crude mixture was extracted three times with Et_2O. The collected organic layer was dried over anhydrous Na_2SO_4 and the solvent evaporated under vacuum. The crude mixture was purified by flash chromatography on silica gel. Yellow-brown oil. Yield 87% (0.209 g). Purified by fast filtration through a plug filled with silica gel using AcOEt as an eluent. ν_{max} cm^{-1} 3355; 1567. ^1H NMR ($CDCl_3$, 300 MHz) δ: 4.61 (dd, J = 12.6, 4.2 Hz, 1H), 4.35 (dd, J = 12.6, 9.4 Hz, 1H), 4.14–4.01 (m, 1H), 2.71–2.63 (m, 1H), 1.89–1.48 (m, 5H), 1.35–0.99 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 125.2 (q, J = 284.5 Hz), 75.3, 55.7 (q, J = 29.1 Hz), 54.8, 34.1, 32.8, 25.9, 24.7, 24.4. HRMS: m/z $[M + H]^+$ calcd for $C_9H_{16}F_3N_2O_2$ 241.1164, found 241.1161.

N^2-Benzyl-3,3,3-trifluoropropan-1,2-diamine (4b)

The title compound was synthesized modifying a reported procedure for the nitro group reduction reaction.[25b] Anhydrous ammonium formate (310 mg, 5 mmol) and Pd/C 10% (95 mg) were added, under an inert atmosphere (Ar), to a solution of **3b** (248 mg, 1 mmol) in anhydrous MeOH. The reaction mixture was kept at reflux for 1.5 h after which it was filtered off to remove the catalyst. The solvent was evaporated under vacuum and 5 mL of water was added; the mixture was extracted three times with Et_2O. The collected organic layers were dried over anhydrous Na_2SO_4 and the solvent evaporated under vacuum. Pale yellow oil. Yield 65% (0.142 g). Purified by fast filtration through a plug filled with silica gel using AcOEt as an eluent. ν_{max} cm^{-1} 3491; 3393. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.39–7.27 (m, 5H), 3.96 (dd, J = 62.6, 13.1 Hz, 2H), 3.11–2.92 (m, 1H), 2.97 (dd, J = 13.3, 3.6 Hz, 1H), 2.74 (dd, J = 13.0, 8.1 Hz, 1H), 1.83 (br, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.4, 128.4 (2C), 128.1 (2C), 127.2, 126.6 (q, J = 284.5 Hz), 60.2 (q, J = 26.0 Hz), 51.7, 40.0. HRMS: m/z $[M + H]^+$ calcd for $C_{10}H_{14}F_3N_2$ 219.1109, found 219.1105.

N-(1-Nitropropan-2-yl)cyclohexanamine (6a)

(*E*)-Aldimine **5a** (1 mmol) was stirred at room temperature (3–18 h) with a five-fold excess of the nitro compound, under solvent free conditions. After removal of the excess nitro compound under vacuum, the crude mixture was purified through a plug filled with silica gel using AcOEt as an eluent. Yellow-brown oil. Yield 95% (0.177 g). ν_{max} cm^{-1} 3355; 1568. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.38–4.27 (m, 1H), 3.56–3.46 (m, 1H), 2.55–2.46 (m, 1H), 1.86–1.55 (m, 7H), 1.17 (d, J = 6.5 Hz, 3H), 1.33–0.99 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 79.8, 53.9, 51.8, 34.2, 33.7, 26.0, 24.8, 24.7, 17.0. HRMS: m/z $[M + H]^+$ calcd for $C_9H_{19}N_2O_2$ 187.1447, found 187.1445.

Acknowledgements

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Notes and references

1 (*a*) *Organofluorine Chemistry: Principles and Commercial Applications*, ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994; (*b*) *Chemistry of Organic Fluorine Compounds II*, ed. M. Hudlicky and A. E. Pavlath, American Chemical Society, Washington, DC, 1995; (*c*) P. Bravo, L. Bruché, M. Crucianelli, F. Viani and M. Zanda, *ACS Symp. Ser.*, 2000, **746**, 98 (Asymmetric Fluoroorganic Chemistry); (*d*) *Organofluorine Compounds: Chemistry and Applications*, ed. T. Hiyama, Springer, New York, 2000; (*e*) V. P. Kukhar, A. E. Sorochinsky and V. A. Soloshonok, *Future Med. Chem.*, 2009, **1**, 793; (*f*) N. Al-Maharik and D. O'Hagan, *Aldrichimica Acta*, 2011, **44**, 65; (*g*) D. O'Hagan, *J. Org. Chem.*, 2012, **77**, 3689.

2 S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330.

3 (*a*) *Biomedicinal Aspects of Fluorine Chemistry*, ed. R. Filler, Y. Kobayashi and L. M. Yagupolskii, Elsevier, Amsterdam, 1993; (*b*) *Biomedical Frontiers of Fluorine Chemistry*, ed. I. Ojima, J. R. McCarthy and J. T. Welch, American Chemical Society, Washington, DC, 1996; (*c*) J.-P. Bégué and D. Bonnet-Delpon, *Chimie Bioorganique et Médicinale du Fluor*, EDP sciences CNRS Editions, 2005; (*d*) K. Mueller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881; (*e*) R. Filler and

R. Saha, *Future Med. Chem.*, 2009, **1**, 777; (*f*) T. Yamazaki, T. Taguchi and I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, ed. I. Ojima, John Wiley & Sons, Ltd, Chichester, UK, 2009, pp. 3–46.
4 B. E. Smart, *J. Fluorine Chem.*, 2001, **109**, 3 and ref. therein.
5 (*a*) K. Mikami, Y. Itoh and M. Yamanaka, *Chem. Rev.*, 2004, **104**, 1; (*b*) J.-A. Ma and D. Cahard, *Chem. Rev.*, 2004, **104**, 6119; (*c*) K. L. Kirk, *Org. Process Res. Dev.*, 2008, **12**, 305.
6 M. Hideyuki, K. Kosuke, Y. Tetsuya, S. Takeshi and K. Yasuo, *J. Fluorine Chem.*, 2010, **131**, 477.
7 L. Carroccia, S. Fioravanti, L. Pellacani and P. A. Tardella, *Synthesis*, 2010, 4096.
8 J.-P. Bégué, D. Bonnet-Delpon, B. Crousse and J. Legros, *Chem. Soc. Rev.*, 2005, **34**, 562.
9 Y. Gong and K. Kato, *Curr. Org. Chem.*, 2004, **8**, 1659.
10 L. Carroccia, S. Fioravanti, L. Pellacani and P. A. Tardella, *Tetrahedron*, 2011, **67**, 5375.
11 (*a*) B. Westermann, *Angew. Chem.*, 2003, **115**, 161, (*Angew. Chem., Int. Ed.*, 2003, **42**, 151); (*b*) E. Marqués-López, P. Merino, T. Tejero and R. Herrera, *Eur. J. Org. Chem.*, 2009, 2401.
12 For a different multi-step synthesis of fluorinated α-nitro amines: V. Yu. Korotaev, A. Yu. Barkov, M. I. Kodess, I. B. Kutyashev, P. A. Slepukhin and A. Ya. Zapevalov, *Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1886.
13 (*a*) *Fluorine Containing Amino Acids: Synthesis and Properties*, ed. V. P. Kukhar and V. A. Soloshonok, Wiley, Chichester, UK, 1994; (*b*) S. Fustero, J. F. Sanz-Cervera, J. Piera, M. Sanchez-Rosello, G. Chiva and A. Simon-Fuentes, *J. Fluorine Chem.*, 2004, **125**, 621; (*c*) J. L. Acena, A. Simon-Fuentes and S. Fustero, *Curr. Org. Chem.*, 2010, **14**, 928.
14 The same fluorinated imines were able to deprotonate *in situ* ethyl nosyloxycarbamate, acting as both base and substrate in aziridination reactions: see ref. 10 and M. Barani, S. Fioravanti, M. A. Loreto, L. Pellacani and P. A. Tardella, *Tetrahedron*, 1994, **50**, 3829.
15 J. Hubner, J. Liebscher and M. Patzel, *Tetrahedron*, 2002, **58**, 10485. To the best of our knowledge only one recent paper reported a base catalyzed aza-Henry reaction performed on fluorinated α,β-unsaturated ketimines: F. Zhang, Z.-J. Liu and J.-T. Liu, *Org. Biomol. Chem.*, 2011, **9**, 3625.
16 S. Fioravanti, L. Pellacani and M. C. Vergari, *Org. Biomol. Chem.*, 2012, **10**, 524.
17 For very recent solvent-free Henry reactions, see: M. Fabris, M. Noè, A. Perosa, M. Selva and R. Ballini, *J. Org. Chem.*, 2012, **77**, 1805.
18 (*a*) C. Gennari, I. Venturini, G. Gislon and G. Schimperna, *Tetrahedron Lett.*, 1987, **28**, 227; (*b*) N. Nishiwaki, K. R. Knudsen, K. V. Gothelf and K. A. Jørgensen, *Angew. Chem.*, 2001, **113**, 3080, (*Angew. Chem., Int. Ed.*, 2001, **40**, 2992).
19 We tested the reactivity of another trifluoromethyl imine N-protected by the *p*-methoxyphenyl (PMP) group. However reacting this imine in the absence of any catalyst no reaction was observed and the reagents were quantitatively recovered; while when $ZrCl_4$ was used as a catalyst an exothermic reaction occurs leading to a complex polymeric mixture.
20 The *syn*/*anti* nomenclature is used according to Masamune convention: (*a*) S. Masamune, S. A. Ali, D. L. Snitman and D. S. Garvey, *Angew. Chem.*, 1980, **92**, 573, (*Angew. Chem., Int. Ed.*, 1980, **19**, 557); (*b*) S. Masamune, T. Kaiho and D. S. Garvey, *J. Am. Chem. Soc.*, 1982, **104**, 5521.
21 The unfluorinated imines (*E*)-**4a–b** were synthesized by a direct condensation reaction between suitable aldehydes and cyclohexylamine using an equimolar ratio, under solvent-free conditions. They were obtained as only *E* isomers and used without further purification.
22 For a similar catalytic process see: (*a*) M. Johannsen and K. A. Jørgensen, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1183; (*b*) Ref. 18*b*.
23 B. Morandi and E. M. Carreira, *Angew. Chem.*, 2011, **123**, 9251, (*Angew. Chem., Int. Ed.*, 2011, **50**, 9085).
24 G. Calderari and D. Seebach, *Helv. Chim. Acta*, 1985, **68**, 1592.
25 (*a*) K. Prasad, X. Jiang, J. S. Slade, J. Clemens, O. Repič and T. J. Blacklock, *Adv. Synth. Catal.*, 2005, **347**, 1769; (*b*) Y. Chi, L. Guo, N. A. Kopf and S. H. Gellman, *J. Am. Chem. Soc.*, 2008, **130**, 5608.
26 D. Lucet, T. Le Gall and C. Mioskowski, *Angew. Chem.*, 1998, **110**, 2724, (*Angew. Chem., Int. Ed.*, 1998, **37**, 2580).
27 (*a*) E. Foresti, G. Palmieri, M. Petrini and R. Profeta, *Org. Biomol. Chem.*, 2003, **1**, 4275; (*b*) R. Ballini and M. Petrini, *Tetrahedron*, 2004, **60**, 1017.
28 (*a*) *Fluorine Containing Amino Acids: Synthesis and Properties*, ed. V. P. Kukhar and V. A. Soloshonok, Wiley, New York, 1995; (*b*) N. C. Yoder and K. Kumar, *Chem. Soc. Rev.*, 2002, **31**, 335; (*c*) M. Zanda, *New J. Chem.*, 2004, **28**, 1401; (*d*) C. Jäckel and B. Koksch, *Eur. J. Org. Chem.*, 2005, 4483; (*e*) R. Smits, C. D. Cadicamo, K. Burger and B. Koksch, *Chem. Soc. Rev.*, 2008, **37**, 1727; (*f*) D. Enders, K. Gottfried and G. Raabe, *Adv. Synth. Catal.*, 2010, **352**, 3147; (*g*) A. Ishii, M. Yasumoto, T. Yamazaki, K. Mogi and Ta. Masuda, *PCT Int. Appl.*, WO 2010026918 A1 20100311, 2010; (*h*) T. Katagiri, Y. Katayama, M. Taeda, T. Ohshima, N. Iguchi and K. Uneyama, *J. Org. Chem.*, 2011, **76**, 9305.
29 (*a*) M. W. Walter, R. M. Adlington, J. E. Baldwin, J. Chuhan and C. J. Schofield, *Tetrahedron Lett.*, 1995, **36**, 7761; (*b*) M. W. Walter, R. M. Adlington, J. E. Baldwin and C. J. Schofield, *J. Org. Chem.*, 1998, **63**, 5179; (*c*) J. Legros, D. Bouvet, B. Crousse, D. Bonnet-Delpon and J. P. Bégué, *Synthesis*, 2000, 838; (*d*) R. P. Singh and J. M. Shreeve, *J. Org. Chem.*, 2000, **65**, 3241; (*e*) G. Hughes, P. N. Devine, J. R. Naber, P. D. O'Shea, B. S. Foster, D. J. McKay and R. P. Volante, *Angew. Chem.*, 2007, **119**, 1871, (*Angew. Chem., Int. Ed.*, 2007, **46**, 1839); (*f*) T. Shibata and S. Noritake, *Jpn. Kokai Tokkyo Koho*, JP 2010209007 A 20100924, 2010.

