Lanthanide reagents in solid phase synthesis

Lisa A. Sloan and David J. Procter*

Received 19th May 2006
First published as an Advance Article on the web 28th June 2006
DOI: 10.1039/b509215a

From solid-supported ytterbium(III) catalysts to linkers cleaved by electron transfer from samarium(II) species, lanthanide reagents are beginning to find widespread application in solid phase organic synthesis. This *tutorial review* introduces the use of lanthanide(III) Lewis acids and lanthanide(IV) oxidants in solid phase chemistry before concentrating on the growing use of lanthanide(II) reagents in the area.

1. Introduction

In recent years lanthanide reagents have played an increasingly important role in many areas across the broad discipline of organic synthesis.[1] This tutorial review will focus on the use of lanthanide reagents in solid phase synthesis and is organised according to the oxidation state of the lanthanide metal in the reagent. A brief illustration of the use of lanthanide(III) and (IV) reagents in solid phase synthesis will be followed by a closer examination of the emerging area of lanthanide(II)-mediated chemistry on the solid phase.

2. Lanthanide(III) reagents

Lanthanide(III) salts are versatile catalysts and have been used widely as water-tolerant Lewis acids in organic synthesis.[2] Such catalysts are now finding increasing use in solid phase synthesis. Wilson has used a ytterbium(III) triflate-catalysed tandem Mannich–Michael reaction of immobilised imines with Danishefsky's diene in a solid-phase synthesis of 2,3-dihydro-4-pyridones such as **1**.[3] A range of common Lewis acid catalysts was screened with ytterbium(III) triflate giving the highest yields in the reaction (Scheme 1).

Barluenga has also reported a solid phase synthesis of substituted 4-piperidones using a similar process involving the reaction of immobilised imines with 2-amino-1,3-butadienes catalysed by ytterbium(III) triflate.[4] Again, the ytterbium(III) Lewis acid was the most effective catalyst for the cycloaddition. Products such as **2** were obtained in good yield and purity as single diastereoisomers (Scheme 2).

Wang has also used ytterbium(III) triflate to catalyse solid phase aza Diels–Alder reactions in an approach to piperidine derivatives.[5] Stirring aminomethylated-polystyrene resin with aldehydes and dienes results in cyclative-capture to give immobilised piperidines **3** that can be cleaved from the support in high yield. Interestingly, $AlCl_3$ and $MgCl_2$ were ineffective catalysts in the reaction (Scheme 3).[5]

Kobayashi has utilised ytterbium(III) triflate-catalysed 1,3-dipolar cycloadditions in a solid phase synthesis of 2-isoxazoline derivatives. Products such as **4** are obtained in high yield and as single diastereoisomers after oxidative cleavage from the polystyrene support (Scheme 4).[6]

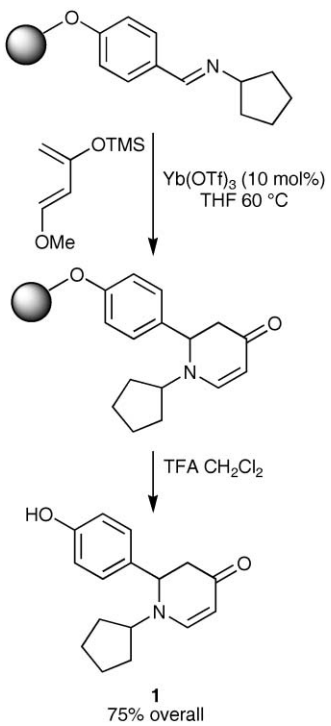
School of Chemistry, Oxford Road, The University of Manchester, Manchester, UK M13 9PL. E-mail: David.J.Procter@manchester.ac.uk; Fax: +44 (0) 161 2754939; Tel: +44 (0) 161 2751425

Lisa A. Sloan

Lisa A. Sloan was born in Enniskillen, Northern Ireland. She received her MSci Degree in Chemistry with Medicinal Chemistry from the University of Glasgow in 2003 and is currently engaged in PhD research under the supervision of David J. Procter at the University of Manchester. Lisa's research is concerned with the application of SmI_2-mediated cyclisations in natural product synthesis. Away from the laboratory, Lisa enjoys running, kickboxing, reading, and cooking.

David J. Procter

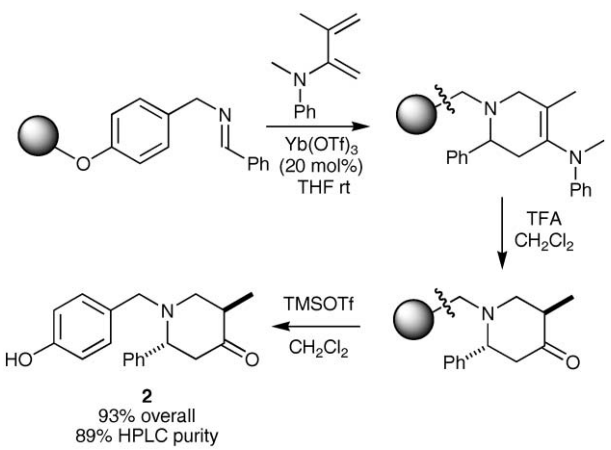
David J. Procter was born in Leyland in Lancashire, England. He obtained his BSc in Chemistry from the University of Leeds in 1992 and his PhD in 1995 working with Professor Chris Rayner. He then spent two years as a postdoctoral research associate with Professor Robert Holton at Florida State University in Tallahassee, USA working on the synthesis of analogues of the anticancer agent Taxol. In late 1997 he took up a Lectureship at the University of Glasgow in Scotland and was promoted to Senior Lecturer in February 2004. In September 2004, he moved to a Readership at the University of Manchester. His research interests lie in the development of new organic reactions, particularly using the lanthanide reagent SmI_2, natural product synthesis and high-throughput chemistry.



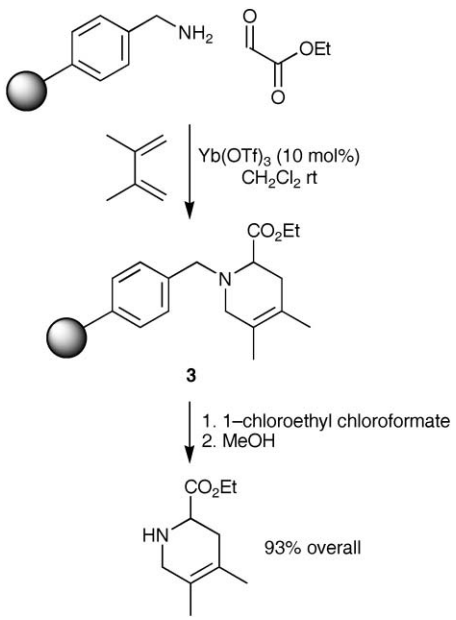
Scheme 1 Ytterbium(III) triflate-catalysed tandem Mannich–Michael reaction in a solid-phase synthesis of 2,3-dihydro-4-pyridones.

Dujardin has used an europium(III)-catalysed heterocycloaddition for the asymmetric solid-phase synthesis of substituted dihydropyrans such as **7**.[7] High levels of diastereoselectivity were observed in the reaction of chiral enol ether **6** with the immobilised heterodiene **5**. A higher loading of the europium(III) salt was required to achieve efficient reactions on resin compared to analogous processes in solution (Scheme 5).[7]

In addition to cycloaddition-type processes, lanthanide(III) salts have been used to catalyse several other classes of reaction. For example, Ganesan has used lanthanum(III) triflate to accelerate the Baylis–Hillman reactions of a supported acrylate with a range of aldehydes.[8] The immobilised adducts were converted to ketone products such as **8** in



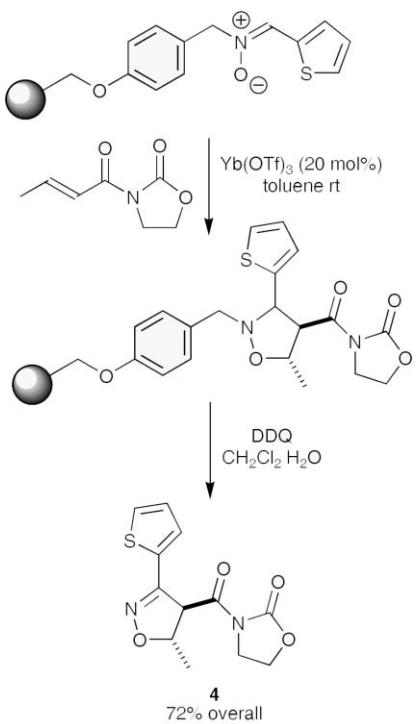
Scheme 2 Solid phase synthesis of 4-piperidones using a ytterbium(III) triflate-catalysed cycloaddition.



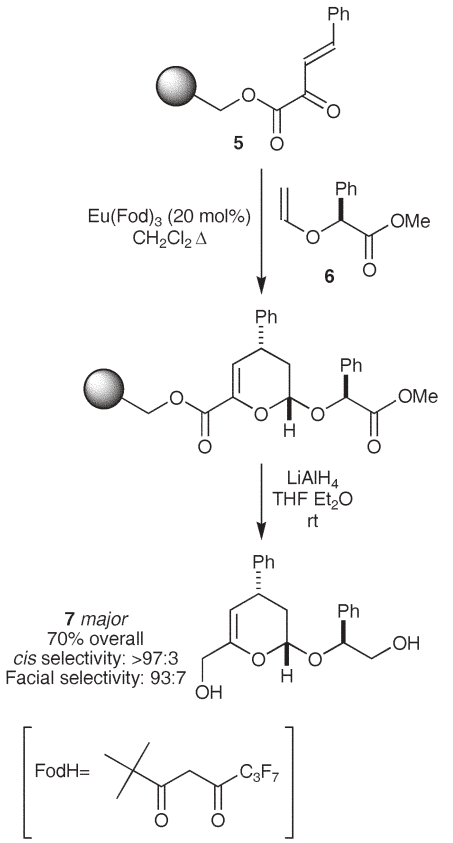
Scheme 3 Ytterbium(III) triflate-catalysed aza Diels–Alder reactions in a solid phase approach to piperidines.

good overall yield using a Heck reaction followed by cleavage from the support (Scheme 6).[8]

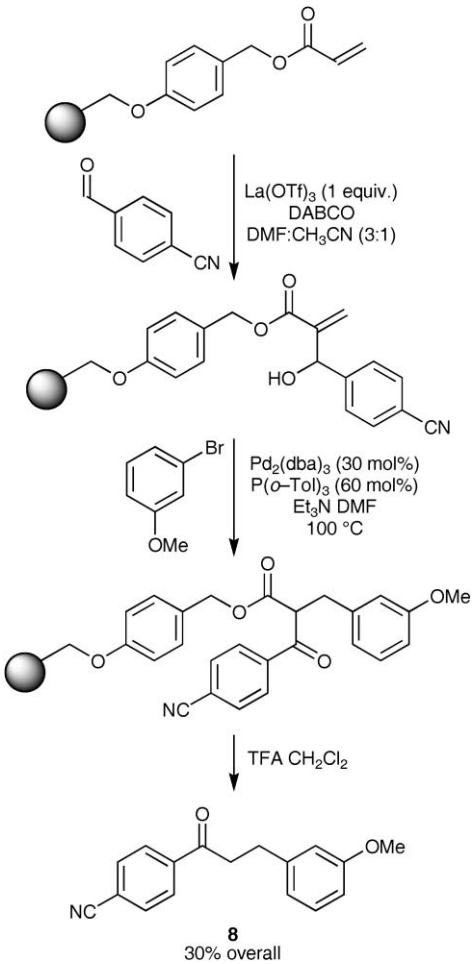
Meldal has exploited the stability of ytterbium(III) triflate under aqueous conditions in his application of the catalyst in an aldol condensation of a peptide aldehyde immobilised on a hydrophilic support.[9] The product **9** was obtained in good yield after cleavage from the support (Scheme 7).



Scheme 4 Ytterbium(III) triflate-catalysed 1,3-dipolar cycloadditions in a solid phase synthesis of 2-isoxazoline derivatives.



Scheme 5 Europium(III)-catalysed heterocycloaddition for the asymmetric solid-phase synthesis of substituted dihydropyrans.



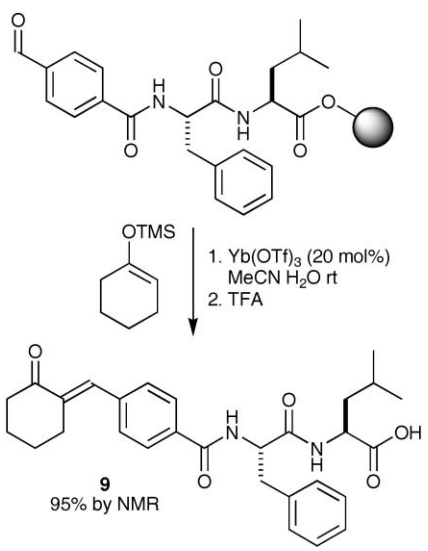
Scheme 6 Lanthanum(III) triflate-mediated Baylis–Hillman reactions of a supported acrylate.

Wang has used ytterbium(III) triflate to mediate the electrophilic cyclisation of a glyoxalate-derived, unsaturated imine **10**.[10] The cyclative cleavage strategy gives lactone **11** in good purity as only the desired product is released from resin and by-products are left attached to the support. The ytterbium(III)-mediated cyclisation proceeded with high *trans* selectivity (Scheme 8). The use of the hydrate of the ytterbium(III) salt proved to be crucial for efficient cyclisation.[10]

Kobayashi has recently reported the immobilisation of lanthanide(III) triflates by micro-encapsulation and has investigated the use of such catalysts in organic synthesis.[11] Janda has immobilised ytterbium(III) triflate using an ionic polymer and shown that the supported reagent is readily recoverable.[12]

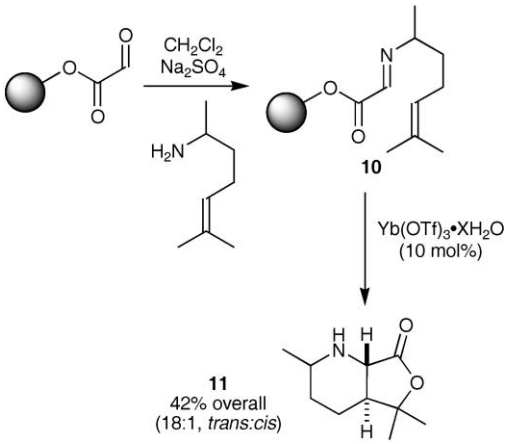
The development of chiral, solid-supported lanthanide(III) catalysts for use in asymmetric synthesis is currently an important area within the field. Shibasaki has developed heterobimetallic catalysts for a range of asymmetric transformations.[13] Many of these catalysts are based on lanthanide(III)-binol complexes. Recent studies have developed polymer-supported, linked-binol lanthanide catalysts, such as **12**, for asymmetric Michael additions. The addition of dibenzylmalonate to cyclohexenone, in the presence of catalyst **12**, gives **13** in good enantiomeric excess (Scheme 9).[14]

Sasai has developed supported lanthanide catalysts for the asymmetric epoxidation of enones.[15] Immobilised ytterbium(III) complexes derived from binol resins **14** and **15**



Scheme 7 Ytterbium(III) triflate-catalysed aqueous aldol condensation to prepare peptide isosteres.

gave epoxide **16** in high enantiomeric excess (Scheme 10). Sasai also showed these catalysts could be recovered and reused with no loss in enantioselectivity.[15]



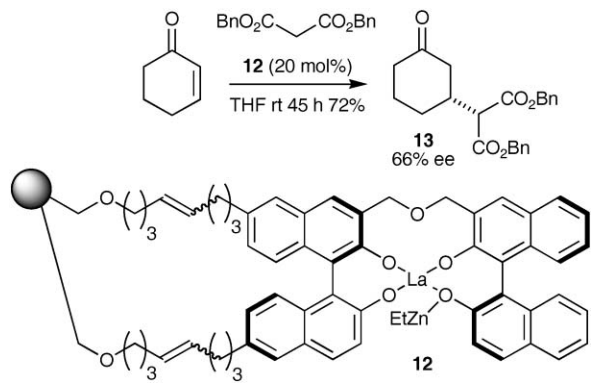
Scheme 8 A ytterbium(III) triflate-catalysed cyclative cleavage strategy.

High enantioselectivities have also been obtained in the ytterbium(III)-catalysed silylcyanation of benzaldehyde using a polymer-supported catalyst developed by Moberg.[16] Catalysts derived from ytterbium(III) chloride and pyridine-bis(oxazoline) ligand **17** immobilised on a Tentagel resin can be recovered and reused up to four times with little loss in activity (Scheme 11).[16]

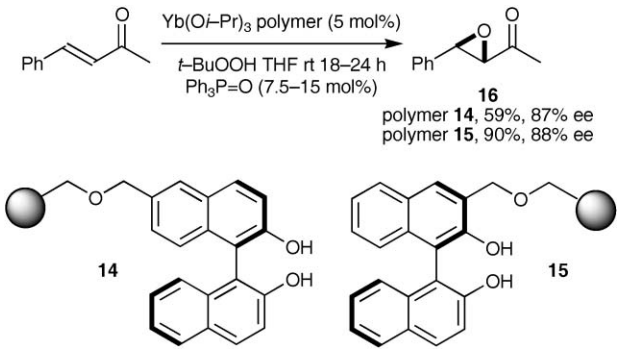
3. Lanthanide(IV) reagents

Cerium(IV) compounds are the most stable tetrapositive lanthanide species and are versatile one-electron oxidising agents. There are few examples of the use of lanthanide(IV) reagents in solid phase synthesis. Still used cerium(IV) ammonium nitrate (CAN) to oxidatively cleave molecular tags from a polymer support in his seminal work on the development of encoding methods for combinatorial chemistry.[17] Acylcarbenes bearing tags were used to encode Merrifield resin by reaction at unfunctionalised sites on the polymer backbone. The resulting encoded resin **18** can then be used for library synthesis. The tag can be read by electron capture gas chromatography (ECGC) after efficient cleavage of the tag using CAN (Scheme 12).[17]

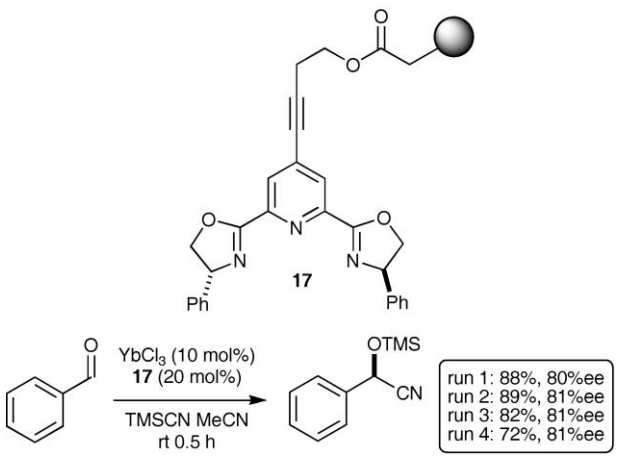
Fukase has used CAN to oxidatively cleave a *p*-acylaminophenyl linker and has illustrated the potential of the linker



Scheme 9 A polymer-supported, linked-binol lanthanide(III) catalyst for asymmetric Michael additions.



Scheme 10 A polymer-supported, binol ytterbium(III) catalyst for asymmetric enone epoxidation.



Scheme 11 A polymer-supported, ytterbium(III) pyridine-bis(oxazoline) catalyst.

system for use in solid-phase carbohydrate synthesis (Scheme 13).[18]

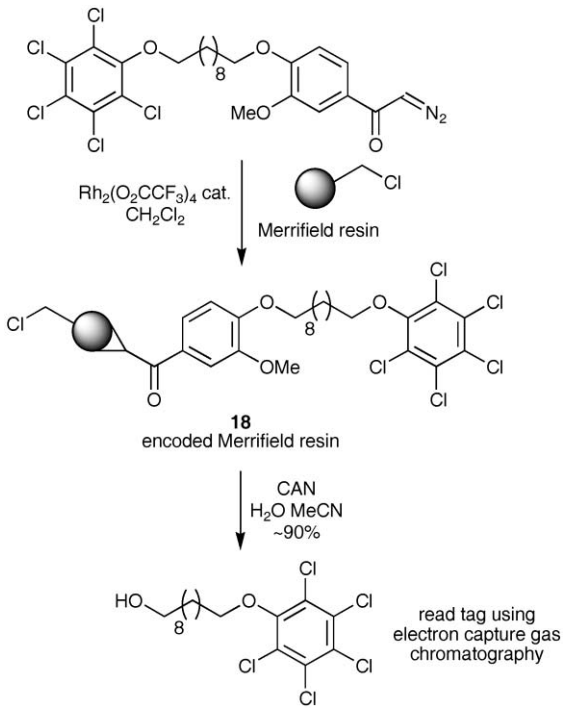
Floreancig has recently described a new solid-phase linker system cleaved by oxidative electron transfer using CAN.[19] The cleavage process is based on the oxidative fragmentation of homobenzylic ethers. On treatment with CAN, vinyl acetate **19**, immobilised on a soluble oligonorbornene scaffold prepared by ring-opening metathesis polymerisation (ROMP), undergoes a cyclorelease process to give pyranone **20** as a single diastereoisomer (Scheme 14).[19]

Cleavage occurs *via* radical fragmentation and formation of the benzylic radical **21** and oxonium ion **22** (Scheme 15).[19] The latter then cyclises to give the observed product **20**.

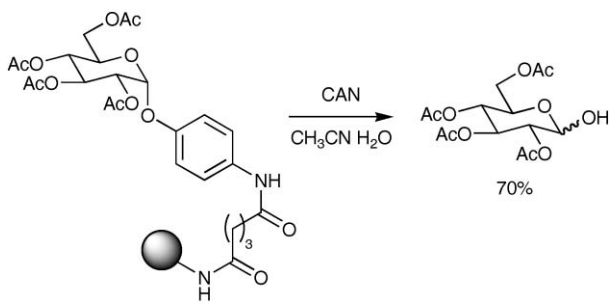
4. Lanthanide (II) reagents

Due to the propensity for lanthanide(II) complexes to revert to the more stable lanthanide(III) oxidation state, these species are one-electron reducing agents. The single electron transfer reagent samarium(II) iodide (SmI_2) has been used extensively to mediate radical and organometallic reactions in solution[20] and has now begun to find application in solid phase organic synthesis.

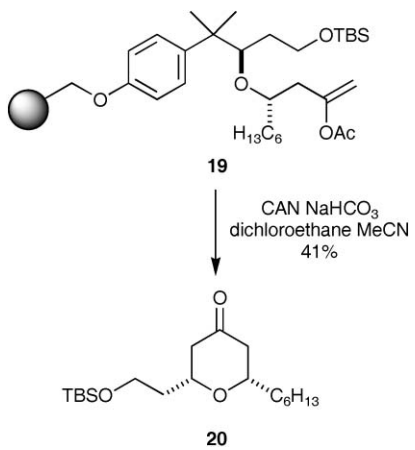
The first use of SmI_2 in solid phase chemistry was reported by Armstrong in 1997.[21] An efficient synthesis of benzofuran



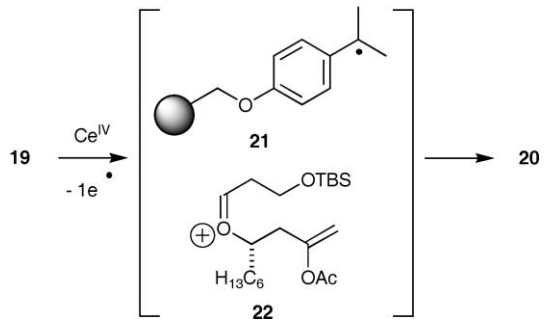
Scheme 12 Cleavage of encoding tags using cerium(IV) ammonium nitrate.



Scheme 13 Cleavage of a linker for carbohydrate synthesis using cerium(IV) ammonium nitrate.



Scheme 14 Cleavage of a homobenzylic ether linker using cerium(IV) ammonium nitrate.



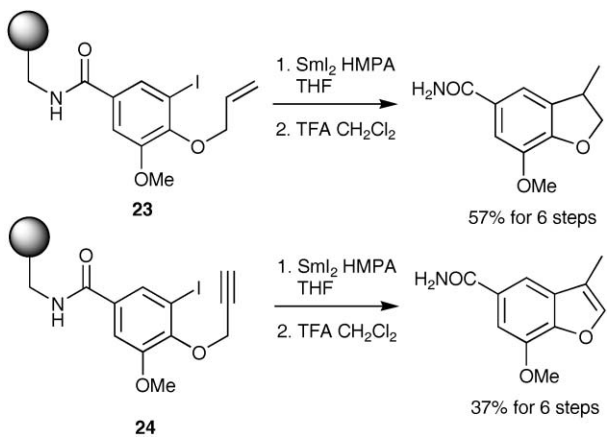
Scheme 15 The mechanism of cleavage of a homobenzylic ether linker using cerium(IV).

derivatives on solid support was achieved by SmI_2-mediated cyclisation of unsaturated aryl iodides such as **23** and **24**, attached to a Rink resin. Benzofuran products were obtained in good yield after cleavage of the products from the support. Armstrong found that substrates immobilised using PEG (polyethylene glycol) grafted resins also underwent efficient cyclisation with the added advantage that samarium(III) salts could be easily washed from the support after the reaction (Scheme 16).[21]

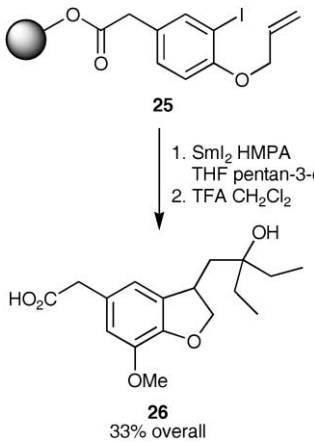
In an extension of his studies, Armstrong carried out sequential processes where the intermediate radicals from the cyclisation of iodides such as **25**, immobilised on a TentaGel support, were reduced further by a second equivalent of SmI_2 and the resultant organosamarium captured by a carbon electrophile to give adducts such as **26** (Scheme 17).[22]

Armstrong's pioneering work was crucial in that it illustrated the compatibility of samarium(II) reagents with the common classes of polymer support.

Linhardt has employed organosamarium additions to carbon electrophiles in a solid phase synthesis of *C*-sialosides.[23] Sialyl donor **27**, immobilised on an amino-functionalised, controlled pore glass support, was treated with SmI_2 in the presence of ketone and aldehyde electrophiles, *e.g.* reaction of **27** with cyclopentanone gave adduct **28** (Scheme 18). Cleavage from the support gave *C*-glycoside **29** in good overall yield. The *C*-glycosylation step proceeds *via* one-electron



Scheme 16 Samarium(II)-mediated cyclisations in a solid phase synthesis of benzofurans.

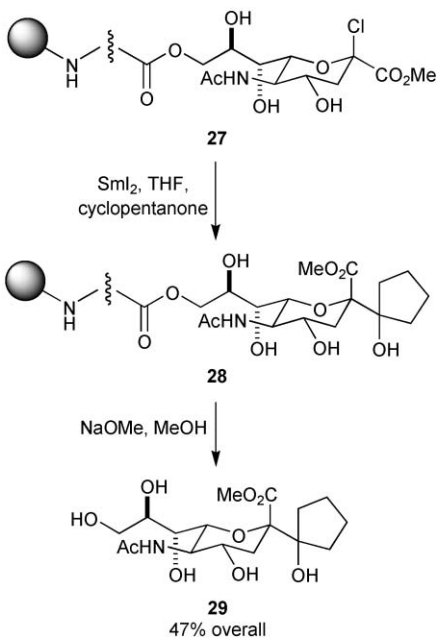


Scheme 17 Radical cyclisation–anion trapping using SmI_2.

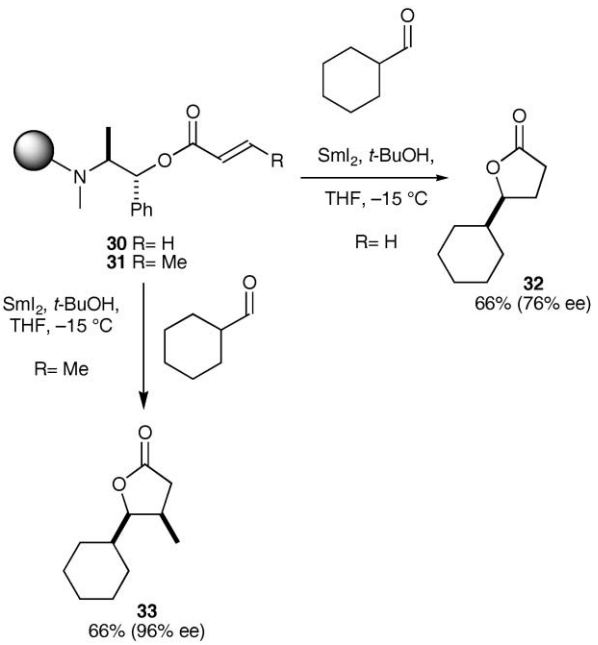
reduction of **27** to give a glycosyl radical that is then reduced further to the corresponding organosamarium.[23]

We have reported the intermolecular reductive coupling of aldehydes and ketones with α,β-unsaturated esters, immobilised using an ephedrine chiral resin, to give enantiomerically enriched γ-butyrolactones.[24]

For example, treatment of acrylate and crotonate ephedrine resins **30** and **31** with cyclohexanecarboxaldehyde, employing SmI_2 in THF with *tert*-butyl alcohol as a proton source, gave lactones **32** and **33** respectively, in moderate yield and good to high enantiomeric excess (Scheme 19). The process can be considered as an example of an asymmetric catch and release process, where a substrate immobilised on a chiral support captures a reactive intermediate, in this case a ketyl radical anion, from solution.[24] The chiral support controls the asymmetry of the capture step and leads to a diastereomeric, resin-bound intermediate that breaks down to release a non-racemic product.



Scheme 18 Reductive coupling of a glycosyl chloride with a ketone using SmI_2.



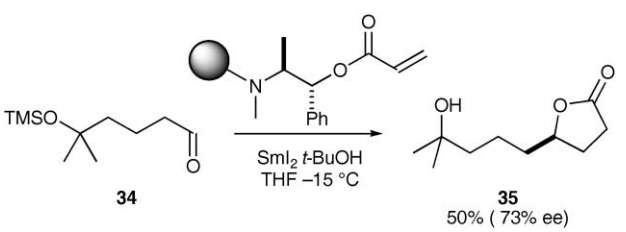
Scheme 19 An asymmetric catch and release approach to γ-butyrolactones using SmI_2.

We have used the approach in a short, asymmetric synthesis of γ-butyrolactone **35**, a moderate DNA-binding metabolite isolated from *Streptomyces* GT61115, starting from aldehyde **34** (Scheme 20).[24]

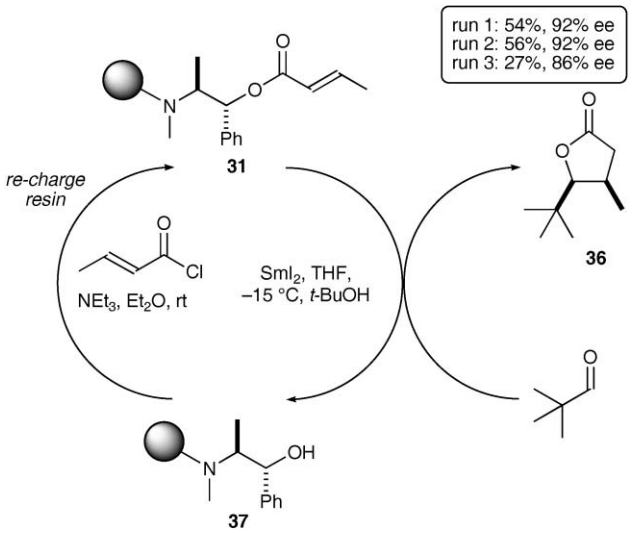
In further studies, we have investigated the feasibility of recycling the chiral ephedrine resin:[25] Employing crotonate resin **31** and 2,2-dimethylpropanal gave lactone **36** in 54% yield and 92% ee (Scheme 21). Recovery of the ephedrine resin **37** and re-esterification with crotonyl chloride gave recycled **31**. Re-treatment with 2,2-dimethylpropanal gave **36** in virtually identical yield and enantiomeric excess. Recovery and re-use for a third time, however, led to a substantially lower yield although the enantioselectivity of the process was still high (86% ee).[25]

SmI_2 is also a useful reagent for functional group reductions. Ito has employed SmI_2 to reduce a nitro group in a solid phase carbohydrate synthesis.[26] Treatment of immobilised monosaccharide **38** with SmI_2 triggers cyclative-cleavage and release of **39** from the support in good yield (Scheme 22).[26]

The mild, neutral electron-transfer conditions associated with the use of SmI_2 makes the reagent ideal for the selective cleavage of linkers in solid phase organic synthesis.



Scheme 20 An application of asymmetric catch and release in target synthesis.



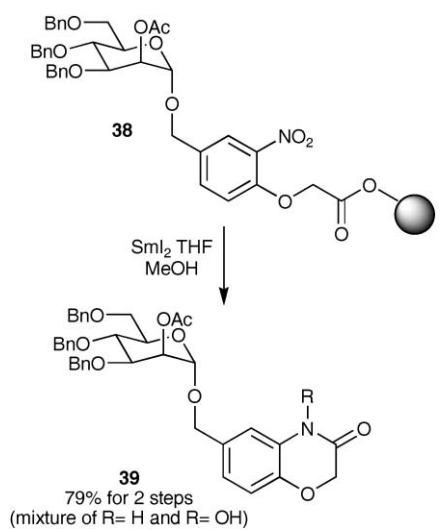
Scheme 21 Recycling of a chiral resin in an asymmetric approach to γ-butyrolactones using SmI_2.

Abell has developed a linker strategy for the synthesis of amides and ureas based on the reduction of N–O bonds by SmI_2.[27] Wang-based hydroxylamine resin **40** was used to prepare a range of immobilised ureas and amides, such as **41**. Traceless cleavage of the linker gave amide **42** in good overall yield and in high purity (Scheme 23).[27]

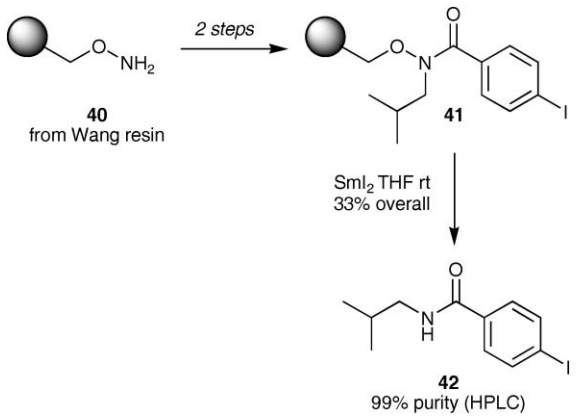
A related linker strategy has been utilised by Taddei in a solid phase approach to β-lactams.[28] Treatment of immobilised substrate **43** with SmI_2 resulted in smooth reduction and release of **44** from the support (Scheme 24), further illustrating the suitability of the electron-transfer cleavage approach for the synthesis of highly functionalised targets (Scheme 24).[28]

A similar N–O linker, cleaved using SmI_2, has been used by Andersson in a solid phase approach to tertiary amines.[29]

De Clercq has utilised a sulfone linker in a solid phase Julia-type olefination process.[30] Olefins were released from α-benzoyloxy sulfone resins, such as **45**, upon reduction with a



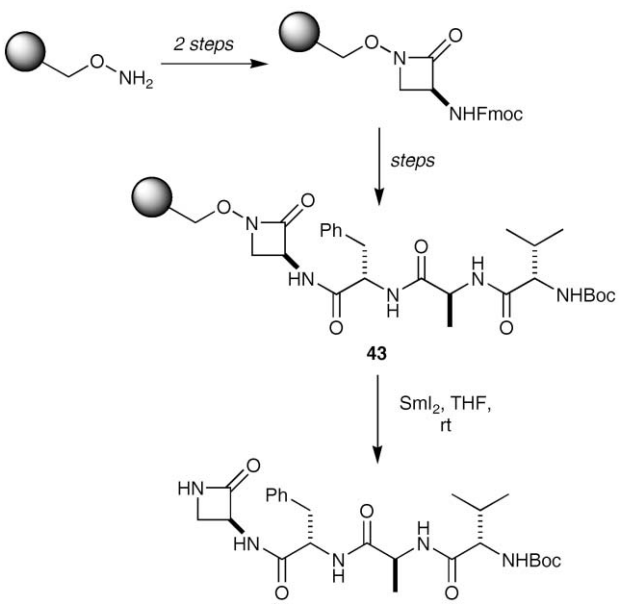
Scheme 22 Nitro group reduction using SmI_2 in a solid phase carbohydrate synthesis.



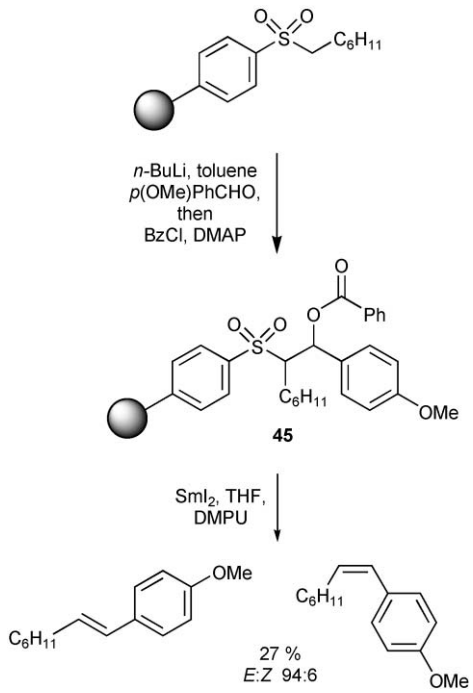
Scheme 23 A solid phase synthesis of amides using an N–O linker cleaved using SmI_2.

single electron transfer reagent and elimination of the sulfone linkage (Scheme 25). SmI_2 proved to be the most suitable reagent for the process and was used with the promoters HMPA and DMPU.[30] The stereoselectivity of the olefination was found to be strongly dependant upon the additive, DMPU giving rise to higher *E* selectivities than HMPA (Scheme 25).

We have developed a new class of linker for the synthesis of carbonyl compounds that is cleaved using SmI_2.[31] The cleavage of α heteroatom-substituted carbonyl or HASC linkers is based on the well-established reduction of an α heteroatom-substituted carbonyl compound to the parent ketone, ester or amide using SmI_2. Lactone **46**, immobilised *via* an oxygen HASC linker, was converted to a range of ketones and amides, including **47** and **48** (Scheme 26). Treatment with SmI_2 released cyclopropyl ketone **49** and morpholine amide **50** respectively from the support in good overall yield.[31]

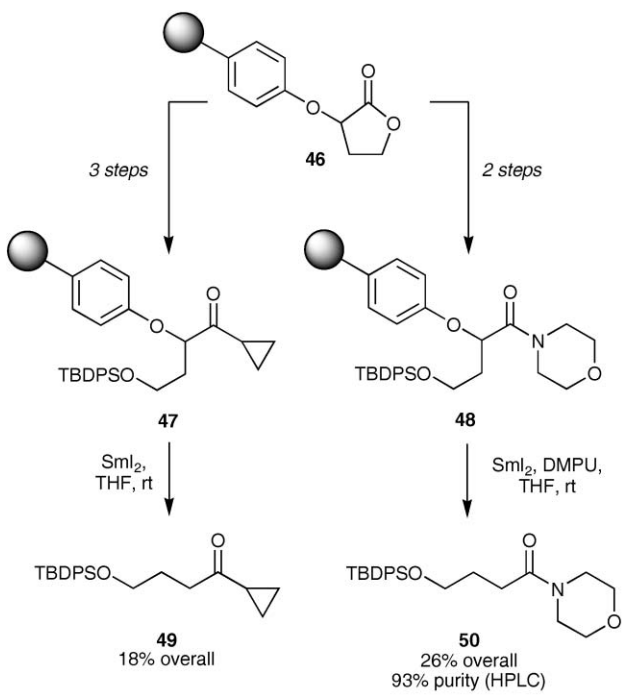


Scheme 24 A solid phase synthesis of β-lactams using an N–O linker cleaved using SmI_2.

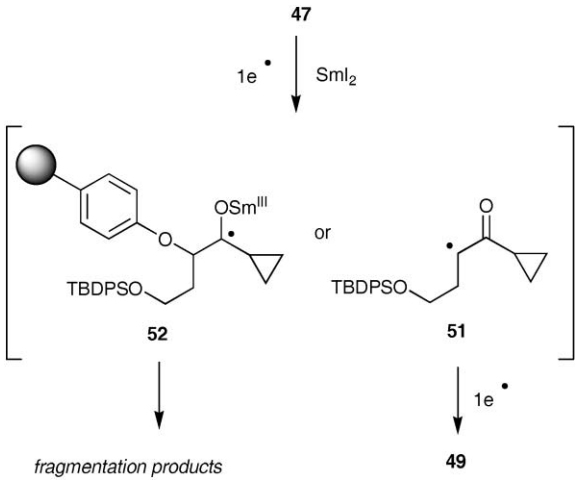


Scheme 25 A solid phase Julia-type olefination process using SmI_2 as the reductant.

We prepared immobilised cyclopropyl ketone **47** to probe the mechanism of the cleavage reaction.[32] Isolation of **49** where the cyclopropyl ring is intact suggests that cleavage proceeds *via* formation of radical **51** rather than ketyl radical anion **52**, formed by single-electron transfer to the ketone carbonyl, as cyclopropylmethyl radical anions are known to undergo facile fragmentation (Scheme 27).[32]



Scheme 26 Solid phase synthesis of ketones and amides using an ether linker cleaved using SmI_2.

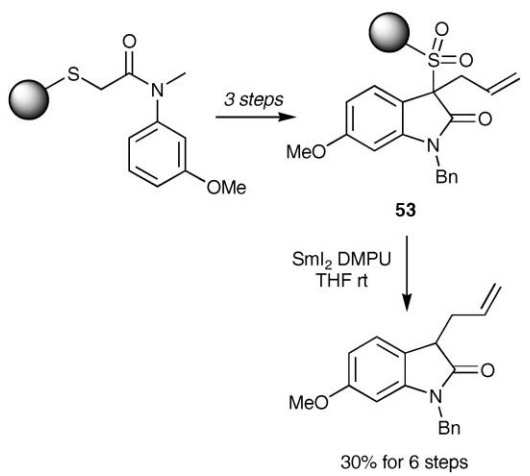


Scheme 27 Mechanistic investigations of the Sm(II)-mediated cleavage of an ether linker.

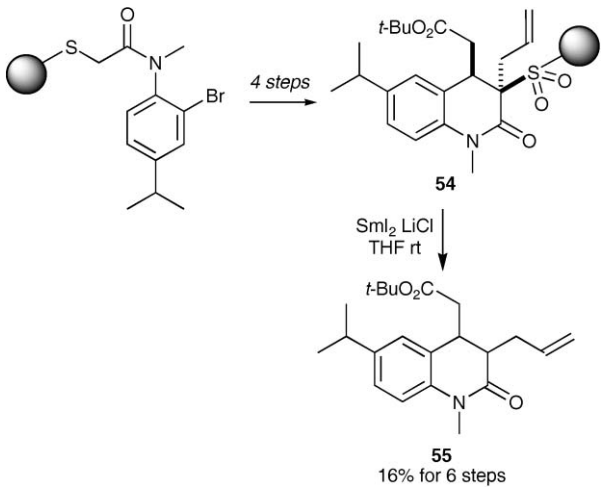
We have also utilised a sulfur HASC linker for the solid phase synthesis of N-heterocycles. A route to oxindoles has been developed that employs the first Pummerer cyclisations on solid phase to construct the heterocyclic ring system.[33] Treatment of immobilised substrates such as **53** with SmI_2 releases oxindoles from the support in good overall yield (Scheme 28).

We have also used the sulfur linker in a route to tetrahydroquinolones that involves a microwave-assisted Heck reaction followed by a Michael cyclisation.[34] At the end of the sequence, tetrahydroquinolines such as **55** are released from the polymer support by reduction of intermediate sulfones **54** with SmI_2. In this case LiCl is used to increase the reducing ability of the lanthanide reagent (Scheme 29).[34]

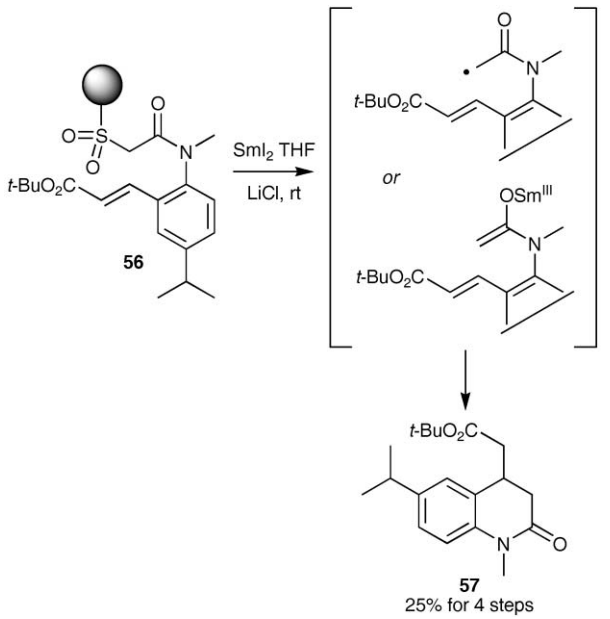
In the same study, we have illustrated the feasibility of a cyclative-cleavage strategy using the linker family.[34] Treatment of immobilised sulfone **56** with SmI_2 results in cleavage and cyclisation to give tetrahydroquinoline **57**. This cyclisation may proceed by either a radical or anionic mechanism (Scheme 30).[34]



Scheme 28 A solid phase route to oxindoles using a sulfide linker cleaved using SmI_2.



Scheme 29 A solid phase route to tetrahydroquinolones using a sulfide linker cleaved using SmI_2.



Scheme 30 Cyclative-cleavage using a sulfide linker cleaved using SmI_2.

We have also shown the sulfide HASC linker to be effective in fluorous phase synthesis, where the polymer phase tag is replaced by a perfluoroalkyl group.[35]

5. Conclusions

As lanthanide(III) compounds approach routine status as reagents for solid phase synthesis, the use of lanthanide(III)-mediated reactions for library synthesis and the development of polymer-supported lanthanide(III) catalysts for asymmetric synthesis have become the focus for future advancements.

In contrast, the use of lanthanide(IV) and lanthanide(II) reagents in solid phase synthesis are areas in their infancy. Successfully harnessing the power of samarium(II) for use with supported substrates, in particular, promises benefits in library synthesis, asymmetric methodology and the design of new linker systems. With the compatibility of the samarium(II) system now established with a variety of polymer supports, the way is clear to exploit the full potential of the low-valent lanthanide reagent in solid phase synthesis.

References

1 P. G. Steel, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2727.
2 S. Kobayashi, *Synlett*, 1994, 689.
3 Y. Wang and S. R. Wilson, *Tetrahedron Lett.*, 1997, **38**, 4021.
4 J. Barluenga, C. Mateos, F. Aznar and C. Valdés, *Org. Lett.*, 2002, **4**, 3667.
5 W. Zhang, W. Xie, J. Fang and P. G. Wang, *Tetrahedron Lett.*, 1999, **40**, 7929.
6 S. Kobayashi and R. Akiyama, *Tetrahedron Lett.*, 1998, **39**, 9211.
7 G. Dujardin, S. Leconte, L. Coutable and E. Brown, *Tetrahedron Lett.*, 2001, **42**, 8849.
8 B. A. Kulkarni and A. Ganesan, *J. Comb. Chem.*, 1999, **1**, 373.
9 A. Graven, M. Grøtli and M. Meldal, *J. Chem. Soc., Perkin Trans. 1*, 2000, 955.
10 Q. Jia, W. Xie, W. Zhang, A. Janczuk, S. Luo, B. Zhang, J. P. Cheng, M. B. Ksebati and P. G. Wang, *Tetrahedron Lett.*, 2002, **43**, 2339.
11 S. Kobayashi, Polymer-Supported Rare Earth Catalysts Used in Organic Synthesis, in *Lanthanides: Chemistry and Use in Organic Synthesis*, ed. S. Kobayashi, Springer, 1999, 285 and references therein.
12 B. Se Lee, S. Mahajan and K. D. Janda, *Tetrahedron Lett.*, 2005, **46**, 807.
13 M. Shibasaki, H. Sasai and T. Arai, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1236.
14 S. Matsunaga, T. Ohshima and M. Shibasaki, *Tetrahedron Lett.*, 2000, **41**, 8473.
15 D. Jayaprakash, Y. Kobayashi, S. Watanabe, T. Arai and H. Sasai, *Tetrahedron: Asymmetry*, 2003, **14**, 1587.
16 S. Lundgren, S. Lutsenko, C. Jönsson and C. Moberg, *Org. Lett.*, 2003, **5**, 3663.
17 H. P. Nestler, P. A. Bartlett and W. C. Still, *J. Org. Chem.*, 1994, **59**, 4723.
18 K. Fukase, K. Egusa, Y. Nakai and S. Kusumoto, *Mol. Diversity*, 1997, **2**, 182.
19 H. Liu, S. Wan and P. E. Floreancig, *J. Org. Chem.*, 2005, **70**, 3814.
20 D. J. Edmonds, D. Johnston and D. J. Procter, *Chem. Rev.*, 2004, **104**, 3371 and references therein.
21 X. Du and R. W. Armstrong, *J. Org. Chem.*, 1997, **62**, 5678.
22 X. Du and R. W. Armstrong, *Tetrahedron Lett.*, 1998, **39**, 2281.
23 S. N. Baytas, Q. Wang, N. A. Karst, J. S. Dordick and R. J. Linhardt, *J. Org. Chem.*, 2004, **69**, 6900.
24 N. J. Kerrigan, P. C. Hutchison, T. D. Heightman and D. J. Procter, *Chem. Commun.*, 2003, 1402.
25 N. J. Kerrigan, P. C. Hutchison, T. D. Heightman and D. J. Procter, *Org. Biomol. Chem.*, 2004, **2**, 2476.
26 S. Manabe, Y. Nakahara and Y. Ito, *Synlett*, 2000, 1241.
27 R. M. Myers, S. P. Langston, S. P. Conway and C. Abell, *Org. Lett.*, 2000, **2**, 1349.
28 M. M. Meloni and M. Taddei, *Org. Lett.*, 2001, **3**, 337.
29 M. Gustafsson, R. Olsson and C.-M. Andersson, *Tetrahedron Lett.*, 2001, **42**, 133.
30 J. N. P. D'herde and P. J. De Clercq, *Tetrahedron Lett.*, 2003, **44**, 6657.
31 F. McKerlie, D. J. Procter and G. Wynne, *Chem. Commun.*, 2002, 584.
32 F. McKerlie, I. M. Rudkin, G. Wynne and D. J. Procter, *Org. Biomol. Chem.*, 2005, **3**, 2805.
33 L. A. McAllister, S. Brand, R. de Gentile and D. J. Procter, *Chem. Commun.*, 2003, 2380.
34 K. L. Turner, T. M. Baker, S. Islam, D. J. Procter and M. Stefaniak, *Org. Lett.*, 2006, **8**, 329.
35 L. A. McAllister, R. A. McCormick, S. Brand and D. J. Procter, *Angew. Chem., Int. Ed.*, 2005, **44**, 452.