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## Abstract

This review highlights the advances in the literature up to July 2008 on the intermolecular reactions of acyclic and cyclic N-acyliminium ions. This is an update of an earlier review in 2000 on this topic and does not include intramolecular addition reactions to N-acyliminium ions which was recently reviewed. This review is presented in two parts, with the first part dealing with acyclic and pyrrolidinone-based N-acyliminium ions. Part II continues with other five-membered heterocyclic derivatives and higher systems.



## Keywords

reactions, addition, intermolecular, i, acyliminium, part, ions, n, CMMB


## Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences


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# Intermolecular Addition Reactions of *N*-Acyliminium Ions (Part I)[1]

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**Abstract:** This review highlights the advances in the literature up to July 2008 on the intermolecular reactions of acyclic and cyclic *N*-acyliminium ions. This is an update of an earlier review in 2000 on this topic and does not include intramolecular addition reactions to *N*-acyliminium ions which was recently reviewed. This review is presented in two parts, with the first part dealing with acyclic and pyrrolidinone-based *N*-acyliminium ions. Part II continues with other five-membered heterocyclic derivatives and higher systems.



**Key words:** *N*-acyliminium ion, nucleophilic addition, cycloaddition, aromatic electrophilic substitution, radical addition, peptides, pyrrolidines, piperidines

## 1 Introduction

This review highlights the advances in the literature up to July 2008 on the intermolecular reactions of acyclic and cyclic *N*-acyliminium ions. This is an update of an earlier review in 2000[2] on this topic and does not include intramolecular addition reactions to *N*-acyliminium ions which was recently reviewed.[3] A review article on addition reactions to related, but less reactive, *N*-acylimines has also been recently published.[4]

The highly reactive nature of *N*-acyliminium ions require that they are generated in situ usually in the presence of the other reactive, electron-rich, nucleophilic partner (NuY, Y = metal, $SiR_3$, $SnR_3$, etc.). In general these intermediates are generated from more stable and isolatable α-substituted *N*-acylamines of the type **1** by treatment with a Lewis acid or sometimes a protic acid (Scheme 1). The reaction of **2** with a nucleophilic species (NuY) then gives α-substituted *N*-acylamine **3**. Compounds **1**–**3** can be acyclic systems or $R^1$ and $R^2$, $R^2$ and $R^3$, $R^1$ and $R^3$ can be taken together to form part of a ring system as shown in the general structures **4**, **5**, and **6**.

Compounds like **1** (X = OH and $NHCO_2R$) are most likely formed in situ from the Lewis acid promoted three-component, one-pot coupling reactions of carbamates, aldehydes (or acetals) and silyl nucleophiles or electron-rich aromatic nucleophiles (Scheme 2).[5,6]

*N*-Acyliminium ions like **11** can also be generated in dichloromethane solution, in the absence of nucleophiles, by the electrochemical oxidation of *N*-trimethylsilylmethyl carbamates like **10** (Scheme 3). These intermediates have been characterised spectroscopically and were sub-

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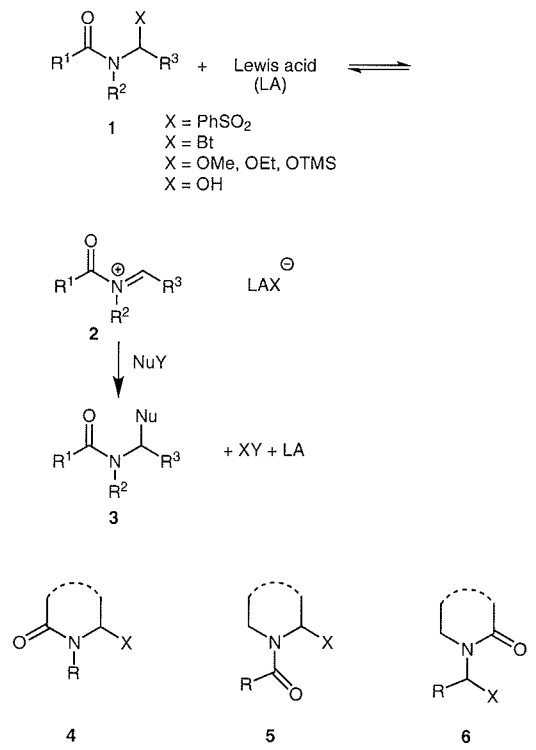
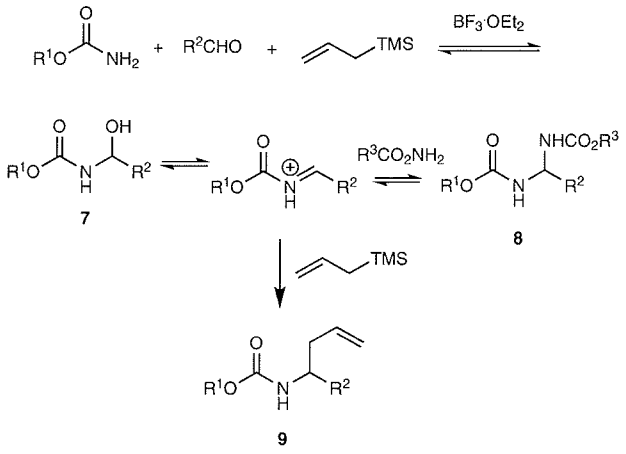
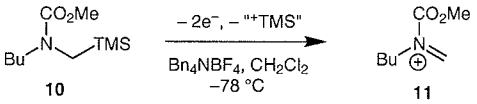



Scheme 1

sequently treated with nucleophiles or dipolarophiles to give addition products.[7–9]




Scheme 2




Scheme 3

## 2 Acyclic *N*-Acyliminium Ions

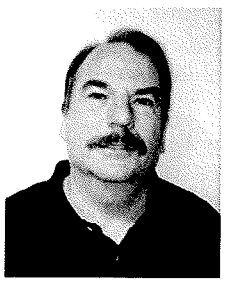
### 2.1 Synthesis of Acyclic *N*-Acyliminium Ion Precursors

Acyclic *N*-acyliminium precursors of the type **1** are generally synthesised from the coupling of an amide or carbamate with an aldehyde in the presence of HX or MX.[4,10]

α-Sulfonyl-*N*-alkyl amides and α-sulfonyl-*N*-alkyl carbamates **12** are useful precursors of acyclic *N*-acylimini-

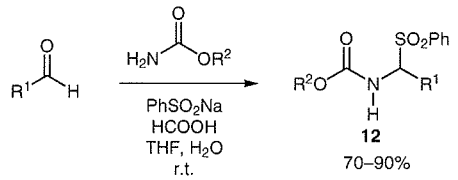
## Biographical Sketches

**Arife Yazici** obtained her MSc degree in chemistry at Hacettepe University-Ankara (Turkey) in 2005. She is currently doing her PhD studies with Professor Stephen Pyne at the University of Wollongong. Her area of study is the total synthesis of Stemona alkaloids.



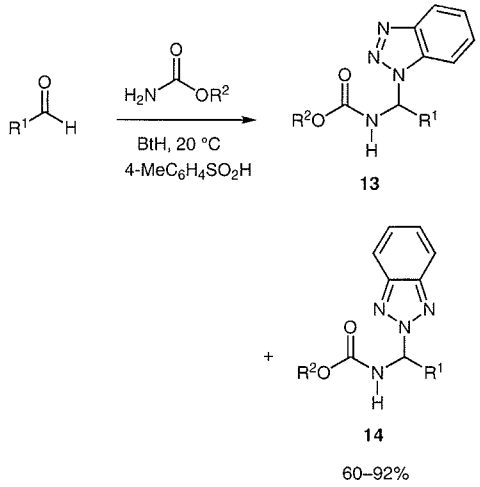
**Stephen G. Pyne** is a Professor of Chemistry at the University of Wollongong (UOW) and Chair of the Division of Organic Chemistry of the Royal Australian Chemical Institute. He obtained his BSc (Hons) degree at the University of Adelaide with Dr. Ralf Massey-Westrop and his PhD degree with Professor Lew Mander (Australian National University) in 1979. After post-doctoral positions with Professor Phil Fuchs (Purdue) and Professor E. J. Corey (Harvard), he was appointed as a lecturer at UOW in 1985. His research interests include the total synthesis of bioactive alkaloids, natural products chemistry, drug design and synthesis, and fullerene chemistry.

um ions since they are often stable solids. They can be prepared by the coupling reaction of amides or carbamates with an aldehyde in the presence of benzenesulfinic acid or its salt (Scheme 4).[11–13]



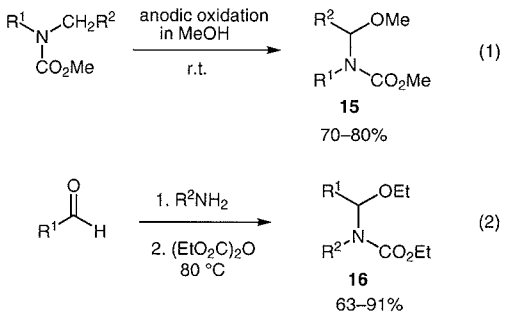

**Scheme 4**

α-Carbamylalkylbenzotriazole derivatives **13** and **14** can be prepared from the coupling of carbamates, benzotriazole and aldehydes (Scheme 5). These benzotriazole adducts are usually formed as a mixture of 1-yl **13** and 2-yl **14** isomers. These regioisomers, however, are both readily converted into the same *N*-acyliminium ion.[6,14,15]



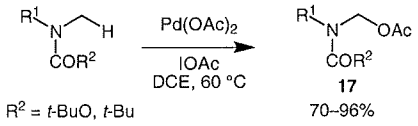

**Scheme 5**

α-Alkoxycarbamates **15** and **16** can be obtained from the electrochemical oxidation of carbamates in methanolic solution[16] (Scheme 6, equation 1) or from the reaction of primary amines with aldehydes, followed by reaction with diethyl pyrocarbonate (Scheme 6, equation 2).[17,18]



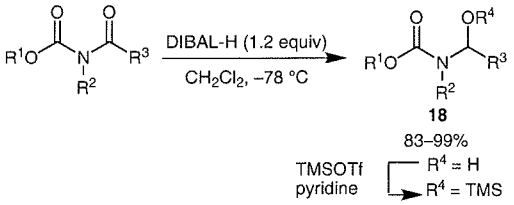

**Scheme 6**

α-Acetoxycarbamate and amide derivatives **17** can be synthesised from the corresponding *N*-methylcarbamates and amides by palladium-catalysed oxidation (Scheme 7).[19]



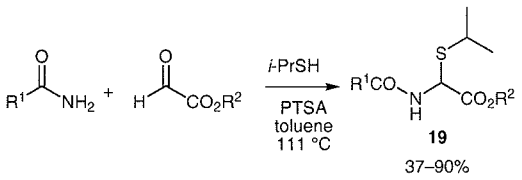

**Scheme 7**

α-Hydroxycarbamate derivatives **18** can be prepared by the partial reduction of imides using diisobutylaluminium hydride (Scheme 8). Although other reducing agents, such as sodium borohydride, are effective for the reduction of cyclic imides, only diisobutylaluminium hydride was effective for acyclic imides.[20,21]



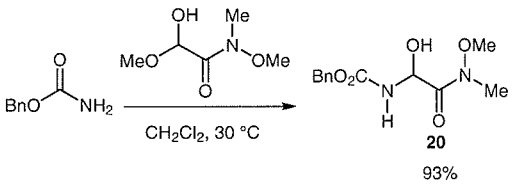

**Scheme 8**

α-Alkylthiocarbamates **19** can be synthesised from the three-component condensation of amides or carbamates with isopropylmercaptan and glyoxylic acid or its ester derivatives (Scheme 9).[22]




**Scheme 9**

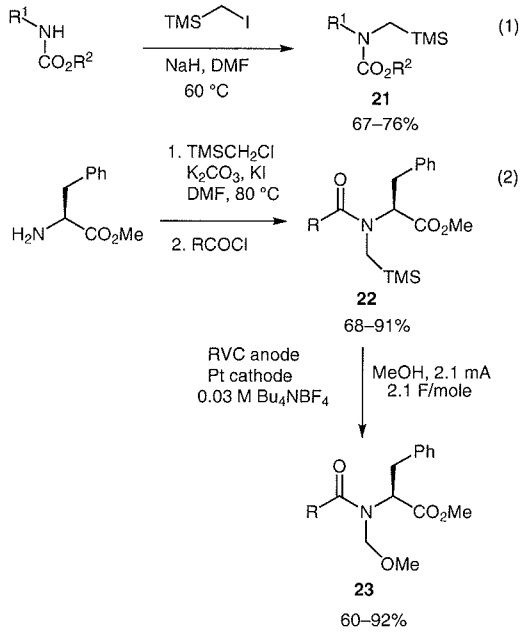
Weinreb amide derivatives **20** can be obtained from the condensation of carbamates with the corresponding hemiacetal (Scheme 10).[23]




**Scheme 10**

Carbamates **21**, having a *N*-silylmethyl substituent, can be easily synthesised from the reaction of carbamates with α-silylalkyl iodides under basic conditions (Scheme 11,

equation 1). They can be used to generate *N*-acyliminium ions by anodic oxidation (Scheme 3).[7–9] Alternatively, these compounds can be prepared by N-alkylation of amines with α-silylalkyl chlorides and then N-acylation of the resulting *N*-silylmethylamine (Scheme 11, equation 2). The *N*-trimethylsilylmethyl amides **22** can be converted into *N*-methoxymethyl carbamates **23** upon anodic oxidation in methanol or by oxidation with ceric ammonium nitrate (see Scheme 18).[24]



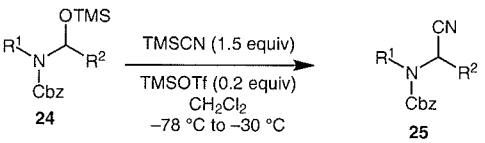

**Scheme 11**

## 2.2 Reactions of Acyclic *N*-Acyliminium Ions

### 2.2.1 Reactions with Nucleophiles

#### 2.2.1.1 Silicon-Based Nucleophiles

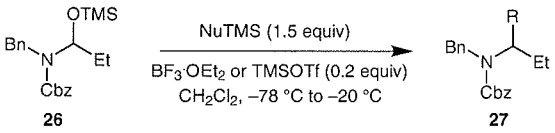
Allylsilanes and silyl enol ethers constitute the largest class of silicon-based nucleophiles that have been treated with in situ generated *N*-acyliminium ions. The α-trimethylsilyloxy carbamates **24** reacted with trimethylsilyl cyanide in the presence of trimethylsilyl triflate (0.2 equiv) at –78 °C to –20 °C to give nitriles **25** in high yields (Scheme 12).[20]




$R^1$ = Bn, Et, *i*-Pr
$R^2$ = Ph, -$(CH_2)_2CH{=}CH_2$, -$(CH_2)_2CHOTBS$, -$CH_2CHBr$, Et

**Scheme 12**

In a limited study the α-trimethylsilyloxy carbamate **26** gave products **27** upon treatment with three different silicon-based nucleophiles (Scheme 13).[20]




| NuTMS | R | Yield (%) |
|---|---|---|
| $CH_2{=}CHCH_2TMS$, | $-CH_2CH{=}CH_2$ | 83 (77)[a] |
| $CH_2{=}C(OTBS)Ph$, | $-CH_2COPh$ | 93 (81)[a] |
| $HC{\equiv}CCH_2TMS$ | $-CH{=}CH{=}CH_2$ | 85 |

[a] yield when TMSOTf used

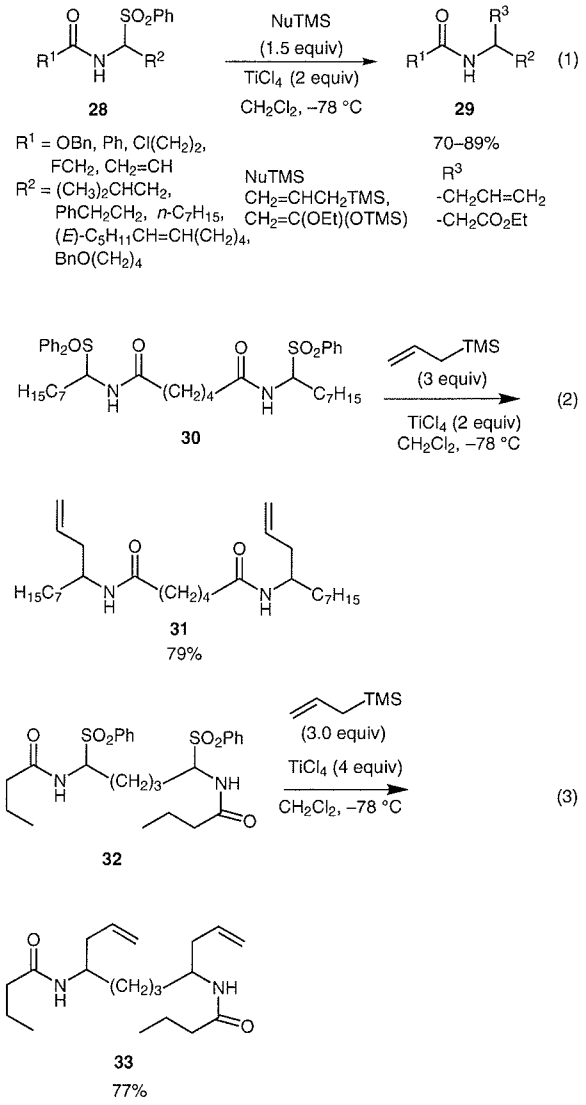
**Scheme 13**

The α-amido sulfones **28** reacted with silicon nucleophiles (1.5 equiv) in the presence of titanium(IV) chloride (2 equiv) to give adducts **29** in 70–89% yields. Halogen-containing substrates were also efficient in the allylation reaction (Scheme 14, equation 1). The bisamido sulfones **30** and **32** were treated with allyltrimethylsilane under the same reaction conditions to give the corresponding bisallylated products **31** and **33** in good yields (Scheme 14, equations 2 and 3).[10]

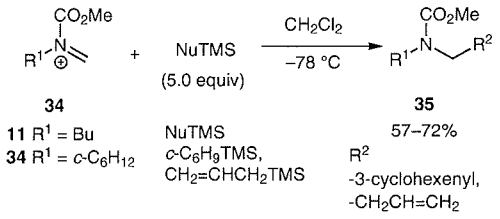
The *N*-acyliminium ions **11** and **34**, which were generated by electrochemical oxidation from the corresponding *N*-silylmethylcarbamates (Scheme 3), reacted with allyltrimethylsilane and 3-trimethylsilylcyclohexene to give the corresponding adducts **35** in 57–72% yields (Scheme 15).[9]

The one-pot three-component coupling reaction of *N*-acyliminium ion **11** with enamine **36** and silicon nucleophiles afforded products **39** in 52–68% yields. The *N*-acyliminium ion **11** first reacted with the enamine **36** to form the new cationic species **37**. The resulting cation, which was assumed to be an equilibrium mixture of **37** and **38**, was then treated with nucleophiles to give the products **39** as diastereomeric mixtures. The major *trans* isomer most likely was a result of attack on the iminium **37** from the face *anti* to the ring C-3 substituent or from an $S_N2$-like attack on the bridged cationic intermediate pyrrolidine **38**. The reaction of the *N*-acyliminium ion **11** with six-membered-ring analogues of enamine **36** and allyltrimethylsilane gave the corresponding six-membered analogues of product **39** in 62% yield and with a *trans*/*cis* ratio of 91:9. Treatment of the *N*-cyclohexyl analogue of the *N*-butyl *N*-acyliminium ion **11** with allyltrimethylsilane afforded the corresponding *N*-cyclohexyl analogue of **39** in 70% yield and with a diastereomeric ratio of 91:9.[25] The analogous *tert*-butyl carbamate of **36** gave the *tert*-butyl analogue of **39** in the same yield and with the same *trans*/*cis* diastereoselectivity (Scheme 16).[26]

The use of vinyl sulfide **40** as an olefinic component in the three-component coupling reaction of the *N*-acyliminium ion **11** and silicon nucleophiles gave the products **41** in 56–75% yields (Scheme 17).[25]

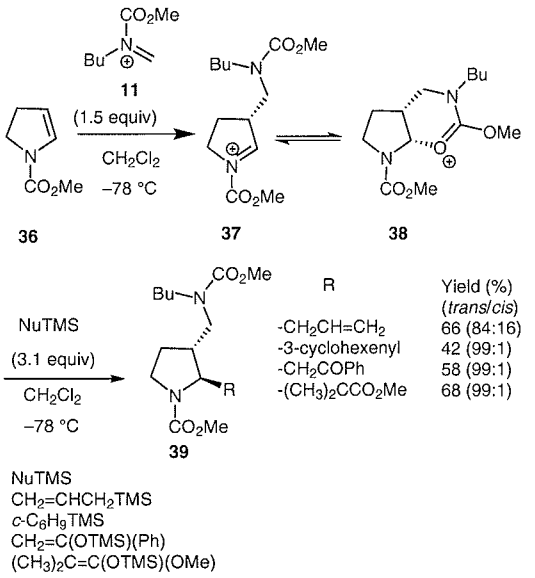



**Scheme 14**

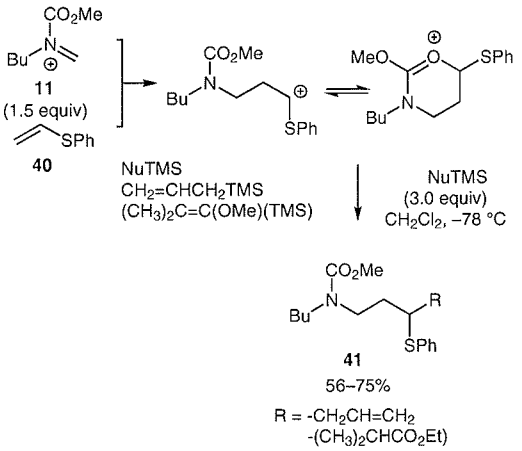



**Scheme 15**

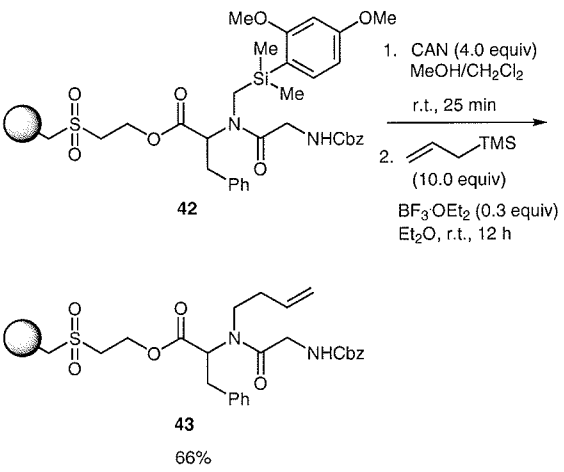
An *N*-acyliminium ion was selectively generated in the polymer-supported dipeptide **42** by oxidation of the *N*-silylmethyl group with ceric ammonium nitrate in methanol. The resulting *N*-methoxymethyl carbamate reacted with allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex to give the polymer-supported allylated product **43**. The yield of **43** was determined to be 66% yield (Scheme 18).[24,27]




**Scheme 16**

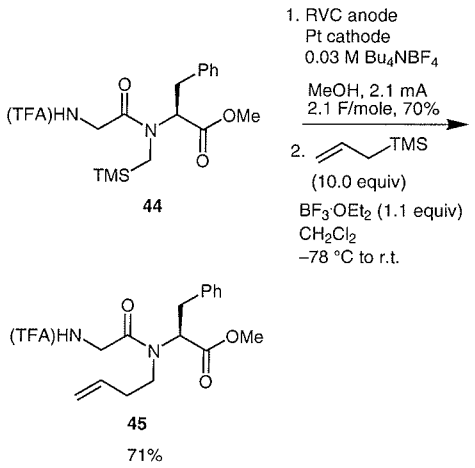



**Scheme 17**



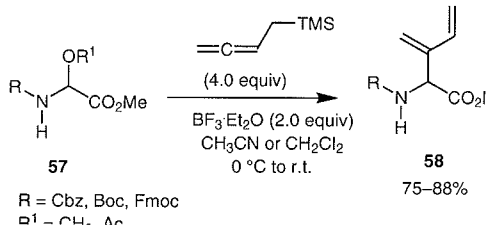

**Scheme 18**

Similarly, anodic oxidation of the trimethylsilyl group in peptide **44** gave the corresponding *N*-methoxymethyl carbamate, which was treated with allyltrimethylsilane and boron trifluoride–diethyl ether complex to give product **45** (Scheme 19).[24,28]



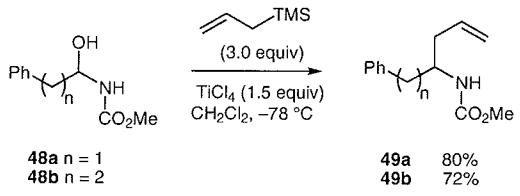

**Scheme 19**

The reaction of the α-benzotriazole carbamate **46** with allyltrimethylsilane gave the allylated product **47** in 80% yield (Scheme 20). The analogous reactions of **46** with buta-2,3-dienylsilane and (furan-2-yloxy)trimethylsilane were less efficient and gave the corresponding adducts **47** in 53% and 51% yields, respectively.[6]



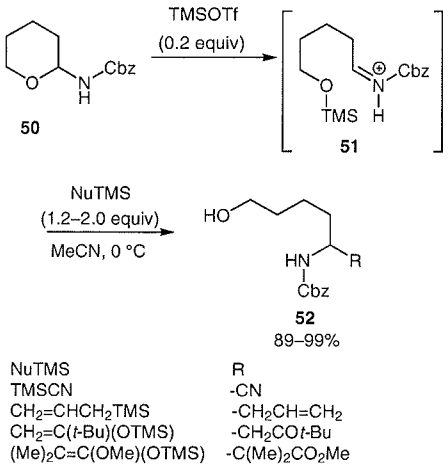

**Scheme 20**

The reaction of the α-hydroxy carbamates **48a** and **48b** with allyltrimethylsilane in the presence of titanium(IV) chloride provided the corresponding allylated products **49a** and **49b** in 80% and 72% yields, respectively (Scheme 21).[21]




**Scheme 21**

The Lewis acid catalysed reactions of the *N*,*O*-acetals **50** and **53** gave the corresponding ring-opened acyclic *N*-acyliminium ions **51**. These reacted smoothly with allyltrimethylsilane, trimethylsilyl cyanide, and ketene silyl acetals to afford the adducts **52** (Scheme 22) and the diastereomeric products **54** and **55** (Scheme 23) in good yields.[29]




**Scheme 22**

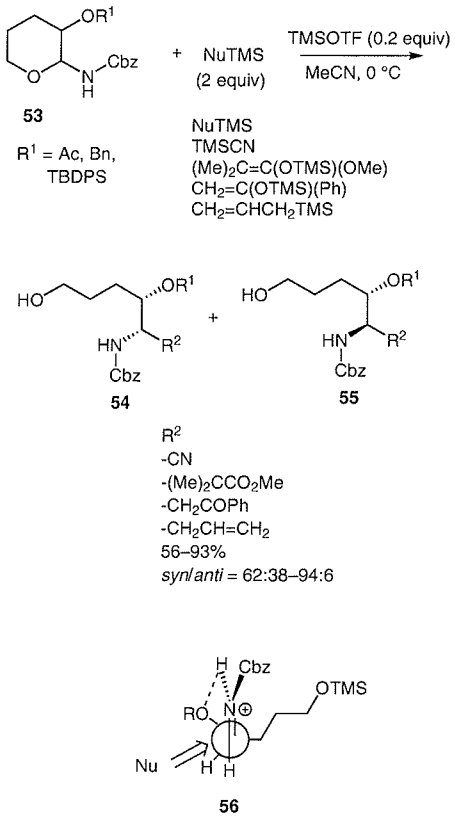
High *syn* selectivity was observed in the adducts from the reactions of the 3-benzyloxycarbonyl acetal **53**. A hydrogen-bonded transition-state model **56**, involving hydrogen-bonding between the proton bound to the iminium nitrogen and the α-oxygen substituent group, was proposed. The nucleophile preferentially attacked from the less-hindered face of the iminium ion (from the side of the α-hydrogen) to give the *syn* product (Scheme 23).[29] The *syn*/*anti* ratio did not vary dramatically with the nature of $R^1$ in **53**.

Allenylmethylsilane reacted with the α-methoxy and α-acetoxy carbamates **57** in the presence of boron trifluoride–diethyl ether complex to give dienes **58** in 75–88% yields (Scheme 24).[30]

The one-pot reaction of carbamates **59** with aldehydes or their acetals and silyl nucleophiles in the presence of boron trifluoride–diethyl ether complex gave adducts **60** in yields ranging from 5% to 92% (Scheme 25). In the same study, treatment of carbamate **59** ($R^1$ = Bn) with vinyl acetate and benzaldehyde in the presence of a catalytic amount of scandium(III) triflate provided product **60** in 28% yield. The reaction did not work with boron trifluoride–diethyl ether complex.[6]

The (benzylsulfonyl)ethyl and (benzylsulfinyl)ethyl carbamates **61a** and **61b** underwent one-pot reactions with aldehydes or their acetals and allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex to afford products **62** in 45–89% yields (Scheme 26).[6]

Similarly, the reaction of carbamate **63** with diethyl acetal **64** and allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex afforded a mixture of the



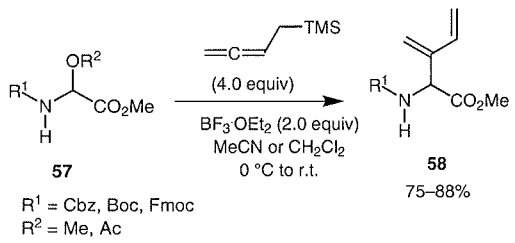

Scheme 23

desired allylated product **65** and the bis-carbamate **66** in 75% yield (Scheme 27). Treatment of **66** with allyltrimethylsilane and boron trifluoride–diethyl ether complex resulted in a 6:4 mixture of compounds **65** and **66**.[6]

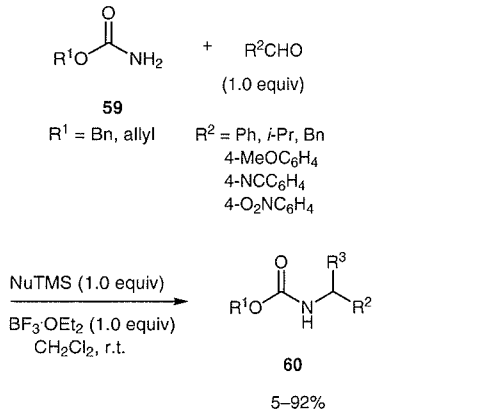
Treatment of resin-bound **67a** with aromatic aldehydes and allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex provided the corresponding allylated products **69** in a range of yields, <5% to 80%, after base-promoted cleavage from the resin (Scheme 28). Use of 4-methoxybenzaldehyde and benzaldehyde resulted in 79% and 80% yields of **69**, respectively, while the use of benzaldehydes having electron-withdrawing groups, 4-cyanobenzaldehyde and 4-nitrobenzaldehyde, gave poor yields of **69** (< 5% and 39%, respectively). The three-component, one-pot reactions of compounds **67b** and **67c** with benzaldehyde and allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex gave the corresponding allylated products **69** in 83% and 57% yields, respectively, after cleavage from the resin.[5]

In a similar study, the one-pot reaction of resin-bound **67a** with aldehydes or their acetals and silicon nucleophiles in the presence of boron trifluoride–diethyl ether complex provided products **70** in 3–80% yields, after cleavage from the resin (Scheme 29).[6]

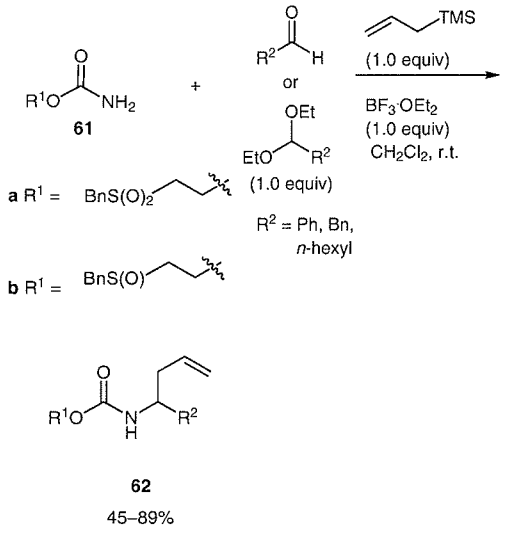
The reaction of Weinreb amide **71** with allyltrimethylsilane under boron trifluoride–diethyl ether complex catalysis gave product **72** in 89% yield (Scheme 30).[23]



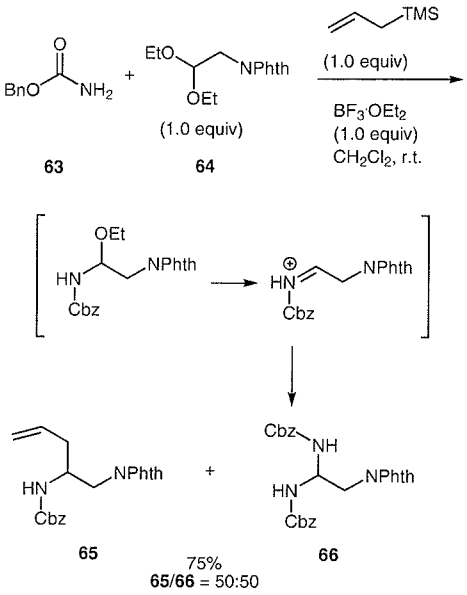

Scheme 24



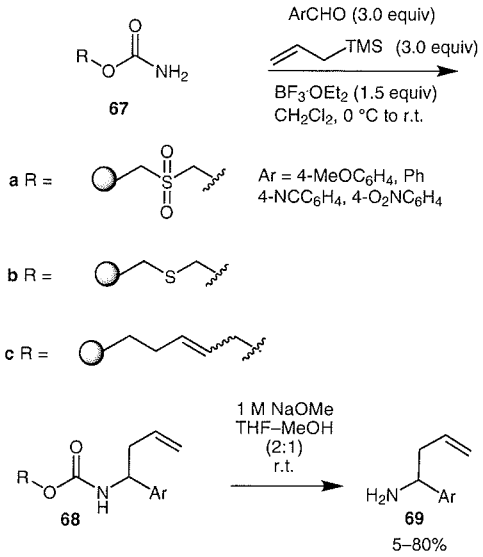

Scheme 25




Scheme 26




Scheme 27

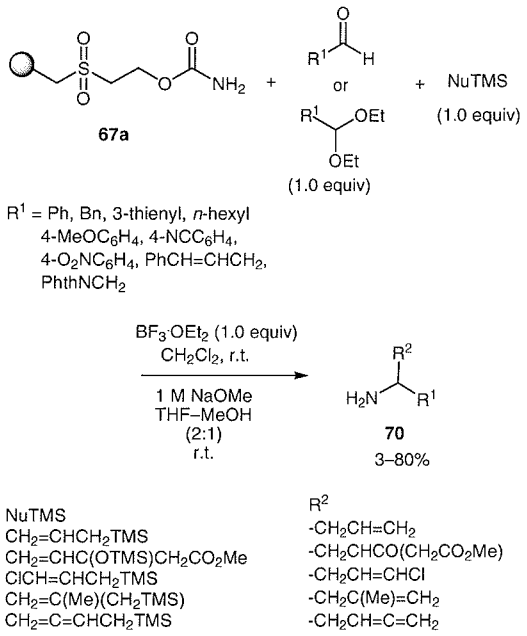



Scheme 28

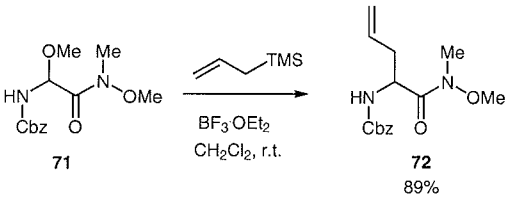
The reaction of immobilised α-benzotriazole carbamates **73a** and **73b** with allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex provided the desired allylated products **74a** and **74b** in 71% and 36% yields, respectively, after cleavage from the resin by sodium methoxide (Scheme 31).[6]

Tin(IV) chloride mediated allylation reaction of oxazolidinone **75** with allyltrimethylsilane provided product **76** in 78% yield (Scheme 32).[31]

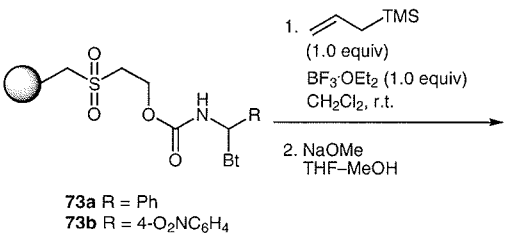
The reactions of oxazolidinone **77** with silicon nucleophiles under boron trifluoride–diethyl ether complex catalysis led to the formation of the desired products **78** in 85–94% yields (Scheme 33).[32]



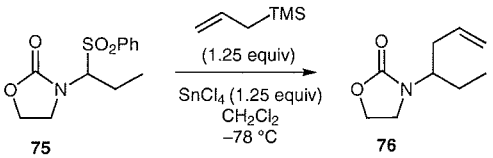

Scheme 29



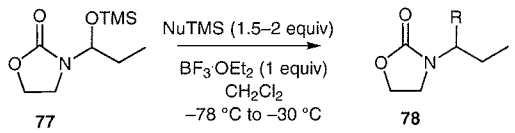

Scheme 30




Scheme 31



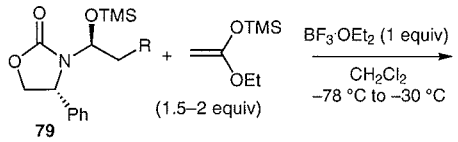

Scheme 32



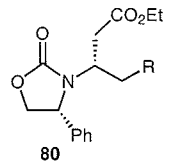

| NuTMS | R | Yield (%) |
|---|---|---|
| $CH_2$=C(OTBS)(OEt) | -$CH_2CO_2Et$ | 94 |
| $CH_2$=$CHCH_2TMS$ | -$CH_2CH$=$CH_2$ | 85 |
| $CH_2$=C(OTMS)(Ph) | -$CH_2COPh$ | 89 |

**Scheme 33**

The boron trifluoride–diethyl ether complex catalysed reaction of chiral oxazolidinones **79** with $CH_2$=C(OTMS)(OEt) yielded products **80** in yields of 47–99% with very high diastereoselectivity (dr = 91:9 to 96:4) (Scheme 34).[32]




R = Me, Et, Bu,
$CH_2CH_2CH$=$CH_2$
$CH_2(CH_2)_7CH_3$
$CH_2CH_2Ph$



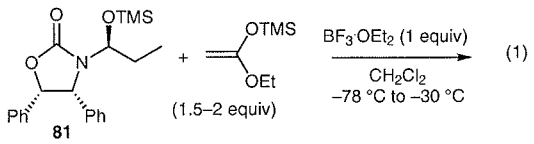

47–99%
*cis*/*trans* = 91:9 to 96:4

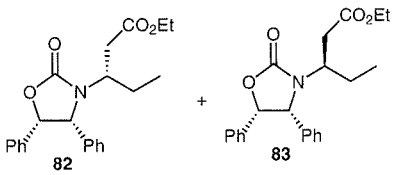
**Scheme 34**

The oxazolidinone **81** reacted with $CH_2$=C(OTMS)(OEt) in the presence of boron trifluoride–diethyl ether complex and provided the products **82** and **83** in a ratio of 95:5 (Scheme 35, equation 1); while the reaction of diastereomer **84** of the oxazolidinone **81** under the same reaction conditions yielded product **82** and **83** in a ratio of 6:94 (Scheme 35, equation 2).[32]

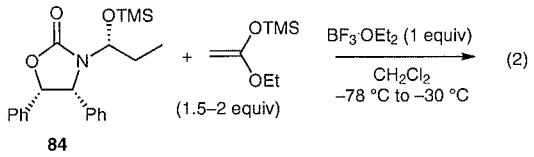
The oxazolidinone **85** was treated with allyltrimethylsilane in the presence of titanium(IV) chloride to provide adducts **86** and **87** in yields of 46–93%, in favour of product **86** (Scheme 36).[33]

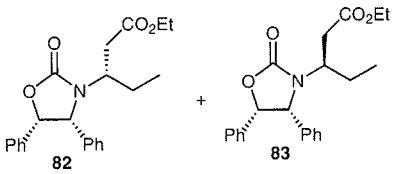
Treatment of the imidazolidinones **88** with silicon nucleophiles under tin(IV) chloride catalysis led to the formation of adducts **89** and **90** in yields of 30–80% (Scheme 37).[31]



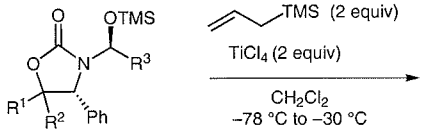

**82**/**83** = 95:5



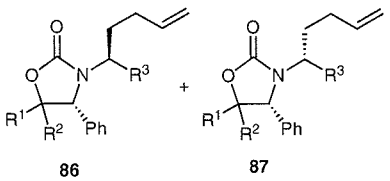




**82**/**83** = 6:94

**Scheme 35**




$R^1$ = *i*-Pr, Ph
$R^2$ = H, Me, Ph
$R^3$ = Et, *i*-Bu,
*i*-Pr, $PhCH_2CH_2$,
*n*-$C_7H_{15}$, $Cl(CH_2)_5$,
$CH_2$=$CH(CH_2)_7$

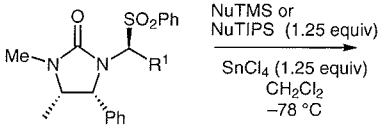



46–93%
*cis*/*trans* = 55:45 to 95:5

**Scheme 36**

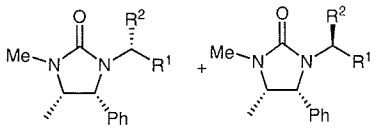
## 2.2.1.2 Aromatic Nucleophiles

The reaction of the *N*-acyliminium ion **11** with substituted benzenes and heteroaromatic compounds afforded the corresponding monoalkylated and dialkylated products **91–94** (Scheme 38). The use of a conventional batch reactor resulted in the formation of both mono- and dialkylated products, except in the cases of toluene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene, where the monoalkylated products **91** were obtained exclusively, in yields of 62–69%. When the reactions were performed in a micromixer-type reactor, however, only the monoalky-




88

$R^1$ = EtCHO, $Ph(CH_2)_2CHO$
$(Me)_2CHCH_2CHO$
$n$-$C_7H_{15}CHO$, $BnO(CH_2)CHO$,
$C_5H_{11}CH{=}CH(CH_2)_2CHO$

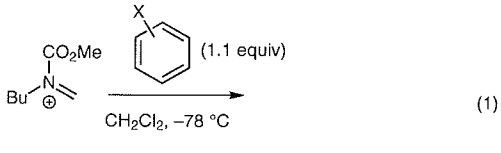


89 90

30–80%
**89/90** = 60:40 to 97:3

| NuTMS | $R^2$ |
|---|---|
| $CH_2{=}C(OTBS)(OEt)$ | $-CH_2CO_2Et$ |
| $CH_2{=}CHCH_2TMS$ | $-CH_2CH{=}CH_2$ |
| $CH_2{=}C(OTMS)(Ph)$ | $-CH_2COPh$ |
| $CH_2{=}C(OTIPS)(OEt)$ | $-CH_2CO_2Et$ |

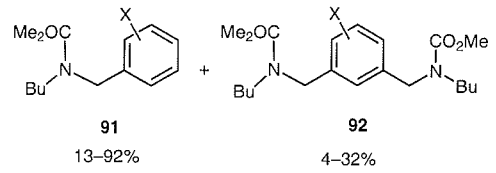
**Scheme 37**




(1)

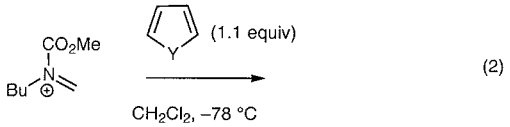
11

ArX
MePh, 1,4-$(Me)_2C_6H_4$, 1,3,5-$(Me)_3C_6H_3$,
MeOPh, 1,2-$(MeO)_2C_6H_4$, 1,3,5-$(MeO)_3C_6H_3$

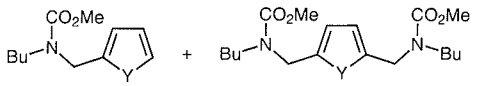


91 92

13–92% 4–32%




(2)



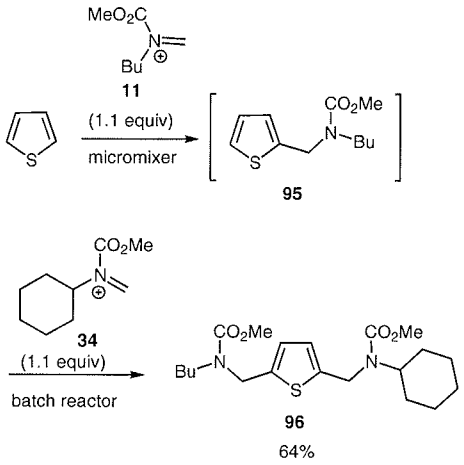
93 94

11–84% 5–28%

**Scheme 38**

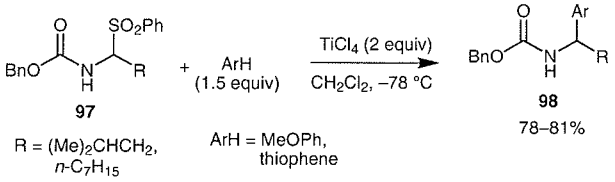
lated products **91** and **93** were obtained, in 26–92% and 39–84% yields, respectively.[9]

The above method, using a micromixer together with pregenerated *N*-acyliminium ions, has been extended to the selective introduction of two different alkyl groups onto aromatic compounds (Scheme 39). Monoalkylation of thiophene was carried out in a micromixer, and the product **95** was directly treated with a different *N*-acyliminium ion **34**, to give the dialkylated product **96** in 64% yield.[9]




**Scheme 39**

The α-amido sulfones **97** gave the corresponding arylated adducts **98** in good yields when treated with electron-rich aromatic compounds in the presence of titanium(IV) chloride (Scheme 40).[10]




97

R = $(Me)_2CHCH_2$, $n$-$C_7H_{15}$

ArH = MeOPh, thiophene

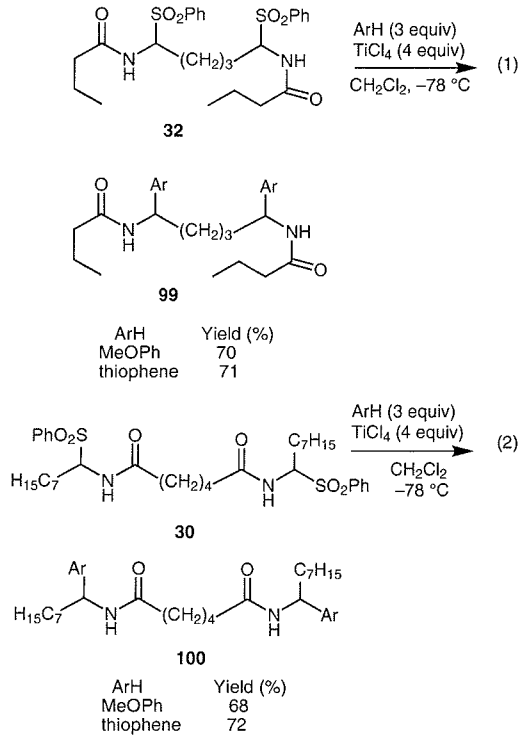
98

78–81%

**Scheme 40**

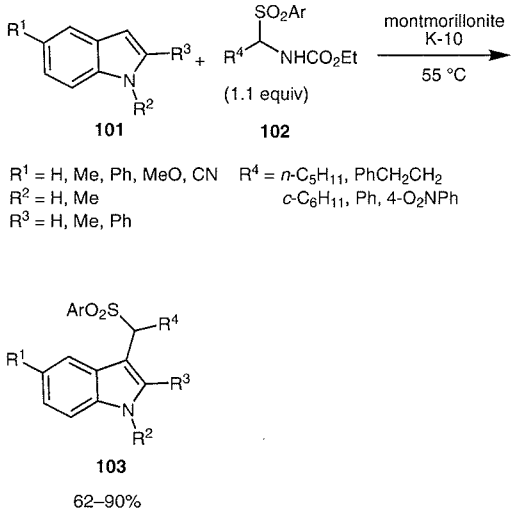
Treatment of bisamido sulfones **32** and **30** with aromatic compounds (1.5 equiv) in the presence of titanium(IV) chloride (2 equiv) resulted in poor yields of monoarylated products due to the formation of bisarylated products and side products. Bisarylation took place efficiently when excess amounts of the aromatic nucleophiles (3 equiv) and titanium(IV) chloride (4 equiv) were used (Scheme 41).[10]

The α-amido sulfones **102** reacted with indoles **101** in the presence of montmorillonite K-10 without solvent to give the 3-substituted indole derivatives **103** (Scheme 42). Unexpectedly, these products retained the toluenesulfonyl group of **102**, instead of its carbamoyl group. The formation of these products **103** has been explained by the mechanism shown in Scheme 43. The *N*-acyliminium ion

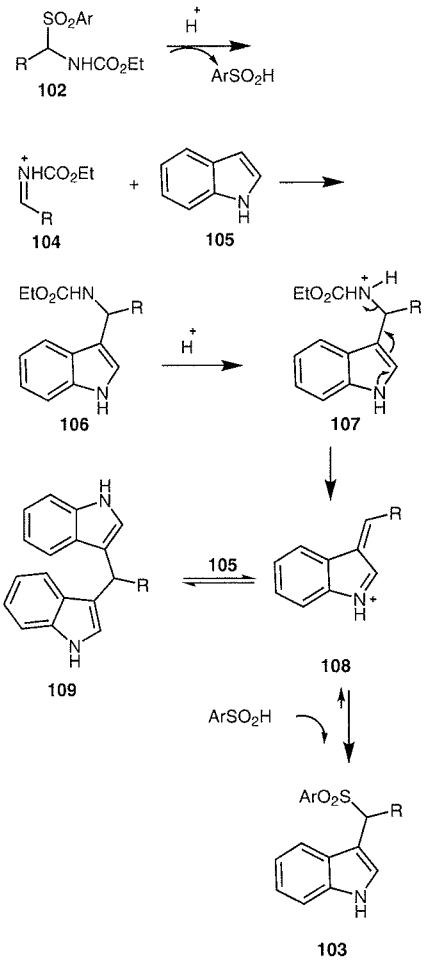



**Scheme 41**

**104** forms from the α-amido sulfone under acidic conditions. The indole **105** attacks the *N*-acyliminium ion **104** to form the expected product **106**, which is then protonated and eliminates the carbamate group. The resulting iminium ion **108** can react with another molecule of indole to give the bisindole **109**, or with the arenesulfinic acid to give the observed product **103**. Since the formation of the bisindole is reversible and product **103** is more stable than the bisindole, the reaction favours the formation of **103**.[34]

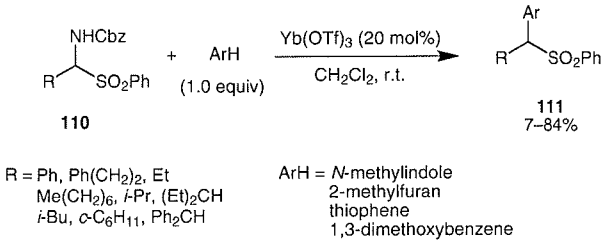



**Scheme 42**




**Scheme 43**

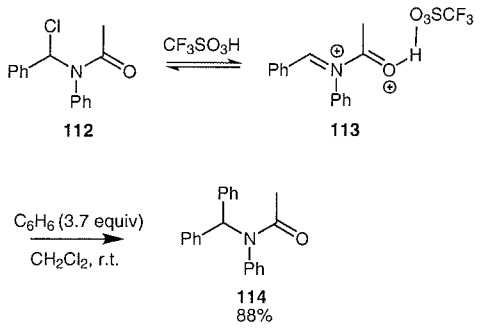
The α-amido sulfones **110** gave products **111** when they were treated with 1,2,4-trimethoxybenzene in the presence of ytterbium(III) triflate at room temperature (Scheme 44). Heteroaromatic compounds gave lower yields of adducts than electron-rich benzene derivatives, which might be the result of formation of a deactivating complex between the heteroaromatic compounds and the Lewis acid.[35]




**Scheme 44**

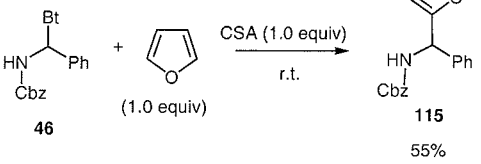
Trifluoromethanesulfonic acid catalysed the reaction of α-chloro amide **112** with benzene and gave the benzhydril

product **114** in 88% yield (Scheme 45).[33] Evidence for the dicationic intermediate **113** has been reported.[36]



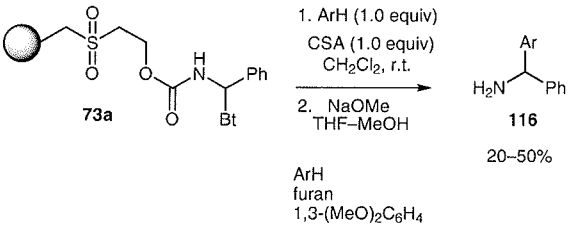

**Scheme 45**

Treatment of the α-benzotriazole carbamate **46** with furan in the presence of camphorsulfonic acid monohydrate afforded product **115** in 55% yield (Scheme 46).[6]




**Scheme 46**

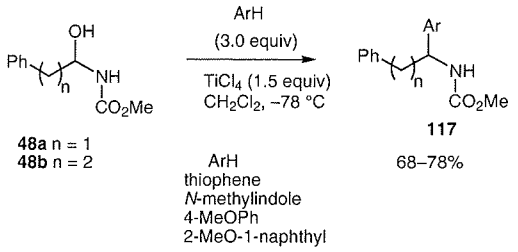
In the same study, the reaction of immobilised α-benzotriazole carbamate **73a** with furan and 1,3-dimethoxybenzene in the presence of camphorsulfonic acid gave products **116** in 50% and 20% yields, respectively, after cleavage from the resin (Scheme 47).[6]



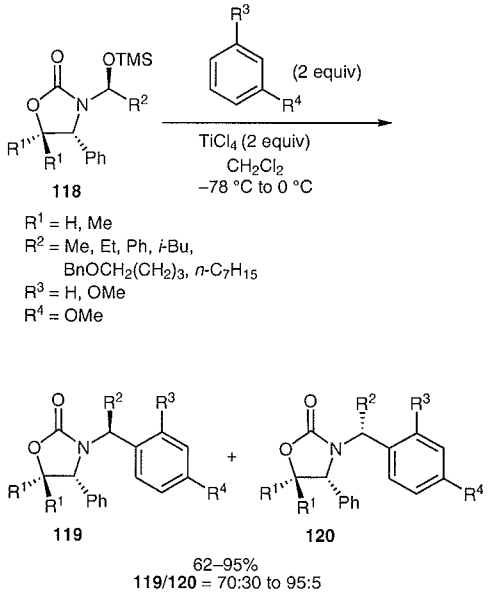

**Scheme 47**

Treatment of the α-hydroxy carbamates **48a** and **48b** with aromatic nucleophiles under titanium(IV) chloride catalysis afforded the desired arylated products **117** in yields ranging from 68% to 78% (Scheme 48).[21]

The oxazolidinones **118** reacted with methoxybenzene and 1,3-dimethoxybenzene in the presence of titanium(IV) chloride to afford the corresponding adducts **119** and **120** in 62–95% yields (Scheme 49).[37]




**Scheme 48**




**Scheme 49**

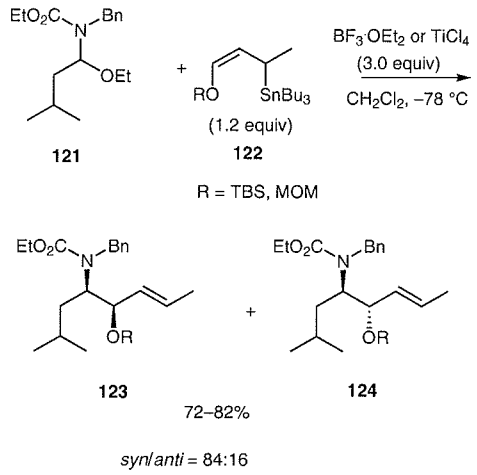
### 2.2.1.3 Organostannanes

Racemic allylic stannanes **122** reacted with *N*-acyliminium ions derived from α-ethoxy carbamate **121** to give the racemic adducts **123** and **124** in good to excellent yields, and with good diastereoselectivities (Scheme 50).[17,18]

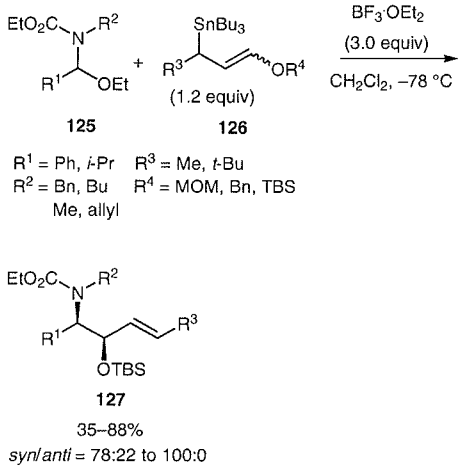
The racemic (*E*)-γ-OTBS derivative of allylic stannane **126** gave only the racemic *syn* adduct **127** from its reaction with α-ethoxy carbamates **125**. The *E*- or *Z*-geometry of the stannane and the nature of the substituents on the iminium ion did not affect the *syn* preference of the reaction (Scheme 51).[17]

The *N*-(2-methoxyphenyl) carbamates **128**, however, underwent highly diastereoselective reactions (dr > 95:5) with the enantiomerically enriched (*S*)-γ-silyloxyallylic stannane **129** to give the *syn* products **130** (Scheme 52). The reason for this enhanced diastereoselectivity, apparently due to the presence of the 2-methoxy group, was not clear.[18]

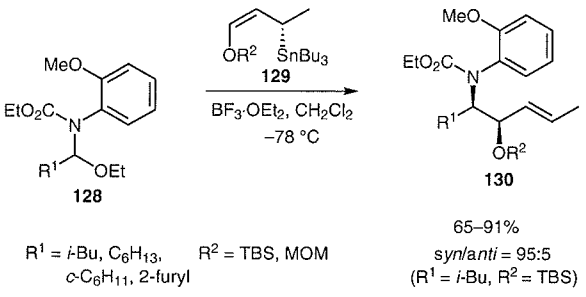
The boron trifluoride–diethyl ether complex promoted reaction of (*R*)-**131** and (*S*)-**132** gave the *syn,anti* adduct **133** as the exclusive product (the matched case) while the corresponding reaction of (*S*)-**131** and (*S*)-**132** gave a 60:40




**Scheme 50**

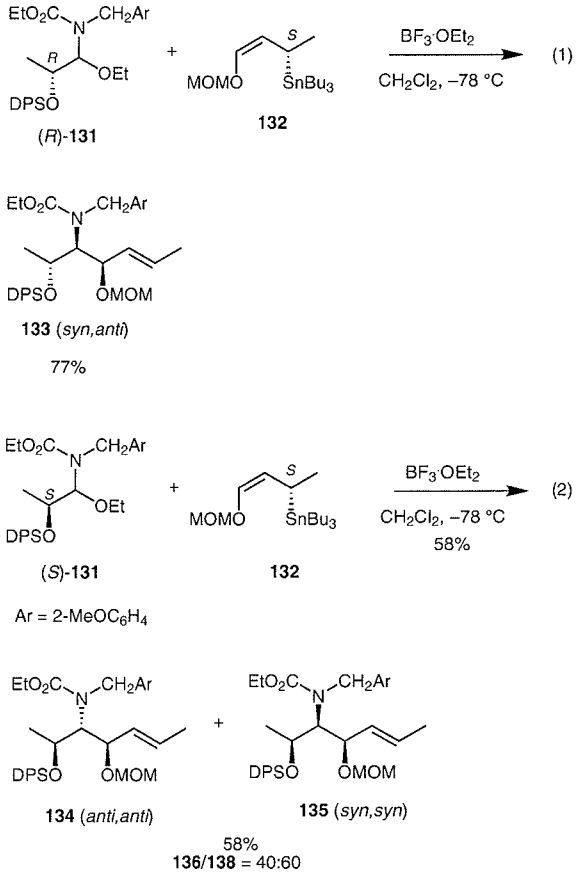



**Scheme 51**



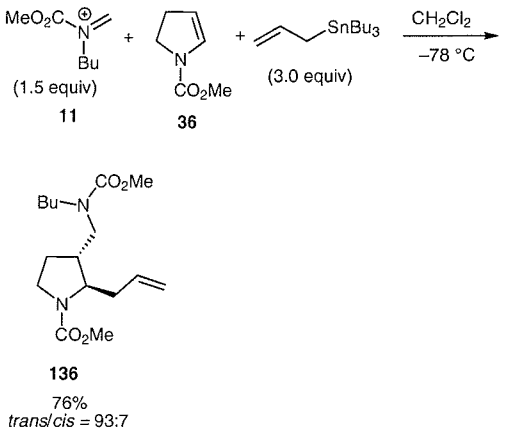

**Scheme 52**

mixture of diastereomers **134** and **135** (mismatched pair) (Scheme 53).[18]



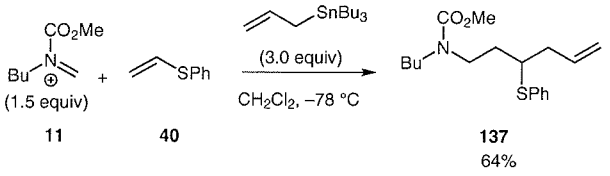

**Scheme 53**

The reaction of the *N*-acyliminium ion **11** with allyltributylstannane and enamine **36** led to the formation of product **136** in a yield of 76% (*trans*/*cis* = 93:7) (Scheme 54).[25]



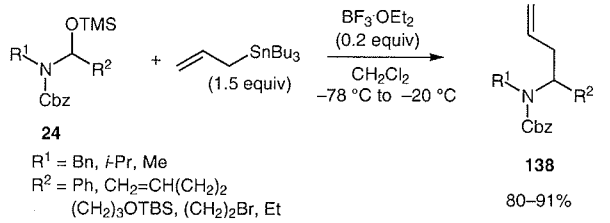

**Scheme 54**

In the same study, the three-component coupling reaction of the *N*-acyliminium ion **11** with vinyl phenyl sulfide **40** and allyltributylstannane provided the corresponding product **137** in 64% yield (Scheme 55).[25]



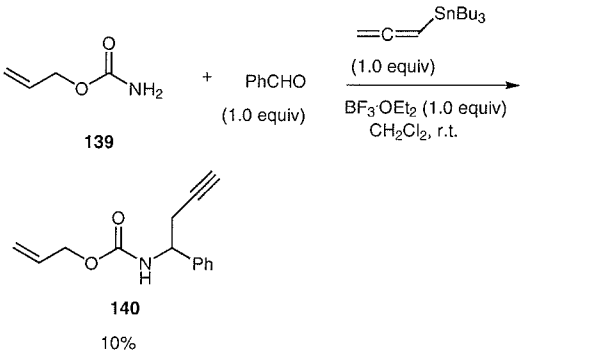

Scheme 55

Treatment of α-silyloxycarbamates **24** with allyltributylstannane in the presence of boron trifluoride–diethyl ether complex provided the desired adducts **138** in yields of 80–91% (Scheme 56).[20]




Scheme 56

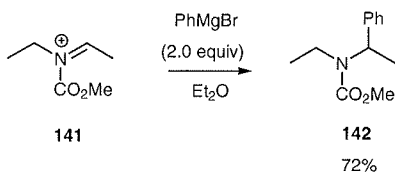
The one-pot reaction of allyl carbamate **139** with benzaldehyde and an allenylstannane nucleophile in the presence of boron trifluoride–diethyl ether complex gave the alkyne product **140** in only 10% yield (Scheme 57).[6]




Scheme 57

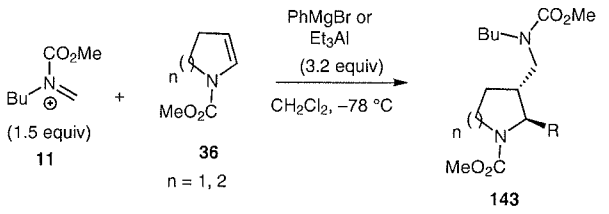
### 2.2.1.4 Organometallic Reagents

The *N*-acyliminium ion **141**, generated from the corresponding carbamate by electrochemical oxidation (Scheme 3), was treated with phenylmagnesium bromide to give the desired adduct **142** in 72% yield (Scheme 58).[38]




Scheme 58

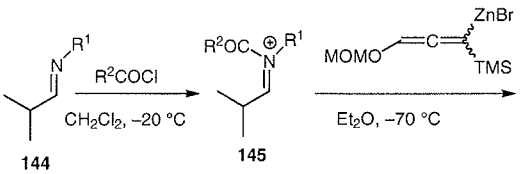
Phenylmagnesium bromide and triethylaluminium each gave the corresponding three-component coupling products **143**, with good diastereoselectivity, when they were added to a solution of **37** and **38** (Scheme 16), formed in situ from the reaction of **11** and **36** (Scheme 59).[25]



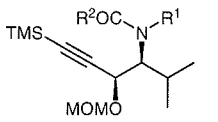

| R | Yield (%) (*trans*/*cis*) |
|---|---|
| Ph (n = 1) | 51 (88:12) |
| Et (n = 1) | 61 (89:11) |
| Ph (n = 2) | 46 (98:2) |
| Et (n = 2) | 71 (61:39) |

Scheme 59

A 3-alkoxyallenylzinc reagent reacted with the *N*-acyliminium ion **145**, which was generated in situ from the treatment of the imine **144** with acyl chlorides, to provide products **146** in yields of 31–96% and with *syn*/*anti* ratios of 61:39 to 74:26 (Scheme 60).[39]




R1 = PMB, allyl, Pr, Cy
R2 = Me, Ph

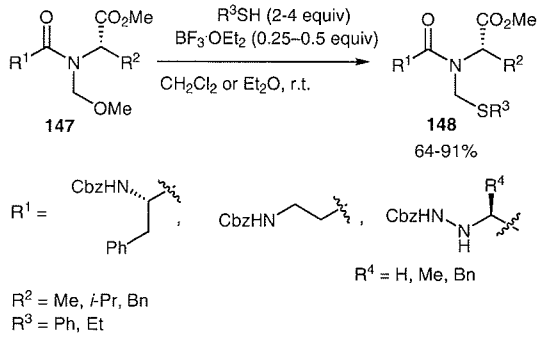



**146**
31–96%
*syn*/*anti* = 61:39–74:26

Scheme 60

### 2.2.1.5 Thiols

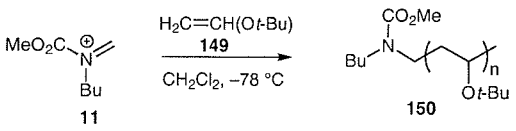
Treatment of *N*-methoxymethyl dipeptides **147** with thiol nucleophiles afforded thiol-substituted dipeptides **148** in 64–91% yields (Scheme 61).[24]




**Scheme 61**

### 2.2.1.6 Alkenes

Generation of *N*-acyliminium ions by low-temperature electrochemical oxidation and the use of a micromixer system were successfully applied to the synthesis of polymers of *tert*-butyl vinyl ether **150** (Scheme 62). The method allowed for the control of molecular-weight distribution.[40]



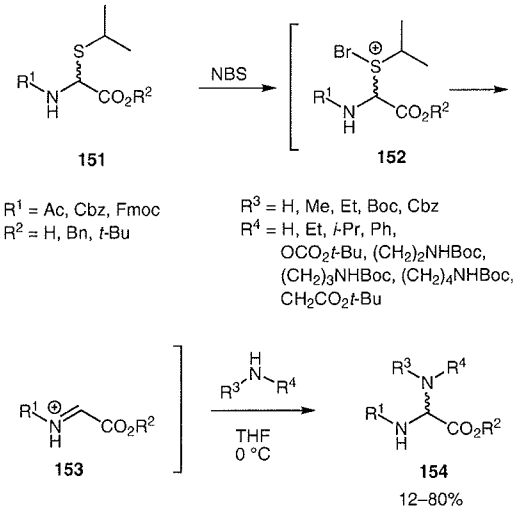

**Scheme 62**

### 2.2.1.7 Nitrogen Nucleophiles

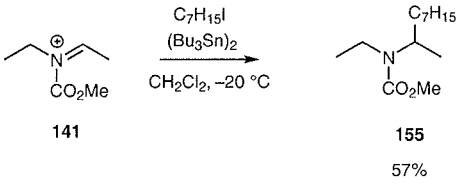
Treatment of the α-isopropylthioglycine derivative **151** with *N*-bromosuccinimide provided bromosulfonium salt **152** which formed the corresponding *N*-acyliminium ion **153**. This intermediate underwent reaction with amines, amides and carbamates to afford products **154** in yields ranging from 12% to 80% (Scheme 63).[22]

### 2.2.1.8 Alkyl Radicals

The *N*-acyliminium ion **141**, generated from the corresponding carbamate by low-temperature electrochemical oxidation, was treated with heptyl iodide in the presence of hexabutyldistannane to afford product **155** in 57% yield (Scheme 64). Decreasing the rate of addition of the distannane had increased the yield from 31% to 57%.[41,42]




**Scheme 63**



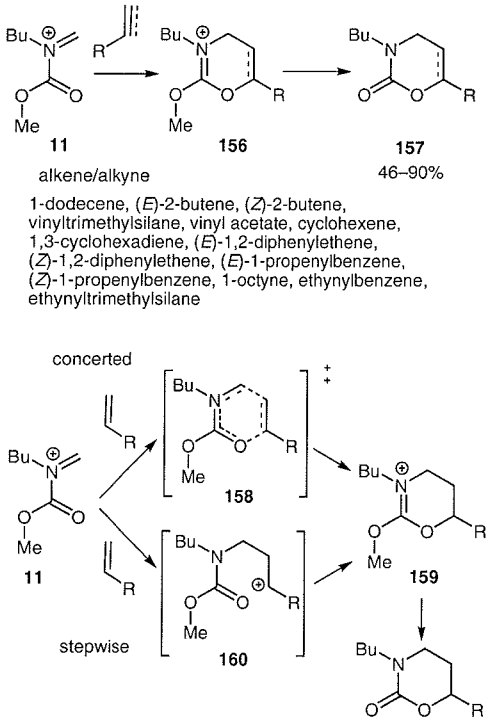

**Scheme 64**

## 2.2.2 Cycloaddition Reactions

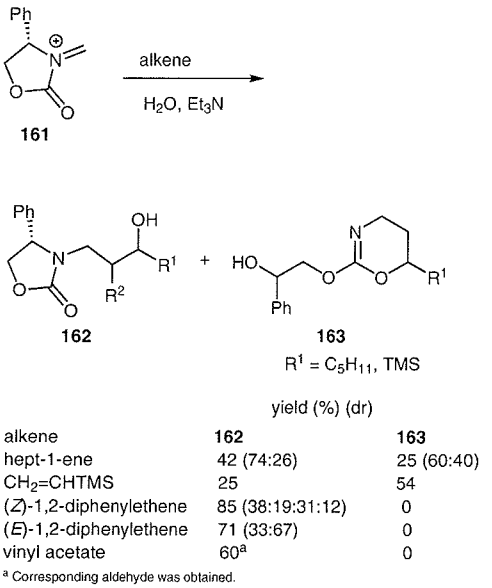
The *N*-acyliminium ion **11** underwent smooth [4+2]-cycloaddition reactions with various alkenes and alkynes (Scheme 65). (*E*)-But-2-ene, (*E*)-1,2-diphenylethene and (*Z*)-propenylbenzene each gave the corresponding *trans* cycloadduct exclusively in 68%, 87%, and 88% yields, respectively, while (*Z*)-but-2-ene gave the *cis* cycloadduct exclusively. These results were consistent with a concerted reaction mechanism. The loss of stereoselectivity in the reaction of (*Z*)-1,2-diphenylethene (*trans*/*cis* = 45:55) and (*E*)-propenylbenzene (*trans*/*cis* = 44:56) suggested a stepwise mechanism in which bond rotation competed with cyclisation in the intermediate **160**. It was concluded that the stereospecificity of the reactions of alkyl-substituted alkenes was consistent with a concerted mechanism, while that observed with aryl-substituted alkenes was consistent with a stepwise mechanism.[8,43]

## 2.2.3 Cationic Carbohydroxylation Reactions

Alkenes underwent cationic carbohydroxylation reaction with the *N*-acyliminium ion **161** to afford products **162** and **163** in combined yields of 60–85% (Scheme 66). The reaction of electrochemically generated **161** with hept-1-ene in the presence of water and triethylamine gave products **162** and **163** in 42% (dr = 74:26) and 25% (dr = 60:40) yields, respectively, while the reaction of vi-




Scheme 65




yield (%) (dr)

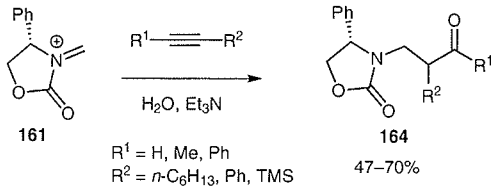
| alkene | 162 | 163 |
|---|---|---|
| hept-1-ene | 42 (74:26) | 25 (60:40) |
| $CH_2$=CHTMS | 25 | 54 |
| (Z)-1,2-diphenylethene | 85 (38:19:31:12) | 0 |
| (E)-1,2-diphenylethene | 71 (33:67) | 0 |
| vinyl acetate | 60[a] | 0 |

[a] Corresponding aldehyde was obtained.

Scheme 66

nyltrimethylsilane with **161** afforded products **162** and **163** in 25% and 54% yields, respectively. The reactions of (*Z*)-1,2-diphenylethene and (*E*)-1,2-diphenylethene with **161** afforded the **162**-type products exclusively in 85% and 71% yields, respectively. The corresponding ketone of product **162** was obtained in 60% yield from the reaction of **161** with vinyl acetate under the same reaction conditions.[44]

The *N*-acyliminium ion **161** reacted with alkynes in water and triethylamine to give the corresponding cationic carbohydroxylation products **164** in yields of 47–70% (Scheme 67).[44]

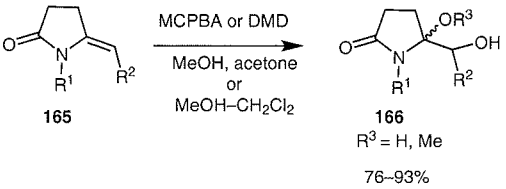



Scheme 67

## 3 Cyclic *N*-Acyliminium Ions

### 3.1 Synthesis of Cyclic *N*-Acyliminium Ion Precursors

Earlier methods for the synthesis of these precursors were reported in the previous review.[2] 5-Alkoxypyrrolidinones **166** were synthesised from the oxidation reactions of 5-alkylidenepyrrolidinones **165** with *m*-chloroperoxybenzoic acid or dimethyldioxirane (DMD) (Scheme 68).[45]

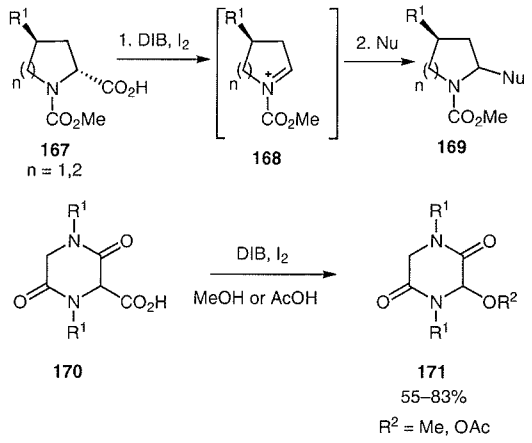



Scheme 68

#### 3.1.1 Preparation of Iminium Ions in situ by Anodic Oxidation

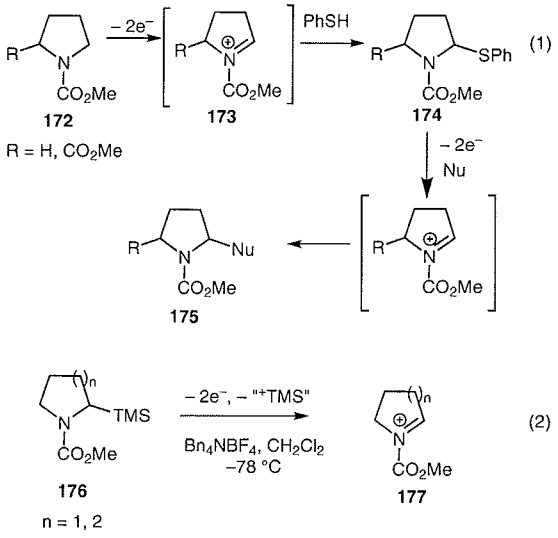
Five-membered-ring *N*-acyliminium ions like **168** can be generated in situ by a one-pot radical decarboxylation–oxidation process using (diacetoxyiodo)benzene (DIB) and iodine. Decarboxylation–oxidation of **167** first formed the *N*-acyliminium ion **168** in situ, then addition of a nucleophile gave addition products **169** (Scheme 69).[46,47] This one-pot decarboxylation–oxidation–nucleophilic addition reaction can be used for the preparation of α-functionalised piperazinediones. Treatment of piperazinedione **170** with (diacetoxyiodo)benzene and iodine in methanol or acetic acid provided the corresponding α-methoxy or α-acetoxy diketopiperazines **171** in 55–83% yields.[48]

Anodic oxidation of compounds **172** in a 1 M lithium perchlorate/nitromethane electrolyte solution in the presence of 50 mM acetic acid generated the *N*-acyliminium ions **173**, which were trapped with thiophenol to give 2-phenylsulfanyl derivatives **174**. Subsequent oxidation of these 2-phenylsulfanyl derivatives also gave rise to the corresponding *N*-acyliminium ions which, when generated in the presence of a nucleophile, gave the expected adducts **175** (Scheme 70, equation 1).[49] The *N*-acyliminium




**Scheme 69**

ions **177** (R = H) can also be formed by low-temperature oxidation of the corresponding carbamates **176** in dichloromethane solution in the absence of nucleophiles (Scheme 70, equation 2).[38,41,42,50]



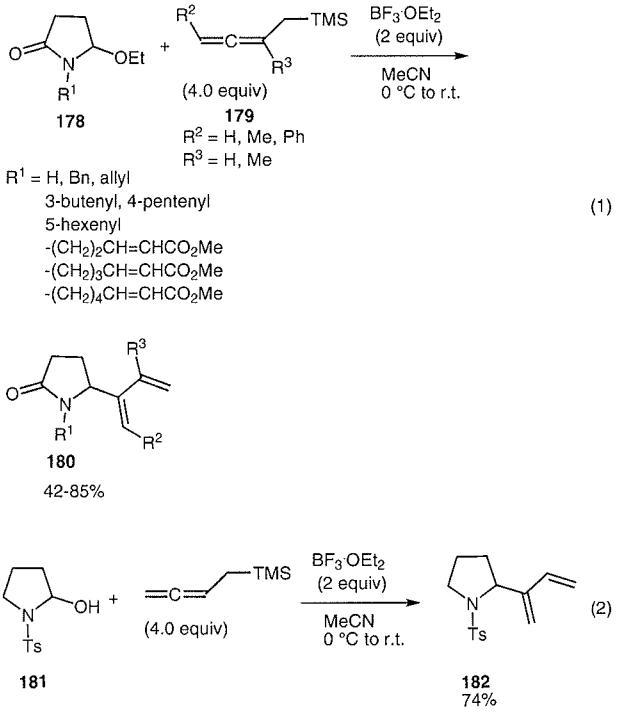

**Scheme 70**

## 3.2 Five-Membered-Ring *N*-Acyliminium Ions

### 3.2.1 Reactions of Pyrrolidinone-Based *N*-Acyliminium Ions with Nucleophiles

#### 3.2.1.1 Silicon-Based Nucleophiles

Allenylmethylsilanes **179** react with 5-ethoxypyrrolidinones **178** in the presence of boron trifluoride–diethyl ether complex in acetonitrile to give the corresponding dienes **180** (Scheme 71, equation 1). Reaction of allenylmethylsilane (**179**, $R^2 = R^3 = H$) with **178** gave 5-substituted pyrrolidinone products in 42–74% yields. Substituted allenylsilanes **179** resulted in formation of products **180** in yields of 65–85%. Product **180** with $R^1 = H$, $R^2 = Me$, $R^3 = H$ was obtained as the pure *E*-isomer, while product **180** with $R^1 = H$, $R^2 = Ph$, $R^3 = H$ was obtained as a 1:1 mixture of isomers. Treatment of the 5-hydroxypyrrolidinone **181** with allenylmethylsilane under the same reaction conditions provided product **182** in 74% yield (Scheme 71, equation 2).[30a]

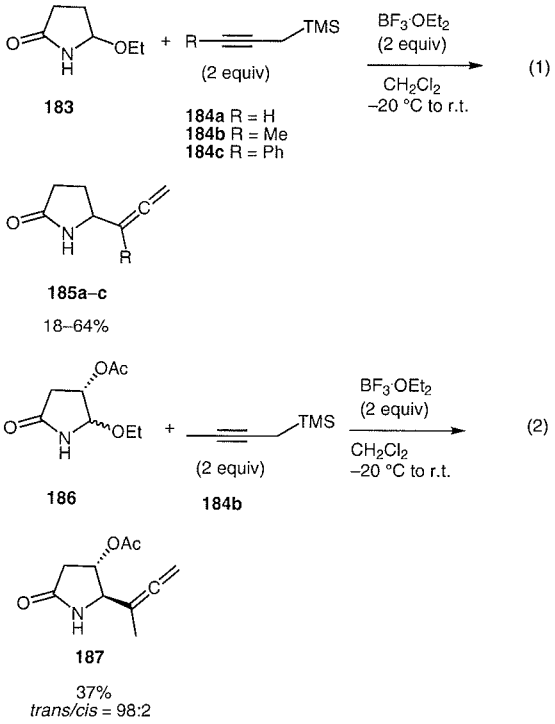



**Scheme 71**

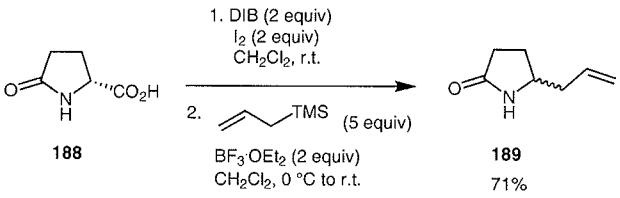
The reaction of 5-ethoxypyrrolidinone **183** with propargylsilanes **184a–c** led to the formation of the 5-allenylpyrrolidinones **185a–c**. Propargyltrimethylsilane (**184a**) and but-2-ynyltrimethylsilane (**184b**) gave allenyl products **185a** and **185b** in 55% and 64% yields, respectively, while phenyl-substituted propargylsilane **184c** gave **128c** in 18% yield (Scheme 72, equation 1). The reaction of 4-acetoxy-5-ethoxypyrrolidinone **186** with propargylsilane **184b** under the same reaction conditions afforded the corresponding product **187** in 37% yield and with very high *trans* selectivity (*trans*/*cis* = 98:2) (Scheme 72, equation 2).[51]

The *N*-acyliminium ion generated from **188** was trapped with allyltrimethylsilane in the presence of boron trifluoride–diethyl ether complex to give allylated product **189** in 71% yield (Scheme 73).[46]

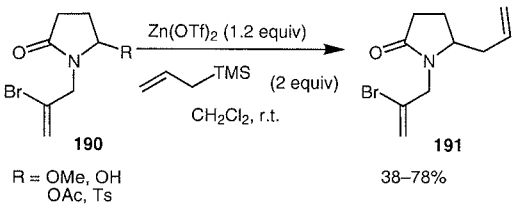
The zinc triflate catalysed reaction of allyltrimethylsilane with the 5-hydroxy-, 5-methoxy-, 5-acetoxy- and 5-sulfonylpyrrolidinones **190** afforded 5-allylated products **191** in moderate to good yields (Scheme 74). The 5-methoxypyrrolidinone derivative of **190** (R = OMe) underwent an addition reaction with a silyl enol ether [$CH_2$=C(OTMS)(Ph)] to give the desired product in 69% yield.[52]




Scheme 72

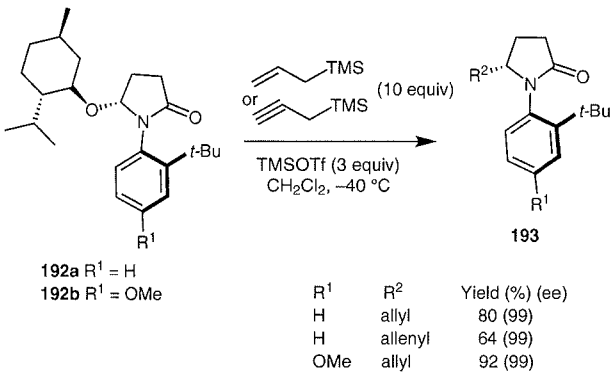



Scheme 73



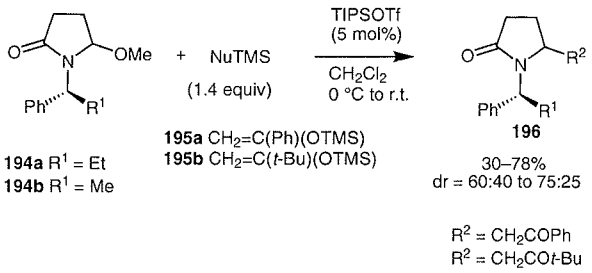

Scheme 74

Pyrrolidinones **192**, having a chiral C–N axis, reacted with allyltrimethylsilane or propargyltrimethylsilane in the presence of trimethylsilyl triflate to give products **193** in ≥99% ee (Scheme 75).[53]




Scheme 75

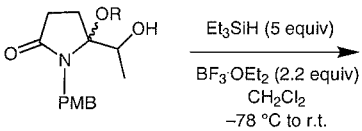
The reaction of **194a** with silyl enol ether **195a** in the presence of triisopropylsilyl triflate (5 mol%) afforded the corresponding ketone **196** in 42% yield and as a 75:25 mixture of diastereomers. The use of toluene as a solvent increased the yield (78%) but lowered the diastereoselectivity (60:40). Treatment of **194b** with **195a** under the same reaction conditions provided the desired ketone product as a mixture of isomers (dr = 60:40) in 55% yield. In that case, using toluene as a solvent did not change the diastereoselectivity but increased the yield to 74%. The reaction of **194b** with **195b** in dichloromethane or toluene afforded the desired ketone **196** with the same diastereomeric ratio of 63:37 and in 30% and 32% yields, respectively (Scheme 76).[54] The reaction of the pyrrolidinone **194b** with **195a** under catalysis by bis(trifluoromethane)sulfonimide (5 mol%) or scandium(III) triflate (5 mol%) afforded the expected ketone as a mixture of isomers (60:40 and 58:42) and in yields of 78% and 81%, respectively.[55]




Scheme 76

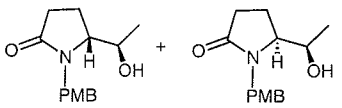
The reaction of the 5-alkoxypyrrolidinone **197** with triethylsilane in the presence of boron trifluoride–diethyl ether complex yielded products **198** in yields of ranging from 86% to 97% favouring the *threo* isomer (Scheme 77, equation 1). Pyrrolidinones **199** with triethylsilane yield-

ed exclusively the *threo* isomer of product **200** under the same experimental conditions (Scheme 77, equation 2).[45]




(1)

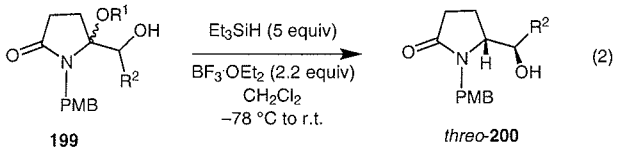
**197a** R = H
**197b** R = Me




*threo*-**198** *erythro*-**198**

| R | Yield (%) (*threo*/*erythro*) |
|---|---|
| **197a** | 89 (97:3) |
| **197b** | 97 (97:3) |
| **197b** | 86[a] (67:33) |

[a] $TiCl_4$ (1.2 equiv) was used.




(2)

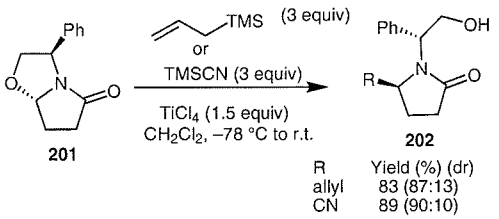
**199**
$R^1$ = H, Me
$R^2$ = $Cl(CH_2)_3$, $n$-$C_{12}H_{25}$

*threo*-**200**
71–77%
*threo*/*erythro* = 99:1 to 100:0

**Scheme 77**

Allyltrimethylsilane and trimethylsilyl cyanide reacted with the pyrrolidinone **201** under titanium(IV) chloride catalysis to give the corresponding 5-allylpyrrolidinone and 5-cyanopyrrolidinones **202** in 83% (dr = 87:13) and 89% (dr = 90:10) yields, respectively (Scheme 78).[56] Treatment of pyrrolidinone **201** with $CH_2$=C(Ph)(OTMS) in the presence of bis(trifluoromethane)sulfonimide (5 mol%) or scandium(III) triflate (5 mol%) gave the corresponding ketone as a 1:1 mixture of isomers and in 81% and 40% yields, respectively. The reaction of **201** with $CH_2$=C(Ph)(TMS), $CH_2$=C(OTMS)(*t*-Bu), and $Me_2C$=C(OMe)(OTMS) under catalysis by triisopropylsilyl triflate afforded the corresponding ketones in 93%, 50%, and 89% yields, respectively.[54,55]

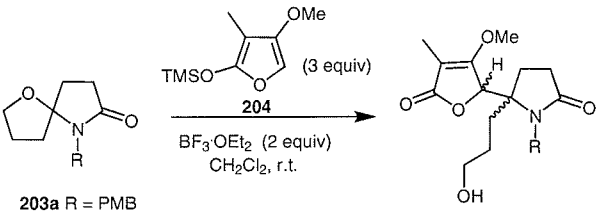
The boron trifluoride–diethyl ether complex catalysed reaction of 2-silyloxyfuran **204** and pyrrolidinone **203a** afforded adduct **205a** as a mixture of diastereomers (dr = 67:33) in 80% yield. The reaction of pyrrolidinone **203b** under the same reaction conditions gave **205b** in 27% yield and as a 1:1 mixture of diastereomers (Scheme 79).[57,58]




**201** **202**

| R | Yield (%) (dr) |
|---|---|
| allyl | 83 (87:13) |
| CN | 89 (90:10) |

**Scheme 78**

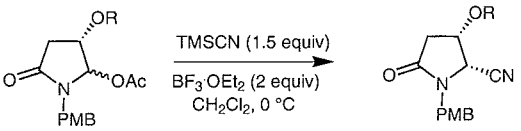



**203a** R = PMB
**203b** R = Bu

**205a** 80% dr = 67:33
**205b** 27% dr = 50:50

**Scheme 79**

Pyrrolidinones **206a,b** reacted with trimethylsilyl cyanide in the presence of boron trifluoride–diethyl ether complex to give the 5-cyanolactams **207a,b** (Scheme 80). Pyrrolidinone **206a** gave rise to **207a** in 98% yield as a 57:43 mixture of *cis* and *trans* isomers. Using toluene as a solvent increased the *cis* selectivity (*cis*/*trans* = 73:27) but lowered the chemical yield (70%). Under the same reaction conditions, **206b** gave **207b** in 98% yield with moderate *trans* selectivity (*trans*/*cis* = 61:39).[59]




**206a** R = TBS
**206b** R = Ac

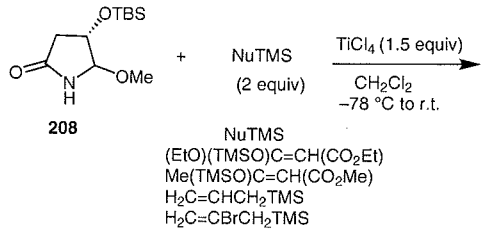
**207**

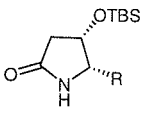
| R | Yield (%) (*cis*/*trans*) |
|---|---|
| TBS | 98 (57:43) |
| TBS | 70 (73:27)[a] |
| Ac | 98 (39:61) |

[a] Toluene was used as a solvent.

**Scheme 80**

The 5-methoxypyrrolidinone **208** underwent addition reactions with silyl enol ethers and allylsilanes in the presence of titanium(IV) chloride to give 5-alkylpyrrolidinones **209** with good *cis* selectivity (Scheme 81).[60]



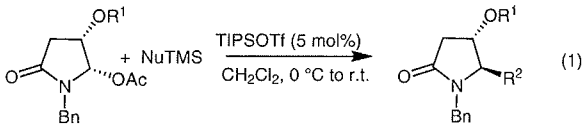




| R | Yield (%) (*cis*/*trans*) |
|---|---|
| -CH(CO$_2$Et)CO$_2$Et | 26 (79:21) |
| -CH(CO$_2$Me)COMe | 52 (90:10) |
| -CH$_2$CH=CH$_2$ | 89 (91:9) |
| -CH$_2$C(Br)=CH$_2$ | 72 (87:13) |

**Scheme 81**

The reaction of the 5-acetoxypyrrolidinones **210a** with **195b** (1.4 equiv) in the presence of triisopropylsilyl triflate in dichloromethane or toluene gave the products **212** in 74% and 64% yields, and with a diastereomeric ratio of >97:<3 and 90:10, respectively, in favour of the *trans* isomer (Scheme 82, equation 1). Treatment of **210a** with **211a** (2.0 equiv) in dichloromethane or toluene afforded the corresponding products **212** in 94% and 72% yields, respectively, and with moderate *trans* selectivity (74:26, 63:37, respectively). The reaction of **210a** with **211b** (1.4 equiv) provided product **212** in 74% yield and with a *trans*/*cis* ratio of >97:<3. The reaction of **210b** with **195a** and **211a** under the same reaction conditions provided the desired products in 80% and 67% yields and with diastereomeric *trans*/*cis* ratios of 87:13 and 30:70, respectively (Scheme 82, equation 1). Although the reactions of **210a** with **195a**,**b** and **211a** afforded the desired products with high *trans* selectivity, the reaction of **210a** with trimethylsilyl cyanide in the presence of triisopropylsilyl triflate in dichloromethane or toluene gave 5-cyanopyrrolidinone **213** with *cis*/*trans* ratios of 57:43 and 60:40, in yields of 82% and 94%, respectively (Scheme 82, equation 2).[54]

In a very similar study, treatment of the 4,5-diacetoxypyrrolidinones **210a**, **206b**, **214** with silyl nucleophiles in the presence of bis(trifluoromethane)sulfonimide (5 mol%) in dichloromethane or acetonitrile provided the desired products **215** with moderate to excellent *trans* diastereoselectivity (Scheme 83, equation 1). The reaction of pyrrolidinone **210a** with trimethylsilyl cyanide under the same reaction conditions yielded the 4,5-*cis*-pyrrolidinone **213** in 87% yield and with a diastereomeric ratio of 66:34 (Scheme 83, equation 2).[55]

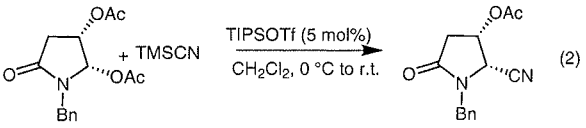



**210a** $R^1$ = Ac
**210b** $R^1$ = TBS

**212**

64–94%
*trans*/*cis* = 63:37 to 97:3

| NuTMS | $R^2$ |
|---|---|
| **195a** CH$_2$=C(Ph)(OTMS) | -CH$_2$COPh |
| **195b** CH$_2$=C(*t*-Bu)(OTMS) | -CH$_2$CO*t*-Bu |
| **211a** CH$_2$=CHCH$_2$TMS | -CH$_2$CH=CH$_2$ |
| **211b** (Me)$_2$C=C(OMe)(OTMS) | -C(Me)$_2$CO$_2$Me |

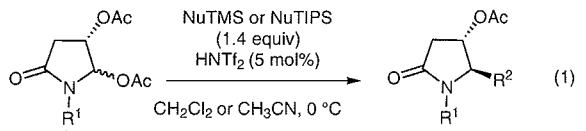



**210a**

**213**

82–94%
*cis*/*trans* = 57:43 to 60:40

**Scheme 82**

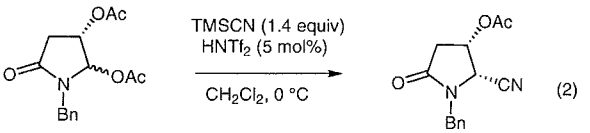



**206b** $R^1$ = PMB
**210a** $R^1$ = Bn
**214** $R^1$ = allyl

**215**

| NuTMS | $R^2$ |
|---|---|
| (Me)$_2$C=C(OMe)(OTMS) | -C(Me)$_2$CO$_2$Me |
| CH$_2$=C(*t*-Bu)(OTMS) | -CH$_2$CO*t*-Bu |
| CH$_2$=CHCH$_2$TMS | -CH$_2$CH=CH$_2$ |
| CH$_2$=C(Ph)(OTMS) | -CH$_2$COPh |
| *c*-C$_6$H$_9$OTMS | -2-cyclohexanonyl |
| CH$_2$=C(OTMS)*t*-Bu | -CH$_2$CO*t*-Bu |
| HC≡CC(OTIPS)=CH$_2$ | -CH$_2$COC≡CH |

55–90%
dr = 99:1–60:40



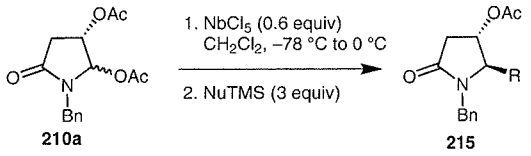

**210a**

**213**

87%
*cis*/*trans* = 66:34

**Scheme 83**

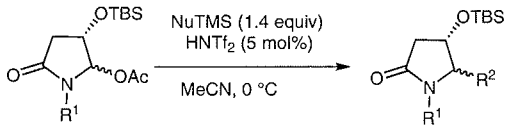
The pyrrolidinone **210a** reacted with allyltrimethylsilane and the silyl enol ether of acetophenone in the presence of niobium(V) chloride to afford adducts **215** in 86% and 81% yields and with moderate *trans* selectivity (Scheme 84).[61] The bismuth(III) triflate catalysed reaction of the pyrrolidinone **210a** with allyltrimethylsilane provided the 5-allylated pyrrolidinone in 82% yield (*trans*/*cis* = 70:30).[62]




| NuTMS | R | Yield (%) (*trans*/*cis*) |
|---|---|---|
| $CH_2CH=CH_2$ | $-CH_2CH=CH_2$ | 86 (67:33) |
| $CH_2=C(OTMS)(Ph)$ | $-CH_2COPh$ | 81 (67:33) |

**Scheme 84**

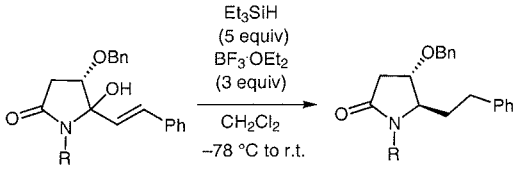
The reactions of pyrrolidinones **206a**, **210b** with silicon nucleophiles in the presence of bis(trifluoromethane)sulfonimide (5 mol%) in acetonitrile gave products **216** in yields ranging from 55% to 95% (Scheme 85).[55,63]




| NuTMS | $R^2$ |
|---|---|
| $CH_2=C(OTMS)t$-Bu | $-CH_2COt$-Bu |
| $c$-$C_6H_9OTMS$ | -2-cyclohexanonyl |
| $CH_2CH=CH_2$ | $-CH_2CH=CH_2$ |
| TMSCN | -CN |
| $(Me)_2C=C(OTMS)(OMe)$ | $-C(Me)_2CO_2Me$ |

**Scheme 85**

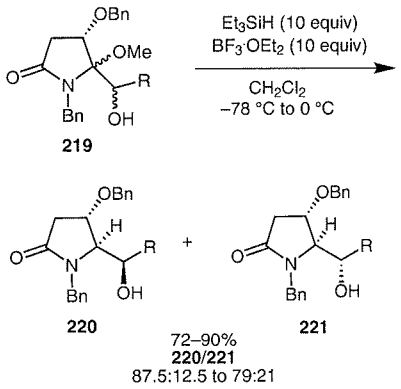
Pyrrolidinone **217** reacted with triethylsilane in the presence of boron trifluoride–diethyl ether complex to give the product **218** in a yield of 83% and with high 4,5-*trans* diastereoselectivity (Scheme 86).[64a]



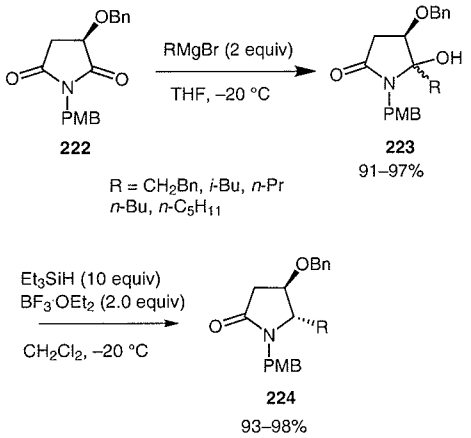

**Scheme 86**

The reaction of pyrrolidinone **219** with triethylsilane in the presence of boron trifluoride–diethyl ether complex provided products **220** and **221** in 72–90% yields, in favour of the *erythro* isomer (*erythro*/*threo* = 87.5:12.5 to 79:21) (Scheme 87).[65]

Treatment of imides **222** with Grignard reagents afforded 5-hydroxy-5-alkylpyrrolidinones **223** which were treated with triethylsilane in the presence of boron trifluoride–diethyl ether complex to give the 4,5-*trans* adducts **224** exclusively in yields of 93–98% (Scheme 88).[66]



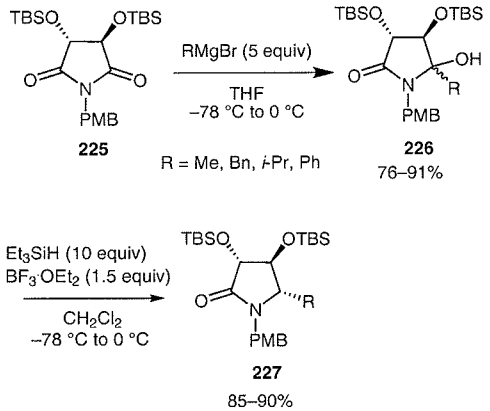

**Scheme 87**




**Scheme 88**

The reaction of imide **225** with Grignard reagents led to the formation of 5,5-disubstituted pyrrolidinones **226** in yields of 76–91%. Treatment of pyrrolidinones **226** with triethylsilane and boron trifluoride–diethyl ether complex provided the 4,5-*trans* isomer **227**, exclusively, in 85–90% yields (Scheme 89).[67]

While the addition of Grignard reagents and hydrides to imides **222** was regioselective and gave adducts of the

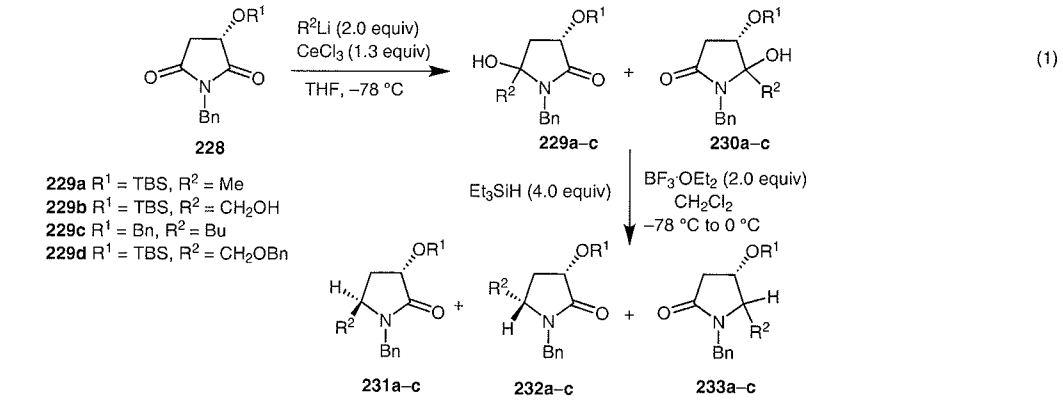



**Scheme 89**

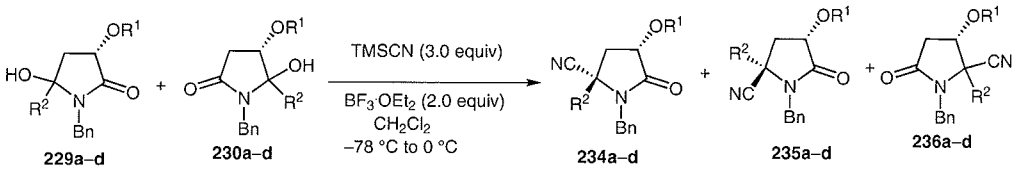
type **223** (Scheme 88), the reactions of organolithium reagents in the presence of cerium(III) chloride with imides **228** afforded regioisomeric mixtures of adducts **229** and **230**. The major adducts are **229**. These mixtures were treated with triethylsilane (Scheme 90, equation 1) in the presence of boron trifluoride–diethyl ether complex to give 3,5-*trans* alkyl-substituted pyrrolidinones. Reaction of triethylsilane with pyrrolidinones **229a**,**230a** and **229b**,**230b** gave products in 55% and 63% yields, respectively, in ratios of (**231**+**232**)/**233** = 73:27 and 75:25, respectively, while products **231c**,**232c** were isolated exclusively in 51% yield from the reaction of pyrrolidinone **229c** with triethylsilane. Similarly the reaction of trimethylsilyl cyanide with pyrrolidinones **229a**,**230a**, **229b**,**230b**, and **229d**,**230d** gave products in 50%, 68%, and 55% yields, respectively, with ratios of (**234**+**235**)/**236** = 73:27, 75:25 and 75:25. Products **234c**,**235c** were obtained exclusively, in 52% yield, from the reaction of imide **229c** with trimethylsilyl cyanide (Scheme 90, equation 2).[68]

Whereas the C-2 and C-5 carbonyl groups of imides **228a–d** reacted with organolithium reagents to give mixtures of the adducts **229** and **230** (Scheme 90), imides **237a–d** reacted only at C-2 and gave products of type **238a–d** with lithium trimethylsilylacetylide. Reduction of these 5-hydroxypyrrolidinones **238a–d** with triethylsilane and boron trifluoride–diethyl ether complex afforded products **239a–d** with very high 4,5-*trans* selectivity (Scheme 91, equation 1). In contrast, the reduction of pyrrolidinones **238a–c** with sodium cyanoborohydride and acetic acid afforded products **239a–c** with moderate 4,5-*cis* selectivity (Scheme 91, equation 2); **238d** gave the *trans* product as major isomer (*trans*/*cis* = 60:40).[65] The 4,5-*cis* isomer **239a** was prepared as a single diastereomer from the titanium chloride catalysed reaction of **240** (Scheme 91, equation 3).[69]

The addition reactions of allyltrimethylsilane to the 5-acetoxy-*N*-allylpyrrolidinones **214a** and **241** afforded products **215** and **242** with 4,5-*trans* selectivity (Scheme 92, equation 1). The highest *trans* selectivity (88:12) was observed from the reaction of pyrrolidinone **214a** with allyltrimethylsilane in the presence of titanium(IV) chloride. The use of indium(III) chloride, tin(IV) chloride or trimethylsilyl triflate as the Lewis acid in this reaction resulted in *trans*/*cis* product ratios of 80:20, 76:24 and 78:22, respectively. Treatment of pyrrolidinone **241** with allyltrimethylsilane under catalysis by boron trifluoride–diethyl ether complex or titanium(IV) chloride gave **242** in 64:36 and 69:31 diastereomeric ratios, respectively. In the same study, the reaction of the pyrrolidinone **243a**

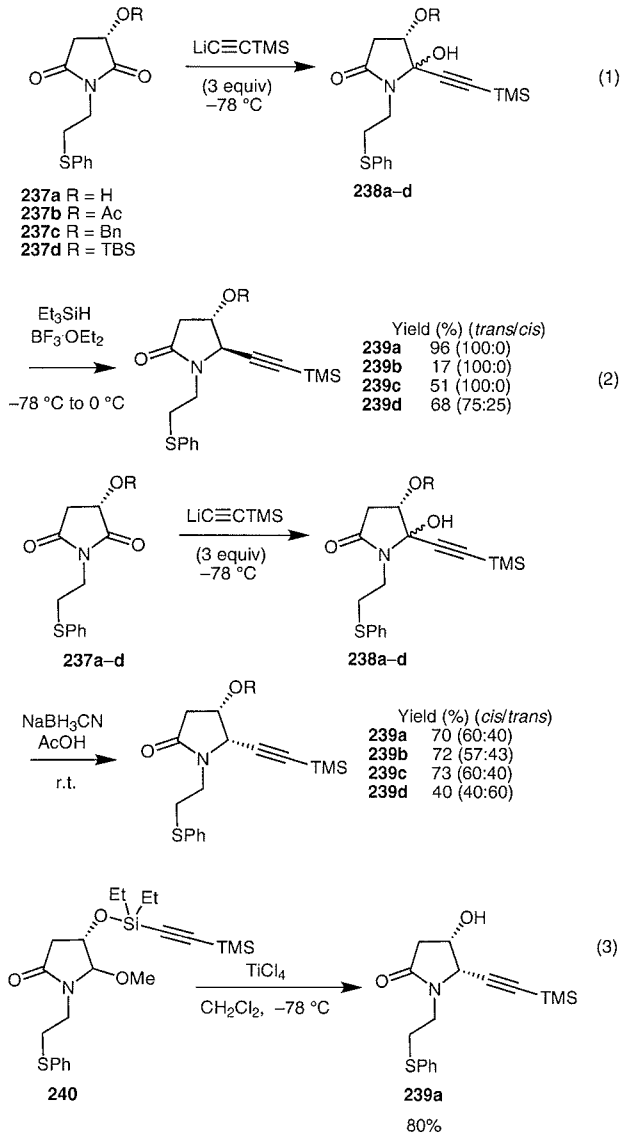



| R¹ | R² | Yield (%) (231/232/233) | 231/232 | (231+232)/233 |
|---|---|---|---|---|
| TBS | Me | 55 | 60:40 | 73:27 |
| TBS | $CH_2OH$ | 63 | 67:33 | 67:33 |
| Bn | Bu | 51 | 95:5 | 100:0 |




| R¹ | R² | Yield (%) (234/235/236) | 234/235 | (234+235)/236 |
|---|---|---|---|---|
| TBS | Me | 50 | 64:36 | 73:27 |
| TBS | $CH_2OH$ | 68 | 95:5 | 67:33 |
| Bn | Bu | 52 | 87:13 | 100:0 |
| TBS | $CH_2OBn$ | 55 | 95:5 | 67:33 |

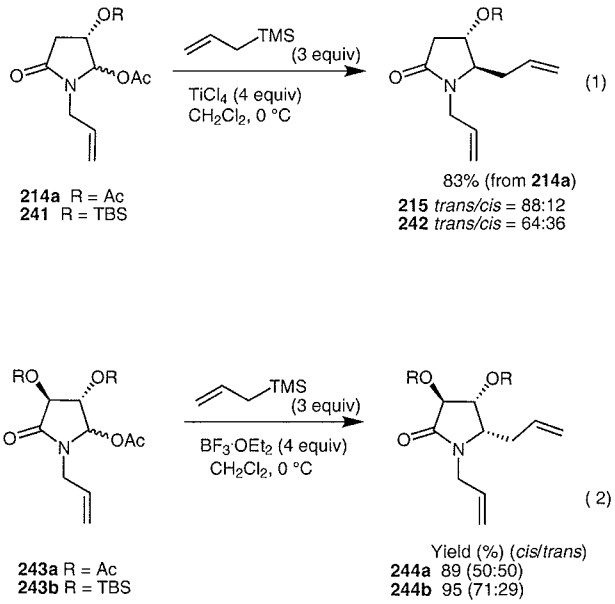
**Scheme 90**




**Scheme 91**

with allyltrimethylsilane afforded the C-5 allylated product **244a** with no selectivity (1:1) under catalysis by boron trifluoride–diethyl ether complex or titanium(IV) chloride, while pyrrolidinone **243b** gave the product **244b** with a *cis*/*trans* ratio of 71:29 under boron trifluoride–diethyl ether complex catalysis (Scheme 92, equation 2).[70]

The pyrrolidinones **245a** and **245b** were subjected to cyanation reaction conditions to afford the corresponding 5-cyanopyrrolidinones **246a**,**247a** and **246b**,**247b** in 96% and 82% yields, respectively (Scheme 93, equation 1). A 4,5-*cis* selectivity (**246a**/**247a** = 84:16) was observed in the reaction of **245a** in toluene. The use of dichloromethane as a solvent decreased the diastereomeric ratio of **246a**/**247a** to 80:20. Pyrrolidinone **245b** gave products with *trans* selectivity with a diastereomeric ratio of 82:18 and 77:23 in dichloromethane and toluene, respectively.



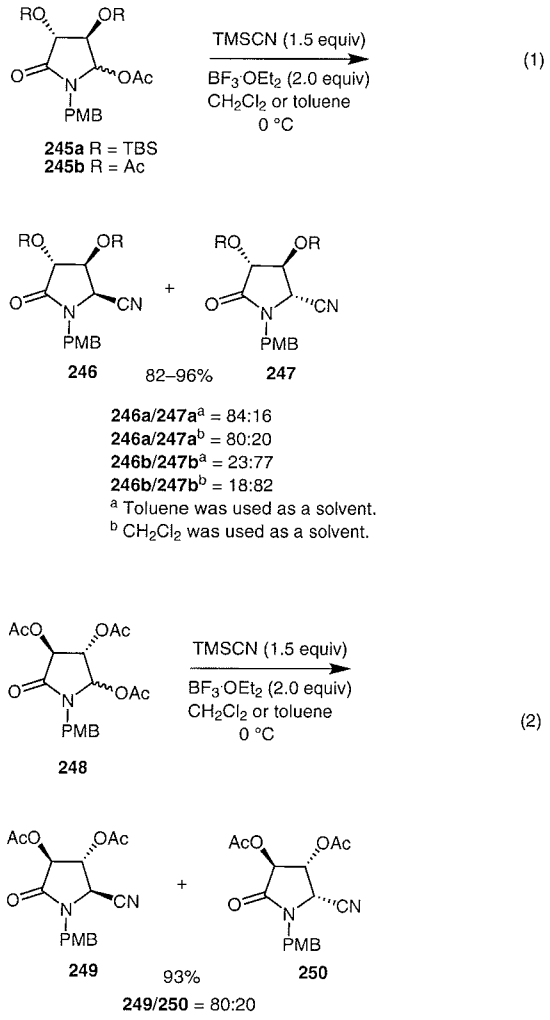

**Scheme 92**

Treatment of pyrrolidinone **248**, the enantiomer of **245b**, with trimethylsilyl cyanide provided products **249** and **250** in 93% yield and as a mixture of isomers (**249**/**250** = 80:20) (Scheme 93, equation 2).[71]

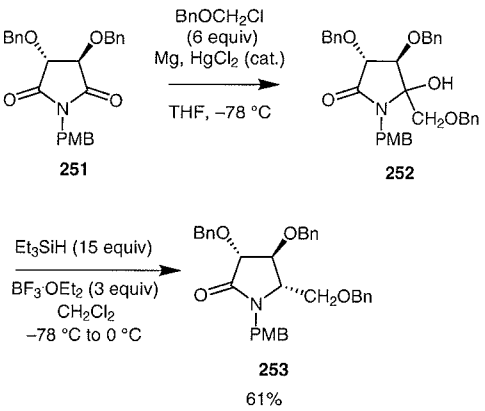
The addition of the Grignard reagent benzyloxymethylmagnesium chloride to imide **251** in the presence of mercury(II) chloride afforded the 5-hydroxypyrrolidinone **252** as a diastereomeric mixture. Treatment of this mixture with triethylsilane gave exclusively the 4,5-*trans* pyrrolidinone **253** in 61% yield (Scheme 94).[72]

Organolithium reagents were treated with imide **254** to afford 5-hydroxy-5-alkylpyrrolidinones **255**. The 4,5-*trans* pyrrolidinones **256** were obtained from the reaction of these 5-hydroxypyrrolidinones **255** with triethylsilane in the presence of boron trifluoride–diethyl ether complex (Scheme 95). Similarly, the reaction of pyrrolidinone **257** with lithium reagents and then triethylsilane under the same reaction conditions provided 4,5-*trans* products **259** in yields of 50–66%.[73]

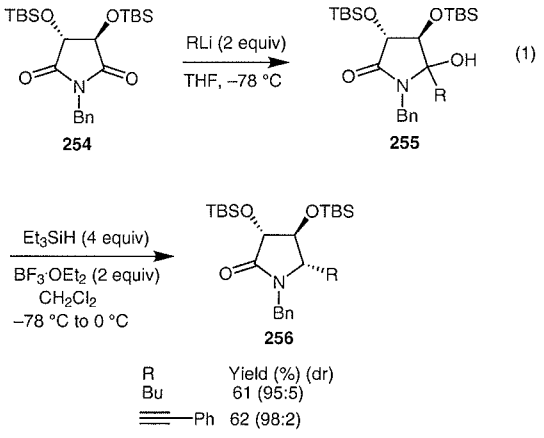
Treatment of **214a** with **260** (1.5 equiv) under triisopropylsilyl triflate catalysis in dichloromethane or diethyl ether gave the desired product **261a** in 50% yield and as a mixture of isomers (*trans*/*cis* = 85:15). The reaction of **243** with **195a** (1.4 equiv) provided the product **261b** with *cis* selectivity (*cis*/*trans* = 73:27) in 73% yield, while the reaction of **243** with **260** afforded product **261c** with no selectivity (dr = 50:50) and in a yield of 55% (Scheme 96).[54]

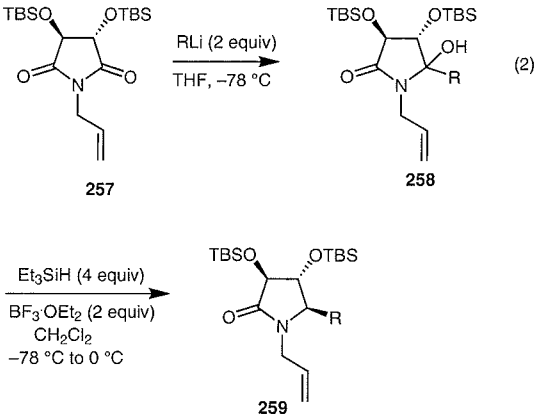



**Scheme 93**

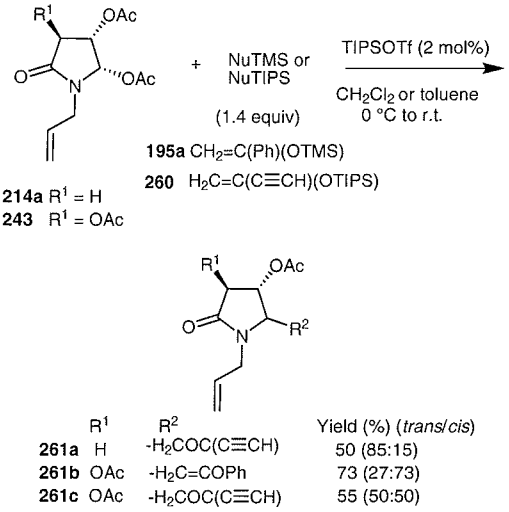



**Scheme 94**



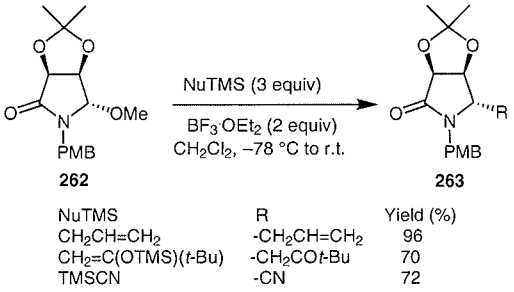




**Scheme 95**




**Scheme 96**

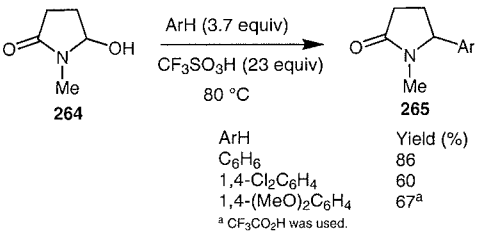
The boron trifluoride–diethyl ether complex promoted reaction of acetonide **262** with allyltrimethylsilane or the trimethylsilyl enol ether of pinacolone provided the corresponding products **263** in 96% and 70% yields, as the single isomers, whereas the reaction of **262** with trimethylsilyl cyanide gave product **263** as a mixture of diastereomers [(2*S*,3*S*,4*S*)/(2*R*,3*S*,4*S*) = 80:20] in 72% yield (Scheme 97).[74]




**Scheme 97**

### 3.2.1.2 Aromatic Nucleophiles

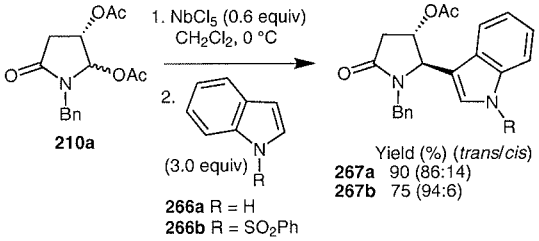
The reaction of benzene and its derivatives with the 5-hydroxypyrrolidinone **264** in the presence of trifluoromethanesulfonic acid or trifluoroacetic acid provided 5-arylpyrrolidinones **265** (Scheme 98). The reaction of benzene with **264** in the presence of trifluoromethanesulfonic acid gave **265** in 86% yield, while the less nucleophilic 1,4-dichlorobenzene gave **265** in 60% yield. 1,4-Dichlorobenzene did not react under trifluoroacetic acid catalysis; however, the more nucleophilic 1,4-dimethoxybenzene gave **265** in 67% yield.[36]



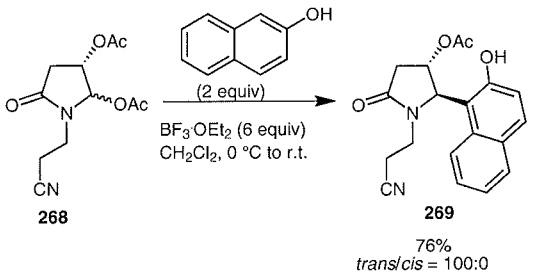

**Scheme 98**

Indole compounds **266a,b** reacted with 4,5-diacetoxypyrrolidinone **210a** in the presence of niobium(V) chloride to give *trans* adducts **267a,b** (Scheme 99). From **266a**, a 90% yield of **267a** (*trans*/*cis* = 86:14) was obtained, while **266b** afforded **267b** in 75% yield with a higher selectivity, *trans*/*cis* = 94:6.[61]

A boron trifluoride–diethyl ether complex mediated addition of 2-naphthol to 4,5-diacetoxypyrrolidinone **268** gave exclusively the *trans* arylated product **269** in 76% yield (Scheme 100).[75]



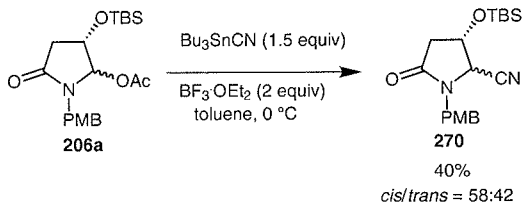

**Scheme 99**




**Scheme 100**

### 3.2.1.3 Organostannanes

5-Acetoxypyrrolidinone **206a** was subjected to cyanation reaction conditions with tributyltin cyanide under boron trifluoride–diethyl ether complex catalysis, and afforded the 5-cyanopyrrolidinone **270** in 40% yield and with low 4,5-*cis* diastereoselectivity (*cis*/*trans* = 58:42) (Scheme 101).[59]

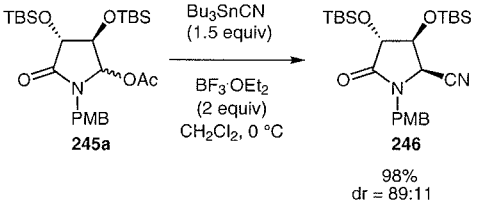



**Scheme 101**

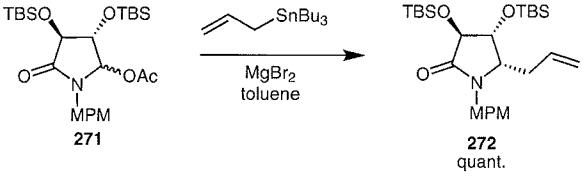
High 4,5-*cis* diastereoselectivity was obtained from the cyanation reaction of the 5-acetoxypyrrolidinone **245a** with tributyltin cyanide in the presence of boron trifluoride–diethyl ether complex. The use of dichloromethane or toluene as a solvent gave product **246** in 98% and 94% yields and with a *cis*/*trans* ratio of 89:11 and 90:10, respectively (Scheme 102).[71]

Treatment of the 5-acetoxypyrrolidinone **271** with allyltributylstannane in the presence of magnesium bromide yielded exclusively the 4,5-*cis* product **272**, and in quantitative yield (Scheme 103).[76]

Pyrrolidinones **214a,b** reacted with allylstannanes in the presence of Lewis acids to give the 5-allylated products **273a,b** (Scheme 104, equation 1). In the reaction of **214a**, titanium(IV) chloride gave the product **273a** with a *cis*/*trans* ratio of 67:33, boron trifluoride–diethyl ether com-

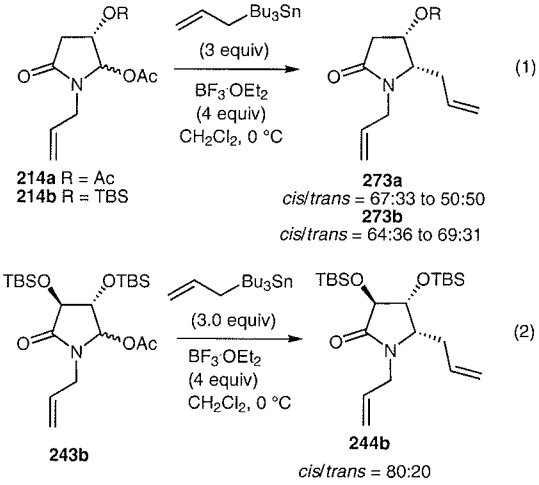



**Scheme 102**



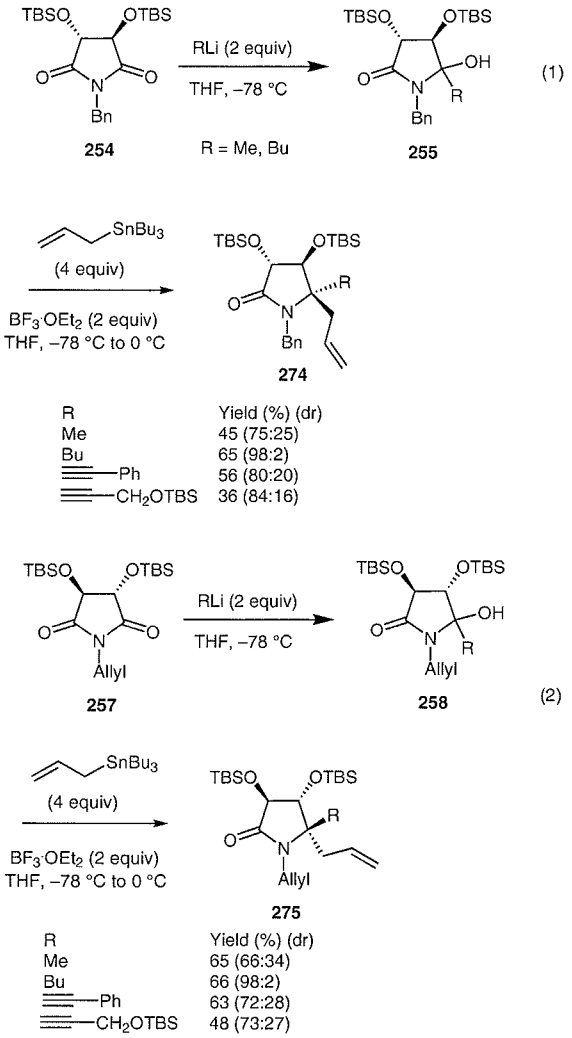

**Scheme 103**

plex gave a *cis*/*trans* ratio of 64:36 and titanium(IV) fluoride gave no selectivity (*cis*/*trans* = 50:50). In the reaction of pyrrolidinone **214b**, boron trifluoride–diethyl ether complex and magnesium bromide each gave a 69:31 mixture of isomers, favouring the *cis* isomer, while titanium(IV) chloride gave a 64:36 mixture of *cis*/*trans* isomers. The reaction of pyrrolidinone **243b** with allyltributyltin in the presence of boron trifluoride–diethyl ether complex provided the 5-allylated product **244b** as a mixture of isomers (*cis*/*trans* = 80:20) (Scheme 104, equation 2).[70]




**Scheme 104**

5-Hydroxypyrrolidinones **255**, obtained from the reaction of organolithium reagents with imides **254**, reacted with allyltributyltin in the presence of boron trifluoride–diethyl ether complex to afford 5-allyl-5-alkylpyrrolidinones **274**. The reaction of the 5-butyl-substituted pyrrolidinone with allyltributylstannane provided **274** in the highest yield (65%, dr = 98:2) (Scheme 105, equation 1). The *N*-allyl analogue, pyrrolidinone **257**, underwent addition reactions under the same conditions to afford products **275** in yields of 48–66% (Scheme 105, equation 2).[73]

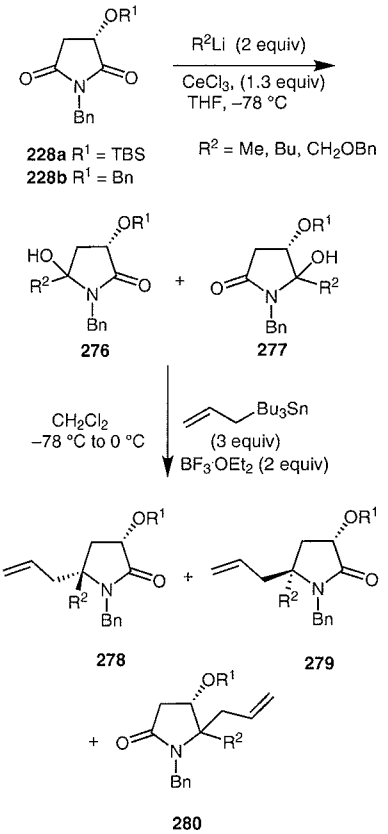



**Scheme 105**

The addition of organolithium compounds to imides **228a,b** gave a mixture of the regioisomers **276** and **277**. These isomers were subjected to allylation reactions with allyltributyltin in the presence of boron trifluoride–diethyl ether complex to give 5-alkyl-5-allylpyrrolidinones **278**, **279** and **280**, respectively. The reaction of pyrrolidinone **228a** with methyllithium and then allyltributyltin gave a mixture of **278**, **279** and **280** [(**278**+**279**)/**280** = 73:27] in 53% yield. Treatment of **228b** with butyllithium and then allyltributyltin gave only products **278** and **279** (**278**/**279** = 88:12) in 55% yield (Scheme 106).[68]

### 3.2.1.4 Organometallic Reagents

Zinc alkynylides, generated in situ, reacted with 5-methoxypyrrolidinone **281** in the presence of zinc triflate to afford the corresponding propargylic adducts **282** (Scheme 107).[52]

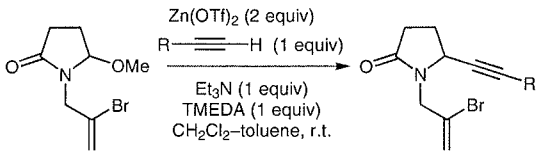



**228a** $R^1$ = TBS
**228b** $R^1$ = Bn

**276** **277** **278** **279** **280**

| $R^1$ | $R^2$ | Yield (%) | **278/279** | **(278+279)/280** |
|---|---|---|---|---|
| TBS | Me | 53 | 70:30 | 60:40 |
| Bn | Bu | 55 | 88:12 | 100:0 |
| Bn | $CH_2OBn$ | 64 | 98:2 | 67:33 |

**Scheme 106**




**281** **282**

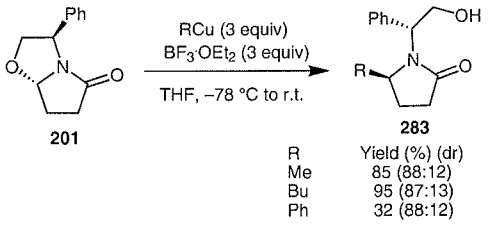
| R | Yield (%) |
|---|---|
| Ph | 58 |
| TMS | 58 |

**Scheme 107**

The reactions of organocopper reagents with pyrrolidinone **201** gave products **283** with good diastereoselectivities (dr = 87:13 to 88:12). Methyl and butyl cuprates gave **283** in 85% and 95% yields, respectively, while phenyl cuprate gave **283** in only 32% yield but also good diastereoselectivity (dr = 88:12) (Scheme 108).[56]

Treatment of the pyrrolidinone **284** with vinylmagnesium bromide in the presence of zinc chloride yielded the product **285** in 65% yield and with a *trans*/*cis* ratio of 80:20 (Scheme 109).[77]

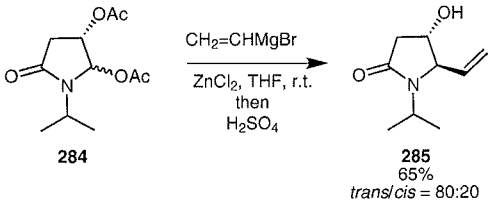
The zinc chloride–diethyl ether complex promoted reaction of pyrrolidinone **286** with Grignard reagents led to




**201** **283**

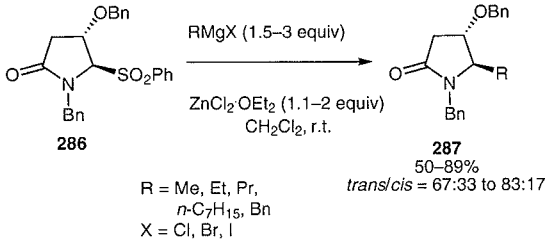
| R | Yield (%) (dr) |
|---|---|
| Me | 85 (88:12) |
| Bu | 95 (87:13) |
| Ph | 32 (88:12) |

**Scheme 108**




**284** **285**
65%
*trans*/*cis* = 80:20

**Scheme 109**



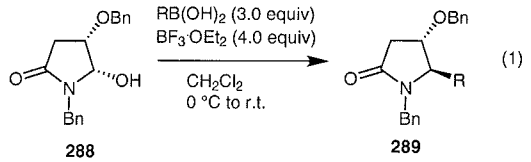

**286** **287**
50–89%
*trans*/*cis* = 67:33 to 83:17

**Scheme 110**

the formation of products **287** in yields of 50–89%, with 4,5-*trans* selectivity (Scheme 110).[78]

Treatment of 4-benzyloxy-5-hydroxypyrrolidinone **288** with boronic acids in the presence of boron trifluoride–diethyl ether complex afforded the corresponding *trans*-4,5-disubstituted pyrrolidinones **289**. The use of 2-furanboronic acid, 2-benzofuranboronic acid, styrylboronic acid, and potassium *trans*-styryltrifluoroborate all resulted in good to high *trans* selectivity. Phenylboronic acid did not react with the pyrrolidinone, but its electron-rich derivatives 4-methoxyphenylboronic acid and 3,4-dimethoxyphenylboronic acid provided 5-arylated pyrrolidinones in 48% and 74% yields (Scheme 111, equation 1). Reaction of **290**, the 4-hydroxy analogue of pyrrolidinone **288**, with 2-furanboronic acid and 3,4-dimethoxyphenylboronic acid gave 4,5-*trans* pyrrolidinones **291** in 65% (dr = 77:23) and 72% (dr = 72:28) yields, respectively. The use of 2-benzofuranboronic acid gave the 4,5-*cis* product in 56% yield and with a diastereomeric ratio of 92:8 (Scheme 111, equation 2).[64a]

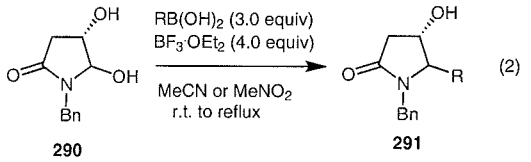
The reaction of pyrrolidinones **210a,b** and **292** with phenylacetylenetrifluoroborate in the presence of boron trifluoride–diethyl ether complex afforded the corresponding products **293** in 69–89% yield, with very high 4,5-*trans* selectivity (*trans*/*cis* = 90:10) (Scheme 112).[64b]




288 289 (1)

| R = | Yield (%) (*trans*/*cis*) |
|---|---|
| (*E*)-PhCH=CH | 47 (91:9) |
| (*E*)-PhCH=CH[a] | 59 (92:8) |
| 2-furyl | 79 (71:29) |
| 2-benzofuranyl | 55 (89:11) |
| 2-thienyl | 72 (38:62) |
| 4-$MeOC_6H_4$ | 48 (72:28) |
| 3,4-$(MeO)_2C_6H_3$ | 74 (74:26) |

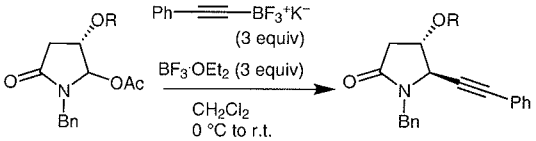
[a] The corresponding $RBF_3K$ was used.




290 291 (2)

| R = | Yield (%) (*trans*/*cis*) |
|---|---|
| (*E*)-PhCH=CH | 20 (9:91) |
| 2-furyl | 65 (77:23) |
| 2-benzofuranyl | 56 (8:92) |
| 3,4-$(MeO)_2C_6H_3$ | 44 (72:28) |

**Scheme 111**

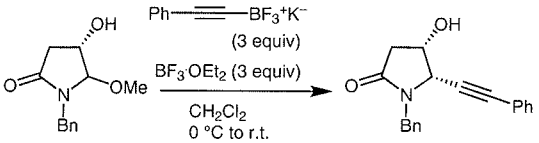



**210a** R = Ac
**210b** R = TBS
**292** R = Bn

**293**

| R | Yield (%) (*trans*/*cis*) |
|---|---|
| Ac | 69 (90:10) |
| TBS | 70 (100:0) |
| Bn | 89 (100:0) |

**Scheme 112**

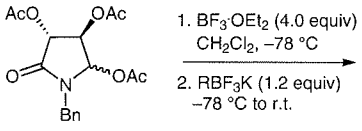



**294** **295** 70%

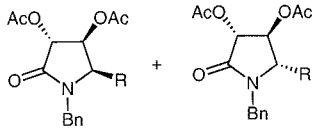
**Scheme 113**

The reaction of **294** with phenylacetylenetrifluoroborate under boron trifluoride–diethyl ether complex catalysis yielded the 4,5-*cis* adduct **295** exclusively in 70% yield (Scheme 113).[64b]

In a similar study, 5-acetoxy-2-pyrrolidinone **296** reacted with potassium organotrifluoroborates under boron trifluoride–diethyl ether complex catalysis to afford the corresponding products **297** and **298** with good 4,5-*syn* diastereoselectivity and in yields of 65–87% (Scheme 114).[79]




**296**




**297** **298**

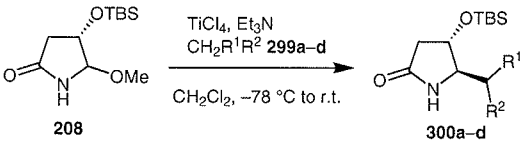
65–87%
**297**/**298** = 70:30 to 90:10

R = Ph, 4-$MeOC_6H_4$, 4-$FC_6H_4$, 3,5-$(CF_3)_2C_6H_3$, 2-$MeC_6H_4$, 3-thienyl, PhC≡C, *n*-BuC≡C, $MeOCH_2C$≡C

**Scheme 114**

### 3.2.1.5 Active Methylene Compounds

The reaction of 4-*tert*-butyldimethylsilyloxy-5-methoxypyrrolidinone **208** with titanium enolates derived from the active methylene compounds **299a–d** gave 4,5-disubstituted pyrrolidinones **300a–d**. Except for the reaction of the enolate derived from **299b** with **208**, high 4,5-*trans* selectivity was observed in these reactions (Scheme 115).[60]



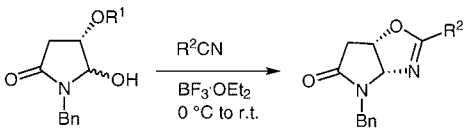

**208** **300a–d**

| | Yield (%) (*trans*/*cis*) |
|---|---|
| **a** $R^1 = R^2 = CO_2Et$ | 74 (90:10) |
| **b** $R^1$ = COMe, $R^2 = CO_2Me$ | 59 (9:91) |
| **c** $R^1$ = CN, $R^2 = CO_2Me$ | 43 (92:8) |
| **d** $R^1 = SO_2Ph$, $R^2 = CO_2Me$ | 50 (95:5) |

**Scheme 115**

### 3.2.1.6 Nitrile Nucleophiles (Ritter Reaction)

Treatment of pyrrolidinones **288** and **290** with nitriles in the presence of boron trifluoride–diethyl ether complex afforded the pyrrolo[2,3-*d*]oxazoles **301** in yields of 80–93% (Scheme 116).[80]




**288** $R^1$ = Bn
**290** $R^1$ = H

$R^2$ = Me, *i*-Pr, Ph, 3,4-$(MeO)_2C_6H_3$

**301** 80–93%

**Scheme 116**

This review continues with the chemistry of *N*-acyliminium ions derived from other five-membered heterocyclic and higher systems in the next issue of *Synthesis*.[1]

## Acknowledgment

We thank the Australian Research Council for supporting our research in this area.

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