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Mini Review

The intramolecular Stille reaction in some target natural product syntheses

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Abstract

A chronological summary of the contributions made by researchers in Nottingham, UK, to developing the scope for the intramolecular Stille reaction in target natural product syntheses, e.g. leinamycin, the virginiamycins, macrolactin A, rhizoxin, the amphidinolides, lophotoxin, and pateamine, is described.

Keywords: Stille reaction; Macrolactones; Macrolactams

1. Introduction

The palladium(0)-catalysed Stille coupling reaction between an organostannane reagent and an organic electrophile has become one of the revered methods for the synthesis of 1,3-dienes and other conjugated polyenes in contemporary organic synthesis [1–3]. Over the past decade, developments and applications of the scope for the reaction in the synthesis of complex macrocyclic structures of natural origin have been really quite awesome [4,5]. A few years ago, we captured a flavour of the momentum in this area in a review of the applications of the *intramolecular* Stille reaction [6]. At the same time, we surveyed the range of methods available for the synthesis of the organostannane and electrophile components used in the reaction. Our research group in Nottingham has been particularly interested in exploring the scope for the intramolecular Stille reaction in the synthesis of macrocyclic constructs for almost a decade, and we would like to believe that we have contributed in a significant way in this area. As a tribute to the late J.K. Stille, we now present a personalised and chronological summary of the contributions we have made to exposing the scope of the intramolecular Stille reaction in target macrocycles of particular biological interest to us over the past decade.

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2. Discussion

2.1. Leinamycin

Leinamycin **1** is a novel antitumor antibiotic substance isolated from *Streptomyces* [7]. Its structure is based on an unusual 1,3-dioxo-1,2-dithiolane ring system which is spiro-fused to a thiazole containing 1,3-diene macrolactam. We began work on the synthesis of the sulphur-containing portion of this structure in 1988, culminating in several approaches to this unit [8]. At the same time, we applied the Stille reaction to the functionalised precursor **2** under what have become known as Farina conditions i.e. $Pd(AsPh_3)_4$,·THF, reflux [9], to produce the macrolactam unit **3** in leinamycin [10]. Although Piers et al. [11] described the first examples of intramolecular Stille reactions, in 5- and 6-ring carbocyclic syntheses, our application to leinamycin was one of the first illustrations of its use in the formation of macrolactams and of relevance to natural products [12,13]. Fukuyama et al. [14] have subsequently published a concise total synthesis of leinamycin using a macrocyclisation strategy not based on the Stille reaction or its variants. This novel natural product and its analogues are presently undergoing extensive biological evaluation [15]. Since this early excursion into the intramolecular Stille reaction we sought other targets to apply the general methodology, including macrolactin A, the virginiamycins, rhizoxin, pateamine, the amphidinolides, and lophotoxin.

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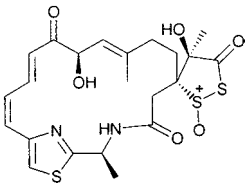

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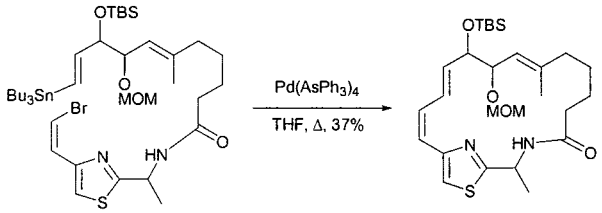

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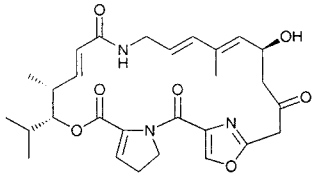
2.2. The virginiamycin 14,15-anhydropristinamycin

The virginiamycins are relatively 'old' antibiotic substances isolated from microorganisms [16]. They show structures based on a common 23-membered macrolide/bis-macrolactam accommodating an oxazole and a conjugated polyene segment. They are used commercially as food additives to improve growth of cattle, and as cholecystokinin (CCK) antagonists for treatment of anxiety and cancer withdrawal [17]. Their total synthesis had been pursued for several decades, but in 1996 the research groups of Meyers [18], Schlessinger [19], and ourselves [20] simultaneously outlined total synthesis of (−)-madumycin (**4**), (−)-virginiamycin M_2 (**5**), and anhydropristinamycin II_B (**6**), respectively.



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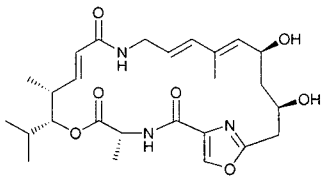

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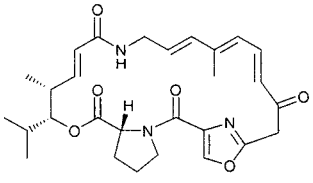

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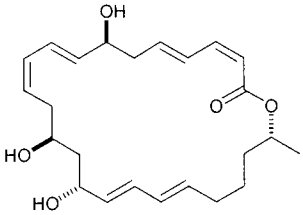
Our own synthesis had, as its focus, the application of the intramolecular Stille reaction from **7** under Farina conditions which led to the macrolactam triene **8** in an acceptable 30% yield. We also applied the same macrocyclisation strategy to a range of alternatively functionalised Stille precursors in a program designed to synthesise other virginiamycin analogues, but none of these was as successful as the conversion **7**→**8**.



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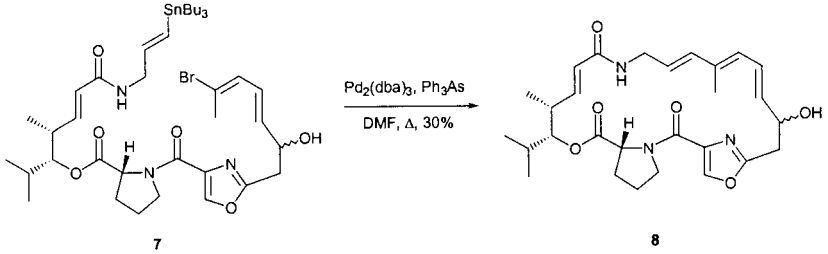

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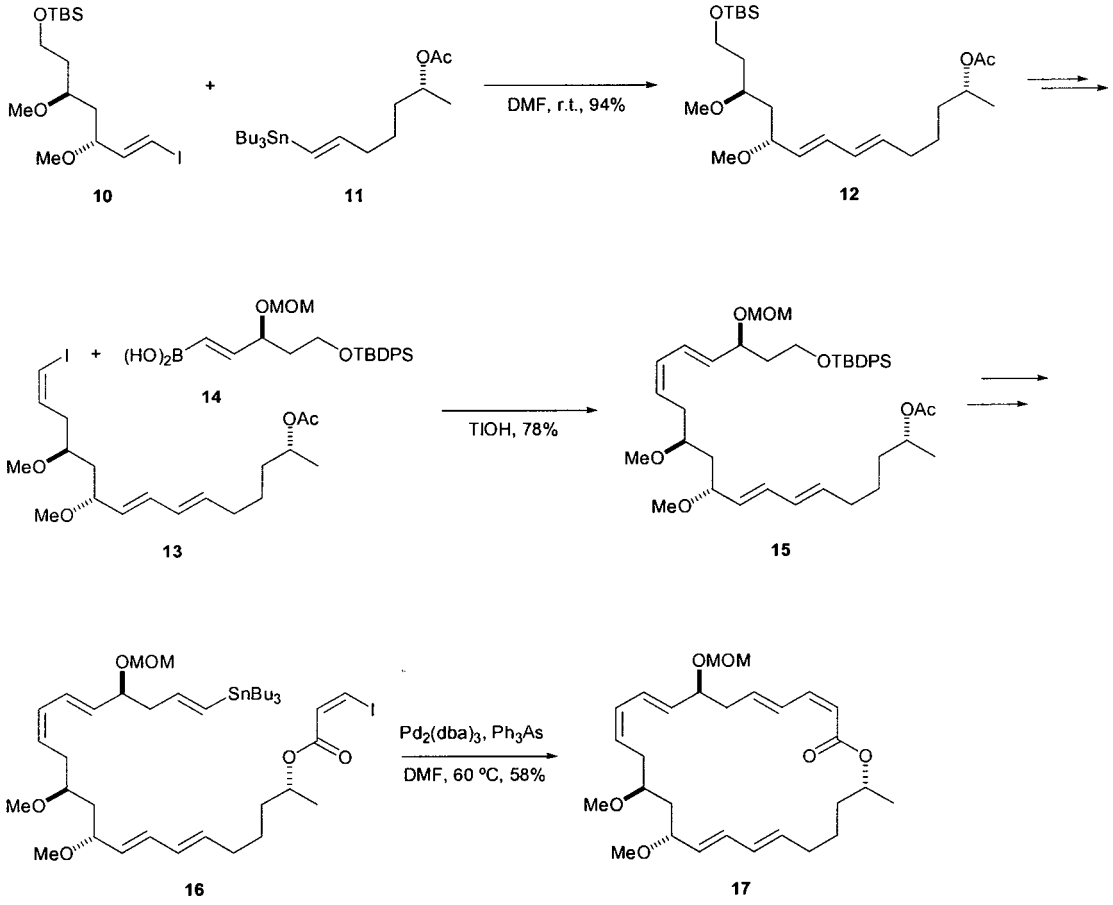
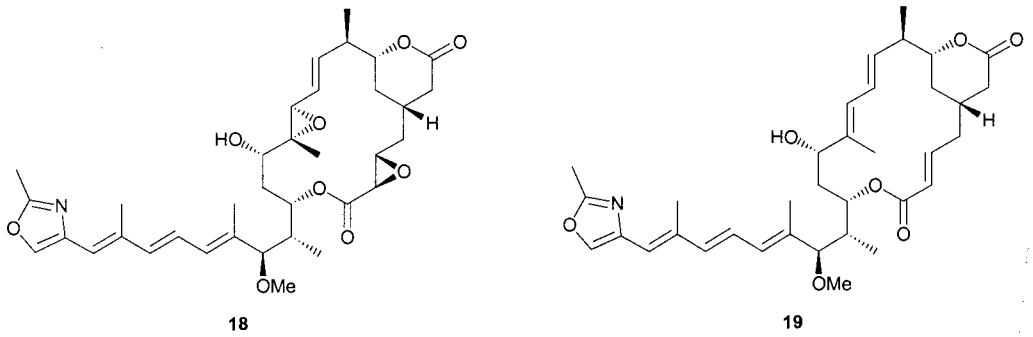
2.3. Macrolactin A

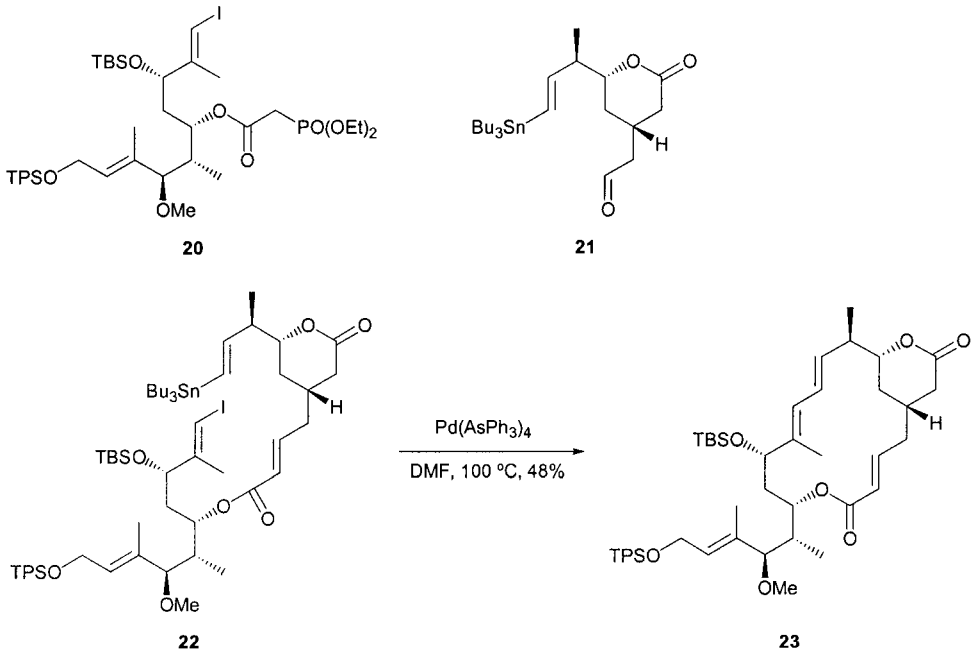
The triple 1,3-diene contained within the macrolide, macrolactin A (**9**), isolated from a deep sea marine bacterium [21], provided us with a unique opportunity to use a combination of inter- and intra-molecular Stille reactions to synthesise this unusual macrocyclic polyene. Macrolactin A is an extremely cytotoxic compound which, amongst other things, inhibits B16–F10 murine melanoma cancer cells and mammalian *Herpes simplex* viruses, and we embarked on its synthesis in 1992 shortly following the publication of its structure. Thus, we first synthesised the iodide **10** and the stannane **11**, and then coupled them to give **12**. The 1,3-diene **12** was later elaborated to the *Z*-vinyl iodide **13**, which was next coupled to the boronic acid **14** [2,22] leading to the *E*,*E*,*Z*,*E* tetraene **15**. The synthesis of the protected macrolactin A was completed by intramolecular coupling from **16** under Farina conditions which led to **17** in an unoptimised 58% yield [23]. Unfortunately, we experienced difficulty in deprotecting the OMe residues in **17** which frustrated us in completing the total synthesis of the natural product. Subsequent to these studies, Smith et al. [24] described an almost identical synthetic strategy using different protecting groups, and these authors were able to secure a synthesis of the natural product.



2.4. Rhizoxin

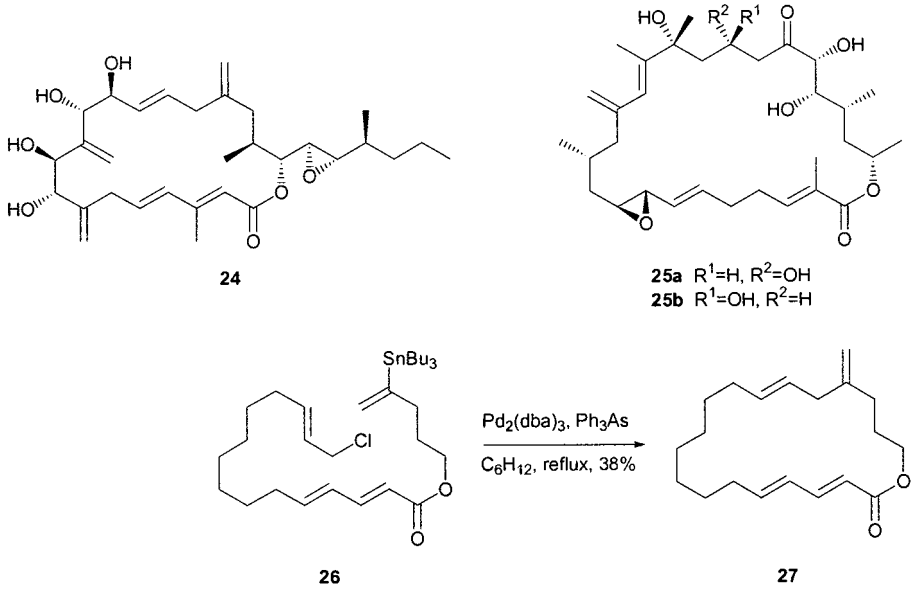
Rhizoxin (**18**) is the most highly functionalised species among a unique class of secondary metabolites, isolated in small quantities from the pathogenic fungus *Rhizopus chinensis*, which is the aetiologic agent of rice seedling blight [25]. Many other related metabolites have been isolated from the fungus including the conjugated 1,3-diene (rhizoxin D) **19**, which is a logical biogenetic precursor to rhizoxin. We embarked on synthetic studies towards rhizoxin in 1993 coincidental with the publication of the first synthesis of this intriguing metabolite by Ohno et al. [26]. A number of other research groups later published syntheses of the didesepoxyrhizoxin **19** [27,28]. Our own design to the polyene macrolide portion in **19** differed from previous approaches in that we chose to use the intramolecular Stille reaction from the vinylstannane–vinyl iodide **22** as a key stratagem. Thus, the precursors **20** and **21** were synthesised and then coupled under Wadsworth–Emmons olefination conditions leading to the unsaturated ester **22**. A Stille cyclisation of **22** under Farina conditions then produced the corresponding polyene macrolide **23** in 48% yield, which was subsequently elaborated to didesepoxyrhizoxin (rhizoxin D) **19** [29].

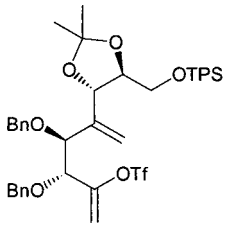




2.5. Amphidinolides A and B

The amphidinolides are an ever-expanding family of polyene, polyol-based macrolides isolated from dinoflagellates of the genus *Amphidinium* which show potent anti-tumour activity [30]. Amphidinolide A (**24**) was the first of the series to be characterised [31], closely followed by amphidinolides B_1 and B_2 (**25a** and **b**), [32]; amphidinolide T5 was described in the literature during 2001 [33]. Amphidinolide A features a 20-membered macrolactone core which accommodates three *exo*-methylene groups, two of which are also parts of 1,4-diene units. Although there was some precedent [34], the equivalent sp^2–sp^3 coupling equivalent of the Stille (sp^2–sp^2) reaction was less commonly used in 1992 when we decided to examine this approach to the core macrolide system in amphidinolide A. Much to our pleasure, a coupling reaction from the vinyl stannane–allyl chloride **26** proceeded quite smoothly under Farina conditions, and gave the macrocyclic 1,4-diene **27** in an agreeable 38% yield [35]. The formation of **27** was accompanied by small amounts of the corresponding *Z*-isomeric and allylic positional isomer products. In contemporaneous studies we have also described a concise synthesis of the unique ene-tetrol unit **28** [36], and very recently we have completed a total synthesis of the amphidinolide A stereostructure **24** involving a novel sp^2–sp^3 Stille reaction from the precursor **29** derived from **28** [37].





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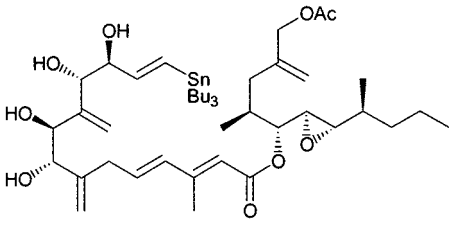

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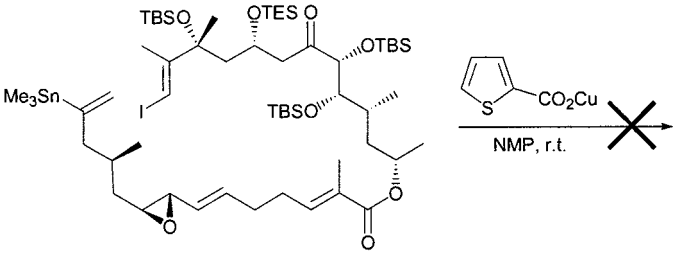
Not all intramolecular Stille reactions we have investigated, however, are successful. A case in point is the approach we made to amphidinolide B (**25**). Thus, we synthesised both the carboxylic acid and the alcohol precursors, and then coupled them to provide the key ester intermediate **30**, but much to our chagrin we have not yet been able to effect a Stille macrocyclisation from **30** to **31**, under a wide range of conditions [38,39]. Instead, the major product from this reaction has been the symmetrical dimer resulting from Piers-type vinylstannane–vinylstannane coupling of **30**. We believe that the problem most likely has its origin in the steric congestion associated with the bulky TBS protected *t*-alcohol adjacent to the vinyl iodide residue in **30**. Further work is now in progress to circumvent this issue, which will hopefully lead to a successful synthesis of amphidinolide B [40].



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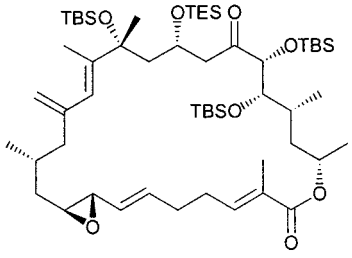

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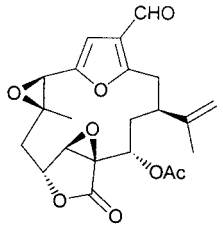
2.6. Lophotoxin

Lophotoxin (**32**) is the name given to a unique furanocembrane isolated from species of the Pacific sea whip *Lophogorgia* [41]. The compound has potent neurotoxic properties and binds in a selective and irreversible manner to acetylcholine recognition sites in nicotinic acetylcholine receptors leading to paralysis and asphyxiation, i.e. it is not a pleasant natural product! Over several years, we have examined a number of synthetic approaches to this deceptively challenging target and its congeners [42]. These studies have recently culminated in a successful synthesis of the desepoxylophotoxin **33** using a strategy based on sequential carbanion alkylation (to **36**) and intramolecular Stille coupling from **36**, using the chiral building blocks **34** and **35**, leading to the furanocembranolide **37**, followed by functional group manipulation [43]. Studies are in progress to effect the regio- and stereochemically controlled bis-epoxidation of **33** leading to lophotoxin itself [44].



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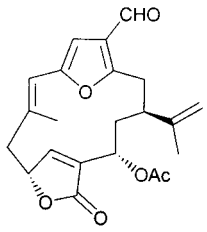

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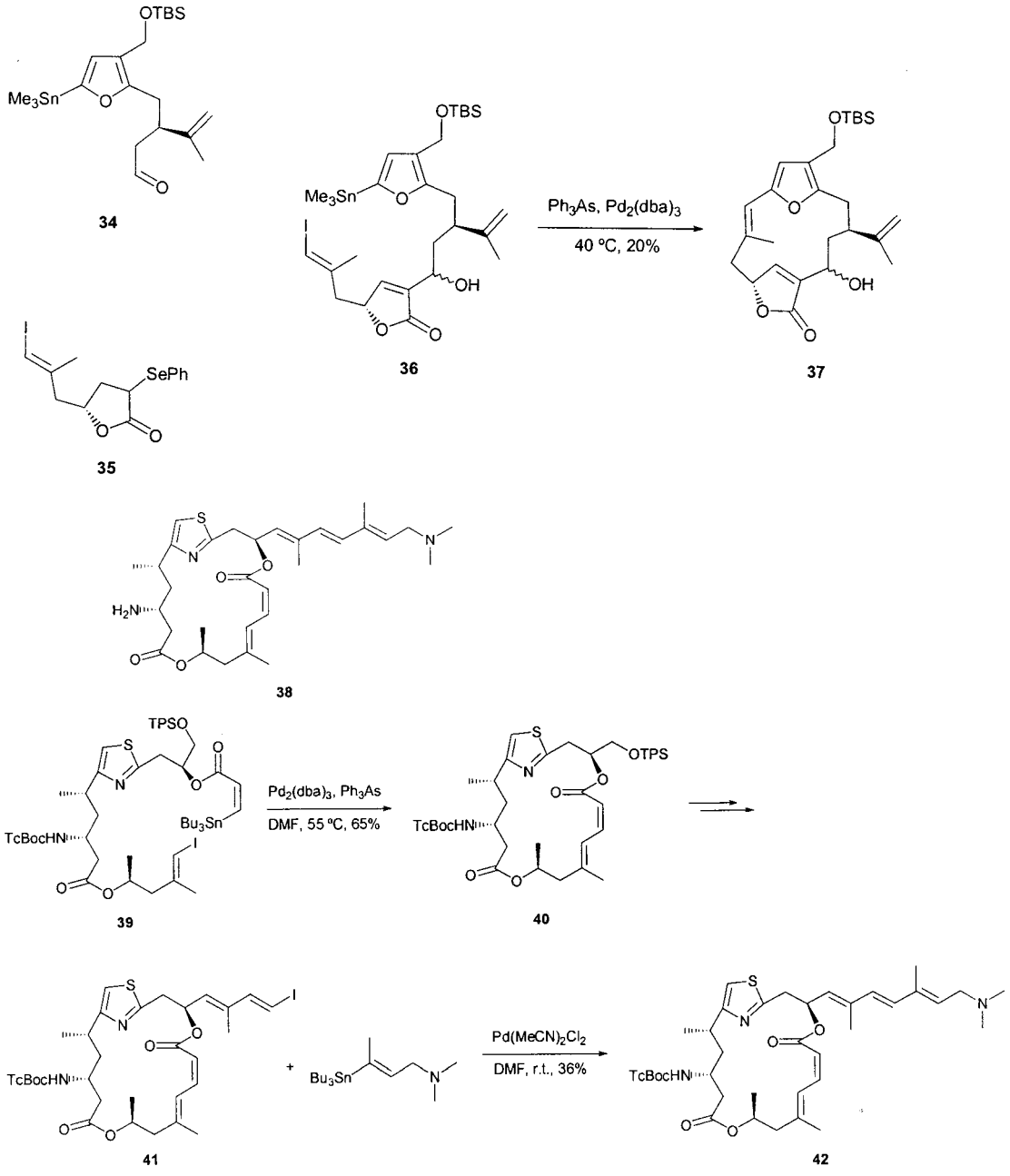
2.7. Pateamine

Pateamine (**38**) is a somewhat striking and unusual natural product which has been isolated from the marine sponge *Mycale* sp. [45]. Its structure shows a unique thiazole-containing 19-membered-bis-lactone core which accommodates a *E*,*Z*-1,3-diene unit and is substituted by an unusual all-*E*-trienamine residue. Pateamine (**38**) exhibits potent immunosuppressant properties with low cytotoxicity. We began synthetic work on this compound in 1994 which climaxed some 5 years later in a total synthesis [46]. Our synthesis featured both the intra- and intermolecular Stille sp^2–sp^2 coupling reactions to elaborate the *E*,*Z* diene macrolide **40** (from **39**) and the all-*E*-polyene side chain portion, viz **41** → **42**, [47]. Coincidentally, we also compared the Stille reaction with the Heck reaction for elaborating

the macrolide portion in pateamine from appropriate precursors [48]. In every respect, and as expected, the Stille coupling approach was immeasurably superior.



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