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REVIEW

The formation of carbon–carbon and carbon–heteroatom bonds using silver tetrafluoroborate as a promoter

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Transition metal promoter;
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Abstract Silver tetrafluoroborate ($AgBF_4$) is a transition metal salt extensively used in organic syntheses. This review provides insight into the use of the silver salt as a promoter in the synthesis of compounds *via* the formation of carbon–carbon and carbon–heteroatom bonds. We summarised articles where $AgBF_4$ plays an important role in the activation of coupling sites. These include the elimination of oxygen and sulphur leaving groups, hydride abstraction, halide abstraction and participation in stereo-selective and regio-specific halogenation reactions. $AgBF_4$-mediation in heterocyclisation reactions, ring-opening and successive cyclisation reactions were also reviewed. The uses of the $AgBF_4$ in the heteroatom–heteroatom bond-forming reaction and in the formation of complexes are beyond the scope of this review and were therefore not considered.

Contents

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1. Introduction

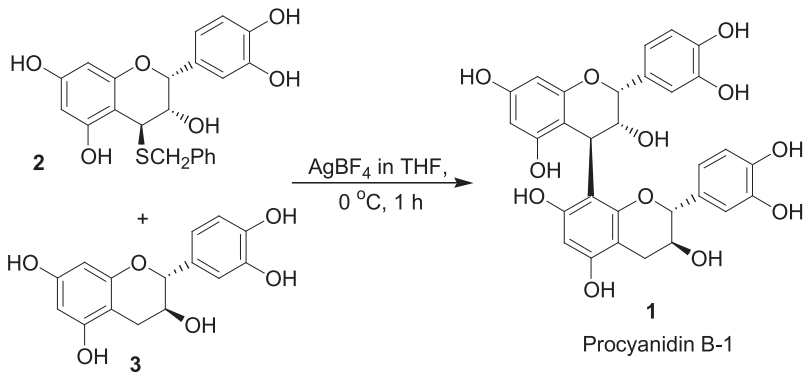
Transition metal promoters, widely used for carbon–carbon, carbon–heteroatom and heteroatom–heteroatom bond formation, are active areas of research in organic chemistry. Silver salts, particularly $AgBF_4$ (a Lewis acid, a white deliquescent crystal inorganic salt), have been used to form carbon–carbon and carbon–heteroatom bonds under mild and environmentally friendly conditions and in good yields (Chen et al., 2010; Steynberg et al., 1998; Barrett et al., 1989). The importance of $AgBF_4$ promoted rearrangements in organic synthetic chemistry has grown significantly over the last four decades (Paquette and Stowell, 1971). A comprehensive search revealed reviewed papers (Álvarez-Corral et al., 2008; Weibel et al., 2008, 2010a,b; Grant and West, 2010; Belmont, 2010; Kawasaki and Yamamoto, 2010; Driver, 2010; Lovely, 2010; Li and He, 2006; Kantorowski and Kurth, 2000) in which varieties of silver-mediated syntheses, including $AgBF_4$-promoted reactions, were summarised. Weibel et al. (2008) comprehensively reviewed a number of articles (Kinsman et al., 1987; Mitasev and Brummond, 2006; Gallagher et al., 1991; Lathbury and Gallagher, 1985, 1986; Davies et al., 1992; Lathbury et al., 1989) that demonstrate interesting $AgBF_4$-promoted hetero-cyclisations through C–N bond formations to provide optically active compounds. Kantorowski and Kurth (2000) reviewed two articles that described the ability of $AgBF_4$ to promote reactions that afford ring expansion to seven-membered rings *via* BF_4^- anion stabilised intermediates.

Silver tetra-fluoroborate ($AgBF_4$) has interesting properties that are attributed to the anion (BF_4^-), but this non-basic, non-nucleophilic, anionic BF_4^- ion has been assumed not to take part in identified reactions (Honeychuck and Hersh, 1989; Rosenthal, 1973) and it is speculated that it stabilises positively charged intermediates (Achilonu et al., 2008). Nevertheless, the participation of BF_4^- in fluorination of compounds has been recorded (Chen et al., 2010, 2012; Cochrane et al., 2013; Wang et al., 2013a,b, 2010; Tang and Ritter, 2011; Shibata et al., 2010; Kirk and Othmer, 1966). Another noteworthy property of $AgBF_4$ is its ability to act as a moderately strong oxidant (one-electron abstraction) (Achilonu et al., 2008). $AgBF_4$ is soluble in H_2O, diethyl ether, tetrahydrofuran (THF), toluene and nitromethane, moderately soluble in benzene and cyclohexene, and insoluble in cyclohexane (Sharpe, 1952). However, when a polar solvent such as acetonitrile or water is used in a reaction system involving $AgBF_4$, the solvent binds and deactivates the $Ag+$ ion that is supposed to be the driving force of the reaction.

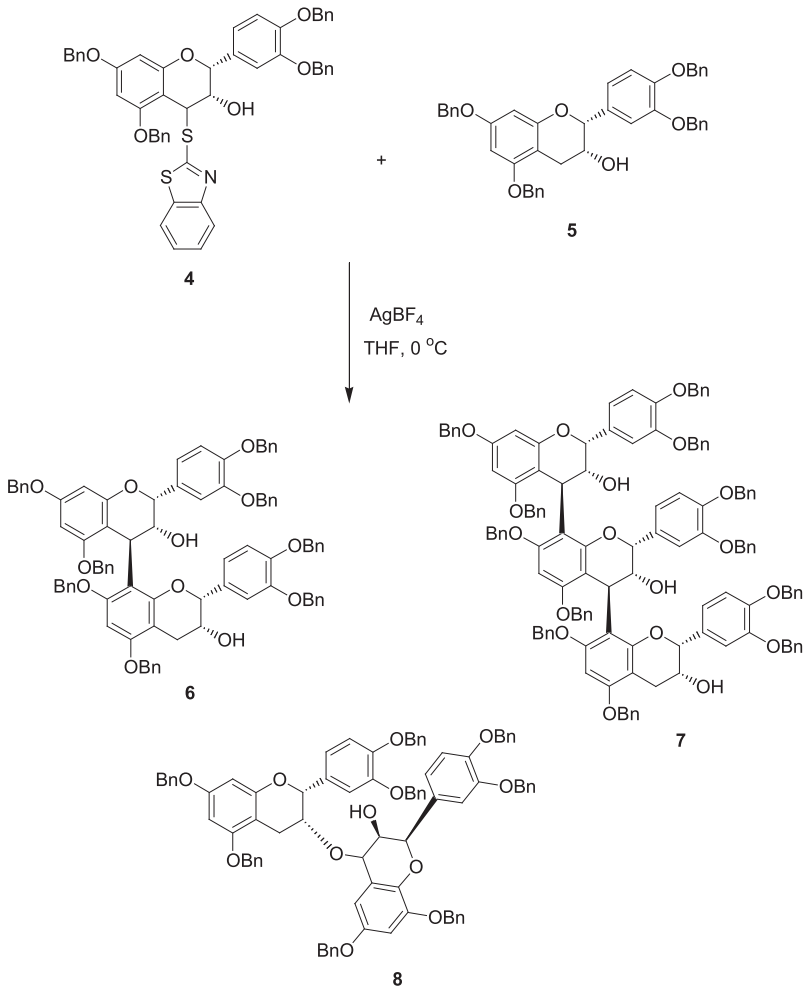
The salt is commonly used to replace halogens. The abstraction of the halide is driven by characteristic precipitation of the appropriate silver halide while activating the actual catalytic species (Broka and Gerlits, 1988). Its importance in cyclisation reactions has also been widely demonstrated (Luo et al., 2005; Liu et al., 2010). In the present review, we summarise the role of $AgBF_4$ in activating oxygen and sulphur leaving groups, in oxidative coupling reactions *via* hydride abstraction, as a reaction promoter through halide abstraction and Ag(I) halide formation, and activity in stereo-selective and regiospecific halogenation reactions. We also considered $AgBF_4$ mediation in heterocyclisation reactions and ring-opening and subsequent cyclisation reactions. Furthermore, we recapitulated complexation with strained σ-bonds with enhanced *p* character, and the activities of the BF_4^- anion in organic synthesis. The use of $AgBF_4$ in heteroatom–heteroatom bond-forming reactions (Álvarez-Corral et al., 2008; Weibel et al., 2008; Grimaldi and Cormons, 1989) and in formation of complexes falls outside the scope of this review and will therefore not be considered.

2. $AgBF_4$-promoted activation of oxygen and sulphur containing leaving groups

The affinity of dimethyl(methylthio)-sulphonium tetrafluoroborate (DMTSF) and $AgBF_4$ towards oxygen and sulphur has been exploited to activate the benzylic C–S and C–O ether leaving groups of flavan-3-ol analogues for carbon nucleophiles. This property has been explored to create good routes to obtain procyanidins **1** under neutral reaction conditions. Trost et al. (1981, 1985) and Barrett 1989 demonstrated the effectiveness of DMTSF and $AgBF_4$ in activating benzylic thioether bond of flavan-3-ol for C–C interflavanyl bond formation. The studies of Thompson and coworkers (1972) revealed that reactions of thiophilic Lewis acids with 4β-benzyl sulphanylepicateehin and catechin activator $AgBF_4$ afforded procyanidin B-1 in improved yield of 38% over DMTSF activator that afforded 22%. Studies by Van Rensburg et al. (1996, 1997) described successful activation of benzylic C–S bond of a benzylsulphanyldihydrochalcone towards the formation of a C–O bond in the synthesis of dihydroflavonols using $AgBF_4$. Steynberg et al. (1998) recorded development of methodologies for C–C interflavanyl bond formation under neutral conditions. The optimised protocol involved treating a mixture of 4β-benzenesulphanylepicatechin **2** and catechin **3** in THF with $AgBF_4$ (2.5 equiv.) for 1 h at 0 °C to obtain procyanidin B-1 in 38% yield (Scheme 1). The formation of 4β-interflavanyl bond is explicable by the thiobenzyl ether being converted by the $AgBF_4$ into relatively stable carbocationic intermediate allowing regioselective attack of the nucleophile *via* C-8 where the HOMO displays maximum amplitude and



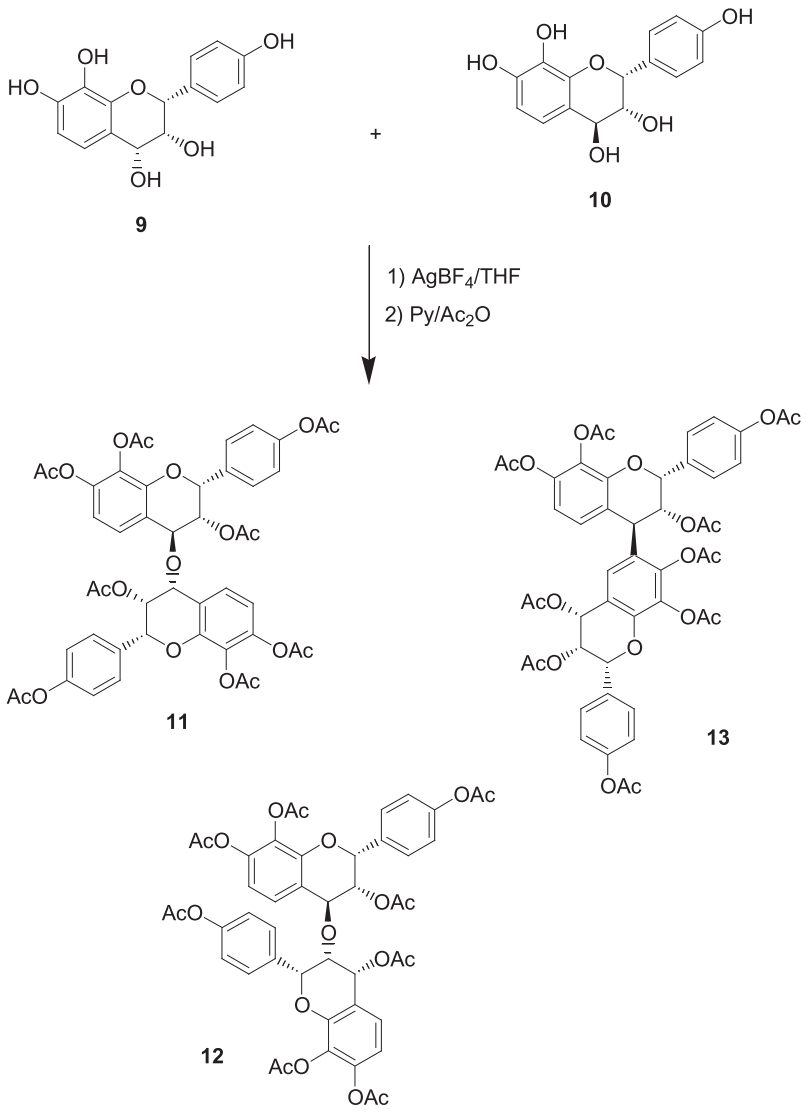
Scheme 1 Interflavanyl bond formation in procyanidins under neutral conditions.



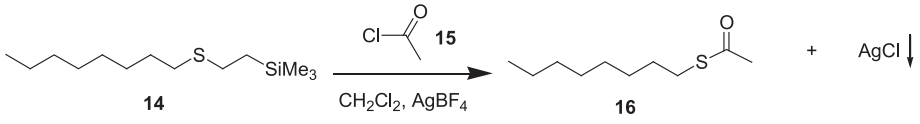
Scheme 2 Synthesis of procyanidin oligomers using the 4-[(2-benzothiazolyl)thio] derivative.

the stereoselectivity by approach from the sterically least hindered side.

Oligomers larger than the tetramer are poorly or not accessible. Favourable chain extension protocols involve activation of 4-(benzylthio)catechin and epicatechin by DMTSF or, preferably by $AgBF_4$. This protocol has exclusive virtue of forming $4 \rightarrow 8$-interflavanyl linked products. On the other hand, a 2-mercaptobenzothiazole is used to avoid the offensive odour associated with 4-thio derivatives. Condensation of **4** and **5** in dry THF in the presence of anhydrous $AgBF_4$ at 0 °C resulted in the formation of $4\beta \rightarrow 8$-dimer **6** (56%), $(4\beta \rightarrow 8)_2$-trimer **7** (14%) and 3-*O*-4-dimer **8** (5%), as presented in Scheme 2. However, the undesired intervention of the 3-hydroxyl group in the chain elongation process could be avoided by protecting this 3-OH group in both the electrophilic **2** and the nucleophilic **3** reaction partners.



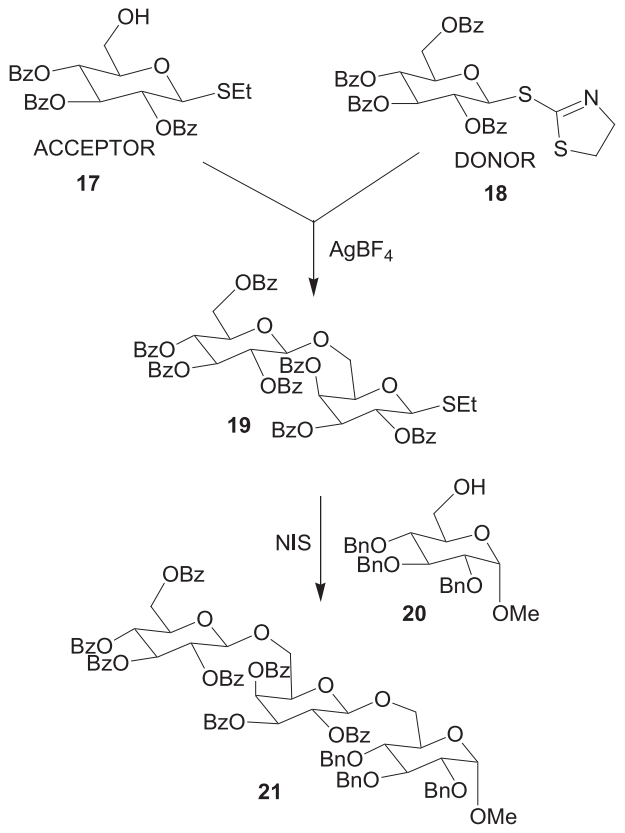
Scheme 3 Synthesis of ether-linked proteracacinidins **11** and **12** and the C–C coupled analogue **13**.



Scheme 4 Conversion of 2-(trimethylsilyl)ethyl sulphide into a thioester.

Additionally, attempts to improve yield with molecular sieves were ineffective. Interestingly, vacuum-drying the $AgBF_4$ immediately before the reaction afforded a series of oligomers ranging from the trimer to the octamer were isolated in a combined yield of 91%. No 4 → 6-linked products were found (Kozikowski et al., 2003).

$AgBF_4$ was used to activate OH groups to synthesise the ether-linked proanthocyanidins, proteracacinidin and promelacacinidin (Bennie et al., 2000; Foo, 1989; Coetzee et al., 1998a,b). The protocol involved treating a mixture of the epioritin-4β- **9** and 4α-ols **10** in dry THF at 0 °C with $AgBF_4$ for 90 min under nitrogen before the reaction was quenched with water. After work-up and purification processes including acetylation, the expected products, epioritin-(4*β* → 4)-epioritin-4α-ol **11** (9%) and epioritin-(4*β* → 3)-epioritin-4α-ol **12** (8%), accompanied by a C–C-linked compound, epioritin-(4*β* → 6)-epioritin-4α-ol **13** (7%) were obtained as the octa-*O*-acetyl derivatives (Scheme 3). Formation of **11** and **12** could be attributed to the activation of the reactive axial C-4 hydroxyl group of **10**, coupled with the outstanding stable equatorial benzylic OH group of 9 serving as the ambient nucleophile. On the other hand, the earlier work by Coetzee et al. (1998a,b) using $AgBF_4$ to activate the free phenolic epioritin-4b-ol **10** towards self-condensation resulted in isolating **12** and **13** from a complex reaction mixture. The stereochemistry of the products can be explained in



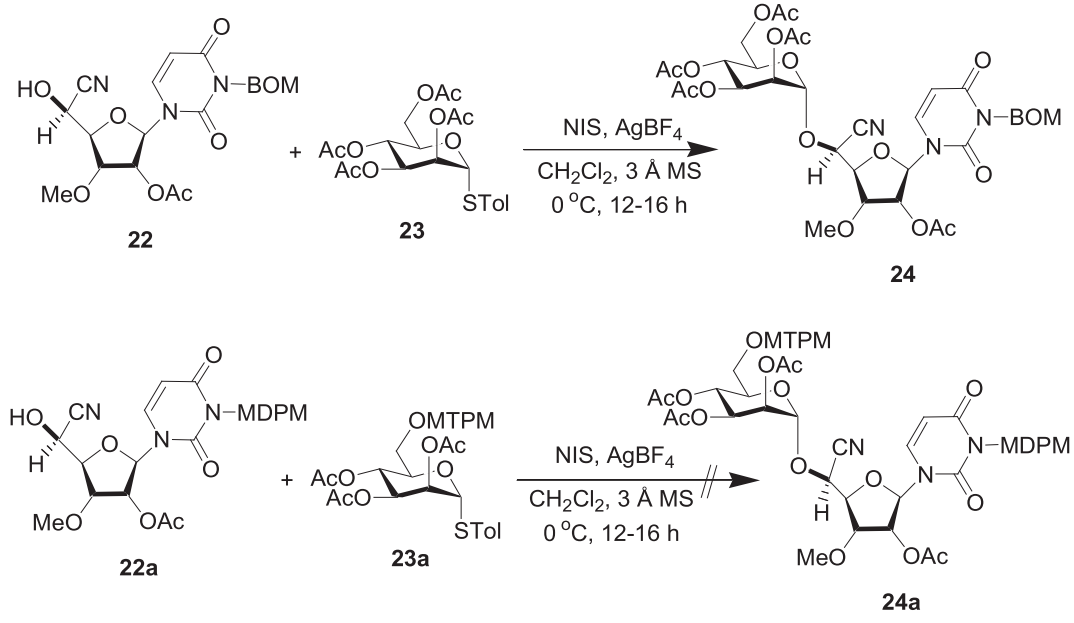
Scheme 5 Synthesis of trisaccharides **21**.

line with neighbouring group mechanism triggered by interaction of the Lewis acid and the near-axial C-4 hydroxyl group of the flavan-3,4-diol **10** (Coetzee et al., 1998a,b).

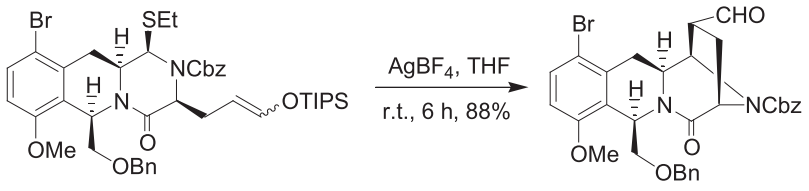
Furthermore, the fact that $AgBF_4$ activates S-containing leaving groups was utilised to cleave the S–C bond and obtained S-octylethanethioate **16** in the presence of acetyl chloride **15** as a trapping agent. It is thus purported that the silver metal complexed with the carbonyl to assist the reaction. Typical experimental protocol involved treatment of 2-(trimethylsilyl)ethyl sulphide **14** (91.4 mg, 0.37 mmol) and **15** (0.5 mL) in dry dichloromethane (CH_2Cl_2) (2 mL) under argon with $AgBF_4$ (75 mg, 0.39 mmol) for 5 min. The reaction mixture diluted with CH_2Cl_2 and saturated aqueous $NaHCO_3$, filtered through celite, the filtrate (CH_2Cl_2) dried over Na_2SO_4 and concentrated to obtain octyl thioacetate in good yield (64.6 mg, 93%) (Scheme 4) (Grundberg et al., 1999).

Thioglycosides are usually activated by NIS/TfOH or NIS/TMSOTf. The glycosyl acetates are commonly activated by $BF_3{\bullet}Et_2O$, while the glycosyl donors such as glycosyl bromides, chlorides, trichloracetimidates, and seleno glycosides are normally triggered by freshly activated AgOTf. Unfortunately, the use of AgOTf is limited by the rigours of dehydration processes to obtain a freshly activated AgOTf before a successful reaction could be conducted. Excitingly, $AgBF_4$ required no prior azeotropic dehydration before usage, and thus makes it preferred reaction promoter over AgOTf in glycosyl synthesis. Accordingly, $AgBF_4$ has been identified as a facile and excellent promoter for the activation of various glycosyl donors such as glycosyl halides, trichloroacetimidates and thioimidates (Pornsuriyasak and Demchenko, 2006; Kaeothip et al., 2008). Kaeothip et al. (2008), demonstrated that glycosylthioimidate **18** could be selectively activated by $AgBF_4$ (20–50 mol%) while the S-ethyl moiety of the glycosyl acceptor **17** remained inert. The activated **18** then couples with the **17** to form intermediate dissacharide **19**. On addition of 2.0 equiv. of N-iodosuccinimide (NIS), the -SEt moiety of **19** was readily activated, and following the addition of a new acceptor (methoxy glycoside **20**) to the reaction system, trisaccharides **21** was afforded in 72% yield (Scheme 5).

Wang et al. (2013) described $AgBF_4$-improved synthesis of capuramycin: demonstrating the effectiveness of $AgBF_4$ in activation of thioglycosides **23** in the mannosylation of uridine derivatives **22**. The authors found that α-selective mannosylation of **22** with **23** was only achieved through the combination

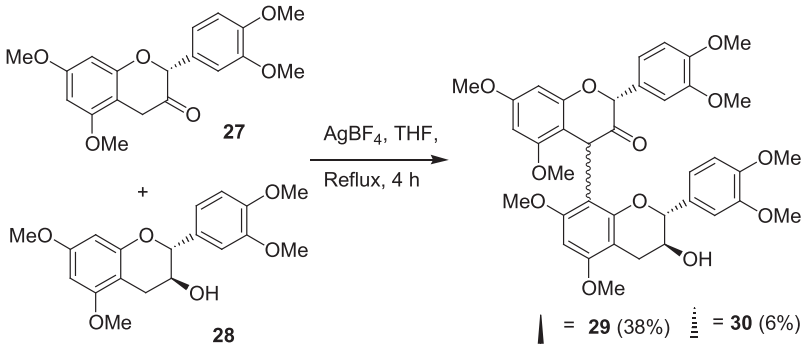


Scheme 6 $AgBF_4$ α-selective mannosylation of **22** with thioglycoside **23**.

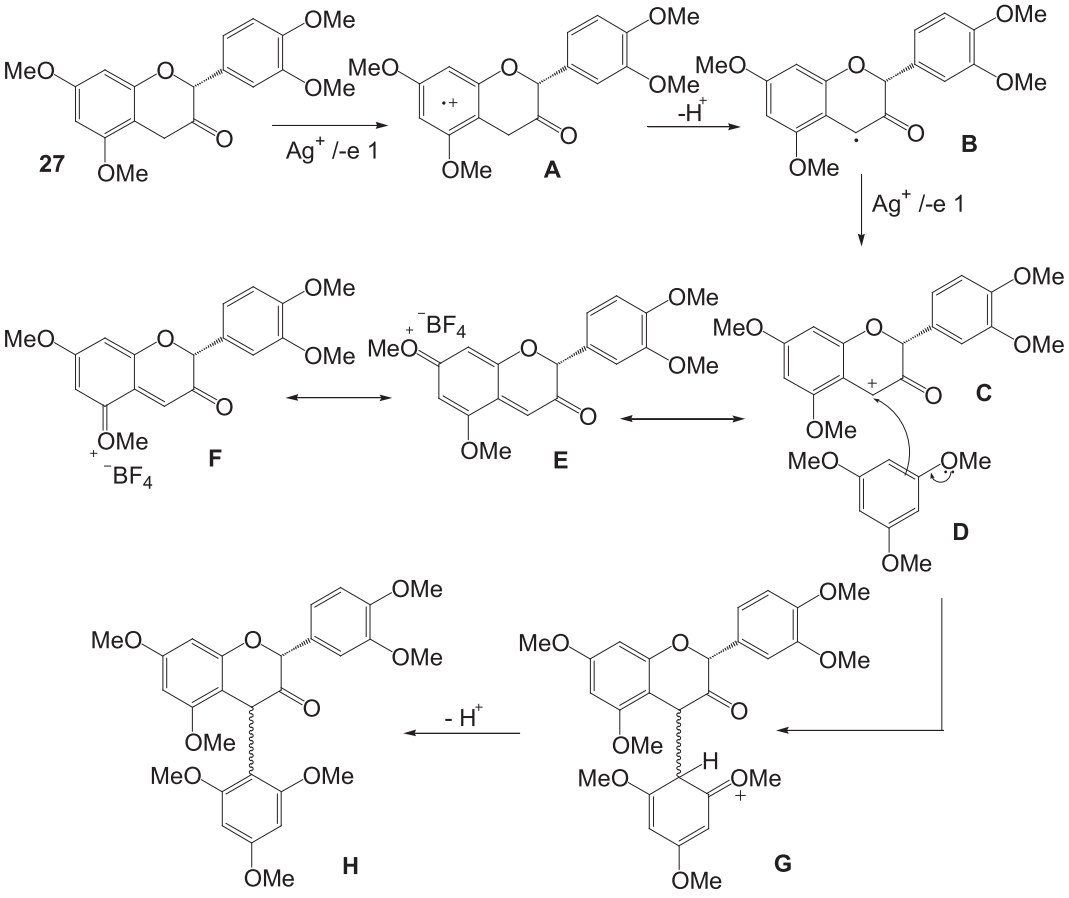


25 26

Scheme 7 Construction of the tetra-cyclic ring of quinocarcin.



Scheme 8 Condensation reaction between **27** and **28**.



Scheme 9 Proposed mechanism for oxidative synthesis of **29** and **30** based on the model reaction.

of NIS and $AgBF_4$ in CH_2Cl_2 at low concentration (0.05 M) and long reaction time (16 h) to afford **24** exclusively in 90% yield. On investigation of the activity of $AgBF_4$ on different substrates, treatment of uridine protected by monomethoxydi phenylmethoxylmethyl (MDPM) **22a** and thioglycoside **23a** with the same NIS/$AgBF_4$, did not provide the desired product but the starting material **24a** was completely consumed to form complex mixtures (Scheme 6) (Kurosu et al., 2009; Wang et al., 2013a,b).

Reacting a THF solution of **25** at room temperature with $AgBF_4$ activates an intramolecular Mannich reaction, leading to efficient 5-*endo*-trig cyclisation to furnish the tetra-cyclic compound **26** with an *exo*-oriented aldehyde function in 88% yield after 6 h. The reaction protocol involved addition to a THF (6 mL) solution of silyl enol ether **25** (137.7 mg, 0.164 mmol), $AgBF_4$ (57.6 mg, 0.294 mmol) at room temperature. The mixture was stirred at room temperature for overnight, and quenched with saturated aqueous $NaHCO_3$ (20 mL) and ethyl acetate (50 mL). After work-up and chromatographic purification, tetracyclic aldehyde **26** (89.6 mg, 88% yield) was obtained as foam (Scheme 7). The $AgBF_4$ served as an activator of both the electrophilic and nucleophilic moieties leading to the efficient 5-*endo*-trig cyclisation (Wu et al., 2008, 2009).

3. $AgBF_4$-promoted oxidative coupling reactions driven by hydride abstraction

$AgBF_4$ can activate C–H groups between a carbonyl and aryl functional group, affording a novel synthesis of proanthocyanidins **29** and **30** (Scheme 8) from 3-oxo-flavans **27**, accessible from readily available flavan-3-ols **28** *via* Dess-Martin periodinane oxidation, thus circumventing the need for C-4 functionalisation. In contrast to flavan-3-ol based syntheses, where the C-3 configuration determines the C-4 configuration, the 3-oxo-flavans have no stereochemistry on C-3 and the C-2 configuration determines absolute configuration on C-4, giving access to hitherto synthetically unavailable 3,4-*cis* procyanidins. Standard coupling method involved a solution of tetra-*O*-methyl-catechin (0.435 mmol) in THF (3 mL), added dropwise to a mixture of $AgBF_4$ (1.1 mmol) and tetra-*O*-methyl-3-oxocatechin (0.145 mmol) in THF (3 mL) and refluxed under nitrogen for 4 h. Filtration on SiO_2 and purifying with silica gel TLC yielded the desired products (Achilonu et al., 2008; Achilonu, 2009).

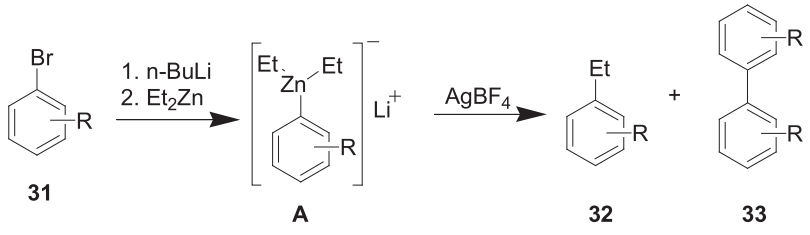
The requirement of an excess of $AgBF_4$ and the observation of a silver mirror (reduction of Ag^1 to Ag^0) may indicate an oxidative mechanism (Scheme 9).

The BF_4^- anion probably assists in stabilising the 4-carbocation **C** *via* the quinone methide tautomer **E.** Another major advantage of this synthesis is that no self-condensation was observed, thus no multiple by-products, as is the case with the conventional syntheses based on a flavan-3-ol with a C-4 leaving group as exemplified by Schemes 2 and 3.

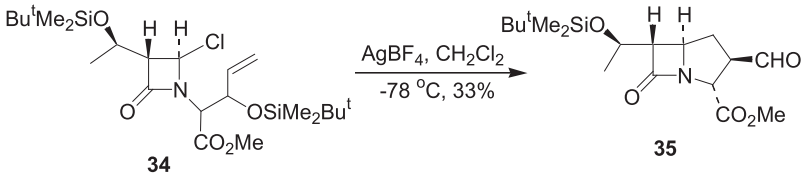
The use of silver as an oxidation agent has been summarised (Álvarez-Corral et al., 2008; Weibel et al., 2008) and will not be comprehensively reviewed here. Hirao et al. (2000), described oxidant-induced coupling reaction between organozinc compounds. Studies have shown cross-coupling reactions of organozinc reagents promoted by transition metal salts as versatile synthetic tools in organic syntheses (Oshima, 1991; Erdik, 1992). $AgBF_4$ is a useful oxidising agent that gives cross-coupling compound, probably *via* a one-electron oxidation process. When 6.0 equiv. of $AgBF_4$ was used instead of the oxovanadium(V) compound, selective cross-coupling reaction between alkyl groups and *o*-methoxy-substituted aryl groups occurred. Metal silver, Ag(0), was detected in the reaction mixture, suggesting that the cross-coupling reaction is induced by one-electron oxidation with Ag(I). Typical protocol includes the cross-coupling of organo-zinc compounds (Hirao et al., 2000), where the mild nature of $AgBF_4$ gave good yields. In their representative procedure, *n*-BuLi (0.75 mmol, 0.49 mL, 1.54 M in hexane) was added to a stirred solution of arylbromide **39** (0.68 mmol) in dry ether (1.4 mL) under argon at room temperature to generate the corresponding aryllithium. After 10 min at room temperature, Et_2-Zn (0.75 mmol, 0.75 mL, 1.0 M in hexane) was added drop-wise to the resulting solution at 0 °C. Ten minutes later, at the same temperature, the resulting solution containing intermediate compound **A** was added to a solution of $AgBF_4$ (801 mg, 4.1 mmol, 6.0 equiv.) in dry ether at 0 °C. The mixture was stirred for 2 h at room temperature. After work-up and purification by column chromatography on silica gel, **32** (65 mg, 70%) and **33** (3 mg, 4%) were obtained (Scheme 10).

4. $AgBF_4$-promoted synthesis driven by halide abstraction

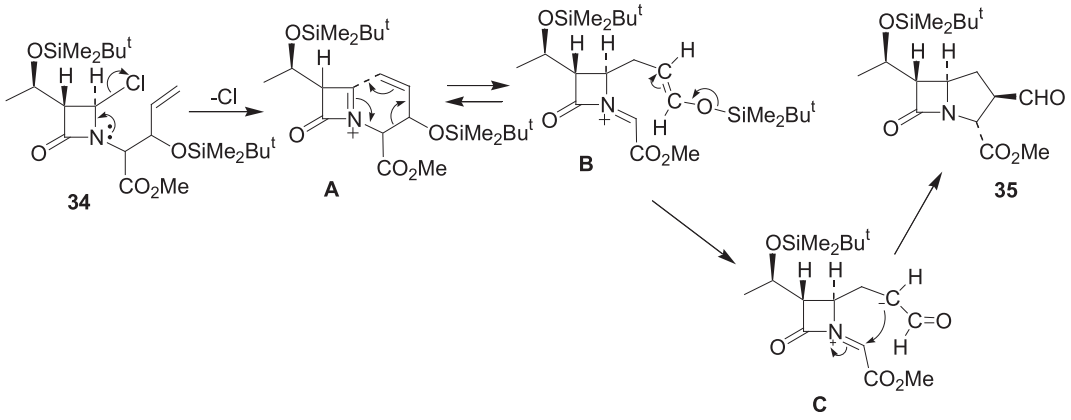
A novel synthetic approach to synthesise carbapenems utilising aza-Cope-Mannich cyclisation was recorded in 1995 (Sakurai et al., 1995). The success of this preparation involved the introduction of a carbon nucleophile into the azetidinones with a leaving group at C-4; suitable for generation of acyliminium intermediate. Authors' first attempt was introducing acetoxy moiety in the C-4 of **34** and several trials to activate the acetoxy group using a variety of acetoxy activating promoters ($Me_3SiOSO_2CF_3$, $Bu^tMe_2SiOSO_2CF_3$, $BF_3{\bullet}OEt_2$) did not yield the desired carbapenem. With chloride as leaving group on the C-4 of **34**, $AgBF_4$ was found to be a suitable silver salt to activate cyclisation of the compound after several attempts



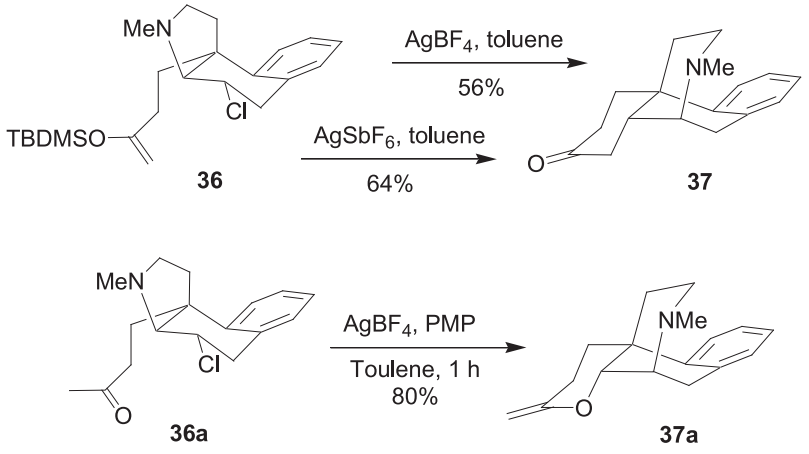
Scheme 10 Cross-coupling reaction of triorgano-zincates **A** using $AgBF_4$.



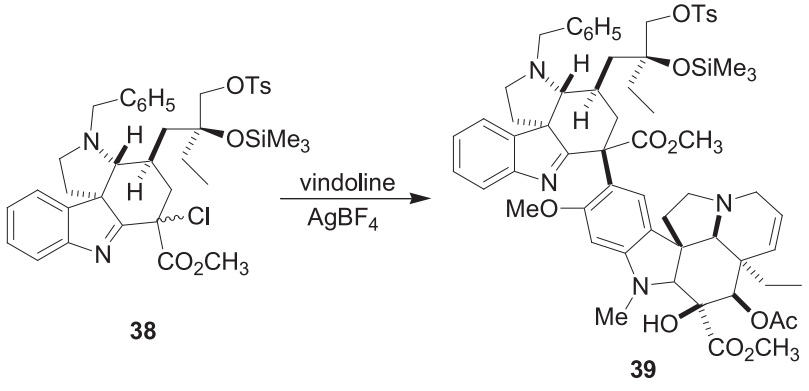
Scheme 11 Synthesis of carbapenems using aza-Cope Mannich cyclisation.



Scheme 12 Plausible mechanism for the $AgBF_4$-catalysed alkene-aza-Cope-Mannich cyclisation of **34**.



Scheme 13 $AgBF_4$-mediated synthesis of morphinans.



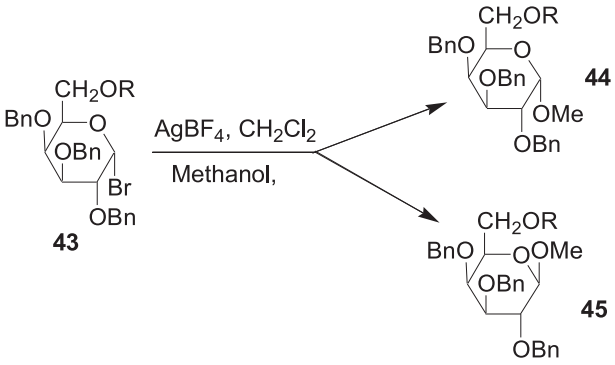
Scheme 14 Synthesis of indolenine **39**.

using a variety of other silver salts with non-nucleophilic counter anions. The reaction procedure includes treating **34** with $AgBF_4$ in CH_2Cl_2 at −78 °C to obtain the desired carbapenam **35** in 33% as a single isomer (Scheme 11). A plausible mechanism for the $AgBF_4$ catalysed alkene-aza-Cope-Mannich cyclisation is presented in Scheme 12.

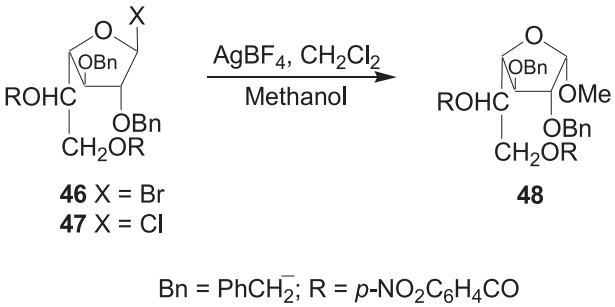
A concise route to a morphinan ring system **37** through silver-promoted reactions has been described (Broka and Gerlits, 1988). It relies on the intramolecular trapping of an aziridinium cation generated *in situ* by the treatment of **36** with $AgBF_4$ or $AgSbF_6$ in toluene. Attempted treatment of unprotected carbonyl group of pyrrolidine **36a** and 1,2,2,6,6-penta methylpiperidine (PMP) with $AgBF_4$ produced **37a**, while reaction of the trimethylsilyl enol ether of the **36a** with $AgBF_4$ also failed to lead to desired product **37**. Interestingly, treatment of a solution of dimethyl-*tert*-butylsilyl (TBDMS) enol ether **36** (54 mg, 0.13 mmol) in 3 mL of toluene with $AgBF_4$ (56 mg, 0.29 mmol) in 2 mL of toluene afforded the desired compound **37** (19 mg, 56%) after purification on preparative silica gel (eluting with 12% $MeOH/CH_2Cl_2$) (Scheme 13). The immediate formation of AgCl precipitate is purported to drive the reaction forward. When THF or CH_3CN solvent is used, lower yield of **37** was obtained. Using $AgSbF_6$ in toluene gave better yield (64%). However, treatment of **36** with AgOAc or AgF failed to afford **37**.

Kuehne et al. (1991) recorded successful enantioselective synthesis of vinblastine, a naturally occurring bioactive binary indole-indoline alkaloid. Here, we summarised accessing the compound *via* the synthesis of the intermediate promoted by $AgBF_4$. The authors established that treating 5 mL dry acetone solution of chloroimine **38** (∼100 mg, 0.14 mmol) and vindoline hydrofluoroborate (63 mg, 0.95 equiv.) with 0.05 mL (2 equiv.) of tetrafluoroboric acid-diethyl ether complex. After 5 min, $AgBF_4$ (56 mg, 2 equiv.) in 2 mL dry acetone was added. After another 5 min, 10 mL of 10% aqueous ammonium hydroxide was added to the heterogenous reaction mixture. Tetracyclic C16′–C14′ *parf* indolenine **39** was obtained as white foam after work-up and concentration under pressure (Scheme 14).

Formation of Lewis salts-promoted C-linked glycosyl compounds through alkyne transfer to the anomeric centre of 2-azido-2-deoxy sugars has been described. However, the use of ZnCl, $TiCl_4$, $BF_3{\bullet}Et_2O$, trimethyltriflate, etc. promoters in alkynylation of sugar bromides by alkynylstannanes are notorious for not giving clean reactions, consequently afford poor α-selectivity and low yields. According to Leteux and Veyrières (1994), coupling of 6-acetyl-azido-3,4-di-*O*-benzyl-2-deoxy-α-d-galactopyranosylbromide **40** with various alkynyltributylstannanes in the presence of silver $AgBF_4$ yields the corresponding stable α, *β*-C-(d-galactopyranosyl)alkynes. The $AgBF_4$ (2 mol. equiv.) was found to initiate a smooth and clean coupling reactions at 0 °C. The authors' typical reaction



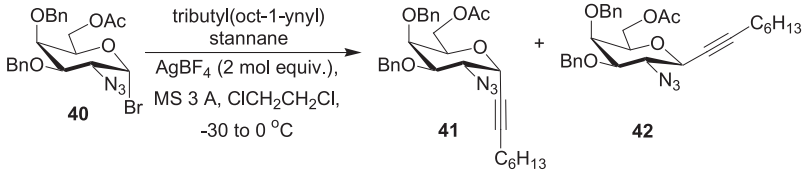
Scheme 16 Methanolysis of 2–*o*-benzylated d-galactopyranosyl halides.



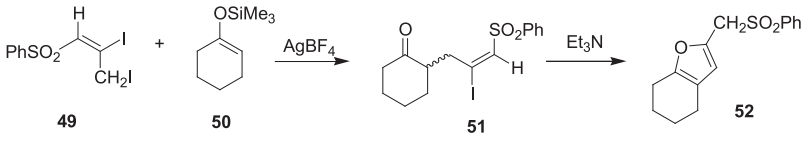
Scheme 17 Methanolysis of 2–*o*-benzylated d-galactofuranosyl halides.

methodology involved stirring a mixture of bromide **40** (1.96 g, 4 mmol), tributyl(oct-1-ynyl)stannane (7.98 g, 20 mmol) and 3 Å molecular sieves (1 g) in dry 1,2-dichloroethane (12 cm^3) at room temperature under argon for 30 min. Then the reaction mixture was cooled to −30 °C, followed by rapid addition of dry $AgBF_4$ (1.56 g, 8 mmol). Thereafter, the temperature was allowed to rise slowly to 0 °C and stirring continued at the same temperature overnight. After work-up and flash chromatography, the α-C-glycoside **41** (1.08 g, 52%) and *β*-C-glycoside **42** (218 mg, 10%) were obtained (Scheme 15).

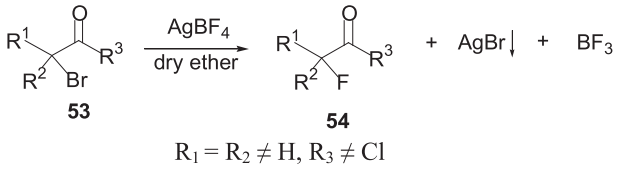
Fréchet and Baer (1975) established that subjecting the CH_2Cl_2 solutions of halides **43**, **46** and **47** to methanolysis in the presence of $AgBF_4$ and excess of methanol, stereoselectively produces ratios of anomeric glycosides, respectively. Galactopyranosylbromide **44** afforded the methyl α- and β-glycosides **44** and **45** in the ratio of (5:95) (Scheme 16). Use of n-Bu^tNBr catalyst afforded **44** and **45** α/β ratio of 70:30, while $Hg(CN)_2$ catalyst gave 3:97. The 2,3-di-*O*-benzyl-5,6-di-*O*-*p*-nitrobenzoyl-β-d-galactofuranosyl bromide **46** gave product **48** (methyl 2,3,5.6-tetra-*O*-benzyl-α-d-galactofurano side) with α/β ratio of (95:5), while the β-d-galactofuranosyl



Scheme 15 Synthesis of α-C-glycopyranosides *via* $AgBF_4$-promoted alkynylation at the anomeric centre.



Scheme 18 Synthesis of substituted furan **52**.

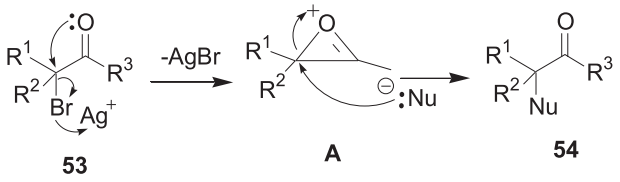


Scheme 19 Synthesis of α-fluorocarbonyl compounds **54**.

chloride **47** yielded the same product with α/β ratio of (100:0) and using catalyst n-Bu^{t}NBr or $Hg(CN)_2$ did not make any difference in α/β ratio of product **48** (Scheme 17). In their representative reaction protocol, $AgBF_4$ (about 95 mg) was added in one portion to a cooled (−78 °C) CH_2Cl_2 solution (10 mL) of glycosyl halide (160 mg) and the reaction mixture was stirred in the dark for 10 min. Methanol (0.5 mL) was introduced and stirring continued for 1 h. After purification, the ratio of anomeric glycosides in the residue was determined by measuring the intensity of the methoxy proton resonances of the ^1H NMR spectrum.

$AgBF_4$ has been used to activate trimethylsilylenols as nucleophiles in substitution reactions. In a study (Padwa and Ishida, 1991), 2,3-diiodo-1-(phenylsulphonyl)-1-propene **49** and (cyclohex-1-enyloxy)trimethylsilane **50** were treated at 25 °C in methylene chloride (0.05 M), with 2.0 equiv. of $AgBF_4$ to effect S_N2 displacement of the terminal halide of **49** and iodo-(phenylsulphonyl) ketone **51** was obtained in 71% yield. Addition of triethylamine in THF at 25 °C cyclised the ketone compound to form the 2-phenylsulphonylmethyl substituted furan **52** (Scheme 18). Other Lewis acids ($TiCl_4$ and ZnCl) reacted with **49** and **50** led only to the destruction of **50** and **49** was recovered unchanged.

A convenient, mild and one-step synthesis of α-fluorocarbonyl compounds, involving only reaction of the appropriate α-bromo compound with $AgBF_4$ in ether has been reported. The fluoride in the BF_4^- anion component of $AgBF_4$ can liberate as an F^- nucleophile. Following this line of thought, α-fluorocarbonyl molecules **54** were prepared *via* substitution of carbonyl α-bromo substituents (Scheme 19), presumably *via* neighbouring group participation by the carbonyl oxygen (Scheme 20) to obtain α-fluorocarbonyl compounds (Fry and Migron, 1979). The authors noted that the reaction is not applicable to terminal bromides or



Scheme 20 Proposed reaction mechanism for α-fluorocarbonyl compounds.

chloroketones. Again, reactions carried out in nucleophilic solvents (methanol) yield the corresponding α-methoxy ketone. Representative protocol involves the reaction of 1.65 g (0.01 mol.) of 2-bromo-2-methyl-3-butanone and 1.95 g (0.01 mol.) of $AgBF_4$ overnight at room temperature in 70 mL of dry ether. After work-up and purification, **54** was obtained in 87% yield.

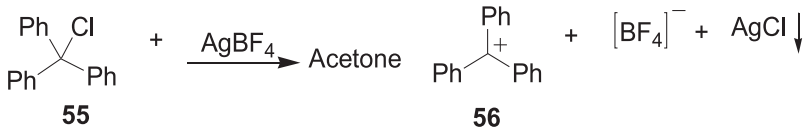
The role of BF_4^- in stabilisation of intermediate carbocations is demonstrated by using $AgBF_4$ to heterolyse a C–Cl bond (Schmitt et al., 2013). The precipitation of AgCl probably plays a thermodynamic role in driving the reaction forward (Scheme 21).

An efficient two-step synthesis of trifluoromethyl sulphides using inorganic fluorides (CsF, HF, HgF_2, $AgBF_4$, etc.) has been described. BF_4^- anion from $AgBF_4$ salt participation in fluorination reactions is the synthesis of trifluoromethyl sulphides has been demonstrated (Suda and Hino, 1981). The procedure involved treatment of an aprotic solution of mercaptan **57** with a base (NaH), and thereafter with CF_2Br_2 or CF_2BrCl. The resulting bromodifluoromethylsulphide **58** was subsequently treated with $AgBF_4$ to obtain the desired trifluoromethyl sulphide **59** in moderate yield (41%) (Scheme 22).

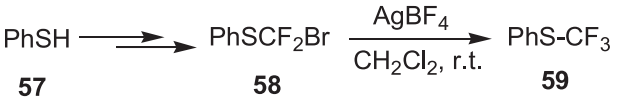
Bloodworth and Bowyer (1987) reported a mild, convenient halogen-exchange route to *gem*-difluorides and trifluorides as promoted by $AgBF_4$. The $AgBF_4$ promotes conversion of dihalides and trihalides into their corresponding fluorides at room or sub-ambient temperatures in moderate to good yields. The exchange-fluorination protocol involved treating substrates **60** or **62** with $AgBF_4$ (1.1 M equiv. per halide) in CH_2Cl_2 for 1 h at room temperature afforded 35–84% yields after appropriate work-up (Scheme 23). The author suggested that the reactions proceeded *via* cationic intermediates, generated by silver-induced halogenation, which went fluorination by BF_4^- anion as demonstrated by the proposed mechanism in Scheme 24.

5. $AgBF_4$-promoted halogenation reactions

$AgBF_4$ activates alkyne moieties *via* π-complexes, as exemplified in the regio- and stereoselective difunctional synthesis of (*Z*)-*β*-haloenol acetates from terminal alkynes (Scheme 25) (Chen et al., 2010). There are few catalytic methods to synthesise the haloenols (OC = CX) bond in one step from terminal alkynes (Barluenga et al., 1990). Out of the reaction promoters (CuI, $Pd(OAc)_2$, $FeCl_3$, HBF_4, $AgBF_4$) used, only $AgBF_4$ could afford the corresponding product in 90% yield; others did not proceed without $AgBF_4$. Actic anhydride was the favourable solvent. DMF and 1,4-dioxane afforded products in lower yield. Representative protocol involved reaction of phenylacetylene **64** (1.0 mmol) and an *N*-halosuccinimide (NXS) (1.2 mmol) in acetic anhydride (2 mL) in the presence of $AgBF_4$ (5 mol%) at 120 °C for 12 h affords 60–90% yield of (*Z*)-*β*-haloenol acetate compounds **65**. These vinyl halides



Scheme 21 Synthesis of a BF_4^- stabilised intermediate carbocation.



Scheme 22 $AgBF_4$-mediated synthesis of trifluoromethyl sulphide.

are important starting materials for transition-metal-catalysed cross-coupling reactions and halogen-metal exchange reactions (Chen et al., 2011).

In 2012, Chen et al. disclosed the first transition-metal-catalysed electrophilic cascade cyclisation reaction of benzodiyne **66** with NXS and $AgBF_4$, which affords halo-containing benzo[*a*]fluorenols **A** at room temperature (10 °C) in moderate to good yields (Scheme 26). Initial reaction attempts on **66** using an electrophile NXS, did not trigger reaction in the presence of catalysts $FeCl_3$, $FeCl.6H_2O$, CuI, $In(OTf)_3$ or $NiCl_2(PPh_3)_2$. Further investigation using silver salts as catalyst revealed that $AgBF_4$ was the best reaction promoter compared with Ag_2CO_3, AgF, $AgNO_3$, and $AgSbF_6$. Optimised reaction condition involved treating a solution of benzodiyne **66** (0.20 mmol) in CH_2Cl_2 (1.0 mL) with a mixture of *N*-iodosuccinimide (0.24 mmol) and $AgBF_4$ (0.01 mmol) in CH_2Cl_2 (0.5 mL) at 10 °C under nitrogen. After 12 h, the reaction mixture was quenched with a saturated ammonium chloride solution (3 mL) and flash column chromatography (ethyl acetate/*n*-hexane, 1:50) afforded **67** (76%) as a light yellow solid. A plausible mechanism is depicted in Scheme 27.

Wang et al., 2013 reported efficient and regioselective fluorination of arenes under various silver-mediated conditions by intercepting the putative silver-complexed aryne intermediates with anions such as ^-F, $^-CF_3$, or $^-SCF_3$. Exploring the reactivity of fluorinating agents and solvents, the author's initial investigation showed that $AgBF_4$ in a polar solvent (toluene) was most effective at promoting the fluorination but ineffective in acetonitrile. AgF afforded 20% yield in acetonitrile, while $AgSbF_6$, CuF, $Cu(MeCN)_4BF_4$, $Cu(MeCN)_4PF_6$, or $[(Au_3)(PPh_3)_3]BF_4$ did not afford any product in both toluene and acetonitrile. The general procedure for the stoichiometric fluorination reaction involved dissolving **68** (0.1 mmol) and $AgBF_4$ (0.15 mmol) in 5.0 mL of toluene under an inert atmosphere, and stirring the mixture at 90 °C for 2 h. Thereafter, the crude reaction mixture was filtered through a small column packed with silica gel and the required product **69** (96% yield) was isolated by column chromatography on silica gel (Scheme 28). A proposed reaction mechanism is shown in Scheme 29.

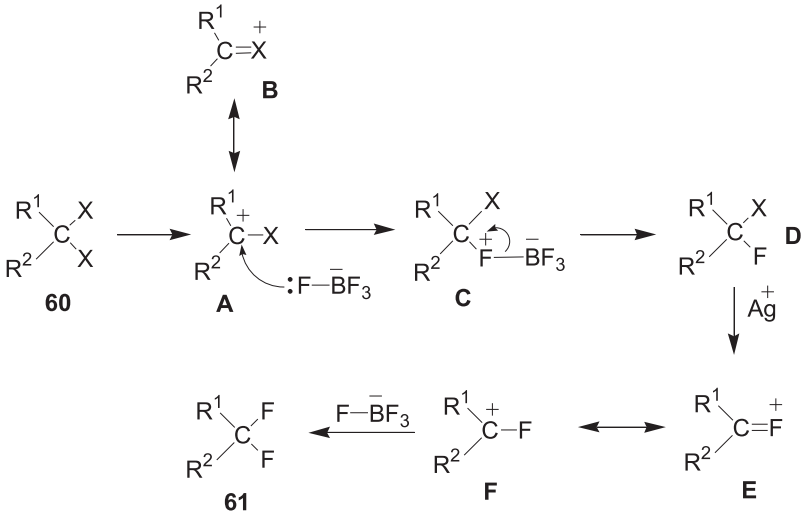
In 2011, Tang and Ritter described direct electrophilic fluorination of aryltrialkoxysilanes with N-Chloromethylfluorot riethylenediammoniumbis(tetra-fluoroborate) fluorinating agent **71** in the presence a silver(I) salt promoter to give functionalised aryl fluorides. The authors established that reaction of **71** and 4-(biphenyl)trethoxysilane **70** gave 4-biphenyl fluoride **72** in less than 4% yield, but on addition of Ag(I) salts (Ag_2O, AgOAc, $AgBF_4$, $AgPF_6$, AgF, etc.) regioselective fluorination was observed and Ag_2O gave the highest yield of the expected product (4-Fluorobiphenyl) **72** (14.3 mg, 83%). Following the optimised reaction procedure, the general protocol involved addition to aryl silane (0.100 mmol, 1.00 equiv.) in acetone (2.0 mL) at 23 °C $AgBF_4$ (0.300 mmol, 2.00 equiv.), barium oxide (17.2 mg, 0.110 mmol), and **71** (70.8 mg, 0.200 mmol). The reaction mixture was stirred for 2 h at 90 °C, cooled to 23 °C, worked up and purified to obtain the desired product in 11% yield (Scheme 30).

In addition to the reactivities of $AgBF_4$ described above, an effective electrophilic trifluoromethylating reagent, (trifluoro methyl)dibenzotellurophenium salt **75** (Scheme 33), was developed (Wang et al., 2010; Shibata et al., 2010). Treatment of telluride **73** with an equimolar mixture of triflic anhydride and DMSO at 0 °C, followed by anion exchange with $AgBF_4$ (Umemoto and Ishihara, 1993) afforded the Umemoto salt **75**. Synthesised trifluoromethylated arenes **77** were obtained by reacting substituted arenes **76** with Umemoto reagents **75**, $Pd(OAc)_2$ and $Cu(OAc)_2$, at 110 °C in a mixture of dichloroethane and 10 equiv. of trifluoroacetic acid to afford 53–88% yield of **77** (Scheme 31) (Shibata et al., 2010).

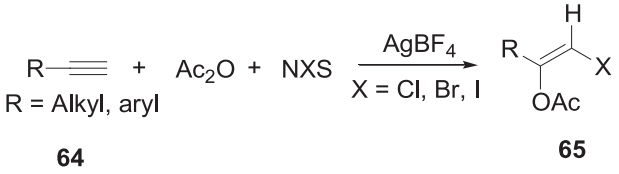
6. Heterocyclisation reactions promoted by $AgBF_4$

In 2005, Luo et al. reported the first example of an efficient silver-catalysed regioselective domino reaction between anilines and alkynes to obtain polysubstituted 1,2-dihydroquinolines. In their initial studies, they explored hydroamination of unactivated alkynes by anilines with a gold/silver catalyst system (e.g. $AuCl_3$/AgOTf), to obtain amines in high yields. Subsequently, examination of AgOTf catalyst alone and Au catalyst alone did not provide these products. Combination of $AgBF_4/HBF_4$ gave the expected product in good yield. Thus, the optimised reaction conditions

Scheme 23 Exchange-fluorination by reaction with $AgBF_4$.



Scheme 24 Mechanism of exchange-fluorination by reaction with $AgBF_4$.



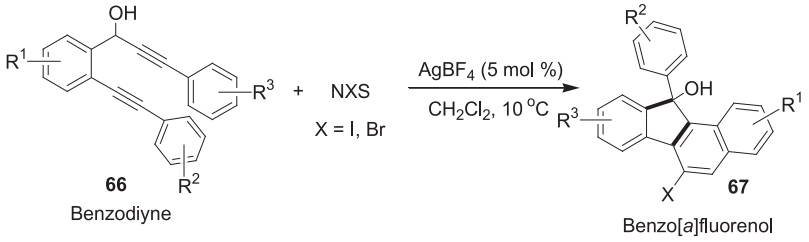
Scheme 25 Highly regio- and stereo-selective synthesis of (*Z*)-*β*-haloenol acetates.

involve treating phenylacetylene **78** (1.0 mmol) and phenylamine **79** (4.0 mmol) with $AgBF_4$ (9.7 mg, 0.05 mmol), hydrogen tetrafluoroborate (HBF_4) (11.2 mg 0.07 mmol) and trifluoroboronetherate ($BF_3{\bullet}Et_2O$) (11.3 mg, 0.08 mmol) as co-catalysts, for 12 h at 160–190 °C gave **80** in 77% yield (Scheme 32). A proposed mechanism is given in Scheme 33 below.

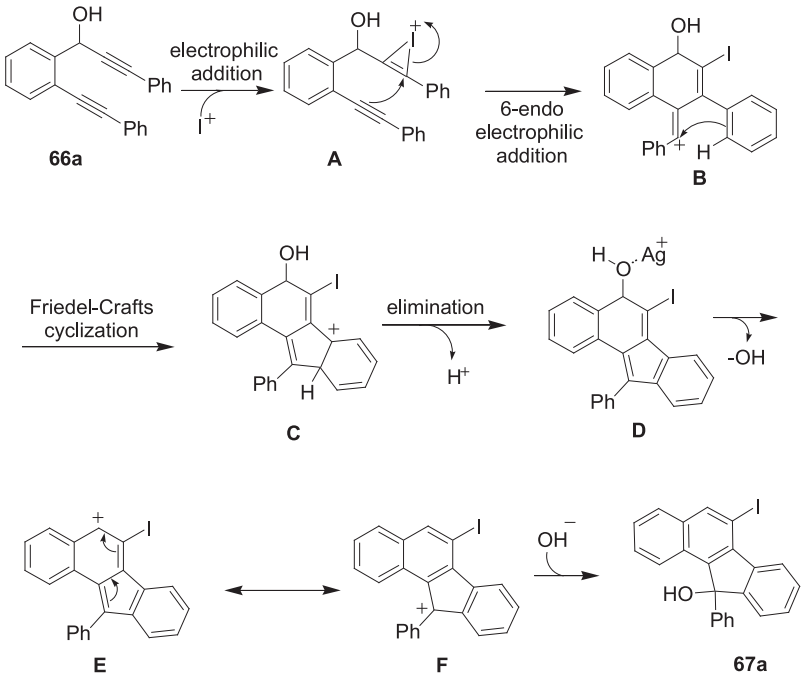
Liu and co-workers (2010) reported an efficient one-pot silver-catalysed and phenyliodine diacetate (PIDA)-mediated synthesis of poly-substituted pyrroles, in which dimethyl but-2-ynedioate **81** was treated with various amines **83** to afford, *via* tandem reactions, corresponding pyrroles in moderate to excellent isolated yields of 53–89% (Liu et al., 2010). The initial studies involved examining various silver catalysts ($AgBF_4$, AgOTf, $AgNO_3$, and Ag_2CO_3) by heating mixtures of **81** and **83** using PIDA as the oxidant in dioxane at 100 °C to obtain the expected product, tetramethyl 1-benzyl-1*H*-pyrrole-2,3,4,5-tetracarboxylate **84**. $AgBF_4$ showed the highest activity for the reaction. They established a facile and highly efficient C–N and C–C bond formation method to construct a direct pyrrole framework (Scheme 34) as described by the proposed reaction mechanism (Scheme 35).

Tang et al. (2010) reported the ammonolysis-cyclisation tandem reactions of various 2-alkynylbenzenamines **85** with tetra-alkyl-thiuram disulphides **86** in the presence of silver catalysts to afford the corresponding 4-methylene-4*H*-benzo[*d*][1,3]thiazin-2-amines **87** in moderate to good yields. They evaluated a series of catalysts such as AgOTf, $AgBF_4$, $AgSbF_6$, AgOAc, $Cu(OTf)_2$ and $Pd(OAc)_2$; solvents such as N-methylpyrrolidine (NMP), toluene, acetronitrile, dichloroethane and DMSO, and temperature from 60 to 120 °C. Interestingly, the studies revealed that $AgBF_4$ was the most effective in terms of yield, 88% at 80 °C after 36 h (Scheme 36). Notably, they discovered that electron-rich aryl groups provided good yields, whereas electron-withdrawing acetyl- or trifluoromethyl-substituted aryl groups lowered the yields. Thus, the general procedure involved reaction of 2-alkynylbenzenamines **85** (0.5 mmol), tetra-alkyl-thiuram disulphides **86** (0.5 mmol), $AgBF_4$ (0.05 mmol), and DMSO (1 mL) at 80 °C for 36 h. After work-up and chromatographic purification, pale yellow solid was obtained in 88% yield (*Z*/*E* = 90:10).

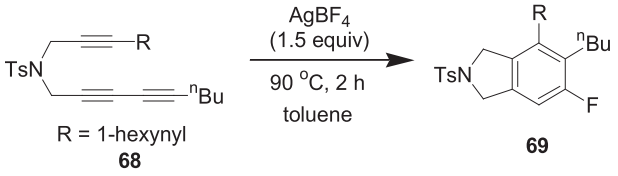
Recent reports (Ko et al., 2013) show that stable bis-cyclometallated gold(III) catalysts **L** exhibit high catalytic activity in organic synthesis *via* gold–silver dual catalysis for substrate activation. They also purported that silver salts are able to work synergistically with bis-cyclometallated gold(III) complexes in the indole alkylation. Thus, treating alkynyl



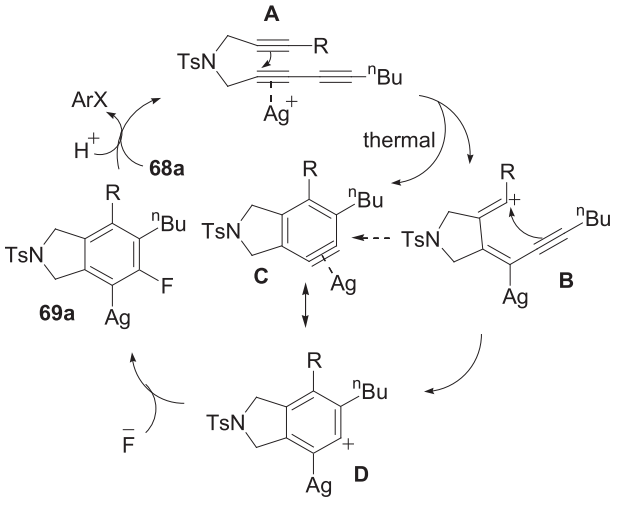
Scheme 26 Synthesis of halo-substituted benzo[*a*]fluorenols.



Scheme 27 Mechanism for $AgBF_4$ catalysed sequential electrophilic cyclisation reaction.

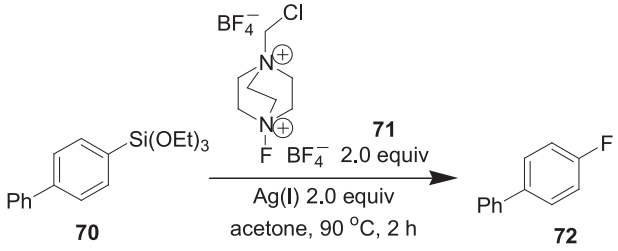


Scheme 28 Synthesis of compound **69**.



Scheme 29 A proposed reaction mechanism for compound **69a**.

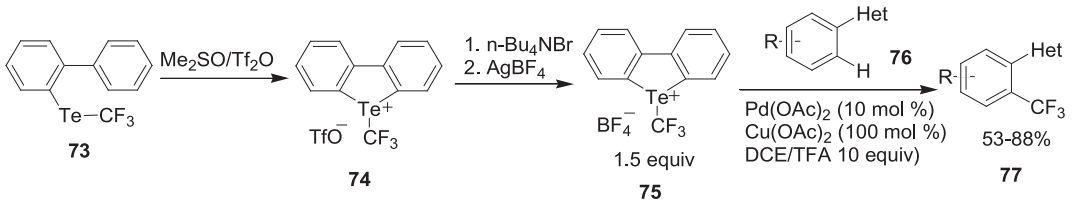
alcohol **88** and indole **89** at room temperature for 2 h with a combination of **L** (2.5 mol%) and $AgBF_4$ (5 mol%) as reaction promoter, gave alkylated indole **90** isolated in 80% yield (Scheme 37). Reaction of **L** in combination with $Zn(OTf)_2$ or $Yb(OTf)_3$ also catalyses the reaction to afford 76% and 39% isolated yields, respectively. However, poor yields (10–13%)



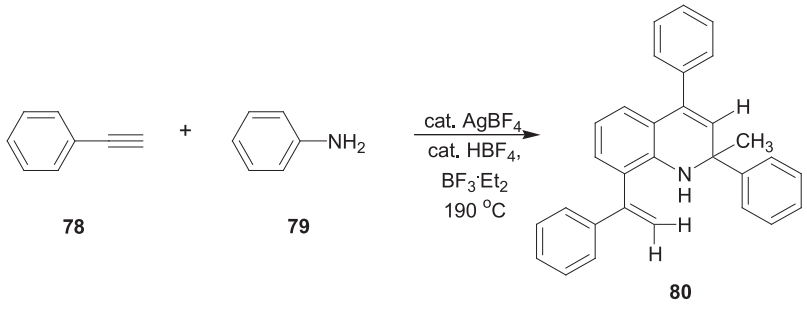
Scheme 30 Silver-mediated synthesis of 4-fluoro-biphenyl.

or no product formation was found when only a single metal catalyst was used.

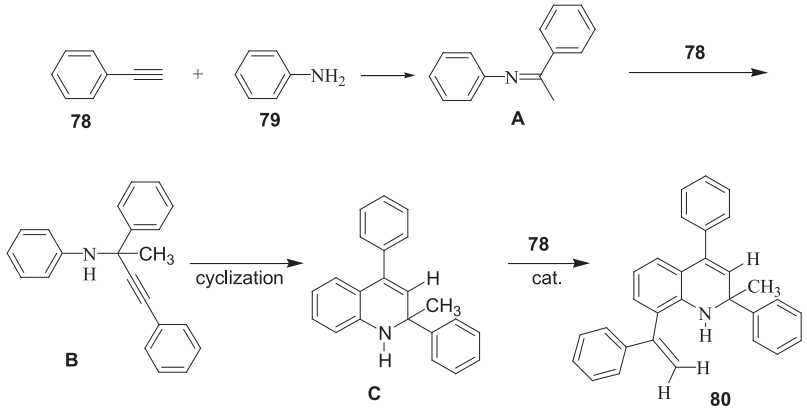
$AgBF_4$ has also been used to generate carbenes from diazo compounds (Xia et al., 2011). Several Ag(I)-containing catalysts were tried for the synthesis of 2,3-dihydrofurans **93**, from 2-diazo-5,5-dimethylcyclohexanedione **91** and styrene **92**. In the reaction, using Ag_2O, Ag_2CO_3, $AgNO_3$, $AgClO_4$, or $AgOSO_2CF_3$ at 70 °C for 10 h gave no cycloadducts, also with $AgBF_4$ (10 mol%) in CH_2Cl_2, THF or CH_3CN solvent at room temperature for 48 h gave no cycloadduct. However, when toluene was used for the same reaction, the expected product **93** was produced in 22% yield. Raising the temperature to 70 °C increased the yield to 47%, and by using the ionic liquid, 1-butyl-3-methylimidazolium tetra-fluoroborate ([Bmim]BF_4), as a co-catalyst, the yield was increased to 71%. The general procedure for the synthesis involves addition of $AgBF_4$ (0.10 mmol) and (Bmim)BF_4 (0.1 mL) to a solution of cyclic diazodicarbonyl **91** (1.0 mmol) and the corresponding olefin **92** (5.0 mmol) in toluene (2.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 24 h, or at 70 °C for 5 h (Scheme 38), and the mechanism is given in Scheme 39.



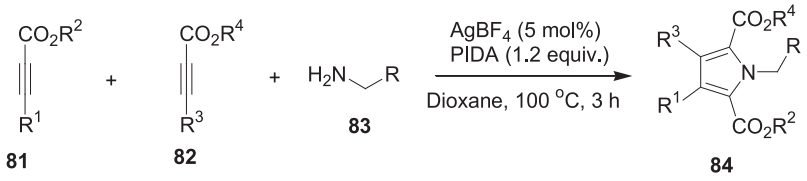
Scheme 31 Synthesis of Umemoto reagent and *ortho*-trifluoromethylation of heterocycle-substituted arenes.



Scheme 32 A silver-catalysed efficient synthesis of 1,2-dihydroquinoline derivatives.



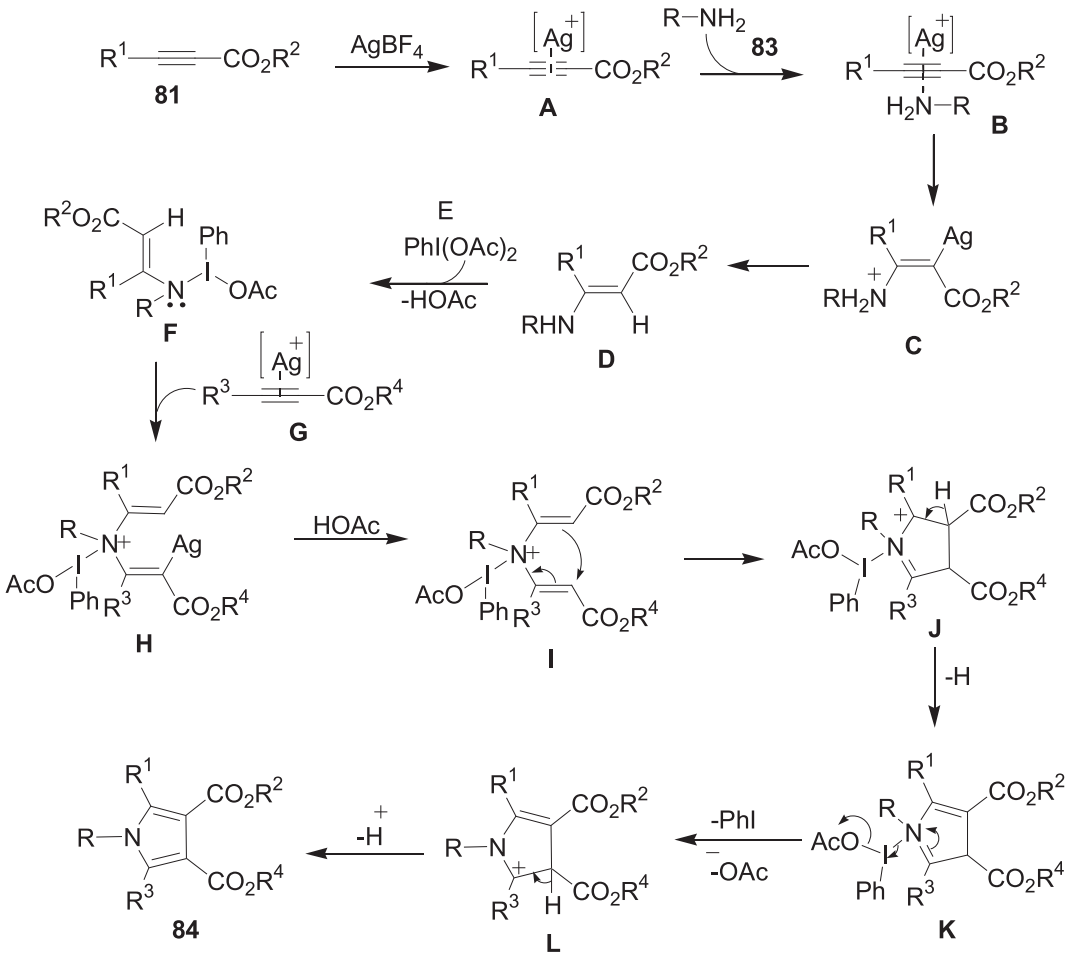
Scheme 33 Proposed mechanism for the synthesis of **80**.



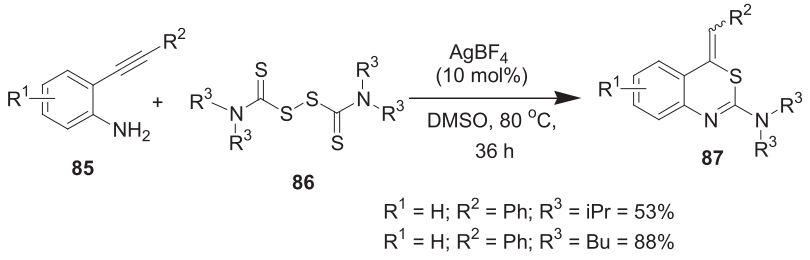
Scheme 34 Synthesis of poly-substituted pyrroles from various alkynoates and amines.

7. $AgBF_4$-promoted strained-ring-opening and cyclisation reactions

Banwell and co-workers (2001) used $AgBF_4$ to open cyclopropane rings and to trap the resulting allylic cation with carbamate nitrogen to synthesise maritinamine *via* an arylated hexahydroindole **95** (64%) from 6,6-dichlorobicyclo[3.1.0]hexane **94**. Subjecting **94** to reaction with $AgBF_4$ in THF at 40 °C resulted in smooth electrocyclic ring-opening of the *gem*-dihalocyclopropane and accompanying π-allyl cation cyclisation to afford the **95** in yields of 65–75%. Typical reaction procedure involves treating a stirred THF (5 mL) solution of **94** (90 mg, 0.20 mmol) with $AgBF_4$ (230 mg, 1.2 mmol) at 40 °C for 21 h. After appropriate work-up and concentration under reduced pressure, the resulting pale-yellow oil was redissolved in THF (2 mL) and triethylamine (0.19 mL, 1.4 mmol) added. The reaction was stirred for 10 min, treated with di-*tert*-butyl dicarbonate (120 mg, 0.54 mmol), and again stirred at 18 °C for 15 h. Work-up and flash chromatographic purification gave carbamate **95** (60 mg, 72%) as a clear,



Scheme 35 A plausible mechanism for the addition/oxidative cyclisation reaction leading to the formation of **84**.

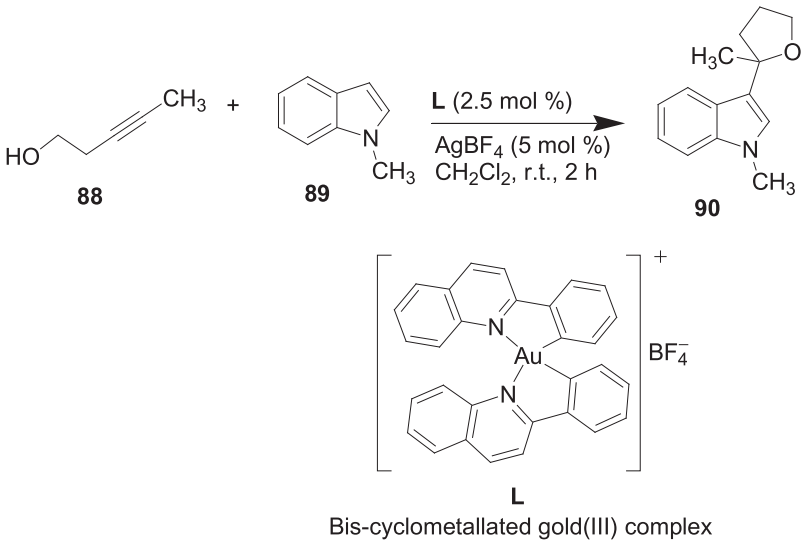


Scheme 36 Synthesis of 4-methylene-4*H*-benzo[*d*][1,3]thiazin-2-amines.

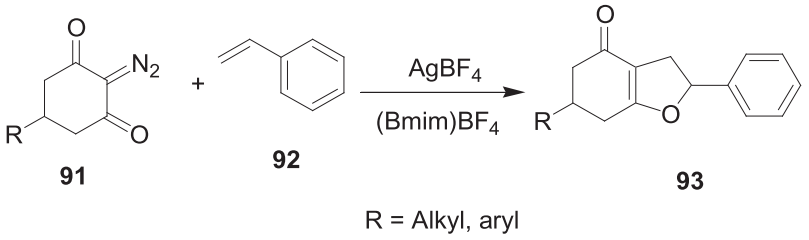
colourless oil. This conversion predictably involves sequence of silver-ion-induced electrocyclic ring-opening of the three membered ring and trapping of the resulting allylic cation by pendant carbamate nitrogen. The formation of maritinamine **97** took two more reaction steps (Scheme 40) (Banwell et al., 2001).

Another example of $AgBF_4$-mediated cyclopropane ring opening and trapping of the intermediate cation with indole is the synthesis of a diastereoisomeric mixture of **101** in 59% combined yield (Scheme 41) (Banwell, 2008; Banwell et al., 2006).

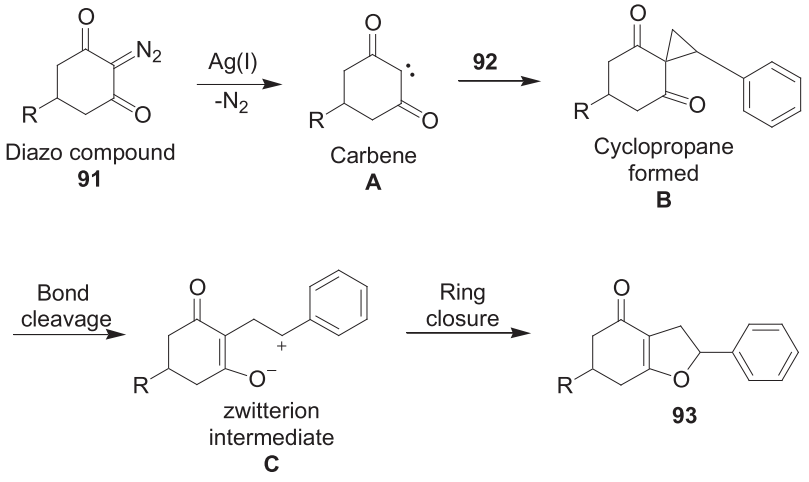
A significant part of the successful synthesis of *ent*-erythramine **105** involves the spirocyclisation of *gem*-dichlorocyclopropane **102** (mixture of diastereoisomers). Successive treatment of THF solution of **102** at −40 to 0 °C with lithium hexamethyldisilazide (LiHMDS) and the resulting conjugate base with $AgBF_4$ at 0–45 °C, gave a diastereoisomeric mixture of desired spirocyclisation products. It was purported that deprotonation step with LiHMDS, and treatment with $Pb(PPh_3)_4$ and dimedone resulted in cleavage of the Alloc-group, and thus afforded products **103** (26%) and its C-3 epimer **104** (30%). Omitting the deprotonation step resulted to dramatic drop in spirocyclisation products, presumably because of the reduced nucleophilicity of the carbamate nitrogen, which could be likened to Boc-protection of the amine group and no spirocyclisation product was detected



Scheme 37 Gold-silver dual catalysed cyclisation–addition reactions of alkynyl alcohol **88** and substituted indoles **89**.



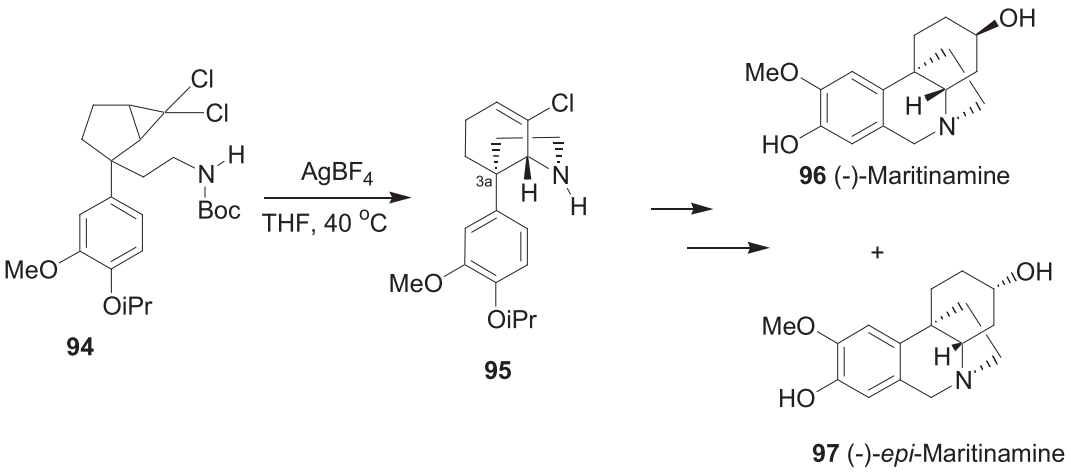
Scheme 38 Synthesis of 2,3-dihydrofurans **93**.



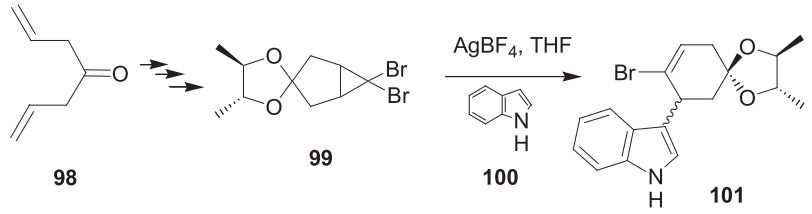
Scheme 39 Proposed reaction mechanism to afford the 2,3-dihydrofuran.

(Banwell, 2008; Stanislawsk et al., 2006). Completion of the synthesis of erythramine **105** took three further steps (Scheme 42).

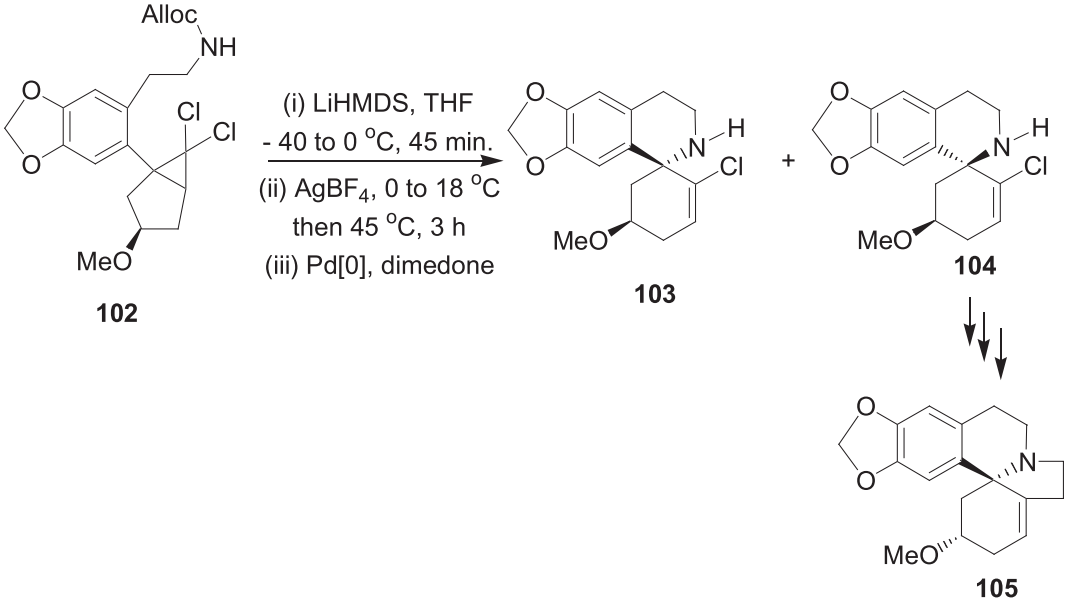
Paquette and Stowell (1971) reported silver(I) ion-catalysed rearrangement of strained σ-bond to synthesise pentacyclo[3.3.2.0.0.3.0]dec-9-ene (snoutene) **108**. Notably, such metal ion catalysed molecular rearrangements have revealed that Ag(I) ions can complex with strained σ bonds (those endowed with enhanced *p* character) to an extent sufficient to permit the operation of otherwise thermally forbidden chemical transpositions. At the onset of this study, an excess amount of $AgBF_4$ was added to dilute deuteriochloroform solutions of **106** at nmr probe temperature (~40 °C). In less than 3 min quantitative conversion to **107** was obtained. For preparative purposes, an acetone solution of **106** in the presence of catalytic amounts of $AgBF_4$ was refluxed for 2 h. The crystalline ester was



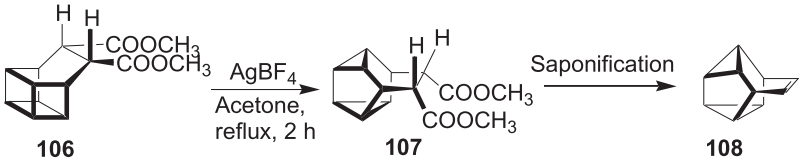
Scheme 40 Synthesis of epi-maritinamine **97.**



Scheme 41 Synthesis of hapalindole C.



Scheme 42 Synthesis of (-)-erythramine **105.**



Scheme 43 Synthesis of snoutene **108**.

saponified and the derived diacid was electrolytically decarboxylated to give snoutene **108** in 17% yield (Scheme 43).

8. Conclusions

A plethora of carbon–carbon and carbon–heteroatom bonds formation promoted by silver tetra-fluoroborate has a long history. Over the years, there have been positive improvements geared towards better understanding of the reaction mechanisms and the associated influence of the reaction conditions on yields and products. Accordingly, $AgBF_4$ salt has become useful transition metal promoter that mediates a variety of reactions through its ability to complex with and activates electron-rich atoms and bonds under mild conditions. The BF_4^- anion has been found valuable in stabilising intermediate cation for smooth nucleophilic attack. The anion also participates in complexing with strained σ-bonds with enhanced *p* character to activate the reaction, and has demonstrated fascinating ability to liberate F^- nucleophile to fluorinate compound. It is therefore plausible to conclude that $AgBF_4$ is a promoter of some intriguing reactions: a versatile and efficient promoter for carbon–carbon and carbon-heteroatom bond formation.

Author contributions

MCA prepared the manuscript and DOU participated in discussions of views represented in the paper.

Conflicts of interest

The authors have no competing financial interests.

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References

Achilonu, MC. 2009. Novel synthetic approaches toward procyanidins and biflavonoids. Ph. D. Thesis, University of the Free State, Bloemfontein, RSA.

Achilonu, M.C., Bonnet, S.L., van der Westhuizen, J.H., 2008. Synthesis of proanthocyanidins. Part 1. The first oxidative formation of the interflavanyl bond in procyanidins. Org. Lett. 10, 3865–3868.

Álvarez-Corral, M., Muñoz-Dorado, M., Rodríguez-García, I., 2008. Silver-mediated synthesis of heterocycles. Chem. Rev. 108, 3174–3198.

Banwell, M.G., 2008. New processes for the synthesis of biologically relevant heterocycles. Pure Appl. Chem. 80, 669–679.

Banwell, M.G., Harvey, J.E., Jolliffe, K.A., 2001. π-Allyl cation cyclisations initiated by electrocyclic ring-opening of *gem*-dihalocyclopropanes: application to the first total syntheses of the crinine-type alkaloids maritinamine and *epi*-maritinamine. J. Chem. Soc. Perkin Trans. 1, 2002–2005.

Banwell, M.G., Ma, X., Taylor, R.M., Willis, A.C., 2006. Concise assembly of the polycyclic frameworks associated with the hapalindole and fischerindole alkaloids. Org. Lett. 8, 4959–4961.

Barluenga, J., Rodríguez, M.A., Campos, P.J.J., 1990. Electrophilic additions of positive iodine to alkynes through an iodonium mechanism. Org. Chem. 55, 3104.

Barrett, A.G.M., Bezuidenhoudt, B.C.B., Howell, A.R., Lee, A.C., 1989. Redox glycosidation *via* thionoester intermediates. J. Org. Chem. 54, 2275.

Belmont, P., 2010. Silver-catalyzed cycloisomerization reactions. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, pp. 143–165.

Bennie, L., Malan, E., Coetzee, J., Ferreira, D., 2000. Structure and synthesis of ether-linked proteracacinidin and promelacacinidin proanthocyanidins from *Acacia caffra*. Phytochemistry 53, 785–793.

Bloodworth, A.J., Bowyer, K.J., 1987. A mild, convenient, halogen-exchange route to *gem*-difluorides and trifluorides. Tetrahedron Lett. 28, 5347–5350.

Broka, C.A., Gerlits, J.F., 1988. Aziridinium cation mediated cyclizations. New routes to the morphinan ring system. J. Org. Chem. 53, 2144–2150.

Chen, Z., Li, J., Jiang, H., Zhu, S., Li, Y., Qi, C., 2010. Silver-catalysed difunctionalization of terminal alkynes: highly regio- and stereoselective synthesis of (Z)-β-haloenol acetates. Org. Lett. 12, 3262–3265.

Chen, X., Chen, D., Lu, Z., Kong, L., Zhu, G., 2011. Palladium-catalyzed coupling of haloalkynes with allylacetate: a regio- and stereoselective synthesis of (Z)-β-haloenol acetates. J. Org. Chem. 76, 6338–6343.

Chen, Z., Zeng, M., Yuan, J., Yang, Q., Peng, Y., 2012. Novel silver tetrafluoroborate catalyzed electrophilic cascade cyclization reaction: a facile approach to the synthesis of halo-substituted benzo[*a*]fluorenols. Org. Lett. 14, 3588–3591.

Cochrane, N.A., Nguyen, H., Gagne, M.R., 2013. Catalytic enantioselective cyclization and C3-fluorination of polyenes. J. Am. Chem. Soc. 135, 628–631.

Coetzee, J., Malan, E., Ferreira, D., 1998a. Oligomeric flavanoids. Part XXVIII: Structure and synthesis of ether-linked [4-O-3]-bis-teracacinidins, a novel class of naturally occurring proanthocyanidins. J. Chem. Res. (S), 526–527; (M), 2287–2296.

Coetzee, J., Malan, E., Ferreira, D., 1998b. Oligomeric flavanoids. Part XXIX: Structure and synthesis of novel ether-linked [4-O-4]-bis-teracacinidins. Tetrahedron 54 (31), 9153–9160.

Davies, I.W., Gallagher, T., Lamont, R.B., Scopes, D.I.C., 1992. Asymmetric synthesis of functionalised pyrrolidines. Highly diastereoselective cyclisations mediated by sulphide and sulphoxide ligands. J. Chem. Soc. Chem. Commun., 335–337.

Driver, T.G., 2010. Silver-catalyzed silylene transfer. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 183–227.

Erdik, E., 1992. Transition metal catalysed reactions of organozinc reagents. Tetrahedron 48, 9577.

Foo, L.Y., 1989. Isolation of [4-*O*-4]-linked bifavanoids from Acacia melanoxylon: firrst examples of a new class of single ether-linked proanthocyanidin dimers. J. Chem. Soc. Chem. Commun. 20, 1505–1506.

Fréchet, J.M., Baer, H.H., 1975. Concerning the problem of stereospecific glycosylation. Synthesis and methanolysis of some 2-*O*-benzylated d-galactopyranosyl and d-galactofuranosyl halides. Can. J. Chem. 53, 670–679.

Fry, A.J., Migron, Y.A., 1979. Convenient new synthesis of α-fluorocarbonyl compounds. Tetrahedron Lett. 36, 3357–3360.

Gallagher, T., Jones, S.W., Mahon, M.F., Molloy, K.C., 1991. Stereoselectivity in electrophile-mediated cyclisations. Ag-catalysed synthesis of disubstituted pyrrolidines; crystal structure of *cis*-5-phenyl-*N*-tosylpyrrolidin-2-yl methyl 4-bromobenzoate. J. Chem. Soc. Perkin Trans. 1, 2193–2198.

Grant, T.N., West, F.G., 2010. Silver(I)-mediated electrocyclic processes. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 117–141.

Grimaldi, J., Cormons, A., 1989. ''Une extension de la théorie de Fredholm''. C. R. Acad. Sci., Ser. 2309, 1753. Subjection of σ-allenicoxime X to AgBF4-promoted cyclization, the alloxime derivative Y; trapped by 1,3-dipolarophile (styrene) yielded disubstitutedpiperidine Z.

Grundberg, H., Andergran, M., Nilsson, U.F., 1999. Conversion of 2-(trimethylsilyl)ethyl sulphides into thioesters. Tetetrahedron Lett. 40, 1811–1814.

Hirao, T., Takada, T., Ogawa, A., 2000. Oxovanadium(V)-induced cross-coupling reaction between two ligands of organozinc compounds. J. Org. Chem. 65, 511–1515.

Honeychuck, R.V., Hersh, W.H., 1989. Coordination of ''noncoordinating'' anions: synthesis, characterization, and X-ray crystal structures of fluorine-bridged $[SbF]^{-}$, [BFJ], and $[PF_6]$-adducts of [R3P(CO),(NO) W]. An unconventional order of anion donor strength. Inorg. Chem. 28, 2869–2886.

Kaeothip, S., Pornsuriyasak, P., Demchenko, A.V., 2008. Silver(I) tetrafluoroborate as a potent promoter for chemical glycosylation. Tetrahedron Lett. 49, 1542–1545.

Kantorowski, E.J., Kurth, M.J., 2000. Expansion to seven-membered rings. Tetrahedron 56, 4317–4353.

Kawasaki, M., Yamamoto, H., 2010. Aldol and related processes. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 167–182.

Kinsman, R., Lathbury, D., Vernon, P., Gallagher, T., 1987. Stereoselectivity in the synthesis of 2,5-disubstituted pyrrolidines. J. Chem. Soc. Chem. Commun., 243–244.

Kirk, R.E., Othmer, D.F., 1966. The chemistry and chemical technology of fluorine. In: Kirk, R.E., Othmer, D.F. (Eds.), Encyclopedia of Chemical Technology. John Wiley & Sons, New York, USA, pp. 566.

Ko, H.-M., Kung, K.K.-Y., Cui, J.-F., Wong, M.-K., 2013. Bis-cyclometallated gold(III) complexes as efficient catalysts for synthesis of propargylamines and alkylated indoles. Chem. Commun. 49, 8869–8871.

Kozikowski, A.P., Tückmantel, W., Böttcher, G., Romanczyk, L.J., 2003. Studies in polyphenol chemistry and bioactivity. 4. Synthesis of trimeric, tetrameric, pentameric, and higher oligomeric epicatechin-derived procyanidins having all $4\beta \rightarrow 8$-interflavan connectivity and their inhibition of cancer cell growth through cell cycle arrest. J. Org. Chem. 68, 1641–1658.

Kuehne, M.E., Matson, P.A., Bornmann, W.G., 1991. Enantioselective syntheses of vinblastine, leurosidine, vincovaline, and 20'-*epi* –vincovaline. J. Org. Chem. 56, 513–528.

Kurosu, M., Li, K., Crick, D.C., 2009. Concise synthesis of capuramycin. Org. Lett. 11 (11), 2393–2396.

Lathbury, D.C., Gallagher, T., 1985. A new approach to cyclic nitrones: application to the synthesis of α, α′-disubstituted piperidines and pyrrolidines. Tetrahedron Lett. 26, 6249–6252.

Lathbury, D., Gallagher, T., 1986. Asymmetric synthesis *via* allenes: synthesis of (*R*)-(–)-coniine. J. Chem. Soc. Chem. Commun., 114–115.

Lathbury, D.C., Shaw, R.W., Bates, P.A., Hursthouse, M.B., Gallagher, T., 1989. Electrophile-mediated cyclisations: regioselective synthesis of substituted cyclic nitrones and crystal structures of the nitronecyclo adducts. J. Chem. Soc. Perkin Trans. 1, 2415–2424.

Leteux, C., Veyrières, A., 1994. Synthesis of α-C-glycopyranosides of d-galactosamine and glucosamine *via* iodocyclization of corresponding glycals and silver tetrafluoroborate-promoted alkynylation at the anomeric centre. J. Chem. Soc. Perkin Trans. 1, 2647–2655.

Li, Z., He, C., 2006. Recent advances in silver-catalyzed nitrene, carbene, and silylene-transfer reactions. Euro. J. Org. Chem., 4313–4322.

Liu, W., Jiang, H., Huang, L., 2010. One-pot silver-catalyzed and PIDA-mediated sequential reactions: synthesis of polysubstituted pyrroles directly from alkynoates and amines. Org. Lett. 12, 312–315.

Lovely, C.J., 2010. Silver carbenoids. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 229–257.

Luo, Y., Li, Z., Li, C.-J., 2005. A Silver-catalyzed domino route toward 1,2-dihydroquinoline derivatives from simple anilines and alkynes. Org. Lett. 7, 2675–2678.

Mitasev, B., Brummond, K.M., 2006. Synthesis of functionalized Δ^3-pyrrolines *via* a Ag(I)-catalyzed cyclization of amino acid derived allenes. Synlett., 3100–3104.

Oshima, K., 1991. Transition metal catalyzed reactions of organozinc compounds. In: Liebiskind, L.S. (Ed.), Advance in organometallic chemistry. JAI Press, London, Vol. 2, p. 101.

Padwa, A., Ishida, M., 1991. Silver tetrafluoroborate induced reaction of trimethylsilyl enol ethers with 2,3-diiodo-1-(phenylsulfonyl)-1-propane as a method for preparing substituted furans. Tetrahedron Lett. 32, 5673–5676.

Paquette, L.A., Stowell, J.C., 1971. Silver(I) ion catalyzed rearrangements of strained bonds. III. The synthesis and degenerate thermal valence isomerization of pentacyclo[3.3.2.0.0.0]dec-9-ene. J. Amer. Chem. Soc. 93, 2459–2463.

Pornsuriyasak, P., Demchenko, A.V., 2006. S-Thaiazolinyl (STaz) glycosides as versatile building blocks for convergent selective, chemoselective, and orthogonal oligosaccharide synthesis. Chem. Eur. J. 12, 6630–6646.

Rosenthal, M.R., 1973. The myth of the non-coordinating anion. J. Chem. Educ. 50, 333.

Sakurai, O., Horikawa, H., Iwasaki, T., 1995. Novel Synthetic approach to carbapenems utilizing aza-cope mannich cyclization. J. Chem. Soc. Chem. Commun., 2527–2528.

Schmitt, C., Wibner, O., Schween, M., 2013. Carbenium-ionen als reaktive zwischenstufen. Chemkon. 20, 59–65.

Sharpe, A.G., 1952. The preparation of silver tetrafluoroborate and silver(I) fluoride. J. Chem. Soc., 4538–4539.

Shibata, N., Matsnev, A., Cahard, D., 2010. Shelf-stable electrophilic trifluoro methylating reagents: a brief historical perspective. Beilstein J. Org. Chem. 6, 1–19.

Stanislawsk, P.C., Willis, A.C., Banwell, M.G., 2006. New protocols for the assembly of the tetracyclic framework associated with the aromatic erythrina alkaloids. Org. Lett. 8, 2143–2146.

Steynberg, P.J., Nel, R.J.J., van Rensburg, H., Benzuidenhoudt, B.C.B., Ferreira, D., 1998. Oligomeric flavonoids. Part 27. Interflavanyl bond formation in procyanidins under neutral conditions. Tetrahedron 54, 8153–8158.

Suda, M., Hino, C., 1981. Preparation of bromodifluoromethylsulphide and its conversion to trlfluoromethylsulphide. Tetrahedron Lett. 22, 1997–2000.

Tang, P., Ritter, T., 2011. Silver-mediated fluorination of aryl silanes. Tetrahedron 67, 4449–4454.

Tang, R.-Y., Luo, P.-S., Zhang, X.-G., Zhong, P., Li, J.-H., 2010. Silver-catalyzed ammonolysis-cyclization tandem reactions of 2-alkynylbenzenamines with tetraalkylthiuramdisulphides leading to 4-methylene-4H-benzo[d][1,3]thiazin-2-amines. Synlett. 9, 1345–1350. Abstract.

Thompson, R.S., Jacques, D., Haslam, E., Tanner, R.J.N.J., 1972. Plant proanthocyanidins. Part I. Introduction; the isolation, structure, and distribution in nature of plant procyanidins. Chem. Soc. Perkin Trans. I, 1387–1399.

Trost, B.M., Murayama, E., 1981. Dimethylmethylthiosulphonium fluoroborate. A chemoselective initiator for thionium ion induced cyclizations. J. Am. Chem. Soc. 103, 6529–6530.

Trost, B.M., Sato, T.J., 1985. Dimethyl(methylthio)sulphonium tetrafluoroborate initiated organometallic additions to and macrocyclizations of thioketals. Am. Chem. Soc. 107, 719–721.

Umemoto, T., Ishihara, S., 1993. Power-variable electrophilic trifluoro methylating agents. S-, *Se-*, and *Te-(*trifluoromethy1)dibenzothio-,

-seleno-, and –tellurophenium salt system. J. Am. Chem. Soc. 115, 2156–2164.

Van Rensburg, H., Van Heerden, P.S., Bezuidenhoudt, B.C.B., Ferreira, D., 1996. The first enantioselective synthesis of trans- and cis-dihydroflavonols. Chem. Commun., 2747–2748

Van Rensburg, H., Van Heerden, P.S., Bezuidenhoudt, B.C.B., Ferreira, D., 1997. Stereoselective synthesis of flavonoids. Part 4. Trans- and c/s-dihydroflavonols. Tetrahedron 53, 14141–14152.

Wang, X., Truesdale, L., Yu, J.-Q., 2010. Pd(II)-catalyzed *ortho*-trifluoro methylation of arenes using TFA as promoter. J. Am. Chem. Soc. 132, 3648–3649.

Wang, Y., Siricilla, S., Aleiwi, B.A., Kurosu, M., 2013a. Improved synthesis of capuramycin and its analogues. Chem. Eur. J. 19, 13847–13858.

Wang, K.-P., Yun, S.Y., Mamidipalli, P., Lee, D., 2013b. Silver-mediated fluorination, trifluoromethylation, and trifluoromethylthiolation of arynes. Chem. Sci. 4, 3205–3211.

Weibel, J.-M., Blanc, A., Pale, P., 2008. Ag-mediated reactions: coupling and heterocyclization reactions. Chem. Rev. 108, 3149–3173.

Weibel, J.-M., Blanc, A., Pale, P., 2010a. Sigmatropic rearrangements and related processes promoted by silver. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 83–116.

Weibel, J.-M., Blanc, A., Pale, P., 2010b. Coupling reactions promoted by silver. In: Harmata, M. (Ed.), Silver in Organic Chemistry. John Wiley and Sons, New Jersey, USA, pp. 285–328.

Wu, Y.-C., Liron, M., Zhu, J., 2008. Asymmetric total synthesis of (-)-quinocarcin. J. Am. Chem. Soc. 130, 7148–7152.

Wu, Y.-C., Bernadat, G., Masson, G., Couturier, C., Schlama, T., Zhu, J., 2009. Synthetic studies on (-)-lemonomycin: an efficient assymmetric synthesis of lemonomycinone amide. J. Org. Chem. 74, 2046–2052.

Xia, L., Lee, Y.R., Kim, S.H., Lyoo, W.S., 2011. $AgBF_4$/[Bmim]BF_4-catalyzed [3 + 2] cycloaddition of cyclic diazodicarbonyl compounds: efficient synthesis of 2,3-dihydrofurans and conversion to 3-acylfurans. Bull. Korean Chem. Soc. 32, 1554–1558.