Application of aluminum triiodide in organic synthesis

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Abstract

The multifaceted reactivity of aluminum triiodide (AlI_3) is reviewed. The oxophilic character of the Lewis acid enables the formation of coordination complexes with esters, ethers, oxiranes, diols, *N*-oxides, and sulfoxides that decompose spontaneously to afford acids, alcohols and olefins *via* ester and ether cleavage, deoxygenation of oxiranes, and deoxydehydration of diols, respectively. As an iodide ion source and hydrogen iodide precursor, the reagent allows iodination and reduction of *N*-oxides, sulfoxides and azides as well as hydroiodination of alkenes and alkynes. Aluminum enolates, generated by treatment of α-haloketones with AlI_3, provide accesses to β-hydroxy ketones, 1,5-diones, and β-iodo Morita-Baylis-Hillman esters.

Keywords: Aluminum triiodide, ester cleavage, ether cleavage, hydroiodination, deoxygenation, deoxydehydration, aluminum enolate

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1. Introduction

Efficient transformations of organic functional groups using conveniently available and inexpensive reagents under mild reaction conditions represent a challenging demand of current organic syntheses. Aluminum triiodide (AlI_3), to this end, has emerged as a non-hazardous and easy to handle reagent toward a broad spectrum of functional groups.[1]

AlI_3 exists as a dimer (Al_2I_6) in the solid state and in aprotic apolar solvents, whereas planar monomer has also been observed in gas phase.[2] The reagent serves as an oxophilic Lewis acid[3,4] and coordinates with Lewis base ligands to form tetrahedral complexes.[5] Due to the unique oxophilicity and Lewis acidity nature, AlI_3 has been extensively applied in organic synthesis.

2. Ester Cleavage

The oxophilic character of AlI_3 enables coordination with esters by the Lewis acidic center (Al^{3+}) through the formation of donor-acceptor complexes. The complexes undergo cleavage at ambient temperature, and their decomposition could be accelerated at elevated temperatures.[6-8] The cleavages were complete within 0.5 hour and afforded corresponding acids in moderate to high yields.[9] Such kind of non-hydrolytic cleavage of esters features the advantage of avoiding strong acidic or basic conditions and is suitable for substrates containing sensitive functional groups. The transformation can be accessed alternatively with trimethyltin hydroxide,[10] lithium iodide,[11] lithium 1-propanethiolate,[12] lithium bromide,[13] and trimethylsilyl iodide (TMSI).[14]

2.1 Scope of substrates

The ester cleavage method was applied to a variety of substrates (**1**) including aromatic ester (**1a**), α,β-unsaturated esters (**1b**, **1c**), halogen-containing ester (**1d**), and aliphatic ester (**1e**), see scheme 1A.[9]

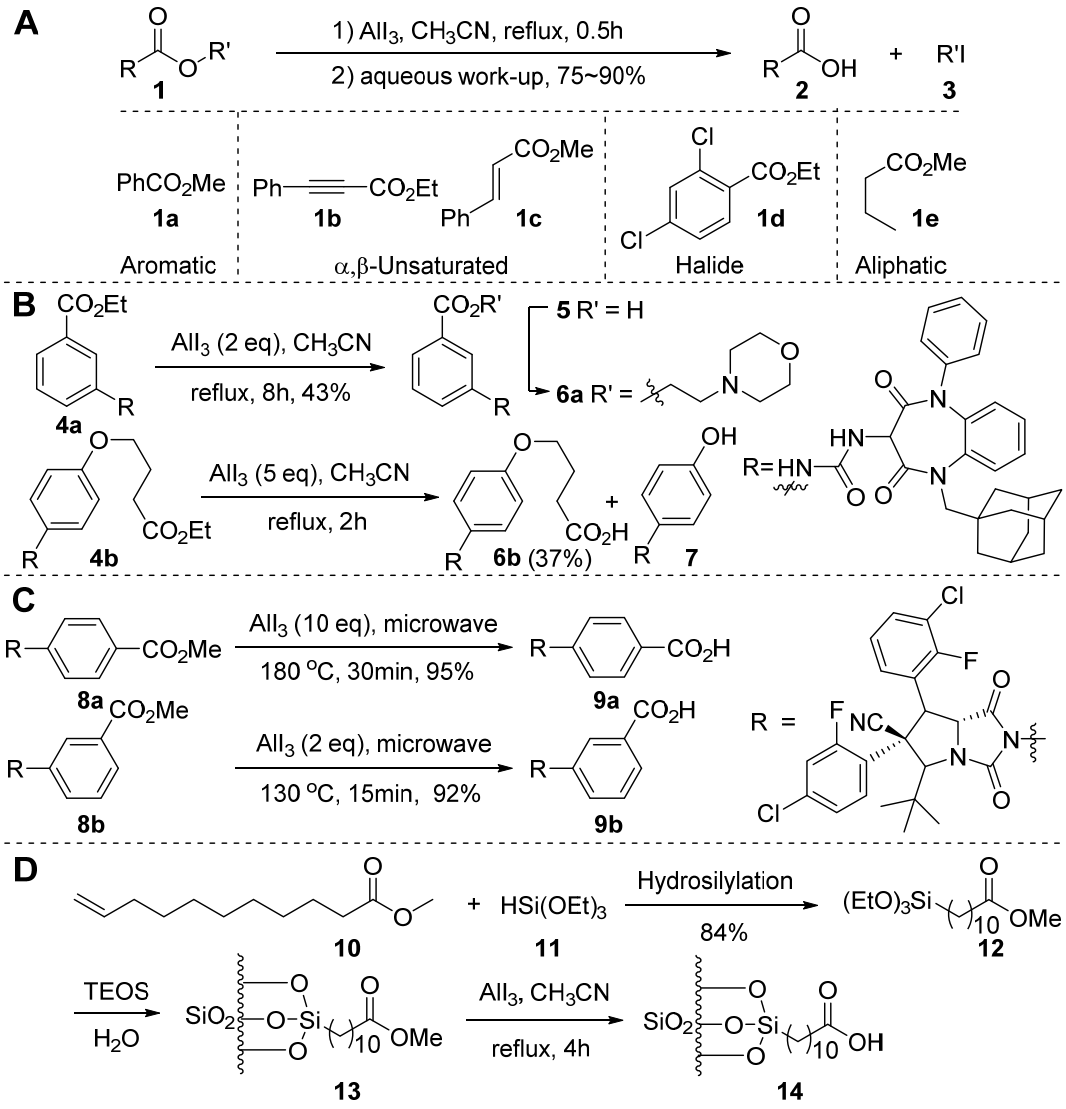
When the method was applied to phenyl esters, however, ester cleavage was superceded by Fries rearrangement. For example, a mixture of benzophenols (p/o=2) were obtained in moderate yields after treatment of phenyl benzoate with AlI_3.[9]

2.2 Application in syntheses of pharmaceutical targets

The method has been applied in syntheses of pharmaceutical targets: (I) A class of potent cholecystokinin B (CCK-B) receptor antagonists were accessed through AlI_3 induced ester cleavage. The cleavages of **4a** and **4b** were complete after refluxing in acetonitrile for several hours with AlI_3 and afforded 1,5-disubstituted benzodiazepines (**6a** and **6b**) in low yields (scheme 1B).[15,16] Trace amount of meta-substituted phenol (**7**) was isolated, and was formed apparently through ether cleavage.[17] (II) Hexahydropyrrolo[1,2-*c*]imidazolones (**9a** and **9b**), a family of effective MDM2-p53 interaction inhibitors and useful drug candidates for treating cancer, were prepared by AlI_3 induced cleavage of **8a** and **8b** in virtually quantitative yields. Microwave irradiation was used to assist the cleavage, and the conversions were complete efficiently in 15~30 minutes (scheme 1C).[18]

2.3 Other applications

An organic-inorganic hybrid material with free carboxylic groups over the surface was prepared by AlI_3 induced ester cleavage of corresponding methyl carboxylate groups. Hydrosilylation of **11** with triethoxysilane (**10**) gave **12**. Sol-gel co-condensation between **12** and tetraethoxysilane (TEOS) afforded nanohybrid material **13**. The surface of **13** was modified by AlI_3 to release terminal carboxylic groups (**14**) for uptake of lanthanide cations (Scheme 1D).[19]



Scheme 1. AlI_3 induced non-hydrolytic ester cleavage. A: Scope of substrates; B: syntheses of CCK-B receptor antagonists; C: syntheses of inhibitors for MDM2-p53 interactions; D: surface modification of an ester terminated silica nanohybrid.

3. Ether Cleavage

Ethers (**15**) tend to form ethereal-AlI_3 complexes (**16**) with AlI_3 as a result of its unique oxophilicity. The complexes underwent noticeable ether cleavages (Figure 1A) that afforded alcohols (**18**) and alkyl iodides. For example, methyl iodide, ethyl iodide and 4-iodobutanol were observed during decomposition of anisole, ethyl ether[20] and tetrahedronfuran complexes, respectively.[6] Ether cleavage reaction was applied in deprotection of alkoxybenzene, 1,3-benzodioxole, and alkylthiophenyl alkyl ether to afford corresponding phenol, pyrocatechol and alkylthiophenol, respectively.[21]

3.1 Regioselectivity

Cleavage of ethers is commonly carried out with Brønsted acids (such as HI-anhydride,[22] HBr-HOAc[23]or HCl-pyridine[24]) or Lewis acids (boron, silicon and metal halides). AlI_3 showed an inversed regioselectivity in ether cleavage compared to boron and silicon halides when a dialkyl ether group and an alkyl aryl ether group coexisted in a substrate. For example when **19** was cleaved by AlI_3, phenol (**20**) was the exclusive product (Figure 1B). By contrast, boron chloride (BCl_3), boron bromide (BBr_3), TMSI and trichlorosilyl iodide preferentially cleaved the aliphatic ether bond and gave 2-phenoxy ethanol (**21**) in moderate yields.[25]

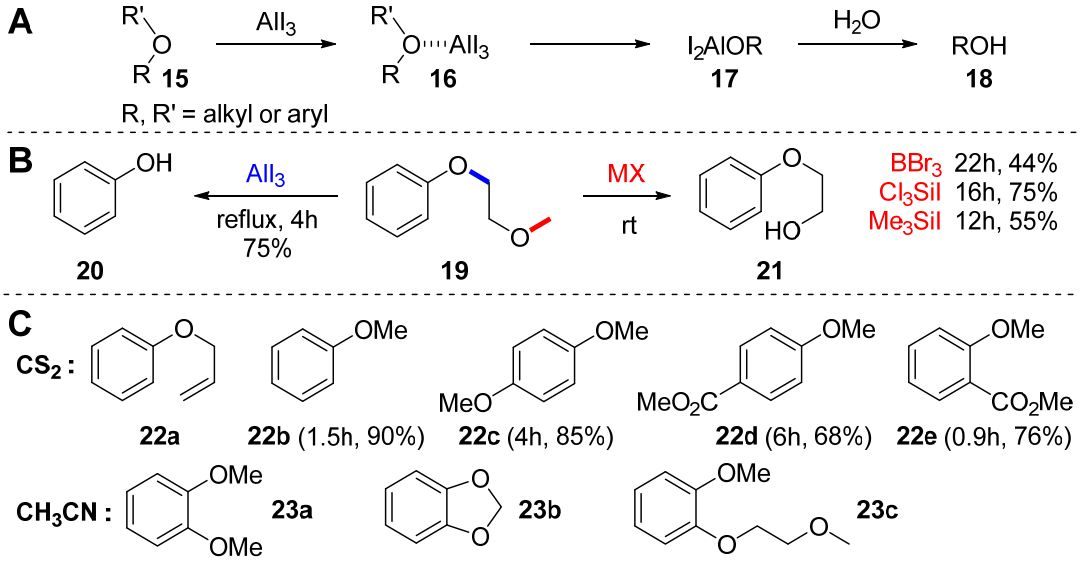


Figure 1. AlI_3 catalyzed cleavage of ethers. A: formation and decomposition of ethereal-AlI_3 complexes; B: regioselectivities induced by variant Lewis acids; C: solvent effects.

3.2 Solvent effects

Deprotection of alkyl aryl ethers (**22a**~**22e**) can be accessed more efficiently in carbon disulfide (CS_2) then in acetonitrile. Surprisingly, cleavage of pyrocatechol derived ethers (**23a**~**23c**) turned faster in acetonitrile (Figure 1C). Meanwhile, it was noted that the ethereal cleavage of **22d** was slower than its *o*-isomer (**22e**). The conversion proceeded possibly *via* chelation mechanism featuring neighboring group participation. Accordingly, demethylation of **22c** occurred in a stepwise manner, and *p*-methoxyphenol was isolated.[25,26]

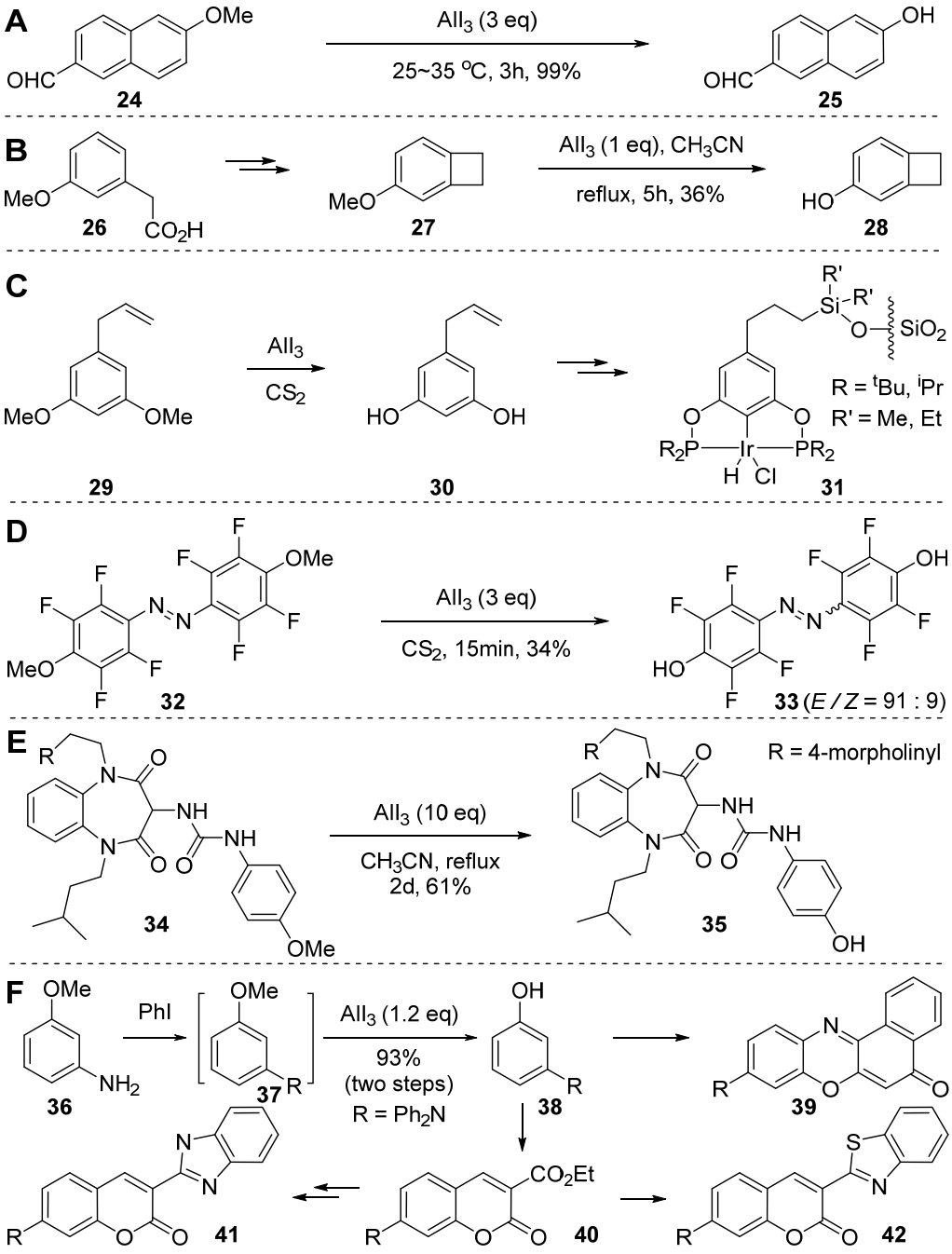
3.3 Deprotection of alkyl aryl ethers

AlI_3 was applied in deprotection of phenolic ethers to afford several phenol intermediates, as depicted in scheme 2. Demethylation of **24** with AlI_3 afforded 2-formyl-6-naphthol (**25**) in almost quantitative yield (Scheme 2A).[27] **28** is a useful performance enhancement additive for engineering thermoplastics such as polycarbonate. A convenient preparation of **28** was accomplished by AlI_3 mediated demethylation of **27**. Failed deprotection attempts include treatments of the ether with BBr_3 and TMSI (Scheme 2B).[28,29] Deprotection of **29** by AlI_3 in refluxing CS_2 furnished 5-allyl

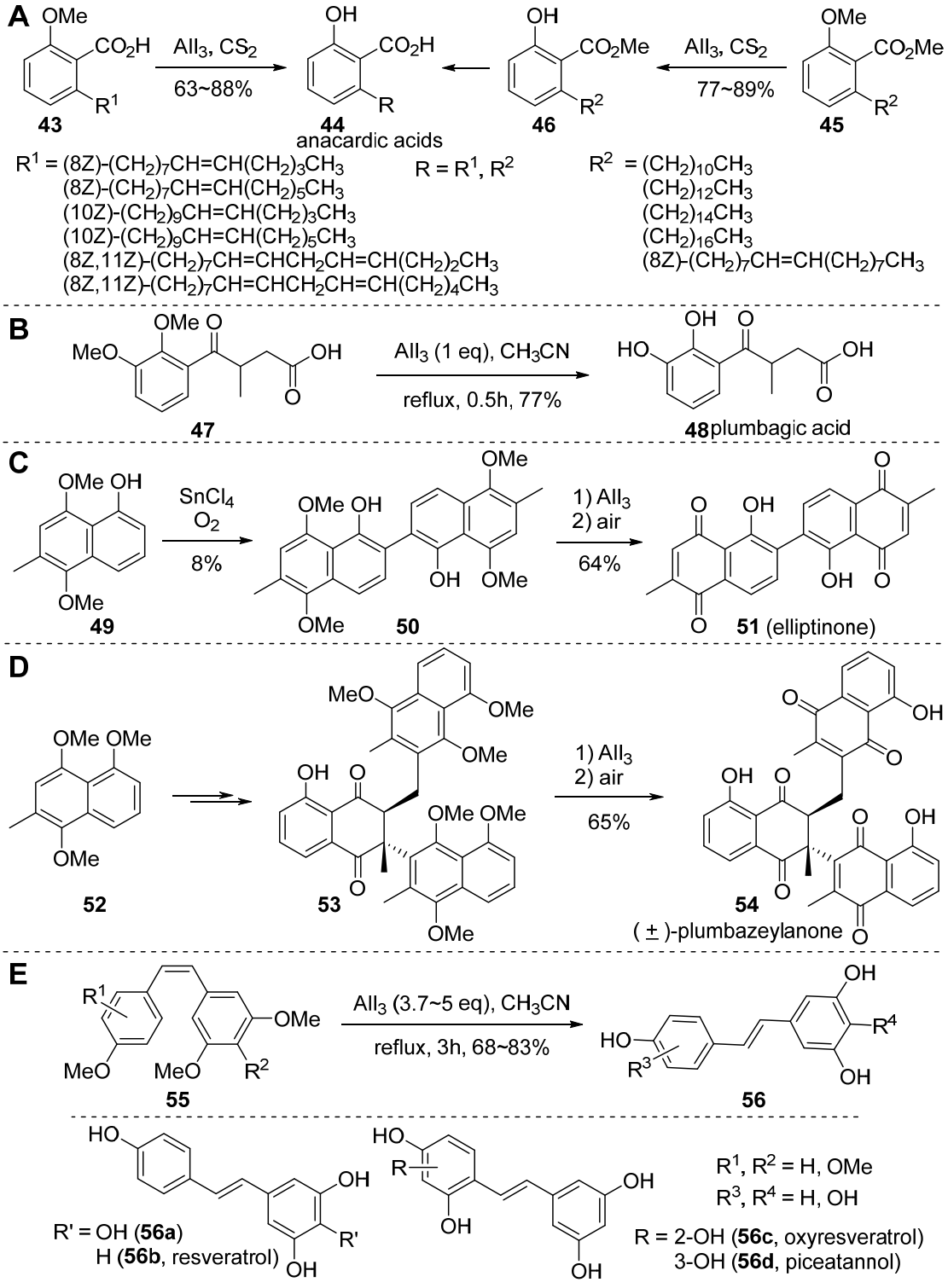
resorcinol (**30**). **30** was further transformed into an organoirridium catalyst loaded on silica (**31**) for converting low molecular weight alkanes into higher molecular weight fuel (Scheme 2C).[30] As an inhibitor of 17α-hydroxylase-$C_{17,20}$-lyase and 5α-reductase for treatment of hormone-dependent prostatic carcinoma, **33** was obtained as a mixture of stereoisomers (*E/Z*=91:9) by demethylation of **32** with AlI_3 in CS_2 (Scheme 2D).[31] 1,5-Dialkyl-1,5-benzodiazepine (**35**), a potent CCK-B receptor antagonist, was synthesized by demethylation of ether **34** with AlI_3 in reflux acetonitrile. Alhough the transformation was sluggish, a large excess of AlI_3 furnished the deprotection in moderate yield (Scheme 2E).[32] The method was applied in syntheses of four coumarin analogues (**39**~**42**) applicable to organic light emitting displays as fluorescent dyes. Key intermediate 3-hydroxytriphenylamine (**38**) was prepared in a two-step procedure: Ulmann coupling of iodobenzene and *m*-anisidine (**36**) furnished anisole **37**; demethylation of **37** with AlI_3 afforded **38** in 93% yield (Scheme 2F).[33]

3.4 Exhaustive demethylation

AlI_3 was applied in syntheses of several naturally occurring phenols (Scheme 3). (I) Anacardic acids (**44**), a class of salicylic acids bearing a long alkyl chain, were achieved by demethylation of relevant ethers (**43** and **46**). The substrates were refluxed with AlI_3 in acetonitrile for 0.5 hour to complete the deprotection and afforded **44** in moderate to high yields (Scheme 3A). For two substrates with (*8Z,11Z*)-aliphatic substituent, limonene was used as hydrogen iodide (HI) scavenger.[34] (II) Plumbagic acid (**48**) was prepared in 77% yield by exhaustive demethylation of ether **47** with AlI_3. The conversion was complete in 0.5 hour in refluxing acetonitrile.[35] It is noteworthy that the generation of I_2 complicated the work-up (Scheme 3B).[36] (III) Elliptinone (**51**), a biaryl natural product, was achieved by exhaustive deprotection of a 2,2'-binaphthol (BNAP, **50**) followed by air oxidation. The BNAP was synthesized by tin tetrachloride ($SnCl_4$) mediated oxidative coupling of α-naphthol (**49**), see Scheme 3C.[37] Deprotection of such 1,4-dimethoxybenzene is typically achieved by cerium ammonium nitrate (CAN) mediated oxidation.[38-39] (IV) In a similar manner (±)-plumbazeylanone (**54**), a trimer of naphthoquinone, was achieved by exhaustive demethylation of ether **53** followed by air oxidation in 65% yield (Scheme 3D).[40] (V) Resveratrol (**56b**) and its derivatives such as oxyresveratrol (**56c**) and piceatannol (**56d**) were obtained by exhaustive deprotection of related phenolic methyl ethers (**55**). The transformations were complete after 3 hours of refluxing in acetonitrile, and afforded polyphenols (**56a**~**56d**) in 68~83% yields.[41-43] Surprisingly, *E*-stilbenes were obtained after treatment of *Z*-stilbenes with AlI_3 (Scheme 3E).[44] Conjugation of *Z*-4-styrylphenolates, a reactive species derived from 4-methoxy-stilbenes, may account for the *E/Z* stereoisomerization.



Scheme 2. Application of AlI_3 in deprotection of phenolic ethers. A: 2-Formyl-6-naphthol; B: 4-hydroxybenzocyclobutane; C: iridium catalyst intermediate; D: 17α-hydroxylase-C17,20-lyase and 5α-reductase inhibitor 4,4'-dihydroxyoxtafluoroazobenzene; E: CCK-B receptor antagonist 1,5-dialkyl-1,5-benzodiazepine; F: OLED material intermediate.



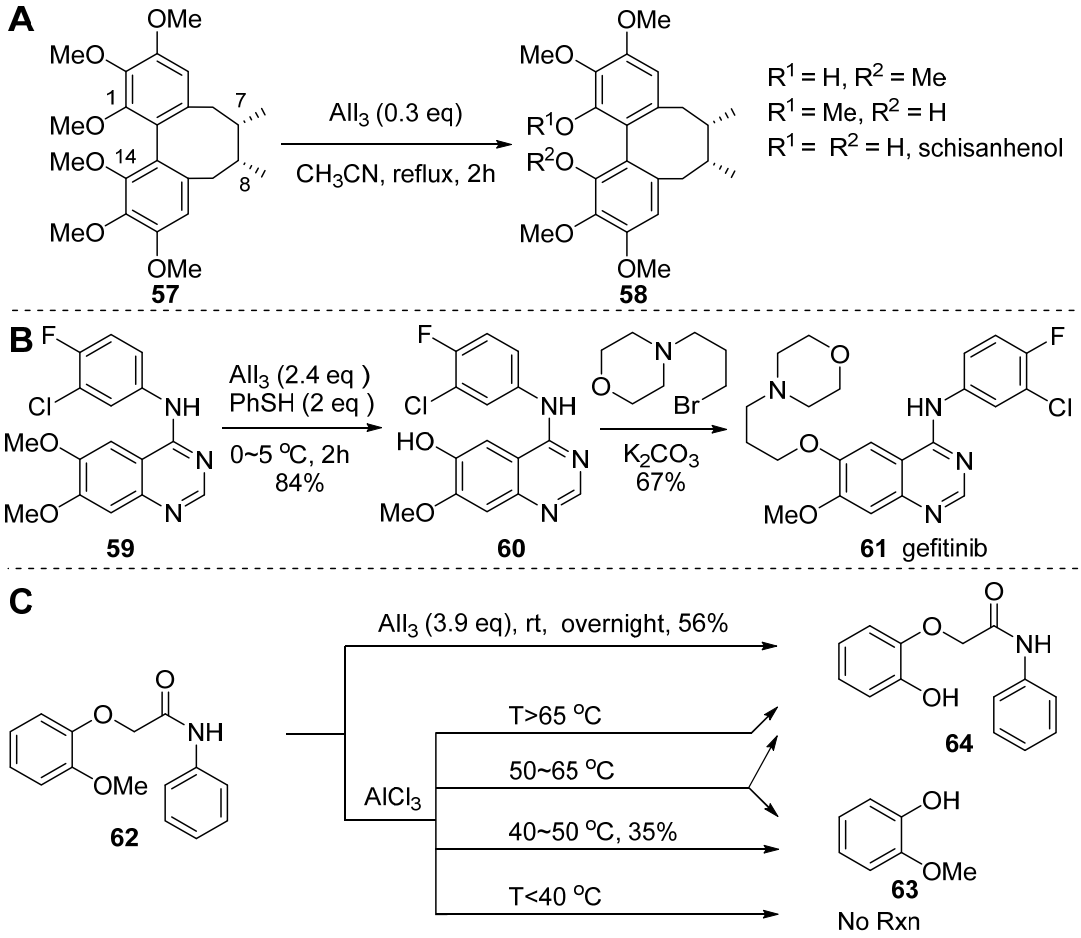
Scheme 3. Application of AlI_3 in syntheses of phenolic natural products. A: Anacardic acids; B: plumbagic acid; C: elliptinone; D: (±)-plumbazeylanone; E: resveratrol analogues.

It should be noted, however, that slight excess AlI_3 is needed for successful exhaustive demethylation; otherwise partial demethylation may occur. For example deprotection of 3,4',5-

trimethoxystilbene (15 mmol) by AlI_3 (36.9 mmol, 2.46 eq) in refluxing acetonitrile afforded **56b** in 15% yield.[45-47] Apparently, failure to remove HI constitutes an factor for the low yield.

3.5 Partial demethylation

As mentioned above, insufficient AlI_3 leads to partial demethylation. In the case of isolable intermediates, regioselective demethylation may be accessed. For example, after treating deoxyschizandrin (**57**) with AlI_3 (0.3eq) in acetonitrile for 2 hours under reflux, several intermediates (**58**) including schisanhenol were separated (in low yields) by preparative thin layer chromatography (Scheme 4A).[48]



Scheme 4. Regioselective demethylation. A: Deprotection of deoxyschizandrin by AlI_3; B: PhSH promoted demethylation of gefitinib intermediate; C: comparisons between AlI_3 and $AlCl_3$ in deprotection of 2-(2-methoxyphenoxy)-*N*-phenylacetamide.

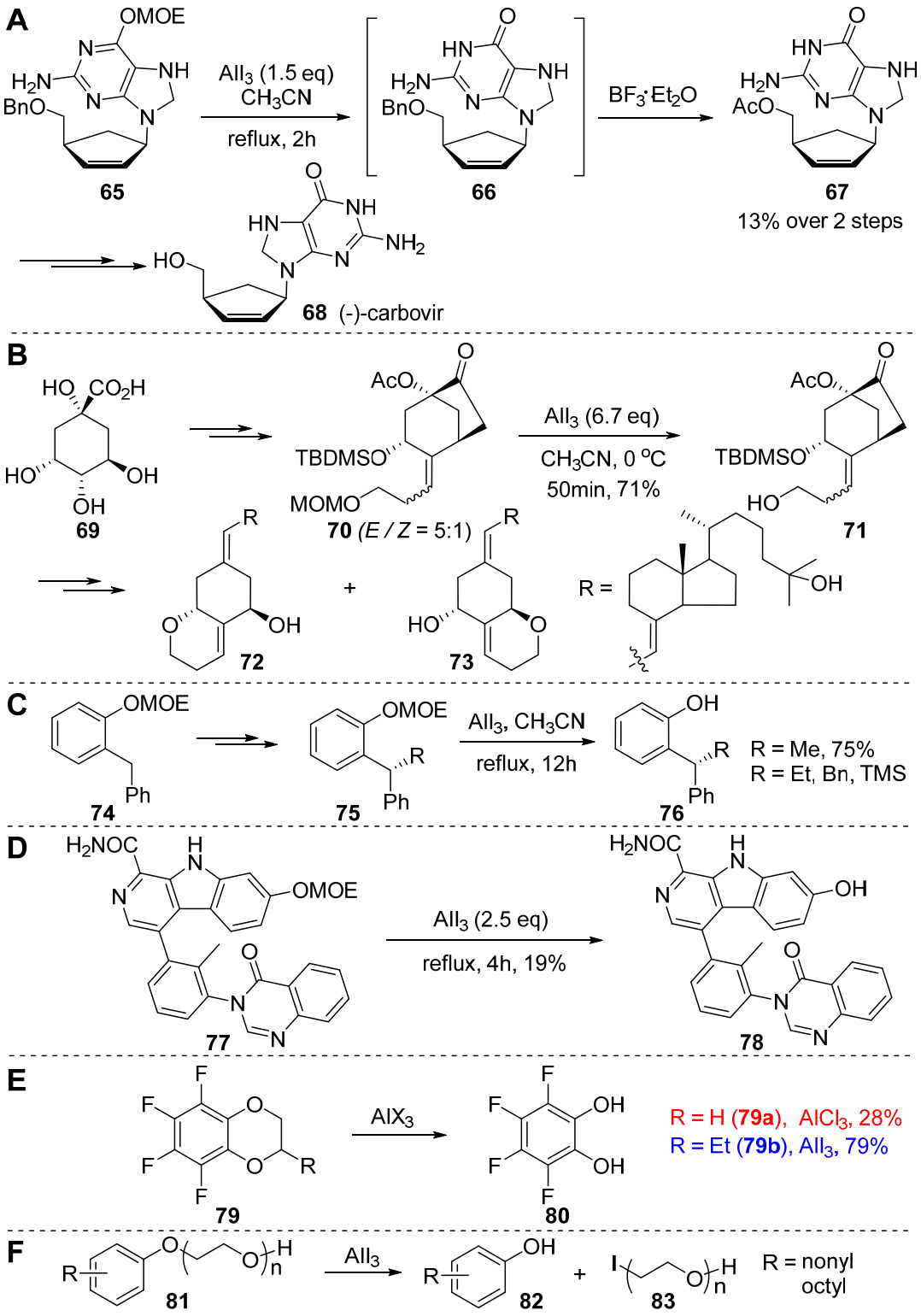
The oxophilic character of AlI_3 could be tuned by thiophenol (PhSH). Thiols and sulfides alone are effective for dealkylation of alkyl aryl ethers.[49] Reagent combinations of aluminum halides-thiols are useful for demethylation of aliphatic and aromatic methyl ethers.[50] In a concise route to gefitinib (**61**), 6,7-dimethoxyquinazoline (**59**) was regioselectively demethylated to give **60** by the

action of PhSH and AlI_3 in 84% yield (Scheme 4B).[51] The method could not be extended to aldehydes due to the formation of hemithioacetals.[52]

Selectivive deprotection of **62** was accomplished with AlI_3 (Scheme 4C). Complicated temperature effects were observed when aluminum trichloride ($AlCl_3$) was used. The desired phenol **64** was not obtained below 50 ^oC. Above 65 ^oC, demethylation proceeded in poor yields. The deprotection was improved by the use of AlI_3 that afforded **64** in 56% yield after stirring overnight at room temperature.[53]

3.6 Removal of methoxymethyl, methoxyethyl and other phenolic protecting groups

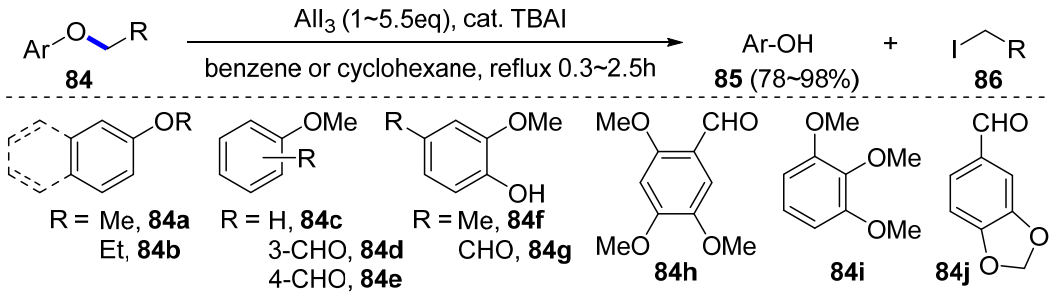
AlI_3 is suitable for removal of aliphatic protecting groups from ethers to release (phenolic) hydroxyl groups (Scheme 5). (I) A synthetic route to (-)-carbovir (**68**) involved the cleavage of methoxyethyl (MOE) group from **65** (Scheme 5A). Deprotection by Brønsted acids was unsuccessful.[54] After treating **65** with AlI_3 in acetonitrile for 2 hours under reflux, the deprotection was complete. The purification, however, was unsatisfactory due to aluminum salt contamination. Hence the intermediate was used directly in the next step, and the yield was 13% over two steps. (II) 1α,25-Dihydroxy-19-norvitamin D_3 is a functional vitamin D metabolite. Syntheses of two analogues (**72** and **73**) of this metabolite involved the removal of a methoxymethyl (MOM) group from intermediate **70** (Scheme 5B). Attempts to furnish the deprotection using hydrogen chloride/isopropanol, trifluoroacetic acid/dichloromethane (DCM), lithium boron tetrafluoride/acetonitrile, trimethylsilyl bromide/DCM and trityl boron tetrafluoride/DCM had failed; butylthiol/magnesium bromide afforded **71** in low yield. The best reagent selected for the deprotection was AlI_3. The reaction proceeded smoothly under a mild condition and afforded **71** in 71% yield. Biological activity of the analogues were 2~3 orders or magnitude lower in *vitro* then 1α,25-dihydroxy-19-norvitamin D_3.[55-57] (III) MOE was attached to a diarylmethane scaffold (**74**) for additional coordinations to reactive lithium species and hence for improved enantiomeric excess (**75**) in asymmetric alkylation (Scheme 5C). The protecting group was removed by AlI_3 to afford (*R*)-2-(1-phenylethyl)phenol (**76**) in 75% yield. Products with other substituents (benzyl, ethyl, and trimethylsilyl) were prepared by the method in acceptable yields for determination of chiral configurations.[58] (IV) AlI_3 was applied in synthesis of carboxamide **78**, a useful kinase inhibitor, by removal of MOE (Scheme 5D).[59] The deprotection afforded **78** in 19% yield after refluxing a mixture of **77** and AlI_3 (2.5eq) in acetonitrile for 4 hours. (V) In a recent synthesis of **80**, tetrafluorobenzodioxin (**79a**) was deprotected by $AlCl_3$ to afford tetrafluorocatechol in 28% yield.[60] A markedly improved method consisted of treating dioxin **79b** with AlI_3 to furnish the catechol in 79% yield (Scheme 5E).[61] (VI) The regioselective preference of AlI_3 for cleaving alkyl aryl ethers has been applied in evaluation of nonylphenol ethoxylates ($NPEO_n$) and octylphenol ethoxylates ($OPEO_n$) in textiles and leathers (Scheme 5F). These ethoxylates are non-ionic surfactants prohibited for domestic use. After cleaving the ethers (**81**), the resultant nonylphenol and octylphenol (**82**) could be quantitatively evaluated by GC-MS.[62-67]



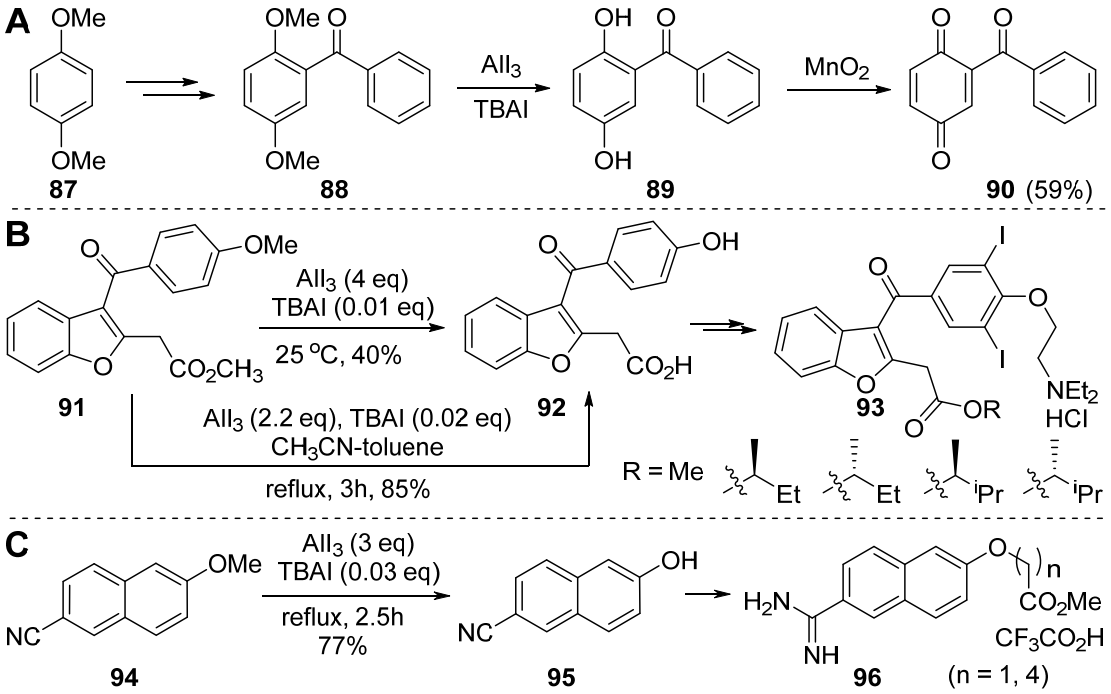
Scheme 5. Removal of phenolic protecting groups. A: (-)-Carbovir intermediate; B: 1α,25-dihydroxy-19-norvitamin D_3 analogue intermediate; C: chiral benzylphenol; D: kinase inhibitor carboline carboxamide; E: 3,4,5,6-tetrafluorocatechol; F: nonylphenol and octylphenol.

3.7 Application of AlI_3-TBAI in exhaustive demethylation

Anderson independently developed an efficient method for deprotection of phenolic alkyl ethers (**84**) by using catalytic tetrabutylammonium iodide (TBAI) as a promoter (Scheme 6). By contrast, TBAI is commonly used in Finkelstein reaction[68] for halide exchange, and the alkyl iodides generated therein can be used to accelerate etherification. The demethylation conversions were complete after stirring for 3 hours in benzene or cyclohexane and afforded phenols in moderate to high yields.[69,70] Extension of the substrate to 3,4,5-trimethoxybenzaldehyde and isovanillin were less satisfactory for either low isolated yields or partial deprotection. Diphenyl ether remained intact under the condition.

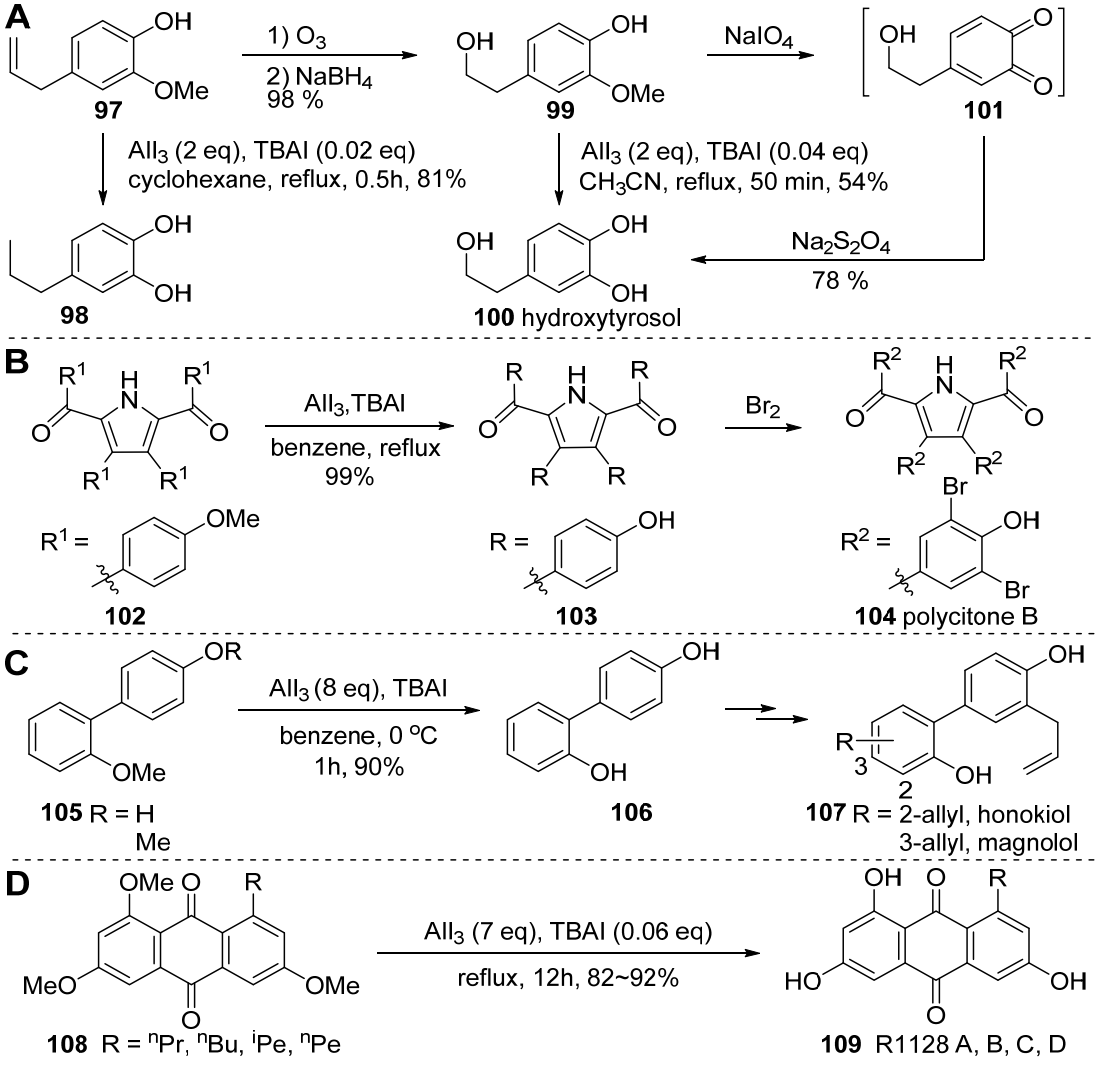


Scheme 6. AlI_3-TBAI induced cleavage of alkyl aryl ethers.



Scheme 7. Syntheses of several intermediates. A: 2-Benzoylhydroquinone; B: pharmaceutical intermediate; C: urokinase inhibitor intermediate 7-cyanon-2-naphthol.

Anderson's method was used in syntheses of several intermediates such as **89**,[71] **92**[72-74] and **95**,[75] see Scheme 8. **89** can be oxidized to benzoquinone **90** by active manganese dioxide (MnO_2) (Scheme 7A). Benzofuran **92** is an intermediate to five pharmaceutical agents (**93**) useful in treating cardiac arrhythmia and congestive heart failure (Scheme 7B). Naphthol **95** is an intermediate to two urokinase inhibitors (**96**), see Scheme 7C.

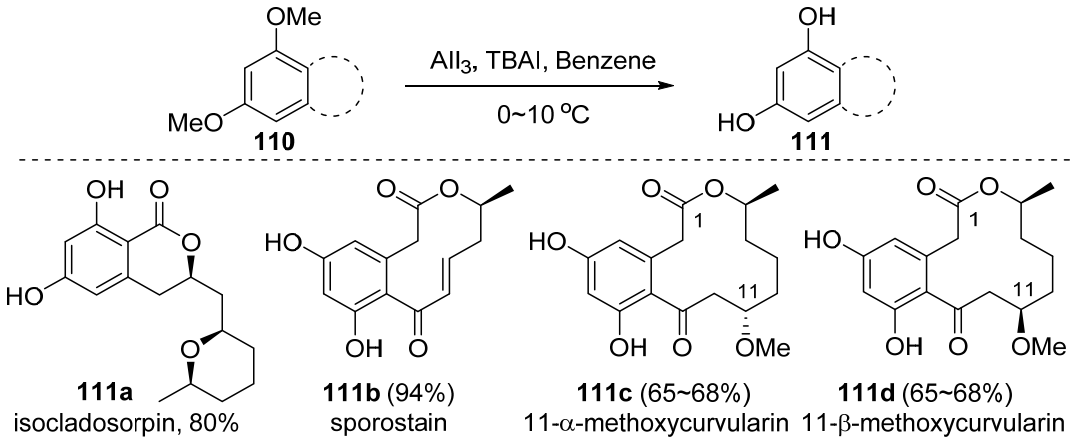


Scheme 8. Syntheses of natural products. A: Hydroxytyrosol; B: polycitone B intermediate; C: honokiol and magnolol intermediate; D: R1128A, B, C, and D.

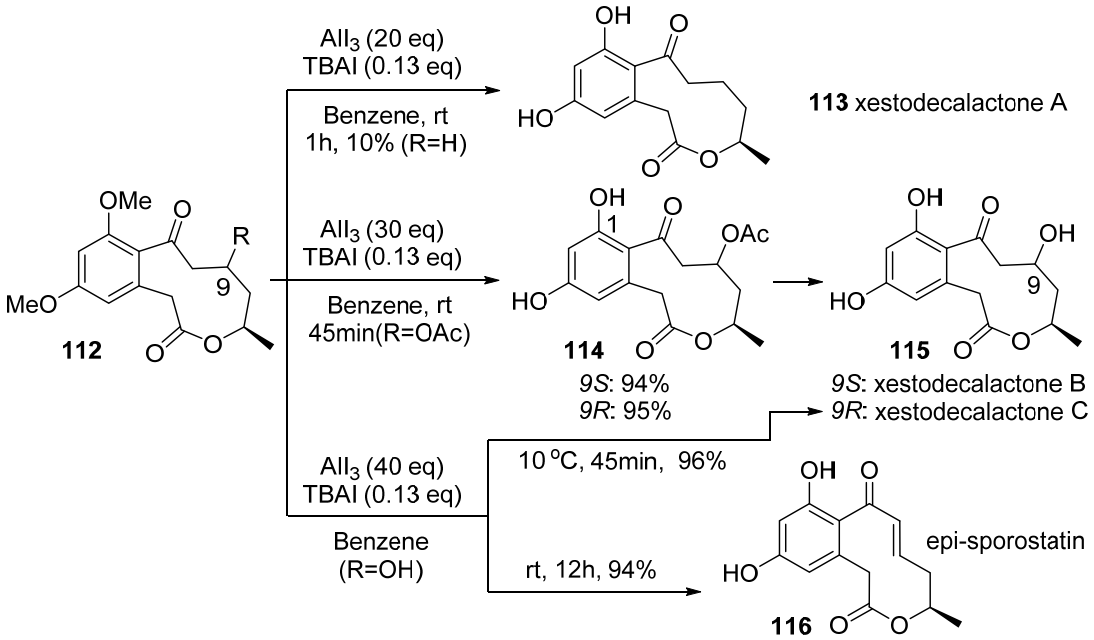
The AlI_3-TBAI reagent combination was applied in synthesis of several natural products (Scheme 8). Hydroxytyrosol (**100**), a natural antioxidant, was obtained by demethylation of **99** with AlI_3-TBAI in 54% yield, see Scheme 8A. Surprisingly, the allylic group para to phenolic hydroxyl group was reduced to propyl group when eugenol (**97**) was demethylated under the condition, and furnished **98** in 81% yield.[76] Polycitone B (**104,** see Scheme 8B),[77] biaryl plural neolignan honokiol and magnolol (**107**, see scheme 8C),[78] and non-steroidal Estrogen receptor antagonists R1128 A~D

(**109**, see Scheme 8D)[79] were accomplished similarly in moderate to high yields. It is noteworthy that deprotection of **108** with BBr_3 resulted in partially demethylated mixtures; besides, the 9,10-anthraquinone skeleton was not affected by AlI_3.

The AlI_3-TBAI combination has also been applied in syntheses of other natural products including isocladosorpin (**111a**),[80] sporostain (**111b**),[81] 11-*α*-methoxycurvularin (**111c**) and 11-*β*-methoxycurvularin (**111d**)[82,83] as well as xestodecalactone A (**113**),[84] B and C (**115**),[85] see Scheme 9 and Scheme 10. A deoxydehydration product (**116**) was obtained from **112** at ambient temperature in 94% yield during the synthesis of xestodecalactone C.[86] The naturally occurring sporostain (**111b**) is an inhibitor of cyclic adenosine 3',5'-monophosphate phosphodiesterase (cAMP-PDE).

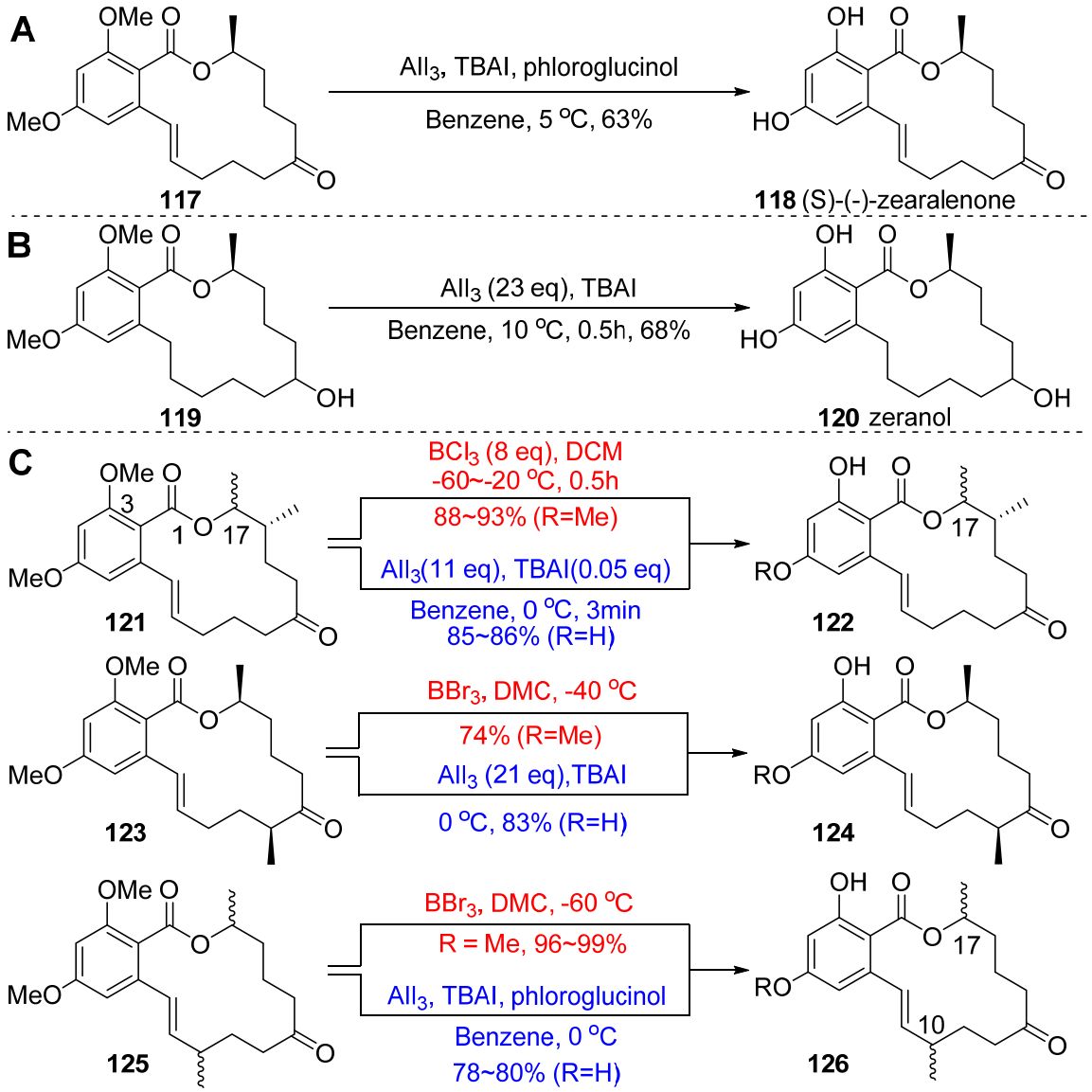


Scheme 9. Syntheses of naturally occurring isocladosorpin, sporostain, 11-α-methoxycurvularin and 11-β-methoxycurvularin *via* exhaustive demethylation.



Scheme 10. Syntheses of xestodecalactone A, B, C and epi-sporostatin.

Lipoxygenase inhibitor (*S*)-(-)-zearalenone (**118**, Scheme 11A)[87], zeranol (**120**, Scheme 11B)[88,89] and several zearalenone analogues (**122**, **124** and **126**, scheme 11C) were prepared by exhaustive demethylation of corresponding resorcinol dimethyl ethers (**121**, **123**, **125**). Regioselective cleavage of the C_3-phenyl methyl ethers was achieved alternatively with BBr_3 or BCl_3 in high yields. Exhaustive deprotection of **121**, **123** and **125** was accomplished by BCl_3-BBr_3 combination,[90,91] and by AlI_3-TBAI.[92-94] Phloroglucinol, a widely used antioxidant, was sacrificed herein to scavenge HI in syntheses of **118** and **126**.



Scheme 11. Syntheses of zearalenone analogues. A: (*S*)-(-)-zearalenone; B: zeranol; C: zearalenone analogues.

4. Deoxygenation and Deoxydehydration

4.1 Deoxygenation of oxiranes

A variety of reagents have been used in deoxygenation of oxiranes to prepare olefins in moderate to low yields and poor retention of stereochemistry.[95] Inspired by the succes of AlI_3 in ether cleavage, Barua and Sarmah extended the reagent to oxiranes (**127a~127g**), see Figure 2. The conversions were complete within 1 hour in moderate to high yields depending on the substrate.[96] For example, treatment of **129** with AlI_3 afforded **130** in 70% yield after refluxing in acetonitrile for 1 hour. Carvone (**131**) was accessed *via* deoxygenation of **130** with AlI_3 in 90% yield after refluxing for 8 hours in acetonitrile. **131** was alternatively prepared by deoxygenation of the sterically less hindered **132** in 87% yield within 0.5 hour (Scheme 12).[96]

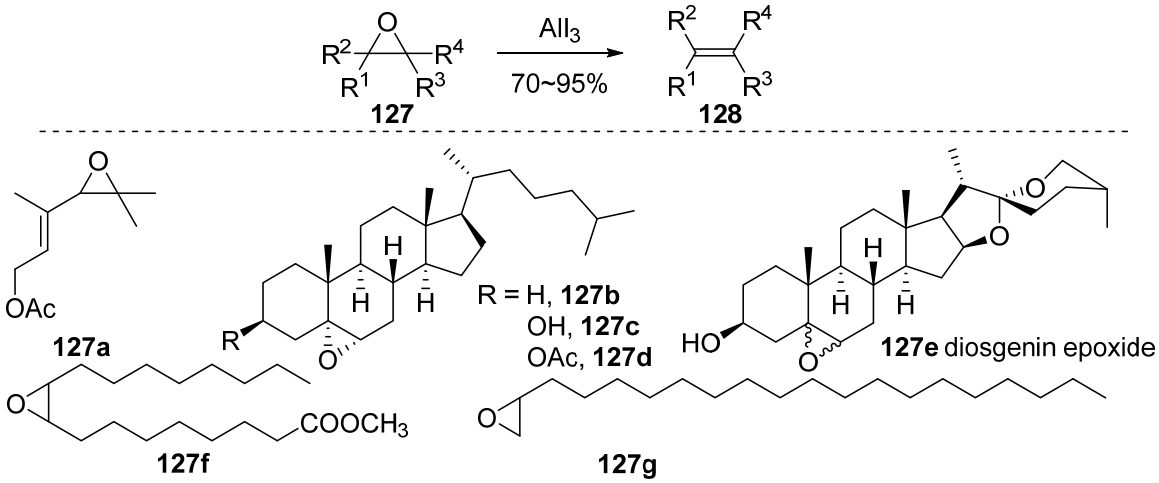
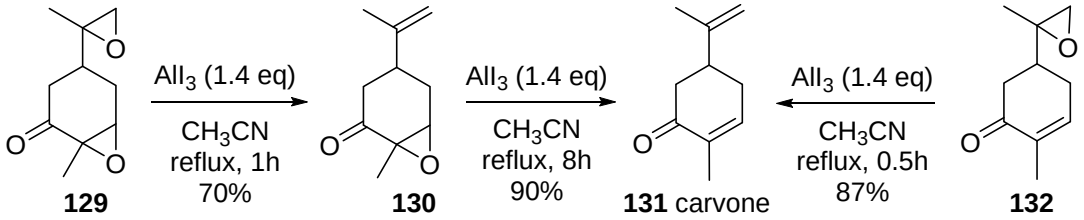


Figure 2. Deoxygenation of oxiranes.



Scheme 12. Synthesis of carvone by deoxygenation.

The mechanism for AlI_3 induced deoxygenation was well illustrated by the study of trichlorooxirane **133** (Figure 3A).[97] Trichloroolefin **136** was obtained in 91% yield after the reaction mixture of AlI_3 and **133** (conducted at room temperature) was loaded on column in place of radial chromatography during workup at 30~32 ^oC for 20 hours, whereas *cis*-iodohydrin **138** was isolated in 50% yield along with **136** (25%) when the column was stored at 35 ^oC for 24 hours. When the reaction was quenched 15 minutes after start, *anti*-iodohydrin **137** was isolated in 95% yield as colorless needles. Apparently *trans*-iodohydrin **135** was involved in the reaction. At lower

temperature, the reaction proceeded through path b with an iodide anion attacking the C-I bond leading to **136**. Accordingly, **138** was accessed at higher temperature *via* path a. **137** was further converted to **133** in basic conditions in 74% yield, and to **138** in 92% yield by treating with either I^- or AlI_3. It is worth noting that deoxygenation of oxarine **139** afforded olefin **140** in 78% yield after stirring for 20 hours with AlI_3; accordingly **140** was oxidized to **139** with 3-chloroperoxybenzoic acid (*m*-CPBA) in high yield, see Figure 3B.

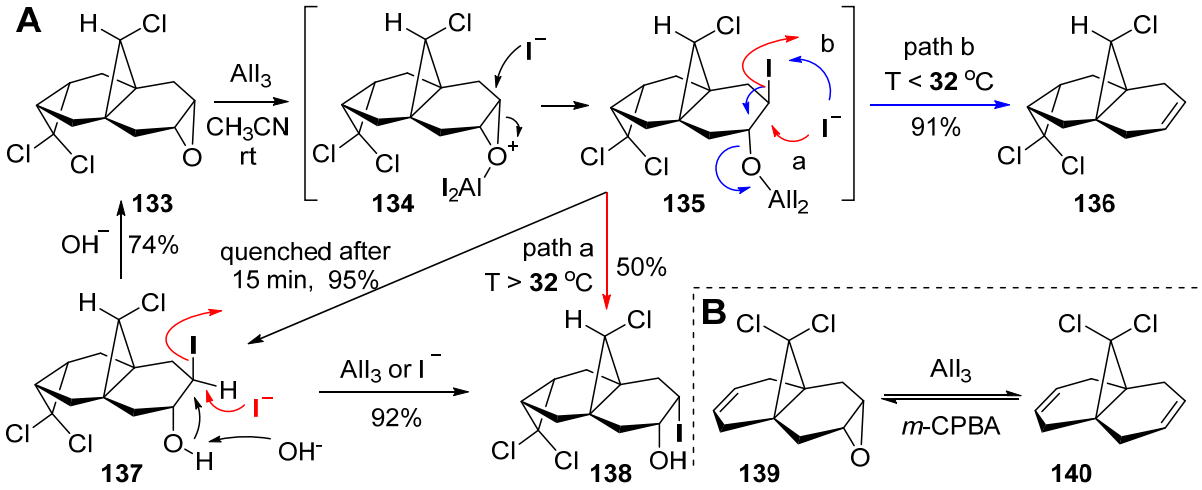


Figure 3. Deoxygenation of oxiranes. A: deoxygenation mechanism; B: reversible epoxidation and deoxygenation.

A class of 1,3-halohydrins (**142**) were prepared through aluminum halide induced ring opening of oxiranes. Treating a mixture of stereoisomers of **141** (exo/endo=15:1) with AlX_3 (X=Cl, Br, I) in DCM or CS_2 (Figure 4), followed by carbocation rearrangements (**143**) and halide transfer (**144**) afforded **142** in 79~84% yields.[98]

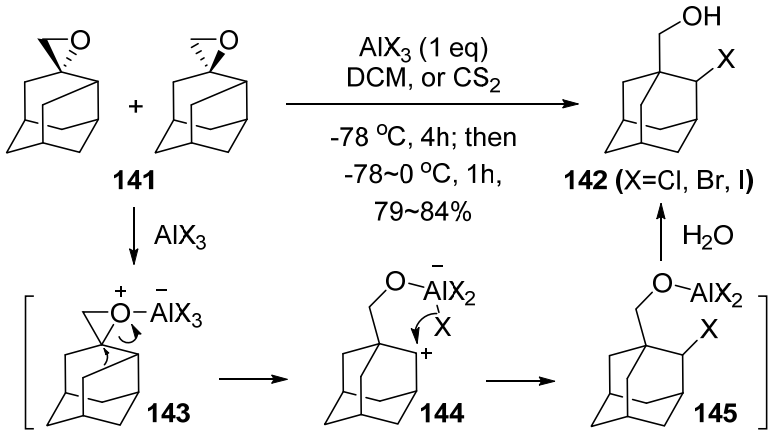


Figure 4. Synthesis of 2-halo-l-(hydroxymethyl)adamantine.

Ring-opening of oxirane by AlI_3 was regioselective in the case of 1,2-decane epoxide. The reaction was complete after stirring for 2 hours in heptane at room temperature, and afforded 1-iodo-2-decanol exclusively. The high regioselectivity was attributed to the larger volume size and higher nucleophilicity of I^-; thus I^- attacked the oxirane from the sterically more accessible terminal site (**148**).[99] Though depicted in stepwise sequences, the reaction may proceed in a concerted manner *via* a four-membered transition state (Figure 5).

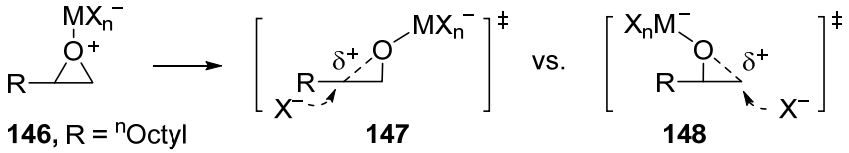
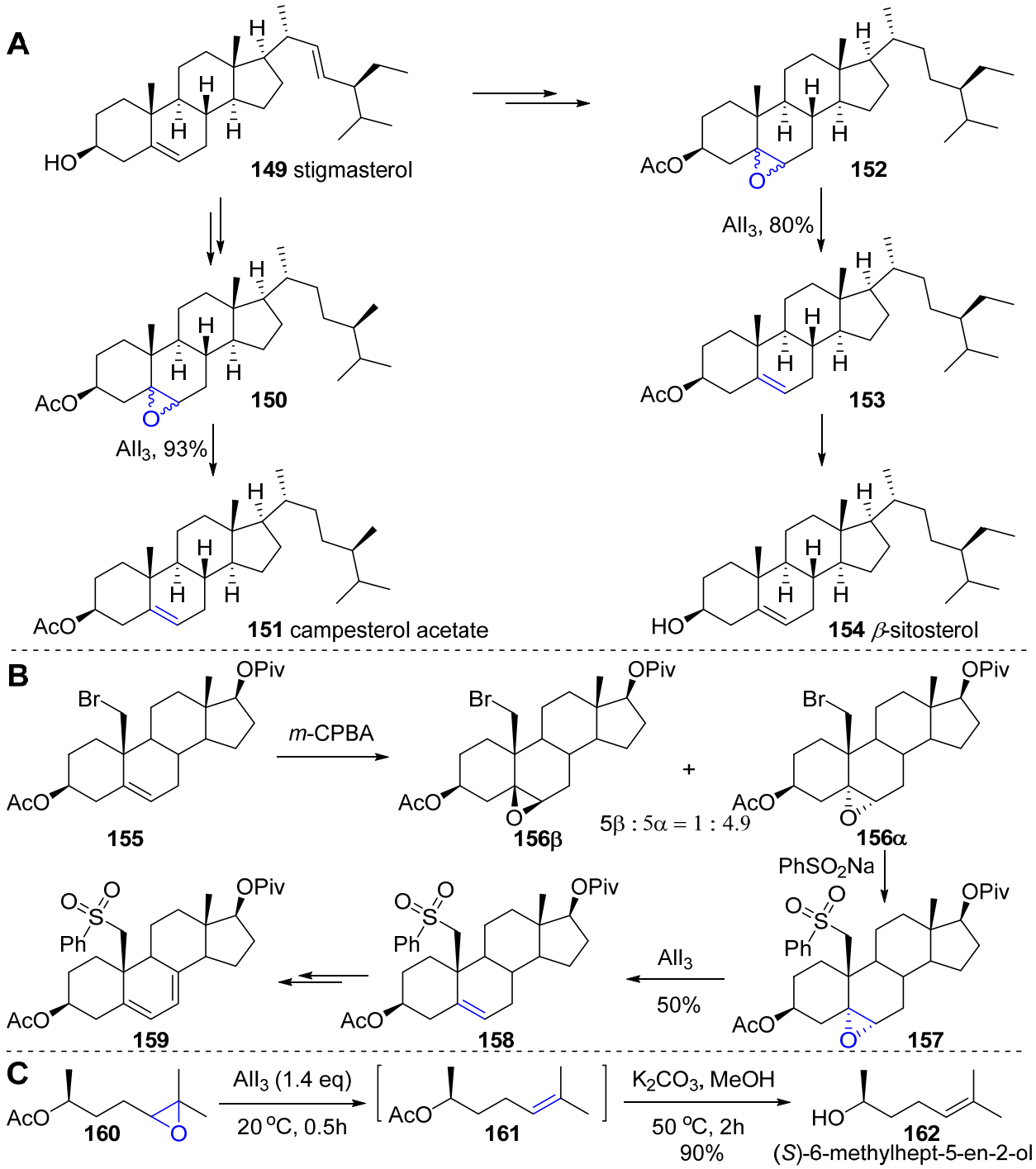


Figure 5. Regioselectivity analysis.

Several natural products were prepared by AlI_3 induced deoxygenation of oxiranes (Scheme 13). An epoxidation-deoxygenation protocol had been applied in syntheses of campesterol acetate (**151**)[100] and β-sitosterol (**154**)[101] commenced from stigmaserol (**149**), see Scheme 13A. Similarly, a 19-phenylsulfonyl provitamin D analogue (**159**) was accomplished. Epoxidation of **155** afforded a mixture of epoxides **156α** and **156β** in a ratio of 4.9:1. **156β** was unreactive under the deoxygenation condition. Successive deoxygenation of **157** afforded **158** in 50% yield (Scheme 13B).[102] (*S*)-6-Methylhept-5-en-2-ol (**162**), an aggregation hormone of gnathotrichus sulcatus, was accessed by deoxygenation of **160** followed by saponification of **161** in 90% yield over two steps (Scheme 13C).[103]



Scheme 13. Syntheses of natural products or intermediates *via* AlI_3 induced deoxygenation of oxiranes. A: β-Sitosterol and campesterol acetate; B: 19-phenylsulfonyl provitamin D analogue; C: (*S*)-6-methylhept-5-en-2-ol.

4.2 Deoxydehydration of diols

Deoxydehydration (DODH) of diols involves the formation of iodohydrins as intermediates, and and affords olefins *via* E_2 elimination. A plausible mechanism is depicted in Figure 6. Treatment of

diol **163** with AlI_3 afforded iodohydrin **165**, **165** then undergone elimination to give olefin **168**. Several olefins (**170** and **173**) were prepared by this method (Scheme 14).[104] It is noteworthy that both c*is*-diol (**169**) and *trans*-diol (**17**) afforded the same olefin (**170**), indicating that the conversion proceeded in a stepwise manner (Scheme 14).

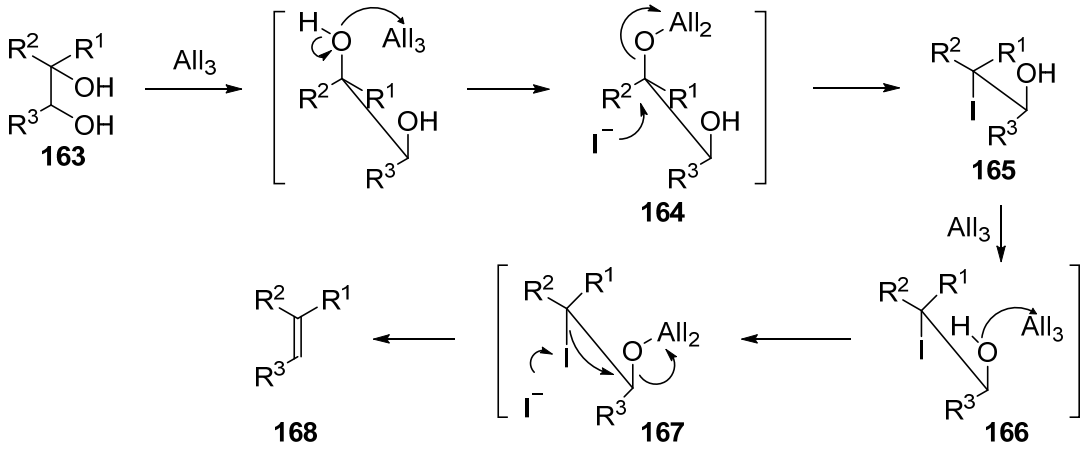
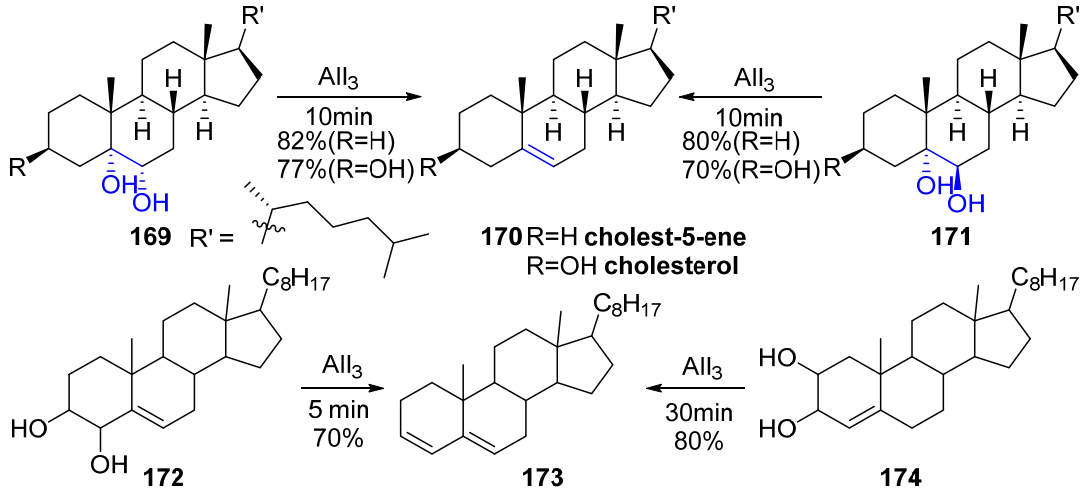
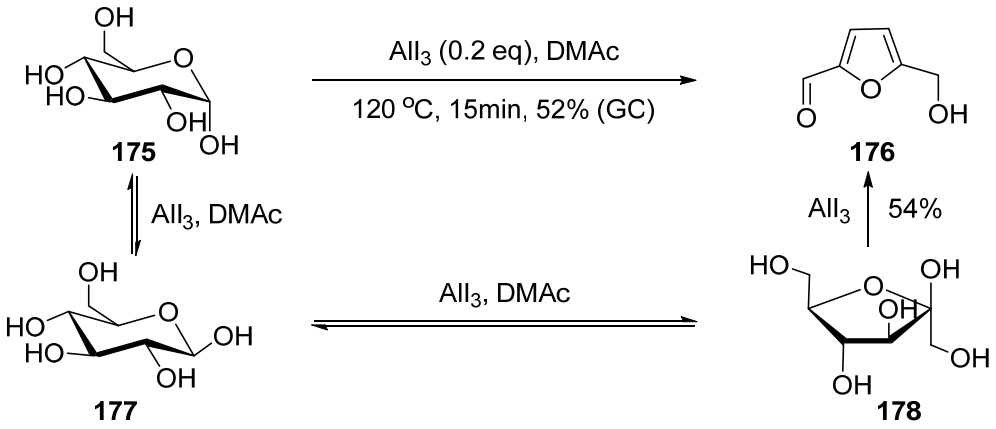


Figure 6. A plausible mechanism for the deoxydehydration of diols.



Scheme 14. Deoxydehydration of diols.

Recently, 5-hydroxymethylfurfural (HMF, **176**), a biomass-derived precursor for biofuel, was accessed through deoxydehydration of α-glucopyranose (**175**) with AlI_3 in dimethylacetamide (DMAc). The conversion involved the α/β isomerization of glucopyranose (**177**), and the following dehydration of **178** furnished HMF in 54% yield (Scheme 15).[105]



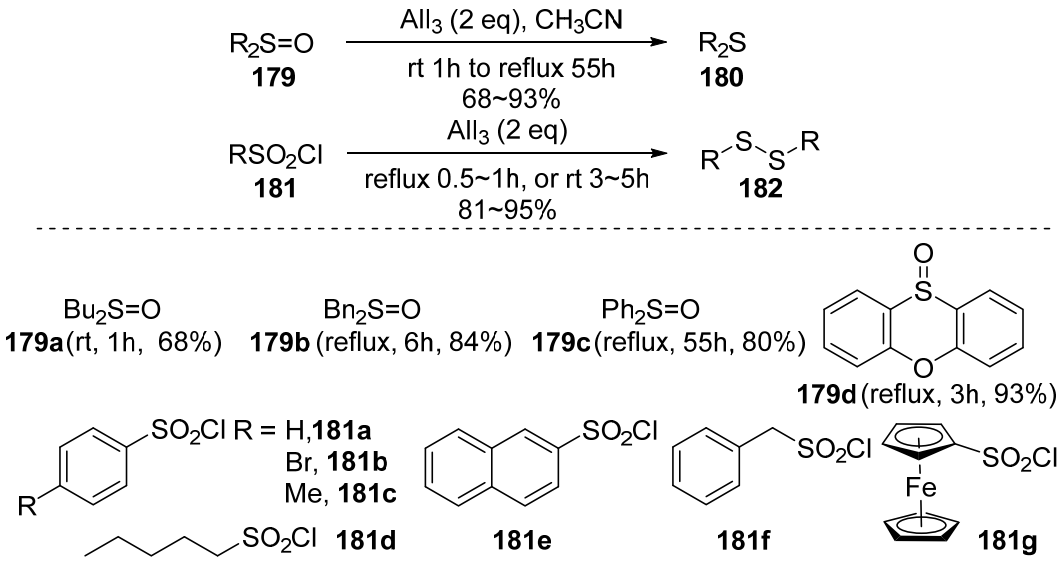
Scheme 15. Transformation of glucose to furfural *via* AlI_3 catalyzed dehydrodeoxygenation.

4.3 Deoxygenation of sulfoxides and sulfonyl chlorides

Sulfoxides and sulfonyl chlorides can be converted into corresponding sulfides and disulfides by sodium iodide (NaI),[106] potassium iodide (KI)[107] or TMSI.[108] AlI_3 is also effective for these transformations. Alkyl and aryl sulfides such as dibutyl sulfide (**180a**), dibenzyl sulfide (**180b**), and diphenyl sulfide (**180c**) were prepared by reduction of sulfoxides (**179a**~**189c**) with AlI_3. The reduction was much slower for aryl sulfoxide (**179c**) compared to alkyl sulfoxide (**179a**). Similarly, reduction of phenoxathiine 10-oxide (**179d**) afforded phenoxathiine (**180d**), see Scheme 16.[109]

Reduction of sulfonyl chlorides (**181**) were complete typically in about 1 hour under reflux or 3~5 hours at room temperature, and afforded disulfides in high yields (Scheme 16).[110] The method was applied in the synthesis of diferrocenyl disulfide from ferrocenesulfonyl chloride (**171g**).[111,112]

A plausible mechanism for the reduction is shown in figure 7. AlI_3 served as an oxophilic agent as well as an I^- source during the transformations. The oxophilic character of AlI_3 induced the formation of **184** and **186**. Cleavage of the sulfinyl bond followed by intramolecular attack of S-I bond iodide *via* an envelope transition state furnished **180**. Thiosulfonic S-ester (RSO_2-SR, **190**) was involved during the reduction of sulfonyl chlorides (**181**); **190** can be further reduced to disulfides (**182**) by AlI_3.[113] HCl-KI reagent system is also effective.[114]



Scheme 16. Deoxygenation of sulfoxides and sulfonyl chlorides.

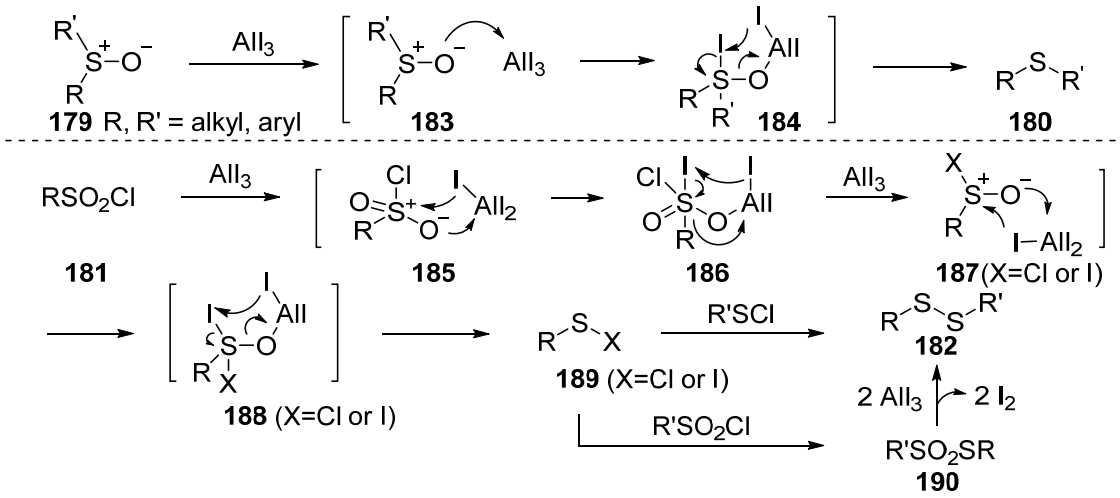


Figure 7. Plausible mechanisms for the deoxygenation of sulfoxides and sulfonyl chlorides.

4.4 Deoxydehydration of oximes

Oximes (**191**) can be reduced to nitriles (**193**) by AlI_3 in moderate to high yields in acetonitrile under reflux for several hours (Figure 8A). The method was extended to substituted aliphatic oximes and arylaldoximes.[115] Reduction of aryl ketoximes (**194**), such as benzophenone oxime and acetophenone oxime, afforded the corresponding anilides (**198**) in moderate yields *via* Beckmann rearrangement (conversions from **195** to **197**), see Figure 8B. Aliphatic ketoximes remained unchanged under the condition.

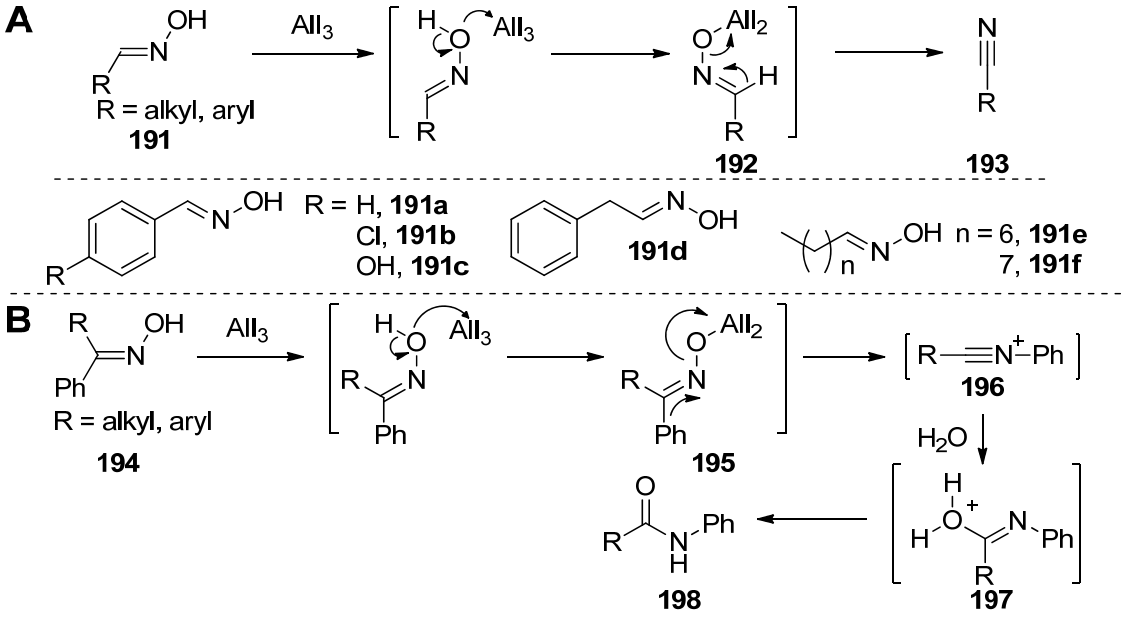


Figure 8. Deoxydehydration of *N*-oxides. A: Scope of substrates and mechanism of reaction; B: AlI_3 induced Beckmann rearrangement of aryl ketoximes.

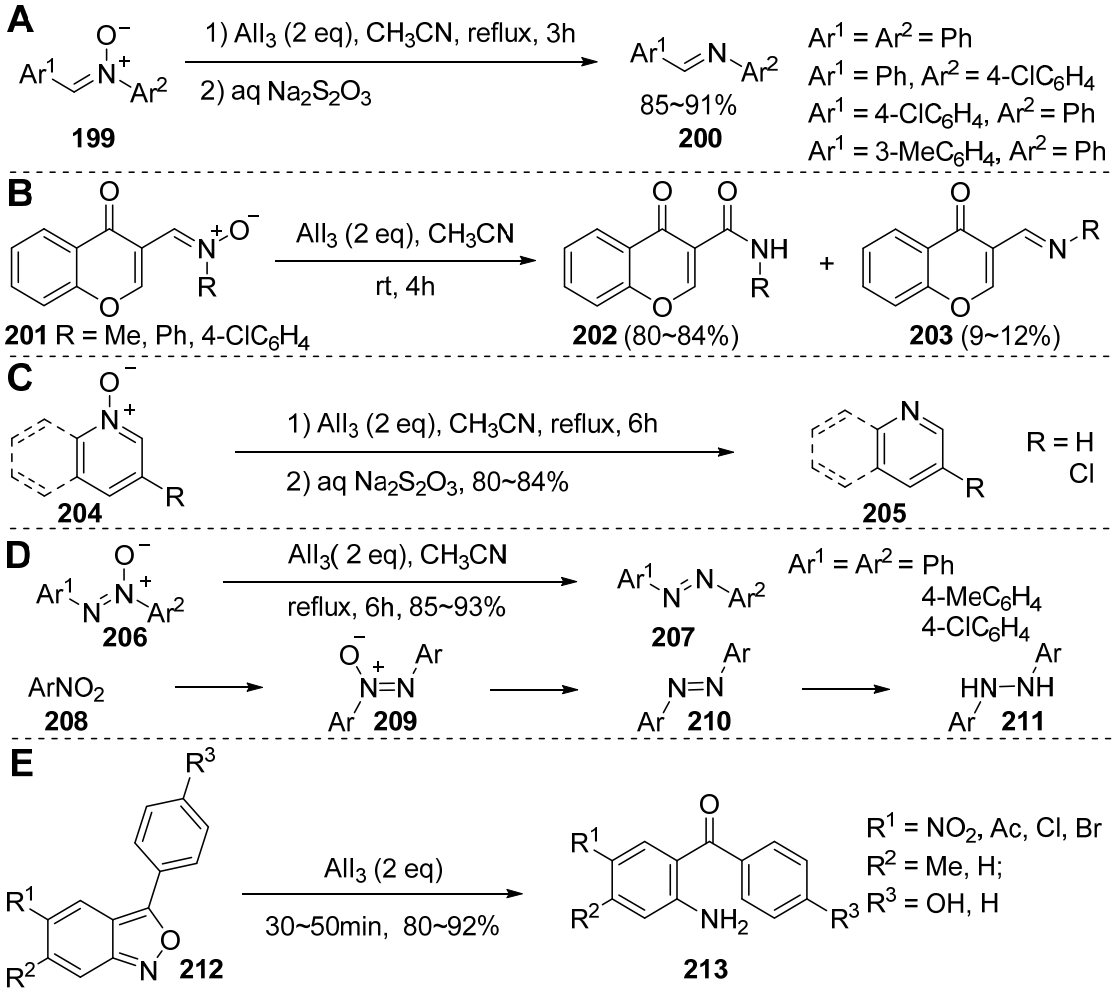
4.5 Deoxygenation of *N*-arylnitrones, azoxyarenes and *N*-heteroarene *N*-oxides

Selective deoxygenation of *N*-arylnitrones (**199**) to *N*-arylimines (**200**) were achieved with AlI_3 in moderate to high yields (Scheme 17A).[116] The imine turned to be a by-product (**203**) when **201** was deoxygenated by the method (Scheme 17B). The conversion was complete after 4 hours of stirring at room temperature in acetonitrile.[117] The major product **202** is a promising lead for selective A_{2B} adenosine receptor ($A_{2B}AR$) antagonist.[118] Ruthenium trichloride is also suitable for deoxygenation of *N*-arylnitrones.[119]

N-heteroarenes (**205**) can be achieved *via* deoxygenation of the corresponding *N*-heteroarene *N*-oxides (**204**) in high yields (Scheme 17C).[116]

Azobenzenes (**207**) are widely used as dyes in industry, and have potent applications in molecular devices.[120-121] Commonly used reagents for preparation of **207** *via* deoxygenation of azoxybenzenes (**206**) include indium trichloride, zinc triflate, and copper(II) triflate.[122] AlI_3 was developed as an efficient deoxygenation agent[116] for syntheses of symmetrical azobenzenes in high yields (Scheme 17D).[123]

2-Aminobenzophenones (**213**), a class of synthetic intermediates for 1,4-benzodiazepines,[124-125] were prepared by Lewis acid catalyzed ring opening of 2,1-benzisoxazoles (**212**).[126] The conversions were complete within 1 hour in the presence of AlI_3 and afforded **213** in high yields (Scheme 17E).[127] The deoxygenationcan can be catalyzed more efficiently by TMSI[128] at room temperature in almost quantitative yields.[129]



Scheme 17. AlI_3 induced deoxygenation of *N*-oxides. A: *N*-arylnitrones; B: chromon-3-yl nitrone; C: *N*-heteroarene *N*-oxides; D: azoxybenzenes; E: preparation of 2-aminobenzophenone from 2,1-benzisoxazole.

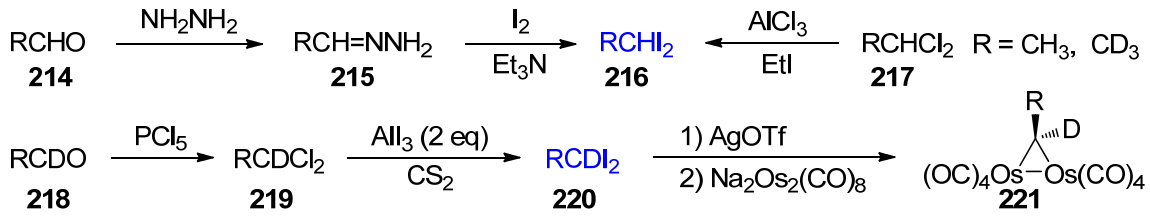
5 Iodination

5.1 Halide exchange reaction

The halide exchange between AlI_3 and alkyl halides is known as the Gustavson method.[130] For example, ethyl bromide underwent iodination within 5 minutes;[6b] and saturated $C_{1\text{-}4}$ alkyl iodides were prepared from aliphatic chlorides.[131] A more practical method for preparation of alkyl iodides is by the use of NaI or TBAI *via* Finkelstein reaction.[68]

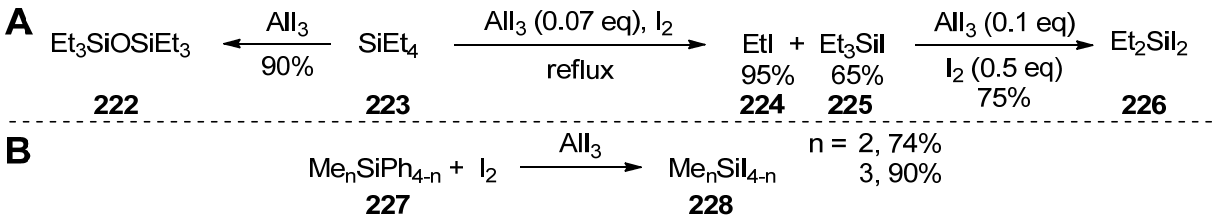
Ethylidine diiodide (**216**), a reagent suitable for the preparation of methylpropane, was made in 30% yield by iodination of Schiff base **215** (synthesized from acetaldehyde **214** and hydrazine). **216** was alternatively prepared through $AlCl_3$ catalyzed halide exchange between ethylidine dichloride (**217**) and ethyl iodide in 60% yield (Scheme 18).[132] Deuterated ethylidine diiodide (**220**) was

prepared in a similar manner by chlorination of deuterated acetaldehyde (**218**) with phosphorus pentachloride, followed by iodination with AlI_3 (2 equivalents). The agent could be further transformed into d^1 (R=CH_3) and d^4 (R=CD_3) isotopologues of (μ_2-$CHCH_3$)-$Os_2(CO)_8$ (**221**) for study of ethylidine surface species on metal surfaces.[133]



Scheme 18. Preparation of ethylidine diiodides *via* AlI_3 catalyzed halogen exchange reactions.

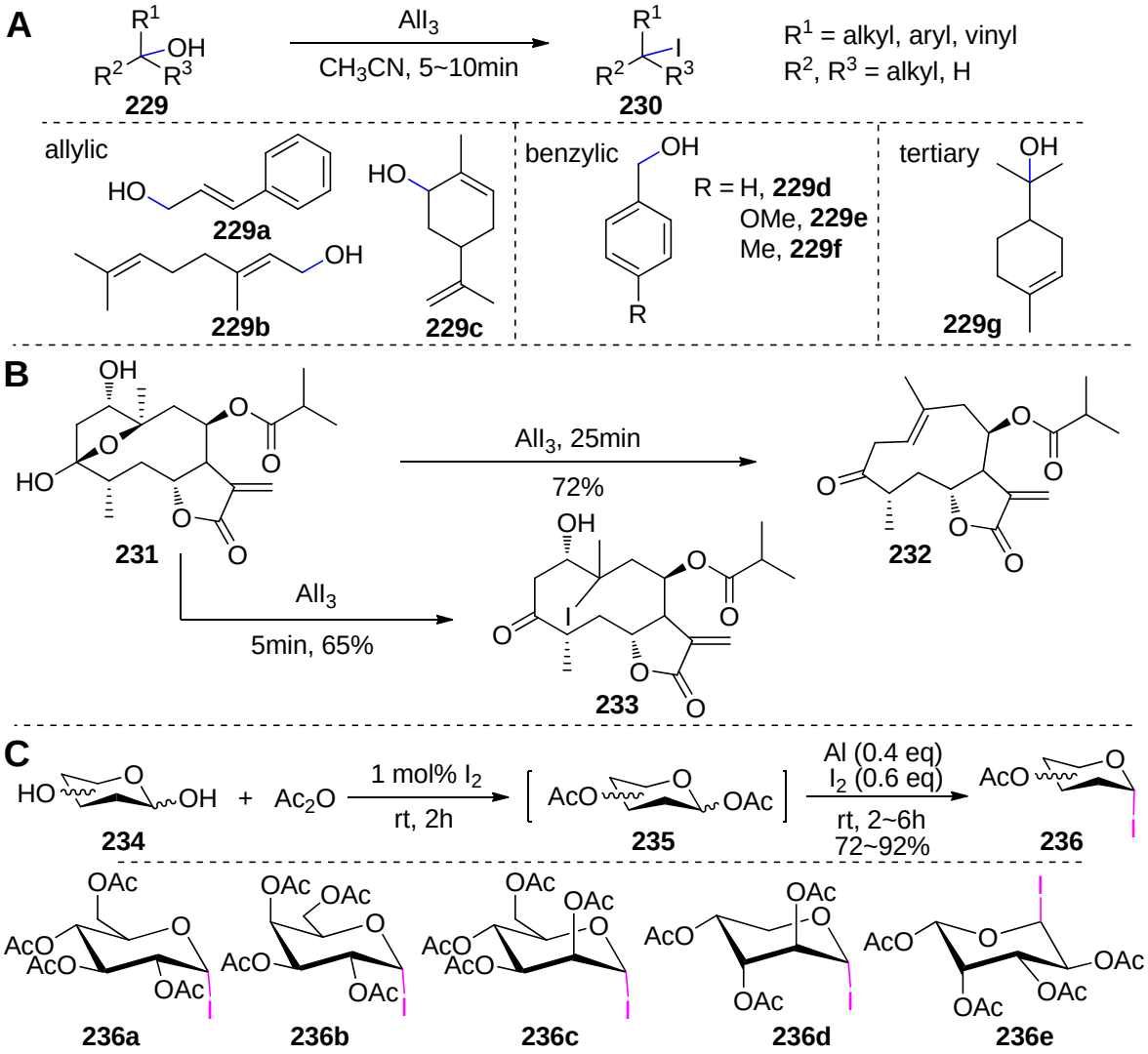
Ethyl and phenyl groups attached to silicon atom can be replaced by iodine (Scheme 19). Triethyl iodosilane (**225**) and diethyldiiodosilane (**226**) can be prepared from tetraethylsilane (**223**) and iodine in the presence of catalytic AlI_3 in moderate yields (Scheme 19A). AlI_3 served as a catalyst in phenyl-iodine exchange reactions between iodine and silanes containing phenyl groups such as Ph_2SiMe_2 or $PhSiMe_3$ (**227**), to give related iodosilanes (**228**), see Scheme 19B.[134,135] This reaction is suitable for the synthesis of cyclic polydiiodosilanes $(I_2Si)_n$, n=4~6.[136,137]



Scheme 19. AlI_3 catalyzed Iodine-halogen/phenyl exchange reactions.

5.2 Iodination of allylic, benzylic, and tertiary alcohols

Allyl, benzyl and tert-alkyl alcohols (**229**) were transformed into corresponding iodides (**230**) by AlI_3 in 5~10 minutes at room temperature in high yields (Scheme 20A).[104] Intramolecular hemiacetal **231** was converted very quickly into iodoketone **233**, whereas prolonged stirring led to olefin **232** (Scheme 20B).[104]



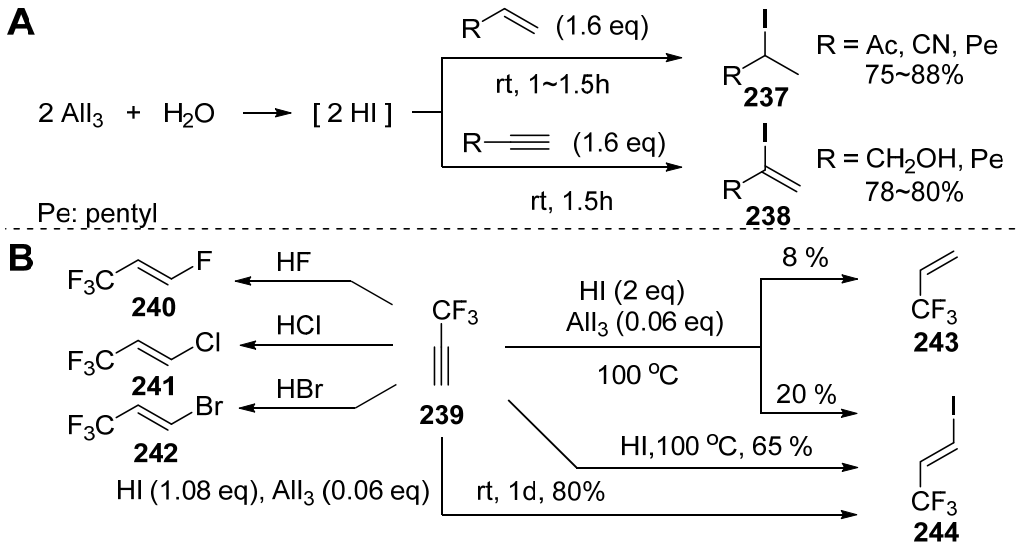
Scheme 20. Iodination of tertiary, benzoyl and allyl alcohols. A: Scope of substrates; B: iodination of an intramolecular hemiacetal; C: one-pot two-step preparation of O-peracetylated glycosol iodides.

Per-*O*-acetylated α-glycosyl iodides (**236**), a class of anomeric intermediates useful for preparation of glycosides,[138] were synthesized from unprotected reducing sugars (**234**) like *D*-glucose, *D*-galactose, *D*-mannose, *D*-arabinose, and *L*-fucose following a one-pot two-step sequence in moderate to high yields (Scheme 20C).[139,140] Reducing sugars (**234**) were acetylated (**235**) by acetic anhydride in the presence of catalytic iodine at room temperature for 2 hours, and the resulting per-*O*-acetylated sugars were stirred with aluminum powder and iodine at ambient temperature to furnish per-*O*-acetylated glycosyl iodides (**236**). Other Lewis acids such as indium triiodide and cerium triiodide were also effective in preparation of such intermediates.[141]

5.3 Hydroiodination of alkenes and alkynes

Hydroiodination of alkenes or alkynes by HI afforded alkyl or alkenyl iodides. Although hydroiodic

acid could be used directly,[142] HI is generally prepared *in situ* for yield consideration. HI generated by hydrolysis of AlI_3 reacted smoothly with alkenes and alkynes, and furnished Markovnikov adducts (**237** and **238**) in moderate yields (Scheme 21A).[143] Other reagents like KI-phosphoric acid (95%)[144], TMSI-H_2O[145], triphenylphosphine (PPh_3)-I_2-H_2O[146] and titanium(IV) iodide-H_2O[147] were also effective.



Scheme 21. AlI_3 mediated hydroiodination. A: Alkenes or alkynes; B: 3,3,3-trifluoropropyne.

Anti-Markovnikov adducts (**240**~**242**, and **244**) were observed during hydrohalogenations of propyne **239** with hydrohalic acids. Reactions between **239** and HX (X=F, Cl, Br) were rapid even in the absence of catalysts such as boron trifluoride (BF_3), $AlCl_3$ and $AlBr_3$. For hydroiodination, however, elevated temperature (100 ^oC) was required. The conversion was improved by catalytic AlI_3 and preceded at room temperature, whereas higher temperature resulted in lower yield (20%) in concurrent with the formation of **243**, see Scheme 21B.[148]

5.4 Electrophilic iodination of secondary and tertiary alkanes

$Cl_3C^+[Al_2I_6Cl]^-$ (**246**), a super electrophile *in situ* prepared by reaction of carbon tetrachloride (CCl_4) and AlI_3 (2 eq), could abstract a hydrogen from secondary or tertiary alkanes (**247**) to form $R^+[Al_2I_6Cl]^-$ species (**248**), see Figure 9. Treating **248** with elementary iodine afforded alkyl iodides (**249**) in moderate to good yields.[149] Another reagent combination useful for the conversion is sodium periodate-potassium iodide-sodium azide.[150]

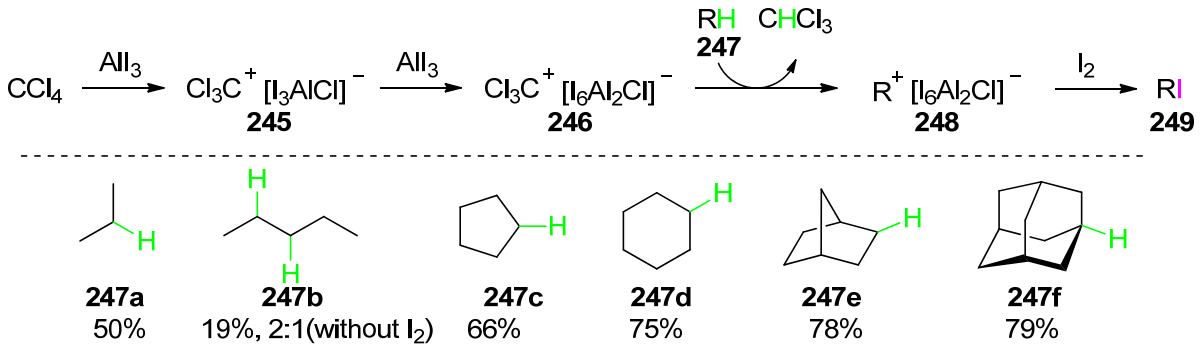


Figure 9. Scope of substrates for AlI_3 catalyzed electrophilic iodination.

6 Deprotection of Ketals

The oxophilic nature of AlI_3 was used in selective deprotection of ketals (**250**). Complete conversions could be achieved within 5~30 minutes in moderate to high yields (Figure 10).[151]

In a synthetic route to franosterol saponin (**255**) from diosgenin (**252**), a cascade transformations of spiral ketal deprotection followed by spontaneous iodination were accomplished by treating the spiral ketal **253** with AlI_3 in 85% yield (Scheme 22).[152]

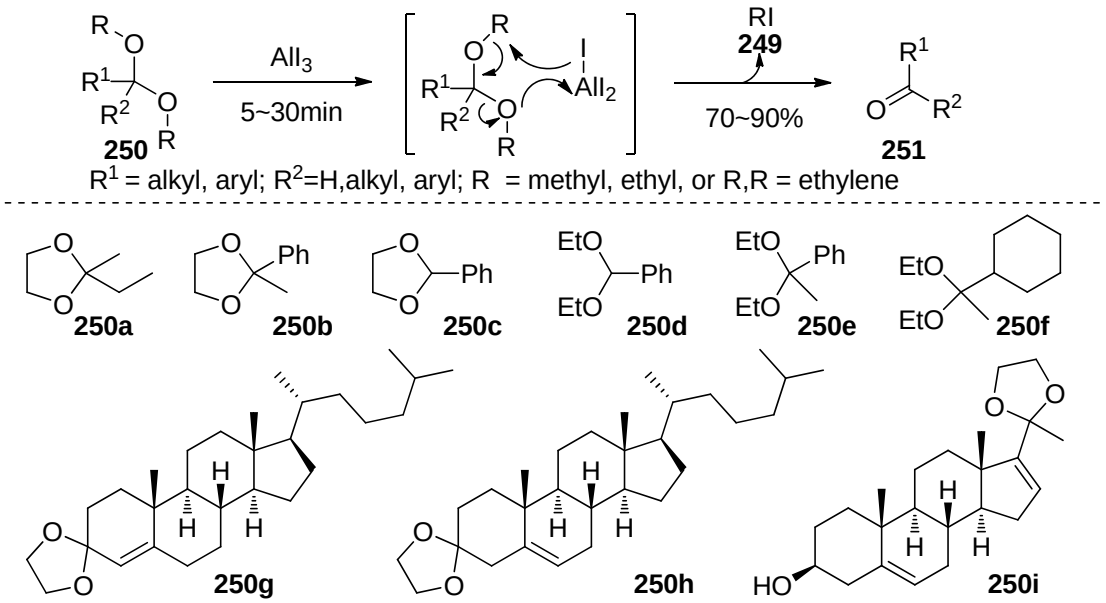
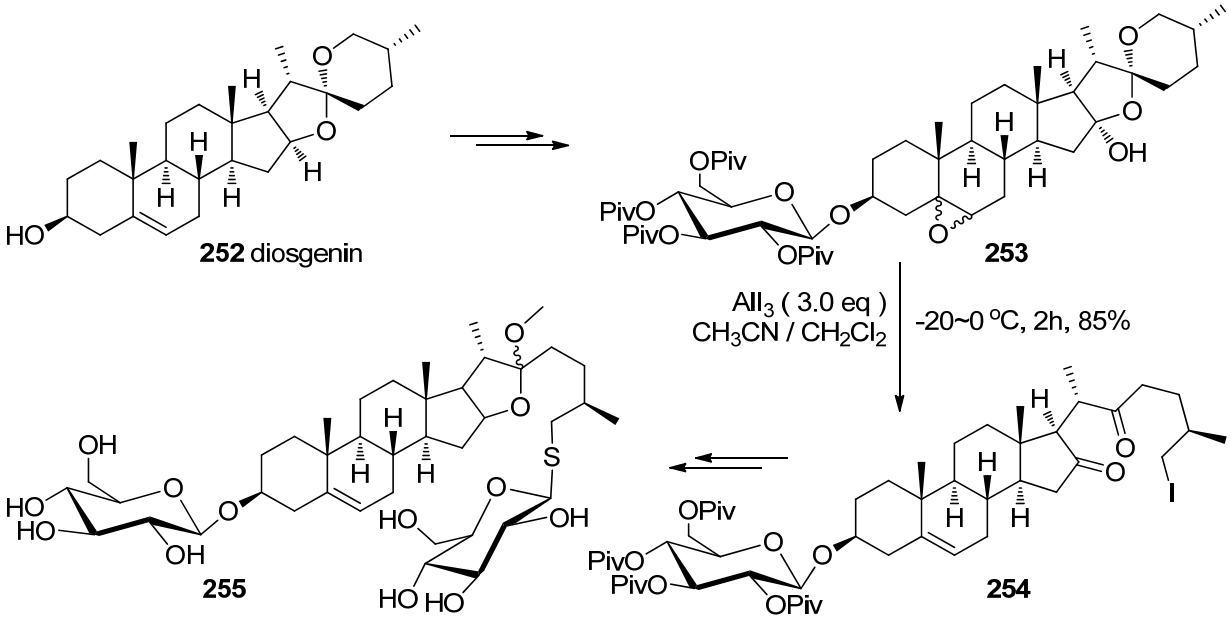


Figure 10. Scope of substrates for AlI_3 catalyzed ketal deprotection.



Scheme 22. Application of AlI_3 in synthesis of a franosterol saponin.

7 Reduction of Quinones

Quinones (**256**) such as 1,4-benzoquinone, 1,2-benzoquinone, 1,4-naphthaquinone, and 9,10-anthraquinone were reduced to corresponding hydroquinones (**257**) in moderate to high yields. AlI_3 served as an oxophilic agent and iodide donor during the transformation (Figure 11A). Reactive species **260** could be trapped by dienophiles like *N*-methylmaleimide and fumaronitrile through Diels-Alder reaction (Figure 11B).[153]

8 Reduction of Azides

8.1 Reduction of azides to primary amines

Numerous methods have been developed for reduction of azides (**263**). Examples include reductions by PPh_3 (Staudinger reaction),[154] thiol,[155] $NaBH_4$-$CoCl_2$-H_2O,[156] and palladium on carbon (catalytic hydrogenation).[157,158] The electro-affinity character of AlI_3 was used in reduction of azides (**263**) to afford corresponding primary amines (**264**) in moderate to high yields (Scheme 23A).[159] Functional groups such as nitro (**263c**), methoxy (**263e**), ethoxycarbonyl (**263k**) and acetoxy groups (**263f** and **263p**) remained unaffected.

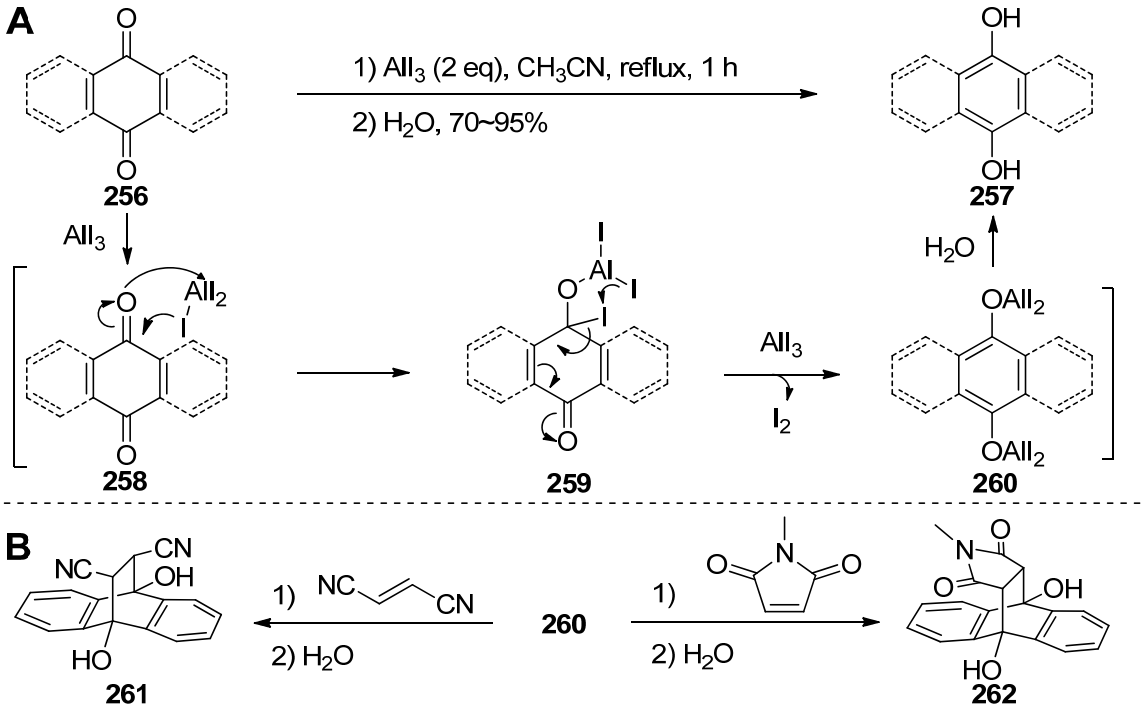
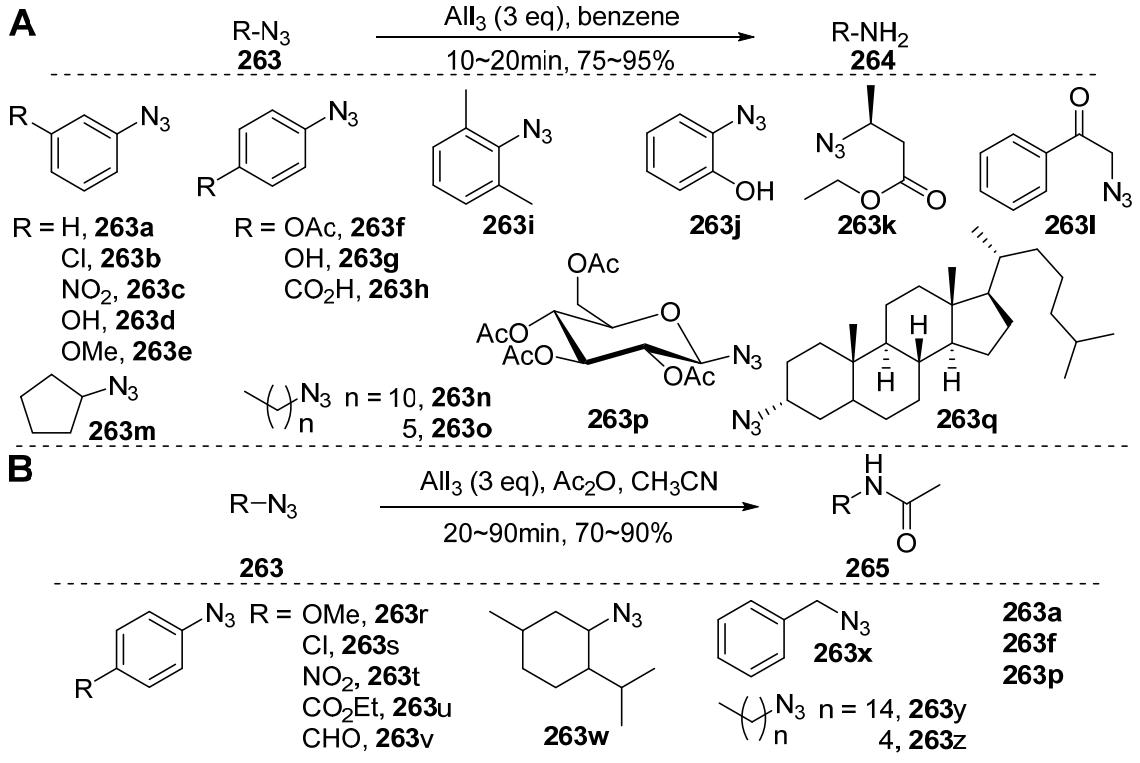


Figure 11. AlI_3 catalyzed reduction of quinine. A:plausible reduction mechanism; B: trapping of reduction intermediate *via* Diels-Alder adduction by *N*-methylmaleimide and fumaronitrile.



Scheme 23. AlI_3 catalyzed reduction of azides. A: Scope of substrates for reducing to primary amine; B: Scope of substrate for reducing to secondary amine in anhydride.

8.2 Reduction of azides to secondary amines

Azides (**263**) can also be transformed into substituted secondary amines (**265**). For example iminophosphorane, derived from reaction of azides and PPh_3 *via* Staudinger reaction, could be trapped by intramolecular ester group to give a lactam,[160] or a carboxylic acid activated by 2,2'-PySeSePy to give an amide.[161] Capturing of iminophosphorane by MeI followed by hydrolysis led to methylamine, whereas reaction of the iminophosphorane with paraformaldehyde followed by reduction afforded mono-methylamine.[162]

In acetic anhydride, reduction of azides (**263**) by AlI_3 afforded acetamide in moderate to high yields (Scheme 23B).[163] It is noteworthy that methoxy (**263r**), acetoxy (**263f**, **263p**), and ethoxycarbonyl (**263u**) groups tolerated the condition.

A plausible reaction mechanism is shown in Figure 12. The electro-affinity character of AlI_3 enabled the formation of **266**, concerted decomposition of **266** afforded iminoaluminane **267**. Treatment of **267** with acetic anhydride led to **269**. Hydrolysis of **267** and **269** afforded **264** and **265**, respectively.

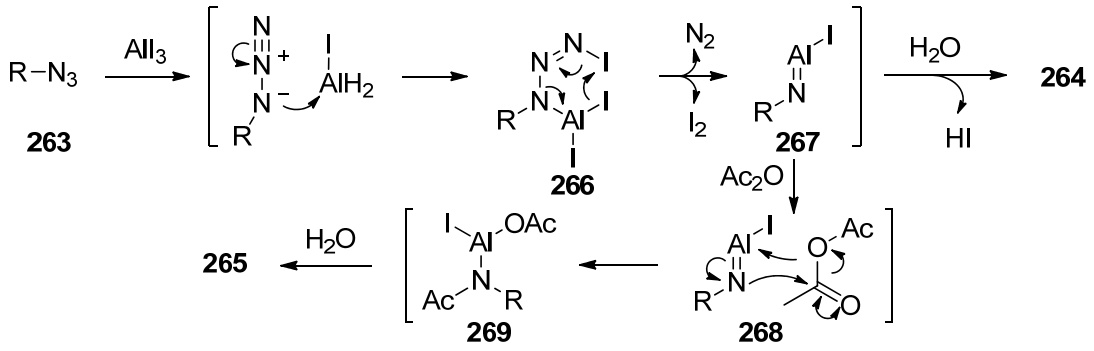


Figure 12. A plausible mechanism for AlI_3 catalyzed reduction of azides.

9 Aluminum Enolate Mediated Reactions

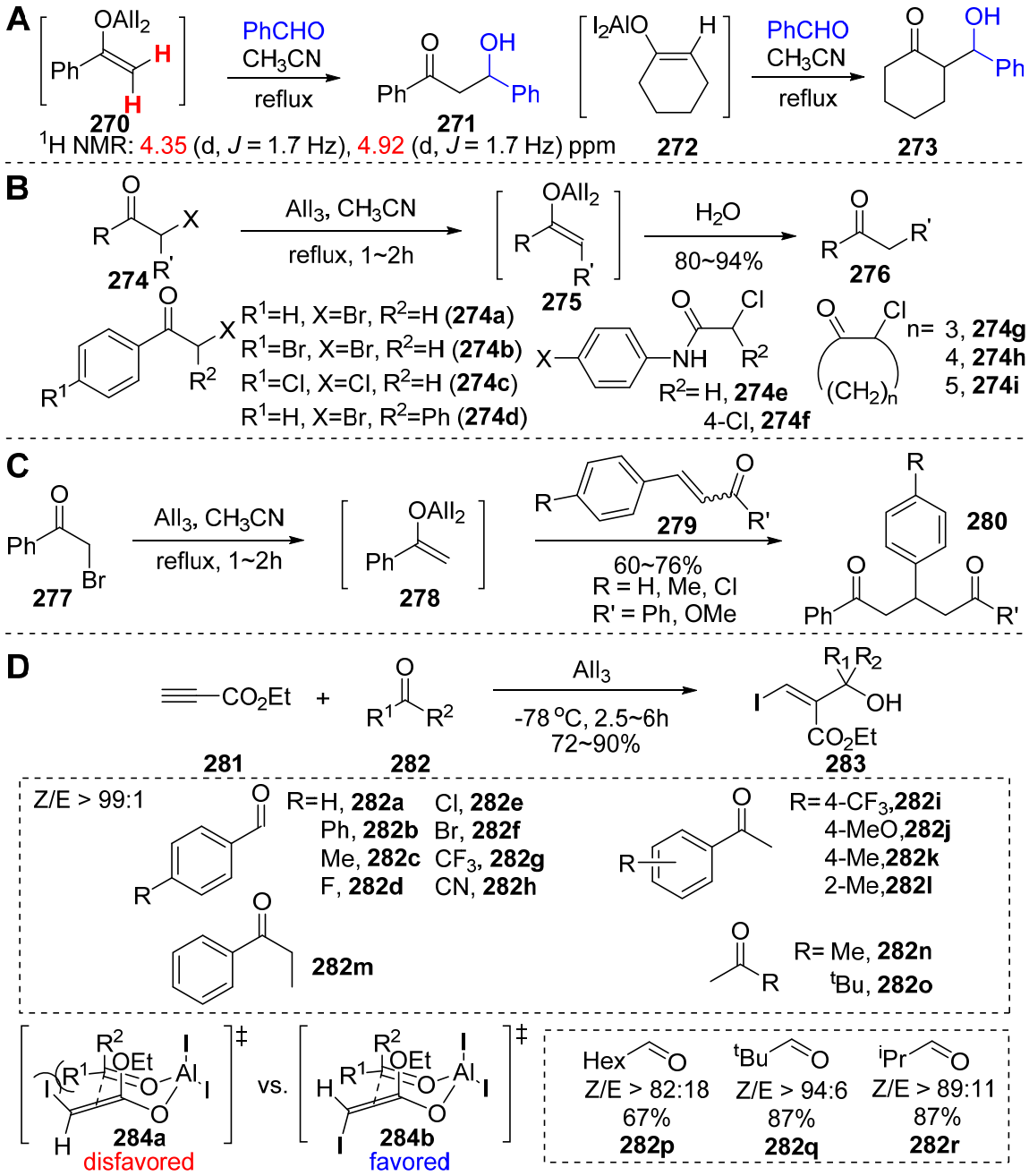
9.1 Generation of aluminum enolates

Application of aluminum enolates in C-C bond formation has garnered scant attention. The existence of aluminum enolate species (**270**), generated by α-bromoacetophenone and AlI_3, was confirmed by ^{1}H NMR spectrum; two doublet peaks (δ 4.35 and 4.92 ppm) were attributed to vinylic protons of **270** (Scheme 24A). Capturing of **270** by benzaldehyde *via* aldol condensation afforded **271**. Similarly, α-halocyclohexanone was transformed to **273** *via* **272**.[164]

9.2 Dehalogenation of α-haloketones

Aluminum enolates (**275**), prepared from α-haloketone, were quenched by water to give corresponding ketones (**276**) deprived of the α-halogen atoms, Scheme 24B.[164] Alternatively, combinations of NaI and Lewis acids such as ferrous chloride, ferric chloride, titanium(IV) chloride, chromium(III) chloride and $AlCl_3$were applied in preparation of acetophenones from α-

chloroacetophenones in 85~88% yields.[165] It was discovered that sodium bromide, sodium chloride, sodium cyanate, sodium thiocyanate, sodium chlorite were also effective when used in combination with Lewis acids.[166]



Scheme 24. Reactions of aluminum enolates. A: Existence of aluminum enolates; B: dehalogenation of α-halocarbonyl compounds; C: Michael addition; D: preparation of *Z*-*β*-Iodo-MBH esters and an explanation of the high Z/E regioselectivity;

9.3 Michael addition

Treating **277** with AlI_3 afforded enolate **278** after refluxing in acetonitrile for 1~2 hours. Capture of **278** with α,β-unsaturated ketones or esters (**279**) *via* Mukaiyama-Michael addition afforded 1,4-Michael adducts (**280**) in 60~76% yields (Scheme 24C).[167]

9.4 Preparation of Morita-Baylis-Hillman esters

AlI_3 induced Morita-Baylis-Hillman (MBH) reactions between aldehydes (**282a**~**282h**) or ketones (**282i**~**282o**) and ethyl propiolate (**281**) afforded β-Iodo esters (**283**) in high yields with high *Z*-stereoselectivity. The regioselectivity was low in the case of aliphatic aldehydes (**282p**~**282r**). The *Z/E*-stereoselectivity was attributed to steric hindrance between iodine and the substituents of carbonyl substrates. Thus transition state **284b** was favored over **284a**, as illustrated in Scheme 24D.[168,169] Other Lewis acids effective in preparation of β-I-MBH esters include magnesium iodide, TMSI[170] and BF_3•Et_2O-TBAI.[171,172] Interestingly, *E*-*β*-I-MBH esters could be achieved stereoselectively with BF_3•Et_2O-TMSI.[171]

9.5 Acetonitrile adduction

In an attempted ring-opening iodination of a cylcoheptanone (**285**), an unexpected acetonitrile adduct (**286**) was obtained in 61% yield (Figure 13a). Aluminum enolate species was possibly involved in the transformation. The tetrahydronfuran moiety remained unchanged probably due to the low reactivity of ring cleavage, whereas deficient Lewis acid (0.95 eq) precluded further conversion. Extension of the condition to other substrates such as cyclohexanone (**287**) failed to give similar products except **288**.[173]

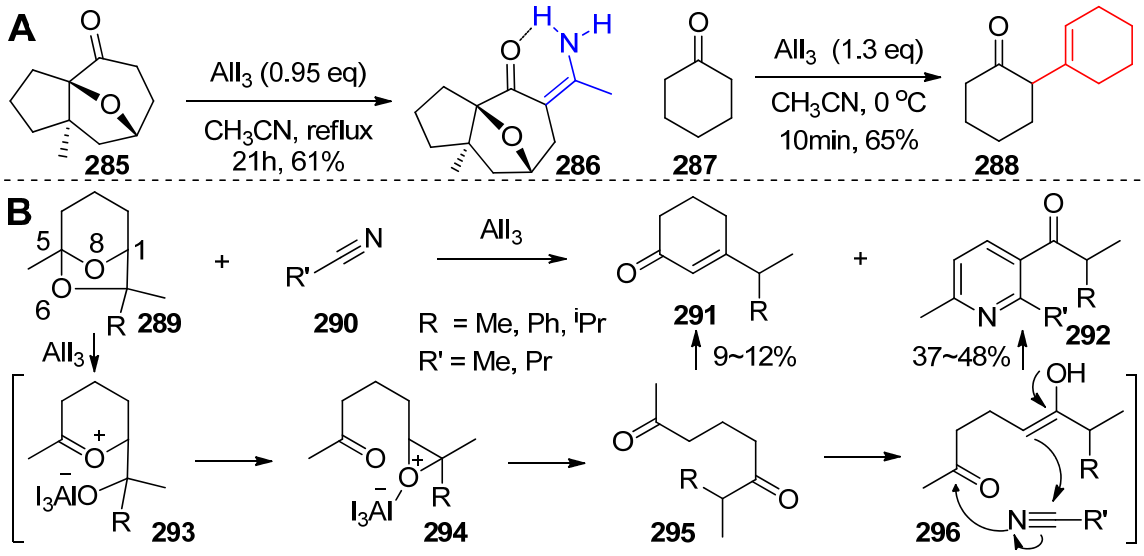


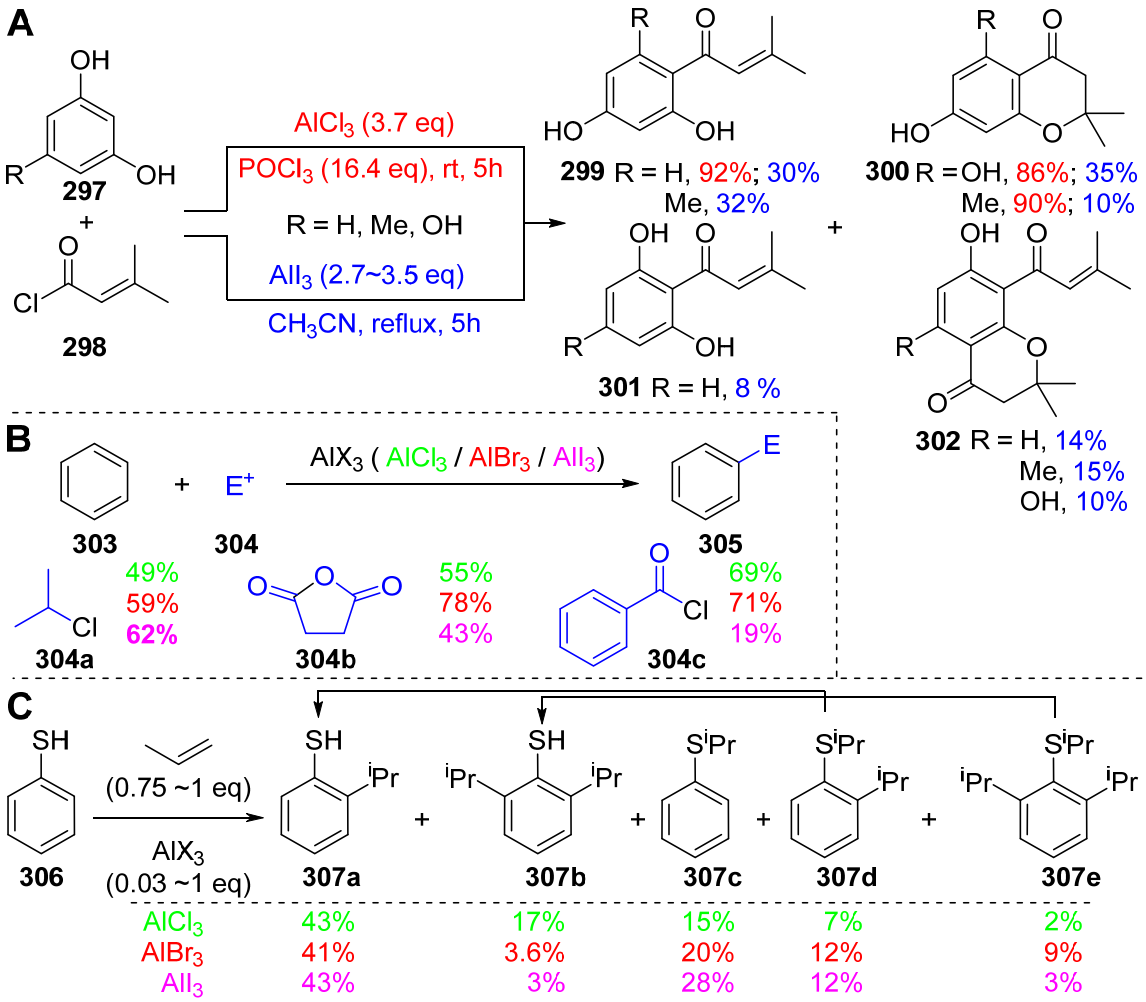
Figure 13. Unexpected adducts. A: Acetonitrile adduct; B: novel pyridine synthesis.

A similar adduct was observed during deprotection of 6,8-dioxobicyclo[3.2.1]octane **289**, a bicyclic ketal, with AlI_3 in acetonitrile. 2,3,6-Trisubstituted pyridine **292** was isolated as major

product in about 40% yield along with cyclohexenone **291** in about 10% yield. Apparently 1,5-diketone **295** was the intermediate *en route* to the products. Aldol condensation of the 1,5-diketone afforded cyclohexenone **291**. Addition of nitriles to enolate **296** of the 1,5-diketone gave pyridines (**292**), see Figure 13B. Other regioisomers, surprisingly, were not observed.[174,175]

10 Friedel-Crafts Acylation and Alkylation

Despite wide applications of $AlCl_3$ and BF_3•Et_2O in Friedel-Crafts acylation and alkylation, use of AlI_3 usually resulted in complicated mixtures of products. For example, treatment of orcinol, resorcinol, and phlorogucinol (**297**) with 3-methylcrotonoyl chloride (**298**) in the presence of $AlCl_3$ and oxyphosphorus chloride ($POCl_3$) led to related acylation product (**299**) or coumarins (**300**) in high yields even at room temperature.[176] The reactions with AlI_3 were sluggish, and the reaction mixtures were complex (**299**~**302**) and in low yields after refluxing in acetonitrile for 5 h, (Scheme 25A).[177]



Scheme 25. AlI_3 catalyzed Friedel-Crafts reactions. A: Acylation; B: comparison of catalytic efficiencies; C: syntheses of isopropylthiophenols.

One potential use of AlI_3 is the alkylation with bulky elecrophiles. Friedel-Crafts alkylation between benzene (**303**) and isopropyl chloride (**304a**) revealed a slightly higher yield when AlI_3 was used as catalyst (Scheme 25B).[178]

In preparation of orthoalkyl thiophenols (**307a** and **307b**) from thiophenol (**306**) and propene, AlX_3 was selected as the alkylation catalyst. 2-Isopropylthiophenol (**307a**) and 2,6-dipropyl-thiophenol (**307b**) were the target products. Thiol ethers (**307c**~**307e**) were further transformed into the corresponding thiols. In alkylation catalyzed by AlI_3, slightly higher portion of mono-alkylated products was obtained (Scheme 25C).[179]

11 Miscellaneous

11.1 Preparation of selenocarbonyl fluorides

Reactive selenocarbonyl fluorides (**309**) were prepared through AlI_3 or diethylaluminum iodide (Et_2AlI) induced the decomposition of $Hg(SeR_F)_2$ (**308**) in octamethylcyclotetrasiloxan (D_4). The products were collected by a *U*-trap cooled in liquid nitrogen in 35~45% yield. Selenocarbonyl fluoride polymerized at low temperature. Thermolysis of the colorless polymers (**310**) released selenocarbonyl fluoride monomers (**309**) and dimers (**311** and **312**), see Scheme 26A.[180-182]

11.2 Triene electrocyclization

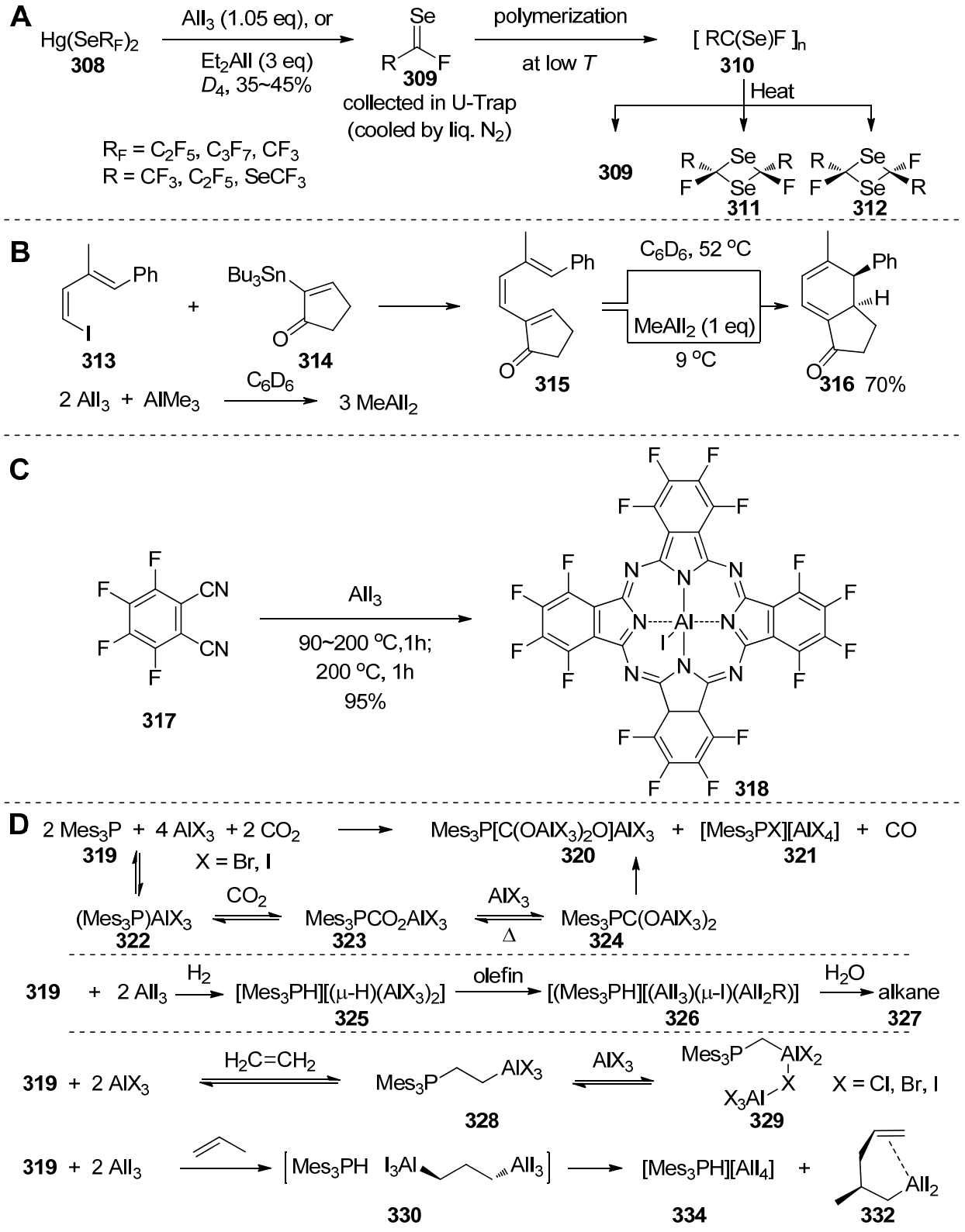
Methylaluminum diiodide ($MeAlI_2$), prepared *in situ* with AlI_3 and $AlMe_3$, was used as an efficient catalyst in asymmetric carba-6π electrocyclization of triene **315** (Scheme 26B).[183] The electrocyclization proceeded at 9 ^oC with an acceleration rate of 600 ($t_{1/2}$=7 minutes) compared to thermocyclization that occurs at 52 ^oC.

11.3 Preparation of a perfluorophthalocyanine

Perfluorophthalocyanine (**318**), a pigment of photoelectronic importance, was prepared by heating perfluorinated *o*-phthalonitrile (**317**) with catalytic AlI_3 at elevated temperatures (Scheme 26C).[184]

11.4 Formation of frustrated Lewis pairs with hindered Lewis bases

Coordination of AlI_3 to Lewis bases affords frustrated Lewis pairs (FLP) with hindered ligands such as $(Mes_3P)AlX_3$ (**322**, Mes=2,4,6-trimethylphenyl). The FLPs were found useful for activation of greenhouse gas carbon dioxide (CO_2), hydrogen gas (H_2), and olefins (Scheme 26D).[185-188] Reaction of **322** with CO_2 afforded **320** and carbon monoxide (CO) *via* **323** and **324**. H_2 can be activated by **319** and AlI_3 to give **325**. Reaction of **325** with olefins afforded **326**, and aqueous work-up of **326** gave the corresponding alkane (**327**). Reactions of ethylene and propene with **319** and AlI_3 afforded **329** and **332**, respectively.



Scheme 26. Other applications of AlI_3. A: Preparation of selenocarbonyl fluoride; B: triene electrocyclization; C: synthesis of perfluorophthalocyanine; D: potential of frustrated Lewis pair $(Mes_3P)(AlI_3)$ in activation of CO_2, H_2, and olefins (ethylene and propylene).

12 Preparation of the Reagent

For general application in organic synthesis, AlI_3 can be prepared *in situ*. Colorless AlI_3 crystal is available by reacting aluminum and iodine in hexane or by reacting aluminum with sublimed iodine in a vitreous pipe at 500~525 ^oC.[189]

12.1 *In situ* preparation of AlI_3

A mixture of aluminum powder or foil (250 mg, 9.3 mmol) and elementary iodine (1.9 g, 15 mmol) were mixed in an inert solvent (benzene, toluene, acetonitrile, carbon disulfide, or cyclohexane, 8 ml). The mixture was stirred under reflux for about 3 h, till the purple color of iodine faded. The solution can be used directly without further purification.[25]

12.2 Preparation of crystalline AlI_3

To a stirred mixture of aluminum foil (3 mmol, 0.1 mm thick) in hexane (100 ml) was added elementary iodine (4.5 mmol). Then the mixture was refluxed under slow argon flush for 1 hour until the purple color faded. Unreacted metal was filtered off while hot. After cooling to room temperature, colorless crystals precipitated and were collected, yield 96%, mp 191 ^oC.[190]

13 Conclusions

AlI_3 is a strong Lewis acid and iodide source. Its unique oxophilicity has been widely and extensively applied in deoxygenation and deoxydehydration of a broad range of substrates such as oxiranes, diols, sulfoxides, sulfonyl chlorides, oximes, *N*-arylnitrones azoxyarenes, and *N*-heteroarene *N*-oxides. It can be used in generation of aluminum enolates from α-haloketones which in turn can be quenched with water to afford dehalogenated products, or be captured by α,β-unsaturated ketone affording Michael addition products. AlI_3 also serves as a precursor of HI in hydroiodination of alkenes or alkynes. Generally AlI_3 is not suitable for application in Friedel-Crafts reactions due to its unique oxophilicity and electroaffinity character. Among the broad range of other synthetic applications, ether cleavage and ester cleavage have been frequently applied in synthesis. Non-hydrolitic ester cleavage is suitable for substrates sensitive to strong acidic or basic conditions. Efficient demethylation of alkyl aryl ethers has made AlI_3 an ideal alternative to BBr_3.

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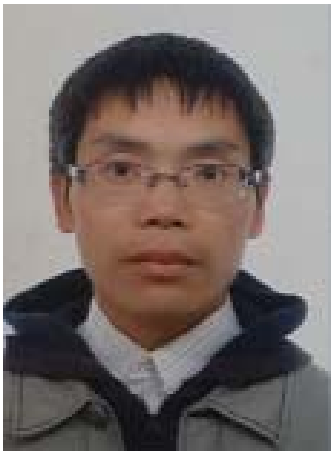

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