

Chapter 2

Lewis or Brønsted Acid-Mediated Transformations of VDCPs

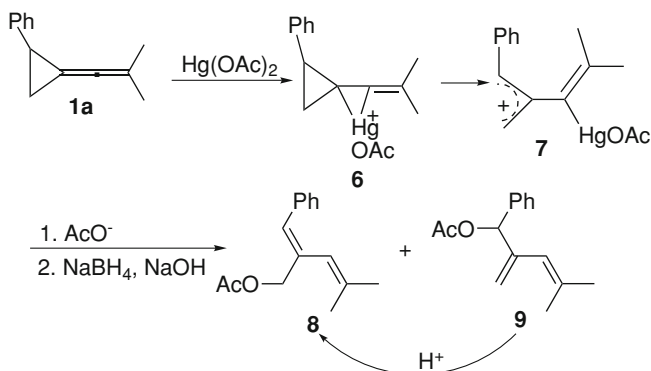
Abstract Lewis or Brønsted acid-mediated intramolecular rearrangement of VDCPs, and the reactions of VDCPs with acetals, aldehydes, ketones, imines, activated alkenes, nitriles, acyl chlorides, and alcohols are described in this chapter.

Keywords Vinylidenecyclopropanes • Intramolecular rearrangement • Cycloaddition reaction • Ring-opening reaction • Mercury acetate-mediated reaction • Lewis acid-mediated reaction • Brønsted acid-mediated reaction

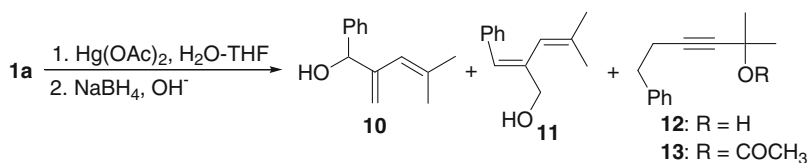
2.1 Mercury Acetate-Mediated Transformations of VDCPs

Pasto et al. reported the mercury acetate-mediated transformations of VDCPs **1** in 1976 [1–5]. Acetoxymercuration of VDCP **1a** followed by reductive demercuration using a great excess of sodium borohydride produced a complex mixture of the monomeric acetates **8** and **9** (60:40 ratio), dimeric diacetates, and bis(acetoxymethyl)mercury compounds. Disrotatory ring-opening of an intermediate spiromercurinium ion **6** (or possible cyclopropyl cation **7** as a transition state) is expected to occur with outward rotation of the phenyl group, i.e., in the least sterically congested manner, to produce an allylic cation which then reacts with acetate to produce products **8** and **9**. In addition, **9** can be cleanly rearranged to **8** in the presence of strong protic acid (Scheme 2.1).

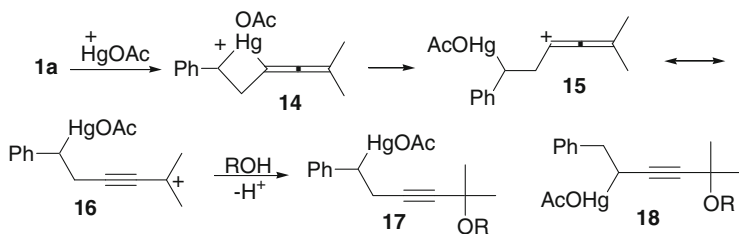
In addition to the formation of alcohols **10** and **11**, which correspond to the acetates **8** and **9** formed in acetoxymercuration of VDCP **1a**, hydroxymercuration of **1a** in 50% aqueous tetrahydrofuran (THF) also resulted in the formation of the acetylenic alcohol **12** (small amounts of acetates **8**, **9**, and **13** are also formed) (Scheme 2.2).



Scheme 2.1 $\text{Hg}(\text{OAc})_2$ -mediated transformation of VDCP **1a**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society



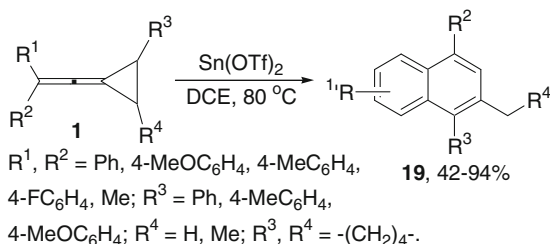
Scheme 2.2 $\text{Hg}(\text{OAc})_2$ -mediated reaction of VDCP **1a** in aqueous THF. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society



Scheme 2.3 Plausible mechanism for the $\text{Hg}(\text{OAc})_2$ -mediated reaction of VDCP **1a**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

The alcohol **12** and acetate **13** may be formed by initial attack by acetoxy-mercury cation on one of the ring bonds, either as shown to produce **17** or alternatively on the $-\text{CH}_2-\text{C}=\text{C}-$ bond to give **18**, both of which would be reduced to **12** and **13** (Scheme 2.3) [6, 7].

Scheme 2.4 $\text{Sn}(\text{OTf})_2$ -catalyzed intramolecular rearrangement of VDCPs **1**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

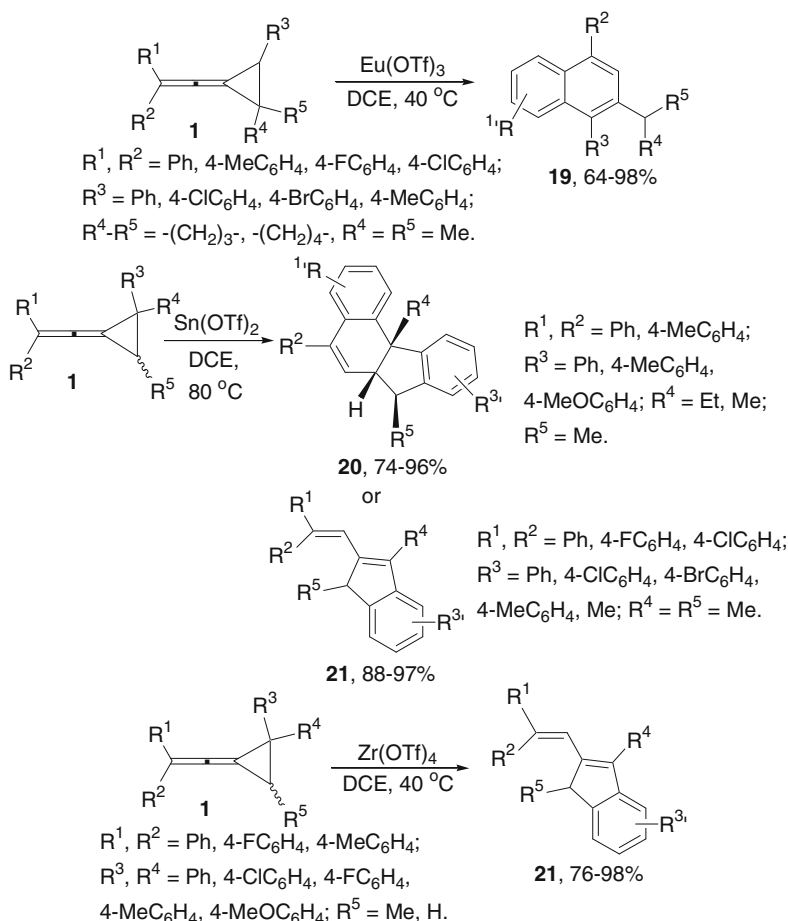


2.2 Lewis or Brønsted Acid-Mediated Intramolecular Rearrangement of VDCPs

During the recent years, Shi et al. have reported a series of Lewis acid-catalyzed rearrangement reactions of VDCPs **1**. For example, in 2005, Shi et al. first found the Lewis acid-catalyzed rearrangement reaction of VDCPs **1**. It was observed that VDCPs **1** could rearrange to naphthalene derivatives **19** in the presence of $\text{Sn}(\text{OTf})_2$, in acceptable to high yields under mild conditions (Scheme 2.4) [1, 8].

Based on this pioneering work, Shi et al. investigated thoroughly the Lewis acid-catalyzed rearrangement reactions of VDCPs **1** having three substituents on the corresponding cyclopropyl rings [9–11]. It was found that the reaction products are highly dependent on the substituents on the corresponding cyclopropyl rings and the electronic nature of the aryl groups on VDCPs **1**. For VDCPs **1** bearing two alkyl groups at the C3 position ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{aryl}; \text{R}^4 = \text{H}; \text{R}^5, \text{R}^6 = \text{alkyl}$), naphthalene derivatives **19** were formed in the presence of Lewis acid $\text{Eu}(\text{OTf})_3$ in DCE at $40\text{ }^\circ\text{C}$. For VDCPs **1** in which $\text{R}^1, \text{R}^2, \text{R}^3 = \text{aryl}$ and $\text{R}^4, \text{R}^5 = \text{alkyl}$ (*syn/anti* isomeric mixture), the corresponding 6*a*H-benzo[*c*]fluorine derivatives **20** were obtained in the *syn*-configuration via a double intramolecular Friedel–Crafts reaction using the substrates without electron-withdrawing substituents on aryl groups or the corresponding indene derivatives **21** were formed via an intramolecular Friedel–Crafts reaction as long as one electron-deficient aryl group was attached. For VDCPs **1** in which $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4 = \text{aryl}$ and $\text{R}^5 = \text{alkyl}$ or H, the corresponding indene derivatives **21** were obtained exclusively via a sterically demanding intramolecular Friedel–Crafts reaction (Scheme 2.5).

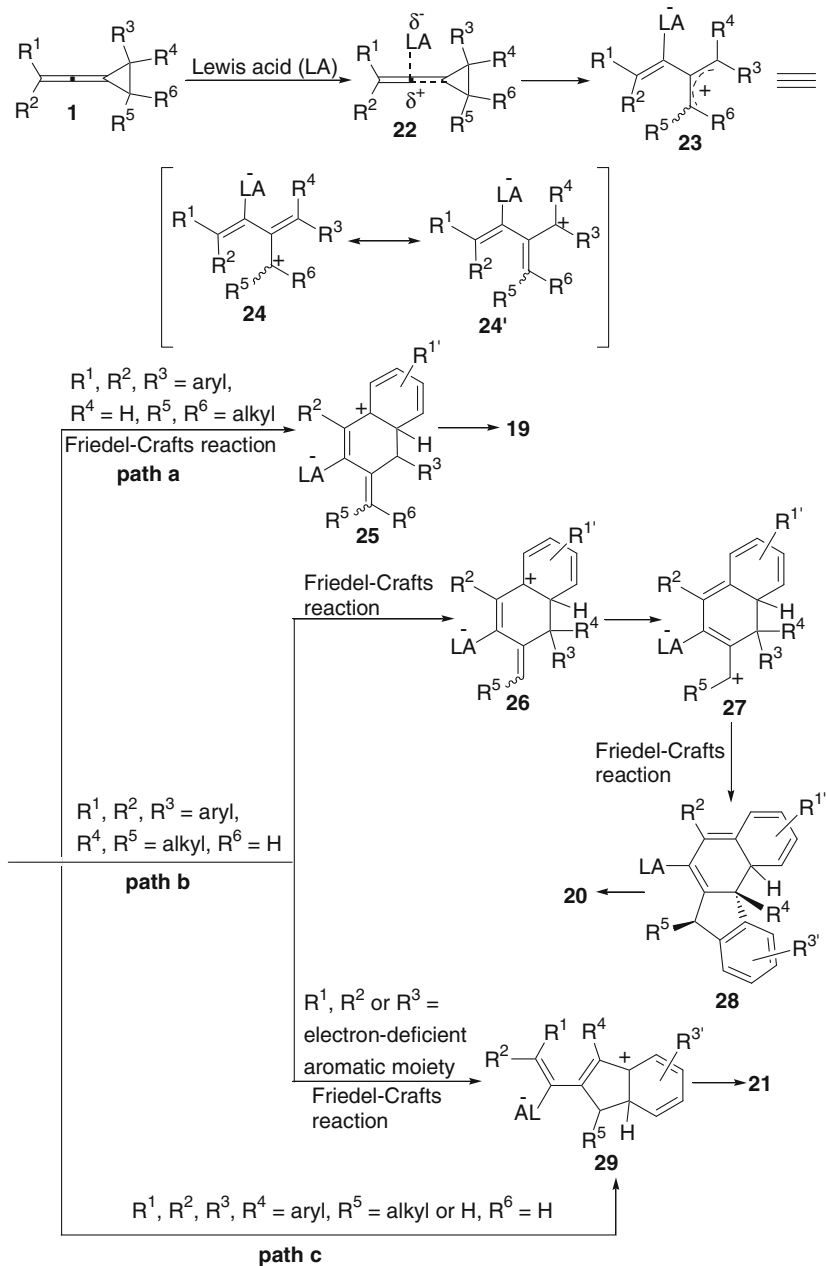
Plausible mechanisms for the formation of naphthalene, 6*a*H-benzo[*c*]fluorine, and indene derivatives are shown as below: the coordination of VDCPs **1** to Lewis acid initially gives 1-cyclopropylvinyl cation **22**, a vinyl group stabilized cyclopropyl cation [12–16], which results in the formation of cyclopropyl ring-opened cationic intermediate **23** or its resonance-stabilized zwitterionic intermediate **24** and **24'**, which is stabilized by the aromatic R^3 group in most cases. The intramolecular Friedel–Crafts reaction [17] produces the cyclized intermediate **25**, from which the thermodynamically favored naphthalene derivatives **19** are formed via successive 1,3-carbocation rearrangement, 1,4-proton shift along with release of Lewis acid or deprotonation and 1,3-proton shift (Scheme 2.6, **path a**) [18].



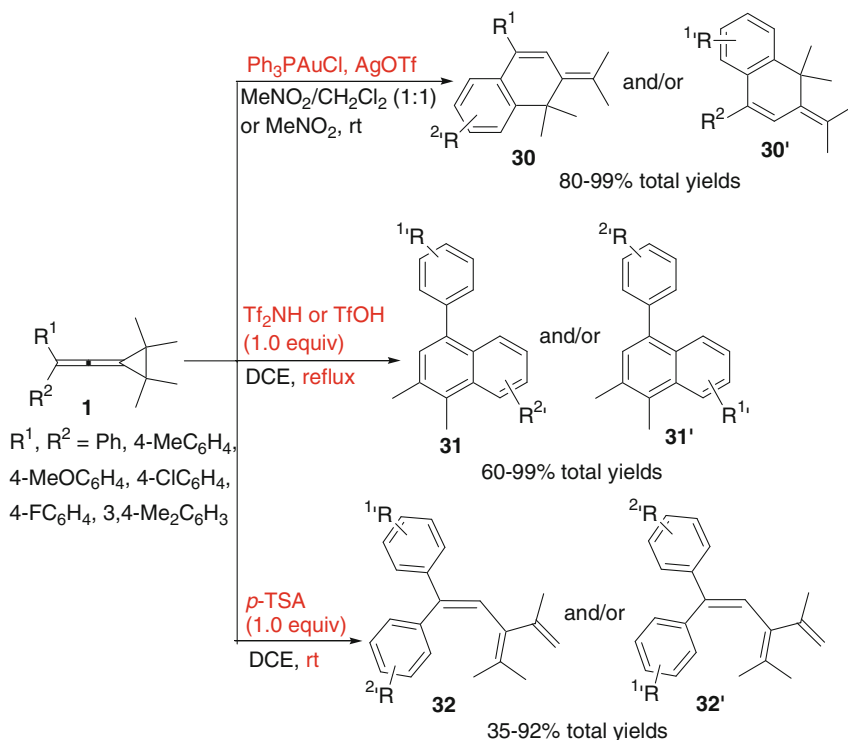
Scheme 2.5 Lewis acid-catalyzed intramolecular rearrangement of VDCPs **1**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

6aH-benzo[*c*]fluorine derivatives **20** can be obtained via a double Friedel–Crafts reaction as shown in **path b** in Scheme 2.6. The formation of indene derivatives **21** is illustrated in **path c** in Scheme 2.6.

Using VDCPs **1** with tetramethyl-substituted cyclopropyl ring ($R^3 = R^4 = R^5 = R^6 = \text{Me}$), interesting intramolecular rearrangement patterns were found in the presence of different Lewis or Brønsted acid catalyst under different reaction temperature. For example, with soft Lewis acid Au(I) as the catalyst, 2-isopropylidene-1,1-dimethyl-1,2-dihydronaphthalene derivatives **30** and/or **30'** were obtained in good to high yields at room temperature (Scheme 2.7) [19], while with hard Brønsted acid such as Tf_2NH ($\text{Tf} = \text{trifluoromethanesulfonyl}$) or toluene-4-sulfonic acid (*p*-TSA) as the catalyst, the corresponding naphthalene



Scheme 2.6 Plausible mechanism for the Lewis acid-catalyzed intramolecular rearrangement of VDCPs **1**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

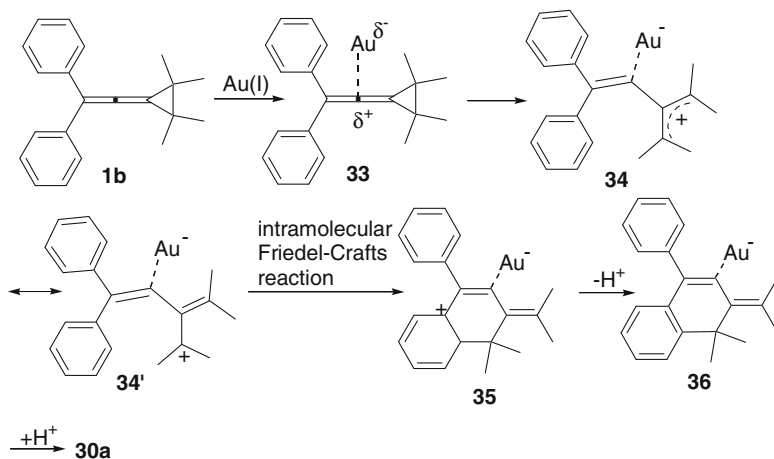


Scheme 2.7 Lewis or Brønsted acid-catalyzed intramolecular rearrangement of VDCPs **1** with tetramethyl groups on the cyclopropyl ring

derivatives **31** and/or **31'** were formed in good to high yields upon heating, along with release of a propene molecule. In addition, in the presence of Brønsted acid such as toluene-4-sulfonic acid (*p*-TSA), the corresponding triene derivatives **32** and **32'** were afforded in moderate to good yields at room temperature (Scheme 2.7) [20]. All ratios of **30** and **30'**, **31** and **31'**, and **32** and **32'** were dependent on the electron character of groups R^1 and R^2 .

Plausible mechanism for the formation of products **30** with VDCP **1b** as the model is shown below: first, the corresponding cyclopropyl ring-opened zwitterionic intermediate **34** or the resonance-stabilized zwitterionic intermediate **34'** is formed from the initial zwitterionic intermediate **33**. Then intramolecular Friedel–Crafts reaction with the adjacent aromatic ring takes place to produce zwitterionic intermediate **35**, which affords the corresponding intermediate **36** via deprotonation. Subsequent protonation of intermediate **36** produces the corresponding product **30a** along with the release of Au(I) catalyst (Scheme 2.8).

Plausible mechanism for the formation of products **31** and **32** is shown below: first, protonation of VDCP **1b** by the Brønsted acid regioselectively gives intermediate **37**, which results in the formation of cyclopropyl ring-opened cationic



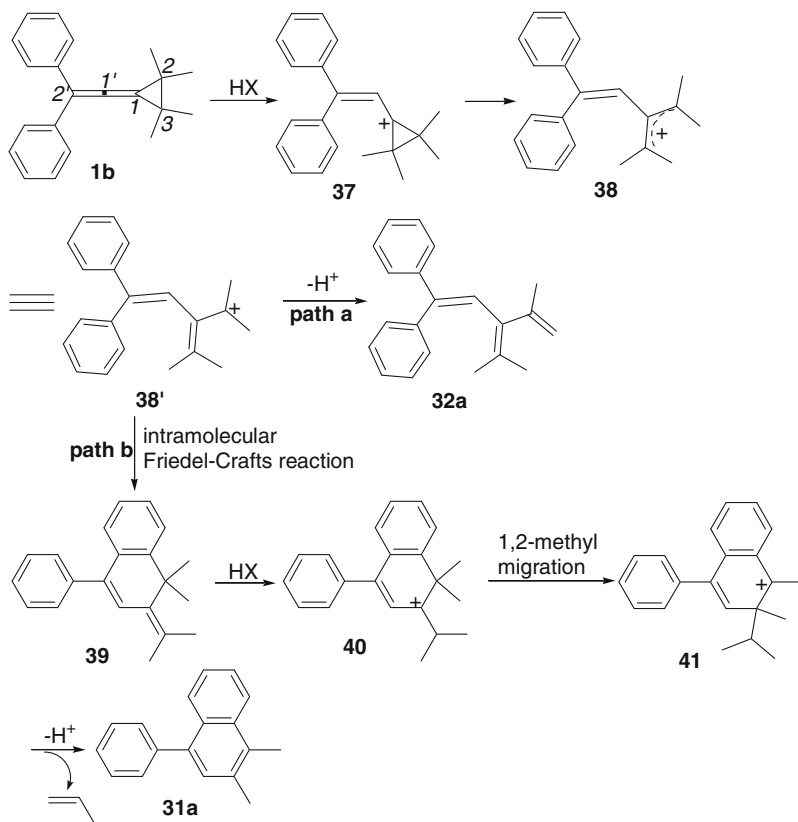
Scheme 2.8 Plausible mechanism for the Au(I)-catalyzed intramolecular rearrangement of VDCP **1b**. Reprinted with the permission from Ref. [19]. Copyright 2011 American Chemical Society

intermediate **38** or **38'**. Then product **32a** will be achieved with release of a proton (Scheme 2.9, **path a**). Alternatively, intermediate **38'** will be transformed to intermediate **39** through an intramolecular Friedel–Crafts reaction (Scheme 2.9, **path b**). Intermediate **39** undergoes subsequent protonation to give intermediate **40**. 1,2-Migration of the methyl group in intermediate **40** gives intermediate **41**, which will produce the final product **31a** with release of a proton and a propene. It is worth noting that this mechanism is postulated on the DFT studies performed with the Gaussian03 program by using the B3LYP method [20].

In the early 2008, Huang et al. reported a Lewis acid TiCl_4 -mediated ring-expansion reaction of bicyclic VDCPs **1** for the formation of medium- and large-size naphthalenacarbocycle derivatives **42** (Scheme 2.10) [21].

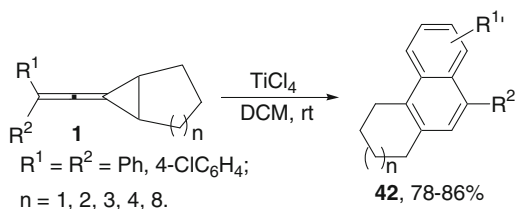
2.3 Lewis or Brønsted Acid-Mediated Reactions of VDCPs with Acetals, Aldehydes and Ketones

Lewis acid Sc(OTf)_3 -catalyzed reactions of VDCPs **1** with acetals **43** were also established for the preparation of indene derivatives **44** and **45**. This reaction is believed to proceed via regioselective addition of oxonium intermediate to VDCPs **1** and the subsequent intramolecular Friedel–Crafts reaction. It was found that the electronic nature of substituent strongly influenced the reaction results, even leading to different products (Scheme 2.11) [1, 22]. In a word, when R^3 , R^4 = aryl, R^5 , R^6 = Me or H, indene derivatives **44** can be formed singly; and while $\text{R}^3 = \text{R}^4 = \text{R}^5 = \text{R}^6 = \text{Me}$, indene derivatives **45** were obtained exclusively.

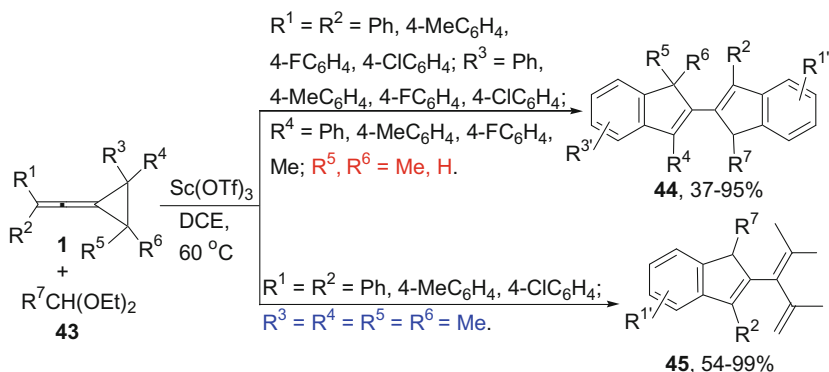


Scheme 2.9 Plausible mechanism for the Brønsted acid-catalyzed intramolecular rearrangement of VDCP **1b**

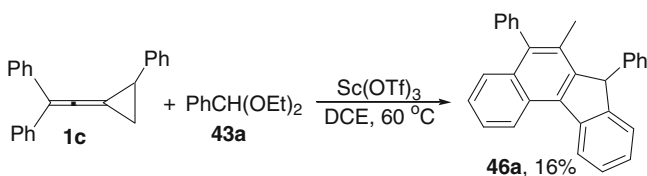
Scheme 2.10 TiCl_4 -mediated ring-expansion of VDCPs **1**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society



Interestingly, the substrate VDCP **1c** with only one phenyl group at the cyclopropyl ring demonstrated a special reactivity under identical reaction conditions. A new product 6-methyl-5,7-diphenyl-7*H*-benzo[*c*]fluorine **46a** along with other unidentified by-products was obtained although the yield (16%) was rather low (Scheme 2.12).



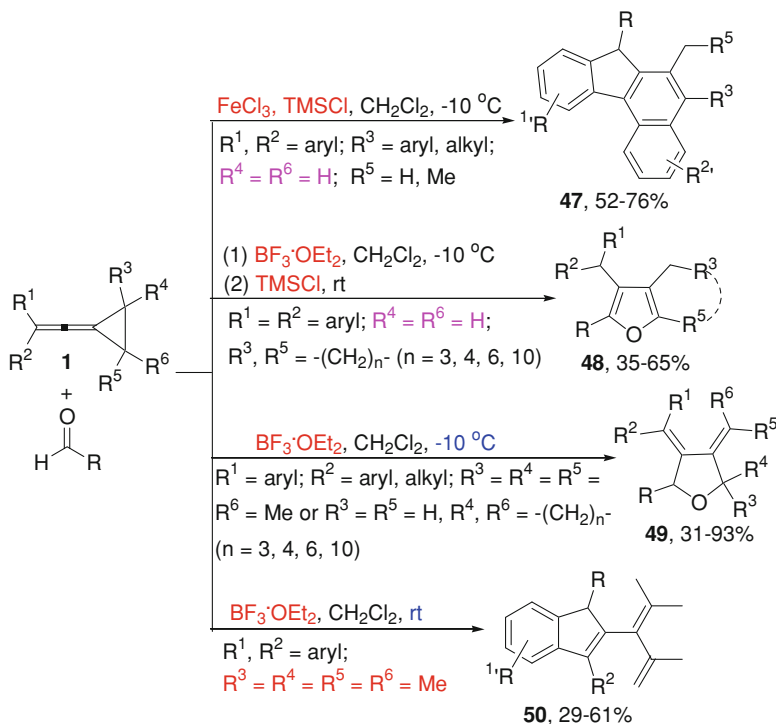
Scheme 2.11 $\text{Sc}(\text{OTf})_3$ -catalyzed reactions of VDCPs **1** with acetals. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society



Scheme 2.12 $\text{Sc}(\text{OTf})_3$ -catalyzed reaction of VDCP **1c** with acetal **43a**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

Huang et al. developed the reactions of VDCPs **1** with aldehydes to provide an efficient and selective method for the synthesis of benzo[*c*]fluorene, tetrahydrofuran, furan, and indene derivatives. A variety of benzo[*c*]fluorene **47**, furan **48**, tetrahydrofuran **49**, and indene derivatives **50** can be obtained selectively depending on the Lewis acid catalysts, the substituents on VDCPs **1**, and the reaction temperature [23–25]. For instance, using $\text{FeCl}_3/\text{TMSCl}$ as the catalyst at -10°C , benzo[*c*]fluorene derivatives **47** can be obtained in moderate to good yields ($R^1, R^2 = \text{aryl}$; $R^3 = \text{aryl, alkyl}$; $R^4 = R^6 = \text{H}$, $R^5 = \text{H, Me}$); first treatment with $\text{BF}_3 \cdot \text{OEt}_2$ at -10°C , then with TMSCl at room temperature, furan derivatives **48** can be achieved in acceptable to moderate yields [$R^1 = R^2 = \text{aryl}$; $R^4 = R^6 = \text{H}$, $R^3, R^5 = -(\text{CH}_2)_n-$ ($n = 3, 4, 6, 10$)]; using $\text{BF}_3 \cdot \text{OEt}_2$ as the catalyst at -10°C , tetrahydrofuran derivatives **49** can be obtained in acceptable to high yields [$R^1 = \text{aryl}$; $R^2 = \text{aryl, alkyl}$; $R^3 = R^4 = R^5 = R^6 = \text{Me}$ or $R^3 = R^5 = \text{H}$, $R^4, R^6 = -(\text{CH}_2)_n-$ ($n = 3, 4, 6, 10$)]; while using $\text{BF}_3 \cdot \text{OEt}_2$ as the catalyst at room temperature, indene derivatives **50** can be formed in low to moderate yields ($R^1, R^2 = \text{aryl}$; $R^3 = R^4 = R^5 = R^6 = \text{Me}$) (Scheme 2.13).

Plausible mechanism for the formation of products **47–50** is outlined below. Initially, the coordination of aldehydes to Lewis acid (LA) gives intermediate **51**, which adds to VDCPs **1** regioselectively to produce intermediate **52**. Then the

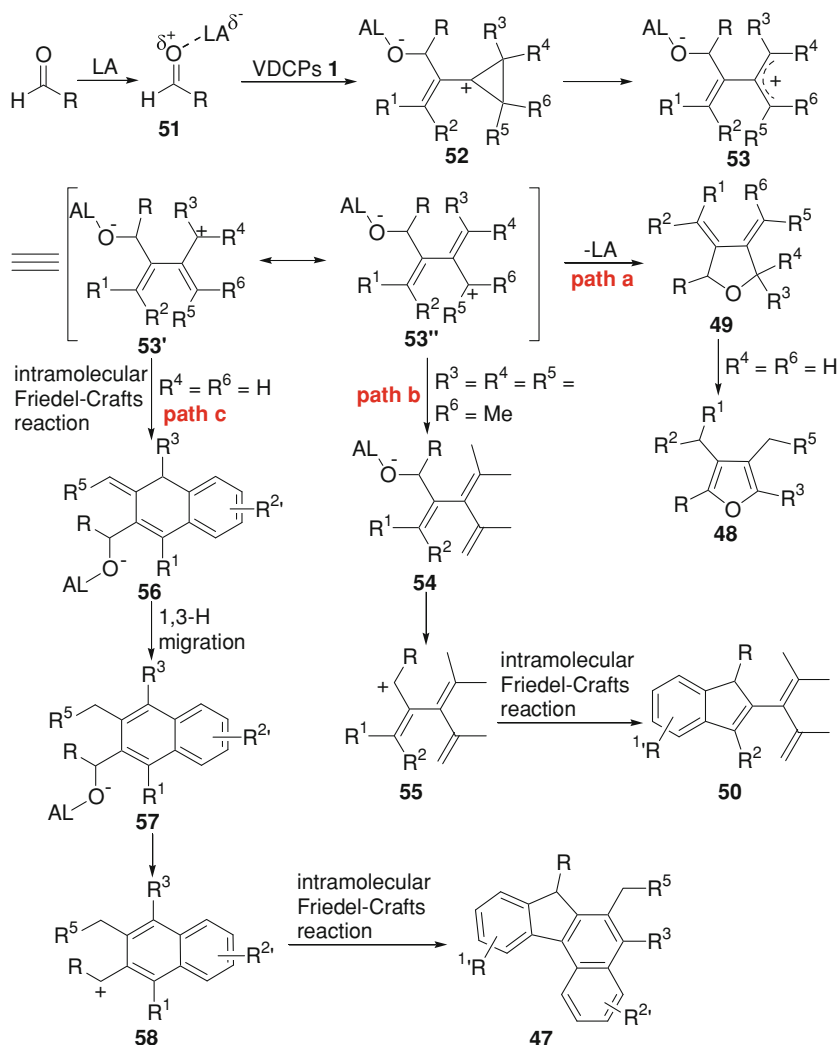


Scheme 2.13 Lewis acid-catalyzed reactions of VDCPs **1** with aldehydes

cyclopropyl ring-opened intermediate **53** or the resonance-stabilized intermediates **53'** and **53''** will be formed. Intramolecular *O*-attack cyclization of intermediate **53'** will afford products **49**. When $\text{R}^4 = \text{R}^6 = \text{H}$, aromatization of **49** will take place to give products **48** (Scheme 2.14, **path a**). When $\text{R}^3 = \text{R}^4 = \text{R}^5 = \text{R}^6 = \text{Me}$, deprotonation of intermediate **53''** will form intermediate **54**, which then transforms to intermediate **55**. The subsequent intramolecular Friedel–Crafts reaction of intermediate **55** furnishes the indene derivatives **50** (Scheme 2.14, **path b**). In addition, when $\text{R}^4 = \text{R}^6 = \text{H}$, intermediate **53'** undergoes intramolecular Friedel–Crafts reaction to give intermediate **56**. Aromatization of **56** produces the thermodynamically favored naphthalene intermediate **57**, which then transforms to intermediate **58**. Finally, intermediate **58** undergoes another intramolecular Friedel–Crafts reaction to give products **47** (Scheme 2.14, **path c**).

Further studies revealed that using VDCPs **1** with functionalized groups on the cyclopropyl ring shown below as the substrates, their reactions with aldehydes will afford the furo[2,3-*b*]furan derivatives **59** in 37–64% yields (Scheme 2.15).

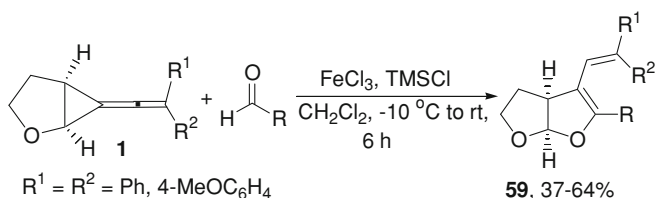
Plausible mechanism for the formation of products **59** is depicted in Scheme 2.16. First, the addition of the Lewis acid-activating aldehydes **51** to VDCPs **1** may occur to give the ring-opened intermediate **60** via proximal cleavage of the cyclopropyl ring. Then an intramolecular cyclization of



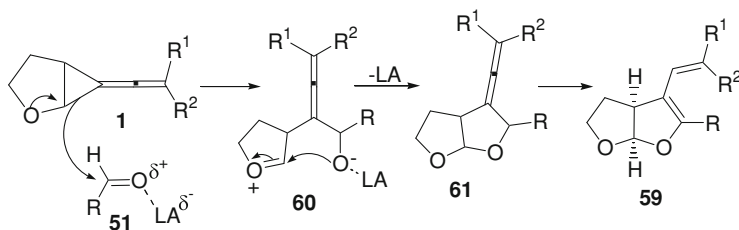
Scheme 2.14 Plausible mechanism for the Lewis acid-catalyzed reactions of VDCPs **1** with aldehydes. Reprinted with the permission from Ref. [25]. Copyright 2011 American Chemical Society

intermediate **60** along with the release of the Lewis acid furnished the [3 + 2] cycloaddition intermediate **61**, which will transform to the final products **59** via 1,3-H shift.

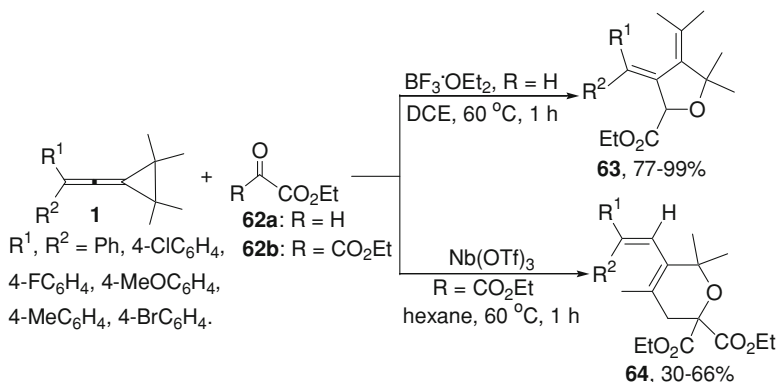
The reactions of VDCPs **1** with activated carbonyl compounds **62** were also investigated and it was found that a number of functionalized tetrahydrofurans **63** and 3,6-dihydropyrans **64** can be formed in moderate to good yields selectively in the presence of different Lewis acids (Scheme 2.17) [26]. In these reactions,



Scheme 2.15 Lewis acid-catalyzed reactions of bicyclic VDCPs **1** with aldehydes

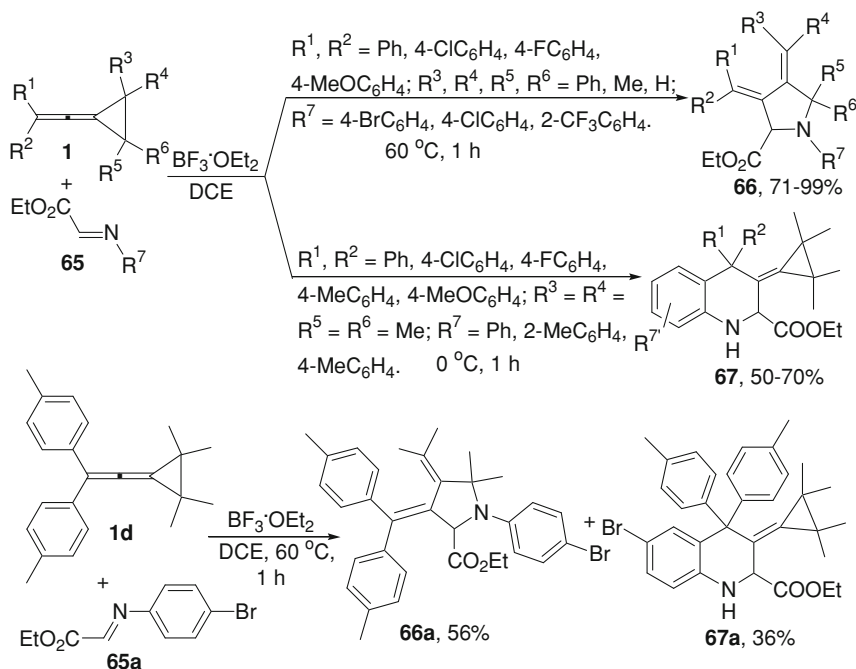


Scheme 2.16 Plausible mechanism for the Lewis acid-catalyzed reactions of bicyclic VDCPs **1** with aldehydes. Reprinted with the permission from Ref. [24]. Copyright 2011 Wiley John and Sons



Scheme 2.17 Lewis acid-catalyzed reactions of VDCPs **1** with activated carbonyl compounds. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

tetrahydrofurans **63** were obtained in 77–99% yields in the reactions of VDCPs **1** with oxo-acetic acid ethyl ester **62a** in the presence of $\text{BF}_3 \cdot \text{OEt}_2$; however, 3,6-dihydropyrans **64** were formed in 30–66% yields in the reactions of VDCPs **1** with 2-oxo-malonic acid diethyl ester **62b** in the presence of Nb(OTf)_3 .

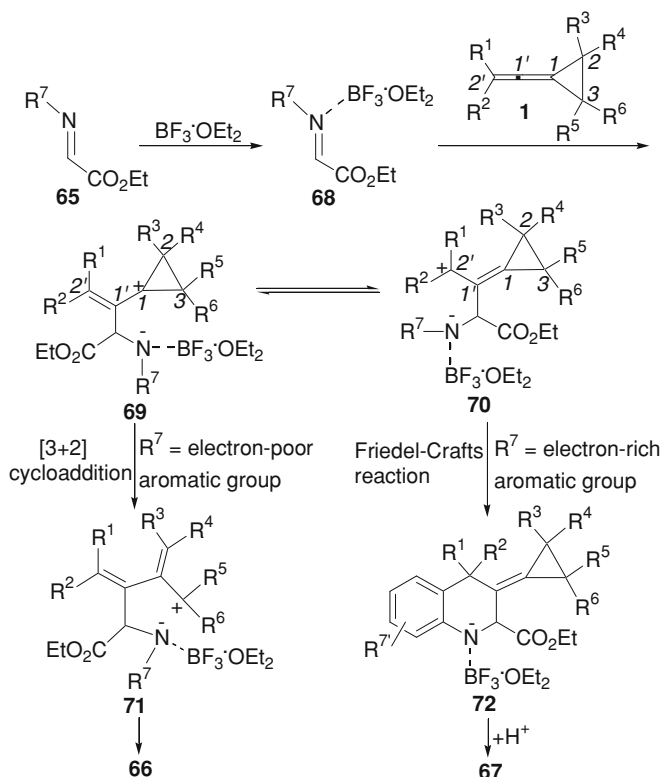


Scheme 2.18 $\text{BF}_3\cdot\text{OEt}_2$ -catalyzed reactions of VDCPs **1** with ethyl (arylimino)acetates. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

2.4 Lewis or Brønsted Acid-Mediated Reactions of VDCPs with Imines and Their Analogs

The scope of Lewis acid-catalyzed reaction of VDCPs **1** was further extended with respect to a series of ethyl (arylimino)acetates **65**, which led to a facile synthetic protocol of pyrrolidine and 1,2,3,4-tetrahydroquinoline derivatives. A number of pyrrolidine derivatives **66** and 1,2,3,4-tetrahydroquinoline derivatives **67** can be obtained selectively in moderate to good yields by the reaction of VDCPs **1** with ethyl (arylimino)acetates **65** in the presence of Lewis acid $\text{BF}_3\cdot\text{OEt}_2$ depending on the electronic nature of both **65** and R^1 or R^2 aromatic groups of **1** [1, 27–29]. Generally, when R^7 group on **65** is an electron-poor aromatic group, the pyrrolidines **66** will be formed solely; when R^7 is an electron-rich aromatic group, the 1,2,3,4-tetrahydroquinolines **67** will be obtained as the sole products. Meanwhile, if R^1 and R^2 are both electron-rich aromatic groups ($R^1 = R^2 = 4\text{-MeC}_6\text{H}_4$ as the example in this case), both of the products **66a** and **67a** can be obtained in spite of R^7 is an electron-poor or -rich group (Scheme 2.18).

Plausible mechanism for the formation of pyrrolidines **66** and 1,2,3,4-tetrahydroquinolines **67** is outlined in Scheme 2.19. First, ethyl (arylimino)acetate **65** is activated by $\text{BF}_3\cdot\text{OEt}_2$ to afford intermediate **68**, which subsequently adds to $\text{C1}'$

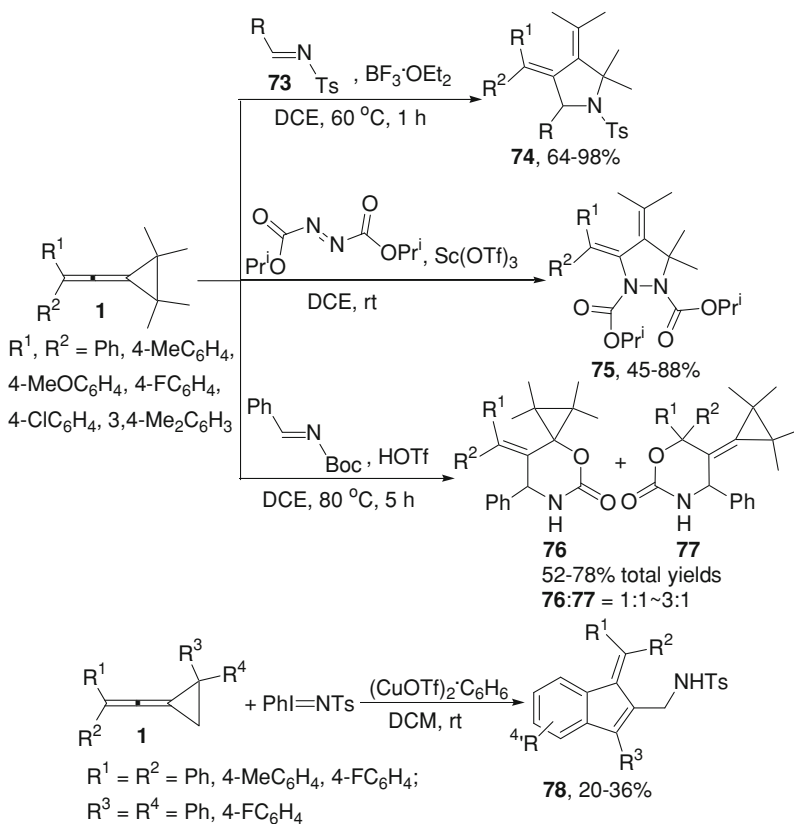


Scheme 2.19 Plausible mechanism for the $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed reactions of VDCPs **1** with ethyl (arylimino)acetates. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

position of VDCPs **1** to give the corresponding allylic carbocationic intermediates **69** and **70** [30–32]. Intermediate **71**, derived from **69** via a cyclopropyl ring-opening process, undergoes cyclization to give the corresponding [3 + 2] cycloaddition products **66** when R^7 is an electron-poor aromatic group. Alternatively, if R^7 is an electron-rich aromatic group, intramolecular Friedel–Crafts reaction takes place from intermediate **70** to give intermediate **72** [33], which finally furnishes products **67** [34–37].

During the ongoing investigations, Shi et al. found that VDCPs **1** can also react with other activated carbon–nitrogen, nitrogen–nitrogen, and iodine–nitrogen double-bond-containing compounds, such as *N*-toluene-4-sulfonyl (*N*-Ts) imines, diisopropylazodicarboxylate (DIAD), *N*-*tert*-butoxycarbonyl (*N*-Boc) aldimine, and *N*-Ts-iminophenylidiodine in the presence of Lewis or Brønsted acid to afford the corresponding cycloadducts in moderate to high yields (Scheme 2.20) [38].

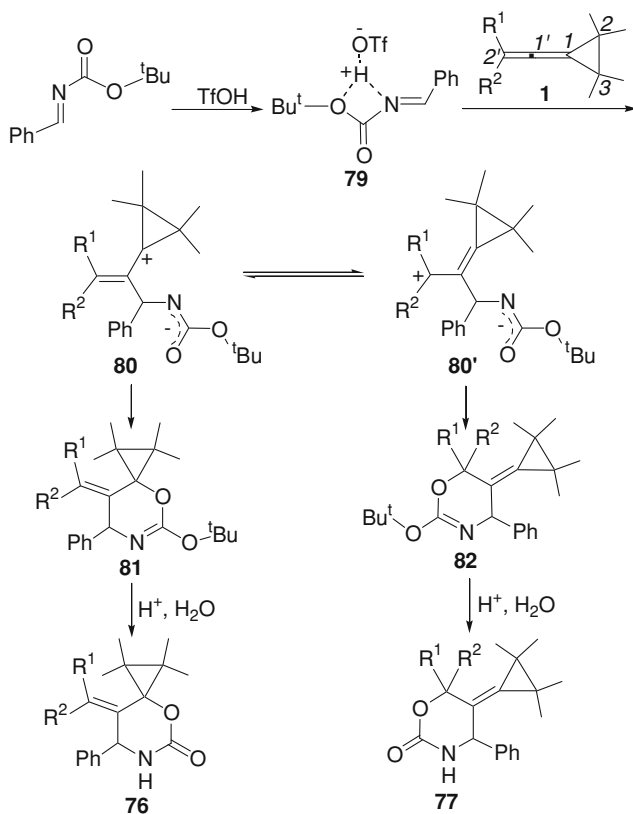
Plausible mechanism for the formation of products **76** and **77** is illustrated in Scheme 2.21. Initially, *N*-Boc aldimine is activated by Brønsted acid TfOH to give



Scheme 2.20 Lewis or Brønsted acid-catalyzed reactions of VDCPs **1** with activated carbon–nitrogen, nitrogen–nitrogen, and iodine–nitrogen double-bond-containing compounds

intermediate **79**, which subsequently adds to the C1' position of VDCPs **1** selectively to afford the corresponding intermediates **80** and **80'**. Then, ring-closure of intermediates **80** and **80'** affords intermediates **81** and **82**, respectively. Finally, hydrolysis of intermediates **81** and **82** furnishes products **76** and **77**, respectively. It was believed that cyclization of intermediates **80** and **80'** is faster than the cyclopropyl ring-opening reaction in this particular case, so the six-membered products **76** and **77** were formed instead of the [3 + 2] cycloaddition products.

Plausible mechanism for the formation of products **78** is outlined below: initially, intermediate **83** is formed by the reaction of Cu(I) with $\text{PhI}=\text{NTs}$ according to the general mechanism in the Cu(I)-catalyzed aziridination of olefin [39]. Then, the reaction of intermediate **83** with VDCPs **1** gives the ring-opened zwitterionic intermediate **84** presumably through nucleophilic attack of the cyclopropyl ring on the nitrene species. The allylic rearrangement of zwitterionic intermediate **84** produces intermediate **85**, which undergoes an intramolecular



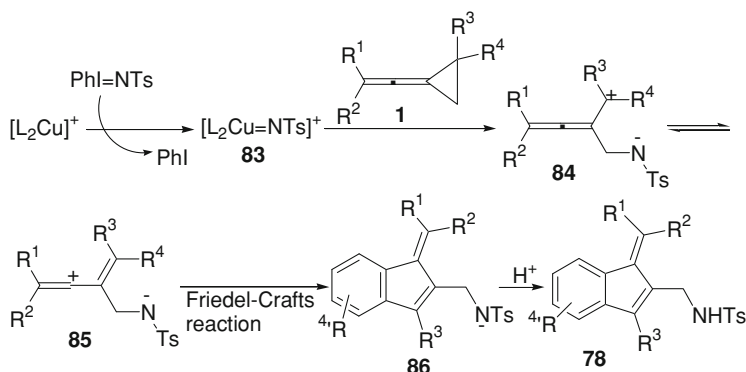
Scheme 2.21 Plausible mechanism for the TfOH-catalyzed reactions of VDCPs **1** with *N*-Boc aldimine

Friedel–Crafts reaction with the R⁴ group to generate intermediate **86**. Protonation of intermediate **86** will furnish products **78** (Scheme 2.22).

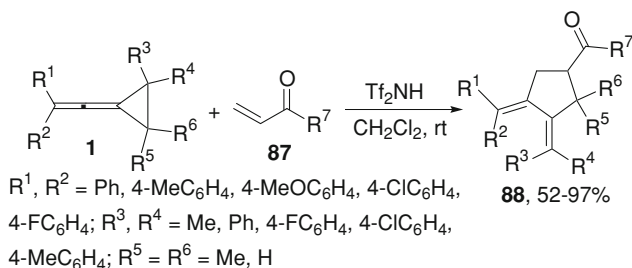
2.5 Brønsted Acid-Mediated Reactions of VDCPs with Activated Alkenes

Further studies showed that VDCPs **1** can also react with activated olefins such as α,β -unsaturated ketones (aldehyde) **87** to give the corresponding [3 + 2] cycloaddition products **88** as the major ones in moderate to high yields (Scheme 2.23) [40].

The formation of products **88** can be rationalized as below with the cycloaddition reaction of VDCP **1b** and methyl vinyl ketone (MVK) as the model: first, MVK is protonated by Tf₂NH to generate intermediate **89a**, which undergoes



Scheme 2.22 Plausible mechanism for the Cu(I)-catalyzed reactions of VDCPs **1** with N -Ts-iminophenyliodinane

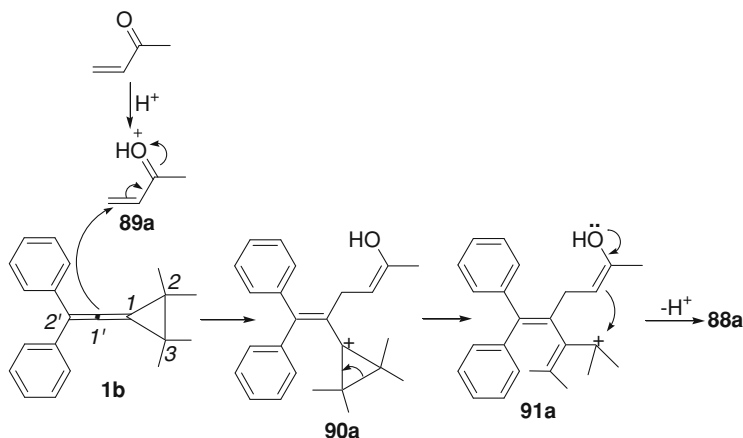


Scheme 2.23 Tf_2NH -catalyzed reactions of VDCPs **1** with activated alkenes

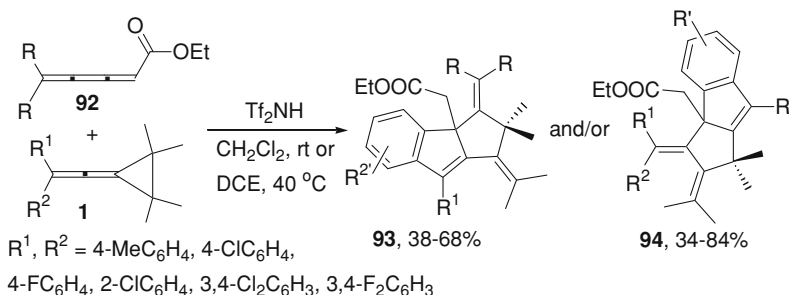
a 1,4-nucleophilic addition reaction with C1' position of VDCP **1b** to give intermediate **90a**. Subsequently, ring opening of the cyclopropyl ring in intermediate **90a** produces intermediate **91a**. Finally, products **88a** will be achieved from intermediate **91a** through intramolecular nucleophilic attack (Scheme 2.24).

In continuing research, ethyl 5,5-diarylpenta-2,3,4-trienoates **92** were also used as the reaction partner catalyzed by Brønsted acid Tf_2NH . It was found that cascade cycloaddition and Friedel–Crafts reactions of VDCPs **1** were achieved to provide a variety of novel polycyclic ester derivatives **93** and/or **94**, depending on the substituents R^1 and R^2 on VDCPs **1**, in moderate to good yields under mild conditions (Scheme 2.25) [41].

Plausible mechanism for these reactions is shown below: similarly, 5,5-diphenylpenta-2,3,4-trienoate **92a** is first protonated by the Brønsted acid catalyst Tf_2NH to produce intermediate **95a**, which will isomerize to the carbocationic intermediate **97a** via an enolate intermediate **96a**. Subsequently, VDCPs **1** undergoes a nucleophilic attack on intermediate **97a** to generate intermediate **98**, which produces intermediate **99** via the ring opening of the cyclopropyl ring. An intramolecular nucleophilic attack generates an intermediate **100**, which should

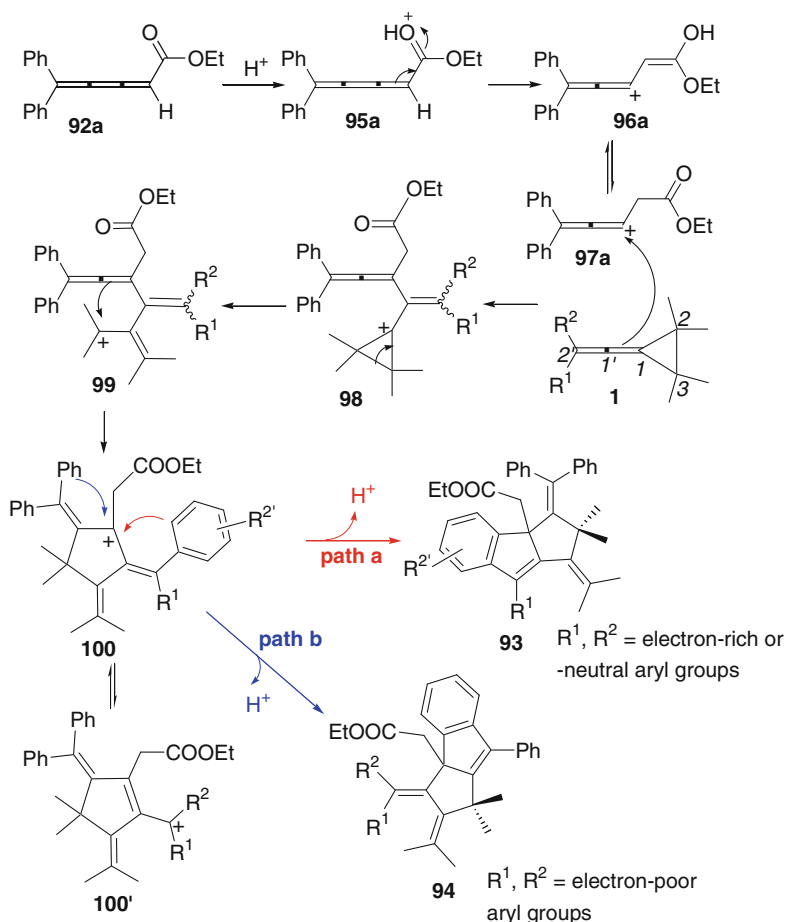


Scheme 2.24 Plausible mechanism for the Brønsted acid-catalyzed reaction of VDCP **1b** with MVK. Reprinted with the permission from Ref. [40]. Copyright 2011 American Chemical Society



Scheme 2.25 Tf_2NH -catalyzed reactions of VDCPs **1** with 5,5-diarylpenta-2,3,4-trienoates **92**

be in equilibrium with intermediate **100'** via allylic rearrangement. It is understandable that the intramolecular Friedel–Crafts reaction is favored for the electron-rich rings of intermediate **100**. Thus, there are two pathways for the intramolecular Friedel–Crafts reaction. For VDCPs **1** bearing moderately electron-donating groups on the phenyl rings or neutral phenyl ring, the intramolecular Friedel–Crafts reaction occurs on the aromatic ring of VDCPs **1** to give the products **93** since R^1 and R^2 are in larger conjugate system which can stabilize the cationic intermediate generated in the Friedel–Crafts reaction (Scheme 2.26, **path a**). On the other hand, for VDCPs **1** bearing electron-withdrawing groups on both of the phenyl rings, the intramolecular Friedel–Crafts reaction occurs on the phenyl ring of 5,5-diphenylpenta-2,3,4-trienoate **92a** to generate products **94** (Scheme 2.26, **path b**).

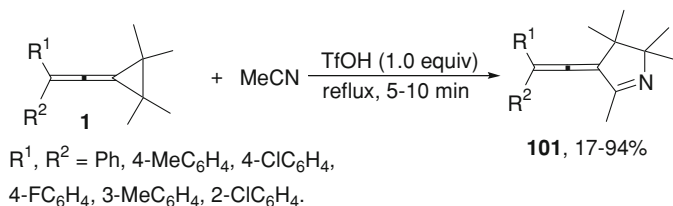


Scheme 2.26 Plausible mechanism for the Brønsted acid-catalyzed reactions of VDCPs **1** with 5,5-diphenylpenta-2,3,4-trienoate **92a**. Reprinted with the permission from Ref. [41]. Copyright 2011 Royal Society of Chemistry

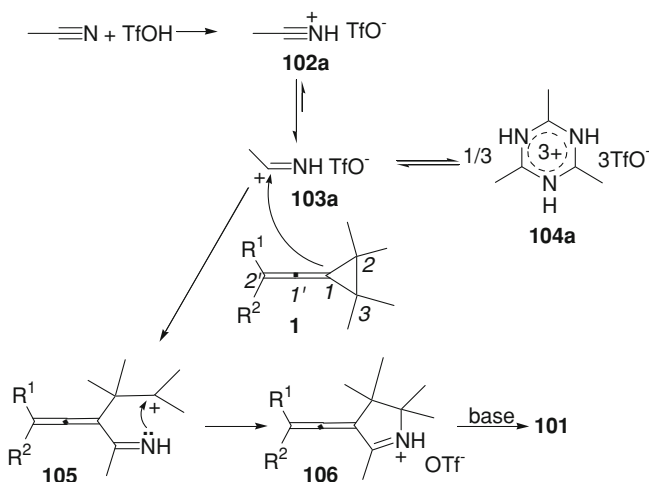
2.6 Brønsted Acid-Mediated Reactions of VDCPs with Nitriles

The Brønsted acid TfOH-catalyzed reactions of VDCPs **1** with MeCN were also investigated in Shi's group and it was reported that the [3 + 2] cycloaddition products, the 3,4-dihydro-2*H*-pyrrole derivatives **101** can be obtained in moderate to excellent yields under reflux within a short time (Scheme 2.27) [1, 42–44]. In these reactions, the four substituents on the cyclopropyl ring of VDCPs **1** should be all methyl groups.

Plausible mechanism for this transformation is outlined in Scheme 2.28. First, there is an equilibrium among intermediates **102a**, **103a**, and **104a** in the reaction



Scheme 2.27 TfOH-catalyzed reactions of VDCPs **1** with acetonitrile. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

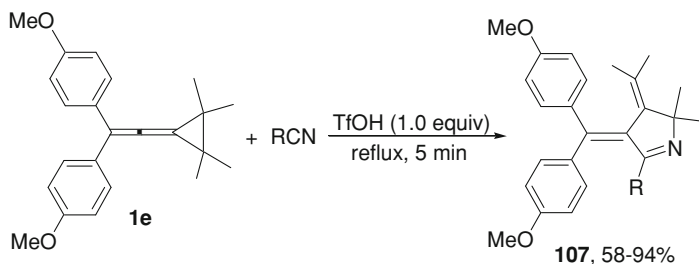


Scheme 2.28 Plausible mechanism for the TfOH-catalyzed reactions of VDCPs **1** with acetonitrile. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

of acetonitrile with TfOH according to the previous literatures [45, 46]. Intermediate **103a** undergoes an electrophilic attack to the C1 position of VDCPs **1** to afford the corresponding ring-opened cationic intermediate **105**, which undergoes the subsequent intramolecular cyclization reaction to give cationic intermediate **106**. Treatment of **106** with a base furnishes products **101**.

For strongly electron-donating 4-methoxyphenyl group substituted VDCP **1e** ($R^1 = R^2 = 4\text{-MeOC}_6\text{H}_4$, $R^3 = R^4 = R^5 = R^6 = \text{Me}$), 3,4-dihydro-2*H*-pyrrole derivatives **107** were formed in moderate to high yields under the same reaction conditions (Scheme 2.29).

Scheme 2.30 shows the plausible mechanism for this [3 + 2] cycloaddition reaction of VDCP **1e** with nitriles mediated by TfOH. Electrophilic attack of intermediate **103** to the C1' position of VDCP **1e** gives intermediate **108**, which immediately undergoes a ring-opening process to afford intermediate **109**.



Scheme 2.29 TFOH-mediated reactions of VDCP **1e** with nitriles. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

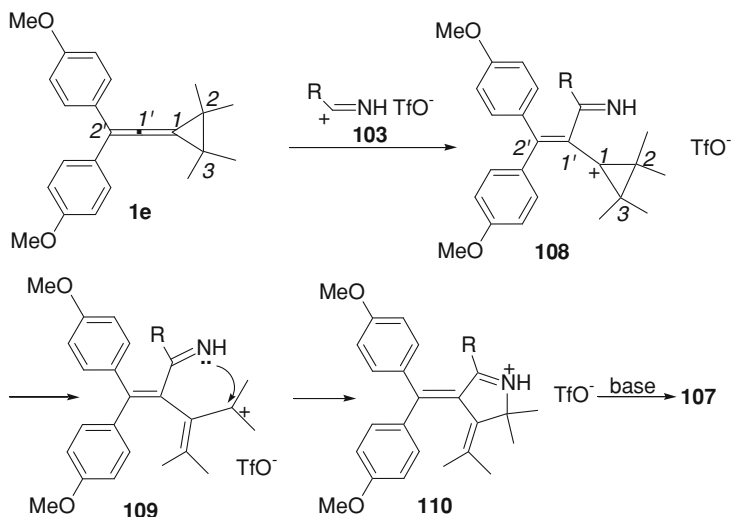
Intramolecular cyclization takes place to give intermediate **110**, which furnishes products **107** by treatment with a base. Maybe the strong electron-donating 4-methoxyphenyl group on VDCP **1e** increases the electron density at C1' position, facilitating the electrophilic attack of cationic intermediate **103**. Therefore, the reaction takes place in a different pathway.

2.7 Lewis Acid-Mediated Reactions of VDCPs with Acyl Chlorides

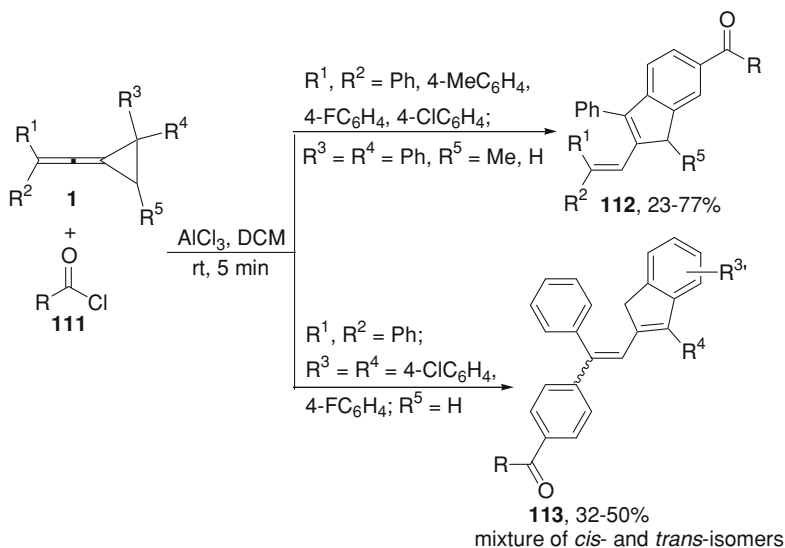
During the investigation on the Lewis acid-mediated chemistry of VDCPs **1**, it was also reported that AlCl_3 -mediated tandem Friedel–Crafts reaction of VDCPs **1** with acyl chlorides **111** afforded the corresponding products **112** or **113** in moderate to good yields under mild conditions within short reaction time (Scheme 2.31) [1, 47, 48]. The control experiment showed that products **112** and **113** can be derived from the corresponding intramolecular rearrangement products of VDCPs **1**.

2.8 Lewis Acid-Mediated Reactions of VDCPs with Alcohols or Ethers

The reactions between VDCPs **1** and 1,1,3-triarylprop-2-yn-1-ols **114** or their methyl ethers **115** in the presence of Lewis acid were also investigated in Shi's group. 4-Dihydro-1*H*-cyclopenta[*b*]-naphthalene derivatives **116** can be obtained in the reactions of VDCPs **1** with 1,1,3-triarylprop-2-yn-1-ols **114** in the presence of $\text{Zr}(\text{OTf})_4$ in DCE at $-20\text{ }^\circ\text{C}$; 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **117** can be formed in the reactions of VDCPs **1**, bearing four methyl groups on the cyclopropyl ring, with 1,1,3-triarylprop-2-yn-1-ol methyl ethers **115** in the presence of $\text{Sc}(\text{OTf})_3$ in DCE at $40\text{ }^\circ\text{C}$ (Scheme 2.32) [49].

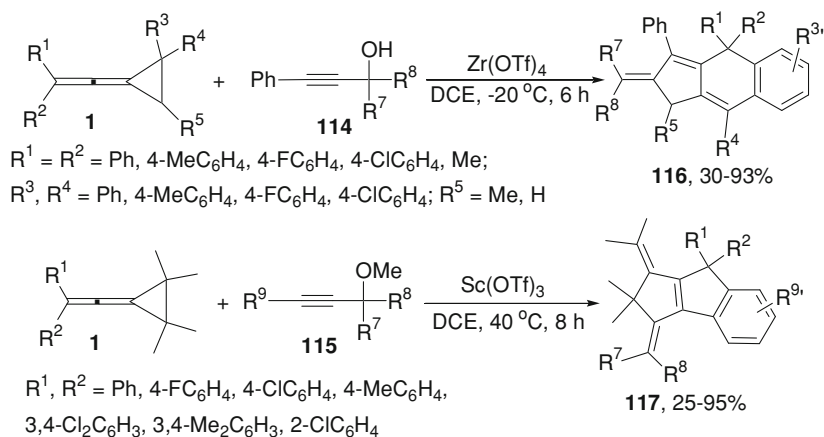


Scheme 2.30 Plausible mechanism for the $TfOH$ -mediated reactions of VDCP **1e** with nitriles. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society



Scheme 2.31 $AlCl_3$ -catalyzed reactions of VDCPs **1** with acyl chlorides. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

Plausible mechanism for the formation of products **116** and **117** is outlined below based on Meyer-Schuster rearrangement [50, 51]. In the presence of a Lewis acid,



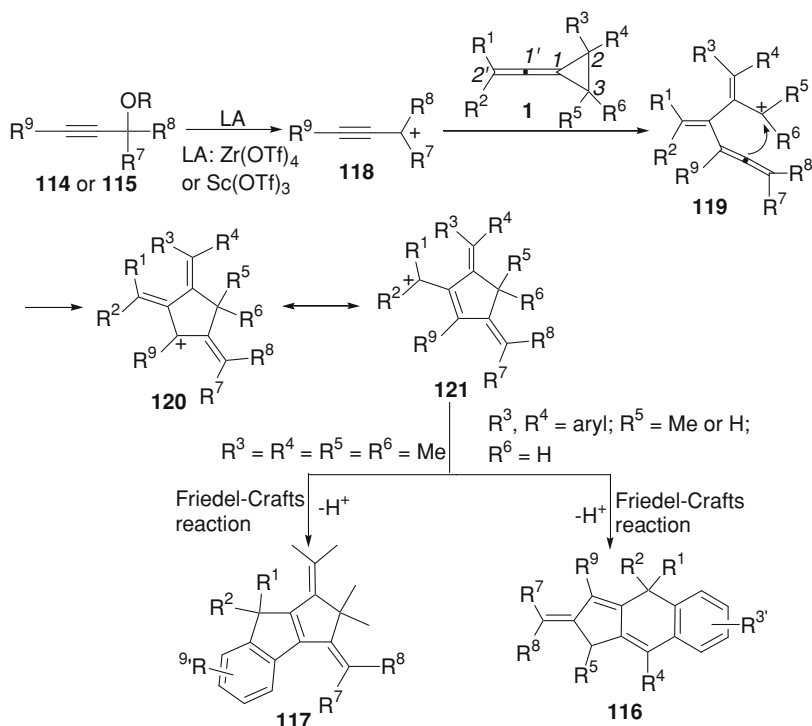
Scheme 2.32 Lewis acid-catalyzed reactions between VDCPs **1** and 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers

propargylic cation intermediate **118** is first produced from 1,1,3-triarylprop-2-yn-1-ols **114** or their methyl ethers **115**. Then nucleophilic attack of C1' position of VDCPs **1** to intermediate **118**, along with allylic rearrangement affords cationic intermediate **119**. Cyclization of intermediate **119** produces cationic intermediate **120** or its resonance-stabilized intermediate **121**. When R³ = R⁴ = R⁵ = R⁶ = Me, a Friedel–Crafts reaction with the adjacent aromatic group takes place to afford products **117**. When R³ and R⁴ are both aromatic groups, a Friedel–Crafts reaction with R³ takes place, presumably due to steric effects, to afford products **116** (Scheme 2.33). In this case, the formation of a stable cationic intermediate **118** is the key step, so when R⁷, R⁸, or R⁹ are aliphatic groups, complex mixtures of products are formed.

Moreover, it was found that for the reactions of VDCPs **1** with **114a**, in which both of R⁷ and R⁸ are 4-methoxyphenyl groups, a novel functionalized methyl-enecyclobutene derivatives **122** were achieved in moderate to high yields instead of the 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **117**. This may be because the intermediate formed, cation **123**, produces allyl cationic intermediate **124**, which can be further stabilized by two electron-rich aromatic groups, through an intramolecular proton transfer. Subsequent cyclization and deprotonation afford products **122** (Scheme 2.34).

Encouraged by these results, Shi et al. further explored such cascade electrophilic attack, followed by Friedel–Crafts reaction process of VDCPs **1** with other electrophiles such as enynols **126**. Using Nd(OTf)₃ as the catalyst, tricyclic compounds **127** can be formed in acceptable to high yields in these cases (Scheme 2.35) [52].

Plausible mechanism for the formation of tricyclic products **127a** is shown in Scheme 2.36. First, the reaction of enynol **126a** with Nd(OTf)₃ generates cationic intermediate **128a**, which can transform to its resonant cationic intermediate **129a**. The reaction of **129a** with VDCP **1b** gives the corresponding cyclopropyl

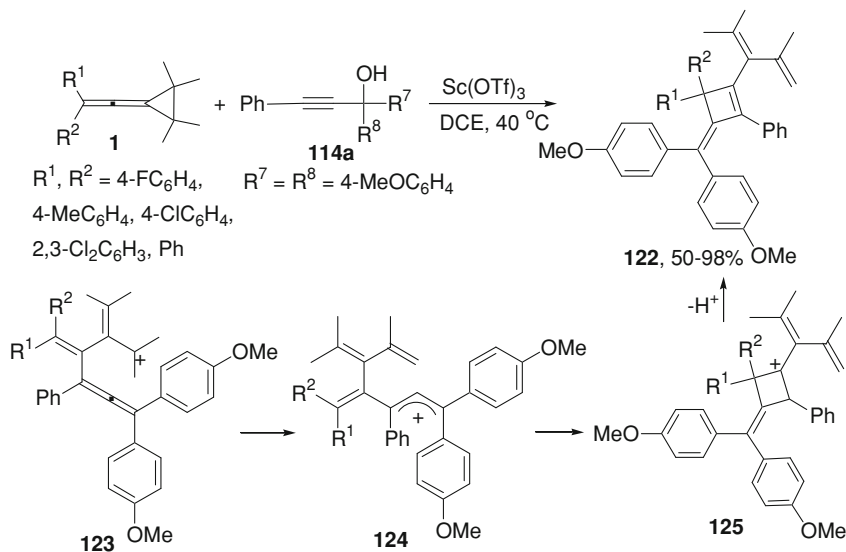


Scheme 2.33 Plausible mechanism for the Lewis acid-catalyzed reactions of VDCPs **1** with 1,1,3-triarylprop-2-yn-1-ols **114** or their methyl ethers **115**

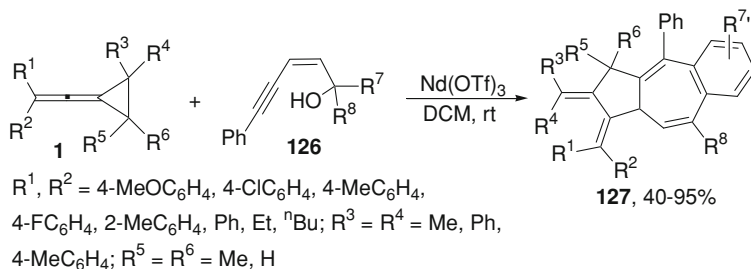
ring-opened π -allylic cationic intermediate **130a**. In this case, the reaction of intermediate **129a** with VDCP **1b** can take place more easily than that of intermediate **128a** presumably because intermediate **129a** is less sterically hindered than intermediate **128a**. Intermediate **130a**, through intramolecular electrophilic attack, affords intermediate **131a**, which undergoes intramolecular Friedel–Crafts reaction to give the final product **127a**.

The reactions were further extended to enol **132a** and dienol **133a**, and the $[3 + 2]$ cycloaddition products **134a** and **135a** were obtained with the reactions of VDCP **1b** (Scheme 2.37).

Plausible mechanism for the formation of products **134a** and **135a** is depicted below: first, treatment of **132a** or **133a** with $\text{Nd}(\text{OTf})_3$ gives cationic intermediate **136**, which will transform to its resonant intermediate **137** via allylic rearrangement. Subsequently, the reaction of intermediate **137** with VDCP **1b** affords the cyclopropyl ring-opened π -allylic cationic intermediate **138**, which can either furnish intermediate **139a** ($n = 1$) or intermediate **140a** ($n = 2$) via intramolecular electrophilic attack. Nucleophilic attack by the in situ generated H_2O at intermediate **139a** affords the final product **134a**. Alternatively, intermediate **140a** undergoes deprotonation to afford the final product **135a** (Scheme 2.38).

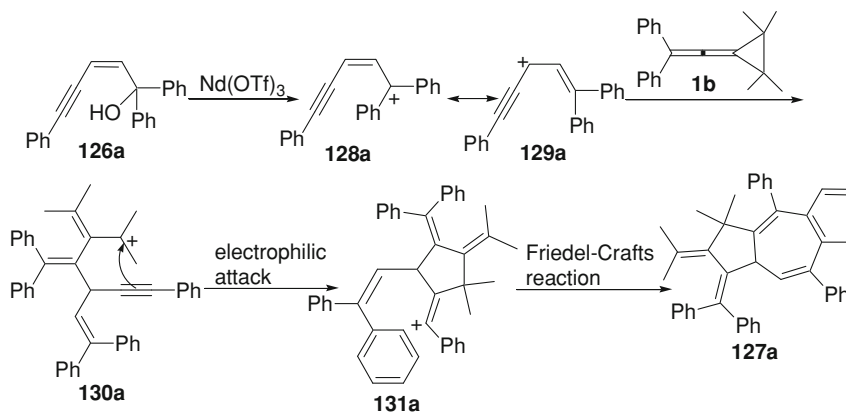


Scheme 2.34 Lewis acid-catalyzed reactions of VDCPs **1** with 1,1,3-triarylprop-2-yn-1-ol **114a**

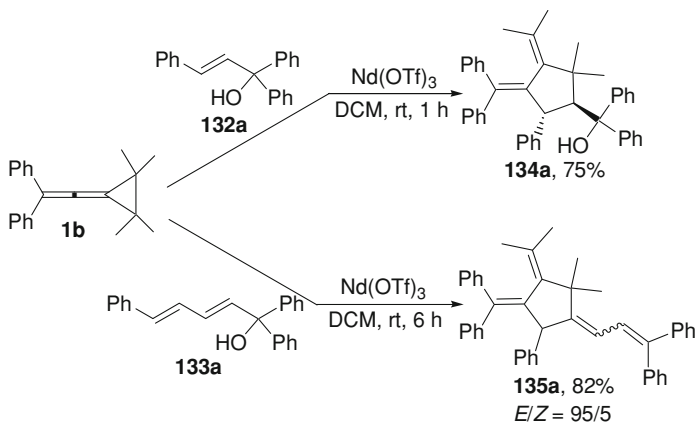


Scheme 2.35 Nb(OTf)₃-catalyzed reactions of VDCPs **1** with enynols **126**

When *N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methyl-*N*-prop-2-ynylbenzene-sulfonamides (1,6-diynes) **141** and *N*-allyl-*N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methylbenzenesulfonamides (1,6-enynes) **142** were tested as the partners, the reactions with VDCPs **1** can produce polycyclic compounds **143** and **144** as well as isopropylidene-3,3-diaryl-4-cyclobut-1-enyl-methyl derivatives **145** in good to high yields depending on the substituents on VDCPs **1** and substrates **141** and **142** [53]. For instance, Lewis acid Sn(OTf)₂ or BF₃·OEt₂-catalyzed reactions of VDCPs **1**, bearing four methyl groups on the cyclopropyl ring, with 1,6-diynes **141** and 1,6-enynes **142** can afford polycyclic compounds **143** in moderate to high yields; in particular, VDCPs **1** bearing two phenyl groups at one carbon of the cyclopropyl ring produced the corresponding polycyclic compounds **144** in



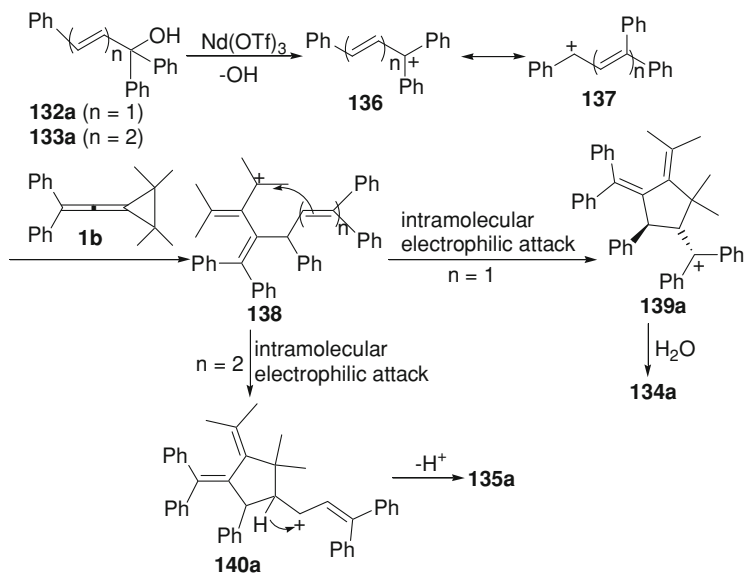
Scheme 2.36 Plausible mechanism for the $\text{Nb}(\text{OTf})_3$ -catalyzed reaction of VDCP **1b** with enynol **126a**



Scheme 2.37 $\text{Nb}(\text{OTf})_3$ -catalyzed reactions of VDCP **1b** with enol **132a** and dienol **133a**

51–60% yields. Moreover, the reactions of VDCPs **1** with substrates **141** or **142** bearing strong electron-donating substituents can give products **145** in moderate to high yields (Scheme 2.39).

Plausible mechanism for the formation of products **143** is outlined below based on a cascade rearrangement [54, 55]: Lewis acid (LA)-activating **141** or **142** will give cationic intermediate **146**, which adds to the C1' position of VDCPs **1** to afford cationic intermediate **147**. Cyclization of intermediate **147** produces



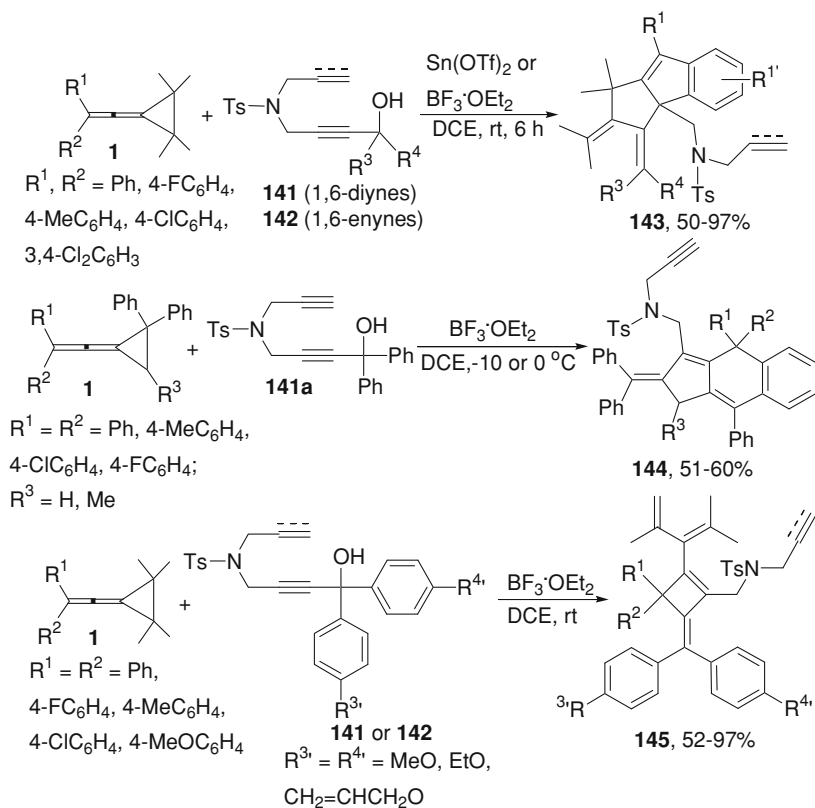
Scheme 2.38 Plausible mechanism for the Nb(OTf)_3 -catalyzed reactions of VDCP **1b** with enol **132a** and dienol **133a**

intermediate **148**, which affords intermediate **149** via the intramolecular Friedel–Crafts reaction with the adjacent aromatic R^3 group. Aromatization of intermediate **149** furnishes polycyclic compounds **143** (Scheme 2.40).

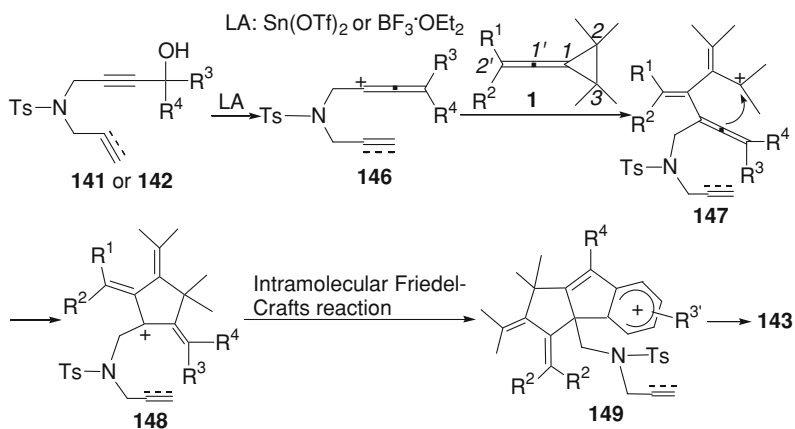
Plausible mechanism for the formation of products **144** is indicated in Scheme 2.41. Similarly, intermediates **146a**, **150** and **151** will be formed in the Lewis acid-catalyzed reactions of **141a** with VDCPs **1**. In this case, the allylic rearrangement of intermediate **151** gives intermediate **152**, which is further stabilized by the two aryl groups and undergoes intramolecular Friedel–Crafts reaction with the adjacent phenyl ring to afford products **144**. The intramolecular Friedel–Crafts reaction with the adjacent phenyl ring of intermediate **152** can take place more easily than that of intermediate **151** since the cyclic cation in intermediate **151** is a sterically tight species which should be more difficult to go through an intramolecular Friedel–Crafts reaction. This is the reason why products **144** were obtained solely in the reactions of VDCPs **1** with two phenyl groups at one carbon of the cyclopropyl ring.

In the case of strong electron-donating groups substituted **141** ($\text{R}^3 = \text{R}^4 =$ strong electron-donating phenyl rings) were used, similarly, intermediate **154** is formed firstly. Then intermediate **154** will transform to intermediate **155** via an intramolecular proton transfer, which can be stabilized by two electron-rich aromatic groups (R^3 and R^4). Finally, the intramolecular cyclization and deprotonation affords products **145** (Scheme 2.42).

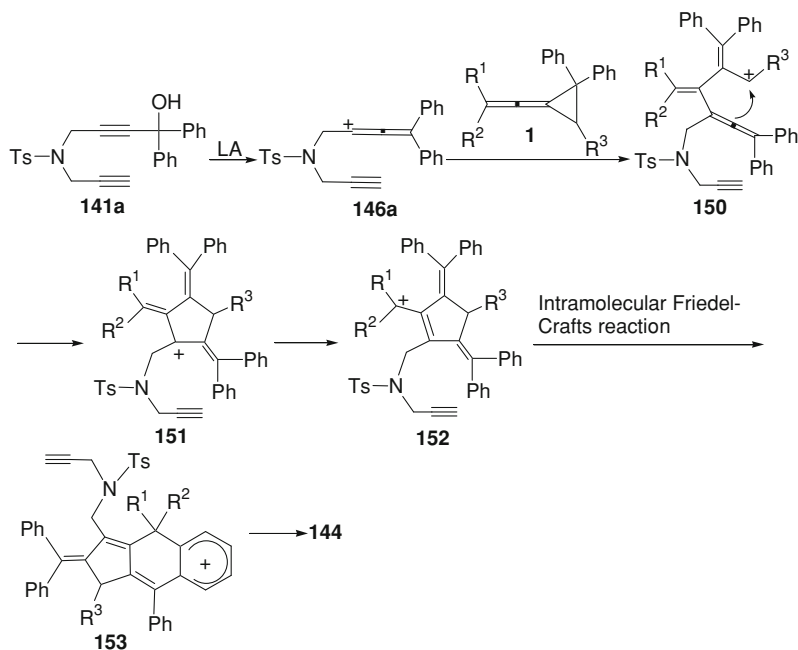
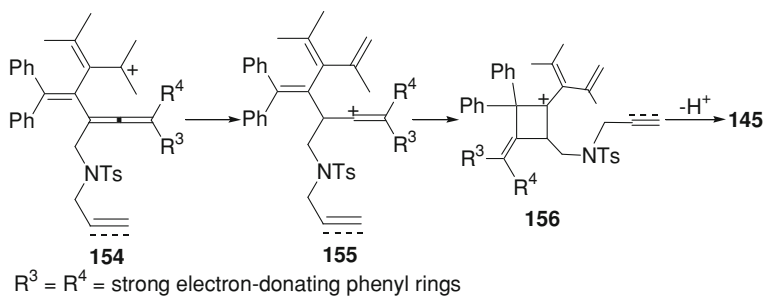
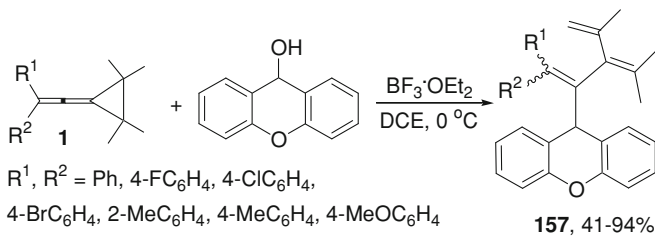
VDCPs **1** can also react with xanthidrol in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ to give the corresponding conjugated triene derivatives **157** in moderate to high yields under mild conditions (Scheme 2.43) [56, 57].

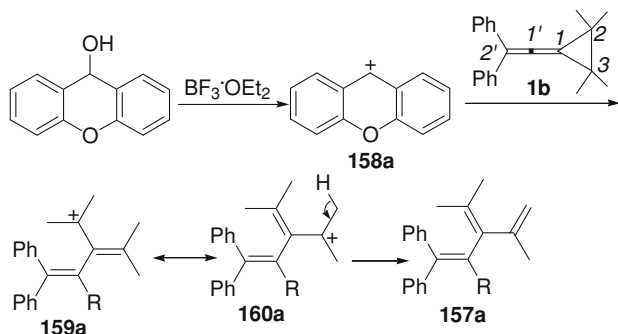


Scheme 2.39 Lewis acid-catalyzed reactions of VDCPs **1** with 1,6-diynes and 1,6-enynes

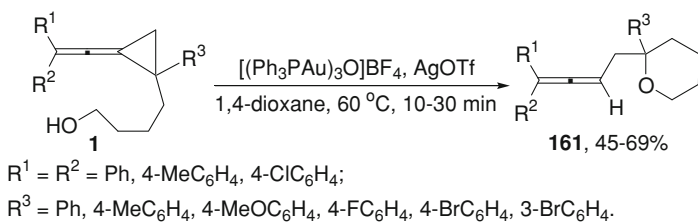


Scheme 2.40 Plausible mechanism for the formation of products **143**

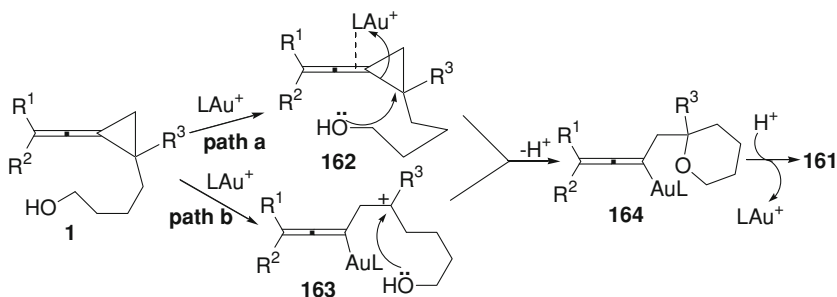
**Scheme 2.41** Plausible mechanism for the formation of products **144****Scheme 2.42** Plausible mechanism for the formation of products **145****Scheme 2.43** $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed reactions of VDCPs **1** with xanthidrol



Scheme 2.44 Plausible mechanism for the $\text{BF}_3\cdot\text{OEt}_2$ -catalyzed reactions of VDCPs **1** with xanthhydrol. Reprinted from Tetrahedron, Vol 66, Wei Yuan, Min Shi, Reactions of vinylidene-cyclopropanes with xanthhydrol and xanthenes, Pages 7104–7111, Copyright 2011, with permission from Elsevier

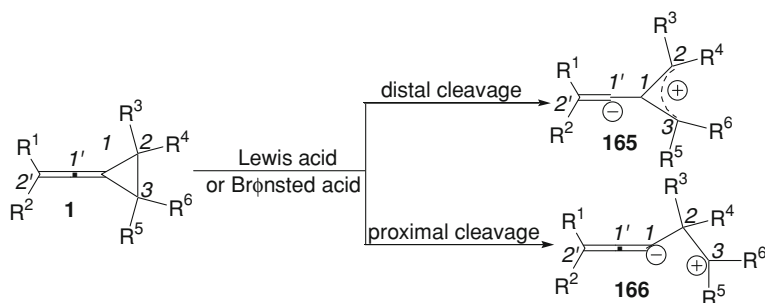


Scheme 2.45 Lewis acid-catalyzed intramolecular ring-opening reaction of VDCPs **1** tethered with alcohol chains



Scheme 2.46 Plausible mechanism for the formation of products **161**. Reprinted with the permission from Ref. [58]. Copyright 2011 American Chemical Society

Plausible mechanism for the reaction of VDCPs **1** with xanthhydrol catalyzed by $\text{BF}_3\cdot\text{OEt}_2$ is outlined in Scheme 2.44 using VDCP **1b** as the model. Initially, intermediate **158a** is formed by treatment of xanthhydrol with $\text{BF}_3\cdot\text{OEt}_2$, which adds to the C1' position of VDCP **1b** to give the cyclopropyl ring-opened resonance-



Scheme 2.47 Brief summary for the Lewis or Brønsted acid-mediated reactions of VDCPs **1**. Reprinted with the permission from Ref. [1]. Copyright 2011 American Chemical Society

stabilized intermediates **159a** and **160a** (allylic cation). Deprotonation of intermediate **160a** affords trienes **157a**.

In 2010, an intramolecular ring-opening reaction of VDCPs **1** tethered with alcohol chains was also established. With the combination of $[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ and AgOTf as the catalyst, allene-functionalized tetrahydropyrans **161** can be formed in moderate yields (Scheme 2.45) [58].

Plausible mechanism for the formation of products **161** is shown in Scheme 2.46. First, Au(I) complex is oxidized to L-Au^+ species by cocatalyst AgOTf prior to attacking VDCPs **1**. The subsequent addition/ring-opening processes can occur through two possible pathways: gold cation works as a Lewis acid to activate the allene functionality, affording intermediate **162** (path a) [59–62]; Au(I) catalyzes the ring opening via formation of cationic intermediate **163** (path b). The intramolecular nucleophilic addition by the hydroxyl group onto the electrophilic carbon centers in intermediates **162** or **163** gives the same intermediate **164**, which produces the corresponding tetrahydropyran derivatives **161** followed by protonation along with the regeneration of Au(I) species for the catalytic cycles.

In summary, the reaction course of VDCPs **1** promoted by Lewis or Brønsted acid can be categorized into the following two patterns: the distal bond and proximal bond cleavage. As can be seen from Scheme 2.47, zwitterionic ions **165** and **166** were formed with these two bond cleavage patterns. To obtain stable zwitterionic ions such as **165** and **166**, the substituents as R^3 , R^4 , R^5 , and R^6 on the cyclopropyl ring cannot be hydrogen atoms at the same time in most cases [1].

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