RSC Advances

REVIEW

View Article Online
View Journal | View Issue

Check for updates

Cite this: *RSC Adv.*, 2020, **10**, 10232

Received 10th February 2020
Accepted 4th March 2020

DOI: 10.1039/d0ra01286f

rsc.li/rsc-advances

Direct cyanation, hydrocyanation, dicyanation and cyanofunctionalization of alkynes

Lifen Peng, *[a] Zhifang Hu,[a] Hong Wang,[a] Li Wu,[a] Yinchun Jiao,[a] Zilong Tang[a] and Xinhua Xu *[b]

In this review, direct cyanation, hydrocyanation, dicyanation, cyanofunctionalization and other cyanation reactions of alkynes were highlighted. Firstly, the use of nitriles and development of cyanation was simply introduced. After presenting the natural properties of alkynes, cyanation reactions of alkynes were classified and introduced in detail. Transition metal catalysed direct cyanation and hydrocyanation of alkynes gave alkynyl cyanides and alkenyl nitriles in good yields. Dicyanation of alkynes produced 1,2-dicyano adducts. Cyanofunctionalization of alkynes afforded functional cyanated compounds. Thiocyanation and selenocyanation yielded the expected functional vinylthiocyanates and vinylselenocyanates. A plausible reaction mechanism is presented if available.

Introduction

The nitrile group, an equivalent to carbonyl, carboxyl, amino and hydroxymethyl groups, has been considered as not only a key building block in many pharmaceuticals and bioactive compounds but also an important and versatile group that can be easily transformed into various derivatives such as nitrogen-containing heterocycles, amides, amines and so on.[1] Meanwhile, nitriles, occurring in lots of natural products and important precursors for amides, amines, esters, carboxylic acids, ketones, aldehydes and alcohols, are versatile intermediates for the preparation of pharmaceuticals, pesticides and organic materials.[2] For example, acrylonitrile[3] is an important monomer for manufacture of plastics, rubbers, fiber, agrochemicals and pharmaceutical, while cyanamides[4] have been widely used as ambidentate ligands in coordination chemistry. Nitriles could be readily obtained by traditional cyanation reactions including Sandmeyer reaction, Rosenmund-von Braun reaction, and other transition-metal[5] catalyzed cyanation reactions applying metal cyanides or metalloid cyanides as cyanide source.[6] But these above protocols usually used toxic metal cyanation reagents and also required prefunctionalization of these cyanation reagents.[7] According to the *12 principles of green chemistry*,[8] a green chemical process should avoid the use of toxic reagents. Thus, many less toxic or green cyanation reagents were discovered, including safe reagent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[9] benzyl cyanide,[10] acetonitrile,[11] *N*,*N*-dimethylformamide (DMF),[12] azobisisobutyronitrile (AIBN),[13] trimethylsilylcyanide (TMSCN),[14] ary(cyano)iodonium triflates,[15] *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS),[16] bis(dialkylamino)cyanoboranes,[17] malononitrile,[18] and so on.

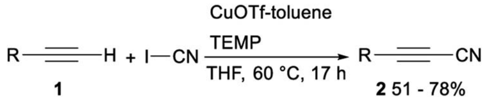
Alkynes are fundamentally useful unsaturated compounds which are omnipresent in many natural products, and pharmaceuticals, agrochemicals and organic materials because of their unique physical, chemical and biological properties.[19] And inherently nucleophilic alkynes are also important intermediates in organic synthesis for preparation of biological active compounds and organic functional compounds used in organic field-effect transistors, organic light-emitting diodes, liquid crystals and dye-sensitised solar cells.[20] Direct cyanation, hydrocyanation, dicyanation and cyanofunctionalization of alkynes, useful protocols for synthesis of interesting nitriles such as acrylonitriles, alkynyl cyanides, dicyano-substituted and cyanofunctionalized derivatives, have attracted more and more attention.[21] In this review, direct cyanation, hydrocyanation, dicyanation and cyanofunctionalization of alkynes are presented. Numerous less toxic or green cyanation reagents are efficient for direct cyanation, hydrocyanation, dicyanation and cyanofunctionalization of alkynes.

Direct cyanation and hydrocyanation of alkynes

In 2013, Okamoto and Ohe reported copper catalysed cyanation of terminal alkynes with cyanogen iodide (ICN). When CuOTf-toluene was applied as a catalyst and tetramethylpiperidine (TEMP) was used as a base, direct cyanation of terminal acetylene **1** with ICN proceeded smoothly and gave the desired alkynyl cyanides **2** in moderate to good yields (Scheme 1).[22]

[a]Key Laboratory of Theoretical Organic Chemistry and Functional Molecule of Ministry of Education, Hunan Provincial Key Laboratory of Controllable Preparation and Functional Application of Fine Polymers, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, P. R. China. E-mail: 1060137@hnust.edu.cn

[b]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China



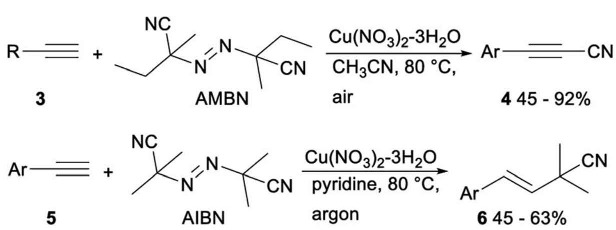
Scheme 1 Copper catalysed cyanation of terminal alkynes with ICN.

Cu-catalyzed direct cyanation of terminal alkynes with AMBN (azobisisoamylonitrile) or AIBN (azobisisobutyronitrile) was demonstrated by Mao and Xu in 2015. As shown in Scheme 2, the desired alkynyl cyanides **4** were obtained in 45–92% yield when terminal acetylene **3** was treated with AMBN and $Cu(OAc)_2$ in acetonitrile at 80 °C under air. While under argon atmosphere, the direct cyanation of terminal alkynes **5** with AIBN occurred and gave the desired addition products isobutyronitriles **6** in moderate yields. The above direct cyanation reactions of terminal alkynes with AMBN or AIBN had remarkable advantages including a less toxic cyanation reagent and wide substrate scope.[23]

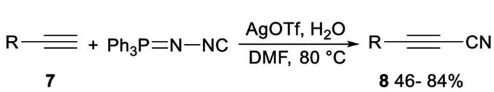
Silver-mediated direct cyanation of terminal alkynes for the synthesis of propionitrile derivatives had been achieved by Wang and Bi. Direct cyanation reaction of terminal alkynes **7** with *N*-isocyanoiminotriphenylphosphorane (NIITP) in the presence of a quantitative amount of AgOTf in DMF produced propionitriles **8** in moderate to good yields (Scheme 3).[24]

A plausible mechanism for this cyanation reaction was shown in Scheme 4, firstly, ethynylbenzene reacted with AgOTf to generate the silver acetylide ***A***. Then, an acetylenic imido complex ***B*** was produced by insertion of NIITP into the silver–carbon bond of ***A***. Finally, the complex ***B*** converted to target 3-phenylpropiolonitrile with the release of AgOH and triphenylphosphine azaylide. This procedure, applying NIITP as a nontoxic, facile "CN" source, was characterized by its operational simplicity, high efficiency with excellent yields, broad substrate scope, and greater functional group tolerance.[24]

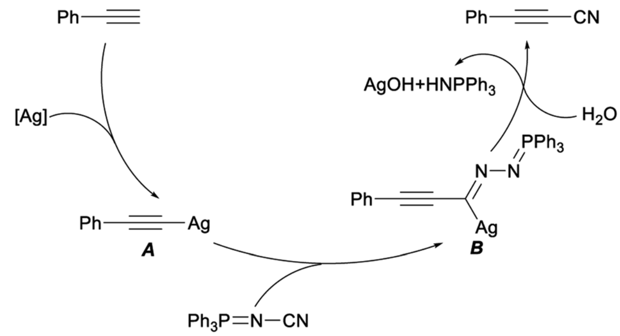
In addition, copper-catalyzed direct cyanation of terminal alkynes with benzoyl cyanide was reported by Li in 2018. This protocol using less toxic, stable and easy to handle benzoyl cyanide as a cyanide source and air as an oxidant provided



Scheme 2 Cu catalysed direct cyanation of terminal alkynes with AMBN or AIBN.



Scheme 3 Silver-mediated direct cyanation of terminal alkynes.

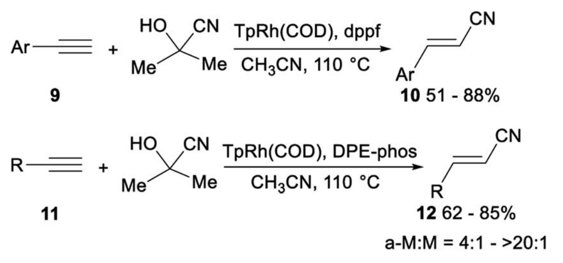


Scheme 4 Plausible mechanism for silver-mediated direct cyanation of terminal alkynes.

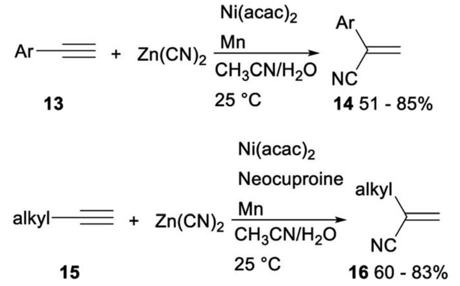
a good alternative to the preparation of 3-arylpropiolonitriles under mild condition.[25]

The first highly stereo- and regioselective hydrocyanation of terminal alkynes with acetone cyanohydrin was reported by Ritter. Treatment of aromatic terminal alkynes **9** with acetone cyanohydrin, dppf, and TpRh(COD) (Tp = (tris(1-pyrazolyl) borohydride)) in CH_3CN and heating at 110 °C afforded the desired anti-Markovnikov alkenyl nitriles **10** in 51–88% yield without the formation of Markovnikov product. Instead of dppf, DPE-phos enabled facile hydrocyanation of aliphatic terminal alkynes with acetone cyanohydrin. Mixing of aliphatic terminal alkynes **11**, acetone cyanohydrin, DPE-phos, and TpRh(COD) (Tp = (tris(1-pyrazolyl)borohydride)) in CH_3CN and heating at 110 °C afforded the desired alkenyl nitriles **12** in 62–85% yield with the ratio of anti-Markovnikov products (a-M) to Markovnikov products (M) from 4 : 1 to >20 : 1 (Scheme 5).[26]

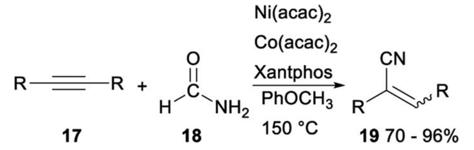
The first efficient and general nickel catalysed hydrocyanation of terminal alkynes with $Zn(CN)_2$ was developed by Liu in 2018. When water was used as a hydrogen source, $Ni(acac)_2$ was applied as a catalyst and Mn was employed as an additive, hydrocyanation of terminal aryl alkynes **13** with $Zn(CN)_2$ proceeded smoothly to afforded the desired Markovnikov addition products **14** in moderate to good yields. Under the above standard reaction conditions of aryl alkynes, the hydrocyanation reactions of terminal aliphatic alkynes with $Zn(CN)_2$ did not proceed completely. While addition of neocuproine as ligand finished the desired functionalized vinyl nitriles **16** in 60–83% yields (Scheme 6). This protocol, avoiding use of the volatile and hazardous reagent like HCN, offered



Scheme 5 Stereo- and regioselective hydrocyanation of terminal alkynes with acetone cyanohydrin.



Scheme 6 Nickel catalysed hydrocyanation of terminal alkynes with $Zn(CN)_2$.



Scheme 8 Ni mediated hydrocyanation of alkynes.

a regioselective method for preparation of functionalized vinyl nitriles with a range of structural diversity under mild reaction conditions.[27]

A reaction mechanism for the above hydrocyanation of terminal alkynes with $Zn(CN)_2$ was tentatively propose. As depicted in Scheme 7, firstly, reduction of $Ni(acac)_2$ with Mn formed Ni(0) species. Then Ni(II) intermediate ***C*** was generated by oxidative addition of water to Ni(0). The alkenyl nickel complex ***D*** was produced by insertion of alkyne to ***C*** *via cis*-addition of Ni–H bond (hydronickelation). Possibly, the stability of the alkenyl nickel species influenced the regioselectivity of this step. The desired nitriles was formed *via* transmetalation of ***D*** with $Zn(CN)_2$ followed by reductive elimination. Alternatively, the same intermediate ***D*** could be also afforded by reaction of nickel π-alkyne complex ***F*** with H_2O. The detailed process for this transformation was not clear yet, it may proceed through oxidative addition of water with ***F*** or cleavage of nickelacyclopropene intermediate ***G*** by water.[27]

In 2019, Yang and Chang reported the first example of Ni-mediated dehydration of formamide to form "CN" and its subsequent catalytic applications in the hydrocyanation of alkynes (Scheme 8). Treatment of acetylenes **17** and formamide with $Ni(acac)_2/Co(acac)_2$/Xantphos catalytic system gave the corresponding acrylonitriles **19** in 70–96%. The above reaction generated "CN" unit from readily available nontoxic organic precursors *via* nickel catalysis, was an efficient protocol for synthesis of vinyl nitriles.[28]

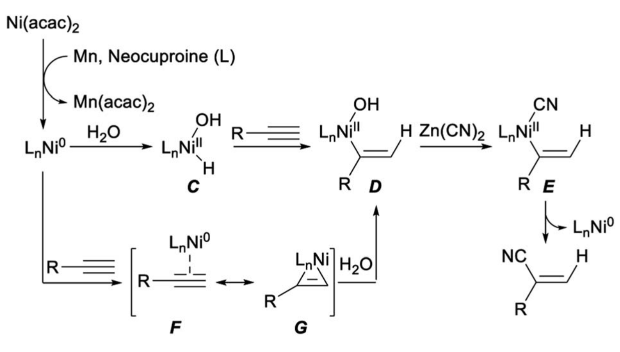
In the same year, Lan and Xiao demonstrated the first asymmetric propargylic radical cyanation *via* a synergetic photoredox/copper catalysis strategy. After irradiating acetylenes **20** and trimethylsilyl cyanide (TMSCN) with visible light (2 × 3 W, purple LEDs, 390 nm) for 24 h in the presence of organic photocatalyst Ph-PTZ, catalyst $Cu(MeCN)_4BF_4$ and chiral bisoxazoline (box) ligand L′, the desired propargyl cyanide products **21** was detected in moderate to excellent yields with 83–98% ee. The above strategy, providing an unprecedented access to optically enriched propargyl cyanides with generally high reaction efficiency and enantioselectivity under mild conditions, not only offered a new way for catalytic asymmetric propargylic functionalization, but also provided a novel dual catalysis system for visible-light-induced asymmetric chemical bond formation (Scheme 9).[29]

Dicyanation of alkynes

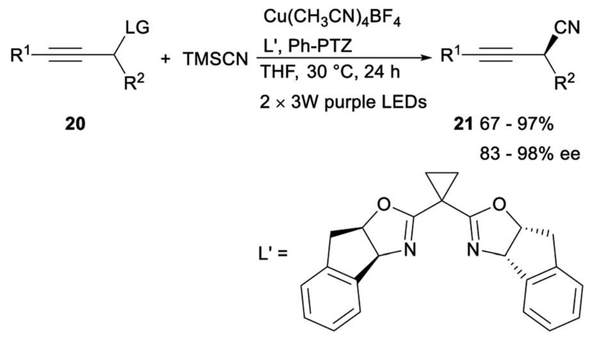
In 2009, Arai reported a palladium(II) catalysed stereoselective 1,2-dicyanation of various alkynes with TMSCN under aerobic conditions. Treatment of alkynes **22** with $PdCl_2$, TMSCN and O_2 in toluene gave the corresponding 1,2-dicyano adducts **23** in 50–82% yields (Scheme 10).[30]

The same research group investigated palladium catalysed dicyanative [4 + 2] cycloaddition of various ene–enynes. As shown in Scheme 11, $Pd(CN)_2$ catalysed 1,2-dicyanation of alkynes **24** with TMSCN in toluene under O_2 proceeded smoothly and gave a mixture of *cis*- and *trans*-adducts or trans only adducts **25** in 56–78% yields.[31]

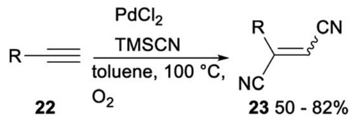
Palladium catalysed dicyanation of carbon–carbon triple bonds under aerobic conditions was also investigated. As shown in Scheme 12, subjection acetylenes **26** to $PdCl_2$ or $Pd(CN)_2$ catalysed dicyanation with TMSCN gave the corresponding products **27** in moderate to good yields.[21c] This above simple and basic method provided a new approach to 1,2-dicyano olefin.



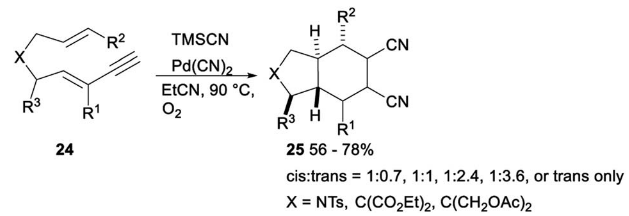
Scheme 7 Plausible mechanism for nickel catalysed hydrocyanation of terminal alkynes with $Zn(CN)_2$.



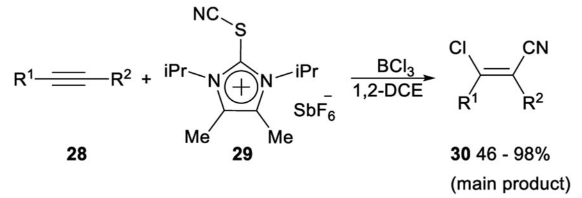
Scheme 9 Asymmetric propargylic radical cyanation.



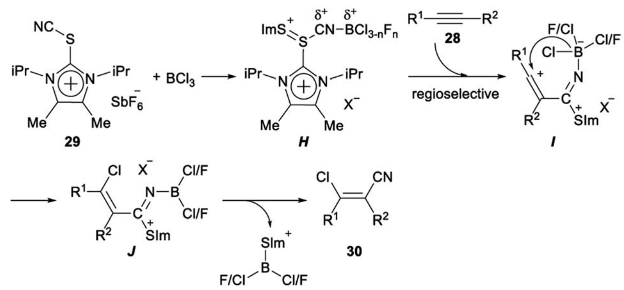
Scheme 10 Palladium(II) catalysed stereoselective 1,2-dicyanation of alkynes.



Scheme 11 Palladium catalysed dicyanative [4 + 2] cycloaddition of ene–enynes.



Scheme 13 Regio- and stereoselective chlorocyanation of alkynes.



Scheme 14 Plausible mechanism of chlorocyanation of alkynes.

Cyanofunctionalization of alkynes

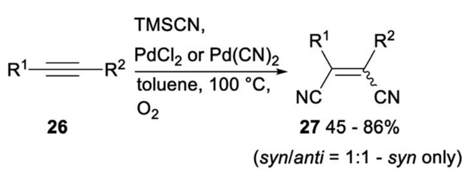
Regio- and stereoselective chlorocyanation of alkynes was reported by Alcarazo in 2017. The reaction of alkynes **28** with thioimidazolium salt **29** in the presence of boron trichloride (BCl_3) was able to provide the desired product **30** in moderate to excellent yields. The stereo- and regioselectivity observed in the above transformation was remarkable. The cyanide group was exclusively incorporated at the unsubstituted carbon atom of terminal alkynes, or at the alkyl-substituted carbon atom of 1-aryl-2-alkyl alkynes. This regioselectivity is typical for an electrophilic mechanism. In both cases, only the *Z* isomer was formed, thus suggesting a *syn*-addition pathway for the reaction (Scheme 13).[32]

The following mechanism for the chlorocyanation reaction was proposed. Initially, Lewis adduct ***H*** which was already partially fluorinated at boron was formed by activation of the cyanating reagent **29**. Vinyl cation ***I*** was generated by regioselective attack of H to the corresponding alkyne **28**. The *syn* transfer of one chloride from boron to the carbocationic center gave iminoborane ***J***, which then produced the desired chlorocyanated products **30** by elimination of the imidazolium–thioborane fragment (Scheme 14).[32]

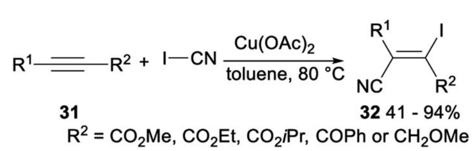
Okamoto and Ohe investigated copper catalysed regio- and stereoselective iodocyanation of alkynes with cyanogen iodide. Subjection of alkyne **31** to $Cu(OAc)_2$ catalysed iodocyanation with ICN afforded the desired iodocyanoalkene **32** in 41–94% (Scheme 15). This reaction, including diiodide formation, selective monocyanation, and second cyanation processes, shew high regio- and stereoselectivity.[33]

In 2016, Chien demonstrated CuI catalysed intramolecular aminocyanation of terminal alkynes. A series of 1-sulfonyl-3-cyanoindoles **34** was obtained in 53–83% yields when aminocyanation ring closure of *N*-(2-ethynylphenyl)-*N*-sulfonylcyanamides **33** was carried out in 1,4-dioxane with CuI as the catalyst, and Na_2CO_3 as the base under argon at 80 °C, and the reaction could be completed within 3 hours (Scheme 16).[34]

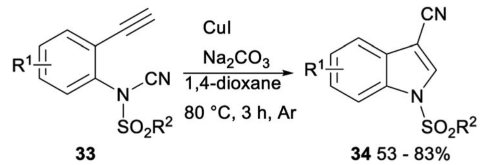
The plausible mechanism was proposed (Scheme 17). First, p-coordination of alkyne and nitrile moieties to the copper centre was occurred to form a substrate–copper complex ***K***. Subsequently, the *N*-tosyl-2-alkynylanilide cyanocopper complex ***L*** was obtained through the heterolytic cleavage of the N–CN bond by the migration of the electrophilic cyano group to the copper centre. Transaminometalation of ***L*** across the alkyne and the following cyanation produced the desired 1-tosyl-3-cyanoindoles **34** *via* the intermediary of the 1-tosylindol-3-yl cyano–copper complex ***M***. Another plausible mechanism was also proposed to start with the formation of Cu–acetylide ***N*** with the increase of π-electron density at the β-carbon. The β-cyano Cu–vinylidene complex ***O*** was formed *via* intramolecular nucleophilic attack of the β-carbon to the electrophilic cyanamide carbon accompanied by the N–CN bond cleavage. ***M*** was afforded by intramolecular nucleophilic attack of the remaining tosyl amide at the α-carbon of the Cu–vinylidene complex ***O***.



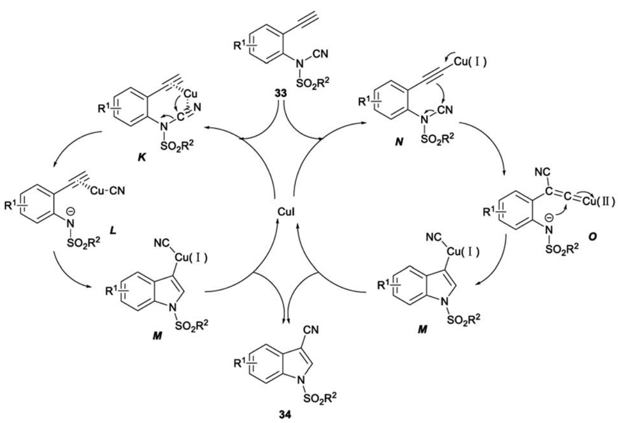
Scheme 12 Palladium catalysed dicyanation of carbon–carbon triple bonds.



Scheme 15 Regio- and stereoselective iodocyanation of alkynes.



Scheme 16 CuI catalysed intramolecular aminocyanation of terminal alkynes.

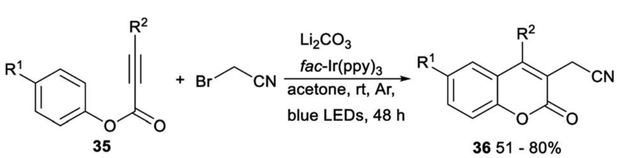


Scheme 17 Plausible mechanism of intramolecular aminocyanation of terminal alkynes.

Protonation of ***M*** furnished the desired product **34** and regained the Cu(I) catalyst to continue the catalytic cycle.[34]

A visible-light-mediated direct cyanomethylation of aryl alkynoates for synthesis of 3-cyanomethylated coumarins was demonstrated by Li in 2018. In the presence of fac-Ir(ppy)$_3$ as a photocatalyst and $NaHCO_3$ as a base under blue-light irradiation in acetone at room temperature, direct cyanomethylation of aryl alkynoates **35** with 2-bromoacetonitrile proceeded smoothly to afford the desired 3-cyanomethylated coumarins **36** in moderate to good yields. This reaction, using cheap and easily available bromoacetonitrile as the cyanomethylation reagent, provided a new method for synthesis of 3-cyanomethylated coumarins (Scheme 18).[35]

A possible reaction mechanism for the above cyanomethylation was propose. Firstly, fac-Ir(III)(ppy)$_3$ was irradiated to the excited state [fac-Ir(III)(ppy)$_3^*$], which was then oxidatively quenched by $BrCH_2CN$ with the formation of a [fac-Ir(IV)(ppy)$_3$]$^+$ complex and a highly reactive radical ***P***. The radical intermediate ***Q***, generated by addition of radical ***P*** to the triple bond of aryl alkynoates **35**, underwent intramolecular spirocyclization and gave the spiroradical intermediate ***R***. The coumarin radical ***T*** was generated by selective ester migration *via* a carboxyl radical ***S***. Then, oxidation of ***T*** by [fac-Ir(IV)(ppy)$_3$]$^+$ formed the cyclohexadienyl cation ***U*** and regenerated fac-Ir(III)(ppy)$_3$. Finally, the desired product **36** was produced by deprotonation of ***U*** assisted by the base (Scheme 19).[35]

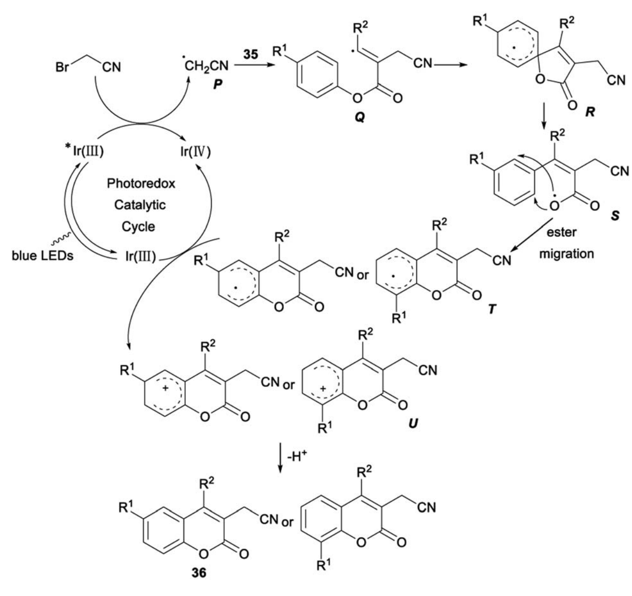


Scheme 18 Cyanomethylation of aryl alkynoates.

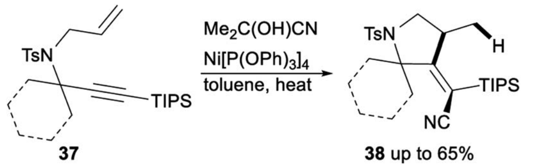
Nickel catalysed carbocyanative cyclization of 1,6-enynes was described by Arai (Scheme 20). When acetone cyanohydrin was used as an inexpensive and easy-to-handle HCN source and Ni[P(OPh$_3$)]$_4$ was applied as a catalyst, carbocyanative cyclization of 1,6-enynes **37** proceeded smoothly in toluene and gave the corresponding products **38** in moderate yields.[36]

Sc(OTf)$_3$ catalysed formal acylcyanation of electron-rich alkynes for synthesis of fully-substituted acrylonitriles was investigated by Zhao and Sun in 2018. The formal acylcyanation of electron-rich alkynes **39** with cyanide **40** proceeded smoothly in the presence of Sc(OTf)$_3$ in $CHCl_3$ under N_2 and gave the corresponding ynamides, thioalkynes or ynol ethers **41** in moderate to excellent yields with remarkable *Z* selectivity. This reaction, featuring mild conditions, high regio- and stereo-selectivity, and a broad scope, offered an efficient protocol to fully-substituted acrylonitriles (Scheme 21).[37]

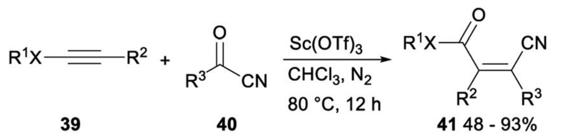
A plausible mechanism for the above formal acylcyanation was proposed in Scheme 22. Sc(OTf)$_3$ could serve to activate the acylnitrile by lowering its LUMO level, thereby increasing its electrophilicity and giving intermediate ***V***. The β-carbon of the ynamide attacked the carbonyl of ***V*** followed by cyclization (*i.e.*, [2 + 2] cycloaddition) to form the oxetane intermediate ***W*** with high regioselectivity because of the high polarization of the alkyne. The desired product **42** was produced by the subsequent electrocyclic opening of the oxetane ***W***. Conrotatory torquoselection in the ring-opening process governed the *syn* selectivity. During the conrotatory ring opening, the CN group rotates inward, so that its π* orbital can favourably interact with the breaking σ(C–O) orbital, thus preferentially delivering the (*Z*)-olefin product.[37]



Scheme 19 Plausible mechanism for cyanomethylation of aryl alkynoates.



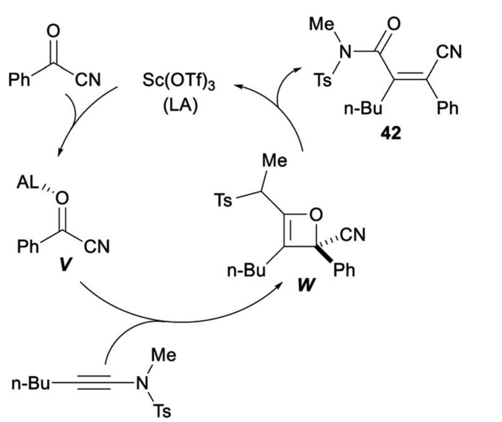
Scheme 20 Carbocyanative cyclization of 1,6-enynes.



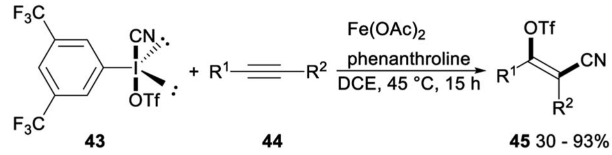
Scheme 21 $Sc(OTf)_3$ catalysed formal acylcyanation of electron-rich alkynes.

Regio- and stereoselective cyanotriflation of alkynes using aryl(cyano)iodonium triflates was reported by Studer in 2016. When 3,5-di(trifluoromethyl)-phenyl(cyano)iodonium triflate **43** was used as the triflate and cyanide source, $Fe(OAc)_2$ in combination with phenanthroline as the catalyst, direct vicinal alkyne cyanotriflation of alkynes **44** occurred with regioselective *syn*-addition of both the CN and OTf groups of **43** to alkynes **44** to give the desired tetrasubstituted alkenes **45** in moderate to excellent yields. This cyanotriflation of alkynes possessed some advantages such as mild conditions, complete regioselectivity, excellent stereoselectivity, and a wide range of functional groups tolerances. And products tetrasubstituted alkenes were useful building blocks in a series of stereospecific palladium catalysed cross-coupling reactions such as Suzuki coupling, Sonogashira reaction and a Buchwald–Hartwig amidation (Scheme 23).[38]

The CuCN-mediated cyclization–cyanation reactions of β-hydroxyalkynes and *o*-alkynylphenol and -aniline derivatives was developed by Pyne. Treatment of β-hydroxyalkynes or *o*-alkynylphenol or -aniline derivatives **46** or **48** with CuCN in DMF afforded the desired 3-cyanobenzofurans **47** or 3-cyanoindoles **49** in moderate to good yields, respectively (Scheme 24).[39]



Scheme 22 Plausible mechanism for $Sc(OTf)_3$ catalysed formal acylcyanation of alkynes.



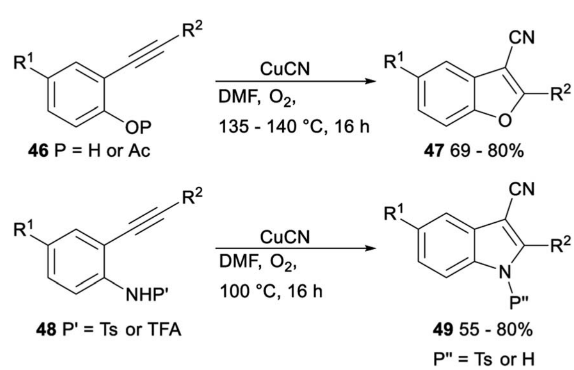
Scheme 23 Regio- and stereoselective cyanotriflation of alkynes.

In 2012, Hiyama demonstrated nickel/Lewis acid catalysed polyfluoroarylcyanation of alkynes. When $Ni(cod)_2$ was used as a catalyst and DPEphos/BPh_3 was employed as a ligand, polyfluoroarylcyanation of polyfluorobenzonitriles **50** with 4-octyne proceeded smoothly and produced the desired adducts **51** in excellent yields (Scheme 25).[40]

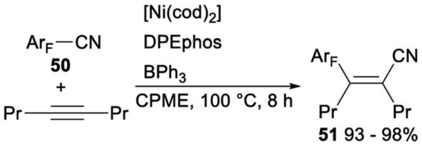
A plausible mechanism for the above nickel/Lewis acid catalysed polyfluoroarylcyanation of alkynes was shown in Scheme 26. The catalytic cycle should be initiated by the formation of the η^2-complex ***Y*** or ***Z***. The following oxidative addition of the C–CN bond to nickel(0) gave ***A′*** after the cyano group nitrogen atom is bound to BPh_3. Insertion of 4-octyne into the ArF–Ni bond in ***A′*** afforded ***C′*** *via* the alkyne-coordinated complex ***B′***. Steric repulsion between the bulkier group Pr and the polyfluorophenyl group on the Ni center in ***B′*** was assumed to be minimal.[40] Finally, C–C bond-forming reductive elimination of **51** from ***C′*** generated a nickel(0) complex to complete the catalytic cycle.[40]

Nickel catalysed hydrocyanative cyclization and three-component cross-coupling reaction between allenes and alkynes was reported by Arai in 2013 (Scheme 27). Subjection of **52** to $Me_2C(OH)CN/[Ni\{P(OPh_3)\}_4]/P(OPh)_3$ catalytic system afforded the corresponding products **53** in 43–70% yields. This protocol offered a new method for the addition of a CN functionality to C–C triple bonds and provided tetra substituted alkenes with highly regio- and stereoselective.[21g]

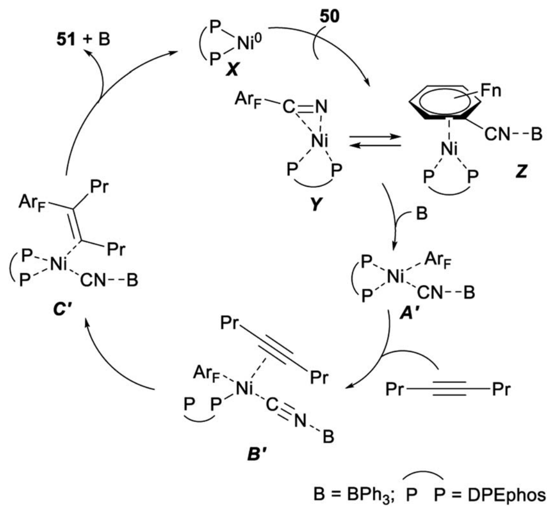
The possible mechanism for the above nickel catalysed hydrocyanative cyclization and three-component cross-coupling reaction between allenes and alkynes was described in Scheme 28. Firstly, a regioselective hydronickelation of the allene occurred and generated a Ni–H species. Then, hydride attacked at the central carbon atom of the allene **52** and would give a π-



Scheme 24 Cyclization–cyanation reactions of β-hydroxyalkynes and *o*-alkynylphenol and -aniline derivatives.



Scheme 25 Nickel/Lewis acid catalysed polyfluoroarylcyanation of alkynes.

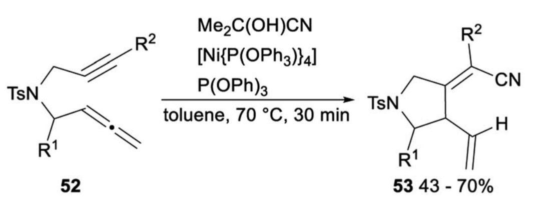


Scheme 26 Plausible mechanism for nickel/Lewis acid catalyzed polyfluoroarylcyanation of alkynes.

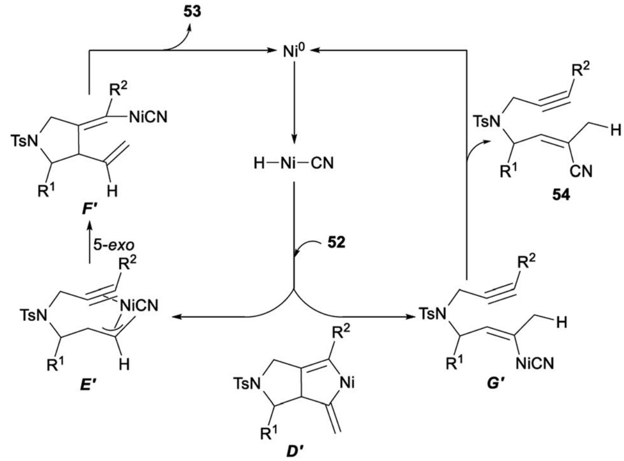
allylnickel intermediate E'. The following 5-exo cyclization of E' gave F'. A subsequent elimination would give the tetrasubstituted alkene **53** stereoselectively together with Ni^0. When the initial C–H bond formation occurred at the terminal allenyl carbon atom, the resulting organonickel species G' was not suitable for cyclization and produced by-products **54** through reductive elimination. Since a cyano functionality was added exclusively to a C–C triple bond in a regio- and stereoselective fashion, it was unlikely that the two vinyl–nickel bonds in D', which could be generated by the oxidative cyclization of **52**, reacted specifically with AC through protonation to give F'.[21g]

Other cyanation of alkynes

In 2018, He reported ultrasound-promoted Brønsted acid ionic liquid catalysed hydrothiocyanation of activated alkynes (Scheme 29). When alkynes **55** was treated with KSCN, BAIL-1



Scheme 27 Nickel catalyzed hydrocyanative cyclization and three-component cross-coupling reaction between allenes and alkynes.

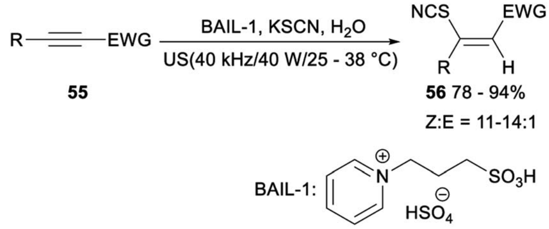


Scheme 28 Plausible mechanism for hydrocyanative cyclization and three-component cross-coupling reaction between allenes and alkynes.

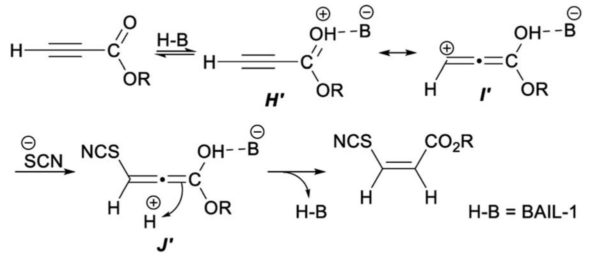
and water at room temperature in minimal solvent under ultrasonic radiation (40 kHz/40 W), the corresponding vinyl thiocyanates **56** was afforded in 78–94% yields. And the catalytic system could be repeated five times without significant influence on the yield. This reaction provided an eco-friendly and practical protocol for the synthesis of *Z*-vinyl thiocyanates, having some features including the abundance and accessibility of raw materials, the usage of recyclable and reusable catalysts, a wide substrate scope with good to high yields, ease of scale-up and high energy efficiency.[41]

A plausible mechanism for the above hydrothiocyanation was proposed in Scheme 30. Firstly, a cationic intermediate G' was generated by protonation of the activated alkyne with BAIL-1. Then H' was further tautomerized into the zwitterionic complex I'. Intermediate J' was produced by the nucleophilic thiocyanate ion attacked the β-carbon of intermediate I'. Finally, the capture of a proton dissociated from water by ultrasonic radiation proceeded from the less hindered face of intermediate J', trans to SCN, thus leading to product *Z*-vinyl thiocyanates.[41]

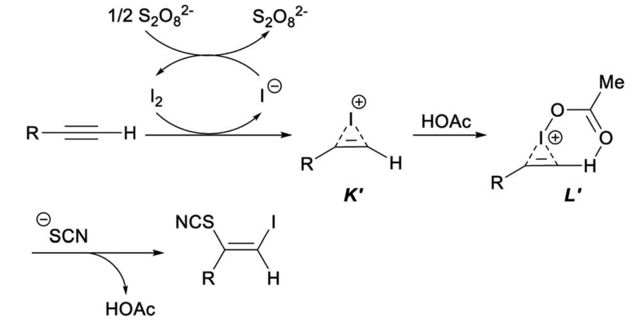
Ultrasonic multicomponent synthesis of (*Z*)-β-iodo vinylthiocyanates *via* hydrothiocyanation of alkynes was also studied. When alkynes **57** was treated with KSCN and I_2 in the presence of $K_2S_2O_8$ as the oxidant in MeCN at room temperature, the corresponding (*Z*)-β-iodo vinylthiocyanates **58** was



Scheme 29 Ultrasound-promoted Brønsted acid ionic liquid catalysed hydrothiocyanation of activated alkynes.



Scheme 30 Plausible mechanism for ultrasound-promoted Brønsted acid ionic liquid catalyzed hydrothiocyanation of activated alkynes.



Scheme 32 Plausible mechanism for ultrasonic multicomponent synthesis of (*Z*)-β-iodo vinylthiocyanates.

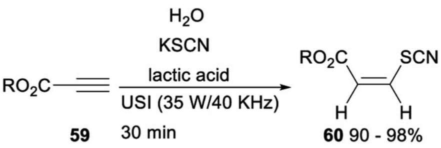
yielded in 82–94% yield with *Z*/*E* from 11 : 1 to 28 : 1 (Scheme 31).[42]

In the plausible mechanism of the above ultrasonic multicomponent synthesis of (*Z*)-β-iodo vinylthiocyanates, an activated iodoirenium ion ***K′*** was formed through the molecular iodine electrophilic addition to alkyne with the release an iodine anion which was oxidized by $(NH_4)_2S_2O_8$ to regenerate I_2 for continuing participation in the reaction. Then, an energetically favourable six-membered ring intermediate ***L′*** was yielded by the coordination of HOAc to intermediate ***K′***. Finally, the thiocyanate anion attacked the less steric hindered carbon atom to give the corresponding product (*Z*)-β-iodo vinylthiocyanates with concomitant release of HOAc to complete the catalytic cycle (Scheme 32).[42]

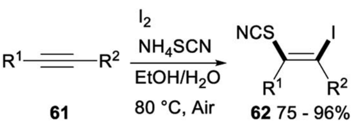
Synthesis of a variety of *Z*-β-thiocyanate alkenyl esters *via* lactic acid catalysed multicomponent hydrothiocyanation of alkynes was established (Scheme 33). After treating alkynes **59** with KSCN in the presence of natural lactic acid under ultrasound conditions for 30 min, the expected *Z*-β-thiocyanate alkenyl esters **60** was formed in excellent yields.[43]

Iodine-mediated regio- and stereoselective iodothiocyanation of alkynes was reported by Zeng and Chen in 2018 (Scheme 34). Iodothiocyanation of alkyne **61** with NH_4SCN in the presence of I_2 as the iodine source and $EtOH/H_2O$ as the solvent at 80 °C under air afforded series of functional β-iodo vinylthiocyanates **62** in good to excellent yields. This protocol proceeding in aqueous ethanol media under mild conditions with good functional group tolerance was a new environmentally friendly, economical and straightforward approach for versatile synthesis of vinyl thiocyanates from readily available and inexpensive NH_4SCN and I_2.[44]

The plausible reaction pathway for the above iodothiocyanation of alkynes was shown in Scheme 35. First, an electrophilic addition of I_2 to the C–C triple bond of substrate **61** led a cyclic iodonium ion ***M′***. And then, nucleophilic attack of SCN^- on a more substituted site of ***M′*** resulted succedent ring opening, which produced the difunctionalized product **62**.[44]



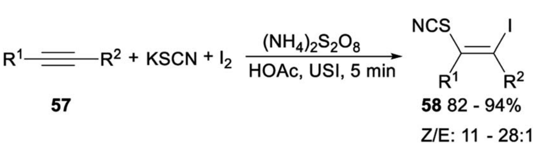
Scheme 33 Synthesis of *Z*-β-thiocyanate alkenyl esters *via* lactic acid catalyzed hydrothiocyanation of alkynes.



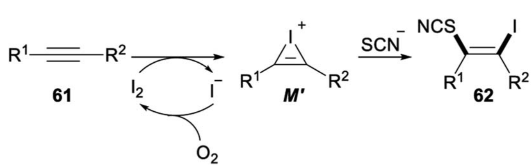
Scheme 34 Iodine-mediated iodothiocyanation of alkynes.

In 2019, He investigated natural deep eutectic solvent catalysed selenocyanation of activated alkynes (Scheme 36). Under ultrasonic radiation, treatment of alkynes **63** with H_2O and KSeCN in natural deep eutectic solvent (ChCl/glycolic acid) afforded the corresponding *Z*-vinylselenolates **64** in 78–94% yields with *Z*/*E* ratio from 14 : 1 to 39 : 1.[45]

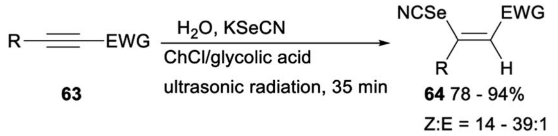
The plausible mechanism for deep eutectic solvent catalysed selenocyanation of activated alkynes was depicted in Scheme 37. First, two hydrogen bonds formed between the oxygen atom of the carboxyl group in alkynes and the H atom of the hydroxyl groups (glycolic acid) in DES, resulting in enhanced polarization of carbonyl group of alkynes (***N′***), which was in resonance with a zwitterionic intermediate ***O′***. Then, an intermediate ***P′***, in which a hydrogen bond formed between the nitrogen-atom of "SeCN" and the H atom of the hydroxyl group (ChCl) in ChCl/



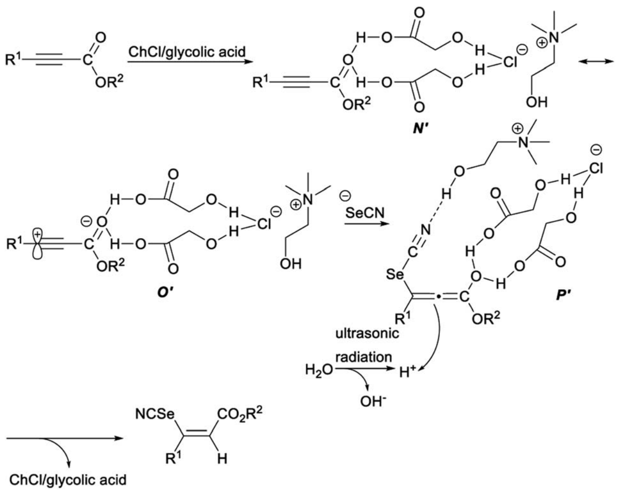
Scheme 31 Ultrasonic multicomponent synthesis of (*Z*)-β-iodo vinylthiocyanates *via* hydrothiocyanation of alkynes.



Scheme 35 Plausible mechanism for iodothiocyanation of alkynes.



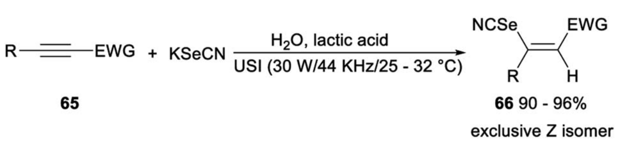
Scheme 36 Deep eutectic solvent catalysed selenocyanation of activated alkynes.



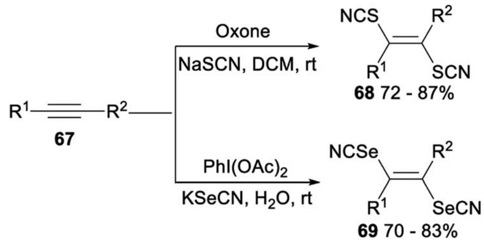
Scheme 37 Plausible mechanism for deep eutectic solvent catalysed selenocyanation of activated alkynes.

glycolic acid, was generated by the attachment of selenocyanate anion to intermediate ***P′***. Finally, the intermediate ***P′*** captured a proton (*in situ* generated by ultrasound-assisted self-ionization of H_2O) on the reverse side of the sterically hindered H-bond activated atom to produce the desired *Z*-vinyl selenocyanates with concomitant release of the DES to fulfil the catalytic cycle.[45]

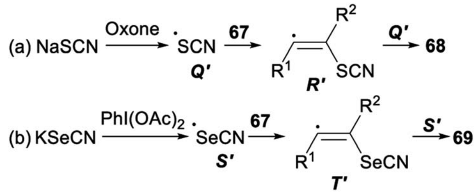
A green selenocyanation of activated alkynes catalysed by lactic acid was achieved by He in 2019. Treatment of a mixture of alkynes **65**, H_2O, KSeCN and lactic acid at ambient temperature under ultrasonic conditions (30 W/44 KHz/25–32 °C) in open air led to the expected *Z*-3-selenocyanatoacrylates and analogues **66** in excellent yields. This protocol, using a minimal amount of lactic acid as reaction media, entirely avoided the usage of organic volatile compounds. And the reaction also had other advantages such as the conversion of substrate was almost quantitative, the pure products could be conveniently collected through water precipitation and the cheap biomass lactic acid could be re-used for five consecutive runs without obvious decrease in catalytic activity (Scheme 38).[46]



Scheme 38 Green selenocyanation of activated alkynes catalysed by lactic acid.



Scheme 39 Stereoselective difunctionalization of alkynes with NaSCN or KSeCN.



Scheme 40 Plausible mechanism for difunctionalization of alkynes with NaSCN or KSeCN.

Stereoselective difunctionalization of alkynes with NaSCN or KSeCN was also reported (Scheme 39). When NaSCN was used as a [SCN] source and oxone was employed as an oxidant, dithiocyanation of alkynes **67** proceeded smoothly in DCM and produced the desired alkenyl dithiocyanates **68** in 72–87% yield. The expected alkenyl diselenocyanates **69** was obtained in good yield when alkynes **67** was treated with KSeCN [SeCN] source and $PhI(OAc)_2$ oxidant in H_2O.[47]

A possible mechanism for the difunctionalization of alkynes was proposed in Scheme 40. Firstly, in the presence of an oxidant oxone or $PhI(OAc)_2$, NaSCN or KSeCN was converted into the SCN radical ***Q′*** or the SeCN radical ***S′***. Then, the anti-Markovnikov addition of ***Q′*** or ***S′*** to alkyne **67** produced the alkenyl radical ***R′*** or ***T′***. Finally, the radical ***Q′*** or ***S′*** attacked more favourably the sterically less hindered side of the alkenyl radical ***R′*** or ***T′*** which could result the formation of desired products **68** and **69**, respectively.[47]

Conclusions

In summary, nitriles were versatile intermediates for preparation of pharmaceuticals, pesticides and organic materials. Inherently nucleophilic alkynes were important intermediates in organic synthesis for preparation of biological active compounds and organic functional compounds. Cyanation reactions of alkynes had attracted more and more attention. Transition metal catalysed direct cyanation and hydrocyanation of alkynes gave the corresponding alkynyl cyanides and alkenyl nitriles in high yields. And dicyanation of alkynes could produce 1,2-dicyano adducts. Cyanofunctionalization of alkynes afforded functional cyanated compounds. Other cyanation of alkynes such as thiocyanation and selenocyanation yielded the expected functional vinylthiocyanates and vinylselenocyanates.

Limitations and perspectives

Although these above cyanation reactions were useful and convenient for synthesis of cyanates, expensive transition metal catalysts like rhodium and palladium complexes were often used to realize reasonable yields in direct cyanation of alkynes. Thus, establishment of cheap catalytic system should be focused in future research. And developing other kind cyanation of alkynes was still in high need.

Conflicts of interest

No conflict of interest exists in this paper, and the paper is approved by all authors for publication. I and my co-authors would like to declare that the work described is original and has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the contents of the paper.

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (No. 21802040, 21877034), the Natural Science Fund Youth Project of Hunan Province (No. 2018JJ3145), the General project of Hunan Education Department (17C0629), and the Open Foundation of Key Laboratory of Theoretical Organic Chemistry and Functional Molecule of Ministry of Education, Hunan University of Science and Technology (No. E21843) for financial support.

Notes and references

1 (*a*) J. M. Sansano, *Angew. Chem.*, 2009, **121**, 2488; (*b*) B.-B. Liu, W.-B. Cao, F. Wang, S.-Y. Wang and S.-J. Ji, *J. Org. Chem.*, 2018, **83**, 11118; (*c*) C. Nájera and J. M. Sansano, *Angew. Chem., Int. Ed.*, 2009, **48**, 2452; (*d*) A. J. Fatiadi, in *Preparation and Synthetic Applications of Cyano Compounds*, ed. S. Patai and Z. Rappoport, Wiley-VCH, New York, 1983; (*e*) X. Wang, S.-Y. Wang and S.-J. Ji, *J. Org. Chem.*, 2014, **79**, 8577; (*f*) E. N. Bess and M. S. Sigman, Linear free energy relationships (LFERs) in asymmetric catalysis, in *Asymmetric Synthesis II: More Methods and Applications*, ed. M. Christmann and S. Bräse, Wiley-VCH, Weinheim, Germany, 2012, p. 363; (*g*) Z. Rappoport, in *Chemistry of the Cyano Group*, John Wiley & Sons, London, 1970, p. 121; (*h*) P. Xu, Y.-M. Zhu, F. Wang, S.-Y. Wang and S.-J. Ji, *Org. Lett.*, 2019, **21**, 683; (*i*) J. W. Han, X.-S. Peng and H. N. C. Wong, *Natl. Sci. Rev.*, 2017, **4**, 892; (*j*) X.-D. Xiong, C.-L. Deng, X.-S. Peng, Q. Miao and H. N. C. Wong, *Org. Lett.*, 2014, **16**, 3252; (*k*) C. Cheng, Z. Cai, X.-S. Peng and H. N. C. Wong, *J. Org. Chem.*, 2013, **78**, 8562; (*l*) X. Wang, X.-P. Xu, S.-Y. Wang, W.-Q. Zhou and S.-J. Ji, *Org. Lett.*, 2013, **15**, 4246.

2 (*a*) A. Kleemann, J. Engel, B. Kutscher and D. Reichert, *Appl. Organomet. Chem.*, 2001, **15**, 726; (*b*) S. Krautwald and E. M. Carreira, in *Comprehensive Organic Transformations: a Guide to Functional Group Preparations*, ed. C. R. Larock, Wiley-VCH, Weinheim, 1989, p. 819; (*c*) J. S. Miller and J. L. Manson, *Acc. Chem. Res.*, 2001, **34**, 563; (*d*) F. F. Fleming and Q. Wang, *Chem. Rev.*, 2003, **103**, 2035.

3 (*a*) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend and A. B. Holmes, *Nature*, 1993, **365**, 628; (*b*) F. F. Fleming, *Nat. Prod. Rep.*, 1999, **16**, 597; (*c*) Z. Rappoport, *The Chemistry of the Cyano Group*, Interscience Publishers, London, 1970; (*d*) R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, VCH, New York, 1989; (*e*) *UllmannQs Encyclopedia of Industrial Chemistry: Acrylonitrile*, ed. P. W. Langvardt, Wiley-VCH, Weinheim, 2011, vol. 1, p. 365; (*f*) *Encyclopedia of Polymer Science and Technology*, ed. H. F. Mark, Wiley, Hoboken, 3rd edn, 2007.

4 (*a*) M. H. Larraufie, G. Maestri, M. Malacria, C. Ollivier, L. Fensterbank and E. Lacote, *Synthesis*, 2012, 1279; (*b*) D. D. Nekrasov, *Russ. J. Org. Chem.*, 2004, **40**, 1387; (*c*) R. J. Crutchley, *Coord. Chem. Rev.*, 2001, **219**, 125.

5 (*a*) L.-F. Peng, Z.-F. Hu, Z.-L. Tang, Y.-C. Jiao and X.-H. Xu, *Chin. Chem. Lett.*, 2019, **30**, 1481; (*b*) K.-J. Liu, X.-L. Zeng, Y. Zhang, Y. Wang, X.-S. Xiao, H. Yue, M. Wang, Z. Tang and W.-M. He, *Synthesis*, 2018, **50**, 4637; (*c*) C. Wu, J. Wang, X.-Y. Zhang, G.-K. Jia, Z. Cao, Z. Tang, X. Yu, X. Xu and W.-M. He, *Org. Biomol. Chem.*, 2018, **16**, 5050; (*d*) R.-N. Yi, Z.-J. Wang, Z.-W. Liang, M. Xiao, X.-H. Xu and N.-B. Li, *Appl. Organomet. Chem.*, 2019, **33**, 4917; (*e*) L.-Y. Xie, S. Peng, L.-L. Jiang, X. Peng, W. Xia, X. Yu, X.-X. Wang, Z. Cao and W.-M. He, *Org. Chem. Front.*, 2019, **2**, 167; (*f*) L.-Y. Xie, Y.-J. Li, J. Qu, Y. Duan, J. Hu, K.-J. Liu, Z. Cao and W.-M. He, *Green Chem.*, 2017, **19**, 5642; (*g*) L.-F. Peng, R.-Z. Li, Z.-L. Tang, J.-Y. Chen, R.-N. Yi and X.-H. Xu, *Tetrahedron*, 2017, **73**, 3099; (*h*) L.-F. Peng, Z.-H. Hu, Q.-C. Lu, Z.-L. Tang, Y.-C. Jiao and X.-H. Xu, *Chin. Chem. Lett.*, 2019, **30**, 2151; (*i*) L.-Y. Xie, S. Peng, F. Liu, Y.-F. Liu, M. Sun, Z. Tang, S. Jiang, Z. Cao and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 7193.

6 (*a*) T. Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 1633; (*b*) C. Galli, *Chem. Rev.*, 1988, **88**, 765; (*c*) K. W. Rosenmund and E. Struck, *Ber. Dtsch. Chem. Ges.*, 1919, **52**, 1749; (*d*) J. Lindley, *Tetrahedron*, 1984, **40**, 1433; (*e*) G. P. Ellis and T. M. Romney-Alexander, *Chem. Rev.*, 1987, **87**, 779; (*f*) P. Anbarasan, T. Schareina and M. Beller, *Chem. Soc. Rev.*, 2011, **40**, 5049; (*g*) Y.-Y. Ping, Q.-P. Ding and Y.-Y. Peng, *ACS Catal.*, 2016, **6**, 5989; (*h*) B. Mondal, K. Acharyya, P. Howlader and P. S. Mukherjee, *J. Am. Chem. Soc.*, 2016, **138**, 1709; (*i*) G. Yan, Y. Zhang and J. Wang, *Adv. Synth. Catal.*, 2017, **359**, 4068.

7 (*a*) J. Zanon, A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2003, **125**, 2890; (*b*) J. Ramnauth, N. Bhardwaj, P. Renton, S. Rakhit and S. P. Maddaford, *Synlett*, 2003, **14**, 2237; (*c*) M. Sundermeier, S. Mutyala, A. Zapf, A. Spannenberg and M. Beller, *J. Organomet. Chem.*, 2003, **684**, 50; (*d*) R. Chidambaram, *Tetrahedron Lett.*, 2004, **45**, 1441; (*e*) J. M. Veauthier, C. N. Carlson, G. E. Collis, J. L. Kiplinger and K. D. John, *Synthesis*, 2005, **16**, 2683; (*f*) H. J. Cristau, A. Ouali, J. F. Spindler and M. Taillefer, *Chem.–Eur. J.*, 2005, **11**, 2483; (*g*) R. S. Jensen, A. S. Gajare, K. Toyota,

M. Yoshifuj and F. Ozawa, *Tetrahedron Lett.*, 2005, **46**, 8645; (*h*) X. Chen, X.-S. Hao, C. E. Goodhue and J.-Q. Yu, *J. Am. Chem. Soc.*, 2006, **128**, 6790; (*i*) F. G. Buono, R. Chidambaram, R. H. Mueller and R. E. Waltermire, *Org. Lett.*, 2008, **10**, 5325; (*j*) X. Jia, D. Yang, S. Zhang and J. Cheng, *Org. Lett.*, 2009, **11**, 4716; (*k*) H. Q. Do and O. Daugulis, *Org. Lett.*, 2010, **12**, 2517; (*l*) A. V. Ushkov and V. V. Grushin, *J. Am. Chem. Soc.*, 2011, **133**, 10999; (*m*) G. Zhang, L. Zhang, M. Hu and J. Cheng, *Adv. Synth. Catal.*, 2011, **353**, 291; (*n*) J. Chen, Y. Sun, B. Liu, D. Liu and J. Cheng, *Chem. Commun.*, 2012, **48**, 449; (*o*) K. W. Rosenmund and E. Struck, *Chem. Ber.*, 1919, **52**, 1749; (*p*) X. Jia, D. Yang, W. Wang, F. Luo and J. Chen, *J. Org. Chem.*, 2009, **74**, 9470; (*q*) D. T. Cohen and S. L. Buchwald, *Org. Lett.*, 2015, **17**, 202; (*r*) G.-Y. Zhang, J.-T. Yu, M.-L. Hu and J. Chen, *J. Org. Chem.*, 2013, **78**, 2710.

8 (*a*) P. T. Anastas and J. C. Warner, *Green Chemistry Theory and Practice*, Oxford University Press, Oxford, 1998; (*b*) A. S. Matlack, *Introduction to Green Chemistry*, Marcel Dekker, New York, 2001; (*c*) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren and P. T. Anastas, *Science*, 2002, **297**, 807; (*d*) L.-Y. Xie, J. Qu, S. Peng, K.-J. Liu, Z. Wang, M.-H. Ding, Y. Wang, Z. Cao and W.-M. He, *Green Chem.*, 2018, **20**, 760; (*e*) K.-J. Liu, S. Jiang, L.-H. Lu, L.-L. Tang, S.-S. Tang, H.-S. Tang, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3038; (*f*) M. Lancaster, *Green Chemistry: An Introductory Text*, RSC Publishing, Cambridge, 2002; (*g*) K.-J. Liu, S. Jiang, L.-H. Lu, L.-L. Tang, S.-S. Tang, H.-S. Tang, Z. Tang, W.-M. He and X. Xu, *Green Chem.*, 2018, **20**, 3683; (*h*) L.-H. Lu, Z. Wang, W. Xia, P. Cheng, B. Zhang, Z. Cao and W.-M. He, *Chin. Chem. Lett.*, 2019, **30**, 1237–1240; (*i*) W.-H. Bao, M. He, J.-T. Wang, X. Peng, M. Sung, Z. Tang, S. Jiang, Z. Cao and W.-M. He, *J. Org. Chem.*, 2019, **84**, 6065–6071; (*j*) W.-H. Bao, C. Wu, J.-T. Wang, W. Xia, P. Chen, Z. Tang, X. Xu and W.-M. He, *Org. Biomol. Chem.*, 2018, **16**, 8403; (*k*) L.-H. Lu, S.-J. Zhou, W.-B. He, W. Xia, P. Chen, X. Yu, X. Xu and W.-M. He, *Org. Biomol. Chem.*, 2018, **16**, 9064; (*l*) L.-Y. Xie, Y. Duan, L.-H. Lu, Y.-J. Li, S. Peng, C. Wu, K.-J. Liu, Z. Wang and W.-M. He, *ACS Sustainable Chem. Eng.*, 2017, **5**, 10407; (*m*) L.-Y. Xie, S. Peng, J.-X. Tan, R.-X. Sun, X. Yu, N.-N. Dai, Z.-L. Tang, X. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2018, **6**, 16976; (*n*) C. Wu, P.-P. Yang, Z.-M. Fu, Y. Peng, X. Wang, Z.-Z. Zhang, F. Liu, W.-Y. Li, Z.-Z. Li and W.-M. He, *J. Org. Chem.*, 2016, **81**, 10664; (*o*) L.-Y. Xie, S. Peng, L.-H. Lu, J. Hu, W.-H. Bao, F. Zeng, Z. Tang, X. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2018, **6**, 7989; (*p*) C. Wu, H.-J. Xiao, S.-W. Wang, M.-S. Tang, Z.-L. Tang, W. Xia, W.-F. Li, C. Zhong and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 2169; (*q*) H. Jiang, X.-Y. Tang, Z.-H. Xu, H.-X. Wang, K. Han, X.-L. Yang, Y.-Y. Zhou, Y.-L. Feng, X.-Y. Yu and Q.-W. Gui, *Org. Biomol. Chem.*, 2019, **17**, 2715.

9 G. Zhang, S. Chen, H. Fei, J. Cheng and F. Chen, *Synlett*, 2012, **23**, 2247.

10 Q. Wen, J. Jin, B. Hu, P. Lu and Y. Wang, *RSC Adv.*, 2012, **2**, 6167.

11 (*a*) Y.-M. Zhu and Z.-M. Shen, *Adv. Synth. Catal.*, 2017, **359**, 3515; (*b*) C.-D. Pan, H.-M. Jin, P. Xu, X. Liu, Y.-X. Cheng and C.-J. Zhu, *J. Org. Chem.*, 2013, **78**, 9494; (*c*) F.-H. Luo, C.-I. Chu and C.-H. Cheng, *Organometallics*, 1998, **17**, 1025.

12 J. Kim and S. Chang, *J. Am. Chem. Soc.*, 2010, **132**, 10272.

13 H. Xu, P.-T. Liu, Y.-H. Li and F.-S. Han, *Org. Lett.*, 2013, **15**, 3354.

14 (*a*) N. Chatani and T. Hanafusa, *J. Chem. Soc., Chem. Commun.*, 1985, 838; (*b*) N. Chatani, T. Takeyasu, N. Horiuchi and T. Hanafusa, *J. Org. Chem.*, 1988, **53**, 3539.

15 (*a*) Z. Shu, W. Ji, X. Wang, Y. Zhou, Y. Zhang and J.-B. Wang, *Angew. Chem., Int. Ed.*, 2014, **53**, 2186; (*b*) M. V. Vita, P. Caramenti and J. Waser, *Org. Lett.*, 2015, **17**, 5832; (*c*) J. T. Reeves, C. A. Malapit, F. G. Buono, K. P. Sidhu, M. A. Marsini, C. A. Sader, K. R. Fandrick, C. A. Busacca and C. H. Senanayake, *J. Am. Chem. Soc.*, 2015, **137**, 9481; (*d*) G. Talavera, J. Peña and M. Alcarazo, *J. Am. Chem. Soc.*, 2015, **137**, 8704; (*e*) R. Frei, T. Courant, M. D. Wodrich and J. Waser, *Chem.–Eur. J.*, 2015, **21**, 2662; (*f*) A. B. Pawar and S. Chang, *Org. Lett.*, 2015, **17**, 660; (*g*) Y.-F. Wang, J. Qiu, D. Kong, Y. Gao, F. Lu, P. G. Karmaker and F.-X. Chen, *Org. Biomol. Chem.*, 2015, **13**, 365; (*h*) Y. Yang and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2014, **53**, 8677; (*i*) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes and F. Glorius, *J. Am. Chem. Soc.*, 2014, **136**, 17722; (*j*) C. Zhu, J.-B. Xia and C. Chen, *Org. Lett.*, 2014, **16**, 247; (*k*) T.-J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu and Y. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 10630; (*l*) T. Hoshikawa, S. Yoshioka, S. Kamijo and M. Inoue, *Synthesis*, 2013, **45**, 874; (*m*) J. P. Brand, D. F. González, S. Nicolai and J. Waser, *Chem. Commun.*, 2011, **47**, 102; (*n*) S. Kamijo, T. Hoshikawa and M. Inoue, *Org. Lett.*, 2011, **13**, 5928; (*o*) P. Anbarasan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 519; (*p*) Y. Yang, Y. Zhang and J. Wang, *Org. Lett.*, 2011, **13**, 5608; (*q*) T. Dohi, K. Morimoto, N. Takenaga, A. Goto, A. Maruyama, Y. Kiyono, H. Tohma and Y. Kita, *J. Org. Chem.*, 2007, **72**, 109; (*r*) P. Anbarasan, H. Neumann and M. Beller, *Chem.–Eur. J.*, 2010, **16**, 4725; (*s*) Y.-Q. Wu, D. C. Limburg, D. E. Wilkinson and G. S. Hamilton, *Org. Lett.*, 2000, **2**, 795.

16 (*a*) J. Cui, J. Song, Q. Liu, H. Liu and Y.-H. Dong, *Chem.–Asian J.*, 2018, **13**, 482; (*b*) R. Lopez and C. Palomo, *Angew. Chem., Int. Ed.*, 2015, **54**, 13170.

17 (*a*) M. Suginome, A. Yamamoto and Y. Ito, *Chem. Commun.*, 2002, 1392; (*b*) M. Suginome, A. Yamamoto and M. Murakami, *J. Am. Chem. Soc.*, 2003, **125**, 6358; (*c*) B. Jiang, Y. Kan and A. Zhang, *Tetrahedron*, 2001, **57**, 1581; (*d*) W. R. Jackson and C. G. Lovel, *J. Chem. Soc., Chem. Commun.*, 1982, 1231; (*e*) N. Chatani and T. Hanafusa, *J. Chem. Soc., Chem. Commun.*, 1985, 838; (*f*) N. Chatani, T. Takeyasu, N. Horiuchi and T. Hanafusa, *J. Org. Chem.*, 1988, **53**, 3539; (*g*) M. Suginome, H. Kinugasa and Y. Ito, *Tetrahedron Lett*, 1994, **35**, 8635; (*h*) Y. Obora, A. S. Baleta, M. Tokunaga and Y. Tsuji, *J. Organomet. Chem.*, 2002, **660**, 173; (*i*) K. Nozaki, N. Sato and H. Takaya, *J. Org. Chem.*, 1994, **59**, 2679.

18 X. Wang, S. Y. Wang and S. J. Ji, *Org. Lett.*, 2013, **15**, 1954.

19 (*a*) P. J. Stang and F. Diederich, *Modern Acetylene Chemistry*, VCH, Weinheim, 1995; (*b*) F. Diederich, P. J. Stang and R. R. Tykwinski, *Acetylene Chemistry*, Willey-VCH Verlag GmbH & CO. KgaA, Weinheim, 2005; (*c*) L.-F. Peng, S.-W. Zhang, B.-H. Wang, M.-S. Xun, Z.-L. Tang, Y.-C. Jiao and X.-H. Xu, *Chin. J. Org. Chem.*, 2018, **38**, 519; (*d*) L.-F. Peng, B.-H. Wang, M. Wang, Z.-L. Tang, Y.-Z. Jiang, Y.-C. Jiao and X.-H. Xu, *J. Chem. Res.*, 2018, **42**, 235; (*e*) Z. Wang, L. Yang, H.-L. Liu, W.-H. Bao, Y.-Z. Tan, M. Wang, Z. Tang and W.-M. He, *Chin. J. Org. Chem.*, 2018, **38**, 2639; (*f*) L.-F. Peng, J.-Y. Lei, L. Wu, Z.-L. Tang, Z.-P. Luo, Y.-C. Jiao and X.-H. Xu, *J. Chem. Res.*, 2018, **42**, 271; (*g*) W.-Y. Li, G.-X. Yin, L. Huang, Y. Xiao, Z.-M. Fu, X. Xin, F. Liu, Z.-Z. Li and W.-M. He, *Green Chem.*, 2016, **18**, 4879; (*h*) C. Wu, Z. Wang, Z. Hu, F. Zeng, X.-Y. Zhang, Z. Cao, Z. Tang, W.-M. He and X.-H. Xu, *Org. Biomol. Chem.*, 2018, **16**, 3177; (*i*) L.-F. Peng, C. Peng, M. Wang, Z.-L. Tang, Y.-C. Jiao and X.-H. Xu, *Chin. J. Org. Chem.*, 2018, **38**, 3048; (*j*) L. Wu, L.-F. Peng, Z.-F. Hu, H. Wang, Z.-L. Tang, Y.-C. Jiao and X.-H. Xu, *J. Chem. Res.*, 2019, **43**, 503.

20 (*a*) G. Mao, A. Orita, L. Fenenko, M. Yahiro, C. Adachi and J. Otera, *Mater. Chem. Phys.*, 2009, **115**, 378; (*b*) L. Fenenko, G. Shao, A. Orita, M. Yahiro, J. Otera, S. Svechnikov and C. Adachi, *Chem. Commun.*, 2007, 2278; (*c*) D. Matsuo, X. Yang, A. Hamada, K. Morimoto, T. Kato, M. Yahiro, C. Adachi, A. Orita and J. Otera, *Chem. Lett.*, 2010, **39**, 1300; (*d*) T. Oyamada, G. Shao, H. Uchiuzou, H. Nakanotani, A. Orita, J. Otera, M. Yahiro and C. Adachi, *Jpn. J. Appl. Phys., Part 2*, 2006, **45**, 46; (*e*) X. Yang, S. Kajiyama, J.-K. Fang, F. Xu, Y. Uemura, N. Koumura, K. Hara, A. Orita and J. Otera, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 687; (*f*) X. Yang, J.-K. Fang, Y. Suzuma, F. Xu, A. Orita, J. Otera, S. Kajiyama, N. Koumura and K. Hara, *Chem. Lett.*, 2011, **40**, 620.

21 (*a*) Y.-N. Cheng, Z. Duan, L.-J. Yu, Z.-X. Li, Y. Zhu and Y.-J. Wu, *Org. Lett.*, 2008, **10**, 901; (*b*) Y. Nakao, T. Yukawa, Y. Hirata, S. Oda, J. Satoh and T. Hiyama, *J. Am. Chem. Soc.*, 2006, **128**, 7116; (*c*) S. Arai, T. Sato, Y. Koike, M. Hayashi and A. Nishida, *Angew. Chem., Int. Ed.*, 2009, **48**, 4528; (*d*) Y. Hirata, A. Yada, E. Morita, Y. Nakao, T. Hiyama, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2010, **132**, 10070; (*e*) Y. Nakao, A. Yada, S. Ebata and T. Hiyama, *J. Am. Chem. Soc.*, 2007, **129**, 2428; (*f*) N. R. Rondla, S. M. Levi, J. M. Ryss, R. A. V. Berg and C. J. Douglas, *Org. Lett.*, 2011, **13**, 1940; (*g*) S. Arai, Y. Amako, X. Yang and A. Nishida, *Angew. Chem., Int. Ed.*, 2013, **52**, 8147; (*h*) Y. Obora, A. S. Baleta, M. Tokunaga and Y. Tsuji, *J. Organomet. Chem.*, 2002, **660**, 173; (*i*) M. Suginome, A. Yamamoto and M. Murakami, *J. Am. Chem. Soc.*, 2003, **125**, 6358; (*j*) M. Suginome, A. Yamamoto and M. Murakami, *Angew. Chem., Int. Ed.*, 2005, **44**, 2380; (*k*) J. Kamiya, S. Kawakami, A. Yano, A. Nomoto and A. Ogawa, *Organometallics*, 2006, **25**, 3562; (*l*) M. Murai, R. Hatano, S. Kitabata and K. Ohe, *Chem. Commun.*, 2011, **47**, 2375; (*m*) D. C. Koester, M. Kobayashi, D. B. Werz and Y. Nakao, *J. Am. Chem. Soc.*, 2012, **134**, 6544; (*n*) N. Chatani, T. Morimoto, M. Toyoshige and S. Murai, *J. Organomet. Chem.*, 1994, **473**, 335; (*o*) I. Kamiya, J. Kawakami, S. Yano, A. Nomoto and A. Ogawa, *Organometallics*, 2006, **25**, 3562; (*p*) C. Najera and J. M. Sansano, *Angew. Chem., Int. Ed.*, 2009, **45**, 2452; (*q*) Y. Nakao, S. Oda and T. Hiyama, *J. Am. Chem. Soc.*, 2004, **126**, 13904; (*r*) Y. Nakao, K. Kanyiva, S. Oda and T. Hiyama, *J. Am. Chem. Soc.*, 2006, **128**, 8146; (*s*) Y. Nakao, S. Ebata, A. Yada, T. Hiyama, M. Ikawa and S. Ogoshi, *J. Am. Chem. Soc.*, 2008, **130**, 12874; (*t*) Y. Cheng, Z. Duan, L. Yu, Z. Li, Y. Zhu and Y. Wu, *Org. Lett.*, 2008, **10**, 901; (*u*) K. Nozaki, N. Sato and H. Takaya, *J. Org. Chem.*, 1994, **59**, 2679; (*v*) Y. Kobayashi, H. Kamisaki, R. Yanada and Y. Takemoto, *Org. Lett.*, 2006, **8**, 2711; (*w*) Y. Nishihara, Y. Inoue, S. Izawa, M. Miyasaka, K. Tanemura, K. Nakajima and K. Takagi, *Tetrahedron*, 2006, **62**, 9872; (*x*) M. Suginome, A. Yamamoto and M. Murakami, *J. Am. Chem. Soc.*, 2003, **125**, 6358; (*y*) M. Suginome, A. Yamamoto and M. Murakami, *Angew. Chem., Int. Ed.*, 2005, **44**, 2380; (*z*) M. Sun, J. Jiang, J.-L. Chen, Q. Yang and X.-Y. Yu, *Tetrahedron*, 2019, **75**, 130456.

22 K. Okamoto, M. Watanabe, N. Sakata, M. Murai and K. Ohe, *Org. Lett.*, 2013, **15**, 5810.

23 G.-W. Rong, J.-C. Mao, Y. Zheng, R.-W. Yao and X.-F. Xu, *Chem. Commun.*, 2015, **51**, 13822.

24 H.-N. Wang, P.-B. Mi, W.-J. Zhao, R. Kumar and X.-H. Bi, *Org. Lett.*, 2017, **19**, 5613.

25 Y. Du and Z. Li, *Tetrahedron Lett.*, 2018, **59**, 4622.

26 F. Ye, J.-T. Chen and T. Ritter, *J. Am. Chem. Soc.*, 2017, **139**, 7184.

27 X.-J. Zhang, X. Xie and Y.-H. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 7385.

28 L. Yang, Y.-T. Liu, Y. Park, S. W. Park and S. Chang, *ACS Catal.*, 2019, **9**, 3360.

29 F.-D. Lu, D. Liu, L. Zhu, L.-Q. Lu, Q. Yang, Q.-Q. Zhou, Y. Wei, Y. Lan and W.-J. Xiao, *J. Am. Chem. Soc.*, 2019, **141**, 6167.

30 S. Arai, T. Sato and A. Nishida, *Adv. Synth. Catal.*, 2009, **351**, 1897.

31 S. Arai, Y. K. Koike, H. Hada and A. Nishida, *J. Org. Chem.*, 2010, **75**, 7573.

32 A. G. Barrado, A. Z. Ski, R. Goddard and M. Alcarazo, *Angew. Chem., Int. Ed.*, 2017, **56**, 13401.

33 N. Sakata, K. Sasakura, G. Matsushita, K. Okamoto and K. Ohe, *Org. Lett.*, 2017, **19**, 3422.

34 Z.-Y. Liao, P.-Y. Liao and T.-C. Chien, *Chem. Commun.*, 2016, **52**, 14404.

35 W. Zhang, C. Yang, Y.-L. Pan, X. Li and J.-P. Cheng, *Org. Biomol. Chem.*, 2018, **16**, 5788.

36 T. Igarashi, S. Arai and A. Nishida, *J. Org. Chem.*, 2013, **78**, 4366.

37 B. Liu, Y. Wang, Y. Chen, Q. Wu, J. Zhao and J.-W. Sun, *Org. Lett.*, 2018, **20**, 3465.

38 X. Wang and A. Studer, *J. Am. Chem. Soc.*, 2016, **138**, 2977.

39 N. K. Swamy, A. Yazici and S. G. Pyne, *J. Org. Chem.*, 2010, **75**, 3412.

40 Y. Minami, H. Yoshiyasu, Y. Nakao and T. Hiyama, *Angew. Chem., Int. Ed.*, 2013, **52**, 883.

41 C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z.-L. Tang, W.-M. He and X.-H. Xu, *Green Chem.*, 2018, **20**, 3683.
42 L.-H. Lu, S. J. Zhou, M. Sun, J.-L. Chen, W. Xia, X.-Y. Yu, X.-H. Xu and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 1574.
43 C. Wu, L. Hong, H. Shu, Q.-H. Zhou, Y. Wang, N. Su, S.-i. Jiang, Z. Cao and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 8798.
44 X.-H. Zeng and L. Chen, *Org. Biomol. Chem.*, 2018, **16**, 7557.
45 C. Wu, H.-J. Xiao, S.-W. Wang, M.-S. Tang, Z.-L. Tang, W. Xia, W.-F. Li, Z. Cao and W.-M. He, *ACS Sustainable Chem. Eng.*, 2019, **7**, 2169.
46 L.-H. Lua, Z. Wang, W. Xia, P. Cheng, B. Zhang, Z. Cao and W.-M. He, *Chin. Chem. Lett.*, 2019, **30**, 1237.
47 L.-H. Lu, S.-J. Zhou, W.-B. He, W. Xia, P. Chen, X.-Y. Yu, X.-H. Xu and W.-M. He, *Org. Biomol. Chem.*, 2018, **16**, 9064.