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Alkynes as a versatile platform for construction of chemical molecular complexity and realization of molecular 3D printing

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The current level of scientific and technological development requires the formation of general tools and techniques. One of the most versatile technologies is 3D printing, which allows fast and efficient creation of materials and biological objects of desired shape and composition. Today, methods have been developed for 3D printing of macro- and nano-sized objects and for production of films and deposited materials with molecular precision but the most promising technology is printing at the molecular level (molecular 3D printing) for the purpose of direct construction of molecular complexity. This process is currently at the initial stage concerning selection of simple molecules to be used as building blocks possessing flexibility, availability and ease of modification. In this review, we examine the possible versatile synthons suitable for preparation of the main types of organic compounds using molecular 3D printing. The surveyed data strongly indicate that alkyne molecules may be used as a building material in a molecular 3D printer working on hydrocarbons.
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I. Introduction

The state-of-the-art of chemical science provides solution to a multitude of important synthetic problems. The major contribution to the development of organic synthesis in recent years has been made by metal-catalyzed reactions, especially cross-coupling, oxidation, metathesis, rearrangements, tandem reactions and other processes, which considerably extended the potential of synthetic chemistry.[1–8] However, the trend towards increasing number and complication of experimental methods suffers from drawbacks such as poor reproducibility of results, high cost of starting compounds, poor accessibility of complex catalysts and difficulty of scaling-up experimental procedures from laboratory to industry. Therefore, of special value is the search for a limited range of versatile synthetic methods and selection of building blocks (platform chemicals) that could serve as the basis for the design of more complicated structures. The modern concept of development of organic chemistry implies rational design of complex organic molecules, *i.e.*, generation of molecular complexity.

The idea of using common building blocks is implemented in natural processes (Fig. 1 *a*,*b*). The biosynthesis of peptide and protein structures makes use of only twenty α-amino acids. Depending on the number and the sequence of amino acid residues, the resulting highly specific peptides and proteins form enzymes, receptors, cell structures and whole organisms (see Fig. 1 *a*). The diversity of nucleic acids, which play the key role in the storage and transfer of genetic information and evolution, is provided by combinations of only five nitrogen bases (see Fig. 1 *b*).

The human activity is also based on the use of general approaches to solve various pure and applied problems. A highly versatile technology is 3D printing, which is capable of fast and efficient fabrication of new materials and biological objects[9–12] of a desired shape (see Fig. 1 *c*). Currently, methods for 3D printing of macro- and nano-sized objects have been developed;[13–16] however, printing at the molecular level for the direct construction of complex molecules seems most promising (see Fig. 1 *d*). A similar concept is inherent in the atomic layer deposition (ALD) of superthin films and supported catalysts, which is based on

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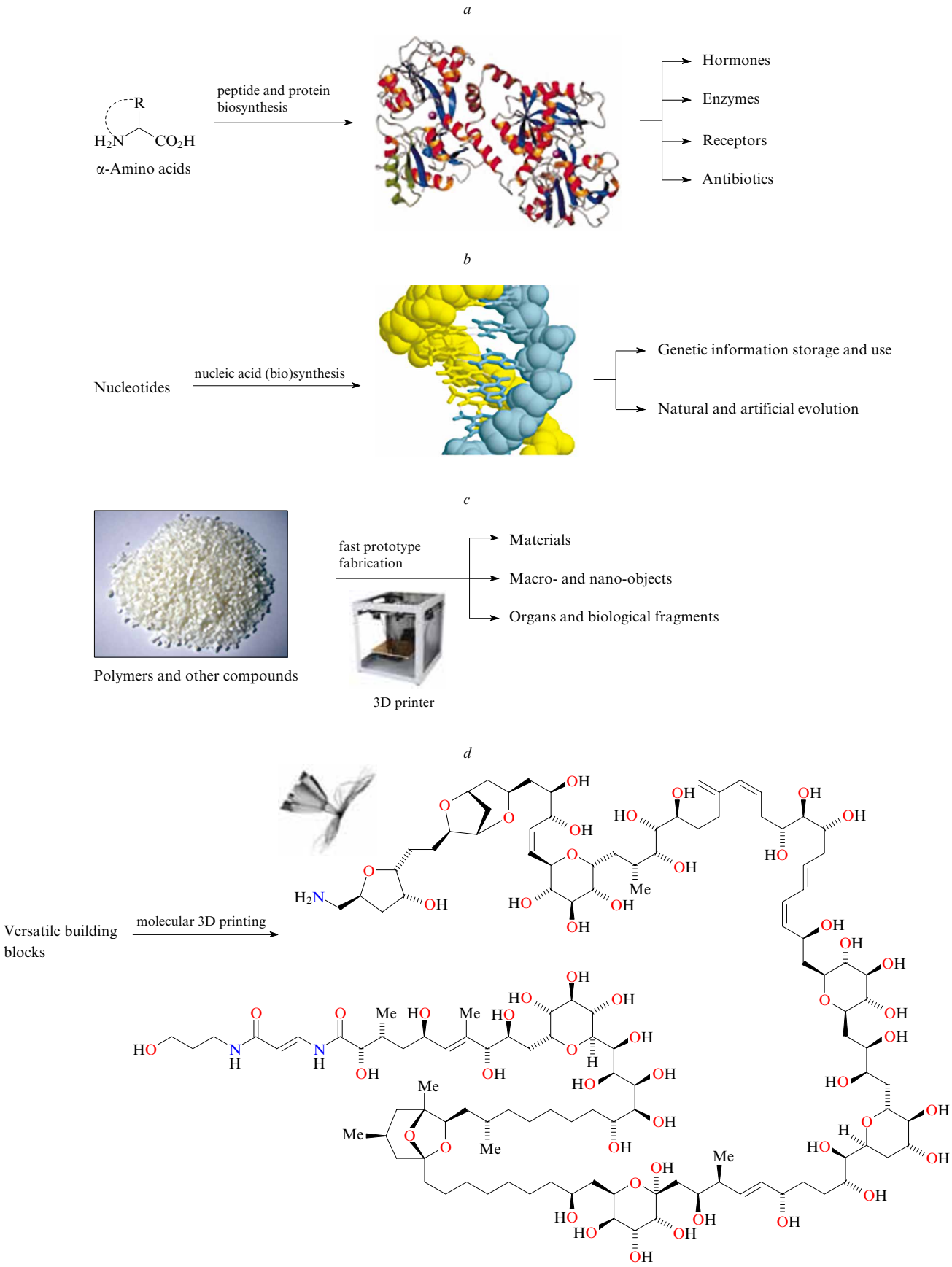


Figure 1. Versatile building blocks in natural and non-natural processes (see text).

gas-phase layer-by-layer coating of the surface by a material with layer thickness up to several angstroms.[17–24]

As regards the direct 3D printing of molecules, today this technology is at its infancy. To develop such technology, it would be necessary to choose a number of simple molecules, distinguished by versatility, easy accessibility and easy modification, as building blocks. Formally, this goal could be achieved with the simplest low-molecular-weight hydrocarbons — methane, ethylene, acetylene and the similar compounds. The key characteristics of hydrocarbons that are crucial for molecular 3D printing are summarized in Table 1. The activation of sp^3-C–H and sp^2-C–H bonds is a complicated process; therefore, among the above types of compounds, acetylene and substituted alkynes appear most suitable substrates. The presence of a multiple bond makes possible atom-economical chemical modification of alkynes under mild conditions, often in good yields and selectivity. Thus, acetylene exhibits, in full measure, the properties that are most important for possible generation of complex molecules: (i) the possibility of two atom-economical addition reactions; (ii) relatively reactive hydrogen atom at each carbon centre; (iii) the absence of unreactive C–H bonds (see Table 1).

The chemistry of the triple bond has been studied in detail, as alkynes have long been used as convenient substrates for the preparation of many classes of organic compounds.[25–32] The chemistry of acetylene derivatives has been the subject of numerous papers and the importance of this research is permanently increasing. In the present review, we do not aim to cover all known reactions of alkynes or to give a detailed analysis of the possible chemical transformations. The purpose of the review is to examine the potential of alkynes as versatile synthons for direct molecular assembly in the future research (see Fig. 1 *d*). The review considers the main types of molecules in which an acetylene moiety plays the key role as well as the most significant classical and recently developed methods for alkyne modification, especially those involving catalysts (Scheme 1).† Particular attention is paid to the methods for generating molecular complexity and to transformations of functionalized molecules.[33]

Table 1. Potential chemical building blocks for a molecular 3D printer.

Building block molecule	Number of low-reactive substituents at the C atom	Number of activated substituents at the C atom	Number of atom-economical steps
	4	0	0
	2	0	1
H–C≡C–H	0	1	2

II. Atom-economical transformations of the triple bond

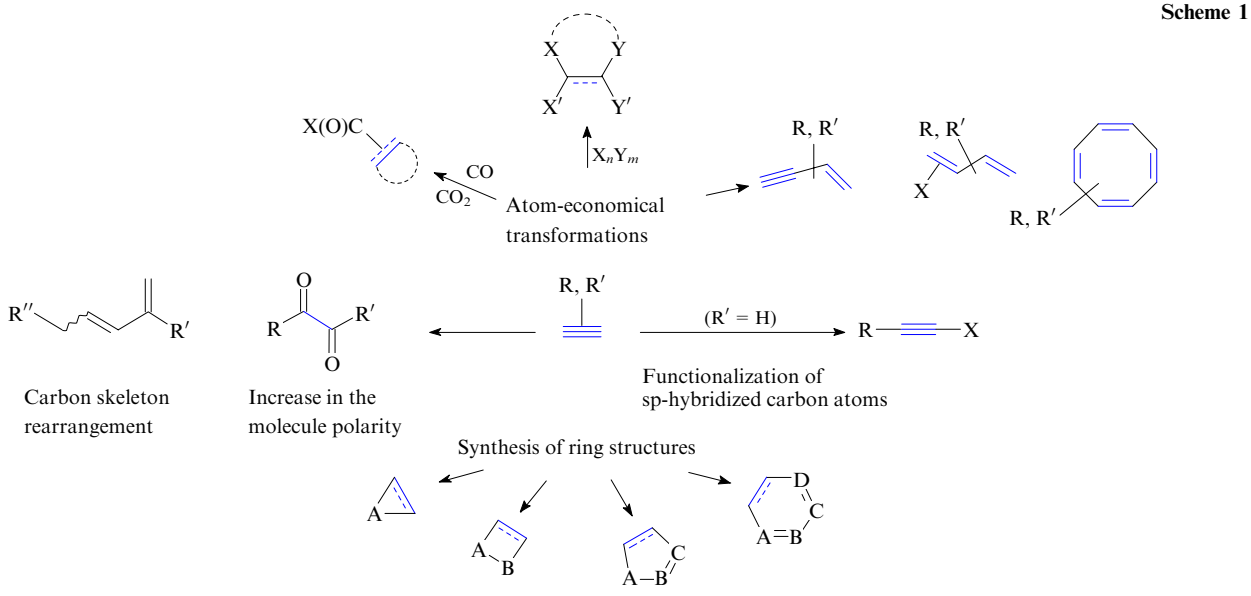
The atom economy plays the key role in the design of complex molecules as this means the absence of side products. All atoms of the starting compounds enter the desired product, in atom-economical reactions, which eliminates the necessity to isolate and purify the products of intermediate steps. This is the key factor for multistep reactions and successive building-up of complexity of molecular structures. Depending on the reaction conditions and the nature of reactants, either unsaturated or saturated products can be obtained. Using intra- and intermolecular annulation, cyclization and various cascade reactions, many types of complex alicyclic and aromatic systems have been synthesized. In addition, dimerization and oligomerization of acetylenes may give rise to polyolefinic products.

II.1. Formation of sp^2- and sp^3-hybridized carbon atoms

The methods for reduction of alkynes to hydrocarbons containing sp^2- and sp^3-hybridized carbon atoms are well-

† Hereinafter, the colour designates the triple bond and its contribution to the reaction products.

Scheme 1



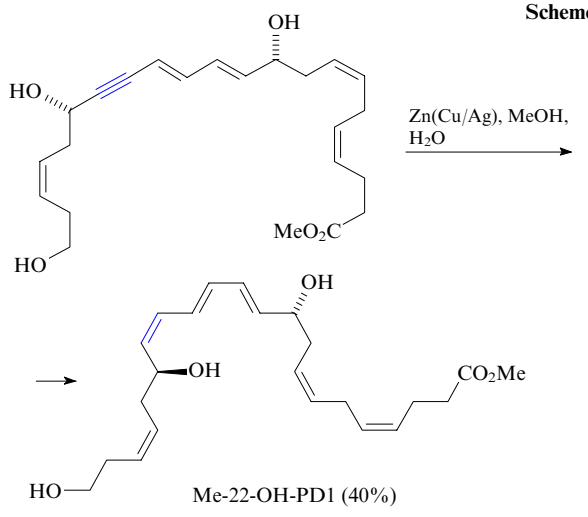
known and widely used in industry.[34] Depending on the alkyne structure and catalyst type, either complete or chemoselective hydrogenation is possible to give alkanes or *cis*- and *trans*-alkenes, respectively. The first hydrogenation catalysts (Pd/C, Pt/C or PtO_2, Raney Ni, Wilkinson's catalyst and so on) had low chemoselectivity. They serve for complete reduction of alkynes to alkanes.[35–39] Currently, there are numerous highly efficient catalytic systems based on Ni,[40,41] Cu,[42,43] Ru,[44] Pd,[45–48] Pt,[49] Nb[50] as well as metal-free systems[51] that are used for alkyne hydrogenation to alkenes and demonstrate high activity and chemoselectivity. The Lindlar catalyst ($Pd-BaSO_4$–quinoline) is the most versatile and readily accessible among the listed systems;[52–56] however, the development of high-performance nanostructured catalysts with a large active surface area that would be easily regenerated is fairly promising.[34]

As a rule, triple bond reduction with transition metal-based reagents results in the formation of *cis*-alkenes,[40–43,45,46] whereas in the case of reducing agents free from transition metals, *e.g.*, aluminium hydride[57,58] or alkali metal amides,[59] the reaction mainly gives *trans*-alkenes.

Active investigations of the possibility of alkyne reduction using alternative sources of hydrogen atoms are in progress. Nanoporous[60,61] and supported[62,63] Au-based catalysts showed remarkable results in the reduction of alkynes to *Z*-alkenes in the presence of water: the selectivity was above 95% with almost complete conversion. The $InCl_3-Et_3SiH$ system reduces alkynes to *trans*-alkenes with a good selectivity (>85%).[64] Shen *et al.*[65] found that the $Pd_2(dba)_3$–phosphine–HCO_2H catalytic system (dba is dibenzylideneacetone) can provide, depending on the reaction conditions (the presence of water and the type of phosphine ligand used), the reduction of alkynes to *cis*- or *trans*-alkenes or to alkanes with a conversion and selectivity of >90%.

Both selective and complete hydrogenation of triple bond are often used in the total syntheses of natural biologically active compounds and their analogues.[66] The key challenge in the reduction of such substrates is the need to minimize the formation of side products resulting from isomerization, racemization, reduction of other reaction centres an so on. In most cases, the desired selectivity of hydrogenation can be achieved by using the Lindlar catalyst but in some cases, more specific reagents are required.

Scheme 2



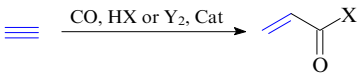
For example, only with the use of the catalytic system containing Zn, Cu and Ag (Boland reagent), was the product of the final step of the synthesis of methyl (4*Z*,7*Z*,10*R*,11*E*,13*E*,15*Z*,17*S*,19*Z*)-10,17,22-trihydroxydocosa-4,7,11,13,15,19-hexaenoate (Me-22-OH-PD1) isolated in a good yield (Scheme 2).[67]

II.2. Construction of a carbon chain with an odd number of atoms

The carbon chain elongation during molecular 3D printing requires an accessible source of one carbon atom, which would react with the triple bond of alkynes to give compounds with odd numbers of carbon atoms. Carbon oxides appear to be the most available reagents for implementing this strategy.

The wide use of alkyne carbonylation and carboxylation methods became possible after Reppe had investigated the reactions of acetylene in the presence of CO with simple inorganic and organic molecules: hydrogen (hydroformylation), oxygen (oxidative carbonylation), water, alcohols, amines and other nucleophiles. The reactions are catalyzed by carbonyls of some transition metals, which were implemented in industrial methods for the production of some α,β-unsaturated carbonyl compounds (Scheme 3).

Scheme 3



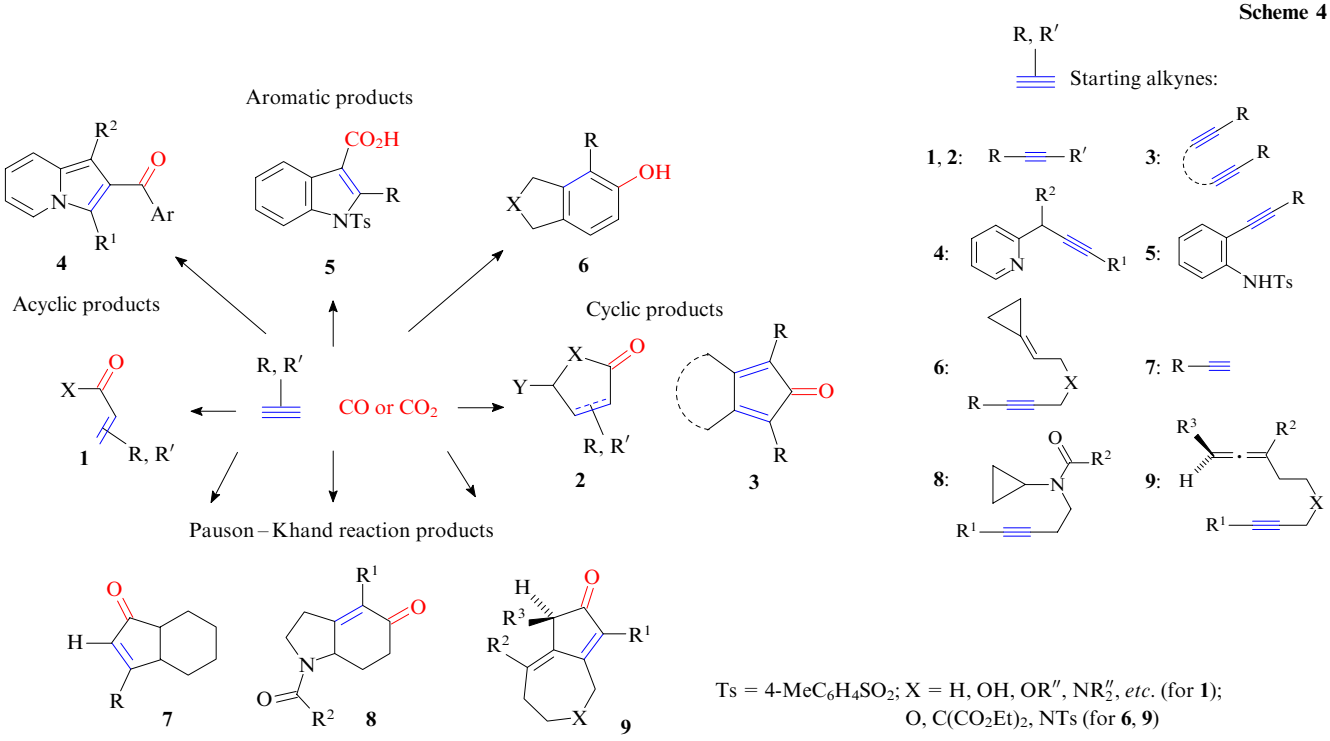
XH = RR′NH, ROH, RSH, HCl; $Y_2 = H_2, O_2$

As a result of further experimental research, the addition reactions of carbon oxides to acetylenes have formed convenient and efficient methods for the preparation of various carbonyl compounds and their derivatives.[68] The methods for regio- and stereoselective synthesis of linear α,β-unsaturated products **1**: aldehydes,[69] carboxylic acids,[70] esters,[71] enamides,[72] carbamates[73] and maleic acid derivatives,[74–76] mainly as *E*-isomers are well known (Scheme 4).‡

Various types of cyclic products **2** have been prepared by reactions of acetylenes with carbon oxides. For instance, maleic anhydride derivatives are formed upon carbonylation of alkynes in the presence of palladium salts[77] or carboxylation catalyzed by $Ni(acac)_2$(bipy) (acac is acetylacetonate, bipy is 2,2′-bipyridine) in the presence of zinc and $MgBr_2$. It is of interest that in the latter case, two CO_2 molecules participate in the ring construction.[78] Recently, conditions have been found for the formation of benzoyl derivatives of ethylene and substituted furanones by carbonylation of internal[79] and terminal[80] acetylenes, respectively, in the presence of arylboronic acids and $[Rh(COD)Cl]_2$ as the catalyst (COD is cycloocta-1,5-diene). Palladium-catalyzed carbonylation of benzylacetylenes in the presence of aryl iodides affords alkylidene derivatives of furanones.[81] The carboxylation of *o*-alkynylalanines in the presence of silver salts gives cyclic carbamates.[82] A series of substituted indenones have been obtained by the Rh-catalyzed reaction of Br-substituted boronic acids with internal alkynes.[83] The formation of

‡ Hereinafter, the starting compounds and the reaction products are numbered in the Schemes in pairs (product **1** is obtained from initial compound **1** and so on).

Scheme 4

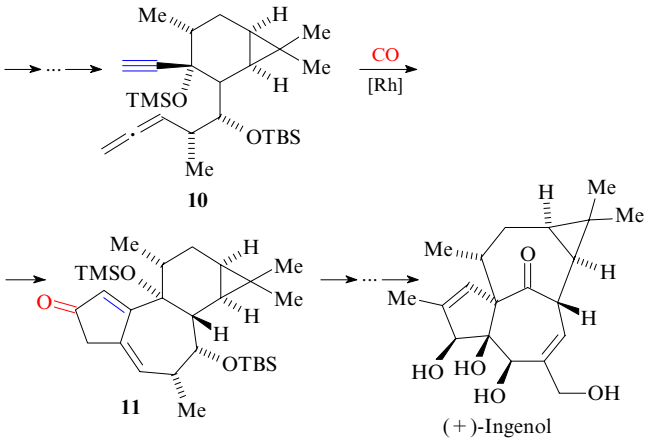


unsaturated lactams in good yields and good regioselectivity upon [2 + 2 + 1]-cycloaddition with amidines, acetylenes and CO in the presence of Bu^n_3SnH and AIBN [AIBN is azobis(isobutyronitrile)] has been reported.[84] Carbonylation of metallacycles formed in the catalytic reaction of two alkyne molecules with $PdCl_2$ in the presence of $CuCl_2$ affords cyclopentadienones **3** with high regioselectivity.[85]

Attempts were made to utilize carbonylation and carboxylation methods for the synthesis of aromatic compounds. Palladium-catalyzed formation of 2-acylated indolizines **4** from propargylpyridines and CO in the presence of ArI has been described.[86] Similarly, 1*H*-indole-3-carboxylic acids **5** were obtained by carboxylation of 2-alkynylanilines in the presence of a Cu catalyst and $ZnMe_2$.[87] By using acetylenes containing a cyclopropylidenealkyl moiety in the carbonylation in the presence of $[Rh(CO)_2Cl]_2$ and silver salts, Kim and Chung[88] unexpectedly obtained bicyclic phenols **6** in good yields.

The Pauson–Khand reaction, the synthetic scope of which is the subject of numerous publications, serves as a method for the preparation of cyclic carbonyl derivatives.[89–96] Zirconium-based catalysts showed good regioselectivity of the intermolecular Pauson–Khand reaction towards the formation of cyclopenten-2-ones **7** from cyclohexene and terminal acetylenes.[97] In recent studies, Bower and co-workers[98] have found that carbonylation of acetylenes containing the N-cyclopropyl moiety under usual conditions ($[Rh(CO)_2Cl]_2$, phosphine) furnishes the reduced indolone derivatives **8** in good yields. An attempt was made to carry out stereoselective intramolecular cyclocarbonylation of allene-yne substrates to bicyclic ketones **9** with >90% enantioselectivity.[99] A similar approach was used in the synthesis of the complex natural terpenoid, (1a*R*,2*S*,5*R*,5a*R*,6*S*,8a*S*,9*R*,10a*R*)-5,5a,6-trihydroxy-4-(hydroxymethyl)-1,1,7,9-tetramethyl-1a,2,5,5a,6,9,10,10a-octahydro-1*H*-2,8*a*-methanocyclopenta[*a*]cyclopropa[*e*][10]annulen-11-one [(+)-ingenol], where cyclocarbonylation of *tert*-butyl{[(1*R*,2*R*)-1-((1*R*,3*R*,4*R*,6*R*)-4,7,7-trimethyl-3-trimethylsilyloxy-3-ethynylbicyclo[4.1.0]heptan-2-yl)-2-methylpenta-3,4-dien-1-yl]oxy}dimethylsilane (**10**) to give (1a*R*,1b*R*,2*R*,3*R*,7b*R*,8*R*,9a*R*)-2-(*tert*-butyldimethylsilyloxy)-1,1,3,8-tetramethyl-7b-(trimethylsilyloxy)-1,1a,1b,2,3,5,7b,8,9,9a-decahydro-6*H*-cyclopropa[3,4]benzo[1,2-*e*]azulen-6-one (**11**) was one of the key steps (Scheme 5).[90]

Scheme 5



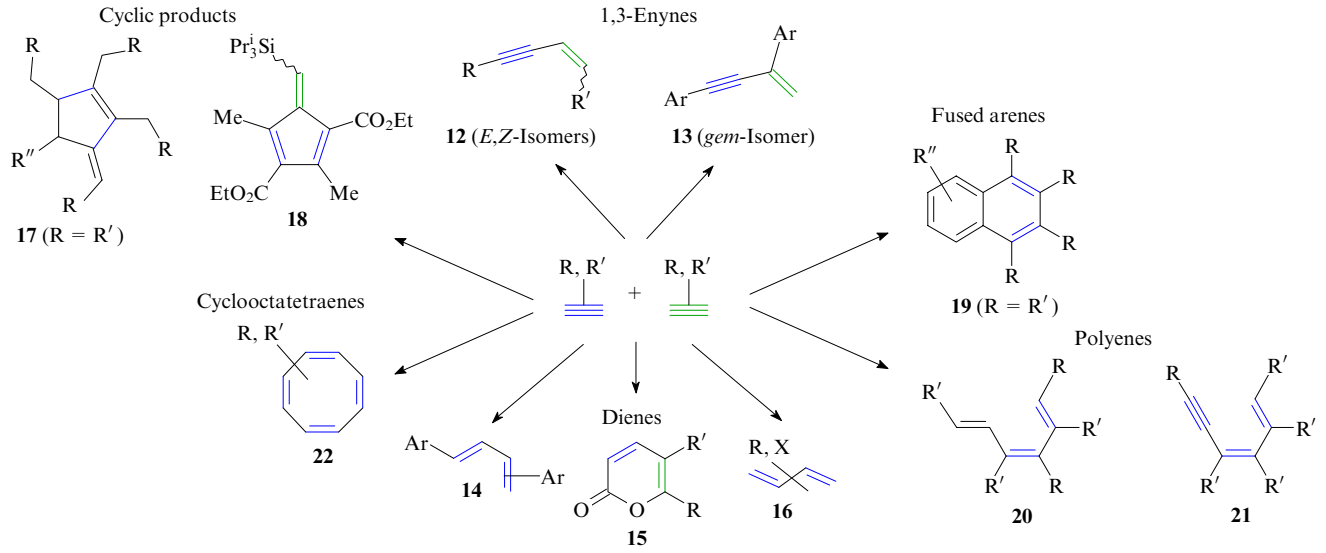
TMS = Me_3Si, TBS = Bu^tMe_2Si

II.3. Elongation of the carbon skeleton of the molecule

A convenient method for the preparation of linear and cyclic products directly from alkynes is di- and oligomerization (Scheme 6). The linear and cyclic conjugated π-systems thus formed are of considerable interest for medicine and materials science.[100]

Hydroalkynylation (dimerization) of terminal acetylenes affords conjugated enynes. The main challenge of this

Scheme 6



For **16**: X = SAr, SeAr, 2-pyridyl, *etc.*

reaction is to choose catalysts that would ensure high chemo-, regio- and stereoselectivities of reactions between different alkynes without substantial contribution of homocoupling, aromatization, tetramerization, oligomerization or other side processes. Previously, it was found that Pd-catalyzed dimerization of arylacetylenes (either a head-to-head or head-to-tail) is affected by the nature of the base used.[101,102] The Rh^{I} phosphine complexes showed good results in the head-to-tail addition of terminal arylacetylenes to propargyl and aminopropargyl derivatives (products **12**).[103] With some catalytic systems, for example, pincer Rh^{I} phosphine complexes[104] or Fe chelate complexes,[105] *cis*-hydroalkynylation was found to predominate. In aqueous acetic acid in the presence of $Pd(PPh_3)_4$, *gem*-isomeric enynes **13** (R = Ar, R′ = H) were formed in good yields.[106]

Dimerization of internal alkynes giving conjugated dienes **14** [107] and Ru-catalyzed dimerization of propiolates, resulting in substituted carboxylate derivatives of pyrones **15**, have been reported.[108] In some cases, substituted dienes **16** are formed upon the addition reactions catalyzed by complexes of Ni,[109–111] Pd,[112–114] Co [115] or Rh.[116] Tsurugi *et al.*[117] discovered an unusual reaction of internal alkynes with lutidine catalyzed by hafnium complexes, resulting in the isolation of methylidene derivatives of cyclopentene **17**. A similar cyclopentadiene product **18** was obtained in the reaction of $Pr^{i}_{3}Si$-substituted acetylene with ethyl butynoate in the presence of $[Rh(COD)_2][BF_4]$.[118]

Dimerization of alkynes taking place together with CH-activation of aromatic substrates has proved efficient for the synthesis of polyaromatic compounds **19**.[119–124] It is important that the formation of substituted aromatic derivatives can be highly regioselective.[121,123]

By the reactions of acrylates with alkynes catalyzed by nickel carbene complexes, triene derivatives **20** were synthesized,[125] while cross-trimerization of internal and terminal alkynes in the presence of nickel phosphine complexes yielded conjugated dienynes **21** in high yields and high regio- and stereoselectivities.[126]

Tetramerization of acetylenes serves as the main method for the preparation of cyclooctatetraene derivatives **22**. Attempts were made to perform selective tetramerization catalyzed, for example, by rhodium [127] or nickel [128–130] complexes; transannulation of cyclic tetraynes to tricyclic derivatives of cyclooctatetraene without participation of metal compounds was reported.[131]

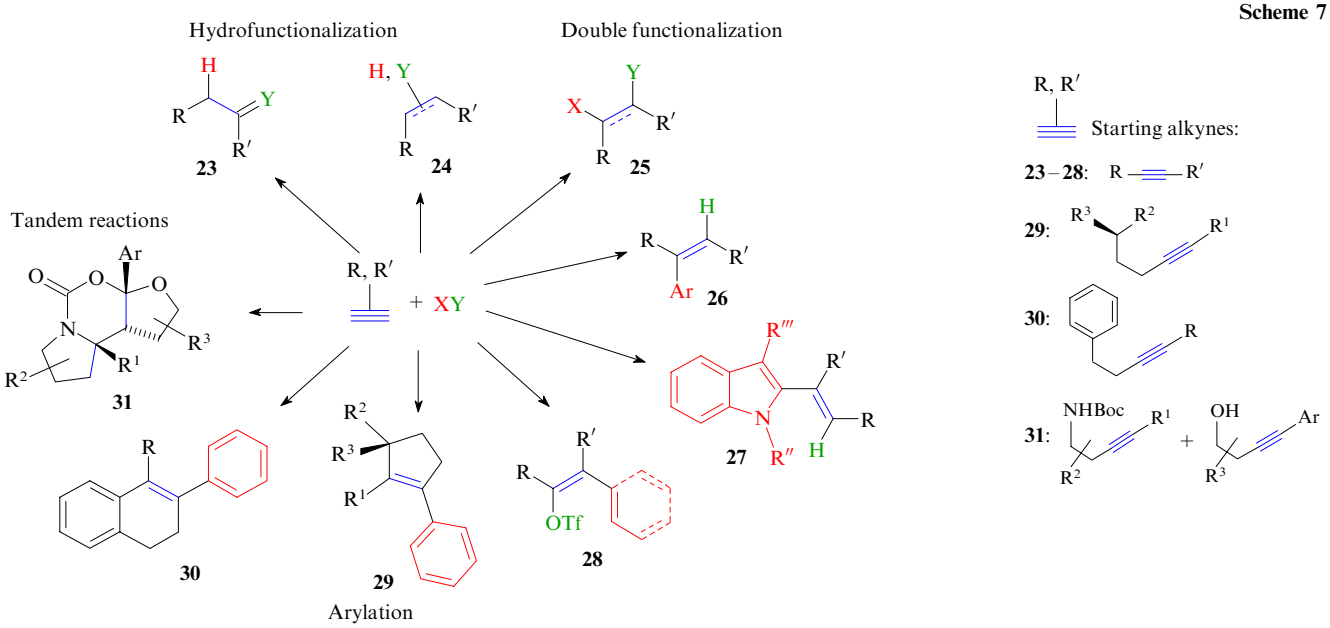
II.4. Formation of carbon–carbon and carbon–heteroatom bonds

Apparently, electrophilic, nucleophilic or radical addition reactions to the triple bond would become the key method for functionalization of alkynes in the molecular 3D printing. This type of reactions comprises a wide diversity of synthetic methods and is extensively employed for the preparation of many classes of unsaturated and saturated compounds.[132–135] Methods for the synthesis of partly or completely substituted aliphatic derivatives [136–139] and various cyclic products of a desired composition and spatial structure *via* formation of new carbon–heteroatom bonds (C–B, C–N, C–O, C–S, C–P [3,133,140–163] and other) having high value for fine organic synthesis and commercial production have been comprehensively studied (Scheme 7).

Numerous papers are devoted to the development of highly efficient catalysts that improve regio- and stereoselectivity of the addition to triple bonds giving products **23**–**25**. Using homogeneous [146] or heterogeneous [144] zinc-based catalytic systems for hydroamination, silver compounds for hydration [150] and rhodium complexes for hydroacylation,[164] terminal alkynes are mainly converted to Markovnikov products. Mixed-ligand amido-imidate titanium complexes [165,166] and ruthenium pyridine complexes [149] catalyze hydroamination and hydration at the terminal carbon atom, respectively. In the presence of Au^{I} triazole complexes, hydroamination of internal alkynes proceeds regioselectively even if the substituents at the triple bond differ only slightly.[145] A highly efficient system for selective hydro- and *gem*-dihydrofluorination of acetylenes comprising an *N*,*N*′-dimethyl-2-pyrimidone complex with HF and a mixed imido-phosphine Au^{I}-based catalyst was found.[167]

An important task is to develop catalytic systems for the reaction of acetylenes with aliphatic [168–171] or aromatic [172–177] substrates to afford new C–C bonds. The

Scheme 7



For **23**, **24**: XY = NH_2R'', H_2O, *etc.*; for **25**: XY = R″SSR″, *etc.*, Tf = F_3CSO_2, Boc = $Bu^tOC(O)$

reactions of acetylenes with alcohols in the presence of $Ni(COD)_2$ give en-2-oles in good yields but with low regioselectivity.[178] The C–H activation of aromatic compounds in the presence of acetylenes was used to prepare substituted styrenes **26**[173,174] and alkenylindoles **27**.[176,177] Gaunt's research group[179] described Cu-catalyzed coupling of internal alkynes with iodonium salts as a method for preparing activated vinyl- or aryl-containing tetrasubstituted alkenes **28**.[179] The same researchers used this method for the synthesis of substituted cyclopentenes **29**[180] and fused cyclohexene derivatives **30**.[181]

The intramolecular and tandem addition reactions to alkynes form an important method for the preparation of carbo- and heterocycles widely used in the synthesis of biologically active compounds.[182,183] Galván *et al.*[184] reported a convenient method for the preparation of several saturated polycycles **31** having potential biological activity *via* isomerization followed by dimerization of readily accessible unsaturated compounds using rhodium complexes as catalysts (see Scheme 7).

Metallation of the triple bond can result in isolation of stable metal vinyl derivatives;[65] however, compounds of this type are formed as intermediates in the catalytic cycles of many triple bond modification reactions. The use of gold-based catalysts for triple bond activation was a breakthrough, as these catalysts showed high performance and selectivity towards both traditional reactions and previously unknown processes involving alkynes: regioselective hydroamination,[185–188] hydroalkoxylation[189] and hydrosulfonation,[190] as well as various cycloaddition and cycloisomerization processes.[191–199] Therefore, catalysis by gold compounds now receives a lot of attention in acetylene chemistry.[200–208]

II.5. Synthesis of cyclic structures

Acetylenes play a key role in the construction of most of the known types of ring molecules.[6,32] A multitude of cyclization and cycloaddition reactions involving triple bond compounds have been studied and are used to prepare aliphatic or aromatic products. Since many cyclic compounds are structural moieties of biologically active molecules,[209] the search for new methods for cyclization of acetylene substrates is highly demanded.

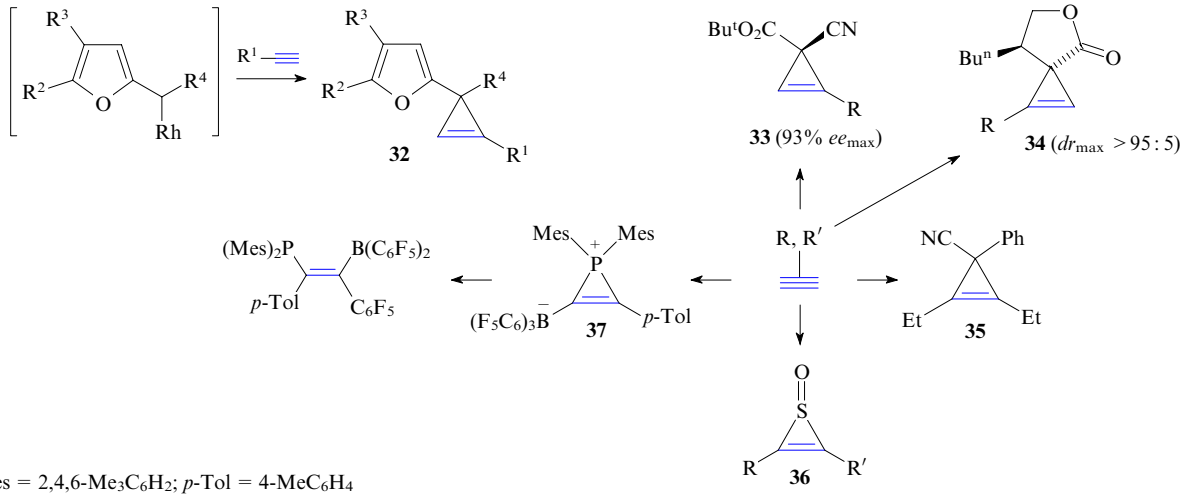
Compounds of C_2A type (see synthesis of ring molecules in Scheme 1). The [2 + 1]-cycloaddition of acetylenes serves as the key method for the preparation of three-membered rings (Scheme 8),[210–216] which have found wide application as important synthetic intermediates and biologically active compounds.[217–224]

A number of studies have been devoted to the development of new [2 + 1]-cycloaddition methods, namely, non-catalyzed[216] and metal carbenoid-involving reactions. Cyclopropene derivatives **32** were prepared by the reaction of acetylenes with furan Rh carbenoids formed *in situ* from alkynyl ketones. Compounds **32** proved to be unstable under reaction conditions and further rearranged to bicyclic products.[215] Considerable attention is paid to the possibility of stereoselective [2 + 1]-cycloaddition; good results were obtained by using catalytic systems based on Au and Rh.[225,226]

Functionalized cyclopropenes **33** were prepared in > 80% yield and enantioselectivity by the Rh_2(*S*-IBAZ)$_4$-catalyzed (IBAZ is the 4-isobutoxycarbonylazetidin-2-one anion) reaction of acetylenes with diazocarbonyl compounds containing electron-withdrawing substituents.[211] Similarly, Rh-catalyzed reactions of alkynes with chiral cyclic diazo compounds afford bicyclic spiro derivatives **34** with a diastereoselectivity of > 93%.[227]

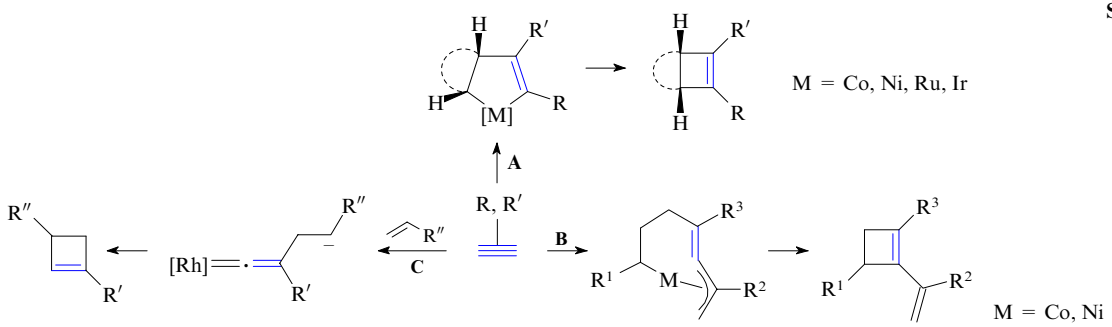
A metal-free method for the preparation of cyclopropenes by treatment of acetylenes with the $PhI(OAc)_2$ iodine(III) reagent is known.[228] The cyclopropanation of acetylenes with iodonium derivatives in the presence of azides affords cyanocyclopropenes (*e.g.*, compound **35**) in moderate yields.[229] In the researchers' opinion, the key intermediate of this reaction is unstable azidoacetylene, which is converted upon N_2 elimination to phenylcyanocarbene, and the latter directly participates in cyclopropanation.

Scheme 8



Mes = 2,4,6-$Me_3C_6H_2$; *p*-Tol = 4-MeC_6H_4

Scheme 9



New methods for the synthesis of three-membered heterocycles are being studied. The reaction of triplet SO with alkynes yielded a number of thiirene oxides **36**.[230] The cyclic products were isolated in low yields (5%–20%); however, note that monosubstituted thiirene oxide derivatives were prepared in this study for the first time. Unusual zwitter-ionic derivatives of phosphirene **37** are formed in the reaction of P-substituted acetylenes with $B(C_6F_5)_3$. These compounds are unstable and they are converted to polysubstituted alkenes on heating above 100 °C.[231]

Compounds of C_2AB type. Four-membered rings are of considerable biological and synthetic value.[232–235] The [2 + 2]-cycloaddition of alkenes to alkynes (the main method for the preparation of cyclobutenes) can be performed as a regio- or chemoselective process (Scheme 9).

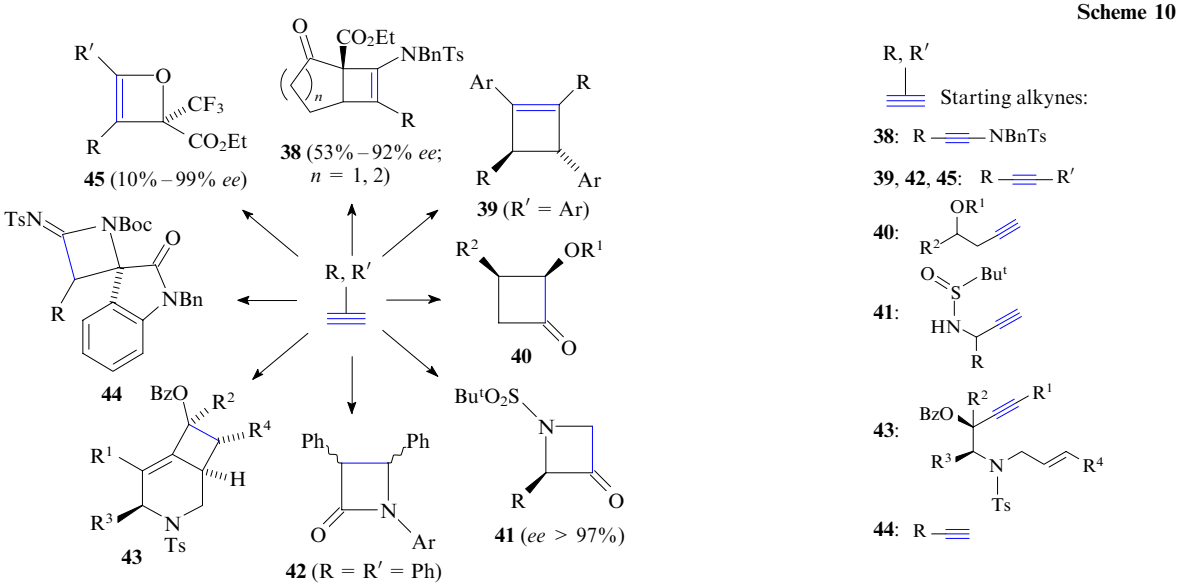
The addition of alkynes to unsaturated substrates with intermediate formation of five-membered metallacycles catalyzed by Co,[236] Ni,[237] Ru[238] or Ir[239] complexes was studied. The cyclobutene ring is formed *via* the subsequent reductive elimination of the metal-containing moiety (pathway **A**). The intermolecular cyclization of alkenynes and acetylenes in the presence of nickel[240] or cobalt[241] compounds follows a different mechanism the key step of which is the formation of an intermediate η^3-dienyl complex (pathway **B**). Unlike the above examples, the cycloaddition of electron-deficient alkenes in the presence of a quinoline-containing rhodium complex and the phosphine co-catalyst proceeds presumably *via* the formation of vinylidene intermediates (pathway **C**).[242]

The most popular modern methods for the preparation of four-membered ring molecules using alkyne substrates are summarized in Scheme 10.

Heterosubstituted acetylenes undergo cycloaddition *via* the formation of heteroallene intermediates (Ficini reaction). When ruthenium complexes are used in reactions of alkynylamides with cyclopentenones and cyclohexenones, the corresponding bicyclic products **38** are formed in high yields and high enantioselectivity.[243] Tetrasubstituted cyclobutene derivatives **39** were obtained by reductive [2 + 2]-cycloaddition of terminal alkynes. Zirconium complexes were found to perform this cyclization with high yields and regio- and stereoselectivity.[244] The stereoselective oxidative cyclization of homopropargylic ethers catalyzed by gold complexes was used to synthesize cyclobutanone derivatives **40** as *cis*-isomers.[245] Under similar conditions, intramolecular oxidative cyclization of propargyl sulfamides affords azetidin-3-one derivatives **41** with high enantioselectivity.[246] The predominant formation of *trans*-substituted azetidin-2-ones **42** was observed in the Cu-catalyzed [2 + 2]-cycloaddition of acetylenes to nitrones (Kinugasa reaction).[247,248] The cyclization of benzoate-substituted 1,7-enynes[249] or 1,7-diynes[250] in the presence of gold complexes gave [4.2.0]azabicyclic products **43** after benzoate group migration and formation of the allene-yne intermediate.

New methods for the preparation of heterocyclic cyclobutane analogues are being vigorously studied (see Scheme 10). Spirocyclic isatin derivatives of (azetidin)-

Scheme 10



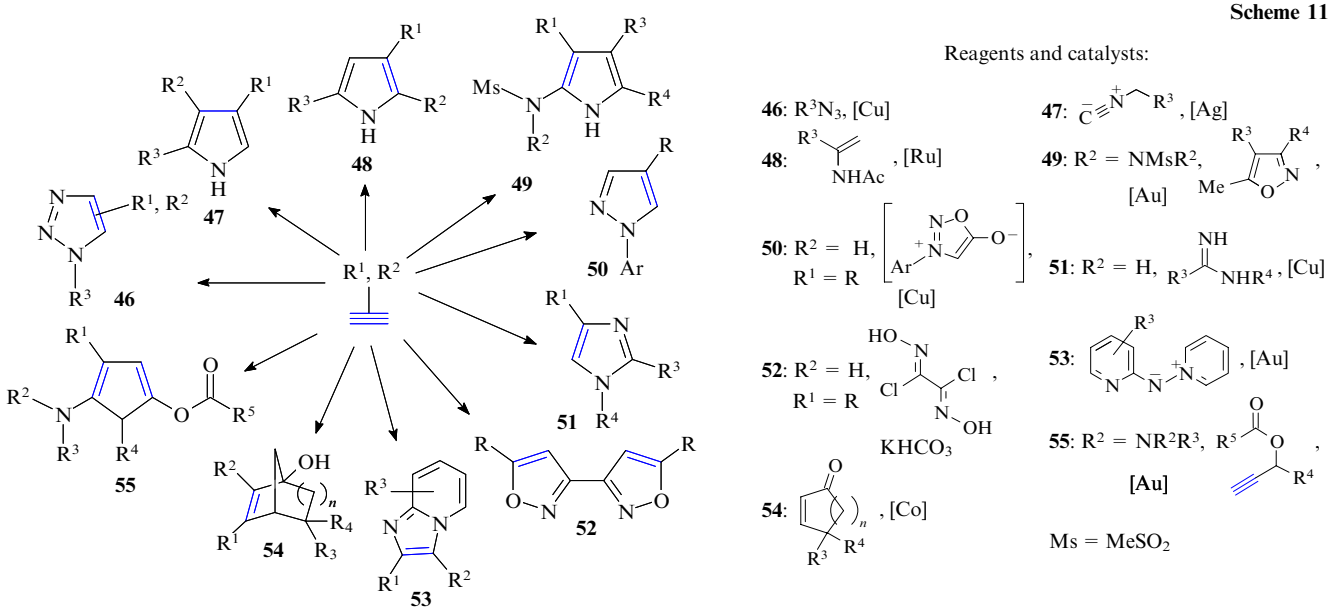
imines **44** were synthesized by stereoselective cyclization of ketimines, formed *in situ* from terminal acetylenes and tosyl azide, with cyclic imines.[251] Some stable CF_3-substituted dehydroxetane derivatives **45** were isolated upon [2 + 2]-cycloaddition of acetylenes to trifluoropyruvate. The use of the chiral Pd-BINAP catalyst [BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] provided high enantioselectivity of this reaction.[252]

Compounds of C_2ABC type. Five-membered rings of virtually any structure can be formed using acetylene synthons. A variety of cycloaddition and cycloisomerization methods are widely used for preparing aliphatic and aromatic compounds of both mono- and polycyclic structures (Scheme 11).

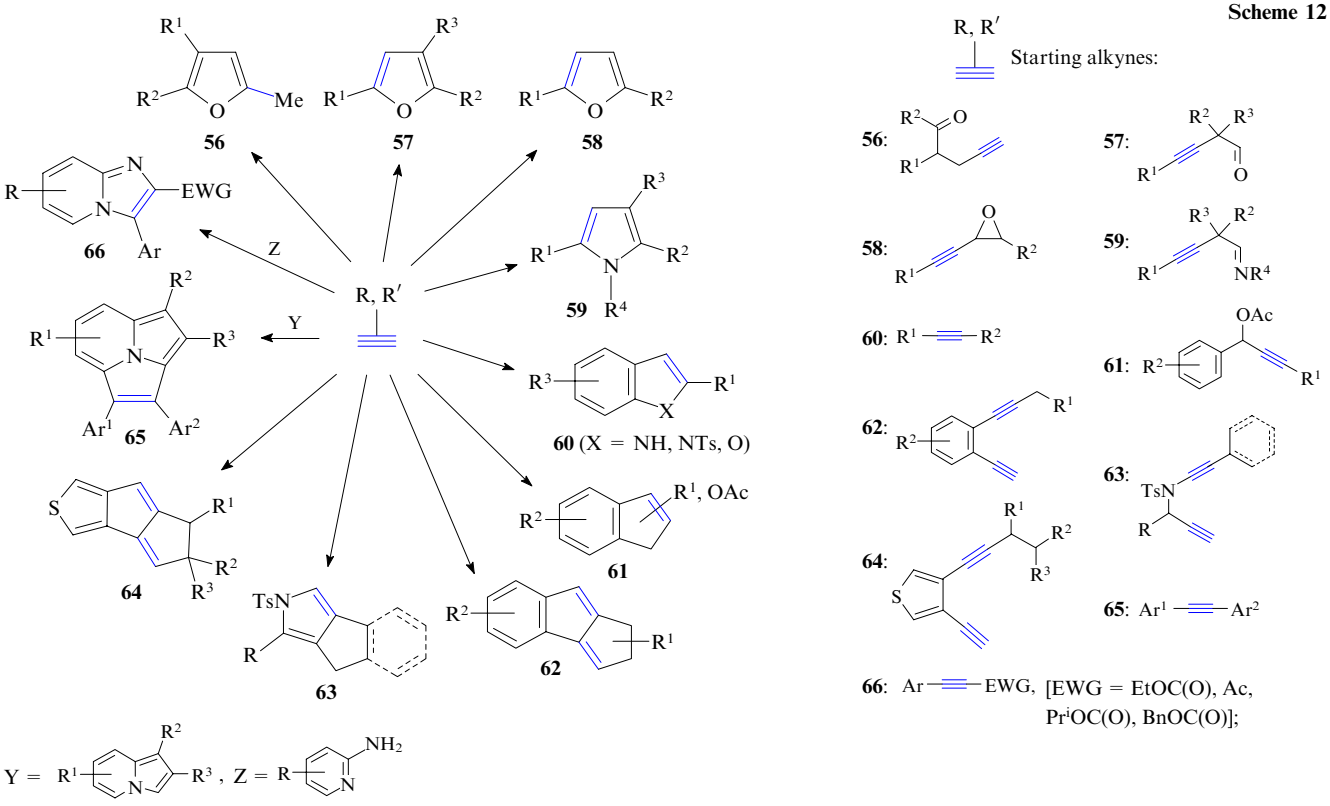
Considerable attention is given to the development of new methods of intermolecular cycloaddition that would be used for the one-step synthesis of functionalized heterocycles from readily accessible reagents. A significant reaction of this type is the regioselective Cu-catalyzed interaction between alkynes and azides giving rise to triazoles **46**. This reaction was studied in the early 21st century by Mendal and Sharpless research groups and found diverse applications.[253–260] Owing to the simplicity of conducting this cyclization, together with high efficiency, this reaction has formed the basis for click chemistry — a fast and reliable method for the fabrication of molecular blocks mimicking biological binding.[261]

Depending on the type of substrates used, various carbo- and heterocycles with the desired positions of substituents can be constructed. For example, as applied to the synthesis of pyrrole derivatives, the Ag-catalyzed reaction of internal alkynes with isonitriles furnished 2,3,4-substituted products **47**,[262, 263] whereas cyclization with enamides in the presence of Ru complexes produced 2,3,5-substituted products **48**.[264] Substituted 2-amino pyrroles **49** were prepared by the unusual reaction of ynamides with oxazoles in the presence of Au complexes.[265]

Scheme 11



Scheme 12



New cycloaddition reactions resulting in the formation of pyrazole (**50**),[266] imidazole (**51**),[264] bioxazole (**52**),[267] imidazopyridine (**53**) derivatives[268] and the similar structures have been developed. The Co-catalyzed [3 + 2]-cycloaddition of internal alkynes to cyclic unsaturated ketones results in bicyclic enols **54**. By using chiral ligands, the researchers performed the cyclization with enantioselectivity of >90%.[269] Hashmi's research group[270] obtained functionalized cyclopentadienes **55** by cyclization of ynamides with propargylic carboxylates in the presence of Au catalysts.

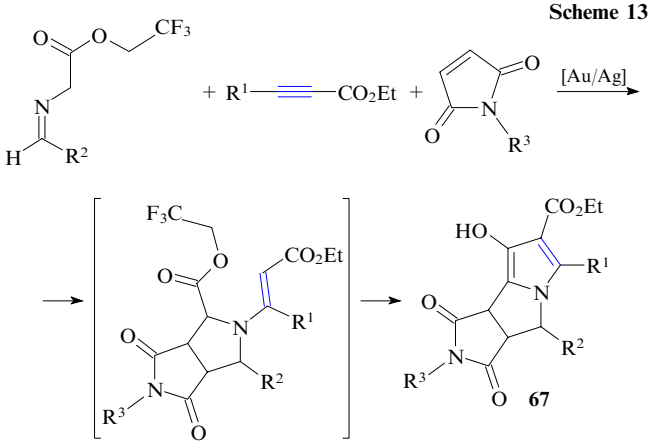
The intramolecular cyclizations of functionalized alkynes are widely used for the synthesis of aliphatic and aromatic heterocycles (Scheme 12).

It is noteworthy that these reactions are quite diverse and provide the desired type of heterocycle by a convenient route. Indeed, some furan derivatives **56**–**58** were synthesized by cyclization of alkynyl ketones,[271,272] homopropargylic aldehydes[273] or acetylenes containing epoxide substituents.[274] New methods for cyclization of functionalized alkynes were found, resulting in the formation of pyrrole (**59**),[273,275] indole and benzofuran (**60**),[276–280] indolizine[281] and indene (**61**)[282] derivatives and other compounds. Zheng *et al.*[283] prepared arylated derivatives of pyrroles, furans and thiophenes by cyclization of butadiynes in the presence of appropriate inorganic compounds. By using Au-based catalysts, di- and tricyclic indene (**62**),[192] pyrrole (**63**)[284] and thiophene (**64**)[285–287] derivatives were prepared from bis-alkyne substrates.

The C—H activation of aromatic substrates catalyzed, most often, by Rh or Au complexes[118,285,288] provided the synthesis of many cyclic products, including derivatives of indole,[118,288,289] benzophosphole oxide[290,291] and other. Double CH-activation of indolizines in the Pd-catalyzed reaction with diarylacetylenes in the presence of oxygen led to tricyclic derivatives **65**.[292] Another important method of annulation that has found wide application for the preparation of indole,[293–295] benzofuran and indene[296] derivatives involves the reaction of functionalized aryl iodides with acetylenes catalyzed by Pd complexes (Larock method). The annulation of aminopyridines in the presence of Cu and Fe compounds resulted in highly regioselective synthesis of substituted imidazopyridines **66**.[297]

An important line of research is the one-step synthesis of complex polycyclic systems containing five-membered heterocycles (domino reactions) from readily accessible substrates. An unusual method was found for the preparation of ethyl 8-hydroxy-1,3-dioxo-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-*a*]pyrrolizine-7-carboxylate derivatives **67** by a three-component reaction of alkynes, alkenes and imines

Scheme 13

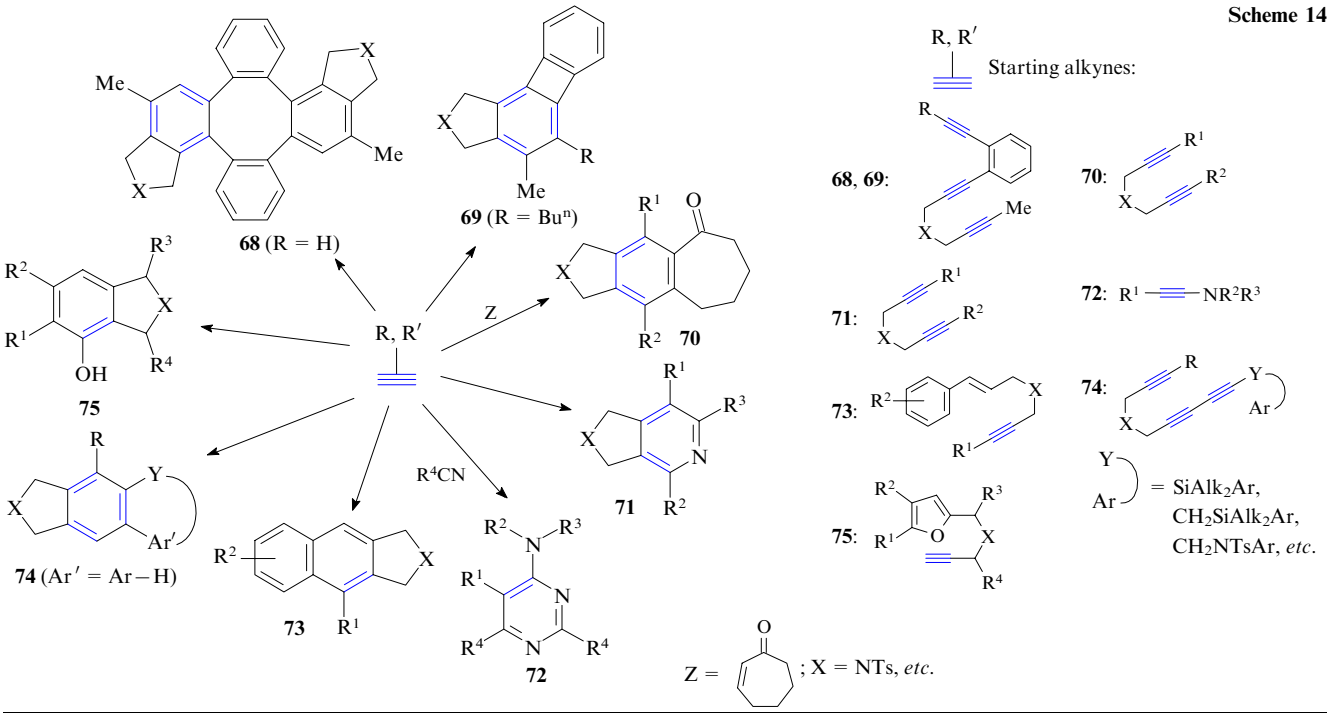


catalyzed by Au complexes in the presence of Ag salts (Scheme 13).[298]

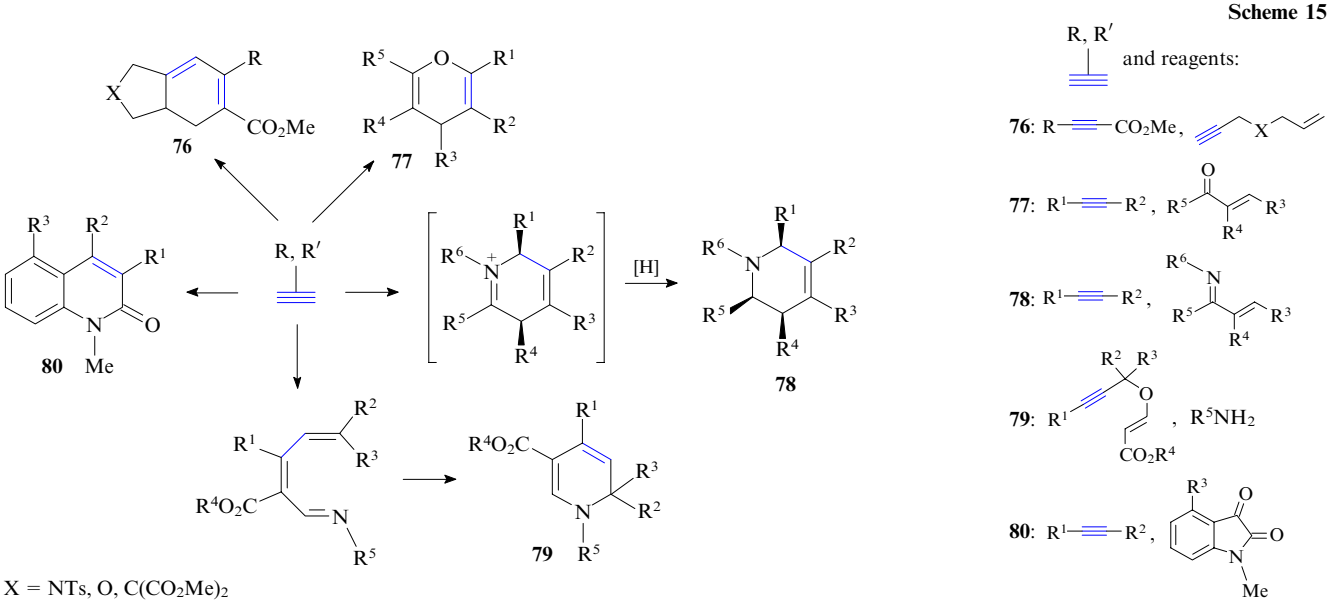
Compounds of the C_2ABCD type. Methods for the construction of six-membered rings with participation of alkynes are rather diverse (Schemes 14–16). Some of them, for example [2+2+2]-cycloaddition or Diels–Alder reactions, are classical methods for the preparation of aromatic and aliphatic carbo- and heterocyclic products. Intramolecular cyclizations and various annulation methods are used for the synthesis of polycyclic systems.

Acetylene derivatives play a key role in the synthesis of aromatic compounds. An early method for the preparation of benzene — trimerization of alkynes — affords, as a rule, a mixture of regioisomers;[299] however, the [2+2+2]-cycloaddition reactions involving isolated diynes are successfully used for the synthesis of some polycyclic aromatic compounds, for example, **68** and **69**.[300–303] Tanaka and coworkers[304] utilized chiral Rh catalysts for enantioselective synthesis of paracyclophanes from cyclic diynes and alkynes. The Ni-catalyzed reactions of 1,6-diynes with tropone yielded fused tricyclic compounds **70** comprising five-, six- and seven-membered rings.[305] Regioselective cycloaddition involving nitriles and two alkyne substrates in the presence of Fe,[306] Ni[307] or Rh[308] complexes is one of the key methods for the synthesis of pyridine derivatives (*e.g.*, compounds **71**). Karad and Liu[309] have found a convenient method for the preparation of 4-aminopyrimidines **72** by [2+2+2]-cycloaddition of ynamides to nitriles catalyzed by Au phosphine complexes.

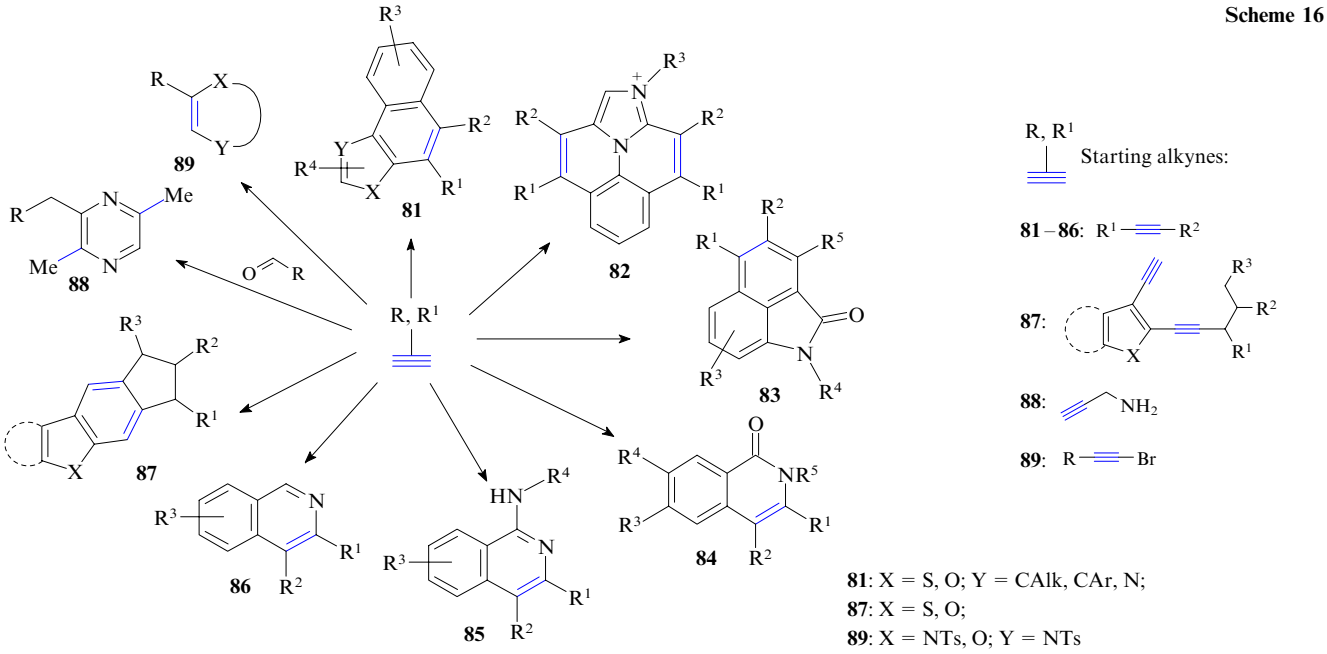
Scheme 14



Scheme 15



Scheme 16



Currently, compounds containing several multiple bonds are mainly utilized as substrates for the synthesis of aromatic derivatives. The most important reactions of this type include cycloaromatization of dienynes[310] as well as the Diels–Alder reactions of 1,3-enynes with alkynes or 1,3-diynes with alkenes, resulting in the formation of benzene derivatives.[311,312] Naphthalene derivatives **73** were prepared by intramolecular Diels–Alder reaction using alkynylstyrene as the diene.[313]

Of considerable interest is the Diels–Alder reaction of 1,3-diynes with acetylenes, giving rise to highly reactive aryne intermediates.[314,315] The addition of relatively unreactive substrates such as non-activated benzene derivatives or alkanes to the arynes affords aromatic derivatives **74** which are difficult to obtain by other methods.[316–318] Wang *et al.*[319] used Au-catalyzed intramolecular cyclization of enediynes to generate aryne intermediates, which were modified to indane derivatives and some heterocyclic fused benzene derivatives. A number of phenols **75** can be prepared by cyclization of alkynylfurans in the presence of $AuCl_3$.[194]

The [2 + 2 + 2]-cycloaddition and modified Diels–Alder reaction are used to construct unsaturated six-membered rings.[320–322] It is important that stereoselective product formation is possible;[323] however, in some cases, substantial amounts of aromatic side products are formed.[324] A number of functionalized cyclohexadienes **76** have been prepared by regioselective cyclization of 1,6-enynes with alkyl propiolates in the presence of Rh complexes (Scheme 15).[325]

Heterodienes can function as alkynophiles, which results in the formation of six-membered heterocycles. Using Ni-catalyzed cycloaddition of α,β-unsaturated ketones to alkynes, substituted pyrans **77** were obtained.[326] Ellman and co-workers[327,328] used the cyclization–reduction tandem process for enamines and acetylenes catalyzed by Rh phosphine complexes for diastereoselective synthesis of substituted tetrahydropyridines **78**. Substituted dihydropyridines **79** are obtained upon cyclization of vinyl propargyl ethers with amines *via* the intermediate formation of azatrienes.[329] The Rh-catalyzed insertion of alkynes into cyclobutanones gives cyclohexenones.[330] The C—C bond activation in isatin by a Rh catalyst in the presence of acetylenes followed by decarbonylation furnishes substituted quinolinones **80**.[331]

The annulation reactions of aromatic compounds involving acetylenes are also widely used for the synthesis of fused cyclic systems (Scheme 16).

Cyclizations that occur *via* metal-promoted C—H-activation of various aromatic carbo- and heterocycles have been thoroughly studied. Fused naphthalene derivatives **81**[332] and tetracyclic aromatic imidazole derivatives **82**[333] were obtained upon Rh-catalyzed C—H-activation of phenyl-substituted heterocycles. You and co-workers[334] found an unusual synthetic route to benzoxindoles **83** by regioselective C—H-activation of 3-carbonylindoles. The annulation of substituted benzamides[335] or benzamidines[336] results in isoquinolone **84** or aminoisoquinoline **85** derivatives, respectively. Substituted isoquinolines **86** were obtained by cyclization of aromatic imines with acetylenes in the presence of a Rh catalyst.[337]

Metal-catalyzed tandem cycloaddition reactions serve for efficient synthesis of six-membered cyclic systems. Hashmi and co-workers[338] prepared heterocyclic indane derivatives **87** by cyclization of bis-alkynyl substrates in the presence of Au complexes. The tandem reaction of aldehydes with propargylamines catalyzed by Au complexes provided the synthesis of pyrazine derivatives **88**.[339]

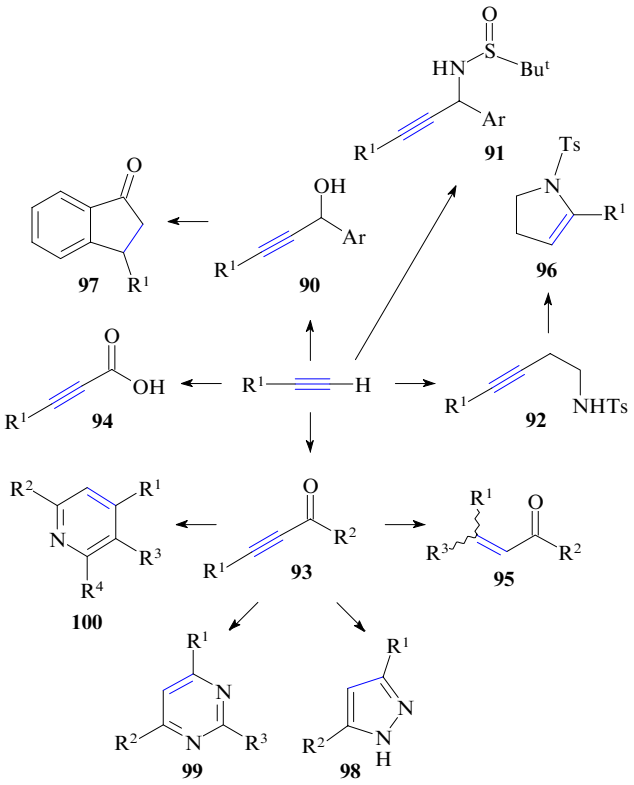
A variety of non-aromatic heterocyclic systems are formed upon cycloisomerization of functionalized acetylenes. For instance, dihydropyran and tetrahydropyridine derivatives were obtained by endo-cyclization of aliphatic and aromatic alkynols, respectively.[340] Similarly, double functionalization of haloalkynes in the presence of Cu compounds results in the formation of several unsaturated heterocycles **89** containing two heteroatoms.[341]

III. Functionalization of sp-hybridized carbon atoms

Owing to the relatively high acidity of the hydrogen atom in terminal alkynes they are converted to the corresponding acetylides on treatment with strong bases or salts of some transition metals. Alkali metal acetylides are strong nucleophiles and, hence, they are used as ethynylating reagents, whereas transition metal (first of all, copper) acetylides play a role of substrates or catalytic cycle participants in most C–H-functionalization reactions.

The nucleophilic reactions of acetylides with carbonyl compounds (Favorsky and Favorsky–Reppe reactions) and their nitrogen analogues [342] as well as carbonylation and carboxylation [343, 344] (Scheme 17) are general methods for the preparation of diverse alkynes (*e.g.*, compounds **90**–**94**), in particular, intermediates of the syntheses of biologically active products,[345–348] cyclic compounds [349–351] and other products.

Scheme 17



Calderone and Santos reported [352] Cu-catalyzed silylation of alkynylcarbonyl compounds, obtained by the reaction of acetylenes with DMF or substituted chloroformates in the presence of Bu^nLi, to give β-silyl-α,β-unsaturated aldehydes and esters, respectively (Structures **95**). The stereoselectivity of this reaction was found to depend on the nature of the substrate: carbonyl derivatives are mainly converted to *Z*-isomers, whereas carboxyl derivatives are converted only to *E*-isomers.[352] Zhdanko and Maier [186] used ring opening in *N*-tosylaziridine for the preparation of aminoethylated derivatives of acetylene **92**, which were further converted to 2-pyrrolines **96** *via* intramolecular cyclization in the presence of Au^I. A convenient method for the preparation of indan-1-ones **97** in high yields by intramolecular cyclization of α-arylpropargyl alcohols **90** in the presence of Rh complexes has been developed. Interestingly, the reaction is accompanied by 1,4-shift of the *ortho*-proton in the aromatic substituent.[349] Alkynes containing a conjugated carbonyl group are convenient substrates for the preparation of heterocyclic products. Murai *et al.*[351] used the reactions of alkynyl ketones **93** with hydrazine hydrate, methylthiourea and alkyl 3-aminocrotonoate to prepare pyrazole (**98**), pyrimidine (**99**) and pyridine (**100**) derivatives, respectively, in good yields.

Methods for the preparation of acetylenes with the C≡C–X (X = N, O, S and so on) bonds are being investigated,[353–356] because compounds of this class are used in the synthesis of poorly accessible aliphatic products [357–361] and functionalized aromatic heterocycles.[268, 362–364]

Dumitrescu and co-workers [364] employed Au-catalyzed [3 + 2]-cycloaddition of N- and O-functionalized acetylenes to pyridine-*N*-aminides for the preparation of a number of substituted oxazoles. The reaction is characterized by high chemoselectivity: cyclization occurs only for the triple bond activated by an electron-donating substituent.

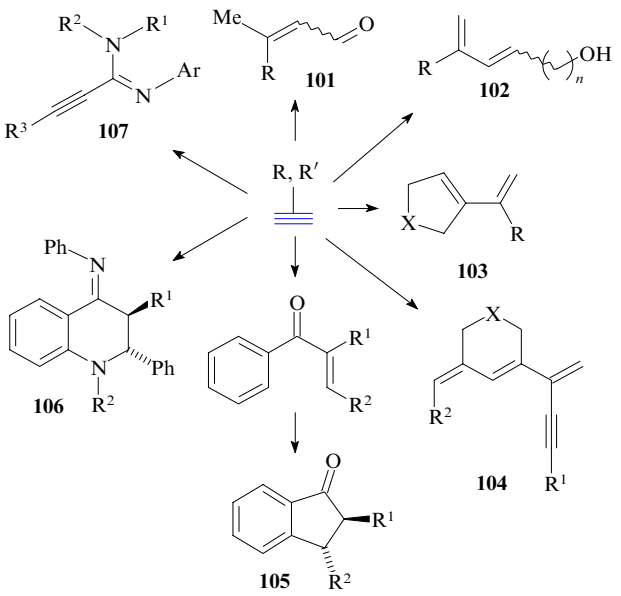
Coupling involving terminal acetylenes has been thoroughly studied. The condensation of alkynes in the presence of Cu^I salts to give 1,3-diynes (Cadiot–Chodkiewicz, Glaser, Eglinton and Hay reactions) is a versatile method for the construction of linear and cyclic structures with high molecular mass.[365, 366] Furthermore, conjugated diacetylenes can undergo heterocyclization. For example, thiophene- and isoxazole-based crown-like macrocyclic systems, prepared in good yields from diyne polyethers on treatment with Na_2S and NH_2OH, respectively, have been recently studied.[367]

The use of Group VIII metal complexes in the presence of Cu^I salts as catalysts largely extended the synthetic scope of acetylene functionalization.[368–370] Currently, cross-coupling of acetylenes with alkyl, vinyl, aryl and acyl halides in the presence of Pd compounds (Sonogashira, Castro–Stephens and Heck reactions) are widely used in the synthesis of poorly accessible intermediates and biologically active compounds.[371–376] In addition, the coupling of aromatic substrates with monosubstituted acetylenes in the presence of CO resulted in the synthesis of 2-alkynyl ketones [350, 365, 377–381] and carbonyl-containing cyclic products.[68, 350, 378, 382]

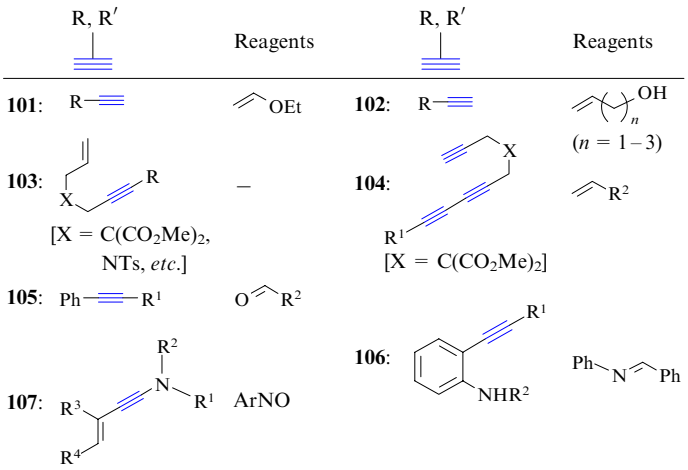
IV. Targeted modification of the carbon core

IV.1. Rearrangement of the carbon skeleton

The intramolecular transformations during molecular 3D printing would require the use of methods for altering the already existing triple-bond carbon group. After the fundamental works of Grubbs, Schrock and other researchers on the use of carbene and alkylidyne complexes in alkene and alkyne metathesis, respectively, this method was introduced into laboratory practice and into industry for the preparation of unsaturated derivatives including a number of highly demanding cyclic compounds, biologically active compounds and polymers.[383–392] However, there are only a limited number of known stable Ru- (Grubbs catalysts), Mo- (Schrock catalysts) and W-based complexes [an example of metathesis catalyzed by gold(I) complexes has also been reported [393]] tolerant to the reaction conditions (especially to the presence of various functional groups) and able



Scheme 18



to perform the metathesis in high yield and high stereo- and chemoselectivity.[394]

Alkynes undergo metathesis with substrates containing both double and triple bonds (Scheme 18). Lhermet and Fürstner[395] obtained Mo and W alkylidyne complexes suitable for carrying out metathesis with terminal alkynes. Enyne metathesis is an important method for the synthesis of poorly accessible linear and cyclic diene derivatives.[396–398] Crotonaldehyde **101** or dienol **102** derivatives with slightly predominating *E*-isomer were obtained by cross-metathesis of alkynes with enol ethers[399] and unsaturated alcohols,[400] respectively, catalyzed by generation II Grubbs catalysts. The intramolecular reactions give, most often, *exo*-cyclization products such as vinylcyclopentenes and their heterocyclic analogues **103**. However, the use of some catalysts ensured the formation of ethylidenecyclohexene derivatives as *endo*-cyclization products (compounds **104**).[401,402] Similar cyclic products of high molecular complexity are formed upon Au-catalyzed cycloisomerization of enynes.[403]

Catalysts for the metathesis of alkynes[404] and diynes giving rise to unsymmetrical diacetylenes have been found.[405,406] Substrates with C—heteroatom multiple bonds can also undergo metathesis. Saito *et al.*[407] used the carbonyl–alkyne metathesis to prepare conjugated phenyl alkenyl ketones, which are converted, in some cases, to indanones **105** *via* further CH-activation. More recently, the same researchers reported[408] the stereoselective synthesis of iminotetrahydroquino moiety of the+lines **106** by the three-component reaction of *ortho*-alkynylanilines, amines and aldehydes; one of the process steps is non-catalyzed metathesis of imines and alkynes. Alkynylamidines **107** were obtained as products of 1,4-metathesis of ene-ynamides with nitrosoarenes.[409] Conditions for nitrile–alkyne metathesis to produce symmetrical alkynes were selected;[410,411] however, this method has not found wide use.

IV.2. Increasing the polarity of carbon moieties

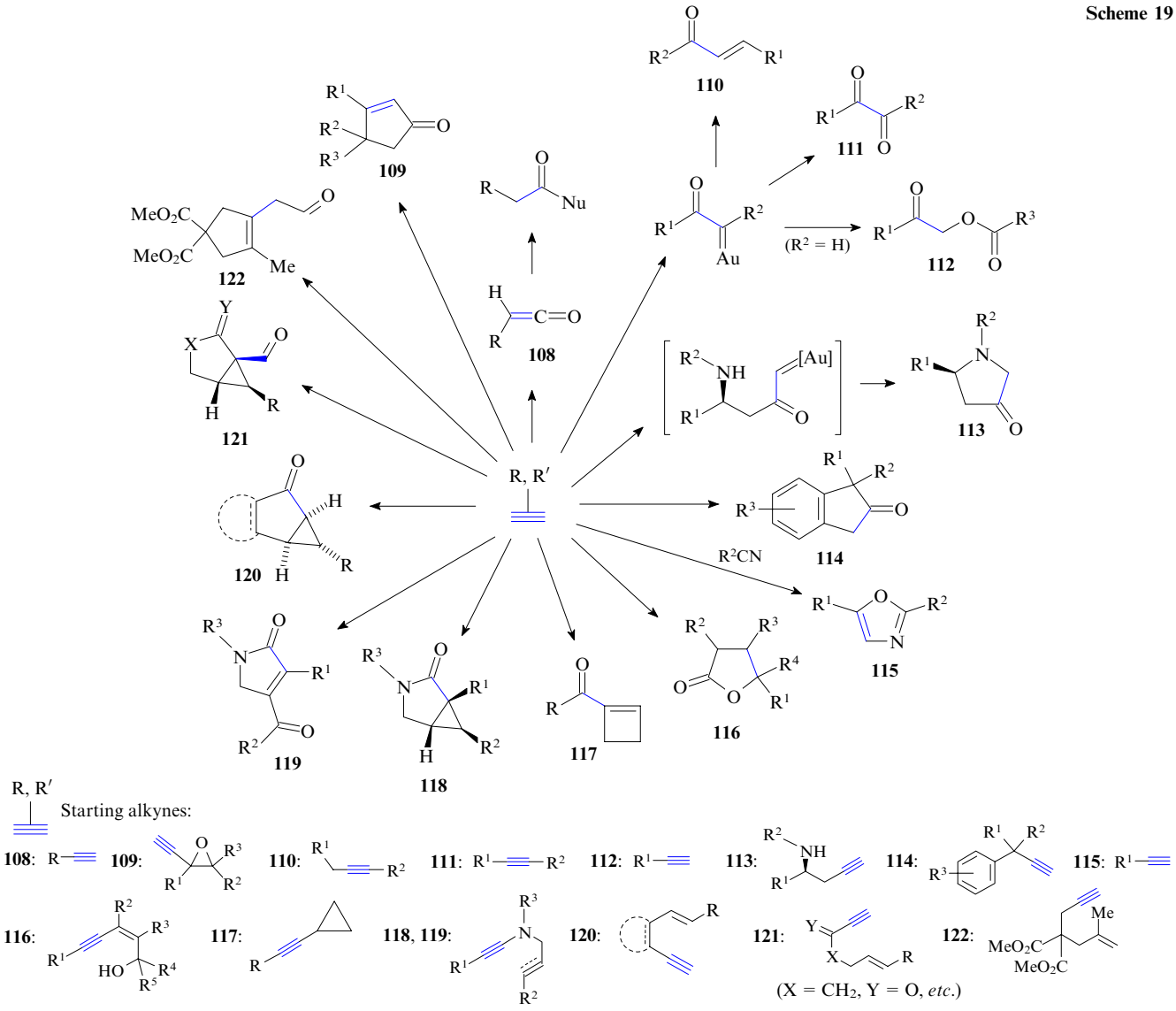
A number of processes during the molecular 3D printing of items with high molecular complexity may require increasing the polarity of some moieties *via* formation of oxygenates. An important synthetic route to these compounds is selective catalytic oxidation of a triple bond. The variation of substrates, oxidants and catalysts allows conduction the oxidation under mild conditions to give products in good yields and selectivity (Scheme 19).

The selective oxidation of alkynes can follow several mechanisms. Some catalyst systems, for example, Mn porphyrin complexes in the presence of oxone, oxidize acetylenes *via* the intermediate formation of unstable oxirene derivatives. The final reaction products — amides — were formed upon the rearrangement of oxirenes to ketenes **108** followed by addition of a nucleophile (Nu).[412] Similarly, ester and amide derivatives were synthesized from alkynes in the presence of Rh complexes. Ketenes formed as intermediates of this reaction result from oxidation of the intermediate Rh vinylidene complexes.[413]

The oxidation of functionalized acetylenes is widely used to prepare carbonyl derivatives which are difficult to obtain by other methods. Gagosz and co-workers[232] studied the Cu-catalyzed selective oxidation of alkynyloxiranes to give cyclopentenones **109**. The alkyne oxidation reactions to form α,β-unsaturated carbonyl compounds **110**[414] or 1,2-dicarbonyl derivatives **111**[415] catalyzed by Au^{I} complexes have been widely investigated in recent years. The intermediates of these reactions are Au α-oxocarbene complexes. These reactions can result in the formation of the products of addition of carboxyl-containing compounds **112**[416] as well as various cyclization products: pyrrolidinones **113**,[417] indanones **114**,[418] oxazoles **115**[419,420] and so on. Mild oxidation of *Z*-enynols catalyzed by Au^{I} phosphine complexes in the presence of AgOTf yielded furanone derivatives **116**.[421] Keto derivatives of cyclobutenes **117** were synthesized by oxidative cycloisomerization of acetylenes with a cyclopropyl substituent in the presence of Au complexes and diphenyl sulfoxide as the oxidant.[422]

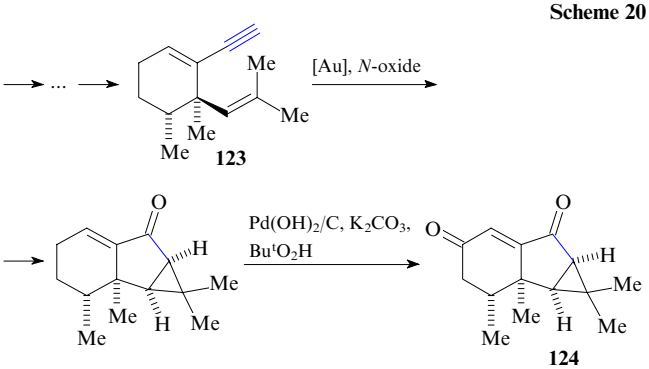
Gold or rhodium oxocarbene complexes can function as cyclopropanating agents. The oxidative cycloisomerization of alkenyl- or alkynyl-ynamides in the presence of Rh^{I} complexes gave 3-azabicyclo[3.1.0]hexane (**118**) and pyrrolidone (**119**) derivatives, respectively.[423] Similarly, Au-catalyzed oxidative cycloisomerization of 1,6-enynes was used to synthesize carbonyl derivatives of bicyclo[3.1.0]hexane (compounds **120** and **121**),[424,425] while in some cases, the

Scheme 19



reactions gave carbonyl cyclopentene derivatives **122**.[426] This approach has also been successfully used in the stereoselective synthesis of the alkaloid (−)-nardoaristolone B (Scheme 20). The oxidative isomerization of (5*R*,6*R*)-5,6-dimethyl-6-(2-methylprop-1-en-1-yl)-1-ethynylcyclohex-1-ene (**123**) gives, in one of the synthetic steps, the desired (1a*S*,1b*R*,2*R*,6a*R*)-1,1,1b,2-tetramethyl-1,1a,1b,2,3,6a-hexahydrocyclopropa[*a*]indene-4,6-dione (**124**) in an overall yield of ~17% over seven steps.[427]

Scheme 20



V. Conclusion

It is beyond doubt that acetylene derivatives possess an enormous synthetic potential. It is important that many reactions involving alkynes often give the desired product in high yield and high chemo-, regio- and stereoselectivities. The ways of triple bond modification are fairly diverse and many atom-economical methods of alkyne functionalization are widely used in fine organic synthesis and in industry. Of particular interest are multistep processes resulting in the formation of aliphatic and aromatic rings from available alkyne substrates.

We demonstrated in this review that using acetylene hydrocarbons provides construction of the required molecular complexity. From this standpoint, the following types of chemical transformations are significant:

(i) interconversions of sp-, sp²- and sp³-hybridized carbon centres;

(ii) elongation of the carbon skeleton by even or odd number of atoms;

(iii) selective formation of C–H, C–C and C–heteroatom bonds;

(iv) functionalization of the existing carbon centres;

(v) active rearrangement of the carbon core;

(vi) adjustment of the polarity of the carbon moieties;

(vii) performing atom-economical transformations without the formation of side products.

It is noteworthy that all these highly important types of transformations are accomplished by means of well-known reactions of alkynes: hydrogenation, carbonylation, carboxylation, di- and oligomerization, addition, cycloaddition, cycloisomerization, metathesis, oxidation and other. The above account and comparative analysis strongly indicate that if a hydrocarbon-based 3D printer is created, alkyne molecules will serve as the building materials.

Of course, now the resolution of three-dimensional printers is insufficient to print directly at the molecular level. However, the rapid development of this area allows one to expect a considerable progress in 3D-printing technology. During the preparation of this review, a study was published demonstrating the possibility of fivefold reduction in size for the three-dimensional printing objects.[428] The three-dimensional direct laser writing technology (3D-DLW) followed by vacuum pyrolysis provided the fabrication of carbon nanorods with a length of < 1 μm and a diameter of < 20 nm, which formed extra strong microsized structures.[428] If further 10-fold enhancement of the three-dimensional design resolution is achieved in the near future, then the direct generation of high molecular complexity will be practically implemented.

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