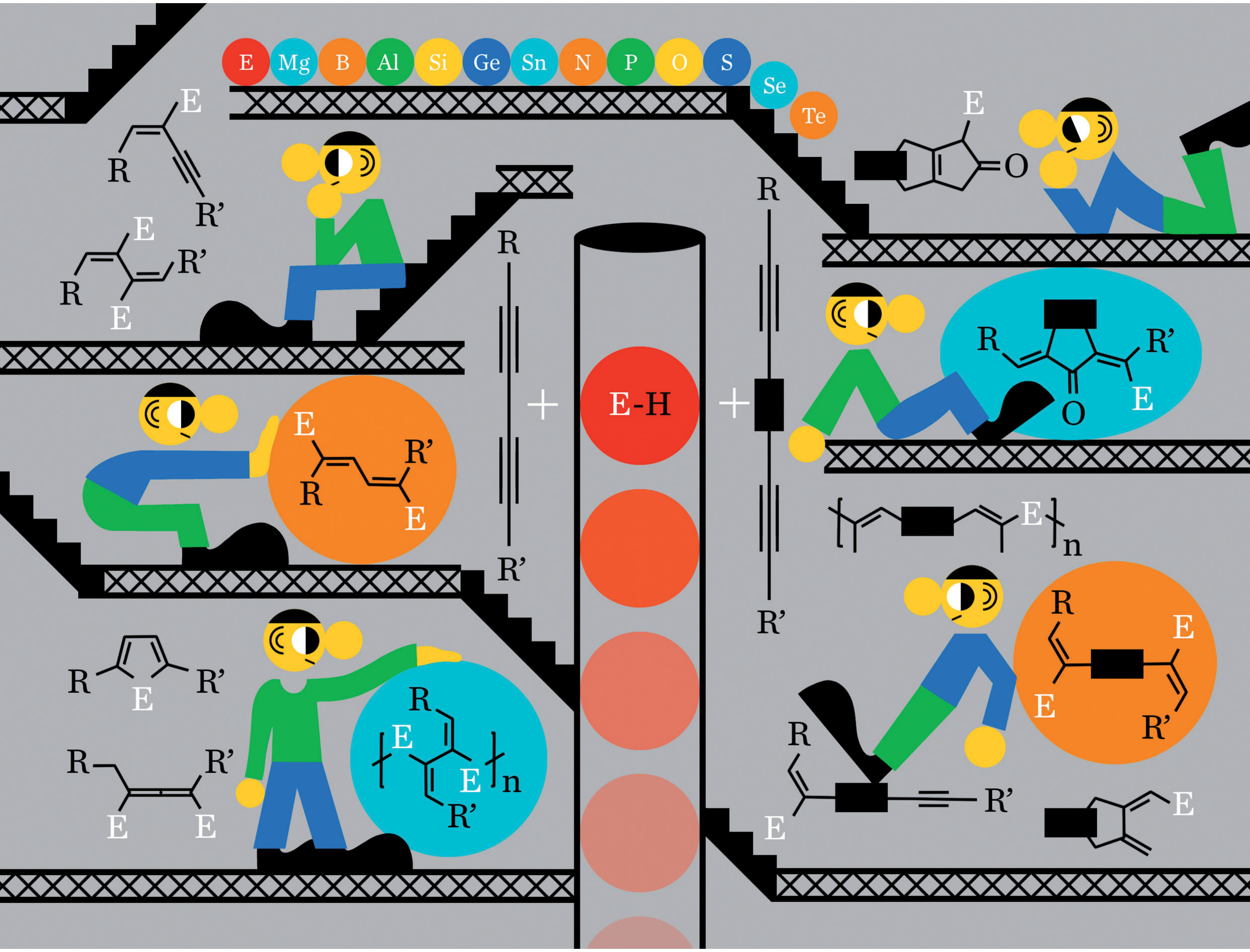
Volume 51
Number 3
7 February 2022
Pages 797–1198

Chem Soc Rev

Chemical Society Reviews

rsc.li/chem-soc-rev



ISSN 0306-0012

ROYAL SOCIETY
OF **CHEMISTRY**

REVIEW ARTICLE
Jędrzej Walkowiak, Rebecca L. Melen *et al.*
Hydroelementation of diynes

Chem Soc Rev

ROYAL SOCIETY OF CHEMISTRY

REVIEW ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Soc. Rev.*, 2022, **51**, 869

Hydroelementation of diynes†

Jędrzej Walkowiak, *[a] Jakub Szyling, [ab] Adrian Franczyk [a] and Rebecca L. Melen *[c]

Received 26th October 2021

DOI: 10.1039/d1cs00485a

rsc.li/chem-soc-rev

This review highlights the hydroelementation reactions of conjugated and separated diynes, which depending on the process conditions, catalytic system, as well as the type of reagents, leads to the formation of various products: enynes, dienes, allenes, polymers, or cyclic compounds. The presence of two triple bonds in the diyne structure makes these compounds important reagents but selective product formation is often difficult owing to problems associated with maintaining appropriate reaction regio- and stereoselectivity. Herein we review this topic to gain knowledge on the reactivity of diynes and to systematise the range of information relating to their use in hydroelementation reactions. The review is divided according to the addition of the E–H (E = Mg, B, Al, Si, Ge, Sn, N, P, O, S, Se, Te) bond to the triple bond(s) in the diyne, as well as to the type of the reagent used, and the product formed. Not only are the hydroelementation reactions comprehensively discussed, but the synthetic potential of the obtained products is also presented. The majority of published research is included within this review, illustrating the potential as well as limitations of these processes, with the intent to showcase the power of these transformations and the obtained products in synthesis and materials chemistry.

---

[a] *Adam Mickiewicz University in Poznan, Center for Advanced Technology, Uniwersytetu Poznanskiego 10, 61-614, Poznan, Poland. E-mail: jedrzej.walkowiak@amu.edu.pl*
[b] *Adam Mickiewicz University in Poznan, Faculty of Chemistry, Uniwersytetu Poznanskiego 8, 61-614, Poznan, Poland*
[c] *Cardiff Catalysis Institute, Cardiff University, School of Chemistry, Park Place, Main Building, Cardiff CF10 3AT, Cymru/Wales, UK. E-mail: MelenR@cardiff.ac.uk*

† This article is dedicated to Prof. Bogdan Marciniec from Adam Mickiewicz University in Poznań (Poland), expert in hydrosilylation reactions, on the occasion of his 80th birthday.

Jędrzej Walkowiak

Jędrzej Walkowiak received his PhD degree (maxima cum laude) in 2009 from Adam Mickiewicz University in Poznań (Poland) with Prof. B. Marciniec. He completed postdoctoral research in Prof. W. Leitner group at the RWTH Aachen in Germany. In 2019, he obtained habilitation in chemical sciences. From 2011 he has been employed at the Center for Advanced Technology, at Adam Mickiewicz University in Poznan, first as an Assistant Professor and from 2020 as Associate Professor. He also received an MBA degree in 2019. His main research concerns homogeneous catalysis, organoboron, and organosilicon chemistry as well as sustainable and green processes.

Jakub Szyling

Jakub Szyling received his PhD degree with honours in 2018 from Adam Mickiewicz University in Poznań, Poland under the supervision of Professor H. Maciejewski and Dr J. Walkowiak. Since 2019, he has been employed as an Assistant Professor at the Faculty of Chemistry, Adam Mickiewicz University and since 2021 at the Center for Advanced Technology. His research is currently focused on the synthesis and application of organoboron compounds in organic synthesis with a great emphasis on green chemistry principles. He is a scientist in the Laboratory of Applied and Sustainable Catalysis working on hydroboration of conjugated compounds.

1. Introduction

Hydroelementation reactions are one of the most prominent transformations in organic and organometallic chemistry, to obtain functionalised compounds from the addition of E–H bonds (E = Mg, B, Al, Si, Ge, Sn, N, P, O, S, Se, Te) to unsaturated C–C bonds in olefins (C=C) or alkynes (C≡C),[1–31] C–N bonds in imines (C=N)[2,32–36] or nitriles (C≡N),[2,33,34,37] and C=O bonds in carbonyl compounds.[2,32–35,38–47] The processes are mostly catalytic but may also occur as uncatalysed. In both cases, the stereo- and regioselectivity of the reaction depends upon the catalyst, reagent, and reaction conditions.

Hydroelementation of alkynes is perhaps the simplest, most straightforward, and atom economic method for the synthesis of unsaturated organometallic or organometalloid compounds. Over the last few decades, several reviews have been published focusing on this subject.[14,17,18,22,25,30,48–61] Particularly useful are hydroboration, hydrosilylation, hydroamination, hydrophosphination, and hydrostannation processes, which lead to important building blocks in organic and materials chemistry. Although many different terminal and internal alkynes have been used in these transformations, literature focused on the hydroelementation of conjugated or separated diynes is much rarer and has never been collated in a review before. The more complex structure of diynes together with the possibility to obtain various isomers or different products (*e.g.*, enynes, dienes, allenes, heterocyclic compounds, polymers), as well as the problems with carrying out monohydroelementation or bishydroelementation selectively, define the complexity of these processes (Scheme 1). For example, as was described by Perry *et al.*, the hydrosilylation of conjugated 1,3-diynes may lead to the formation of nine different products.[62] The difficulties in distinction in the reactivity of both C≡C bonds and the potential for overreduction are the most problematic issues reported. Actually, because of the synthetic potential of diyne hydrometallative products in the production of natural compounds, pharmaceuticals, or highly conjugated materials, within the last two decades, the subject is getting more explored.[63–71]

Working on the hydroboration and hydrosilylation of various unsaturated compounds and especially on the reactivity of conjugated 1,3-diynes in these processes, we have found that literature information is often scattered, with no detailed procedures or much discussion on the process optimisation or methodology.[72–87] Therefore, we have decided to build a comprehensive and critical compendium focused on this subject, which will systemise the existing knowledge on the hydroelementation of diynes in relation to the formation of different products. We will also show the possible applications of the obtained products in the synthesis of fine chemicals and materials. The review is divided into subchapters according to the type of hydroelementation reactions according to the element group of the periodic table of elements: hydromagnesation, hydroboration, hydroalumination, hydrosilylation, hydrogermylation, hydrostannation, hydroamination, hydrophosphination, hydration, hydrothiolation, hydroselenation, and hydrotelluration. Each hydroelementation reaction type is then subdivided into conjugated and separated diynes, and the type of product formed (enynes, dienes, heterocyclic compounds, and polymers). This comprehensive review will be helpful for all advanced researchers and newcomers working on the synthesis of organometallic compounds and their further applications in organic chemistry, synthesis of natural compounds, pharmaceuticals, with the emphasis placed on the process regio- and stereoselectivity.

2. Hydromagnesation

2.1. Hydromagnesation of conjugated 1,4-diaryl-1,3-diynes

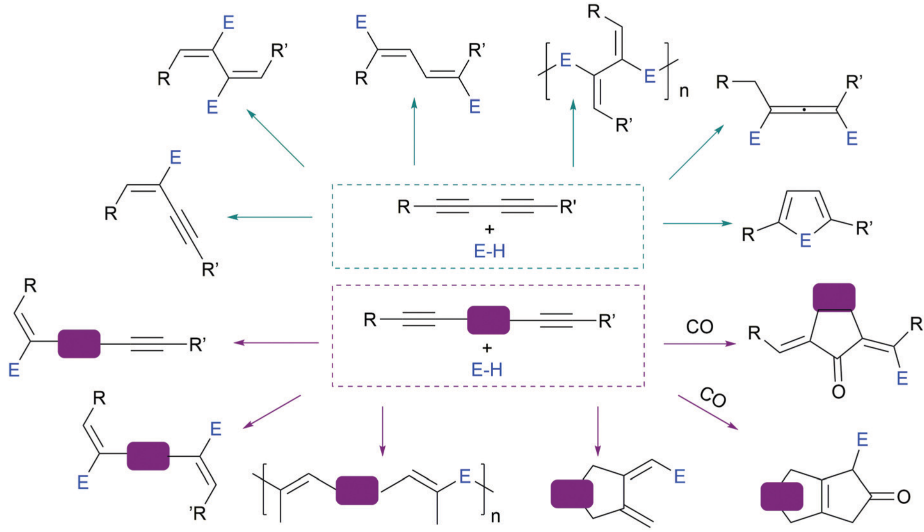
Hydromagnesation of alkynes is just limited to a few examples, which were performed in the presence of nickel, titanium, or

Adrian Franczyk

Adrian Franczyk received his PhD degree with honors in 2014 from Adam Mickiewicz University in Poznań (Poland), under the supervision of Professor B. Marciniec and Professor K. Matyjaszewski. During his education, he did internships at Mitsubishi Chemical Corporation (Yokohama, Japan), Universidade de Lisboa (Portugal), and Carnegie Mellon University (Pittsburgh, US). Since 2015 he has been employed at the Center for Advanced Technology, at Adam Mickiewicz University in Poznan as an Assistant Professor. His research is currently focused on the synthesis, characterisation, and application of molecular and macromolecular organosilicon compounds.

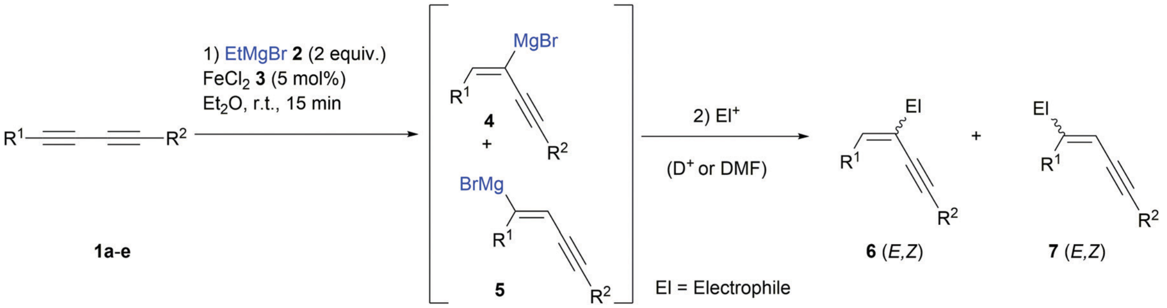
Rebecca Melen

Rebecca Melen studied for her PhD degree at the University of Cambridge (UK) with Professor D. S. Wright. Following Postdoctoral studies in Toronto (Canada) with Professor D. W. Stephan and Heidelberg (Germany) with Professor L. H. Gade, she took up a position at Cardiff University (UK) in 2014 where she is now a Professor in Inorganic Chemistry. In 2018, she was awarded an EPSRC early career fellowship and she was the 2019 recipient of the RSC Harrison Meldola Memorial Prize. Her research interests include diverse aspects of main group reactivity and catalysis, including the applications of main group chemistry in organic synthesis.



E = Mg, B, Al, Si, Ge, Sn, N, P, O, S, Se, Te

Scheme 1 Possible products obtained from the hydroelementation of conjugated 1,3-diynes and separated 1,*n*-diynes. Only selected products and their isomers are presented.

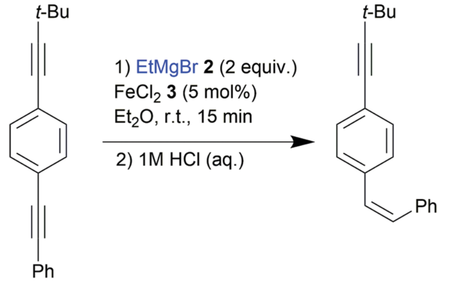


Scheme 2 Hydromagnesation of conjugated 1,3-diynes **1a–e** with ethylmagnesium bromide **2** catalysed by $FeCl_2$ **3**.

iron complexes.[88–95] Hydromagnesation of conjugated and separated diynes was reported only by Nakamura *et al.*, who synthesised alkenylmagnesium compounds using EtMgBr **2** as a hydrogen source and $FeCl_2$ **3** as a catalyst.[96] The reaction occurred with 1,2-diarylalkynes and 1,3-diynes **1a–e** with high (*Z*)-selectivity, in short reaction time (15 min), at room temperature. For the reaction 5 mol% of an iron catalyst was used. Under the applied reaction conditions, the alkenes were unreactive, so no overreduction was observed. Moreover, only one C≡C bond in the diynes **1a–e** was converted to the magnesium derivative **4** or **5** (regioisomers), which then was treated with an electrophile (HCl, D_2O, allyl bromide, or DMF) giving products with H, D, allyl or CHO groups respectively **6**, **7** (Scheme 2 and Table 1). Other iron complexes (*e.g.*, $FeCl_3$ **8**, $Fe(acac)_2$ **9**, $Fe(acac)_3$ **10**) were also active in this transformation but gave products with lower yields. Primary alkyl magnesium derivatives were also active in this reaction (except for bulky isobutylmagnesium bromide), as well as secondary alkyl Grignard compounds (with cyclohexyl or cyclopentyl groups). The magnesium compound had to be used in a 2.0 to 2.5-fold excess to obtain high conversion of alkyne or diyne, but the necessity of this excess was not clear. The source of hydrogen was from the magnesium compound, which was determined from the reaction of 1,2-diphenylethyne with deuterated d_5-ethylmagnesium bromide. Both diynes with electron-donating and electron-withdrawing groups attached to aryl rings were transformed into enynes with high regio- and stereoselectivity. The stereoselectivity was slightly lower for electron-rich reagents **1c** and **1d** (Table 1, entries 4 and 5). When the unsymmetrically substituted diyne with phenyl and trimethylsilyl groups **1e**

Table 1 Hydromagnesation of conjugated 1,3-diynes **1a–e** with ethylmagnesium bromide **2** followed by the electrophilic substitution

Entry	$R^1{=}R^2$	1	Electrophile	6-*E*/*Z*	6 : 7	Isol. yield of 6 [%]
1	Ph	**1a**	D^+	14 : 86	>99 : 1	63
2	Ph	**1a**	DMF	97 : 3	>99 : 1	50
3	$4\text{-}FC_6H_4$	**1b**	D^+	11 : 89	97 : 3	63
4	$4\text{-}MeC_6H_4$	**1c**	D^+	25 : 75	97 : 3	55
5	$4\text{-}MeOC_6H_4$	**1d**	D^+	22 : 78	97 : 3	65
	$R^1 \neq R^2$					
6	$R^1 = Me_3Si$, $R^2 = Ph$	**1e**	DMF	17 : 83	98 : 2	55



11 **12**, 64%, *E*/*Z* = 1:99

Scheme 3 Selective hydromagnesation of unsymmetrically substituted 1,4-diethynylbenzene **11** with ethylmagnesium bromide **2** catalysed by $FeCl_2$ **3**.

was used, the addition of magnesium compound **2** occurred at the C≡C bond to which the phenyl ring was attached (Table 1, entry 6). Moreover, the lack of reactivity of alkyl-substituted alkynes permitted the selective functionalisation of 1-(3,3-dimethylbut-1-yn-1-yl)-4-(phenylethynyl)benzene **11**, which reacted at the diarylalkyne site. Only a small amount (7%) of diene was formed in the reaction mixture as a side product (Scheme 3). As it was shown for hydromagnesation of alkynes, the catalytic system tolerates many functional groups (*e.g.*, halogens, amines, phenoxide, alkenes).

3. Hydroboration

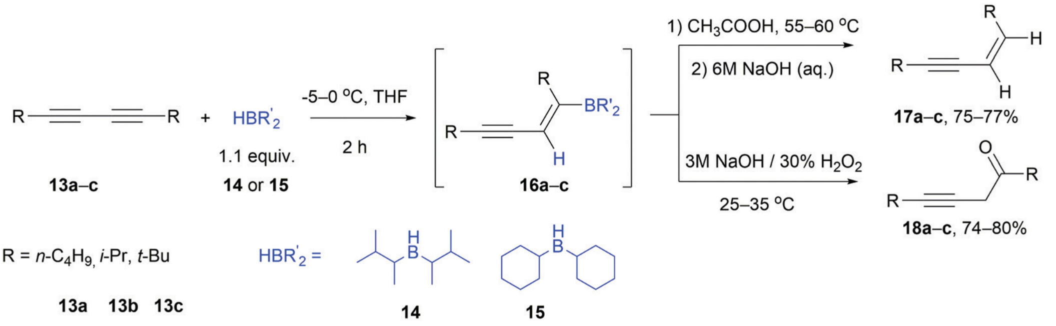
Organoboron compounds constitute important building blocks in the synthesis of structurally advanced organic and organometallic compounds due to their versatile reactivity in many catalytic and noncatalytic couplings and deborylation reactions, together with their low toxicity and moderate stability. There are numerous papers focused on the synthesis and applications of organoboron compounds, especially arylboronic acids and vinyl boranes.[97–110] The hydroboration reaction is still the most important and useful transformation in the synthesis of boranes because of its straightforward procedure, 100% atom economy, the possibility to control process regio- and stereoselectivity by the application of a catalyst or modification of the reagent steric properties or process conditions. The hydroboration of monoalkynes furnishing important alkenylborane building blocks is well established in the literature and has been discussed in several reviews.[1,2,4,7,10,12,48] Hydroboration of conjugated and separated diynes, because of the increased complexity of their structure, is much more challenging in the case of selectivity control. Moreover, the possibility for carrying out mono-, bishydroboration, polyaddition reactions and cyclisation reactions with these reagents creates the possibility to obtain various products, which have been used in the synthesis of natural compounds, pharmaceuticals (*e.g.*, anticancer rizoxin D, cytotoxic nannocystin Ax, ivorenolides),[111–119] dyes,[120] π-conjugated compounds, or heterocycles.[121–123] The information in this section is divided according to the type of reagent used: conjugated or separated diynes, as well as the formation of different products: enynes, dienes, heterocyclic compounds, and polymers.

3.1. Hydroboration of conjugated 1,3-diynes

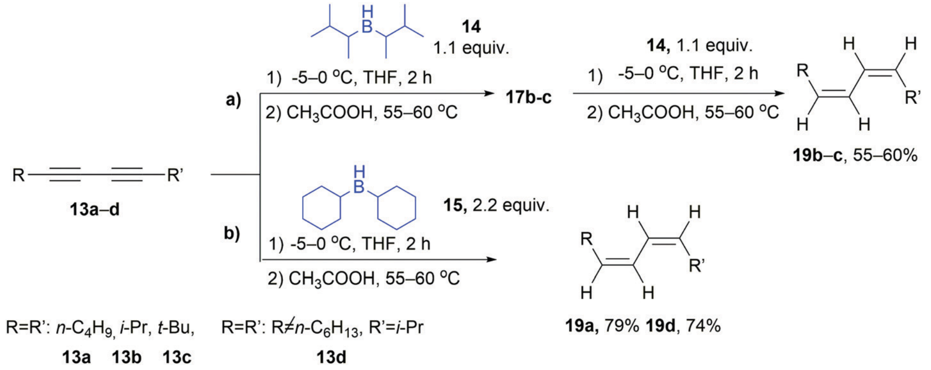
Hydroboration of conjugated 1,3-diynes is the simplest procedure for the synthesis of boryl-substituted 1,3-enynes or bisboryl-substituted 1,3-dienes, but the transition metal-catalysed selective addition of the B–H bond to the C≡C bond is limited only to three recently published examples.[72,124,125]

The first selective hydroboration of 1,3-diynes was reported by Zweifel and Ponso. Noncatatalytic reduction of alkyl-substituted buta-1,3-diynes **13a–c** was carried out using disiamylborane (bis(3-methyl-2-butyl)borane) **14** or less bulky dicyclohexylborane **15**. The monohydroboration of dodeca-5,7-diyne **13a**, 2,7-dimethylocta-3,5-diyne **13b** and 2,2,7,7-tetramethyl-octa-3,5-diyne **13c** with disiamylborane **14** (used in 1.1-fold excess) occurred with high regio- and stereoselectivity at 0–5 °C within 3 h. Protonolysis of the enynylborane intermediate **16a** (obtained in the reaction of **13a** with **14**) with acetic acid at 55–60 °C for 5 h furnished (*Z*)-5-dodecen-7-yne **17a** (83%), (*Z*,*Z*)-dodeca-5,7-diene (7%), and only traces of unreacted diyne **13a**. Bulkier diyne **13c** yielded the bishydroboration products only in trace amounts. Oxidation of the monohydroboration products with $NaOH/H_2O_2$ (30%) afforded the acetylenic ketones **18a–c** in high yields >70% (Scheme 4).

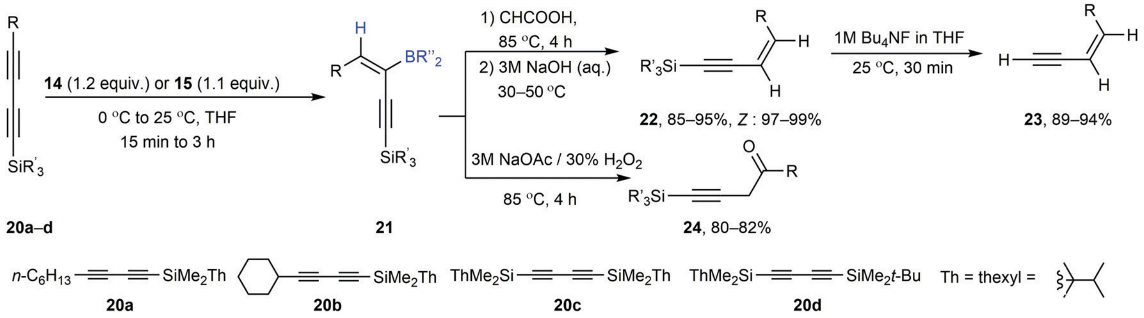
The boryl group was attached to the external carbon atom, which was proved by protonolysis with deuterated acetic acid. NMR analysis indicated that deuterium was attached to the internal carbon atom (95(±3%)). Synthesis of (*Z*,*Z*)-bisborylated dienes was more effective when less hindered borane **15** was



Scheme 4 Non-catalytic hydroboration of symmetrical dialkyl-substituted 1,3-diynes **13a–c** with disiamylborane **14** and dicyclohexylborane **15** followed by protonolysis or oxidation towards enynes **17a–c** or α,β-acetylenic ketones **18a–c**.



Scheme 5 Non-catalytic hydroboration of 1,4-dialkyl 1,3-diynes **13a–d** with boranes **14** and **15** towards (*Z*,*Z*)-dienes: (a) two-step method when **14** was used; (b) one-step procedure for **15**.

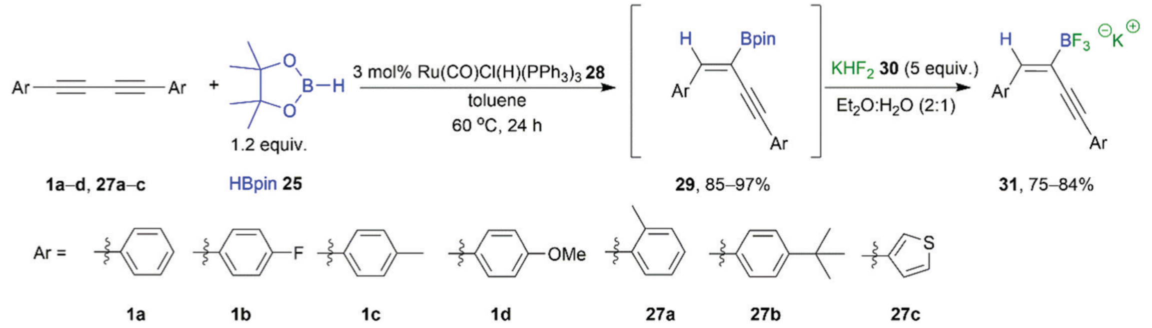


Scheme 6 Functionalisation of silyl-substituted 1,3-diynes **20a–d** with boranes **14** and **15**, and further synthesis of silyl-substituted enynes **22**, terminal enynes **23**, and silyl-functionalised ketones **24**.

used and could also be reacted with the non-symmetrically substituted diyne *e.g.*, 2-methyldodeca-3,5-diyne **13d**. In the case of hindered diynes **13b** and **13c**, the reduction was carried stepwise using borane **14** to obtain (*Z*,*Z*)-diene, by the hydroboration protonolysis of the first triple bond and the subsequent repetition of these processes. The application of **14** instead of **15** was caused due to the fact that dienes **19** formed in the reaction with **15** have a similar boiling point to the side product cyclohexanol, making the distillation method ineffective for their separation (Scheme 5). The analogous experiment with deuterium labeling proved that the second boryl group is attached to the external carbon atom of the second $C\equiv C$ bond, showing the directing induction effect of the firstly attached boryl group.[126]

The same group reported that for unsymmetrically substituted 1,3-diynes with silyl and alkyl or cycloalkyl groups attached to the opposite sides of **20a–d**, monohydroboration predominantly occurred at the $C\equiv C$ bond without the silyl group. Application of the more hindered borane **14**, as well as the structure of silyl groups (trimethyl, (*tert*-butyl)dimethyl, dimethylthexyl) influenced the reaction selectivity. For symmetrical 1,4-bis(trimethylsilyl)-1,3-butadiyne, the addition of sterically hindered **14** occurred at positions C^1 and C^2 in the ratio 26 : 74. The high regioselectivity of the reaction towards the product with borane at C^2 position was obtained when the bulky dimethylthexylsilyl substituent was attached in **20c** and **20d**.[127] The obtained products were further transformed into silyl-functionalised ketones **24** or enynes **22–23** with the above-described procedure (Scheme 6).[126]

These alkylboryl-substituted enynes (**16**, **21**) are difficult to handle due to their low stability, therefore the hydroboration of diynes with alkoxyboranes (*e.g.*, pinacolborane **25** or catecholborane **26**) is much more desirable. Moreover, alkoxyboranes are easy to use and non-flammable. However, due to the lower acidity of the B–H bond in comparison to alkylboranes, the addition of alkoxyboranes to unsaturated $C\equiv C$ bonds requires the application of a catalyst to accelerate the process. Relating to this, our recent paper focused on the selective monohydroboration of 1,4-diaryl-buta-1,3-diynes **1a–d**, **27a–c** with pinacolborane **25** in the presence of $Ru(CO)Cl(H)(PPh_3)_3$ **28**. Compound **28** has previously been described as an active catalyst in hydroboration of terminal- or internal monoalkynes in conventional and novel, green reaction media (supercritical CO_2 ($scCO_2$), ionic liquids (ILs), polyethylene glycol, (PEG)).[72,75,76,128,129] The reaction proceeded effectively for various diynes possessing electron-withdrawing or electron-donating substituents on the aryl ring, as well as for heterocyclic 1,4-di(thiophen-3-yl)buta-1,3-diyne **27c**. Alkyl-substituted diynes yielded boryl-substituted enynes by *cis*-addition of borane to the $C\equiv C$ bond, but the postreaction mixture also consisted of other monoborylated enynes, bisboryl-functionalised dienes, and some undefined products. Thus, the electronic properties of diynes have an important influence on



Scheme 7 Monohydroboration of symmetrical 1,4-diaryl-buta-1,3-diynes **1a–d** and **27a–c** with pinacoloborane **25** in the presence of $Ru(CO)Cl(H)(PPh_3)_3$ catalyst **28**.

the process regio- and stereoselectivity. Under the optimised reaction conditions (3 mol% of $Ru(CO)Cl(H)(PPh_3)_3$ **28**, 60 °C, 24 h, with a small excess of borane **25** (1.2 equiv.)), the boryl-substituted enynes **29** were obtained with high yields (85–97%). Due to their instability during purification by column chromatography, the products were directly transformed to the corresponding stable trifluoroborane salts **31** with KHF_2 **30** furnishing the desired products with 75–84% yield (Scheme 7).

The regioselectivity of the process was confirmed by NOESY and X-ray diffraction analysis for product **29** obtained in the hydroboration of **27b** with **25** (Fig. 1). The borane **25** was added to the C≡C bond in a *syn*-manner according to the anti-Markownikow rule, with the boron group attached to the less shielded internal carbon atom in **29.** We have also proposed the mechanism of the process according to the stoichiometric reactions monitored by ^{1}H NMR and 1D selective gradient NOESY. The process initiates from the insertion of diyne **1a–d** or **27a–c** into the Ru–H bond of catalyst **28** forming but-3-en-1-yn-3-yl complex **32.** The addition of borane **25** then leads to a σ-bond metathesis between Ru–C and B–H (**33**), followed by the elimination of the product **29** and regeneration of the initial Ru-hydride complex **28** (Scheme 8 and Fig. 1).

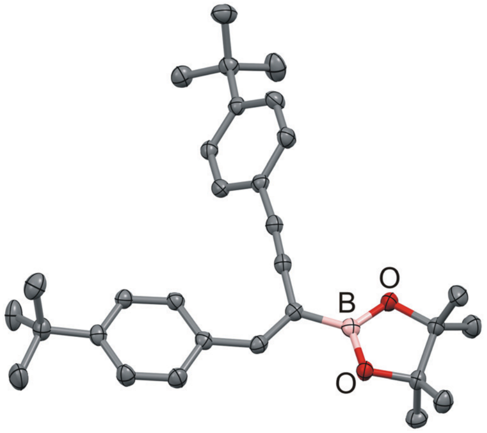
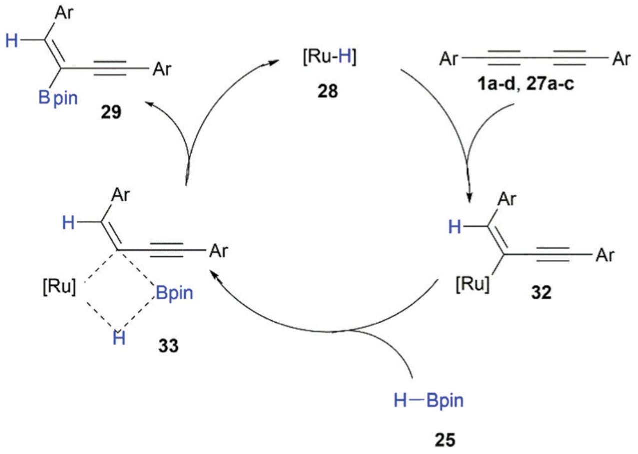
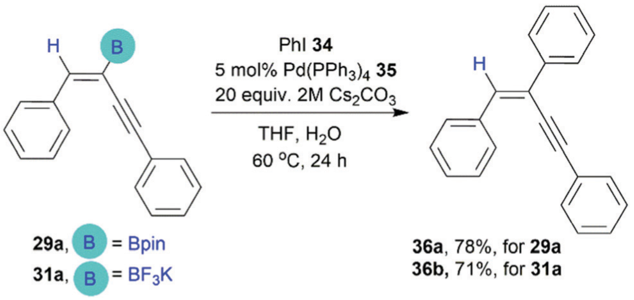


Fig. 1 Molecular structure of 2-(4,4,5,5,-tetramethyl-1,3,2-dioxaborol-anyl)-1,4-bis(4-*tert*-butylphenyl)but-1-en-3-yne **29** obtained in the hydroboration of **27b** with **25** in the presence of catalyst **28**.[72]



Scheme 8 Proposed catalytic cycle for the hydroboration of 1,3-diynes **1a–d**, **27a–c** with pinacolborane **25** in the presence of $[Ru(CO)Cl(H)(PPh_3)_3]$ **28**.



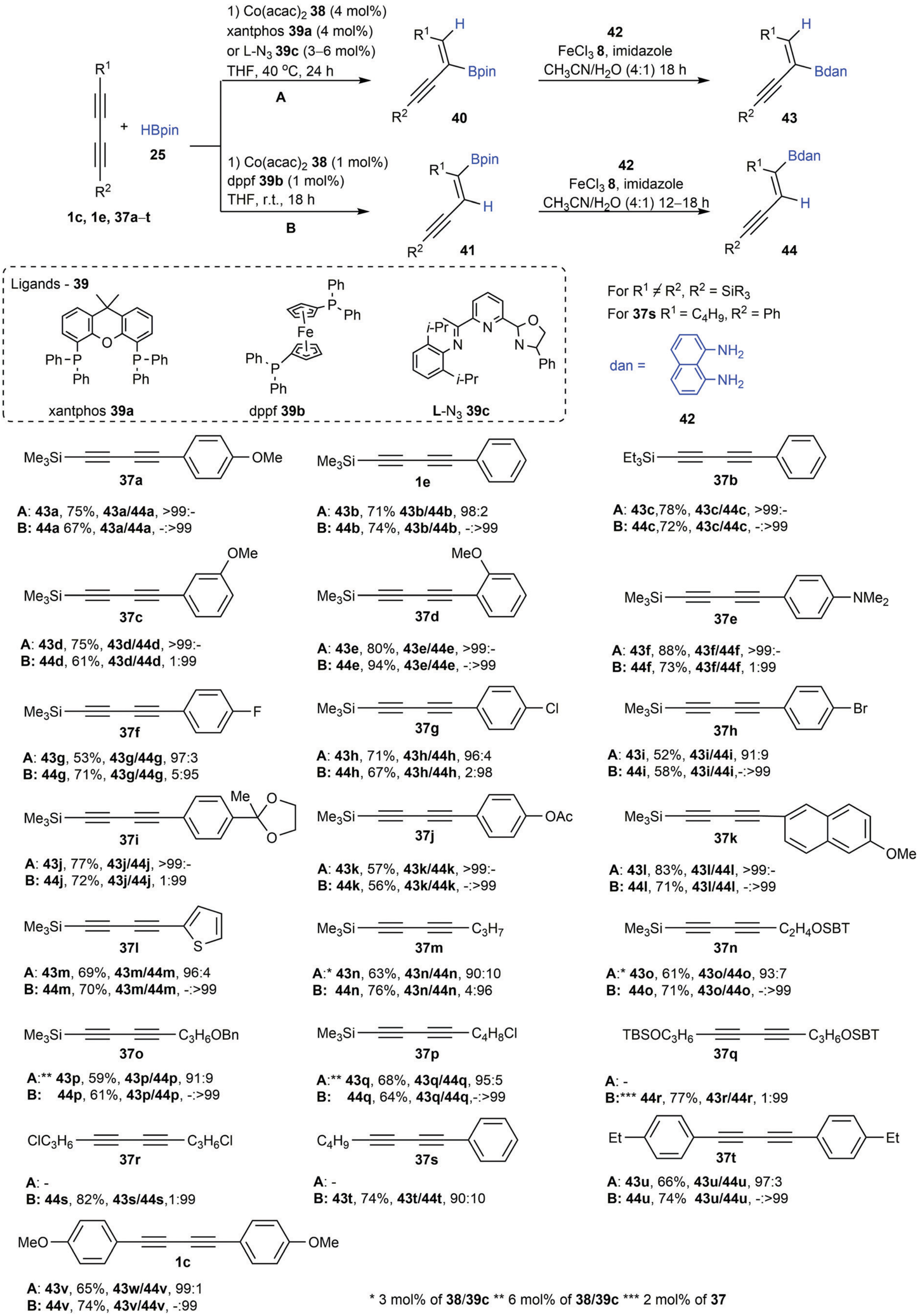
Scheme 9 Suzuki–Miyaura coupling of enynes **29a** and **31a** with iodobenzene **34**.

The utility of the resulting boryl-substituted 1,4-diaryl-but-1-en-3-ynes was presented in the Suzuki coupling reaction of pinacoloborane derivative **29a** and trifluoroborate salt **31a** with iodobenzene **34** using 5 mol% of $Pd(PPh_3)_4$ **35.** The reaction occurred with the retention of the configuration and (*Z*)-1,2,4-triphenylbut-1-en-3-yne **36a–b** was formed with high yields 71% and 78%, respectively (Scheme 9).[72]

Ge *et al.* reported an interesting method for the synthesis of boryl-substituted enynes from unsymmetrical and symmetrical 1,3-diynes **1c**, **1e**, **37a–t** in the presence of a cobalt catalyst generated from inexpensive and stable Co(acac)$_2$ **38** and bidentate phosphine ligands **39a–c**. The authors showed that the regioselectivity of the process was dependent on the bidentate phosphine ligand used. When Co(acac)$_2$/xantphos **38**/**39a** was used, enynes with boron groups attached to the internal carbon atom were formed **40**. However, when applying dppf **39b** as a ligand, the opposite regioselectivity was observed, furnishing the product functionalised with borane at the external position **41**. The pinacolborane derivatives were further transformed to more stable 1,8-diaminonaphthalene boronates **43** and **44** respectively, with 1,8-diaminonaphthalene **42**, which were easier to isolate (Scheme 10).[125] To find the answer to this different reactivity pathway, the authors carried out a reaction with deuterated DBpin **45** (Scheme 11a). The formation of products with different regioselectivity was also confirmed using 1D NOE and 2D HMBC NMR correlations. For the Co(acac)$_2$/xantphos **38**/**39a** catalyst, the reaction occurred through the formation of Co–H intermediate **48**, while for Co(acac)$_2$/dppf **38**/**39b** the process proceeded through the Co–borane species **50** (Scheme 11b). For both catalytic systems, several boryl-substituted enynes **40** and **41** were formed using an equimolar amount of reagents. When silyl groups were attached to one alkyne, the borane was added to the second triple bond with different (aryl, heteroaryl, or alkyl) substituents. The products were obtained with excellent regioselectivity and yield. For alkyl-substituted diynes, better selectivity was obtained when L-N$_3$ **39c** was used as a ligand instead of xphos **39a**. The catalytic systems tolerate a lot of functional groups in the diyne structure. No significant changes in their reactivity were observed (Scheme 10).[125] The utility of the resulting boryl-functionalised 1,3-enynes was presented in the bromodeborylation reaction with CuBr$_2$ **52**, as well as the Pd-catalysed Suzuki–Miyaura and Hiyama coupling reactions (Scheme 12).

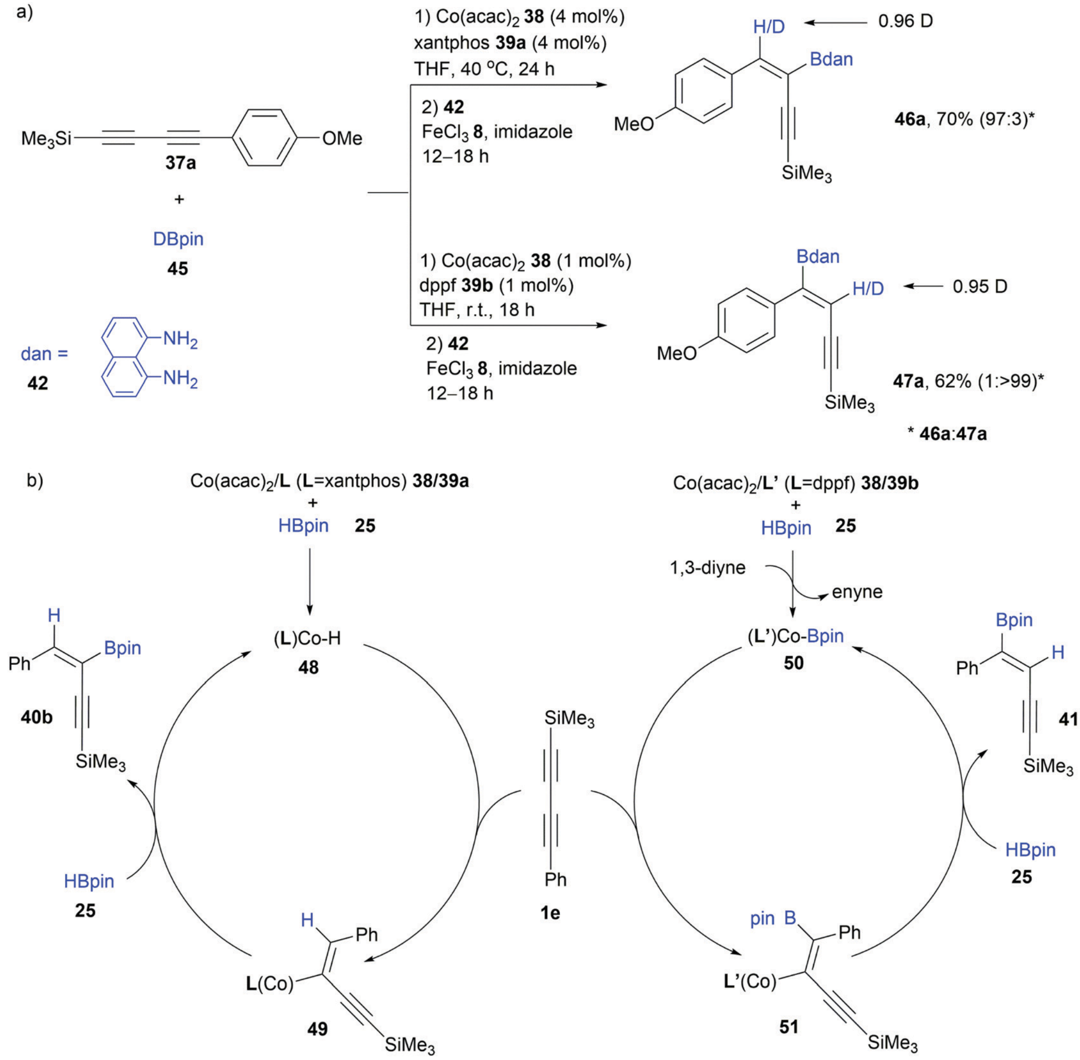
Applying a CuCl **55**/P(*p*-Tol)$_3$/NaO*t*–Bu catalytic system, it was possible to carry out formal hydroboration of symmetrical and unsymmetrical 1,3-diynes **1a–b**, **1d–e**, **13a**, **13c**, **27a**, and **60a–e** with bis(pinacolato)diboron **61** and methanol as a proton source. The process was carried out under strictly assigned conditions (11 °C for 6 h) with 5 mol% of CuCl **55**, 6 mol% of phosphine, and 10 mol% of the base. Reactions with weaker donating phosphines (P(OEt)$_3$ or PPh$_3$) resulted in lower yields and longer reaction times, with some exceptions. For diynes with *tert*-butyl **13c**, 4-methoxyphenyl **1d**, cyclohexyl **60a** groups, P(OEt)$_3$ was applied, while for 4-fluorophenyl-substituted diyne **1b**, PPh$_3$ was successfully used. The boryl group was attached at the external carbon position of the 1,3-diyne and only for sterically hindered 2,2,7,7-tetramethyl-octa-3,5-diyne **13c** the regioselectivity was reversed and the borane was bonded to the less shielded internal carbon atom. When hydroboration of unsymmetrically functionalised diynes with aryl and alkyl groups in the terminal position was carried out, the reaction occurred at a more accessible C$\equiv$C bond. Diynes bearing a silyl group were characterised by their strong directing effect, where the functionalisation proceeded at the triple bond situated further from the silyl group.[124] The same observation was noticed in the noncatalytic hydroboration of silyl-substituted diynes.[127] The resulting pinacolborane derivatives **62** were then transformed to their potassium trifluoroborate analogs **63** with KHF$_2$ **30**. When unsymmetrical 1,4-diaryl-diyne was used, a 1 : 1 mixture of regioisomers was formed due to the similar reactivity of both C$\equiv$C bonds (Scheme 13). Using this catalytic system, different regioisomers were formed with the boryl group attached to the internal carbon bond in comparison to the previously described works on noncatalytic or Ru–H catalysed hydroboration.[72,126,130] The obtained products were subsequently derivatised by Suzuki–Miyaura coupling with iodobenzene **34** using PdCl$_2$ **64**/dppf **39b** as a catalyst and KOH as a base, as well as deborylated to enynes with acetic acids. Moreover, it was possible to carry out selective desilylation of silylboryl-substituted enynes with K$_2$CO$_3$/MeOH while Bpin remained unreactive under applied process conditions.

Very recently, Taniguchi and co-workers reported the first *trans*-hydroboration of 1,3-diyne derivatives **60a** and **65a–l** under radical conditions in the presence of AIBN (2,2′-azobis(isobutyronitrile)) **67** or ACCN ((1,1′-azobis(cyclohexane-1-carbonitrile))) **68** as an azo initiator and *tert*-dodecanethiol **69** (TDT) as a polarity-reversal catalyst. The addition of an N-heterocyclic carbene borane **66** to symmetrical and unsymmetrical 1,3-diynes gave (*E*)-alkynylalkenyl boranes **70** in high selectivity (*E*/*Z* = 95/5) and good isolated yields (51–77%). Interestingly, a 4-fold excess of the borane **66** with diynes **65a–l** and **60a** caused the formation of bisadducts in inconsiderable amounts. The protocol was suitable for 1,3-diynes with different substituents (*n*-alkyl, *c*-alkyl, propargyl ether, silyl) however, hydroboration of 1,4-diphenylbuta-1,3-diyne **1a** under the standard conditions gave a mixture of undefined products due to different rate of hydrogen atom transfer for aryl and alkyl or silyl substituted 1,3-diynes. It is worth noting that obtained NHC-based boryl functionalised enynes **70**, in contrast to pinacolborane-based enynes, are bench-stable compounds and can be easily purified by silica-column chromatography (Scheme 14). The authors proposed the mechanism of this anti-selective hydroboration of 1,3-diynes which in the first step involved the thermal decomposition of azo initiator AIBN **67** or ACCN **68** and formation of thiyl radical **71** from thiol **69**. The abstraction of the hydrogen atom from NHC–borane **66** by the radical **71** yielded NHC–boryl radical **72**. Subsequently, the regioselective addition of boryl-radical **72** to 1,3-diyne **60a**, **65a–l** gave alkenyl radical **73** conjugated to the alkyne moiety. The presence of thiol TDT **69** promoted the hydrogen atom transfer step and formation of thiyl radical **71** which abstracted hydrogen atom from NHC–borane **66** and closed radical chain. The authors suggested that the bisadducts **74** would not be efficiently formed since the presence of electron-rich NHC–borylalkenyl group of **73** would cause polarity mismatching during the addition of nucleophilic NHC–boryl radical **72** (Scheme 15). **70a** could be easily converted to the corresponding (*Z*)-1-aryl-1,3-enyne derivatives **77a** and **77b** through a one-pot procedure involving chlorination and hydrolysis of the boron moiety with *N*-chlorosuccinimide (NCS) **78** and water followed by a Suzuki–Miyaura coupling with aryl iodides **75** and **76** (Scheme 16).[131]



* 3 mol% of **38**/**39c** ** 6 mol% of **38**/**39c** *** 2 mol% of **37**

Scheme 10 Selective hydroboration of conjugated diynes **1c**, **1e** and **37a–t** using Co(acac)$_2$ **38** as a catalyst and different ligands: path A – xantphos **39a** or L-N$_3$ **39c**; path B – dppf **39b**.



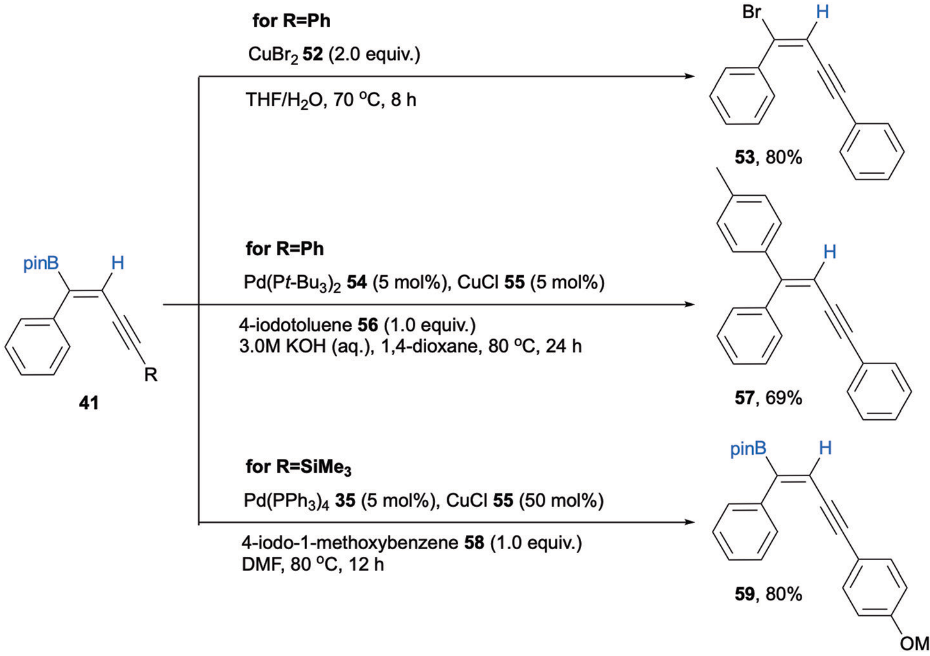
Scheme 11 (a) Mechanistic study on the hydroboration of conjugated diynes with **38**/**39a** and **38**/**39b** with DBpin **45**; (b) proposed catalytic cycles for Co-catalysed regiodivergent hydroboration of 1,3-diynes.

3.2. Hydroboration of separated 1,*n*-diynes

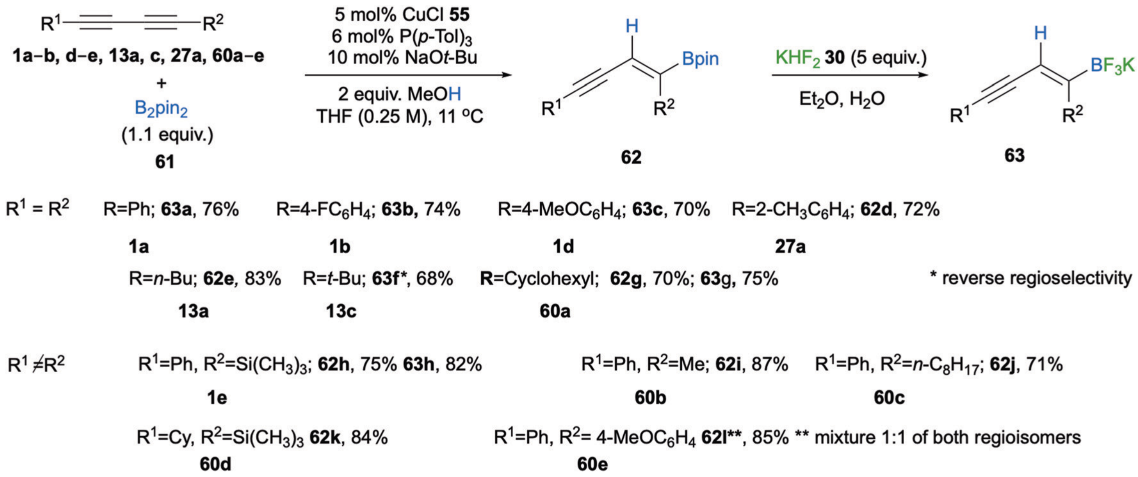
The hydroboration of separated 1,*n*-diynes leads to the formation of various products from boryl-substituted enynes and bisboryl-substituted dienes, towards cyclic products, which are important building blocks in the synthesis of natural compounds, that can be used in *e.g.*, Diels–Alder reactions. The selectivity of the hydroboration processes depends on the catalyst type and reagent structure. Their choice is essential to direct the desired course of the reaction. In this section, the synthesis of molecular boryl-derivatives is presented, while the formation of macromolecular compounds is described in Section 3.3.

Selective hydroboration of the separated 1,6-diynes, 1-pinacolboryl-hepta-1,6-diyne **79a** or 1-pinacolboryl-octa-1,7-diyne **79b**, occurred at the terminal C≡C bond with the *syn*-addition of pinacolborane **25** in the presence of 5 mol% Cp_2ZrHCl **80** as a catalyst (according to Wang's procedure)[132] or using $HBBr_2–SMe_2$ **81**, which was further transformed with pinacol **82** to generate stable boryl derivatives **83a–b** in 94–95% yield. The obtained diborylenynes **83a–b** were further cyclised using Cp_2ZrCl_2 **84** and *n*-BuLi **85** followed by treatment with anhydrous HCl in diethyl ether. The resulting products **87a–b** possessing boryl groups attached to C_{sp^2} and C_{sp^3} were used in Suzuki coupling reactions with iodoarenes in typical conditions, applying the commonly used $Pd(PPh_3)_4$ **35** as a catalyst. Here the reaction occurred exclusively on C_{sp^2}–B bond, because of its much higher reactivity in this coupling reaction (Scheme 17).[130]

Wang's procedure was also used for the bishydroboration of aminodiyne **90** with pinacolborane **25**. (*E*,*E*)-Bis(vinylboronate ester) **91** was obtained in 54% yield. When the modified Srebrnik procedure was used, the same product was formed but with opposite (*Z*,*Z*)-stereoselectivity **93**.[133] Here reaction of diyne **90** with *n*-BuLi **85** (2 equiv.) in Et_2O at −78 °C, which was then transferred to a solution of 2 equiv. of PINBOP **92**, followed by the addition of HCl. The crude bis-alkynyl-Bpin was then added to a solution of Schwartz reagent Cp_2ZrHCl **80**,



Scheme 12 Transformation of borylsilyl-substituted enynes **41** in bromodeborylation, Suzuki–Miyaura and Hiyama coupling reactions.

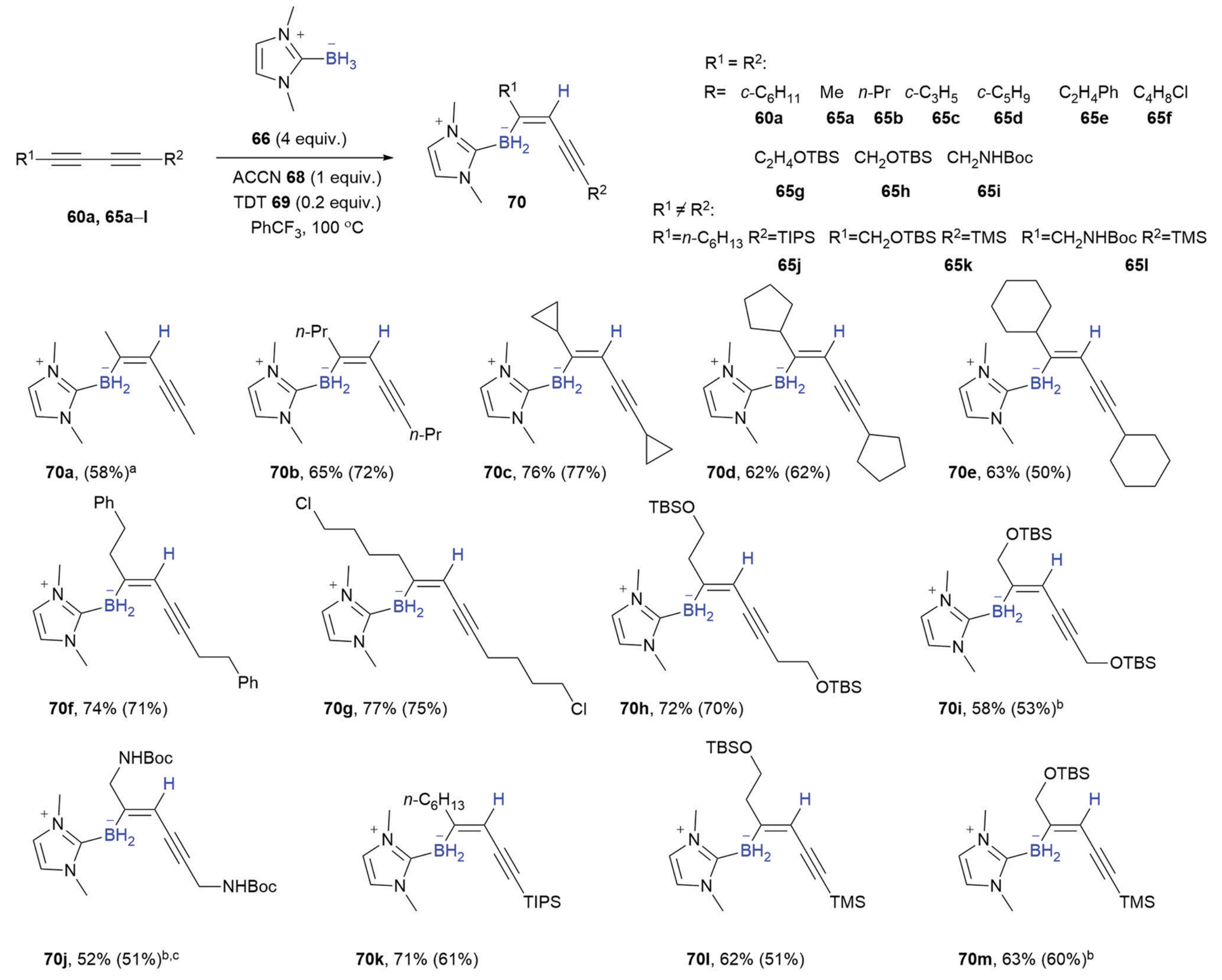


Scheme 13 Monohydroboration of symmetrical and nonsymmetrical conjugated diynes with bis(pinacolato)diboron **61** and methanol as a proton source catalysed by a CuCl **55**/P(p-Tol)$_3$/NaOt–Bu system.

and the obtained zirconocene was then hydrolysed to the bisborylated diene **93** in 49% yield (Scheme 18).[134] Wang's and Srebrnik's procedures were also applied for the formation of other (*E*,*E*)- or (*Z*,*Z*)-vinyl boronate esters with moderate yields, which were further cyclised using PdCl$_2$(PPh$_3$)$_2$ **94** to various cyclic polyenes with controlled (*E*,*E*), (*Z*,*Z*) or (*E*,*Z*) selectivities **95–104** (Schemes 18 and 19).[134]

Non-catalytic hydroboration of diyne **105** with sterically hindered di(iso-pinocampheyl)borane (^{l}Ipc$_2$BH) **106** was carried out in THF at 0 °C yielded the desired selective hydroboration of the Me-substituted alkyne. Addition of bromodienoate **107**, Pd(PPh$_3$)$_4$ **35**, and TlOEt to the product provided the targeted cross-coupling product **109** in 83% yield with excellent regioselectivity (>95 : 5) (Scheme 20). This method was developed and used as a part of the synthesis of the natural compound *Apoptolidin An* isolated from actinomycete identified as *Nocardiopsis sp*, which possesses cytotoxic properties. Interestingly, the application of the less hindered pinacolborane **25**, cateholborane **26**, or dicyclohexylborane **15**, led to the mixture of isomers in the reaction.

Hydroboration of chiral binol derived diynes **110a–e** was carried out with Piers borane (HB(C$_6$F$_5$)$_2$) **111** in mesitylene to **112a–e**. After 5 min, tri(*tert*-butyl)phosphine **113** was added to **112** to generate a frustrated Lewis pair *in situ*. This system was used for the enantioselective reduction of enol silyl ethers **114a–u** under 40 bars of H$_2$. After workup with TBAF



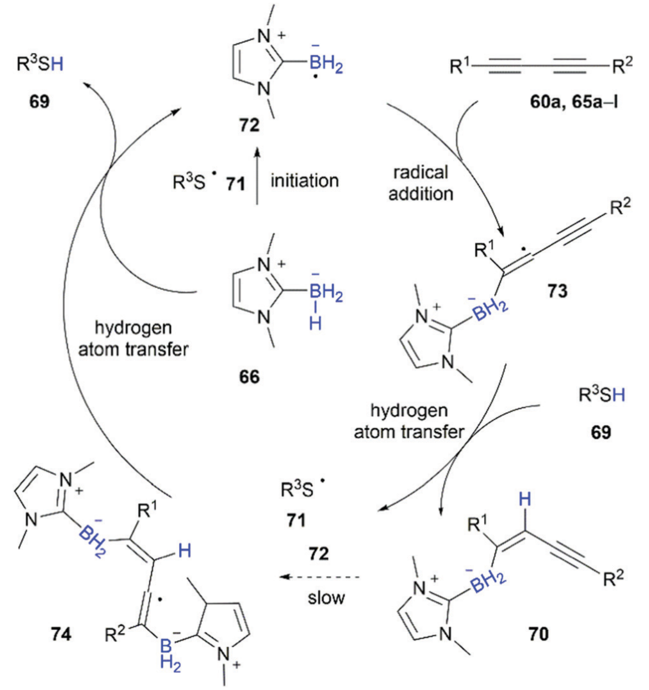
[a] Estimated by ^1H NMR. [b] AIBN **67** was used instead of ACCN **68** at 80 °C. [c] Ph_3CSH was used instead of TDT **69**.

Scheme 14 Radical *trans*-hydroboration of 1,3-diynes **60a** and **65a–l** with an N-heterocyclic carbene borane **66** in the presence of thiol **69** as a polarity-reversal catalyst.

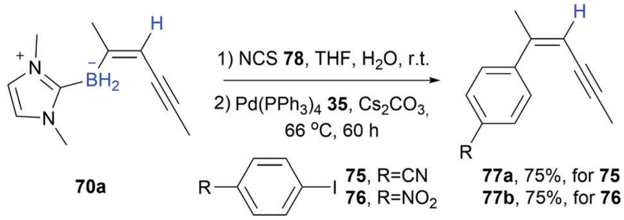
(tetrabutylammonium fluoride) **108**, chiral secondary alcohols **115a–u**, with excellent yields and enantioselectivities (87–99% ee) were obtained. The catalytic alkenylborane activity **112a–e** (Lewis acidity) was tuned by conjugation of the system as well as the type of electron-rich or deficient substituents attached to the binaphthyl ring (Scheme 21).[135]

Ruthenium catalysts have not only been used in the hydroboration of conjugated 1,3-diynes[72] but also in the hydroboration of separated diynes **116a–c.**[136] In this case, application of ruthenium hydride pincer complex [Ru(*t*-BuPNP)(H)$_2$(H$_2$)] **117** (PNP = 1,3-bis(di-*tert*-butyl-phosphinomethyl)pyridine) permitted anti-Markownikow *trans*-hydroboration leading to (*Z*)-vinyl boranates **118** under mild reaction conditions (r.t., 24 h, toluene). Generally, the system was active in the reaction with various terminal alkynes, but very good yields and selectivities were also obtained in bishydroboration of hepta-1,6-diyne **116a**, deca-1,9-diyne **116b** and 1,4-diethynylbenzene **116c** (Scheme 22).

The complex [Ru(PNP)(H){(μ-H)$_2$Bpin}] **119**, which is formed in the reaction of **117** with pinacolborane **25**, with the simultaneous evolution of H$_2$, was found to be the catalyst for this transformation which was structuraly characterised (Scheme 23). Based on stoichiometric reactions, DFT calculations, and catalytic transformation with deuterated d$_1$-phenylacetylene, the mechanism of this transformation was determined. **119** is generated by the formation of the ruthenium hydride complex with a covalent bond Ru–B through σ-bond metathesis. **119** is subsequently further substituted with an alkyne generating complex **120.** Then dihydrogen migration led to η^1-vinylidene complex **121.** Complex **122** is then formed by the coupling between borane and vinylidene ligands. Coordination of pinacolborane **25** followed by σ-bond metathesis releases product **124** and generates complex **125.** The addition of the next alkyne molecule regenerates complex **120** closing the catalytic cycle. The (*Z*)-stereochemistry of the product is determined in the reaction



Scheme 15 Proposed mechanism of radical *trans*-hydroboration of 1,3-diynes **60a** and **65a–l** with an N-heterocyclic carbene borane **66**.

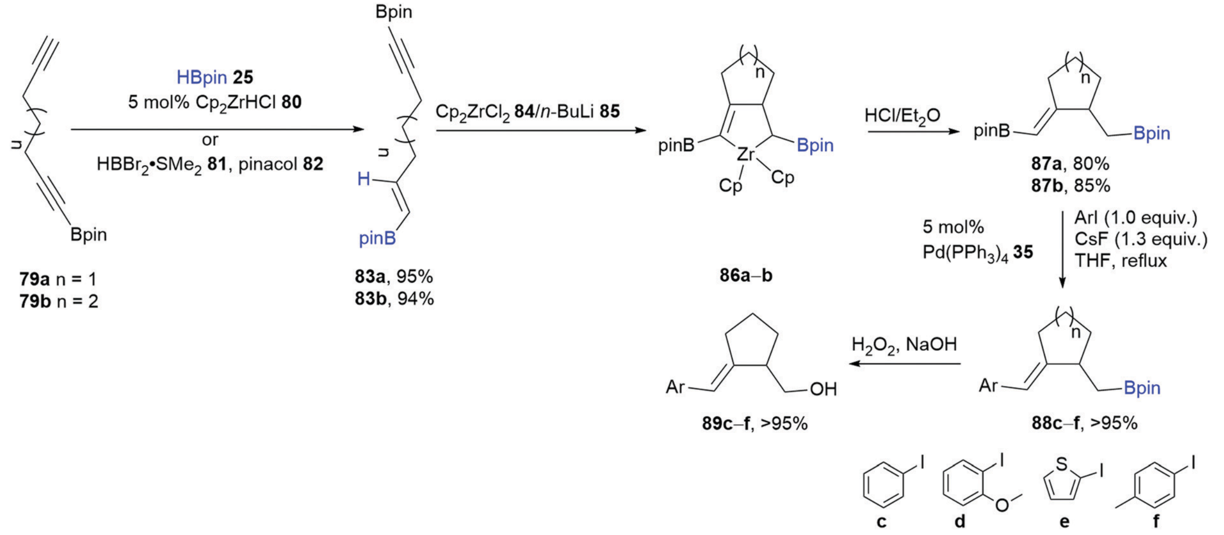


Scheme 16 Derivatisation of **70a** in Pd-catalysed Suzuki–Miyaura coupling.

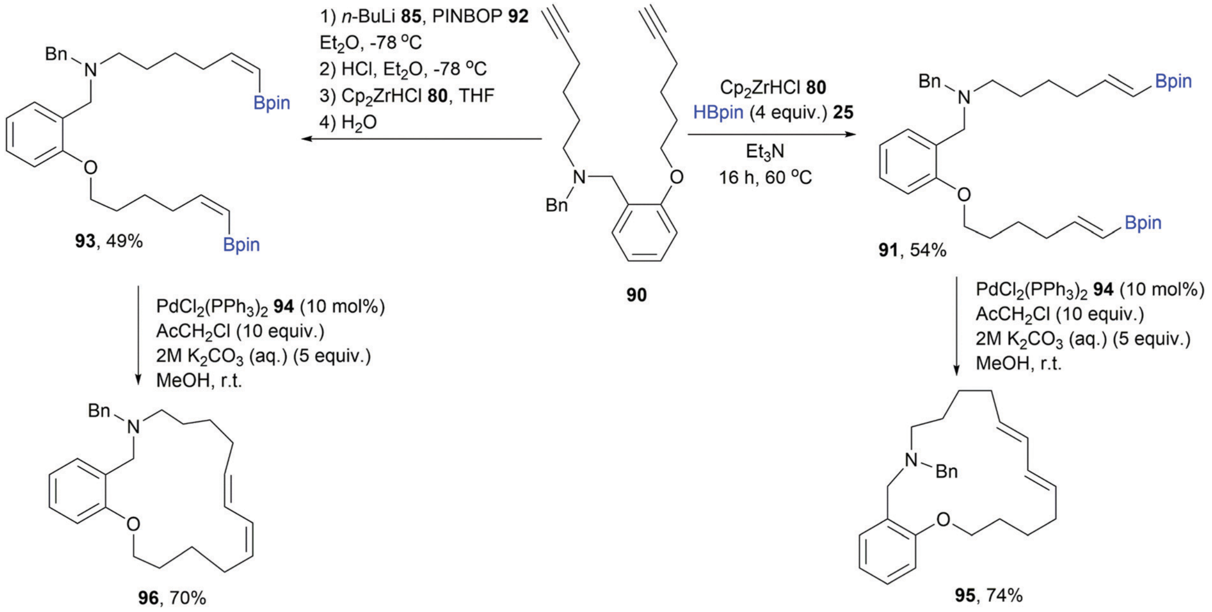
sequence from **120** to **122**, presumably reflecting steric interactions in the formation of complex **121.**[136]

Applying the low-valent Co catalyst **126**, generated *in situ* from CoCl$_2$/phenanthroline, TBAF **108**, and pinacolborane **25**, it was possible to carry out the cyclisation/hydroboration of 1,6-diynes **116a**, **127a–r**, and **129** yielding cyclic 1,3-dienylborons **128.** No other work has been reported on this type of cyclisation of diynes, although analogous systems with enynes and dienes have been published.[137–142] This reaction was observed to be more effective in dilute solutions. Different ligands and activators, *e.g.*, TMSCH$_2$Li, KOAc, *t*-BuOK could be used, but TBAF **108** and **126** were the most efficient. It was found that the system was active using various 1,6-diynes **116a** and **127a–r** with different substituents, *e.g.*, ketone, amide, nitrile, or sulfone. Not only *C*-tethered but also *N*- and *O*-tethered 1,6-diynes were reactive in this transformation furnishing heterocyclic compounds **128a–s**. Interestingly the reaction with 1,7-diyne failed in most cases with only one example using 4,4,5,5-tetraester **129** which underwent cyclisation/hydroboration to the six-membered ring product **130** (Scheme 24).

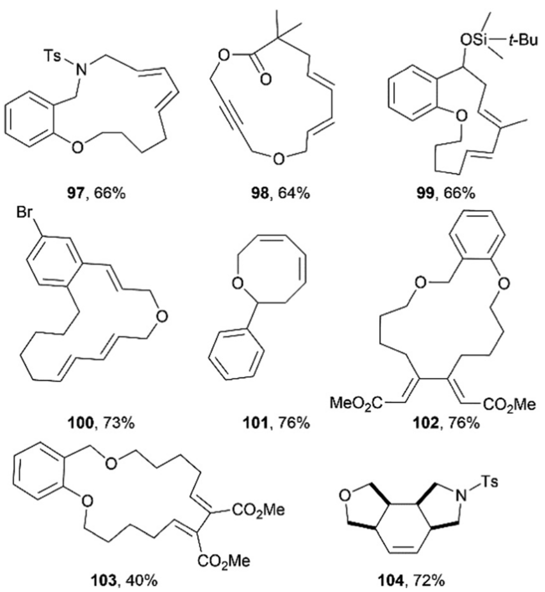
The mechanism of this transformation was proposed according to the stoichiometric reactions and experiments with DBpin **45.** The reaction is initiated by the formation of low-valent Co complex **131** in the reaction of **L**-CoCl$_2$ **126** with HBpin **25** (DBpin **45**) and TBAF **108**, which reduces the Co(II) to Co(0). In the next step coordination of diyne **116a**, or **127a–r** to **132**, occurs followed by the oxidative cyclisation to form a five-membered cobalt-containing cyclic intermediate **133. 133** then undergos σ-bond metathesis with **25** (transition state **134**) to give intermediate **135.** Reductive elimination of the product **128a–s** from **135** regenerates the low-valent cobalt species **131** (Scheme 25).[123] The utility of 1,3-dienylborones **128a–s** as building blocks was tested for **128a** in Diels–Alder, oxidation, chlorodeborylation, and Suzuki–Miyaura coupling reactions (Scheme 26).



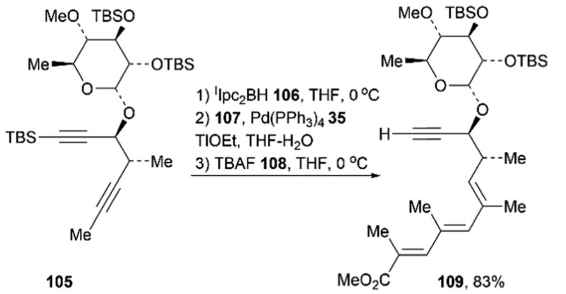
Scheme 17 Hydroboration of 1,*n*-diynes **79a–b** to borylated enynes according to Wang's procedure followed by the cyclisation and deborylation processes.



Scheme 18 Synthesis of macrocyclic dienes **95** and **96** applying the hydroboration reaction of aminodiyne **90** under Wang's and Srebrnik's procedures.

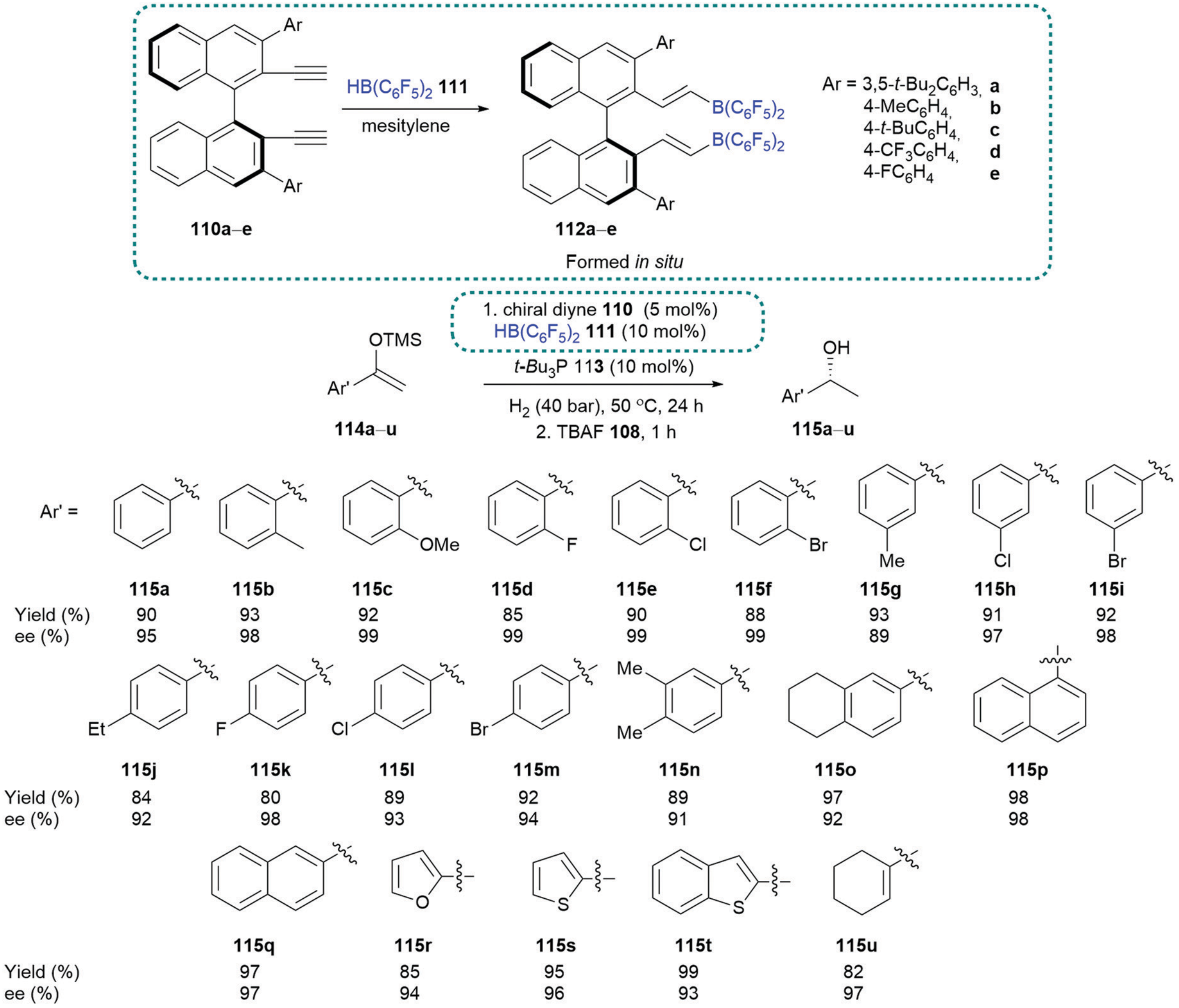


Scheme 19 Synthesis of macrocyclic dienes **97–103** and **104** based on the hydroboration/Pd-catalysed cyclisation of 1,*n*-diynes.

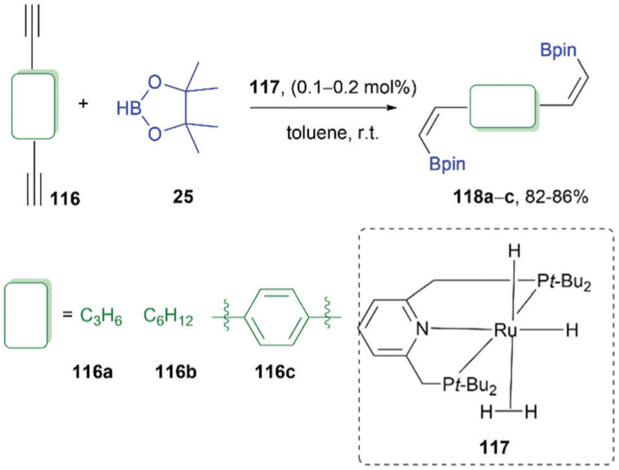


Scheme 20 Towards the synthesis of natural compound *Apoptolidin An*. Hydroboration of diyne **105** with $^{\text{I}}$Ipc$_2$BH **106** followed by the Suzuki–Miyaura coupling with **107** to give **109**.

Taniguchi *et al.* reported another type of hydroboration of benzo[3,4]cyclo-dec-3-ene-1,5-diynes **144a–m** which, following a borylative radical cyclisation, permitted the formation of 5-borylated 6,7,8,9-tetra-hydrobenzo[a]azulenes products **145a–m.**[143,144] The boryl radicals were formed from N-heterocyclic carbene–boranes **146** with radical initiators, of which di-*tert*-butyl hyponitrite (TBHN) **147** was the most effective. The homolytic bond dissociation energies of N-heterocyclic carbene boranes are much lower than those which possess typical boryl hydrides, and therefore these compounds might be used as precursors for rather stable boryl radicals **148.** The reaction occurred according to a radical chain mechanism by the intramolecular addition of the boryl radical followed by the cyclisation process. Under the optimised reaction conditions, 100 °C, trifluoromethylbenzene, 0.4 equiv. of TBHN **147**, and 5-fold excess of NHC–borane **146** products were obtained with moderate yields, which slightly varies depending on the substituents in both reagents: borane **146** and diyne **144** (Scheme 27). The obtained borylated compound **145a** was subsequently transformed in a one-pot cascade reaction into deborylated products **150a–c** and **151a–c** in the following reactions with *N*-chlorosuccinimide (NCS) **78** and then a Suzuki–Miyaura coupling with aryl iodides. Depending on the reaction conditions (path A or B), a different distribution of products was observed (Scheme 28).[143,144] The mechanism of this transformation was discussed based on the formation of borepin **156** from cyclic diyne **152** and NHC–boryl radical **148,** whose formation was initiated by the homolysis of the di-*tert*-butyl peroxide activator. The obtained radical **148** was added to diyne **152** to form alkenyl radical **153,** which was transformed to the hydroboration product by a



Scheme 21 Asymmetric hydrogenation of silyl enol ethers **114a–u** using frustrated Lewis pairs catalysts based on alkenyl boronates **112a–e** formed *in situ* in the hydroboration of diynes **110a–e** with Piers borane **111**.



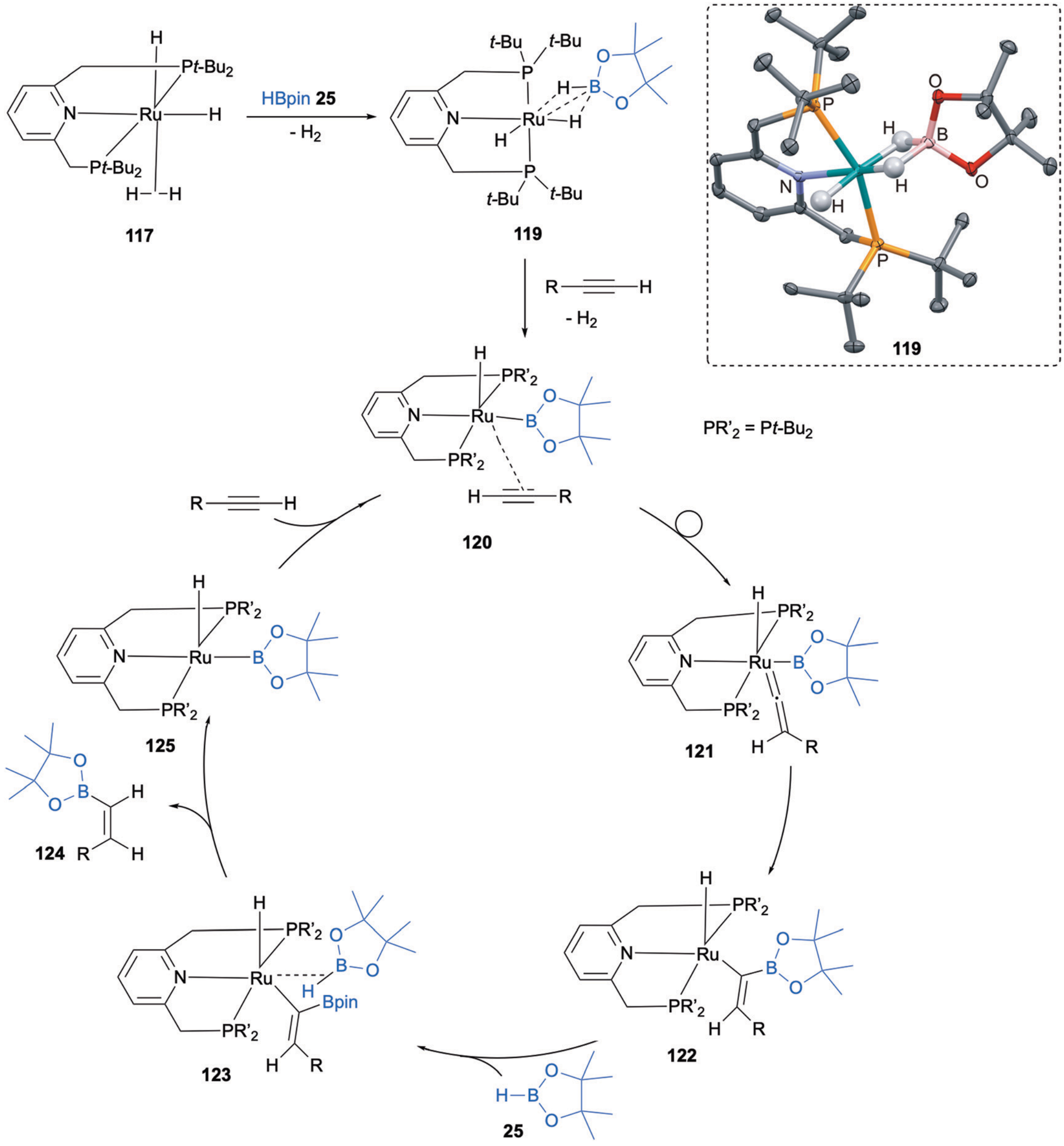
Scheme 22 Hydroboration of terminal separated diynes **116a–c** with pinacolborane **25** catalysed by Ru-complex **117**.

hydrogen atom transfer from NHC–borane **148.** Alkenyl borane **154** has two remaining B–H bonds and can undergo a second hydroboration to give product **156** (Scheme 29).[145]

3.3. Hydroboration of separated 1,*n*-diynes in the synthesis of macromolecular compounds

Non-catalytic hydroboration of internal and terminal diynes with alkyl or aryl spacers between ethynyl groups with dihydroboranes can lead to the formation of polymers, which possess a boryl group attached to C_{sp^2} determining their further reactivity. In most cases, sterically hindered thexylborane **157**, mesitylborane **158**, or tripylborane **159** have been used as hydroboration agents.

The foundation research carried out by Chujo *et al.*, used thexylborane **157** in the polyaddition process to terminal octa-1,7-diyne **160**, as well as internal 3,9-dodecadiyne **161a**, 3,8-undecadiyne **161b**, 3,10-tridecadiyne **161c**, 3,9-dodecadiyne **161d**, which occurred in THF, at 0 °C. When terminal diyne **160** was used, the polymer **162**, possessing 20% of the branched structure was obtained, which was visible by the gelation of the reaction mixture. The cross-linking structure occurred because

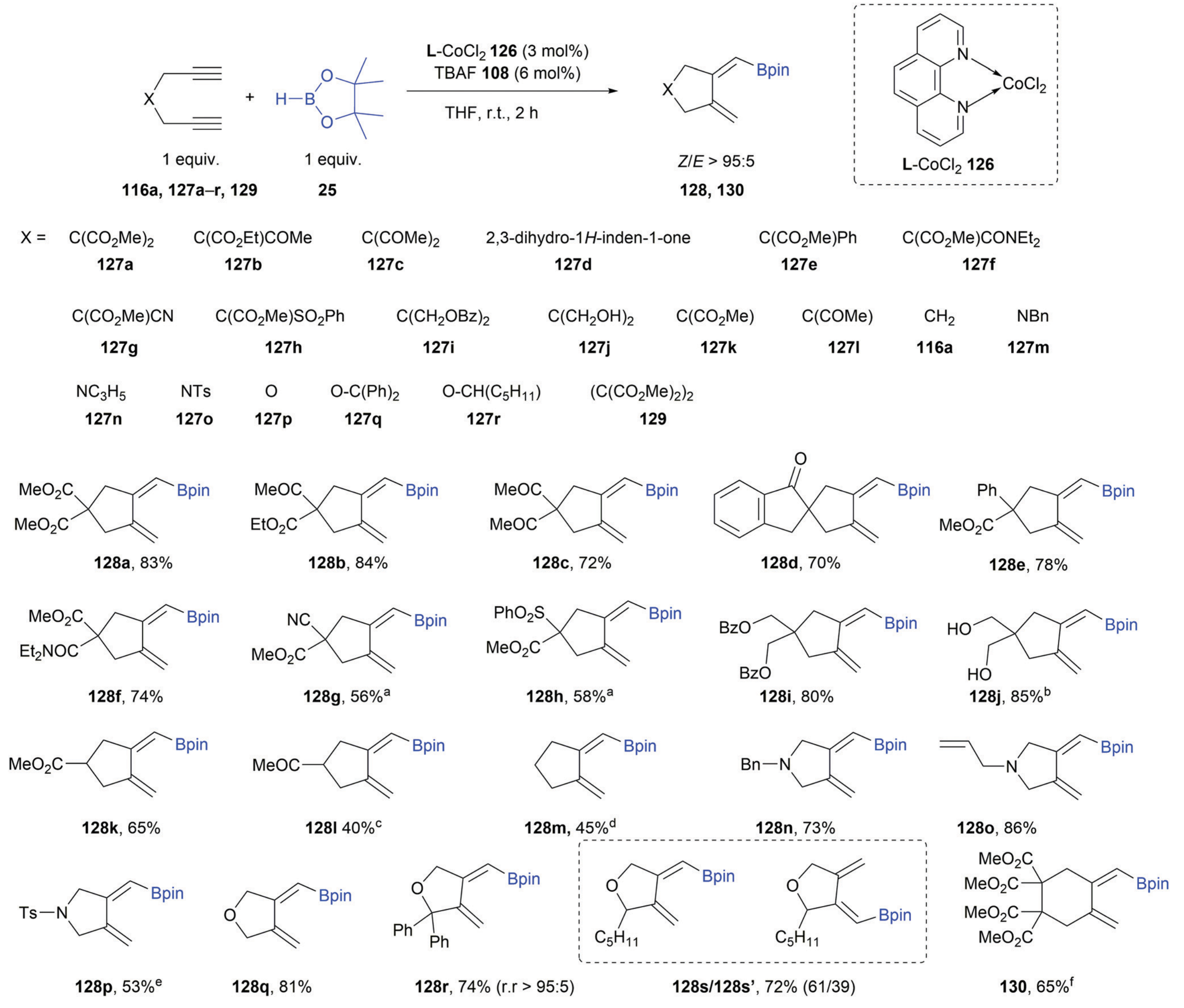


Scheme 23 Mechanism of *Z*-selective hydroboration of alkynes and diynes using Ru–pincer complex **117**.

of the easy access of the second borane molecule to the unshielded vinylborane bond in the subsequent hydroboration process. This branched structure caused the broadening of the molecular weight distribution of the polymer. When internal diynes **161** were used, the linear polymers **163** were mostly formed, which was determined by the observation of vinylic groups in ^{1}H NMR spectra (Scheme 30).[145]

When mesitylborane **158** was used as a hydroborating agent, no gelation and crosslinking were observed due to its high steric hindrance. The linear polymers **165** were formed from terminal separated diynes **116b**, **c**, **160**, and **164a–i** with good or moderate yields (35–95%) and moderate molecular weights (Scheme 31 and Table 2). The solvent type was observed to have a big influence on the products yields (Table 2, entries 1–4). Moreover, the temperature and the diyne type are also important factors for the reaction course. The best results were obtained for polymerisation of **160** in deuterated $CDCl_3$, but for most of the examples, THF was used. The polymers were more stable to air-oxidation than the products obtained by hydroboration with thexylborane **157**. The application of diynes with chromophores permitted the synthesis of polymers with optoelectronic properties.[146] The organoboron polymer prepared from diethynylbenzene **116c** and mesitylborane **158** was subsequently subjected to reaction with iodine to form poly(phenylene–butadienylene) **166** (Scheme 32).[146–150]

The same authors described the application of hydroboration with tripylborane **159** as a method for producing optoelectronic polymers **167a–d** using various 1,4-diethynylbenzenes as starting monomers (Scheme 33). The obtained polymers with chromophores **167a–d** emitted green or blue light, while their



[a] 2.0 equiv. of **25**, [b] 1.5 equiv. of **25**, [c] 10 h; [d] 3.0 equiv. of **116a**, [e] 1.5 equiv. of **127o**, [f] 24 h.

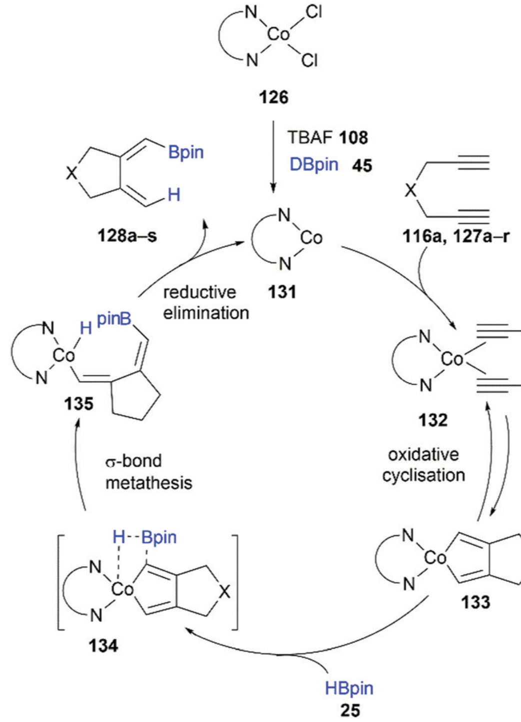
Scheme 24 Cobalt catalysed hydroboration/cyclisation of 1,6-diynes **116a**, **127a–r**, and 1,7-diyne **129** with HBpin **25**.

photostability depended on the electron density of the substituents in the comonomers. Moreover, conjugated polymers containing boron atoms in their backbone are known to extend π-conjugation through the vacant p-orbital of the boron atom. The authors used Gaussian 03 and theoretical calculations using DFT methods at the B3LYP/6-31G(d,p)/B3LYP/6-31G(d,p) level to calculate the bandgap in the polymers. The results showed that the bandgap decreased significantly with increasing the number of repeating mers in the polymer, showing that conjugation length was extended in polymer *via* the vacant p-orbital of the boron atoms.[147–150]

Using the same theoretical methods, it was possible to calculate the reactivity of C═C bonds depending on the R-groups attached to the aryl ring in the polymer by calculating the bond order. The bond order was found to be $OCH_3 < CH_3 < H$, while the stability was in the opposite order $OCH_3 > CH_3 > H$.[150] The polymerisation was also carried out for optically active diyne **168** with tripylborane **159.** A chiroptical activity was induced to the polymer **169** *via* the chiral side chain (Scheme 34).[151]

4. Hydroalumination of conjugated and separated diynes

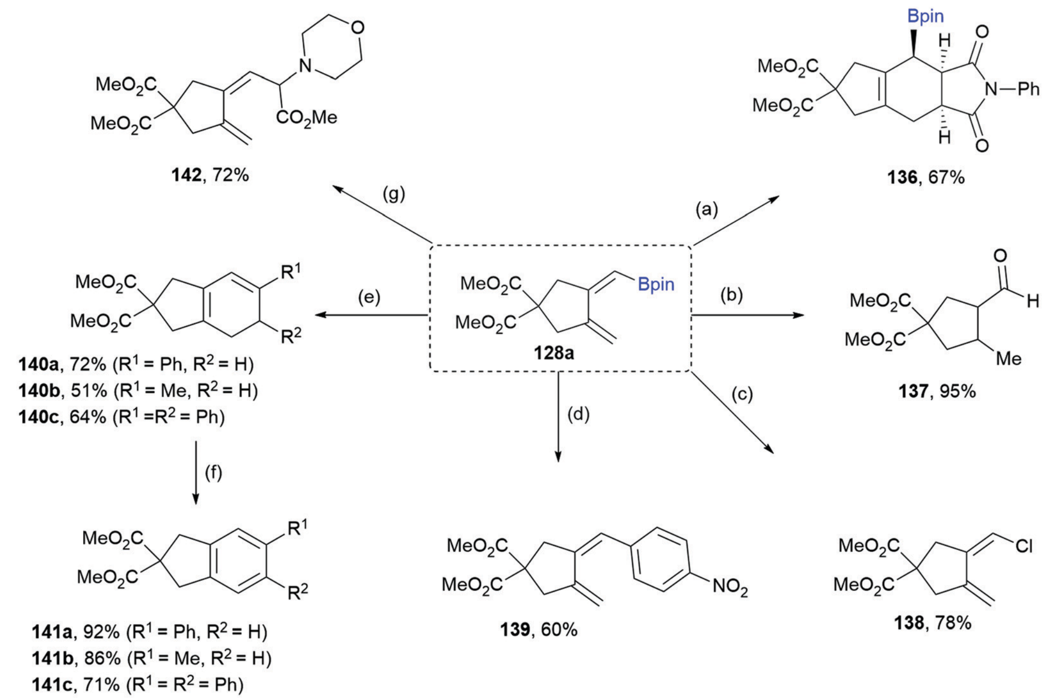
The addition of an Al–H bond to the C≡C bond of a diyne may proceed *via* mono- or bishydroalumination for the synthesis of metallated enynes or dienes, which can be further used in the chemical transformation towards the synthesis of natural products or *fine chemicals*. In comparison to boranes, there is a limited availability of organoaluminium hydrides which is



Scheme 25 Proposed mechanism for the Co-catalysed hydroboration/cyclisation of 1,6-diynes **116a** and **127a–r**.

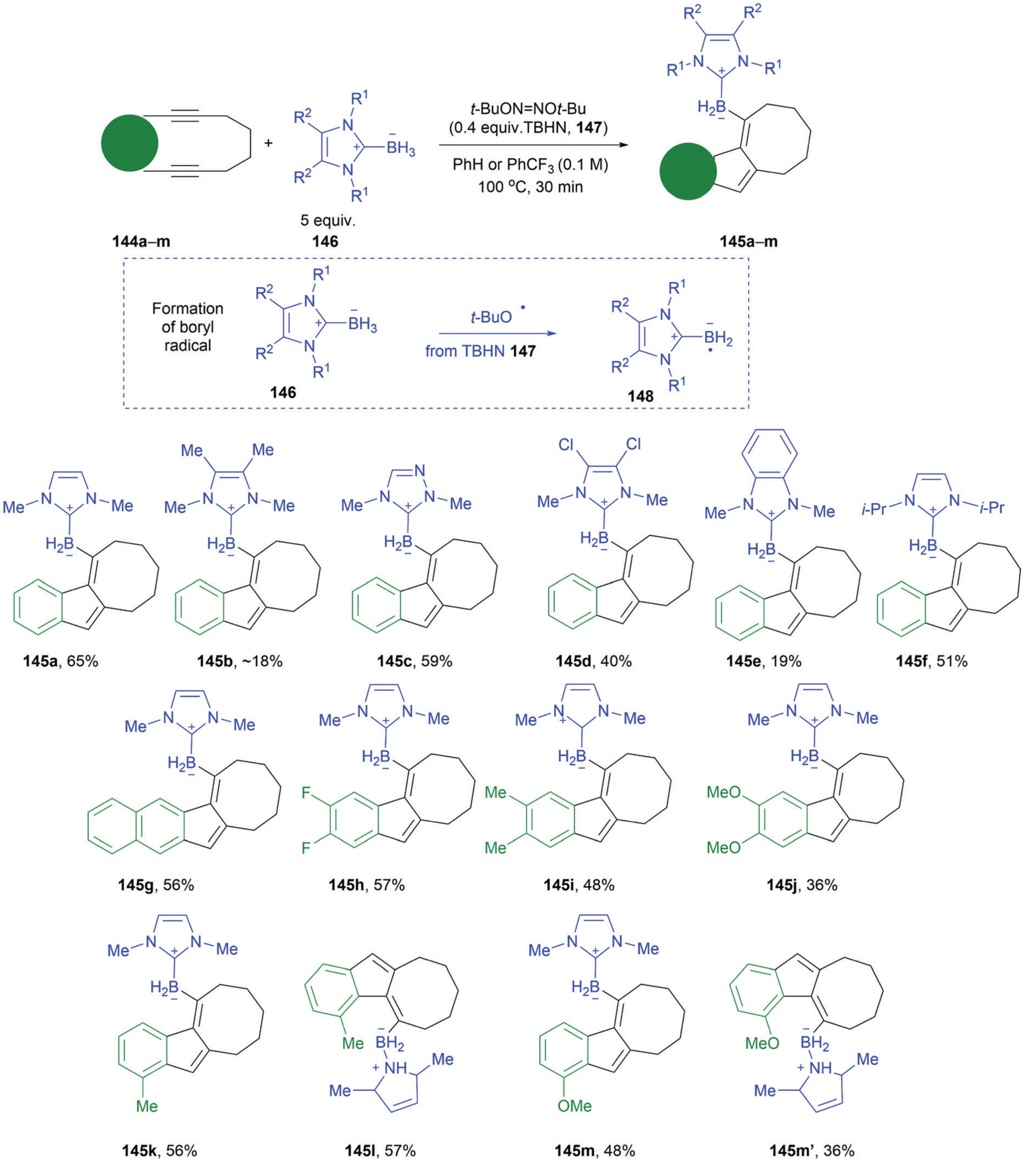
responsible for just a small number of papers focused on the hydroalumination of alkynes and diynes.[152,153]

In 1977, Zewifel described the hydroalumination of 1,3-diynes with lithium di(*iso*-butyl)methylaluminium hydride **172**, which was formed in the reaction of di(*iso*-butyl)aluminium hydride **170** with methyllithium **171**. The reaction occurred in diglyme at room temperature furnishing lithium enynylaluminate **173**. The rate of hydroalumination was found to be dependant upon the solvent and, when 1,2-dimethoxyethane or THF were used, the yields were much lower. The hydroalumination of the second C≡C bond in **13a–c, 65d** was not observed even when a 50% excess of aluminum hydride **172** was used (Scheme 35).[154] The reaction was highly stereoselective, which was confirmed with the exclusive formation of (*E*)-enynes **174a–d** after hydrolysis of obtained aluminate.[154] Deuterolisys of the aluminate in D_2O was used to prove the reaction regioselectivity. More than 98% deuterium was placed at the less shielded internal carbon bond **175**. The products **173** were additionally transformed to enyonic acids **176** in the reaction with CO_2. The reaction was only selective for symmetrical diynes **13a–c, 65d** (Scheme 35). In the case of 2,2-dimethyldeca-3,5-diyne **177**, two regioisomers **178** and **179** were obtained with comparable yields (Scheme 36). The opposite (*Z*)-isomer **16** to **173** was obtained by the same authors using hydroboration reaction.[126] To apply this transformation to unsymmetrically substituted diynes, reagents with electronically different substituents attached to C≡C bonds



Reaction conditions: (a) N-phenylmaleimide, THF, r.t., 15 h; (b) H_2O_2/NaOH, THF, r.t., 3 h; (c) $CuCl_2$ **143**, THF/H_2O 70 °C, 10 h; (d) p-nitroiodobenezne **76**, $Pd(PPh_3)_4$ **35**/K_2CO_3, toluene/H_2O/MeOH, 80 °C, 12 h; (e) alkenyl bromides or iodides, $Pd(PPh_3)_4$ **35**/MeONa, toluene/MeOH, 80-100 °C, 15 h; (f) 2,3-dicyano-5,6-dichlorobenzoquinone, toluene, 100 °C, 3 h; (g) 1. glyoxilic, morpholine, hexafluoropropan-2-ol, r.t., 8 h; 2. $TMSCH_2N_2$, THF, 4 h.

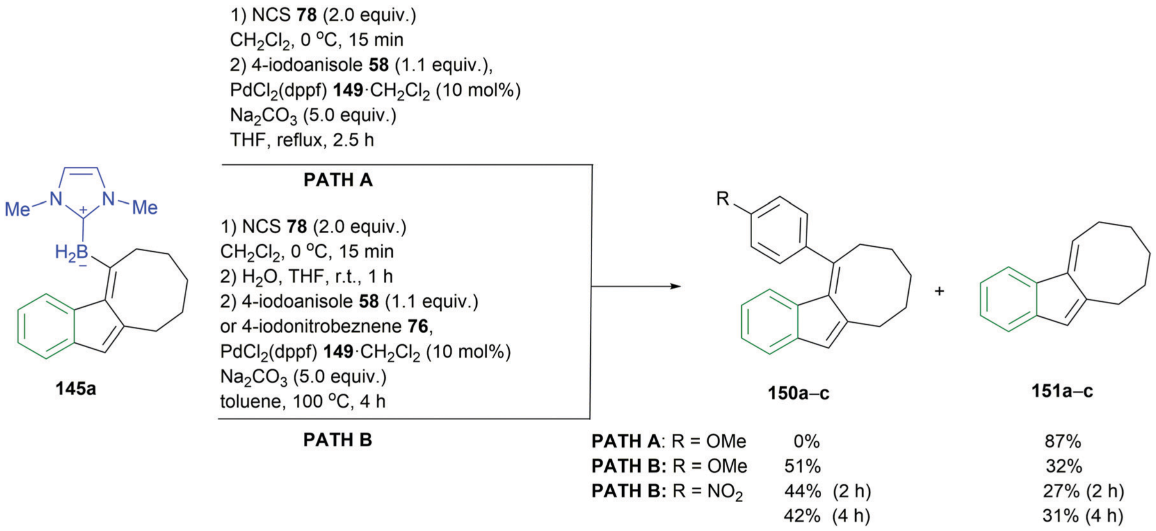
Scheme 26 Application of product **128a** as a building block in organic chemistry.



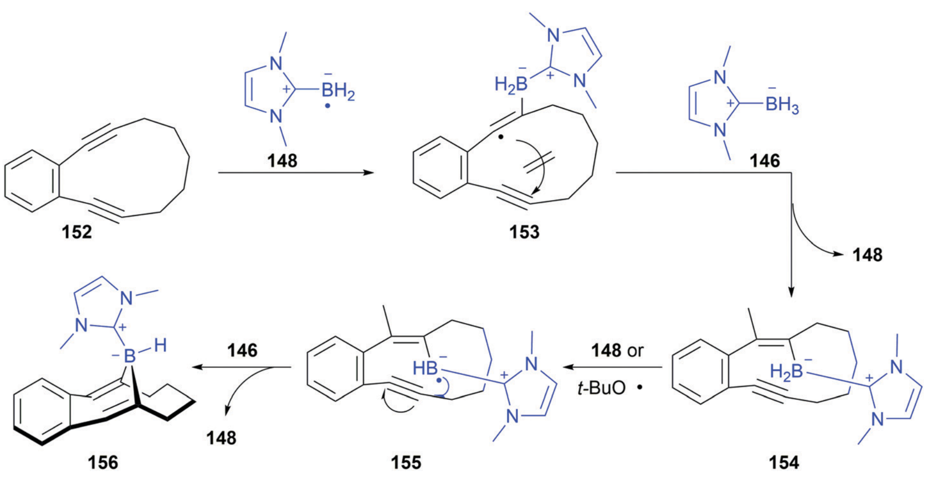
Scheme 27 Products formed in the reaction of diynes **144a–m** with boryl radical **148** generated from N-heterocyclic carbene boranes **146**.

were used **180a–c**. The trimethylsilyl group was attached to one alkyne, while an alkyl or cycloalkyl group was included on the other alkyne. The presence of the silyl protecting group made the second triple bond more susceptible to nucleophilic attack by the aluminum hydride **181** (Scheme 37). This strong activating effect from the silyl group was proved by the reaction of equimolar amounts of two different diynes: silyl-substituted **180a** and alkyl-substituted deca-4,6-diyne **65b**. Within the process, the silyl-substituted diyne **180a** was converted to enyne **182a**, while diyne **65b** was unreactive.[152] The obtained enynes following deprotonation **182a–d** were subjected to a second hydroalumination reaction with i-Bu$_2$AlH **170**. Here, the aluminate was attached to the C$_1$ atom with silyl group **183a–d** and then hydrolysed to **184a–d**. This regiochemistry was analysed according to the deuterolysis reaction, indicating more than 95% of D atoms at the C$_1$ position (Scheme 37).

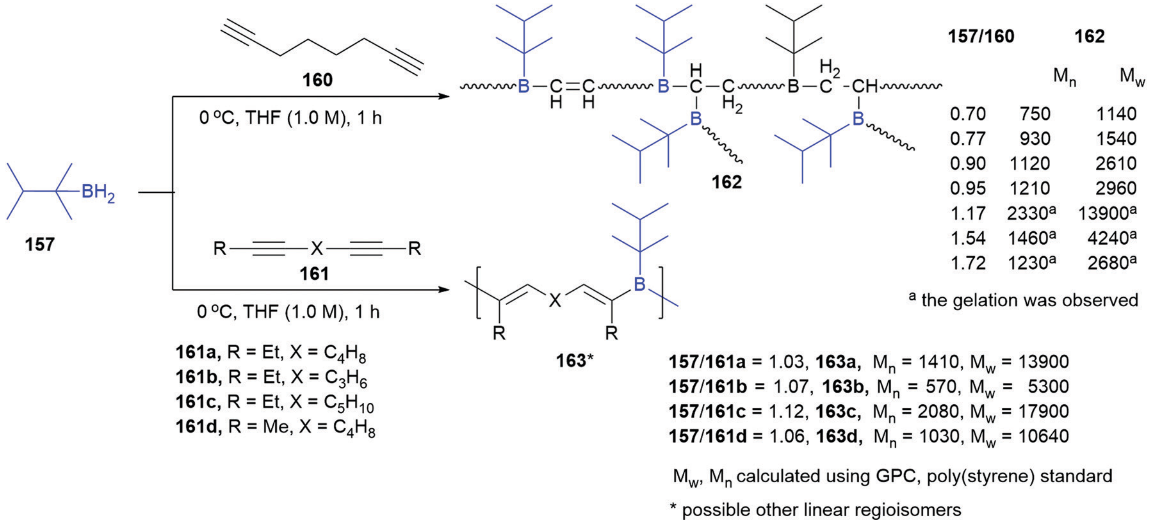
The hydroalumination and hydroboration reactions were applied in the synthesis of insect pheromone *Bombykol* **187** applying a desilylation procedure with KF × 2H$_2$O in DMF. The product **187** was obtained in high *trans*-selectivity in 81% yield (Scheme 38).[152]



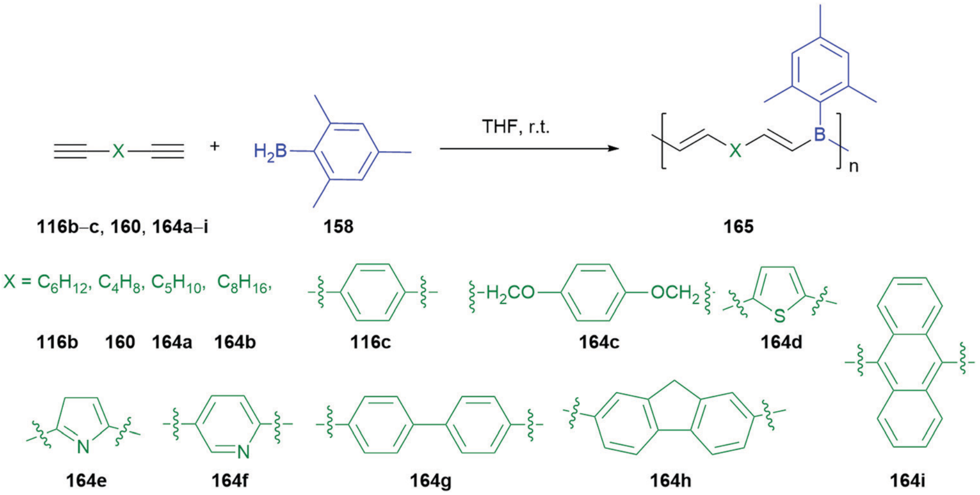
Scheme 28 Suzuki–Miyaura coupling of **145a** with iodoarenes **58** or **76**.



Scheme 29 Proposed mechanism for the formation of borepin **156** based on radical hydroboration.



Scheme 30 Noncatalytic hydroboration of terminal octa-1,7-diyne **160** and internal separated diynes **161a–d** with thexylborane **157**.



Scheme 31 Non-catalytic hydroboration of terminal separated diynes (**116b–c**, **160**, **164a–i**) with mesitilborane **158**. The results of the polymerisation are presented in Table 2.

Table 2 Results of polymerisation of terminal separated diynes **116b–c**, **160**, **164a–i** with mesitilborane **158** based on the hydroboration reaction

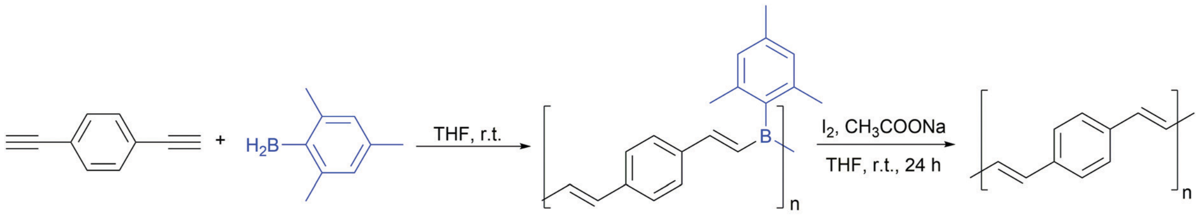
Entry	Diyne	Diyne:**158**	M_n	M_w	M_w/M_n	Yield of **165** [%]
1	**160**	n.a.[d]	5600	9600	1.7	35
2[a]	**160**	n.a.[d]	4200	5900	1.4	63
3[b]	**160**	n.a.[d]	12 600	28 600	2.3	80
4[c]	**160**	n.a.[d]	4700	8100	1.7	56
5	**164a**	n.a.[d]	7100	13 200	1.9	39
6	**116b**	n.a.[d]	6300	12 600	2.0	38
7	**164b**	n.a.[d]	6100	13 400	2.2	48
8	**164c**	n.a.[d]	810	1270	1.6	n.a.
9	**116c**	n.a.[d]	10 500	24 400	2.3	47
10	**116c**	1.17	6500	16 000	2.5	71
11	**164d**	1.27	3000	4800	1.6	58
12	**164e**	1.03	3000	5900	2.0	57
13	**164f**	1.21	2900	4500	1.6	36
14	**164g**	1.27	5100	10 500	2.1	95
15	**164h**	1.24	2800	4200	1.5	71
16	**164i**	1.22	1300	1700	1.5	67

Reaction conditions: THF, room temperature, isolated after precipitation in MeOH. [a] 50 °C. [b] $CDCl_3$. [c] CH_2Cl_2. [d] A small excess of diyne **116b–c**, **160** or **164a–i** was added to the THF solution of **158** (1.0 M).

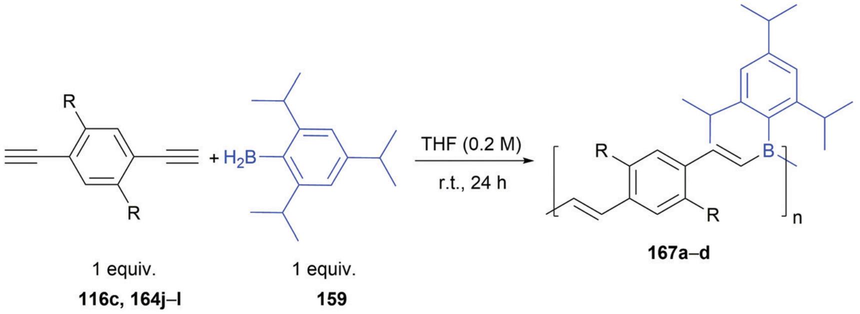
Hydroalumination of 1,4-bis(trimethylsilyl)-1,3-butadiyne **180c** and 1,4-bis(trimethylsilylethynyl)benzene **188** with di(*tert*-butyl)aluminium hydride **189** proceeded *via cis*-addition of the Al–H bond to both C≡C bonds in the diyne. Due to the directing effect of the silyl group, both organoaluminium groups were attached to the carbon atoms possessing the silicon atom. Within this reaction, the kinetic dienes **190** and **191** with (*Z*,*Z*)-stereoselectivity were formed. Increasing the temperature to 60 °C degrees caused the rearrangement of diene towards the thermodynamic product with (*E*,*E*)-configuration **193**. The exclusive formation of this isomer occurred when 1,4-bis-(trimethylsilylethynyl)benzene **188** was used as an initial reagent. In the case of 1,4-bis(trimethylsilyl)-1,3-butadiyne **180c** upon heating, a mixture of different products was obtained. The formation of both products: kinetic and thermodynamic were confirmed using NMR spectroscopy and X-ray analysis. The rearrangement of isomers from (*Z*,*Z*) **191** to (*E*,*E*) **192** took 7 days, while the total consumption of initial diynes in the first hydroalumination step was carried out for 15 or 3 hours respectively (Scheme 39). The formation of products **190**, **191**, **193** was confirmed by X-ray analyses (Fig. 2).[155]

5. Hydrosilylation

The subject focused on the hydrosilylation of diynes is the most documented of all hydroelementation processes discussed in this review. This is owing to the fact that the products are useful synthons in organic chemistry. The presence of the silyl group in the product structures, as well as other functional groups (hydrosilylation is a highly tolerant reaction), these compounds



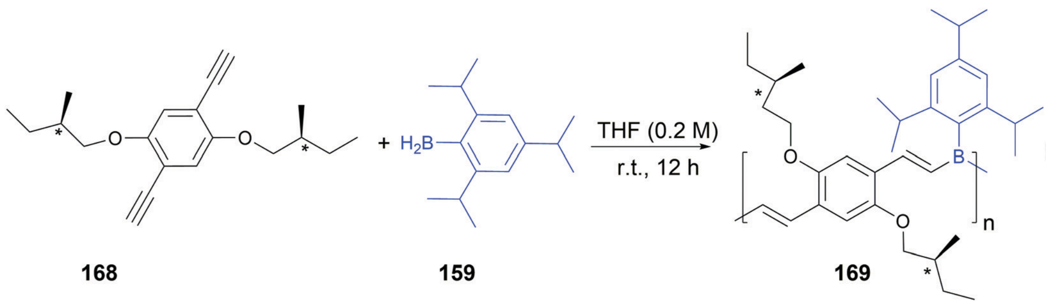
Scheme 32 Synthesis of poly(phenylene-butadienylene) **166**.



			167			
diyne	yield (%)		M_n	M_w	M_w/M_n	DP
116c	64	**a**	4100	6900	1.68	12
164j	79	**b**	4700	9500	2.00	13
164k	75	**c**	4200	7100	1.71	10
164l	32	**d**	4200	5900	1.41	8.8

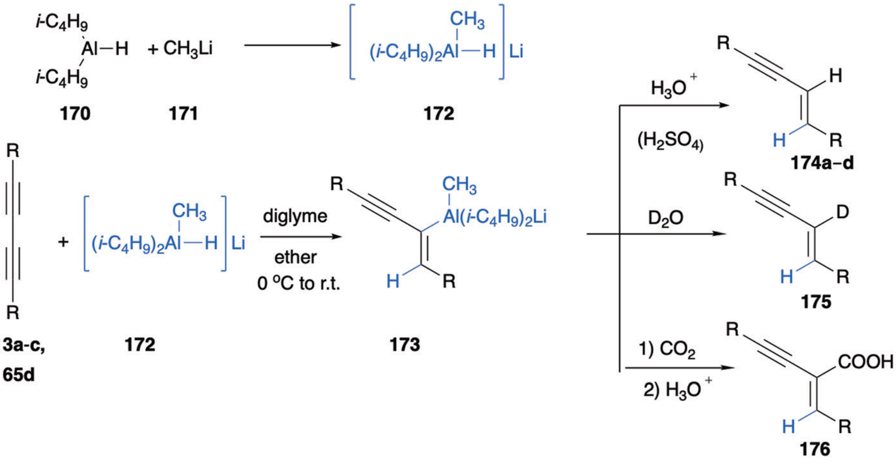
R = H,	$-CH_3$,	$-OCH_3$,	$-CF_3$
116c	**164j**	**164k**	**164l**

Scheme 33 Hydroborative polyaddition of 1,4-diethynylbenzenes (**116c**, **164j–l**) with tripylborane **159**.



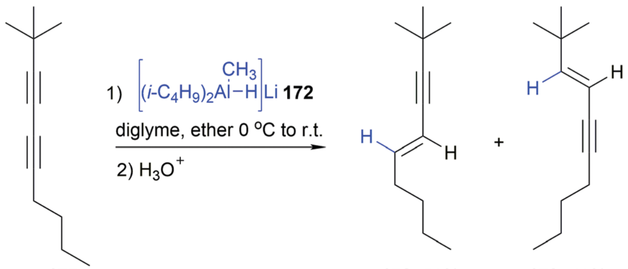
(73%)
M_n = 5600, M_w = 11 500,
M_w/M_n = 2.05

Scheme 34 Hydroborative polyaddition of tripylborane **159** to chiral diyne **168**.



	R = *n*-C_4H_9	*i*-C_3H_7	*t*-C_4H_9	c-C_5H_9
	174a	**174b**	**174c**	**174d**
Yield (%)	92	89	91	80
Isomer purity (%)	99	98	98	96

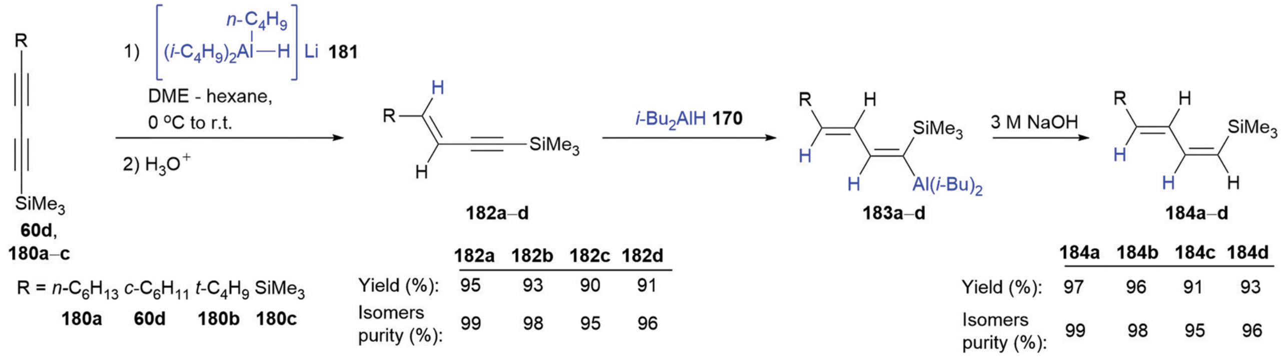
Scheme 35 Synthesis of (*E*)-enynes **174a–d** and enyonic acids **176** in the hydroalumination/hydrolysis or oxidation reactions.



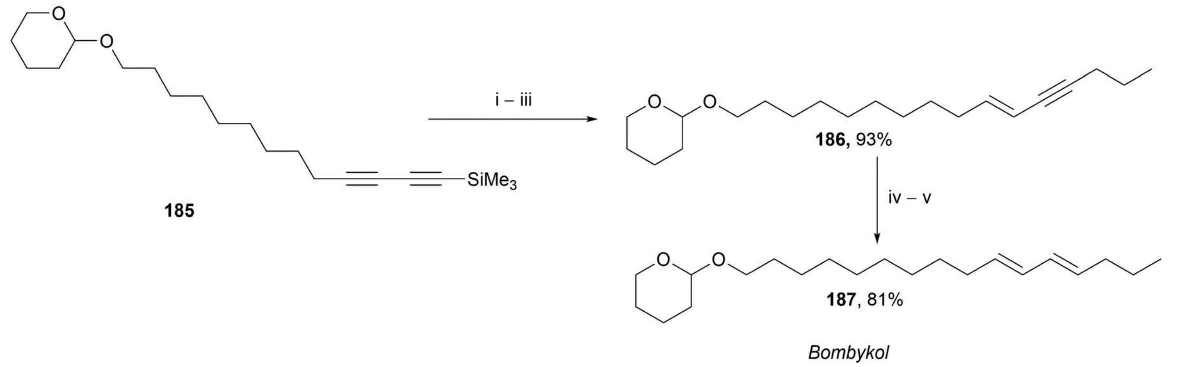
177 **178**, 58% **179**, 42%

Scheme 36 Hydroalumination/hydrolysis of unsymmetrical 2,2-dimethyl-deca-3,5-diyne **177** with **172**.

might be applied in various transformations leading to fine organic and organometallic compounds and materials.[67,68,156–162] This broad applicability is a result of the ease of substitution of the silyl group with a broad range of functional groups, as well as the formation of different silylated products: 1,3-enynes, allenes, polymers, or cyclic compounds, depending on the type of diyne starting material (conjugated or separated with alkyl or aryl spacers). Moreover, silyl-substituted compounds are easy to handle, simple for isolation, stable in air, and active in many chemical transformations. Additionally, the hydrosilylation of diynes, when an appropriate catalyst is chosen, might be carried

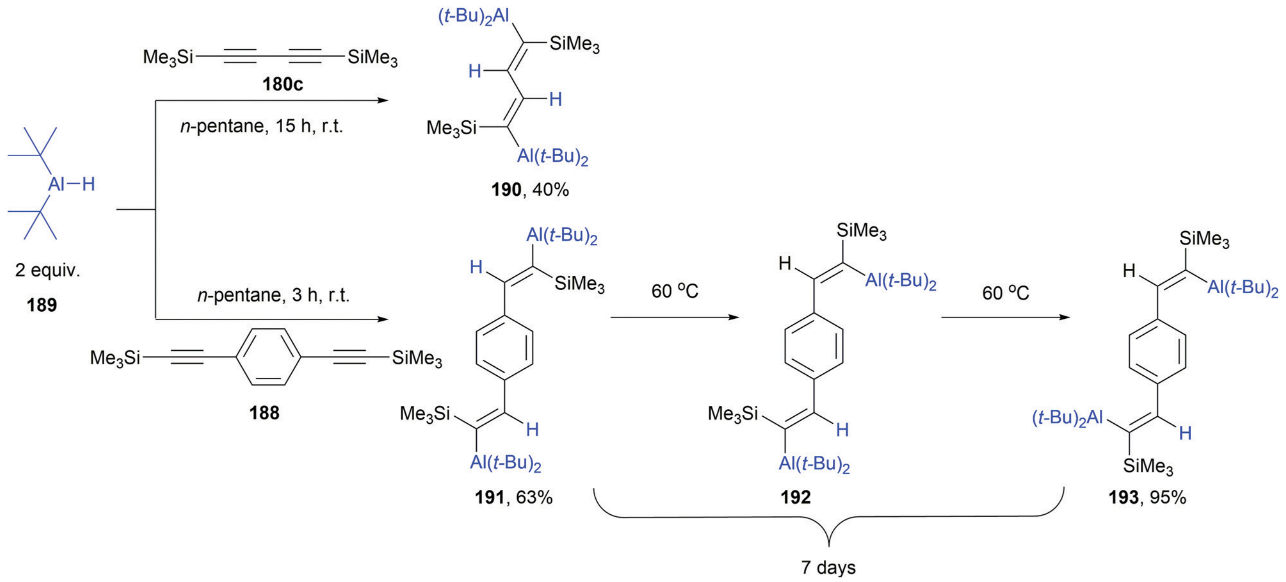


Scheme 37 Synthesis of silylated buta-1,3-dienes **184a–d** *via* two-step hydroalumination/hydrolysis reactions.



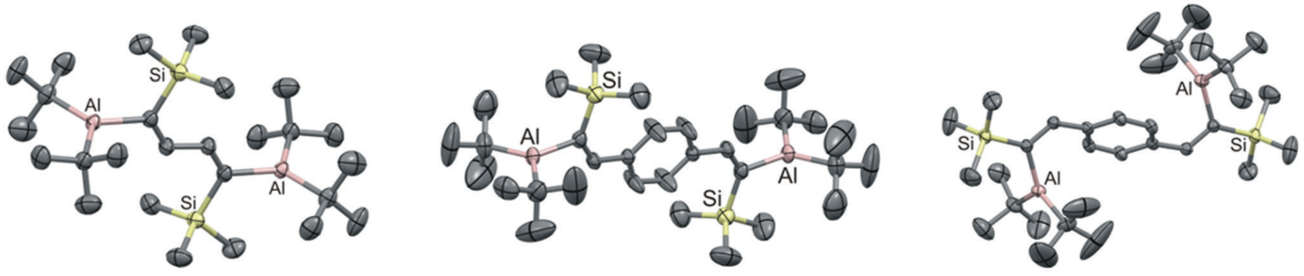
i) Li[AlH(*i*-Bu)$_2$*n*-Bu] **181**/DME-hexane, 25 °C, 1 h; 3 M HCl; ii) KF x 2H$_2$O/DMF, 25 °C; iii) *n*-BuLi **85**/hexane-diglyme, -78 °C to 25 °C, *n*-C$_3$H$_7$Br/25 °C to 80 °C, 18 h; iv) Disiamylborane **14**/THF, 0 °C, 3 h; AcOH, 60 °C, 5 h, H$_2$O$_2$, NaOH, 30 °C to 50 °C; v) MeOH, 3 M HCl.

Scheme 38 Synthesis of insect pheromone Bombykol **187** with hydroalumination, desilylation, and hydroboration steps.



Scheme 39 Kinetic **190** and **191** and thermodynamic products **193** in the hydroalumination of diynes **180c** and **188** with HAl(*t*-Bu)$_2$ **189**.

out in a 100% atom economic way yielding a single product. Such an approach is especially important owing to the simplification of separation steps. Therefore, considering the reaction methodology, conditions, and application of a specific type of catalyst (often tailored-made) is of prior importance, especially when such complex diyne molecules are used as reagents.[68,73,74,156,163] The simplicity of the hydrosilylation process, its high tolerance towards various functional groups present in the reagent



190 **191** **193**

Fig. 2 Molecular structures of kinetic **190**, **191** and thermodynamic **193** wich were obtained in the hydroalumination reaction of **180c** and **188** with $HAl(t\text{-}Bu)_2$ **189**.[155]

structures, as well as the diversity of the selectivities, which can be tuned by the proper choice of the catalyst, has rendered this transformation the first choice for the synthesis of organosilicon compounds. The reactivity of the silyl group in coupling reactions or desilylation processes has allowed the application of the resulting compounds (*e.g.*, 1,3-enyne or 1,3-diene fragments), in the synthesis of natural or biologically active compounds.[67,68,156–160]

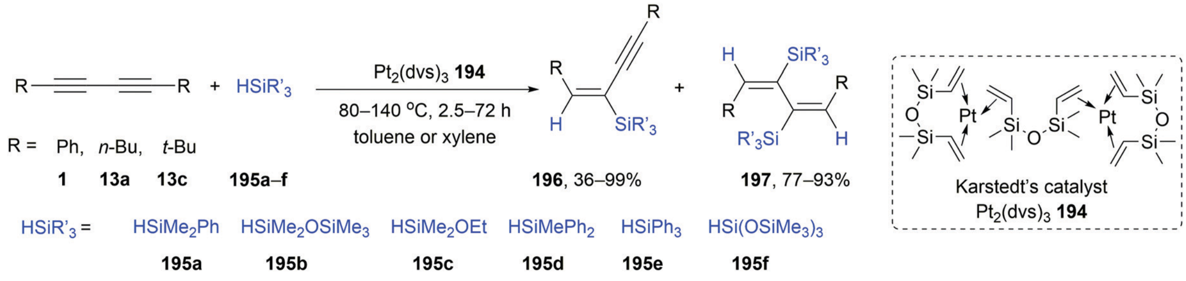
To systemise the results in this section, the information is ordered according to the hydrosilylation of conjugated 1,3-diynes, 1,*n*-diynes, as well as the formation of various products, 1,3-enynes, allenes, polymers, or cyclic compounds.

5.1. Hydrosilylation of conjugated 1,3-diynes towards molecular and macromolecular unsaturated organosilicon compounds

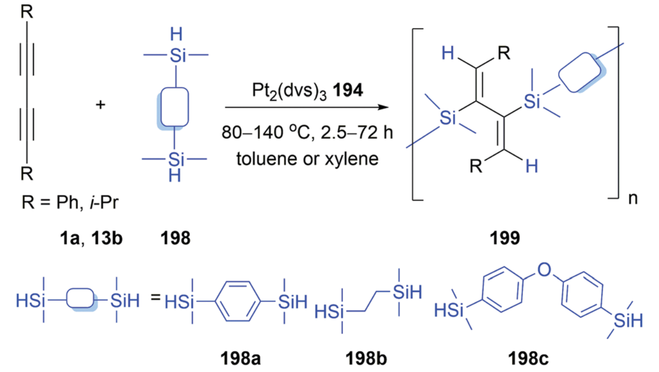
The hydrosilylation of conjugated 1,3-diynes is a straightforward and 100% atom economic method, which occurs *via* the addition of the Si–H bond to the C≡C bond, but due to the presence of two such alkyne groups, the formation of a specific single product with high selectivity is a challenging task. Depending on the type of the catalyst, reagents, their concentration, ratio, and process conditions, silylated 1,3-enynes, 1,3-dienes, or allenes can be formed, frequently as a complex mixture of products (up to nine different compounds can potentially be formed).[62,73,74,156,164] Many papers describe the hydrosilylation of monoalkynes,[14,41,48,49,51] but the addition of the Si–H bond to 1,3-diynes is much more demanding and limited only to a few papers. The hydrosilylation of 1,3-diynes occurs mainly in the presence of noble metal complexes (Rh, Pt, Pd, Ru). There are also some examples of the application of less expensive Ni or Co catalysts. However, in the majority of examples there was little discussion of the influence of the reagent structure, reaction conditions, or the nature of the catalyst on the reaction outcome. Our recent papers focused on the hydrosilylation of 1,3-diynes with silanes or silsesquioxanes in the presence of commercially available platinum complexes give the first detailed research which discusses the influence of several parameters on the hydrosilylation selectivity.[73,74,165]

In a report by Perry *et al.* the synthesis of conjugated polymers from 1,3-diynes and bis(silylhydrides) were described. The products were obtained *via* hydrosilylation reactions in the presence of Karstedt's catalyst **194**. To check whether the double Si–H addition to the 1,3-diyne had occurred, the authors carried out model reactions using monohydrosilanes **195a–f** with methyl, phenyl, or trimethylsiloxy groups with 1,4-diphenylbuta-1,3-diyne **1a**, dodeca-5,7-diyne **13a**, and 2,2,7,7-tetramethyl-octa-3,5-diyne **13c**. Bissilyl adducts **197** were obtained under harsh reaction conditions (120–145 °C) in xylene. The silyl-substituted but-3-en-1-ynes **196** were obtained for less bulky silanes **195a** and **195b** under lower temperature (80 °C) in toluene. Not only were the steric properties of silanes important but also the 1,3-diyne used influenced the formation of monosilyl or bissilylated adducts. The functionalisation of bulky **13c** gave exclusively the silyl-substituted enyne **196** (75–99%) (Scheme 40). The hydrosilylation occurred according to the *syn*-addition with the silyl group attached to the most internal carbon atom.

Furthermore, the polymerisations were carried out with dihydrosilanes **198a–c** which furnished polymers **199** with a



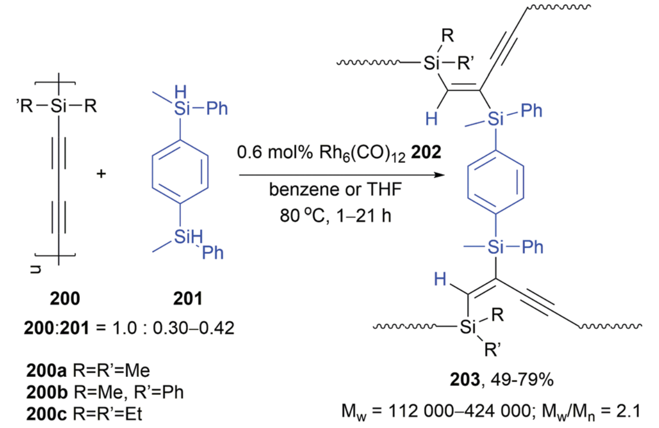
Scheme 40 Hydrosilylation of symmetrical 1,3-diynes **1a**, **13a**, and **13c** with silanes **195a–f** in the presence of Karstedt's catalyst **194**.



Scheme 41 Hydrosilylation of symmetrical 1,3-diynes **1a**, **13b** with dihydrosilanes **198a–c** catalysed by Karstedt's catalyst **194**.

Table 3 Parameters of polymers **199** obtained in the hydrosilylation reaction of conjugated diynes **1a** and **13b** with dihydrosilanes **198a–c**

			199			
Entry	Diyne	198	M_n	M_w	M_w/M_n	State
1	**1a**	**198a**	9540	4130	2.31	Solid
2	**1a**	**198b**	n.a.	n.a.	n.a.	n.a.
3	**1a**	**198c**	16 190	6490	2.50	Solid
4	**13b**	**198a**	19 770	8020	2.47	Liquid
5	**13b**	**198c**	17 610	7190	2.45	Liquid



Scheme 42 Rh-catalysed crosslinking of polymers with conjugated C≡C bonds **200** with 1,4-bis(methylphenylsilyl)benzene **201**.

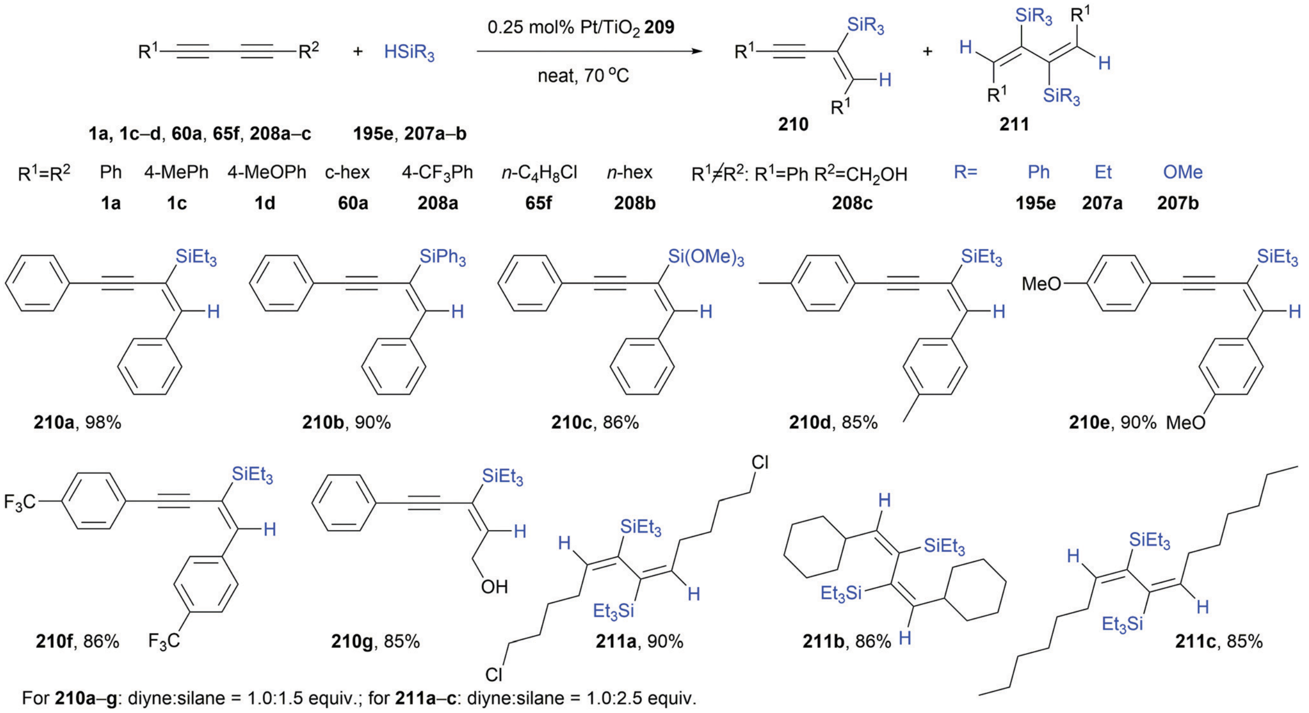
(*Z*,*Z*)-2,3-disubstituted-1,3-butadiene mers. The main products were linear polymers **199**, but a few percent of cyclic oligomers were formed as well. Most of the cyclic products and low molecular weight linear polymers were separated by precipitation in MeOH : acetone = 3 : 1 solution, which presence was confirmed by MALDI and SEC analysis. The authors reported also that the rate of polymerisation depended on the catalyst **194** concentration, but did not influence the molecular weight of the polymers and polydispersity, which varies from 2.0 to 2.61 for specific reagents (Scheme 41 and Table 3).[62]

The hydrosilylation of poly[(dimethylsilylene, methylphenylsilylene, and diethylsilylene)but-1,3-diyne] **200a–c** with 1,4-bis(methylphenylsilyl)benzene **201** was selectively carried out at 80 °C in the presence of 0.5 mol% of $Rh_6(CO)_{16}$ **202**, with a **200 : 201** ratio = 1 : 0.3–0.42 (Scheme 42). Applying the catalyst **202**, the addition to only one alkynyl group in the polymer occurred, while other Rh complexes, *e.g.*, $Rh(acac)(CO)_2$ **204** and $RhCl(PPh_3)_3$ **205** also yielded allenes. H_2PtCl_6 **206** additionally catalysed depolymerisation reaction. The polymers **203** were obtained with 49–79% yield, the M_w = 112 000–424 000, and M_w/M_n = 2.1. The higher the molecular weight of **203**, the longer reaction time was needed. The catalyst activity was checked in the model reaction of poly[(dimethyl-silylene)buta-1,3-diyne] **200a** with triethylsilane **207a**.[166]

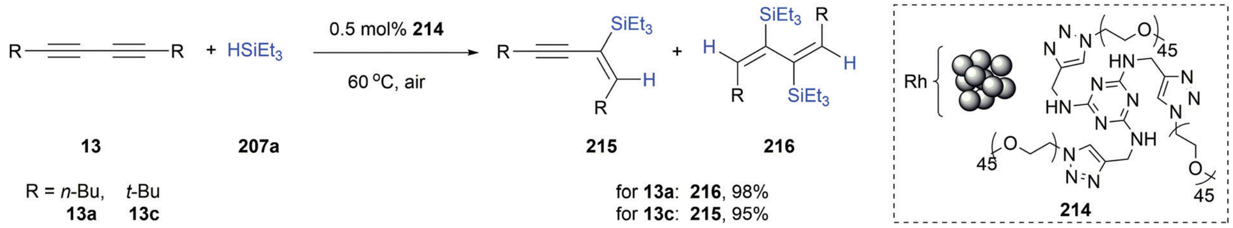
Escribano's group used a heterogeneous monometallic or bimetallic catalyst with active calcinated or non-calcinated platinum supported on titania in the hydrosilylation of symmetrical 1,4-diaryl **1a**, **1c–d**, **208a**, or 1,4-dialkyl-substituted-1,3-diynes **60a**, **65f**, **208b**, and one unsymmetrical diyne **208c** with silanes **195e** and **207a–b**. The best activity occurred using Pt/TiO_2 catalyst **209** (Scheme 43). Under the optimised reaction conditions (0.25 mol% of Pt/TiO_2 **209**, 70 °C, solvent-free conditions), depending on the reagent structures, monohydrosilylation or bishydrosilylation resulted. Electronically different diaryl-1,3-diynes underwent hydrosilylation using three silanes (Et_3SiH **207a**, Ph_3SiH **195e**, $(MeO)_3SiH$ **207b**) giving silylated 1,3-enynes **210a–g** with high yields (85–98%). The hydrosilylation of electron-rich reagents was much faster than for electron-poor diynes and occurred with higher yields. Bishydrosilylation of diynes was possible only for the dialkyl-substituted reagents **60a**, **65f**, and **208b** using 2.5 equiv. of silane **207a**. Additionally, the hydrosilylation of unsymmetrical 5-phenylpenta-2,4-diyn-1-ol **208c** with Et_3SiH **207a** gave silylated 1,3-enyne **210g** as a product with 75% isolated yield. For the reaction of 1,4-diphenylbuta-1,3-diyne **1a** with triethylsilane **207a**, catalyst **209** was filtered and three times recycled, giving the product **210a** with 100, 70, and 15% in the following cycles. The significant decrease of the product yield was caused by the Pt leaching, which was confirmed by ICP-MS analysis (the catalyst **209** contained 22% of initial Pt loading after the third cycle). The products **210** and **211** were obtained with (*E*)-stereochemistry and with the silicon atom bonded to the internal carbon atom of the conjugated system.[167]

Another heterogeneous catalyst, which was used in the hydrosilylation of alkynes and 1,3-diynes was based on Rh nanoparticles **214** synthesised by the reduction of $RhCl_3$ **213** with $NaBH_4$ **212** and their further stabilisation in a nitrogen-rich poly(oxyethylate) derivative. The catalyst was used for hydrosilylation of dodeca-5,7-diyne **13a** and 2,2,7,7-tetramethylocta-3,5-diyne **13c** with triethylsilane **207a** used in a 4.0–6.0 fold excess. The more hindered diyne **13c** gave monosilylated enyne **215**, while the less shielded **13a** gave bissilylated diene **216** with excellent isolated yields (95% and 98% respectively) (Scheme 44).[168] Palladium nanoparticles were also tested for single alkyne examples.[169,170]

The hydrosilylation of conjugated symmetrical 1,3-diynes **1a**, **13c**, and **180c** with mono- or dihydrosilanes **195a**, **207a**, **217** was carried out in the presence of various Ni(0) **218–220** or



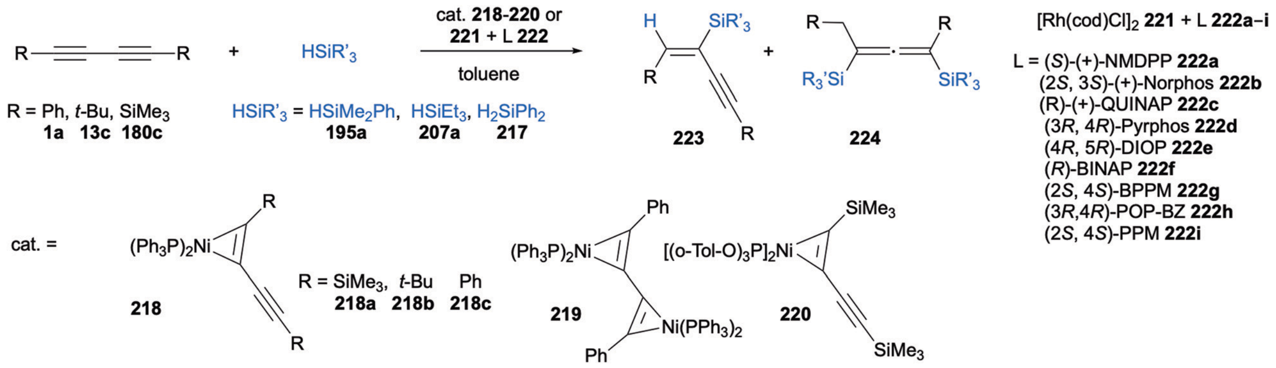
Scheme 43 Solvent-free mono- and bishydrosilylation of 1,3-diynes **1a**, **1c–d**, **60a**, **65f**, **208a–c** with silanes **195e**, **207a–b** catalysed by Pt/TiO_2 **209**.



Scheme 44 Hydrosilylation of symmetric diynes **13a** and **13c** with triethylsilane **207a** using Rh nanoparticles stabilised with nitrogen-rich poly(oxyethylenate) derivative **214**.

Rh(I) **221** complexes with the addition of different chiral or non-stereoselective ligands **222a–i**. In all experiments, the silane was used in a 3.5 to 4.0-fold excess with respect to the diyne. The bishydrosilylated allene **224** was obtained for 1,4-bis(trimethylsilyl)buta-1,3-diyne **180c**, while for diynes substituted with *tert*-butyl **13c** and phenyl **1a** groups, a mixture of silyl-substituted enyne **223** and allene **224** was formed (Scheme 45). The synthetic procedure was quite enigmatic, and the silane was used in high excess with no equimolar reagent ratios tested (Table 4).[164,171,172]

A recent publication from our group details the application of commercially available catalysts: $Pt_2(dvs)_3$ **194**, $Pt(PPh_3)_4$ **225**, or PtO_2 **226** in the hydrosilylation of various symmetrical 1,4-disubstituted buta-1,3-diynes (**1a**, **13c**, **65a**, **227a–b**) with sterically and electronically different triethyl-**207a** and triphenylsilane **195e**. Comprehensive optimisation studies were carried out to find the most suitable conditions that permitted obtaining either the monosilylated enynes or bissilyated dienes with high stereo- and regioselectivity. The application of a Pt catalyst led to the *syn*-addition of silane to the C≡C bond and the formation of the alkenyl silane with the silyl group attached to the internal carbon atom. This was confirmed by the crystal structures of the products **228h** and **228i** (Fig. 3), as well as with ^1H–^{13}C HSQC and NOESY 2D NMR. Within the study, an equimolar ratio of reagents was reported for the first time, which is in agreement with the atom economy policy and simplifies the separation procedure, additionally reducing the process costs. Pt Karstedt's catalyst **194** was used for the synthesis of bisadducts **229**, whereas the less active PtO_2 **226** and $Pt(PPh_3)_4$ **225** were capable of the synthesis of monosilylated enynes **228** (Scheme 46). Moreover, the influence of the reaction temperature on reaction selectivity was noticeable. For monohydrosilylation, 40 °C or lower temperature gave better selectivity. The structure of the reagents has also an important role in reaction selectivity. For sterically hindered diynes **13c** and **227b** and triphenylsilane **195e**, only monoadducts **228h** and **228e** were obtained. The products **228a–j** and **229a–d** were isolated with 82–98% yield and were fully characterised.[73]



Scheme 45 Catalytic hydrosilylation of symmetrical conjugated diynes **1a**, **13c**, **180c** with silanes **195a**, **207a**, and **217** in the presence of $L_2Ni(0)$-butadiyne **218–220** and $[Rh(cod)Cl]_2$ **221** + L **222** complexes.

Table 4 Hydrosilylation of 1,3-diynes with $L_2Ni(0)$-butadiyne **218–220** and $[Rh(cod)Cl]_2$ **221** + L **222a–i** complexes

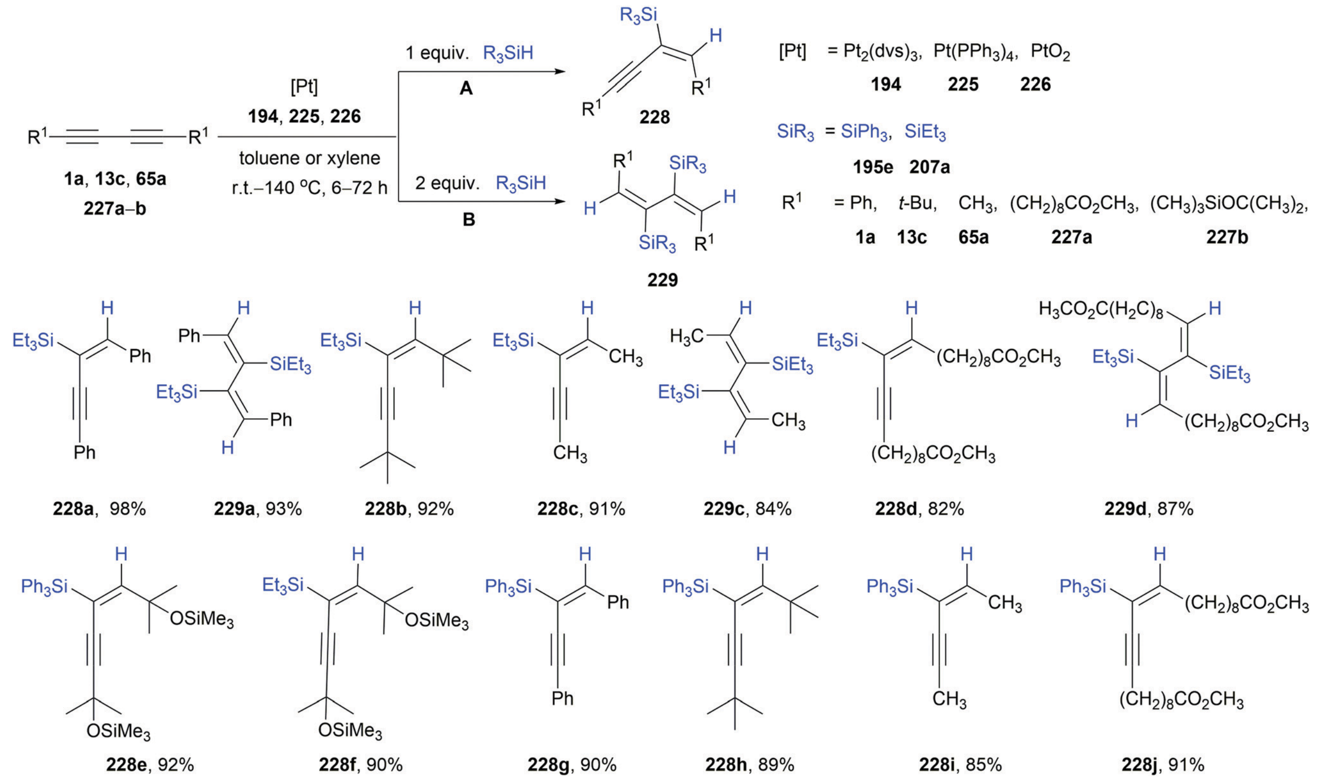
Entry	Cat[a]	Diyne	Silane	[Diyne]:[silane]	*T* [°C]	*t* [h]	Yield [%]	Selectivity of (223/224) [%]	Isolation method	Isolated yield (223/224) [%]
1	**218a**	**180c**	**217**	1.0/3.5	80	2	100	2/91	Distillation	—/49
2	**218a**	**180c**	**217**	1.0/2.5	80	2	92	20/61	Distillation	
3	**218a**	**13c**	**217**	1.0/3.5	80	1	100	3/78	Chromatography	
4	**218a**	**13c**	**217**	1.0/3.5	80	6	100	1/80	Chromatography	—/78
5	**218a**	**13c**	**195a**	1.0/3.5	80	2	100	51/31	Solvent evaporation	
6	**218a**	**13c**	**195a**	1.0/3.5	80	6	100	53/33	Chromatography	
7	**218a**	**13c**	**207a**	1.0/3.5	80	6	66	59/—	Chromatography	50/—
8	**218a**	**13c**	**207a**	1.0/3.5	80	30	100	89/—	Precipitation/crystallization	74/—
9	**218b**	**180c**	**217**	1.0/3.5	80	6	100	—/92	Chromatography	78(0/78)
10	**218c**	**180c**	**217**	1.0/3.5	80	6	100	—/92	Chromatography	93(6/93)
11	**219**	**180c**	**217**	1.0/3.5	80	6	100	—/90	Chromatography	77(0/77)
12	**220**	**180c**	**217**	1.0/3.5	80	12	87	20/59	Chromatography	n.a.
13	**222a**	**13c**	**195a**	1.0/4.0	70	24	91	90/1	Chromatography	75(75/0)
14	**222b**	**13c**	**195a**	1.0/4.0	70	24	90	90/1	Column chromatography	n.a.
15	**222c**	**13c**	**195a**	1.0/4.0	70	24	99	92/7	Column chromatography	n.a.
16	**222d**	**13c**	**195a**	1.0/4.0	70	24	71	67/4	Column chromatography	n.a.
17	**222e**	**13c**	**195a**	1.0/4.0	70	24	78	53/25	Column chromatography	n.a.
18	**222f**	**13c**	**195a**	1.0/4.0	70	24	71	41/30	Column chromatography	n.a.
19	**222g**	**13c**	**195a**	1.0/4.0	70	24	77	56/21	Column chromatography	n.a.
20	**222h**	**13c**	**195a**	1.0/4.0	70	24	91	56/35	Column chromatography	n.a.
21	**222i**	**13c**	**195a**	1.0/4.0	70	24	93	66/27	Column chromatography	n.a.

[a] For **222a–i** the catalyst $[Rh(cod)Cl]_2$ **221** was used. Only ligand is placed in the table.

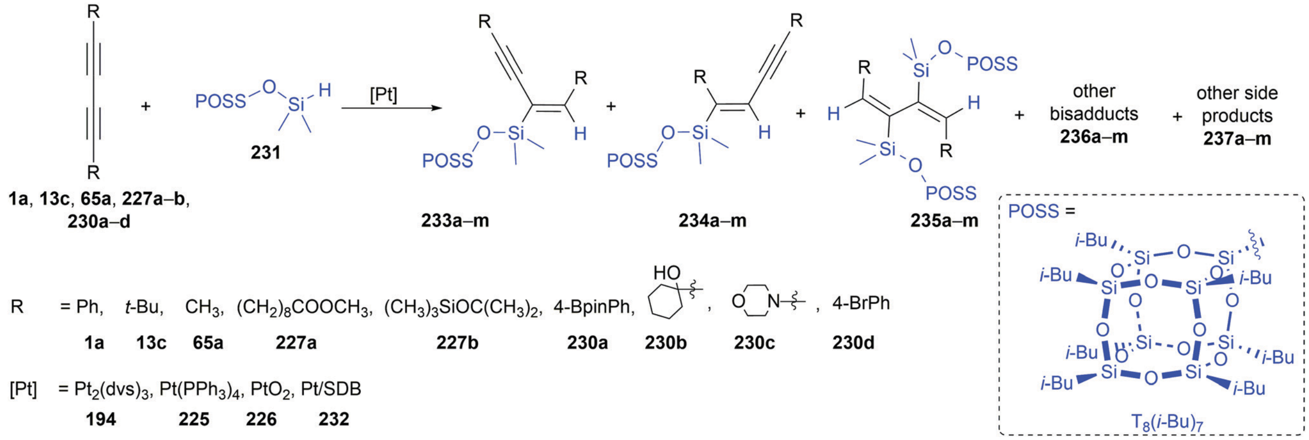
228h **228i**

Fig. 3 Crystal structures of **228h** and **228i** were obtained *via* monohydrosilylation of diynes **13c**, and **65a** with triphenylsilane **195e**.[73]

The same catalytic systems **194**, **225**, **226**, and heterogeneous Pt/SDB **232**, and the equimolar ratio of reagents were used in the hydrosilylation of 1,4-symmetrically substituted 1,3-diynes **1a**, **13c**, **65a**, **227a–b**, **230a–d** with 1-dimethylsiloxy-3,5,7,9,11,13,15-hepta-*iso*-butylpentacyclo-$[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}]$ octasiloxane ($(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$) **231** yielding silsesquioxane



Scheme 46 Hydrosilylation of conjugated 1,3-diynes **1a**, **13c**, **65a**, **227a–b** with triphenylsilane **195e** and triethylsilane **207a** in the presence of commercially available platinum catalysts **194**, **225**, and **226**.



Scheme 47 Hydrosilylation of 1,3-diynes **1a**, **13c**, **65a**, **227a–b**, and **230a–d** with silsesquioxane **231** using equimolar amounts of reagents and commercially available Pt-complexes.

products with several functionalities attached to the enyne **233a–m**, **234a–m**, or diene moieties **235a–m**, **236a–m**, *e.g.*, 4-boronic acid pinacol ester, 4-bromophenyl, hydroxyl groups, making them potentially useful nanobuilding blocks in polymerisation or Suzuki–Miyaura, Sonogashira, Heck, and Hiyama coupling reactions.[74] The process selectivity depended on the catalyst type and concentration, as well as the structure of the reagent. For hindered 1,3-diynes as **13c** or **227b**, only silsesquioxyl-substituted enynes **235** were formed (Scheme 47 and Table 5). Alkenylsilsesquioxanes have already been used in materials chemistry, in the synthesis of OLEDs, liquid crystals, or porous biocompatible materials. The attachment of silsesquioxanes as pendant groups to the conjugated molecular or macromolecular compounds is known to increase material brightness, color stability, and their solubility in organic solvents, or to improve the mechanical or thermal properties of the final products.[173–176] Similar systems were obtained by the use of incompletely condensed silsesquioxanes **238a–b.** In these cases,

Table 5 The optimised reaction conditions for the hydrosilylation of 1,3-diynes **1a**, **13c**, **65a**, **227a–b**, and **230a–d** with silsesquioxane **231**

Entry	Diyne	[Pt]	[**231**]:[diyne]:[Pt]	T [°C]	t [h]	Selectivity of **233/234/235/236/237**[a]
1	**1a**	**194**	$1:1:4\times10^{-4}$	100	24	**a**, 85/0/5/2/8
2	**1a**	**225**	$1:1:4\times10^{-2}$	40	24	**a**, 85/0/2/2/11
3	**1a**	**232**	$1:1:4\times10^{-2}$	100	24	**a**, 83/0/9/0/8
4	**13c**	**194**	$1:1:2\times10^{-4}$ $1:1:2\times10^{-3}$	100	24 2	**b**, 93/7/0/0/0 **b**, 93/7/0/0/0
5	**65a**	**194**	$1:1:4\times10^{-2}$	100	0.5	**c**, 76/24/0/0/0
6	**65a**	**194**	$1:1:4\times10^{-2}$	100	2	**c**, 86/5/9/0/0
7	**65a**	**194**	$1:1:4\times10^{-2}$	40	24	**c**, 83/17/0/0/0
8	**65a**	**194**	$2.3:1:2\times10^{-4}$	100	24	**d**, 0/0/91/9/0
9	**227a**	**194**	$2:1:2\times10^{-4}$	100	6	**e**, 17/0/83/0/0
10	**227b**	**194**	$1:1:4\times10^{-4}$	100	48	**f**, 100/0/0/0/0
11	**230a**	**194**	$1:1:4\times10^{-4}$	100	48	**g**, 95/0/5/0/0
12	**230a**	**194**	$2:1:4\times10^{-3}$	100	48	**h**, 0/0/69/0/31
13	**230b**	**194**	$1:1:4\times10^{-4}$	100	24	**i**, 91/9/0/0/0
14	**230b**	**194**	$2:1:2\times10^{-4}$	100	24	**j**, 0/12/88/0/0
15	**230c**	**194**	$2:1:2\times10^{-3}$	100	72	**k**, 0/0/87/13/0
16	**230d**	**194**	$1:1:4\times10^{-2}$	40	48	**l**, 73/0/5/3/19
17	**230d**	**194**	$2:1:2\times10^{-4}$	100	96	**m**, 6/0/80/0/14

[a] Conversion of diynes in all experiments was complete. Toluene was used as a solvent: $m_{\mathrm{S1}}/V_{\mathrm{tol.}}$ = 50 mg mL^{-1}.

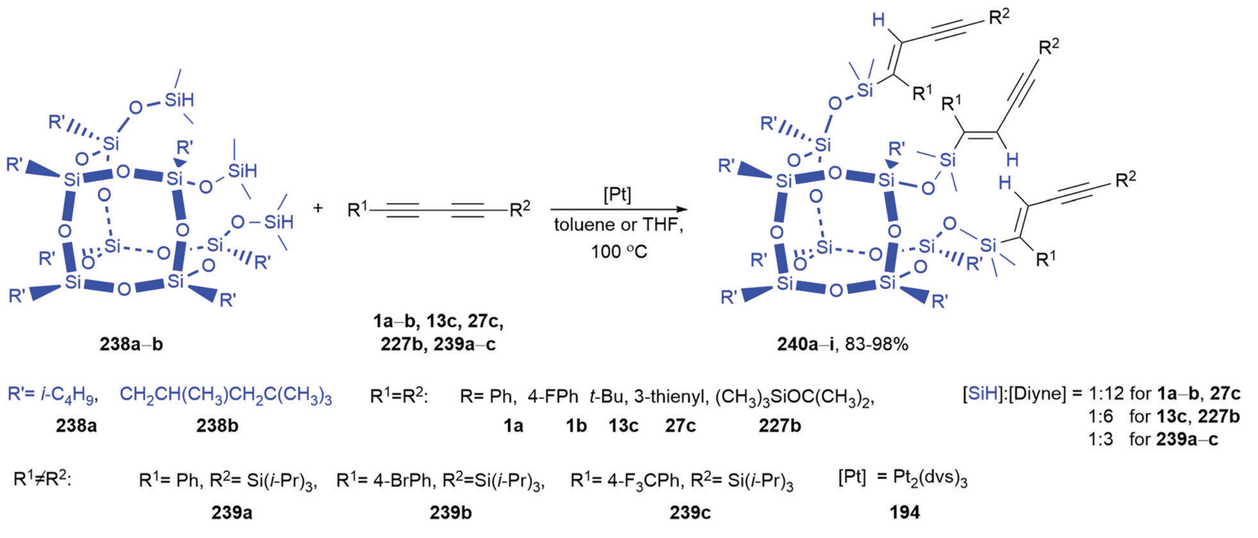
a stoichiometric amount of diyne was used for unsymmetrical diynes with Si(i-Pr)$_3$ groups **239a–c**. An excess of diyne (6–12 mol) compared to silsesquioxanes was necessary when symmetrically substituted diynes **1a–b**, **13c**, **27c**, and **227b** were tested. All the target products **240a–i** were formed with a very high selectivity of 99% (Scheme 48).[165]

The hydrosilylation of 1,4-bis(trimethylsilyl)buta-1,3-diyne **180c** with triethylsilane **207a** using RhCl(PPh$_3$)$_3$ **205**, H$_2$PtCl$_6$ **206**, Pt(PPh$_3$)$_4$ **225**, and Pd(PPh$_3$)$_4$ **35** was also described in 1984 by Hiyama *et al.*, but complex mixtures of bissilylated allenes and monosilyl-substituted enynes were obtained, regardless of the catalyst used.[177] Better selectivity was observed when silyl-substituted butenynes **241** in analogous reactions were used.[178]

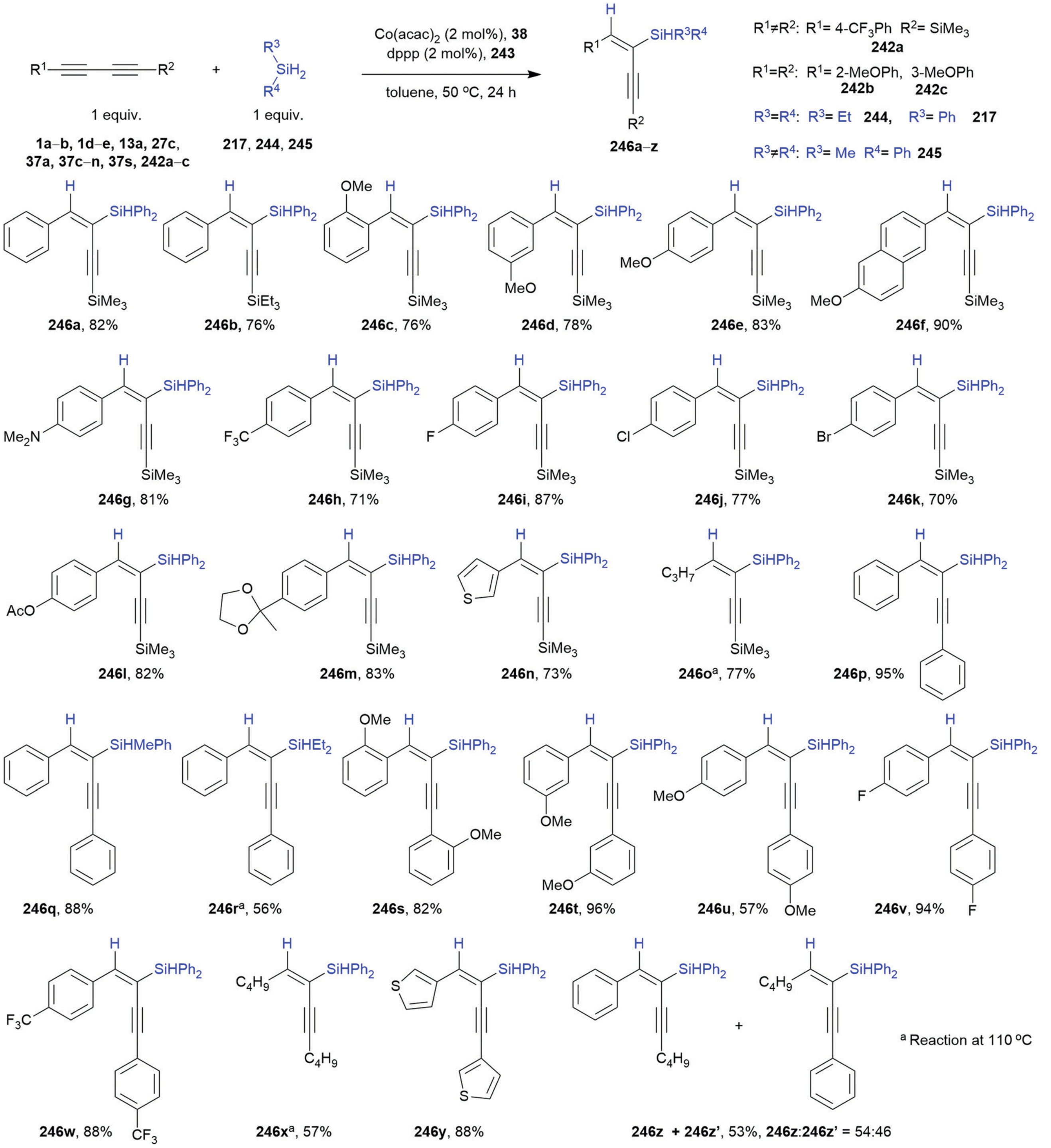
Recent work published by Ge *et al.* focused on the hydrosilylation of symmetrically or unsymmetrically substituted 1,3-diynes **1a–b**, **1d–e**, **13a**, **27c**, **37a**, **37c–n**, **37s**, and **242a–c** catalysed by inexpensive Co(acac)$_2$ complex **38** with xantphos **39a**, dppf **39b**, or dppp **243** ligands with dihydrosilanes (Scheme 49). The authors previously reported the effectiveness of this system in the hydrosilylation of alkynes.[179,180] Moreover, other Co-catalysed systems for terminal and internal alkynes hydrosilylation have been recently published.[181–185] Under the optimised conditions of 2 mol% of Co(acac)$_2$ **38**, 2 mol% of dppp **243**, 50 °C, toluene, after 24 h, several silylated enynes **246a–z** were obtained with high yields and selectivity as confirmed by GC-MS and NMR analyses. The electronic effects of substituents attached to the aryl ring were not noticeable, and the catalyst was tolerant towards many functional groups. Mainly diphenylsilane **217**, but also diethylsilane **244** and methylphenylsilane **245** were used as silylating agents.[156]

The authors proposed the mechanism of this transformation, which started from the generation of Co-hydride complex **247** in the reaction with H$_2$SiPh$_2$ **217**, in the presence of dppp **243**. The insertion of 1,3-diyne **37** or **242** into the Co–H bond generated the vinylcobalt intermediate **248**, which directly reacted with dihydrosilane **217** with the elimination of the desired product – (*E*)-1-en-3-yn-2-ylsilane **246** and regeneration of initial catalyst **247** (Scheme 50).[156] The utility of silyl-substituted 1,3-enynes **246e** and **246p** as building blocks in organic synthesis was presented in the desilylation reaction by oxidation to ketone **250** and silanols (**251**, **253**), protodesilylation to enynes **249**, and Hiyama and Sonogashira coupling reactions (Scheme 51) furnishing products **252** and **255** respectively.[156]

Another example of Co-catalysed hydrosilylation of 1,3-diynes (symmetrical and one nonsymmetrical reagent) was recently reported by Chen *et al.*[163] Cobalt tridentate complexes N$^{\mathrm{C}}$NN–CoX$_2$ were previously reported as effective systems for hydrosilylation of alkynes.[186] The catalyst obtained from CoBr$_2$

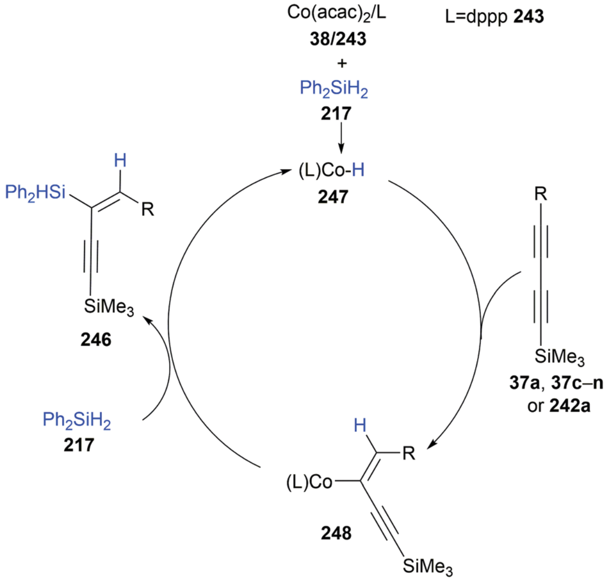


Scheme 48 Hydrosilylation of 1,3-diynes **1a–b**, **13c**, **27c**, **227b**, and **239a–c** with silsesquioxanes **238a–b** catalysed by Karstedt's catalyst **194**.



Scheme 49 Co-Catalysed selective hydrosilylation of conjugated symmetrical and nonsymmetrical diynes **1a–b**, **1d–e**, **13a**, **27c**, **37a**, **37c–n**, **37s**, and **242a–c** with dihydrosilanes **217**, **244**, and **245**.

256 and tridentate ligand **257** transpired to be highly active in the hydrosilylation of various 1,3-diynes **1a–e**, **27b–c**, **37t**, **208a**, **208c**, **230d**, **242b–c**, and **258a–q** with electron-donating and electron-withdrawing groups (Scheme 52). Several ligands were tested, but the best results were obtained when **257** was used. The high conversion of diynes was obtained within 5 minutes at room temperature. A longer reaction time was required for fluoro, chloro, bromo, trifluoromethyl, and cyano electron-withdrawing groups to obtain satisfying yields of **260a–ad**. The alkenyl-substituted diyne reacted in the hydrosilylation process under the applied conditions without addition to the C=C bond. Excellent regioselectivity was observed in the hydrosilylation of an unsymmetrical diyne. The mechanism of this transformation started from the formation of active



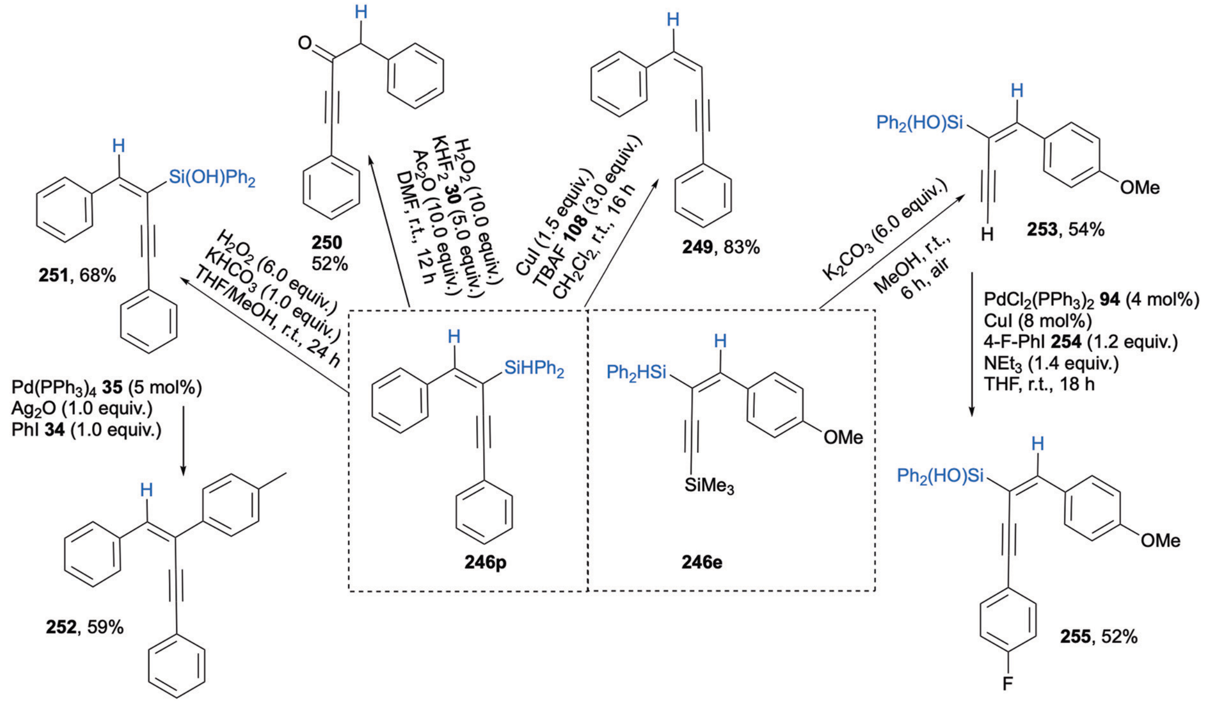
Scheme 50 Proposed catalytic cycle for the hydrosilylation of 1,3-diynes with dihydrosilanes in the presence of Co-catalyst formed *in situ* from Co(acac)$_2$ **38** and dppp **243**.

complex **261** in the reaction with NaHBEt$_3$ **259** and Ph$_2$SiH$_2$ **217** followed by the coordination of 1,3-diyne **1a–e**, **27b–c**, **37t**, **208a**, **208c**, **230d**, **242b–c**, **258a–q** to form intermediate **262**. The 1,3-diyne inserts to the Co–Si bond yielding the vinylcobalt species **263**. The reaction with the second molecule of Ph$_2$SiH$_2$ **217** causes the catalyst **261** regeneration and evolution of the silylated enyne product **260a–ad** (Scheme 53).

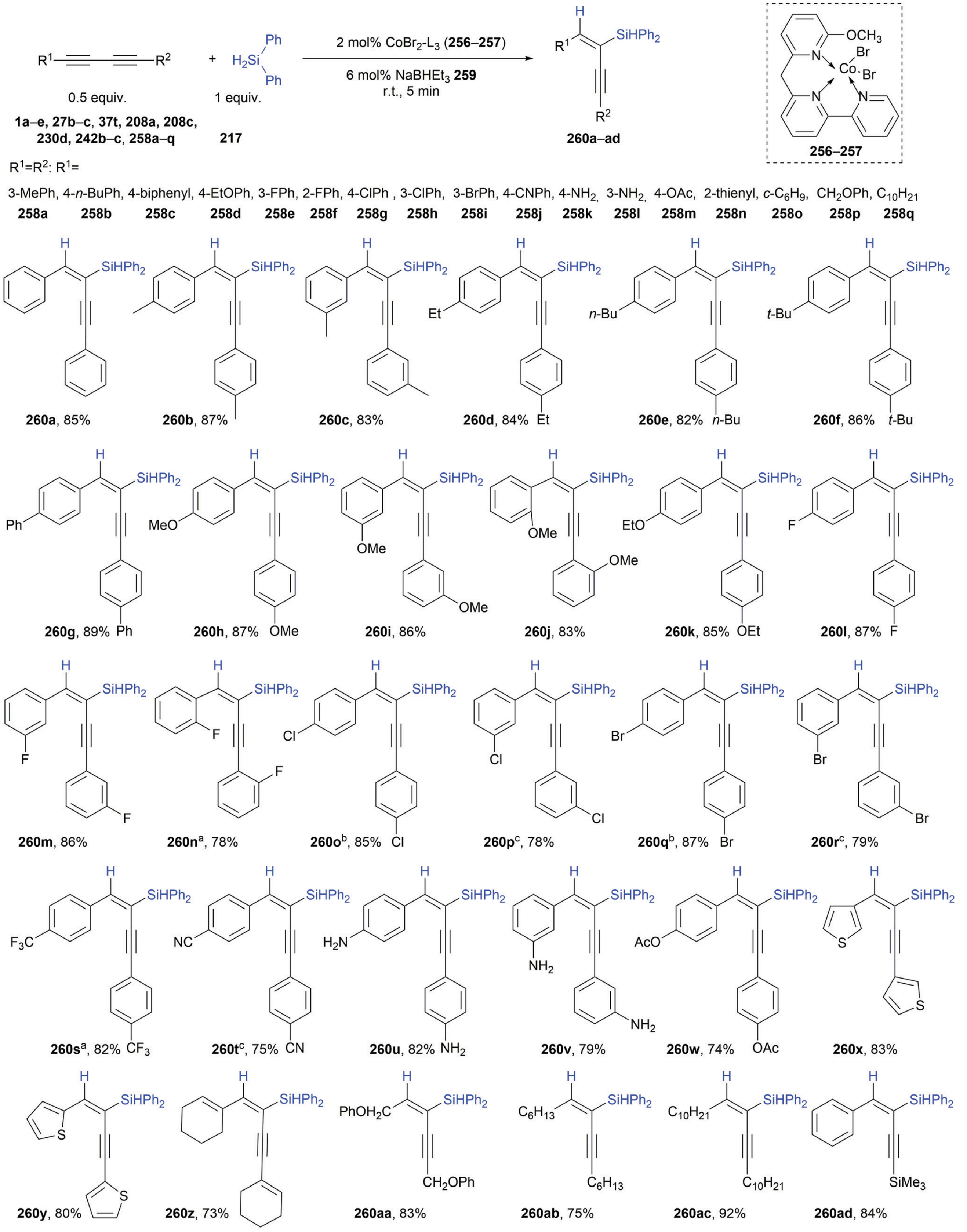
The enyne **260a** was desilylated according to the procedure described by Ge,[156] and then hydrosilylated again with diphenylsilane **217** to silylated 1,3-diene **264**. Two regioisomers with silyl groups attached to the internal and external C bond were formed in the ratio 15 : 85 with a high yield of 95%. The double bond in enyne was unreactive under the applied reaction conditions.[163]

Chen *et al.* tested several cobalt complexes in hydrosilylation of 1,3-diynes **1a–e**, **27b–c**, **37t**, **208a**, **208c**, **230d**, **242b–c**, **258a–i**, **258k–q**, **265a–c** (Scheme 54). Among tested catalytic systems synthesised from the commercially available materials, CoCl$_2$-dppp (1 mol%, **266**) exhibited the best regio- and stereoselectivity (in the presence of 3 mol% NaHBEt$_3$ **259**). A variety of (*E*)-2-silyl-1,3-enynes **268a–ah** were obtained in high yields through monohydrosilylation at the internal carbon of the 1,3-diyne unit *via syn*-addition. Good functional (alkoxy, amine, halides, esters, heterocyclics) tolerance was achieved by testing more than thirty substrates. A mechanism of 1,3-diyne hydrosilylation was proposed (Scheme 55) in which CoCl$_2$-dppp **266** initially reacts with NaHBEt$_3$ **259** to afford the low-valent cobalt(I) hydride intermediate **269**. Subsequently, the coordination of 1,3-diyne with **269** is followed by the migratory insertion of one of the alkynyl groups into the Co–H bond and forms the intermediate **270**. In the end, Ph$_2$SiH$_2$ **217** reacts with **270** and as a result, the alkenylsilanes (**268a–ah**) are obtained, accompanied by the regeneration of **269**.[187]

Zhan *et al.* studied the hydrosilylation of 1,3-diynes catalysed by Ni(acac)$_2$ **273** with a series of organophosphine ligands screened in THF at room temperature. First, the use of xantphos **39a** as the ligand showed moderate regioselectivity and

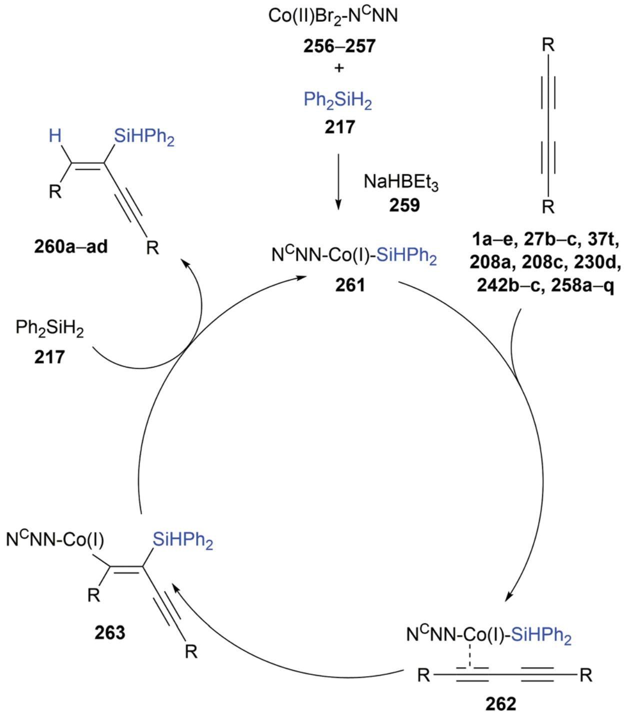


Scheme 51 Applications of silyl-functionalised enynes **246e** and **246p** as building blocks.



Reaction time: [a] 15 min; [b] 1 h; [c] 3 h.

Scheme 52 Monohydrosilylation of conjugated 1,3-diynes **1a–e**, **27b–c**, **37t**, **208a**, **208c**, **230d**, **242b–c**, **258a–q** with diphenylsilane **217** catalysed by a $CoBr_2$ **256**/N^{C}NN-tridentate ligand **257** system.



Scheme 53 Proposed mechanism of the hydrosilylation of 1,3-diynes with Co-catalyst with tridentate N^{C}NN-ligand **256–257**.

yield. Several other commercially available phosphorus ligands were examined, however, the results were less than satisfactory. Therefore, from vinyl-functionalised xantphos monomer, through solvothermal polymerisation, POL–xantphos **274** was obtained and employed as a heterogeneous ligand for nickel catalysed 1,3-diyne hydrosilylation. Unsymmetrical and symmetrical 1,3-diynes **1a**, **1e**, **37f**, **37h**, **180a**, **239a**, and **271a–b** were reacted with silanes **217**, **245**, **272** yielding the corresponding silyl-functionalised 1,3-enynes **275a–x** (Scheme 56). The authors claimed that, due to the microporous structure of immobilised system Ni(acac)$_2$/POL–xantphos **273**/**274**, the selectivity of the process increased compared to the system based on the monomeric xantphos ligand. Based on the experimental results a hydrometalation pathway with a Ni(0) intermediate for this Ni-catalysed hydrosilylation of 1,3-diynes was proposed (Scheme 57). In the mechanism, the nickel precursor is reduced *in situ* by phenylsilane **272** to form Ni(0) **276**, and then oxidative addition of the silane generates **277**. Reaction with the 1,3-diyne generates **278** which then leads to the alkenyl nickel intermediate **279** after the insertion of the alkyne into the Ni–Si bond. The final product **275a–x** is obtained by C–H reductive elimination with the return of the Ni(0) active species **276** into the catalytic cycle. The recyclability of the catalytic system based on Ni(acac)$_2$/POL–xantphos **273**/**274** was examined for the hydrosilylation of 1,4-diphenylbuta-1,3-diyne **1a** and PhSiH$_3$ **272**. After five runs, the Ni/POL–xantphos **273**/**274** reacted with nearly no loss of activity and selectivity demonstrating the good reusability of this catalytic system.[188]

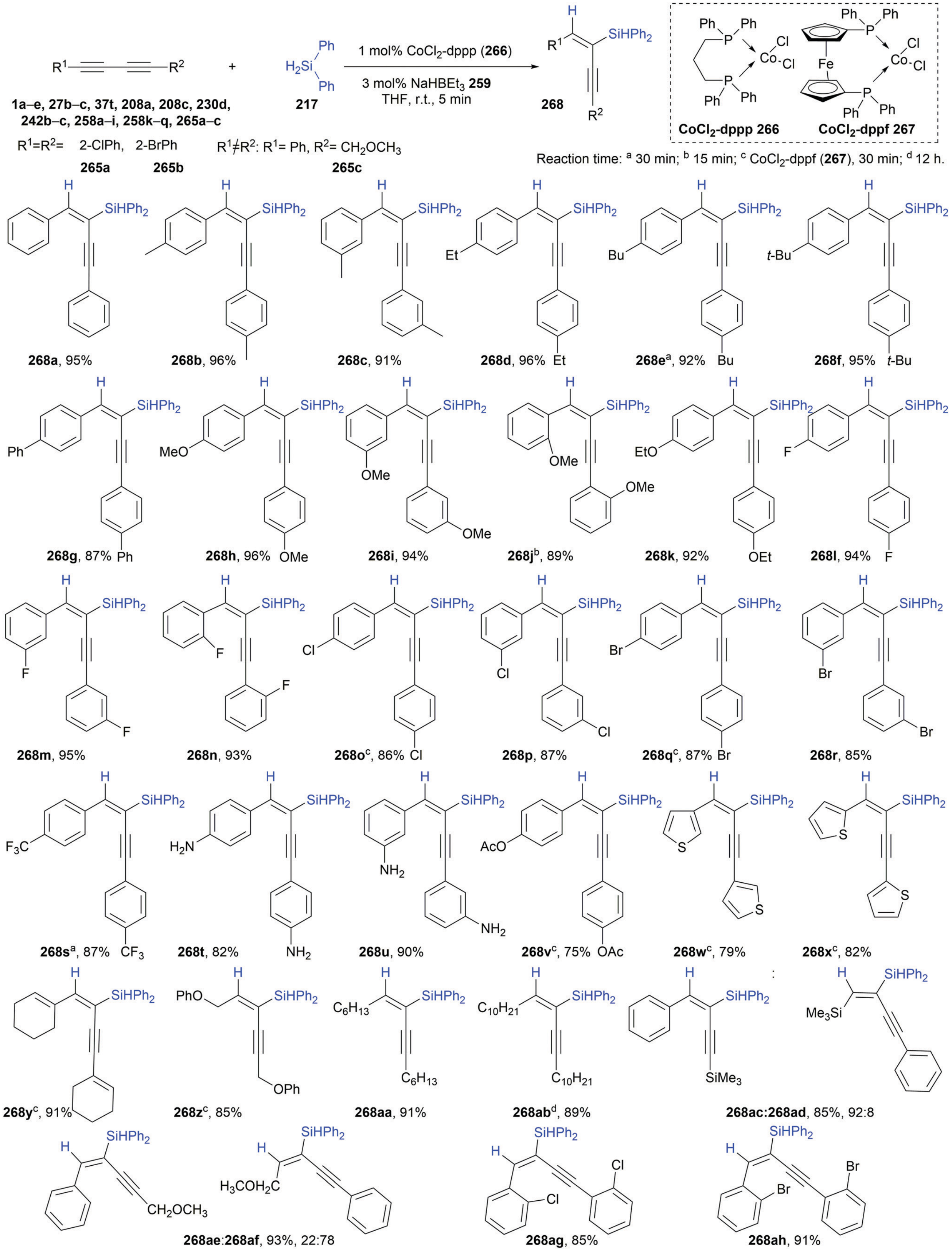
When the hydrosilylation occurs as a *trans*-addition, cyclic siloles **283** and **284** are formed. The reaction proceeded in the presence of 20 mol% of [Cp*Ru(MeCN)$_3$]PF$_6$ **281**, which was described as an effective *trans*-hydrosilylation catalyst of alkynes.[189] The symmetrical and nonsymmetrical 1,4-disubstituted-buta-1,3-diynes **1b–d**, **27c**, **60e**, **258i**, **258o**, and **280a–f** reacted with 9-silafluorene **282** or diphenylsilane **217** to the corresponding 2,5-diarylsiloles **283** and **284** with moderate to good yields. It was found that electron-donating groups attached to the aryl ring facilitated the process, while electron-withdrawing functions, *e.g.*, acetyl group **280b**, rendered the process more sluggish (Scheme 58).

The process occurred stepwise. After the first *trans*-hydrosilylation, the intramolecular second *trans*-addition proceeds. The obtained siloles were characterised by high fluorescence maxima.[190] The same catalytic system ([Cp*Ru(MeCN)$_3$]PF$_6$ **281**) was used by Trost *et al.* in the hydrosilylation of diynols which was one of the stages in the total synthesis of biologically important natural products.[191] In this study, diynols **285** and **289** were reacted with dimethylethoxysilane **286** and benzyldimethylsilane **290**, respectively. It was observed that the partial reduction of C≡C to *trans* C=C led to the enynols **287** and **291**, and is directed by the propargyl alcohol fragments of the diynols (Scheme 59).[191]

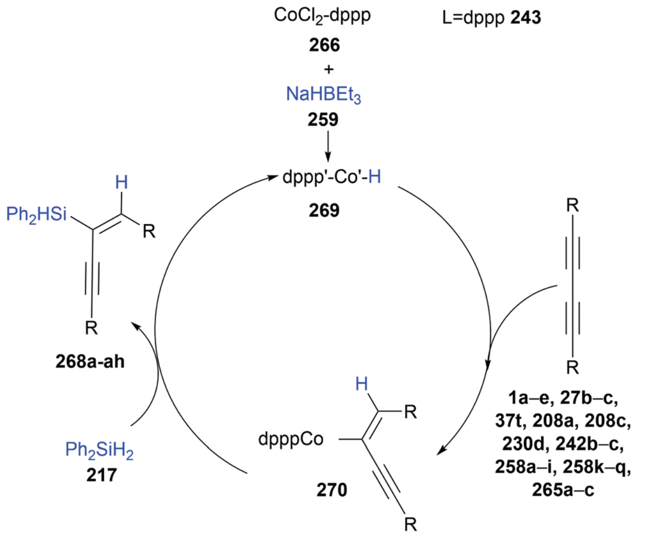
5.2. Hydrosilylation of separated diynes – synthesis of molecular unsaturated linear compounds

Selective hydrosilylation of α,ω-diynes with CH$_2$OCH$_2$ **127p**, C$_4$H$_8$ **160**, and CH$_2$NHCH$_2$ **293** spacers were successfully carried out using the [Pt(IPr*OMe)(dvs)] **294** catalyst with bulky NHC ligand (where IPr*OMe = 1,3-bisimidazol-2-ylidene) and dimethylphenylsilane **195a** under the typical anti-Markownikow manner. The hydrosilylation of the C≡C bonds leads to (*E*)-products, while the formation of monosilylated enyne **295** or bissilylated diene **296** can be distinguished with different reagents stoichiometry: diyne : silane = 1 : 1 or 1 : 2. The exclusive formation of silylated enyne was furnished for diyne **160**, while in the case of diynes with heteroatoms **127p** and **293** a small amount (up to 4%) of bissilylated diene **296** was observed when equimolar reagents ratio were used. Bishydrosilylation was carried out quantitatively for **127p** and **293**, while for octa-1,7-diyne **160** a complex reaction mixture consisting of (β-*E*)/(β-*Z*)/α isomers in 77 : 20 : 3 ratio were formed (Scheme 60).[192] The single example of hydrosilylation of deca-1,9-diyne **116b** with diphenylsilane **217** was also carried out by Leitner *et al.*, who used ruthenium pincer complex [Ru(*t*-BuPNP)(H$_2$)(H)$_2$] **117** [*t*-BuPNP = 2,6-bis(di(*tert*-butyl)phosphinomethyl)pyridine], which was also active in the addition of B–H bonds to alkynes and diynes.[136] The bissilylate diene **297** (*E*) : (*Z*) = 91 : 9 was obtained using an equimolar ratio of the neat reagents and 0.2 mol% of Ru **117** within 16 h at 50 °C. No dehydrogenative coupling reaction occurred, which was visible in the case of sterically hindered terminal alkynes (Scheme 61).[193]

The thermal hydrosilylation of α,ω-diynes was also used for the modification of silica surface Si(100) **298** used in the preparation of monolayers for electrodes in the reaction of diynes (*e.g.*, nona-1,8-diyne **164a**) with silica enriched with the Si–H bonds **299**. The products **300** were next modified in



Scheme 54 Monohydrosilylation of conjugated 1,3-diynes **1a–e**, **27b–c**, **37t**, **208a**, **208c**, **230d**, **242b–c**, **258a–i**, **258k–q**, and **265a–c** with diphenylsilane **217** catalysed by $CoCl_2$-dppp **266** or $CoCl_2$-dppf **267**.

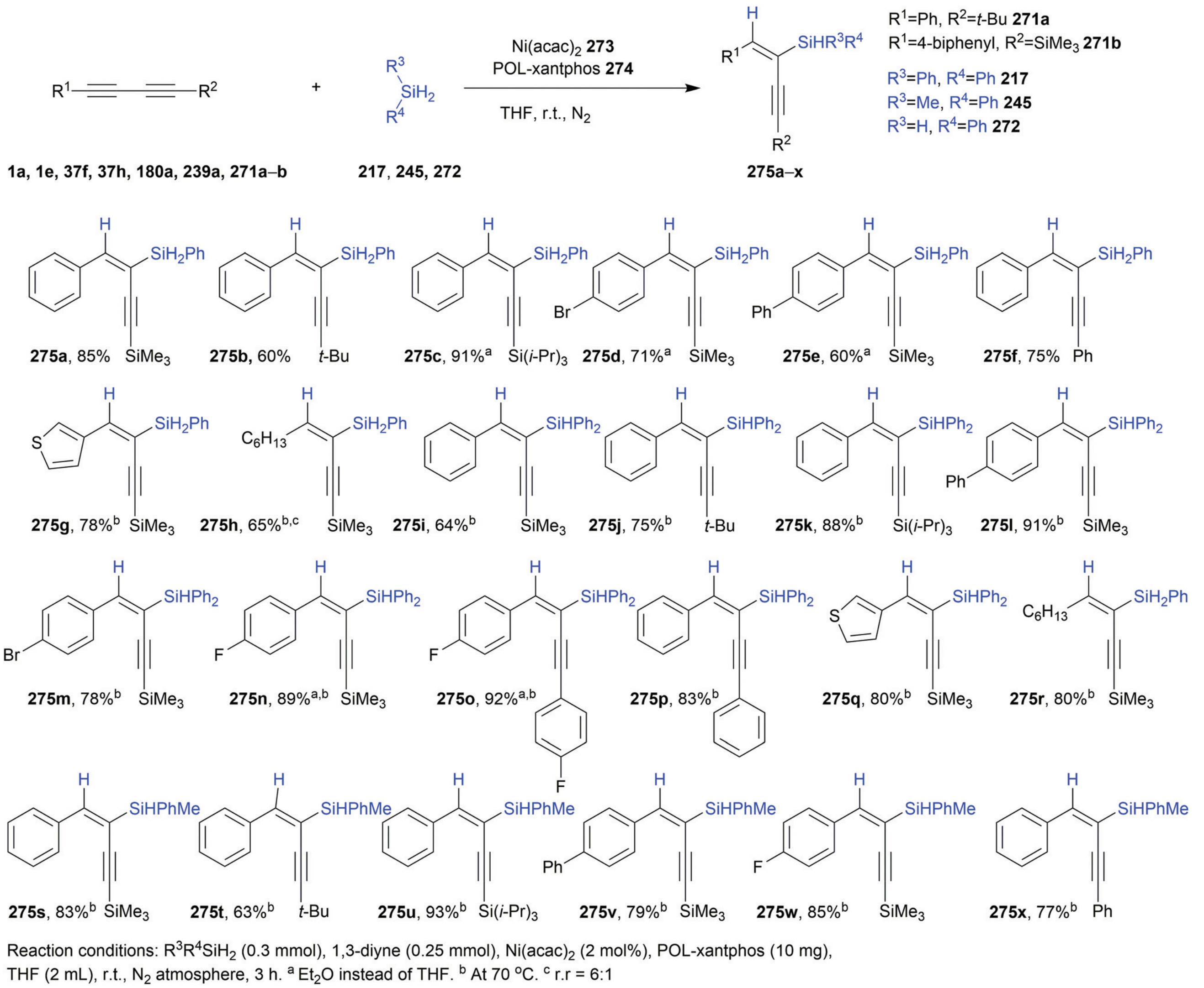


Scheme 55 Proposed mechanism of the hydrosilylation of 1,3-diynes with Co-dppp **266**.

"click" chemistry with azides **301a–d** by Husigen-type cycloaddition (Scheme 62).[194–197]

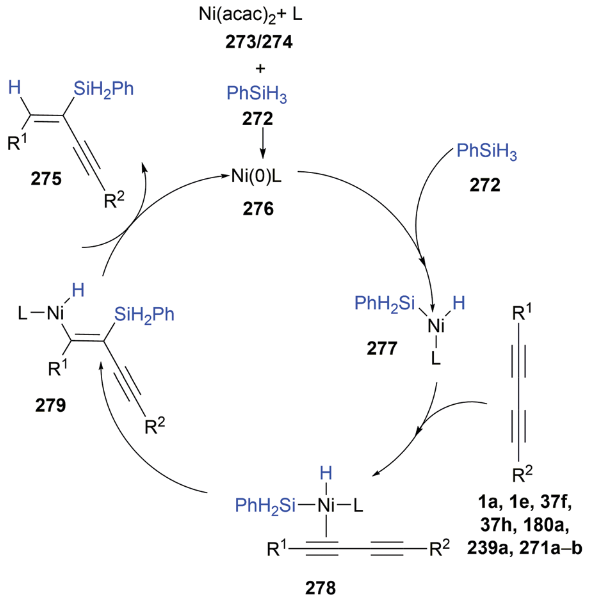
A broad range of diyne and triyne π-electron bridges arenes **116c**, **304a–f** (aryl cores = phenyl, azulene, fluorene, carbazole, 9,9′-spirobi[fluorene], 1,1′-binaphtalene) were hydrosilylated with chlorodimethylsilane **305** in the presence of Karstedt's catalyst **194** in a *syn*-addition manner towards (*E*)-silylated products **306** with high yields and selectivities. The reactions occurred with the best yield in Et_2O, at room temperature for 6–12 h with 3 mol% of a Pt-catalyst **194** (Scheme 63). The influence of the solvent on reagents conversion was visible and when THF or toluene was used a much lower conversion was observed. Good results were also obtained for the hydrosilylation of 1,3,5-triethynyllbenezene **304a** with H_2PtCl_6 **206** and Pt/C **307** in toluene. The rhodium catalysts on the other hand were less active.

The product **306a** possessing halogen attached to silicon atom was further functionalised by a substitution reaction with lithiated chromophores **312, 314,** or $LiAlH_4$ **308** in stoichiometric



Reaction conditions: $R^3R^4SiH_2$ (0.3 mmol), 1,3-diyne (0.25 mmol), $Ni(acac)_2$ (2 mol%), POL-xantphos (10 mg), THF (2 mL), r.t., N_2 atmosphere, 3 h. ^{a} Et_2O instead of THF. ^{b} At 70 °C. ^{c} r.r = 6:1

Scheme 56 Monohydrosilylation of conjugated 1,3-diynes **1a**, **1e**, **37f**, **37h**, **180a**, **239a** and **271a–b** with $Ni(acac)_2$ **273** immobilised on POL–xantphos **274**.



Scheme 57 Proposed mechanism of the hydrosilylation of 1,3-diynes with Ni(acac)$_2$/POL–xantphos **273/274**.

reactions, followed by the subsequent hydrosilylation reaction with 4-ethynylbenzonitrile **310**.[198] The presence of the SiMe$_2$ bridge between chromophores facilitates intramolecular photo-induced charge transfer process and interrupts the π-conjugated chains (Scheme 64).[199–201]

5.3. Hydrosilylation of separated diynes – synthesis of conjugated polymers

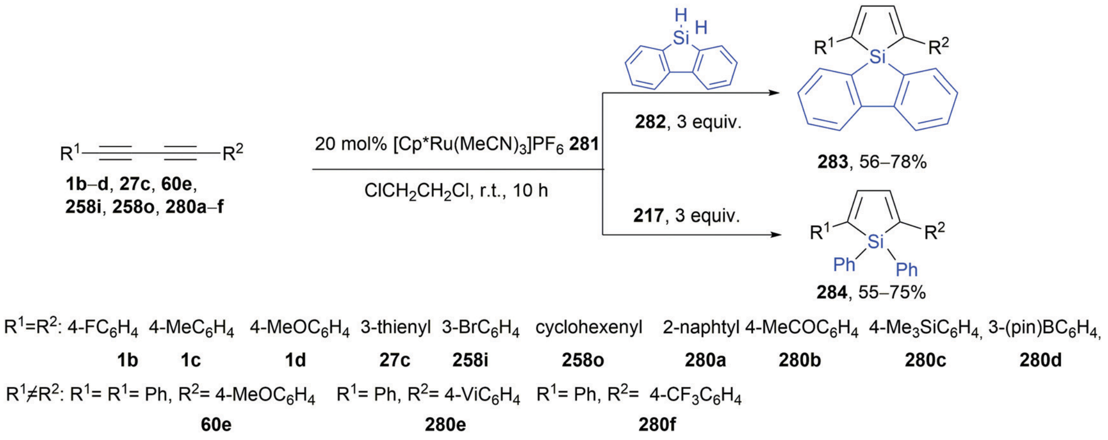
In 2008, Trogler and Sanchez published a review regarding the synthesis and application of functionalised polymers delocalised through silicon, which can be obtained by a hydrosilylation reactions of diynes. The authors discussed the properties and applications of such polymers in detail, therefore within this review we focus only on the synthetic aspects in the formation of such macromolecular compounds.[68]

Luh *et al.* reported the RhCl(PPh$_3$)$_3$ **205** catalysed hydrosilylation of 1,4-diethynylarenes **116c**, **164k**, and **316a–d** with disilanes **317a–b** obtained in the NiCl$_2$(PPh$_3$)$_2$ **319** catalysed reaction of dithiolano-substituted arenes **320** with Me$_2$(*i*-PrO)SiCH$_2$MgCl **321**, followed by the reduction of alkoxy group with LiAlH$_4$ **308**. The process was carried out with 0.5 mol% RhCl(PPh$_3$)$_3$ **205** with an equimolar ratio of reagents. The molecular weight of the obtained polymers was a function of reagents concentration and reaction time. Increasing both parameters led to a higher molecular weight of **318** being obtained (Scheme 65).[202,203]

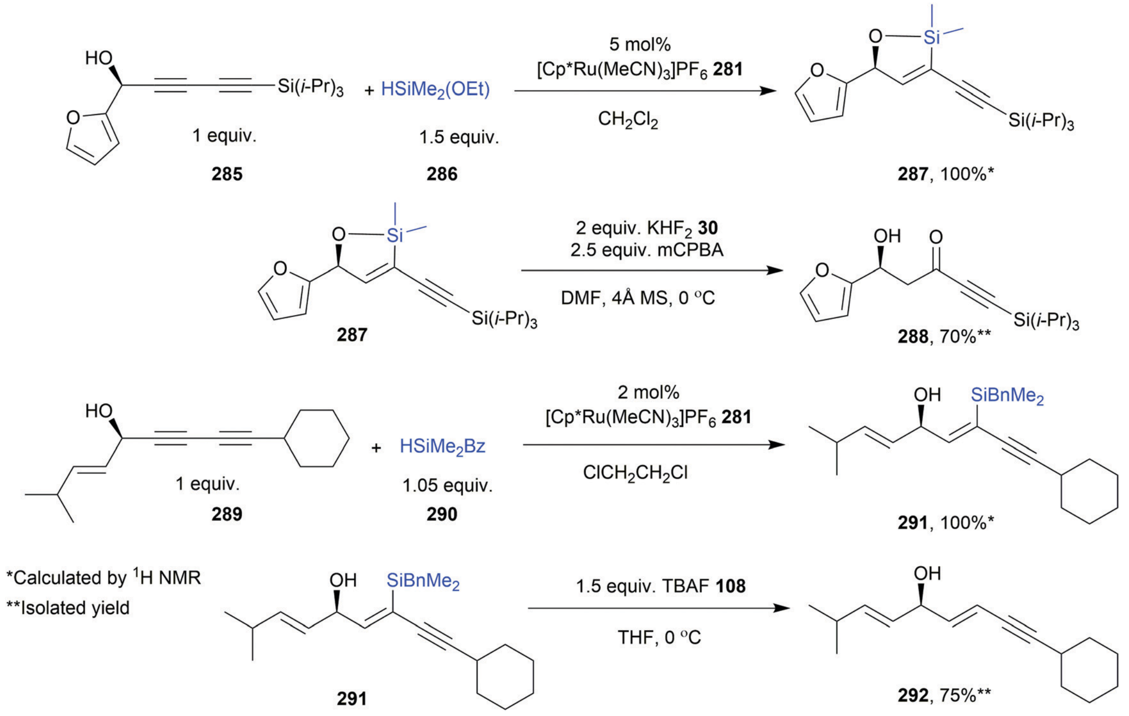
The synthesis of poly(silyl-vinylenes) was also carried out in the presence of Pt-catalysts, in particular Speier's catalyst H$_2$PtCl$_6$ **206**, with the predominant formation of polymer **322** with (*E*)-β-regioselectivity, sometimes in addition to α-silylated mers in residual amounts. The formation of both isomers was due to the steric freedom of the monomers, which did not possess any bulky substituents responsible for preventing α-silylation. The products were obtained with low M_w (Schemes 66, 67 and Table 6).[204–206]

Platinum-based Karstedt's catalyst **194** was used in the polymerisation of aromatic diynes **327a–d** with two different types of silsesquioxanes: octakis(hydrodosilsesqioxane) T^{H}_{8} **328**[207] and double-decker-shaped silsesquioxane (DDSQ) with two hydrido functions **329**.[208] Hydrosilylation with T^{H}_{8} **328** was carried out with the use of 2.1–2.4 mol% of **194**. The total consumption of reagents was observed in 2 h, but the reaction mixture was homogeneous even after 24 h, with the M_w ranging from 10 000 to 34 000, depending on the diyne **327a–d** used. The polymerisation was carried out in an equimolar ratio of the reagents, at room temperature. When the diyne **327** : T^{H}_{8} **328** ratio was increased to 1 : 1.55, the M_w of polymer **330a–e** increased to 87 000, but crosslinking with T^{H}_{8} **328** was observed. ^{1}H NMR spectra did not detect CH–sp^3 bonds in the post-reaction mixture, which indicated that the C≡C bonds are much more reactive than the C=C bonds (Scheme 68 and Table 7).[207]

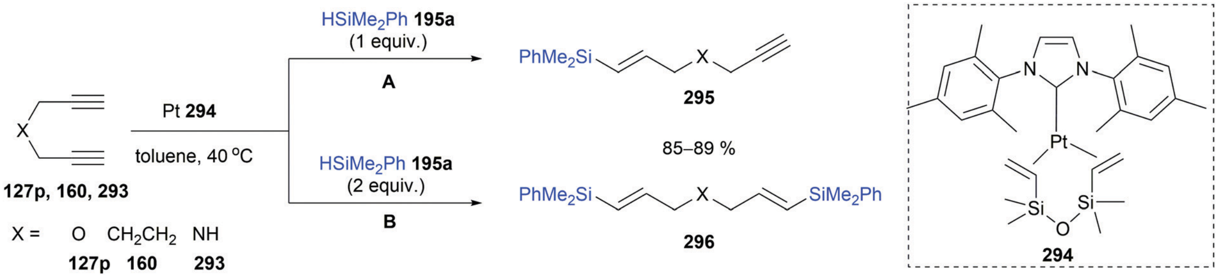
The same conclusions were obtained for the polymerisation with DDSQ **329**. The linear polymers **331a–d** were obtained for



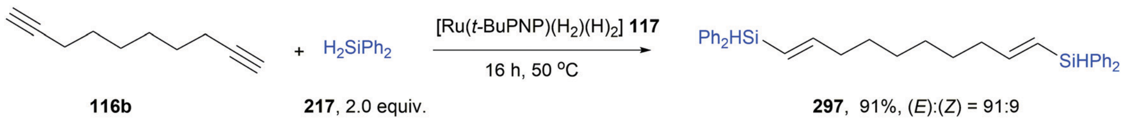
Scheme 58 Double trans-hydrosilylation of 1,4-diarylbuta-1,3-diynes leading to 2,5-diarylsiloles **283–284** catalysed by Ru complex **281**.



Scheme 59 Hydrosilylation of diynols **285** and **289** by silanes **286** and **290**, in the presence of $[Cp^*Ru(MeCN)_3]PF_6$ **281**.



Scheme 60 Hydrosilylation of 1,3-diynes with dimethylphenylsilane **195a** using a Pt catalyst **294** and an equimolar ratio of reagents.

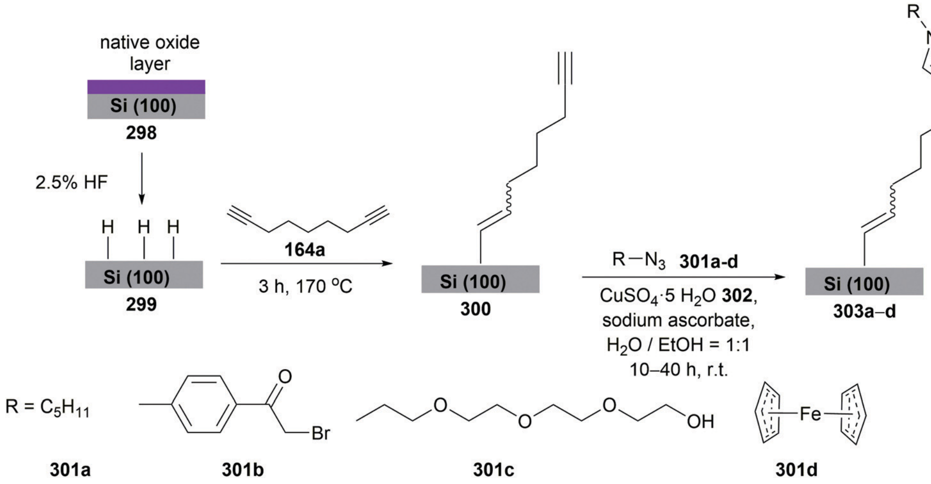


Scheme 61 Hydrosilylation of deca-1,9-diyne **116b** with diphenylsilane **217** in the presence of Pincer type complex **117**.

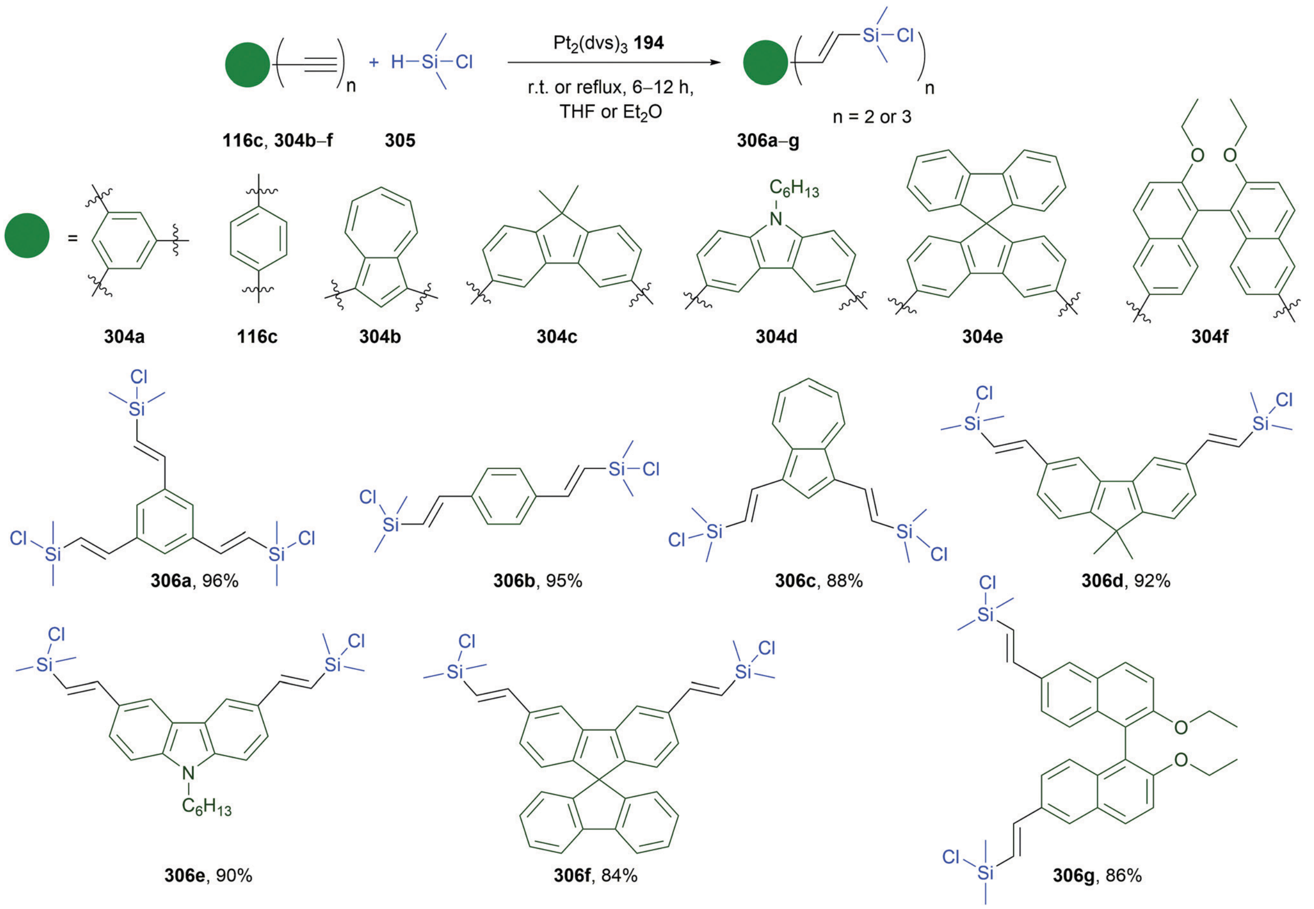
internal diynes **327** (yield 90–97%, M_n = 11 900–29 100, M_w/M_n = 2.9–4.9) after 24 h at 100 °C with 0.2 mol% of Karstedt's catalyst **194**. When 1,4-diethynylbenzene **116c** was used as a monomer, the insoluble polymer was achieved within 30 minutes, due to the subsequent crosslinking reaction of the less shielded vinyl bonds (Scheme 69 and Table 8).[208]

The same group synthesised polymer **333** by the hydrosilylation of (1,4-bis(4-(tetrahydroxypyranyloxy)phenyl)ethenyl)benzene **332** with dihydrido-DDSQ **329** used in equal amounts with $Pt_2(dvs)_3$ **194** as the catalyst. The reaction was carried out in toluene, at 100 °C for 7 h. The THP groups in **333** were further hydrolysed to give **334**, and the polymer with 10 wt% MBHP **335** and 1.5 wt% PTMA **336** was applied as a chemically amplified negative-working photoresist system **337** (Scheme 70).[209] Incorporation of silsesquioxane into the polymer chain or as a pendant group enhances many properties of the final materials: mechanical, thermal, fire or oxygen resistance.[173,176]

$Pd_2(dba)_3$ **338**/PCy_3 was also used as an effective catalyst in the polymerisation of diethynylarenes with dihydrosilanes.[210–212] Yamashita *et al.* used 0.1 mol% $Pd_2(dba)_3$ **338**/0.2 mol% PCy_3 and

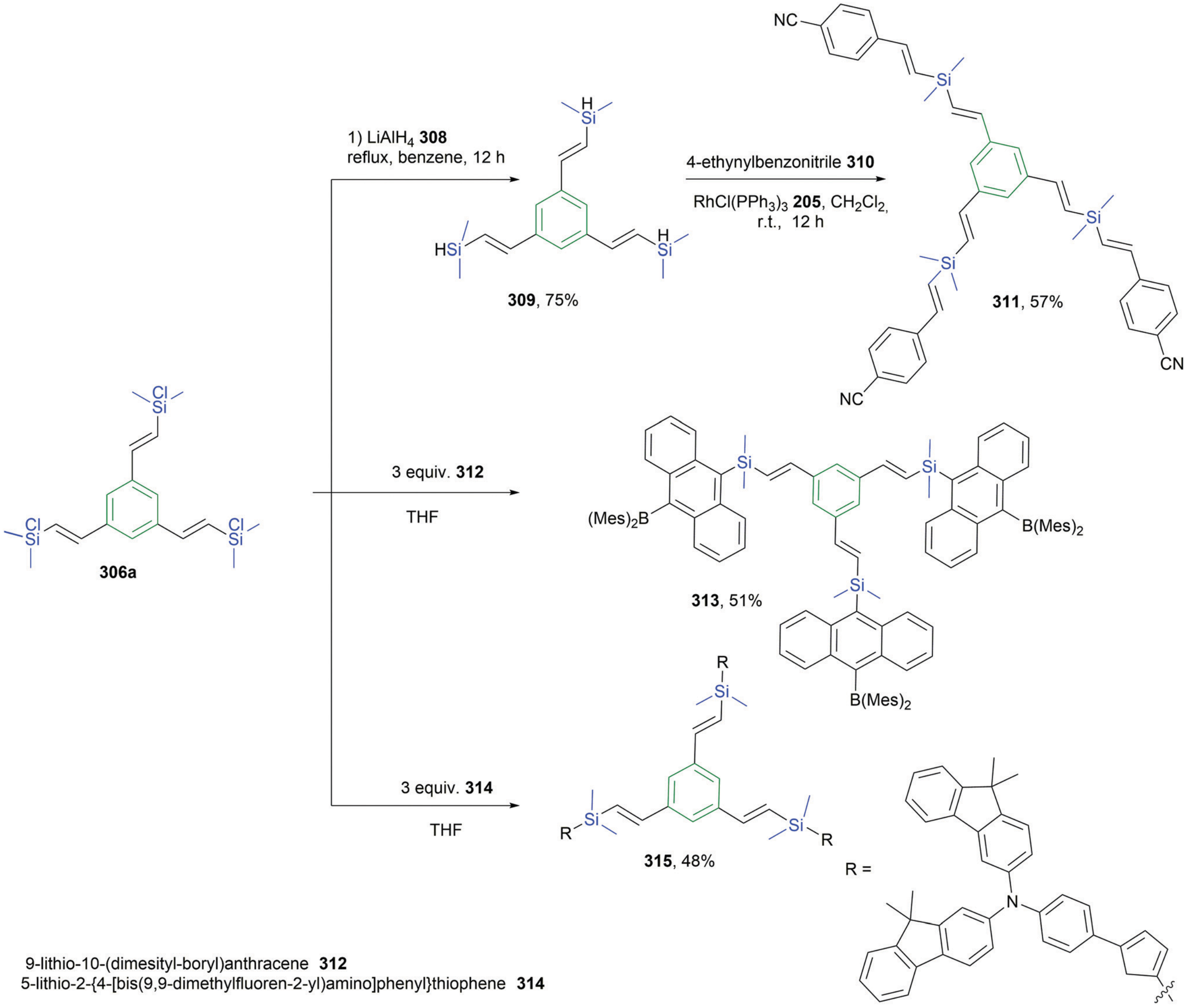


Scheme 62 Modification of Si-layer in hydrosilylation reaction with diynes and Husigen-type cycloaddition.

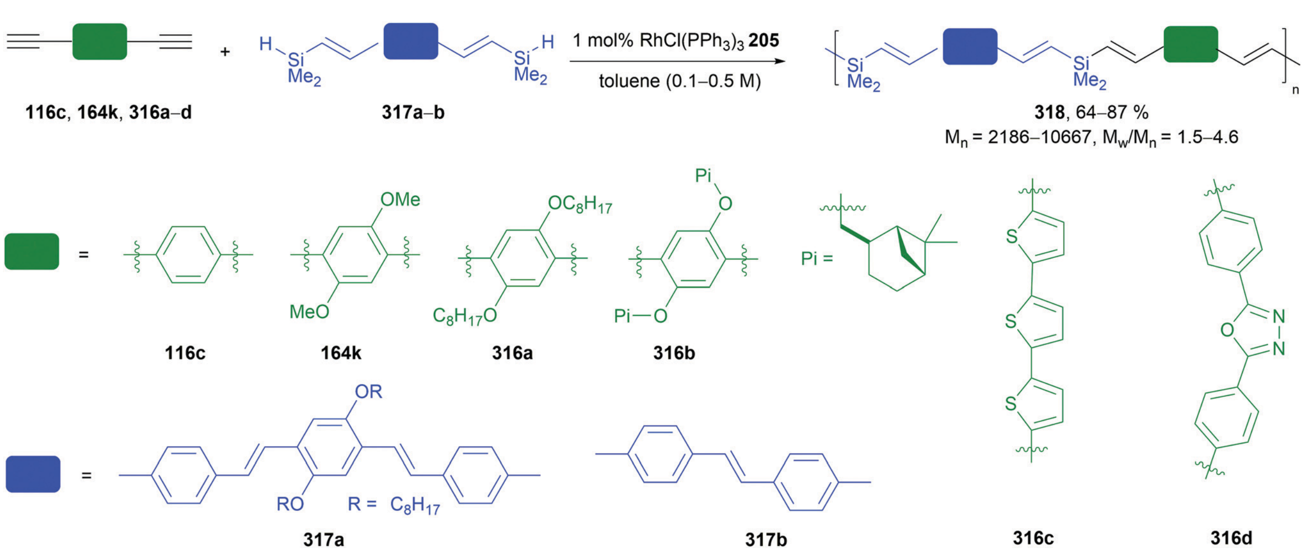


Scheme 63 Hydrosilylation of 1,*n*-diynes **116c**, **304b–f** and 1,3,5-triethynylbenzene **304a**, with chlorodimethylsilane **305** in the presence of Karstedt's catalyst **194**.

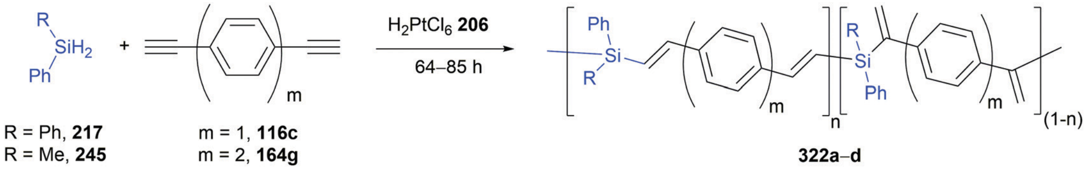
an equimolar ratio of silane (Ph_2SiH_2 **217**, $MePhSiH_2$ **245** and $Ph(H_2C{=}CH)SiH_2$ **339**) in the hydrosilylation of *p*-diethylnybenzene **116c** and *m*-diethynylbenzene **324** at 70–110 °C for 0.5–9 h yielding polymers **340a–f** with 84–91% yield and M_w = 12 000 to 49 000. The reaction occurred mostly through the *syn*-addition with the silyl group attached to β-carbon atom, but some other possible isomers (β,α) and (α,α) were also presented in the reaction mixture what was distinguished



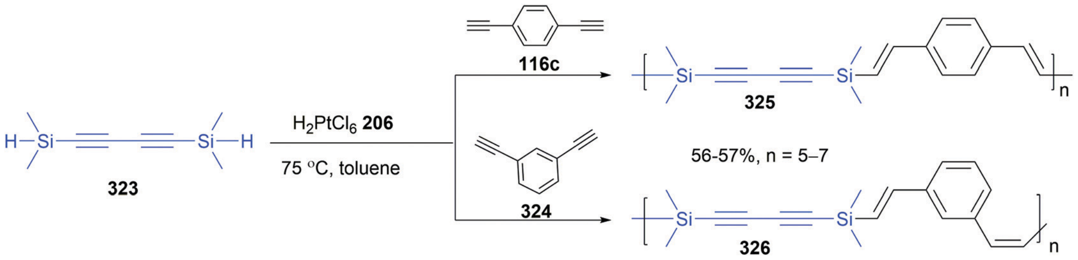
Scheme 64 Modification of **306a** possessing Si–Cl bonds with chromophors.



Scheme 65 Polyaddition of disilanes **317a–b** to diynes **116c**, **164k**, and **316a–d** towards the synthesis of conjugated polymers **318**.



Scheme 66 Hydrosilylation of diynes **116c**, **164g** with **217** and **245** catalysed by H_2PtCl_6 **206**.



Scheme 67 Hydrosilylation of 1,4-diethynylbenzene **116c** and 1,3-diethynylbenzene **324** with 1,4-dimethylsilylbuta-1,3-diyne **323**.

Table 6 Hydrosilylation of diynes **116c**, **164g** with **217** and **245** (Scheme 66)

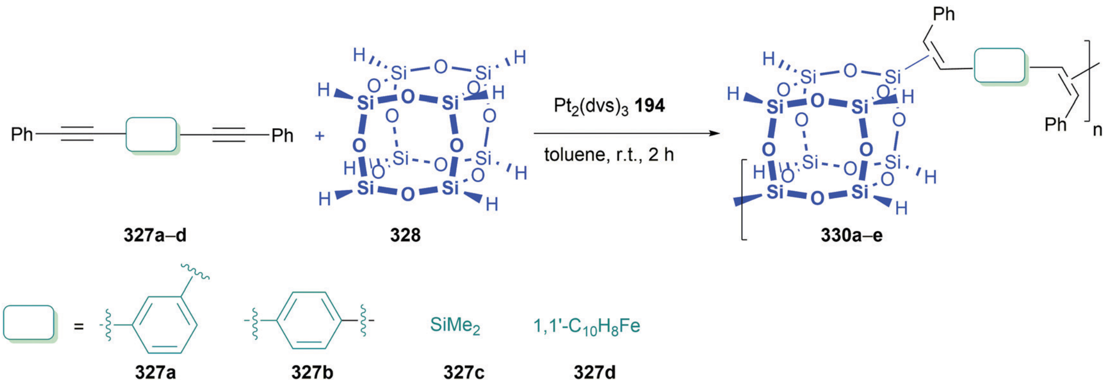
Entry	Silane	Diyne	Polymer	Yield [%]	M_n	M_w	M_w/M_n[a]	n[bc]	x[d]
1	**217**	**116c**	**322a**	92	2800	7200	1.7	9[b](19)[c]	0.92
2	**217**	**164g**	**322b**	77	1550	3000	3.1	4(4)	0.96
3	**245**	**116c**	**322c**	77	3000	5200	2.6	12(11)	0.82
4	**245**	**164g**	**322d**	79	3000	9200	1.9	9(5)	0.85

[a] Poly(styrene) standard. [b] Number of repeat units calculated from GPC data. [c] Number of repeat units calculated from ^1H NMR data. [d] x-value was calculated from the relative intensity of vinyl peak to vinylidene peak in ^1H NMR spectrum.

with ^1H and ^{29}Si NMR. The signals at $\delta = -15.7$ and -15.6 ppm for **340** seemed to arise from the –CH═CH–Si–CH═CH–(β,β) linkages, while the signal at $\delta = -13.4$ ppm in the ^{29}Si NMR spectrum could be signed to the –CH═CH–Si–C(═CH$_2$)–(β,α) linkages. The coupling constants J_{H-H} in the ^1H NMR spectrum also confirmed the predominant formation of the (*E*)-product. Since the Pd-complex **338** only catalysed the addition of the Si–H bond to the C≡C bond it was possible to prepare polymers with vinyl function attached to Si-atom **340e–f**, which can be then transformed in further reactions (Scheme 71 and Table 9).[210]

Rao *et al.* used the same strategy for the formation of macromolecular compounds, but to build a crosslinked matrix. They used 1,3,5-triethynylbenzene **304a** or 1,3,5-triethynyl-2,4,6-trimethylborazine **342** in different ratios **245**:(**116c** or **324**):(**304a** or **342**) = 100 : 95 : 5, 100 : 90 : 10, and 100 : 80 : 20. The reaction time was 4.5 h and the polymers **343a–i** were precipitated in propan-1-ol before gelation. Depending on the ratio of momers and crosslinking agents, different molecular weights of **343a–i** were obtained, with the highest M_w = 110 000–130 000 for a 100 : 80 : 20 ratio. The degree of crosslinking influenced the thermal stability of polymers (Scheme 72 and Table 10).[211]

The same group also used phenylsilane **272** as a monomer possessing three Si–H bonds in an equimolar hydrosilylation reaction with 1,4-diethynyl-**116c** or 1,3-diethynylbenzene **324** with the $Pd_2(dba)_3$ **338**/PCy_3 catalytic system to furnish polymers **344** with different ratios of regioisomers (β,β) : (β,α) : (α,α) = 60 : 35 : < 5. The presence of a free Si–H bond in the polymer structure **344** allowed its further modification with different

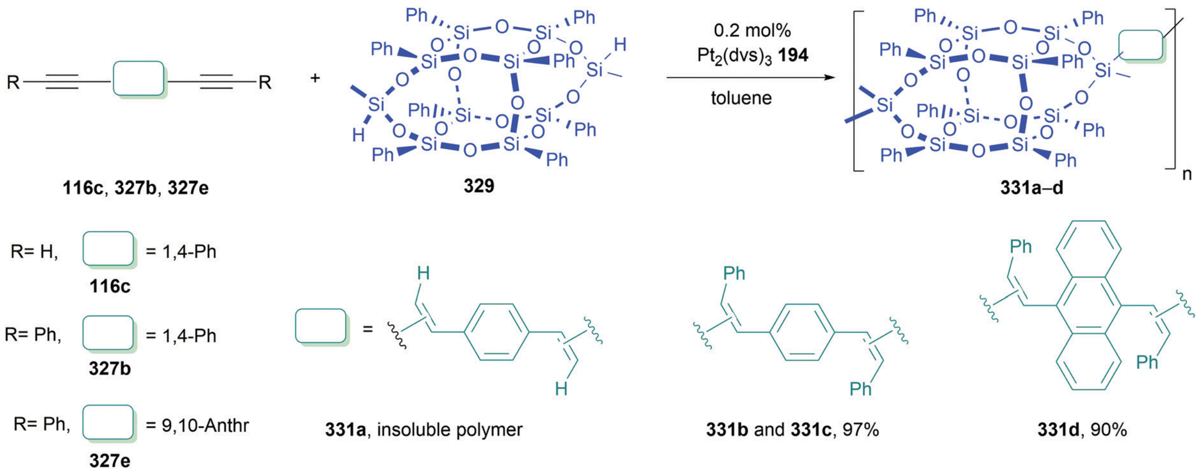


Scheme 68 Hydrosilylation of diynes **327a–d** with silsesquioxane **328** in the presence of Karstedt's catalyst **194**.

Table 7 Hydrosilylation of diynes **327a–d** with silsesquioxane **328** (Scheme 68)

Entry	Diyne	Polymer	Diyne/**330** in polymer[b]	M_w[c]	M_w/M_n[c]	T_{d1}[d] [°C]	T_{d5}[d] [°C]	Residue at 984 °C[d] [%]
1	**327a**	**330a**	1.23	21 000	2.03	534	1000	95.4
2[a]	**327a**	**330b**	1.55	87 000	2.29	501	748	94.1
3	**327b**	**330c**	1.22	34 000	1.79	477	788	93.8
4	**327c**	**330d**	1.17	26 000	1.65	454	649	93.4
5	**327d**	**330e**	1.59	10 000	1.79	486	841	92.9

Reaction conditions: **327** : **328** = 1 : 1, Karstedt's catalyst $Pt_2(dvs)_3$ **194** 5 μL, toluene, r.t., 2 h. [a] **327a** : **328** = 1.5 : 1. [b] Based on elemental analysis. [c] Determined by GPC with poly(styrene) standard. [d] Based on TGA in N_2.



Scheme 69 Hydrosilylation of diynes **116c**, **327b** and **327e** with silsesquioxane DDSQ **329**.

Table 8 Hydrosilylation of diynes **116c**, **327b** and **327e** with silsesquioxane DDSQ **329** (Scheme 69)

Entry	Diyne	Polymer	Feed ratio **329**/diyne	Time [h]	Yield [%]	M_n[a]	M_w/M_n[a]	T_d[b]	T_g[c]
1	**116c**	**331a**	1	0.5	—	—	—		
2	**327b**	**331b**	1.2	24	97	14 600	2.9	489	156
3	**327b**	**331c**	1	24	97	29 100	4.1	518	153
4	**327e**	**331d**	1	24	90	11 900	4.9	301	—

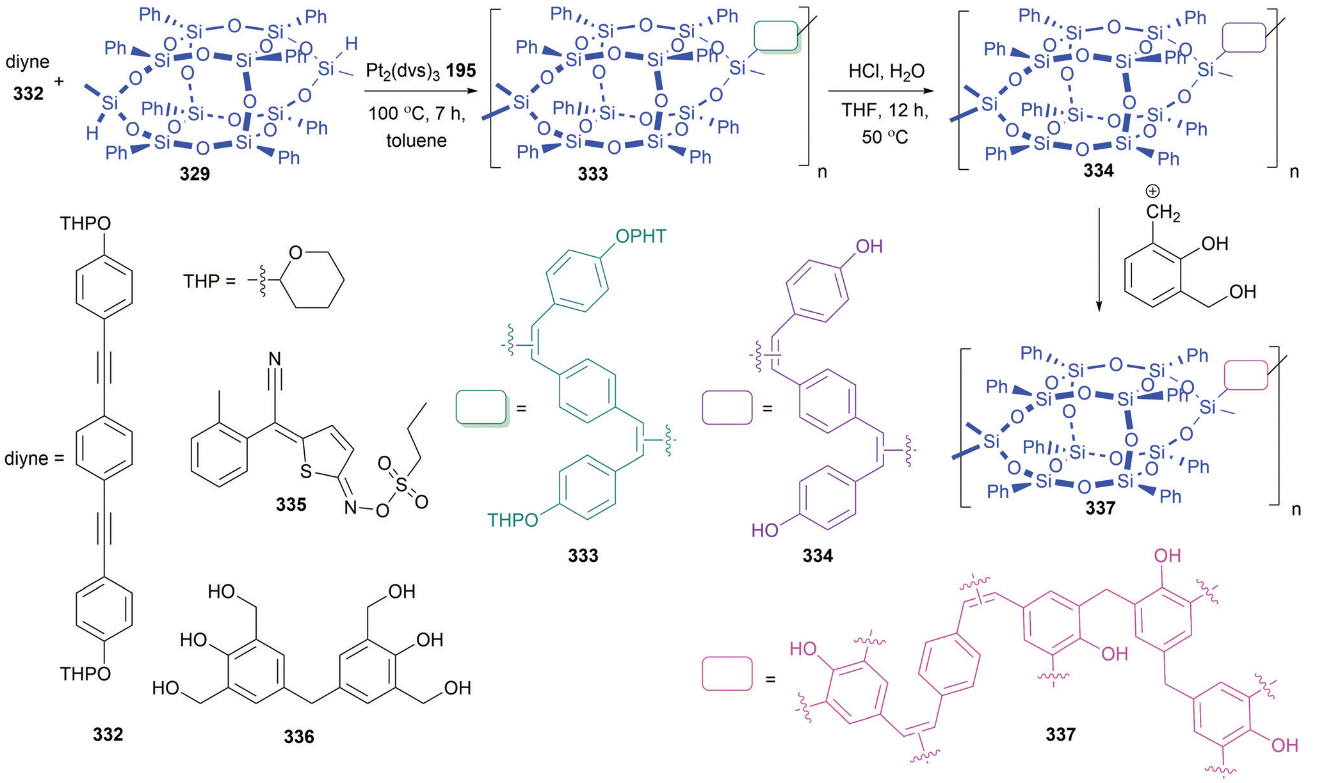
Pre-precipitated in MeOH. [a] Determined by GPC with poly(styrene) standard. [b] TGA, 10 °C min^{-1} in N_2. [c] DSC, second heating, 10 °C min^{-1} in N_2.

ethynylarenes **345a–b**, **346** in the next step towards functional polymers **347a–d.** Therefore, some additional functional groups or chromophores were included in the polymer **347a–d** as pendant groups (Scheme 73 and Table 11).[212]

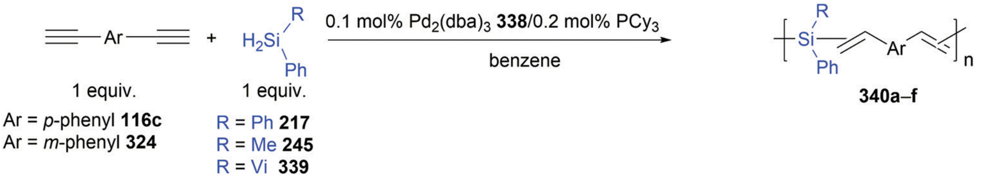
$RhI(PPh_3)_3$ **351** was reported as the selective catalyst for hydrosilylation of alkynes, in which the stereoselectivity can be tuned by altering the reaction temperature. When the reaction was carried out at 80 °C, the formation of (*E*)-alkenylsilane occurred, while at 0 °C the (*Z*)-isomer was predominantly formed.[213] The same observations were visible for hydrosilylative polyaddition of dihydrosilanes with diethynylarenes. The products were obtained with high yields and stereoselectivity depended on the reaction conditions. The coupling constants for ethenyl hydrogens were typical for (*Z*)- or (*E*)-isomers. At elevated temperatures (80 °C), polymers **353** with (*E*) regioselectivity were mainly formed ((*E*) > 93%), while at 0 °C (*Z*)-isomers **354** were synthesised ((*Z*) > 91%) With more sterically hindered silanes 1,4-bis[methyl(3,3,3-trifluoropropylsilyl)]benzene **349** and 1,3-bis[methyl(3,3,3-trifluoroprorylsilyl)]benzene **350**, the polymerisation was carried out in the presence of $[RhI(cod)]_2$ **352.** All polymers **353–354** were obtained with high yields 54–96% and M_n = 5000–22 000 (Scheme 74).[213–215]

The same catalyst was used in the synthesis of hyperbranched polymers by the homopolymerisation of bis(4-ethynylphenyl)methylsilane **355**. The process resulted in polymer **356** with the (*E*)-regularity in 95% yield.[216] Dendrimeric structures were also obtained in the reaction of bis(1-ethynylphenyl)dimethylsilane **327c** with dichloromethylsilane **357** in the presence of a Pt/C catalyst **307** (10% of Pt).

Bishydrosilylation leading to saturated products and α-hydrosilylation was not visible. The further substitution of halogen in **358** with 1,4-bislithium-1,2,3,4-tetraphenylbuta-1,3-diene **359** led to siloles **360**, while the reaction with lithiumethynylbenzene **361** led to the product **362** that can be further hydrosilylated with dichloromethylsilane **357** to build a more branched product (Scheme 75).[217]



Scheme 70 Hydrosilylation of diyne **332** with silsesquioxane **329** followed by the hydrolysis.



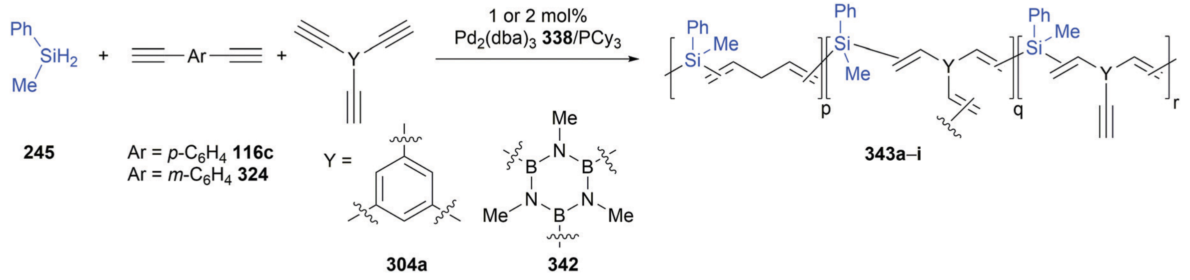
Scheme 71 Pd-catalysed hydrosilylation polyaddition of dihydrosilanes (**217**, **245**, **339**) to diynes (**116c**, **324**) catalysed by $Pd_2(dba)_3$ **338**/PCy_3.

Table 9 Results of Pd **338**-catalysed hydrosilylation of diynes (**116c**, **324**) with dihydrosilanes (**217**, **245**, **339**) with diynes (Scheme 71)

					340				
Entry	Arene	Silane	T [°C]	t [h]		Yield [%]	M_w[a]	M_w/M_n[a]	α:β[b]
1	**116c**	**217**	70	1	**a**	90	53 000	6.8	82 : 18
2	**324**	**217**	70	8	**b**	94	12 000	3.6	79 : 21
3	**116c**	**217**	70	0.5	**c**	86	49 000	6.6	78 : 22
4	**324**	**217**	70	2	**d**	85	20 000	4.2	78 : 22
5[c]	**116c**	**339**	110	6	**e**	91	20 000	4.6	70 : 30
6[c]	**324**	**339**	110	9	**f**	88	12 000	3.8	75 : 25

[a] Estimated by GPC using poly(styrene) standards. [b] Estimated from the ^1H and/or ^{29}Si NMR spectra. [c] $PdCl_2(PCy_3)_2$ **341** was used in place of $Pd_2(dba)_3$ **338**/PCy_3.

Sanchez *et al.* reported a special type of hydrosilylation of diynes using dihydrosiloles **282** and **368**. The reaction was carried out with different transition metal catalysts based upon Rh, Pt, and Pd catalysts (*e.g.*, $Pt_2(dvs)_2$ **194**, $RhCl(PPh_3)_3$ **205**, $Pd(PPh_3)_4$ **35**). The best results according to polymer molecular weight, yield, and selectivity were obtained when heterogeneous H_2PtCl_6 **206** was used in boiling toluene. The reactions were carried out for 10 min–12 h. Very bulky 2,3,4,5-tetraphenylsilole **368**, as well as silafluorene **282**, were used in these polyaddition reactions. The process occurred by *cis*-addition of the Si–H bond to the C≡C bond of diyne forming exclusively (*E*)-products. In the case of other complexes, α-hydrosilylation or desilylative coupling was also observed. During the reaction, the selectivity was controlled sterically and kinetically. Less bulky groups such as silafluorene **282** required more accurate temperature control. At lower temperatures, (*E*)-products were obtained, while at higher temperature complex mixture of β- and α-hydrosilylation was observed. Bulky reagents such as siliptycene (1,1-dihydrido-4,5,8,9-bis(triptycene)silafluorene) **369d** remained completely unreactive towards polyaddition. The structure of diyne also influenced the polydispersity and molecular weight of the polymers **370** and **371** (Scheme 76). Obtained polymers were used as luminescence chemosensors for explosives. Cyclic siloles increase the efficiency of application of

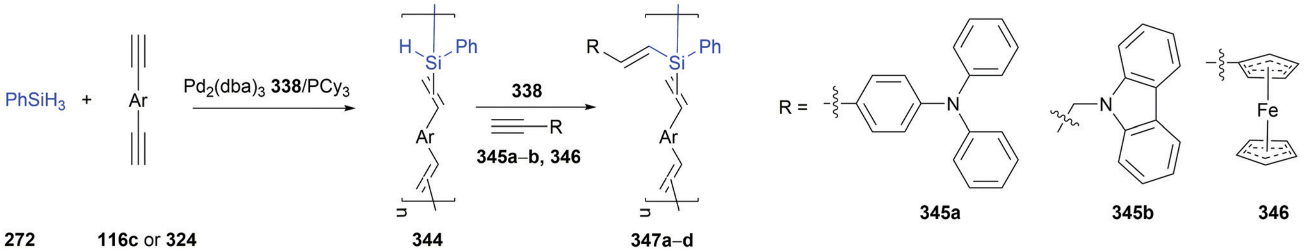


Scheme 72 Pd-catalysed **338** polyaddition of methylphenylsilane **245** to diynes **116c** and **324** with different ratios of crosslinking agent **304a** and **342**.

Table 10 Results of polyaddition of silane **245** to diynes **116c**, **324** with different ratios of crosslinking agent **304a**, **342** in the presence of Pd-catalyst **338** (Scheme 72)

Entry	Diyne	Crosslin. agent	Diyne : crosslin. agent	T [°C]	t [h]	Polymer, yield [%][a]	M_w[b]	M_w/M_n[b]
1	**116c**	—	100 : 0	60	4	**343a**, 75	24 000	3.8
2	**116c**	**304a**	95 : 5	60	4	**343b**, 70	26 000	4.1
3	**116c**	**304a**	90 : 10	60	4.5	**343c**, 68	30 000	5.0
4	**116c**	**304a**	80 : 20	60	3.5	**343d**, 80	130 000	16
5	**116c**	**342**	80 : 20	80	4.5	**343e**, 70	59 000	7.2
6	**324**	—	100 : 0	70	5	**343f**, 65	15 000	3.1
7	**324**	**304a**	95 : 5	70	4	**343g**, 70	21 000	4.0
8	**324**	**304a**	90 : 10	70	5	**343h**, 64	59 000	9.7
9	**324**	**304a**	80 : 20	70	3	**343i**, 75	110 000	14

[a] Reaction conditions: **245** (0.5 mmol), diyne + crosslinking agent (0.5 mmol), **338** (0.005–0.01 mmol, P/Pd = 2), toluene. [b] Estimated by GPC using poly(styrene) standard.



Scheme 73 Synthesis of polymers **347a–d** *via* hydrosilylation reactions.

Table 11 Results of the synthesis of polymers **347a–d** *via* hydrosilylation reactions (Scheme 73)

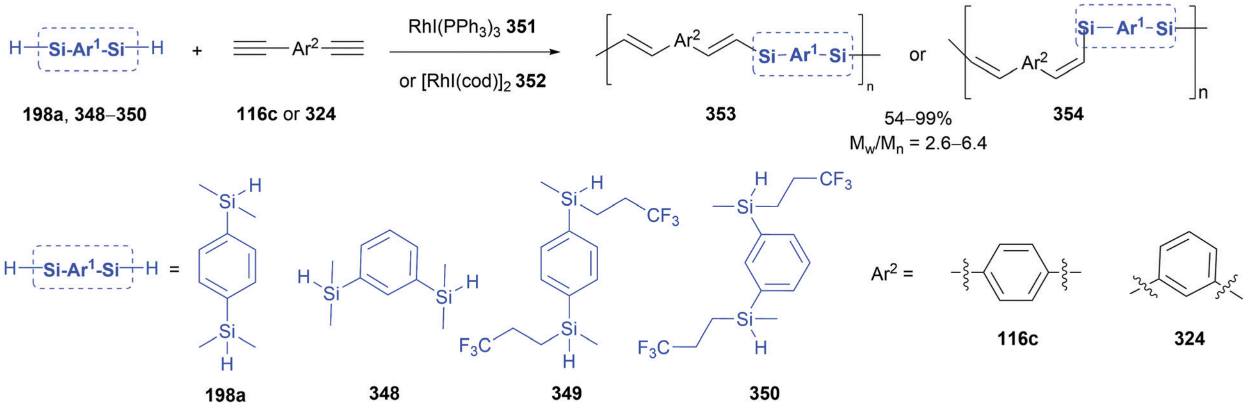
Entry	Diyne	Alkyne	Polymer[a]	Yield[b] [%]	M_w[c]	M_w/M_n[c]
1	**116c**	**345a**	**347a**	80	112 000	7.5
2	**324**	**345a**	**347b**	79	56 000	9.4
3	**116c**	**345b**	**347c**	85	61 000	5.7
4	**324**	**346**	**347d**	85	42 000	4.1

[a] **272** (0.3 mmol), diyne **116c** or **324** (0.3 mmol), alkyne **345a–b**, **346** (0.315 mmol), Pd$_2$(dba)$_3$ **338**/PCy$_3$ (0.042 mmol in total, P/Pd = 2), benzene. [b] Purified by precipitation in benzene/2-propanol. [c] Estimated by GPC with poly(styrene) standards.

these vinylene-silole polymers as light-emitting diodes (LEDs), luminescent sensors, or organic charge carrier materials.[68,218–220]

5.4. Cyclisation of 1,*n*-diynes by hydrosilylation reactions

Silanes and 1,*n*-diynes were also used in the hydrosilylation/cyclisation to silylated (*Z*)-1,2-dialkylidenecyclohexanes, useful synthons in the synthesis of fine chemicals. The reactions occurred in the presence of metal complexes including Ni, Rh, Ru, Pd, Pt, but there are several limitations of each catalytic system. Described by Tamao *et al.*, Ni(0) complexes catalysed the cyclisation of 1,7-diynes **160**, **372–375**, while 1,6-diynes were not active in this transformation.[157,221] Different types of trialkyl, trialkoxysilanes, and silazanes **376a–e** were applied as reagents. The reactions were carried out in the presence of Ni(acac)$_2$ (1 mol%) **273**/DIBAH (2 mol%) **170**, at 50–100 °C, for 6–24 h. The higher the temperature and the longer the reaction time, the lower yield of exocyclic diene was obtained, due to the subsequent polymerisation process. The cyclisation of terminal diynes occurred with moderate or good yield (47–73%) with the exclusive or predominant formation of (*Z*)-product. The process was effective also for optically active diyne **372**. The asymmetric diyne **373** containing nitrogen led to the silyl-substituted tricyclic alkaloid-type dienes **379** with lower selectivity (*Z*)/(*E*) (**379a**/**379b**) = 79 : 21, suggesting a directing effect of the



Scheme 74 Temperature tunable stereoselective hydrosilylation of diynes **116c**, **324** with disilanes **198a**, **348–350** in the presence of $RhI(PPh_3)_3$ **351** and $[RhI(cod)]_2$ **352** catalysts.

nitrogen atom, which can easily coordinate to the metal centre. The internal diyne **374** was less reactive and reacted only under higher reaction temperatures and using accelerating triphenylphosphine as an additive. Unsymmetrical diyne **375** containing one terminal and one internal C≡C bond reacted with the silane from the less shielded terminal acetylene furnishing a single regioisomer **381** in the post-reaction mixture (Scheme 77).[157,221]

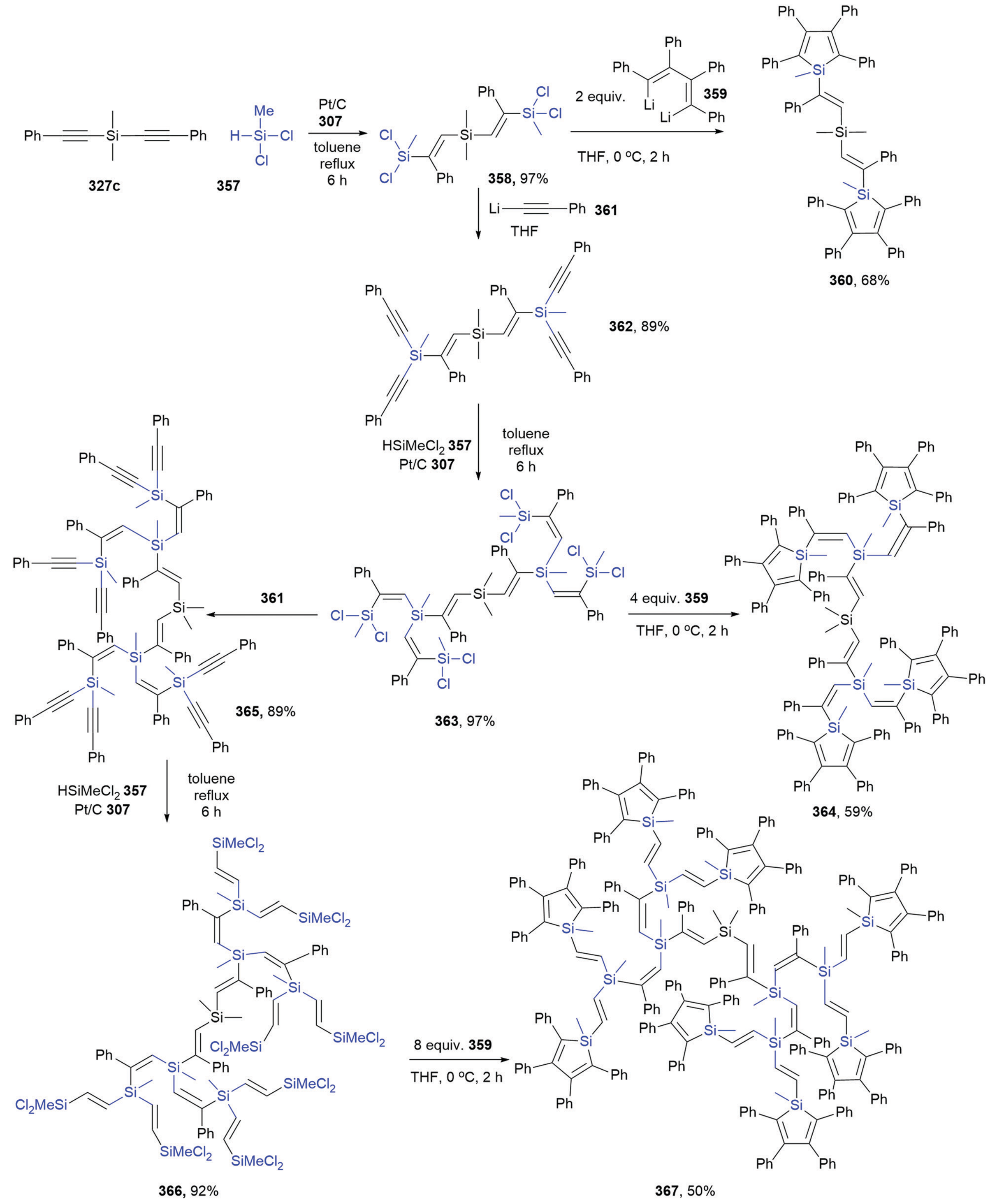
The mechanism of this transformation (Scheme 78) started from the insertion of one of the C≡C bonds (less shielded) to the Ni–Si bond, generated by the oxidative addition of silane **376a–e** to metal centre **382**. The insertion of the second acetylene group to the Ni–vinyl bond **384** and reductive elimination of the exocyclic diene **381** closed the catalytic cycle. The insertion of acetylene to the Ni–H bond can be eliminated, because of the lack of other isomers in the post-reaction mixture.[157,221] This Ni-catalysed reaction was possible only for 1,7-diynes. 1,6- or 1,8-diynes in the hydrosilylation process gave only polymeric products. To cyclise 1,6-diynes with hydrodisilanes, the reaction was catalysed with 5 mol% of $Ni(acac)_2$ **273**/DIBAH **170**/PEt_3 and the mechanism proceeded with the formation of Ni-silylene intermediate.[157] The obtained exocyclic dienes with (*Z*)-selectivity were used as reagents in Diels–Alder reactions, or the silyl groups were reacted in C–C bond forming reactions with aryl halides in Hiyama coupling reactions (Scheme 79).[157,221]

Widenhoefer *et al.* developed cationic Pt-complex, formed *in situ* from (phen)$PtMe_2$ **399** (phen = phenanthroline) and $B(C_6F_5)_3$ **401** that was highly active and selective in the cyclisation/hydrosilylation reactions of 1,6- and 1,7-diynes **127a**, **127k**, **127p**, and **394a–l** leading to silylated 1,2-dialkylidenecyclopentanes **402–410** and 1,2-dialkylidenecyclohexane **411**, with high (*Z*)-selectivity ((*Z*)/(*E*) > 8 : 1). The catalyst was found to be inactive in the cyclisation/hydrosilylation of separated dienes (for which palladium analogs were active), making this process highly selective.[222–225] The reactions were carried out for 10 min–3 h at 110 °C in toluene for different silanes **207a**, **395–398** (Scheme 80).[158]

The same group developed a diimine cationic Pt complex, [PhN=C(Me)C(Me)=NPh]$PtMe_2$ **400**, which was much more active and selective than the complex with phenanthroline **399**. The products **402–411** were obtained in 15 min at 110 °C or 85 min at 70 °C with higher selectivity towards (*Z*)-isomer (*Z*) : (*E*) >30 : 1. The electronic and steric properties of the diimine ligands were found to have an important influence on the cyclisation/hydrosilylation reaction. The rate of the process decreased with the increase of the electron density and steric bulk of the ligand. The structure of silane and diyne also influenced the reaction rate. When $HSi(i\text{-}Pr)_3$ **398** was used instead of $HSiEt_3$ **207a**, the reaction was 10 times slower. The catalytic system was tolerant towards many functional groups including *inter alia* sulfones, amides, ketones (Scheme 80).[159]

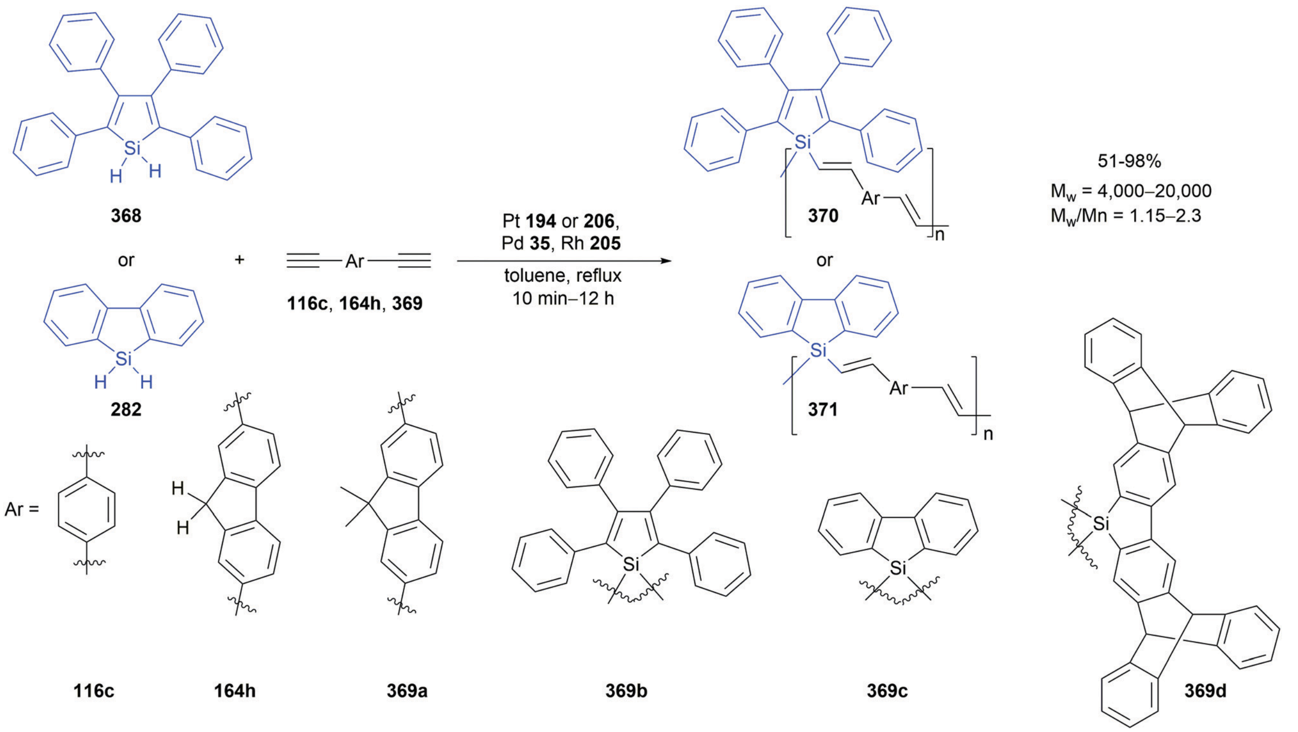
The authors proposed the mechanism of this transformation (Scheme 81). Initially CO or $B(C_6F_5)_3$ **401** abstracts the methyl group from the pre-catalyst **400** forming the Pt-cationic complex **412** upon coordination to the diyne substrate. Oxidative addition of the silane, which occurred readily, even at −30 °C leads to complex **413.** Loss of CH_4 leads to **414.** Next, the insertion of the alkyne into the Pt–Si bond occurs leading to **415**, followed by the β-migratory insertion of the coordinated second alkyne group and formation of the platinum dienyl intermediate **416.** The oxidative addition of silane **207a** or **395–398** formed **417.** Elimination of the product **402–411** and the coordination of diyne regenerates the initial catalyst **414.** The obtained cyclic products were used in protodesilylation and Diels–Alder transformations. Examples of these processes are presented in Scheme 82 using **402a** as a reagent.[158,159]

Several papers discussed the application of Rh complexes in the synthesis of 1,2-dialkylidenecyclopentanes. The use of the popular Wilkinson's complex **205** in this transformation was reported by Matsuda *et al.*[226,227] The exact catalyst, which facilitated the formation of cyclic compounds was the complex $Rh(H)(SiR_3)Cl(PPh_3)_2$ **438**, which was obtained by oxidative addition of silane to the metal centre. The order and time of addition of silane and diyne were important for the reaction course. When reagents **127a, 127k, 127p, 195a** and **394a–l** were added 1,2-dialkilidenecyclopentane **434** was formed immediately. In other cases, indane **435** was formed as the main product (Scheme 83). Scheme 84 shows various dialkilidenecyclopentanes

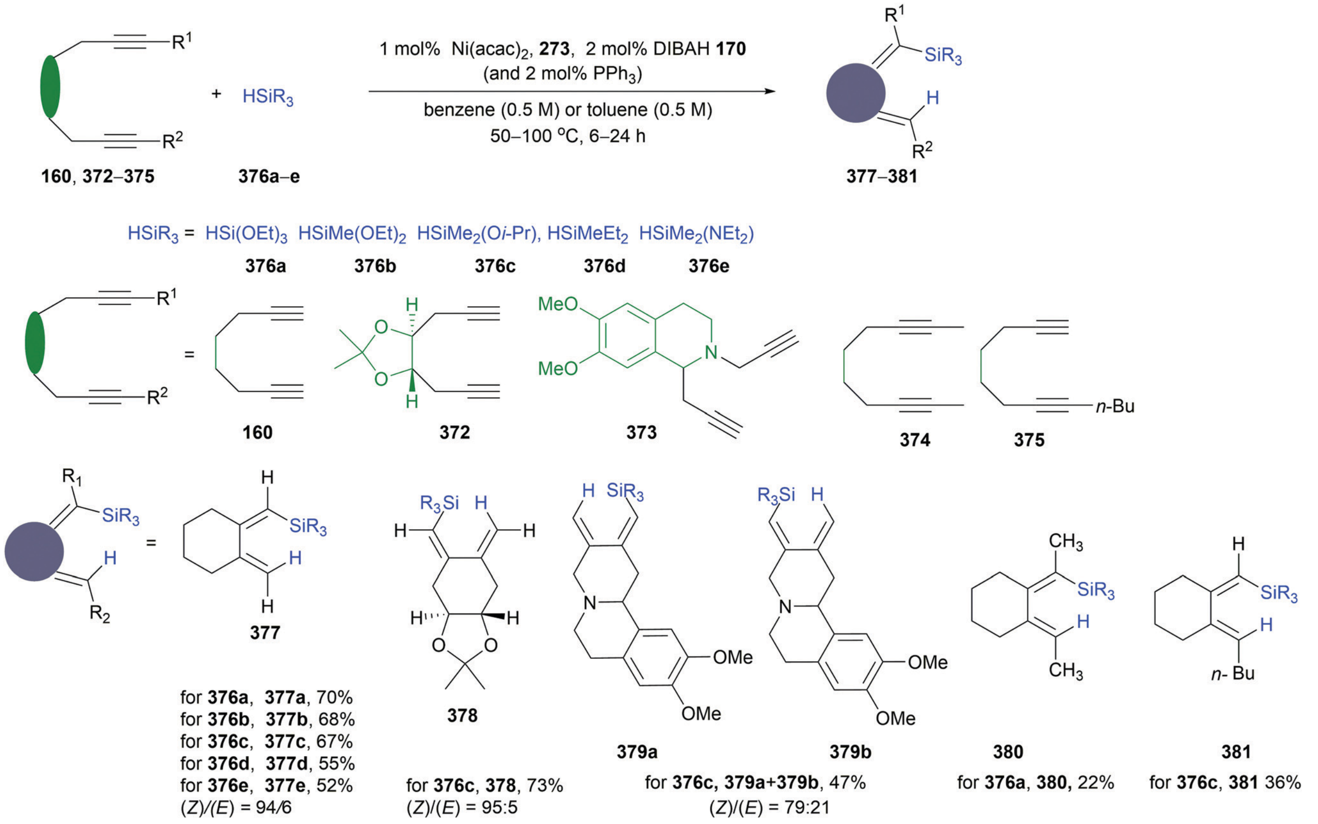


Scheme 75 Preparation of hyperbranched organosilicon compounds using hydrosilylation of diynes.

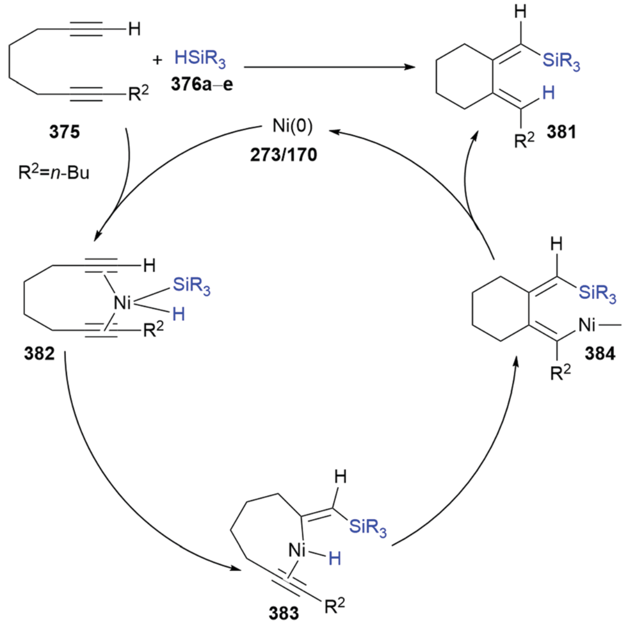
434 obtained within this transformation in the presence of **438.** Depending on the catalyst structure (*E*)- or (*Z*)-cyclic isomers were obtained. When mono- or bidentate electron-donating phosphine ligands are coordinated to the metal centre $\mathrm{RhCl(PPh_3)_3}$ **205** or $\mathrm{[Rh(cod)(dppb)][PF_6]}$ **439,** the insertion of the second alkyne group is slowed down giving time to convert the (*Z*)-isomer **434** into (*E*)-product **434.** For $\mathrm{Rh_4(CO)_{12}}$ **440** with electron-withdrawing CO ligands, the insertion process is much faster, and there is no time



Scheme 76 Hydrosilylation of diethynylarenes **116c**, **164h**, **369a–d** with 1,10-dihydridosiloles **282** and **368** catalysed by transition metal complexes.



Scheme 77 Synthesis of 1,2-dialkylidenecyclohexanes **377–381** *via* catalytic cyclisation of 1,7-diynes **160**, **372–375** with silanes **376a–e** catalysed by Ni(0) complex **273**.



Scheme 78 Mechanism of cyclisation *via* hydrosilylation of 1,7-diynes with silanes catalysed by Ni(0) complex generated *in situ* from **273**/**170**.

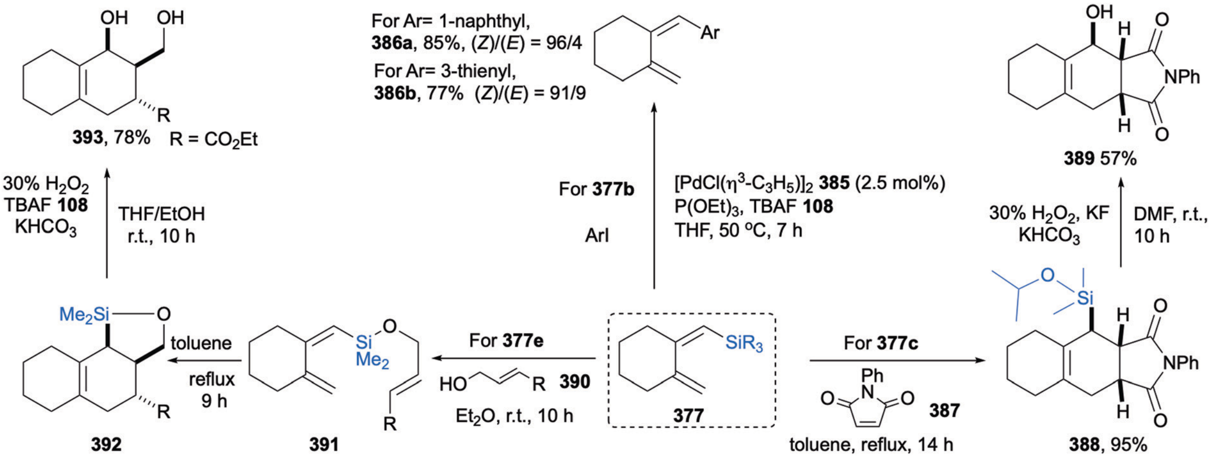
for the formation of (*E*)-isomer (Scheme 85).[226,227] The obtained products were used in Diels–Alder transformations with different dienophiles, as well as in the hydrogenation process catalysed by the Pd/C **446** system, followed by the homologation reaction (Scheme 86).

Ojima *et al.* reported several papers based on the cyclisation/hydrosilylation of 1,6-diynes **127o–p**, **450a–f** in the presence of rhodium complexes **204**, **451–452** and different pressures of CO.[66,67,228–230] The course of the reaction strictly depended on the reagents (silane, diyne) structure, the type of the catalyst, as well as the pressure of CO. When $Rh_2Co_2(C0)_{12}$ **451**, $Rh(acac)(CO)_2$ **204** or $Rh(t\text{-}BuNC)_4Co(CO)_4$ **452** were used, the corresponding bicyclo[3.3.0]octenones **453–455** were obtained in 82–93% yield *via* carbobicyclisation with the incorporation of CO (15–50 bar) (Scheme 87 and Table 12). Under lower CO pressures (1–2 bar), no reaction with CO was observed and typical dialkilidenecycloalkanes were formed.[230] Moreover, the steric hindrance of silane or diyne influenced the formation of a specific product. Additionally, the C_4 position in 1,6-diynes **450a–f** exerts marked influence on the product distribution. When the heteroatom is at the C_4 position 1,2-hydrosilylation is the main process, while 1,4-hydrosilylation is favoured with 4,4-*gem*-disubstitution with ester groups.[228] Products **453** can easily isomerise quantitatively to **454** in the presence of $RhCl_3{\cdot}3H_2O$ **213** as a catalyst in ethanol under 50 °C.

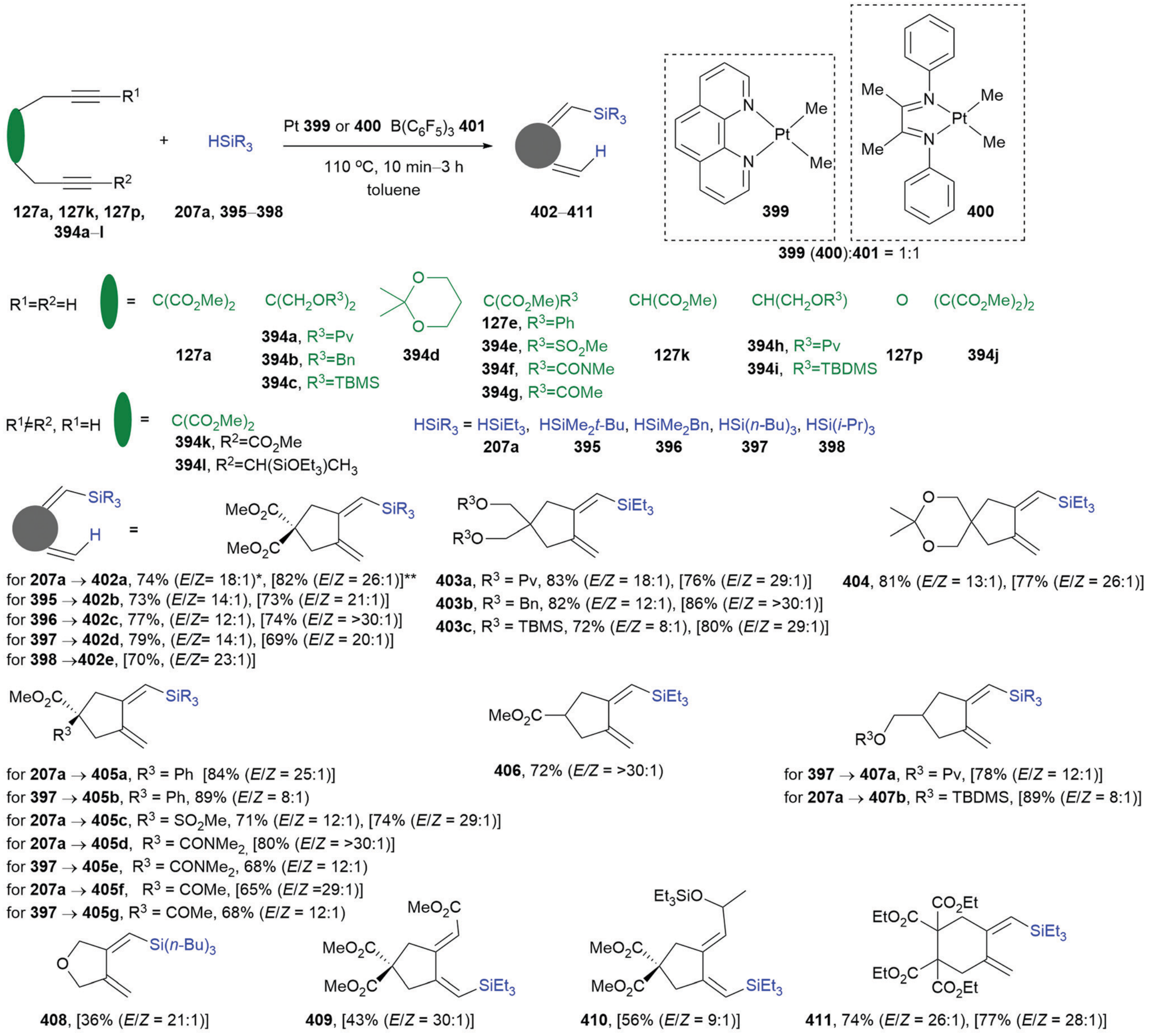
A detailed mechanism of this transformation was also presented which explained the formation of various cyclic products. The product outcome was found to be dependent on the further transformations of complex **459** formed in the carbocylisation of **457** to **458**, followed by CO insertion and subsequent carbocyclization to bicyclic **460.** When a 1,3-[Rh]-shift occurred from **460**, the complex **461** is formed, which then after reductive elimination furnishes product **453.** When β-hydride elimination occurred from **460**, the dienone–M–H complex **462** is formed or/and bicyclic diene **464.** The addition of the M–H species leads to intermediates **463** or **465**, which next (*via* addition of the next silane and reductive elimination of R_3Si–[Rh]) accomplishes the products **454** or **455.** The formation of **455** was observed only for the product which was able to form a stable aromatic pyrrole product (Scheme 88).[229]

Ojima discussed also that endiynes **466** (dodec-11-ene-1,6-diyne or their heteroatom analogs) reacted with silanes ($PhMe_2$SiH **195a**, Et_3SiH **207a**, or $(t\text{-}Bu)Me_2SiH$ **395**) in the presence of $Rh(acac)(CO)_2$ **204** in unique silylative cascade carbonylative carbotricyclisation process, at room temperature and under ambient pressure of CO. The reaction yielding fused 5-7-5 tricyclic products 5-oxo-1,3*a*,4,5,7,9-hexahydro-3*H*-cyclopenta[*e*]azulenes **467** or their heteroatom congeners. Within this process, functionalised polycyclic compounds were obtained that are useful synthons in the synthesis of natural products (Scheme 89).[66,67]

Using the same $[Rh(acac)(CO)_2]$ complex **204**, it was possible to carry out hydrosilylative cyclisation with carbonylation of



Scheme 79 Transformations of 1,2-dialkylidenecyclohexanes with vinylsilyl group **377** in Diels–Alder and Hiyama coupling reactions.

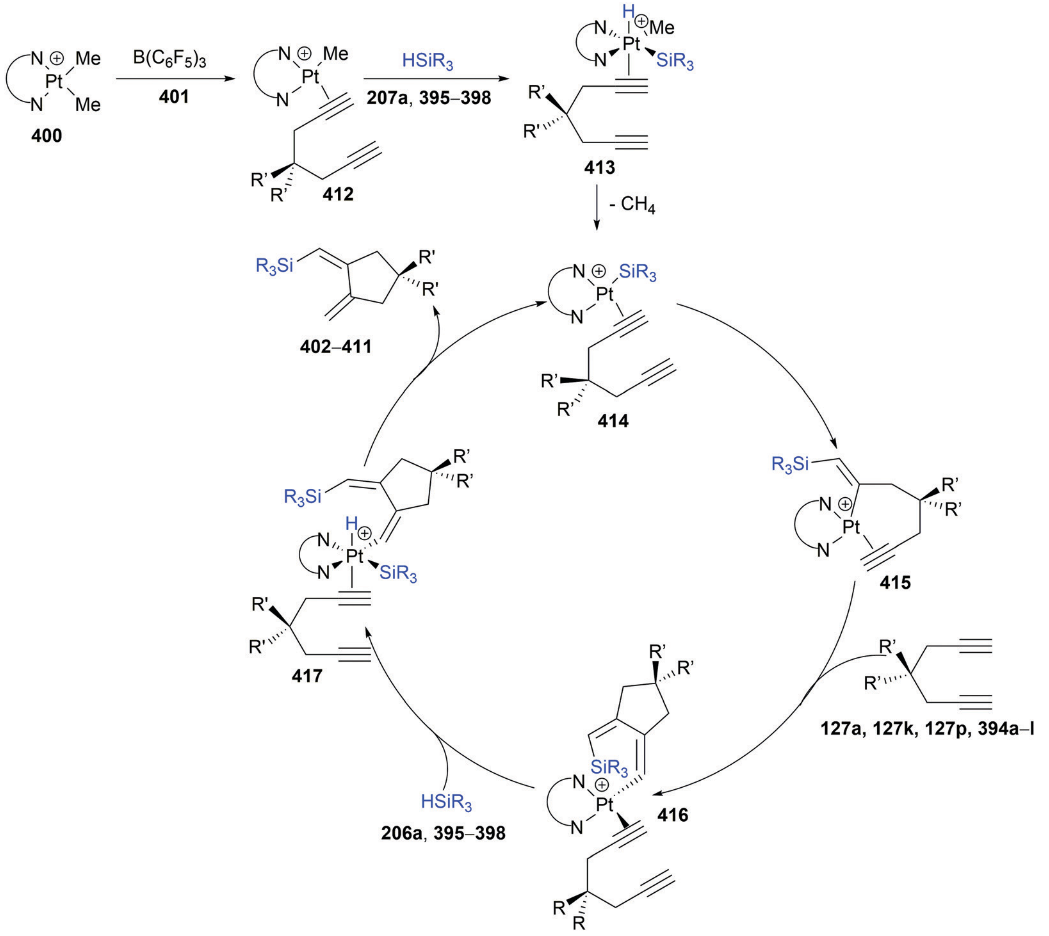


* Results for 399 used as a catalyst, 3 h. ** Results for 400 used as a catalyst, 10–100 min.

Scheme 80 Cyclisation/hydrosilylation of diynes **127a**, **127k**, **127p**, and **394a–l** catalysed by a 1 : 1 mixture of Pt catalyst (**399** or **400**) and $B(C_6F_5)_3$ **401** in toluene at 110 °C towards exocyclic dienes **402–411**.

various 1,5-diynes with aromatic, olefinic, and ethylene tethered spacers **468** under the ambient pressure of CO (1 atm.). The reaction furnished various 2,5-dialkylidenecyclopentanones **469** in good yields. In this example, the insertion of CO was favoured to build a five-membered ring and avoid high strains. The products **469a–m** were obtained with moderate or high yields 30–92%, which varies with both reagent structures (Scheme 90).[231] The mechanism of carbonylative cyclisation of 1,5-diynes **468** using $[Rh(acac)(CO)_2]$ **204** started from silylrhodation, followed by the insertion of CO to **471** to form acylrhodium species **472**, then acylrhodation to the second alkynyl group forms the 5-membered ring **473** (Scheme 91).[231]

Cyclisation/hydrosilylation of 1,6-, 1,7- and 1,8-diynes **127a**, **127o–p**, **160**, **164a**, **474a–d** was carried out in the presence of ionic Pd complex $[(\eta^3\text{-}C_3H_5)Pd(cod)][PF_6]$ **476** with chlorodimethyl-**305**, dichloromethyl-**357**, and trichlorosilane **475**. The reaction occurred at room temperature in CH_2Cl_2 and products (*Z*)-1-methylene-2-silylmethylenecycloalkanes **477** were obtained in good yields, which were further transformed to their ethoxy analogs **478** (Scheme 92). For unsymmetrical diyne 2-butynyl propargyl ether **474b**, it was found by NOE analysis that the silyl group is attached to the internal C≡C bond, suggesting that the formation of the regioisomer **478f** was due to the fact, that the reaction started from the hydropalladation at the terminal alkyne site to **481**, instead of the insertion of the alkyne into the metal–Si bond. The further steps in the plausible mechanism are: intramolecular carbopalladation, the formation of cyclised (*Z*)-alkenylpalladium intermediate **482**, and finally σ-metathesis with a hydrosilane,



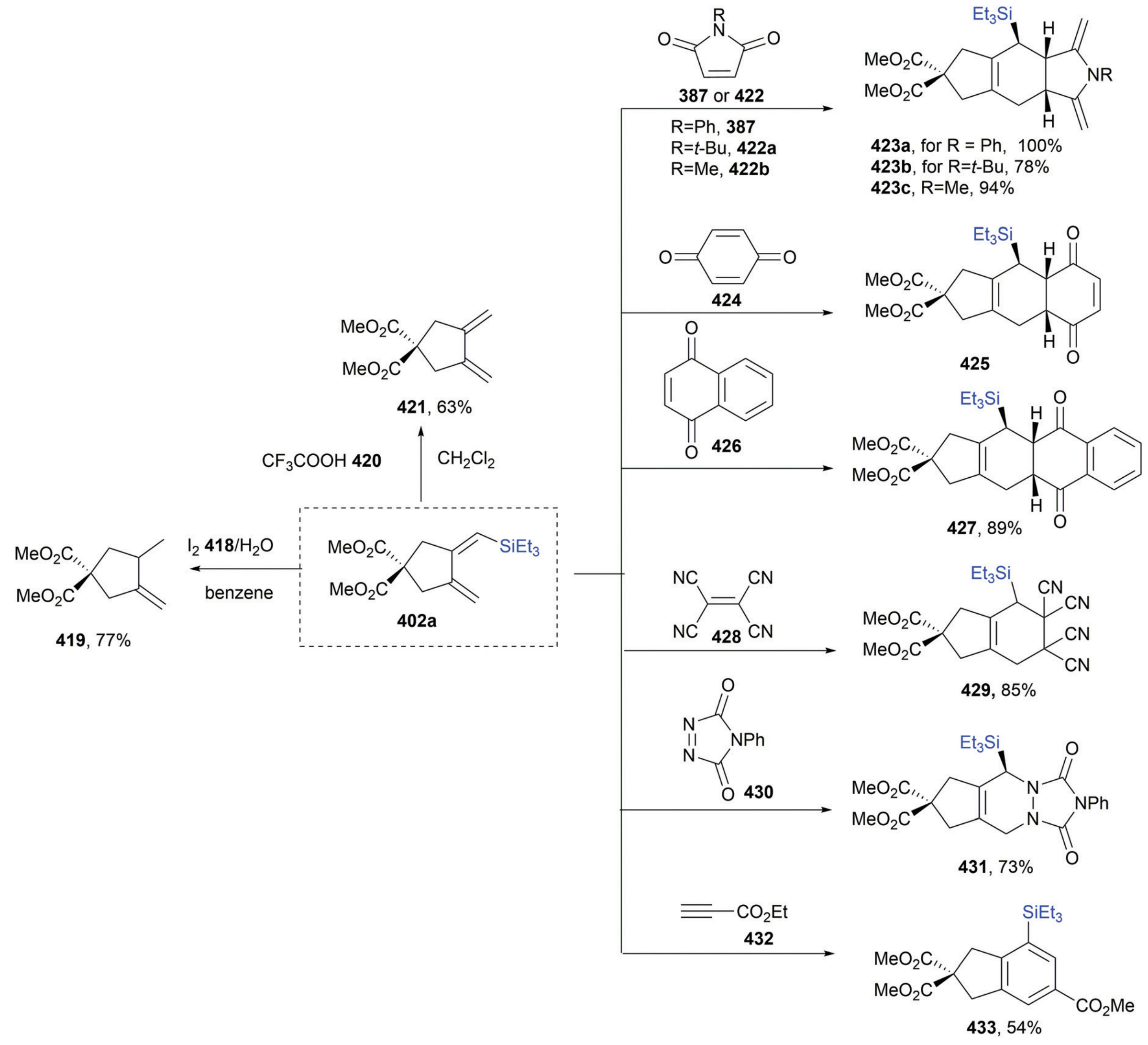
Scheme 81 Mechanism of the hydrosilylation/cyclisation reaction of separated diynes in the presence of Pt-diimine complex **400** and $B(C_6F_5)_3$ **401**.

followed by the product release **477** and regeneration of the initial catalyst **479** (Scheme 93).[232–234]

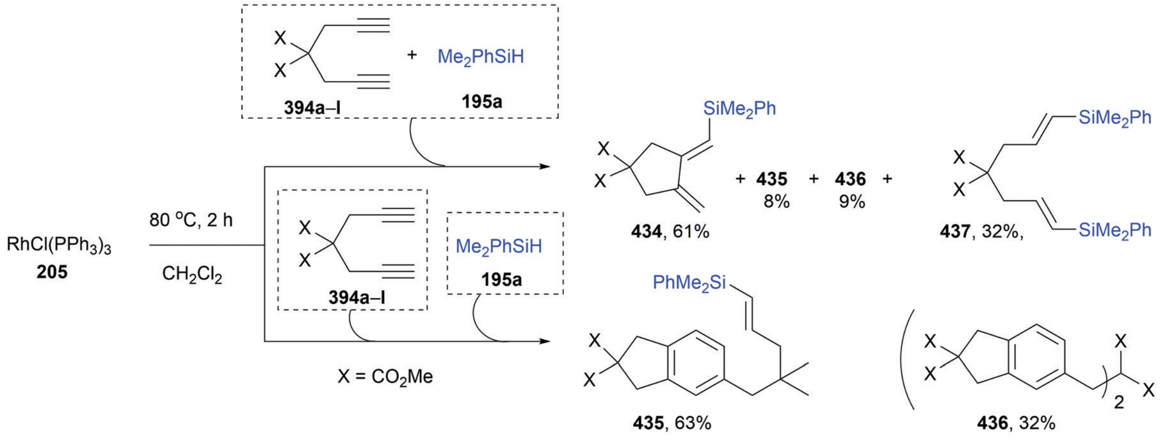
Liu and Wiedenhoefer reported that the cationic rhodium complex $[Rh(BINAP)(cod)][BF_4]$ **485** (BINAP = ((±)-2,2-bis(diphenylphosphino)binaphthyl)) is as an effective catalyst (10 mol%) in the cyclisation/hydrosilylation reaction of terminal and internal 1,*n*-diynes **127a, 483a–m** with silanes **195d**, **207a**, and **484** leading to 1,2-dialkilidynecycloalkanes **486a–p** with high yield and high diastereoselectivity (Scheme 94). The higher the concertation of silane the lower the selectivity. The best results were obtained when triethylsilane **207a** was used (1.0–1.7 M) and was added slowly to the reaction mixture. The mechanism of this transformation is similar to that previously described for Pt-complexes (Scheme 81).[160] The obtained silylated 1,2-dialkilidynecycloalkanes **486** were further used in the Diels–Alder reaction with 4-phenyl[1,2,4]triazole-3,5-dione **430** at 0 °C for 30 min (Scheme 95).

Another example that involved the reaction of diynes **116a**, **127c**, **127o–p**, **488a–c**, *tert*-butyldimethylsilane **395**, and CO, which furnished two different catechol derivatives **490** and **491**, was carried out in the presence of $[Ru_3(CO)_{12}]$ **489**/PCy_3. Product **490** was the primary product, which can be readily hydrosilylated to **491** when 6 equiv. of silane **395** was used. In the case of a lower excess of **395**, product **490** was visible in the reaction mixture. The best results were obtained using acetonitrile as a solvent. Various terminal and internal diynes were used as reagents giving products with moderate yields (Scheme 96).[235] The mechanism of the process involves the formation of an oxycarbyne complex **493** as an intermediate and the process requires the introduction of two CO molecules into the diyne structure. A carbyne/CO coupling yields intermediate **493** was previously tested for tungsten.[235] Analog complexes to **495** for alkynes were determined for other metals, *e.g.*, Nb, Ta, V, Ta. Katz *et al.* reported the formation of a similar product in the reaction of $(CO)_4BrM{\equiv}CCH_3$ (M = Cr, W) with diyne.[236] This proved that the proposed mechanism is plausible (Scheme 97).

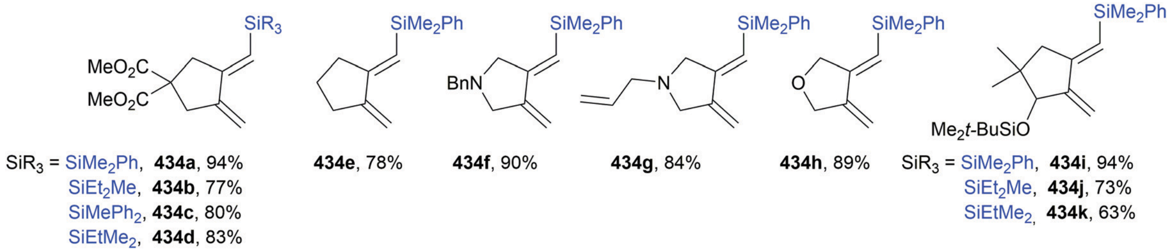
Lewis acids such as $AlCl_3$ **496** and $EtAlCl_2$ **497** were successfully applied for the hydrosilylation of alkynes with trialklylsilanes, which occurred as a *syn*-addition of the Si–H bond to the C≡C bond with the formation of the *trans*-product.[57,237] The mechanism of this transformation assumes the formation of a zwitterionic intermediate by the coordination of **496** or **497** to the acetylenic bond. Next, the hydride of silane attacks the electron-deficient carbon atom from the opposite site to AlX_3 with the formation of ate-complex. The coupling between the



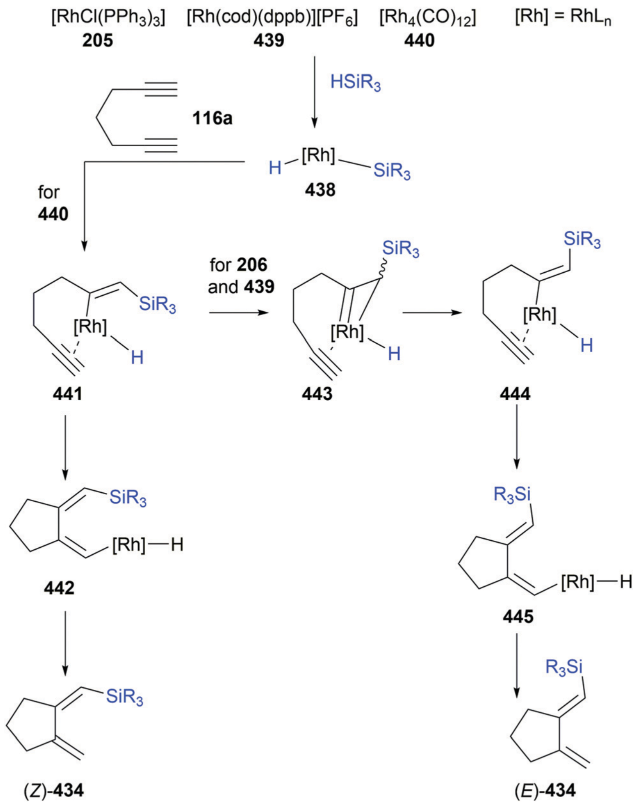
Scheme 82 Chemical transformation of **402a** in Diels–Alder and protodesilylation.



Scheme 83 Possible silylative cyclisation reactions of diynes **394a–l** with dimethylphenylsilane **195a**. Different products were formed depending on the order of reagent addition.



Scheme 84 Dialkilidenecyclopentanes **434a–l** obtained from the silylative cyclisation of diynes with silanes in the presence of Rh(H)(SiR$_3$)Cl(PPh$_3$)$_2$ **438**.



Scheme 85 Proposed mechanism for the formation of (*Z*)- and (*E*)-isomers of **434** in the silylative cyclisation reaction in the presence of Rh-catalysts **205**, **439**, or **440**.

silyl cation and vinyl group furnishes the silylated olefin with retention of configuration. The same catalysts **496** and **497** were also used in the hydrosilylation of hepta-1,6-diyne **116a** and octa-1,7-diyne **160**, using 4 equiv. of triethylsilane **207a**. For a shorter chain of terminal diyne **116a**, the cyclic product **498** was obtained in 60% yield, while for octa-1,7-diyne **160**, 1,8-bistriethylsilyl-octa-1,7-diene **499** was formed predominantly (Scheme 98).[237] Formation of bissilylated diene using this Lewis catalyst contrasts with the cyclization process *via* hydrosilylation, which occurred in the presence of Ni or Rh catalysts.[157,221]

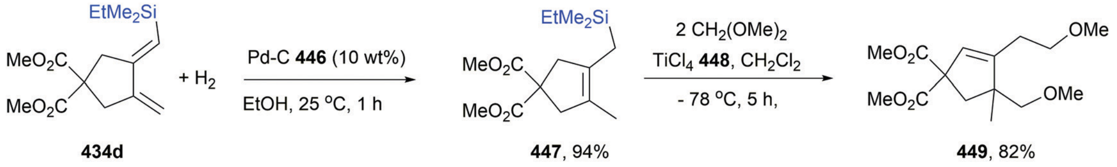
6. Hydrogermylation of conjugated and separated diynes

Hydrogermylation of diynes is limited only to two examples, which describe the formation of 2,5-disubstituted germoles[238] or germylene–divinylene polymers.[239]

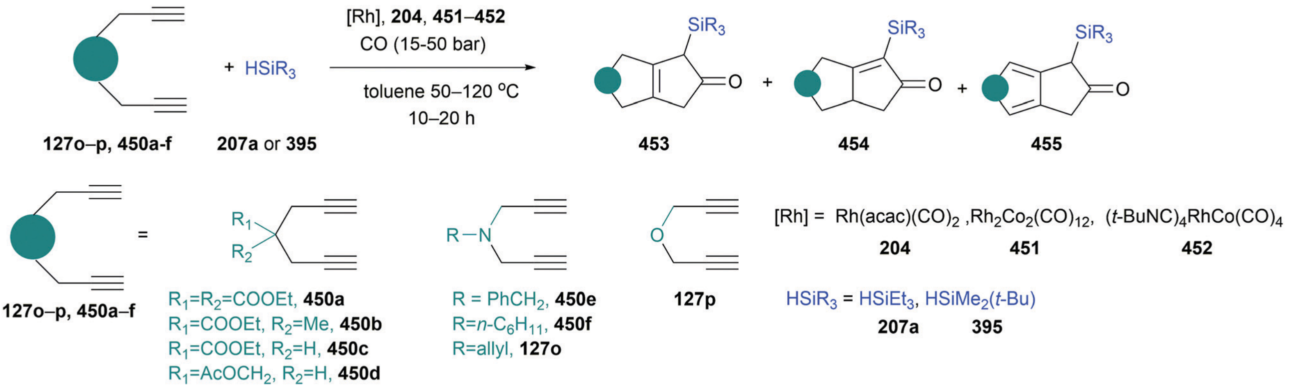
Murakami *et al.* developed a *trans*-hydrogermylation of conjugated symmetrical and nonsymmetrical 1,3-diynes **1a–b**, **1d**, **27c**, **60e**, **258i**, **258o**, **500a–d** with diphenylgermane **501** in the presence of $[Cp^*Ru(MeCN)_3][PF_6]$ **281** wich yielded cyclic germoles **502a–o** with good or moderate yields (Scheme 99).

The same complex **281** was previously used by Trost *et al.* in the *trans*-hydrosilylation of alkynes,[56,189,240,241] but its activity in the reaction with conjugated diynes was much lower than for hydrogermylation (Table 13). The double addition of diphenylgermane **501** to 1,4-diphenyl-buta-1,3-diyne **1a** occurred with a much higher yield in comparison to the hydrosilylation reaction (93% *vs.* 29%) (Scheme 58).[156] The hydrogermylation reaction was carried out with 3 equiv. of germane **501** and 10 mol% of Ru catalyst **281**, but a lower excess of reagent **501** was also possible (1.2 equiv.).

The reaction was efficient for diaryl-substituted diynes with different functional groups (silyl, boryl, methoxy, bromo, fluoro) or compounds with heteroaryl substituents **27c**, **500b**. The presence of strongly electron-withdrawing nitro groups in the para position **500a** was responsible for the lower product yield (40%, **502i**). No reactions were observed for diynes with alkyl groups (hexa-2,4-diyne **65a**) and silyl functionalities (1,4-bis(trimethylsilyl)buta-1,3-diyne **180c**). When dibutylgermane **503** was used as a reagent, the reaction was less effective, even with 20 mol% of **281**. Applying conjugated 1,8-diphenylocta-1,3,5,7-tetrayne **504**, diphenylgermane **501** (6 equiv.), and 20 mol% of



Scheme 86 Hydrogenation of dialkilidenecyclopentane **434d** followed by a Ti-catalysed homologation reaction.



Scheme 87 Silacarbocyclisation of 1,6-diynes **127o–p** and **450a–f** catalysed by various Rh complexes **204**, and **451–452**.

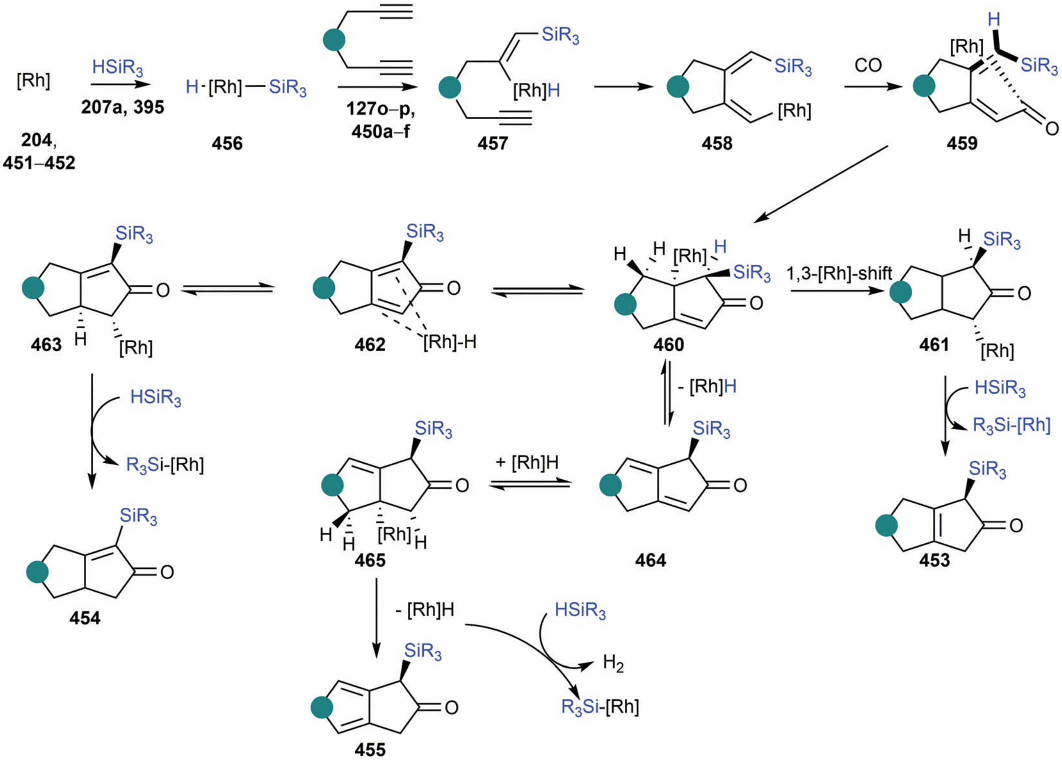
Table 12 Results of silacarbocyclisation of 1,6-diynes **127o–p** and **450a–f** catalysed by various Rh complexes **204**, and **451–452**

Entry	Diyne	Silane	Rh	CO (bar)	T [°C]	Yield[a] [%] **453/454/455**
1	**450a**	**395**	**451**	15	50	93/0/0
2			**204**	15	50	93/0/0
3			**452**	15	50	82/0/0
4	**450b**	**395**	**204**	50	50	70/0/0
5	**450c**	**395**	**204**	50	50	47/16/0
6	**450d**	**395**	**204**	50	120	73/0/0
7	**450e**	**395**	**204**	50	65	0/18/70
8	**450e**	**395**	**452**	50	65	0/10/57
9	**450f**	**207a**	**204**	50	65	0/0/58
10	**450f**	**207a**	**452**	50	65	0/62/0
11	**127o**	**395**	**204**	50	66	0/22/56
12	**127p**	**395**	**204**	50	65	27/22/0

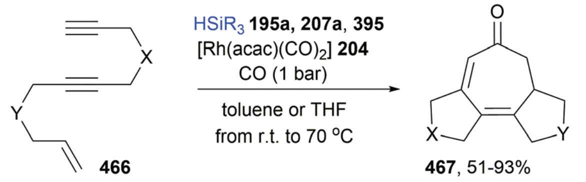
[a] Isolated yield, reaction time 10–20 h.

Ru complex **281** it was also possible to obtain 2,2′-bigermole **505** with 56% yield (Scheme 100).[238]

Diphenylgermane **501** was also used as a reagent in the hydrogermylation of various diynes, with aryl or alkyl spacers between the C≡C bonds leading to germylene–divinylene polymers. The polymerisation was effectively catalysed in the presence of 0.9 mol% of Pd catalysts ($Pd_2(dba)_3$ **338**/$2PCy_3$, $PdCl_2(PCy_3)_2$ **341**). The reactions were carried out at 50–90 °C and the polymers **506** were obtained with M_w = 12 000–83 000 and M_w/M_n = 3.3–12.0 (Scheme 101). They were isolated by precipitation in benzene/propan-2-ol solution. Due to the high conjugation, the germylene–divinylene polymers **506a–d** indicated intense light emission depending on the structures of the monomers. The best results were obtained for anthrylene



Scheme 88 Various catalytic pathways in silacarbocyclisation of 1,6-diynes **127o–p** and **450a–f** furnishing products **453–455**.



Scheme 89 Carobocyclisation of enediynes **466** catalysed by Rh catalyst **204**. Construction of functionalised fused 5-7-5 ring systems **467**.

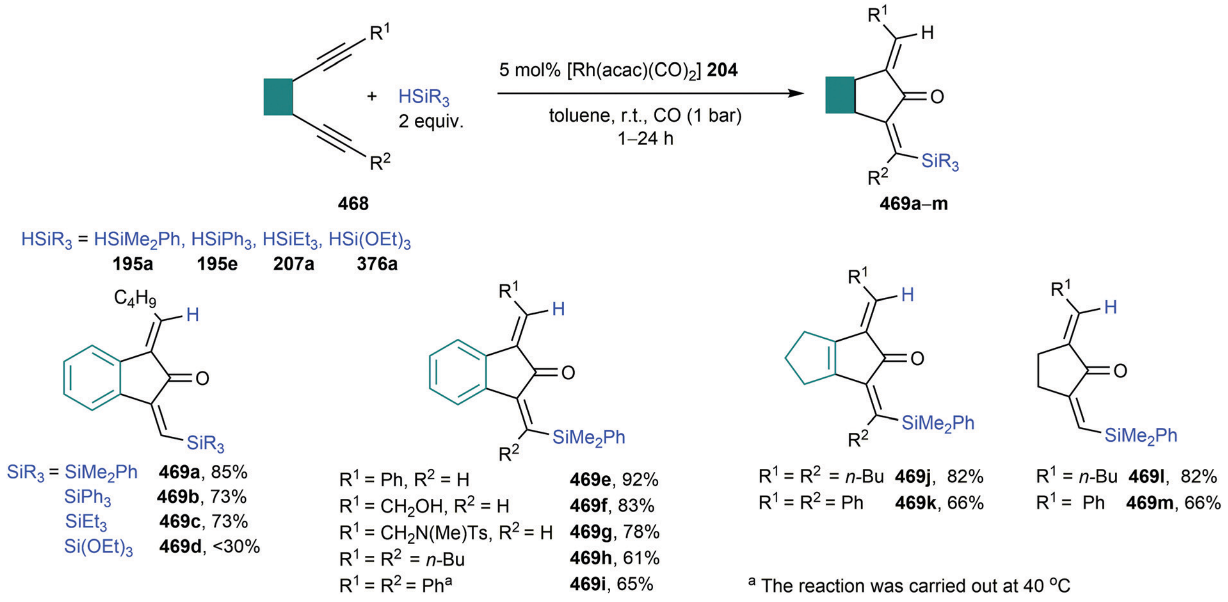
polymer which gave intense and broad UV-Vis spectra from 420 to ≥600 nm with λ_{max} peaks at 440, 464, and 534 nm.[239]

7. Hydrostannation

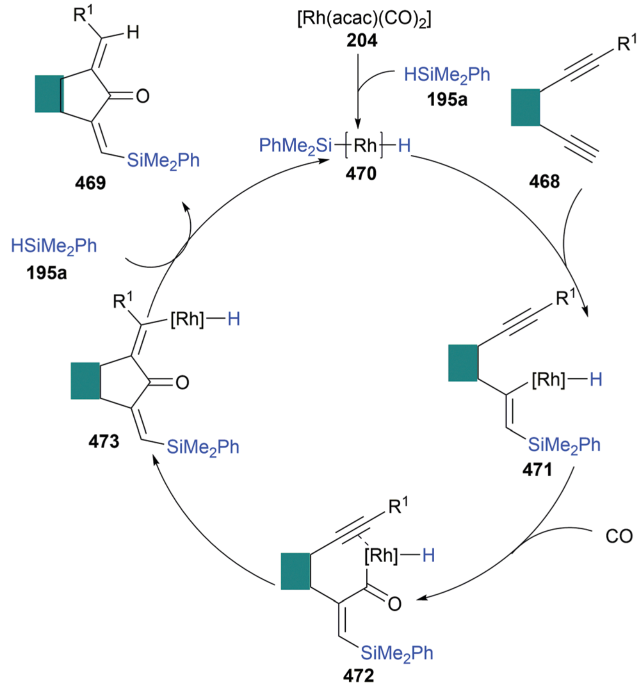
Alkenylstannanes are useful building blocks in the synthesis of various organic compounds (also complex molecules as pharmaceuticals or natural compounds) due to their ability to the formation of the new C–C bonds in Stille coupling reactions.[242–247] The hydrostannation of alkynes, which can occur under a free radical manner, in the presence of a transition–metal catalyst or *via* a hydrogen atom transfer reaction (with trialkyltin hydride used as a nucleophilic species), is the most convenient and popular method for the synthesis of alkenylstannanes.[18,54–56] Despite several papers focused on the hydrostannation of alkynes, the literature concerning the addition of the Sn–H bond to the C≡C bonds in diynes is limited to a few examples based on radical or transition metal-catalyzed transformations.

7.1. Radical hydrostannation of conjugated and separated diynes

Radical hydrostannation was successfully applied in the reaction with 1,3-diynes,[248] as well as diynes possessing an aryl spacer between the C≡C bonds.[249]



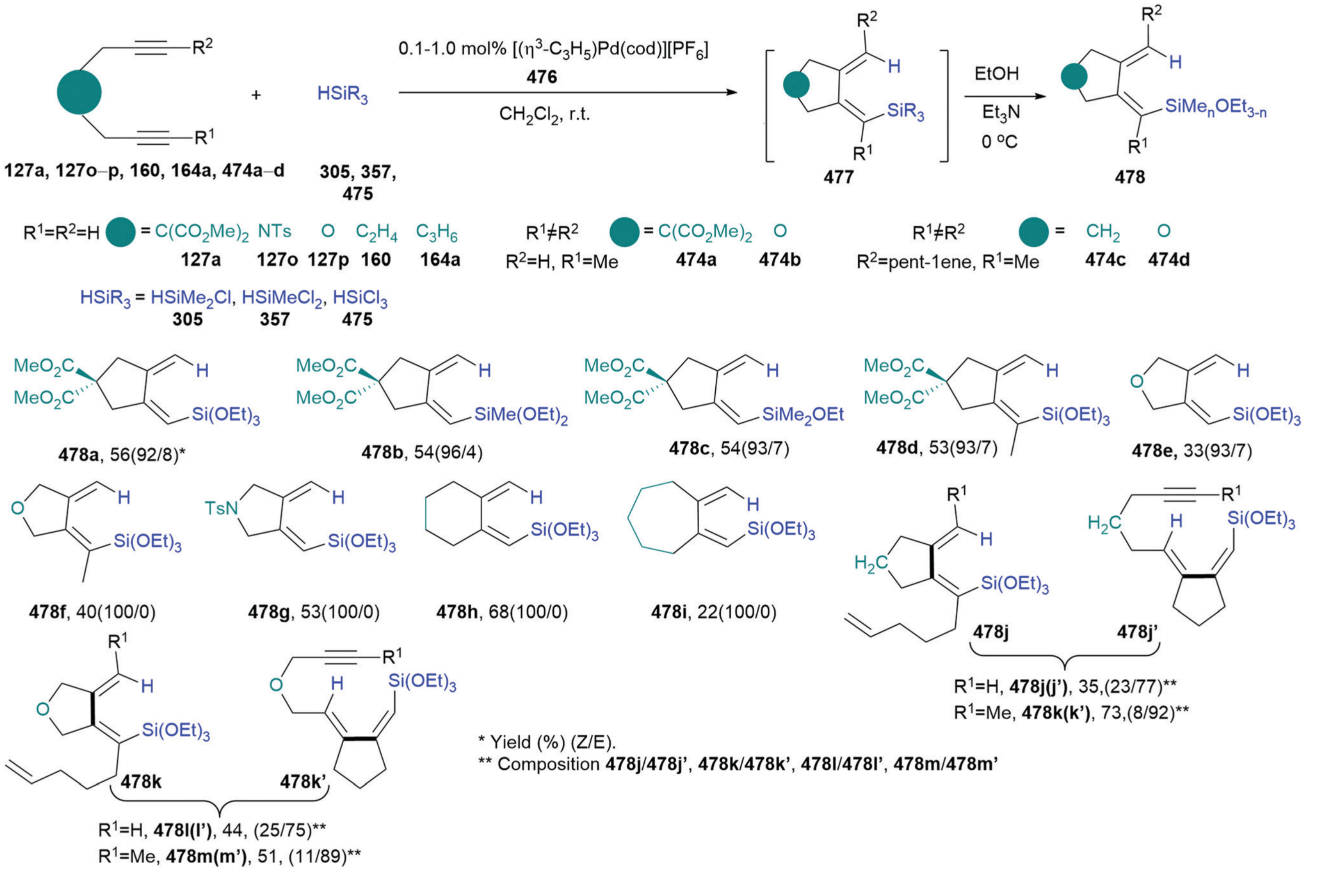
Scheme 90 Carbonylative hydrosilylation of 1,5-diynes **468** with silanes **195a**, **195e**, **207a**, **376a** in the presence of [Rh(acac)(CO)$_2$] **204** and 1 bar of CO.



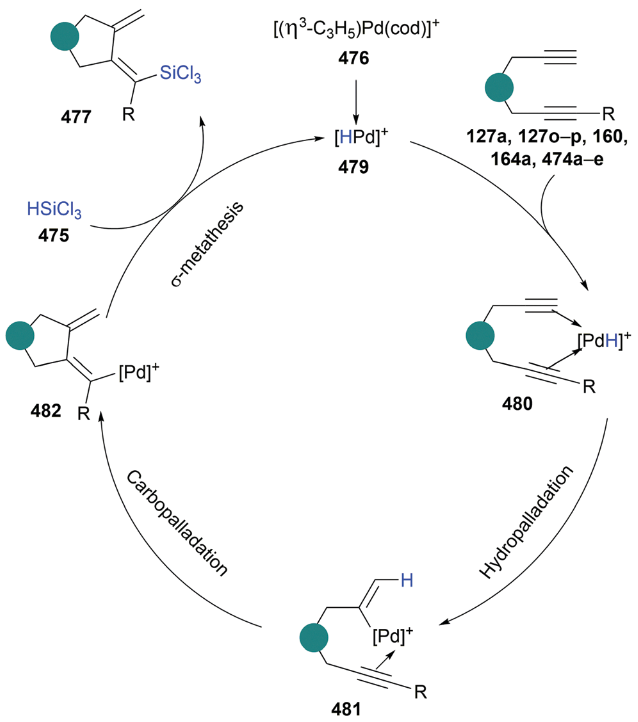
Scheme 91 Proposed mechanism of carbonylative silylcarbocyclisation of 1,5-diynes **468** with silanes catalysed by [Rh(acac)(CO)$_2$] **204**.

Konno *et al.* reported selective radical hydrostannation of 5-benzyloxy-1-trifluoromethyl-5-methyl-hexa-1,3-diyne **507** with tributyltin hydride **508**. The radical is generated from HSn(n-Bu)$_3$ **508** in the presence of Et$_3$B **509** and oxygen (Scheme 102).

Despite the fact that even eight different products might be obtained in hydrostannation due to the presence of double C≡C bonds and different substituents in terminal positions, some of the products might be eliminated. The attack of the radical on the carbon in position β- or γ-can be excluded



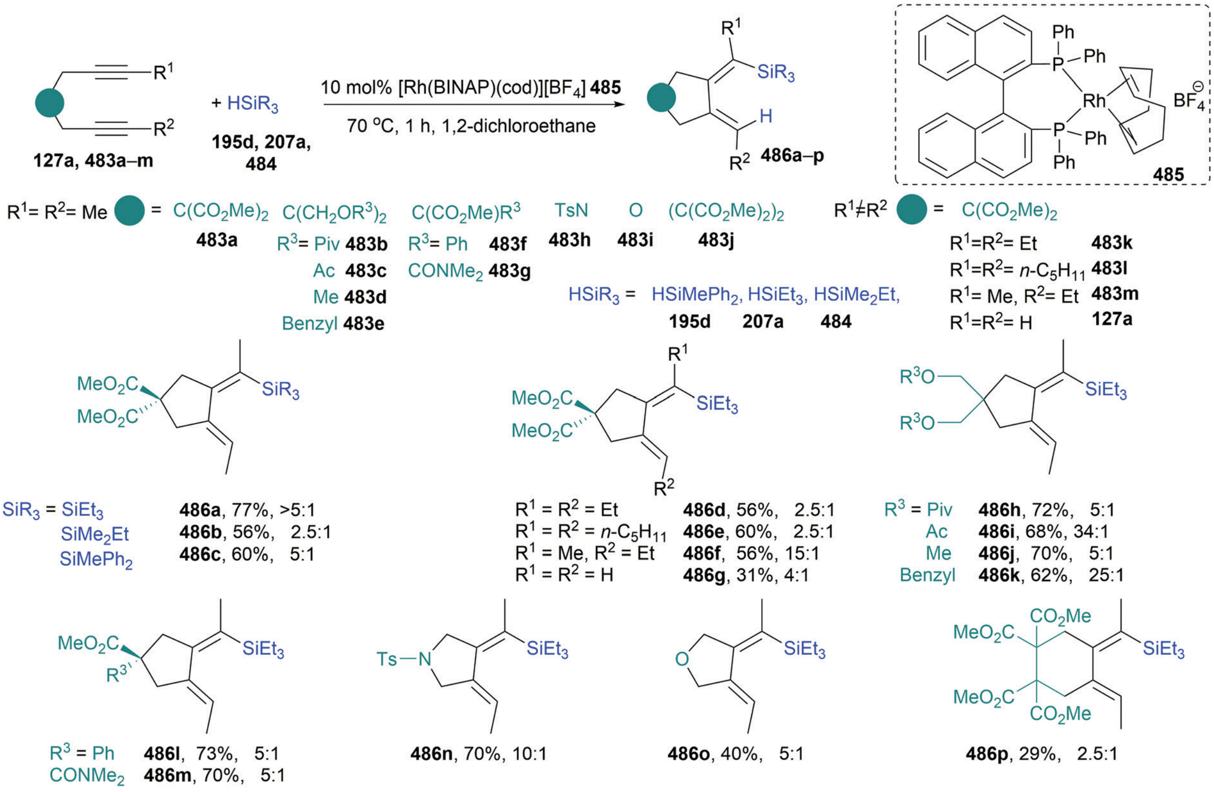
Scheme 92 Cyclisation–hydrosilylation functionalisation of 1,6-, 1,7- and 1,8-diynes **127a**, **127o–p**, **160**, **164a**, **474a–d** catalysed by $[(\eta^3\text{-}C_3H_5)Pd(cod)][PF_6]$ **476**.



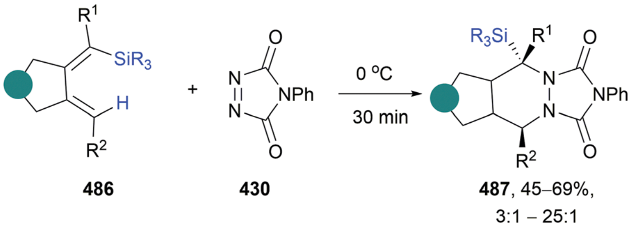
Scheme 93 Mechanism of the cyclisation–hydrosilylation reaction of separated diynes catalysed $[(\eta^3\text{-}C_3H_5)Pd(cod)][PF_6]$ **476**.

because of the lack of resonance of the vinyltin radical. The radical, which has a nucleophilic character attacks the more electrophilic α-carbon atom in **507** with a strong electron-withdrawing CF_3 group. Moreover, the bulky group in δ-position limits the access of the organotin group, therefore product **510** is formed with high regio- and stereoselectivity (Scheme 103). The obtained enyne **510** was generated in 75% yield and was further used in the synthesis of CF_3-substituted (*Z*)-enediyne **517** compounds in iododestannylation/Sonogashira coupling reactions (Scheme 104).[248]

The radical hydrostannation of various diynes and triynes **102c** and **264a–e** was carried out stereoselectively with tributyltin hydride **508**. In the two cases, the (*E*)-products **521a** and **521c** were exclusively formed. The hydrostannation of other diynes **264a–c**, and **264e** occurred with lower selectivity, but still with an excess of the (*E*)-products **521** (Scheme 105). To obtain high selectivity, an elevated temperature (80 °C) has to be maintained. Under lower temperatures, the conversion was not complete and other isomers were also formed. The authors proved the (*E*)-selectivity of the products through ^{1}H NMR spectroscopy by the large coupling constant of the vinyl group (J_{H-H} = 18–19 Hz) and the characteristic values for tin hydrogen coupling (J_{Sn-H} = 124–138 Hz). For 1,3,5-tris[(*E*)-2-(tributylstannyl)vinyl]benzene **521f**, the authors carried out Stille coupling with various bromo-substituted chromophores **522** in the



Scheme 94 Cyclisation–hydrosilylation of 1,6- and 1,7-diynes **127a**, **483a–m** catalysed by Rh complex **485**.

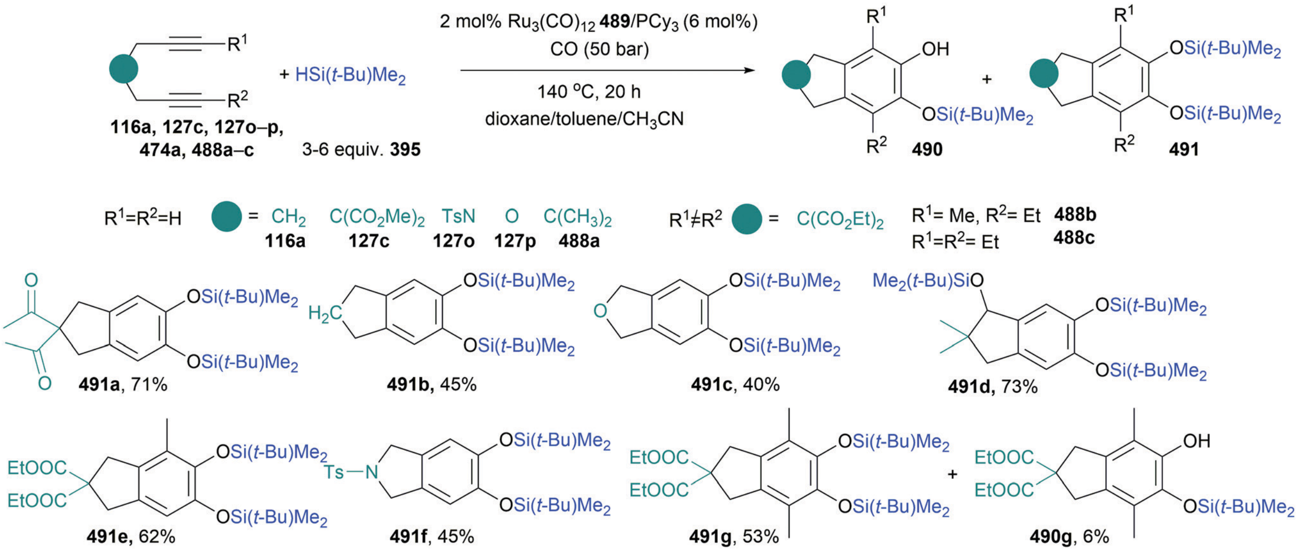


Scheme 95 Cycloaddition of 1,2-dialkilidynecycloalkanes **486** with 4-phenyl[1,2,4]triazole-3,5-dione at 0 °C **430** *via* Diels–Alder reactions.

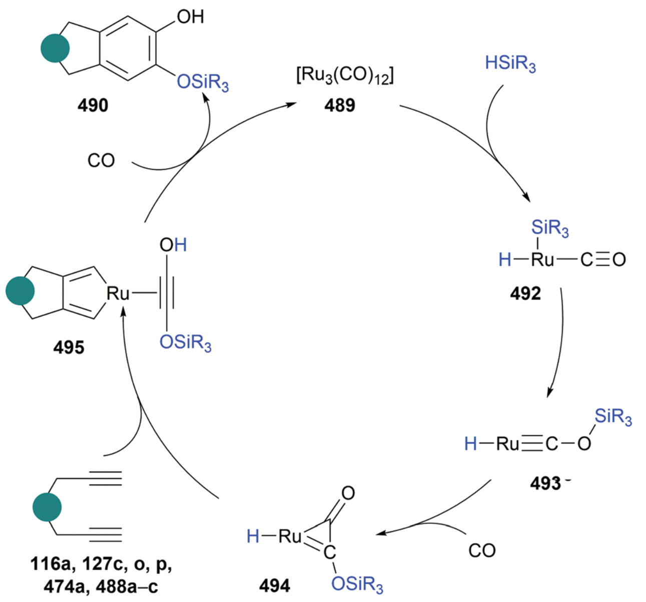
presence of $PdCl_2(PPh_3)_2$ **94** catalyst and CsF **523** or CuI **519** as additives. The products were obtained with moderate or good yield with the retention of the configuration, showing the utility of organotin compounds (Scheme 106).[249] Previously published papers described that radical hydrostannation of diynes led to the mixture of various isomers, which is in opposition to the above-reported results.[250]

The non-catalysed addition of organotin compounds to the C$\equiv$C bond in elevated temperatures occurs relatively easily due to the weak Sn–H bond. The application of dihydrides in the hydrostannation of diynes may lead to cyclic or polymeric products which can be controlled by appropriate selection of the substrates and reaction conditions.[251] The addition of Bu_2SnH_2 **525** to penta-1,4-diyne **526a** in refluxing heptane followed by heating the reaction mixture to 200 °C gave a six-membered heterocycle **528a** with 43% yield. The product was distilled from a viscous polymeric residue together with the small amount of five-membered by-product **530a**. Generally, the terminal addition (path A) of the Sn–H bond to the C$\equiv$C bonds yielded a six-membered heterocycles **528**, whereas the non-terminal addition (path B) led to five-membered adducts **530** (Scheme 107). The regioselectivity could be controlled by the proper selection of the substituents attached to C_{sp} carbon. When the hepta-2,5-diyne **526b** or 1-phenyl-1,4-pendadiyne **526f** were used the five-membered heterocycles **530b** and **530f** were formed as the major regioisomers. The application of monoalkyl-substituted 1,4-diynes **526c–e** on the other hand gave in an excess stannabenzene derivatives **528c–e**. The authors suggested that radical-stabilising substituents in 1,4-diynes mainly led to stannoles **530**, whereas 6-substituted hexa-1,4-diynes **526g–i** gave the six-membered adducts **528g–i** (Scheme 107).[252,253] The substitution of CH_2 spacer between alkynyl groups, in the case of 3-organyl-substituted 1,5-diynes, did not influence process regioselectivity leading mainly to the six-membered products.[254–256]

The hydrostannation of diynes possessing the p-block element as a linker between alkynyl groups gave in major an attractive six-membered rings with two heteroatoms, which are useful synthons in organic synthesis. For instance, the hydrostannation of (dialkylamino)dialkynylboranes **531a–c** with dimethylstannane **532** yielded 1,1-dimethyl-1-stanna-4-bora-2,5-cyclohexadies **533**, which could be further converted *via* *trans*-amination to 4-amino derivatives **534** or *via* solvolysis of **533** to alkoxy derivatives **535**. These latter were precursors for 4-alkyl-1,1-dimethyl-1-stanna-4-boracyclohexadienes **537** or lithium-1,1,2,4,4,6-hexamethyl-1-stanna-4-borata-2,5-cyclohexadiene which



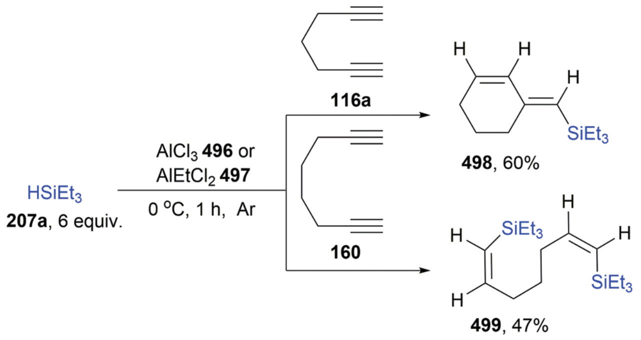
Scheme 96 $Ru_3(CO)_{12}$ **489** catalysed carbocyclisation of 1,6-diynes **116a**, **127c**, **127o–p**, **488a–c** with HSi(*t*-Bu)Me_2 **395** and CO.



Scheme 97 Mechanism of the Ru-catalyzed **489** reaction of 1,6-diynes with silanes and CO.

were obtained in high yield **536** (Scheme 108).[257] Analogous ring systems with different heteroatoms could also be obtained for the hydrostannation of diynes containing Si, Sn, or P atoms as spacers between alkynyl groups.[258–260]

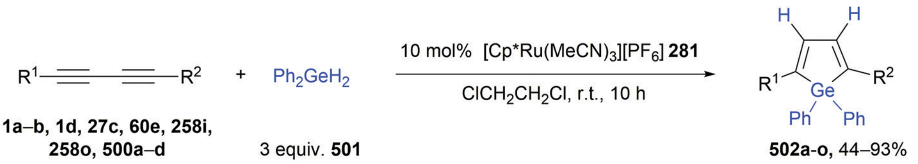
The diyne structure, as well as reaction conditions, have a crucial influence on the product formed. The hydrostannation of α,ω-diynes, such as 1,4-diethynylbenzene **116c**, nona-1,8-diyne **164a**, and hexa-1,5-diyne **541** with diorganotin dihydrides **525**, **532**, **538–540** at high temperatures gave rubber-like polymers. However, for hexa-1,5-diyne **541** small amounts of 1-stanna-2,6-cycloheptadiene **544** derivatives were isolated as well. The polymer formation occurred *via* intermolecular poly-addition of alkenyldiorganoltin hydride **542** whereas, the cyclic product is obtained through its intramolecular cyclisation (Scheme 109). The molecular weight of the polymers depended on both the α,ω-diynes, and organotin compounds (Table 14).[261] Similar observations were made when *p*-phenylene-bis(dimethyltin hydride) **545** was used in the poly-addition to α,ω-diynes.[262]



Scheme 98 Lewis acid (**496** or **497**) catalysed hydrosilylation of hepta-1,6-diyne **116a** or octa-1,7-diyne **160**.

The appropriate selection of the reaction condition was also crucial for the synthesis of tin-containing seven-membered heterocycles (stannepines) by the hydrostannation of (*Z*)-endiynes. Mild reaction conditions and the presence of base led to the desired heterocycles instead of polymeric material.[263]

The hydrostannation of *o*-diethynylbenzene **545** with diorganotin hydrides **532**, **538**, **540**, and **546** yielded, in addition to polymers **549**, the seven and fourteen-membered tin-containing heterocycles (**547** and **548**) with low or moderate yields.[264,265] The highest yield of the fourteen-membered ring system was observed for **548d** when ethylphenyltin dihydride **546** was used, whereas the benzostannepin **547b** was formed in 22% yield when diethyltin dihydride **538** was applied. Nevertheless, in all cases, the polymers were the main products (Scheme 110 and Table 15).



Scheme 99 Double *trans*-hydrogermylation of 1,3-diynes **1a–b**, **1d**, **27c**, **60e**, **258i**, **258o**, and **500a–d** with diphenylgermane **501** in the presence of $[Cp^*Ru(MeCN)_3][PF_6]$ **281**.

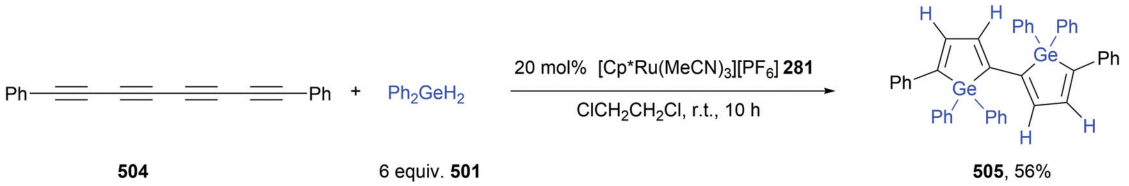
Table 13 Synthesis of 2,5-disubstituted germoles **502a–o** *via* double *trans*-hydrogermylation of 1,3-diynes with diphenylgermane **501**

Entry	R^1	R^2	Diyne	Product	Isolated yield [%]
1	Ph	Ph	**1a**	**502a**	93 (90)[b]
2	4-FC_6H_4	4-FC_6H_4	**1b**	**502b**	66
3	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**1d**	**502c**	80
4	3-Thienyl	3-Thienyl	**27c**	**502d**	94
5	3-BrC_6H_4	3-BrC_6H_4	**258i**	**502e**	93
6	Cyclohexen-1-yl	Cyclohexen-1-yl	**258o**	**502f**	70
7	2-Naphtyl	2-Naphtyl	**280a**	**502g**	87
8	3-(pin)BC_6H_4	3-(pin)BC_6H_4	**280d**	**502h**	91
9	4-$O_2NC_6H_4$	4-$O_2NC_6H_4$	**500a**	**502i**	40
10	5-Pyrimidyl	5-Pyrimidyl	**500b**	**502j**	69
11	Ph	4-$MeOC_6H_4$	**60e**	**502k**	95
12	Ph	4-CNC_6H_4	**500c**	**502l**	71
13	Ph	4-ViC_6H_4	**280e**	**502m**	87
14	4-MeC_6H_4	*n*-C_6H_{13}	**500d**	**502n**	44
15	4-$Me_3SiC_6H_4$	4-$Me_3SiC_6H_4$	**500e**	**502o**	75

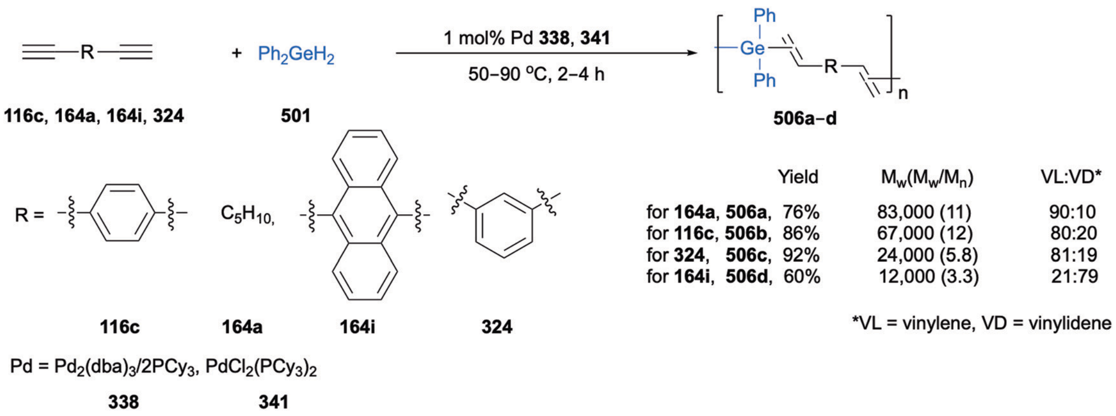
[a] Diyne : **501** = 1 : 3, 1,2-dicholoroethane, r.t., 10 mol% of $[Cp^*Ru(MeCH)_3][PF_6]$ **281**. [b] 1.2 equiv. of **501**.

The obtained heterocyclic compounds and polymeric materials could be readily transformed with the retention of configuration into alkenyl iodides by the reaction with I_2 **418**. Polymer degradation with iodine **418** revealed that the polymer product contained *Z*,*Z*-, *Z*,*E*- and *E*,*E*-units.[265]

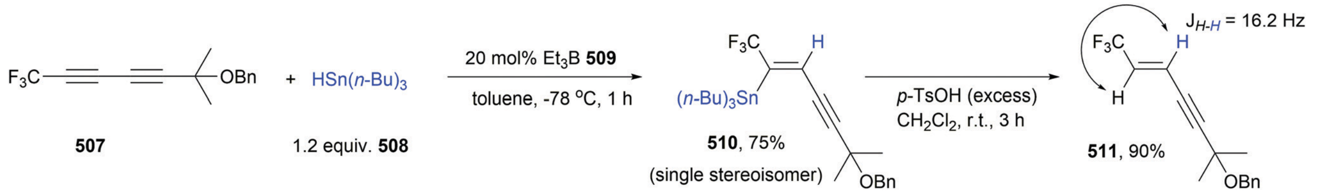
The tin-containing six-membered heterocycles are attractive precursors in the preparation of various 15 group heterobenzenes.[266,267] In 1971, Ashe reported the synthesis of arsabenzene **555** based on the arsenic/tin exchange. The l,4-dihydro-l,l-dibutylstannobenzene **528a** was converted in a one-step procedure to desired product **555** through the reaction with the arsenic trichloride **553**. Similarly, **528a** reacted with phosphorus tribromide **550** to give phosphabenzene **552.**[268] The same research group extended the scope of 15 group heterobenzenes to stibabenzenes **558**[269] and bismabenzene **561**[270] in an analogous manner. However, treatment of l,4-dihydro-l,l-dibutylstannobenzene **528a** with $SbCl_3$ **556** or $BiCl_3$ **559** gave 1-chloro-1-stibacyclohexa-2,5-diene **557** or 1-chloro-1-bismacyclohexa-2,5-diene **560**, respectively. The group 15 heterobenzenes underwent Diels–Alder reactions with hexafluorobutyne **562** to give **563.** The reactivity of heterobenzenes increased with the higher atomic number of heteroatom. For instance, stilabenzene **558** reacted rapidly with hexafluorobutyne **562** at 0 °C, arsabenzene **555** at



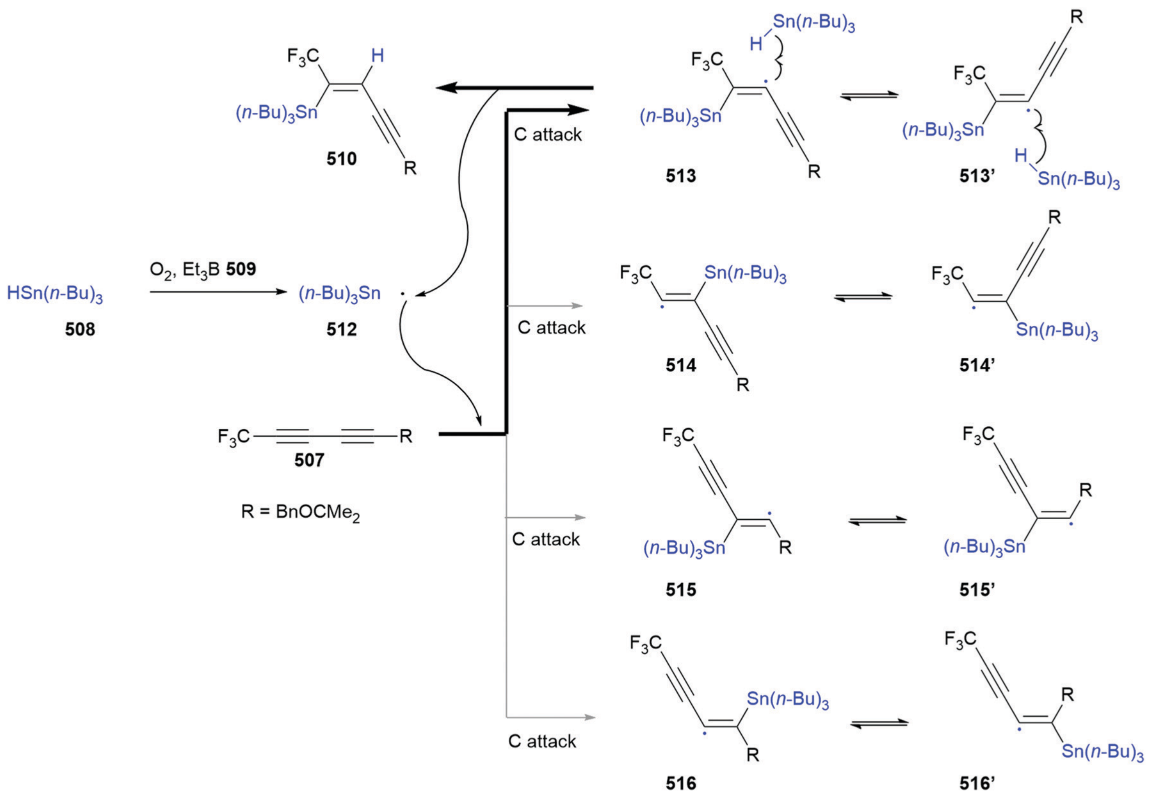
Scheme 100 Synthesis of 2,2-bisgermole **505** in hydrogermylation reaction of 1,8-diphenylocta-1,3,5,7-tetrayne **504** with diphenylgermane **501**.



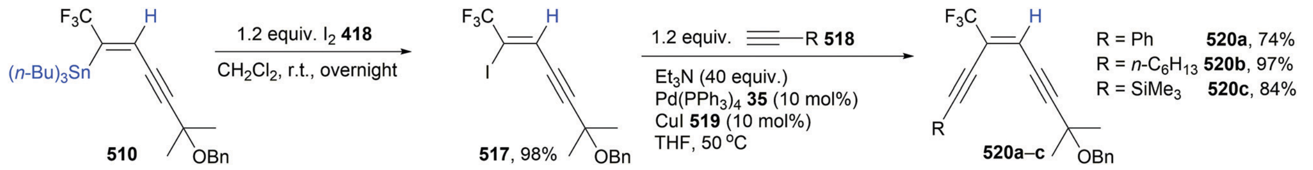
Scheme 101 Polymerisation of 1,*n*-diynes **116c**, **164a**,**164i**, and **324** with diphenylgermane **501** *via* hydrogermylation reaction catalysed by Pd-complexes **338** and **341**.



Scheme 102 Radical hydrostannation of conjugated diyne **507** with tributyltin **508** followed by the assignment of the stereoselectivity in the destannation reaction.



Scheme 103 Proposed mechanism of the radical hydrostannation of diyne **507** with tributyltin hydride **508**.



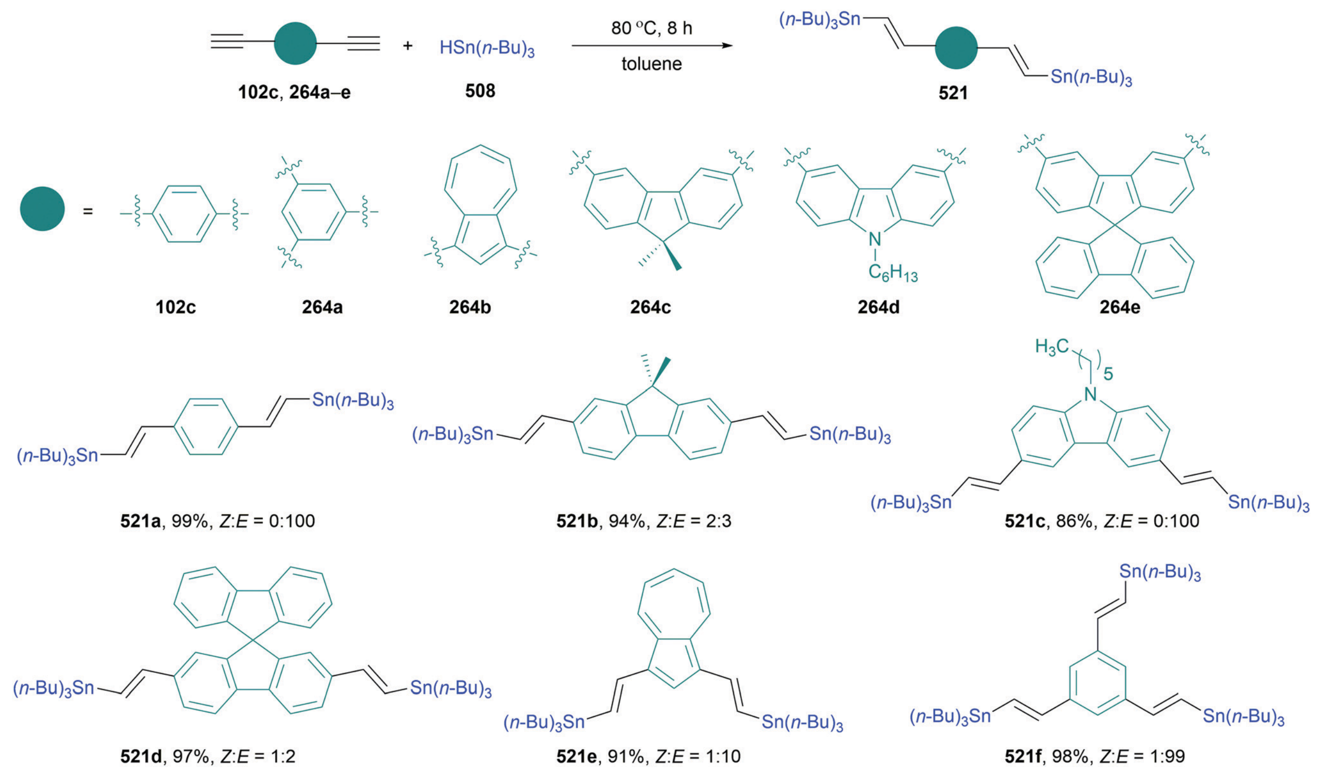
Scheme 104 Synthesis of stereo-defined CF$_3$-substituted (*Z*)-enediyne compounds **520a–c** in iododestannylation/Sonogashira coupling reactions.

room temperature, whereas phospabenzene **552** was converted to Diels–Alder adduct at 100 °C (Scheme 111).[270] The 2- and 4-subtituted heterobenzenes could be also synthesised through hydrostannation of appropriate 1,4-diynes. Further transformation of the stannabeznes to the phospha- or arsabeznene derivatives could also be achieved.[271–273] The same procedure was adopted to the formation of borabenzenes.[253]

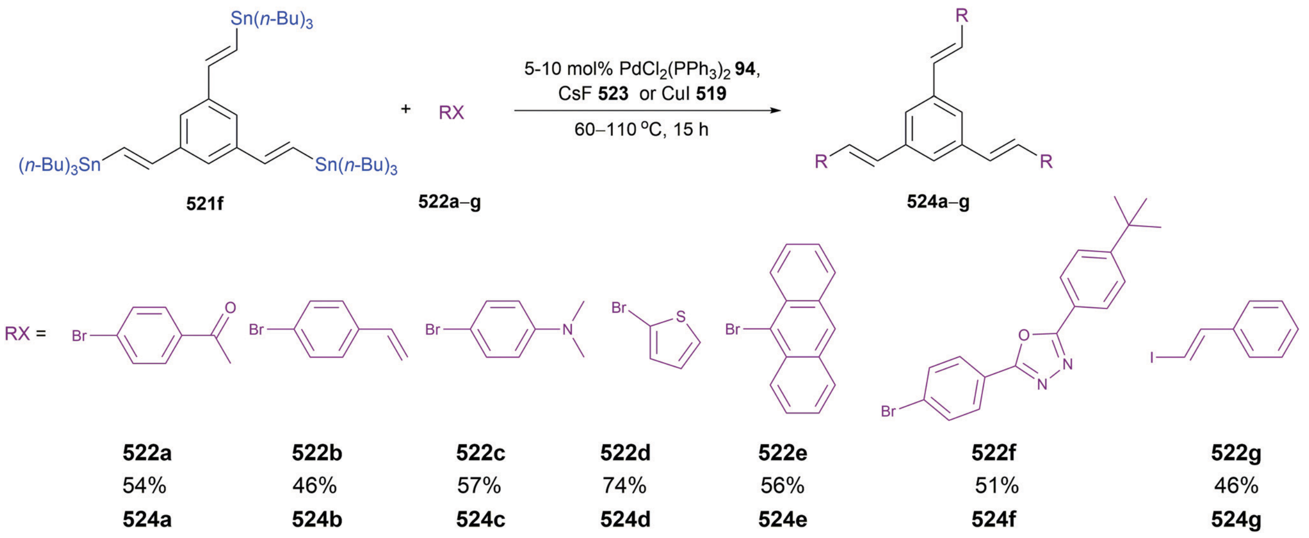
The hydrostannation of penta-1-4-diyne **526a** with Bu$_2$SnH$_2$ **525** was used in the synthesis of 13-thiaarachidonic acid **573**. Compounds **573** is a time- and O$_2$-dependent irreversible inhibitor of soybean lipoxygenase and was prepared in reaction sequence presented in Scheme 112.[274] The process was characterised by excellent stereoselectivity and satisfactory yields of each of the individual reaction steps.

7.2. Transition metal-catalysed hydrostannation of diynes

The phosphine-free palladium Pearlman's catalyst Pd(OH)$_2$/C **575** was found to be effective in the hydrostannation of 1,6-diynes **127a**, **127j**, **127m**, **127p**, **394d** and **574a–c** with HSn(*n*-Bu)$_3$ **508**, which generated 1,2-dialkylidenecyclopentenes with the

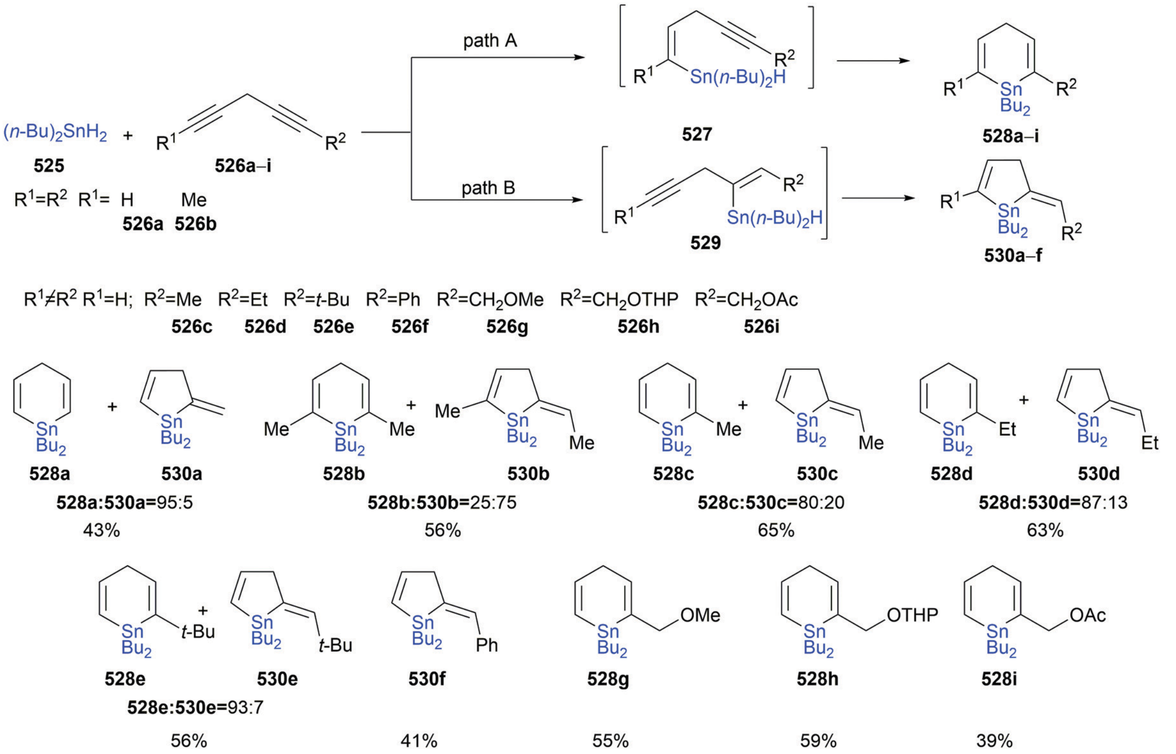


Scheme 105 Radical hydrostannation of diynes and triynes **102c**, **264a–e** with tributyltin hydride **508**.

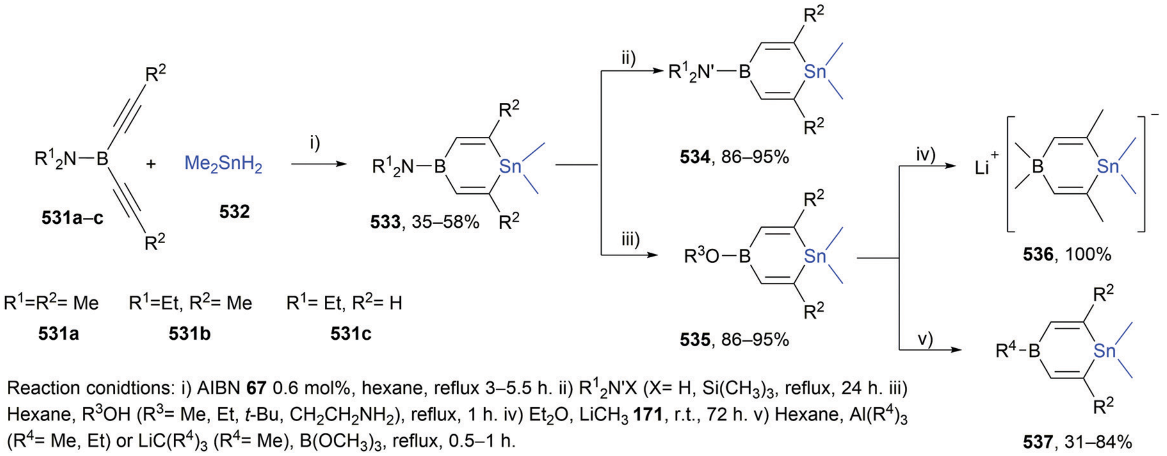


Scheme 106 Cross-coupling reaction of electrophiles RX **522** with 1,3,5-tris[(*E*)-2-(tributylstannyl)vinyl]benzene **521f** catalysed by $PdCl_2(PPh_3)_2$ **94**.

tributylstannyl group **576.** This stannylative coupling was effective for various 1,6-diynes, including those possessing hydroxyl groups or protected alcohols, as well as reagents with heteroatoms in the propargylic position. The reactions occurred with high yields of the products **576** (58–95% yield) (Scheme 113). Several other complexes such as $Pd_2(dba)_3$ **338,** Pd/C **446,** $Pd(acac)_2$ **577** gave the desired cyclised product **576a** with the yield >75%. Adding 1 or 2 equiv. of PPh_3 or dppb to $Pd_2(dba)_3$ **338,** gave a complex post-reaction mixture with less than 15% of **576a.** The authors suggested that the phosphine coordinates to the metal centre, blocking the possibility chelate formation with the 1,6-diynes **127a, 127j, 127m, 127p, 394d,** and **574a–c.** The mechanism of the process begins with the oxidative addition of $HSn(n\text{-}Bu)_3$ **508** and chelation of the 1,6-diyne to give **579.** The formation of the product might occur within two possible pathways based on stannylpalladation (path A) or hydropalladation/carbopalladation (path B) (Scheme 114). There was no information on which cycle is more probable. Terminally substituted 1,6-diynes **584a–c** were also reactive in this cyclisation

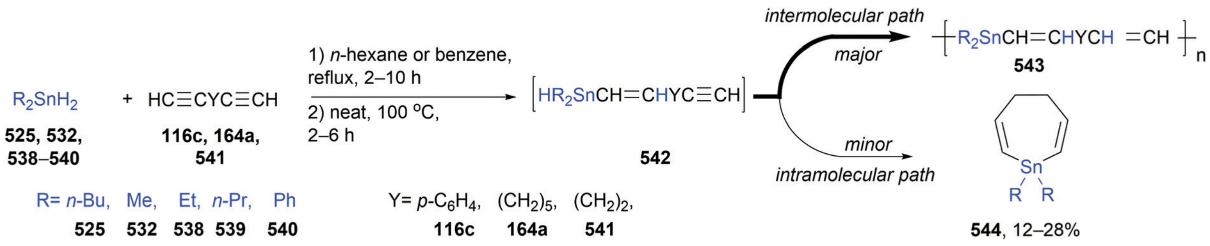


Scheme 107 Synthesis of stannabenzens **528** and stannoles **530** *via* hydrostannation of hepta-2,5-diyne **526b** and 1,4-diynes **526a** and **526c–i**.



Reaction conidtions: i) AIBN **67** 0.6 mol%, hexane, reflux 3–5.5 h. ii) R$^1{}_2$N'X (X= H, Si(CH$_3$)$_3$, reflux, 24 h. iii) Hexane, R^{3}OH (R^3= Me, Et, *t*-Bu, CH$_2$CH$_2$NH$_2$), reflux, 1 h. iv) Et$_2$O, LiCH$_3$ **171**, r.t., 72 h. v) Hexane, Al(R^4)$_3$ (R^4= Me, Et) or LiC(R^4)$_3$ (R^4= Me), B(OCH$_3$)$_3$, reflux, 0.5–1 h.

Scheme 108 Hydrostannation of (dialkylamino)dialkynylboranes **531a–c** with dimethylthin dihydride **532**, and further transformations.



Scheme 109 Synthesis of linear polymers **543** through the hydrostannation of α,ω-diynes **116c**, **164a**, **541** with diorganotin dihydrides **525**, **532**, **538–540**.

Table 14 Results of hydrostannation of α,ω-diynes **116c**, **164a**, **541** with diorganotin dihydrides **525**, **532**, **538–540** (Scheme 109)

Entry	α,ω-Diyne	R_2SnH_2	Molecular weight, M_w	Degree of polym., n
1	**541**	**540**	75 000[a]	170
2	**541**	**532**	—[b]	—
3	**541**	**538**	—[b]	—
4	**541**	**539**	50 000	180
5	**541**	**525**	50 000	160
6	**164a**	**540**	100 000	250
7	**164a**	**525**	45 000	130
8	**116c**	**540**	65 000	160

[a] Molecular weight of benzene-soluble fraction. [b] Polymer insoluble in benzene after heating under vacuum.

Table 15 Results for hydrostannation of *o*-diethynylbenzene **545** with diorganotin hydrides **532**, **538**, **540**, and **546** (Scheme 110)

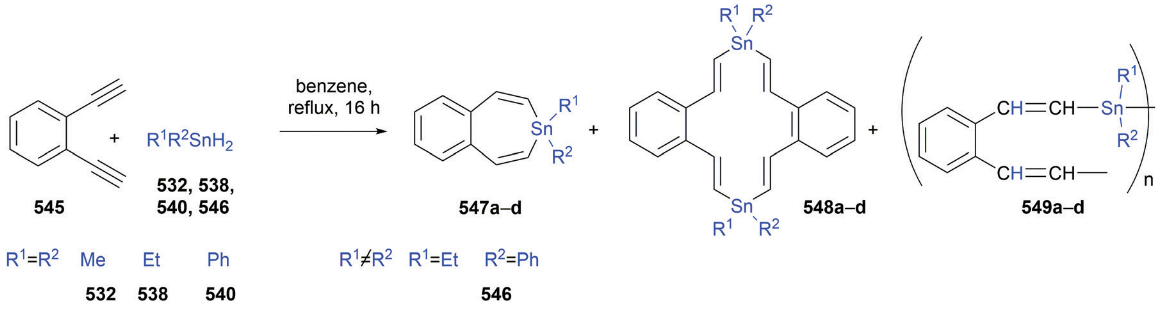
	$R^1\ R^2SnH_2$				Yield [%]		
Entry					**547**	**548**	**549**
1	**532**	Me	Me	**a**	10(6)[a]	—	80
2	**538**	Et	Et	**b**	22(17)[a]	—	50
3	**540**	Ph	Ph	**c**	—	17(12)[a]	70
4	**546**	Ph	Et	**d**	5	41(25)[a]	50

[a] Yield (%) after extensive purification.

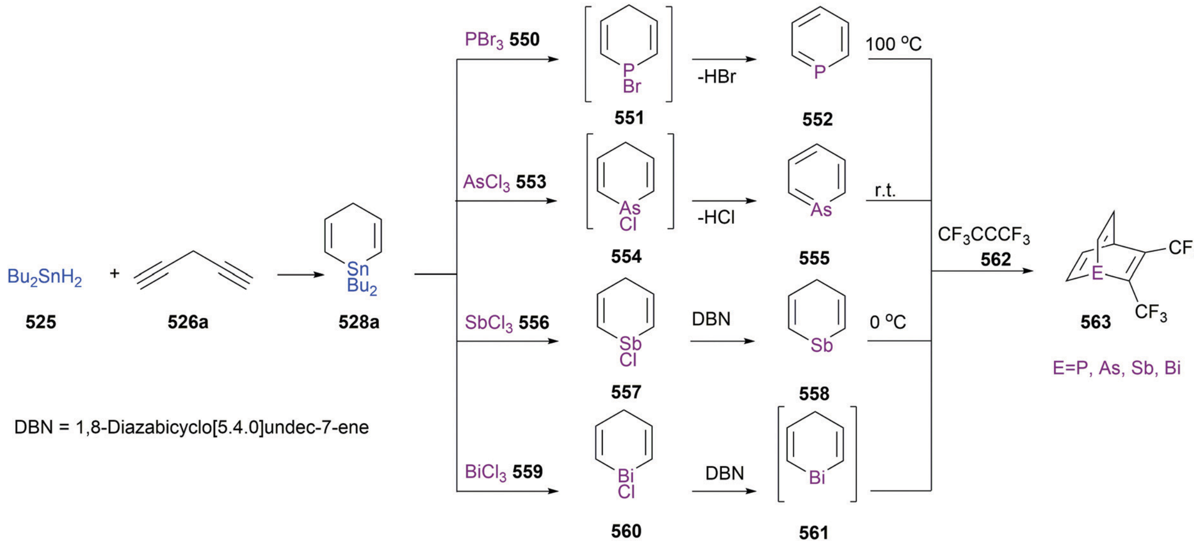
reaction, but the electronic properties of the diyne substituents strongly influenced the selectivity, and a mixture of cyclised **585** and **586** and linear **587** vinylstannanes were generated. The linear product was predominantly formed (**587c**, 59%) in the case of hydrostannylation of the silyl-substituted reagent **584c** (Scheme 115).[275,276] The obtained dialkylidenecyclopentenes functionalised with stannyl group **576a–c** were used in several destannylation reactions: Diels–Alder with *N*-phenyl maleimide **387** to **588** followed by protodestannylation to **589**, Stille coupling with *p*-iodoanisole **58**, and homocoupling of **576a**, showing the high utility of this reagent in organic synthesis (Scheme 116).

Furstner *et al.* reported that conjugated 1,3-diynes **594**, as well as non-conjugated 1,*n*-diynes **595** (with an unprotected hydroxyl group in the propargyl position), underwent double or site-selective *trans*-monohydrostannation depending on the reaction conditions in the presence of catalytic $[Cp^*RuCl]_4$ **596**. The process was found to be temperature-dependent. When the reaction was carried out in boiling 1,2-dichloroethane (at 80 °C), the site-selective reaction is favoured, while at a lower temperature (especially at −40 °C) bishydrostannylation occurred in a large amount. Irrespective of the alcohol type (primary, secondary, or tertiary) the *trans*-hydrostannylation occurred with high selectivity (Scheme 117). Additionally, the type of substituent attached to the second alkyne influence the process selectivity with bulkier groups giving better selectivity towards *trans*-hydrostannation. The selectivity of the stannylation of diyne **594** from the propargylic side resulted from the hydrogen bonding of OH with the polarised [Ru–Cl] bond of **596**. The propargylic alcohol readily forms an adduct with the Ru-complex under room or higher temperature, while binding the alkyne occurs only at a lower temperature. The reaction was also effective for *trans*-monohydrostannation of 1,*n*-diynes **595** to give products **599a–e** (Scheme 118). The strong directing effect of the hydroxyl group in the propargylic position was responsible for the high process selectivity. The stannyl-substituted products might be directly transformed to (*E*)-conjugated enynes by the protodestannation reaction with copper diphenylphosphinate $CuOP(O)Ph_2$ **601** in DMF. The site-selective *trans*-hydrostannation was applied in the total synthesis of typhonoside series of glycolipids **608** and **614**, which have neuroprotective properties (Scheme 119). Moreover, the application of this transformation permitted for late-stage modification of the bioactive compound, which was illustrated by the synthesis of the fluoroalkene sphingosine analog. The replacement of tin with fluorine was carried out with F-TEDA-PF_6 **615** in the presence of silver phosphinate $AgOP(O)Ph_2$ **616**.[63]

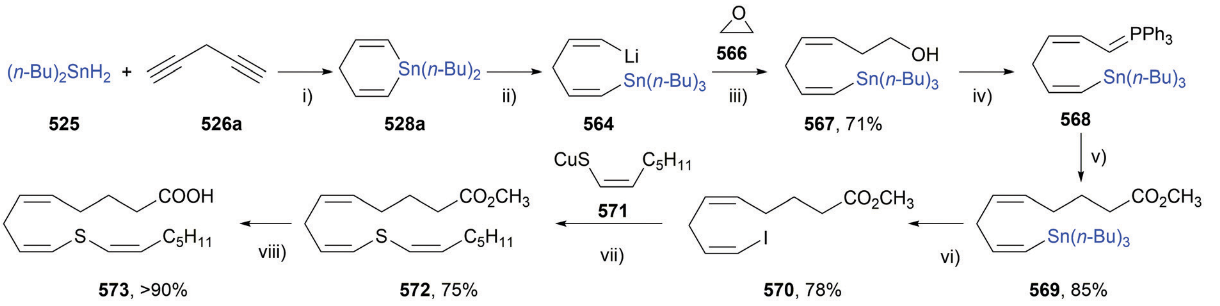
In 1990 Zhang *et al.* reported the palladium- and molybdenum-catalysed addition of Sn–H to C≡C bonds leading to vinylstannanes in high regio- and stereoselectivity. Although the authors described in detail the hydrostannation of mono alkynes, a few examples of diyne reactivity was also reported. The readily available and air-stable catalyst $PdCl_2(PPh_3)_2$ **94** was applied in the hydrostannation of symmetrical and unsymmetrical 1,3-diynes. The addition of $HSn(n\text{-}Bu)_3$ **508** to symmetrically substituted dodeca-3,5-diyne **13a** under mild reaction conditions and a short reaction time (10 min) gave (*E*)-enyne **618a** in 78% yield. The n-Bu_3Sn moiety was attached to the carbon atom contiguous to the C≡C unit. The further addition of Sn–H bond to the unreacted triple C≡C bond was not possible and led to the decomposition of **618a**. Similar regio- and stereoselectivity was observed when unsymmetrically substituted diyne **617** terminated with ethynyl group was used. In turn, the hydrostannation of deca-1,3-diyn-1-yltrimethylsilane



Scheme 110 Hydrostannation of *o*-diethynylbenzene **545** with diorganotin hydrides **532**, **538**, **540**, and **546**.

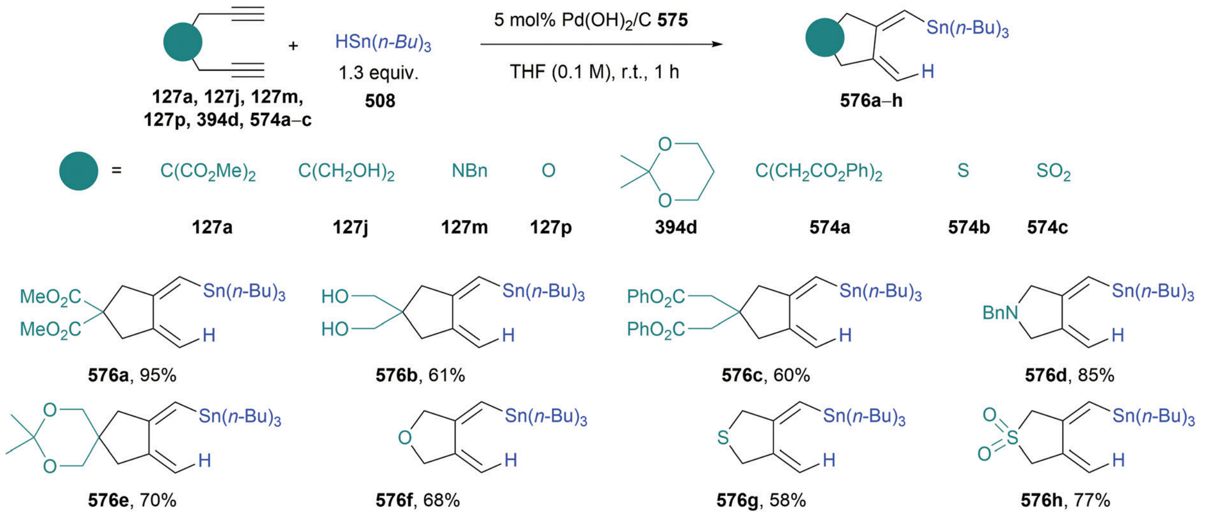


Scheme 111 Synthesis of heterobenzenes **552**, **555**, **558**, and **561** through the 15 group element/tin exchange.

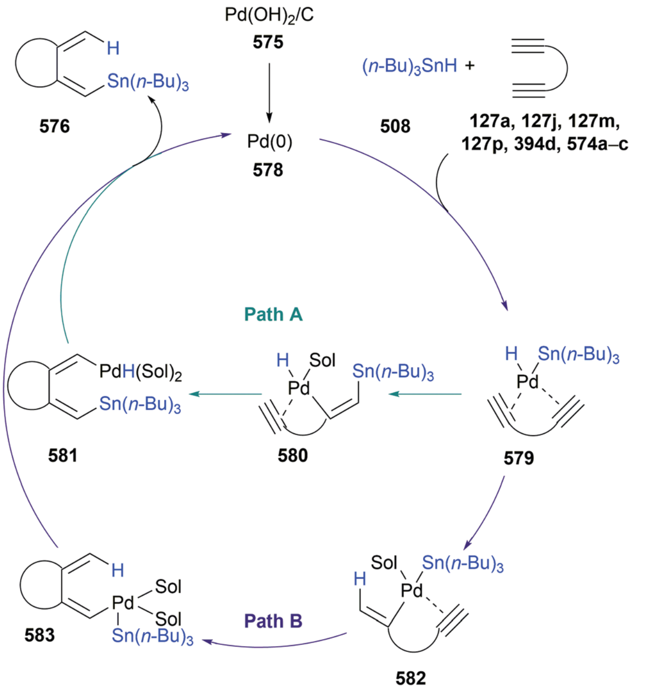


i) heptan, reflux, AIBN **67**, ii) *n*-BuLi **85**, -40 °C, 1.5 h, iii) $BF_3•Et_2O$ **565**, iv) a)TsCl, pyridine, 0 °C–r.t., 5 h, b) NaI, acetone, reflux, 4 h, c) PPh_3, MeCN, 14 h, d) LDA, -78 °C, 1 h, v) HMPA, -78 °C, 40 min. vi) I_2 **418**, DCM, pyridine, -45 °C, 1.5 h, vii) DMF, 105 °C, 6 h, viii) LiOH/DME = 1/1, r.t., 4 h.

Scheme 112 Synthetic path to 13-thiaarachidonic acid **573** *via* hydrostannation of penta-1-4-diyne **526a**.



Scheme 113 The stannylative coupling of 1,6-diynes **127a**, **127j**, **127m**, **127p**, **394d**, and **574a–c** with tributyltin hydride **508** catalysed by $Pd(OH)_2/C$ **575**.



Scheme 114 Proposed mechanism of stannylative coupling of 1,6-diynes with tributyltin hydride **508**. Both pathways A and B are possible.

180a gave monohydrostannation product **618b** in 86% yield. The presence of trimethylsilyl moiety caused the addition of Sn–H to C$\equiv$C bond adjacent to the alkyl substituents. Intriguingly, the hydrostannation of 1,2-bis(trimethylsilyl)ethyne did not occur at all, thus the SiMe$_3$ moiety in **180a** could be considered as a directing group (Scheme 120).[277]

The same palladium catalyst PdCl$_2$(PPh$_3$)$_2$ **94** was applied for the tin-functionalised dienynes by the hydrostannation of (*Z*)- or (*E*)-endiynes with HSn(*n*-Bu$_3$) **508** in just 20 minutes at room temperature. The protocol was suitable for the symmetrical and unsymmetrical (*Z*)-endiynes **619a–j** with various (aryl, alkyl, alkoxy, silyl) substituents. Among many possible isomers only α-products with the tin atom located on the carbon atom adjacent to C$=$C bond, were formed. Nevertheless, very high selectivity was noticed only for symmetrical (*Z*)-endiynes. In the case of unsymmetrical (*Z*)-trideca-5-en-3,7-diyn-1-ol **619e** an equimolar mixture of α-isomers and α′-isomers was observed since, the HSn(*n*-Bu$_3$) **508** did not distinguish in its addition between the two triple bonds. Intriguingly, the hydrostannation of SiMe$_3$ substituted unsymmetrical diynes with HSn(*n*-Bu)$_3$ **508** gave exclusively α-isomers, thus the silyl moiety acted as a directing group. The addition of Sn–H bond occurred on the silyl-unsubstituted C$\equiv$C bond with tin moiety attached at C$_\alpha$ (Scheme 121).[278]

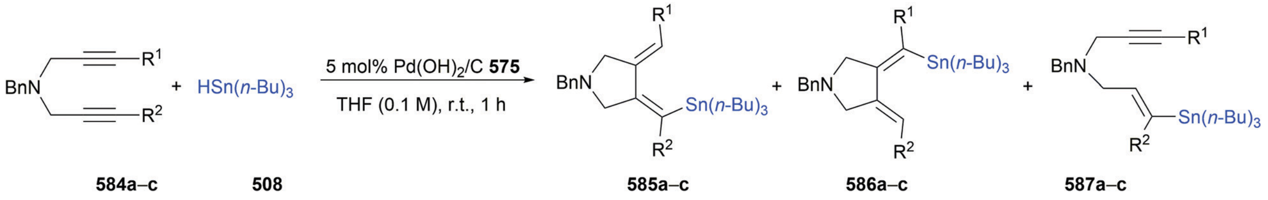
Notably, the geometry of endiynes double bond had a crucial influence on reaction regioselectivity. The hydrostannation of unsymmetrical (*E*)-endiynes **621a–d** in the same reaction conditions gave a mixture of α- and β-isomers even in the presence of the directing SiMe$_3$ group. However, the silyl-substituted C$\equiv$C bond, similar to hydrostannation of (*Z*)-endiynes, remained unreactive. The ratio of α- and β-isomers was dependent on the second substituent and ranging from 64 : 36 to 94 : 6 (Scheme 122).[278]

(*Z*,*E*)-Stannylated dienynes **620** were also found to be attractive building blocks in organic synthesis. Bujard *et al.* reported the synthesis of (*Z*,*E*)-dienediynes through the iododestannylation of **620d** and **620i** with NIS **624** and subsequent Pd/Cu catalysed coupling of vinyl iodide **625** with terminal alkyne **626a–c**. The process was highly stereoselective and gave desired products **627a–c** in good isolated yields (47–51%) (Scheme 123). The authors suggested that the obtained acyclic dienediynes are promising substrates for the synthesis of more complex molecules such as neocarzinostatin chromophore which was found to be an antitumor antibiotic.[279,280]

Kazmaier *et al.* described the Mo(CO)$_3$(NC-*t*-Bu)$_3$ **629** catalysed hydrostannation of C$\equiv$C bonds. Although in the report a detailed research on hydrostannation of alkynes was presented, a single example of hydrostannation of a diyne was presented. The hydrostannation of diynoic ester **628**, possessing internal and terminal triple C$\equiv$C bonds, with HSn(*n*-Bu)$_3$ **508** occurred preferentially at the internal C$\equiv$C bond bearing electron-withdrawing group. The reaction was relatively selective leading to a mixture of α- and β-isomers (**630**/**631** = 82/18) in 74% isolation yield (Scheme 124).[281]

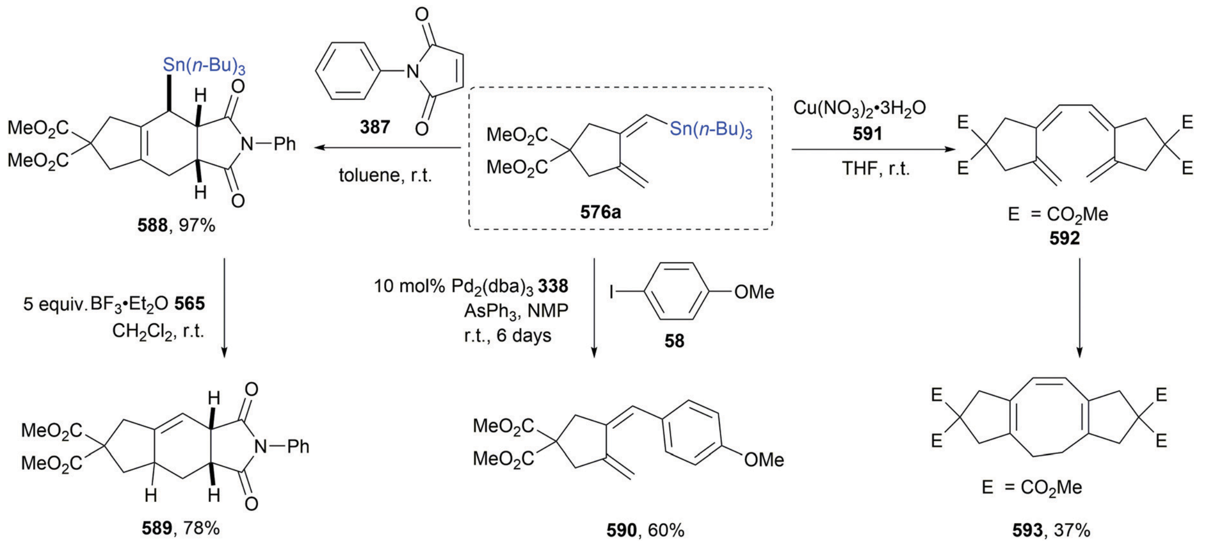
8. Hydroamination

Compounds (acyclic and heterocyclic) possessing carbon–nitrogen bonds are omnipresent in an array of chemicals, especially

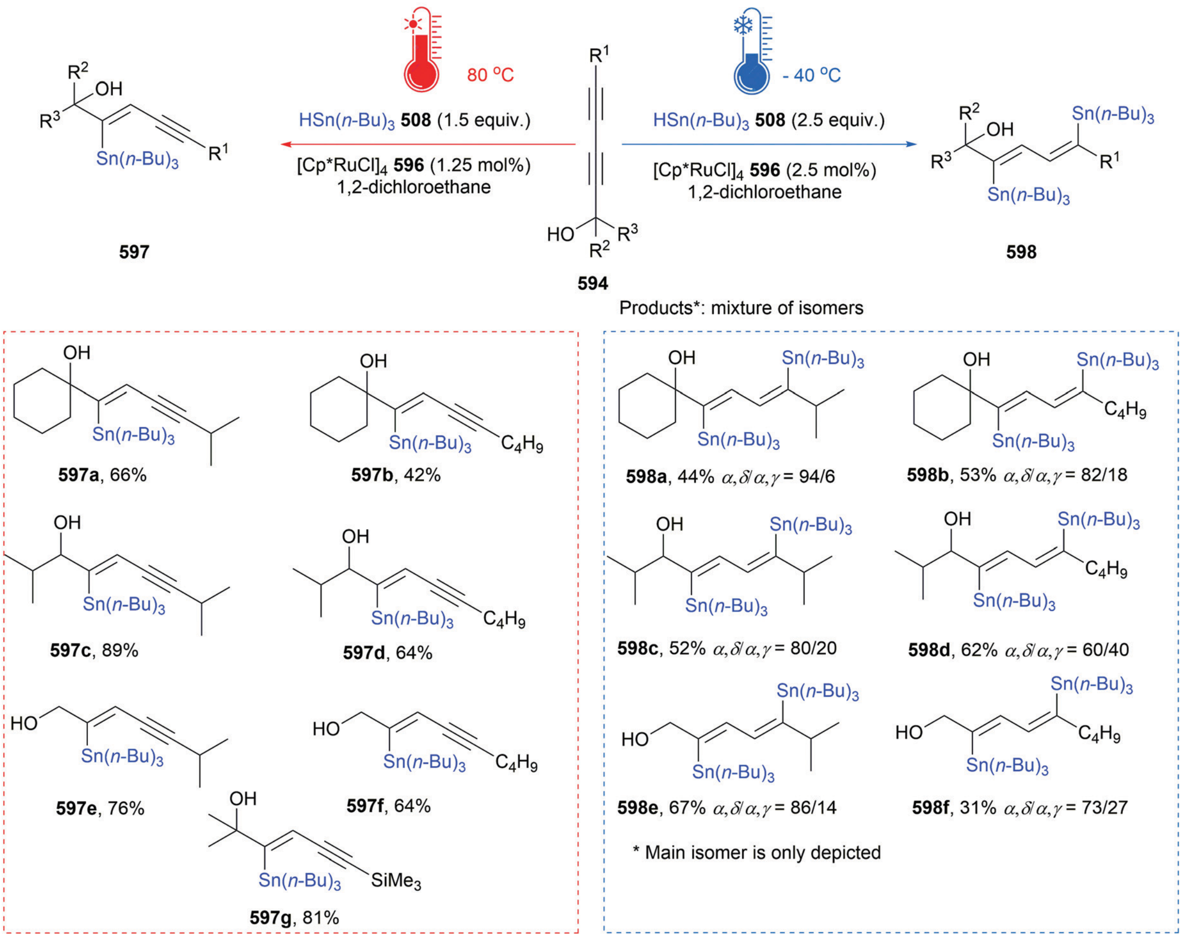


	Selectivity	Isolated yield
For **584a** (R^1= H, R^2 = C(O)CH$_2$CH$_3$)	**585a/586a/587a** =1/0/0	**585a**, 64%
For **584b** (R^1= H, R^2 = CH(OH)C$_3$H$_7$)	**585b/586b/587b** =9/2/1	**585b**, 42%, **586b**, 14%
For **584c** (R^1=H, R^2 = SiMe$_3$)	**585c/586c/587c** =0/0/1	**587c**, 59%

Scheme 115 Hydrostannation of terminally substituted diynes **584** with tributyltin hydride **508** catalysed by Pd(OH)$_2$/C **575**.

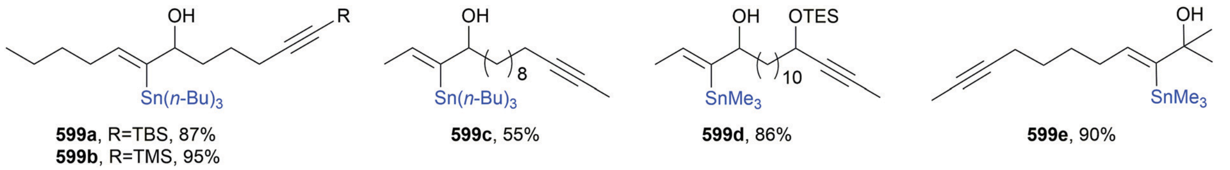


Scheme 116 Chemical transformations of dienyl stannane **576a**.

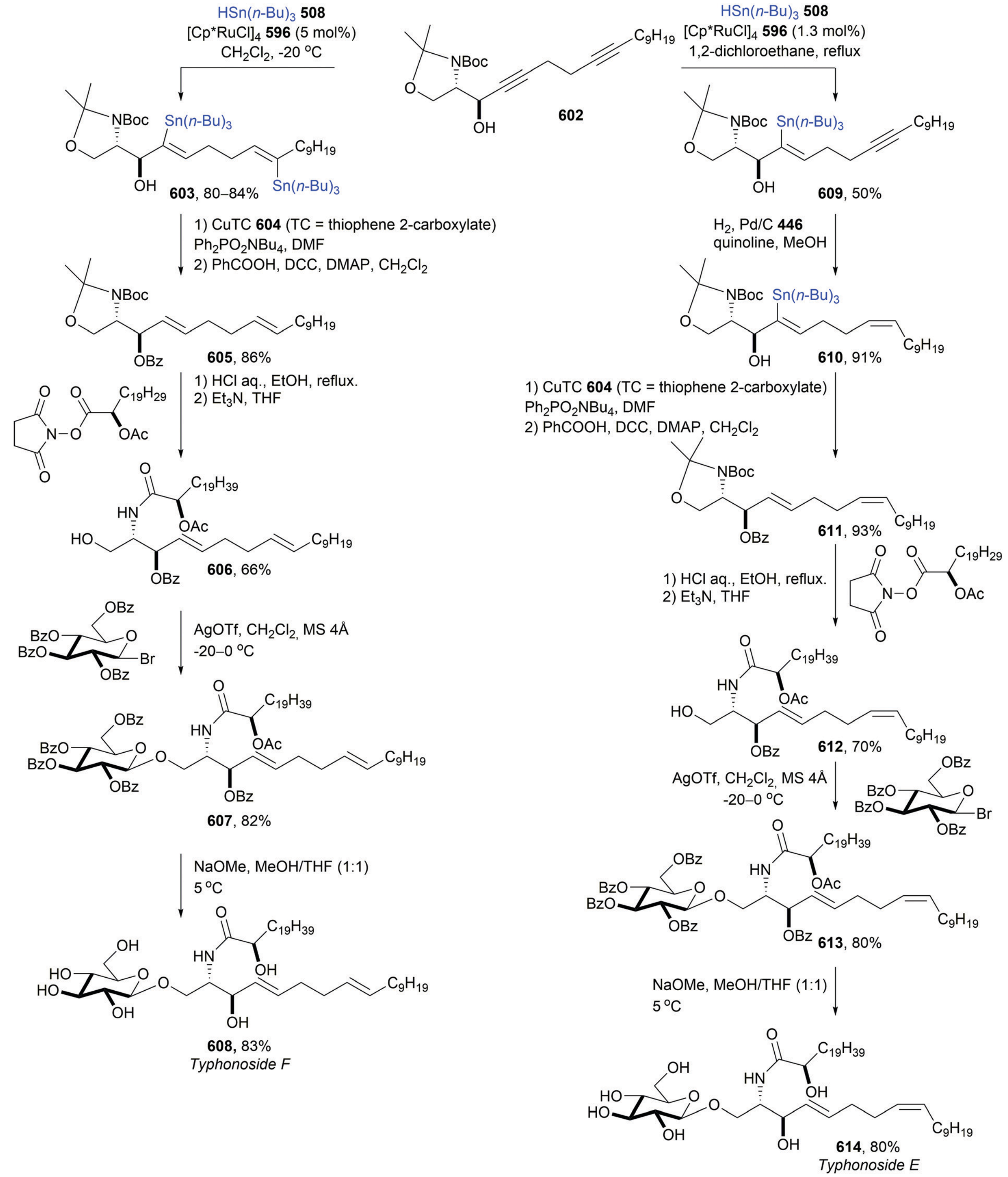


Scheme 117 Temperature tunable *trans*-hydrostannation of 1,3-diynes **594** with tributyltin hydride **508** catalysed by [Cp*RuCl]$_4$ **596**.

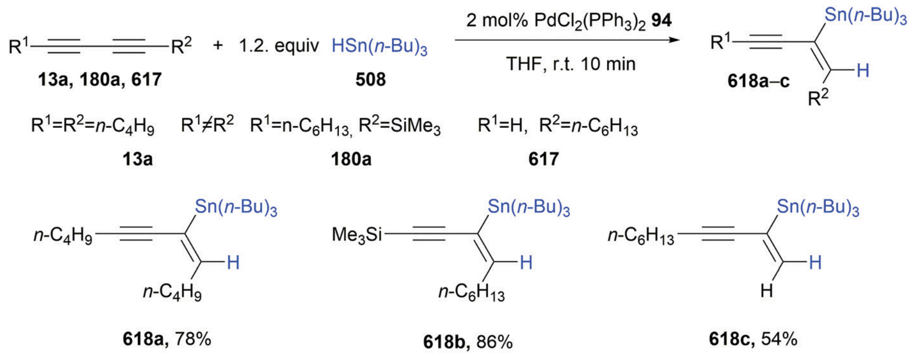
in natural compounds, agrochemicals, pharmaceuticals, or cosmetics.[22,282–288] They are produced on a gram scale as *fine chemicals*, as well as in feedstock in tonnage scale in the industry. A limited number of chemical transformations leading



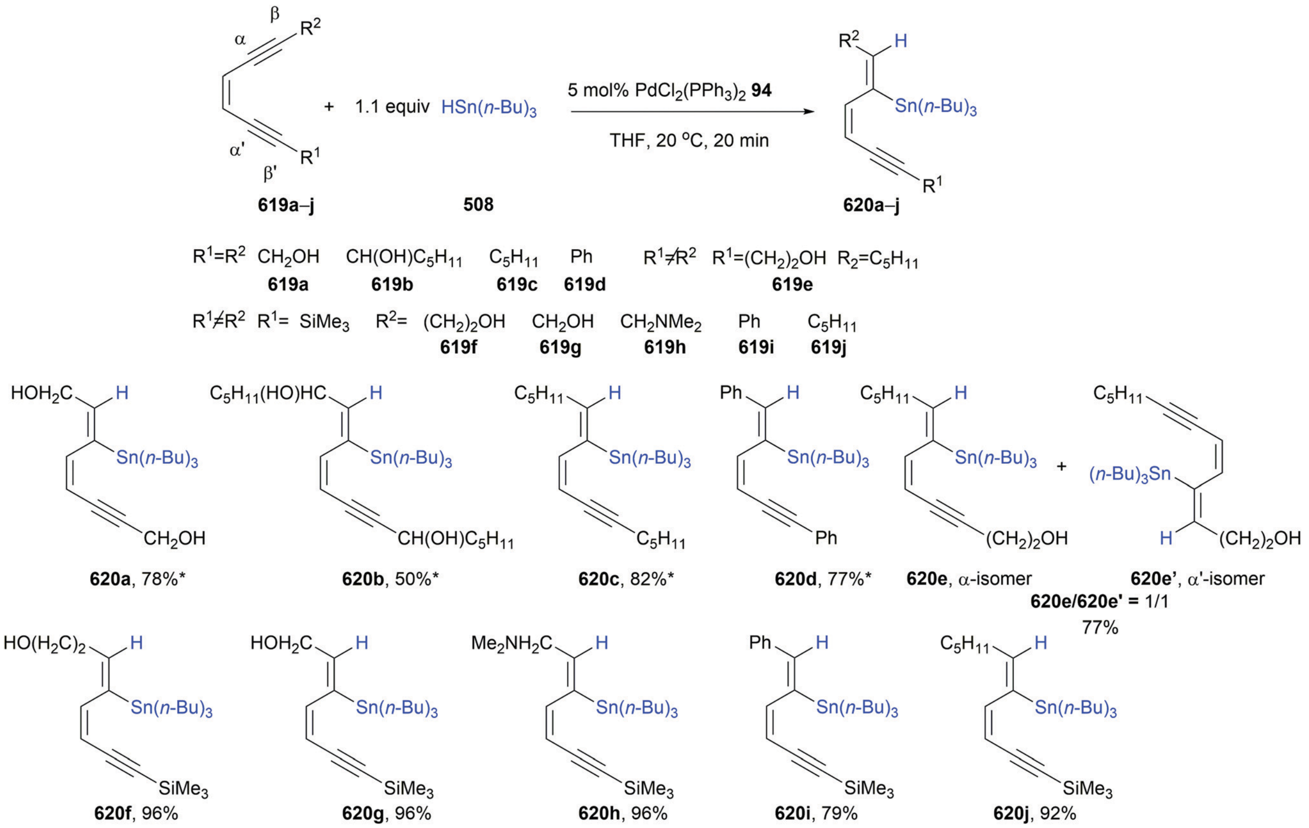
Scheme 118 Products obtained by the site-selective *trans*-hydrostannation of 1,*n*-diynes **595** using $[Cp^*RuCl]_4$ **596** (1–2 mol%) and 1.05–1.2 equiv. of $HSn(n\text{-}Bu_3)_3$ **508** or $HSnMe_3$ **600**.



Scheme 119 Synthesis of *Typhonoside F* **608** and *Thphonoside E* **614** with *trans*-stannylation step of diyne **602**.



Scheme 120 Hydrostannation of 1,3-diynes **13a**, **180a**, **617** with $HSn(n\text{-}Bu)_3$ **508** (1.2 equiv.) catalysed by $PdCl_2(PPh_3)_2$ **94** (2 mol%).

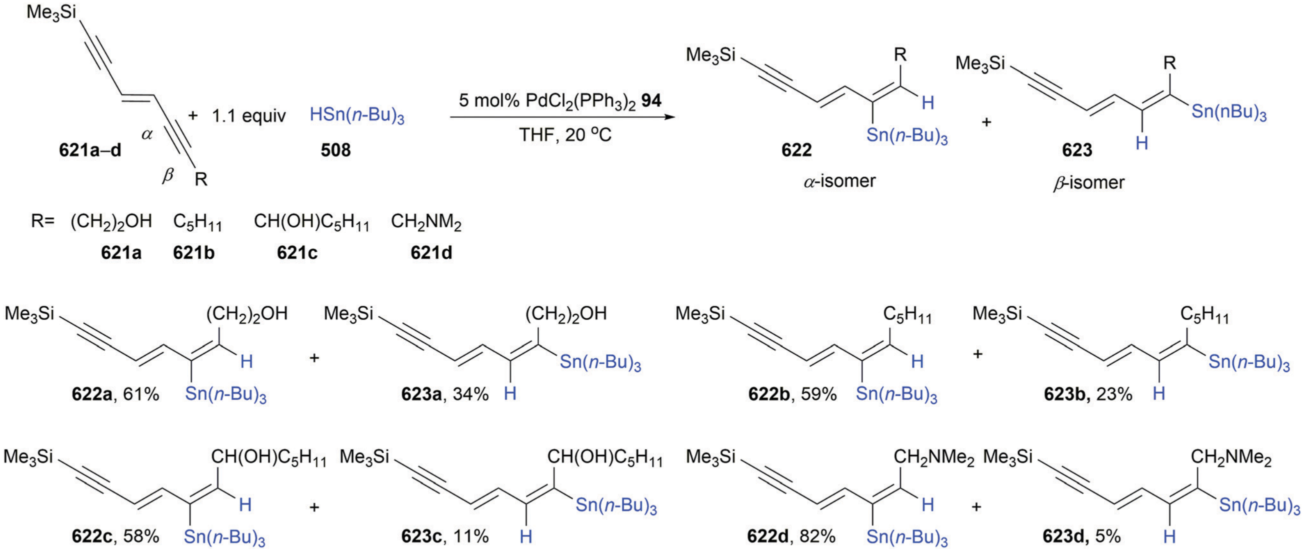


Scheme 121 Synthesis of dienynes *via* hydrostannation of (*Z*)-dienynes **619a–j** with $HSn(n\text{-}Bu)_3$ **508** catalysed by $PdCl_2(PPh_3)_2$ **94** (5 mol%).

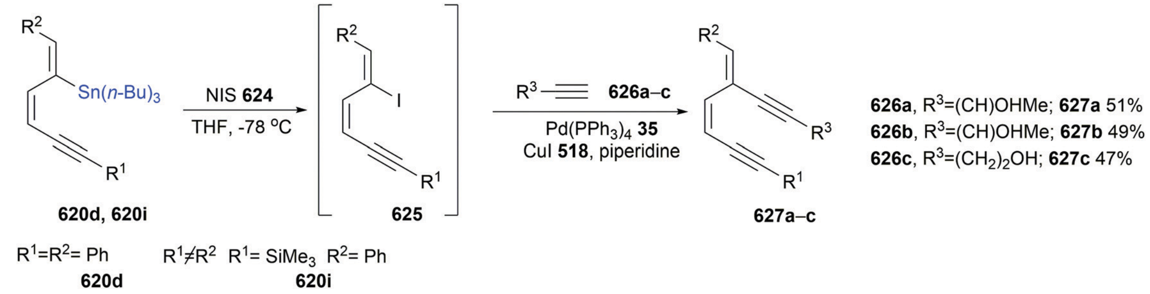
to the formation of the C–N bonds in stoichiometric reactions led to the intensive development of hydroamination reactions, which simply introduce the N-atom to the compound structure, and occurs by the addition of the N–H bond to the unsaturated C–C bonds in olefins and alkynes.[19–22,29,289–293] This 100% atom economic method mostly requires the application of a catalyst to (i) overcome the repulsion electrostatic effect between the high electron-dense unsaturated C≡C bond and the strong Lewis base (electron-rich amine 1° or 2°, ammonia, or hydrazine), and (ii) to facilitate this addition reaction due to the high energy difference between both types of bonds.[294] The hydroamination of (non)conjugated diynes leads to various products, but intramolecular cyclisation is of utmost importance to produce N-heterocyclic compounds, *e.g.*, indoles, pyrroles, pyrazoles, pyrimidines.

8.1. Noncatalytic hydroamination of conjugated 1,3-diynes

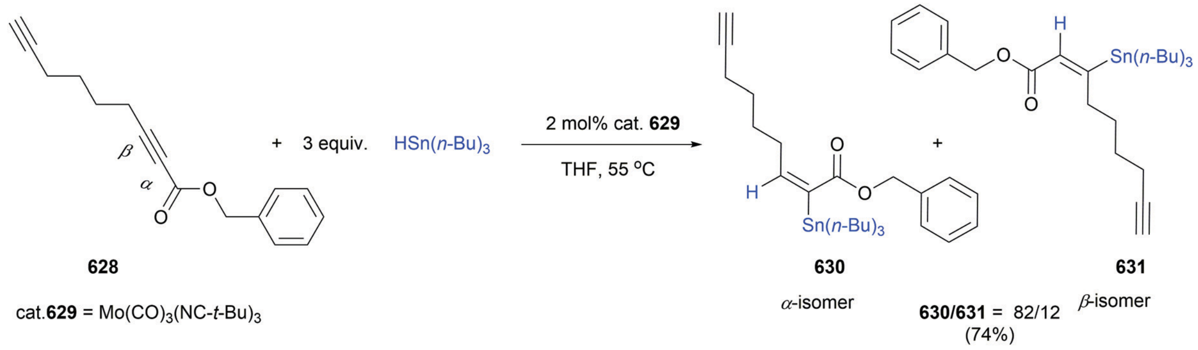
The origins of noncatalytic hydroamination of 1,3-diynes date back to the 1960s and 1970s, which was briefly described in the review published in 2002, which focused on the heterocyclisation of diynes.[295] Different hydroamination agents (*e.g.*, ammonia **632**, hydrazine **633**, substituted hydrazines **634**, amines **635**, diamines **636–637**, hydroxylamine **638**, 2-aminoethan-1-ol **639**, guanidine **640**) were used in this transformation. Depending on the type of



Scheme 122 Synthesis of dienynes **622** and **623** *via* hydrostannation of (*E*)-dienynes **621a–d** with HSn(n-Bu)$_3$ **508** catalysed by PdCl$_2$(PPh$_3$)$_2$ **94** (5 mol%).



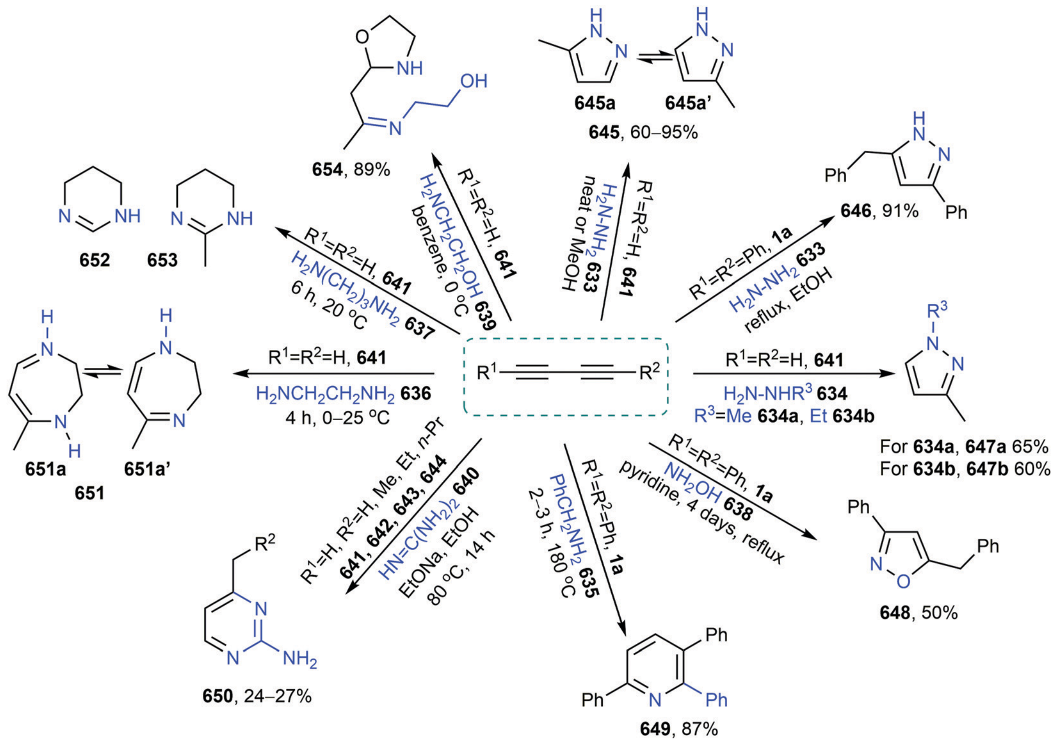
Scheme 123 Synthesis of (*Z*,*E*)-dienediynes *via* iododestannylation of **620d**, **620i**, and vinyl iodide **625** coupling with terminal alkynes **626a–c** catalysed by CuI/Pd(PPh$_3$)$_4$ **518**/**35**.



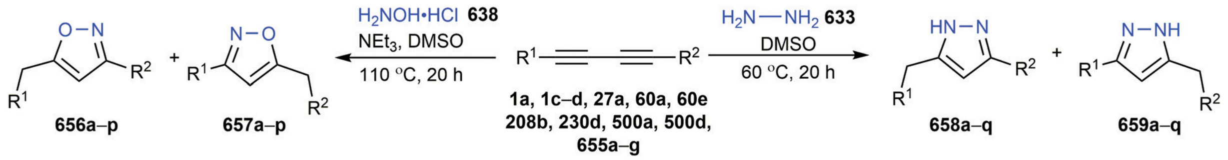
Scheme 124 Mo(CO)$_3$(NC-t-Bu)$_3$ **629** catalysed hydrostannation of diynoic ester **628**.

reagents and reaction conditions various heterocyclic products (*e.g.*, pyrazoles **645–647**, pyridines **649**, diazepines **651**, pyrimidines **650**, isoxazole **648**) were obtained (Scheme 125).[295–298]

The Cope-type hydroamination of conjugated 1,3-diynes occurs under noncatalytic and relatively mild conditions, while the reactivity of the substrates depends on the electronic structure of the 1,3-diyne. A reduction of the electronic density on the C≡C bond has a positive influence on the reaction yield and formation of the hydroaminated product. Therefore, the electron-withdrawing groups attached to the benzene ring in



Scheme 125 Examples of noncatalytic hydroamination of conjugated 1,3-diynes.



Scheme 126 Synthesis of 3,5-disubstituted isoxazoles (**656**, **657**) and pyrazoles (**658**, **659**) in the Cope-type hydroamination reactions of 1,3-diynes.

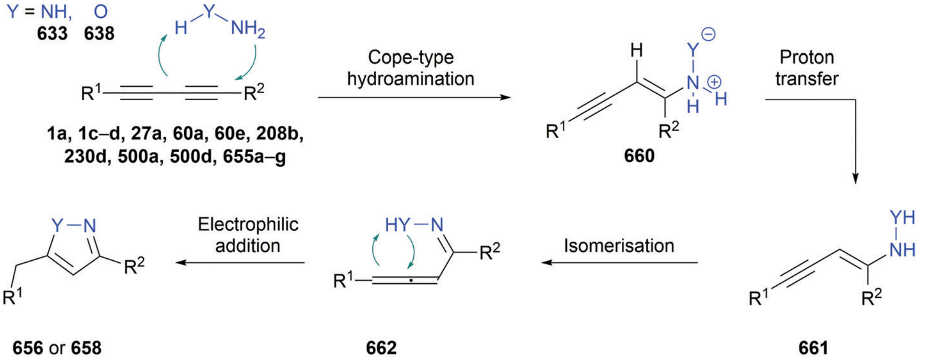
1,4-diphenyl-buta-1,3-diyne permitted the desired products to be isolated in higher yields, while electron-donating groups caused the opposite effect. Bao *et al.* have reported the synthesis of 3,5-disubstituted isoxazoles or pyrroles (Scheme 126) by the Cope-type intramolecular hydroamination of 1,3-diynes **1a**, **1c–d**, **27a**, **60a**, **60e**, **208b**, **230d**, **500a**, **500d**, **655a–g** with hydroxylamine **639** or hydrazine **633** respectively.[299,300] Both reactions occurred at elevated temperatures (110 °C or 60 °C) in DMSO and using an excess of hydroaminating reagent **633** or **639** (1.5–4.0 equiv.) to provide the full conversion of 1,3-diynes. Triethylamine (Et_3N) was used as the most effective base in the synthesis of isoxazoles **656–657**. The reactions yielded isoxazoles **656** and **657** in 61–92% or pyrazoles **658** and **659** in 60–93% isolated yields (Table 16). The high selectivity for unsymmetrical diynes was obtained when the reagent was substituted with groups with a distinct difference in electronic properties (*e.g.*, hexyl- and 4-nitrophenyl).[299,300] The mechanism of intermolecular Cope-type hydroamination of 1,3-diynes occurred *via* the formation of intermediate **661** in a proton-transfer process, which further undergoes isomerisation to the allenyl oxime intermediate **662**, followed by the electrophilic cycloaddition towards 3,5-disubstituted isoxazoles **656** or pyrazoles **658** (Scheme 127).[299,300] Moreover, the same group developed a one-pot procedure for the synthesis of heterocycles *via* Glasser coupling of alkynes followed by intramolecular hydroamination. The final products were obtained in comparable yields.[299,300]

The hydroamination with hydroxylamine **638** or hydrazine **633** was carried out also for symmetrical **663a–f** (Scheme 128) and nonsymmetrical 1,3-diyne indole derivatives **668** (Scheme 129). The reactions were conducted in eco-friendly PEG-400 as a solvent, which facilitates a proton transfer to the allenyl intermediate, which according to the DFT calculations is the rate-determining step of the process. Applying PEG-400 as a solvent, it was possible to shorten the reaction time from 20 h to 2–6 h, and to carry out the reactions under milder conditions.[301,302] Additionally, *N*-substituted products were obtained by the application of arylhydrazines **665a–d** (Schemes 128 and 129).[302]

3,5-Disubstituted pyrazoles **674a–d** were synthesised using the Cope-type hydroamination in a sustainable manner by the application of a continuous flow process, starting from terminal alkynes **518a** and **672a–c** and hydrazine **633**. Two coil

Table 16 Synthesis of 3,5-disubsituted isoxazoles (**656**, **657**) pyrazoles (**658**, **659**) in Cope-type hydroamination reactions with hydrazine **633** and hydroxylamine **638**

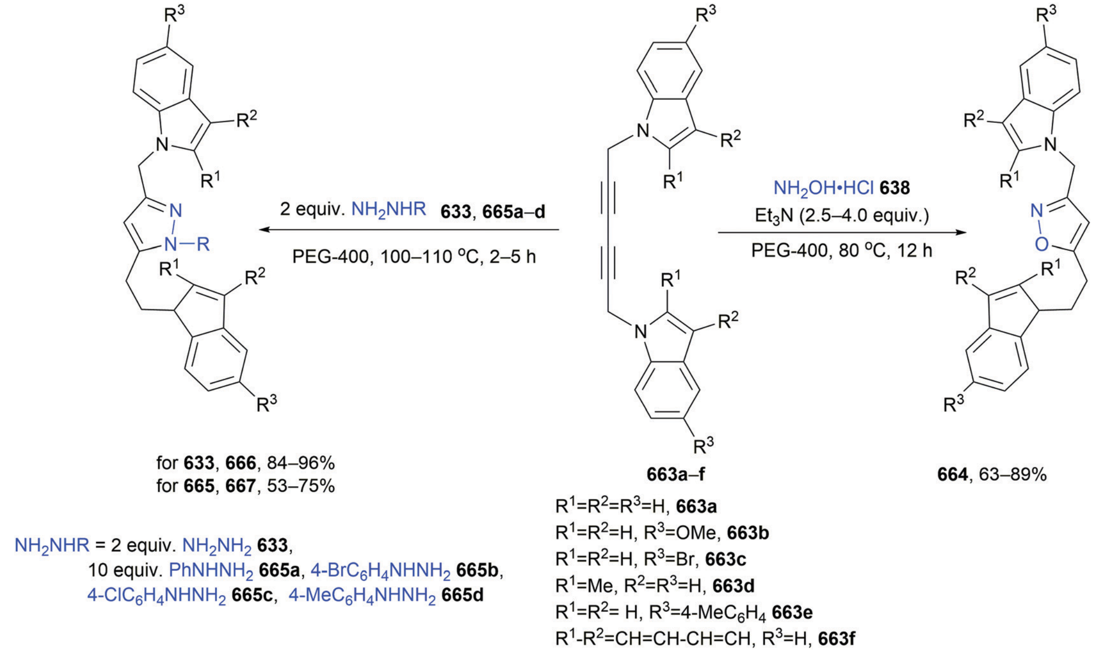
	Yield [%]		Diyne			Yield [%]	
Entry	656	657	R^1	R^2		658	659
	656 = **657**					**658** = **659**	
1	**656a**, 86		Ph	Ph	**1a**	**658a**, 83	
2	**656b**, 81		*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**1d**	**658b**, 76	
3	**656c**, 84		*p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$	**1c**	**658c**, 78	
4	**656d**, 81		*m*-MeC$_6$H$_4$	*m*-MeC$_6$H$_4$	**27a**	**658d**, 78	
5	**656e**, 91		*p*-BrC$_6$H$_4$	*p*-BrC$_6$H$_4$	**230d**	**658e**, 93	
6	**656f**, 98		*p*-NO$_2$C$_6$H$_4$	*p*-NO$_2$C$_6$H$_4$	**500a**	**658f**, 93	
7	**656g**, 66		*n*-Hexyl	*n*-Hexyl	**208b**	**658g**, 60	
8	**656h**, 89		*c*-Hexyl	*c*-Hexyl	**60a**	**658h**, 76	
	656 ≠ **657**					**658**≠**659**	
9	**656i**, 41	**657i**, 32	Ph	*p*-MeOC$_6$H$_4$	**60e**	**658i**, 47	**659i**, 35
10	**656j**, 72	**657j**, 9	*p*-FC$_6$H$_4$	*p*-MeOC$_6$H$_4$	**655a**	**658j**, 52	**659j**, 31
11	**656k**, 87	**657k**, 0	*p*-NO$_2$C$_6$H$_4$	*p*-MeOC$_6$H$_4$	**655b**	**658k**, 58	**659k**, 30
12	**656l**, 78	**657l**, 0	Ph	*n*-Hexyl	**655c**	**658l**, 72	**659l**, 11
13	**656m**, 81	**657m**, 0	Ph	*c*-Hexyl	**655d**	**658m**, 70	**659m**, 18
14	**656n**, 89	**657n**, 0	*p*-NO$_2$C$_6$H$_4$	*n*-Hexyl	**655e**	**658n**, 88	**659n**, 0
15	**656o**, 94	**657o**, 0	*p*-NO$_2$C$_6$H$_4$	*c*-Hexyl	**655f**	**658o**, 70	**659o**, 0
16	**656p**, 64	**657p**, 12	*p*-MeC$_6$H$_4$	*n*-Hexyl	**500d**	—	Hexyl
17	—	—	*p*-NO$_2$C$_6$H$_4$	Ph	**655g**	**658q**, 54	**659q**, 27



Scheme 127 Mechanism of Cope-type hydroamination of 1,3-diynes **1a**, **1c–d**, **27a**, **60a**, **60e**, **208b**, **230d**, **500a**, **500d**, **655a–g**.

reactors were combined, the temperature, the volume of the coils, and reagent flow rates, which influence the residence times, which were carefully chosen to obtain high product yields of **1a**, **1c**, **27c**, and **258a** in the Glasser coupling of alkynes and hydroamination process. For the homocoupling of alkynes **518a**, **672a–c** a 3.5 mL coil, alkyne concentration 0.75 M in DMSO, 120 °C, and 0.1 mL min^{-1} flow (residence time: 35 minutes) were used. After the reactor outlet, the thiourea **673** scavenger column was applied to trap the copper (CuBr$_2$ **52**) used as a catalyst for the Glaser reaction. The hydroamination was carried out in a 17.5 mL coil with hydrazine **633** in DMSO (0.1–0.2 mL min^{-1}) at 140 °C. The 87.5 min residence time was sufficient for the total conversion of 1,3-diynes **1a**, **1c**, **27c**, and **258a** yielding the appropriate pyrazoles **674a–d** in 90–98% (isolated yields: 84–90%). The system was active for 16 hours for subsequent continuous flow Glaser coupling/hydroamination of 3-ethynylthiophene **27c** with hydrazine **633**, leading to 0.52 g of pure 3-(thiophen-3-yl)-5-(thiophen-3-ylmethyl)-1*H*-pyrazole **674d** in 81% isolated yield. The ICP analysis detected only residue amounts of Cu (3 ppm), showing a high efficiency of the in-line Cu-scavenger (Scheme 130).[303]

This noncatalytic hydroamination was also used in the synthesis of 2,4,6-pyrimidines **677a–o**, which possess biological activities (*e.g.*, antitumor, antifungal, anticancer, anticonvulsant), luminescence properties, or are the component of nucleic acids. They can be effectively synthesised from diaryl or monoaryl-substituted 1,3-diynes (**1a–d**, **27b**, **258a**, **258e**, **258h**, and **675**), and amidines **676** (acetamide hydrochloride **676a**, benzamidine hydrochloride **676b** or formamidine acetate **676c**), which are used as bidentate nucleophiles in the presence of Et$_3$N as a base. The reaction occurred effectively in DMSO under a high temperature (160 °C), with the reagent ratio [diyne] : [**676**] : [Et$_3$N] = 1 : 3 : 3. The products **677a–o** were obtained with 46–88% isolated yields, with the highest efficiency for electron-poor 1,3-diynes with electron-withdrawing groups (Scheme 131).[304]



for **633**, **666**, 84–96%
for **665**, **667**, 53–75%

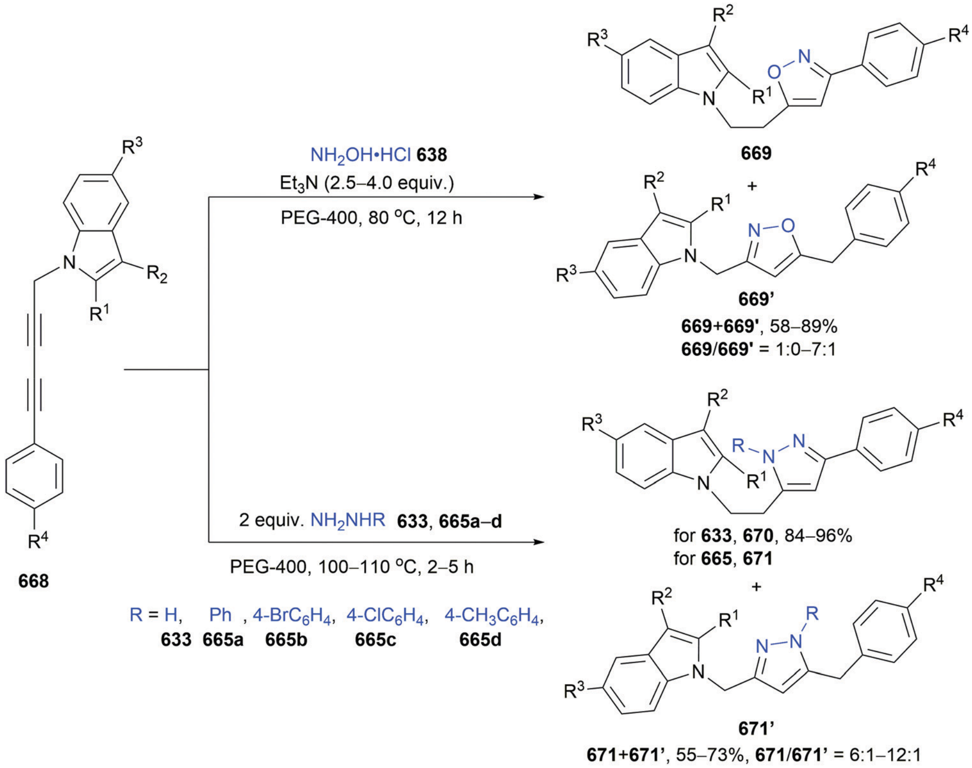
663a–f

664, 63–89%

NH_2NHR = 2 equiv. NH_2NH_2 **633**,
10 equiv. $PhNHNH_2$ **665a**, $4\text{-}BrC_6H_4NHNH_2$ **665b**,
$4\text{-}ClC_6H_4NHNH_2$ **665c**, $4\text{-}MeC_6H_4NHNH_2$ **665d**

$R^1=R^2=R^3=H$, **663a**
$R^1=R^2=H$, $R^3=OMe$, **663b**
$R^1=R^2=H$, $R^3=Br$, **663c**
$R^1=Me$, $R^2=R^3=H$, **663d**
$R^1=R^2=H$, $R^3=4\text{-}MeC_6H_4$ **663e**
$R^1\text{-}R^2=CH=CH\text{-}CH=CH$, $R^3=H$, **663f**

Scheme 128 Synthesis of 3,5-disubstituted-1,2-isoxazoles **664** and 3,5-disubstituted 1*H*-pyrazoles **666** and **667** in the hydroamination process.



669

669'

669+669', 58–89%
669/669' = 1:0–7:1

for **633**, **670**, 84–96%
for **665**, **671**

671'

671+671', 55–73%, **671/671'** = 6:1–12:1

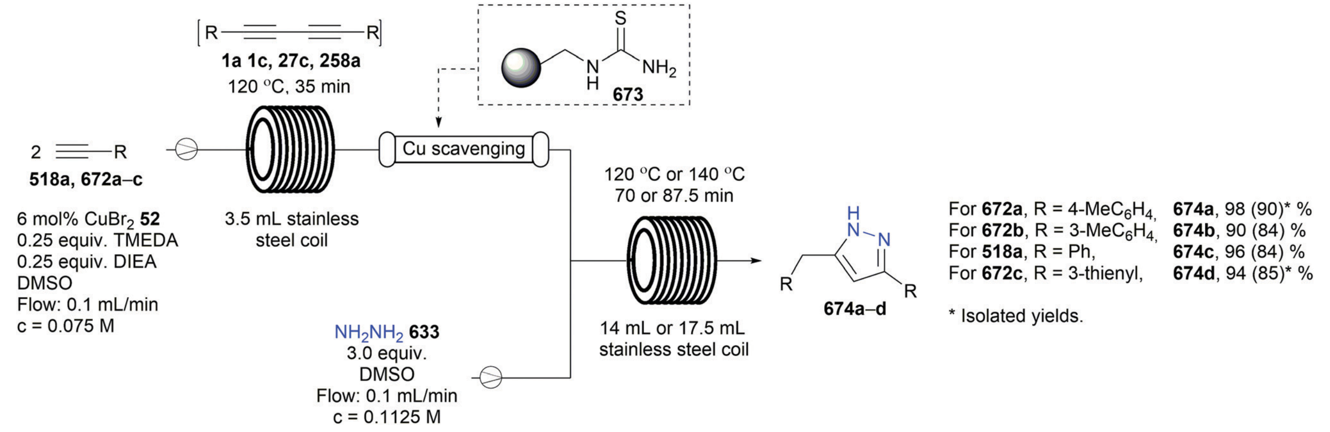
668

R = H, Ph, $4\text{-}BrC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}CH_3C_6H_4$,
633 **665a** **665b** **665c** **665d**

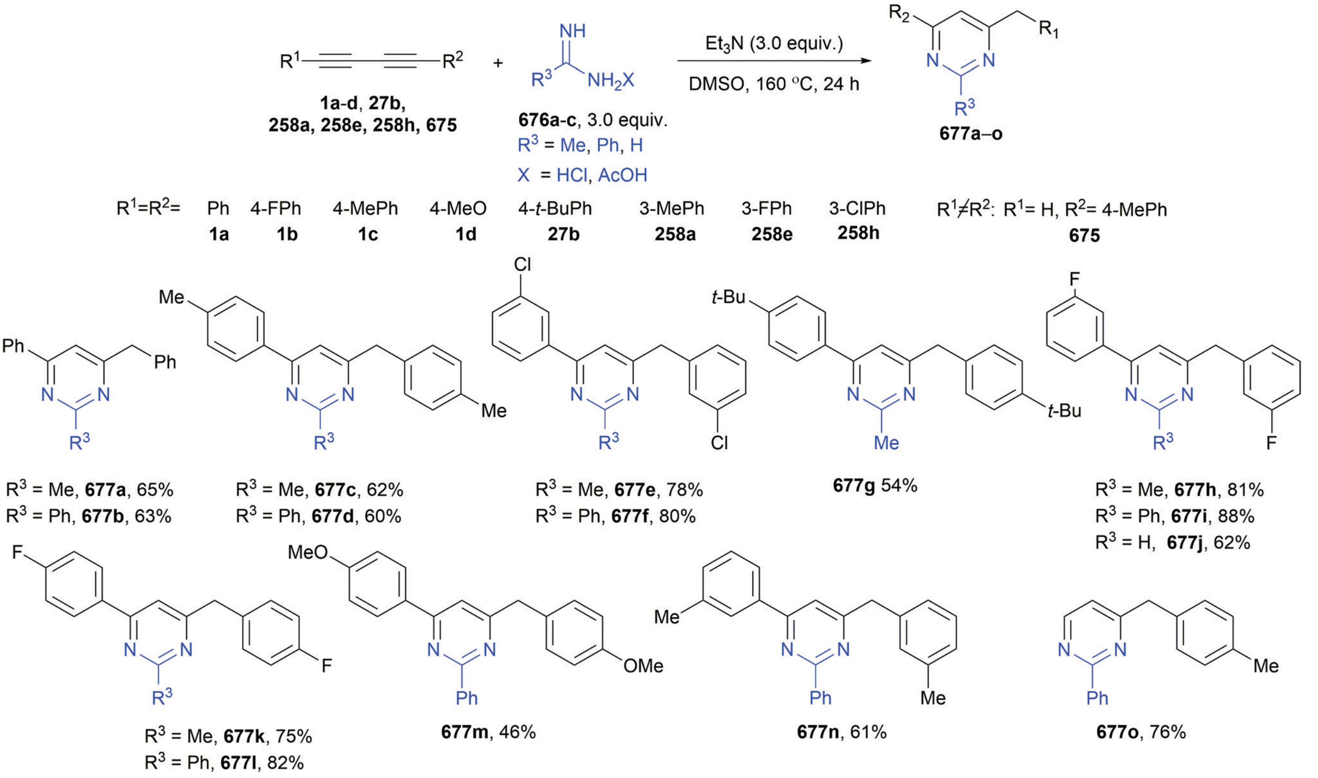
Scheme 129 Synthesis of 3,5-disubstituted-1,2-isoxazoles **669** and 3,5-disubstituted 1*H*-pyrazoles **670** and **671** from nonsymmetrical diynes **668** in the hydroamination process.

8.2. Catalytic hydroamination of conjugated 1,3-diynes and separated diynes

The hydroamination of conjugated, as well as nonconjugated diynes, is often catalysed by homogeneous transition metal catalysts (Au, Ag, Cu, Pd) as well as non-noble metal or main group element complexes (Ti, Ni, Co, Ca). Among them, Au complexes have found a prominent position in their application for catalytic hydroamination. The hydroamination reaction



Scheme 130 Synthesis of pyrazoles **674a–d** in a two-step continuous flow process based on the Glaser coupling of **518a** and **672a–c** to diynes and their hydroamination with hydrazine **633**.

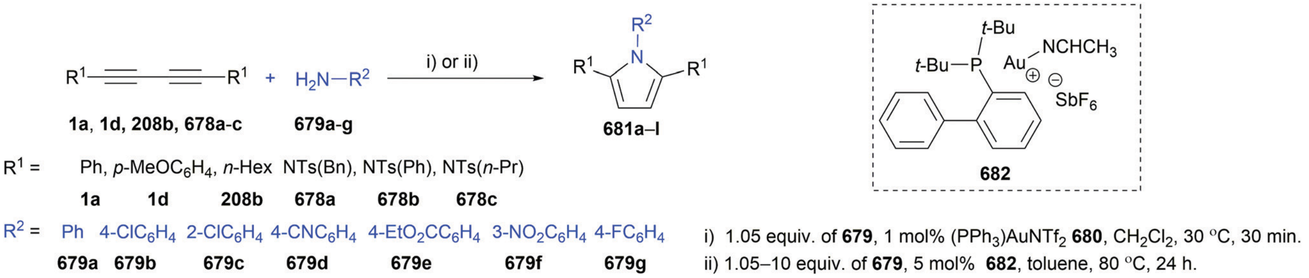


Scheme 131 Synthesis of substituted pyrimidines **677a–o** by the hydroamination reaction of diynes **1a–d**, **27b**, **258a**, **258e**, **258h**, and **675** with aminides **676**.

constitutes one of the steps in the synthesis of natural products as *e.g.*, indolizidine alkaloid (±)-Monomorine, pharmaceuticals or agrochemicals.[64,305–307]

Skrydstrup *et al.* reported the synthesis of electron-rich 2,5-diamidopyrroles, 1,2,5-trisubstituted pyrroles, as well as pyrazoles using a hydroamination reaction in the presence of Au(I)-complexes. These products are difficult to synthesise according to other methods. Using $(Ph_3P)AuNTf_2$ **680** and only a slight excess of aniline **679a** (1.05 equiv.), appropriate 2,5-diamidopyrroles were obtained in 30 min, under low temperature (30 °C) in CH_2Cl_2. The anilines with electron-withdrawing groups in the *para* position required a longer reaction time (60 min). The trisubstituted products were obtained after 24 h using different Au **680** and **682** catalysts in toluene and at elevated temperatures (80 °C), (Scheme 132 and Table 17).[308]

The cationic gold(I) catalyst supported by a cyclic(alkyl)-(amino)carbene (CAAC) generated *in situ* from an equimolar mixture of AuCl(CAAC) **684**/$KB(C_6F_5)_4$ was able to activate NH_3 **632** and NH_2NH_2 **633** in the hydroamination reactions of alkynes, and conjugated and non-conjugated diynes **1a, 65a,**



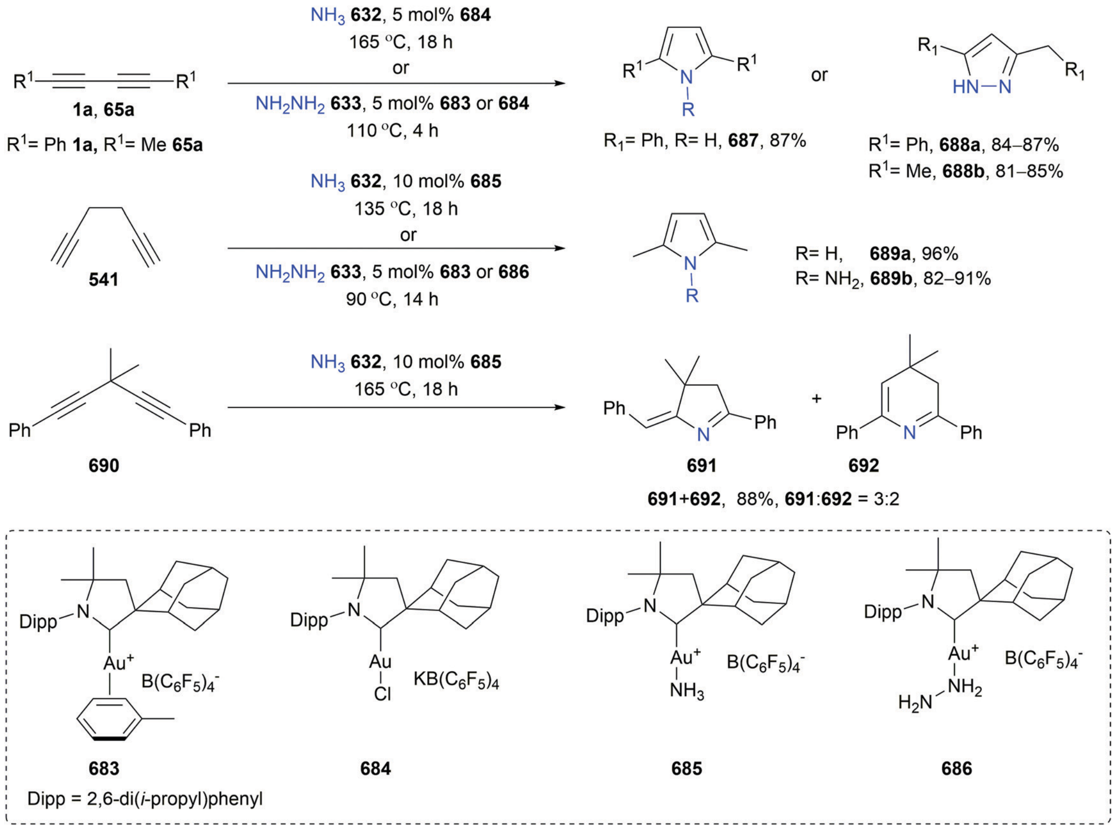
Scheme 132 Gold-catalysed hydroamination of diynes **1a**, **1d**, **208b**, and **678a–c** with anilines **679a–g**. Synthesis of pyrroles **681a–l**.

Table 17 Synthesis of pyrroles **681** in Au-catalysed hydroamination reactions of diynes **1a**, **1d**, **208b**, and **678a–c** with anilines **679a–g** and phenylhydrazine **665a** (Scheme 132)

Entry	Diyne	Amine	Reaction conditions	Product	Yield [%]
1	**1a**	**679a**	(ii)	**681a(b)**[a]	49 (56)[a]
2	**1d**	**679a**	(ii)	**681c(d)**[a]	48(63)[a]
3	**678a**	**679a**	(i)	**681e**	96
4	**678a**	**679c**	(i)	**681f**	95
5	**678a**	**679d**	(i)	**681g**	95
6	**678a**	**679e**	(i)	**681h**	94
7	**678b**	**679b**	(i)	**681i**	95
8	**678c**	**679f**	(i)	**681j**	93
9	**678c**	**679g**	(i)	**681k**	94
10	**208b**	**679a**	(ii)	**681l**	24

[a] Phenylhydrazine **665a** was used as a reagent.

541, 690 (Scheme 133). These hydroaminating reagents are powerful reductive agents, which can form saturated products, as well as metal nanoparticles, therefore their use in the formation of the new C–N bonds is problematic. The gold centre is capable of NH_3 **632** or NH_2NH_2 **633** addition if it is coordinated by the CAAC ligand and rendered cationic by Cl^- abstraction. The same Ag complex: (CAAC)AgCl **692**/$KB(C_6F_5)_4$ or $NH_4B(C_6F_5)_4$ **685** did not cause the activation of NH_3 **632.** The coordination of NH_3 **632** or NH_2NH_2 **633** led to a typical Werner complex immediately. The same happened when the alkyne was added to the initial catalyst, η-2 bounded to the gold atom. The reaction occurred according to the insertion mechanism. The addition of NH_3 **632** to 1,4-diphenyl-buta-1,3-diyne **1a** or hexa-1,5-diyne **541,** occurred according to the Markovnikow rule, followed by the ring-closing hydroamination to give pyrroles



Scheme 133 Au-catalysed (**683–686**) hydroamination of diynes with NH_3 **632** and NH_2NH_2 **633**. Synthesis of pyrroles and pyrazoles.

with high yields: 87% for **688** and 96% for **689a.** The same reaction with 3,3-dimethyl-1,5-diphenylpenta-1,4-diyne **690** formed two products: Markovnikov six-membered ring and anti-Markovnikov five-membered heterocycles **691** and **691′** in a 2 : 3 ratio. Similar activity was observed for the reaction with hydrazine **633** where pyrroles or pyrazoles were formed (Scheme 133).[309,310]

Amphiphilic gold nanoparticles: Au-HS/SO_3H-PMO(Et) **693**, obtained with a narrow particle distribution 1–2 nm (which is important for their high catalytic activity) permitted the reactions to be carried out with organic reagents in an aqueous solution without using any organic solvents. The intramolecular hydroamination of hexa-2,4-diyne **65a** in water occurred with high yields of the product **676** (87%). Moreover, the addition of catalytic amount of H_2SO_4 to AuCl(PPh_3) **694** (used as a homogeneous catalyst) was also successful, but the yields were much lower than for the reaction catalysed by nanoparticles **693.**[311]

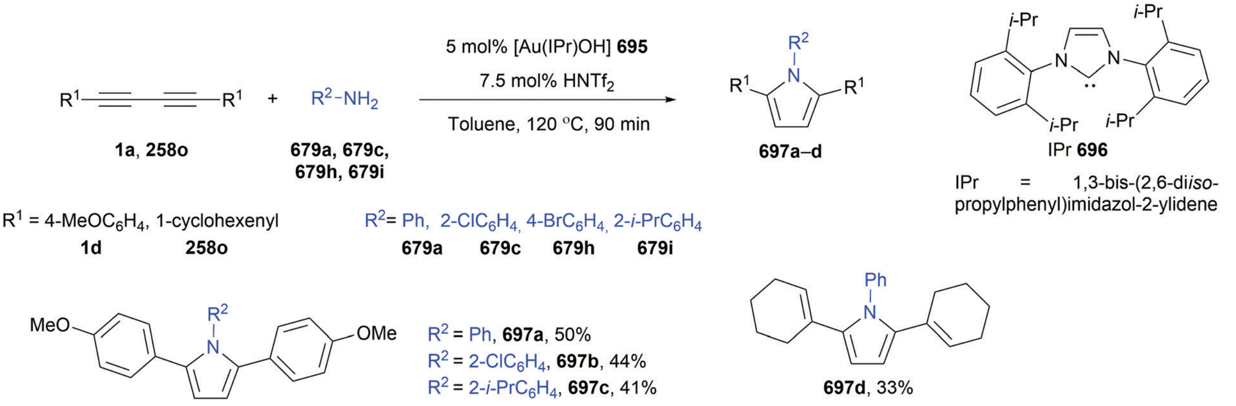
Nolan *et al.* described the application of 5 mol% of [Au(IPr)OH] **695** (IPr = 1,3-bis-(2,6-di-*iso*-propylphenyl)imidazol-2-ylidene **696**) as a precatalyst for the hydroamination and hydration of conjugated 1,3-diynes **1a** and **258o** to pyrroles **697a–d** and furans respectively. The active cationic form of the catalyst is formed in the presence of 7.5 mol% of $HNTf_2$. Microwave irradiation was used as a heating source, and the reaction was carried out at 120 °C for 90 min (Scheme 134).[312] The results were similar to those obtained by Skrydstrup (see Scheme 132).[308]

Ohno *et al.* developed a method for the formation of various fused indoles and indolines using gold catalysts. Depending on the catalyst and ligands type different products were selectively formed with very good yields.[313–315] The first paper focused on the synthesis of aryl-annulated[α]carbazoles **700** *via* gold-catalysed 5-*endo-dig* hydroamination of diynes followed by 6-*endo-dig* hydroarylation. The type of phosphine ligand attached to the gold atom **699a–c** has a strong impact on the diyne **698a–s** conversion. Particularly, when bulky biarylphosphine ligands were used, the dissociation of the catalyst from a substrate is accelerated, improving the possibility for activation of the appropriate C≡C bond for hydroamination, even in the case of reagents with electron-rich aryl groups (*p*-MeC_6H_4, **698a** *p*-$MeOC_6H_4$ **698b**). The reaction was sluggish when *o*-CNC_6H_4 **698e** was used probably due to the interaction of CN group with the catalyst. The process was carried out in the presence of R_3PAuCl **699**/AgOTf systems yielding aryl-annulated[α]-carbazoles **700** with very good yields (Scheme 135).[313] Carbazoles **700c** and **700n** showed good antifungal activity against *T. metagrophytes* and modest activity against *T. rubrum*.[313]

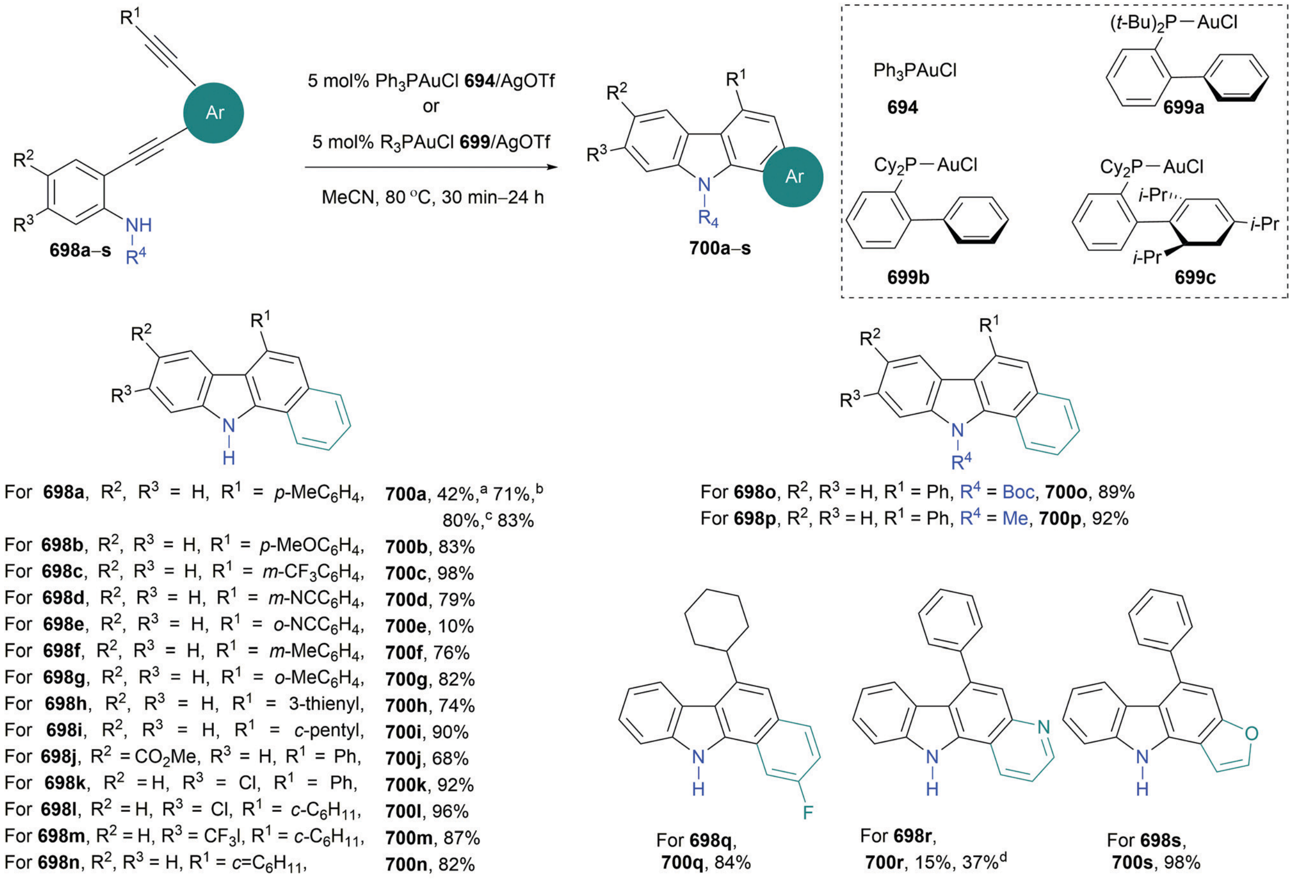
Applying this method it was also possible to synthesize dihydrobenzoindole **702** and **703** and azepino-**705a** oxepino-[3,4-*b*]indole **705b** and cyclohepta[*b*]indole **705c** derivatives with moderate to good yields (Scheme 136). The authors proposed the mechanism of this transformation, which started from the activation of diyne **698t** by gold catalysts **699** to **706.** Next the 5-*endo-dig* cyclisation furnishes the indolylgold intermediate **707**. After proto-deuaration the cyclised product **708** is formed. It is activated by the gold catalyst, which promotes 6-*endo-dig* cyclisation at the C-3 position of the indole, followed by the rearomatisation to arylgold species **709**. The cycle is finished with the proto-deauration of **709** and production of fused carbazole **700t**, with the subsequent regeneration of the initial catalyst **699** (Scheme 137).

The same group developed a method for the synthesis of fused indolines **716** and indoles **712** from anilines functionalised with diyne group **710** catalysed by gold complexes. The formation of both products is controlled by the reagent, ligand, and solvent. When IPr **696** ligands and protic solvents were used the fused indoles **712** were predominantly formed. While Buchwald's type ligands (*e.g.*, JohnPhos **714** and BrettPhos **715**) and nonpolar solvents (*e.g.*, toluene) promoted the synthesis of indolines **716** as the main products. The most active catalyst for the preparation of indoles was $IPrAuNTf_2$ (5 mol%) **711,** while for the synthesis of indolines John-$PhosAuNTf_2$ **713** was applied (Scheme 138 and Table 18).

The catalytic systems **711** and **713** were tolerant to many electron-donating and electron-withdrawing functional groups in the diyne structures. For **710g** (with highly electron-withdrawing CN group R^1) the indole **712g** was formed with very low yield (17%), while propellane type indoline **716g** was not formed regardless of the method A or B. Moreover the influence of the position of substituents in phenyl ring of aniline influences the products yields. When the ring was

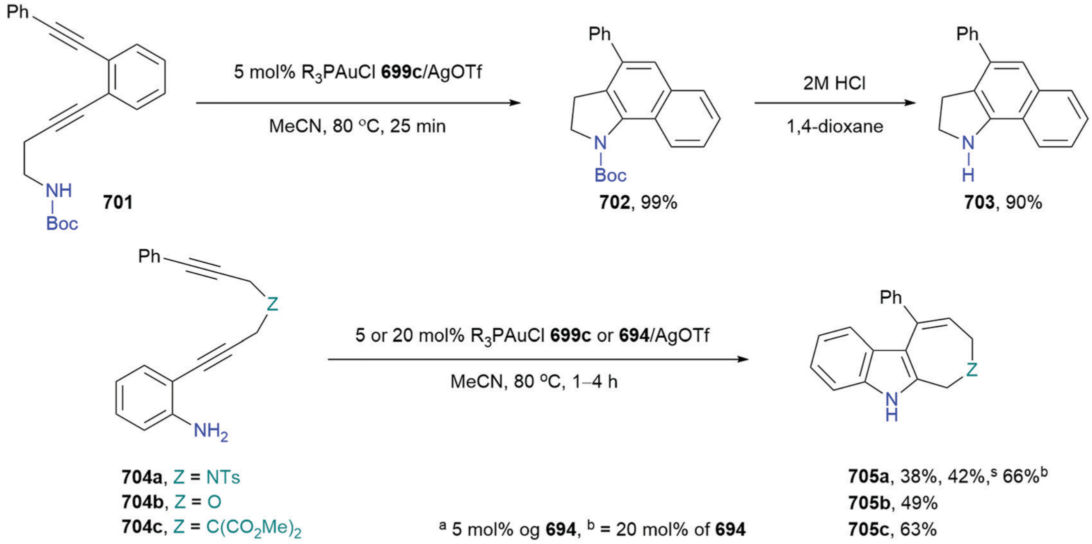


Scheme 134 Synthesis of pyrroles **697a–d** in the hydroamination of 1,3-diynes in the presence of [Au(IPr)OH] **695**.



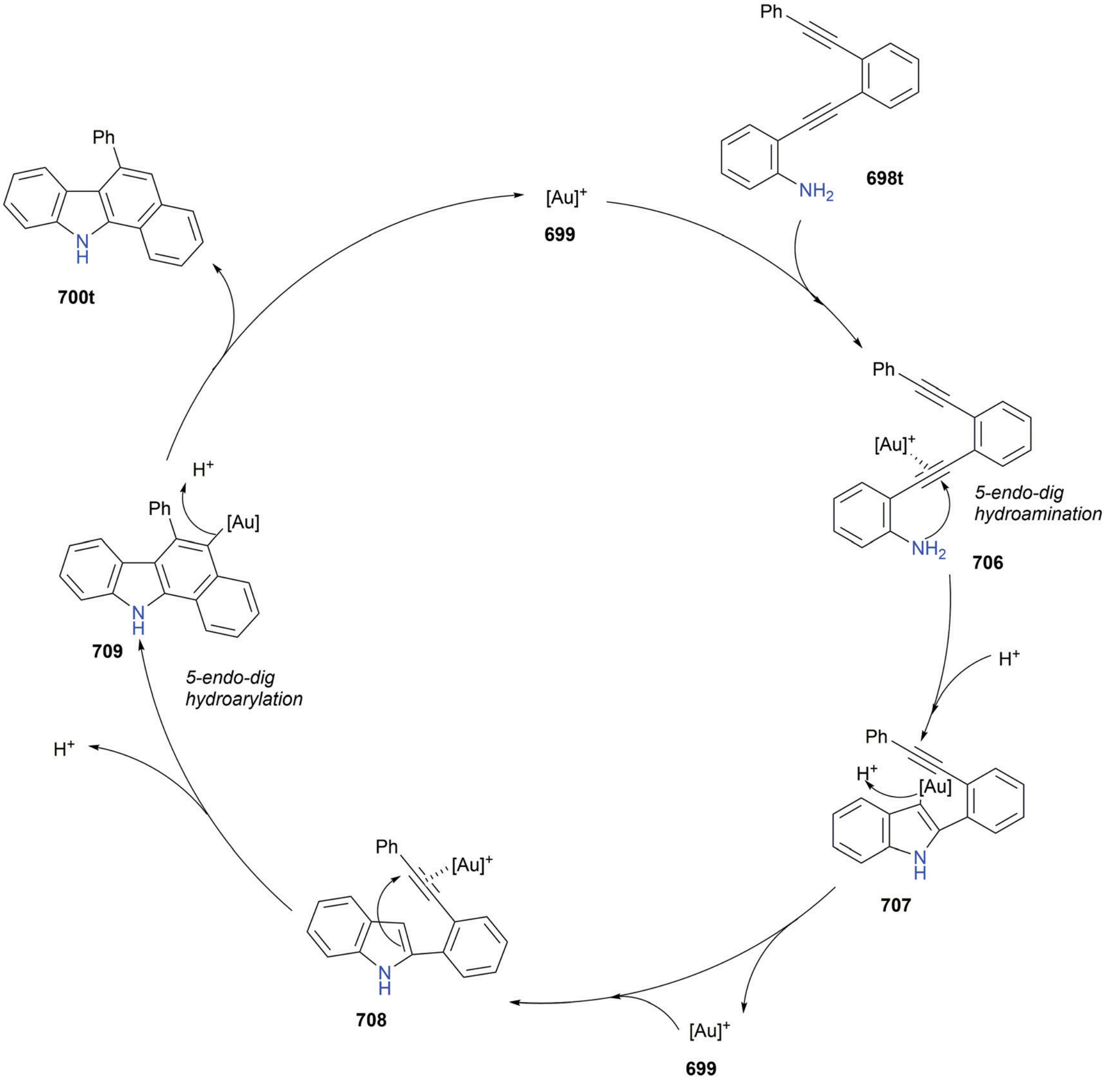
Reaction conditions: 5 mol% of **699c,** AgOTf (5 mol%), 3–24h, [a] For **694**, [b] For **699a**, [c] For **699b**, [d] 20 mol% of **699c** and AgOTf.

Scheme 135 Synthesis of aryl-annulated[α]carbazoles *via* gold-catalysed 5-*endo-dig* hydroamination of diynes followed by 6-*endo-dig* hydroarylation.

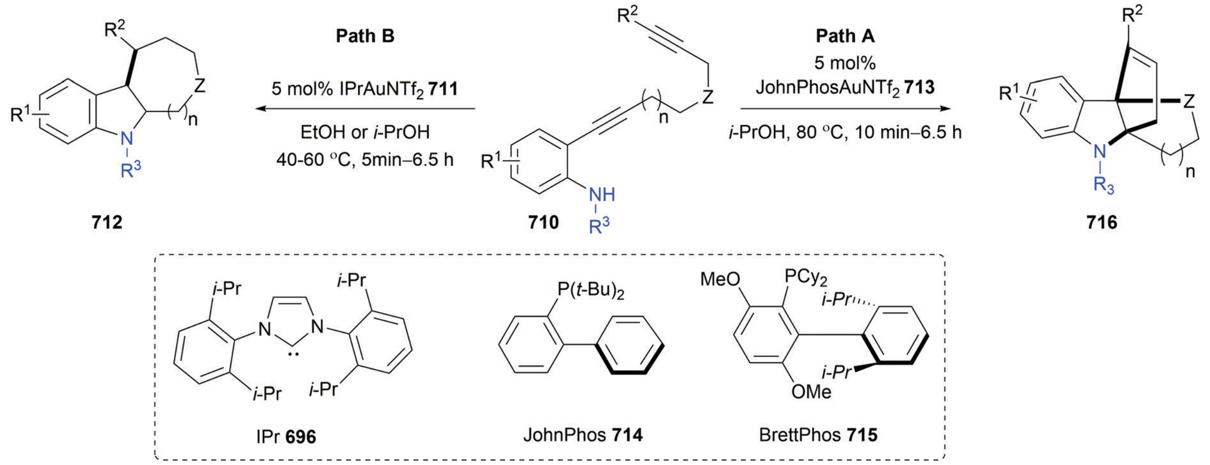


Scheme 136 Synthesis of indoles in Au catalysed hydroamination and *endo-dig* cyclisation.

substituted in the *ortho* position to alkyne, **710h** propellane type indoline **716h** was formed in moderate yield (44%), while oxocine-fused indole was not detected at all. The steric repulsion between *o*-Br and phenyl groups interferes with the formation of indole **712h.** When the length of the chain between both C≡C bonds was shorter as in **710u,** the propellane type indoline **716u** is



Scheme 137 Proposed mechanism of the synthesis of fused carbazole **700t** in the hydroamination/cyclisation reactions catalysed by gold complexes **699**.



Scheme 138 Synthesis of fused indolines **716** and indoles **712** catalysed by gold complexes **711** and **713**.

Table 18 Reagents scope in the gold catalysed synthesis of fused indolines **716a–w** and indoles **712a–w**

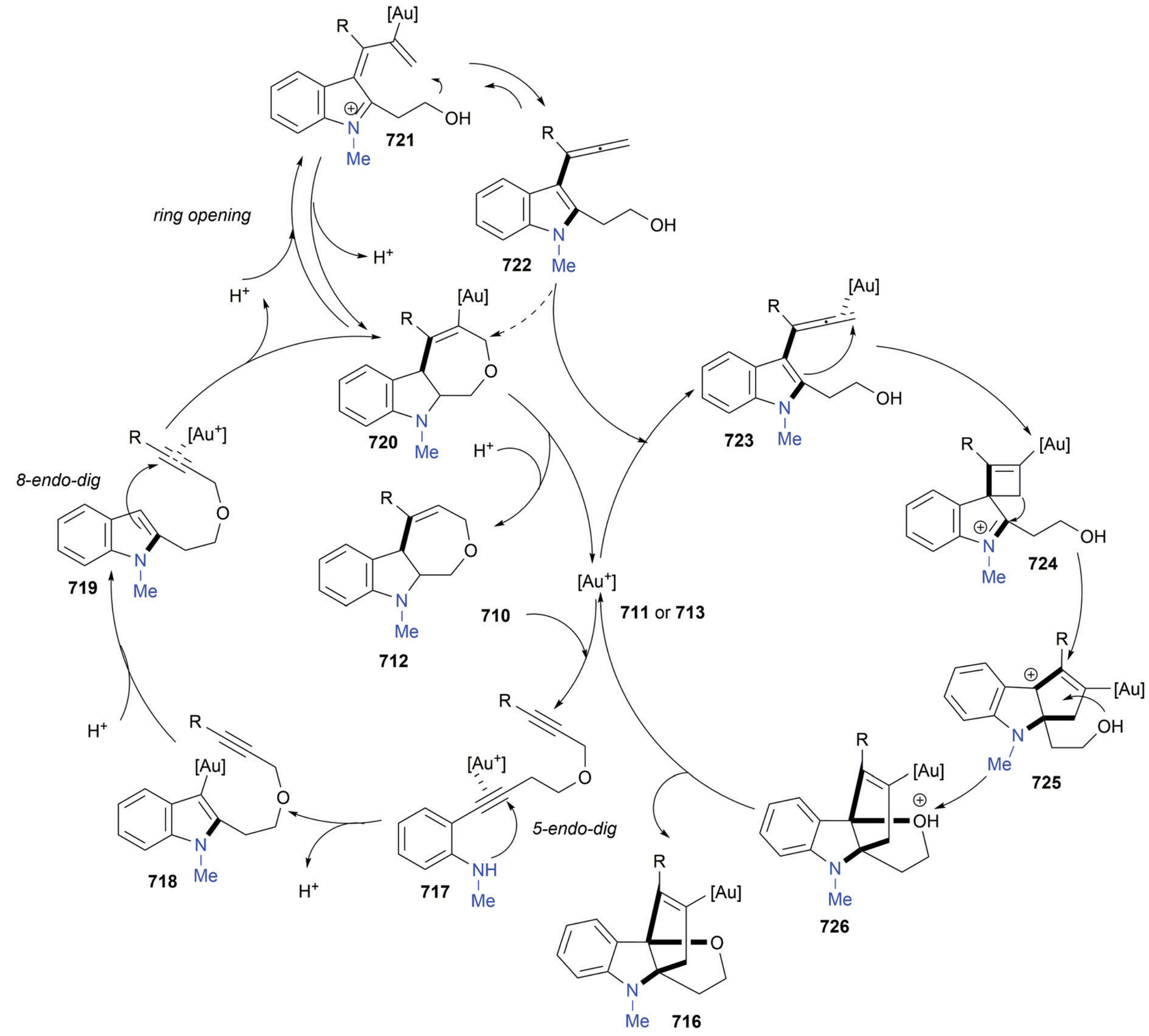
Entry	710	R^1	R^2	R^3	*n*	*Z*	Method	Yield **716** [%]	Yield **712** [%]
1	**710a**	H	Ph	Me	1	0	A	**716a**, 11	**712a**, 82
2							B	**716a**, 88	**712a**, 8
3	**710b**	4-F	Ph	Me	1	O	A	**716b**, 3	**712b**, 68
4							B	**716b**, 67	**712b**, 22
5	**710c**	4-Cl	Ph	Me	1	O	A	**716c**, trace	**712c**, 64
6							B	**716c**, 79	**712c**, 13
7	**710d**	4-Br	Ph	Me	1	O	A	**716d**, 6	**712d**, 62
8							B	**716d**, 82	**712d**, 11
9	**710e**	4-Me	Ph	Me	1	O	A	**716e**, 3	**712e**, 77
10							B	**716e**, 77	**712e**, 6
11	**710f**	4-MeO	Ph	Me	1	O	A	**716f**, 3	**712f**, 77
12							B	**716f**, 77	**712f**, 6
13	**710g**	4-CN	Ph	Me	1	O	A^a	**716g**, 0	**712g**, 17
14							B	**716g**, 0	**712f**, 5
15	**710h**	3-Br	Ph	Me	1	O	A	**716h**, 0	**712h**, 0
16							B	**716h**, 44	**712h**, 0
17	**710i**	2-Br	Ph	Me	1	O	A	**716i**, trace	**712i**, 71
18							B	**716i**, 80	**712i**, 9
19	**710j**	H	4-ClC$_6$H$_4$	Me	1	O	A	**716j**, $<$10	**712j**, 73
20							B	**716j**, 77	**712j**, 8
21	**710k**	H	4-BrC$_6$H$_4$	Me	1	O	A	**716k**, $<$15	**712k**, 56
22							B	**716k**, 69	**712k**, 4
23	**710l**	H	4-CNC$_6$H$_4$	Me	1	O	A	**716l**, $<$11	**712l**, 73
24							B	**716l**, 74	**712l**, 6
25	**710m**	H	4-MeC$_6$H$_4$	Me	1	O	A^a	**716m**, $<$12	**712m**, 53
26							B	**716m**, 76	**712m**, 10
27	**710n**	H	4-MeOC$_6$H$_4$	Me	1	O	A^a	**716n**, $<$14	**712n**, 22
28							B	**716n**, 67	**712n**, 0
29	**710o**	H	4-ClC$_6$H$_4$	Me	1	O	A	**716o**, $<$7	**712o**, 71
30							B	**716o**, 74	**712o**, 8
31	**710p**	H	2-ClC$_6$H$_4$	Me	1	O	A	**716p**, $<$12	**712p**, 70
32							B	**716p**, 26	**712p**, 27
33	**710q**	H	1-naphthyl	Me	1	O	A	**716q**, $<$9	**712q**, 63
34							B	**716q**, 52	**712q**, 0
35	**710r**	H	Me	Me	1	O	A^b	**716r**, 8	**712r**, 16
36							B	**716r**, 34	**712r**, 5
37							C	**716r**, 82	**712r**, trace
38	**710s**	H	Ph	H	1	O	A	**716s**, 7	**712s**, 32
39							B	**716s**, 18	**712s**, 0
40	**710t**	H	Ph	Bn	1	O	A	**716t**, trace	**712t**, 56
41							B	**716t**, 77	**712t**, 8
42	**710u**	H	Ph	Me	0	O	A	**716u**, 0	**712u**, 63
43							B	**716u**, 0	**712u**, 44
44	**710v**	H	Ph	Me	2	O	A	**716v**, 0	**712v**, 0
45							B	**716v**, 28	**712v**, 0
46	**710w**	H	Ph	Me	1	NTs	A	**716w**, 0	**712w**, 63
47							B	**716w**, 0	**712w**, 67

Reaction conditions: A: 5 mol% IPrAuNTf$_2$ **711**;EtOH or *i*-PrOH, 40–60 °C, 5 min–6.5 h; B: 5 mol% JohnPhosAuNTf$_2$ **713**, *i*-PrOH, 80 °C, 10 min–6.5 h. [a] Additional 5 mol% of **711** was added. [b] The reaction was carried out in *i*-PrOH with the addition of MS3 Å at 80 °C.

not obtained due to the higher ring strain, whlie for longer chains as in **710v** no nine-membered ring fused indole **712v** was produced, while **716v** was obtained in 28% (Table 18).

The mechanism of this transformation, in which hydroamination is a crucial step was proposed according to the experiments. Activation of alkyne with gold **717** is responsible for 5-*endo-dig* cyclisation followed by the protodeauratiom towards the indole. Next, the activation of the second alkyne group promotes the 8-*endo-dig* hydroarylation of **719** to intermediate **720**. The subsequent protodeuaration of **720** furnishes oxocine fused indole **712**. The intermediate **720** can be easily opened to cationic intermediate **721**. Elimination of the gold from **721** leads to allene **722**, which is essential for obtaining propellane-type indoline **716** (Scheme 139).[315] Protic solvents accelerate the protodeauration of vinyl-gold intermediate **720** yielding oxocine-fused indoles **712**. The same influence is observed for electron-donating IPr ligand **696**. When allene **722** is formed the mechanism is favoured to obtained propellane-type indolines **716**. The DFT calculations for this transformation was also used to help underpin the reaction mechanism.[316] A detailed discussion on the influence of substituents attached to the nitrogen atom in aniline, in the diyne, and the aryl ring on process selectivity and product yields and mechanism of the process were comprehensively discussed by the authors in several papers.[313–315]

Wiest, Helquist *et al.* applied a hydroamination reaction for the desymmetrisation of diynes **727a–c**, **730a–c**, **732** in the



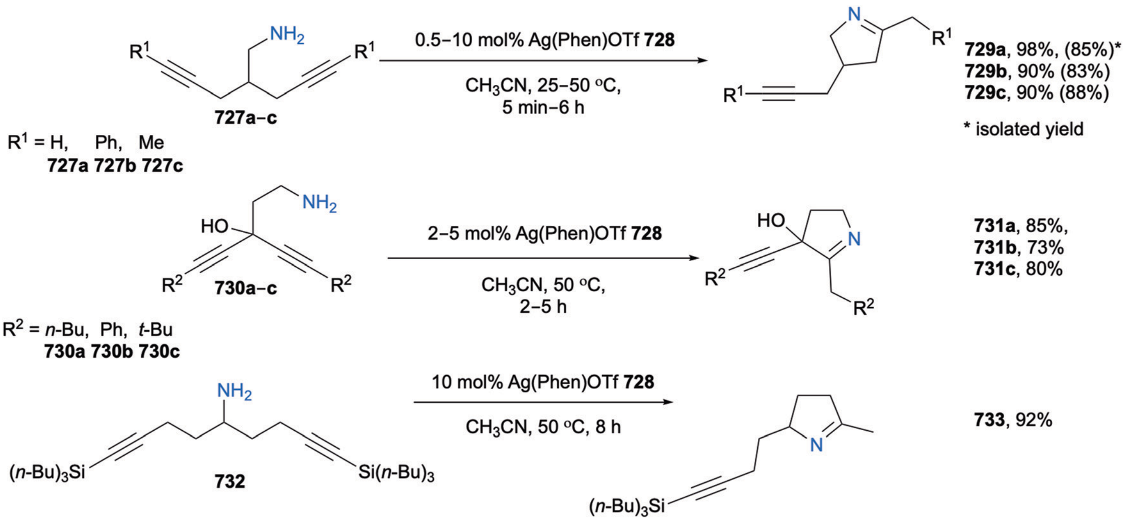
Scheme 139 Proposed mechanism of the synthesis of fused indolines **716** and indoles **712** catalysed by gold complexes.

presence of Ag(phen)OTf **728** yielding to 1-pyrrolines **729a–c**, **731a–c**, or **733** with two entirely different, orthogonal functional groups, which are capable of further functionalisation. The reaction occurred under mild reaction conditions (25–50 °C), with the low catalyst **728** loadings (0.5–2.0 mol%) (Scheme 140).[64] Additionally, this method was applied to the synthesis of natural indolizidine alkaloid (±)-monomorine **743**, which started from the hydroamination/cyclisation of diyne **734** synthesised from 4-bromo-1-butyne followed by the several steps illustrated in Scheme 141.[64]

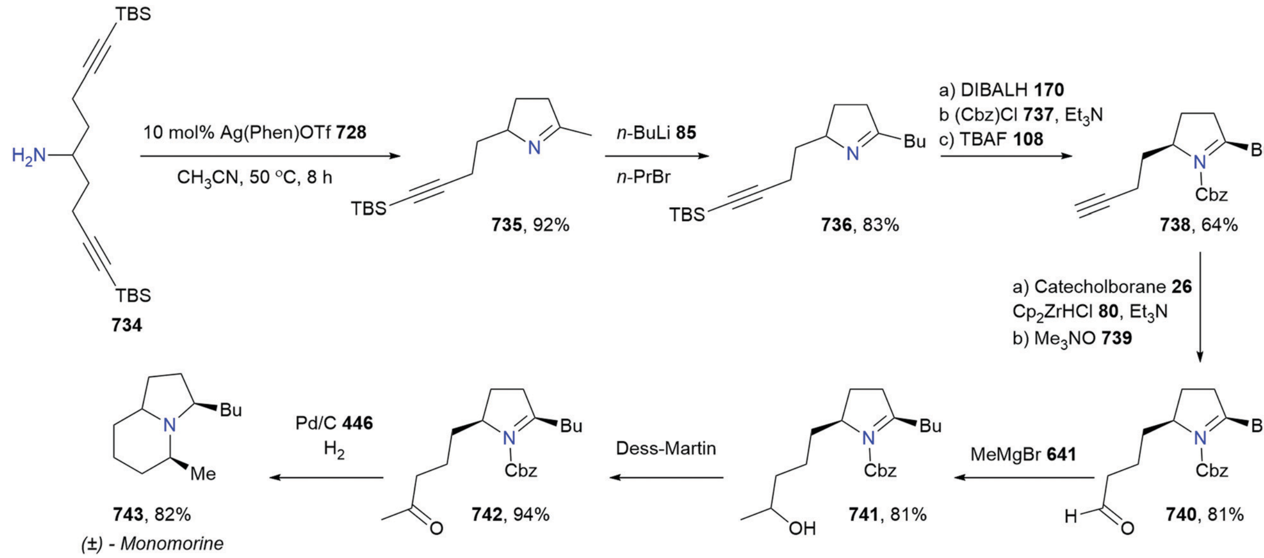
In the hydroaminative cyclisation of diynes was used also $AgSbF_6$ **746** as a catalyst. The process was developed for the synthesis of naphthol-indole derivatives **750a–l** from 1,3-diynes **745a–l** and sulfoxonium ylides **744** in a one-pot cascade reaction (i) intramolecular hydroamination/cyclisation of diyne-substituted anilines **745a–l** to **750a–l**, and (ii) $[RhCp^*Cl_2]_2$ **748** catalysed arene *ortho*-C–H bond activation. Indoles functionalised in the C2 position **750** were obtained with good yields with high functional groups tolerance (Scheme 142).[317]

The system generated *in situ* from $TiCl_4$ **448** by the addition of *t*-$BuNH_2$ **751** in toluene is an active catalyst for the hydroamination of alkynes and 1,3-diynes with hydrazine **633** leading to indole or pyrrole derivatives respectively. Using 20 mol% of $TiCl_4$ **448**, at 105 °C for 18 h, the reagents (anilines **679a–b** and dodeca-5,7-diyne **13a**) are quantitatively converted to the products mixture of mono- and bishydroamination of diyne **13a**. The pyrroles **752** were obtained as the main products in 30% yield (Scheme 143).[318]

$CpCo(C_2H_4)_2$ **755** was applied in the hydroaminative coupling of α,ω-diynes **79b**, **160**, **753a–j** with various amides **754a–f**, which resulted in the formation of dienamides **757–758** with high regio- and stereoselectivity (Scheme 144 and Table 19). Such compounds can be used as reagents in Diels–Alder reaction, in the synthesis of polycyclic compounds as well as natural product derivatives. They can be also synthesised from alkynes by a co-oligomerisation reaction with *N*-vinyl amides or Ti-catalysed coupling with ynamides.[319,320] The mechanism of Co-mediated reaction started from the oxidative addition of



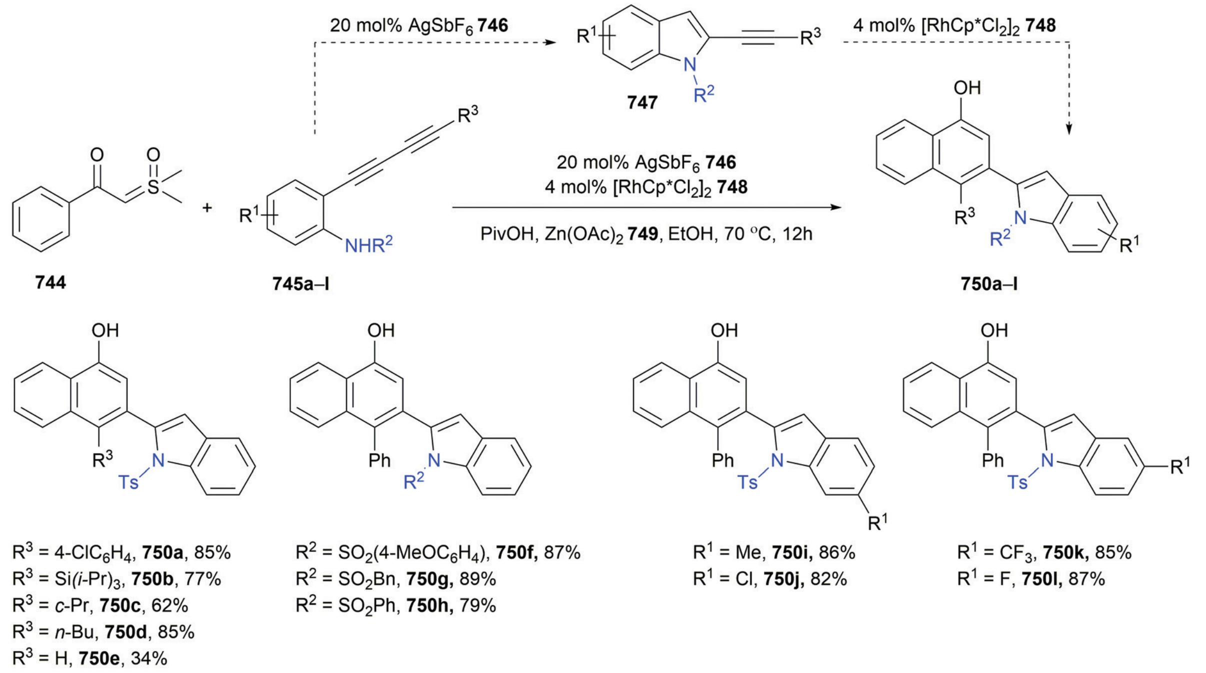
Scheme 140 Desymmetrisation of diynes **727a–c**, **730a–c**, **732** *via* intramolecular hydroamination.



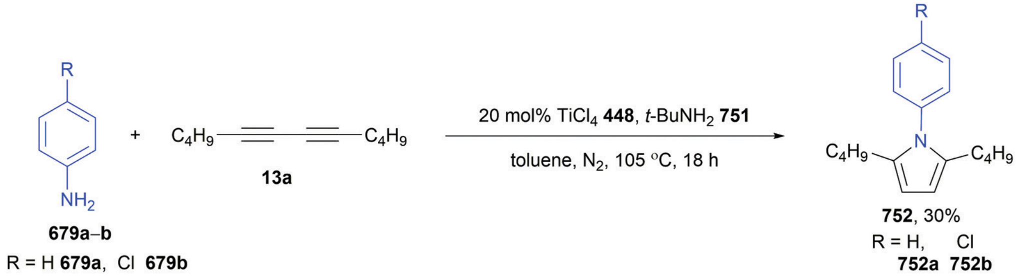
Scheme 141 Synthesis of the alkaloid (±)-*Monomorine* **743** with the hydroamination step.

diyne **79b**, **160**, or **753a–j** to the metal centre of **755** with the formation of cobalt–cyclopentadiene **760**, followed by the formation of 18 electron *N*-coordinated complex **761**. Proton transfer from nitrogen to carbon then takes place to generate intermediate **762**, which subsequently rearranges to *N*-coordinated cobaltcyclopentene **763**, that tautomerises to product **764**. The regioselectivity is controlled by the proton transfer step to the least hindered carbon atom in cobaltcyclopentadiene (Scheme 145). The reaction occurring according to this mechanism permitted several amidated 1,2-dimethylenecycloalkanes to be obtained in moderate to good yields (24–81%) (Scheme 144 and Table 19).[321]

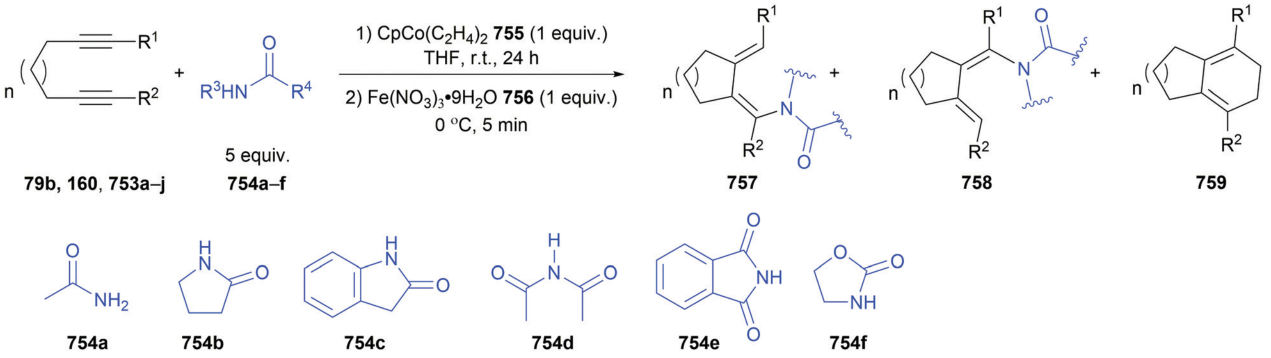
Shimada and Yamamoto have developed a different approach applying hydroamination reaction in the C–C bond cleavage in diynes **1a**, **13a**, **617**, and **765a–f** with *o*-aminophenols **766a–h**. The transformation leads to 2-substituted benzoxazoles **769** and **771** and ketones **770** and **772**. The reaction occurred according to two possible pathways in the presence of $Ru_3(CO)_{12}$ **489** with NH_4PF_6 **767** by the C≡C (path A) or C–C single (path B) bond cleavage. The formation of more sterically hindered benzoxazoles **769** is favourable. Additionally, the bulky groups in the diyne (*e.g.*, *t*-butyl **765c**) led to the almost exclusive formation of product (**769**, **769** : **771** = 30 : 1) with 81% yield. For substituted *o*-amimophenols **766d–f** in positions 4 and 5 with strong electron-donating or electron-withdrawing groups, the reactions were sluggish. Ru-catalyst **489** was found to be more effective in the reaction with terminal diynes **765a–f**, while internal diynes **1a** and **13a** proceeded better with $Pd(NO_3)_2$ **768** (Scheme 146). The key step in the bond cleavage is the hydroamination of one of the C≡C bonds of **765a–f** with **766**, followed by the



Scheme 142 Synthesis of naphtol–indole derivatives **750a–l** from 1,3-diynes **745a–l** and sulfoxonium ylides **744** catalysed by $[RhCp^*Cl_2]_2$ **748**/$AgSbF_6$ **746** system.



Scheme 143 Synthesis of pyrroles **752** in the hydroamination of dodeca-5,7-diyne **13a** with anilines **679** in the presence of $TiCl_4$ **448**/*t*-$BuNH_2$ **751**.



Scheme 144 Hydroaminative coupling of substituted α,ω-diynes **79b**, **160**, and **753a–j** with amides **754a–f** catalysed by Co catalyst **755**.

tautomerisation leading to α,β-unsaturated imines **774**. The addition of the second molecule of *o*-aminophenols **766** to **765** yielded β-aminoimines **775** and their tautomers **777**, which further undergoes intramolecular cyclisation to ketals **776** and **778**. The final step leading to benzoxazoles **769** and **771** occurred by the C–C bond cleavage through a retro-Mannich-type reaction (Scheme 147).[322]

The copper-catalysed synthesis of pyrroles *via* hydroamination of diynes was first published in 1965.[323] 0.1 mol% of CuCl **55** was used for the hydroamination/cyclisation of 1,3-diynes

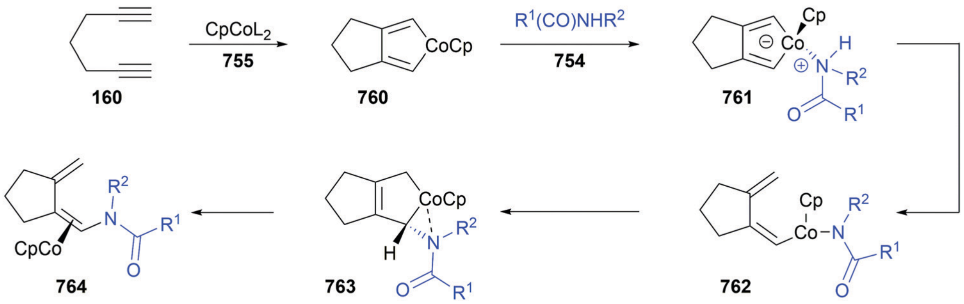
Table 19 Hydroaminative coupling of substituted α,ω-diynes with dienamides **754**

Entry	Diyne	754	Yield 757 : 758 : 759 [%]
			757 = 758 : 759
1	$R^1 = R^2 = H$, $n = 2$, **160**	**754a**	24 : 0
2		**754b**	55 : 0
3		**754c**	65 : 0
4		**754d**	32 : 0
5		**754e**	81 : 0
6		**754f**	69 : 0
7	$R^1 = R^2 = SiMe_3$, $n = 1$, **753a**	**754e**	64 : 0
8	$R^1 = R^2 = Ph$, $n = 1$, **753b**	**754e**	48 : 0
9	$R^1 = R^2 = CMe_2OH$, $n = 2$, **753c**	**754e**	58 : 0
10	$R^1 = R^2 = CO_2Me$, $n = 2$, **753d**	**754e**	0 : 70
11	$R^1 = R^2 = Bpin$, $n = 2$, **79b**	**754e**	0 : 60
			757 : 758 : 759
12	$R^1 = H$, $R^2 = SiMe_3$, $n = 1$, **753e**	**754e**	72 : 0 : 0
13	$R^1 = H$, $R^2 = SiMe_3$, $n = 2$, **753f**	**754e**	66 : 0 : 0
		754c	14 : 65 : 0
14	$R^1 = H$, $R^2 = Ph$, $n = 2$, **753g**	**754e**	70 : 0 : 0
15	$R^1 = H$, $R^2 = Ph$, $n = 2$, **753g**	**754c**	78 : 0 : 0
16	$R^1 = Ph$, $R^2 = SiMe_3$, $n = 2$, **753h**	**754e**	62 : 18 : 0
17	$R^1 = H$, $R^2 = CMe_2OH$, $n = 2$, **753i**	**754e**	70 : 0 : 0
18	$R^1 = H$, $R^2 = Bpin$, $n = 2$, **753j**	**754e**	22 : 13 : 0

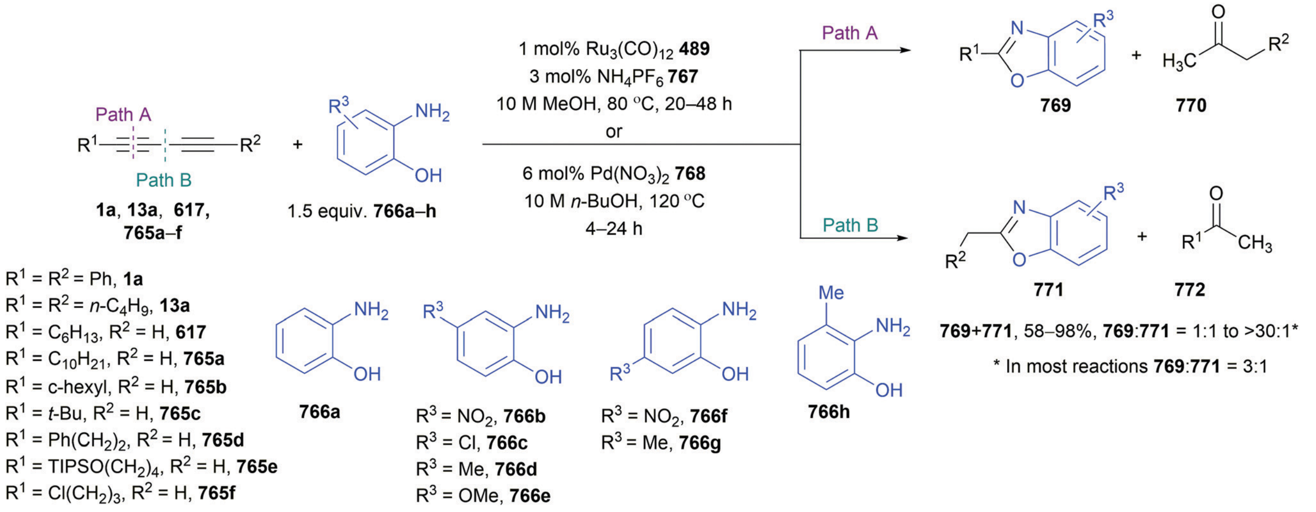
Reaction conditions: (1) $CpCo(C_2H_4)_2$ **755** (1 equiv.), **754** (5 equiv.), THF, r.t., 24 h, then: (2) $Fe(NO_3)_2 \cdot 9H_2O$ **756** (1 equiv.), 0 °C, 5 min.

1a, **1d**, **65a**, **208b**, **258n**, **781a–c** with aromatic and aliphatic primary amines **679a**, **679c**, **679g**, **782a–i** and ammonia **632**. The reaction was carried out in MeOH, EtOH, 1,4-dioxane, or DMF for 1 h, at 150–180 °C, furnishing pyrroles **783a–w** in moderate yields. Increasing the catalyst **55** concentration to 10 mol%, under solvent-free conditions, and with 10 equiv. of amine **679** and **782** it was possible to obtain almost quantitative yields of pyrroles **783** in 24 h (Scheme 148).[324,325] The same catalytic system was applied in the synthesis of 2,2′-bipyrrolle derivatives possessing four aryl groups in 1, 1′, 5, 5′ positions. The reaction was carried out with CuCl **55** as a catalyst, in DMF at 90–150 °C.[326,327]

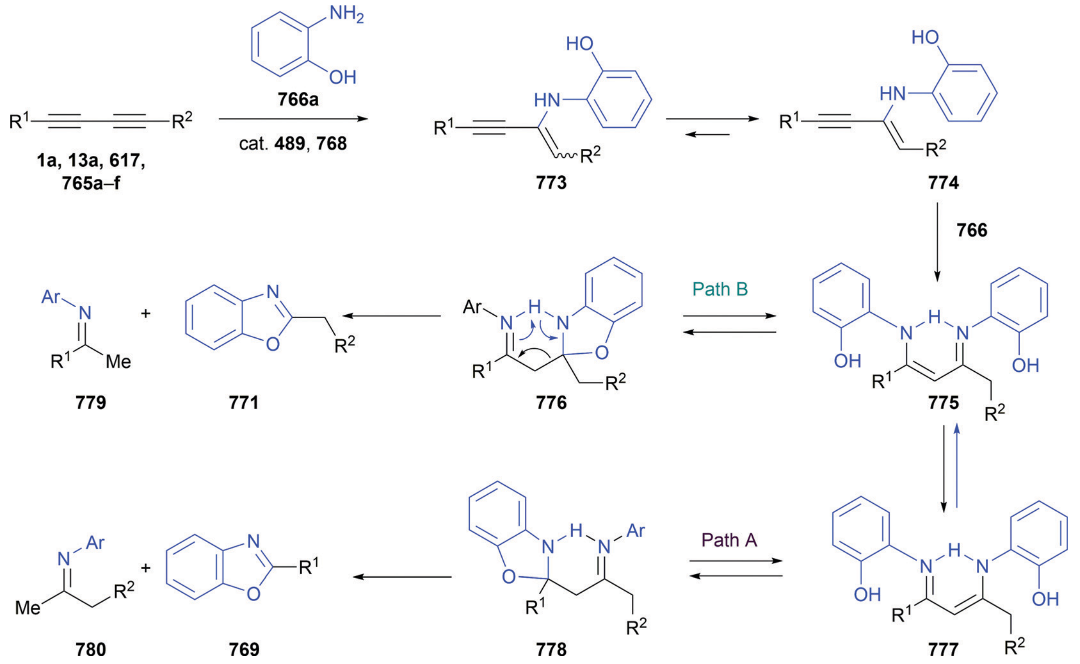
Modified Ullmann conditions (CuI **519**/L/Cs_2CO_3, where L = 1,10-phenatrholine, L-proline, (*E*)-4-hydroxy-L-proline) were used for the synthesis of *N*-alkenynes in hydroamination/amidation reaction of 1,4-diaryl-1,3-diynes **1a**, **1c–d**, **27b** with heterocyclic indoles **784a–d**, azoles **784e–h**, pyrazole **784i** and cyclic or acyclic amides **754b**, **785a–c**. The reaction yielded a mixture of (*Z*)- and (*E*)-*N*-alkenynes **786–796** with an excess of the (*Z*)-isomer in the range of 60–95%, and 75–95% yields for cyclic reagents **784a–i**, **754b**, and exclusive formation of (*E*)-isomer for acyclic amides **785a–c**. In the latter case, the yield was reduced to low to moderate values 10–41% (Scheme 149).



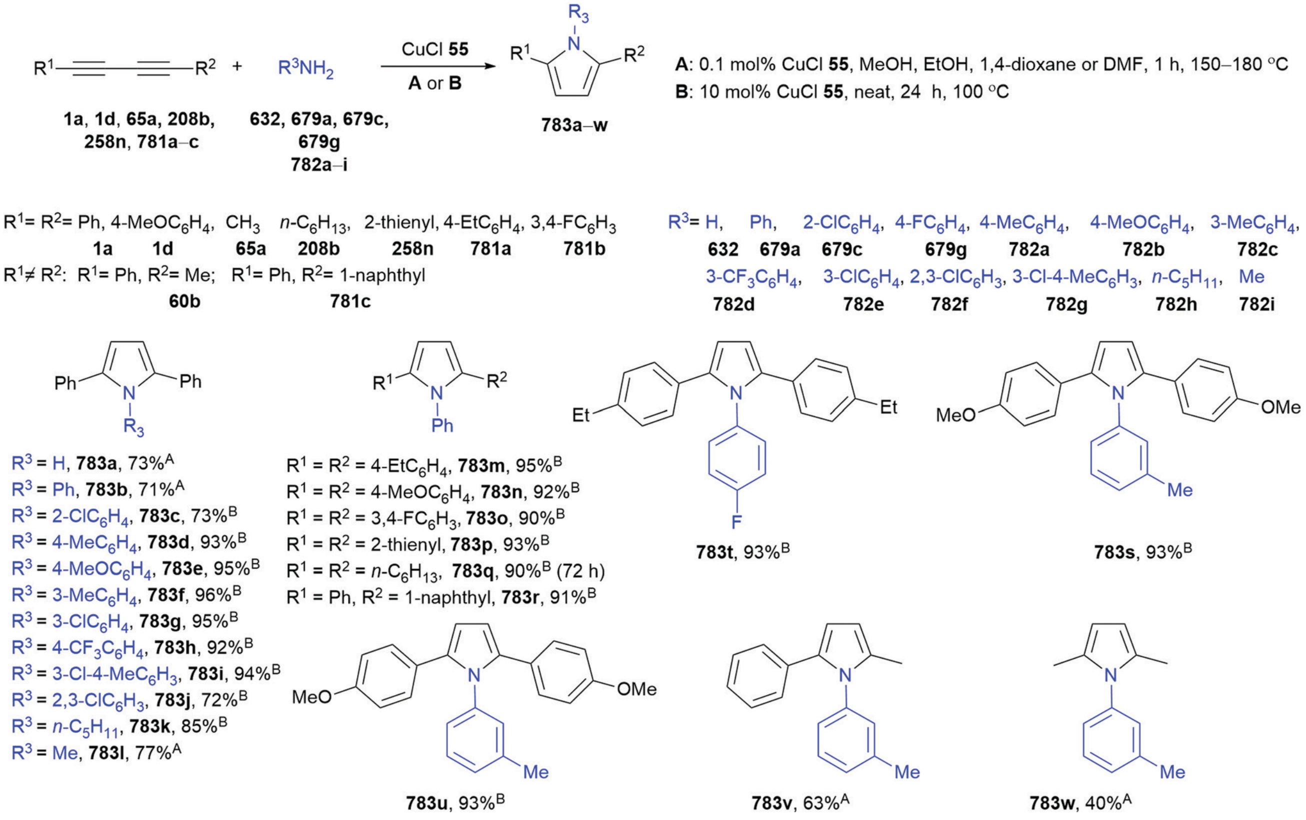
Scheme 145 Mechanism of hydroaminative coupling of diyne **160** with amides **754** catalysed by $CpCo(C_2H_4)_2$ **755**.



Scheme 146 Carbon–carbon bond cleavage of diynes **1a**, **13a**, **617**, and **767a–f** with 2-aminophenols **766a–h** catalysed by $Ru_3(CO)_{12}$ **489** and $Pd(NO_3)_2$ **768**.

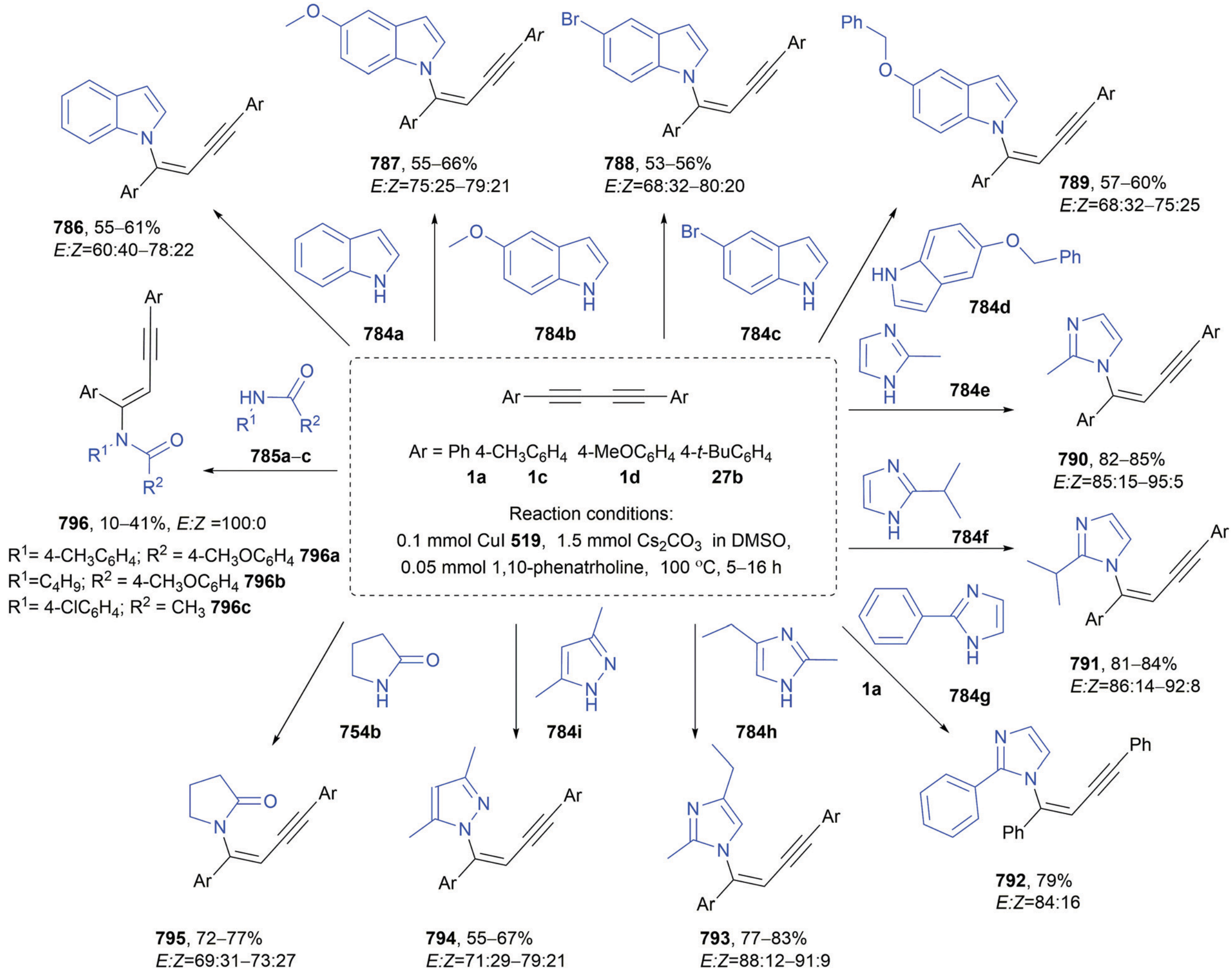


Scheme 147 Mechanism of C–C bond cleavage in diynes **1a**, **13a**, **617**, and **765a–f** based on the hydroamination reaction with 2-aminophenol **766a** catalysed by $Ru_3(CO)_{12}$ **489** or $Pd(NO_3)_2$ **768**.



Scheme 148 Synthesis of 1,2,5-trisubstituted pyrroles **783** by CuCl **55** catalysed cycloaddition of 1,3-diynes **1a**, **1d**, **65a**, **208b**, **258n**, **781a–c** with amines **679a**, **679c**, **679g**, **782a–i** and ammonia **632**.

The authors assumed that the hydroamination reaction occurred *via* an oxidative addition/reductive elimination mechanism with the addition of the N–H bond to Cu^I **519** as an initial step of the mechanism. The insertion of diyne **1a, 1c–d, 27b** to the Cu–N

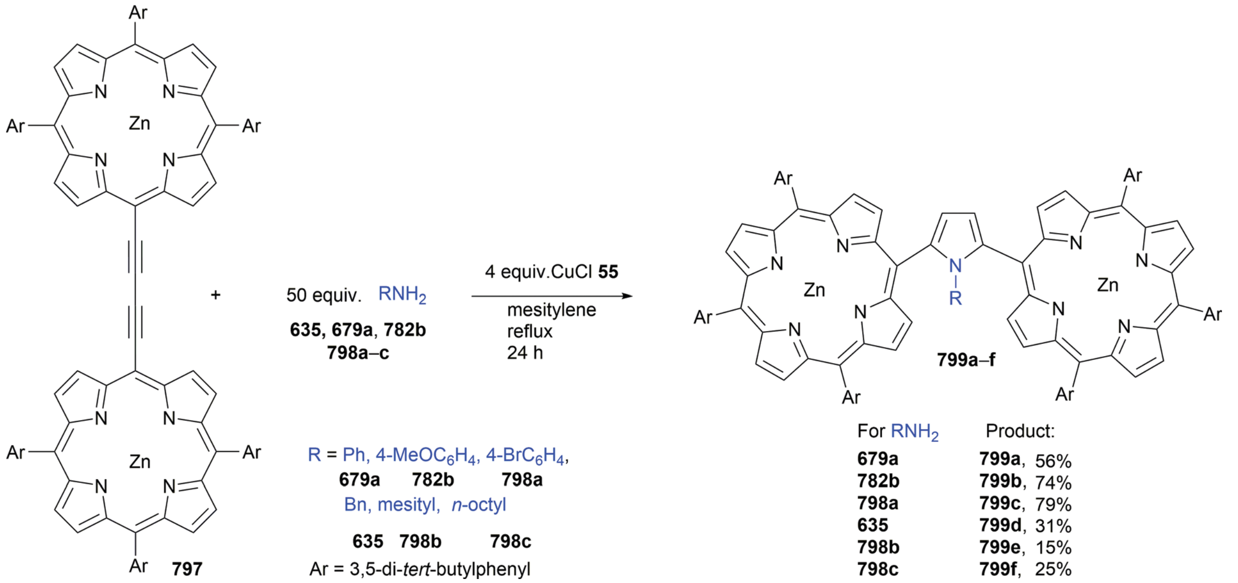


Scheme 149 Hydroamination/hydroamidation of 1,3-diynes (**1a**, **1c–d**, **27b**) under modified Ullmann conditions.

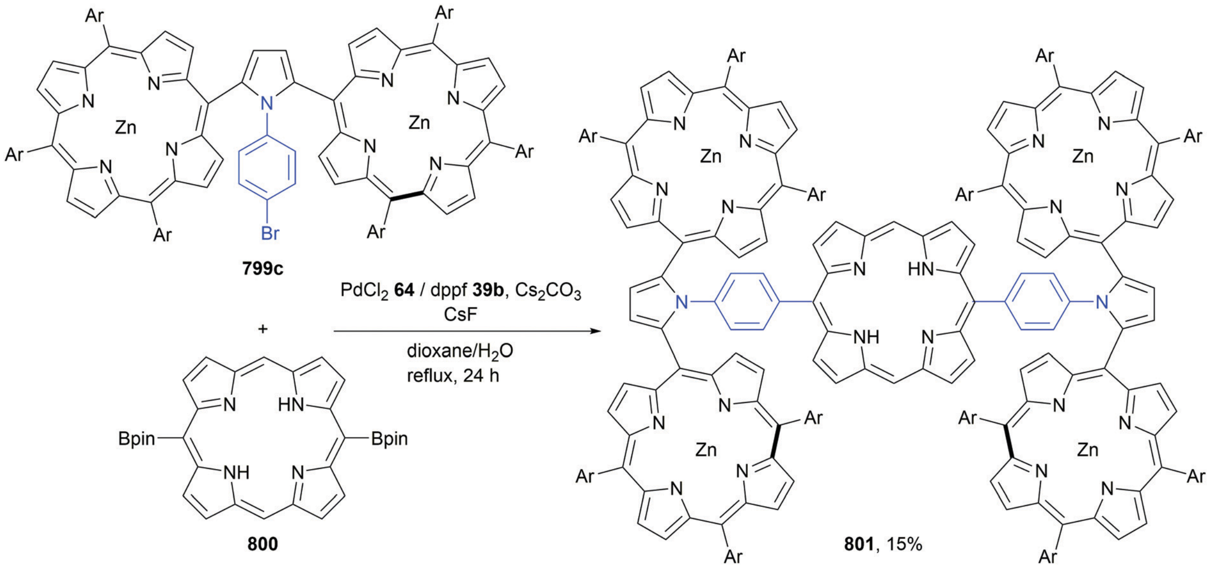
bond, followed by the reductive elimination of *N*-alkenyne **786–796** is postulated as the next stage of the mechanism. The system was not efficient for alkyl-substituted 1,3-diynes and unsymmetrical reagents.[328]

CuCl **55** was used also for the hydroamination of *meso*,*meso'*-1,3-butadiyne-bridged Zn(II) diporphyrin **797** with various amines **635, 679a, 782b, 798a–c** to *meso*,*meso'*-pyrrole-bridged Zn(II) diporphyrins **799a–f**. The structure of diporphyrin **799** was confirmed by the single-crystal X-ray diffraction method. The bulky mesitylamine **798b** and octylamine **798c** were less active in the hydroamination reaction (Scheme 150). Moreover, it was possible to modify in Suzuki–Miyaura coupling reaction of diporphyrin with 4-bromophenyl substituted pyrrole **799c** with porphyrin possessing Bpin **800** groups to **801** with 15% yield. As a catalyst $PdCl_2$ **64**/dppf **39b** was used. (Scheme 151).[329]

3- or 4-Aminomethylpyrroles **806a–k** and aminomethylfurans **807a–i** bearing a sulfur group were obtained by the hydoamination/cyclisation reaction of *N*- or *O*-tethered 1,6-diynes **802** and **803a–d** with a sulfur substituent attached to one of the alkynyl group using two catalytic systems $Ni(hfa)_2$ hydrate **805** (10 mol%)/DBU (Method A) or $Ni(hfa)_2$ hydrate **805**/$PdCl_2(PPh_3)_2$ **94**/DBU (Method B) in DMSO at room temperature (Scheme 152). The products were obtained with good yields (50–92%) using cyclic and acyclic amines **804a–n** between 2–72 h (Table 20). The possible mechanism of this transformation started from the isomerisation of diyne (**802, 803**) to alkyne-allene **809** or allene-allene **810** intermediates *via* a carbanion **808,** followed by its coordination to the Ni atom **805** with a sulfur ligand. This activates the alkyne moiety **812** towards intermolecular attack by the amine **804.** This leads to the diamino metal intermediate **815** through intermediates **813** and **814.** Next, the second intramolecular cyclisation towards **816** occurred, followed by the formation of **817.** Its protonolysis and isomerisation yields the product **806** or **807** and regenerates the catalyst. Less nucleophilic amines might react with water according to path II with the formation of side product **811** (Scheme 153). The presence of the sulfur group in the products **806** permitted their further functionalisation such as the introduction of formyl or acetyl groups (**819a–c, 820**) which are then susceptible to subsequent modification in other chemical transformations, or the reaction with the strong base leading to 1*H*-pyrrole **821** (Scheme 154).[330]



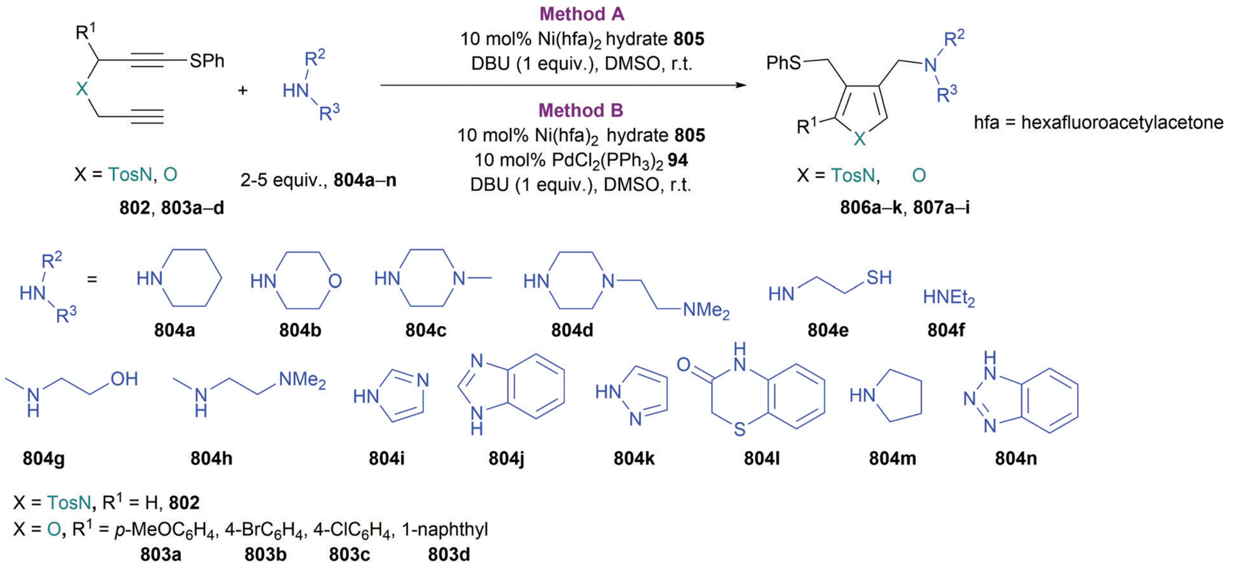
Scheme 150 Synthesis of *meso,meso′*-pyrrole-bridged Zn(II) diporphyrins **799a–f** in Cu(I)-mediated annulation of *meso,meso′*-1,3-butadiyne-bridged Zn(II) diporphyrin **797** with various amines.



Scheme 151 Synthesis of Zn(II)-free base hybrid porphyrin pentamer **801** in Suzuki–Miyaura coupling reaction of **799c** with **800**.

Another approach to N-heterocyclic 1,2,5-trisubstituted pyrroles **826a–e** and **829a–c** was based on the hydroamination reaction of separated 1,4- or 1,5-diynes **822a–b**, **541**, or **827** with primary amines (aniline **679a**, benzylamine **635**, or 4-methoxybenzylaniline **782b**) with the subsequent 5-*endo* dig or 5-*exo* dig cyclisation in the presence of Ti(NMe$_2$)$_2$(dpma) **823** or Ti(NMe$_2$)$_2$(dmpm) **827** as a catalyst. The addition of amine **679a** or **635** occurred according to the Markovnikov rule. The hydroamination of unsymmetrical 1,4-diynes with aryl and alkyl substituents led exclusively to the product with amine attached to the β-carbon to aryl substituent **826a–e**, while nonsubstituted 1,4-diynes led to the dihydroamination product, since the second hydroamination of the terminal alkyne is faster than the intermolecular cyclisation reaction. In the case of internal or terminal 1,5-diynes **541**, **827**, the cyclisation was faster than the hydroamination of the second C$\equiv$C bond, and the cyclic pyrroles **829a–c** were formed exclusively (Scheme 155). This method is an alternative of Paal–Knorr synthesis to pyrroles, especially when unsymmetrical 1,4-diketones are used as reagents.[331]

Wasterhausen *et al.* published several papers on the hydroamination reactions of alkynes and conjugated 1,4-diphenylbuta-1,3-diyne **1a** in the presence of heterobimetallic complexes constructed from Ca- and K-complexes **830** and **839.** The homometallic Ca- or K-catalysts were inactive in the hydroamination reactions. Depending on the structure of the complex

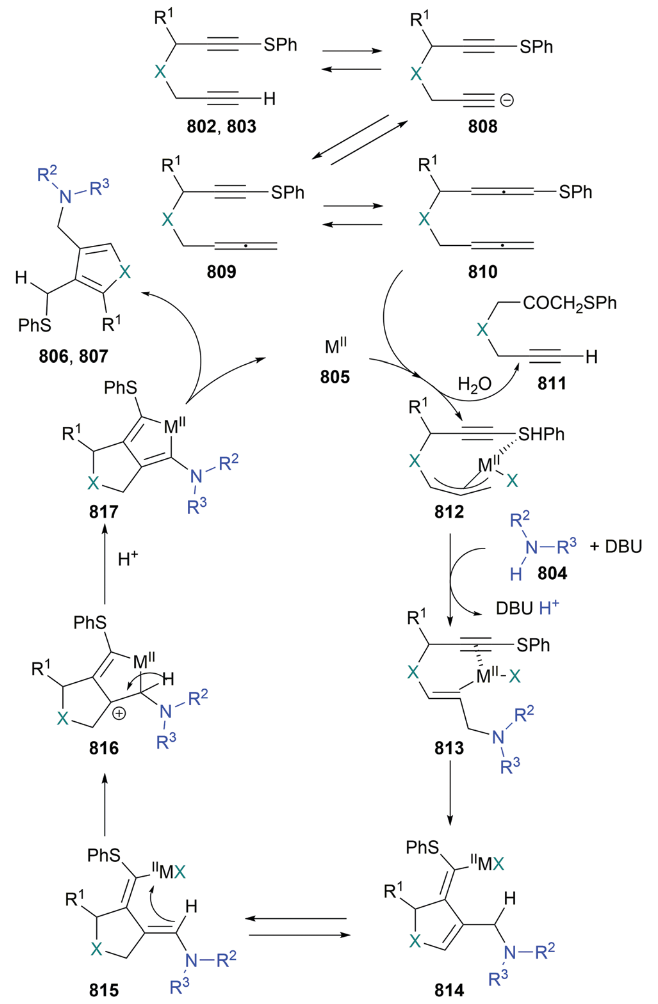


Scheme 152 Hydroamination/cyclisation of sulfur-substituted 1,6-diynes **802** and **803a–d** with secondary amines **804a–n** catalysed by Ni(hfa)$_2$ **805**.

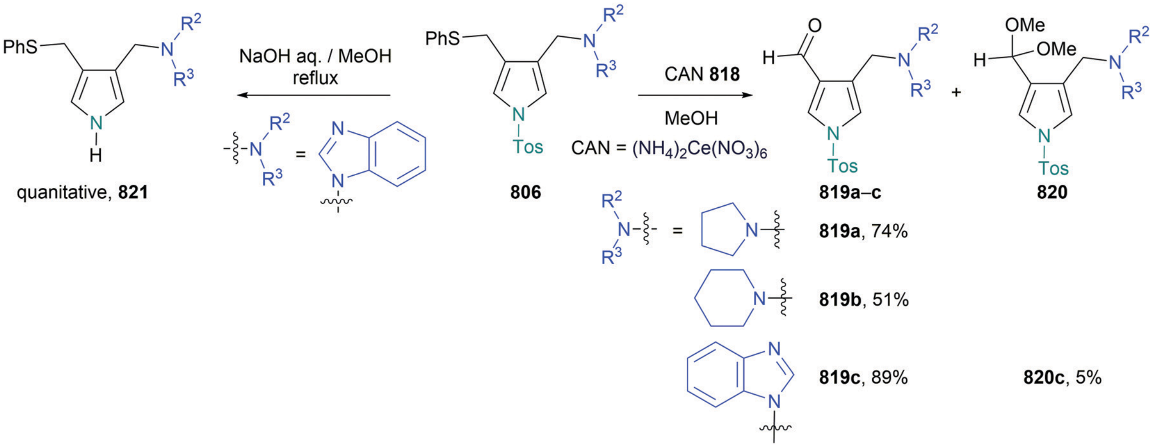
Table 20 Synthesis of 3- or 4-aminomethylpyrroles **806a–k** and aminomethylfurans **807a–i** by hydroamination/cyclisation of 1,6-diynes **802** and **803a–d** with amines **804a–n** catalysed by Ni(hfa)$_2$ **805**

Entry	Diyne	Amine	Method	Time [h]	Yield [%]
1	**802**	**804a**	A	4	**806a**, 79,
2			B	8	**806a**, 100
3		**804b**	A	6	**806b**, 77
4			B	8	**806b**, 88
5		**804c**	A	6	**806c**, 75
6			B	8	**806c**, 100
7		**804d**	A	8	**806d**, 50
8			B	8	**806d**, 76
9		**804e**	B	8	**806e**, 43
10		**804f**	A	8	**806f**, 49
11			B	8	**806f**, 82
12		**804g**	A	8	**806g**, 71
13			B	72	**806g**, 84
14		**804h**	B	72	**806h**, 66
15		**804i**	A	4	**806i**, 70
16			B	4	**806i**, 43
17		**804j**	A	7	**806j**, 74
18			B	1	**806j**, 92
19		**804k**	A	4	**806k**, 48
20			B	2	**806k**, 53
21	**803a**	**804a**	A	6	**807a**, 63
22		**804c**	A	8	**807b**, 71
23		**804j**	B	8	**807c**, 71
24		**804l**	B	8	**807d**, 70
25	**803b**	**804m**	B	8	**807e**, 61
26		**804n**	B	72	**807f**, 39
27	**803c**	**804j**	A	4	**807g**, 55
28		**804m**	B	72	**807h**, 61
29	**803d**	**804m**	B	1	**807i**, 69

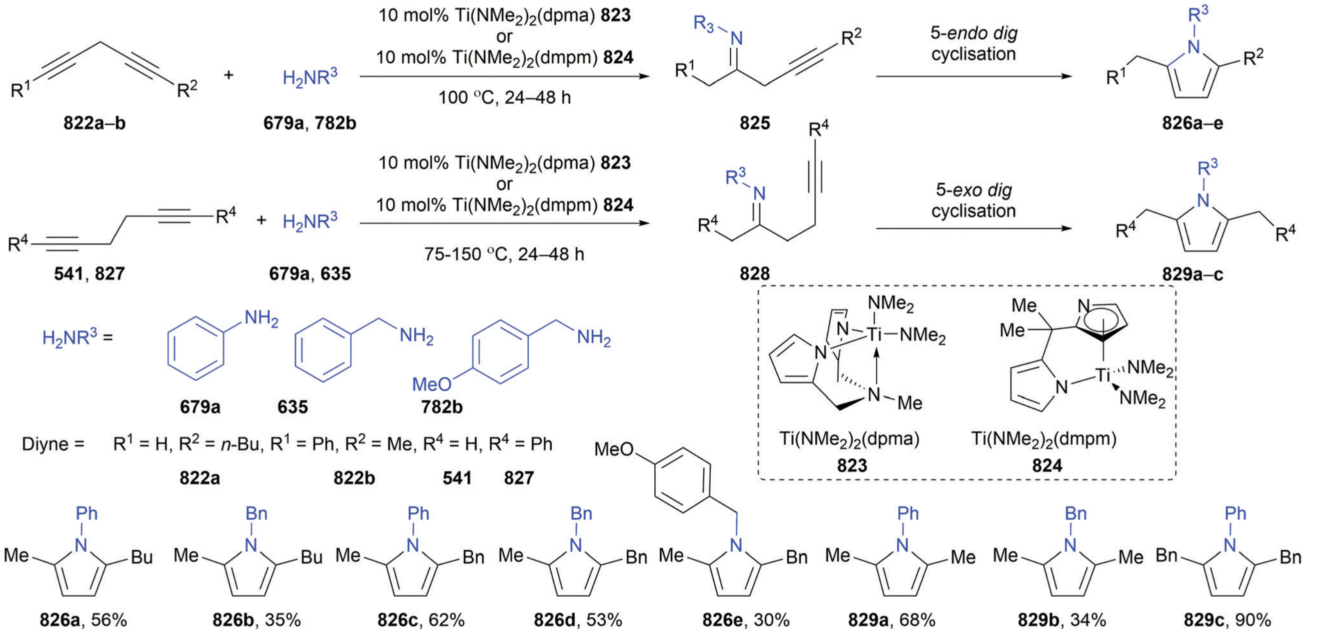
and amine, various products were formed such as cyclic cyclohepta-1,2,4,6-tetraenes **832a–b** and **833**, pyrroles **834a–d**, aminated enynes **836a–c, 840–841**, or bisaminated dienes **837a–b.** The reactions under room temperature lead to thermodynamic products, *e.g.*, cyclohepta-1,2,4,6-tetraenes **832a–b** or **833**, while at higher temperatures, kinetic pyrrole products **834a–d** were formed. The structure of amines has a significant



Scheme 153 Mechanism of hydroamination/cyclisation of sulfur-substituted 1,6-diynes **802** and **803** with secondary amines **804** catalysed by Ni(hfa)$_2$ **805**.



Scheme 154 Chemical transformations of aminomethylpyrroles **806** towards formyl or acetyl-functionalised products (**819a–c**, **820**) or 1-*H*-pyrrole **821**.



Scheme 155 Ti-Catalysed **823** and **824** hydroamination/cyclisation of 1,4-diynes **822a–b** or 1,5-diynes **541**, **827**. Synthesis of 1,2,5-trisubstituted pyrroles **826a–e** and **829a–c**.

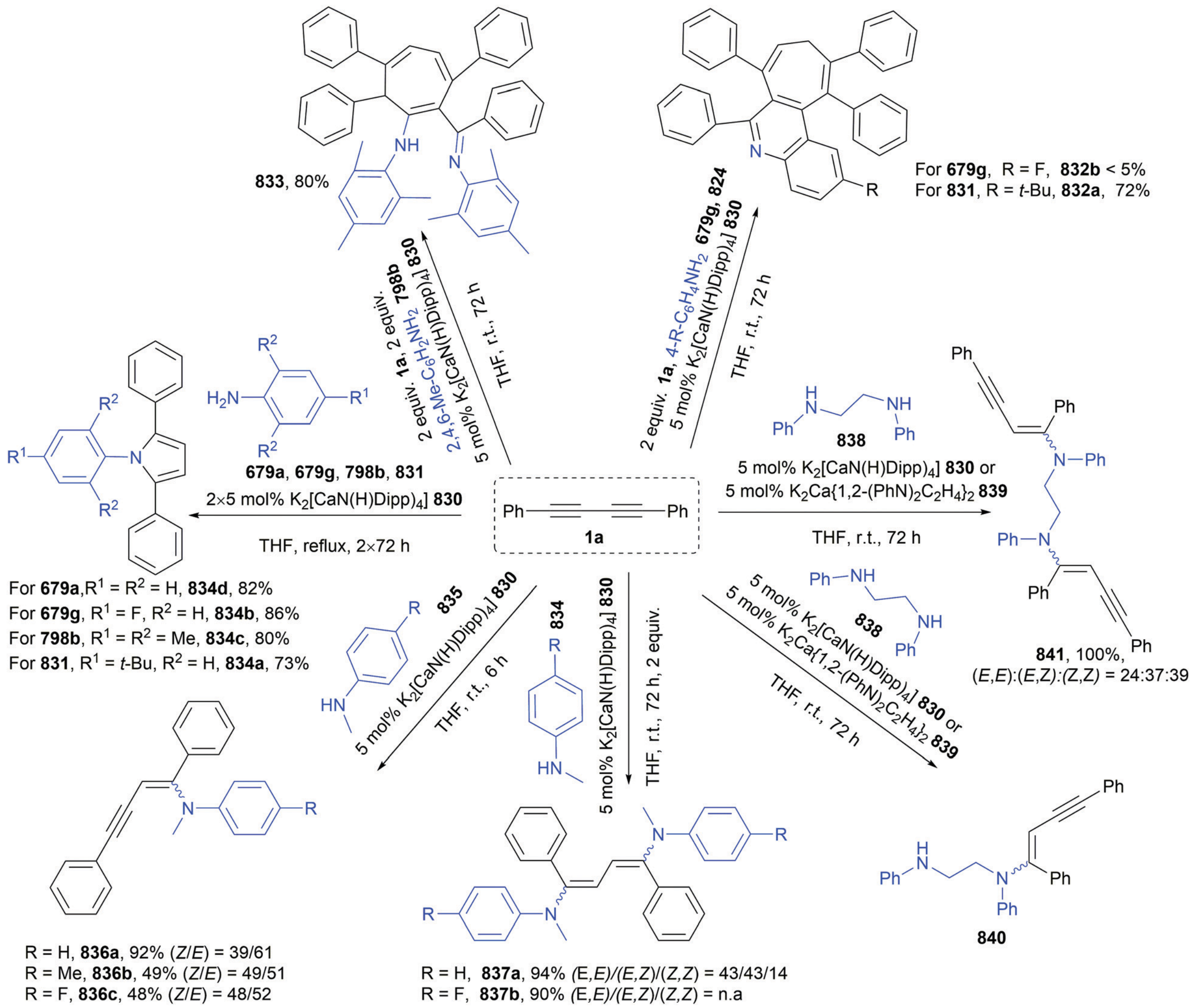
influence on the product type (Scheme 156.). The authors discussed in detail the mechanisms of these transformations, which differ according to the hydroamination reagent.[294]

9. Hydrophosphination

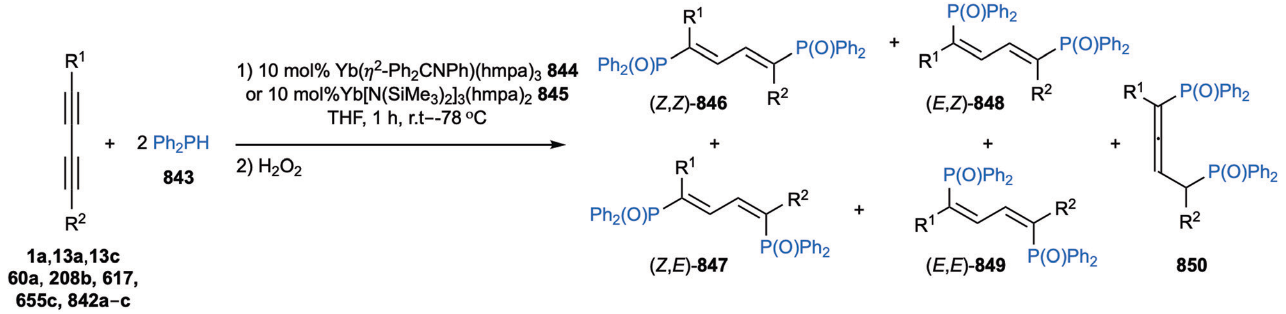
Unsaturated organophosphorus compounds have found several applications as building blocks in organic synthesis, (chiral) ligands for catalyst formation, biologically active compounds, or in the preparation of flame retardant materials.[332–337] They are also used in medicinal- or agrochemistry, as components of drugs, which are used in *e.g.*, bone, calcium-metabolism or neurological diseases, antiviral and antibacterial systems, enzymes inhibitors.[337–345] They are commonly applied as monodentante as well as chelating ligands in various chemical transformations.[332–334,339] The synthesis of vinylicphoshpines can be carried out using the hydrophosphination reaction.[30,59,346] This type of addition reaction was also used in the reaction with conjugated and separated diynes, but, unlike hydroamination, the examples are limited only to a few papers.

9.1. Hydrophosphination of conjugated and non-conjugated diynes

Hydrophosphination of conjugated 1,3-diynes **1a, 13a, 13c, 60a, 208b, 617, 655c,** and **842a–c** with Ph_2PH **843** was carried out in the presence of ytterbium complexes $[Yb(\eta^2\text{-}Ph_2CNPh)(hmpa)_3]$ **844** or $[Yb[N(SiMe_3)_2]_3(hmpa)_2]$ **845.** The reaction occurred according to the double addition of two diphenylphosphine



Scheme 156 Hydroamination of 1,4-diphenylbuta-1,3-diyne **1a** catalysed by heterobimetallic K and Ca complexes **830** and **839**.



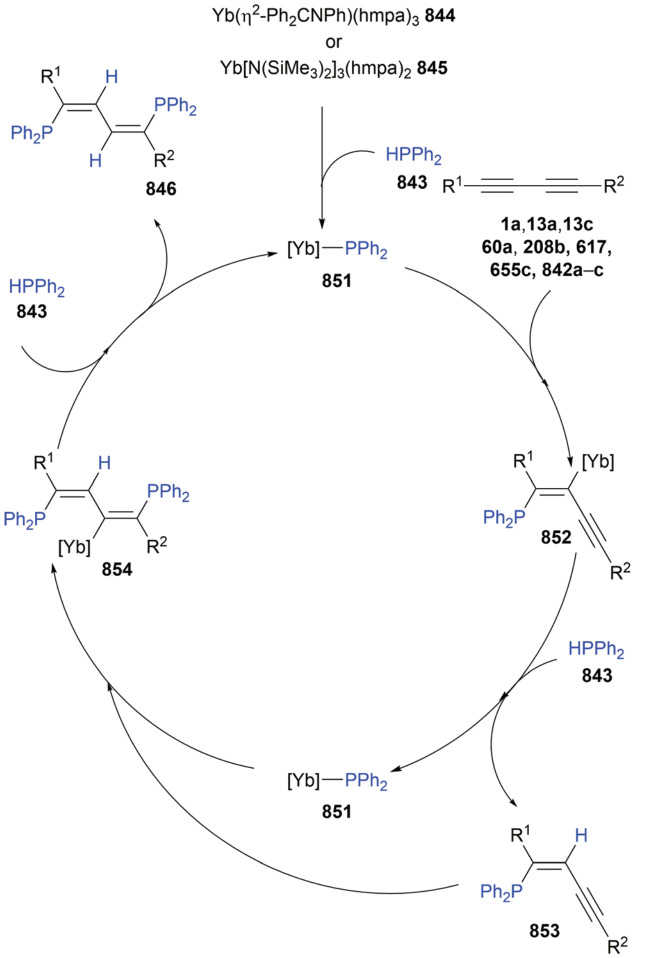
Scheme 157 Double hydrophosphination of conjugated diynes with diphenylphosphine **843** catalysed by Yb-complexes **844–845**.

843 molecules to the C≡C bonds of diyne, even at low temperatures −35 to (−78) °C, and the formation of bis(diphenylphosphinyl)-dienes **846–849** with high yields but relatively low selectivities (Scheme 157 and Table 21). The stereochemistry of the process was kinetically and thermodynamically controlled and the formation of the specific isomer depended on the structure of diyne. Hydrophosphination of disubstituted diynes predominantly formed (*Z*,*Z*)-**846** isomers with a minor amount of (*Z*,*E*)-**847** butadiene. Terminal diynes yielded (*E*,*Z*)-butadiene **848** as the main product, while the sterically hindered

Table 21 Double hydrophosphination of conjugated diynes with diphenylphosphine **843** catalysed by Yb-complexes **844–845**

Entry	Diyne	Cat.	T [°C]	Total yield [%]	Selectivity [%] **846 : 847 : 848 : 849 : 850**
1	$R^1 = R^2$ = Ph, **1a**	**845**	−78	28	0 : 0 : 0 : 100 : 0
2	$R^1 = R^2$ = *n*-Bu, **13a**	**844**	−15	92	67 : 33 : 0 : 0 : 0
3	$R^1 = R^2$ = *t*-Bu, **13c**	**844**	r.t.	89	0 : 0 : 0 : 0 : 100
4		**845**	r.t.	80	0 : 0 : 0 : 0 : 100
5	$R^1 = R^2$ = *c*-C_6H_{11}, **60a**	**844**	−15	74	86 : 14 : 0 : 0 : 0
6	$R^1 = R^2$ = *n*-Hex, **208b**	**844**	−15	82	74 : 26 : 0 : 0 : 0
7		**845**	−15	82	61 : 39 : 0 : 0 : 0
8	R^1 = Ph, R^2 = *n*-Hex, **655c**	**844**	−15	98	73 : 27 : 0 : 0 : 0
9		**845**	−15	95	72 : 28 : 0 : 0 : 0
10	R^1 = H, R^2 = *n*-Hex, **617**	**844**	−78[a]	80	0 : 0 : 61 : 39 : 0
11		**845**	−78[a]	89	6 : 0 : 75 : 19 : 0
12	R^1 = 4-MeOC_6H_4, R^2 = *n*-Hex, **842a**	**844**	−15	85	73 : 19 : 8 : 0 : 0
13	R^1 = H, R^2 = *n*-Bu, **842b**	**844**	−78[a]	89	16 : 0 : 64 : 20 : 0
14	R^1 = H, R^2 = Ph, **842c**	**844**	−78	—	Polymerisation

[a] −78 °C for 1 h then r.t. for 2 h.



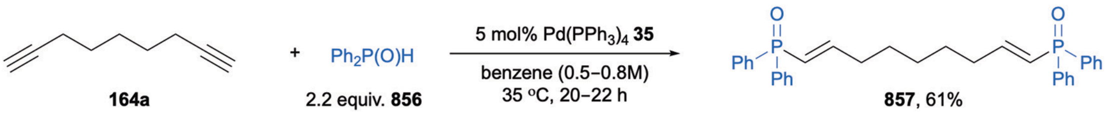
Scheme 158 The mechanism of hydrophosphination of 1,3-diynes catalysed by Yb-complexes **844** and **845**.

1,4-ditertbutyl-buta-1,3-diyene **13c** was quantitatively converted to allenic product **850**. The reaction started from the formation of the [Yb]–PPh_2 complex **851**, which underwent anti-addition to diyne to form enynylyterbium complex **852**. Protonation of **852** with Ph_2PH **843** yields diphenylphosphine-substituted enyne **853** and regenerates ytterbium–phosphide active complex **851**. Repetition of this process provided the bishydrophosphination product **846**. The products were easily oxidised with H_2O_2 to phosphine oxides, which were easier to isolate (Scheme 158).[347,348] The formation of diphenylphosphine-substituted enyne **853** in the reaction was also possible using an equimolar ratio of reagents and a shorter the reaction time of up to 30 minutes. After oxidation with H_2O_2, the (*Z*)-products were predominantly formed.

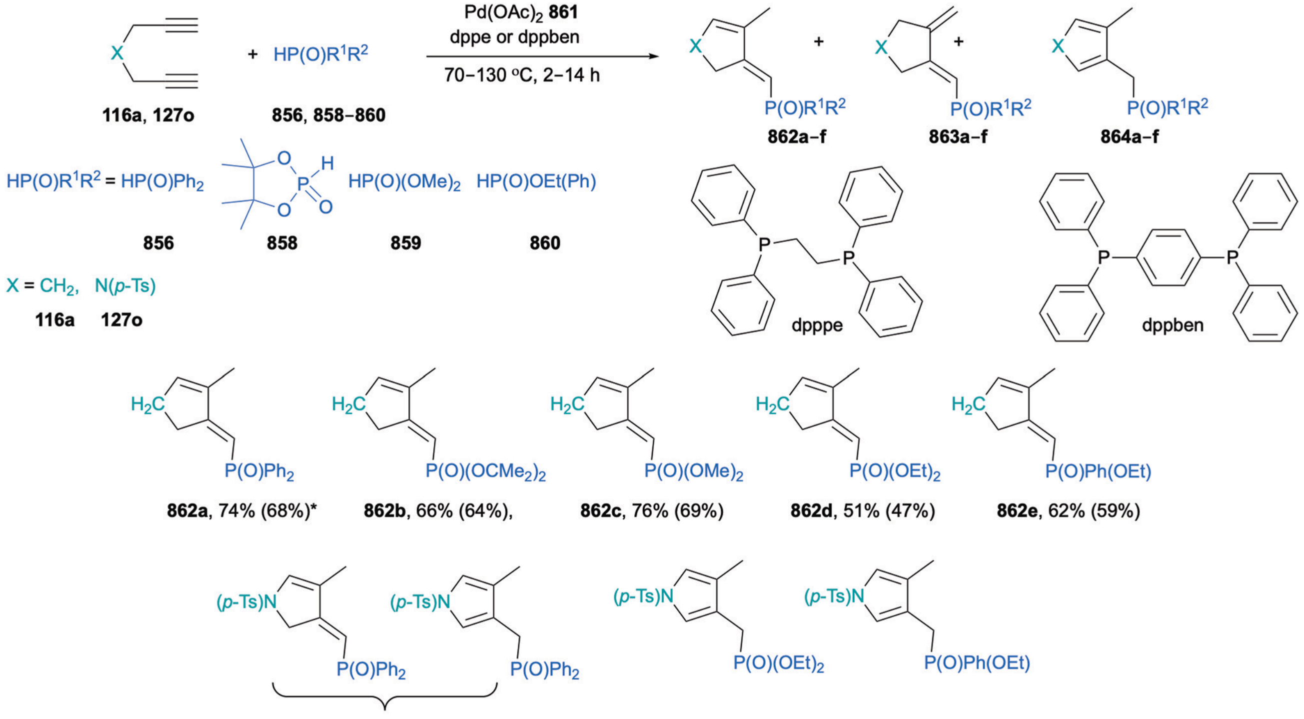
Tanaka *et al.* developed the hydrophospinylation reaction of alkynes in the presence of $Pd(PPh_3)_4$ **35** or $PdMe_2(PR_3)_2$ **855** (PR_3=PPh_3 or $PPhMe_2$, PPh_2Me, PEt_3, PMe_3) catalysts. All these complexes catalysed the synthesis of alkenyldiphenylphosphine oxides from alkynes and $Ph_2P(O)H$ **856**. Less basic phosphines (*e.g.*, PPh_3, PPh_2Me) accelerate the formation of anti-Markovnikov products, whereas application of more basic phosphines *e.g.*, PMe_3 or PEt_3 increases the amount of the geminal regioisomer. The best results were obtained when 5 mol% of $Pd(PPh_3)_4$ **35** was used at 35 °C. This method was used also for hydrophosphinylation of nona-1,8-diyne **164a** derivatives towards 1,9-diphosphinyl-nona-1,8-diene **857** when 2.2 equiv. of $Ph_2P(O)H$ **856** and $Pd(PPh_3)_4$ **35** was used (Scheme 159).[349]

The same authors reported Pd-catalysed hydrophosphinylative carbocyclisation of α,ω-diynes. The reaction occurred in the presence of 5 mol% $Pd(OAc)_2$ **861** and chelating phosphine ligands such as ethylenebis(diphenylphosphine) (dppe) or 1,2-bis(diphenylphosphino)benzene (dppben) at 70 °C in chlorobenzene, toluene, ethylbenzene, or dioxane. The carbocyclisation was the most effective for 1,7-heptadiyne derivatives, while longer or shorter α,ω-diynes were less susceptible to cyclisation, and linear hydrophophinylatve products were mainly obtained. Scheme 160 presents the formation of various products, which depends on the reagents used (diynes **116a** or **127o**, and phosphorus compounds **856**, or **858–860**).[350] For diyne **116a** product **862** is mainly formed, while for **127o** product **864** is predominantly obtained (Scheme 160).

Hydrophosphinylative carbocyclisation was also reported by Yamamoto *et al.* but, instead of Pd-complexes, ruthenium catalysts **281a–c** with cyclopentadiene ligands (responsible for the formation of the active ruthenacyclopentatriene intermediate) were used. The best results were obtained for $[Cp^*Ru(MeCN)_3]PF_6$ **281a** for which exocyclic 1,3-dienylphosphine oxides **866a–j** were exclusively formed, under the optimised reaction conditions using $HP(O)Ph_2$ **856**. In the case of complexes **281b–c**, the hydrative cyclisation product **867** was formed as well. To suppress the formation of these by-products molecular sieves 4 Å were added to the reaction mixture. The $[Cp^*Ru(MeCN)_3]PF_6$ **281a** was used in 5–10 mol%, depending on the reactivity of diynes **865a–j**. The substituents in the tether position have a significant influence on the product yields. The more hindered these groups, the lower the



Scheme 159 Hydrophosphination of nona-1,8-diyne **164a** with $Ph_2P(O)H$ **856** and $Pd(PPh_3)_4$ **35**.



*Isolated yields in brackets.

Scheme 160 Hydrophosphination of α,ω-diynes **116a** and **127o** with phosphines catalysed by $Pd(OAc)_2$ **861** with chelating ligands dpppe and dppben.

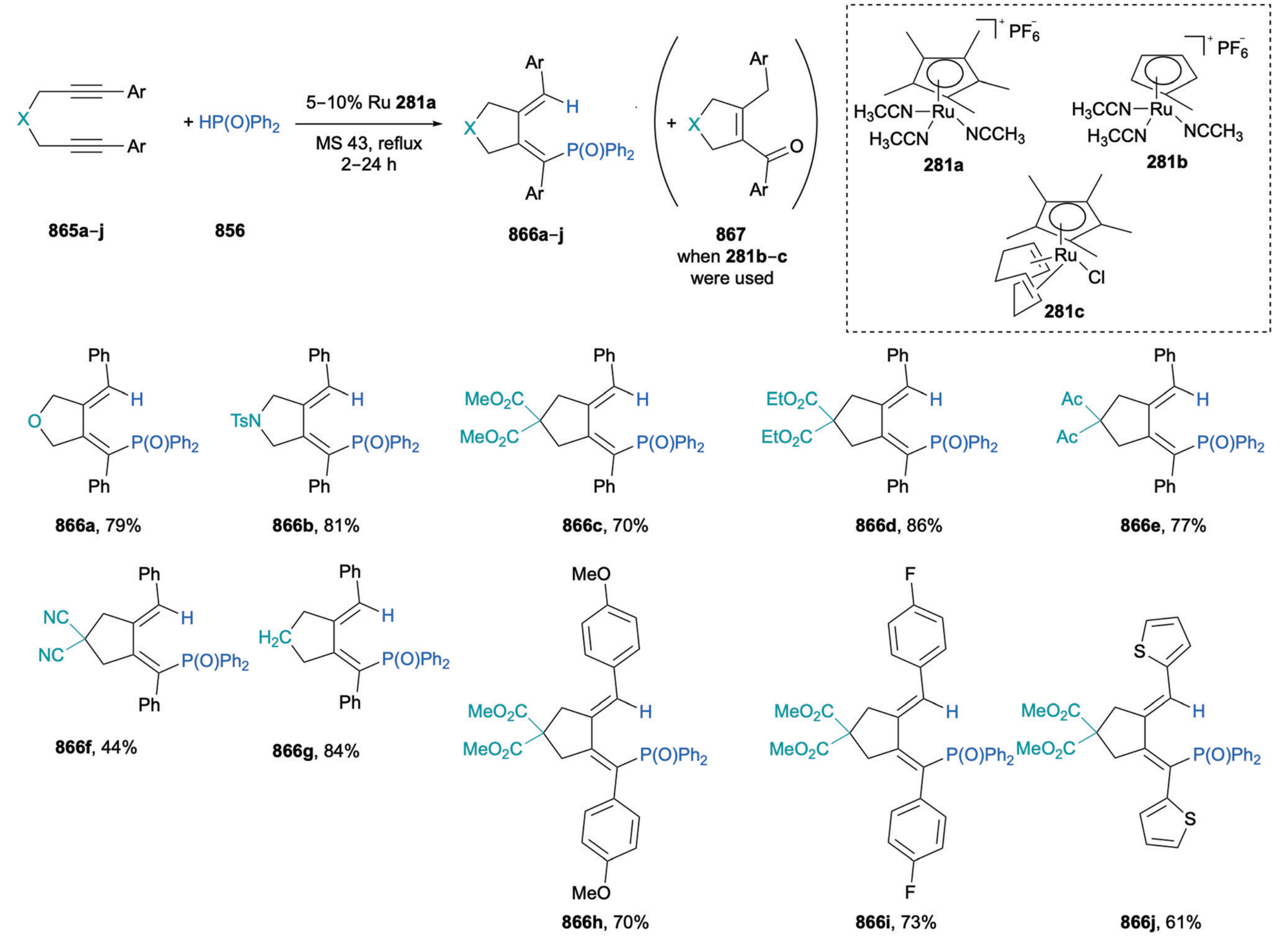
yields of the desired products **866a–j** observed. To obtain the desired cyclic product, 1,6-heptadiyne derivatives need to be used with the aryl substituents in the terminal position (Scheme 161). When shorter chain diynes such as 1,5-hexadiyne, or reagents with alkyl substituents in terminal positions were used, the reaction did not occur or the products were formed in low yield. The aryl terminal groups accelerate the formation of active ruthenacyclopentatriene intermediate, which is essential for this transformation.

The mechanism of this transformation was proposed based on DFT calculations. The reaction started with the oxidative cyclisation of bis(alkyne) complex **868**. The rate-determining step was found to be H-atom transfer, which leads to the monocarbenoid with a phosphinate ligand **869**. The intramolecular attack of phosphorus on the remaining carbenoid carbon generates oxaphospharuthenatricycle **870** followed by the formation of (*Z*)-4-diene complex **871**. The addition of diyne **865** and $HP(O)Ph_2$ **856** generates product **866** and regenerates the active catalytic intermediate **868** (Scheme 162).[351]

Hydrophosphinylation of symmetrical 1,4-diphenyl or 1,4-*tert*-butyl-buta-1,3-diynes (**1a** or **13c**) was also carried out in the presence of a main group element catalyst $[(thf)_4Ca(PPh_2)_2]$ **872**. The composition of the postreaction-mixture depended on the phosphorus reagent. When diphenylphosphane oxide $HP(O)Ph_2$ **856** was used as reagent, 1,4-diphenyl-2,3-bis(diphenyl-phosphoryl)-buta-1,3-diene **873** or 2,2,7,7-tetramethyl-3,6-bis-(diphenyl-phosphoryl)-4-octyne **874** were selectively formed in the reaction with 1,4-diphenylbuta-1,3-diyne **1a** or 1,4-di-*tert*-butylbuta-1,3-diyne **13c** respectively in very good yields (80–82%). The reaction with Ph_2PH **843** yielded different products in 1,4- or 1,3 phoshponylation (**875–876**). These differences in process selectivity are due to the different base-acid interactions between calcium catalyst **872** and Ph_2PH **843** or $HP(O)Ph_2$ **856.** Rather, strong Ca–O interactions are responsible for the closeness of the alkali metal to reactive multiple C–C bonds (Scheme 163).[352]

10. Hydration of conjugated 1,3- and separated 1,*n*-diynes

Hydration of 1,3- and 1,*n*-diynes is limited to several examples, which are focused on the catalytic activation of the water molecule and diyne with various catalysts mostly based on transition metals. This transformation leads to many important



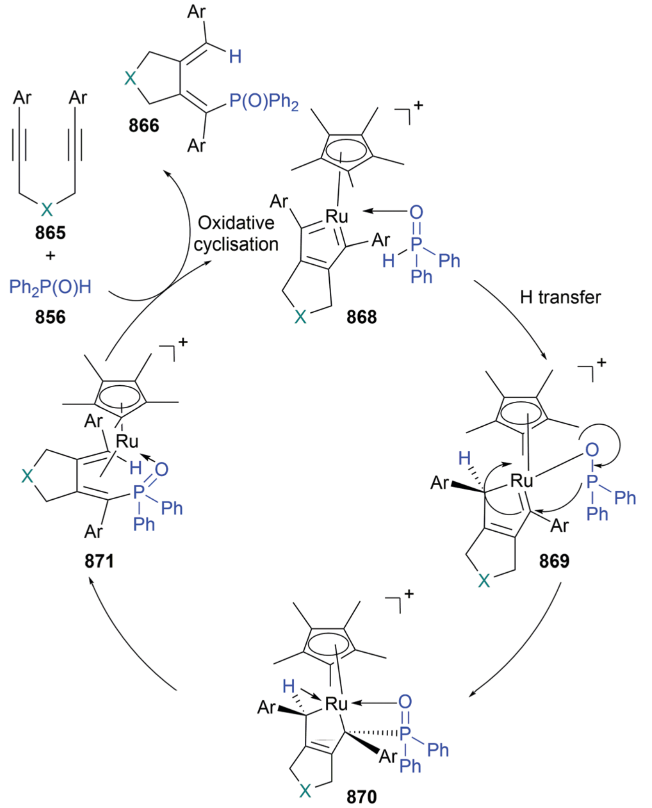
Scheme 161 Ru-catalysed **281** hydrophosphinylative cyclisation of 1,6-diynes **865a–j** towards exocyclic 1,3-dienylphosphine oxides **866a–j**.

building blocks, especially in cyclisation reactions to furanes, 3-(2*H*)-furanones, or γ-pyrones. The obtained products are used in the synthesis of antitumor agents, antibiotics, natural and bioactive compounds.[353–355] The addition of water to the C≡C triple bond may also yield carbonyl compounds *via* tautomerisation of the hydroxylated enyne.

Hydration or hydration/cyclisation reactions are simple and 100% atom economic transformations, which can provide the desired products in a straightforward procedure, without (or with a small number of) side-products. Therefore, they are a useful alternative to common methods, that require the application of complex reagents and multi-step procedures. Most of the catalytic systems for selective hydration reactions of diynes, which are based on predominately gold, ruthenium and palladium complexes, were developed within the last two decades.

The first papers on the hydration of diynes were published in the 1960s and apply mercuric salts. The addition of water to undeca-1,7-diyne **877** provided a mixture of two diketones, undecane-2,7-dione **878** and undecane-2,8-dione **879** with moderate yields and low selectivity.[356,357] A modified procedure was used by Constantino *et al.* in the preparation of natural marine compound 1-(2,6,6-trimethyl-4-hydroxy-cyclohexenyl)-1,3-butanedione **880**, which possess antibiotic activity. They used $HgSO_4$ and formic acid (85%) in the hydration step. The compound was formed in 50% crude yield. The same system was applied for hydration of other cyclohexyl-substituted diynes. The terminal C≡C group was hydrated at first, followed by the reduction of the second alkynyl group.[358]

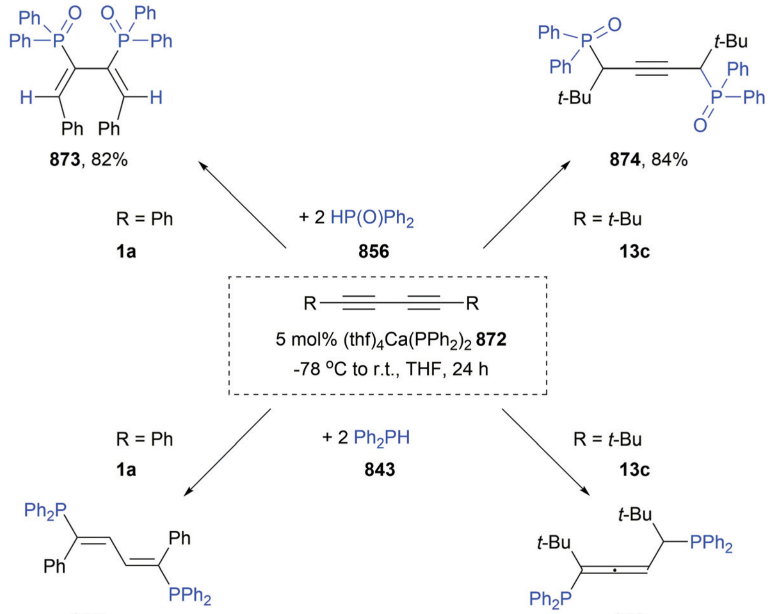
Ruthenium catalysed hydrative cyclisation of various diynes was studied in detail by Trost *et al.*[359–364] They have found that simple cationic $[Cp^*Ru(CH_3CN)_3]PF_6$ **281a** complex, which catalyses many different transformations such as alkyne–alkyne coupling reactions (*e.g.*, dimerisation, trimerisation)[365–368] or cycloaddition reactions with dienes,[369] isocyanates,[370] nitriles,[371] can be effectively used in diyne hydrative cyclisation or cycloisomerisation reactions (Scheme 164).[359–364] Depending on the structure of the diyne, different mechanisms for the reaction occur. Internal diynes can directly react with water in the presence of catalytic amounts of the Ru complex **281a** (3–10 mol%) producing five- or six-membered enones with moderate or excellent yields. The same catalyst was used for the dimerisation of propargylic alcohol and a further intramolecular cycloisomerisation reaction (Scheme 164). Tertiary or secondary propargylic



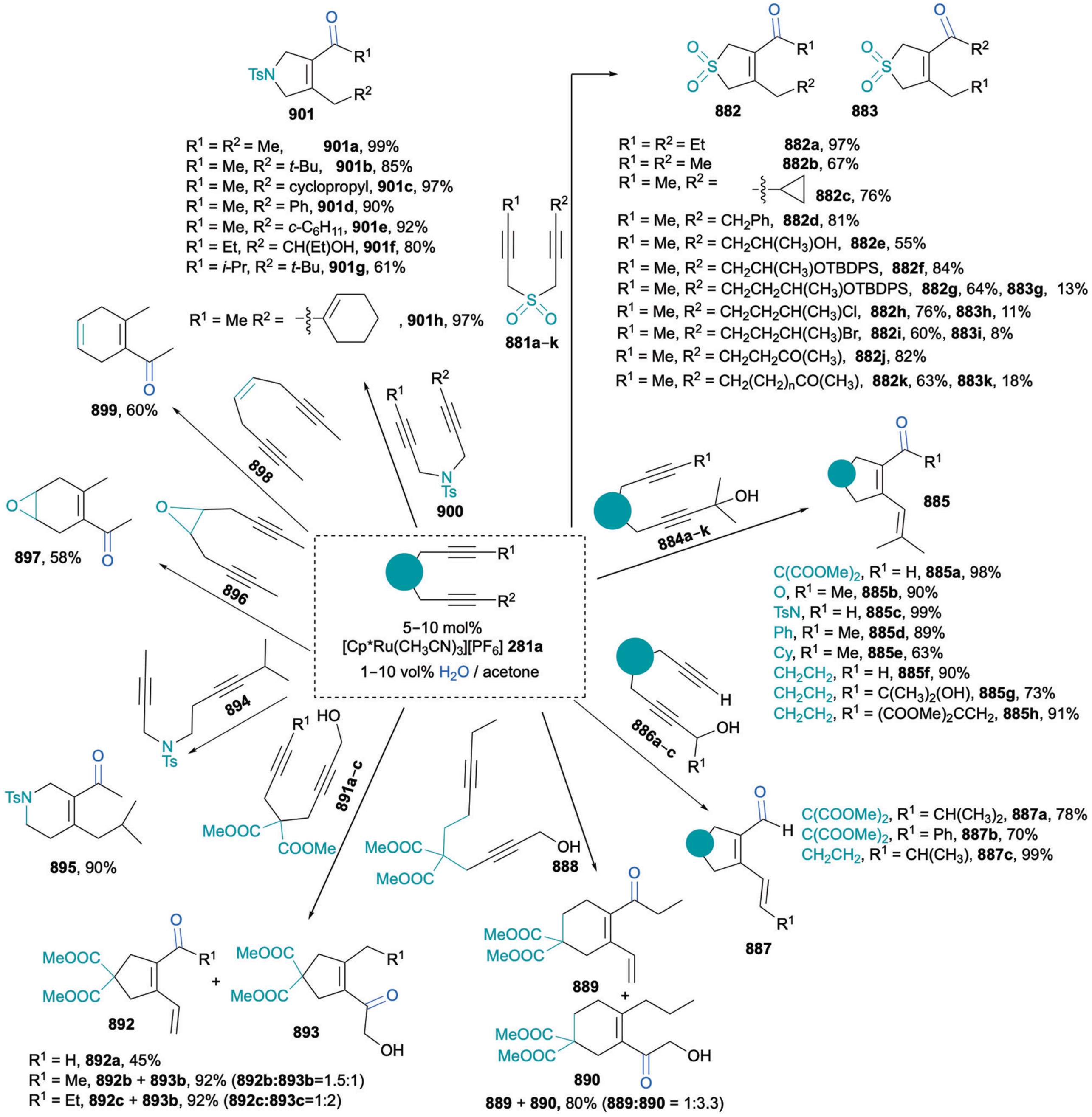
Scheme 162 Proposed catalytic cycle for hydrophosphinylative coupling reaction.

alcohols cycloisomerise to α,β,γ,δ-unsaturated aldehydes and ketones, while primary propargylic alcohols also gave the hydrated cyclised product. The key step in both paths of mechanism (Cycle A and Cycle B) starts from the reseonance invocation to ruthenacyclopentatriene **904.** For primary propargylic alcohol diynes, the addition of water might occur to two carbene carbons yielding intermediates **905** and **910.** The hydrative cyclisation process leads to the rearrangement of **905** to **907**, followed by a hydride shift and protontion to the product **909.** In the case of cyclodimerisation, compound **910** is rearranged to **911** which, after hydride shift and β-hydroxide elimination or protonation and water elimination, leads to product **913** (Scheme 165). The mechanism common for secondary and tertiary propargylic alcohols (which possess better-leaving groups) occurs mainly *via* Cycle B. The detailed mechanistic studies on the activation of a water molecule by ruthenacyclopentatriene **904** were studied by Yamamoto *et al.* Using DFT calculation, they postulated the formation of half-open oxaruthenocene as an initial step of the mechanism.[372] The methodology was used in the cyclisation of various diynes (Scheme 164). Moreover, the directing effect of carbonyl group attached to the C≡C in the δ- or ε-position was observed, by the coordination of C=O to ruthenacyclopentadiene complex **914.**[360] Hydrative cyclisation was a step in the formation of natural compounds: tricyclic alkaloids *Cylindricine C* **920** (Scheme 166), while cycloisomerisation was used in the synthesis of (+)-α-kainic acid **933** (Scheme 167).[362,364] Moreover, the cyclised products were applied in both intra- and intermolecular Diels–Alder reactions.[360,361]

Another example of the application of hydration process is the formation of functionalised benzene derivatives **936a–e** in the aromatisation of enediynes **934a–e** catalysed by 10 mol% $[TpRu(PPh_3)(CH_3CN)_2][PF_6]$ **935** (Tp = tris(1-pyrazolyl)borate) (Scheme 168).[373] The process is also possible for the addition of other nucleophiles than H_2O (*e.g.*, aniline, acetylacetone, pyrroles, and dimethyl malonate) to non-functionalised enediynes



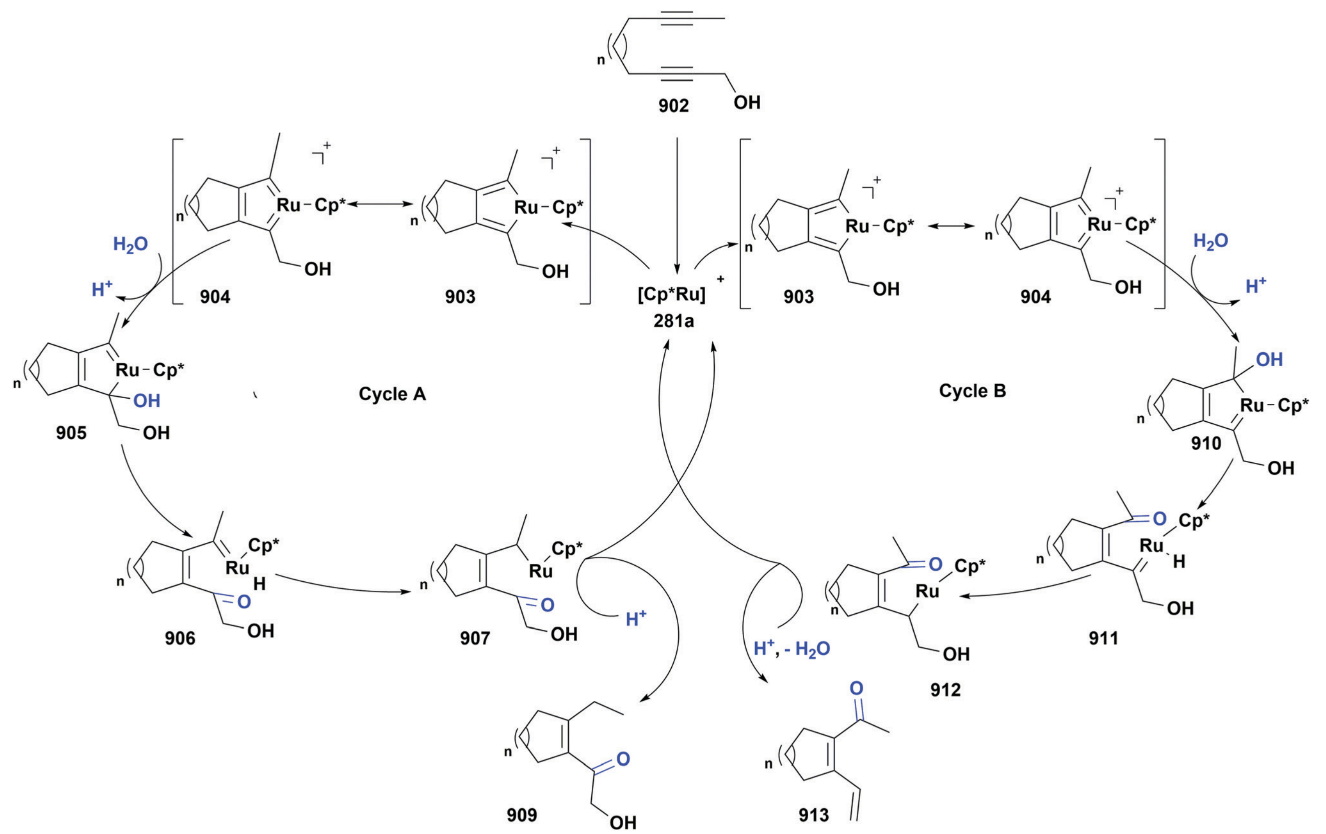
Scheme 163 Intermolecular hydrophosphanylation of butadiynes **1a** and **13c** with diphenylphosphane oxide **856** and diphenylphoshpine **843** catalysed by $(thf)_4Ca(PPh_2)_2$ **872**.



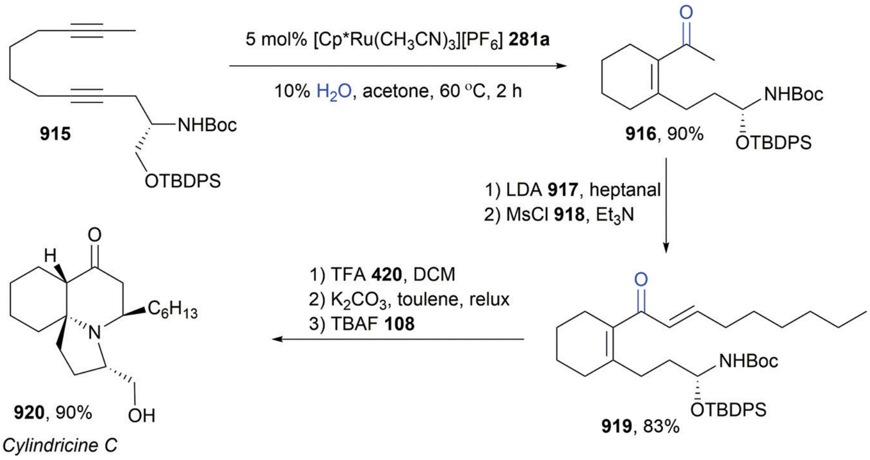
Scheme 164 Hydrative cyclisation/cyclodimerisation of separated diynes catalysed by $[Cp^*Ru(CH_3CN)_3][PF_6]$ **281a**.

934. The addition is highly selective and the attack occurs at the more electron-rich alkyne carbon yielding various functionalised aromatic compounds **936a–e** depending on the nucleophile. The mechanism was proposed according to the reactions with D_2O. These experiments proved that the catalytically active species is a ruthenium-π-alkyne complex instead of the ruthenium-vinylidene intermediate, which is a characteristic step in Saito-Myers cyclisation (Scheme 169).[373]

Gold complexes are another big class of catalysts, which have been used in the hydration of conjugated and separated diynes. The presence of water was essential for the hydrative cyclisation. In 2010, Skrydstrup *et al.* published that 1,3-diynes can be converted in a hydration reaction towards 2,5-disubstituted furans **946** (Scheme 170) or in a hydroamination process to 1,2,5-trisubstituted pyrroles **681** (Scheme 132). Au(I) complexes such as $(Ph_3P)AuNTf_2$ **680** and SPhosAuNTf$_2$ **945** were able to catalyse these two reactions under mild conditions. Complex **945** was more active in hydration reaction since H_2O is a better nucleophile when 1,4-diaryl or dialkylbuta-1,3-diynes were used. Within this methodology, it was possible to furnish a selection of 2,5-diamidofurans **946k–m** in 45 minutes with good to moderate yields (Table 22, entries 14–17). To obtain



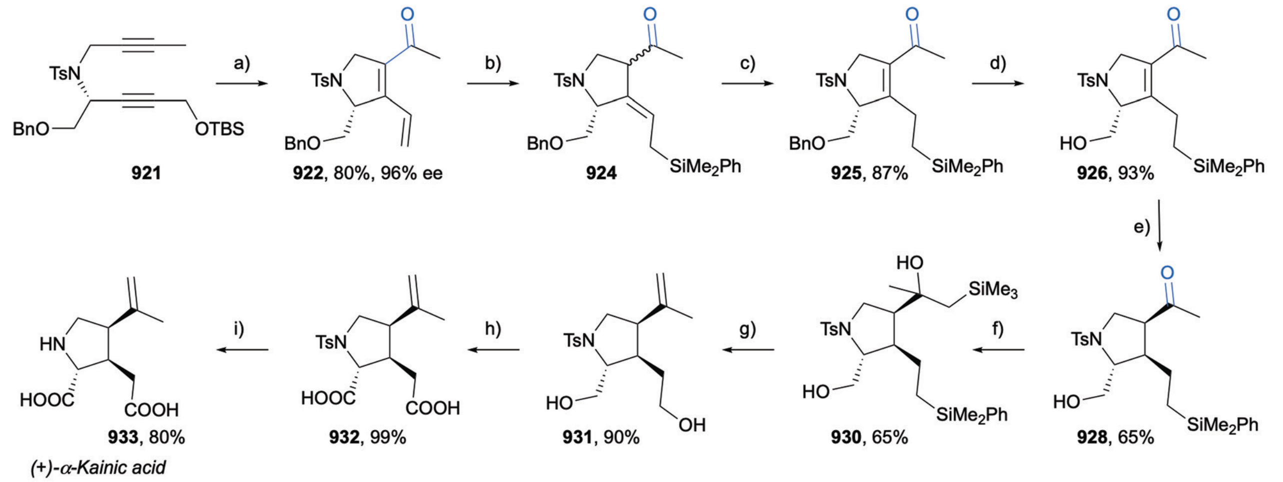
Scheme 165 Hydrative cyclisation (Cycle A) and cyclodimerisation (Cycle B) mechanism based on the reaction of primary diynols with H_2O in the presence of $[Cp^*Ru(CH_3CN)_3][PF_6]$ **281a**.



Scheme 166 Synthesis of alkaloid *Cylindricine C* **920** with the hydrative cyclisation step.

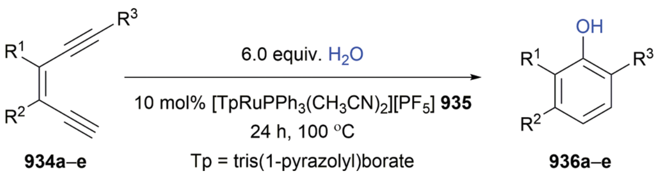
high yields in the case of the hydration of symmetrical **1a, 1c–d**, and non-symmetrical diraryl-**944b** or dialkyl-substitued **208b** diynes using complex **945**, 24 hour reaction times were necessary. Moreover, increasing the polarisation of the diyne by the introduction of electron-donating OMe groups led to a small amount of side products (Scheme 170). When D_2O was used instead of H_2O, furans **946e** with deuterium atom at 3,4-position were synthesied.[308]

The same products were formed, when [Au(IPr)OH] **695** was used as a precursor. The reaction proceeded only in the presence of Brønsted acid HX, which generated the active complex [Au(IPr)]X **947** *in situ*. $HNTf_2$ was the most effective in the model reaction with 1,4-diphenybuta-1,3-diyne **1a.** Poorer results were observed when HBF_4 **948** and HPF_6 **949** were used (77% *vs.* 37–39%). No catalyst activity was noticed for the complex with SbF_6^- or OTf^- groups. Elevated temperatures



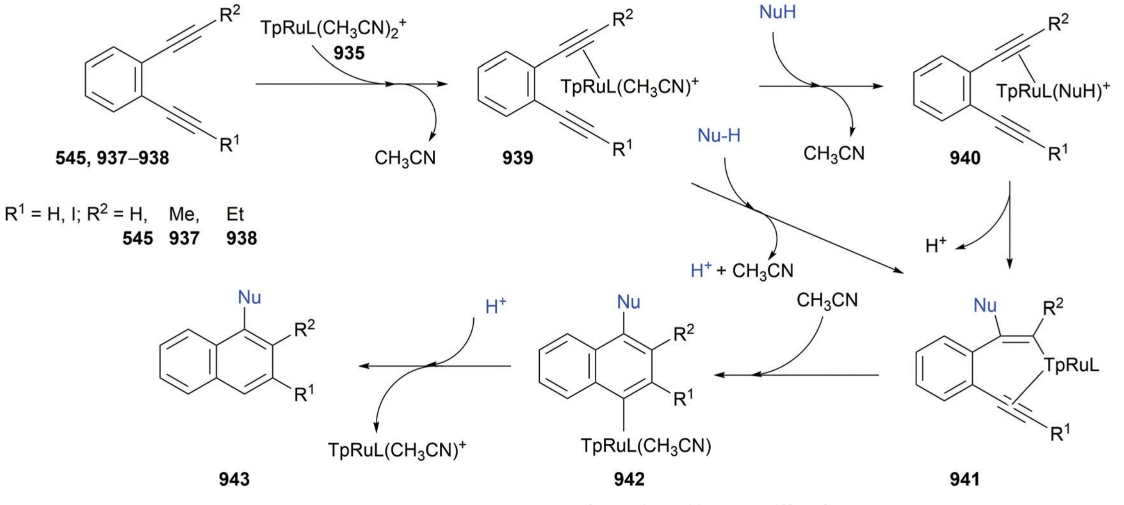
a) 10 mol% [Cp*Ru(CH$_3$CN)$_3$][PF$_6$] **281a**, 2% H_2O/acetone, 40 °C, 1 equiv. malonic acid; b) Li[SiMe$_2$Ph] **923**, CuCN, THF, -79–0 °C. 2.8:1 dr; c) DBU, beznene, reflux; d) 5% Pd/C **446**, HCOOH:MeOH (1:1); e) 20 mol% [Ir(cod)Py(PCy$_3$)][PF$_6$] **927**, 138 bar H$_2$, 1 equiv. B(O-*i*Pr)$_3$; f) Li(CH$_2$SiMe$_3$) **929**, THF, -78 °C; g) 1) HF, H_2O CH$_3$CN, 2) KH, *t*-BuOOH, TBAF **108**, DNF, 65 °C; h) 8 N Jones' reagent, acetone. r.t.; i) 1) Li, NH$_3$ **632**, THF, -78 °C, 2) ambertile CG-50.

Scheme 167 Multistep synthesis of (+)-α-Kainic Acid **933** with the cycloisomerisation step.

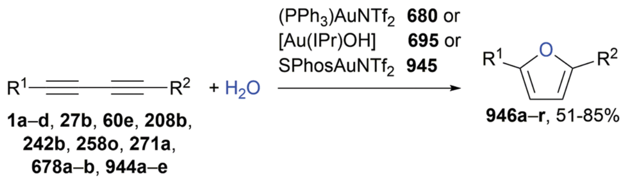


For **934a** R^1, R^2 = -(CH$_2$)$_3$-, R^3 = H, **936a,** 77%
For **934b** R^1, R^2 = -(CH$_2$)$_3$-, R^3 = Me, **936b,** 71%
For **934c** R^1, R^2 = -(CH$_2$)$_4$-, R^3 = H, **936c,** 74%
For **934d** R^1, R^2 = -(CH$_2$)$_4$-, R^3 = Me, **936d,** 70%
For **934e** R^1 = H, R^2 = *n*-C$_6$H$_{13}$, R^3 = Me, **936e,** 78%

Scheme 168 Aromatisation of endiynes **934a–e** *via* a hydration process catalysed by [TpRu(PPh$_3$)(CH$_3$CN)$_2$][PF$_6$] **935**.



Scheme 169 The general mechanism of aromatisation reaction catalysed by [TpRu(PPh$_3$)(CH$_3$CN$_2$)][PF$_6$] **935** in the presence of various nucleophiles.



Scheme 170 Gold(I) catalysed synthesis of 2,5-disubstituted furans **946a–r**.

are needed to perform the reaction with the [Au(IPr)OH] **695**/HX system. Additionally, the type of substituents attached to buta-1,3-diyne skeleton is important for the reaction. Diynes with aryl groups in the terminal positions were the most active in the formation of 2,5-disubstituted furanes **946.** For the diyne with cyclohexene groups (**258o**) the reaction was less effective, while reagents with dialkyl sidechains in positions 1,4 did not

Table 22 Results of gold(I) catalysed synthesis of 2,5-disubstituted furans **946a–r**

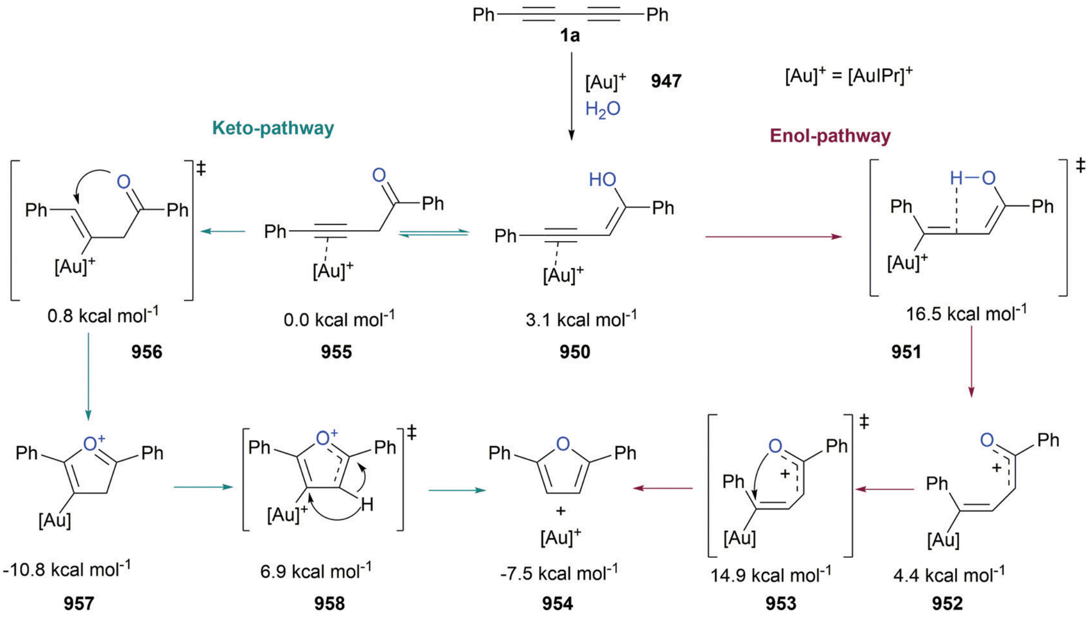
Entry	Diyne	R^1	R^2	Method[a,b,c,d]	Yield of **946a–r** [%]	
1	**1a**	Ph	Ph	b	**a**	73
2	**1b**	4-FC_6H_4	4-FC_6H_4l	c	**b**	82
3	**1c**	4-MeC_6H_4	4-MeC_6H_4	b	**c**	80
4				c	**c**	82
5	**1d**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	b	**d**	84
6				b, d	**e**	79
7				c	**d**	82
8	**27b**	4-*t*-BuC_6H_4	4-*t*-Bu-C_6H_4	c	**f**	84
9	**60e**	4-$MeOC_6H_4$	Ph	c	**g**	65
10	**208b**	*n*-C_6H_{13}	*n*-C_6H_{13}	b	**h**	68
11	**242b**	2-$MeOC_6H_4$	2-$MeOC_6H_4$	c	**i**	71
12	**258o**	*c*-C_6H_9	*c*-C_6H_9	c	**j**	75
13	**271a**	Ph	*t*-Bu	c	**k**	62
14	**678a**	NTs(Bn)	NTs(Bn)	a	**l**	85
15	**678b**	NTs(Ph)	NTs(Ph)	a	**m**	51
16	**944a**	NTs(*i*-Pr)	NTs(*i*-Pr)	a	**m**	82
17				c	**n**	77
18	**944b**	4-$MeOC_6H_4$	4-BrC_6H_4	c	**o**	82
20	**944c**	4-$MeOC_6H_4$	*c*-C_6H_9	c	**p**	72
21	**944d**	4-$MeOC_6H_4$	*n*-Bu	c	**q**	64
22	**944e**	4-$MeOC_6H_4$	2-$MeOC_6H_4$	c	**r**	71

[a] 1.4 equiv. H_2O, 2 mol% $(PPh_3)AuNTf_2$ **680**, THF, 60 °C, 45 min. [b] 10.0 equiv. H_2O, 2–5 mol% SPhosAuNTf$_2$ **945**, THF, 60 °C, 24 h. [c] H_2O, 1 mol% [Au(IPr)OH] **695**, 1.5 mol% HNTf$_2$ dioxane, 80 °C, 4 h. [d] D_2O used.

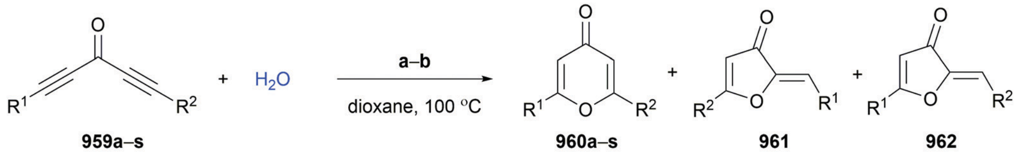
lead to the desired products. When one of these group was substituted with an aryl ring, the reaction occurred with good yield (Scheme 170 and Table 22). According to stoichiometric experiments and DFT calculations, it was proved that the reaction proceeded *via* hydration of the one C≡C bond. Two pathways are possible through the keto or enolate form. It was determined that the keto-pathway is favoured by 9.6 kcal mol^{-1} (Scheme 171).[312]

Hydration of conjugated diynes was used for the synthesis of 6,5,6-trioxabispiroacetal moieties, the spacers between the steroid cores. Steroid diynediols were used as reagents, while JohnPhos-Au(MeCN)SbF$_6$ **682** was applied as a catalyst.[374,375]

Sanz *et al.* reported the Au-catalysed hydration-oxacyclisation reactions of 1,4-diyn-3-ones **959a–s**, which were obtained from ethyl lactate as carbonyl source, a feedstock derived from biomass. Depending on the catalytic system composition it was possible to carry out the selective synthesis of 4-pyrones **960a–s** or 3(2*H*)-furanones **961–962.** Such compounds possess many biological activities, *e.g.*, phenoxans, funicones and rapicones indicate anti-HIV activity.[376,377] The reaction can be tuned by the ligand attached to the gold complex, the presence or absence of silver salts, and the counteranion. When 5 mol% of IPrAuNTf$_2$ **711** was used 4-pyrones **960a–s** were predominantly formed (5 : 1–20 : 1), while applying 5 mol% of AuCl(PPh$_3$) **694**/AgSbF$_6$ **746** 3(2*H*)-furanones **961–962** were obtained (1 : 11–1 : 20). Both products were formed in moderate yields of 65–86%. The lowest yield of 3(2*H*)-furanones **961** was obtained for alkyl-substituted diynones. This pathway was much more effective for aryl- or heteroaryl-functionalised diynones, while 4-pyrones **960a–s** were furnished with similar yields regardless of the type of substituents (Scheme 172 and Table 23). This is an alternative method towards 4-pyrones and furanones, which are typically made by multistep condensation cyclisation reactions of carbonyl compounds.[378] The mechanism of this transformation was demonstrated from the reaction with D_2O. The key step in the formation of 4-pyrones **960** or 3(2*H*)-furanones **961** is the hydration of diynone **959**, which might proceed according to Michael or anti-Michael addition. Both pathways are possible and depending on the catalytic system. Next, the intramolecular oxacyclisation occurred leading to Au-intermediates **965** or **966.** Finally, protodeauration affords the final products with the



Scheme 171 Possible catalytic pathways for Au promoted hydrative cyclisation of 1,4-diphenylbuta-1,3-diyne **1a**.



a: 5 mol% IPrAuNTf$_2$ **711**, 1 h, 0.5. mmol of **959a–s**, H_2O (1 mL), dioxane (2 mL)
b: 5 mol% AuCl(PPh$_3$) **694** / AgSbF$_6$ **746**, 5 h, 0.5 mmol of **959**, H_2O (1 mL), dioxane (2 mL)

Scheme 172 Synthesis of 4-pyrones **960a–s** and 3(2*H*)-furanones **961** and **962** in the hydration–oxacyclisation of symmetrically and non-symmetrically substituted diynones **959** catalysed by Au(I) complexes.

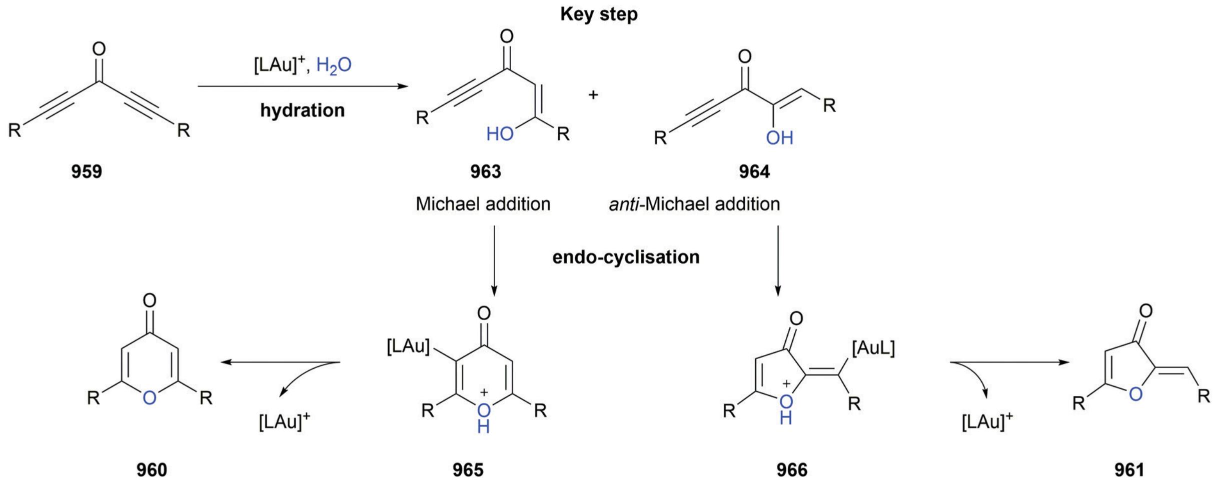
Table 23 Results of the hydration-oxacyclisation reactions of symmetrically and non-symmetrically substituted diynones catalysed by Au(I) complexes

Entry	Diynones **959**	R^1	R^2	Method^{ab}	Selectivity **960**/(**961** + **962**)^c	**961**/**962**^{c}	Product, yield^d [%]
					960/(**961** = **962**)	—	
1	**a**	Ph	Ph	a	9/1	—	**960a**, 73
2				b	1/18	—	**961a**, 80
3	**b**	*p*-Tol	*p*-Tol	a	10/1	—	**960b**, 81
4				b	1/11	—	**961b**, 77
5	**c**	4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	a	12/1	—	**960c**, 83
6				b	1/>20	—	**961c**, 81
7	**d**	3-MeOC$_6$H$_4$	3-MeOC$_6$H$_4$	a	>20/1	—	**960d**, 78
8				b	1/>20	—	**961d**, 79
9	**e**	4-FC$_6$H$_4$	4-FC$_6$H$_4$	a^e	10/1	—	**960e**, 79
10				b^e	1/10	—	**961e**, 70
11	**f**	3-Th^f	3-Th^f	a	5/1	—	**961f**, 70
12				b	1/18	—	**961f**, 79
13	**g**	2-Th^f	2-Th^f	a	1/18	—	**961g**, 74
14	**h**	*n*-Bu	*n*-Bu	a	>20/1	—	**960h**, 81
15				b^g	1.5/1	—	**961h**, 35
16	**i**	*c*-C$_3$H$_5$	*c*-C$_3$H$_5$	a	>20/1	—	**960i**, 80
17				b^g	2.5/1	—	**961i**, 26
18	**j**	(CH$_2$)$_2$Ph	(CH$_2$)$_2$Ph	a	>20/1	—	**960j**, 86
19	**k**	*c*-C$_6$H$_9$	*c*-C$_6$H$_9$	a	>20/1	—	**960k**, 67
20	**l**	C(CH$_3$)=CH$_2$	C(CH$_3$)=CH$_2$	a	>20/1	—	**960l**, 74
21	**m**	CH$_2$O(4-MeOC$_6$H$_4$)	CH$_2$O(4-MeOC$_6$H$_4$)	a	>20/1	—	**960m**, 65
22	**n**	CH$_2$O[3,5-(MeO)$_2$C$_6$H$_3$]	CH$_2$O[3,5-(MeO)$_2$C$_6$H$_3$]	a	>20/1	—	**960n**, 70
					(**960**/(**961** + **962**))		
23	**o**	Ph	*n*-Bu	a	>20/1	—	**960o**, 82
24				b	1/1.25	1/10	**960o**, 35, **961o**, 42
25	**p**	Ph	*c*-C$_3$H$_5$	b	1/1.1	14/1	**960p**, 37, 961p, 35
26	**q**	Ph	4-MeOC$_6$H$_4$	b	1/20	3/1	**961q**, 71
27	**r**	4-FC$_6$H$_4$	4-MeOC$_6$H$_4$	b	1/10	4/1	**960r**, 8, 961r, 72
28	**s**	Ph	H	a	>20/1	—	**960s**, 74
				b	>20/1	—	**960s**, 76

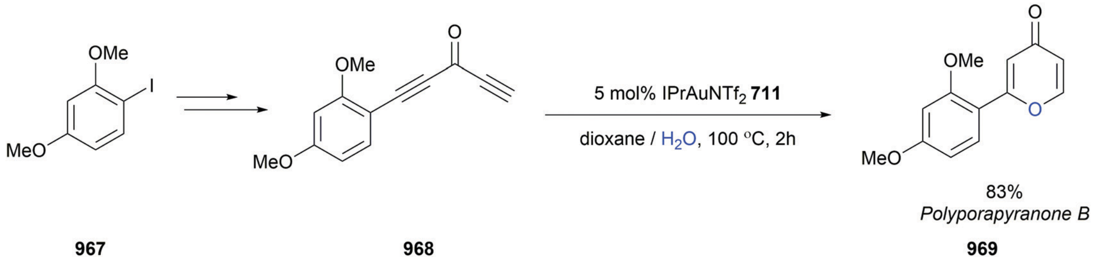
[a] Method a: 5 mol% IPrAuNTf$_2$ **711**, 1 h, 0.5. mmol of **959**, H_2O (1 mL), dioxane (2 mL). [b] Method b: 5 mol% AuCl(PPh$_3$)$_3$ **694**/AgSbF$_6$ **746**, 5 h, 0.5 mmol of **959**, H_2O (1 mL), dioxane (2 mL). [c] Determined by ^{1}H NMR analysis. [d] Isolated yields after column chromatography. [e] 10 mol% of catalyst was used. [f] Th = thienyl. [g] 8 hours.

elimination of the catalytic species. The regioselectivity is controlled by hydration step, not by a 6-*endo vs.* 5-*exo* oxacyclisation reaction (Scheme 173). The Michael or anti-Michael addition of water also had an influence on the synthesis of furanones and pyrones when unsymmetrically substituted diynones **959o–s** were used. Anti-Michael addition was favoured with the more electron-poor alkyne group causing the synthesis of furanones in a higher amount.[378] This methodology was used in the preparation of *Polyporapyranone B* **969**, which is naturally occurring γ-pyrone in sea-grass derived fungi *Polyporales* (Scheme 174). The hydration–oxacyclisation reaction is the final step in the synthesis of this bioactive compound, proceeded by Sonogashira coupling of 2,4-dimethoxyiodobenzene **967** with propargylic alcohol, oxidation, the addition of ethynylmagnesium bromide, and the next oxidation step. Finally, both products, which could be prepared on a gram scale, were utilised in further transformations leading to pyrylium salts, that can be used as photoredox catalysts or in the reaction with *N*-nucleophilic reagents to functionalised N-heterocycles (Scheme 175).[378]

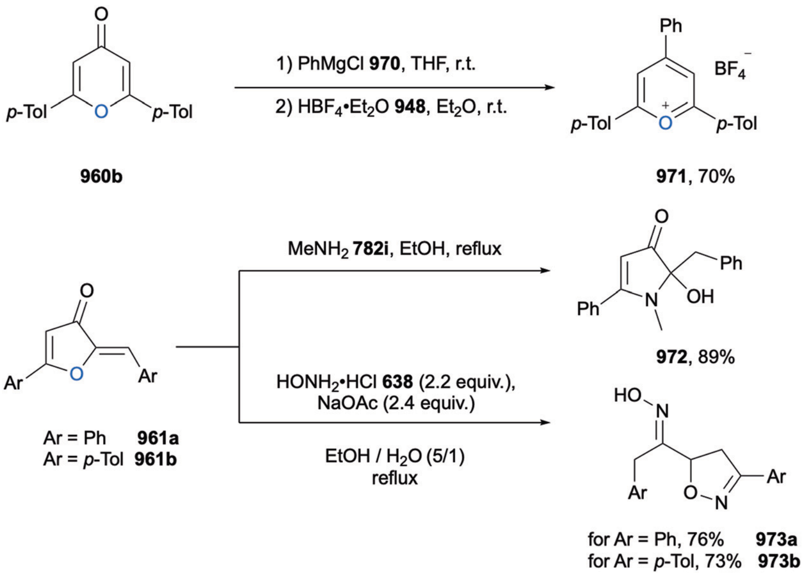
Diynones **959** were also converted to 4-pyranones **960** in the presence of TfOH **974**, which promotes the hydration reaction, followed by cyclisation. The reaction occurred under metal-free conditions, making the process more legitimate in the case of the process economy (no expensive gold catalysts) and sustainability. Under the optimised conditions (1 equiv. TfOH **974**, 100 °C, 36 h) various symmetrically and non-symmetrically 2,6-substituted 4-pyranonens **960** were obtained with good yields (57–82%). Other acids as *e.g.*, *p*-TSA or PhCOOH were much less



Scheme 173 Michael and anti-Michael hydration as a key step in hydration–oxacyclisation reactions of diynones **959** in the presence of Au-complexes $IPrAuNTf_2$ **711** and $AuCl(PPh_3)_3$ **694**/$AgSbF_6$ **746**.

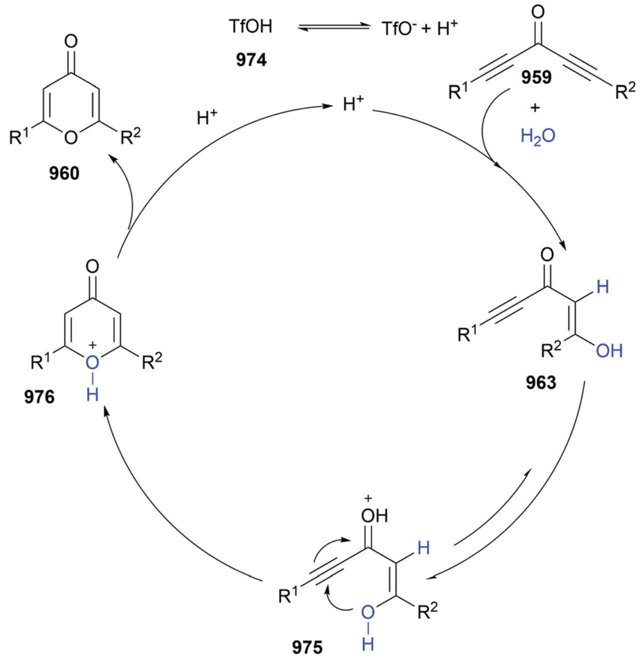


Scheme 174 The final hydration-oxacyclisation step in the preparation of *Polyporapyranone B* **969**.



Scheme 175 Transformations of 4-pyranone **960b** and furanones **961a** and **961b**.

active than TfOH **974**. Diynones **959** substituted in the terminal position with aryl groups bearing electron-donating groups (*e.g.*, Me, *t*-Bu, OMe) gave products with slightly better yields, than those with electron-withdrawing groups (*e.g.*, F, Cl). The mechanism of the reaction starts from the activation of carbonyl group in diynone **959** by TfOH **974** and nucleophilic



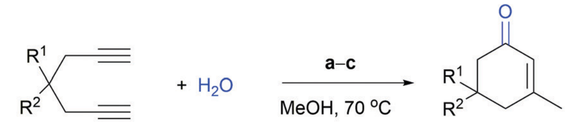
Scheme 176 Proposed mechanism of hydration/cyclisation of diynones **959** catalysed by TfOH **974**.

addition of water to the C≡C triple bond followed by a keto–enol tautomerisation towards intermediate **963**. Subsequently the protonation and C–C bond rotation, which occurred under elevated temperature leads to species **975**. The cycle is subsequently closed by the intramolecular nucleophilic attack of the oxohydryl group to the second C≡C to give cyclic intermediate **976**, which furnished 4-pyrorone **960** after deprotonation (Scheme 176).[379]

$MeAuPPh_3$ **978** or $(PPh_3)AuNO_3$ **979** with trifluoromethanesulfonic acid (TfOH) **974** are active catalysts in the hydrative cyclisation of 1,6-heptadiynes **116a**, **127a**, **127e**, **127j**, **394b**, **394g**, **450a**, **450c**, and **977a–o** functionalised with various different groups, *e.g.*, alkoxy, esters, carboxyl, carbonyl, phenyl, or nitrile (Scheme 177).[380,381] Other acids as mineral H_2SO_4 or heteropolyacids $H_3PW_{12}O_{40}$ **982a**, $H_3PMo_{12}O_{40}$ **982b**, and $H_4SiW_{12}O_{40}$ **982c** were also used as co-catalysts and permitted the isolation of the corresponding 3-methyl-hex-2-enone but with lower yields. The proposed mechanism of this transformation assumes the formation of an active Au^+ species in the first step. The coordination of diyne, followed by the H_2O attack then leads to intermediate **983**, which further isomerises to gold cyclohexanone complex **984** by the intramolecular attack of enolic ion to the gold cation binding through the C≡C bond. Product **981** is then released through a tandem double bond isomerisation process and gold catalyst elimination (Scheme 178).[380]

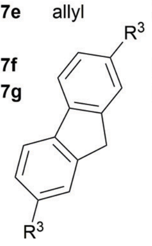
Moreover, ILs were used as solvents and immobilisation media for $(PPh_3)AuNO_3$ **979**. The best results were obtained for $[BMIM][BF_4]$, allowing to obtain stable products with yields of 72–78% in six cycles of hydrative cyclisation of **127a**. Such strategy permitted the recycling of the expensive gold catalyst. No information about catalyst leaching was presented.[381]

The same authors discovered that the $Pt(cod)Cl_2$ **980** catalyst with TfOH **974** as a co-catalyst is active in the hydrative cyclisation of the same reagents (1,6-heptadiynes): **116a**, **127a**,



116a, 127a, 127e, 127j, 394b, 394g, 450a, 450c, 977a–o

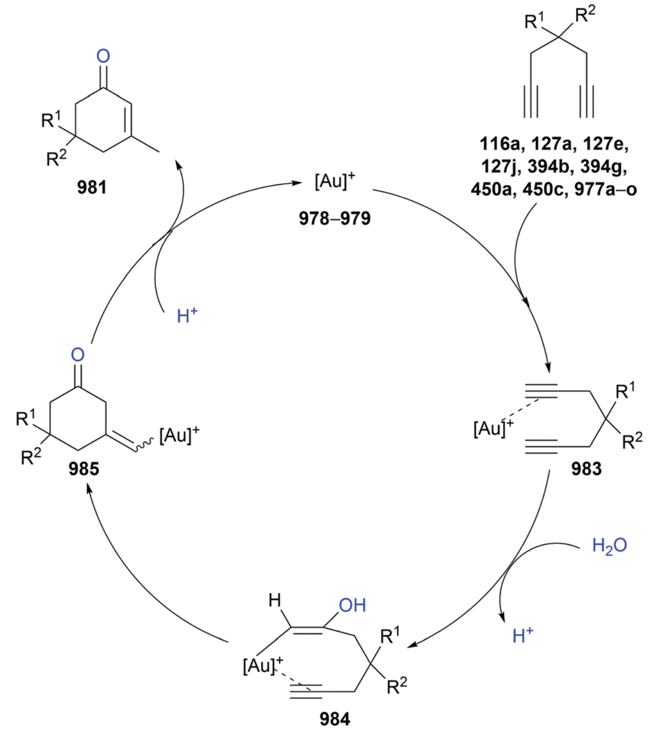
981

Diyne	$R^1 = R^2$	Yield of **981**
116a	H	**a** 51%[a]
127a	CO_2Me	**b** 89%,[a] 72%,[b] 75%[c]
127j	CH_2OH	**c** 54%,[b] 39%[c]
394b	$BnOCH_2$	**d** 91%,[a]
450a	CO_2Et	**e** 71%,[a] 82%,[b] 88%[c]
977a	CO_2i-Pr	**f** 87%[a]
977b	$MeOCH_2$	**g** 71%,[a] 65%[c]
977c	COOH	**h** 40%[a]
977d	CH_2OMe	**i** 96%[b]
977e	allyl	**j** 83%[b]
977f		**k** 75%,[b] 48%[c] R^3 = H,
977g		**l** 63%[b] R^3 = Cl

Diyne	$R^1 \neq R^2$	Yield of **981**
127e	R^1 = Ph, $R^2 = CO_2Me$	**k** 69%,[a] 69%[c]
394g	R^1 = COMe, R^2 = COOMe	**l** 65%,[b] 62%[c]
450c	R^1 = H, $R^2 = CO_2Et$	**m** 90%[b]
977h	R^1 = H, $R^2 = CO_2Et$	**n** 90%,[a] 75%[c]
977i	R^1 = H, $R^2 = CH_2OH$	**o** 91%[b]
977j	R^1 = Ph, R^2 = CN	**p** 47%[a]
977k	R^1 = COPh, R^2 = COOEt	**q** 60%[b]
977l	$R^1 = P(O)Ph_2$, $R^2 = CO_2Et$	**r** 73%[a]
977m	$CH(CH_3)OH$, $R^2 = CO_2Me$	**s** 50%,[b] 47%[c]
977n	R^1 = allyl, R^2 = H	**t** 71%[b]
977o	CH_2OH, $R^2 = CH_2OH$	**u** 61%[c]

a: 2 mol% $MeAu(PPh_3)$ **978**, 100 mol% H_2O, 50 mol% TfOH **974**, 10 min–3 h
b: 5 mol% $(PPh_3)AuNO_3$ **979**, 50 mol% $MeSO_3H$, $[bmim][BF_4]$, 1–5 h
c: 5 mol% $Pt(cod)Cl_2$ **980**, TfOH **974**, [diyne]:[H_2O]:[TfOH] = 1:1:0.5, 3–13 h

Scheme 177 Au(I)- or Pt(II)-catalysed **978–980** hydrative cyclisation of terminal 1,6-diynes **116a**, **127a**, **127e**, **127j**, **394b**, **394g**, **450a**, **450c**, **977a–o**.



Scheme 178 Plausible mechanism of hydrative cyclisation of 1,6-diynes catalysed by Au(I) complexes **978–979**.

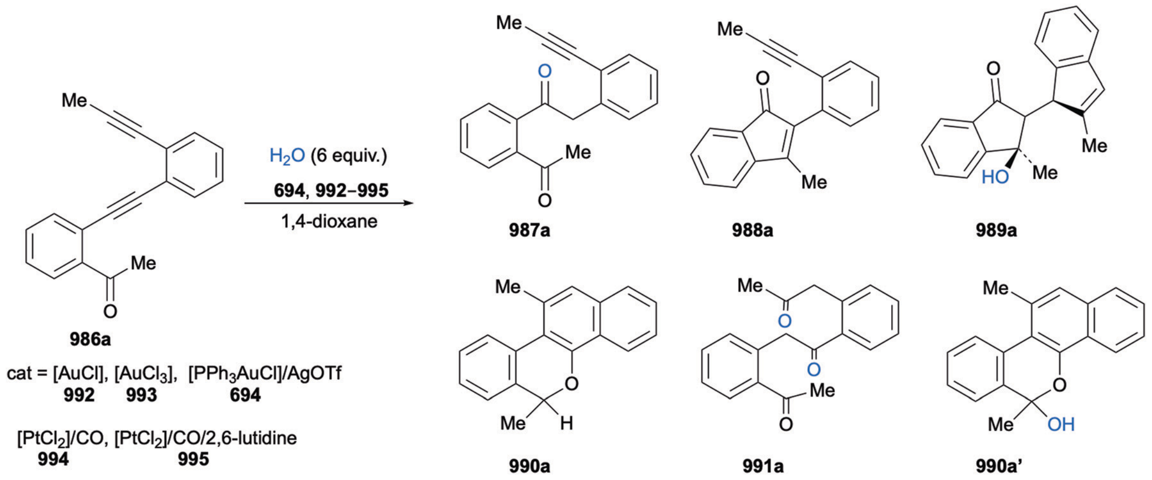
Table 24 Influence of the catalyst (Pt or Au) on the products and yields in the hydration/cyclisation reactions of **986a**

Entry	Cat[a]	Process conditions	Yield of products[c] [%]
1	**992**	25 °C, 12 h	**987a**, 65
2	**992**	100 °C, 12 h	**988a**, 63
3	**993**	100 °C, 14 h	**988a**, 74
4	**694**	25 °C, 14 h	**989a**, 78, dr = 2 : 1
5	**994**	100 °C, 5 h	990a, 61
6	**995**[b]	100 °C, 12 h	**991a**, 47, 990a, 12

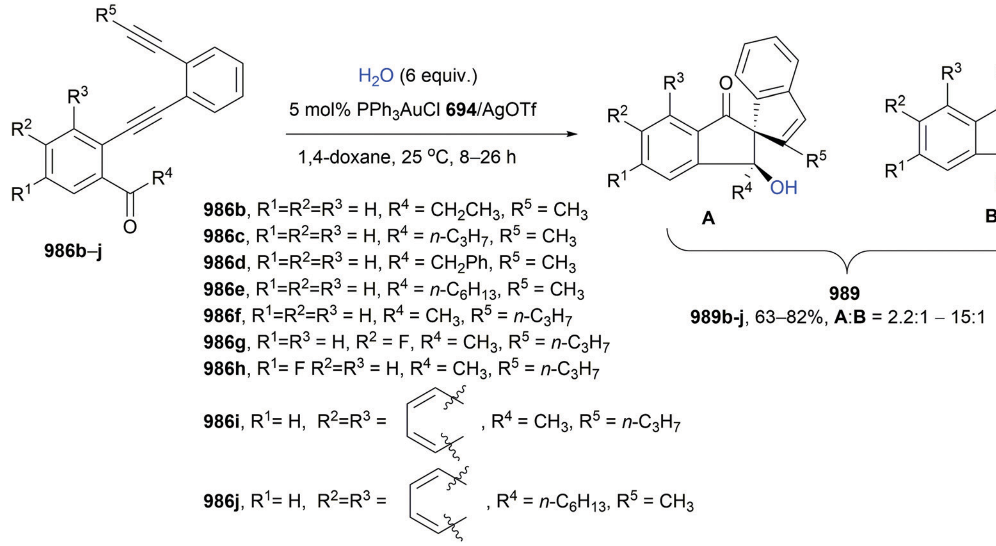
[a] 5 mol% for **694**, **992–993** catalyst, 8 mol% for **994–995**, 1,4 dioxane, [**986a**] = [0.15 M]. [b] 10 mol% of 2,6 lutidine. [c] Isolated yields.

127e, **127j**, **394b**, **394g**, **450a**, **450c**, **977a–o** functionalised in position 4. This catalytic system furnishes 3-methyl-hex-2-enone **981** with good yields (Scheme 177). The mechanism of the reaction was similar to that presented for Au-catalyst in Scheme 178. Interestingly Ru- or Pd-complexes were not active in this transformation.[382]

Liu *et al.* reported platinum and gold-catalysed hydrative cyclisation or carbocyclisation of oxo diynes or triynes, which led to benzopyrones and bicyclic spiro ketones.[383–385] As a model reagent, diynone **986a** was used which gave products **987a–991a** depending on the catalyst used (Scheme 179 and Table 24). Simple AuCl **992** led to diketone product **987a,** when the hydration step was carried out at room temperature. Increasing the temperature to 100 °C provided 1-*H*-inden-1-one **988a** as the main product, while spiroketone **989a** was obtained using PPh_3AuCl **694**/AgOTf as a catalyst. Product **987a** is an intermediate in the synthesis of spiro ketone **989a.** Switching from gold to a platinum catalyst, by application of $PtCl_2$/CO **994,** the chemoselectivity was directed to benzoisochromene **990a.** Triketone **991a** was formed when 10 mol% of lutidine was added to the catalytic system. The yield towards **990a** was improved by the application of 1 atm of CO, which role is to increase the nucleophilcity of Pt(II) by the formation of $PtCl_2(CO)_n$. Moreover, CO was essential to increase the process selectivity to **990a.** PPh_3AuCl **694**/AgOTf produced spiro ketones **989b–j** with a very good yields (63–88%), depending on the substrate **986b–j** (Scheme 180). The authors postulated that the ketone group accelerates the hydration of proximate C(1)–carbon of the neighboring alkyne (according to intermediate **996**). The obtained diketone **987a** undergoes a Conia–ene transformation[386] based on the attack of its enol form **997** at the π-alkyne group to form indenyl ketone **998.** A subsequent gold-or proto-catalysed aldol reaction formed spiro ketone **989a** (Scheme 181). Whereas $PtCl_2$/CO **994** catalyses the transformation of various diynones **986** to isochromenes **990,** hydrative cyclisation of diynones **986** and **999** or diynals **1002** catalysed by $PtCl_2$ **1000** furnishes benzoisochromenes **1001** or



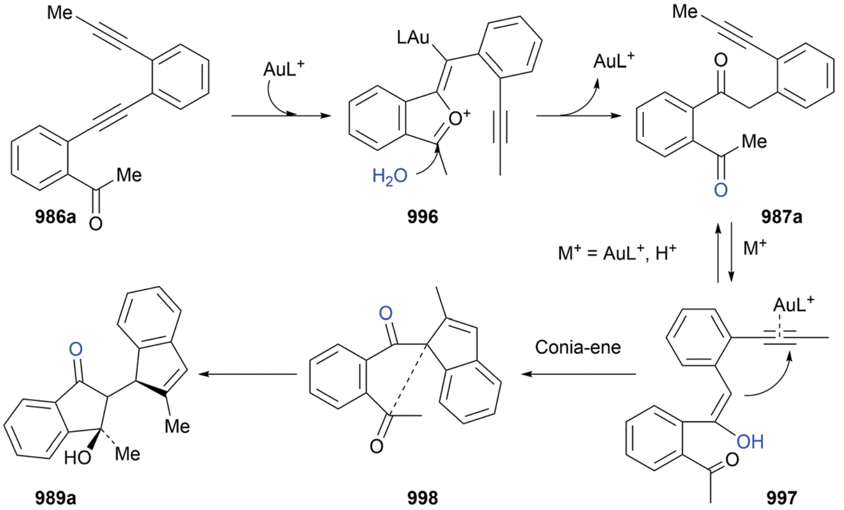
Scheme 179 Chemoselectivity of the hydration/cyclisation process depending on the catalyst type: Pt- or Au-based.



986b, $R^1=R^2=R^3$ = H, R^4 = CH_2CH_3, R^5 = CH_3
986c, $R^1=R^2=R^3$ = H, R^4 = n-C_3H_7, R^5 = CH_3
986d, $R^1=R^2=R^3$ = H, R^4 = CH_2Ph, R^5 = CH_3
986e, $R^1=R^2=R^3$ = H, R^4 = n-C_6H_{13}, R^5 = CH_3
986f, $R^1=R^2=R^3$ = H, R^4 = CH_3, R^5 = n-C_3H_7
986g, $R^1=R^3$ = H, R^2 = F, R^4 = CH_3, R^5 = n-C_3H_7
986h, R^1= F $R^2=R^3$ = H, R^4 = CH_3, R^5 = n-C_3H_7
986i, R^1= H, $R^2=R^3$ = , R^4 = CH_3, R^5 = n-C_3H_7
986j, R^1= H, $R^2=R^3$ = , R^4 = n-C_6H_{13}, R^5 = CH_3

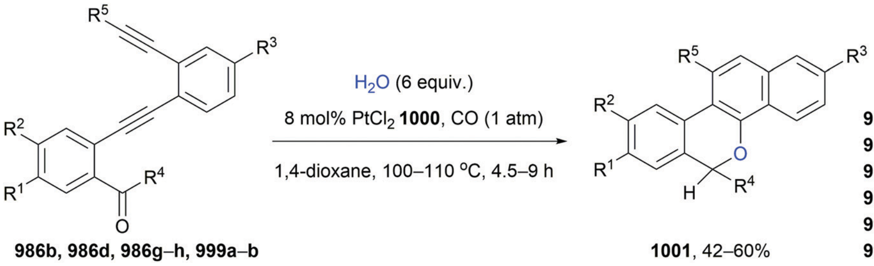
989b-j, 63–82%, **A**:**B** = 2.2:1 – 15:1

Scheme 180 PPh_3AuCl **694**/AgOTf catalysed synthesis of spiro ketones *via* hydration/cyclisation reactions.



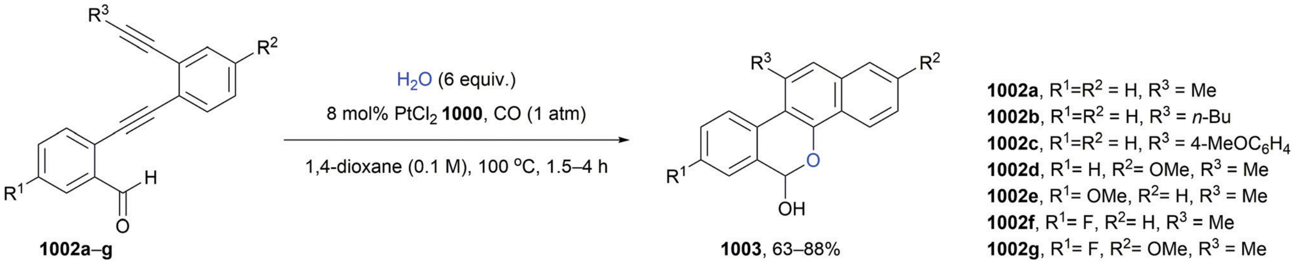
Scheme 181 Mechanism of the hydration/cyclisation reaction of diynone **986a** to spiro ketone **989a** catalysed by PPh_3AuCl **694**/AgOTf.

primary lactol derivatives **1003** (Schemes 182 and 183). The mechanism of this transformation was proposed on the basis of the reaction with D_2O. The diynone **986a** leads to the formation of benzopyriliums **1004**, which is transformed to triketone **1005**. Next, the aldol condensation of **1005** catalysed by a Brønsted acid or $PtCl_2$ **1000** produces 1-naphtol **1007** *via* enol intermediate **1006**. Finally, the tetracyclic ketal **990′** is formed, which is reduced by D_2O. Oxonium intermediate **1010** then undergoes hydride

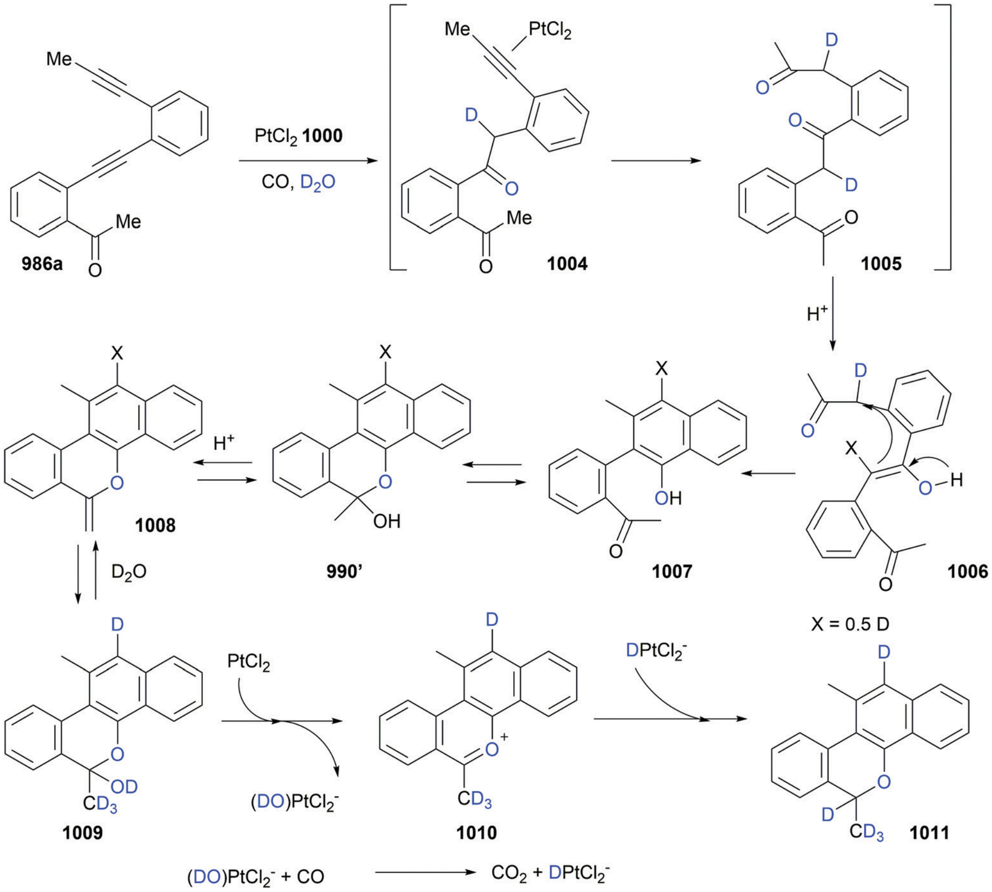


986b, $R^1=R^2=R^3$ = H, R^4 = CH_2CH_3, R^5 = CH_3
986d, $R^1=R^2=R^3$ = H, R^4 = CH_2Ph, R^5 = CH_3
986g, $R^1=R^3$ = H, R^2 = F, R^4 = CH_3, R^5 = n-C_3H_7
986h, R^1= F $R^2=R^3$ = H, R^4 = CH_3, R^5 = n-C_3H_7
999a, $R^1=R^2$ = H R^3 = OMe, R^4 = CH_3, R^5 = n-C_3H_7
999b, $R^1=R^3$ = H R^2 = OMe, R^4 = CH_3, R^5 = n-C_3H_7

Scheme 182 Hydration/cyclisation of diynones **986b**, **986d**, **986g–h**, **999a–b** to benzoisochromenes **1001** catalysed by $PtCl_2$ **1000**.



Scheme 183 Hydration/cyclisation of diynals **1002a–g** to primary lactol derivatives **1003** catalysed by $PtCl_2$ **1000**.



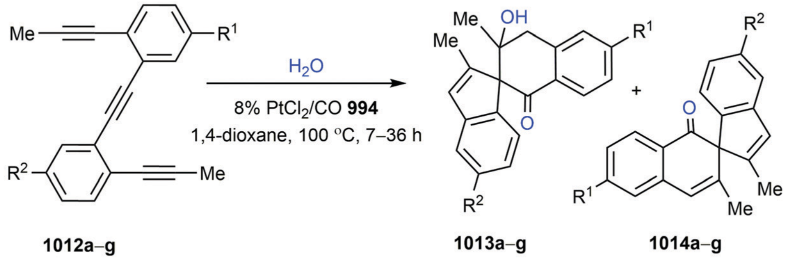
Scheme 184 Plausible mechanism including the secondary hydrogenation of primary ketal product **990′** to beznoisochromenes catalysed by $PtCl_2$ **1000**.

addition by $DPtCl_2$. Its formation from CO and $HOPtCl_2^-$ was reported in the literature (Scheme 184).[387]

In the case of triynes **1012a–g** and **1015a–m**, applying $PtCl_2$/CO **994** (or more active PtI_2/CO **1016**) as a catalyst led to nucleophilic hydration of the alkyne moiety, followed by the cyclisation led to tetracyclic **1013a–g** and **1014a–g**, or bicyclic spiro ketones **1017a–m** with excellent selectivity (Scheme 185). The authors postulated that the formation of products occurred according to two hydration processes, further alkyne insertion, and aldol condensation. The type of product which is formed depends on the order of the hydration process. Spiro ketones **1017a–m** are synthesised when the initial hydration occurred at the central diphenyl alkynes. When the outer alkyne is hydrated at first, tetracyclic ketones **1013a–g** and **1014a–g** were effectively synthesised. Both types of products were formed in good yields (Scheme 185).[383,384]

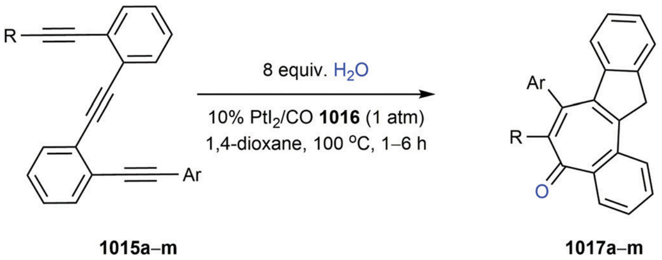
Conjugated 1,3-diynes can be converted to 2,5-disubstituted furans using a simple and cheap copper(I) catalyst **519**, which constitutes an alternative to reactions catalysed by much more expensive Au(I) complexes.[308,312,388] The formation of furans can occur directly from haloalkynes **1018a–n** and **1019a–n** *via* preliminary Glaser coupling to 1,3-diynes **1a–d**, **27c**, **37t**, **230d**, **258a**, **258g–h**, **265a**, **500b**, **1020a–b** or direct hydration of diynes **60e**, **655a**, **1020c–e**, followed by cyclisation. As a base, KOH was

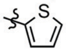
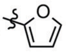
Synthesis of bicyclic spiro ketones



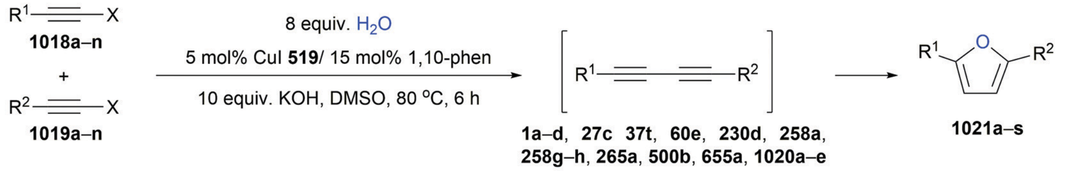
For **1012a**, R^1 = OMe, R^2 = CF_3, **1013a**, 54%, **1014a**, 17%
For **1012b** R^1 = Me, R^2 = CF_3, **1013b**, 44%, **1014b**, 36%
For **1012c** R^1 = H, R^2 = CF_3, **1013c**, 23%, **1014c**, 38%
For **1012d** R^1 = Me, R^2 = F, **1013d**, 47%, **1014d**, 26%
For **1012e** R^1 = Me, R^2 = H, **1013e**, 51%, **1014e**, 26%
For **1012f** R^1 = Me, R^2 = H, **1014f**, 76%
For **1012g** R^1 = OMe, R^2 = F, **1014g**, 61%

Synthesis of tetracyclic compounds



For **1015a**, R = Me, Ar = 4-$MeOC_6H_4$, **1017a**, 83%
For **1015b**, R = Me, Ar = 4-MeC_6H_4, **1017b**, 74%
For **1015c**, R = Me, Ar = 3,4-$(MeO)_2C_6H_3$, **1017c**, 76%
For **1015d**, R = Me, Ar = 3,4-$(OCH_2O)C_6H_3$, **1017d**, 85%
For **1015e**, R = Me, Ar = C_6H_5, **1017e**, 12%
For **1015f**, R = Me, Ar = , **1017f**, 62%
For **1015g**, R = Me, Ar = , **1017g**, 62%
For **1015h**, R = H, Ar = 4-$MeOC_6H_4$, **1017h**, 67%
For **1015i**, R = H, Ar = 4-MeC_6H_4, **1017i**, 65%
For **1015j**, R = H, Ar = 3,4-$(MeO)_2C_6H_3$, **1017j**, 61%
For **1015k**, R = H, Ar = 3,4-$(OCH_2O)C_6H_3$, **1017k**, 72%
For **1015l**, R = *n*-Bu, Ar = 4-$MeOC_6H_4$, **1017l**, 43%
For **1015m**, R = *n*-Bu, Ar = 3,4-$(OCH_2O)C_6H_3$, **1017m**, 62%

Scheme 185 $PtCl_2$/CO **994** or PtI_2/CO **1016** catalysed synthesis of tetracyclic ketones **1013a–g** and **1014a–g** or bicyclo spiro ketones **1017a–m** *via* hydration/cyclisation of triynes **1012a–g** and **1015a–m**.



1018 = 1019

From alkynyl halides

1018a, R^1 = R^2 = Ph, **1021a**, 93%
1018b, R^1 = R^2 = *p*-Me-C_6H_4, **1021b**, 90%
1018c, R^1 = R^2 = *m*-Me-C_6H_4, **1021c**, 87%
1018d, R^1 = R^2 = *p*-Et-C_6H_4, **1021d**, 90%
1018e, R^1 = R^2 = *p*-F-C_6H_4, **1021e**, 84%
1018f, R^1 = R^2 = *p*-Cl-C_6H_4, **1021f**, 85%
1018g, R^1 = R^2 = *o*-Cl-C_6H_4, **1021g**, 75%
1018h, R^1 = R^2 = *m*-Cl-C_6H_4, **1021h**, 68%
1018i, R^1 = R^2 = *p*-Br-C_6H_4, **1021i**, 8%
1018j, R^1 = R^2 = *p*-CF_3-C_6H_4, **1021j**, 74%
1018k, R^1 = R^2 = *p*-MeO-C_6H_4, **1021k**, 85%
1018l, R^1 = R^2 = *p*-EtO-C_6H_4, **1021l**, 71%
1018m, R^1 = R^2 = thiophene, **1021m**, 84%
1018n, R^1 = R^2 = pirydine, **1021n**, 75%

R^1 = R^2 = *p*-CF_3-C_6H_4 **1020a**
R^1 = R^2 = *p*-EtO-C_6H_4 **1020b**

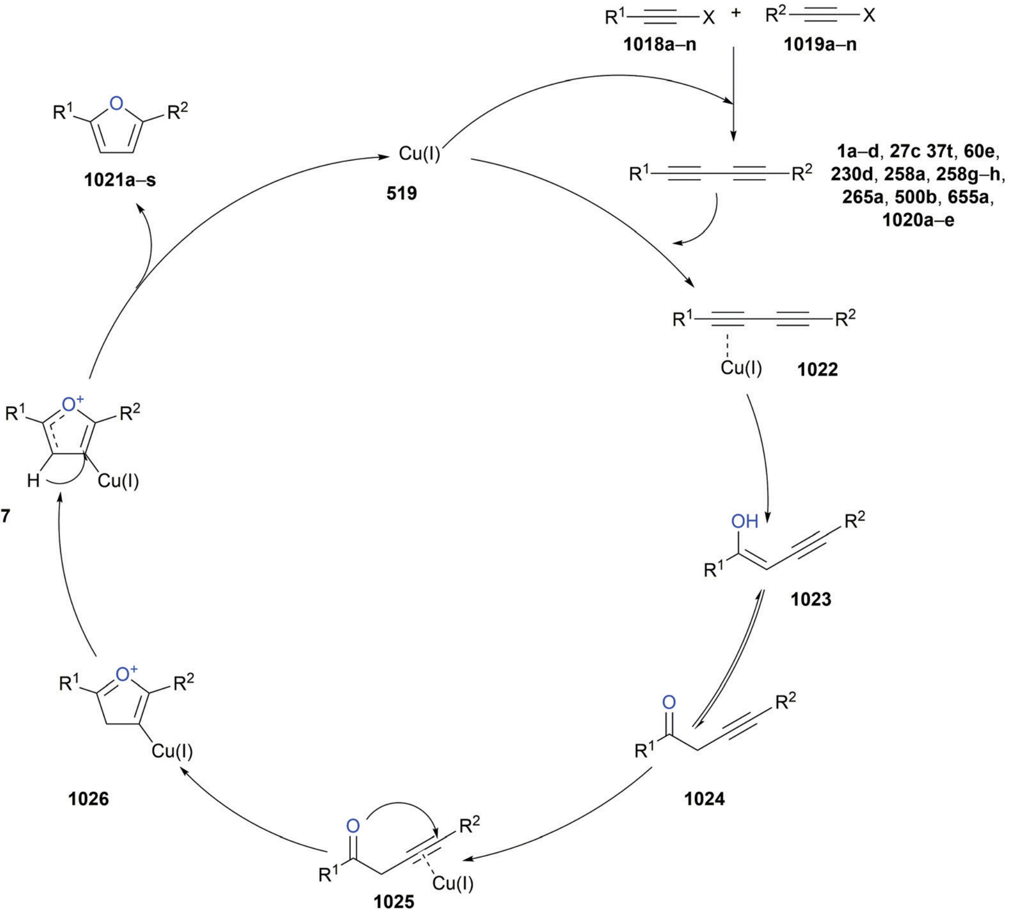
From diynes

60e, R^1 = *p*-$MeOC_6H_4$, R^2 = Ph, **1021o**, 92%
655a, R^1 = *p*-FC_6H_4, R^2 = *p*-$MeOC_6H_4$, **1021p**, 87%
1020c, R^1 = *p*-ClC_6H_4, R^2 = *p*-$MeOC_6H_4$, **1021q**, 90%
1020d, R^1 = *p*-MeC_6H_4, R^2 = *p*-$MeOC_6H_4$, **1021r**, 84%
1020e, R^1 = *p*-$MeOC_6H_4$, R^2 = thiophene, **1021s**, 87%

Scheme 186 Synthesis of 2,5-disubstituted furans **1021a–s** *via* Glaser coupling and hydration process catalysed by CuI **519**/1,10-phen system.

used, and CuI **519**/1,10-phen was much more active than CuCl **55** or CuBr **1022** (Scheme 186). The mechanism of both subsequent processes: Glasser coupling and hydration is presented in Scheme 187.

The hydration of 1,3-diyne alcohols was also catalysed by non-metal systems, based on base-functionalised ionic liquids under an atmosphere of CO_2. The best results were obtained using [HDBU][BenIm] which possess moderate basicity. DFT calculations proved that the process started from the reaction of 2-methyl-6-phenylhexa-3,5-diyn-2-ol **1028** with CO_2, followed by intramolecular cyclisation, which was estimated to be the rate-determining step in this reaction. Then the cyclic



Scheme 187 Mechanism for the synthesis of 2,5-disubstituted furans **1021a–s** from haloalkynes **1018a–n** and **1019a–n**.

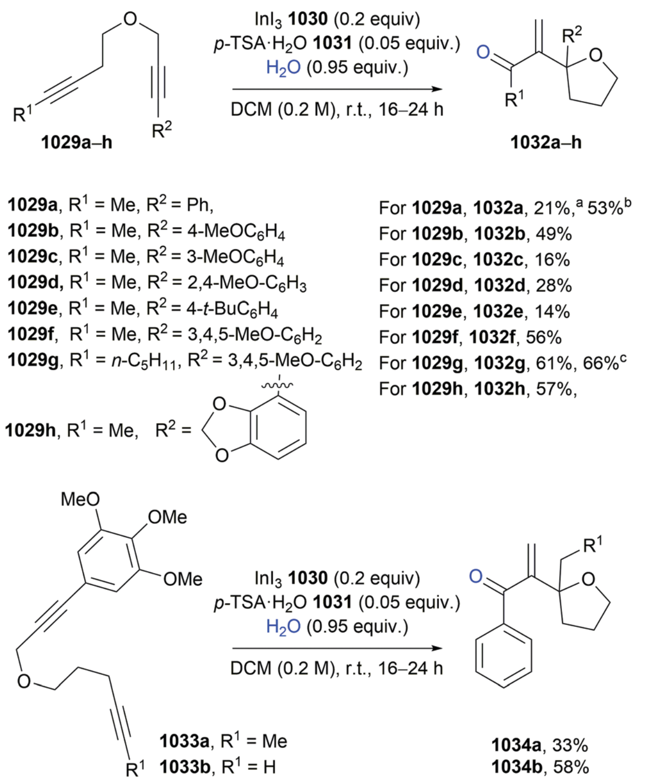
carbonate is hydrolysed and CO_2 is released by the base [BenIm]. Finally 3(2*H*)-furanone is formed through isomerisation with the base catalyst and the intramolecular cyclisation. Much better results were obtained when protic ILs were used.[389]

Performing the hydration/cyclisation process with InI_3 **1030** as a catalyst and *para*-toluene sulfonic acid (*p*-TSA) **1031** as a co-catalyst, it was possible to obtain 2-disubstituted tetrahydrofurans **1032a–h** and **1034a–b** from 1,7- or 1,8-diynyl ethers **1029a–h** and **1033a–b** with moderate yields. The products contain an exocyclic enone part. The best yields were obtained for reagents bearing with nucleophilic aryl groups in the terminal positions (Scheme 188).[390] The authors also postulated the mechanism of the reaction, which started from the activation of homopropargylic alkyne by chelation of InI_3 **1030**, with the ether oxygen atom. This accelerates the initial 7-*endo-dig* cyclisation with the nucleophilic aryl alkyne. The presence of such an aryl ring is necessary for the desired reaction course. Next, hydration occurred, which furnishes enol **1037**, which *via* elimination process leads to acyclic cross-conjugated dienone **1038**. The mechanism is concluded by the protonation of **1038** to tertiary carbocation **1039** and its cyclisation to the desired 2-disubstituted tetrahydrofurans (Scheme 189).[390]

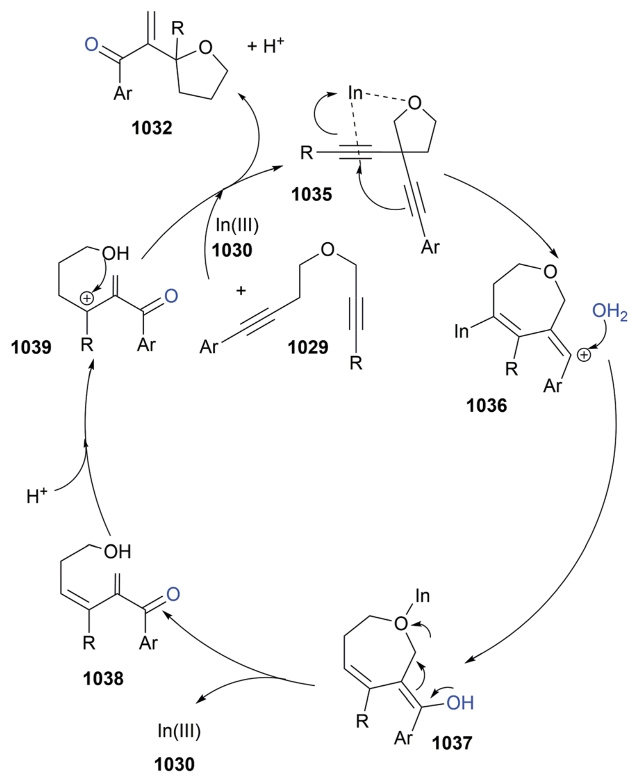
In addition to the application of metal based catalysts in the hydration reaction of diynes, there are also some examples focused on photocatalytic processes. Photohydration of non-symmetricaly substituted conjugated 1,3-diynes **781c**, **1040a–g** with an aryl (naphthyl, phenyl, 4-$MeOC_6H_4$, 4-$CH_3COOC_6H_4$ 4- or 3-$CF_3C_6H_4$, 4- or 3-$NO_2C_6H_4$) or alkyl groups (*tert*-butyl, methyl) occurred in an aqueous sulphuric acid solution. The acidity influences the ration of products **1041** and **1042**, which differs in the hydration of a specific C≡C bond. A medium-acidity gives quantitative yields of hydration, and azulene-quenching postulating that the singlet excited state furnishes both **1041** and **1042** photoadducts. The triplet excited state yields only **1041** photoadducts when R is an alkyl group. Moreover, the type of the substituent attached to the aryl group has an influence on the photohydration process is in the order of 3-NO_2 > 4-NO_2 > 3-CF_3 > 4-CF_3 > 4-CO_2CH_3. Depending on the reagent, various products with a carbonyl group attached to the C≡C or allenic structures were obtained, which are presented in the mechanism shown in Scheme 190.[391,392]

11. Hydrothiolation of conjugated 1,3-diynes

Hydrothiolation of conjugated diynes is carried out mostly according to two pathways: (i) nucleophilic addition of thiols



Scheme 188 Synthesis of 2-disubstituted tetrahydrofurans **1032a–h** and **1034a–b** *via* hydrative cyclisations of 1,7-and 1,8-diynyl ethers **1029a–h** and **1033a–b** catalysed by InI_3 **1030**.

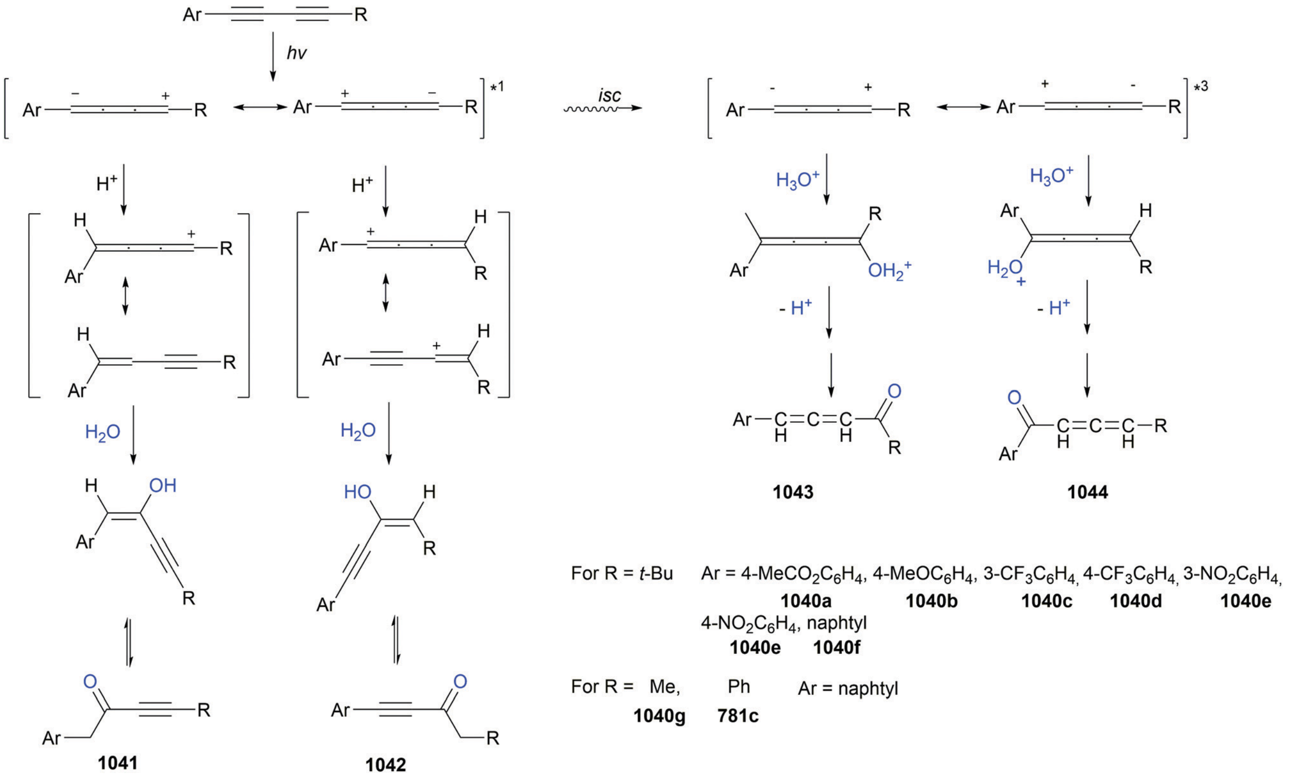


Scheme 189 Proposed mechanism for hydrative cyclisation of 1,7-diynyl ethers **1029** catalysed by InI_3 **1030**.

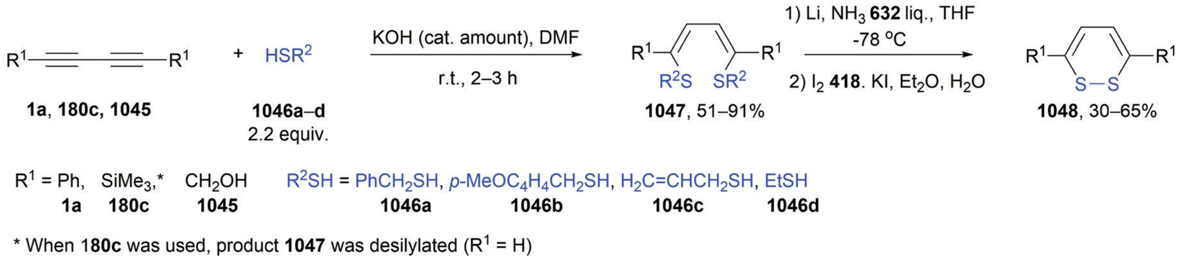
to unsaturated carbon–carbon bonds in the presence of various alkaline metal bases or, (ii) according to radical processes. Vinyl sulfides obtained in the hydrothiolation reactions are the components of several drugs used in the Alzheimer's, Parkinson's, cancer, or AIDS diseases.[393,394] They are also important building blocks in organic synthesis, which might be easily converted to carboxylic acids, ketones, or aldehydes in a thio-Claisen rearrangement. They can also be used in Michael, Peterson, or Diels–Alder transformations as well being easily reductively cleaved.[395–401] Vinylsulfides were isolated in the biologically active compounds *e.g.*, Griseoviridin from *Streptomyces graminofaciens* or benzylthiocrellidone from *Crella spinulata*.[402–404]

Nucleophilic addition of thiolate anions to C≡C bonds in alkynes and diynes occurs mainly according to a *trans*-addition reaction with the generation of (*Z*)-vinylic isomers. The formation of these nucleophilic species occurred predominantly in the reactions with strong bases (*e.g.*, hydroxides: KOH, NaOH, or alkoxides: NaOR or KOR). In most cases, the other possible isomers are accomplished by the post-reaction mixture. The addition of thiols **1046a–d** to conjugated 1,3-diynes **1a**, **180c**, **1045** led to the formation of 1,4-dithiol-1,4-disubstituted dienes **1047**. The reaction occurred in a stepwise process. First, the monothiolate 1,3-enyne is formed, which then is hydrothiolated to 1,4-dithiol-1,4-disubstituted dienes **1047**. The obtained products can be cyclised to dithiins **1048** by deprotection of the thiol group with Li in liquid NH_3 **632**, followed by the oxidation of thiolate anions with I_2 **418** in KF. These cyclic compounds **1048** can be potentially used as antiviral compounds or antibiotics. During the hydrothiolation of 1,4-TMS-substituted buta-1,3-diyne **180c**, the desilylation reaction occurred (Scheme 191).[405–408] Changing the reaction conditions, by applying a different solvent (DMSO), led to the formation of biologically active thiophenes **1051a–f** with moderate isolated yields (51–66%), instead of thio-substituted buta-1,3-dienes **1047** when EtOH or DMF were used.[406,409] The 1,2-addition product of arylmethanethiol **1046a** or **1049a–c** led to the corresponding enyne **1050**. The thiophene was formed by the cyclisation of enenyne thiol **1050**, which occurs from the nucleophilic attack of benzyl anion on C_{sp} bond in the second alkynyl group of **1050** (Scheme 192).[410,411]

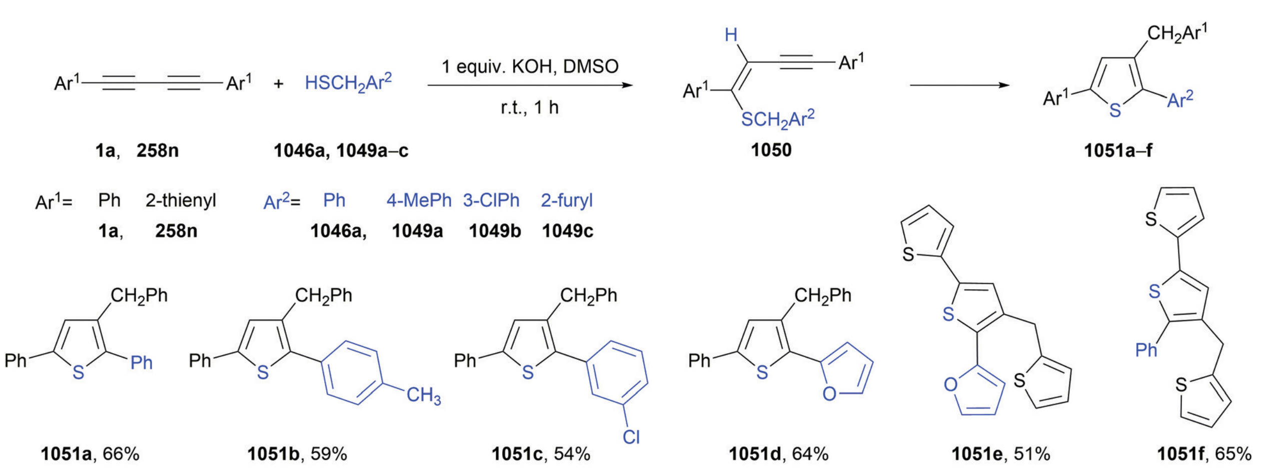
The synthesis of thiophenes and other cyclic compounds from diynes was briefly reviewed by Maretina and Trofimov.[295] The paper presented the procedures that were published mostly in 1960–1980 and are focused on the addition of sulfide ions to conjugated diynes yielding thiols. Very good results were obtained in the case of the formation of thiols when Na_2S **1052** was used as a reagent in KOH/DMSO. When a quantitative amount of Na_2S **1052** and KOH was applied thiophene **1053** was formed from buta-1,3-diyne with excellent yield up to 99%. The process occurred *via* hydrothiolation of diyne followed by cyclisation. Nonhydroxylic polar solvents *e.g.*, DMSO or *N*-methylpyrrolidone should be used in this transformation, because these solvents did not decrease the activity of anions by their solvation.[295] By replacing KOH with TBAOH **1056** and benzylthiol



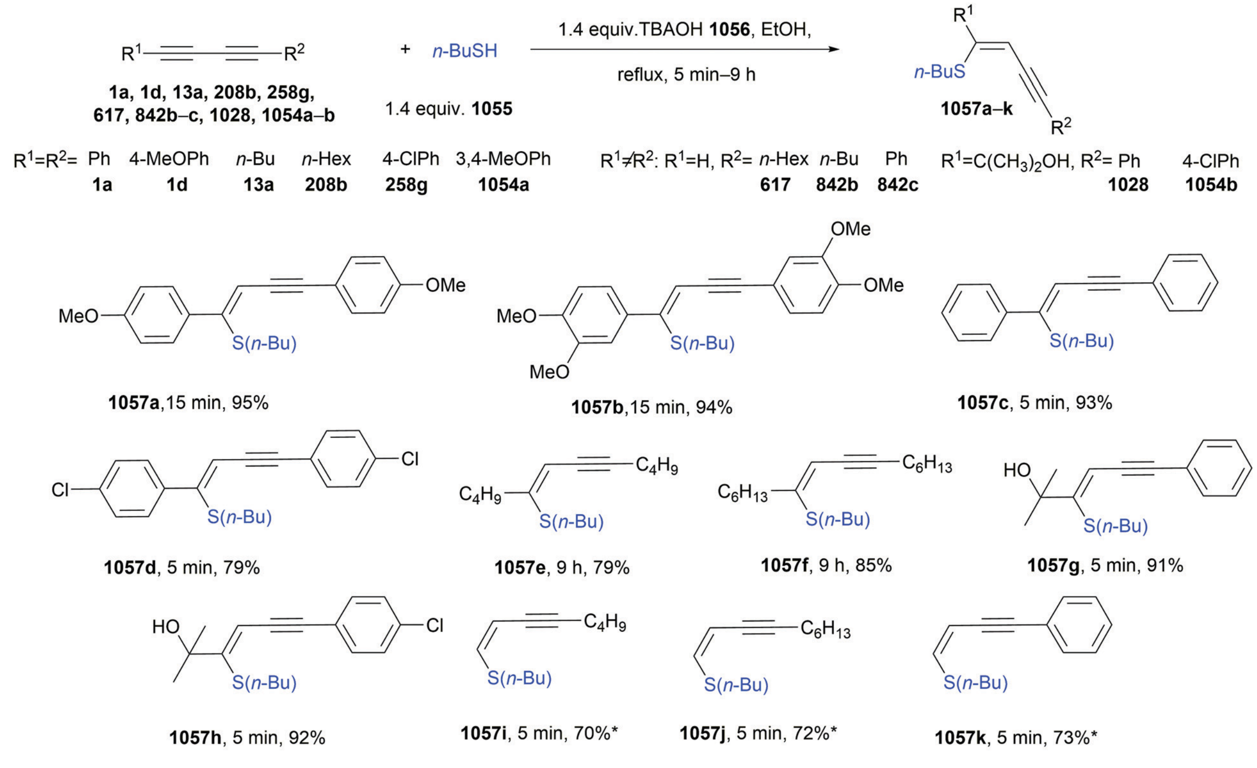
Scheme 190 Mechanism of the photohydration of conjugated 1,3-diynes **781c**, **1040a–g**.



Scheme 191 Nucleophilic hydrothiolation of 1,4-disubstituted-buta-1,3-diynes **1a**, **180c**, **1045** followed by cyclisation to 1,2-dithiins **1048**.

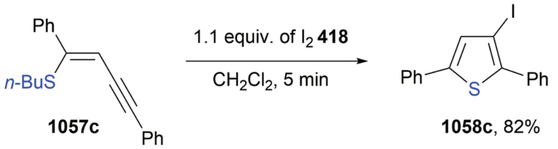


Scheme 192 Hydrothiolation/cyclisation of aryl-substiuted 1,3-diynes **1a**, **258n** with arylmethanethiols **1046a** or **1049a–c**.



* Mixtures of (*Z*)-thiobutenynes and divinyl disulfides were obtained.

Scheme 193 Hydrothiolation of buta-1,3-diynes with *n*-BuSH **1055** in the presence of TBAOH **1056** as a base.

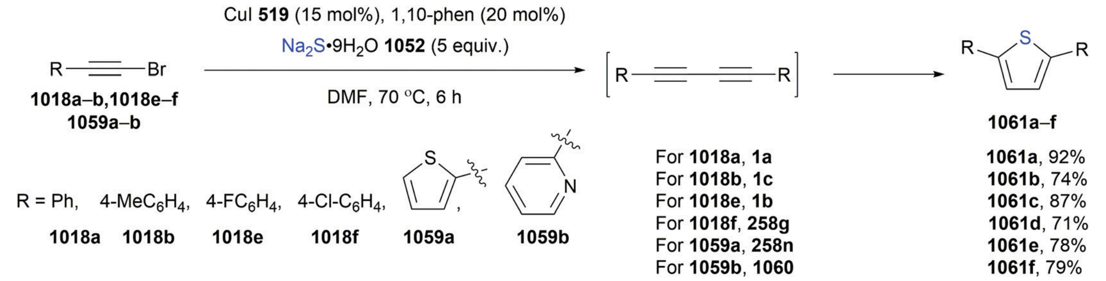


Scheme 194 Electrophilic cyclisation of **1057c** towards 3-iodothiophene **1058c**.

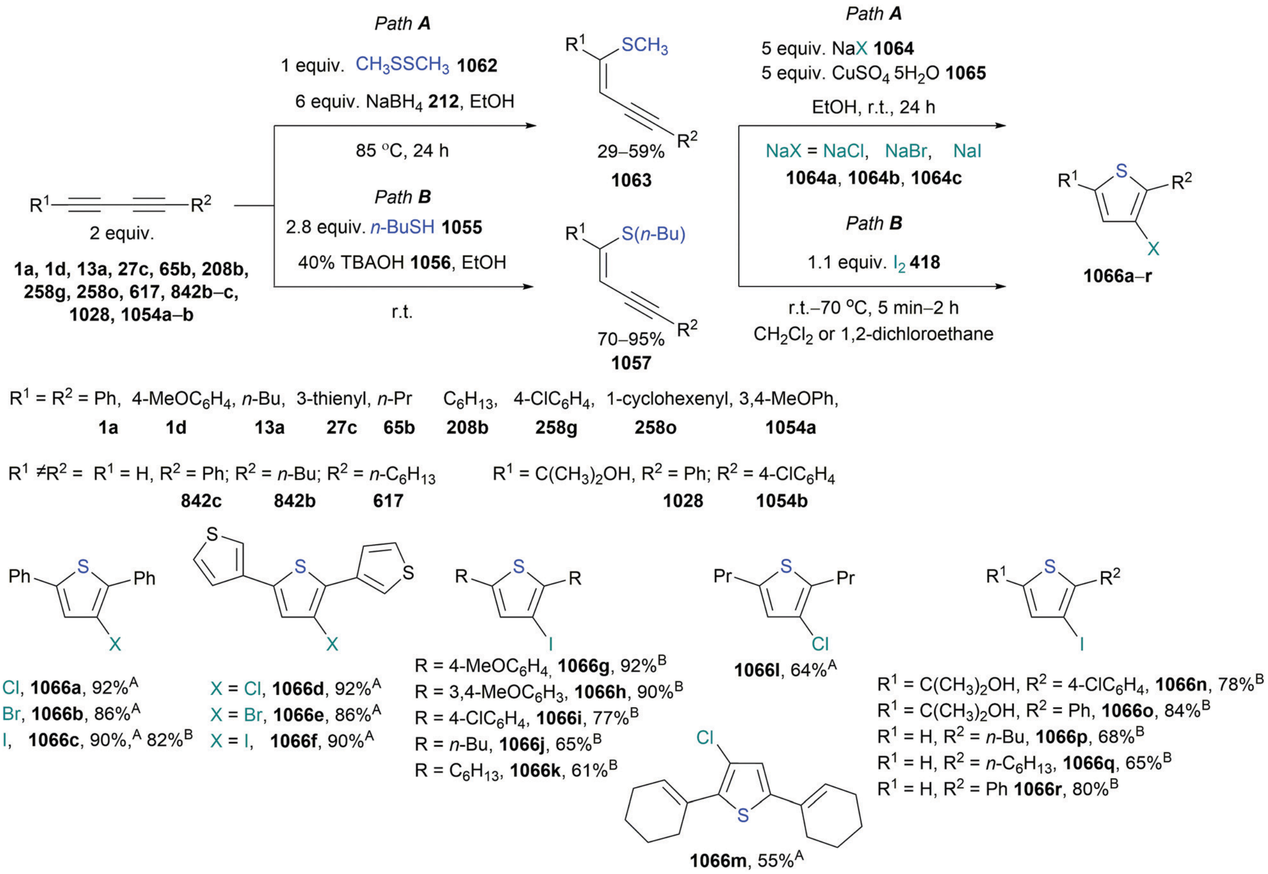
1046a with butyl analog **1055** it was possible to shorten the reaction time to just 5 minutes and to increase the product yields and selectivity. (*Z*)-Thiobutenynes **1057a-k** were obtained exclusively for symmetrical and unsymmetrical diynes **1a, 1d, 13a, 208b, 258g, 617, c, 1028, 1054a–b** with sterically different substituents in positions C_1 and C_4. Hydrothiolation using the reductive system *n*-C_4H_9SH **1055**/TBAOH **1056** is more efficient because it is a stronger base which, due to its phase-transfer ability, increases the solubility of reagents in the organic phase and accelerates the formation of the butylthiolate anion (Scheme 193).[412] In the presence of iodine **418**, the obtained (*Z*)-organylthioenynes underwent electrophilic cyclisation towards 3-iodothiophenes **1058.** The reaction was tested using 1.0 equiv. of **1057c** and 1.1 equiv. of I_2 **418** (Scheme 194).

Thiophenes **1061a–f** were obtained also from haloalkynes **1018** and **1059** from a Glaser reaction to conjugated 1,3-diynes **1a–c, 258g, 258n,** and **1060** followed by the hydrothiolation to sulfanyl substituted enynes, which further cyclises to thiophenes possessing different aryl or heteroaryl groups in positions 2- and 5- **1061a–f.** The reactions were catalysed by a CuI **519**/1,10-phen system and proceeded with high products yields. As a hydrothiolation agent, $Na_2S{\cdot}9H_2O$ **1052** was used (Scheme 195). The mechanism of this transformation was previously described for the analgous hydration process (Scheme 187).[388]

The synthesis of 3-halosubstituted thiophenes **1066** from simple aryl or alkyl-functionalised conjugated buta-1,3-diynes **1a, 1d, 13a, 27c, 65b, 208b, 258g, 258o, 617, 842b–c, 1028,** and **1054a–b** was described by Kesharwani *et al.* They proposed a two-step procedure yielding 3-chloro, 3-bromo and 3-iodothiophenes **1066** based on hydrothiolation reaction of 1,4-diaryl or 1,4-dialkyl-substituted diynes with methyl disulfide **1062** in the presence of $NaBH_4$ **212** as a hydrogen source and, electrophilic cyclisation of the obtained sulfanyl modified enynes **1063** with natrium halides **1064a–c** (NaCl, NaBr, NaI) in the presence of $CuSO_4{\cdot}5H_2O$ **1065** (Scheme 196).[413] This methodology has a positive impact on the environment, because it uses the green solvent ethanol and simple inorganic salts. In many cases it also gave better results than typical methods used for the preparation of halothiophenes (Scheme 196).[413–415] The mechanism of the cyclisation proposed the formation of $CuCl_2$ in the first step from $CuSO_4$ **1065** and NaCl **1064a**, which can easily coordinate to the C≡C triple bond in the enyne to **1067.** Nucleophilic attack of sulfur provided intermediate **1068** that eliminates the methyl group attached to the sulfur atom *via* an S_N2 substitution reaction by the chloride anion yielding intermediate **1069.** Reductive elimination furnished the desired



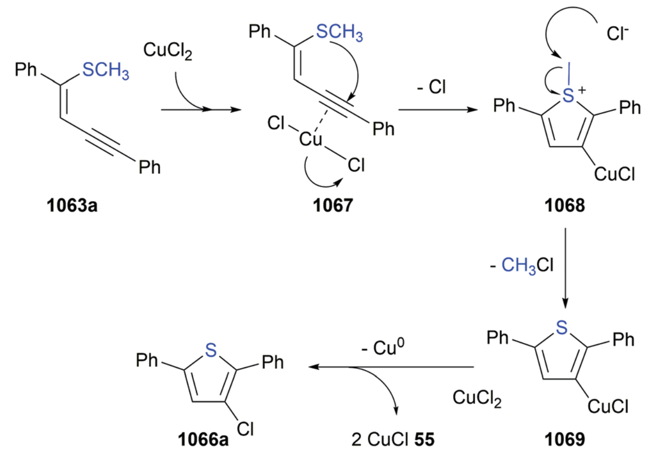
Scheme 195 Synthesis of 2,5-disubstituted thiophenes **1061** from haloalkynes in Glaser coupling/hydrothiolation/cyclisation reactions catalysed by CuI **519**/1,10-phen.



Scheme 196 Synthesis of 3-halothiophenes **1066** in hydrothiolation/electrophilic cyclisation reactions.

halothiophene **1066a,** while the Cu(0) is oxidised to CuCl **55** by $CuCl_2$ (Scheme 197). In the case of the application of NaBr **1064b** and NaI **1064c,** $CuBr_2$ **52** and CuI_2 can easily release I_2 **418** and Br_2, and by applying these as electrophiles forms of bromo- and iodothiophenes.[413] 3,4-Dichloro-substituted thiophenes **1071** can be formed in the reaction of 1,4-diarylsubstituted buta-1,3-diynes with sulfur chloride **1070.** Products **1071** were obtained with 18–80% yields.[295,416] Excellent yields and selectivities of (*Z*)-thioenynes **1074a–l** were obtained when disulfides **1073** (PhSSPh **1073a,** BuSSBu **1073b**) were used as reagents. Oganylthiolate anions were generated *in situ* with $NaBH_4$ **212.** The application of disulfide **1073a–b** may constitute an alternative towards the use of toxic and bad-smelling thiols (Scheme 198).[417]

A sustainable and clean method for obtaining thiobutenynes **1074/1075** was carried out in the presence of KF/Al_2O_3 as a catalyst, using glycerol or poly(ethylene glycol) (M_w = 400, PEG400) as a green solvent. Applying this system, it was possible to decrease the amount of the catalyst employed, and the generation of inorganic products is reduced to a minimum. The products were extracted in hexane/ethyl acetate and KF/Al_2O_3 was directly used in following cycles. The reaction was effective for various diynes substituted in the terminal position with electron-withdrawing or electron-donating



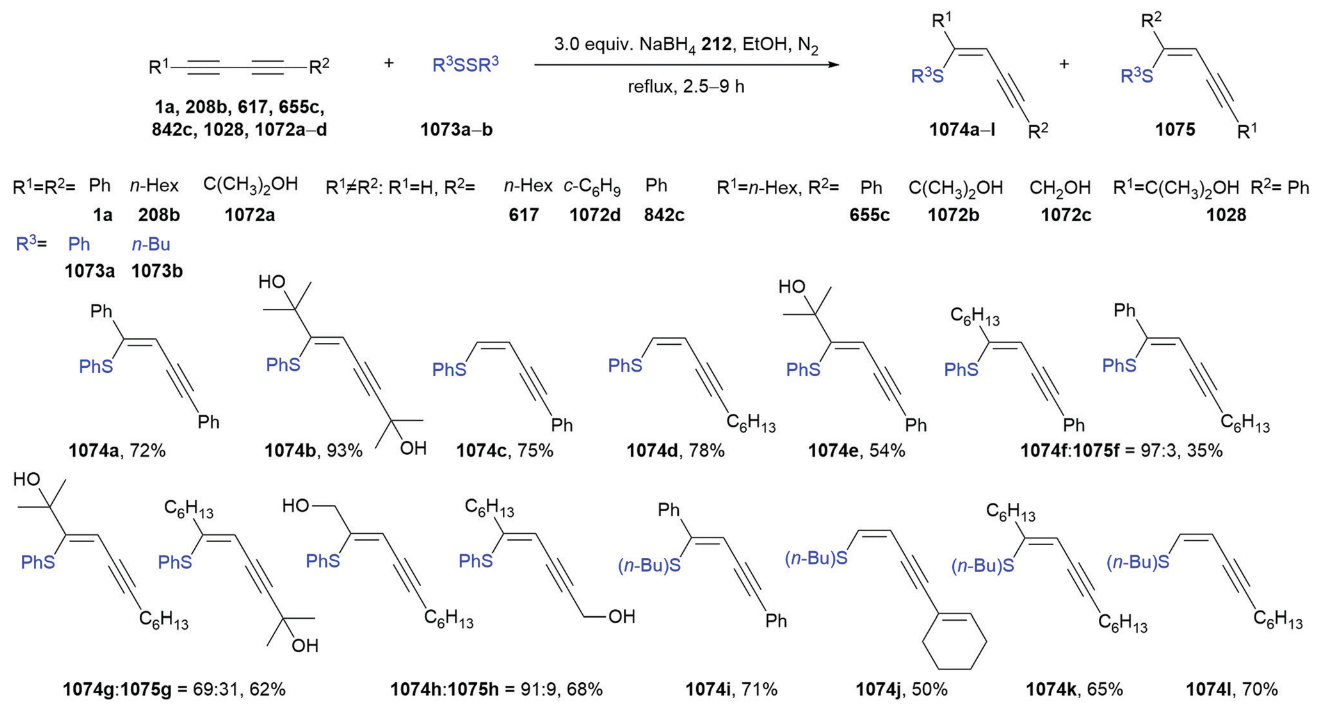
Scheme 197 Proposed mechanism for chlorocyclisation of 1-methylsulphanyl-1,4-diphenyl-buta-1-en-3-yne **1063a** catalysed by Cu(II).

groups. The reaction was optimised for the use of an equimolar ratio of reagents. The best results were accomplished when 90 °C was used and the reaction was carried out for 6 hours. A lower temperature led to lower yields, while higher temperatures reduced the selectivity. Under the optimal conditions' product **1074** with (*Z*)-geometry was obtained in excess, in the ratio 90 : 10 to 100 : 0 depending on the reagent structure. The yields of the (*Z*)-1,4-diphenyl-2-(phenylthio)but-1-en-3-yne **1074a** in the three repetitive batches reached 93%, 89%, 80% respectively (64%, 55%, 48% isolated yield).[418]

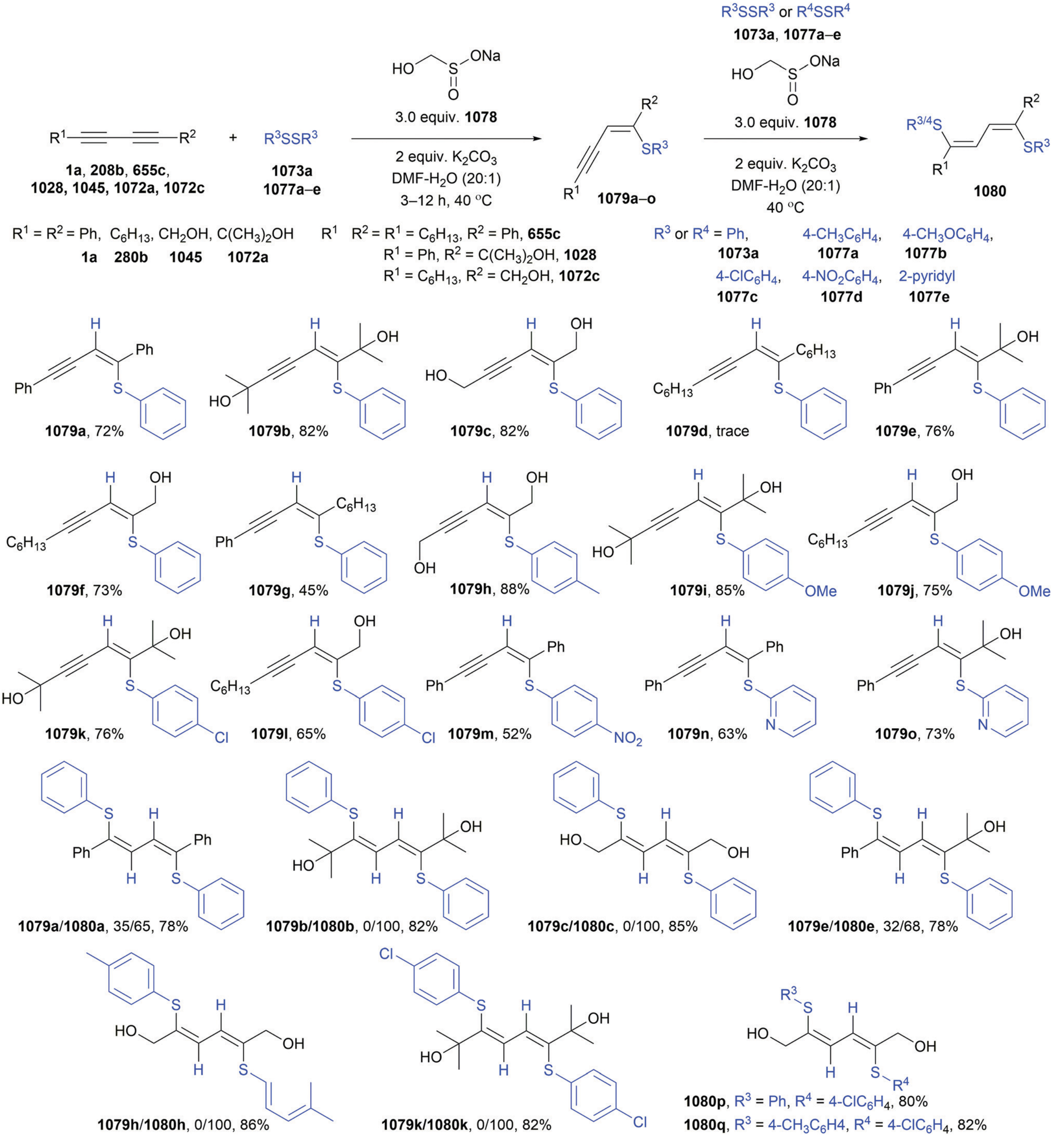
Perin *et al.* proved that the addition of phenyldisulfide **1073a** to 1,4-diphenylbuta-1,3-diyne **1a** using the same conditions (NaBH$_4$ **212**, PEG400, 30 °C) may be accelerated applying microwave irradiation as a heating source. It was possible to reduce the reaction time to 85 minutes from 24 hours under traditional conditions with a slightly better yield of **1074a** (96% *vs.* 82%). Moreover, by increasing the temperature to 90 °C, 1,4-diphenyl-1,4-di(phenylthio)buta-1,3-diene **1076** was selectively formed in good yield (65% *vs.* 69%).[419]

The hydrothiolation of 1,3-butadiynes **1a**, **208b**, **655c**, **1028**, **1045**, **1072a**, and **1072c** were carried also using various diaryl disulfides **1073a** or **1077a–e**, sodium hydroxymethanesulfinate **1078** (rongalite **1078**, HOCH$_2$SO$_2$Na), and potassium carbonate. Rongalite **1078** was applied as a reducing agent cleaving the bond of disulfide. When disulfide was used in 0.5 equiv. to the diyne, (*Z*)-1-sulfanyl-but-1-en-3-ynes **1079a–o** were obtained with isolated yields in the range 45–86%. Increasing the temperature to 70 °C and an equimolar ratio of diyne and disulfide, it was possible to obtain a mixture monothiolation **1079a–o** and bisthiolation **1080** products with moderate yields. Moreover, the introduction of two different arylthiol groups to the product was possible by subsequent hydrothiolation of diyne with two others disulfides. The reaction did not occur for benzyl and alkyl-substituted disulfides (Scheme 199). The mechanism of this transformation started by the decomposition of rongalite **1078** to formaldehyde **1081** and HSO$_2^-$ **1082** in the presence of the base. Next, the single-electron transfer to disulfide **1073a** leads to anionic **1084** and radical species **1085**. The radical thiolate **1085** is then reduced to its ionic form **1084** by another single electron transfer from radical HSO$_2^\bullet$. **1083**. Addition of thiolate **1084** to diyne **1a** followed by the protonation of the intermediate **1086** yields the desired product **1079a** (Scheme 200).

Moreover, bishydrothiolation was also carried out in a sequence of one-pot reactions. Sonogashira coupling of



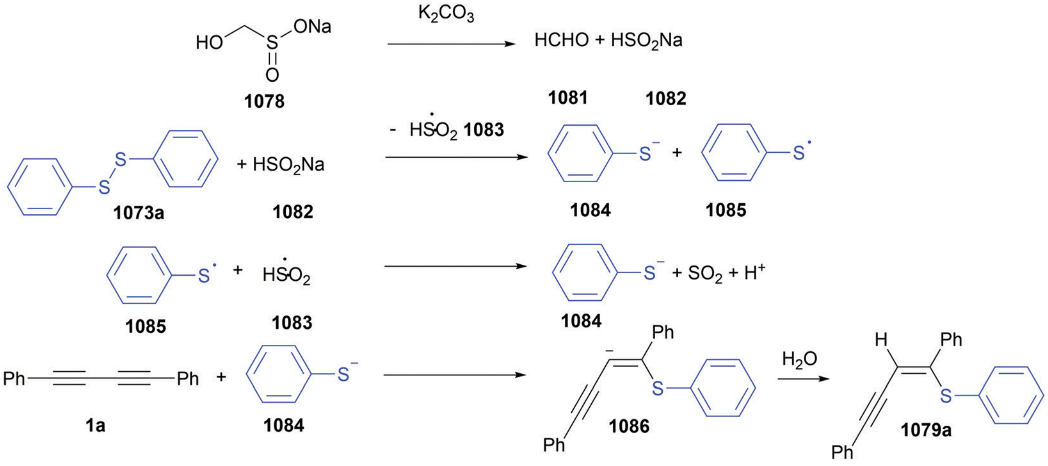
Scheme 198 Synthesis of (*Z*)-1-organothiobut-1-en-3-ynes **1074a–l** by the hydrothiolation of buta-1,3-diynes using disulfides **1073a–b**.



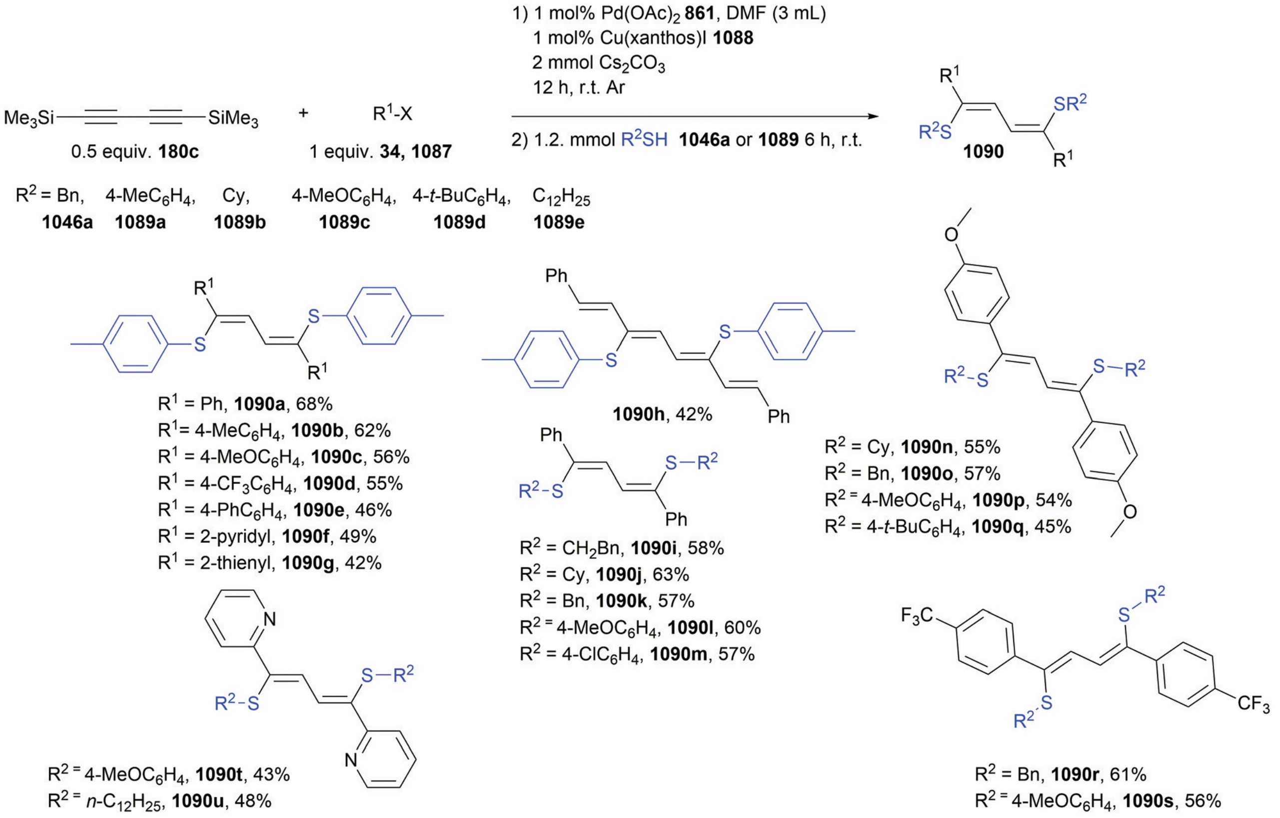
Scheme 199 Hydrothiolation of conjugated 1,3-diynes **1a**, **208b**, **655c**, **1028**, **1045**, **1072a**, and **1072c** in the presence of rongalite **1078**.

1,4-bis(trimethylsilyl)buta-1,3-diyne **180c** with aryl halides **1087** followed by bishydrothilation of the obtained 1,4-bisarylbuta-1,3-diyne with various thiols **1046a** and **1089a** to (*Z*,*Z*)-1,4-diarylbuta-1,3-dienes **1090.** The formation of the new C–C bonds was catalysed by Pd(OAc)$_2$ (1 mol%) **861** and Cu(xantphos)I (1 mol%) **1088,** while double hydrothiolation was promoted by basic Cs$_2$CO$_3$. The whole process occurred with moderate or good yields, with high regio- and stereoselectivity (Scheme 201).[420] The mechanism of this transformation started with the generation of the sulfur anion from thiol **1046a** or **1089** in the presence of base a (BH). The hydrothiolation step then occurs with the formation of intermediate **1091.** The (*Z*)-isomer **1093** is formed in the presence of thiol **1089a** or base according to the protonation step. Subsequent hydrothiolation of obtained enyne **1093** furnished (1*Z*,4*Z*)-bis-sulfanylbuta-1,3-diene **1090a** (Scheme 202).[420]

The addition of aminothiols **1094a–e** to buta-1,3-diyne **641** was carried out in ammonia **632,** which was used as a solvent



Scheme 200 Mechanism of the hydrothiolation of 1,3-diynes in the presence of rongalite **1078**.

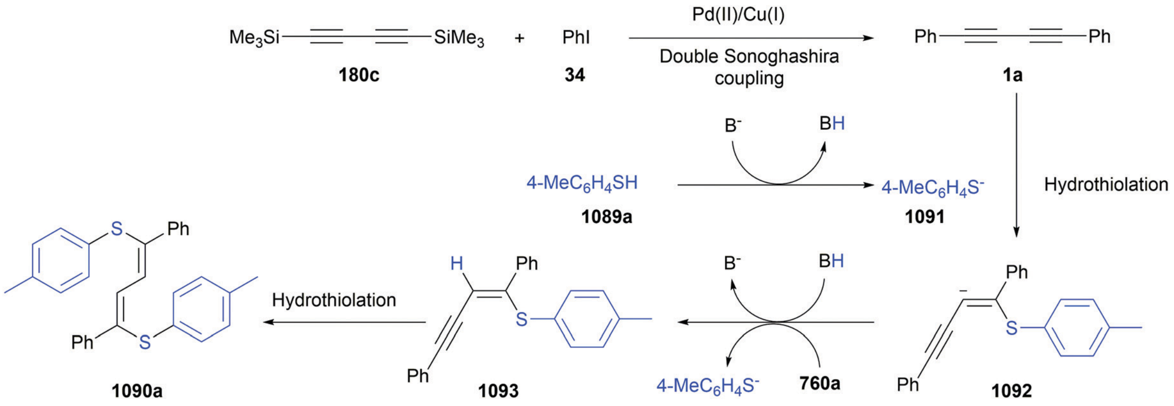


Scheme 201 One-pot Sonogashira coupling/bishydrothiolation of 1,4-bis(trimethylsilyl)buta-1,3-diyne **180c** catalysed by Pd(OAc)$_2$ **861**/Cu(xanthphos)I **1088**/Cs$_2$CO$_3$ system.

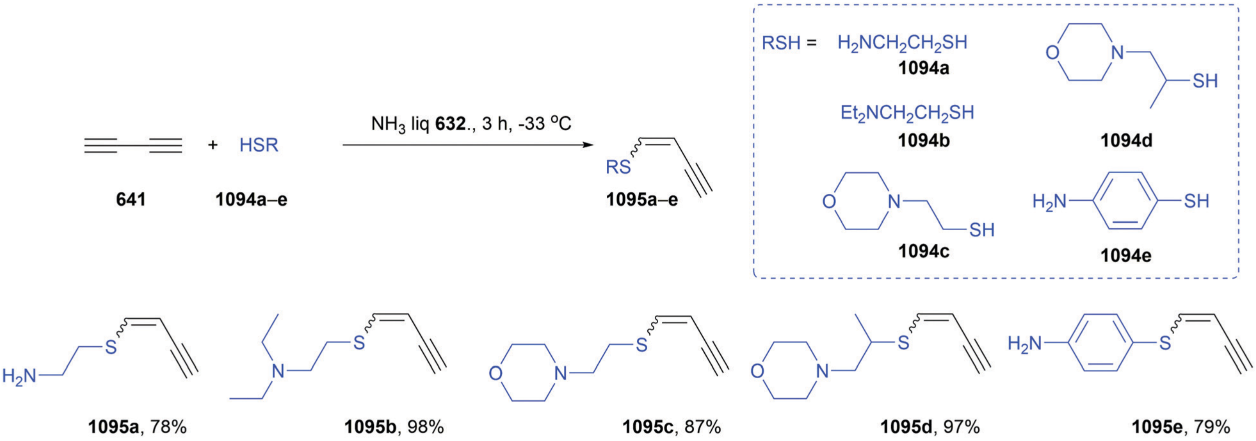
and base at the same time. HS$^-$ anions are 280 times more reactive than NH$_2$$^-$, therefore the addition of aminothiols **1094a–e** to the C≡C bonds occurred from the S-side. The enyne sulfides **1095a–e** were obtained in 78–98% yield (Scheme 203).[421]

12. Hydroselenation of 1,3-diynes

Alkenyl selenides are an important class of organoselenium compounds, which have broad applications in organic chemistry leading to a vast spectrum of valuable products.[422–426] These molecules can be prepared by various synthetic pathways however, the most frequently employed method for their preparation is the hydroselenation of the C≡C bond by nucleophilic organoselenolate anions. The synthesis and application of organoselenium compounds, especially selenophenes, has been summarised in many books and reviews,[422,423,425,427–434] nevertheless the hydroselenation of diynes have not been comprehensively reviewed.



Scheme 202 Mechanism of one-pot Sonogashira/hydrothiolation reactions of 1,4-bis(trimethylsilyl)buta-1,3-diyne **180c** catalysed by Pd(OAc)$_2$ **861**/Cu(xanthphos)I **1088**/Cs$_2$CO$_3$ system.



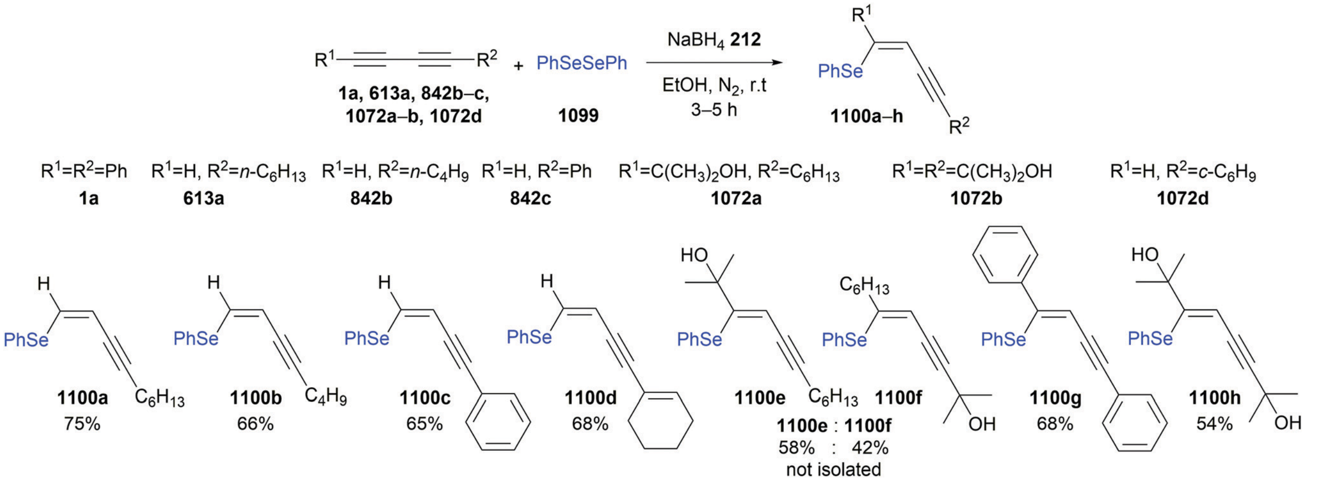
Scheme 203 Hydrothiolation of buta-1,3-diyne **641** with aminothiols **1094a–e**.

Scheme 204 Synthesis of 2,5-substituted selenophene **1098** compounds.

The first example addition of a Se–H bond to diynes was reported by Taylor *et al.* in 1968.[435] The addition of H$_2$Se **1097** to symmetrical and unsymmetrical 1,3-diynes **1a**, **208c**, **1045**, **1072a**, **1096a–b** was catalysed by the Ag$^+$ cations and led to 2,5-disubstituted selenophenes **1098a–f** in good yields (Scheme 204).

Dabdoub *et al.* developed an alternative and efficient synthetic protocol employing the phenylselenolate anion which was generated *in situ* by the reaction of Ph$_2$Se$_2$ **1099** with sodium borohydride **212** in ethanol, instead of using toxic hydrogen selenide. Hydroselenation of 1,4-substituted-1,3-butadiynes **1a**, **613a**, **842b–c**, **1072a–b**, **1072d** occurred with excellent regio-, stereo- and chemoselectivity smoothly leading to (*Z*)-1-phenylseleno-1,4-diorganyl-1-buten-3-ynes **1100a–h** in high yields. However, reacting 2-hydroxy-2-methyl-3,5-dodecadiyne **1072a** with Ph$_2$Se$_2$ **1099** and NaBH$_4$ **212** in ethanol under reflux, gave a mixture of regioisomers (**1100e**/**1100f** = 58/42) which was confirmed by ^{1}H NOESY experiments (Scheme 205).[436]

A similar strategy was applied by Zeni *et al.* who used various diorganodiselenides **1112a–e** in the preparation of (*Z*)-selenoenynes **1113a–o** through the hydroselenation of symmetrical and unsymmetrical 1,3-diynes **1a**, **1c**, **13a**, **37s**, **842b–c**, **1028**, **1045**, **1072a**, and **1111**. The obtained products were further cyclised with different electrophiles such as I$_2$ **418**, ICl **1114a**, PhSeBr **1114b**, or PhSeCl **1114c** to 3-substituted selenophenes



Scheme 205 Hydroselenation of symmetrical and unsymmetrical 1,4-diorganyl-1,3-butadiynes **1a**, **613a**, **842b–c**, **1072a–b**, **1072d** with Ph_2Se_2 **1099**.

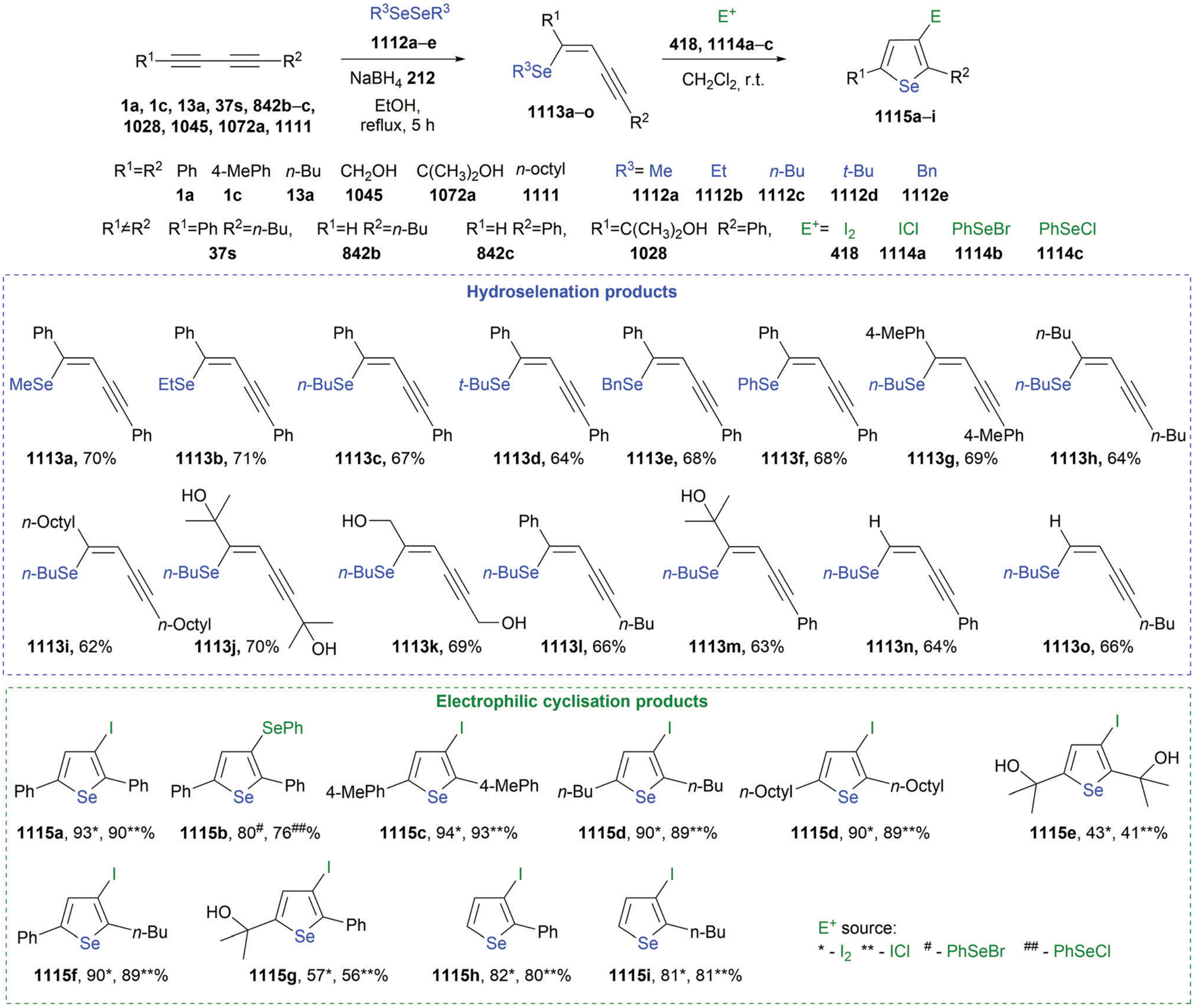
1115a–i in good yields. The electrophilic cyclisation did not occur for (*Z*)-1-(phenylseleno)-1,4-diphenyl-but-1-en-3-yne **1113f** even when using harsh reaction conditions. The authors also presented the versatility of these compounds for many transformations such as Sonogashira coupling, halogen-metal exchange reaction, or Ullmann-type C–O bond forming reactions (Scheme 206).[437]

An analogous protocol was applied by Kesharwan *et al.* who used sodium halides **1064a–c** as a source of electrophilic halogens for the synthesis of halogenated selenophenes **1115a**, **1116**. The hydroselenation of 1,4-diphenyl-1,3-diyne **1a** by Me_2Se_2 **1112a** in the presence of $NaBH_4$ **212** in ethanol gave for (*Z*)-1-(benzylseleno)-1,4-diphenyl-but-1-en-3-yne **1113a** in 60% yield which was transformed to halogenated selenophenes **1115a** and **1116** (Scheme 207a). The protocol was also suitable for the preparation of halogenated thiophenes (Scheme 196).[413] The replacement of electrophiles to a base such as *t*-BuOK in the cyclisation step is also efficient for the synthesis of selenophenes **1119** through selenoenynes **1113e** and **1118** intermediates. The hydroselenation of 1,3-diynes **1a, 1c–d, 27a, 258a,** or **280a** with Bn_2Se_2 **1112e** in the presence of $NaBH_4$ **212** in ethanol was limited to its symmetrical derivatives, and the reaction yields were significantly lower for bulky diynes (Scheme 207b). The authors suggested that 3-benzyl-substituted selenophenes **1119** could be highly promising building blocks for the preparation of polysubstituted selenophenes.[438]

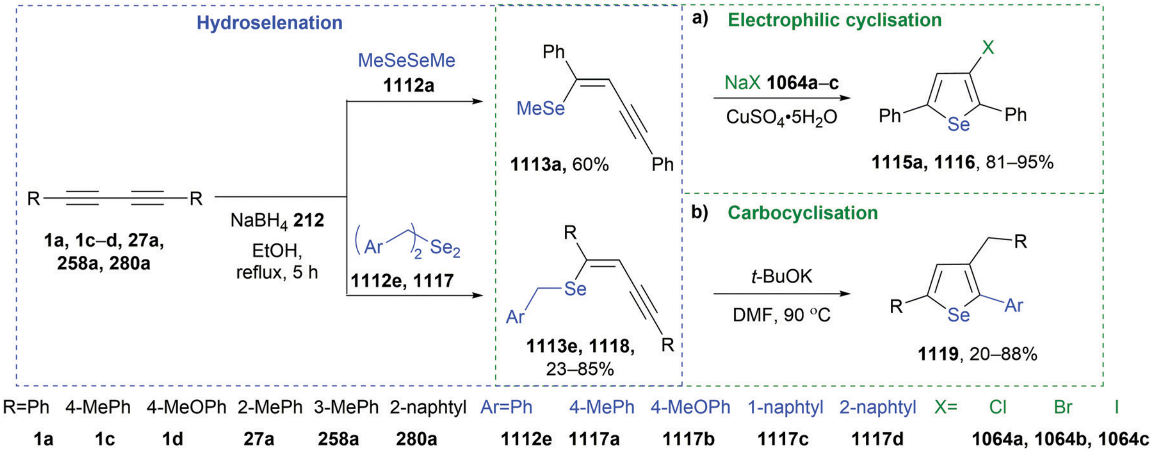
The hydroselenation of diynes was also adopted to synthesise more complex structures such as tetrapyrrolic macrocycles. Chauhan *et al.* presented the preparation of selenium core-modified porphyrinogens based on the hydroselenation of diynediols **1072b**, **1121a–b** with *in situ* generated sodium selenide **1122** in the presence of MeOH and CH_3COOAg in the first step. The obtained selephones **1123** were further transformed to selenophene dipyrranes and used in 3 + 1 condensation reactions with the corresponding diols in the presence of boron trifluoride **565**. It was proved by UV-Vis, fluorescence and ^1H NMR spectroscopy that the selenium core-modified porphyrinogens have a coordination ability to detect of Hg^{2+} cations.[439] The same group reported the preparation of porphomethenes **1128**, porphodimethenes **1127**, and porphotrimethenes **1129** using the same methodology including diynediol hydroselenation followed by 3 + 1 condensation of the selenatripyrranes **1125** with selenophene-2,5-diols **1123** and subsequent oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone **1126** (DDQ). Similar to porphyrinogens, the obtained macrocycles showed the binding affinity with Hg^{2+} anions (Scheme 208).[440]

Lopes *et al.* described the application of deep eutectic solvents (DES), commonly considered as the third generation of ionic liquids, in the preparation of vinyl selenides. Although the report concerns mainly the synthesis of (*E*)-1,2-bisorganylseleno alkenes through the hydroselenation of alkynes, the utilisation of symmetrical buta-1,3-diynes was also presented. Diphenyl selenide **1099** reacted with 1,4-diphenyl-1,3-diyne **1a** or hexa-2,4-diyne-1,6-diol **1045** in the presence of $NaBH_4$ **212** in a choline chloride/urea (1/2) mixture at 90 °C to give corresponding (*Z*)-selenoenynes **1100g** and **1130** with excellent selectivity and high yields (Scheme 209a).[441] A similar strategy based on the application of green solvents was used by Lara *et al.* who applied a poly(ethylene glycol) (PEG 400) as an alternative for DES. Depending on the reaction temperature, the (*Z*)-selenoenynes **1100g–h** and **1132a–b** or (*Z*,*Z*)-1,4-bisselenobuta-1,3-dienes **1133a–c** were obtained in the reaction of diorganodiselenides **1099**, **1112c**, and **1131** with the symmetrical 1,3-diynes **1a**, **1045**, **1072a** in the presence of $NaBH_4$ **212**. The process is highly stereoselective exclusively leading to the corresponding products in high yields. The reaction time was reduced from 24 to 1.25 h by the application of microwave radiation (MW) as a heating method (Scheme 209b).[419]

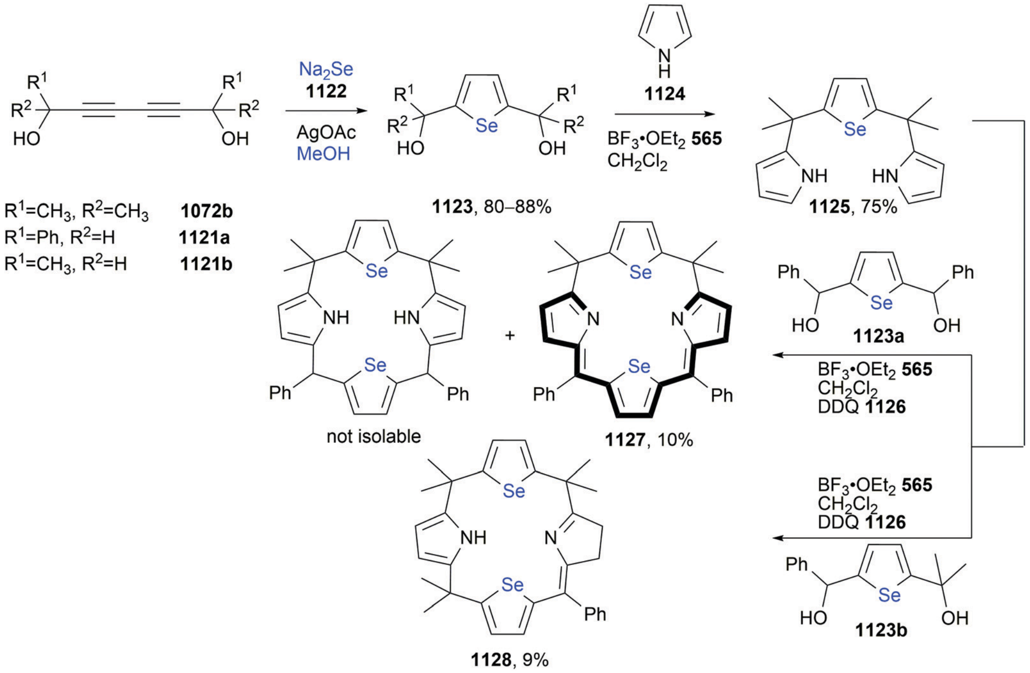
An interesting protocol for the synthesis of (*Z*)-1-(organoselanyl or sulfanyl)enynes was developed by Venkateswarlu *et al.* who utilised sodium hydroxymethanesulfinate (rongalite) **1078** as a reducing agent instead of commonly used $NaBH_4$ **212**. The hydroselenation of 1,3-diynes **1a**, **208b**, **655c**, **1028**, **1045**, **1072a–b** was carried out in the presence of potassium carbonate in a DMF–H_2O (20 : 1) mixture and under mild reaction



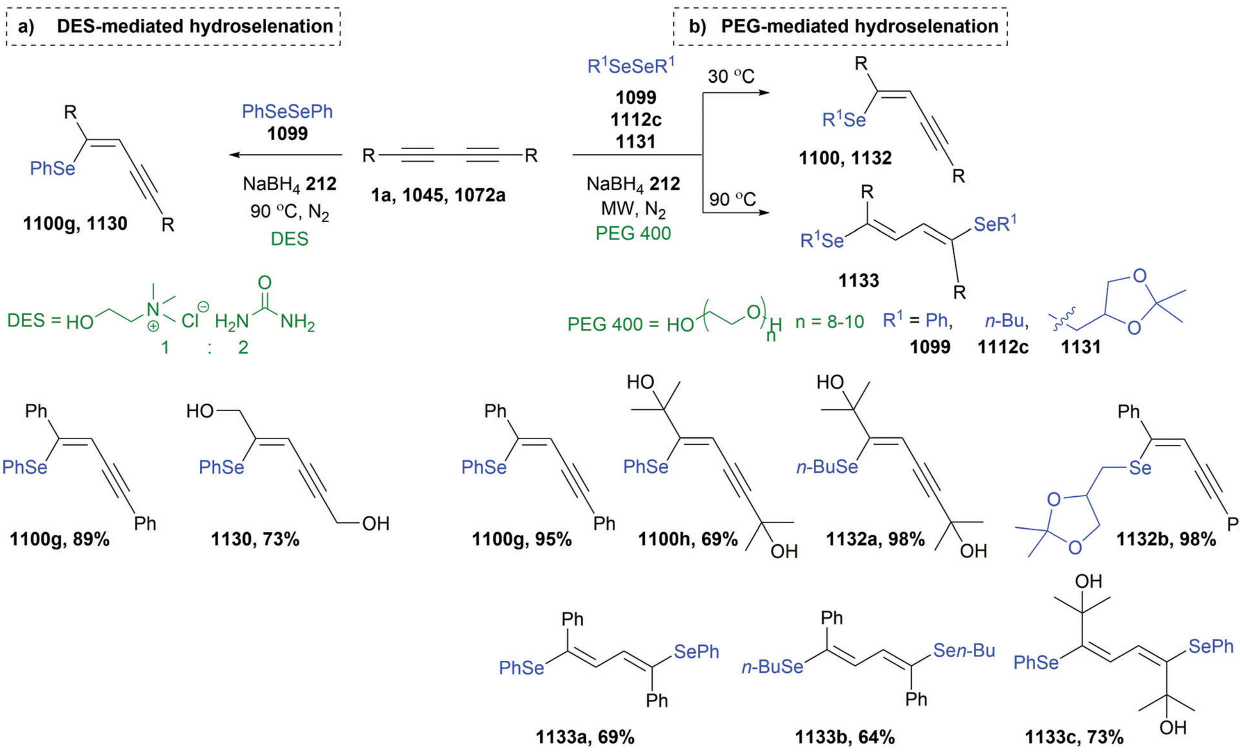
Scheme 206 Synthesis of 3-iodoselenophene **1115a–i** compounds *via* electrophilic cyclisation of selenoenynes **1113a–o**.



Scheme 207 Synthesis of 3-substituted selenophenes **1115a**, **1116**, and **1119** through (a) electrophilic cyclisation or (b) carbocyclisation of selenoenynes.

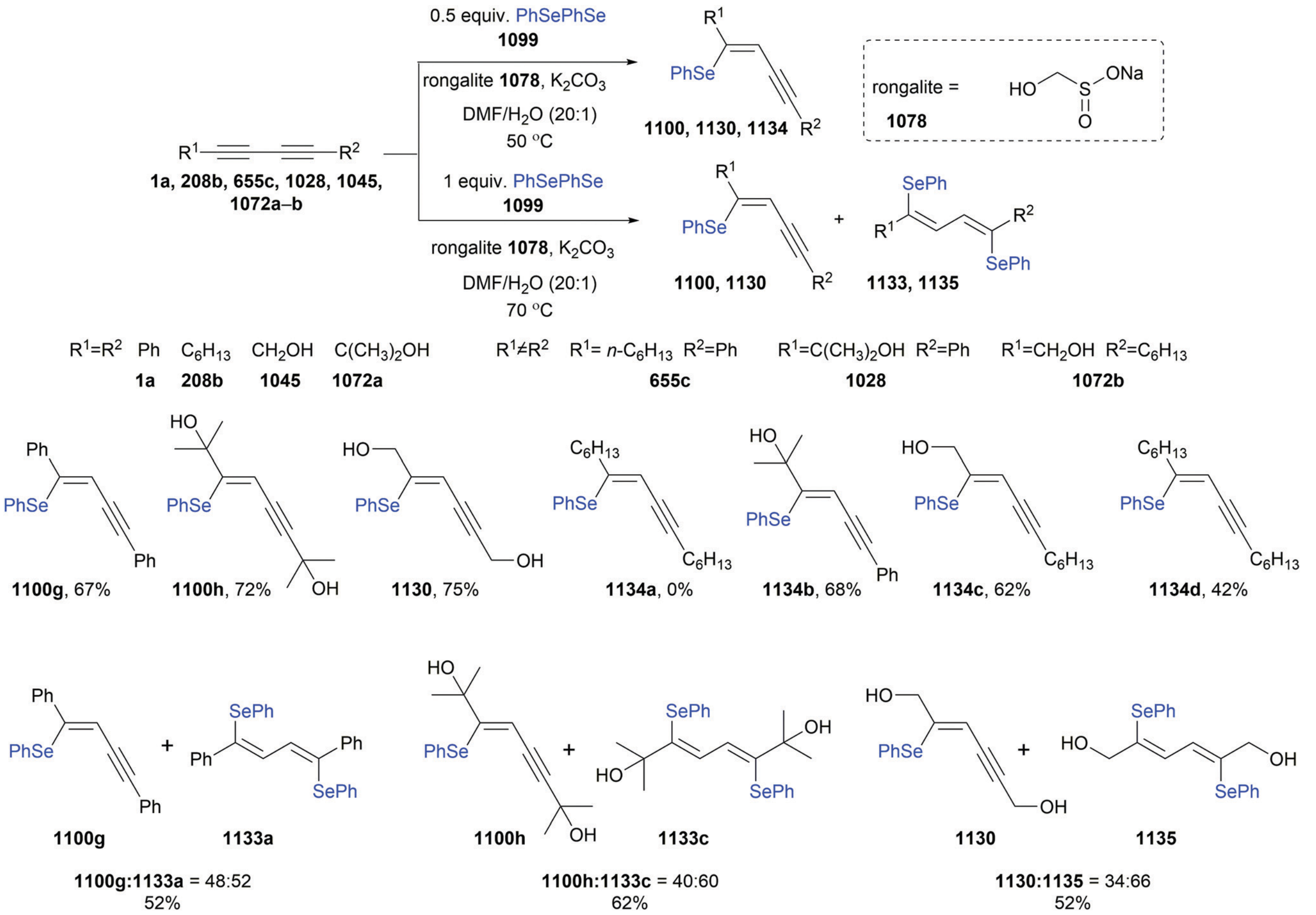


Scheme 208 Selected examples for the synthesis of porphomethenes **1128** and porphodimethenes **1127**.

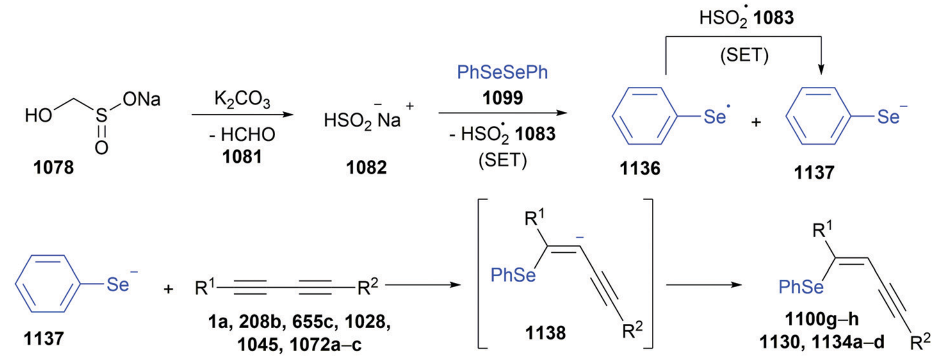


Scheme 209 Hydroselenation of symmetrical substituted 1,3-diynes **1a**, **1045**, **1072a** in (a) DES and (b) PEG 400.

conditions leading exclusively to (*Z*)-isomers **1100g–h, 1130** and **1134a–d.** It is worth noting that the discussed procedure was suitable for symmetrical and unsymmetrical 1,3-diynes, however, it failed when an aliphatic diacetylene such as hexadeca-7,9-diyne **208b** was applied. The low reactivity of **208b** in this transformation can be explained in the same manner as hydrothiolation,[442] by weak stabilisation of transition state which is dependent on steric and electronic factors. Depending on reaction conditions it was possible to obtain mono- or bis-hydroselenation products. The hydroselenation of 1,3-diynes



Scheme 210 Hydroselenation of symmetrical and unsymmetrical substituted 1,3-diynes **1a**, **208b**, **655c**, **1028**, **1045**, **1072a–b** with diphenyl diselenide **1099** in a presence of rongalite **1078** as a reducing agent.



Scheme 211 Mechanism for the hydroselenation of diynes in the presence of rongalite **1078**.

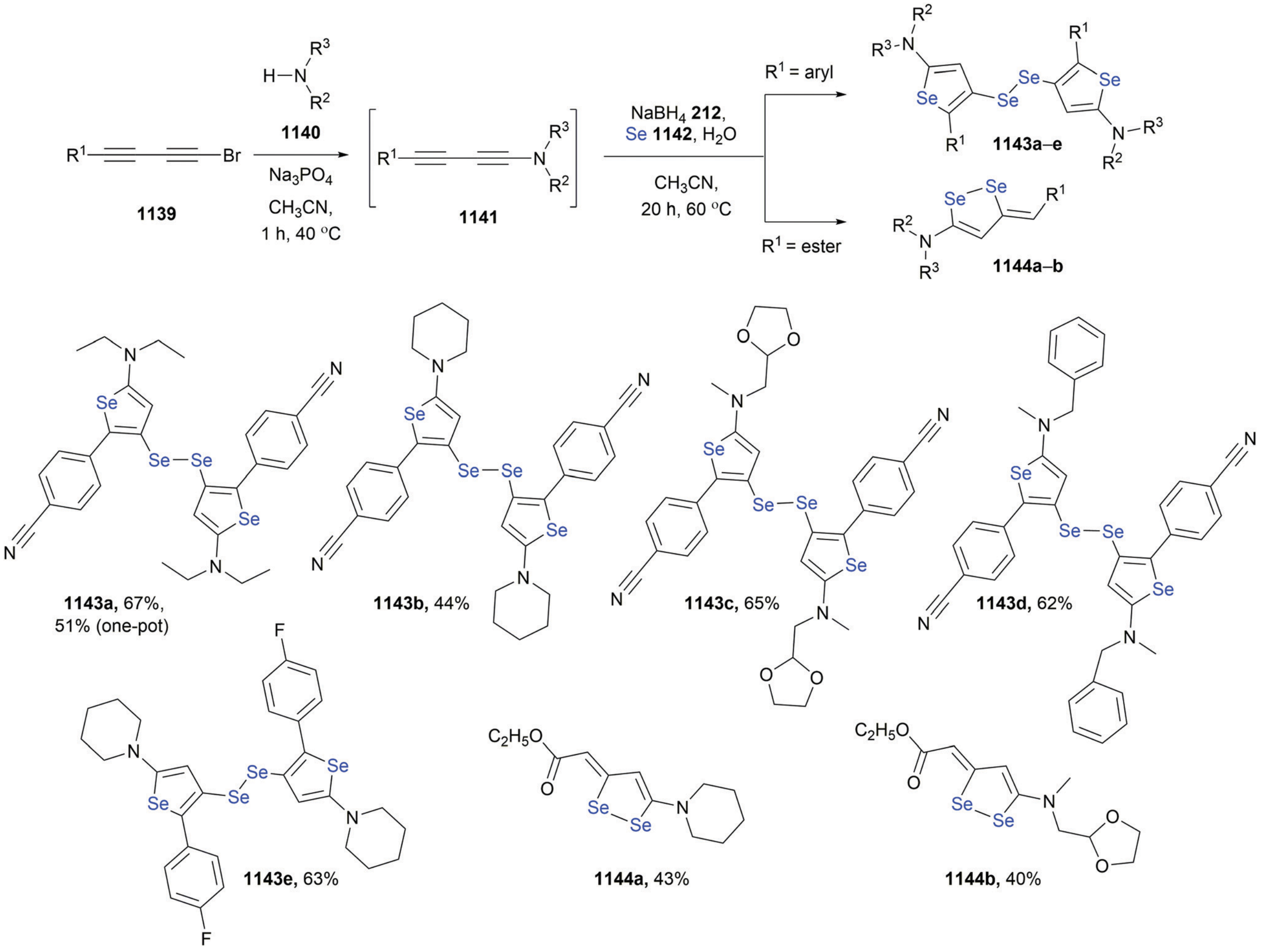
performed at a lower temperature (50 °C) and with 0.5 eq. of Ph_2Se_2 **1099** furnished (*Z*)-1-(organoselanyl)enynes **1100g–h, 1130** and **1134a–d,** whereas application of 1.0 equiv. of Ph_2Se_2 **1099** and a higher temperature (70 °C) yielded a mixture of mono- and bishydroselenation products (Scheme 210). The presented protocol is also adequate for sulfanyl derivatives (Scheme 199).[443] The mechanistic studies for the reaction were performed based on hydrothiolation of diynes (Scheme 200), however, it also can be extended to hydroselenation.[444] It involves the reduction of Ph_2Se_2 **1099** with the generation of the $PhSe^-$ anion **1137** followed by hydroselenation of the 1,3-diyne. In the initial step, the rongalite **1078** is decomposed in the presence of K_2CO_3 to formaldehyde **1081** and $HSO_2^-Na^+$ **1082.** Single electron transfer (SET) gives anion **1137** and radical **1136.** Another SET reduces **1136** to **1137**. The *trans*-addition of the benzeneselenolate anion **1137** to the 1,3-diyne gives intermediate **1138** which is protonated to yields (*Z*)-1-(organoselanyl)enynes **1100g–h, 1130** and **1134a–d** (Scheme 211).[443]

The hydroselenation of 1,3-diynes was utilised by Męcik *et al.* for the synthesis of di(selenophen-3-yl)diselenides **1143a–e** and 3-methylene-3*H*-1,2-diselenoles **1144a–b**. These uncommon selenium heterocycles were only formed when 1-amino-4-aryl-buta-1,3-diynes or 1-amino-4-ester-buta-1,3-diynes **1141** (synthesised from 1-bromobutadiynes **1139** and secondary amine **1140**) were used. The reaction of 1-aminobutadiynes **1141** with generated *in situ* sodium selenide led to desired products **1143a–e** and **1144a–b**, instead of excepted selenophenes, in moderate to high yields.

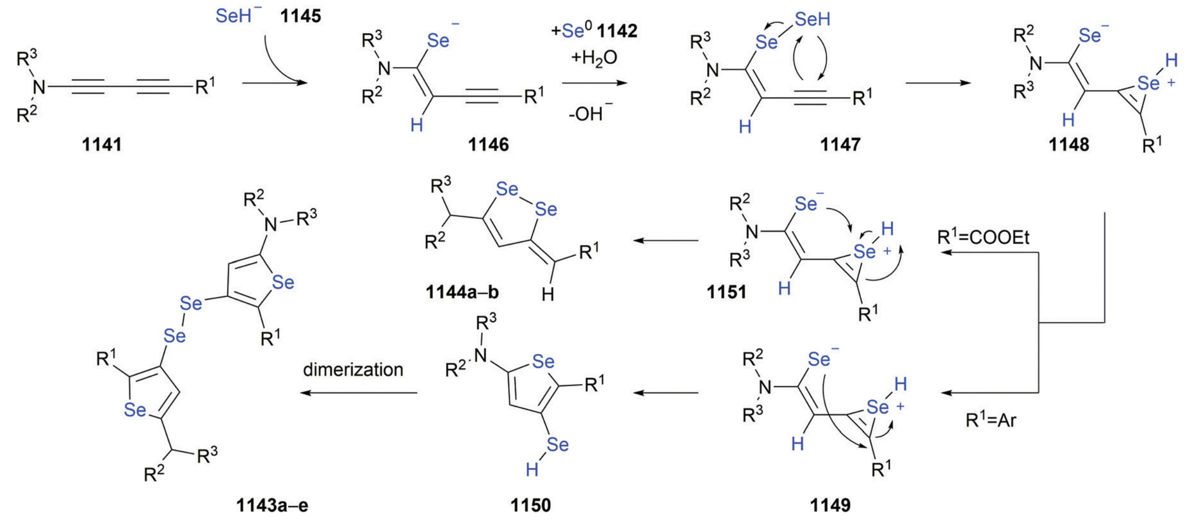
Simple diaryl or dialkyl-1,3-butadiynes led to classical selenophenes or did not react at all thus, the presence of amine group in diyne structure was crucial for the synthesis of di(selenophen-3-yl)diselenides **1143a–e** and 3-methylene-3*H*-1,2-diselenoles **1144a–b.** It is worth noting that this protocol could be also adopted in a one-step strategy without the isolation of 1-aminobutadiynes **1141**, by the addition of sodium selenide solution to the reaction mixture directly after the amination step (Scheme 212). The authors proposed the mechanism of this transformation, which started from the hydroselenation of 1,3-butadiyne by the nucleophilic attack of generated *in situ* SeH^- anion **1145** to $C\equiv C$ bond. Subsequently, the bisselenide **1147** is formed and transformed to selenirenium ion **1148**, which undergos nucleophilic attack to a carbon atom (for aryl-substituted diynes) **1149** and its dimerisation with the generation of di(selenophen-3-yl)diselenides **1143a–e**. For ester-substituted diynes occurs an internal nucleophilic attack of Se^- to Se^+ **1151** and further rearrangement to 3-methylene-3*H*-1,2-diselenoles **1144a–b** (Scheme 213).[445]

13. Hydrotelluration of 1,3-diynes

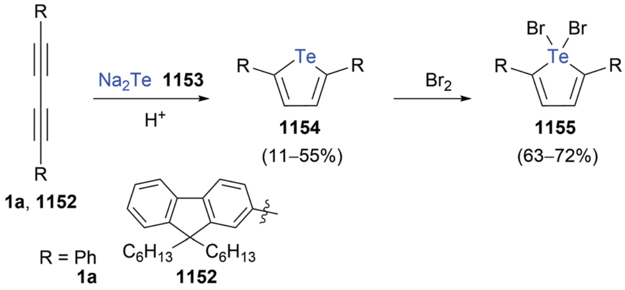
Unsaturated organotellurium compounds, especially vinylic tellurides have found numerous applications in organic synthesis due to their high reactivity, tolerance towards many functional groups and the possibility for carbon–carbon bond formation. This has been covered in previous reviews.[431,433,434,446–448] This versatile class of tellurium compounds is also an important intermediate in the synthesis of tellurophenes which have applications in material chemistry[430,447,449–455] and biological chemistry.[433,456] Among many synthetic strategies towards unsaturated organotellurium compounds, the hydrotelluration



Scheme 212 Synthesis of di(selenophen-3-yl)diselenides **1143** and diselenoles **1144** from 1-bromobutadiynes **1139**.



Scheme 213 The mechanism for the hydroselenation of 1-aminodiynes **1141**.

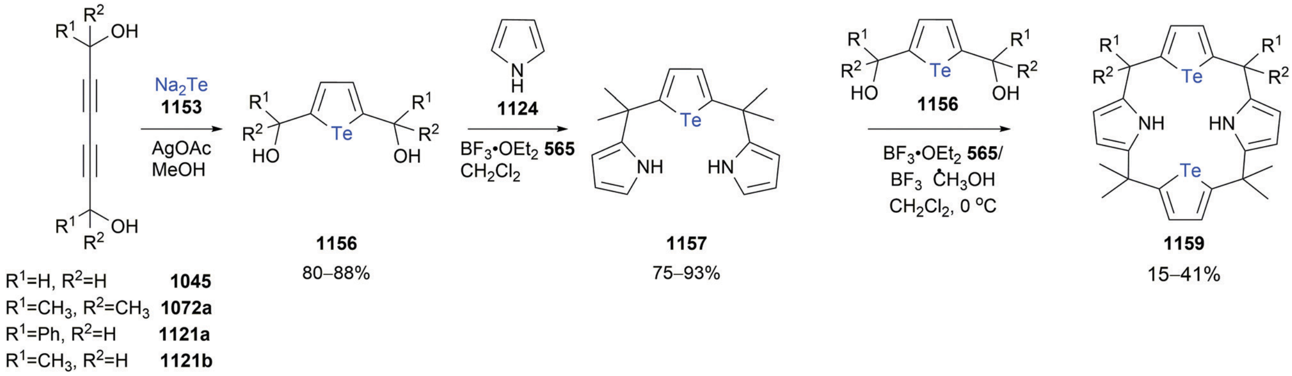


Scheme 214 Synthesis of π-conjugated 2,5-substituted tellurophene compounds **1154** and **1155**.

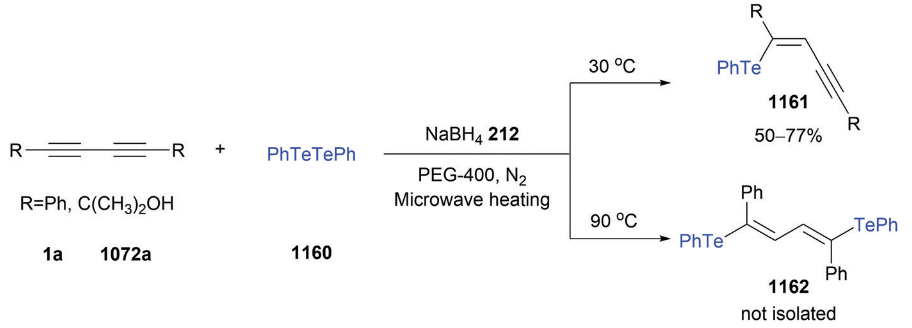
of diynes is a highly efficient and stereoselective method for enynyl tellurides which are useful building blocks in modern chemistry. Since the first synthesis of tellurophene by the interaction of 1,3-butadiyne **1a** and **1152** with Na_2Te **1153** in methanol developed by Mack's in 1966,[457] the several papers describing hydrotelluration of diynes appeared[458–468] which was also covered by Detty[431] and Zeni.[446,469] In this chapter the recent development of functionalisation of diynes by tellurium compounds will be presented.

Seferos *et al.* reported π-conjugated 2,5-substituted tellurophene **1154** compounds which were synthesised *via* ring-closing reactions of 1,4-substituted butadiynes **1a** and **1152** in the presence of Na_2Te **1153** and a protic solvent (Scheme 214). This synthetic procedure avoids harsh reaction conditions and degradation of the tellurophene ring. The oxidation of tellurophene **1154** through Br_2 addition to **1155** changed the measured optical absorption spectrum and oxidation potential which was confirmed by absorption spectroscopy and DFT calculations. The authors suggested that this class of compounds might have potential applications as semiconducting materials or as transition metal-free catalysts for energy storage reactions.[453,470,471]

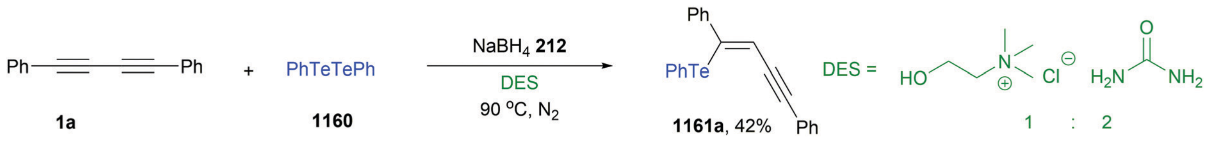
A similar approach was applied by Chauhan *et al.* who synthesised a series of calixpyrroles and calixphyrins by the interaction of diynediols **1045**, **1072a**, **1121a–b**, and AgOAc in MeOH with an aqueous solution of Na_2Te **1153**. Subsequent 3 + 1 condensation of telluratdipyrranes **1157** or telluratripyrranes **1158** with corresponding tellurophene-2,5-diols **1156** in the presence of BF_3–etherate **565** gave desired products (Scheme 215). The obtained compounds had a binding affinity with Hg^{2+} cations which was confirmed by spectroscopy studies. A described



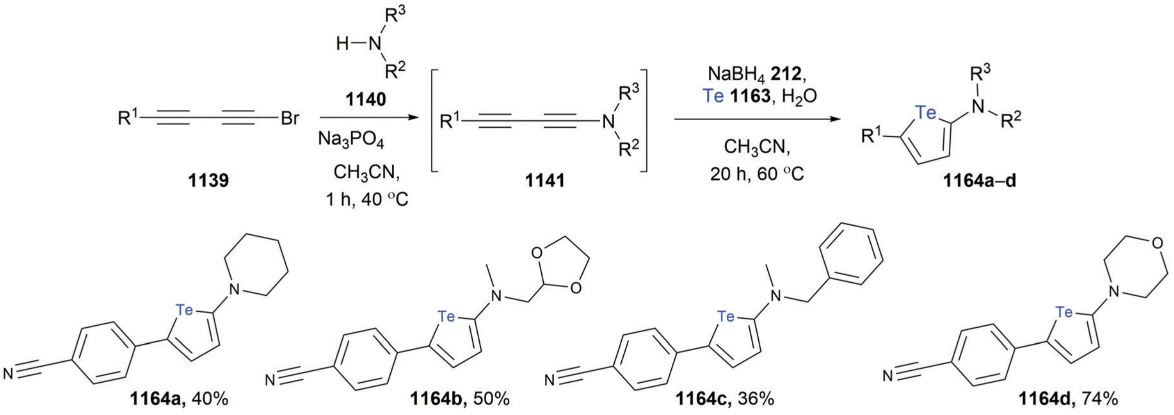
Scheme 215 Synthesis of core-modified porphyrinogens **1159**.



Scheme 216 Hydrotelluration of 1,3-diynes **1a** and **1072a** in PEG-400.



Scheme 217 Hydrotelluration of 1,4-diphenylbuta-1,3-diyne **1a** in DES.



Scheme 218 Synthesis of tellurophenes **1164** from 1-bromobutadiynes **1139** in the one-pot strategy.

synthetic protocol could also be applied for selenophenoediols (see Section 11.2).[439,440]

Application of environmentally-friendly poly(ethylene glycol, M_w = 400) in the selective synthesis of (*Z*)-telluroenynes **1161** and (*Z*,*Z*)-1,4-bis-tellurobuta-1,3-dienes **1162** in the reaction of symmetrical diynes with diphenyl telluride **1160** and $NaBH_4$ **212** as a reducing agent was reported by Perin *et al.* The process was found to be temperature-dependent. When the reaction was carried out at 30 °C, the (*Z*)-telluroenynes **1162** were obtained with excellent selectivity while higher temperatures (90 °C) led to (*Z*,*Z*)-1,4-bis-tellurobuta-1,3-diene **1162** (Scheme 216). The use of microwave radiation as an alternative heating source furnished desired products in a few minutes instead of several hours. The protocol is also suitable for selenium and sulfur derivatives.[419]

Deep eutectic solvents (DES) composed with the choline chloride (ChCl) and urea mixture (1 : 2) could be applied as another green solvent in the synthesis of organoseleno alkenes and mono-chalcogenated (*Z*)-alkenynes. The hydrotelluration of **1a** with diphenyl telluride **1160** in the presence of $NaBH_4$ **212** led to the (*Z*)-1-phenyltelluro-1,4-diphenyl-but-1-en-3-yne **1161a** with excellent regio- and stereoselectivity and moderate isolated yield (42%) (Scheme 217).[441]

Męcik *et al.* reported the synthesis of tellurophenes **1164a–d** by the reaction of 1-aminobutadiynes **1141** with sodium telluride **1153** which was generated *in situ* from Te **1163** and $NaBH_4$ **212**. The 1-aminobutadiynes **1141** were prepared from 1-bromobutadiynes **1139** and used without purification step leading to 2-aminotellurophenes **1164a–d** in good yields. Intriguingly, the application of sodium selenide **1122** gave di(selenophen-3-yl)-diselenides **1143** and methylene-3*H*-1,2-diselenoles **1144** instead of simple selenophenes (Scheme 212). The authors suggested that it might be caused by the lower stability of Te–Te bond compared with the Se–Se bond (Scheme 218).[445]

14. Conclusions and outlook

Conjugated and separated diynes constitute a special class of compounds, which due to their structural and electronic versatility that can be tuned by the presence of various functional groups attached to the $C\equiv C$ bonds, as well as by the spacer between both $C\equiv C$ bonds, create a "chemical mine" for developing fine organometallic and organic chemicals. The combination of these compounds with hydroelementation reagents, chosen from main group elements, permits an incredibly diverse array of products (enynes, dienes, allenes, cyclic compounds, heterocycles, polymers) to be obtained. Due to the presence of the unsaturated C–C bonds, as well as main group elements in their structures, these are extremely useful building blocks in the synthesis of tailor-made materials, pharmaceuticals, natural compounds analogs, and structurally advanced organic molecules. The review presents the library of the reactions, reagents, products, and catalysts for the hydroelementation of conjugated and separated diynes and can be used as a guidebook for planning the synthesis of advanced compounds *via* hydroelementation processes. The problems with the selective activation of the one or two $C\equiv C$ bonds, possible overreduction, and the stereo- and regioselectivity of hydroelementation processes are the biggest challenges that need to be overcome during the reduction of diynes. This can be achieved by the proper choice of reagents (steric and electronic properties have a significant influence on the process selectivity) catalyst, and reaction conditions. The number of examples that produce only one product and one isomer is however limited. Therefore, there is still a lot of scope for developing catalytic systems that might be highly selective, active, and stable as well as being straightforward from a synthetic perspective. Bearing in mind that the hydroelementation reaction is a 100% atom economic process, searching for highly effective and selective methods, which might be applied using an equimolar ratio of reagents is of prior importance. The products obtained in the hydroelementation reactions of conjugated and separated diynes can be used as important synthons in organic synthesis. Several demetallation, coupling, and addition reactions were presented in this review to demonstrate the power of the products obtained in the hydrometallation of diynes. In the future, improvements in the catalyst effectiveness and availability, selectivity, and productivity need to be undertaken to make the hydroelementation process straightforward for the formation of different products. Control of the process regio- and stereoselectivity is the biggest task for all chemists, which are focused on the synthesis of fine chemicals.

Abbreviations

acac	Acetylacetone
ACCN	((1,1-Azobis(cyclohexane-1-carbonitrile)))
BINAP	2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene
bmin	1-Butyl-3-methylimidazolium
Bn	Benzyl
BPPM	4-(Diphenylphosphino)-2-[di(phenylphosphino)methyl]pyrrolidine
CAAC	Cyclic(alkyl)(amino)carbene
CAN	Ammonium cerium(IV) nitrate
Cbz	Benzyloxycarbonyl
cod	1,5-Cyclooctadiene
m-CPBA	3-Chlorobenzene-1-carboperoxoic acid
Cy	Cyclohexyl
t-BuPNP	2,6-Bis(di(*tert*-butyl)phosphinomethyl)pyridine
dba	Dibenzylideneacetone
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCC	Dicyclohexylcarbodiimide
DDSQ	Double-decker-shaped silsesquioxane
DDQ	2,3-Dichloro-5,6-dicyanobenzoquinone
DES	Deep eutectic solvent
DIBAH	Di(iso-butyl)aluminum hydride
Dipp	2,6-Di(iso-propyl)phenyl
DMAP	4-(Dimethylamino)pyridine
dmpm	5,5-Dimethyldipyrrolylmethane
dpma	*N*,*N*-Di(pyrrolyl-alpha-methyl)-*N*-methylamine
DP	Polymerisation degree
dppb	1,4-Bis(diphenylphosphino)butane
dppben	1,2-Bis(diphenylphosphino)benzene
dppe	Ethylenebis(diphenylphosphine)
dppf	1,1′-Ferrocenediyl-bis(diphenylphosphine)
dppp	1,3-Bis(diphenylphosphino)propane
dvs	1,1,3,3-Tetramethyl-1,3-divinyldisiloxane
DIEA	*N*,*N*-Di-iso-propylethylamine
DIOP	2,3-*O*-Iso-propylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
F-TEDA	1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)
hfa	Hexafluoroacetone
hmpa	Hexamethylphosphoramide
IL	Ionic liquid
^{l}Ipc$_2$BH	Di-iso-pinocampheylborane
IPr*OMe	1,3-Bisimidazol-2-ylidene
LDA	Lithium diisopropylamide
MBPH	4,4′-Methylenebis[2,6-bis(hydroxymentyl)]phenol
Ms	Methanesulfonyl
MS	Molecular sieves
M_w	Molecular weight
MW	Microwave radiation
NCS	*N*-Chlorosuccinimide
NHC	N-Heterocyclic carbene
NIS	*N*-Iodosuccinimide
NMDPP	Neomenthyldiphenylphosphine
Norphos	2,3-Bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene
NTf$_2$	Bis(trifluoromethane)sulfonimide
OTf	Trifluoromethanesulfonate
PEG	Poly(ethylene glycol)

pin	Pinacol
PINBOP	2-Iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolan
pivOH	Pivalic acid
PNP	1,3-Bis(di-*tert*-butyl-phosphinomethyl)pyridine
POP-BZ	1-Benzyl-3,4-bis((diphenylphosphaneyl)oxy)pyrrolidine
PPM	4-(Diphenylphosphaneyl)-2-((diphenylphosphaneyl)methyl)pyrrolidine
PTMA	(5-Propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-2(methylphenyl)acetonitrile
pv	Pivaldehyde
PyrPhos	3,4-Bis-diphenylphosphino-pyrrolidine
QUINAP	1-(2-Diphenylphosphino-1-naphthyl)isoquinoline
scCO$_2$	Supercritical CO$_2$
SET	Single electron transfer
TBAF	Tetrabutylammonium fluoride
TBHN	Di-*tert*-butyl hyponitrite
TBDMS	*Tert*-butyldimethylsilyl
TC	Thiophene 2-carboxylate
TDT	*Tert*-dodecanethiol
THP	Tetrahydropyranyl
TIPS	Tri(iso-propyl)silyl
TMEDA	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
TMS	Trimethylsilyl
Tos	Toluenesulfonyl
TP	Tris(1-pyrazolyl)borate
p-TSA	*para*-Toluenesulfonic acid
xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We are grateful for the financial support of the National Science Centre (Poland) grants no. UMO-2018/31/G/ST4/04012, UMO-2019/34/E/ST4/00068 and UMO-2019/32/C/ST4/00235, as well as the EPSRC grant no. EP/R026912/1.

References

1 X. Wang, Y. Wang, W. Huang, C. Xia and L. Wu, *ACS Catal.*, 2021, **11**, 1–18.
2 M. Wang and Z. Shi, *Chem. Rev.*, 2020, **120**, 7348–7398.
3 G. J. P. Perry, T. Jia and D. J. Procter, *ACS Catal.*, 2020, **10**, 1485–1499.
4 L. Mao and S. K. Bose, *Adv. Synth. Catal.*, 2020, **362**, 4174–4188.
5 A. D. Bage, K. Nicholson, T. A. Hunt, T. Langer and S. P. Thomas, *ACS Catal.*, 2020, **10**, 13479–13486.
6 W. Fan, L. Li and G. Zhang, *J. Org. Chem.*, 2019, **84**, 5987–5996.
7 Z. Zuo, H. Wen, G. Liu and Z. Huang, *Synlett*, 2018, 1421–1429.
8 J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15–34.
9 A. Maity and T. S. Teets, *Chem. Rev.*, 2016, **116**, 8873–8911.
10 M. D. Greenhalgh, A. S. Jones and S. P. Thomas, *ChemCatChem*, 2015, **7**, 190–222.
11 L. Zhang and Z. Huang, *Synlett*, 2013, 1745–1747.
12 M. Zaidlewicz, in *Encyclopedia of Chemical Technology*, ed. Kirk-Othmer, John Wiley & Sons, Inc., New York, 5th edn, 2005, vol. 13, pp. 631–684.
13 W. Meng, X. Feng and H. Du, *Acc. Chem. Res.*, 2018, **51**, 191–201.
14 B. Marciniec, H. Maciejewski, C. Pietraszuk and P. Pawluc, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils, W. Herrmann, M. Beller and R. Paciello, Wiley-VCH Verlag GmbH & Co. KGaA, 2018, vol. 2, pp. 569–620.
15 J. Chen and Z. Lu, *Org. Chem. Front.*, 2018, **5**, 260–272.
16 C. Chatgilialoglu, C. Ferreri, Y. Landais and V. I. Timokhin, *Chem. Rev.*, 2018, **118**, 6516–6572.
17 B. Marciniec, *Hydrosilylation: A Comprehensive Reviews on Recent Advances*, Springer, 2010.
18 K. J. Hale, S. Manaviazar and H. A. Watson, *Chem. Rec.*, 2019, **19**, 238–319.
19 A. Trowbridge, S. M. Walton and M. J. Gaunt, *Chem. Rev.*, 2020, **120**, 2613–2692.
20 R. Y. Liu and S. L. Buchwald, *Acc. Chem. Res.*, 2020, **53**, 1229–1243.
21 P. Colonna, S. Bezzenine, R. Gil and J. Hannedouche, *Adv. Synth. Catal.*, 2020, **362**, 1550–1563.
22 M. Patel, R. K. Saunthwal and A. K. Verma, *Acc. Chem. Res.*, 2017, **50**, 240–254.
23 K. Lauder, A. Toscani, N. Scalacci and D. Castagnolo, *Chem. Rev.*, 2017, **117**, 14091–14200.
24 A. A. Trifonov, I. V. Basalov and A. A. Kissel, *Dalton Trans.*, 2016, **45**, 19172–19193.
25 M. T. Pirnot, Y.-M. Wang and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2016, **55**, 48–57.
26 L. Huang, M. Arndt, K. Goossen, H. Heydt and L. J. Goossen, *Chem. Rev.*, 2015, **115**, 2596–2697.
27 A. L. Reznichenko, A. J. Nawara-Hultzsch and K. C. Hultzsch, *Top. Curr. Chem.*, 2014, **343**, 191–260.
28 K. G. Nelson and C. H. Larsen, *Synlett*, 2014, 2681–2685.
29 K. D. Hesp and M. Stradiotto, *ChemCatChem*, 2010, **2**, 1192–1207.
30 D. Wei and C. Darcel, *J. Org. Chem.*, 2020, **85**, 14298–14306.
31 R. Castarlenas, A. Di Giuseppe, J. J. Perez-Torrente and L. A. Oro, *Angew. Chem., Int. Ed.*, 2013, **52**, 211–222.
32 C. C. Chong and R. Kinjo, *ACS Catal.*, 2015, **5**, 3238–3259.
33 K. Kucinski and G. Hreczycho, *Green Chem.*, 2020, **22**, 5210–5224.
34 N. S. Shaikh, *ChemistrySelect*, 2019, **4**, 6753–6777.
35 J. R. Hummel, J. A. Boerth and J. A. Ellman, *Chem. Rev.*, 2017, **117**, 9163–9227.

36 O. Riant, in *Modern Reduction Methods*, ed. P. G. Andersson and I. J. Munslow, Wiley-VCH Verlag GmbH & Co. KGaA, 2008, pp. 321–337.

37 D. Hayrapetyan and A. Y. Khalimon, *Chem. – Asian J.*, 2020, **15**, 2575–2587.

38 S. Chakraborty, P. Bhattacharya, H. Dai and H. Guan, *Acc. Chem. Res.*, 2015, **48**, 1995–2003.

39 M. Zaidlewicz and M. M. Pakulski, in *Science of Synthesis, Stereoselective Synthesis*, ed. G. A. Molander, Georg Thieme Verlag, 2011, vol. 2, pp. 59–131.

40 V. M. Uvarov and D. A. de Vekki, *J. Organomet. Chem.*, 2020, **923**, 121415.

41 D. Wei and C. Darcel, *Chem. Rev.*, 2019, **119**, 2550–2610.

42 H. Wang and S. L. Buchwald, *Org. React.*, 2019, **100**, 121–194.

43 R. Shi, Z. Zhang and X. Hu, *Acc. Chem. Res.*, 2019, **52**, 1471–1483.

44 A. Raya-Baron, P. Ona-Burgos and I. Fernandez, *ACS Catal.*, 2019, **9**, 5400–5417.

45 M. Zaranek and P. Pawluc, *ACS Catal.*, 2018, **8**, 9865–9876.

46 K. Riener, M. P. Hoegerl, P. Gigler and F. E. Kuehn, *ACS Catal.*, 2012, **2**, 613–621.

47 R. H. Morris, *Chem. Soc. Rev.*, 2009, **38**, 2282–2291.

48 Z. Cheng, J. Guo and Z. Lu, *Chem. Commun.*, 2020, **56**, 2229–2239.

49 W. Gao and S. Ding, *Synthesis*, 2020, 3549–3563.

50 A. Fuerstner, *J. Am. Chem. Soc.*, 2019, **141**, 11–24.

51 J. Sun and L. Deng, *ACS Catal.*, 2016, **6**, 290–300.

52 J. Peng, Y. Bai, J. Li and G. Lai, *Curr. Org. Chem.*, 2011, **15**, 2802–2815.

53 T. G. Frihed and A. Fuerstner, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 135–160.

54 M. Alami, A. Hamze and O. Provot, *ACS Catal.*, 2019, **9**, 3437–3466.

55 L. T. Leung and P. Chiu, *Pure Appl. Chem.*, 2006, **78**, 281–285.

56 B. M. Trost and Z. T. Ball, *Synthesis*, 2005, 853–887.

57 N. Asao and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1071–1087.

58 Z. Tashrifi, M. Mohammadi Khanaposhtani, M. Biglar, B. Larijani and M. Mahdavi, *Asian J. Org. Chem.*, 2020, **9**, 969–991.

59 L. Rosenberg, *ACS Catal.*, 2013, **3**, 2845–2855.

60 A. Dondoni and A. Marra, *Eur. J. Org. Chem.*, 2014, 3955–3969.

61 Z. T. Ball, in *Comprehensive Organometallic Chemistry*, ed. D. M. P. Mingos and R. H. Crabtree, Elsevier Ltd, 3rd edn, 2007, vol. 10, pp. 789–813.

62 R. J. Perry, M. Karageorgis and J. Hensler, *Macromolecules*, 2007, **40**, 3929–3938.

63 X. Mo, A. Letort, D.-A. Rosca, K. Higashida and A. Fürstner, *Chem. – Eur. J.*, 2018, **24**, 9667–9674.

64 V. B. R. Iska, V. Verdolino, O. Wiest and P. Helquist, *J. Org. Chem.*, 2010, **75**, 1325–1328.

65 M. Handa, K. A. Scheidt, M. Bossart, N. Zheng and W. R. Roush, *J. Org. Chem.*, 2008, **73**, 1031–1035.

66 I. Ojima, A. T. Vu, J. V. McCullagh and A. Kinoshita, *J. Am. Chem. Soc.*, 1999, **121**, 3230–3231.

67 B. Bennacer, M. Fujiwara, S.-Y. Lee and I. Ojima, *J. Am. Chem. Soc.*, 2005, **127**, 17756–17767.

68 J. C. Sanchez and W. C. Trogler, *Macromol. Chem. Phys.*, 2008, **209**, 1527–1540.

69 C. Raviola, S. Protti, D. Ravelli and M. Fagnoni, *Chem. Soc. Rev.*, 2016, **45**, 4364–4390.

70 J. Xuan and A. Studer, *Chem. Soc. Rev.*, 2017, **46**, 4329–4346.

71 A. M. Asiri and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2016, **45**, 4471–4503.

72 T. Sokolnicki, J. Szyling, A. Franczyk and J. Walkowiak, *Adv. Synth. Catal.*, 2020, **362**, 177–183.

73 J. Walkowiak, K. Salamon, A. Franczyk, K. Stefanowska, J. Szyling and I. Kownacki, *J. Org. Chem.*, 2019, **84**, 2358–2365.

74 K. Stefanowska, A. Franczyk, J. Szyling and J. Walkowiak, *ChemCatChem*, 2019, **11**, 4848–4853.

75 J. Szyling, A. Franczyk, K. Stefanowska, H. Maciejewski and J. Walkowiak, *ACS Sustainable Chem. Eng.*, 2018, **6**, 10980–10988.

76 J. Szyling, A. Franczyk, K. Stefanowska and J. Walkowiak, *Adv. Synth. Catal.*, 2018, **360**, 2966–2974.

77 K. Stefanowska, A. Franczyk, J. Szyling, M. Pyziak, P. Pawluc and J. Walkowiak, *Chem. – Asian J.*, 2018, **13**, 2101–2108.

78 K. Stefanowska, A. Franczyk, J. Szyling, K. Salamon, B. Marciniec and J. Walkowiak, *J. Catal.*, 2017, **356**, 206–213.

79 J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chemistry*, 2017, **23**, 10997–11000.

80 J. L. Carden, L. J. Gierlichs, D. F. Wass, D. L. Browne and R. L. Melen, *Chem. Commun.*, 2019, **55**, 318–321.

81 D. M. C. Ould, T. T. P. Tran, J. M. Rawson and R. L. Melen, *Dalton Trans.*, 2019, **48**, 16922–16935.

82 Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381–2384.

83 L. C. Wilkins, J. L. Howard, S. Burger, L. Frentzel-Beyme, D. L. Browne and R. L. Melen, *Adv. Synth. Catal.*, 2017, **359**, 2580–2584.

84 J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. – Eur. J.*, 2017, **23**, 10997–11000.

85 D. M. C. Ould and R. L. Melen, *Chem. – Eur. J.*, 2018, **24**, 15201–15204.

86 D. Willcox, J. L. Carden, A. J. Ruddy, P. D. Newman and R. L. Melen, *Dalton Trans.*, 2020, **49**, 2417–2420.

87 D. M. C. Ould, J. L. Carden, R. Page and R. L. Melen, *Inorg. Chem.*, 2020, **59**, 14891–14898.

88 F. Sato, *J. Organomet. Chem.*, 1985, **285**, 53–64.

89 F. Sato, H. Watanabe, Y. Tanaka, T. Yamaji and M. Sato, *Tetrahedron Lett.*, 1983, **24**, 1041–1044.

90 Y. Gao and F. Sato, *J. Chem. Soc., Chem. Commun.*, 1995, 659–660.

91 U. M. Dzhemilev, O. S. Vostrikova, R. M. Sultanov and A. R. Gimaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2156–2159.

92 U. M. Dzhemilev, A. G. Ibragimov, R. A. Saraev and P. P. Muslukhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2385–2389.

93 P. J. Kocienski, C. J. Love, R. J. Whitby, G. Costello and D. A. Roberts, *Tetrahedron*, 1989, **45**, 3839–3848.

94 B. B. Snider, M. Karras and R. S. E. Conn, *J. Am. Chem. Soc.*, 1978, **100**, 4624–4626.

95 R. Santhoshkumar, Y.-C. Hong, C.-Z. Luo, Y.-C. Wu, C.-H. Hung, K.-Y. Hwang, A.-P. Tu and C.-H. Cheng, *ChemCatChem*, 2016, **8**, 2210–2213.

96 L. Ilies, T. Yoshida and E. Nakamura, *J. Am. Chem. Soc.*, 2012, **134**, 16951–16954.

97 N. D. J. Hiller, N. A. do Amaral, E. Silva, T. A. Tavares, R. X. Faria, M. N. Eberlin and D. de Luna Martins, *Eur. J. Org. Chem.*, 2020, 4841–4877.

98 X. Yang, S. J. Kalita, S. Maheshuni and Y.-Y. Huang, *Coord. Chem. Rev.*, 2019, **392**, 35–48.

99 A. Stubelius, S. Lee and A. Almutairi, *Acc. Chem. Res.*, 2019, **52**, 3108–3119.

100 J. P. G. Rygus and C. M. Crudden, *J. Am. Chem. Soc.*, 2017, **139**, 18124–18137.

101 J. Pyziak, J. Walkowiak and B. Marciniec, *Chem. – Eur. J.*, 2017, **23**, 3502–3541.

102 J. W. B. Fyfe and A. J. B. Watson, *Chem*, 2017, **3**, 31–55.

103 L. Xu, S. Zhang and P. Li, *Chem. Soc. Rev.*, 2015, **44**, 8848–8858.

104 D. G. Hall, in *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, ed. D. G. Hall, Wiley-VCH Verlag GmbH & Co. KGaA, 2 edn, 2011, vol. 1, pp. 1–133.

105 C. M. Crudden, B. W. Glasspoole and C. J. Lata, *Chem. Commun.*, 2009, 6704–6716.

106 S. Darses and J.-P. Genet, *Chem. Rev.*, 2008, **108**, 288–325.

107 K. M. Korch and D. A. Watson, *Chem. Rev.*, 2019, **119**, 8192–8228.

108 E. Marques-Lopez and R. P. Herrera, in *Multicomponent Reactions: Concepts and Applications for Design and Synthesis*, ed. R. P. Herrera and E. Marqués-López, John Wiley & Sons, Inc., 2015, pp. 127–148.

109 S. Roscales and A. G. Csákÿ, *Chem. Soc. Rev.*, 2014, **43**, 8215–8225.

110 L. Xu, S. Zhang and P. Li, *Chem. Soc. Rev.*, 2015, **44**, 8848–8858.

111 H. Itoh and M. Inoue, *Chem. Rev.*, 2019, **119**, 10002–10031.

112 P. Karier, F. Ungeheuer, A. Ahlers, F. Anderl, C. Wille and A. Fürstner, *Angew. Chem., Int. Ed.*, 2019, **58**, 248–253.

113 S. Gao, J. Chen and M. Chen, *Chem. Sci.*, 2019, **10**, 3637–3642.

114 Z. Meng, L. Souillart, B. Monks, N. Huwyler, J. Herrmann, R. Müller and A. Fürstner, *J. Org. Chem.*, 2018, **83**, 6977–6994.

115 K.-Q. Ma, Y.-H. Miao, X. Li, Y.-Z. Zhou, X.-X. Gao, X. Zhang, J.-B. Chao and X.-M. Qin, *RSC Adv.*, 2017, **7**, 16005–16014.

116 S. Schaubach, K. Gebauer, F. Ungeheuer, L. Hoffmeister, M. K. Ilg, C. Wirtz and A. Fürstner, *Chem. – Eur. J.*, 2016, **22**, 8494–8507.

117 M. de Léséleuc, É. Godin, S. Parisien-Collette, A. Lévesque and S. K. Collins, *J. Org. Chem.*, 2016, **81**, 6750–6756.

118 F. Ungeheuer and A. Fürstner, *Chem. – Eur. J.*, 2015, **21**, 11387–11392.

119 S. F. Mayer, A. Steinreiber, R. V. A. Orru and K. Faber, *J. Org. Chem.*, 2002, **67**, 9115–9121.

120 P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem., Int. Ed.*, 2000, **39**, 2632–2657.

121 J. Wang, Y. Shen, S. Kessel, P. Fernandes, K. Yoshida, S. Yagai, D. G. Kurth, H. Möhwald and T. Nakanishi, *Angew. Chem., Int. Ed.*, 2009, **48**, 2166–2170.

122 J.-N. Tisserant, R. Hany, E. Wimmer, A. Sánchez-Ferrer, J. Adamcik, G. Wicht, F. Nüesch, D. Rentsch, A. Borgschulte, R. Mezzenga and J. Heier, *Macromolecules*, 2014, **47**, 721–728.

123 Q. Huang, M.-Y. Hu and S.-F. Zhu, *Org. Lett.*, 2019, **21**, 7883–7887.

124 D. X. Li, Y. E. Kim and J. Yun, *Org. Lett.*, 2015, **17**, 860–863.

125 H. L. Sang, C. Wu, G. G. D. Phua and S. Ge, *ACS Catal.*, 2019, **9**, 10109–10114.

126 G. Zweifel and N. L. Polston, *J. Am. Chem. Soc.*, 1970, **92**, 4068–4071.

127 E. C. Stracker, W. Leong, J. A. Miller, T. M. Shoup and G. Zweifel, *Tetrahedron Lett.*, 1989, **30**, 6487–6490.

128 J. Szyling, A. Franczyk, K. Stefanowska, M. Klarek, H. Maciejewski and J. Walkowiak, *ChemCatChem*, 2018, **10**, 531–539.

129 J. Szyling, J. Walkowiak, T. Sokolnicki, A. Franczyk, K. Stefanowska and M. Klarek, *J. Catal.*, 2019, **376**, 219–227.

130 G. Desurmont, S. Dalton, D. M. Giolando and M. Srebnik, *J. Org. Chem.*, 1997, **62**, 8907–8909.

131 K. Takahashi, S. J. Geib, K. Maeda, D. P. Curran and T. Taniguchi, *Org. Lett.*, 2021, **23**, 1071–1075.

132 Y. D. Wang, G. Kimball, A. S. Prashad and Y. Wang, *Tetrahedron Lett.*, 2005, **46**, 8777–8780.

133 L. Deloux and M. Srebnik, *J. Org. Chem.*, 1994, **59**, 6871–6873.

134 R. G. Iafe, D. G. Chan, J. L. Kuo, B. A. Boon, D. J. Faizi, T. Saga, J. W. Turner and C. A. Merlic, *Org. Lett.*, 2012, **14**, 4282–4285.

135 X. Ren, G. Li, S. Wei and H. Du, *Org. Lett.*, 2015, **17**, 990–993.

136 C. Gunanathan, M. Hölscher, F. Pan and W. Leitner, *J. Am. Chem. Soc.*, 2012, **134**, 14349–14352.

137 P. I. Kitov and D. R. Bundle, *Org. Lett.*, 2001, **3**, 2835–2838.

138 T. Xi and Z. Lu, *ACS Catal.*, 2017, **7**, 1181–1185.

139 S. Yu, C. Wu and S. Ge, *J. Am. Chem. Soc.*, 2017, **139**, 6526–6529.

140 N. Cabrera-Lobera, P. Rodríguez-Salamanca, J. C. Nieto-Carmona, E. Buñuel and D. J. Cárdenas, *Chem. – Eur. J.*, 2018, **24**, 784–788.

141 C. Wang and S. Ge, *J. Am. Chem. Soc.*, 2018, **140**, 10687–10690.

142 C. Wu, J. Liao and S. Ge, *Angew. Chem., Int. Ed.*, 2019, **58**, 8882–8886.

143 M. Shimoi, I. Kevlishvili, T. Watanabe, K. Maeda, S. J. Geib, D. P. Curran, P. Liu and T. Taniguchi, *Angew. Chem., Int. Ed.*, 2020, **59**, 903–909.

144 T. Watanabe, D. Hirose, D. P. Curran and T. Taniguchi, *Chem. – Eur. J.*, 2017, **23**, 5404–5409.

145 Y. Chujo, I. Tomita, Y. Hashiguchi and T. Saegusa, *Macromolecules*, 1992, **25**, 33–36.

146 Y. Chujo, Y. Sasaki, N. Kinomura and N. Matsumi, *Polymer*, 2000, **41**, 5047–5051.

147 N. Matsumi and Y. Chujo, *Spec. Publ. - R. Soc. Chem.*, 2000, **253**, 51–58.

148 N. Matsumi, M. Miyata and Y. Chujo, *Macromolecules*, 1999, **32**, 4467–4469.

149 N. Matsumi, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 1998, **120**, 5112–5113.

150 A. Nagai, T. Murakami, Y. Nagata, K. Kokado and Y. Chujo, *Macromolecules*, 2009, **42**, 7217–7220.

151 F. Matsumoto and Y. Chujo, *Pure Appl. Chem.*, 2009, **81**, 433–437.

152 J. A. Miller and G. Zweifel, *J. Am. Chem. Soc.*, 1983, **105**, 1383–1384.

153 V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics*, 2004, **23**, 4160–4165.

154 G. Zweifel, R. A. Lynd and R. E. Murray, *Synthesis*, 1977, 52–53.

155 W. Uhl and F. Breher, *J. Organomet. Chem.*, 2000, **608**, 54–59.

156 H. L. Sang, Y. Hu and S. Ge, *Org. Lett.*, 2019, **21**, 5234–5237.

157 K. Tamao, K. Kobayashi and Y. Ito, *Synlett*, 1992, 539–546.

158 J. W. Madine, X. Wang and R. A. Widenhoefer, *Org. Lett.*, 2001, **3**, 385–388.

159 X. Wang, H. Chakrapani, J. W. Madine, M. A. Keyerleber and R. A. Widenhoefer, *J. Org. Chem.*, 2002, **67**, 2778–2788.

160 C. Liu and R. A. Widenhoefer, *Organometallics*, 2002, **21**, 5666–5673.

161 K. Kanamori and K. Nakanishi, *Chem. Soc. Rev.*, 2011, **40**, 754–770.

162 B. A. Kamino and T. P. Bender, *Chem. Soc. Rev.*, 2013, **42**, 5119–5130.

163 D. Kong, B. Hu, M. Yang, D. Chen and H. Xia, *Organometallics*, 2019, **38**, 4341–4350.

164 A. Tillack, C. Koy, D. Michalik and C. Fischer, *J. Organomet. Chem.*, 2000, **603**, 116–121.

165 K. Stefanowska, J. Szyling, J. Walkowiak and A. Franczyk, *Inorg. Chem.*, 2021, **60**, 11006–11013.

166 M. Ishikawa, E. Toyoda, T. Horio and A. Kunai, *Organometallics*, 1994, **13**, 26–27.

167 F. Alonso, R. Buitrago, Y. Moglie, A. Sepulveda-Escribano and M. Yus, *Organometallics*, 2012, **31**, 2336–2342.

168 W. Guo, R. Pleixats, A. Shafir and T. Parella, *Adv. Synth. Catal.*, 2015, **357**, 89–99.

169 M. Planellas, W. Guo, F. Alonso, M. Yus, A. Shafir, R. Pleixats and T. Parella, *Adv. Synth. Catal.*, 2014, **356**, 179–188.

170 C. Bal Reddy, A. K. Shil, N. R. Guha, D. Sharma and P. Das, *Catal. Lett.*, 2014, **144**, 1530–1536.

171 A. Tillack, D. Michalik, C. Koy and M. Michalik, *Tetrahedron Lett.*, 1999, **40**, 6567–6568.

172 A. Tillack, S. Pulst, W. Baumann, H. Baudisch, K. Kortus and U. Rosenthal, *J. Organomet. Chem.*, 1997, **532**, 117–123.

173 H. Zhou, Q. Ye and J. Xu, *Mater. Chem. Front.*, 2017, **1**, 212–230.

174 K. L. Chan, P. Sonar and A. Sellinger, *J. Mater. Chem.*, 2009, **19**, 9103–9120.

175 Z. Yang, M. Gao, W. Wu, X. Yang, X. W. Sun, J. Zhang, H.-C. Wang, R.-S. Liu, C.-Y. Han, H. Yang and W. Li, *Mater. Today*, 2019, **24**, 69–93.

176 B. Dudziec, P. Żak and B. Marciniec, *Polymers*, 2019, **11**, 506–545.

177 T. Kusumoto and T. Hiyama, *Chem. Lett.*, 1985, 1405–1408.

178 T. Kusumoto, K. Ando and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1280–1290.

179 C. Wu, W. J. Teo and S. Ge, *ACS Catal.*, 2018, **8**, 5896–5900.

180 W. J. Teo, C. Wang, Y. W. Tan and S. Ge, *Angew. Chem., Int. Ed.*, 2017, **56**, 4328–4332.

181 C. Chen, T. R. Dugan, W. W. Brennessel, D. J. Weix and P. L. Holland, *J. Am. Chem. Soc.*, 2014, **136**, 945–955.

182 Z. Zuo, J. Yang and Z. Huang, *Angew. Chem., Int. Ed.*, 2016, **55**, 10839–10843.

183 J. Guo, X. Shen and Z. Lu, *Angew. Chem., Int. Ed.*, 2017, **56**, 615–618.

184 S. Zhang, J. J. Ibrahim and Y. Yang, *Org. Lett.*, 2018, **20**, 6265–6269.

185 J. Guo and Z. Lu, *Angew. Chem., Int. Ed.*, 2016, **55**, 10835–10838.

186 D. Kong, B. Hu and D. Chen, *Chem. – Asian J.*, 2019, **14**, 2694–2703.

187 D. Kong, B. Hu, M. Yang, D. Gong, H. Xia and D. Chen, *Organometallics*, 2020, **39**, 4437–4443.

188 Y. Yang, Y.-N. Jiang, Z.-Y. Lin, J.-H. Zeng, Z.-K. Liu and Z.-P. Zhan, *Org. Chem. Front.*, 2021, **8**, 4826–4832.

189 B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2005, **127**, 17644–17655.

190 T. Matsuda, S. Kadowaki and M. Murakami, *Chem. Commun.*, 2007, 2627–2629.

191 B. M. Trost, V. S. Chan and D. Yamamoto, *J. Am. Chem. Soc.*, 2010, **132**, 5186–5192.

192 P. Zak, M. Bolt and C. Pietraszuk, *Eur. J. Inorg. Chem.*, 2019, 2455–2461.

193 C. Conifer, C. Gunanathan, T. Rinesch, M. Hölscher and W. Leitner, *Eur. J. Inorg. Chem.*, 2015, 333–339.

194 S. Ciampi, P. K. Eggers, G. Le Saux, M. James, J. B. Harper and J. J. Gooding, *Langmuir*, 2009, **25**, 2530–2539.

195 S. Ciampi, T. Böcking, K. A. Kilian, M. James, J. B. Harper and J. J. Gooding, *Langmuir*, 2007, **23**, 9320–9329.

196 S. Ciampi, T. Böcking, K. A. Kilian, J. B. Harper and J. J. Gooding, *Langmuir*, 2008, **24**, 5888–5892.

197 S. A. A. Ahmad, S. Ciampi, S. G. Parker, V. R. Goncales and J. J. Gooding, *ChemElectroChem*, 2019, **6**, 211–220.

198 T. Lee, I. Jung, K. H. Song, C. Baik, S. Kim, D. Kim, S. O. Kang and J. Ko, *Organometallics*, 2004, **23**, 4184–4191.

199 S. E. Gradwell and C. L. Kepler, *Macromolecules*, 2002, **35**, 2871–2872.

200 H. K. Kim, M.-K. Ryu, K.-D. Kim, S.-M. Lee, S.-W. Cho and J.-W. Park, *Macromolecules*, 1998, **31**, 1114–1123.

201 A. Kunai, E. Toyoda, I. Nagamoto, T. Horio and M. Ishikawa, *Organometallics*, 1996, **15**, 75–83.

202 R.-M. Chen, K.-M. Chien, K.-T. Wong, B.-Y. Jin, T.-Y. Luh, J.-H. Hsu and W. Fann, *J. Am. Chem. Soc.*, 1997, **119**, 11321–11322.

203 Y.-J. Cheng, T.-Y. Hwu, J.-H. Hsu and T.-Y. Luh, *Chem. Commun.*, 2002, 1978–1979.

204 D. S. Kim and S. C. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 2933–2940.

205 D. Y. Son, D. Bucca and T. M. Keller, *Tetrahedron Lett.*, 1996, **37**, 1579–1582.

206 G. K. Rickle, *J. Appl. Polym. Sci.*, 1994, **51**, 605–612.

207 T. Kobayashi, T. Hayashi and M. Tanaka, *Chem. Lett.*, 1998, 763–764.

208 M. Seino, T. Hayakawa, Y. Ishida, M.-A. Kakimoto, K. Watanabe and H. Oikawa, *Macromolecules*, 2006, **39**, 3473–3475.

209 Y. Ishida, T. Hayakawa, M.-A. Kakimoto and Y. Kimae, *J. Photopolym. Sci. Technol.*, 2008, **21**, 155–159.

210 H. Yamashita, M. S. de Leon, S. Channasanon, Y. Suzuki, Y. Uchimaru and K. Takeuchi, *Polymer*, 2003, **44**, 7089–7093.

211 T. V. Rao, H. Yamashita, Y. Uchimaru, J.-I. Sugiyama and K. Takeuchi, *Polymer*, 2005, **46**, 9736–9741.

212 T. V. Rao, H. Yamashita, Y. Uchimaru, M. Asai and K. Takeuchi, *Chem. Lett.*, 2003, **32**, 580–581.

213 A. Mori, E. Takahisa, Y. Yamamura, T. Kato, A. P. Mudalige, H. Kajiro, K. Hirabayashi, Y. Nishihara and T. Hiyama, *Organometallics*, 2004, **23**, 1755–1765.

214 A. Mori, E. Takahisa, H. Kajiro, Y. Nishihara and T. Hiyama, *Macromolecules*, 2000, **33**, 1115–1116.

215 K.-i. Sumiya, G. Kwak, F. Sanda and T. Masuda, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 2774–2783.

216 G. Kwak and T. Masuda, *Macromol. Rapid Commun.*, 2002, **23**, 68–72.

217 H.-J. Son, W.-S. Han, H. Kim, C. Kim, J. Ko, C. Lee and S. O. Kang, *Organometallics*, 2006, **25**, 766–774.

218 J. C. Sanchez, S. A. Urbas, S. J. Toal, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Macromolecules*, 2008, **41**, 1237–1245.

219 J. C. Sanchez and W. C. Trogler, *J. Mater. Chem.*, 2008, **18**, 3143–3156.

220 J. C. Sanchez, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Chem. Mater.*, 2007, **19**, 6459–6470.

221 K. Tamao, K. Kobayashi and Y. Ito, *J. Am. Chem. Soc.*, 1989, **111**, 6478–6480.

222 R. A. Widenhoefer and M. A. DeCarli, *J. Am. Chem. Soc.*, 1998, **120**, 3805–3806.

223 R. A. Widenhoefer and C. N. Stengone, *J. Org. Chem.*, 1999, **64**, 8681–8692.

224 T. Pei and R. A. Widenhoefer, *Org. Lett.*, 2000, **2**, 1469–1471.

225 N. S. Perch, T. Pei and R. A. Widenhoefer, *J. Org. Chem.*, 2000, **65**, 3836–3845.

226 T. Muraoka, I. Matsuda and K. Itoh, *Organometallics*, 2002, **21**, 3650–3660.

227 T. Muraoka, I. Matsuda and K. Itoh, *Tetrahedron Lett.*, 1998, **39**, 7325–7328.

228 I. Ojima, J. Zhu, E. S. Vidal and D. F. Kass, *J. Am. Chem. Soc.*, 1998, **120**, 6690–6697.

229 I. Ojima, D. F. Kass and J. Zhu, *Organometallics*, 1996, **15**, 5191–5195.

230 I. Ojima, D. A. Fracchiolla, R. J. Donovan and P. Banerji, *J. Org. Chem.*, 1994, **59**, 7594–7595.

231 T. Shibata, N. Nakagawa, Y. Ueno and K. Endo, *Organometallics*, 2008, **27**, 1342–1344.

232 T. Uno, S. Wakayanagi, Y. Sonoda and K. Yamamoto, *Synlett*, 2003, 1997–2000.

233 S. Wakayanagi, T. Shimamoto, M. Chimori and K. Yamamoto, *Chem. Lett.*, 2005, **34**, 160–161.

234 T. Shimamoto, T. Hirano, H. Nishimoto and K. Yamamoto, *Chem. Lett.*, 2006, **35**, 846–847.

235 N. Chatani, Y. Fukumoto, T. Ida and S. Murai, *J. Am. Chem. Soc.*, 1993, **115**, 11614–11615.

236 T. M. Sivavec and T. J. Katz, *Tetrahedron Lett.*, 1985, **26**, 2159–2162.

237 T. Sudo, N. Asao, V. Gevorgyan and Y. Yamamoto, *J. Org. Chem.*, 1999, **64**, 2494–2499.

238 T. Matsuda, S. Kadowaki, Y. Yamaguchi and M. Murakami, *Org. Lett.*, 2010, **12**, 1056–1058.

239 H. Yamashita, S. Channasanon and Y. Uchimaru, *Chem. Lett.*, 2006, **35**, 398–399.

240 B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2003, **125**, 30–31.

241 B. M. Trost, Z. T. Ball and T. Joege, *J. Am. Chem. Soc.*, 2002, **124**, 7922–7923.

242 M. M. Heravi and L. Mohammadkhani, *J. Organomet. Chem.*, 2018, **869**, 106–200.

243 P. Devendar, R.-Y. Qu, W.-M. Kang, B. He and G.-F. Yang, *J. Agric. Food Chem.*, 2018, **66**, 8914–8934.

244 A. Skhiri, R. Ben Salem, J.-F. Soule and H. Doucet, *ChemCatChem*, 2017, **9**, 2895–2913.

245 C. Cordovilla, C. Bartolome, J. M. Martinez-Ilarduya and P. Espinet, *ACS Catal.*, 2015, **5**, 3040–3053.

246 B. Carsten, F. He, H. J. Son, T. Xu and L. Yu, *Chem. Rev.*, 2011, **111**, 1493–1528.

247 S. Pascual and A. M. Echavarren, in *Tin Chemistry: Fundamentals, Frontiers, and Applications*, ed. A. G. Davies, M. Gielen, K. H. Pannell and E. R. T. Tiekink, John Wiley & Sons Ltd, 2008, pp. 579–606.

248 T. Konno, M. Kishi, T. Ishihara and S. Yamada, *Tetrahedron*, 2014, **70**, 2455–2463.

249 I. Jung, T. Lee, S. O. Kang and J. Ko, *Synthesis*, 2005, 986–992.

250 C. Rim and D. Y. Son, *Org. Lett.*, 2003, **5**, 3443–3445.

251 A. J. Ashe, *J. Org. Chem.*, 1982, 125–155.

252 A. J. Ashe III and W.-T. Chan, *J. Org. Chem.*, 1979, **44**, 1409–1413.

253 A. J. Ashe III and P. Shu, *J. Am. Chem. Soc.*, 1971, **93**, 1804–1805.

254 G. E. Herberich, E. Bauer, J. Hengesbach, U. Kölle, G. Huttner and H. Lorenz, *Chem. Ber.*, 1977, **110**, 760–772.

255 V. G. Märkl, P. Hofmeister and F. Kneidl, *Tetrahedron Lett.*, 1976, **17**, 3125–3128.

256 G. Märkl and F. Kneidl, *Angew. Chem., Int. Ed.*, 1973, **12**, 931–932.

257 H. O. Berger, H. Nöth, G. Rub and B. Wrackmeyer, *Chem. Ber.*, 1980, **113**, 1235–1244.

258 G. Märkl and D. Matthes, *Tetrahedron Lett.*, 1976, **17**, 2599–2602.

259 G. E. Herberich and B. Heßner, *Z. Naturforsch. B*, 1978, **33**, 180–182.

260 G. E. Herberich and M. Thönnessen, *J. Organomet. Chem.*, 1979, **177**, 357–363.

261 J. G. Noltes and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1962, **81**, 41–48.

262 A. J. Leusink, J. G. Noltes, H. A. Budding and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 609–620.

263 A. Ashe, F. Drone, C. Kausch, J. Kroker and S. Al-Taweel, *Pure Appl. Chem.*, 1990, **62**, 513–517.

264 A. J. Leusink, J. G. Noltes, H. A. Budding and G. J. M. van der Kerk, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 1036–1038.

265 A. J. Leusink, H. A. Budding and J. G. Noltes, *J. Organomet. Chem.*, 1970, **24**, 375–386.

266 A. J. Ashe, *Eur. J. Inorg. Chem.*, 2016, 572–574.

267 D. Chen, Y. Hua and H. Xia, *Chem. Rev.*, 2020, **120**, 12994–13086.

268 A. J. Ashe III, *J. Am. Chem. Soc.*, 1971, **93**, 3293–3295.

269 A. J. Ashe III, *J. Am. Chem. Soc.*, 1971, **93**, 6690–6691.

270 A. J. Ashe III and M. D. Gordon, *J. Am. Chem. Soc.*, 1972, **94**, 7596–7597.

271 P. Jutzi and J. Baumgärtner, *J. Organomet. Chem.*, 1978, **148**, 257–266.

272 A. J. Ashe, W.-T. Chan and E. Perozzi, *Tetrahedron Lett.*, 1975, **16**, 1083–1086.

273 A. J. Ashe and W.-T. Chan, *Tetrahedron Lett.*, 1975, **16**, 2749–2752.

274 E. J. Corey, M. d'Alarcao and K. S. Kyler, *Tetrahedron Lett.*, 1985, **26**, 3919–3922.

275 M. Lautens, N. D. Smith and D. Ostrovsky, *J. Org. Chem.*, 1997, **62**, 8970–8971.

276 M. Lautens, T. Rovis, N. D. Smith and D. Ostrovsky, *Pure Appl. Chem.*, 1998, **70**, 1059–1064.

277 H. X. Zhang, F. Guibe and G. Balavoine, *J. Org. Chem.*, 1990, **55**, 1857–1867.

278 F. Ferri and M. Alami, *Tetrahedron Lett.*, 1996, **37**, 7971–7974.

279 N. Ishida, K. Miyazaki, K. Kumagai and M. Rikimaru, *J. Antibiot.*, 1965, **18**, 68–76.

280 M. Bujard, F. Ferri and M. D. Alami, *Tetrahedron Lett.*, 1998, **39**, 4243–4246.

281 U. Kazmaier, D. Schauss and M. Pohlman, *Org. Lett.*, 1999, **1**, 1017–1019.

282 X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, *Chem. Rev.*, 2016, **116**, 7330–7396.

283 J.-R. Chen, X.-Q. Hu, L.-Q. Lu and W.-J. Xiao, *Acc. Chem. Res.*, 2016, **49**, 1911–1923.

284 Y.-M. Wang, A. D. Lackner and F. D. Toste, *Acc. Chem. Res.*, 2014, **47**, 889–901.

285 M. K. Ghorai, D. P. Tiwari and A. Bhattacharyya, in *Stereoselective Synthesis of Drugs and Natural Products*, ed. V. Andrushko and N. Andrushko, John Wiley & Sons, Inc., 2013, vol. 2, pp. 1173–1210.

286 K. C. Hultzsch, *Adv. Synth. Catal.*, 2005, **347**, 367–391.

287 S. Hong and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673–686.

288 E. McDonald, K. Jones, P. A. Brough, M. J. Drysdale and P. Workman, *Curr. Top. Med. Chem.*, 2006, **6**, 1193–1203.

289 S. Bestgen and P. W. Roesky, in *Early Main Group Metal Catalysis: Concepts and Reactions*, ed. S. Harder, Wiley-VCH Verlag GmbH & Co. KGaA, 2020, pp. 59–91.

290 J. Hannedouche and E. Schulz, *Organometallics*, 2018, **37**, 4313–4326.

291 A. L. Reznichenko and K. C. Hultzsch, in *Organic Reactions*, ed. Evans A., Wiley-VCH Verlag GmbH & Co. KGaA, 2015, vol. 88, pp. 1–554.

292 A. L. Reznichenko and K. C. Hultzsch, in *Chiral Amine Synthesis*, ed. T. C. Nugent, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 341–375.

293 R. Severin and S. Doye, *Chem. Soc. Rev.*, 2007, **36**, 1407–1420.

294 S. Ziemann, S. Krieck, H. Goerls and M. Westerhausen, *Organometallics*, 2018, **37**, 924–933.

295 I. A. Maretina and B. A. Trofimov, *Advances in Heterocyclic Chemistry*, Academic Press, 2002, vol. 82, pp. 157–259.

296 W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, 1969, **34**, 999–1001.

297 X. Feng, B. Tong, J. Shen, J. Shi, T. Han, L. Chen, J. Zhi, P. Lu, Y. Ma and Y. Dong, *J. Phys. Chem. B*, 2010, **114**, 16731–16736.

298 A. J. Chalk, *Tetrahedron Lett.*, 1972, **13**, 3487–3490.

299 L. Wang, X. Yu, X. Feng and M. Bao, *Org. Lett.*, 2012, **14**, 2418–2421.

300 L. Wang, X. Yu, X. Feng and M. Bao, *J. Org. Chem.*, 2013, **78**, 1693–1698.

301 M. M. Bassaco, M. P. Fortes, D. F. Back, T. S. Kaufman and C. C. Silveira, *RSC Adv.*, 2014, **4**, 60785–60797.

302 M. M. Bassaco, M. P. Fortes, T. S. Kaufman and C. C. Silveira, *RSC Adv.*, 2015, **5**, 21112–21124.

303 S. B. Otvos, A. Georgiades, D. Ozsvar and F. Fulop, *RSC Adv.*, 2019, **9**, 8197–8203.

304 R. Singha and J. K. Ray, *RSC Adv.*, 2014, **4**, 44052–44055.

305 D. O'Hagan, *Nat. Prod. Rep.*, 2000, **17**, 435–446.

306 A. Glisan King and J. Meinwald, *Chem. Rev.*, 1996, **96**, 1105–1122.

307 A. Mitchinson and A. Nadin, *J. Chem. Soc., Perkin Trans. I*, 2000, 2862–2892.

308 S. Kramer, J. L. H. Madsen, M. Rottlander and T. Skrydstrup, *Org. Lett.*, 2010, **12**, 2758–2761.

309 V. Lavallo, G. D. Frey, B. Donnadieu, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2008, **47**, 5224–5228.

310 R. Kinjo, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2011, **50**, 5560–5563.

311 F.-X. Zhu, W. Wang and H.-X. Li, *J. Am. Chem. Soc.*, 2011, **133**, 11632–11640.

312 P. Nun, S. Dupuy, S. Gaillard, A. Poater, L. Cavallo and S. P. Nolan, *Catal. Sci. Technol.*, 2011, **1**, 58–61.

313 K. Hirano, Y. Inaba, N. Takahashi, M. Shimano, S. Oishi, N. Fujii and H. Ohno, *J. Org. Chem.*, 2011, **76**, 1212–1227.

314 Y. Tokimizu, S. Oishi, N. Fujii and H. Ohno, *Angew. Chem., Int. Ed.*, 2015, **54**, 7862–7866.

315 A. Yamaguchi, S. Inuki, Y. Tokimizu, S. Oishi and H. Ohno, *J. Org. Chem.*, 2020, **85**, 2543–2559.

316 Y. Duan, Y. Liu, S. Bi, B. Ling, Y.-Y. Jiang and P. Liu, *J. Org. Chem.*, 2016, **81**, 9381–9388.

317 R. Liu, Y. Wei and M. Shi, *ChemCatChem*, 2020, **12**, 5903–5906.

318 L. Ackermann and R. Born, *Tetrahedron Lett.*, 2004, **45**, 9541–9544.

319 H. Tsujita, Y. Ura, S. Matsuki, K. Wada, T.-A. Mitsudo and T. Kondo, *Angew. Chem., Int. Ed.*, 2007, **46**, 5160–5163.

320 R. Tanaka, S. Hirano, H. Urabe and F. Sato, *Org. Lett.*, 2003, **5**, 67–70.

321 V. Gandon, C. Aubert, M. Malacria and K. P. C. Vollhardt, *Chem. Commun.*, 2008, 1599–1601.

322 T. Shimada and Y. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 6646–6647.

323 K. E. Schulte, J. Reisch and H. Walker, *Chem. Ber.*, 1965, **98**, 98–103.

324 Q. Zheng and R. Hua, *Tetrahedron Lett.*, 2010, **51**, 4512–4514.

325 T. Matsuda, in *Transition-Metal-Mediated Aromatic Ring Construction*, ed. K. Tanaka, 2013, pp. 537–547.

326 S. Matsumoto, T. Kobayashi and K. Ogura, *Heterocycles*, 2005, **66**, 319–332.

327 M. Takeda, S. Matsumoto and K. Ogura, *Heterocycles*, 2001, **55**, 231–236.

328 S. Gupta, P. K. Agarwal, M. Saifuddin and B. Kundu, *Tetrahedron Lett.*, 2011, **52**, 5752–5757.

329 C. Maeda, H. Shinokubo and A. Osuka, *Org. Lett.*, 2010, **12**, 1820–1823.

330 H. Nagata, Y. Sugimoto, Y. Ito, M. Tanaka and M. Yoshimatsu, *Tetrahedron*, 2014, **70**, 1306–1316.

331 B. Ramanathan, A. J. Keith, D. Armstrong and A. L. Odom, *Org. Lett.*, 2004, **6**, 2957–2960.

332 W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029–3070.

333 Y.-G. Zhou, *Acc. Chem. Res.*, 2007, **40**, 1357–1366.

334 S. E. Denmark and J. Fu, *Chem. Rev.*, 2003, **103**, 2763–2794.

335 S. C. Cullen and T. Rovis, *Org. Lett.*, 2008, **10**, 3141–3144.

336 S. V. Levchik and E. D. Weil, *Polym. Int.*, 2005, **54**, 11–35.

337 A. A.-A. Al-Quntar, O. Baum, R. Reich and M. Srebnik, *Arch. Pharm.*, 2004, **337**, 76–80.

338 J. Hiratake and J. i. Oda, *Biosci., Biotechnol., Biochem.*, 1997, **61**, 211–218.

339 P. Cheruku, A. Paptchikhine, T. L. Church and P. G. Andersson, *J. Am. Chem. Soc.*, 2009, **131**, 8285–8289.

340 N. A. Bondarenko, I. N. Lermontova, G. N. Bondarenko, N. S. Gulyukina, T. M. Dolgina, S. O. Bachurin and I. P. Beletskaya, *Pharm. Chem. J.*, 2003, **37**, 226–228.

341 D.-Y. Wang, X.-P. Hu, J. Deng, S.-B. Yu, Z.-C. Duan and Z. Zheng, *J. Org. Chem.*, 2009, **74**, 4408–4410.

342 K. Moonen, E. Van Meenen, A. Verwée and C. V. Stevens, *Angew. Chem., Int. Ed.*, 2005, **44**, 7407–7411.

343 H. Bräuner-Osborne, J. Egebjerg, E. Ø. Nielsen, U. Madsen and P. Krogsgaard-Larsen, *J. Med. Chem.*, 2000, **43**, 2609–2645.

344 V. Devreux, J. Wiesner, H. Jomaa, J. Rozenski, J. Van der Eycken and S. Van Calenbergh, *J. Org. Chem.*, 2007, **72**, 3783–3789.

345 K. Schlüter, R. D. Walter, B. Bergmann and T. Kurz, *Eur. J. Med. Chem.*, 2006, **41**, 1385–1397.

346 Y. Sarazin and J.-F. Carpentier, in *Early Main Group Metal Catalysis: Concepts and Reactions*, ed. S. Harder, Wiley-VCH Verlag GmbH & Co. KGaA, 2020, pp. 93–121.

347 K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani and K. Takehira, *J. Org. Chem.*, 2003, **68**, 6554–6565.

348 K. Komeyama, D. Kobayashi, Y. Yamamoto, K. Takehira and K. Takaki, *Tetrahedron*, 2006, **62**, 2511–2519.

349 L.-B. Han, N. Choi and M. Tanaka, *Organometallics*, 1996, **15**, 3259–3261.

350 J. Kanada, K.-i. Yamashita, S. K. Nune and M. Tanaka, *Tetrahedron Lett.*, 2009, **50**, 6196–6199.

351 Y. Yamamoto, K. Fukatsu and H. Nishiyama, *Chem. Commun.*, 2012, **48**, 7985–7987.

352 T. M. A. Al-Shboul, H. Goerls, S. Krieck and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2012, 5451–5455.

353 D. B. Borders, P. Shu and J. E. Lancaster, *J. Am. Chem. Soc.*, 1972, **94**, 2540–2541.

354 Y.-L. Yan and S. M. Cohen, *Org. Lett.*, 2007, **9**, 2517–2520.

355 T. Koyama, Y. Kawazoe, A. Iwasaki, O. Ohno, K. Suenaga and D. Uemura, *J. Antibiot.*, 2016, **69**, 348–351.

356 A. Jennen and E. Bajoit, *Compt. Rend.*, 1960, **250**, 2218–2219.

357 I. D. Campbell, N. A. Dobson and G. Eglinton, *J. Chem. Soc.*, 1964, 1092–1096.

358 M. G. Constantino, P. M. Donate and N. Petragnani, *J. Org. Chem.*, 1986, **51**, 387–390.

359 B. M. Trost and M. T. Rudd, *J. Am. Chem. Soc.*, 2002, **124**, 4178–4179.

360 B. M. Trost and X. Huang, *Org. Lett.*, 2005, **7**, 2097–2099.

361 B. M. Trost and X. Huang, *Chem. – Asian J.*, 2006, **1**, 469–478.

362 B. M. Trost and M. T. Rudd, *Org. Lett.*, 2003, **5**, 4599–4602.

363 B. M. Trost and M. T. Rudd, *J. Am. Chem. Soc.*, 2003, **125**, 11516–11517.

364 B. M. Trost and M. T. Rudd, *J. Am. Chem. Soc.*, 2005, **127**, 4763–4776.

365 B. M. Trost, J.-P. Surivet and F. D. Toste, *J. Am. Chem. Soc.*, 2004, **126**, 15592–15602.

366 B. M. Trost and F. D. Toste, *J. Am. Chem. Soc.*, 2002, **124**, 5025–5036.

367 Y. Yamamoto, J.-i. Ishii, H. Nishiyama and K. Itoh, *J. Am. Chem. Soc.*, 2004, **126**, 3712–3713.

368 Y. Yamamoto, T. Arakawa, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.*, 2003, **125**, 12143–12160.

369 J. A. Varela, L. Castedo and C. Saá, *Org. Lett.*, 2003, **5**, 2841–2844.

370 Y. Yamamoto, H. Takagishi and K. Itoh, *Org. Lett.*, 2001, **3**, 2117–2119.

371 Y. Yamamoto, R. Ogawa and K. Itoh, *J. Am. Chem. Soc.*, 2001, **123**, 6189–6190.

372 Y. Yamamoto, K. Yamashita and H. Nishiyama, *Chem. Commun.*, 2011, **47**, 1556–1558.

373 A. Odedra, C.-J. Wu, T. B. Pratap, C.-W. Huang, Y.-F. Ran and R.-S. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 3406–3412.

374 I. Volchkov, K. Sharma, E.-J. Cho and D.-S. Lee, *Chem. – Asian J.*, 2011, **6**, 1961–1966.

375 R. M. Valdez-Garcia, C. Alarcon-Manjarrez, A. Galano, B. Rodriguez-Molina, M. Flores-Alamo and M. A. Iglesias-Arteaga, *Eur. J. Org. Chem.*, 2019, 4916–4927.

376 D. Garey, M.-l. Ramirez, S. Gonzales, A. Wertsching, S. Tith, K. Keefe and M. R. Peña, *J. Org. Chem.*, 1996, **61**, 4853–4856.

377 M. Ehrlich and T. Carell, *Eur. J. Org. Chem.*, 2013, 77–83.

378 M. Solas, M. A. Munoz, S. Suarez-Pantiga and R. Sanz, *Org. Lett.*, 2020, **22**, 7681–7687.

379 Y.-L. Xu, Q.-H. Teng, W. Tong, H.-S. Wang, Y.-M. Pan and X.-L. Ma, *Molecules*, 2017, **22**, 109–123.

380 C. Zhang, D.-M. Cui, L.-Y. Yao, B.-S. Wang, Y.-Z. Hu and T. Hayashi, *J. Org. Chem.*, 2008, **73**, 7811–7813.

381 D.-M. Cui, Y.-N. Ke, D.-W. Zhuang, Q. Wang and C. Zhang, *Tetrahedron Lett.*, 2010, **51**, 980–982.

382 C. Zhang, J.-F. Qi, D.-M. Cui, Q. Wang and X.-L. Wang, *Molecules*, 2010, **15**, 5045–5052.

383 H.-K. Chang, S. Datta, A. Das, A. Odedra and R.-S. Liu, *Angew. Chem., Int. Ed.*, 2007, **46**, 4744–4747.

384 H.-K. Chang, Y.-C. Liao and R.-S. Liu, *J. Org. Chem.*, 2007, **72**, 8139–8141.

385 A. Das, H.-K. Chang, C.-H. Yang and R.-S. Liu, *Org. Lett.*, 2008, **10**, 4061–4064.

386 J. J. Kennedy-Smith, S. T. Staben and F. D. Toste, *J. Am. Chem. Soc.*, 2004, **126**, 4526–4527.

387 A. Das, H.-K. Chang, C.-H. Yang and R.-S. Liu, *Org. Lett.*, 2008, **10**, 4061–4064.

388 H. Jiang, W. Zeng, Y. Li, W. Wu, L. Huang and W. Fu, *J. Org. Chem.*, 2012, **77**, 5179–5183.

389 K. Chen, G. Shi, W. Zhang, H. Li and C. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 14198–14201.

390 A. L. Gibeau and J. K. Snyder, *Org. Lett.*, 2011, **13**, 4280–4283.

391 S. C. Shim and T. S. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1739–1743.

392 S. C. Shim, Y. S. Chae and E. K. Baek, *Bull. Korean Chem. Soc.*, 1997, **18**, 364–366.

393 G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik and T. W. von Geldern, *J. Med. Chem.*, 2001, **44**, 1202–1210.

394 S. F. Nielsen, E. Ø. Nielsen, G. M. Olsen, T. Liljefors and D. Peters, *J. Med. Chem.*, 2000, **43**, 2217–2226.

395 M. See Waters, J. A. Cowen, J. C. McWilliams, P. E. Maligres and D. Askin, *Tetrahedron Lett.*, 2000, **41**, 141–144.

396 T. Satoh, D. Taguchi, C. Suzuki and S. Fujisawa, *Tetrahedron*, 2001, **57**, 493–500.

397 P. G. Guerrero, M. J. Dabdoub, F. A. Marques, C. L. Wosch, A. C. M. Baroni and A. G. Ferreira, *Synth. Commun.*, 2008, **38**, 4379–4394.

398 F. Foubelo, A. Gutiérrez and M. Yus, *Tetrahedron Lett.*, 1999, **40**, 8173–8176.

399 M. Hojo, H. Harada, J. Yoshizawa and A. Hosomi, *J. Org. Chem.*, 1993, **58**, 6541–6542.

400 J. P. Dittami, X. Y. Nie, H. Nie, H. Ramanathan, C. Buntel, S. Rigatti, J. Bordner, D. L. Decosta and P. Williard, *J. Org. Chem.*, 1992, **57**, 1151–1158.

401 M. Kolb, *Synthesis*, 1990, 171–190.

402 E. Marcantoni, M. Massaccesi, M. Petrini, G. Bartoli, M. C. Bellucci, M. Bosco and L. Sambri, *J. Org. Chem.*, 2000, **65**, 4553–4559.

403 C. Kuligowski, S. Bezzenine-Lafollée, G. Chaume, J. Mahuteau, J.-C. Barrière, E. Bacqué, A. Pancrazi and J. Ardisson, *J. Org. Chem.*, 2002, **67**, 4565–4568.

404 H. Wai Lam, P. A. Cooke, G. Pattenden, W. M. Bandaranayake and W. A. Wickramasinghe, *J. Chem. Soc., Perkin Trans. I*, 1999, 847–848.

405 M. Koreeda and W. Yang, *Synlett*, 1994, 201–203.

406 W. Schroth, F. Billig and G. Reinhold, *Angew. Chem., Int. Ed.*, 1967, **6**, 698–699.

407 M. Koreeda and W. Yang, *J. Am. Chem. Soc.*, 1994, **116**, 10793–10794.

408 W. Schroth, S. Dunger, F. Billig, R. Spitzner, R. Herzschuh, A. Vogt, T. Jende, G. Israel, J. Barche, D. Ströhl and J. Sieler, *Tetrahedron*, 1996, **52**, 12677–12698.

409 A. Zschunke, C. Mügge, E. Hintzsche and W. Schroth, *J. Prakt. Chem. - Chemiker Ztg*, 1992, **334**, 141–146.

410 F. Freeman, H. Lu and E. Rodriguez, *Tetrahedron Lett.*, 1993, **34**, 1753–1756.

411 F. Freeman, H. Lu, Q. Zeng and E. Rodriguez, *J. Org. Chem.*, 1994, **59**, 4350–4354.

412 A. S. Santana, D. B. Carvalho, N. S. Casemiro, G. R. Hurtado, L. H. Viana, N. M. Kassab, S. L. Barbosa, F. A. Marques, P. G. Guerrero and A. C. M. Baroni, *Tetrahedron Lett.*, 2012, **53**, 5733–5738.

413 T. Kesharwani, K. A. Giraudy, J. L. Morgan, C. Kornman and A. D. Olaitan, *Tetrahedron Lett.*, 2017, **58**, 638–641.

414 M. Shahid, R. S. Ashraf, Z. Huang, A. J. Kronemeijer, T. McCarthy-Ward, I. McCulloch, J. R. Durrant, H. Sirringhaus and M. Heeney, *J. Mater. Chem.*, 2012, **22**, 12817–12823.

415 A. S. Santana, D. B. Carvalho, N. S. Cassemiro, L. H. Viana, G. R. Hurtado, M. S. Amaral, N. M. Kassab, P. G. Guerrero, S. L. Barbosa, M. J. Dabdoub and A. C. M. Baroni, *Tetrahedron Lett.*, 2014, **55**, 52–55.

416 K. E. Schulte, H. Walker and L. Rolf, *Tetrahedron Lett.*, 1967, **8**, 4819–4821.

417 M. J. Dabdoub, V. B. Dabdoub, E. J. Lenardao, G. R. Hurtado, S. L. Barbosa, P. G. Guerrero, Jr., C. E. D. Nazario, L. H. Viana, A. S. Santana and A. C. M. Baroni, *Synlett*, 2009, 986–990.

418 D. Alves, M. Sachini, R. G. Jacob, E. J. Lenardão, M. E. Contreira, L. Savegnago and G. Perin, *Tetrahedron Lett.*, 2011, **52**, 133–135.

419 R. G. Lara, L. K. Soares, R. G. Jacob, R. F. Schumacher and G. Perin, *J. Braz. Chem. Soc.*, 2016, **27**, 2046–2054.

420 Y. Li, J. Wu, H. Li, Q. Sun, L. Xiong and G. Yin, *Org. Chem. Front.*, 2021, **8**, 628–634.

421 A. N. Volkov and K. A. Volkova, *Russ. J. Org. Chem.*, 2004, **40**, 1679–1681.

422 B. Banerjee and M. Koketsu, *Coord. Chem. Rev.*, 2017, **339**, 104–127.

423 F. V. Singh and T. Wirth, *Catal. Sci. Technol.*, 2019, **9**, 1073–1091.

424 A. L. Stein, F. N. Bilheri and G. Zeni, *Chem. Commun.*, 2015, **51**, 15522–15525.

425 G. Perin, E. J. Lenardão, R. G. Jacob and R. B. Panatieri, *Chem. Rev.*, 2009, **109**, 1277–1301.

426 G. Sartori, J. S. Neto, A. P. Pesarico, D. F. Back, C. W. Nogueira and G. Zeni, *Org. Biomol. Chem.*, 2013, **11**, 1199–1208.

427 A. D. Sonawane, R. A. Sonawane, M. Ninomiya and M. Koketsu, *Adv. Synth. Catal.*, 2020, **362**, 3485–3515.

428 P. S. Hellwig, T. J. Peglow, F. Penteado, L. Bagnoli, G. Perin and E. J. Lenardão, *Molecules*, 2020, **25**, 5907.

429 Y. D. Maksym, F. P. Maksym and V. V. Valerii, *Curr. Org. Synth.*, 2017, **14**, 683–690.

430 F. Vilela, Z. Vobecka and P. J. Skabara, in *PATAI'S Chemistry of Functional Groups*, ed. I. Marek, 2014, pp. 1–30.

431 M. E. Logan, M. A. Lang and M. R. Detty, in *PATAI's Chemistry of Functional Groups*, ed. I. Marek, John Wiley & Sons, Ltd, 2014, pp. 1–82.

432 C. R. B. Rhoden and G. Zeni, *Org. Biomol. Chem.*, 2011, **9**, 1301–1313.

433 C. W. Nogueira, G. Zeni and J. B. T. Rocha, *Chem. Rev.*, 2004, **104**, 6255–6286.

434 C. W. Bird, G. W. H. Cheeseman and A. B. Hörnfeldt, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, pp. 935–971.

435 R. F. Curtis, S. N. Hasnain and J. A. Taylor, *Chem. Commun.*, 1968, 365a–365a.

436 M. J. Dabdoub, A. C. M. Baroni, E. J. Lenardão, T. R. Gianeti and G. R. Hurtado, *Tetrahedron*, 2001, **57**, 4271–4276.

437 D. Alves, C. Luchese, C. W. Nogueira and G. Zeni, *J. Org. Chem.*, 2007, **72**, 6726–6734.

438 D. A. Barancelli, C. I. Acker, P. H. Menezes and G. Zeni, *Org. Biomol. Chem.*, 2011, **9**, 1529–1537.

439 S. Ahmad, K. K. Yadav, S. J. Singh and S. Chauhan, *RSC Adv.*, 2014, **4**, 3171–3180.

440 S. Ahmad, K. K. Yadav, S. Bhattacharya, P. Chauhan and S. M. S. Chauhan, *J. Org. Chem.*, 2015, **80**, 3880–3890.

441 E. F. Lopes, L. C. Gonçalves, J. C. G. Vinueza, R. G. Jacob, G. Perin, C. Santi and E. J. Lenardão, *Tetrahedron Lett.*, 2015, **56**, 6890–6895.

442 M. J. Dabdoub, V. B. Dabdoub, E. J. Lenardao, G. R. Hurtado, S. L. Barbosa, P. G. Guerrero, C. E. Nazario, L. H. Viana, A. S. Santana and A. C. Baroni, *Synlett*, 2009, 986–990.

443 C. Venkateswarlu and S. Chandrasekaran, *Synthesis*, 2015, 395–410.

444 V. Ganesh and S. Chandrasekaran, *Synthesis*, 2009, 3267–3278.

445 P. Męcik, B. Pigulski and S. Szafert, *Org. Lett.*, 2021, **23**, 1066–1070.

446 G. Zeni, D. S. Lüdtke, R. B. Panatieri and A. L. Braga, *Chem. Rev.*, 2006, **106**, 1032–1076.

447 E. Rivard, *Chem. Lett.*, 2015, **44**, 730–736.

448 N. Petragnani and H. A. Stefani, in *Tellurium in Organic Synthesis*, Second Edition, ed. N. Petragnani and H. A. Stefani, Academic Press, London, 2007, pp. 285–328.

449 X. Wu, L. Lv, L. Hu, Q. Shi, A. Peng and H. Huang, *ChemPhysChem*, 2019, **20**, 2600–2607.

450 C. A. Braun, D. Zomerman, I. de Aguiar, Y. Qi, W. T. Delgado, M. J. Ferguson, R. McDonald, G. L. C. de Souza, G. He, A. Brown and E. Rivard, *Faraday Discuss.*, 2017, **196**, 255–268.

451 L. Lv, X. Wang, X. Wang, L. Yang, T. Dong, Z. Yang and H. Huang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 34620–34629.

452 E. I. Carrera, A. E. Lanterna, A. J. Lough, J. C. Scaiano and D. S. Seferos, *J. Am. Chem. Soc.*, 2016, **138**, 2678–2689.

453 E. I. Carrera and D. S. Seferos, *Dalton Trans.*, 2015, **44**, 2092–2096.

454 R. S. Ashraf, I. Meager, M. Nikolka, M. Kirkus, M. Planells, B. C. Schroeder, S. Holliday, M. Hurhangee, C. B. Nielsen, H. Sirringhaus and I. McCulloch, *J. Am. Chem. Soc.*, 2015, **137**, 1314–1321.

455 J. Fernández-Lodeiro, M. F. Pinatto-Botelho, A. A. Soares-Paulino, A. C. Gonçalves, B. A. Sousa, C. Princival and A. A. Dos Santos, *Dyes Pigm.*, 2014, **110**, 28–48.

456 J. Malmström, M. Jonsson, I. A. Cotgreave, L. Hammarström, M. Sjödin and L. Engman, *J. Am. Chem. Soc.*, 2001, **123**, 3434–3440.

457 W. Mack, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 896.

458 D. P. Sweat and C. E. Stephens, *J. Organomet. Chem.*, 2008, **693**, 2463–2464.

459 J. P. Marino and H. N. Nguyen, *J. Org. Chem.*, 2002, **67**, 6841–6844.

460 S. Ng, H. Ding and H. Chan, *Chem. Lett.*, 1999, 1325–1326.

461 M. J. Dabdoub, A. Justino, P. G. Guerrero and J. Zukerman-Schpector, *Organometallics*, 1998, **17**, 1901–1903.

462 M. J. Dabdoub, V. B. Dabdoub, M. A. Pereira and J. Zukerman-Schpector, *J. Org. Chem.*, 1996, **61**, 9503–9511.

463 M. J. Dabdoub and V. B. Dabdoub, *Tetrahedron*, 1995, **51**, 9839–9850.

464 M. J. Dabdoub, V. B. Dabdoub and J. V. Comasseto, *Tetrahedron Lett.*, 1992, **33**, 2261–2264.

465 M. R. Detty, J. W. Hassett, B. J. Murray and G. A. Reynolds, *Tetrahedron*, 1985, **41**, 4853–4859.

466 F. Fringuelli and A. Taticchi, *J. Chem. Soc., Perkin Trans. I*, 1972, 199–203.

467 T. J. Barton and R. W. Roth, *J. Organomet. Chem.*, 1972, **39**, C66–C68.

468 A. Ulman, J. Manassen, F. Frolow and D. Rabinovich, *Tetrahedron Lett.*, 1978, **19**, 1885–1886.

469 C. R. Rhoden and G. Zeni, *Org. Biomol. Chem.*, 2011, **9**, 1301–1313.

470 T. M. McCormick, A. A. Jahnke, A. J. Lough and D. S. Seferos, *J. Am. Chem. Soc.*, 2012, **134**, 3542–3548.

471 E. I. Carrera, T. M. McCormick, M. J. Kapp, A. J. Lough and D. S. Seferos, *Inorg. Chem.*, 2013, **52**, 13779–13790.