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Mini Review

New cascade and multiple cross-coupling reactions for the efficient construction of complex molecules

Armin de Meijere *, Paultheo von Zezschwitz, Hanno Nüske, Baldur Stulgies

Institut für Organische Chemie, Georg-August-Universität Göttingen, Tammannstr. 2, D-37077 Göttingen, Germany

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Abstract

Multiple palladium-catalyzed cross-coupling reactions of the Heck, Suzuki and Stille types on oligofunctionalized cycloalkenes and arenes can be performed in very high yields. While Heck type reactions on 1,2-dibromocycloalkenes or 2-bromocyclohexenyl triflates lead only to the twofold coupling products, the Stille coupling of the latter substrates occurs chemoselectively at the site of the triflate leaving group to give bromobutadienes which readily undergo subsequent Heck reactions. The thus obtained 1,3,5-hexatrienes undergo thermal 6π-electrocyclizations to furnish bicyclic skeletons, among others cyclohexenone-annelated systems after acidic work-up. Cascades of carbopalladation, rearrangement and [4+2] cycloaddition with bicyclopropylidene, aryl iodides and dienophiles constitute a new class of three-component reactions with a remarkable combinatorial potential, especially since they can be performed on the solid phase using the triazene linker. With nucleophiles instead of dienophiles yet another domino reaction consisting of carbopalladation, rearrangement and nucleophilic substitution can be performed with bicyclopropylidene, aryl or alkenyl iodides and C-, O- and N-centered nucleophiles to give a wide variety of interesting compounds. Under properly adjusted conditions even sixfold coupling reactions on hexabromoarenes can be achieved. When using Heck type reactions the initially formed intermediates en route to hexaalkenylarenes undergo intramolecular ring closures to yield multi-component mixtures of isomers of the expected products, but sixfold Stille and Suzuki couplings give pure hexaalkenylarenes in up to 73% yield. Crystal structure analyses reveal that depending on the nature of the alkenyl groups the six arms are positioned either on the same side of the central ring making it an interesting cup-shaped molecule or alternating above and below the central plane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cross-coupling; Palladium-catalysis; Alkenylboronates; Cascade reactions; Combinatorial synthesis

1. Introduction

Increasing the efficiency of organic chemical transformations is one of the major goals in todays synthetic methodology development [1]. One important way to achieve increased efficiency is by combining several steps of the same or different transformations into single-pot operations [2]. For a number of years, we have been engaged in developing multiple cross-coupling reactions, predominantly of the Heck, Stille, and Suzuki types, and frequently we have combined such coupling cascades with cycloadditions or other transformations [3].

2. Results and discussion

The Mizoroki–Heck reaction has been extensively reviewed in recent years [4]. This cross-coupling of alkenyl or aryl halides or perfluoroalkylsulfonates can easily be employed for oligohaloalkenes and -arenes, and we have shown some time ago, that the twofold coupling of 1,2-dibromocycloalkenes can give high yields of (E,Z,E)-1,3,5-hexatrienes which are perfectly set up for a thermal 6π-electrocyclization [5a]. The overall sequence is a new method for cyclohexadiene-annelation onto five-, six-, and seven-membered rings [5b]. Competition experiments have shown that the second coupling step in this twofold Heck coupling occurs about 50 times faster than the first one, especially when the coupled alkene contains an electron-withdrawing group as in styrenes and acrylates [5], two

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* Corresponding author. Fax: +49-551-39-9475.
E-mail address: armin.demeijere@chemie.uni-goettingen.de (A. de Meijere).

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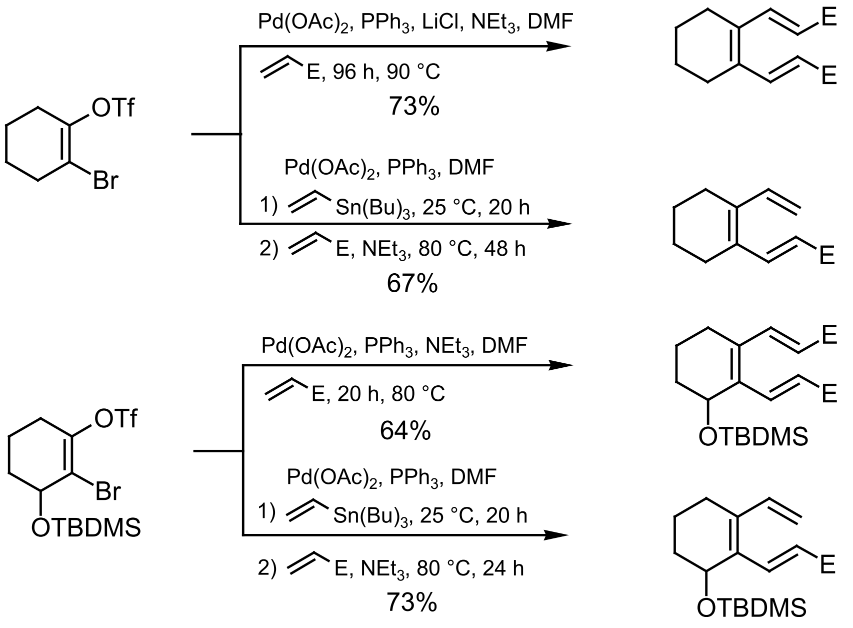
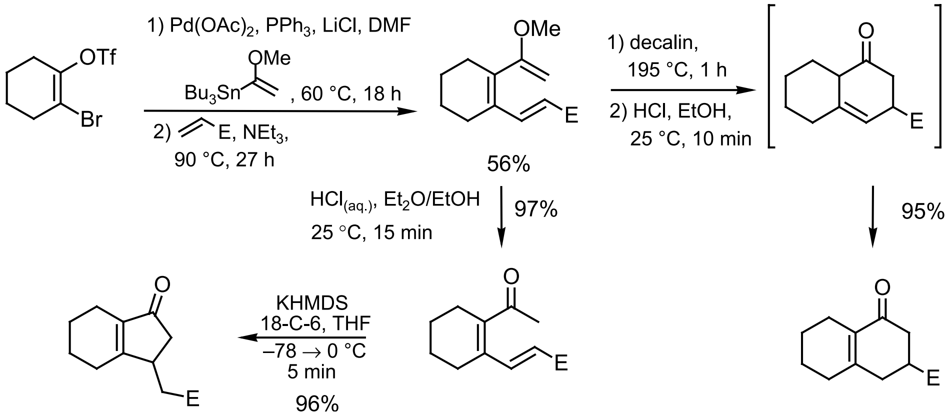


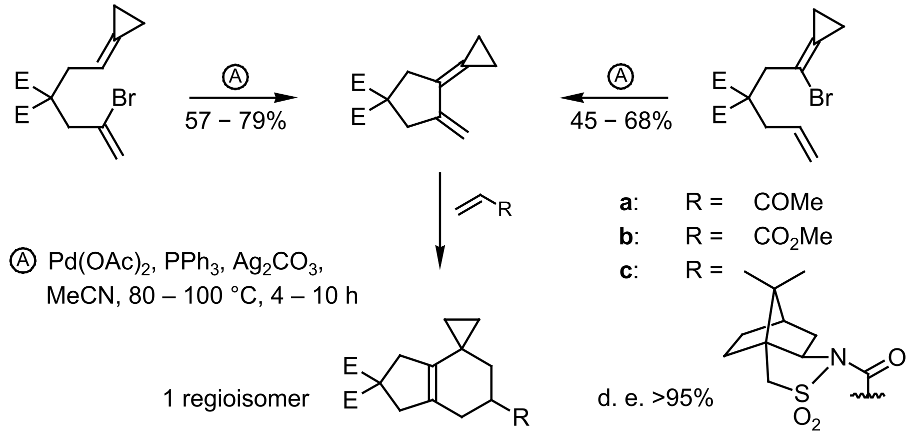
Scheme 1. Unsymmetrically 1,6-disubstituted 1,3,5-hexatrienes from 2-bromocyclohexenyl triflates. E = CO_2t-Bu.

typical substrates for Heck couplings. Under Heck conditions, therefore, 2-bromocyclohexenyl triflates in spite of their two different leaving groups, simply undergo twofold Heck coupling with *tert*-butyl acrylate to give the corresponding products in 73 and 64% yield, respectively (Scheme 1). However, under modified conditions, i.e. without the added triethylamine, these bromoenol triflates undergo a completely selective Stille coupling [6] with tributylethenylstannane at room temperature, and the products can then be coupled with *tert*-butyl acrylate after addition of triethylamine at 80 °C to give the Stille–Heck cross-coupling products in 67 and 73% overall yield [7].

Thus, the door is open to other combinations of Stille and Heck couplings, e.g. with functionally substituted vinylstannanes, such as α-methoxyvinylstannane which is easily prepared from lithiated methyl vinyl ether and tributylstannyl chloride. Although the Stille coupling in this case requires 60 °C for 18 h, it is still selective for the triflate leaving group in the substrate, and subsequent Heck coupling with methyl acrylate gives the twofold cross-coupling product in 56% yield (Scheme 2). This product can be directly hydrolyzed to a methyl ketone, the enolate of which undergoes an intramolecular Michael addition to yield a tetrahydroindanone derivative, but it can also be heated in decalin at 195 °C for 1 h to give the cyclization product. This was not isolated, but immediately hydrolyzed by acid work-up and gave methyl 2-oxobi[4.4.0]dec-1(6)-en-4-carboxylate (Scheme 2) originating by acid-catalyzed rearrangement of the initial hydrolysis product [7]. The overall process constitutes a cyclohexenone annelation procedure, and as such it complements the well known Robinson annelation. For certain applications, the current methodology may be favorable, as the obtained products have the carbonyl group and the adjacent double bond



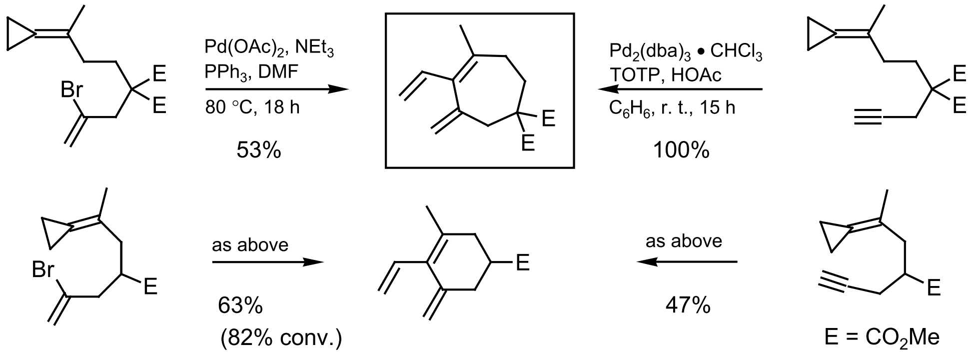
Scheme 2. A new access to bicyclo[4.4.0]decenones and bicyclo[4.3.0]nonenones [7]. E = CO_2Me.



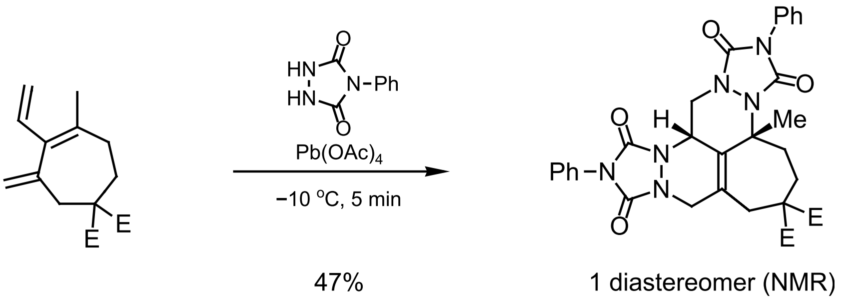
Scheme 3. Intramolecular Heck reactions of 2-bromo-1,6-dienes incorporating methylenecyclopropane units [8a].

in positions different from those of the Robinson annelation products.

In another effort, we have shown that intramolecular Heck couplings to yield bisexodialkylidenecycloalkanes can favorably be combined with a subsequent Diels–Alder reaction in a one-pot operation [8]. This protocol consistently gives better yields than the two-step procedure with intermediate isolation of the diene, and it is particularly favorable when the intermediate diene is prone to undergo polymerization such as a 1-cyclopropylidene-2-methylenecyclopentane (Scheme 3). Such dienes are rather sensitive and can be isolated at best in 40% yield. However, the one-pot operation in the presence of a dienophile gives the intramolecular coupling-cycloadduct in up to 79% overall yield. This reaction is completely regioselective, and with a chirally modified dienophile such as the acryloyl derivative of the Oppolzer sultame also occurs completely diastereoselectively [8a]. It is noteworthy, that the same cyclization–cycloaddition sequence could not be brought about with analogous bromodienes that contained an isopropylidene instead of the methylenecyclopropane moiety at either end. However, the spirocyclopropane unit in the final product is a mimic of a *gem*-dimethyl group, and, if necessary, it can actually be converted to a *gem*-dimethyl fragment by catalytic hydrogenation over a platinum catalyst in acetic acid. This successful coupling of bromodienes featuring methylenecyclopropane units, without ring opening, was surprising in light of literature reports on palladium-catalyzed cycloadditions of methylenecyclopropane derivatives with ring opening [9]. Therefore, it appeared logical to try out systems, in which the methylenecyclopropane unit contained a tetrasubstituted double bond, so that β-hydride elimination, which is required to form the intermediate dienes in the previous case, would be blocked or at least retarded, as it would have to go into a three-membered ring with formation of a highly strained cyclopropene. Model 2-bromo-1,6-dienes with an additional methyl group attached at the vinylic position of the methylenecyclopropane terminator were put together and treated with the typical Heck catalyst cocktail, at first in the presence of methyl acrylate (Scheme 4). Surprisingly, the product did not contain the acrylate unit, and according to the tether length between the vinyl bromide and the methylenecyclopropane unit in the starting materials, a larger ring had been formed than that anticipated by the usual *n–exo–trig*-ring closure. Cross-conjugated trienes were formed in moderate to good yields not only from the bromodienes, but also from enynes with the same substitution pattern under the enyne-cycloisomerization conditions developed by Trost et al. [11]. The mechan-



Scheme 4. Cross-conjugated trienes by an intramolecular Pd-catalyzed reaction with a methyl-substituted methylenecyclopropane terminator [10].



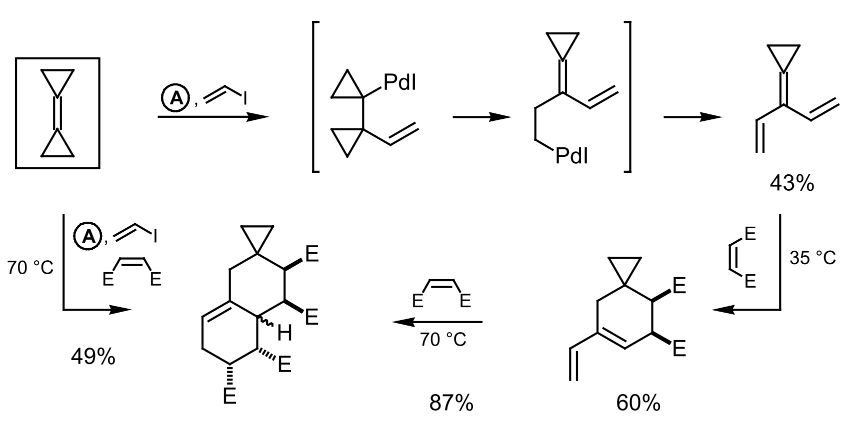
Scheme 5. Cross-conjugated trienes for domino-Diels–Alder reactions [13]. E = CO_2Me.

istic implications of these transformations are quite interesting. Cross-conjugated trienes, which are easily accessible along this route, are favorably set up for domino-Diels–Alder reactions, also called 'transmissive cycloadditions' by Tsuge et al. [12] earlier on, and indeed, the methylene-vinylcycloheptane derivative did undergo successive Diels–Alder reactions with the highly reactive *N*-phenyltriazolinedione (PTAD) generated by lead tetraacetate oxidation of the *N*-phenylurazole precursor (Scheme 5) [13].

The formation of cross-conjugated trienes from systems with a methyl-substituted methylenecyclopropane terminator led to the concept of carrying out such a reaction in an intermolecular fashion. Probably the most appropriate methylenecyclopropane for such a case is bicyclopropylidene, a highly strained alkene which has a tetrasubstituted double bond and is a methylenecyclopropane in both directions [14]. Thus, regioselectivity problems would be excluded from the start. Indeed, bicyclopropylidene, when treated with iodoethene in the presence of a typical palladium precatalyst, gave 3-cyclopropylidenepenta-1,4-diene in 43% yield. The latter did react with dimethyl maleate at 35 °C at its vinylmethylenecyclopropane moiety, and the newly created 1,3-diene unit in the primary product required 70 °C to undergo the Diels–Alder reaction with dimethyl maleate, and furnished the spirocyclopropanated octahydronaphthaline derivative (Scheme 6) [10].

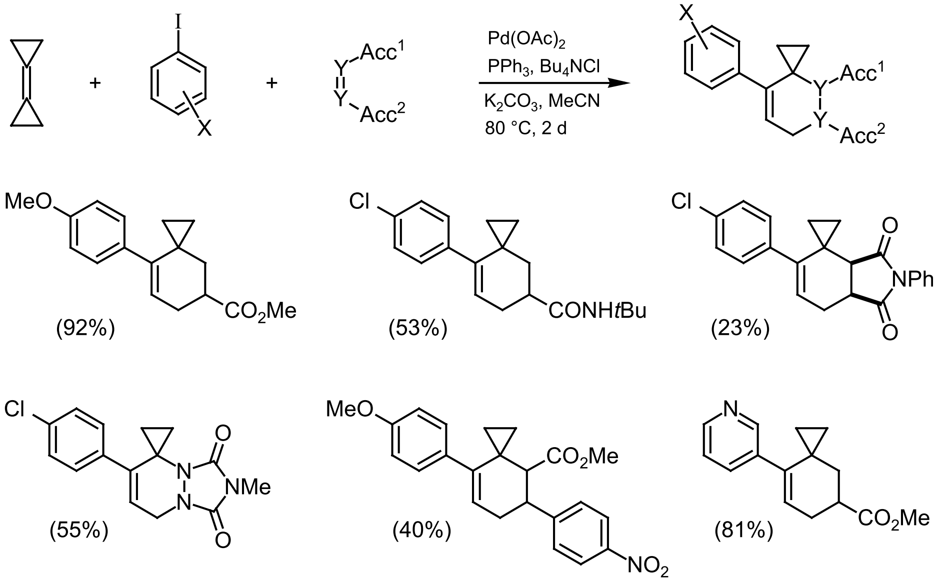
The same product was obtained in 49% yield, when bicyclopropylidene, iodoethene and dimethyl maleate were treated with the palladium catalyst in one pot at 70 °C. The fact that no direct coupling product of iodoethene and dimethyl maleate was observed, indicates that the carbopalladation of the double bond in bicyclopropylidene with the initially formed vinylpalladium iodide occurs more rapidly than that of the double bond in dimethyl maleate. The first formed carbopalladation intermediate, which contains a cyclopropylpalladium iodide as well as a cyclopropylcarbinylpalladium iodide moiety, undergoes a rapid cyclopropylcarbinyl to homoallyl rearrangement, and the latter intermediate, by β-hydride elimination, furnishes the observed cross-conjugated triene (Scheme 6).

This new three-component reaction can be carried out with a large variety of aryl halides, most favorably iodides (Scheme 7) [10,15]. The yields in this coupling-cycloaddition sequence are particularly high with the parent iodobenzene applying the Jeffery protocol for Heck reactions, and working with as little solvent as possible [16]. The combinatorial potential of this reaction has been demonstrated with the preparation of a library of more than 150 different compounds on a synthesizing robot. Hetero atoms can be brought in with



Ⓐ: $Pd(OAc)_2$, PPh_3, NEt_3, DMF, 80 °C, 4 h.

Scheme 6. An inter–intermolecular domino of Heck and Diels–Alder reactions [10].



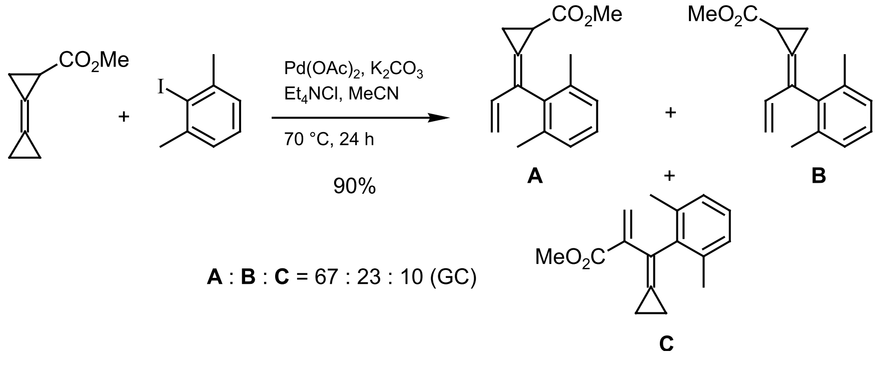
Scheme 7. The combinatorial potential of the new three-component reaction [10,15].

the dienophile as well as with the iodoarene (Scheme 7), and the combinatorial diversity can be further increased by the use of substituted bicyclopropylidene derivatives (Scheme 8).

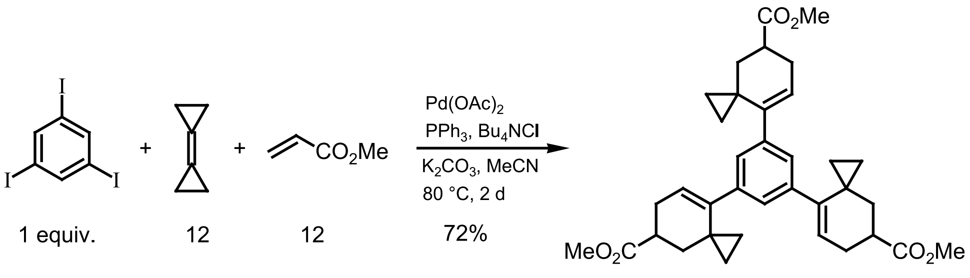
The vinylmethylenecyclopropane intermediates, which are prone to undergo polymerization, can be isolated when the aryl substituent is 2,6-disubstituted. For instance, with 2,6-dimethyliodobenzene, methyl bicyclopropylidenecarboxylate gave in very high yield (90%) a mixture of three isomeric aryldiene products, in which isomer A predominated with 67% (Scheme 8) [17].

This cross-coupling-rearrangement–cycloadditon sequence can be carried out twice, e.g. with 1,2- or 1,4-diiodobenzene. The latter reaction, in which six new C,C-bonds are formed, gives a single diastereomer in up to 83% yield. The corresponding threefold sequence with 1,3,5-triiodobenzene, in which nine new C,C-bonds are formed in a single operation, gives the coupling-cycloaddition product in 72% yield (Scheme 9).

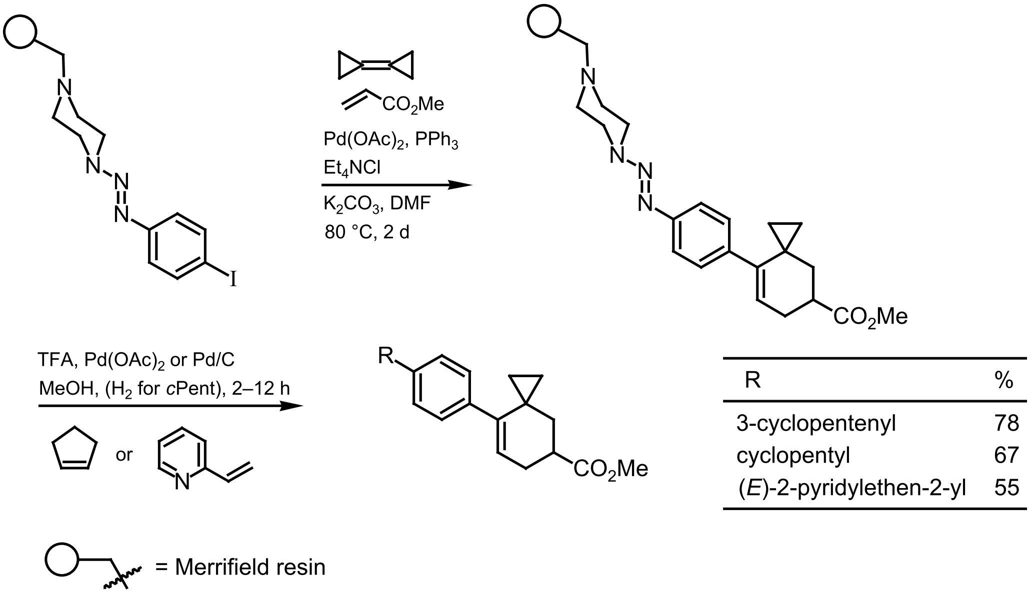
The fourfold reaction with 1,2,4,5-tetraiodobenzene was also successful (47% yield), but the sixfold sequence starting from hexaiodobenzene gave a mixture of



Scheme 8. Regioselective carbopalladation of methyl bicyclopropylidenecarboxylate [17].



Scheme 9. Nine new C–C-bonds in a single operation [16].



R	%
3-cyclopentenyl	78
cyclopentyl	67
(*E*)-2-pyridylethen-2-yl	55

Scheme 10. Combination of cross-coupling, Diels–Alder reaction and cross coupling with a combinatorial potential [16].

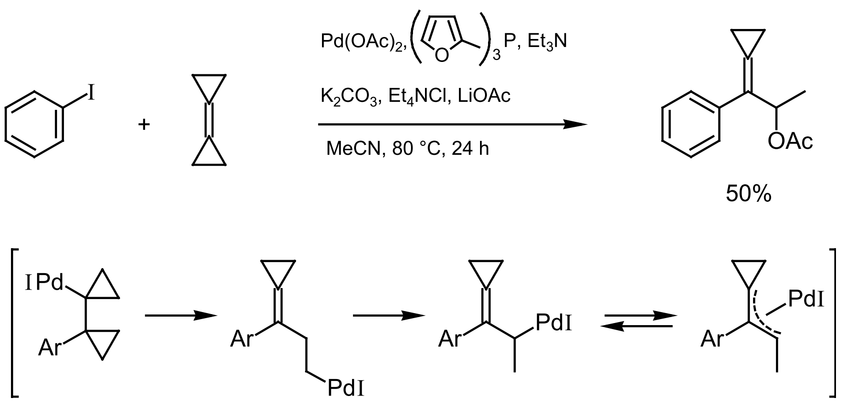
compounds, in which the sixfold coupling-cycloadditon product, at best, was a minor component.

This new three-component reaction can also be carried out on the solid phase with all the advantages of solid phase reactions in terms of facile automatization and ease of work up. Applying the triazene linker methodology, which was recently developed by Bräse et al. [18], iodobenzene bound to a Merrifield resin was treated with bicyclopropylidene and methyl acrylate in the presence of a palladium catalyst cocktail (Jeffery protocol) to yield the coupling-cycloadduct (Scheme 10) [16].

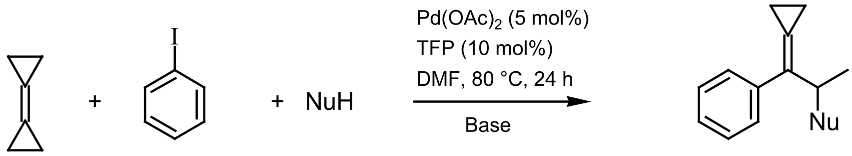
The triazene linker has two favorable features, in that it can be cleaved off without leaving a trace, or else in combination with yet another cross-coupling step. Upon treatment with trifluoroacetic acid, a diazonium ion is formed first, and when this occurs in the presence of a palladium catalyst and another Heck-coupling partner such as cyclopentene or 2-vinylpyridine, the cleavage–cross-coupling products are obtained in rather good yields (55–78%) [16].

Yet another new three-component reaction mode involving bicyclopropylidene, an iodoarene and a nucleophile, was first observed as a side reaction, but could be further developed to predominate by tuning the conditions. It is essential to use tris(2-furyl)phosphine as a ligand to achieve good yields of the cross-coupling-nucleophilic substitution product, e.g. with acetate ion, arising from a π-allylpalladium intermediate (Scheme 11) [19].

Apparently, under these conditions the homoallylpalladium iodide intermediate, formed by the cyclopropylcarbinyl to homoallyl rearrangement, isomerizes to yield a π-allylpalladium, and the latter is regioselectively attacked by the acetate ion. This type of regioselectivity in nucleophilic substitutions of (1,1-dimethyleneallyl)palladium intermediates has been observed previously in our group [20]. In the current case, the π-



Scheme 11. Domino reaction of bicyclopropylidene involving a homoallyl- to allylpalladium rearrangement [19].



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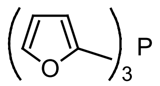
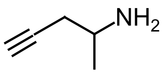
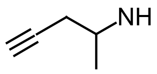
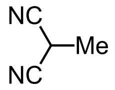
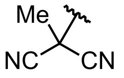
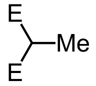
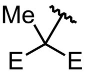


NuH	Base	Nu	%
$BnNH_2$	—	BnNH	60
$i$$BuNH_2$	—	iBuNH	85
$t$$BuNH_2$	—	tBuNH	95
	Et_3N		38
	Et_3N		77
	Et_3N		57
	E = CO_2Et		

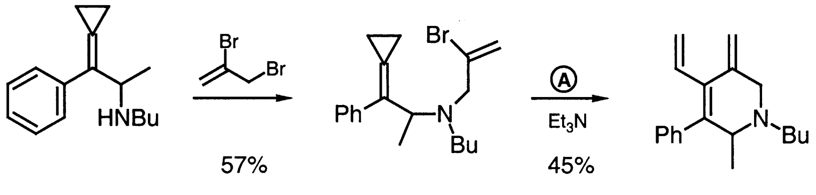
Scheme 12. The same building block, but another three-component reaction [19].

allylpalladium intermediate most probably is formed by β-hydride elimination and readdition of the hydridopalladium species with the reverse regiochemistry. This sequence of events, i.e. carbopalladation of the double bond in a methylenecyclopropane derivative, ring opening of a cyclopropylcarbinyl- to a homoallylpalladium intermediate, β-hydride elimination with readdition to give a π-allylpalladium intermediate, and finally trapping of the latter with external or internal carbon and heteroatom nucleophiles, has previously been observed and explored for synthetic applications by Fournet et al. [21,22].

The recent observation for the behavior of bicyclopropylidene opened up a new frontier, in that its cross-coupling with an iodoarene can be combined with a nucleophilic substitution. Nitrogen-centered nucleophiles can be employed with particularly high yields (up to 95%), but carbon nucleophiles also work well (Scheme 12) [19].

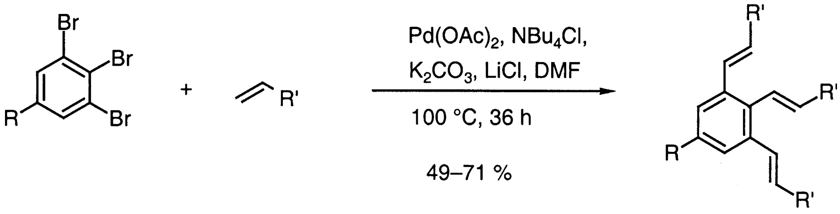
The coupling–substitution product from iodobenzene, bicyclopropylidene and n-butylamine can be further elaborated upon. Thus, treatment with 2,3-dibromopropene gave a bromodiene which could be converted by an intramolecular cross coupling to a heterocyclic cross-conjugated triene (Scheme 13) [17b], which is set up for domino-Diels–Alder reactions in analogy to the carbocyclic systems mentioned above (Scheme 5).

Twofold cross-coupling reactions of dihaloarenes have been reported as early as 1972 by Heck et al. [23], however, the same group claimed in 1990 that a threefold cross-coupling even of an activated 1,2,3-triiodobenzene derivative could not be achieved [24]. By choosing the proper conditions, i.e. in this case using the Jeffery protocol, we were able to establish threefold cross-coupling reactions with unsubstituted and 5-substituted 1,2,3-tribromobenzene derivatives in rather good yields (49–71%) (Scheme 14) [25].



Ⓐ : $Pd(OAc)_2$ (5 mol%), Ph_3P (10 mol%), DMF, 80 °C, 24 h

Scheme 13. Bicyclopropylidene, yet another dimension [17b].



R	H	H	H	NO$_2$	NO$_2$	NH$_2$
R'	Ph	CO$_2$Me	*p*-Me-Ph	Ph	CO$_2$Me	Ph

Scheme 14. Efficient threefold Heck coupling of 1,2,3-tribomobenzenes under Jeffery conditions [25].

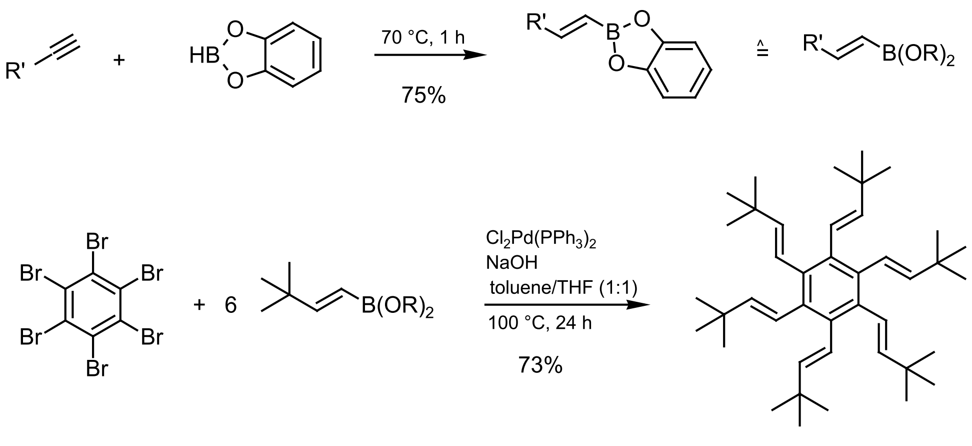
This observation naturally triggered attempts to carry out fourfold, fivefold and even sixfold alkenylations of the corresponding oligobromobenzene derivatives. In fact, the sixfold coupling of hexabromobenzene with styrene occurred with a remarkable efficiency, and gave in very good yield a product showing the correct relative molecular mass of the sixfold coupling product, but NMR-spectroscopy disclosed that this product was a multi-component mixture of different isomers arising from intramolecular ring closures between vicinal phenylvinyl substituents. Pure isomers have never been isolated from this mixture, yet the reason for these side reactions was elaborated by model studies of the twofold coupling of 1,2-dibromobenzene with different alkenes [26]. Once the mechanism of this side reaction had been rationalized, it was obvious how this difficulty could be circumvented, namely by applying the Suzuki instead of the Heck coupling [27].

Incidentally, the first ever sixfold Suzuki coupling that Peter Prinz tried in our laboratory, was that of catechol *tert*-butylethenylboronate which was prepared by hydroboration of *tert*-butylacetylene with catecholborane, and this reaction gave the sixfold coupling product in up to 73% yield (Scheme 15) [28].

When analogous coupling reactions of hexabromobenzene were attempted with styryl- or *n*-hexyl-substituted boronates, the sixfold coupling products could not be obtained. Apparently, the steric demand of the *tert*-butyl groups is beneficial for this sixfold coupling to occur with such high yields, and this may have to do with attractive van der Waals interactions during the self assembly in the consecutive coupling steps. An X-ray crystal structure analysis disclosed that all six arms of the hexakis(*tert*-butylethenyl)benzene (Scheme 15) are on the same side of the molecule, making it an interestingly cup-shaped molecule (Fig. 1).

However, the *tert*-butyl groups are not essential for a hexavinylbenzene to have this shape in the crystal, since even the unsubstituted hexaethenylbenzene has the same structural feature [29]. On the other hand, the six *tert*-butyl-substituted arms on a benzene ring do not necessarily lead to a cup-shaped molecule, since hydrogenation of the hexakis(*tert*-butylethenyl)benzene, which occurred readily in hexane solution at room temperature, gave the corresponding hexakis(*tert*-butylethyl)benzene (89% yield) which, in the crystal, had its six arms alternating up and down (Scheme 16).

Yet, the sixfold coupling went reasonably well, whenever the *tert*-butyl groups were mimicked with groups of similar size. Thus, the hexakis(2-adamantylethenyl)-substituted benzene could be obtained by a sixfold Suzuki coupling [28], and the hexakis(trimethylsilylethenyl)-substituted compound was obtained by a sixfold Stille coupling [6] of hexabromobenzene with tri-



Scheme 15. The solution: sixfold Suzuki coupling [28].

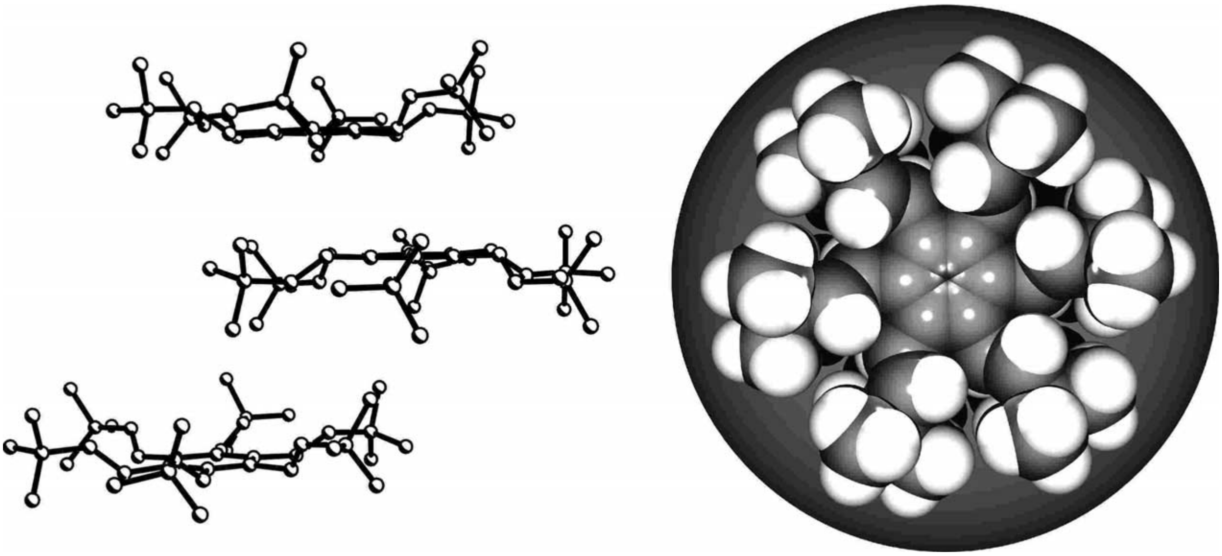
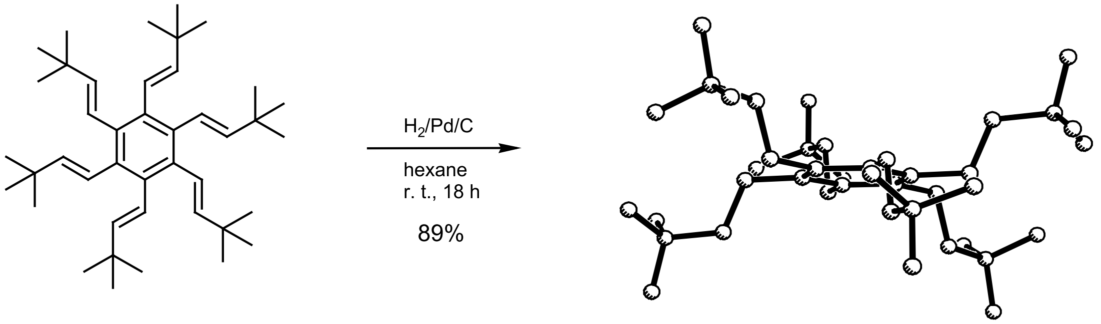
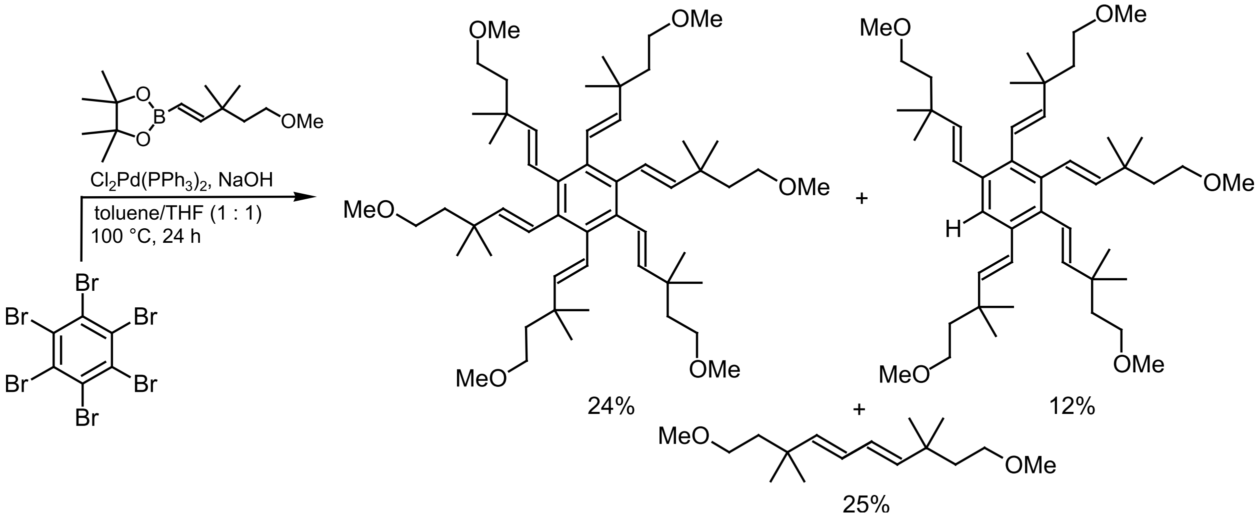


Fig. 1. Hexakis(*tert*-butylethenyl)benzene—a cup-shaped molecule (at least in the crystal) [28].



Scheme 16. Catalytic hydrogenation of hexakis-(2-*tert*-butylethenyl)benzene [28].



Scheme 17. A functionally substituted hexakis(*tert*-alkylethenyl)benzene by sixfold Suzuki cross coupling of hexabromobenzene [30].

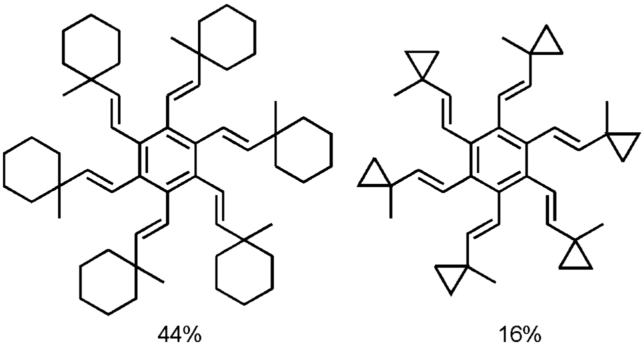


Fig. 2. More hexakisalkenylbenzene derivatives by sixfold Suzuki couplings [30].

n-butyl(2-trimethylsilylethenyl)stannane [28]. With other mimics of the *tert*-butyl group, such as the 1-methylcyclohexyl or the smaller 1-methylcyclopropyl groups the sixfold Suzuki coupling also worked moderately well (Fig. 2) [30].

In these latter cases, the pentakis(1-methylcycloalkylethenyl)benzene derivatives arising from five-fold coupling and single reduction, were the major products (53 and 40% yield, respectively) (Fig. 2).

A functionally substituted hexakis(*tert*-alkylethenyl)benzene could be obtained by sixfold Suzuki coupling of a correspondingly methoxymethyl-substituted *tert*-butylethenylboronate (Scheme 17) [30].

This compound, in contrast to the parent hexakis(*tert*-butylethenyl)benzene, turned out to have its six arms alternating up and down, at least in the crystal (Fig. 3).

An eightfold Suzuki coupling of octabromonaphthalene could not be brought about, however, the sixfold coupling of catechol *tert*-butylethenylboronate with hexabromotriphenylene succeeded particularly well with a 93% yield of the corresponding product (Scheme 18) [30].

3. Conclusion

Multiple cross-coupling reactions of dihalocycloalkenes and oligohaloarenes can be achieved in very high yields, if the conditions are properly adjusted. Combination of Stille- and Heck-type couplings of 2-bromocyclohexenyl triflates with subsequent thermal 6π-electrocyclization and hydrolysis lead to cyclohexenone-annelated systems. Cascades of carbopalladation, rearrangement and [4+2] cycloaddition or nucleophilic substitutions with bicyclopropylidene, aryl iodides and dienophiles or nucleophiles constitute two new classes of

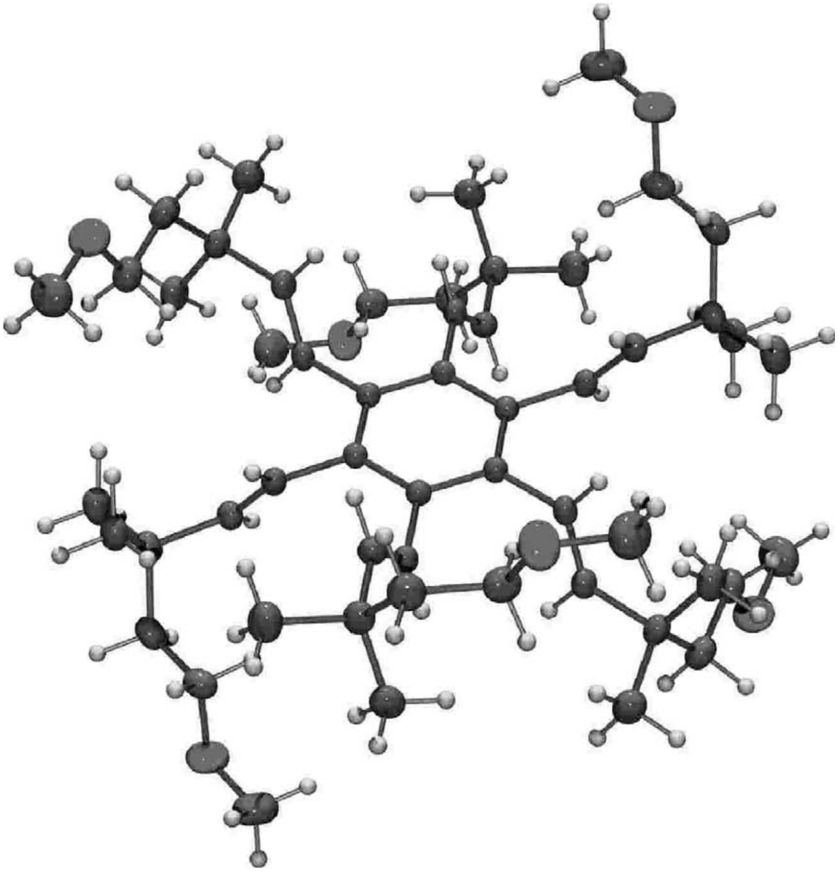
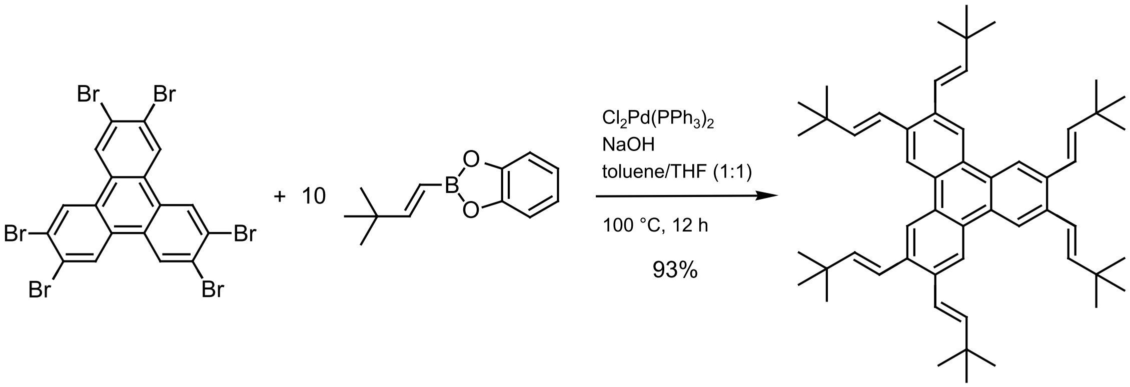


Fig. 3. A surprise: the functionally substituted six arms are up and down [30].



Scheme 18. Sixfold Suzuki coupling of hexabromotriphenylene [30].

three-component reactions with a remarkable combinatorial potential. Sixfold Suzuki and Stille couplings of hexabromoarenes lead to interesting cup-shaped molecules with extraordinary efficiency.

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