Carbocupration/Zinc Carbenoid Homologation and β-Elimination Reactions for a New Synthesis of Allenes − Application to the Enantioselective Synthesis of Chiral Allenes by Deracemization of sp^3-Organometallic Derivatives

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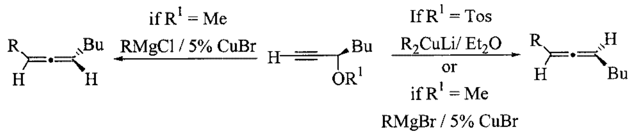
A new and straightforward carbocupration/zinc homologation/β-elimination reaction sequence allows the one-pot synthesis of polysubstituted allenes from acetylenic sulfoxides in excellent isolated chemical yields. Secondary zinc carbenoids were used for the homologation reaction, and so a new synthesis of 1,1-diiodoalkanes is described. This methodology also allows the synthesis of chiral allenes through thermodynamic equilibration of secondary organometallic derivatives.

I. Introduction

Allenes are an important class of molecules with high chemical reactivity, due to their cumulated double bonds.[1] The most popular method for their preparation is the treatment of propargylic derivatives with organocopper reagents.[2] Since the first report, by Crabbe et al.,[3] many authors have used modified organocopper reagents, with stoichiometric or catalytic amounts of copper salt. The propargylic substrate itself varies from ethers and epoxides to various esters of greater or lesser reactivity.[4] Matters concerning the mechanism and the stereochemistry of this substitution reaction have been elucidated by the use of chiral propargylic esters.[5] In this case, an overall *anti* process between the nucleophile and the leaving group, through a Cu^{III} intermediate, was postulated.[6] On the other hand, when the reaction is performed on chiral propargylic ethers rather than esters, the stereochemical outcome is dependant on the experimental conditions:[7] (1) with the use of a stoichiometric amount of organocopper reagent, the reaction proceeds by carbometalation across the alkyne, followed by *anti* β-elimination,[8] while (2) with the use of a catalytic amount of copper salt in the presence of alkylmagnesium halide, the reaction also proceeds by carbometallation, but this is then followed by either *syn* or *anti* β-elimination according to the nature of the Grignard reagent halide, BuMgCl promoting the *syn* elimination whereas BuMgBr and BuMgI promote an *anti* elimination (Scheme 1).[9]



Scheme 1. Stereochemical outcome of the carbometalation of propargylic derivatives

The stereochemistry therefore depends on the organometallic reagents, on the solvent, and on the type of leaving group used. In many cases, however, allenes are contaminated by the presence of alkynyl isomers resulting from direct S_N2 processes (particularly for the preparation of mono- and 1,1-disubstituted propadienes).[10] Several factors influence this distribution and as a consequence, tedious separations are required.[11]

We therefore wished to develop an alternative and general approach that would avoid the formation of these isomeric alkynes in the reaction mixture. We have recently reported preliminary studies[12] based on the use of a totally different concept, and we would like to describe our results in full here with an application to the synthesis of chiral allenes.

II. Results and Discussion

It is well known that monoalkylcopper reagents **1** react with α,β-acetylenic sulfoxides **2** in a highly stereoselective manner to produce excellent yields of β-β′ alkylated α,β-

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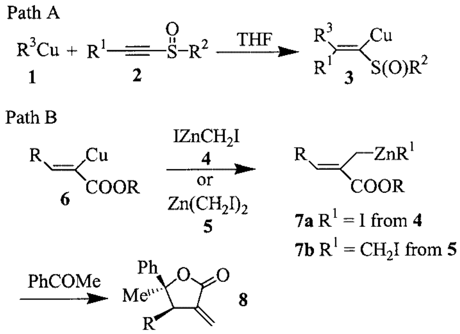
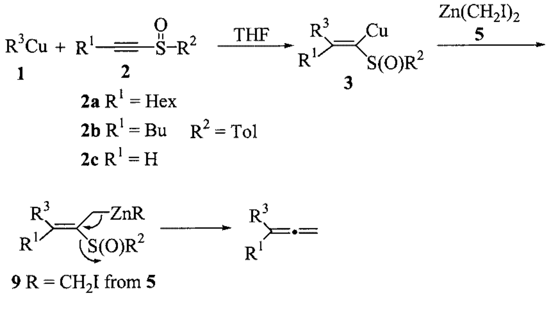
ethylenic sulfoxides **3** (Scheme 2, path A).[13] The product of *cis* addition of R^3 and Cu to the triple bond was formed exclusively, and the addition took place even with terminal acetylenic sulfoxides (R^1 = H).[13]



Scheme 2. Carbocupration of alkynyl sulfoxide and zinc homologation of vinylcopper

On the other hand, zinc carbenoids[14] such as (iodomethyl)zinc iodide (**4**)[15] or bis(iodomethyl)zinc (**5**),[16] principally used for cyclopropanation reactions,[17] have recently found new applications for homologation of organocopper derivatives and provide new zinc-copper species.[18] When applied to vinylcopper derivatives such as **6**, the corresponding allylic zinc compounds **7a** and **7b** were quantitatively formed and efficiently trapped with carbonyl derivatives to produce α-methylene-γ-butyrolactones **8** with excellent stereoselectivities (Scheme 2, path B).[19]

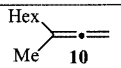
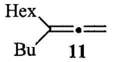
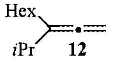
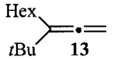
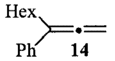
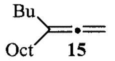
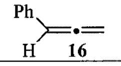
We therefore reasoned that (1) carbocupration of alkynyl sulfoxides **2** by use of an organocopper reagent (generated by the addition of 1 equiv. of RMgBr to 1 equiv. of CuBr in THF) according to path A in Scheme 2, followed by (2) zinc homologation of the resulting vinylcopper compound **3** with the primary zinc sp^3-carbenoid **5** (prepared by treatment of Et_2Zn with CH_2I_2 in THF) should result in the formation of the allylzinc derivative **9**, and (3) a spontaneous *syn* β-elimination[20] should give the corresponding allene in a one-pot operation as shown in Scheme 3.



Scheme 3. General scheme for the carbocupration/zinc homologation/β-elimination sequence

We indeed found that this combined three-step reaction afforded mono- and 1,1-disubstituted propadienes in excellent isolated yields as described in Scheme 3 and Table 1.

Table 1. Synthesis of 1,1-disubstituted allenes

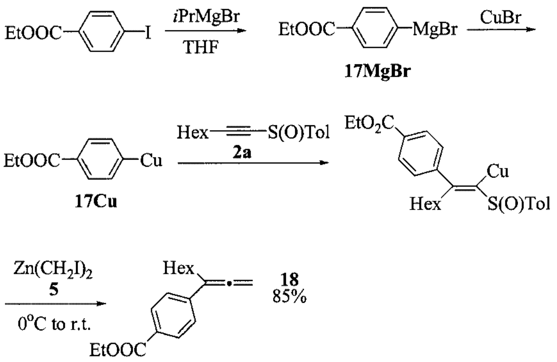
Entry	R^1	R^3	allenes	Yield (%)[a]
1	Hex **2a**	Me	 **10**	75
2	Hex **2a**	Bu	 **11**	80
3	Hex **2a**	*i*Pr	 **12**	65
4	Hex **2a**	*t*Bu	 **13**	50
5	Hex **2a**	Ph	 **14**	95
6	Bu **2b**	Oct	 **15**	80
7	H **2c**	Ph	 **16**	85

[a] Based on pure isolated products.

The scope of this reaction is broad, since primary (Me, Bu, and Oct; Entries 1, 2, and 6), secondary (Entry 3), and even tertiary alkyl groups (Entry 4) all added cleanly to alkynyl sulfoxides **2a** and **2b** to afford the corresponding vinylcopper species and then to the allene through the homologation/β-elimination sequence. Although the yield decreases slightly, as would be expected, with the degree of substitution on the alkylcopper compound (compare Entries 1, 2, and 6 to 3 and 4),[21] the reaction proceeded smoothly in all cases. Even arylcopper adds cleanly to both the octynyl and the ethynyl sulfoxides (**2a** and **2c**, respectively) to give the corresponding allenes in excellent yields (Table 1, Entries 5 and 7). The exact nature of the allylic intermediate **9** is not known, but it can be viewed as a mixed zinc-copper cluster.

It is interesting to note that although the methyl and the phenyl carbocupration reactions are known to be very sluggish reactions,[21] the slight activation generated by the sulfoxide moiety allows the reaction to proceed.

The recently reported iodine/magnesium exchange reaction for the preparation of functionalized magnesium reagents[22] also enhances the scope of the synthesis of 1,1-disubstituted propadiene. Indeed, treatment of ethyl 4-iodobenzoate with *i*PrMgBr gave the corresponding functionalized arylmagnesium halide **17MgBr** (Scheme 4). The organocopper compound **17Cu** was produced through a transmetalation reaction with copper salt, and added to the alkynyl sulfoxide **2a** as described in Scheme 4. This is the first example of a carbocupration reaction between an alkyne and a functionalized aryl derivative and it occurred quantitatively.[23] Addition of **2a** to the functionalized organocopper reagent **17Cu** at room temperature, followed by the homologation/β-elimination reaction, then gave the expected allene **18** in 85% isolated yield (based on the starting

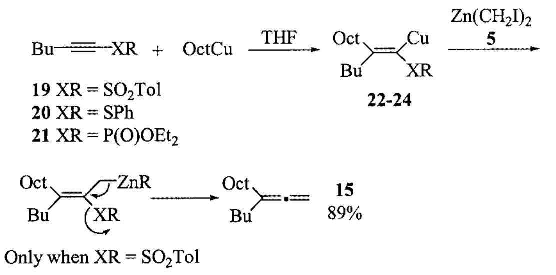


Scheme 4. Preparation of functionalized allenes

4-ethyl iodobenzoate after five consecutive steps, Scheme 4).

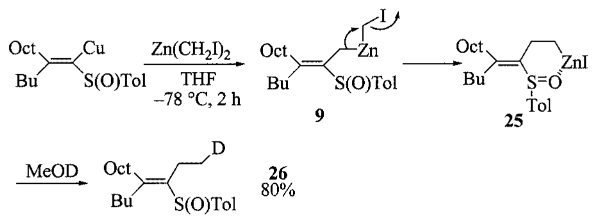
When the carbocupration of **2b** with an octylcopper reagent was followed by the homologation reaction with (iodomethyl)zinc iodide (**4**) instead of the bis(iodomethyl)zinc (**5**) and then β-elimination, the yield of **15** was lower (70%).

Several different heterosubstituted alkynes, such as alkynyl sulfone **19**,[24] alkynyl sulfide **20**,[25] and alkynylphosphonate **21**,[26] were tested in this sequence. In all cases the carbocupration reaction with an octylcopper reagent gave the expected vinylcopper derivatives **22**−**24**, but only the alkynyl sulfone gave the corresponding allene **15** (Scheme 5) on treatment with the zinc carbenoid **5**.



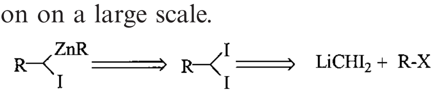
Scheme 5. Allene synthesis from alkynyl sulfones

The homologation step with the carbenoid has to be performed between 0 °C and room temperature in order to provide spontaneous β-elimination. At lower temperature, the more reactive allylic organometallic derivative **9** (Scheme 3) underwent a second homologation reaction (intra- or intermolecularly) to give the homoallylzinc compound **25** in good yield (the homoallylzinc derivative **25** is much less reactive than the parent allylzinc compound **9**). The presence of this organometallic derivative was confirmed by the isolation of **26** after treatment with MeOD.



Scheme 6. Double homologation reaction

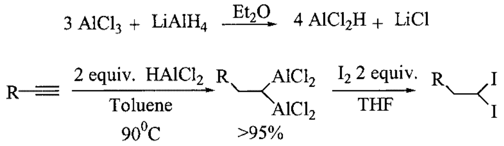
We then turned our attention to the synthesis of 1,3-di- and 1,1,3-trisubstituted propadienes.[27] In this context, it was necessary to perform the homologation reaction with a secondary zinc carbenoid. Their uses in organic synthesis, however, are mainly limited[28] to their in situ preparation for cyclopropanation reactions.[29] Moreover, secondary carbenoid derivatives are generally prepared from geminal dihaloalkanes by metal/halogen exchange and more specifically from 1,1-diiodoalkanes, since they are far more reactive than the other halogens (Scheme 7).[30] Unfortunately, 1,1-diiodoalkanes are also more difficult to prepare because of this high C−I bond reactivity. Indeed, few methods have been reported for their preparation,[31] and to date the more versatile approach is based on alkylation of diiodomethyllithium or diiodomethylsodium with reactive electrophiles.[32] The major drawback of this strategy is that these reactants are unstable at temperatures above −95 °C, which precludes preparation on a large scale.



Scheme 7. Preparation of secondary carbenoids

Preparation of Geminal Dihaloalkane Derivatives

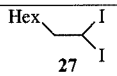
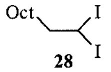
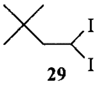
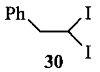
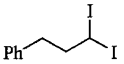
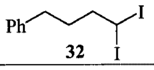
We thus needed a more general approach for the preparation of 1,1-diiodoalkanes, allowing access to a large variety of carbon skeletons on multigram scales. For this purpose, we investigated the iodolysis of dimetalated sp^3-alkanes[33] and − more specifically − the iodolysis of 1,1-dialuminioalkanes.[34] Although they are readily accessible by double hydroalumination of 1-alkynes with DIBAL-H,[34] the use of a hydroaluminating reagent without a transferable alkyl group, such as dichloroaluminium hydride ($HAlCl_2$),[35] turned out to be the most successful. This reagent was easily obtained by mixing aluminium chloride with lithium aluminium hydride[36] as described in Scheme 8 and Table 2.



Scheme 8. Double hydroalumination reaction of alkynes

The LiCl formed during the preparation of $HAlCl_2$ is not troublesome for the following step and no separation was required. The double hydroalumination of various alkynes with $HAlCl_2$ occurs in very high yields (> 95%) even on a large scale (except for Entry 3, Table 2). Moreover, the addition of 2 equiv. of I_2 at 0 °C results in the formation of 1,1-diiodoalkane derivatives **27**−**32** as described in Scheme 8 and Table 2. In the experiments described in Entries 1, 2, and 6 the yields of 1,1-diiodoalkanes are good. For the double hydroalumination of *tert*-butylacetylene (Entry 3)

Table 2. Synthesis of 1,1-diiodoalkanes

Entry	R	Products	Yield (%)[a]
1	Hexyl	 **27**	81
2	Octyl	 **28**	75
3	*ter*Bu	 **29**	52
4	Ph	 **30**	50
5	PhCH$_2$	 **31**	46
6	PhCH$_2$CH$_2$	 **32**	75

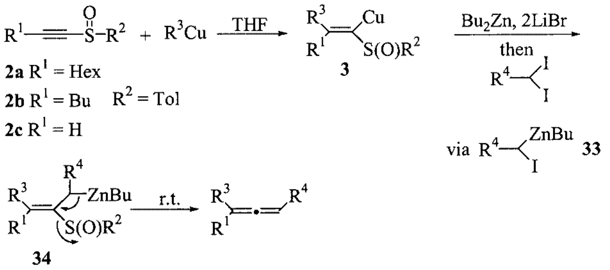
[a] Based on pure isolated products.

the yield is lower since it was difficult to obtain the corresponding bis[1,1-(dichloroaluminio)]-3,3-dimethylbutane in good yield (the starting material is very volatile). The presence of an electron-withdrawing substituent on the triple bond, as in phenylacetylene (Entry 4), increases the acidity of the acetylenic hydrogen atom and hence results in increased metalation during the double hydroalumination. Thus, treatment of phenylacetylene with 2 mol-equiv. of $HAlCl_2$ in toluene produces the expected product but a possible metalation of the triple bond could impair the yield of the bis(alane) (Entry 4). In a similar way, when the reaction is performed on 3-phenyl-1-propyne (Entry 5) the presence of acidic benzylic and propargylic hydrogen atoms decreases the yield. Moreover, the hydrolysis of the reaction mixture is also a crucial step and needs to be done at 0 °C. Indeed, after iodinolysis, 2 equiv. of the strong Lewis acid $IAlCl_2$ are present in the reaction and can affect the chemical yield.[37]

Synthesis of 1,3-Di- and 1,1,3-Trisubstituted Propadiene Derivatives

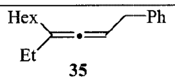
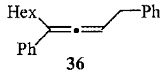
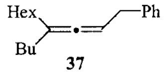
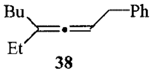
Once this new route to a large quantity of 1,2-diiodoalkanes was resolved, we came back to the preparation of 1,3-di- and 1,1,3-trisubstituted propadiene derivatives by our methodology. As discussed previously, it was necessary to perform the homologation reaction with a secondary zinc carbenoid. However, as their uses in organic synthesis had always been limited to their in situ preparation, we designed our strategy in such a way that, as soon as the secondary zinc carbenoid had been formed in the reaction mixture, it would react with the vinylcopper compound **3**.

Indeed, after the carbocupration of **2a** or **2b**, dibutylzinc (prepared by treatment of 2 equiv. of *n*BuLi with $ZnBr_2$) was added to the reaction mixture first, followed by the 1,1-diiodoalkane **27** or **30** at room temperature as described in Scheme 9. The expected 1,3-di- and 1,1,3-trisubstituted allenes were formed in excellent yields within 30 min, as reported in Table 3.



Scheme 9. General scheme for the carbocupration/secondary zinc homologation/β-elimination sequence

Table 3. Synthesis of 1,3-di- and 1,1,3-trisubstituted allenes

Entry	R^1	R^3	R^4	allenes	Yield (%)[a]
1	Hex **2a**	Et	CH$_2$Ph	 **35**	90
2	Hex **2a**	Ph	CH$_2$Ph	 **36**	84
3	Hex **2a**	Bu	CH$_2$Ph	 **37**	85
4	Bu **2b**	Et	CH$_2$Ph	 **38**	80
5	H **2c**	Et	CH$_2$Ph	 **39**	82
6	H **2c**	Oct	Bu	 **40**	85

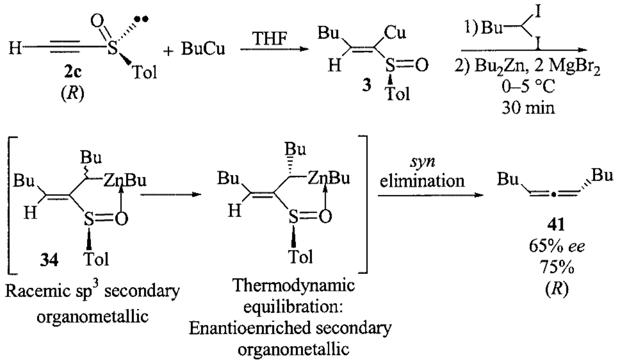
[a] Based on pure isolated products.

A plausible mechanism for this reaction can be described as follows: the secondary carbenoid **33** formed in situ (generated by the reaction between Bu_2Zn, 2 LiBr, and **30**)[38] reacted with the vinylcopper compound **3** to give the homologated product **34** as an unstable intermediate, which underwent an instantaneous β-elimination to furnish the corresponding allenes **35−40** (see Table 3) in excellent yields.[12]

Enantioselective Synthesis of Allenes

Finally, we wanted to use this new approach for the asymmetric synthesis of allenes. In this case, the critical step is the equilibration of the sp^3-allylic organometallic compound **34** before the β-elimination reaction (see Scheme 10). Intramolecular chelation between the zinc organometallic compound and a heteroatom of **34** is thus necessary. An *anti* relationship between the tolyl and the alkyl groups, through a thermodynamic equilibration[39] (or deracemization if related to an existing chiral center), should therefore be expected. Van der Kerk et al.[40] established that dialkylzinc reagents bearing heteroatoms at the γ position, such as $Zn[(CH_2)_3ZR]_2$ with Z = N, O, S are chelated, monomeric species in benzene solution, and display a spiro structure with N coordinating better than O, and O better than

S. If so, then the presence of a double bond in **34** should not change this intramolecular chelation (Scheme 10). The preparation of our starting material, chiral ethynyl *p*-tolyl sulfoxide (**2c**), was performed by sulfinylation of the commercially available 1-(trimethylsilyl)acetylene with (*R*)-menthyl sulfinate, by the previously reported method.[41]



Scheme 10. Enantioselective synthesis of dibutylallenes

When chiral sulfoxide **2c** of (*R*) configuration was treated with BuCu·$MgBr_2$, followed by our standard zinc homologation/β-elimination conditions (as described in Scheme 9) optically active dibutylallene **41** of (*R*) configuration was obtained in good yield and in 51% enantiomeric excess. The enantiomeric excess of the dibutylallene was determined by gas chromatography analysis with a cyclodextrin-B stationary phase.[42] The absolute configuration of the starting material and of the final allene implies that the intermediate allylic zinc derivative **34** undergoes an epimerization into the most stable intermediate in which the tolyl and the butyl groups are indeed *anti* to each other, followed by a *syn* β-elimination as described in Scheme 10. When the same reaction was performed between 5 and 10 °C (instead of at room temperature) the enantiomeric excess increased slightly, to 58% in comparable yield. After several experiments, we found that the best enantiomeric excess (*ee* 65% and 75% yield) was obtained when the zinc carbenoid was prepared by treatment of the 1,1-diiodoalkane with Bu_2Zn, 2 $MgBr_2$ (by treatment of $ZnBr_2$ with 2 equiv. of BuMgBr) and when the reaction mixture was stirred between 0 and 5 °C for 30 min as described in Scheme 10.

This effect of the magnesium salt on the enantioselectivity of the reaction indicates that further investigations are needed to elucidate the mechanism of this reaction completely. As mentioned before, the exact nature of the allylic intermediate **34** is unknown and could be regarded as a mixed cluster (zinc-copper- or magnesium-type). However, as the reaction is a relatively fast process (maximum 30 min at 5 °C), the possible racemization of the chiral allene by a reversible single-electron-transfer process mediated by the organocopper compound, cuprates or by Cu^0, does not play an important role in this reaction.[43] Indeed, on the principle that a good ligand to copper might avoid the formation of Cu^0 by decomposition of the organocopper species and therefore the racemization process, the same reaction was performed with a complexed copper salt such as a triethyl phosphite complexed copper salt.[7] No improvement in the enantioselectivity was observed (*ee* 60%, but in a lower yield of 50%).

Conclusion

The formation of several polysubstituted allenes from acetylenic sulfoxides and sulfones can be achieved in an easy and straightforward way. This sequence involves carbocupration followed by a zinc carbenoid homologation and finally by a *syn* β-elimination reaction. This strategy also allowed the preparation of functionalized allenes in a one-pot procedure. The separation of the final allene is very easy in all cases, since no isomeric alkynes can be formed as nonpolar products.

A new synthesis of 1,1-diiodoalkanes by a double hydroalumination reaction of terminal alkynes is also reported, and allows the syntheses of secondary carbenoids and thus of 1,3-di- and 1,1,3-trisubstituted allenes. Finally, a thermodynamic equilibration (or deracemization) of secondary organometallic derivatives before the *syn* β-elimination opens a new route to chiral 1,3-disubstituted allenes.

Experimental Section

General: Experiments involving organometallic compounds were carried out under a positive pressure of dry argon. All glassware was oven-dried at 150 °C overnight and assembled quickly while hot under a stream of argon. Liquid nitrogen was used as a cryogenic fluid and all indicated temperatures, unless otherwise stated, refer to internal values. Diethyl ether and THF were distilled from sodium benzophenone ketyl. Diethylzinc (1 M solution in hexane), *n*-butyllithium (1.6 M solution in hexane), diiodomethane, zinc bromide, and copper(I) bromide were purchased from Aldrich Chemical Co Inc. Grignard reagents were prepared and titrated before use. $ZnBr_2$ was melted under a stream of argon and handled as a 1 M solution in diethyl ether. Organolithium reagents were titrated with 2-butanol (1 M in toluene) with 1,10-phenanthroline as indicator. NMR spectra were recorded with Bruker AC 400 or Bruker AC 200 machines in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard (0.1%) in ^1H NMR spectra. In ^{13}C NMR spectra, $CDCl_3$ (δ = 77.2 ppm) was used as a reference.

General Procedure for the Synthesis of 1,1-Disubstituted Allenes: A solution of alkynyl sulfoxide (2 mmol) in 3 mL of THF was added at −70 °C to a suspension of organocopper compound (2 mmol Grignard reagent + 2 mmol CuBr) in 9 mL of THF and the mixture was kept at that temperature for 30 min. It was then allowed to warm to 20 °C over 30 min. Meanwhile, diiodomethane (0.97 mL, 12 mmol) was added at −50 °C to a stirred solution of diethylzinc (0.75 M in hexane, 6 mmol) in 8 mL of THF. It was then allowed to warm to 0 °C over 30 min and kept at that temperature for 15 min. The zinc carbenoid solution was then again cooled to −50 °C, transferred by cannula to the vinylcopper solution, and kept at 20 °C for 5 min. The reaction mixture was then stirred for another 10 min at 25 °C and then quenched with 2:1 aqueous NH_4Cl/NH_4OH solution. After conventional diethyl ether workup, the crude product was purified by filtering through silica gel with hexane as eluent.

General Procedure for the Synthesis of 1,3-Di- and 1,1,3-Trisubstituted Allenes: A solution of alkynyl sulfoxide (2 mmol) in 3 mL of THF was added at −70 °C to a suspension of organocopper compound (2 mmol Grignard reagent + 2 mmol CuBr) in 9 mL of THF and the mixture was kept at that temperature for 30 min. It was then allowed to warm to 20 °C over 30 min. Meanwhile, *n*-butyllithium (1.5 M in hexane, 8 mmol) was added at −40 °C to a stirred solution of zinc bromide (0.91 g, 4 mmol) in 8 mL of THF. It was then kept at 0 °C for 30 min and for another 30 min at 25 °C. The dibutylzinc solution was then added to the vinylcopper solution by syringe and stirred for 5 min. Next, a solution of 1,1-diidophenylethane in 8 mL of THF was added dropwise over 10 min. The reaction mixture was then stirred for another 30 min at 25 °C and was then quenched with 2:1 aqueous NH_4Cl/NH_4OH solution. After conventional diethyl ether workup, the crude product was purified by filtering through silica gel with hexane as eluent.

3-Methyl-1,2-nonadiene (10):[44] Colorless liquid. Isolated yield 75% (200 mg). ^{1}H NMR: δ = 0.83 (t, *J* = 6.5 Hz, 3 H), 1.238−1.42 (m, 8 H), 1.64 (t, *J* = 3 Hz, 3 H), 1.87−1.95 (m, 2 H), 4.53−4.59 (m, 2 H) ppm. ^{13}C NMR: δ = 14.05, 18.67, 22.68, 27.44, 29, 31.79, 33.56, 73.65, 98.41, 206.29 ppm. $C_{10}H_{18}$ (138.24): calcd. C 86.87, H 13.12; found C 86.91, H 13.10.

3-Butyl-1,2-nonadiene (11): Colorless liquid. Isolated yield 80%. (290 mg). ^{1}H NMR: δ = 0.83 (m,6 H), 1.26−1.43 (m, 12 H), 1.87−1.9 (m, 4 H), 4.58−4.64 (m, 2 H) ppm. ^{13}C NMR: δ = 13.92, 14.04, 22.48, 22.7, 27.58, 29.1, 29.81, 31.82, 31.9, 32.21, 75.09, 103.26, 205.84 ppm. $C_{13}H_{24}$ (180.32): calcd. C 86.58 H, 13.41; found C 86.52 H, 13.47.

3-(Isopropyl)-1,2-nonadiene (12): Colorless liquid. Isolated yield 65%. (215 mg). ^{1}H NMR: δ = 0.83 (t, *J* = 6.4 Hz, 3 H) 0.98 (d, *J* = 6.9 Hz, 6 H), 1.24−1.42 (m, 8 H), 1.86−1.95 (m, 2 H), 1.96−2.21 (m, 1 H), 4.63−4.68 (m, 2 H) ppm. ^{13}C NMR: δ = 14.08, 21.64, 22.73, 27.81, 29.21, 29.79, 30.38, 30.46, 31.87, 76.46, 109.77, 204.88 ppm.

3-*tert*-Butyl-1,2-nonadiene (13): Colorless liquid. Isolated yield. 50%. (180 mg). ^{1}H NMR: δ = 0.83 (t, *J* = 6.13 Hz, 3 H), 1.02 (s, 9 H), 1.24−1.41 (m, 8 H), 1.85−1.9 (m, 2 H), 4.61−4.67 (m,2 H) ppm. ^{13}C NMR: δ = 14.09, 22.73, 26.59, 27.58, 28.29, 29.08, 29.28, 31.9, 76.8, 112.65, 204.66 ppm.

3-Phenyl-1,2-nonadiene (14):[45] Colorless liquid. Isolated yield 95%. (380 mg). ^{1}H NMR: δ = 0.86 (t, *J* = 6.5 Hz, 3 H), 1.26−1.59 (m, 8 H), 2.38−2.45 (m, 2 H), 5.05 (t, *J* = 3.3 Hz, 2 H), 7.19−7.43 (m, 5 H) ppm. ^{13}C NMR: δ = 14.08, 22.71, 27.89, 29.16, 29.55, 31.78, 77.9, 105.12, 125.99, 126.48, 128.29, 136.56, 208.69 ppm. $C_{15}H_{20}$ (200.31): calcd. C 89.93 H, 10.06; found C 89.87 H, 10.14.

3-Butyl-1,2-undecadiene (15): Colorless liquid. Isolated yield 80%. (330 mg). ^{1}H NMR: δ = 0.83 −0.92(m, 6 H), 1.24−1.43 (m, 16 H), 1.87−1.92 (m, 4 H), 4.59−4.64 (m, 2 H) ppm. ^{13}C NMR: δ = 13.82, 13.96, 22.31, 22.55, 27.47, 29.19, 29.27, 29.36, 29.58, 29.67, 31.78, 32.06, 74.96, 103.23, 205.67 ppm. $C_{15}H_{28}$ (208.37): calcd. C 86.45, H 13.54; found C 86.62, H 13.48.

1-Phenylpropadiene (16):[46] Colorless oil. Isolated yield 85%. (200 mg). ^{1}H NMR: δ = 5.12 (d, *J* = 6.8 Hz, 2 H), 6.12 (t, *J* = 6.8 Hz, 1 H), 7.14−7.35 (m, 5 H) ppm.

Ethyl 4-(1-Hexylpropa-1,2-dienyl)benzoate (18): Colorless oil. Isolated yield 85%. (465 mg). ^{1}H NMR: δ = 0.83 (t, *J* = 6.4 Hz, 3 H), 1.24−1.52 (m, 11 H), 2.36−2.41 (m, 2 H), 4.28 (q, *J* = 7 Hz, 2 H), 5.07 (t, *J* = 3.2 Hz, 3 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.94(d, *J* = 8.31 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.93, 14.21, 22.53, 27.69, 28.94, 29.22, 31.58, 60.63, 78.35, 104.75, 125.65, 128.14, 129.46, 141.34, 166.31, 209.25 ppm. $C_{18}H_{24}O_2$ (272.37): calcd. C 79.36 H, 8.88; found C 79.86 H, 9.21.

4-Ethyl-1-phenyl-2,3-decadiene (35): Colorless oil. Isolated yield 90%. (435 mg). ^{1}H NMR: δ = 0.84 (t, *J* = 6.4 Hz, 3 H), 0.93 (t, *J* = 7.4 Hz, 3 H), 1.26−1.38 (m, 8 H), 1.85−1.98 (m, 4 H), 3.298 (d, *J* = 6.9 Hz, 2 H), 5.2−5.3 (m, 1 H), 7.14−7.32 (m, 5 H) ppm. ^{13}C NMR: δ = 12.37, 14.09, 22.67, 25.72, 27.75, 29.07, 31.84, 32.77, 36.55, 91.78, 106.73, 125.88, 128.22, 128.56, 141.11, 201.22 ppm. $C_{18}H_{26}$ (242.39): calcd. C 89.18 H, 10.81; found C 89.24 H, 10.63.

1,4-Diphenyl-2,3-decadiene (36): Colorless oil. Isolated yield 84%. (490 mg). ^{1}H NMR: δ = 0.97 (t, *J* = 6.3 Hz, 3 H), 1.38−1.68 (m, 6 H), 2.4−2.56 (m, 4 H), 3.54 (d, *J* = 7.1 Hz, 2 H), 5.73−5.79 (m, 1 H), 7.16−7.52 (m, 10 H) ppm. ^{13}C NMR: δ = 14.07, 22.62, 27.98, 29.1, 30.09, 31.75, 35.93, 93.66, 106.33, 126.02, 126.11, 126.44, 128.24, 128.36, 128.51, 129.74, 137.27, 140.43, 204.44 ppm.

4-Butyl-1-phenyl-2,3-decadiene (37): Colorless oil. Isolated yield 85%. (455 mg). ^{1}H NMR: δ = 0.94 (t, *J* = 6.85 Hz, 3 H), 1.36−1.51 (m, 12 H), 1.96−1.99 (m, 4 H), 3.37 (d, *J* = 6.9 Hz, 2 H), 5.25−5.35 (m, 1 H), 7.22−7.39 (m, 5 H) ppm. ^{13}C NMR: δ = 13.96, 14.07, 22.42, 22.65, 27.72, 29.07, 29.95, 31.83, 32.46, 32.75, 36.49, 91.07, 104.84, 125.87, 128.19, 128.53, 141.11, 201.52 ppm. $C_{20}H_{30}$ (270.44): calcd. C 88.81 H, 11.18; found C 88.76 H, 11.21.

4-Ethyl-1-phenyl-2,3-octadiene (38): Colorless oil. Isolated yield 80%. (345 mg). ^{1}H NMR: δ = 0.84 (t, *J* = 6.9 Hz, 3 H), 0.93 (t, *J* = 7.4 Hz, 3 H), 1.25−1.44 (m, 4 H), 1.85−1.96 (m, 4 H), 3.298 (d, *J* = 7 Hz, 2 H), 5.2−5.3 (m, 1 H), 7.14−7.32 (m, 5 H) ppm. ^{13}C NMR: δ = 12.37, 13.98, 22.42, 25.69, 29.95, 32.43, 36.55, 91.71, 106.73, 125.88, 128.22, 128.58, 141.14, 201.19 ppm.

1-Phenyl-2,3-pentadiene (39):[47] Colorless oil. Isolated yield 82%. (260 mg). ^{1}H NMR: δ = 0.99 (t, *J* = 7.4 Hz, 3 H), 2.07−1.92 (m, 2 H), 3.32 (dd, *J* = 2.8, 6.9 Hz, 2 H), 5.15−5.32 (m, 2 H), 7.15−7.33 (m, 5 H) ppm.

5,6-Pentadecadiene (40):[48] Colorless oil. Isolated yield 85%. (355 mg). ^{1}H NMR: δ = 0.83 (t, *J* = 7 Hz, 3 H), 088 (t, *J* = 7 Hz, 3 H), 1.2−1.39 (m, 16 H), 1.93−2.03 (m, 4 H), 4.99−5.06 (dt, *J* = 4.6, 9.4 Hz, 2 H) ppm. ^{13}C NMR: δ = 13.89, 14.03, 22.16, 22.51, 28.29, 28.72, 29.03, 29.11, 29.58, 29.67, 31.09, 31.59, 74.45, 90.90, 203.86 ppm.

Double Homologated Product 26: Colorless oil. Isolated yield 80%. (780 mg). ^{1}H NMR: δ = 0.64 (t, *J* = 7.2 Hz, 2 H), 0.79 (t, *J* = 6.6HZ, 3 Hz), 0.88 (t, *J* = 6.9 Hz, 3 H), 1.19−1.48 (m, 16H0, 2−2.6 (m, 6 H), 2.29 (s, 3 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.32 (D, *J* = 7.9HZ, 2 H) ppm. ^{13}C NMR: δ = 13.70, 13.84, 14.9 (t), 16.95, 17.02, 21.03, 22.44, 22.64, 27.94, 28.99, 29.21, 29.66, 31.32, 31.48, 31.61, 32.40, 124.22, 129.34, 139.84, 140.63, 140.82, 150.39 ppm.

General Procedure for the Synthesis of 1,1-Diiodoalkanes: An ethereal solution of $LiAlH_4$ (1.09 M, 1.51 mL, 1.65 mmol, 0.55 equiv.) was added at room temperature to a suspension of aluminium chloride (0.66 g, 4.95 mmol, 1.65 equiv.) in 3 mL of pentane and 7.5 mL of diethyl ether. After the mixture had been stirred for 5 min, the solvents were removed at room temperature under vacuum (20 Torr) through $CaCl_2$ to give a white suspension of LiCl and $HAlCl_2$ (6.6 mmol, 2.2 equiv.). Toluene (6 mL) was then added, followed by 1-alkyne (3 mmol, 1 equiv.). The reaction mixture was heated at 90 °C for 3 h to give the bis-1,1-(dichloroaluminio)alkane. After the mixture had been cooled to 0 °C, THF (20 mL) was added and a solution of iodine (1.675 g, 6.6 mmol, 2.2 equiv.) in cold THF (20 mL) was then added. The reaction mixture was warmed to room temperature and stirred for 15 min and was then transferred into a cold solution (0 °C) of aqueous HCl (1 M, 100 mL). After the mixture had been stirred for 5 min, the aqueous layer was extracted with diethyl ether, and the collected organic phases were washed with aq. $Na_2S_2O_3$ and saturated brine and then dried with $MgSO_4$. After filtration and evaporation of the solvents, the residue was chromatographed on silica gel.

1,1-Diiodooctane (27):[49] Isolated yield 81%. (890 mg). ^1H NMR: $\delta = 0.86$ (t, $J = 5.5$ Hz, 3 H), 1.26 (m, 10 H), 2.33 (q, $J = 7.2$ Hz), 2 H), 5.09 (t, $J = 6.5$ Hz, 1 H) ppm.

1,1-Diiodododecane (28): Isolated yield 75%. (885 mg). ^1H NMR: $\delta =$ 0.86 (t, $J = 5.5$ Hz, 3 H), 1.26 (m, 10 H), 2.33 (q, $J = 7.2$ Hz), 2 H), 5.09 (t, $J = 6.5$ Hz, 1 H) ppm.

1,1-Diiodo-3,3-dimethylbutane (29):[50] Isolated yields 52%. (525 mg). ^1H NMR: $\delta = 0.96$ (s, 9 H), 2.92 (d, $J = 6.4$ Hz, 2 H), 5.17 (t, $J = 6.4$ Hz, 1 H) ppm.

1,1-Diiodo-2-phenylethane (30):[51] Isolated yields 50%. (540 mg). ^1H NMR: $\delta = 3.7$ (d, $J = 7.4$ Hz, 2 H), 5.08 (t, $J = 7.4$ Hz, 1 H), 7.2−7.35 (m, 5 H) ppm.

1,1-Diiodo-3-phenylpropane (31):[49] Isolated yields 46%. (515 mg). ^1H NMR: $\delta = 2.12$ (q, $J = 7.0$ Hz, 2 H), 2.69 (t, $J = 5.8$ Hz, 1 H), 4.98 (t, $J = 5.8$ Hz, 1 H), 7.17−7.35 (m, 5 H) ppm.

1,1-Diiodo-4-phenylbutane (32): Isolated yields 75%. (870 mg). ^1H NMR: $\delta = 1.76$ (m, 2 H), 2.39 (dt, $J = 6.6$ Hz, 8.37 Hz, 2 H), 2.66 (t, $J = 7.7$ Hz, 2 H), 5.09 (t, $J = 6.4$ Hz, 1 H), 7.15−7.29 (m, 5 H) ppm.

Enantioselective Synthesis of 5,6-Undecadiene 41:[53] A solution of chiral ethynyl sulfoxide[41] (2 mmol) in THF (3 mL) was added at −70 °C to a suspension of organocopper compound (2 mmol Grignard reagent + 2 mmol CuBr) in 9 mL of THF and the mixture was kept at that temperature for 30 min. It was then warmed to 20 °C over 30 min. Meanwhile, *n*-butylmagnesium bromide (1 M solution in Et_2O, 8 mmol, 8 mL) was added at −40 °C to a stirred solution of zinc bromide (0.91 g, 4 mmol) in 8 mL of THF. It was then kept at 0 °C for 30 min and for another 30 min at 25 °C. The dibutylzinc solution was then added to the vinylcopper solution by syringe and the mixture was stirred for 5 min. A solution of 1,1-diiodopentane in THF (8 mL) was then added dropwise at 0 °C over 10 min. The reaction mixture was then stirred for another 30 min between 0 and 5 °C and then quenched with 2:1 aqueous NH_4Cl/NH_4OH solution. After conventional diethyl ether workup, the crude product was purified by filtering through silica gel with hexane as eluent. Dibutylallene was obtained in 75% isolated yield and in 65% enantiomeric excess.[42] $[\alpha]_D^{25} = -44.2$ ($c =$ 1.25, $HCCl_3$).[52] ^1H NMR: $\delta = 1.0$ (t, $J = 8$ Hz, 6 H), 1.44−1.6 (m, 8 H), 2 (t, $J = 10$ Hz, 4 H), 5.2 (m, $J = 10$ Hz, 2 H) ppm. ^{13}C NMR: $\delta = 13.9$, 22.2, 28.8, 31.5, 90.8, 204 ppm. IR 1370, 1450, 1960, 2980 ppm.

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[1] For reviews, see: [1a] L. Brandsma, H. D. Verkruijsse in *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier, New York, **1981**. [1b]W. Smadja, *Chem. Rev.* **1983**, *83*, 263. [1c] D. J. Pasto, *Tetrahedron* **1984**, *40*, 2805. [1d] J. A. Marshall, *Chem. Rev.* **2000**, *100*, 3163. [1e] A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2000**, *39*, 3590.

[2] [2a] H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, Wiley-Interscience, New York, **1984**. [2b] *Modern Organocopper Chemistry* (Ed.: N. Krause), Wiley-VCH, Weinheim, **2002**.

[3] P. Rona, P. Crabbe, *J. Am. Chem. Soc.* **1968**, *90*, 4733.

[4] A. Alexakis, I. Marek, P. Mangeney, J. F. Normant, *Tetrahedron* **1991**, *47*, 1677.

[5] C. R. Johnson, D. S. Dhanoa, *J. Org. Chem.* **1987**, *52*, 1887.

[6] J. M. Dollat, J. L. Luche, P. Crabbe, *J. Chem. Soc., Chem. Commun.* **1977**, 761.

[7] A. Alexakis, I. Marek, P. Mangeney, J. F. Normant, *J. Am. Chem. Soc.* **1990**, *112*, 8042.

[8] A. Alexakis, J. F. Normant, J. Villieras, *J. Mol. Catal.* **1975/1976**, *1*, 43.

[9] I. Marek, P. Mangeney, A. Alexakis, J. F. Normant, *Tetrahedron Lett.* **1986**, *27*, 5499.

[10] [10a] M. H. Nantz, D. M. Bender, S. Janaki, *Synthesis* **1993**, 577. [10b] M. P. Doyle, V. Bagheri, E. E Claxton, *J. Chem. Soc., Chem. Commun.* **1990**, 46. [10c] P. Crabbe, E. Barreiro, J. M. Dollat, J. L. Luche, *J. Chem. Soc., Chem. Commun.* **1976**, 183. [10d] J. Tsuji, T. Sugiura, I. Minami, *Synthesis* **1987**, 603. [10e] A. G. Myers, B. Zheng, *J. Am. Chem. Soc.* **1996**, *118*, 4492. [10f] T. Satoh, Y. Kuramochi, Y. Inoue, *Tetrahedron Lett.* **1999**, *40*, 8815.

[11] R. S. Brinkmeyer, T. MacDonald, *J. Chem. Soc., Chem. Commun.* **1978**, 876.

[12] J. P. Varghese, P. Knochel, I. Marek, *Org. Lett.* **2000**, *2*, 2849.

[13] [13a] W. E. Truce, M. J. Lusch, *J. Org. Chem.* **1974**, *39*, 3174. [13b] W. E. Truce, M. J. Lusch, *J. Org. Chem.* **1978**, *43*, 2252.

[14] For a review on zinc carbenoids, see: W. B. Motherwell, C. J. Nutley, *Contemp. Org. Synth.* **1994**, *1*, 219.

[15] D. Seyferth, H. Dertouzos, L. J. Todd, *J. Organomet. Chem.* **1965**, *4*, 18.

[16] For a detailed study on the structure of halomethylzinc reagents, see: [16a] A. B. Charette, J. F. Marcoux, C. Molinaro, A. Beauchemin, C. Brochu, E. Isabel, *J. Am. Chem. Soc.* **2000**, *122*, 4508. [16b] S. E. Denmark, J. P. Edwards, S. R. Wilson, *J. Am. Chem. Soc.* **1992**, *114*, 2592. [16c] S. E. Denmark, S. P. O'Connor, *J. Org. Chem.* **1997**, *62*, 3390. [16d] S. E. Denmark, J. P. Edwards, *J. Org. Chem.* **1991**, *56*, 6974.

[17] [17a] A. B. Charette, J. F. Marcoux, *Synlett* **1995**, 1197. [17b] A. B. Charette, B. Côté, J. F. Marcoux, *J. Am. Chem. Soc.* **1991**, *113*, 8166. [17c] A. B. Charette, H. Juteau, *J. Am. Chem. Soc.* **1994**, *116*, 2651. [17d] S. E. Denmark, S. P. O′Connor, *J. Org. Chem.* **1997**, *62*, 584.

[18] [18a] P. Knochel, N. Jeong, M. J. Rozema, M. C. P Yeh, *J. Am. Chem. Soc.* **1989**, *111*, 6474. [18b] P. Knochel, T. S. Chou, H. G. Chen, M. C. P. Yeh, M. J. Rozema, *J. Org. Chem.* **1989**, *54*, 5202. [18c] P. Knochel, S. Achyutha Rao, *J. Am. Chem. Soc.* **1990**, *112*, 6146.

[19] [19a] S. Achyutha Rao, P. Knochel, *J. Am. Chem. Soc.* **1992**, *114*, 7579. [19b] S. Achyutha Rao, M. J. Rozema, P. Knochel, *J. Org. Chem.* **1993**, *58*, 2694. [19c] P. Wipf, C. Kendall, *Org. Lett.* **2001**, *3*, 2773.

[20] [20a] *Organosulfur Chemistry, Synthetic and Stereochemical Aspects* (Ed.: P. Page), Academic Press, San Diego, **1998**. [20b]A radical β-elimination of vinyl sulfoxide for the synthesis of allenes was recently published: B. Delouvrie, E. Lacote, L. Fensterbank, M. Malacria, *Tetrahedron Lett.* **1999**, *40*, 3565. [20c] An anionic β-elimination of vinyl sulfoxide for the synthesis of allenes has also been published: G. H. Posner, P. W. Tang, J. P. Mallano, *Tetrahedron Lett.* **1978**, *19*, 3995.

[21] J. F. Normant, A. Alexakis, *Synthesis* **1981**, 841.

[22] M. Rottlander, L. Boymond, L. Berillon, A. Leprete, G. Varchi, S. Avolio, H. Laaziri, G. Quequiner, A. Ricci, G. Cahiez, P.

Knochel, *Chem. Eur. J.* **2000**, *6*, 767 and references cited therein.

[23] Carbocupration of functionalized alkyl groups was reported previously: S. Achyutha Rao, P. Knochel, *J. Am. Chem. Soc.* **1991**, *113*, 5735.

[24] P. Vermeer, C. de Graaf, J. Meijer, *Recl. Trav. Chim. Pays Bas* **1974**, *93*, 24.

[25] [25a] H-J. Cristau, M-B. Gasc, X. Y. Mbianda, *J. Organomet. Chem.* **1994**, *474*, C14. [25b] J. M. Gil, D. Y. Oh, *J. Org. Chem.* **1999**, *64*, 2950.

[26] [26a] J. Meijer, P. Vermeer, *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 14. [26b] V. Fiandanese, G. Marghese, F. Naso, *Tetrahedron Lett.* **1978**, 5131.

[27] [27a] K. Ruitenberg, H. Klein, J. Meijer, E. A. Oostveen, P. Vermeer, *J. Organomet. Chem.* **1982**, *224*, 399. [27b] W. de Graaf, J. Boersma, G. van Koten, C. J. Elsevier, *J. Organomet. Chem.* **1989**, *378*, 115. [27c] S. Ma, A. Zhang, *J. Org. Chem.* **1998**, *63*, 9601.

[28] For a selective reaction of secondary zinc carbenoid generated from geminal sp^3-dimetallic species, see: F. Chemla, I. Marek, J. F. Normant, *Synlett* **1993**, 665.

[29] A. B. Charette, J. Lemay, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1090.

[30] J. Villieras, C. Bacquet, J. F. Normant, *Bull. Soc. Chim. Fr.* **1975**, 1797.

[31] [31a] A. G. Martinez, A. H. Fernandez, R. M. Alvarez, J. O. Barcina, C. G. Gomez, L. R. Subramanian, *Synthesis* **1993**, 1063. [31b] D. H. R. Barton, G. Bashiardes, J-L. Fourrey, *Tetrahedron* **1988**, *44*, 147. [31c] A. G. Martinez, A. H. fernandez, R. M. Alvarez, A. G. Fraile, J. B. Calderon, J. O. Barcina, M. Hanack, L. R. Subramanian, *Synthesis* **1986**, 1076.

[32] P. Charreau, M. Julia, J. N. Verpeaux, *Bull. Soc. Chim. Fr.* **1990**, *127*, 275.

[33] I. Marek, J. F. Normant, *Chem. Rev.* **1996**, *96*, 3241.

[34] A. M. Piotrowski, D. B. Malpass, M. P. Boleslawski, J. J. Eisch, *J. Org. Chem.* **1988**, *53*, 2829.

[35] [35a] G. Wilke, H. Muller, *Justus Liebigs Ann. Chem.* **1960**, *629*, 222. [35b] J. J. Eisch, H. Gopal, S. G. Rhee, *J. Org. Chem.* **1975**, *40*, 2064.

[36] The lithium aluminium hydride was used as an ethereal solution, which was titrated either by the iodometric method: H. Felkin, *Bull. Soc. Chim. Fr.* **1951**, *18*, 347, or with salicylaldehyde phenylhydrazone as indicator: B. E. Love, E. G. Jones, *J. Org. Chem.* **1999**, *64*, 3755.

[37] L. Aufauvre, P. Knochel, I. Marek, *Chem. Commun.* **1999**, 2207.

[38] A. Shabli, J. P. Varghese, P. Knochel, I. Marek, *Synlett* **2001**, 818.

[39] For epimerization of carbanionic centers into the thermodynamic product, see. [39a] P. G. Mc Dougal, B. D. Condon, M. D. Lafosse, Jr., A. M. Lauro, D. Vanderveer, *Tetrahedron Lett.* **1988**, *29*, 2547. [39b] R. Hoffmann, M. Bewersdorf, *Tetrahedron Lett.* **1990**, *31*, 67. [39c] D. R. Williams, J. G. Philipps, J. C. Huffman, *J. Org. Chem.* **1981**, *46*, 4101. [39d] A. Krief, M. Hobe, *Tetrahedron Lett.* **1992**, *33*, 6527. [39e] A. Krief, M. Hobe, *Tetrahedron Lett.* **1992**, *33*, 6529. [39f] P. Beak, J. E. Hunter, Y. M. Jun, A. P. Wallin, *J. Am. Chem. Soc.* **1987**, *109*, 5403. [39g] W. H. Miles, S. L. Riviera, J. D. Rosario, *Tetrahedron Lett.* **1992**, *33*, 305. [39h] A. I. Meyers, J. Guiles, J. S. Warmus, M. A. Gonzales, *Tetrahedron Lett.* **1991**, *32*, 5505. [39i] W. H. Pearson, A. C. Lindbeck, *J. Am. Chem. Soc.* **1991**, *113*, 8546. [39j] W. H. Pearson, A. C. Lindbeck, J. W. Kampf, *J. Am. Chem. Soc.* **1993**, *115*, 2622. [39k] S. Norsikian, I. Marek, J. F. Poisson, J. F. Normant, *Chem. Eur. J.* **1999**, *5*, 2055.

[40] [40a] H. K. Hofstee, J. Boersma, J. D. Van der Meulen, G. J. M. Van der Kerk, *J. Organomet. Chem.* **1978**, *153*, 245. [40b] K. H. Thiele, M. Heinrich, W. Bruser, S. Z. Schroder, *Z. Anorg. Allg. Chem.* **1977**, *432*, 221.

[41] [41a] H. Kosugi, M. Kitaoka, K. Tagami, A. Takahashi, H. Uda, *J. Org. Chem.* **1987**, *52*, 1078. [41b] J. L. Garcia Ruano, A. Esteban Gamboa, A. M. Martin Castro, J. H. Rodriguez, M. I. Lopez-Solera, *J. Org. Chem.* **1998**, *63*, 3324. [41c] K. K. Andersen, W. Gaffield, N. E. Papanikolau, J. W. Foley, R. I. Perkins, *J. Am. Chem. Soc.* **1964**, *86*, 5637 and references cited therein.

[42] We found that the chiral cyclodex-B (film thickness 0.25μm and column dimensions 30 × 0.321 mm) was very efficient for the separation of 1,3-dialkylallenes such as dibutylallene, butylethylallene, butylpropylallene, butylisopropylallene, phenylethylallene, phenylpropylallene and phenylisopropylallene.

[43] [43a] A. Claesson, L. I. Ollson, *J. Chem. Soc., Chem. Commun.* **1979**, 524. [43b] J. H. B. Chenser, J. A. Howard, B. Mile, *J. Am. Chem. Soc.* **1985**, *107*, 4190.

[44] D. Michelot, J. C. Clinet, G. Linstrumelle, *Synth. Commun.* **1982**, *12*, 739.

[45] H. Yorimitsu, J. Tang, K. Okada, H. Shinokubo, K. Oshima, *Chem. Lett.* **1998**, 11.

[46] A. Mahmood, T. Arnauld, A. G. M. Barrett, X. D. C. Braddock, K. Flack, P. A. Procopiou, *Org. Lett.* **2000**, *2*, 551.

[47] L. N. Cherkasov, V. A. Kormer, Kh. V. Bal'yan, A. A. Petrov, *Zh. Org. Khim.* **1966**, *2*, 1573.

[48] T. Harada, T. Katsuhira, A. Osada, K. Iwazaki, K. Maejima, A. Oku, *J. Am. Chem. Soc.* **1996**, *118*, 11377.

[49] A. Garcia Martinez, R. Martinez Alvarez, S. Martinez Gonzalez, L. R. Subramanian, M. Conrad, *Tetrahedron Lett.* **1992**, *33*, 2043.

[50] K. H. Heopold, R. G Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 464.

[51] R. W. Hoffmann, O. Knopff, A. Kusche, *Angew. Chem. Int. Ed.* **2000**, *39*, 1462.

[52] W. H. Pirckle, C. W. Boeder, *J. Org. Chem.* **1978**, *43*, 1950.

[53] A. Mori, J. Fujiwara, K. Maruoka, H. Yamamoto, *J. Organomet. Chem.* **1985**, *285*, 83.

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