Synthesis of Allenes by 1,6-Addition of Organocuprates to Acceptor-Substituted Enynes: Scope and Limitations

Michael Hohmann[+] and Norbert Krause*[+]

Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 22, 64287 Darmstadt, F.R.G.

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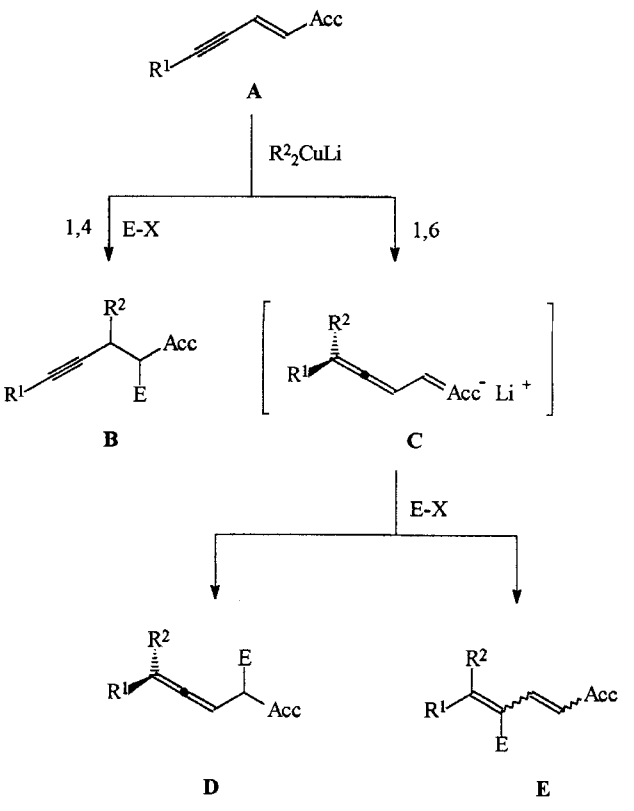
Acyclic acceptor-substituted conjugated enynes bearing sulfonyl, sulfinyl, sulfonate, nitro, amide, cyano, and oxazolidino groups at the double bond were synthesized and the regioselectivity of their reaction with organocuprates was examined. All Michael acceptors except enynes with nitro and amide functions underwent 1,6-additions, and the allenyl enolates thus formed were trapped with electrophiles in order to obtain the corresponding allenes. A qualitative reactivity scale for these reactions was established. The dependence of the regioselectivity of both the cuprate addition and the subsequent electrophilic capture on the acceptor group and the substitution pattern of the allenyl enolate were studied. Cyclic 2-en-4-ynoates with endocyclic double bonds were synthesized and treated with organocuprates to afford an exocyclic allene in one case.

Allenes are important target molecules in organic chemistry because of the appearance of the allene moiety in several natural products[1,2]. Additionally, their high reactivity allows the conversion of allenes into many other molecules, e.g. in cyclization reactions[1,3], making them again more interesting from the synthetic point of view. Recently, a new route to β-allenic carbonyl compounds with complex substitution patterns by 1,6-addition of organocuprates to acceptor-substituted enynes has been established[4]. Spectroscopic investigations of this reaction provided new insights into the mechanisms of cuprate conjugate additions[5]. So far, the 1,6-addition has been applied successfully to the synthesis of allenes with ester, thioester, keto, lactone, and dioxanone groups[4,6]. It seemed interesting to extend this method to enynes with different electron acceptors in order to obtain allenes with new functional groups. Besides that, only acyclic allenes have been prepared by 1,6-addition until now. Therefore, we applied this method to 2-en-4-ynoates with an endocyclic double bond in order to synthesize exocyclic allenes.

In cuprate addition reactions with acceptor-substituted enynes **A** two problems of regioselectivity have to be considered[4]. First, the cuprate may add in a 1,4 (→ **B**) or a 1,6-fashion (→ **C**) to the enyne. In the latter case, reaction of the allenyl enolate **C** with an electrophile can take place at the α-carbon (→ allenes **D**) or at the γ-carbon atom (→ dienes **E**).



1. Preparation of Acceptor-Substituted Enynes

The enynes bearing sulfur-containing groups as acceptor substituent were synthesized by the same route. 4,4-Dimethyl-2-pentynal (**2**) was obtained by formylation of 3,3-dimethyl-1-butyne (**1**) with DMF[7a]. Reaction of this aldehyde with the anion of methyl phenyl sulfone (**3**) gave the alcohol **4a**, which was converted into the enyne **5a** by treatment with methanesulfonyl chloride and mesylate elimination with DBU[6,8]. The yield over these three steps was 48%. The starting material for the enynes **5b**, **11** and **12**, 2-butynal, was obtained by reduction of methyl tetrolate (**6**)

[+] New address: Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, F.R.G.

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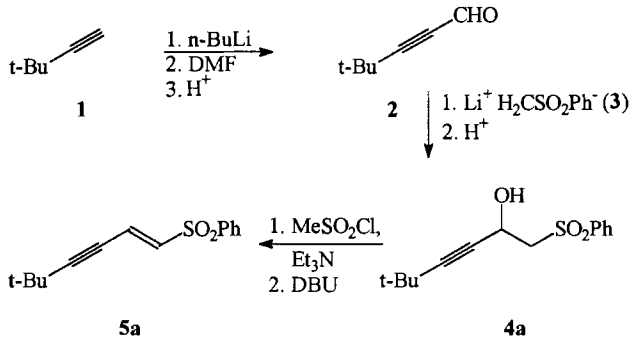
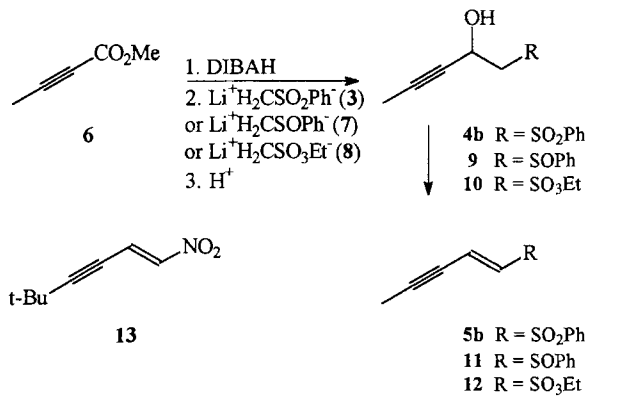
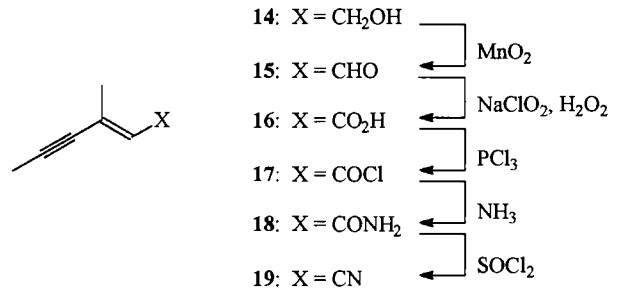
with DIBAH[9]. In situ conversion of the aldehyde with **3**, the anions of methyl phenyl sulfoxide (**7**) and ethyl methanesulfonate (**8**), respectively, provided the alcohols **4b**, **9** and **10**, which were converted into the enynes **5b**, **11** and **12** as described above in 61, 15 and 26% yield, respectively. The known nitro-substituted enyne **13**[10] was synthesized analogously from aldehyde **2** and nitromethane.

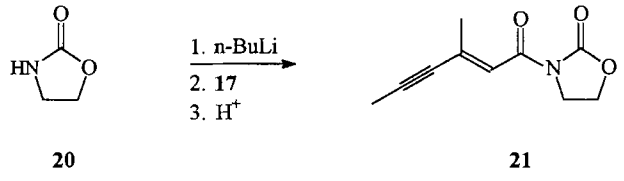


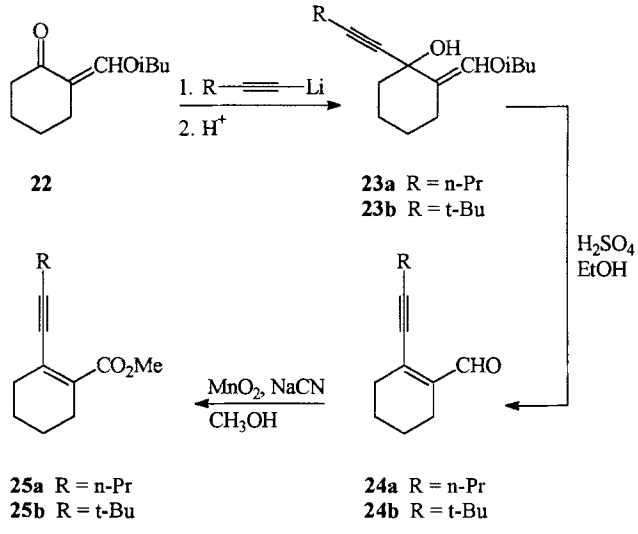


The amide **18** was obtained from the known alcohol (*E*)-3-methyl-2-hexen-4-yn-1-ol (**14**)[7b,c,11]. Oxidation of **14** with activated MnO_2 to the aldehyde **15** and further with $H_2O_2/NaClO_2$ to the carboxylic acid **16**[12] (91% yield) was followed by the conversion to the acid chloride **17** with PCl_3[13a]. Treatment with aqueous ammonia afforded the amide **18** in 83% yield[13b]. The nitrile **19** was readily accessible in 73% yield from the amide **18** by dehydration with thionyl chloride.

The enyne **21**, bearing on oxazolidino substituent, was prepared by deprotonation of 2-oxazolidinone (**20**) and reaction with the acid chloride **17** in 27% yield[14]. The cyclic esters **25a** and **25b** were obtained in three steps starting with the known enol ether **22**[15,16]. Nucleophilic addition of the lithium acetylides derived from *n*-pentyne or 3,3-dimethylbutyne furnished the alcohols **23a** and **23b**, which were converted into the aldehydes **24a** and **24b** by treatment with sulfuric acid in 35 and 36% yield, respectively[16]. Oxidative esterification with activated MnO_2, NaCN and methanol resulted in the formation of the 2-en-4-ynoates **25a** and **25b** in 49 and 21% yield, respectively[17].

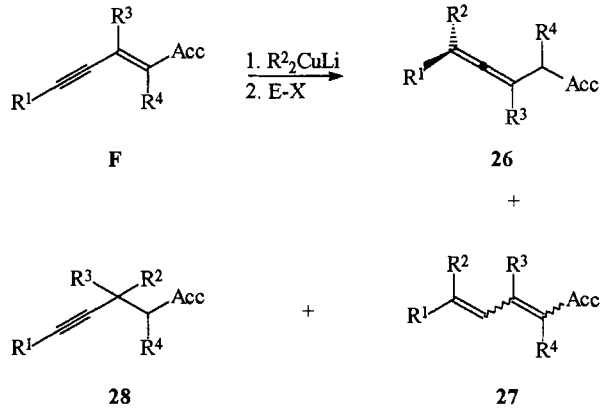


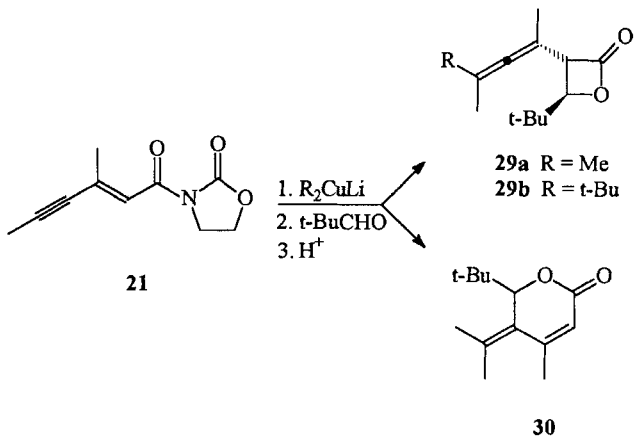




2. Addition Experiments

The first addition experiment was carried out with enyne **5a** and lithium dimethylcuprate under the usual conditions for 1,6-additions to 2-en-4-ynoates[4,6], i.e. at −20 °C with 2 equiv. of the cuprate. Besides starting material, only traces of allene could be detected after protonation with dilute sulfuric acid. This was also the case when 5 equiv. of the cuprate were used and the temperature was raised slowly to 20 °C. The addition of 5 equiv. of TMSCl to the cuprate solution prior to addition of the enyne gave a dimeric product[6a] which was not characterized further. The best result was obtained by using TMSOTf as Lewis acid, added to the enyne before addition to the solution of the cuprate[6b]. Under these conditions, the allene **26a** could be isolated with 23% yield. Compared to **5a**, the sterically less demanding enyne **5b** should be more reactive. Accordingly,





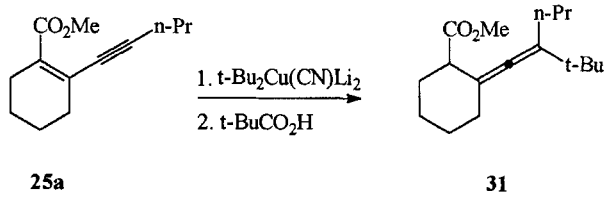


Table 1

Entry	Enyne	Product	R^1	$R^{2a)}$	R^3	R^4	Acc	Work-up[b]	Yield	A : D[c] (%)
1	5a	26a	t-Bu	Me	H	H	SO_2Ph	B	23%[d]	>99 : <1
2	5b	26b	Me	Me	H	H	SO_2Ph	A	45%[e]	>99 : <1
3	5a	28a	t-Bu	t-Bu	H	H	SO_2Ph	B	69%	f)
4	5b	26a	Me	t-Bu	H	H	SO_2Ph	B	91%	>99 : <1
5	11	26c	Me	t-Bu	H	H	SOPh	C	g)	
6	12	26d	Me	Me	H	H	SO_3Et	C	31%	70 : 30
7	12	26e	Me	t-Bu	H	H	SO_3Et	A	49%	>99 : <1
8	13	28b	t-Bu	t-Bu	H	H	NO_2	A	24%	f)
9	19	27a	Me	Me	Me	H	CN	A/C	74%	<1 : >99[h]
10	19	26f	Me	Me	Me	CH(t-Bu)OH	CN	D	34%	>99 : <1[i]
11	19	26g	Me	t-Bu	Me	H	CN	A	65%	>95 : <5
12	21	29a/30	Me	Me		j)	Oxazol.	D	58%	1 : 1
13	21	29b	Me	t-Bu		j)	Oxazol.	D	77%	>99 : <1
14	25a	31	n-Pr	t-Bu		k)	CO_2Et	C	42%	>99 : <1

[a] Cuprates used: $Me_2CuLi \cdot LiI$ for R^2 = Me, $t\text{-}Bu_2Cu(CN)Li_2$ for R^2 = t-Bu. – [b] Workup procedure A: sat. NH_4Cl solution; procedure B: 2 N H_2SO_4; procedure C: pivalic acid, −80°C; procedure D: pivalic aldehyde, −80°C. – [c] Allene:diene ratio (determined by ^{1}H-NMR spectroscopy). – [d] In the presence of 1 equiv. of TMSOTf. – [e] In the presence of 1 equiv. of TMSI. – [f] 1,4-Addition product. – [g] The product could not be purified. – [h] Workup procedure A: *Z*:*E* ratio of dienes = 1.8:1; procedure C: *Z*:*E* ratio of dienes = 5:1. – [i] Dienes **27** (R^4 = H) were formed as byproduct. – [j] Cyclization with elimination of the oxazolidino group. – [k] C-2 and C-3 are ring carbon atoms.

treatment with 2 equiv. of lithium dimethylcuprate in the presence of 1 equiv. of TMSI as Lewis acid furnished allene **26b** in 45% yield (Table 1, entry 2). The use of 5 equiv. of the higher order cuprate Me_3CuLi_2[18] gave this allene in 16% yield.

In 1,6-addition reactions with 2-en-4-ynoates, lithium di-*tert*-butylcyanocuprate proved to be more reactive than lithium dimethylcuprate[6b]. Likewise, enyne **5a** was consumed completely within 1 h at −20°C when treated with 5 equiv. of $t\text{-}Bu_2Cu(CN)Li_2$. However, the product turned out to be the 1,4-addition product **28a**, obtained in 69% yield (entry 3). In contrast to this, reaction of enyne **5b** with the cyanocuprate gave the same allene **26a** as enyne **5a** with Me_2CuLi, but this time at −20°C with 5 equiv. of the cuprate in 91% yield (entry 4).

Addition of lithium dimethylcuprate to the sulfinyl-substituted enyne **11** proceeded very slowly, even in the presence of Lewis acids at elevated temperature. A mixture of products, mainly consisting of the conjugated dienes, was isolated in low yield and not characterized further. Reaction with $t\text{-}Bu_2Cu(CN)Li_2$, however, furnished the allene **26c**. Since the sulfoxide moiety is chiral, this compound exists as two diastereomers; the cuprate addition proceeds with a modest diastereoselectivity of 3:1. Allene **26c** turned out to be very sensitive, and attempts to purify it by chromatography or kugelrohr distillation failed.

Since the sulfonate group is a stronger electron acceptor than the sulfoxide group, corresponding enynes should be more reactive. Indeed, treatment of enyne sulfonate **12** with 5 equiv. of lithium dimethylcuprate and protonation with pivalic acid[4] resulted in the formation of a 3.3:1 mixture of allene **26d** and the corresponding conjugated dienes. Since the yield was very low, the reaction was carried out with 2 equiv. of the cuprate in the presence of 2 equiv. of TMSOTf, giving a 70:30 allene/diene mixture in 31% yield (entry 6). As observed for the sulfones **5**, these problems could be circumvented by using lithium di-*tert*-butylcyanocuprate for the addition: Enyne **12** was consumed completely within 1 h by treatment with 2 equiv. of the cuprate at −30°C, and the expected allene **26e** was obtained as the only product in 49% yield (entry 7).

Next, we turned our attention to nitro-substituted enynes. These Michael acceptors were expected to be the most polarized and reactive compounds examined in this work. Indeed, upon addition of lithium dimethylcuprate the enyne **13** was consumed within a few minutes at −20°C. The NMR spectra of the crude product showed no allene signals but resonances that could be attributed to the 1,4-addition

product. The addition was repeated with t-$Bu_2Cu(CN)Li_2$ and this time the 1,4-adduct **28b** was isolated in 24% yield (entry 8). Thus, it seems that the 1,4-addition is strongly favored for nitroenynes; however, it might be possible to achieve 1,6-addition to nitro-substituted enynes with a sterically less demanding group attached to the triple bond. Therefore, 1-nitro-1-penten-3-yne was synthesized in analogy to the enyne **13**, but cuprate additions resulted in complex mixtures, again containing the 1,4-adduct as major product.

Another class of enynes with nitrogen-containing acceptors are 2-en-4-ynoic amides. It was found earlier that 5-phenyl-2-penten-4-ynoic diethylamide does not react with cuprates[4a]. Amide **18** synthesized in this work should be more reactive because the substituent at C-5 is much smaller and because there are no substituents at the nitrogen atom. However, also this amide proved to be totally unreactive towards cuprates, even in the presence of Lewis acids at room temperature.

Like amides, 2-en-4-ynenitriles are rather unreactive Michael acceptors. For example, (*E*)-6,6-dimethyl-2-hepten-4-ynenitrile does not undergo addition reactions with cuprates; rather, isomerization of the double bond takes place[5]. Here, nitrile **19** which is easily accessible from the amide **18** was tested as starting material for the 1,6-addition; since this acceptor bears no bulky substituents, it should be more reactive than the *tert*-butyl-substituted nitrile mentioned above. Accordingly, upon treatment with 2 equiv. of lithium dimethylcuprate the enyne **19** was consumed completely within 2 h at −20 °C, but protonation with aqueous ammonium chloride solution provided only the known conjugated dienes **27a** (*Z*:*E* = 1.8:1) in 74% yield. The use of pivalic acid as protonating agent did not alter the undesired regioselectivity of the protonation, changing only the *Z*:*E* ratio to 5:1 (entry 9). In order to obtain allenes, the allenyl enolate formed by reaction of **19** with lithium dimethylcuprate had to be trapped at C-2 with other soft electrophiles[4c–e]. Addition of methyl triflate to the solution of the enolate provided a complex mixture, containing conjugated dienes but no allene. However, by addition of pivalic aldehyde the expected allene **26f** was produced in 34% yield (entry 10). Another possibility of disfavoring protonation of allenyl enolates at C-4 is the attachment of bulky substituents to C-5[4]. Thus, addition of lithium di-*tert*-butylcyanocuprate to nitrile **19** and protonation with aqueous ammonium chloride gave the allene **26g** in 65% yield (entry 11).

Another interesting substrate for cuprate additions is the oxazolidinone **21**. Although possessing an amide structure, a stronger acceptor property was expected for this compound. However, the reactivity towards $Me_2CuLi \cdot LiI$ is quite low, giving a complex mixture containing the corresponding conjugated dienes. Trapping of the allenyl enolate with pivalic aldehyde furnished a 1:1 mixture of allene **29a** and diene **30** in 58% yield (entry 12). Thus, the reaction of the enolate with the aldehyde is not regioselective but takes place both at C-2 and C-4; subsequent cyclization with elimination of the oxazolidino group gives the observed products. The structure of the β-lactone **29a** could be assigned on the basis of a typical carbonyl resonance at 1820 cm^{-1} in the IR spectrum. Only one isomer was formed as shown by GC and NMR spectroscopy; for the vicinal protons of the β lactone ring of **29a**, a coupling constant of $J_{2,3}$ = 4.5 Hz was observed. The analogous reaction of **21** with t-$Bu_2Cu(CN)Li_2$ and pivalic aldehyde furnished only the allene **29b** (77% yield, 1.2:1 mixture of diastereomers) without traces of conjugated dienes (entry 13). Thus, the introduction of the bulky *tert*-butyl group into the 5-position allows reaction of the enolate with pivalic aldehyde at C-2 only. The configuration of the β-lactone ring was determined to be *trans* with an NOE-difference spectrum showing an intensity enhancement of 3-H upon irradiation of the resonance of the 1′-methyl group. The coupling constant of $J_{2,3}$ = 4.4 Hz found for **29b** is very similar to that observed for **29a**; therefore, it can be concluded that the latter also possesses the *trans* configuration.

Finally, conjugate cuprate additions to the two cyclic 2-en-4-ynoates **25** were examined. Of these, only **25a** could be converted into the corresponding allene. However, the reactivity was quite low compared with acyclic analogs. The 1,6-addition of lithium dimethylcuprate took several hours at room temperature to give the conjugated diene although pivalic acid was used as proton source. Trapping of the enolate with pivalic aldehyde failed, probably due to the strong steric hindrance at the allenyl enolate. In contrast, addition of t-$Bu_2Cu(CN)Li_2$ furnished allene **31** as a 1:1 mixture of diastereomers in 42% yield. Here, the reactivity is comparable to acyclic 2-en-4-ynoates. The sterically more hindered cyclic ester **25b** did not react with lithium dimethylcuprate even after 12 h at room temperature and in the presence of Lewis acids. With lithium di-*tert*-butylcyanocuprate a reaction took place but the complex product mixture formed did not contain any allene and was not characterized further.

3. Discussion

In this work a qualitative reactivity scale of different acceptor-substituted enynes towards organocuprates has been established. According to the reaction times necessary for complete consumption of the starting material, the reactivity decreases in the following order, taking into account the results of our earlier work[4]:

Acceptor = $-NO_2 > -COR, -CO_2R, -COSR > -CN, -SO_3R, -Oxazolidino > -SO_2R > -SOR \gg -CONH_2$

It must be mentioned that this order is valid for lithium dimethylcuprate; the reactivity towards lithium di-*tert*-butylcyanocuprate is significantly higher and the differences between the enynes are diminished. 2-En-4-ynoic amides are the only substrates examined here that do not react with organocuprates, showing that the amide function is too weak an acceptor for conjugate addition reactions. The cyclic enynoates **25** are much less reactive than acyclic esters; this is probably due to the twofold substitution at a double bond which disfavors the initial attack of the cuprate to form a π complex at this position[5]. Nevertheless, use of

the more reactive lithium di-*tert*-butylcyanocuprate in combination with pivalic acid as protonating agent enabled us to obtain the exocyclic allene **31**.

With regard to the two problems of regioselectivity mentioned in the introduction, the following observations have been made:

1. Regioselectivity of the Cuprate Addition: With the exception of nitroenynes which give 1,4-addition products, all reactive Michael acceptors examined undergo 1,6-addition reactions with organocuprates. The reason for this deviating behavior is not clear at present. With enynesulfone **5a**, a dependence of the regioselectivity of the cuprate addition on steric properties was found: Whereas lithium dimethylcuprate gives the 1,6-adduct, the *tert*-butylcyanocuprate adds in a 1,4-fashion. In contrast to this, the regioselectivity of cuprate additions to all other reactive enynes is independent of steric factors. The 1,6-addition of t-$Bu_2Cu(CN)Li_2$ to the chiral sulfoxide **11** takes place with (modest) diastereoselectivity, whereas analogous additions to 2-en-4-ynoates bearing chiral ester groups are not stereoselective[6a].

2. Regioselectivity of the Reaction of Allenyl Enolates with Electrophiles: The protonation of allenyl enolates takes place regioselectively at C-2 to give allenes for the enolates obtained from enynes with ester, thioester and sulfonyl groups; in some cases, the weak and bulky pivalic acid has to be employed as proton source in order to obtain pure allenes[4]. In the case of keto, sulfoxide, sulfonate and nitrile enolates, mixtures of allenes and dienes are formed; the regioselectivity of the protonation can be shifted to attack at C-2 by attachment of bulky substituents to C-5. In the case of enynenitrile **19**, pure allene **26g** could be obtained by regioselective trapping of the allenyl enolate with pivalic aldehyde. This method, however, could not be successfully applied to the enolate obtained from oxazolidinone **21** and lithium dimethylcuprate; instead, a 1:1 mixture of regioisomers **29a** and **30** was obtained. For the first time we observed attack of pivalic aldehyde at C-4 of an allenyl enolate, although this regioselectivity was found by Hulce et al.[19] in reactions of keto allenyl enolates. Additionally, this is the first example of an enyne with an acceptor function serving also as leaving group, thus giving access to allenic β-lactones and dihydropyranes. Again, the introduction of the bulky *tert*-butyl group into the C-5 position shifted this balance towards reaction of the electrophile at C-2, giving allene **29b** exclusively. Thus, the regioselectivity of the reaction of allenyl enolates with electrophiles shows a complex dependence on the steric and electronic properties of enolate and electrophile. In the case of β-lactones **29**, the trapping reaction with pivalic aldehyde is also stereoselective since only the *trans* products are formed.

In concluding this account, we have shown that the 1,6-addition of organocuprates to acceptor-substituted enynes can be applied to the synthesis of allenes with ester, keto, thioester, sulfonate, sulfone, sulfoxide, nitrile, and oxazolidone functions. A qualitative reactivity scale for these reactions has been established, allowing an estimation of the feasibility of a desired transformation. We expect that these developments will enhance the utilization of functionalized allenes both as target molecules and as starting materials for further transformations.

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Experimental

IR: Beckman-IR-5A and Perkin-Elmer 125. – ^1H, ^{13}C NMR: Bruker WM-300 with $CDCl_3$ as solvent and internal standard (δ = 7.27 [^1H NMR], δ = 77.05 [^{13}C NMR]). Abbreviations for the DEPT spectra: $+CH_3$, CH; $-CH_2$; x C(quat.). – Mass spectra: Varian MAT 311 A. – All reactions were carried out in thoroughly dried glassware under nitrogen or argon. Diethyl ether and THF were distilled from $LiAlH_4$ and potassium/benzophenone, respectively, prior to use. Dichloromethane and cyclohexane were distilled from CaH_2. All other reagents were used without further purification. Column chromatography was carried out with silica gel (70–230 mesh, Merck).

Due to the lability of some allenes towards oxidation and polymerization, correct elemental analyses could not be obtained in every case.

(E)-5,5-Dimethyl-1-phenylsulfonyl-1-hexen-3-yne (**5a**)[6a,b,8]: To a solution of 2.58 g (16.5 mmol) of methyl phenyl sulfone (**3**) in 40 ml of THF was added dropwise with stirring at 0 °C 11.0 ml (16.5 mmol) of a 1.5 M solution of *n*BuLi in hexane. A pink product precipitated. After stirring at 0 °C for 1 h the suspension was cooled to −80 °C and a solution of the crude aldehyde **2**[7a] (about 14.0 mmol) in 25 ml of THF was added dropwise. After 1 h the mixture was allowed to warm to room temp. A clear yellow solution formed which was treated with 15 ml of a satd. NH_4Cl solution. After separation of the layers the aqueous layer was extracted several times with diethyl ether. The combined organic layers were washed with brine and dried with $MgSO_4$; the solvent was removed in vacuo. The crude alcohol **4a** was dissolved in 25 ml of dichloromethane, and 2.46 g (24.3 mmol) of triethylamine (1.75 equiv.). was added to the solution. To this mixture 1.99 g (17.4 mmol) of methanesulfonyl chloride (1.25 equiv.) was slowly added at −50 °C. The cooling bath was removed and the suspension was allowed to warm to 0 °C within 30 min. 5.08 g (33.4 mmol) of DBU (2.4 equiv.) was added dropwise at this temperature. A clear dark solution formed. After stirring for 2 h at room temp. the mixture was diluted with diethyl ether, washed three times with water and dried with $MgSO_4$. After removal of the solvent the crude product was chromatographed (diethyl ether/cyclohexane, 1:3); yield 1.78 g (51%) of **5a** as colorless crystals. M.p. 92 °C. – IR: $\tilde{\nu}$ = 3060, 2980 (s, CH), 2240 (s, C≡C), 1600 cm^{-1} (s, C=C). – ^1H NMR: δ = 1.23 [s, 9H, $C(CH_3)_3$], 6.59 (d, 1H, *J* = 15.2 Hz, 1-H), 6.78 (d, 1H, *J* = 15.2 Hz, 2-H), 7.51–7.65 (m, 3H, phenyl-H), 7.86–7.90 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 28.5 (x, C-5), 30.3 [+, $C(CH_3)_3$], 74.2 (x, C-3), 111.6 (x, C-4), 124.7 (+), 127.9 (t), 129.5 (+), 133.7 (+), 137.7 (+, C-1/C-2/phenyl), 140.2 (x, phenyl). – MS: *m/z* (%) = 248 (13) [M^+], 91 (100). – $C_{14}H_{16}O_2S$ (248.3): Calcd. C 67.71, H 6.49; found C 67.62, H 6.42.

(E)-1-Phenylsulfonyl-1-penten-3-yne (**5b**)[6a,b,9]: To a solution of 2.45 g (25.0 mmol) of methyl 2-butynoate (**6**) in 50 ml of diethyl ether was added dropwise at −105 °C 25 ml (25.0 mmol) of a 1.0 M solution of DIBAH in hexane. The temperature was kept below −100 °C during the addition. In a second flask, to a solution of 3.12 g (20.0 mmol) of methyl phenyl sulfone (**3**) in 50 ml of THF was added 12.5 ml (20.0 mmol) of a 1.6 M solution of *n*BuLi in

hexane at −20°C. The mixture was cooled to −80°C and the content of the first flask was transferred to the second under argon pressure via a teflon tubing. The resulting suspension was allowed to warm to room temp. to give a clear solution. After 1 h the mixture was hydrolyzed with 100 ml of a satd. NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted several times with diethyl ether. The separation was complicated by aluminium salts, which could be dissolved by addition of 2 N HCl. The combined organic layers were washed with brine and dried with $MgSO_4$; the solvent was removed in vacuo. The crude alcohol **4b** was treated as described for **4a** with 3.54 g (35.0 mmol) of triethylamine, 2.86 g (25.0 mmol) of methanesulfonyl chloride, and 5.54 g (36.5 mmol) of DBU. The crude product was recrystallized from cyclohexane to furnish 2.50 g (61%) of **5b** as colorless crystals. M.p. 91−92°C. − IR: $\tilde{\nu}$ = 3060 (s, CH), 2220 (s, C≡C), 1600 cm^{-1} (s, C=C). − ^1H NMR: δ = 2.01 (d, 3H, *J* = 2.4 Hz, 5-H), 6.59 (d, 1H, *J* = 15.4 Hz, 1-H), 6.73 (dq, 1H, *J* = 15.4/2.4 Hz, 2-H), 7.51−7.66 (m, 3H, phenyl-H), 7.78−7.92 (m, 2H, phenyl-H). − ^{13}C NMR: δ = 5.0 (+, C-5), 74.8 (x, C-3), 99.7 (x, C-4), 124.7 (+), 127.9 (+), 129.5 (+), 133.8 (+), 138.0 (+, C-1/C-2/phenyl), 140.0 (x, phenyl). − MS: *m/z* (%) = 206 (15) [M^+], 125 (100). − $C_{11}H_{10}O_2S$ (206.3): Calcd. C 64.05, H 4.89; found C 64.18, H 4.91.

(E)-1-Phenylsulfinyl-1-penten-3-yne (**11**)[6a,b,9]: Compound **11** was prepared as described for **5b** by starting from 2.22 g (22.6 mmol) of methyl 2-butynoate (**6**), 22.6 ml (22.6 mmol) of a 1.0 M solution of DIBAH in hexane, 2.54 g (18.1 mmol) of methyl phenyl sulfoxide (**7**), and 11.3 ml (18.1 mmol) of a 1.6 M solution of *n*BuLi in hexane. The crude alcohol **9** was treated with 2.66 g (26.3 mmol) of triethylamine, 2.15 g (18.8 mmol) of methanesulfonyl chloride and 4.10 g (27.0 mmol) of DBU. The reaction mixture was stirred for 18 h at room temp. The crude product was chromatographed (diethyl ether/cyclohexane, 3:1) to furnish 520 mg (15%) of the enyne **11** as slightly yellow crystals. M.p. 73−76°C (cyclohexane). − IR: $\tilde{\nu}$ = 3040 (s, CH), 2230 (s, C≡C), 1590 cm^{-1} (s, C=C). − ^1H NMR: δ = 1.98 (d, 3H, *J* = 2.5 Hz, 5-H), 6.45 (dq, 1H, *J* = 15.2/2.4 Hz, 2-H), 6.63 (d, 1H, *J* = 15.2 Hz, 1-H), 7.46−7.65 (m, 5H, phenyl-H). − ^{13}C NMR: δ = 4.9 (+, C-5), 75.8 (x, C-4), 95.0 (x, C-3), 117.6 (+), 125.1 (+), 129.9 (+), 131.7 (+), 144.0 (+, C-1/C-2/phenyl), 143.7 (x, phenyl). − MS: *m/z* (%) = 190 (5) [M^+], 142 (100). − $C_{11}H_{10}OS$ (190.3): Calcd. C 69.44, H 5.30; found C 69.55, H 5.34.

(E)-Ethyl 1-Penten-3-ynesulfonate (**12**)[6a,b,9]: Compound **12** was prepared as described for **11** by starting from 2.45 g (25.0 mmol) of **6**, 25 ml (25.0 mmol) of a 1.0 M solution of DIBAH in hexane, 2.48 g (20.0 mmol) ethyl methanesulfonate (**8**), and 13.8 ml (20.0 mmol) of a 1.45 M solution of *n*BuLi in hexane. The crude alcohol **10** was treated with 2.84 (28.0 mmol) of triethylamine, 2.29 g (20.0 mmol) of methanesulfonyl chloride and 5.84 g (38.4 mmol) of DBU. Chromatography (diethyl ether/cyclohexane, 1:1) furnished 0.90 g (26%) of **12** as a yellow oil. − IR: $\tilde{\nu}$ = 3060, 2980 (w, CH), 2220 (s, C≡C), 1600 cm^{-1} (s, C=C). − ^1H NMR: δ = 1.37 (t, 3H, *J* = 7.1 Hz, $SO_3CH_2CH_3$), 2.04 (d, 3H, *J* = 2.4 Hz, 5-H), 4.17 (q, 2H, *J* = 7.1 Hz, $SO_3CH_2CH_3$), 6.47 (d, 1H, *J* = 15.3 Hz, 1-H), 6.66 (dq, 1H, *J* = 15.3/2.4 Hz, 2-H). − ^{13}C NMR: δ = 4.9 (+, C-5), 15.0 (+, $SO_3CH_2CH_3$), 67.3 (−, $SO_3CH_2CH_3$), 74.4 (x, C-3), 99.7 (x, C-4), 126.6 (+, C-1/C-2), 132.1 (+, C-1/C-2). − MS: *m/z* (%) = 174 (25) [M^+], 39 (100). − $C_7H_{10}O_3S$ (174.3): Calcd. C 48.26, H 5.79; found C 48.43, H 5.84.

(E)-3-Methyl-2-hexen-4-ynoic Acid (**16**)[12]: A solution of 8.25 g (75.0 mmol) of alcohol **14**[7b,c,11] in 75 ml of diethyl ether was added dropwise to a suspension of 130 g (1.50 mol) of activated MnO_2 (Merck) in 400 ml of diethyl ether with vigorous stirring and ice cooling. The mixture was stirred for 4 h at room temp. and filtered through Celite. Removal of the solvent from the filtrate in vacuo furnished the crude aldehyde **15** which was dissolved in 50 ml of acetonitrile and treated with a solution of 1.60 g (18.3 mmol) of NaH_2PO_4 in 30 ml of water and 8.1 ml (73.0 mmol) of 30% H_2O_2. To this mixture a solution of 11.2 g (98.0 mmol) of $NaClO_2$ (80%) in 100 ml of water was added dropwise within 1 h with stirring at 10°C. The formation of oxygen could be observed. After the addition was complete, stirring was continued for 1 h and then about 0.5 g of Na_2SO_3 was added to destroy the excess HOCl and H_2O_2. The mixture was acidified with 2 N HCl and extracted three times with diethyl ether. The combined organic extracts was dried with $MgSO_4$ and the solvent was removed in vacuo to furnish 7.91 g (91%) of the crude acid **16** as slightly yellow crystals. Recrystallization of a sample from toluene gave colorless needles with m.p. 102−104°C. − IR: $\tilde{\nu}$ = 2950 (w, OH), 2870 (w, CH), 2220 (w, C≡C), 1710 (s, C=O), 1615 cm^{-1} (s, C=C). − ^1H NMR: δ = 2.00 (s, 3H, 6-H), 2.27 (d, 3H, *J* = 1.4 Hz, 3-CH_3), 5.99 (q, 1, *J* = 1.4 Hz, 2-H), 10.23 (br. s, 1H, CO_2H). − ^{13}C NMR: δ = 4.7 (+, C-6), 20.6 (+, 3-CH_3), 82.2 (x, C-4/C-5), 93.1 (x, C-4/C-5), 122.6 (+, C-2), 141.9, (x, C-3), 171.8 (x, C-1). − MS: *m/z* (%) = 124 (100) [M^+], 77 (55). − Since the acid **16** polymerized rapidly, a correct elemental analysis could not be obtained.

(E)-3-Methyl-2-hexen-4-ynamide (**18**)[13]: To 3.42 g (27.5 mmol) of the crude acid **16** was added with ice cooling 1.51 g (11.0 mmol) of PCl_3, and the mixture was kept at 50°C for 3 h. The mixture became liquid and H_3PO_3 precipitated. The crude chloride **17** was decanted and dissolved in 50 ml of dry dioxane. 20 ml (0.28 mol) of 25% aqueous ammonia was added at 0°C. After stirring for 10 min at room temp. the mixture was diluted with 300 ml of water and acidified with 2 N HCl. A colorless product precipitated. Filtration and drying of the solid furnished 2.82 g (83%) of the amide **18** as colorless needles. M.p. 155−156°C (toluene). − IR: $\tilde{\nu}$ = 3360 (s, NH), 3180 (s, NH), 2220 (C≡C), 1670 (s, C=O), 1605 cm^{-1} (s, C=C). − ^1H NMR (in [D_6]acetone): δ = 1.95 (s, 3H, 6-H), 2.21 (d, 3H, *J* = 1.4 Hz, 3-CH_3), 6.08 (q, 1H, *J* = 1.4 Hz, 2-H), 6.25 (br. s, 1H, NH_2), 6.76 (br. s, 1H, NH_2). − ^{13}C NMR: δ = 3.9 (+, C-6), 19.4 (+, 3-CH_3), 83.0 (x, C-4/C-5), 89.0 (x, C-4/C-5), 127.0 (+, C-2), 134.3 (x, C-3), 168.0 (x, C-1). − MS: *m/z* (%) = 123 (100) [M^+], 77 (61). − C_7H_9NO (123.2): Calcd. C 68.27, H 7.37, N 11.37; found C 67.86, H 7.33, N 10.92.

(E)-3-Methyl-2-hexen-4-ynenitrile (**19**): To 0.99 g (8.0 mmol) of the amide **18** 4.76 g (40.0 mmol) of $SOCl_2$ was added and the mixture was heated at reflux for 2.5 h during which time it was protected against moisture. A brown oil formed. Excess $SOCl_2$ was removed in vacuo and the crude product was purified by kugelrohr distillation. 610 mg (73%) of the known nitrile **19**[20] was obtained as colorless liquid. B.p. 90°C/12 mbar.

(E)-3-(3-Methyl-1-oxo-2-hexen-4-yn-1-yl)-2-oxazolidinone (**21**)[14]: To a solution of 3.92 g (45.0 mmol) of 2-oxazolidinone (**20**) in 150 ml of THF was added 31 ml (45.5 mmol) of a 1.45 M solution of n-BuLi in hexane at −80°C within 10 min. To this mixture the crude acid chloride **17**, prepared from 6.21 g (50.0 mmol) of **16** was added. After stirring for 30 min at −80°C the mixture was allowed to warm to room temp. within 30 min. It was then hydrolyzed with 30 ml of a satd. NH_4Cl solution. Most of the THF was removed in vacuo and the residue was extracted twice with dichloromethane. The combined organic layers were washed with 1 N NaOH and brine and subsequently dried with $MgSO_4$, and the solvent was removed in vacuo. Storage of the remaining brown oil at 5°C furnished 2.37 g (27%) of **21** as a yellow solid. M.p. 61−63°C, slightly yellow needles (hexane). − IR: $\tilde{\nu}$ = 3100, 2980, 2920, 2780 (m,

CH), 2220 (s, C≡C), 1780, 1760 (s, C=O), 1595 cm^{-1} (s, C=C). – ^1H NMR: δ = 2.00 (s, 3H, 6′-H), 2.28 (d, 3H, *J* = 1.4 Hz, 3′-CH_3), 4.04 (t, 2H, *J* = 8.2 Hz, 4-H), 4.40 (t, 2H, *J* = 8.2 Hz, 5-H), 7.26 (ps, 1H, 2′-H). – ^{13}C NMR: δ = 4.7 (+, C-6′), 21.3 (+, 3′-CH_3), 42.7 (–, C-4), 61.9 (–, C-5), 82.8 (x, C-4′/C-5′), 93.2 (x, C-4′/C-5′), 121.9 (+, C-2′), 141.1 (x, C-3′), 153.3 (x, C-2), 165.2 (x, C-1′). – MS: *m/z* (%) = 193 (27) [M^+], 107 (100). – $C_{10}H_{11}NO_3$ (193.2): Calcd. C 62.17, H 5.74, N 7.25; found C 62.20, H 5.84, N 7.24.

2-(1-Pentyn-1-yl)-1-cyclohexenecarbaldehyde (**24a**)[16]: To a solution of 3.58 g (52.5 mmol) of 1-pentyne in 125 ml of THF was added dropwise at −80 °C 37 ml (55.0 mmol) of a 1.5 M solution of n-BuLi. The mixture was warmed to −10 °C and dropwise addition of 9.11 g (50.0 mmol) of **22**[15,16] in 25 ml of THF followed. The temperature was kept below 20 °C during the addition, and the color of the reaction mixture turned red-brown. After stirring for 5 h at room temp. the mixture was hydrolyzed with 120 ml of ice-cold water. The aqueous layer was saturated with NH_4Cl and extracted three times with diethyl ether. The combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo. The crude alcohol **23a** thus obtained was dissolved in 150 ml of a 1:1 mixture of ethanol and 2 N H_2SO_4. After stirring at room temp. for 3 h the mixture was diluted with 600 ml of water and extracted 8 times with diethyl ether. The combined organic layers were washed with 2 N NaOH and brine, dried with $MgSO_4$, and the solvent was removed in vacuo. Chromatography (cyclohexane/diethyl ether, 10:1) afforded 3.08 g (35%) of the aldehyde **24a** as a yellow liquid. – IR: $\tilde{\nu}$ = 2930, 2860, 2830 (s, CH), 2210 (m, C≡C), 1670 (s, C=O), 1600 cm^{-1} (m, C≡C). – ^1H NMR: δ = 0.99 (t, 3H, *J* = 7.3 Hz, 5′-H), 1.52–1.67 (m, 6H, 4-, 5-, 4′-H), 2.21–2.39 (m, 6H, 3-, 6-, 3′-H), 10.16 (s, 1H, CHO). – ^{13}C NMR: δ = 13.6 (+, C-5′), 21.2 (–), 21.7 (–), 22.0 (–), 22.1 (–), 32.9 (–, C-3/C-4/C-5/C-6/C-3′/C-4′), 78.2 (x, C-1′), 100.6 (x, C-2′), 141.3 (x, C-1/C-2), 141.8 (x, C-1/C-2), 193.4 (+, CHO). – MS: *m/z* (%) = 176 (4) [M^+], 148 (100). – Due to the lability of this aldehyde, a correct elemental analysis could not be obtained.

Methyl 2-(1-Pentyn-1-yl)-1-cyclohexenecarboxylate (**25a**)[17]: A solution of 1.66 g (9.40 mmol) of the aldehyde **24a** in 20 ml of methanol was added dropwise to a mixture of 10.8 g (0.12 mol) of activated MnO_2 (Merck), 1.57 g (32.0 mmol) of NaCN and 0.56 g (9.30 mmol) of acetic acid in 100 ml of methanol. After stirring for 3 d the reaction mixture was filtered through a pad of Celite and the residue was washed with a 1:1 mixture of methanol and water. The filtrate was diluted with sufficient water to give two layers upon addition of diethyl ether. After four extractions of the aqueous layer with diethyl ether the combined organic layers were dried with $MgSO_4$ and the solvent was removed in vacuo. Chromatography (cyclohexane/diethyl ether, 10:1) furnished 0.95 g (49%) of the ester **25a** as a colorless oil. – IR: $\tilde{\nu}$ = 2930, 2860, 2830 (s, CH), 2210 (w, C≡C), 1710 (s, C=O), 1610 cm^{-1} (m, C=C). – ^1H NMR: δ = 1.01 (t, 3H, *J* = 7.4 Hz, 5′-H), 1.52–1.56 (m, 6H, 4-, 5-, 4′-H), 2.29–2.39 (m, 6H, 3-, 6-, 3′-H), 3.74 (s, 3H, CO_2CH_3). – ^{13}C NMR: δ = 13.6 (+, C-5′), 21.8 (–), 21.9 (–), 22.3 (–), 26.2 (–), 32.9 (–, C-3/C-4/C-5/C-6/C-3′/C-4′), 51.5 (+, CO_2CH_3), 80.0 (x, C-1′), 98.1 (x, C-2′), 129.5 (x, C-1/C-2), 132.7 (x, C-1/C-2), 168.1 (x, CO_2CH_3). – MS: *m/z* (%) = 206 (4) [M^+], 178 (100). – $C_{13}H_{18}O_2$ (206.3): Calcd. C 75.69, H 8.80; found C 75.45, H 8.92.

2-(3,3-Dimethyl-1-butyn-1-yl)-1-cyclohexenecarbaldehyde (**24b**)[16]: Compound **24b** was prepared as described for **24a** by starting from 27.3 g (0.15 mol) of **22**[15,16] in 75 ml of THF, 12.9 g (0.16 mol) of 3,3-dimethyl-1-butyne (**1**) in 35 ml THF and 114 ml (0.17 mol) of a 1.45 M solution of n-BuLi in hexane. The crude alcohol **23b** was dissolved in a mixture of 225 ml of ethanol and 225 ml of 2 N H_2SO_4. Of 20.5 g of the crude aldehyde thus obtained, 5.0 g was chromatographed (cyclohexane/diethyl ether, 20:1) to afford 2.53 g (36%) of **24b** as a yellow oil – IR: $\tilde{\nu}$ = 2960, 2930, 2860, 2830 (s, CH), 2210 (w, C≡C), 1670 (s, C=O), 1600 cm^{-1} (m, C=C). – ^1H NMR: δ = 1.24 [s, 9H, $C(CH_3)_3$], 1.56–1.66 (m, 4H, 4-, 5-H), 2.17–2.36 (m, 4H, 3-, 6-H), 10.14 (s, 1H, CHO). – ^{13}C NMR: δ = 21.2 (–), 22.0 (–), 28.4 (x, C-3′), 30.8 [+, $C(CH_3)_3$)], 32.8 (–, C-3/C-4/C-5/C-6), 76.5 (x, C-1′), 108.5 (x, C-2′), 141.1 (x, C-1/C-2), 141.5 (x, C-1/C-2), 193.4 (+, CHO). – MS: *m/z* (%) = 190 (21) [M^+], 175 (100). – Due to the lability of this aldehyde, a correct elemental analysis could not be obtained.

Methyl 2-(3,3-Dimethyl-1-butyl-1-yl)-1-cyclohexenecarboxylate (**25b**)[17]: Compound **25b** was prepared as described for **25a** by starting from 1.58 g (8.3 mmol) of the aldehyde **24b** in 20 ml of methanol, 9.56 g (0.11 mol) of MnO_2, 1.38 g (28.2 mmol) of NaCN, and 0.49 g (8.2 mmol) of acetic acid in 80 ml of methanol. The reaction proceeded very slowly and could not be accelerated by additional MnO_2. It was interrupted after 4 d although 10% of the starting material were still present. Chromatography (cyclohexane/diethyl ether, 10:1) furnished 380 mg (21%) of the ester **25b** as a colorless oil. – IR: $\tilde{\nu}$ = 2980, 2940, 2860 (s, CH), 2220 (w, C≡C), 1715 (s, C=O), 1610 cm^{-1} (m, C=C). – ^1H NMR: δ = 1.25 [s, 9H, $C(CH_3)_3$], 1.55–1.65 (m, 4H, 4-, 5-H), 2.23–2.34 (m, 4H, 3-, 6-H), 3.74 (s, 3H, CO_2CH_3). – ^{13}C NMR: δ = 21.7 (–), 21.8 (–), 26.3 (–), 32.7 (–, C-3/C-4/C-5/C-6), 28.3 (x, C-3′), 30.8 [+, $C(CH_3)_3$], 51.3 (+, CO_2CH_3), 79.3 (x, C-1′), 105.8 (x, C-2′), 129.0 (x, C-1/C-2), 133.0 (x, C-1/C-2), 168.4 (+, CO_2CH_3). – MS: *m/z* (%) = 220 (20) [M^+], 205 (100). – $C_{14}H_{20}O_2$ (220.3): Calcd. C 76.33, H 9.15; found C 76.38, H 9.22.

General Procedure for the Preparation of Allenes by 1,6-Addition of Organocuprates to Acceptor-Substituted Enynes[5,6]: To a suspension of 2.0 mmol of copper(I) iodide or cyanide in 10 ml of diethyl ether 4.0 mmol of the organolithium compound in diethyl ether (MeLi) or pentane (t-BuLi) was added dropwise. The temperature was kept at −20 to −10 °C (MeLi) and −30 °C (t-BuLi), respectively. The mixture was stirred for 30 min and a solution of 1.0 mmol of the enyne in 5 ml of diethyl ether was added dropwise at −20 to −30 °C. If the reaction was performed in the presence of a Lewis acid, 1.0 mmol of the Lewis acid was added to the solution of the enyne prior to addition of the cuprate. The reaction was followed by GC or TLC and interrupted when the starting material was consumed completely. For the enynes with a low reactivity towards the organocuprates this could be achieved by long reaction times and increase of the temperature, respectively. In some cases it was necessary to use a larger excess of cuprate to achieve complete conversion.

Workup Procedure A: The mixture was hydrolyzed by addition of 3 ml of a satd. NH_4Cl solution with vigorous stirring. The copper salts and the aqueous layer were removed by filtration through Celite. The solvent was removed in vacuo and the crude product purified by chromatography.

Workup Procedure B: The mixture was hydrolyzed with 3 ml of 2 N H_2SO_4 and treated further as described under A.

Workup Procedure C: The mixture was cooled to −80 °C and added via a teflon tubing under argon pressure to a stirred solution of 0.51 g (5.0 mmol) of pivalic acid in 10 ml of diethyl ether, which was kept at −80 °C. After warming to room temp. 3 ml of water was added, and the mixture was filtrated through Celite. The filtrate was washed twice with a satd. $NaHCO_3$ solution (to remove excess acid) and once with brine. The solution was dried with

$MgSO_4$ and the solvent was removed in vacuo prior to chromatography.

Workup Procedure D: The mixture was cooled to −80°C and a solution of 172 mg (2.0 mmol) of pivalic aldehyde in 3 ml of diethyl ether was added dropwise. After 1 h the temperature was raised to −20°C, the mixture was hydrolyzed with 5 ml of a satd. NH_4Cl solution and treated further as described under A.

4,5,5-Trimethyl-1-phenylsulfonyl-2,3-hexadiene (**26a**): a) Prepared from 248 mg (1.0 mmol) of **5a**, 381 mg (2.0 mmol) of CuI, 2.2 ml (4.0 mmol) of MeLi (1.85 M solution in diethyl ether), and 222 mg (1.0 mmol) of trimethylsilyl triflate; temperature −20 to −5°C, reaction time 5 h; workup procedure B. Purification by chromatography (cyclohexane/diethyl ether, 2:1) yielded 60 mg (23%) of **26a** as a colorless oil. – b) From 206 mg (1.0 mmol) of **5b**, 448 mg (5.0 mmol) of CuCN and 6.2 ml (10.0 mmol) of t-BuLi (1.62 M solution in pentane); temperature −20°C, reaction time 1 h; workup procedure B. Purification by chromatography (cyclohexane/diethyl ether, 1.5:1) yielded 240 mg (91%) of **26a** as colorless crystals; m.p. 55–57°C. – IR: $\tilde{\nu}$ = 2960, 2860 (s, CH), 1960 cm^{-1} (w, C=C=C). – ^1H NMR: δ = 0.89 [s, 9H, $C(CH_3)_3$], 1.40 (d, 3H, *J* = 2.7 Hz, 4-CH_3), 3.68/3.74 (2dd, 2H, 2 × *J* = 10.2/7.4 Hz, 1-H), 5.02 (tq, 1H, *J* = 7.4/2.7 Hz, 2-H), 7.50–7.66 (m, 3H, phenyl-H), 7.88–7.95 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 14.4 (+, CH_3), 28.8 [+, $C(CH_3)_3$], 33.3 (x, C-5), 58.2 (−, C-1), 79.3 (+, C-2), 111.1 (x, C-4), 128.7 (+), 129.2 (+), 133.7 (+), 138.6 (x, phenyl), 205.2 (x, C-3). – MS: *m/z* (%) = 264 (100) [M^+], 248 (19). – $C_{15}H_{20}O_2$ (264.4): Calcd. C 68.15, H 7.62; found C 68.05, H 7.82.

4-Methyl-1-phenylsulfonyl-2,3-pentadiene (**26b**): From 206 mg (1.0 mmol) of **5b**, 381 mg (2.0 mmol) of CuI, 2.2 ml (4.0 mmol) of MeLi (1.85 M in diethyl ether), and 200 mg (1.0 mmol) of iodotrimethylsilane; temp. −20 to 0°C, time: 2 h; workup procedure A. Chromatography with cyclohexane/diethyl ether (2:1) gave 100 mg (45%) of **26b** as a slightly yellow oil. – IR: $\tilde{\nu}$ = 2980, 2910 (s, CH), 1970 cm^{-1} (w, C=C=C). – ^1H NMR: δ = 1.39 (d, 6H, *J* = 2.7 Hz, 5-H), 3.67 (d, 2H, *J* = 7.8 Hz, 1-H), 4.97 (t × sept, 1H, *J* = 7.8/2.7 Hz, 2-H), 7.50–7.65 (m, 3H, phenyl-H), 7.85–7.96 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 19.7 (+, CH_3), 57.7 (−, C-1), 77.9 (+, C-2), 97.7 (x, C-4), 128.8 (+), 129.0 (+), 133.6 (+), 138.4 (x, phenyl), 206.9 (x, C-3). – MS: *m/z* (%) = 222 (6) [M^+], 97 (100). – $C_{12}H_{14}O_2S$ (222.3): Calcd. C 64.83, H 6.35; found C 65.19, H 6.53.

2-(1,1-Dimethylethyl)-5,5-dimethyl-1-phenylsulfonyl-3-hexyne (**28a**): From 248 mg (1.0 mmol) of **5a**, 448 mg (5.0 mmol) of CuCN and 6.0 ml (10.0 mmol) of t-BuLi (1.67 M in pentane); temp. −20°C, time 2 h; workup procedure B. Chromatography with cyclohexane/diethyl ether (2:1) furnished 210 mg (69%) of **28a** as colorless crystals; m.p. 105–107°C. – IR: $\tilde{\nu}$ = 2970, 2870 (s, CH), 2220 cm^{-1} (w, C≡C). – ^1H NMR: δ = 0.94 [s, 9H, $C(CH_3)_3$], 0.96 [s, 9H, $C(CH_3)_3$], 2.59 (dd, 1H, *J* = 9.7/2.2 Hz, 2-H), 3.21 (dd, 1H, *J* = 14.3/9.7 Hz, 1-H), 3.30 (dd, 1H, *J* = 14.3/2.2 Hz, 1-H), 7.53–7.69 (m, 3H, phenyl-H), 7.93–7.97 (m, 2H, phenyl-H). – ^{13}C NMR: δ = 27.0 [+, 2-$C(CH_3)_3$], 27.2 (x, C-5), 31.0 [+, 4-$C(CH_3)_3$], 34.5 [x, 2-$C(CH_3)_3$], 38.2 (+, C-2), 58.5 (−, C-1), 77.3 (x, C-3), 92.6 (x, C-4), 128.7 (+), 129.1 (+), 133.7 (+), 139.7 (x, phenyl). – MS: *m/z* (%) = 306 (53) [M^+], 279 (100). – $C_{18}H_{26}O_2S$ (306.5): Calcd. C 70.54, H 8.55; found C 70.03, H 8.45.

4,5,5-Trimethyl-1-phenylsulfinyl-2,3-hexadiene (**26c**): From 143 mg (0.75 mmol) of **11**, 336 mg (3.8 mmol) of CuCN and 4.7 ml (7.5 mmol) of t-BuLi (1.6 M solution in pentane); temp. −30 to −15°C, time 2 h; workup procedure C. Chromatography (cyclohexane/diethyl ether, 1:3) yielded 130 mg of **26c** (yellow oil) as a 3:1 mixture of diastereomers and two other products. Decomposition upon kugelrohr distillation. – ^1H NMR: δ = 0.94/0.96 [2s, 9H, $C(CH_3)_3$], 1.48/1.54 (2d, 3H, 2 × *J* = 2.8 Hz, 4-CH_3), 3.31–3.56 (2 × 2dd, 2H, *J* = 12.9/8.3 Hz, 1-H), 4.82/4.92 (2 × tq, 2H, *J* = 7.7/2.8 Hz, 2-H), 7.39–7.66 (m, 5H, phenyl-H). – ^{13}C NMR: δ = 14.7 (+, 4-CH_3), 28.7/28.9 [+, $C(CH_3)_3$], 33.2 (x, C-5), 57.8/58.1 (−, C-1), 79.2/79.3 (+, C-2), 110.3/110.4 (x, C-4), 124.5/124.7 (+), 129.1/129.3 (+), 131.0/131.2 (+), 143.1 (x, phenyl), 204.7/204.9 (x, C-3).

Ethyl 4-Methyl-2,3-pentadienesulfonate (**26d**): From 174 mg (1.0 mmol) of **12**, 381 mg (2.0 mmol) of CuI, 2.2 ml (4.0 mmol) of MeLi (1.85 M in diethyl ether), and 222 mg (1.0 mmol) of trimethylsilyl triflate; temp. −20 to −10°C, time 1 h; workup procedure C. Chromatography (cyclohexane/diethyl ether, 2:1) provided 60 mg (31%) of **26d** as a yellow oil. The product was a 70:30 mixture of the allene **26d** and the corresponding diene **27**. – IR: $\tilde{\nu}$ = 2980, 2920, 2870 (s, CH), 1970 cm^{-1} (w, C=C=C). – ^1H NMR: δ = 1.40 (t, 3H, *J* = 7.1 Hz, $SO_3CH_2CH_3$), 1.73 (d, 6H, *J* = 2.8 Hz, 4-CH_3), 3.68 (d, 2H, *J* = 7.6 Hz, 1-H), 4.25 (q, 2H, *J* = 7.1 Hz, $SO_3CH_2CH_3$), 5.09 (m, 1H, 2-H). – ^{13}C NMR: δ = 15.2 (+, $SO_3CH_2CH_3$), 20.0 (+, 4-CH_3), 51.9 (−, C-1), 67.0 (−, $SO_3CH_2CH_3$), 77.7 (+, C-2), 98.3 (x, C-4), 206.4 (x, C-3). – MS: *m/z* (%) = 190 (20) [M^+], 79 (100). – $C_8H_{14}O_3S$ (190.3): Calcd. C 50.50, H 7.42; found C 51.97, H 7.61.

Ethyl 4,5,5-Trimethyl-2,3-hexadienesulfonate (**26e**): From 174 mg (1.0 mmol) of **12**, 179 mg (2.0 mmol) of CuCN and 2.5 ml (4.0 mmol) of t-BuLi (1.6 M solution in pentane); temp. −30°C, time 45 min; workup procedure A. Chromatography with cyclohexane/diethyl ether (3:1) gave 115 mg (49%) of **26e** as a slightly yellow oil. – IR: $\tilde{\nu}$ = 2960, 2870 (s, CH), 1960 cm^{-1} (m, C=C=C). – ^1H NMR: δ = 1.05 [s, 9H, $C(CH_3)_3$], 1.39 (t, 3H, *J* = 7.2 Hz, $SO_3CH_2CH_3$), 1.71 (d, 3H, *J* = 2.7 Hz, 4-CH_3), 3.68 (d, 2H, *J* = 7.2 Hz, 1-H), 4.30 (q, 2H, *J* = 7.2 Hz, $SO_3CH_2CH_3$), 5.13 (tq, 1H, *J* = 7.2/2.4 Hz, 2-H). – ^{13}C NMR: δ = 14.7 (+, $SO_3CH_2CH_3$/4-CH_3), 15.2 (+, $SO_3CH_2CH_3$/4-CH_3), 28.9 [+, $C(CH_3)_3$], 33.6 [x, $C(CH_3)_3$], 52.2 (−, C-1), 66.7 (−, $SO_3CH_2CH_3$), 79.1 (+, C-2), 111.7 (x, C-4), 204.9 (x, C-3). – MS: *m/z* (%) = 232 (<1) [M^+], 107 (100). – $C_{11}H_{20}O_3S$ (232.4): Calcd. C 56.87, H 8.68; found C 57.60, H 8.62.

2-(1,1-Dimethylethyl)-5,5-dimethyl-1-nitro-3-hexyne (**28b**): From 153 mg (1.0 mmol) of **13**[10], 179 mg (2.0 mmol) of CuCN and 2.7 ml (4.0 mmol) of t-BuLi (1.5 M in pentane); temp. −20°C, time 2 h; workup procedure A. Chromatography (cyclohexane/diethyl ether, 10:1) provided 50 mg (24%) of **28b** as a yellow oil. – IR: $\tilde{\nu}$ = 2960, 2870 (s, CH), 2240 (w, C≡C), 1560 cm^{-1} (s, N=O). – ^1H NMR: δ = 1.02 [s, 9H, 4-$C(CH_3)_3$], 1.18 [s, 9H, 2-$C(CH_3)_3$], 3.02 (dd, 1H, *J* = 4.6/10.8 Hz, 2-H), 4.28 (dd, 1H, *J* = 10.8/11.5 Hz, 1-H), 4.47 (dd, 1H, *J* = 4.6/11.5 Hz, 1-H). – ^{13}C NMR: δ = 27.5 [+, 4-$C(CH_3)_3$], 31.1 [+, 2-$C(CH_3)_3$], 33.4 (x, C-5), 35.4 [x, 2-$C(CH_3)_3$], 42.3 (+, C-2), 77.6 (−, C-1), 75.0 (x, C-3), 94.4 (x, C-4). – MS: *m/z* (%) = 211 (5) [M^+], 57 (100). – $C_{12}H_{21}NO_2$ (211.3): Calcd. C 68.21, H 10.02, N 6.63; found C 69.33, H 10.27, N 5.13.

3,5-Dimethyl-2,4-hexadienenitrile (**27a**): From 105 mg (1.0 mmol) of **19**, 381 mg (2.0 mmol) of CuI and 2.2 ml (4.0 mmol) of MeLi (1.85 M solution in diethyl ether); temp. −20°C, reaction time 2 h; workup procedure A. Chromatography with cyclohexane/diethyl ether (3:1) yielded 90 mg (74%) of the known nitrile **27a**[21] as a 1.8:1 mixture of (*Z*/*E*) isomers. Workup procedure *C* furnished a 5:1 (*Z*/*E*) mixture.

2-(1-Hydroxy-2,2-dimethylpropyl)-3,5-methyl-3,4-hexadienenitrile (**26f**): The reaction was carried out as described for **27a**. Workup procedure D with 172 mg (2.0 mmol) of pivalic aldehyde. Chromatography with cyclohexane/diethyl ether (2:1) yielded 70 mg (34%) of **26f**) as slightly yellow crystals; m.p. 68–71°C. Dienes **27a** (*E*/*Z*

mixture) were isolated as byproduct. – IR: $\tilde{\nu}$ = 3500 (OH), 2980, 2960, 2920, 2880 (s, CH), 2260 (s, C≡N), 1980 cm^{-1} (w, C=C=C). – ^1H NMR: δ = 1.01 [s, 9H, $C(CH_3)_3$], 1.72/1.74 (2s, 6H, 5-CH_3) 1.78 (s, 3H, 3-CH_3), 2.18 (d, 1H, *J* = 5.2 Hz, OH), 3.24 (d, 1H, *J* = 1.8 Hz, 2-H), 3.39 (dd, 1H, *J* = 5.2/1.8 Hz, 1'-H). – ^{13}C NMR: δ = 18.2 (+), 20.3 (+), 20.8 (+, 3-CH_3/5-CH_3), 26.2 [+, $C(CH_3)_3$], 35.5 [x, $C(CH_3)_3$], 39.5 (+, C-2), 78.0, (+, C-1'), 93.6 (x, C-3/C-5), 98.5 (x, C-3/C-5), 118.8 (x, C-1), 199.9 (x, C-4). – MS: *m/z* (%) = 207 (65) [M^+], 198 (100). – $C_{13}H_{21}NO$ (207.3): Calcd. C 75.31, H 10.21, N 6.76; found C 75.55, H 10.24, N 6.70.

3,5,6,6-Tetramethyl-3,4-heptadienenitrile (**26g**): Prepared from 79 mg (0.75 mmol) of **19**, 134 mg (1.5 mmol) of CuCN and 1.9 ml (3.0 mmol) of t-BuLi (1.6 M in pentane); temp. –30°C, reaction time 1 h, workup procedure A. Chromatography (cyclohexane/diethyl ether, 10:1) gave 80 mg (65%) of **26g** as a yellow oil. – IR: $\tilde{\nu}$ = 2960, 2860 (s, CH), 2250, 2220 cm^{-1} (m, C≡N). – ^1H NMR: δ = 1.03 [s, 9H, $C(CH_3)_3$], 1.67 (s, 3H, 3-CH_3/5-CH_3), 1.73 (s, 3H, 3-CH_3/5-CH_3), 2.97 (s, 2H, 2-H). – ^{13}C NMR: δ = 14.9 (+, 3-CH_3/5-CH_3), 18.9 (+, 3-CH_3/5-CH_3), 23.9 (–, C-2), 29.0 [+, $C(CH_3)_3$], 34.1 (x, C-6), 89.5 (x, C-3/C-5), 97.2 (x, C-3/C-5), 117.7 (x, C-1), 198.6 (x, C-4). – MS: *m/z* (%) = 163 (5) [M^+], 121 (100). – A correcct elemental analysis of this labile allene could not be obtained.

2-(1,3-Dimethyl-1,2-butadien-1-yl)-3-(1,1-dimethylethyl)-β-propiolactone) (**29a**) and *6-(1,1-Dimethylethyl)-5,6-dihydro-4-methyl-5-(methylethenylidene)-2H-pyran-2-one* (**30**): Prepared from 97 mg (0.5 mmmol) of **21**, 476 mg (2.5 mmol) of CuI, 2.8 ml (5.0 mmol) of MeLi (1.85 M solution in diethyl ether), and 431 mg (5.0 mmol) of pivalic aldehyde; temp. –20°C, time 2 h; workup procedure D. Chromatography (cyclohexane/diethyl ether, 1:3) gave 30 mg (29%) of **29a** and 30 mg (29%) of **30** as yellow oils.

29a: IR: $\tilde{\nu}$ = 2960, 2910, 2870 (s, CH), 1820 cm^{-1} (s, C=O). – ^1H NMR: δ = 0.99 [s, 9H, $C(CH_3)_3$], 1.67/1.71 (2s, 6H, 3'-CH_3), 1.79 (s, 3H, 1'-CH_3), 3.75 (d, 1H, *J* = 4.5 Hz, 2-H), 4.12 (d, 1H, *J* = 4.5 Hz, 3-H). – ^{13}C NMR: δ = 17.5 (+, 1'-CH_3), 20.4/20.7 (+, 3'-CH_3), 24.4 [+, $C(CH_3)_3$], 32.7 [x, $C(CH_3)_3$], 54.7 (+, C-2), 84.0 (+, C-3), 91.2 (x, C-1'/C-3'), 97.8 (x, C-1'/C-3'), 169.5 (x, C-1), 199.5 (x, C-2'). – MS: *m/z* (%) = 208 (63) [M^+], 193 (100). – $C_{13}H_{20}O_2$ (208.3): Calcd. C 74.96, H 9.68; found C 74.27, H 9.90.

30: IR: $\tilde{\nu}$ = 2960, 2910, 2870 (s, CH), 1700 (s, C=O), 1630 cm^{-1} (m, C=C). – ^1H NMR: δ = 0.93 [s, 9H, $C(CH_3)_3$], 1.88 (s, 3H, 1'-CH_3), 1.96 (s, 3H, 1'-CH_3), 2.21 (d, 3H, *J* = 1.3 Hz, 4-CH_3), 5.04 (s, 1H, 6-H), 5.74 (q, 1H, *J* = 1.3 Hz, 3H). – ^{13}C NMR: δ = 23.3 (+), 23.5 (+), 23.8 (+, 4-CH_3/1'-CH_3), 27.1 [+, $C(CH_3)_3$], 38.1 [x, $C(CH_3)_3$], 86.4 (+, C-6), 118.9 (+, C-3), 125.1 (x), 140.2 (x), 152.6 (x, C-4/C-5/C-1'), 164.4 (x, C-2). – MS: *m/z* (%) = 208 (100) [M^+], 152 (100). – $C_{13}H_{20}O_2$ (208.3): Calcd. C 74.96, H 9.68; found C 73.85, H 9.74.

3-(1,1-Dimethylethyl)-2-(1,3,4,4-tetramethyl-1,2-pentadien-1-yl)-β-propiolactone (**29b**): Prepared from 145 mg (0.75 mmol) of **21**, 134 mg (1.5 mmol) of CuCN, 1.9 ml (3.0 mmol) of t-BuLi (1.6 M solution in diethyl ether), and 431 mg (5.0 mmol) of pivalic aldehyde; temp. –20°C, time 1.5 h; workup procedure D. Chromatography with cyclohexane/diethyl ether (10:1) provided 145 mg (77%) of **29b** (1:1 mixture of diastereomers) as a colorless oil. – IR: $\tilde{\nu}$ = 2960, 2870 (s, CH), 1990 (w, C=C=C), 1830 cm^{-1} (s, C=O). – ^1H NMR: δ = 0.96/0.98 [2s, 9H, $C(CH_3)_3$], 1.01/1.03 [2s, 9H, $C(CH_3)_3$], 1.65/1.68 (2s, 3H, 3'-CH_3), 1.78/1.79 (2s, 3H, 1'-CH_3), 3.71 (d, 1H, *J* = 4.4 HZ, 2-H), 4.10/4.13 (2d, 1H, 2 × *J* = 4.4 Hz, 3-H). – ^{13}C NMR: δ = 14.9/15.1 (2+, 1'-CH_3), 17.8/18.1 (2+, 3'-CH_3), 24.5/24.6 [2+, 3-$C(CH_3)_3$], 29.1/29.2 [2+, 3'-$C(CH_3)_3$], 32.7/32.9 [2x, 2-$C(CH_3)_3$], 34.0/34.2 [2x, 3'-$C(CH_3)_3$], 54.6/54.8 (2+, C-2), 84.0/84.2 (2+, C-3), 92.6/92.7 (2x, C-1'), 111.4/111.6 (2x, C-3'), 169.5 (x, C-1), 197.9/198.1 (2x, C-2'). – NOE experiment: Irradiation at δ = 1.79 (1'-CH_3) gave an intensity enhancement of the resonance at δ = 4.13 (3-H). – MS: *m/z* (%) = 250 (3) [M^+], 149 (100). – $C_{16}H_{26}O_2$ (250.4): Calcd. C 76.75, H 10.47; found C 75.45, H 10.15.

Methyl 2-[(2-(1,1-Dimethylethyl)-2-pentenylidene]-1-cyclohexanecarboxylate (**31**): Prepared from 206 mg (1.0 mmol) of **25a**, 179 mg (2.0 mmol) of CuCN and 2.4 ml (4.0 mmol) of t-BuLi (1.7 M in pentane); temp. –20°C, time 1.5 h; workup procedure C. Chromatography with cyclohexane/diethyl ether (20:1) furnished 110 mg (42%) of **31** (1:1 mixture of diastereomers) as a yellow oil. – IR: $\tilde{\nu}$ = 2940, 2860 (s, CH), 1735 cm^{-1} (C=O). – ^1H NMR: δ = 0.90/0.91 (2t, 3H, 2 × *J* = 7.4 Hz, 5'-H), 0.99/1.00 [2s, 9H, $C(CH_3)_3$], 1.27–2.32 (m, 12H, 3-, 4-, 5-, 6-, 3'-, 4'-H), 3.02 (m, 1H, 1-H), 3.60/3.61 (2s, 3H, CO_2CH_3). – ^{13}C NMR: δ = 14.3 (+, C-5'), 21.2 (–), 21.5 (–), 24.7 (–), 27.4 (–), 29.4 (–), 31.9 (–, C-3/C-4/C-5/C-6/C-3'/C-4'), 29.4 [+, $C(CH_3)_3$], 34.0 [x, $C(CH_3)_3$], 47.6 (+, C-1), 51.3 (+, CO_2CH_3), 103.1 (x, C-2/C-2'), 114.8 (x, C-2/C-2'), 174.1 (x, CO_2CH_3), 193.7 (x, C-1'). – MS: *m/z* (%) = 264 (28) [M^+], 207 (100). – $C_{17}H_{28}O_2$ (264.4): Calcd. C 77.22, H 10.67; found C 77.22, H 10.72.

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