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Electrophilic Addition of Propargylic Cations to Allenes: Formation of Crowded Chloro- and Azido-Enynes by Trapping of the Resulting Allylic Cations with TMSX (X = Cl, N_3): A Synthetic and Computational Study

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Propargylic cations, generated by the ionization of propargyl alcohols with catalytic amounts of $Bi(OTf)_3$, react with aryl-substituted allenes to generate incipient allylic cations that are quenched in the presence of TMSCl to form a number of sterically crowded chloro-enynes as a mixture of *Z* and *E* isomers with a strong preference for the *Z* alkenes. Several other metallic triflates, $M(OTf)_3$ (M = Sc, Yb, La), as well as bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$ also promote this reaction with similar conversions and stereoselectivity. Although trapping with TMSBr and TMSI gave intractable mixtures, trapping with $TMSN_3$ in a couple of cases led to the isolation of the corresponding isomeric azido-enynes, albeit in lower isolated yields and lower stereoselectivity. Competitive formation of the Meyer–Schuster rearrangement products was also observed. Sterically crowded chloro-allenes did not form adducts with propargyl alcohols, instead they underwent a skeletal rearrangement under the influence of $Bi(OTf)_3$ to form 2-chloro-butadienes. The results of DFT calculations indicated that the relative *anti*/*syn* energies of the propargyl cation and the energy difference between the *Z*/*E* isomeric products are too small to explain the stereochemical preference observed for the enynes. A study of the transition state in the crucial C–C bond-forming step by DFT indicated that rotation of the benzylic portion away from the propargyl cation may be a key factor in favoring the *anti* isomer of the allylic cation.

Introduction

Allenes are being increasingly recognized as powerful and versatile building blocks in organic synthesis and progress in this area, in particular in the past two decades, has rapidly changed their old image of being highly unstable and difficult to work with.[1,2]

To date, many examples of electrophilic addition to allenes with control of regio- and stereoselectivity have been reported.[3] Lewis acid activation and the formation of incipient allylic cations has led to successful ring-closing reactions for the construction of heterocyclic compounds.[4]

Meng and Ma reported the condensation of allylic alcohols with 1-aryl- and 1,1-diaryl-substituted allenes in the presence of ZnX_2 to form allylic halides and indenes.[5] In connection with a number of studies in our laboratory focusing on C–C bond-forming reactions with propargylic cations employing metallic triflates or bismuth nitrate as catalyst and ionic liquids as solvent[6–9] and our continuing interest in propargyl/allenyl carbocation generation and chemistry,[10] we report herein on the reaction of aryl-substituted allenes with a series of propargylic alcohols by using metallic triflates as catalyst in the presence of TMSX to form sterically crowded halo-enyne derivatives. A computational study aimed at probing the origin of the observed stereoselectivity that leads to the formation of *Z* alkenes is also reported.

Results and Discussion

The reaction of allene **1a** with propargylic alcohol **2a** in the presence of 1.1 equiv. of TMSCl and 5 mol-% $Bi(OTf)_3$ in DCM at 0 °C gave the corresponding chloro-enyne adduct **3aa** (Scheme 1) in 65% isolated yield as a mixture of *Z* and *E* isomers in a ratio of 92:8, as determined by NMR spectroscopy.

The isomers were identified on the basis of the nuclear Overhauser difference (NOED) (see Figure 1) and 2D NMR spectroscopy. For compound **3aa** (*Z*), irradiation of H_c (δ = 7.02 ppm) resulted in a strong NOE enhancement of H_d (δ = 5.01 ppm) with no enhancement in H_a/H_b (δ = 4.42/3.99 ppm). Irradiation of H_d (δ = 5.01 ppm) resulted in a strong NOE enhancement of H_c (δ = 7.02 ppm) and a very weak enhancement of H_a/H_b. When H_a/H_b (δ = 4.42/

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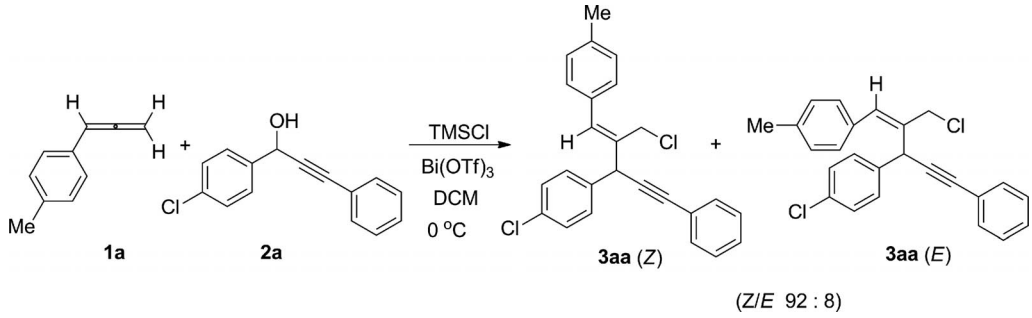


Scheme 1. Coupling of aryl-allene **1a** with propargylic alcohol **2a**.

3.99 ppm) were irradiated separately, strong NOE enhancement of the geminal proton was observed with a very weak enhancement of H_c (δ = 7.02 ppm) and H_d (δ = 5.01 ppm). For compound **3ab** (*E*), when H_a/H_b (δ = 3.98/4.12 ppm) were irradiated separately, a strong NOE enhancement of the geminal proton was observed and a very weak enhancement of H_c (δ = 6.91 ppm), but no NOE effects were detected between H_a/H_b and H_d (δ = 5.38 ppm). Similarly, irradiation of H_c (δ = 6.91 ppm) resulted in only a weak NOE effect on H_a/H_b (δ = 3.98/4.12 ppm) and no NOE enhancement of H_d (δ = 5.38 ppm). These NOE measurements were corroborated by COSY and HSQC NMR spectroscopy. The COSY spectrum of **3aa** shows a correlation between H_c (δ = 7.02 ppm) and H_d (δ = 5.01 ppm), but no

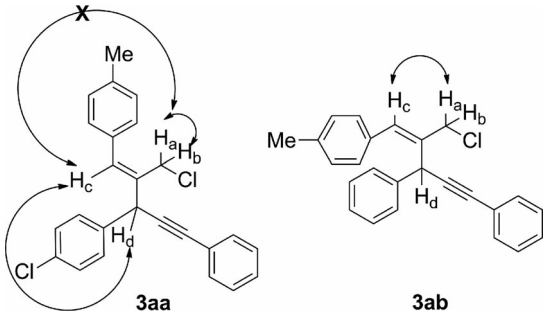


Figure 1. NOE effects in **3aa** and **3ab**.

Table 1. Survey of catalysts in the reaction of **1a** with **2a** to form **3aa**.

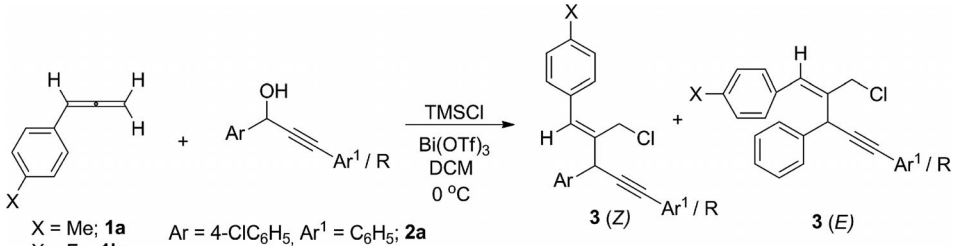
Entry	Catalyst[a]	*T* [°C]	*Z*/*E*[b]	Yield[c] [%]
1	$Bi(OTf)_3$	0	92:8	65
2.	$Sc(OTf)_3$	0	90:10	58
3.	$Yb(OTf)_3$	0	87:13	56
4.	$La(OTf)_3$	0	88:12	62
5.	$Bi(NO_3)\cdot 5H_2O$	0	90:10	57
6.	$Bi(OTf)_3$	–20	91:9	55
7.	$Bi(OTf)_3$	–40	91:9	50

[a] Catalyst loading 5 mol-%. [b] Isomer ratios determined by NMR spectroscopy. [c] Isolated yield.

Table 2. Scope of the reaction of allenes **1** with propargylic alcohols **2**.

Entry	Allene	Propargylic alcohol	Product	Yield[a] [%]	*Z*/*E*[b]
1.	**1a**	**2a**	**3aa**	65	91:9
2.	**1a**	**2b**	**3ab**	60	92:8
3.	**1a**	**2c**	**3ac**	58	89:11
4.	**1a**	**2d**	**3ad**	63	91:9
5.	**1a**	**2e**	**3ae**	64	92:8
6.	**1a**	**2f**	**3af**	65	87:13
7.	**1a**	**2g**	**3ag**	59	91:9
8.	**1a**	**2h**	**3ah**	55	89:11
9.	**1a**	**2i**	**3ai**	62	93:7
10.	**1b**	**2f**	**3bf**	52	72:28
11.	**1b**	**2h**	**3bh**	52	80:20
12.	**1c**	**2c**	**3cc**	51	82:18
13.	**1c**	**2h**	**3ch**	51	73:27

[a] Isolated yield. [b] Isomer ratios determined by NMR spectroscopy.



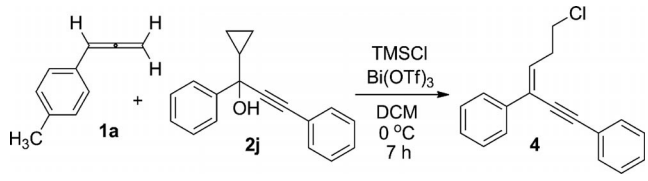
X = Me; **1a**
X = F; **1b**
X = H; **1c**

Ar = 4-ClC_6H_5, Ar^1 = C_6H_5; **2a**
Ar = C_6H_5, Ar^1 = C_6H_5; **2b**
Ar = 4-MeC_6H_5, Ar^1 = C_6H_5; **2c**
Ar = 4-BrC_6H_5, Ar^1 = C_6H_5; **2d**
Ar = 4-FC_6H_5, Ar^1 = C_6H_5; **2e**
Ar = 2-Thienyl, Ar^1 = C_6H_5; **2f**
Ar = C_6H_5, R = *n*Bu; **2g**
Ar = 4-MeC_6H_5, R = *n*Bu; **2h**
Ar = 4-FC_6H_5, R = *n*Bu; **2i**

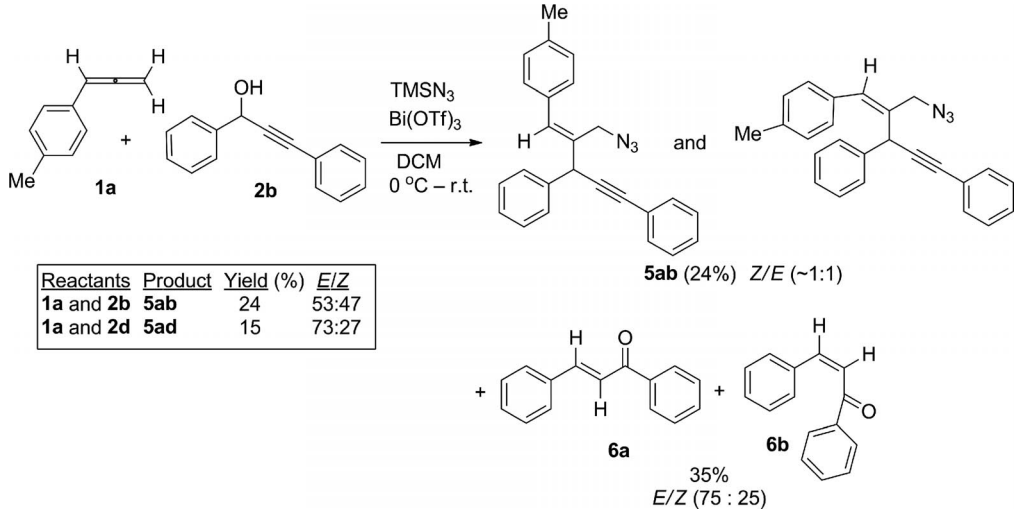
Scheme 2. Condensation of propargylic alcohols **2a**–**2i** with aryl-allenes **1a**–**1c** in the presence of TMSCl and catalytic amounts of $Bi(OTf)_3$.

interaction with the methylene protons. The HSQC NMR spectrum confirmed the C/H connectivity between CH_2 (for **3aa**; δ = 42.1 ppm) and H_a/H_b (δ = 4.42/3.99 ppm), and between CH_2 (δ = 42.0 ppm) and H_d (δ = 5.01 ppm). The H_c proton at δ = 7.02 ppm shows long-range coupling with the *C*H signal at δ = 132.3 ppm. High-field proton spectra provide a diagnostic tool for the detection/identification of *Z*/*E* isomeric products (see selected NMR spectra in Supporting Information).

In the search for other catalysts that could promote this transformation, the reaction was repeated with other metallic triflates (M = Sc, Yb, La) and bismuth nitrate pentahydrate. The results (Table 1) demonstrate that this C–C bond-forming transformation works well with all of these catalysts, but with minor variations in the isolated yields and isomer ratios, although the use of excess $Bi(OTf)_3$ (20 mol-%) gave complex mixtures. Lowering the reaction

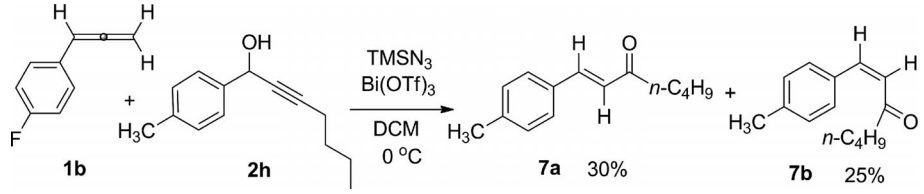


Scheme 3. Formation of compound **4** from propargylic alcohol **2j**.

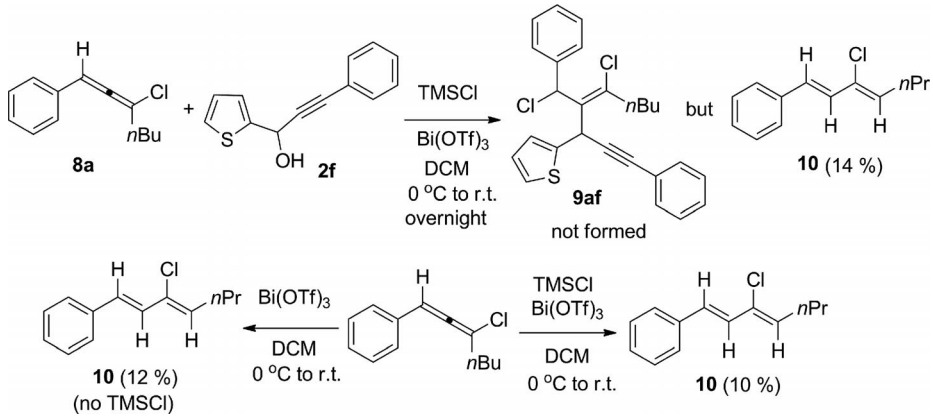


Reactants	Product	Yield (%)	*E*/*Z*
1a and **2b**	**5ab**	24	53:47
1a and **2d**	**5ad**	15	73:27

Scheme 4. Reaction of **1a** with **2b** in the presence of $TMSN_3$ and $Bi(OTf)_3$.



Scheme 5. Reaction of **1b** with **2h** in the presence of $TMSN_3$ and $Bi(OTf)_3$.



Scheme 6. Reaction of crowded chloro-allene **8a** with **2f** in the presence of TMSCl and $Bi(OTf)_3$. Formation of chlorobutadiene **10** and independent synthesis of **10**.

temperature appeared to have no notable influence on the *Z*/*E* ratio (Table 1).

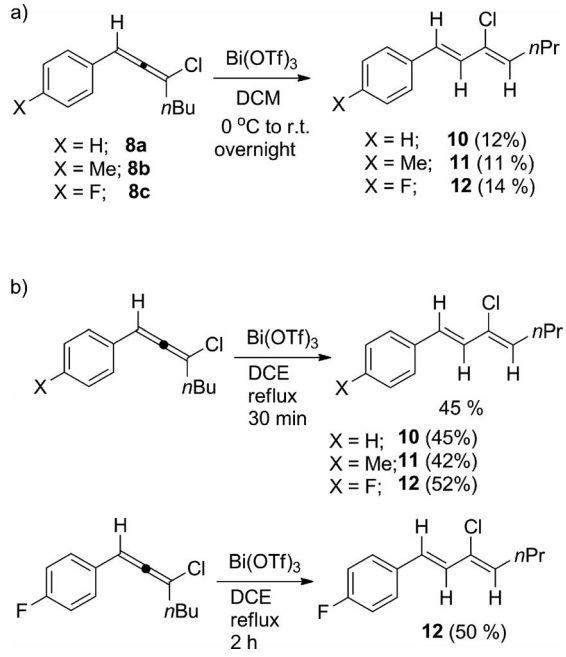
Having established the feasibility of this novel C–C bond-forming reaction, we set out to determine the scope of the transformation (Scheme 2 and Table 2). Thus, propargylic alcohols **2a**–**2i** were treated with aryl-allenes **1a**–**1c** in the presence of a slight excess of TMSCl and catalytic amounts of $Bi(OTf)_3$.

The chloro-enyne derivatives **3aa**–**3ai** were isolated in yields of 55–65% as *Z*/*E* mixtures with a strong preference for the formation of the *Z* alkene (typically 9:1). The chloro-enyne derivatives **3bf**, **3bh**, **3cc**, and **3ch** were obtained in similar isolated yields of 51–52%, but with smaller ratios of *Z*/*E*.

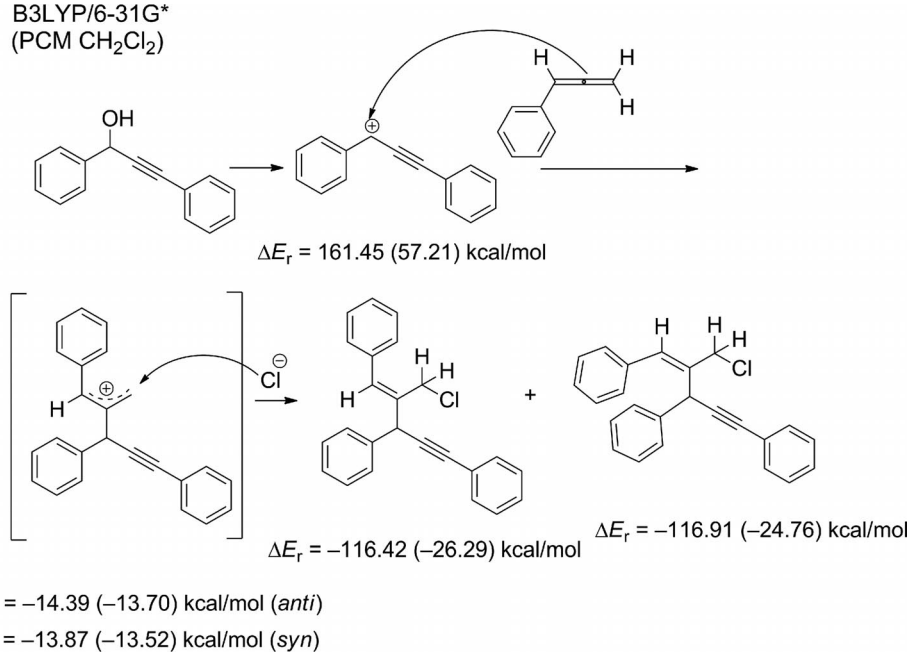
In an attempt to induce a Lewis acid catalyzed $Z \rightarrow E$ isomerization, isolated chloro-enyne adduct **3bf** was heated at reflux in 1,2-dichloroethene (DCE) for 5 h in the presence of $Bi(OTf)_3$, but no noticeable change in the *Z*/*E* ratio was observed by NMR spectroscopy. This suggests that the *Z*/*E* ratios reflect a kinetic distribution and that the formation of the *E* isomer by subsequent isomerization of the initially formed *Z* isomer is unlikely.

The reaction of aryl-allene **1a** with propargylic alcohol **2j** did not produce the expected coupling adduct; the allene remained unreacted (TLC monitoring) and chloro-enyne **4** was isolated in 73% yield (Scheme 3). Compound **4** was formed by a well-known rearrangement of the α-cyclopropyl carbocation derived from **2j** and trapping with TMSCl.[6]

Unfortunately, when TMSCl was replaced by TMSBr or TMSI, the reactions were no longer clean. Although the allene was consumed (TLC monitoring), the corresponding halo-enyne was only formed in low yields along with other unidentified compounds in complex mixtures that could not be separated. A complex mixture was also formed with TMSCN. With $TMSN_3$, the azido-enyne derivative **5ab** was isolated, albeit in low yield, along with the Meyer–Schuster rearrangement products[11,12] **6a** and **6b** as an *E*/*Z* mixture, which were separated (Scheme 4). Remarkably, in the case of **5ab**, the proportion of the *E* isomer was notably higher (*E*/*Z*, 53:47). In addition, the azido-enyne **5ad** was obtained



Scheme 7. Formation of 2-chlorobutadienes **10**–**12** from chloro-allenes in a) DCM at room temp. and b) in DCE at reflux.



Scheme 8. B3LYP/6-31G* relative energies for the *anti* and *syn* configurations of the allyl cation and the derived Z and *E* chloro-enynes (values in parentheses were determined by the PCM method with DCM as solvent).

from the reaction of the same allene **1a** with **2d** in a modest isolated yield (15%) as an isomeric mixture in which the *E* isomer prevailed (*E*/*Z*, 73:27). However, the targeted azido-enyne adduct was not obtained from the reaction of fluorophenyl-allene **1b** and propargylic alcohol **2h**. Instead only the Meyer–Schuster rearrangement products **7a/7b** were isolated (Scheme 5).

The facile synthesis of crowded halo-allenes (such as **8a** in Scheme 6) by the reaction of propargylic alcohols with *N*-halosuccinimide/PPh_3[13] encouraged us to explore their reaction with propargylic alcohols. We had hoped that the introduction of steric crowding at the other end of the allenyl moiety may alter the regioselectivity of nucleophilic attack by TMSCl on the resulting allyl cation, hence forming different types of crowded chloro-enynes, for example, **9af**. The reaction of **8a** with the propargyl alcohol **2f** (Scheme 6) did not, however, lead to the successful isolation of the expected coupling adduct **9af**. Instead, the chlorobutadiene **10** was formed by a skeletal rearrangement involving the *n*-butyl side-chain under the influence of $Bi(OTf)_3$ and was isolated in modest yield out of an otherwise complex reaction mixture that could not be separated. Independent control experiments (Scheme 6) confirmed that the formation of compound **10** is independent of **2f** and TMSCl and only requires the presence of catalytic amounts of $Bi(OTf)_3$. The formation of **10** from **8a** was also observed by using $Sc(OTf)_3$.

To check the generality of this transformation, chloroallenes **8b** and **8c** were synthesized[13] and tested (Scheme 7, a). The corresponding 2-chlorobutadienes **11** and **12** were formed in the presence of catalytic amounts of $Bi(OTf)_3$ in DCM and were isolated in low yields. A significant improvement in the isolated yields was observed by heating the chloro-allenes in DCE at reflux and by employing short reaction times (Scheme 7, b).

Although the mechanistic details have not been established for this transformation, it is seemingly a Lewis acid catalyzed electrocyclic reaction involving a hydride shift from the *n*-butyl methylene and migration of the double bond.

Probing the Origin of the Stereoselectivity in the Formation of the Chloro-Enynes

The plausible mechanistic pathway depicted in Scheme 8 was evaluated by means of DFT calculations both in the gas phase and with CH_2Cl_2 as solvent. The computed energies of the isomeric chloro-enynes are similar (difference of less than 1 kcal/mol in the gas phase). The incorporation of solvation effects (by means of PCM computations) led to an increase in the energy difference to around 2 kcal/mol in favor of the *Z* alkene, but it is still too small to account for the strong preference for the *anti* orientation of the allyl cation and subsequent formation of the *Z* alkene. To shed some light on this issue, the kinetics of the process were considered by characterizing the corresponding transition state for the formation of the allyl cation, which is the step determining the *anti*/*syn* isomerism.

In the transition state (TS), the originally linear allene starts to bend and the vinyl moiety becomes perpendicular to the benzyl fragment (Figure 2, structure a). This TS could in principle generate either a *syn* or *anti* allyl cation. After the transition state, the reaction proceeds downhill with rotation of the benzyl group away from the propargyl moiety to yield the *anti* isomer of the allylic cation (the reaction profile is shown in Figure 3, a). Rotation in the opposite direction generates repulsive interactions between

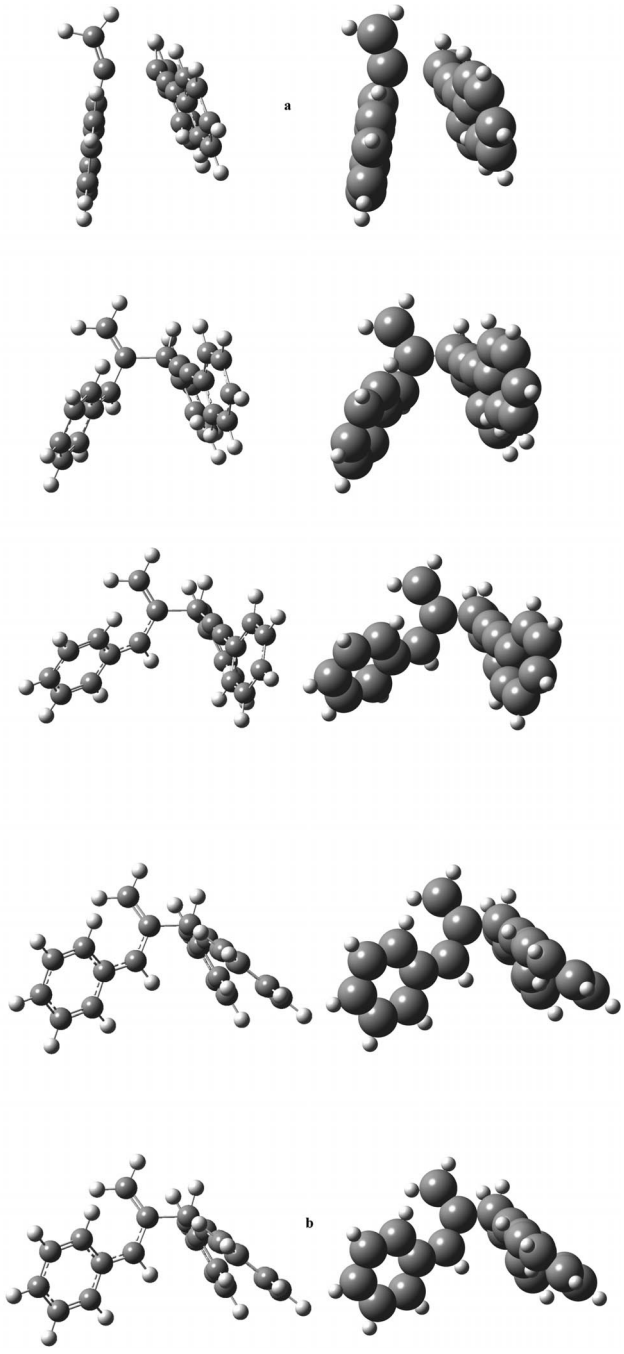


Figure 2. Intermediate structures going downhill from the transition for the propargyl cation/allene coupling reaction (a) to the *anti*-allylic cation (b). The structures are shown in ball-and-stick and space-filling modes by using van der Waals radii.

the proximate hydrogen atoms leading to a higher potential energy surface for the formation of the *syn* allylic cation (Figure 2, structure b and Figure 3, b). This mechanistic picture may explain the experimental observations regarding the preference for the formation of the *Z*-chloro-enynes, however, the preferred formation of the *E* isomer in the case of the azido derivatives **5ab** and **5ad** remains a mystery.

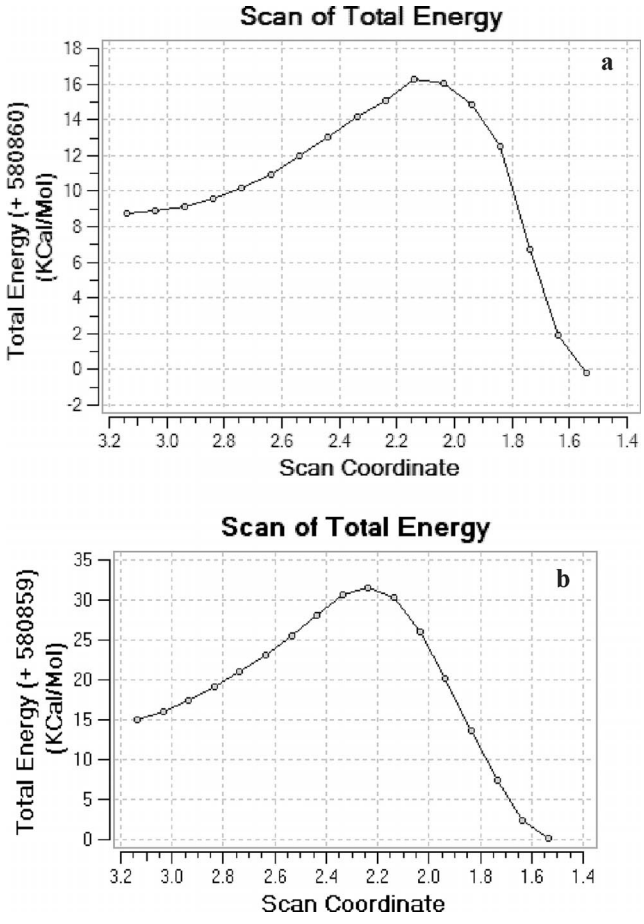


Figure 3. Reaction profiles for the coupling reaction: (a) formation of the *anti* allylic cation and (b) constraining the geometry of the reactants in a *syn* disposition to obtain the *syn*-allylic cation. The *x* axis corresponds to the length (in Å) of the forming bond.

Conclusions

We have shown that the propargylic cations generated by the ionization of propargylic alcohols with catalytic amounts of $Bi(OTf)_3$ react with various aryl-substituted allenes to form incipient allylic cations that are quenched by TMSCl to produce a number of sterically crowded chloro-enynes as *Z*/*E* isomeric mixtures with a preference for the formation of the Z stereoisomer. Two azido-enynes were also formed by using $TMSN_3$. A study of the transition state for the crucial C–C bond-forming step by DFT calculations indicates that rotation of the benzylic portion away from the propargyl cation may be a key factor in favoring the *anti* isomer of the allylic cation. An interesting skeletal rearrangement was observed in crowded chloro-allenes bearing an *n*-butyl group, which produced 2-chlorobutadienes.

Experimental Section

Computational Procedures: Calculations were performed with the Gaussian 09 suite of programs.[14] The structures were fully optimized by DFT using the B3LYP[15] functional and the 6-31G* basis set. Harmonic vibrational frequency calculations were performed to characterize all computed stationary points as minima (no imaginary frequencies) or transition states (one imaginary frequency). Solvation effects were considered by performing energy minimizations in CH_2Cl_2 (dielectric constant ε = 8.93) using the SCRF-polarized continuum model (PCM).[16]

General Experimental Methods: The substituted allenes[17] and propargyl alcohols[18] were synthesized according to the reported methods. The Lewis acid catalysts employed were purchased and used without further purification. Reactions were carried out in 10 mL round-bottomed flasks under N_2. Dichloromethane (DCM) was dried with molecular sieves. Column chromatography was performed on silica gel (200–400 mesh). NMR spectra were recorded in $CDCl_3$ with a Varian 500 MHz NMR spectrometer. The mass spectra of the isomeric mixtures were recorded by using the ES-API method at the Mass Spectrometer facility at the University of South Florida. Owing to their fragile nature, intact molecular ions were observed only in some cases, typically accompanied by substantial fragmentation.

General Synthetic Procedure: Trimethylsilyl halide (TMSX) or trimethylsilyl azide ($TMSN_3$; 0.60 mmol) followed by $Bi(OTf)_3$ (0.05 mol-%) were added to a mixture of 1-arylallene (0.5 mmol) and propargylic alcohol (0.5 mmol) in dichloromethane (2 mL) at 0 °C under nitrogen. The reaction mixture was stirred for 4–5 h at 0 °C. After completion (monitored by TLC), the reaction mixture was directly passed through a column of silica gel and the products were eluted with hexane. The isomeric mixtures could not be separated by column chromatography and were isolated as isomeric mixtures. The azido-enynes were purified by preparative TLC.

(*Z*)-2-(Chloromethyl)-3-(4-chlorophenyl)-5-phenyl-1-(*p*-tolyl)pent-1-en-4-yne (3aa, *Z*/*E* = 91:1): Yield: 65%; viscous yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.48–7.45 (m, 4 H), 7.37–7.36 (m, 3 H), 7.34–7.32 (m, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.02 (s, 1 H), 5.01 (d, *J* = 1.0 Hz, 1 H), 4.42 (d, *J* = 11.5 Hz, 1 H), 3.99 (d, *J* = 11.5 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.8, 137.6, 136.1, 133.3, 133.0, 132.3, 131.6, 129.7, 129.2, 128.9, 128.6, 128.3, 128.2, 123.0, 88.1, 86.4, 42.1, 42.0, 21.2 ppm. MS (ES-API): *m*/*z* = 256 [M – $C_8H_5Cl]^+$, 389.0 [M – 1]$^+$, 390.1 [M]$^+$, 391 [M + 1]$^+$, 282, 256, 130. Minor isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.44 (s), 4.27 (dd), 4.08 (dd) ppm.

(*Z*)-2-(Chloromethyl)-3,5-diphenyl-1-(*p*-tolyl)pent-1-en-4-yne (3ab, *Z*/*E* = 92:8): Yield: 60%; viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.51–7.47 (m, 4 H), 7.38–7.37 (m, 3 H), 7.32–7.28 (m, 6 H), 7.19 (d, *J* = 7.5 Hz, 2 H), 7.05 (s, 1 H), 5.02 (d, *J* = 1.0 Hz, 1 H), 4.40 (d, *J* = 11.0 Hz, 1 H), 3.98 (d, *J* = 11.5 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.4, 137.5, 136.7, 133.4, 132.1, 131.8, 129.3, 128.9, 128.7, 128.5, 128.3, 128.2, 127.5, 123.4, 88.8, 86.2, 42.6, 42.3, 21.3 ppm. MS (ES-API): *m*/*z* = 357 [M + H]$^+$, 279 [M – Ph]$^+$. Minor isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.48 (s), 4.29 (dd), 4.06 (dd) ppm.

(*Z*)-2-(Chloromethyl)-5-phenyl-1,3-di(*p*-tolyl)pent-1-en-4-yne (3ac, *Z*/*E* = 89:11): Yield: 58%; viscous pale-yellow liquid. ^{1}H NMR

($CDCl_3$, 500 MHz): δ = 7.46–7.44 (m, 2 H), 3.37 (d, J = 8.5 Hz, 2 H), 7.30–7.26 (m, 5 H), 7.18–7.16 (m, 4 H), 7.04 (s, 1 H), 4.96 (s, 1 H), 4.38 (d, J = 11.5 Hz, 1 H), 3.95 (d, J = 11.5 Hz, 1 H), 2.35 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.5, 137.2, 136.8, 136.4, 133.5, 131.9, 131.8, 131.7, 129.6, 129.3, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 123.5, 89.1, 86.1, 42.3, 42.2, 21.3, 21.2 ppm. MS (ES-API): m/z = 366/369 $[M - H]^+$, 267, 239, 130. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.41 (s), 4.28 (dd), 4.04 (dd) ppm.

(*Z*)-3-(4-Bromophenyl)-2-(chloromethyl)-5-phenyl-1-(*p*-tolyl)pent-1-en-4-yne (3ad, *Z*/*E* = 91:1): Yield: 63%; yellow solid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.51 (d, J = 8.5 Hz, 2 H), 7.48–7.46 (m, 2 H), 7.39 (d, J = 8.5 Hz, 2 H), 7.33–7.31 (m, 3 H), 7.27 (d, J = 8.5 Hz, 2 H), 7.20 (d, J = 8.5 Hz, 2 H), 7.00 (s, 1 H), 4.99 (d, J = 1.0 Hz, 1 H), 4.40 (d, J = 11.0 Hz, 1 H), 3.98 (d, J = 11.0 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.4, 137.6, 136.1, 133.0, 132.4, 131.8, 131.7, 131.6, 130.1, 129.2, 128.6, 128.3, 128.2, 123.0, 121.4, 88.0, 86.4, 42.1, 21.2 ppm. MS (ES-API): m/z = 435/433/431/429 $[M]^+$, 280, 242, 130. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.41 (s), 4.26 (dd), 4.07 (dd) ppm.

(*Z*)-2-(Chloromethyl)-3-(4-fluorophenyl)-5-phenyl-1-(*p*-tolyl)pent-1-en-4-yne (3ae, *Z*/*E* = 92:8): Yield: 64%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.50–7.47 (m, 4 H), 7.33–7.32 (m, 3 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.09–7.06 (m, 2 H), 7.01 (s, 1 H), 5.01 (s, 1 H), 4.41 (d, J = 11.5 Hz, 1 H), 3.99 (d, J = 11.5 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 162.2 (d, J = 245.0 Hz), 137.7, 136.6, 133.2, 132.3, 131.8, 130.1 (d, J = 7.3 Hz), 129.3, 128.7, 128.3 (d, J = 10.2 Hz), 123.2, 115.7 (d, J = 21.3 Hz), 88.5, 86.5, 42.2, 42.0, 21.3 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –115.1 (m) ppm. MS (ES-API): m/z = 373 $[M - H]^+$, 267, 239, 130. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.44 (s), 4.24 (dd), 4.07 (dd) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.19, 135.1, 131.9, 129.5, 128.8, 128.4 ppm.

(*Z*)-2-(Chloromethyl)-5-phenyl-3-thienyl-1-(*p*-tolyl)pent-1-en-4-yne (3af, *Z*/*E* = 87:13): Yield: 65%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.50–7.48 (m), 7.33–7.30 (m), 7.27–7.26 (m), 7.20 (d), 7.16–7.15 (m), 7.10 (s), 7.00–6.98 (m), 5.29 (s), 4.43 (d), 4.12 (d), 2.37 (s) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 143.1, 137.7, 136.2, 133.1, 132.2, 131.8, 129.3, 128.7, 128.4, 126.9, 126.3, 125.3, 123.1, 88.0, 85.9, 42.0, 38.1, 21.4 ppm. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.52 (s), 4.39 (dd), 4.23 (dd) ppm.

(*Z*)-2-(Chloromethyl)-3-phenyl-1-(*p*-tolyl)non-1-en-4-yne (3ag, *Z*/*E* = 91:9): Yield: 59%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.43–7.41 (m, 2 H), 7.36–7.33 (m, 2 H), 7.28–7.25 (m, 3 H), 7.18 (d, J = 8.5 Hz, 2 H), 6.96 (s, 1 H), 4.76 (d, J = 1.5 Hz, 1 H), 4.35 (d, J = 11.5 Hz, 1 H), 3.91 (d, J = 11.5 Hz, 1 H), 2.37 (s, 3 H), 2.28 (dt, J_1 = 1.5, J_2 = 7.0 Hz, 2 H), 1.56–1.51 (m, 2 H), 1.46–1.42 (m, 2 H), 0.92 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 140.1, 137.4, 137.3, 133.6, 131.6, 129.2, 128.7, 128.7, 128.4, 127.3, 86.6, 79.2, 42.3, 42.1, 31.1, 22.1, 21.3, 18.7, 13.7 ppm. MS (ES-API): m/z = 335 $[M - H]^+$, 337, 353, 267, 239, 130. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.23 (s), 4.23 (dd), 3.97 (dd) ppm.

(*Z*)-2-(Chloromethyl)-1,3-di(*p*-tolyl)non-1-en-4-yne (3ah, *Z*/*E* = 89:11): Yield: 55%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.30 (d, J = 8.0 Hz, 2 H), 7.26–7.24 (m, 2 H), 7.19–7.18 (m, 2 H), 7.17–7.14 (m, 4 H), 7.09 (m, 2 H), 6.97 (s, 1 H), 4.72 (d, J = 1.5 Hz, 1 H), 4.34 (d, J = 11.0 Hz, 1 H), 3.90 (d, J = 11.0 Hz, 1 H), 2.36 (s, 3 H), 2.34 (s, 3 H), 2.28 (dt, J_1 = 1.5, J_2 = 7.0 Hz, 2 H), 1.55–1.52 (m, 2 H), 1.45–1.43 (m, 2 H), 0.93 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.4, 137.3, 137.1, 136.9, 133.7, 131.5, 129.4, 129.2, 128.7, 128.3, 86.4, 79.4, 42.3, 41.7, 31.1, 22.1, 21.3, 21.2, 18.8, 13.7 ppm. MS (ES-API): m/z = 351 $[M + H]^+$, 335, 313, 291, 277. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.21 (s), 4.23 (dd), 3.97 (dd) ppm.

(*Z*)-2-(Chloromethyl)-3-(4-fluorophenyl)-1-(*p*-tolyl)non-1-en-4-yne (3ai, *Z*/*E* = 93:7): Yield: 62%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.40–7.38 (m, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 2 H), 7.05–7.02 (m, 2 H), 6.92 (s, 1 H), 4.75 (d, J = 1.5 Hz, 1 H), 4.35 (d, J = 11.5 Hz, 1 H), 3.91 (d, J = 11.5 Hz, 1 H), 2.36 (s, 3 H), 2.28 (dt, J_1 = 1.5, J_2 = 7.0 Hz, 2 H), 1.56–1.52 (m, 2 H), 1.46–1.41 (m, 2 H), 0.92 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 161.9 (d, J = 244.3 Hz), 137.4, 137.0, 135.7, 133.3, 131.7, 129.8 (d, J = 8.3 Hz), 129.2, 128.5, 115.4 (d, J = 21.2 Hz), 86.7, 78.8, 42.1, 41.3, 30.9, 22.0, 21.2, 18.6, 13.6 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –113.4 (m) ppm. MS (ES-API): m/z = 353 $[M - H]^+$, 355 $[M + H]^+$, 371. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.19 (s), 4.21 (dd), 3.97 (dd), 0.89 (t) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 135.7, 129.2, 129.0, 128.7 ppm.

(*Z*)-2-(Chloromethyl)-1-(4-fluorophenyl)-5-phenyl-3-thienylpent-1-en-4-yne (3bf, *Z*/*E* = 72:28): Yield: 52%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.42–7.40 (m), 7.31–7.28 (m), 7.26–7.23 (m), 7.19–7.18 (m), 7.06 (d, J = 8.5 Hz), 7.01–6.98 (m), 6.92–6.89 (m), 5.20 (s, 1 H), 4.27 (d, J = 11.5 Hz, 1 H), 4.00 (d, J = 11.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 162.2 (d, J = 246.2 Hz), 142.7, 137.0, 131.76, 131.71, 131.0, 130.4 (d, J = 8.2 Hz), 128.3 (d, J = 6.5 Hz), 126.8, 126.3, 125.3, 125.1, 122.9, 115.5 (d, J = 21.2 Hz), 87.6, 85.9, 41.5, 37.9 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –113.6 (m) ppm. MS (ES-API): m/z = 367 $[M + H]^+$, 280, 242. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.40 (s), 4.32 (dd), 4.13 (dd) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 142.2, 136.1, 132.0, 131.9, 130.3 (d, J = 8.3 Hz), 130.0, 128.4, 127.0, 125.7, 122.8, 115.6 (d, J = 21.3 Hz), 87.1, 84.5, 45.1, 34.2 ppm.

(*Z*)-2-(Chloromethyl)-1-(4-fluorophenyl)-3-(*p*-tolyl)non-1-en-4-yne (3bh, *Z*/*E* = 80:20): Yield: 52%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.35–7.32 (m, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.08–7.04 (m), 6.94 (s, 1 H), 4.72 (d, J = 1.5 Hz, 1 H), 4.27 (d, J = 11.0 Hz, 1 H), 3.88 (d, J = 11.0 Hz, 1 H), 2.35 (s, 3 H), 2.27 (dt, J_1 = 1.5, J_2 = 7.0 Hz, 2 H), 1.56–1.51 (m), 1.47–1.41 (m), 0.92 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 162.0 (d, J = 265.0 Hz), 138.3, 137.0, 136.9, 130.5, 130.4 (d, J = 9.2 Hz), 129.5, 128.2, 127.5, 115.5 (d, J = 21.3 Hz), 86.6, 79.2, 41.9, 41.7, 31.1, 22.1, 21.2, 18.7, 13.7 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –114.3 (m) ppm. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.39–7.36 (m), 7.23–7.22 (m), 7.19–7.10 (m), 6.89 (s), 5.09 (s), 4.24 (dd), 3.95 (dd), 2.32 (s), 2.29 (dt), 0.96 (t) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 136.8, 135.4, 132.6, 132.5, 130.6, 129.2, 128.7, 115.6 (d, J = 21.3 Hz), 45.4, 37.3, 22.1. 21.1 ppm.

(*Z*)-2-(Chloromethyl)-1,5-diphenyl-3-(*p*-tolyl)pent-1-en-4-yne (3cc, *Z*/*E* = 82:18): Yield: 51%; viscous pale-yellow liquid. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.39–7.36 (m, 2 H), 7.32–7.29 (m, 6 H), 7.22–7.19 (m, 4 H), 7.10 (d, J = 7.5 Hz, 2 H), 7.00 (d, J = 1.5 Hz, 1 H), 4.91 (d, J = 1.0 Hz, 1 H), 4.29 (d, J = 11.5 Hz, 1 H), 3.87 (d, J = 11.5 Hz, 1 H), 2.27 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.4, 137.1, 136.3, 136.2, 131.7, 131.6, 129.5, 128.6, 128.5, 128.29, 128.25, 128.0, 127.5, 123.3, 88.8, 86.0, 42.0, 21.1 ppm. MS (ES-API): m/z = 357 $[M + H]^+$, 315, 297. Minor isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.45–7.43 (m), 5.33 (s), 4.23 (dd), 3.97 (dd), 2.25 (s) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 129.2, 128.7, 128.6, 128.3, 128.1, 127.4 ppm.

(*Z*)-2-(Chloromethyl)-1-phenyl-3-(*p*-tolyl)non-1-en-4-yne (3ch, *Z*/*E* = 73:27): Yield: 51%; viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38–7.35 (m, 4 H), 7.31–7.30 (m, 3 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.01 (d, J = 1.0 Hz, 1 H), 4.74 (d, J = 2.0 Hz, 1 H), 4.33 (d, J = 11.0 Hz, 1 H), 3.90 (d, J = 11.0 Hz, 1 H), 2.35 (s, 3 H), 2.27 (dt, J = 1.5, J_2 = 7.5 Hz, 2 H), 1.54–1.51 (m), 1.47–1.43 (m), 0.92 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.1, 137.07, 137.0, 136.6, 131.4, 129.4, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 127.54, 127.52, 86.5, 79.3, 42.2, 41.6, 31.1, 22.1, 21.2, 18.8, 13.7 ppm. MS (ES-API): m/z = 337 $[M + H]^+$, 339, 315, 297. Minor isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41–7.39 (m), 7.24 (d), 7.11 (d), 6.95 (s), 5.17 (s), 4.26 (dd), 3.97 (dd), 2.33 (s), 2.30 (dt), 0.96 (t) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.2, 136.7, 135.6, 129.8, 127.4, 45.4, 37.4, 21.1, 13.7 ppm.

(*E*)-2-(Azidomethyl)-3,5-diphenyl-1-(*p*-tolyl)pent-1-en-4-yne (5ab, *E*/*Z* = 53:47): Yield: 24%; viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47–7.46 (m), 7.44–7.40 (m), 7.35–7.29 (m), 7.28–7.19 (m), 7.15–7.14 (m), 7.09 (s), 6.73 (s, 1 H), 5.36 (s, 1 H), 4.06 (d, J = 13.0 Hz, 1 H), 3.72–3.69 (m, 2 H), 2.28 (s) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 139.2, 138.1, 134.8, 133.3, 131.9, 129.4, 128.7, 128.46, 128.40, 128.34, 127.6, 123.3, 87.8, 85.1, 53.3, 37.8, 21.4 ppm. Other isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.99 (s, 1 H), 3.86 (dd, J_1 = 1.0, J_2 = 14.5 Hz, 1 H), 4.80 (s, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.5, 135.1, 133.2, 132.5, 131.8, 130.1, 129.2, 128.9, 128.8, 128.3, 128.2, 127.5, 88.5, 86.3, 49.2, 43.9, 21.3 ppm.

(*E*)-2-(Azidomethyl)-3-(4-bromophenyl)-5-phenyl-1-(*p*-tolyl)pent-1-en-4-yne (5ad, *E*/*Z* = 73:27): Yield: 15%; viscous pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55–7.53 (m), 7.51–7.48 (m), 7.46–7.45 (m), 7.40 (d), 7.37–7.35 (m), 7.33–7.32 (m), 7.31–7.29 (m), 7.24 (d), 7.18–7.17 (m), 6.83 (s, 1 H), 5.38 (s, 1 H), 3.92 (dd, J_1 = 1.5, J_2 = 15.0 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.7, 137.3, 134.3, 133.0, 132.8, 131.9, 131.7, 130.7, 130.0, 129.5, 129.3, 128.5, 123.0, 121.3, 87.2, 85.5, 53.3, 37.4, 21.4 ppm. Minor isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.04 (s), 4.85 (s), 4.15 (d), 3.82–3.78 (m), 2.36 (s) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 138.3, 137.7, 134.7, 133.0, 132.8, 132.5, 132.0, 131.8, 129.3, 128.9, 128.8, 128.4, 123.1, 121.5, 87.8, 86.7, 49.2, 43.4, 21.3 ppm.

(*E*)-1-(*p*-Tolyl)hept-1-en-3-one (7a) and (*Z*)-1-(*p*-Tolyl)hept-1-en-3-one (7b): These Meyer–Schuster products were formed in a ratio of 6:5 (by NMR). **7a**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.54 (d, J = 16.0 Hz, 1 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 6.72 (d, J = 16.0 Hz, 1 H), 2.67 (t, J = 7.0 Hz, 2 H), 2.39 (s, 3 H), 1.69–1.66 (m, 2 H), 1.42–1.37 (m, 2 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 200.8, 142.3, 140.8, 131.8, 129.6, 128.2, 125.3, 40.6, 26.5, 22.4, 21.5, 13.9 ppm. **7b**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.48 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.78 (d, J = 12.5 Hz, 1 H), 6.15 (d, J = 12.5 Hz, 1 H), 2.48 (t, J = 7.5 Hz, 2 H), 2.37 (s, 3 H), 1.60–1.57 (m, 2 H), 1.32–1.28 (m, 2 H), 0.88 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 203.4, 139.9, 139.4, 132.4, 129.7, 128.9, 127.6, 43.4, 26.3, 22.2, 21.4, 13.8 ppm.

6-Chloro-1,3-diphenylhex-3-en-1-yne (4): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.74–7.23 (m, 2 H), 7.60–7.58 (m, 2 H), 7.44–7.39 (m, 5 H), 7.37–7.35 (m, 1 H), 6.54 (t, J = 7.5 Hz, 1 H), 3.77 (t, J = 7.0 Hz, 2 H), 3.09 (q, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.6, 132.9, 131.6, 128.5, 128.5, 128.4, 128.0, 126.2, 126.1, 123.1, 96.2, 86.1, 43.6, 34.4 ppm.

(1*E*,3*Z*)-3-Chloro-1-phenylhepta-1,3-diene (10): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43–7.41 (m, 2 H), 7.34–7.31 (m, 3 H), 7.24 (d, J = 6.5 Hz, 1 H), 6.90 (d, J = 15.5 Hz, 1 H), 6.77 (d, J = 15.5 Hz, 1 H), 5.88 (t, J = 7.5 Hz, 1 H), 2.37–2.32 (m, 2 H), 1.51–1.47 (m, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 136.6, 132.3, 131.9, 130.8, 128.6, 127.7, 126.7, 126.7, 31.1, 21.9, 13.8 ppm. GC–MS: m/z = 206 $[M]^+$.

(1*E*,3*Z*)-3-Chloro-1-(*p*-tolyl)hepta-1,3-diene (11): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.32 (d, J = 8.0 Hz, 2 H), 7.13 (d, J = 7.5 Hz, 2 H), 6.87 (d, J = 15.5 Hz, 1 H), 6.73 (d, J = 15.5 Hz, 1 H), 5.85 (t, J = 7.5 Hz, 1 H), 2.35–2.32 (m, 5 H), 1.51–1.47 (m, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.7, 133.8, 132.4, 131.3, 130.0, 129.3, 126.6, 125.8, 31.1, 21.9, 21.1, 13.8 ppm. GC–MS: m/z = 220 $[M]^+$.

(1*E*,3*Z*)-3-Chloro-1-(4-fluorophenyl)hepta-1,3-diene (12): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.39–7.37 (m, 2 H), 7.03–6.96 (m, 2 H), 6.85 (d, J = 15.0 Hz, 1 H), 6.90 (d, J = 15.5 Hz, 1 H), 5.87 (t, J = 7.5 Hz, 1 H), 2.36–2.32 (m, 2 H), 1.51–1.47 (m, 2 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 162.4 (d, J = 246.2 Hz), 132.8 (d, J = 3.6 Hz), 132.2, 132.0, 128.8, 128.1 (d, J = 7.37 Hz), 126.5 (d, J = 1.8 Hz), 115.6 (d, J = 21.2 Hz), 31.1, 21.9, 13.8 ppm. GC–MS: m/z = 224 $[M]^+$.

Supporting Information (see footnote on the first page of this article): Selected ^{1}H and ^{13}C{^{1}H} NMR spectra.

Acknowledgments

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