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Rhodium- and Palladium-Catalyzed 1,5-Substitution Reactions of 2-En-4-yne Acetates and Carbonates with Organoboronic Acids

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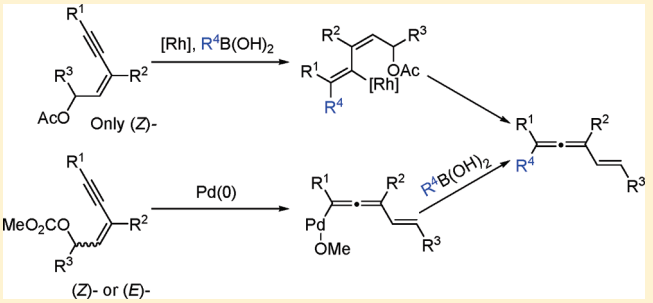
Supporting Information

ABSTRACT: Two methods involving the rhodium-catalyzed reaction of 2-en-4-yne acetates and the palladium-catalyzed reaction of 2-en-4-yne carbonates with organoboronic acids were investigated; both afforded exclusively the (*E*)-configured vinylallenes. The coordinative interaction of the rhodium with the acetate group promoted the *δ*-elimination of Rh(I)-OAc from the alkenylrhodium intermediate **II** in both *syn* and *anti* modes, with the *syn*-elimination being the major path. DFT calculations revealed that a conformer of this intermediate (**II**), which can lead to the (*E*)-configured vinylallene product via the *syn*-elimination mode, is energetically the most favorable conformer. The rhodium-catalyzed procedure is not applicable to reactions involving (*E*)-configured enyne acetates, because the geometry of the alkenylrhodium intermediate that is derived from the corresponding (*E*)-enyne acetate would not allow such coordinative interaction to occur. The palladium-catalyzed method, which proceeds through formation of the *σ*-vinylallenylpalladium intermediate, **B**, is suitable for both the (*E*)- and (*Z*)-configured enyne carbonates and appears to have a wider scope for both organoboronic acids and enyne substrates. The palladium-catalyzed reaction of an enantiomerically enriched enyne carbonate proceeded with racemization.



INTRODUCTION

Grignard, organocopper, organolithium, and organozinc reagents are traditional nucleophilic organometallic reagents that are used for carbon−carbon coupling reactions. However, these reagents are highly moisture- and air-sensitive, have very short shelf-lives, and can tolerate only few electrophilic groups. Hence, use of these organometallic reagents requires protection of electrophilic functional groups, strict anhydrous conditions, and an inert atmosphere.

For these reasons, there has been an increasing trend toward adopting reagents that are relatively cheap, easy-to-handle, and tolerant to a wide range of functionalities and solvents during C−C bond-forming reactions. Importantly, the rather lower reactivity of these reagents is compensated by performing the reactions in the presence of transition metal catalysts.

A classical example of these efforts is transition-metal-catalyzed biaryl-forming reactions. Kumada, Negishi, Stille, and Suzuki couplings are well-known transition-metal-catalyzed reactions. All of them involve the coupling of aryl halides or pseudoaryl halides with different types of organometallic reagents. Among them, the Suzuki reaction is the most popular and has found wide application in industrial processes and in laboratory syntheses since it utilizes organoboron reagents that have several advantages over its competitors.[1]

Organoboron reagents, particularly those bearing aryl and alkenyl units, are convenient and versatile reagents because they are widely available, thermally stable, inert to water and oxygen, relatively nontoxic, and tolerant to a wide range of reactive functional groups.[2] For these reasons, organoboron reagents are often used, with convenience, in transition-metal-catalyzed C−C bond-forming reactions.[2a,3]

Some of the leading applications in the use of organoboron reagents as a source for soft nucleophiles are[4] the rhodium(I)-catalyzed conjugate addition of aryl- or alkenylboronic acids to α,*β*-unsaturated reagents,[4,5] addition of arylboronic acids to aldehydes via Rh(I) catalysis (which is an alternative to the commonly known Grignard reaction),[6] Rh(I)-catalyzed hydroarylation of internal alkynes with aryl- or alkenylboronic reagents,[7] 1,3-S_N2'-type substitution reactions of propargylic reagents leading to allenic products,[8] and Rh(I)-catalyzed ring-opening reactions of oxabicyclic alkenes with organoborons.[9]

It has been previously established that conjugated enynes with a leaving group at the allylic position undergo 1,5-(S_N2'')-substitution with organometallic nucleophiles leading to vinylallenes (Scheme 1).

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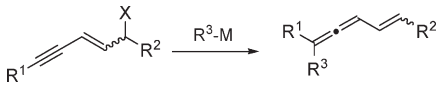
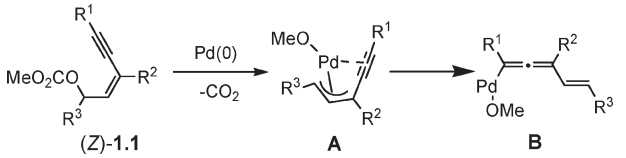
Scheme 1. Reaction of 2-En-4-yne Reagents and Organometals



Scheme 2. Palladation of 2-En-4-yne Carbonate Leading to σ-Vinylallenylpalladium(II) Species



Goré and Dulcere found that the reaction of 2,4-enyne halides with methylmagnesium iodide or trimethylsilylmagnesium chloride (or trimethylsilyllithium) proceeds via an S_N2''-type nucleophilic substitution yielding an *E*/*Z* mixture of vinylallenes.[10] The method, however, is not general, since other Grignard reagents completely failed to form the desired vinylallenes. Krause et al. devised a more general method; they determined that (*E*)-2-en-4-yne acetates can effectively undergo S_N2'' type alkylation with various lithium cuprates affording an *E*/*Z* mixture of vinylallenes.[11]

However, to the best of our knowledge, there has been no report involving any 1,5-substitution reactions of 2,4-enynes with organoboron reagents,[12] and therefore it was our intention to introduce the transition-metal-catalyzed organoboronic combination as a new method for the arylative and alkenylative reactions of 2-en-4-yne reagents. A part of our related study discloses that organoboron reagents can also be utilized as a nucleophilic aryl source for conjugated enyne acetates in the presence of a rhodium(I) complex to provide vinylallenes.

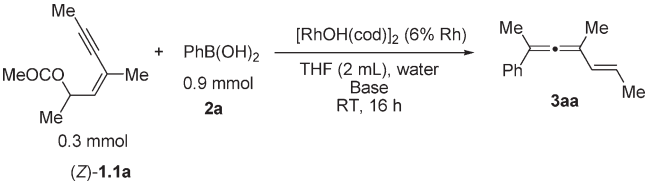
Another part of this report involves studies on the Pd(0)-catalyzed reaction of organoboronic acids with conjugated enynes bearing a carbonate substituent in the allylic position. We have recently reported that the Pd(0)-catalyzed carbonylation of carbonates of secondary (*Z*)-2-en-4-yne alcohols in the presence of CO in an alcohol medium proceeded through the formation of a σ-vinylallenylpalladium(II) complex (**B**) leading with high selectivity to 2,3,5-trienoates, while showing no traces of allylic substitution products (Scheme 2).[13]

It has been already shown that σ-allenylpalladium(II) species are also reactive toward transmetalation-type reactions with organoboronic acids leading to arylallenes.[14] To this end, we purposely investigated the Pd(0)-catalyzed 1,5-substitution reactivity of the 2,4-enyne carbonates with organoboronic reagents.

RESULTS AND DISCUSSION

Rh(I)-Catalyzed Reaction of 2-En-4-yne Acetates and Organoborons. The reaction of a (*Z*)-configured enyne acetate **1.1a** with 3 equiv of phenylboronic acid proceeded in THF solvent, at room temperature, and in the presence of $[RhCl(cod)]_2$ (6% Rh), 3 equiv of KOH, and 0.1 mL of water to yield the desired phenyl-substituted vinylallene **3aa** product, which however was accompanied by significant amounts of nonseparable intricate isomers of the vinylallene with unassigned structures (Table 1, entry 1).

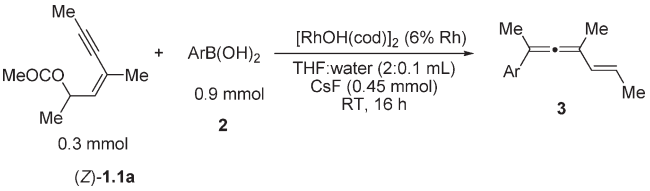
Table 1. Effect of Base and Water Additives on the Rh(I)-Catalyzed Reaction of (*Z*)-Enyne Acetate 1.1a with Phenylboronic Acid



entry	base (equiv)	water (mL)	conversion (%)[a]	yield, **3aa** (%)[a]
1[b]	KOH (3)	0.1	78	58
2	CsF (3)	0.1	100	55
3	CsF (2)	0.1	100	75
4	CsF (1.5)	0.1	100	85
5	CsF (1.1)	0.1	95	75
6	CsF (1.5)		25	20
7	CsF (1.5)	0.05	77	67
8	CsF (1.5)	0.2	55	42
9	KF (3)	0.1	40	38
10	CsOH (1.5)	0.1	100	50
11	Cs_2CO_3 (1.5)	0.1	82	40

[a] Determined by ^1H NMR using benzaldehyde as internal standard. [b] Rhodium complex charged was $[RhCl(cod)]_2$.

Table 2. Rh(I)-Catalyzed Reaction of the (*Z*)-Enyne Acetate 1.1a with Arylboronic Acids



entry	Ar	product	yield (%)
1	**2a** Ph	**3aa**	82
2	**2b** 4-$CF_3C_6H_4$	**3ab**	76
3	**2c** 4-$MeCOC_6H_4$	**3ac**	77
4	**2d** 4-MeC_6H_4	**3ad**	83
5	**2e** 3-MeC_6H_4	**3ae**	86
6	**2f** 3-ClC_6H_4	**3af**	77
7	**2g** 2-$MeOC_6H_4$	**3ag**	83
8	**2h** 2-naphthyl	**3ah**	76
9	**2i** 3-thienyl	**3ai**	81

The reaction halted after a period of time, and the conversion was incomplete even with higher loadings of Rh at the beginning of the reaction, indicating that a change in the composition of the reaction medium (possibly due to an increased concentration of the acetate dispelled from the enyne substrate) lowered the activity of the rhodium significantly.

The complete conversion of (*Z*)-**1.1a** could be attained by substituting the base with CsF (entry 2) in the presence of $[RhOH(cod)]_2$ complex. The formation of isomeric byproducts

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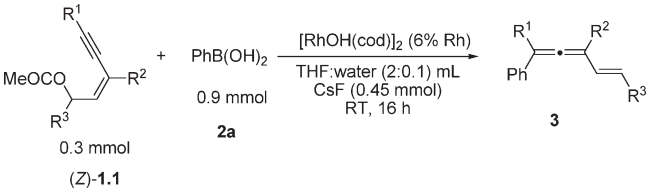
Table 3. Rh(I)-Catalyzed Reaction of (*Z*)-Enyne Acetates with Phenylboronic Acid



entry	substrate	R^1	R^2	R^3	product	isolated yield (%)
1	(*Z*)-**1.1b**	Bu	Me	Me	**3ba**	72
2	(*Z*)-**1.1c**	Cy	Me	Me	**3ca**	70
3	(*Z*)-**1.1d**	Bu	Bu	Me	**3da**	75
4	(*Z*)-**1.1e**	Bu	Ph	Me	**3ea**	73
5	(*Z*)-**1.1f**	Me	Me	Bu	**3fa**	79
6	(*Z*)-**1.1g**	Me	Me	*i*-Pr	**3ga**	77

could be minimized and thereby high yields of **3aa** product could be achieved by decreasing the CsF addition to 1.5 equiv (entries 2−5). The fine adjustment of the amount of added water seemed highly critical for the effectiveness of the process; the arylative substitution reaction did not proceed to completion when the reaction medium contained less or higher than 0.1 mL of water (entries 6−8). KF salt could not be an alternative flouride source (entry 9), and the use of other Cs compounds instead of CsF was useless (entries 10 and 11).[15]

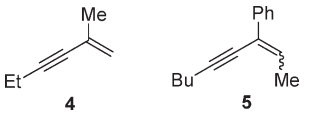
The above-shown finding represents the first example of an arylative S_N2''-type reaction for 2-en-4-yne reagents. In contrast to their transformation with organocopper and Grignard reagents, the resulting vinylallene had the vinylic group exclusively in (*E*)-configuration.

Having established the effective conditions, an array of substituted boronic acids were then subjected to the reactions with the enyne acetate (*Z*)-**1.1a** (Table 2). The reaction tolerated both electron-withdrawing and -donating groups on the *meta* and *para* positions, giving rise to high yields of the corresponding arylated vinylallene products **3aa**−**3af** (entries 1−6). A sterically congested organoboronic acid (**2g**), 2-naphthylboronic acid, and 3-thienylboronic acid were also suitable components for the reaction, yielding related products **3ag**−**3ai** with isolated yields in the range of 76−83% (entries 7−9).[16]

The scope of the arylation method was also surveyed for a range of acetates of secondary (*Z*)-enynols. The method appeared suitable for the enyne acetates bearing butyl ((*Z*)-**1.1b**) or cyclohexyl ((*Z*)-**1.1c**) groups on the alkynyl moiety (R^1, Table 3, entries 1 and 2), butyl ((*Z*)-**1.1d**), or phenyl ((*Z*)-**1.1e**) groups in the R^2 position (entries 3 and 4) and butyl ((*Z*)-**1.1f**) or isopropyl ((*Z*)-**1.1g**) groups on the allylic carbon (R^3, entries 5 and 6), affording the corresponding vinylallenes in good yields when reacted with phenylboronic acid (70−79%).[17]

The Rh(I)-catalyzed reaction of the acetate of an enantiomerically enriched enynol reagent, (*R*,*Z*)-**1.1a** (94.5% ee) with phenylboronic acid under the optimal conditions proceeded with partial racemization and yielded (*S*)-(+)-vinylallene as the major enantiomer (82% isolated yield, 40% ee, $[\alpha]^{25}_D = +0.33$ (*c* 0.29, $CHCl_3$)) (Scheme 3).[18,19]

The reaction should involve the regioselective *cis*-1,2-addition of the *in situ* generated phenylrhodium(I) species across the carbon−carbon triple bond, which should be directed through the dual coordinative interaction of rhodium with alkynyl and acetate moieties (**I**), to afford the alkenylrhodium(I) intermediate (**II**) (Scheme 3).[7,8] It should be noted that the application of the rhodium-catalyzed protocol on enynes **4** and **5**, which lack a leaving group at the allylic carbon, resulted in complex mixtures of various isomers of mono- and diarylated products.



The subsequent δ-elimination of [Rh]-OAc and double bond migration may take place concurrently via both *anti* and *syn* modes,[20] *syn*-deacetylation being the major path, to produce the enantiomers of arylated vinylallene products and regenerating the active Rh(I) catalyst for the next cycle. Alternatively, the formation of a benzylidene-π-allylrhodium intermediate (**III**) may precede the deacetylation step.[12,19]

However, in both instances, the elimination step should be activated via the coordination of the rhodium and the oxygen functionality.[20] Indeed, we found that the Rh-mediated protocol is not applicable to (*E*)-configured enyne acetates; an analogous reaction with (*E*)-**1.1a** furnished a dienyl acetate structure (**6**) as the major product (62% NMR yield), and consequently, formation of the desired vinylallene product was less than 10% (Scheme 4). This result indicates that the alkenylrhodium intermediate **II**′, which is formed via rhodoarylation of (*E*)-**1.1a**, could not undergo the δ-elimination of [Rh]-OAc, preferring instead demetalation to yield a hydroarylated product (**6**).[7] The intermediate **II**′ cannot maintain a suitable geometry that is amenable to interaction with Rh(I)-OAc, this being a suspected prerequisite to the elimination step.

For better rationalization of the observed enantioselective outcome of the rhodium-mediated reaction of (*R*,*Z*)-**1.1a** with phenylboronic acid, we performed conformational analyses by carrying out density functional theory (DFT) calculations for intermediate **II**. The conformations were investigated by considering different combinations of rotations about four different single carbon−carbon bonds (Θ_1−Θ_4), as depicted in Figure 1, and 81 conformers were obtained. Then, more rotations were performed so as to achieve conformers that included the rhodium and the acetate groups in suitable relative proximity to one other for effective coordination (typically 2.239−2.286 Å), a necessary condition for the subsequent Rh-OAc elimination step leading to **3**.

The overall conformational analysis yielded a minimum energy that was associated with the conformer **ES** as shown in Figure 2. Interestingly, this conformer could potentially follow a [Rh]-OAc elimination path leading to the product (*S*)-**3aa**. The other structures, which are assigned the identifiers **ER**, **ZS**, and **ZR** (Figure 2), represent the conformers of local minimum energies and potentially lead to the products (*E*,*R*)-, (*Z*,*S*)-, and (*Z*,*R*)-**3aa**, respectively. The fact that the conformer **ER** had a potential energy that is 4.1 kcal/mol higher than that of the conformer **ES** may account for the resulting enantiomeric ratio of the **3aa** products. The relative energies of **ZR** and **ZS** as compared to **ES** are about 6.9 and 8.8 kcal/mol higher, respectively. It should be noted that no (*Z*)-configured vinylallene production was observed in the course of this study.

Pd(0)-Catalyzed Reaction of 2-En-4-yne Carbonates and Organoborons. The catalyst system used for the Pd(0)-catalyzed

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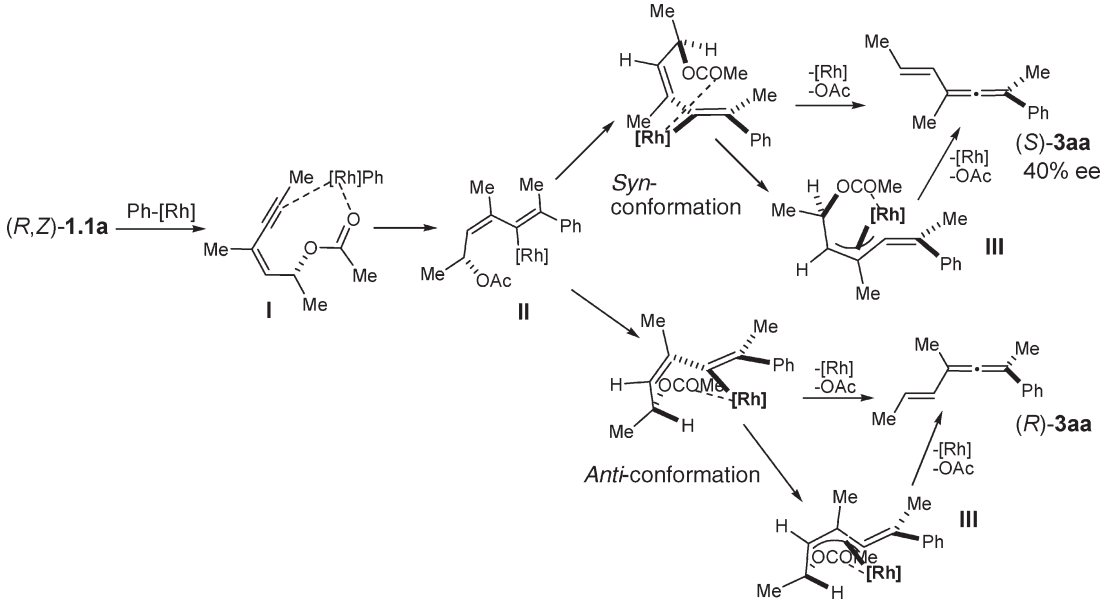
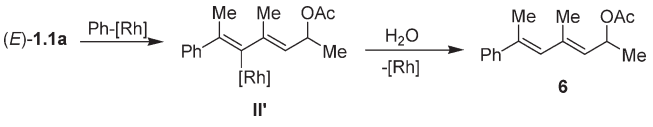
Scheme 3. Machanism and Stereochemistry of Rh(I)-Catalyzed Arylation of (*R*,*Z*)-2-En-4-yne Acetate 1.1a



Scheme 4. Rh(I)-Catalyzed Arylation of (*E*)-1.1a



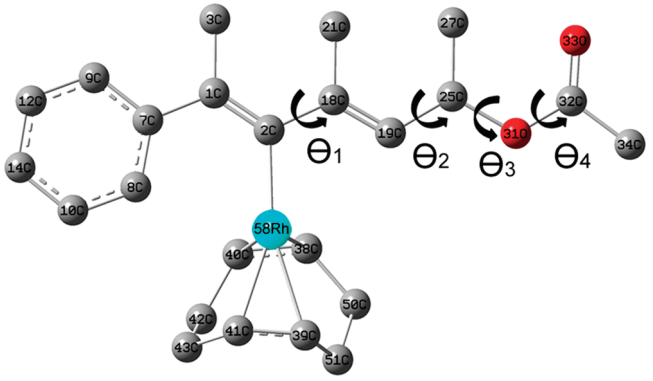


Figure 1. Rotational angles on the structure of intermediate **II**, which was used in conformational search (hydrogen atoms are omitted for clarity).

reactions of 2,4-enyne carbonates with organoboronic acids was $Pd_2(dba)_3CHCl_3/PPh_3$, since this combination already proved its activity for Pd(0)-catalyzed alkoxycarbonylation of conjugated (*Z*)-enyne carbonates, which led to vinylallenyl esters.[13] Indeed, a related (*E*)-configured and phenyl-functionalized vinylallene **3aa** was produced via the reaction of a (*Z*)-2-en-4-yne carbonate **1.2a** with phenylboronic acid in the presence of $Pd_2(dba)_3CHCl_3$ (3 mol % Pd) and PPh_3 (12 mol %) in dry THF and at 65 °C, albeit the reaction did not proceed to completion (Table 4, entry 1). The formation of **3aa** dictates formation of a σ-vinylallenylpalladium(II) intermediate and its subsequent transmetalation with the organoboronic acid (Schemes 2 and 5).

The presence of small amounts of water seems beneficial for the reaction; with its presence, the reaction of the enyne carbonate (*Z*)-**1.2a** with phenylboronic acid proceeded with complete conversion to give the **3aa** in high yields (entries 2 and 3). The application of a lower reaction temperature (50 °C) significantly reduced the efficacy of the process (entry 4), and the method can also be run at a lower Pd loading (2 mol %) (entry 5).

The scope of the Pd(0)-catalyzed method appears to be remarkably wider for both organoboronic acid and enyne carbonate substrate partners as compared to the Rh(I)-catalyzed version. The reaction of (*Z*)-**1.2a** with the highly electron-deficient *p*-CF_3 (**2b**) or 3,4-difluoro substituted phenylboronic (**2j**) acids and 3-pyridylboronic acid (**2k**) afforded moderate yields of vinylallene products (Table 5, entries 1−3). Nevertheless the reactions with *ortho*-, *para*-, and *meta*-substituted electron-rich and moderately electron-poor phenylboronic acids, 1- and 2-naphthylboronic acids (**2m** and **2h**, respectively), as well as 3-thienylboronic acid (**2i**) provided the corresponding arylated vinylallene products at yields ranging between 73% and 92% within relatively short reaction times (typically 1 h) (entries 4−11). In contrast to the Rh(I)-catalyzed version, alkenylboronic acids also proved to be an applicable class of organoboron reagents for the proposed Pd(0)-catalyzed method. A divinylallene structure **3an** was produced at a yield of 74% when (*Z*)-**1.2a** reacted with 1-pentenylboronic acid for 1 h (entry 12).

The methodology can tolerate without problem phenyl ((*Z*)-**1.2h**), butyl ((*Z*)-**1.2b**), cyclohexyl ((*Z*)-**1.2c**), as well as highly bulky *tert*-butyl ((*Z*)-**1.2i**) groups on the alkynyl terminus of the enyne carbonates (R^1, Table 6, entries 1−4). Their reaction with phenylboronic acid under the optimal conditions provided the corresponding vinylallenes in good to high yields (58−88%). A moderate yield (50%, entry 5) of the vinylallene **3ja** was produced when R^1 is H ((*Z*)-**1.2j**). The product **3ja**, nonetheless, was formed at a higher yield (82%, entry 6) from the reaction of the (*Z*)-enyne carbonate where R^1 was a $SiMe_3$ group ((*Z*)-**1.2k**)

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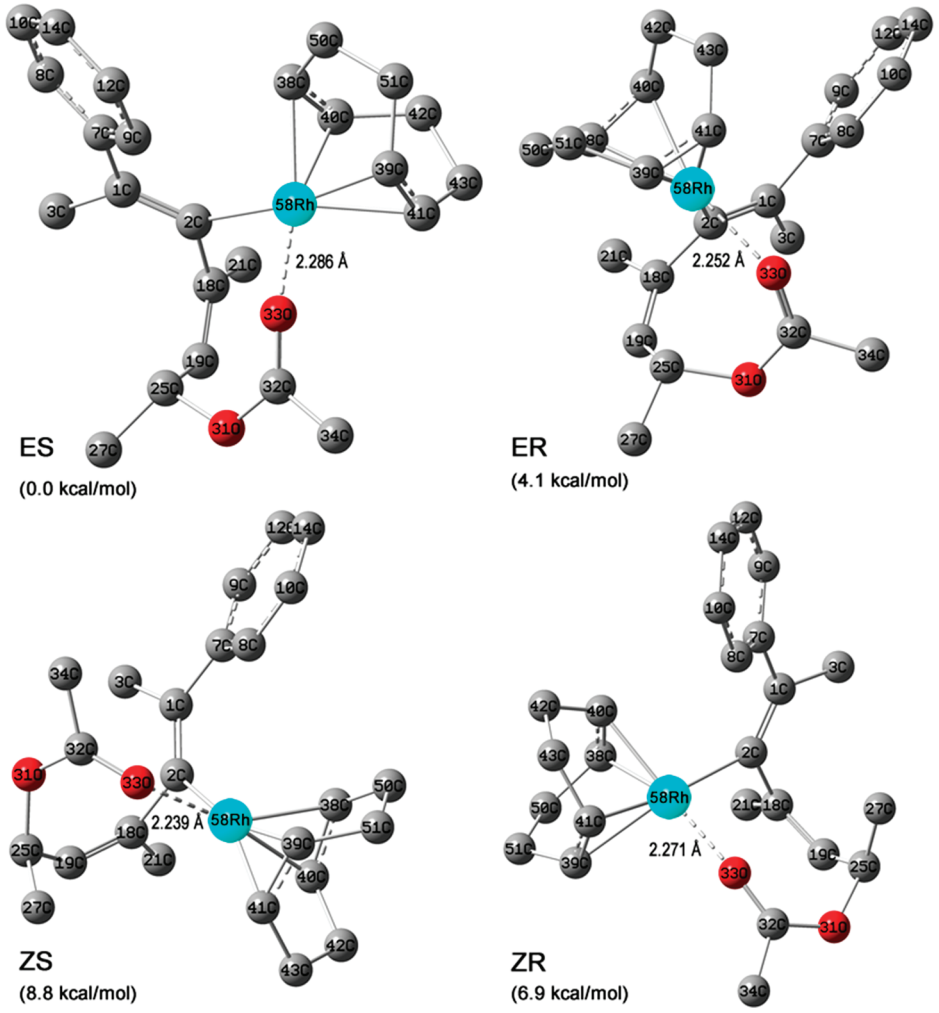
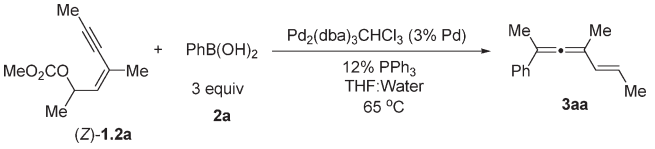


Figure 2. Optimized conformers for the intermediate **II** (hydrogen atoms are omitted for clarity and the energy values are relative energies).

Table 4. Effect of Reaction Conditions on the Pd(0)-Catalyzed Reaction of the (*Z*)-Enyne Carbonate 1.2a with Phenylboronic Acid

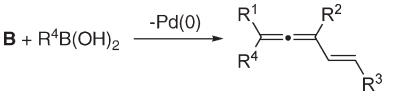


entry	(*Z*)-**1.2a** (mmol)	THF/water (mL)	time (h)	conversion (%)	yield (%)[a]
1	0.1	2.5:0	6	71	67
2	0.1	2.5:0.2	2	100	89
3	0.2	5:0.4	1	100	(84)[b]
4[c]	0.2	5:0.4	23	50	43
5[d]	0.1	2.5:0.2	2	100	85

[a] Determined by ^{1}H NMR using benzaldehyde as internal standard. [b] Isolated yield. [c] 50 °C. [d] 2% Pd and 8% PPh_3.

upon the involvement of a desilylation process (entry 6).[21] Substituting the methyl group in the R^2 position with a butyl group ((*Z*)-**1.2d**) had no significant effect on the activity of the enyne carbonate substrate (80% yield, entry 7); however, the corresponding vinylallene yields were relatively lower when R^2 was H ((*Z*)-**1.2l**) or a phenyl group ((*Z*)-**1.2e**) (61% and 64%, entries 8 and 9, respectively).

Scheme 5. Transmetalation of *σ*-Vinylallenylpalladium(II) and Organoboronic Acid



The effect of variation of allylic substitution on the activity of the enyne carbonate was also assessed. The method was rather successful also for the enyne substrates in which R^3 was butyl ((*Z*)-**1.2f**, 76%) or isopropyl ((*Z*)-**1.2g**, 92%) groups; however, an enyne carbonate of a primary alcohol (R^3 = H) led to a low yield of (44%) of vinylallene product **3ma** (entries 10−12).

In contrast to the Rh-mediated procedure, the Pd-catalyzed method was also successful when used with (*E*)-configured 2,4-enyne carbonates (Table 7); (*E*)-**1.2a** afforded the vinylallene product **3aa** in a yield of 69%, which is somewhat lower than that

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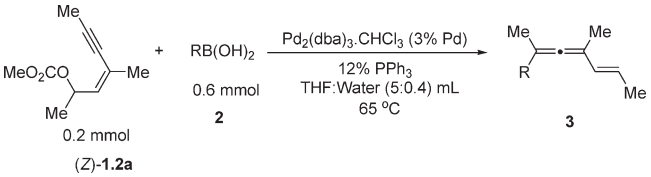
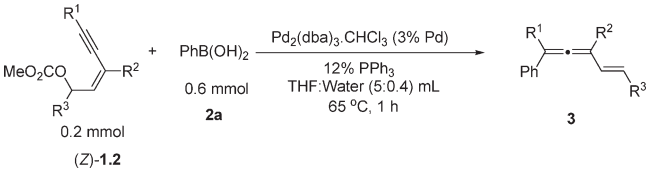
Table 5. Pd(0)-Catalyzed Reaction of the (*Z*)-Enyne Carbonate 1.2a with Organoboronic Acids



entry	R	time (h)	product	yield (%)
1	**2b** 4-$CF_3C_6H_4$	8	**3ab**	56
2	**2j** 3,4-$F_2C_6H_4$	24	**3aj**	58
3	**2k** 3-pyridyl	6	**3ak**	59
4	**2c** 4-$MeCOC_6H_4$	2	**3ac**	79
5	**2d** 4-MeC_6H_4	1	**3ad**	92
6	**2e** 3-MeC_6H_4	1	**3ae**	80
7	**2g** 2-$MeOC_6H_4$	1	**3ag**	88
8	**2l** 2-FC_6H_4	1	**3al**	82
9	**2h** 2-naphthyl	1	**3ah**	75
10	**2m** 1-naphthyl	1	**3am**	83
11	**2i** 3-thienyl	1	**3ai**	73
12	**2n** 1-pentenyl	1	**3an**	74

Table 6. Pd(0)-Catalyzed Reaction of (*Z*)-Enyne Carbonates with Phenylboronic Acid

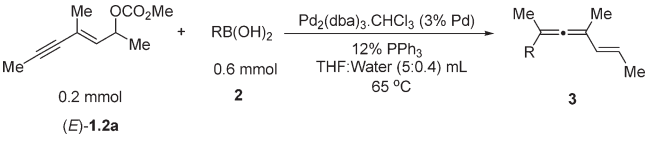


entry	substrate	R^1	R^2	R^3	product	yield (%)
1	(*Z*)-**1.2h**	Ph	Me	Me	**3ha**	88
2	(*Z*)-**1.2b**	Bu	Me	Me	**3ba**	82
3	(*Z*)-**1.2c**	Cy	Me	Me	**3ca**	67
4[a]	(*Z*)-**1.2i**	*t*-Bu	Me	Me	**3ia**	58
5	(*Z*)-**1.2j**	H	Me	Me	**3ja**	50
6	(*Z*)-**1.2k**	Me_3Si	Me	Me	**3ja**	82 (R^1 = H)[b]
7	(*Z*)-**1.2d**	Bu	Bu	Me	**3da**	80
8	(*Z*)-**1.2l**	Bu	H	Me	**3la**	61
9	(*Z*)-**1.2e**	Bu	Ph	Me	**3ea**	64
10[c]	(*Z*)-**1.2f**	Me	Me	Bu	**3fa**	76
11	(*Z*)-**1.2g**	Me	Me	*i*-Pr	**3ga**	92
12	(*Z*)-**1.2m**	Bu	Me	H	**3ma**	44

[a] 3 h. [b] Desilylated product. [c] 2 h.

obtained from its (*Z*)-configured isomer when reacted with phenylboronic acid at 65 °C for 1 h (entry 1). Nevertheless, in contrast with the reactivity of (*Z*)-**1.2a**, the same yield could also be achieved at 50 °C (entry 2); however, at this lower reaction temperature, the conversion was incomplete when using (*Z*)-**1.2a** (see Table 4, entry 4). The activity of the Pd-catalysis, however, was insufficient at room temperature; the conversion was low and consequently gave rise to a small yield of the desired vinylallene product (entry 3).

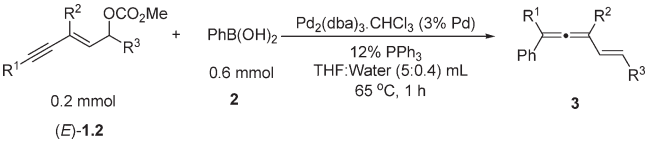
Table 7. Pd(0)-Catalyzed Reaction of the (*E*)-Enyne Carbonate 1.2a with Organoboronic Acids



entry	R	time (h)	product	yield (%)
1	**2a** Ph	1	**3aa**	69
2[a]		1		69
3[b]		6		25
4	**2b** 4-$CF_3C_6H_4$	5	**3ab**	61
5	**2c** 4-$MeCOC_6H_4$	10	**3ac**	81
6	**2d** 4-MeC_6H_4	1	**3ad**	77
7	**2e** 3-MeC_6H_4	1	**3ae**	76
8	**2g** 2-$MeOC_6H_4$	1	**3ag**	75
9	**2l** 2-FC_6H_4	1	**3al**	77
10	**2m** 1-naphthyl	1	**3am**	71
11	**2i** 3-thienyl	1	**3ai**	77
12	**2k** 3-pyridyl	10	**3ak**	71
13	**2n** 1-pentenyl	1	**3an**	74

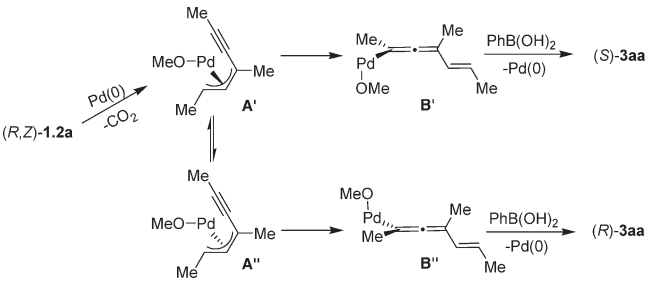
[a] 50 °C. [b] RT.

Table 8. Pd(0)-Catalyzed Reaction of (*E*)-Enyne Carbonates with Phenylboronic Acid



entry	substrate	R^1	R^2	R^3	product	yield (%)
1	(*E*)-**1.2b**	Bu	Me	Me	**3ba**	78
2	(*E*)-**1.2h**	Ph	Me	Me	**3ha**	87
3	(*E*)-**1.2f**	Me	Me	Bu	**3fa**	75
4	(*E*)-**1.2g**	Me	Me	*i*-Pr	**3ga**	83
5	(*E*)-**1.2n**	Me	H	Me	**3na**	<10

Scheme 6. Mechanism and Stereochemistry of Pd(0)-Catalyzed Arylation of (*R,Z*)-2-En-4-yne Carbonate 1.2a



(*E*)-**1.2a** reacted with various electron-rich and electron-poor, as well as sterically encumbered phenylboronic acids successfully to produce the related vinylallenes in good yields (entries 4–9).

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1-Napthyl, heteroaryl, and alkenylboronic acids were also suitable components (entries 10−13).

The enyne reagents with butyl ((*E*)-**1.2b**) or phenyl substituent on the alkynyl carbon ((*E*)-**1.h**) and butyl ((*E*)-**1.2f**) or isopropyl ((*E*)-**1.2 g**) groups on the allylic carbon all gave rise to high yields of the corresponding vinylallene products when reacted with phenylboronic acid (Table 8, entries 1−4). Interestingly, however, the reaction of an (*E*)-enyne carbonate ((*E*)-**1.2n**), where R^2 is H, with phenylboronic acid, in contrast to its analogue (*Z*)-configured substrate ((*Z*)-**1.2l**), gave rise to an intricate mixture of products, containing less than 10% of the corresponding phenylated vinylallene (entry 5).

No center-to-axis chirality transfer selectivity could be demonstrated with the existing method, as is the reported case for the Pd(0)-catalyzed alkoxycarbonylation applications with these substrates.[13] The relevant reaction of an enantiomerically enriched enyne carbonate (*R*,*Z*)-**1.2a** (94.5% ee) with phenylboronic acid led to a racemic mixture of the product.

The catalytic cycle should involve an oxidative cleavage leading to a π−allylpalladium intermediate (**A′**) and subsequent isomerization of this intermediate to **A″** could be the basis for the observed racemization (Scheme 6).[22] The shift of palladium to the distal alkynyl carbon yields a racemate of **3aa**.

CONCLUSION

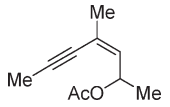
In this report, the first examples of the transition-metal-catalyzed 1,5-substitution reactions of 2-en-4-yne reagents with a leaving group in the allylic position and organoboronic acids are presented. The reactions produced vinylallenes with an exclusively (*E*)-configuration in both Rh(I)- and Pd(0)-catalyzed procedures. Rh(I)-catalyzed reactions proceeded via typically S_N2''-type substitution of (*Z*)-2-en-4-yne acetates, which is triggered by *cis*-addition of *in situ* formed nucleophilic arylrhodium(I) species. The δ-elimination of Rh(I)-OAc, which is promoted via coordinative interactions, took place in both *syn* and *anti* modes, with the *syn*-elimination being the dominant route. The (*E*)-configured enynes are not suitable reagents for the Rh(I)-catalyzed method, since geometrical constraints prohibit the required coordinative interactions. The Pd(0)-catalyzed method can be employed for conjugated enynes that contain a carbonate functionality in the allylic position and is applicable for a wider range of organoboronic acids and both (*E*)- and (*Z*)-configured enyne substrates. For an enantiomerically enriched (*Z*)-enyne carbonate, the Pd(0)-catalyzed method led to complete racemization, in contrast to the Rh(I)-catalyzed method.

EXPERIMENTAL SECTION

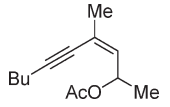
General. The synthesized reactants and vinylallene products were analyzed by GC and GC−MS and isolated by column chromatography using a hexane/ethyl acetate eluent. The vinylallene products are colorless or light yellow oil, and coupling constants of olefinic protons and NOE studies confirmed (*E*)-configured structures. NMR spectra were recorded within $CDCl_3$ or C_6D_6 solvents.[23] Infrared spectra were obtained by ATR method with neat samples. Enantiomeric excess values were determined by an HPLC method with an OD column (25 cm × 0.46 cm) and using hexane eluent (1 mL/min; racemic (*Z*)-**3aa** eluted at the retention times of 4.0 (*R*) and 4.2 (*S*) minutes). The $Pd_2(dba)_3CHCl_3$,[24] $[RhCl(cod)]_2$,[25] and $[RhOH(cod)]_2$[26] complexes were synthesized in laboratory.

Preparation of the Enyne Substrates. The synthesis of enyne carbonate (*Z*)-**1.2k** involved the Sonogashira coupling of ethynyltrimethylsilane with a corresponding vinyl iodide reagent as described elsewhere.[13] The enyne carbonate containing a terminal alkynyl group ((*Z*)-**1.2j**) was obtained via desilylation[27] of a corresponding Me_3Si substituted 2,4-enynol ((Z)-4-methyl-6-(trimethylsilyl)hex-3-en-5-yn-2-ol) and the following conversion of the hydroxyl group to carbonate. The methods for the syntheses of all other (*Z*)-enyne carbonates are described elsewhere.[13] Acetates and carbonates of (*E*)-2-en-4-yn-1-ols were synthesized following the described methods starting from (*E*)-pent-2-en-4-yn-1-ol reagent.[13] Racemic enyne acetates and (*S*)-**1.1a** were prepared by acetylation[11a] of the corresponding enynol reagents, which were synthesized as described previously.[13] All substrates were colorless oils.

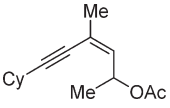
(*Z*)-1.1a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (dq, *J* = 8.8, 6.8 Hz, 1H), 5.56 (dq, *J* = 8.8, 1.2 Hz, 1H), 2.01 (s, 3H), 1.97 (s, 3H), 1.81 (d, *J* = 1.2 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 134.9, 121.5, 91.7, 77.7, 70.3, 23.5, 21.5, 20.5, 4.5; IR (ν_{max}/cm^{-1}) 2982, 2233, 1730, 1639, 1433, 1235, 1152, 1046; MS (EI, *m*/*z*) 166 (11, M^+), 151 (37), 137 (4), 123 (100), 109 (92), 91 (98), 79 (33); HRMS (EI) calcd for $C_{10}H_{14}O_2$ (M^+) 166.0988, found 166.0993.



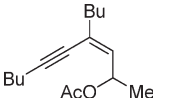
(*Z*)-1.1b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dq, *J* = 8.4, 6.4 Hz, 1H), 5.56 (dq, *J* = 8.4, 1.4 Hz, 1H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.02 (s, 3H), 1.83 (d, *J* = 1.6 Hz, 3H), 1.38−1.58 (m, 4H), 1.29 (d, *J* = 6.4 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 134.9, 121.6, 96.4, 78.6, 70.4, 30.9, 23.6, 22.1, 21.5, 20.4, 19.3, 13.7; IR (ν_{max}/cm^{-1}) 2941, 2870, 2223, 1736, 1636, 1371, 1232, 1036; MS (EI, *m*/*z*) 208 (8, M^+), 193 (8), 179 (4), 165 (100), 151 (24), 137 (14), 123 (49), 109 (88), 91 (82), 79 (47); HRMS (EI) calcd for $C_{13}H_{20}O_2$ (M^+) 208.1458, found 208.1455.



(*Z*)-1.1c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78−5.66 (m, 1H), 5.56 (dq, *J* = 8.4, 0.8 Hz, 2H), 2.55−2.48 (m, 1H), 2.01 (s, 3H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.83−1.76 (m, 2H), 1.66−1.74 (m, 2H), 1.43−1.53 (m, 3H), 1.30−1.37 (m, 3H), 1.35 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 134.8, 128.6, 121.8, 100.5, 78.5, 70.3, 63.4, 32.8, 29.8, 26.0, 24.9, 23.6, 21.5, 20.4; IR (ν_{max}/cm^{-1}) 2971, 2929, 2854, 2212, 1737, 1448, 1368, 1234, 1153, 1041; MS (EI, *m*/*z*) 234 (10, M^+), 219 (12), 191 (89), 177 (19), 149 (26), 131 (31), 117 (24), 109 (100), 91 (51), 77 (25); HRMS (EI) calcd for $C_{15}H_{22}O_2$ (M^+) 234.1614, found 234.1616.

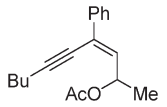


(*Z*)-1.1d. ^{1}H NMR (400 MHz, C_6D_6) δ 6.25 (dq, *J* = 8.4, 6.4 Hz, 1H), 5.67 (d, *J* = 8.8 Hz, 1H), 2.15 (t, *J* = 6.8 Hz, 2H), 2.11 (t, *J* = 8.0 Hz, 2H), 1.69 (s, 3H), 1.56 (quint, *J* = 7.6 Hz, 2H), 1.42−1.31 (m, 4H), 1.38 (d, *J* = 6.4 Hz, 3H), 1.30−1.20 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.4, 135.1, 126.7, 97.1, 78.5, 70.1, 37.4, 31.1, 30.8, 22.4, 22.2, 21.0, 20.7, 19.4, 14.1, 13.7; IR (ν_{max}/cm^{-1}) 2955, 2932, 2865, 2216, 1742, 1631, 1457, 1369, 1237, 1041; MS (EI, *m*/*z*) 250 (3, M^+) 235 (10), 221 (3), 207 (80), 190 (28), 161 (33), 151 (68), 133 (48), 119 (51), 105 (100), 91 (98), 77 (34); HRMS (EI) calcd for $C_{16}H_{26}O_2$ (M^+) 250.1927, found 250.1928.

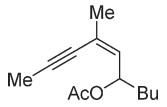


dx.doi.org/10.1021/jo200201r |*J. Org. Chem.* 2011, 76, 5959–5971

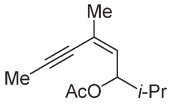
(*Z*)-1.1e. ^{1}H NMR (400 MHz, C_6D_6) δ 7.70−7.65 (m, 2H), 7.17−7.04 (m, 3H), 6.42 (dq, J_{AB}= 8.4, 6.4 Hz, 1H), 6.34 (d, J_{AB} = 8.4 Hz, 1H), 2.18 (t, J = 6.8 Hz, 2H), 1.70 (s, 3H), 1.44−1.29 (m, 4H), 1.42 (d, J = 6.4 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.4, 138.2, 135.3, 128.7, 128.4, 126.7, 126.2, 99.2, 77.4, 70.4, 31.0, 22.3, 20.9, 20.5, 19.5, 13.7; IR (ν_{max}/cm^{-1}) 2960, 2932, 2865, 2233, 1739, 1368, 1234, 1039, 761, 693; MS (EI, *m*/*z*) 270 (6, M$^+$) 255 (6), 227 (63), 211 (16), 185 (42), 167 (100), 153 (94), 141 (33), 128 (34), 115 (37), 91 (23), 77 (14); HRMS (EI) calcd for $C_{18}H_{22}O_2$ (M$^+$) 270.1614, found 270.1613.



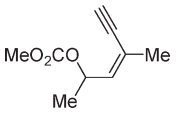
(*Z*)-1.1f. ^{1}H NMR (400 MHz, C_6D_6) δ 6.12 (dt, J = 8.4, 6.8 Hz, 1H), 5.55 (dq, J = 8.6, 1.0 Hz, 1H), 1.83−1.74 (m, 2H), 1.76 (d, J = 1.2 Hz, 3H), 1.72 (s, 3H), 1.60 (s, 3H), 1.38−1.25 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.4, 134.7, 122.6, 91.8, 78.6, 73.3, 34.9, 27.6, 23.6, 22.9, 20.9, 14.2, 4.05; IR (ν_{max}/cm^{-1}) 2958, 2922, 2857, 2232, 1738, 1634, 1363, 1371, 1234, 1018, 953; MS (EI, *m*/*z*) 208 (5, M$^+$), 193 (14), 165 (59), 151 (43), 123 (28), 109 (100), 91 (49), 79 (32); HRMS (EI) calcd for $C_{13}H_{20}O_2$ (M$^+$) 208.1458, found 208.1456.



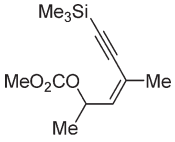
(*Z*)-1.1g. ^{1}H NMR (400 MHz, C_6D_6) δ 6.01 (dd, J = 8.8, 6.4 Hz, 1H), 5.55 (dq, J = 8.8, 0.8 Hz, 1H), 1.98 (octet, J = 6.8 Hz, 1H), 1.77 (d, J = 1.6 Hz, 3H), 1.72 (s, 3H), 1.60 (s, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.3, 132.7, 123.6, 91.7, 78.8, 77.4, 33.0, 23.8, 20.8, 18.4, 18.1, 4.10; IR (ν_{max}/cm^{-1}) 2963, 2920, 2876, 2240, 1733, 1637, 1435, 1369, 1232, 1017, 972, 606; MS (EI, *m*/*z*) 194 (4, M$^+$), 179 (2), 151 (41), 137 (8), 119 (24), 109 (100), 91 (15), 79 (13); HRMS (EI) calcd for $C_{12}H_{18}O_2$ (M$^+$) 194.1301, found 194.1307.



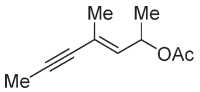
(*Z*)-1.2j. ^{1}H NMR (400 MHz, C_6D_6) δ (dq, J = 8.0, 6.5 Hz, 1H), 5.56 (d, J = 8.0 Hz, 1H), 3.34 (s, 3H), 2.80 (s, 1H), 1.58 (d, J = 1.2 Hz, 3H), 1.26 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 155.6, 138.0, 120.4, 83.4, 81.4, 73.8, 54.1, 22.7, 20.2; FTIR (ν_{max}/cm^{-1}) 2957, 2931, 2860, 2244, 146 1441, 1258, 1033, 944, 791, 762, 697; MS (EI, *m*/*z*) 168 (2, M$^+$), 153(4), 109(100), 91(77), 77(44); HRMS (EI) calcd for $C_9H_{12}O_3$ (M$^+$) 168.0781, found 168.0780.



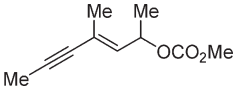
(*Z*)-1.2k. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (dq, J_{AB} = 8.8, 1.6 Hz, 1H), 5.62 (dq, J = 6.4, 1.2 Hz, 1H), 3.76 (s, 3H), 1.85 (d, J = 0.8 Hz, 3H), 1.37 (d, J = 6.8 Hz, 3H), 0.2 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.9, 121.4, 102.7, 100.5, 74.1, 54.7, 23.0, 20.1, −0.01; FTIR (ν_{max}/cm^{-1}) 2958, 2147, 1747, 1442, 1254, 1036, 880, 837, 791, 760, 634; MS (EI, *m*/*z*) 240 (12, M$^+$), 225 (3), 197 (3), 181 (100), 165 (35), 149 (88), 136 (13), 121 (22), 107 (12), 97 (23), 89 (64), 73 (63), 59 (33); HRMS (EI) calcd for $C_{12}H_{20}O_3Si$ (M$^+$) 240.1176, found 240.1165.



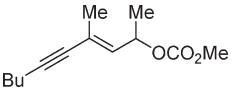
(*E*)-1.1a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (d, J_{AB} = 9.2, 1H), 5.54−5.61 (dq, J_{AB} = 8.8, 6.4 Hz, 1H), 2.01(s, 3H), 1.93(s, 3H), 1.85 (d, J = 0.8 Hz, 3H), 1.27 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 134.8, 121.8, 84.7, 81.8, 67.5, 21.4, 20.5, 18.2, 4.3; FTIR (ν_{max}/cm^{-1}) 2980, 2918, 2228, 1731, 1638, 1443, 1370, 1234, 1154, 1040, 1015, 943, 864, 610; MS (EI, *m*/*z*) 166 (13, M$^+$), 151 (30), 123 (100), 109 (79), 91 (87), 79 (26).



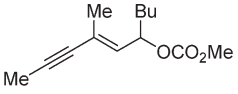
(*E*)-1.2a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (d, J = 9.2 Hz, 1H), 5.43 (dq, J = 9.2, 6.4 Hz, 1H), 3.75 (s, 3H), 1.92 (s, 3H), 1.87 (d, J = 1.2 Hz, 3H), 1.33 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 134.0, 122.4, 85.0, 81.7, 71.6, 54.7, 20.5, 18.2, 4.3; FTIR (ν_{max}/cm^{-1}) 2981, 2957, 2920, 2853, 2227, 1742, 1639, 1441, 1327, 1255, 1154, 1034, 938, 898, 864, 791; MS (EI, *m*/*z*) 182 (13, M$^+$), 167 (5), 123 (100), 107 (84), 91 (99), 79 (62).



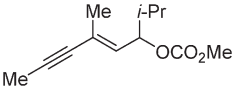
(*E*)-1.2b. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (d, J = 8.8 Hz 1H), 5.48 (dq, J = 8.8, 6.5 Hz, 1H), 3.75 (s, 3H), 2.29 (t, J = 7.0 Hz, 2H), 1.88 (s, 3H), 1.50 (quint, J = 6.8 Hz, 2H), 1.41 (sext, J = 7.6 Hz, 2H), 1.34 (d, J = 6.4 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR: (101 MHz, $CDCl_3$) δ 155.3, 133.9, 122.5, 89.6, 82.6, 71.7, 54.7, 30.9, 22.1, 20.5, 19.1, 18.3, 13.7; FTIR (ν_{max}/cm^{-1}) 2958, 2933, 2873, 2220, 1743, 1638, 1441, 1326, 1257, 1154, 1036, 939, 865, 792; MS (EI, *m*/*z*) 224 (6, M$^+$), 182 (9), 165 (70), 149 (50), 133 (19), 119 (41), 105 (77), 91 (100), 77 (53).



(*E*)-1.2f. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (d, J = 9.2, 1H), 5.26−5.32 (m, 1H), 3.75 (s, 3H), 1.93 (s, 1H), 1.88 (d, J = 1.2 Hz, 3H), 1.68−1.77 (m, 1H), 1.49−1.58 (s, 1H), 1.37−1.24 (m, 4H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 133.1, 123.2, 85.0, 82.0, 75.2, 55.0, 34.2, 27.1, 23.0, 18.4, 14.1, 4.3; FTIR (ν_{max}/cm^{-1}) 2957, 2930, 2862, 2222, 1743, 1638, 1441, 1380, 1321, 1259, 1152, 1091, 1036, 933, 879, 866, 791; MS (EI, *m*/*z*) 224 (4, M$^+$), 167 (31), 148 (26), 133 (19), 123 (38), 119 (51), 105 (47), 91 (94), 77 (56).

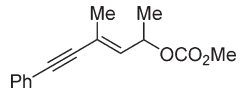


(*E*)-1.2g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (d, J = 9.6 Hz, 1H), 5.07 (dd, J = 9.6, 7.0 Hz, 1H), 3.75 (s, 3H), 1.93 (s, 3H), 1.89 (d, J = 1.2 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 131.5, 124.0, 85.0, 81.9, 79.6, 54.8, 32.5, 18.5, 18.3, 17.9, 4.3; FTIR (ν_{max}/cm^{-1}) 2960, 2920, 2876, 2222, 1743, 1639, 1441, 1254, 966, 934, 791; MS (EI, *m*/*z*) 210 (9, M$^+$), 195 (3), 167 (100), 151 (85), 135 (41), 123 (42), 119 (92), 108 (71), 91 (82), 77 (59).

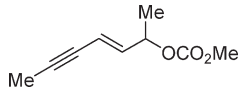


(*E*)-1.2h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.45 (m, 2H), 7.28−7.33 (m, 3H), 5.87 (dq, J = 8.8, 1.2 Hz, 1H), 5.50 (dq, J = 8.8, 6.4 Hz, 1H), 3.77 (s, 3H), 2.00 (d, J = 1.2 Hz, 3H), 1.39 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ155.3, 135.5, 131.7, 128.4, 123.3, 121.9, 91.3, 88.5, 71.6, 54.8, 20.4, 18.0; FTIR (ν_{max}/cm^{-1}) 3059, 2982, 2956,

2923, 1741, 1489, 1441, 1328, 1255, 1142, 1036, 942, 866, 754, 690; MS (EI, *m*/*z*) 244 (6, M^+), 185 (100), 167 (90), 153 (95), 152 (88), 141 (44), 128 (38), 115 (54), 102 (22), 91 (35), 77 (36).



(*E*)-1.2n. ^{1}H NMR (400 MHz, C_6D_6) δ 5.99 (dd, J_{AB} = 15.6, 6.8 Hz, 1H), 5.67 (d, J_{AB} = 15.6 Hz, 1H), 5.15 (quint, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 1.90 (d, *J* = 1.6 Hz, 3H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.0, 139.6, 112.9, 87.9, 75.4, 54.7, 20.1, 4.3; FTIR (ν_{max}/cm^{-1}) 2984, 2958, 2920, 2854, 2223, 1743, 1638, 1441, 1255, 1036, 941, 871, 790; MS (EI, *m*/*z*) 168 (3, M^+), 153 (3), 109 (100), 91 (83), 77 (47).

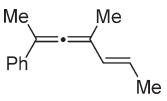


General Method for the Rhodium-Catalyzed Synthesis of Vinylallenes with (*Z*)-2-En-4-yne Acetates and Arylboronic Acids. To an oven-dried flask containing **1.1** (0.3 mmol) and **2** (0.9 mmol, 3 equiv) was added CsF (0.45 mmol, 1.5 equiv), $[RhOH(cod)]_2$ (6 mol % Rh), degassed water (0.1 mL), and dry THF (2.0 mL), successively, under Ar. The reaction mixture was stirred magnetically at room temperature for 16 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using hexane/ethyl acetate as eluent to give **3**.

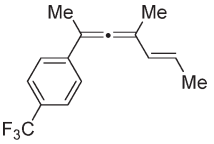
General Method for the Palladium-Catalyzed Synthesis of Vinylallenes with (*Z*)-or (*E*)-2-En-4-yne Carbonates and Arylboronic Acids. A mixture of $Pd_2(dba)_3CHCl_3$ (3% Pd) and PPh_3 (12%) in dry THF (1 mL) was stirred for 15 min under Ar. Then, the dry THF (4 mL) solution of **1.2** (0.2 mmol), **2** (0.6 mmol, 3 equiv), and degassed water (0.4 mL) was added successively. The mixture was stirred magnetically in an oil bath preheated at 65 °C. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate), affording the product **3**.

Computational Details. The geometry optimizations were performed by using the density functional theory (DFT) with Becke three parameter Lee, Yang, and Parr, (B3LYP)[28] functional and LANL2DZ basis set implemented in Gaussian 09 software.[29] The imaginary frequencies have been checked with the frequencies for these structures. The geometry analysis is shown in Supporting Information for some selected geometrical parameters. The natural Bond Orbital (NBO) and Mulliken charges were used for the charge analysis.

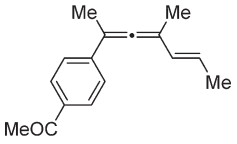
3aa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.38 (m, 2H), 7.28−7.33 (m, 2H), 7.14−7.21 (m, 1H), 6.06 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.64 (dq, *J* = 16.0, 6.8 Hz, 1 H), 2.09 (s, 3H), 1.90 (s, 3H), 1.80 (dd, *J* = 6.8, 1.6 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.40−7.46 (m, 2H), 7.14−7.21 (m, 2H), 7.02−7.08 (m, 1H), 6.15 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.51 (dq, *J* = 15.6, 6.4 Hz, 1H), 2.02 (s, 3H), 1.85 (s, 3H), 1.63 (dd, *J* = 6.8, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 137.8, 129.2, 128.3, 126.4, 125.8, 124.5, 101.8, 99.6, 18.3, 17.1, 15.5; ^{13}C NMR (101 MHz, C_6D_6) δ 207.5, 138.2, 129.9, 128.7, 126.9, 126.4, 124.5, 102.3, 100.4, 18.3, 17.3, 15.6; FTIR (ν_{max}/cm^{-1}) 3029, 2981, 2911, 1933, 1598, 1491, 1444, 1367, 1065, 1026, 961, 757, 690, 603, 594; MS (EI, *m*/*z*) 184 (100, M^+), 169 (98), 154 (86), 141 (70), 128 (51), 115 (36), 105 (19), 91 (30), 77 (15); HRMS (ESI) calcd for $C_{14}H_{17}$ (MH^+) 185.1325, found 185.1324.



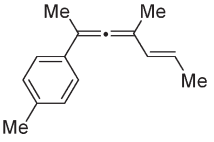
3ab. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J_{AB} = 8.0 Hz, 2H), 7.44 (d, J_{AB} = 8.0 Hz, 2H), 6.05 (dq, *J* = 16.0, 2.0 Hz, 1H), 5.64 (dq, *J* = 15.6, 6.8 Hz, 1H), 2.1 (s, 3H), 1.91 (s, 3H), 1.79 (dd, *J* = 6.8, 1.6 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.08 (dd, *J* = 15.2, 1.6 Hz, 1H), 5.50 (dq, *J* = 15.6, 6.4 Hz, 1H), 1.87 (s, 3H), 1.80 (s, 3H), 1.62 (dd, *J* = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 141.7, 128.5, 128.3 (q, *J* = 32 Hz), 125.9, 125.4, 125.1 (q, *J* = 3.9 Hz), 124.4 (q, *J* = 270 Hz), 102.5, 99.0, 18.3, 17.0, 15.3; ^{13}C NMR (100 MHz, C_6D_6) δ 208.2, 141.9, 128.9 (q, *J* = 32 Hz), 128.9, 126.4, 125.5 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 263 Hz), 102.9, 99.6, 18.4, 17.0, 15.4; FTIR (ν_{max}/cm^{-1}) 2987, 2928, 2855, 1933, 1616, 1323, 1164, 1114, 1074, 1014, 840, 607; MS (EI, *m*/*z*) 252 (100, M^+), 237 (82), 222 (21), 209 (43), 197 (64), 183 (26), 168 (36), 153 (39), 141 (17), 128 (14), 115 (13), 91 (16); HRMS (EI) calcd for $C_{15}H_{15}F_3$ (M^+) 252.1120, found 252.1119.



3ac. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, J_{AB} = 8.0 Hz, 2H), 6.04 (dq, J_{AB} = 15.6, 1.6 Hz, 1H), 5.68 (dq, *J* = 15.2, 6.8 Hz, 1H), 2.57 (s, 3H), 2.1 (s, 3H), 1.9 (s, 3H), 1.80 (dd, *J* = 6.4, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 197.7, 143.0, 135.0, 128.43, 128.39, 125.8, 125.4, 102.4, 99.4, 26.6, 18.4, 17.0, 15.3; FTIR (ν_{max}/cm^{-1}) 2925, 2850, 1930, 1681, 1601, 1357, 1266, 959, 838, 646, 602; MS (EI, *m*/*z*) 226 (100, M^+), 211 (57), 183 (37), 168 (43), 153 (39), 141 (24), 128 (19), 115 (21), 91 (11); HRMS (ESI) calcd for $C_{16}H_{19}$ (MH^+) 227.1430, found 227.1429.

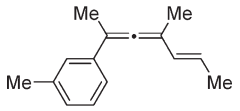


3ad. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J_{AB} = 8.0, 2H), 7.11 (d, J_{AB} = 8.0 Hz, 2H), 6.06 (dq, *J* = 16.0, 2.0 Hz, 1H), 5.64 (dq, *J* = 15.6, 6.4 Hz, 1H), 2.32 (s, 3H), 2.07 (s, 3H), 1.80 (s, 3H), 1.79 (dd, *J* = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 136.1, 134.8, 129.5, 129.0, 125.7, 124.3, 101.7, 99.5, 21.1, 18.3, 17.2, 15.5; FTIR (ν_{max}/cm^{-1}) 3038; 2982, 2921, 2850, 1510, 1444, 1370, 1025, 963, 816, 590; MS (EI, *m*/*z*) 198 (100, M^+), 183 (93), 168 (82), 153 (48), 141 (36), 128 (33), 115 (35), 105 (18), 91 (30), 77 (19); HRMS (ESI) calcd for $C_{15}H_{19}$ (MH^+) 199.1481, found 199.1481.

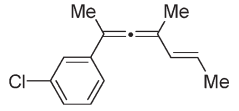


3ae. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.41 (m, 3H), 7.02−7.05 (m, 1H), 6.10 (dq, *J* = 15.2, 1.6 Hz, 1H), 5.67 (dq, *J* = 15.2, 6.4 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H), 1.93 (s, 3H), 1.83 (dd, *J* = 6.8, 1.6 Hz, 3 H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (s, 1H), 7.27−7.33 (m, 1H), 7.12−7.16 (m, 1H), 6.88−6.94 (m, 1H), 6.19 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.50 (dq, *J* = 15.2, 6.4 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 1.87 (s, 3H), 1.62 (dd, *J* = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 138.79, 137.8, 129.4, 128.2, 127.3, 126.6, 124.3, 123.0, 101.6, 99.6, 21.6, 18.3, 17.3, 15.5; ^{13}C NMR (100 MHz, C_6D_6) δ 207.5, 138.2, 138.0, 130.0, 128.7, 127.8, 127.1, 124.5, 123.6, 102.2, 100.4, 21.5, 18.4, 17.5, 15.7; FTIR (ν_{max}/cm^{-1}) 3013, 2918, 2855, 1933, 1604, 1488, 1444, 1376, 1028, 962, 781, 696; MS (EI, *m*/*z*) 198 (100, M^+), 183 (87), 168 (78), 153 (47), 141 (37), 128 (32), 115 (34), 105 (17), 91 (32); HRMS (ESI) calcd for $C_{15}H_{19}$ (MH^+) 199.1481, found 199.1481.

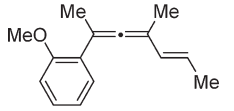
dx.doi.org/10.1021/jo200201r |*J. Org. Chem.* 2011, 76, 5959–5971



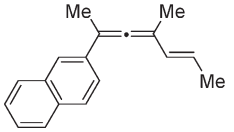
3af. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.32 (m, 1H), 7.21−7.23 (m, 2H), 7.13−7.17 (m, 1H), 6.04 (dq, J = 15.6, 1.6 Hz, 1H), 5.67 (dq, J = 15.6, 6.8 Hz, 1H), 2.07 (s, 3H), 1.89 (s, 3H), 1.81 (dd, J = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 140.1, 134.4, 129.5, 128.9, 126.5, 126.0, 125.3, 124.1, 102.5, 99.0, 18.5, 17.3, 15.6; FTIR (ν_{max}/cm^{-1}) 3034, 2982, 2916, 2855, 1933, 1592, 1566, 1475, 1443, 1417, 1368, 1106, 1080, 1067, 1027, 961, 776, 748, 687, 609; MS (EI, m/z) 218 (97, M$^+$), 203 (70), 183 (33), 175 (19), 168 (100), 153 (77), 141 (45), 128 (31), 115 (33), 102 (12), 91 (21), 77 (20); HRMS (ESI) calcd for $C_{14}H_{16}Cl$ (MH$^+$) 219.0935, found 219.0936.



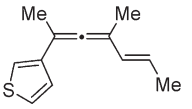
3ag. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.41 (m, 2H), 6.84−6.93 (m, 2H), 6.10 (dq, J = 15.6, 1.6 Hz, 1H), 5.54 (dq, J = 16.0, 6.8 Hz, 1H), 3.81 (s, 3H), 2.07 (s, 3H), 1.84 (s, 3H), 1.78 (dd, J = 6.4, 1.6 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.36 (dd, J = 7.6, 1.6 Hz, 1H), 7.06 (dt, J = 8.0, 1.2 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 6.28 (dq, J = 15.6, 1.6 Hz, 1H), 5.46 (dq, J = 15.6, 6.4 Hz, 1H), 3.33 (s, 3H), 2.22 (s, 3H), 1.88 (s, 3H), 1.64 (dd, J = 6.4, 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 157.0, 130.1, 129.2, 128.1, 127.9, 123.4, 120.5, 111.4, 98.5, 97.2, 55.7, 19.6, 18.3, 15.7; ^{13}C NMR (101 MHz, C_6D_6) δ 208.2, 157.6, 130.9, 129.9, 128.8, 127.9, 123.3, 120.9, 111.7, 99.1, 98.3, 55.2, 20.0, 18.4, 16.0; FTIR (ν_{max}/cm^{-1}) 2924, 1596, 1578, 1491, 1434, 1245, 1029, 962, 749, 603; MS (EI, m/z) 214 (23, M+), 199 (100), 184 (38), 165 (34), 152 (25), 141 (25), 135 (78), 128 (29), 115 (34), 91 (30), 77 (28); HRMS (ESI) calcd for $C_{15}H_{19}$ (MH$^+$) 215.1430, found 215.1430.



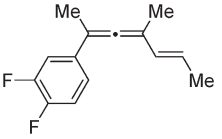
3ah. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78−7.87 (m, 2H), 7.70−7.77 (m, 2H), 7.54−7.59 (m, 1H), 7.40−7.52 (m, 2H), 6.14 (dq, J = 16.0, 1.0 Hz, 1H), 5.72 (dq, J = 15.5, 6.5 Hz, 1H), 2.25 (s, 3H), 1.97 (s, 3H), 1.85 (d, J = 5.5 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.72−7.77 (m, 2H), 7.58−7.67 (m, 3H), 7.20−7.30 (m, 2H), 6.19 (dq, J = 15.6, 2.4 Hz, 1H), 5.54 (dq, J = 15.6, 6.8 Hz, 1H), 2.14 (s, 3H), 1.89 (s, 3H), 1.64 (dd, J = 6.4, 1.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.0, 135.4, 133.8, 132.5, 129.3, 128.1, 127.71, 127.68, 126.2, 125.6, 125.5, 124.8, 123.5, 102.2, 100.1, 18.5, 17.4, 15.7; ^{13}C NMR (101 MHz, C_6D_6) δ 208.3, 135.6, 134.4, 133.0, 129.7, 128.4, 128.2, 126.4, 125.9, 125.8, 124.8, 124.0, 102.6, 100.7, 18.4, 17.4, 15.7; FTIR (ν_{max}/cm^{-1}) 3053, 2982, 2915, 1929, 1629, 1597, 1505, 1371, 1025, 961, 854, 817, 783, 745; MS (EI, m/z) 234 (100, M$^+$), 219 (88), 204 (81), 189 (27), 178 (43), 165 (25), 152 (20), 141 (15); HRMS (ESI) calcd for $C_{18}H_{19}$ (MH$^+$) 235.1481, found 235.1481.



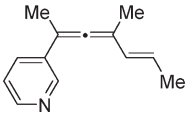
3ai. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.23 (m, 1H), 7.01−7.05 (m, 2H), 6.27 (dq, J = 15.6, 1.6 Hz, 1H), 5.96 (dq, J = 15.6, 6.4 Hz, 1H), 2.06 (s, 3H), 1.87 (s, 3H), 1.79 (dd, J = 6.8, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 140.1, 129.3, 126.9, 125.2, 124.5, 118.7, 103.3, 99.1, 18.3, 17.7, 15.6; FTIR (ν_{max}/cm^{-1}) 3103, 2987, 2922, 2855, 1929, 1442, 1368, 1247, 1183, 1026, 962, 864, 775, 644; MS (EI, m/z) 190 (95, M$^+$), 175 (100), 160 (45), 147 (32), 142 (59), 134 (23), 129 (17), 115 (25); HRMS (ESI) calcd for $C_{12}H_{15}S$ (MH$^+$) 191.0889, found 191.0889.



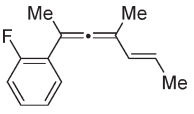
3aj. ^{1}H NMR (400 MHz, C_6D_6) δ 7.06−7.14 (m, 1H), 6.77−6.84 (m, 1H), 6.66−6.75 (m, 1H), 6.04 (dq, J = 15.6, 1.6 Hz, 1H), 5.48 (dq, J = 15.6, 6.4 Hz, 1H), 1.80 (s, 3H), 1.76 (s, 3H), 1.61 (dd, J = 6.8, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 207.0, 150.8 (dd, J = 236, 12.2 Hz), 149.6 (dd, J = 246, 12.9 Hz), 135.6 (t, J = 5.0 Hz), 129.1, 125.4, 122.1 (dd, J = 6.1, 3.1 Hz), 117.2 (d, J = 16.8 Hz), 115.0 (d, J = 17.5 Hz), 18.1, 17.0, 15.2; FTIR (ν_{max}/cm^{-1}) 3037, 2986, 2928, 2859, 1933, 1735, 1603, 1515, 1445, 1289, 962, 817, 773; MS (EI, m/z) 220 (100, M$^+$), 205 (82), 190 (56), 177 (55), 165 (43), 151 (33), 141 (29), 127 (21), 91 (22), 77 (6); HRMS (ESI) calcd for $C_{14}H_{15}F_2$ (MH$^+$) 221.1136, found 221.1137.



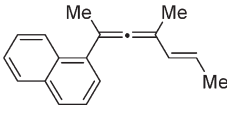
3ak. ^{1}H NMR (400 MHz, C_6D_6) δ 8.88−8.92 (m, 1H), 8.42−8.47 (m, 1H), 7.34−7.37 (m, 1H), 6.70−7.38 (m, 1H), 6.04 (dq, J = 15.6, 1.2 Hz, 1H), 5.48 (dq, J = 15.6, 6.8 Hz, 1H), 1.86 (s, 3H), 1.76 (s, 3H), 1.6 (dd, J = 7.2, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 207.4, 148.3, 133.5, 132.6, 129.2, 125.3, 123.1, 103.0, 98.0, 18.3, 16.8, 15.4; FTIR (ν_{max}/cm^{-1}) 3037, 2985, 2924, 2858, 1932, 1569, 1479, 1445, 1417, 1378, 1020, 962, 806, 708, 605; MS (EI, m/z) 185 (68, M$^+$), 170 (100), 154 (48), 142 (13), 128 (15), 115 (12), 106 (14), 91 (10), 77 (12); HRMS (EI) calcd for $C_{13}H_{15}N$ (M$^+$) 185.1199, found 185.1199.



3al. ^{1}H NMR (500 MHz, C_6D_6) δ 7.19−7.25 (m, 1H), 6.76−6.85 (m, 3H), 6.18 (d, J = 15.5 Hz, 1H), 5.46 (dq, J = 15.5, 6.5 Hz, 1H), 2.10 (s, 3H), 1.83 (s, 3H), 1.61 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 208.7, 160.5 (d, J = 248 Hz), 129.9, 129.6 (d, J = 3.8 Hz), 128.5 (d, J = 7.6 Hz), 128.4, 124.5, 124.2 (d, J = 3.8 Hz), 116. (d, J = 23.1 Hz), 100.5, 95.8, 19.4 (d, J = 2.0 Hz), 18.4, 15.7; FTIR (ν_{max}/cm^{-1}) 3038, 2923, 2854, 1907, 1576, 1490, 1445, 1368, 1220, 1037, 961, 753, 601; MS (EI, m/z) 202 (100, M$^+$), 187 (74), 165 (57), 159 (52), 152 (50), 146 (44), 133 (35), 123 (35), 109 (30), 91 (14), 77 (9); HRMS (EI) calcd for $C_{14}H_{15}F$ (M$^+$) 202.1152, found 202.1147.

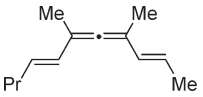


3am. ^{1}H NMR (400 MHz, C_6D_6) δ 8.40−8.46 (m, 1H), 7.63−7.69 (m, 1H), 7.53−7.58 (m, 1H), 7.33−7.43 (m, 2H), 7.21−7.30 (m, 2H), 6.26 (dq, J = 15.6, 1.6 Hz, 1H), 5.43 (dq, J = 15.6, 6.8 Hz, 1H), 2.16 (s, 3H), 1.83 (s, 3H), 1.62 (dd, J = 6.8, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 206.8, 138.0, 134.7, 131.8, 130.3, 128.9, 127.7, 126.2, 126.1, 126.0, 125.8, 125.5, 124.2, 99.6, 98.8, 21.7, 18.4, 15.9; FTIR (ν_{max}/cm^{-1}) 3057, 2918, 2879, 2723, 1939, 1734, 1439, 1030, 960, 799, 775; MS (EI, m/z, M$^+$): 234 (26), 219 (100), 204 (63), 189 (32), 178 (16), 165 (26), 152 (14); HRMS (EI) calcd for $C_{18}H_{18}$ (M$^+$), 234.1403, found 234.1403.

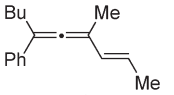


dx.doi.org/10.1021/jo200201r |J. Org. Chem. 2011, 76, 5959–5971

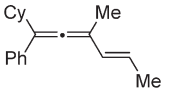
3an. ^{1}H NMR (400 MHz, C_6D_6) δ 6.08−6.23 (m, 2H), 5.53 (dt, J = 15.6, 6.8 Hz, 1H), 5.45 (dq, J = 15.6, 6.4 Hz, 1H), 2.00 (q, J = 7.2 Hz, 2H), 1.85 (s, 3H), 1.82 (s, 3H), 1.62 (dd, J = 6.8, 1.6 Hz, 3H), 1.33 (sext, J = 7.6 Hz, 2H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 209.5, 130.5, 129.5, 129.2, 123.8, 99.79, 99.75, 35.4, 23.1, 18.3, 16.1, 16.0, 13.9; FTIR (ν_{max}/cm^{-1}) 3037, 2959, 2927, 2872, 1929, 1439, 1377, 1032, 961, 586; MS (EI, m/z, M$^+$): 176 (51), 161 (14), 147 (42), 133 (31), 119 (100), 105 (75), 91 (59), 77 (25); HRMS (EI) calcd for $C_{13}H_{20}$ (M$^+$) 176.1560, found 176.1552.



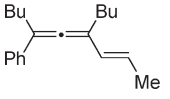
3ba. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.41 (m, 2H), 7.28−7.34 (m, 2 H), 7.17−7.23 (m, 1H), 6.10 (dq, J = 15.6, 1.6 Hz, 1H), 5.67 (dq, J = 15.6, 6.6 Hz, 1H), 2.47 (t, J = 7.6 Hz, 2H), 1.93 (s, 3H), 1.83 (dd, J = 6.6, 2.0 Hz, 3H), 1.53 (quint, J = 7.2 Hz, 2H), 1.44 (sext, J = 7.6 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H); ^{1}H NMR (400 MHz, C_6D_6) δ 7.45−7.49 (m, 2H), 7.15−7.22 (m, 2H), 7.03−7.10 (m, 1H), 6.19 (dq, J = 15.6, 1.6 Hz, 1H), 5.67 (dq, J = 15.6, 6.6 Hz, 1H), 2.42 (t, J = 7.6 Hz, 2H), 1.87 (s, 3H), 1.64 (dd, J = 6.8, 1.6 Hz, 3H), 1.56 (quint, J = 7.6 Hz, 2H), 1.36 (sext, J = 7.6 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 137.8, 129.6, 128.4, 126.5, 126.3, 124.4, 105.1, 103.2, 30.3, 30.2, 22.6, 18.5, 15.7, 14.1; ^{13}C NMR (101 MHz, C_6D_6) δ 207.3, 138.0, 129.9, 128.7, 126.9, 126.7, 124.4, 105.7, 105.6, 30.6, 30.5, 22.9, 18.4, 15.7, 14.2; FTIR (ν_{max}/cm^{-1}) 3025, 2957, 2928, 2859, 1931, 1599, 1492, 1446, 1376, 961, 757, 693; MS (EI, m/z) 226 (13, M$^+$), 211 (7), 197 (13), 184 (50), 169 (100), 155 (37), 141 (31), 128 (23), 115 (21), 91 (25), 77 (8); HRMS (EI) calcd for $C_{17}H_{22}$ (M$^+$) 226.1716, found 226.1712.



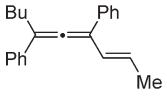
3ca. ^{1}H NMR (400 MHz, C_6D_6) δ 7.44−7.57 (m, 2H), 7.17−7.21 (m, 2H), 7.02−7.09 (m, 1H), 6.19 (dq, J = 15.6, 1.6 Hz, 1H), 5.54 (dq, J = 15.6, 6.8 Hz, 1H), 2.44−2.52 (m, 1H), 1.95−2.03 (m, 2H), 1.87 (s, 3H), 1.65 (dd, J = 6.8, 1.6 Hz, 3H), 1.59−1.73 (m, 3H), 1.24−1.32 (m, 4H), 1.11−1.19 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 207.1, 137.8, 130.2, 128.7, 127.2, 126.8, 124.2, 112.2, 104.3, 38.6, 33.3, 33.5, 27.0, 26.8, 18.4, 15.9; FTIR (ν_{max}/cm^{-1}) 3021, 2924, 2851, 1928, 1598, 1493, 1446, 961, 764, 693; MS (EI, m/z) 252 (18, M$^+$), 237 (18), 223 (31), 195 (26), 183 (100), 169 (50), 155 (48), 141 (30), 128 (29), 115 (25), 91 (36), 77 (12); HRMS (EI) calcd for $C_{19}H_{24}$ (M$^+$) 252.1873, found 252.1871.



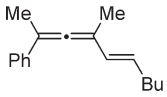
3da. ^{1}H NMR (400 MHz, C_6D_6) δ 7.46−7.53 (m, 2H), 7.16−7.23 (m, 2H), 7.03−7.09 (m, 1H), 6.14 (dd, J = 15.7, 1.6 Hz, 1H), 5.65 (dq, J = 15.7, 6.7 Hz, 1H), 2.46 (t, J = 8.0 Hz, 2H), 2.26 (t, J = 7.6 Hz, 2H), 1.66 (dd, J = 6.8, 1.5 Hz, 3H), 1.54−1.64 (m, 4H), 1.30−1.41 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 206.8, 138.0, 129.4, 128.7, 126.9, 126.5, 124.1, 108.7, 107.3, 30.8, 30.61, 30.60, 29.6, 23.2, 23.0, 18.6, 14.3, 14.2; FTIR (ν_{max}/cm^{-1}) 3023, 2956, 2927, 2858, 1597, 1493, 1448, 1377, 961, 757, 692; MS (EI, m/z) 268 (2, M$^+$), 239 (4), 226 (3), 211 (39), 183 (33), 169 (100), 155 (38), 141 (48), 128 (14), 115 (17), 91 (28), 77 (8); HRMS (EI) calcd for $C_{20}H_{28}$ (M$^+$) 242.1485, found 242.1485.



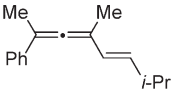
3ea. ^{1}H NMR (400 MHz, C_6D_6) δ 7.50−7.57 (m, 4H), 7.12−7.20 (m, 4H), 7.02−7.09 (m, 2H), 6.27 (dq, J = 15.6, 2.0 Hz, 1H), 5.96 (dq, J = 15.6, 6.8 Hz, 1H), 2.47 (t, J = 7.6 Hz, 1H), 2.46 (t, J = 7.6 Hz, 1H), 1.62 (dd, J = 6.8, 1.6 Hz, 3H), 1.54−1.65 (m, 2H), 1.31 (sext, J = 15.6, 2H), 0.82 (t, J = 15.6 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 207.7, 137.3, 137.1, 128.9, 128.8, 128.7, 127.9, 127.4, 127.2, 127.0, 126.5, 111.3, 109.1, 30.6, 30.5, 23.0, 18.5, 14.2; FTIR (ν_{max}/cm^{-1}) 3026, 2956, 2929, 2858, 1597, 1492, 1445, 960, 756, 692; MS (EI, m/z) 288 (8, M$^+$), 259 (19), 246 (168), 231 (100), 215 (77), 202 (28), 165 (16), 155 (20), 128 (21), 115 (28), 91 (26), 77 (13); HRMS (EI) calcd for $C_{22}H_{24}$ (M$^+$) 288.1873, found 288.1876.



3fa. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.43 (m, 2H), 7.31−7.36 (m, 2H), 7.21−7.24 (m, 1H), 6.08 (dt, J = 19.6, 1.6 Hz, 1H), 5.66 (dt, J = 15.6, 7.2 Hz, 1H), 2.13−2.20 (m, 2H), 2.13 (s, 3H), 1.93 (s, 3H), 1.32−1.48 (m, 4H), 0.94 (t, J = 7.6 Hz, 3H); ^{1}H NMR (500 MHz, C_6D_6) δ 7.40−7.46 (m, 2H), 7.12−7.20 (m, 2H), 7.00−7.09 (m, 1H), 6.20 (dt, J = 15.5, 1.5 Hz, 1H), 5.60 (dt, J = 12.5, 6.0 Hz, 1H), 2.00−2.10 (m, 2H), 2.03 (d, J = 3.0 Hz, 3H), 1.89 (d, J = 3.0, 3H), 1.20−1.22 (m, 4H), 0.84 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 137.8, 130.08, 128.3, 127.9, 126.4, 125.9, 101.9, 99.6, 32.7, 31.8, 22.3, 17.1, 15.5, 14.0; ^{13}C NMR (126 MHz, C_6D_6) δ 207.7, 138.2, 130.2, 128.7, 128.6, 126.9, 126.4, 102.4, 100.4, 33.1, 32.1, 22.7, 17.3, 15.7, 14.2; FTIR (ν_{max}/cm^{-1}) 3027, 2956, 2925, 2863, 1933, 1492, 1444, 1367, 1027, 963, 758, 692, 604, 596; MS (EI, m/z) 226 (38, M$^+$), 211 (21), 197 (9), 183 (100), 168 (52), 155 (83), 141 (55), 128 (40), 115 (37), 105 (28), 91 (33), 77 (21); HRMS (ESI) calcd for $C_{17}H_{23}$ (MH$^+$) 227.1794, found 227.1795.

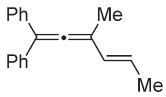


3ga. ^{1}H NMR (400 MHz, C_6D_6) δ 7.32−7.50 (m, 2H), 7.10−7.20 (m, 2H), 7.00−7.08 (m, 1H), 6.20 (dd, J = 15.8, 1.4 Hz, 1H), 5.59 (dd, J = 15.6, 7.0 Hz, 1H), 2.21−2.32 (m, 1H), 2.03 (s, 3H), 1.89 (s, 3H), 0.956 (d, J = 7.2 Hz, 3H), 0.953 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 207.9, 138.2, 137.0, 128.7, 126.9, 126.4, 125.9, 102.3, 100.4, 31.9, 22.7, 17.3, 15.7; FTIR (ν_{max}/cm^{-1}) 3027, 2958, 2867, 1933, 1597, 1492, 1465, 1444, 1366, 1066, 1029, 964, 758, 692, 603; MS (EI, m/z) 212 (47, M$^+$), 197 (100), 182 (32), 169 (31), 165 (29), 155 (48), 141 (36), 128 (35), 115 (29), 91 (24), 77 (15); HRMS (EI) calcd for $C_{16}H_{20}$ (M$^+$) 212.1560, found 212.1551.

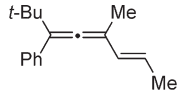


3ha. ^{1}H NMR (500 MHz, C_6D_6) δ 7.46−7.50 (m, 4H), 7.14−7.23 (m, 4H), 7.05−7.10 (m, 2H), 6.16 (dq, J = 15.5, 1.5 Hz, 1H), 5.50 (dq, J = 15.8, 6.5 Hz, 1H), 1.84 (s, 3H), 1.61 (dd, J = 7.0, 1.5 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 209.5, 137.9, 129.2, 129.1, 128.8, 127.4, 125.4, 110.2, 103.5, 18.4, 15.6; FTIR (ν_{max}/cm^{-1}) 3029, 2925, 1715, 1598, 1492, 1445, 962, 900, 839, 768, 738, 695, 630; MS (EI, m/z) 246 (100, M$^+$), 231 (24), 215 (70), 202 (27), 189 (12), 165 (17), 153 (21), 128 (10), 115 (14), 91 (9), 77 (8); HRMS (EI) calcd for $C_{19}H_{18}$ (M$^+$) 246.14030, found 246.13960.

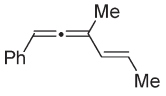
dx.doi.org/10.1021/jo200201r |J. Org. Chem. 2011, 76, 5959–5971



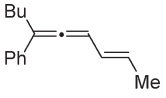
3ia. ^{1}H NMR (400 MHz, C_6D_6) δ 7.30−7.35 (m, 2H), 7.11−7.17 (m, 2H), 7.04−7.10 (m, 1H), 6.22 (dq, J = 15.6, 1.6 Hz, 1H), 5.42 (dq, J = 6.8, 15.6 Hz, 1H), 1.79 (s, 3H), 1.64 (dd, J = 6.4, 1.6 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 204.7, 138.6, 130.8, 129.9, 128.2, 126.8, 123.6, 115.6, 101.0, 35.4, 30.3, 18.4, 16.2; FTIR (ν_{max}/cm^{-1}) 3018, 2965, 2902, 2866, 1442, 1361, 960, 755, 737, 698, 570; MS (EI, m/z) 226 (7, M$^+$), 196 (6), 181 (6), 169 (100), 154 (72), 141 (25), 128 (24), 115 (19), 91 (26), 77 (12); HRMS (EI) calcd for $C_{17}H_{22}$ (M$^+$) 226.1716, found 226.1710.



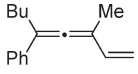
3ja. ^{1}H NMR (400 MHz, C_6D_6) δ 7.24−7.28 (m, 2H), 7.08−7.15 (m, 2H), 6.90−7.04 (m, 1H), 6.23 (s, 1H), 6.12 (d, J = 15.6 Hz, 1H), 5.50 (dq, J = 15.6, 6.4 Hz, 1H), 1.82 (d, J = 2.8 Hz, 3H), 1.60 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 208.7, 135.6, 129.1, 128.9, 127.3, 127.1, 125.2, 104.2, 99.7, 18.3, 15.5; FTIR (ν_{max}/cm^{-1}) 3024, 2871, 1932, 1598, 1495, 1448, 960, 825, 742, 692, 631; MS (EI, m/z) 170 (75, M$^+$), 155 (100), 141 (24), 128 (45), 115 (36), 102 (8), 91 (28), 77 (20); HRMS (EI) calcd for $C_{13}H_{14}$ (M$^+$), 170.1090, found 170.1084.



3la. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.36 (m, 2H), 7.35−7.28 (m, 2H), 7.22−7.16 (m, 1H), 6.15 (dt, J = 10.0, 2.8 Hz, 1H), 5.92 (ddq, J_{AB} = 15.2, 10.4, 1.2 Hz, 1H), 5.74 (dq, J_{AB} = 15.2, 6.8 Hz, 1H), 2.49−2.41 (m, 2H), 1.77 (dd, J = 6.0, 1.2 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 137.0, 128.5, 127.9, 126.8, 126.7, 126.3, 107.1, 97.3, 30.2, 30.0, 22.6, 18.4, 14.1; FTIR (ν_{max}/cm^{-1}) 2956, 2926, 2857, 1931, 1492, 1447, 1026, 962, 758, 692; MS (EI, m/z) 212 (5, M$^+$), 170 (48), 155 (100), 141 (28), 128 (19), 115 (20), 91 (21), 77 (6); HRMS (EI) calcd for $C_{16}H_{20}$ (M$^+$) 212.1560, found 212.1554.



3ma. ^{1}H NMR (400 MHz, C_6D_6) δ 7.39−7.45 (m, 2H), 7.15−7.21 (m, 2H), 7.02−7.09 (m, 1H), 6.51 (dd, J = 17.2, 10.4 Hz, 1H), 5.12 (dd, J = 17.2, 1.2 Hz, 1H), 4.99 (dd, J = 10.8, 0.8 Hz, 1H), 2.39 (t, J = 7.6 Hz, 2H), 1.84 (s, 3H), 1.51 (quint, J = 7.6 Hz, 2H), 1.33 (sext, J = 7.6 Hz, 2H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 208.3, 137.5, 136.1, 128.8, 127.0, 126.7, 112.9, 106.0, 103.9, 30.4, 30.3, 22.8, 14.9, 14.2; FTIR (ν_{max}/cm^{-1}) 3026, 2957, 2929, 2859, 1931, 1613, 1493, 1455, 896, 759, 739, 694; MS (EI, m/z, M$^+$): 212 (2, M$^+$), 197 (1), 170 (54), 155 (100), 141 (35), 128 (23), 115 (31), 91 (23), 77 (12); HRMS (EI) calcd for $C_{16}H_{20}$ (M$^+$) 212.1560, found 212.1560.



■ ASSOCIATED CONTENT

Supporting Information. Calculated DFT parameters and ^{1}H and ^{13}C spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) No successful results could be obtained by the use of 1-naphthyl-, 3-pyridyl-, and 1-pentenylboronic acids.
(17) The reactions of enynes with *tert*-butyl, $SiMe_3$, or Ph substituents on the R^1 position ($R^2 = R^3 = Me$) and of a primary enyne acetate ($R^1 = R^2 = Me$, $R^3 = H$) were highly sluggish and afforded the related vinylallene products in very low yields, usually <20%. The reactions of enynes with $R^1 = H$, $R^2 = R^3 = Me$ and $R^1 = R^3 = Me$, $R^2 = H$ gave complex mixtures.
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