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Palladium-Catalyzed Coupling of Alkynes with Unactivated Alkenes in Ionic Liquids: A Regio- and Stereoselective Synthesis of Functionalized 1,6-Dienes and Their Analogues

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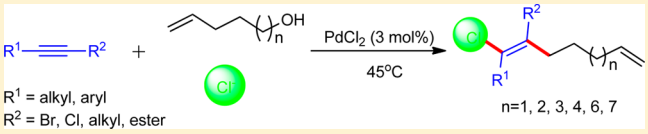
Supporting Information

ABSTRACT: A palladium-catalyzed regio- and stereoselective intermolecular tandem reaction of alkynes and unactivated 1,6-enols in ionic liquids is described, providing a practical, efficient, and versatile method for the synthesis of functionalized 1,6-dienes in moderate to good yields. The present reaction has high functional-group tolerance and gives products on a gram scale. Mechanistic studies indicate that the reaction might proceed via a chain-walking mechanism.



INTRODUCTION

During recent years, transition-metal-catalyzed transformations for the construction of highly functionalized and complex molecules in a convenient and concise manner has become a rapidly expanding area of research, owing in part to readily accessible starting materials and versatile approaches.[1] Toward this end, there has been a growing interest in the application of palladium-catalyzed processes, since they usually proceed under mild reaction conditions and are tolerant of many functional groups.[2] In this regard, nucleopalladation of alkynes has proved to be a very effective and convenient method for the construction of both carbon−carbon and carbon−heteroatom bonds in a rather versatile and atom-economical way.[3] Although significant contributions have been made to this research area,[4] most of the methods still have some limitations: (i) in contrast to other conventional solvents, the use of environmentally friendly ionic liquids (ILs) is attractive; (ii) high selectivities, including chemo-, regio-, and stereoselectivity, are still being sought; (iii) the trapping of alkenylpalladium intermediates with readily available materials, such as unactivated alkenes, is also desirable.

The 1,6-diene moiety has been recognized as a privileged fragment that can be found in many natural products and drug candidates and exhibits potential biological activities.[5] Consequently, many representative methodologies have been developed for the synthesis of functionalized 1,6-dienes, including [2 + 2] cycloaddition of allenynes,[6] Pd-catalyzed allylation,[7] and Pd-catalyzed decarboxylative protonation.[8] Although classical methods for the preparation of 1,6-diene skeletons are widely recognized in the early research, these syntheses generally involve multiple steps, harsh reaction conditions, and/or complicated workup procedures. Very recently, Ryu and co-workers discovered an elegant method for the stereoselective synthesis of 2-bromo-1,6-dienes based on the bromine-radical-mediated rearrangement and addition reaction of alkylidenecyclopropanes.[9] However, complex substrates are required in these radical reactions. Despite the significant progress that has been achieved, the development of facile approaches that may allow for the straightforward preparation of structurally diverse functionalized 1,6-dienes from easily available starting materials needs to be pursued. Driven by our interest in nucleopalladation and Pd-catalyzed cross-coupling reactions in ionic liquids,[10] herein we disclose for the first time an efficient and practical method for the synthesis of functionalized 1,6-dienes via the Pd-catalyzed intermolecular cross-coupling reaction of alkyne derivatives with unactivated alkenes in ionic liquids, which allows the selective construction of (1*E*)- or (1*Z*)-1,6-dienes in a highly stereoselective fashion. In this reaction, the ionic liquid not only acts as a solvent in the reaction but also provides the excess halide ions to control the *Z*/*E* selectivity.[10f]

RESULTS AND DISCUSSION

Our investigation was initiated by using the reaction of (bromoethynyl)benzene (**1a**) and pent-4-en-1-ol (**2a**) as a model system (Table 1). First, the reactions without aqueous HCl or $PdCl_2$ failed to afford the desired product **3a**, thus showing the pivotal role of these reagents in the reaction (entries 1 and 2). To our delight, in the presence of 3 mol % $PdCl_2$ in 0.50 mL of [Bmim]Cl as the solvent with 0.25 mL of 12 mol/L HCl(aq) as an additive, the starting materials were consumed within 12 h at room temperature, providing 1,6-diene **3a** in 38% yield with high *Z* stereoselectivity (*Z*/*E* = 98/2 by GC) (entry 3).[11] Furthermore, the reaction temperature was also varied, and 45 °C gave the best yield (entry 5). Neither higher nor lower reaction temperatures were beneficial for the conversion (entries 3, 4, and 6). Gratifyingly, a clear improvement in the yield was observed when 0.35 mL of HCl(aq) was used (entry 8). Subsequently, various palladium sources were also tested (entries 10−12), and $PdCl_2$ proved to

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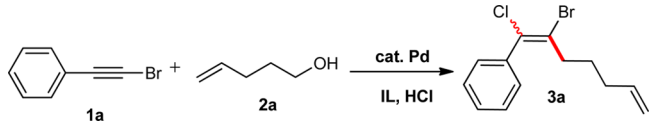
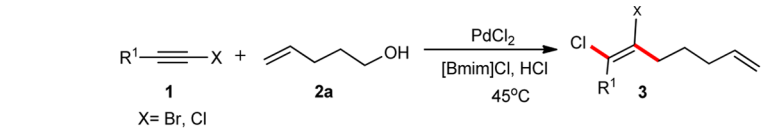
Table 1. Optimization of the Reaction Conditions[a]

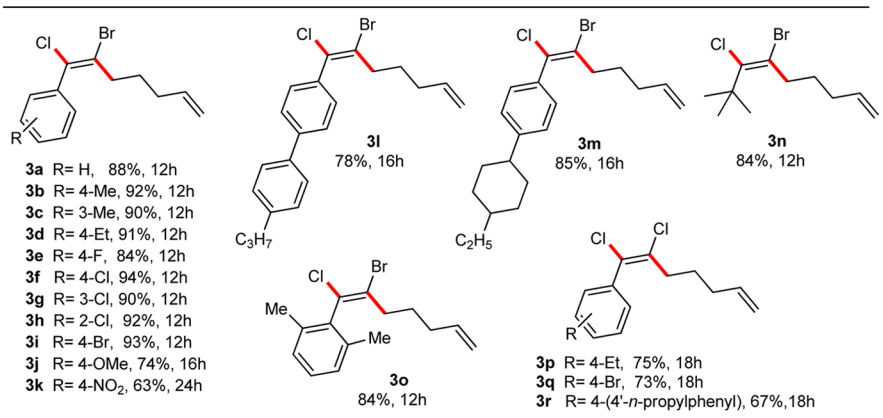


entry	ionic liquid	additive (mL)	[Pd]	T (°C)	yield (%)[b]	Z/E
1	[Bmim]Cl	–	$PdCl_2$	rt	nr	–
2	[Bmim]Cl	HCl (0.25)	–	rt	nr	–
3	[Bmim]Cl	HCl (0.25)	$PdCl_2$	rt	38	98/2
4	[Bmim]Cl	HCl (0.25)	$PdCl_2$	35	58	98/2
5	[Bmim]Cl	HCl (0.25)	$PdCl_2$	45	76	98/2
6	[Bmim]Cl	HCl (0.25)	$PdCl_2$	50	61	96/4
7	[Bmim]Cl	HCl (0.30)	$PdCl_2$	45	80	98/2
8	[Bmim]Cl	HCl (0.35)	$PdCl_2$	45	98 (88)	98/2
9	[Bmim]Cl	HCl (0.40)	$PdCl_2$	45	92	98/2
10	[Bmim]Cl	HCl (0.35)	$Pd(OAc)_2$	45	58	98/2
11	[Bmim]Cl	HCl (0.35)	$Pd(PPh_3)_4$	45	nd	–
12	[Bmim]Cl	HCl (0.35)	$Pd(PPh_3)_2Cl_2$	45	47	98/2
13[c]	[Bmim]Cl	–	$PdCl_2$	45	81	84/16
14	$[C_2OHmim]Cl$	HCl (0.35)	$PdCl_2$	45	70	98/2
15	$[C_2O_2mim]Cl$	HCl (0.35)	$PdCl_2$	45	87	98/2
16[d]	–	HCl (0.35)	$PdCl_2$	45	91	73/27
17	–	HCl (0.35)	$PdCl_2$	45	85	56/44
18[e]	–	HCl (0.35)	$PdCl_2$	45	39	51/49

[a]Unless otherwise noted, the reaction was performed with **1a** (0.5 mmol), **2a** (0.6 mmol), Pd catalyst (0.025 mol), and ionic liquid (0.5 mL) for 12 h. The 1*Z*/1*E* ratios were determined by GC. n.r. = no reaction; n.d. = not determined. [b]Determined by GC using dodecane as the internal standard. The value in parentheses is the isolated yield. [c]6.0 equiv of LiCl was used. [d]0.5 mL of HOAc was used. [e]0.5 mL of DMF was used.

Table 2. Pd(II)-Catalyzed Coupling Reaction of Haloalkynes with 2a in [Bmim]Cl[a]





[a]Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $PdCl_2$ (3 mol %), [Bmim]Cl (0.5 mL), and HCl (0.35 mL) under an atmosphere of air at 45 °C. Reactions were monitored for completion by TLC.

be optimal, affording **3a** in 98% GC yield while the other palladium sources did not show apparent positive effects (entries 10–12). Cheap and readily available alkaline metal salts seemed to be less efficient for the reaction. When LiCl was employed, the reaction yield was 81% (entry 13). Further examination of the ionic liquid effects revealed that [Bmim]Cl was the most suitable solvent for this transformation (entries 8, 14, and 15). Notably, various conventional solvents, such as HOAc and DMF, were examined under the same reaction conditions and significantly decreased the yields and stereoselectivities (entries 16–18). Thus, the optimized reaction conditions were affirmed as follows: 3 mol % $PdCl_2$ as the catalyst and 0.35 mL of HCl(aq) as the additive in [Bmim]Cl at 45 °C for 12 h.

Subsequently, we explored the scope of the reaction between **2a** and a variety of haloalkynes under the optimized reaction conditions (Table 2). All of the bromoalkynes and the chloroalkynes reacted smoothly and afforded the corresponding 1,6-diene products **3a–r** in moderate to high yields (63–94%). Aromatic alkynyl bromides with either electron-rich or

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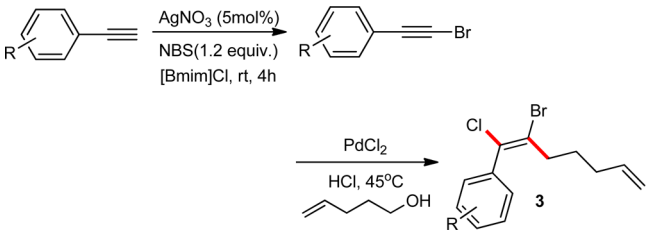
electron-poor groups attached to the benzene ring were able to react with **2a** to give the corresponding alkynylation products in good to excellent yields. Moreover, the reaction tolerated a variety of substituents, including F, Cl, Br, NO_2, OMe, and even bulky ethylcyclohexyl groups. As for the sterically hindered bromoalkynes **1h** and **1o**, the reaction furnished the corresponding products (*Z*)-**3h** and (*Z*)-**3o** in yields similar to that of (*Z*)-**3f** or (*Z*)-**3b**. Interestingly, alkyl alkynyl bromides such as 1-bromo-3,3-dimethylbut-1-yne (**1n**) could also undergo this transformation in good yields. Furthermore, the reaction was found to be applicable to various chloroalkynes, although the reaction of chloroalkynes was relatively sluggish (Table 2, **3p**–**r**). In terms of the stereoselectivity, all of the products obtained in the presence of an excess of chloride ions and acid in a polar solvent resulted from trans addition.[12] The site of halogen addition to asymmetric acetylenes was controlled by electronic factors.[13]

Next, the one-pot synthesis of (1*Z*)-1,2-dihalo-1,6-dienes from alkynes were examined, and the results are summarized in Table 3. After the Ag-catalyzed reaction of alkynes was completed,[14] **2a** and HCl solution were added to the resultant mixture. The reaction mixture was then treated at 45 °C. A similar yield of **3a** was observed in the reaction of phenylacetylene (**1a**) (Table 3, entry 1). The reactions of arylacetylenes **1a**–**c**, **1m**, and **1o** bearing an electron-donating group at the 4- or 3-position of the benzene ring produced the desired products in good yields (entries 1–3, 6, and 7). Moreover, relatively high yields were also observed in the reactions of arylacetylenes **1e** and **1k** bearing an electron-withdrawing group on the benzene ring. The desired products **3e** and **3k** were isolated in 81 and 57% yield, respectively (entries 4 and 5). This appreciably simplifies the preparation of 1,2-dihalo-1,6-dienes.

Table 3. One-Pot Synthesis of (1*Z*)-1,2-Dihalo-1,6-dienes from Terminal Alkynes in Ionic Liquids[a,b]



entry	alkyne **1**	product **3**	yield (%)
1	**1a**, R = H	**3a**	80
2	**1b**, R = 4-Me	**3b**	88
3	**1c**, R = 3-Me	**3c**	83
4	**1e**, R = 4-F	**3e**	81
5	**1k**, R = 4-NO_2	**3k**	57
6	**1m**, R = 4-(4′- ethylcyclohexyl)	**3m**	71
7	**1o**, R = 2,6-dimethyl	**3o**	73

[a]Reaction conditions for the first step: alkyne (0.6 mmol), NBS (0.72 mmol), and $AgNO_3$ (5 mol %, 4.2 mg) in [Bmim]Cl (1.00 mL) under an atmosphere of air at room temperature for 4 h. [b]Reaction conditions for the second step: HCl (12 N, 0.35 mL), **2a** (0.5 mmol), and $PdCl_2$ (3 mol %) in a sealed tube at 45 °C.

More interestingly, the chloropalladation of alkynoates under similar reaction conditions could also initiate this domino-type reaction with various alkenes to give functionalized 1,6-diene products. Representative results are summarized in Table 4. Generally, aromatic alkynoates with either an electron-donating or electron-withdrawing group on the benzene ring were able to generate the corresponding products in good to excellent yields with high stereoselectivity (**5a**–**o**), which presumably originated from the selective *trans*-chloropalladation of alkynes. Various functional groups, including alkyl, fluoro, chloro, bromo, cyano, ester, and trifluoromethyl groups, were compatible with the reaction conditions. The electronic properties of the substituents on the aromatic alkynoates did not have a significant influence on the reaction efficiency. Notably, a vinyl group was tolerated under the standard reaction conditions, providing **5e** in 90% yield with high *Z* stereoselectivity. Substitution at the 4-position or 3-position of the aromatic ring had a slight impact (**5b**, **5c** and **5k**, **5l**). Especially, the substrate substituted with two electron-donating groups gave a good yield (**5h**). Interestingly, other alkynoates such as a methyl ester (**4p**) and a benzyl ester (**4q**) could be converted into the corresponding products **5p** and **5q** in excellent yields as well. Furthermore, besides the aryl alkynoates, alkyl alkynoates were also found to be suitable substrates under the standard conditions (**5r** and **5s**).

In addition, we were interested in extending the method to other alkynes to prepare a variety of highly functionalized 1,6-diene derivatives (Scheme 1). Remarkably, asymmetrical internal alkynes participated well in this reaction. For example, but-1-yn-1-ylbenzene (**6a**) reacted smoothly with **2a** to afford the 1,6-diene product (*Z*)-**7a** in 61% yield (eq 1). In contrast to other types of alkynes, symmetrical internal alkynes such as 1,2-diphenylethyne (**6b**) failed to react with **2a** to afford the desired products under the standard reaction conditions (eq 2). Moreover, according to the literature reports,[15] 1,2-diphenylethyne was relatively sluggish in the nucleopalladation of alkynes. Given our experimental results, we thought that steric hindrance plays a very important role in this reaction transformation. Nevertheless, aliphatic 1,4-dichlorobut-2-yne (**6c**) was employed successfully in the synthesis of the 1,6-diene product (*Z*)-**7b** in 78% yield with excellent stereoselectivity (eq 3).

Thus far, we have developed a highly efficient and stereoselective method for the synthesis of chlorinated (1*E*)- and (1*Z*)-1,6-diene derivatives. After the effects of alkynes had been examined thoroughly, we decided to employ a series of long-chain 1,*n*-enols **2** in this transformation. As such, hex-5-en-1-ol (**2b**), hept-6-en-1-ol (**2c**), oct-7-en-1-ol (**2d**), dec-10-en-1-ol (**2e**), and undec-11-en-1-ol (**2f**) were allowed to react under the optimal conditions, and good to excellent yields of the desired products were obtained (Table 5, **8a**–**e**).

To further indicate the universality of this reaction, the scope of the reaction was expanded to other types of long-chain 1,*n*-enols (Scheme 2). Gratifyingly, this method was successfully applied to pent-4-en-2-ol (**2g**) and hept-6-en-3-ol (**2h**), and these substrates were smoothly converted to the desired products in 88% and 82% yield, respectively (eqs 4 and 5). The regioselectivity was elucidated by GC and NMR analysis.

To prove the practicality of the present method in the synthesis of halogenated 1,6-dienes, a gram-scale synthesis of **3a** was performed, and the result is shown in Scheme 3. When 1.8 g of **1a** was utilized, 2.27 g of product **3a** (80% yield) was obtained.

To demonstrate the synthetic utility of this protocol, we further examined the resulting products in transition-metal-catalyzed cross-coupling reactions. For instance, we studied the Suzuki–Miyaura coupling[16] of halogenated 1,6-diene com-

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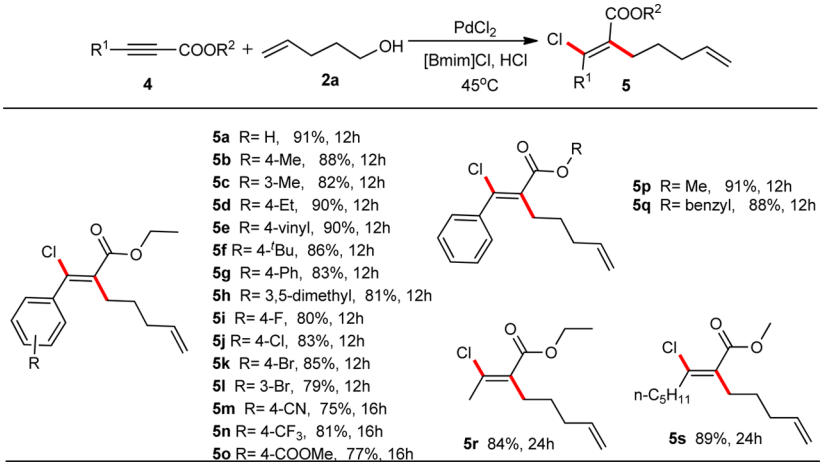
Table 4. Pd(II)-Catalyzed Coupling Reaction of Alkynoates with 2a in [Bmim]Cl[a]



[a]Reaction conditions: **4** (0.5 mmol), **2a** (0.6 mmol), $PdCl_2$ (3 mol %), [Bmim]Cl (0.5 mL), and HCl (0.35 mL) under an atmosphere of air at 45 °C. Reactions were monitored for completion by TLC.

Scheme 1. Pd(II)-Catalyzed Coupling Reaction of Alkynes with 2a in [Bmim]Cl

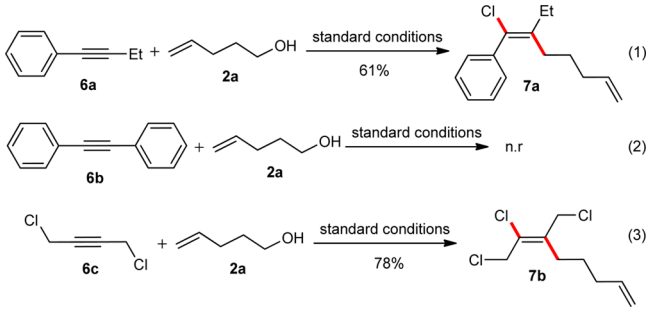
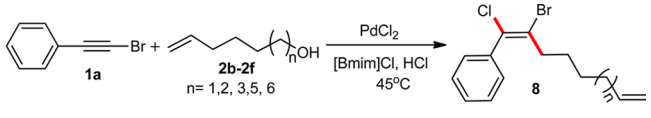
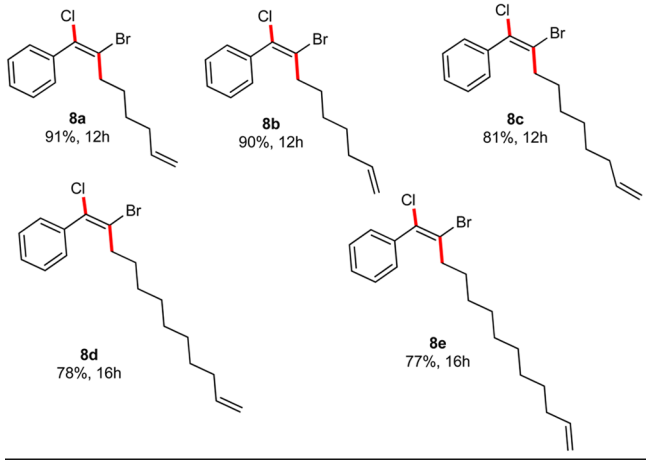


Table 5. Pd(II)-Catalyzed Coupling Reaction of 1a with Long-Chain Enols 2 in [Bmim]Cl[a]

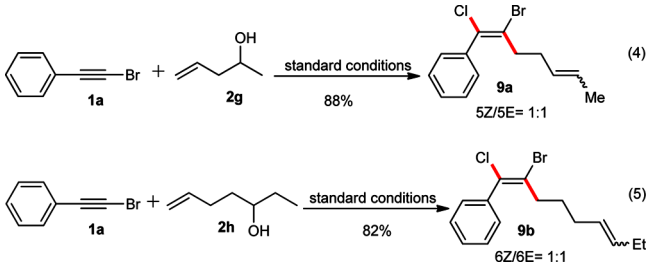




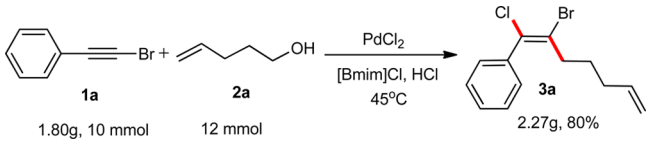
[a]Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), $PdCl_2$ (3 mol %), [Bmim]Cl (0.5 mL), and HCl (0.35 mL) under an atmosphere of air at 45 °C. Reactions were monitored for completion by TLC.

pounds with phenylboronic acid derivatives. Treatment of (*Z*)-ethyl 2-(chloro(phenyl)methylene)hept-6-enoate (**5a**) with (4-

Scheme 2. Pd(II)-Catalyzed Coupling Reaction of Enols with 1a in [Bmim]Cl



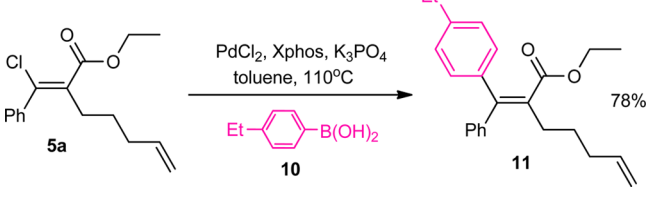
Scheme 3. Gram-Scale Synthesis of 3a[a]



[a]Reaction conditions: **1a** (10 mmol, 1.80 g), **2a** (12 mmol, 1.03 g), $PdCl_2$ (5 mol %, 52.80 mg), [Bmim]Cl (5 mL), and HCl (3.5 mL) under an atmosphere of air at 45 °C for 18 h.

ethylphenyl)boronic acid (**10**) under the standard conditions (0.25 mmol of **3s**, 3.0 equiv of **10**, 5 mol % $PdCl_2$, 10 mol % Xphos, 3.0 equiv of K_3PO_4, and 0.5 mL of toluene at 110 °C for 10 h) afforded a high yield of the target product **11** (Scheme 4). In addition, the resulting 1-chloro-1,6-dienes and 1,2-dihalo-1,6-dienes could serve as useful intermediates for the rapid synthesis of stereodefined tetrasubstituted alkenes, which represent another class of challenging targets in organic synthesis.

Scheme 4. Pd-Catalyzed Suzuki–Miyaura Reaction of (*Z*)-5a



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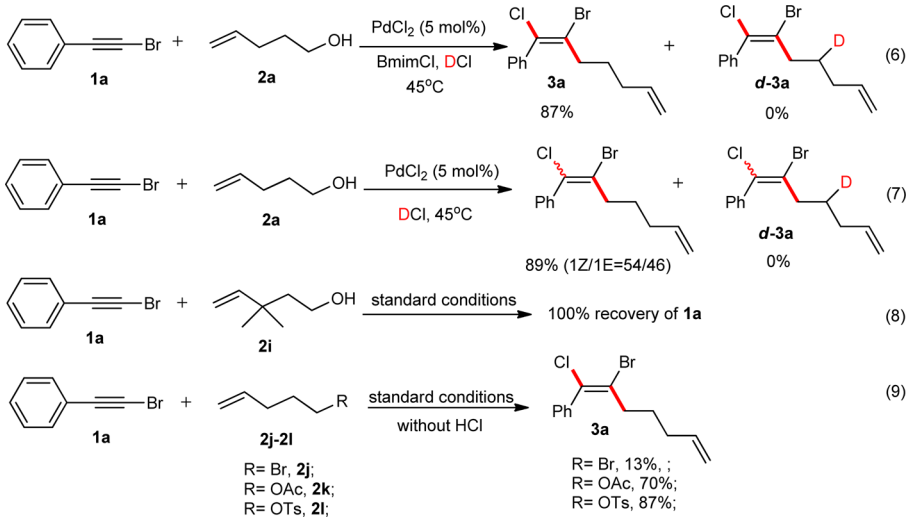
Scheme 5. Control Experiments



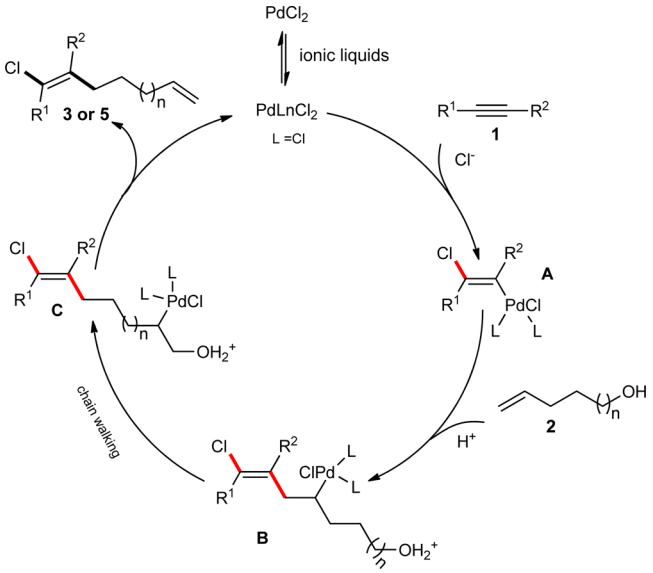
Several control experiments were also carried out to get more insights into this unique transformation (Scheme 5). Under the standard conditions, the reaction of **1a** with **2a** in DCl(aq) did not give the deuterated 1,6-diene product, but (*Z*)-**3a** was obtained in 87% yield (eq 6). Furthermore, when **1a** and **2a** were allowed to react in DCl(aq) without ionic liquid, similarly no deuterated 1,6-diene product could be detected while (*Z*)-**3a** was obtained with lower stereoselectivity (eq 7). The deuterated experiment results were identified by NMR analysis. All of these observations indicated that external proton is not involved in this chemical process. That is, direct protonolysis of the carbon−palladium bond does not occur in this case. Also, when 3,3-dimethylpent-4-en-1-ol (**2i**) was employed to react with **1a** under the standard conditions, no reaction occurred at all (eq 8), which indicates that the *β*-hydrogen of the carbon−palladium bond is important for this transformation. Finally, a control experiment employing alkenes with different leaving groups was carried out, and the desired product (*Z*)-**3a** was obtained under similar conditions (eq 9). These results suggest that alkenes with a better leaving group could also smoothly be converted to the corresponding products in the absence of HCl(aq).

On the basis of the above results and the literature,[3,17] a tentative mechanism involving chain walking is proposed in Scheme 6. The Pd complex is initially formed in situ in the IL,[10a,f] and vinylpalladium intermediate **A** is formed by *trans*-chloropalladation of the alkyne in a polar solvent system[12] in the presence of excess chloride ions.[18] Then, intermediate **A** can undergo alkene insertion to generate Pd−alkyl intermediate **B**. Subsequently, **B** undergoes rapid *β*-hydride elimination and reinsertion to change the position of the metal on the alkyl chain, producing intermediate **C**. Finally, *β*-heteroatom elimination affords the target product. Noticeably, although the chain-walking mechanism has been widely incorporated into many olefin polymerization processes,[19] its use for carbon−carbon bond formation in small organic molecules, especially for unactivated long-chain enols, has rarely been investigated.[20]

CONCLUSION

In summary, we have developed a practical, efficient, and versatile method for the synthesis of functionalized (1*E*)- and

Scheme 6. Proposed Mechanism



(1*Z*)-1,6-dienes and their analogues with high regio- and diastereoselectivities in moderate to excellent yields. The employment of ionic liquids under mild conditions makes this transformation green and practical. The key step in the present reaction is likely to involve a chain-walking process. Most importantly, this methodology provides a new tool for the construction of diversely substituted 1,6-diene derivatives from inexpensive starting materials.

EXPERIMENTAL SECTION

General Methods. Melting points were measured using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC−MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF254). Unless otherwise noted, purchased chemicals were used without further

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purification. The ionic liquids ([Bmim]Cl,[21] [C_2OHmim]Cl,[22] and [C_2O_2mim]Cl[23]) were synthesized using reported procedures. The bromoalkynes,[14] chloroalkynes,[24] and alkynoates[25] were prepared according to the literature.

General Procedure. Alkyne (0.5 mmol), **2** (0.6 mmol), $PdCl_2$ (3 mol %), ionic liquid (0.5 mL), and HCl (0.35 mL) were mixed in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred under an atmosphere of air at 45 °C. After the reaction was completed, 10 mL of ethyl acetate was added into the tube. The combined organic layers were washed with brine to neutral, dried over $MgSO_4$, and concentrated in vacuum. Purification of the residue by preparative TLC afforded the desired products.

*(Z)-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)benzene (**3a**).* Yield: 88% (124.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.34 (m, 5H), 5.76−5.66 (m, 1H), 4.98−4.92 (m, 2H), 2.50−2.46 (m, 2H), 1.99 (dd, J = 14.2, 7.0 Hz, 2H), 1.76−1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.5, 131.1, 128.9, 128.7, 128.6, 127.4, 115.1, 37.5, 32.5, 28.2; IR (KBr) ν_{max}/cm^{-1} 3077, 2965, 1642, 1607, 1451, 1285, 920, 794; MS (EI) m/z 115, 128, 141, 163, 169, 195, 205, 207, 249, 284; HRMS (EI) calcd for $C_{13}H_{14}ClBr$ 283.9967, found 283.9960.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-methylbenzene (**3b**).* Yield: 92% (137.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.16 (m, 4H), 5.74−5.64 (m, 1H), 4.95−4.89 (m, 2H), 2.45 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.96 (dd, J = 14.0, 7.0 Hz, 2H), 1.72−1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.8, 134.6, 131.2, 129.2, 128.5, 127.0, 115.0, 37.6, 32.5, 28.6, 21.3; IR (KBr) ν_{max}/cm^{-1} 3079, 2921, 1641, 1603, 1418, 920, 760; MS (EI) m/z 115, 129, 142, 155, 163, 183, 219, 221, 263, 298; HRMS (EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0119.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-3-methylbenzene (**3c**).* Yield: 90% (134.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.23 (m, 1H), 7.16−7.09 (m, 3H), 5.73−5.63 (m, 1H), 4.94−4.88 (m, 2H), 2.44 (t, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.96 (dd, J = 14.0, 7.0 Hz, 2H), 1.69 (dt, J = 14.8, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.7, 137.4, 131.2, 129.6, 129.2, 128.4, 127.1, 125.7, 115.1, 37.5, 32.5, 28.2, 21.4; IR (KBr) ν_{max}/cm^{-1} 3077, 2960, 1600, 1538, 1456, 918, 760; MS (EI) m/z 115, 129, 142, 155, 163, 183, 219, 221, 265, 298; HRMS (EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0117.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-ethylbenzene (**3d**).* Yield: 91% (141.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.18 (m, 4H), 5.74−5.64 (m, 1H), 4.95−4.88 (m, 2H), 2.66 (q, J = 7.6 Hz, 2H), 2.46 (m, 2H), 1.96 (dd, J = 14.0, 7.0 Hz, 2H), 1.72−1.65 (m, 2H), 1.27−1.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 137.8, 134.8, 131.3, 128.6, 128.0, 127.0, 115.0, 37.6, 32.5, 28.6, 28.2, 15.3; IR (KBr) ν_{max}/cm^{-1} 3077, 2960, 1635, 1600, 1520, 1456, 761; MS (EI) m/z 115, 128, 143, 155, 176, 197, 233, 235, 257, 279, 312; HRMS (EI) calcd for $C_{15}H_{18}ClBr$ 312.0280, found 312.0274.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-fluorobenzene (**3e**).* Yield: 84% (126.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.09−7.04 (m, 2H), 5.73−5.63 (m, 1H), 4.95−4.89 (m, 2H), 2.44−2.41 (m, 2H), 1.96 (dd, J = 14.0, 7.0 Hz, 2H), 1.72−1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (J = 248.1 Hz), 137.6, 133.5 (J = 3.5 Hz), 130.6 (J = 8.4 Hz), 130.0, 127.7, 115.7 (J = 21.7 Hz), 115.2, 37.5, 32.5, 28.1; IR (KBr) ν_{max}/cm^{-1} 3079, 2916, 1641, 1503, 1232, 922, 731; MS (EI) m/z 107, 109, 133, 146, 159, 181, 187, 213, 223, 225, 267, 302; HRMS (EI) calcd for $C_{13}H_{13}FClBr$ 301.9873, found 301.9868.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-chlorobenzene (**3f**).* Yield: 94% (149.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.26−7.24 (m, 2H), 5.73−5.63 (m, 1H), 4.96−4.90 (m, 2H), 2.44−2.41 (m, 2H), 1.96 (dd, J = 14.0, 7.0 Hz, 2H), 1.72−1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.9, 134.9, 130.0, 129.8, 128.9, 128.0, 115.3, 37.5, 32.5, 28.2; IR (KBr) ν_{max}/cm^{-1} 3081, 2920, 1642, 1487, 922, 748; MS (EI) m/z 113, 139, 152, 165, 191, 207, 229, 253, 281, 305, 307, 318; HRMS (EI) calcd for $C_{13}H_{13}Cl_2Br$ 317.9578, found 317.9570.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-3-chlorobenzene (**3g**).* Yield: 90% (143.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 3H), 7.21−7.19 (m, 1H), 5.73−5.63 (m, 1H), 4.96−4.90 (m, 2H), 2.46−2.42 (m, 2H), 1.97 (q, J = 7.2 Hz, 2H), 1.73−1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.5, 134.4, 129.8, 129.5, 129.1, 128.8, 128.4, 126.9, 115.3, 37.5, 32.4, 28.1; IR (KBr) ν_{max}/cm^{-1} 3079, 2930, 1600, 1520, 1456, 918, 760; MS (EI) m/z 75, 101, 125, 127, 149, 162, 168, 185, 203, 205, 241, 243, 285, 318; HRMS (EI) calcd for $C_{13}H_{13}Cl_2Br$ 317.9578, found 317.9573.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-2-chlorobenzene (**3h**).* Yield: 92% (146.2 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.42 (m, 1H), 7.34−7.27 (m, 3H), 5.70−5.60 (m, 1H), 4.93−4.86 (m, 2H), 2.37−2.22 (m, 2H), 1.95−1.90 (m, 2H), 1.74−1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.2, 133.2, 130.6, 130.4, 130.1, 129.2, 127.7, 127.1, 115.0, 37.4, 32.5, 27.5; IR (KBr) ν_{max}/cm^{-1} 3080, 2929, 1640, 1500, 1480, 920, 740; MS (EI) m/z 114, 127, 149, 162, 164, 197, 203, 205, 241, 318; HRMS (EI) calcd for $C_{13}H_{13}Cl_2Br$ 317.9578, found 317.9573.

*(Z)-1-Bromo-4-(2-bromo-1-chlorohepta-1,6-dien-1-yl)benzene (**3i**).* Yield: 93% (168.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.20−7.18 (m, 2H), 5.73−5.63 (m, 1H), 4.96−4.90 (m, 2H), 2.43 (t, J = 7.6 Hz, 2H), 1.96 (dd, J = 14.0, 7.2 Hz, 2H), 1.72−1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.4, 131.8, 130.3, 129.9, 128.0, 123.1, 115.3, 37.5, 32.4, 28.2; IR (KBr) ν_{max}/cm^{-1} 3080, 2921, 1643, 1480, 735; MS (EI) m/z 88, 115, 128, 149, 162, 193, 204, 206, 285, 287, 362; HRMS (EI) calcd for $C_{13}H_{13}ClBr_2$ 361.9073, found 361.9065.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-ethoxybenzene (**3j**).* Yield: 74% (121.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.22 (m, 2H), 6.88−6.84 (m, 2H), 5.74−5.64 (m, 1H), 4.96−4.89 (m, 2H), 4.05 (q, J = 7.2 Hz, 2H), 2.45 (t, J = 7.6 Hz, 2H), 1.96 (dd, J = 14.4, 7.2 Hz, 2H), 1.68 (dt, J = 14.8, 7.6 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.8, 131.2, 130.0, 128.1, 126.8, 115.1, 114.4, 63.6, 37.6, 28.2, 14.8; IR (KBr) ν_{max}/cm^{-1} 3079, 2921, 1640, 1500, 1475, 916, 752; MS (EI) m/z 77, 102, 115, 131, 166, 185, 194, 213, 249, 277, 328; HRMS (EI) calcd for $C_{15}H_{18}OClBr$ 328.0230, found 328.0225.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-nitrobenzene (**3k**).* Yield: 63% (103.6 mg) as a yellow solid; mp 116.3−117.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26−8.18 (m, 2H), 7.60−7.51 (m, 2H), 5.72−5.62 (m, 1H), 4.93−4.90 (m, 2H), 2.45 (t, J = 8.0 Hz, 2H), 1.97 (q, J = 7.2 Hz, 2H), 1.75−1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.3, 132.8, 129.8, 128.5, 123.9, 123.6, 115.5, 37.5, 32.4, 28.1; IR (KBr) ν_{max}/cm^{-1} 3078, 2980, 1636, 1522, 1490, 1435, 924, 711; MS (EI) m/z 102, 115, 128, 149, 162, 169, 214, 232, 249, 251, 289, 314, 329; HRMS (EI) calcd for $C_{13}H_{13}BrClNO_2$ 328.9818, found 328.9814.

*(Z)-4-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4′-propyl-1,1′-biphenyl (**3l**).* Yield: 78% (156.8 mg) as a yellow solid; mp 160.5−161.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.27−7.21 (m, 2H), 5.74−5.64 (m, 1H), 4.96−4.88 (m, 2H), 2.63 (t, J = 8.0 Hz, 2H), 2.52−2.48 (m, 2H), 1.98 (dd, J = 14.4, 7.2 Hz, 2H), 1.75−1.63 (m, 4H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.7, 137.7, 137.5, 136.0, 131.0, 129.1, 129.0, 127.4, 127.0, 126.9, 115.1, 37.7, 37.6, 32.5, 28.3, 24.5, 13.9; IR (KBr) ν_{max}/cm^{-1} 3078, 2926, 1640, 1504, 1416, 920, 752; MS (EI) m/z 101, 115, 133, 152, 165, 189, 202, 217, 245, 259, 287, 288, 323, 325, 369, 389, 402; HRMS (EI) calcd for $C_{22}H_{24}ClBr$ 402.0750, found 402.0746.

*(Z)-1-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-4-(4-ethylcyclohexyl)benzene (**3m**).* Yield: 85% (167.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.18 (m, 4H), 5.73−5.63 (m, 1H), 4.93−4.87 (m, 2H), 1.98−1.88 (m, 6H), 1.72−1.65 (m, 2H), 1.49−1.39 (m, 2H), 1.31−1.18 (m, 4H), 1.07−1.00 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 137.8, 134.8, 131.3, 128.6, 127.0, 115.0, 44.4, 39.1, 37.5, 34.2, 33.1, 32.5, 30.0, 28.2, 11.5; IR (KBr) ν_{max}/cm^{-1} 3080, 2921, 2851, 1640, 1450, 920, 750; MS (EI) m/z 69, 91, 111, 115, 141, 153, 169, 203, 205, 235, 250, 285, 287,

315, 359, 394; HRMS (EI) calcd for $C_{21}H_{28}ClBr$ 394.1063, found 394.1059.

(Z)-6-Bromo-7-chloro-8,8-dimethylnona-1,6-diene (**3n**). Yield: 84% (110.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85−5.75 (m, 1H), 5.07−5.00 (m, 2H), 2.77−2.73 (m, 2H), 2.10 (q, J = 7.2 Hz, 2H), 1.76 (dt, J = 15.2, 7.6 Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 137.8, 126.7, 115.3, 40.5, 38.8, 33.1, 31.4, 28.7; IR (KBr) ν_{max}/cm^{-1} 3081, 2923, 1500, 745; MS (EI) m/z 67, 79, 93, 107, 108, 121, 149, 169, 187, 209, 229, 251, 264; HRMS (EI) calcd for $C_{11}H_{18}ClBr$ 264.0280, found 264.0276.

(Z)-2-(2-Bromo-1-chlorohepta-1,6-dien-1-yl)-1,3-dimethylbenzene (**3o**). Yield: 84% (131.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−6.98 (m, 3H), 5.72−5.62 (m, 1H), 4.94−4.87 (m, 2H), 2.32 (s, 3H), 2.30−2.27 (m, 2H), 2.26 (s, 3H), 1.91 (dd, J = 14.4, 7.2 Hz, 2H), 1.65−1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.8, 136.1, 133.9, 131.3, 130.1, 128.9, 127.2, 126.8, 114.9, 37.3, 32.5, 27.8, 21.2, 19.2; IR (KBr) ν_{max}/cm^{-1} 3079, 2923, 1640, 1446, 920, 756; MS (EI) m/z 115, 128, 141, 162, 169, 177, 197, 198, 233, 235, 245, 285, 312; HRMS (EI) calcd for $C_{15}H_{18}ClBr$ 312.0280, found 312.0272.

(Z)-1-(1,2-Dichlorohepta-1,6-dien-1-yl)-4-ethylbenzene (**3p**). Yield: 75% (100.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.19 (m, 5H), 5.75−5.65 (m, 1H), 4.95−4.89 (m, 2H), 2.67 (q, J = 7.6 Hz, 2H), 2.40 (t, J = 7.6 Hz, 2H), 1.97 (dd, J = 14.4, 7.2 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 137.8, 134.6, 133.6, 128.8, 128.5, 128.0, 115.0, 35.5, 32.6, 28.6, 27.2, 15.3; IR (KBr) ν_{max}/cm^{-1} 3079, 2960, 1600, 1458, 760; MS (EI) m/z 115, 128, 141, 149, 169, 177, 197, 199, 203, 205, 233, 239, 241, 243, 268; HRMS (EI) calcd for $C_{15}H_{18}Cl_2$ 268.0786, found 268.0783.

(Z)-1-Bromo-4-(1,2-dichlorohepta-1,6-dien-1-yl)benzene (**3q**). Yield: 73% (116.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.50 (m, 2H), 7.21−7.18 (m, 2H), 5.74−5.64 (m, 1H), 4.96−4.91 (m, 2H), 2.36 (t, J = 7.6 Hz, 2H), 1.97 (dd, J = 14.4, 7.2 Hz, 2H), 1.72−1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.1, 134.7, 131.8, 130.5, 128.1, 123.2, 115.3, 35.5, 32.6, 27.2; IR (KBr) ν_{max}/cm^{-1} 3079, 2980, 1636, 1490, 1430, 738; MS (EI) m/z 114, 127, 149, 162, 184, 197, 218, 241, 265, 285, 318; HRMS (EI) calcd for $C_{13}H_{13}BrCl_2$ 317.9578, found 317.9572.

(Z)-4-(1,2-Dichlorohepta-1,6-dien-1-yl)-4′-propyl-1,1′-biphenyl (**3r**). Yield: 67% (120.0 mg) as a yellow solid; mp 158.1−159.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.58 (m, 2H), 7.53−7.50 (m, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.26 (m, d, J = 9.2 Hz, 2H), 5.75−5.65 (m, 1H), 4.96−4.89 (m, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.44 (t, J = 7.6 Hz, 2H), 1.99 (dd, J = 14.4, 7.2 Hz, 2H), 1.76−1.64 (m, 4H), 0.98 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.7, 137.7, 137.5, 135.8, 134.0, 129.3, 129.0, 128.2, 127.0, 126.9, 115.1, 37.7, 35.6, 32.6, 31.3, 24.5, 13.9; IR (KBr) ν_{max}/cm^{-1} 3080, 2927, 1640, 1501, 921, 756; MS (EI) m/z 101, 115, 133, 152, 165, 178, 189, 202, 204, 227, 245, 287, 323, 325, 358; HRMS (EI) calcd for $C_{22}H_{24}Cl_2$ 358.1225, found 358.1248.

(Z)-Ethyl 2-(Chloro(phenyl)methylene)hept-6-enoate (**5a**). Yield: 91% (126.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.34 (m, 5H), 5.71−5.61 (m, 1H), 4.93−4.88 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.29 (t, J = 8.0 Hz, 2H), 1.97 (dd, J = 14.4, 7.2 Hz, 2H), 1.54−1.47 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 137.7, 137.3, 133.5, 131.4, 129.0, 128.5, 128.4, 115.0, 61.3, 33.0, 31.3, 27.5, 14.2; IR (KBr) ν_{max}/cm^{-1} 3078, 2981, 1725, 1638, 1480, 1440, 1287, 758; MS (EI) m/z 63, 77, 91, 105, 115, 128, 141, 163, 169, 177, 197, 204, 233, 243, 249, 278; HRMS (ESI) calcd for $C_{16}H_{19}ClNaO_2^+$ 301.0966, found 301.0972.

(Z)-Ethyl 2-(Chloro(p-tolyl)methylene)hept-6-enoate (**5b**). Yield: 88% (128.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.24 (m, 2H), 7.19−7.17 (m, 2H), 5.73−5.63 (m, 1H), 4.95−4.89 (m, 2H), 4.36−4.28 (m, 2H), 2.38 (s, 3H), 2.32−2.28 (m, 2H), 1.97 (dd, J = 14.4, 7.2 Hz, 2H), 1.50 (dt, J = 15.2, 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 139.1, 137.8, 134.4, 133.0, 129.4, 129.1, 128.4, 115.0, 61.2, 33.1, 31.4, 27.6, 21.3, 14.2; IR (KBr) ν_{max}/cm^{-1} 3075, 2925, 1724, 1645, 1538, 1455, 754; MS (EI) m/z 91, 105, 115, 129, 139, 141, 163, 183, 199, 211, 257, 277, 292; HRMS (ESI) calcd for $C_{17}H_{21}ClNaO_2^+$ 315.1122, found 315.1127.

(Z)-Ethyl 2-(Chloro(m-tolyl)methylene)hept-6-enoate (**5c**). Yield: 82% (119.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 1H), 7.18−7.14 (m, 3H), 5.72−5.62 (m, 1H), 4.94−4.88 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 2.31−2.27 (m, 2H), 1.97 (q, J = 7.2 Hz, 2H), 1.54−1.47 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 138.2, 137.8, 137.2, 133.3, 131.6, 129.1, 128.3, 125.5, 115.0, 61.2, 33.0, 31.3, 27.5, 21.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3076, 2961, 1723, 1643, 1495, 1440, 756; MS (EI) m/z 105, 115, 129, 139, 163, 191, 211, 247, 277, 292; HRMS (ESI) calcd for $C_{17}H_{21}ClNaO_2^+$ 315.1122, found 315.1123.

(Z)-Ethyl 2-(Chloro(4-ethylphenyl)methylene)hept-6-enoate (**5d**). Yield: 90% (137.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.73−5.63 (m, 1H), 4.94−4.88 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.67 (q, J = 7.6 Hz, 2H), 2.37−2.26 (m, 2H), 1.98 (dd, J = 14.4, 7.2 Hz, 2H), 1.51 (dt, J = 15.2, 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.3, 137.8, 134.6, 133.1, 131.6, 128.5, 127.9, 115.0, 61.2, 33.0, 31.3, 28.7, 27.5, 15.3, 14.2; IR (KBr) ν_{max}/cm^{-1} 3078, 2958, 1726, 1638, 1515, 1280, 755; MS (EI) m/z 115, 128, 153, 177, 205, 225, 279, 306; HRMS (ESI) calcd for $C_{18}H_{23}ClNaO_2^+$ 329.1279, found 329.1284.

(Z)-Ethyl 2-(Chloro(4-vinylphenyl)methylene)hept-6-enoate (**5e**). Yield: 90% (136.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.72 (dd, J = 17.6, 10.8 Hz, 1H), 5.80 (d, J = 17.6 Hz, 1H), 5.73−5.63 (m, 1H), 4.95−4.89 (m, 2H), 4.34 (q, J = 7.2 Hz, 1H), 2.33−2.29 (m, 2H), 1.98 (dd, J = 14.4, 7.2 Hz, 2H), 1.51 (dt, J = 15.2, 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 138.3, 137.7, 136.5, 136.0, 133.5, 131.2, 128.8, 126.2, 115.2, 115.1, 61.3, 33.0, 31.4, 27.5, 14.2; IR (KBr) ν_{max}/cm^{-1} 3077, 2981, 1725, 1643, 1455, 1268, 754; MS (EI) m/z 115, 131, 153, 175, 195, 203, 230, 232, 269, 304; HRMS (ESI) calcd for $C_{18}H_{22}ClO_2^+$ 305.1303, found 305.1307.

(Z)-Ethyl 2-((4-(tert-Butyl)phenyl)chloromethylene)hept-6-enoate (**5f**). Yield: 86% (143.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.72−5.62 (m, 1H), 4.93−4.87 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.35−2.28 (m, 2H), 1.98 (q, J = 7.2 Hz, 2H), 1.50 (dd, J = 15.2, 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 152.2, 137.8, 134.2, 133.1, 131.6, 128.2, 125.3, 114.9, 61.2, 34.7, 33.0, 31.3, 31.2, 27.5, 14.2; IR (KBr) ν_{max}/cm^{-1} 3075, 2961, 1726, 1514, 1480, 1440, 1259, 755; MS (EI) m/z 115, 141, 169, 181, 197, 209, 225, 245, 277, 299, 319, 321, 334; HRMS (ESI) calcd for $C_{20}H_{27}ClNaO_2^+$ 357.1592, found 357.1592.

(Z)-Ethyl 2-([1,1′-Biphenyl]-4-ylchloromethylene)hept-6-enoate (**5g**). Yield: 83% (146.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.57 (m, 4H), 7.47−7.37 (m, 5H), 5.74−5.64 (m, 1H), 4.96−4.89 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.38−2.33 (m, 2H), 2.00 (dd, J = 14.2, 7.2 Hz, 2H), 1.59−1.50 (m, 2H), 1.39 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 141.9, 140.2, 137.7, 136.1, 133.6, 131.2, 129.0, 128.9, 127.8, 127.1, 127.0, 115.1, 61.3, 33.0, 31.4, 27.6, 14.2; IR (KBr) ν_{max}/cm^{-1} 3072, 2928, 1725, 1642, 1484, 1453, 758; MS (EI) m/z 115, 139, 165, 178, 191, 203, 207, 225, 245, 253, 280, 291, 319, 354; HRMS (ESI) calcd for $C_{22}H_{23}ClNaO_2^+$ 377.1279, found 377.1279.

(Z)-Ethyl 2-(Chloro(3,5-dimethylphenyl)methylene)hept-6-enoate (**5h**). Yield: 81% (123.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.97 (s, 2H), 5.73−5.63 (m, 1H), 4.95−4.86 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 2.33 (s, 6H), 2.29 (t, J = 8.0 Hz, 2H), 1.98 (q, J = 7.2 Hz, 2H), 1.50 (dd, J = 15.2, 7.6 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 138.0, 137.8, 137.1, 133.1, 130.7, 126.2, 114.9, 61.2, 33.0, 29.7, 27.5, 21.2, 14.2; IR (KBr) ν_{max}/cm^{-1} 3075, 2925, 1644, 1563, 1480, 1455, 754; MS (EI) m/z 115, 128, 143, 155, 177, 197, 207, 225, 271, 306; HRMS (ESI) calcd for $C_{18}H_{23}ClNaO_2^+$ 329.1279, found 329.1280.

(Z)-Ethyl 2-(Chloro(4-fluorophenyl)methylene)hept-6-enoate (**5i**). Yield: 80% (118.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.33 (m, 2H), 7.10−7.06 (m, 2H), 5.72−5.62 (m, 1H), 4.95−4.89 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 2.29−2.26 (m, 2H), 1.97 (q, J

= 7.2 Hz, 2H), 1.54−1.46 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 162.8 (*J* = 248.0 Hz), 137.6, 133.3 (*J* = 3.5 Hz), 130.5 (*J* = 8.3 Hz), 130.3, 115.5 (*J* = 21.8 Hz), 115.1, 61.3, 33.0, 31.3, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3076, 2928, 1726, 1643, 1506, 1446, 1267, 755; MS (EI) *m*/*z* 107, 109, 123, 133, 147, 159, 177, 187, 209, 222, 251, 261, 296; HRMS (ESI) calcd for $C_{16}H_{18}FClNaO_2^+$ 319.0872, found 319.0875.

(Z)-Ethyl 2-(Chloro(4-chlorophenyl)methylene)hept-6-enoate (**5j**). Yield: 83% (129.5 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.72−5.62 (m, 1H), 4.95−4.90 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.29−2.26 (m, 2H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.54−1.46 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 137.6, 135.6, 135.1, 134.1, 130.1, 129.9, 128.7, 115.2, 61.4, 32.9, 31.3, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3087, 2959, 1726, 1645, 1516, 1268, 754; MS (EI) *m*/*z* 125, 139, 151, 168, 183, 203, 205, 231, 277, 283, 312; HRMS (ESI) calcd for $C_{16}H_{18}Cl_2NaO_2^+$ 335.0576, found 335.0577.

(Z)-Ethyl 2-((4-Bromophenyl)chloromethylene)hept-6-enoate (**5k**). Yield: 85% (151.3 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.72−5.62 (m, 1H), 4.95−4.90 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.29−2.25 (m, 2H), 1.97 (dd, *J* = 14.2, 7.2 Hz, 2H), 1.50 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 137.5, 136.1, 134.1, 131.7, 130.2, 130.1, 123.3, 115.2, 61.4, 33.0, 31.3, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3075, 2927, 1726, 1642, 1482, 1452, 1267, 753; MS (EI) *m*/*z* 115, 149, 153, 168, 195, 207, 227, 247, 275, 293, 323, 356; HRMS (ESI) calcd for $C_{16}H_{18}BrClNaO_2^+$ 379.0071, found 379.0074.

(Z)-Ethyl 2-((3-Bromophenyl)chloromethylene)hept-6-enoate (**5l**). Yield: 79% (140.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 2H), 5.72−5.62 (m, 1H), 4.95−4.90 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.30−2.26 (m, 2H), 1.98 (q, *J* = 7.2 Hz, 2H), 1.51 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 139.1, 137.5, 134.4, 132.1, 131.5, 130.0, 129.5, 127.2, 122.4, 115.2, 61.4, 32.9, 31.2, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3074, 2981, 1727, 1644, 1560, 1465, 754; MS (EI) *m*/*z* 115, 129, 141, 170, 185, 213, 241, 283, 315, 356; HRMS (ESI) calcd for $C_{16}H_{18}BrClNaO_2^+$ 379.0071, found 379.0060.

(Z)-Ethyl 2-(Chloro(4-cyanophenyl)methylene)hept-6-enoate (**5m**). Yield: 75% (113.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.70−5.60 (m, 1H), 4.94−4.90 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.28−2.24 (m, 2H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.50 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 141.6, 137.3, 135.2, 132.3, 129.4, 128.9, 118.1, 115.4, 112.9, 61.6, 32.9, 31.2, 27.3, 14.2; IR (KBr) ν_{max}/cm^{-1} 3076, 2925, 1725, 1644, 1500, 1456, 755; MS (EI) *m*/*z* 113, 127, 140, 154, 166, 194, 216, 249, 268, 294, 303; HRMS (ESI) calcd for $C_{17}H_{18}ClNNaO_2^+$ 326.0918, found 326.0920.

(Z)-Ethyl 2-(Chloro(4-(trifluoromethyl)phenyl)methylene)hept-6-enoate (**5n**). Yield: 81% (140.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.71−5.61 (m, 1H), 4.94−4.89 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.29−2.25 (m, 2H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.55−1.47 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 140.7, 137.5, 134.7, 133.1, 131.2, 129.5, 129.0, 125.6, 125.5, 115.2, 61.5, 32.9, 31.2, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3076, 2929, 2362, 1727, 1644, 1515, 1455, 755; MS (EI) *m*/*z* 115, 133, 153, 183, 197, 209, 237, 259, 283, 311, 346; HRMS (ESI) calcd for $C_{17}H_{18}ClF_3NaO_2^+$ 369.0840, found 369.0838.

(Z)-Methyl 4-(1-Chloro-2-(ethoxycarbonyl)hepta-1,6-dien-1-yl)-benzoate (**5o**). Yield: 77% (129.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.70−5.60 (m, 1H), 4.94−4.88 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 2.30−2.26 (m, 2H), 1.96 (q, *J* = 7.2 Hz, 2H), 1.54−1.47 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.4, 141.5, 137.5, 134.4, 130.6, 130.1, 129.7, 128.6, 115.2, 61.4, 52.3, 32.9, 31.3, 27.4, 14.2; IR (KBr) ν_{max}/cm^{-1} 3079, 2926, 1725, 1642, 1437, 756; MS (EI) *m*/*z* 115, 128, 149, 153, 195, 207, 227, 249, 273, 301, 336; HRMS (ESI) calcd for $C_{18}H_{21}ClNaO_4^+$ 359.1021, found 359.1025.

(Z)-Methyl 2-(Chloro(phenyl)methylene)hept-6-enoate (**5p**). Yield: 91% (120.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (m, 5H), 5.71−5.61 (m, 1H), 4.94−4.88 (m, 2H), 3.87 (s, 3H), 2.31−2.27 (m, 2H), 1.96 (q, *J* = 7.2 Hz, 2H), 1.53−1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 137.7, 137.2, 133.2, 131.9, 129.1, 128.5, 115.1, 52.2, 33.0, 31.3, 27.6; IR (KBr) ν_{max}/cm^{-1} 3075, 2926, 1729, 1644, 1516, 756; MS (EI) *m*/*z* 105, 115, 128, 169, 177, 197, 221, 229, 264; HRMS (ESI) calcd for $C_{15}H_{17}ClNaO_2^+$ 287.0809, found 287.0806.

(Z)-Benzyl 2-(Chloro(phenyl)methylene)hept-6-enoate (**5q**). Yield: 88% (149.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.40−7.35 (m, 8H), 5.65−5.55 (m, 1H), 5.31 (s, 2H), 4.89−4.85 (m, 2H), 2.31−2.27 (m, 2H), 1.92 (q, *J* = 7.2 Hz, 2H), 1.49−1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 137.6, 137.3, 135.5, 133.1, 132.1, 129.1, 128.6, 128.5, 128.4, 128.4, 115.0, 67.1, 33.0 31.3, 27.5; IR (KBr) ν_{max}/cm^{-1} 3069, 2924, 1725, 1643, 1549, 1518, 755; MS (EI) *m*/*z* 115, 128, 167, 169, 205, 207, 260, 306, 340; HRMS (ESI) calcd for $C_{21}H_{21}ClNaO_2^+$ 363.1122, found 363.1123.

(Z)-Ethyl 2-(1-Chloroethylidene)hept-6-enoate (**5r**). Yield: 84% (90.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83−5.73 (m, 1H), 5.04−4.97 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.33 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.16 (s, 3H), 2.08 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.58−1.50 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 137.9, 131.2, 131.0, 115.2, 61.0, 33.0, 30.3, 27.3, 22.7, 14.1; IR (KBr) ν_{max}/cm^{-1} 3083, 2930, 1644, 1515, 1436, 755; MS (EI) *m*/*z* 55, 67, 79, 91, 97, 107, 129, 153, 171, 181, 207, 216; HRMS (ESI) calcd for $C_{11}H_{17}ClNaO_2^+$ 239.0809, found 239.0809.

(Z)-Methyl 3-Chloro-2-(pent-4-en-1-yl)oct-2-enoate (**5s**). Yield: 89% (114.8 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82−5.72 (m, 1H), 5.04−4.97 (m, 2H), 3.78 (s, 3H), 2.41−2.37 (m, 2H), 2.34−2.31 (m, 2H), 2.07 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.62−1.50 (m, 4H), 1.35−1.29 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 137.8, 136.0, 130.9, 115.2, 51.9, 35.2, 33.0, 30.1, 27.6, 27.1, 22.4, 13.8; IR (KBr) ν_{max}/cm^{-1} 3077, 2930, 1645, 1547, 1454, 753; MS (EI) *m*/*z* 55, 79, 91, 107, 121, 125, 149, 163, 173, 191, 223, 258; HRMS (ESI) calcd for $C_{14}H_{23}ClNaO_2^+$ 281.1279, found 281.1283.

(E)-(1-Chloro-2-ethylhepta-1,6-dien-1-yl)benzene (**7a**). Yield: 61% (71.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 3H), 7.18−7.16 (m, 2H), 5.78−5.68 (m, 1H), 4.98−4.92 (m, 2H), 2.54 (q, *J* = 7.2 Hz, 2H), 2.42 (q, *J* = 8.0 Hz, 2H), 2.02 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.39 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.2, 136.5, 132.6, 128.5, 128.0, 126.8, 114.8, 34.2, 33.3, 28.9, 27.4, 13.0; IR (KBr) ν_{max}/cm^{-1} 3079, 2968, 1538, 1457, 754; MS (EI) *m*/*z* 65, 77, 91, 103, 115, 128, 157, 169, 192, 207, 234; HRMS (EI) calcd for $C_{15}H_{19}Cl$ 234.1175, found 234.1173.

(Z)-7,8-Dichloro-6-(chloromethyl)octa-1,6-diene (**7b**). Yield: 78% (88.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85−5.75 (m, 1H), 5.08−5.01 (m, 2H), 4.30 (s, 2H), 4.26 (s, 2H), 2.36 (t, *J* = 8.0 Hz, 2H), 2.11 (q, *J* = 7.2 Hz, 2H), 1.62 (dt, *J* = 10.4, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.5, 129.8, 115.6, 44.9, 43.8, 33.3, 30.5, 27.4; IR (KBr) ν_{max}/cm^{-1} 3086, 2926, 1523, 1271, 720; MS (EI) *m*/*z* 77, 91, 105, 113, 126, 153, 177, 226; HRMS (EI) calcd for $C_9H_{13}Cl_3$ 226.0083, found 226.0075.

(Z)-(2-Bromo-1-chloroocta-1,7-dien-1-yl)benzene (**8a**). Yield: 91% (135.6 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.30 (m, 5H), 5.78−5.68 (m, 1H), 4.95−4.91 (m, 2H), 2.44 (t, *J* = 7.6 Hz, 2H), 1.95 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.64−1.56 (m, 2H), 1.29 (dt, *J* = 14.4, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 137.6, 130.9, 128.9, 128.7, 128.6, 127.6, 114.7, 37.8, 33.2, 28.3, 27.6; IR (KBr) ν_{max}/cm^{-1} 3078, 2983, 1600, 1455, 1420, 720; MS (EI) *m*/*z* 102, 129, 131, 174, 183, 211, 254, 298; HRMS (EI) calcd for $C_{14}H_{16}ClBr$ 298.0124, found 298.0118.

(Z)-(2-Bromo-1-chlorononа-1,8-dien-1-yl)benzene (**8b**). Yield: 90% (140.4 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.35 (m, 3H), 7.32−7.30 (m, 2H), 5.80−5.70 (m, 1H), 4.98−4.91 (m, 2H), 2.42 (t, *J* = 8.0 Hz, 2H), 1.99 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.59 (dt, *J* = 14.8, 7.6 Hz, 2H), 1.32−1.25 (m, 2H), 1.24−1.16 (m,

2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.6, 130.8, 128.7, 128.5, 127.7, 114.4, 37.9, 33.6, 28.7, 28.4, 27.9; IR (KBr) ν_{max}/cm^{-1} 3076, 2981, 1632, 1445, 1424, 736; MS (EI) *m*/*z* 115, 137, 144, 146, 165, 172, 174, 200, 211, 246, 281, 312; HRMS (EI) calcd for $C_{15}H_{18}ClBr$ 312.0280, found 312.0276.

(Z)-(2-Bromo-1-chlorodeca-1,9-dien-1-yl)benzene (**8c**). Yield: 81% (132.0 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.34 (m, 3H), 7.32−7.30 (m, 2H), 5.82−5.72 (m, 1H), 4.99−4.91 (m, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 1.98 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.59−1.56 (m, 2H), 1.33−1.30 (m, 2H), 1.21−1.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.6, 130.7, 128.8, 128.7, 128.5, 127.8, 114.3, 37.9, 33.7, 28.8, 28.7, 28.6, 28.3; IR (KBr) ν_{max}/cm^{-1} 3074, 2980, 1628, 1430, 726; MS (EI) *m*/*z* 95, 115, 129, 151, 163, 183, 195, 211, 218, 241, 243, 245, 326; HRMS (EI) calcd for $C_{16}H_{20}ClBr$ 326.0437, found 326.0430.

(Z)-(2-Bromo-1-chlorododeca-1,11-dien-1-yl)benzene (**8d**). Yield: 78% (138.1 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 3H), 7.33−7.30 (m, 2H), 5.85−5.75 (m, 1H), 5.00−4.91 (m, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 2.02 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.59−1.55 (m, 2H), 1.36−1.31 (m, 2H), 1.26−1.18 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.6, 130.7, 128.8, 128.7, 128.5, 127.8, 114.1, 37.9, 33.8, 29.3, 29.1, 29.0, 28.9, 28.9, 28.4; IR (KBr) ν_{max}/cm^{-1} 3078, 2980, 1633, 1490, 1445, 728; MS (EI) *m*/*z* 115, 129, 157, 183, 200, 202, 237, 275, 317, 354; HRMS (EI) calcd for $C_{18}H_{24}ClBr$ 354.0750, found 354.0746.

(Z)-(2-Bromo-1-chlorotrideca-1,12-dien-1-yl)benzene (**8e**). Yield: 77% (141.7 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.35 (m, 3H), 7.32−7.30 (m, 2H), 5.86−5.76 (m, 1H), 5.01−4.91 (m, 2H), 2.42 (t, *J* = 7.6 Hz, 2H), 2.03 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.59−1.55 (m, 2H), 1.37−1.32 (m, 2H), 1.26−1.18 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.6, 130.7, 128.8, 128.7, 128.5, 127.8, 114.1, 38.0, 33.8, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 28.4; IR (KBr) ν_{max}/cm^{-1} 3079, 2985, 1637, 1504, 1445, 724; MS (EI) *m*/*z* 95, 115, 129, 151, 157, 171, 191, 218, 253, 289, 368; HRMS (EI) calcd for $C_{19}H_{26}ClBr$ 368.0906, found 368.0903.

(2-Bromo-1-chlorohepta-1,5-dien-1-yl)benzene (**9a**). Yield: 88% (124.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.50−5.38 (m, 1H), 5.29−5.20 (m, 1H), 2.49−2.42 (m, 2H), 2.35−2.30 (m, 1H), 2.28−2.23 (m, 1H), 1.61 (d, *J* = 6.4 Hz, 1.5H), 1.55 (d, *J* = 6.8 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6 (137.5), 131.3 (131.2), 128.9 (128.8), 128.8 (127.8), 128.7 (128.7), 128.5 (128.5), 127.0 (126.9), 126.5 (125.7), 38.2 (37.9), 31.8 (26.4), 17.9 (12.8); IR (KBr) ν_{max}/cm^{-1} 3049, 2983, 1600, 1501, 1464, 720; MS (EI) *m*/*z* 115, 150, 169, 205, 231, 252, 284; HRMS (EI) calcd for $C_{13}H_{14}ClBr$ 283.9967, found 283.9964.

(2-Bromo-1-chlorononа-1,6-dien-1-yl)benzene (**9b**). Yield: 82% (127.9 mg) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.30 (m, 5H), 5.39−5.29 (m, 1H), 5.27−5.16 (m, 1H), 2.45−2.41 (m, 2H), 1.99−1.86 (m, 4H), 1.68−1.60 (m, 2H), 0.917 (d, *J* = 7.6 Hz, 1.5H), 0.883 (d, *J* = 7.6 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6 (137.5), 132.9 (132.5), 130.9 (130.8), 128.8 (128.8), 128.7 (128.6), 128.5 (128.5), 127.9 (127.8), 127.6 (127.4), 37.8 (37.5), 31.2 (20.5), 29.1 (28.9), 26.0 (25.5), 14.2 (13.8); IR (KBr) ν_{max}/cm^{-1} 3044, 2987, 1605, 1500, 1445, 728; MS (EI) *m*/*z* 115, 128, 141, 155, 197, 237, 249, 298, 312; HRMS (EI) calcd for $C_{15}H_{18}ClBr$ 312.0280, found 312.0274.

(Z)-Ethyl 2-((4-Ethylphenyl)(phenyl)methylene)hept-6-enoate (**11**). Yield: 78% (67.9 mg) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 3H), 7.18−7.16 (m, 2H), 7.08−7.02 (m, 4H), 5.79−5.69 (m, 1H), 4.98−4.89 (m, 2H), 3.96 (q, *J* = 7.6 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.36 (dd, *J* = 9.2, 6.4 Hz, 2H), 2.02 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.58 (dt, *J* = 18.4, 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 145.7, 143.5, 141.1, 139.7, 138.3, 133.2, 129.1, 128.6, 128.1, 127.5, 127.4, 114.7, 60.4, 33.5, 31.7, 28.6, 28.2, 15.5, 13.6; IR (KBr) ν_{max}/cm^{-1} 3077, 2965, 1710, 1643, 1500, 1454, 755; MS (EI) *m*/*z* 91, 115, 119, 143, 153, 165, 179, 191, 195, 205, 219, 245, 247, 259, 274, 293, 319, 348; HRMS (ESI) calcd for $C_{24}H_{28}NaO_2^+$ 371.1982, found 371.1980.

■ ASSOCIATED CONTENT

Supporting Information

Spectral data for all new compounds and NOE studies of the stereochemistry of **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews, see: (a) Negishi, E.; Coperet, C.; Ma, S.; Liou, S. Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365−393. (b) Zeni, G.; Larock, R. C. *Chem. Rev.* **2004**, *104*, 2285−2309. (c) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644−4680. (d) Patil, N. P.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395−3442. (e) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.* **2012**, *41*, 5588−5598. (f) Chow, W. K.; Yuen, O. Y.; Choy, P. Y.; So, C. M.; Lau, C. P.; Wong, W. T.; Kwong, F. Y. *RSC Adv.* **2013**, *3*, 12518−12539. (g) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084−3213.

(2) For reviews, see: (a) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114−4133. (b) Kambe, N.; Iwasaki, T.; Terao, J. *Chem. Soc. Rev.* **2011**, *40*, 4937−4947. (c) Sundararaju, B.; Achard, M.; Bruneau, C. *Chem. Soc. Rev.* **2012**, *41*, 4467−4483. (d) Yamamoto, Y. *Chem. Rev.* **2012**, *112*, 4736−4769. (e) Nikishkin, N. I.; Huskens, J.; Verboom, W. *Org. Biomol. Chem.* **2013**, *11*, 3583−3602.

(3) For selected examples, see: (a) Wang, Z.; Lu, X. *J. Org. Chem.* **1996**, *61*, 2254−2255. (b) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252−7263. (c) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; Wiley Interscience: New York, 2002. (d) Patil, N. T.; Huo, Z.; Bajracharya, G. B.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 3612−3614. (e) Panda, N.; Mothkuri, R. *J. Org. Chem.* **2012**, *77*, 9407−9412.

(4) For reviews, see: (a) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400−3420. (b) Sigman, M. S.; Jensen, D. R. *Acc. Chem. Res.* **2006**, *39*, 221−229. (c) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981−3019. (d) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851−863.

(5) (a) Iwashima, M.; Terada, I.; Okamoto, K.; Iguchi, K. *J. Org. Chem.* **2002**, *67*, 2977−2981. (b) Mondal, S.; Yadav, R. N.; Ghosh, S. *Org. Biomol. Chem.* **2011**, *9*, 4903−4913.

(6) Mukai, C.; Hara, Y.; Miyashita, Y.; Inagaki, F. *J. Org. Chem.* **2007**, *72*, 4454−4461.

(7) (a) Bhar, S.; Chaudhuri, S. K.; Sahu, S. G.; Panja, C. *Tetrahedron* **2001**, *57*, 9011−9016. (b) Gan, K.-H.; Jhong, C.-J.; Yang, S.-C. *Tetrahedron* **2008**, *64*, 1204−1212.

(8) Park, B. R.; Kim, K. H.; Kim, J. N. *Bull. Korean Chem. Soc.* **2010**, *31*, 2057−2060.

(9) Kippo, T.; Hamaoka, K.; Ryu, I. *J. Am. Chem. Soc.* **2013**, *135*, 632−635.

(10) For selected examples, see: (a) Yang, S.-R.; Jiang, H.-F.; Li, Y.-Q.; Chen, H.-J.; Luo, W.; Xu, Y.-B. *Tetrahedron* **2008**, *64*, 2930−2937. (b) Zhou, P.; Huang, L.; Jiang, H.; Wang, A.; Li, X. *J. Org. Chem.* **2010**,

75, 8279−8282. (c) Li, Y.; Liu, X.; Jiang, H.; Liu, B.; Chen, Z.; Zhou, P. *Angew. Chem., Int. Ed.* **2011**, *50*, 6341−6345. (d) Huang, L.; Wang, Q.; Liu, X.; Jiang, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 5696−5700. (e) Wen, Y.; Huang, L.; Jiang, H.; Chen, H. *J. Org. Chem.* **2012**, *77*, 2029−2034. (f) Wu, W.; Jiang, H. *Acc. Chem. Res.* **2012**, *45*, 1736−1748. (g) Li, J.; Yang, S.; Huang, L.; Chen, H.; Jiang, H. *RSC Adv.* **2013**, *3*, 11529−11532.

(11) See: Bianchini, R.; Chiappe, C.; Moro, G. L.; Lenoir, D.; Lemmen, P.; Goldberg, N. *Chem.—Eur. J.* **1999**, *5*, 1570−1580.

(12) (a) Wang, Z.; Lu, X. *J. Org. Chem.* **1996**, *61*, 2254−2255. (b) Zhang, Q.; Lu, X.; Han, X. *J. Org. Chem.* **2001**, *66*, 7676−7684. (c) Zhao, L.; Lu, X.; Xu, W. *J. Org. Chem.* **2005**, *70*, 4059−4063. (d) Wu, W.; Kong, A.; Lu, X. *J. Org. Chem.* **2006**, *71*, 3854−3858.

(13) Kaneda, K.; Uchiyama, T.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55−63.

(14) For representative preparations of bromoalkynes from terminal alkynes, see: (a) Abele, E.; Rubina, K.; Abele, R.; Gaukhman, A.; Lukevics, E. *J. Chem. Res., Synop.* **1998**, 618−619. (b) Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151−1154. (c) Mu, Z.; Shu, L.; Fuchs, H.; Mayor, M.; Chi, L. *J. Am. Chem. Soc.* **2008**, *130*, 10840−10841.

(15) (a) Huang, J.; Zhou, L.; Jiang, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 1945−1949. (b) Wen, Y.; Huang, L.; Jiang, H.; Chen, H. *J. Org. Chem.* **2012**, *77*, 2029−2034.

(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(17) Kochi, T.; Hamasaki, T.; Aoyama, Y.; Kawasaki, J.; Kakiuchi, F. *J. Am. Chem. Soc.* **2012**, *134*, 16544−16547.

(18) For selected examples, see: (a) Lu, X.; Zhu, G.; Ma, S. *Tetrahedron Lett.* **1992**, *33*, 7205−7206. (b) Lu, X.; Zhu, G. *J. Org. Chem.* **1995**, *60*, 1087−1089. (c) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics* **2001**, *20*, 3724−3728. (d) Zhang, Q.; Xu, W.; Lu, X. *J. Org. Chem.* **2005**, *70*, 1505−1507.

(19) For selected examples, see: (a) Chen, M. S.; White, M. C. *Science* **2007**, *318*, 783−787. (b) Okada, T.; Park, S.; Takeuchi, D.; Osakada, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 6141−6143. (c) Wasa, M.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 3680−3681. (d) Takeuchi, D. *J. Am. Chem. Soc.* **2011**, *133*, 11106−11109. (e) Liu, P.; Ye, Z.; Wang, W.; Li, B.-G. *Macromolecules* **2013**, *46*, 72−82.

(20) Ma, S.; Yu, Z. *Angew. Chem., Int. Ed.* **2003**, *42*, 1955−1957.

(21) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765−1766.

(22) Branco, L. C.; Rosa, J. N.; Moura, R. J. J.; Afonso, C. A. M. *Chem.—Eur. J.* **2002**, *8*, 3671−3677.

(23) Miao, C.-X.; He, L.-N.; Wang, J.-Q.; Wang, J.-L. *Adv. Synth. Catal.* **2009**, *351*, 2209−2216.

(24) Sasson, Y.; Webster, O. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1200−1201.

(25) Pan, C.; Luo, F.; Wang, W.; Ye, Z.; Cheng, J. *Tetrahedron Lett.* **2009**, *50*, 5044−5046.