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Synthesis of 1,4-dienes by Pd(II)-catalyzed haloallylation of alkynes with allylic alcohols in ionic liquids

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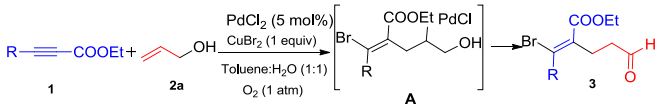
ABSTRACT

A Pd-catalyzed haloallylation of alkynes with allyl alcohols in ionic liquids has been reported. Both chloroallylation and bromoallylation can be easily carried out with high selectivity. A variety of 1,4-dienes were formed in moderate to excellent yields. The reaction system of the Pd catalyst as well as the ionic liquid can be recycled for several times. And the ionic liquid acts as not only a solvent in the reaction, but also provides the excess halide ions to control *Z*/*E* selectivity and acts as a ligand inhibit the β-hydride elimination.

1. Introduction

In recent decades, the synthesis of 1,4-dienes has attracted much attention, and a series of synthetic approaches related to the reaction of alkynes have been developed.[1,2] Among these strategies, palladium-catalyzed haloallylation of alkynes with allylic moiety has been recognized to be an effective method because of the good selectivity and mild reaction conditions. Although allylic alcohols are commercially available, the allylating reagents in the reaction have usually been limited to allylic chlorides, allylic bromides, and allylic acetates.[2] Obviously, it will greatly enlarge the scope and synthetic application field of alkyne haloallylation if allylic alcohols can be directly used in the reaction. In our previous work, we successfully performed the reaction to produce 1,4-dienes in an aqueous media by employing alkynes and allyl alcohols.[2f] Upon exploring the reaction, it was found that the ionic liquids worked more efficiently for this process and produced 1,4-dienes in high selectivity with moderate to excellent yields. Herein, we report a method for highly efficient synthesis of 1,4-dienes by Pd(II)-catalyzed haloallylation of alkynes with allyl alcohols in aqueous ionic liquids.

One of the complications in palladium-catalyzed alkyne/allyl alcohol reaction is the strong tendency for the alkylpalladium intermediates to undergo a β-hydride elimination to yield γ,δ-unsaturated carbonyl compounds (Scheme 1).[3] Obviously, if β-hydride elimination was suppressed, alternative reactions of the alkylpalladium species would be promoted. In our previous work,[4] it was found that β-hydride elimination could be inhibited in a $PdCl_2$-[Bmim]Cl–HCl system. In this system, the ionic liquid provides the excess chloride ions to control *Z*/*E* selectivity[5] and acts as a ligand inhibit the β-hydride elimination.[4]



Scheme 1. Palladium-catalyzed bromoalkylation of alkynoates.

Thus, we chose this system to investigate the palladium-catalyzed alkyne/allyl alcohol reaction.

2. Results and discussion

Synthesis of (1Z) or (1E) 1,4-dienes. The reaction of ethyl 3-phenylpropiolate (**1a**) and prop-2-en-1-ol (**2a**) was first investigated

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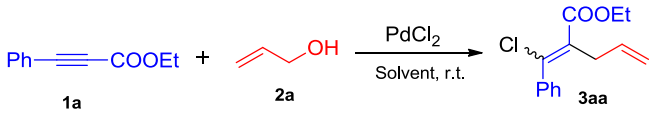
in the presence of 5 mol % of $PdCl_2$ in 1 mL mixed solvents ([Bmim]Cl:12 N aqueous HCl=3:1). To our delight, the reaction produced the desired (*Z*)-**3aa** in 98% GC yield with an excellent *Z*-stereoselectivity (*Z*/*E*=98/2 by GC) after stirring for 24 h at room temperature and no carbonyl compounds were detected. The results demonstrated that β-hydride elimination could be inhibited. Encouraged by this result, we further investigated the reaction conditions and the results are listed in Table 1.

Table 1
Optimization of reaction conditions[a]



Entry	Solvent (mL)	Pd (mol %)	GC yield[b] (%)	*Z*/*E*[c]
1	[Bmim]Cl (0.75)+12 N HCl (0.25)	5	98	98/2
2	[Bmim]Cl (0.75)+12 N HCl (0.15)	5	78	98/2
3	[Bmim]Cl (0.75)+12 N HCl (0.1)	5	55	98/2
4[d]	[Bmim]Cl (0.75)+12 N HCl (0.25)	5	87	95/5
5	[Bmim]Cl (0.5)+12 N HCl (0.25)	5	97	98/2
6	[Bmim]Cl (0.5)+H_2O (0.25)	5	—	—
7	[Bmim]BF_4(0.5)+12 N HCl (0.25)	5	87	78/22
8	[Bmim]PF_6 (0.5)+12 N HCl (0.25)	5	83	63/37
9	[C_2OHmim]Cl(0.5)+12 N HCl (0.25)	5	93	95/5
10	[BuPy]Cl(0.5)+12 N HCl (0.25)	5	88	94/6
11	H_2O (0.5)+12 N HCl (0.25)	5	93	61/39
12	DMSO (0.5)+12 N HCl (0.25)	5	93	61/39
13[e]	12 N HCl (0.25)	5	93	71/29
14[f]	12 N HCl (0.25)	5	95	77/23
15	[C_2O_2mim]Cl (0.5)+H_2O (0.1)	5	94	98/2
16	[C_2O_2mim]Cl (0.5)+H_2O (0.25)	5	98	98/2
17	[C_2O_2mim]Cl (0.5)+H_2O (0.5)	5	89	98/2
18	[C_2O_2mim]Cl (0.5)+H_2O (0.25)	2	90	98/2
19	[C_2O_2mim]Cl (0.5)+H_2O (0.25)	3	98	98/2
20	[C_2O_2mim]Cl (0.5)+HCl (0.25)	3	100	>98/2
21[g]	Second	—	100	>98/2
22[h]	Third	—	100	>98/2
23[i]	Fourth	—	98	>98/2
24[j]	Fifth	—	83	>98/2
25[k]	Sixth	—	100	>98/2
26[l]	Seventh	—	100	>98/2

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), and $PdCl_2$ were stirred in different solvents.
[b] Conversions analyzed by GC/MS are based on 1a.
[c] The ratios of 1*Z*/1*E*.
[d] The reaction was performed at 50 °C.
[e] With 4 equiv of NaCl.
[f] With 4 equiv of LiCl.
[g] The second run after entry 20, after extracted with ethyl ether.
[h] The third run after entry 21, after extracted with ethyl ether.
[i] The fourth run after entry 22, after extracted with ethyl ether.
[j] The fifth run after entry 23, after extracted with ethyl ether.
[k] The sixth run after entry 24, after extracted with ethyl ether, and HCl (0.02 mL) was added.
[l] The seventh run after entry 25, after extracted with ethyl ether, and HCl (0.02 mL) was added.

As shown in Table 1, decreasing the amount of [Bmim]Cl only resulted in slight decrease in the yields (entries 1 and 5) and decreasing the amount of HCl resulted in sharply decreased conversion. It might mean that acidic medium favored this transformation. And the reaction proceeded smoothly in the 0.25 mL HCl (entries 1–3, 6). The reaction was subsequently investigated in the replacement of [Bmim]Cl by other ionic liquids (Fig. 1), such as [Bmim]BF_4, [Bmim]PF_6, [C_2OHmim]Cl, [BuPy]Cl, and [C_2O_2mim]Cl (entries 7–10 and 15). Interestingly, the reaction still gave the desired (*Z*)-**3aa** in 94% GC yield in [C_2O_2mim]Cl and H_2O without using HCl (entry 15). Furthermore, various the conventional solvents were examined under the same reaction conditions, such as H_2O and DMSO, significantly decreased the yields and stereoselectivities (entries 11, 12). Other halide sources, such as NaCl and LiCl, were tested as a convenient source of halogens, unfortunately, the products were produced in lower selectivities (entries 13,14). Accordingly, different catalytic loading and the solvent systems were examined to improve the reaction efficiency (entries 15–20). After many attempts, 3 mol % of $PdCl_2$ as the catalyst, 0.5 mL of [C_2O_2mim]Cl and 0.25 mL of HCl as the solvent were found to be the best choices, providing **3aa** in 100% yield with an excellent *Z*-stereoselectivity (*Z*/*E*>98/2 by GC). Moreover, diallyl ether was observed in the reaction mixture.[6]

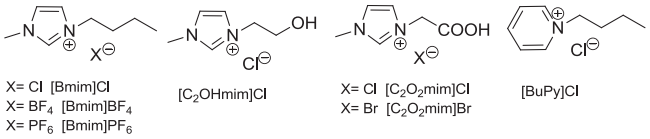
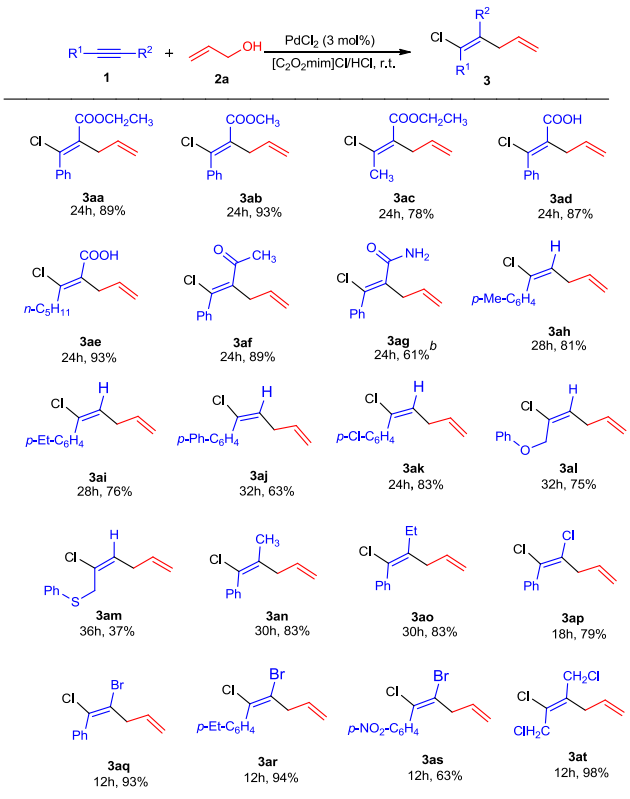


Fig. 1. Ionic liquids applied in this work.

On the basis of the optimized reaction conditions, we next examined the reuse of the palladium catalyst in [C_2O_2mim]Cl. The results indicated that the catalyst was successfully recycled five times with excellent yields. The reaction rate dropped significantly at the fifth cycle, probably due to the decreased amount protons and halide sources of ionic liquid. When 0.02 mL HCl solution was added, the reaction gave the desired (*Z*)-**3aa** in 100% GC yield (Table 1, entries, 25, 26). However, it should be emphasized that the present system realized five repetitions of the reaction without any addition of the catalyst with excellent yield and good selectivity. The catalyst solution could be stored for several days without decrease in the activity or regioselectivity.

With the optimized reaction conditions in hand, we further investigated the scope and limitation of this reaction. The representative results are summarized in Scheme 2. In most cases, the allylation reactions proceeded smoothly and gave the desired (1*Z*)- or (1*E*)-1-chloro-1,4-dienes in good to excellent yields with extremely high selectivity. What interesting is the substrate 3-phenylpropiolic acid (**1d**) and oct-2-ynoic acid (**1e**), which resulted in the introduction of a carboxylic acid moiety directly into the 1,4-diene without the need for functional group protection and deprotection. Aliphatic alkynes also participated well in this reaction, and resulted in the (1*Z*)-1-chloro-1,4-dienes in a highly selectivity fashion and with good yields. For instance, the (*Z*)-methyl 2-(1-chloroethylidene) pent-4-enoate (**3ac**) and (*Z*)-2-allyl-3-chlorooct-2-enoic acid (**3ae**) were generated in 78% and 93% yields, respectively, and with excellent selectivity. The more challenging 4-phenylbut-3-yn-2-one (**1f**) and 3-phenylpropiolamide (**1g**) showed good stability under the similar reaction conditions, providing **3af** and **3ag** in 89% and 61% yield, respectively. It is noteworthy that the terminal acetylenes (**1h**–**m**) also gave the desired 1,4-dienes rather than cotrimerization products in our previous study.[2f] Finally, we also examined the steric effect for this reaction. For example, the reaction of 1-ethynyl-4-methylbenzene (**1h**) afforded **3ah** in 81% yield, and 4-ethynyl-1,1′-biphenyl (**1j**) led to **3aj** in 63% yield, which indicated a little steric effect on the reaction. In sharp contrast, symmetric internal alkynes, such as 1,2-diphenylethyne and 1,2-bis(4-methoxyphenyl)ethyne, failed to react with **2a** to afford the desired product under the standard reaction conditions. Unfortunately, but-2-yne-1,4-diol also failed to afford the desired product. Both electron-rich and electron-poor phenylethynyl bromides were reacted with but-3-en-1-ol (**2a**) to give the corresponding 1,4-diene products **3aq**–**as** in good to excellent yields. Moreover, the reaction was found to be applicable to chloroalkyne, although the reaction of chloroalkynes was relatively

sluggish (**3ap**). In terms of the selectivity, all the products obtained in the presence of an excess of chloride ions and acid in a polar solvent resulted from trans addition.[2b,2c,7] The site of halogen addition to unsymmetric acetylenes was controlled by electronic factors.[8]

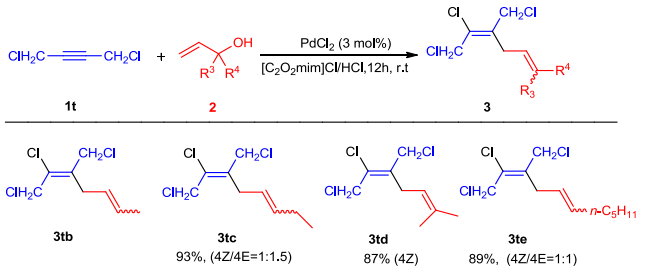


[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $PdCl_2$ (3 mol%), $[C_2O_2mim]Cl$ (0.5 mL) and HCl (0.25 mL) under the atmosphere of air at room temperature. Reaction was monitored by TLC for the completion of the reaction. Yields referred to isolated yields.
[b] without HCl

Scheme 2. Pd(II)-catalyzed coupling reaction of alkynes with allyl alcohol in $[C_2O_2mim]Cl$.

After the effect of alkynes had been examined, a series of secondary allyl alcohols was investigated in this transformation. Generally, the reaction of allylic alcohols with a terminal C–C double bond with 1,4-dichlorobut-2-yne (**1t**) produced the desired products. For example, methyl, ethyl and pentyl allylic alcohols (**2b**, **2c**, **2e**) gave 1,4-dienes in good to excellent yields with mixture of *E* and *Z* isomers (Scheme 3). Meanwhile, 2-methylbut-3-en-2-ol (**2d**) afforded the product (*Z*)-**3td** in good yield. However, the allylic alcohols with an internal C–C double bond failed to give the desired products. For example, while crotyl alcohol, 3-methylbut-2-en-1-ol and (*E*)-hept-2-en-1-ol with alkynes were performed under the same reaction conditions, no 1,4-diene products were detected and the alkynes were recovered after 24 h.

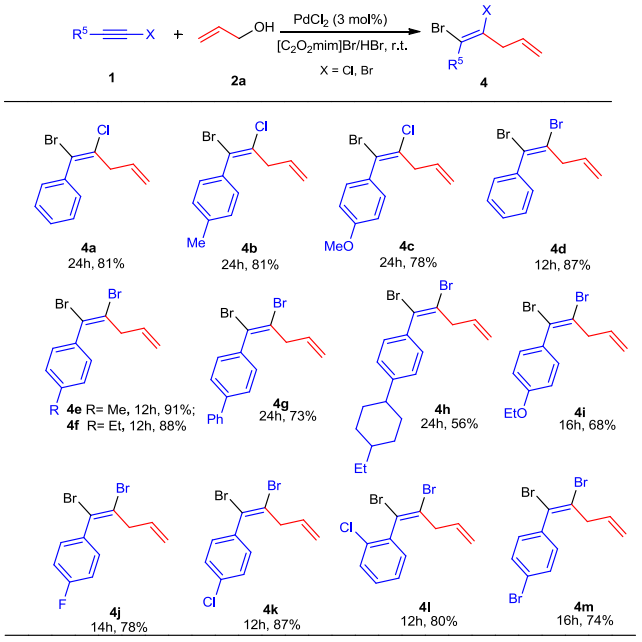
After the chloroallylation of alkyne with allylic alcohols was investigated thoroughly, we turned our attention to the bromoallylation of alkynes with allylic alcohols. Haloalkynes are one kind of the most important intermediates and versatile building blocks in organic synthesis.[9] Very recently, they are widely used as one of the coupling partners in transition- metal-catalyzed carbon–carbon (heteroatom) bond formations via cross-coupling reactions in our previous studies.[10] Based on these results, we chose haloalkynes as substrates to react with allyl alcohol in a mixed



[a] Reaction conditions: **1t** (0.5 mmol), **2** (0.6 mmol), $PdCl_2$ (3 mol%), $[C_2O_2mim]Cl$ (0.5 mL) and HCl (0.25 mL) under the atmosphere of air at room temperature. Yields referred to isolated yields. The ratios of 4Z/4E were determined by NOE.

Scheme 3. $PdCl_2$-catalyzed allylation of 1,4-dichloro- but-2-yne(**1t**) in $[C_2O_2mim]Cl$.

solvent of $[C_2O_2mim]Br$ and HBr (Scheme 4). Fortunately, the bromoallylation of haloalkynes proceeded well. Alkynyl chlorides whether possessing electron-donating groups or electron-withdrawing groups on the benzene ring could undergo the transformation in moderate yields (**4a**, **4b**, and **4c**). For bromoalkynes with a variety of substituted groups on the benzene ring, including Me, Et, X, Ph, OEt, and even the bulky ethylcyclohexyl group, the reaction could afford desired products in moderate to good yields (**4d**–**m**).

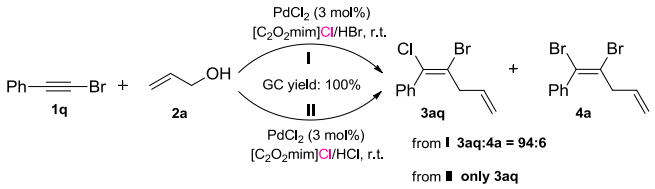


[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), $PdCl_2$ (3 mol%), $[C_2O_2mim]Br$ (0.5 mL) and HBr (0.25 mL) under the atmosphere of air at room temperature. Reaction was monitored by TLC for the completion of the reaction. Yields referred to isolated yields.

Scheme 4. Pd(II)-catalyzed cross-coupling reaction of haloalkynes with allyl alcohol in $[C_2O_2mim]Br$.

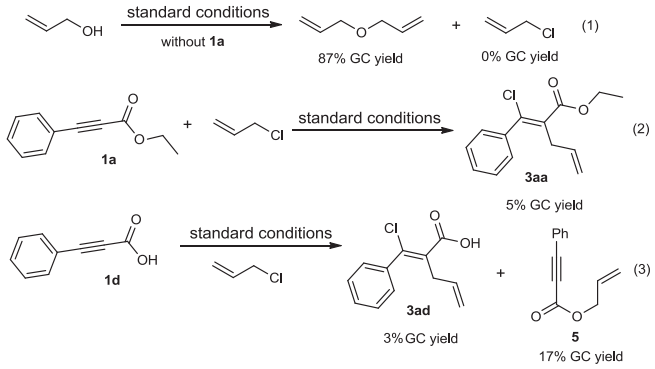
In contract, when (bromoethynyl)benzene (**1q**) was allowed to react with prop-2-en-1-ol (**2a**) in $PdCl_2$–$[C_2O_2mim]Cl$–HBr system under similar reaction condition, the reaction lost its regiospecificity, with the two mixed differentially halogenated 1,4-dienes **3aq** and **4a** (Scheme 5).

Plausible Reaction Mechanism. In order to understand the reaction mechanism of this unique transformation, several control experiments were performed under the standard reaction conditions (Scheme 6). The controlled experiment without alkyne was



Scheme 5. Contrast experiments.

performed, diallyl ether was observed in 87% GC yield and no allyl chloride was obtained (Eq. 1). Furthermore, When ethyl 3-phenylpropiolate (**1a**) was allowed to react with allyl chloride under the standard conditions, however, product **3aa** was detected with only 5% GC yield and 1a almost completely recovered (Eq. 2). Finally, employed 3-phenylpropiolic acid (**1d**) as the alkyne component and trace desired product **3ad** was detected by GC–MS and allyl 3-phenylpropiolate **5** was obtained in 17% GC yield and 70% **1d** was recovered (Eq. 3). Therefore, these results suggested that the reaction might not proceed via the allylic halide intermediate.

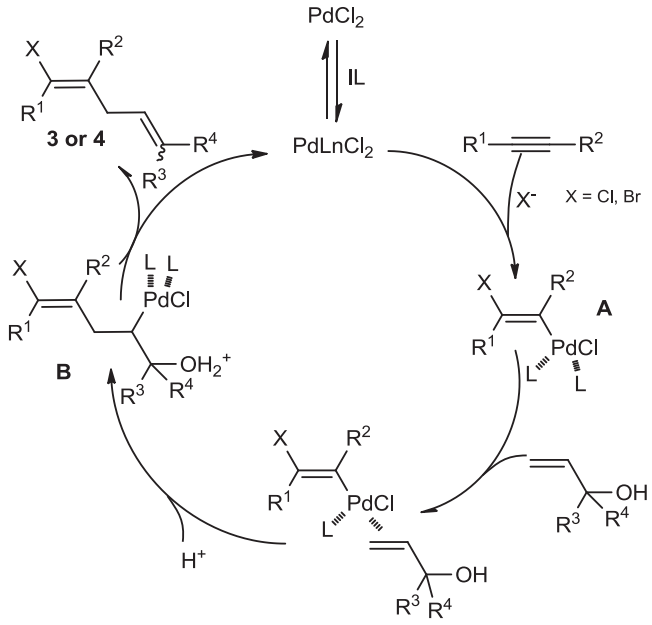


Scheme 6. Control experiments.

On the basis of our previous reports and experimental data,[2f,4] a plausible mechanism for the Pd-catalyzed haloallylation of alkynes with allylic alcohols in ionic liquids is illustrated in Scheme 7. Pd-alkenyl intermediate **A** is initially formed by *trans*-halopalladation of the alkynes **1** in the presence of an excess of halide ions in ionic liquids.[4,7] Subsequently, intermediate **A** undergoes alkene insertion to generate a Pd-alkyl intermediate **B**, which could complex with ionic liquids ligand efficiently to inhibit β-hydride elimination according to our previous report.[4b] With the aid of the proton of HCl, which can protonize the hydroxyl group of the intermediate B, then the product **3** or **4** was formed through *trans*-β-OH elimination of the intermediate **B** and the active Pd(II) specie was regenerated. Here, the ionic liquid plays an important role in the reaction. It not only acts as a solvent, but also provides the excess halide ions to control the *trans*-halopalladation of the alkynes, and also to stabilize the intermediate **B**[4b] and inhibit the β-hydride elimination.

3. Conclusion

In summary, we have developed an efficient method for the synthesis of 1,4-dienes by Pd(II)-catalyzed haloallylation of alkynes with allyl alcohols via β-OH elimination of alkylpalladium intermediates in the mixed solvent of ionic liquids and HCl. Both chloroallylation and bromoallylation can be easily carried out with high selectivity in moderate to excellent yields. Moreover, the Pd catalyst as well as the ionic liquid can be recycled several times.



Scheme 7. A plausible reaction mechanism.

This process provides a new methodology for constructing 1,4-dienes from alkynes and allylic alcohols.

4. Experimental section

4.1. General methods

Melting points were measured with a BÜCHI B-545 melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. Mass spectra were recorded on a Shimadzu GC–MS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. High-resolution mass spectra were obtained with Shimadazu LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. The ionic liquids ([Bmim]Cl,[11] [Bmim]BF_4,[12] [Bmim]PF_6,[12] [C_2OHmim]Cl,[13] [BuPy]Cl,[14] [C_2O_2mim]Cl,[15] and [C_2O_2mim]Br[15]) were synthesized using the procedure reported by other authors. The bromoalkynes[10] and chloroalkynes[16] were prepared according to the literature. Other reagents were purchased as reagent grade and used without further purification.

4.2. General procedure for the synthesis of 1,4-dienes

A mixture of alkynes **1** (0.5 mmol), **2** (0.6 mmol), palladium chloride (3.2 mg, 3 mol %), ionic liquid (0.5 mL), HX (0.25 mL) in a test tube (10 mL) equipped with a magnetic stirring bar. The mixture was stirred under the atmosphere of air at room temperature. After the reaction was completed, 10 mL ethyl acetate (3×10 mL) 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 on a preparative TLC afforded the desired products. Residual ionic liquid obtained

after the workup was stirred with diethyl ether (2×10 mL) for 15 min, and the ethereal layer was decanted. The ionic liquid was then directly used for the next runs without further dry and reused for up to five runs.

*4.2.1. (Z)-Ethyl 2-(chloro(phenyl)methylene)pent-4-enoate (**3aa**).* Yield: 89% (111.3 mg) as a yellow oil; IR (KBr) *ν* 3074, 2983, 2930, 1725, 1637, 1485, 1443, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.36 (m, 5H), 5.82–5.72 (m, 1H), 5.11 (dd, *J*=8.4, 0.8 Hz, 1H), 5.07 (dd, *J*=10.8, 0.8 Hz, 1H), 4.32 (q, *J*=7.1 Hz, 2H), 3.05 (d, *J*=6.0 Hz, 2H), 1.35 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.5, 137.2, 133.9, 133.4, 130.8, 129.3, 128.4, 117.2, 61.3, 36.2, 14.2 ppm; MS (EI) *m/z*: 115, 128, 141, 177, 205, 250; HRMS(ESI) calcd for $C_{14}H_{15}ClO_2Na$ (M^++Na) 273.0653, found 273.0655.

*4.2.2. (Z)-Methyl 2-(chloro(phenyl)methylene)pent-4-enoate (**3ab**).* Yield: 93% (109.7 mg) as a yellow oil; IR (KBr) *ν* 3078, 2951, 2907, 1731, 1638, 1489, 1436, 705 cm^{-1}; ^1H NMR (400 MHz $CDCl_3$): *δ* 7.40–7.34 (m, 5H), 5.81–5.71 (m, 1H), 5.10 (dd, *J*=4.8, 0.8 Hz, 1H), 5.07 (dd, *J*=5.2, 0.8 Hz, 1H), 3.84 (s, 3H), 3.04 (d, *J*=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 167.9, 137.1, 133.9, 133.8, 130.6, 129.3, 128.4, 128.3, 117.2, 52.1, 36.2 ppm; MS (EI) *m/z* 115, 129, 141, 177, 201, 236; HRMS(ESI) calcd for $C_{13}H_{14}ClO_2$ (M^++H) 237.0677, found 237.0678.

*4.2.3. (Z)-Ethyl 2-(1-chloroethylidene)pent-4-enoate (**3ac**).* Yield: 78% (73.3 mg) as a yellow oil; IR (KBr) *ν* 2921, 2851, 1632, 1369, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 5.81–5.71 (m, 1H), 5.10 (dd, *J*=8.8, 1.2 Hz, 1H), 5.05 (dd, *J*=15.6, 1.2 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 3.08 (d, *J*=6.0 Hz, 2H), 2.18 (s, 3H), 1.31 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.4, 133.4, 133.3, 128.5, 116.7, 61.0, 34.9, 23.1, 14.1 ppm; MS (EI) *m/z* 77, 79, 107, 115, 143, 153, 188; HRMS(ESI) calcd for $C_9H_{13}ClO_2Na$ (M^++Na) 211.0496, found 211.0493.

*4.2.4. (Z)-2-(Chloro(phenyl)methylene)pent-4-enoic acid (**3ad**).* Yield: 87% (96.6 mg) as a yellow oil; IR (KBr) *ν* 3075, 2923, 1699, 1641, 1489, 1413, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.44–7.36 (m, 5H), 5.88–5.78 (m, 1H), 5.10 (dd, *J*=4.8, 1.2 Hz, 1H), 5.07 (dd, *J*=6.0, 1.2 Hz, 1H), 3.09 (d, *J*=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 172.6, 137.4, 136.9, 133.9, 129.5, 129.3, 128.5, 128.2, 117.2, 36.1 ppm; MS (EI) *m/z* 115, 141, 142, 143, 177, 222; HRMS(ESI) calcd for $C_{12}H_{10}ClO_2$ (M^-−H) 221.0375, found 221.0377.

*4.2.5. (Z)-2-Allyl-3-chlorooct-2-enoic acid (**3ae**).* Yield: 93% (100.4 mg) as a yellow oil; IR (KBr) *ν* 3082, 2930, 1698, 1642, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 5.85–5.75 (m, 1H), 5.12 (dd, *J*=10.0, 1.2 Hz, 1H), 5.08 (dd, *J*=16.4, 1.2 Hz, 1H), 3.14 (d, *J*=6.0 Hz, 2H), 2.45 (t, *J*=7.6 Hz, 2H), 1.66–1.59 (m, 2H), 1.36–1.26 (m, 4H), 0.906 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 172.5, 141.9, 133.7, 126.8, 116.7, 36.5, 34.5, 31.1, 27.1, 22.4, 13.9 ppm; HRMS(ESI) calcd for $C_{11}H_{18}ClO_2$ (M^-−H) 215.0844, found 215.0845.

*4.2.6. (Z)-3-(Chloro(phenyl)methylene)hex-5-en-2-one (**3af**).* Yield: 77% (84.7 mg) as a colorless oil; IR (KBr) *ν* 3081, 2936, 1694, 1645, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.37 (m, 5H), 5.80–5.70 (m, 1H), 5.10 (dd, *J*=10.4, 1.6 Hz, 1H), 5.07 (dd, *J*=16.0, 1.2 Hz, 1H), 3.02 (d, *J*=6.0 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 203.5, 138.6, 137.0, 133.8, 130.4, 129.3, 128.9, 128.4, 117.5, 36.5, 31.0 ppm; MS (EI) *m/z* 115, 128, 141, 143, 163, 183, 185, 205, 220; HRMS(EI) calcd for $C_{13}H_{13}ClO$ 220.0655, found 220.0647.

*4.2.7. (Z)-2-(Chloro(phenyl)methylene)pent-4-enamide (**3ag**).*[21] Yield: 61% (67.4 mg) as a white solid.; mp=163.4–164.7 °C; IR (KBr) *ν* 3074, 2983, 2930, 1725, 1637, 1485, 1443, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.42–7.37 (m, 5H), 6.02 (s, 1H), 5.96 (s, 1H), 5.85–5.75 (m, 1H), 5.10 (dd, *J*=10.0, 1.2 Hz, 1H), 5.08 (dd, *J*=10.8, 0.8 Hz, 1H), 3.07 (d, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.5, 137.1, 133.9, 130.7, 129.3, 128.5, 117.4, 36.5 ppm; MS (EI) *m/z* 115, 128, 141, 143, 168, 184, 186, 221; HRMS(EI) calcd for $C_{12}H_{12}ClNO$ 221.0607, found 221.0603.

*4.2.8. (E)-1-(1-Chloropenta-1,4-dien-1-yl)-4-methylbenzene (**3ah**).* Yield: 81% (77.8 mg) as a yellow oil; IR (KBr) *ν* 3077, 2924, 1694, 1511, 1432, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.23–7.17 (m, 4H), 6.11 (s, 1H), 5.81–5.71 (m, 1H), 5.07 (dd, *J*=8.0, 1.2 Hz, 1H), 5.04 (dd, *J*=9.2, 1.2 Hz, 1H), 3.14 (d, *J*=6.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 140.9, 137.4, 134.8, 134.7, 128.9, 128.1, 117.3, 114.1, 45.1, 21.3 ppm; MS (EI) *m/z* 77, 91, 115, 129, 142, 157, 192; HRMS(EI) calcd for $C_{12}H_{13}Cl$ 192.0706, found 192.0703.

*4.2.9. (E)-1-(1-Chloropenta-1,4-dien-1-yl)-4-ethylbenzene (**3ai**).* Yield: 76% (78.3 mg) as a yellow oil; IR (KBr) *ν* 3078, 2965, 2928, 1726, 1692, 1457, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.25–7.20 (m, 4H), 6.11 (s, 1H), 5.82–5.72 (m, 1H), 5.08 (dd, *J*=6.4, 1.2 Hz, 1H), 5.04 (dd, *J*=8.8, 1.2 Hz, 1H), 3.15 (d, *J*=6.8 Hz, 2H), 2.66 (q, *J*=7.6 Hz, 2H), 1.25 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 143.7, 140.9, 135.0, 134.7, 128.1, 127.7, 117.3, 114.1, 41.5, 28.6, 15.3 ppm; MS (EI) *m/z* 115, 128, 141, 143, 155, 171, 177, 206; HRMS(EI) calcd for $C_{13}H_{15}Cl$ 206.0862, found 206.0860.

*4.2.10. (E)-4-(1-Chloropenta-1,4-dien-1-yl)-1,1′-biphenyl (**3aj**).* Yield: 63% (80.1 mg) as a yellow solid; mp=137.3–138.1 °C; IR (KBr) *ν* 3064, 2925, 1687, 1602, 1517, 1449, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.62–7.59 (m, 4H), 7.46–7.40 (m, 4H), 7.36–7.33 (m, 1H), 6.17 (s, 1H), 5.85–5.75 (m, 1H), 5.11 (dd, *J*=6.8, 0.8 Hz, 1H), 5.07 (dd, *J*=16.0, 0.8 Hz, 1H), 3.20 (d, *J*=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 140.7, 140.6, 140.5, 136.7, 134.6, 128.8, 128.7, 127.4, 127.1, 126.8, 117.5, 114.6, 41.4 ppm; MS (EI) *m/z* 73, 77, 91, 115, 141, 152, 165, 178, 191, 203, 219, 254; HRMS(EI) calcd for $C_{17}H_{15}Cl$ 254.0862, found 254.0858.

*4.2.11. (E)-1-Chloro-4-(1-chloropenta-1,4-dien-1-yl)benzene (**3ak**).* Yield: 83% (87.9 mg) as a yellow oil; IR (KBr) *ν* 3086, 2924, 1682, 1589, 1488, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.35–7.31 (m, 4H), 6.01 (t, *J*=8.0 Hz, 1H), 5.85–5.75 (m, 1H), 5.09 (dd, *J*=8.8, 1.2 Hz, 1H), 5.06 (dd, *J*=9.2, 1.2 Hz, 1H), 2.81 (dt, *J*=6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 135.4, 135.2, 134.6, 130.5, 130.0, 128.5, 127.7, 116.0, 33.7 ppm; MS (EI) *m/z* 115, 142, 177, 212; HRMS(EI) calcd for $C_{11}H_{10}Cl_2$ 212.0160, found 212.0158.

*4.2.12. (E)-((2-Chlorohexa-2,5-dien-1-yl)oxy)benzene (**3al**).* Yield: 75% (78.1 mg)as a yellow oil; IR (KBr) *ν* 3075, 2926, 1640, 1493, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.29–7.26 (m, 2H), 6.97–6.92 (m, 3H), 6.03 (s, 1H), 5.84–5.74 (m, 1H), 5.12 (dd, *J*=8.8, 1.2 Hz, 1H), 5.09 (dd, *J*=10.4, 1.2 Hz, 1H), 4.73 (s, 2H), 2.95 (d, *J*=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 158.4, 137.3, 134.2, 129.6, 121.1, 117.8, 116.3, 114.7, 64.7, 36.6 ppm; MS (EI) *m/z* 79, 94, 157, 173, 208; HRMS(ESI) calcd for $C_{12}H_{13}ClONa$ (M^++Na) 231.0547, found 231.0550.

*4.2.13. (E)-(2-Chlorohexa-2,5-dien-1-yl)(phenyl)sulfane (**3am**).* Yield: 37% (41.4 mg) as a yellow oil; IR (KBr) *ν* 3063, 2923, 1580, 1477, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.34 (m, 4H), 7.29–7.27 (m, 1H), 7.22–7.19 (m, 1H), 6.08 (s, 1H), 5.95 (dd, *J*=6.4, 0.8 Hz, 1H), 5.89 (dd, *J*=9.2, 0.8 Hz, 1H), 3.83 (s, 2H), 3.57 (d, *J*=2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 136.2, 135.6, 131.5, 130.8, 129.6, 128.9, 128.8, 127.1, 126.7, 121.2, 37.1, 31.6 ppm; MS (EI) *m/z* 110, 135, 147, 186, 207, 224; HRMS(ESI) calcd for $C_{12}H_{14}ClS$ (M^++H) 225.0499, found 225.0502.

*4.2.14. (E)-(1-Chloro-2-methylpenta-1,4-dien-1-yl)benzene (**3an**).* Yield: 83% (79.7 mg) as a yellow oil; IR (KBr) *ν* 3064, 2926,

1722, 1599, 1490, 1447, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 5.80–5.70 (m, 1H), 5.06 (dd, J=8.4, 1.2 Hz, 1H), 5.00 (dd, J=10.8, 1.2 Hz, 1H), 2.78 (d, J=6.0 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 135.3, 132.2, 128.9, 128.2, 128.0, 127.4, 116.5, 39.6, 19.7 ppm; MS (EI) m/z 51, 77, 91, 115, 129, 142, 157, 177, 192; HRMS(EI) calcd for $C_{12}H_{13}Cl$ 192.0706, found 192.0703.

*4.2.15. (E)-(1-Chloro-2-ethylpenta-1,4-dien-1-yl)benzene (**3ao**).* Yield: 83% (85.5 mg) as a yellow oil; IR (KBr) ν 3079, 2968, 1641, 1457, 755/cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.31 (m, 2H), 7.23–7.19 (m, 3H), 5.77–5.67 (m, 1H), 5.04 (dd, J=10.8, 1.2 Hz, 1H), 5.00 (dd, J=16.0, 1.2 Hz, 1H), 3.17 (d, J=6.4 Hz, 2H), 2.55 (q, J=7.2 Hz, 2H), 1.22 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 134.6, 133.8, 133.7, 128.6, 127.9, 126.9, 116.1, 39.1, 29.1, 12.8 ppm; MS (EI) m/z 77, 91, 115, 129, 141, 143, 177, 179, 206; HRMS(EI) calcd for $C_{13}H_{15}Cl$ 206.0862, found 206.0858.

*4.2.16. (Z)-(1,2-Dichloropenta-1,4-dien-1-yl)benzene (**3ap**).*[2j] Yield: 79% (83.7 mg) as a yellow oil; IR (KBr) ν 3075, 2924, 1625, 1488, 1429, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 5H), 5.88–5.78 (m, 1H), 5.17 (dd, J=10.2, 1.2 Hz, 1H), 5.12 (dd, J=17.2, 1.2 Hz, 1H), 3.11 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 133.2, 131.2, 129.4, 129.1, 128.7, 128.5, 117.8, 40.6 ppm; MS (EI) m/z 115, 141, 142, 162, 177, 197, 212; HRMS(EI) calcd for $C_{11}H_{10}Cl_2$ 212.0160, found 212.0157.

*4.2.17. (Z)-(2-Bromo-1-chloropenta-1,4-dien-1-Yl)benzene (**3aq**).*[2j] Yield: 93% (118.9 mg) as a yellow oil; IR (KBr) ν 3074, 2980, 1637, 1490, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 5H), 5.87–5.77 (m, 1H), 5.16 (dd, J=10.2, 1.2 Hz, 1H), 5.11 (dd, J=17.2, 1.2 Hz, 1H), 3.19 (d, J=4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 133.8, 132.3, 129.1, 128.6, 128.5, 124.1, 117.7, 42.6 ppm; MS (EI) m/z 115, 142, 177, 256; HRMS(EI) calcd for $C_{11}H_{10}ClBr$ 255.9654, found 255.9650.

*4.2.18. (Z)-1-(2-Bromo-1-chloropenta-1,4-dien-1-yl)-4-ethylbenzene (**3ar**).* Yield: 94% (133.5 mg) as a yellow oil; IR (KBr) ν 3072, 2981, 1635, 1450, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J=8.0 Hz, 2H), 7.19 (d, J=8.0 Hz, 2H), 5.88–5.78 (m, 1H), 5.17 (dd, J=10.2, 1.2 Hz, 1H), 5.13 (dd, J=16.8, 1.2 Hz, 1H), 3.22 (d, J=4.8 Hz, 2H), 2.69–2.63 (m, 2H), 1.24 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 134.5, 133.9, 132.5, 128.5, 128.0, 123.6, 117.6, 42.6, 28.7, 15.3 ppm; MS (EI) m/z 115, 128, 141, 155, 169, 176, 190, 205, 207, 249, 257, 271, 284; HRMS(EI) calcd for $C_{13}H_{14}ClBr$ 283.9967, found 283.9962.

*4.2.19. (Z)-1-(2-Bromo-1-chloropenta-1,4-dien-1-yl)-4-nitrobenzene (**3as**).* Yield: 63% (94.8 mg) as a yellow oil; IR (KBr) ν 3071, 2982, 1635, 1490, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26–8.18 (m, 2H), 7.63–7.55 (m, 2H), 5.89–5.79 (m, 1H), 5.23 (dd, J=10.2, 1.2 Hz, 1H), 5.14 (dd, J=17.2, 1.2 Hz, 1H), 3.21 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 143.3, 132.8, 129.7, 126.3, 123.8, 123.6, 118.1, 42.6 ppm; MS (EI) m/z 115, 141, 149, 157, 176, 178, 205, 222, 224, 266, 301; HRMS(EI) calcd for $C_{11}H_9ClBr\,NO_2$ 300.9505, found 300.9497.

*4.2.20. (Z)-5,6-Dichloro-4-(chloromethyl)hexa-1,4-diene (**3at**).* Yield: 98% (97.1 mg) as a yellow oil; IR (KBr) ν 3088, 2928, 1523, 1272, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.83–5.73 (m, 1H), 5.17 (dd, J=3.2, 1.2 Hz, 1H), 5.13 (dd, J=10.2, 2.8 Hz, 1H), 4.29 (s, 2H), 4.25 (s, 2H), 3.12 (dt, J=6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.1, 130.5, 117.9, 44.9, 43.6, 34.8 ppm; MS (EI) m/z 77, 91, 127, 129, 163, 165, 198; HRMS(EI) calcd for $C_7H_9Cl_3$ 197.9770, found 197.9766.

*4.2.21. (Z)-1,2-Dichloro-3-(chloromethyl)hepta-2,5-diene:(E)-1,2-dichloro-3-(chloromethyl) hepta-2,5-diene=1:1.4] (**3bt**).* Yield: 90% (95.4 mg) as a yellow oil; IR (KBr) ν 3023, 2926, 1637, 1443, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.70–5.52 (m, 1H), 5.41–5.28 (m, 1H), 4.31 (d, J=6.8 Hz, 2H), 4.23 (s, 2H), 3.12 (d, J=7.6 Hz, 0.85H), 3.03 (d, J=6.4 Hz, 1.15H), 1.73–1.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.3, 129.9, 129.7, 128.9, 127.6, 125.7, 125.0, 45.0, 44.9, 43.7, 43.6, 33.7, 28.4, 17.9, 12.9 ppm; MS (EI) m/z 91, 105, 141, 143, 177, 212; HRMS(EI) calcd for $C_8H_{11}Cl_3$ 211.9926 found 211.9923.

*4.2.22. [(Z)-1,2-Dichloro-3-(chloromethyl)octa-2,5-diene:(E)-1,2-dichloro-3-(chloromethyl)octa-2,5-diene=1:1.5] (**3ct**).* Yield: 93% (105.1 mg) as a yellow oil; IR (KBr) ν 3017, 2931, 1636, 1443, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.63–5.53 (m, 1H), 5.38–5.21 (m, 1H), 4.31 (d, J=4.8 Hz, 2H), 4.23 (s, 2H), 3.11 (d, J=7.2 Hz, 0.8H), 3.04 (d, J=6.4 Hz, 1.2H), 2.18–2.11 (m, 0.8H), 2.07–2.00 (m, 1.2H), 1.03–0.96 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.4, 135.9, 135.3, 129.9, 129.7, 123.5, 123.4, 44.9, 43.6, 33.8, 28.7, 25.5, 20.7, 14.1, 13.5 ppm; MS (EI) m/z 91, 119, 155, 184, 193, 226; HRMS(EI) calcd for $C_9H_{13}Cl_3$ 226.0083 found 226.0081.

*4.2.23. (Z)-1,2-Dichloro-3-(chloromethyl)-6-methylhepta-2,5-diene (**3dt**).* Yield: 87% (98.3 mg) as a yellow oil; IR (KBr) ν 3027, 2923, 1635, 1442, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.05–5.02 (m, 1H), 4.32 (s, 2H), 4.22 (s, 2H), 3.06 (d, J=7.2 Hz, 2H), 1.72 (d, J=5.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 135.6, 129.3, 119.2, 45.0, 43.7, 29.6, 25.7, 17.9 ppm; MS (EI) m/z 119, 191, 193, 226; HRMS(EI) calcd for $C_9H_{13}Cl_3$ 226.0083 found 226.0082.

*4.2.24. [(Z)-1,2-Dichloro-3-(chloromethyl)undeca-2,5-diene:(E)-1,2-dichloro-3-(chloromethyl) undeca-2,5-diene=1:1] (**3et**).* Yield: 89% (119.3 mg) as a yellow oil; IR (KBr) ν 3015, 2927, 1636, 1448, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.61–5.51 (m, 1H), 5.38–5.24 (m, 1H), 4.31 (d, J=4.8 Hz, 2H), 4.23 (s, 2H), 3.16 (d, J=7.2 Hz, 1H), 3.04 (d, J=6.8 Hz, 1H), 2.12 (q, J=7.2 Hz, 1H), 2.01 (q, J=7.2 Hz, 1H), 1.43–1.24 (m, 6H), 0.92–0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.4, 134.6, 133.8, 129.9, 129.6, 124.3, 123.9, 45.0, 44.9, 43.6, 33.8, 32.4, 31.5, 31.4, 29.2, 28.9, 28.7, 27.3, 22.5, 22.4, 14.0 ppm; MS (EI) m/z 67, 77, 91, 113, 127, 149, 163, 184, 198, 268; HRMS(EI) calcd for $C_{12}H_{19}Cl_3$ 268.0552, found 268.0549.

*4.2.25. (Z)-(1-Bromo-2-chloropenta-1,4-dien-1-yl)benzene (**4a**).* Yield: 81% (103.7 mg) as a yellow oil; IR (KBr) ν 3077, 2924, 1610, 1489, 1438, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 5H), 5.87–5.77 (m, 1H), 5.15 (d, J=10.0 Hz, 1H), 5.10 (d, J=16.8 Hz, 1H), 3.08 (d, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 133.9, 133.0, 128.9, 128.8, 128.5, 120.5, 117.8, 40.8 ppm; MS (EI) m/z 115, 141, 162, 177, 223, 256; HRMS(EI) calcd for $C_{11}H_{10}ClBr$ 255.9654, found 255.9652.

*4.2.26. (Z)-1-(1-Bromo-2-chloropenta-1,4-dien-1-yl)-4-methylbenzene (**4b**).* Yield: 81% (109.4 mg) as a yellow oil; IR (KBr) ν 3081, 2924, 1641, 1458, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24–7.12 (m, 4H), 5.87–5.77 (m, 1H), 5.14 (dd, J=10.0, 1.2 Hz, 1H), 5.10 (dd, J=17.2, 1.2 Hz, 1H), 3.08 (dt, J=6.4, 1.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 135.9, 133.6, 133.1, 129.2, 128.7, 120.7, 117.7, 40.9, 21.3 ppm; MS (EI) m/z 115, 142, 177, 197, 270; HRMS(EI) calcd for $C_{12}H_{12}ClBr$ 269.9811, found 269.9808.

*4.2.27. (Z)-1-(1-Bromo-2-chloropenta-1,4-dien-1-yl)-4-methoxybenzene (**4c**).* Yield: 78% (111.5 mg) as a yellow oil; IR (KBr) ν 3079, 2925, 1640, 1460, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.24 (m, 2H), 6.89–6.86 (m, 2H), 5.88–5.78 (m, 1H), 5.15 (dd, J=10.4, 1.2 Hz, 1H), 5.10 (dd, J=17.2, 1.6 Hz, 1H), 3.82 (s, 3H), 3.08 (dt, J=6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 133.5, 133.2, 131.1, 130.2, 120.7, 117.7, 113.8, 55.4, 40.9 ppm; MS (EI) m/z 75, 102,

128, 141, 157, 171, 207, 286; HRMS(EI) calcd for $C_{12}H_{12}OClBr$ 285.9760, found 285.9756.

*4.2.28. (Z)-(1,2-Dibromopenta-1,4-dien-1-yl)benzene (**4d**).*[2k] Yield: 87% (130.5 mg) as a yellow oil; IR (KBr) ν 3082, 2923, 1645, 1450, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 5H), 5.85–5.75 (m, 1H), 5.15 (dd, J=10.4, 1.2 Hz, 1H), 5.09 (dd, J=17.2, 1.2 Hz, 1H), 3.16 (d, J=6.0, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 133.7, 128.9, 128.6, 127.2, 123.8, 117.7, 43.0 ppm; MS (EI) m/z 115, 142, 180, 193, 226, 228, 285, 287, 289, 300; HRMS(EI) calcd for $C_{11}H_{10}Br_2$ 299.9149, found 299.9147.

*4.2.29. (Z)-1-(1,2-Dibromopenta-1,4-dien-1-yl)-4-methylbenzene (**4e**).* Yield: 91% (142.8 mg) as a yellow oil; IR (KBr) ν 3079, 2921, 1641, 1506, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22–7.15 (m, 4H), 5.86–5.76 (m, 1H), 5.15 (dd, J=10.4, 1.2 Hz, 1H), 5.09 (dd, J=17.2, 1.2 Hz, 1H), 3.17 (d, J=6.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 136.3, 133.8, 129.2, 128.4, 126.8, 124.1, 117.6, 43.0, 21.3 ppm; MS (EI) m/z 115, 128, 141, 156, 160, 234, 238, 314; HRMS(EI) calcd for $C_{12}H_{12}Br_2$ 313.9306, found 313.9303.

*4.2.30. (Z)-1-(1,2-Dibromopenta-1,4-dien-1-yl)-4-ethylbenzene (**4f**).* Yield: 88% (144.3 mg) as a yellow oil; IR (KBr) ν 3079, 2967, 1602, 1456, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 4H), 5.87–5.77 (m, 1H), 5.16 (dd, J=10.4, 1.2 Hz, 1H), 5.12 (dd, J=16.4, 1.2 Hz, 1H), 3.18 (d, J=4.8 Hz, 2H), 2.69–2.63 (m, 2H), 1.25 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.5, 133.8, 128.5, 127.9, 126.8, 124.2, 117.6, 43.1, 28.7, 15.3 ppm; MS (EI) m/z 115, 128, 141, 155, 170, 328; HRMS(EI) calcd for $C_{13}H_{14}Br_2$ 327.9462, found 327.9460.

*4.2.31. (Z)-4-(1,2-Dibromopenta-1,4-dien-1-yl)-1,1′-biphenyl (**4g**).* Yield: 73% (137.2 mg) as a yellow solid; mp=157.5–158.7 °C; IR (KBr) ν 3080, 2921, 1640, 1504, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.56 (m, 4H), 7.45–7.33 (m, 5H), 5.88–5.78 (m, 1H), 5.17 (dd, J=10.0, 1.2 Hz, 1H), 5.12 (dd, J=17.2, 1.2 Hz, 1H), 3.22 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.1, 138.0, 133.7, 129.0, 128.9, 127.8, 127.3, 127.2, 127.1, 43.1 ppm; MS (EI) m/z 109, 165, 189, 202, 218, 376; HRMS(EI) calcd for $C_{17}H_{14}Br_2$ 375.9462, found 375.9458.

*4.2.32. (Z)-1-(1-Bromo-2-chloropenta-1,4-dien-1-yl)-4-(4-ethylcyclohexyl)benzene (**4h**).* Yield: 56% (114.8 mg) as a yellow oil; IR (KBr) ν 3080, 2921, 1640, 1504, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 2H), 7.21–7.17 (m, 2H), 5.86–5.76 (m, 1H), 5.15 (dd, J=10.0, 1.2 Hz, 1H), 5.10 (dd, J=16.8, 1.6 Hz, 1H), 3.18 (dt, J=6.0, 1.2 Hz, 2H), 2.50–2.43 (m, 1H), 1.92–1.86 (m, 4H), 1.48–1.39 (m, 2H), 1.27–1.18 (m, 3H), 1.09–1.02 (m, 2H), 0.908 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 136.5, 133.9, 128.5, 126.9126.8, 124.2, 117.6, 44.4, 43.0, 39.1, 34.2, 33.1, 29.9, 11.6 ppm; MS (EI) m/z 111, 141, 155, 168, 253, 410; HRMS(EI) calcd for $C_{19}H_{24}ClBr$ 410.0245, found 410.0243.

*4.2.33. (Z)-1-(1,2-Dibromopenta-1,4-dien-1-yl)-4-ethoxybenzene (**4i**).* Yield: 68% (116.9 mg) as a yellow oil; IR (KBr) ν 3079, 2926, 1640, 1476, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.25 (m, 2H), 6.87–6.84 (m, 2H), 5.86–5.76 (m, 1H), 5.15 (dd, J=10.4, 1.6 Hz, 1H), 5.10 (dd, J=16.8, 1.6 Hz, 1H), 4.04 (q, J=7.2 Hz, 2H), 3.18 (dt, J=6.4, 1.2 Hz, 2H), 1.42 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 133.8, 131.3, 129.9, 126.6, 124.1, 117.5, 114.3, 63.6, 43.0, 14.8 ppm; MS (EI) m/z 115, 128, 158, 186, 237, 267, 344; HRMS(EI) calcd for $C_{13}H_{14}OBr_2$ 343.9411, found 343.9407.

*4.2.34. (Z)-1-(1,2-Dibromopenta-1,4-dien-1-yl)-4-fluorobenzene (**4j**).* Yield: 78% (124.0 mg) as a yellow oil; IR (KBr) ν 3079, 2916, 1641, 1595, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.08–7.02 (m, 2H), 5.86–5.76 (m, 1H), 5.16 (dd, J=10.0, 1.2 Hz, 1H), 5.10 (dd, J=17.2, 1.2 Hz, 1H), 3.16 (t, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (J=248.2 Hz), 135.2 (J=3.4 Hz), 133.4, 130.5 (J=8.2 Hz), 127.7, 122.7, 117.7, 115.6 (J=21.7 Hz), 43.0 ppm; MS (EI) m/z 106, 133, 160, 180, 197, 224, 318; HRMS(EI) calcd for $C_{11}H_9Br_2F$ 317.9055, found 317.9053.

*4.2.35. (Z)-1-Chloro-4-(1,2-dibromopenta-1,4-dien-1-yl)benzene (**4k**).* Yield: 87% (145.3 mg) as a yellow oil; IR (KBr) ν 3080, 2920, 1641, 1486, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2H), 7.27–7.26 (m, 2H), 5.85–5.75 (m, 1H), 5.17 (dd, J=9.6, 0.8 Hz, 1H), 5.09 (dd, J=16.4, 0.8 Hz, 1H), 3.17 (d, J=6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.9, 133.4, 129.9, 128.8, 127.8, 122.4, 117.8, 43.0 ppm; MS (EI) m/z 113, 115, 141, 176, 257, 334; HRMS(EI) calcd for $C_{11}H_9ClBr_2$ 333.8760, found 333.8757.

*4.2.36. (Z)-1-Chloro-2-(1,2-dibromopenta-1,4-dien-1-yl)benzene (**4l**).* Yield: 80% (133.5 mg) as a yellow oil; IR (KBr) ν 3077, 2921, 1640, 1469, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 7.22–7.20 (m, 1H), 5.85–5.75 (m, 1H), 5.17 (dd, J=10.0, 1.2 Hz, 1H), 5.10 (dd, J=17.2, 1.2 Hz, 1H), 3.16 (d, J=6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 134.3, 133.3, 129.8, 129.1128.7, 128.2, 126.8, 121.9, 117.9, 43.1 ppm; MS (EI) m/z 113, 115, 141, 176, 222, 257, 334; HRMS(EI) calcd for $C_{11}H_9ClBr_2$ 333.8760, found 333.8757.

*4.2.37. (Z)-1-Bromo-4-(1,2-dibromopenta-1,4-dien-1-yl)benzene (**4m**).* Yield: 74% (139.8 mg) as a yellow oil; IR (KBr) ν 3080, 2923, 1641, 1483, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 2H), 7.22–7.19 (m, 2H), 5.85–5.75 (m, 1H), 5.16 (dd, J=10.0, 1.2 Hz, 1H), 5.09 (dd, J=17.2, 1.2 Hz, 1H), 3.15 (d, J=6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 133.4, 131.8, 130.2, 127.8, 123.2, 122.5, 117.8, 43.0 ppm; MS (EI) m/z 115, 141, 220, 222, 378; HRMS(EI) calcd for $C_{11}H_9Br_3$ 377.8254, found 377.8251.

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Supplementary data

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