DOI: 10.1002/chem.200901927

Applications of Allylsamarium Bromide as a Grignard Reagent and a Single-Electron Transfer Reagent in the One-Pot Synthesis of Dienes and Trienes

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Abstract: The utility of allylsamarium bromide, both as a nucleophilic reagent and a single-electron transfer (SET) reagent in the reaction of α-halo, γ-halo-α,β-unsaturated ketones and esters with allylsamarium bromide is reported for the first time in this paper. From a synthetic point of view, a general, efficient and experimentally simple one-pot method for the preparation of 1,4-dienes and trienes is developed. A possible mechanism of the transformation is proposed.

Keywords: alkenes · allylsamarium bromide · reaction mechanisms · samarium · single-electron transfer

Introduction

Alkenes are useful compounds in a large number of synthetic applications including epoxidation, hydroxylation, dihydroxylation, haloetherification and so forth. Especially dienes and trienes not only play an important role in the synthesis of many ligands, but also are found in the structure of numerous natural products and pharmaceutical agents.[1] Therefore, the synthesis of dienes and trienes is a very important issue in synthetic chemistry.[2] For alkene synthesis, one can use the condensation-type reaction of carbonyl compounds such as the Wittig reaction[3] or related reactions.[4] However, the condensation-type reaction is not effective for the synthesis of dienes and trienes, and although there are many other methods for the preparation of di- and trienes,[5,6] these methods suffer from disadvantages such as difficult-to-synthesise substrates, harsh reaction conditions, multistep procedures and so forth.

Since the pioneering work of Kagan in 1980,[7] applications of samarium diiodide as a mild, neutral, selective and versatile single-electron transfer (SET) reducing and coupling reagent in organic synthesis have already been well documented in several reviews,[8] and a variety reactions mediated by metallic samarium and other samarium reagents have also been reported.[9] Zhang first reported the convenient preparation of allylsamarium(II) bromide and used it successfully in Grignard-type reactions.[10] Compared to allylmagnesium bromide,[11] allylsamarium bromide is not as active, and it does not give rise to coupling by-products during preparation. However, that allylsamarium bromide can play the role of a SET reagent has not been reported.

We presume that allylsamarium(II) can be used as a SET reagent, like SmI_2. The question of whether allylsamarium bromide could play the role of a Grignard reagent and a SET reagent prompted us to conduct a study on the reaction of α-halo and γ-halo-α,β-unsaturated ketones and esters with allylsamarium bromide. We report herein the reaction of α-haloketones and esters with allylsamarium bromide under mild conditions; this one-pot transformation afforded di- and trienes in good yield, which, to our knowledge, has not been studied so far.

Results and Discussion

Several features of SmI_2 reductions that were exhibited in previous studies[12] led us to investigate the function of allylsamarium as a reductant for α-haloketones and esters. As shown in Scheme 1 and Table 1, the role of allylsamarium reduction has been proved. The α-haloketone and ester undergo reduction at −78 °C upon addition of the substrate in THF/MeOH to a solution of allylsamarium in THF, making it the reagent of choice for this transformation.

Encouraged by the above-mentioned reaction, we found that when α-haloketones **1** were treated with allylsamarium bromide (**2**) in THF at room temperature, 1,4-dienes **3** were obtained in good yields (Scheme 2). The α-haloketones and

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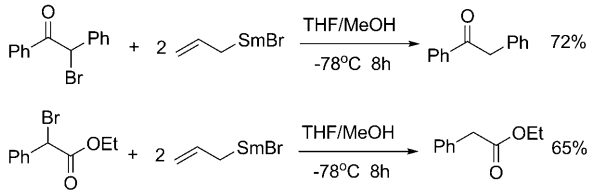
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901927.

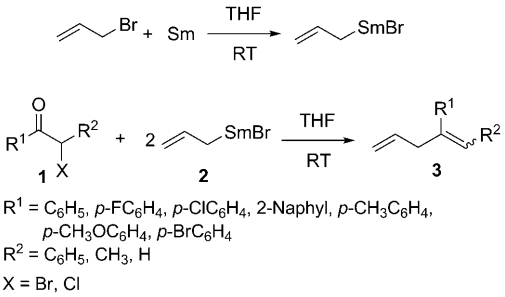


Scheme 1. Reduction of an α-haloketone and an ester with allylsamarium bromide.

Table 1. Comparison of the effect of ratio, temperature and solvent in the reduction of 2-bromo-1,2-diphenylethanone with allylsamarium bromide.

Entry	Ratio [substrate/ allylsamarium bromide]	T [°C]	Solvent	Yield[a] [%]
1	1:1	−78	THF/MeOH	26
2	1:2	−78	THF/MeOH	72
3	1:2	−78	THF	45
4	1:2	25	THF/MeOH	20

[a] Isolated yields based on 2-bromo-1,2-diphenylethanone.



Scheme 2. Reactions of α-haloketones with allylsamarium bromide.

allylsamarium bromide were used in a ratio of 1:2. All reactions were completed within 30 min, and good yields of 1,4-dienes were isolated. The product formation was ascertained by TLC monitoring, and the product isolation was achieved by quenching the reaction with dilute hydrochloric acid followed by a standard workup. The results were shown in Table 2.

Generally, the expected products can be obtained with good to excellent yields. Compared to α-chloroketones, α-bromoketone substrates result in higher yields, the reason probably is that the Br atom has better leaving ability than Cl. However, aromatic α-haloketones bearing a 4-methoxy group on the aromatic ring, showed poor yields (Table 2, entries 9 and 13). For the substrates (R^2=H), the corresponding 1,4-dienes have a pair of isomers. The Z isomer was the main product.

In addition, we also investigated the reaction of allylsamarium with an aliphatic α-haloketone (α-chlorocyclohexanone; **4**), and the corresponding 1,4-diene **5** was obtained successfully in moderate yield (50%; Scheme 3).

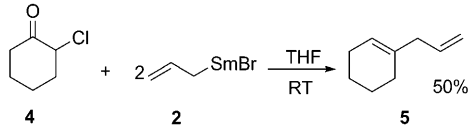
A plausible mechanism for this transformation is proposed in Scheme 4. Firstly, the ketone **A** undergoes allylation leading to the intermediate **B**. Then the halogen atom of intermediate **B** coordinates with allylsamarium bromide to afford intermediate **C**, which is followed by a *trans* elimination (a sequential single-electron transfer process) to give to the desired product **D**.

The stereochemistry of the reaction can be explained by the mechanism. We obtained the steady conformation **K** at the B3LYP/6-31G level (Scheme 5). In the process of allylation, the orientation of allyl anion attacking the plain of carbonyl decides the stereochemistry of the terminal product. There are two attacking paths shown in Scheme 5. In path a, the allyl anion attacks from the back of the plain of carbon-

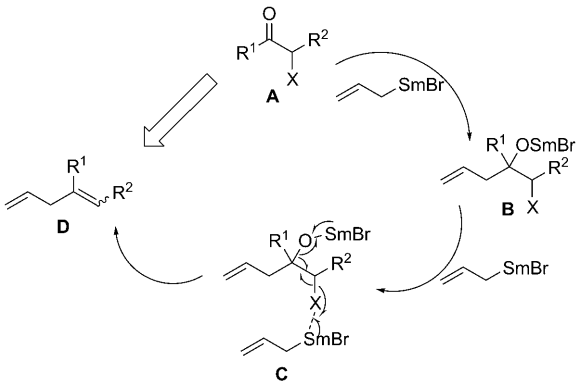
Table 2. Reactions of α-haloketones with allylsamarium bromide.

Entry	R^1	R^2	X	Yields[a] [%]	Z/E[b,c]
1	C_6H_5	C_6H_5	Cl	83	3.4:1
2	C_6H_5	C_6H_5	Br	80	5.3:1
3	4-FC_6H_4	H	Br	97	–
4	4-ClC_6H_4	H	Br	91	–
5	4-ClC_6H_4	H	Cl	70	–
6	C_6H_5	H	Br	95	–
7	2-Naphthyl	H	Br	95	–
8	4-$CH_3C_6H_4$	H	Br	83	–
9	4-$CH_3OC_6H_4$	H	Br	40	–
10	C_6H_5	CH_3	Br	90	4.9:1
11	C_6H_5	CH_3	Cl	85	3.4:1
l2	4-$CH_3C_6H_4$	CH_3	Cl	60	4.2:1
13	4-$CH_3OC_6H_4$	CH_3	Cl	35	6.0:1
14	4-ClC_6H_4	CH_3	Cl	75	4.0:1
15	4-BrC_6H_4	CH_3	Cl	60	3.6:1

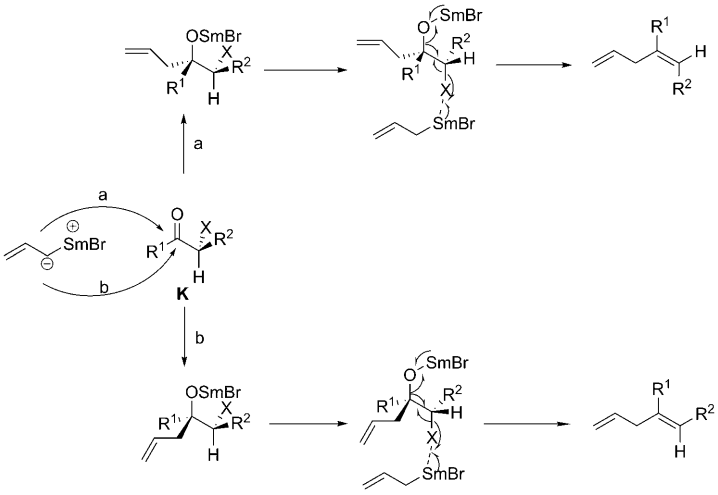
[a] Isolated yields based on α-haloketones. [b] The stereochemistry of the C=C bond of the 1,4-dienes was assigned based on the literature.[13] [c] The ratio Z/E was obtained from ^{1}H NMR spectroscopy.



Scheme 3. The reaction of allylsamarium bromide with an aliphatic α-haloketone.

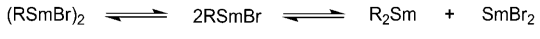


Scheme 4. Plausible mechanisms for the reaction of α-haloketones with allylsamarium bromide.



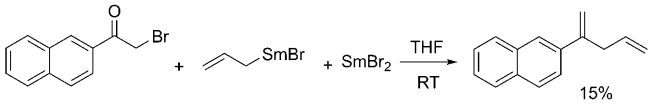
Scheme 5. The two attacking pathways decide the stereochemistry of the terminal products.

yl, then the bromine atom, acting as a ligand, coordinates with another equivalent of allylsamarium bromide followed by *trans* elimination leading to the *E* isomer. In contrast, in path b, allyl anion attacks from the front of the plain. As a result, the *Z* isomer was obtained. Because of the hindrance from the bulk and electron-repelling effect of the halogen atom, the allyl anion attacks the carbonyl from the side of R^2 group. So the reaction that followed the path b leads to *Z* alkenes.



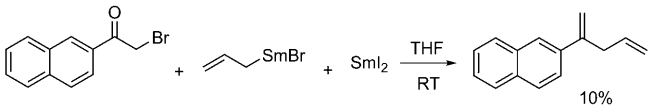
Scheme 6. The Schlenk equilibrium[14] in allylsamarium bromide solution.

Because of the Schlenk equilibrium[14] (Scheme 6) in allylsamarium bromide solution, it is possible that samarium dibromide could be the actual SET reagent. Therefore, we replaced the second molecular allylsamarium bromide by samarium dibromide to check this possibility. We carried out the reaction shown in Scheme 7. The ratio of 2-bromo-1-



Scheme 7. The reaction of 2-bromo-1-(naphthalen-2-yl)ethanone with allylsamarium bromide and samarium dibromide.

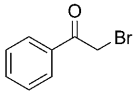
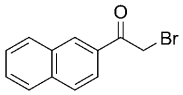
(naphthalen-6-yl)ethanone, allylsamarium bromide and samarium dibromide was 1:1:1. Evidently, the yield of desired product decreased seriously. This means that the second equivalent of allylsamarium bromide could not be replaced by samarium dibromide to facilitate the elimination step. Samarium diiodide was also checked in the reaction. Similarly, it did not facilitate the elimination step, but resulted in some side reactions, which was reflected from the poor yield (Scheme 8).



Scheme 8. The reaction of 2-bromo-1-(naphthalen-2-yl)ethanone with allylsamarium bromide and samarium diiodide.

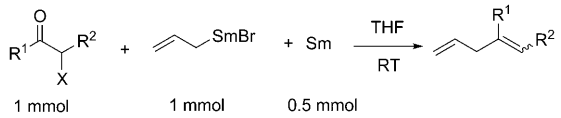
When the second equivalent of allylsamarium bromide was replaced by Sm powder, we obtained successfully the expected product in good yields (Table 3, entries 3 and 6),

Table 3. Reactions of α-haloketones with allylsamarium bromide and Sm powder in different ratios.

Entry	Substrate	Ratio	Yields[a] [%]
1		1:1:0	45
2		1:2:0	95
3		1:1:0.5	80
4		1:1:0	43
5		1:2:0	95
6		1:1:0.5	65

[a] Isolated yields based on α-haloketones.

but compared to the corresponding reaction without Sm powder (Table 3, entries 2 and 5), the yields were lower. This indicates that Sm powder can replace the second equivalent of allylsamarium bromide as an electron transfer reagent to some extent. Unfortunately, the loading of samarium powder also leads to some undesired reactions resulting in lower yields (Scheme 9, Table 3).



Scheme 9. The reaction of 2-bromo-1-(naphthalen-2-yl)ethanone with allylsamarium bromide and samarium powder.

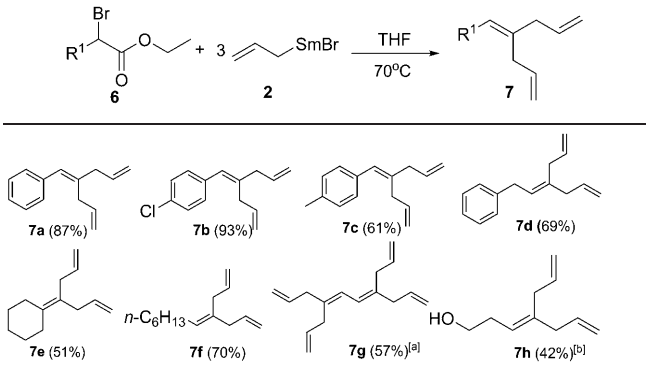
Moreover, we were pleased to find that the reaction was successfully extended to α-haloesters, which proved that the allylsamarium bromide was a SET reagent too. Firstly, we investigated the ratio of α-haloester to allylsamarium bromide (Table 4), which showed that the best ratio was 1:3. We next investigated the effect of temperature on the reaction yields of products. The results (Table 4, entries 6–8) showed clearly that the yields were improved remarkably under refluxing conditions.

Table 4. Comparison of the effect of ratio and temperature in the reaction of ethyl 2-bromo-2-phenylacetate and the allylsamarium bromide.[a]

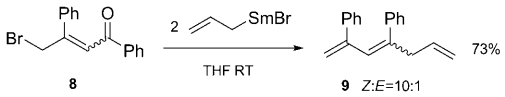
Entry	Ratios [substrate/ allylsamarium bromide]	T [°C]	t [h]	Yield[b] [%]
1	1:2	25	0.5	28
2	1:2.5	25	0.5	43
3	1:3	25	0.5	65
4	1:4	25	0.5	67
5	1:5	25	0.5	70
6	1:3	0	6	60
7	1:3	25	0.5	65
8	1:3	70	1	87

[a] All reaction were performed under a N_2 atmosphere. [b] Overall isolated yields after silica gel chromatography.

Table 5. Reactions of α-haloesters with allylsamarium bromide.

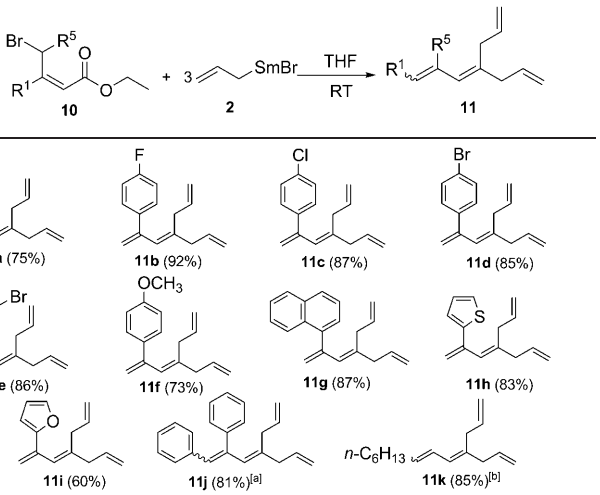


[a] Diethyl 2,3-dibromosuccinate as the substrate. [b] α-Bromo-γ-butyrolactone as the substrate.



Scheme 10. Reactions of γ-halo-α,β-unsaturated ketones with allylsamarium bromide.

Table 6. Reactions of γ-halo-α,β-unsaturated esters with allylsamarium bromide.



[a] Whether it is a Z or E configuration cannot be determined. [b] Z/E Configuration in a ratio of 1:6.4.

With the optimised reaction conditions, a variety of aromatic α-haloesters were prepared and treated with allylsamarium bromide. The results in Table 5 show that aromatic α-haloesters bearing a 4-chloro group on the aromatic ring give higher yields (**7b**, **7c**). To broaden the scope further, the reaction of allylsamarium bromide with aliphatic α-haloesters was also investigated, and the corresponding products were obtained successfully in moderate yields. Compared with the aromatic α-haloesters, the aliphatic α-haloesters did not have much higher activity; for instance, when they were treated with allylsamarium bromide at ambient temperature, the products (Table 5, **7e–h**) were not detected at all. When the reactions were run at reflux temperature, the corresponding products were obtained in moderate yields.

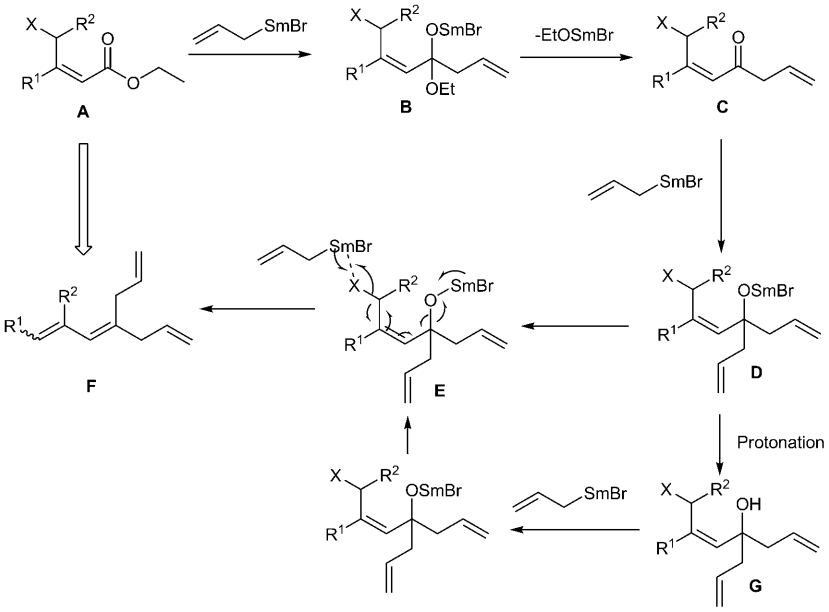
Based on the preceding section, we discuss the reaction of allylsamarium with γ-halo-α,β-unsaturated ketone. The experimental results summarised in Scheme 10 show the potential synthetic utility of the new route to disubstituted alkenes. One sample of **9** was obtained in good yield and stereochemistry (**9** as Z/E configuration in a ratio of 10:1).

It is worth mentioning that the use of γ-halo-α,β-unsaturated esters as the substrates can also react with the allylsamarium bromide to give trienes (Table 6, **11a–k**), which proved that the allylsamarium bromide was a SET reagent too. Treatment of **10** with exactly three equivalents of allylsamarium bromide followed by quenching with 1 N HCl cleanly provided **11** in good yields, but the substrates bearing electron-withdrawing groups on the aromatic ring showed higher yields. It should be emphasised here that the corresponding triene **11k** was obtained with good control of stereochemistry (**11k** as E configuration, see the ^{1}H and ^{13}C NMR spectra in the Supporting Information).

A possible mechanism for the reaction of haloesters with allylsamarium bromide is proposed in Scheme 11. Firstly, ester **A** undergoes allylation leading to the intermediate **B**, which converts to the compound **C**. Allylation of **C** with another allylsamarium bromide affords the intermediate **D** (its protonation-product **G** was separated), which undergoes a sequential SET process to afford the desired product **F**. At the same time, the intermediate **G** can also be converted to the target product by using two equivalents of allylsamarium bromide, which has been proved by experimentation.

Conclusion

In summary, we found allylsamarium bromide is not only a nucleophilic reagent but also a SET reagent that is efficiently applied to the synthesis of 1,4-dienes and trienes bz using α-halo, γ-halo-α,β-unsaturated ketones and esters as substrates. It is a new way and a general, efficient and experi-



Scheme 11. A possible mechanism about the reactions of haloesters with allylsamarium bromide.

mentally simple one-pot method for preparation of 1,4-dienes and trienes. Further investigation of the application of allylsamarium bromide demonstrated in this paper is in progress.

Experimental Section

General: THF was distilled from sodium benzophenone immediately prior to use. All reactions were conducted under a N_2 atmosphere. Metallic Sm and all solvents were purchased from commercial sources and were used without further purification. Flash column chromatography was carried out on Merck silica gel (300–400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts in ^1H NMR spectra are reported in parts per million downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal ($\delta = 77.50$ ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

Materials: All reactions were carried out under an atmosphere of N_2. The starting materials were prepared by published methods.[15] The other chemicals were purchased from the Aldrich or Acros chemical companies and were used without further purification. Petroleum ether (PE) that was used refers to the 30–60 °C boiling point fraction of petroleum.

General procedure for the synthesis of 1,2-diphenylethanone: Allyl bromide (2.1 mmol) and Sm (2.0 mmol) were suspended in dry THF (10 mL) under a N_2 atmosphere at RT. The mixture was stirred for about 5 min, and a purple colour formed. The stirring was continued until the Sm powder disappeared (1 h), after which time the resulting purple colour slurry of allylsamarium bromide formed was cooled to −78 °C and treated with a solution of the 2-bromo-1,2-diphenylethanone substrate (1.0 mmol) in MeOH (0.03 mL) and THF (2 mL). The resultant yellow mixture was stirred for 8 h at −78 °C, warmed to RT and then was quenched with dil aq HCl. The resulting mixture was extracted with Et_2O (3×10 mL), the Et_2O solution was washed with sat. NaCl (3×10 mL), and dried over anhyd $MgSO_4$. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded 1,2-diphenylethanone.

General procedure for the synthesis of 1,4-dienes: Allyl bromide (2.1 mmol) and Sm (2.0 mmol) were suspended in dry THF (10 mL) under a N_2 atmosphere at RT. The mixture was stirred for about 5 min, and a purple colour formed. The stirring was continued until the Sm powder disappeared (1 h). Then the solution of substrates (α-haloketones) was added dropwise (the reaction was monitored by TLC). The mixture was stirred for 20–30 min and then was quenched with dil aq HCl. The resulting mixture was extracted with Et_2O (3×10 mL), the Et_2O solution was washed with sat. NaCl (3×10 mL), and dried over anhyd $MgSO_4$. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded 1,4-dienes (300–400 mesh, petroleum ether 30–60 °C as eluent).

General procedure for the synthesis of trienes: Allyl bromide (3.1 mmol) and Sm (3.0 mmol) were suspended in dry THF (10 mL) under a N_2 atmosphere at RT. The mixture was stirred for about 5 min, and a purple colour formed. The stirring was continued until the Sm powder disappeared (1 h). Then the solution of substrates (α-halo or γ-halo-α,β-unsaturated esters) was added dropwise, and the reaction was monitored by TLC. The mixture was stirred for 20–30 min and then was quenched with dil aq HCl. The resulting mixture was extracted with Et_2O (3×10 mL), the Et_2O solution was washed with sat. NaCl (3×10 mL), and dried over anhyd $MgSO_4$. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded trienes (300–400 mesh, petroleum ether 30–60 °C as eluent).

General procedure for the reaction of 2-bromo-1-(naphthalen-6-yl)ethanone with allysamarium bromide and samarium dibromide:[16] 2-Bromo-1-(naphthalen-6-yl)ethanone (1 mmol) was added dropwise into the mixture of prepared allyl samarium bromide (1 mmol) and $SmBr_2$ (1 mmol) under a N_2 atmosphere at RT. A similar procedure was adopted for the reaction 2-bromo-1-(naphthalen-6-yl)ethanone, allylsamarium bromide and SmI_2. The work-up was similar to the procedure for the synthesis of 1,4-dienes.

General procedure for the reaction of α-haloketones with allysamarium bromide and Sm powder: Allyl bromide (1 mmol) and Sm (1.5 mmol) were suspended in dry THF (10 mL) under a N_2 atmosphere at RT. The mixture was stirred for about 5 min, and a purple colour formed. The stirring was continued about 1 h. Then the solution of substrate (1.0 mmol) was added dropwise. The work-up was similar to the procedure for the synthesis of 1,4-dienes.

(*Z*,*E*)-1,2-Diphenyl-1,4-pentadiene (3a, b): Compounds **3a**,**b** were obtained according to the general procedure. Colourless oil; yield: 83% (**3a**) and 80% (**3b**); $R_f = 0.82$ (PE); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.23$ (d, $^3J_{H,H} = 6.0$ Hz, 2H; $CH_2CH{=}CH_2$; *Z* isomer), 3.48 (d, $^3J_{H,H} = 5.62$ Hz, 2H; $CH_2CH{=}CH_2$; *E* isomer), 5.06–5.15 (m, 2H; $CH_2{=}CH$), 5.85–5.94 (m, 1H; $CH{=}CH_2$), 6.45 (s, 1H; CHAr; *Z* isomer), 6.94–7.53 ppm (m, 10H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 35.07$ ($CHCH{=}CH_2$; *E* isomer), 45.17 ($CHCH{=}CH_2$; *Z* isomer), 117.15, 116.87 ($2\times CH_2{=}CH$), 126.73, 126.95, 127.32, 127.44, 127.48, 127.77, 128.30, 128.74, 128.83, 128.93, 129.03, 129.19, 129.50, 129.93, 136.31, 136.45, 137.76, 138.29, 141.64, 141.67 ppm ($16\times C_{Ar}$, $4\times C_{alkene}$); HRMS (EI^+): *m*/*z* calcd for $C_{17}H_{16}$: 220.1252 $[M]^+$; found: 220.1255.

2-(4-Fluorophenyl)-1,4-pentadiene (3c): Compound **3c** was obtained according to the general procedure. Colourless oil; yield: 97%; $R_f = 0.95$ (PE); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.22$ (d, $^3J_{H,H} = 6.4$ Hz, 2H; CH_2CH), 5.03–5.13 (m, 3H; $CH_{2a}{=}C$, $CH_2{=}CH$), 5.34 (s, 1H; $CH_{2b}{=}C$), 5.83–5.93 (m, 1H; $CH{=}CH_2$), 6.98–7.03 (m, 2H; Ar), 7.38–7.42 ppm (m,

2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=40.10 (CH_2CH), 113.60, 117.12 136.45, 145.71 (4×C_{alkene}), 115.53 ($^4J_{C,F}$=21.3 Hz), 128.06 ($^3J_{C,F}$=7.7 Hz), 137.38 ($^2J_{C,F}$=3.3 Hz), 162.73 ppm ($^1J_{C,F}$=244.9 Hz, 4×C_{Ar}); HRMS (EI$^+$): *m*/*z* calcd for $C_{11}H_{11}F$: 162.0845 [*M*]$^+$; found: 162.0839.

2-(4-Chlorophenyl)-1,4-pentadiene (3d,e): Compounds **3d**,**e** were obtained according to the general procedure. Colourless oil; yield: 91% (**3d**) and 70% (**3e**); R_f=0.90 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.22 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH), 5.06–5.13 (m, 3H; CH_{2a}=C, CH_2=CH), 5.38 (s, 1H; CH_{2b}=C), 5.82–5.92 (m, 1H; C*H*=CH_2), 7.27–7.37 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=39.88 (CH_2CH), 114.23 (CH_2=C), 117.22 (CH_2=CH), 127.79, 128.86, 133.67, 136.30, 139.73, 145.60 ppm (4×C_{Ar}, 2×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{11}H_{11}{}^{35}Cl$: 178.0549 [*M*]$^+$; found: 178.0569.

2-Phenyl-1,4-pentadiene (3f): Compound **3f** was obtained according to the general procedure. Colourless oil; yield: 95%; R_f=0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.25 (d, $^3J_{H,H}$=6.0 Hz, 2H; CH_2CH), 5.05–5.14 (m, 3H; CH_{2a}=C, CH_2=CH), 5.39 (s, 1H; CH_{2b}=C), 5.86–5.94 (m, 1H; C*H*=CH_2), 7.24–7.45 ppm (m, 5H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=39.97 (CH_2CH), 113.64 (CH_2=C), 116.96 (CH_2=CH), 126.45, 127.92, 128.73, 136.66, 141.38, 146.76 ppm (4×C_{Ar}, 2×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{11}H_{12}$: 144.0939 [*M*]$^+$; found: 144.1009.

2-(2-Naphthyl)-1,4-pentadiene (3g): Compound **3g** was obtained according to the general procedure. Colourless oil; yield: 95%; R_f=0.82 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.37 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH), 5.08–5.21 (m, 3H; CH_{2a}=C, CH_2=CH), 5.55 (s, 1H; CH_{2b}=C), 5.93–5.99 (m, 1H; C*H*=CH_2), 7.42–7.85 ppm (m, 7H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=39.97 (CH_2CH), 114.21 (CH_2=C), 117.06 (CH_2=CH), 124.91, 125.15, 126.32, 126.59, 127.98, 128.54, 128.68, 133.24, 133.78, 136.67, 138.50, 146.53 ppm (10×C_{Ar}, 2×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{15}H_{14}$: 194.1096 [*M*]$^+$; found: 194.1090.

2-(4-Methylphenyl)-1,4-pentadiene (3h): Compound **3h** was obtained according to the general procedure. Colourless oil; yield: 83%; R_f=0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.34 (s, 3H; CH_3), 3.24 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH), 5.05–5.13 (m, 3H; CH_{2a}=C, CH_2=CH), 5.36 (s, 1H; CH_{2b}=C), 5.85–5.95 (m, 1H, C*H*=CH_2), 7.12–7.14 (m, 2H; Ar), 7.33–7.35 ppm (m, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.58 (CH_3), 39.98 (CH_2CH), 112.82 (CH_2=C), 116.85 (CH_2=CH), 126.31, 129.42, 136.78, 137.68, 138.39, 146.53 ppm (4×C_{Ar}, 2×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_{14}$: 158.1096 [*M*]$^+$; found: 158.1103.

2-(4-Methoxyphenyl)-1,4-pentadiene (3i): Compound **3i** was obtained according to the general procedure. Colourless oil; yield: 40%; R_f=0.91 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.23 (d, $^3J_{H,H}$=6 Hz, 2H; CH_2CH), 3.81 (s, 3H; OCH_3), 5.01–5.13 (m, 3H; CH_{2a}=C, CH_2=CH), 5.32 (s, 1H; CH_{2b}=C), 5.85–5.95 (m, 1H, C*H*=CH_2), 6.86 (d, $^3J_{H,H}$=8.8 Hz, 2H; Ar), 7.39 ppm (d, $^3J_{H,H}$=8.8 Hz, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=40.07 (CH_2CH), 55.74 (OCH_3), 112.00 (CH_2=C), 114.06 (CH_2=CH), 116.82, 127.56, 133.78, 136.87, 146.02, 159.53 ppm (4×C_{Ar}, 2×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_{14}O$: 174.1045 [*M*]$^+$; found: 174.1037.

(*Z*,*E*)-2-Phenyl-1-methyl-1,4-pentadiene (3j,k): Compounds **3j**,**k** were obtained according to the general procedure. Colourless oil; yield: 90% (**3j**) and 85% (**3k**); R_f=0.81 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.59 (d, $^3J_{H,H}$=6.8 Hz, 3H; CH_3; *E* isomer), 1.79 (d, $^3J_{H,H}$=6.8 Hz, 3H; CH_3; *Z* isomer), 3.08 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH=CH_2; *E* isomer), 3.26 (d, $^3J_{H,H}$=5.6 Hz, 2H; CH_2CH=CH_2; *Z* isomer), 4.96–5.09 (m, 2H; CH_2=CH), 5.54–5.60 (m, 1H; C*H*CH_3; *E* isomer), 5.79–5.96 (m, 2H; C*H*CH_3, C*H*=CH_2), 7.16–7.37 ppm (m, 7H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.72 (CH_3; *Z* isomer), 15.26 (CH_3; *E* isomer), 34.57 (CH_2CH; *Z* isomer), 43.82 (CH_2CH; *E* isomer), 115.61, 116.28, 122.72, 124.77, 126.43, 126.92, 126.96, 128.46, 128.63, 128.97, 136.14, 137.13, 138.02, 143.60 ppm (8×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_{14}$: 158.1096 [*M*]$^+$; found: 158.1100.

(*Z*,*E*)-2-(4-Methylphenyl)-1-methyl-1,4-pentadiene (3l): Compound **3l** was obtained according to the general procedure. Colourless oil; yield: 60%; R_f=0.95 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.60 (d, $^3J_{H,H}$=6.8 Hz, 3H; CHCH_3; *E* isomer), 1.78 (d, $^3J_{H,H}$=7.2 Hz, 3H; CHCH_3; *Z* isomer), 2.32 (s, 3H; $ArCH_3$; *Z* isomer), 2.34 (s, 3H; $ArCH_3$; *E* isomer), 3.07 (d, $^3J_{H,H}$=6.8 Hz, 2H; CHCH_2; *E* isomer), 3.24 (d, $^3J_{H,H}$=6.8 Hz, 2H; CHCH_2; *Z* isomer), 4.97–5.09 (m, 2H; CH=CH_2), 5.52–5.57 (m, 1H; C=C*H*; *E* isomer), 5.81–5.93 (m, 2H; C=C*H*, CH_2=C*H*), 7.06–7.27 ppm (m, 5H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.65 (CHCH_3; *Z* isomer), 15.29 (CHCH_3; *E* isomer), 21.51 (ArCH_3; *Z* isomer), 21.65 (ArCH_3; *E* isomer), 34.53 (CH_2CH; *Z* isomer), 43.86 (CH_2CH; *E* isomer), 115.55, 116.18, 122.45, 123.91, 126.29, 128.84, 129.17, 129.34, 136.23, 136.58, 137.27, 137.81, 140.65 ppm (7×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{13}H_{16}$: 172.1252 [*M*]$^+$; found: 172.1249.

(*Z*,*E*)-2-(4-Methoxyphenyl)-1-methyl-1,4-pentadiene (3m): Compound **3m** was obtained according to the general procedure. Colourless oil; yield: 35%; R_f=0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.60 (d, $^3J_{H,H}$=6.8 Hz, 3H; CHCH_3; *E* isomer), 1.77 (d, $^3J_{H,H}$=6.8 Hz, 3H; CHCH_3; *Z* isomer), 3.06 (d, $^3J_{H,H}$=5.6 Hz, 2H; CHCH_2; *E* isomer), 3.23 (d, $^3J_{H,H}$=4.8 Hz, 2H; CHCH_2; *Z* isomer), 3.80 (s, 3H, OCH_3; Z isomer), 3.81 (s, 3H; OCH_3; *E* isomer), 4.96–5.09 (m, 2H; CH=CH_2), 5.51–5.56 (m, 1H; C=C*H*; *E* isomer), 5.76–5.86 (m, 2H; C=C*H*, CH_2=C*H*), 6.82–7.31 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.62 (CHCH_3; *Z* isomer), 15.30 (CHCH_3; *E* isomer), 34.59 (CH_2CH; *Z* isomer), 43.93 (CH_2CH; *E* isomer), 55.65 (OCH_3, *E* isomer), 55.71 (OCH_3, *Z* isomer), 113.83, 113.98, 155.55, 116.15, 122.35, 123.13, 127.45, 130.04, 136.26, 137.41, 158.82 ppm (6×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{13}H_{16}O$: 188.1201 [*M*]$^+$; found: 188.1194.

(*Z*,*E*)-2-(4-Chlorophenyl)-1-methyl-1,4-pentadiene (3n): Compound **3n** was obtained according to the general procedure. Colourless oil; yield: 75%; R_f=0.78 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.58 (d, $^3J_{H,H}$=6.8 Hz, 3H; CHCH_3; *E* isomer), 1.79 (d, $^3J_{H,H}$=7.2 Hz, 3H; CHCH_3; *Z* isomer), 3.05 (d, $^3J_{H,H}$=6.4 Hz, 2H; CHCH_2; *E* isomer), 3.22 (d, $^3J_{H,H}$=6.4 Hz, 2H; CHCH_2; *Z* isomer), 4.97–5.07 (m, 2H; CH=CH_2), 5.56–5.61 (m, 1H; C=C*H*; *E* isomer), 5.71–5.87 (m, 1H; CH_2=C*H*), 5.90–5.95 (m, 1H; C=CH; *Z* isomer), 7.09–7.31 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.72 (CHCH_3; *Z* isomer), 15.24 (CHCH_3; *E* isomer), 34.41 (CH_2CH; *Z* isomer), 43.70 (CH_2CH; *E* isomer), 115.85, 116.57, 123.48, 125.33, 127.73, 128.66, 128.70, 128.76, 130.36, 132.63, 135.78, 136.78, 136.99, 139.67, 141.97 ppm (8×C_{Ar}, 7×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_{13}{}^{35}Cl$: 192.0706 [*M*]$^+$; found: 192.0716.

(*Z*,*E*)-2-(4-Bromophenyl)-1-methyl-1,4-pentadiene (3o): Compound **3o** was obtained according to the general procedure. Colourless oil; yield: 60%; R_f=0.81 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.57 (d, $^3J_{H,H}$=6.0 Hz, 3H; CHCH_3; *E* isomer), 1.78 (d, $^3J_{H,H}$=7.2 Hz, 3H; CHCH_3; *Z* isomer), 3.04 (d, $^3J_{H,H}$=6.0 Hz, 2H; CHCH_2; *E* isomer), 3.22 (d, $^3J_{H,H}$=5.2 Hz, 2H; CHCH_2; *Z* isomer), 4.97–5.07 (m, 2H; CH=CH_2), 5.56–5.61 (m, 1H; C=C*H*; *E* isomer), 5.71–5.86 (m, 1H; CH_2=C*H*), 5.90–5.95 (m, 1H, C=CH; *Z* isomer), 7.03–7.46 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.74 (CHCH_3; *Z* isomer), 15.25 (CHCH_3; *E* isomer), 34.36 (CH_2CH; *Z* isomer), 43.64 (CH_2CH; *E* isomer), 115.88, 116.61, 120.77, 123.51, 125.44, 128.12, 130.74, 131.62, 131.66, 135.77, 136.76, 137.03, 142.44 ppm (7×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{12}H_{13}{}^{81}Br$: 238.0180 [*M*]$^+$; found: 238.0190; *m*/*z* calcd for $C_{12}H_{13}{}^{79}Br$: 236.0201 [*M*]$^+$; found: 236.0207.

1-Allylcyclohex-1-ene (5): Compound **5** was obtained according to the general procedure. Colourless oil; yield: 50%; R_f=0.92 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.54–1.64 (m, 4H; $CH_{2a}CH_{2b}$), 1.92–2.00 (m, 4H; $CH_{2c}CH_{2d}$), 2.66 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH), 4.98–5.04 (m, 2H; CH=CH_2), 5.43 (m, 1H; CH=C), 5.75–5.85 ppm (m, 1H; C*H*=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.96, 23.44, 25.77, 25.81 (4×CH_2), 43.03 (CH_2CH), 115.92, 122.35, 136.79, 137.46 ppm (4×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for C_9H_{14}: 122.1096 [*M*]$^+$; found: 122.1090.

(2-Allylpenta-1,4-dienyl)benzene (7a): Compound **7a** was obtained according to the general procedure. Colourless oil; yield: 90%; R_f=0.82 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.90–2.99 (m, 4H; 2×CH_2CH), 5.08–5.14 (m, 4H; 2×CH=CH_2), 5.81–5.94 (m, 2H; 2×C*H*=CH_2), 6.40 (s, 1H; CH=C), 7.17–7.33 ppm (m, 5H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=35.83, 41.98 (2×CH_2CH), 116.64, 117.06, 126.77, 127.77, 128.58, 128.93, 136.38, 136.81, 138.43, 139.13 ppm (4×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{14}H_{16}$: 184.1252 [*M*]$^+$; found: 184.1256.

1-(2-Allylpenta-1,4-dienyl)-4-chlorobenzene (7b): Compound **7b** was obtained according to the general procedure. Colourless oil; yield: 93%; R_f=0.84 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89–2.95 (m, 4H; 2×

CH_2CH), 5.07–5.14 (m, 4H; 2×CH=CH_2), 5.80–5.91 (m, 2H; 2×CH=CH_2), 6.34 (s, 1H; CH=C), 7.14–7.27 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=35.78, 42.00 (2×CH_2CH), 116.79, 117.29, 126.61, 128.71, 130.21, 132.48, 136.00, 136.50, 136.82, 139.95 ppm (4×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{14}H_{15}{}^{35}Cl$: 218.0862 $[M]^+$; found: 218.0859; $C_{14}H_{15}{}^{37}Cl$: 220.0833 $[M]^+$; found: 220.0856.

1-(2-Allylpenta-1,4-dienyl)-4-methylbenzene (7c): Compound **7c** was obtained according to the general procedure. Colourless oil; yield: 61%; R_f=0.95 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.33 (s, 3H; CH_3), 2.89–2.99 (m, 4H; 2×CH_2CH), 5.08–5.12 (m, 4H; 2×CH=CH_2), 5.82–5.92 (m, 2H; 2×CH=CH_2), 6.37 (s, 1H; CH=C), 7.10–7.15 ppm (m, 4H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.62 (CH_3), 35.84, 42.03 (2× CH_2CH), 116.55, 116.96, 127.62, 128.83, 129.29, 135.51, 136.38, 136.45, 136.92, 138.41 ppm (4×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{15}H_{18}$: 198.1409 $[M]^+$; found: 198.1418.

(3-Allylhexa-2,5-dienyl)benzene (7d): Compound **7d** was obtained according to the general procedure. Colourless oil; yield: 69%; R_f=0.75 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.77–2.89 (m, 4H; 2×CH_2CH=CH_2), 3.38 (d, $^3J_{H,H}$=7.2 Hz, 2H; CH_2CH=C); 5.01–5.09 (m, 4H; 2×CH=CH_2), 5.44 (t, $^3J_{H,H}$=7.2 Hz, 1H; CH=C), 5.72–5.84 (m, 2H; 2×CH=CH_2), 7.16–7.28 ppm (m, 5H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=34.57, 35.09 (2×CH_2CH=CH_2), 41.85 (ArCH), 116.02, 116.56, 126.04, 126.28, 128.82, 128.83, 136.20, 136.63, 137.15, 141.73 ppm (4×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{15}H_{18}$: 198.1409 $[M]^+$; found: 198.1414.

Hepta-1,6-dien-4-ylidenecyclohexane (7e): Compound **7e** was obtained according to the general procedure. Colourless oil; yield: 51%; R_f=0.83 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.51–1.57 (m, 6H; $CH_2CH_2CH_2$), 2.15 (t, $^3J_{H,H}$=6.0 Hz, 4H; CH_2CCH_2), 2.77 (d, $^3J_{H,H}$=5.6 Hz, 4H; 2×CH_2CH), 4.94–5.01 (m, 4H; 2×CH=CH_2), 5.69–5.79 ppm (m, 2H; 2×CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=27.38, 28.83, 31.08 (2×CH_2), 36.62 (CH_2CH), 114.91, 124.18, 136.73, 137.48 ppm (4×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{13}H_{20}$: 176.1565 $[M]^+$; found: 176.1557.

4-Allylundeca-1,4-diene (7f): Compound **7f** was obtained according to the general procedure. Colourless oil; yield: 70%; R_f=0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, $^3J_{H,H}$=7.2 Hz, 3H; CH_3), 1.27–1.33 (m, 8H; $CH_2CH_2CH_2CH_2$OH), 1.98–2.03 (m, 2H; CH_2CH=C), 2.71–2.78 (m, 4H; 2×CH_2CH=CH_2), 4.97–5.04 (m, 4H; 2×CH=CH_2), 5.24 (t, $^3J_{H,H}$=7.2 Hz, 1H; CH=C), 5.68–5.82 ppm (m, 2H; 2×CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.59 (CH_3), 23.16, 28.37, 29.57, 30.38, 32.30 (CH_2 $CH_2CH_2CH_2CH_2$), 35.07, 41.83 (2×CH_2CH=CH_2), 115.61, 116.18, 127.86, 135.38, 136.66, 137.59 ppm (6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{14}H_{24}$: 192.1878 $[M]^+$; found: 192.1867.

4,7-Diallyldeca-1,4,6,9-tetraene (7g): Compound **7g** was obtained according to the general procedure. Colourless oil; yield: 57%; R_f=0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.81–2.92 (m, 8H; 4×CH_2CH=CH_2), 5.00–5.06 (m, 8H; 4×CH=CH_2), 5.70–5.84 (m, 4H; 4×CH=CH_2), 6.11 ppm (s, 2H; CHCH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=35.47, 42.35 (2×CH_2CH), 116.11, 116.82, 122.64, 136.22, 136.89, 137.80 ppm (6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{22}$: 173.1331 $[M-C_3H_5]^+$; found: 173.1300.

4-Allylhepta-3,6-dien-1-ol (7h): Compound **7h** was obtained according to the general procedure. Yellow oil; yield: 42%; R_f=0.33 (PE/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.84 (brs, 1H; OH); 2.30–2.35 (m, 2H; CH_2CH=C), 2.76–2.82 (m, 4H; 2×CH_2CH=CH_2), 3.62–3.65 (t, $^3J_{H,H}$=6.4 Hz, 2H; CH_2OH), 5.00–5.66 (m, 4H; 2×CH=CH_2), 5.26 (t, $^3J_{H,H}$=7.2 Hz, 1H; CH=C), 5.73–5.81 ppm (m, 2H; 2×CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ=31.86 (CH_2CH_2OH), 35.13 (C_aH_2CH=CH_2), 41.86 (C_bH_2CH=CH_2), 62.85 (CH_2OH), 115.95, 116.65, 122.87, 136.28, 137.03, 139.12 ppm (6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{10}H_{16}$: 152.1501 $[M]^+$; found: 152.1512.

(*Z*,*E*)-Hepta-1,3,6-triene-2,4-diyldibenzene (9): Compound **9** was obtained according to the general procedure. Colourless oil; yield: 73%; R_f=0.86 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.15 (d, $^3J_{H,H}$=6.4 Hz, 2H; CH_2CH; *Z* isomer). 3.34 (d, $^3J_{H,H}$=4.8 Hz, 2H; CH_2CH; *E* isomer), 4.80 (s, 1H; CH_{2a}=C), 4.96–5.04 (m, 2H; CH_2=CH), 5.20 (s, 1H; CH_{2b}=C), 5.76–5.86 (m, 1H; CH=CH_2), 6.15 (s, 1H; CH=C; *Z* isomer), 6.50 (s, 1H; CH=C; *E* isomer), 7.03–7.29 ppm (m, 10H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ=44.13 (CH_2CH), 116.91, 117.11, 126.98, 127.12, 127.80, 128.33, 128.55, 128.68, 128.80, 136.43, 141.22, 141.24, 143.26, 145.23 ppm (8×C_{Ar}, 6×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{19}H_{18}$: 246.1409 $[M]^+$; found: 246.1418.

(4-Allylhepta-1,3,6-trien-2-yl)benzene (11a): Compound **11a** was obtained according to the general procedure. Colourless oil; yield: 75%; R_f=0.87 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 2.92 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 5.00–5.14 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.52 (s, 1H; CH_{2b}=C), 5.71–5.92 (m, 2H; 2×CH=CH_2), 6.05 (s, 1H; CH=C), 7.24–7.31 (m, 3H; Ar), 7.40 ppm (d, $^3J_{H,H}$=8.0 Hz, 2H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.22, 41.32 (2× CH_2CH), 114.43, 116.49, 117.02, 126.93, 127.37, 127.99, 128.67, 136.75, 136.83, 140.73, 141.31, 145.12 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{18}$: 210.1409 $[M]^+$; found: 210.1404.

1-(4-Allylhepta-1,3,6-trien-2-yl)-4-fluorobenzene (11b): Compound **11b** was obtained according to the general procedure. Colourless oil; yield: 92%; R_f=0.92 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.90 (t, $^3J_{H,H}$=8.0 Hz, 4H; 2×CH_2CH), 5.00–5.12 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.46 (s, 1H; CH_{2b}=C), 5.71–5.92 (m, 2H; 2×CH=CH_2), 6.01 (s, 1H; CH=C), 6.97–7.02 (m, 2H; Ar), 7.34–7.38 ppm (m, 2H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.24, 41.33 (2×CH_2CH), 114.27 ($^4J_{C,F}$=9.0 Hz),115.36, 115.64, 116.60, 117.15, 127.18, 128.57 ($^3J_{C,F}$=8.3 Hz), 136.69 ($^2J_{C,F}$=3.7 Hz), 141.08, 144.13, 162.91 ppm ($^1J_{C,F}$=245.3 Hz, 4×C_{Ar}, 7×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{17}F$: 228.1314 $[M]^+$; found: 228.1315.

1-(4-Allylhepta-1,3,6-trien-2-yl)-4-chlorobenzene (11c): Compound **11c** was obtained according to the general procedure. Colourless oil; yield: 87%; R_f=0.90 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89 (d, $^3J_{H,H}$=8.0 Hz, 4H; 2×CH_2CH), 5.00–5.15 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.50 (s, 1H; CH_{2b}=C), 5.70–5.91 (m, 2H; 2×CH=CH_2), 6.00 (s, 1H; CH=C), 7.24–7.33 ppm (m, 4H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.26, 41.33 (2×CH_2CH), 114.89,116.64, 117.18, 126.88, 128.26, 128.83, 133.85, 136.62, 139.79, 141.34, 144.09 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{17}{}^{35}Cl$ (M^+): 244.1019; found: 244.1020; $C_{16}H_{17}{}^{37}Cl$: 246.0989 $[M]^+$; found: 246.0979.

1-(4-Allylhepta-1,3,6-trien-2-yl)-4-bromobenzene (11d): Compound **11d** was obtained according to the general procedure. Colourless oil; yield: 85%; R_f=0.90 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89 (d, $^3J_{H,H}$=8.0 Hz, 4H; 2×CH_2CH), 4.99–5.16 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.50 (s, 1H; CH_{2b}=C), 5.70–5.91 (m, 2H; 2×CH=CH_2), 5.99 (s, 1H; CH=C), 7.26 (d, $^3J_{H,H}$=8.0 Hz, 2H; Ar), 7.43 (d, $^3J_{H,H}$=8.0 Hz, 2H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.25, 41.32 (2×CH_2CH), 114.96, 116.65, 117.20, 122.03, 126.77, 128.59, 131.77, 136.59, 140.23, 141.38, 144.10 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{17}{}^{79}Br$: 288.0514 $[M]^+$; found: 288.0514; m/z calcd for $C_{16}H_{17}{}^{81}Br$: 290.0493 $[M]^+$; found: 290.0515.

1-(4-Allylhepta-1,3,6-trien-2-yl)-2-bromobenzene (11e): Compound **11e** was obtained according to the general procedure. Colourless oil; yield: 86%; R_f=0.88 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.75 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 2.82 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 4.91–5.13 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.36 (s, 1H; CH_{2b}=C), 5.61–5.86 (m, 2H; 2×CH=CH_2), 6.00 (s, 1H; CH=C), 7.10–7.56 ppm (m, 4H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=35.94, 42.00 (2×CH_2CH), 116.44, 117.04, 119.26, 122.84, 127.35, 127.68, 129.05, 130.98, 133.24, 136.34, 136.65, 139.68, 143.96, 146.51 ppm (6×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{16}H_{17}{}^{79}Br$: 288.0514 $[M]^+$; found: 288.0514; $C_{16}H_{17}{}^{81}Br$: 290.0493 $[M]^+$; found: 290.0515.

1-(4-Allylhepta-1,3,6-trien-2-yl)-4-methoxybenzene (11f): Compound **11f** was obtained according to the general procedure. Colourless oil; yield: 73%; R_f=0.78 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 2.93 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2CH), 3.81 (s, 3H; OCH_3), 5.00–5.13 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.45 (d, $^3J_{H,H}$=4.0 Hz, 1H; CH_{2b}=C), 5.72–5.93 (m, 2H; 2×CH=CH_2), 6.03 (s, 1H; CH=C), 6.86 (d, $^3J_{H,H}$=12.0 Hz, 2H; Ar), 7.34 ppm (d, $^3J_{H,H}$=8.0 Hz, 2H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.25, 41.30 (2×CH_2CH), 55.77 (OCH_3), 112.72, 114.04, 116.47, 117.00, 127.59, 128.07, 133.84, 136.84, 136.98, 140.55, 144.43, 159.68 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): m/z calcd for $C_{17}H_{20}O$: 240.1514 $[M]^+$; found: 240.1514.

1-(4-Allylhepta-1,3,6-trien-2-yl)naphthalene (11g): Compound **11g** was obtained according to the general procedure. Colourless oil; yield: 87%; R_f=0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.94 (s, 4H; 2×CH_2CH), 5.00–5.16 (m, 4H; 2×CH_2=CH), 5.23 (s, 1H; CH_{2a}=C), 5.65 (s, 1H; CH_{2b}=C), 5.74–5.95 (m, 2H; 2×C*H*=CH_2), 6.16 (s, 1H; CH=C), 7.40–7.78 ppm (m, 8H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.34, 41.38 (2×CH_2CH), 114.99, 116.57, 117.09, 125.07, 125.96, 126.32, 126.56, 127.40, 128.01, 128.26, 128.69, 133.36, 133.81, 136.82, 138.58, 140.96, 145.04 ppm (9×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{17}H_{20}$: 260.1565 $[M]^+$; found: 260.1564.

2-(4-Allylhepta-1,3,6-trien-2-yl)thiophene (11h): Compound **11h** was obtained according to the general procedure. Colourless oil; yield: 83%; R_f=0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.89 (d, $^3J_{H,H}$=8.0 Hz, 2H), 2.95 (d, $^3J_{H,H}$=8.0 Hz, 2H), 5.00–5.12 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.55 (s, 1H; CH_{2b}=C), 5.72–5.92 (m, 2H; 2×C*H*=CH_2), 6.08 (s, 1H; CH=C), 6.95–6.99 (m, 2H; Ar), 7.18 ppm (d, $^3J_{H,H}$=4.8 Hz, 1H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.32, 41.05 (2×CH_2CH), 112.74, 116.61, 117.18, 124.95, 125.12, 126.14, 127.84, 136.56, 136.86, 138.66, 141.39, 145.66 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{14}H_{16}S$: 216.0973 $[M]^+$; found: 216.0974.

2-(4-Allylhepta-1,3,6-trien-2-yl)furan (11i): Compound **11i** was obtained according to the general procedure. Colourless oil; yield: 60%; R_f=0.82 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.88 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2=CH), 2.95 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2=CH), 5.03–5.13 (m, 5H; 2×CH_2=CH, CH_{2a}=C), 5.67 (s, 1H; CH_{2b}=C), 5.73–5.91 (m, 2H; 2×C*H*=CH_2), 6.00 (s, 1H; CH=C), 6.23 (d, $^3J_{H,H}$=3.2 Hz, 1H; Ar), 6.36–6.37 (m, 1H; Ar), 7.37 ppm (s, 1H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.35, 41.17 (2×CH_2CH), 107.59, 111.30, 111.65, 116.60, 117.16, 124.07, 134.47, 136.57, 136.84, 141.78, 142.57, 154.70 ppm (4×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{14}H_{16}O$: 200.1201 $[M]^+$; found: 200.1200.

(*Z*,*E*)-(4-Allylhepta-1,3,6-triene-1,2-diyl)dibenzene (11j): Compound **11j** was obtained according to the general procedure. Colourless oil; yield: 81%; R_f=0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.86 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2=CH), 2.99 (d, $^3J_{H,H}$=8.0 Hz, 2H; CH_2=CH), 4.98–5.10 (m, 4H; 2×CH_2=CH), 5.69–5.89 (m, 2H; CH_2=C), 6.04 (s, 1H; C*H*=CCH_2), 6.57 (s, 1H; C*H*=CCH), 6.95–7.27 ppm (m, 10H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.13, 42.01 (2×CH_2CH), 116.43, 117.02, 126.97, 127.68, 128.37, 128.94, 129.62, 129.72, 129.80, 130.93, 136.80, 136.84, 137.63, 139.69, 139.89, 140.93 ppm (8×C_{Ar}, 8×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{22}H_{22}$: 286.1722 $[M]^+$; found: 286.1721.

(*Z*,*E*)-4-Allyltrideca-1,4,6-triene (11k): Compound **11k** was obtained according to the general procedure. Colourless oil; yield: 85%; R_f=0.86 (PE); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, $^3J_{H,H}$=6.8 Hz, 3H; CH_3CH_2), 1.28–1.37 (m, 8H; 4×CH_2), 2.08 (q, $^3J_{H,H}$=7.0 Hz, 2H; CH_2CH_2CH; *E* isomer), 2.17 (q, $^3J_{H,H}$=7.0 Hz, 2H; CH_2CH_2CH; *Z* isomer), 2.77 (d, $^3J_{H,H}$=7.2 Hz, 2H; CCH_2CH), 2.89 (d, $^3J_{H,H}$=6.0 Hz, 2H), 5.00–5.06 (m, 4H; 2×CH_2=CH), 5.38–5.44 (m, 1H; C*H*=CH; *Z* isomer),5.61–5.68 (m, 1H; C*H*=CH; *E* isomer), 5.70–5.83 (m, 2H; C*H*=CH_2), 5.88 (d, $^3J_{H,H}$=8.0 Hz, 1H; CH=C), 6.17–6.27 ppm (m, 1H; C*H*=$CHCH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.61, 23.13, 29.40, 29.93, 32.23 ($CH_3CH_2CH_2CH_2CH_2$), 33.44 (CH_2CH_2CH), 35.51, 41.88 (2×CH_2CH), 116.04, 116.73, 126.47, 127.11, 134.68, 136.16, 136.31, 136.88 ppm (8×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{16}H_{26}$: 218.2035 $[M]^+$; found: 218.2036.

(*Z*)-4-Allyl-7-bromo-6-phenylhepta-1,5-dien-4-ol (G, R^1=Ph; R^2=H; X=Br): Compound **G** was obtained according to the general procedure. Colourless oil; yield: 86%; R_f=0.55 (PE/EtOAc 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.34 (s, 1H; OH), 2.39–2.52 (m, 4H; 2×CH_2CH), 4.82 (s, 2H; CH_2Br), 5.17–5.23 (m, 4H; 2×CH_2CH), 5.76 (s, 1H; CH=C), 5.81–5.95 (m, 2H; 2×C*H*=CH_2), 7.25–7.42 ppm (m, 5H; Ar); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.66, 46.79 (2×CH_2CH), 46.94 (CH_2Br), 75.99 (COH), 120.30, 126.91, 128.24, 128.92, 133.37, 137.63, 137.83, 139.40, 141.90 ppm (4×C_{Ar}, 5×C_{alkene}); HRMS (EI$^+$): *m*/*z* calcd for $C_{16}H_{19}{}^{79}$BrO: 306.0619 $[M]^+$; found: 306.0614.

Acknowledgements

We thank the Program for Hi-Tech Research of Jiangsu Science and Technology Department (BE2008063), Innovation Fund for Small Technology-based Firms (08C26223201851), Innovator Fund of Suzhou Government (ZXJ0726), Suzhou LAC Co., LTD and Suzhou Chiral Chemistry Co., LTD (www.suzhoulac.com) for financial support.

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Received: July 11, 2009
Published online: December 11, 2009

