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Tetrahedron 60 (2004) 1913–1920
Tetrahedron

# A convenient method for the preparation of α-vinylfurans by phosphine-initiated reactions of various substituted enynes bearing a carbonyl group with aldehydes

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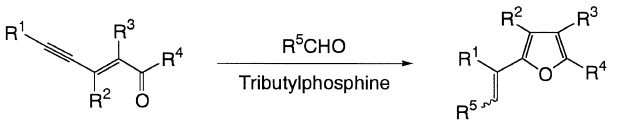
Received 14 July 2003; accepted 9 December 2003

**Abstract**—α-Vinylfurans were obtained by phosphine-initiated cyclization of various enynes bearing a carbonyl group at the ene end in the presence of various aldehydes, in moderate to high yields. The reaction may consist of 1,6-addition of phosphine to the enynes, ring closure, and Wittig reaction between the ylid resulting from cyclization and an aldehyde. Thus, various aldehydes were able to be used in the reaction. The reaction was influenced greatly by the substituents at the acetylene position ($R^1$) and the α-position of the carbonyl group ($R^3$).


## 1. Introduction

The development of cyclization reactions is of vital importance in organic chemistry, so that the cyclic systems found in naturally occurring products can be constructed. A number of cyclic systems containing one oxygen atom are present in nature (e.g., hydrofuran, furan, pyran ring). Furan rings, one example of five-membered heterocycles, are found in a lot of naturally occurring products.[1] The furan ring is not only present as key structural units in naturally occurring products, but is also important in the pharmaceutical industry.[2] Therefore, there has been interest in the synthesis of polysubstituted furans, and a number of useful synthetic methods for furans have been reported, by many synthetic chemists.[3] The Paal–Knorr method,[4] the Feist–Benary method,[5] etc. are known as long-standing methods for furan ring construction. Conjugated enynols are useful and important key intermediates for direct furan ring construction.[6] In our previous communication,[7] we described a novel synthetic method for the preparation of α-vinylfurans in high yields by a phosphine-initiated reaction of the simple 2-penten-4-yn-1-one system with benzaldehyde in dichloromethane. Kim et al. have reported furan ring construction by reaction of alkynic acetal, aldehyde and phosphine.[8] Trialkylphosphines are mild, useful reagents in various organic reactions,[9] including the addition of alcohols to acetylenes having electron-withdrawing groups,[10] isomerization of ynones, ynoates, and ynamides to the corresponding (2*E*, 3*E*)-diene[11] and polyenes.[12] Trost et al. have reported phosphine-catalyzed cyclization of ω-hydroxylynoates to the corresponding tetrahydrofuran or tetrahydropyran derivatives.[13] Herein, we wish to describe in detail the preparation of multi-substituted enynes (**1A**–**C**) and phosphine-initiated furan ring construction with a vinyl group at the α-position, by reaction of the various enynes (**1**) in the presence of various aldehydes (Scheme 1).




1 2

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | |
|---|---|---|---|---|
| Bu | H | H | Ph | Aa |
| Bu | H | H | Me | Ab |
| Ph | H | H | Ph | Ac |
| Ph | H | H | Me | Ad |

| $R^1$ | $R^2$ | $R^3$ | $R^4$ | |
|---|---|---|---|---|
| Bu | Bu | H | Me | Ba |
| Bu | Ph | H | Me | Bb |
| Bu | H | Et | Ph | Ca |
| Bu | H | Ph | Ph | Cb |

**Scheme 1.**

## 2. Results and discussions

### 2.1. Preparation of various enynes (1)

The synthesis of enynes (**1Aa**–**1Ad**; $R^2$=$R^3$=H) with disubstituted olefinic moieties was carried out by the reaction of ynals (**3**) with Wittig reagent (**4**) (Y. 69–82%) (Eq. 1 in Scheme 2). The enynes (**1Ba** and **1Bb**; $R^3$=H) with

*Keywords*: Cyclization; Vinyl furans; Enynes; Phosphine; Wittig reaction.
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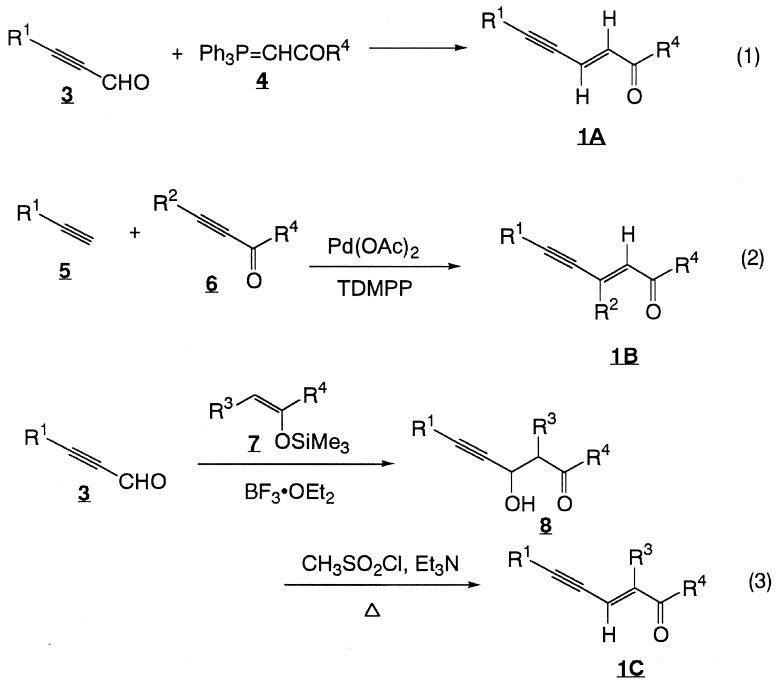
doi:10.1016/j.tet.2003.12.034




**Scheme 2.**

trisubstituted olefinic moieties were prepared by the procedure reported by Trost et al. from terminal alkynes (**5**) and ynones (**6**), in 87 and 40% yields, respectively (Eq. 2 in Scheme 2).[14] The enynes (**1Ca** and **1Cb**; $R^2$=H) with trisubstituted olefinic moieties were synthesized in two steps by acidic aldol reaction of ynal (**3**) with silyl enol ether (**7**), followed by dehydration of the aldol products in 69 and 64% yields (two steps), respectively (Eq. 3 in Scheme 2). As mentioned above, the three types of enynes (**1A**–**1C**) were prepared conveniently by modification of the known methods.

## 2.2. Phosphine-initiated cyclization of 1

The tributylphosphine-initiated ($Bu_3P$; 1 equiv.) cyclization of **1** in the presence of a stoichiometric amount of benzaldehyde was tried by using **1Aa** in $CH_2Cl_2$ for 6 h at room temperature, to obtain α-vinylfuran (**2Aa**) in 83% yield. **1Aa** was almost entirely consumed within 1 h under these conditions, as shown by GC analysis, and it was found that the reaction proceeded very smoothly under the mild conditions. From the NMR, IR, and MS spectra, the compound obtained was determined to be **2Aa**, containing an α-vinyl furan skeleton. **2Aa** contained a small amount of geometrical isomer† (*E*:*Z*=90:10) and an NOE experiment was carried out to determine the geometry of the major isomer in **2Aa**. The geometry of the major product was determined to be the *E*-isomer because no effect was observed between the olefinic proton of the vinyl group and the proton at the allylic position in the experiment (Fig. 1).

Furthermore, the reaction was carried out in the presence of stoichiometric amounts of triphenylphosphine or triethylamine instead of tributylphosphine. Although the corresponding furan (**2Aa**) was obtained in 73% yield after 6 h in the presence of triphenylphosphine, in the case of triethylamine the reaction did not proceed, and mostly **1Aa** was recovered. Moreover, when the amount of tributylphosphine was reduced to a 0.5 stoichiometric equiv., the yield was reduced approximately by half. These results may suggest the mechanism shown in Scheme 3. The reaction may be initiated by 1,6-addition of phosphine to **1**, followed by cyclization to yield the ylid (**8**) as an intermediate, and then Wittig reaction of **9** with an aldehyde may take place to give the furan (**2**) which has a double bond at the α-position. It is known that ylids stabilized by an aromatic ring, such as **9**, generally give an *E*-isomer as the major product.[15] Thus, the *E*-isomer might be obtained as the major product in this reaction. The reaction might not proceed in the presence of triethylamine due to prevention of the generation of **9**. Furthermore, the reaction might be stoichiometric with regard to the amount

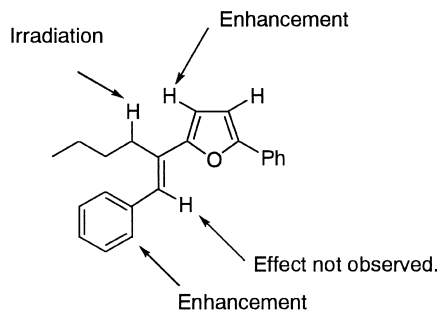
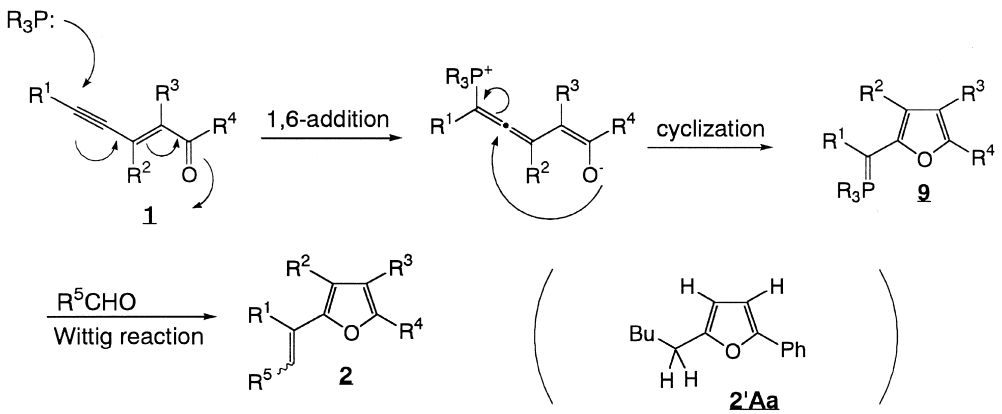



**Figure 1.** DNOE experiment for **2Aa**.

† We were not able to separate the isomers because their physical properties were almost identical, the products were slightly unstable at rt in air, and the amount of minor isomer in the mixture was very small. We presumed the minor product was a geometric isomer of the major product because **2′Aa** containing no double bonds was obtained as a single product in the reaction of **1Aa** with water in the presence of tributylphosphine and the found value almost agreed with the calculated value in the elemental analysis of the mixture of major and minor products, as described below.




**Scheme 3.**

of phosphine because the phosphine was converted to the corresponding phosphine oxide as shown in the suggested reaction mechanism. Therefore, the yield might decrease if the amount of phosphine is reduced. To detect the formation of the ylid (**9**), **1Aa** in $CH_2Cl_2$ was treated with tributylphosphine (1 equiv.) in the presence of water (5 equiv.) without aldehyde. The furan (**2′Aa**) containing no double bonds at the α-position was then obtained as a single product after hydrolysis[16] of the ylid, in 58% yield. **2′Aa** was not obtained when **1Aa** was treated with tributylphosphine without water and aldehyde. These results may suggest formation of the ylid (**9**) in the reaction process.

The reaction of various substituted enynes (**1A**–**1C**) was carried out in $CH_2Cl_2$ at room temperature (Table 2). The influence of substituents $R^1$ and $R^4$ was examined by using **1Aa**–**1Ad** (runs 1–4). When $R^1$=alkyl groups (i.e., **1Aa** and **1Ab**; runs 1 and 2), **2Aa** and **2Ab** were obtained in 83 and 56% yields, respectively. On the other hand, when $R^1$=aromatic (i.e., **1Ac** and **1Ad**; runs 3 and 4), the reaction gave a complex mixture containing only a small amount of the corresponding furan. From these results, it was found that the yields were markedly influenced by $R^1$ rather than by $R^4$. In the cases of **1Ac** and **1Ad**, **8** stabilized by two aromatic rings might be generated as the intermediate, based on the mechanism described above. Generally, such an ylid is too inert to react with aldehyde.[17] Therefore, the corresponding furans might not be obtained in the reactions with **1Ac** and **1Ad**. Furthermore, the reaction was investigated by using enynes (**1B** and **1C**) with trisubstituted olefinic moieties to examine the influence of $R^2$ and $R^3$ in this reaction. In the case of enynes (**1Ba** and **1Bc**; runs 5 and 6), the yield was not influenced by the type of substituent on the double bond. In contrast to this result, the substituent $R^3$ greatly affected the yield. In the case of $R^3$=alkyl group (i.e., **1Ca**), although **1Ca** was almost entirely consumed, the corresponding furan was not obtained, due to unknown side-reactions (run 7). When the reaction was retried by using triphenylphosphine, as a milder initiator than tributylphosphine, **1Ca** was almost exclusively recovered. This result may be attributable to the stability of the enolate in the suggested reaction mechanism. Thus, in the case of $R^3$=alkyl group, the enolate might become unstable due to the electron-donating effect of the alkyl substituent, compared with the case of $R^3$=H. When **1Cb** ($R^3$=phenyl group) was used as substrate, the reaction proceeded smoothly to give the corresponding furan in good yield (run 8). The phenyl group might stabilize the enolate by the resonance effect. These results suggest that the substituent $R^3$ may be important for control of the stability of the enolate. Although all the substituents ($R^1$–$R^4$) in the enynes (**1**) were effective for obtaining α-vinylfurans (**2**) as mentioned above, the substituents were not so effective for geometrical selectivity.‡ The α-vinylfurans (**2**) were obtained regardless of the kind of substituents, with high geometrical selectivity (runs 1, 2, 5, 6, and 8) (Table 1).

**Table 1**. Synthesis of furans from various enynes (**1**) and benzaldehyde[a]

| Run | $R^1$ | $R^2$ | $R^3$ | $R^4$ | | Yield[b]/% | *E*:*Z*[c] |
|---|---|---|---|---|---|---|---|
| 1 | Bu | H | H | Ph | Aa | 83 | 90:10 |
| 2 | Bu | H | H | Me | Ab | 56 | >99 (E) |
| 3 | Ph | H | H | Ph | Ac | 0 | |
| 4 | Ph | H | H | Me | Ad | 0 | |
| 5 | Bu | Bu | H | Me | Ba | 64 | 91:9 |
| 6 | Bu | Ph | H | Me | Bb | 63 | 93:7 |
| 7 | Bu | H | Et | Ph | Ca | 0 | |
| 8 | Bu | H | Ph | Ph | Cb | 70 | 90:10 |

[a] The reaction of **1** with benzaldehyde (1 equiv.) was carried out at room temperature for 5 h in the presence of tributylphosphine (1 equiv.).
[b] Isolated yield ($SiO_2$, ethyl acetate and hexane eluent).
[c] Determined by $^1$H NMR spectroscopy (400 MHz, $CDCl_3$).

**Table 2**. Synthesis of furans from **1Aa** and various carbonyl compounds[a]

| Run | Carbonyl compounds | Yield[b]/% | *E*:*Z*[c] |
|---|---|---|---|
| 1 | PhCHO | 83 | 90:10 |
| 2 | EtCHO | 92 | 80:20 |
| 3 | *trans*-PhCH=CHCHO | 90 | 79:21 |
| 4 | *p*-$MeOC_6H_4CHO$ | 89 | 92:8 |
| 5 | *p*-$MeC_6H_4COCH_3$ | 0 | |

[a] The reaction of **1** with various carbonyl compounds (1 equiv.) was carried out at room temperature for 5 h in the presence of tributylphosphine (1 equiv.).
[b] Isolated yield ($SiO_2$, ethyl acetate and hexane eluent).
[c] Determined by $^1$H NMR spectroscopy (400 MHz).

The reaction of **1Aa** with various carbonyl compounds was also examined on the basis of the suggested reaction mechanism (Scheme 3). Although ketones were not suitable, various aldehydes were able to be used in this reaction. Furthermore, the aldehyde substituents ($R^5$) had a

‡ Although attempts to separate the isomers were unsuccessful, we presumed the major isomer of all obtained α-vinylfurans was the *E*-form, from the suggested mechanism mentioned above.

greater affect on the geometry of α-vinylfurans (**2**) than the substituents ($R^1$–$R^4$) in the enynes (**1**).‡ (Table 2)

## 3. Conclusion

In this paper we described a novel phosphine-initiated cyclization of enynes bearing a carbonyl group at the ene end, in the presence of aldehydes, to obtain α-vinylfurans. Although the reaction was influenced by some substituents in the enyne compounds, the furans were obtained easily with high geometrical selectivity in moderate to high yields. We believe this reaction could become an important and convenient method for the synthesis of compounds containing α-vinylfuran skeletons, which are currently being investigated in detail.

## 4. Experimental

### 4.1. Materials and instruments

Tetrahydrofuran (THF), diethyl ether and benzene were dried over sodium benzophenone ketyl and distilled under nitrogen. Dichloromethane, dimethylformamide (DMF) and triethyl amine were dried over calcium hydride and then purified by distillation. Tributylphosphine and all aldehydes were purified by distillation. Triphenylphosphine was purified by recrystallization from ethyl acetate and dried in vacuo. Other commercially available chemicals were used without purification.

Infrared (IR) spectra were obtained with a JASCO FT/IR 8000 infrared spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on JNM-FX90 or AL400 spectrometers, in $CDCl_3$ (using tetramethylsilane as an internal standard). MS spectra were measured with a JMS-AX500 mass spectrometer. Elemental analysis was carried out by using Yanagimoto MT-5.

### 4.2. Synthesis of enynes

Enynes (**1A**, $R^2$=$R^3$=H) with disubstituted olefinic moieties were synthesized by Wittig reaction of the corresponding ynals (**3**) with phosphoranes (**4**).

The ynals were prepared from terminal acetylenes and DMF by modification of the method described in literature.[18]

**4.2.1. 2-Heptynal (3a).** *n*-Butyllithium (1.54 M in hexane, 39.6 mL, 61.0 mmol) was added dropwise to a solution of 1-hexyne (5.00 g, 61.0 mmol) in diethyl ether (40 mL) at −70 °C under nitrogen. After 30 min, dried DMF (6.68 g, 91.5 mmol) was added, and then the temperature of the mixture was allowed to rise to room temperature, and stirring was continued for 30 min. The mixture was poured into ice water and acidified slightly with conc. hydrochloric acid. The mixture was then neutralized with sodium hydrogen carbonate until a pH between 6 and 7 was reached. The organic layer was separated and the aqueous layer was extracted four times with 25 mL of ethyl acetate. The combined organic solution was dried over magnesium sulfate. After evaporation of the solvents, the residue was purified by vacuum distillation to give 2-heptynal (5.19 g, 47.2 mmol, 86%: colorless oil, $bp_{14}$ 58–60 °C); IR (neat) 2959, 3310, 2961, 2872, 2282, 2202, 1670, 1138 cm$^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.93 (t, *J*=6.4 Hz, 3H, $CH_3CH_2$–), 1.14–1.89 (m, 4H, –$CH_2$–), 2.42 (t, *J*=6.4 Hz, 2H, $CH_2C{\equiv}C$–), 9.18 (s, 1H, –CHO).

**4.2.2. Phenyl-2-propynal (3b).** Similarly, phenyl-2-propynal (**3b**) (colorless oil, $R_f$=0.45 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was synthesized and then purified by column chromatography on silica gel (hexane/ethyl acetate=20/1). Yield 97%; IR (neat) 3301, 2984, 2856, 2239, 2189, 1736, 1661, 1489 cm$^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 7.1–7.8 (5H, Ph–), 9.41 (s, 1H, –CHO).

Phosphoranes were prepared from corresponding α-haloketones and triphenylphosphine in two steps by modification of the method described in the literature.[19]

**4.2.3. Phenylcarbonylmethylenetriphenylphosphorane (4a).** A solution of α-bromoacetophenone (4.53 g, 22.8 mmol) in benzene (15 mL) was added dropwise to a solution of triphenylphosphine (5.96 g, 22.8 mmol) in benzene (15 mL) under nitrogen. The mixture was stirred overnight and the resulting phosphonium salt was filtered. The precipitate was washed with benzene and collected to dry in vacuo. The dried phosphonium salt was suspended in a mixture of water (250 mL) and methanol (250 mL), and the mixture was stirred for 1 h. Aqueous sodium hydroxide (2.00 M) was added to the mixture until a pH between 7 and 8 was reached. The mixture was then stirred vigorously for 1 h. The phosphorane precipitate was filtered and washed water. After drying in vacuo, the phosphorane was recrystallized from ethyl acetate and dried under vacuum to obtain 7.39 g (19.1 mmol, yield 89%, white crystal) of pure product; IR (neat) 3051, 2361, 1971, 1896, 1824, 1774, 1588, 1522 cm$^{-1}$. $^1$H NMR (90 MHz, δ, ppm) 4.44 (bd, *J*=24.3 Hz, 1H, P=C*H*–), 7.22–8.14 (20H, Ph).

**4.2.4. Methylcarbonylmethylenetriphenylphosphorane (4b).** Similarly, methylcarbonylmethylenetriphenylphosphorane (**4b**) was obtained from triphenylphosphine and bromoacetone in 69% yield as a white crystal; IR (neat) 3049, 2990, 2912, 1572, 1535, 1481, 1437 cm$^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 2.09 (d, *J*=1.9 Hz, 3H, $CH_3$), 3.29–4.06 (br, 1H, P=C*H*–), 7.32–7.84 (15H, Ph).

**4.2.5. *trans*-1-Phenyl-2-nonen-4-yn-1-one (1Aa).** 2-Heptynal (1.00 g, 9.09 mmol) was added slowly to a mixture of phenylcarbonylmethylenetriphenylphosphorane (3.45 g, 9.09 mmol) in $CH_2Cl_2$ (56 mL). The mixture was stirred at room temperature for 5 h and then concentrated by using an evaporator. Hexane (100 mL) was added to the mixture, and the triphenylphosphine oxide crystals were filtered. The filtrate was concentrated by using an evaporator, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate=100/1) to obtain the enyne (**1Aa**, 1.53 g, 7.20 mmol) in 79% yield (pale yellow oil, $R_f$=0.63 on TLC: $SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 2959, 2934, 2872, 2210, 1660, 1591, 1448, 1290 cm$^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.93 (t, *J*=6.6 Hz, 3H, $CH_3$–), 1.24–1.57 (m, 4H, –$CH_2$–), 2.42 (dt, *J*=2.3, 6.8 Hz, 2H, –$CH_2C{\equiv}$,

6.68 (dt, $J$=15.6, 2.3 Hz, 1H, ≡CC*H*═), 7.29 (d, $J$=15.6 Hz, 1H, ═C*H*CO–), 7.44–7.58 (m, 3H, Ph), 7.89–8.00 (m, 2H, Ph).

Similarly, other **1A** were synthesized from their corresponding ynals and phosphoranes.

**4.2.6. *trans*-3-Decen-5-yn-2-one (1Ab).** Yield 82%, colorless oil, $R_f$=0.53 on TLC ($SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 2961, 2936, 2872, 2213, 1693, 1674, 1595, 1356 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 0.93 (t, $J$=7.2 Hz, 3H, $CH_3$–), 1.26–1.74 (m, 4H, –C$H_2$–), 2.25 (s, 3H, C$H_3$CO), 2.24 (t, $J$=7.2 Hz, 2H, ≡CC$H_2$–), 6.36 (d, $J$=18.0 Hz, 1H, ═C*H*CO–), 6.55 (dt, $J$=18.0, 2.3 Hz, 1H, ≡CC*H*═).

**4.2.7. *trans*-1,5-Diphenyl-2-penten-4-yn-1-one (1Ac).** Yield 69%, pale yellow solid, mp 46 °C, $R_f$=0.72 on TLC ($SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 3063, 2191, 1661, 1597, 1580, 1337, 1308, 1254, 1211 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 7.01 (d, $J$=16.2 Hz, 1H, –C*H*═CHCO–), 7.20–7.80 (9H, ═C*H*CO–, Ph), 7.80–8.10 (m, 2H, Ph).

**4.2.8. *trans*-6-Phenyl-3-hexen-5-yn-2-one (1Ad).** Yield 75%, pale yellow solid, mp 104 °C, $R_f$=0.38 on TLC ($SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 3038, 3015, 2195, 1657, 1590, 1489, 1445, 1363 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 2.24 (s, 3H, C$H_3$CO–), 6.28 (d, $J$=16.1 Hz, 1H, ≡CC*H*═), 6.49 (d, $J$=16.1 Hz, 1H, ═C*H*CO–), 7.20–7.56 (m, 5H, Ph).

Enynes (**1B**) with trisubstituted olefinic moieties were prepared by the palladium-catalyzed cross coupling reaction of ynones with terminal alkynes described in the literature.[14] The ynones used in the cross coupling reaction were prepared as follows:[20]

**4.2.9. 3-Octyn-2-one (6a).** *n*-Butyllithium (1.54 M in hexane, 39.6 mL, 61.0 mmol) was added dropwise to a solution of 1-hexyne (5.00 g, 61.0 mmol) in THF (60 mL) at −70 °C. After 30 min, acetic anhydride (12.4 g, 122 mmol) was added to the mixture over 30 min and the mixture was then stirred for an additional 20 min. The temperature was then allowed to rise to 0 °C, and aqueous ammonium chloride (3 M, 100 mL) was poured into the mixture, followed by dropwise addition of concentrated aqueous ammonia, over 30 min. The mixture was extracted four times with 25 mL of ethyl acetate. The combined organic solution was washed twice with 50 mL of saturated aqueous ammonium chloride solution and then dried over magnesium sulfate. After solvent evaporation, the residue was purified by vacuum distillation to give 3-octyn-2-one (4.60 g, 37.1 mmol, yield 68%: colorless oil, $bp_{22}$ 71–77 °C); IR (neat) 3335, 2961, 2212, 1678, 1466, 1625, 1300, 1234 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 0.93 (t, $J$=7.4 Hz, 3H, C$H_3$CH$_2$–), 1.14–1.89 (m, 4H, –C$H_2$–), 2.32 (s, 3H, $CH_3$CO–), 2.36 (t, $J$=7.4 Hz, 2H, –C$H_2$C≡C–).

**4.2.10. 4-Phenyl-3-butyn-2-one (6b).** *n*-Butyllithium (1.54 M in hexane, 31.8 mL, 49.0 mmol) was added dropwise to a solution of ethynylbenzene (5.00 g, 49.0 mmol) in THF (28 mL), at −30 °C. After 30 min, a solution of zinc chloride (6.69 g, 49 mmol) in THF (18 mL) was added dropwise to the mixture. The temperature of the mixture was allowed to rise to 0 °C. After 30 min, acetylchloride (3.85 g, 49.0 mmol) was added. The mixture was stirred at 0 °C for 5 h and then poured into saturated aqueous ammonium chloride. The mixture was extracted four times with 25 mL of ethyl acetate and then dried over magnesium sulfate. After evaporation of the solvents, the residue was purified by column chromatography ($SiO_2$, hexane/ethyl acetate=100/1) to give 4-phenyl-3-butyn-2-one (4.70 g, 32.6 mmol, 67% yield, pale yellow oil, $R_f$=0.48 on TLC; $SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 2202, 1674, 1359, 1280, 1157, 978, 758, 690 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 2.44 (s, 3H, C$H_3$–), 7.25 (5H, Ph–).

**4.2.11. (3*E*)-4-Butyl-3-decen-5-yn-2-one (1Ba).** Tris (2,6-dimethoxyphenyl)phosphine (0.092 g, 0.261 mmol) was added to a suspension of palladium (II) acetate (0.035 g, 0.156 mmol) in benzene (9 mL). After 5 min, **6a** (1.00 g, 8.06 mmol) was added, and the mixture was stirred for 10 min. 1-Hexyne (0.661 g, 8.06 mmol) was then added slowly to the mixture, and the stirring was continued for 24 h. The mixture was subsequently concentrated in vacuo. The residue was purified by column chromatography ($SiO_2$, hexane/ethyl acetate=100/1) to obtain **1Ba** (1.45 g, 7.03 mmol) (colorless oil, $R_f$=0.63 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) in 87% yield; IR (neat) 2932, 2872, 2214, 1682, 1590, 1356, 1169 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 0.94 (t, $J$=7.6 Hz, 6H, C$H_3$–) 1.36–1.58 (8H, –C$H_2$–), 2.17 (s, 3H, C$H_3$CO–), 2.36 (t, $J$=6.4 Hz, –C$H_2$CH═), 2.69 (t, $J$=7.62 Hz, 2H, –CH$_2$C≡), 6.34 (s, 1H, ═C*H*CO–).

**4.2.12. (3*E*)-4-phenyl-3-decen-5-yn-2-one (1Bb).** Similarly, (3*E*)-4-phenyl-3-decen-5-yn-2-one (**1Bb**) (pale yellow oil, $R_f$=0.63 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was prepared by the palladium catalyzed reaction (reaction time: 4 h) of **6b** and 1-hexyne in 40% yield; IR (neat) 2959, 2231, 1685, 1657, 1361, 1259, 763, 692 $cm^{-1}$; $^1H$ NMR (90 MHz, $\delta$, ppm) 0.96 (t, $J$=6.6 Hz, 6H, C$H_3$–) 1.36–1.66 (4H, –C$H_2$–), 2.56 (s, 3H, C$H_3$CO–), 2.58 (t, $J$=6.6 Hz, 2H, –CH$_2$C≡), 6.71 (s, 1H, ═C*H*CO–), 7.34 (m, 5H, Ph–).

Enynes (**1C**) with trisubstituted olefinic moieties were synthesized from 2-heptynal (**3a**) and silyl enol ethers (**7**) in two steps. The silyl enol ethers were prepared as follows, by modification of the method described in the literature:[21]

**4.2.13. 1-phenyl-1-trimethylsiloxy-1-butene (7a).** Butyllithium (1.54 M in hexane, 21.9 mL, 33.7 mmol) was added slowly at 0 °C to a solution of diisopropylamine (3.40 g, 33.7 mmol) and THF (150 mL). After 10 min, 1-phenyl-1-butanone (5.00 g, 33.7 mmol) was added slowly to the solution at −78 °C. The mixture was stirred for a further 30 min, and then chlorotrimethylsilane (4.39 g, 40.5 mmol) was added at the same temperature. The solution was allowed to warm slowly from −78 °C to room temperature. After 12 h, the solvent had almost evaporated completely, and hexane was added. The resulting precipitate was removed and the obtained filtrate was evaporated, and purified by distillation to obtain **7a** (colorless oil, $bp_7$ 75–80 °C) (7.01 g, 31.9 mmol, 95% yield); IR (neat) 2963, 1649, 1446, 1342, 1251, 1074, 843 $cm^{-1}$; $^1H$ NMR

(90 MHz, δ, ppm) 0.13 (s, 9H, C$H_3$Si–), 1.04 (t, $J$=7.4 Hz, 3H, C$H_3$–), 2.22 (q, $J$=7.4 Hz, 2H, –C$H_2$C═), 5.23 (t, $J$=7.2 Hz, 1H, –C$H$═), 7.22–7.44 (m, 5H, Ph–).

**4.2.14. 1,2-Diphenyl-1-trimethylsiloxyethene (7b).** Colorless oil, $bp_7$ 125–140 °C) was prepared similarly in 48% yield; IR (neat) 2959, 1630, 1448, 1350, 1253, 1066, 897, 846 $cm^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.13 (s, 9H, C$H_3$Si–), 6.29 (s, 1H, –C$H$═), 7.15–7.88 (m, 10H, Ph–).

**4.2.15. 2-Ethyl-1-phenyl-2-nonen-4-yn-1-one (1Ca). 1Ca** was synthesized via 2-ethyl-3-hydroxy-1-phenyl-4-nonyn-1-one. 2-Ethyl-3-hydroxy-1-phenyl-4-nonyn-1-one (**8a**): Trifluoroborone diethyl ether complex (1.97 g, 13.9 mmol) was added dropwise at −78 °C to a solution of **3a** (1.00 g, 9.09 mmol) and **7a** (2.00 g, 9.09 mmol) in $CH_2Cl_2$ (25 mL). After 1 h, the mixture was poured into cold water (100 mL), and neutralized with sodium bicarbonate until a pH of 7 was attained. After separation of the organic layer, the aqueous phase was extracted four times with 25 mL of ethyl acetate. The combined organic phase was dried over magnesium sulfate. After solvent evaporation, the residue was purified by column chromatography ($SiO_2$, hexane/ethyl acetate=20/1) to give **8a** (2.15 g, 8.33 mmol) (pale yellow oil, $R_f$=0.10 and 0.20 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) as a diastereo mixture (The diastereo ratio was estimated from the $^1$H NMR spectrum as 1:1.5) in 92% yield; IR (neat) 3443, 2963, 2229, 1676, 1448, 1205, 1028, 704 $cm^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.78 (t, $J$=7.0 Hz, 3H, C$H_3$–), 0.91 (t, $J$=7.0 Hz, 3H, C$H_3$–), 1.17–1.80 (m, –C$H_2$–, 4H), 2.86 (br, 1H, –OH) (this peak may be attributable to the minor diastereoisomer), 3.20 (br, 1H, –O$H$), 3.68 (q, $J$=6.6 Hz, 1H, –C$H$(Et)CO–), 4.64 (br, 1H, –C$H$(OH)–), 7.00–8.00 (m, 5H, Ph–). Methanesulfonyl chloride (0.177 g, 1.55 mmol) and then triethylamine (0.157 g, 1.55 mmol) were added at 0 °C to a solution of **8a** (diastereo mixture) (0.400 g 1.55 mmol) in $CH_2Cl_2$ (1.5 mL). This mixture was refluxed for 3 h and then poured into saturated aqueous ammonium chloride (25 mL). After separation of the organic layer, the aqueous phase was extracted four times with 15 mL portions of ethyl acetate. The combined organic phase was dried over magnesium sulfate. After evaporation of the solvents, the residue was purified by column chromatography ($SiO_2$, hexane/ethyl acetate=20/1) to give **1Ca** (0.280 g, 1.17 mmol) (pale yellow oil, $R_f$=0.58 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) as a single isomer in 75.2% yield; IR (neat) 2963, 2208, 1774, 1649, 1597, 1250, 1057, 880, 720 $cm^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.96 (t, $J$=7.9 Hz, 3H, C$H_3$–), 1.12 (t, $J$=7.9 Hz, 3H, C$H_3$–), 1.32–1.90 (m, –C$H_2$–, 4H), 2.48 (t, $J$=7.8 Hz, 2H, –C$H_2$C≡), 3.76 (q, $J$=7.9 Hz, 2H, –C$H_2$C═), 6.10 (s, 1H, –C$H$═), 7.28–7.76 (m, 5H, Ph–).

**4.2.16. 1,2-Diphenyl-2-nonen-4-yn-1-one (1Cb).** Similarly, 1,2-diphenyl-2-nonen-4-yn-1-one (**1Cb**) was prepared as a single isomer via 3-hydroxy-1,2-diphenyl-4-nonyn-1-one (**8b**) in two steps. **8b** (pale yellow oil, $R_f$=0.33 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of diastereoisomers (1:1.7) in 81% yield; IR (neat) 3458, 2959, 2231, 1678, 1450, 1205, 1047, 700 $cm^{-1}$; $^1$H NMR (400 MHz, δ, ppm) 0.81 (t, $J$=7.3 Hz, 3H, C$H_3$–), 1.32–1.60 (m, –C$H_2$–, 4H), 2.12 (t, $J$=6.8 Hz, 2H, –C$H_2$C≡), 2.80 (br, 1H, –O$H$), 4.80 (d, $J$=6.3 Hz, 1H, –C$H$Ph–), 5.12 (d, $J$=6.3 Hz, 1H, –C$H$(OH)–), 7.00–8.00 (m, 10H, Ph–). 0.82 (t, $J$=7.3 Hz, 3H, C$H_3$–), 1.32–1.60 (m, –C$H_2$–, 4H), 2.13 (t, $J$=6.8 Hz, 2H, –C$H_2$C≡), 3.15 (br, 1H, –O$H$), 4.80 (d, $J$=7.8 Hz, 1H, –C$H$Ph–), 5.06 (d, $J$=7.8 Hz, 1H, –C$H$(OH)–), 7.00–8.00 (m, 10H, Ph–). **1Cb** (pale yellow oil, $R_f$=0.48 on TLC; $SiO_2$, hexane/ethyl acetate=4/1); IR (neat) 2959, 2208, 1657, 1591, 1259, 1068, 731, 696 $cm^{-1}$; $^1$H NMR (90 MHz, δ, ppm) 0.88 (t, $J$=7.7 Hz, 3H, C$H_3$–), 1.11–1.69 (m, 4H, –C$H_2$–), 2.34 (dt, $J$=2.6, 7.7 Hz, 2H, –C$H_2$C≡), 6.30 (t, $J$=2.6 Hz, 1H, –C$H$═), 7.11–8.09 (m, 10H, Ph–).

**4.2.17. Phosphine-initiated cyclization of 1. 2-(1-Butyl-2-phenylethenyl)-5-phenylfuran (2Aa).** Tributylphosphine (190 mg, 0.943 mmol) was added at room temperature to a solution of **1Aa** (200 mg, 0.943 mmol) and benzaldehyde (100 mg, 0.943 mmol) in $CH_2Cl_2$ (1.9 mL). After stirring for 5 h, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate=200/1) to give 236 mg (83%) of **2Aa** as a mixture of geometric isomers; colorless oil, $R_f$=0.63 on TLC (hexane/ethyl acetate=4/1); IR (neat) 3059, 2957, 1685, 1599, 1483, 1468, 1449, 1024, 785, 758, 692 $cm^{-1}$; $^1$H NMR (400 MHz, δ, ppm) 0.95 (t, $J$=7.3 Hz, 3H, C$H_3$–), 1.44 (m, 2H, $CH_3$C$H_2$–), 1.66 (m, 2H, –$CH_2$C$H_2$$CH_2$–), 2.53 (t, $J$=7.6 Hz, 2H, –C$H_2$-furan; minor isomer), 2.61 (t, $J$=8.3 Hz, 2H, –$CH_2$$CH_2$C$H_2$–), 6.23 (d $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.45 (d, $J$=3.4 Hz, 1H, furan-H), 6.56 (d $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.68 (d, $J$=3.4 Hz, 1H, furan-H) 7.19 (s, 1H, –C$H$═), 7.20–7.75 (m, 10H, Ph),; $^{13}$C NMR (100 MHz, δ, ppm; major isomer) 13.9 ($CH_3$), 23.0 (–$CH_2$–), 28.2 (–$CH_2$–), 32.0 (–$CH_2$–), 107.0 (CH in furan ring), 108.6 (CH in furan ring), 123.7 (Ph), 124.2 (═*C*HPh), 126.6 (Ph), 127.3 (Ph), 128.3 (Ph), 128.7 (Ph), 128.8 (Ph), 130.8 (Ph), 131.6 (Ph), 137.5 (>*C*═CHPh), 153.0 (O–C in furan ring), 155.2 (O–C in furan ring). MS (EI, *m*/*z*) 302 ($M^+$). Anal. Calcd for $C_{22}H_{22}O$: C 87.38, H 7.33. Found: C 87.41, H 7.65.

Similarly, the cyclization was carried out by using various enynes and aldehydes in the presence of tributylphosphine.

**4.2.18. 2-(1-Butyl-2-phenylethenyl)-5-methylfuran (2Ab).** 2-(1-Butyl-2-phenylethenyl)-5-methylfuran (**2Ab**) (pale yellow oil, $R_f$=0.75 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained in 56% yield; IR (neat) 2957, 2930, 2870, 1701, 1653, 1599, 1456 $cm^{-1}$; $^1$H NMR (400 MHz, δ, ppm) 0.93 (t, $J$=7.4 Hz, 3H, C$H_3$–), 1.41 (m, 2H, –C$H_2$–), 1.63 (m, 2H, –C$H_2$–), 2.34 (d, $J$=0.8 Hz, 3H, C$H_3$-furan), 2.53 (t, $J$=8.2 Hz, 2H, –C$H_2$C═), 6.00 (dq, $J$=3.2, 0.8 Hz, 1H, furan-H), 6.26 (d, $J$=3.2 Hz, 1H, furan-H) 7.01 (s, 1H, –C$H$═), 7.20–7.50 (m, 5H, Ph); $^{13}$C NMR (100 MHz, δ, ppm) 13.8 ($CH_3$), 13.9 ($CH_3$), 22.9 (–$CH_2$–), 28.1 (–$CH_2$–), 31.9 (–$CH_2$–), 107.1 (CH in furan ring), 107.2 (CH in furan ring), 122.4 (═*C*HPh), 126.0 (Ph), 127.9 (Ph), 128.4 (Ph), 131.4 (Ph), 137.4 (>*C*═CHPh), 150.5 (O–*C* in furan ring), 153.7 (O–*C* in furan ring). MS (EI, *m*/*z*) 240 ($M^+$). Anal. Calcd for $C_{17}H_{20}O$: C 84.96, H 8.39. Found: C 84.60, H 8.52.

**4.2.19. 2-(1-Butyl-2-phenylethenyl)-3-butyl-5-methylfuran (2Ba).** Pale yellow oil, $R_f$=0.63 on TLC; $SiO_2$,

hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 64% yield; IR (neat) 2957, 2860, 1616, 1458, 1259, 750, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.74 (t, $J$=7.1 Hz, 3H, $CH_3-$; minor isomer), 0.84 (t, $J$=7.2 Hz, 3H, $CH_3-$), 0.92 (t, $J$=7.6 Hz, 3H, $CH_3-$), 1.20–1.60 (m, 8H, $-CH_2-$), 1.80 (t, $J$=7.6 Hz, 2H, $-CH_2$-furan; minor isomer), 2.28 (s, 3H, $CH_3$-Furan), 2.51 (t, $J$=7.6 Hz, 2H, $CH_2$-furan), 2.61 (t, $J$=7.6 Hz, 2H, $-CH_2C=$), 5.80 (s, 1H, furan-H; minor isomer), 5.92 (s, 1H, furan-H), 6.46 (s, 1H, $-CH=$; minor isomer), 6.62 (s, 1H, $-CH=$), 6.46 (s, 1H, $-CH=$; minor isomer), 7.20–7.50 (m, 5H, Ph),; $^{13}C$ NMR (100 MHz, $\delta$, ppm) 13.6 ($CH_3$), 13.9 ($CH_3$), 14.0 ($CH_2$), 22.5 ($CH_2$), 22.7 ($CH_2$), 25.7 ($CH_2$), 28.7 ($CH_2$), 31.4 ($CH_2$), 32.5 ($CH_2$), 109.0 (CH in furan ring), 122.8 (Bu–C in furan), 126.0 (Ph), 126.1 (PhCH=), 127.9 (Ph), 128.4 (Ph), 133.7 (Ph), 137.6 (>$C$=CHPh), 148.9 (O–$C$ in furan ring), 149.4 (O–$C$ in furan ring). MS (EI, $m/z$) 296 ($M^+$). Anal. Calcd for $C_{21}H_{28}O$: C 85.08, H 9.52. Found: C 85.03, H 9.71.

**4.2.20. 2-(1-Butyl-2-phenylethenyl)-5-methyl-3-phenylfuran (2Bb).** Pale yellow oil, $R_f$=0.68 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 63% yield; IR (neat) 3026, 2926, 1740, 1601, 1444, 1126, 956, 763 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.84 (t, $J$=7.2 Hz, 3H, $CH_3-$), 1.26 (m, 2H, $-CH_2-$), 1.51 (m, 2H, $-CH_2-$), 2.33 (d, $J$=0.8 Hz, 3H, $CH_3$-furan), 2.39 (d, $J$=0.8 Hz, 3H, $CH_3$-furan), 2.42 (t, $J$=8.0 Hz, 2H, $-CH_2C=$; minor isomer), 2.58 (t, $J$=8.0 Hz, 2H, $CH_2C=$), 6.16 (q, $J$=0.8 Hz, 1H, furan-H), 6.24 (q, $J$=0.8 Hz, 1H, furan-H, minor isomer), 6.58 (s, 1H, $-CH=$; minor isomer), 6.77 (s, 1H, $-CH=$), 7.20–7.50 (m, 10H, Ph); $^{13}C$ NMR (100 MHz, $\delta$, ppm; major isomer) 13.8 ($CH_3$), 13.9 ($CH_3$), 22.8 ($CH_2$), 28.6 ($CH_2$), 31.5 ($CH_2$), 109.6 (CH in furan ring), 123.3 (Ph–$C$ in furan), 126.4 (=$C$HPh), 126.5 (Ph), 128.0 (Ph), 128.1 (Ph), 128.4 (Ph), 128.5 (Ph), 133.1 (Ph), 135.0 (Ph), 137.4 (>$C$=CHPh), 149.1 (O–$C$ in furan ring), 150.2 (O–$C$ in furan ring). MS (EI, $m/z$) 316 ($M^+$). Anal. Calcd for $C_{23}H_{24}O$: C 87.30, H 7.64. Found: C 86.86, H 7.87.

**4.2.21. 2-(1-Butyl-2-phenylethenyl)-4,5-diphenylfuran (2Cb).** Pale yellow oil, $R_f$=0.60 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 70% yield; IR (neat) 2959, 2870, 1703, 1599, 1446, 1147, 763, 696 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.88 (t, $J$=7.6 Hz, 3H, $CH_3-$), 1.38 (m, 2H, $-CH_2-$), 1.63 (m, 2H, $-CH_2-$), 2.47 (t, $J$=7.6 Hz, 2H, $-CH_2C=$; minor isomer), 2.56 (t, $J$=8.2 Hz, 2H, $-CH_2C=$), 6.24 (s, 1H, furan-H; minor isomer), 6.47 (s, 1H, furan-H), 7.14 (s, 1H, $-CH=$), 7.10–7.55 (m, 15H, Ph); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 14.0 ($CH_3$), 23.2 ($CH_2$), 28.4 ($CH_2$), 32.1 ($CH_2$), 110.7 (CH in furan ring), 124.2 (Ph–$C$ in furan), 124.5 (=$C$HPh), 126.0 (Ph), 126.5 (Ph), 127.1 (Ph), 127.3 (Ph), 128.2 (Ph), 128.3 (Ph), 128.5 (Ph), 128.6 (Ph), 128.7 (Ph), 130.9 (Ph), 131.2 (Ph), 134.2 (Ph), 137.3 (>$C$=CHPh), 147.3 (O–$C$ in furan ring), 154.1 (O–$C$ in furan ring). MS (EI, $m/z$) 378 ($M^+$). Anal. Calcd for $C_{28}H_{26}O$: C 88.85, H 6.92. Found: C 88.64, H 7.14.

**4.2.21. 2-Pentyl-5-phenylfuran (2′Aa).** Colorless oil, $R_f$=0.63 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained in 58% yield; IR (neat) 2957, 2930, 2870, 1738, 1685, 1599, 1483, 1024, 785, 758 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.91 (t, $J$=7.0 Hz, 3H, $CH_3-$), 1.37 (m, 4H, $-CH_2-$), 1.69 (m, 2H, $-CH_2-$), 2.67 (t, $J$=7.6 Hz, 2H, $-CH_2$-furan), 6.05 (d, $J$=3.20 Hz, 1H, furan-H), 6.54 (d, $J$=3.2 Hz, 1H, furan-H), 7.21 (m, 1H, –Ph), 7.34 (m, 2H, Ph), 7.62 (m, 2H, Ph); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 14.2 ($CH_3$), 22.6 ($CH_2$), 27.9 ($CH_2$), 28.3 ($CH_2$), 31.5 ($CH_2$), 105.5 (CH in furan ring), 106.7 (CH in furan ring), 123.2 (Ph), 126.5 (Ph), 128.4 (Ph), 131.1 (Ph), 151.9 (O–$C$ in furan ring), 156.2 (O–$C$ in furan ring). MS (EI, $m/z$) 214 ($M^+$). Anal. Calcd for $C_{15}H_{18}O$: C 84.07, H 8.47. Found: C 84.00, H 8.60.

**4.2.22. 2-(1-Butyl-2-ethylethenyl)-5-phenylfuran.** Pale yellow oil, $R_f$=0.73 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 92% yield; IR (neat) 2959, 2932, 1606, 1523, 1485, 1458, 1024, 783, 758, 688 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.94 (t, $J$=7.2 Hz, 3H, $CH_3-$), 0.96 (t, $J$=7.2 Hz, 3H; minor isomer), 1.09 (t, $J$=7.6 Hz, 3H, $CH_3-$), 1.12 (t, $J$=7.6 Hz, 2H, $CH_3-$; minor isomer), 1.39 (m, 2H, $-CH_2-$), 1.49 (m, 2H, $-CH_2-$), 1.74 (quint, $J$=7.6 Hz, 2H, $CH_3CH_2CH=$; minor isomer), 2.24 (quint, $J$=7.6 Hz, 2H, $CH_3CH_2CH=$), 2.38 (t, $J$=7.2 Hz, 2H, $-CH_2CH_2C=$), 2.50 (t, $J$=7.2 Hz, 2H, $-CH_2CH_2C=$; minor isomer), 5.45 (t, $J$=7.2 Hz, 1H, $-CH=$; minor isomer), 6.15 (t, $J$=7.6 Hz, 1H, $-CH=$), 6.26 (d, $J$=3.2 Hz, 1H, furan-H), 6.34 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.63 (d, $J$=3.2 Hz, 1H, furan-H), 6.67 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 7.10–7.80 (m, 5H, Ph); $^{13}C$ NMR (100 MHz, $\delta$, ppm; major isomer) 14.0 ($CH_3$), 14.3 ($CH_3$), 21.2 ($CH_2$), 22.8 ($CH_2$), 27.6 ($CH_2$), 31.8 ($CH_2$), 106.2 (CH in furan ring), 106.4 (CH in furan ring), 123.2 (Ph), 126.6 (=$C$HPh), 127.5 (Ph), 128.3 (Ph), 128.9 (Ph), 130.7 (>$C$=CHPh), 151.8 (O–$C$ in furan ring), 154.9 (O–$C$ in furan ring). MS (EI, $m/z$) 254 ($M^+$). Anal. Calcd for $C_{18}H_{22}O$: C 84.99, H 8.72. Found: C 84.72, H 8.79.

**4.2.23. 2-(1-Butyl-4-phenyl-1,3-butadienyl)-5-phenylfuran.** Pale yellow oil, $R_f$=0.73 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 90% yield; IR (neat) 3032, 2957, 2932, 1606, 1532, 1506, 1250, 1176, 1035, 758, 690 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.94 (t, $J$=7.2 Hz, 3H, $CH_3-$; minor isomer), 0.97 (t, $J$=7.6 Hz, 3H, $CH_3-$), 1.44 (m, 2H, $-CH_2-$), 1.61 (m, 2H, $-CH_2-$), 2.46 (t, $J$=7.6 Hz, 2H, $-CH_2CH_2C=$; minor isomer), 2.60 (t, $J$=7.2 Hz, 2H, $-CH_2CH_2C=$), 6.21 (d, $J$=11.6 Hz, 1H, PhCH=CHC$H$=; minor isomer), 6.44 (d, $J$=3.6 Hz, 1H, furan-H), 6.49 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.64 (d, $J$=15.6 Hz, 1H, PhC$H$=CH–; minor isomer), 6.68 (d, $J$=3.20 Hz, 1H, furan-H), 6.72 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.73 (d, $J$=15.2 Hz, 1H, PhC$H$=CH–), 6.95 (d, $J$=11.6 Hz, 1H, PhCH=CHC$H$=), 7.16 (dd, $J$=11.6, 15.6 Hz, 1H, PhCH=C$H$–), 7.20–7.80 (m, 10H, Ph) 7.96 (dd, $J$=11.6, 15.6 Hz, 1H, PhCH=C$H$–; minor isomer); $^{13}C$ NMR (100 MHz, $\delta$, ppm; major isomer) 13.9 ($CH_3$). 22.8 ($CH_2$), 28.0 ($CH_2$), 32.3 ($CH_2$), 107.0 (CH in furan ring), 108.5 (CH in furan ring), 123.4 (Ph), 123.8 (PhCH=CH–$C$H=), 124.6 (PhCH=$C$H–), 126.0 (Ph), 127.0 (Ph), 127.0 (Ph), 128.3 (Ph), 130.4 (=CH–CH=$C$<), 130.7 (Ph), 132.6 (Ph$C$H=CH–), 137.5 (Ph), 152.8 (O–$C$ in furan ring), 154.7 (O–$C$ in furan ring). MS (EI, $m/z$) 328 ($M^+$). Anal.

Calcd for $C_{24}H_{24}O$: C 87.76, H 7.37. Found: C 87.34, H 7.53.

**4.2.24. 2-[1-Butyl-2-(*p*-methoxyphenyl)ethenyl]-5-phenylfuran.** Pale yellow oil, $R_f$=0.70 on TLC; $SiO_2$, hexane/ethyl acetate=4/1) was obtained as a mixture of geometric isomers in 89% yield; IR (neat) 2957, 29.32, 1606, 1524, 1506, 1464, 1250, 1176, 758 $cm^{-1}$; $^1H$ NMR (400 MHz, $\delta$, ppm) 0.88 (t, $J$=6.8 Hz, 3H, C$H_3$–; minor isomer), 0.96 (t, $J$=7.2 Hz, 3H, C$H_3$–), 1.45 (m, 2H, –C$H_2$–), 1.66 (m, 2H, –C$H_2$–), 2.51 (t, $J$=8.0 Hz, 2H, –CH$_2$C$H_2$CH=; minor isomer), 2.60 (t, $J$=8.0 Hz, 2H, –CH$_2$C$H_2$CH=), 3.80 (s, 3H, C$H_3$O–; minor isomer), 3.82 (s, 3H, C$H_3$O–), 6.24 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.42 (d, $J$=3.6 Hz, 1H, furan-H), 6.57 (d, $J$=3.6 Hz, 1H, furan-H; minor isomer), 6.68 (d, $J$=3.6 Hz, 1H, furan-H), 6.91 (m, 2H, MeOPh–; minor isomer), 6.92 (m, 2H, MeOPh–), 7.13 (s, 1H, –C$H$=), 7.20–7.80 (m, 7H, Ph, MeOPh–); $^{13}C$ NMR (100 MHz, $\delta$, ppm) 13.9 ($CH_3$), 23.0 ($CH_2$), 28.2 ($CH_2$), 31.8 ($CH_2$), 55.1 ($CH_3O$), 106.7 (CH in furan ring), 107.7 (CH in furan ring), 113.1 ($p$-Me$C_6H_4$–), 123.3 (Ph), 123.5 (Ph), 126.8 (–CH=), 128.3 (Ph), 129.7 ($p$-MeO$C_6H_4$–), 129.8 ($p$-MeO$C_6H_4$–, Ph), 130.5 (>$C$=CH–), 152.4 (O–$C$ in furan ring), 155.1 (O–$C$ in furan ring), 158.0 ($p$-Me$C_6H_4$–),. MS (EI, $m/z$) 332 ($M^+$). Anal. Calcd for $C_{23}H_{24}O_2$: C 83.10, H 7.28. Found: C 82.98, H 7.52.

## Acknowledgements

We are grateful to Dr. Shin Ono Ms. Yukiko Hoshino at Toyama Univ. for performing the elemental analysis.

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