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Gold(I) catalysed sequential dehydrative cyclisation/ intermolecular [4+2] cycloaddition of alkynyldienols onto activated alkynes/ alkenes: A facile route to substituted norbornadienes/norbornenes

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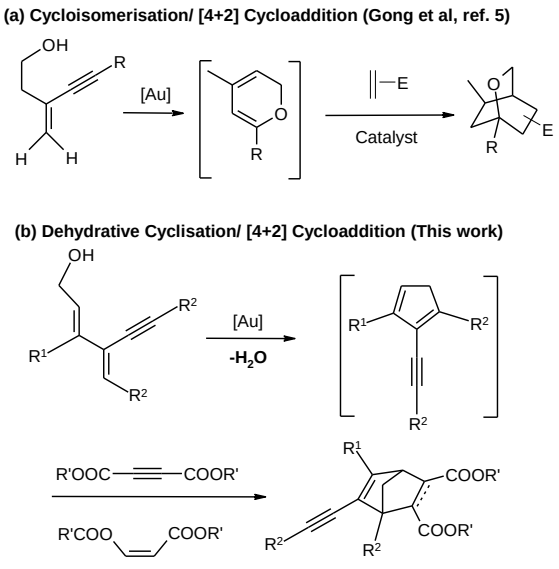
One-pot synthesis of highly substituted norbornadienes/ norbornenes *via* gold-catalysed dehydrative cyclisation of alkynyldienol, followed by intermolecular [4+2] cycloaddition of *in situ* generated cyclopentadiene and activated alkynes/ alkenes is described. The precursors, alkynyldienols, are obtained *via* sequential Sonogashira cross-coupling of 3-bromoenals, alkyne addition and reduction. Yields of the enynals and multisubstituted norbornadienes in all the cases are good to excellent.

Introduction

In recent years, homogeneous gold catalysis has emerged as a fast growing research area in organic synthesis due to its proven potential as a powerful tool for the construction of carbon-carbon and carbon-heteroatom bonds.[1] Generally, gold salts activate alkynes, alkenes and allenes towards a variety of organic transformations including cycloaddition,[2] and cyclisation/ cycloisomerisation.[3] In particular, [4+2] cycloaddition reactions catalysed by gold salts have been employed effectively for the construction of a huge number of carbo-/hetero-cyclic frameworks from acyclic precursors.[4] In this context, recently, gold catalysed sequential hydroalkoxylation followed by [4+2] cycloaddition of enyne alcohols with dienophiles leading to oxa bridged tricyclic compounds was reported by Gong and co-workers (Scheme 1a).[5] Bridged carbo-/heterocycles are important core structures present in many natural products[6]/ pharmaceuticals[7] and are useful as chiral reagents in organic synthesis.[8] In particular, norbornadiene and its derivatives are used as precursors to other polycycles/ natural products[9] and as ligands for metal complexes, which in turn are useful in homogeneous catalysis.[10] Polymerisation of norbornadiene derivatives is also a subject of recent interest.[11] Of recent interest is the diaryl substituted norbornadienes with red-shifted absorption for molecular solar thermal energy storage.[12] Even though there are several methods for the preparation of norbornadiene derivatives by cycloaddition of cyclopentadiene and alkynes,[13] dehydrative intermolecular cycloaddition of alkynyldienols *via* cyclopentadiene as an intermediate, is a point not reported in the literature so far. As part of an ongoing study on gold catalysis for the synthesis of various carbo-heterocycles,[14] herein, we disclose our results on the formation of functionalized norbornadienes/ norbornenes by using gold(I)-catalysed ***dehydrative*** cycloaddition of alkynyldienols with activated alkynes or alkenes (Scheme 1b). This reaction is ***quite different*** from that shown in Scheme 1a. The synthesis of precursors, alkynyldienols, by the reduction of the products from an interesting alkyne addition in the Sonogashira coupling is also described.



Scheme 1 Au(I)-catalysed (a) cycloisomerisation followed by cycloaddition and (b) dehydrative cycloaddition of alkynyldienols.

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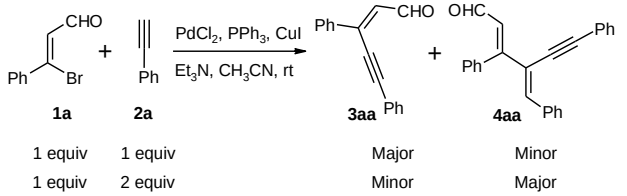
Results and discussion

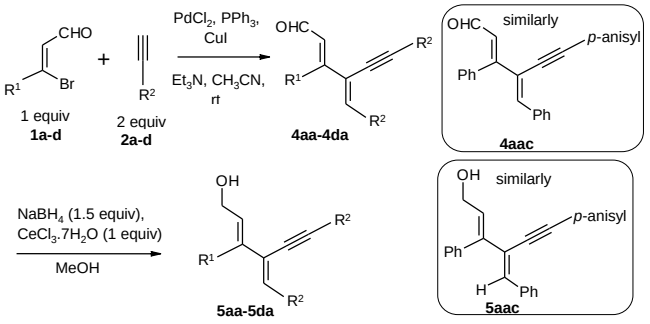
(i) Synthesis of alkynyldienals and alkynyldienols

Initially, we performed Sonogashira cross coupling of 3-bromoenal (**1a**)[15a] with phenylacetylene **2a** (1:1 molar stoichiometry ratio) that led to expected coupling product, alkynylenal (**3aa**)[15] along with a trace amount of alkynyldienal (**4aa**) (Scheme 2). Interestingly, yield of alkynyldienal (**4aa**) was enhanced by increasing the stoichiometry of phenylacetylene. It is important to note that this type of sequential cross coupling followed by alkyne addition is not reported in the literature. We then applied this method using 3-bromoenals (**1a-d**)[16] and terminal alkynes (1:2 molar stoichiometry) to obtain the alkynyldienals (**4aa-4da**) (Table 1). Yields were good to excellent in all the cases. Using $NaBH_4/CeCl_3$ system,[17] alkynyldienals (**4aa-4da**) were reduced to the alkynyldienols (**5aa-5da**) in high yields. The stereochemistry in compounds **4ab** and **5aa** was confirmed by X-ray crystallography (Figures 1 and S95). It is important to note that in this product, R^1 and -CHO are *cis* to each other as per literature while the same groups are *trans* in **1a**. It is likely that the initially formed Sonogashira product undergoes further alkyne addition under the conditions employed to lead to compound of type **4**. A possible rationalization for the isomerization is that addition-elimination of triethylamine to the α,β-unsaturated aldehyde function (a good Michael acceptor) may take place, allowing rotation about the bond to the aldehyde function.[18]



Scheme 2 Reaction of 3-bromoenal (**1a**) with phenylacetylene (**2a**) leading to alkynylenal (**3aa**) and alkynyldienal (**4aa**).

Table 1 Synthesis of alkynyldienals (**4**) and alkynyldienols (**5**) from 3-bromoenals (**1**) and terminal alkynes (**2**) using palladium catalysis and $NaBH_4$reduction.[a]



Entry	Aldehyde **1** R^1 =	Alkyne **2** R^2 = or $R^2 \neq R^2$	Product **4** (yield %)[b]	Product **5** (yield %)[b]
1	Ph (**1a**)	Ph (**2a**)	**4aa** (90)	**5aa** (97)
2	Ph (**1a**)	*p*-MeC_6H_4 (**2b**)	**4ab** (91)	**5ab** (96)
3	Ph (**1a**)	*p*-$MeOC_6H_4$ (**2c**)	**4ac** (96)	**5ac** (99)
4	Ph (**1a**)	*m*-FC_6H_4 (**2d**)	**4ad** (95)	**5ad** (97)
5	*p*-MeC_6H_4 (**1b**)	Ph (**2a**)	**4ba** (88)	**5ba** (96)
6	*p*-MeC_6H_4 (**1b**)	*p*-MeC_6H_4 (**2b**)	**4bb** (80)	**5bb** (96)
7	*p*-FC_6H_4 (**1c**)	Ph (**2a**)	**4ca** (91)	**5ca** (97)
8	*p*-FC_6H_4 (**1c**)	*p*-MeC_6H_4 (**2b**)	**4cb** (87)	**5cb** (96)
9	*p*-$MeOC_6H_4$ (**1d**)	Ph (**2a**)	**4da** (85)	**5da** (97)
10	Ph (**1a**)	Ph (**2a**) followed by *p*-$MeOC_6H_4$ (**2c**)[a]	**4aac** (88)[c]	**5aac** (88)[c]

[a]Reaction conditions: Bromo substrate (**1**) (1 equiv) and alkyne (2 equiv), $PdCl_2$ (3 mol %), PPh_3 (6 mol %) and CuI (6 mol %) were used. [b]Isolated yields. [c]unsymmetrical alkynyldienal; 1 equiv of **2a** followed by one equiv of **2c** were added.

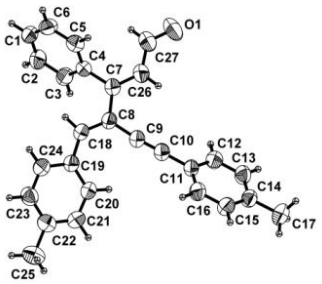
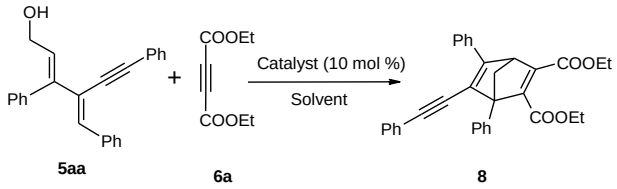


Fig. 1. ORTEP (probability level 50%) of compound **4ab**. Selected bond lengths [Å] with esds in parentheses: O(1)-C(27) 1.209(2), C(7)-C(8) 1.483(2), C(8)-C(9) 1.432(2), C(9)-C(10) 1.195(2), C(10)-C(11) 1.430(2), C(8)-C(18) 1.356(2).

(ii) Synthesis of norbornadienes 8-23

After having the alkynyldienol precursors in hand, we chose alkynyldienol (**5aa**) and diethylacetylene dicarboxylate (DEAD) (**6a**) as model substrates for optimisation studies (Table 2). Initially, we treated **5aa** with DEAD in the presence of AuCl (10 mol %) in dioxane at 80 °C for 5h, that resulted in the dehydrative [4+2] cycloaddition product, norbornadiene **8**, in 75 % yield (entry 1). At room temperature, there was no reaction (entry 2). To our delight, when the reaction was performed at 50 °C for 5h, norbornadiene (**8**) was obtained in excellent yield (86 %) (entry 3). In the case of other catalysts like $AuCl_3$, PPh_3AuCl and $PPh_3AuCl/AgSbF_6$, the yield was good (entries 5-7), but marginally lower than that in entry 3. In the absence of gold catalyst, reaction did not proceed (entry 8). On the other hand, yields of the cycloaddition product **8** did not improve in solvents like THF, toluene, 1,2-dichloroethane, DMF, dichloromethane or nitromethane in place of dioxane (entries 9-13). Thus dioxane was proved to be an efficient reaction medium for this dehydrative cycloaddition. Accordingly, the reaction conditions were optimised as follows: AuCl (10 mol %) in dioxane at 50 °C.

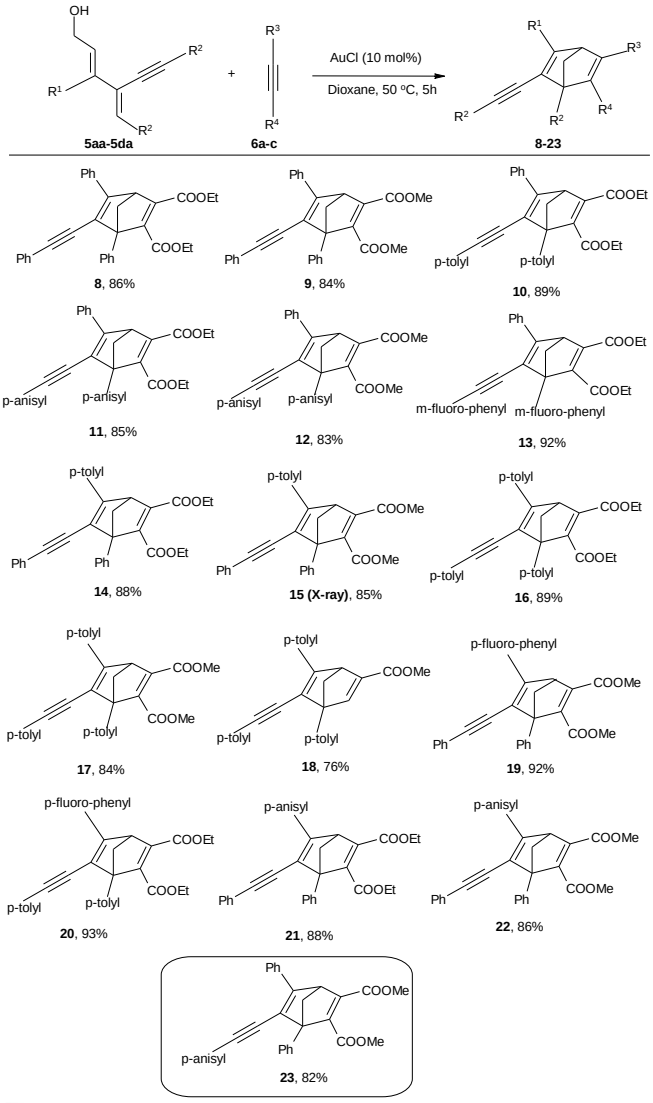
Table 2 Optimisation table for the gold-catalysed dehydrative cycloaddition of alkynyldienol (**5aa**) with diethylacetylene dicarboxylate (**6a**)[a]



Entry	Catalyst	Solvent	Temp (^oC) /Time (h)	Yield (%)[b]
1	AuCl	Dioxane	80/5	75
2	AuCl	Dioxane	rt/8	NR
3	**AuCl**	**Dioxane**	**50/5**	**86**
4[c]	AuCl	Dioxane	50/5	54
5	$AuCl_3$	Dioxane	50/5	71
6	PPh_3AuCl	Dioxane	50/8	75
7	$PPh_3AuCl/AgSbF_6$	Dioxane	50/5	79
8[d]	-	Dioxane	50/6	NR
9	AuCl	THF	50/5	56
10	AuCl	Toluene	50/6	52
11	AuCl	DCE	50/6	51
11	AuCl	DMF	50/5	Trace
12	AuCl	DCM	50/5	Trace
13	AuCl	$MeNO_2$	50/5	51

[a]Reaction conditions: **5aa** (1 equiv), **6a** (1 equiv), catalyst (10 mol %) and solvent (2.0 mL) at the specified temperature and time under dry nitrogen. [b]Isolated yields. [c]5 mol % of catalyst was used. [d]Alkynyldienol (**5aa**) was completely recovered. NR = No Reaction.

By using above optimal reaction conditions, we then checked its applicability for differently substituted alkynyldienols (**5aa-5da and 5aac**) and activated alkynes (**6a-c**). These reactions afforded the functionalized norbornadienes (**8-23**) in good to excellent yields without any difficulty in isolation (Scheme 3). Alkynyldienol precursors having electron withdrawing groups furnished better yields when compared with those containing electron donating groups. In the present reaction, partially activated alkyne H-C≡C(CO_2Me) was also well tolerated and gave good yield of the corresponding product **18**. Less activated alkyne like diphenyl acetylene did not work in this reaction. The structure of compound **15** was proven by X-ray crystallography (Fig. 2).



Scheme 3 Synthesis of functionalized norbornadienes **8-23**.

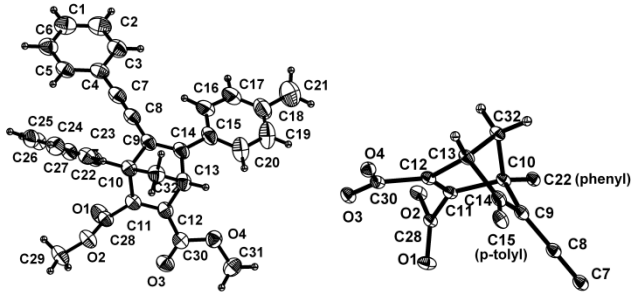
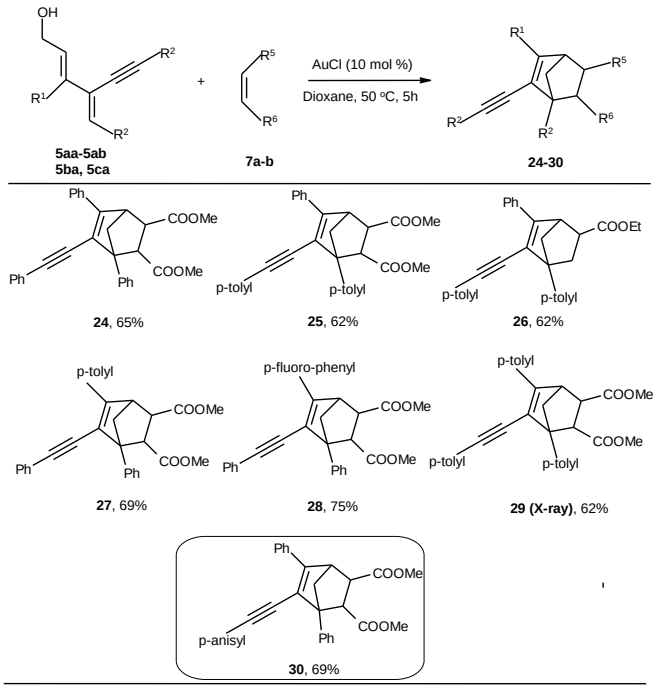


Fig. 2. ORTEP [probability level 30% (left drawing)] of compound **15**. Selected bond lengths [Å] with esds in parentheses: C(9)-C(10) 1.569(4), C(9)-C(14) 1.348(4), C(10)-C(11) 1.554(4), C(10)-C(32) 1.543(4), C(11)-C(12) 1.328(4), C(12)-C(13) 1.535(4), C(13)-C(14) 1.539(5), C(13)-C(32) 1.531(4). On the picture on the right, norbornene part is highlighted.

(iii) Extension to the synthesis of norbornenes 24-30

Interestingly, the present cycloaddition reaction was successfully extended to activated alkenes. Thus the reaction of alkynyldienols with ethyl acrylate/ dimethyl maleate instead

of alkyne substrate furnished the desired products **24-30** in good yields (Scheme 4). The structure of compound **29** was proven by X-ray crystallography (Fig. 3) that suggests exo-isomer. Thus it is possible that the major product in these reactions has a similar stereochemistry. However, it appears that there were diastereomers/isomers (HPLC/^{1}H NMR/ X-ray structure of **25**, See ESI) although this was not indicated in the structure of **29**.



Scheme 4 Reaction of alkynyldienol with ethyl acrylate or dimethyl maleate leading to norbornenes **24-30**.

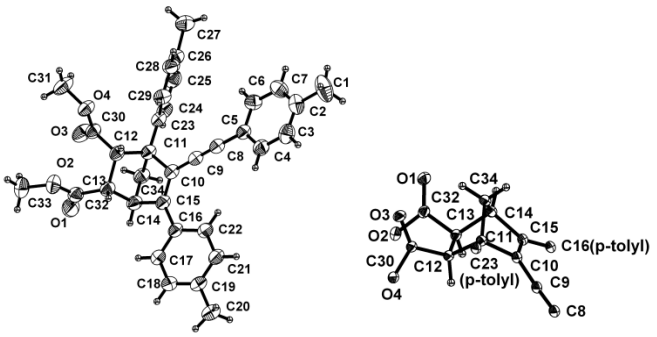
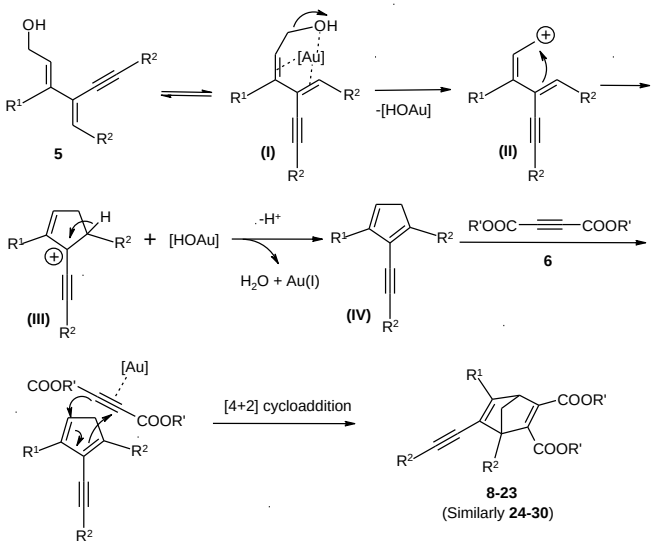


Fig. 3. ORTEP (probability level 30%, left drawing) of compound **29**. Selected bond lengths [Å] with esd's in parentheses: C(8)-C(9) 1.202(2), C(9)-C(10) 1.411(2), C(10)-C(11) 1.543(2), C(11)-C(12) 1.584(2), C(11)-C(34) 1.537(2), C(12)-C(13) 1.568(2), C(13)-C(14) 1.550(2), C(14)-C(15) 1.514(2), C(14)-C(34) 1.526(2), C(15)-C(16) 1.468(2). On the picture on the right, the exo-stereochemistry in the norbornene part is highlighted.

(iv) Possible pathway for the formation of norbornadienes/ norbornenes via gold catalysis

A plausible pathway for the formation of functionalized norbornadienes **8-30** is shown in Scheme 5. We assume that this reaction occurs *via* gold-catalysed dehydration of alkynyldienol followed by [4+2] cycloaddition.[19] Initially, alkynyl *trans*-dienol (**5**) may isomerise to intermediate *cis*-dienol (**I**);[20] then gold catalyst may activate the diene and hydroxyl part. Dehydroxylation[21] will lead to allylic carbocation (**II**). This intermediate may undergo cycloisomerisation resulting in cyclic carbocation (**III**). Subsequent deprotonation furnishes the cyclopentadiene (**IV**)[22] formation one of this intermediate could be detected by the HRMS analysis of the crude reaction mixture (see ESI) which then reacts with activated alkynes or alkenes *via* intermolecular [4+2] cycloaddition[23] leading to the desired products **8-30**. In this reaction, it appears that the alkyne group on the substrate is a requirement for the stabilization of the cationic intermediate.[24]



Scheme 5 Plausible pathway for the formation of functionalized norbornadienes/ norbornenes.

Conclusions

We have developed a new route to norbornadienes/ norbornenes derivatives *via* dehydrative cyclisation followed by intermolecular [4+2] cycloaddition of alkynyldienols and activated alkynes under mild conditions. The present method was successfully extended to activated alkenes also. Alkynyldienol precursors were synthesized by reduction of corresponding alkynyldienals, which were prepared by the Sonogashira cross coupling followed by alkyne addition of 3-bromoenals and terminal alkynes. Strucutral proof has been provided for the key precursors as well as products.

Experimental

General information:

Solvents were dried according to known methods as appropriate.[25] ^{1}H and ^{13}C NMR spectra (Bruker ^{1}H-400 MHz or 500MHz and ^{13}C-100 MHz or 125 MHz) were recorded using a

400 MHz or 500 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ (δ = 0). IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and were uncorrected. Elemental analyses were carried out on a Thermo Finnigan EA1112 analyzer. Mass spectra were recorded using Shimadzu GC-MS or LC-MS instruments. High resolution mass spectra (HR-MS) were performed using a BRUKUR-MAXIS mass spectrometer with ESI-QTOF-II method. Single crystal X-ray data were collected at 298 K on Bruker AXS-SMART or Oxford diffractometer using Mo-K_α (λ = 0.71073 Å) or Cu-K_α (λ = 1.54184 Å) radiation. The structures were solved by direct methods and refined by full matrix least-squares methods using standard procedures.[26] 3-Bromo-acrylic aldehydes were synthesized by following a literature procedure.[15]

General procedure for the synthesis of substituted alkynyldienals 4aa-4da and 4aac: To a stirred solution of (*Z*)-3-bromo-3-phenylacrylaldehyde **1** (5.00 mmol) in CH_3CN (16 mL) was added triethylamine (1 mL), $PdCl_2$ (0.026 g, 0.15 mmol), PPh_3 (0.079 g, 0.30 mmol), CuI (0.057 g, 0.30 mmol) and terminal acetylene **2** (10.00 mmol) at rt and the mixture stirred for 5h. After completion of the reaction, saturated NH_4Cl solution (30 mL) was added followed by extraction with diethyl ether (3x50 mL). The combined organic layer was stripped of the volatiles under vacuum. The crude product was purified by column chromatography using silica gel with hexane/ethyl acetate (10:1) mixture as the eluent. Compounds **4aa-4da** and **4aac** are new.

(2E,4E)-4-benzylidene-3,6-diphenylhex-2-en-5-ynal 4aa: Yellow solid, yield 1.50 g (90%); m.p. 94-96 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.43 (d, *J* = 8.0 Hz, 1H), 7.92-7.90 (m, 2H), 7.58-7.56 (m, 2H), 7.51-7.50 (m, 3H), 7.41-7.36 (m, 7H), 7.27-7.26 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 160.8, 143.6, 135.4, 134.9, 131.7, 130.3, 130.1, 129.9, 129.2, 129.1, 129.0, 128.6, 128.5, 122.8, 122.6, 99.2, 85.6; IR (KBr) ν 3079, 2844, 2197, 1666, 1447, 1337, 1129, 751 cm^{-1}; LC/MS m/z: 335 $[M+1]^+$; Anal. Calcd. for $C_{25}H_{18}O$: C, 89.79; H, 5.43. Found: C, 89.62; H, 5.51.

(2E,4E)-4-(4-methylbenzylidene)-3-phenyl-6-*p*-tolylhex-2-en-5-ynal 4ab: Yellow solid, yield 1.65 g (91%); m.p. 100-102 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.41 (d, *J* = 8.0 Hz, 1H), 7.84-7.82 (m, 2H), 7.50-7.46 (m, 7H), 7.23-7.21 (m, 4H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.70 (s, 1H), 2.41 (s, 3H, ArCH_3), 2.37 (s, 3H, ArCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 161.1, 144.0, 140.4, 139.3, 135.0, 132.8, 131.5, 130.4, 130.2, 129.4, 129.2, 129.0, 128.9, 128.4, 121.8, 119.7, 99.4, 85.3, 21.7,21.6; IR (KBr) ν 3057, 2833, 2191, 1660, 1441, 1183, 871, 706 cm^{-1}; LC/MS m/z: 363 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.34; H, 6.18.

(2E,4E)-4-(4-methoxybenzylidene)-6-(4-methoxyphenyl)-3-phenylhex-2-en-5-ynal 4ac: Bright yellow solid, yield 1.90 g (96%); m.p. 109-111 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.41 (d, *J* = 8.0 Hz, 1H), 7.94-7.92 (m, 2H), 7.55-7.50 (m, 7H), 7.37-6.90 (m, 5H), 6.68 (s, 1H), 3.88 (s, 3H, ArOCH_3), 3.86 (s, 3H, ArOCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 161.4, 160.9, 160.1, 142.7, 135.2, 133.1, 131.9, 130.3, 128.9, 128.5$_1$, 128.5$_0$, 128.4, 120.4, 114.9, 114.3, 113.9, 99.1, 84.8, 55.4; IR (KBr) ν 2981, 2833, 2192, 1655, 1611, 1573, 1337, 1129, 833, 701 cm^{-1}; LC/MS m/z: 395 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.91; H, 5.56.

(2E,4E)-4-(4-fluorobenzylidene)-6-(4-fluorophenyl)-3-phenylhex-2-en-5-ynal 4ad: Yellow solid, yield 1.75 g (95%); m.p. 106-108 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.44 (d, *J* = 8.0 Hz, 1H), 7.82-7.79 (m, 1H), 7.52-7.31 (m, 9H), 7.24 (br s, 1H), 7.15-7.05 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.74 (br s, 1H);); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.8, 162.6 (d, ^1J(F-*C*) = 244.0 Hz), 162.5 (d, ^1J(F-*C*) = 246.0 Hz, F*C*), 159.9, 142.3, 142.2, 137.3 (d, ^3J(F-*C*) = 8.0 Hz), 134.5, 130.3 (d, ^3J(F-*C*) = 10.0 Hz), 129.9 (d, ^3J(F-*C*) = 9.0 Hz), 129.6, 129.3, 128.6, 127.6, 126.3, 124.0 (d, ^3J(F-*C*) = 10.0 Hz), 123.7, 118.4 (d, ^2J(F-*C*) = 23.0 Hz), 117.0 (d, ^2J(F-*C*) = 21.0 Hz), 116.6 (d, ^2J(F-*C*) = 21.0 Hz), 116.0 (d, ^2J(F-*C*) = 22.0 Hz), 98.4, 86.0; IR (KBr) ν 3074, 2844, 2190, 1666, 1573, 1453, 1129, 877, 779 cm^{-1}; LC/MS m/z: 371 $[M+1]^+$; Anal. Calcd. for $C_{25}H_{16}F_2O$: C, 81.07; H, 4.35. Found: C, 81.19; H, 4.31.

(2E,4E)-4-benzylidene-6-phenyl-3-*p*-tolylhex-2-en-5-ynal 4ba: Orange solid, yield 1.52 g (87.5%); m.p. 80-82 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.47 (d, *J* = 8.0 Hz, 1H), 7.94-7.92 (m, 2H), 7.60-7.57 (m, 2H), 7.42-7.25 (m, 10H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 2.47 (s, 3H, ArCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.3, 160.9, 143.5, 139.2, 135.5, 131.8, 131.7, 130.4, 130.1, 129.9, 129.2, 129.0, 128.6, 128.4, 122.9, 122.7, 99.1, 85.8, 21.4; IR (KBr) ν 3058, 2833, 2181, 1660, 1567, 1179, 1129, 751, 685 cm^{-1}; LC/MS m/z: 349 $[M+1]^+$; Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.45; H, 5.86.

(2E,4E)-4-(4-methylbenzylidene)-3,6-di-*p*-tolylhex-2-en-5-ynal 4bb: Bright yellow solid, yield 1.50 g (80%); m.p. 105-107 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.44 (d, *J* = 8.4 Hz, 1H), 7.85-7.83 (m, 2H), 7.48-7.46 (m, 2H), 7.30-7.18 (m, 8H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.75 (s, 1H), 2.46 (s, 3H, ArCH_3), 2.41 (s, 3H, ArCH_3), 2.38 (s, 3H, ArCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.3, 161.3, 143.3, 140.3, 139.2, 139.0, 132.9, 132.0, 131.5, 130.4, 130.1, 129.3, 129.2, 129.1, 128.8, 121.9, 119.7, 99.3, 85.4, 21.6$_2$, 21.6$_0$, 21.4; IR (KBr) ν 3019, 2838, 2197, 1665, 1545, 1177, 1128, 668 cm^{-1}; LC/MS m/z: 377 $[M+1]^+$; Anal. Calcd. for $C_{28}H_{24}O$: C, 89.33; H, 6.43. Found: C, 89.21; H, 6.37.

(2E,4E)-4-benzylidene-3-(4-fluorophenyl)-6-phenylhex-2-en-5-ynal 4ca: Yellow solid, yield 1.60 g (91%); m.p. 101-103 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.44. (d, *J* = 8.4 Hz, 1H), 7.93-7.91 (m, 2H), 7.58-7.56 (m, 2H), 7.42-7.35 (m, 8H), 7.23-7.19 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.73 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.6, 163.1 (d, ^1J(F-C) = 248.0 Hz, F*C*), 159.5, 143.4, 135.3, 132.2, 132.1, 131.7, 130.1, 130.0, 129.6, 129.1, 128.6 (d, ^3J(F-C) = 12.0 Hz), 122.7, 122.5, 115.8 (d, ^2J(F-C) = 22.0 Hz), 99.3, 85.5; IR (KBr) ν 3069, 2838, 2190, 1666, 1579, 1332, 1134, 833, 756 cm^{-1}; LC/MS m/z: 353 $[M+1]^+$; Anal. Calcd. for $C_{25}H_{17}FO$: C, 85.21; H, 4.86. Found: C, 85.36; H, 4.91.

(2E,4E)-3-(4-fluorophenyl)-4-(4-methylbenzylidene)-6-*p*-tolylhex-2-en-5-ynal 4cb: Yellow solid, yield 1.65 g (87%); m.p. 102-104 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.43 (d, *J* = 8.2 Hz, 1H), 7.86-7.84 (m, 2H), 7.49-7.46 (m, 2H), 7.37-7.33 (m,

2H), 7.23-7.18 (m, 6H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.68 (s, 1H), 2.42 (s, 3H, ArCH_3), 2.39 (s, 3H, ArCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.0, 163.1 (d, ^1J(F-*C*) = 247.0 Hz, F*C*), 159.9, 143.2, 140.6, 139.3, 132.7, 132.2, 132.1, 131.5, 131.0, 130.1, 129.4, 129.3, 121.8, 119.6, 115.7 (d, ^2J(F-*C*) = 22.0 Hz), 99.6, 85.2, 21.6$_2$, 21.6$_0$; IR (KBr) ν 3025, 2832, 2197, 1671, 1507, 1178, 821, 669 cm^{-1}; LC/MS m/z: 381 [M+1]$^+$; Anal. Calcd. for $C_{27}H_{21}FO$: C, 85.24; H, 5.56. Found: C, 85.12; H, 5.48.

(2E,4E)-4-benzylidene-3-(4-methoxyphenyl)-6-phenylhex-2-en-5-ynal 4da: Yellow solid, yield 1.55 g (85%); m.p. 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.47 (d, *J* = 8.0 Hz, 1H), 7.93-7.92 (m, 2H), 7.60-7.57 (m, 2H), 7.43-7.36 (m, 7H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.97-6.90 (m, 3H), 6.80 (s, 1H), 3.87 (s, 3H, ArOCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.1, 160.5, 159.5, 143.5, 136.2, 135.5, 131.6, 130.1, 129.9, 129.6, 129.1, 128.6, 128.4, 122.8, 122.5, 115.8, 114.6, 99.1, 85.6, 55.4; IR (KBr) ν 3052, 2833, 2195, 1660, 1485, 1129, 800, 690 cm^{-1}; LC/MS m/z: 365[M+1]$^+$; Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69 H, 5.53. Found: C, 85.52; H, 5.61.

(2*E*,4*E*)-4-benzylidene-6-(4-methoxyphenyl)-3-phenylhex-2-en-5-ynal (4aac): Yellow solid, yield 1.6 g (88%); m.p. 115-117 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.45-9.44 (m, 1H), 7.93-7.92 (m, 2H), 7.54-7.52 (m, 5H), 7.39-7.28 (m, 5H), 6.98-6.94 (m, 3H), 6.73 (s, 1H), 3.88 (s, 3H, ArOCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.2, 160.9, 160.2, 142.9, 135.6, 134.9, 133.2, 130.3, 130.0, 129.8, 129.2, 129.1, 128.4$_4$, 128.4$_0$, 123.0, 114.7, 114.3, 99.4, 84.5, 55.4; IR (KBr) ν 2827, 2197, 1666, 1606, 1507, 1326, 1288, 1129, 696 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{26}H_{21}O_2$: 365.1542; Found: 365.1545.

General procedure for the synthesis of substituted alkynyldienols 5aa-5da and 5aac: To a stirred solution of (2E,4E)-4-benzylidene-3,6-diphenylhex-2-en-5-ynal (2.00 mmol) and $CeCl_3 7H_2O$ (2.00 mmol) were dissolved in methanol (15 mL) then the reaction mixture was kept at 0 ^{o}C, $NaBH_4$ (3.00 mmol) was added mixture stirred further for 1h. After completion of the reaction, methanol was evoparated then H_2O (10 mL) was added followed by extraction with ethylacetate (3x15 mL). The combined organic layer was stripped of the volatilities under vacuum. The crude product was purified by column chromatography using silica gel with hexane/ethyl acetate (20:1) mixture as the eluent. Compounds **5aa-5da** and **5aac** are new.

(2E,4E)-4-benzylidene-3,6-diphenylhex-2-en-5-yn-1-ol 5aa: Orange solid, yield 0.650 g (96.7%); m.p. 96-98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 7.6 Hz, 2H), 7.59-7.57 (m, 2H), 7.46-7.24 (m, 11H), 6.76 (t, *J* = 6.8 Hz, 1H), 6.43 (s, 1H), 4.13 (d, *J* = 6.8 Hz, 2H), 1.46 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.1, 137.9, 137.3, 136.4, 131.5, 130.5, 129.7, 129.3, 128.6, 128.4$_7$, 128.4$_6$, 128.3, 128.1, 127.7, 123.4, 123.2, 97.9, 87.1, 60.8; IR (KBr) ν 3392, 3052, 2190, 1594, 1490, 1447, 756, 701 cm^{-1}; LC/MS m/z: 337 [M+1]$^+$; Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.12; H, 5.93.

(2E,4E)-4-(4-methylbenzylidene)-3-phenyl-6-*p*-tolylhex-2-en-5-yn-1-ol 5ab: Orange gummy solid, yield 0.70 g (96.%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 8.0 Hz, 2H), 7.48-7.40 (m, 5H), 7.23-7.14 (m, 6H), 6.40 (t, *J* = 6.8 Hz, 1H), 6.36 (s, 1H), 4.11 (d, *J* = 6.8 Hz, 2H), 2.41 (s, 3H, ArCH_3), 2.36 (s, 3H, ArCH_3), 1.65 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.3, 138.7, 138.4, 137.7, 137.4, 133.7, 131.4, 129.9, 129.7, 129.3, 129.2, 128.9, 128.4, 127.6, 122.4, 120.3, 98.1, 86.6, 60.9, 21.6, 21.4; IR (neat) ν 3413, 2926, 2198, 1611, 1507, 1041, 811 cm^{-1}; LC/MS m/z: 365 [M+1]$^+$; Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.79; H, 6.71.

(2E,4E)-4-(4-methoxybenzylidene)-6-(4-methoxyphenyl)-3-phenylhex-2-en-5-yn-1-ol 5ac: Orange gummy liquid, yield 0.78 g (98.5%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44-7.22 (m, 5H), 6.95-6.70 (m, 4H), 6.70 (t, *J* = 6.4 Hz, 1H), 6.32 (s, 1H), 4.10 (d, *J* = 6.8 Hz, 2H), 3.88 (s, 3H, ArOCH_3), 3.83 (s, 3H, ArOCH_3), 1.60 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.8, 159.6, 143.5, 137.6, 136.9, 132.9, 130.8, 129.7, 129.4, 128.4, 127.6, 121.3, 115.5, 114.2, 113.6, 97.8, 86.1, 60.9, 55.4, 55.3; IR (neat) ν 3408, 2948, 2838, 2194, 1600, 1507, 1255, 1030, 833 cm^{-1}; LC/MS m/z: 397 [M+1]$^+$; Anal. Calcd. for $C_{27}H_{24}O_3$: C, 81.79; H, 6.01. Found: C, 81.62; H, 6.15.

(2E,4E)-4-(3-fluorobenzylidene)-6-(3-fluorophenyl)-3-phenylhex-2-en-5-yn-1-ol 5ad: Orange solid, yield 0.720 g (96.8%); m.p. 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (m, 1H), 7.46-7.20 (m, 10H), 7.11-7.08 (m, 1H), 7.00-6.96 (m, 1H), 6.72 (t, *J* = 6.8 Hz, 1H), 6.39 (s, 1H), 4.12 (d, *J* = 6.4 Hz, 2H), 1.52 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6 (d, ^1J(F-*C*) = 244.0 Hz, F*C*), 162.5 (d, ^1J(F-*C*) = 244.0 Hz), 142.5, 138.4 (d, ^3J(F-*C*) = 8.0 Hz), 136.9, 136.8, 131.3, 130.2 (d, ^3J(F-*C*) = 9.0 Hz), 129.7, 129.5, 128.6, 127.9, 127.5, 125.5, 124.7 (d, ^3J(F-*C*) = 9.0 Hz), 124.3, 118.3 (d, ^2J(F-*C*) = 23.0 Hz), 116.2 (d, ^2J(F-*C*) = 21.0 Hz), 115.5, 115.4 (d, ^2J(F-*C*) = 22.0 Hz), 97.2, 87.4, 60.8; IR (KBr) ν 3578, 2195, 1611, 1583, 1441, 1178, 1019, 959, 712 cm^{-1}; LC/MS m/z: 373 [M+1]$^+$; Anal. Calcd. for $C_{25}H_{18}F_2O$: C, 80.63; H, 4.87. Found: C, 80.76; H, 4.81.

(2E,4E)-4-benzylidene-6-phenyl-3-*p*-tolylhex-2-en-5-yn-1-ol 5ba: Orange solid, yield 0.670 g (95.7%); m.p. 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 7.6 Hz, 2H), 7.57-7.56 (m, 2H), 7.34-7.32 (m, 5H), 7.29-7.23 (m, 3H), 7.12-7.10 (m, 2H), 6.73 (t, *J* = 6.8 Hz, 1H), 6.45 (s, 1H), 4.13 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H, ArCH_3), 1.42 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.1, 137.8, 137.4, 136.5, 134.2, 131.6, 130.4, 129.6, 129.3, 129.1, 128.6, 128.5, 128.3, 128.1, 123.5, 123.3, 97.8, 87.2, 60.9, 21.3; IR (KBr) ν 3397, 3013, 2865, 2192, 1490, 1446, 1095, 1013, 755, 685cm^{-1}; LC/MS m/z: 351 [M+1]$^+$; Anal. Calcd. for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 89.23; H, 6.41.

(2E,4E)-4-(4-methylbenzylidene)-3,6-di-*p*-tolylhex-2-en-5-yn-1-ol 5bb: Orange solid, yield 0.730 g (96.4%); m.p. 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.25-7.10 (m, 8H), 6.72 (t, *J* = 6.8 Hz, 1H), 6.40 (s, 1H), 4.12 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H, ArCH_3), 2.41 (s, 3H, ArCH_3), 2.36 (s, 3H, ArCH_3), 1.46 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.3, 138.6, 138.3, 137.6, 137.3, 134.3, 133.8, 131.4, 129.8, 129.6, 129.3, 129.2, 129.1, 128.9, 122.6, 120.3, 98.1, 86.7, 60.9, 21.6, 21.4, 21.3; IR (KBr) ν 3403, 2915, 2197, 1611, 1512, 1025, 959, 811 cm^{-1}; LC/MS m/z: 377 [M-1]$^+$; Anal. Calcd. for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.74; H, 6.85.

(2E,4E)-4-benzylidene-3-(4-fluorophenyl)-6-phenylhex-2-en-5-yn-1-ol 5ca: Orange solid, yield 0.690 g (97.4%); m.p. 112-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 7.6 Hz, 2H), 7.56-7.55 (m, 2H), 7.34-7.28 (m, 6H), 7.22-7.19 (m, 2H), 7.16-7.12 (m, 2H), 6.74 (t, *J* = 6.4 Hz, 1H), 6.39 (s, 1H), 4.11 (d, *J* = 6.4 Hz, 2H), 1.49 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6 (d, ^{1}J(F-C) = 246.0 Hz, F*C*), 142.1, 137.8, 136.2, 133.1, 131.6, 131.5,131.4, 130.9, 129.3, 128.6 (d, ^{3}J(F-C) = 14.0 Hz), 128.2, 123.3, 123.1, 115.5 (d, ^{2}J(F-*C*) = 21.0 Hz, FC=*C*), 98.1, 86.9, 60.8; IR (KBr) ν 3260, 2367, 2193, 1594, 1501, 1222, 1013, 844, 696 cm^{-1}; LC/MS m/z: 355 [M+1]$^{+}$; Anal. Calcd. for $C_{25}H_{19}FO$: C, 84.72; H, 5.40. Found: C, 84.56; H, 5.48.

(2E,4E)-3-(4-fluorophenyl)-4-(4-methylbenzylidene)-6-*p*-tolylhex-2-en-5-yn-1-ol 5cb: Orange solid, yield 0.730 g (95.5%); m.p. 115-117 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.21-7.12 (m, 8H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.33 (s, 1H), 4.01 (d, *J* = 6.8 Hz, 2H), 2.40 (s, 3H, ArC*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 1.60 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.3, (d, ^{1}J(F-*C*) = 245.0 Hz), 142.3, 138.8, 138.6, 137.6, 133.5, 133.3, 131.4, (d, ^{3}J(F-*C*) = 6.0 Hz), 130.4, 129.3, 128.9, 122.4, 120.2, 115.5, (d, ^{2}J(F-*C*) = 21.0 Hz), 98.3, 86.5, 60.8, 21.6, 21.4; IR (KBr) ν 3567, 3019, 2192, 1600, 1512, 1157, 822 cm^{-1}; LC/MS m/z: 383 [M+1]$^{+}$; Anal. Calcd. for $C_{27}H_{23}FO$: C, 84.79; H, 6.06. Found: C, 84.65; H, 6.13.

(2E,4E)-4-benzylidene-3-(4-methoxyphenyl)-6-phenylhex-2-en-5-yn-1-ol 5da: Orange solid, yield 0.71 g (97%); m.p. 114-116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 7.6 Hz, 2H), 7.59-7.57 (m, 2H), 7.42-7.28 (m, 6H), 7.18-7.16 (m, 2H), 7.00-6.98 (m, 2H), 6.74 (t, *J* = 6.8 Hz, 1H), 6.50 (s, 1H), 4.16 (d, *J* = 6.8 Hz, 2H), 3.89 (s, 3H, ArOC*H*$_3$)1.52 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.1, 142.8, 137.8, 136.5, 131.5, 130.9, 130.5, 129.4, 129.3, 128.5$_4$, 128.5$_0$, 128.3, 128.2, 123.7, 123.3, 113.9, 97.9, 87.3, 60.9, 55.3; IR (KBr) ν 3414, 2915, 2185, 1611,1512, 1485, 1255, 1025, 751, 696 cm^{-1}; LC/MS m/z: 367 [M+1]$^{+}$; Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.36; H, 6.12.

(2*E*,4*E*)-4-benzylidene-6-(4-methoxyphenyl)-3-phenylhex-2-en-5-yn-1-ol (5aac): Pale yellow solid, yield 0.65 g (88%); m.p. 121-123 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 8.0 Hz, 2H), 7.53-7.24 (m, 10H), 6.94 (~d, *J* ~ 8.0 Hz, 2H), 6.76 (t, *J* = 7.0 Hz, 1H), 6.40 (s, 1H), 4.13 (d, *J* = 7.0 Hz, 2H), 3.85 (s, 3H) 1.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.9, 143.1, 137.4, 137.2, 136.6, 130.5, 129.8, 128.5, 128.2, 128.1, 127.7, 123.6, 115.4, 114.2, 98.1, 85.9, 60.8, 55.4; IR (KBr) ν 3671, 1649, 1600, 1507, 1293, 1162, 1060, 690 cm^{-1}; HRMS (ESI): *m/z* [M + Na]$^{+}$ calcd. for $C_{26}H_{22}O_2Na$: 389.1517; Found: 389.1516.

Synthesis of substituted bicyclo[2.2.1]hepta-2,5-diene carboxylates 8-30: General Procedure: To a stirred solution of (*2E,4E*)-4-benzylidene-3,6-diphenylhex-2-en-5-yn-1-ol (0.5 mmol), dialkyl dicarboxylate (0.5 mmol) in dioxane (2 mL) was added AuCl (0.05 mmol) at rt under nitrogen atmosphere. The solution was stirred at 50 ^{o}C till the starting material was consumed [*Note*: The reaction mixture using **5bb** in the absence of DMAD, showed a peak in HRMS at 361.1958 that corresponds to [M+H]$^{+}$ peak (calcd: 361.1912) for the corresponding cyclopentadiene]. Solvent was removed under vacuum and the crude product was purified by column chromatography using silica gel with hexane/ethyl acetate (10:1) mixture as the eluent to obtain one of the products **8-30**.

Compound 8: Orange gummy liquid, yield 0.205 g (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, *J* = 6.8 Hz, 2H), 7.63 (d, *J* = 6.4 Hz, 2H), 7.48-7.28 (m,11H), 4.61 (s, 1H), 4.30-4.25 (m, 2H), 4.16-4.14 (m, 2H), 2.93 (d, *J* = 6.4 Hz, 1H), 2.75 (d, *J* = 6.0 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.12 (t, *J* = 5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4, 163.1, 160.0, 158.0, 143.7, 136.1, 134.9, 131.1, 130.4, 128.6, 128.4, 128.3$_3$, 128.3$_0$, 128.0, 127.9, 127.6, 126.9, 123.6, 105.0, 86.3, 73.5, 70.7, 61.3, 61.2, 52.0, 14.1, 14.0; IR (neat) ν 3052, 2981, 1737, 1715, 1627, 1447, 1370, 1030, 756 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^{+}$ calcd. for $C_{33}H_{29}O_4$: 489.2067; Found: 489.2066.

Compound 9: Orange gummy solid; yield 0.193 g (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 7.2 Hz, 2H), 7.60-7.58 (m, 2H), 7.47-7.45 (m, 5H), 7.37-7.28 (m, 6H), 4.62 (s, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 2.93 (d, *J* = 5.6 Hz, 1H), 2.77 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.8, 163.5, 160.1, 157.7, 143.7, 135.9, 134.7, 131.6, 131.1, 130.4, 128.6, 128.5, 128.3, 128.0, 127.8, 127.7, 126.9, 123.6, 105.1, 86.1, 73.6, 70.7, 54.0, 52.2, 51.9; IR (neat) ν 3055, 2983, 2172, 1725, 1703, 1627, 1442, 1378, 1036, 758 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^{+}$ calcd. for $C_{31}H_{25}O_4$: 461.1754; Found: 461.1750.

Compound 10: Orange solid; yield 0.23 g (89%); m.p. 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12-8.02 (m, 2H), 7.63-7.12 (m, 11H), 4.59 (s, 1H), 4.29-4.24 (m, 2H), 4.17-4.14 (m, 2H), 2.91-2.90 (m, 1H), 2.73-2.71 (m, 1H), 2.43 (s, 3H, ArC*H*$_3$), 2.38 (s, 3H, ArC*H*$_3$), 1.33 (t, *J* = 5.8 Hz, 3H), 1.15 (t, *J* = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.5, 163.1, 160.2, 157.5, 143.6, 138.5, 137.1, 135.0, 133.1, 131.0, 130.7, 129.2, 129.1, 128.7, 128.4, 127.8, 127.0, 120.7, 105.1, 85.8, 73.3, 70.7, 61.3, 61.1, 51.9, 21.6, 21.2, 14.1, 14.0; IR (KBr) 2975, 2871, 2193, 1745, 1715, 1638, 1370, 1310, 1036, 767 cm^{-1}; HRMS (ESI): *m/z* [M^{+}+Na] Calcd. for $C_{35}H_{32}O_4Na$: 539.2199; Found: 539.2196.

Compound 11: Orange gummy solid, yield 0.232 g (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11-8.09 (m, 2H), 7.56-7.54 (m, 2H), 7.46-7.43 (m, 2H), 7.35-7.28 (m, 3H), 7.00-6.97 (m, 2H), 6.87-6.85 (m, 2H), 4.58 (s, 1H), 4.33-4.23 (m, 2H), 4.17-4.14 (m, 2H), 3.87 (s, 3H, ArOC*H3*), 3.83 (s, 3H, ArOC*H*$_3$), 2.90 (d, *J* = 8.8 Hz, 1H), 2.70 (d, *J* = 8.8 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.5, 163.1, 160.2, 159.7, 159.0, 156.7, 143.5, 135.0, 132.5, 130.9, 129.1, 128.4, 128.0, 127.9,126.8, 115.9, 114.0, 113.3, 105.1, 85.2, 72.9, 70.7, 61.2, 61.1, 55.3$_1$, 55.3$_0$, 51.8, 14.1, 14.0; IR (neat) ν 3046, 2931, 2832, 2180, 1731, 1715, 1604, 1468, 1369, 1177, 1029, 827 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^{+}$ calcd. for $C_{35}H_{33}O_6$: 549.2278; Found: 549.2272.

Compound 12: Yellow solid, yield 0.215 g (83%); m.p.120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J* = 8.0 Hz, 2H), 7.52-7.29 (m, 7H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.60 (s, 1H), 3.86 (s, 3H, ArOC*H*$_3$), 3.82 (s, 3H, ArOC*H*$_3$), 3.80 (s, 3H, ArCOOC*H*$_3$), 3.69 (s, 3H, ArCOOC*H*$_3$), 2.89 (d, *J* = 7.2 Hz, 1H), 2.71 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

(ppm) 167.0, 163.5, 160.3, 159.8, 159.1, 156.5, 143.6, 134.9, 132.6, 130.9, 129.0, 128.4$_4$, 128.4$_0$, 128.2, 126.8, 115.8, 114.1, 113.4, 105.4, 85.1, 73.0, 70.7, 55.3$_2$, 55.3$_0$, 52.2, 51.8; IR (KBr) ν 3003, 2942, 2175, 1732, 1715, 1605, 1507, 1118, 1036, 827, 762, 696 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{33}H_{29}O_6$: 521.1965; Found: 521.1963.

Compound 13: Yellow solid, yield 0.235 g (92%); m.p. 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08-7.81 (m, 2H), 7.59-7.26 (m, 7H), 7.11-7.00 (m, 4H), 4.61-4.60 (m, 1H), 4.27- 4.15 (m, 4H), 2.93-2.90 (m, 1H), 2.75-2.70 (m, 1H), 1.34-1.28 (m, 3H), 1.17-1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 162.5 (d, ^1J(F-*C*) = 243.0 Hz, F*C*), 162.9, 162.4 (d, ^1J(F-*C*) = 245.0 Hz, F*C*), 159.2, 143.8, 138.5, 136.7 (d, ^3J(F-*C*) = 8.0 Hz, F*C*), 130.0, 129.6 (d, ^3J(F-*C*) = 8.0 Hz, F*C*), 129.0, 128.6, 127.0, 125.2 (d, ^3J(F-*C*) = 10.0 Hz, F*C*), 123.6, 117.8, 117.6, 115.7 (d, ^2J(F-*C*) = 21.0 Hz, F*C*), 115.5 (d, ^2J(F-*C*) = 22.0 Hz, F*C*), 114.7 (d, ^2J(F-*C*) = 21.0 Hz, F*C*), 103.7, 86.8, 73.6, 72.8, 70.7, 61.5, 61.3, 52.1, 14.1, 14.0; IR (KBr) ν 3069, 2975, 2191, 1723, 1704, 1633, 1485, 1364, 1249, 1135, 784, 696 cm^{-1}; HRMS (ESI): m/z [M + H]$^+$ calcd. for $C_{33}H_{27}F_2O_4$: 525.1878; Found: 525.1875.

Compound 14: Orange gummy liquid, yield 0.220 g (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11-8.00 (m, 2H), 7.62 -7.60 (m, 1H), 7.51-7.25 (m, 11H), 4.58 (s, 1H), 4.30-4.24 (m, 2H), 4.16-4.12 (m, 2H), 2.90 (d, *J* = 5.6 Hz, 1H), 2.72 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H, ArC*H*$_3$), 1.34-1.29 (m, 3H), 1.13-1.08 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4, 163.1, 160.0, 158.1, 143.6, 138.7, 136.2, 132.1, 131.0, 129.2, 128.7, 128.4, 128.3, 128.0, 127.9, 127.6, 126.9, 123.8, 104.7, 86.5, 73.4, 70.7, 61.2, 61.1, 51.9, 21.4, 21.2, 14.1; IR (neat) ν 3063, 2986, 2932, 2191, 1732, 1716, 1633, 1370, 1260, 1107, 762 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{34}H_{31}O_4$: 503.2223; Found: 503.2221.

Compound 15: Orange solid, yield 0.20 g (84.5%); m.p. 118-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00-7.97 (m, 2H), 7.58-7.57 (m, 2H), 7.47-7.39 (m, 3H), 7.32-7.25 (m, 7H), 4.59 (s, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 2.90 (d, *J* = 6.8 Hz, 1H), 2.74 (d, *J* = 6.8 Hz, 1H), 2.40 (s, 3H, Ar C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.9, 164.0, 160.2, 157.8, 143.7, 138.8, 136.0, 132.0, 131.0, 129.2, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7, 126.8, 123.7, 105.0, 86.3, 73.4, 70.7, 52.3, 51.9, 21.5; IR (KBr) ν 2980, 2942, 2193, 1725, 1709, 1638, 1325, 1260, 1117, 761, 690 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{32}H_{27}O_4$: 475.1909; Found: 475.1908.

Compound 16: Orange gummy solid, yield 0.236 g (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.28-7.23 (m, 6H), 7.14-7.12 (m, 2H), 4.56 (s, 1H), 4.33-4.24 (m, 2H), 4.16-4.13 (m, 2H), 2.88 (d, *J* = 8.8 Hz, 1H), 2.70 (d, *J* = 8.4 Hz, 1H), 2.41 (s, 3H, ArC*H*$_3$), 2.40 (s, 3H, ArC*H*$_3$), 2.37 (s, 3H, ArC*H*$_3$), 1.36-1.29 (m, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.5, 163.1, 160.2, 157.5, 151.8, 143.6, 138.5, 138.3, 137.0, 132.2, 130.1, 129.1, 129.0, 128.6, 127.8, 126.8, 120.8, 104.8, 86.0, 73.2, 70.7, 63.0, 61.2, 61.0, 51.9, 21.4, 21.2, 14.1, 14.0, 13.9; IR (neat) ν 2975, 2916, 2193, 1752, 1715, 1622, 1512, 1260, 1107. 816 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$; calcd. for $C_{36}H_{35}O_4$: 531.2535; Found: 531.2529.

Compound 17: Orange solid, 0.21 g (84%); m.p. 113-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.28-7.23 (m, 6H), 7.14-7.12 (m, 2H), 4.57 (s, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 2.89 (d, *J* = 6.8 Hz, 1H), 2.71 (d, *J* = 7.0 Hz, 1H), 2.42 (s, 3H, ArC*H*$_3$), 2.41 (s, 3H, ArC*H*$_3$), 2.37 (s, 3H, ArC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0, 163.6, 160.4, 157.3, 143.6, 138.6, 138.4, 137.2, 133.0, 132.1, 131.3, 131.0, 129.5, 129.2, 129.1, 128.7, 127.7, 126.8, 120.7, 105.1, 85.8, 73.2, 70.7, 52.2, 51.8, 21.6, 21.5, 21.3; IR (KBr) ν 3025, 2943, 2194, 1742, 1715, 1644, 1518, 1321, 1118, 816 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{34}H_{31}O_4$: 503.2223; Found: 503.2220.

Compound 18: Orange solid, yield 0.168 g (76%; purity ca 96%); m.p. 118-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 12.0 Hz, 2H), 7.32-7.13 (m, 9H), 4.18 (t, *J* ~ 1.6 Hz, 1H), 3.64 (s, 3H), 2.65 (m, 1H), 2.56 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H, ArC*H*$_3$), 2.41 (s, 3H, ArC*H*$_3$), 2.40 (s, 3H, ArC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.3, 158.1, 153.9, 150.3, 138.3, 138.2, 136.2, 135.1, 132.5, 131.0, 130.1, 129.1$_2$, 129.1$_0$, 128.6, 128.2, 126.0, 121.0, 104.5, 86.8, 73.3, 70.3, 51.9, 51.4, 21.6, 21.4, 21.2; IR (KBr) ν 3025, 2915, 2186, 1720, 1605, 1436, 1179, 822, 734 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{32}H_{29}O_2$: 445.2168; Found: 445.2167. The assignment is tentative but a triplet with a small *J* value of 1.6 Hz at δ 4.18 (for C*H*-CH_2) is indication that the olefinic proton is 4-bonds away as assigned.

Compound 19: Orange solid, yield 0.22 g (92%); m.p. 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08-8.05 (m, 2H), 7.58-7.56 (m, 2H), 7.48-7.40 (m, 3H), 7.32-7.30 (m, 5H), 7.16-7.11 (m, 2H), 4.56 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.91(d, *J* = 6.4 Hz, 1H), 2.76 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.8, 164.0, 162.7 (d, ^1J(F-*C*) = 248.0 Hz, F*C*), 160.2, 156.7, 143.5, 135.8, 131.6, 131.1, 130.0$_1$, 130.0$_0$, 128.7, 128.4, 128.1, 127.8, 126.9, 123.4, 115.5 (d, ^2J(F-*C*) = 22.0 Hz, F*C*), 105.1, 85.8, 73.5, 70.7, 52.4, 52.3; IR (KBr) ν 3058, 2948, 2195, 1732, 1715, 1644, 1605, 1227, 1129, 762 cm^{-1}; HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_{31}H_{24}FO_4$: 479.1659; Found: 479.1656.

Compound 20: Yellow solid, yield 0.235 g (93%); m.p. 120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01-7.98 (m, 2H), 7.60-7.48 (m, 2H), 7.26-7.21 (m, 4H), 7.14-7.10 (m, 4H), 4.57-4.52 (m, 1H), 4.27- 4.22 (m, 2H), 4.16-4.13 (m, 2H), 2.88 (d, *J* = 6.8 Hz, 1H), 2.69 (d, *J* = 6.8 Hz, 1H), 2.41 (s, 3H, ArC*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 1.31 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4, 164.0, 161.7 (d, ^1J(F-*C*) = 291.0 Hz, F*C*), 157.5, 156.5, 143.4, 138.6, 137.2, 133.0, 130.1, 129.2, 128.7 (d, ^3J(F-*C*) = 13.0 Hz, F*C*), 127.8, 126.8, 120.5, 115.4 (d, ^2J(F-*C*) = 21.0 Hz, F*C*), 114.9, 114.7, 105.0, 85.5, 73.3, 70.7, 61.3, 61.2, 52.0, 21.6, 21.2, 14.1, 14.0; IR (KBr) ν 2975, 2926, 2186, 1725, 1715, 1655, 1600, 1512, 1266, 1019, 833 cm^{-1}; HRMS (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{35}H_{31}FO_4Na$: 557.2104; Found: 557.2102.

Compound 21: Yellow gummy liquid, yield 0.227 g (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 8.8 Hz, 2H), 7.65-7.63 (m, 2H), 7.48-7.28 (m, 8H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.60 (s, 1H), 4.29-4.24 (m, 2H), 4.17-4.15 (m, 2H), 3.88 (s, 3H, ArOC*H*$_3$), 2.91 (d, *J* = 5.6 Hz, 1H), 2.72 (d, *J* = 5.6 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.5, 163.2, 160.1, 159.9, 157.8, 143.5, 136.2, 131.0, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 123.8, 113.9,

113.4, 104.3, 86.7, 73.3, 70.5, 61.2, 61.1, 55.4, 52.0, 14.1, 14.0; IR (neat) ν 2980, 2898, 2192, 1725, 1704, 1599, 1260, 1035, 755 cm^{-1}; HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{34}H_{31}O_5$: 519.2172; Found:519.2172.

Compound 22: Orange solid, yield 0.21 g (86%); m.p. 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09-8.05 (m, 2H), 7.60-7.59 (m, 1H), 7.58-7.46 (m, 3H), 7.34-7.00 (m, 6H), 6.99-6.98 (m, 2H), 4.60 (s, 1H), 3.88 (s, 3H, ArOC*H*$_3$), 3.81 (s, 3H), 3.70 (s, 3H), 2.90 (d, *J* = 5.6 Hz, 1H), 2.74 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.0, 163.5, 159.1, 157.7, 143.5, 134.8, 131.1, 131.0, 129.0, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 126.9, 113.9, 113.4, 105.1, 86.2, 73.3, 72.9, 70.8, 55.3, 52.3, 51.9; IR (KBr) ν 2936, 2833, 2188, 1732, 1715, 1621, 1436, 1260, 762 cm^{-1}; HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{27}O_5$: 491.1859; Found: 491.1854.

Compound 23: Yellow solid, yield 0.20 g (82%); m.p. 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10-8.08 (m, 2H), 7.60-7.59 (m, 2H), 7.60-7.33 (m, 8H), 7.28-7.26 (m, 2H), 6.87-6.85 (m, 2H), 4.60 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 2.92 (d, *J* = 8.0 Hz, 1H), 2.76 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.8, 163.5, 160.1, 160.0, 156.5, 143.8, 136.0, 134.9, 132.6, 131.1, 130.7, 127.9, 127.6, 126.8, 126.0, 115.8, 114.0, 113.9, 105.4. 85.0, 73.6, 70.7, 55.4, 55.3, 52.1, 51.9; IR (KBr) ν 2943, 1765, 1726, 1633, 1600, 1315, 1244, 827, 756 cm^{-1}; HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{26}O_5Na$: 513.1678; Found: 513.1677.

Compound 24: Yellow solid, yield 0.150 g (65%); m.p. 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.94-7.93 (m, 2H), 7.92-7.53 (m, 2H), 7.51-7.28 (m, 11H), 3.94 (s, 1H), 3.69 (s, 3H), 3.59 (d, *J* = 10.0 Hz, 1H), 3.33 (s, 3H), 3.11 (d, *J* = 8.0 Hz, 1H), 2.90 (d, *J* = 9.5 Hz, 1H), 2.32 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.9, 172.3, 151.7, 137.3, 134.0, 131.2, 128.6,128.5$_0$, 128.5$_0$, 128.4, 128.3, 128.1, 127.6, 127.2, 126.6, 123.3, 101.1, 85.6, 66.4, 53.3, 52.1, 51.5, 50.4, 45.8, 45.3; IR (KBr) ν 2952, 2192, 1748, 1726, 1436, 1332, 1200, 1025, 756, 690 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{26}O_4Na$ $[M^+$+Na]: *m/z* 485.1729; Found: 485.1729.

Compound 25: Yellow solid, yield 0.145 g (62%); m.p.146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.91 (~d, *J* = 6.4 Hz, 1H), 7.84-7.83 (d, *J* = 6.4 Hz, 1H), 7.52-7.10 (m, 11H), 3.91-3.90 (2 s or a d, 1H), 3.70 (s, 3H), 3.58-3.54 (m, 1H), 3.33-3.31 (2 s, 3H), 3.10-3.07 (m, 1H), 2.89-2.86 (m, 1H), 2.40-2.36 (4 s, total 6H), 2.30-2.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.3, 151.2, 151.1, 138.5$_1$, 138.5$_0$, 138.4, 137.5, 136.5, 134.3, 134.2, 131.1, 131.0, 129.2, 129.0, 128.3, 128.2, 127.5, 127.0, 126.5$_2$, 126.5$_0$, 120.4, 120.3, 101.2, 85.2, 66.3, 66.2, 53.4, 53.3, 52.0, 51.4$_2$, 51.4$_0$, 50.5$_4$, 50.5$_0$, 45.8, 45.3, 45.2, 21.5, 21.3, 21.2; IR (KBr) ν 2948, 2186, 1737, 1726, 1600, 1430, 1195, 1052, 811 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{31}O_4$ $[M^+$+H] *m/z* 491.2223; Found: 491.2222. The multiplet pattern observed for this compound may indicate two inseparable diastereomers/isomers, but NMR spectrum of a single crystal also showed the same pattern (ESI and see below for X-ray data).

Compound 26: Yellow gummy solid, yield 0.131 g (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.61 (m, 2H), 7.59-7.40 (m, 2H), 7.34-7.22 (m, 5H), 7.08-7.05 (m, 4H), 4.01-3.96 (m, 2H), 3.62-3.58 (m, 1H), 3.54-3.53 (m, 1H), 2.48-2.44 (m, 1H), 2.41 (s, 3H, ArC*H*$_3$), 2.33 (s, 3H, ArC*H*$_3$), 2.05-1.98 (m, 2H), 1.84-1.82 (m, 1H), 1.03 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 151.9, 137.9, 136.8, 136.1, 134.9, 131.0, 130.1, 128.9, 128.5, 128.3, 127.9, 127.5, 127.0, 123.1, 98.6, 87.0, 66.6, 60.4, 56.4, 47.4, 44.7, 33.6, 21.5, 21.1, 13.9; IR (neat) ν 2981, 2860, 2203, 1726, 1600, 1266, 1173, 811 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{30}O_2Na$ $[M^+$+Na] *m/z* 469.2144; Found: 469.2147.

Compound 27: Yellow solid, yield 0.165 g (69%); m.p. 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.53-7.19 (m, 12H), 3.92 (s, 1H), 3.69 (s, 3H), 3.56-3.55 (m, 1H), 3.34-3.32 (2 s, 3H), 3.11-3.08 (m, 1H), 2.91-2.88 (m, 1H), 2.41-2.40 (2 s, 3H), 2.32-2.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.9, 172.3, 151.7, 151.6, 138.6, 137.4, 136.6, 134.2, 134.1, 131.3, 131.2, 129.3, 128.5$_4$, 128.5$_0$, 128.3$_2$, 128.3$_0$, 127.6, 127.2, 126.6, 126.5, 123.4, 100.9, 85.8$_2$, 85.8$_0$, 66.3, 66.1, 53.4, 53.3, 52.1, 51.6, 51.5, 50.5, 50.4, 45.8, 45.3, 45.2, 21.4, 21.2; IR (KBr) ν 2942, 2196 (w), 1742, 1732, 1430, 1326, 1195, 1041, 756, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{32}H_{28}O_4Na$ $[M^+$+Na] *m/z* 499.1886; Found: 499.1887. The multiplet pattern observed for this compound may indicate two inseparable diastereomers/isomers. Variable temperature ^{1}H NMR spectra (-20- 80 °C; toluene-d_8) did not show any change. HPLC (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate) showed it to be a mixture of isomers/diastereomers.

Compound 28: Yellow solid, yield 0.18 g (75%); m.p. 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94-7.93 (br m, 2H), 7.53-7.28 (m, 10H), 7.16-7.09 (m, 2H), 3.95-3.90 (2 s, 1H), 3.70 (s, 3H), 3.61-3.55 (m, 1H), 3.36-3.33 (2 s, total 3H), 3.13-3.10 (m, 1H), 2.92-2.90 (m, 1H), 2.33-2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.7, 172.2, 172.1, 162.3 (d, ^1J(F-*C*) = 298.0 Hz, F*C*), 151.8, 150.6, 137.2, 133.9, 133.2$_1$, 133.2$_0$, 131.2, 130.1 (d, ^3J(F-*C*) = 8.0 Hz, F*C*), 128.6, 128.5, 128.4$_2$, 128.4$_0$, 127.6, 127.3, 126.6, 123.1, 115.5 (d, ^2J(F-*C*) = 21.4 Hz, F*C*), 114.4 (d, ^2J(F-*C*) = 21.1 Hz, F*C*), 101.2, 101.1, 85.4, 66.4, 65.7, 53.4, 53.3, 52.1, 51.6, 51.5, 50.4$_4$, 50.4$_0$, 45.9, 45.8, 45.5, 45.3; IR (KBr) ν 2997, 2942, 2186, 1748, 1726, 1600, 1436, 1337, 1195, 833, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{31}H_{25}FO_4Na$ $[M^+$+Na] *m/z* 503.1635, Found 503.1635. The multiplet pattern observed for this compound may indicate two inseparable diastereomers/isomers, but NMR spectrum of a single crystal also showed the same pattern.

Compound 29: Orange yellow solid, yield 0.156 g (62%); m.p. 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28-7.20 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 1H), 3.68 (s, 3H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.33 (s, 3H), 3.07 (d, *J* = 9.6 Hz, 1H), 2.86 (d, *J* = 9.2 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 2.26 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.0, 172.4, 151.1, 138.4$_3$, 138.4$_2$, 136.5, 134.4, 131.3, 131.1, 129.2, 129.1, 128.3, 128.2, 127.3, 126.5, 120.4, 101.0, 85.4, 66.0, 53.4, 52.0, 51.5, 50.5, 45.7, 45.2, 21.6, 21.4, 21.2; IR (KBr) ν 2942, 1753, 1742, 1435, 1337, 1120, 1052, 816 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{33}O_4$ $[M^+$+H] *m/z* 505.2379; Found 505.2376. Chiral HPLC (isopropanol/hexane; 5:95; chiralpack AS-H column; 0.5 mL/min flow rate) trace showed it to be a mixture of

suggested the presence of two isomers (enantiomers). X-ray structure was determined for this compound.

Compound 30: Orange yellow solid, yield 0.170 g (69%); m.p. 158-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* ~ 8.0 Hz, 2H), 7.54-7.52 (m, 2H), 7.45-7.34 (m, 6H), 7.23-7.21 (m, 2H), 6.85-6.83 (m, 2H), 3.93 (s, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.56 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H), 3.11 (d, *J* = 8.0 Hz, 1H), 2.90 (d, *J* = 7.5 Hz, 1H), 2.31 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.9, 172.3, 159.8, 150.4, 137.5, 134.2, 132.8, 128.5$_2$, 128.5$_0$, 128.4, 128.3, 127.6, 127.2, 126.5, 115.4, 114.0, 101.4, 84.5, 66.4, 55.3, 53.3, 52.1, 51.5, 50.5, 45.7, 45.2; IR (KBr) ν 2943, 1743, 1740, 1600, 1436, 1249, 1025, 838, 701 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{28}O_5Na$ [M^++Na] *m/z* 515.1835; Found 515.1836.

Compound 31: The precursor α,β,γ,δ-unsaturated aldehyde was synthesized by following literature procedure.[27] Reduction of the aldehyde by using $NaBH_4$/MeOH afforded compound **31**. Oily liquid, yield 0.39 g (by starting with 2 mmol of the corresponding aldehyde, 89%), ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55-7.51 (m, 1H), 7.43-7.38 (m, 3H), 7.12-7.10 (m, 2H), 6.26 (t, *J* ~ 6.0 Hz, 1H), 5.52 (d, *J* ~ 15.6 Hz, 1H), 4.13 (d, *J* ~ 6.0 Hz, 2H), 3.73 (s, 3H), 1.71 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.5, 147.6, 140.9, 138.9, 135.5, 129.0, 128.6, 128.0, 120.9, 60.2, 51.5; IR (neat) ν 2942, 1720, 1621, 1435, 1314, 1167 cm^{-1}; HRMS ESI: Calcd. for $C_{13}H_{15}O_3$ [M^++H]: *m/z* 219.1021; Found: 219.1025.

***X-ray Data*:** X-ray structures for compounds **4ab, 5aa**, **15**, **25**, and **29** were determined. The CCDC numbers are CCDC 1061733-1061737.

Compound 4ab: $C_{27}H_{22}O$, *M* = 362.45, Triclinic, Space group *P-1*, *a* = 8.7294 (17) Å, *b* = 9.0226 (18) Å, *c* = 13.246(3) Å, α = 89.48 (3)°, β = 79.49 (3)°, γ = 89.81 (3)°, *V* = 1025.7(3) Å^3, *Z* = 2, μ = 0.070 mm^{-1}, data/restraints/parameters: 4022/0/255, R indices (I> 2σ(I)): R1 = 0.0463, *w*R2 (all data) = 0.1379, CCDC No. 1061733.

Compound 5aa: $C_{25}H_{20}O$, *M* = 336.41, Monoclinic, Space group *P2(1)/c*, *a* = 20.9391 (5) Å, *b* = 19.6321 (17) Å, *c* = 19.0212 (5) Å, β = 99.008 (2)°, *V* = 7722.8 (3) Å^3, *Z* = 16, μ = 0.531 mm^{-1}, data/restraints/parameters: 14836/2/945, R indices (I> 2σ(I)): R1 = 0.0555, *w*R2 (all data) = 0.1639, CCDC No. 1061734.

Compound 15: $C_{32}H_{26}O_4$, *M* = 474.32, Monoclinic, Space group *C*2/c, *a* = 40.6890(12) Å, *b* = 7.9939(2) Å, *c* = 15.8777(7) Å, β = 101.669(3)°, *V* = 5057.7(3) Å^3, *Z* = 8, μ = 0.650 mm^{-1}, data/restraints/parameters: 4029/0/328, R indices (I> 2σ(I)): R1 = 0.0653, *w*R2 (all data) = 0.2091. CCDC No. 1061735.

Compound 25: $C_{33}H_{30}O$, *M* = 490.57, Triclinic, Space group *P_-1*, *a* = 9.648(4) Å, *b* = 12.704(5) Å, *c* = 13.199(5) Å, α = 118.354(5)°, β = 94.509(6)°, γ = 101.854(6)°, *V* = 1363.8(8) Å^3, *Z* = 2, μ = 0.077 mm^{-1}, data/restraints/parameters: 4785/0/337, R indices (I> 2σ(I)): R1 = 0.1102, *w*R2 (all data) = 0.3477. The data quality was moderate. Although there were no 'A' type alerts in checkcif, there was additional residual density near *p*—position of the phenyl ring connected to alkene, possibly as a result of two isomers/diastereomers crystallizing together. CCDC No. 1061736. The ORTEP is given in the ESI.

Compound 29: $C_{34}H_{32}O_4$, *M* = 504.60, Triclinic, Space group *P_-1*, *a* = 10.0941(5) Å, *b* = 12.7419(5) Å, *c* = 13.2345(8) Å, α = 117.981(5)°, β = 94.366(5)°, γ = 104.498(4)°, *V* = 1417.55(12) Å^3, *Z* = 2, μ = 0.077 mm^{-1}, data/restraints/parameters: 5417/0/343, R indices (I> 2σ(I)): R1 = 0.0497, *w*R2 (all data) = 0.1563. CCDC No. 1061737.

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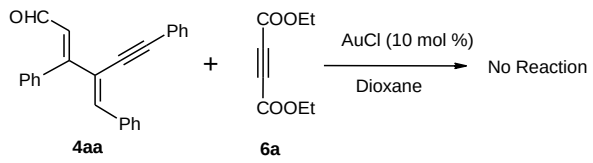
18 We thank a referee for this suggestion. It is also possible that isomerisation takes place via PPh_3 mediation.

19 It should be noted that the cycloaddition reaction of alkynyldienal (**4aa**) with diethylacetylene dicarboxylate (**6a**) under the optimised conditions mentioned in the text did not lead to any product. Even with increase in temperature, starting materials remained unreacted. If we assume that this reaction may go *via* [4+2] cycloaddition followed by dehydration, we should have obtained the cycloaddition product.



4aa **6a**

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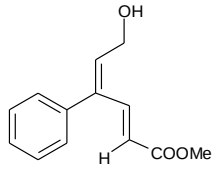
24 This statement is corroborated by the result that compound **31** did not undergo the dehydrative cyclisation/ intermolecular [4+2] cycloaddition with DMAD.



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