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Divergence in the Reactivity between Amine- and Phosphine-Catalyzed Cycloaddition Reactions of Allenoates with Enynals: One-Pot Gold-Catalyzed Synthesis of Trisubstituted Benzofurans from the [3 + 2] Cycloadduct via 1,2-Alkyl Migration and Dehydrogenation

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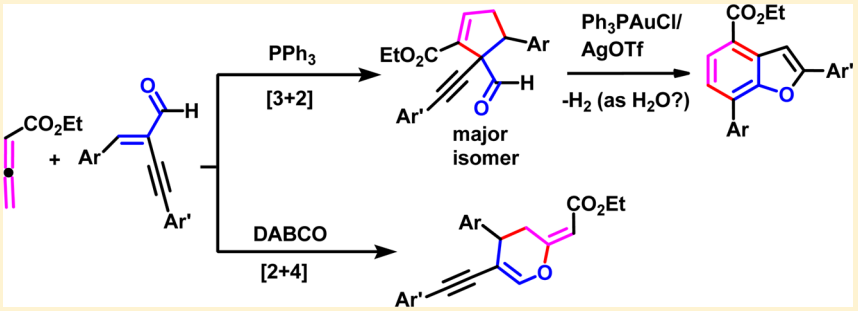
Supporting Information



ABSTRACT: Regioselective synthesis of functionalized dihydropyran derivatives by DABCO-catalyzed [2 + 4] cycloaddition of allenoates with enynals or enynones has been developed. Phosphine-catalyzed [3 + 2] cycloaddition of allenoates with enynals provides 1,1-alkyne (aldehyde)-substituted cyclopentenes wherein enynals act as electrophiles. These alkyne-tethered cyclopentenes upon [Au]/[Ag] catalysis lead to substituted benzofurans via 1,2-alkyl migration and dehydrogenation (aromatization). One-pot reaction of allenoates with enynals using sequential phosphine and gold catalysis is also reported. The cyclopentene obtained from the PPh_3-catalyzed reaction of allenoate $H_2C{=}C{=}CH(COO\text{-}t\text{-}Bu)$ with enynal undergoes decarboxylation under the [Au]/[Ag] catalysis and forms a carboxylate-free benzofuran. The structures of key products are confirmed by single-crystal X-ray analysis.

INTRODUCTION

Organocatalytic reactions constitute a powerful platform for organic chemists for numerous cyclization reactions. Among these, Lewis base catalyzed cycloaddition has emerged as an efficient method for the construction of synthetically useful heterocyclics and natural products.[1] Allenoates, by virtue of the reactive cumulative double bonds, have been utilized as versatile synthons in many such transformations. DABCO-catalyzed [2 + 2],[2] [3 + 3],[3] and [2 + 4][4] annulation reactions of allenoates are also well established. Here, allenoate acts as a two- or three-carbon unit to afford four- and six-membered heterocycles. On the other hand, phosphine-catalyzed [3 + 2] cycloaddition of 2,3-butadienoates (allenoates) with activated alkenes in which allenoates function as three-carbon synthons, discovered by Lu et al., has emerged as a powerful tool in organic synthesis.[5] On the basis of this principle, further investigations showed that allenoates, depending on the substituents, can also undergo [2 + 2 + 2], [1 + 4], [4 + 2], and [2 + 4] annulation reactions.[6−10] To the best of our knowledge, enynals and enynones remain rather unexplored in DABCO-catalyzed reactions with allenoates, and only enynones have been explored in phosphine-catalyzed reactions.[11]

In the above context, one set of reactions that is pertinent to this study is shown in Scheme 1. Allenes do undergo cycloaddition even in the absence of bases,[12] but the facile organocatalytic DABCO-catalyzed [2 + 4] cycloaddition of allenoates that take place in a manner different from that using phosphine catalysis, and leading to synthetically useful heterocycles, has held a greater attraction for synthetic chemists in recent years.[4d] Compounds **1**−**3** shown in Scheme 1 are some representative examples in which cycloaddition takes place at 2,3-positions of the allenoate;[4a,c,d] also included in the scheme is a reaction in the absence of DABCO wherein the cycloaddition takes place at the 1,2-positions of the allenoate (cf. compounds **4a,b**). These reactions are atom-economical, and the yields are generally high.

The second set of reactions involves phosphine-catalyzed cycloaddition of allenoates shown in Scheme 2. The cyclopentene ring system of type **5a**/**5b** has been synthesized by Fu and co-workers,[13] and multifunctional compounds of type **7** have been reported by Zhang and co-workers[11] by phosphine-activated reactions of allenoates with enynones bestowed with

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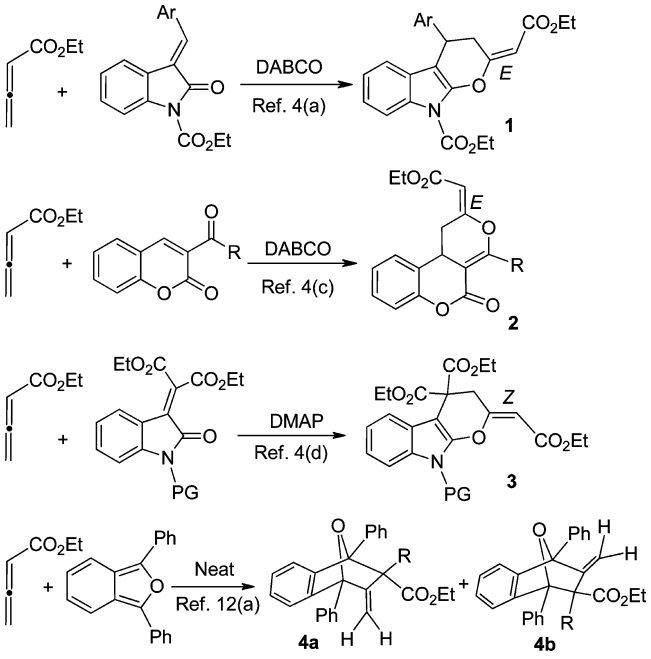
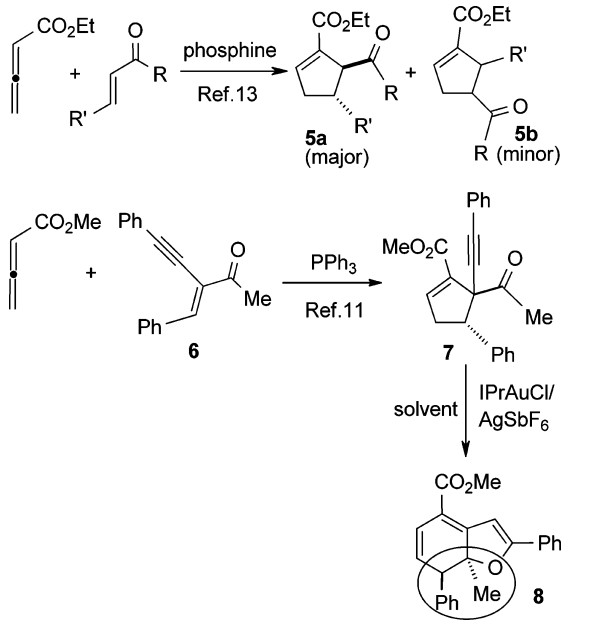
Scheme 1. Representative Examples of Amine-Catalyzed (and Neat) Cycloaddition Reactions of Allenoates



Scheme 2. Examples of Phosphine-Catalyzed Cycloaddition Reactions of Allenoates



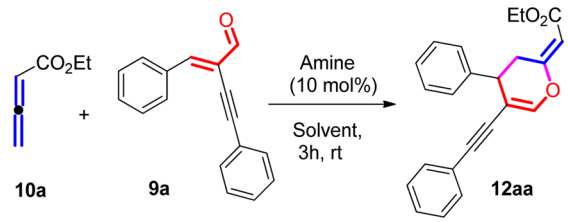
alkyne functionality. What is more interesting is that compounds of type **7**, by making use of the aurophilic alkyne moiety, undergo regiodivergent rearrangements involving 1,2-alkyl migration to lead to highly functionalized dihydrobenzofurans **8**;[11] to our knowledge, this is the only report using such substrates in the literature. We surmised that simply replacing the keto group [C(O)Me] in the precursor **6** by an aldehyde group followed by dehydrogenation (or aromatization) should lead to trisubstituted benzofurans. Also, instead of isolating any intermediate, it should be possible to develop a one-pot synthesis for such useful benzofurans by [3 + 2] cycloaddition and gold-catalyzed alkyl migration.

In line with the above literature, and in continuation of our interest in developing allene chemistry,[14] we contemplated utilizing the readily accessible substrates of type **9** (prepared by starting with cinnamaldehyde[15]) in DABCO-catalyzed [2 + 4] annulation with allenoates that can provide substituted dihydropyrans in high regioselectivity. The latter class of compounds can be valuable precursors in the pharmaceutical industry.[16] Additionally, the residual alkyne functionality in the products can later be used for further transformations. We also report PPh_3-catalyzed [3 + 2] cycloaddition of allenoates **10** with enynals **9** resulting in cyclopentenes possessing reactive aldehyde and alkyne functionalities on the same carbon. This feature is utilized in the [Au]/[Ag]-catalyzed 1,2-alkyl migration strategy[17] that involves an additional *dehydrogenation* (aromatization) step for the synthesis of trisubstituted benzofurans.

RESULTS AND DISCUSSION

(i) DABCO-Catalyzed Reactions of Allenoates with Enynals and Enynones. For the amine-catalyzed [2 + 4] cycloaddition, we chose DABCO as the catalyst with ethyl 2,3-butadienoate (**10a**) and (*E*)-2-benzylidene-4-phenylbut-3-ynal (**9a**) as substrates to afford dihydropyran **12aa**. Although toluene has been effectively used as a solvent in such reactions,[2b,4a,d] in our case, 1,4-dioxane worked better (Table 1, entry 4). The reaction mixture showed a single product, and

Table 1. DABCO-Catalyzed [2 + 4] Cycloaddition Leading to Functionalized Dihydropyrans[a]



entry	catalyst	solvent	yield of **12aa**[b] (%)
1	DABCO	$(EtO)_2CO$	73
2	DABCO	toluene	55
3	DABCO	DCM	61
4	**DABCO**	**1,4-dioxane**	**82**
5	DABCO	THF	68
6	DBU	1,4-dioxane	trace[c]
7	DMAP	1,4-dioxane	trace[c]
8	DMAP	toluene	10
9	Et_3N	1,4-dioxane	N.R.[d]
10	none	1,4-dioxane	N.R.[e]

[a]Reaction conditions: enynal **9** (1.0 mmol), allenoate **10** (1.2 mmol), catalyst (10 mol %), solvent (2 mL), rt for 3 h unless otherwise noted. [b]Isolated yields. [c]Complex mixture of products with only a trace of **12aa**. [d]Reaction was carried out at 70 °C for 2 days. [e]At 100 °C also there was no reaction.

the yields given are after isolation by column chromatography. Other solvents like diethyl carbonate and dichloromethane gave lower yields (entries 1−3). In the case of toluene, reaction was incomplete even after 6 h. When bases such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and DMAP (4-(dimethylamino)pyridine) were used, a mixture of products with only a trace amount of the [2 + 4] cycloadduct was observed (entries 6 and 7). Triethylamine was ineffective for this reaction (entry

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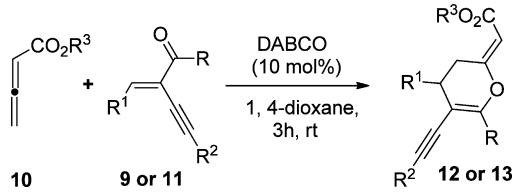
9), even after 2 days. In the absence of catalyst, the desired product was not observed even at 100 °C (entry 10). Hence, we chose DABCO (10 mol %) as the organocatalyst and 1,4-dioxane (2 mL) as a solvent (entry 4) for this [2 + 4] cycloaddition reaction.

We then investigated the substrate scope for the above [2 + 4] cycloaddition reaction of allenoates with enynals as well as enynones (Table 2). The reaction was smooth, and the

Table 2. Substrate Scope for the DABCO-Catalyzed [2 + 4] Cycloaddition of Allenoates (10) with Enynals (9) or Enynones (11)[a]



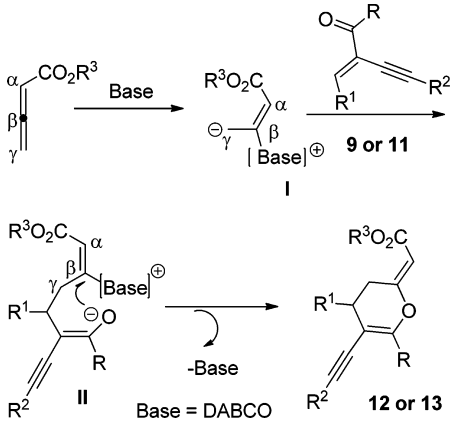
R/R^1/R^2/R^3	product	yield[b] (%)
H/Ph/Ph/Et	**12aa**	82
H/Ph/4-MeOC$_6$H$_4$/Et	**12ba**	70
H/Ph/4-MeC$_6$H$_4$/Et	**12ca**	72
H/Ph/2-MeC$_6$H$_4$/Et	**12da**	71
H/Ph/4-FC$_6$H$_4$/Et	**12ea**	80
H/Ph/3-FC$_6$H$_4$/Et	**12fa**	73
H/Ph/4-ClC$_6$H$_4$/Et	**12ga** (X-ray)	78
H/Ph/4-BrC$_6$H$_4$/Et	**12ha**	64
H/4-MeOC$_6$H$_4$/Ph/Et	**12ia**	60
H/4-NO$_2$C$_6$H$_4$/Ph/Et	**12ja**	62
H/3-FC$_6$H$_4$/Ph/Et	**12ka**	86
H/Ph/SiMe$_3$/Et	**12la**	62
H/Ph/*n*-Bu/Et	**12ma**	57
H/Ph/cyclohexenyl/Et	**12na**	67
Ph/Ph/Ph/Et	**13aa**	84
4-MeO-C$_6$H$_4$/Ph/Ph/Et	**13ba**	87
Me/Ph/Ph/Et	**13ca** (X-ray)	85

[a]Conditions: enynal/enynone (0.4 mmol), allenoate (0.48 mmol), DABCO (10 mol %), 1,4-dioxane (2 mL) at rt for 3 h (for compounds **12**) or 1 h (for compounds **13**). [b]Isolated yields.

corresponding dihydropyrans were obtained in 57−87% yield with high regioselectivity. Interestingly, enynones consistently gave much better yields. Electron-releasing or -withdrawing groups on the phenyl rings gave satisfactory results (compounds **12ba−da** and **12ia−ja**). Halogen-substituted enynals also showed good reactivity and resulted in 64−86% yield (compounds **12ea−ha** and **12ka**). With R^2 = alkyl we also observed the [2 + 4] cycloadduct in good yield (compound **12ma**). When this methodology was applied to ethyl 2,3-butadienoate **10a** and enynones (**11a−c**), the desired [2 + 4] annulation products **13aa−ca** were obtained in excellent yields and high regioselectivity within 1 h. The structure and stereochemistry of the annulation products **12ga** and **13ca** were further confirmed by X-ray crystallography (Figures S1 and S2, Supporting Information). In both cases, *E*-stereochemistry at the exocyclic double bond is observed.

On the basis of literature reports,[2b,9c,18] a plausible pathway for the formation of substituted dihydropyrans is shown in Scheme 3. Initially, allenoate provides zwitterionic intermediate **I** upon addition of the Lewis base. In the presence of DABCO, enynal/enynone interacts with intermediate **I** resulting in **II**,

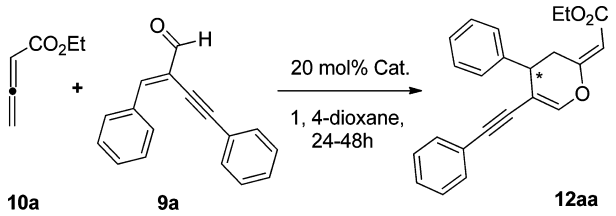
Scheme 3. DABCO-Catalyzed [2 + 4] Cycloaddition of Allenoates with Enynals/Enynones



which undergoes intramolecular attack of oxygen nucleophile at the *β*-position of the allenoate and concomitant elimination of the base affording the substituted dihydropyran **12** or **13** as well as regeneration of the DABCO catalyst. This concomitant elimination of the base (DABCO) will allow the stereochemistry at the olefinic double bond to remain intact.

On the basis of the above mechanism, it should be possible to induce chirality in compounds **12** and **13** by using chiral amines as catalysts.[19] Initially, we attempted the reaction of allenoate **10a** and enynal **9a** by using simple chiral amine cinchonine (20 mol %) in 1,4-dioxane as the solvent (cf. Table 3). Compound **12aa** was obtained in 23% yield with 79% ee

Table 3. Development of Asymmetric [2 + 4] Cycloaddition of Allenoate (10a) with Enynal (9a) Using Chiral Amines[a]



entry	catalyst	*T* (°C)/time (h)	yield[b] (%)	ee[c] (%)
1	cinchonine	rt (48)	30	85
2	cinchonine	80 (24)	23	79
3	cinchonine	15 (48)	42	86
4	(DHQD)$_2$PHAL	rt (48)	35	93

[a]Conditions: enynal (0.3 mmol), allenoate (0.36 mmol), chiral amine (20 mol %), 1,4-dioxane (1 mL). [b]Isolated yields. [c]Determined by HPLC on a chiral stationary phase using a Chiralcel AD-H column.

after 24 h at rt. An increase in the temperature to 80 °C led to a decrease in both the yield and the ee. By using (DHQD)$_2$PHAL as the catalyst, we observed an enhancement in the ee of compound **12aa**, but the yield of the product was only moderate.

(ii) Triphenylphosphine-Catalyzed Reaction of Allenoates with Enynals. In contrast to the above, in the presence of PPh$_3$ as a catalyst, allenoates underwent [3 + 2] cycloaddition with enynals to afford cyclopentenes. Thus, by using 10 mol % of PPh$_3$ as a catalyst, reaction of ethyl-2,3-butadienoate (**10a**) with (*E*)-2-benzylidene-4-phenylbut-3-ynal (**9a**) provided **14aa** and **15aa** in a combined yield of 76% in a 5:1 ratio (Table 4, entry 1). We screened several solvents like

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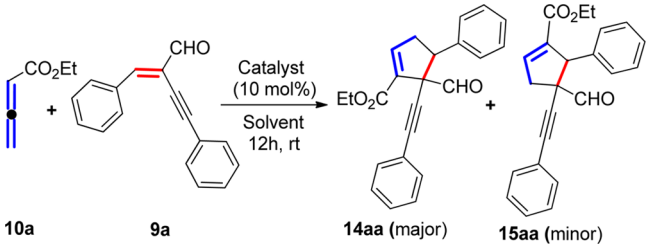
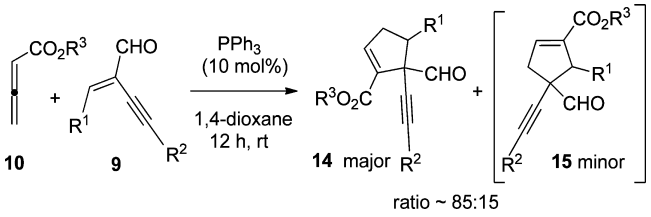
Table 4. Survey of Reaction Conditions for the PPh_3-Catalyzed [3 + 2] Cycloaddition Leading to Functionalized Cyclopentenes[a]



entry	catalyst	solvent	yield (%)[b] of 14 + 15
1	PPh_3	toluene	76[c]
2	PPh_3	CH_3CN	48
3	PPh_3	DMF	54
4	PPh_3	THF	74
5	PPh_3	PEG-400	33
6	PPh_3	$(EtO)_2CO$	72
7	PPh_3	DCM	35
8	PPh_3	EtOH	57
9	**PPh_3**	**1,4-dioxane**	**80**
10	PPh_3	1,4-dioxane	76[d]
11	PPh_3	1,4-dioxane	77[e]
12	dppe	1,4-dioxane	56
13	PCy_3	1,4-dioxane	45
14	PFu_3	1,4-dioxane	N.R.[f]
15	PBu_3	1,4-dioxane	complex

[a]Reaction conditions: enynal (1.0 mmol), allenoate (1.2 mmol), catalyst (10 mol %), solvent (5 mL), rt for 12 h unless otherwise noted. [b]Isolated yields (includes pure major isomer + the remaining mixture containing both the isomers obtained during isolation). [c]Starting material enynal remained. [d]One equiv of allene was used. [e]50 mol % of PPh_3 was used. [f]Reaction was carried out at 70 °C for 2 days.

Table 5. Substrate Scope for the Phosphine-Catalyzed [3 + 2] Cycloaddition of Allenoates (10) with Enynals (9)[a]



Entry	$R^1/R^2/R^3$	products	combined % yield of 14 + 15[b] (isomer ratio)
1	Ph/Ph/Et	**14aa + 15aa**	80 (5:1.0)
2	Ph/4-$MeOC_6H_4$/Et	**14ba + 15ba**	88 (5:0.8)
3	Ph/4-MeC_6H_4/Et	**14ca + 15ca**	74 (5:1.0)
4	Ph/2-MeC_6H_4/Et	**14da + 15da**	83 (5:0.9)
5	Ph/4-$O_2NC_6H_4$/Et	**14ea + 15ea**	68 (5:1.5)
6	Ph/2-$O_2NC_6H_4$/Et	**14fa + 15fa**	62 (5:1.5)
7	Ph/4-FC_6H_4/Et	**14ga + 15ga**	64 (5:1.0)
8	Ph/3-FC_6H_4/Et	**14ha + 15ha**	72 (5:0.9)
9	Ph/4-ClC_6H_4/Et	**14ia + 15ia**	65 (5:0.8)
10	Ph/4-BrC_6H_4/Et	**14ja + 15ja**	55 (5:0.9)
11	4-$MeOC_6H_4$/Ph/Et	**14ka + 15ka**	80 (5:0.9)
12	4-$O_2NC_6H_4$/Ph/Et	**14la + 15la**	58 (5:2.0)
13	4-FC_6H_4/Ph/Et	**14ma + 15ma**	77 (5:1.3)
14	3-FC_6H_4/Ph/Et	**14na + 15na**	75 (5:0.9)
15	Ph/$SiMe_3$/Et	**14oa + 15oa**	77 (5:0.9)
16	Ph/Ph/Me	**14ab + 15ab**	74 (5:0.9)
17	Ph/Ph/Bn	**14ac + 15ac**	77 (5:1.0)

[a]Conditions: enynal **9** (1.0 mmol), allenoate **10** (1.2 mmol), PPh_3 (0.1 mmol), 1,4-dioxane (5 mL), rt for 12 h. [b]Isolated yields (isomer ratio based on ^1H NMR spectra of crude reaction mixture is shown in parentheses).

CH_3CN, DMF, THF, $(EtO)_2CO$, DCM, EtOH, and 1,4-dioxane (entries 2–9), and to our delight, the [3 + 2] cycloaddition product was obtained in 80% combined yield by using dioxane as the solvent. Phosphine catalysts like dppe [1,2-bis(diphenylphosphino)ethane] and PCy_3 decreased the yield of the cycloadduct (entries 12 and 13), while trifurylphosphine (PFu_3) (entry 14) was ineffective. Vigorous reaction took place when tributylphosphine (PBu_3) was used as the catalyst, but only a mixture of products was obtained (entry 15). Thus, PPh_3 was the best catalyst for the [3 + 2] cycloaddition reaction. Use of 1.0 equiv of **10a** lowered the yield (entry 10); an excess of **10a** did not improve the yield. Increasing the catalyst loading to 50 mol % slightly diminished the yield of desired product (entry 11). Thus, conditions under entry 9 gave the best results.

After establishing the optimized reaction conditions, we turned our attention to the substrate scope and limitations of triphenylphosphine-catalyzed [3 + 2] cycloaddition between allenoates and 2-(1-alkynyl)-2-alken-1-als (Table 5). Both electron-donating and -withdrawing groups on ring R^2 gave the desired [3 + 2] cycloadducts (entries 2–10) in good yields, but electron-releasing groups enhanced the yield. Similarly, both electron-donating and -withdrawing groups on ring R^1 also worked well, but the electron-withdrawing $-NO_2$ group marginally reduced the yield (entries 11–14). The yields were good even for R^2 = Me_3Si (entries 15). Allenoates with R^3 = Me or Bn also afforded good yields (entries 16 and 17). The reaction was completed within 12 h. The major isomers (**14aa–oa** and **14ab–ac**) as viscous liquids were isolated in pure form in all cases. Among the minor isomers, we have isolated **15aa**, **15ea**, and **15na** in pure form. All of these compounds are rather unstable at room temperature (25 °C) for >1 day and hence had to be preserved at low temperatures. The structure of the minor isomer **15aa** was confirmed by single-crystal X-ray structural analysis (Figure S3, Supporting Information).

(iii) Gold-Catalyzed Ring Transformation and 1,2-Alkyl Migration of Cyclopentenes 14. Compounds of type **14** have a reactive −CHO and an alkyne group juxtaposed on the same carbon and are consequently interesting substrates in gold catalysis. The alkynophilic character of gold(I),[20] therefore, is what we wanted to exploit in the next step. Thus, we used the 1,2-alkyl migration strategy[17] on compounds **14aa–oa** and **14ab–ac** for the construction of substituted benzofurans under gold catalysis. To begin, the reaction of functionalized cyclopentene **14aa** with 5 mol % each of gold(I) carbene complex (IPrAuCl) and AgOTf at rt for 3 days in dioxane afforded substituted benzofuran **16aa** in 50% yield (Table 6, entry 1). In the absence of AgOTf, this transformation was forbidden (entry 2). Use of a Ph_3PAuCl/AgOTf catalytic system at rt for 2 days resulted in 65% yield (entry 3). Fortunately, increasing the temperature to 100 °C increased the yield to 76% (entry 5) within 24 h. Among the tested solvents, dioxane showed better results (entries 5–9). Although AgOTf itself is active, only 58% yield was obtained in this case (entry 10). Gold catalysts like AuCl and $NaAuCl_4·2H_2O$ gave very poor yields. Furthermore, increasing the catalytic loading did not benefit this transformation. Thus, the optimal reaction

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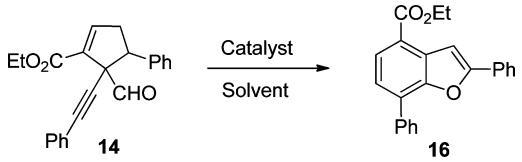
Table 6. Details on Screening of Solvents and Catalysts for the Synthesis of Benzofurans 16[a]



entry	catalyst (5 mol %)	solvent	time	T (°C)	yield[b] (%)
1	IPrAuCl/AgOTf	1,4-dioxane	3 days	rt	50
2	IPrAuCl	1,4-dioxane	3 days	rt	NR
3	$Ph_3PAuCl/AgOTf$	1,4-dioxane	2 days	rt	65
4	$Ph_3PAuCl/AgSbF_6$	1,4-dioxane	2 days	rt	61
5	**$Ph_3PAuCl/AgOTf$**	**1,4-dioxane**	**24 h**	**100**	**76**
6	$Ph_3PAuCl/AgOTf$	DCE	24 h	80	67
7	$Ph_3PAuCl/AgOTf$	CH_3CN	24 h	100	44
8	$Ph_3PAuCl/AgOTf$	MeOH	2 days	80	25
9	$Ph_3PAuCl/AgOTf$	DMF	2 days	100	24
10	AgOTf	1,4-dioxane	24 h	100	58
11	AuCl/AgOTf	1,4-dioxane	2 days	100	20
12	$NaAuCl_4.2H_2O$/AgOTf	1,4-dioxane	2 days	100	28

[a]Conditions: one of the functionalized cyclopentenes **14** (0.3 mmol), [Au] catalyst (5 mol %), [Ag] catalyst (5 mol %), and 1,4-dioxane (2 mL) were used. [b]Isolated yields.

conditions for this transformation are $Ph_3PAuCl/AgOTf$ (5 mol %) and 1,4-dioxane (2 mL) as a solvent at 100 °C for 24 h.

Having the optimal reaction conditions in hand, we explored the substrate scope of the reaction by using various [3 + 2] cycloadducts **14**. The results are summarized in Scheme 4. The yields were, in general, good to excellent. A point worth noting here is that the substrate **14oa** undergoes elimination of the trimethylsilyl group resulting in **16oa** in excellent yield. As can be seen readily, cycloisomerized compounds (benzofurans) **16** have two fewer hydrogen atoms than their precursors, suggesting dehydrogenation. To our knowledge, such a dehydrogenation leading to aromatization has not been reported thus far in related systems. For the sake of foolproof evidence, the structures of **16aa** and **16fa** were confirmed by X-ray structural analysis (Figures S4 and S5, Supporting Information).

In the above reactions, if the allenoate used is $H_2C{=}C{=}CH(COO\text{-}t\text{-}Bu)$ (**10d**), the final product (**17**) after gold catalysis is the one in which decarboxylation also has taken place (Scheme 5). This feature may perhaps be used in cases when one does not require the carboxylate group in the aromatic ring.

(iv) One-Pot Synthesis of Benzofurans from Allenoates and Enynals: Combined Phosphine and Gold Catalysis. Synthetically, it is best if we can devise a one-pot strategy since this would alleviate the problem of isolating intermediates. The yields, therefore, will at least be marginally higher. Indeed, in the above synthesis, we could accomplish this, and the results are shown in Scheme 6. The overall yield of the substituted benzofurans **16** was 5−6% higher than that from the two-step method involving isolation of intermediate cyclopentenes of type **14**.

(v) Plausible Pathway for the Gold-Catalyzed Cycloisomerization/Alkyl Migration/Dehydrogenation of Cyclopentenes 14. Initially, gold activated the alkyne end of **14aa** to generate **III** (Scheme 7). Subsequent intramolecular attack of carbonyl oxygen leads to spirobicyclic intermediate **IV**.[17a,e] 1,2-Alkyl migration in **V** results in allylic cationic vinyl gold intermediate **VI**. Intermediate **VII**/**VII′** is formed by deprotonation of **VI** (by pathway a or pathway b). Protodeauration of **VII**/**VII′** followed by aromatization results in the functionalized benzofuran **16**. Removal of two hydrogen atoms (aromatization) may have taken place by elimination of water. At least in our case, it appears that pathway (a) is favored because the product mixture (starting from **14aa**) immediately after column chromatography exhibits the presence of compound **16aa** and another species with a CH_2 group [^1H and ^{13}C (DEPT) NMR; see the Supporting Information] consistent with the presence of **VIII**. Over a period of ca. 24 h, this intermediate disappeared, and only the product **16aa** was observed.

■ CONCLUSIONS

We have developed DABCO-catalyzed regioselective synthesis of functionalized dihydropyrans by the [2 + 4] cycloaddition of allenoates with enynals or enynones. In the absence of DABCO there was no reaction. In contrast, triphenylphosphine-catalyzed reaction of the same substrates (allenoates and enynals) takes place via [3 + 2] cycloaddition to afford highly functionalized cyclopentenes. The latter compounds are utilized in [Au]/[Ag]-catalyzed cycloisomerization/1,2-alkyl migration/dehydrogenation (aromatization) resulting in trisubstituted benzofurans. Synthesis of these trisubstituted benzofurans is accomplished by a direct one-pot route from the allenoate and enynal. Interestingly, the intermediate cyclopentene obtained from the allenoate $H_2C{=}C{=}CH(COO\text{-}t\text{-}Bu)$ undergoes facile decarboxylation under the [Au]/[Ag] catalysis to lead to a carboxylate-free benzofuran.

■ EXPERIMENTAL SECTION

General Experimental Conditions. Chemicals and solvents were purified when required according to standard procedures.[21] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded using 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. For TLC, glass microslides were coated with silica gel GF_{254} (mesh size 75 μm), and spots were identified using an iodine or UV chamber as appropriate. For column chromatography, silica gel of 100−200 mesh size was used. LC−MS or HRMS (ESI-TOF) equipment was used to record mass spectra for isolated compounds where appropriate. HPLC analysis was performed using Daicel Chiralpak AD-H.

Enynals **9** and enynones **11** were prepared by using standard literature reports.[15] Allenes **10a**−**d**[22] were prepared by following a reported method.

(i) Representative Procedure for the Preparation of Compounds 12aa−na and 13aa−ca. To a solution of 2-(1-alkynyl)-2-alken-1-al **9** or 2-(1-alkynyl)-2-alken-1-one **11** (0.4 mmol) in dry 1,4-dioxane (2 mL), DABCO (0.04 mmol) followed by alkyl 2,3-butadienoate **10a** (0.48 mmol) was added. The vessel was stoppered under nitrogen atmosphere, and the contents were stirred for 3 h (for compounds **12**) or 1 h (for compounds **13**) at rt. The completion of the reaction was monitored by TLC. Later, the solvent was removed under vacuum, and the crude product was purified by column chromatography by using silica gel with ethyl acetate/hexane (1:99) mixture as the eluent to afford the corresponding dihydropyrans **12** or **13**.

*(E)-Ethyl 2-(4-phenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12aa**):* yield 0.112 g (82%, white solid); mp 64−66

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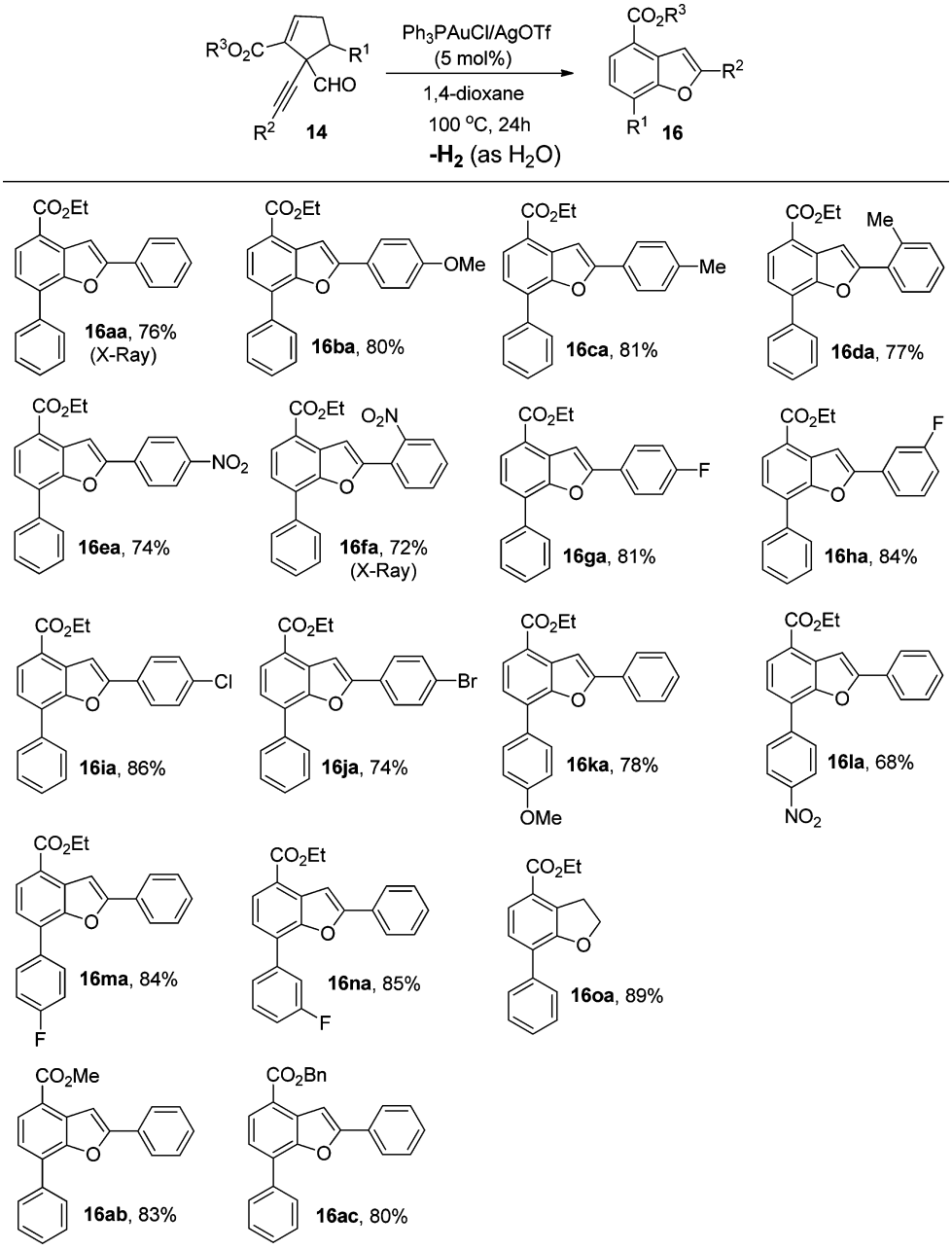
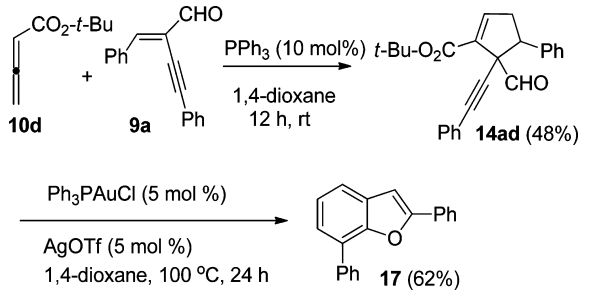
J. Org. Chem. 2015, 80, 4084−4096

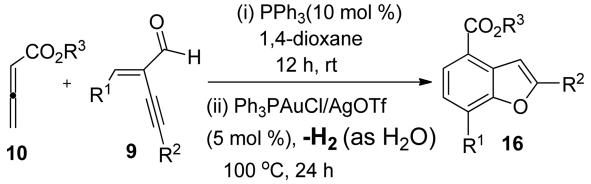
Scheme 4. Gold-Catalyzed Synthesis of Substituted Benzofurans 16 from Highly Functionalized [3 + 2] Cyclopentenes 14



Scheme 5. Decarboxylative Pathway in the Reaction of Allenoate 10d with Enynal 9a



Scheme 6. One-Pot Reaction of Allenoates (10) with Enynals (9) Leading to Substituted Benzofurans 16



16aa, 65% (X-ray)	**16fa**, 58% (X-ray)	**16ka**, 70%	**16ab**, 70%
16ba, 74%	**16ga**, 67%	**16la**, 50%	**16ac**, 73%
16ca, 68%	**16ha**, 62%	**16ma**, 71%	
16da, 66%	**16ia**, 65%	**16na**, 72%	
16ea, 64%	**16ja**, 52%	**16oa**, 74%	

°C; IR (KBr) 3085, 2976, 2909, 2202, 1698, 1649, 1490, 1380, 1353, 1266, 1161, 1123, 843, 755, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 4H), 7.31−7.27 (m, 6H), 7.07 (s, 1H), 5.64 (s, 1H),

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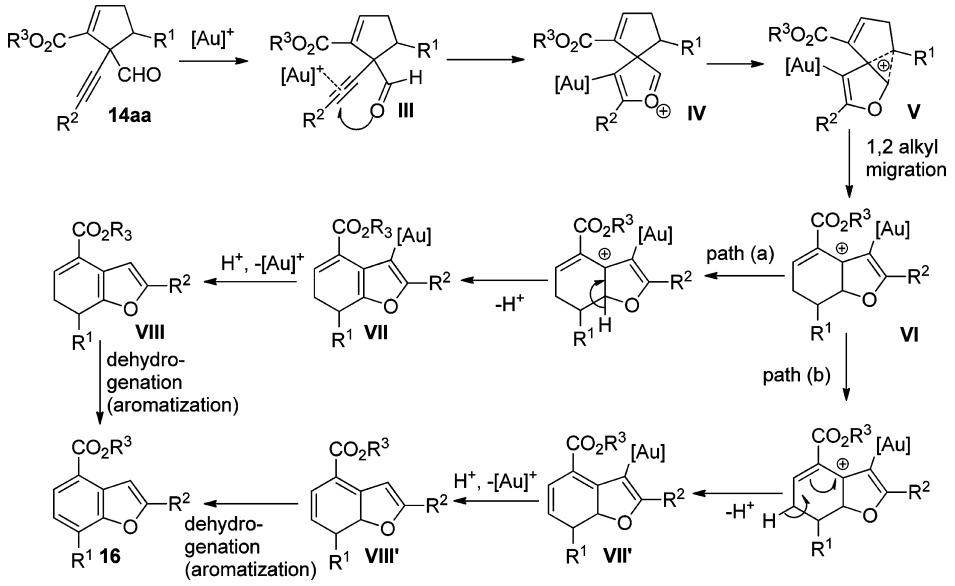
Scheme 7. Plausible Pathway for the Gold-Catalyzed Transformation Leading to 16



4.19−4.06 (m, 2H), 3.83−3.77 (m, 2H), 3.35−3.28 (m, 1H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.2, 145.7, 140.8, 131.2, 128.5, 128.2, 128.0, 127.6, 127.1, 123.2, 104.4, 100.8, 91.5, 85.5, 59.8, 38.8, 29.9, 14.2; LC/MS m/z 345 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.36; H, 5.79. The enantiomeric excess was determined by HPLC using Daicel Chiralpak AD-H column at 254 nm (hexane/2-propanol = 90:10), 0.5 mL/min; t_R = 11.2 min (major), 10.2 min (minor); $[\alpha]_D^{25}$ −89.0 (c = 0.09, $CHCl_3$), 93% ee.

*(E)-Ethyl 2-(5-((4-methoxyphenyl)ethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ba**):* yield 0.105 g (70%, white solid); mp 86−88 °C; IR (KBr) 3090, 2970, 2838, 1710, 1655, 1512, 1441, 1381, 1238, 1151, 1123, 1030, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 4H), 7.25−7.23 (m, 1H), 7.19 (d, J = 8.8 Hz, 2H), 7.01 (s, 1H), 6.78 (d, J = 8.8 Hz, 2H), 5.58 (s, 1H), 4.15−4.03 (m, 2H), 3.78 (s, 3H), 3.75−3.72 (m, 2H), 3.29−3.24 (m, 1H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.4, 159.4, 145.1, 140.8, 132.7, 128.5, 127.6, 127.0, 115.3, 113.9, 104.6, 100.7, 91.4, 84.1, 59.8, 55.3, 38.9, 29.9, 14.2; HRMS (ESI) calcd for $C_{24}H_{23}O_4$ $[M^+ + H]$ m/z 375.1596, found 375.1591.

*(E)-Ethyl 2-(4-phenyl-5-(p-tolylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ca**):* yield 0.103 g (72%, white solid); mp 98−100 °C; IR (KBr) 3019, 2986, 1710, 1660, 1512, 1370, 1353, 1173, 1151, 1123, 866, 811, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.27 (m, 4H), 7.25−7.23 (m, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.02 (s, 1H), 5.59 (s, 1H), 4.16−4.03 (m, 2H), 3.81−3.73 (m, 2H), 3.29−3.24 (m, 1H), 2.31 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.3, 145.4, 140.8, 138.1, 131.1, 129.0, 128.5, 127.6, 127.0, 120.1, 104.5, 100.7, 91.7, 84.8, 59.8, 38.9, 29.9, 21.4, 14.2; LC/MS m/z 359 $[M + 1]^+$. Anal.Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.31; H, 6.12.

*(E)-Ethyl 2-(4-phenyl-5-(o-tolylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12da**):* yield 0.100 g (71%, white solid); mp 68−70 °C; IR (KBr) 3080, 3025, 2975, 2203, 1710, 1655, 1616, 1485, 1452, 1375, 1348, 1173, 1030, 860, 756, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 7.28−7.23 (m, 2H), 7.19−7.14 (m, 2H), 7.13−7.08 (m, 1H),7.05 (s, 1H), 5.63 (s, 1H), 4.16−4.07 (m, 2H), 3.77−3.74 (m, 1H), 3.68−3.63 (m, 1H), 3.45−3.40 (m, 1H), 2.14 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.4, 145.4, 141.0, 139.9, 131.4, 129.3, 128.6, 128.0, 127.7, 127.1, 125.4, 123.0, 104.7, 100.7, 90.6, 89.4, 59.9, 39.1, 30.1, 20.4, 14.3; LC/MS m/z 359 $[M + 1]^+$. Anal.Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.34; H, 6.25.

*(E)-Ethyl 2-(5-((4-fluorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ea**):* yield 0.116 g (80%, white solid); mp 88−90 °C; IR (KBr) 3085, 2970, 2208, 1704, 1649, 1501, 1381, 1359, 1222, 1178, 1156, 1123, 866, 833, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 2H), 7.30−7.26 (m, 3H), 7.23−7.19 (m, 2H), 7.03 (s, 1H), 6.94 (d, J = 8.6 Hz, 2H), 5.60 (s, 1H), 4.16−4.03 (m, 2H), 3.77−3.72 (m, 2H), 3.32−3.26 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.1, 162.3 (J = 247.5 Hz), 145.7, 140.7, 133.1 (J = 8.3 Hz), 128.5, 127.6, 127.1, 119.3, 115.5 (J = 21.9 Hz), 104.2, 100.9, 90.4, 85.2, 59.9, 38.8, 29.9,14.2; LC/MS m/z 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.12; H, 5.23.

*(E)-Ethyl 2-(5-((3-fluorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12fa**):* yield 0.106 g (73%, gummy liquid); IR (neat) 3074, 2981, 2197, 1704, 1649, 1605, 1578, 1490, 1381, 1266, 1156, 1123, 866, 789 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H), 7.30−7.25 (m, 3H), 7.23−7.17 (m, 1H), 7.05 (s, 1H), 7.03−7.00 (m, 1H), 6.98−6.91 (m, 2H), 5.62 (s, 1H), 4.15−4.06 (m, 2H), 3.78−3.72 (m, 2H), 3.35−3.29 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.0, 162.3 (J = 244.8 Hz), 146.2, 140.6, 129.8 (J = 8.3 Hz), 128.6, 127.6, 127.2, 127.1, 125.0 (J = 9.6 Hz), 117.9 (J = 22.5 Hz), 115.3 (J = 20.9 Hz), 104.1, 101.1, 90.4, 86.6, 59.9, 38.8, 29.9,14.2; LC/MS m/z 361 $[M - 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.03; H, 5.19.

*(E)-Ethyl 2-(5-((4-chlorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ga**):* yield 0.151 g (78%, white solid); mp 118−120 °C; IR (KBr) 3085, 2970, 2893, 2208, 1715, 1638, 1484, 1375, 1353, 1260, 1145, 1117, 854, 821, 706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.29−7.26 (m, 3H), 7.22 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.04 (s, 1H), 5.60 (s, 1H), 4.16−4.03 (m, 2H), 3.77−3.71 (m, 2H), 3.33−3.26 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.0, 146.0, 140.7, 133.9, 132.4, 128.6, 127.6, 127.1, 121.7, 104.2, 101.0, 90.4, 86.6, 59.9, 38.8, 29.9, 14.2; HRMS (ESI) calcd for $C_{23}H_{20}ClO_3$ $[M^+ + H]$ m/z 379.1101, found 379.1101. This compound was crystallized from an acetonitrile/hexane (2:1) mixture at room temperature. The X-ray structure was determined for this compound.

*(E)-Ethyl 2-(5-((4-bromophenyl)ethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ha**):* yield 0.108 g (64%, white solid); mp 118−120 °C; IR (KBr) 2986, 2202, 1704, 1632, 1479, 1375, 1254, 860, 810, 706, 651 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.29−7.24 (m, 3H), 7.08 (d, J = 8.4 Hz, 2H), 7.04 (s, 1H), 5.61 (s, 1H), 4.16−4.05 (m, 2H), 3.77−3.72 (m, 2H), 3.33−3.27 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.0, 146.0, 140.7, 132.6, 131.5, 128.6, 127.6, 127.2, 122.1, 104.2, 101.0, 90.5, 86.8, 59.9, 38.8,

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29.9,14.2; HRMS (ESI) calcd for $C_{23}H_{20}BrO_3$ [M^+ + H], [M^+ + 2 + H] m/z 423.0596, 425.0596, found 423.0597, 425.0585.

*(E)-Ethyl 2-(4-(4-methoxyphenyl)-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ia**):* yield 0.090 g (60%, gummy liquid); IR (neat) 2986, 2937, 2899, 2833, 2208, 1704, 1649, 1512, 1447, 1375, 1260, 1151, 1123, 1036, 838, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.25 (m, 5H), 7.22 (d, J = 8.8 Hz, 2H), 7.03 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 5.60 (s, 1H), 4.15−4.05 (m, 2H), 3.83−3.72 (m, 1H), 3.79 (s, 3H), 3.71 (t, J = 5.4 Hz, 1H), 3.23−3.17 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.4, 158.6, 145.5, 132.9, 131.3, 128.6, 128.2, 128.0, 123.2, 104.7, 100.8, 91.4, 85.7, 59.9, 55.3, 38.0, 30.1, 14.3; LC/MS m/z 375 [M + 1]$^+$. Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.91; H, 5.85.

*(E)-Ethyl 2-(4-(4-nitrophenyl)-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ja**):* yield 0.097 g (62%, gummy liquid); IR (neat) 3080, 2981, 2208, 1704, 1655, 1600, 1523, 1485, 1353, 1156, 1118, 1041, 860, 751, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.24 (br s, 5H), 7.08 (s, 1H), 5.64 (s, 1H), 4.14−4.05 (m, 2H), 3.90−3.85 (m, 2H), 3.28−3.21 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 162.8, 148.3, 147.2, 146.4, 131.2, 128.6, 128.3, 123.9, 122.7, 102.9, 101.7, 92.0, 84.7, 60.1, 38.9, 29.3, 14.2; LC/MS m/z 390 [M + 1]$^+$. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.82; H, 4.87; N, 3.68.

*(E)-Ethyl 2-(4-(3-fluorophenyl)-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ka**):* yield 0.125 g (86%, white solid); mp 58−60 °C; IR (KBr) 2980, 2203, 1704, 1644, 1616, 1589, 1485, 1447, 1375, 1353, 1255, 1167, 1129, 855, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.27 (m, 6H), 7.09 (d, J = 7.6 Hz, 1H), 7.04 (s, 1H), 7.03−6.94 (m, 2H), 5.62 (s, 1H), 4.17−4.04 (m, 2H), 3.83−3.78 (m, 1H), 3.75 (t, J = 5.4 Hz, 1H), 3.26−3.21 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.6, 162.9 (J = 244.6 Hz), 145.9, 143.3, 131.2, 130.0 (J = 8.0 Hz), 128.3, 128.1, 123.3, 123.0, 114.6 (J = 21.8 Hz), 114.1 (J = 20.9 Hz), 103.7, 101.2, 91.6, 85.2, 59.9, 38.6, 29.6, 14.2; LC/MS m/z 363 [M + 1]$^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.15; H, 5.32.

*(E)-Ethyl 2-(4-phenyl-5-((trimethylsilyl)ethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12la**):* yield 0.136 g (62%, white solid); mp 66−68 °C; IR (KBr) 3030, 2959, 2899, 2142, 1709, 1644, 1623, 1452, 1375, 1249, 1145, 1041, 844, 756, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.31 (m, 2H), 7.29−7.24 (m, 3H), 6.98 (s, 1H), 5.58 (s, 1H), 4.15−4.03 (m, 2H), 3.78−3.73 (m, 1H), 3.66 (t, J = 5.6 Hz, 1H), 3.24−3.19 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H) 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.2, 146.5, 140.6, 128.4, 128.0, 127.5, 127.0, 104.4, 101.2, 100.8, 96.7, 59.8, 38.5, 29.6, 14.2, −0.17; LC/MS m/z 341 [M + 1]$^+$. Anal. Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.10. Found: C, 70.36; H, 7.21.

*(E)-Ethyl 2-(5-(hex-1-yn-1-yl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12ma**):* yield 0.074 g (57%, gummy liquid); IR (neat) 3030, 2959, 2926, 2866, 1742, 1704, 1644, 1496, 1452, 1370, 1260, 1123, 866, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.25−7.22 (m, 3H), 6.86 (s, 1H), 5.54 (s, 1H), 4.12−4.02 (m, 2H), 3.77−3.72 (m, 1H), 3.60 (t, J = 5.6 Hz, 1H), 3.19−3.14 (m, 1H), 2.19 (t, J = 7.2 Hz, 2H), 1.40−1.35 (m, 2H), 1.29−1.24 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.5, 144.6, 141.0, 128.4, 127.5, 126.9, 104.7, 100.3, 92.3, 76.3, 59.7, 39.0, 30.7, 30.0, 21.8, 19.1, 14.2, 13.6; LC/MS m/z 325 [M + 1]$^+$. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.83; H, 7.41.

*(E)-Ethyl 2-(5-(cyclohex-1-en-1-ylethynyl)-4-phenyl-3,4-dihydro-2H-pyran-2-ylidene)acetate (**12na**):* yield 0.093 g (67%, gummy liquid); IR (neat) 3063, 3025, 2975, 2932, 2855, 1704, 1649, 1490, 1452, 1375, 1255, 1129, 1036, 734, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.31 (m, 2H), 7.27−7.23 (m, 3H), 6.93 (s, 1H), 5.95 (b s, 1H), 5.57 (s, 1H), 4.14−4.05 (m, 2H), 3.81−3.76 (m, 1H), 3.67 (t, J = 5.6 Hz, 1H), 3.24−3.19 (m, 1H), 2.07−2.01 (m, 4H), 1.61−1.54 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.4, 144.9, 140.8, 134.5, 128.4, 127.5, 126.9, 120.6, 104.7, 100.5, 93.4, 82.8, 59.8, 38.9, 29.9, 29.0, 25.6, 22.2. 21.4, 14.2; HRMS (ESI) calcd for $C_{23}H_{25}O_3$ [M^+ + H] m/z 349.1803, found 349.1803.

*(E)-Ethyl 2-(4,6-diphenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**13aa**):* yield 0.141 g (84%, white solid); mp 90−92 °C; IR (KBr) 2932, 1704, 1638, 1485, 1381, 1271, 1151, 1129, 838, 751, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.50−7.44 (m, 3H), 7.37−7.36 (m, 4H), 7.29−7.25 (m, 4H), 7.21−7.19 (m, 2H), 5.72 (s, 1H), 4.20−4.06 (m, 2H), 3.98−3.92 (m, 2H), 3.36−3.29 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.2, 153.5, 141.2, 133.3, 131.0, 129.5, 128.6, 128.3, 127.9, 127.7, 127.1, 123.5, 100.4, 100.2, 94.8, 88.0, 59.8, 40.8, 30.0, 14.3; LC/MS m/z 421 [M + 1]$^+$. Anal. Calcd for $C_{29}H_{24}O_3$: C, 82.83; H, 5.75. Found: C, 82.73; H, 5.71.

*(E)-Ethyl 2-(6-(4-methoxyphenyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**13ba**):* yield 0.157 g (87%, white solid); mp 78−80 °C; IR (KBr) 2975, 2904, 2833, 1704, 1644, 1595, 1507, 1381, 1249, 1123, 1019, 827, 740, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.48−7.41 (m, 3H), 7.36−7.30 (m, 4H), 7.28−7.25 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 5.71 (s, 1H), 4.18−4.07 (m, 2H), 3.97−3.94 (m, 2H), 3.78 (s, 3H), 3.33−3.27 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.4, 159.4, 152.7, 141.2, 133.4, 132.5, 129.4, 128.5, 127.9, 127.8,127.7, 127.0, 115.7, 113.9, 100.7, 100.0, 94.9, 86.6, 59.8, 55.3, 40.9, 30.1, 14.3; LC/MS m/z 451 [M + 1]$^+$. Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.85; H, 5.76.

*(E)-Ethyl 2-(6-methyl-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (**13ca**):* yield 0.124 g (85%, white solid); mp 60−62 °C; IR (KBr) 3030, 2970, 2203, 1699, 1655, 1490, 1436, 1381, 1277, 1233, 1162, 1129, 1047, 838, 751, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 5H), 7.25 (br s, 5H), 5.57 (s, 1H), 4.16−4.03 (m, 2H), 3.81−3.76 (m, 1H), 3.73 (t, J = 5.6 Hz, 1H), 3.23−3.17 (m, 1H), 2.27 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.1, 154.7, 141.5, 131.4, 131.0, 130.8, 128.6, 128.5, 128.2, 127.8, 127.6, 126.9, 123.6, 100.0, 99.3, 93.8, 86.9, 59.8, 39.2, 30.0, 18.4, 14.3; HRMS (ESI) calcd for $C_{24}H_{23}O_3$ [M^+ + H] m/z 359.1647, found 359.1647. This compound was crystallized from ethyl acetate/hexane (2:1) mixture at room temperature. The X-ray structure was determined for this compound.

(ii) Representative Procedure for the Synthesis of Functionalized Cyclopentenes 14aa−oa, 14ab−ad, 15aa, 15ea, and 15na. To a solution of 2-(1-alkynyl)-2-alken-1-als **9** (1.0 mmol) in dry 1,4-dioxane (5 mL) was added PPh_3 (0.1 mmol) followed by alkyl 2,3-butadienoate **10a−d** (1.2 mmol). The vessel was stoppered under nitrogen atmosphere, and the contents were stirred for 12 h at rt. The progress of the reaction was monitored by TLC. Later, the solvent was removed under vacuum, and crude product was purified by column chromatography by using silica gel with ethyl acetate/hexane (1:49) mixture as the eluent to afford the corresponding cyclopentenes. The minor isomer had a slightly lower R_f value and hence eluted after the major isomer. All of the major isomers were obtained in a pure state; the minor isomer was isolated in a pure state in three cases.

*Ethyl 5-formyl-4-phenyl-5-(phenylethynyl)cyclopent-1-ene carboxylate (**14aa**):* yield 0.231 g (67%, gummy liquid); IR (neat) 3057, 3025, 2981, 2197, 1710, 1627, 1490, 1375, 1326, 1255, 1129, 1101, 1030, 767, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.34−7.30 (m, 5H), 7.27−7.21 (m, 3H), 7.18−7.14 (m, 3H), 4.32−4.19 (m, 3H), 3.10−2.93 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 162.9, 146.5, 138.5, 137.3, 131.6, 129.0, 128.3, 128.1, 127.5, 122.6, 89.9, 85.1, 63.8, 61.1, 51.8, 37.5, 14.2; LC/MS m/z 345 [M + 1]$^+$. Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.12; H, 5.91.

*Ethyl 2-formyl-3-phenyl-2-(phenylethynyl)cyclopent-3-enecarboxylate (**15aa**):* yield 0.045 g (13%, white solid); mp 92−94 °C; IR (KBr) 3063, 3030, 2981, 2203, 1715, 1496, 1447, 1375, 1255, 1200, 1096, 762, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.38−7.30 (m, 3H), 7.28−7.22 (m, 3H), 7.20−7.16 (m, 2H), 6.97−6.95 (m, 3H), 4.50 (s, 1H), 4.13−4.02 (m, 2H), 3.34−3.29 (m, 1H), 2.95−2.91 (m, 1H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 163.5, 141.5, 138.3, 137.1, 131.6, 128.6, 128.4, 128.3,

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J. Org. Chem. 2015, 80, 4084−4096

128.1, 127.4, 122.2, 89.5, 85.0, 60.6, 58.5, 54.9, 39.2, 14.0; LC/MS *m/z* 345 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.15; H, 5.76. This compound was crystallized from ethyl acetate/hexane (2:1) mixture at room temperature. X-ray structure was determined for this compound.

*Ethyl 5-formyl-5-((4-methoxyphenyl)ethynyl)-4-phenylcyclopent-1-enecarboxylate (**14ba**):* yield 0.284 g (76%, gummy liquid); IR (neat) 2981, 2932, 2838, 2203,1704, 1595, 1512, 1458, 1381, 1260, 1173, 1036, 838, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.33−7.27 (m, 5H), 7.11 (d, J = 8.8 Hz, 3H), 6.76 (d, J = 8.6 Hz, 2H), 4.31−4.17 (m, 3H), 3.77 (s, 3H, -OCH_3), 3.08−2.91 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 162.9, 159.6, 146.3, 138.7, 137.4, 133.1, 129.0, 128.6, 128.1, 127.4, 114.7, 114.1, 113.7, 89.8, 83.6, 63.8, 61.0, 55.2, 51.8, 37.5, 14.2; LC/MS *m/z* 375 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.85; H, 5.98.

*Ethyl 5-formyl-4-phenyl-5-(p-tolylethynyl)cyclopent-1-enecarboxylate (**14ca**):* yield 0.205 g (61%, gummy liquid); IR (neat) 3061, 3030, 2975, 2197, 1704, 1633, 1507, 1463, 1375, 1332, 1260, 1134, 1025, 822, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.34−7.29 (m, 5H), 7.13−7.12 (m, 1H), 7.08−7.03 (m, 4H), 4.29−4.18 (m, 3H), 3.05−2.96 (m, 2H), 2.31 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 162.9, 146.4, 138.6, 138.4, 137.4, 131.6, 129.0, 128.9, 128.1, 127.5, 119.6, 90.1, 84.4, 63.8, 61.1, 51.8, 37.5, 21.5,14.3; LC/MS *m/z* 359 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.36; H, 6.09.

*Ethyl 5-formyl-4-phenyl-5-(o-tolylethynyl)cyclopent-1-enecarboxylate (**14da**):* yield 0.250 g (70%, gummy liquid); IR (neat) 3063, 3030, 2981, 2191, 1709, 1616, 1490, 1457, 1369, 1254, 1030, 761, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.34−7.28 (m, 5H), 7.19−7.10 (m, 4H), 7.06 (t, J = 7.6 Hz, 1H), 4.30−4.21 (m, 3H), 3.11−2.94 (m, 2H), 2.16 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 162.9, 146.3, 140.3, 138.6, 137.6, 131.9, 129.3, 128.9, 128.3, 128.2, 127.4, 125.3, 122.4, 88.8, 64.0, 61.1, 51.5, 37.4, 20.4, 14.2; LC/MS *m/z* 359 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.31; H, 6.25.

*Ethyl 5-formyl-5-((4-nitrophenyl)ethynyl)-4-phenylcyclopent-1-enecarboxylate (**14ea**):* yield 0.221 g (57%, gummy liquid); IR (neat) 3063, 2975, 2931, 2844, 2235, 1731, 1709, 1632, 1594, 1512, 1342, 1265, 1106, 860, 755, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.09 (d, J = 9.2 Hz, 2H), 7.37−7.24 (m, 7H), 7.19−7.17 (m, 1H), 4.32−4.21 (m, 3H), 3.13−2.98 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 162.7, 147.2, 147.1, 138.3, 136.3, 132.4, 129.4, 128.8, 128.3, 127.7, 123.4, 90.7, 88.1, 64.2, 61.2, 51.4, 37.6, 14.2; LC/MS *m/z* 389 $[M]^+$. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.85; H, 4.87; N, 3.68.

*Ethyl 2-formyl-2-((4-nitrophenyl)ethynyl)-3-phenylcyclopent-3-enecarboxylate (**15ea**):* yield 0.043 g (11%, gummy liquid); IR (neat) 3112, 2975, 2910, 2838, 2230, 1732, 1710, 1638, 1595, 1518, 1353, 1249, 1096, 855, 756, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.05 (d, J = 8.8 Hz, 2H), 7.38−7.30 (m, 3H), 7.24 (d, J = 7.2 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.98 (s, 1H), 4.54 (s, 1H), 4.15−4.02 (m, 2H), 3.37−3.31 (m, 1H), 2.99−2.94 (m, 1H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 163.2, 147.1, 141.1, 138.1, 137.1, 132.3, 129.0, 128.5, 128.4, 127.6, 123.4, 90.6, 87.6, 60.7, 58.5, 55.2, 39.2, 14.0; LC/MS *m/z* 389 $[M]^+$. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 71.12; H, 4.96; N, 3.71.

*Ethyl 5-formyl-5-((2-nitrophenyl)ethynyl)-4-phenylcyclopent-1-enecarboxylate (**14fa**):* yield 0.185 g (48%, gummy liquid); IR (neat) 3058, 3030, 2981, 2236, 1732, 1710, 1627, 1611, 1529, 1348, 1266, 1129, 1107, 1025, 745, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.47−7.44 (m, 1H), 7.41−7.37 (m, 1H), 7.32−7.23 (m, 5H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 (s, 1H), 4.29−4.19 (m, 3H), 3.16−3.09 (m, 1H), 3.02−2.94 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 162.7, 149.6, 146.9, 138.1, 136.9, 135.0, 132.7, 128.9, 128.8, 128.2, 127.6, 124.5, 117.9, 93.3, 85.2, 64.3, 61.3, 51.7, 37.5, 14.2; LC/MS *m/z* 390 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.85; H, 4.86; N, 3.72.

*Ethyl 5-((4-fluorophenyl)ethynyl)-5-formyl-4-phenylcyclopent-1-enecarboxylate (**14ga**):* yield 0.192 g (53%, gummy liquid); IR (neat) 3063, 3030, 2975, 2849, 2197, 1704, 1633, 1606, 1507, 1381, 1332, 1238, 1129, 1025, 838, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.32−7.27 (m, 5H), 7.14−7.11 (m, 3H), 6.92 (t, J = 8.4 Hz, 2H), 4.33−4.18 (m, 3H), 3.09−2.93 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 162.9, 162.5 (J = 247.9 Hz), 146.5, 138.6, 137.1, 133.5 (J = 8.3 Hz), 128.9, 128.1, 127.5, 118.7, 115.4 (J = 21.9 Hz), 88.9, 84.8, 63.9, 61.1, 51.6, 37.5, 14.2; LC/MS *m/z* 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.32; H, 5.21.

*Ethyl 5-((3-fluorophenyl)ethynyl)-5-formyl-4-phenylcyclopent-1-enecarboxylate (**14ha**):* yield 0.233 g (61%, gummy liquid); IR (neat) 3063, 3036, 2981, 2197, 1704, 1606, 1578, 1490, 1370, 1271, 1036, 789, 701, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.37−7.29 (m, 5H), 7.21−7.14 (m, 2H), 6.99−6.93 (m, 2H), 6.85−6.82 (m, 1H), 4.33−4.19 (m, 3H), 3.10−2.94 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 162.8, 162.2 (J = 244.8 Hz), 146.7, 138.5, 137.0, 129.7 (J = 8.5 Hz), 128.9, 128.2, 127.6 (J = 5.6 Hz), 124.4 (J = 9.4 Hz), 118.5 (J = 22.7 Hz), 115.7 (J = 21.1 Hz), 88.7, 86.2, 63.9, 61.1, 51.6, 37.5, 14.2; LC/MS *m/z* 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.31; H, 5.24.

*Ethyl 5-((4-chlorophenyl)ethynyl)-5-formyl-4-phenylcyclopent-1-enecarboxylate (**14ia**):* yield 0.214 g (57%, gummy liquid); IR (neat) 3030, 2986, 2931, 2899, 2844, 1720, 1627, 1490, 1375, 1331, 1266, 1123, 1085, 1025, 838, 756, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.36−7.27 (m, 5H), 7.20 (d, J = 8.4 Hz, 2H), 7.14−7.13. (m, 1H), 7.07 (d, J = 8.4 Hz, 2H), 4.31−4.18 (m, 3H), 3.10−2.94 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 162.8, 146.6, 138.5, 137.0, 134.3, 132.9, 128.9, 128.5, 128.1, 127.5, 121.1, 88.8, 86.1, 63.9, 61.1, 51.6, 37.5, 14.2; LC/MS *m/z* 379 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}ClO_3$: C, 72.92; H, 5.06. Found: C, 72.85; H, 5.13.

*Ethyl 5-((4-bromophenyl)ethynyl)-5-formyl-4-phenylcyclopent-1-enecarboxylate (**14ja**):* yield 0.197 g (47%, gummy liquid); IR (neat) 3061, 3030, 2980, 2933, 2200, 1713, 1628, 1581, 1486, 1455, 1394, 1372, 1327, 1257, 1105, 1069, 1031, 825, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.37−7.27 (m, 7H), 7.14 (s, 1H), 7.00 (d, J = 8.0 Hz, 2H), 4.28−4.18 (m, 3H), 3.09−2.95 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 162.8, 146.7, 138.5, 136.9, 133.1, 131.4, 128.9, 128.2, 127.5, 122.6, 121.6, 88.9, 86.4, 64.0, 61.1, 51.6, 37.5, 14.3; LC/MS *m/z* 421 $[M - 2]^+$ and 423 $[M]^+$. Anal. Calcd for $C_{23}H_{19}BrO_3$: C, 65.26; H, 4.52. Found: C, 65.36; H, 4.48.

*Ethyl 5-formyl-4-(4-methoxyphenyl)-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14ka**):* yield 0.239 (68%, gummy liquid); IR (neat) 3063, 2981, 2932, 2904, 2833, 2060, 1715, 1611, 1512, 1496, 1441, 1370, 1321, 1244, 1178, 1129, 1036, 827, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.27−7.23 (m, 7H), 7.12 (s, 1H), 6.87 (d, J = 8.4 Hz, 2H), 4.33−4.12 (m, 2H), 4.13 (t, J = 8.8 Hz, 1H), 3.80 (s, 3H), 3.04−2.89 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 162.9, 159.0, 146.5, 137.4, 131.7, 130.4, 130.0, 128.3, 128.1, 122.7, 113.5, 89.8, 85.2, 63.8, 61.0, 55.3, 51.3, 37.8, 14.2; LC/MS *m/z* 375 $[M + 1]^+$. Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.85; H, 5.98.

*Ethyl 5-formyl-4-(4-nitrophenyl)-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14la**):* yield 0.166 g (40%, gummy liquid); IR (neat) 3080, 2986, 2849, 2208, 1715, 1600, 1529, 1359, 1260, 1112, 849, 762, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.18 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.30−7.21 (m, 3H), 7.15−7.11 (m, 3H), 4.38−4.21 (m, 3H), 3.05−3.02 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 162.6, 147.3, 146.4, 145.6, 137.3, 131.5, 130.0, 128.8, 128.3, 123.2, 122.0, 90.8, 84.1, 63.7, 61.3, 50.2, 37.4, 14.2; LC/MS *m/z* 390 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 71.06; H, 4.87; N, 3.68.

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*Ethyl 4-(4-fluorophenyl)-5-formyl-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14ma**):* yield 0.223 g (62%, gummy liquid); IR (neat) 3063, 2981, 2197, 1715, 1600, 1512, 1222, 1162, 1036, 833, 751, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.32−7.23 (m, 5H), 7.20−7.18 (m, 2H), 7.12−7.11 (m, 1H), 7.02 (t, J = 8.4 Hz, 2H), 4.33−4.17 (m, 3H), 2.97 (d, J = 8.4 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 162.8, 162.2 (J = 244.3 Hz), 146.2, 137.3, 134.3, 131.6, 130.5 (J = 7.9 Hz), 128.5, 128.2, 122.4, 115.4 (J = 21.1 Hz), 90.2, 84.8, 63.8, 61.1, 50.7, 37.7, 14.2; LC/MS m/z 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.15; H, 5.32.

*Ethyl 4-(3-fluorophenyl)-5-formyl-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14na**):* yield 0.251g (63%, gummy liquid); IR (neat) 3068, 2975, 2198, 1704, 1611, 1584, 1485, 1370, 1326, 1244, 1123, 1019, 789, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.31−7.23 (m, 4H), 7.22−7.19 (m, 2H), 7.11−7.08 (m, 3H), 7.02−6.97 (m, 1H), 4.32−4.20 (m, 3H), 3.00−2.97 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 162.7 (J = 243.9 Hz), 146.0, 141.2, 137.3, 131.6, 129.6, 129.5, 128.5, 128.2, 124.8, 122.4, 115.9 (J = 21.5 Hz), 114.4 (J = 20.9 Hz), 90.3, 84.6, 63.7, 61.1, 50.9, 37.4, 14.2; LC/MS m/z 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.31; H, 5.23.

*Ethyl 3-(3-fluorophenyl)-2-formyl-2-(phenylethynyl)cyclopent-3-enecarboxylate (**15na**):* yield 0.048 g (12%, white solid); mp 100−102 °C; IR (KBr) 3058, 2981, 2937, 1704, 1627, 1611, 1595, 1490, 1447, 1370, 1337, 1244, 1118, 1101, 1063, 844, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.35−7.30 (m, 1H), 7.27−7.18 (m, 3H), 7.05−6.94 (m, 6H), 4.52 (s, 1H), 4.15−4.05 (m, 2H), 3.34−3.28 (m, 1H), 2.96−2.91 (m, 1H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 163.2, 162.9 (J = 243.9 Hz), 141.7, 141.1, 136.9, 131.5, 129.7, 129.6, 128.5, 128.2, 124.4, 122.0, 115.4 (J = 21.6 Hz), 114.3 (J = 20.9 Hz), 89.9, 84.5, 60.7, 58.3, 54.4, 39.4, 14.0; LC/MS m/z 363 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{19}FO_3$: C, 76.23; H, 5.28. Found: C, 76.45; H, 5.13.

*Ethyl 5-formyl-4-phenyl-5-((trimethylsilyl)ethynyl)cyclopent-1-enecarboxylate (**14oa**):* yield 0.222 g (65%, gummy liquid); IR (neat) 3036, 2959, 2899, 2844, 2164, 1721, 1627, 1496, 1381, 1321, 1249, 1112, 1036, 849, 756, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.29−7.26 (m, 5H), 7.08 (s, 1H), 4.31−4.18 (m, 2H), 4.11 (t, J = 8.4 Hz, 1H), 3.02−2.86 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 162.8, 146.4, 138.4, 137.3, 129.0, 127.9, 127.3, 100.9, 95.0, 64.0, 61.0, 51.8, 37.4, 14.2, −0.31; LC/MS m/z 341 $[M + 1]^+$. Anal. Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.10. Found: C, 70.45; H, 7.18.

*Methyl 5-formyl-4-phenyl-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14ab**):* yield 0.202 g (62%, gummy liquid); IR (neat) 3058, 3036, 2948, 2849, 2197, 1721, 1622, 1485, 1441, 1332, 1260, 1129, 1025, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.37−7.29 (m, 5H), 7.27−7.22 (m, 3H), 7.18 (d, J = 7.6 Hz, 2H), 7.14 (s, 1H), 4.21 (t, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.11−2.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 163.3, 146.8, 138.4, 137.0, 131.7, 129.0, 128.4, 128.1, 127.5, 122.6, 89.9, 84.9, 63.8, 52.1, 51.8, 37.5; HRMS (ESI) calcd for $C_{22}H_{19}O_3$ $[M^+ + H]$ m/z 331.1334, found 331.1331.

*Benzyl 5-formyl-4-phenyl-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14ac**):* yield 0.274 g (64%, gummy liquid); IR (neat) 3063, 3030, 2943, 2203, 1715, 1622, 1600, 1490, 1463, 1332, 1255, 1151, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.43−7.31 (m, 10H), 7.30−7.20 (m, 4H), 7.14−7.12 (m, 2H), 5.35−5.19 (m, 2H), 4.23 (t, J = 8.4 Hz, 1H), 3.11−3.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 162.7, 147.3, 138.5, 136.8, 135.7, 131.7, 129.0, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 122.6, 90.1, 85.0, 66.8, 63.9, 51.8, 37.6; LC/MS m/z 407 $[M + 1]^+$. Anal. Calcd for $C_{28}H_{22}O_3$: C, 82.74; H, 5.46. Found: C, 82.58; H, 5.41.

*tert-Butyl 5-formyl-4-phenyl-5-(phenylethynyl)cyclopent-1-enecarboxylate (**14ad**):* yield 0.175 g (48%, gummy liquid); IR (neat) 3062, 3031, 2978, 2932, 2201, 1710, 1634, 1600, 1491, 1455, 1392, 1368, 1273, 1254, 1167, 1030, 847, 757, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.48−7.47 (m, 2H), 7.35−7.23 (m, 6H), 7.14 (d, J = 7.2 Hz, 2H), 6.96 (s, 1H), 4.75 (s, 1H), 3.59−3.54 (m, 1H), 2.82−2.77 (m, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 163.0, 141.2, 137.8, 136.7, 131.8, 128.9, 128.6, 128.4, 128.2, 127.8, 122.4, 88.8, 86.6, 80.8, 61.9, 56.2, 38.8, 27.8; LC/MS m/z 373 $[M + 1]^+$. Anal. Calcd for $C_{25}H_{24}O_3$: C, 80.62; H, 6.49. Found: C, 80.48; H, 6.41.

(iii) (a) General Procedure for the Synthesis of Benzofurans 16 and 17 from Cyclopentenes 14. To a dry Schlenk tube were added Ph_3PAuCl (5 mol %), AgOTf (5 mol %) and dry 1,4-dioxane solvent (1 mL). The contents were stirred at room temperature for 0.5 h in the dark. Later, cyclopentene **14** (0.3 mmol) in 1,4-dioxane (1 mL) was added to the above mixture, and the contents were stirred at 100 °C for 24 h. After completion of the reaction, as monitored by TLC, the solvent was evaporated under vacuum. Benzofurans **16** and **17** were isolated by column chromatography by using an EtOAc/hexane mixture (1:99) as the eluent.

(b) General Procedure for the One-Pot Synthesis of Benzofurans 16 and 17 from Allenoates 10 and Enynals 9. To a solution of 2-(1-alkynyl)-2-alken-1-als **9** (0.5 mmol) in dry 1,4-dioxane (3 mL) was added PPh_3 (0.05 mmol) followed by alkyl 2,3-butadienoate **10a−d** (0.6 mmol). The vessel was stoppered under nitrogen atmosphere, and the contents were stirred for 12 h at rt. The progress of the reaction was monitored by TLC. Later, the solvent was removed under vacuum (to remove excess of allenoate). In the meantime, to a dry Schlenk tube were added Ph_3PAuCl (5 mol %), AgOTf (5 mol %), and dry 1,4-dioxane (1 mL). The contents were stirred at room temperature for 0.5 h in dark. To this catalytic system was added the above mixture in dioxane (1 mL), and the contents were stirred at 100 °C for 24 h. After completion of the reaction, as monitored by TLC, the solvent was evaporated under vacuum. Benzofuran **16** or **17** was isolated by column chromatography by using an EtOAc/hexane mixture (1:99) as the eluent.

*Ethyl 2,7-diphenylbenzofuran-4-carboxylate (**16aa**):* yield 0.078 g (76%, white solid); mp 84−86 °C; IR (KBr) 2980, 1726, 1447, 1375, 1282, 1222, 1140, 1030, 811, 756, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.93 (d, J = 7.2 Hz, 2H), 7.76.(s, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.51−7.46 (m, 4H), 7.40 (t, J = 7.2 Hz, 1H), 4.53−4.48 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 157.8, 152.3, 135.7, 130.8, 130.0, 129.4, 129.2, 128.9, 128.8, 128.5, 126.1, 125.4, 123.2, 121.4, 102.7, 60.9, 14.6; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $[M^+ + H]$ m/z 343.1334, found 343.1334. This compound was crystallized from ethanol at room temperature. X-ray structure was determined for this compound.

*Ethyl 2-(4-methoxyphenyl)-7-phenylbenzofuran-4-carboxylate (**16ba**):* yield 0.089 g (80%, white solid); mp 68−70 °C; IR (KBr) 2964, 2926, 2833, 1704, 1606, 1501, 1381, 1266, 1178, 1041, 816, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 8.8 Hz, 2H), 7.61.(s, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.49−7.45 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 4.52−4.47 (m, 2H), 3.88 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 160.4, 158.0, 152.1, 139.3, 135.8, 131.2, 129.1, 128.9, 128.8, 128.4, 126.9, 126.0, 122.8, 122.7, 121.0, 114.4, 101.1, 60.9, 55.4, 14.5; HRMS (ESI) calcd for $C_{24}H_{21}O_4$ $[M^+ + H]$ m/z 373.1440, found 373.1441.

*Ethyl 7-phenyl-2-(p-tolyl)benzofuran-4-carboxylate (**16ca**):* yield 0.081 g (76%, white solid); mp 70−72 °C; IR (KBr) 2921, 1726, 1441, 1386, 1266, 1145, 1041, 806, 756, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.99−7.97 (m, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.70.(s, 1H), 7.60−7.56 (m, 2H), 7.50−7.46 (m, 2H), 7.29−7.27 (m, 2H), 4.53−4.48 (m, 2H), 2.42 (s, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 158.1, 152.1, 139.3, 135.8, 130.9, 129.6, 129.3, 128.9, 128.8, 128.4, 127.2, 126.0, 125.3, 122.9, 121.2, 101.9, 60.9, 21.5, 14.5; HRMS (ESI) calcd for $C_{24}H_{21}O_3$ $[M^+ + H]$ m/z 357.1490, found 357.1486.

*Ethyl 7-phenyl-2-(o-tolyl)benzofuran-4-carboxylate (**16da**):* yield 0.082 g (77%, white solid); mp 70−72 °C; IR (KBr) 2981, 1704, 1375, 1282, 1266, 1216, 1140, 1036, 767, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.89−7.88 (m, 1H), 7.65 (s, 1H), 7.58−7.51 (m, 3H), 7.46 (t, J = 7.2 Hz, 1H), 7.33 (br s, 3H), 4.53−4.48 (m, 2H), 2.66 (s, 3H), 1.51 (t, J = 7.2 Hz,

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3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 157.7, 151.9, 136.2, 135.7, 131.5, 130.6, 129.9, 129.5, 129.4, 129.0, 128.9, 128.8, 128.4, 128.3, 126.2, 126.0, 123.1, 121.4, 106.3, 60.9, 22.2, 14.5; HRMS (ESI) calcd for $C_{24}H_{20}O_3Na$ [M^+ + Na] m/z 379.1310, found 379.1310.

*Ethyl 2-(4-nitrophenyl)-7-phenylbenzofuran-4-carboxylate (**16ea**):* yield 0.086 g (74%, yellow solid); mp 142−144 °C; IR (KBr) 2915, 2860, 1704, 1606, 1529, 1343, 1266, 1162, 1036, 860, 816, 745, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.8 Hz, 2H), 7.97.(s, 1H), 7.95−7.93 (m, 2H), 7.62−7.56 (m, 3H), 7.51 (t, J = 7.4 Hz, 1H), 4.54−4.49 (m, 2H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 154.9, 152.8, 147.6, 135.7, 135.3, 130.0, 129.9, 129.0, 128.8$_3$, 128.7$_6$, 126.7, 125.7, 124.6, 124.6, 124.4, 122.1, 106.3, 61.1, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}NO_5$ [M^+ + H] m/z 388.1185, found 388.1187.

*Ethyl 2-(2-nitrophenyl)-7-phenylbenzofuran-4-carboxylate (**16fa**):* yield 0.084 g (72%, yellow solid); mp 100−102 °C; IR (KBr) 2937, 1715, 1529, 1474, 1381, 1364, 1282, 1260, 1216, 1151, 1036, 981, 838, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 1H), 7.87−7.83 (m, 4H), 7.76.(s, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.57−7.53 (m, 4H), 7.45 (t, J = 7.4 Hz, 1H), 4.52−4.47 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 152.9, 152.7, 148.5, 135.1, 132.2, 130.3, 130.1, 129.9, 129.7, 128.8, 128.7, 126.5, 124.3, 124.1, 124.0, 122.1, 107.1, 61.1, 14.5; HRMS (ESI) calcd for $C_{23}H_{17}NO_5Na$ [M^+ + Na] m/z 410.1005, found 410.1007. This compound was crystallized from chloroform/hexane (2:1) mixture at room temperature. X-ray structure was determined for this sample.

*Ethyl 2-(4-fluorophenyl)-7-phenylbenzofuran-4-carboxylate (**16ga**):* yield 0.087 g (81%, white solid); mp 64−66 °C; IR (KBr) 2986, 1709, 1610, 1507, 1370, 1293, 1266, 1227, 1162, 1036, 910, 816, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.96−7.94 (m, 2H), 7.91−7.88 (m, 2H), 7.69.(s, 1H), 7.58 (t, J = 7.4 Hz, 2H), 7.50−7.46 (m, 2H), 7.17 (d, J = 8.6 Hz, 2H), 4.53−4.47 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.2 (J = 248.4 Hz), 156.9, 152.2, 135.7, 130.7, 129.4, 128.5, 127.2 (J = 8.2 Hz), 126.2 (J = 13.2 Hz), 123.2, 121.4, 116.0 (J = 21.9 Hz), 102.4, 60.9, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}FO_3$ [M^+ + H] m/z 361.1240, found 361.1242.

*Ethyl 2-(3-fluorophenyl)-7-phenylbenzofuran-4-carboxylate (**16ha**):* yield 0.091 g (84%, white solid); mp 106−108 °C; IR (KBr) 2959, 1721, 1611, 1480, 1375, 1277, 1222, 1140, 1030, 849, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.78.(s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.61−7.57 (m, 3H), 7.53−7.49 (m, 2H), 7.47−7.41 (m, 1H), 7.11−7.07 (m, 1H), 4.53−4.48 (m, 2H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.1 (J = 244.4 Hz), 156.3, 152.3, 135.6, 132.0 (J = 8.2 Hz), 130.6, 130.5, 130.4, 129.6, 128.9, 128.6, 126.3, 123.7, 121.6, 121.0, 116.0 (J = 21.2 Hz), 112.2 (J = 23.4 Hz), 103.7, 61.0, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}FO_3$ [M^+ + H] m/z 361.1240, found 361.1237.

*Ethyl 2-(4-chlorophenyl)-7-phenylbenzofuran-4-carboxylate (**16ia**):* yield 0.097 g (86%, white solid); mp 116−118 °C; IR (KBr) 2981, 1699, 1479, 1381, 1282, 1282, 1266, 1151, 1096, 1041, 822, 756, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H), 7.58 (t, J = 7.4 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.53−4.47 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 156.6, 152.3, 135.6, 135.0, 130.6, 129.5, 129.2, 128.9, 128.8, 128.5, 126.5, 126.2, 123.4, 121.5, 103.1, 61.0, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}ClO_3$ [M^+ + H] m/z 377.0944, found 377.0944.

*Ethyl 2-(4-bromophenyl)-7-phenylbenzofuran-4-carboxylate (**16ja**):* yield 0.093 g (74%, white solid); mp 120−122 °C; IR (KBr) 2981, 1710, 1589, 1479, 1381, 1282, 1255, 1151, 1041, 811, 756, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 8.8 Hz, 3H), 7.60−7.56 (m, 4H), 7.49 (t, J = 8.0 Hz, 2H), 4.53−4.47 (m, 2H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 156.6, 152.3, 135.6, 132.1, 130.6, 129.5, 128.9, 128.8, 128.5, 126.7, 126.3, 123.5, 123.2, 121.5, 103.2, 61.0, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}BrO_3$ [M^+ + H] and [M^+ + H + 2] m/z 421.0438, 423.0439, found 421.0440, 423.0422.

*Ethyl 7-(4-methoxyphenyl)-2-phenylbenzofuran-4-carboxylate (**16ka**):* yield 0.087 g (78%, white solid); mp 74−76 °C; IR (KBr) 3057, 2926, 2833, 1704, 1605, 1512, 1446, 1369, 1282, 1254, 1156, 1029, 805, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.94 (t, J = 7.2 Hz, 4H), 7.61.(s, 1H), 7.50−7.45 (m, 3H), 7.41−7.40 (m, 1H), 7.11 (d, J = 8.8 Hz, 2H), 4.52−4.47 (m, 2H), 3.92 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 159.9, 157.7, 152.1. 130.7, 130.1, 129.7, 129.1, 128.9, 128.1, 126.2, 125.3, 122.6, 120.8, 114.3, 102.7, 60.8, 55.4, 14.5; LC/MS m/z 373 [M + 1]$^+$. Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.26; H, 5.48.

*Ethyl 7-(4-nitrophenyl)-2-phenylbenzofuran-4-carboxylate (**16la**):* yield 0.079 g (68%, yellow solid); mp 148−150 °C; IR (KBr) 2920, 1715, 1594, 1583, 1512, 1375, 1353, 1260, 1145, 1040, 860, 816, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.4 Hz, 2H), 8.15−8.08 (m, 3H), 7.91 (d, J = 7.6 Hz, 2H), 7.77.(s, 1H), 7.53−7.43 (m, 4H), 4.55−4.49 (m, 2H), 1.52 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.2, 152.2, 147.6, 142.2, 131.1, 129.6, 129.5, 129.0, 126.7, 126.2, 125.4, 124.0, 123.2, 123.0, 102.7, 61.2, 14.5; HRMS (ESI) calcd for $C_{23}H_{18}NO_5$ [M^+ + H] m/z 388.1185, found 388.1181.

*Ethyl 7-(4-fluoro)phenyl)-2-phenylbenzofuran-4-carboxylate (**16ma**):* yield 0.091 g (84%, white solid); mp 100−102 °C; IR (KBr) 2975, 1710, 1600, 1529, 1375, 1288, 1216, 1140, 1036, 921, 816, 756, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.97−7.90 (m, 4H), 7.75.(s, 1H), 7.50−7.39 (m, 4H), 7.29. (s, 1H), 7.25 (s, 1H), 4.53−4.48 (m, 2H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.9 (J = 247.0 Hz), 157.8, 152.1, 131.7, 130.8, 130.6 (J = 8.0 Hz), 129.9, 129.2, 128.9, 128.3, 126.1, 125.3, 122.9, 121.5, 115.8 (J = 21.3 Hz), 102.7, 60.9, 14.5; HRMS (ESI) calcd for $C_{23}H_{17}FO_3Na$ [M^++ Na] m/z 383.1060, found 383.1060.

*Ethyl 7-(3-fluorophenyl)-2-phenylbenzofuran-4-carboxylate (**16na**).* Yield 0.092 g (85%, white solid); mp 58−60 °C; IR (KBr) 2981, 1715, 1605, 1474, 1441, 1375, 1282, 1195, 1134, 1030, 849, 795, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.77−7.72 (m, 3H), 7.58−7.49 (m, 4H) 7.43 (t, J = 7.4 Hz, 1H), 7.22−7.17 (m, 1H), 4.55−4.50 (m, 2H), 1.53 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 163.0 (J = 244.1 Hz), 157.9, 152.1, 137.8 (J = 8.1 Hz), 130.9, 130.2 (J = 8.2 Hz), 129.8, 129.3, 128.9, 128.0, 126.1, 125.4, 124.5 (J = 2.8 Hz), 123.0, 122.0, 115.8 (J = 22.5 Hz), 115.3 (J = 20.9 Hz), 102.7, 61.0, 14.5; LC/MS m/z 361 [M + 1]$^+$. Anal. Calcd for $C_{23}H_{17}FO_3$: C, 76.65; H, 4.75. Found: C, 76.53; H, 4.71.

*Ethyl 7-phenyl-2,3-dihydrobenzofuran-4-carboxylate (**16oa**):* yield 0.072 g (89%, gummy liquid); IR (neat) 2975, 2860, 1710, 1595, 1507, 1403, 1277, 1211, 1134, 1030, 975, 756, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.38−7.35 (m, 2H), 4.67 (t, J = 8.8 Hz, 2H), 4.42−4.36 (m, 2H), 3.62 (t, J = 8.8 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 157.8, 152.8, 146.6, 136.5, 130.6, 128.5, 127.9, 127.8, 127.3, 126.0, 122.3, 71.6, 60.8, 31.2, 14.4; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ [M^+ + H] m/z 269.1177, found 269.1178.

*Methyl 2,7-diphenylbenzofuran-4-carboxylate (**16ab**):* yield 0.082 g (83%, white solid); mp 118−120 °C; IR (KBr) 2964, 1715, 1606, 1430, 1375, 1288, 1140, 904, 816, 756, 685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.93 (d, J = 7.6 Hz, 1H), 7.74.(s, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 8.6 Hz, 4H), 7.40 (t, J = 7.2 Hz, 2H), 4.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 157.9, 152.2, 135.7, 130.8, 130.0, 129.5, 129.2, 128.9, 128.8, 128.5, 126.2, 125.4, 123.2, 121.1, 102.7, 52.0; HRMS (ESI) calcd for $C_{22}H_{17}O_3$ [M^+ + H] m/z 329.1177, found 329.1175.

*Benzyl 2,7-diphenylbenzofuran-4-carboxylate (**16ac**):* yield 0.097 g (80%, white solid); mp 118−120 °C; IR (KBr) 3052, 1699, 1578, 1447, 1381, 1260, 1156, 1041, 762, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 6.8 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.75.(s, 1H), 7.58−7.39 (m, 12H), 5.50(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 157.9, 152.3, 136.3, 135.7, 131.0, 129.9, 129.6, 129.2, 128.9$_1$, 128.8$_7$, 128.8, 128.7, 128.5, 128.3, 128.2,

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J. Org. Chem. 2015, 80, 4084−4096

126.3, 125.4, 123.2, 121.0, 102.7, 66.7; LC/MS m/z 405 $[M + 1]^+$. Anal. Calcd for $C_{28}H_{20}O_3$: C, 83.15; H, 4.98. Found: C, 83.06; H, 4.91.

2,7-Diphenylbenzofuran (17): yield 0.050 g (62%, gummy liquid); IR (neat) 3063, 3030, 2921, 2849, 1737, 1688, 1600, 1474, 1408, 1266, 1216, 1162, 904, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 7.2 Hz, 2H), 7.59−7.54 (m, 3H), 7.46 (t, J = 7.6 Hz, 4H), 7.38−7.31 (m, 2H), 7.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 152.0, 136.6, 130.4, 130.0, 128.8, 128.7, 128.6, 127.6, 125.3, 125.0, 123.9, 123.6, 120.1, 101.5; LC/MS m/z 271 $[M + 1]^+$; HRMS (ESI) calcd for $C_{20}H_{15}O$ $[M^+ + H]$ m/z 271.1123, found 271.1109. Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.75; H, 5.27;

(iv) X-ray Data. X-ray data for compounds **12ga**, **13ac**, **15aa**, **16aa**, and **16fa** were collected using Mo Kα (λ = 0.710 73 Å) radiation. The structures were solved and refined by standard methods.[23]

12ga: $C_{23}H_{19}ClO_3$, M = 378.83, triclinic, space group P-1, a = 8.2508(4) Å, b = 11.0623(5) Å, c = 11.3405(5) Å, V = 978.61(8) $Å^3$, α = 103.306(4), β = 95.478(4), γ = 100.9(4), Z = 2, μ = 1.887 mm^{-1}, data/restraints/parameters 3469/0/247, R indices ($I > 2\sigma(I)$) R1 = 0.0648, wR2 (all data) = 0.2040, CCDC no. 1049092.

13ac: $C_{24}H_{22}O_3$, M = 358.42, monoclinic, space group $P2(1)/n$, a = 15.467(3) Å, b = 5.7705(10) Å, c = 22.341(5) Å, β = 99.10(2), V = 1968.9(7) $Å^3$, Z = 4, μ = 0.079 mm^{-1}, data/restraints/parameters: 4472/0/246, R indices ($I > 2\sigma(I)$): R1 = 0.0701, wR2 (all data) = 0.1746, CCDC no. 1049093.

15aa: $C_{23}H_{20}O_3$, M = 344.39, monoclinic, space group $P2(1)/n$, a = 11.8106(11) Å, b = 8.1876(9) Å, c = 19.816(3) Å, β = 104.297(11), V = 1856.9(4) $Å^3$, Z = 4, μ = 0.081 mm^{-1}, data/restraints/parameters: 3263/0/240, R indices ($I > 2\sigma(I)$): R1 = 0.0599, wR2 (all data) = 0.1865, CCDC no. 1049094.

16aa: $C_{23}H_{18}O_3$, M = 342.37, orthorhombic, space group $Pca2_1$, a = 12.3414(4) Å, b = 20.8549(6) Å, c = 6.9482(2) Å, V = 1788.32(10) $Å^3$, Z = 4, μ = 0.669 mm^{-1}, data/restraints/parameters: 2117/0/236, R indices ($I > 2\sigma(I)$): R1 = 0.0411, wR2 (all data) = 0.1049, CCDC no. 1049095.

16fa: $C_{23}H_{17}NO_5$, M = 387.38, monoclinic, space group $C2/c$, a = 15.4744(3) Å, b = 16.1876(3) Å, c = 15.6267(3) Å, V = 3850.85(13) $Å^3$, Z = 8, μ = 0.784 mm^{-1}, data/restraints/parameters: 3692/0/263, R indices ($I > 2\sigma(I)$): R1 = 0.0666, wR2 (all data) = 0.1592, CCDC no. 1049096.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ORTEP drawings as shown by X-ray crystallography (CIF) and copies of $^1H/^{13}C$ NMR spectra of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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