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Brønsted Acid-Catalyzed Cycloisomerization of But-2-yne-1,4-diols with or without 1,3-Dicarbonyl Compounds to Tri- and Tetrasubstituted Furans

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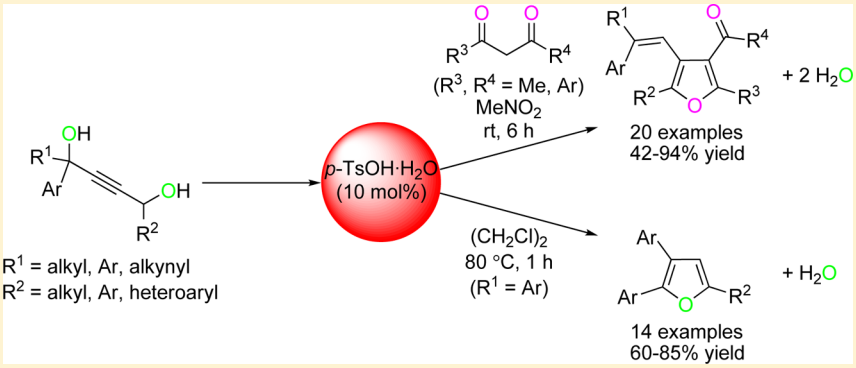
Supporting Information



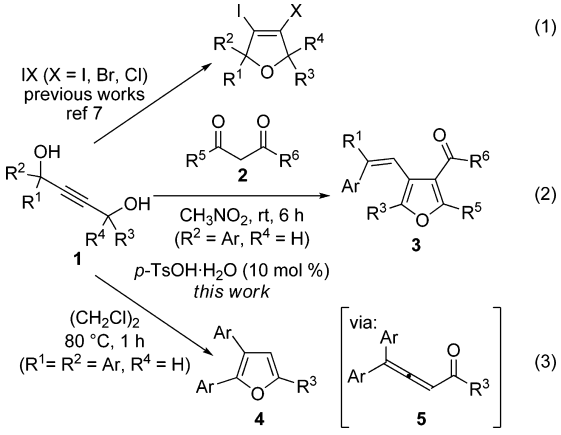
ABSTRACT: A Brønsted acid-catalyzed method to prepare tri- and tetrasubstituted furans efficiently from cycloisomerization of but-2-yne-1,4-diols with or without 1,3-dicarbonyl compounds is described. By taking advantage of the orthogonal modes of reactivity of the alcoholic substrate through slight modification of the reaction conditions, a divergence in product selectivity was observed. At room temperature, *p*-TsOH·H_2O-mediated tandem alkylation/cycloisomerization of the propargylic 1,4-diol with the *β*-dicarbonyl compound was found to selectively occur to provide the tetrasubstituted furan product. On the other hand, increasing the reaction temperature to 80 °C was discovered to result in preferential *p*-TsOH·H_2O-catalyzed dehydrative rearrangement of the unsaturated alcohol and formation of the 2,3,5-trisubstituted furan adduct.

INTRODUCTION

Furans occupy an important place in the heterocyclic family of compounds because of their prevalence as a key structural component in a myriad of natural and pharmaceutical products and ability to serve as a versatile building block in organic synthesis.[1,2] While this has led to a myriad of impressive approaches for furan synthesis being developed over the years,[1−3] there remains a need for new methods for their construction with selective control substitution of patterns from starting materials and a catalytic system that are readily accessible, atom-economical, and low cost.

Over the past decade, the use of unsaturated alcohols in Brønsted acid-catalyzed synthetic strategies directed toward the assembly of carbocyclic and heterocyclic compounds has received an increasing amount of attention.[4−7] For example, we recently reported a method for the synthesis of 3-halohydrofurans that relied on TfOH-mediated hydroxylation/halocyclization of cyclopropyl methanols with H_2O and N-halosuccinimide (NXS, X = I, Br, Cl) or Selectfluor.[5a] Further exploration of this field led us to examine the potential Brønsted acid-catalyzed reactivity of readily available propargylic 1,4-diols **1** (Scheme 1). Thus far, the cycloisomerization chemistry of this class of compounds has been reported only in electrophilic halocyclizations in the presence of a stoichiometric amount of a halogen source, such as I_2, to give 3,4-dihalodihydrofurans

Scheme 1. Design of Propargylic 1,4-Diol-Based Approaches for the Synthesis of Furan Derivatives



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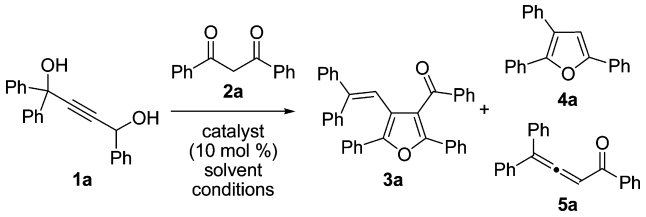
(Scheme 1, eq 1).[7] In contrast, a catalytic rearrangement process involving Brønsted acid-induced ionization of a propargylic 1,4-diol, which results in the formation the aromatic oxygen heterocycle is not known. As part of effects to develop this type of reaction, we report herein that *p*-TsOH·H_2O can mediate tandem alkylation/cycloisomerization of but-2-yne-1,4-diols **1** with 1,3-dicarbonyl compounds **2** (Scheme 1, eq 2). This process provides a convenient synthetic route to tetrasubstituted furans **3** in 42−94% yield for a wide variety of substrates under mild conditions at room temperature. In the course of this study, our discovery that a synthetic route to 2,3,5-trisubstituted furans **4** in 60−85% yield from *p*-TsOH·H_2O-catalyzed dehydrative rearrangement of the starting 1,4-diol under slightly modified reaction conditions is also presented (Scheme 1, eq 3). A notable observation we have made for this latter furan forming process is that it occurs via the in situ formed allenyl ketone intermediate **5**, the cycloisomerization chemistry of which has been extensively studied under transition metal catalysis.[8]

RESULTS AND DISCUSSION

All the but-2-yne-1,4-diols examined in this work were prepared from reaction of the corresponding aldehyde and substituted prop-2-yn-1-ol pretreated with LDA following literature procedures.[9] With 1,1,4-triphenylbut-2-yne-1,4-diol **1a** and 1,3-diphenylpropane-1,3-dione **2a** as the model substrates in hand, we then began by focusing on a variety of Brønsted acid catalysts to test our hypothesis (Table 1). This revealed that

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	conditions (°C)/(h)	yield (%) 3a	4a	5a
1	*p*-TsOH·H_2O	$MeNO_2$	rt/6	92	–	–
2[b]	*p*-TsOH·H_2O	$MeNO_2$	rt/6	68	–	–
3[c]	*p*-TsOH·H_2O	$MeNO_2$	rt/6	85	–	–
4	TfOH	$MeNO_2$	rt/6	20	–	–
5	TFA	$MeNO_2$	rt/6	72	–	–
6	Tf_2NH	$MeNO_2$	rt/6	25	–	–
7	HCl	$MeNO_2$	rt/6	–[d]	–	–
8	*p*-TsOH·H_2O	CH_2Cl_2	rt/6	20	–	–
9	*p*-TsOH·H_2O	1,4-dioxane	rt/6	–[e]	–	–
10	*p*-TsOH·H_2O	PhMe	80/1	–	53	–
11[f]	*p*-TsOH·H_2O	PhMe	80/1	–	58	–
12[f]	*p*-TsOH·H_2O	$(CH_2Cl)_2$	80/1	–	80	–
13[c,f]	*p*-TsOH·H_2O	$(CH_2Cl)_2$	80/1	–	70	–
14[f]	*p*-TsOH·H_2O	$(CH_2Cl)_2$	80/0.5	–	30	54
15[f]	*p*-TsOH·H_2O	$MeNO_2$	80/1	–	55	–
16[f]	*p*-TsOH·H_2O	CH_3CN	80/1	–	20	44

[a]All reactions were performed with **1a**:**2a** ratio = 1:2 and 10 mol % of catalyst. [b]Reaction performed with 5 mol % of catalyst. [c]Reaction performed without the exclusion of air. [d]Mixture of unknown decomposition products obtained on the basis of TLC and ^1H NMR analysis of the reaction mixture. [e]No reaction observed on the basis of TLC and ^1H NMR analysis of the reaction mixture. [f]Reaction performed in the absence of **2a**.

subjecting **1a** (1 equiv) and **2a** (2 equiv) in $MeNO_2$ with 10 mol % of *p*-TsOH·H_2O at room temperature for 6 h gave the best result (entry 1). Under these conditions, (4-(2,2-diphenylvinyl)-2,5-diphenylfuran-3-yl)(phenyl)methanone **3a** was afforded in 92% yield. The structure of the furan product was determined by ^1H NMR measurements and comparison with the X-ray crystal structure analysis of three closely related adducts (vide infra). Lower product yields of 68 and 85% were obtained on decreasing the catalyst loading from 10 to 5 mol % or in the absence of a nitrogen atmosphere (entries 2 and 3). Similarly, lower product yields were found on repeating the reaction with TFA, TfOH or Tf_2NH in place of *p*-TsOH·H_2O as the catalyst or employing CH_2Cl_2 in place of $MeNO_2$ as the solvent (entries 4−6 and 8). Changing the catalyst from *p*-TsOH·H_2O to HCl or solvent from $MeNO_2$ to 1,4-dioxane were the only instances in which either recovery of the starting material in near quantitative yield or decomposition was found (entries 7 and 9). Unexpectedly, 2,3,5-triphenylfuran **4a** was afforded in 53% yield when $MeNO_2$ was replaced by toluene as the solvent at 80 °C for 1 h because of the heterogeneity of the reaction mixture at room temperature (entry 10). The unprecedented formation of **4a** via a mechanistically intriguing dehydrative rearrangement of **1a** prompted us to additionally examine this transformation more closely to establish a second set of reaction conditions to this class of substituted furans (entries 11−16). This initially showed that a comparable yield of the trisubstituted furan was found on repeating the reaction in the absence of the 1,3-dicarbonyl compound (entry 11). Our studies subsequently showed changing the solvent from toluene to 1,2-dichloroethane gave **4a** in 80% yield (entry 12). In contrast, lower product yields were obtained in the absence of a nitrogen atmosphere, or on replacing 1,2-dichloroethane with MeCN or $MeNO_2$ as the solvent, or reducing the reaction time from 1 h to 30 min (entries 13−16). Reactions with MeCN as solvent or conducted for 30 min also afforded the allenyl ketone byproduct **5a** in 44 and 54% yield, respectively (entries 14 and 16).[8] On the basis of the above results, reaction of **1a** with **2a** in the presence of 10 mol % of *p*-TsOH·H_2O in $MeNO_2$ at room temperature for 6 h provided the optimum conditions to the tetrasubstituted furan. On the other hand, reaction of **1a** with 10 mol % of *p*-TsOH·H_2O in 1,2-dichloroethane at 80 °C for 1 h gave the best conditions to the trisubstituted product.

With the two optimized conditions to access tetra- and trisubstituted furans in hand, we first turned to assessing the scope of the bimolecular reaction for a series of 1,3-dicarbonyl compounds and propargylic 1,4-diols (Table 2). These experiments showed that with *p*-TsOH·H_2O as the catalyst and $MeNO_2$ as the solvent, the conditions proved to be broad, and a variety of tetrasubstituted furans could be furnished in good to excellent yields from the corresponding substrates **1b−r** and **2a−d**. Reactions of starting 1,4-diols **1b−g**, containing para-substituted electron-withdrawing or electron-donating aryl groups at R^1 and R^2, with **2a** gave **3b−g** in excellent yields of 78−86%. The presence of a second alkyne moiety at R^1 was found to have no influence on the course of the reaction, with **3h** afforded in 82% yield. Likewise, replacing the phenyl substituent at R^3 with derivatives of the aromatic structure containing an electron-withdrawing (**1j**,**k**) or electron-donating (**1l**) group at the para position of the ring afforded the corresponding furan products **3j−l** in excellent yields of 89−91%. Similarly, the tetrasubstituted furans **3n−r** with a pendant alkyl, cyclohexyl, 1-napthyl or 2-thiophene functional group

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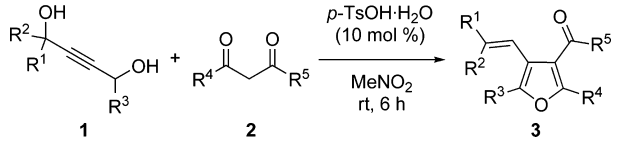
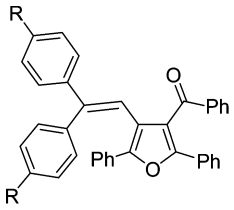
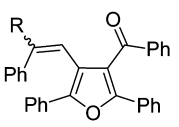
Table 2. Tandem Cycloisomerizations of 1b−r with 2a−d Catalyzed by *p*-TsOH·H_2O[a]

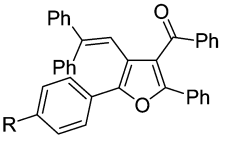




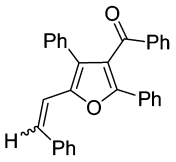
3b: R = F (78%)
3c: R = Cl (83%)
3d: R = Br (86%)
3e: R = Me (80%)



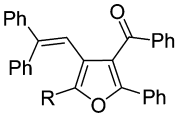
3f: R = *p*-Br(C_6H_4) (83%)[b]
3g: R = *p*-Me(C_6H_4) (85%)[c]
3h: R = C≡CPh (82%)[d]
3i: R = *t*-Bu (42%)[e]



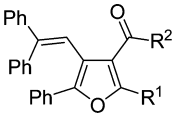
3j: R = F (89%)
3k: R = Br (91%)
3l: R = *t*-Bu (89%)



6m: (45%)[d]



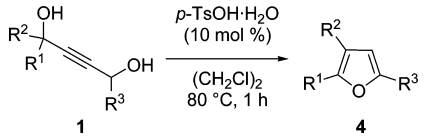
3n: R = 1-napthyl (72%)
3o: R = 2-thiophene (81%)
3p: R = cyclohexyl (85%)
3q: R = Me (74%)
3r: R = *t*-Bu (86%)

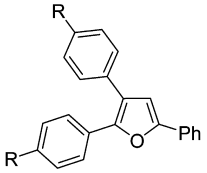


3s: R^1 = Me, R^2 = Ph (83%)
3t: R^1 = R^2 = *p*-MeO(C_6H_4) (94%)
3u: R^1 = R^2 = Me (85%)

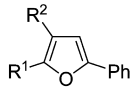
[a]All reactions were performed with **1**:**2** ratio = 1:2 and 10 mol % of *p*-TsOH·H_2O in $MeNO_2$ at rt for 6 h. [b]Product obtained as a 1.3:1 mixture of *E*/*Z* isomers. [c]Product obtained as a 1.1:1 mixture of *E*/*Z* isomers. [d]Product obtained as a 1:1 mixture of *E*/*Z* isomers. [e]Product obtained as a 1:2 mixture of *E*/*Z* isomers.

Table 3. Tandem Cycloisomerizations of 1b−r Catalyzed by *p*-TsOH·H_2O[a]

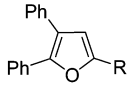




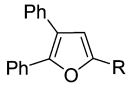
4b: R = F (80%)
4c: R = Cl (80%)
4d: R = Br (81%)
4e: R = Me (79%)



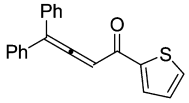
4f': R^1 = Ph, R^2 = *p*-Br(C_6H_4)
4f'': R^1 = *p*-Br(C_6H_4), R^2 = Ph (83%)[b]
4g': R^1 = Ph, R^2 = *p*-Me(C_6H_4)
4g'': R^1 = *p*-Me(C_6H_4), R^2 = Ph (82%)[c]
4h: R^1 = C≡CPh, R^2 = Ph (-)[d]
4i: R^1 = *t*-Bu, R^2 = Ph (-)[d]



4j: R = *p*-F(C_6H_4) (81%)
4k: R = *p*-Br(C_6H_4) (83%)
4l: R = *p*-(*t*-Bu)(C_6H_4) (85%)
4m: R = H (-)[d]



4n: R = 1-napthyl (60%)
4p: R = cyclohexyl (74%)
4q: R = Me (62%)
4r: R = *t*-Bu(82%)



5o: (68%)

[a]All reactions were performed at the 0.16 mmol scale with 10 mol % of *p*-TsOH·H_2O in 1,2-dichloroethane at 80 °C for 1 h. [b]Product obtained as an inseparable 2.5:1 mixture of regioisomers. [c]Product obtained as an inseparable 3.3:1 mixture of regioisomers. [d]Mixture of decomposition products obtained that could not be identified by ^{1}H NMR analysis or mass spectrometry.

at R^3 were obtained in 72−86% yield from the corresponding reactions of starting alcohols **1n−r** with **2a**. This contrasted to the analogous reactions where the phenyl substituent at R^1 was replaced with a *t*-Bu group (**1i**) or both carbinol carbon centers are secondary alcohols (**1m**) with **2a**. Reaction of the former was the only example found to give the corresponding furan **3i** in a lower yield of 42%. Moreover, reaction of the latter was found to furnish the tetrasubstituted furan regiosiomer **6m** in 45% yield.

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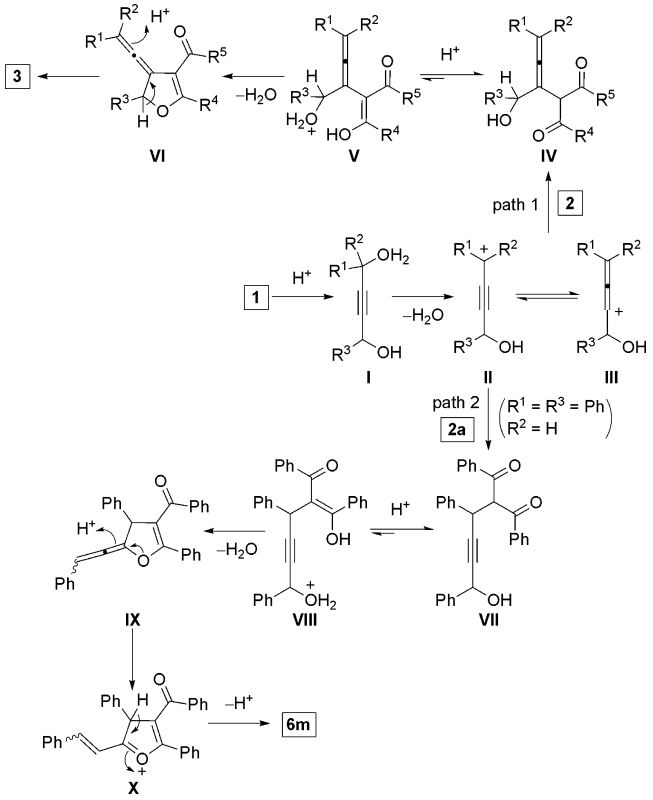
On the other hand, reactions of 1,3-dicabonyl compounds bearing a methyl or Ar group (**2b–d**) with **1a** were found to proceed well and provide **3s–u** in excellent yields. For reactions in which $R^1 \neq R^2$, the tetrasubstituted furan products were also obtained as a mixture of *E*/*Z* isomers in a ratio of up to 2:1 based on ^{1}H NMR measurements of the respective crude mixtures. The structure of the furan products were also determined on the basis of X-ray crystallographic analysis of **3d**, **3q**, **3r**, and **6m**.[10]

We next sought to define the scope of the intramolecular reaction with the same set of propargylic 1,4-diols compounds **1b–r**, and the results are summarized in Table 3. Overall, this led us to find the cyclization reactions to proceed well on applying the *p*-TsOH·H_2O-catalyzed conditions in 1,2-dichloroethane described in Table 1, entry 12. Under these conditions, the corresponding 2,3,5-trisubstituted furans **4b–g**, **4j–l**, **4n**, and **4p–r** were afforded in 60–85% yield. For reactions of **1f** and **1g**, the corresponding 2,3,5-trisubstituted adducts were also obtained as mixture of regioisomers in ratios of up to 3.3:1, comparable to those reported for the metal-catalyzed cycloisomerization of allenyl ketones.[11] Reactions of **1h,i**, **1m**, and **1o** were the only instances in which no product formation was observed. In our hands, reactions of **1h,i** and **1m** were found to give a mixture of decomposition products that could not be identified by ^{1}H NMR analysis or mass spectrometry. For **1o**, the allenyl ketone **5o** was the only product obtained in 68% yield, even on prolonging the reaction time to 5 h.

Tentative mechanisms for the present *p*-TsOH·H_2O-catalyzed tri- and tetrasubstituted furan forming reactions are outlined in Schemes 2 and 3. For the formation of the tetrasubstituted oxygen heterocycle, this could involve protonation of **1** by the Brønsted acid at the tertiary carbinol oxygen center (Scheme 2).

Scheme 2. Tentative Mechanism for *p*-TsOH·H_2O-Catalyzed Cycloisomerization of 1 in the Presence of 2



This leads to the protonated analogue **I**, which undergoes dehydration to give the alkynyl substituted carbocation **II** and its allenic resonance form **III**. At room temperature, nucleophilic attack at the acetylenic carbon center in **II** or allenic carbon center in **III** by **2** would then to give the alkylated adduct **IV** (Scheme 2, path 1). Subsequent isomerization to its enolate form and protonation of the remaining hydroxyl moiety by *p*-TsOH·H_2O would provide cationic tautomer **V**. Intramolecular nucleophilic substitution of the enolic oxygen onto the carbon center of the protonated hydroxyl group of this newly formed species followed by aromatization of the resulting hydrofuran **VI** obtained would then deliver the tetrasubstituted furan **3**. In these reactions, trapping at the sterically less hindered carbon center of the putative ionized species **II** or **III** could be one possible reason for the obtained product regioselectivities.[12] Such a pathway would limit any unfavorable steric interactions between the substituents of the tertiary carbocationic center and the incoming carbon nucleophile. The selective formation of **3s** could be due to attack of the more nucleophilic and less sterically bulky methyl ketone over that of the phenyl ketone in intermediate **V**. The regioisomer **6m** from **1m** could be due to the direct alkylation by **2a** of a presumably more reactive carbocationic species of **II** generated from the secondary 1,4-diol **1m** (Scheme 2, path 2).[13] This would give the propargylic adduct **VII**, which can isomerize to its enolate form and protonation at the remaining hydroxyl moiety by *p*-TsOH·H_2O to form cationic tautomer **VIII**. Cyclization of this cationic intermediate involving nucleophilic substitution of the enolic oxygen onto the carbon center of the protonated hydroxyl group would give **IX**, which can undergo aromatization via **X** to afford **6m**.

At 80 °C, it is thought that deprotonation of **II** preferentially occurs at the secondary carbinol carbon center to give the cumenol **XI** that readily isomerizes to the allenyl ketone **5** (Scheme 3).[14] In a manner similar to that reported for the analogous metal-catalyzed allenoate/allenyl ketone cyclizations,[8] this is followed by intramolecular addition of the carbonyl oxygen onto the allene moiety of the adduct triggered by the Brønsted acidic conditions (Scheme 3, route a). A [1,2]-aryl shift of the resultant cyclic oxonium intermediate **XII** would give **XIII**, which then aromatizes to provide the 2,3,5-trisubstituted furan **4**. Alternatively, the allenyl ketone **5** could isomerize to the corresponding vinyl cationic species **XV** via **XIV**, which would then undergo a [1,2]-aryl shift to give the disubstituted variant **XVI** (Scheme 3, route b). Cycloaddition involving attack of the enolic hydroxyl group onto the carbocationic carbon center of this species followed by deprotonation would then give **4**.

To demonstrate that the allenyl ketone **5** is the actual intermediate that leads to the formation of the trisubstituted adduct, we first examined the reaction of **5a** with 10 mol % of *p*-TsOH·H_2O in 1,2-dichloroethane at 80 °C for 1 h (Scheme 4, eq 1). This afforded **4a** in 86% yield, comparable to that directly obtained from **1a** as described in Table 1, entry 12. The mechanistic premise put forward in Scheme 3 for the formation of the allenyl ketone **5** via the cumenol **XI** was also supported by the following deuterium labeling experiments (Scheme 4, eq 2–4). Exposing a solution of **1a**-d_6 in 1,2-dichloroethane with *p*-TsOH·H_2O (10 mol %) under the conditions shown in Scheme 4, eq 2, gave **4a**-d_5 in 72% yield but with no retention of D content at C3 in the product, as determined by both ^{1}H NMR analysis and GC–MS measurements. In contrast, repeating the reactions of **1a**-d_6 and **1a** with 10 equiv of D_2O

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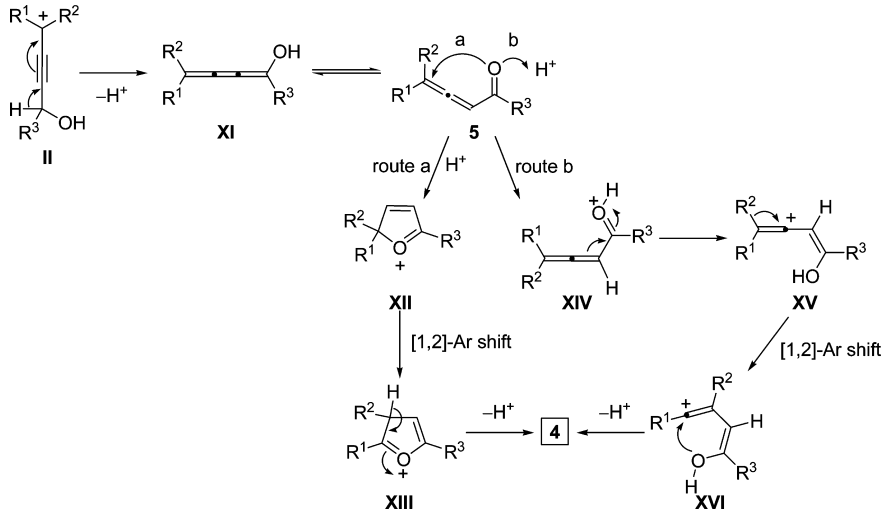
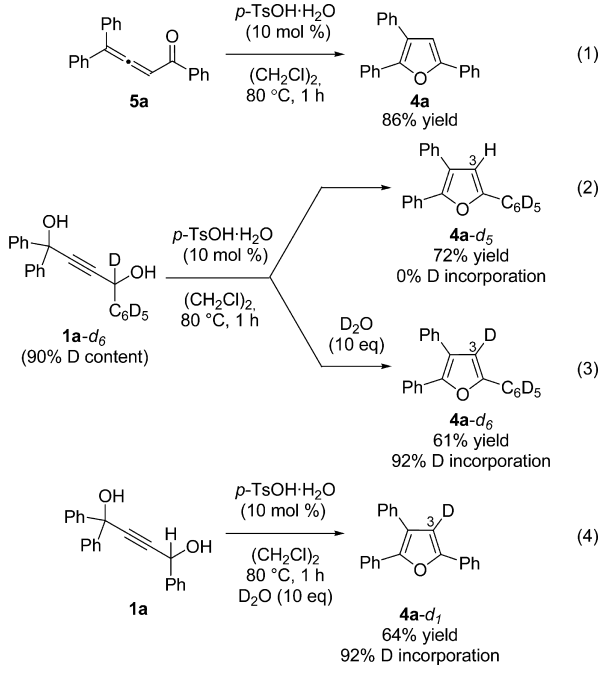
Scheme 3. Tentative Mechanism for Cycloisomerization of 1 Catalyzed by *p*-TsOH·H_2O



Scheme 4. Control Experiments with 1a, 1a-d_6 and 5a Catalyzed by *p*-TsOH·H_2O



afforded **4a**-d_6 and **4a**-d_1 in 61 and 64% yield and with a D content of 92%, incorporated at C3 of the adduct on the basis of ^{1}H NMR analysis and GC−MS measurements (Scheme 4, eq 3 and 4).

CONCLUSION

In summary, an efficient Brønsted acid-catalyzed synthetic route to tetrasubstituted furans from but-2-yne-1,4-diols and 1,3-dicarbonyl compounds under mild conditions at room temperature has been reported. The intriguing reactivities of the propargylic 1,4-diol at an elevated reaction temperature of 80 °C was also discovered and exploited to prepare the 2,3,5-trisubstituted class of furans. By judiciously applying one of these two reaction temperatures and solvent medium, our studies showed that a divergence in product selectivity was possible. Efforts to explore the synthetic applications of the present reactions are currently underway and will be reported in due course.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed under a nitrogen atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using precoated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and a gradient solvent system (*n*-hexane/EtOAc as eluent). ^{1}H and ^{13}C NMR spectra were measured on 300, 400, and 500 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Infrared spectra were recorded on a FTIR spectrometer. Solid samples were examined as a thin film between NaCl salt plates. High resolution mass spectra (HRMS) were obtained using a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

Experimental Procedure for Preparation of Substituted But-2-yne-1,4-diols (1a)−(1r).[9,15] To a solution of the appropriate aldehyde or ketone (2.7 mmol) in THF (5 mL) was added dropwise ethynylmagnesium bromide (0.5 M THF solution; 2.9 mL; 3.5 mmol) at room temperature. The resulting solution was stirred for a further 1−10 h at the same temperature. On completion, the reaction mixture was quenched by adding saturated NH_4Cl (50 mL) and extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with water (25 mL), brine (25 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave the propargylic alcohol intermediate **7**. To a solution of diisopropylamine (0.47 g, 4.6 mmol) in anhydrous THF (5 mL) was added butyl lithium (1.6 M hexane solution; 2.9 mL; 4.6 mmol) at −78 °C in a dropwise manner. The resulting solution was stirred for 1 h prior to slow addition of **7** (1.3 mmol) in THF at −78 °C. The resulting mixture was stirred at the same temperature for 1 h. The appropriate aldehyde (2.0 mmol) in THF (2 mL) was added to the reaction mixture and allowed to stir for a further 1 h at the same temperature. On completion, the reaction mixture was quenched by adding saturated NH_4Cl (50 mL) and extracted with EtOAc (2 × 25 mL). The combined organic layers were washed with water (25 mL), brine (25 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 4:1) gave the title compound.

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General Procedure for Optimizing the Brønsted Acid-Catalyzed Reactions of (1a) with (2a). The Brønsted acid catalyst (8−16 μmol) was added to the respective solvent (2 mL) at room temperature prior to adding the starting materials. A solution of **1a** (0.16 mmol) and **2a** (0.32 mmol) in 2 mL of the same solvent was then added dropwise to the solution of the Brønsted acid at room temperature. The resulting mixture was stirred at for 6 h at the same temperature. On completion, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) to give **3a**.

General Procedure for Optimizing the Brønsted Acid-Catalyzed Reactions of (1a). To a solution of *p*-TsOH·H_2O (16 μmol) in the respective solvent (2 mL) was added a solution of **1a** (0.16 mmol) in the same solvent at room temperature. The resulting mixture was then stirred at 80 °C for 1 h. On completion, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave **4a** and/or **5a**.

Representative Procedure for Brønsted Acid-Catalyzed Intermolecular Reactions of (1) with (2). To a solution of *p*-TsOH·H_2O (16 μmol) in $MeNO_2$ (2 mL) at room temperature was added dropwise the propargylic 1,4-diol **1** (0.16 mmol) and 1,3-dicarbonyl compound **2** (0.32 mmol) dissolved in $MeNO_2$ (2 mL). The resulting mixture was stirred at room temperature for 6 h and monitored by TLC analysis. The solvent was concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave the tetrasubstituted furan **3**.

Representative Procedure for Brønsted Acid-Catalyzed Intramolecular Reactions of (1). To a solution of *p*-TsOH·H_2O (16 μmol) in 1,2-dichloroethane (2 mL) at room temperature was added dropwise the propargylic 1,4-diol **1** (0.16 mmol) dissolved in 1,2-dichloroethane (2 mL). The resulting mixture was stirred at 80 °C for 1 h and monitored by TLC analysis. On completion, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave the trisubstituted furan **4**.

Procedure for Brønsted Acid-Catalyzed Reaction of (5a). To a solution of *p*-TsOH·H_2O (16 μmol) in 1,2-dichloroethane (2 mL) at room temperature was added dropwise **5** (0.16 mmol) dissolved in 1,2-dichloroethane (2 mL). The resulting mixture was stirred at 80 °C for 1 h. On completion, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave **4a**.

Representative Procedure for Brønsted Acid-Catalyzed Reactions of (1a) and (1a-d_6) in the Presence of D_2O. To a solution of *p*-TsOH·H_2O (16 μmol) in 1,2-dichloroethane (2 mL) at room temperature was added dropwise the propargylic 1,4-diol **1** (0.16 mmol) dissolved in 1,2-dichloroethane (2 mL) followed by the addition of D_2O (1.6 mmol). The resulting mixture was stirred at 80 °C for 1 h and monitored by TLC analysis. On completion, the reaction mixture was cooled down to room temperature and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 9:1) gave **4a**-d_1 or **4a**-d_6 with a D content incorporated at C3 on the basis of ^{1}H NMR analysis and GC−MS measurements or **4a**-d_5 when D = 0%.

1,1,4-Triphenylbut-2-yne-1,4-diol (1a). Yield 85%; wt 0.25 g; white solid: mp 139−141 °C; ^{1}H NMR (CD_3OD, 300 MHz) δ 7.61−7.55 (m, 6H), 7.36−7.15 (m, 9H), 5.57 (s, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 145.7, 141.3, 128.1, 127.7, 127.6, 127.0, 126.5, 125.8, 88.8, 86.7, 73.7, 63.7; IR (neat, cm^{-1}) 3419, 3018, 2399, 1635, 1556, 1419, 1215, 1004, 927, 771, 669; HRMS (ESI) calcd for $C_{22}H_{19}O_2$ $[M + H]^+$ 315.1385, found 315.1378.

1,1-bis(4-Fluorophenyl)-4-phenylbut-2-yne-1,4-diol (1b). Yield 69%; wt 0.098 g; light brown solid: mp 131−133 °C; ^{1}H NMR ($CDCl_3$+CD_3OD, 400 MHz) δ 7.54−7.50 (m, 5H), 7.38−7.28 (m, 3H), 7.21−7.17 (m, 1H), 6.99−6.94 (m, 4H), 5.53 (s, 1H), 2.68 (bs, 2H); ^{13}C NMR ($CDCl_3$+CD_3OD, 100 MHz) δ 163.5, 160.9, 140.9, 140.5, 129.3, 129.2, 128.5, 128.3, 127.8, 127.7, 126.5, 115.3, 115.09, 115.05, 114.8, 114.6, 88.7, 87.0, 73.0, 64.0; IR (neat, cm^{-1}) 3442, 3018, 2399, 1645, 1602, 1521, 1473, 1423, 1338, 1215, 1097, 1014, 927, 758, 669, 624; HRMS (ESI) calcd for $C_{22}H_{17}O_2F_2$ $[M + H]^+$ 351.1197, found 351.1214.

1,1-bis(4-Chlorophenyl)-4-phenylbut-2-yne-1,4-diol (1c). Yield 75%; wt 0.10 g; white solid: mp 120−122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45−7.42 (m, 6H), 7.37−7.32 (m, 3H), 7.25−7.22 (m, 4H), 5.50 (s, 1H), 3.47 (bs, 1H), 2.82 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.84, 142.82, 139.9, 133.9, 128.8, 128.7, 128.5, 127.3, 126.6, 88.4, 87.5, 73.5, 64.6; IR (neat, cm^{-1}) 3446, 3018, 2399, 1489, 1404, 1215, 1093, 1014, 927, 775, 669; HRMS (ESI) calcd for $C_{22}H_{17}O_2Cl_2$ $[M + H]^+$ 383.0606, found 383.0594.

1,1-bis(4-Bromophenyl)-4-phenylbut-2-yne-1,4-diol (1d). Yield 78%; wt 0.10 g; white solid: mp 133−135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41−7.23 (m, 13H), 5.44 (s, 1H), 3.86 (bs, 1H), 3.20 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.34, 143.31, 139.8, 131.5, 128.8, 128.7, 128.5, 127.7, 127.67, 126.6, 125.6, 122.1, 88.3, 87.4, 73.6, 64.5; IR (neat, cm^{-1}) 3419, 3018, 2399, 2088, 1635, 1516, 1417, 1215, 1010, 927, 771, 669; HRMS (ESI) calcd for $C_{22}H_{17}O_2Br_2$ $[M + H]^+$ 470.9595, found 470.9602.

4-Phenyl-1,1-di-*p*-tolylbut-2-yne-1,4-diol (1e). Yield 81%; wt 0.11 g; light brown solid: mp 140−142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54−7.52 (m, 2H), 7.47 (d, 4H, J = 8.2 Hz), 7.39−7.33 (m, 3H), 7.12 (d, 4H, J = 8.0), 5.56 (s, 1H), 3.04 (bs, 1H), 2.61 (bs, 1H), 2.32 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.0, 140.3, 137.4, 128.9, 128.6, 128.4, 126.7, 125.9, 89.6, 86.6, 74.2, 64.7, 21.0; IR (neat, cm^{-1}) 3419, 3018, 2399, 2088, 1637, 1560, 1516, 1473, 1419, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ $[M + H]^+$ 343.1698, found 343.1690.

1-(4-Bromophenyl)-1,4-diphenylbut-2-yne-1,4-diol (1f). Yield 76%; wt 0.10 g; yellow solid: mp 109−111 °C; dr ratio = 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53−7.24 (m, 14H), 5.50 (s, 1H, diastereomer A or B), 5.49 (s, 1H, diastereomer A or B), 3.40 (bs, 1H), 2.80 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 143.8, 140.0, 131.3, 128.7, 128.6, 128.4, 128.0, 127.8, 126.6, 125.9, 121.8, 88.8, 87.2, 74.0, 64.6; IR (neat, cm^{-1}) 3446, 3018, 2399, 1635, 1521, 1473, 1419, 1215, 1010, 927, 756, 669; HRMS (ESI) calcd for $C_{22}H_{18}O_2Br$ $[M + H]^+$ 393.0490, found 393.0481.

1,4-Diphenyl-1-*p*-tolylbut-2-yne-1,4-diol (1g). Yield 75%; wt 0.11 g; white solid: mp 123−125 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56−7.23 (m, 12H), 7.10 (d, 2H, J = 7.7 Hz), 5.52 (s, 1H), 3.13 (bs, 1H), 2.65 (bs, 1H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 141.9, 140.3, 137.5, 129.0, 128.6, 128.4, 128.2, 127.7, 126.7, 126.0, 89.5, 86.8, 74.3, 64.6, 21.0; IR (neat, cm^{-1}) 3439, 3018, 2088, 1637, 1508, 1419, 1215, 1016, 927, 758, 669; HRMS (ESI) calcd for $C_{23}H_{21}O_2$ $[M + H]^+$ 329.1542, found 329.1541.

1,4,6-Triphenylhexa-2,5-diyne-1,4-diol (1h). Yield 82%; wt 0.11 g; light brown solid: mp 129−131 °C; ^{1}H NMR ($CDCl_3$+CD_3OD, 500 MHz) δ 7.86−7.84 (m, 2H), 7.56−7.29 (m, 13H), 5.53 (s, 1H, diastereomer A or B), 5.52 (s, 1H, diastereomer A or B), 3.32 (bs, 2H); ^{13}C NMR ($CDCl_3$+CD_3OD, 125 MHz) δ 142.0, 140.3, 131.5, 128.5, 128.3, 128.2, 128.1, 128.0, 126.6, 126.5, 125.7, 122.0, 89.2, 86.3, 84.5, 84.3, 84.2, 64.8, 63.8, 63.7; IR (neat, cm^{-1}) 3018, 2399, 1516, 1419, 1215, 927, 769, 669; HRMS (ESI) calcd for $C_{24}H_{19}O_2$ $[M + H]^+$ 339.1385, found 339.1387.

5,5-Dimethyl-1,4-diphenylhex-2-yne-1,4-diol (1i). Yield 79%; wt 0.12 g; colorless oil: inseparable mixture with benzylic alcohol (1:1 ratio); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57−7.51 (m, 4H), 7.37−7.23 (m, 6H, (4H, benzylic)), 5.50 (s, 1H), 4.60 (s, 2H, (benzylic)), 2.83 (bs, 1H), 2.75 (bs, 1H), 0.99 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.9, 140.8, 140.6, 128.6, 128.5, 128.3, 127.6, 127.4, 127.1, 127.0, 126.6, 89.8, 85.5, 78.9, 65.2, 64.6, 39.5, 25.4; IR (neat, cm^{-1}) 3383, 3014, 2972, 2401, 1953, 1726, 1600, 1492, 1454, 1392, 1215, 1136, 1078, 1001, 906, 756, 700, 667; HRMS (ESI) calcd for $C_{20}H_{23}O_2$ $[M + H]^+$ 295.1698, found 295.1686.

4-(4-Fluorophenyl)-1,1-diphenylbut-2-yne-1,4-diol (1j). Yield 71%; wt 0.22 g; white solid: mp 113−115 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53−7.51 (m, 4H), 7.41−7.38 (m, 2H), 7.29−7.21 (m, 6H), 6.97 (t, 2H, J = 8.6 Hz), 5.42 (s, 1H), 3.54 (bs, 1H), 3.19 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.8, 161.8, 144.7 (d, 1C, J_{C-F} = 10.1 Hz),

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136.2 (d, 1C, J_{C-F} = 11.4 Hz), 128.78, 128.71, 128.5, 128.0, 126.1, 115.7, 115.5, 89.7, 86.8, 74.6, 64.0; IR (neat, cm^{-1}) 3421, 3018, 2399, 1635, 1508, 1419, 1215, 1014, 927, 771, 669; HRMS (ESI) calcd for $C_{22}H_{18}O_2F$ $[M + H]^+$ 333.1291, found 333.1279.

4-(4-Bromophenyl)-1,1-diphenylbut-2-yne-1,4-diol (1k). Yield 73%; wt 0.27 g; light brown solid: mp 166−168 °C; ^1H NMR ($CDCl_3$+CD_3OD, 500 MHz) δ 7.58−7.55 (m, 4H), 7.48−7.40 (m, 4H), 7.31−7.19 (m, 6H), 5.49 (s, 1H); ^{13}C NMR ($CDCl_3$+CD_3OD, 125 MHz) δ 145.15, 145.10, 139.9, 131.6, 131.58, 131.55, 128.6, 128.5, 128.3, 128.2, 127.8, 127.6, 126.0, 125.97, 125.95, 122.1, 89.4, 86.3, 74.0, 63.4; IR (neat, cm^{-1}) 3419, 3018, 2399, 2088, 1635, 1521, 1419, 1215, 1010, 927, 771, 669; HRMS (ESI) calcd for $C_{22}H_{18}O_2Br$ $[M + H]^+$ 393.0490, found 393.0487.

4-(4-*tert*-Butylphenyl)-1,1-diphenylbut-2-yne-1,4-diol (1l). Yield 78%; wt 0.27 g; white solid: mp 162−164 °C; ^1H NMR ($CDCl_3$+CD_3OD, 400 MHz) δ 7.59 (d, 4H, J = 7.3 Hz), 7.46 (d, 2H, J = 7.8 Hz), 7.38 (d, 2H, J = 7.8 Hz) 7.29−7.21 (m, 6H) 5.50 (s, 1H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$+CD_3OD, 100 MHz) δ 151.2, 145.2, 145.1, 137.6, 128.1, 127.4, 126.5, 126.02, 126.00, 125.4, 89.0, 86.8, 74.0, 63.8, 34.5, 31.2; IR (neat, cm^{-1}) 3439, 3018, 2399, 1635, 1419, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{26}H_{27}O_2$ $[M + H]^+$ 371.2011, found 371.2013.

1,4-Diphenylbut-2-yne-1,4-diol (1m). Yield 87%; wt 0.15 g; light brown solid: mp 117−119 °C; ^1H NMR ($CDCl_3$+CD_3OD, 400 MHz) δ 7.52 (d, 4H, J = 7.2 Hz), 7.35−7.26 (m, 6H), 5.47 (s, 2H), 3.32 (bs, 2H); ^{13}C NMR ($CDCl_3$+CD_3OD, 100 MHz) δ 140.6, 128.4, 128.1, 126.63, 126.62, 86.1, 86.0, 63.9; IR (neat, cm^{-1}) 3585, 3018, 2399, 1653, 1521, 1456, 1419, 1338, 1217, 1122, 1014, 927, 771, 698, 669; HRMS (ESI) calcd for $C_{16}H_{15}O_2$ $[M + H]^+$ 239.1072, found 239.1082.

4-(Naphthalen-1-yl)-1,1-diphenylbut-2-yne-1,4-diol (1n). Yield 71%; wt 0.12 g; white solid: mp 121−123 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.22−7.82 (m, 2H), 7.80 (d, 1H, J = 8.2 Hz), 7.74 (d, 1H, J = 7.0 Hz), 7.56−7.46 (m, 6H), 7.37 (t, 1H, J = 7.6 Hz), 7.25−7.18 (m, 6H), 6.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.6, 144.5, 135.2, 133.9, 130.4, 129.3, 128.6, 128.2, 127.6, 126.3, 125.9, 125.8, 125.1, 124.6, 123.9, 89.8, 86.8, 74.4, 62.9; IR (neat, cm^{-1}) 3439, 3018, 2399, 2088, 1633, 1519, 1423, 1215, 1014, 927, 771, 669; HRMS (ESI) calcd for $C_{26}H_{21}O_2$ $[M + H]^+$ 365.1542, found 365.1545.

1,1-Diphenyl-4-(thiophen-2-yl)but-2-yne-1,4-diol (1o). Yield 82%; wt 0.12 g; pale yellow solid: mp 156−158 °C; ^1H NMR ($CDCl_3$+CD_3OD, 500 MHz) δ 7.62−7.58 (m, 4H), 7.31−7.21 (m, 7H), 7.14 (bd, 1H, J = 3.4 Hz), 6.95−6.94 (m, 1H), 5.73 (s, 1H), 3.04 (bs, 2H); ^{13}C NMR ($CDCl_3$+CD_3OD, 125 MHz) δ 145.1, 145.0, 144.8, 128.2, 127.6, 126.8, 126.1, 126.0, 125.8, 125.5, 88.4, 86.1, 74.0, 59.8; IR (neat, cm^{-1}) 3441, 3018, 2399, 2088, 1635, 1516, 1419, 1215, 1014, 927, 771, 669; HRMS (ESI) calcd for $C_{20}H_{17}O_2S$ $[M + H]^+$ 321.0949, found 321.0965.

4-Cyclohexyl-1,1-diphenylbut-2-yne-1,4-diol (1p). Yield 86%; wt 0.13 g; white solid: mp 141−143 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, 4H, J = 7.6 Hz), 7.32−7.22 (m, 6H), 4.26 (d, 1H, J = 5.9 Hz), 3.18 (bs, 1H), 2.19 (bs, 1H), 1.86−1.58 (m, 5H), 1.28−1.01 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.9, 128.2, 127.6, 125.9, 88.3, 87.4, 74.4, 67.2, 44.1, 28.6, 28.1, 26.4, 25.87, 25.84; IR (neat, cm^{-1}) 3446, 3018, 2399, 1647, 1521, 1419, 1338, 1215, 1016, 927, 771, 669; HRMS (ESI) calcd for $C_{22}H_{25}O_2$ $[M + H]^+$ 321.1855, found 321.1870.

1,1-Diphenylpent-2-yne-1,4-diol (1q). Yield 80%; wt 0.09 g; white solid: mp 109−111 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, 4H, J = 7.1 Hz), 7.30−7.20 (m, 6H), 4.56 (q, 1H, J = 6.6 Hz), 3.47 (bs, 1H), 2.92 (bs, 1H), 1.44 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.8, 128.2, 127.7, 126.01, 126.00, 89.0, 86.7, 74.2, 58.4, 24.0; IR (neat, cm^{-1}) 3419, 3018, 2397, 1645, 1489, 1448, 1328, 1215, 1020, 925, 758, 669; HRMS (ESI) calcd for $C_{17}H_{17}O_2$ $[M + H]^+$ 253.1229, found 253.1227.

5,5-Dimethyl-1,1-diphenylhex-2-yne-1,4-diol (1r). Yield 82%; wt 0.11 g; white solid: mp 163−165 °C; ^1H NMR ($CDCl_3$+CD_3OD, 400 MHz) δ 7.58−7.22 (m, 10H), 4.10 (s, 1H), 3.63 (bs, 2H), 1.01 (s, 9H); ^{13}C NMR ($CDCl_3$+CD_3OD, 100 MHz) δ 145.4, 145.3, 127.9, 127.3, 126.5, 125.89, 125.87, 88.1, 86.6, 73.9, 70.8, 35.9, 25.2; IR (neat, cm^{-1}) 3689, 3018, 2962, 2397, 1521, 1419, 1215, 1004, 927, 769, 667; HRMS (ESI) calcd for $C_{20}H_{23}O_2$ $[M + H]^+$ 295.1698, found 295.1706.

1,1,-Triphenylbut-2-yne-1,4-diol (1a-d_6). Yield 81%; wt 0.12 g; white solid: mp 141−143 °C; ^1H NMR ($CDCl_3$+CD_3OD, 400 MHz) δ 7.59 (d, 4H, J = 7.6 Hz), 7.30−7.20 (m, 6H), 3.2 (bs, 2H); ^{13}C NMR ($CDCl_3$+CD_3OD, 100 MHz) δ 145.18, 145.12, 140.4, 128.0, 127.4, 125.96, 125.94, 89.0, 86.6, 77.3, 73.9; IR (neat, cm^{-1}) 3446, 3018, 2399, 1635, 1521, 1423, 1215, 1029, 927, 771, 669; HRMS (ESI) calcd for C_{22} $^1H_{14}$ $^2H_5O_2$ $[M + H]^+$ 320.1699, found 320.1686.

(4-(2,2-Diphenylvinyl)-2,5-diphenylfuran-3-yl)(phenyl)-methanone (3a). Wt 0.073 g; yellow solid: mp 124−126 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.89−7.87 (m, 2H), 7.55−7.20 (m, 16H), 7.10−6.90 (m, 7H), 6.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1, 152.3, 149.6, 146.6, 142.8, 138.8, 137.1, 132.7, 130.66, 130.61, 129.8, 129.5, 128.79, 128.71, 128.5, 128.3, 128.2, 128.0, 127.95, 127.90, 127.8, 127.7, 127.1, 127.0, 125.5, 122.7, 121.0, 118.1; IR (neat, cm^{-1}) 3018, 1734, 1653, 1597, 1483, 1446, 1327, 1215, 1074, 1026, 898, 758, 669; HRMS (ESI) calcd for $C_{37}H_{26}O_2Na$ $[M + Na]^+$ 525.1831, found 525.1830.

(4-(2,2-bis(4-Fluorophenyl)vinyl)-2,5-diphenylfuran-3-yl)-(phenyl)methanone (3b). Wt 0.059 g; yellow solid: mp 173−175 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86−7.84 (m, 2H), 7.54−6.84 (m, 20H), 6.75 (s, 1H), 6.62 (t, 1H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1, 163.8, 163.4, 161.4, 161.0, 152.4, 152.3, 149.8, 149.7, 145.5 (d, 1C, J_{C-F} = 14.2 Hz), 142.6, 138.9, (d, 1C, J_{C-F} = 12.2 Hz), 138.6, 137.1, 136.7, 134.8, 132.9, 132.7, 132.4, 132.3, 130.58 (d, 1C, J_{C-F} = 24.6 Hz), 129.9, 129.8, 129.7, 129.49, 129.41, 128.84, 128.83, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.96, 127.93 (d, 1C, J_{C-F} = 10.0 Hz), 127.2, 127.1, 125.5, 122.6, 122.5, 120.8, 118.1, 118.0, 115.0, 114.9, 114.8, 114.7; IR (neat, cm^{-1}) 3392, 3018, 2397, 1647, 1506, 1444, 1328, 1215, 898, 756; HRMS (ESI) calcd for $C_{37}H_{24}O_2F_2Na$ $[M + Na]^+$ 561.1642, found 561.1631.

(4-(2,2-bis(4-Chlorophenyl)vinyl)-2,5-diphenylfuran-3-yl)-(phenyl)methanone (3c). Wt 0.061 g; pale yellow solid: mp 195−197 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 7.4 Hz), 7.49−7.17 (m, 15H), 7.08 (d, 2H, J = 8.4 Hz), 6.87 (d, 2H, J = 8.4 Hz), 6.81 (d, 2H, J = 8.4 Hz), 6.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.0, 152.4, 150.1, 144.1, 140.7, 137.0, 136.4, 134.0, 133.8, 132.9, 131.8, 130.3, 129.6, 129.5, 129.2, 128.8, 128.6, 128.39, 128.31, 128.25, 128.1, 128.0, 127.1, 125.5, 122.3, 120.5, 118.9; IR (neat, cm^{-1}) 3442, 3018, 2399, 1647, 1506, 1490, 1417, 1338, 1215, 1091, 1014, 927, 777, 669; HRMS (ESI) calcd for $C_{37}H_{25}O_2Cl_2$ $[M + H]^+$ 571.1232, found 571.1252.

(4-(2,2-bis(4-Bromophenyl)vinyl)-2,5-diphenylfuran-3-yl)-(phenyl)methanone (3d). Wt 0.060 g; pale yellow solid: mp 209−211 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 7.6 Hz), 7.80−7.17 (m, 15H), 7.01 (dd, 4H, J_1 = 6.5, J_2 = 8.0 Hz), 6.79 (s, 1H), 6.75 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.0, 152.4, 150.1, 144.2, 141.1, 137.4, 136.4, 132.9, 132.1, 131.3, 131.1, 130.3, 129.8, 129.5, 129.2, 128.8, 128.6, 128.3, 128.17, 128.10, 127.2, 125.5, 122.3, 122.2, 120.4, 119.0; IR (neat, cm^{-1}) 3680, 3018, 2399, 1653, 1597, 1521, 1489, 1419, 1328, 1215, 1070, 1010, 929, 908, 756, 667; HRMS (ESI) calcd for $C_{37}H_{25}O_2Br_2$ $[M + H]^+$ 659.0221, found 659.0221.

(4-(2,2-di-*p*-Tolylvinyl)-2,5-diphenylfuran-3-yl)(phenyl)-methanone (3e). Wt 0.061 g; pale yellow solid: mp 176−178 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.91 (d, 2H, J = 7.4 Hz), 7.51−7.37 (m, 7H), 7.34 (t, 1H, J = 7.4 Hz), 7.22−7.18 (m, 5H), 7.07 (dd, 4H, J_1 = 8.1, J_2 = 17.7 Hz), 6.81 (d, 2H, J = 8.0 Hz), 6.74 (d, 2H, J = 7.9 Hz), 6.70 (s, 1H), 2.35 (s, 3H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.0, 152.0, 149.7, 146.4, 140.2, 137.5, 137.2, 136.9, 136.0, 132.4, 130.7, 130.6, 129.8, 129.6, 128.79, 128.72, 128.5, 128.4, 128.29, 128.25, 127.8, 127.7, 127.2, 127.1, 125.4, 122.7, 121.4, 116.8, 21.2, 21.1; IR (neat, cm^{-1}) 3018, 2399, 1653, 1598, 1516, 1419, 1336, 1215, 1026, 929, 771, 669; HRMS (ESI) calcd for $C_{39}H_{31}O_2$ $[M + H]^+$ 531.2324, found 531.2321.

(4-(2-(4-Bromophenyl)-2-phenylvinyl)-2,5-diphenylfuran-3-yl)(phenyl)methanone (3f). Wt 0.061 g; pale yellow solid: mp 155−157 °C; E/Z ratio = 1.3:1; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H, J = 8.2 Hz), 7.53−7.31 (m, 9H), 7.29−7.16 (m, 8H), 7.05−6.76

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(m, 5H), 6.71 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1 (1C, *E* or *Z* isomer), 191.0 (1C, *E* or *Z* isomer), 152.5, 152.3, 150.0, 149.7, 145.49, 145.40, 142.2, 141.7, 138.2, 137.9, 137.0, 136.4, 132.8, 132.7, 132.2, 131.1, 131.0, 130.5, 130.4, 129.8, 129.6, 129.4, 129.3, 128.8, 128.6, 128.5, 128.2, 128.1, 128.08, 128.02, 127.9, 127.16, 127.11, 125.5, 121.98, 121.95, 120.75, 120.72, 118.6, 118.4; IR (neat, cm^{-1}) 3442, 3018, 2399, 1653, 1521, 1419, 1338, 1215, 1026, 927, 769, 669; HRMS (ESI) calcd for $C_{37}H_{25}O_2BrNa$ $[M + Na]^+$ 603.0936, found 603.0942.

(2,5-Diphenyl-4-(2-phenyl-2-(*p*-tolyl)vinyl)furan-3-yl)-(phenyl)methanone (3g). Wt 0.066 g; pale yellow solid: mp 161−163 °C; *E*/*Z* ratio = 1.1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89−7.37 (m, 9H), 7.35−7.12 (m, 9H), 7.06−6.95 (m, 3H), 6.90 (d, 1H, *J* = 6.9 Hz), 6.79 (d, 1H, *J* = 8.0 Hz), 6.72 (s, 1H), 6.70 (d, 1H, *J* = 5.0 Hz). 2.32 (s, 3H, *E* or *Z* isomer), 2.10 (s, 3H, *E* or *Z* isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1 (1C, *E* or *Z* isomer), 191.0 (1C, *E* or *Z* isomer), 152.2, 152.1, 149.8, 149.5, 146.58, 146.52, 143.07, 143.05, 138.9, 137.6, 137.3, 137.2, 136.8, 135.9, 132.6, 130.67, 130.61, 129.88, 129.83, 129.5, 128.78, 128.73, 128.57, 128.50, 128.4, 128.3, 128.26, 128.23, 128.21, 127.99, 127.94, 127.8, 127.76, 127.74, 127.1, 127.0, 125.5, 122.8, 122.6, 121.3, 121.0, 117.5, 117.3; IR (neat, cm^{-1}) 3419, 3018, 2399, 1647, 1506, 1338, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{38}H_{28}O_2Na$ $[M + Na]^+$ 539.1987, found 539.1994.

(4-(2,4-Diphenylbut-1-en-3-yn-1-yl)-2,5-diphenylfuran-3-yl)-(phenyl)methanone (3h). Wt 0.063 g; yellow solid: mp 118−120 °C; *E*/*Z* ratio = 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85−7.73 (m, 4H), 7.53−7.16 (m, 19H), 7.06−6.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.1 (1C, *E* or *Z* isomer), 190.9 (1C, *E* or *Z* isomer), 153.3, 152.7, 149.9, 149.7, 138.4, 137.9, 136.7, 136.4, 132.8, 132.7, 131.67, 131.61, 130.6, 130.2, 129.9, 129.6, 129.3, 129.0, 128.85, 128.81, 128.7, 128.6, 128.39, 128.34, 128.29, 128.24, 128.21, 128.1, 128.09, 128.03, 128.00, 127.9, 127.8, 127.4, 127.2, 127.1, 126.3, 126.2, 125.9, 125.1, 123.2, 122.9, 122.4, 119.9, 119.3, 98.0, 91.2, 89.9, 87.7; IR (neat, cm^{-1}) 3442, 3018, 2399, 1653, 1489, 1215, 1026, 927, 773, 669; HRMS (ESI) calcd for $C_{39}H_{27}O_2$ $[M + H]^+$ 527.2011, found 527.2006.

(4-(3,3-Dimethyl-2-phenylbut-1-en-1-yl)-2,5-diphenylfuran-3-yl)(phenyl)methanone (3i). Wt 0.034 g; pale yellow solid: mp 145−147 °C; *E*/*Z* ratio = 1:2; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, 1H, *J* = 7.4 Hz), 7.76 (d, 2H, *J* = 7.4 Hz), 7.67 (d, 1H, *J* = 7.2 Hz), 7.45−7.02 (m, 25H), 6.81 (d, 2H, *J* = 6.9 Hz), 6.50 (s, 1H, *E* or *Z* isomer), 6.11 (s, 1H, *E* or *Z* isomer), 1.35 (s, 9H, *E* or *Z* isomer), 1.14 (s, 9H, *E* or *Z* isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.9 (1C, *E* or *Z* isomer), 193.7 (1C, *E* or *Z* isomer), 156.2, 152.3, 151.3, 150.4, 147.8, 146.9, 145.9, 141.3, 137.39, 137.35, 133.4, 133.3, 132.0, 131.9, 129.8, 129.78, 129.71, 129.5, 129.4, 129.2, 129.1, 128.6, 128.5, 128.4, 128.32, 128.30, 128.2, 128.0, 127.9, 127.8, 127.5, 127.24, 127.21, 126.8, 126.3, 126.2, 125.8, 122.3, 121.6, 116.0, 110.6, 37.1, 36.0, 30.9, 29.7; IR (neat, cm^{-1}) 3414, 3018, 2399, 1653, 1521, 1419, 1325, 1215, 1020, 927, 779, 669; HRMS (ESI) calcd for $C_{35}H_{31}O_2$ $[M + H]^+$ 483.2324, found 483.2326.

(4-(2,2-Diphenylvinyl)-5-(4-fluorophenyl)-2-phenylfuran-3-yl)(phenyl)methanone (3j). Wt 0.069 g; pale yellow solid: mp 143−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (dd, 2H, J_1 = 5.4, J_2 = 8.5 Hz), 7.56 (d, 2H, *J* = 7.7 Hz), 7.50−7.48 (m, 2H), 7.40 (t, 1H, *J* = 7.2 Hz), 7.25−6.96 (m, 15H), 6.89 (d, 2H, *J* = 7.3 Hz), 6.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.1, 163.6, 161.1, 152.2, 148.7, 146.9, 142.7, 138.8, 137.0, 132.7, 130.5, 129.8, 129.4, 128.5, 128.0 (d, 1C, J_{C-F} = 26.1 Hz), 128.00, 127.86, 127.81, 127.7, 127.4, 127.3, 127.0, 126.9 (d, 1C, J_{C-F} = 16.8 Hz), 126, 122.7, 120.6, 117.7, 115.9, 115.7; IR (neat, cm^{-1}) 3419, 3018, 2399, 1653, 1516, 1417, 1328, 1215, 927, 769, 669; HRMS (ESI) calcd for $C_{37}H_{26}O_2F$ $[M + H]^+$ 521.1917, found 521.1916.

(5-(4-Bromophenyl)-4-(2,2-diphenylvinyl)-2-phenylfuran-3-yl)(phenyl)methanone (3k). Wt 0.067 g; pale yellow solid: mp 181−183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, 2H, *J* = 8.5 Hz), 7.56−7.49 (m, 7H), 7.41 (t, 1H, *J* = 7.3 Hz), 7.27−7.20 (m, 7H), 7.11−6.97 (m, 5H), 6.89 (d, 2H, *J* = 7.0 Hz), 6.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.0, 152.5, 148.5, 147.1, 142.6, 138.7, 137.0, 132.8, 131.9, 130.5, 129.8, 129.4, 129.3, 128.6, 128.3, 128.2, 128.08, 128.01, 127.9, 127.8, 127.0, 126.9, 122.8, 121.8, 121.5, 117.5; IR (neat, cm^{-1}) 3446, 3018, 2399, 1653, 1521, 1479, 1419, 1215, 1008, 927, 771, 669; HRMS (ESI) calcd for $C_{37}H_{26}O_2Br$ $[M + H]^+$ 581.1116, found 581.1128.

(5-(4-(*tert*-Butyl)phenyl)-4-(2,2-diphenylvinyl)-2-phenylfuran-3-yl)(phenyl)methanone (3l). Wt 0.067 g; yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, 2H, *J* = 8.5 Hz), 7.53−7.36 (m, 7H), 7.24−7.18 (m, 8H), 7.09−6.88 (m, 7H), 6.72 (s, 1H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.1, 152.0, 151.1, 149.9, 146.3, 142.9, 138.8, 137.1, 132.6, 130.6, 129.8, 129.6, 128.4, 128.28, 128.23, 127.9, 127.8, 127.77, 127.70, 127.0, 125.7, 125.3, 122.6, 120.4, 118.3, 34.7, 31.2; IR (neat, cm^{-1}) 3441, 3018, 2399, 1653, 106, 1417, 1338, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{41}H_{35}O_2$ $[M + H]^+$ 559.2637, found 559.2644.

(4-(2,2-Diphenylvinyl)-5-(naphthalen-1-yl)-2-phenylfuran-3-yl)(phenyl)methanone (3n). Wt 0.054 g; brown oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06−8.03 (m, 1H), 7.83−7.79 (m, 4H), 7.53−7.6.79 (m, 20H), 6.66 (s, 1H), 6.61−6.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.0, 152.8, 150.2, 146.3, 142.8, 139.2, 137.1, 133.8, 133.1, 131.0, 130.1, 130.0, 129.7, 129.5, 129.2, 128.7, 128.4, 128.3, 128.27, 128.23, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.9, 126.3, 126.0, 125.9, 125.1, 122.8, 122.4, 117.2; IR (neat, cm^{-1}) 3439, 3018, 2399, 1651, 1489, 1446, 1323, 1215, 1132, 1074, 898, 756, 696, 669; HRMS (ESI) calcd for $C_{41}H_{29}O_2$ $[M + H]^+$ 553. 2168, found 553.2161.

(4-(2,2-Diphenylvinyl)-2-phenyl-5-(thiophen-2-yl)furan-3-yl)(phenyl)methanone (3o). Wt 0.064 g; yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, 2H, *J* = 7.5 Hz), 7.48−7.27 (m, 13H), 7.22 (d, 1H, *J* = 5.0 Hz), 7.13−6.91 (m, 6H), 6.87 (d, 2H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.6, 150.4, 148.5, 142.7, 142.2, 141.0, 137.2, 133.7, 132.1, 129.8, 129.6, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.4, 127.3, 126.2, 125.7, 121.7, 121.0, 112.9; IR (neat, cm^{-1}) 3394, 3018, 2399, 1654, 1597, 1490, 1446, 1215, 929, 906, 767, 669; HRMS (ESI) calcd for $C_{35}H_{25}O_2S$ $[M + H]^+$ 509.1575, found 509.1594.

(5-Cyclohexyl-4-(2,2-diphenylvinyl)-2-phenylfuran-3-yl)-(phenyl)methanone (3p). Wt 0.067 g; yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, 2H, *J* = 7.5 Hz), 7.40−7.02 (m, 18H), 6.60 (s, 1H), 2.53−2.46 (m, 1H), 1.74−1.47 (m, 7H), 1.25−1.13 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.3, 156.4, 151.4, 145.2, 143.1, 139.8, 137.3, 132.8, 130.8, 129.9, 128.2, 128.1, 128.0, 127.9, 127.5, 127.3, 126.7, 121.6, 118.3, 117.8, 36.6, 30.9, 26.3, 25.8; IR (neat, cm^{-1}) 3446, 3018, 2399, 2308, 1647, 1506, 1338, 1215, 927, 767, 669; HRMS (ESI) calcd for $C_{37}H_{33}O_2$ $[M + H]^+$ 509.2481, found 509.2474.

(4-(2,2-Diphenylvinyl)-5-methyl-2-phenylfuran-3-yl)-(phenyl)methanone (3q). Wt 0.064 g; pale yellow solid: mp 143−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, 2H, *J* = 7.1 Hz), 7.43−7.37 (m, 3H), 7.29−7.07 (m, 15H), 6.56 (s, 1H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.4, 151.6, 148.9, 145.4, 143.0, 140.0, 137.3, 132.9, 130.6, 129.9, 129.7, 128.2, 128.19, 128.17, 128.0, 127.9, 127.5, 127.2, 126.6, 121.8, 120.0, 117.7, 12.5; IR (neat, cm^{-1}) 3018, 2399, 1653, 1597, 1489, 1215, 1074, 1022, 929, 771, 669; HRMS (ESI) calcd for $C_{32}H_{25}O_2$ $[M + H]^+$ 441.1855, found 441.1855.

(5-(*tert*-Butyl)-4-(2,2-diphenylvinyl)-2-phenylfuran-3-yl)-(phenyl)methanone (3r). Wt 0.070 g; pale yellow solid: mp 125−127 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, 2H, *J* = 7.1 Hz), 7.39−7.33 (m, 3H), 7.23−7.11 (m, 8H), 7.04−6.92 (m, 7H), 6.69 (s, 1H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.5, 158.4, 150.8, 144.6, 143.3, 139.1, 137.4, 132.3, 130.8, 129.9, 129.7, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.46, 127.42, 126.9, 122.2, 119.1, 117.9, 34.3, 29.3; IR (neat, cm^{-1}) 3419, 3016, 2972, 2432, 2399, 1651, 1598, 1519, 1489, 1423, 1319, 1215, 1074, 1028, 927, 781, 667; HRMS (ESI) calcd for $C_{35}H_{31}O_2$ $[M + H]^+$ 483.2324, found 483.2324.

(4-(2,2-Diphenylvinyl)-2-methyl-5-phenylfuran-3-yl)-(phenyl)methanone (3s). Wt 0.058 g; yellow solid: mp 108−110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, 2H, *J* = 7.2 Hz), 7.47−7.22 (m, 11H), 7.10−7.01 (m, 5H), 6.83 (d, 2H, *J* = 7.0 Hz), 6.75 (s, 1H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.6, 154.7, 148.8, 145.8, 142.9, 139.0, 137.9, 132.3, 130.8, 129.77, 129.74, 128.7, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 125.3, 122.8, 119.2, 118.4, 31.6; IR (neat, cm^{-1}) 3018, 2399, 1647, 1521, 1419, 1215, 927,

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771, 669; HRMS (ESI) calcd for $C_{32}H_{25}O_2$ $[M + H]^+$ 441.1855, found 441.1866.

(4-(2,2-Diphenylvinyl)-2-(4-methoxyphenyl)-5-phenylfuran-3-yl)(4-methoxyphenyl)methanone (3t). Wt 0.084 g; yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, 2H, J = 7.2 Hz), 7.53−7.45 (m, 4H), 7.38 (t, 2H, J = 7.6 Hz), 7.30−7.13 (m, 6H), 7.01−6.88 (m, 5H), 6.75 (s, 1H), 6.74−6.69 (m, 4H), 3.80 (s, 3H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.9, 163.2, 159.7, 152.0, 149.0, 146.4, 142.9, 138.9, 132.2, 130.8, 130.6, 130.2, 128.7, 128.5, 128.3, 128.0, 127.7, 127.6, 125.4, 122.5, 121.7, 120.9, 118.2, 113.7, 113.2, 55.4, 55.2; IR (neat, cm^{-1}) 3680, 3441, 3018, 2839, 2399, 1645, 1598, 1500, 1419, 1334, 1255, 1215, 1170, 1136, 1029, 927, 900, 767, 669; HRMS (ESI) calcd for $C_{39}H_{31}O_4$ $[M + H]^+$ 563.2222, found 563.2226.

1-(4-(2,2-Diphenylvinyl)-2-methyl-5-phenylfuran-3-yl)-ethanone (3u). Wt 0.051 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, 2H, J = 7.3 Hz), 7.39−7.19 (m, 8H), 7.14−7.05 (m, 3H), 6.92 (s, 1H), 6.91−6.89 (m, 2H), 2.48 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.2, 156.4, 148.1, 146.2, 142.6, 139.1, 130.6, 130.0, 128.4, 128.3, 128.2, 127.9, 127.7, 127.49, 127.40, 125.5, 124.2, 118.9, 117.8, 30.5, 14.4; IR (neat, cm^{-1}) 3442, 3018, 2399, 1668, 1516, 1444, 1361, 1215, 1118, 927, 771, 669; HRMS (ESI) calcd for $C_{27}H_{23}O_2$ $[M + H]^+$ 379.1698, found 379.1697.

2,3,5-Triphenylfuran (4a). Wt 0.037 g; pale yellow solid: mp 91−93 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, 2H, J = 7.8 Hz), 7.61 (d, 2H, J = 8.0 Hz), 7.47−7.24 (m, 11H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 147.9, 134.3, 131.1, 130.5, 128.76, 128.72, 128.6, 128.4, 127.54, 127.51, 127.3, 126.1, 124.5, 123.8, 109.4; IR (neat, cm^{-1}) 3439, 3018, 2962, 2399, 1635, 1556, 1419, 1261, 1215, 1097, 1014, 929, 775, 698, 669; HRMS (ESI) calcd for $C_{22}H_{17}O$ $[M + H]^+$ 297.1279, found 297.1291.

2,3-bis(4-Fluorophenyl)-5-phenylfuran (4b). Wt 0.037 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, 2H, J = 7.6 Hz), 7.55−7.37 (m, 6H), 7.29 (t, 1H, J = 7.4 Hz), 7.08 (t, 2H, J = 8.6 Hz), 7.01 (t, 2H, J = 8.7 Hz), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4, 160.9, 152.6, 147.0, 130.3, 130.2, 128.7, 127.9 (d, 1C, J_{C-F} = 31.8 Hz), 127.6, 123.8, 123.2, 115.8, 115.6, 115.4, 109.2; IR (neat, cm^{-1}) 3442, 3018, 2399, 1653, 1521, 1473, 1419, 1338, 1217, 1014, 927, 958, 669; HRMS (ESI) calcd for $C_{22}H_{15}OF_2$ $[M + H]^+$ 333.1091, found 333.1085.

2,3-bis(4-Chlorophenyl)-5-phenylfuran (4c). Wt 0.038 g; yellow solid: mp 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, 2H, J = 7.4 Hz), 7.51 (d, 2H, J = 8.6 Hz), 7.42 (t, 2H, J = 7.6 Hz), 7.36 (s, 4H), 7.32−7.25 (m, 3H), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.0, 146.9, 133.46, 133.43, 132.4, 130.1, 129.9, 129.2, 129.0, 128.8, 128.7, 127.8, 127.3, 123.8, 123.7, 109.1; IR (neat, cm^{-1}) 3018, 2854, 2399, 1489, 1261, 1215, 1093, 1014, 952, 931, 831, 775, 669; HRMS (ESI) calcd for $C_{22}H_{15}OCl_2$ $[M + H]^+$ 365.0500, found 365.0512.

2,3-bis(4-Chlorophenyl)-5-phenylfuran (4d). Wt 0.038 g; yellow solid: mp 154−156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, 2H, J = 7.4 Hz), 7.52 (d, 2H, J = 8.3 Hz), 7.43−7.40 (m, 6H), 7.32−7.28 (m, 3H), 6.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.1, 146.9, 132.9, 132.0, 131.7, 130.2, 130.1, 129.6, 128.8, 127.9, 127.5, 123.9, 121.6, 121.5, 109.1; IR (neat, cm^{-1}) 3439, 3018, 2399, 2104, 1635, 1516, 1419, 1215, 1010, 927, 754, 669; HRMS (ESI) calcd for $C_{22}H_{14}OBr_2Na$ $[M + Na]^+$ 474.9309, found 474.9297.

5-Phenyl-2,3-di-*p*-tolylfuran (4e). Wt 0.037 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (d, 2H, J = 7.2 Hz), 7.51 (d, 2H, J = 8.2 Hz), 7.40 (t, 2H, J = 7.7 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.28 (d, 1H, J = 7.4 Hz), 7.19 (d, 2H, J = 7.8 Hz), 7.12 (d, 2H, J = 8.0 Hz), 6.78 (s, 1H), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 148.0, 137.3, 136.8, 131.4, 130.8, 130.6, 129.3, 129.0, 128.7, 128.5, 127.3, 126.0, 123.8, 123.7, 109.4, 21.3, 21.2; IR (neat, cm^{-1}) 3676, 3018, 1602, 1512, 1472, 1419, 1252, 1215, 1097, 1017, 929, 757, 669; HRMS (ESI) calcd for $C_{24}H_{21}O$ $[M + H]^+$ 325.1592, found 325.1579.

2-(4-Bromophenyl)-3,5-diphenylfuran (4f). Wt 0.039 g; yellow oil: regioisomeric ratio = 2.5:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 2H, J = 7.9 Hz), 7.60−7.27 (m, 12H), 6.80 (s, 1H, regioisomer of **4i**′ or **4i**″), 6.78 (s, 1H, regioisomer of **4i**′ or **4i**″); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.8, 148.1, 146.7, 134.0, 133.2, 131.8, 131.5, 130.8, 130.3, 129.9, 128.8, 128.7, 128.6, 128.5, 127.79, 127.75, 127.70, 127.5, 127.4, 126.2, 125.1, 123.88, 123.85, 121.3, 109.6, 108.9; IR (neat, cm^{-1}) 3444, 3018, 2399, 1716, 1506, 1417, 1338, 1215, 929, 771, 669; HRMS (ESI) calcd for $C_{22}H_{16}OBr$ $[M + H]^+$ 375.0385, found 375.0383.

3,5-Diphenyl-2-(*p*-tolyl)furan (4g). Wt 0.038 g; brown solid: mp 142−144 °C; regioisomeric ratio = 3.3:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, 2H, J = 7.9 Hz), 7.62 (d, 1H, J = 7.7 Hz), 7.50−7.45 (m, 1H), 7.40 (t, 2H, J = 7.6 Hz), 7.36 (d, 2H, J = 7.9 Hz), 7.32−7.18 (m, 6H), 7.12 (d, 1H, J = 8.0 Hz, A or B isomer), 6.80 (s, 1H, regioisomer of **4j**′ or **4j**″), 6.79 (s, 1H, regioisomer of **4j**′ or **4j**″), 2.39 (s, 1H, regioisomer of **4j**′ or **4j**″), 2.34 (s, 1H, regioisomer of **4j**′ or **4j**″); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 147.7, 137.0, 131.3, 131.2, 130.6, 129.4, 129.1, 128.7, 128.68, 128.64, 128.5, 128.3, 127.4, 127.3, 126.1, 126.0, 124.5, 123.8, 123.7, 109.5, 109.3, 21.2; IR (neat, cm^{-1}) 3676, 3018, 1602, 1512, 1489, 1419, 1261, 1215, 1097, 1020, 929, 756, 669; HRMS (ESI) calcd for $C_{23}H_{19}O$ $[M + H]^+$ 311.1436, found 311.1425.

5-(4-Fluorophenyl)-2,3-diphenylfuran (4j). Wt 0.038 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75−7.71 (m, 2H), 7.60−7.59 (m, 2H), 7.47−7.24 (m, 8H), 7.14−7.09 (m, 2H), 6.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4, 161.4, 151.9, 148.1, 134.3, 131.2, 128.9, 128.8, 128.6, 127.7, 127.5, 127.1 (d, 1C, J_{C-F} = 13.1 Hz), 126.3, 125.8, 125.7, 124.7, 116.1, 115.9, 109.3; IR (neat, cm^{-1}) 3419, 3018, 2962, 2399, 1653, 1604, 1498, 1442, 1261, 1215, 1157, 1097, 1012, 952, 933, 837, 756, 696, 669; HRMS (ESI) calcd for $C_{22}H_{16}OF$ $[M + H]^+$ 315.1185, found 315.1180.

5-(4-Bromophenyl)-2,3-diphenylfuran (4k). Wt 0.039 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62−7.57 (m, 4H), 7.53 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 7.2 Hz), 7.40−7.23 (m, 6H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 148.2, 134.0, 131.9, 130.8, 129.4, 128.7, 128.6, 128.4, 127.7, 127.4, 126.1, 125.2, 124.6, 121.2, 110.0; IR (neat, cm^{-1}) 3439, 3018, 2962, 2399, 2088, 1637, 1521, 1485, 1419, 1261, 1215, 1097, 1008, 929, 779, 669; HRMS (ESI) calcd for $C_{22}H_{16}OBr$ $[M + H]^+$ 375.0385, found 375.0385.

5-(4-*tert*-Butylphenyl)-2,3-diphenylfuran (4l). Wt 0.040 g; yellow solid: mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70 (d, 2H, J = 8.4 Hz), 7.61−7.59 (m, 2H), 7.48−7.23 (m, 10H), 6.76 (s, 1H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 150.6, 147.5, 134.4, 131.2, 128.7, 128.6, 128.3, 127.8, 127.3, 127.2, 126.0, 125.6, 124.4, 123.6, 108.9, 34.6, 31.2; IR (neat, cm^{-1}) 3419, 3018, 2399, 1647, 1506, 1456, 1338, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{26}H_{25}O$ $[M + H]^+$ 353.1905, found 353.1900.

5-(Naphthalen-1-yl)-2,3-diphenylfuran (4n). Wt 0.028 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.58 (d, 1H, J = 8.4 Hz), 7.91 (d, 1H, J = 7.5 Hz), 7.87−7.85 (m, 2H), 7.66 (d, 2H, J = 7.3 Hz), 7.58−7.51 (m, 5H), 7.41 (t, 2H, J = 7.4 Hz), 7.36−7.24 (m, 4H), 6.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.2, 148.3, 134.3, 134.0, 131.1, 130.2, 128.8, 128.75, 128.70, 128.6, 128.4, 128.1, 127.5, 127.3, 126.7, 126.2, 126.09, 126.01, 125.5, 125.3, 124.2, 113.7; IR (neat, cm^{-1}) 3018, 2399, 1600, 1502, 1442, 1215, 1097, 1016, 923, 777, 696, 669; HRMS (ESI) calcd for $C_{26}H_{19}O$ $[M + H]^+$ 347.1436, found 347.1432.

5-Cyclohexyl-2,3-diphenylfuran (4p). Wt 0.034 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52−7.40 (m, 4H), 7.35−7.24 (m, 5H), 7.21−7.17 (m, 1H), 6.13 (s, 1H), 2.73−2.66 (m, 1H), 2.13−1.71 (m, 5H), 1.52−1.25 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 146.2, 134.9, 131.6, 128.6, 128.5, 128.2, 126.9, 126.8, 125.9, 122.7, 107.4, 37.2, 31.5, 26.1, 25.9; IR (neat, cm^{-1}) 3446, 3018, 2399, 1647, 1516, 1417, 1338, 1215, 1014, 927, 775, 669; HRMS (ESI) calcd for $C_{22}H_{23}O$ $[M + H]^+$ 303.1749, found 303.1736.

5-Methyl-2,3-diphenylfuran (4q). Wt 0.028 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, 2H, J = 7.5 Hz), 7.40−7.19 (m, 8H), 6.15 (s, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.3, 146.7, 134.7, 131.4, 128.58, 128.55, 128.3, 127.0, 126.9, 125.9, 123.1, 110.1, 13.5; IR (neat, cm^{-1}) 3419, 3018, 2343, 1637, 1521, 1419, 1328, 1215, 925, 771, 669; HRMS (ESI) calcd for $C_{17}H_{15}O$ $[M + H]^+$ 235.1123, found 235.1118.

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5-(*tert*-Butyl)-2,3-diphenylfuran (4r). Wt 0.038 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, 2H, J = 7.4 Hz), 7.42 (d, 2H, J = 7.2 Hz), 7.33 (bt, 2H, J = 7.2 Hz), 7.26, (bt, 3H, J = 7.8 Hz), 7.19 (d, 1H, J = 7.0 Hz), 6.12 (s, 1H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.2, 146.2, 134.9, 131.7, 128.6, 128.5, 128.2, 126.9, 126.8, 125.9, 122.6, 106.6, 32.7, 29.1 IR (neat, cm^{-1}) 3419, 3018, 2399, 1647, 1521, 1419, 1338, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{20}H_{21}O$ $[M + H]^+$ 277.1592, found 277.1602.

2,3,5-Triphenylfuran (4a-d_1). Wt 0.029 g; yellow solid: mp 94−96 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, 2H, J = 7.7 Hz), 7.62 (d, 2H, J = 7.4 Hz), 7.48−7.25 (m, 11H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.5, 147.9, 134.3, 131.1, 130.5, 128.76, 128.71, 128.6, 128.4, 127.53, 127.51, 127.3, 126.1, 124.4, 123.8, 109.4; IR (neat, cm^{-1}) 3439, 3018, 2962, 2399, 1635, 1556, 1419, 1261, 1215, 1097, 1014, 929, 775, 698, 669; HRMS (ESI) calcd for C_{22} $^1H_{16}$ ^2HO $[M + H]^+$ 298.1342, found 298.1332.

2,3,5-Triphenylfuran (4a-d_5). Wt 0.033 g; yellow solid: mp 91−93 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61−746 (m, 4H), 7.38 (t, 2H, J = 7.4 Hz), 7.34−7.24 (m, 4H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.5, 147.8, 134.3, 131.1, 130.3, 128.7, 128.6, 128.4, 128.2, 128.0, 127.5, 127.3, 126.1, 124.5, 123.6, 114.6, 109.4; IR (neat, cm^{-1}) 3446, 3018, 2399, 1602, 1516, 1419, 1215, 1022, 927, 775, 669; HRMS (ESI) calcd for C_{22} $^1H_{12}$ ^2H_5O $[M + H]^+$ 302.1593, found 302.1604.

2,3,5-Triphenylfuran (4a-d_6). Wt 0.028 g; pale yellow oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62−7.46 (m, 4H), 7.40−7.23 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.8, 134.3, 131.1, 130.3, 128.7, 128.6, 128.4, 128.2, 127.9, 127.4, 127.3, 126.1, 124.4, 123.4, 123.0, 109.4; IR (neat, cm^{-1}) 3421, 3018, 2926, 2399, 1602, 1502, 1477, 1442, 1379, 1213, 1099, 1022, 954, 779, 694, 669; HRMS (ESI) calcd for C_{22} $^1H_{11}$ ^2H_6O $[M + H]^+$ 303.1656, found 303.1659.

1,4,4-Triphenylbuta-2,3-dien-1-one (5a). Wt 0.040 g; brown color oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, J = 7.7 Hz), 7.50 (t, 1H, J = 7.3 Hz), 7.39−7.25 (m, 12H), 6.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 216.1, 191.5, 137.4, 134.2, 132.7, 128.76, 128.72, 128.6, 128.34, 128.33, 113.7, 96.5; IR (neat, cm^{-1}) 3439, 3018, 2399, 1635, 1521, 1419, 1259, 1215, 1097, 1016, 927, 848, 771, 669; HRMS (ESI) calcd for $C_{22}H_{17}O$ $[M + H]^+$ 297.1279, found 297.1292.

4,4-Diphenyl-1-(thiophen-2-yl)buta-2,3-dien-1-one (5o). Wt 0.032 g; brown color oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.799−7.790 (m, 1H), 7.60 (bd, 1H, J = 4.9 Hz), 7.40−7.34 (m, 10H), 7.05 (bt, 1H, J = 4.3 Hz), 6.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.8, 181.9, 143.0, 134.0, 133.8, 132.6, 128.7, 128.6, 128.4, 127.9, 127.1, 114.5, 96.8; IR (neat, cm^{-1}) 3439, 3018, 2399, 1625, 1521, 1416, 1242, 1215, 1095, 1011, 927, 771, 669; HRMS (ESI) calcd for $C_{20}H_{15}OS$ $[M + H]^+$ 303.0844, found 303.0856.

(2,4-Diphenyl-5-styrylfuran-3-yl)(phenyl)methanone (6m). Wt 0.04 g; pale yellow solid: mp 146−148 °C; E/Z ratio = 1:1; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84−7.81 (m, 2H), 7.68 (d, 1H, J = 7.1 Hz), 7.61 (d, 1H, J = 7.1 Hz), 7.48 (d, 2H, J = 7.6 Hz), 7.42−7.15 (m, 14H), 6.98 (d, 1H, J = 16.1 Hz), 6.65 (d, 1H, J = 12.5 Hz, E or Z isomer), 6.37 (d, 1H, J = 12.5 Hz, E or Z isomer); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.6 (1C, E or Z isomer), 193.3 (1C, E or Z isomer), 151.6, 148.4, 137.2, 136.8, 133.47, 133.42, 131.5, 129.8, 129.6, 129.5, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.38, 128.35, 127.97, 127.92, 127.5, 126.59, 126.52, 126.0, 122.8, 115.3, 114.4; IR (neat, cm^{-1}) 3442, 3018, 2399, 1635, 1521, 1417, 1338, 1215, 927, 771, 669; HRMS (ESI) calcd for $C_{31}H_{23}O_2$ $[M + H]^+$ 427.1698, found 427.1706.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all starting materials and products, GC−MS spectra of **4a**-d_1, **4a**-d_5, **4a**-d_6, and CIF files of **3d**, **3q**, **3r**, and **6m**. 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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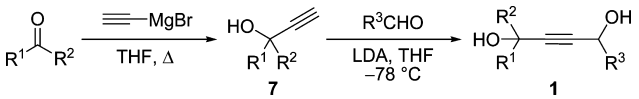

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