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Multisubstituted Furan Formation from (*Z*)- or (*E*)-Enynyl Acetates: Tandem Reactions Accelerated by Electron-Donating Groups on Aromatic Rings

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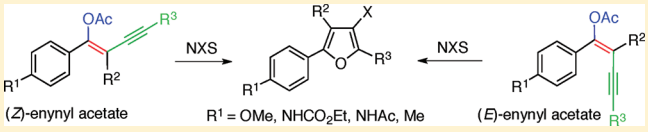
Supporting Information

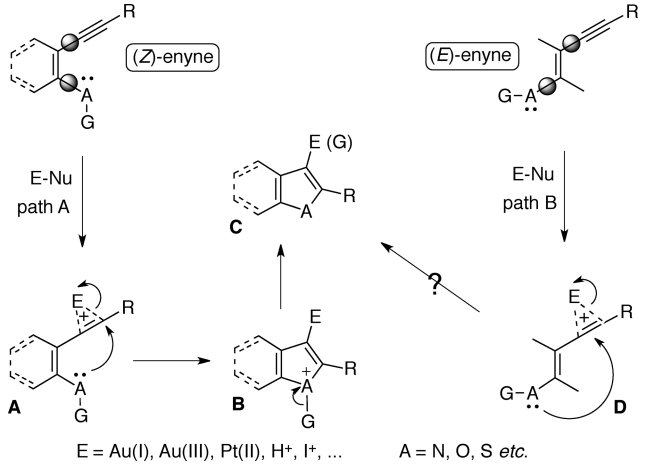
ABSTRACT: Multisubstituted furans were readily prepared from (*Z*)- or (*E*)-conjugated enynyl acetates with NXS under metal-free conditions at room temperature via the same haloallenyl ketone intermediates. This tandem haloallenyl ketone formation–furan formation reaction sequence was accelerated by electron-donating groups on the aromatic rings.



INTRODUCTION

Among heterocycles, five- and six-membered heterocycles are the most common structural motifs appearting in natural products and are found in industrial intermediates and pharmaceuticals. Of the various synthetic methodologies, cyclization reactions of simple acyclic compounds are attractive ways to construct these heterocycles.[1] Electrophilic cyclizations have been achieved as an efficient method in the synthesis of indoles, pyrroles, furans, and thiophenes employing electrophiles such as transition metals[2] and/or halogenation reagents.[3] The typical course of these cyclization reactions involves (i) coordination of the electrophilic source to the unsaturated carbon–carbon bond of the (*Z*)-enyne to generate **A**; (ii) nucleophilic attack of the heteroatom on the activated intermediate to produce **B**; and (iii) facile removal[4] or rearrangement[5] of the group G bonded to the heteroatom to generate the heterocyclic products **C** (Scheme 1, path A). We have reported the tandem synthesis of indoles and isoquinolines through a similar reaction pathway catalyzed by $In(OTf)_3$ or $PtCl_2$ as a π-electron coordination metal catalyst.[6] On the other hand, the same cyclization reaction from (*E*)-enyne stereoisomers has not been reported because of their steric factors (path B). Recently, we have communicated a regio- and stereoselective (*Z*)- or (*E*)-haloenol ester synthesis.[7] Various (*Z*)- and (*E*)-enynyl acetates could be obtained by Sonogashira coupling reaction of (*Z*)- or (*E*)-haloenol esters and alkynes. Here, we report the synthesis of multisubstituted furans from these (*Z*)- or (*E*)-enynyl acetates. Without requiring a metal catalyst, these tandem reactions were accelerated by electron-donating groups on the aromatic rings.

Scheme 1. Synthesis of Heteroaromatics C from (*Z*)- or (*E*)-Enyne Stereoisomers



RESULTS AND DISCUSSION

The starting materials, (*Z*)- or (*E*)-enynyl acetates **1** or **2**, were readily synthesized regio- and stereoselectively from consecutive Sonogashira coupling reaction of (*Z*)- or (*E*)-iodoenyl acetates **F** or **G**, obtained from the reaction of alkyne **E** with NIS and acetic acid according to our method.[7] The results are summarized in Table 1.

Our initial investigation focused on the optimization of electrophilic source to unsaturated carbon–carbon bond. We hypothesized that $PtCl_2$-catalyzed cyclization reaction might provide a convenient access to furans.[6c] Contrary to our expectations, the reaction did not occur at all (Table 2, entry 1). Recently, Jiang and co-workers reported the iodocyclization reaction of (*Z*)-enynyl acetate **1** ($R^1 = R^2 = H$) with iodine to produce 2,5-substituted 3-iodofurans under basic conditions.[8] We examined the same reaction with **1a** and iodine, but furan **3a** was obtained in low yield (Table 2, entry 2). Next we treated **1a** with NXS as the electrophilic source directed against the triple bond of **1a**. Most substrates **1** could afford the corresponding 2,4,5-trisubstituted 3-halofurans **3a–3k′** with

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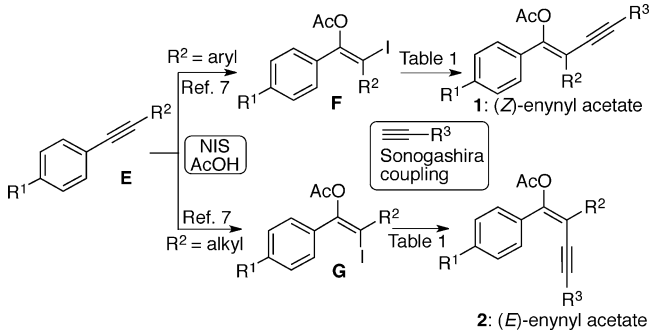
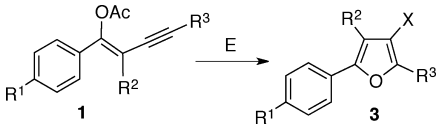
Table 1. Stereoselective Synthesis of (*Z*)- and (*E*)-Enynyl Acetates



entry	R^1	R^2	R^3	1 or 2	yield (%) (*Z*:*E*)
1	OMe	Ph	*p*-MeC_6H_4	**1a**	95 (*Z*)
2	OMe	Ph	Ph	**1b**	quant (20:1)
3	OMe	Ph	cyclohexyl	**1c**	86 (14:1)
4	OMe	Ph	^{n}Bu	**1d**	90 (25:1)
5	OMe	*p*-$MeOC_6H_4$	Ph	**1e**	99 (10:1)
6	OMe	*p*-MeC_6H_4	Ph	**1f**	81 (11:1)
7	OMe	*p*-FC_6H_4	Ph	**1g**	88 (9:1)
8	$NHCO_2Et$	Ph	*p*-MeC_6H_4	**1h**	97 (25:1)
9	NHAc	Ph	*p*-MeC_6H_4	**1i**	quant (14:1)
10	OMe	^{n}Bu	Ph	**2a**	96 (*E*)
11	OMe	^{n}Bu	*p*-$MeOC_6H_4$	**2b**	87 (*E*)
12	OMe	^{n}Bu	*p*-MeC_6H_4	**2c**	86 (*E*)
13	OMe	^{n}Bu	*p*-FC_6H_4	**2d**	96 (*E*)
14	OMe	^{n}Bu	^{n}Bu	**2e**	81 (*E*)
15	OMe	cyclohexyl	*p*-MeC_6H_4	**2f**	72 (*E*)
16	OMe	Ph	^{n}Bu	**2g**	76 (*E*)
17	$NHCO_2Et$	^{n}Bu	*p*-MeC_6H_4	**2h**	93 (*E*)
18	NHAc	^{n}Bu	*p*-MeC_6H_4	**2i**	69 (*E*)
19	Me	^{n}Bu	*p*-MeC_6H_4	**2j**	82 (*E*)

Table 2. Multisubstituted Furan 3 Synthesis with (*Z*)-Enynyl acetate 1



entry	(*Z*)-enynyl acetate **1**	E	time (h)	furan **3**	yield (%)
1[a]	**1a** (R^1 = OMe, R^2 = Ph, R^3 = *p*-MeC_6H_4)	$PtCl_2$	24.00		recovery of **1a**
2[b]	**1a**	I_2	6.00	**3a** (R^1 = OMe, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = I)	(12)[c]
3[d]	**1a**	NBS	2.00	**3b** (R^1 = OMe, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = Br)	90
4[d]	**1a**	NIS	0.25	**3a** (R^1 = OMe, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = I)	71
5[d]	**1b** (R^1 = OMe, R^2 = Ph, R^3 = Ph)	NIS	1.00	**3c** (R^1 = OMe, R^2 = Ph, R^3 = Ph, X = I)	61
6[d]	**1c** (R^1 = OMe, R^2 = Ph, R^3 = cyclohexyl)	NIS	4.50	**3d** (R^1 = OMe, R^2 = Ph, R^3 = cyclohexyl, X = I)	61
7[d]	**1d** (R^1 = OMe, R^2 = Ph, R^3 = ^{n}Bu)	NIS	6.00	**3e** (R^1 = OMe, R^2 = Ph, R^3 = ^{n}Bu, X = I)	67
8[d]	**1e** (R^1 = OMe, R^2 = *p*-$MeOC_6H_4$, R^3 = Ph)	NIS	0.25	**3f** (R^1 = OMe, R^2 = *p*-$MeOC_6H_4$, R^3 = Ph, X = I)	56
9[d]	**1f** (R^1 = OMe, R^2 = *p*-MeC_6H_4, R^3 = Ph)	NBS	1.00	**3g** (R^1 = OMe, R^2 = *p*-MeC_6H_4, R^3 = Ph, X = Br)	(81)[c]
10[d]	**1f**	NIS	0.50	**3h** (R^1 = OMe, R^2 = *p*-MeC_6H_4, R^3 = Ph, X = I)	50
11[d]	**1g** (R^1 = OMe, R^2 = *p*-FC_6H_4, R^3 = Ph)	NIS	1.50	**3i** (R^1 = OMe, R^2 = *p*-FC_6H_4, R^3 = Ph, X = I)	59
12[d]	**1h** (R^1 = $NHCO_2Et$, R^2 = Ph, R^3 = *p*-MeC_6H_4)	NIS	0.25	**3j** (R^1 = $NHCO_2Et$, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = I)	57
13[d]	**1i** (R^1 = NHAc, R^2 = Ph, R^3 = *p*-MeC_6H_4)	NIS	6.00	**3k** (R^1 = NHAc, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = I)	21
				3k′ (R^1 = NAc_2, R^2 = Ph, R^3 = *p*-MeC_6H_4, X = I)	23

[a]Compound **1a** (1 equiv) and $PtCl_2$ (0.1 equiv) in toluene at 70 °C. [b]Compound **1a** (1 equiv), I_2 (1.5 equiv), and $NaHCO_3$ (1.5 equiv) in CH_2Cl_2 at room temp.[8] [c]The yield was obtained from ^{1}H NMR, because **3a** or **3g** was obtained as inseparable mixture with another structurally unknown compound. [d]Compound **1** (1 equiv) and NXS (1.2 equiv) in DCE/MeCN = 1/1 at room temp.

NXS (Table 2, entries 3–13). Unfortunately, the reactions were accompanied by some structurally unknown byproduct. Therefore, we obtained moderate yields of the iodofurans **3** (Table 2, entries 4–8, 10–13). NBS gave higher product yields than the yields obtained with NIS, although longer reaction times were needed (Table 2, entries 3, 4, 9 and 10). The

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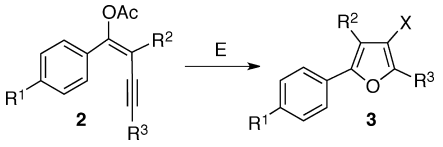
Table 3. Multisubstituted Furan 3 Synthesis with (*E*)-Enynyl Acetate 2



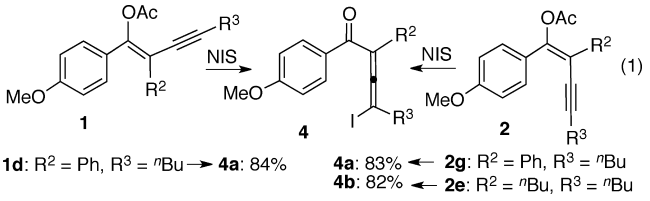
entry	(*E*)-enynyl acetate **2**	E	time (h)	furan **3**	yield (%)
1[a]	**2a** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = Ph)	$PtCl_2$	24.0		recovery of **2a**
2[b]	**2a**	I_2	20.0	**3l** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = Ph, X = I)	51
3[c]	**2a**	NBS	1.0	**3m** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = Ph, X = Br)	91
4[c]	**2a**	NCS	24.0		recovery of **2a**
5[c]	**2a**	NIS	2.0	**3l** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = Ph, X = I)	92
6[c]	**2b** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-$MeOC_6H_4$)	NIS	0.5	**3n** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-$MeOC_6H_4$, X = I)	82
7[c]	**2c** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4)	NIS	1.0	**3o** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4, X = I)	95
8[c]	**2d** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-FC_6H_4)	NIS	2.0	**3p** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = *p*-FC_6H_4, X = I)	93
9[c]	**2e** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = ^{n}Bu)	NIS	4.0	**3q** (R^1 = OMe, R^2 = ^{n}Bu, R^3 = ^{n}Bu, X = I)	77
10[c]	**2f** (R^1 = OMe, R^2 = cyclohexyl, R^3 = *p*-MeC_6H_4)	NIS	4.5	**3r** (R^1 = OMe, R^2 = cyclohexyl, R^3 = *p*-MeC_6H_4, X = I)	67
11[c]	**2g** (R^1 = OMe, R^2 = Ph, R^3 = ^{n}Bu)	NIS	5.0	**3e** (R^1 = OMe, R^2 = Ph, R^3 = ^{n}Bu, X = I)	69
12[c]	**2h** (R^1 = $NHCO_2Et$, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4)	NIS	1.0	**3s** (R^1 = $NHCO_2Et$, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4, X = I)	78
13[c]	**2i** (R^1 = NHAc, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4)	NIS	8.0	**3t** (R^1 = NHAc, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4, X = I)	36
				3t′ (R^1 = NAc_2, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4, X = I)	44
14[c]	**2j** (R^1 = Me, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4)	NIS	5.0	**3u** (R^1 = Me, R^2 = ^{n}Bu, R^3 = *p*-MeC_6H_4, X = I)	84

[a]Compound **2a** (1 equiv) and $PtCl_2$ (0.1 equiv) in toluene at 70 °C. [b](*E*)-Enynyl acetate **2a** (1 equiv), I_2 (1.5 equiv), and $NaHCO_3$ (1.5 equiv) in CH_2Cl_2 at room temp.[8] [c]Compound **2** (1 equiv) and NXS (1.2 equiv) in DCE/MeCN = 1/1 at room temp. [d]Compound **2j** (1 equiv), NIS (1.2 equiv), $Pd(OAc)_2$ (a little), and CuI (a little) in DCE/MeCN = 1/1 at room temp.

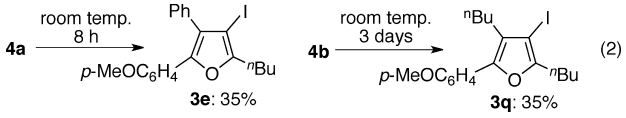
reaction rate seemed to depend on the substituent R^3: the reaction was faster when R^3 was an aromatic substituent rather than an aliphatic substituent (Table 2, entries 4−7). The nature of the R^2 group on the double bond had a slight effect on the reaction rate (Table 2, entries 5, 8, 10 and 11). Interestingly, intermediates were observed on TLC in the case of slow reactions (≥1 h) (vide infra). The reaction of the compound **1i** having the *N*-acetyl electron-donating substituent as R^1 afforded the corresponding furan **3k** together with *N*-diacetylated product **3k′**, probably arising from *N*-acetylation of **3k** by transfer from *O*-acetyl group of starting compound **1i**.

Next, we examined the reaction of various (*E*)-enynyl acetate **2** with some electrophiles, applying the standard conditions used for the formation of **3** from (*Z*)-enynyl acetate **1**. As expected from the structural factors, the $PtCl_2$-catalyzed cyclization reaction did not proceed (Table 3, entry 1). According to the mechanism proposed by Jiang and co-workers,[8] we assumed that (*E*)-enynyl acetate **2** also would not react with I_2. Contrary to our expectations, furan **3l** could be formed in 51% yield (Table 3, entry 2). Bromofuran **3m** was obtained from **2a** by using NBS (Table 3, entry 3). The use of NCS resulted in recovery of starting material **2a** (Table 3, entry 4). Surprisingly, most of the substrates **2** could be converted into multisubstituted furans **3** in higher yields than the yields of the reaction with (*Z*)-enynyl acetate **1** and NIS (Table 3, entries 5−14). With respect to the reactivity, similar tendencies with the results obtained from (*Z*)-enynyl acetate **1** were observed: (i) aromatic substituent R^3 underwent a facile furan formation (Table 3, entries 5−9) and (ii) the reaction proceeded via the intermediate (vide infra). The furan formation reaction mentioned here can proceed under mild and metal-free conditions and can provide a powerful methodology toward the synthesis of diversely substituted furans.

In an effort to understand the reaction mechanism, we attempted to isolate and identify the reaction intermediate (eq 1). When either (*Z*)- or (*E*)-enynyl acetates **1d** or **2g** was stirred with NIS at room temperature for only 10 min, the same



allenylketone **4a** was obtained. Compound **4b** was also obtained from **2e**. Because allenylketone **4** was relatively unstable, **4a** or **4b** was gradually isomerized in low yield under neutral conditions into the corresponding furan **3e** or **3q** after storage at room temperature (eq 2).



On the basis of the results obtained above, we propose a plausible reaction mechanism (Scheme 2). Initially, electrophilic addition of NXS to the triple bond of (*Z*)- or (*E*)-enynyl acetates **1** or **2** was assisted by an electron-donating group (EDG) at the para-position on the aromatic ring of **1** or **2** to afford haloallenyl ketone intermediate **4** through ionic intermediate **H**. EDG of haloallenyl ketone **4** also assisted in the formation of intermediate **I**. Intramolecular Michael-type migration of X to the conjugated polyene moiety, leading to haloirenium zwitterion **J**, which subsequently underwent 1,2-halogen migration and nucleophilic attack of oxygen anion, furnished 3-halofuran **3**. Gevorgyan and co-workers reported furan **3** formation from iodoallenylketone **4** (EDG = H, R^2 = Ph, R^3 = ^{n}Bu, X = I) via 1,2-iodomigration with Au(III)-catalyst at room temperature for 3 days.[9] In our experiment, enynyl

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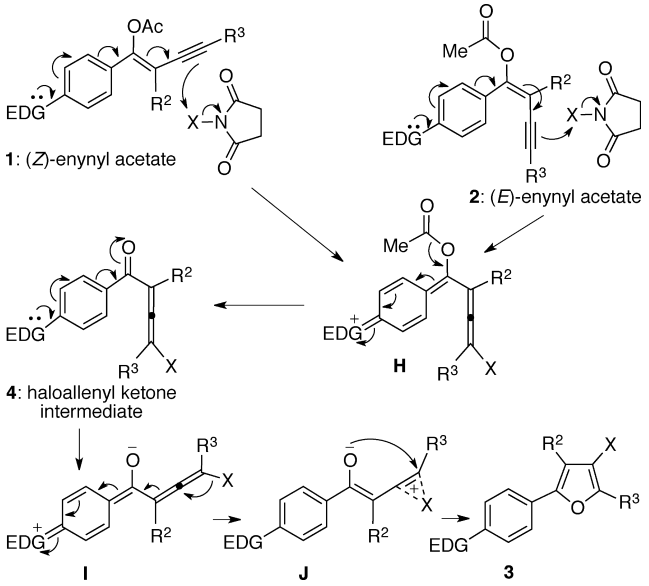
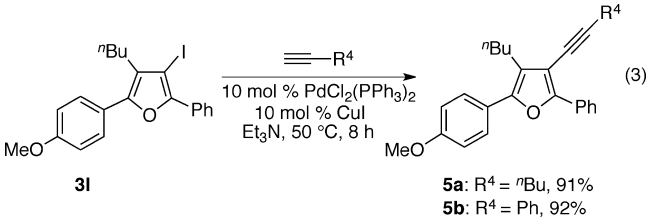
Scheme 2. Plausible Reaction Mechanism for the Synthesis of Furans



acetate **1d** or **2g** (EDG = OMe, R^2 = Ph, R^3 = ^{n}Bu) gave furan **3e** at room temperature after 5−6 h under metal-free conditions (Table 2, entry 7, and Table 3, entry 11). These results suggest that the EDG on the aromatic ring assisted in the formation of furan **3**.

Halofurans are attractive and important building blocks that provide sites for further functionalization, for example, C−C, C−N, or C−S bond formation.[10] To further explore the utility of our methodology, we studied the Sonogashira coupling reaction of 3-iodofuran **3l** with terminal alkynes. The corresponding 2,3,4,5-tetrasubstituted furans **5a** and **5b** were obtained in high yields (eq 3).



CONCLUSION

In summary, we have demonstrated a highly efficient multisubstituted furan synthesis under metal-free conditions from (*Z*)- or (*E*)-enynyl acetates with NXS via the same haloallenyl ketone intermediates. This tandem allenyl ketone formation−furan formation reaction sequence was accelerated by electron-donating groups on the aromatic rings. Our approach allows for excellent regioselective synthesis of 2,4,5-trisubstituted 3-halofurans. The 3-iodofuran was also utilized for the transformation to a tetrasubstituted furan by Pd-catalyzed coupling reaction.

EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on 600 MHz spectrometer. Chemical shifts are reported in δ (ppm) from tetramethylsilane as an internal standard. Data are reported as follows: chemical shifts, relative integration value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). Infrared spectra were obtained using an FT spectrometer. Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} TLC plates.

General Procedure for the Preparation of (*Z*)- and (*E*)-Enynyl Acetates 1 and 2. To a solution of (*Z*)- or (*E*)-iodoenol acetate (0.5 mmol) in Et_3N (3 mL) were added $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13 mg, 0.05 mmol), CuI (4.7 mg, 0.025 mmol), and alkyne (0.75 mmol), and the mixture was stirred at 50 °C under nitrogen. The reaction was monitored by TLC to establish completion. Saturated aqueous NH_4Cl solution was added to the reaction mixture and extracted with AcOEt (three times). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated at the reduced pressure. Column chromatography on silica gel using hexanes/ethyl acetate as an eluent afforded **1** or **2**.

*(Z)-1-(4-Methoxyphenyl)-2-phenyl-4-(p-tolyl)but-1-en-3-yn-1-yl Acetate (**1a**).* White solid: ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, dd, J = 7.6, 2.1 Hz), 7.33 (2H, d, J = 8.2 Hz), 7.25−7.23 (3H, m), 7.16 (2H, d, J = 8.9 Hz), 7.12 (2H, d, J = 7.6 Hz), 6.71 (2H, dd, J = 6.9, 2.1 Hz), 3.75 (3H, s), 2.35 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.6, 159.9, 151.6, 138.5, 136.1, 130.2, 129.6, 129.1, 128.3, 127.6, 126.6, 120.2, 113.7, 113.5, 95.7, 86.8, 55.2, 21.5, 21.0; IR ($CHCl_3$, cm^{-1}) 1763, 1606, 1507, 1464, 1445, 1370, 1300, 1253, 1195, 1174, 1094, 1033, 1016; MS (EI) m/z = 382 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{22}O_3$ 382.1569, found 382.1568.

*(Z)-1-(4-Methoxyphenyl)-2,4-diphenylbut-1-en-3-yn-1-yl Acetate (**1b**).* Yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.44 (2H, dd, J = 3.2, 1.6 Hz), 7.38 (2H, dd, J = 7.9, 1.7 Hz), 7.32−7.31 (3H, m), 7.27−7.23 (3H, m), 7.16 (2H, d, J = 8.9 Hz), 6.72 (2H, d, J = 8.9 Hz), 3.76 (3H, s), 2.32 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.5, 160.0, 151.9, 136.0, 131.4, 130.3, 129.6, 128.3, 128.3, 127.7, 126.5, 123.3, 113.6, 95.4, 87.4, 55.2, 21.0; IR ($CHCl_3$, cm^{-1}) 1759, 1606, 1511, 1489, 1443, 1370, 1254, 1174, 1095, 1032, 1027; MS (EI) m/z = 368 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{20}O_3$ 368.1412, found 368.1412.

*(Z)-4-Cyclohexyl-1-(4-methoxyphenyl)-2-phenylbut-1-en-3-yn-1-yl Acetate (**1c**).* Orange solid: ^{1}H NMR ($CDCl_3$) δ 7.30 (2H, dd, J = 7.6, 2.1 Hz), 7.22−7.18 (3H, m), 7.11 (2H, d, J = 8.9 Hz), 6.69 (2H, d, J = 8.9 Hz), 3.75 (3H, s), 2.60 (1H, s), 2.27 (3H, s), 1.84−1.72 (4H, m), 1.51 (3H, br s), 1.34 (3H, br s); ^{13}C NMR ($CDCl_3$) δ 168.5, 159.7, 150.9, 136.7, 130.2, 129.6, 128.1, 127.4, 126.9, 114.1, 113.5, 101.0, 78.4, 55.2, 32.7, 29.9, 25.9, 24.8, 21.0; IR ($CHCl_3$, cm^{-1}) 2935, 2856, 1757, 1607, 1510, 1445, 1369, 1298, 1251, 1236, 1196, 1176, 1153, 1060, 1032, 837; MS (EI) m/z = 374 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{26}O_3$ 374.1882, found 374.1887.

*(Z)-1-(4-Methoxyphenyl)-2-phenyloct-1-en-3-yn-1-yl Acetate (**1d**).* Pale yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.30 (2H, dd, J = 7.6, 2.1 Hz), 7.21−7.19 (3H, m), 7.10 (2H, d, J = 8.9 Hz), 6.69 (2H, d, J = 8.9 Hz), 3.74 (3H, s), 2.41 (2H, t, J = 7.2 Hz), 2.26 (3H, s), 1.56−1.53 (2H, m), 1.47−1.45 (2H, m), 0.93 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.6, 159.7, 151.0, 136.7, 130.2, 129.6, 128.2, 127.4, 126.8, 114.1, 113.5, 97.0, 78.4, 55.2, 30.9, 22.0, 21.0, 19.5, 13.6; IR ($CHCl_3$, cm^{-1}) 2961, 2936, 1757, 1606, 1510, 1465, 1444, 1370, 1296, 1252, 1176, 1151, 1029; MS (EI) m/z = 348 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{24}O_3$ 348.1725, found 348.1724.

*(Z)-1,2-Bis(4-methoxyphenyl)-4-phenylbut-1-en-3-yn-1-yl Acetate (**1e**).* Orange solid: ^{1}H NMR ($CDCl_3$) δ 7.44−7.43 (2H, m), 7.32−7.30 (5H, m), 7.19 (2H, dd, J = 6.9, 2.1 Hz), 6.79 (2H, dd, J = 6.9, 2.1 Hz), 6.73 (2H, dd, J = 6.9, 2.1 Hz), 3.79 (3H, s), 3.77 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.6, 159.9, 159.1, 151.1, 131.4, 130.8, 130.2, 129.7, 129.3, 128.3, 128.2, 126.8, 123.4, 113.8, 113.6, 113.1, 95.3, 87.6, 55.2, 21.0; IR ($CHCl_3$, cm^{-1}) 2961, 2937, 1757, 1607, 1577, 1512, 1490, 1464, 1443, 1370, 1299, 1293, 1256, 1243, 1193, 1174, 1115, 1090, 1029, 1020, 836; MS (EI) m/z = 398 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{22}O_4$ 398.1518, found 398.1518.

*(Z)-1-(4-Methoxyphenyl)-4-phenyl-2-(p-tolyl)but-1-en-3-yn-1-yl Acetate (**1f**).* Orange solid: ^{1}H NMR ($CDCl_3$) δ 7.43 (2H, dd, J = 3.2, 1.6 Hz), 7.31−7.26 (5H, m), 7.18 (2H, d, J = 8.9 Hz), 7.05 (2H, d, J = 8.2 Hz), 6.72 (2H, d, J = 8.9 Hz), 3.75 (3H, s), 2.31 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.6, 159.9, 151.5, 137.5, 133.0, 131.4, 130.2, 129.5, 129.1, 128.3, 128.2, 126.7, 123.4, 113.6, 95.3, 87.6, 55.2,

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21.2, 21.0; IR ($CHCl_3$, cm^{-1}) 1757, 1606, 1508, 1490, 1464, 1443, 1370, 1300, 1254, 1193, 1174, 1091, 1029, 1016, 989, 837; MS (EI) m/z = 382 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{22}O_3$ 382.1569, found 382.1565.

*(Z)-2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-4-phenylbut-1-en-3-yn-1-yl Acetate (**1g**).* Yellow solid: ^1H NMR ($CDCl_3$) δ 7.44 (2H, dd, J = 3.2, 1.6 Hz), 7.36−7.31 (5H, m), 7.16 (2H, d, J = 8.2 Hz), 6.94 (2H, t, J = 8.6 Hz), 6.73 (2H, d, J = 8.2 Hz), 3.77 (3H, s), 2.31 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.5, 163.0, 161.4, 160.1, 152.1, 132.1, 132.1, 131.5, 131.4, 131.4, 130.3, 129.4, 128.5, 128.4, 126.4, 123.2, 115.5, 115.3, 113.7, 113.5, 112.6, 95.7, 87.2, 55.2, 21.0; IR ($CHCl_3$, cm^{-1}) 2937, 2840, 1762, 1605, 1507, 1490, 1465, 1443, 1370, 1301, 1254, 1238, 1194, 1174, 1158, 1101, 1088, 1029, 1014, 840; MS (EI) m/z = 386 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{19}FO_3$ 386.1318, found 386.1315.

*(Z)-1-(4-((Ethoxycarbonyl)amino)phenyl)-2-phenyl-4-(p-tolyl)-but-1-en-3-yn-1-yl Acetate (**1h**).* Orange solid: ^1H NMR ($CDCl_3$) δ 7.38−7.36 (2H, m), 7.33 (2H, d, J = 8.2 Hz), 7.24−7.22 (5H, m), 7.15 (2H, d, J = 8.2 Hz), 7.12 (2H, d, J = 8.2 Hz), 6.58 (1H, br s), 4.20 (2H, q, J = 7.1 Hz), 2.35 (3H, s), 2.32 (3H, s), 1.29 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 153.3, 151.3, 138.6, 138.6, 136.0, 131.4, 129.7, 129.7, 129.1, 129.0, 128.4, 127.8, 120.2, 117.8, 114.4, 96.2, 86.7, 61.4, 21.5, 21.0, 14.5; IR ($CHCl_3$, cm^{-1}) 3433, 2985, 1762, 1734, 1609, 1586, 1522, 1509, 1445, 1411, 1370, 1316, 1238, 1194, 1180, 1015, 843, 818; MS (EI) m/z = 439 (M^+); HRMS (EI) m/z calcd for $C_{28}H_{25}NO_4$ 439.1784, found 439.1783.

*(Z)-1-(4-Acetamidophenyl)-2-phenyl-4-(p-tolyl)but-1-en-3-yn-1-yl Acetate (**1i**).* Brown solid: ^1H NMR ($CDCl_3$) δ 7.58 (1H, s), 7.35−7.32 (4H, m), 7.27−7.24 (5H, m), 7.12 (4H, t, J = 8.9 Hz), 2.35 (3H, s), 2.33 (3H, s), 2.12 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.5, 151.1, 138.7, 138.5, 135.9, 131.4, 129.6, 129.5, 129.1, 128.5, 127.9, 120.1, 118.9, 114.6, 96.3, 86.6, 24.6, 21.5, 21.0; IR ($CHCl_3$, cm^{-1}) 3434, 1762, 1693, 1603, 1589, 1516, 1508, 1445, 1405, 1370, 1314, 1248, 1196, 1179, 1095, 1015, 846; MS (EI) m/z = 409 (M^+); HRMS (EI) m/z calcd for $C_{27}H_{23}NO_3$ 409.1678, found 409.1681.

*(E)-1-(4-Methoxyphenyl)-2-(phenylethynyl)hex-1-en-1-yl Acetate (**2a**).* Orange oil: ^1H NMR ($CDCl_3$) δ 7.77 (2H, d, J = 8.9 Hz), 7.37−7.37 (2H, m), 7.31−7.29 (3H, m), 6.89 (2H, d, J = 8.9 Hz), 3.82 (3H, s), 2.29 (2H, t, J = 7.9 Hz), 2.25 (3H, s), 1.67−1.63 (2H, m), 1.42−1.41 (2H, m), 0.96 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 159.8, 150.4, 131.3, 129.0, 128.3, 128.0, 127.6, 123.6, 113.3, 112.1, 94.0, 88.4, 55.3, 31.0, 30.1, 22.4, 20.8, 14.0; IR ($CHCl_3$, cm^{-1}) 2961, 2933, 1751, 1608, 1512, 1490, 1465, 1443, 1370, 1299, 1251, 1176, 1098, 1058; MS (EI) m/z = 348 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{24}O_3$ 348.1725, found 348.1732.

*(E)-1-(4-Methoxyphenyl)-2-((4-methoxyphenyl)ethynyl)hex-1-en-1-yl Acetate (**2b**).* Yellow oil: ^1H NMR ($CDCl_3$) δ 7.77 (2H, d, J = 8.9 Hz), 7.31 (2H, d, J = 8.9 Hz), 6.88 (2H, d, J = 8.9 Hz), 6.83 (2H, d, J = 8.2 Hz), 3.81 (3H, s), 3.80 (3H, s), 2.28 (2H, t, J = 7.6 Hz), 2.24 (3H, s), 1.64−1.63 (2H, m), 1.42−1.40 (2H, m), 0.95 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 159.7, 159.5, 149.7, 132.7, 128.9, 127.7, 115.8, 114.0, 113.3, 112.3, 94.0, 87.0, 55.3, 55.2, 31.0, 30.1, 22.3, 20.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2961, 2935, 2839, 1751, 1607, 1570, 1507, 1465, 1442, 1370, 1289, 1248, 1196, 1176, 1099, 1056, 1033, 834; MS (EI) m/z = 378 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{26}O_4$ 378.1831, found 378.1830.

*(E)-1-(4-Methoxyphenyl)-2-(p-tolylethynyl)hex-1-en-1-yl Acetate (**2c**).* Yellow oil: ^1H NMR ($CDCl_3$) δ 7.77 (2H, d, J = 8.9 Hz), 7.27 (2H, d, J = 7.6 Hz), 7.11 (2H, d, J = 7.6 Hz), 6.88 (2H, d, J = 8.9 Hz), 3.82 (3H, s), 2.35 (3H, s), 2.28 (2H, t, J = 7.9 Hz), 2.25 (3H, s), 1.66−1.61 (2H, m), 1.42−1.40 (2H, m), 0.95 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 159.7, 150.0, 138.2, 131.1, 129.0, 128.9, 127.6, 120.5, 113.3, 112.2, 94.2, 87.7, 55.2, 31.0, 30.1, 22.3, 21.5, 20.8, 14.0; IR ($CHCl_3$, cm^{-1}) 2959, 2932, 2862, 1753, 1607, 1508, 1464, 1441, 1369, 1298, 1250, 1196, 1177, 1098, 1055, 1034, 837; MS (EI) m/z = 362 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{26}O_3$ 362.1882, found 362.1882.

*(E)-2-((4-Fluorophenyl)ethynyl)-1-(4-methoxyphenyl)hex-1-en-1-yl Acetate (**2d**).* Orange oil: ^1H NMR ($CDCl_3$) δ 7.74 (2H, d, J = 8.9 Hz), 7.34−7.33 (2H, m), 6.99 (2H, t, J = 8.6 Hz), 6.89 (2H, d, J = 8.2 Hz), 3.82 (3H, s), 2.28 (2H, t, J = 7.6 Hz), 2.24 (3H, s), 1.64−1.62 (2H, m), 1.42−1.41 (2H, m), 0.96 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 168.6, 163.2, 161.5, 159.8, 150.5, 133.1, 133.1, 129.0, 127.6, 119.7, 119.7, 115.6, 115.5, 113.3, 112.0, 92.7, 88.1, 55.3, 30.9, 30.1, 22.3, 20.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2961, 2934, 1755, 1608, 1506, 1465, 1442, 1370, 1299, 1251, 1238, 1196, 1177, 1155, 1098, 1094, 1056, 1033, 893, 837; MS (EI) m/z = 366 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{23}FO_3$ 366.1631, found 366.1632.

*(E)-2-Butyl-1-(4-methoxyphenyl)oct-1-en-3-yn-1-yl Acetate (**2e**).* Yellow oil: ^1H NMR ($CDCl_3$) δ 7.70 (2H, d, J = 8.9 Hz), 6.84 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.33 (2H, t, J = 6.9 Hz), 2.21 (3H, s), 2.17 (2H, dd, J = 8.2, 6.9 Hz), 1.58−1.48 (4H, m), 1.42−1.34 (4H, m), 0.93−0.90 (6H, m); ^{13}C NMR ($CDCl_3$) δ 168.8, 159.4, 149.1, 128.8, 127.7, 113.2, 112.7, 95.5, 78.8, 55.2, 31.4, 30.6, 30.0, 22.4, 22.0, 20.8, 19.4, 14.0, 13.6; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 2874, 2862, 1753, 1608, 1511, 1466, 1442, 1370, 1297, 1252, 1239, 1195, 1177, 1085, 1035, 836; MS (EI) m/z = 328 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{28}O_3$ 328.2038, found 328.2035.

*(E)-2-Cyclohexyl-1-(4-methoxyphenyl)-4-(p-tolyl)but-1-en-3-yn-1-yl Acetate (**2f**).* Orange oil: ^1H NMR ($CDCl_3$) δ 7.76 (2H, d, J = 8.9 Hz), 7.27 (2H, d, J = 7.6 Hz), 7.11 (2H, d, J = 8.2 Hz), 6.87 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.47−2.43 (1H, m), 2.34 (3H, s), 2.25 (3H, s), 1.82−1.69 (4H, m), 1.61−1.55 (3H, m), 1.32−1.24 (3H, m); ^{13}C NMR ($CDCl_3$) δ 168.9, 159.7, 148.9, 138.1, 131.1, 129.1, 129.0, 127.8, 120.6, 117.6, 113.2, 95.1, 86.3, 55.2, 39.2, 31.2, 26.4, 25.9, 21.5, 20.8; IR ($CHCl_3$, cm^{-1}) 2934, 1755, 1607, 1512, 1451, 1370, 1251, 1196, 1177, 1062, 1034, 837; MS (EI) m/z = 388 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{28}O_3$ 388.2038, found 388.2037.

*(E)-1-(4-Methoxyphenyl)-2-phenyloct-1-en-3-yn-1-yl Acetate (**2g**).* Orange oil: ^1H NMR ($CDCl_3$) δ 7.83 (2H, d, J = 8.9 Hz), 7.48 (2H, d, J = 8.2 Hz), 7.34 (2H, t, J = 7.6 Hz), 7.28−7.25 (1H, m), 6.89 (2H, d, J = 8.9 Hz), 3.84 (3H, s), 2.34 (2H, t, J = 6.9 Hz), 1.98 (3H, s), 1.51−1.50 (2H, m), 1.41−1.37 (2H, m), 0.90 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 168.9, 160.0, 150.0, 137.6, 129.2, 128.4, 128.1, 127.5, 127.4, 113.3, 112.7, 95.9, 79.4, 55.3, 30.5, 22.0, 20.8, 19.5, 13.6; IR ($CHCl_3$, cm^{-1}) 2961, 1936, 1757, 1608, 1511, 1465, 1444, 1370, 1306, 1294, 1252, 1237, 1195, 1178, 1150, 1062, 1033, 1011, 834, 809; MS (EI) m/z = 348 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{24}O_3$ 348.1725, found 348.1725.

*(E)-1-(4-((Ethoxycarbonyl)amino)phenyl)-2-(p-tolylethynyl)hex-1-en-1-yl Acetate (**2h**).* Orange oil: ^1H NMR ($CDCl_3$) δ 7.78 (2H, d, J = 8.9 Hz), 7.37 (2H, d, J = 8.2 Hz), 7.26 (2H, d, J = 7.6 Hz), 7.11 (2H, d, J = 7.6 Hz), 6.65 (1H, br s), 4.23 (2H, q, J = 7.1 Hz), 2.34 (3H, s), 2.29 (2H, t, J = 7.9 Hz), 2.24 (3H, s), 1.65−1.61 (2H, m), 1.41−1.40 (2H, m), 1.31 (3H, t, J = 6.9 Hz), 0.95 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 153.3, 149.7, 138.2, 138.2, 131.1, 129.9, 129.0, 128.3, 120.4, 117.6, 113.0, 94.6, 87.5, 61.3, 31.1, 30.0, 22.3, 21.4, 20.7, 14.5, 13.9; IR ($CHCl_3$, cm^{-1}) 2961, 2932, 1734, 1611, 1586, 1521, 1508, 1410, 1370, 1256, 1237, 1195, 1183, 1097, 1066, 1016, 892, 818; MS (EI) m/z = 419 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{29}NO_4$ 419.2097, found 419.2106.

*(E)-1-(4-Acetamidophenyl)-2-(p-tolylethynyl)hex-1-en-1-yl Acetate (**2i**).* Orange solid: ^1H NMR ($CDCl_3$) δ 7.77 (2H, d, J = 8.2 Hz), 7.47−7.45 (3H, m), 7.26 (2H, d, J = 7.6 Hz), 7.10 (2H, d, J = 8.2 Hz), 2.34 (3H, s), 2.29 (2H, t, J = 7.6 Hz), 2.25 (3H, s), 2.15 (3H, s), 1.64−1.63 (2H, m), 1.41−1.40 (2H, m), 0.95 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.9, 168.3, 149.6, 138.4, 138.1, 131.2, 130.7, 129.1, 128.2, 120.3, 118.8, 113.2, 94.7, 87.4, 31.1, 30.1, 24.6, 22.4, 21.5, 20.8, 14.0; IR ($CHCl_3$, cm^{-1}) 3435, 2961, 2931, 2862, 1755, 1691, 1608, 1588, 1518, 1515, 1507, 1405, 1370, 1315, 1299, 1239, 1194, 1182, 1099, 1055, 1017, 1003, 893; MS (EI) m/z = 389 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{27}NO_3$ 389.1991, found 389.1997.

*(E)-1-(p-Tolyl)-2-(p-tolylethynyl)hex-1-en-1-yl Acetate (**2j**).* Yellow oil: ^1H NMR ($CDCl_3$) δ 7.72 (2H, d, J = 8.2 Hz), 7.27 (2H, d, J = 7.6 Hz), 7.17 (2H, d, J = 8.2 Hz), 7.11 (2H, d, J = 7.6 Hz), 2.35 (3H, s), 2.34 (3H, s), 2.30 (2H, t, J = 7.6 Hz), 2.24 (3H, s), 1.65−1.63 (2H, m), 1.42−1.40 (2H, m), 0.95 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.7, 150.3, 138.6, 138.2, 132.2, 131.2, 129.1, 128.6, 127.4, 120.5, 113.1, 94.4, 87.6, 31.1, 30.1, 22.4, 21.5, 21.4, 20.8, 14.0; IR ($CHCl_3$, cm^{-1}) 2961, 2929, 2863, 1757, 1539, 1507, 1370, 1236, 1195, 1184, 1099, 1055, 893, 810; MS (EI) m/z = 346 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{26}O_2$ 346.1933, found 346.1940.

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General Procedure of the Synthesis of Multisubstituted Furans from (*Z*)- or (*E*)-Enynyl Acetates. To a solution of (*Z*)-enynyl acetates **1** or (*E*)-enynyl acetates **2** (0.1 mmol) in 1,2-dichloroethane (0.25 mL) and MeCN (0.25 mL) was added NXS (0.12 mmol), and the mixture was stirred at room temperature. After the completion of the reaction was confirmed by TLC, 10% $Na_2S_2O_3$ aqueous solution was added for quenching. The aqueous layer was extracted with AcOEt (two times). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography to give **3**.

3-Iodo-5-(4-methoxyphenyl)-4-phenyl-2-(p-tolyl)furan (**3a**). White needle: mp 99−100 °C; ^{1}H NMR ($CDCl_3$) δ 7.99 (2H, d, J = 8.2 Hz), 7.46−7.43 (3H, m), 7.36−7.35 (4H, m), 7.27 (2H, d, J = 8.2 Hz), 6.78 (2H, d, J = 8.9 Hz), 3.76 (3H, s), 2.40 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.1, 150.2, 148.3, 138.1, 134.2, 130.6, 129.1, 128.6, 128.0, 127.6, 127.0, 126.4, 126.2, 123.0, 113.8, 70.3, 55.2, 21.4; IR ($CHCl_3$, cm^{-1}) 2937, 1612, 1571, 1513, 1497, 1487, 1464, 1444, 1375, 1301, 1252, 1179, 1106, 1068, 1034, 942, 835; MS (EI) m/z = 466 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{19}IO_2$ 466.0430, found 466.0432.

3-Bromo-5-(4-methoxyphenyl)-4-phenyl-2-(p-tolyl)furan (**3b**). Colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.97 (2H, d, J = 8.2 Hz), 7.44−7.40 (7H, m), 7.27 (2H, d, J = 8.2 Hz), 6.79 (2H, d, J = 8.9 Hz), 3.78 (3H, s), 2.40 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.2, 147.8, 147.3, 137.9, 132.4, 130.5, 129.2, 128.7, 127.9, 127.1, 127.1, 125.6, 123.4, 123.0, 113.9, 100.3, 55.2, 21.4; IR ($CHCl_3$, cm^{-1}) 2938, 2839, 1611, 1513, 1501, 1488, 1464, 1444, 1420, 1379, 1301, 1254, 1178, 1110, 1073, 1034, 969, 943, 835, 809; MS (EI) m/z = 418 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{19}BrO_2$ 418.0568, found 418.0562.

3-Iodo-5-(4-methoxyphenyl)-2,4-diphenylfuran (**3c**). White needle: mp 127−128 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (2H, d, J = 7.6 Hz), 7.47−7.43 (5H, m), 7.37−7.35 (5H, m), 6.78 (2H, d, J = 8.9 Hz), 3.77 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.2, 149.9, 148.6, 134.1, 130.7, 130.4, 128.7, 128.4, 128.1, 128.0, 127.1, 126.4, 126.4, 122.9, 113.9, 71.0, 55.2; IR ($CHCl_3$, cm^{-1}) 1611, 1570, 1512, 1489, 1464, 1445, 1376, 1301, 1253, 1179, 1112, 1065, 1030, 963, 942, 835; MS (EI) m/z = 452 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{17}IO_2$ 452.0273, found 452.0272.

2-Cyclohexyl-3-iodo-5-(4-methoxyphenyl)-4-phenylfuran (**3d**). White needle: mp 122−124 °C; ^{1}H NMR ($CDCl_3$) δ 7.43−7.26 (7H, m), 6.76 (2H, d, J = 8.9 Hz), 3.77 (3H, s), 2.88−2.84 (1H, m), 1.90 (4H, dt, J = 36.7, 6.9 Hz), 1.76−1.65 (3H, m), 1.44−1.30 (3H, m); ^{13}C NMR ($CDCl_3$) δ 158.7, 158.2, 147.4, 134.1, 130.4, 128.5, 127.6, 126.8, 123.5, 123.5, 113.7, 69.5, 55.2, 37.8, 31.1, 26.2, 25.9; IR ($CHCl_3$, cm^{-1}) 2935, 2856, 1616, 1512, 1489, 1451, 1444, 1300, 1252, 1236, 1198, 1179, 1034, 988, 953, 835; MS (EI) m/z = 458 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{23}IO_2$ 458.0743, found 458.0748.

2-Butyl-3-iodo-5-(4-methoxyphenyl)-4-phenylfuran (**3e**). Colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.42−7.35 (3H, m), 7.31−7.29 (4H, m), 6.76 (2H, d, J = 8.9 Hz), 3.76 (3H, s), 2.79 (2H, t, J = 7.6 Hz), 1.74−1.71 (2H, m), 1.46−1.44 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 158.8, 155.1, 147.8, 134.2, 130.4, 128.5, 127.6, 126.8, 123.7, 123.5, 113.8, 71.2, 55.2, 30.3, 27.7, 22.3, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 1610, 1512, 1488, 1466, 1443, 1299, 1252, 1179, 1034, 835; MS (EI) m/z = 432 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{21}IO_2$ 432.0586, found 432.0583.

3-Iodo-4,5-bis(4-methoxyphenyl)-2-phenylfuran (**3f**). White needle: mp 99−100 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (2H, d, J = 7.6 Hz), 7.46 (2H, t, J = 7.9 Hz), 7.38−7.36 (3H, m), 7.27 (2H, d, J = 8.9 Hz), 6.99 (2H, d, J = 8.9 Hz), 6.79 (2H, d, J = 8.9 Hz), 3.88 (3H, s), 3.77 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.4, 159.1, 149.7, 148.6, 131.8, 130.5, 128.4, 128.1, 127.0, 126.4, 126.2, 126.1, 123.1, 114.2, 113.9, 71.8, 55.2; IR ($CHCl_3$, cm^{-1}) 2961, 2839, 1612, 1518, 1499, 1465, 1443, 1300, 1289, 1251, 1178, 1032, 942, 835; MS (EI) m/z = 482 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{19}IO_3$ 482.0379, found 482.0386.

3-Bromo-5-(4-methoxyphenyl)-2-phenyl-4-(p-tolyl)furan (**3g**). White solid: ^{1}H NMR ($CDCl_3$) δ 8.09 (2H, d, J = 6.9 Hz), 7.46−7.41 (4H, m), 7.33 (1H, t, J = 7.2 Hz), 7.29−7.25 (4H, m), 6.80 (2H, d, J = 8.9 Hz), 3.77 (3H, s), 2.42 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.2, 148.0, 146.8, 137.7, 131.6, 130.3, 129.5, 129.5, 129.2, 128.5, 127.8, 127.1, 125.6, 123.0, 113.9, 101.2, 55.2, 21.4; IR ($CHCl_3$, cm^{-1}) 2961, 2935, 2839, 1608, 1520, 1499, 1465, 1379, 1301, 1254, 1238, 1197, 1179, 1114, 1068, 1032, 942; MS (EI) m/z = 418 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{19}BrO_2$ 418.0568, found 418.0559.

3-Iodo-5-(4-methoxyphenyl)-2-phenyl-4-(p-tolyl)furan (**3h**). White needle: mp 117−119 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (2H, d, J = 8.2 Hz), 7.45 (2H, t, J = 7.6 Hz), 7.40−7.34 (3H, m), 7.26−7.25 (4H, m), 6.79 (2H, t, J = 5.8 Hz), 3.77 (3H, s), 2.43 (3H, s); ^{13}C NMR ($CDCl_3$) δ 159.1, 149.8, 148.6, 137.8, 131.0, 130.5, 129.5, 128.4, 128.1, 127.0, 126.4, 126.4, 123.1, 113.9, 71.4, 55.2, 21.4; IR ($CHCl_3$, cm^{-1}) 1613, 1604, 1519, 1499, 1482, 1301, 1253, 1179, 1032, 941, 835; MS (EI) m/z = 466 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{19}IO_2$ 466.0430, found 466.0429.

3-(4-Fluorophenyl)-4-iodo-2-(4-methoxyphenyl)-5-phenylfuran (**3i**). White solid: mp 137−139 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d, J = 7.6 Hz), 7.47 (2H, t, J = 7.9 Hz), 7.38−7.32 (5H, m), 7.16 (2H, t, J = 8.6 Hz), 6.80 (2H, d, J = 8.9 Hz), 3.79 (3H, s); ^{13}C NMR ($CDCl_3$) δ 163.4, 161.8, 159.3, 150.1, 148.8, 132.5, 132.4, 130.3, 130.0, 130.0, 128.4, 128.2, 127.1, 126.4, 125.4, 122.7, 115.9, 115.7, 114.0, 71.0, 55.3; IR ($CHCl_3$, cm^{-1}) 1606, 1517, 1498, 1301, 1254, 1236, 1197, 1179, 1157, 1065, 1031, 943, 841, 810; MS (EI) m/z = 470 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{16}FIO_2$ 470.0179, found 470.0183.

Ethyl (4-(4-Iodo-3-phenyl-5-(p-tolyl)furan-2-yl)phenyl)carbamate (**3j**). Pale yellow solid: mp 180−181 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (2H, d, J = 8.2 Hz), 7.46−7.44 (3H, m), 7.36 (4H, t, J = 7.9 Hz), 7.28−7.26 (4H, m), 6.54 (1H, br s), 4.21 (2H, q, J = 7.1 Hz), 2.41 (3H, s), 1.30 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 153.4, 150.5, 148.0, 138.3, 137.3, 134.0, 130.6, 129.1, 128.7, 128.1, 127.6, 127.0, 126.5, 126.3, 125.3, 118.3, 70.4, 61.3, 21.4, 14.5; IR ($CHCl_3$, cm^{-1}) 3434, 1733, 1614, 1593, 1584, 1518, 1498, 1413, 1236, 1197, 1098, 1061, 942, 821; MS (EI) m/z = 523 (M^+); HRMS (EI) m/z calcd for $C_{26}H_{22}INO_3$ 523.0644, found 523.0647.

N-(4-(4-Iodo-3-phenyl-5-(p-tolyl)furan-2-yl)phenyl)acetamide (**3k**). Colorless needle: mp 236−239 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (2H, d, J = 8.2 Hz), 7.48−7.34 (9H, m), 7.28 (2H, d, J = 8.2 Hz), 7.18 (1H, br s), 2.41 (3H, s), 2.16 (3H, s); ^{13}C NMR ($CDCl_3$) δ 168.2, 150.6, 147.8, 138.3, 137.2, 134.0, 130.6, 129.1, 128.8, 128.1, 127.5, 127.3, 126.5, 126.2, 119.5, 70.5, 24.7, 21.4; IR ($CHCl_3$, cm^{-1}) 3435, 2926, 1691, 1603, 1517, 1497, 1407, 1370, 1315, 942, 822, 812; MS (EI) m/z = 493 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{20}INO_2$ 493.0539, found 493.0538.

N-Acetyl-N-(4-(4-iodo-3-phenyl-5-(p-tolyl)furan-2-yl)phenyl)-acetamide (**3k′**). Pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.01 (2H, d, J = 8.2 Hz), 7.54−7.47 (5H, m), 7.37 (2H, d, J = 6.2 Hz), 7.29 (2H, d, J = 8.2 Hz), 7.01 (2H, d, J = 8.9 Hz), 2.42 (3H, s), 2.27 (6H, s); ^{13}C NMR ($CDCl_3$) δ 172.9, 151.3, 146.9, 138.7, 138.2, 133.8, 130.7, 130.4, 129.2, 129.1, 128.9, 128.8, 128.4, 127.3, 126.6, 126.4, 70.9, 26.9, 21.4; IR ($CHCl_3$, cm^{-1}) 2925, 1712, 1607, 1511, 1497, 1445, 1417, 1370, 1293, 1245, 1108, 1068, 1028, 1015, 942, 822; MS (EI) m/z = 535 (M^+); HRMS (EI) m/z calcd for $C_{27}H_{22}INO_3$ 535.0644, found 535.0641.

3-Butyl-4-iodo-2-(4-methoxyphenyl)-5-phenylfuran (**3l**). White needle: mp 36−38 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (2H, d, J = 6.9 Hz), 7.59 (2H, d, J = 8.9 Hz), 7.43 (2H, t, J = 7.6 Hz), 7.32 (1H, t, J = 7.2 Hz), 6.97 (2H, d, J = 8.9 Hz), 3.84 (3H, s), 2.62 (2H, t, J = 8.2 Hz), 1.63−1.60 (2H, m), 1.50−1.45 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 159.0, 149.5, 148.2, 130.5, 128.3, 127.8, 127.1, 126.2, 124.6, 123.8, 114.1, 71.3, 55.3, 31.8, 26.8, 22.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 1615, 1605, 1506, 1483, 1465, 1292, 1253, 1236, 1198, 1178, 1040, 946, 834; MS (EI) m/z = 432 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{21}IO_2$ 432.0586, found 432.0585.

3-Bromo-4-butyl-5-(4-methoxyphenyl)-2-phenylfuran (**3m**). Pale yellow needle: mp 36 °C; ^{1}H NMR ($CDCl_3$) δ 8.04 (2H, d, J = 8.2 Hz), 7.61 (2H, d, J = 8.9 Hz), 7.43 (2H, t, J = 7.9 Hz), 7.31 (1H, t, J = 7.6 Hz), 6.98 (2H, d, J = 8.9 Hz), 3.86 (3H, s), 2.66 (2H, t, J = 7.9 Hz), 1.65−1.61 (2H, m), 1.47−1.46 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 159.1, 147.7, 146.4, 130.1, 128.4, 127.6, 127.0, 125.4, 123.8, 122.4, 114.1, 101.8, 55.3, 31.6, 24.7, 22.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2961, 2933, 2862, 1604, 1506, 1486, 1465, 1457, 1443, 1293, 1252, 1237, 1178, 1045, 1027, 950, 834; MS (EI) m/z = 384 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{21}BrO_2$ 384.0725, found 384.0717.

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*3-Butyl-4-iodo-2,5-bis(4-methoxyphenyl)furan (**3n**).* White needle: mp 64−66 °C; ^{1}H NMR ($CDCl_3$) δ 7.97 (2H, d, J = 8.9 Hz), 7.58 (2H, d, J = 8.9 Hz), 6.97 (4H, dd, J = 8.6, 1.7 Hz), 3.85 (6H, s), 2.61 (2H, t, J = 8.2 Hz), 1.62−1.61 (2H, m), 1.48−1.46 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 159.3, 158.9, 149.7, 147.6, 127.8, 127.0, 124.3, 123.9, 123.4, 114.1, 113.7, 69.8, 55.3, 31.8, 26.8, 22.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 2935, 1615, 1507, 1495, 1465, 1442, 1305, 1294, 1251, 1178, 1099, 1038, 946, 834; MS (EI) m/z = 462 (M^+); HRMS (EI) m/z calcd for $C_{22}H_{23}IO_3$ 462.0692, found 462.0687.

*3-Butyl-4-iodo-2-(4-methoxyphenyl)-5-(p-tolyl)furan (**3o**).* White needle: mp 49−50 °C; ^{1}H NMR ($CDCl_3$) δ 7.93 (2H, d, J = 8.2 Hz), 7.58 (2H, d, J = 8.9 Hz), 7.23 (2H, d, J = 8.9 Hz), 6.96 (2H, d, J = 8.9 Hz), 3.84 (3H, s), 2.61 (2H, dd, J = 9.3, 7.2 Hz), 2.38 (3H, s), 1.63−1.60 (2H, m), 1.48−1.46 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 159.0, 149.8, 147.8, 137.8, 129.0, 127.8, 127.0, 126.2, 124.4, 123.9, 114.1, 70.6, 55.3, 31.8, 26.8, 22.8, 21.3, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 1616, 1507, 1494, 1465, 1457, 1443, 1292, 1252, 1237, 1197, 1178, 1098, 1040, 946, 834, 821; MS (EI) m/z = 446 (M^+); HRMS (EI) m/z calcd for $C_{22}H_{23}IO_2$ 446.0743, found 446.0743.

*3-Butyl-5-(4-fluorophenyl)-4-iodo-2-(4-methoxyphenyl)furan (**3p**).* Colorless needle: mp 51−52 °C; ^{1}H NMR ($CDCl_3$) δ 8.02 (2H, dd, J = 4.8, 2.4 Hz), 7.58 (2H, d, J = 8.9 Hz), 7.12 (2H, t, J = 8.6 Hz), 6.98 (2H, d, J = 8.2 Hz), 3.86 (3H, s), 2.61 (2H, t, J = 8.2 Hz), 1.62−1.60 (2H, m), 1.50−1.45 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 163.1, 161.5, 159.1, 148.8, 148.2, 128.2, 128.1, 127.1, 126.9, 126.8, 124.5, 123.7, 115.4, 115.3, 114.1, 71.1, 55.3, 31.8, 26.8, 22.8, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 1615, 1597, 1506, 1493, 1466, 1291, 1253, 1238, 1178, 1159, 1094, 1040, 946, 838; MS (EI) m/z = 450 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{20}FIO_2$ 450.0492, found 450.0494.

*2,4-Dibutyl-3-iodo-5-(4-methoxyphenyl)furan (**3q**).* Colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.48 (2H, d, J = 8.9 Hz), 6.94 (2H, d, J = 8.9 Hz), 3.83 (3H, s), 2.70 (2H, t, J = 7.6 Hz), 2.52 (2H, t, J = 8.2 Hz), 1.67−1.64 (2H, m), 1.57−1.55 (2H, m), 1.43−1.39 (4H, m), 0.96 (3H, t, J = 7.6 Hz), 0.94 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 158.6, 154.6, 147.2, 126.7, 124.3, 122.2, 114.0, 71.7, 55.3, 31.9, 30.2, 27.6, 26.6, 22.7, 22.2, 13.9, 13.8; IR ($CHCl_3$, cm^{-1}) 2960, 2933, 2874, 2862, 1616, 1601, 1576, 1559, 1506, 1466, 1457, 1443, 1292, 1250, 1178, 1041, 1017, 834; MS (EI) m/z = 412 (M^+); HRMS (EI) m/z calcd for $C_{19}H_{25}IO_2$ 412.0899, found 412.0894.

*3-Cyclohexyl-4-iodo-2-(4-methoxyphenyl)-5-(p-tolyl)furan (**3r**).* White viscous oil: ^{1}H NMR ($CDCl_3$) δ 7.86 (2H, d, J = 8.2 Hz), 7.45 (2H, d, J = 8.9 Hz), 7.21 (2H, d, J = 8.2 Hz), 6.96 (2H, d, J = 8.9 Hz), 3.85 (3H, s), 2.80−2.78 (1H, m), 2.37 (3H, s), 1.95−1.75 (7H, m), 1.37−1.24 (3H, m); ^{13}C NMR ($CDCl_3$) δ 159.53, 150.90, 148.91, 137.89, 129.83, 128.89, 127.89, 127.49, 126.93, 124.09, 113.77, 66.54, 55.31, 37.30, 31.34, 26.92, 25.97, 21.33; IR ($CHCl_3$, cm^{-1}) 2931, 1615, 1506, 1494, 1465, 1450, 1294, 1251, 1176, 1045, 1029, 939, 836; MS (EI) m/z = 472 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{25}IO_2$ 472.0899, found 472.0901.

*Ethyl (4-(3-Butyl-4-iodo-5-(p-tolyl)furan-2-yl)phenyl)carbamate (**3s**).* White needle: mp 135−137 °C; ^{1}H NMR ($CDCl_3$) δ 7.93 (2H, d, J = 8.2 Hz), 7.61 (2H, d, J = 8.9 Hz), 7.45 (2H, d, J = 8.2 Hz), 7.24 (2H, d, J = 8.2 Hz), 6.63 (1H, br s), 4.25 (2H, q, J = 7.1 Hz), 2.64−2.63 (2H, m), 2.39 (3H, s), 1.63−1.60 (2H, m), 1.48−1.47 (2H, m), 1.33 (3H, t, J = 7.2 Hz), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 153.5, 150.1, 147.5, 138.0, 137.2, 129.0, 127.7, 126.3, 126.3, 125.3, 118.7, 70.8, 61.4, 31.7, 26.9, 22.8, 21.4, 14.6, 13.9; IR ($CHCl_3$, cm^{-1}) 3435, 2961, 2933, 1733, 1585, 1522, 1411, 1316, 1258, 1185, 1098, 1066, 946, 839; MS (EI) m/z = 503 (M^+); HRMS (EI) m/z calcd for $C_{24}H_{26}INO_3$ 503.0957, found 503.0950.

*N-(4-(3-Butyl-4-iodo-5-(p-tolyl)furan-2-yl)phenyl)acetamide (**3t**).* Pale yellow solid: mp 168−170 °C; ^{1}H NMR ($CDCl_3$) δ 7.93 (2H, d, J = 8.2 Hz), 7.61 (2H, d, J = 8.9 Hz), 7.58 (2H, d, J = 8.9 Hz), 7.37 (1H, br s), 7.25 (2H, t, J = 7.6 Hz), 2.63 (2H, t, J = 8.2 Hz), 2.39 (3H, s), 2.20 (3H, s), 1.64−1.58 (2H, m), 1.50−1.45 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.3, 150.2, 147.3, 138.0, 137.0, 129.0, 127.6, 127.1, 126.3, 126.1, 125.5, 119.8, 70.9, 31.7, 26.9, 24.7, 22.8, 21.4, 13.9; IR ($CHCl_3$, cm^{-1}) 3435, 2961, 2932, 1690, 1599, 1586, 1517, 1509, 1405, 1370, 1314, 1237, 1197, 946 809; MS (EI) m/z = 473 (M^+); HRMS (EI) m/z calcd for $C_{23}H_{24}INO_2$ 473.0852, found 473.0855.

*N-Acetyl-N-(4-(3-butyl-4-iodo-5-(p-tolyl)furan-2-yl)phenyl)-acetamide (**3t′**).* White solid: mp 104−106 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (2H, d, J = 8.2 Hz), 7.76 (2H, d, J = 8.9 Hz), 7.26 (2H, d, J = 8.2 Hz), 7.21 (2H, d, J = 8.2 Hz), 2.68 (2H, t, J = 8.2 Hz), 2.40 (3H, s), 2.33 (6H, s), 1.66−1.63 (2H, m), 1.51−1.50 (2H, m), 1.01 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 173.0, 151.0, 146.5, 138.4, 138.0, 131.5, 129.1, 129.0, 127.4, 127.2, 126.5, 126.4, 71.0, 31.6, 27.0, 22.8, 21.4, 13.9; IR ($CHCl_3$, cm^{-1}) 2961, 2933, 1713, 1506, 1370, 1292, 1238, 1197, 1035, 1014, 946, 821; MS (EI) m/z = 515 (M^+); HRMS (EI) m/z calcd for $C_{25}H_{26}INO_3$ 515.0957, found 515.0956.

*3-Butyl-4-iodo-2,5-di-p-tolylfuran (**3u**).* White needle: mp 49−50 °C; ^{1}H NMR ($CDCl_3$) δ 7.94 (2H, d, J = 8.2 Hz), 7.56 (2H, d, J = 8.2 Hz), 7.24 (4H, d, J = 7.6 Hz), 2.64 (2H, t, J = 8.2 Hz), 2.39 (6H, s), 1.63−1.61 (2H, m), 1.48−1.47 (2H, m), 0.99 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 150.0, 147.9, 137.9, 137.3, 129.3, 129.0, 128.3, 127.8, 126.3, 125.5, 125.2, 70.8, 31.7, 26.9, 22.8, 21.4, 21.3, 13.9; IR ($CHCl_3$, cm^{-1}) 2960, 2928, 2862, 1507, 1493, 1467, 1457, 1100, 946, 822; MS (EI) m/z = 430 (M^+); HRMS (EI) m/z calcd for $C_{22}H_{23}IO$ 430.0794, found 430.0791.

*Allenylketone **4a**.* Orange oil: ^{1}H NMR ($CDCl_3$) δ 8.01 (2H, d, J = 8.9 Hz), 7.47 (2H, d, J = 8.2 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.32 (1H, d, J = 7.6 Hz), 6.97 (2H, d, J = 8.9 Hz), 3.90 (3H, s), 2.47−2.43 (2H, m), 1.46−1.45 (2H, m), 1.23−1.21 (2H, m), 0.83 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 202.2, 190.4, 163.9, 132.1, 132.0, 130.5, 128.8, 128.3, 128.0, 113.8, 108.0, 68.8, 55.5, 40.0, 31.1, 21.4, 13.6; IR ($CHCl_3$, cm^{-1}) 2961, 2935, 2874, 2862, 1652, 1601, 1575, 1509, 1465, 1314, 1260, 1167, 1031, 857, 842; MS (EI) m/z = 432 (M^+); HRMS (EI) m/z calcd for $C_{21}H_{21}IO_2$ 432.0586, found 432.0587.

*Allenylketone **4b**.* Orange oil: ^{1}H NMR ($CDCl_3$) δ 7.86 (2H, d, J = 8.2 Hz), 6.93 (2H, d, J = 8.9 Hz), 3.88 (3H, s), 2.46−2.43 (2H, m), 2.30 (2H, t, J = 7.2 Hz), 1.53−1.33 (6H, m), 1.12−1.10 (2H, m), 0.95 (3H, t, J = 7.2 Hz), 0.77 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 206.3, 192.2, 163.0, 131.2, 130.9, 113.4, 107.5, 66.9, 55.4, 39.5, 31.0, 29.6, 28.1, 22.4, 21.1, 13.9, 13.6; IR ($CHCl_3$, cm^{-1}) 2961, 2933, 2874, 1643, 1602, 1509, 1466, 1312, 1257, 1032, 843; MS (EI) m/z = (M^+); HRMS (EI) m/z calcd for $C_{19}H_{25}IO_2$ 412.0899, found 412.0899.

Sonogashira Coupling Reaction of 3-Iodofuran 3 with Terminal Alkynes. To a solution of 3-iodofuran **3** (0.1 mmol) in Et_3N (1 mL) were added $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol), CuI (1.9 mg, 0.01 mmol), and alkyne (0.3 mmol), and the mixture was stirred at 50 °C under nitrogen. The reaction was monitored by TLC to establish completion. Saturated aqueous NH_4Cl solution was added to the reaction mixture and extracted with AcOEt (three times). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated at the reduced pressure. Column chromatography on silica gel using hexane/ethyl acetate as an eluent afforded **5**.

*3-Butyl-4-(hex-1-yn-1-yl)-2-(4-methoxyphenyl)-5-phenylfuran (**5a**).* Pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 8.13 (2H, d, J = 7.6 Hz), 7.62 (2H, d, J = 8.2 Hz), 7.40 (2H, t, J = 7.9 Hz), 7.27 (1H, t, J = 6.9 Hz), 6.97 (2H, d, J = 8.2 Hz), 3.85 (3H, s), 2.69 (2H, t, J = 7.9 Hz), 2.55 (2H, t, J = 6.9 Hz), 1.67−1.66 (4H, m), 1.56−1.55 (2H, m), 1.46−1.44 (2H, m), 0.98 (3H, t, J = 7.2 Hz), 0.97 (3H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 158.8, 151.4, 147.1, 130.8, 128.4, 127.3, 127.0, 124.3, 124.1, 124.0, 114.1, 107.4, 97.3, 73.1, 55.3, 31.8, 30.9, 24.5, 22.8, 22.0, 19.5, 14.0, 13.6; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 2873, 2862, 1605, 1572, 1507, 1465, 1443, 1294, 1250, 1177, 1035, 834; MS (EI) m/z = 386 (M^+); HRMS (EI) m/z calcd for $C_{27}H_{30}O_2$ 386.2246, found 386.2252.

*3-Butyl-2-(4-methoxyphenyl)-5-phenyl-4-(phenylethynyl)furan (**5b**).* Pale yellow needle: mp 63−65 °C; ^{1}H NMR ($CDCl_3$) δ 8.18 (2H, d, J = 8.2 Hz), 7.65 (2H, d, J = 7.6 Hz), 7.56 (2H, d, J = 6.9 Hz), 7.44 (2H, t, J = 7.2 Hz), 7.40−7.36 (3H, m), 7.30 (1H, t, J = 6.9 Hz), 6.99 (2H, d, J = 8.9 Hz), 3.86 (3H, s), 2.78 (2H, t, J = 7.6 Hz), 1.76−1.74 (2H, m), 1.50−1.49 (2H, m), 0.98 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 158.9, 152.2, 147.5, 131.3, 130.6, 128.5, 128.4, 128.1, 127.7, 127.1, 124.6, 123.9, 123.7, 123.7, 114.1, 106.7, 96.0, 82.5, 55.3, 31.8,

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24.5, 22.8, 14.0; IR ($CHCl_3$, cm^{-1}) 2960, 2934, 2862, 1607, 1598, 1572, 1507, 1484, 1464, 1443, 1295, 1250, 1178, 1136, 1028, 967, 834; MS (EI) m/z = 406 (M^+); HRMS (EI) m/z calcd for $C_{29}H_{26}O_2$ 406.1933, found 406.1924.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all new compounds. 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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