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Regio- and Stereoselective Multisubstituted Enol Ester Synthesis

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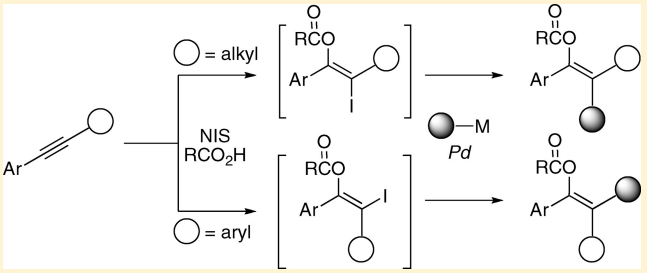
Supporting Information

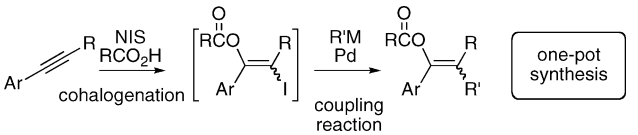
ABSTRACT: Regio- and stereoselective cohalogenation of alkynes with NXS (X = Br, I) was achieved, and the stereoselectivity of the resulting alkenes was dependent on the substituent on the alkyne. Cohalogenation and successive cross-coupling gave multisubstituted enol esters in a one-pot process.



The regio- and stereoselective synthesis of multisubstituted alkenes has provided a particular challenge in organic synthesis.[1] Multisubstituted enol esters and ethers, members of the multisubstituted alkenes, are important constituents in drugs such as Nileprost,[2] and also versatile synthons in organic synthesis, readily engaging in a range of transformations including regioselective Diels–Alder reactions,[3] [3 + 2] cycloaddition,[4] asymmetric hydrogenation,[5] and Pd-catalyzed enantioselective allylations.[6] Cohalogenation, the simultaneous introduction of a halogen atom and a suitable nucleophile across carbon–carbon multiple bonds, is a useful reaction.[7] Alkenyl halides obtained from cohalogenation reaction of alkynes are important intermediates in multisubstituted alkene syntheses because they can be further functionalized via transition-metal-catalyzed cross-coupling reactions. If regio- and stereoselectivity of cohalogenation could be controlled and if successive cross-coupling could be conducted, this method would be ideally suited for diversity-oriented[8] multisubstituted alkene synthesis. Although alkenyl iodides are suitable substrates for these cross-coupling reactions, the examples of coiodination of alkynes are mostly confined to intramolecular transformations, including iodolactonization,[9] in which an intramolecular nucleophile attacks the activated alkyne leading to a cyclized product. We herein report regio- and stereoselective cohalogenation of alkynylbenzene derivatives. Furthermore, we conducted the one-pot synthesis of multisubstituted enol esters via successive cohalogenation and cross-coupling reactions (Scheme 1).

First, we examined the reaction of alkynes **1** having various aromatic substituents with NXS (X = Cl, Br, I) as the electrophilic halogenation reagent and AcOH as the nucleophile (Table 1). Although NXS has been used to activate alkynes in iodocyclizations,[9] there are a few reports of the stereoselective synthesis of iodoalkenes from alkynes, electrophilic iodine reagent, and external nucleophile.[10] The reaction with

Scheme 1. Regio- and Stereoselective Multisubstituted Enol Ester Synthesis



alkynylbenzenes having electron-donating groups such as OMe, $NHCO_2Et$, or NHAc on the aromatic ring proceeded smoothly to afford the iodoalkenes **2a–c** in good to excellent yields as a single *E*-isomer (vide infra) (entries 1–3). When methyl-substituted **1d** was used, reactivity and selectivity decreased (entry 4). Unsubstituted **1e**, *p*-fluoro- and *p*-nitro-substituted **1f** and **1g** did not react under these conditions (entries 5–7). To examine the effect of the substituent position on the aromatic ring, the reaction was carried out using alkynylbenzenes, having *o*- or *m*-methoxy group. *o*-Methoxy-alkynylbenzene **1h** gave the iodoalkene **2h** as a single *E*-isomer in 63% yield together with 2-butyl-3-iodobenzofuran **3** in 16% yield (entry 8). It appears that intermolecular reaction with AcOH is more favorable than intramolecular attack of oxygen at the alkyne triple bond.[11] As expected, the reaction with *m*-methoxyalkynylbenzene **1i**, NIS, and AcOH did not undergo the cohalogenation reaction, resulting in recovery of starting material (entry 9). When NBS was used, bromoalkene **2a′** was obtained in 91% yield after prolonged reaction time (entry 10). The use of NCS resulted in recovery of **1a** (entry 11). Electron-rich heteroaromatic-substituted alkyne **1j** also participated in this reaction, whereas electron-deficient pyridine-substituted **1k** led to complex mixture (entries 12 and 13). The electronic bias

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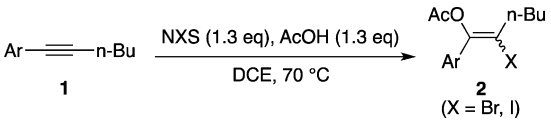
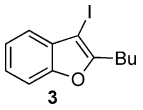
Table 1. Effect of the Aromatic Substituent



entry	1	Ar	X	time (h)	2	yield (%)
1	**1a**	*p*-$MeOC_6H_4$	I	1	**2a**	quant (*E*)
2	**1b**	*p*-$EtCO_2NHC_6H_4$	I	1	**2b**	95 (*E*)
3	**1c**	*p*-$AcNHC_6H_4$	I	1	**2c**	70 (*E*)
4	**1d**	*p*-MeC_6H_4	I	4	**2d**	70 (*E*/*Z* = 10:1)
5	**1e**	C_6H_5	I	4	**2e**	trace
6	**1f**	*p*-FC_6H_4	I	22		recovery of **1f**
7	**1g**	*p*-$NO_2C_6H_4$	I	22		recovery of **1g**
8	**1h**	*o*-$MeOC_6H_4$	I	1	**2h**	63 (*E*)[a]
9	**1i**	*m*-$MeOC_6H_4$	I	2		recovery of **1i**
10	**1a**	*p*-$MeOC_6H_4$	Br	4	**2a′**	91 (*E*/*Z* = 10:1)
11	**1a**	*p*-$MeOC_6H_4$	Cl	3		recovery of **1a**
12	**1j**	2-thiophenyl	I	2	**2j**	58 (*E*)
13	**1k**	2-pyridyl	I	2		decomposed

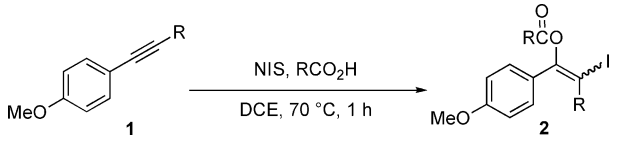
[a]2-Butyl-3-iodobenzofuran **3** was obtained in 16% yield.

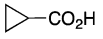


of the groups on both carbons of the triple bond plays an important role in attack of the nucleophile. Regioselective addition of AcOH was assumed to occur by preferential attack on a more electrophilic carbon.[12]

We next explored the effects of the alkynyl substituent R and the nucleophile NuH (Table 2). Alkynylbenzenes bearing alkyl

Table 2. Reaction of Alkynylbenzene 1 with NIS and Nucleophile



entry[a]	1	R	RCO_2H	2	yield (%)
1	**1l**	$(CH_2)_3OTs$	AcOH	**2l**	98 (*E*)
2	**1m**	cyclohexyl	AcOH	**2m**	91 (*E*)
3	**1n**	C_6H_5	AcOH	**2n**	quant. (*E*:*Z* = 1:8)
4	**1o**	*p*-MeC_6H_4	AcOH	**2o**	quant. (*E*:*Z* = 1:10)
5	**1p**	*p*-FC_6H_4	AcOH	**2p**	89 (*E*:*Z* = 1:9)
6	**1q**	*p*-$MeOC_6H_4$	AcOH	**2q**	87 (*E*:*Z* = 1:10)
7	**1r**	*m*-$MeOC_6H_4$	AcOH	**2r**	82 (*E*:*Z* = 1:6)
8	**1a**	Bu		**2s**	quant. (*E*)
9	**1a**	Bu	$PhCO_2H$	**2t**	quant. (*E*)

[a]Entries 1, 2, 8, and 9: NIS (1.3 equiv), RCO_2H (1.3 equiv). Entries 3–7: NIS (2 equiv), RCO_2H (2 equiv).

substituents on the acetylene terminus gave (*E*)-**2** in good yields (entries 1, 2, 8, and 9). In contrast to the results of alkyl-substituted substrates, the reaction of aryl-substituted substrates exhibited *Z*-selectivity and the ratios of *E*/*Z* were about 1:9 (entries 3–7). The use of alcohol instead of carboxylic acid failed to afford the desired iodoalkenes under these conditions. Halogenation with NXS often needs various NXS-activating coreagent, such as BF_3, CF_3CO_2H, *p*-TsOH, [hydroxy(tosyloxy)iodo]benzene, CF_3SO_3H.[13] It is conceivable that carboxylic acids behave not only as nucleophile but also as NIS-activating reagent.

We could not determine the stereochemistry of the products by NOE experiments. Fortunately, we were able to recrystallize compounds **2l**, **2m**, **2n**, and **2o** and obtain the results of X-ray analysis.[14] Alkyl-substituted **2l** and **2m** were *E*-products (*anti* addition products), while compounds **2n** and **2o**, which were major products from aryl-substituted alkynylbenzenes, were *Z*-products (*syn* addition products). The stereochemistries of **2p**–**r** were confirmed by ^1H NMR chemical shifts of the acetyl protons as compared with the corresponding protons of **2n** and **2o**, namely the acetyl peaks of the *E* isomers were shifted to upfield (Figure 1).

In an earlier report, the reaction of alkyne and electrophilic iodine reagent ($IPy_2 \cdot BF_4$, ICl) yielded *E*-iodoalkene through cyclic iodonium ion intermediates and nucleophilic *anti*-attack. When the steric hindrance of alkynyl substituents increases, nucleophiles will interact to a greater extent with the iodine atom of the iodonium ion, hence yielding an overall *syn*-addition.[10a,c] Spectroscopic and theoretical investigations of electrophilic halogenation reactions of alkynes have also been reported.[15] Recently, Laali and co-workers reported[16] a theoretical study on halogen addition to terminal alkynes by density functional theory (DFT) and gauge-independent atomic orbital (GIAO)-DFT calculations. To obtain further information on stereoselectivity, we performed ^1H NMR spectroscopic analysis using the reaction of **1n** with NIS and AcOH. After 10 min, approximately half of the starting material **1n** still remained: the *E*/*Z* ratio of **2n** was 2:1. Over time, the amount of the *Z*-isomer gradually increased. After the completion of the reaction (1 h), the final *E*/*Z* ratio was 1:10. This observation indicates that the isomerization of the double bond occurred under the reaction conditions. However, the mechanistic basis for the different stereoselectivity remains unclear.

The resulting iodoalkenes **2**, which were stable at room temperature, could be functionalized by cross-coupling reactions (Scheme 2). Suzuki coupling of **2a** with several boronic acids gave multisubstituted enol esters **4a**–**c** in good yields.

Finally, we undertook the one-pot synthesis of multisubstituted enol esters **4** or **5** from alkynylbenzene **1a** or **1n** (Scheme 3). After the formation of **2a** or **2n** was confirmed by TLC, an aqueous solution of $Na_2S_2O_3$ was added to the reaction mixture to decompose extra NIS, then successive Suzuki coupling reaction produced multisubstituted enol esters **4a**–**c** or **5a**–**c** in good yields.

In summary, we have developed a regio- and stereoselective cohalogenation of alkynylbenezenes, which have electron-donating groups at the *para*-position on the aromatic ring. The stereoselectivity of the reaction is dependent upon the substituent on the acetylene terminus. Alkyl-substituted alkynylbenzene proceeded via *anti*-addition, affording *E*-iodoalkene, while aryl-substituted alkynylbenzene exhibited a preference for *syn*-selectivity. The resulting iodoalkene was utilized for the transformation through a Pd-catalyzed coupling reaction. A one-pot regio- and stereoselective cohalogenation/Suzuki-coupling reaction was also achieved.

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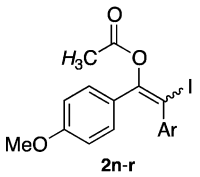
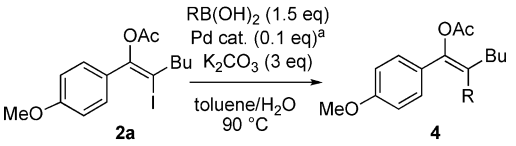


entry	2	Ar	major isomer δ (ppm)	minor isomer δ (ppm)
1	**2n**	C_6H_5	2.30 (*Z*)[a]	1.83
2	**2o**	*p*-MeC_6H_4	2.30 (*Z*)[a]	1.85
3	**2p**	*p*-FC_6H_4	2.28	1.85
4	**2q**	*p*-$MeOC_6H_4$	2.28	1.86
5	**2r**	*m*-$MeOC_6H_4$	2.29	1.86

Figure 1. ^{1}H NMR Chemical Shift of OCOCH_3 of Compound **2**. Footnote: (a) Determined by X-ray crystallography.

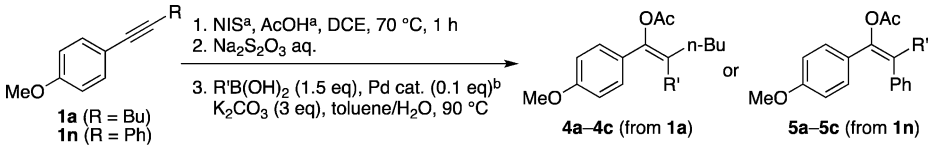
Scheme 2. Cross-Coupling Reaction Using Compound 2a



4	R	yield (%)
4a	C_6H_5	quant.
4b	β-styryl	89
4c	α-styryl	97

[a]$PdCl_2(PPh_3)_2$ was used for coupling with $PhB(OH)_2$. $Pd(OAc)_2$ and PPh_3 (0.2 equiv) were used for coupling with 2-phenylvinylboronic acid or 1-phenylvinylboronic acid.

Scheme 3. One-Pot Synthesis of Multisubstituted Enol Esters 4 and 5



4	R'	yield (%)	5	R'	yield (%)
4a	C_6H_5	85	**5a**	C_6H_5	92
4b	β-styryl	75	**5b**	β-styryl	71
4c	α-styryl	72	**5c**	α-styryl	86

[a]**1a**: NIS (1.3 equiv), AcOH (1.3 equiv). **1n**: NIS (2.0 equiv), AcOH (2.0 equiv). [b]See Scheme 2.

EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H NMR spectral data were recorded in $CDCl_3$ solutions on a 600 MHz spectrometer, and ^{13}C NMR were recorded in $CDCl_3$ 151 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm), and the signals are described as br (broad singlet), d (doublet), dd (doublet of doublet), m (multiple), q (quartet), s (singlet), and t (triplet). Coupling constants (J values) are given in Hz. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded at an ionizing voltage of 30 eV. Column chromatography was carried out on silica gel (70−140 μM). All reactions were monitored using TLC on silica gel plates. All of the reagents were used directly as obtained commercially or synthesized according to literature procedures. NIS and NCS were purchased from Tokyo Chemical Industry Co., Ltd., NBS was purchased from a commercial supplier. Alkynylbenzenes **1a**,[17] **1d**,[17b] **1f**,[17a] **1g**,[18] **1h**,[17c] **1i**,[17c] **1j**,[19] **1k**,[20] **1m**,[21] **1n**,[17b17d,21] **1o**,[21,22] **1p**,[21] **1q**,[21] and **1r**[23] and benzofuran **3**[24] are all known compounds. 1-Phenyl-1-hexyne (**1e**) was purchased from a commercial supplier.

*Ethyl (4-(Hex-1-yn-1-yl)phenyl)carbamate (**1b**).* 4-Iodoaniline (300 mg, 1.37 mmol), ethyl chloroformate (522 mL, 5.48 mmol), and K_2CO_3 (1.1 g, 8.22 mmol) were stirred in 5 mL of acetone at room temperature for 2 h.[25] Then the reaction mixture was diluted with water. The organic phase was separated, and the aqueous phase was extracted with AcOEt (three times). Theorganic fractions were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The solids were diluted with chloroform and filtered through a short silica gel column chromatography using 5:1 hexanes/ethyl acetate as an eluent. The product was used in the following step without further purification.

To a solution of the above compound in Et_3N/MeCN (1:1, 6 mL) was added $PdCl_2(PPh)_2$ (29 mg, 0.041 mmol), CuI (8 mg, 0.041 mmol) and 1-hexyne (205 mL, 1.78 mmol) and stirred at room temperature 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 Na_2SO_4, and concentrated at the reduced pressure. Column chromatography on silica gel using 10:1 hexanes/ethyl acetate as an eluent afforded 314 mg (93%, two steps) of **1b** as orange solid. Mp: 108−109 °C (colorless needles from $CHCl_3$−AcOEt). ^{1}H NMR ($CDCl_3$) δ: 7.34−7.29 (4H, m), 6.57 (1H, s), 4.22 (2H, q, J = 7.1 Hz), 2.39 (2H, t, J = 7.2 Hz), 1.60−1.55 (2H, m), 1.50−1.44 (2H, m), 1.31 (3H, t, J = 6.9 Hz), 0.94 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 153.3, 137.2, 132.3, 129.1, 118.9, 118.1, 89.7, 80.1, 61.4, 30.9, 22.0, 19.1, 14.5, 13.7. IR ($CHCl_3$, cm^{-1}): 3435, 2961, 2934, 1732, 1609, 1582, 1518, 1504, 1410, 1252, 1065, 837. MS (EI): m/z = 245 (M^+). HRMS (EI): m/z calcd for $C_{15}H_{19}NO_2$ 245.1416, found 245.1410.

*N-(4-(Hex-1-yn-1-yl)phenyl)acetamide (**1c**).* One drop of concd H_2SO_4 was added to a stirred solution of 4-iodoaniline (300 mg, 1.15 mmol) in acetic anhydride (5 mL).[26] The resulting mixture was stirred at room temperature for 5 min, quenched with water, and extracted with CH_2Cl_2 (three times). The combined organic layers were washed with water, brine and dried with anhydrous Na_2SO_4. The solvent was removed and the crude product was crystallized from ethanol to give the *N*-acetyl derivative as a crystalline solid (293 mg, 83%). To a solution of the above compound (220 mg, 0.84 mmol) in Et_3N/MeCN (1:1, 6 mL) was added $PdCl_2(PPh)_2$ (21 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), and 1-hexyne (126 mL, 1.1 mmol) and stirred at room temperature 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,

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dried over anhydrous Na_2SO_4, and concentrated at the reduced pressure. Column chromatography on silica gel using hexanes/ethyl acetate (5:1−2:1) as an eluent afforded 178 mg (98%) of **1c** as orange solid. ^{1}H NMR ($CDCl_3$) δ: 7.72 (1H, s), 7.44 (2H, d, J = 8.2 Hz), 7.32 (2H, d, J = 8.2 Hz), 2.39 (2H, t, J = 7.2 Hz), 2.15 (3H, s), 1.60−1.55 (2H, m), 1.50−1.45 (2H, m), 0.94 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.5, 137.2, 132.2, 119.8, 119.4, 90.0, 80.1, 30.8, 24.5, 21.0, 19.1, 13.6. IR ($CHCl_3$, cm^{-1}): 3436, 3008, 2961, 2935, 1691, 1583, 1518, 1510, 1402, 1370, 1311, 1290, 1239, 1197, 1110, 1003, 842, 809. MS (EI): m/z = 215 (M^+). HRMS (EI): m/z calcd for $C_{14}H_{17}NO$ 215.1310, found 215.1304.

*5-(4-Methoxyphenyl)pent-4-yn-1-yl 4-Methylbenzenesulfonate (**1l**).* To a solution of 4-iodoanisole (468 mg, 2 mmol) in Et_3N/MeCN (4:1, 5 mL) were added $PdCl_2(PPh)_2$ (42 mg, 0.06 mmol), CuI (11 mg, 0.06 mmol), and 4-pentyn-1-ol (223 mL, 2.4 mmol) and stirred at room temperature under nitrogen for 4.5 h. 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 Na_2SO_4, and concentrated at the reduced pressure. Column chromatography on silica gel using hexanes/ethyl acetate (3:1) as an eluent afforded 380 mg (quant) of alkynylated product. Under an nitrogen atmosphere, to a solution of the above compound (325 mg, 1.55 mmol) in CH_2Cl_2 (15 mL) were added *p*-toluenesulfonyl chloride (414 mg, 2.17 mmol), Et_3N (324 mL, 2.33 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (114 mg, 0.93 mmol) and stirred at room temperature for 4 h.[27] The mixture was diluted with AcOEt and washed with water (two times), saturated aqueous NH_4Cl, brine, dried ($MgSO_4$), and concentrated. Purification by silica gel column chromatography (hexane/AcOEt (5:1)) gave **1j** (534 mg, quant) as a colorless solid. Mp: 31−32 °C (colorless needles from $CHCl_3$−AcOEt). ^{1}H NMR ($CDCl_3$) δ: 7.80 (2H, d, J = 8.2 Hz), 7.30 (2H, d, J = 7.6 Hz), 7.22 (2H, d, J = 8.9 Hz), 6.80 (2H, d, J = 8.9 Hz), 4.20 (2H, t, J = 6.2 Hz), 3.79 (3H, s), 2.45 (2H, t, J = 6.9 Hz), 2.39 (3H, s), 1.94−1.89 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 159.1, 144.70, 132.9, 132.8, 129.8, 127.9, 115.5, 113.7, 85.9, 81.4, 69.0, 55.2, 28.0, 21.6, 15.6. IR ($CHCl_3$, cm^{-1}): 2839, 1608, 1510, 1465, 1362, 1290, 1246, 1237, 1176, 1098, 1019, 978, 957, 932, 833, 811. MS (EI): m/z = 344 (M^+). HRMS (EI): m/z calcd for $C_{19}H_{20}O_4S$ 344.1082, found 344.1076.

General Procedure for Cohalogenation of Alkynylbenzenes. To a solution of alkynylbenzene **1** (0.1 mmol) and NIS in 1,2-dichloroethane (0.5 mL) was added AcOH, and the mixture was stirred at 70 °C. After completion of the reaction (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 **2**.

*(E)-2-Iodo-1-(4-methoxyphenyl)hex-1-en-1-yl Acetate (**2a**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.42 (2H, d, J = 8.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.52 (2H, t, J = 7.2 Hz), 2.11 (3H, s), 1.58−1.53 (2H, m), 1.37 (2H, td, J = 14.8, 7.6 Hz), 0.95 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.4, 159.7, 146.1, 131.1, 130.0, 113.2, 96.4, 55.2, 37.9, 31.1, 21.7, 20.6, 13.9. IR ($CHCl_3$, cm^{-1}) 3034, 1753, 1607, 1510, 1296, 1175, 1022. MS (EI): m/z = 374 (M^+). HRMS (EI): m/z calcd for $C_{15}H_{19}IO_3$ 374.0379, found 374.0383.

*(E)-2-Bromo-1-(4-methoxyphenyl)hex-1-en-1-yl Acetate (**2a′**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.46 (2H, d, J = 8.9 Hz), 6.87 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.52 (2H, t, J = 7.6 Hz), 2.13 (3H, s), 1.62−1.57 (2H, m), 1.40−1.34 (2H, m), 0.95 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.4, 159.6, 143.6, 130.6, 127.8, 118.7, 113.2, 55.2, 34.9, 29.8, 21.8, 20.7, 13.8. IR ($CHCl_3$, cm^{-1}): 2961, 1756, 1608, 1511, 1370, 1298, 1249, 1174, 1086, 1024. MS (EI): m/z = 326 (M^+). HRMS (EI): m/z calcd for $C_{15}H_{19}BrO_3$ 326.0518, found 326.0507.

*(E)-1-(4-((Ethoxycarbonyl)amino)phenyl)-2-iodohex-1-en-1-yl Acetate (**2b**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.43 (2H, d, J = 8.6 Hz), 7.36 (2H, d, J = 8.6 Hz), 6.74 (1H, s), 4.22 (2H, q, J = 7.1 Hz), 2.52 (2H, t, J = 7.2 Hz), 2.11 (3H, s), 1.58−1.53 (2H, m), 1.40−1.34 (2H, m), 1.30 (3H, t, J = 7.2 Hz), 0.95 (3H, t, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.4, 153.4, 145.8, 138.4, 132.3, 130.6, 117.6, 96.6, 61.3, 37.9, 31.1, 21.6, 20.6, 14.5, 13.9. IR ($CHCl_3$, cm^{-1}): 3433, 2961, 1736, 1609, 1587, 1522, 1408, 1371, 1314, 1238, 1194, 1180, 1065, 841. MS (EI): m/z = 431 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{22}INO_4$ 431.0594, found 431.0591.

*(E)-1-(4-Acetamidophenyl)-2-iodohex-1-en-1-yl Acetate (**2c**).* Yellow solid. Mp: 132−134 °C (colorless plate from AcOEt). ^{1}H NMR ($CDCl_3$) δ: 7.48 (2H, d, J = 8.9 Hz), 7.44 (2H, d, J = 8.9 Hz), 7.26 (1H, s), 2.53 (2H, t, J = 7.6 Hz), 2.18 (3H, s), 2.11 (3H, s), 1.58−1.53 (2H, m), 1.39−1.35 (2H, m), 0.95 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.5, 145.7, 138.3, 133.2, 130.5, 118.9, 96.7, 37.9, 31.0, 24.6, 21.6, 20.6, 13.9. IR ($CHCl_3$, cm^{-1}): 3435, 3036, 2959, 2932, 2874, 1753, 1694, 1589, 1514, 1402, 1369, 1312, 1240, 1192, 1180, 1076, 1015, 810. MS (EI): m/z = 401 (M^+). HRMS (EI): m/z calcd for $C_{16}H_{20}INO_3$ 401.0488, found 401.0483.

*(E)-2-Iodo-1-(p-tolyl)hex-1-en-1-yl Acetate (**2d**).* Yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.37 (2H, d, J = 8.2 Hz), 7.15 (2H, d, J = 8.2 Hz), 2.53 (2H, t, J = 7.6 Hz), 2.35 (3H, s), 2.10 (3H, s), 1.58−1.53 (2H, m), 1.40−1.35 (2H, m), 0.95 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.3, 146.3, 138.8, 134.7, 129.6, 128.6, 96.5, 37.8, 31.1, 21.7, 21.4, 20.6, 13.9. IR ($CHCl_3$, cm^{-1}): 2959, 2930, 2874, 1753, 1510, 1456, 1369, 1236, 1196, 1182, 1076, 1016, 700. MS (EI): m/z = 358 (M^+). HRMS (EI): m/z calcd for $C_{15}H_{19}IO_2$ 358.0430, found 358.0429.

*(E)-2-Iodo-1-(2-methoxyphenyl)hex-1-en-1-yl Acetate (**2h**).* Orange oil. ^{1}H NMR ($CDCl_3$) δ: 7.40 (1H, dd, J = 7.6, 1.7 Hz), 7.33 (1H, td, J = 7.9, 1.7 Hz), 6.96−6.90 (2H, m), 3.86 (3H, s), 2.53 (2H, t, J = 7.4 Hz), 2.09 (3H, s), 1.59−1.54 (2H, m), 1.42−1.37 (2H, m), 0.96 (3H, t, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.3, 157.0, 144.1, 132.7, 130.5, 126.9, 120.1, 111.1, 100.0, 55.8, 37.1, 31.3, 21.6, 20.6, 13.9. IR ($CHCl_3$, cm^{-1}): 2960, 2934, 1751, 1598, 1490, 1465, 1436, 1369, 1288, 1257, 1236, 1195, 1114, 1077, 1050, 1018. MS (EI): m/z = 374 (M^+). HRMS (EI): m/z calcd for $C_{15}H_{19}IO_3$ 374.0379, found 374.0378.

*(E)-2-Iodo-1-(thiophen-2-yl)hex-1-en-1-yl Acetate (**2j**).* Dark brown oil. ^{1}H NMR ($CDCl_3$) δ: 7.43 (1H, q, J = 1.6 Hz), 7.33 (1H, q, J = 2.1 Hz), 7.02 (1H, dd, J = 4.8, 3.4 Hz), 2.56 (2H, t, J = 7.6 Hz), 2.20 (3H, s), 1.58−1.53 (2H, m), 1.39−1.34 (2H, m), 0.94 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.23, 140.6, 138.3, 129.8, 126.7, 126.5, 97.3, 38.9, 31.1, 21.7, 20.5, 13.9. IR ($CHCl_3$, cm^{-1}): 2960, 2933, 2874, 1761, 1603, 1466, 1427, 1370, 1237, 1194, 1079, 1016, 965. MS (EI): m/z = 374 (M^+). HRMS (EI): m/z calcd for $C_{12}H_{15}IO_2S$ 349.9837, found 349.9839.

*(E)-2-Iodo-1-(4-methoxyphenyl)-5-(tosyloxy)pent-1-en-1-yl Acetate (**2l**).* Pale yellow solid. Mp: 72−73 °C (colorless plates from hexane−Et_2O). ^{1}H NMR ($CDCl_3$) δ: 7.81 (2H, d, J = 6.9 Hz), 7.39−7.35 (4H, m), 6.86 (2H, d, J = 8.2 Hz), 4.07 (2H, t, J = 6.2 Hz), 3.81 (3H, d, J = 1.4 Hz), 2.64 (2H, t, J = 7.2 Hz), 2.46 (3H, s), 2.13 (3H, s), 1.92 (2H, t, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 168.5, 159.9, 147.6, 144.8, 133.1, 131.0, 129.9, 129.5, 127.9, 113.2, 93.0, 69.0, 55.2, 34.3, 28.2, 21.7, 20.6. IR ($CHCl_3$, cm^{-1}): 1754, 1609, 1510, 1366, 1298, 1245, 1176, 1027. MS (EI): m/z = 530 (M^+). HRMS (EI): m/z calcd for $C_{21}H_{23}IO_6S$ 530.0260, found 530.0253.

*(E)-2-Cyclohexyl-2-iodo-1-(4-methoxyphenyl)vinyl Acetate (**2m**).* Pale yellow solid. Mp: 82−83 °C (colorless needles from hexane−Et_2O). ^{1}H NMR ($CDCl_3$) δ: 7.39 (2H, d, J = 8.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.12 (3H, s), 2.01−1.96 (1H, m), 1.81 (2H, d, J = 6.9 Hz), 1.68 (1H, d, J = 12.4 Hz), 1.62−1.60 (2H, m), 1.45−1.36 (4H, m), 1.22−1.17 (1H, m). ^{13}C NMR ($CDCl_3$) δ: 168.5, 159.6, 144.5, 131.4, 130.5, 113.2, 107.3, 55.2, 42.0, 33.1, 25.7, 25.6, 20.7. IR ($CHCl_3$, cm^{-1}): 2934, 2856, 1751, 1607, 1510, 1450, 1297, 1247, 1197, 1174, 1028, 912, 836. MS (EI): m/z = 400 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{21}IO_3$ 400.0535, found 400.0527.

*(E)-2-Iodo-1-(4-methoxyphenyl)-2-phenylvinyl Acetate ((E)-**2n**).* Yellow needle. ^{1}H NMR ($CDCl_3$) δ: 7.59 (2H, d, J = 8.9 Hz), 7.41 (2H, dd, J = 8.2, 1.4 Hz), 7.34 (2H, t, J = 7.9 Hz), 7.26 (1H, t, J = 7.6 Hz), 6.92 (2H, d, J = 8.9 Hz), 3.84 (3H, s), 1.83 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.7, 160.1, 147.1, 140.9, 131.1, 129.4, 128.5, 128.2, 113.4, 99.9, 88.2, 55.3, 20.4. IR ($CHCl_3$, cm^{-1}): 1757, 1608, 1370, 1299, 1250, 1196, 1174, 1046, 1031. MS (EI): m/z = 394 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{15}IO_3$ 394.0066, found 394.0069.

*(Z)-2-Iodo-1-(4-methoxyphenyl)-2-phenylvinyl Acetate ((Z)-**2n**).* Yellow solid. Mp: 126−128 °C (pale yellow plates from hexane−Et_2O). ^{1}H NMR ($CDCl_3$) δ: 7.28 (2H, d, J = 6.9 Hz),

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7.22−7.17 (3H, m), 7.07 (2H, d, J = 8.9 Hz), 6.65 (2H, d, J = 8.2 Hz), 3.72 (3H, s), 2.29 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.0, 159.6, 149.9, 140.8, 130.2, 130.1, 128.4, 128.1, 125.8, 113.5, 89.9, 55.1, 21.4. IR ($CHCl_3$, cm^{-1}): 2840, 1764, 1606, 1511, 1464, 1443, 1369, 1300, 1253, 1195, 1174, 1059, 1032, 922. MS (EI): m/z = 394 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{15}IO_3$ 394.0066, found 394.0067.

*(E)-2-Iodo-1-(4-methoxyphenyl)-2-(p-tolyl)vinyl Acetate ((E)-**2o**).* Pale yellow plates. ^{1}H NMR ($CDCl_3$) δ: 7.58 (2H, d, J = 8.9 Hz), 7.31 (2H, d, J = 8.2 Hz), 7.14 (2H, d, J = 8.2 Hz), 6.92 (2H, d, J = 8.9 Hz), 3.84 (3H, s), 2.35 (3H, s), 1.85 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.8, 160.0, 146.8, 138.1, 138.0, 131.1, 129.7, 128.9, 128.4, 113.4, 99.9, 88.8, 55.3, 21.3, 20.5. IR ($CHCl_3$, cm^{-1}): 1757, 1608, 1513, 1370, 1298, 1251, 1196, 1173, 1045, 1031. MS (EI): m/z = 408 (M^+). HRMS (EI): m/z calcd for $C_{18}H_{17}IO_3$ 408.0222, found 408.0230.

*(Z)-2-Iodo-1-(4-methoxyphenyl)-2-(p-tolyl)vinyl Acetate ((Z)-**2o**).* Yellow solid. Mp: 85−86 °C (yellow needles from hexane−AcOEt). ^{1}H NMR ($CDCl_3$) δ: 7.17 (2H, d, J = 8.2 Hz), 7.08 (2H, d, J = 8.9 Hz), 7.01 (2H, d, J = 7.6 Hz), 6.66 (2H, d, J = 8.9 Hz), 3.73 (3H, s), 2.30 (3H, s), 2.28 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.0, 159.5, 149.5, 138.1, 137.9, 130.1, 130.0, 129.1, 125.9, 113.5, 90.3, 55.1, 21.4, 21.3. IR ($CHCl_3$, cm^{-1}): 2936, 1762, 1606, 1512, 1506, 1465, 1442, 1369, 1300, 1252, 1193, 1175, 1116, 1059, 1032, 922. MS (EI): m/z = 408 (M^+). HRMS (EI): m/z calcd for $C_{18}H_{17}IO_3$ 408.0222, found 408.0223.

*2-(4-Fluorophenyl)-2-iodo-1-(4-methoxyphenyl)vinyl Acetate (**2p**).* Compound **2p** was obtained as a mixture of isomer. Yellow oil. IR ($CHCl_3$, cm^{-1}): 1762, 1600, 1511, 1506, 1464, 1370, 1300, 1252, 1239, 1192, 1174, 1060, 1032, 922, 843, 811. MS (EI): m/z = 412 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{14}FIO_3$ 411.9972, found 411.9973. (*Z*)-**2p**: ^{1}H NMR ($CDCl_3$) δ: 7.26 (2H, td, J = 5.8, 2.7 Hz), 7.02 (2H, t, J = 8.6 Hz), 6.92−6.87 (2H, m), 6.66 (2H, d, J = 8.9 Hz), 3.72 (3H, s), 2.27 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 167.9, 162.9, 161.3, 159.7, 150.3, 136.9, 136.9, 132.1, 132.0, 130.2, 125.6, 115.5, 115.4, 113.6, 88.5, 55.2, 21.34. (*E*)-**2p**: ^{1}H NMR ($CDCl_3$) δ: 7.57 (2H, d, J = 8.2 Hz), 7.40 (2H, q, J = 4.8 Hz), 7.02 (2H, t, J = 8.6 Hz), 6.92−6.87 (2H, m), 3.83 (3H, s), 1.84 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.6, 160.2, 147.5, 132.4, 131.0, 130.4, 130.4, 129.2, 115.3, 115.1, 114.4, 113.4, 86.8, 55.3, 20.4.

*2-Iodo-1,2-bis(4-methoxyphenyl)vinyl Acetate (**2q**).* Compound **2q** was obtained as a mixture of isomers. Yellow oil. IR ($CHCl_3$, cm^{-1}): 1762, 1605, 1511, 1506, 1465, 1457, 1370, 1293, 1250, 1196, 1174, 1059, 1032, 838. MS (EI): m/z = 424 (M^+). HRMS (EI): m/z calcd for $C_{18}H_{17}IO_4$ 424.0172, found 424.0173. (*Z*)-**2q**: ^{1}H NMR ($CDCl_3$) δ: 7.21 (2H, d, J = 8.9 Hz), 7.08 (2H, d, J = 8.2 Hz), 6.73 (2H, d, J = 8.2 Hz), 6.66 (2H, d, J = 8.9 Hz), 3.77 (3H, s), 3.72 (3H, s), 2.27 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.0, 159.5, 159.2, 149.3, 133.1, 131.5, 130.1, 126.0, 113.8, 113.5, 90.2, 55.2, 55.1, 21.4. (*E*)-**2q**: ^{1}H NMR ($CDCl_3$) δ: 7.57 (2H, d, J = 8.2 Hz), 7.36 (2H, d, J = 8.2 Hz), 6.91 (2H, d, J = 8.2 Hz), 6.86 (2H, d, J = 8.2 Hz), 3.83 (3H, s), 3.82 (3H, s), 1.85 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.7, 160.0, 159.3, 146.7, 133.2, 131.1, 129.9, 129.7, 113.5, 113.4, 88.6, 55.3, 55.3, 20.5.

*2-Iodo-2-(3-methoxyphenyl)-1-(4-methoxyphenyl)vinyl Acetate (**2r**).* Compound **2r** was obtained as a mixture of isomers. Yellow oil. IR ($CHCl_3$, cm^{-1}) 1759, 1606, 1511, 1482, 1430, 1370, 1288, 1253, 1238, 1195, 1059, 811. MS (EI): m/z = 424 (M^+). HRMS (EI): m/z calcd for $C_{18}H_{17}IO_4$ 424.0172, found 424.0168. (*Z*)-**2r**: ^{1}H NMR ($CDCl_3$) δ: 7.12−7.08 (3H, m), 6.85−6.84 (2H, m), 6.73 (1H, d, J = 7.6 Hz), 6.66 (2H, d, J = 8.2 Hz), 3.72 (3H, s), 3.70 (3H, s), 2.28 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 167.9, 159.6, 159.2, 149.9, 142.0, 130.0, 129.4, 125.8, 122.5, 115.3, 114.3, 113.5, 89.5, 55.2, 55.1, 21.4. (*E*)-**2r**: ^{1}H NMR ($CDCl_3$) δ: 7.59 (2H, d, J = 8.9 Hz), 7.24 (1H, t, J = 7.2 Hz), 7.00 (1H, d, J = 6.9 Hz), 6.95 (1H, s), 6.92 (2H, d, J = 8.2 Hz), 6.81 (1H, dd, J = 8.2, 2.7 Hz), 3.84 (3H, s), 3.81 (3H, s), 1.85 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 168.7, 160.1, 159.2, 147.2, 131.1, 129.4, 129.2, 120.8, 114.3, 113.7, 113.4, 87.9, 55.3, 55.3, 20.5.

*(E)-2-Iodo-1-(4-methoxyphenyl)hex-1-en-1-yl Cyclopropanecarboxylate (**2s**).* Pale yellow solid. ^{1}H NMR ($CDCl_3$) δ: 7.41 (2H, d, J = 8.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 3.81 (3H, s), 2.53 (2H, t, J = 7.6 Hz), 1.70−1.66 (1H, m), 1.59−1.53 (2H, m), 1.41−1.34 (2H, m), 1.03−1.00 (2H, m), 0.95 (3H, t, J = 7.2 Hz), 0.92−0.89 (2H, m). ^{13}C NMR ($CDCl_3$) δ: 172.3, 159.6, 146.1, 131.1, 129.9, 113.1, 96.2, 55.2, 37.8, 31.0, 21.7, 13.9, 12.6, 8.8. IR ($CHCl_3$, cm^{-1}): 2960, 2933, 1743, 1740, 1608, 1510, 1465, 1457, 1385, 1297, 1244, 1235, 1176, 1142, 1099, 1033. MS (EI): m/z = 400 (M^+). HRMS (EI): m/z calcd for $C_{17}H_{21}IO_3$ 400.0535, found 400.0543.

*(E)-2-Iodo-1-(4-methoxyphenyl)hex-1-en-1-yl Benzoate (**2t**).* Colorless oil. ^{1}H NMR ($CDCl_3$) δ: 8.07 (2H, dd, J = 8.2, 1.4 Hz), 7.59 (1H, t, J = 7.6 Hz), 7.52 (2H, d, J = 8.2 Hz), 7.46 (2H, t, J = 7.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 3.79 (3H, s), 2.60 (2H, t, J = 7.6 Hz), 1.61−1.56 (2H, m), 1.39−1.33 (2H, m), 0.91 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 164.0, 159.8, 146.2, 133.6, 131.2, 129.0, 129.8, 129.1, 128.6, 113.2, 96.4, 55.2, 38.0, 31.2, 21.6, 13.9. IR ($CHCl_3$, cm^{-1}): 2960, 2933, 1733, 1608, 1507, 1465, 1452, 1297, 1270, 1242, 1175, 1085, 1066, 1025, 833, 810. MS (EI): m/z = 436 (M^+). HRMS (EI): m/z calcd for $C_{20}H_{21}IO_3$ 436.0535, found 436.0544.

General Procedure for One-Pot Synthesis of Multisubsutituted Enol Esters. To a solution of alkynylbenzene **1** (0.1 mmol) and NIS in 1,2-dichloroethane (0.5 mL) was added AcOH, and the mixture was stirred at 70 °C for 1 h. A 10% $Na_2S_2O_3$ aqueous solution was added for quenching and the mixture stirred for 5 min. Then toluene, boronic acid (1.5 equiv), Pd catalyst (0.1 equiv), and K_2CO_3 (3 equiv) were added, and the mixture was stirred at 90 °C. 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 **4** and **5**.

*(E)-1-(4-Methoxyphenyl)-2-phenylhex-1-en-1-yl Acetate (**4a**).* Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.21−7.11 (5H, m), 7.01 (2H, d, J = 8.9 Hz), 6.62 (2H, d, J = 8.9 Hz), 3.70 (3H, s), 2.44 (2H, t, J = 7.2 Hz), 2.21 (3H, s), 1.32−1.29 (4H, m), 0.86 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 169.2, 158.6, 142.8, 139.5, 130.5, 130.1, 129.5, 128.2, 128.1, 126.6, 113.1, 55.0, 32.5, 29.4, 22.5, 21.0, 13.8. IR ($CHCl_3$, cm^{-1}): 2959, 2932, 1751, 1609, 1510, 1464, 1443, 1369, 1296, 1250, 1238, 1196, 1177, 1090, 1036, 837. MS (EI): m/z = 324 (M^+). HRMS (EI): m/z calcd for $C_{21}H_{24}O_3$ 324.1725, found 324.1717.

*(E)-1-(4-Methoxyphenyl)-2-((E)-styryl)hex-1-en-1-yl Acetate (**4b**).* Yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.36 (2H, d, J = 8.9 Hz), 7.31−7.25 (4H, m), 7.19 (1H, t, J = 6.9 Hz), 6.92−6.90 (3H, m), 6.65 (1H, d, J = 16.5 Hz), 3.84 (3H, s), 2.41 (2H, t, J = 7.9 Hz), 2.19 (3H, s), 1.57−1.41 (4H, m), 0.97 (3H, t, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 169.4, 159.6, 146.4, 137.7, 130.8, 128.9, 128.6, 127.9, 127.6, 127.2, 126.3, 126.1, 113.6, 55.3, 30.7, 26.7, 23.0, 21.0, 14.0. IR ($CHCl_3$, cm^{-1}): 2960, 2934, 1747, 1606, 1510, 1465, 1369, 1296, 1251, 1193, 1175, 1101, 1054, 1033, 839. MS (EI): m/z = 350 (M^+). HRMS (EI): m/z calcd for $C_{23}H_{26}O_3$ 350.1882, found 350.1885.

*(E)-1-(4-Methoxyphenyl)-2-(1-phenylvinyl)hex-1-en-1-yl Acetate (**4c**).* Yellow oil. ^{1}H NMR ($CDCl_3$) δ: 7.56 (2H, d, J = 6.9 Hz), 7.37−7.28 (5H, m), 6.70 (2H, d, J = 8.2 Hz), 5.49 (1H, s), 4.97 (1H, s), 3.73 (3H, s), 2.22 (3H, s), 2.10 (2H, t, J = 7.6 Hz), 1.36−1.26 (4H, m), 0.86 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ: 169.2, 159.0, 145.6, 143.9, 138.9, 130.5, 129.3, 128.5, 128.3, 127.8, 126.8, 116.1, 113.1, 55.1, 29.9, 29.4, 22.4, 20.9, 13.9. IR ($CHCl_3$, cm^{-1}) 2962, 2935, 1757, 1714, 1601, 1513, 1254, 1239, 1175, 1031. MS (EI): m/z = 350 (M^+). HRMS (EI): m/z calcd for $C_{23}H_{26}O_3$ 350.1882, found 350.1884.

*1-(4-Methoxyphenyl)-2,2-diphenylvinyl Acetate (**5a**).* Pale yellow solid. ^{1}H NMR ($CDCl_3$) δ: 7.33−7.23 (5H, m), 7.17−7.15 (5H, m), 7.10−7.08 (2H, m), 6.70 (2H, d, J = 8.9 Hz), 3.75 (3H, s), 1.98 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 169.9, 159.2, 143.8, 140.3, 140.0, 130.8, 130.3, 129.0, 128.1, 128.1, 128.1, 127.2, 127.0, 113.4, 55.1, 20.9. IR ($CHCl_3$, cm^{-1}): 1754, 1608, 1512, 1444, 1370, 1293, 1250, 1237, 1170, 1055, 1033, 835. MS (EI): m/z = 344 (M^+). HRMS (EI): m/z calcd for $C_{23}H_{20}O_3$ 344.1412, found 344.1417.

*(1E,3E)-1-(4-Methoxyphenyl)-2,4-diphenylbuta-1,3-dien-1-yl Acetate (**5b**).* Yellow solid. ^{1}H NMR ($CDCl_3$) δ: 7.35−7.21 (11H, m), 7.01 (2H, d, J = 8.9 Hz), 6.63 (2H, d, J = 8.9 Hz), 6.22 (1H, d, J = 15.8 Hz), 3.72 (3H, s), 2.35 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 169.1, 159.0, 144.6, 137.5, 136.8, 133.0, 131.1, 129.9, 129.1, 128.6, 128.5, 127.8, 127.7, 127.4, 126.6, 125.8, 113.2, 55.1, 21.1. IR ($CHCl_3$, cm^{-1}): 1755, 1603, 1510, 1492, 1443, 1370, 1296, 1253, 1237, 1176, 1125, 1040,

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1022, 836. MS (EI): m/z = 370 (M^+). HRMS (EI): m/z calcd for $C_{25}H_{22}O_3$ 370.1569, found 370.1569.

*(Z)-1-(4-Methoxyphenyl)-2,3-diphenylbuta-1,3-dien-1-yl Acetate (**5c**).* Orange oil. ^{1}H NMR ($CDCl_3$) δ: 7.50 (2H, d, J = 8.2 Hz), 7.30−7.10 (10H, m), 6.69 (2H, d, J = 8.2 Hz), 5.64 (1H, s), 5.29 (1H, s), 3.73 (3H, s), 1.83 (3H, s). ^{13}C NMR ($CDCl_3$) δ: 169.1, 159.2, 147.6, 144.9, 139.9, 138.6, 130.4, 130.3, 128.3, 128.1, 128.0, 127.5, 127.0, 126.7, 117.0, 113.4, 113.4, 55.1, 20.6. IR ($CHCl_3$, cm^{-1}): 1761, 1654, 1600, 1511, 1258, 1167, 1032, 837. MS (EI): m/z = 370 (M^+). HRMS (EI): m/z calcd for $C_{25}H_{22}O_3$ 370.1569, found 370.1571.

■ ASSOCIATED CONTENT

Supporting Information

1H and 13C NMR spectra of obtained compounds. Thermal ellipsoid plots of the crystallographic structures of **2l**−**o**. X-ray data for compounds **2l**−**o** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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