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Indium(III) Chloride Catalyzed Conjugate Addition Reaction of Alkynylsilanes to Acrylate Esters

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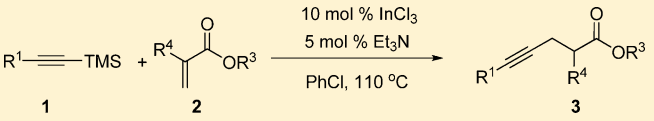
Supporting Information

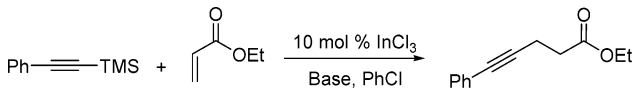
ABSTRACT: A novel and efficient procedure for the synthesis of δ,γ-alkynyl esters by the conjugate addition of alkynylsilanes to acrylate esters in the presence of a catalytic amount of indium(III) chloride has been developed. This method provides a rapid and efficient access to substituted δ,γ-alkynyl esters.



The importance of the chemistry of the carbon−carbon triple bond has been well recognized since this functional group has been shown to be one of the main building blocks of organic and material chemistry.[1] The conjugate addition of alkynes to α,β-unsaturated carbonyl compounds is a powerful strategy for constructing a new sp−sp^3 C−C bond.[2] However, the one-pot synthesis of δ,γ-alkynyl esters directly from alkynes with α,β-unsaturated esters catalyzed by a catalytic amount of Lewis acid is much less studied. Recently, efficient conjugate additions of terminal alkynes to acrylate esters in the presence of $Ru_3(CO)_{12}$/halide[3] or $Pd(OAc)_2$/NHCs,[4] which led to the synthesis of δ,γ-alkynyl esters, have been reported. Nevertheless, with either method, the peculiarity and high cost of such catalyst are a barrier to its large-scale use. Therefore, the development of a general, efficient, cheap, and readily available catalyst for the formation of δ,γ-alkynyl esters by the conjugate addition reaction is of significance. Herein, we describe a highly efficient conjugate addition reaction for the synthesis of δ,γ-alkynyl esters directly from alkynylsilanes and acrylate esters using indium(III) chloride as catalyst.

The $InCl_3$-catalyzed conjugate addition of alkynylsilanes to acrylate esters proceeded smoothly to give δ,γ-alkynyl esters.[5] First, using 1-phenyl-2-trimethylsilylacetylene (**1a**) with ethyl acrylate (**2a**) as a model substrate, the effects of the additives, such as organic and inorganic bases, in the conjugate addition were investigated (Table 1). In the absence of bases, treatment of 1-phenyl-2-trimethylsilylacetylene (**1a**) with ethyl acrylate (**2a**) in the presence of $InCl_3$ gave ethyl 5-phenylpent-4-ynoate (**3aa**) in 60% yield (Table 1, entry 1). When using alkali metal salts or Et_3N as additives, δ,γ-alkynyl ester **3aa** was obtained in higher yields (Table 1, entries 2−6). Especially, in the presence of Et_3N, the yield of product **3aa** increased up to 92% (Table 1, entry 6). When other organic bases such as $(i\text{-Pr})_2NH$, pyridine, and $HOCH_2CH_2NH_2$ were used, the yield of **3aa** dramatically decreased to 10−30% (Table 1, entries 7−9). Moreover, the use of sodium acetate and sodium bicarbonate led to product **3aa** in lower yields (Table 1, entries 10 and 11). A control experiment confirmed that in the absence of $InCl_3$ the reaction led to recovery of starting materials. The results

Table 1. Effect of Additives[a]



1a **2a** **3aa**

entry	base	yield[b] (%)
1		60
2	Li_2CO_3	65
3	Na_2CO_3	68
4	K_2CO_3	80
5	Cs_2CO_3	70
6	Et_3N	92
7	$(i\text{-Pr})_2NH$	20
8	pyridine	30
9	$HOCH_2CH_2NH_2$	10
10	CH_3COONa	5
11	$NaHCO_3$	10
12	Et_3N (20 mol %)	0

[a]Reaction conditions: alkynylsilane **1a** (0.3 mmol), ethyl acrylate **2a** (0.45 mmol), $InCl_3$ (10 mol % to **1a**), additives (5 mol % to **1a**), PhCl (2.0 mL), 110 °C, sealed tube, 24 h. [b]Isolated yield of pure product based on **1a**.

showed that $InCl_3/Et_3N$ is the best combination for promoting conjugate addition of alkynylsilanes to acrylate esters. Interestingly, when the amount of Et_3N was increased to 20 mol %, the reaction led to 1,4-diphenylbuta-1,3-diyne, which is the coupling product of phenylacetylene under the strong base conditions (Table 1, entry 12).[6] Therefore, 5 mol % Et_3N was selected as the base of choice for further screening reactions.

With this optimal base in hand, a variety of Lewis acid catalysts and solvents were screened using 1-phenyl-2-trimethylsilylacetylene **1a** with ethyl acrylate **2a** as a model system (Table 2). Initially, the reaction of **1a** and **2a** gave **3aa** in 92% yield in the presence of 10 mol % $InCl_3$ and 5 mol % Et_3N in chlorobenzene

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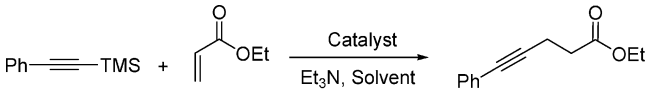
Table 2. Optimization of Reaction Conditions[a−c]



1a 2a 3aa

entry	catalyst	solvent	yield[d] (%)
1	$InCl_3$	PhCl	92
2	$InCl_3$ (5 mol %)	PhCl	82
3	$InCl_3$ (20 mol %)	PhCl	93
4	$Sc(OTf)_3$	PhCl	80
5[e]	$Bi(OTf)_3$	PhCl	70
6	$Fe(OTf)_3$	PhCl	50
7	$In(OTf)_3$	PhCl	20
8	$InCl_3$	CH_3CN	10
9	$InCl_3$	$PhCH_3$	5

[a]Reaction conditions: alkynylsilane **1a** (0.3 mmol), ethyl acrylate **2a** (0.45 mmol), catalyst (10 mol % to **1a**), Et_3N (5 mol % to **1a**), solvent (2.0 mL), 110 °C, sealed tube, 24 h. [b]Inactive catalysts: $InBr_3$, InCl, $FeCl_3$, $ZnCl_2$, CuCl, $BiCl_3$, $Cu(OTf)_2$, $Zn(OTf)_2$, AgOTf. [c]Inactive solvents: CH_3NO_2, DCE, THF, DMF, DMSO. [d]Isolated yield of pure product based on **1a**. [e]The reaction time was prolonged to 56 h.

at 110 °C for 24 h. When the amount of $InCl_3$ was decreased to 5 mol %, the yield of product **3aa** decreased to 82% (Table 2, entry 2). However, no improvement in the yield of **3aa** could be obtained, as the amount of $InCl_3$ was increased to 20 mol % (Table 2, entry 3). The conjugate addition of alkynylsilane **1a** to ethyl acrylate **2a** using $Sc(OTf)_3$, $Bi(OTf)_3$, $Fe(OTf)_3$, or $In(OTf)_3$ also provided the product **3aa** in 80%, 70%, 50%, and 20% yields, respectively (Table 2, entries 4−7). Nevertheless, in the presence of other metal catalysts, such as $InBr_3$, InCl, $FeCl_3$, $ZnCl_2$, CuCl, $BiCl_3$, $Cu(OTf)_2$, $Zn(OTf)_2$, or AgOTf, the product **3aa** was not obtained at all. Further optimization suggested that solvents had a strong effect on this process. The reactions were obviously restrained when they were performed in CH_3CN or toluene (Table 2, entries 8 and 9). In other solvents, such as CH_3NO_2, DCE, THF, DMF, and DMSO, most of starting material **1a** was recovered. Hence, it was concluded that the best conditions involved 10 mol % $InCl_3$ and 5 mol % Et_3N, in chlorobenzene at 110 °C for 24 h.

With these optimal conditions in hand, we examined the scope of this conjugate addition reaction. Typical results are shown in Table 3. Phenylacetylene **1b** reacted with ethyl acrylate **2a** in the presence of 50 mol % $InCl_3$ afforded the desired product **3aa** in 56% yield, whereas when using 1-phenyl-2-trimethylsilylacetylene **1a** instead, the yield of product **3aa** dramatically increased to 92% (Table 3, entries 1 vs 2).[7] Among the alkynylsilanes **1a**−**1h** that were examined, alkynylsilane **1c** (R^1 = 4-MeO-C_6H_4) gave the most desirable result, providing the *δ*,*γ*-alkynyl ester **3ca** in 96% yield (Table 3, entry 3 vs entries 2 and 4, 5). Substrate **1d** possessing an electron-withdrawing group (R^1 = 4-Br-C_6H_4) at the benzene ring also reacted smoothly and afforded the desired product **3da** in 78% yield (Table 3, entry 4). However, alkynylsilanes bearing a strong electron-withdrawing group on the benzene ring (R^1 = 4-CN-C_6H_4, 4-CH_3OOC-C_6H_4, or 4-CF_3-C_6H_4) treated with ethyl acrylate **2a** failed to afford the desired products. Obviously, electron-rich alkynylsilanes provided the desired products in higher yields than electron-poor alkynylsilanes did, along with the shorter reaction time (Table 3, entry 3 vs entry 4). Reactions of alkynylsilanes **1** with methyl acrylate (**2b**), *n*-butyl acrylate (**2c**), isobutyl acrylate (**2d**) gave the corresponding *δ*,*γ*-alkynyl esters **3ab**−**3db** in 75−93% yields (Table 3, entries 6−15). Substrate alkynylsilanes bearing a heterocyclic aromatic substituent such as 3-[(trimethylsilyl)ethynyl]-thiophene (R^1 = 3-thienyl) **1f** treated with methyl acrylate **2b** led to the desired product **3fb** in 89% yield (Table 3, entry 16). Remarkablely, the reaction of 1-phenyl-2-trimethylsilylacetylene **1a** and methyl methacrylate **2e** led to the desired product **3ae** in 68% yield under the optimal condition (Table 3, entry 17). Moreover, 1-hexyne **1g** reacted with ethyl acrylate **2a** in the presence of 50 mol % $InCl_3$ giving **3ga** in 55% yield, while using trimethyl(1-hexynyl)silane **1h** instead, the yield of the product **3ga** increased to 86% (Table 3, entries 18 and 19). Unfortunately, the reaction of 1-cyclohexenylethyne or 3,3-dimethyl-1-butyne with ethyl acrylate **2a** failed to give the corresponding products.

To our delight, alkynylsilanes such as **1a**, **1e**, and **1f**, reacted smoothly with 1,6-hexanediol diacrylate **2f** in the presence of 20 mol % $InCl_3$ and 10 mol % Et_3N giving the corresponding products **3af**, **3ef**, and **3ff** in 85%, 89%, and 82% yields, respectively (Scheme 1).

Also, 1,4-bis(2-(trimethylsilyl)ethynyl)benzene **1i** reacted smoothly with ethyl acrylate **2a** in the presence of 20 mol % $InCl_3$ and 10 mol % Et_3N in chlorobenzene at 110 °C for 6 h, affording **4ia** in 85% yield, while the conjugate addition led to the symmetrical *δ*,*γ*-alkynyl esters **3ia** in 72% yield when the reaction time was prolonged to 24 h (Scheme 2).

Interestingly, alkynylsilane **1d** was treated with methyl acrylate **2b** (1.5 equiv) under the optimal condition affording methyl 5-(4-bromophenyl)-4-pentynoate **3db** in 75% yield as usual (Table 3, entry 15). However, when the reaction time was prolonged to 48 h under the same conditions, it led finally to 1,5-ketoester **4db**, due to the hydration of **3db** (Scheme 3). This is in sharp contrast to the hydration of alkynes where the reaction always performs under the rigorous conditions.[8]

Finally, substrate **1a** also reacted with ethyl vinyl ketone **2g** to give 2-benzyl-5-ethylfuran **3ag** in 65% yield under the optimal condition (Scheme 4). This result indicated that $InCl_3$-catalyzed conjugate addition of alkynylsilanes to vinyl ketone afforded *δ*,*γ*-alkynyl ketone, which generated substituted furan by a 5-*exo*-*dig* cyclization.[9]

In summary, we have developed an effective conjugate addition reaction of alkynylsilanes to acrylate esters, which was catalyzed by the commercially available indium catalyst in the presence of Et_3N. The alkyl- and aryl-substituted alkynylsilanes with acrylate esters are readily available. This reaction system can be carried out under mild conditions that give a rapid access to a variety of *δ*,*γ*-alkynyl esters.

EXPERIMENTAL SECTION

General Description. Melting points are uncorrected. NMR spectra were in $CDCl_3$ (^1H at 500 MHz and ^{13}C at 125 MHz or ^1H at 400 MHz and ^{13}C at 100 MHz). Column chromatography was performed on silica gel (300−400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

General Procedure for Synthesis of *δ*,*γ*-Alkynyl Esters 3 and 4. The reaction mixture of alkynylsilanes **1** (0.3 mmol), acrylate esters **2** (0.45 mmol), indium trichloride (0.03 mmol), Et_3N (0.015 mmol), and chlorobenzene (2.0 mL) in a 10 mL sealed tube was stirred at 110 °C and monitored periodically by TLC. Upon completion, chlorobenzene was removed under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (EtOAc/hexane) to afford corresponding *δ*,*γ*-alkynyl esters **3** and **4**.

Ethyl 5-Phenyl-4-pentynoate[3b] (3aa). Pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) *δ* 1.28 (t, *J* = 7.1 Hz, 3H), 2.62 (t, *J* = 7.3 Hz, 2H),

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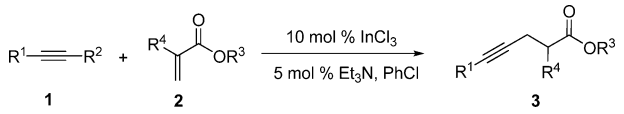
2.73 (t, J = 7.6 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 7.27−7.28 (m, 3H), 7.37−7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ14.2, 15.4, 33.7, 60.7, 81.2, 88.0, 123.6, 127.7, 128.2, 131.7, 171.8; IR (KBr) ν_{max} 3059, 2925, 2208, 1737, 1597, 1490 cm^{-1}; MS m/z = 203 [M + H$^+$].

Ethyl 5-(4-Methoxyphenyl)-4-pentynoate[3b] (3ca). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 3H), 2.59 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 7.3 Hz, 2H), 3.76 (s, 3H), 4.16 (q, J = 7.1 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 7.30 (d, J = 8.9 Hz, 2H); ^{13}C NMR

Table 3. Synthesis of δ,γ-Alkynyl Esters 3 Catalyzed by $InCl_3/Et_3N$[a]



1 2 3

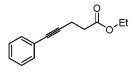
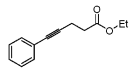
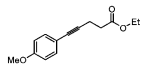
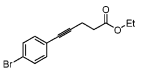
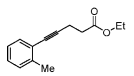
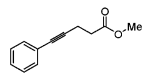
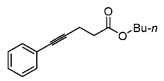
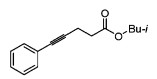
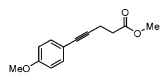
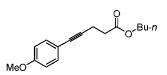
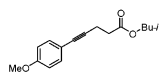
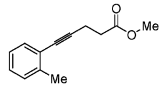
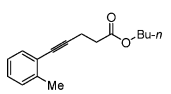
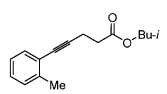
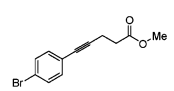
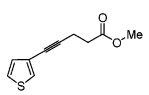
Entry	Alkynylsilane	Acrylate ester	Product	Yield (%)[b]
1	**1a:** R^1 = Ph; R^2 = TMS	**2a:** R^3 = Et; R^4 = H	**3aa:** 	92
2[c]	**1b:** R^1 = Ph; R^2 = H	**2a:** R^3 = Et; R^4 = H	**3aa:** 	56
3[d]	**1c:** R^1= 4-MeO-C_6H_4; R^2 = TMS	**2a:** R^3 = Et; R^4 = H	**3ca:** 	96
4	**1d:** R^1 = 4-Br-C_6H_4; R^2 = TMS	**2a:** R^3 = Et; R^4 = H	**3da:** 	78
5	**1e:** R^1 = 2-Me-C_6H_4 ; R^2 = TMS	**2a:** R^3 = Et; R^4 = H	**3ea:** 	88
6	**1a:** R^1 = Ph; R^2 = TMS	**2b:** R^3 = Me; R^4 = H	**3ab:** 	89
7	**1a:** R^1 = Ph; R^2 = TMS	**2c:** R^3 = *n*-Bu; R^4 = H	**3ac:** 	86
8	**1a:** R^1 = Ph; R^2 = TMS	**2d:** R^3 = *i*-Bu; R^4 = H	**3ad:** 	85
9[d]	**1c:** R^1 = 4-MeO-C_6H_4; R^2 = TMS	**2b:** R^3 = Me; R^4 = H	**3cb:** 	93
10[d]	**1c:** R^1 = 4-MeO-C_6H_4; R^2 = TMS	**2c:** R^3 = *n*-Bu; R^4 = H	**3cc:** 	90
11[d]	**1c:** R^1 = 4-MeO-C_6H_4; R^2 = TMS	**2d:** R^3 = *i*-Bu; R^4 = H	**3cd:** 	86
12	**1e:** R^1 = 2-Me-C_6H_4; R^2 = TMS	**2b:** R^3 = Me; R^4 = H	**3eb:** 	87
13	**1e:** R^1 = 2-Me-C_6H_4; R^2 = TMS	**2c:** R^3 = *n*-Bu; R^4 = H	**3ec:** 	87
14	**1e:** R^1 = 2-Me-C_6H_4; R^2 = TMS	**2d:** R^3 = *i*-Bu; R^4 = H	**3ed:** 	86
15	**1d:** R^1 = 4-Br-C_6H_4; R^2 = TMS	**2b:** R^3 = Me; R^4 = H	**3db:** 	75
16	**1f**: R^1 = 3-Thienyl; R^2 = TMS	**2b:** R^3 = Me; R^4 = H	**3fb:** 	89

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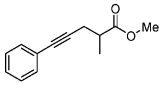
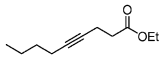
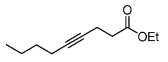
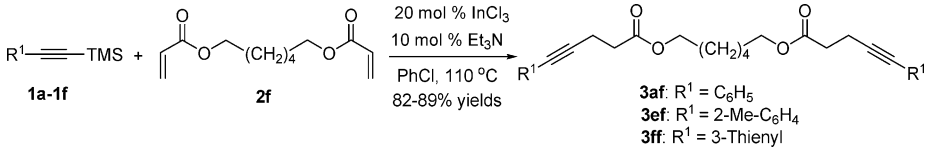
Table 3. continued

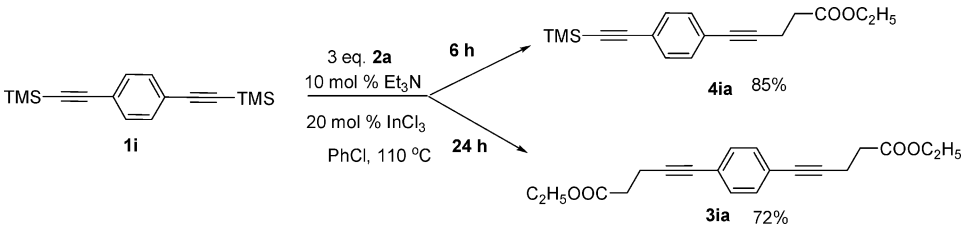
Entry	Alkynylsilane	Acrylate ester	Product	Yield (%)[b]
17	**1a:** R^1 = Ph; R^2 = TMS	**2e:** R^3 = Me; R^4 = Me	**3ae:** 	68
18[c]	**1g**: R^1 = *n*-Bu; R^2 = H	**2a:** R^3 = Et; R^4 = H	**3ga:** 	55
19	**1h**: R^1 = *n*-Bu ; R^2 = TMS	**2a:** R^3 = Et; R^4 = H	**3ga:** 	86

[a]Reaction conditions: alkynylsilanes **1** (0.3 mmol), acrylate esters **2** (0.45 mmol), $InCl_3$ (10 mol % to **1**), Et_3N (5 mol % to **1**), PhCl (2.0 mL), 110 °C, sealed tube, 24 h. [b]Isolated yield of pure product based on **1**. [c]The amount of $InCl_3$ was 50 mol % to **1**, without adding the additives Et_3N, and the reaction time was prolonged to 48 h. [d]All of the reaction times of alkynylsilane **1c** with acrylate esters **2** were shortened to 16 h under the same condition.

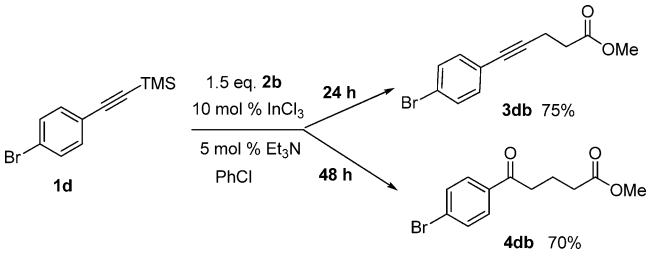
Scheme 1. Synthesis of δ,γ-Alkynyl Esters 3af−3ff from Alkynylsilanes 1a−1f and 1,6-Hexanediol Diacrylate



Scheme 2. Synthesis of δ,γ-Alkynyl Esters 3ia and 4ia from Alkynylsilane 1i and Ethyl Acrylate 2a



Scheme 3. Synthesis of 1,5-Ketoester 4db from Alkynylsilane 1d and Methyl Acrylate 2b



(100 MHz, $CDCl_3$) δ 14.2, 15.3, 33.7, 55.1, 60.5, 80.8, 86.3, 113.7, 115.6, 132.8, 159.1, 171.9; IR (KBr) ν_{max} 3040, 2935, 2044, 1733, 1607, 1510 cm^{-1}; MS *m*/*z* = 233 [M + H^+].

Ethyl 5-(4-Bromophenyl)-4-pentynoate[3b] (3da). Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.1 Hz, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 6.6 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.4, 33.5, 60.6, 80.1, 89.3, 121.9, 122.5, 131.4, 133.0, 171.8. IR (KBr) ν_{max} 3034, 2928, 2242, 1737, 1585, 1486 cm^{-1}; MS *m*/*z* = 282 [M + H^+].

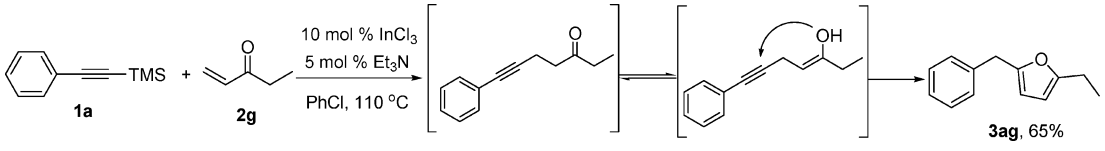
Ethyl 5-(2-Methylphenyl)-4-pentynoate (3ea). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.1 Hz, 3H), 2.40 (s, 3H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 7.07−7.13 (m, 1H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 15.5, 20.5, 33.9, 60.6, 80.0, 92.0, 123.3, 125.4, 127.7, 129.3, 131.8, 139.9, 171.9; IR (KBr) ν_{max} 3062, 2982, 2235, 1737, 1601, 1486 cm^{-1}; MS *m*/*z* = 217 [M + H^+]. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.92; H, 7.19.

Methyl 5-Phenyl-4-pentynoate[4] (3ab). Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 2.64 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 3.72 (s, 3H), 7.28−7.29 (m, 3H), 7.38−7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.3, 33.4, 51.8, 81.2, 87.9, 123.5, 127.8, 128.2, 131.6, 172.3; IR (KBr) ν_{max} 3034, 2953, 2228, 1742, 1598, 1587, 1491 cm^{-1}; MS *m*/*z* = 189 [M + H^+].

***n*-Butyl 5-Phenyl-4-pentynoate[4] (3ac).** Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.33−1.44 (m, 2H), 1.58−1.68 (m, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 2H), 7.27−7.28 (m, 3H), 7.37−7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 15.4, 19.1, 30.6, 33.8, 64.5, 81.1, 88.0, 123.5, 127.7, 128.1, 131.7, 171.9; IR (KBr) ν_{max} 3055, 2960, 2204, 1736, 1599, 1491 cm^{-1}; MS *m*/*z* = 231 [M + H^+].

Isobutyl 5-Phenyl-4-pentynoate (3ad). Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, *J* = 6.7 Hz, 6H), 1.95 (m, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 3.91 (d, *J* = 6.6 Hz, 2H),

Scheme 4. Synthesis of 2-Benzyl-5-ethylfuran 3ag from Alkynylsilane 1a and Ethyl Vinyl Ketone 2g



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7.26−7.27 (m, 3H), 7.37−7.39 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 19.0, 27.7, 33.7, 70.7, 81.1, 88.0, 123.5, 127.7, 128.1, 131.5, 171.9. IR (KBr) ν_{max} 3055, 2963, 2214, 1738, 1599, 1491 cm^{-1}; MS m/z = 231 [M + H$^+$]. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.06; H, 8.02.

Methyl 5-(4-Methoxyphenyl)-4-pentynoate (3cb). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, J = 7.3 Hz, 2H), 2.71 (t, J = 6.7 Hz, 2H), 3.71 (s, 3H), 3.78 (s, 3H), 6.80 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 33.6, 51.7, 55.2, 80.9, 86.3, 113.8, 115.7, 132.9, 159.2, 172.4; IR (KBr) ν_{max} 3002, 2954, 2225, 1739, 1607, 1511 cm^{-1}; MS m/z = 219 [M + H$^+$]. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.32; H, 6.79.

***n*-Butyl 5-(4-Methoxyphenyl)-4-pentynoate (3cc).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 1.43−1.34 (m, 2H), 1.66−1.58 (m, 2H), 2.61 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 3.78 (s, 3H), 4.12 (t, J = 6.7 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 15.4, 19.1, 30.7, 33.8, 55.2, 64.5, 80.9, 86.4, 113.8, 115.7, 132.9, 159.2, 172.1; IR (KBr) ν_{max} 3041, 2958, 2220, 1736, 1607, 1510 cm^{-1}; MS m/z = 261 [M + H$^+$]. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.61; H, 7.88.

Isobutyl 5-(4-Methoxyphenyl)-4-pentynoate (3cd). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 6.7 Hz, 6H), 1.93 (m, 1H), 2.61 (t, J = 6.7 Hz, 2H), 2.70 (t, J = 7.2 Hz, 2H), 3.76 (s, 3H), 3.89 (d, J = 6.6 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 7.30 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 18.9, 27.6, 33.7, 55.1, 70.6, 80.8, 86.3, 113.7, 115.6, 132.8, 159.1, 171.9; IR (KBr) ν_{max} 3041, 2961, 2046, 1733, 1607, 1509 cm^{-1}; MS m/z = 261 [M + H$^+$]. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.60; H, 7.88.

Methyl 5-(2-Methylphenyl)-4-pentynoate (3eb). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.65 (t, J = 7.7 Hz, 2H), 2.78 (t, J = 7.1 Hz, 2H), 3.72 (s, 3H), 7.07−7.12 (m, 1H), 7.17 (dd, J = 5.1, 1.1 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 20.5, 33.7, 51.7, 80.1, 91.8, 123.2, 125.4, 127.7, 129.2, 131.8, 140.0, 172.3; IR (KBr) ν_{max} 3062, 2952, 2233, 1741, 1601, 1486 cm^{-1}; MS m/z = 203 [M + H$^+$]. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 7.12.

***n*-Butyl 5-(2-Methylphenyl)-4-pentynoate (3ec).** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.4 Hz, 3H), 1.38−1.40 (m, 2H), 1.61−1.63 (m, 2H), 2.40 (s, 3H), 2.64 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.1 Hz, 2H), 4.13 (t, J = 6.7 Hz, 2H), 7.07−7.13 (m, 1H), 7.17 (dd, J = 5.1, 1.1 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 15.6, 19.1, 20.6, 30.6, 33.9, 64.5, 80.1, 92.0, 123.3, 125.4, 127.7, 129.2, 131.8, 140.0, 172.0; IR (KBr) ν_{max} 3062, 2960, 2236, 1737, 1601, 1487 cm^{-1}; MS m/z = 245 [M + H$^+$]. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.32; H, 8.38.

Isobutyl 5-(2-Methylphenyl)-4-pentynoate (3ed). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, J = 6.7 Hz, 6H), 1.96 (m, 1H), 2.40 (s, 3H), 2.66 (t, J = 7.8 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 3.92 (d, J = 6.7 Hz, 2H), 7.07−7.13 (m, 1H), 7.17 (dd, J = 5.1, 1.2 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 19.0, 20.6, 27.7, 33.9, 70.7, 80.0, 92.0, 123.3, 125.3, 127.7, 129.2, 131.8, 140.0, 171.9; IR (KBr) ν_{max} 3023, 2963, 2231, 1738, 1601, 1486 cm^{-1}; MS m/z = 245 [M + H$^+$]. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C,78.46; H, 8.37.

Methyl 5-(4-Bromophenyl)-4-pentynoate (3db). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (t, J = 7.5 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 3.71 (s, 3H), 7.23 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 33.2, 51.8, 80.2, 89.2, 121.9, 122.5, 131.4, 133.0, 172.2; IR (KBr) ν_{max} 3032, 2926, 2269, 1734, 1589, 1486 cm^{-1}; MS m/z = 268 [M + H$^+$]. Anal. Calcd for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 53.82; H, 4.38.

Methyl 5-(3-Thienyl)-4-pentynoate (3fb). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.4 Hz, 2H), 3.72 (s, 3H), 7.06 (d, J = 4.8 Hz, 1H), 7.23 (dd, J = 4.5, 3.2 Hz, 1H), 7.36 (s, 1H); ^{13}C NMR (125 MH7z, $CDCl_3$) δ 15.3, 33.4, 51.8, 76.3, 87.5, 122.5, 125.0, 128.0, 129.9, 172.4; IR (KBr) ν_{max} 3108, 2953, 2204, 1739, 1596, 1490 cm^{-1}; MS m/z = 195 [M + H$^+$]. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.19. Found: C, 61.66; H, 5.44.

Methyl 2-Methyl-5-phenylpent-4-ynoate (3ae). Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (d, J = 6.9 Hz, 3H), 2.60 (m, 1H), 2.73−2.80 (m, 2H), 3.72 (s, 3H), 7.27−7.29 (m, 3H), 7.38−7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 23.6, 38.9, 51.9, 82.1, 87.0, 123.5, 127.5, 128.2, 131.5, 175.5; IR (KBr) ν_{max} 3034, 2953, 2223, 1742, 1598, 1587, 1491 cm^{-1}; MS m/z = 203 [M + H$^+$]. Anal. Calcd for $C_{10}H_{10}O_2S$: C, 77.20; H, 6.98. Found: C, 77.06; H, 7.21.

Ethyl 5-*n*-Butyl-4-pentynoate (3ga). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 4H), 1.23 (t, J = 7.2 Hz, 3H), 1.38 (m, 4H), 2.09 (t, J = 6.9 Hz, 2H), 2.45 (t, J = 4.2 Hz, 3H), 4.12 (q, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 14.1, 14.7, 18.3, 21.8,31.0, 34.1, 60.4, 78.0, 81.0, 172.1. IR (KBr) ν_{max} 2953, 2164, 1740 1460, 1360 cm^{-1}; MS m/z =183 [M + H$^+$]. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.26; H, 10.11.

5-Phenyl-pent-4-ynoic Acid 6-(5-phenyl-pent-4-ynoyloxy)-hexyl Ester[10] (3af). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35−1.38 (m, 4H), 1.59−1.63 (m, 4H), 2.62 (t, J = 7.3 Hz, 4H), 2.73 (t, J = 7.5 Hz, 4H), 4.09 (t, J = 6.6 Hz, 4H), 7.26−7.28 (m,6H), 7.37−7.39 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 25.6, 28.5, 33.0, 64.6, 81.2, 88.0, 123.5, 127.8, 128.2, 131.6, 172.0. IR (KBr) ν_{max} 3056, 2938, 2240, 1732, 1598, 1572, 1491 cm^{-1}; MS m/z = 431 [M + H$^+$]. Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11; H, 7.02. Found: C, 78.36; H, 6.88.

5-(2-Methylphenyl)-pent-4-ynoic Acid 6-(5-(2-Methylphenyl)-pent-4-ynoyloxy)-hexyl Ester[10] (3ef). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35−1.40 (m, 4H), 1.60−1.65 (m, 4H), 2.39 (s, 6H), 2.64 (t, J = 7.7 Hz, 4H), 2.77 (t, J = 7.0 Hz, 4H), 4.12 (t, J = 6.6 Hz, 4H), 7.06−7.12 (m, 2H), 7.17 (dd, J = 5.1, 1.1 Hz, 4H), 7.34 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 20.5, 25.6, 28.5, 33.9, 64.6, 80.1, 91.9, 123.2, 125.4, 127.7, 129.3, 131.8, 140.0, 171.9; IR (KBr) ν_{max} 3060, 2982, 2238, 1735, 1608, 1498 cm^{-1}; MS m/z = 459 [M + H$^+$]. Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.43. Found: C, 78.40; H, 7.68.

5-Thiophen-3-yl-pent-4-ynoic Acid 6-(5-Thiophen-3-yl-pent-4-ynoyloxy)-hexyl Ester[10] (3ff). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35−1.38 (m, 4H), 1.61−1.63 (m, 4H), 2.60 (t, J = 7.2 Hz, 4H), 2.71 (t, J = 7.1 Hz, 4H), 4.10 (t, J = 6.6 Hz, 4H), 7.05 (dd, J = 4.9, 1.0 Hz, 2H), 7.22 (dd, J = 4.9, 3.0 Hz, 2H), 7.35 (d, J = 1.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 25.6, 28.5, 33.7, 87.6, 64.6, 76.3, 122.6, 125.0, 128.0, 130.0, 171.9. IR (KBr) ν_{max} 3106, 2934, 2208, 1731, 1521, 1465 cm^{-1}; MS m/z = 443 [M + H$^+$]. Anal. Calcd for $C_{24}H_{26}O_4S_2$: C, 65.13; H, 5.92. Found: C, 64.96; H, 6.08.

Diethyl 5,5′-(1,4-Phenylene)dipent-4-ynoate[11] (3ia). Brown solid; mp: 82−83 °C; ^{1} H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 6H), 2.60 (t, J = 7.1 Hz, 4H), 2.72 (t, J = 7.8 Hz, 4H), 4.17 (q, J = 7.1 Hz, 4H), 7.28 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 15.3, 33.5, 60.6, 80.8, 89.6, 122.9, 131.3, 171.8. IR (KBr) ν_{max} 3066, 2928, 2220, 1729, 1521, 1499 cm^{-1}; MS m/z = 327 [M + H$^+$]. Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.48; H, 6.93.

Ethyl 5-(4-(2-(Trimethylsilyl)ethynyl)phenyl)pent-4-ynoate[11] (4ia). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H), 2.61 (t, J = 7.8 Hz, 2H), 2.73 (t, J = 7.8 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 14.2, 15.4, 29.8, 33.6, 60.7, 80.9, 90.1, 95.8, 104.7, 122.4, 123.7, 131.4, 131.7, 171.8. IR (KBr) ν_{max} 3055, 2930, 2219, 1730, 1535, 1496 cm^{-1}; MS m/z = 299 [M + H$^+$]. Anal. Calcd for $C_{18}H_{22}O_2Si$: C, 72.44; H, 7.43. Found: C, 72.58; H, 7.26.

Methyl 5-(4-Bromophenyl)-5-oxopentanoate (4db). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03−2.09 (m, 2H), 2.44 (t, J = 7.2 Hz, 2H), 3.01 (t, J = 7.2 Hz, 2H), 3.67 (s, 3H), 7.59 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 29.7, 33.0, 37.4, 51.6, 128.2, 129.6, 131.9, 135.5, 173.6, 198.3. IR (KBr) ν_{max} 3066, 2952, 1736, 1687, 1586, 1484 cm^{-1}; MS m/z = 286 [M + H$^+$]. Anal. Calcd for $C_{12}H_{13}BrO_3$: C, 50.55; H, 4.60. Found: C, 50.73; H, 4.45.

2-Benzyl-5-ethylfuran[9] (3ag). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 3H), 2.60 (q, J = 7.5 Hz, 2H), 3.93 (s, 2H), 5.86 (s, 2H), 7.19−7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 21.6, 34.8, 104.8, 106.7, 127.1, 128.8, 128.9, 138.6, 152.7,

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156.6; IR (KBr) ν_{max} 3033, 2973,1564, 1496, 1454, 1012, 706 cm^{-1}; MS m/z = 187 [M + H^+].

■ ASSOCIATED CONTENT

Supporting Information

Spectra data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) δ,γ-Alkynyl esters **3ia** and **4ia** were synthesized by the reactions of alkynylsilane **1i** (0.5 mmol) with ethyl acrylate **2a** (1.5 mmol) in the presence of indium trichloride (0.1 mmol) and Et_3N (0.05 mmol).