Article

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Regio- and Stereoselective Carboindation of Internal Alkynyl Ethers with Organosilicon or -stannane Nucleophiles

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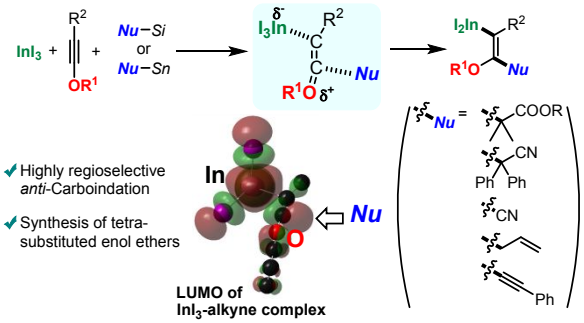
Supporting Information Placeholder



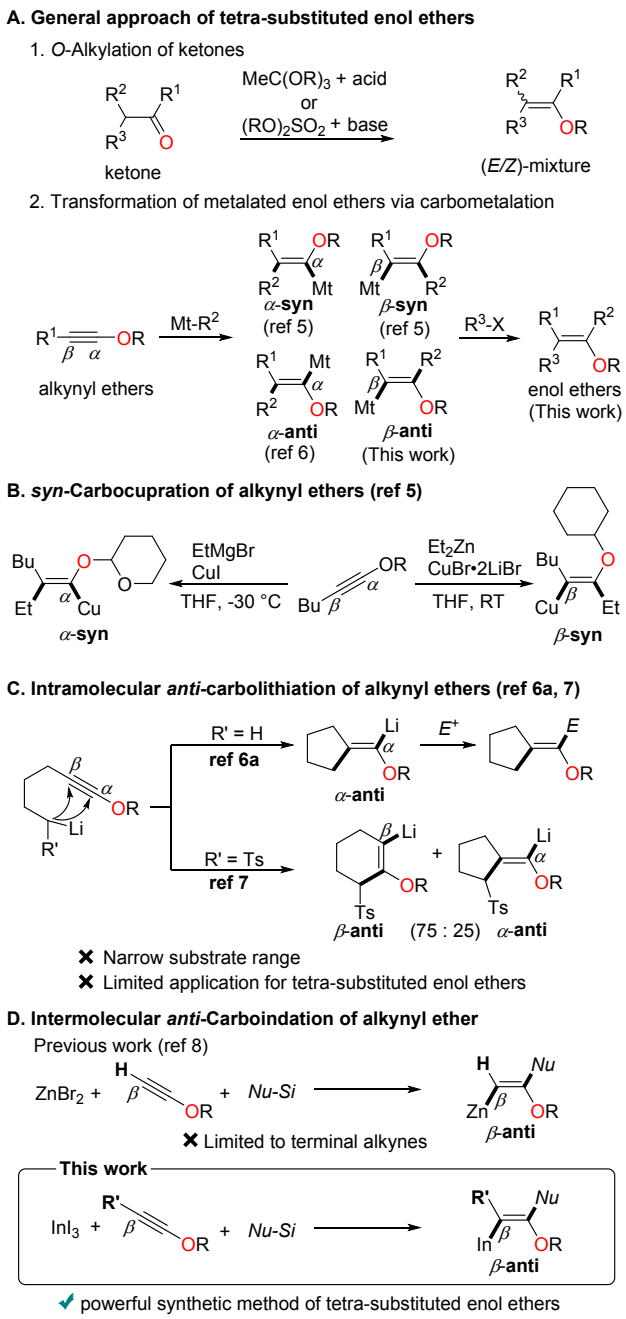
ABSTRACT: We achieved regio- and stereoselective carboindation of terminal and internal alkynyl ethers using InI_3 and organosilicon or -stannane nucleophiles to synthesize (*Z*)-*β*-alkoxyalkenylindiums. The carbometalation regio- and stereoselectively proceeded in *anti*-addition fashion, which was confirmed by X-ray diffraction analysis of (*Z*)-*β*-alkoxyalkenylindium products. Theoretical calculation on the carboindation of alkynyl ethers to elucidate the effect of an alkoxy group were conducted in parallel with calculations on a carbon analogue of the alkynyl ether. Reaction profiles and computational data of carboindation suggest that the alkoxy group enhances the interaction between InI_3 and an alkyne moiety and reduces the activation energy. Many types of carbon nucleophiles such as silyl ketene acetals, silyl ketene imines, a silyl cyanide, an alkynyl stannane, and an allylic stannane were applicable to the present reaction system to give highly functionalized metalated enol ethers (*β*-alkoxyalkenylindiums). The prepared *β*-alkoxyalkenylindiums were transformed to various functionalized tetra-substituted enol ethers by iodination followed by Suzuki coupling. The synthesis of a 7-membered ring compound containing a phenol ether moiety was accomplished using a sequential process that included the present stereoselective carboindation.

■ INTRODUCTION

Multi-substituted enol ethers are an important class of building blocks in organic synthesis due to an electron-rich π-bond and its various reactivities.[1] Actually, valuable synthetic transformations of enol ethers, such as the Diels-Alder reaction[2] and Claisen rearrangement,[3] are well established. There are two general approaches for the synthesis of highly substituted enol ethers. One is *O*-alkylation of ketones under acidic or basic conditions,[4] and another is the transformation of metalated enol ethers prepared via the carbometalation of internal alkynyl ethers. The former method often exhibits less stereoselectivity to give *E*/*Z* mixtures due to an inability to control isomers. (Scheme 1, A1). In contrast, the latter is a promising strategy to exclusively synthesize one isomer from among several possible isomers. However, this strategy has not been well established, because the regio- and stereoselective carbometalation of internal alkynyl ethers is a difficult process (Scheme 1, A2). For *syn*-carbometalations, Marek reported a *syn*-carbocupration of internal alkynyl ethers in the preparation of individual *α*-**syn** or *β*-**syn** alkoxyalkenylcoppers.[5] By changing an OR group from cyclohexyloxy (-OCy) to 2-tetrahydropyranyloxy (-OTHP), the regioselectivity of alkoxyalkenylcoppers was converted from *β*-**syn** to *α*-**syn** (Scheme 1, B). In contrast, the *anti*-carbometalation of internal alkynyl ethers remains a challenge. Only intramolecular *anti*-carbolithiations of an internal alkynyl ether for *α*-**anti** and *β*-**anti** alkoxyalkenyllithiums has been reported (Scheme 1, C). In the case of *α*-**anti**, however, the substrate scope was narrow and only 5-membered ring compounds were obtained.[6] A carbolithiation for the production of *β*-**anti** was also established by using organolithium species derived from an alkyl sulfone.[7] In this case, the produced alkenyllithium was not useful for further transformations because it was quenched by the acidic protons in the starting material. In addition, the regioselectivity of the alkenyllithium was low.

Recently, we reported a regioselective *anti*-carbozincation of terminal alkynyl ethers[8] using $ZnBr_2$ and silyl ketene acetals to give *β*-alkoxyalkenylzincs bearing an ester moiety, and also established a selective synthetic method for tri-substituted enol ethers (Scheme 1, D, previous work). By continuing the investigation to establish a more versatile carbometalation, we discovered that an indium trihalide was effective in the carbometalation of both terminal and internal alkynyl ethers. Herein, we describe a method for the synthesis of tetra-substituted enol ethers by carbometalation of internal alkynyl ethers via the use of InI_3 and organosilicon or -stannane nucleophiles (Scheme 1D, this work).

Scheme 1. Syntheses of tetra-substituted enol ethers

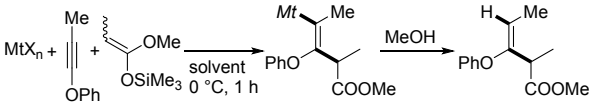


■ RESULTS AND DISCUSSION

Optimization of the Reaction Conditions

Based on our previous work for the carbozincation of terminal alkynyl ethers using $ZnBr_2$,[8] we investigated the carbometalation of internal alkynyl ether **1a** with silyl ketene acetal **2a** (Table 1). $ZnBr_2$, **1a**, and **2a** were mixed in CH_2Cl_2 at 0 °C and then stirred for 1 h. After quenching with MeOH only a 10% yield of **3aa** was obtained (Table 1, entry 1). $ZnBr_2$ was ineffective in the carbometalation of internal alkynyl ethers in contrast to that of terminal versions.[8] We recently reported that $BiBr_3$,[9a] $AlBr_3$,[9b] $GaBr_3$,[9c] and $InBr_3$[9d] are effective in the carbometalation of simple alkynes. When these metal salts were examined, $InBr_3$ gave (*E*)-**3aa** as a single isomer in 66% yield and the others resulted in lower yields or in no reaction (Table 1, entries 2-6). Finally, InI_3 gave the highest yield (Table 1, entry 7). The reason that In salts exhibit more efficient reactivity than Al, Zn, or Ga salts would be that the large lobe of LUMO on an indium atom effectively interacts with the π-orbital of an internal alkyne. Typical Lewis acids such as BF_3·OEt_2, $SnBr_4$, and $FeBr_3$ were not suitable to this carbometalation (See supporting information (SI), Table S1). Chloroform, diethyl ether, and toluene as solvents gave the desired product **3aa** in 68, 66, and 58% yields, respectively (Table 1, entries 8, 9, and 10). A non-polar solvent such as hexane (Table 1, entry 11) and a highly coordinative solvent such as THF (Table 1, entry 12) did not give the product. Therefore, the reaction conditions of entry 7 proved to be optimal.

Table 1. Optimization for the carbometalation of internal alkynyl ether **1a**[a]



entry	MtX_n	solvent	yield[b] of **3aa** (%)
1	$ZnBr_2$	CH_2Cl_2	10
2	$BiBr_3$	CH_2Cl_2	0
3	$AlBr_3$	CH_2Cl_2	0
4	$GaBr_3$	CH_2Cl_2	37
5	$InCl_3$	CH_2Cl_2	15
6	$InBr_3$	CH_2Cl_2	66
7	InI_3	CH_2Cl_2	73
8	InI_3	$CHCl_3$	68
9	InI_3	Et_2O	66
10	InI_3	toluene	58
11	InI_3	hexane	trace
12	InI_3	THF	0[c]

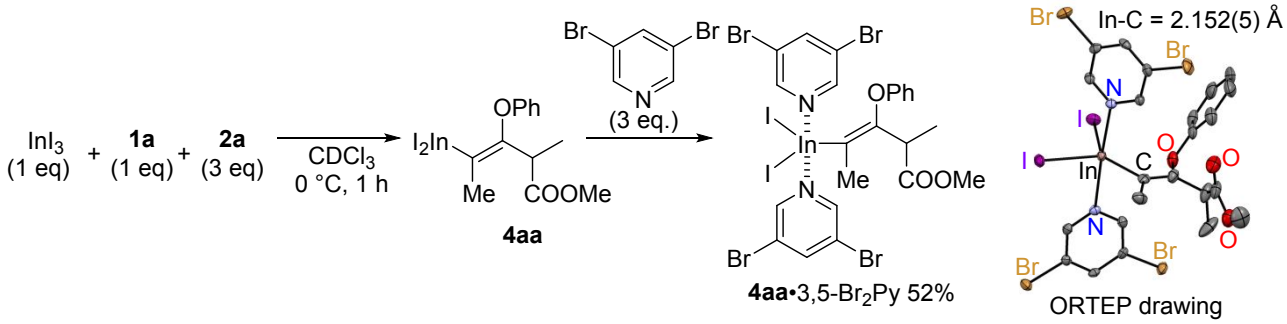
[a]Reaction conditions: MtX_n (0.5 mmol), **1a** (0.5 mmol), **2a** (1.5 mmol), CH_2Cl_2 (1 mL), 0 °C, and 1 h. [b]Yields were determined

by ^{1}H-NMR using $Cl_2CHCHCl_2$ as an internal standard. [c]Starting materials were recovered.

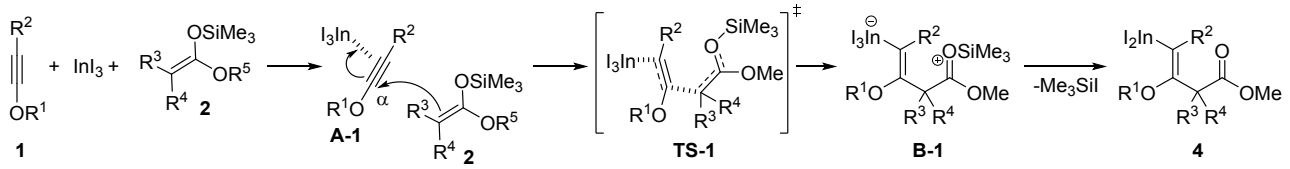
Isolation and Characterization of Alkenylindium 4

The produced alkenylindiums in carboindation were characterized by NMR spectroscopy and X-ray diffraction analysis. After the carboindation of alkynyl ether **1a** using InI_3 and silyl ketene acetal **2a** in $CDCl_3$ at 0 °C for 1 h, the *in situ* ^{1}H NMR showed a full conversion of **1a** and production of alkenylindium **4aa**. The addition of 3,5-dibromopyridine to the reaction mixture generated a white precipitate. After removal of the volatiles *in vacuo*, washing with hexane, and extraction with Et_2O, recrystallization of the obtained solid from CH_2Cl_2/hexane gave a single crystal. X-ray analysis revealed the structure of alkenylindium coordinated by 3,5-dibromopyridine **4aa**·3,5-Br_2Py (Scheme 2).[10] The *trans* geometry between an InI_2 group and a substituent derived from silyl ketene acetal **2a** in the phenoxyalkene moiety supported an *anti*-addition mechanism. The length of the C-In bond (2.152(5) Å) is similar to that of a typical In-C(sp^2) bond.[11] The geometry around an indium atom is a distorted trigonal bipyramid. An alkenyl group and two iodine atoms occupy equatorial positions, and two 3,5-dibromopyridines occupy axial positions.

Scheme 2. Isolation and ORTEP drawing of **4aa**·3,5-Br_2Py produced by carboindation



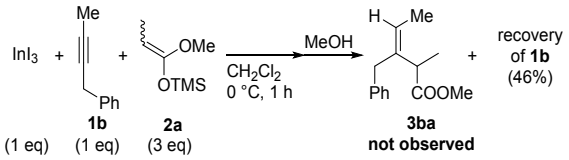
Scheme 3. Reaction mechanism



Elucidation of the Reaction Mechanism Using Theoretical Calculation

A plausible mechanism for the carboindation of alkynyl ether **1** using InI_3 and silyl ketene acetal **2** is shown in Scheme 3. First, a carbon-carbon triple bond of alkyne **1** coordinates to InI_3 to increase the positive charge at an α-carbon of the OR^1 group (**A-1**).[12] The nucleophilic attack of silyl ketene acetal **2** to the α-carbon atom occurs at the opposite side of InI_3 to give zwitterionic alkenyl indium **B-1** through transition state **TS-1**.[13] Then, elimination of Me_3SiI from **B-1** affords alkenyl indium **4**. Simple internal alkyne **1b**, 1-phenylbut-2-yne (carbon analogue of **1a**), was not applicable to this transformation in contrast to **1a** (Scheme 4).

Scheme 4. Carboindation of internal alkyne **1b**



The role of an alkoxy group in the reaction mechanism was investigated by DFT calculation (B3LYP/DGDZVP(for In and I) and 6-31+g**(for others)). Reaction profiles for alkynyl ether **1a** (red line) and simple alkyne **1b** (blue line) are shown in Figure 1. In the reaction of alkynyl ether **1a**, the smaller activation energy ($\Delta G^{\ddagger}$ = 17.9 kcal/mol) is estimated for **TS-1a**,[14] whereas the activation energy in the reaction of **1b** is very high ($\Delta G^{\ddagger}$ = 36.1 kcal/mol).

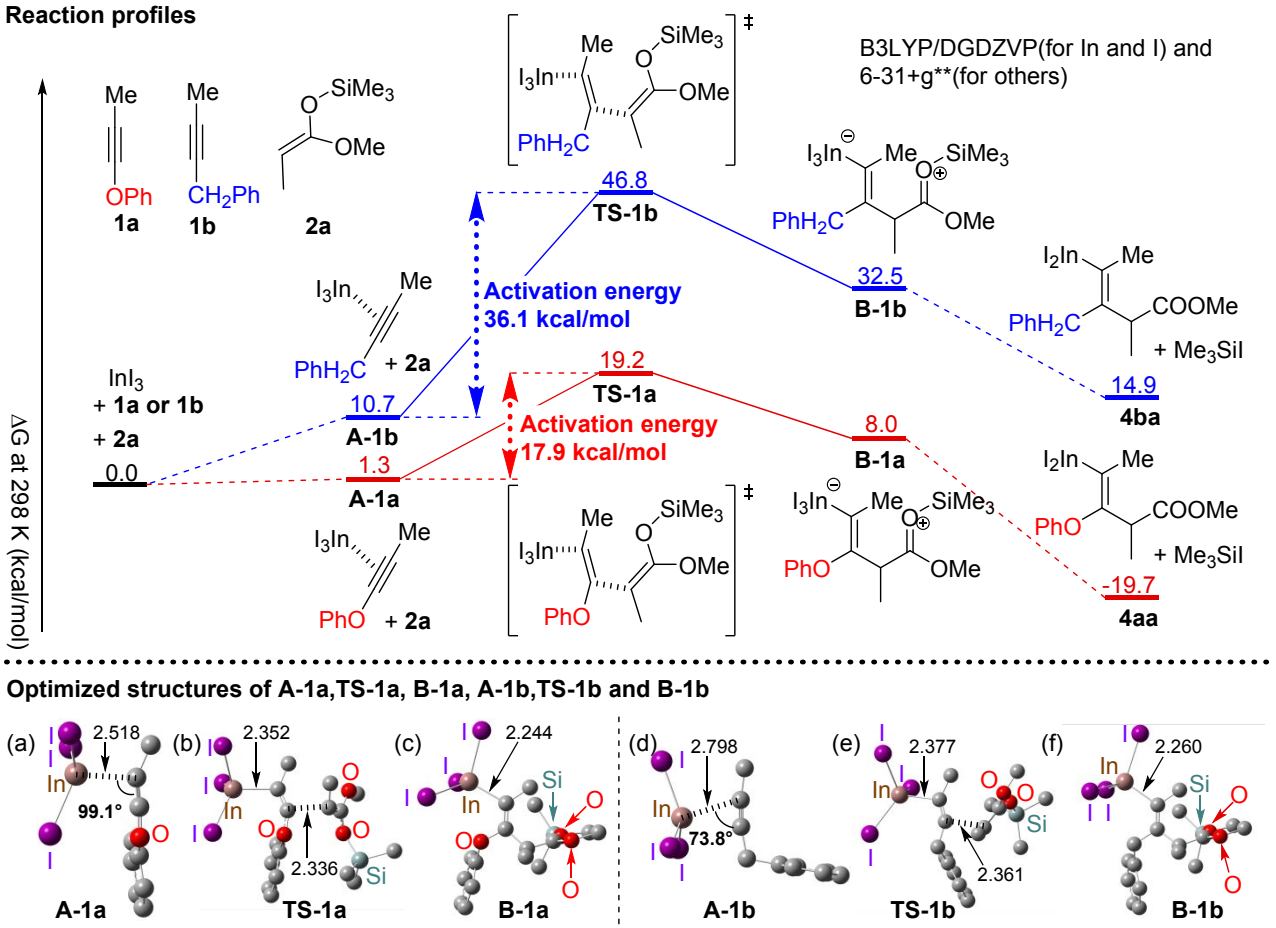
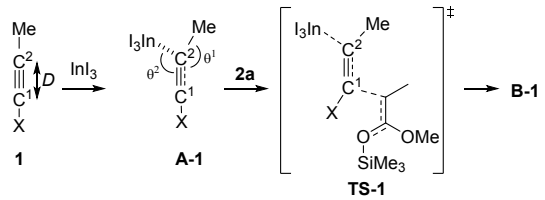


Figure 1. Reaction profiles and optimized structures of **A-1**, **TS-1,** and **B-1**

We considered geometrical parameters, enthalpies, and the NBO charges of **1a**, **1b**, **A-1a**, **A-1b**, **TS-1a**, and **TS-1b** to reveal the details of an activation mode of alkynes (**1a** and **1b**) by InI_3 (Table 2).[9b] In the complexation between InI_3 and **1a** (**A-1a**), coordination of **1a** to InI_3 considerably changes the length of the carbon-carbon triple bond (*D*) from 1.209 to 1.236 Å, the oxygen-carbon bond (C^1-O) from 1.314 to 1.276 Å, and the angle of Me-C^2-C^1 (θ^1) from 180.0° to 150.4°. The angle of In-C^2-C^1(θ^2) in **A-1a** is an obtuse angle, 99.1°, and the length of In-C^2 is 2.518 Å shorter than that of In-C^1 (see Figure 1, (a)). These geometrical changes suggest that the indium atom effectively interacted with the C^2-atom rather than with the C^1-atom to withdraw π-electrons from a triple bond. On the other hand, in case of the coordination of simple internal alkyne **1b** to InI_3 (**A-1b**), the changes of *D* and θ^1 are smaller than

those to **1a**, the angle of In-C^2-C^1(θ^2) is acute (see Figure 1, (d)), and the indium atom interacted with both C^1- and C^2 atoms. Although there are two distinguishable activation modes of alkynes (**A-1a** and **A-1b**), the two optimized transition states (**TS-1a** and **TS-1b**) are relatively similar (see Figure 1, (b) and (e)). Because the changes in geometrical parameters such as θ^1, θ^2, D, and In-C^2 in a path from **A-1a** to **TS-1a** are smaller than the corresponding changes in a path from **A-1b** to **TS-1b**, the activation energy in the carboindation of **1a** was smaller than that in **1b**. It is noteworthy that the small change in the In-C^2 bond represented an effective interaction between the indium and C^2 atoms in **A-1a** due to a conjugative electron donation from the OPh group (The changes of the In-C^2 bond length from **A-1a** to **TS-1a** and from **A-1b** to **TS-1b** amount to 0.166 Å and 0.421 Å, respectively.). The changes in the NBO charges on C^1- and C^2-atoms were helpful in evaluating the degree of the indium-alkyne interaction. The coordination of **1a** to InI_3 (**A-1a**) resulted in an increase of positive charge on the C^1-atom (from 0.299 to 0.448). The considerable changes in the charges of **A-1a** reduced the stabilization, but the strong bond-forming interaction of In with C^2 atoms compensated for the disadvantage. The positive charge on the C^1-atom that is required by the nucleophilic attack of **2a** is sufficiently increased in **A-1a**. The actual change is slight in the charge of the C^1-atom between **A-1a** and **TS-1a** (from 0.448 to 0.436). On the other hand, the large change in the NBO charge of the C^1-atom between **A-1b** and **TS-1b** (from -0.041 to 0.151) led to a higher level of activation energy. Therefore, the conjugative donation of an alkoxy group accelerates the interaction of an indium atom with the C^2-atom to assist the regioselective carboindation.

Table 2. Geometrical parameters[a] and the NBO charges of **1a**, **1b**, **A-1a**, **A-1b**, **TS-1a**, and **TS-1b**



	D^b (Å)	In-C^2 (Å)	C^1-X (Å)	θ^1 (°)	θ^2 (°)	NBO charge C^1	NBO charge C^2
1a	1.209	-	1.314	180.0	-	+0.299	-0.134
A-1a	**1.236**	**2.518**	**1.276**	**150.4**	**99.1**	**+0.448**	**-0.305**
TS-1a	1.282	2.352	1.298	134.5	113.3	**+0.436**	**-0.411**
1b	1.212	-	1.469	180.0	-	-0.047	-0.002
A-1b	**1.224**	**2.798**	1.475	**172.0**	**73.8**	**-0.041**	**-0.009**
TS-1b	1.275	2.377	1.478	137.8	113.7	**+0.151**	**-0.331**

[a]Optimized by B3LYP/6-31+G(d,p) for H, C, O and DGDZVP for In, I, at 298.15 K. [b]D is bond length of C^1-C^2.

The stereochemistry of carboindation to lead to an *anti*-addition fashion is explained by the LUMO of **A-1a** including the π* orbital of the alkyne moiety (Figure 2). The π* orbital fragment is localized at the C^1 atom. In addition, the lobe located on the opposite side to InI_3 (indicated by arrows) is larger. In contrast, another lobe on the C^1 atom, which is located on the same side of InI_3, is smaller and is sterically blocked by InI_3. Therefore, the nucleophilic attack of silyl ketene acetal **2a** should occur from the opposite side to InI_3 to achieve the *anti*-carboindation.

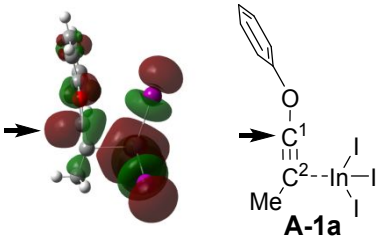


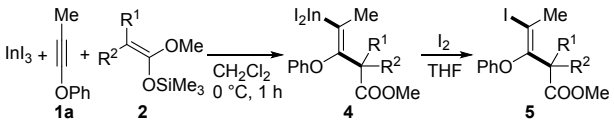
Figure 2. Explanation of the stereochemistry of carboindation by the LUMO of **A-1a**

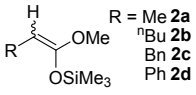
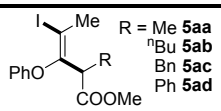
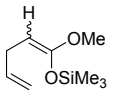
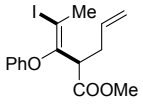
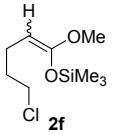
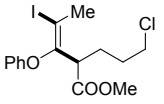
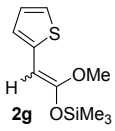
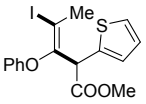
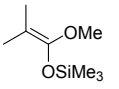
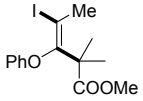
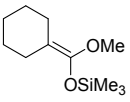
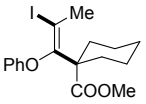
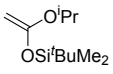
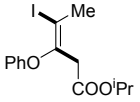
Scope and Limitations of Organosilicon Nucleophiles

With the optimized reaction conditions in hand (Table 1, entry 7), the scope of silyl ketene acetals **2** was investigated (Table 3). To synthesize tetra-substituted enol ethers, the alkenylindium **4aa** prepared from **1a**, InI_3, and

2a was treated with I_2 to give the iodinated enol ether **5aa** in a 76% yield with retention of the stereochemistry of **4aa**. Various types of silyl ketene acetals **2** were applicable to the carboindation/iodination process. Monoalkyl- and monoaryl-substituted silyl ketene acetals were suitable substrates to give the desired products (**5aa-d**) (Table 3, entries 1-4). Allyl-substituted silyl ketene acetal **2e** proved to be a feasible nucleophile (Table 3, entry 5). The chloride moiety tolerated the reaction conditions (Table 3, entry 6). Carboindation using 2-thienyl-substituted silyl ketene acetal **2g** afforded **5ag** in a yield of 20% (Table 3, entry 7), because **2g** would be decomposed in the presence of a stoichiometric amount of InI_3. Dialkylsilyl ketene acetals (**2h** and **2i**) gave the corresponding enol ethers in medium to high yields (**5ah** and **5ai**) (Table 3, entries 8 and 9). On the other hand, non-substituted silyl ketene acetal **2j** resulted in a complicated mixture (Table 3, entry 10).

Table 3. Scope and limitations of silyl ketene acetals **2**[a]



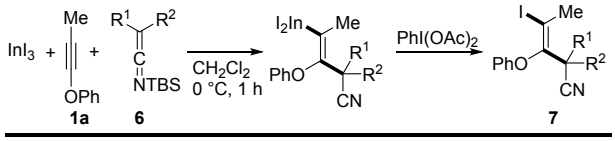
entry	substrate **2**	product **5**	yield[b]
1	 R = Me **2a**, ^{n}Bu **2b**, Bn **2c**, Ph **2d**	 R = Me **5aa**, ^{n}Bu **5ab**, Bn **5ac**, Ph **5ad**	76%
2			64%
3			69%
4			72%
5	 **2e**	 **5ae**	69%
6	 **2f**	 **5af**	86%
7	 **2g**	 **5ag**	20%
8	 **2h**	 **5ah**	54%
9	 **2i**	 **5ai**	80%
10	 **2j**	 **5aj**	0%

[a]Reaction conditions: InI_3 (0.5 mmol), **1a** (0.5 mmol), **2** (1.5 mmol), I_2 (1.5 mmol), CH_2Cl_2 (1 mL), 0 °C, and 1 h. [b]Isoated yields.

The scope of silyl ketene imines **6** was shown in Table 4. The iodinated products **7** were obtained when the reaction mixture was treated with $PhI(OAc)_2$ instead of I_2 for iodination of the alkenylindiums.[15] Carboindation of **1a** with various α-alkyl-α-phenyl-substituted silyl ketene imines (**6a**, **6b**, and **6c**) followed by iodination smoothly gave iodinated enol ethers (**7aa**, **7ab**, and **7ac**) bearing a CN group (Table 4, entries 1-3). A diphenylcyanomethyl group was successfully installed using **6d** (Table 4, entry 4). Silyl ketene imines bearing either an electron donating group (**6e**) or an electron withdrawing group (**6f**) gave the corresponding

compounds **7ae** and **7af** in moderate yields, respectively (Table 4, entries 5 and 6). Thienyl-substituted silyl ketene imine **6g** was applicable, although the yield was low (Table 4, entry 7). Oxidative iodination gave iodinated (*Z*)-alkenes selectively from (*Z*)-alkenylindium with the retention of the stereochemistry of the alkene moiety in all cases.

Table 4. Scope of silyl ketene imines **6**

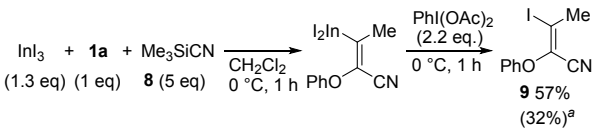


entry	substrate **6**	product **7**	yield[b]
1	R = Me **6a**	R = Me **7aa**	90%
2	Et **6b**	Et **7ab**	90%
3	^{i}Pr **6c**	^{i}Pr **7ac**	41%
4	**6d**	**7ad**	89%
5	**6e**	**7ae**	67%
6	**6f**	**7af**	76%
7	**6g**	**7ag**	27%

[a]Reaction conditions: InI_3 (0.5 mmol), **1a** (0.5 mmol), **6** (1.0 mmol), $PhI(OAc)_2$ (1.0 mmol), CH_2Cl_2 (1 mL), 0 °C, and 1 h. [b]Isoated yields. TBS = *tert*-butyldimethylsilyl.

Me_3SiCN **8** also worked as a nucleophile to afford the corresponding product **9**. *anti*-Carboindation of **1a** using 1 equivalent of InI_3 and 4 equivalents of Me_3SiCN followed by iodination by $PhI(OAc)_2$ afforded product **9** in a 32% yield. Increasing the amount of InI_3 and Me_3SiCN improved the yield of **9** to 57% (Scheme 5).

Scheme 5. *anti*-Carboindation using Me_3SiCN **8**



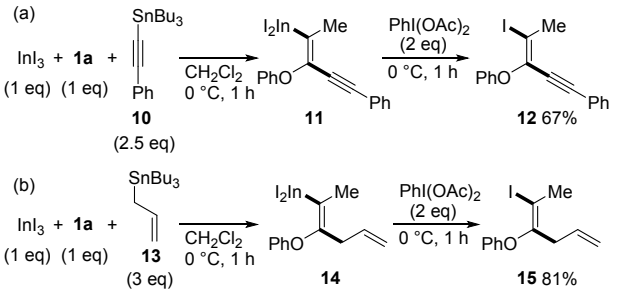
[a]Using InI_3 (1 eq) and Me_3SiCN (4 eq).

We attempted to use other types of organosilicon nucleophiles such as an alkynylsilane and an allylsilane, but these were not applicable to the present carboindation (see SI, Table S3).

Organostannane Nucleophiles for Carboindation

To construct versatile carbon skeletons, instead of organosilicon nucleophiles, we applied more nucleophilic organostannanes to the carboindation system. The use of alkynylstannane **10** in the carboindation of **1a** gave the iodinated enol ether **12** in a 67% yield with the treatment of $PhI(OAc)_2$ (Scheme 6a). The *Z*-form structure of **12** was determined by X-ray diffraction analysis.

Scheme 6. Carboindation using organostannane nucleophiles



The complex between alkenylindium **11** and 3,5-dibromo pyridine was successfully analyzed by X-ray crystallography, which revealed that an *anti*-addition mechanism led to a *trans*-

orientation between the indium and alkynyl groups (Figure 3).

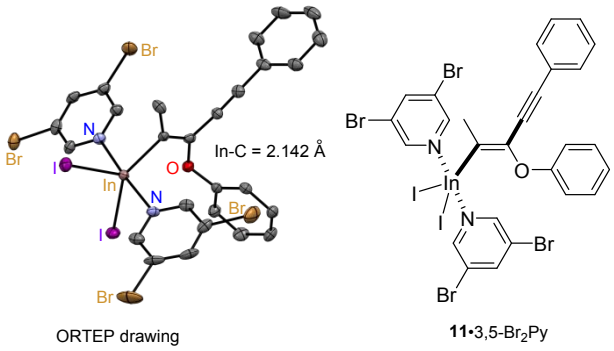


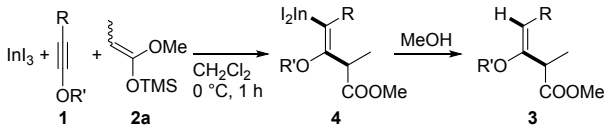
Figure 3. ORTEP drawing of **11**·3,5-Br_2Py

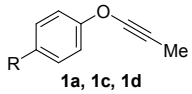
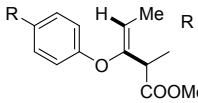
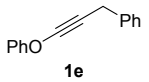
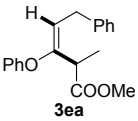
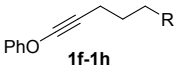
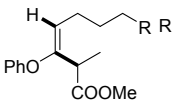
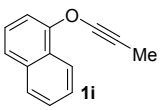
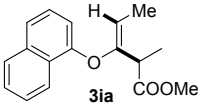
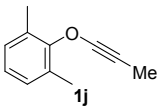
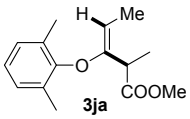
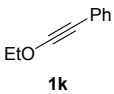
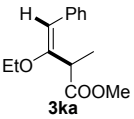
Allylstannane **13** was also applicable to the *anti*-carboindation of **1a** to afford iodinated compound **15** in an 81% yield (Scheme 6b). The reaction of alkynes with an allylstannane in the presence of Lewis acids such as $EtAlCl_2$ or $ZrCl_4$ are known to give alkenylstannanes as products via an *anti*-addition/transmetalation mechanism.[16] Furthermore, in a previous experience with the carboindation of simple alkynes, we found that organostannane nucleophiles were inapplicable. It is noted that enhancing the reactivity of a carbon-carbon multiple-bond in carboindation by an alkoxy group extends the scope of suitable nucleophiles.

Scope and Limitations of Alkynes

As shown in Table 5, various types of alkynyl ethers **1** were applied to the present carboindation system. Aryl alkynyl ethers bearing an electron-withdrawing group **1b** or an electron donating group **1c** on an aryl ring gave the corresponding products **3ca** and **3da** in high yields, respectively (Table 5, entries 2 and 3). Chloro (**3fa**), methoxy (**3ga**), and phenyl groups (**3ea** and **3ja**) endured these conditions (Table 5, entries 4-7). 1-Naphtyl alkynyl ether **1h** was successfully transformed to product **3ha** in an 85% yield (Table 5, entry 8). However, bulky aryl alkynyl ether **1j** did not give the desired product (Table 5, entry 9). The carboindation of phenyl acetylene bearing an ethoxy group (**1k**) exclusively formed the desired carbon-carbon bond at a carbon-bearing ethoxy group, although the yield of **3ka** was low (Table 5, entry 10).

Table 5. Scope and limitations of internal alkynyl ethers **1**[a]



entry	substrate **1**	product **3**			yield[b]
1	 **1a, 1c, 1d**		R = H	**3aa**	72%
2			Cl	**3ca**	73%
3			OMe	**3da**	80%
4	 **1e**	 **3ea**			45%
5	 **1f-1h**		R = Cl	**3fa**	68%
6			OMe	**3ga**	56%
7			Ph	**3ha**	57%
8	 **1i**	 **3ia**			85%
9	 **1j**	 **3ja**			0%
10	 **1k**	 **3ka**			25%

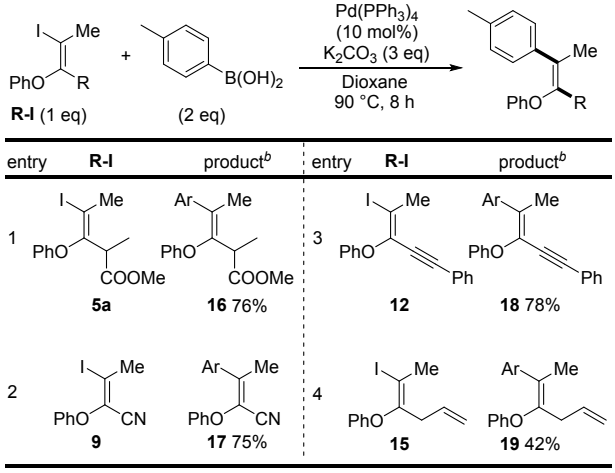
[a]Reaction conditions: InI_3 (0.5 mmol), **1a** (0.5 mmol), **2a** (1.5 mmol), I_2 (1.5 mmol), CH_2Cl_2 (1 mL), 0 °C, and 1 h. [b]Isoated yields.

Application of Synthesized Iodinated Enol Ethers to Suzuki Cross-Coupling Reactions

Cross-coupling reactions were conducted using iodinated enol ethers prepared by the carboindation/iodination process (Table 6).[17] Iodinated compound **5a** underwent Suzuki coupling with *p*-tolylboronic acid to give tetra-substituted enol ether **16** in a 76% yield with no

loss of stereochemistry in the alkene moiety of **5a**. Other iodinated compounds such as **9**, **12,** and **15** also gave corresponding products in moderate to high yields. Generally, the stereo- and regioselective synthesis of tetra-substituted enol ethers is a difficult process.[18] This approach could be one of the most reliable tools for the selective synthesis of multi-substituted enol ethers.

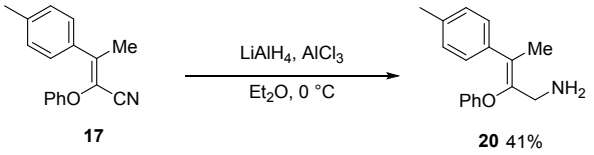
Table 6. Synthesis of tetra-substituted enol ethers by Suzuki reaction[a]



[a]Reaction conditions: **R-I** (1 eq), *p*-tolylboronic acid (2 eq), K_2CO_3 (3 eq), $Pd(PPh_3)_4$ (10 mol%). Solvent, temperature, and reaction time are given in the table. [b]Isoated yields. Ar = *p*-Me-C_6H_4

Further transformation of **17** to amine **20** was performed by reduction[19] using lithium aluminum hydride and aluminum chloride in a 41% yield (Scheme 7). Compound **20** is a precursor of α-amino ketone, which is commonly found in biological molecules, natural products, and active pharmaceutical ingredients.[20]

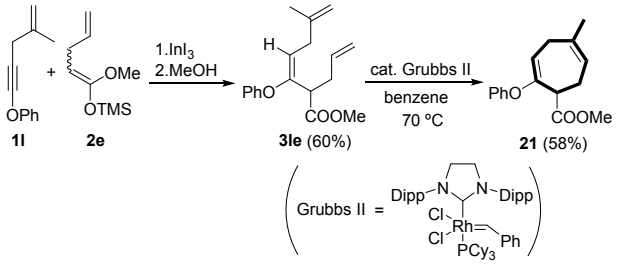
Scheme 7. Further reduction to amine 20



Applications of Synthesized Multi-substituted Enol Ethers to the Construction of a 7-Membered Ring Compound

The developed carboindation was applied to the synthesis of a 7-membered ring compound, which is an important carbon framework in natural compounds such as cyanthiwigin,[21a] pseudolaric acid A,[21b] and sphenolobane-type diterpenoids.[21c] The *anti*-carboindation of **1l** using InI_3 and **2e** gave triene compound **3le** in a 60% yield with no stereoisomers. Triene compound **3le** underwent intramolecular olefin metathesis[21b] by Grubbs catalyst to produce 7-membered ring compound **21** (Scheme 8). The perfect stereoselective synthesis of enol ether **3le** led to an easy and efficient access to cyclic compounds.

Scheme 8. Construction of a 7-memberd ring using a Grubbs catalyst



■ CONCLUSION

In conclusion, we achieved regio- and stereoselective carboindation of alkynyl ethers using organometallic nucleophiles and InI_3 to synthesize *β*-alkoxyalkenylindiums. An efficient synthetic method for tetra-substituted enol ethers was established via a sequential process including the present carboindation. The reaction proceeded in an *anti*-addition fashion, which was confirmed by X-ray diffraction

analysis of *β*-alkoxyalkenylindiums. We discovered that an oxygen atom bonding at an alkyne moiety boosted carboindation by increasing the interaction of InI_3 and the alkyne moiety and stabilizing its transition state. The scope of nucleophiles was considerably wide, and silyl ketene acetals, silyl ketene imines, an alkynyl stannane, and an allyl stannane were applicable. The prepared *β*-alkoxyalkenylindiums were successfully transformed to functionalized tetra-substituted enol ethers through various organic reactions such as halogenation and halogenation/Suzuki coupling.

■ EXPERIMENTAL SECTION

General Information NMR spectra were recorded on JEOL JNM-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (δ = 0 for ^{1}H NMR) and residual $CDCl_3$ (δ = 77.0 for ^{13}C NMR) as an internal reference. All new compounds were characterized by ^{1}H, ^{13}C{^{1}H}, ^{13}C off-resonance techniques, DEPT, COSY, HMQC, and HMBC. Infrared (IR) spectra were recorded on a JASCO FT/IR-6200 Fourier transform infrared spectrophotometer. Positive EI and CI High-resolution mass spectra were recorded on a magnetic sector type mass spectrometer (JEOL JMS-700). Column chromatographies were performed with silica gel or alumina. Purification by recycled HPLC or GPC was performed using a SHIMADZU recycling HPLC system (SPD-20A, RID-10A, DGU-20A, LC-6AD, and FCV-20H2) from the Japan Analytical Industry Co. (NEXT recycling preparative GPC). Reactions were carried out in dried solvents under a nitrogen atmosphere, unless otherwise stated. An oil bath was used for reactions requiring heating. Reagents were purchased from Aldrich or Tokyo Chemical Industry Co., Ltd. (TCI), Wako Pure Chemical Industries, Ltd., and used either after purification by distillation or without purification for solid substrates. Bulb-to-Bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. X-ray diffraction analysis was carried out using Rigaku XtaLAB Synergy with Hypix-6000HE.

Material Dehydrated solvents, CH_2Cl_2, $CHCl_3$, DMF, Et_2O, toluene, hexane, benzene, 1,4-dioxane, and THF, were purchased from Wako Pure Chemical Industries and used as obtained. Alkynyl ethers **1a**[22a] and **1d**[22a] were prepared by modified reported methods[22a], and these compounds were reported. Alkynyl ether **1k**[22b] was prepared by reported methods[22b]. The preparation and characterization of alkynyl ethers **1c**, **1e-1j**, and **1l** are described below. Internal alkyne **1b**[22c] was synthesized using a procedure reported in the literature. Silyl ketene acetals **2a**,[23a] **2b**,[23b] **2c**,[23c] **2d**,[23b] **2e**,[23d] **2f**,[8] **2g**,[8] **2i**,[23b] and **2j**[23e] were prepared by known methods and these compounds were reported. Silyl ketene imines **6a**,[24a] **6b**,[24a] **6c**,[24b] **6d**,[24c] **6e**,[24a] **6f**,[9b] and **6g**[24d] were prepared by known methods and these compounds were reported. InI_3 (indium iodide, 99.99%) was purchased from Kojundo Chemical Laboratory Co., Ltd.. All other reagents were commercially available.

***Phenyl prop-1-ynyl ether (1a)*[22a]**

A solution of *n*-BuLi (1.6 M hexane solution, 160 mmol, 100 mL) was added dropwise to a solution of 1,2-dichloro-1-phenoxyethene (79.8 mmol, 15.1 g) in Et_2O (200 mL) at -78 °C. Then, the mixture was warmed to -20 °C and stirred for 2 h. MeI (100 mmol, 15.2 g) and HMPA (160 mmol, 26.4 g) were added to the reaction mixture at -20 °C and stirred at 50 °C for 8 h. The mixture was poured into hexane (200 mL) and sat. NH_4Cl aq (100 mL) and then extracted with hexane (50 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography and then by distillation (bp. 60 °C, 12 torr) to give the desired product as a yellow oil (7.90 g, 75%). This is a known compound, and the spectroscopic data were identical to that found in the literature.[22a]

4-Chlorophenyl prop-1-ynyl ether (1c)

A solution of *n*-BuLi (1.6 M hexane solution, 50 mmol, 32 mL) was added dropwise to a solution of 1,2-dichloro-1-(4-chlorophenoxy)ethene (20 mmol, 4.4 g) in Et_2O (40 mL) at -78 °C. Then, the mixture was warmed to -20 °C and stirred for 2 h. MeI (43 mmol, 6.5 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (49 mmol, 6.3 g) were added to the reaction mixture at -20 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (100 mL) and sat. NH_4Cl aq (50 mL) and then extracted with

hexane (20 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by alumina column chromatography to give the desired product as a yellow oil (2.20 g, 66%).; IR: (neat) 2288 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.29 (d, J = 9.2 Hz, 2H), 7.19 (d, J = 9.2 Hz, 2H), 1.88 (s, 3H, 3-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.9 (C), 129.4 (CH), 128.9 (C), 116.2 (CH), 81.8 (C), 40.6 (C), 1.7 (CH_3); HRMS: (EI, 70 eV) Calculated: (C_9H_7ClO) 166.0815 (M^+) Found: 166.0813.

4-Methoxyphenyl prop-1-ynyl ether (1d) [22a]

A solution of *n*-BuLi (1.6 M hexane solution, 6 mmol, 3.8 mL) was added dropwise to a solution of ethynyl 4-methoxyphenyl ether[8] (6.1 mmol, 0.90 g) in THF (10 mL) at -78 °C. Then, the mixture was warmed to -20 °C and stirred for 2 h. MeI (9.2 mmol, 1.3 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (4.2 mmol, 0.53 g) were added to the reaction mixture at -20 °C, and stirred at 25 °C for 1 h. The mixture was poured into hexane (20 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by alumina column chromatography to give the desired product as a yellow oil (0.53 g, 54%). This is a known compound, and the spectroscopic data were identical to that reported in the literature.[22a]

Phenyl 3-phenylprop-1-ynyl ether (1e)

A solution of *n*-BuLi (1.6 M hexane solution, 11 mmol, 6.8 mL) was added dropwise to a solution of ethynyl phenyl ether[8] (10.0 mmol, 1.18 g) in THF (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. Benzyl bromide (10.0 mmol, 1.71 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (10.0 mmol, 1.29 g) were added to the reaction mixture at -78 °C and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography, and then by distillation (bp. 160 °C, 0.35 torr) to give the desired product as a yellow oil (0.533 g, 26%).; IR: (neat) 2280 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.42-7.10 (m, 10H, OPh and 3-Ph), 3.71 (s, 2H, 3-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.2 (s), 137.6 (s), 129.6 (d), 128.4 (d), 127.8 (d), 126.5 (d), 124.0 (d), 114.8 (d), 85.1 (s), 42.5 (s), 23.6 (t); HRMS: (EI, 70 eV) Calculated: ($C_{15}H_{12}O$) 208.0887 (M^+) Found: 208.0891.

Phenyl 5-chloropent-1-ynyl ether (1f)

A solution of *n*-BuLi (1.6 M hexane solution, 10 mmol, 6.3 mL) was added dropwise to a solution of ethynyl phenyl ether (9.22 mmol, 1.09 g) in THF (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. 1-Bromo-3-chloropropane (9.81 mmol, 1.60 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (10.4 mmol, 1.34 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography, and then by distillation (bp. 130 °C, 0.71 torr) to give the desired product as a colorless oil (0.803 g, 45%).; IR: (neat) 2279 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.35 (t, J = 8.0 Hz, 2H, *m*), 7.24 (d, J = 8.0 Hz, 2H, *o*), 7.13 (t, J = 8.0 Hz, 1H, *p*), 3.70 (t, J = 6.8 Hz, 2H, 5-H_2), 2.48 (t, J = 6.8 Hz, 2H, 3-H_2), 2.00 (quint, J = 6.8 Hz, 2H, 4-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.1 (s), 129.6 (d), 124.1 (d), 114.8 (d), 83.9 (s), 43.8 (t), 42.6 (s), 31.9 (t), 14.7 (t); HRMS: (EI, 70 eV) Calculated: ($C_{11}H_{11}ClO$) 194.0498 (M^+) Found: 194.0499.

Phenyl 5-methoxypent-1-ynyl ether (1g)

A solution of *n*-BuLi (1.6 M hexane solution, 11 mmol, 6.8 mL) was added dropwise to a solution of ethynyl phenyl ether (10.0 mmol, 1.18 g) in THF (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. 1-Iodo-3-methoxypropane (8.23 mmol, 1.71 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (9.53 mmol, 1.22 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography, and then by distillation (bp. 110 °C, 0.14 torr) to give the desired product as a yellow oil (0.775 g, 50%).; IR: (neat) 2278 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.34 (t, J = 7.8 Hz, 2H, *m*), 7.25 (d, J = 7.8 Hz, 2H, *o*), 7.11 (t, J = 7.8 Hz, 1H, *p*), 3.50 (t, J = 7.1 Hz, 2H, 5-H_2), 3.35 (s, 3H, OMe), 2.37 (t, J = 7.1 Hz, 2H, 3-H_2), 1.82 (quint, J = 7.1 Hz, 2H, 4-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.3 (s), 129.5 (d), 123.9 (d), 114.7 (d), 83.4 (s), 71.3 (t), 58.7 (q), 43.9 (s), 29.3 (t), 14.0 (t).; HRMS: (EI, 70 eV) Calculated: ($C_{12}H_{14}O_2$) 190.0994 (M^+) Found: 190.0992.

Phenyl 5-phenylpent-1-ynyl ether (1h)

A solution of *n*-BuLi (1.6 M hexane solution, 10 mmol, 6.3 mL) was added dropwise to a solution of ethynyl phenyl ether (9.43 mmol, 1.11 g) in THF (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. (3-Bromopropyl)benzene (8.83 mmol, 2.03 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (10.5 mmol, 1.35 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography, and then by distillation (bp. 200 °C, 0.71 torr) to give the desired product as a colorless oil (0.800 g, 34%).; IR: (neat) 2277 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38-7.11 (m, 10H, OPh and 5-Ph), 2.77 (t, J = 7.2 Hz, 2H, 5-H_2), 2.30 (t, J = 7.2 Hz, 2H, 3-H_2), 1.88 (quint, J = 7.2 Hz, 2H, 4-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.3 (s), 141.8 (s), 129.5 (d), 128.5 (d), 128.3 (d), 125.8 (d), 123.9 (d), 114.8 (d), 83.7 (s), 44.2 (s), 34.9 (t), 31.0 (t), 16.8 (t).; HRMS: (EI, 70 eV) Calculated: ($C_{17}H_{16}O$) 236.1201(M^+) Found: 236.1199.

1-Naphthyl prop-1-ynyl ether (1i)

A solution of *n*-BuLi (1.6 M hexane solution, 20 mmol, 13 mL) was added dropwise to a solution of 1,2-dichloro-1-(1-naphthoxy)ethene[25] (9.95 mmol, 2.38 g) in Et_2O (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. MeI (20.6 mmol, 2.93 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (13.5 mmol, 1.73 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by alumina column chromatography to give the desired product as a yellow oil (0.544 g, 30%).; IR: (neat) 2295 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 8.20-8.17 (m, 1H), 7.86-7.84 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.54-7.52 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 1.98 (s, 3H, 13-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 152.2 (s), 134.3 (s), 127.5 (d), 126.7 (d), 126.1 (d), 125.3 (d), 123.7 (s), 123.6 (d), 120.8 (d), 108.1 (d), 82.0 (s), 41.2 (s), 1.8 (q); HRMS: (EI, 70 eV) Calculated: ($C_{13}H_{10}O$) 182.0732 (M^+) Found: 182.0734.

2,6-Dimethylphenyl prop-1-ynyl ether (1j)

A solution of *n*-BuLi (1.6 M hexane solution, 20 mmol, 13 ml) was added dropwise to a solution of 1,2-dichloro-1-(2,6-dimethylphenoxy)ethene[26] (9.87 mmol, 2.15 g) in Et_2O (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. MeI (20.6 mmol, 2.93 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (13.1 mmol, 1.70 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by alumina column chromatography to give the desired product as a yellow oil (0.269 g, 17%).; IR: (neat) 2282 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.01 (m, 3H, 3-H x 2, 4-H), 2.37 (s, 6H, 2-Me x 2), 1.72 (s, 3H, 3'-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 153.8 (s), 129.4 (s), 129.0 (d), 125.6 (d), 86.1 (s), 32.0 (q), 15.9 (s), 1.5 (q); HRMS: (EI, 70 eV) Calculated: ($C_{11}H_{12}O$) 160.0888 (M^+) Found: 160.0889.

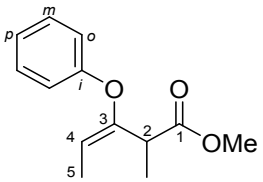
Phenyl 4-methylpent-4-en-1-ynyl ether (1l)

A solution of *n*-BuLi (1.6 M hexane solution, 11 mmol, 7.0 mL) was added dropwise to a solution of ethynyl phenyl ether (9.75 mmol, 1.15 g) in THF (20 mL) at -78 °C. Then, the mixture was stirred for 1 h at -78 °C. 3-Bromo-2-methylprop-1-ene (9.18 mmol, 1.71 g) and *N*,*N*'-dimethylpropyleneurea (DMPU) (9.53 mmol, 1.22 g) were added to the reaction mixture at -78 °C, and stirred at 50 °C for 8 h. The mixture was poured into hexane (50 mL) and sat. NH_4Cl aq (10 mL) and then extracted with hexane (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by short alumina column chromatography to give the desired product as a yellow oil (0.937 g, 50%).; IR: (neat) 2281 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.34 (t, *J* = 7.7 Hz, 2H, *m*), 7.26 (d, *J* = 7.7 Hz, 2H, *o*), 7.11 (t, *J* = 7.7 Hz, 1H, *p*), 5.07 (s, 1H, 5-H^A), 4.85 (s, 1H, 5-H^B), 2.99 (s, 2H, 3-H_2), 1.83 (s, 3H, 4-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.2 (s), 141.4 (s), 129.5 (d), 124.0 (d), 114.8 (d), 111.2 (t), 85.2 (s), 41.8 (s), 26.1 (t), 22.1 (q); HRMS: (EI, 70 eV) Calculated: 172.0888 (M^+) ($C_{12}H_{12}O$) Found: 172.0890.

General procedure for the carboindation of alkynyl ether 1 using InI_3 and a silyl ketene acetal 2 to give enol ether 3 (Table 6)

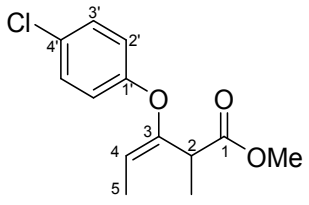
Alkynyl ether **1** (0.50 mmol) was added to a solution of InI_3 (0.50 mmol) and a silyl ketene acetal **2** (1.50 mmol) in dichloromethane (1 mL). The mixture was stirred at 0 °C for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography.

Methyl (E)-2-methyl-3-phenoxypent-3-enoate (3aa)



Phenyl prop-1-ynyl ether **1a** (0.442 mmol, 0.0584 g) was added to a solution of InI_3 (0.514 mmol, 0.255 g) and methylketene methyl trimethylsilyl acetal **2a** (1.64 mmol, 0.263 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.074 g, 76%).; IR: (neat) 1745 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.29 (t, *J* = 7.7 Hz, 2H, *m*), 7.05 (t, *J* = 7.7 Hz, 1H, *p*), 7.00 (d, *J* = 7.7 Hz, 2H, *o*), 4.72 (q, *J* = 7.1 Hz, 1H, 4-H), 3.72 (s, 3H, OMe), 3.69 (q, *J* = 7.3 Hz, 1H, 2-H), 1.63 (d, *J* = 7.1 Hz, 3H, 5-H_3), 1.43 (d, *J* = 7.3 Hz, 3H, 2-Me).; ^{13}C NMR: (100 MHz, $CDCl_3$) 173.3 (C, C-1), 156.2 (C, *i*), 154.1 (C, C-3), 129.4 (CH, *m*), 123.2 (CH, *p*), 119.9 (CH, *o*), 103.4 (CH, C-4), 52.1 (CH_3, OMe), 39.6 (CH, C-2), 14.3 (CH_3, 2-Me), 11.4 (CH_3, C-5).; HRMS: (EI, 70 eV) Calculated: ($C_{13}H_{16}O_3$) 220.1099 (M^+) Found: 220.1103.

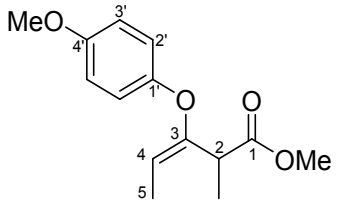
Methyl (E)-3-(4-chlorophenoxy)-2-methylpent-3-enoate (3ca)



A solution of 4-chlorophenyl prop-1-ynyl ether **1c** (0.505 mmol, 0.0842 g) was added to a solution of InI_3 (0.545 mmol, 0.270 g) and methylketene methyl trimethylsilyl

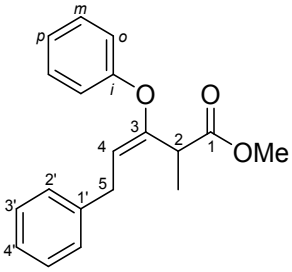
acetal 2a (1.58 mmol, 0.253 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.093 g, 73%). The structure of **3ca** was determined by ^{1}H-NOE experiment and 2D spectra of the compound.; IR: (neat) 1743 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.18 (d, *J* = 8.7 Hz, 2H, 3'-H x 2), 6.88 (d, *J* = 8.7 Hz, 2H, 2'-H x 2), 4.67 (q, *J* = 7.2 Hz, 1H, 4-H), 3.64 (s, 3H, OMe), 3.62 (q, *J* = 7.2 Hz, 1H, 2-H), 1.56 (d, *J* = 7.2 Hz, 3H, 2-Me), 1.35 (d, *J* = 7.2 Hz, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.0 (s, C-1), 154.8 (s, C-1'), 153.8 (s, C-3), 129.4 (d, C-2'), 128.1 (s, C-3'), 121.0 (d, C-2'), 104.2 (d, C-4), 52.1 (q, OMe), 39.5 (s, C-2), 14.2 (q, 2-Me), 11.4 (q, C-5); HRMS: (EI, 70 eV) Calculated: ($C_{13}H_{15}ClO_3$) 254.0710 (M^+) Found: 254.0711.

Methyl (E)-3-(4-methoxyphenoxy)-2-methylpent-3-enoate (3da)



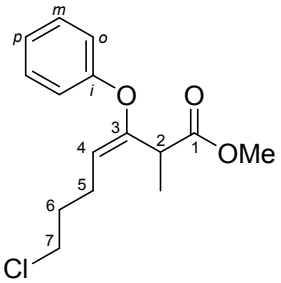
A solution of (4-methoxyphenyl)(prop-1-ynyl)ether **1d** (0.524 mmol, 0.0850 g) was added to a solution of InI_3 (0.551 mmol, 0.273 g) and methylketene methyl trimethylsilyl acetal **2a** (1.76 mmol, 0.282 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.105 g, 80%).; IR: (neat) 1743 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 6.92 (d, *J* = 9.2 Hz, 2H, 2'-H x 2), 6.83 (d, *J* = 9.2 Hz, 2H, 3'-H x 2), 4.54 (q, *J* = 7.2 Hz, 1H, 4-H), 3.78 (s, 3H, 4'-OMe), 3.74 (s, 3H, 1-OMe), 3.68 (q, *J* = 7.2 Hz, 1H, 2-H), 1.59 (d, *J* = 7.2 Hz, 3H, 5-H_3), 1.44 (d, *J* = 7.2 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.3 (s, C-1), 155.7 (s, C-4'), 155.3 (s, C-3), 149.1 (s, C-1'), 121.6 (d, C-2'), 114.4 (d, C-3'), 100.6 (d, C-4), 55.5 (q, 4'-OMe), 52.0 (q, 1-COOMe), 39.5 (d, C-2), 14.3 (q, 2-Me), 11.3 (q, C-5); HRMS: (EI, 70 eV) Calculated: ($C_{14}H_{18}O_4$) 250.1205 (M^+) Found: 250.1209.

Methyl (E)-2-methyl-3-phenoxy-5-phenylpent-3-enoate (3ea)



Phenyl 3-phenylprop-1-ynyl ether **1e** (0.522 mmol, 0.109 g) was added to a solution of InI_3 (0.547 mmol, 0.269 g) and methylketene methyl trimethylsilyl acetal **2a** (1.60 mmol, 0.256 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.064 g, 43%).; IR: (neat) 1739 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.29-7.27 (m, 4H, *m* and 3'-H x 2), 7.19-7.17 (m, 3H, 2'-H x 2 and 4'-H), 7.06-7.03 (m, 3H, *p* and *o*), 4.83 (t, *J* = 8.0 Hz, 1H, 4-H), 3.80 (q, *J* = 7.1 Hz, 1H, 2-H), 3.73 (s, 3H, OMe), 3.43 (dd, *J* = 16.0, 8.0 Hz, 2H, 5-*H*H), 3.37 (dd, *J* = 16.0, 8.0 Hz, 2H, 5-H*H*), 1.49 (d, *J* = 7.1 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.1 (C, C-1), 155.8 (C, *i*), 155.0 (C, C-3), 140.4 (C, C-1'), 129.5 (CH, *m*), 128.4 (CH), 128.1 (CH), 126.1 (CH), 123.6 (CH, *p*), 120.3 (CH, *o*), 106.7 (CH, C-4), 52.1 (CH_3, OMe), 39.9 (CH, C-2), 32.5 (CH_2, C-5), 14.6 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: ($C_{19}H_{20}O_3$) 296.1412 (M^+) Found: 296.1413.

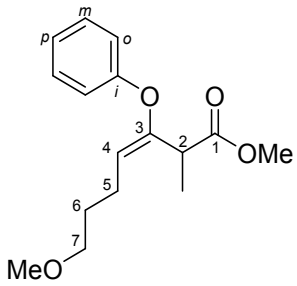
Methyl (E)-7-chloro-2-methyl-3-phenoxyhept-3-enoate (3fa)



Phenyl 5-chloropent-1-ynyl ether **1f** (0.532 mmol, 0.104 g) was added to a solution of InI_3 (0.529 mmol, 0.262 g) and methylketene methyl trimethylsilyl acetal **2a** (1.59 mmol, 0.254 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a transparent oil (0.097 g, 64%).; IR: (neat) 1741 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz,

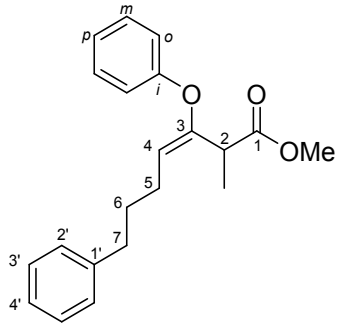
$CDCl_3$) 7.31 (t, *J* = 7.7 Hz, 2H, *m*), 7.08 (t, *J* = 7.7 Hz, 1H, *p*), 7.00 (d, *J* = 7.7 Hz, 2H, *o*), 4.56 (t, *J* = 7.3 Hz, 1H, 4-H), 3.75-3.72 (m, 4H, OMe and 2-H), 3.54-3.53 (m, 2H, 7-H_2), 2.21 (q, *J* = 7.3 Hz, 2H, 5-H_2), 1.79 (quint, *J* = 7.3 Hz, 2H, 6-H_2), 1.46 (d, *J* = 7.0 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.0 (C, C-1), 155.8 (C, *i*), 155.3 (C, C-3), 129.5 (CH, *m*), 123.5 (CH, *p*), 120.2 (CH, *o*), 106.3 (CH, C-4), 52.1 (CH_3, OMe), 44.1 (CH_2, C-7), 39.9 (CH, C-2), 32.5 (CH_2, C-6), 23.4 (CH_2, C-5), 14.6 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: ($C_{15}H_{19}ClO_3$) 282.1023 (M^+) Found: 282.1025.

Methyl (E)-7-methoxy-2-methyl-3-phenoxyhept-3-enoate (3ga)



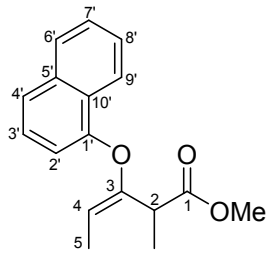
Phenyl 5-methoxypent-1-ynyl ether **1g** (0.532 mmol, 0.101 g) was added to a solution of InI_3 (0.541 mmol, 0.268 g) and methylketene methyl trimethylsilyl acetal **2a** (1.61 mmol, 0.258 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.079 g, 53%).; IR: (neat) 1745 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.29 (t, *J* = 7.7 Hz, 2H, *m*), 7.06 (t, *J* = 7.7 Hz, 1H, *p*), 7.01 (d, *J* = 7.7 Hz, 2H, *o*), 4.66 (t, *J* = 7.5 Hz, 1H, 4-H), 3.74-3.69 (m, 4H, 2-H and COOMe), 3.35 (t, *J* = 6.2 Hz, 2H, 7-H_2), 3.31 (s, 3H, 7-OMe), 2.11 (q, *J* = 7.5 Hz, 2H, 5-H_2), 1.63-1.56 (m, 2H, 6-H_2), 1.44 (d, *J* = 6.9 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.1 (C, C-1), 156.1 (C, *i*), 154.2 (C, C-3), 129.4 (CH, *m*), 123.2 (CH, *p*), 119.9 (CH, *o*), 108.2 (CH, C-4), 71.6 (CH_2, C-7), 58.5 (CH_3, 7-OMe), 52.0 (CH_3, 1-OMe), 39.8 (CH, C-2), 29.7 (CH_2, C-6), 22.9 (CH_2, C-5), 14.6 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: ($C_{16}H_{22}O_4$) 278.1518 (M^+) Found: 278.1517.

Methyl (E)-2-methyl-3-phenoxy-7-phenylhept-3-enoate (3ha)



Phenyl 5-phenylpent-1-ynyl ether **1h** (0.494 mmol, 0.116 g) was added to a solution of InI_3 (0.515 mmol, 0.255 g) and methylketene methyl trimethylsilyl acetal **2a** (1.53 mmol, 0.245 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.093 g, 57%).; IR: (neat) 1743 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.30-7.27 (m, 4H, Ar), 7.19-7.15 (m, 3H, Ar), 7.06 (t, *J* = 7.7 Hz, 1H, *p*), 7.01 (d, *J* = 7.7 Hz, 2H, *o*), 4.70 (t, *J* = 7.7 Hz, 1H, 4-H), 3.71 (s, 3H, OMe), 3.64 (q, *J* = 7.7 Hz, 1H, 2-H), 2.60 (t, *J* = 7.7 Hz, 2H, 7-H_2), 2.10-2.04 (m, 2H, 5-H_2), 1.72-1.62 (m, 2H, 6-H_2), 1.43 (d, *J* = 7.7 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.2 (s, C-1), 156.2 (s, *i*), 153.9 (s, C-3), 142.1 (s, C-1'), 129.4 (d), 128.34 (d), 128.29 (d), 125.7 (d), 123.2 (d, *p*), 119.9 (d, *o*), 108.8 (d, C-4), 52.1 (q, OMe), 39.9 (d, C-2), 35.3 (t, C-7), 31.7 (t, C-6), 26.0 (t, C-5), 14.6 (q, 2-Me); HRMS: (EI, 70 eV) Calculated: ($C_{21}H_{24}O_3$) 324.1725 (M^+) Found: 324.1721.

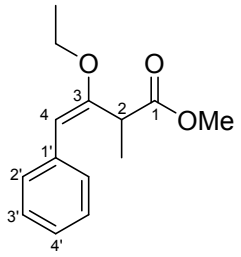
Methyl (E)-2-methyl-3-(naphthalen-1-yloxy)pent-3-enoate (3ia)



A solution of 1-naphthyl prop-1-ynyl ether **1i** (0.500 mmol, 0.0912 g) was added to a solution of InI_3 (0.547 mmol, 0.269 g) and methylketene methyl trimethylsilyl acetal **2a** (1.60 mmol, 0.256 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.116 g, 82%).; IR: (neat) 1743 (C=O) cm^{-1};

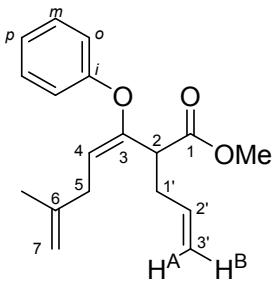
^{1}H NMR: (400 MHz, $CDCl_3$) 8.06-8.05 (m, 1H), 7.83-7.81 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H, 4'-H), 7.47-7.46 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H, 3'-H), 7.10 (d, *J* = 8.0 Hz, 1H, 2'-H), 4.58 (q, *J* = 7.2 Hz, 1H, 4-H), 3.82-3.75 (m, 4H, OMe and 2-H), 1.60 (d, *J* = 7.2 Hz, 3H, 5-H_3), 1.56 (d, *J* = 7.2 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.4 (s, C-1), 154.3 (s, C-3), 151.5 (s, C-1'), 134.8 (s, C-5'), 127.7 (d), 127.4 (s, C-10'), 126.3 (d), 125.8 (d), 125.7 (d), 123.6 (d, C-4'), 122.1 (s), 115.2 (d, C-2'), 102.0 (d, C-4), 52.1 (q, OMe), 39.8 (d, C-2), 14.6 (q, 2-Me), 11.4 (q, C-5); HRMS: (EI, 70 eV) Calculated: ($C_{17}H_{18}O_3$) 270.1256 (M^+) Found: 270.1257.

Methyl (E)-3-ethoxy-2-methyl-4-phenylbut-3-enoate (3ka)



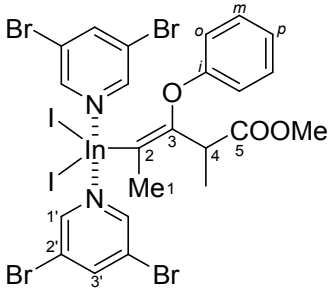
Ethyl phenylethynyl ether **1k** (0.517 mmol, 0.0756 g) was added to a solution of InI_3 (0.555 mmol, 0.275 g) and methylketene methyl trimethylsilyl acetal **2a** (1.79 mmol, 0.287 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.0301 g, 25%). The structure of **3ka** was determined by ^{1}H-NOE experiment and 2D spectra of the compound.; IR: (neat) 1744 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.31 (t, *J* = 7.5 Hz, 2H, 7-H x 2), 7.24 (d, *J* = 7.5 Hz, 2H, 6-H x 2), 7.18 (t, *J* = 7.5 Hz, 1H, 8-H), 5.68 (s, 1H, 4-H), 3.87-3.85 (m, 2H, OCH_2CH$_3$), 3.78 (q, *J* = 7.2 Hz, 1H, 2-H), 3.70 (s, 3H, OMe), 1.33 (d, *J* = 7.2 Hz, 3H, 2-Me), 1.31 (t, *J* = 6.9 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.5 (s, C-1), 156.7 (s, C-3), 137.0 (s, C-5), 128.8 (d, C-6), 128.3 (d, C-7), 125.7 (d, C-8), 100.9 (d, C-4), 62.9 (t, OCH_2CH$_3$), 52.0 (q, OMe), 40.5 (d, C-2), 14.9 (q, 2-Me), 14.3 (q, OCH$_2$CH_3); HRMS: (EI, 70 eV) Calculated: 234.1256 (M^+) ($C_{14}H_{18}O_3$) Found: 234.1260.

Methyl (E)-2-allyl-6-methyl-3-phenoxyhepta-3,6-dienoate (3le)



Phenyl(4-methylpent-4-en-1-ynyl)ether **1l** (0.500 mmol, 0.086 g) was added to a solution of InI_3 (0.533 mmol, 0.264 g) and allylketene methyl trimethylsilyl acetal **2e** (1.55 mmol, 0.289 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. The mixture was poured into ethyl acetate (20 mL) and sat. $NaHCO_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as colorless oil (0.085 g, 60%).; IR: (neat) 1742 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.31 (t, *J* = 7.7 Hz, 2H, *m*), 7.08 (t, *J* = 7.7 Hz, 1H, *o*), 7.02 (d, *J* = 7.7 Hz, 2H, *p*), 5.85 (ddt, *J* = 17.1, 10.1 and 7.0 Hz, 1H, 2'-H), 5.17 (dd, *J* = 17.1 and 1.7 Hz, 1H, 3'-H^A), 5.07 (dd, *J* = 10.1, 1.7 Hz, 1H, 3'-H^B), 4.69-4.68 (m, 3H, 4-H, 7-H x 2), 3.72 (s, 3H, OMe), 3.63 (dd, *J* = 8.8 and 6.4 Hz, 1H, 2-H), 2.79-2.64 (m, 2H, 1'-H_2), 2.70 (d, *J* = 8.0 Hz, 2H, 5-H_2), 1.69 (s, 3H, 6-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.1 (s, C-1), 155.5 (s, *i*), 153.1 (s, C-3), 144.3 (s, C-6), 135.4 (d, C-2'), 129.5 (d, *m*), 123.7 (d, *p*), 120.6 (d, *q*), 116.9 (t, C-3'), 110.6 (t, C-7), 106.4 (d, C-4), 52.1 (q, OMe), 45.3 (d, C-2), 34.6 (t, C-5), 33.1 (t, C-1'), 22.5 (q, 6-Me); HRMS: (EI, 70 eV) Calculated: ($C_{18}H_{22}O_3$) 286.1569 (M^+) Found: 286.1570.

(Z)-(5-Methoxy-4-methyl-5-oxo-3-phenoxypent-2-en-2-yl)indium diiodide bis-3,5-dibromopyridine complex (4aa·3,5-Br$_2$Py)



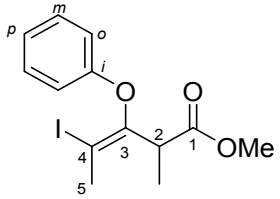
All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard glove box techniques. Phenyl prop-1-ynyl ether **1a** (1.02 mmol, 0.135 g) was added to a solution of InI_3 (1.02 mmol, 0.505 g) and methylketene methyl trimethylsilyl acetal **2a** (3.70 mmol, 0.594 g) in $CDCl_3$ (2 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. To obtain a suitable crystal to X-ray crystallography analysis, 3,5-dibromopyridine (2.62 mmol, 0.621 g) was added to the reaction mixture at room temperature to give an immediately suspended solution.

After the volatiles were removed in vacuo, the residue was washed with hexane (2 mL x 5) and extracted using diethyl ether (2 mL x 5). The volatiles were removed to give alkenylindiums 3,5-dibromopyridine complex as a white solid (0.567 g, 52%). The solid was recrystallized in hexane/dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **4aa**·3,5-Br_2Py was confirmed by X-ray crystallography analysis (CCDC 1908815).; ^{1}H NMR: (400 MHz, $CDCl_3$) 8.75 (d, J = 1.9 Hz, 4H, 1'-H x 4), 8.11 (t, J = 1.9 Hz, 2H, 3'-H x 2), 7.17 (t, J = 7.7 Hz, 2H, *m*), 6.95 (t, J = 7.7 Hz, 1H, *p*), 6.80 (d, J = 7.7 Hz, 2H, *o*), 3.64 (s, 3H, OMe), 3.52 (q, J = 7.2 Hz, 1H, 4-H), 1.97 (s, 3H, 1-H_3), 1.31 (d, J = 7.2 Hz, 3H, 4-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.6 (s, C-5), 155.5 (s, *i*), 152.9 (s, C-3), 148.1 (d, C-1'), 143.6 (d, C-3'), 132.0 (s, C-2), 129.4 (d, *m*), 123.0 (d, *p*), 121.4 (s, C-2'), 116.9 (d, *o*), 52.2 (q, OMe), 40.7 (s, C-4), 16.8 (q, C-1), 15.0 (q, 4-Me).

General procedure for the carboindation of alkynyl ether 1 using InI_3 and a silyl ketene acetal 2 to give an iodinated enol ether 5 (Table 3)

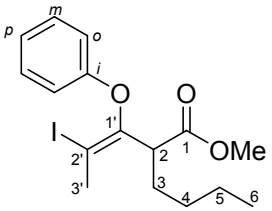
Alkynyl ether **1** (0.50 mmol) was added to a solution of InI_3 (0.50 mmol) and a silyl ketene acetal **2** (1.5 mmol) in dichloromethane (1 mL). The mixture was stirred at 0 °C for 1 h. And then, 4.5 M of I_2 in tetrahydrofuran solution (1.8 mmol/ 4 mL) was added, and then the resultant mixture was stirred at room temperature for 1 h. The mixture was quenched using 10 wt% $Na_2S_2O_3$ aq (10 mL) and was extracted with ethyl acetate (3 x 10 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography.

Methyl (Z)-4-iodo-2-methyl-3-phenoxypent-3-enoate (5aa)



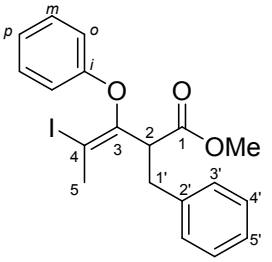
Phenyl prop-1-ynyl ether **1a** (0.469 mmol, 0.0620 g) was added to a solution of InI_3 (0.521 mmol, 0.258 g) and methylketene methyl trimethylsilyl acetal **2a** (1.55 mmol, 0.249 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless liquid (0.123 g, 76%). The structure of **5aa** was determined by ^{1}H-NOE experiment and 2D spectra of the compound.; IR: (neat) 1742 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.27 (t, J = 7.8 Hz, 2H, *m*), 7.01-6.97 (m, 3H, *o* and *p*), 3.76 (q, J = 7.2 Hz, 1H, 2-H), 3.55 (s, 3H, OMe), 2.60 (s, 3H, 5-H_3), 1.32 (d, J = 7.0 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.8 (C, C-1), 155.1 (C, *i*), 149.6 (C, C-3), 129.3 (CH, *m*), 122.3 (CH, *p*), 116.1 (CH, *o*), 88.5 (C, C-4), 52.1 (CH_3, OMe), 40.2 (CH, C-2), 27.3 (CH_3, C-5), 14.4 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: 346.0066 (M^+) ($C_{13}H_{15}IO_3$) Found: 346.0064.

Methyl (Z)-2-(2-iodo-1-phenoxyprop-1-en-1-yl)hexanoate (5ab)



Phenyl prop-1-ynyl ether **1a** (0.481 mmol, 0.0636 g) was added to a solution of InI_3 (0.535 mmol, 0.265 g) and butylketene methyl trimethylsilyl acetal **2b** (1.45 mmol, 0.295 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.120 g, 64%).; IR: (neat) 1743 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.27 (t, J = 8.0 Hz, 2H, *m*), 7.00 (t, J = 7.7 Hz, 1H, *p*), 6.95 (d, J = 7.7 Hz, 2H, *o*), 3.63 (t, J = 7.5 Hz, 1H, 2-H), 3.48 (s, 3H, OMe), 2.63 (s, 3H, 3'-H_3), 1.89-1.70 (m, 2H, 3-H_2), 1.32-1.27 (m, 4H, 4-H_2 and 5-H_2), 0.89 (t, J = 7.0 Hz, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.3 (C, C-1), 155.1 (C, *i*), 148.8 (C, C-1'), 129.3 (CH, *m*), 122.3 (CH, *p*), 116.1 (CH, *o*), 89.4 (C, C-2'), 51.9 (CH, OMe), 45.9 (CH_3, C-2), 29.3 (CH_2), 28.7 (CH_2, C-3), 27.5 (CH_2, C-3'), 22.5 (CH_2), 13.9 (CH_3, C-6); HRMS: (EI, 70 eV) Calculated: 388.0535 (M^+) ($C_{16}H_{21}IO_3$) Found: 388.0531.

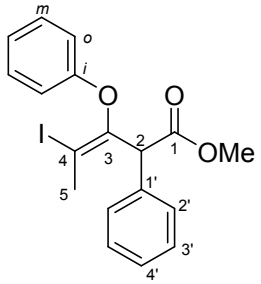
Methyl (Z)-2-benzyl-4-iodo-3-phenoxypent-3-enoate (5ac)



Phenyl prop-1-ynyl ether **1a** (0.548 mmol, 0.0724 g) was added to a solution of InI_3 (0.521 mmol, 0.258 g) and benzylketene methyl trimethylsilyl acetal **2c** (1.54 mmol,

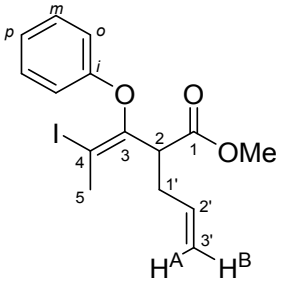
0.363 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.152 g, 69%).; IR: (neat) 1743 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.27-7.21 (m, 7H, 1'-Ph and *m*), 7.03-6.96 (m, 3H, *o* and *p*), 3.89 (dd, *J* = 8.5, 6.5 Hz, 1H, 2-H), 3.39 (s, 3H, OMe), 3.15 (dd, *J* = 13.3, 6.5 Hz, 1H, 1'-*H*H), 3.08 (dd, *J* = 14.0, 8.7 Hz, 1H, 1'-H*H*), 2.29 (s, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.6 (s, C-1), 155.0 (s, *i*), 147.4 (s, C-3), 138.3 (s, C-2'), 129.3 (d), 129.1 (d), 128.3 (d), 126.6 (d), 122.3 (d, *p*), 116.1 (s, *o*), 90.7 (s, C-4), 51.9 (q, OMe), 48.0 (d, C-2), 35.0 (t, C-1'), 27.2 (q, C-5'); HRMS: (EI, 70 eV) Calculated: 422.0379 (M^+) ($C_{19}H_{19}IO_3$) Found: 422.0380.

Methyl (Z)-4-iodo-3-phenoxy-2-phenylpent-3-enoate (5ad)



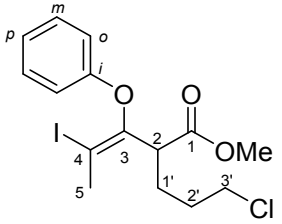
Phenyl prop-1-ynyl ether **1a** (0.479 mmol, 0.0633 g) was added to a solution of InI_3 (0.520 mmol, 0.258 g) and phenylketene methyl trimethylsilyl acetal **2d** (1.52 mmol, 0.337 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.140 g, 68%).; IR: (neat) 1743 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.33-7.21 (m, 7H, 2-Ph and *m*), 6.97 (t, *J* = 7.7 Hz, 1H, *p*), 6.91 (d, *J* = 7.7 Hz, 2H, *o*), 4.93 (s, 1H, 2-H), 3.53 (s, 3H, OMe), 2.60 (s, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.0 (C, C-1), 155.0 (C, *i*), 147.9 (C, C-3), 134.6 (C, C-1'), 129.2 (CH), 129.1 (CH), 128.4 (CH), 127.7 (CH), 122.1 (CH, *p*), 116.0 (CH, *o*), 89.8 (C, C-4), 52.4 (C, OMe), 51.8 (CH_3, C-2), 27.7 (CH_3, C-5); HRMS: (EI, 70 eV) Calculated: 408.0222 (M^+) ($C_{18}H_{17}IO_3$) Found: 408.0225.

Methyl (Z)-2-allyl-4-iodo-3-phenoxypent-3-enoate (5ae)



Phenyl prop-1-ynyl ether **1a** (0.545 mmol, 0.0720 g) was added to a solution of InI_3 (0.517 mmol, 0.256 g) and allylketene methyl trimethylsilyl acetal **2e** (1.79 mmol, 0.335 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a brown oil (0.133 g, 69%).; IR: (neat) 1741 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.27 (t, *J* = 8.0 Hz, 2H, *m*), 7.00 (t, *J* = 8.0 Hz, 1H, *p*), 6.95 (d, *J* = 8.0 Hz, 2H, *o*), 5.76 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H, 2'-H), 5.11 (dd, *J* = 16.9, 1.5 Hz, 1H, 3'-H^A), 5.06 (dd, *J* = 10.3, 1.5 Hz, 1H, 3'-H^B), 3.73 (t, *J* = 6.6 Hz, 1H, 4-H), 3.48 (s, 3H, OMe), 2.62 (s, 3H, 5-H_3), 2.57-2.47 (m, 2H, 1'-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.6 (s, C-1), 155.1 (s, *i*), 148.0 (s, C-3), 134.6 (d, C-2'), 129.3 (d, *m*), 122.3 (d, *p*), 117.4 (t, C-3'), 116.1 (d, *o*), 89.8 (s, C-4), 52.0 (q, OMe), 46.0 (d, C-2), 33.1 (t, C-1'), 27.6 (q, C-5); HRMS: (EI, 70 eV) ;Calculated: 372.0222 (M^+) ($C_{15}H_{17}O_3I$) Found: 372.0216.

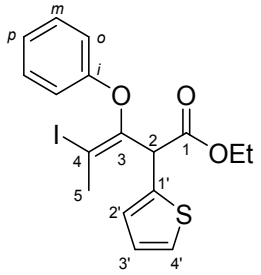
Methyl (Z)-2-(3-chloropropyl)-4-iodo-3-phenoxypent-3-enoate (5af)



Phenyl prop-1-ynyl ether **1a** (1.05 mmol, 0.139 g) was added to a solution of InI_3 (1.07 mmol, 0.530 g) and 3-chloropropylketene methyl trimethylsilyl acetal **2f** (3.08 mmol, 0.687 g) in dichloromethane (2 mL)at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (8 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (25 mL) and sat. $Na_2S_2O_3$ aq (10

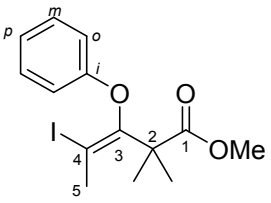
mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow oil (0.367 g, 86%).; IR: (neat) 1742 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.27 (t, J = 7.7 Hz, 2H, *m*), 7.01 (t, J = 7.7 Hz, 1H, *p*), 6.95 (d, J = 7.7 Hz, 2H, *o*), 3.66 (t, J = 8.9 Hz, 1H, 2-H), 3.53 (t, J = 6.5 Hz, 2H, 3'-H_2), 3.49 (s, 3H, OMe), 2.63 (s, 3H, 5-H_3), 2.04-1.73 (m, 4H, 1'-H_2 and 2'-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 170.7 (s, C-1), 154.8 (s, *i*), 148.2 (s, C-3), 129.3 (d, *m*), 122.5 (d, *p*), 116.1 (d, *o*), 89.8 (d, C-4), 52.0 (q, OMe), 45.0 (d, C-2), 44.4 (t, C-3'), 30.0 (t, C-2'), 27.5 (q, C-5), 26.2 (t, C-1'); HRMS: (EI, 70 eV) Calculated: 407.9989 (M^+) ($C_{15}H_{18}ClO_3I$) Found: 407.9991.

Ethyl (Z)-4-iodo-3-phenoxy-2-(thien-2-yl)pent-3-enoate(5ag)



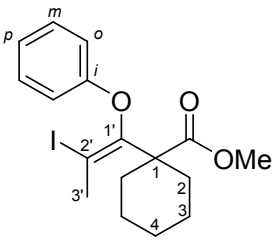
Phenyl prop-1-ynyl ether **1a** (0.468 mmol, 0.0619 g) was added to a solution of InI_3 (0.531 mmol, 0.263 g) and thien-2-ylketene methyl trimethylsilyl acetal **2g** (1.79 mmol, 0.409 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow oil (0.161 g, 20%).; IR: (neat) 1741 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.22-7.26 (m, 3H, 4'-H and *m*), 7.01-6.89 (m, 5H, 2'-H, 3'-H, *o* and *p*), 5.14 (s, 1H, 2-H), 4.05-3.98 (m, 2H, O$CH_2$$CH_3$), 2.64 (s, 3H, 5-$H_3$), 1.18 (t, J = 7.2 Hz, 3H, OCH_2CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.7 (s, C-1), 155.0 (s, *i*), 147.9 (s, C-3), 136.2 (s, C-1'), 129.3 (d, *m*), 127.2 (d, C-2'), 126.3 (d, C-3'), 125.8 (d, C-4'), 122.4 (d, *p*), 116.2 (d, *o*), 90.0 (s, C-4), 62.0 (t, O$CH_2$$CH_3$), 47.1 (d, C-2), 27.8 (q, C-5), 13.9 (q, OCH_2CH_3); HRMS: (EI, 70 eV) Calculated: 427.9943 (M^+) ($C_{17}H_{17}SIO_3$) Found: 427.9938.

Methyl (Z)-4-iodo-2-methyl-3-phenoxypent-3-enoate (5ah)



Phenyl prop-1-ynyl ether **1a** (0.480 mmol, 0.0635 g) was added to a solution of InI_3 (0.518 mmol, 0.257 g) and dimethylketene methyl trimethylsilyl acetal **2h** (1.43 mmol, 0.250 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.093 g, 54%). The solid was recrystallized in dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **5ah** was confirmed by X-ray crystallography analysis (CCDC 1908814).; mp: 52-53 °C; IR: (KBr) 1742 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.31 (t, J = 7.7 Hz, 2H, *m*), 7.08 (d, J = 7.7 Hz, 2H, *o*), 7.01 (t, J = 7.7 Hz, 1H, *p*), 3.79 (s, 3H, OMe), 2.44 (s, 3H, 5-H_3), 1.41 (s, 6H, 2-Me x 2); ^{13}C NMR: (100 MHz, $CDCl_3$) 176.2 (C, C-1), 156.3 (C, *i*), 152.8 (C, C-3), 129.5 (CH, *m*), 121.7 (CH, *p*), 115.3 (CH, *o*), 89.2 (C, C-4), 52.6 (CH_3, OMe), 47.7 (C, C-2), 27.3 (CH_3, C-5), 25.6 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: 360.0222 (M^+) ($C_{14}H_{17}IO_3$) Found: 360.0222.

Methyl (Z)-1-(2-iodo-1-phenoxyprop-1-en-1-yl)cyclohexane-1-carboxylate (5ai)



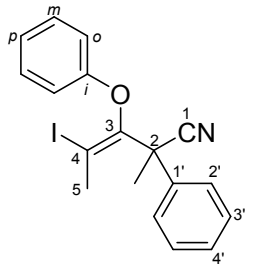
Phenyl prop-1-ynyl ether **1a** (0.535 mmol, 0.0707 g) was added to a solution of InI_3 (0.503 mmol, 0.249 g) and (methoxytrimethylsiloxymethylene)cyclohexane **2i** (1.62 mmol, 0.348 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, 0.45 M of I_2 in a tetrahydrofuran solution (4 mL) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate =

88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow solid (0.161 g, 80%).; mp: 65-69 °C; IR: (KBr) 1730 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.30 (t, *J* = 8.0 Hz, 2H, *m*), 7.07 (d, *J* = 8.0 Hz, 2H, *o*), 7.00 (t, *J* = 8.0 Hz, 1H, *p*), 3.77 (s, 3H, OMe), 2.53 (s, 3H, 3'-H_3), 2.07 (m, 2H), 1.80-1.28 (m, 8H); ^{13}C NMR: (100 MHz, $CDCl_3$) 175.0 (C, 1-*C*OOMe), 156.3 (C, *i*), 152.9 (C, C-1'), 129.4 (CH, *m*), 121.6 (CH, *p*), 115.3 (CH, *o*), 90.6 (C, C-2'), 52.6 (C, C-1), 52.2 (CH_3, OMe), 33.7 (CH_2), 27.3 (CH_3, C-3'), 25.1 (CH_2), 22.6 (CH_2); HRMS: (CI, 70 eV) Calculated: 401.0614 ($[M + H]^+$) ($C_{17}H_{22}IO_3$) Found: 401.0613.

General procedure for the carboindation of alkynyl ether 1 using InI_3 and a silyl ketene imine 6 to give an iodinated enol ether 7 (Table 4)

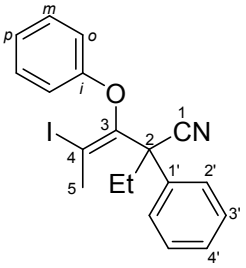
Alkynyl ether **1** (0.50 mmol) was added to a solution of InI_3 (0.50 mmol) and silyl ketene imine **6** (1.0 mmol) in dichloromethane (1 mL). The mixture was stirred at 0 °C for 1 h. And then, iodobenzene diacetate (1.0 mmol) was added, and the resultant mixture was stirred at room temperature for 1 h. The mixture was quenched using 10 wt% $Na_2S_2O_3$ aq (10 mL) and was extracted with ethyl acetate (3 x 10 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography.

(Z)-4-Iodo-2-methyl-3-phenoxy-2-phenylpent-3-enenitrile (7aa)



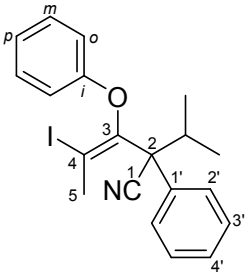
Phenyl prop-1-ynyl ether **1a** (0.536 mmol, 0.0708 g) was added to a solution of InI_3 (0.548 mmol, 0.272 g) and *tert*-butyldimethylsilyl methylphenylketene imine **6a** (1.03 mmol, 0.253 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.07 mmol, 0.344 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a colorless oil (0.187 g, 90%).; IR: (neat) 2236 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.53 (d, *J* = 7.6 Hz, 2H, 2'-H x 2), 7.42-7.36 (m, 5H, *m*, 3'-H x 2 and 4'-H), 7.10-7.08 (m, 3H, *p*, *o*), 2.35 (s, 3H, 2-Me), 1.70 (s, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.8 (C, *i*), 148.0 (C, C-3), 140.9 (C, C-1'), 130.1 (CH, *m*), 129.3 (CH), 128.0 (CH), 125.1 (CH, C-2'), 122.5 (CH), 120.6 (C, C-1), 114.9 (CH), 94.5 (C, C-4), 45.2 (C, C-2), 29.4 (CH_3, C-5), 28.4 (CH_3, 2-Me); HRMS: (EI, 70 eV) Calculated: 389.0277 (M^+) ($C_{18}H_{16}NOI$) Found: 389.0280.

(Z)-4-Iodo-2-ethyl-3-phenoxy-2-phenylpent-3-enenitrile (7ab)



Phenyl prop-1-ynyl ether **1a** (0.539 mmol, 0.0712 g) was added to a solution of InI_3 (0.572 mmol, 0.283 g) and *tert*-butyldimethylsilyl ethylphenylketene imine **6b** (1.15 mmol, 0.298 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (0.944 mmol, 0.304 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow solid (0.196 g, 90%). The solid was recrystallized in dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **7ab** was confirmed by X-ray crystallography analysis (CCDC 1908816).; mp: 121-124 °C; IR: (KBr) 2235 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.48 (d, *J* = 8.2 Hz, 2H, 2'-H x 2), 7.40-7.34 (m, 5H, 3'-H x 2, 4'-H and *m*), 7.08 (m, 3H, *o* and *p*), 2.34 (s, 3H, 5-H_3), 2.16-2.01 (m, 2H, 2-CH_2CH$_3$), 0.68 (t, *J* = 7.2 Hz, 3H, 2-CH$_2$CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.0 (s, *i*), 148.9 (s, C-3), 138.3 (s, C-1'), 130.1 (d, *m*), 128.9 (d), 128.0 (d), 126.1 (d, C-2'), 122.4 (d, *p*), 119.4 (s, C-1), 114.9 (d, *o*), 94.9 (s, C-4), 50.8 (s, C-2), 32.8 (t, 2-*C*H$_2$CH$_3$), 28.3 (q, C-5), 8.9 (q, 2-CH$_2$*C*H$_3$).; HRMS: (EI, 70 eV) Calculated: 403.0433 (M^+) ($C_{19}H_{18}NOI$) Found: 403.0428.

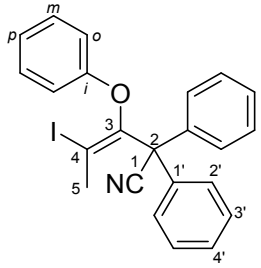
(Z)-4-Iodo-2-isopropyl-3-phenoxy-2-phenylpent-3-enenitrile (7ac)



Phenyl prop-1-ynyl ether **1a** (0.495 mmol, 0.0655 g) was added to a solution of InI_3 (0.561 mmol, 0.278 g) and *tert*-butyldimethylsilyl isopropylphenylketene imine **6c** (1.02 mmol, 0.280 g) in dichloromethane (1 mL) at 0 °C. The

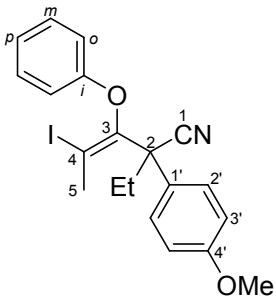
mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.01 mmol, 0.304 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow solid (0.0862 g, 41%).; mp: 101-111 °C; IR: (KBr) 2234 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$); 7.44-7.26 (m, 7H, 2-Ph and *m*), 7.04 (t, *J* = 7.7 Hz, 1H, *p*), 6.97 (d, *J* = 7.7 Hz, 2H, *o*), 2.62-2.52 (m, 1H, 2-C*H*$(CH_3)_2$), 2.43 (s, 3H, 5-H_3), 1.06 (d, *J* = 6.5 Hz, 3H, 2-CH(C*H*$_3$)(CH_3)), 0.83 (d, *J* = 6.5 Hz, 3H, 2-CH(CH_3) (C*H*$_3$)); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.6 (s, *i*), 148.4 (s, C-3), 135.2 (s, C-1'), 129.7 (d, *m*), 128.4 (d), 128.0 (s), 127.7 (s), 122.3 (s, *p*), 119.8 (s, C-1), 115.3 (s, *o*), 95.0 (s, C-4), 55.1 (s, C-2), 34.7 (d, 2-*C*H$(CH_3)_2$), 29.2 (q, C-5), 19.4 (q, 2-CH(*C*H_3)(CH_3)), 18.8 (q, 2-CH(CH_3)(*C*H_3)); HRMS: (EI, 70 eV) Calculated: 417.0590 (M^+) ($C_{20}H_{20}NOI$) Found: 417.0585.

(Z)-4-Iodo-3-phenoxy-2,2-diphenylpent-3-enenitrile (7ad)



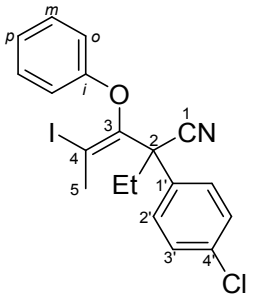
Phenyl prop-1-ynyl ether **1a** (0.532 mmol, 0.0703 g) was added to a solution of InI_3 (0.551 mmol, 0.273 g) and *tert*-butyldimethylsilyl diphenylketene imine **6d** (1.00 mmol, 0.308 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then iodobenzene diacetate (0.995 mmol, 0.321 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow solid (0.202 g, 84%).; mp: 107-114 °C; IR: (KBr) 2239 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.35-7.18 (m, 10H, 2-Ph x 2), 7.06 (t, *J* = 7.9 Hz, 2H, *m*), 6.86 (t, *J* = 7.9 Hz, 1H, *p*), 6.60 (d, *J* = 7.9 Hz, 2H, *o*), 2.53 (s, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.1 (C, *i*), 146.3 (C, C-3), 137.4 (C, C-1'), 129.1 (CH), 128.4 (CH, *m*), 128.1 (CH), 127.9 (CH), 122.1 (CH, *p*), 120.2 (C, C-1), 115.0 (CH, *o*), 95.3 (C, C-4), 54.8 (C, C-2), 29.6 (CH_3, C-5); HRMS: (EI, 70 eV) Calculated: 451.0433 (M^+) ($C_{23}H_{18}NOI$) Found: 451.0430.

(Z)-2-Ethyl-4-iodo-2-(4-methoxyphenyl)-3-phenoxypent-3-enenitrile (7ae)



Phenyl prop-1-ynyl ether **1a** (0.536 mmol, 0.0709 g) was added to a solution of InI_3 (0.567 mmol, 0.281 g) and *tert*-butyldimethylsilyl ethyl(4-methoxyphenyl)ketene imine **6e** (0.984 mmol, 0.280 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (0.998 mmol, 0.321 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.156 g, 67%).; mp: 130-138 °C;IR: (KBr) 2235 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.40-7.35 (m, 4H, *m* and 2'-H x 2), 7.08-7.06 (m, 3H, *o* and *p*), 6.91 (d, *J* = 8.9 Hz, 2H, 3'-H x 2), 3.83 (s, 3H, OMe), 2.37 (s, 3H, 5-H_3), 2.08-2.02 (m, 2H, 2-C$H_2$$CH_3$), 0.69 (t, *J* = 7.3 Hz, 3H, 2-CH_2CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 159.0 (s, C-4'), 156.0 (s, *i*), 149.1 (s, C-3), 130.2 (s, C-1'), 130.0 (d, *m*), 127.3 (d, C-2'), 122.4 (d, *p*), 119.6 (s, C-1), 114.8 (d, *o*), 114.1 (d, C-3'), 94.8 (s, C-4), 55.3 (q, OMe), 50.1 (s, C-2), 32.8 (t, 2-*C*$H_2$$CH_3$), 28.3 (q, C-5), 8.9 (q, 2-CH_2*C*H_3); HRMS: (EI, 70 eV) Calculated: 433.0539 (M^+) ($C_{20}H_{20}NO_2I$) Found: 433.0536.

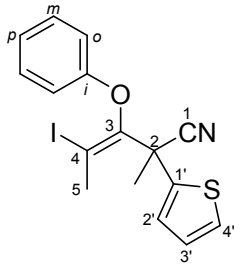
(Z)-2-(4-Chlorophenyl)-2-ethyl-4-iodo-3-phenoxypent-3-enenitrile (7af)



Phenyl prop-1-ynyl ether **1a** (0.527 mmol, 0.0696 g) was added to a solution of InI_3 (0.547 mmol, 0.271 g) and *tert*-butyldimethylsilyl ethyl(4-chlorophenyl)ketene imine **6f** (1.08 mmol, 0.316 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.02 mmol, 0.329 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at

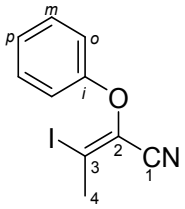
room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.175 g, 76%).; mp: 120-134 °C; IR: (KBr) 2236 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.41-7.39 (m, 6H, *m*, 2'-H x 2 and 3'-H x 2), 7.09 (t, *J* = 7.7 Hz, 1H, *p*), 7.05 (d, *J* = 7.7 Hz, 2H, *o*), 2.36 (s, 3H, 5-H_3), 2.07 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 0.69 (t, *J* = 7.3 Hz, 3H, CH_2CH_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.9 (s, *i*), 148.5 (s, C-3), 136.9 (s), 134.0 (s), 130.1 (d, *m*), 129.1 (d), 127.5 (d), 122.6 (d, *p*), 119.0 (s, C-1), 114.8 (d, *o*), 95.0 (s, C-4), 50.3 (s, C-2), 32.7 (t, CH_2CH_3), 28.3 (q, C-5), 8.9 (q, CH_2CH_3); HRMS: (EI, 70 eV) Calculated: 437.0043 (M^+) ($C_{19}H_{17}ClNOI$) Found: 437.0043.

(Z)-4-Iodo-2-methyl-3-phenoxy-2-(thien-2-yl)pent-3-enenitrile (7ag)



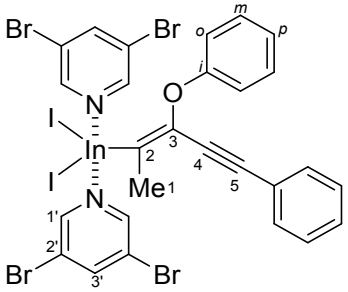
Phenyl prop-1-ynyl ether **1a** (0.534 mmol, 0.0706 g) was added to a solution of InI_3 (0.554 mmol, 0.274 g) and *tert*-butyldimethylsilyl methyl(thien-2-yl)ketene imine **6g** (1.04 mmol, 0.261 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.02 mmol, 0.329 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow oil (0.058 g, 27%).; IR: (neat) 2237 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.36 (t, *J* = 7.7 Hz, 2H, *m*), 7.29 (dd, *J* = 5.2, 1.2 Hz, 1H, 2'-H), 7.18 (dd, *J* = 3.7, 1.2 Hz, 1H, 4'-H), 7.07 (t, *J* = 7.7 Hz, 1H, *p*), 7.03 (d, *J* = 7.7 Hz, 2H, *o*), 6.96 (dd, *J* = 5.2, 3.7 Hz, 1H, 3'-H), 2.57 (s, 3H, 5-H_3), 1.84 (s, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.6 (C, *i*), 147.4 (C, C-3), 143.9 (C, C-1'), 130.0 (CH, *m*), 126.8 (CH, C-3'), 125.9 (CH, C-2'), 125.3 (CH, C-4'), 122.6 (CH, *p*), 120.1 (C, C-1), 114.9 (CH, *o*), 95.8 (C, C-4), 41.5 (C, C-2), 29.9 (CH_3, 2-Me), 28.7 (CH_3, C-5); HRMS: (EI, 70 eV) Calculated: 394.9841 (M^+) ($C_{16}H_{14}NOIS$) Found: 394.9844.

(Z)-3-Iodo-2-phenoxybut-2-enenitrile (9)



Phenyl prop-1-ynyl ether **1a** (1.19 mmol, 0.157 g) was added to a solution of InI_3 (1.52 mmol, 0.756 g) and trimethylsilyl cyanide (5.90 mmol, 0.586 g) in dichloromethane (3 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (2.63 mmol, 0.847 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (20 mL), and then extracted with ethyl acetate (20 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) to give the product as a yellow oil (0.194 g, 57%).; IR: (neat) 2215 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.37 (t, *J* = 7.7 Hz, 2H, *m*), 7.17 (t, *J* = 7.7 Hz, 1H, *p*), 7.03 (d, *J* = 7.7 Hz, 2H, *o*), 2.83 (s, 3H, 4-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.3 (s, *i*), 129.9 (s, *m*), 128.1 (s, C-1), 124.6 (s, *p*), 116.9 (s, *o*), 110.8 (s, C-2), 104.5 (s, C-3), 27.9 (q, C-4); HRMS: (EI, 70 eV) Calculated: 284.9651 (M^+) ($C_{10}H_8NOI$) Found: 284.9653.

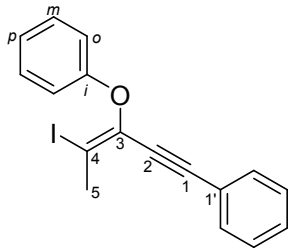
(Z)-(3-Phenoxy-5-phenylpent-2-en-4-yn-2-yl)indium diiodide bis-3,5-dibromopyridine complex (11·3,5-Br_2Py)



All preparations and manipulations were carried out under an anhydrous N_2 atmosphere using standard glove box techniques. Phenyl prop-1-ynyl ether **1a** (1.02 mmol, 0.135 g) was added to a solution of InI_3 (0.496 mmol, 0.246 g) and tributyl(phenylethynyl)stannane **10** (1.44 mmol, 0.563 g) in CH_2Cl_2 (2 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. To obtain a suitable crystal for X-ray crystallography analysis, 3,5-dibromopyridine (1.91 mmol, 0.451 g) was added to the reaction mixture at room temperature to give an immediately suspended solution. After the volatiles were removed in vacuo, the residue was washed with hexane (2 mL x 5), extracted by diethyl ether (2 mL x 5), and then the volatiles were removed in vacuo to give a pale brown solid. This solid was washed with hexane (2 mL x 5) and then the volatiles were removed in vacuo to give a crude product that included a small amount of Bu_3SnX. The crude product

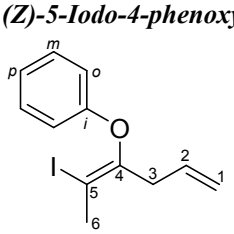
was purified by recrystallization of a hexane/dichloromethane solution to yield the desired complex as a white solid (31%, 0.171 g). The structure of **11**·3,5-Br_2Py was confirmed by X-ray crystallography analysis (CCDC 1908821). ^{1}H NMR: (400 MHz, $CDCl_3$) 8.70 (d, J = 1.9 Hz, 4H, 1'-H x 4), 8.06 (t, J = 1.9 Hz, 2H, 3'-H x 2), 7.29-7.23 (m, 7H, 5-Ph and *m*), 7.00 (t, J = 7.7 Hz, 1H, *p*), 6.85 (d, J = 7.7 Hz, 2H, *o*), 2.23 (s, 3H, 1-H_3);^{13}C NMR: (100 MHz, $CDCl_3$) 155.2 (s, *i*), 148.4 (d, C-1'), 143.0 (d, C-3'), 140.8 (br, C-2), 138.0 (s, C-3), 131.6 (d), 129.1 (d, *m*), 128.9 (d), 128.3 (d), 123.1 (d, *p*), 121.9 (s, C-6), 121.4 (s, C-2'), 117.1 (d, *o*), 96.5 (s, C-5), 80.9 (s, C-4), 18.6 (q, C-1).

(Z)-4-Iodo-3-phenoxy-1-phenyl-pent-3-en-1-yne (12)



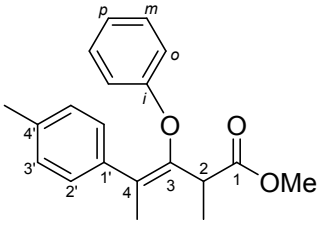
Phenyl prop-1-ynyl ether **1a** (0.537 mmol, 0.0710 g) was added to a solution of InI_3 (0.560 mmol, 0.278 g) and tributyl(phenylethynyl)stannane **10** (1.27 mmol, 0.497 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.09 mmol, 0.354 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.130 g, 67%). The solid was recrystallized in dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **12** was confirmed by X-ray crystallography analysis (CCDC 1908819).; mp: 109 °C; IR: (KBr) 2204 (C≡C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.35-7.26 (m, 7H, 1-Ph and *m*), 7.10-7.08 (m, 3H, *o* and *p*), 2.79 (s, 3H, 5-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.4 (s, *i*), 136.3 (s, C-3), 131.4 (d), 129.3 (d, *m*), 129.0 (d), 128.3 (d), 123.1 (d, *p*), 121.7 (s, C-1'), 117.5 (d, *o*), 96.7 (s, C-1), 92.9 (s, C-4), 79.9 (s, C-2), 28.1 (q, C-5); HRMS: (EI, 70 eV) Calculated: 360.0013 (M^+) ($C_{17}H_{13}OI$) Found: 360.0007.

(Z)-5-Iodo-4-phenoxy-hex-4-en-1-ene (15)



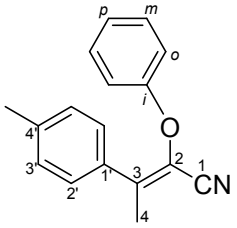
Phenyl prop-1-ynyl ether **1a** (0.531 mmol, 0.0702 g) was added to a solution of InI_3 (0.539 mmol, 0.267 g) and allyltributylstannane **13** (1.65 mmol, 0.548 g) in dichloromethane (1 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, iodobenzene diacetate (1.00 mmol, 0.323 g) was added to the reaction mixture at 0 °C, and the resultant mixture was stirred at room temperature for 1 h. The mixture was poured into ethyl acetate (20 mL) and sat. $Na_2S_2O_3$ aq (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 95:5, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a yellow oil (0.130 g, 81%). The structure of **15** was determined by ^{1}H-NOE experiment and 2D spectra of the compound.; IR: (neat) 1593 (C=C) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.30 (t, J = 7.7 Hz, 2H, *m*), 7.04 (t, J = 7.7 Hz, 1H, *p*), 6.92 (d, J = 7.7 Hz, 2H, *o*), 5.74 (ddt, J = 16.2, 10.9, 6.3 Hz, 1H, 2-H), 5.05 (d, J = 10.9 Hz, 1H, 1-H^A), 5.04 (d, J = 16.2 Hz, 1H, 1-H^B), 3.06 (d, J = 6.3 Hz, 2H, 3-H_2), 2.54 (s, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 154.9 (s, *i*), 150.1 (s, C-4), 132.5 (d, C-2), 129.6 (d, *m*), 122.5 (d, *p*), 117.0 (t, C-1), 116.8 (d, *o*), 84.6 (s, C-5), 32.5 (t, C-3), 26.8 (q, C-6); HRMS: (EI, 70 eV) Calculated: 300.0011 (M^+) ($C_{12}H_{13}OI$) Found: 300.0012.

Methyl (Z)-2-methyl-3-phenoxy-4-(p-tolyl)pent-3-enoate (16)



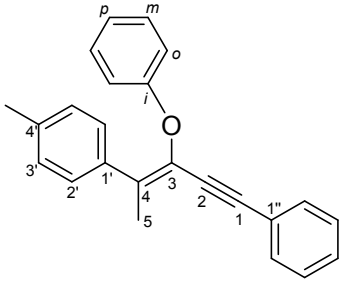
$Pd(PPh_3)_4$ (0.019 mmol, 0.0220 g) was added to a solution of methyl (*Z*)-4-iodo-2-methyl-3-phenoxypent-3-enoate **5aa** (0.194 mmol, 0.0671 g), *p*-tolylboronic acid (0.388 mmol, 0.0527 g), and K_2CO_3 (0.581 mmol, 0.0803 g) in 1,4-dioxane (1 mL) at room temperature. The mixture was stirred at 90 °C for 8 h. Then, the mixture was poured into ethyl acetate (20 mL) and brine (10 mL) and extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a brown oil. (0.0459 g, 76%).; IR: (neat) 1742 (C=O) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.19 (d, J = 8.2 Hz, 2H, 2'-H x 2), 7.09 (t, J = 7.9 Hz, 2H, *m*), 6.97 (d, J = 8.2 Hz, 2H, 3'-H x 2), 6.84-6.78 (m, 3H, *p* and *o*), 3.76 (q, J = 7.3 Hz, 1H, 2-H), 3.60 (s, 3H, OMe), 2.21 (s, 3H, 4'-Me), 2.11 (s, 3H, 4-Me), 1.39 (d, J = 7.3 Hz, 3H, 2-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 173.3 (s, C-1), 156.8 (s, *i*), 144.3 (s, C-3), 136.9 (s, C-1'), 136.2 (s, C-4'), 128.9 (s, *m*), 128.5 (s, C-3'), 127.8 (s, C-2'), 124.8 (s, C-4), 121.2 (s, *p*), 116.0 (s, *o*), 51.9 (s, OMe), 41.6 (s, C-2), 21.1 (s, 4'-Me), 18.9 (s, 4-Me), 14.5 (s, 2-Me); HRMS: (EI, 70 eV) Calculated: 310.1569 (M^+) ($C_{20}H_{22}O_3$) Found: 310.1565.

(Z)-2-Phenoxy-3-(p-tolyl)but-2-enenitrile (17)



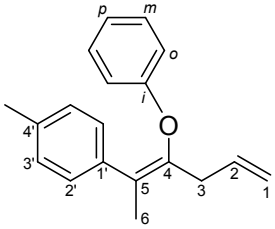
$Pd(PPh_3)_4$ (0.0346 mmol, 0.0403 g) was added to a solution of methyl (*Z*)-3-iodo-2-phenoxybut-2-enenitrile **8** (0.485 mmol, 0.138 g), *p*-tolylboronic acid (1.10 mmol, 0.150 g) and K_2CO_3 (1.47 mmol, 0.204 g) in 1,4-dioxane (5 mL) at room temperature. The mixture was stirred at 90 °C for 8 h. Then, the mixture was poured into ethyl acetate (20 mL) and brine (10 mL) and extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.0901 g, 75%). The solid was recrystallized in dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **17** was confirmed by X-ray crystallography analysis (CCDC 1908823).; mp: 60-68 °C; IR: (KBr) 2213 (C≡N) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.37-7.33 (m, 4H, 6'-H x 2 and *m*), 7.15 (d, *J* = 8.2 Hz, 2H, 3'-H x 2), 7.11 (t, *J* = 7.6 Hz, 1H, *p*), 7.02 (d, *J* = 7.6 Hz, 2H, *o*), 2.44 (s, 3H, 8-Me), 2.33 (s, 3H, 4-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 155.5 (C, *i*), 140.0 (C, C-2), 139.5 (C, C-4'), 132.4 (C, C-1'), 129.8 (CH, *m*), 129.1 (CH, C-2'), 127.8 (CH, C-3'), 123.8 (CH, *p*), 121.5 (C, C-1), 116.6 (CH, *o*), 114.7 (C, C-2), 21.3 (CH_3, 4'-Me), 19.9 (CH_3, C-4); HRMS: (EI, 70 eV) Calculated: 249.1154 (M^+) ($C_{17}H_{15}NO$) Found: 249.1157.

(Z)-3-Phenoxy-1-phenyl-4-(p-tolyl)pent-3-en-1-yne (18)



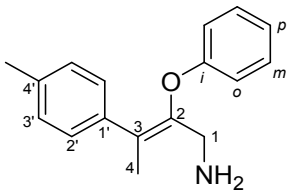
$Pd(PPh_3)_4$ (0.0261 mmol, 0.0301 g) was added to a solution of methyl (*Z*)-4-iodo-3-phenoxy-1-phenyl-pent-3-en-1-yne **12** (0.229 mmol, 0.0825 g), *p*-tolylboronic acid (0.482 mmol, 0.0656 g) and K_2CO_3 (0.785 mmol, 0.108 g) in 1,4-dioxane (1 mL) at room temperature. The mixture was stirred at 90 °C for 8 h. Then, the mixture was poured into ethyl acetate (20 mL) and brine (10 mL) and extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 92:8, column length 11 cm and diameter 2.7 cm) and GPC to give the product as a white solid (0.0577 g, 78%). The solid was recrystallized in dichloromethane solvent to give a crystal suitable for X-ray crystallography analysis. The structure of **18** was confirmed by X-ray crystallography analysis (CCDC 1908822).; mp: 130-136 °C; IR: (KBr) 2200 (C≡C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.38 (d, *J* = 8.2 Hz, 2H, 2'-H x 2), 7.30-7.27 (m, 7H, 1-Ph and *m*), 7.10-7.07 (m, 4H, 3'-H x 2 and *o*), 7.02 (t, *J* = 7.3 Hz, 1H, *p*), 2.41 (s, 3H, 5-H_3), 2.31 (s, 3H, 4'-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.6 (C, *i*), 137.3 (C, C-4'), 135.1 (C, C-1'), 131.3 (CH), 130.7 (C, C-4), 129.9 (C, C-3), 129.2 (CH, *m*), 128.7 (CH, C-3'), 128.5 (CH), 128.2 (CH), 127.8 (CH, C-2'), 122.5 (C, C-1"), 122.3 (CH, *p*), 117.3 (CH, *o*), 95.4 (C, C-1), 84.3 (C, C-2), 21.2 (CH_3, 4'-Me), 20.1 (CH_3, C-5); HRMS: (EI, 70 eV) Calculated: 324.1514 (M^+) ($C_{24}H_{20}O$) Found: 324.1515.

(Z)-4-Phenoxy-5-(p-tolyl)hex-4-en-1-ene (19)



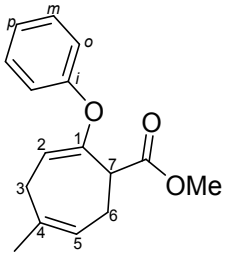
$Pd(PPh_3)_4$ (0.0101 mmol, 0.0117 g) was added to a solution of methyl (*Z*)-5-iodo-4-phenoxy-hex-4-en-1-ene **15** (0.104 mmol, 0.0313 g), *p*-tolylboronic acid (0.226 mmol, 0.0307 g) and K_2CO_3 (0.408 mmol, 0.0564 g) in 1,4-dioxane (0.5 mL) at room temperature. The mixture was stirred at 90 °C for 8 h. Then, the mixture was poured into ethyl acetate (20 mL) and brine (10 mL) and extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as colorless oil (0.0099 g, 36%). The structure of **19** was determined by ^1H-NOE experiment and 2D spectra of the compound.; IR: (neat) 1595 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.23-7.21 (m, 4H, 2'-H x 2 and *m*), 7.03 (d, *J* = 7.9 Hz, 2H, 3'-H x 2), 6.94 (t, *J* = 7.3 Hz, 1H, *p*), 6.88 (d, *J* = 7.6 Hz, 2H, *o*), 5.85 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H, 2-H), 5.10 (ddt, *J* = 16.8, 1.6, 1.6 Hz, 1H, 1-H^A), 5.06 (ddt, *J* = 10.2, 1.6, 1.6 Hz, 1H, 1-H^B), 3.09 (dd, *J* = 6.4, 1.6 Hz, 2H, 3-H_2), 2.26 (s, 3H, 4'-Me), 2.09 (s, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.6 (C, *i*), 143.9 (C, C-4), 137.1 (C, C-1'), 136.0 (C, C-4'), 133.7 (CH, C-2), 129.3 (CH, *m*), 128.5 (CH, C-3'), 127.6 (CH, C-2'), 123.0 (C, C-5), 121.5 (CH, *p*), 116.8 (CH, *o*), 116.1 (CH_2, C-1), 33.9 (CH_2, C-3), 21.1 (CH_3, 4'-Me), 18.6 (CH_3, C-6); HRMS: (EI, 70 eV) Calculated: 264.1514 (M^+) ($C_{19}H_{20}O$) Found: 264.1513.

***(Z)-2-Phenoxy-3-(p-tolyl)but-2-en-1-ylamine (20)*[19]**



A solution of (*Z*)-2-phenoxy-3-(*p*-tolyl)but-2-enenitrile **17** (0.095 mmol, 0.024 g) was added to a suspension of $LiAlH_4$ (0.47 mmol, 0.018 g) and $AlCl_3$ (0.15 mmol, 0.020 g) in diethyl ether (0.25 mL) at 0 °C. The reaction mixture was stirred for 18 h and then, the reaction mixture was quenched with an aqueous solution of NaOH (20 wt%) at 0 °C. The organic phase was separated off, and the aqueous phase was extracted three times with portions of diethyl ether. The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 70:30, column length 11 cm and diameter 2.7 cm) to give the product as a yellow liquid (0.0098 g, 41%).; IR: (neat) 3373 (N-H,br) cm^{-1}, 1594 (C=C) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.24-7.22 (m, 4H, Ar), 7.04 (d, *J* = 7.7 Hz, 2H, Ar), 6.95 (t, *J* = 7.7 Hz, 1H, *p*), 6.89 (d, *J* = 7.7 Hz, 2H, *o*), 3.57 (s, 2H, 1-H_2), 2.27 (s, 3H, 4'-Me), 2.15 (s, 3H, 4-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 156.5 (s, *i*), 146.6 (s, C-3), 136.8 (s, C-1'), 136.3 (s, C-4'), 129.5 (d), 128.6 (d), 127.5 (d), 123.1 (s, C-2), 121.6 (d, *p*), 116.4 (d, *o*), 39.7 (t, C-1), 21.1 (q, 4'-Me), 18.5 (q, C-4); HRMS: (EI, 70 eV) Calculated: 253.1467 (M^+) ($C_{17}H_{19}NO$) Found: 253.1464.

7-methoxycarbonyl-4-methyl-1-phenoxycyclohepta-1,4-diene (21)



A solution of methyl (*E*)-2-allyl-6-methyl-3-phenoxyhepta-3,6-dienoate **3le** (0.467 mmol, 0.134 g) and (1,3-bis(2,4,6-trimethylphenyl)-2-midazolidinylidene)dichloro(phenylmethylene)(tricycloh exylphosphine)ruthenium [Grubbs catalyst 2nd Generation] (0.020 mmol, 0.017 g) in benzene (1 mL) was stirred for 2 h at 70 °C. The reaction was monitored ^1H-NMR. After the reaction was completed, the mixture was poured into ethyl acetate (20 mL) and brine (10 mL), and then extracted with ethyl acetate (10 x 3 mL). The collected organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 88:12, column length 11 cm and diameter 2.7 cm) and GPC to give the product as colorless oil (0.049 g, 41%).; IR: (neat) 1740 (C=O) cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) 7.30 (t, *J* = 7.7 Hz, 2H, *m*), 7.06-7.02 (m, 3H, *p* and *o*), 5.53 (t, *J* = 6.6 Hz, 1H, 5-H), 5.13 (t, *J* = 5.8 Hz, 1H, 2-H), 3.71 (s, 3H, OMe), 3.46 (m, 1H, 7-H), 2.79 (dd, *J* = 18.1, 5.8 Hz, 1H, 6-*H*H), 2.69-2.62 (m, 2H, 6-H*H* and 3-*H*H), 2.51-2.48 (m, 1H, 3-H*H*), 1.75 (s, 3H, 4-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 172.8 (C, 7-*C*OOMe), 156.0 (C, *i*), 153.0 (C, C-1), 140.8 (C, C-4), 129.5 (CH, *m*), 123.0 (CH, *p*), 121.0 (CH, C-5), 119.4 (CH, *o*), 108.8 (CH, C-2), 52.1 (CH_3, OMe), 46.8 (CH, C-7), 29.1 (CH_2, C-3), 27.5 (CH_2, C-6), 25.3 (CH_3, 4-Me); HRMS: (EI, 70 eV) Calculated: 258.1256 (M^+) ($C_{16}H_{18}O_3$) Found: 258.1254.

■ COMPUTATIONAL DETAILS

Quantum chemical calculations of the mechanism of reaction between an indium-alkyne complex **A-1** and silyl ketene acetal **2a** were performed under vacuum at 298 K and 1 bar. All calculations and geometry optimizations were performed using the B3LYP/6-31+G(d,p) for H, C and O, and DGDZVP for In and I level of theory. Stationary points, minima, and transition states on the potential energy surface were identified by vibrational analysis. Transition state structures were verified by the presence of one negative eigenvalue reaction path, which was followed by intrinsic reaction coordinate (IRC) analysis and an inspection of the displacement along the vibrational mode corresponding to the imaginary frequency. Gibbs free energies were calculated as a sum of the single-point electronic energy and thermal correction to the Gibbs free energy. All quantum chemical computations were performed using the Gaussian09 rev.C.01.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Optimization of Reaction Conditions (Table S1 and Table S2)

Scope of organosilicon nucleophile (Table S3)

X-ray crystallographic data (Figure S1-7 and Table 4-10)

NOE experiments

Calculated data (Figure S8 and Table S11-12)

Cartesian coordinates of the compounds

Copies of ^1H and ^{13}C NMR spectra of materials and products

CIF files of X-ray crystal analysis

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Notes

The authors declare no competing financial interest.

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(10) When the volatiles was removed without addition of pyridine, the reaction mixture was complicated. In this case, the produced alkenylindium might be protonated or decomposed.

(11) Reported In-C bond distances in the crystal of Ph_3In were from 2.11(2) to 2.15(2)Å. Malone

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