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# Gold-Catalyzed Regio- and Stereoselective Addition of Carboxylic Acids to Iodoalkynes: Access to (*Z*)-β-Iodoenol Esters and 1,4-Disubstituted (*Z*)-Enynyl Esters

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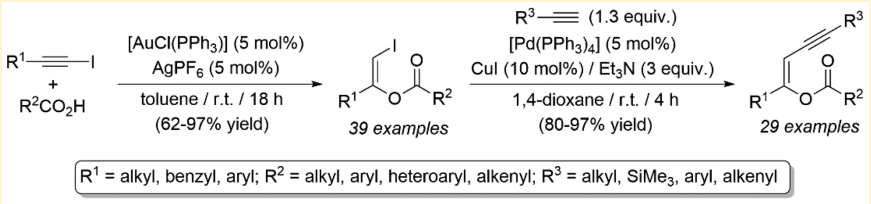
Supporting Information




**ABSTRACT:** In the presence of catalytic amounts of the Au(I) cation $[Au(PPh_3)]^+$, a large variety of (*Z*)-β-iodoenol esters (39 examples) could be synthesized under mild reaction conditions through the regio- and stereospecific intermolecular addition of carboxylic acids to iodoalkynes. Sonogashira coupling of representative (*Z*)-β-iodoenol esters with terminal alkynes, alkynols, and 1,3-enynes allowed also the access to different 1,4-disubstituted (*Z*)-enynyl esters in excellent yields.

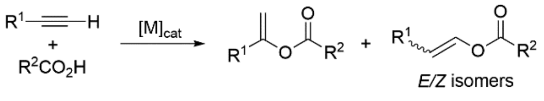
## INTRODUCTION

The intermolecular addition of carboxylic acids to alkynes represents one of the most efficient and atom-economical approaches currently available for the preparation of enol esters,[1] which are relevant compounds for synthetic chemistry and polymerization processes.[2] Since the report by Shvo and Rotem in 1983 employing $Ru_3(CO)_{12}$,[3] the vast majority of catalytic systems employed so far are based on ruthenium complexes, due to their high efficiency and functional groups tolerance.[4,5] A number of catalysts involving other late transition metals, such as rhenium,[6] rhodium,[7] iridium,[8] palladium,[9] gold,[10] and silver,[11] have also proven useful to promote these hydrocarboxylation reactions.[12] Although the use of unactivated internal alkynes, which due to steric grounds require much higher activation energies, has resulted in many cases problematic, effective systems for these challenging substrates have seen the light very recently.[5a,h,10] In addition, for the particular case of terminal alkynes, catalysts capable of controlling the regio- and stereoselectivity of the addition process are known, thus allowing the preferential formation of one of the three possible enol ester isomers (Scheme 1).[4]

On the other hand, easily accessible haloalkynes RC≡CX (X = Cl, Br, I) are a significant class of building blocks in organic chemistry, and remarkable efforts have been devoted in recent years to their selective hydrofunctionalization.[13] In this context, the hydration of haloalkynes has proven to be a very simple and efficient method for accessing α-halomethyl ketones (RC(=O)$CH_2$X),[14] while the addition of thiols,[15] phenols,[16] diphenyl phosphate,[17] amines/amides,[15a,18] and sulfonic acids[19] has allowed the preparation of a large variety of 2-functionalized-1-haloalkenes (NuCR=CHX), via regioselective nucleophilic attack of the heteroatom on the electrophilic C-2 carbon of the haloalkyne.[20] Metal catalysts have certainly played a key role in the development of this chemistry.[14a−f,15b,17,20b−d] However, an important gap in the field concerns the intermolecular addition of carboxylic acids to access β-haloenol esters, a process that, to the best of our knowledge, has not been yet reported.[21] In fact, despite the enormous synthetic potential of these functionalized olefins,[22] there are still relatively few methods available for their preparation.[23]

Among the most general, we can mention (Scheme 2): (i) the silver-catalyzed difunctionalization of terminal alkynes reported by Jiang and co-workers, which allows the stereoselective access to (*Z*)-haloenol acetates;[23b] (ii) the cohalogenation of internal aromatic alkynes using a combination of a carboxylic acid and *N*-iodosuccinimide (NIS) described by Yanada's group, which generates the corresponding β-iodoenol esters as mixtures of *E*/*Z* stereoisomers;[23c] and (iii) the haloacyloxylation processes developed by Xia and Baell groups,

**Scheme 1. Catalytic Addition of Carboxylic Acids to Terminal Alkynes**

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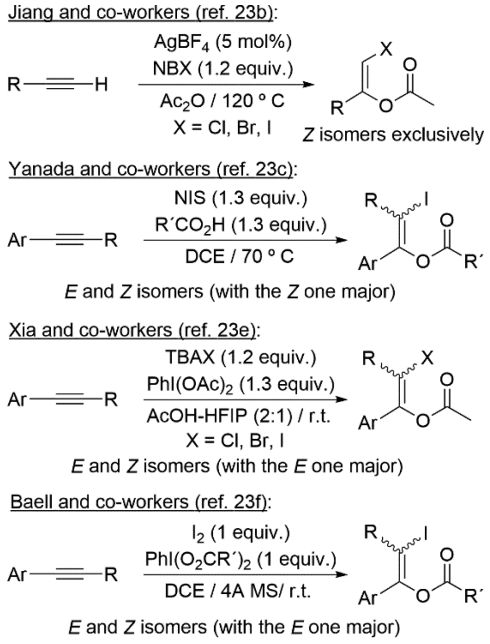
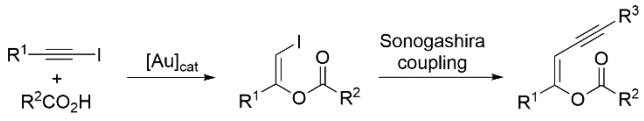
**Scheme 2. General Approaches to β-Haloenol Esters Currently Available**




which give a broad access to β-haloenol esters from terminal and internal aromatic alkynes with high *E*-selectivity.[23e,f]

With all these precedents in mind, we considered that the development of a catalytic system able to promote the intermolecular hydrocarboxylation of haloalkynes with carboxylic acids should be greatly appreciated. In this context, very recently, we communicated the synthesis of a small family of (*Z*)-β-iodoenol acetates through a gold(I)-catalyzed regio- and stereospecific addition of acetic acid to aliphatic iodoalkynes.[24] In addition, we also demonstrated the synthetic utility of these functionalized iodoolefins for the preparation of valuable chiral homobenzylic acetates, through their Suzuki arylation and subsequent rhodium-catalyzed asymmetric hydrogenation.[24] Herein, a full report on the scope of the gold(I)-catalyzed hydrocarboxylation of iodoalkynes is presented, as well as the synthesis of a diverse family of 1,4-disubstituted (*Z*)-enynyl esters via Sonogashira coupling reactions of the resulting (*Z*)-β-iodoenol esters (Scheme 3).

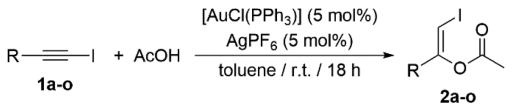
**Scheme 3. Synthesis of (*Z*)-β-Iodoenol and (*Z*)-Enynyl Esters from Iodoalkynes Described Herein**




## RESULTS AND DISCUSSION

In our preliminary communication,[24] we reported the preparation of the (*Z*)-β-iodoenol acetates **2a–f,h** by treatment of the corresponding aliphatic iodoalkyne **1a–f,h** with 1 equiv of acetic acid in the presence of 5 mol% of the gold(I) complex [AuCl(PPh$_3$)] and the silver(I) salt AgPF$_6$.[25] Compounds **2a–f,h** were isolated in 76–90% performing the reactions in toluene at r.t. for 5 h.[24] As shown now in Table 1, the yields could be slightly improved extending the reaction time to 18 h (88–97%; entries 1–6 and 8). Under these new conditions,

**Table 1. Gold-Catalyzed Addition of Acetic Acid to Different Iodoalkynes[a]**



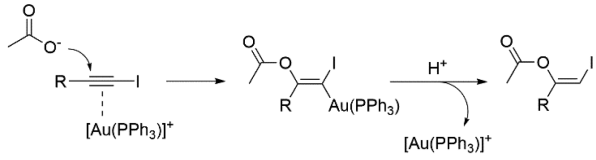

**1a-o** **2a-o**

| entry | alkyne **1** | yield **2** (%)[b] |
|---|---|---|
| 1 | R = $^n$Pr (**1a**) | **2a**; 95 |
| 2 | R = $^n$Bu (**1b**) | **2b**; 93 |
| 3 | R = $^n$Pent (**1c**) | **2c**; 96 |
| 4 | R = $^n$Hex (**1d**) | **2d**; 97 |
| 5 | R = $CH_2CH_2{}^i$Pr (**1e**) | **2e**; 97 |
| 6 | R = $^c$Pr (**1f**) | **2f**; 88 |
| 7 | R = $^c$Pent (**1g**) | **2g**; 72 |
| 8 | R = Cy (**1h**) | **2h**; 94 |
| 9 | R = Bn (**1i**) | **2i**; 76 |
| 10 | R = $CH_2$Bn (**1j**) | **2j**; 79 |
| 11 | R = $CH_2CH_2$Bn (**1k**) | **2k**; 82 |
| 12 | R = Ph (**1l**) | **2l**; 74 |
| 13 | R = 4-$C_6H_4$Me (**1m**) | **2m**; 91 |
| 14 | R = 4-$C_6H_4$F (**1n**) | **2n**; 84 |
| 15 | R = 4-$C_6H_4$Br (**1o**) | **2o**; 79 |

[a]Reaction conditions: iodoalkyne **1** (1 mmol), glacial acetic acid (1 mmol), [AuCl(PPh$_3$)] (0.05 mmol), AgPF$_6$ (0.05 mmol), toluene (3 mL), r.t., 18 h. [b]Isolated yield after chromatographic purification.

other iodoalkynes **1g,i–o**, including aromatic examples, were cleanly converted into the corresponding (*Z*)-β-iodoenol acetates **2g,i–o**, with isolated yields ranging from 72 to 91% (entries 7 and 9–15). The reactions proceeded in all the cases with complete regio- and stereoselectivity. Thus, aside from **2a–o**, the only species detected by NMR in the crudes were the unreacted starting materials and, in some cases, traces of the enol acetates RC(OAc)=CH$_2$ resulting from the partial carbon-iodide bond cleavage of the products. Such a regio- and stereoselectivity is not surprising giving that (i) the C-2 carbon of the haloalkyne is the more electrophilic one,[14–20] and (ii) the nucleophilic Nu-H additions to π-alkyne-gold complexes usually proceed in an *anti*-fashion (Scheme 4).[26]

**Scheme 4. Proposed Mechanism for the Gold-Catalyzed Addition of Acetic Acid to Iodoalkynes**




Regarding this last point, blank experiments conducted separately with [AuCl(PPh$_3$)] and AgPF$_6$ alone did not lead to the formation of the desired β-iodoenol acetates, thus confirming that the cationic species [Au(PPh$_3$)]$^+$ is responsible for the catalytic activity observed.[27]

On the other hand, although the reactions collected in Table 1 were systematically carried out on a 1 mmol scale, we would like to stress that they can be scaled up without major problems. As a representative example, a reaction conducted with 1-iodooct-1-yne (**1d**) on a 10 mmol scale (2.5 g) allowed the preparation of 2.72 g (92% yield) of (*Z*)-1-iodooct-1-en-2-yl acetate (**2d**).



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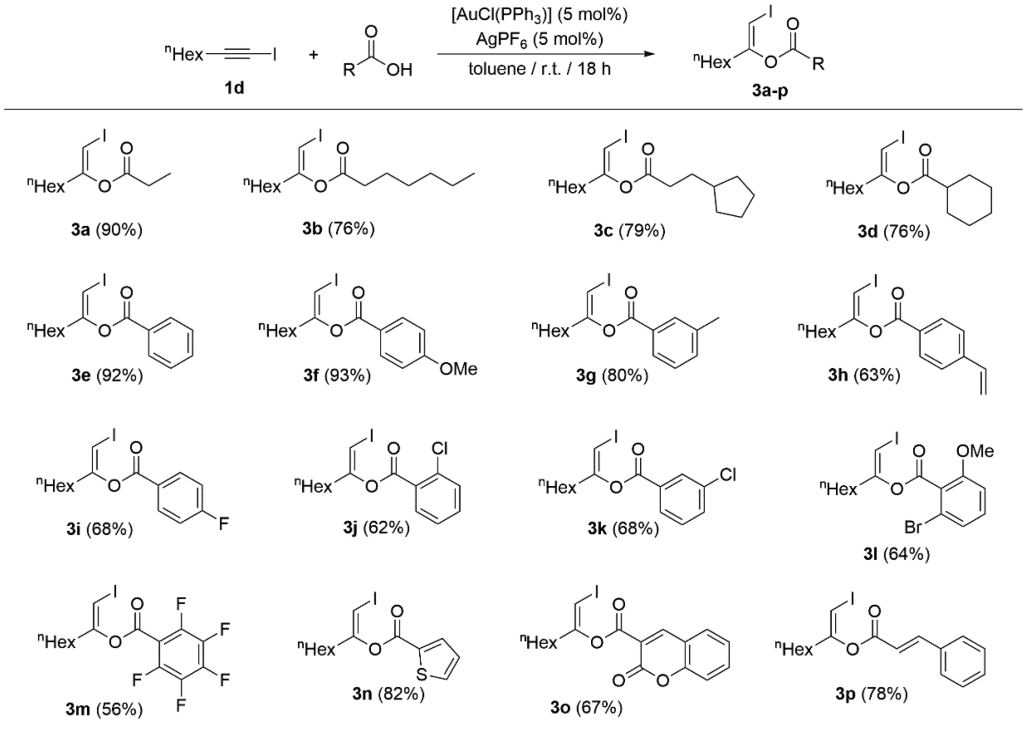
**Scheme 5. Catalytic Addition of Different Carboxylic Acids to 1-Iodooct-1-yne (1d)**




In order to assess in more detail the scope of the process, the addition of a number of other carboxylic acids to 1-iodooct-1-yne (**1d**) was explored under identical experimental conditions (Scheme 5). To our delight, the catalytic reaction proved to be broadly applicable, and the novel (*Z*)-*β*-iodoenol esters **3a**–**p** could be synthesized with complete regio- and stereoselectivity in 56–93% yield, starting from different aliphatic, aromatic, heteroaromatic, heterocyclic, and *α*,*β*-unsaturated carboxylic acids. However, we must note that, compared to acetic acid (entry 4 in Table 1), yields were in general lower, due probably to the higher steric demand of the acids employed. In the case of substituted benzoic acids, electronic effects also influence the reaction, with the electron-donating substituents leading in general to higher yields.

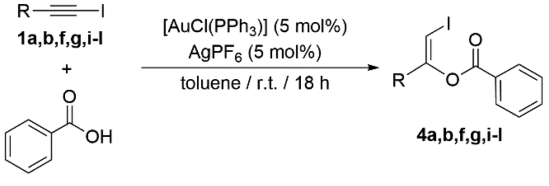
Further evidence of the generality of the process were gained in the reaction of benzoic acid with iodoalkynes **1a,b,f,g,i**–**l** which, regardless of their aliphatic or aromatic nature, cleanly underwent the addition process to generate the corresponding (*Z*)-*β*-iodoenol esters **4a,b,f,g,i**–**l** in 68–85% yield (Scheme 6).

One of the main applications of haloalkenes is their use in the construction of polysubstituted olefins through transition-metal-catalyzed cross-coupling reactions. In this context, we previously demonstrated the utility of the aliphatic (*Z*)-*β*-iodoenol acetates **2a**–**f,h** as starting materials for the preparation of a broad family of (*Z*)-1-alkyl-2-arylvinyl acetates by Pd-catalyzed Suzuki coupling with arylboronic acids, products that were subsequently hydrogenated in the presence of chiral Rh(I) catalysts to generate enantiomerically enriched homobenzylic acetates.[24] To further demonstrate the synthetic utility of the (*Z*)-*β*-iodoenol esters generated through our gold-catalyzed hydrocarboxylation reactions, their Sonogashira coupling with terminal alkynes was now explored as an entry route to 1,4-disubstituted (*Z*)-enynyl esters. We would like to remark here that (*Z*)-enynyl acetates have recently found application as starting materials for the preparation of polysubstituted furans via metal-catalyzed or iodine-induced electrophilic cyclization.[22a,c,23e,28]

As shown in Scheme 7, employing (*Z*)-1-iodooct-1-en-2-yl acetate/benzoate (**2d**/**3e**) and (*Z*)-2-iodo-1-phenylvinyl acetate (**2l**) as model substrates, a large variety of 1,4-disubstituted (*Z*)-enynyl esters **5a**–**j**, **6a**–**j** and **7a**–**i** could be easily synthesized in excellent yields (80–96%) under classical Sonogashira conditions, using different terminal alkynes, 1,3-enynes, and propargylic alcohols as coupling partners.[29]

In summary, we have developed a wide scope procedure for the synthesis of (*Z*)-*β*-iodoenol esters through the unprecedented catalytic hydrocarboxylation of readily available iodoalkynes with carboxylic acids.[30] The process, which is catalyzed by the *in situ* generated gold(I) cation $[Au(PPh_3)]^+$, proceeds with complete regio- and stereoselectivity under mild conditions, affording the desired products in moderate to excellent yields. The usefulness of the resulting (*Z*)-*β*-iodoenol esters, some of them previously employed by us as starting materials for the synthesis of valuable chiral homobenzylic acetates,[24] was further demonstrated herein with the preparation of a broad family of 1,4-disubstituted (*Z*)-enynyl esters via Sonogashira coupling with different terminal alkynes.

**Scheme 6. Catalytic Addition of Benzoic Acid to Different Iodoalkynes**




R = $^n$Pr (**4a**; 84%), $^n$Bu (**4b**; 85%), $^c$Pr (**4f**; 71%), $^c$Pent (**4g**; 68%), Bn (**4i**; 72%), $CH_2Bn$ (**4j**; 75%), $CH_2CH_2Bn$ (**4k**; 76%), Ph (**4l**; 69%)



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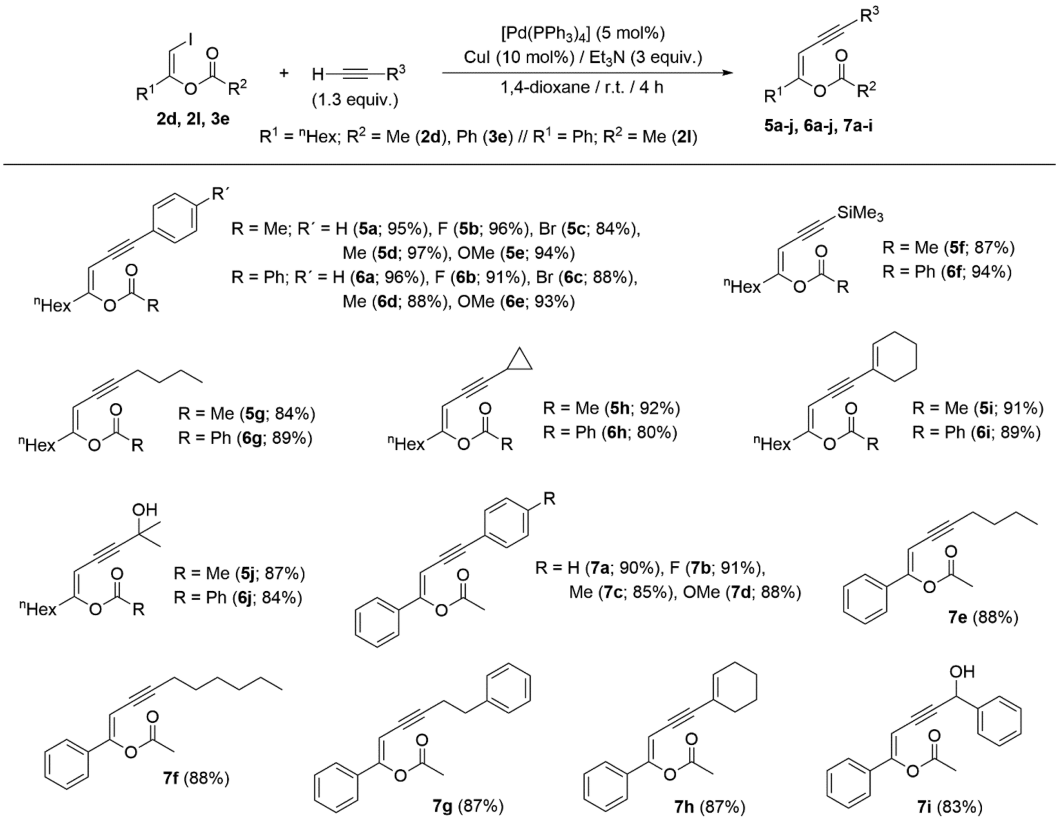
**Scheme 7. Synthesis of 1,4-Disubstituted (*Z*)-Enynyl Esters from the (*Z*)-β-Iodoenol Esters 2d, 2l, and 3e**




## EXPERIMENTAL SECTION

All the manipulations were performed under argon atmosphere using vacuum-line and standard sealed-tube techniques. Solvents were dried by standard methods and distilled under argon before use.[31] All reagents were obtained from commercial suppliers and used as received, with the exception of complexes [AuCl(PPh$_3$)][32] and [Pd(PPh$_3$)$_4$],[33] and the iodoalkynes **1a–o**,[34] which were prepared by following the methods reported in the literature. For column chromatography, silica gel of 230–400 mesh was employed. For NMR spectra, the chemical shift values (δ) are given in parts per million and are referred to the residual peak of the deuterated solvent employed ($^1$H and $^{13}$C) or to the CFCl$_3$ standard ($^{19}$F). HRMS data were obtained on a QTOF mass spectrometer.

**General Procedure for the Catalytic Addition of Carboxylic Acids to Iodoalkynes.** Under an argon atmosphere, the corresponding iodoalkyne **1** (1 mmol) and carboxylic acid (1 mmol), [AuCl(PPh$_3$)] (0.024 g; 0.05 mmol), AgPF$_6$ (0.012 g; 0.05 mmol), and toluene (3.0 mL) were introduced into a Teflon-capped sealed tube, and the reaction mixture stirred at room temperature for 18 h in the absence of light. The solvent was then removed *in vacuo* and the resulting oily residue purified by flash column chromatography over silica gel using diethyl ether/hexane (1:10) as eluent. Characterization data for the isolated (*Z*)-β-iodoenol esters are as follows:

*(Z)-1-Iodopent-1-en-2-yl Acetate (**2a**).* Yellow oil. Yield: 0.241 g (95%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.83 (s, 1H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.24 (s, 3H), 1.58–1.46 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.5, 157.8, 65.3, 36.4, 21.0, 19.7, 13.4 ppm. IR (film): ν = 1767 (s, C═O), 1639 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 276.9694, [M+Na$^+$] (calcd for C$_7$H$_{11}$O$_2$INa: 276.9696).

*(Z)-1-Iodohex-1-en-2-yl Acetate (**2b**).* Yellow oil. Yield: 0.249 g (93%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.82 (s, 1H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 1.49–1.44 (m, 2H), 1.37–1.32 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.5, 158.0, 65.2, 34.2, 28.4, 22.0, 21.0, 13.7 ppm. IR (film): ν = 1762 (s, C═O), 1638 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 290.9848, [M+Na$^+$] (calcd for C$_8$H$_{13}$O$_2$INa: 290.9852).

*(Z)-1-Iodohept-1-en-2-yl Acetate (**2c**).* Yellow oil. Yield: 0.271 g (96%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.82 (s, 1H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 1.50–1.46 (m, 2H), 1.32–1.27 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.5, 158.0, 65.2, 34.4, 31.0, 26.0, 22.3, 21.0, 13.9 ppm. IR (film): ν = 1761 (s, C═O), 1637 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 305.0004, [M+Na$^+$] (calcd for C$_9$H$_{15}$O$_2$INa: 305.0009).

*(Z)-1-Iodooct-1-en-2-yl Acetate (**2d**).* Yellow oil. Yield: 0.287 g (97%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.82 (s, 1H), 2.36 (t, *J* = 8.2 Hz, 2H), 2.23 (s, 3H), 1.50–1.45 (m, 2H), 1.34–1.28 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.4, 158.0, 65.1, 34.4, 31.5, 28.6, 26.3, 22.5, 21.0, 14.0 ppm. IR (film): ν = 1763 (s, C═O), 1638 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 319.0153, [M+Na$^+$] (calcd for C$_{10}$H$_{17}$O$_2$INa: 319.0165).

*(Z)-1-Iodo-5-methylhex-1-en-2-yl Acetate (**2e**).* Yellow oil. Yield: 0.274 g (97%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.83 (s, 1H), 2.36 (t, *J* = 7.8 Hz, 2H), 2.24 (s, 3H), 1.57–1.50 (m, 1H), 1.41–1.34 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.5, 158.2, 65.1, 35.2, 32.4, 27.4, 22.3, 21.0 ppm. IR (film): ν = 1766 (s, C═O), 1639 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 305.0005, [M+Na$^+$] (calcd for C$_9$H$_{15}$O$_2$INa: 305.0009).

*(Z)-1-Cyclopropyl-2-iodovinyl Acetate (**2f**).* Yellow oil. Yield: 0.222 g (88%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.87 (d, *J* = 0.6 Hz, 1H), 2.21 (s, 3H), 1.74–1.68 (m, 1H), 0.76–0.73 (m, 2H), 0.68–0.65 (m, 2H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.3, 158.1, 63.9, 21.0, 14.8, 5.5 ppm. IR (film): ν = 1764 (s, C═O), 1628 (m, C═C) cm$^{-1}$. HRMS (ESI): *m*/*z* 274.9534, [M+Na$^+$] (calcd for C$_7$H$_9$O$_2$INa: 274.9539).

*(Z)-1-Cyclopentyl-2-iodovinyl Acetate (**2g**).* Colorless oil. Yield: 0.202 g (72%). $^1$H NMR (CDCl$_3$, 300 MHz): δ = 5.91 (d, *J* = 1.0 Hz, 1H), 2.83–2.72 (m, 1H), 2.23 (s, 3H), 1.86–1.84 (m, 2H), 1.69–1.53 (m, 6H) ppm. $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ = 167.4, 160.5, 64.7, 45.2, 30.3, 24.7, 21.1 ppm. IR (film): ν = 1765 (s, C═O), 1629



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(m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 302.9850, [M+$Na^+$] (calcd for $C_9H_{13}O_2INa$: 302.9852).

*(Z)-1-Cyclohexyl-2-iodovinyl Acetate (**2h**).* Yellow oil. Yield: 0.276 g (94%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.85 (s, 1H), 2.29−2.15 (m, 1H), 2.23 (s, 3H), 1.91−1.88 (m, 2H), 1.77−1.65 (m, 3H), 1.32−1.12 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.4, 161.8, 65.1, 43.5, 30.5, 25.9, 25.8, 21.1 ppm. IR (film): $\nu$ = 1765 (s, C═O), 1629 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 317.0003, [M+$Na^+$] (calcd for $C_{10}H_{15}O_2INa$: 317.0009).

*(Z)-1-Iodo-3-phenylprop-1-en-2-yl Acetate (**2i**).* Yellow oil. Yield: 0.230 g (76%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.38−7.22 (m, 5H), 5.79 (s, 1H), 3.68 (s, 2H), 2.20 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.5, 156.8, 135.5, 129.2, 128.7, 127.1, 67.6, 40.5, 21.0 ppm. IR (film): $\nu$ = 1759 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 324.9694, [M+$Na^+$] (calcd for $C_{11}H_{11}O_2INa$: 324.9696).

*(Z)-1-Iodo-4-phenylbut-1-en-2-yl Acetate (**2j**).* Yellow oil. Yield: 0.250 g (79%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.35−7.30 (m, 2H), 7.26−7.19 (m, 3H), 5.85 (s, 1H), 2.86−2.81 (m, 2H), 2.74−2.69 (m, 2H), 2.23 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.6, 157.0, 140.2, 128.5, 128.3, 126.3, 66.3, 36.1, 32.8, 21.0 ppm. IR (film): $\nu$ = 1759 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 338.9849, [M+$Na^+$] (calcd for $C_{12}H_{13}O_2INa$: 338.9852).

*(Z)-1-Iodo-5-phenylpent-1-en-2-yl Acetate (**2k**):*[35] Yellow oil. Yield: 0.271 g (82%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.33−7.28 (m, 2H), 7.24−7.17 (m, 3H), 5.86 (s, 1H), 2.66 (t, $J$ = 7.8 Hz, 2H), 2.41 (t, $J$ = 6.9 Hz, 2H), 2.25 (s, 3H), 1.88−1.78 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.5, 157.5, 141.3, 128.4 (2C), 126.0, 65.7, 34.9, 33.9, 27.9, 21.0 ppm.

*(Z)-2-Iodo-1-phenylvinyl Acetate (**2l**):*[23b] Yellow oil. Yield: 0.213 g (74%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.47−7.44 (m, 2H), 7.39−7.36 (m, 3H), 6.66 (s, 1H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.3, 155.0, 133.6, 129.4, 128.8, 125.2, 68.5, 21.0 ppm.

*(Z)-2-Iodo-1-(4-methylphenyl)vinyl Acetate (**2m**):*[23b] Yellow oil. Yield: 0.275 g (91%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.33 (d, $J$ = 8.1 Hz, 2H), 7.17 (d, $J$ = 8.1 Hz, 2H), 6.57 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.4, 155.1, 139.6, 130.9, 129.5, 125.1, 67.2, 21.3, 21.0 ppm.

*(Z)-1-(4-Fluorophenyl)-2-iodovinyl Acetate (**2n**):*[22d] Yellow oil. Yield: 0.257 g (84%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.45−7.40 (m, 2H), 7.08−7.02 (m, 2H), 6.58 (s, 1H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.3, 163.2 (d, $J$ = 250.0 Hz), 154.1, 130.0 (d, $J$ = 3.3 Hz), 127.2 (d, $J$ = 8.4 Hz), 115.8 (d, $J$ = 22.1 Hz), 68.0, 21.0 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −111.1 ppm.

*(Z)-1-(4-Bromophenyl)-2-iodovinyl Acetate (**2o**).* Yellow solid. Yield: 0.290 g (79%). Mp 76−79 °C. $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.49 (d, $J$ = 8.7 Hz, 2H), 7.30 (d, $J$ = 8.7 Hz, 2H), 6.68 (s, 1H), 2.36 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.3, 154.1, 132.6, 132.0, 126.7, 123.6, 69.3, 21.0 ppm. IR (KBr): $\nu$ = 1763 (s, C═O), 1604 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 388.8642, [M+$Na^+$] (calcd for $C_{10}H_8O_2BrINa$: 388.8644).

*(Z)-1-Iodooct-1-en-2-yl Propionate (**3a**).* Orange oil. Yield: 0.279 g (90%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.81 (s, 1H), 2.52 (q, $J$ = 7.8 Hz, 2H), 2.36 (t, $J$ = 7.2 Hz, 2H), 1.49−1.41 (m, 2H), 1.36−1.28 (m, 6H), 1.25 (t, $J$ = 7.8 Hz, 3H), 0.89 (t, $J$ = 6.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 170.9, 158.0, 64.9, 34.4, 31.5, 28.6, 27.7, 26.3, 22.5, 14.0, 9.1 ppm. IR (film): $\nu$ = 1759 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 333.0308, [M+$Na^+$] (calcd for $C_{11}H_{19}O_2INa$: 333.0322).

*(Z)-1-Iodooct-1-en-2-yl Heptanoate (**3b**).* Yellow oil. Yield: 0.278 g (76%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.81 (s, 1H), 2.49 (t, $J$ = 7.5 Hz, 2H), 2.37 (t, $J$ = 7.8 Hz, 2H), 1.79−1.70 (m, 2H), 1.50−1.29 (m, 14H), 0.93−0.87 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 170.3, 158.0, 64.9, 34.5, 34.3, 31.5, 31.4, 28.8, 28.6, 26.3, 24.8, 22.5 (2C), 14.0 (2C) ppm. IR (film): $\nu$ = 1760 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 389.0933, [M+$Na^+$] (calcd for $C_{15}H_{27}O_2INa$: 389.0948).

*(Z)-1-Iodooct-1-en-2-yl 3-Cyclopentylpropanoate (**3c**).* Colorless oil. Yield: 0.299 g (79%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 5.79 (s, 1H), 2.49 (t, $J$ = 7.6 Hz, 2H), 2.35 (t, $J$ = 7.6 Hz, 2H), 1.86−1.74 (m, 5H), 1.55−1.44 (m, 6H), 1.34−1.27 (m, 6H), 1.16−1.11 (m, 2H), 0.88 (t, $J$ = 6.4 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 170.4, 158.0, 64.8, 39.6, 34.4, 33.6, 32.4, 31.4, 31.0, 28.6, 26.3, 25.1, 22.5, 14.0 ppm. IR (film): $\nu$ = 1760 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 401.0945, [M+$Na^+$] (calcd for $C_{16}H_{27}O_2INa$: 401.0948).

*(Z)-1-Iodooct-1-en-2-yl Cyclohexanecarboxylate (**3d**).* Orange oil. Yield: 0.277 g (76%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.79 (s, 1H), 2.53−2.43 (m, 1H), 2.36 (t, $J$ = 7.8 Hz, 2H), 2.08−2.03 (m, 2H), 1.85−1.80 (m, 2H), 1.69−1.24 (m, 14H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 172.5, 157.9, 64.7, 43.2, 34.4, 31.5, 29.0, 28.5, 26.3, 25.7, 25.3, 22.5, 14.0 ppm. IR (film): $\nu$ = 1755 (s, C═O), 1638 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 387.0782, [M+$Na^+$] (calcd for $C_{15}H_{25}O_2INa$: 387.0791).

*(Z)-1-Iodooct-1-en-2-yl Benzoate (**3e**).* Yellow oil. Yield: 0.329 g (92%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.19−8.16 (m, 2H), 7.67−7.62 (m, 1H), 7.54−7.49 (m, 2H), 5.95 (s, 1H), 2.52 (t, $J$ = 7.2 Hz, 2H), 1.58−1.51 (m, 2H), 1.39−1.31 (m, 6H), 0.90 (t, $J$ = 6.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.2, 158.2, 133.7, 130.2, 129.3, 128.6, 65.2, 34.6, 31.5, 28.6, 26.4, 22.5, 14.1 ppm. IR (film): $\nu$ = 1738 (s, C═O), 1639 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 381.0307, [M+$Na^+$] (calcd for $C_{15}H_{19}O_2INa$: 381.0322).

*(Z)-1-Iodooct-1-en-2-yl 4-Methoxybenzoate (**3f**).* Yellow oil. Yield: 0.361 g (93%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.12 (d, $J$ = 9.0 Hz, 2H), 6.99 (d, $J$ = 9.0 Hz, 2H), 5.91 (s, 1H), 3.90 (s, 3H), 2.50 (t, $J$ = 7.2 Hz, 2H), 1.57−1.52 (m, 2H), 1.37−1.26 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.9, 162.9, 158.3, 132.3, 121.5, 113.8, 65.0, 55.5, 34.6, 31.5, 28.6, 26.4, 22.5, 14.0 ppm. IR (film): $\nu$ = 1731 (s, C═O), 1606 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 411.0412, [M+$Na^+$] (calcd for $C_{16}H_{21}O_3INa$: 411.0428).

*(Z)-1-Iodooct-1-en-2-yl 3-Methylbenzoate (**3g**).* Yellow oil. Yield: 0.298 g (80%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.99−7.97 (m, 2H), 7.47−7.38 (m, 2H), 5.94 (s, 1H), 2.51 (t, $J$ = 7.5 Hz, 2H), 2.46 (s, 3H), 1.58−1.53 (m, 2H), 1.39−1.31 (m, 6H), 0.90 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.3, 158.2, 138.4, 134.4, 130.7, 129.1, 128.5, 127.4, 65.1, 34.6, 31.5, 28.6, 26.4, 22.5, 21.3, 14.0 ppm. IR (film): $\nu$ = 1736 (s, C═O), 1639 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 395.0479, [M+$Na^+$] (calcd for $C_{16}H_{21}O_2INa$: 395.0484).

*(Z)-1-Iodooct-1-en-2-yl 4-Vinylbenzoate (**3h**).* Colorless oil. Yield: 0.242 g (63%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.13 (d, $J$ = 8.4 Hz, 2H), 7.54 (d, $J$ = 8.4 Hz, 2H), 6.79 (dd, $J$ = 17.7 and 10.8 Hz, 1H), 5.92 (d, $J$ = 17.7 Hz, 1H), 5.94 (s, 1H), 5.44 (d, $J$ = 10.8 Hz, 1H), 2.51 (t, $J$ = 7.5 Hz, 2H), 1.57−1.50 (m, 2H), 1.40−1.30 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.0, 158.2, 142.7, 135.9, 130.6, 128.3, 126.3, 117.0, 65.2, 34.6, 31.5, 28.6, 26.4, 22.5, 14.1 ppm. IR (film): $\nu$ = 1736 (s, C═O), 1638 (m, C═C), 1607 (s, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 407.0474, [M+$Na^+$] (calcd for $C_{17}H_{21}O_2INa$: 407.0478).

*(Z)-1-Iodooct-1-en-2-yl 4-Fluorobenzoate (**3i**).* Orange oil. Yield: 0.256 g (68%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.21−8.17 (m, 2H), 7.22−7.16 (m, 2H), 5.95 (s, 1H), 2.51 (t, $J$ = 7.5 Hz, 2H), 1.57−1.52 (m, 2H), 1.37−1.30 (m, 6H), 0.89 (t, $J$ = 6.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 166.2 (d, $J$ = 255.3 Hz), 162.2, 158.1, 132.8 (d, $J$ = 9.4 Hz), 125.5, 115.8 (d, $J$ = 22.1 Hz), 65.3, 34.5, 31.5, 28.6, 26.4, 22.5, 14.0 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −104.2 ppm. IR (film): $\nu$ = 1739 (s, C═O), 1639 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 399.0221, [M+$Na^+$] (calcd for $C_{15}H_{18}O_2FINa$: 399.0228).

*(Z)-1-Iodooct-1-en-2-yl 2-Chlorobenzoate (**3j**).* Colorless oil. Yield: 0.243 g (62%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.09 (dd, $J$ = 7.8 and 1.0 Hz, 1H), 7.54−7.37 (m, 3H), 5.97 (s, 1H), 2.52 (t, $J$ = 7.5 Hz, 2H), 1.61−1.55 (m, 2H), 1.41−1.31 (m, 6H), 0.90 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 161.8, 158.0, 134.3, 133.2, 132.0, 131.3, 129.0, 126.7, 65.5, 34.5, 31.5, 28.6, 26.4, 22.5, 14.0 ppm. IR (film): $\nu$ = 1750 (s, C = O), 1639 (m, C = C) $cm^{-1}$. HRMS (ESI): $m/z$ 393.0112, [M+$H^+$] (calcd for $C_{15}H_{19}O_2ClI$: 393.0113).

*(Z)-1-Iodooct-1-en-2-yl 3-Chlorobenzoate (**3k**).* Colorless oil. Yield: 0.267 g (68%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.15−8.04 (m, 2H), 7.63−7.59 (m, 1H), 7.43 (dd, $J$ = 7.8 and 7.8 Hz, 1H), 5.96



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(s, 1H), 2.50 (t, $J$ = 7.8 Hz, 2H), 1.57−1.52 (m, 2H), 1.38−1.31 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 162.0, 158.0, 134.8, 133.7, 131.0, 130.2, 129.9, 128.3, 65.5, 34.5, 31.5, 28.6, 26.4, 22.5, 14.0 ppm. IR (film): $\nu$ = 1741 (s, C=O), 1639 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 414.9936, [M+Na$^+$] (calcd for $C_{15}H_{18}O_2ClINa$: 414.9932).

*(Z)-1-Iodooct-1-en-2-yl 2-Bromo-6-methoxybenzoate (**3l**).* Orange oil. Yield: 0.299 g (64%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.60−7.57 (m, 2H), 6.96 (dd, $J$ = 9.0 and 3.3 Hz, 1H), 5.96 (s, 1H), 3.86 (s, 3H), 2.52 (t, $J$ = 7.2 Hz, 2H), 1.60−1.55 (m, 2H), 1.39−1.27 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 162.1, 158.6, 158.0, 135.3, 131.5, 119.5, 117.0, 112.4, 65.5, 55.7, 34.4, 31.5, 28.6, 26.4, 22.5, 14.1 ppm. IR (film): $\nu$ = 1755 (s, C=O), 1640 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 488.9526, [M+Na$^+$] (calcd for $C_{16}H_{20}O_3BrINa$: 488.9533).

*(Z)-1-Iodooct-1-en-2-yl Pentafluorobenzoate (**3m**).* Yellow oil. Yield: 0.251 g (56%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 6.05 (t, $J$ = 1.0 Hz, 1H), 2.49 (td, $J$ = 7.6 and 1.0 Hz, 2H), 1.58−1.53 (m, 2H), 1.38−1.31 (m, 6H), 0.90 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 157.6, 155.3, 144.7 (m), 143.0 (m), 137.8 (m), 107.4, 66.1, 34.4, 31.4, 28.5, 26.1, 22.5, 14.0 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −136.5 (m, 2F), −147.1 (m, 1F), −159.9 (m, 2F) ppm. IR (film): $\nu$ = 1757 (s, C=O), 1652 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 470.9835, [M+Na$^+$] (calcd for $C_{15}H_{14}F_5O_2INa$: 470.9851).

*(Z)-1-Iodooct-1-en-2-yl Thiophene-2-carboxylate (**3n**).* Yellow oil. Yield: 0.298 g (82%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.94 (d, $J$ = 3.9 Hz, 1H), 7.65 (d, $J$ = 4.5 Hz, 1H), 7.16 (dd, $J$ = 4.5 and 3.9 Hz, 1H), 5.93 (s, 1H), 2.49 (t, $J$ = 7.2 Hz, 2H), 1.56−1.49 (m, 2H), 1.36−1.29 (m, 6H), 0.88 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 158.5, 157.8, 134.8, 133.7, 132.5, 128.1, 65.6, 34.6, 31.5, 28.6, 26.4, 22.5, 14.1 ppm. IR (film): $\nu$ = 1731 (s, C=O), 1640 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 386.9875, [M+Na$^+$] (calcd for $C_{13}H_{17}O_2INaS$: 386.9886).

*(Z)-1-Iodooct-1-en-2-yl 2-oxo-2H-chromene-3-carboxylate (**3o**).* Yellow oil. Yield: 0.285 g (67%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.71 (s, 1H), 7.70−7.65 (m, 2H), 7.38−7.34 (m, 2H), 5.92 (s, 1H), 2.48 (t, $J$ = 7.6 Hz, 2H), 1.55−1.51 (m, 2H), 1.34−1.26 (m, 6H), 0.86 (t, $J$ = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 159.0, 158.0, 156.2, 155.4, 149.8, 134.9, 129.9, 125.0, 117.7, 117.0, 116.9, 65.6, 34.4, 31.4, 28.6, 26.3, 22.5, 14.0 ppm. IR (film): $\nu$ = 1770 (br, C=O), 1609 (br, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 449.0215, [M+Na$^+$] (calcd for $C_{18}H_{19}O_4INa$: 449.0220).

*(Z)-1-Iodooct-1-en-2-yl (E)-Cinnamate (**3p**).* Yellow oil. Yield: 0.299 g (78%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.86 (d, $J$ = 15.9 Hz, 1H), 7.62−7.59 (m, 2H), 7.46−7.43 (m, 3H), 6.57 (d, $J$ = 15.9 Hz, 1H), 5.90 (s, 1H), 2.46 (t, $J$ = 7.5 Hz, 2H), 1.56−1.51 (m, 2H), 1.38−1.29 (m, 6H), 0.90 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.3, 158.0, 146.9, 134.1, 130.8, 129.0, 128.3, 116.8, 65.1, 34.6, 31.5, 28.6, 26.4, 22.5, 14.1 ppm. IR (film): $\nu$ = 1733 (s, C=O), 1634 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 407.0463, [M+Na$^+$] (calcd for $C_{17}H_{21}O_2INa$: 407.0478).

*(Z)-1-Iodopent-1-en-2-yl Benzoate (**4a**).* Yellow oil. Yield: 0.265 g (84%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.19−8.16 (m, 2H), 7.68−7.62 (m, 1H), 7.54−7.49 (m, 2H), 5.95 (s, 1H), 2.50 (t, $J$ = 7.5 Hz, 2H), 1.65−1.53 (m, 2H), 0.98 (t, $J$ = 7.5 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.2, 157.9, 133.7, 130.2, 129.2, 128.6, 65.3, 36.5, 19.8, 13.5 ppm. IR (film): $\nu$ = 1737 (s, C=O), 1639 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 338.9844, [M+Na$^+$] (calcd for $C_{12}H_{13}O_2INa$: 338.9852).

*(Z)-1-Iodohex-1-en-2-yl Benzoate (**4b**).* Yellow oil. Yield: 0.281 g (85%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.20−8.16 (m, 2H), 7.68−7.62 (m, 1H), 7.54−7.49 (m, 2H), 5.95 (s, 1H), 2.52 (t, $J$ = 6.9 Hz, 2H), 1.57−1.50 (m, 2H), 1.43−1.35 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.2, 158.2, 133.7, 130.2, 129.2, 128.6, 65.2, 34.3, 28.6, 22.1, 13.8 ppm. IR (film): $\nu$ = 1739 (s, C=O), 1639 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 352.9999, [M+Na$^+$] (calcd for $C_{13}H_{15}O_2INa$: 353.0009).

*(Z)-1-Cyclopropyl-2-iodovinyl Benzoate (**4f**).* Orange oil. Yield: 0.223 g (71%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.17−8.14 (m, 2H), 7.68−7.62 (m, 1H), 7.54−7.49 (m, 2H), 6.00 (d, $J$ = 1.0 Hz, 1H), 1.91−1.82 (m, 1H), 0.82−0.76 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.1, 158.3, 133.7, 130.2, 129.1, 128.6, 63.9, 15.0, 5.7 ppm. IR (film): $\nu$ = 1738 (s, C=O), 1632 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 336.9685, [M+Na$^+$] (calcd for $C_{12}H_{11}O_2INa$: 336.9696).

*(Z)-1-Cyclopentyl-2-iodovinyl Benzoate (**4g**).* Orange oil. Yield: 0.233 g (68%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.19−8.16 (m, 2H), 7.67−7.62 (m, 1H), 7.54−7.49 (m, 2H), 6.04 (d, $J$ = 1.2 Hz, 1H), 2.99−2.89 (m, 1H), 1.93−1.90 (m, 2H), 1.72−1.59 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.1, 160.6, 133.6, 130.2, 129.3, 128.6, 64.8, 45.4, 30.5, 24.7 ppm. IR (film): $\nu$ = 1737 (s, C=O), 1630 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 364.9996, [M+Na$^+$] (calcd for $C_{14}H_{15}O_2INa$: 365.0009).

*(Z)-1-Iodo-3-phenylprop-1-en-2-yl Benzoate (**4i**).* Orange oil. Yield: 0.262 g (72%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.14−8.11 (m, 2H), 7.67−7.62 (m, 1H), 7.53−7.48 (m, 2H), 7.35−7.27 (m, 5H), 5.89 (s, 1H), 3.82 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.3, 157.1, 135.7, 133.7, 130.2, 129.3, 129.0, 128.7, 128.6, 127.1, 67.7, 40.7 ppm. IR (film): $\nu$ = 1727 (s, C=O), 1601 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 386.9842, [M+Na$^+$] (calcd for $C_{16}H_{13}O_2INa$: 386.9852).

*(Z)-1-Iodo-4-phenylbut-1-en-2-yl Benzoate (**4j**).* Orange oil. Yield: 0.284 g (75%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.21−8.18 (m, 2H), 7.68−7.65 (m, 1H), 7.57−7.52 (m, 2H), 7.35−7.21 (m, 5H), 5.97 (s, 1H), 2.94−2.83 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.3, 157.1, 140.2, 133.8, 130.3, 129.1, 128.6, 128.5, 128.4, 126.3, 66.3, 36.3, 32.9 ppm. IR (film): $\nu$ = 1732 (s, C=O), 1602 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 400.9998, [M+Na$^+$] (calcd for $C_{17}H_{15}O_2INa$: 401.0009).

*(Z)-1-Iodo-5-phenylpent-1-en-2-yl Benzoate (**4k**).* Orange oil. Yield: 0.298 g (76%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.21−8.18 (m, 2H), 7.67−7.65 (m, 1H), 7.56−7.51 (m, 2H), 7.34−7.19 (m, 5H), 5.99 (s, 1H), 2.71 (t, $J$ = 7.5 Hz, 2H), 2.58 (t, $J$ = 7.2 Hz, 2H), 1.97−1.87 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.2, 157.7, 141.4, 133.7, 130.2, 129.2, 128.6, 128.5 (2C), 126.0, 65.8, 35.0, 34.1, 28.1 ppm. IR (film): $\nu$ = 1737 (s, C=O), 1601 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 415.0150, [M+Na$^+$] (calcd for $C_{18}H_{17}O_2INa$: 415.0165).

*(Z)-2-Iodo-1-phenylvinyl Benzoate (**4l**).* Orange oil. Yield: 0.242 g (69%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.32−8.29 (m, 2H), 7.73−7.68 (m, 1H), 7.61−7.52 (m, 4H), 7.39−7.37 (m, 3H), 6.79 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.2, 155.2, 134.0, 133.7, 130.4, 129.5, 128.9, 128.8, 128.7, 125.2, 68.5 ppm. IR (film): $\nu$ = 1771 (s, C=O), 1604 (m, C=C) $cm^{-1}$. HRMS (ESI): $m/z$ 372.9682, [M+Na$^+$] (calcd for $C_{15}H_{11}O_2INa$: 372.9696).

**General Procedure for the Preparation of the 1,4-Disubstituted (*Z*)-Enynyl Esters.** Under an argon atmosphere, [$Pd(PPh_3)_4$] (0.058 g; 0.05 mmol), CuI (0.019 g; 0.1 mmol), the corresponding (*Z*)-$\beta$-iodoenol ester (1 mmol), and 1,4-dioxane (3 mL) were introduced into a Teflon-capped sealed tube, and the resulting suspension stirred at room temperature for 10 min. Then, $Et_3N$ (0.420 mL; 3 mmol) and the appropriate terminal alkyne (1.3 mmol) were added, and the mixture stirred at room temperature for 4 h in the absence of light. The volatiles were then removed *in vacuo* and the resulting residue purified by flash column chromatography over silica gel using diethyl ether/hexane (1:10) as eluent. Characterization data for the isolated (*Z*)-enynyl esters are as follows:

*(Z)-1-Phenyldec-3-en-1-yn-4-yl Acetate (**5a**).*[22a] Yellow oil. Yield: 0.256 g (95%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.43−7.40 (m, 2H), 7.33−7.30 (m, 3H), 5.45 (s, 1H), 2.34 (t, $J$ = 7.5 Hz, 2H), 2.26 (s, 3H), 1.53−1.41 (m, 2H), 1.39−1.28 (m, 6H), 0.91 (t, $J$ = 6.9 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.9, 160.3, 131.4, 128.3, 128.2, 123.3, 97.7, 93.8, 83.2, 33.9, 31.5, 28.7, 26.2, 22.5, 20.8, 14.1 ppm.

*(Z)-1-(4-Fluorophenyl)dec-3-en-1-yn-4-yl Acetate (**5b**).*[22a] Yellow oil. Yield: 0.277 g (96%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.40−7.35 (m, 2H), 7.04−6.98 (m, 2H), 5.43 (s, 1H), 2.33 (t, $J$ = 7.2 Hz, 2H), 2.25 (s, 3H), 1.51−1.49 (m, 2H), 1.36−1.28 (m, 6H), 0.91 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.9, 162.4 (d, $J$ = 249.5 Hz), 160.4, 133.2 (d, $J$ = 8.3 Hz), 119.4 (d, $J$ = 3.5 Hz), 115.5


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(d, $J$ = 22.2 Hz), 97.5, 92.7, 82.9, 33.8, 31.5, 28.7, 26.2, 22.5, 20.8, 14.0 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −111.1 ppm.

*(Z)-1-(4-Bromophenyl)dec-3-en-1-yn-4-yl Acetate (**5c**).* Yellow oil. Yield: 0.293 g (84%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.44 (d, $J$ = 8.4 Hz, 2H), 7.26 (d, $J$ = 8.5 Hz, 2H), 5.43 (s, 1H), 2.33 (t, $J$ = 7.8 Hz, 2H), 2.25 (s, 3H), 1.59−1.49 (m, 2H), 1.38−1.31 (m, 6H), 0.91 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.8, 160.7, 132.8, 131.5, 122.4, 122.3, 97.5, 92.6, 84.4, 33.9, 31.5, 28.7, 26.2, 22.5, 20.8, 14.0 ppm. IR (film): $\nu$ = 2210 (w, C≡C), 1759 (s, C═O), 1653 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 371.0607, [M+Na$^+$] (calcd for $C_{18}H_{21}O_2BrNa$: 371.0617).

*(Z)-1-(4-Methylphenyl)dec-3-en-1-yn-4-yl Acetate (**5d**).* Yellow oil. Yield: 0.275 g (97%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.31 (d, $J$ = 8.1 Hz, 2H), 7.12 (d, $J$ = 8.1 Hz, 2H), 5.44 (s, 1H), 2.36 (s, 3H), 2.33 (t, $J$ = 8.1 Hz, 2H), 2.26 (s, 3H), 1.52−1.50 (m, 2H), 1.37−1.32 (m, 6H), 0.92 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 160.0, 138.3, 131.3, 129.0, 120.3, 97.8, 94.0, 82.6, 33.8, 31.5, 28.7, 26.3, 22.5, 21.5, 20.8, 14.0 ppm. IR (film): $\nu$ = 2201 (w, C≡C), 1761 (s, C═O), 1652 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 307.1659, [M+Na$^+$] (calcd for $C_{19}H_{24}O_2Na$: 307.1669).

*(Z)-1-(4-Methoxyphenyl)dec-3-en-1-yn-4-yl Acetate (**5e**).*[22a] Yellow oil. Yield: 0.282 g (94%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.34 (d, $J$ = 8.7 Hz, 2H), 6.84 (d, $J$ = 8.7 Hz, 2H), 5.43 (s, 1H), 3.81 (s, 3H), 2.32 (t, $J$ = 7.5 Hz, 2H), 2.25 (s, 3H), 1.54−1.49 (m, 2H), 1.38−1.31 (m, 6H), 0.91 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 159.6, 159.5, 132.8, 115.5, 113.9, 97.8, 93.8, 81.9, 55.2, 33.8, 31.5, 28.7, 26.3, 22.5, 20.8, 14.0 ppm.

*(Z)-1-(Trimethylsilyl)dec-3-en-1-yn-4-yl Acetate (**5f**).* Colorless oil. Yield: 0.232 g (87%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 5.23 (s, 1H), 2.25 (t, $J$ = 7.6 Hz, 2H), 2.20 (s, 3H), 1.49−1.44 (m, 2H), 1.34−1.28 (m, 6H), 0.88 (t, $J$ = 6.4 Hz, 3H), −0.18 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.7, 161.6, 99.3, 98.7, 97.7, 33.8, 31.5, 28.6, 26.1, 22.5, 20.7, 14.0, −0.1 ppm. IR (film): $\nu$ = 2136 (m, C≡C), 1766 (s, C═O), 1649 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 289.1593, [M+Na$^+$] (calcd for $C_{15}H_{26}O_2NaSi$: 289.1594).

*(Z)-Tetradec-7-en-9-yn-7-yl Acetate (**5g**).* Yellow oil. Yield: 0.210 g (84%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.20 (s, 1H), 2.35−2.30 (m, 2H), 2.25 (t, $J$ = 7.2 Hz, 2H), 2.21 (s, 3H), 1.49−1.44 (m, 6H), 1.32−1.29 (m, 6H), 0.95−0.87 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 158.9, 98.0, 94.9, 74.1, 33.6, 31.5, 30.8, 28.6, 26.2, 22.5, 21.8, 20.7, 19.1, 14.0, 13.5 ppm. IR (film): $\nu$ = 2220 (w, C≡C), 1763 (s, C═O), 1653 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 273.1825, [M+Na$^+$] (calcd for $C_{16}H_{26}O_2Na$: 273.1825).

*(Z)-1-Cyclopropyldec-3-en-1-yn-4-yl Acetate (**5h**).* Yellow oil. Yield: 0.215 g (92%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 5.15 (s, 1H), 2.22 (t, $J$ = 7.6 Hz, 2H), 2.20 (s, 3H), 1.47−1.40 (m, 2H), 1.36−1.27 (m, 7H), 0.88 (t, $J$ = 6.8 Hz, 3H), 0.83−0.78 (m, 2H), 0.70−0.66 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 168.0, 159.2, 98.1, 97.9, 69.3, 33.6, 31.5, 28.6, 26.2, 22.5, 20.8, 14.0, 8.7, 0.3 ppm. IR (film): $\nu$ = 2116 (w, C≡C), 1761 (s, C═O), 1653 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 257.1515, [M+Na$^+$] (calcd for $C_{15}H_{22}O_2Na$: 257.1517).

*(Z)-1-(Cyclohex-1-en-1-yl)dec-3-en-1-yn-4-yl Acetate (**5i**).* Colorless oil. Yield: 0.249 g (91%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 6.07 (br, 1H), 5.33 (s, 1H), 2.27 (t, $J$ = 7.2 Hz, 2H), 2.22 (s, 3H), 2.12−2.10 (m, 4H), 1.65−1.59 (m, 4H), 1.48−1.45 (m, 2H), 1.32−1.29 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 159.2, 134.8, 120.8, 97.9, 95.9, 80.6, 33.8, 31.5, 29.2, 28.7, 26.2, 25.7, 22.5, 22.3, 21.5, 20.8, 14.0 ppm. IR (film): $\nu$ = 2194 (w, C≡C), 1763 (s, C═O), 1653 (m, C═C), 1623 (w, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 297.1823, [M+Na$^+$] (calcd for $C_{18}H_{26}O_2Na$: 297.1825).

*(Z)-2-Hydroxy-2-methyldodec-5-en-3-yn-6-yl Acetate (**5j**).* Orange oil. Yield: 0.219 g (87%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 5.18 (s, 1H), 2.68 (s, 1H), 2.22 (t, $J$ = 6.9 Hz, 2H), 2.18 (s, 3H), 1.49 (s, 6H), 1.43−1.41 (m, 2H), 1.31−1.24 (m, 6H), 0.86 (t, $J$ = 6.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.9, 160.2, 98.7, 97.1, 75.8, 65.3, 33.7, 31.5, 31.3, 28.6, 26.1, 22.5, 20.7, 14.0 ppm. IR (film): $\nu$ = 3434 (br, OH), 2222 (w, C≡C), 1763 (s, C═O), 1655 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 275.1621, [M+Na$^+$] (calcd for $C_{15}H_{24}O_3Na$: 275.1618).

*(Z)-1-Phenyldec-3-en-1-yn-4-yl Benzoate (**6a**).* Yellow oil. Yield: 0.319 g (96%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.25−8.22 (m, 2H), 7.65−7.50 (m, 3H), 7.22−7.18 (m, 5H), 5.58 (s, 1H), 2.52 (t, $J$ = 6.9 Hz, 2H), 1.63−1.60 (m, 2H), 1.43−1.32 (m, 6H), 0.94 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.9, 160.8, 133.5, 131.3, 130.2, 129.6, 128.6, 128.1, 128.0, 123.3, 97.9, 94.1, 83.5, 34.0, 31.6, 28.8, 26.4, 22.6, 14.1 ppm. IR (film): $\nu$ = 2198 (w, C≡C), 1733 (s, C═O), 1646 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 355.1661, [M+Na$^+$] (calcd for $C_{23}H_{24}O_2Na$: 355.1669).

*(Z)-1-(4-Fluorophenyl)dec-3-en-1-yn-4-yl Benzoate (**6b**).* Yellow oil. Yield: 0.318 g (91%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.21−8.18 (m, 2H), 7.68−7.63 (m, 1H), 7.54−7.49 (m, 2H), 7.14−7.09 (m, 2H), 6.90−6.85 (m, 2H), 5.52 (s, 1H), 2.48 (t, $J$ = 7.2 Hz, 2H), 1.60−1.58 (m, 2H), 1.38−1.29 (m, 6H), 0.91 (t, $J$ = 6.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.8, 162.2 (d, $J$ = 249.2 Hz), 160.9, 133.5, 133.0 (d, $J$ = 8.4 Hz), 130.1, 129.5, 128.5, 119.3, 115.4 (d, $J$ = 22.0 Hz), 97.6, 92.7, 83.1, 34.0, 31.5, 28.7, 26.3, 22.5, 14.0 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −111.3 ppm. IR (film): $\nu$ = 2204 (w, C≡C), 1739 (s, C═O), 1646 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 373.1578, [M+Na$^+$] (calcd for $C_{23}H_{23}O_2FNa$: 373.1574).

*(Z)-1-(4-Bromophenyl)dec-3-en-1-yn-4-yl Benzoate (**6c**).* Yellow oil. Yield: 0.362 g (88%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.21−8.19 (m, 2H), 7.68−7.63 (m, 1H), 7.55−7.50 (m, 2H), 7.31 (d, $J$ = 8.4 Hz, 2H), 6.99 (d, $J$ = 8.5 Hz, 2H), 5.53 (s, 1H), 2.49 (t, $J$ = 7.2 Hz, 2H), 1.67−1.56 (m, 2H), 1.46−1.30 (m, 6H), 0.92 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.8, 161.4, 133.6, 132.6, 131.4, 130.1, 129.4, 128.6, 122.3, 122.2, 97.6, 93.0, 84.7, 34.1, 31.5, 28.7, 26.3, 22.5, 14.1 ppm. IR (film): $\nu$ = 2206 (w, C≡C), 1737 (s, C═O), 1643 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 433.0774, [M+Na$^+$] (calcd for $C_{23}H_{23}O_2BrNa$: 433.0773).

*(Z)-1-(4-Methylphenyl)dec-3-en-1-yn-4-yl Benzoate (**6d**).* Yellow oil. Yield: 0.304 g (88%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.20−8.18 (m, 2H), 7.65−7.61 (m, 1H), 7.52−7.28 (m, 2H), 7.04 (d, $J$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 5.52 (s, 1H), 2.47 (t, $J$ = 7.2 Hz, 2H), 2.28 (s, 3H), 1.58−1.56 (m, 2H), 1.39−1.30 (m, 6H), 0.89 (t, $J$ = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.9, 160.4, 138.1, 133.4, 131.1, 130.1, 129.6, 128.9, 128.5, 120.2, 97.9, 94.3, 82.7, 33.9, 31.5, 28.7, 26.4, 22.5, 21.4, 14.0 ppm. IR (film): $\nu$ = 2204 (w, C≡C), 1736 (s, C═O), 1648 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 369.1820, [M+Na$^+$] (calcd for $C_{24}H_{26}O_2Na$: 369.1825).

*(Z)-1-(4-Methoxyphenyl)dec-3-en-1-yn-4-yl Benzoate (**6e**).* Yellow oil. Yield: 0.337 g (93%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.22−8.19 (m, 2H), 7.65−7.62 (m, 1H), 7.54−7.49 (m, 2H), 7.10 (d, $J$ = 8.7 Hz, 2H), 6.72 (d, $J$ = 8.7 Hz, 2H), 5.53 (s, 1H), 3.76 (s, 3H), 2.45 (t, $J$ = 7.5 Hz, 2H), 1.60−1.57 (m, 2H), 1.40−1.29 (m, 6H), 0.91 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.9, 160.0, 159.4, 133.4, 132.7, 130.1, 129.6, 128.5, 115.5, 113.8, 98.0, 94.1, 82.1, 55.2, 33.9, 31.6, 28.7, 26.4, 22.5, 14.0 ppm. IR (film): $\nu$ = 2203 (w, C≡C), 1735 (s, C═O), 1648 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 385.1768, [M+Na$^+$] (calcd for $C_{24}H_{26}O_3Na$: 385.1774).

*(Z)-1-(Trimethylsilyl)dec-3-en-1-yn-4-yl Benzoate (**6f**).* Yellow oil. Yield: 0.308 g (94%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.17−8.14 (m, 2H), 7.64−7.59 (m, 1H), 7.51−7.46 (m, 2H), 5.33 (s, 1H), 2.42 (t, $J$ = 7.5 Hz, 2H), 1.55−1.53 (m, 2H), 1.35−1.28 (m, 6H), 0.89 (t, $J$ = 6.6 Hz, 3H), −0.02 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.6, 162.3, 133.4, 130.1, 129.6, 128.4, 99.6, 98.8, 97.8, 33.9, 31.5, 28.7, 26.2, 22.5, 14.0, −0.4 ppm. IR (film): $\nu$ = 2125 (m, C≡C), 1757 (s, C═O), 1672 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 351.1742, [M+Na$^+$] (calcd for $C_{20}H_{28}O_2NaSi$: 351.1751).

*(Z)-Tetradec-7-en-9-yn-7-yl Benzoate (**6g**).* Yellow oil. Yield: 0.278 g (89%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.15−8.13 (m, 2H), 7.62−7.58 (m, 1H), 7.50−7.46 (m, 2H), 5.29 (s, 1H), 2.37 (t, $J$ = 7.6 Hz, 2H), 2.19−2.15 (m, 2H), 1.56−1.49 (m, 2H), 1.35−1.19 (m, 10H), 0.87 (t, $J$ = 6.8 Hz, 3H), 0.68 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.8, 159.3, 133.2, 130.1, 129.7, 128.4, 98.2, 95.2, 74.2, 33.7, 31.5, 30.6, 28.7, 26.3, 22.5, 21.7, 19.1, 14.0, 13.4 ppm. IR (film): $\nu$ = 2220 (w, C≡C), 1738 (s, C═O), 1653 (m, C═C)



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$cm^{-1}$. HRMS (ESI): $m/z$ 335.1982, $[M+Na^+]$ (calcd for $C_{21}H_{28}O_2Na$: 335.1981).

*(Z)-1-Cyclopropyldec-3-en-1-yn-4-yl Benzoate (**6h**).* Yellow oil. Yield: 0.237 g (80%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16−8.14 (m, 2H), 7.65−7.62 (m, 1H), 7.53−7.49 (m, 2H), 5.27 (s, 1H), 2.39 (t, $J$ = 7.6 Hz, 2H), 1.57−1.50 (m, 2H), 1.38−1.21 (m, 7H), 0.89 (t, $J$ = 6.8 Hz, 3H), 0.67−0.63 (m, 2H), 0.47−0.43 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.8, 159.6, 133.3, 130.0, 129.7, 128.4, 98.4, 98.0, 69.4, 33.7, 31.5, 28.7, 26.4, 22.5, 14.0, 8.5, 0.2 ppm. IR (film): $\nu$ = 2114 (w, C≡C), 1755 (s, C═O), 1663 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 319.1677, $[M+Na^+]$ (calcd for $C_{20}H_{24}O_2Na$: 319.1674).

*(Z)-1-(Cyclohex-1-en-1-yl)dec-3-en-1-yn-4-yl Benzoate (**6i**).* Yellow oil. Yield: 0.299 g (89%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16−8.14 (m, 2H), 7.63−7.59 (m, 1H), 7.50−7.47 (m, 2H), 5.84 (m, 1H), 5.42 (s, 1H), 2.42 (t, $J$ = 7.6 Hz, 2H), 1.97 (br, 2H), 1.89 (br, 2H), 1.60−1.48 (m, 6H), 1.40−1.28 (m, 6H), 0.88 (t, $J$ = 6.8 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 163.8, 159.6, 134.6, 133.3, 130.1, 129.7, 128.4, 120.7, 98.0, 96.1, 80.7, 33.9, 31.5, 28.8, 28.7, 26.4, 25.6, 22.5, 22.2, 21.4, 14.0 ppm. IR (film): $\nu$ = 2193 (w, C≡C), 1738 (s, C═O), 1653 (m, C═C), 1623 (w, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 359.1983, $[M+Na^+]$ (calcd for $C_{23}H_{28}O_2Na$: 359.1981).

*(Z)-2-Hydroxy-2-methyldodec-5-en-3-yn-6-yl Benzoate (**6j**).* Orange oil. Yield: 0.264 g (84%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.17−8.14 (m, 2H), 7.66−7.61 (m, 1H), 7.53−7.48 (m, 2H), 5.33 (s, 1H), 2.42 (t, $J$ = 7.2 Hz, 2H), 1.74 (br, 1H), 1.58−1.52 (m, 2H), 1.20−1.31 (m, 6H), 1.32 (s, 6H), 0.90 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.7, 160.8, 133.5, 130.0, 129.4, 128.5, 98.9, 97.3, 75.9, 65.3, 33.8, 31.5, 31.1, 28.7, 26.2, 22.5, 14.0 ppm. IR (film): $\nu$ = 3423 (br, OH), 2222 (w, C≡C), 1736 (s, C═O), 1650 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 337.1768, $[M+Na^+]$ (calcd for $C_{20}H_{26}O_3Na$: 337.1774).

*(Z)-1,4-Diphenylbut-1-en-3-yn-1-yl Acetate (**7a**).*[22a] White solid. Mp 106−109 °C. Yield: 0.236 g (90%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.55−7.52 (m, 2H), 7.50−7.46 (m, 2H), 7.43−7.35 (m, 6H), 6.21 (s, 1H), 2.42 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 167.9, 155.7, 133.4, 131.5, 129.7, 128.8, 128.5, 128.4, 124.6, 123.2, 97.9, 97.1, 84.1, 20.7 ppm.

*(Z)-4-(4-Fluorophenyl)-1-phenylbut-1-en-3-yn-1-yl Acetate (**7b**).*[22a] Yellow solid. Mp 85−88 °C. Yield: 0.255 g (91%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.54−7.39 (m, 7H), 7.08−7.02 (m, 2H), 6.18 (s, 1H), 2.41 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.8, 162.6 (d, $J$ = 250.1 Hz), 155.7, 133.3 (d, $J$ = 8.2 Hz), 129.7, 128.7, 124.6, 119.3, 115.7 (d, $J$ = 22.1 Hz), 97.7, 95.9, 83.8, 20.7 ppm. $^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz): $\delta$ = −110.4 ppm.

*(Z)-4-(4-Methylphenyl)-1-phenylbut-1-en-3-yn-1-yl Acetate (**7c**).*[22a] Yellow solid. Mp 102−104 °C. Yield: 0.235 g (85%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.54−7.51 (m, 2H), 7.42−7.35 (m, 5H), 7.16 (d, $J$ = 8.1 Hz, 2H), 6.20 (s, 1H), 2.41 (s, 3H), 2.39 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 155.4, 138.7, 133.5, 131.4, 129.6, 129.2, 128.7, 124.5, 120.1, 98.0, 97.3, 83.5, 21.5, 20.7 ppm.

*(Z)-4-(4-Methoxyphenyl)-1-phenylbut-1-en-3-yn-1-yl Acetate (**7d**).*[22a] Yellow solid. Mp 130−132 °C. Yield: 0.257 g (88%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.53−7.50 (m, 2H), 7.42−7.37 (m, 5H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.19 (s, 1H), 3.85 (s, 3H), 2.41 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 159.9, 155.1, 133.5, 133.0, 129.5, 128.8, 124.5, 115.3, 114.1, 98.1, 97.4, 83.0, 55.3, 20.7 ppm.

*(Z)-1-Phenyloct-1-en-3-yn-1-yl Acetate (**7e**).* Yellow oil. Yield: 0.213 g (88%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.47−7.44 (m, 2H), 7.38−7.34 (m, 3H), 5.97 (t, $J$ = 2.1 Hz, 1H), 2.42 (td, $J$ = 6.9 and 2.1 Hz, 2H), 2.35 (s, 3H), 1.57−1.46 (m, 4H), 0.96 (t, $J$ = 7.2 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 154.8, 133.6, 129.3, 128.7, 124.4, 98.7, 98.5, 75.0, 30.8, 21.9, 20.7, 19.5, 13.6 ppm. IR (film): $\nu$ = 2217 (m, C≡C), 1770 (s, C═O), 1625 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 265.1200, $[M+Na^+]$ (calcd for $C_{16}H_{18}O_2Na$: 265.1199).

*(Z)-1-Phenyldec-1-en-3-yn-1-yl Acetate (**7f**).*[22a] Yellow oil. Yield: 0.238 g (88%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.47−7.44 (m, 2H), 7.38−7.34 (m, 3H), 5.96 (t, $J$ = 2.4 Hz, 1H), 2.40 (td, $J$ = 6.9 and 2.4 Hz, 2H), 2.35 (s, 3H), 1.60−1.31 (m, 8H), 0.92 (t, $J$ = 6.6 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.0, 154.7, 133.6, 129.3, 128.7, 124.3, 98.8, 98.5, 75.0, 31.4, 28.7, 28.6, 22.6, 20.7, 19.8, 14.1 ppm.

*(Z)-1,6-Diphenylhex-1-en-3-yn-1-yl Acetate (**7g**).* Colorless oil. Yield: 0.253 g (87%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.49−7.45 (m, 2H), 7.42−7.33 (m, 5H), 7.30−7.24 (m, 3H), 5.98 (t, $J$ = 2.4 Hz, 1H), 2.92 (t, $J$ = 7.5 Hz, 2H) 2.73 (td, $J$ = 7.2 and 2.4 Hz, 2H), 2.28 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.1, 155.0, 140.5, 133.5, 129.4, 128.7, 128.5, 128.4, 126.4, 124.4, 98.3, 97.7, 75.6, 35.1, 22.0, 20.7 ppm. IR (film): $\nu$ = 2214 (w, C≡C), 1765 (s, C═O), 1694 (m, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 313.1198, $[M+Na^+]$ (calcd for $C_{20}H_{18}O_2Na$: 313.1199).

*(Z)-4-(Cyclohex-1-en-1-yl)-1-phenylbut-1-en-3-yn-1-yl Acetate (**7h**).*[22a] White solid. Mp 87−90 °C. Yield: 0.232 g (87%). $^1H$ NMR ($CDCl_3$): $\delta$ = 7.49−7.46 (m, 2H), 7.39−7.35 (m, 3H), 6.17 (br, 1H), 6.10 (s, 1H), 2.37 (s, 3H), 2.18−2.15 (m, 4H), 1.70−1.62 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 167.9, 154.7, 135.7, 133.5, 129.4, 128.7, 124.4, 120.8, 99.4, 98.2, 81.6, 29.1, 25.8, 22.3, 21.4, 20.7 ppm.

*(Z)-5-Hydroxy-1,5-diphenylpent-1-en-3-yn-1-yl Acetate (**7i**).* Orange oil. Yield: 0.242 g (83%). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.59 (d, $J$ = 6.9 Hz, 2H), 7.50−7.36 (m, 8H), 6.04 (d, $J$ = 1.5 Hz, 1H), 5.66 (d, $J$ = 1.5 Hz, 1H), 2.67 (br, 1H), 2.21 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta$ = 168.1, 156.6, 140.6, 133.2, 129.8, 128.8, 128.7, 128.4, 126.7, 124.7, 97.1, 96.6, 81.1, 65.1, 20.6 ppm. IR (film): $\nu$ = 3413 (br, OH), 2214 (w, C≡C), 1766 (s, C═O), 1625 (w, C═C) $cm^{-1}$. HRMS (ESI): $m/z$ 315.099426, $[M+Na^+]$ (calcd for $C_{19}H_{16}O_3Na$: 315.0992).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02712.

Copies of the NMR spectra of all the (*Z*)-β-iodoenol and (*Z*)-enynyl esters synthesized in this work and synthesis, characterization data, and NMR spectra of compounds **10** and **11** (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) The intramolecular version of this reaction also presents a high synthetic interest since it provides an easy entry to enol-lactones. For selected recent examples, see: (a) Nebra, N.; Monot, J.; Shaw, R.; Martin-Vaca, B.; Bourissou, D. *ACS Catal.* **2013**, *3*, 2930−2934. (b) Tomás-Mendivil, E.; Toullec, P. Y.; Borge, J.; Conejero, S.; Michelet, V.; Cadierno, V. *ACS Catal.* **2013**, *3*, 3086−3098.



DOI: 10.1021/acs.joc.6b02712
*J. Org. Chem.* 2017, 82, 1507−1516

(c) Espinosa-Jalapa, N. A.; Ke, D.; Nebra, N.; Le Goanvic, L.; Mallet-Ladeira, S.; Monot, J.; Martin-Vaca, B.; Bourissou, D. *ACS Catal.* **2014**, *4*, 3605−3611. (d) Nagendiran, A.; Verho, O.; Haller, C.; Johnston, E. V.; Bäckvall, J.-E. *J. Org. Chem.* **2014**, *79*, 1399−1405. (e) Rodríguez-Álvarez, M. J.; Vidal, C.; Díez, J.; García-Álvarez, J. *Chem. Commun.* **2014**, *50*, 12927−12929. (f) López-Reyes, M. E.; Toscano, A.; López-Cortés, J. G.; Alvarez-Toledano, C. *Asian J. Org. Chem.* **2015**, *4*, 545−551. (g) Ke, D.; Espinosa, N. A.; Mallet-Ladeira, S.; Monot, J.; Martin-Vaca, B.; Bourissou, D. *Adv. Synth. Catal.* **2016**, *358*, 2324−2331. (h) Medran, N. S.; Villalba, M.; Mata, E. G.; Testero, S. A. *Eur. J. Org. Chem.* **2016**, *2016*, 3757−3764. (i) Ferré, M.; Cattoën, X.; Wong Chi Man, M.; Pleixats, R. *ChemCatChem* **2016**, *8*, 2824−2831.

(2) See, for example: (a) Kleman, P.; González-Liste, P. J.; García-Garrido, S. E.; Cadierno, V.; Pizzano, A. *Chem. - Eur. J.* **2013**, *19*, 16209−16212. (b) Kleman, P.; González-Liste, P. J.; García-Garrido, S. E.; Cadierno, V.; Pizzano, A. *ACS Catal.* **2014**, *4*, 4398−4408. (c) Liu, X.; Coutelier, O.; Harrisson, S.; Tassaing, T.; Marty, J.-D.; Destarac, M. *ACS Macro Lett.* **2015**, *4*, 89−93. (d) Foarta, F.; Landis, C. R. *J. Org. Chem.* **2016**, *81*, 11250−11255.

(3) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689−1691.

(4) (a) Bruneau, C. *Top. Organomet. Chem.* **2011**, *43*, 203−230. and references cited therein (b) Dixneuf, P. H. *Catal. Lett.* **2015**, *145*, 360−372 and references cited therein..

(5) For selected recent examples, see: (a) Kawatsura, M.; Namioka, J.; Kajita, K.; Yamamoto, M.; Tsuji, H.; Itoh, T. *Org. Lett.* **2011**, *13*, 3285−3287. (b) Cadierno, V.; Francos, J.; Gimeno, J. *Organometallics* **2011**, *30*, 852−862. (c) Saha, S.; Ghatak, T.; Saha, B.; Doucet, H.; Bera, J. K. *Organometallics* **2012**, *31*, 5500−5505. (d) Nishiumi, M.; Miura, H.; Wada, K.; Hosokawa, S.; Inoue, M. *ACS Catal.* **2012**, *2*, 1753−1759. (e) Cheung, K.-C.; Wong, W.-L.; So, M.-H.; Zhou, Z.-Y.; Yan, S.-C.; Wong, K.-Y. *Chem. Commun.* **2013**, *49*, 710−712. (f) Jena, R. K.; Bhattacharjee, M. *Eur. J. Org. Chem.* **2015**, *2015*, 6734−6738. (g) Jeschke, J.; Gäbler, C.; Lang, H. *J. Org. Chem.* **2016**, *81*, 476−484. (h) Jeschke, J.; Engelhardt, T. B.; Lang, H. *Eur. J. Org. Chem.* **2016**, *2016*, 1548−1554.

(6) (a) Hua, R.; Tian, X. *J. Org. Chem.* **2004**, *69*, 5782−5784. (b) Ye, S.; Leong, W. K. *J. Organomet. Chem.* **2006**, *691*, 1216−1222.

(7) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Bruneau, C.; Dixneuf, P. H. *Organometallics* **1990**, *9*, 1155−1160. (b) Lumbroso, A.; Vautravers, N. R.; Breit, B. *Org. Lett.* **2010**, *12*, 5498−5501. (c) Lumbroso, A.; Koschker, P.; Vautravers, N. R.; Breit, B. *J. Am. Chem. Soc.* **2011**, *133*, 2386−2389. (d) Wei, S.; Pedroni, J.; Meißner, A.; Lumbroso, A.; Drexler, H.-J.; Heller, D.; Breit, B. *Chem. - Eur. J.* **2013**, *19*, 12067−12076.

(8) (a) Nakagawa, H.; Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2003**, *44*, 103−106. (b) Merola, J. S.; Ladipo, F. T. *Polyhedron* **2014**, *70*, 125−132.

(9) (a) Lu, X.; Zhu, G.; Ma, S. *Tetrahedron Lett.* **1992**, *33*, 7205−7206. (b) Wakabayashi, T.; Ishii, Y.; Murata, T.; Mizobe, Y.; Hidai, M. *Tetrahedron Lett.* **1995**, *36*, 5585−5588. (c) Tsukada, N.; Takahashi, A.; Inoue, Y. *Tetrahedron Lett.* **2011**, *52*, 248−250. (d) Smith, D. L.; Goundry, W. R. F.; Lam, H. W. *Chem. Commun.* **2012**, *48*, 1505−1507.

(10) (a) Wang, Y.; Wang, Z.; Li, Y.; Wu, G.; Cao, Z.; Zhang, L. *Nat. Commun.* **2014**, *5*, 3470. (b) Chary, B. C.; Kim, S. *J. Org. Chem.* **2010**, *75*, 7928−7931. (c) Dupuy, S.; Gasperini, D.; Nolan, S. P. *ACS Catal.* **2015**, *5*, 6918−6921.

(11) (a) Ishino, Y.; Nishiguchi, I.; Nakao, S.; Hirashima, T. *Chem. Lett.* **1981**, *10*, 641−644. (b) Yin, J.; Bai, Y.; Mao, M.; Zhu, G. *J. Org. Chem.* **2014**, *79*, 9179−9185.

(12) Although rare, some metal-free hydrocarboxylation reactions of alkynes have also been described in the literature: (a) Fan, M.-J.; Li, G.-Q.; Liang, Y.-M. *Tetrahedron* **2006**, *62*, 6782−6791. (b) Xu, S.; Liu, J.; Hu, D.; Bi, X. *Green Chem.* **2015**, *17*, 184−187. (c) Wen, Z.; Tian, C.; Borzov, M. V.; Nie, W. *Huaxue Xuebao* **2016**, *74*, 498−502. (d) Huang, H.; Zhang, X.; Yu, C.; Li, X.; Zhang, Y.; Wang, W. *ACS Catal.* **2016**, *6*, 8030−8035.

(13) (a) Wu, W.; Jiang, H. *Acc. Chem. Res.* **2014**, *47*, 2483−2504. (b) Jiang, H.; Zhu, C.; Wu, W. *Haloalkyne Chemistry*; Springer: Heidelberg, 2016.

(14) (a) Xie, L.; Wu, Y.; Yi, W.; Zhu, L.; Xiang, J.; He, W. *J. Org. Chem.* **2013**, *78*, 9190−9195. (b) Ghosh, N.; Nayak, S.; Prabagar, B.; Sahoo, A. K. *J. Org. Chem.* **2014**, *79*, 2453−2462. (c) Chen, Z.-W.; Ye, D.-N.; Ye, M.; Zhou, Z.-G.; Li, S.-H.; Liu, L.-X. *Tetrahedron Lett.* **2014**, *55*, 1373−1375. (d) Ye, Q.; Cheng, T.; Zhao, Y.; Zhao, J.; Jin, R.; Liu, G. *ChemCatChem* **2015**, *7*, 1801−1805. (e) Zeng, M.; Huang, R.-X.; Li, W.-Y.; Liu, X.-W.; He, F.-L.; Zhang, Y.-Y.; Xiao, F. *Tetrahedron* **2016**, *72*, 3818−3822. (f) Zou, H.; He, W.; Dong, Q.; Wang, R.; Yi, N.; Jiang, J.; Pen, D.; He, W. *Eur. J. Org. Chem.* **2016**, *2016*, 116−121. (g) Ye, M.; Wen, Y.; Li, H.; Fu, Y.; Wang, Q. *Tetrahedron Lett.* **2016**, *57*, 4983−4986.

(15) (a) Xu, H.; Gu, S.; Chen, W.; Li, D.; Dou, J. *J. Org. Chem.* **2011**, *76*, 2448−2458. (b) Rajesh, N.; Prajapati, D. *RSC Adv.* **2014**, *4*, 32108−32112. (c) Liu, G.; Kong, L.; Shen, J.; Zhu, G. *Org. Biomol. Chem.* **2014**, *12*, 2310−2321.

(16) Wang, S.; Li, P.; Yu, L.; Wang, L. *Org. Lett.* **2011**, *13*, 5968−5971.

(17) Chary, B. C.; Kim, S.; Shin, D.; Lee, P. H. *Chem. Commun.* **2011**, *47*, 7851−7853.

(18) (a) Burley, G. A.; Davies, D. L.; Griffith, G. A.; Lee, M.; Singh, K. *J. Org. Chem.* **2010**, *75*, 980−983. (b) Yamagishi, M.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2011**, *13*, 4873−4875. (c) Yamagishi, M.; Okazaki, J.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2012**, *14*, 34−37.

(19) Zeng, X.; Liu, S.; Shi, Z.; Xu, B. *Org. Lett.* **2016**, *18*, 4770−4773.

(20) Hydrohalogenation reactions to afford 1,2-dihaloalkenes have also been described: (a) Chen, Z.; Jiang, H.; Li, Y.; Qi, C. *Chem. Commun.* **2010**, *46*, 8049−8051. (b) Zhu, G.; Chen, D.; Wang, Y.; Zheng, R. *Chem. Commun.* **2012**, *48*, 5796−5798. (c) Li, Y.; Liu, X.; Ma, D.; Liu, B.; Jiang, H. *Adv. Synth. Catal.* **2012**, *354*, 2683−2688. (d) Gómez-Herrera, A.; Nahra, F.; Brill, M.; Nolan, S. P.; Cazin, C. S. J. *ChemCatChem* **2016**, *8*, 3381−3388.

(21) Intramolecular examples of this reaction to give haloenol lactones, promoted by mercury salts and gold catalysts, are known. See, for example: (a) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459−5466. (b) Dai, W.; Katzenellenbogen, J. A. *J. Org. Chem.* **1991**, *56*, 6893−6896. (c) Harkat, H.; Weibel, J.-M.; Pale, P. *Tetrahedron Lett.* **2006**, *47*, 6273−6276. (d) Harkat, H.; Dembelé, A. Y.; Weibel, J.-M.; Blanc, A.; Pale, P. *Tetrahedron* **2009**, *65*, 1871−1879.

(22) See, for example: (a) Chen, Z.; Huang, G.; Jiang, H.; Huang, H.; Pan, X. *J. Org. Chem.* **2011**, *76*, 1134−1139. (b) Chen, X.; Chen, D.; Lu, Z.; Kong, L.; Zhu, G. *J. Org. Chem.* **2011**, *76*, 6338−6343. (c) Okamoto, N.; Yanada, R. *J. Org. Chem.* **2012**, *77*, 3944−3951. (d) Chen, Z.; Ye, D.; Xu, G.; Ye, M.; Liu, L. *Org. Biomol. Chem.* **2013**, *11*, 6699−6702.

(23) See, for example: (a) Barluenga, J.; Rodríguez, M. A.; Campos, P. J. *J. Org. Chem.* **1990**, *55*, 3104−3106. (b) Chen, Z.; Li, J.; Jiang, H.; Zhu, S.; Li, Y.; Qi, C. *Org. Lett.* **2010**, *12*, 3262−3265. (c) Okamoto, N.; Miwa, Y.; Minami, H.; Takeda, K.; Yanada, R. *J. Org. Chem.* **2011**, *76*, 9133−9138. (d) Chawla, R.; Singh, A. K.; Yadav, L. D. S. *Synlett* **2013**, *24*, 1558−1562. (e) Xia, X.-F.; Gu, Z.; Liu, W.; Wang, N.; Wang, H.; Xia, Y.; Gao, H.; Liu, X. *Org. Biomol. Chem.* **2014**, *12*, 9909−9913. (f) Priebbenow, D. L.; Gable, R. W.; Baell, J. *J. Org. Chem.* **2015**, *80*, 4412−4418.

(24) González-Liste, P. J.; León, F.; Arribas, I.; Rubio, M.; García-Garrido, S. E.; Cadierno, V.; Pizzano, A. *ACS Catal.* **2016**, *6*, 3056−3060.

(25) The use of the $[AuCl(PPh_3)]/AgPF_6$ combination to promote the catalytic addition of carboxylic acids to nonhalogenated alkynes was previously described by Kim and co-workers. See ref 10b.

(26) See, for example: (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896−7936. (b) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211. (c) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410−3449. (d) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395−403. (e) Gorin, D. J.; Sherry, B. D.; Toste, F. D.



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*Chem. Rev.* **2008**, *108*, 3351. (f) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208−3221. (g) Obradors, C.; Echavarren, A. M. *Chem. Commun.* **2014**, *50*, 16−28. (h) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028−9072.

(27) Additional experiments demonstrated the need of using silver(I) salts containing noncoordinating anions, since identical reactions performed with AgOAc, AgOTs, or AgOTf led to the recovery of the starting iodoalkynes unchanged (both $AgPF_6$ and $AgSbF_6$ can be used without major differences in yields). On the other hand, we also noted that: (i) As previously observed by Kim and co-workers (ref 10b), the catalytic system $[AuCl(PPh_3)]/AgPF_6$ was very sensitive to the solvent employed, the yields decreasing drastically in DCM, DCE, or MeOH. (ii) An increase of the temperature (60 °C) results, as expected, in faster conversions, but the side products $RC(OAc)=CH_2$ are formed in larger quantities. (iii) The reactions also proceed with a lower Au loading (i.e., 2 mol%), but much longer times (48 h) are, in this case, needed to obtain the (*Z*)-*β*-iodoenol acetates **2** in similar yields.

(28) (a) Chen, Z.-W.; Luo, M.-T.; Wen, Y.-L.; Ye, M.; Zhou, Z.-G.; Liu, L.-X. *Synlett* **2014**, *25*, 2341−2344. (b) Lee, H.; Yi, Y.; Jun, C.-H. *Adv. Synth. Catal.* **2015**, *357*, 3485−3490.

(29) The preparation of enynes **5a**,**b**,**e** and **7a**−**d**,**f**,**h** was previously described by Jiang and co-workers employing (*Z*)-*β*-bromoenol acetates as starting materials. See ref 22a.

(30) The present hydrocarboxylation process is not restricted to iodoalkynes, bromo- and cloroalkynes can also participate in the reaction. Thus, employing identical experimental conditions, we were able to synthesize (*Z*)-1-bromooct-1-en-2-yl acetate (**10**) and (*Z*)-2-chloro-1-(4-methylphenyl)vinyl acetate (**11**) in 73 and 69% yield by reacting 1-bromooct-1-yne (**8**) or 1-(chloroethynyl)-4-methylbenzene (**9**), respectively, with acetic acid. Details are given in the Supporting Information.

(31) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, 2003.

(32) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133−4136.

(33) Coulson, D. R.; Satek, L. C.; Grim, S. O. *Inorg. Synth.* **2007**, *13*, 121−124.

(34) (a) Luithle, J. E. A.; Pietruszka, J. *Eur. J. Org. Chem.* **2000**, *2000*, 2557−2562. (b) Reddy, K. R.; Venkateshwar, M.; Maheswari, C. U.; Kumar, P. S. *Tetrahedron Lett.* **2010**, *51*, 2170−2173. (c) Usanov, D. L.; Yamamoto, H. *J. Am. Chem. Soc.* **2011**, *133*, 1286−1289.

(35) Ochiai, M.; Tsuchimoto, Y.; Hayashi, T. *Tetrahedron Lett.* **2003**, *44*, 5381−5384.



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