Tetrahedron 65 (2009) 1846–1855

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Gold-catalyzed efficient preparation of linear α-haloenones from propargylic acetates

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ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form 23 November 2008
Accepted 24 November 2008
Available online 24 December 2008

ABSTRACT

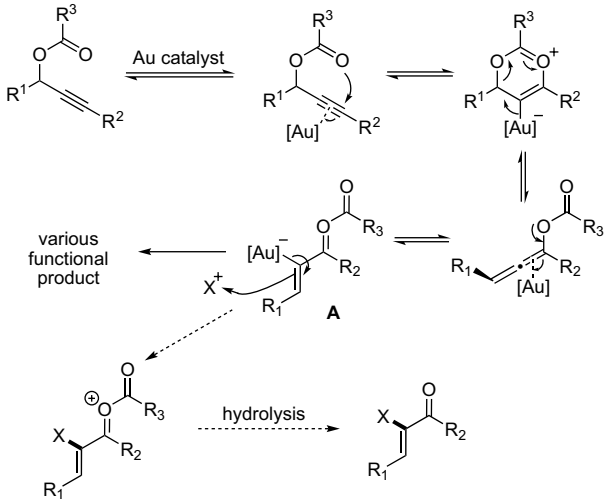
Versatile linear α-iodo- and α-bromoenones are prepared efficiently from readily accessible propargylic acetates using 2 mol % of $Au(PPh_3)NTf_2$. This reaction is easy to execute and has broad substrate scope. Good to excellent *Z*-selectivities are observed in the cases of propargylic acetates derived from aliphatic aldehydes.

1. Introduction

α-Haloenones, especially α-iodoenones, are important synthetic intermediates and can undergo transition metal-catalyzed cross-coupling reactions following Negishi's protocols,[1] readily installing various substituents including alkyl, alkenyl, alkynyl, and aryl groups at the enone α-position.

A range of methods for the synthesis of α-haloenones have been developed. For α-bromoenones, brominations of enones using commercially available or in situ generated bromine are the most studied and straightforward approach[2] although the strong reactivity of Br_2 prevents the inclusion of delicate functional groups. α-Iodoenones are much better substrates for transition metal-catalyzed cross-coupling reactions,[1] and their synthesis can be achieved from enones using a combination of I_2 and a nucleophilic base (e.g., pyridine,[3] DMAP,[4] and quinuclidine[4]). However, this Michael addition-based method is limited with linear enone substrates.[5] Although iodination of C–Si[6] bonds with ICl or C–Sn[7] bonds with I_2 can afford linear α-iodoenones, the need of more functionalized starting materials can be undesirable. McNelis reported that propargylic alcohols could be converted directly into linear α-iodoenones using NIS (*N*-iodosuccinimide) and a catalytic amount of hydroxy(tosyloxy)iodobenzene;[8] unfortunately, this potentially versatile method for α-iodoenone synthesis is limited to secondary alkynols; moreover, its scope was not well defined as only a few special examples of this chemistry were reported. We concluded that an efficient and general preparative method for linear α-haloenones is still much needed. Herein, we give a full account of our effort in addressing this need using Au catalysis.

Propargylic acetates are readily available starting materials and can be easily prepared from aldehydes/ketones, terminal alkynes, and acetic anhydride. They are versatile substrates for Au catalysis[9] and can undergo either 1,2-acetoxyl migration[10] or 3,3-rearrangement.[11,12] We originated and have since continued studies on Au-catalyzed tandem reactions of propargylic esters involving 3,3-rearrangement. In our design, the in situ generated carboxyallenes could be further activated by the very same Au catalyst to form Au-containing oxocarbenium **A** (Scheme 1). Intermediate **A** contains various functionalities including oxocarbenium, C–C double bond, activated acyl group, and potentially nucleophilic Au–C(sp^2) bond; moreover, due to the ease of substrate preparation, various functional groups can be easily incorporated into oxocarbenium



Scheme 1. Au-catalyzed tandem reactions of propargylic esters and the design for α-haloenone formation.

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0040-4020/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.tet.2008.11.107

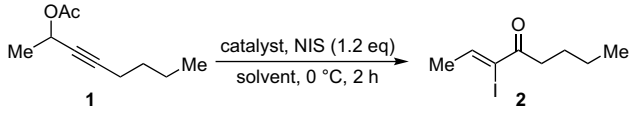
A (i.e., in R^1, R^2, and R^3). As a result, **A** is expected to have rich chemistry. Indeed, based on this design, we have developed several useful methods for efficient synthesis of highly functionalized 2,3-indoline-fused cyclobutanes,[11] cyclopentenones,[13a] α-alkylidene-β-diketones,[13b] alkenyl enol esters/carbonates,[13c] and enones.[13d,14] Several other research groups have also developed efficient synthetic methods sharing the design.[15] A notable observation in some of these studies is that the Au–C(sp^2) bond in **A** can react with intramolecular electrophiles[16,17] including iminiums[11] and activated acyl groups.[13b] We surmise that this Au–C(sp^2) bond could react with electrophilic halogens intermolecularly, leading to efficient formation of α-haloenones upon hydrolysis (Scheme 1).[18] In fact, iodinations of Au–C(sp^2) bonds with NIS had been realized in isolated examples.[19]

2. Results and discussion

We chose oct-3-yn-2-yl acetate (**1**) as substrate and NIS[18] as the 'I^+' source to study the reaction (Table 1). Stable Au(PPh_3)NTf_2 was first used for its ease of preparation and handling.[20] To our delight, the desired reaction did happen with 2 mol % of the catalyst, and α-iodoenone **2** was formed in anhydrous acetone in 95% yield albeit without much *Z*/*E* selectivity (entry 1).

To improve the stereoselectivity, we examined different solvents (entries 2 and 3). However, the improvement was moderate and, moreover, at the expense of the reaction yield. After some experimentation, we found that a small amount of water in acetone dramatically enhanced the *Z*/*E* selectivity, and only *Z*-**2** was observed when acetone/H_2O (40:1) was used as solvent (entry 4). To our delight, the low yield could be overcome by decreasing the amount of H_2O. Hence, 61% and 80% yields of **2** were obtained when the ratios of acetone/H_2O were 200:1 (entry 5) and 400:1 (entry 6), respectively; importantly, the excellent *Z*/*E* selectivity (>99:1) remained unchanged. Finally, when the ratio of H_2O and acetone is 1:800 (about 1.4 equiv of H_2O to **1**, entry 7), the yield of α-iodoenone **2** was improved to 95%, and the stereoselectivity (*Z*/*E*=45:1) remained high. Although previous studies[6,7] showed that the double bond of α-iodoenones could isomerize under acidic conditions, ^{1}H NMR experiments showed that under the optimized reaction conditions (i.e., entry 7) the *Z*/*E* ratio of **2** was constant throughout the reaction and did not noticeably change at 0 °C after extended time. Other Au catalysts (e.g., entries 8–10) and $PtCl_2$ (entry 11) gave less desirable results, and no reaction was observed with NIS alone (entry 12).

Table 1
Gold-catalyzed reactions of propargylic acetate **1** with NIS to form α-iodoenone **2**



1 **2**

Entry[a]	Catalyst	Solvent	Yield[b] [%]	*Z*/*E*[c]
1	2 mol % Au(PPh_3)NTf_2	Anhyd. acetone	95	3:2
2	2 mol % Au(PPh_3)NTf_2	Wet CH_2Cl_2	85	6:1
3	2 mol % Au(PPh_3)NTf_2	$MeNO_2$[d]	78	3:1
4	2 mol % Au(PPh_3)NTf_2	Acetone/H_2O (40:1)	35[e]	>99:1
5	2 mol % Au(PPh_3)NTf_2	Acetone/H_2O (200:1)	61	>99:1
6	2 mol % Au(PPh_3)NTf_2	Acetone/H_2O (400:1)	80	>99:1
7	**2 mol % Au(PPh_3)NTf_2**	**Acetone/H_2O (800:1)**	**95**[f]	**45:1**
8	2 mol % Au(III)[g]	$ClCH_2CH_2Cl$[h]	95	6:1
9	2 mol % Au(I)[i]	Acetone/$_2$O (800:1)	40[j]	>99:1
10	2 mol % $[(PhP_3Au)_3O]^+NTf_2^-$	Acetone/H_2O (800:1)	6[k]	—
11	2 mol % $PtCl_2$	Toluene[l]	12.5	>99:1
12	No catalyst	Acetone/H_2O (800:1)	0[m]	—

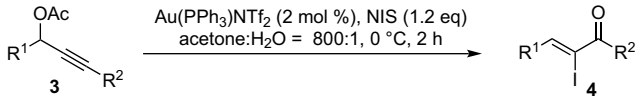
[a] Reaction concentration is 0.05 M.
[b] Estimated by ^{1}H NMR using diethyl phthalate as internal reference.
[c] The geometries of enone **2** were determined by NOESY1D experiments.
[d] Regular, without drying.
[e] Acetate **1** (17%) was left unreacted.
[f] Isolated yield (89%).
[g] Dichloro(2-pyridinecarboxylato)gold(III).
[h] Heating at 80 °C for 0.5 h.
[i] (2-Biphenyl)$Cy_2PAuNTf_2$.
[j] Starting material (47%) left after 2 h.
[k] Mostly starting material left after 4.5 h.
[l] Heating at 80 °C for 2 h.
[m] No reaction.

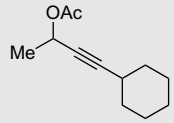
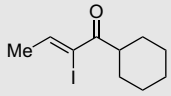
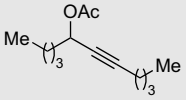
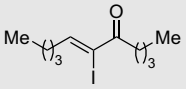
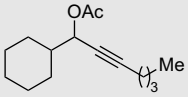
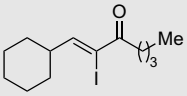
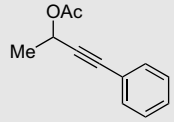
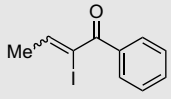
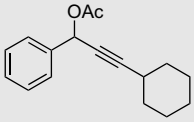
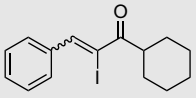
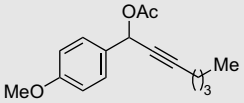
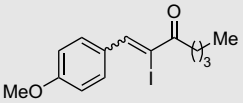
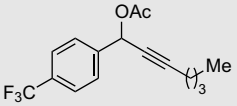
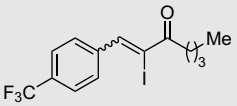
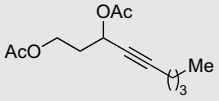
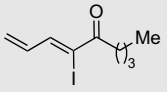
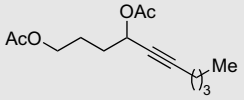
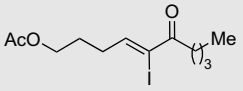
With the optimized reaction conditions in hand, we first studied propargylic acetates derived from various aldehydes, and the results are summarized in Table 2. For all the substrates studied, good to excellent yields of α-iodoenones with β-monosubstitution were obtained. When R^1 and R^2 were both alkyl groups, excellent stereoselectivities favoring the *Z*-isomer were observed (entries 1–3, 8, and 9). In the case of **3c**, the sterically demanding cyclohexyl group at the propargylic position slowed the reaction, and the addition of 10 mol % of $AgNTf_2$ helped to complete the reaction in 3 h (entry 3). The role of $AgNTf_2$ was likely to scavenge I^- and thus prevent Au(PPh_3)NTf_2 from being deactivated by the halide.[21] Notably, in the cases of aryl-containing substrates **3d**–**g**, the *Z*/*E* selectivities were marginal (entries 4–7), and in entry 5 *E*-**4e** was the major isomer. Aryl groups of different electronic natures underwent this reaction smoothly, affording **4f** and **4g** in 84% and 96% yields, respectively. Particularly noteworthy is that no iodination of the anisole ring in **4f** was observed. To our surprise, ester **3h** with a 2-acetoxyethyl at the propargylic position underwent concurrent HOAc elimination, yielding *Z*-α-iododienone **4h** in 80% yield (entry 8). In contrast, ester **3i** with a longer carbon tether expectedly yielded α-iodoenone **4i** in an excellent yield. Interestingly, when the acetyl groups of **4h** and **4i** were replaced with TBS groups, the corresponding substrates reacted to give complicated mixtures. ^{1}H NMRs indicated that desilylation happened during reaction. Although the reaction conditions are normally considered mild, Au(PPh_3)NTf_2 is acidic enough to promote facile desilylation and HOAc elimination (entry 8).

The scope of this α-iodoenone formation can be readily extended to propargylic acetates derived from ketones. As shown in Table 3, under the same reaction conditions, acetates prepared from linear ketones such as acetone (i.e., **5a**) and 3-methylbutan-2-one (i.e., **5e**) underwent smooth Au-catalyzed reactions, affording β,β-disubstituted α-iodoenones in excellent yields (entries 1 and 5). In the latter case, the diastereoselectivity was expectedly low.[22] Similarly, substrates derived from cyclic ketones including cyclopentanone (entry 2), cyclohexanone (entries 3, 6, and 7), and cycloheptanone (entry 4) reacted efficiently, and the corresponding α-iodoenones were all isolated in excellent yields. In addition, the alkyne terminus allowed various substituents including primary (entries 1–5) and secondary (entry 6) alkyl groups as well as phenyl group (entry 7). Remarkably, under this reaction conditions, no enynes[13d] formed via elimination of HOAc were observed, suggesting that Au(PPh_3)NTf_2 activates the C–C triple bond selectively.

Although α-bromoenones are less desirable than α-iodoenones for cross-coupling reactions,[1] they are useful in various synthetic transformations, including exchanging the Br with a CF_3 group,[23] Stille coupling,[24] and synthesizing allenes via 2-bromoallylic alcohols.[25] To our delight, the protocol for α-iodoenone formation can be readily applied for α-bromoenone synthesis. In this case, NBS was used as the 'Br^+' source. As shown in Table 4, propargylic acetates derived from acetaldehyde (e.g., entry 1) and benzaldehyde (e.g., entry 5) served as excellent substrates, affording α-bromoenones **8a** and **8e**, respectively, in excellent yields. Moreover, the *E*/*Z* selectivities paralleled to those observed with α-iodoenones. Hence, *Z*-**8a** with alkyl substituents was almost exclusively formed, while α-bromoenone **8e** with a β-phenyl group was isolated as a mixture with the *E*-isomer slightly favored. Propargylic acetates

Table 2
Formation of β-monosubstituted α-iodoenones



Entry[a]	Propargylic acetate **3**		α-Iodoenone **4**		*Z*/*E*	Yield[b] [%]
1		**3a**		**4a**	12:1	82
2		**3b**		**4b**	10:1	94
3		**3c**		**4c**	19:1	91[c]
4		**3d**		**4d**	1.2:1	75[d]
5		**3e**		**4e**	1:2	97[e]
6		**3f**		**4f**	1:1	84
7		**3g**		**4g**	5:1	96[f]
8		**3h**		**4h**	*Z* only	80[g]
9		**3i**		**4i**	>50:1	83

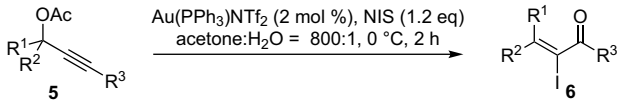
[a] Substrate concentration is 0.05 M.
[b] Isolated yield.
[c] $AgNTf_2$ (10 mol %) was added, and the reaction time was 3 h.
[d] The reaction took 3 h.
[e] The reaction finished in 0.5 h.
[f] $AgNTf_2$ (10 mol %) was added.
[g] Elimination of acetic acid happened during the reaction.

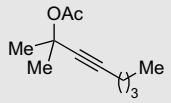
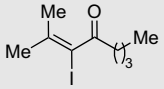
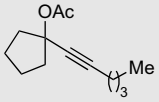
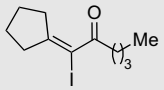
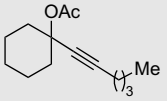
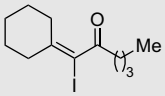
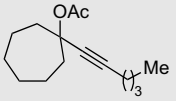
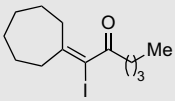
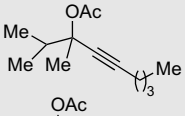
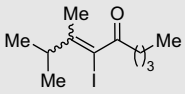
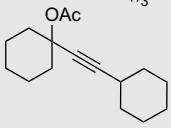
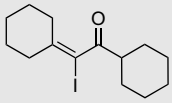
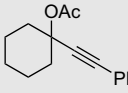
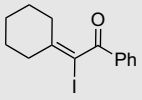
derived from ketones reacted smoothly as well, yielding α-bromoenones **8b**–**8d** all in close to quantitative yields.

Further extension of this chemistry to α-fluoroenones using various electrophilic fluorine reagents such as Selectfluor® and *N*-fluorobenzenesulfonimide was not successful under the established reaction conditions.

Scheme 2 shows the proposed reaction mechanism using propargylic acetates derived from aldehydes as substrate. An initial Au-catalyzed 3,3-rearrangement of the substrate is well documented and highly likely;[13,14] moreover, this acetoxy migration is necessary for regioselective installation of the carbonyl group in the final product. The resulting intermediate, carboxyallene **7**, can proceed to α-haloenones via two different paths: (a) react directly with NXS (X=I or Br); (b) be further activated by the same Au^I catalyst to generate Au-containing cation **A** (Scheme 1). Path a will lead to oxocarbenium **B** with the halo group trans to R^1 (i.e., *E*-isomer) selectively as NXS should approach the more electron-rich enolic C–C double bond from the less hindered face (i.e., synperiplanar to H), while path b would afford product **4** with the halo group cis to R^1 (i.e., *Z*-isomer) as our previous studies[13] suggested repeatedly a cis relationship between $Au(PPh_3)$ and R^1 in intermediates **A** and **C**[26] and iodination of Au–C(sp^2)

Table 3
Formation of β,β-disubstituted α-iodoenones



Entry[a]	Propargylic acetate **5**		α-Iodoenone **6**		Yield[b] [%]
1		**5a**		**6a**	96
2		**5b**		**6b**	87
3		**5c**		**6c**	91
4		**5d**		**6d**	99
5		**5e**		**6e**	88[c]
6		**5f**		**6f**	96
7		**5g**		**6g**	83

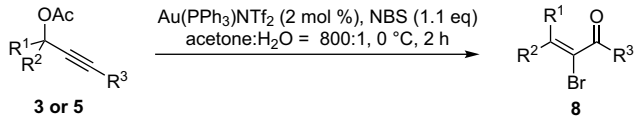
[a] Substrate concentration is 0.05 M.
[b] Isolated yield.
[c] *Z*/*E*=1:2.2.

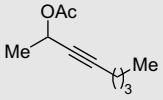
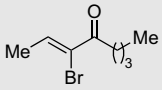
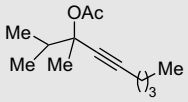
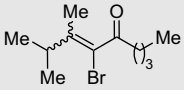
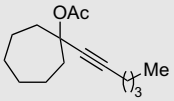
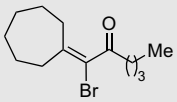
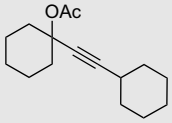
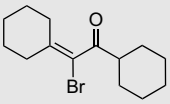
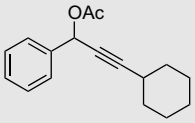
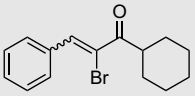
bonds[18] is stereospecific or highly stereoselective. These two paths yield the same product but with opposite stereoselectivities. To shed more light on the mechanism, reactions were run in NMR tube and the *Z*/*E* ratios were monitored by ^{1}H NMR. When propargylic ester **3c** with all alkyl substituents was treated with NIS and $Ph_3PAuNTf_2$ (2 mol %), a constant *Z*/*E* ratio of 19:1 was observed during the reaction while the intermediate carboxyallene was not detected. Quite on the opposite, when ester **3e** with a phenyl group at the propargylic position was studied, an opposite stereoselectivity (*Z*/*E*=1:2) with the *E*-α-iodoenone slightly favored was detected invariably throughout the reaction. Interestingly, in this case, 90% of substrate **3e** was converted into carboxyallene **7** in 5 min while the completion of the reaction took much longer (30 min). The accumulation of **7** in this case allows path a to participate, which can explain the low and opposite stereoselectivity. Moreover, when a 1:1 mixture of **3e** and its corresponding carboxyallene[27] was mixed with NIS without the Au^I catalyst, the carboxyallene reacted to yield *E*-**4e** predominantly (*Z*/*E*=1:6 throughout the reaction) while **3e** remained unchanged. These studies suggest that substrates with all alkyl substituents proceed predominantly along path b, where carboxyallene **7** is a transient intermediate and is converted into **A** and eventually **C** rapidly in the presence of the Au^I catalyst and H_2O; on the contrary, aryl-containing esters such as **3d**, **3e**, **3f**, and **3g** reacted via both paths a and b due to facile 3,3-rearrangement and substantial accumulation of **7**, thus leading to diminished or even opposite stereoselectivities.

H_2O played a key role in controlling the stereoselectivity of the reaction studied during reaction condition optimization. Our proposed mechanism offers ready explanation: under anhydrous conditions where only small amount of adventitious H_2O was present, hydrolysis of **A** is very slow and, therefore, **A** can equilibrate back to **7**. As discussed previously, accumulation of **7** would make path a significant, leading to increased amount of the *E*-isomer and decreased selectivity (Table 1, entry 1). When sufficient amount of H_2O is present, hydrolysis of **A** into **C** is fast, therefore affording *Z*-**2** highly selective.

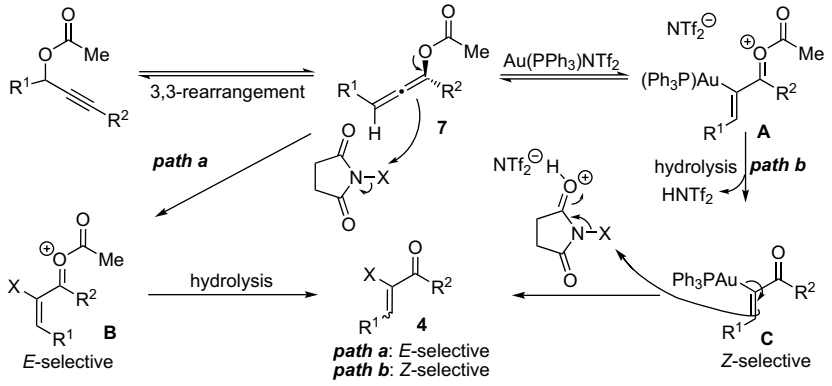
The potential influence of H_2O on the Au(I) complex is worth discussing. Cationic $Ph_3PAu(I)$ complexes are known to react with H_2O under basic conditions to form $[(Ph_3PAu)_3O]^+X^-$.[28] In our reaction, it is unlikely that $Ph_3PAuNTf_2$ is converted into $[(Ph_3PAu)_3O]^+NTf_2^-$ in the presence of H_2O as the trisgold(I)oxonium complex should not be formed in a significant amount under acidic conditions. Moreover, this trigold(I)oxonium complex was not catalytically active enough as only 6% of **2** was formed in 4.5 h (Table 1, entry 10). Nolan and co-workers proposed $I^tBuAuOH$ as the catalyst for their enone formation reaction from propargylic acetates involving gold–allenolate intermediates in THF/H_2O.[14] Although Ph_3PAuOH might be formed along with $HNTf_2$ in equilibrium with $Ph_3PAuNTf_2$ and H_2O, the formation of a similar Ph_3PAu–allenolate intermediate (i.e., **D**, Scheme 3) is less likely in our system: firstly, it cannot explain the observed high *Z*-stereoselectivities with aliphatic substrates as iodination of **D** should favor the formation of *E*-α-haloenones due to sterics; secondly, this approach cannot explain the observed formation of acetoxyallenes during the reaction (e.g., in the case of **3e**).

Table 4
Reaction scope for the formation of α-bromoenones

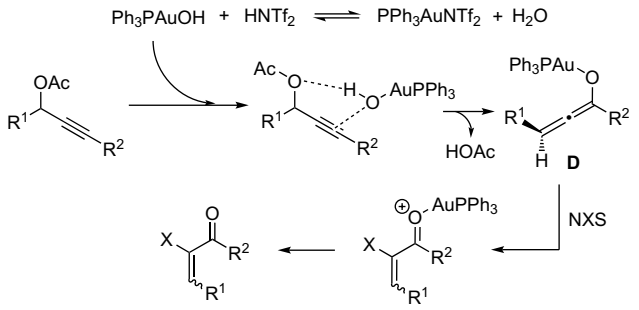


Entry[a]	Propargylic acetate		α-Bromoenones **8**		*Z*/*E*	Yield[b] [%]
1		**1**		**8a**	>99:1	85
2		**5e**		**8b**	1:1.4	93
3		**5d**		**8c**	—	95
4		**5f**		**8d**	—	96
5		**3e**		**8e**	1:5	86[c]

[a] Substrate concentration is 0.05 M.
[b] Isolated yield.
[c] $AgNTf_2$ (10 mol %) was added.



Scheme 2. Proposed reaction mechanism.



Scheme 3. Further mechanistic considerations.

In summary, we have developed an efficient synthesis of linear α-haloenones from readily accessible propargylic acetates. This reaction not only has broad substrate scopes but also offers good to excellent *Z*-selectivities in the case of aliphatic propargylic acetates derived from aldehydes. The low catalyst loading (2 mol %), mostly excellent yields (75–99%), and mild reaction conditions (0 °C and 2 h) are additional features that promise this reaction as a highly useful method for practical α-haloenone preparation.

3. Experimental

3.1. General information

Anhydrous acetone was purchased from Acros Organics and used without further purification. Anhydrous tetrahydrofuran in

Pure-Pac™ from Aldrich was used directly without further purification. Flash column chromatography was performed over silicycle silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 500 MHz Unity plus spectrometer and a Varian 400 MHz spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Waters micromass ZQ detector using electron spray method.

3.2. General procedure A: preparation of propargylic acetates

To a solution of a terminal alkyne (11 mmol) in anhydrous THF (42 mL) at −78 °C under N_2 was added *n*-BuLi (2.5 M solution in hexanes, 4.2 mL, 10.5 mmol). The reaction mixture was stirred at the same temperature for 15 min before the addition of a ketone/aldehyde (10 mmol). The resulting mixture was allowed to warm to 0 °C gradually and stirred for an additional hour. Upon the addition of acetic anhydride (2.4 mL, 25 mmol), the reaction mixture was warmed to room temperature and stirred for 2 h before quenched with aqueous $NaHCO_3$. The mixture was extracted with Et_2O (3×30 mL), and the combined organic phases were washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate=20:1) to yield the desired acetate.

3.2.1. 1-Methylhept-2-ynyl acetate (**1**)

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (qt, 1H, J=6.8, 2.0 Hz), 2.20 (td, 2H, J=7.0, 2.0 Hz), 2.06 (s, 3H), 1.53–1.34 (m, 7H), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 85.6, 78.6, 60.9, 30.6, 21.9, 21.8, 21.2, 18.4, 13.6; IR (neat): 2989, 2960, 2937, 2874, 2249, 1744, 1467, 1453, 1371; MS (ES^+) calculated for $[C_{10}H_{16}NaO_2]^+$: 191.1; found: 191.0.

3.2.2. 3-Cyclohexyl-1-methylprop-2-ynyl acetate (**3a**)

Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (qt, 1H, J=6.5, 2.0 Hz), 2.40–2.36 (m, 1H), 2.07 (s, 3H), 1.79–1.67 (m, 4H), 1.50–1.39 (m, 7H), 1.32–1.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 89.5, 78.5, 60.9, 32.4, 28.9, 25.8, 24.8, 21.9, 21.2; IR (neat): 2988, 2933, 2856, 2244, 1741, 1592, 1450, 1317, 1340, 1309, 1224, 1170, 1592, 1450; MS (ES^+) calculated for $[C_{12}H_{18}NaO_2]^+$: 217.3; found: 217.2.

3.2.3. 1-Butylhept-2-ynyl acetate (**3b**)

Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (t, 1H, J=6.5 Hz), 2.21 (td, 2H, J=7.0, 1.7 Hz), 2.07 (s, 3H), 1.77–1.69 (m, 2H), 1.49 (quintet, 2H, J=7.2 Hz), 1.43–1.31 (m, 6H), 0.93–0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 86.1, 77.6, 64.6, 34.8, 30.6, 27.2, 22.2, 21.9, 21.2, 18.4, 13.9, 13.6; IR (neat): 2959, 2935, 2871, 2864, 2242, 1743, 1468, 1433, 1371, 1351, 1234, 1161, 1108, 1019, 959; MS (ES^+) calculated for $[C_{13}H_{22}NaO_2]^+$: 233.3; found: 233.3.

3.2.4. 1-Cyclohexylhept-2-ynyl acetate (**3c**)

Yield: 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (d, 1H, J=6.0 Hz), 2.21 (t, 2H, J=7.0 Hz), 2.07 (s, 3H), 1.84–1.58 (m, 5H), 1.49 (quintet, 2H, J=7.2 Hz), 1.39 (sextet, 2H, J=7.2 Hz), 1.27–1.03 (m, 6H), 0.90 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 86.8, 76.4, 68.8, 42.0, 30.6, 28.6, 28.0, 26.2, 25.8, 25.7, 21.9, 21.1, 18.4, 13.6; IR (neat): 2960, 2931, 2856, 2239, 1742, 1593, 1452, 1432, 1370, 1231, 1119, 1018, 977; MS (ES^+) calculated for $[C_{15}H_{24}NaO_2]^+$: 259.4; found: 259.2.

3.2.5. 1-Methyl-3-phenylprop-2-ynyl acetate (**3d**)

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.33–7.27 (m, 3H), 5.67 (q, 1H, J=6.6 Hz), 2.11 (s, 3H), 1.58 (d, 3H, J=6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 131.8, 128.6, 128.2, 122.2, 87.4, 84.5, 60.8, 21.5, 21.1; IR (neat): 3058, 2990, 2939, 2247, 1743, 1599, 1491, 1444, 1372; MS (ES^+) calculated for $[C_{12}H_{12}NaO_2]^+$: 211.1; found: 210.9.

3.2.6. 3-Cyclohexyl-1-phenylprop-2-ynyl acetate (**3e**)

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.39–7.31 (m, 3H), 6.49 (d, 1H, J=2.0 Hz), 2.49–2.44 (m, 1H), 2.09 (s, 3H), 1.82–1.79 (m, 2H), 1.73–1.66 (m, 2H), 1.54–1.43 (m, 3H), 1.36–1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 137.8, 128.7, 128.5, 127.7, 92.3, 76.6, 66.0, 32.37, 32.35, 29.1, 25.8, 24.8, 21.2; IR (neat): 3090, 3066, 3035, 2932, 2855, 2236, 1742, 1604, 1588, 1495, 1450, 1369; MS (ES^+) calculated for $[C_{17}H_{20}NaO_2]^+$: 279.1; found: 279.1.

3.2.7. 1-(4-Methoxyphenyl)hept-2-ynyl acetate (**3f**)

Yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, 2H, J=8.5 Hz), 6.89 (d, 2H, J=8.5 Hz), 6.42 (s, 1H), 3.81 (s, 3H), 2.27 (t, 2H, J=7.0 Hz), 2.07 (s, 3H), 1.52 (quintet, 2H, J=7.2 Hz), 1.41 (sextet, 2H, J=7.2 Hz), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 159.9, 129.9, 129.3, 113.8, 88.1, 76.8, 65.8, 55.3, 30.5, 21.9, 21.2, 18.5, 13.6; IR (neat): 3072, 3037, 3003, 2959, 2935, 2873, 2838, 2292, 2234, 1741, 1611, 1587, 1514, 1465, 1443, 1428, 1369, 1343, 1305, 1279, 1251, 1229, 1175, 1144, 1110, 1034, 1015, 952, 909, 832; MS (ES^+) calculated for $[C_{16}H_{20}NaO_3]^+$: 283.3; found: 283.2.

3.2.8. 1-(4-Trifluoromethylphenyl)hept-2-ynyl acetate (**3g**)

Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 6.48 (t, 1H, J=2.0 Hz), 2.27 (td, 2H, J=7.2, 2.4 Hz), 2.11 (s, 3H), 1.52 (quintet, 2H, J=7.2 Hz), 1.40 (sextet, 2H, J=7.2 Hz), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 141.5, 130.8 (q, J_{C-F}=32 Hz), 127.9, 125.6 (q, J_{C-F}=3.7 Hz), 123.9 (q, J_{C-F}=270.0 Hz), 89.2, 76.0, 65.3, 30.4, 21.9, 21.0, 18.5, 13.5; IR (neat): 3067, 2962, 2935, 2876, 2295, 2236, 1928, 1746, 1622, 1590, 1468, 1422, 1371, 1327, 1227, 1168, 1129, 1109, 1068, 1018, 959, 922, 850, 836; MS (ES^+) calculated for $[C_{16}H_{17}NaO_2]^+$: 321.3; found: 321.2.

3.2.9. 1,1-Dimethylhept-2-ynyl acetate (**5a**)

Yield: 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (t, 2H, J=7.0 Hz), 2.01 (s, 3H), 1.64 (s, 6H), 1.48 (p, 2H, J=7.6 Hz), 1.39 (sextet, 2H, J=7.6 Hz), 0.90 (t, 3H, J=7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 84.6, 81.3, 72.6, 30.6, 29.3, 22.1, 21.9, 18.4, 13.6; IR (neat): 2987, 2960, 2936, 2875, 2245, 1747, 1586, 1468, 1434, 1368, 1329, 1266, 1245, 1196, 1016, 953, 822; MS (ES^+) calculated for $[C_{11}H_{18}NaO_2]^+$: 205.1; found: 205.1.

3.2.10. 1-Hex-1-ynylcyclopentyl acetate (**5b**)

Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22–2.15 (m, 4H), 2.12–2.04 (m, 2H), 2.02 (s, 3H), 1.74–1.70 (m, 4H), 1.50–1.44 (m, 2H), 1.43–1.35 (m, 2H), 0.90 (t, 3H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 85.3, 81.0, 80.5, 40.5, 30.7, 23.2, 21.9, 18.5, 13.6; IR (neat): 2960, 2933, 2875, 2246, 1746, 1593, 1453, 1435, 1367, 1334, 1241, 1124, 1016, 970; MS (ES^+) calculated for $[C_{13}H_{20}NaO_2]^+$: 231.1; found: 231.1.

3.2.11. 1-Hex-1-ynylcyclohexyl acetate (**5c**)

Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.254 (t, 2H, J=7.2 Hz), 2.11–2.06 (m, 2H), 2.03 (s, 3H), 1.84–1.77 (m, 2H), 1.63–1.29 (m, 10H), 0.91 (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 86.8, 80.0, 76.1, 37.4, 30.8, 25.3, 22.7, 22.1, 21.9, 18.5, 13.6; IR (neat): 2936, 2861, 2244, 1746, 1600, 1447, 1431, 1367, 1301, 1264, 1230, 1184, 1131, 1034, 1020, 965; MS (ES^+) calculated for $[C_{14}H_{22}NaO_2]^+$: 245.2; found: 245.1.

3.2.12. 1-Hex-1-ynylcycloheptyl acetate (**5d**)

Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24–2.17 (m, 4H), 2.06–2.04 (m, 2H), 2.01 (s, 3H), 1.57–1.37 (m, 12H), 0.90 (t, 3H, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 86.0, 81, 2, 79.5, 40.5, 30.7, 28.2, 22.2, 21.9, 18.5, 13.6; IR (neat): 2936, 2861, 2244, 1746, 1600, 1447, 1431, 1367, 1301, 1264, 1230, 1184, 1131, 1034, 1020, 965; MS (ES^+) calculated for $[C_{15}H_{24}NaO_2]^+$: 257.2; found: 259.2.

*3.2.13. 1-Isopropyl-1-methylhept-2-ynyl acetate (**5e**)*

Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (t, 2H, J=7.2 Hz), 2.16 (heptet, 1H, J=6.6 Hz), 2.01 (s, 3H), 1.61 (s, 3H), 1.53–1.43 (m, 2H), 1.42–1.37 (m, 2H), 1.01 (d, 3H, J=6.6 Hz), 0.97 (d, 3H, J=6.6 Hz), 0.90 (t, 3H, J=7.2 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$) δ 169.4, 86.2, 79.6, 79.2, 37.4, 30.8, 23.5, 22.1, 21.9, 18.4, 17.5, 17.2, 13.6; IR (neat): 2965, 2936, 2876, 2244, 1746, 1559, 1458, 1436, 1371, 1336, 1243, 1129, 1060, 1014, 942; MS (ES^+) calculated for $[C_{13}H_{22}NaO_2]^+$: 233.2; found: 233.2.

*3.2.14. 1-Cyclohexylethynylcyclohexyl acetate (**5f**)*

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47–2.43 (m, 1H), 2.13–2.08 (m, 2H), 2.02 (s, 3H), 1.82–1.24 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 91.0, 80.2, 76.2, 37.5, 32.6, 28.9, 26.0, 25.3, 24.6, 22.9, 22.2; IR (neat): 2933, 2857, 2663, 2237, 1746, 1615, 1447, 1367, 1229, 1184, 1022; MS (ES^+) calculated for $[C_{16}H_{24}NaO_2]^+$: 271.2; found: 271.1.

*3.2.15. 1-Phenylethynylcyclohexyl acetate (**5g**)*

Yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.44 (m, 2H), 7.29–7.28 (m, 3H), 2.24–2.19 (m, 2H), 2.07 (s, 3H), 1.93–1.88 (m, 2H), 1.70–1.65 (m, 4H), 1.59–1.53 (m, 1H), 1.39–1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 131.8, 128.2, 128.1, 122.8, 89.1, 86.2, 75.9, 37.1, 25.2, 22.7, 22.0; IR (neat): 3082, 3057, 3035, 3023, 2937, 2861, 2667, 2229, 2203, 1743, 1675, 1599, 1573, 1491, 1444, 1367, 1346, 1312, 1264, 1229, 1163, 1138, 1071, 1041, 1022, 959; MS (ES^+) calculated for $[C_{16}H_{18}NaO_2]^+$: 265.3; found: 265.2.

3.3. General procedure for propargylic acetates 3h and 3i

A solution of 1-hexyne (1.30 g, 15.8 mmol) in THF (50 ml) was cooled to −78 °C in a dry ice-acetone bath under nitrogen, and *n*-BuLi (1.6 M in hexanes, 9.17 mL, 14.64 mmol) was added dropwise in 15 min. After addition, a solution of 4-(*tert*-butyldimethylsilyloxy)propionaldehyde (for **3h**, 2.3 g, 12.2 mmol) or 4-(*tert*-butyldimethylsilyloxy)butyraldehyde (for **3i**, 2.5 g, 12.2 mmol) in THF (10 mL) was added dropwise, the resulting reaction mixture was allowed to warm to room temperature gradually. The reaction was quenched by the addition of saturated NH_4Cl (30 mL). The aqueous layer was extracted with Et_2O (3×50 mL). The combined organic layer was washed with brine (100 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The desired alcohol was obtained as a clear liquid via bulb-to-bulb distillation (~50% yield in two steps).

To a solution of the above alcohol (1 mmol) in THF (5 mL) was added TBAF (1 M in THF, 1 mL). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was cooled down in an ice-water bath, and Et_3N (0.3 mL, 3 mmol) and DMAP (cat.) were added followed by dropwise addition of CH_3COCl (0.18 mL, 2.5 mmol). The resulting mixture was allowed to rise to room temperature and stirred for 4 h. The reaction was quenched by the addition of water (20 mL). The organic layer was extracted with Et_2O (3×15 mL). The combined organic layer was washed with brine (50 mL), dried with $MgSO_4$, filtered, and concentrated to give an oily residue, which was purified by flash column chromatography to give diacetate **3h** or **3i**.

*3.3.1. 3-Acetoxynon-4-ynyl acetate (**3h**)*

Yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (tt, 1H, J=6.8, 2.0 Hz), 4.25–4.15 (m, 2H), 2.20 (td, 2H, J=6.8, 2.0 Hz), 2.13–2.03 (m, 8H), 1.51–1.45 (m, 2H), 1.41–1.36 (m, 2H), 0.90 (t, 3H, J=6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.0, 87.0, 76.5, 61.5, 60.4, 34.1, 30.4, 21.9, 21.0, 20.9, 18.3, 13.5; IR (neat): 2960, 2936, 2874, 2247, 1744, 1592, 1459, 1432, 1370, 1232, 1159, 1045, 960; MS (ES^+) calculated for $[C_{13}H_{20}NaO_4]^+$: 263.1; found: 263.2.

*3.3.2. 4-Acetoxydec-5-ynyl acetate (**3i**)*

Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40–5.38 (m, 1H), 4.10 (t, 2H, J=4.8 Hz), 2.21 (t, 2H, J=6.8 Hz), 2.08 (s, 3H), 2.06 (s, 3H), 1.83–1.74 (m, 4H), 1.48 (sextet, 2H, J=8 Hz), 1.39 (sextet, 2H, J=8 Hz), 0.91 (t, 3H, J=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 170.0, 86.7, 64.0, 63.9, 31.7, 30.5, 24.3, 21.9, 21.1, 21.0, 18.4, 13.6; IR (neat): 3308, 2960, 2935, 2337, 1741, 1592, 1430, 1370, 1232, 1023; MS (ES^+) calculated for $[C_{14}H_{22}NaO_4]^+$: 277.1; found: 277.2.

3.4. Au(I)-catalyzed formation of α-haloenones

To a solution of propargylic acetate **3** or **5** (0.2 mmol) in anhydrous acetone (4 mL) cooled in ice-water bath were added H_2O (0.005 ml, 1.39 equiv) and $Au(PPh_3)NTf_2$ (0.05 M in acetone, 0.08 mL). The solution was treated with NIS (0.24 mmol, 1.2 equiv) or NBS (0.22 mmol, 1.1 equiv). The reaction mixture was stirred for 2 h before quenched with NEt_3 (one drop) and aqueous $Na_2S_2O_3$ (5 mL). The mixture was extracted with Et_2O (3×8 mL). The combined organic phases were washed with H_2O (10 mL) and brine (10 mL), dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate=50:1) to yield the desired α-haloenone.

*3.4.1. 3-Iodooct-2-en-4-one (**2**)*

Yield: 89%. *Z*/*E*=45:1. ^{1}H NMR (400 MHz, $CDCl_3$) (major isomer) δ 7.11 (q, 1H, J=6.8 Hz), 2.81 (t, 2H, J=7.6 Hz), 2.07 (d, 3H, J=6.8 Hz), 1.63 (quintet, 2H, J=7.6 Hz), 1.34 (sextet, 2H, J=7.6 Hz), 0.92 (t, 3H, J=7.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (major isomer) δ 194.9, 146.8, 114.3, 37.5, 30.3, 27.1, 23.9, 22.3, 13.8; IR (neat): 2958, 2932, 2871, 1702, 1683, 1611, 1464, 1413, 1373, 1288, 1262, 1238, 1288, 1262, 1238, 1171, 1113, 1072; MS (ES^+) calculated for $[C_8H_{13}NaIO]^+$: 275.0; found: 275.0.

*3.4.2. 1-Cyclohexyl-2-iodobut-2-en-1-one (**4a**)*

Yield: 82%. *Z*/*E*=12:1. ^{1}H NMR (500 MHz, $CDCl_3$) (major isomer) δ 7.08 (q, 1H, J=7.0 Hz), 3.14 (q, 1H, J=7.0 Hz), 2.08 (d, 3H, J=7.0 Hz), 1.80–1.78 (m, 4H), 1.48–1.22 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) (major isomer) δ 198.2, 146.1, 113.9, 45.4, 29.9, 25.8, 25.7, 24.0; IR (neat): 3019, 2932, 2855, 2664, 1678, 1611, 1463, 1450, 1372, 1287, 1264, 1241, 1188, 1163, 1131, 1109, 1081, 1071, 1030, 974, 895, 884, 824; MS (ES^+) calculated for $[C_{10}H_{15}NaIO]^+$: 301.0; found: 300.9.

*3.4.3. 6-Iodoundec-6-en-5-one (**4b**)*

Yield: 94%. *Z*/*E*=10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (t, 1H, J=6.8 Hz), 2.82 (t, 2H, J=7.2 Hz), 2.42 (q, 2H, J=7.6 Hz), 1.67–1.50 (m, 4H), 1.45–1.30 (m, 4H), 0.97–0.89 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.0, 151.2, 112.4, 37.7, 37.6, 29.7, 27.1, 22.4, 22.3, 13.8, 13.8; IR (neat): 3351, 2958, 2930, 2872, 2735, 1683, 1604, 1465, 1413, 1379, 1291, 1236, 1167, 1123, 1088, 934; MS (ES^+) calculated for $[C_{11}H_{19}INaO]^+$: 317.0; found: 317.0.

*3.4.4. 1-Cyclohexyl-2-iodohept-1-en-3-one (**4c**)*

Yield: 91%. *Z*/*E*=19:1. $AgNTf_2$ (10 mol%) was added together with $Au(PPh_3)NTf_2$ and a column basified with Et_3N was used for purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, 1H, J=9 Hz), 2.80 (t, 2H, J=15 Hz), 2.60–2.52 (m, 1H), 1.82–1.68 (m, 5H), 1.60 (quintet, 2H, J=7.5 Hz), 1.41–1.31 (m, 4H), 1.27–1.20 (m, 3H), 1.92 (t, 3H, J=7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 155.7, 109.9, 46.8, 37.6, 30.7, 27.2, 25.7, 25.2, 22.3, 13.8; IR (neat): 3351, 2928, 2852, 2662, 2351, 1683, 1601, 1448, 1278, 1224, 1169, 1128, 1089, 968; MS (ES^+) calculated for $[C_{13}H_{21}INaO]^+$: 343.1; found: 343.0.

*3.4.5. 2-Iodo-1-phenylbut-2-en-1-one (**4d**)*

Yield: 75%. *Z*/*E*=1.2:1. Compound *Z*-**4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 2H, J=8 Hz), 7.55 (t, 2H, J=8 Hz), 7.44 (t, 2H,

J=8 Hz), 6.73 (q, 1H, J=8 Hz), 2.09 (d, 3H, J=8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.9, 149.7, 135.8, 132.4, 129.6, 128.4, 110.5, 23.6; IR (neat): 3297, 3059, 2924, 2851, 2356, 1993, 1658, 1606, 1577, 1446, 1371, 1314, 1260, 1179, 1120, 1060, 1025, 965; MS (ES^+) calculated for $[C_{10}H_9INaO]^+$: 295.0; found: 295.0. Compound *E*-**4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, J=8 Hz), 7.61 (t, 2H, J=8 Hz), 7.49 (t, 2H, J=8 Hz), 6.67 (q, 1H, J=8 Hz), 1.67 (d, 3H, J=8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 140.8, 134.0, 133.6, 129.9, 128.9, 90.4, 18.7; IR (neat): 3053, 2916, 2850, 2347, 1666, 1596, 1448, 1329, 1227, 1174, 1115, 1012; MS (ES^+) calculated for $[C_{10}H_9INaO]^+$: 295.0; found: 295.0.

*3.4.6. 1-Cyclohexyl-2-iodo-3-phenylpropenone (**4e**)*

Yield: 97%. *Z*/*E*=1:2. Compound *Z*-**4e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.75–7.70 (m, 2H), 7.46–7.43 (m, 3H), 3.33 (tt, 1H, J=11.5, 3 Hz), 1.92–1.83 (m, 4H), 1.74–1.72 (m, 1H), 1.54–1.46 (m, 2H), 1.42–1.23 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 145.6, 135.9, 130.0, 129.5, 128.3, 107.2, 45.6, 30.0, 25.8; IR (neat): 3334, 3057, 3023, 2930, 2853, 2662, 1674, 1591, 1491, 1445, 1366, 1262, 1186, 1150, 1112, 1013, 925; MS (ES^+) calculated for $[C_{15}H_{17}INaO]^+$: 363.0; found: 362.9. Compound *E*-**4e**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.32–7.31 (m, 3H), 7.19–7.17 (m, 2H), 2.47 (tt, 1H, J=11, 3.5 Hz), 1.82 (d, 2H, J=11.5 Hz), 1.68–1.54 (m, 2H), 1.58–1.54 (m, 1H), 1.39–1.32 (m, 2H), 1.16–1.02 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 143.0, 136.7, 129.0, 129.6, 128.1, 96.3, 49.5, 29.5, 25.6, 25.6; IR (neat): 3352, 3057, 3024, 2930, 2853, 2662, 1687, 1598, 1572, 1494, 1448, 1366, 1312, 1289, 1236, 1141, 1071, 1007, 926, 814; MS (ES^+) calculated for $[C_{15}H_{17}INaO]^+$: 363.0; found: 362.9.

*3.4.7. 2-Iodo-1-(4-methoxyphenyl)hept-1-en-3-one (**4f**)*

Yield: 84%. *Z*/*E*=1.05:1. Compound *Z*-**4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.90 (d, 2H, J=8.8 Hz), 6.98 (d, 2H, J=8.8 Hz), 3.87 (s, 3H), 2.97 (t, 2H, J=8 Hz), 1.70 (quintet, 2H, J=7.2 Hz), 1.39 (sextet, 2H, J=7.6 Hz), 0.95 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 161.4, 146.1, 132.0, 127.6, 113.8, 104.6, 55.4, 37.8, 27.4, 22.4, 13.9; IR (neat): 3003, 2957, 2932, 2871, 2838, 1674, 1604, 1587, 1568, 1509, 1463, 1255, 1148, 1029, 826; MS (ES^+) calculated for $[C_{14}H_{17}INaO_2]^+$: 367.0; found: 366.9. Compound *E*-**4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.13 (d, 2H, J=8.8 Hz), 6.84 (d, 2H, J=8.8 Hz), 3.81 (s, 3H), 2.54 (t, 2H, J=7.6 Hz), 1.56 (quintet, 2H, J=7.2 Hz), 1.24 (sextet, 2H, J=7.6 Hz), 0.83 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 160.2, 142.6, 129.7, 129.2, 114.0, 94.7, 55.3, 40.2, 26.4, 22.1, 13.7; IR (neat): 3271, 2957, 2930, 2870, 1685, 1604, 1509, 1456, 1293, 1255, 1178, 1122, 1032; MS (ES^+) calculated for $[C_{14}H_{17}INaO_2]^+$: 267.0; found: 267.0.

*3.4.8. 2-Iodo-1-(4-trifluoromethylphenyl)hept-1-en-3-one (**4g**)*

Yield: 96%. *Z*/*E*=5:1. Compound *Z*-**4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.81 (d, 2H, J=8.4 Hz), 7.70 (d, 2H, J=8.4 Hz), 2.99 (t, 2H, J=7.2 Hz), 1.71 (quintet, 2H, J=7.2 Hz), 1.40 (sextet, 2H, J=7.2 Hz), 0.96 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 144.8, 139.8, 131.6 (q, J_{C-F}=32.4 Hz), 129.8, 125.6 (q, J_{C-F}=3.72 Hz), 124.0 (q, J_{C-F}=270.8 Hz), 110.2, 38.4, 27.3, 22.5, 14.1; IR (neat): 3070, 2960, 2934, 2874, 1681, 1598, 1466, 1412, 1324, 1168, 1128, 1068, 1017, 885, 827; MS (ES^+) calculated for $[C_{14}H_{14}NaF_3IO]^+$: 405.0; found: 404.9. Compound *E*-**4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 2H, J=8.4 Hz), 7.38 (s, 1H), 7.31 (d, 2H, J=8.4 Hz), 2.55 (t, 2H, J=7.2 Hz), 1.56 (quintet, 2H, J=7.2 Hz), 1.24 (sextet, 2H, J=7.2 Hz), 0.83 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 140.7, 139.5, 130.7 (q, J_{C-F}=32.4 Hz), 128.2, 125.7 (q, J_{C-F}=3.75 Hz), 123.8 (q, J_{C-F}=270.6 Hz), 99.68, 40.0, 26.0, 22.0, 13.7; IR (neat): 3070, 2960, 2923, 2870, 1699, 1597, 1459, 1421, 1324, 1168, 1126, 1068, 1017, 874, 830; MS (ES^+) calculated for $[C_{14}H_{14}NaF_3IO]^+$: 405.0; found: 404.9.

*3.4.9. 4-Iodonona-1,3-dien-5-one (**4h**)*

Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, 1H, J=10 Hz), 6.78 (td, 1H, J=16.5, 10 Hz), 5.88 (d, 1H, J=17 Hz), 5.76 (d, 1H, J=10 Hz), 2.87 (t, 2H, J=7.5 Hz), 1.65 (quintet, 2H, J=7.5 Hz), 1.36 (sextet, 2H, J=7.5 Hz), 0.93 (t, 3H, J=7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 146.2, 139.3, 128.9, 110.6, 37.7, 27.1 22.3, 13.9; IR (neat): 3274, 2958, 2331, 1682, 1597, 1456, 1597, 1457, 1261, 1123, 1042. MS (ES^+) calculated for $[C_9H_{13}INaO]^+$: 286.9; found: 286.6.

*3.4.10. 4-Iodo-5-oxonon-3-enyl acetate (**4i**)*

Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, 1H, J=6.8 Hz), 4.13 (t, 2H, J=6.4 Hz), 2.82 (t, 2H, J=7.2 Hz), 2.50 (q, 2H, J=7.2 Hz), 2.07 (s, 3H), 1.90 (quintet, 2H, J=7.2 Hz), 1.63 (quintet, 2H, J=7.6 Hz), 1.35 (sextet, 2H, J=7.6 Hz), 0.93 (t, 3H, J=6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.9, 171.0, 149.8, 113.0, 63.5, 37.7, 34.6, 27.1, 26.7, 22.3, 21.0, 13.8; IR (neat): 3271, 2958, 2872, 1738, 1683, 1604, 1456, 1366, 1241, 1159, 1118, 1044; MS (ES^+) calculated for $[C_{12}H_{19}INaO_3]^+$: 361.0; found: 360.9.

*3.4.11. 3-Iodo-2-methyloct-2-en-4-one (**6a**)*

Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (t, 2H, J=7.2 Hz), 2.03 (s, 3H), 1.96 (s, 3H), 1.61 (quintet, 2H, J=7.2 Hz), 1.35 (sextet, 2H, J=7.2 Hz), 0.93 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.3, 144.3, 95.5, 40.5, 30.3, 26.4, 22.3, 21.9, 13.8; IR (neat): 2958, 2932, 2873, 1688, 1601, 1464, 1441, 1406, 1380, 1368, 1258, 1238, 1155, 1105, 1044, 910, 842; MS (ES^+) calculated for $[C_9H_{15}NaIO]^+$: 289.0; found: 289.0.

*3.4.12. 1-Cyclopentylidene-1-iodohexan-2-one (**6b**)*

Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (t, 2H, J=7.2 Hz), 2.70 (tt, 2H, J=7.2, 1.2 Hz), 2.47 (tt, 2H, J=7.2, 1.2 Hz), 1.89 (quintet, 2H, J=7.2 Hz), 1.72 (quintet, 2H, J=7.2 Hz), 1.58 (quintet, 2H, J=7.2 Hz), 1.34 (sextet, 2H, J=7.2 Hz), 0.92 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 166.4, 92.3, 44.4, 41.8, 36.1, 28.7, 26.9, 24.9, 22.3, 13.9; IR (neat): 2959, 2936, 2872, 1674, 1573, 1466, 1452, 1413, 1379, 1306, 1289, 1264, 1172, 1158, 1137, 1088, 911; MS (ES^+) calculated for $[C_{11}H_{17}NaIO]^+$: 315.0; found: 315.0.

*3.4.13. 1-Cyclohexylidene-1-iodohexan-2-one (**6c**)*

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (t, 2H, J=7.2 Hz), 2.41 (t, 2H, J=5.6 Hz), 2.33 (t, 2H, J=5.6 Hz), 1.66–1.50 (m, 8H), 1.35 (sextet, 2H, J=7.2 Hz), 0.93 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.5, 149.2, 92.4, 40.3, 39.6, 32.9, 28.0, 27.4, 26.3, 25.9, 22.3, 13.8; IR (neat): 2957, 2932, 2857, 1694, 1606, 1464, 1448, 1404, 1350, 1260, 1221, 1145, 1077, 1069, 984, 854; MS (ES^+) calculated for $[C_{12}H_{19}NaIO]^+$: 329.0; found: 329.0.

*3.4.14. 1-Cycloheptylidene-1-iodohexan-2-one (**6d**)*

Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (t, 2H, J=7.2 Hz), 2.47–2.42 (m, 4H), 1.69–1.49 (m, 10H), 1.35 (sextet, 2H, J=7.2 Hz), 0.93 (t, 3H, J=7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.4, 151.4, 96.1, 41.5, 40.4, 33.5, 29.2, 28.5, 28.0, 26.4, 26.1, 22.3, 13.8; IR (neat): 2956, 2927, 2857, 1688, 1599, 1464, 1457, 1404, 1351, 1266, 1160, 1132, 1081, 957, 909; MS (ES^+) calculated for $[C_{13}H_{21}NaIO]^+$: 343.0; found: 343.0.

*3.4.15. 4-Iodo-2,3-dimethylnon-3-en-5-one (**6e**)*

Yield: 88%. *Z*/*E*=1:2.31. ^{1}H NMR (500 MHz, $CDCl_3$) (major isomer) δ 2.83 (quintet, 1H, J=7.0 Hz), 2.79 (t, 2H, J=7.5 Hz), 1.88 (s, 3H), 1.61 (quintet, 2H, J=7.5 Hz), 1.35 (quintet, 2H, J=7.5 Hz), 1.02 (d, 6H, J=7.0 Hz), 0.93 (t, 3H, J=7.5 Hz); ^{1}H NMR (500 MHz, $CDCl_3$) (minor isomer) δ 2.94 (quintet, 1H, J=7.0 Hz), 2.78 (t, 2H, J=7.5 Hz), 1.77 (s, 3H), 1.61 (quintet, 2H, J=7.5 Hz), 1.35 (quintet, 2H, J=7.5 Hz), 1.02 (d, 6H, J=7.0 Hz), 0.93 (t, 3H, J=7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) (major isomer) δ 202.5, 150.6, 95.9, 40.3, 39.8, 33.5, 26.3, 22.3, 21.0, 19.7, 13.8; ^{13}C NMR (125 MHz, $CDCl_3$) (minor isomer)

δ 202.7, 149.5, 93.9, 40.3, 39.8, 33.5, 26.3, 22.3, 21.6, 14.6, 13.8; IR (neat): 2962, 2932, 2872, 1695, 1620, 1615, 1464, 1404, 1385, 1363, 1342, 1225, 1151, 1101, 1062, 983, 900; MS (ES^+) calculated for $[C_{11}H_{19}NaIO]^+$: 317.1; found: 317.0.

*3.4.16. 1-Cyclohexyl-2-cyclohexylidene-2-iodoethanone (**6f**)*

Yield: 96%. ^1H NMR (500 MHz, $CDCl_3$) δ 3.03 (tt, 1H, *J*=11, 3.0 Hz), 2.42 (t, 2H, *J*=7.5 Hz), 2.30 (t, 2H, *J*=6 Hz), 1.92 (d, 2H, *J*=12.5 Hz), 1.80–1.77 (m, 2H), 1.69–1.50 (m, 7H), 1.41–1.10 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 149.4, 91.8, 47.5, 39.6, 33.4, 28.8, 28.0, 27.4, 25.9, 25.8, 25.7; IR (neat): 3351, 2930, 2853, 2609, 1684, 1616, 1448, 1350, 1309, 1219, 1149, 1084, 982; MS (ES^+) calculated for $[C_{14}H_{21}INaO]^+$: 355.0; found: 355.0.

*3.4.17. 2-Cyclohexylidene-2-iodo-1-phenylethanone (**6g**)*

Yield: 83%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J*=8 Hz), 7.50 (t, 1H, *J*=7.6 Hz), 7.48 (t, 2H, *J*=7.6 Hz), 2.55 (t, 2H, *J*=6 Hz), 2.22 (t, 2H, *J*=6 Hz), 1.75–1.69 (m, 2H), 1.60–1.54 (m, 2H), 1.47–1.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 149.6, 134.0, 133.7, 130.0, 128.7, 87.7, 38.9, 33.2, 27.5, 27.4, 25.8; IR (neat): 3308, 3061, 2932, 2854, 2668, 2201, 1966, 1908, 1817, 1777, 1664, 1632, 1596, 1579, 1448, 1311, 1221, 1173, 1022, 982, 824; MS (ES^+) calculated for $[C_{14}H_{15}INaO]^+$: 349.0; found: 349.0.

*3.4.18. 3-Bromooct-2-en-4-one (**8a**)*

Yield: 85%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (q, 1H, *J*=7.0 Hz), 2.77 (t, 2H, *J*=7.5 Hz), 2.01 (d, 3H, *J*=7.0 Hz), 1.62 (quintet, 2H, *J*=7.5 Hz), 1.35 (sextet, 2H, *J*=7.5 Hz), 0.92 (t, 3H, *J*=7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 139.5, 128.9, 38.4, 26.7, 22.3, 18.2, 13.8; IR (neat): 3042, 2960, 2933, 2873, 1689, 1622, 1466, 1415, 1378, 1288, 1268, 1177, 1154, 1114, 1096, 1075, 972; MS (ES^+) calculated for $[C_8H_{13}NaBrO]^+$: 227.1; found: 227.0.

*3.4.19. 4-Bromo-2,3-dimethylnon-3-en-5-one (**8b**)*

Yield: 93%. *E*/*Z*=1.4:1. ^1H NMR (500 MHz, $CDCl_3$) (major isomer): δ 2.99 (septet, 1H, *J*=6.5 Hz), 2.75 (t, 2H, *J*=7.5 Hz), 1.84 (s, 3H), 1.60 (quintet, 2H, *J*=7.5 Hz), 1.35 (sextet, 2H, *J*=7.5 Hz), 1.03 (d, 6H, *J*=6.5 Hz), 0.92 (t, 3H, *J*=7.5 Hz); ^1H NMR (minor isomer): δ 3.16 (septet, 1H, *J*=7.0 Hz), 2.77 (t, 2H, *J*=7.5 Hz), 1.81 (s, 3H), 1.60 (quintet, 2H, *J*=7.5 Hz), 1.35 (sextet, 2H, *J*=7.5 Hz), 1.03 (d, 6H, *J*=7.0 Hz), 0.92 (t, 3H, *J*=7.5 Hz); ^{13}C NMR (mixture of two isomers) (125 MHz, $CDCl_3$) δ 200.6, 200.5, 148.6, 116.8, 115.3, 41.2, 41.1, 35.1, 32.7, 26.4, 26.3, 22.3, 20.8, 19.5, 17.2, 15.1, 13.9, 13.8; IR (neat): 2962, 2933, 2873, 1690, 1594, 1464, 1407, 1363, 1256, 1232, 1159, 1102, 1061, 987; MS (ES^+) calculated for $[C_{11}H_{19}NaBrO]^+$: 269.1; found: 269.0.

*3.4.20. 1-Bromo-1-cycloheptylidenehexan-2-one (**8c**)*

Yield: 95%. ^1H NMR (500 MHz, $CDCl_3$) δ 2.77 (t, 2H, *J*=7.5 Hz), 2.49 (q, 4H, *J*=6.5 Hz), 1.70–1.65 (m, 4H), 1.60 (quintet, 2H, *J*=7.5 Hz), 1.56–1.51 (m, 4H), 1.35 (sextet, 2H, *J*=7.5 Hz), 0.92 (t, 3H, *J*=7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 150.6, 117.4, 41.2, 37.4, 33.6, 29.1, 28.6, 27.8, 26.4, 25.7, 22.3, 13.9; IR (neat): 2928, 2953, 2858, 2678, 1703, 1688, 1683, 1584, 1464, 1455, 1405, 1379, 1350, 1267, 1244, 1163, 1134, 1084, 1049, 980, 958, 920; MS (ES^+) calculated for $[C_{13}H_{21}NaBrO]^+$: 295.1; found: 295.0.

*3.4.21. 2-Bromo-1-cyclohexyl-2-cyclohexylideneethanone (**8d**)*

Yield: 96%. ^1H NMR (500 MHz, $CDCl_3$) δ 3.00 (tt, 1H, *J*=11.0, 3.5 Hz), 2.43 (t, 2H, *J*=6.0 Hz), 2.28 (t, 2H, *J*=5.5 Hz), 1.91–1.88 (m, 2H), 1.79–1.77 (m, 2H), 1.68–1.56 (m, 6H), 1.38–1.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 145.9, 112.7, 47.5, 34.4, 32.7, 28.5, 27.9, 27.2, 26.0, 25.8, 25.7; IR (neat): 2931, 2854, 2667, 1689, 1608, 1449, 1365, 1310, 1269, 1242, 1225, 1151, 1120, 1087, 1070, 1045, 1016, 983; MS (ES^+) calculated for $[C_{14}H_{21}NaBrO]^+$: 307.1; found: 307.2.

*3.4.22. 2-Bromo-1-cyclohexyl-3-phenylpropenone (**8e**)*

Yield: 93%. *Z*/*E*=1:6. Compound *E*-**8e**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.26–7.25 (m, 3H), 7.19 (s, 1H), 7.14–7.13 (m, 2H), 2.45 (tt, 1H, *J*=11.5, 3.5 Hz), 1.77–1.75 (m, 2H), 1.64–1.61 (m, 2H), 1.31–1.22 (m, 4H), 1.08–0.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 138.8, 135.9, 130.4, 128.7, 128.2, 119.7, 49.4, 28.7, 25.7, 25.5; IR (neat): 3059, 3026, 2931, 2854, 1695, 1602, 1575, 1447, 1144, 928, 754, 697; MS (ES^+) calculated for $[C_{15}H_{17}NaBrO]^+$: 315.1; found: 315.0.

3.5. Preparation of $[(Ph_3PAu)_3O]^+NTf_2^-$

To a solution of $Ph_3PAuNTf_2$ (74 mg, 0.1 mmol) in methanol (10 mL) at room temperature under nitrogen was added KOH (10 mg, 0.178 mol) and $NaNTf_2$ (137 mg, 0.455 mmol). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated and the residue was extracted with chloroform (3 mL×2). After filtration, hexane (20 mL) was added to the filtrate. The precipitation was collected by filtration, washed with hexanes (10 mL), and dried under vacuum to afford the desired Au complex (46 mg, yield 88%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.51 (m, 9H), 7.48–7.44 (m, 18H), 7.37–7.34 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9 (d, ^3J (^{13}C–^{31}P)=13.4 Hz), 132.3 (d, ^4J (^{13}C–^{31}P)=2.9 Hz), 129.4 (d, ^2J (^{13}C– ^{31}P)=11.6 Hz), 128.3 (d, ^1J (^{13}C–^{31}P)=63.5 Hz), 120.3(q, *J* (^{13}C–^{19}F)=319.8 Hz); IR (neat): 3055, 2988, 2306, 1422, 1265; (ES^+) calculated for $[(Ph_3PAu)_3O]^+[C_{54}H_{45}Au_3OP_3]^+$: 1393.2, found: 1392, 1409; ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 24.5; ^{19}F NMR (376.2 MHz, $CDCl_3$) δ 81.4.

Acknowledgements

This work is supported in part by NSF CAREER award (CHE-0748484), ACS PRF (43905-G1), ORAU and Merck. The acquisition of an NMR spectrometer and upgrade of an existing NMR spectrometer are funded by NSF CHE-0521191.

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