Regular Article

Synthesis of α-Acyloxyketone Derivatives *via* the Platinum-Catalyzed Migration of Propargylic Esters

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The synthesis of α-acyloxyketones *via* the migration of a propargylic ester followed by the intramolecular nucleophilic addition of the resulting allene was achieved using a cationic platinum catalyst. The optimized conditions for this transformation were determined to be 3 mol% of $Pt(cod)Cl_2$, 3 mol% of $AgNTf_2$, and 3 eq of water in toluene at 100°C, and these conditions were successfully applied to the synthesis of a wide variety of α-aryl-α-acyloxyketones. The mechanism of this reaction was evaluated in detail based on the results of isotope labeling experiments using $H_2{}^{18}O$.

Key words platinum; propargylic ester migration; α-acyloxyketone

α-Acyloxyketone, which is a protected form of α-hydroxyketone, is a fundamental structure that can be found in a broad range of natural products and bioactive compounds, including hainanmurpanin,[1] paniculatin[2] and murpaniculol senecioate[3] (Fig. 1). α-Acyloxyketone has also been used as a simple starting material for the stereoselective synthesis of a variety of different structures, including numerous 1,2-diols[4–8] and heterocyclic systems.[9–11] Based on the importance of α-acyloxyketones to chemistry, the development of a concise synthetic method for the preparation of α-acyloxyketone derivatives is important. Although a wide variety of synthetic methods have been investigated to date,[12,13] reports pertaining to the direct synthesis of α-acyloxyketone **III** by the oxidation of alkyne **I** are rare, most likely because of the difficulties associated with suppressing the over-oxidation of the product and controlling the regioselectivity of the reaction[14–16] (Chart 1). To allow for the direct synthesis of α-acyloxyketone **III** from alkyne **I**, several researchers directed their attention towards the transition metal-catalyzed migration of propargylic esters[17–20] to affect a facile oxidative transformation.[21–30] For example, in 1991, Schick and Mahrwald[21] reported that the treatment of propargyl acetate **1** with $PdCl_2(MeCN)_2$ gave a 1 : 1 mixture of α-acyloxyketone **2** and α,β-unsaturated ketone **3** *via* the rearrangement of the acetyl group (Chart 2(a)). Ohfune *et al.*[24] also reported the synthesis of α-acyloxy-α′-siloxyketone **4** using a gold catalyst (Chart 2(b)). Under Ohfune's conditions, it was observed that substrates without a silyl group did not undergo the reaction, and it was therefore assumed that the silyl group was essential for stabilizing the β cation of reaction intermediate **5** (or **6**). Although these reactions provided facile access to the α-acyloxyketones **2** and **4** from the readily accessible propargyl esters **1** and **3**, several opportunities still remained to improve on this reaction in terms of the selectivity and substrate scope.

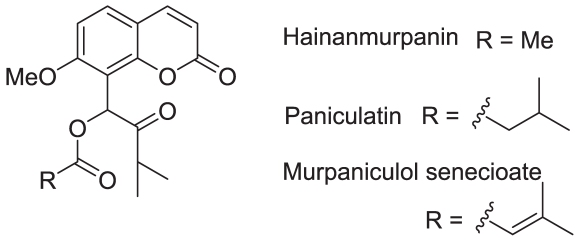

Fig. 1. Selected Natural Products Containing an α-Acyloxyketone Moiety

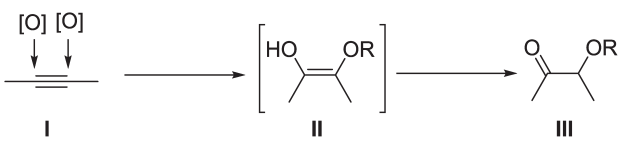

Chart 1. Concept for the Synthesis of α-Acyloxyketones by the Oxidation of an Alkyne

For improving the scope of this reaction, we focused on enhancing the π-acidity of the transition metal catalyst (*i.e.*, palladium, gold or platinum catalyst) by decreasing its electron density.[17–20] If allene **9**, which was derived from **7**, could be strongly activated by a π-acidic transition metal catalyst, then the addition of the internal ester or a water molecule to the allene would give α-acyloxyketone **8** without the requirement for a neighboring group to stabilize the transition state (Chart 3). Given that propargyl ester **7** can be readily prepared by the Sonogashira coupling of an alkyne bearing a propargyl ester to an aryl halide or the nucleophilic addition of a suitable acetylide to an aldehyde followed by acylation, this transformation could be used as a concise method for a preparation of α-acyloxyketones. In this paper, we describe our recent efforts towards the synthesis of α-acyloxyketones based on the platinum-catalyzed migration of propargylic esters.

Results and Discussion

Pivaloyl ester **11a** was selected as a model substrate to investigate the synthesis of α-acyloxyketone **12a** because it would avoid the undesired hydrolysis of the ester (Table 1). Several gold and platinum catalysts were initially screened against the model substrate in toluene at 60°C (Table 1, entries 1–7). Cationic gold catalysts derived from the reaction of AuCl or $AuCl_3$ with $AgNTf_2$ did not give the desired product **12a** (Table 1, entries 1, 2). To reduce the cationic property of the catalyst, we investigated the use of $Au(PPh_3)Cl$ and $Pt(PPh_3)_2Cl_2$ with $AgNTf_2$. However, these two systems also

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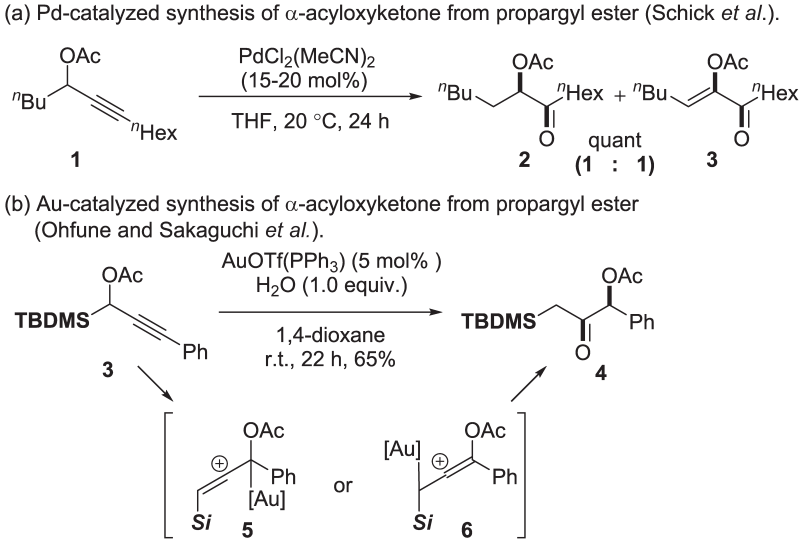


Chart 2. Synthesis of α-Acyloxyketones from Propargyl Esters Using a Metal Catalyst

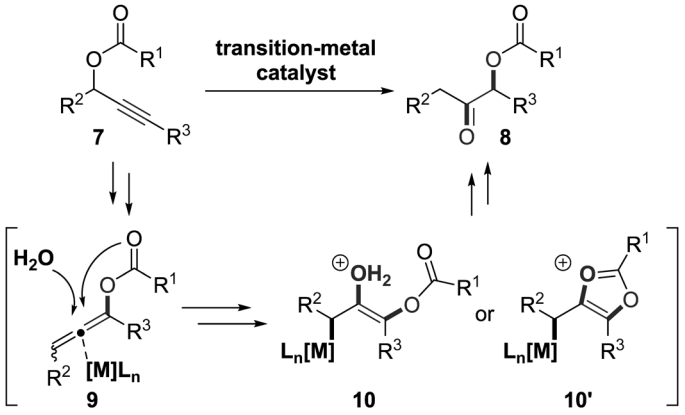
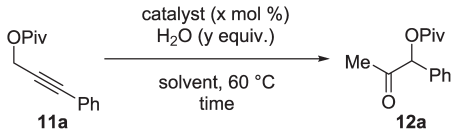


Chart 3. Synthetic Strategy for α-Acyloxyketone

failed to provide any of the desired product **12a**, presumably because the phosphine ligand was strongly coordinated to the metal for decreasing its cationic character (Table 1, entries 3, 4). Based on this result, we proceeded to investigate the use of a CO atmosphere and cyclooctadiene, which have been reported to weakly coordinate to metals.[31–35] While the reaction using 10 mol% of $PtCl_2$ under an atmosphere of CO gave the desired product **12a** in 14% yield, the use of 10 mol% of $Pt(cod)Cl_2/AgNTf_2$ provided **12a** in a much greater yield of 75% within 1 h (Table 1, entries 5, 6).[36] Interestingly, reactions using only $Pt(cod)Cl_2$ or $AgNTf_2$ did not provide any of the desired product (Table 1, entries 7, 8). Taken together, these results indicated that the use of a cationic platinum catalyst with a weakly coordinating ligand would be important for the success of this reaction. Further screening experiments confirmed that the previously reported conditions[21,24] were not effective for this transformation (Table 1, entries 9–11). We then proceeded to investigate the possibility of reducing the amount of catalyst added to the reaction using the $Pt(cod)Cl_2/AgNTf_2$ catalytic system (Table 1, entry 6).[37] A reduction in the amount of catalyst to 3 mol% led to a decrease in the yield to 44%, despite the reaction time being extended to 12 h (Table 1, entry 12). Consideration of the reaction mechanism (*vide infra*) revealed that water would be required for the hydrolysis of the reaction intermediate, and we subsequently investigated the addition of three equivalents of water to the reaction mixture. As anticipated, the yield of the reaction was improved to 63% following the addition of 3 eq, with the reaction reaching completion within 2 h (Table 1, entry 13). The impact of raising the reaction temperature to 100°C was also investigated and led to a decrease in the reaction time (Table 1, entry 14). Based on these results, the optimized conditions were set as follows: 3 mol% of $Pt(cod)Cl_2$, 3 mol% of $AgNTf_2$ and 3 eq of water in toluene at 100°C. To the best of our knowledge, this work represents the first reported example of the migration of a propargylic ester catalyzed by a monocationic Pt catalyst, which was generated *in situ* from neutral $Pt(cod)Cl_2$ and $AgNTf_2$.

With the optimized conditions in hand, we proceeded to investigate the scope of the reaction using a variety of different substrates (Table 2). Substrates **11b**–**g** bearing an electron-withdrawing group at the *para*-position of the phenyl ring (*i.e.*, halogen, ester, nitrile, nitro or trifluoromethyl group) gave the corresponding α-alkoxyketones **12b**–**g** in 69–89% yields (Table 2, entries 1–6). In contrast, substrates bearing an electron-donating group at the para position, such as a methyl or methoxy group, gave much lower yields of the corresponding α-alkoxyketone products, with the *para*-methoxy substrate

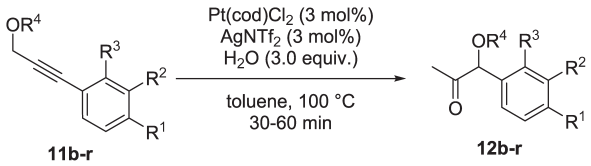
Table 1. Investigation of the Reaction Conditions[a)]



Entry	Catalyst	Solvent	x	y	Time	Yield[b)]
1	$AuCl/AgNTf_2$	Toluene	10	None	24 h	N.D.[c)]
2	$AuCl_3/AgNTf_2$	Toluene	10	None	24 h	N.D.[c)]
3	$Au(PPh_3)Cl/AgNTf_2$	Toluene	10	None	24 h	N.D.[c)]
4	$Pt(PPh_3)_2Cl_2/AgNTf_2$	Toluene	10	None	24 h	N.R.
5	$PtCl_2/CO$	Toluene	10	None	24 h	14%[d)]
6	$Pt(cod)Cl_2/AgNTf_2$	Toluene	10	None	1 h	75%
7	$Pt(cod)Cl_2$	Toluene	10	None	24 h	N.R.
8	$AgNTf_2$	Toluene	10	None	24 h	N.R.
9	$PdCl_2(MeCN)_2$	THF	20	None	18 h	Trace
10	$PdCl_2(MeCN)_2/AgNTf$	Toluene	10	None	24 h	N.D.
11	$Au(PPh_3)Cl/AgSbF_6$	1,4-Dioxane	10	1.0	6 h	Trace
12	$Pt(cod)Cl_2/AgNTf_2$	Toluene	3	None	12 h	44%
13	$Pt(cod)Cl_2/AgNTf_2$	Toluene	3	3.0	2 h	63%
14[e)]	$Pt(cod)Cl_2/AgNTf_2$	Toluene	3	3.0	30 min	67%

a) Reactions were carried out using **11a** (0.3 mmol), platinum catalyst (x mol%) and silver additive (x mol%) in solvent (6 mL) with or without H_2O (3.0 eq) at 60°C. *b*) Isolated yield. *c*) Complex mixture containing starting material **11a**. *d*) NMR yield. *e*) The reaction was conducted at 100°C.

Table 2. Substrate Scope[a)]



Entry	Substrate	R^1	R^2	R^3	R^4	Product	Yield[b)]
1	**11b**	Cl	H	H	Piv	**12b**	77%
2	**11c**	Br	H	H	Piv	**12c**	69%
3	**11d**	CO_2Me	H	H	Piv	**12d**	82%
4	**11e**	CN	H	H	Piv	**12e**	81%
5	**11f**	NO_2	H	H	Piv	**12f**	84%
6	**11g**	CF_3	H	H	Piv	**12g**	89%
7	**11h**	Me	H	H	Piv	**12h**	47%
8[c)]	**11i**	OMe	H	H	Piv	**12i**	Trace
9	**11j**	H	OMe	H	Piv	**12j**	58%
10	**11k**	H	NO_2	H	Piv	**12k**	84%
11[d)]	**11l**	H	H	OMe	Piv	**12l**	0%[e)]
12[d)]	**11m**	H	H	NO_2	Piv	**12m**	0%[e)]
13[f)]	**11n**	H	H	H	Ac	**12n**	35%
14[g)]	**11o**	H	H	H	Isobutyryl	**12o**	48%
15[g)]	**11p**	H	H	H	Bz	**12p**	32%
16[h)]	**11q**	H	H	H	(*p*-MeO)Bz	**12q**	14%
17	**11r**	H	H	H	(*p*-NO_2)Bz	**12r**	64%

a) Reactions were carried out using **11** (1.0 eq), $Pt(cod)Cl_2$ (3 mol%), $AgNTf_2$ (3 mol%), H_2O (3.0 eq) and toluene at 100°C. *b*) Isolated yield. *c*) The reaction was performed for 7 h. *d*) No reaction. *e*) The reaction was performed for 24 h. *f*) The reaction was performed for 10 h. *g*) The reaction was performed for 2 h. *h*) The reaction was performed for 32 h.

providing only a trace amount of the product (Table 2, entries 7, 8). Substrates bearing a methoxy or nitro group at the *meta*-position reacted smoothly to afford the desired products **12j** and **12k**, with the electron-withdrawing group providing a better yield (84%) than the electron-donating group (58%) (Table 2, entries 9, 10). In sharp contrast, substrates **11l** and **11m** bearing a substituent at the *ortho*-position of their phenyl ring failed to provide any of the desired products (Table 2, entries 11, 12). The failure of these substrates can be rationalized by the chelation of the functional groups to the cationic platinum catalyst, which would result in a decrease in the ability of the catalyst to activate the alkyne, as shown in Fig. 2. Several acyl groups were examined instead of the pivaloyl group, and the results revealed that the use of a smaller ester such

as acetyl or isobutyryl group resulted in lower yields of 35 and 48%, respectively (Table 2, entries 13, 14). To determine the effect of the electronic state of the ester of the outcome of the reaction, we also investigated several non- and mono-substituted benzoyl groups. The results of these reactions revealed that the use of an aromatic ring bearing an electron-withdrawing group gave a better yield than an aromatic ring bearing an electron-donating group or no substituent at all (Table 2, entries 15–17).

A plausible mechanism for this reaction was proposed based on the results provided above (Chart 4). The initially coordination of the cationic platinum catalyst to the alkyne would give the activated alkyne **A**, which would undergo an intramolecular nucleophilic addition reaction with the ester to give **B**. If the R^2 substituent was an aryl group, it would stabilize the transition state for the 6-*endo* cyclization. The ring opening of cyclic intermediate **B** would give the allene intermediate **C**. The ester would then attacked the central carbon of the allene, which would be activated by the platinum catalyst, to give the five membered cyclic intermediates **D** and **E** (path a).[38] Intermediates **D** and **E** would then be converted to α-acyloxy ketone **H** *via* sequential proto-demetallation[39] and hydrolysis reactions. Substrate **11r** reacted much more effectively than **11q** (Table 2, entries 16, 17). It would be rationalized that intermediate **F** would be readily hydrolyzed by water, because the presence of an electron withdrawing group on the R^1 substituent would lead to a reduction in the electron density of the carbonyl carbon. However, an alternative pathway could occur involving the intermolecular nucleophilic addition of H_2O (path b). In this case, H_2O would directly attack the central carbon of the allene intermediate to give intermediate **I**, which would be converted to α-acyloxyketone **H** *via* sequential protodemetallation and tautomerization reactions. It is noteworthy, however, that this route makes it difficult to explain the differences observed in the reactions of substrates **11r** and **11q**.

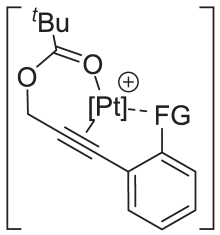


Fig. 2. Proposed Chelation of the Catalyst to the *ortho*-Substituent in Substrates **11l** and **11m**

Several isotope experiments were performed using $H_2{}^{18}O$ to develop deeper insights into the reaction mechanism. For path (a), it was envisaged that the carbonyl oxygen of the ester would be labeled with ^{18}O. In contrast, if the reaction proceeded through path (b), then it was envisaged that the ^{18}O atom would be captured as a ketone oxygen. In practice, when $H_2{}^{18}O$ was added to the reaction mixture instead of $H_2{}^{16}O$ under the optimal conditions, the reaction gave a mixture of mono-labeled products **13** and **14** along with unlabeled **12a** and di-labeled **15** as a 3 : 1 : 3 mixture[40,41] (Chart 5, eq. 1). The treatment of unlabeled **12a** with $H_2{}^{18}O$ under the optimized

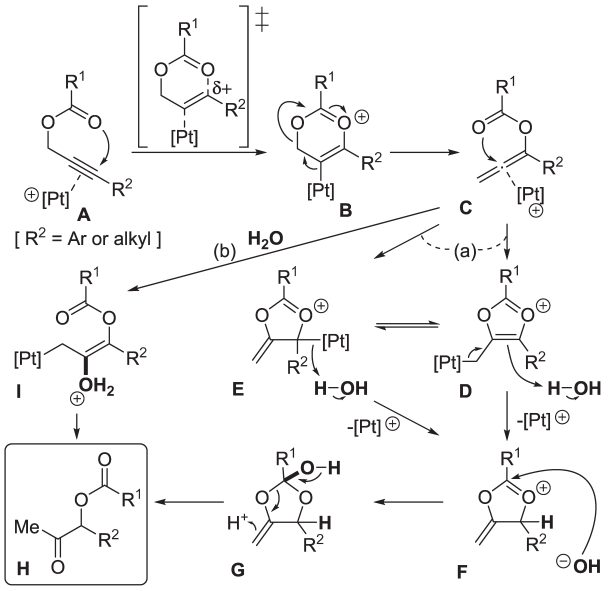


Chart 4. Plausible Mechanism with Internal Alkynes

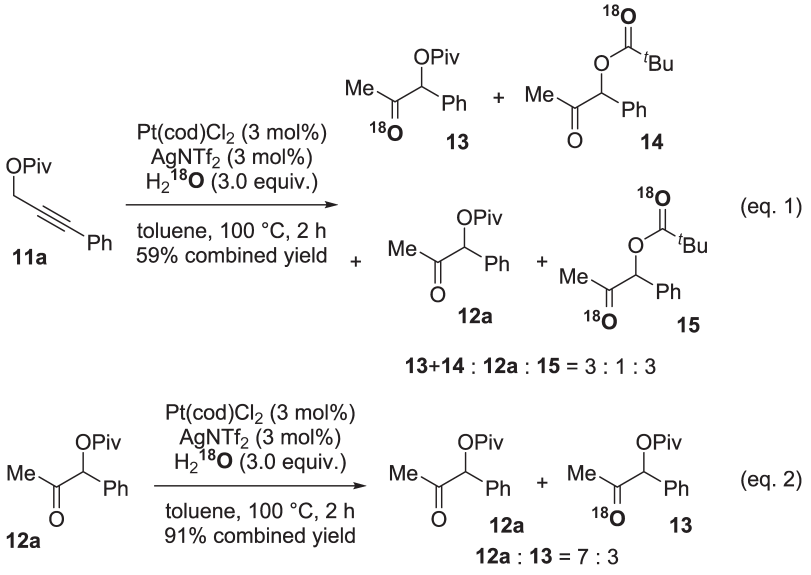


Chart 5. Isotope Labeling Experiments Using $H_2{}^{18}O$

conditions gave mono-labeled **13** without the hydrolysis of the ester (**12a**:**13**=7:3, eq. 2). This result indicated that the ketone carbonyl oxygen could be interconverted with water under the reaction conditions and that di-labeled **15** was most likely produced by addition of $H_2{}^{18}O$ to **14** with the elimination of $H_2{}^{16}O$. The production of **14** therefore suggested that path (a) was likely to be mechanism for the reaction, however path (b) cannot be ruled out.

To determine the effect of the other substituents on the outcome of the reaction, we proceeded to investigate substrates bearing an alkyl or aryl group on the propargylic position of the alkyne (Chart 6). In the case of substrate **11s** bearing an alkyl group instead of the aryl group, the reaction gave the desired *α*-alkoxyketone **12s** albeit in a low yield. This result indicated that the initial 6-*exo*-dig cyclization could occur to give the product **12s**, although the alkyl substituent did not adequately stabilize the transition state. Unexpectedly, the reaction of substrate **11t** bearing a phenyl group at the propargylic position gave a complex mixture. In contrast, substrate **11u** bearing a terminal alkyne and phenyl group at its propargylic position was converted to compound **12u** along with a small amount of the regioisomer **12u′**. Interestingly, the reaction of substrate **11v** bearing a terminal alkyne and an alkyl group at its propargylic position gave regioisomer **12v′** as the major product.

The differences observed in the regioselectivity of these

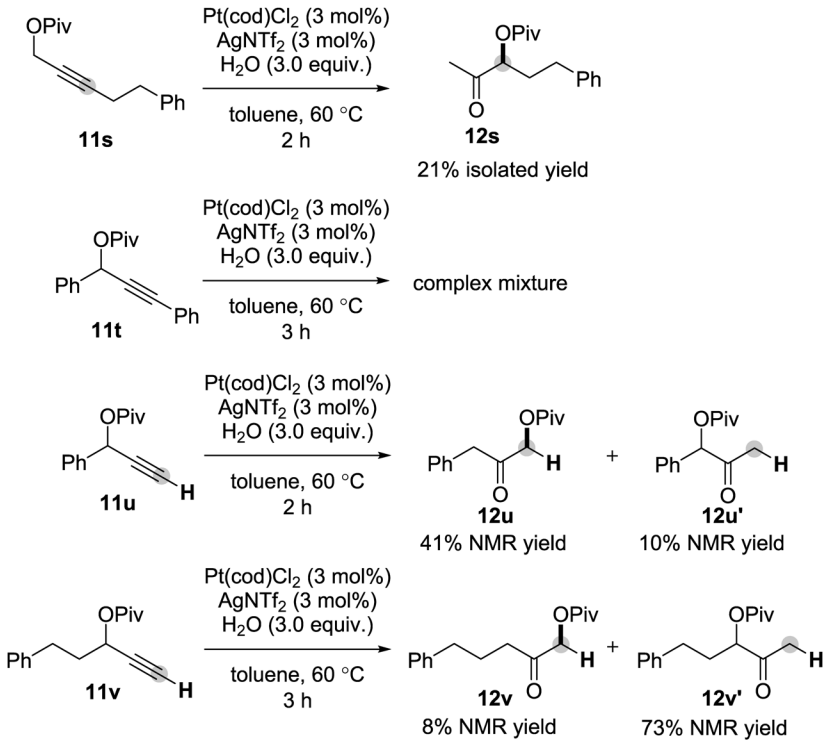


Chart 6. Switch in the Regioselectivity of the Reaction

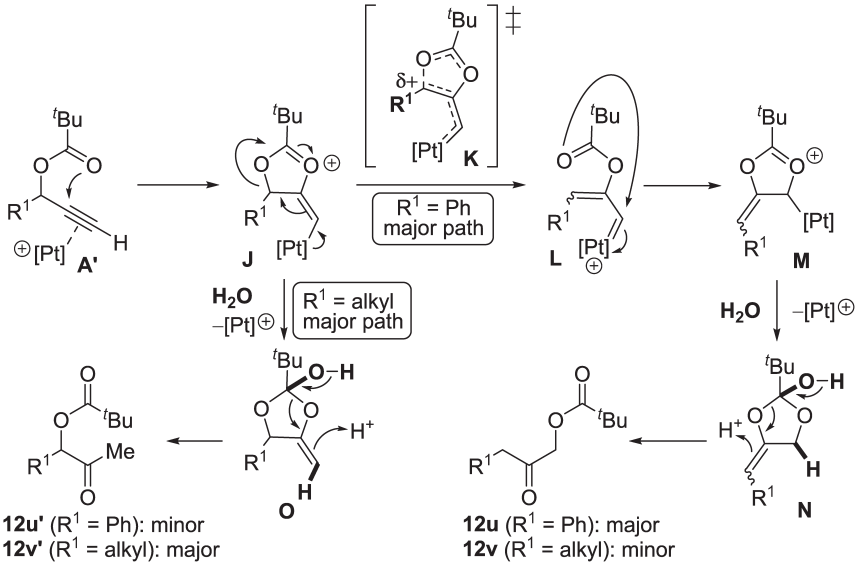


Chart 7. Plausible Mechanism with Terminal Alkynes

reactions can be rationalized as follows (Chart 7). Substrates containing a terminal alkyne would undergo a 5-*exo*-dig cyclization rather than a 6-*endo*-dig cyclization in the absence of a cation-stabilizing substituent to give intermediate **J**. It was assumed that the use of a phenyl group as the R^1 substituent would stabilize the partial cation in transition state **K** to produce the platinum carbene **L**. The subsequent intramolecular addition of the ester to the carbene would give intermediate **M**, which would be converted to *α*-acyloxyketone **12u** *via* sequential protodemetallation and hydrolysis reactions. In contrast, the use of an alkyl group as the R^1 substituent instead of an aryl group would lead to a reduction in the stabilizing effect of transition state **K**. Thus, the subsequent protodemetallation and hydrolysis *via* intermediate **O** would be preferable to give regioisomer **12v′** as the major product rather than the formation of the carbene intermediate **L**.

Conclusion

The Pt-catalyzed facial oxidation of alkynes for the synthesis of *α*-acyloxyketones has been investigated in detail. The cationic nature of the platinum catalyst [$Pt(cod)Cl_2$/$AgNTf_2$] was found to be particularly important for this transformation. The substrate scope of the optimized reaction was investigated as well as the reaction mechanism using $H_2{}^{18}O$. Taken together, the results of these experiments suggested that the *α*-acyloxyketone products were being formed *via* the Pt-catalyzed migration of the propargylic ester moiety followed by the intramolecular nucleophilic addition of the ester to the allene in intermediate **C**. This reaction could also be used for the regioselective synthesis of *α*-aryl-*α*-acyloxyketones.

Experimental

General Experimental Details Unless otherwise noted, all reactions were performed under argon. $Pt(cod)Cl_2$ and $AgNTf_2$ were purchased from Sigma-Aldrich. Toluene was purchased from Wako Pure Chemical Industries, Ltd. Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received. Propargyl alcohols were prepared according to the known procedures using Sonogashira coupling with 2-propyn-1-ol and aryl iodides or nucleophilic addition of terminal alkynes to aldehydes.

Analytical thin-layer chromatography was performed with Merck Silica gel 60. Silica gel column chromatography was performed with Kanto silica gel 60 (particle size, 63–210 μm) or Fuji Silysia BW-300. All melting points (mp) were determined on BÜCHI Melting Point M-565. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL JNM-LA 500 at 500 MHz. Chemical shifts are reported relative to Me_4Si (δ 0.00). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); sep (septet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a JEOL JNM-LA 500 at 126 MHz. Chemical shifts are reported relative to chloroform-d_3 ($CDCl_3$) (δ 77.0). Infrared spectra were recorded on a Fourier transform (FT)/IR-4100 (JASCO). Low and high resolution mass spectra were recorded on JEOL JMS-HX/HX 110 A.

Preperation of Propargyl Esters

3-Phenylprop-2-yn-1-yl Pivalate (**11a**)[42]

To the solution of 3-phenyl-2-propyn-1-ol (1.32 g, 10.0 mmol), NEt_3 (7.0 mL, 50.0 mmol) and 4-(dimethylamino)pyridine (DMAP) (127.5 mg, 1.05 mmol) in methylene chloride (CH_2Cl_2) (50 mL) at 0°C was added pivaloyl chloride (1.35 mL, 11.0 mmol) slowly under Ar and the mixure was warmed to room temperature. After stirring for 2 h, the mixture was quenched with water and extracted with chloroform ($CHCl_3$). The combined extracts were washed with 1.0 M aqueous solution of HCl and 3.0 M aqueous solution of NaOH, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (hexane/CH_2Cl_2=75/25) to give **11a** (1.89 g, 88%) as a colorless oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47–7.44 (m, 2H), 7.35–7.29 (m, 3H), 4.89 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.9, 131.9, 128.7, 128.3, 122.3, 86.1, 83.3, 52.8, 38.8, 27.1; IR (attenuated total reflectance (ATR)) 2974, 2236, 1279, 1136 cm^{-1}; MS (FAB$^+$) *m/z*=217 ([M+H]$^+$); high resolution (HR)-MS (FAB$^+$) Calcd for $C_{14}H_{17}O_2$ [M+H]$^+$: 217.1229. Found: 217.1238.

3-(4-Chlorophenyl)prop-2-yn-1-yl Pivalate (**11b**)

The reaction was performed according to the procedure for **11a**. A white solid; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.39–7.36 (m, 2H), 7.31–7.27 (m, 2H), 4.87 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 134.7, 133.1, 128.6, 120.8, 85.0, 84.3, 52.7, 38.8, 27.1; IR (ATR) 2972, 2234, 1726, 1277, 1142, 828 cm^{-1}; MS (FAB$^+$) *m/z*=250 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{15}ClO_2$ [M]$^+$: 250.0761. Found: 250.0755.

3-(4-Bromophenyl)prop-2-yn-1-yl Pivalate (**11c**)

The reaction was performed according to the procedure for **11a**. A white solid; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47–7.43 (m, 2H), 7.33–7.29 (m, 2H), 4.87 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 133.3, 131.6, 123.0, 121.2, 85.0, 84.5, 52.7, 38.8, 27.1; IR (ATR) 2974, 2236, 1733, 1486, 1278, 1140, 842 cm^{-1}; MS (FAB$^+$) *m/z*=294 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{15}{}^{79}BrO_2$ [M]$^+$: 294.0255. Found: 294.0265.

Methyl 4-(3-(Pivaloyloxy)prop-1-yn-1-yl)benzoate (**11d**)

The reaction was performed according to the procedure for **11a**. A white solid: mp 58.1–58.9°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, 2H, *J*=8.0 Hz), 7.51 (d, 2H, *J*=8.0 Hz), 4.90 (s, 2H), 3.92 (s, 3H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 166.4, 131.8, 129.9, 129.4, 126.9, 86.3, 85.3, 52.6, 52.3, 38.8, 27.1; IR (ATR) 2969, 2240, 1720, 1273, 1144, 862 cm^{-1}; MS (FAB$^+$) *m/z*=275 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{19}O_4$ [M+H]$^+$: 275.1283. Found: 275.1284.

3-(4-Cyanophenyl)prop-2-yn-1-yl Pivalate (**11e**)

The reaction was performed according to the procedure for **11a**. An orange oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.63–7.60 (m, 2H), 7.54–7.52 (m, 2H), 4.90 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.7, 132.4, 132.0, 127.2, 118.3, 112.1, 87.8, 84.3, 52.4, 38.8, 27.1; IR (ATR) 2974, 2229, 1732, 1278, 1134, 840 cm^{-1}; MS (FAB$^+$) *m/z*=242 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{16}NO_2$ [M+H]$^+$: 242.1181. Found: 242.1178.

3-(4-Nitrophenyl)prop-2-yn-1-yl Pivalate (**11f**)

The reaction was performed according to the procedure for **11a**. A yellow oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.21–8.17 (m, 2H), 7.61–7.58 (m, 2H), 4.92 (s, 2H), 1.26 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.7, 147.3, 132.6, 129.1, 123.5, 88.7, 84.1, 52.4, 38.8, 27.1; IR (ATR) 2975, 1734, 1520, 1343, 1278, 1136, 854 cm^{-1}; MS (FAB$^+$) *m/z*=262 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{16}NO_4$ [M+H]$^+$: 262.1079.

Found: 262.1082.

3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl Pivalate (**11g**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.59–7.53 (m, 4H), 4.90 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 132.1, 130.4 (q, J=32.4 Hz), 126.1, 125.2 (q, J=3.6 Hz), 123.8 (q, J=272.3 Hz), 85.8, 84.7, 52.5, 38.8, 27.1; IR (ATR) 2977, 1734, 1321, 1278, 1125, 842 cm^{-1}; MS (FAB$^+$) m/z=284 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{15}F_3O_2$ [M]$^+$: 284.1024. Found: 284.1017.

3-(*p*-Tolyl)prop-2-yn-1-yl Pivalate (**11h**)

The reaction was performed according to the procedure for **11a**. A white solid; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, 2H, J=8.0 Hz), 7.12 (d, 2H, J=8.0 Hz), 4.88 (s, 2H), 2.40 (s, 3H), 1.24 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.9, 138.8, 131.8, 129.0, 119.2, 86.3, 82.6, 52.9, 38.8, 27.1, 21.5; IR (ATR) 2978, 2235, 1721, 1278, 1148, 822 cm^{-1}; MS (FAB$^+$) m/z=231 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{19}O_2$ [M+H]$^+$: 231.1385. Found: 231.1385.

3-(4-Methoxyphenyl)prop-2-yn-1-yl Pivalate (**11i**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.41–7.38 (m, 2H), 6.85–6.82 (m, 2H), 4.88 (s, 2H), 3.81 (s, 3H), 1.24 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.9, 159.8, 133.4, 114.3, 113.9, 86.1, 81.2, 55.2, 53.0, 38.8, 27.1; IR (ATR) 2972, 2231, 1732, 1510, 1249, 1140, 1034, 833 cm^{-1}; MS (FAB$^+$) m/z=247 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{19}O_3$ [M+H]$^+$: 247.1334. Found: 247.1328.

3-(3-Methoxyphenyl)prop-2-yn-1-yl Pivalate (**11j**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.22 (dd, 1H, J=8.0 Hz), 7.05 (d, 1H, J=8.0 Hz), 6.89 (d, 1H, J=8.0 Hz), 4.89 (s, 2H), 3.80 (s, 3H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 159.2, 129.3, 124.4, 123.2, 116.6, 115.3, 86.0, 83.1, 55.3, 52.8, 38.8, 27.1; IR (ATR) 2973, 2240, 1735, 1481, 1292, 1144, 1048, 787 cm^{-1}; MS (FAB$^+$) m/z=246 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{18}O_3$ [M]$^+$: 246.1256. Found: 246.1260.

3-(3-Nitrophenyl)prop-2-yn-1-yl Pivalate (**11k**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 8.19 (d, 1H, J=8.1 Hz), 7.75 (d, 1H, J=8.1 Hz), 7.51 (dd, 1H, J=8.1 Hz), 4.91 (s, 2H), 1.26 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 148.0, 137.5, 129.3, 126.7, 124.1, 123.4, 86.1, 83.6, 52.4, 38.8, 27.1; IR (ATR) 2973, 1733, 1532, 1350, 1279, 1138 cm^{-1}; MS (FAB$^+$) m/z=261 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{15}NO_4$ [M]$^+$: 261.1001. Found: 261.0994.

3-(2-Methoxyphenyl)prop-2-yn-1-yl Pivalate (**11l**)

The reaction was performed according to the procedure for **11a**. A brown oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.44–7.41 (m, 1H), 7.33–7.28 (m, 1H), 6.93–6.86 (m, 2H), 4.94 (s, 2H), 3.88 (s, 3H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.9, 160.1, 134.0, 130.1, 120.4, 111.4, 110.6, 87.3, 82.5, 55.8, 53.1, 38.8, 27.1; IR (ATR) 2972, 2237, 1732, 1494, 1266, 1143, 1026 cm^{-1}; MS (FAB$^+$) m/z=247 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{19}O_3$ [M+H]$^+$: 247.1334. Found: 247.1336.

3-(2-Nitrophenyl)prop-2-yn-1-yl Pivalate (**11m**)

The reaction was performed according to the procedure for **11a**. A yellow oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.07–8.04 (m, 1H), 7.65–7.62 (m, 1H), 7.60–7.56 (m, 1H), 7.50–7.46 (m, 1H), 4.95 (s, 2H), 1.27 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.8, 149.7, 134.9, 132.8, 129.0, 124.6, 117.7, 91.4, 81.3, 52.6, 38.8, 27.1; IR (ATR) 2975, 1735, 1529, 1345, 1280, 1141 cm^{-1}; MS (FAB$^+$) m/z=262 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{16}NO_4$ [M+H]$^+$: 262.1079. Found: 262.1078.

3-Phenylprop-2-yn-1-yl Acetate (**11n**)[43]

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47–7.44 (m, 2H), 7.36–7.29 (m, 3H), 4.91 (s, 2H), 2.14 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 170.3, 131.9, 128.8, 128.3, 122.1, 86.4, 82.9, 52.8, 20.8; IR (ATR) 2939, 2240, 1747, 1225, 1034 cm^{-1}; MS (FAB$^+$) m/z=174 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{11}H_{10}O_2$ [M]$^+$: 174.0681. Found: 174.0682.

3-Phenylprop-2-yn-1-yl Isobutyrate (**11o**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47–7.44 (m, 2H), 7.36–7.29 (m, 3H), 4.91 (s, 2H), 2.67–2.59 (m, 1H), 1.21 (d, 6H, J=7.2 Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 176.5, 131.9, 128.7, 128.3, 122.2, 86.3, 83.1, 52.7, 33.9, 18.9; IR (ATR) 2976, 2238, 1740, 1148 cm^{-1}; MS (FAB$^+$) m/z=202 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{13}H_{14}O_2$ [M]$^+$: 202.0994. Found: 202.0997.

3-Phenylprop-2-yn-1-yl Benzoate (**11p**)[44]

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.13–8.08 (m, 2H), 7.60–7.56 (m, 1H), 7.50–7.43 (m, 4H), 7.36–7.29 (m, 3H), 5.16 (s, 2H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 165.9, 133.2, 131.9, 129.8, 129.6, 128.7, 128.4, 128.3, 122.2, 86.6, 83.0, 53.3; IR (ATR) 3064, 2944, 2232, 1727, 1271, 1108 cm^{-1}; MS (FAB$^+$) m/z=236 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{12}O_2$ [M]$^+$: 236.0837. Found: 236.0841.

3-Phenylprop-2-yn-1-yl 4-Methoxybenzoate (**11q**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.08–8.04 (m, 2H), 7.50–7.46 (m, 2H), 7.36–7.29 (m, 3H), 6.95–6.91 (m, 2H), 5.13 (s, 2H), 3.87 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 165.7, 163.6, 131.9, 128.7, 128.3, 122.2, 122.0, 113.6, 86.4, 83.3, 55.4, 53.0 (one carbon is missing); IR (ATR) 3057, 2936, 2229, 1716, 1605, 1257, 1168, 1098, 1030 cm^{-1}; MS (FAB$^+$) m/z=266 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{17}H_{14}O_3$ [M]$^+$: 266.0943. Found: 266.0948.

3-Phenylprop-2-yn-1-yl 4-Nitrobenzoate (**11r**)

The reaction was performed according to the procedure for **11a**. A yellow solid: mp 59.0–60.1°C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.34–8.26 (m, 4H), 7.51–7.46 (m, 2H), 7.38–7.31 (m, 3H), 5.21 (s, 2H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 164.1, 150.7, 135.0, 131.9, 131.0, 129.0, 128.4, 123.6, 121.8, 87.2, 82.2, 54.2; IR (ATR) 3112, 2955, 2230, 1719, 1526, 1347, 1263, 1097 cm^{-1}; MS (FAB$^+$) m/z=281 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{11}NO_4$ [M]$^+$: 281.0688. Found: 281.0692.

5-Phenylpent-2-yn-1-yl Pivalate (**11s**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.32–7.27 (m, 2H), 7.24–7.20 (m, 3H), 4.65–4.63 (m, 2H), 2.83 (t, 2H, J=7.6 Hz), 2.53–2.49 (m, 2H), 1.22 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.9, 140.4, 128.4, 128.4, 126.3, 86.3, 75.0, 52.7, 38.7, 34.8, 27.1, 21.0; IR (ATR) 2974, 2235, 1735, 1280, 1146 cm^{-1}; MS (FAB$^+$) m/z=245 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{21}O_2$ [M+H]$^+$: 245.1542. Found: 245.1542.

1,3-Diphenylprop-2-yn-1-yl Pivalate (**11t**)[42]

The reaction was performed according to the procedure for

11a. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.59–7.55 (m, 2H), 7.48–7.45 (m, 2H), 7.42–7.28 (m, 6H), 6.67 (s, 1H), 1.24 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.2, 137.5, 131.9, 128.7, 128.7, 128.6, 128.2, 127.4, 122.2, 86.7, 85.8, 65.8, 38.8, 27.0 ; IR (ATR) 2972, 2231, 1733, 1273, 1138 cm^{-1}; MS (FAB$^+$) m/z=292 ([M]$^+$); HR-MS (FAB$^+$) Calcd for $C_{20}H_{20}O_2$ [M]$^+$: 292.1463. Found: 292.1462.

1-Phenylprop-2-yn-1-yl Pivalate (**11u**)[45)]

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.53–7.49 (m, 2H), 7.41–7.34 (m, 3H), 6.42 (d, 1H, J=2.3 Hz), 2.62 (d, 1H, J=2.3 Hz), 1.22 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.1, 136.8, 128.8, 128.6, 127.2, 80.4, 75.1, 65.0, 38.7, 26.9; IR (ATR) 3290, 2974, 1736, 1270, 1141 cm^{-1}; MS (FAB$^+$) m/z=216 ([M$^+$]); HR-MS (FAB$^+$) Calcd for $C_{14}H_{16}O_2$ [M]$^+$: 216.1150. Found: 216.1149.

5-Phenylpent-1-yn-3-yl Pivalate (**11v**)

The reaction was performed according to the procedure for **11a**. A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.31–7.27 (m, 2H), 7.23–7.17 (m, 3H), 5.33 (td, 1H, J_1=2.0 Hz, J_2=6.6 Hz), 2.83–2.73 (m, 2H), 2.47 (d, 1H, J=2.0 Hz), 2.17–2.04 (m, 2H), 1.23 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 177.3, 140.7, 128.5, 128.4, 126.2, 81.1, 73.5, 63.0, 38.7, 36.2, 31.1, 27.0; IR (ATR) 3293, 2974, 1735, 1279, 1146 cm^{-1}; MS (FAB$^+$) m/z=245 ([M$^+$]); HR-MS (FAB$^+$) Calcd for $C_{16}H_{21}O_2$ [M]$^+$: 245.1542. Found: 245.1547.

General Procedure for the Synthesis of α-Acyloxyketone

2-Oxo-1-phenylpropyl Pivalate (**12a**)

To the solution of Pt(cod)Cl_2 (3.4 mg, 0.009 mmol), $AgNTf_2$ (3.5 mg, 0.009 mmol) and H_2O (16 μL, 0.9 mmol) in toluene (4 mL) at 0°C was added 3-phenylprop-2-yn-1-yl pivalate **1a** (64.9 mg, 0.3 mmol) dissolved in toluene (0.5 mL) using syringe. After three repeats of rinsing the syringe with toluene (0.5 mL) and addition of the rinsed solution to the reaction mixture, the mixture was warmed to room temperature. After stirring for 30 min at the same temperature, the mixture was warmed to 100°C. When the starting material disappeared (checked by TLC), the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The obtained residue was purified by silica gel column chromatography (hexane/EtOAc=97.5/2.5) to give **12a** (46.8 mg, 67%) as a colorless oil.: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.45–7.36 (m, 5H), 5.92 (s, 1H), 2.12 (s, 3H), 1.29 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 202.0, 177.8, 133.5, 129.1, 129.0, 127.6, 80.7, 38.7, 27.1, 25.9; IR (ATR) 2974, 1725, 1146 cm^{-1}; MS (FAB$^+$) m/z=235 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{18}O_3$ [M+H]$^+$: 235.1334. Found: 235.1337.

1-(4-Chlorophenyl)-2-oxopropyl Pivalate (**12b**)

The reaction was performed according to the procedure for **12a** and gave **12b** in 77% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.40–7.34 (m, 4H), 5.89 (s, 1H), 2.12 (s, 3H), 1.29 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.7, 177.6, 135.2, 132.0, 129.2, 128.9, 79.8, 38.7, 27.0, 25.9; IR (ATR) 2975, 1728, 1491, 1147 cm^{-1}; MS (FAB$^+$) m/z=269 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{18}ClO_3$ [M+H]$^+$: 269.0944. Found: 269.0940.

1-(4-Bromophenyl)-2-oxopropyl Pivalate (**12c**)

The reaction was performed according to the procedure for **12a** and gave **12c** in 69% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.56–7.50 (m, 2H), 7.32–7.28 (m, 2H), 5.87 (s, 1H), 2.13 (s, 3H), 1.28 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.6, 177.6, 132.5, 132.1, 129.2, 123.4, 79.9, 38.7, 27.0, 25.9; IR (ATR) 2974, 1725, 1487, 1140 cm^{-1}; MS (FAB$^+$) m/z=313 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{18}{}^{79}BrO_3$ [M+H]$^+$: 313.0439. Found: 313.0432.

Methyl 4-(2-Oxo-1-(pivaloyloxy)propyl)benzoate (**12d**)

The reaction was performed according to the procedure for **12a** and gave **12d** in 82% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.08 (d, 2H, J=8.6 Hz), 7.51 (d, 2H, J=8.6 Hz), 5.98 (s, 1H), 3.93 (s, 3H), 2.14 (s, 3H), 1.30 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.5, 177.5, 166.4, 138.3, 130.8, 130.1, 127.4, 80.1, 52.2, 38.7, 27.0, 25.9; IR (ATR) 2975, 1726, 1281, 1146 cm^{-1}; MS (FAB$^+$) m/z=293 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{21}O_5$ [M+H]$^+$: 293.1389. Found: 293.1389.

1-(4-Cyanophenyl)-2-oxopropyl Pivalate (**12e**)

The reaction was performed according to the procedure for **12a** and gave **12e** in 81% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.73–7.70 (m, 2H), 7.58–7.54 (m, 2H), 5.97 (s, 1H), 2.17 (s, 3H), 1.31 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.3, 177.3, 138.6, 132.6, 128.0, 118.1, 113.0, 79.7, 38.7, 27.0, 26.0; IR (ATR) 2975, 2230, 1728, 1140 cm^{-1}; MS (FAB$^+$) m/z=260 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{18}NO_3$ [M+H]$^+$: 260.1287. Found: 260.1289.

1-(4-Nitrophenyl)-2-oxopropyl Pivalate (**12f**)

The reaction was performed according to the procedure for **12a** and gave **12f** in 84% yield as a yellow oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.27 (d, 2H, J=8.6 Hz), 7.63 (d, 2H, J=8.6 Hz), 6.02 (s, 1H), 2.19 (s, 3H), 1.32 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.2, 177.3, 148.2, 140.5, 128.2, 124.1, 79.5, 38.8, 27.0, 26.0; IR (ATR) 2976, 1729, 1524, 1348, 1140 cm^{-1}; MS (FAB$^+$) m/z=280 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{18}NO_5$ [M+H]$^+$: 280.1185. Found: 280.1180.

2-Oxo-1-(4-(trifluoromethyl)phenyl)propyl Pivalate (**12g**)

The reaction was performed according to the procedure for **12a** and gave **12g** in 89% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.67 (d, 2H, J=8.0 Hz), 7.57 (d, 2H, J=8.0 Hz), 5.98 (s, 1H), 2.16 (s, 3H), 1.31 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.5, 177.5, 137.5, 131.2 (q, J=32.8 Hz), 127.0, 125.9 (q, J=4.0 Hz), 123.8 (q, J=272.3 Hz), 79.9, 38.8, 27.0, 25.9; IR (ATR) 2979, 1733, 1326, 1137 cm^{-1}; MS (FAB$^+$) m/z=303 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{18}F_3O_3$ [M+H]$^+$: 303.1208. Found: 303.1196.

2-Oxo-1-(p-tolyl)propyl Pivalate (**12h**)

The reaction was performed according to the procedure for **12a** and gave **12h** in 47% yield as a yellow oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, 2H, J=8.0 Hz), 7.21 (d, 2H, J=8.0 Hz), 5.88 (s, 1H), 2.36 (s, 3H), 2.11 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 202.1, 177.9, 139.1, 130.5, 129.6, 127.6, 80.5, 38.7, 27.1, 25.9, 21.2; IR (ATR) 2975, 1729, 1146 cm^{-1}; MS (FAB$^+$) m/z=249 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{21}O_3$ [M+H]$^+$: 249.1491. Found: 249.1494.

1-(3-Methoxyphenyl)-2-oxopropyl Pivalate (**12j**)

The reaction was performed according to the procedure for **12a** and gave **12j** in 58% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.31 (dd, 1H, J=7.9 Hz), 7.01 (d, 1H, J=7.9 Hz), 6.96–6.90 (m, 2H), 5.89 (s, 1H), 3.82 (s, 3H), 2.12 (s, 3H), 1.29 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.9, 177.7, 159.9, 134.9, 130.0, 119.9, 114.5, 113.1, 80.5, 55.2, 38.7, 27.1, 25.8; IR (ATR) 2973, 1727, 1277, 1147, 1042 cm^{-1}; MS (FAB$^+$) m/z=265 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{15}H_{21}O_4$ [M+H]$^+$: 265.1440. Found: 265.1436.

1-(3-Nitrophenyl)-2-oxopropyl Pivalate (**12k**)

The reaction was performed according to the procedure for **12a** and gave **12k** in 84% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.32–8.23 (m, 2H), 7.78 (d, 1H, J=8.0 Hz), 7.62 (dd, 1H, J=8.0 Hz), 6.03 (s, 1H), 2.21 (s, 3H), 1.32 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.5, 177.3, 148.5, 135.8, 133.4, 130.0, 123.9, 122.2, 79.3, 38.8, 27.0, 26.1; IR (ATR) 2975, 1729, 1533, 1351, 1142 cm^{-1}; MS (FAB$^+$) m/z=280 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{18}NO_5$ [M+H]$^+$: 280.1185. Found: 280.1190.

2-Oxo-1-phenylpropyl Acetate (**12n**)[46]

The reaction was performed according to the procedure for **12a** and gave **12n** in 35% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.43–7.40 (m, 5H), 5.98 (s, 1H), 2.20 (s, 3H), 2.11 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.7, 170.3, 133.1, 129.4, 129.1, 128.1, 80.9, 26.1, 20.7; IR (ATR) 2934, 1733, 1234 cm^{-1}; MS (FAB$^+$) m/z=193 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{11}H_{13}O_3$ [M+H]$^+$: 193.0865. Found: 193.0865.

2-Oxo-1-phenylpropyl Isobutyrate (**12o**)

The reaction was performed according to the procedure for **12a** and gave **12o** in 48% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.44–7.38 (m, 5H), 5.95 (s, 1H), 2.75–2.67 (m, 1H), 2.12 (s, 3H), 1.28 (d, 3H, J=7.2 Hz), 1.21 (d, 3H, J=7.2 Hz); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.9, 176.4, 133.3, 129.2, 129.0, 127.9, 80.6, 33.8, 26.0, 19.0, 18.7; IR (ATR) 2976, 1728, 1149 cm^{-1}; MS (FAB$^+$) m/z=221 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{13}H_{17}O_3$ [M+H]$^+$: 221.1178. Found: 221.1181.

2-Oxo-1-phenylpropyl Benzoate (**12p**)[47]

The reaction was performed according to the procedure for **12a** and gave **12p** in 32% yield as a colorless oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.12 (d, 2H, J=8.0 Hz), 7.61–7.40 (m, 8H), 6.20 (s, 1H), 2.20 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.8, 165.8, 133.5, 133.4, 129.9, 129.3, 129.2, 129.1, 128.5, 127.9, 81.3, 26.1; IR (ATR) 3064, 1721, 1277, 1110 cm^{-1}; MS (FAB$^+$) m/z=255 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{15}O_3$ [M+H]$^+$: 255.1021. Found: 255.1019.

2-Oxo-1-phenylpropyl 4-Methoxybenzoate (**12q**)

The reaction was performed according to the procedure for **12a** and gave **12q** in 14% yield as a colorless oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.08 (d, 2H, J=8.6 Hz), 7.55–7.38 (m, 5H), 6.94 (d, 2H, J=8.6 Hz), 6.17 (s, 1H), 3.87 (s, 3H), 2.19 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 202.2, 165.5, 163.8, 133.6, 132.0, 129.2, 129.1, 127.9, 121.6, 113.7, 81.0, 55.5, 26.0; IR (ATR) 3066, 2934, 1714, 1607, 1259, 1168, 1102, 1029 cm^{-1}; MS (FAB$^+$) m/z=285 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{17}H_{16}O_4$ [M+H]$^+$: 285.1127. Found: 285.1121.

2-Oxo-1-phenylpropyl 4-Nitrobenzoate (**12r**)

The reaction was performed according to the procedure for **12a** and gave **12r** in 64% yield as a yellow oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.32–8.25 (m, 4H), 7.54–7.44 (m, 5H), 6.24 (s, 1H), 2.19 (s, 3H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 200.6, 163.9, 150.7, 134.7, 132.6, 131.0, 129.8, 129.3, 128.2, 123.6, 82.0, 26.2; IR (ATR) 3059, 1723, 1528, 1347, 1279, 1103 cm^{-1}; MS (FAB$^+$) m/z=300 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{14}NO_5$ [M+H]$^+$: 300.0872. Found: 300.0873.

4-Oxo-1-phenylpentan-3-yl Pivalate (**12s**)

The reaction was performed according to the procedure for **12a** and gave **12s** in 21% yield as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.29 (dd, 2H, J_1=J_2=7.7 Hz), 7.23–7.15 (m, 3H), 4.95 (dd, 1H, J_1=8.6 Hz, J_2=4.3 Hz), 2.78–2.64 (m, 2H), 2.15–2.02 (m, 5H), 1.29 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 205.5, 177.9, 140.4, 128.6, 128.4, 126.3, 77.7, 38.8, 32.0, 31.4, 27.1, 26.0; IR (ATR) 2972, 1729, 1151 cm^{-1}; MS (FAB$^+$) m/z=263 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{16}H_{23}O_3$ [M+H]$^+$: 263.1647. Found: 263.1656.

2-Oxo-3-phenylpropyl Pivalate (**12u**)

The reaction was performed according to the procedure for **12a** and gave **12u** in 41% NMR yield (containing 10% NMR yield of **12u′**) as a colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.35–7.19 (m, 5H), 4.68 (s, 2H), 3.73 (s, 2H), 1.25 (s, 9H); ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 201.2, 177.7, 132.8, 129.4, 128.7, 127.2, 67.4, 46.1, 38.6, 27.0; IR (ATR) 2975, 1732, 1285, 1158 cm^{-1}; MS (FAB$^+$) m/z=235 ([M+H]$^+$); HR-MS (FAB$^+$) Calcd for $C_{14}H_{19}O_3$ [M+H]$^+$: 235.1334. Found: 235.1333.

2-Oxo-5-phenylpentyl Pivalate (**12v**)

The reaction was performed according to the procedure for **12a** and gave **12v** in 8% NMR yield (containing 73% NMR yield of **12v′**) as a colorless oil. These products couldn't be isolated from each other, so ^{1}H-NMR of the mixtures (in a ratio of **12v**:**12v′**=0.11:1.00) was reported; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.27–7.31 (m, 2.22H, **12v**+**12v′**), 7.23–7.15 (m, 3.33H, **12v**+**12v′**), 4.95 (dd, 1H, J_1=8.6 Hz, J_2=4.3 Hz, **12v′**), 4.58 (s, 0.22H, **12v**), 2.78–2.62 (m, 2.22H, **12v**+**12v′**), 2.40 (t, 0.22H, J=7.3 Hz, **12v**), 2.15–2.02 (m, 5H, **12v′**), 1.99–1.91 (m, 0.22H, **12v**), 1.29 (s, 9H, **12v′**), 1.25 (s, 0.99H, **12v′**). Compound **12v′** is the same as compound **12s**.

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Conflict of Interest The authors declare no conflict of interest.

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References and Notes

1) Yang J. S., Du M. H., *Huaxue Xuebao*, **42**, 1308 (1984).
2) Steck W., *Can. J. Chem.*, **50**, 443–445 (1972).
3) Kinoshita T., Wu J.-B., Ho F.-C., *Chem. Pharm. Bull.*, **44**, 1208–1211 (1996).
4) Husain S. M., Stillger T., Dünkelmann P., Lödige M., Walter L., Breitling E., Pohl M., Bürchner M., Krossing I., Müller M., Romano D., Molinari F., *Adv. Synth. Catal.*, **353**, 2359–2362 (2011).
5) Nadkarni D., Hallissey J., Mojica C., *J. Org. Chem.*, **68**, 594–596 (2003).
6) Fujita M., Hiyama T., *J. Org. Chem.*, **53**, 5405–5415 (1988).
7) Fujita M., Hiyama T., *J. Org. Chem.*, **53**, 5415–5421 (1988).
8) Takahashi T., Miyazawa M., Tsuji J., *Tetrahedron Lett.*, **26**, 5139–5142 (1985).
9) Loner C. M., Luzzio F. A., Demuth D. R., *Tetrahedron Lett.*, **53**, 5641–5644 (2012).
10) Pei W., Li S., Nie X., Li Y., Pei J., Chen B., Wu J., Ye X., *Synthesis*, **1998**, 1298 (1998).
11) Davidson D., Weiss M., Jelling M., *J. Org. Chem.*, **2**, 328–334 (1937).
12) Lifchits O., Demoulin N., List B., *Angew. Chem. Int. Ed.*, **50**, 9680–

9683 (2011).
13) Hiett N. P., Lynam J. M., Welby C. E., Whitwood A. C., *J. Organomet. Chem.*, **696**, 378–387 (2011).
14) Patil A. S., Mo D.-L., Wang H.-Y., Mueller D. S., Anderson L., *Angew. Chem. Int. Ed.*, **51**, 7799–7803 (2012).
15) Tellitu I., Serna S., Herrero M. T., Moreno I., Domínguez E., SanMartin R., *J. Org. Chem.*, **72**, 1526–1529 (2007).
16) Zhu Z., Espenson J. H., *J. Org. Chem.*, **60**, 7728–7732 (1995).
17) Kazem Shiroodi R., Gevorgyan V., *Chem. Soc. Rev.*, **42**, 4991 (2013).
18) Wang S., Zhang G., Zhang L., *Synlett*, **2010**, 692–706 (2010).
19) Marion N., Nolan S. P., *Angew. Chem. Int. Ed.*, **46**, 2750 (2007).
20) Marco-Contelles J., Soriano E., *Chem. Eur. J.*, **13**, 1350–1357 (2007).
21) Mahrwald R., Schick H., *Angew. Chem. Int. Ed. Engl.*, **30**, 593–594 (1991).
22) Fernández C., Diouf O., Momán E., Gómez G., Fall Y., *Synthesis*, **2005**, 1701–1705 (2005).
23) Vijaykumar D., Mao W., Kirschbaum K. S., Katzenellenbogen J. A., *J. Org. Chem.*, **67**, 4904–4910 (2002).
24) Sakaguchi K., Okada T., Shinada T., Ohfune Y., *Tetrahedron Lett.*, **49**, 25–28 (2008).
25) Ji K., Zhao Y., Zhang L., *Angew. Chem. Int. Ed.*, **52**, 6508–6512 (2013).
26) Cai S., Liu Z., Zhang W., Zhao X., Wang D. Z., *Angew. Chem. Int. Ed.*, **50**, 11133–11137 (2011).
27) Zheng H., Huo X., Zhao C., Jing P., Yang J., Fang B., She X., *Org. Lett.*, **13**, 6448–6451 (2011).
28) Oh C. H., Karmakar S., *J. Org. Chem.*, **74**, 370–374 (2009).
29) Buzas A., Gagosz F., *Org. Lett.*, **8**, 515–518 (2006).
30) Zheng H., Zheng J., Yu B., Chen Q., Wang X., He Y., Yang Z., She X., *J. Am. Chem. Soc.*, **132**, 1788–1789 (2010).
31) Chaudhuri R., Pawar S. K., Pati K., Liu R.-S., *Adv. Synth. Catal.*, **354**, 2241–2250 (2012).
32) Lu L., Liu X.-Y., Shu X.-Z., Yang K., Ji K.-G., Liang Y.-M., *J. Org. Chem.*, **74**, 474–477 (2009).
33) Shu X.-Z., Ji K.-G., Zhao S.-C., Zheng Z.-J., Chen J., Lu L., Liu X.-Y., Liang Y.-M., *Chem. Eur. J.*, **14**, 10556–10559 (2008).
34) Cho E. J., Lee D., *Adv. Synth. Catal.*, **350**, 2719–2723 (2008).
35) Zhang G., Catalano V. J., Zhang L., *J. Am. Chem. Soc.*, **129**, 11358–11359 (2007).
36) The reaction likely proceeded by a small amount of water present in the solvent, although water was not added to the reaction.
37) Several other silver salts including $AgSbF_6$, AgOTf and $AgBF_4$ were also investigated, but only trace amounts of the desired product were obtained.
38) Correa A., Marion N., Fensterbank L., Malacria M., Nolan S. P., Cavallo L., *Angew. Chem. Int. Ed.*, **47**, 718–721 (2008).
39) Mokar B. D., Liu R.-S., *J. Chem. Soc., Chem. Commun.*, **50**, 8966 (2014).
40) This ratio was estimated by comparing intensities of the mass spectral peaks of the mixture.
41) Because the reaction solvent would contain a small amount of $H_2{}^{16}O$, unlabeled **12a** would be observed.
42) Yu Y., Yang W., Rominger F., Hashmi A. S. K., *Angew. Chem. Int. Ed.*, **52**, 7586–7589 (2013).
43) Nishimoto Y., Okita A., Yasuda M., Baba A., *Org. Lett.*, **14**, 1846–1849 (2012).
44) Hazra C. K., Oestreich M., *Org. Lett.*, **14**, 4010–4013 (2012).
45) Rettenmeier E., Schuster A. M., Rudolph M., Rominger F., Gade C. A., Hashmi A. S. K., *Angew. Chem. Int. Ed.*, **52**, 5880 (2013).
46) Wang D., Cai R., Sharma S., Jirak J., Thummanapelli S. K., Akhmedov N. G., Zhang H., Liu X., Petersen J. L., Shi X., *J. Am. Chem. Soc.*, **134**, 9012–9019 (2012).
47) Zhang B., Zhu S.-F., Zhou Q.-L., *Tetrahedron*, **69**, 2033–2037 (2013).