Gold-Catalyzed Diastereoselective Synthesis of α-Fluoroenones from Propargyl Acetates

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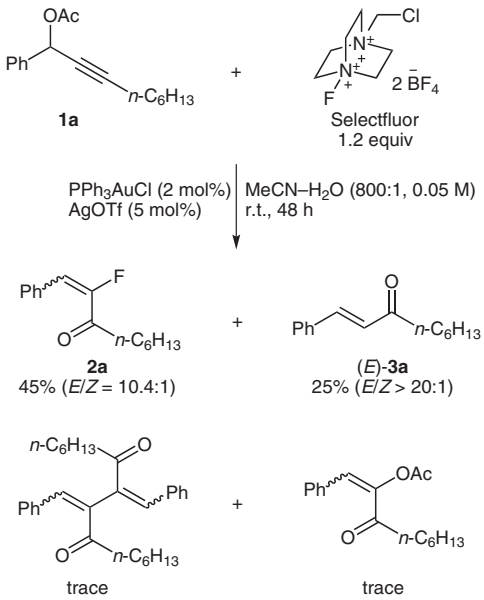
Abstract: A diastereoselective preparation of α-fluoroenones from propargyl acetates has been developed proceeding via a gold-catalyzed rearrangement–fluorination cascade. Control reactions are consistent with a mechanism involving a gold-mediated 3,3-sigmatropic shift followed by a direct, nongold-catalyzed electrophilic fluorination of the allenyl acetate intermediate.

Key words: gold, fluorine, catalysis, diastereoselectivity, rearrangement

Fluorinated compounds are becoming increasingly important as pharmaceuticals and agrochemicals.[2] As such, methods for the introduction of fluorine into complex organic molecules are in high demand. In recent years, significant research attention has focused on the development of transition-metal-catalyzed approaches to C–F bond formation.[3] In 2007, Sadighi and co-workers reported the direct gold-catalyzed hydrofluorination of alkynes with $Et_3N{\cdot}3HF$[4] whilst, the following year, our group reported the first gold-catalyzed fluorination protocol using an electrophilic source of fluorine.[5] Therein, trifluorinated pyranones were obtained upon the gold(I)-mediated cascade cyclization–fluorination of β-hydroxy-α,α-difluoroynones in the presence of Selectfluor. More recently, gold(I) catalysts have been used in combination with Selectfluor to perform oxidative coupling reactions[6] between in situ generated organogold intermediates and benzoates,[7] arylboronic acids,[8] and nonactivated arenes.[9] These transformations are thought to involve Au^I/Au^{III} redox cycles where Selectfluor acts as a stoichiometric oxidant.

In 2009, Zhang and coworkers reported the cascade [3,3]-sigmatropic rearrangement–homodimerization of propargyl acetates catalyzed by gold(I) complexes in the presence of Selectfluor.[10] In the course of this study, α-fluoroenones were observed as minor side products. This observation led us to investigate whether, through optimization of the reaction conditions, α-fluoroenones could be efficiently prepared via this method.[11] These compounds, which contain a $C(sp^2)$–F moiety, are important synthetic intermediates towards fluoroalkenes, which have found applications as peptidomimetics.[12] Currently, synthetic routes towards α-fluoroenones are scarce and are limited to multistep protocols.[13] In this paper, we report the diastereoselective synthesis of these biologically relevant compounds directly from propargyl acetates. In addition, control experiments suggest that a mechanistic scenario involving a cascade gold-catalyzed rearrangement followed by an electrophilic fluorination not involving an organogold intermediate is operational.

As a preliminary study, propargyl acetate **1a** was synthesized and treated with Selectfluor (1.2 equiv), Ph_3PAuCl (2 mol%), and AgOTf (5 mol%) in acetonitrile–water (800:1, 0.05 M) at room temperature for 48 hours. Pleasingly, α-fluoroenones (*E*)-**2a** and (*Z*)-**2a**, resulting from a cascade [3,3]-sigmatropic rearrangement–fluorination process were observed as the major products and isolated in 45% yield. The reaction proceeded with high diastereoselectivity delivering the *E*-isomer as the major product (crude *E*/*Z* ratio = 10.4:1).[14] Importantly, the *E*- and *Z*-isomers could be easily separated by column chromatography. The protonated enone (*E*)-**3a** was also isolated from the reaction mixture in 25% yield (*E*/*Z* > 20:1) whilst trace amounts of products resulting from homocoupling of the propargyl acetate and oxidative cross-coupling with an acetate group were observed by NMR and mass spectrometry (Scheme 1).[10]



Scheme 1 Preliminary studies

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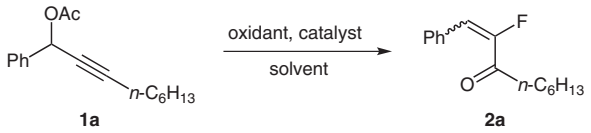
With the aim of identifying standard reaction conditions, optimization studies were carried out using **1a** as a model substrate (Table 1). SIPrAuCl/AgOTf [SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene], was identified as the catalytic system of choice for this transformation, delivering **2a** in 53% isolated yield (68% yield estimated by ^{19}F NMR, entry 2) when heated with Selectfluor in acetonitrile at 80 °C for two hours. Whilst the reaction was still successful with SIPrAuCl in the absence of the silver co-catalyst, this system resulted in a lower yield of fluoroenones (entry 3). AuCl and $AuCl_3$ were less effective catalysts for the rearrangement–fluorination process whilst no fluorinated products were observed in the absence of catalyst or when using 2 mol% of AgOTf or $PtCl_2$ (entries 4–8). Alternative electrophilic fluorinating reagents such as *N*-fluorobenzenesulfonimide (NFSI) and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate were not suitable (entries 12, 13). The yield of fluoroenones and the *E*/*Z* selectivity could be improved upon lowering the reaction temperature to room temperatue and increasing the amount of catalyst (5 mol%), silver co-catalyst (12.5 mol%) and fluorinating reagent (2 equiv). Under these conditions, α-fluoroenones **2a** were isolated in 70% overall yield in a crude *E*/*Z* ratio of 12.5:1 after 48 hours (entry 14).

In order to investigate the effect of the propargyl acetate substitution, substrates **1a**–**k** were prepared according to literature procedures[11a] and treated with Selectfluor and SIPrAuCl/AgOTf in acetonitrile (Table 2).[15] In most cases, the reactions were heated to 40 °C to encourage complete conversion of the starting material in a reasonable reaction time (<72 h). For propargyl acetates **1a**–**h**, which contain only one substituent at the propargylic position, the rearrangement–fluorination process was found to proceed with preferential *E* selectivity. The best diastereoselectivity was observed for substrates bearing a phenyl group (entries 1, 2). In all cases, the *E*- and *Z*-isomers were separable by column chromatography. The *p*-nitrophenyl substituted substrate **1c** was well-tolerated, affording the corresponding (*E*)-α-fluoroenone in 64% yield with an estimated *E*/*Z* ratio of 9.4:1 (entry 3). By contrast, the *p*-methoxyphenyl-substituted variant **1d** led to a complex mixture of products (entry 4). Substrates **1e** and **1f**, bearing alkyl substituents at the propargylic position, reacted successfully with the highest yield and the best diastereoselectivity being observed for the cyclohexyl-substituted compound (yield 80%, *E*/*Z* ratio = 5.2:1, entries 5, 6). The process was less tolerant of propargyl acetates with alkyl substituents at both the propargylic and alkynyl positions. For these compounds, the correspond-

Table 1 Optimization Studies

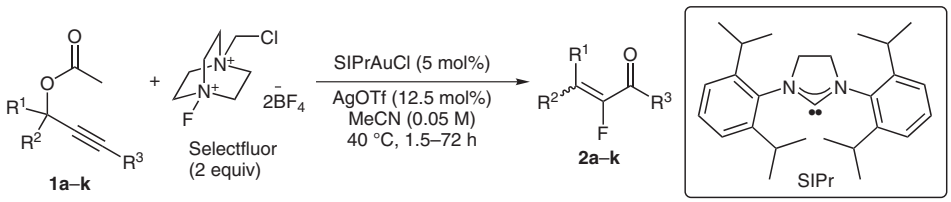


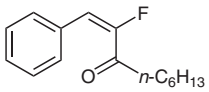
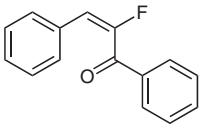
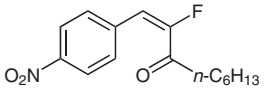
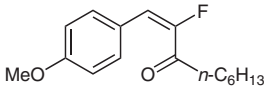
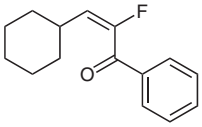
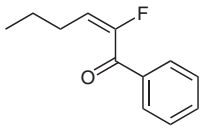
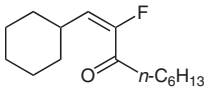
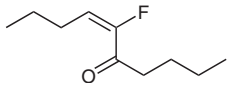
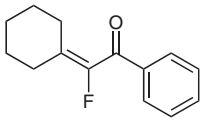
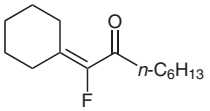
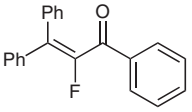
1a **2a**

Entry	Catalyst (mol%)	Conditions[a]	Yield (%)[b]	*E*/*Z*[c]
1	Ph_3PAuCl (2), AgOTf (5)	Selectfluor, MeCN, 80 °C, 2 h	64 (40)	4.4:1
2	SIPrAuCl (2), AgOTf (5)	Selectfluor, MeCN, 80 °C, 2 h	68 (53)	4.2:1
3	SIPrAuCl (2)	Selectfluor, MeCN, 80 °C, 2 h	59	4.0:1
4	AuCl (2)	Selectfluor, MeCN, 80 °C, 2 h	40	3.6:1
5	$AuCl_3$ (2)	Selectfluor, MeCN, 80 °C, 2 h	4	Z only
6	AgOTf (2)	Selectfluor, MeCN, 80 °C, 66 h	–	–
7	$PtCl_2$ (2)	Selectfluor, MeCN, 80 °C, 66 h	trace	–
8	no catalyst	Selectfluor, MeCN, 80 °C, 66 h	–	–
9	SIPrAuCl (2), AgOTf (5)	Selectfluor, MeCN, r.t., 48 h	71	11.6:1
10	SIPrAuCl (5), AgOTf (12.5)	Selectfluor, MeCN, r.t., 48 h	81	10.2:1
11	SIPrAuCl (5), AgOTf (12.5)	Selectfluor, acetone, r.t., 48 h	5	1:4
12	SIPrAuCl (5), AgOTf (12.5)	NFSI, CH_2Cl_2, r.t., 48 h	–	–
13	SIPrAuCl (5), AgOTf (12.5)	[A],[d] MeCN, r.t., 48 h	–	–
14	SIPrAuCl (5), AgOTf (12.5)	Selectfluor (2 equiv), MeCN, r.t., 48 h	100 (70)	12.5:1

[a] Solvent concentration = 0.05 M; 1.2 equiv of oxidant unless otherwise stated.
[b] Yield of **2a** estimated by ^{19}F NMR on the crude reaction mixture with fluorobenzene as internal reference. Isolated yields are in parentheses.
[c] *E*/*Z* ratio determined by ^{19}F NMR on the crude reaction mixture.
[d] [A] = 1-Fluoro-2,4,6-trimethylpyridinium tetrafluoroborate.

Table 2 Rearrangement–Fluorination of Propargyl Acetates **1a–k**



Entry	Propargyl acetate	R^1	R^2	R^3	Time (h)	Major product	Yield (%)[a]	*E*/*Z*[b]
1[c]	**1a**	Ph	H	*n*-C_6H_{13}	48		70 (*E*)-**2a** 64 (*Z*)-**2a** 6	12.5:1
2	**1b**	Ph	H	Ph	24		62 (*E*)-**2b** only	12.2:1
3	**1c**	4-$O_2NC_6H_4$	H	*n*-C_6H_{13}	20		64 (*E*)-**2c** only	9.4:1
4	**1d**	4-$MeOC_6H_4$	H	*n*-C_6H_{13}	20		–[d]	–
5	**1e**	Cy	H	Ph	48		80 (*E*)-**2e** 68 (*Z*)-**2e** 12	5.2:1
6	**1f**	*n*-Pr	H	Ph	72		63 (*E*)-**2f** 42 (*Z*)-**2f** 21	2:1
7	**1g**	Cy	H	*n*-C_6H_{13}	72		29 (*E*)-**2g** only	3.3:1
8	**1h**	*n*-Pr	H	*n*-Bu	72		39 (*E*)-**2h** 19 (*Z*)-**2h** 18	1.4:1
9	**1i**	-$(CH)_5$-		Ph	1.5		**2i** 85	–
10	**1j**	-$(CH)_5$-		*n*-C_6H_{13}	3.5		**2j** 58	–
11	**1k**	Ph	Ph	Ph	24		**2k** 58	–

[a] Isolated yield.
[b] Crude *E*/*Z* ratio determined by ^{19}F NMR. The *E*- and *Z*-isomers were separable by column chromatography.
[c] Reaction performed at r.t.
[d] Complex reaction mixture.

ing α-fluoroenones were isolated in low yields with poor *E*/*Z* selectivities (entries 7, 8). Notably, unlike (*E*)-**2a**,[14] when (*E*)-**2g** (*E*/*Z* > 20:1) was subjected to the reaction conditions, isomerization was observed (*E*/*Z* = 4:1). Substrates **1i–k**, bearing two identical substituents at the propargylic position, reacted readily affording the corresponding α-fluoroenones **2i–k** in moderate to high yields up to 85% (entries 9–11). Compound **2k** was crystalline and allowed for unambiguous assignment of the structure by X-ray crystallographic analysis (Figure 1).

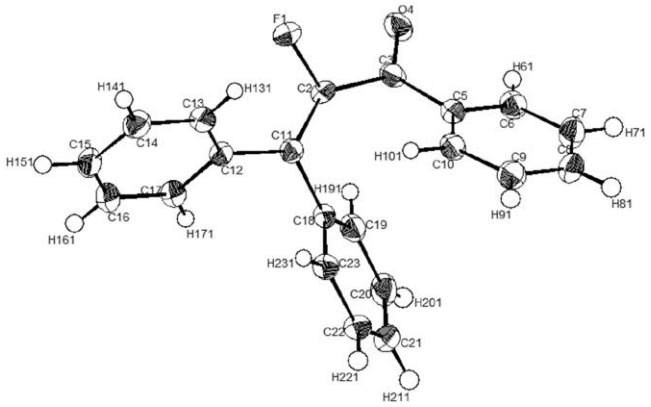
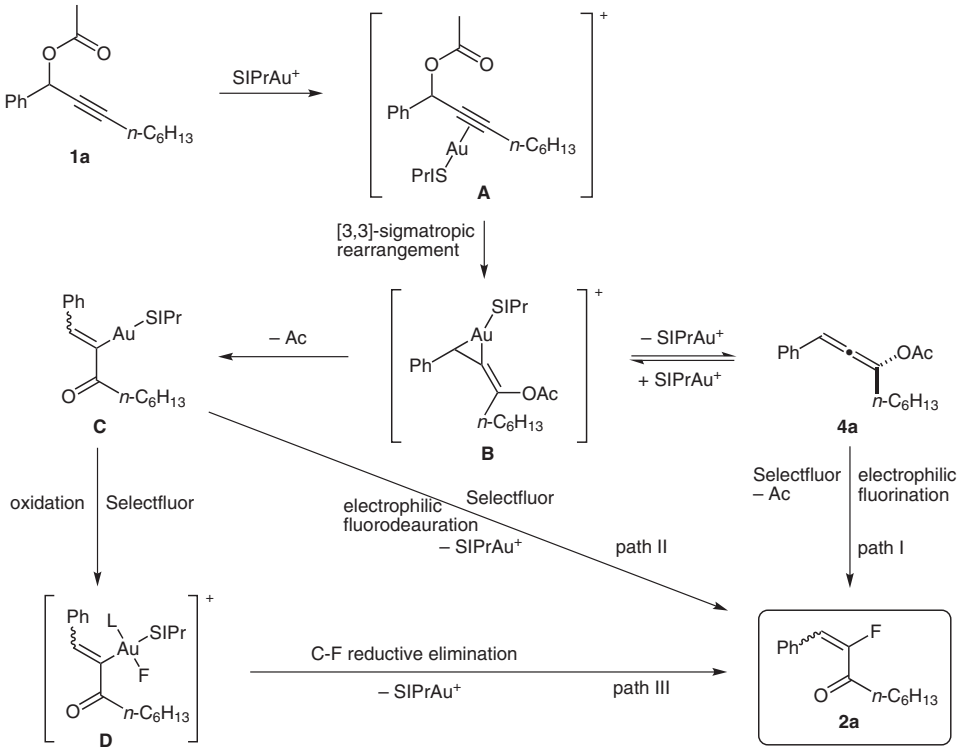


Figure 1 Crystal structure of **2k**

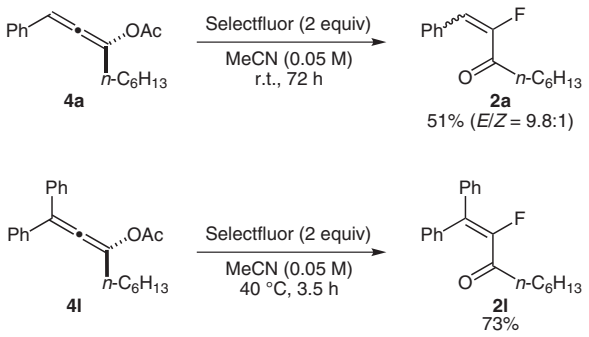
With the scope and limitations of the process established, our attention turned to the reaction mechanism. We envisage three possible mechanistic pathways, all proceeding via an initial gold-catalyzed rearrangement (Scheme 2).[16] Initial coordination of a cationic [SIPrAu]$^+$ species, generated upon treatment with silver(I), to the alkyne (intermediate **A**) followed by a [3,3]-sigmatropic shift affords the allenyl intermediate **B**. DFT calculations on similar substrates have suggested that this intermediate features the gold(I) coordinated to the external double bond.[17] At this stage, decomplexation of the gold could lead to the uncoordinated allenyl acetate **4a**, which, in the presence of Selectfluor could deliver **2a** upon electrophilic fluorination (path I). Alternatively, intermediate **B** could undergo a rearrangement involving the loss of an acetyl group to afford the vinylgold(I) complex **C**. Direct electrophilic 'fluorodeauration' of this species by Selectfluor would deliver the α-fluoroenones **2a** and regenerate the catalyst (path II). The third pathway involves the oxidation of intermediate **C** by Selectfluor to the square planar gold(III) fluoride complex **D**. The C–F bond-forming reductive elimination from this species would again deliver the desired product and regenerate the gold(I) catalyst (path III).

To distinguish between path I and paths II/III, the allenyl acetate **4a** was prepared independently from **1a**[18] and treated with Selectfluor in acetonitrile without gold. After 72 hours at room temperature, α-fluoroenones **2a** were isolated in 51% yield in a crude *E*/*Z* ratio of 9.8:1. In addition, allenyl acetate **4l**[19] led cleanly to the expected α-fluoroenone **2l** in 73% yield when exposed to Selectfluor in acetonitrile at 40 °C for 3.5 hours (Scheme 3). These control reactions suggest that path I, a direct, nongold-catalyzed fluorination pathway is operative for these two compounds. This observation stands in contrast to the mechanism proposed (path III) in a recent report by Nevado et al. which was published during the preparation of this manuscript.[20] The *E* selectivity observed through-



Scheme 2 Plausible reaction mechanisms

out this study is also consistent with a direct electrophilic fluorination mechanism where Selectfluor approaches the allene from the least hindered face. Indeed, previous studies involving intermediates of type **C** would predict a *Z*-selective fluorination if paths II or III were operating.[11] Although gold(III) fluoride complexes of type **D** have been suggested in the literature, these have not been isolated or spectroscopically characterized. Studies to determine the extent to which a gold-catalyzed fluorination pathway (paths II and III) competes with direct electrophilic fluorination (path I) are ongoing in our laboratory.



Scheme 3 Electrophilic fluorination of allenes **4a** and **4l**

In conclusion, we have developed a diastereoselective preparation of α-fluoroenones from propargyl acetates via a gold-catalyzed cascade rearrangement–fluorination process. Control reactions support a mechanism involving a gold-mediated 3,3-sigmatropic shift followed by a direct, nongold-catalyzed electrophilic fluorination of the allenyl acetate intermediate.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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References and Notes

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(14) Compounds (*E*)-**2a** and (*Z*)-**2a** were stable towards isomerization under the reaction conditions implying that the observed diastereoselectivity is under kinetic control.

(15) **General Procedure for Rearrangement–Fluorination Process**
Selectfluor (2 equiv), SIPrAuCl (5 mol%), and silver trifluoromethanesulfonate (12.5 mol%) were added to a solution of the propargyl acetate (1 equiv) in MeCN (0.05 M). The mixture was stirred at r.t. or 40 °C until TLC showed consumption of the propargyl acetate (1.5–72 h). H_2O was added, and the mixture was extracted with EtOAc (3×). The combined organic fractions were washed with brine, dried with anhyd $MgSO_4$, filtered, and the solvents removed in vacuo. The crude mixture was purified by column chromatography on silica gel.
Preparation of 2a
The general procedure was followed using **1a** (500 mg, 1.94 mmol), Selectfluor (1.37 g, 3.87 mmol), SIPrAuCl (60 mg, 0.10 mmol), and AgOTf (62 mg, 0.24 mmol) in MeCN (39 mL). The reaction was stirred for 48 h at r.t. ^{19}F NMR analysis on the crude reaction mixture indicated an *E*/*Z* ratio of 12.5:1. Purification by column chromatography on silica gel (hexane–Et_2O = 20:1) afforded the product (*E*)-**2a** as a yellow oil (290 mg, yield 64%) as well as (*Z*)-**2a** as a yellow solid (24 mg, yield 6%).
(*E*)-2-Fluoro-1-phenylnon-1-en-3-one [(*E*)-2a]
R_f = 0.50 (hexane–Et_2O = 9:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.64 (m, 2 H), 7.35–7.40 (m, 3 H), 6.70 (d, 1 H, *J* = 25.3 Hz), 2.65 (dt, 2 H, *J* = 7.1, 3.5 Hz), 1.63 (tt, 2 H, *J* = 7.3, 7.1 Hz), 1.27–1.36 (m, 6 H), 0.90 (dd, 3 H, *J* = 6.8,

6.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.6 (d, *J* = 38 Hz), 153.1 (d, *J* = 258 Hz), 130.9 (d, *J* = 10 Hz), 130.0 (d, *J* = 2 Hz), 129.2, 128.2, 119.7 (d, *J* = 27 Hz), 40.2 (d, *J* = 2 Hz), 31.6, 28.8, 23.2 (d, *J* = 2 Hz), 22.5, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –114.9 (dt, *J* = 25, 4 Hz). IR (neat): 1708 (C = O). HRMS (ESI$^+$): *m/z* calcd for $C_{15}H_{19}FNaO^+$ [M + Na]$^+$: 257.1314; found: 257.1312.

(*Z*)-2-Fluoro-1-phenylnon-1-en-3-one [(*Z*)-2a]

Mp 30 °C. R_f = 0.42 (hexane–Et_2O = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.70 (m, 2 H), 7.38–7.44 (m, 3 H), 6.83 (d, 1 H, *J* = 36.9 Hz), 2.74 (dt, 2 H, *J* = 7.3, 2.3 Hz), 1.69 (tt, 2 H, *J* = 7.5, 7.3 Hz), 1.27–1.41 (m, 6 H), 0.91 (dd, 3 H, *J* = 7.0, 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1 (d, *J* = 32 Hz), 154.1 (d, *J* = 272 Hz), 131.2 (d, *J* = 4 Hz), 130.6 (d, *J* = 9 Hz), 129.7 (d, *J* = 3 Hz), 128.8, 114.9 (d, *J* = 6 Hz), 38.0, 31.6, 28.8, 23.5 (d, *J* = 2 Hz), 22.5, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ = –125.0 (d, *J* = 37 Hz). IR (CH_2Cl_2): 1697 (C = O). HRMS (FI$^+$): *m/z* calcd for $C_{15}H_{19}FO$ [M]$^+$: 234.1420; found: 234.1414.

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(19) Allenyl acetate **4l** was isolated as the only acetylated product during the attempted preparation of the corresponding propargyl acetate **1l** according to the procedure of ref. 11a. This compound is presumably formed via a spontaneous 3,3-sigmatropic rearrangement of **1l**.
(20) de Haro, T.; Nevado, C. *Chem. Commun.* **2010**, in press; DOI: 10.1039/c002679d.