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Stereoselective Synthesis of α-Trifluoromethyl Enones by Au^I/Cu^I-Co-Catalyzed Tandem 1,3-Acyloxy Migration/Trifluoromethylation Reaction of Propargyl Acetates

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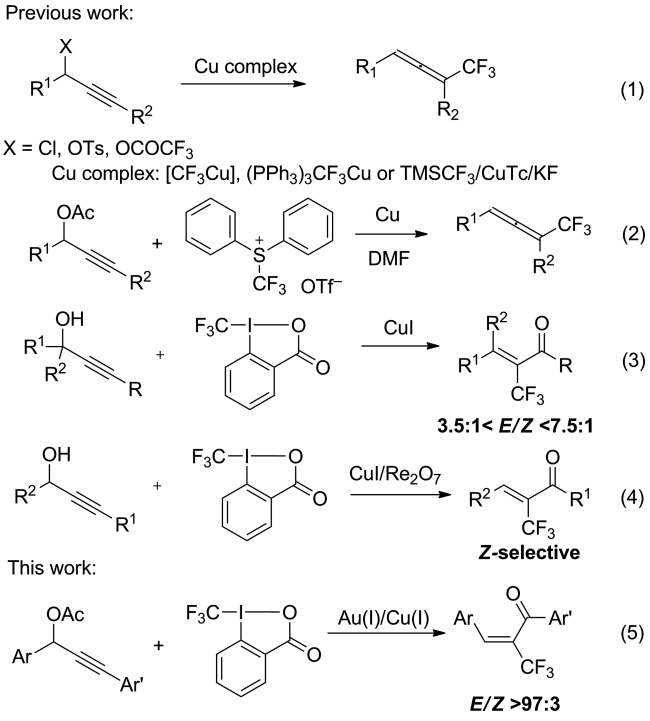
Keywords: Synthetic methods / Trifluoromethylation / Gold / Copper / Stereooselectivity / Enones

Au^I/Cu^I-co-catalyzed tandem 1,3-acyloxy migration/trifluoromethylation reaction of propargyl esters to give α-trifluoromethyl enones in moderate yields and with excellent stereoselectivity is described. It is proposed that the reaction proceeds through the 1,3-acyloxy migration of the propargyl esters catalyzed by Au^I to produce an allenic intermediate, followed by its trifluoromethylation to give the final product.

Introduction

Compounds that contain a trifluoromethyl moiety have proved to be very important in pharmaceuticals and agrochemicals owing to its unique properties, such as metabolic stability, strong electronegativity, and good lipophilicity.[1] Consequently, intensive research efforts have been made towards the development of versatile approaches for incorporation of trifluoromethyl functionality.[2] In recent years, transition-metal-mediated or -catalyzed trifluoromethylation reactions have emerged as powerful synthetic tools because of their high level of functional group tolerance and mild reaction conditions.[3] However, in these studies, gold has never been reported to be involved in trifluoromethylation reactions except in the trifluoromethylation of gold complexes.[4] In this paper, we describe the Au^I/Cu^I-co-catalyzed tandem 1,3-acyloxy migration/trifluoromethylation reaction of propargyl esters to α-trifluoromethyl enones, which to date has been largely unexplored.[5]

Propargyl esters and halides have been found to be valuable building blocks in synthetic chemistry.[6] Trifluoromethylation of these intermediates by employing a $CuCF_3$ reagent prepared in advance or generated in situ from nucleophilic trifluoromethyl sources has been reported, but these processes give trifluoromethyl-allenes as final products (Scheme 1, Equation 1).[7] We have also found that the use of electrophilic trifluoromethylating reagent (*S*-trifluoromethyl)diphenyl sulfonium triflate results in the same conversion in the presence of copper powder (Scheme 1, Equation 2).[8] During the preparation of this manuscript, Liu and co-workers reported a domino copper-catalyzed trifluoromethylated Meyer–Schuster rearrangement reaction of propargyl alcohols with Togni's reagent **II** that leads



Scheme 1. Trifluoromethylation reactions of propargyl halides and esters; DMF = dimethylformamide.

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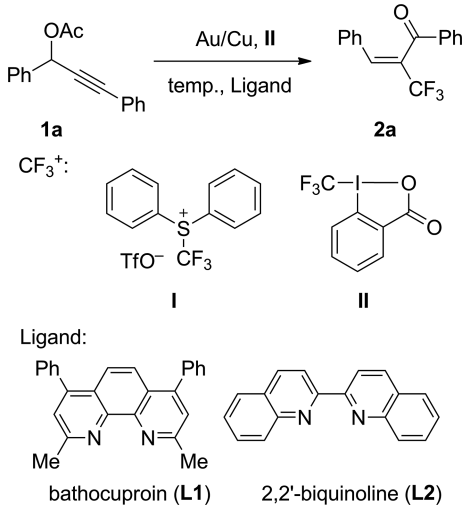
to α-trifluoromethyl enone products (Scheme 1, Equation 3).[9] However, the transformation works less well for a 1-aryl-substituted substrate (R^1 = Ar) than for 1,1-dialkyl-substituted or 1-alkyl-substituted substrates, and only one example of a 1-aryl-substituted substrate was described in 34% yield. Furthermore, stereoselectivity is an issue that remains to be addressed. Interestingly, Sodeoka and coworkers found that dual catalysis with copper and rhenium for trifluoromethylation of propargyl alcohols resulted in *Z*-selectivity (Scheme 1, Equation 4).[10] It is well known that propargylic esters undergo 1,3-acyloxy migration catalyzed by gold to give allenic intermediates,[11] which could applied to a variety of further transformations. In continuation of our research interest into the chemistry of trifluoromethylation,[8,12] we have investigated the Au^I/Cu^I-co-catalyzed tandem 1,3-acyloxy migration/trifluoromethylation reaction of 1-arylpropargyl esters; a transformation that gives α-trifluoromethyl enones with excellent stereoselectivity (*E*/*Z* > 97:3; Scheme 1, Equation 5).

Results and Discussion

Our initial attempts at gold-catalyzed electrophilic trifluoromethylation reactions of propargylic esters in acetonitrile failed, although similar halogenation reactions have been reported (Table 1, Entries 1–3).[13] In dichloromethane, a trace amount of desired product was detected by ^{19}F NMR spectroscopy (Table 1, Entry 4). The presence of CuTc improved the yield slightly (Table 1, Entry 5). An examination of the copper source showed that $(MeCN)_4CuPF_6$ gave better results (Table 1, Entries 7 versus 5 and 6). The use of a AuCl/AgOTf catalytic system instead of AuCl resulted in a lower yield (Table 1, Entry 8). Other catalytic systems composed of various gold complexes and silver triflate were not effective (Table 1, Entries 9–11). However, we found that a catalytic amount of a ligand was favorable for this reaction (Table 1, Entries 12 and 13) and 2,2′-biquinoline was identified as a suitable ligand (Table 1, Entry 13). The reaction in 1,2-dichloroethane (DCE) proceeded much better in 52% yield (Table 1, Entry 14). A rise in the reaction temperature led to an inferior result (Table 1, Entry 15), whereas a decrease in temperature gave a slightly higher yield (Table 1, Entry 16). Gold complex $Ph_3PAuNTf_2$, prepared by anion metathesis between Ph_3PAuCl and $AgNTf_2$, served as a highly efficient and air-stable catalyst.[14] In our reaction system this catalyst gave superior results (Table 1, Entry 17). Use of both the gold and copper complexes were necessary for this conversion, and the absence of either significantly suppressed the desired transformation. This difference indicates that this reaction proceeds through a different path relative to that of the reported halogenation reaction (Table 1, Entries 18 and 19).[13] Without the presence of gold complex, substrate **1a** remained intact (Table 1, Entry 18). Without the presence of copper complex, the reaction was complex and only trace substrate **1a** remained (Table 1, Entry 19). Another copper source, CuOTf, was also suitable, even with a lower loading (Table 1, Entries 20 and 21).

Table 1. Au^I/Cu^I-co-catalyzed trifluoromethylation reactions of **1a**[a].



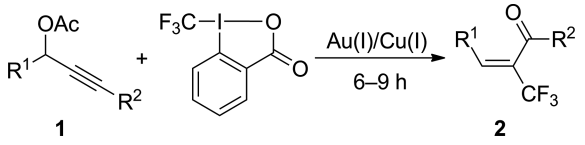
Entry	Au	Cu	Solvent	Temp.	Yield [%][b]
1[c]	PPh_3AuCl	–	CH_3CN	60	0
2	PPh_3AuCl	–	CH_3CN	60	0
3	AuCl	–	CH_3CN	60	0
4	AuCl	–	CH_2Cl_2	45	trace
5	AuCl	CuTc	CH_2Cl_2	45	11
6	AuCl	$Cu(OTf)_2$	CH_2Cl_2	45	10
7	AuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	12
8[d]	AuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	5
9[d]	PPh_3AuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	13
10[d]	IPrAuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	11
11[d]	SIPrAuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	8
12[d],[e]	Ph_3PAuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	24
13[d],[f]	Ph_3PAuCl	$(MeCN)_4CuPF_6$	CH_2Cl_2	45	30
14[f],[g]	Ph_3PAuCl	$(MeCN)_4CuPF_6$	DCE	45	52
15[f],[g]	Ph_3PAuCl	$(MeCN)_4CuPF_6$	DCE	80	46
16[f],[g]	Ph_3PAuCl	$(MeCN)_4CuPF_6$	DCE	r.t.	53
17[f]	$Ph_3PAuNTf_2$	$(MeCN)_4CuPF_6$	DCE	r.t.	64
18[f]	–	$(MeCN)_4CuPF_6$	DCE	r.t.	0
19[f]	$Ph_3PAuNTf_2$	–	DCE	r.t.	trace
20[f]	$Ph_3PAuNTf_2$	CuOTf	DCE	r.t.	64
21[f],[h]	$Ph_3PAuNTf_2$	CuOTf	DCE	r.t.	68

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 equiv.), **II** (1.0 equiv.), [Au] (10 mol-%), [Cu] (10 mol-%), in solvent (3 mL). [b] Determined by ^{19}F NMR spectroscopy. [c] Reagent **I** (1.0 equiv.) was used instead of **II**. [d] AgOTf (10 mol-%) was added. [e] Bathocuproin **L1** (10 mol-%) was added. [f] 2,2′-Biquinoline **L2** (10 mol-%) was added. [g] $AgPF_6$ (10 mol-%) was added. [h] CuOTf (5 mol-%) was used.

To explore the scope of this trifluoromethylation reaction the optimized conditions (Table 1, Entry 21) were applied to the reaction of a variety of propargyl esters with Togni's reagent. As shown in Table 2, the reaction proceeded well with a variety of substrates and gave the corresponding trifluoromethylation products in moderate yields and with excellent stereoselectivity (*E*/*Z* > 97:3). Irrespective of whether the aryl group at the 1-position contained an electron-withdrawing or electron-donating group, the products were obtained in moderate yields (Table 2, Entries 1–9). Substrates with electron-donating groups on the 3-phenyl ring were converted smoothly into the expected products (Table 2,

Entries 10–13), whereas the transformations of substrates with electron-withdrawing groups on 3-phenyl ring were quite complex. This tandem reaction cannot be applied well to alkyl-substituted substrates (Table 2, Entries 14 and 15).

Table 2. Au^I/Cu^I-co-catalyzed trifluoromethylation reaction of propargyl acetates[a].



1 2

Entry	R^1	R^2	**2**, Yield [%][b]
1	Ph	Ph	**2a**, 56
2	4-Me-C_6H_4	Ph	**2b**, 46
3	4-Ph-C_6H_4	Ph	**2c**, 58
4	2-Cl-C_6H_4	Ph	**2d**, 49
5	3-Cl-C_6H_4	Ph	**2e**, 40
6	3-F-C_6H_4	Ph	**2f**, 38
7	4-Br-C_6H_4	Ph	**2g**, 45
8	3,5-Br_2-C_6H_3	Ph	**2h**, 40
9	4-MeO_2C-C_6H_4	Ph	**2i**, 42
10	Ph	4-Ph-C_6H_4	**2j**, 60
11	Ph	4-MeO-C_6H_4	**2k**, 68
12	Ph	3-Me-C_6H_4	**2l**, 45
13	Ph	4-pentyl-C_6H_4	**2m**, 52
14	Ph	*n*Bu	**2n**, 25[c]
15	Cy	Ph	**2o**, 9[c]

[a] Propargyl acetate (0.3 mmol, 1.0 equiv.), II (1 equiv.), $Ph_3PAuNTf_2$ (10%), CuOTf (5%) and 2,2′-biquinoline (10%) in DCE (3 mL) at room temperature. [b] Isolated yields. [c] Determined by ^{19}F NMR spectroscopy.

The structure of product **2i** was determined by single-crystal X-ray diffraction (Figure 1).[15] The structures of the other products were determined by analogy.

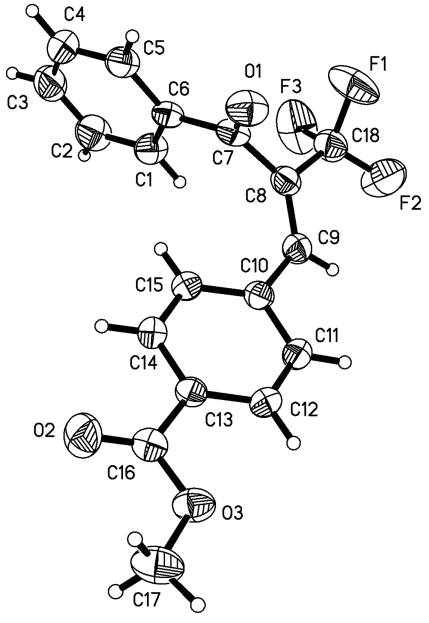
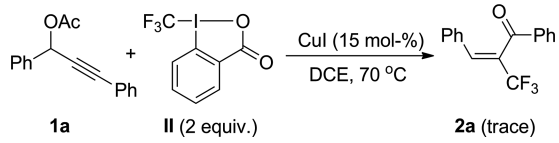


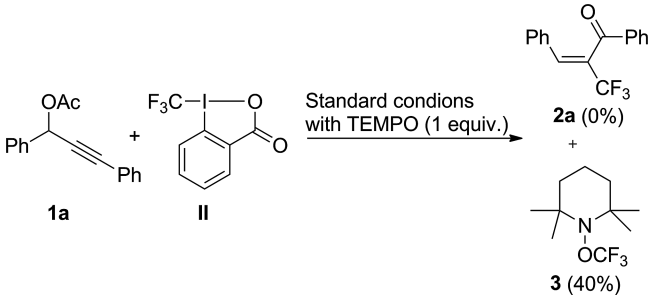
Figure 1. Crystal structure of **2i**.

The group of Liu has previously described the copper-catalyzed trifluoromethylation reaction of propargyl alcohols to afford α-trifluoromethyl enones.[9] Unfortunately, their reaction conditions are not suitable for the trifluoromethylation reaction of propargyl esters, even though 2 equiv. of Togni's reagent was used (Scheme 2). Therefore, Liu's and our protocols are complementary for the trifluoromethylation reaction of different substrates that lead to α-trifluoromethyl enones.



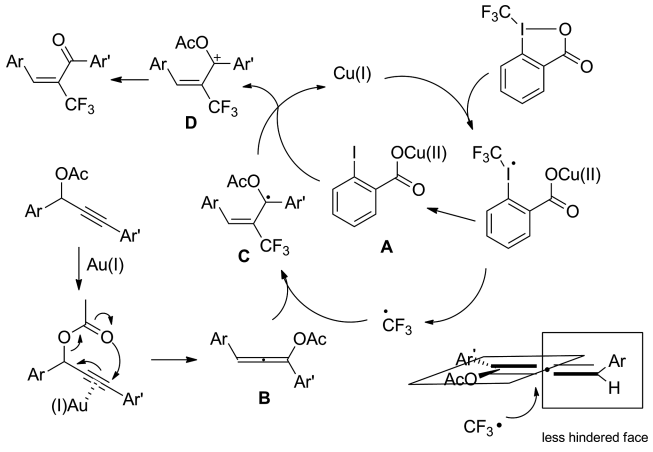
Scheme 2. Attempts at the trifluoromethylation reaction of propargyl acetate by using a previously described method.[9]

The trifluoromethylation of propargyl esters might involve a radical process. Well-known radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) can suppress the desired reaction completely (Scheme 3). A radical trap reaction gave TEMPO-CF_3 complex **3** in 40% yield as determined by ^{19}F NMR spectroscopy.



Scheme 3. Examination of a radical process.

On the basis of our and related reports,[2h,2i,11] we propose the reaction mechanism as shown in Scheme 4. The redox reaction of Togni's reagent with Cu^I affords Cu^{II} (intermediate **A**) and a trifluoromethyl radical. The trifluoromethyl radical is trapped by allenic intermediate **B**, which



Scheme 4. Proposed mechanism for the trifluoromethylation reaction of propargyl acetates.

is generated from the propargyl esters in the presence of gold, to selectively give radical intermediate **C** with the CF_3 group *trans* to Ar (*E*-selective isomer). The trifluoromethyl radical should approach the more electron-rich enolic C–C double bond from the less-hindered face. Subsequent oxidization of radical intermediate **C** by Cu^{II} releases Cu^{I} and cationic intermediate **D**, which is transformed into the final product.

Conclusions

In conclusion, we have described Au^{I}/Cu^{I}-cocatalyzed tandem 1,3-acyloxy migration/trifluoromethylation reactions of 1-arylpropargyl esters to give α-trifluoromethyl enones with excellent stereoselectivity and in moderate yields. Both gold and copper complexes were necessary for this transformation. To the best of our knowledge, this is the first report of the trifluoromethylation reaction of organic intermediates in which gold is involved.

Experimental Section

General Information: ^1H, ^{13}C and ^{19}F NMR spectra were recorded with a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^1H, ^{13}C and ^{19}F NMR were recorded as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet). Mass spectra were obtained on a GC-MS. HRMS data were recorded in EI or ESI mode.

General Procedure for the Preparation of Propargyl Acetates: Propargyl acetates were synthesized according to the procedure reported in literature.[12]

1,3-Diphenylprop-2-yn-1-yl Acetate (1a): Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.56 (m, 2 H), 7.50–7.45 (m, 2 H), 7.43–7.33 (m, 3 H), 7.33–7.24 (m, 3 H), 6.70 (s, 1 H), 2.11 (s, 3 H) ppm.

3-Phenyl-1-(*p*-tolyl)prop-2-yn-1-yl Acetate (1b): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.46 (m, 4 H), 7.41–7.28 (m, 3 H), 7.26–7.21 (m, 2 H), 6.72 (s, 1 H), 2.39 (s, 3 H), 2.13 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.86, 138.93, 134.33, 131.92, 129.39, 128.77, 128.29, 127.84, 122.20, 86.89, 85.83, 66.02, 21.25, 21.16 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2924, 2229, 2202, 1739, 1490, 1368, 1219, 1012, 815, 755, 690 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{16}O_2$ 264.1150; found 264.1147.

1-([1,1′-Biphenyl]-4-yl)-3-phenylprop-2-yn-1-yl Acetate (1c): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.55 (m, 6 H), 7.52–7.47 (m, 2 H), 7.47–7.40 (m, 2 H), 7.39–7.28 (m, 4 H), 6.75 (s, 1 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.86, 141.97, 140.52, 136.13, 131.94, 128.84, 128.83, 128.30, 127.58, 127.47, 127.19, 122.09, 87.16, 85.57, 65.90, 21.18 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3031, 2229, 1738, 1487, 1218, 1008, 754, 691 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{18}O_2$ 326.1307; found 326.1310.

1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-yl Acetate (1d): Yellow solid, m.p. 73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.83 (m, 1 H), 7.51–7.46 (m, 2 H), 7.44–7.39 (m, 1 H), 7.38–7.28 (m, 5 H), 6.98 (s, 1 H), 2.15 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.43, 134.54, 133.45, 131.93, 130.20, 129.80, 129.50, 128.85, 128.24, 127.10, 121.94, 87.32, 84.54, 63.31, 20.86 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 2229, 1742, 1474, 1369, 1215, 1214, 1014, 954, 913, 752, 689 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}ClO_2$ 284.0604; found 284.0601.

1-(3-Chlorophenyl)-3-phenylprop-2-yn-1-yl Acetate (1e): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 7.55–7.42 (m, 3 H), 7.40–7.27 (m, 5 H), 6.66 (s, 1 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.58, 139.16, 134.56, 131.94, 129.99, 129.10, 129.01, 128.35, 127.86, 125.91, 121.82, 87.48, 84.98, 65.29, 21.02 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2230, 1740, 1368, 1215, 1014, 788, 755, 688 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}ClO_2$ 284.0604; found 284.0602.

1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-yl Acetate (1f): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.44 (m, 2 H), 7.41–7.27 (m, 6 H), 7.14–6.99 (m, 1 H), 6.68 (s, 1 H), 2.15 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.71, 162.77 (d, J = 246.8 Hz), 139.50 (d, J = 7.4 Hz), 131.93, 130.24 (d, J = 8.2 Hz), 128.97, 128.32, 123.35 (d, J = 3.0 Hz), 121.79, 115.91 (d, J = 21.2 Hz), 114.75 (d, J = 22.6 Hz), 87.33, 84.90, 65.29 (d, J = 2.0 Hz), 21.08 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2230, 2228, 1742, 1594, 1489, 1215, 1014, 755, 688 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}FO_2$ 268.0900; found 268.0906.

1-(4-Bromophenyl)-3-phenylprop-2-yn-1-yl Acetate (1g): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 2 H), 7.49–7.45 (m, 4 H), 7.34–7.29 (m, 3 H), 6.65 (s, 1 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.68, 136.25, 131.89, 131.84, 129.48, 128.95, 128.31, 123.09, 121.82, 87.36, 85.02, 65.40, 21.07 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2229, 1738, 1487, 1368, 1217, 1010, 818, 754, 689 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}BrO_2$ 328.0099; found 328.0104.

1-(3,5-Dibromophenyl)-3-phenylprop-2-yn-1-yl Acetate (1h): White solid, m.p. 73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.63 (m, 3 H), 7.54–7.44 (m, 2 H), 7.42–7.29 (m, 3 H), 6.60 (s, 1 H), 2.16 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.46, 140.84, 134.52, 131.95, 129.49, 129.13, 128.34, 123.10, 121.52, 87.92, 84.20, 64.49, 21.00 ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2962, 2927, 2232, 1741, 1559, 1214, 1014, 855, 755, 737, 688 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{12}Br_2O_2$ 405.9204; found 405.9206.

Methyl 4-(1-Acetoxy-3-phenylprop-2-yn-1-yl)benzoate (2i): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10–8.03 (m, 2 H), 7.70–7.61 (m, 2 H), 7.52–7.42 (m, 2 H), 7.36–7.27 (m, 3 H), 6.72 (s, 1 H), 3.91 (s, 3 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.64, 166.53, 141.86, 131.90, 130.57, 129.97, 128.97, 128.30, 127.58, 121.78, 87.55, 84.88, 65.46, 52.21, 21.03 ppm. IR (KBr): $\tilde{\nu}$ = 2952, 2230, 1721, 1275, 1216, 1106, 1015, 756, 690 cm^{-1}. HRMS (EI): calcd. for $C_{19}H_{16}O_4$ 308.1049; found 308.1050.

3-([1,1′-Biphenyl]-4-yl)-1-phenylprop-2-yn-1-yl Acetate (1j): Yellow solid, m.p. 110 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.51 (m, 8 H), 7.51–7.30 (m, 6 H), 6.72 (s, 1 H), 2.14 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.88, 141.53, 140.18, 137.14, 132.35, 128.99, 128.86, 128.72, 127.83, 127.73, 127.03, 126.95, 120.93, 86.93, 86.19, 66.14, 21.19 ppm. IR (KBr): $\tilde{\nu}$ = 3062, 3033, 2300, 1739, 1486, 1369, 1220, 1013, 951, 840, 763, 697 cm^{-1}. HRMS (EI): calcd. for $C_{23}H_{18}O_2$ 326.1307; found 326.1310.

3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-yl Acetate (1k): Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.55 (m, 2 H), 7.48–7.31 (m, 5 H), 6.88–6.78 (m, 2 H), 6.70 (s, 1 H), 3.79 (s, 3 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.84, 159.98, 137.37, 133.43, 128.86, 128.64, 127.77, 114.13, 113.89, 87.08, 84.25, 66.22, 55.26, 21.15 ppm. IR (KBr): $\tilde{\nu}$ = 2935, 2838, 2228, 1736, 1605, 1509, 1218, 1014, 831, 697 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{16}O_3$ 280.1099; found 280.1102.

1-Phenyl-3-(*m*-tolyl)prop-2-yn-1-yl Acetate (1l): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.56 (m, 2 H), 7.44–7.35 (m, 3 H), 7.33–7.26 (m, 2 H), 7.22–7.17 (m, 1 H), 7.16–7.12 (m, 1 H), 6.69 (s, 1 H), 2.31 (s, 3 H), 2.12 (s, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.86, 137.98, 137.19, 132.49, 129.70, 128.97, 128.94, 128.68, 128.18, 127.82, 121.85, 87.24, 85.17, 66.11, 21.18 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 3035, 2922, 2234, 1737, 1368, 1218, 1013, 949, 784, 691 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{16}O_2$ 264.1150; found 264.1147.

3-(4-Pentylphenyl)-1-phenylprop-2-yn-1-yl Acetate (1m): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 2 H), 7.46–7.30 (m, 5 H), 7.14–7.09 (m, 2 H), 6.70 (s, 1 H), 2.59 (t, J = 7.6 Hz, 2 H), 2.12 (s, 3 H), 1.64–1.55 (m, 2 H), 1.42–1.21 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.83, 144.00, 137.28, 131.82, 128.87, 128.63, 128.37, 127.79, 119.18, 87.29, 84.87, 66.15, 35.84, 31.37, 30.86, 22.48, 21.14, 13.99 ppm. IR (KBr): $\tilde{\nu}$ = 2956, 2928, 2857, 2230, 1740, 1509, 1455, 1386, 1220, 1013, 697 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{24}O_2$ 320.1776; found 320.1780.

General Trifluoromethylation Procedure for the Propargyl Acetates: PPh_3AuNTf_2 (22.2 mg, 0.03 mmol), CuOTf (3.2 mg, 0.015 mmol), Togni's reagent II (94.8 mg, 0.3 mmol), propargyl acetate (0.3 mmol), and DCE (3 mL) were added sequentially to a flame-dried tube under argon. The tube was then sealed and the resulting mixture was stirred at room temperature. When the reaction was complete, as monitored by ^{19}F NMR spectroscopy, the crude reaction mixture was filtered through a short pad of silica gel and eluted with CH_2Cl_2. After evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/dichloromethane) to afford the desired product.

(*E*)-1,3-Diphenyl-2-(trifluoromethyl)prop-2-en-1-one (2a): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 2 H), 7.53–7.46 (m, 2 H), 7.39–7.31 (m, 2 H), 7.29–7.13 (m, 5 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.61 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.65, 136.91 (q, J = 5.9 Hz), 135.38, 134.26, 131.94, 130.12, 129.58, 129.53, 128.75, 128.69 (q, J = 30.1 Hz), 128.66, 122.28 (q, J = 274.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3063, 1665, 1450, 1292, 1157, 1121, 935, 687 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{11}F_3O$ 276.0762; found 276.0760.

(*E*)-1-Phenyl-3-(*p*-tolyl)-2-(trifluoromethyl)prop-2-en-1-one (2b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.82 (m, 2 H), 7.50 (tt, J = 7.5, 1.4 Hz, 1 H), 7.44 (s, 1 H), 7.39–7.32 (m, 2 H), 7.16–7.10 (m, 2 H), 7.01–6.95 (m, 2 H), 2.22 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.44 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.93, 140.62, 136.83 (q, J = 6.0 Hz), 135.47, 134.21, 129.65, 129.60, 129.42, 129.09, 128.76, 127.51 (q, J = 29.8 Hz), 122.43 (q, J = 274.2 Hz), 21.25 ppm. IR (KBr): $\tilde{\nu}$ = 3050, 1662, 1450, 1293, 1190, 1148, 1057, 953, 924, 849, 723, 699, 649 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}F_3O$ 290.0918; found 290.0923.

(*E*)-3-([1,1′-Biphenyl]-4-yl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2c): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.95 (m, 2 H), 7.57–7.47 (m, 4 H), 7.47–7.37 (m, 6 H), 7.37–7.30 (m, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.40 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.79, 142.79, 139.60, 136.44 (q, J = 5.9 Hz), 135.46, 134.37, 130.80, 130.17, 129.65, 128.86, 128.85, 128.44 (q, J = 29.9 Hz), 127.96, 127.25, 126.93, 122.39 (q, J = 274.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 3033, 1665, 1291, 1121, 798, 724, 697 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{15}F_3O$ 352.1075; found 352.1077.

(*E*)-3-(2-Chlorophenyl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.73 (m, 3 H), 7.43 (tt, J = 7.4, 1.4 Hz, 1 H), 7.34–7.22 (m, 3 H), 7.17–7.07 (m, 2 H), 6.96 (td, J = 7.6, 0.6 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.19 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.74, 135.50, 134.81 (q, J = 6.1 Hz), 134.13, 133.79, 131.06, 131.01, 130.73 (q, J = 30.2 Hz), 130.52, 129.48, 129.28, 128.59, 126.79, 121.91 (q, J = 274.7 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 1668, 1594, 1292, 1162, 1058, 757, 717, 687 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{10}ClF_3O$ 310.0372; found 310.0369.

(*E*)-3-(3-Chlorophenyl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.83 (m, 2 H), 7.51 (tt, J = 7.4, 1.4 Hz, 1 H), 7.45–7.40 (m, 1 H), 7.39–7.33 (m, 2 H), 7.24–7.21 (m, 1 H), 7.19–7.15 (m, 1 H), 7.11–7.08 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.88 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.08, 135.32 (q, J = 6.0 Hz), 135.23, 134.65, 134.48, 133.67, 130.27 (q, J = 30.2 Hz), 130.07, 129.92, 129.49, 128.85, 127.26, 122.00 (q, J = 274.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3066, 2320, 1665, 1369, 1287, 1214, 1160, 927, 908, 785, 683, 616 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{10}ClF_3O$ 310.0372; found 310.0377.

(*E*)-3-(3-Fluorophenyl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2f): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.85 (m, 2 H), 7.52 (tt, J = 7.4, 1.6 Hz, 1 H), 7.44 (s, 1 H), 7.41–7.34 (m, 2 H), 7.19–7.11 (m, 1 H), 7.06–7.00 (m, 1 H), 6.98–6.87 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.87 (s, 3 F), –110.80 to –110.89 (m, 1 F). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.13, 162.43 (d, J = 247.7 Hz), 135.40 (qd, J = 5.9, 2.6 Hz), 135.20, 134.49, 134.01 (d, J = 7.9 Hz), 130.34 (d, J = 8.3 Hz), 130.17 (q, J = 29.9 Hz), 129.53, 128.85, 125.22 (d, J = 2.9 Hz), 122.01 (q, J = 274.5 Hz), 117.08 (d, J = 21.2 Hz), 116.13 (d, J = 22.7 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3069, 1665, 1585, 1234, 1123, 789, 683 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{10}F_4O$ 294.0668; found 294.0669.

(*E*)-3-(4-Bromophenyl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2g): White solid, m.p. 69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.79 (m, 2 H), 7.52 (tt, J = 7.4, 1.3 Hz, 1 H), 7.43–7.34 (m, 3 H), 7.33–7.27 (m, 2 H), 7.13–7.06 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.74 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.32, 135.45 (q, J = 6.0 Hz), 135.14, 134.57, 131.98, 130.89, 130.83, 129.56, 129.44 (q, J = 30.1 Hz), 128.91, 124.67, 122.11 (q, J = 274.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2926, 1666, 1489, 1309, 1285, 1160, 1127, 1074, 1011, 917, 818, 687 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{10}BrF_3O$ 353.9867; found 353.9866.

(*E*)-3-(3,5-Dibromophenyl)-1-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2h): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.81 (m, 2 H), 7.53 (tt, J = 7.4, 1.2 Hz, 1 H), 7.47 (s, 1 H), 7.43–7.33 (m, 3 H), 7.31–7.27 (m, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.06 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.51, 135.30, 135.23, 135.18, 134.68, 133.76 (q, J = 6.0 Hz), 131.74 (q, J = 30.4 Hz), 130.78, 129.37, 128.95, 123.12, 121.72 (q, J = 274.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3067, 1666, 1548, 1277, 1163, 1128, 926, 751, 739, 665 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_9Br_2F_3O$ 431.8972; found 431.8973.

(*E*)-Methyl 4-(2-benzoyl-3,3,3-trifluoroprop-1-en-1-yl)benzoate (2i): White solid, m.p. 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.79 (m, 4 H), 7.54–7.46 (m, 2 H), 7.38–7.27 (m, 4 H), 3.82 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.95 (d, J = 1.5 Hz, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.04, 166.02, 136.19, 135.57 (q, J = 5.9 Hz), 135.11, 134.55, 131.23, 130.75 (q, J = 30.3 Hz), 129.79, 129.52, 129.32, 128.86, 121.96 (q, J = 274.6 Hz), 52.22 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 1723, 1666, 1266, 1110, 812, 798, 688, 671 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{13}F_3O_3$ 334.0817; found 334.0820.

(*E*)-1-([1,1′-Biphenyl]-4-yl)-3-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2j): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06–7.91 (m, 2 H), 7.63–7.52 (m, 5 H), 7.49–7.36 (m, 3 H), 7.35–7.28 (m, 2 H), 7.25–7.18 (m, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.50 (d, J = 2.3 Hz, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.16, 146.85, 139.41, 136.70 (q, J = 5.9 Hz), 134.07, 131.96, 130.19, 130.13, 129.54, 128.90, 128.73 (q, J = 30.3 Hz), 128.71, 128.43, 127.36, 127.21, 122.28 (q, J = 275.1 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 3032, 1663, 1599, 1292, 1156, 1121, 765, 690 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{15}F_3O$ 352.1075; found 352.1078.

(*E*)-1-(4-Methoxyphenyl)-3-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2k): White solid, m.p. 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.76 (m, 2 H), 7.42 (q, J = 1.1 Hz, 1 H), 7.31–7.15 (m, 5 H), 6.87–6.76 (m, 2 H), 3.78 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.74 (d, J = 1.1 Hz, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.93, 164.55, 136.05 (q, J = 6.0 Hz), 132.11, 132.06, 130.02, 129.53, 128.85 (q, J = 29.9 Hz), 128.67, 128.51, 122.39 (q, J = 274.2 Hz), 114.10, 55.43 ppm. IR (KBr): $\tilde{\nu}$ = 2843, 1656, 1594, 1266, 1244, 1156, 1120, 847, 691 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}F_3O_2$ 306.0868; found 306.0865.

(*E*)-3-Phenyl-1-(*m*-tolyl)-2-(trifluoromethyl)prop-2-en-1-one (2l): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.70–7.65 (m, 1 H), 7.48 (q, J = 1.2 Hz, 1 H), 7.35–7.29 (m, 1 H), 7.28–7.15 (m, 6 H), 2.32 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.56 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.84, 138.67, 136.74 (q, J = 5.9 Hz), 135.34, 135.20, 132.01, 130.10, 129.84, 129.53, 128.78 (q, J = 30.3 Hz), 128.67, 128.64, 127.14, 122.31 (q, J = 274.3 Hz), 21.19 ppm. IR (KBr): $\tilde{\nu}$ = 3010, 1667, 1291, 1156, 1122, 942, 755, 690, 660 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{13}F_3O$ 290.0918; found 290.0921.

(*E*)-1-(4-*n*-Pentylphenyl)-3-phenyl-2-(trifluoromethyl)prop-2-en-1-one (2m): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.75 (m, 2 H), 7.46 (s, 1 H), 7.34–7.08 (m, 7 H), 2.58 (t, J = 7.6 Hz, 2 H), 1.68–1.48 (m, 2 H), 1.40–1.19 (m, 4 H), 0.86 (t, J = 6.5 Hz, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.62 (s, 3 F) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.20, 150.35, 136.46 (q, J = 5.9 Hz), 133.19, 132.05, 129.99, 129.78, 129.55, 128.92 (q, J = 29.7 Hz), 128.84, 128.63, 122.35 (q, J = 274.3 Hz), 35.99, 31.35, 30.48, 22.41, 13.92 ppm. IR (KBr): $\tilde{\nu}$ = 2957, 2931, 2859, 1664, 1603, 1271, 1158, 1123, 756, 691 cm^{-1}. HRMS (EI): calcd. for $C_{21}H_{21}F_3O$ 346.1545; found 346.1549.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of all products and the crystal data and structural refinement details of **2i**.

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[1] a) M. Schlosser, *Angew. Chem. Int. Ed.* **2006**, *45*, 5432–5446; *Angew. Chem.* **2006**, *118*, 5558–5572; b) C. Isanbor, D. O'Hagan, *J. Fluorine Chem.* **2006**, *127*, 303–319; c) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; d) S. Purser, P. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330.

[2] For recent reviews, see: a) R. Lundgren, M. Stradiotto, *Angew. Chem. Int. Ed.* **2010**, *49*, 9322–9324; b) T. Furuya, A. Kamlet, T. Ritter, *Nature* **2011**, *473*, 470–477; c) O. Tomashenko, V. Grushin, *Chem. Rev.* **2011**, *111*, 4475–4521; d) T. Besset, C. Schneider, D. Cahard, *Angew. Chem. Int. Ed.* **2012**, *51*, 5048–5050; e) A. Studer, *Angew. Chem. Int. Ed.* **2012**, *51*, 8950–8958; f) X.-F. Wu, H. Neumann, M. Beller, *Chem. Asian J.* **2012**, *7*, 1744–1754; g) Y. D. Ye, M. S. Sanford, *Synlett* **2012**, *23*, 2005–2013; For recent examples, see: h) R. Zhu, S. L. Buchwald, *J. Am. Chem. Soc.* **2012**, *134*, 12462–12465; i) Q. Yu, S. Ma, *Chem. Eur. J.* **2013**, *19*, 13304–13308; j) N. Iqbal, J. Jung, S. Park, E. J. Cho, *Angew. Chem. Int. Ed.* **2014**, *53*, 539–542; k) P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu, Y.-M. Liang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7629–7633.

[3] a) G. Liu, P. Chen, *Synthesis* **2013**, *45*, 2919–2939; b) X. Wu, X. Liu, *Synlett* **2013**, *24*, 1882–1886; c) J. Xu, X. Liu, Y. Fu, *Tetrahedron Lett.* **2014**, *55*, 585–594; d) G. Landelle, A. Panossian, S. Pazenok, J. P. Vors, F. R. Leroux, *Beilstein J. Org. Chem.* **2013**, *9*, 2476–2536; e) T. Liu, Q. Shen, *Eur. J. Org. Chem.* **2012**, 6679–6687.

[4] a) A. Tamaki, S. A. Magennis, J. K. Kochi, *J. Am. Chem. Soc.* **1974**, *96*, 6140–6148; b) A. Johnson, R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.* **1976**, 1360; c) R. D. Sanner, J. H. Satcher, M. W. Droege, *Organometallics* **1989**, *8*, 1498–1506; d) E. Bernhardt, M. Finze, H. Willner, *J. Fluorine Chem.* **2004**, *125*, 967–973; e) D. Zopes, S. Kremer, H. Scherer, L. Belkoura, I. Pantenburg, W. Tyrra, S. Mathur, *Eur. J. Inorg. Chem.* **2011**, 273–280; f) S. Martinez-Salvador, J. Fornies, A. Martin, B. Menjon, *Angew. Chem. Int. Ed.* **2011**, *50*, 6571–6574; g) S. Martinez-Salvador, L. R. Falvello, A. Martin, B. Menjon, *Chem. Eur. J.* **2013**, *19*, 14540–14552.

[5] a) G. H. Rasmusson, R. D. Brown, G. E. Arth, *J. Org. Chem.* **1975**, *40*, 672–675; b) X. S. Fei, W. S. Tian, Q. Y. Chen, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1139–1142; c) G. Chadalapaka, I. Jutooru, A. McAlees, T. Stefanac, S. Safe, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 2633–2639; d) B. Sam, T. Montgomery, M. Krische, *Org. Lett.* **2013**, *15*, 3790–3793; e) Z. Fang, Y. Ning, P. Mi, P. Liao, X. Bi, *Org. Lett.* **2014**, *16*, 1522–1525.

[6] a) S. Yu, S. Ma, *Chem. Commun.* **2011**, *47*, 5384–5418; b) M. Yoshida, *Heterocycles* **2013**, *87*, 1835; c) S. Ma, *Eur. J. Org. Chem.* **2004**, 1175–1183.

[7] a) D. J. Burton, G. A. Hartgraves, J. Hsu, *Tetrahedron Lett.* **1990**, *31*, 3699–3702; b) B. Jean-Philippe, M. Christian, M. N. Robert, G. V. Heinz, *J. Chem. Soc. Perkin Trans. 1* **1991**, 2147–2149; c) T. Zhao, K. Szabó, *Org. Lett.* **2012**, *14*, 3966–3969; d) Y. Miyake, S.-i. Ota, M. Shibata, K. Nakajima, Y. Nishibayashi, *Chem. Commun.* **2013**, *49*, 7809–7811.

[8] Y. L. Ji, J. J. Kong, J. H. Lin, J. C. Xiao, Y. C. Gu, *Org. Biomol. Chem.* **2014**, *12*, 2903–2906.

[9] Y.-P. Xiong, M.-Y. Wu, X.-Y. Zhang, C.-L. Ma, L. Huang, L.-J. Zhao, B. Tan, X.-Y. Liu, *Org. Lett.* **2014**, *16*, 1000–1003.

[10] H. Egami, T. Ide, M. Fujita, T. Tojo, Y. Hamashima, M. Sodeoka, *Chem. Eur. J.* **2014**, *20*, 12061–12065.

[11] a) L. Zhang, *J. Am. Chem. Soc.* **2005**, *127*, 16804–16805; b) J. Zhao, C. Hughes, F. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436–7437; c) D. Garayalde, E. Gómez-Bengoa, X. Huang, A. Goeke, C. Nevado, *J. Am. Chem. Soc.* **2010**, *132*, 4720–4730; d) Y. Yu, W. Yang, F. Rominger, A. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7586–7589; e) D. Wang, Y. Zhang, R. Cai, X. Shi, *Beilstein J. Org. Chem.* **2011**, *7*, 1014–1020; f) P. Nun, S. Gaillard, A. M. Slawin, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 9113–9115.

[12] a) C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, *Angew. Chem. Int. Ed.* **2011**, *50*, 1896–1900; b) C.-P. Zhang, J. Cai, C.-B. Zhou, X.-P. Wang, X. Zheng, Y.-C. Gu, J.-C. Xiao, *Chem. Commun.* **2011**, *47*, 9516–9518; c) C.-P.

Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, *Chem. Commun.* **2011**, *47*, 6632–6634; d) X. Wang, J. Lin, C. Zhang, J. Xiao, X. Zheng, *Chin. J. Chem.* **2013**, *31*, 915–920; e) X. P. Wang, J. H. Lin, C. P. Zhang, J. C. Xiao, X. Zheng, *Beilstein J. Org. Chem.* **2013**, *9*, 2635–2640.

[13] a) V. Gouverneur, M. Hopkinson, G. Giuffredi, A. Gee, *Synlett* **2010**, 2737–2742; b) T. de Haro, C. Nevado, *Chem. Commun.* **2011**, *47*, 248–249; c) M. Yu, G. Zhang, L. Zhang, *Tetrahedron* **2009**, *65*, 1846–1855; d) M. Yu, G. Zhang, L. Zhang, *Org. Lett.* **2007**, *9*, 2147–2150; e) D. Wang, X. Ye, X. Shi, *Org. Lett.* **2010**, *12*, 2088–2091.

[14] N. Mezailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133–4136.

[15] CCDC-987085 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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