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Cu-Promoted Oxidative Trifluoromethylation of Terminal Alkynes with Difluoromethylene Phosphobetaine†

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Difluoromethylene phosphobetaine ($Ph_3P^+CF_2CO_2^-$, PDFA), a known difluorocarbene reagent, was found to be able to efficiently trifluoromethylate terminal alkynes in the presence of Cu(I) and potassium fluoride. The transformation proceeded smoothly to afford the corresponding trifluoromethylated acetylenes in moderate yields.

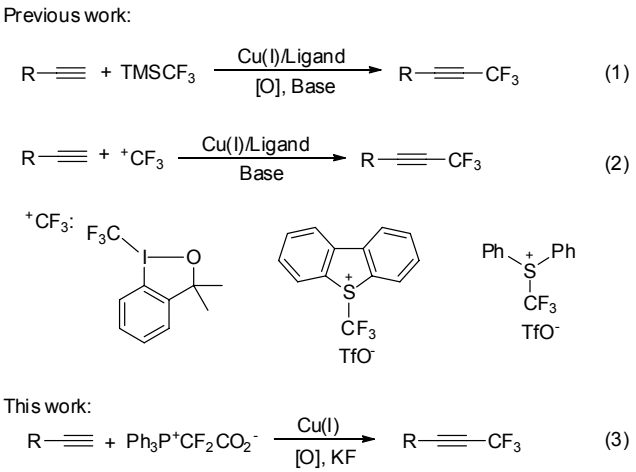
Keywords copper, difluoromethylene phosphobetaine, trifluoromethylation, alkynes, difluorocarbene

Introduction

The introduction of a trifluoromethyl moiety into an organic molecule usually results in a profound effect on its physical, chemical and biological properties.[1] Due to the versatility of this functionality, intensive research efforts have been directed towards the exploration of efficient and practical methods for trifluoromethylation.[2] The past years have witnessed the great advances in transition metal-mediated trifluoromethylation.[2b,3] However, despite these outstanding achievements, the current methods usually employ trifluoromethyl derivatives as trifluoromethylating reagents, such as Ruppert-Prakash reagent Me_3SiCF_3,[4] Umemoto's reagent,[5] Togni's reagents,[6] Langlois' reagent,[7] *S*-(trifluoromethyl)diphenylsulfonium triflate,[8] trifluoroiodomethane[9] and fluoroform.[10] The studies on trifluoromethylation with the utilization of difluorocarbene precursors,[11] a valuable strategy from the perspective of theoretical investigation, have been largely ignored. In continuation of our research interest in the chemistry of difluorocarbene[12] and trifluoromethylation,[8,13] we have now investigated the Cu-promoted oxidative trifluoromethylation of terminal alkynes with difluoromethylene phosphobetaine ($Ph_3P^+CF_2CO_2^-$, PDFA) giving trifluoromethylated acetylenes, a process via difluorocarbene species.

Qing and coworkers found that the nucleophilic reagent, $TMSCF_3$, was efficient for the trifluoromethylation of terminal alkynes leading to trifluoromethylated acetylenes (Scheme 1, reaction 1).[14] Such limitations as high reaction temperature, large excess amount of $TMSCF_3$, and a stoichiometric amount of copper complex prompted them to explore alternative protocols (Scheme 1, reaction 1).[15] It was reported that electrophilic trifluoromethylating reagent, Togni's reagent,[16] Umemoto's reagent,[17] or *S*-(trifluoromethyl)diphenylsulfonium triflate,[13b] could also achieve trifluoromethylation of terminal alkynes in the presence of Cu(I) (Scheme 1, reaction 2). All of these procedures involve the use of expensive trifluoromethylating reagent. We have shown that difluoromethylene phosphobetaine, easily accessible via a quaternization reaction of triphenylphosphine and potassium bromodifluoroacetate,[18] was an efficient difluorocarbene reagent.[12] We envisioned that difluorocarbene generated in situ from this reagent could be captured by fluoride to yield trifluoromethide intermediate, thus leading to oxidative trifluoromethylation of terminal alkynes promoted by Cu(I) (Scheme 1, reaction 3).

Scheme 1 Trifluoromethylation of terminal alkynes



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† Dedicated to Professor Chengye Yuan and Professor Li-Xin Dai on the occasion of their 90th birthdays.

Experimental

^{1}H and ^{13}C NMR spectra were recorded with TMS as the internal standard. ^{19}F NMR spectra were recorded with $CFCl_3$ (positive for downfield shifts) as the external standards. High resolution mass data were recorded on a Waters Micromass GCT Preminer instrument. Low resolution mass data were recorded on an Agilent Technologies GC-MS instrument. Flash column chromatography was carried out using 300—400 mesh silica gel.

General procedure for the trifluoromethylation of terminal alkynes

A dried Schlenk tube was charged with alkyne (0.15 mmol), $Ph_3P^+CF_2CO_2^-$ (214 mg, 0.6 mmol), *p*-chloranil (111 mg, 0.45 mmol), $Cu(MeCN)_4PF_6$ (224 mg, 0.6 mmol), KF (35 mg, 0.6 mmol), 18-crown-6 (159 mg, 0.6 mmol) and DMF (2 mL) under N_2. The resulting mixture was stirred at 40 ℃ for 2 h. After being cooled to room temperature, the mixture was subjected to flash column chromatography to afford pure product.

4-(3,3,3-Trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (**3a**):[13b] 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65—7.58 (m, 6H), 7.51—7.45 (m, 2H), 7.43—7.37 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.68 (s, 3F); GC-MS (EI) *m*/*z*: 246.1 ($[M]^+$).

4-Propyl-4'-(3,3,3-trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (**3b**): White solid, 68% yield; m.p. 144—145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 4H), 7.50 (d, J=8.2 Hz, 2H), 7.27 (d, J=8.2 Hz, 2H), 2.63 (t, J=7.6 Hz, 2H), 1.73—1.63 (m, 2H), 0.97 (t, J=7.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.64 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 143.66 (s), 143.04 (s), 136.98 (s), 132.86 (q, J=1.5 Hz), 129.13 (s), 127.05 (s), 126.95 (s), 116.82 (q, J=1.9 Hz), 114.65 (q, J=255.4 Hz), 86.70 (q, J=6.4 Hz), 76.10 (q, J=50.7 Hz), 37.70 (s), 24.51 (s), 13.83 (s); IR (neat) ν: 2964, 2936, 2880, 2253, 1913, 1601, 1496, 1467, 1401, 1386, 1319, 1222, 1143, 1003, 874, 831, 807, 757, 720, 671, 606, 588, 519 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{15}F_3$ 288.1126, found 288.1128.

1-(*tert*-Butyl)-4-(3,3,3-trifluoroprop-1-yn-1-yl)-benzene (**3c**):[13b] 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=8.2 Hz, 2H), 7.41 (d, J=8.2 Hz, 2H), 1.33 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.56 (s, 3F); GC-MS (EI) *m*/*z*: 226.1 ($[M]^+$).

2-(3,3,3-Trifluoroprop-1-yn-1-yl)-9*H*-fluorene (**3d**):[13b] 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83—7.75 (m, 2H), 7.72 (s, 1H), 7.57 (d, J=7.5 Hz, 2H), 7.45—7.34 (m, 2H), 3.91 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.47 (s, 3F); GC-MS (EI) *m*/*z*: 258.1 ($M]^+$).

1-Pentyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3e**):[19] 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J=8.2 Hz, 2H), 7.20 (d, J=8.2 Hz, 2H), 2.3 (t, J=7.63 Hz, 2H), 1.66—1.57 (m, 2H), 1.38—1.26 (m, 4H), 0.89 (t, J=6.9 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.58 (s, 3F); GC-MS (EI) *m*/*z*: 240.1 ($[M]^+$).

1-[(1*S*,4*R*)-4-Propylcyclohexyl]-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3f**): White solid, 69% yield; m.p. 60—61 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=8.2 Hz, 2H), 7.23 (d, J=8.2 Hz, 2H), 2.54—2.45 (m, 1H), 1.92—1.83 (m, 4H), 1.50—1.30 (m, 5H), 1.26—1.18 (m, 2H), 1.11—0.99 (m, 2H), 0.91 (t, J=7.2 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.56 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.26 (s), 132.43 (q, J=1.5 Hz), 127.20 (s), 115.72 (q, J=1.8 Hz), 114.95 (q, J=256.2 Hz), 87.00 (q, J=6.5 Hz), 75.15 (q, J=52.4 Hz), 44.73 (s), 39.62 (s), 36.94 (s), 33.99 (s), 33.35 (s), 20.00 (s), 14.36 (s); IR (neat) ν: 3409, 3037, 2954, 2874, 2847, 2250, 2185, 1608, 1511, 1468, 1446, 1417, 1314, 1218, 1189, 1164, 1136, 968, 875, 836, 827, 726, 613, 555 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{21}F_3$ 294.1595, found 294.1597.

1-Phenoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)-benzene (**3g**):[14] 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, J=8.7 Hz, 2H), 7.43—7.37 (m, 2H), 7.23—7.17 (m, 1H), 7.09—7.03 (m, 2H), 6.97 (d, J=8.7 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.58 (s, 3F); GC-MS (EI) *m*/*z*: 262.1 ($[M]^+$).

1-Methoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)-benzene (**3h**):[13b] 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J=8.8 Hz, 2H), 6.89 (d, J=8.8 Hz, 2H), 3.84 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.39 (s, 3F); GC-MS (EI) *m*/*z*: 200.0 ($[M]^+$).

1-Ethoxy-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3i**):[13b] 71% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 4.06 (q, J=7.0 Hz, 2H), 1.43 (t, J=7.0 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –49.35 (s, 3F); GC-MS (EI) *m*/*z*: 214.1 ($[M]^+$).

2-Methoxy-6-(3,3,3-trifluoroprop-1-yn-1-yl)naphthalene (**3j**):[14] 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H), 7.73 (d, J=9.0 Hz, 1H), 7.72 (d, J=8.5 Hz, 1H), 7.50 (dd, J=8.5, 1.5 Hz, 1H), 7.20 (dd, J=9.0, 2.4 Hz, 1H), 7.12 (d, J=2.4 Hz, 1H), 3.94 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –49.47 (s, 3F); GC-MS (EI) *m*/*z*: 250.1 ($[M]^+$).

1-Bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3k**):[13b] 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=8.5 Hz, 2H), 7.42 (d, J=8.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –50.05 (s, 3F); GC-MS (EI) *m*/*z*: 247.9 ($[M]^+$).

1-Nitro-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3l**):[17] 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, J=8.8 Hz, 2H), 7.75 (d, J=8.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –50.60 (s, 3F); GC-MS (EI) *m*/*z*: 215.0 ($[M]^+$).

3-(3,3,3-Trifluoroprop-1-yn-1-yl)quinoline (**3m**): White solid, 30% yield; m.p. 80—81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, J=1.7 Hz, 1H), 8.41 (d, J=1.7 Hz, 1H), 8.14 (d, J=8.3 Hz, 1H), 7.85—7.79 (m, 2H), 7.63 (t, J=7.5 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: –50.16 (s, 3F); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.08 (s), 147.86 (s), 140.86 (q, J=1.6 Hz), 131.68

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(s), 129.59 (s), 127.97 (s), 127.92 (s), 126.55 (s), 114.60 (q, J=257.9 Hz), 112.60 (q, J=1.9 Hz), 83.82 (q, J=6.5 Hz), 78.51 (q, J=52.8 Hz); IR (neat) ν: 3046, 2246, 1850, 1727, 1619, 1570, 1531, 1490, 1461, 1413, 1355, 1300, 1257, 1124, 1018, 985, 960, 916, 906, 868, 818, 753, 693, 640, 616, 545, 528, 513, 475, 420 cm^{-1}; HRMS (EI) calcd for $C_{12}H_6F_3N$ 221.0452, found 221.0455.

1-(5-(3,3,3-Trifluoroprop-1-yn-1-yl)thiophen-2-yl)-ethanone (**3n**):[13b] 66% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J=3.9 Hz, 1H), 7.43 (d, J=3.8 Hz, 1H), 2.57 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −50.44 (s, 3F); GC-MS (EI) m/z: 218.0 ($[M]^+$).

(5,5,5-Trifluoropent-3-yn-1-yl)benzene (**3o**):[14] 71% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32 (t, J=7.6 Hz, 2H), 7.27−7.24 (m, 1H), 7.23−7.19 (m, 2H), 2.89 (t, J=7.5 Hz, 2H), 2.63−2.56 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −49.65 (t, J=3.4 Hz, 3F); GC-MS (EI) m/z: 198.1 ($[M]^+$).

Results and Discussion

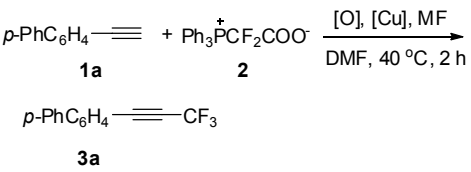
With the use of CsF as fluoride source and *p*-chloranil as oxidant, copper powder can not promote the trifluoromethylation of 4-ethynylbiphenyl with PDFA (Table 1, Entry 1). $Cu(MeCN)_4BF_4$ seemed to be a suitable copper source albeit low yield was obtained (Table 1, Entries 4 vs. 1−3). The examination of other oxidants showed that DDQ was more effective for this transformation (Table 1, Entries 5 vs. 4 and 6−8).

In our previous studies, we found that low-polarity solvent such as *p*-xylene was favorable for the generation of difluorocarbene. In this trifluoromethylation, difluorocarbene should be an important intermediate. However, the desired conversion was not observed with *p*-xylene or dichloromethane as solvent (Table 1, Entries 9, 10). The reaction in other polar solvents could also occur (Table 1, Entries 12, 13), but the inferior results obtained prompted us to further screen the reaction conditions in DMF. Increasing the amount of PDFA, CsF, oxidant and copper source improved the yield significantly (Table 1, Entries 14 vs. 5). The combined system composed of KF and 18-crown-6 instead of CsF was also efficient for this trifluoromethylation, albeit in lower yield (Table 1, Entries 15 vs. 14). Interestingly, superior results were obtained with the use of the same combined system as fluoride source and $Cu(MeCN)_4PF_6$ as copper source (Table 1, Entries 16 vs. 14). The yield was further increased by employing *p*-chloranil as oxidant (Table 1, Entry 17). The reaction was quite sensitive to the reaction temperature, as could be seen from the results that elevating the temperature resulted in lower yields (Table 1, Entries 18, 19).

With the optimized reaction conditions in hand (Table 1, Entry 17), we investigated the substrate scope of Cu-promoted oxidative trifluoromethylation of terminal alkynes with PDFA. As shown in Table 2, the reaction proceeded well with a variety of substrates to afford the corresponding trifluoromethylation products. Irrespective of whether the aryl group was substituted by an electron-withdrawing group or an electron-donating group, the products were obtained in moderate yields (**3a**−**3l**). The reaction was applicable to heteroaromatic substrates (**3m**, **3n**). Low yield obtained in the case of azo-aromatic substrate (**3m**) might be because this substrate could also act as a ligand to coordinate with copper complex. The attempt for trifluoromethylation of aliphatic alkyne was also successful (**3o**).

On the basis of results achieved above and related reports, we propose the reaction proceeds by the mechanism as shown in Scheme 2. The decarboxylation of PDFA generates phosphonium ylide, the dissociation

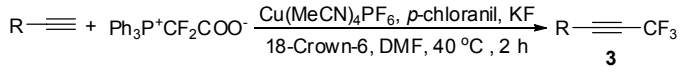
Table 1 Screening of reaction conditions for the oxidative trifluorometylation of 4-ethynylbiphenyl with PDFA[a]



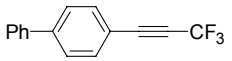
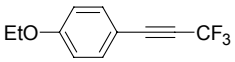
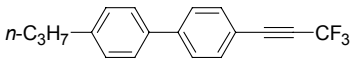
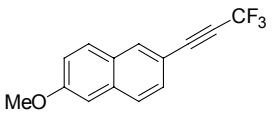
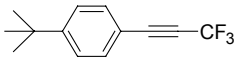
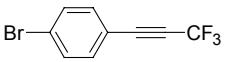
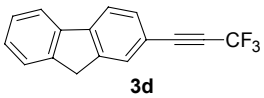
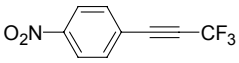
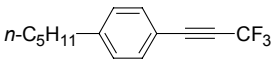
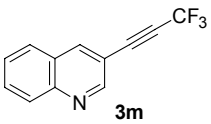
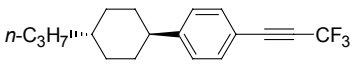
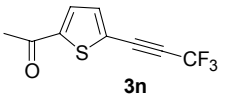
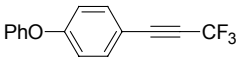
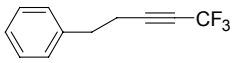
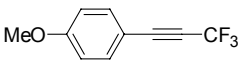
Entry	Cu	MF	Oxidant	Yield[b]/%
1	Cu	CsF	*p*-Chloranil	Trace
2	CuI	CsF	*p*-Chloranil	5
3	$Cu(MeCN)_4PF_6$	CsF	*p*-Chloranil	9
4	$Cu(MeCN)_4BF_4$	CsF	*p*-Chloranil	19
5	$Cu(MeCN)_4BF_4$	CsF	DDQ	32
6	$Cu(MeCN)_4BF_4$	CsF	DIB[c]	ND
7	$Cu(MeCN)_4BF_4$	CsF	DTBP[d]	1
8	$Cu(MeCN)_4BF_4$	CsF	$AgNO_3$	ND
9[e]	$Cu(MeCN)_4BF_4$	CsF	DDQ	ND
10[f]	$Cu(MeCN)_4BF_4$	CsF	DDQ	ND
11[g]	$Cu(MeCN)_4BF_4$	CsF	DDQ	ND
12[h]	$Cu(MeCN)_4BF_4$	CsF	DDQ	29
13[i]	$Cu(MeCN)_4BF_4$	CsF	DDQ	24
14[j]	$Cu(MeCN)_4BF_4$	CsF	DDQ	51
15[j,k]	$Cu(MeCN)_4BF_4$	KF	DDQ	41
16[j,k]	$Cu(MeCN)_4PF_6$	KF	DDQ	58
17[j,k]	$Cu(MeCN)_4PF_6$	KF	*p*-Chloranil	70
18[j,k,l]	$Cu(MeCN)_4PF_6$	KF	*p*-Chloranil	53
19[j,k,m]	$Cu(MeCN)_4PF_6$	KF	*p*-Chloranil	37

[a] Reaction conditions: **1** (0.15 mmol), **2** (0.3 mmol), MF (0.3 mmol), oxidant (0.3 mmol), copper complex (0.3 mmol) and solvent (2.0 mL); [b] determined by ^{19}F NMR with trifluoromethylbenzene as an internal standard; ND=not detected; [c] (diacetoxyiodo)benzene; [d] di-*tert*-butyl Peroxide; [e] *p*-xylene was used as solvent; [f] DCM was used as solvent; [g] acetonitrile was used as solvent; [h] DMA was used as solvent; [i] NMP was used as solvent; [j] **2** (0.6 mmol), MF (0.6 mmol), oxidant (0.45 mmol), copper source (0.6 mmol); [k] 18-crown-6 (0.6 mmol) was used as additive; [l] the reaction was performed at 60 ℃; [m] the reaction was performed at 80 ℃.

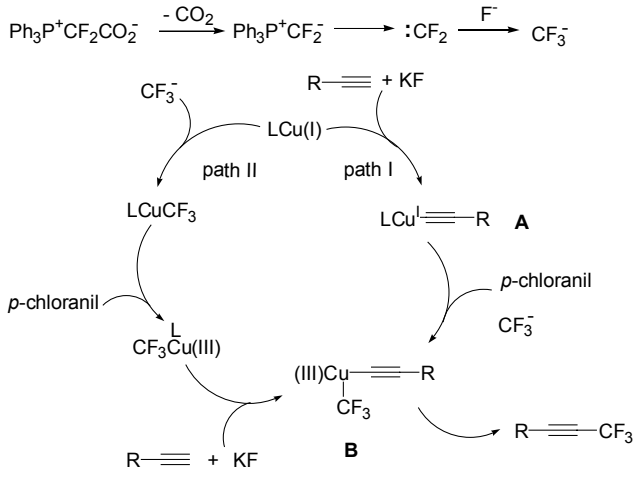
Table 2 Cu-promoted oxidative trifluoromethylation of terminal alkynes with PDFA (isolated yields)



3

Product	Yield/%	Product	Yield/%
 **3a**	56	 **3i**	71
 **3b**	68	 **3j**	61
 **3c**	59	 **3k**	61
 **3d**	86	 **3l**	68
 **3e**	54	 **3m**	30
 **3f**	69	 **3n**	66
 **3g**	66	 **3o**	71
 **3h**	54		

Scheme 2 The proposed reaction mechanism



of which yields difluorocarbene intermediate.[12] The facile capture of difluorocarbene by fluoride gives trifluoromethide.[11a,11b] Two pathways exist for the Cu-promoted trifluoromethylation of terminal alkynes.[14] In the presence of KF acting as a base, ligand exchange of alkyne with copper complex affords intermediate **A** (path I), the oxidation of which by *p*-chloranil and the following ligand exchange generate intermediate **B**. The reductive elimination of intermediate **B** gives the final product. Another possibility is that ligand exchange occurs between trifluoromethide and copper complex to yield [$CuCF_3$]. The subsequent oxidation and further ligand exchange also yield intermediate **B**.

Conclusions

In conclusion, we have described the Cu-promoted oxidative trifluoromethylation of terminal alkynes with difluoromethylene phosphobetaine. The utilization of difluorocarbene precursor, difluoromethylene phosphobetaine, as trifluoromethylating reagent has proved to be quite successful in the presence of potassium fluo-

ride. The studies on the application of PDFA in other reactions are currently underway.

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