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Straightforward and Efficient Deuteration of Terminal Alkynes with Copper Catalysis

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Abstract: The mild and effective preparation of deuterated organic molecules is an active area of research due to their important applications. Herein, we report an air-stable and easy to access copper(I) complex as catalyst for the deuteration of mono-substituted alkynes. Reactions were carried out in technical solvents and in the presence of air, to obtain excellent deuterium incorporation in a range of functionalised alkynes.

Keywords: alkyne; deuteration; copper; catalysis

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1. Introduction

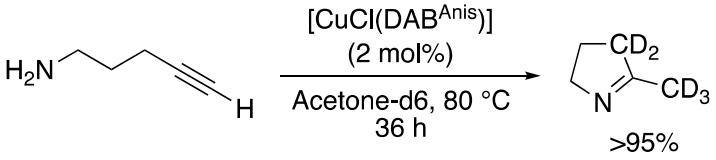
Deuterium-labelled organic compounds are powerful probes in mechanistic studies as well as the investigation of biological systems [1]. Deuterated compounds often display improved pharmacokinetic profiles and lower toxicity while retaining their pharmacodynamic properties, as they are metabolised at lower rates due to stronger C–D bonds compared to C–H ones [2–4]. Deuterated terminal alkynes are particularly valuable as they are precursors of a range of deuterated molecules. For example, they might produce *E*-/*Z*-alkenes and alkanes via hydrogenation [5], ketones after hydration [6] and various aromatic derivatives through cotrimerisation [7].

Both bases and transition metal catalysts have been employed to access deuterated alkynes. While water-sensitive BuLi [8] and Grignard reagents [9] or corrosive triazabicyclododecene [10] have been reported for this transformation, much milder conditions can be used with NEt_3 in D_2O/THF [5], potassium carbonate in D_2O and acetonitrile [11,12] or KOH in DMSO-d6 [13]. Despite the simplicity of these systems, they still require exclusion of moisture to ensure the reported high levels of isotopic enrichment.

Considering the rich reactivity of alkynes with d block elements, surprisingly few transition metals have been reported for the deuteration of terminal alkynes. A ruthenium(II) pincer complex displayed high activity in this transformation [14] but this methodology required the use of a glove-box and a costly catalyst [15]. Alternatively, silver trifluoroacetate in D_2O/DCM can also be used [16,17], but overall copper has been more widely used other deuteration reactions, such as that of aldimine esters [18], terminal alkenes to form deuterated alkanes [19], or aryl halides to access deuterated aromatic derivatives [20]. While copper-mediated reactions involving alkynes have also been reported, these focus mainly on (transfer) deuteration to form deuterated alkenes or alkanes [21,22] and to the best of our knowledge the only deuterated alkynes generated in the presence of copper were reported during the study of stoichiometric reactions of copper(I) –acetylide complexes with CD_3COOD [23]. Hence, an unexpensive, air and moisture compatible metal system for the deuteration of terminal alkynes remains a challenge.

We recently reported $[Cu(NCMe)_4]BF_4$ as a convenient and effective catalyst for the intramolecular hydroamination of alkynes [24]. In our preliminary studies, we screened other copper catalysts with 1-aminopentyne as the model substrate in different deuterated solvents. When acetone-d6 was used with a complex bearing a diazabutadiene (DAB)

ligand, the obtained pyrrolidine was partially deuterated (Scheme 1) [25]. NMR studies showed that while the hydroamination step was sluggish with this catalyst, the deuteration of the model substrate was complete within 2 h of heating, confirming a rapid acetylenic deuteration step prior to the cyclisation [26].



Scheme 1. Copper-mediated formation of pyrrolidine-d5.

Herein, we report the optimisation and scope of a copper-mediated deuteration of alkynes that does not require any precautions to minimise the presence of moisture or oxygen.

2. Results and Discussion

In this study we considered an array of copper(I) complexes bearing different types of ancillary ligands. For the reader's convenience the structures and acronyms of complexes tested in this study are shown in Figure 1. All of these complexes were prepared following the literature reports, are air and moisture stable and do not require any particular precaution for their manipulation or storage.

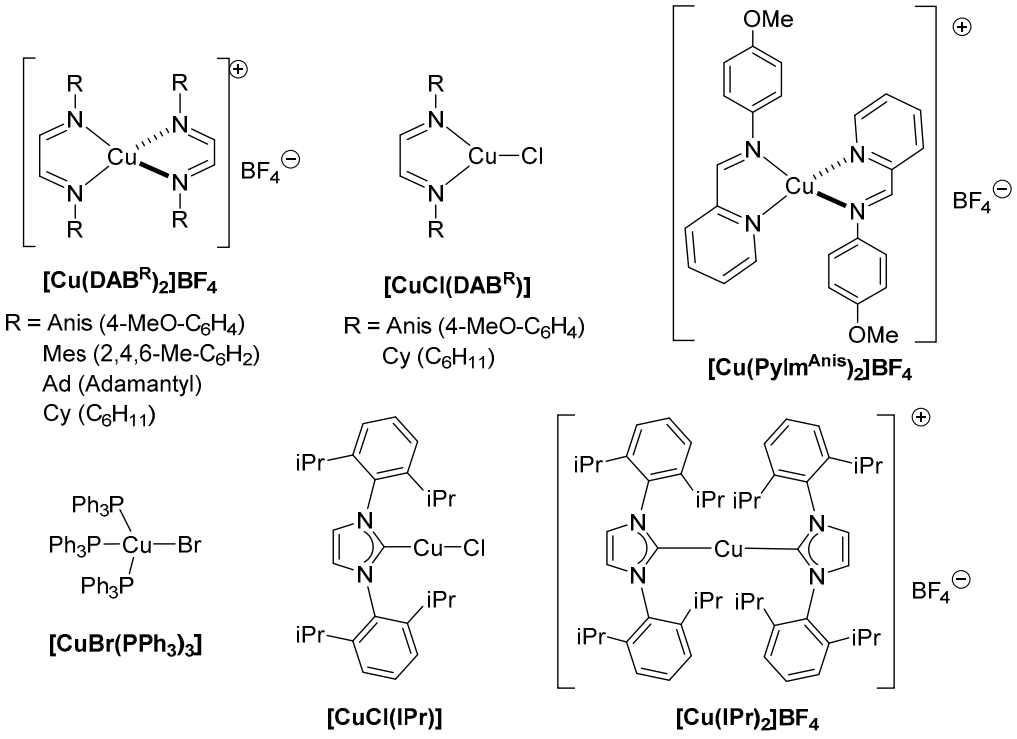
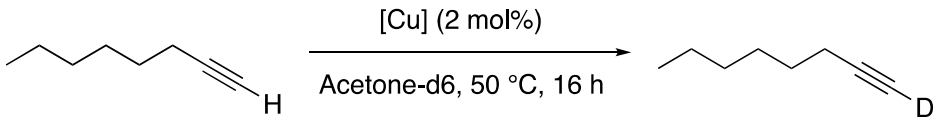


Figure 1. Copper(I) complexes screened in this work.

Catalysts with DAB, pyridylimine (PyIm), phosphine or N-heterocyclic carbenes ligands were screened with 1-octyne as model substrate in technical deuterated acetone in the presence of air (Table 1).

Table 1. Copper(I) catalyst screening [a].



1a **1a-D**

Entry	[Cu]	1a-D (%) [b]	Entry	[Cu]	1a-D (%) [b]
1	$[Cu(DAB^{Anis})_2]BF_4$	92	8	$[CuCl(DAB^{Anis})]$	7
2	$[Cu(DAB^{Mes})_2]BF_4$	29	9	$[CuCl(DAB^{Cy})]$	54
3	$Cu(DAB^{Ad})_2]BF_4$	10	10	$[CuBr(PPh_3)_3]$	11
4	$[Cu(DAB^{Cy})_2]BF_4$	69	11	[CuCl(IPr)]	22
5	$[Cu(PyIm^{Anis})_2]BF_4$	23	12	CuCl	19
6	$[Cu(IPr)_2]BF_4$	54	13	–	15
7	$[Cu(NCMe)_4]BF_4$	18	14 [c]	$[Cu(DAB^{Anis})_2]BF_4$	67

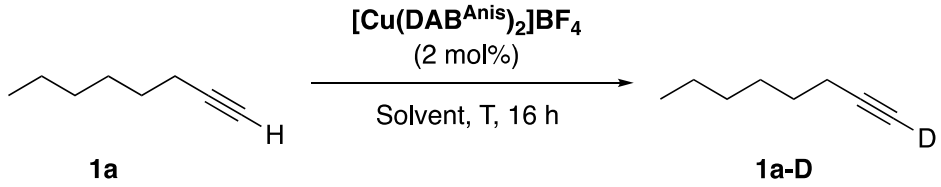
[a] Reaction conditions: 1-Octyne **1a** (0.4 mmol), [Cu] (2 mol%), acetone-d6 (0.5 mL), 50 °C, 16 h. [b] ^{1}H NMR yields are the average two independent reactions and were calculated with respect to 1,3,5-trimethoxybenzene as the internal standard. [c] [Cu] (1 mol%).

The highest conversion into amide **1a-D** was obtained with homoleptic complex $[Cu(DAB^{Anis})_2]BF_4$ (Table 1, entry 1), while related DAB complexes or an heteroleptic analogue led to lower yields in **1a-D** (Table 1, entries 2–4 and 8). Only moderate yields were obtained with any of the other complexes shown in Figure 1, and simple copper salts were inactive, giving comparable results to that of a blank experiment (Table 1, entries 7, 12 and 13). No by-product formation was observed in any of these experiments.

When the model reaction was carried out with 1 mol% of $[Cu(DAB^{Anis})_2]BF_4$, a lower NMR yield of 67% was obtained (Table 1, entry 14). Hence, the reaction media and temperature were optimised next (Table 2). Very low yields were observed in acetone-d6 at room temperature (Table 2, entry 2), and among the other deuterated solvents tested, $CDCl_3$ showed the best performance, although yields were still significantly lower than acetone-d6 (Table 2, entry 4). Furthermore, reactions in deuterated methanol were not reproducible and it was not possible to accurately quantify the deuterium incorporation in acetonitrile-d3 due to the overlap of the **1a** acetylenic signal and residual acetonitrile (Table 2, entries 3 and 6).

Next, we reacted a range of commercially available alkynes **1** with the selected catalyst, although reaction conditions had to be slightly modified in some cases (Table 3). Either higher reaction temperatures or copper loadings were beneficial with different substrates as illustrated with products **1l-D**, **1o-D**, **1r-D** and **1s-D** (Table 3, entries 12, 15, 18 and 19). In general, excellent deuterium incorporation was observed with substrates featuring diverse functional groups, including di- and tri-ynes. The reaction was sensitive to steric hindrance (Table 3, entries 4–6) and in the case of malonate **1o-D**, the best selectivity towards acetylenic deuteration was achieved at 50 °C, whereas a higher temperature led to an increase in deuteration at both the acetylenic and alpha positions (Table 3, entry 15).

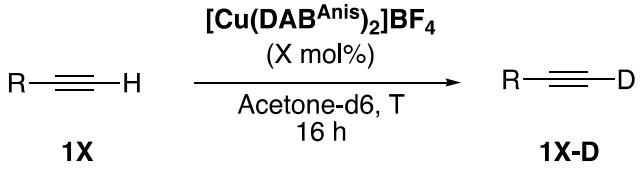
Table 2. Final optimisation [a].



Entry	Solvent	T (°C)	1a-D (%) [b]
1	Acetone-d6	50	92
2	Acetone-d6	RT	16
3	Methanol-d4	50	N.D.
4	$CDCl_3$	50	63
5	Toluene-d8	50	12
6	Acetonitrile-d3	50	N.D.

[a] Reaction conditions: 1-Octyne **1a** (0.4 mmol), $[Cu(DAB^{Anis})_2]BF_4$ (2 mol%), solvent (0.5 mL), T, 16 h. [b] ^1H NMR yields are the average two independent reactions and were calculated with respect to 1,3,5-trimethoxybenzene as the internal standard.

Table 3. Scope of the reaction [a].



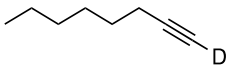
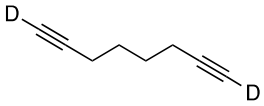
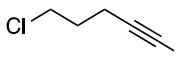
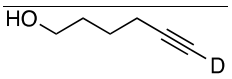
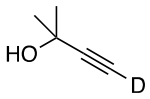
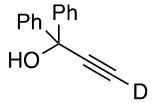
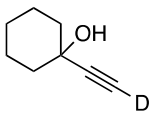
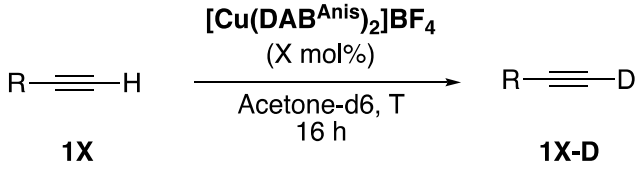
Entry	Deuterated Alkyne		[Cu] (mol%)	T (°C)	1X-D(%) [b]
1		**1a-D**	2	50	92
2		**1b-D**	2	50	85
3		**1c-D**	4	50	94
4		**1d-D**	2	50	87
5		**1e-D**	2	50	48
6		**1f-D**	2	50	15
7		**1g-D**	2	50	93

Table 3. *Cont*.



1X **1X-D**

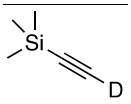
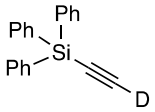
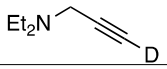
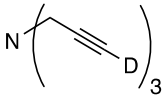
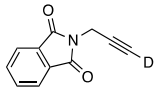
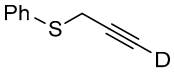
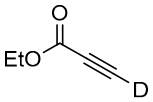
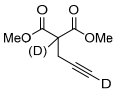
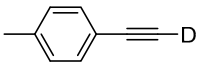
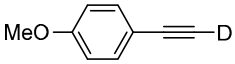
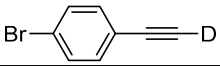
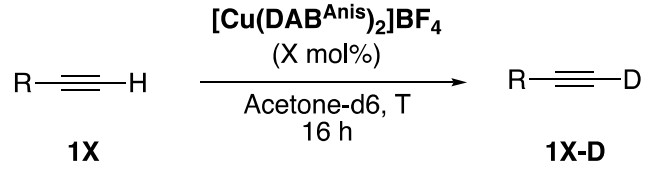
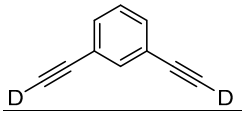
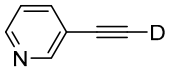
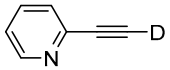
Entry	Deuterated Alkyne		[Cu] (mol%)	T (°C)	1X-D(%) [b]
8		**1h-D**	2	50	56
9		**1i-D**	5	50	91
10		**1j-D**	2 4	50 50	64 81
11		**1k-D**	4	50	90
12		**1l-D**	2 4 2	50 50 rfx	21 41 >95
13 [c]		**1m-D**	2	50	>95
14 [c]		**1n-D**	2	rfx	77
15 [d]		**1o-D**	2 2 2	60 50 rt	93 (66) 84 (<5) [c] 16 (<5)
16		**1p-D**	2 2	rfx 50	33 20
17		**1q-D**	2	50	85
18		**1r-D**	2 2 4	rfx 50 50	94 51 53
19		**1s-D**	2 2	rfx 50	94 46

Table 3. *Cont.*



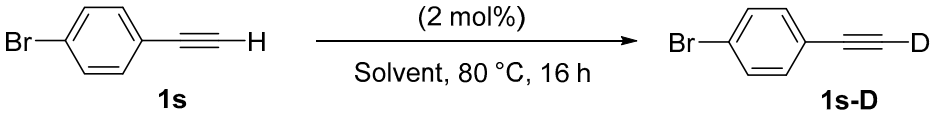
Entry	Deuterated Alkyne		[Cu] (mol%)	T (°C)	1X-D(%) [b]
20 [c]		**1t-D**	2	50	93
21		**1u-D**	2	50	95
22		**1v-D**	2	50	91

[a] Reactions carried out with 0.4 mmol of alkyne **1X**. [b] ^{1}H NMR yields are the average two independent reactions and were calculated with respect to 1,3,5-trimethoxybenzene as the internal standard. [c] Dibromomethane was used as internal standard. [d] D-incorporation at the α-position in brackets.

Together with the significant functional group tolerance, the present catalytic system has the advantage of not requiring the exclusion of water from the reaction media. Indeed, all reactions were carried out in technical acetone-d6 (no molecular sieves were used for storing the solvent between different experiments) and even when one additional equivalent of water with respect to the alkyne was added, a 59% conversion into **1a-D** was still obtained.

While acetone-d6 is not the most expensive deuterium source, its use as solvent in larger scale would significantly increase the overall cost of the process. Hence, we investigated the effect of using our deuterium source as a reagent, rather than solvent. We selected toluene as (co)solvent to avoid H/D-scrambling with **1s-D** as model substrate (Table 4). Pleasingly, comparable results were obtained when using 17, 8 or 6 equivalents of acetone-d6 (Table 4, entries 1–3) and 76% of **1s-D** was still detected when using only one equivalent of deuterated solvent (Table 4, entry 4).

Table 4. Additional solvent optimisation [a].



Entry	Acetone-d6/Toluene (*v*:*v*)	Acetone-d6 (equiv)	1s-D (%) [b]
1	1:0	17	92
2	1:1	8	88
3	3:7	6	88
4	1:16	1	76

[a] Reaction conditions: 1-bromo-4-ethynylbenzene **1s** (0.4 mmol), [Cu(DAB^{Anis})$_2$]BF$_4$ (2 mol%), solvent (0.5 mL), 80 °C, 16 h. [b] ^{1}H NMR yields are the average of two independent reactions and were calculated with respect to 1,3,5-trimethoxybenzene as the internal standard.

With these conditions in hand, we prepared two deuterated alkynes in the gram scale. **1l-D** and **1s-D** were selected as they are not volatile compounds and starting from 1.2 g of

each alkyne, the desired deuterated analogues were isolated analytically pure in excellent yields after an aqueous work-up (Figure 2).

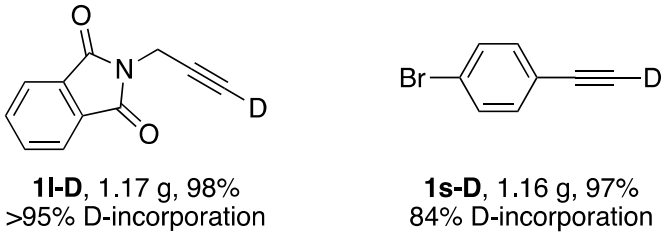


Figure 2. Gram-scale deuteration reactions.

In terms of mechanism, we believe these reactions proceed with the intermediacy of well-established copper–acetylide species [27]. We considered, however, the activation of terminal alkynes via π-coordination and the ^{1}H NMR spectra of an equimolar mixture of 1-octyne and [Cu(DAB^{Anis})$_2$]BF$_4$ in acetone-d6 were recorded at temperatures ranging from −80 to 50 °C. Only changes in the chemical shift of the acetylenic environment were observed in these spectra. This signal appeared at 2.73 ppm at −80 °C, compared to 2.23 ppm for the free alkyne. At 20 °C, only a small shift of 0.08 ppm was detected, and this was further reduced to zero at 50 °C, the standard reaction temperature for our deuteration reactions (Supplementary Materials). These changes in chemical shift are clearly smaller to reported values for 1-hexyne and copper(I) triflate, a stronger Lewis acid [23]. While such interactions cannot be ruled out from the catalytic cycle, these observations provide support to the involvement of copper–acetylide intermediates, maybe supported as well by some free DAB ligand in the reaction mixture [28].

3. Materials and Methods

3.1. General Considerations

All chemicals were obtained from commercial sources and used without further purification. NMR spectra were measured on Bruker AVANCE 400 spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz) at 20 °C unless stated otherwise. The chemical shifts (δ) are given in ppm relatively to a tetramethylsilane standard or the residual solvent signal. The multiplicity is given in br, s, d, t, q and m for broad, singlet, doublet, triplet, quartet and multiplet. Mass spectra (MS) were recorded on a Micromass Autospec Premier, Micromass LCT Premier or a VG Platform II spectrometer using EI, ESI or APCI techniques at the Mass Spectroscopy Service of Imperial College London.

All copper complexes were prepared following reported procedures and the obtained spectroscopic data were in accordance with the literature. [Cu(DAB^R)$_2$]BF$_4$ [28], [CuCl(DAB^{Anis})] [28], [Cu(PyIm^{Anis})$_2$]BF$_4$ [29], [CuBr(PPh$_3$)$_3$] [30], [CuCl(IPr)] [31], [Cu(IPr)$_2$]BF$_4$ [32], [Cu(NCMe)$_4$]BF$_4$ [33].

3.2. Copper-Mediated Deuteration of Alkynes

General procedure: In a 20 mL microwave vial, alkyne **1** (0.4 mmol), [Cu(DAB^{Anis})$_2$]BF$_4$ (5.5 mg, 2 mol%), 4–5 mg of 1,3,5-trimethoxybenzene (or 8 µL of dibromomethane) and acetone-d6 (0.5 mL) were loaded and sealed with an aluminium cap. The reaction mixture was heated at 50 °C for 16 h, then cooled to room temperature and transferred to an NMR tube. In all examples, no by-products were observed and the overall mass balance was >95%. Reported NMR yields are the average of two independent experiments and were determined with respect to the internal standard.

1-Deutero-oct-1-yne (1a-D)

Using the general procedure, the title compound was obtained from oct-1-yne (59 µL, 0.4 mmol) with 92% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 2.16 (t, *J* = 6.8 Hz, 2H, CH$_2$–C≡), 1.53–1.24 (m, 8H, CH$_2$), 0.89 (t, *J* = 6.6 Hz, 3H, CH$_3$). Residual acetylenic proton signal appeared at 2.23 ppm (t, *J* = 2.6 Hz);

^{13}C NMR (100 MHz, acetone-d6): 84.6 (t, *J* = 8 Hz, *C*≡C–D), 69.6 (t, *J* = 38 Hz, C≡*C*–D), 32.2, 29.4. Residual signals from the starting material appeared at 85.1 and 69.8 ppm.

HRMS (EI+) m/z: Calcd for $C_8H_{12}D$ $[M]^+$ 110.1086; Found 110.1082.

1,8-Deutero-octa-1,7-diyne (1b-D)

Using the general procedure, the title compound was obtained from octa-1,7-dyne (53 µL, 0.4 mmol) with 85% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 2.20 (t, *J* = 6.8 Hz, 4H, CH_2–C≡), 1.67–1.53 (m, 4H, $(CH_2)_2$). Residual acetylenic proton signal appeared at 2.32 ppm (t, *J* = 2.8 Hz).

^{13}C NMR (100 MHz, acetone-d6): δ 84.1 (t, *J* = 8 Hz, *C*≡C–D), 69.8 (t, *J* = 38 Hz, C≡*C*–D), 28.2 (*C*H_2–C≡), 18.2 (CH_2). Residual signals from the starting material appeared at 84.6 and 70.0 ppm.

HRMS (EI+) m/z: Calcd for $C_8H_8D_2$ $[M]^+$ 108.0908; Found 108.0913.

5-Chloro-1-deutero-pent-1-yne (1c-D)

Using the general procedure with $[Cu(DAB^{Anis})_2]BF_4$ (11 mg, 4 mol%), the title compound was obtained from 5-chloropent-1-yne (44 µL, 0.4 mmol) with 94% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 3.71 (t, *J* = 6.4 Hz, 2H, CH_2Cl), 2.39–2.34 (m, 2H, CH_2–C≡), 1.99–1.92 (m, 2H, CH_2). The residual acetylenic signal overlapped with the propargylic environment.

^{13}C NMR (100 MHz, acetone-d6): δ 82.8 (t, *J* = 8 Hz, *C*≡C–D), 70.5 (t, *J* = 38 Hz, C≡*C*–D), 44.3, 32.1, 16.1. Residual signals from the starting material appeared at 83.2 and 70.7 ppm.

HRMS (ESI) m/z: Calcd for C_5H_6D $[M\text{-}Cl]^+$ 68.0605; Found 68.0611.

5-Deuterohex-5-yn-1-ol (1d-D)

Using the general procedure, the title compound was obtained from hex-5-yn-1-ol (44 µL, 0.4 mmol) with 87% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 3.54 (t, *J* = 6.0 Hz, 2H, CH_2OH), 2.18 (t, *J* = 5.8 Hz, 2H, CH_2–C≡), 1.68–1.46 (m, 4H, CH_2). The residual acetylenic proton signal appeared at 2.31 ppm (br t).

^{13}C NMR (100 MHz, acetone-d6): δ 84.8 (t, *J* = 8 Hz, *C*≡C–D), 69.9 (t, *J* = 38 Hz, C≡*C*–D), 62.0, 32.9, 26.1, 18.8. Residual signals from the starting material appeared at 85.3 and 70.1 ppm.

HRMS (ESI) m/z: Calcd for C_6H_9DO $[M]^+$ 99.0794; Found 99.0760.

4-Deutero-2-methylbut-3-yn-2-ol (1e-D)

Using the general procedure, the title compound was obtained from 2-methyl-3-butyn-2-ol (39 µL, 0.4 mmol) with 48% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 1.42 (s, 6H, CH_3). The residual acetylenic proton signal appeared at 2.75 ppm (s).

^{13}C NMR (100 MHz, acetone-d6): δ 90.3 (t, *J* = 8 Hz, *C*≡C–D), 70.5 (t, *J* = 38 Hz, C≡*C*–D), 64.7, 32.1. Residual signals from the starting material appeared at 90.7 and 70.7 ppm.

HRMS (ESI) m/z: Calcd for C_5H_7DO $[M]^+$ 85.0638; Found 85.0633.

3-Deutero-1,1-diphenylprop-2-yn-1-ol (1f-D)

Using the general procedure, the title compound was obtained from 1,1-diphenyl-2-propyn-1-ol (4g, 83 mg) with 15% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 7.70–7.67 (m, 4H, H^{Ar}), 7.36–7.32 (m, 4H, H^{Ar}), 7.28–7.23 (m, 2H, H^{Ar}). The residual OH and acetylenic proton signals appeared at 5.80 (s) and 3.39 ppm (s), respectively.

1-Deutero-ethynyl-1-cyclohexanol (1g-D)

Using the general procedure, the title compound was obtained from 1-ethynyl-1-cyclohexanol (50 mg, 0.4 mmol) with 93% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 1.89–1.74 (m, 2H), 1.74–1.60 (m, 2H), 1.60–1.40 (m, 5H), 1.33–1.14 (m, 1H). Residual acetylenic proton signal appeared at 2.81 ppm (s).

^{13}C NMR (100 MHz, acetone-d6): δ 88.9 (t, *J* = 7 Hz, *C*≡C–D), 72.3 (t, *J* = 35 Hz, C≡*C*–D), 67.7 (C–OH), 40.5 (CH_2), 25.9 (CH_2), 23.6 (CH_2). Residual signals from the starting material appeared at 89.3 and 72.5 ppm.

HRMS (ESI) m/z: Calcd for $C_8H_{11}DO$ $[M]^+$ 125.0954; Found 125.0952.

Deutero(trimethylsilyl)acetylene (1h-D)

Using the general procedure, the title compound was obtained from trimethylsilylacetylene (57 µL, 0.4 mmol) with 56% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 0.16 (s, 9H, CH_3). The residual acetylenic signal appeared at 2.86 ppm (s).

^{13}C NMR (100 MHz, acetone-d6): δ 96.0 (t, *J* = 36 Hz, C≡*C*–D), 90.2 (t, *J* = 6 Hz, *C*≡C–D), -0.52. Residual signals from the starting material appeared at 92.6 and 90.7 ppm.

HRMS (EI) m/z: Calcd for C_5H_9DSi $[M]^+$ 99.0615; Found 99.0621.

Deutero(triphenylsilyl)acetylene (1i-D)

Using the general procedure with $[Cu(DAB^{Anis})_2](BF_4)$ (18 mg, 5 mol%), the title compound was obtained from (triphenylsilyl)acetylene (114 mg, 0.4 mmol) with 91% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 7.79–7.63 (m, 6H, H^{Ar}), 7.52–7.33 (m, 9H, H^{Ar}). The residual acetylenic signal appeared at 2.48 ppm (s).

^{13}C NMR (100 MHz, acetone-d6): δ 136.2, 133.8, 131.1, 129.1, 100.6 (t, *J* = 36 Hz, C≡*C*–D), 85.1 (t, J = 6 Hz, *C*≡C–D). Residual signals from the starting material appeared at 100.8 and 85.6 ppm.

HRMS (EI+) m/z: Calcd for $C_{20}H_{15}DSi$ $[M]^+$ 285.4391; Found 285.4372.

3-Deutero *N*,*N*-diethyl-prop-2-ynyl amine (1j-D)

Using the general procedure with $[Cu(DAB^{Anis})_2]BF_4$ (11 mg, 4 mol%), the title compound was obtained from *N*,*N*-diethyl-prop-2-ynyl amine (55 µL, 0.4 mmol) with 81% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 3.39 (s, 2H, CH_2N), 2.50 (q, *J* = 6.4 Hz, 4H, NCH_2CH_3), 1.01 (t, *J* = 6.4 Hz, 6H, CH_3). The residual acetylenic signal appeared at 2.58 ppm (t, *J* = 2.0 Hz).

^{13}C NMR (100 MHz, acetone-d6): δ 79.4 (t, *J* = 8 Hz, *C*≡C–D), 74.5 (t, *J* = 38 Hz, C≡*C*–D), 47.3, 41.5, 13.7. Residual signals from the starting material appeared at 79.8 and 74.7 ppm.

HRMS (EI+) m/z: Calcd for $C_7H_{12}DN$ $[M]^+$ 112.1105; Found 112.1111.

Tris(prop-2-ynyl-3-deutero)amine (1k-D)

Using the general procedure with $[Cu(DAB^{Anis})_2]BF_4$ (11 mg, 4 mol%), the title compound was obtained from tris(2-propynyl)amine (57 µL, 0.4 mmol) with 90% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 3.45 (s, 6H, CH_2). The residual acetylenic signal appeared at 2.73 ppm (br s).

^{13}C NMR (101 MHz, acetone-d6): δ 9.4 (t, *J* = 8 Hz, *C*≡C–D), 75.0 (t, *J* = 38 Hz, C≡*C*–D), 42.5. Residual signals from the starting material appeared at 79.8 and 75.2 ppm.

HRMS (APCI): Calcd for $C_9H_7D_3N$ $[M^+]$: 135.0996, found: 135.0996.

2-(Prop-2-ynyl-3-deutero)isoindoline-1,3-dione (1l-D)

Using the general procedure at 80 °C, the title compound was obtained from *N*-propargylic phthalamide (74 mg, 0.4 mmol) with >95% deuterium incorporation.

***Gram scale synthesis*:** *N*-Propargylic phthalamide (1.2 g, 6.4 mmol) was reacted in a mixture of acetone-d6/toluene (3:7, 3.5 mL) at 80 °C for 16 h in the presence of $[Cu(DAB^{Anis})_2]BF_4$ (89 mg, 0.13 mmol, 2 mol%). The reaction mixture was cooled down to room temperature, then poured onto an aqueous saturated solution of Na_4EDTA. The aqueous phase was extracted with EtOAc, washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The title compound was obtained as a light brown solid (1.17 g, 98% yield) with >95% deuterium incorporation.

The spectroscopic data for the title compound is in accordance with the literature [11].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 5.3; 2.8 Hz, 2H), 7.72 (dd, *J* = 5.3; 2.8 Hz, 2H), 4.43 (s, 2H, CH_2). The residual acetylenic signal appeared at 2.22 ppm (s).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.9, 134.2, 131.9, 123.5, 71.2 (t, *J* = 38 Hz, C≡C–D), 26.9. Residual signal from the starting material appeared at 71.5 ppm.

Phenyl(prop-2-ynyl-3-deutero)sulphane (1m-D)

Using the general procedure, the title compound was obtained from phenyl propargyl sulphide (55 µL, 0.4 mmol) with >95% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 7.48–7.42 (m, 2H, H^{Ar}), 7.35 (t, *J* = 7.5 Hz, 2H, H^{Ar}), 7.25 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 3.75 (s, 2H, CH_2). The residual acetylenic signal appeared at 2.69 ppm (t, *J* = 2.6 Hz).

^{13}C NMR (100 MHz, acetone-d6): δ 136.8, 130.6, 130.3, 127.9, 80.8 (t, *J* = 8 Hz, *C*≡C–D), 73.1 (t, *J* = 38 Hz, C≡*C*–D), 22.7. Residual signals from the starting material appeared at 81.2, 73.4 and 21.7 ppm.

HRMS (EI+) m/z: Calcd for C_9H_7DS $[M]^+$ 149.0409; Found 149.0411.

Ethyl Deuteropropiolate (1n-D)

Using the general procedure in refluxing acetone-d6, the title compound was obtained from ethyl propiolate (41 µL, 0.4 mmol) with 77% deuterium incorporation.

^{1}H NMR (400MHz, acetone-d6): δ 4.22 (q, *J* = 7.1 Hz, 2H, CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3). The residual acetylenic signal appeared at 3.80 ppm.

^{13}C NMR (101 MHz, acetone-d6): δ 153.7, 76.8 (t, *J* = 40 Hz, C≡*C*–D), 75.7 (t, *J* = 8 Hz, *C*≡C–D), 63.2, 14.6. The residual signals from the starting material appeared at 77.1 and 76.1 ppm.

HRMS (APCI) m/z: Calcd for $C_5H_5DO_2$ $[M]^+$ 99.0431; Found 99.0435.

Dimethyl-2-(3-deutero-prop-2-ynyl) (deutero)malonate (1o-D)

Using the general procedure, the title compound was obtained from dimethyl-2-(prop-2-yn-1-yl)malonate (71 µL, 0.4 mmol) with 84% deuterium incorporation. When the same reaction was carried out at 60 °C, the title compound was obtained with 93% deuterium incorporation at the acetylenic position and 66% deuterium incorporation at the homopropargylic position.

Monodeuterated compound:

^{1}H NMR (400 MHz, acetone-d6): δ 3.71 (s, 6H, CH_3), 3.67 (t, *J* = 7.7 Hz, 1H, CH), 2.72 (d, *J* = 7.7 Hz, 2H, CH_2). The residual acetylenic signal appeared at 2.45 ppm (s br).

^{13}C NMR (101 MHz, acetone-d6): δ 169.3, 80.8 (t, *J* = 8 Hz, *C*≡C–D), 72.1 (t, *J* = 38 Hz, C≡*C*–D), 53.4, 52.0, 19.3. Residual signals from the starting material appeared at 81.3 and 72.3 ppm.

Bisdeuterated compound:

^{1}H NMR (400 MHz, acetone-d6): δ 3.71 (s, 6H, CH_3), 3.67 (t, *J* = 7.7 Hz, 1H, CH), 2.72 (d, mboxemphJ = 7.7 Hz, 2H, CH_2). Residual signals from the starting material appeared at 3.67 (t, *J* = 7.7 Hz) and 2.45 ppm (s br).

^{13}C NMR (101 MHz, acetone-d6): δ 169.3, 80.8 (t, *J* = 8 Hz, *C*≡C–D), 72.1 (t, *J* = 38 Hz, C≡*C*–D), 53.4, 51.7 (t, *J* = 21 Hz, MeOC(O)C–D), 19.3. Residual signals from the starting material appeared at 81.3, 72.3 and 52.0 ppm.

HRMS (APCI): Calcd. for $C_8H_8D_2O_4$ $[M]^+$: 172.0699, found: 172.0713.

1-Deutero-3,3-diethoxyprop-1-yne (1p-D)

Using the general procedure in refluxing acetone-d6, the title compound was obtained from 3,3-diethoxypropyne (57 µL, 0.4 mmol) with 33% deuterium incorporation. Deuteration was confirmed by HRMS.

^{1}H NMR (400 MHz, acetone-d6): δ 5.25 (s, 1H, CH), 3.75–3.61 (m, 2H), 3.61–3.43 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H, CH_3). The residual acetylenic signal appeared at 3.08 ppm (t, *J* = 2.0 Hz).

HRMS (APCI): Calcd. for $C_7H_{11}DO_2$ $[M]^-$: 129.0906, found: 129.0911.

1-Deutero-*p*-tolylacetylene (1q-D)

Using the general procedure, the title compound was obtained from *p*-tolylacetylene (51 µL, 0.4 mmol) with 85% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 7.39 (d, *J* = 8.0 Hz, 2H, H^{Ar}), 7.19 (d, *J* = 8.0 Hz, 2H, H^{Ar}), 2.33 (s, 3H, CH_3). The residual acetylenic signal appeared at 3.57 (s).

^{13}C NMR (100 MHz, acetone-d6): δ 139.7 (C^{Ar}), 132.6 (CH^{Ar}), 130.0 (CH^{Ar}), 120.1 (C^{Ar}), 83.9 (t, *J* = 8 Hz, *C*≡C–D), 78.1 (t, *J* = 38 Hz, C≡*C*–D), 21.4 (CH_3). Residual signals from the starting material appeared at 84.3 and 78.4 ppm.

HRMS (ESI) m/z: Calcd for C_9H_8D $[M+H]^+$ 118.0767; Found 118.0772.

1-Deutero-*p*-anisylacetylene (1r-D)

Using the general procedure in refluxing acetone-d6, the title compound was obtained from *p*-anisylacetylene (52 µL, 0.4 mmol) with 94% deuterium incorporation after evaporation of the reaction solvent under reduced pressure. Spectroscopic data for this compound are in accordance with the literature [29].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.8 Hz, 2H, H^{Ar}), 6.82 (d, *J* = 8.8 Hz, 2H, H^{Ar}), 3.78 (s, 3H, CH_3). The residual acetylenic signal appeared at 3.00 (s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8 (C^{Ar}), 133.5 (CH^{Ar}), 114.0 (C^{Ar}), 113.8 (CH^{Ar}), 83.1 (t, *J* = 7 Hz, *C*≡C–D), 75.5 (t, *J* = 38 Hz, C≡*C*–D), 55.2 (CH_3). Residual signals from the starting material appeared at 83.6 and 75.8 ppm.

1-Bromo-4-(deuteroethynyl)-benzene (1s-D)

Using the general procedure in refluxing acetone-d6, the title compound was obtained from 1-bromo-4-ethynylbenzene (73 mg, 0.4 mmol) with 94% deuterium incorporation after evaporation of the reaction solvent under reduced pressure.

***Gram scale synthesis*:** 1-Bromo-4-ethynylbenzene (1.2 g, 6.6 mmol) was reacted in a mixture of acetone-d6/toluene (3:7, 3.5 mL) at 80 °C for 16 h in the presence of $[Cu(DAB^{Anis})_2]BF_4$ (91 mg, 0.13 mmol, 2 mol%). The reaction mixture was cooled down to room temperature, then poured onto an aqueous saturated solution of Na_4EDTA. The aqueous phase was extracted with EtOAc, washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The title compound was obtained as a light brown solid (1.16 g, 97% yield) with 84% deuterium incorporation.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.3 Hz, 2H, H^{Ar}), 7.34 (d, *J* = 8.3 Hz, 2H, H^{Ar}). The residual acetylenic signal appeared at 3.14 (s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4 (CH^{Ar}), 131.5 (CH^{Ar}), 123.0 (C^{Ar}), 121.0 (C^{Ar}), 82.0 (t, *J* = 8 Hz, *C*≡C–D), 78.1 (t, *J* = 39 Hz, C≡*C*–D). Residual signals from the starting material appeared at 82.4 and 78.1 ppm.

HRMS (ESI) m/z: Calcd for C_8H_5DBr $[M+H]^+$ 181.9710; Found 181.9705.

1,3-Bis(deuteroethynyl)benzene (1t-D)

Using the general procedure, the title compound was obtained from 1,3-diethynylbenzene (53 µL, 0.4 mmol) with 93% deuterium incorporation.

^{1}H NMR (400 MHz, acetone-d6): δ 7.58 (s, 1H, H^{Ar}), 7.54–7.49 (m, 2H, H^{Ar}), 7.40 (t, *J* = 7.7 Hz, 1H, H^{Ar}). The residual acetylenic signal appeared at 3.71 ppm (s).

^{13}C NMR (101 MHz, acetone-d6): δ 136.3, 133.6, 130.3, 124.2, 83.1 (t, *J* = 8 Hz, *C*≡C–D), 80.4 (t, *J* = 38 Hz, C≡*C*–D). Residual signals from the starting material appeared at 83.6 and 80.6 ppm.

HRMS (APCI): Calcd. for $C_{10}H_4D_2$ $[M]^+$: 128.0589, found: 128.0593.

3-(Deuteroethynyl)pyridine (1u-D)

Using the general procedure, the title compound was obtained from 3-ethynylpyridine (41 mg, 0.4 mmol) with 95% deuterium incorporation. Spectroscopic data for this compound is in agreement with the literature [34].

^{1}H NMR (400 MHz, acetone-d6): δ 8.71 (br s, 2H, H^{Ar}), 7.89 (d, *J* = 7.8 Hz, 1H, H^{Ar}), 7.43 (br s, 1H, H^{Ar}). The residual acetylenic signal appeared at 3.90 (s).

^{13}C NMR (100 MHz, acetone-d6): δ 153.1 (CH^{Ar}), 149.9 (CH^{Ar}), 139.5 (CH^{Ar}), 82.3 (t, *J* = 38 Hz, C≡C–D), 80.7 (t, *J* = 7 Hz, *C*≡C–D). Residual signals from the starting material appeared at 82.6 and 81.9 ppm.

2-(Deuteroethynyl)pyridine (1v-D)

Using the general procedure, the title compound was obtained from 2-ethynylpyridine (41 µL, 0.4 mmol) with 91% deuterium incorporation. Spectroscopic data for this compound are in agreement with the literature [35].

^{1}H NMR (400 MHz, acetone-d6): δ 8.58 (d, *J* = 2.1 Hz, 1H, H^{Ar}), 7.80 (td, *J* = 7.7; 2.1 Hz, 1H, H^{Ar}), 7.56 (d, *J* = 7.7 Hz, 1H, H^{Ar}), 7.43–7.33 (m, 1H, H^{Ar}). The residual acetylenic signal appeared at 3.80 ppm (s).

^{13}C NMR (100 MHz, acetone-d6): δ 150.8 (CH^{Ar}), 143.2 (C^{Ar}), 137.2 (CH^{Ar}), 128.3 (CH^{Ar}), 124.4 (CH^{Ar}), 83.4 (t, *J* = 8 Hz, *C*≡C–D), 78.3 (t, *J* = 39 Hz, C≡*C*–D). Residual signals from the starting material appeared at 83.8 and 78.5 ppm.

4. Conclusions

$[Cu(DAB^{Anis})_2]BF_4$ is a convenient and effective catalyst for the deuteration of terminal alkynes using technical acetone-d6 as the deuterium source. A wide range of alkynes including examples with other functional groups such as alcohols, silanes, amines, thioethers, esters and aromatic substituents, readily produced their deuterated analogues with complete mass recovery and high deuterium incorporation. For larger scale reactions, a toluene/acetone-d6 combination can be used as the reaction media to keep costs down without compromising on the catalytic performance. Furthermore, the present methodology is compatible with the presence of water and oxygen and all reactions were carried out in technical solvents with no precautions to minimise the presence of moisture or air.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13040648/s1. ^{1}H and ^{13}C NMR for the reported deuterated alkynes, figures for the ^{1}H NMR spectra of **1a** and $[Cu(DAB^{R})_2]BF_4$ at different temperatures.

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