ACS OMEGA

Article

Cite This: ACS Omega 2018, 3, 18065−18077

http://pubs.acs.org/journal/acsodf

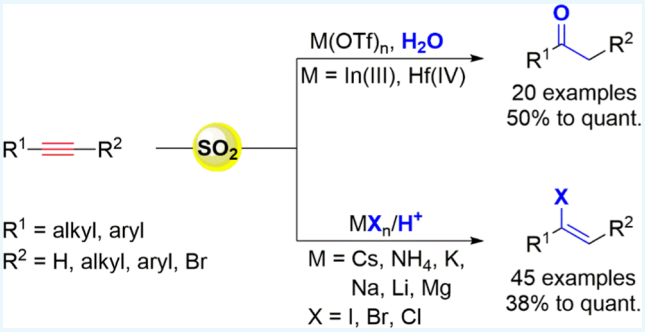
In(III) and Hf(IV) Triflate-Catalyzed Hydration and Catalyst-free Hydrohalogenation of Aryl Acetylenes in Liquid Sulfur Dioxide

Krista Suta and Māris Turks*

Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena Street 3, LV-1048 Riga, Latvia

Supporting Information

ABSTRACT: The use of liquid sulfur dioxide as a reaction solvent to promote chemical transformations of alkynes has been explored. First, a combination of liquid SO_2 and $In(OTf)_3$ or $Hf(OTf)_4$ as a catalyst allows to perform hydration of aryl alkynes under mild conditions without a direct addition of Brønsted acid. Second, novel catalyst-free conditions for the synthesis of α-vinyl iodides, bromides, and chlorides from aryl alkynes have been developed in liquid SO_2 using group I and II metal halides and ammonium iodide as the halide ion sources.



INTRODUCTION

Alkyne hydration is an atom-efficient strategy toward carbonyl compounds.[1−3] Traditionally, the synthesis of ketones by Markovnikov addition of water to the C≡C bond is carried out using stoichiometric amount of toxic Hg(II) salts under strongly acidic conditions.[4] A great number of alternative hydration conditions, including transition-metal catalysis, have been developed over the past decades.[1−3,5−12] Also, several metal-free systems based on the combination of strong protic acid (e.g., TsOH or TfOH) with weakly acidic and hydrogen-bond-forming reaction medium have been reported.[13,14] Recently, several procedures for metal triflate-catalyzed alkyne hydration have been established revealing contributory effect of triflate ion on the Lewis acid properties of the corresponding metal ion and its ability to activate the C≡C bond. In 2013, Gao et al. developed In(III) triflate-catalyzed hydration of both terminal and internal alkynes in the presence of catalytic amount of *p*-TsOH in 1,2-dichloroethene.[15] After 3 years, Zeng et al. employed the same catalyst for hydration of 1-haloalkynes in acetic acid.[16] A similar substrate scope was examined for Ga(III) triflate-catalyzed reaction in acetic acid by Liang et al. in 2015,[17] while a combination of Cu(II) triflate and acetic acid published by Jha group in 2014 is applicable only for aryl acetylenes.[18] To the best of our knowledge, there are only two reports that describe triflate-catalyzed alkyne hydration in the absence of Brønsted acid additive. These reactions are carried out in ethyl acetate at elevated temperatures in the presence of Cu(II)[19] or Ag(I)[20] triflate as a catalyst. The latter is effective only for terminal alkynes. Besides employing these Brønsted acid-free protocols, catalyst loading has to be increased to 10−20 mol % instead of 0.2−2.5 mol % used in the methods mentioned previously.

Also, vinyl halides are versatile intermediates in organic synthesis, especially as substrates for the transition metal-catalyzed C−C cross-coupling reactions. Hydrohalogenation of alkynes is one of the easiest ways to obtain these valuable compounds.[21] The hydrohalogenation regioselectivity of a terminal C≡C bond mainly depends on the choice of reagents. As the direct addition of HX (X = I, Br or Cl) to the alkyne is nonselective and often leads to low yield and undesirable side reactions, various multicomponent reagent systems have been developed to obtain one regioisomer, exclusively. Highly regioselective methods for the synthesis of α-vinyl bromides and iodides from terminal alkynes include alkyne haloboration[22] or Ni(II)-catalyzed hydroalumination[23] and subsequent acidic workup or addition of halonium source, respectively. Another strategy is *in situ* generation of HX (X = I, Br) employing following combinations of reagents: trimethylsilyl iodide/H_2O,[24] trimethylsilyl chloride (TMSCl)/NaI/H_2O,[25] TMSCl/LiBr/tetraethylammonium bromide,[26] CuO·HBF_4/I_2/Et_3SiH,[27] and BI_3/*N*,*N*-diethylaniline.[28] Recently, Kawaguchi et al. have published a method for the synthesis of α-vinyl iodides using iodine and $Ph_2P(O)H$.[29] The latter reduces iodine as well as serves as a proton source. Later, they made an improvement by replacing $Ph_2P(O)H$ with PPh_3 and water.[30] This modification allowed to perform a sequential C−C cross-coupling reaction in the same pot. Another recently published approach toward the α-vinyl iodides from terminal alkynes is a $CeCl_3$·$7H_2O$-catalyzed hydroiodination employing NaI as the iodide ion source.[31] Although highly regioselective, most of these methods are not

Received: August 4, 2018
Accepted: December 4, 2018
Published: December 21, 2018

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

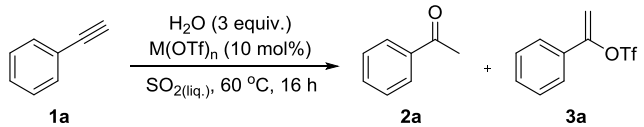
atom-efficient and lead to a high amount of both organic and inorganic wastes. In contrast, selective synthesis of α-vinyl chlorides from monosubstituted acetylenes is poorly studied. The latest examples include direct Markovnikov addition of HCl to the alkynes catalyzed by [Cp*RuCl(cod)][32] or commercially available nanogold catalyst.[33]

As the alkyne hydration and hydrohalogenation can be facilitated by Lewis acid additives, we became curious to explore whether liquid SO_2 as a solvent bearing Lewis acid properties will have the same promoting effect. Due to its relatively high boiling point (bp −10.05 °C) and low vapor pressure (ca. 3 bar at 20 °C) compared to other gases,[34] SO_2 can be easily liquefied and handled in its liquid state. Compared to conventional solvents, liquid SO_2 has some considerable advantages: (1) it dissolves both organic and inorganic salts, due to the high dipole moment (1.6 D);[35] (2) it is commercially available (≤5 EUR/kg) in high purity (99.98%, H_2O content ≤50 ppm); and (3) its removal from the reaction mixture does not require heating under reduced pressure. Since Walden observations of carbenium ion stability in liquid SO_2 at the beginning of the 20th century,[36] the application of liquid SO_2 as a solvent has been slowly expanded.[37−47]

RESULTS AND DISCUSSION

Prompted by the fact that metal triflates are an emerging catalyst class in hydroelementation reactions in general and that besides the title reactions, also triflate-catalyzed protocols for hydroalkoxylation,[48,49] hydroamination,[50,51] and hydrothiolation[52,53] are known, we started our study by screening a series of metal triflates $M(OTf)_n$ as catalysts for the alkyne hydration in liquid SO_2 employing phenyl acetylene (**1a**) as a model substrate (Table 1). In almost all cases, a formation of the desired acetophenone (**2a**) was observed. Conversion to **2a** did not exceed 13% in the presence of Cu(I,II)[a] and Yb(III) triflates (Table 1, entries 1−3), while the use of Al(III), Bi(III), or Ag(I)[a] triflate improved the conversion of the starting material to above 60% (Table 1, entries 4−6). Sc(III) and In(III) triflates exhibited comparably high catalytic activity providing >70% of acetophenone (**2a**) (Table 1, entries 7 and 8), but $Hf(OTf)_4$ proved to be the most active hydration catalyst providing full conversion (Table 1, entry 9). The presence of vinyl triflate **3a** (Table 1, entries 3 and 6) in the crude reaction mixture may point to the reaction mechanism through this compound as an intermediate. To the best of our knowledge, this is the first report on $Hf(OTf)_4$-catalyzed alkyne hydration.

Table 1. Catalyst Screening for the Alkyne Hydration in Liquid SO_2[a]



		^{1}H NMR yields of products **2a**, **3a**, and recovered starting material **1a** (%)[b]		
entry	catalyst $M(OTf)_n$ (10 mol %)	**1a**	**2a**	**3a**
1	$CuOTf{\cdot}C_6H_6$	73	1	0
2	$Cu(OTf)_2$	67	8	0
3	$Yb(OTf)_3{\cdot}nH_2O$	58	13	1
4	$Al(OTf)_3$	18	49	0
5	$Bi(OTf)_3$	12	62	0
6	AgOTf	26	64	6
7	$Sc(OTf)_3$	11	72	0
8	$In(OTf)_3$	8	75	0
9	$Hf(OTf)_4$	0	80	0

[a]Reactions were carried out using **1a** (1 mmol), $M(OTf)_n$ (10 mol %), and H_2O (3 equiv) in liquid SO_2 (25 ± 5 g) at 60 °C for 16 h in a pressure reactor. [b]Determined by ^{1}H NMR spectra on the crude reaction mixture using diphenyl methane as an internal standard, samples were prepared by filtration of reaction mixture in $CHCl_3$ through a celite layer.

Based on economic considerations, $In(OTf)_3$ was the catalyst of choice for further optimization of the reaction conditions (see Table S3, Supporting Information). It was found that 10 mol % loading of $In(OTf)_3$ and 100 °C are the optimal conditions for the hydration of phenyl acetylene (**1a**) in liquid SO_2 (Table S3, entry 4). To avoid a practical problem associated with the isolation of rather volatile product **2a**, we continued the optimization studies with 4-ethynylbiphenyl (**1b**). Using this more reactive substrate, catalyst loading could be reduced to 1 mol % and the temperature to 60 °C without a significant loss in the product yield (Table S3, entry 7). Moreover, a formation of the desired ketone **2b** was observed even in the absence of the catalyst at elevated temperature (20% isolated yield at 105 °C: Table S3, entry 6). On the other hand, when the amount of the water additive was reduced to 1 equiv in the presence of catalyst, the conversion of acetylene **1b** diminished, considerably (Table S3, entry 9).

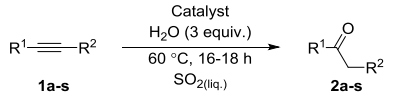
It is also worth mentioning that the hydration of phenyl acetylene (**1a**) practically did not proceed in conventional solvents such as EtOAc, MeCN, dimethyl sulfoxide, 1,4-dioxane, and sulfolane under optimized reaction conditions (3 equiv H_2O, 10 mol % $In(OTf)_3$, 100 °C).

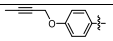
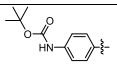
To test the Brønsted acidity of the reaction medium, we performed a control experiment: a solution of PhNHBoc (1 equiv) and H_2O (3 equiv) in liquid SO_2 was heated at conditions equal to those for the optimized hydration process of 4-ethynylbiphenyl (**1b**) (Table S3, entry 7). The acid-labile test substrate was recovered with 96% isolated yield after chromatographic purification. This experiment shall indicate that the overall acidity of the system should not be considered as significantly acidic. We hypothesize that liquid SO_2 as solvent is a weak Lewis acid and is not efficient in stabilizing HSO_3^- anion. Therefore, the equilibrium $SO_2 + 2H_2O \rightarrow H_3O^+ + HSO_3^-$ is not efficiently shifted to the right in the liquid SO_2 medium.

Substrate scope for In(III) or Hf(IV) triflate-catalyzed alkyne hydration in liquid SO_2 under optimized conditions is summarized in Table 2. The reactivity of an alkyne and consequently a choice of the catalyst and its loading depend on the electronic effects of the substituents. Hence, phenyl acetylenes **1d−j** containing electron-donating substituents (Alk-, AlkO-, ArO-) reacted smoothly in the presence of ≤1 mol % $In(OTf)_3$ (Table 2, entries 6−12). It should be mentioned that the hydration occurred only to the benzylic position of diyne **1j**, leaving the internal C≡C bond of the side chain unreacted (Table 2, entry 12). Taking alkyne **1f** as an example, we demonstrated that the hydration procedure can be performed in gram scale by using a substrate/solvent mass ratio of 1:20 (Table 2, entry 8). Despite the presence of Lewis basic nitrogen in *para*-amino-substituted phenyl acetylenes **1k,l**, the corresponding aryl ketones **2k,l** were isolated in good

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

Table 2. Substrate Scope for In(III) and Hf(IV) Triflate-Catalyzed Alkyne Hydrations in Liquid SO_2[a]



Entry	Substrate **1a-s**	R^1	R^2	Catalyst		Yield of compound **2** (%)[b]
				$M(OTf)_n$	mol%	
1[c]	**1a**		H	$In(OTf)_3$	10	**2a**, quant.[d]
2	**1b**		H	$In(OTf)_3$	1	**2b**, 89
3	**1c**		H	$In(OTf)_3$	1	**2c**, 22
4				$In(OTf)_3$	5	**2c**, 76[d]
5				$Hf(OTf)_4$	1	**2c**, quant.
6	**1d**		H	$In(OTf)_3$	0.5	**2d**, quant.
7	**1e**		H	$In(OTf)_3$	0.5	**2e**, quant.
8	**1f**		H	$In(OTf)_3$	0.5	**2f**, quant.
9	**1g**		H	$In(OTf)_3$	0.5	**2g**, quant.
10	**1h**		H	$In(OTf)_3$	0.5	**2h**, 95
11	**1i**		H	$In(OTf)_3$	0.5	**2i**, quant.
12	**1j**		H	$In(OTf)_3$	1	**2j**, 87
13	**1k**		H	$In(OTf)_3$	1	**2k**, 70
14	**1l**		H	$In(OTf)_3$	1	**2l**, 50
15	**1m**		H	$In(OTf)_3$	5	**2m**, 56
16	**1n**		H	$In(OTf)_3$	1	**2n**, 74[d]
17	**1o**		H	$In(OTf)_3$	1	**2o**, 79[d]
18	**1p**		Me	$In(OTf)_3$	5	**2p**, 9[e]
19[f]				$Hf(OTf)_4$	5	**2p**, 82
20[f]	**1q**		*n*-Bu	$Hf(OTf)_4$	5	**2q**, 53
21[f]	**1r**		Ph	$Hf(OTf)_4$	5	**2r**, 66
22[g]	**1s**		Br	$In(OTf)_3$	10	**2s**, 55

[a]The reactions were carried out using **1** (0.5−4.5 mmol) in liquid SO_2 (25 ± 5 g) in a pressure reactor. [b]Isolated yield, if not stated otherwise. [c]The reaction was carried out at 100 °C. [d]Determined by ^1H NMR using diphenyl methane as an internal standard. [e]Gas chromatography (GC)−mass spectrometry (MS) analysis of the reaction extract: 88% **1p**, 9% **2p**. [f]The reaction was carried out at 70 °C. [g]The reaction was carried out at 80 °C; formation of 1-(1,2-dibromovinyl)-4-propylbenzene as a side product was observed.

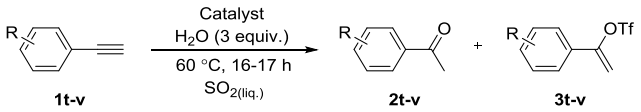
DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

yields (Table 2, entries 13 and 14). Even *N*-Boc-protected aniline **1m** as an acid-labile substrate provided product **2m** with 56% yield (Table 2, entry 15). Also, heterocyclic substrate like 3-ethynylthiophene (**1n**) was compatible with our newly developed hydration conditions in liquid SO_2 in the presence of 1 mol % $In(OTf)_3$ (Table 2, entry 16).

An enhanced hydration reactivity in the presence of $Hf(OTf)_4$ was demonstrated in the cases of substrates **1c** and **1p** (Table 2, entries 5 and 19). Thus, a quantitative yield of **2c** was obtained in the presence of 1 mol % $Hf(OTf)_4$, whereas 5 mol % $In(OTf)_3$ provided lower yield (Table 2, entry 5 vs 4). This was even more pronounced for the substrate **1p**, where the switch between both catalysts changed the yield from 9 to 82% (Table 2, entry 18 vs 19). $Hf(OTf)_4$ performed well also for other disubstituted acetylenes like **1q,r** (Table 2, entries 20 and 21), whereas 1-haloalkyne **1s** was converted to the corresponding α-haloketone **2s** in the presence of 10 mol % $In(OTf)_3$ (Table 2, entry 22). Although aliphatic alkynes did not react under the optimized reaction conditions, cyclopropyl acetylene (**1o**) formed the hydration product **2o** in good yield (Table 2, entry 17). Such a result could be explained by the ability of cyclopropyl ring to stabilize the α-vinyl carbenium ion.[54]

Phenyl acetylenes **1t−v** with electron-withdrawing substituents had notably reduced reactivity compared to the substrates containing electron-donating groups (Table 3).

Table 3. In(III) and Hf(IV) Triflate-Catalyzed Hydrations of Electron-Poor Aryl Acetylenes 1t−v in Liquid SO_2[a]



1t-v 2t-v 3t-v

					compound distribution in the reaction mixture (%)[b]		
entry	1	R	catalyst	mol %	1	2	3
1	**1t**	4-F	$In(OTf)_3$	5	66	32	2
2			$In(OTf)_3$	10		>99[c]	
3			$Hf(OTf)_4$	1	24	73	3
4			$Hf(OTf)_4$	5		>99[c]	
5	**1u**	2-F	$In(OTf)_3$	10	58	27	15
6			$Hf(OTf)_4$	5	70	30	
7	**1v**	4-CF_3	$In(OTf)_3$	10	97		3
8			$Hf(OTf)_4$	10	44		56 (45)[d]

[a]The reactions were carried out using **1** (0.6−1.2 mmol) in liquid SO_2 (25 ± 5 g) in a pressure reactor. [b]Determined by GC−MS. [c]Quant. yield: determined by ^1H NMR spectroscopy using diphenyl methane as an internal standard. [d]Isolated yield based on the initial amount of triflate ion.

Thus, despite the positive mesomeric effect of fluorine atom, its negative inductive effect reduces the reactivity of *p*-fluorophenyl acetylene (**1t**) (Table 3, entries 1−4). As a result, to reach full conversion of alkyne **1t**, 5 mol % $Hf(OTf)_4$ or 10 mol % $In(OTf)_3$ was required (Table 3, entries 4 and 2). Interestingly, for a sterically hindered *o*-fluoro-substituted analogue **1u**, 10 mol % $In(OTf)_3$ provided higher conversion of starting material than 5 mol % $Hf(OT)_4$ (Table 3, entry 5 vs 6). Employing alkyne **1v**, practically no ketone **2v** was observed (Table 3, entries 7 and 8). Instead, under $Hf(OTf)_4$-catalyzed conditions, the corresponding vinyl triflate **3v** was formed and isolated in 45% yield based on the initial triflate content in the reaction mixture (Table 3, entry 8).

Generation of vinyl triflates **3a** (Table 1, entries 3 and 6) and **3t−v** (Table 3, entries 1, 3, 5, 7, and 8) might indicate that the hydration proceeds through these species as the intermediates (see Scheme S1, Supporting Information). Stability of triflate **3** is higher when the benzylic carbenium ion intermediate during the hydrolysis process is destabilized with the electron-withdrawing groups. At first sight, we cannot exclude that the transformation **1** → **3** can occur due to the presence of trace amounts of triflic acid, which might be released after hydrolysis of the metal triflate.[55−59] Therefore, a control experiment **1b** → **2b** was performed in the presence of TfOH (1 mol %) (see Table S3, entry 8, Supporting Information). The latter provided product **2b** only with 15% isolated yield contrary to 89% in the presence of $In(OTf)_3$ (Table S3, entry 8 vs 7). At this point, we conclude that under the developed experiment conditions, trace amounts of TfOH, which might be present in the reaction mixture, can act as a background mediator, but the observed excellent catalytic activity of $In(OTf)_3$ and $Hf(OTf)_4$ should be mainly attributed to the nonhydrolyzed salt.

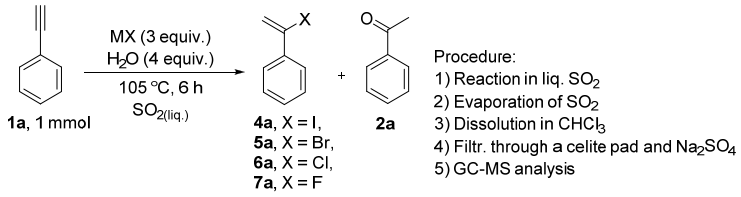
Inspired by the successful alkyne hydration employing liquid SO_2 as the solvent, we next turned our attention to alkyne hydrohalogenation. With reference to the Lewis acid-catalyzed hydroiodination of alkynes published by Bartoli et al.,[31] we screened a reactivity of the group I and II metal halides and ammonium halides toward phenyl acetylene (**1a**) in liquid SO_2 under constant conditions (Table 4). The tested fluorides turned out to be unreactive under these conditions. For chlorides, slightly higher reactivity was observed, although the content of the desired α-vinyl chloride **6a** in the reaction filtrate did not exceed 13% (GC−MS). LiBr and $MgBr_2{\cdot}6H_2O$ exhibited the highest reactivity among bromides, providing 96 and 77% (GC−MS) contents of α-bromostyrene (**5a**) in the reaction filtrate, respectively. Finally, all tested iodides led to the consumption of the starting material. LiI led to a mixture of acetophenone (**2a**) and unidentified side products. Also, NaI provided ketone **2a** from alkyne **1a**, albeit in a quantitative manner. Gratifyingly, K, Cs, and ammonium iodides provided the desired vinyl iodide **4a** in a good to excellent content with less than 5% of ketone **2a** as an impurity (GC−MS). We can assume that the relatively unstable α-iodostyrene does further hydrolyze to acetophenone (**2a**) under the investigated reaction conditions.

We suggest that the difference of the reactivity among halides could be explained by their solubility in liquid SO_2. It is known that the alkali metal halides are soluble in liquid SO_2, but their solubility decreases in the order $I^- > Br^- > Cl^- > F^-$.[60] Furthermore, the ability of sulfur dioxide to bind fluoride ion in a stable fluorosulfite ion can explain that the reactivity of fluorides is completely suppressed under these conditions.[39] At the same time, a difference between halides bearing the same anion indicates that also cationic part of salt has its own effect on the course of the reaction. It should be mentioned that NH_4I was identified as a novel source of both H^+ and I^- ions required for alkyne hydroiodination. NH_4I as a reagent does not require the water additive, which makes the experimental procedure even simpler.

With the screening results in hand (Table 4), we turned to the investigation of the substrate scope. It was found that each hydrohalogenation system still required a "secondary optimization" depending on the used substrates. The investigated

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

Table 4. Halide Reactivity Screening for Alkyne Hydrohalogenation in Liquid SO_2[a]



Entry	MX	I^-			Br^-			Cl^-			F^-		
		1a	**4a**	**2a**	**1a**	**5a**	**2a**	**1a**	**6a**	**2a**	**1a**	**7a**	**2a**
1	Li^+	-	-	48	-	96	<1	89	11	-	>99	-	-
2	Na^+	-	-	>99	97	2	<1	99	<1	<1	>99	-	-
3	K^+	-	96	4	96	4	-	98	1	1	>99	-	-
4	Cs^+	-	90	4	87	11	-	not tested			>99	-	-
5[b]	Mg^{2+}	not tested			14	77	1	86	13	2	>99	-	-
6	NH_4^+	16	83	1	99	1	-	98	<1	<1	94	-	6

[a]The reactions were carried out in liquid SO_2 (25 ± 5 g) in a pressure reactor; the numbers describe the composition of the crude reaction mixture determined by GC−MS; the best results are highlighted in green. [b]$MgBr_2{\cdot}6H_2O$ or $MgCl_2{\cdot}6H_2O$ was used, respectively.

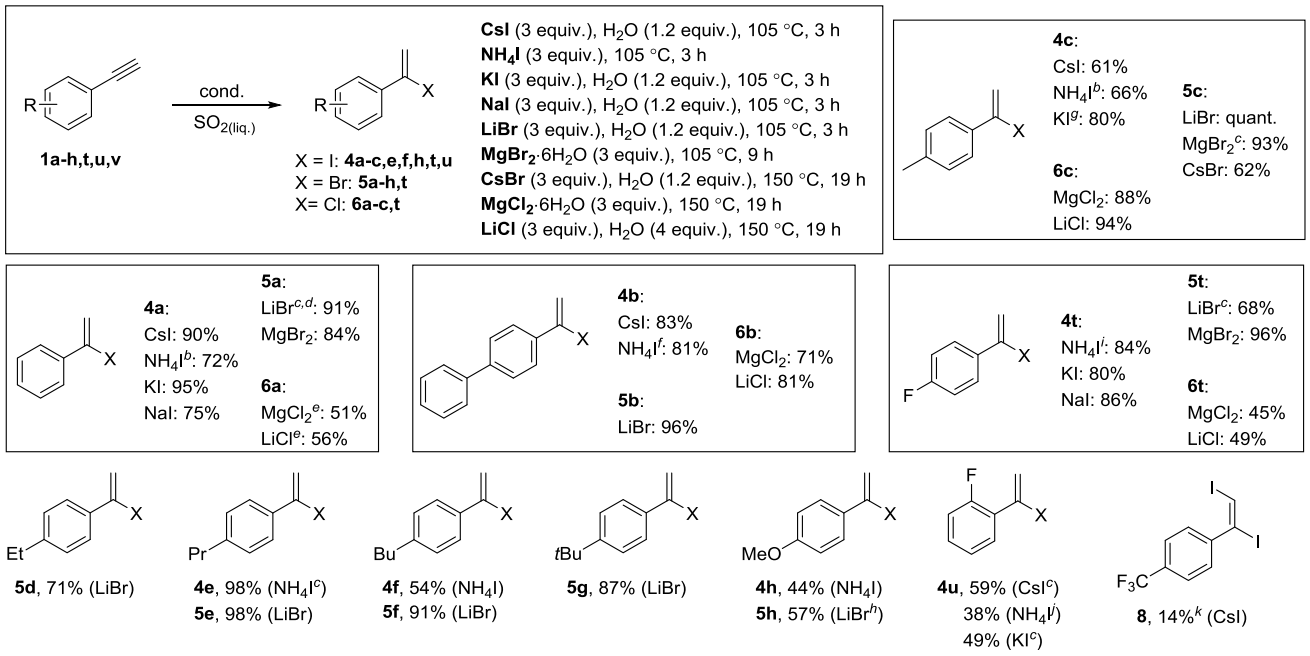
alkyne hydrohalogenations proceeded cleanly and provided easily analyzable mixtures of α-vinyl halide, unreacted starting material, and ketone. Therefore, product yields were determined by ^1H NMR spectroscopy using internal standard. The full data set can be found in the Supporting Information (CsI: Tables S4 and S5; NH_4I: Table S6; KI: Table S7; NaI: Table S8; LiBr: Tables S9 and S10; CsBr and $MgBr_2{\cdot}6H_2O$: Table S11; LiCl and $MgCl_2{\cdot}6H_2O$: Table S12). The substrate scope of hydrohalogenation of terminal aryl acetylenes is depicted in Scheme 1. NH_4I, LiBr, NaI, KI, and CsI appeared to be the most reactive halides, which required 3 h at 105 °C to provide optimal yields of the expected products. Also, $MgBr_2{\cdot}6H_2O$ was reasonably reactive, albeit it required 9 h at 105 °C and a higher excess (3 equiv). In the least reactive category, we can place CsBr, $MgCl_2{\cdot}6H_2O$, and LiCl, which required much higher temperature (150 °C) and prolonged reaction times (19 h).

The yields of hydroiodination products exhibited the largest data scattering. This can be explained by a compromise between the aryl alkyne reactivity and the hydrolytic stability of the formed vinyl iodide. In general, electron-donating substituents (Scheme 1; **1b**: R = Ph, **1c**: R = Me, **1e**: R = Pr) and weakly deactivation substituents (**1t**: R = F) gave good to excellent yields of products **4a−c**, **4e**, and **4t**. Strong electron-donating substituents (**1b**: R = OMe) and ortho-substituted systems (e.g., **1u**) resulted in mediocre yields of vinyl iodides due to the formation of ketone side product or diminished reactivity, respectively. In this context, it is clear that only salts bearing non-Lewis acidic cations (NH_4^+, Na^+, K^+, Cs^+) can be successfully used in hydroiodination reactions in liquid SO_2 (see also remark on the synthesis of vinyl bromide **5h** in the presence of LiBr; vide infra). Finally, substrate **1v** possessing F_3C substituent stayed rather intact and gave 14% of a side product, which was identified as 1-(1,2-diiodovinyl)-4-(trifluoromethyl)benzene (**8**). We have also tested $NaHSO_3$ as an additional proton source for alkyne protonation step (see Table S6, entry 10, Supporting Information), but this led to a reduced rate of the hydrohalogenation reaction. On the other hand, triphenylphosphine as a reductant of molecular iodine possibly formed in the reaction mixture slightly improved the conversion of alkynes **1** to the desired iodides **4** (Table S6, entries 3, 7, and 15).

Next, we turned our attention to the synthesis of α-vinyl bromides **5**. First, the reactivity of LiBr was tested (Scheme 1, see Tables S9 and S10, Supporting Information). The influence of the substituent electronic effects on the course of the reaction was not so significant as in the case of vinyl iodide synthesis. Thus, aryl acetylenes **1a−g** provided up to quantitative yields of α-vinyl bromides **5a−g**. By employing alkyne **1a**, we demonstrated that the hydrobromination can be excellently performed (91% of product **5a**) in gram scale using a substrate/solvent mass ratio of 1:14. In contrast to iodides, no formation of the corresponding 1,2-dibromides was observed. Interestingly, a combination of more reactive alkyne **1h**, LiBr (3 equiv), and H_2O (1.2 equiv) in liquid sulfur dioxide already at −10 °C provided the expected halide **5h** in 57% yield. On the other hand, the same combination at 105 °C

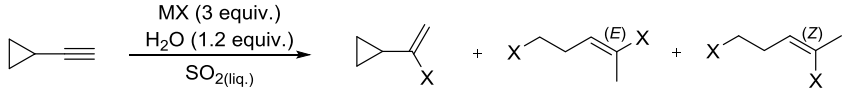
DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

Scheme 1. Hydrohalogenation of Terminal Aryl Acetylenes 1 in Liquid SO_2[a]



[a]The reactions were carried out using **1** (0.6−1.1 mmol) in liquid SO_2 (25 ± 5 g) in a pressure reactor; yields were determined by ^{1}H NMR spectroscopy using diphenyl methane or *m*-tolyl aldehyde (for **4h** and **5h**) as an internal standard; if not stated otherwise. [b]0.5 equiv PPh_3 was added. [c]Reaction time 6 h. [d]Concentration substrate/solvent 1:14 (g/g). [e]Reaction time 24 h. [f]Reaction carried out at 70 °C for 14 h. [g]Reaction carried out at 80 °C. [h]Reaction carried out in a two-neck round-bottom flask equipped with a dry ice condenser at −10 °C for 6 h. [i]Reaction carried out using 1.2 equiv NH_4I at 80 °C for 18 h. [j]Reaction time 14 h. [k]Isolated yield.

Table 5. Hydrohalogenation of Cyclopropyl Acetylene (1o) in Liquid SO_2[a]



			^{1}H NMR yields (%)[b]		
entry	MX	cond	9	10	11
1	CsI	A	9a, 23	10a, 16	11a, 7
2		B	9a, 55	10a, 23	11a, 7
3	NH_4I	A		10a, 54	11a, 29
4		B	9a, 42	10a, 17	11a, 7
5	LiBr	A		10b, 58	11b, 27
6		B		10b, 66	11b, 27

[a]Reactions were carried out using **1o** (1.2 mmol) in liquid SO_2 (25 ± 5 g) in a pressure reactor; reaction with NH_4I was performed without the water additive. [b]Determined by ^{1}H NMR spectroscopy using diphenyl methane as an internal standard.

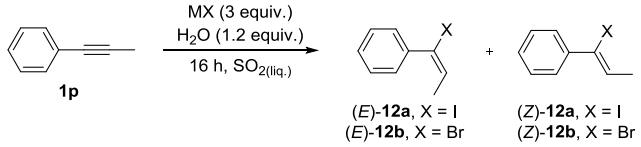
provided ketone **2h** (Table S10, entry 1). On the contrary, the tested iodides did not react at such a low temperature. We also discovered that the formation of ketone **2** was facilitated when methanol instead of water was used as a proton source for the hydrobromination of alkyne **1e** (Table S9, entry 13). $MgBr_2 \cdot 6H_2O$ behaved similar to LiBr, although a prolonged reaction time was required to provide sufficient conversion of the starting material (Scheme 1 and Table S11, Supporting Information). Also, CsBr can be used as a bromide source (transformation **1c** → **5c**), albeit it required harsher reaction conditions and provided only 62% of product **5c** (Scheme 1, see Table S11, entry 3, Supporting Information).

On the basis of the successful modification of reaction conditions in bromide series, we also explored a possibility to enhance the reactivity of chloride ion sources. A comparable reactivity was observed when $MgCl_2 \cdot 6H_2O$ or LiCl was used at 150 °C (Scheme 1 and see Table S12, Supporting Information). Alkynes **1b** and **1c** containing weakly electron-donating groups reacted smoothly, and the expected *α*-vinyl chlorides **6b** and **6c** were obtained in good yields (Table S12, entries 3−6). When less reactive phenyl acetylene (**1a**) or 4-fluorophenyl acetylene (**1t**) was subjected to the same conditions, reaction yields were affected by incomplete conversion of the starting material (Table S12, entries 1, 2, 7, and 8).

Unfortunately, acetylenes containing acyclic aliphatic substituents did not form the desired *α*-vinyl halides under the developed conditions. LiBr was absolutely unreactive, but CsI

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

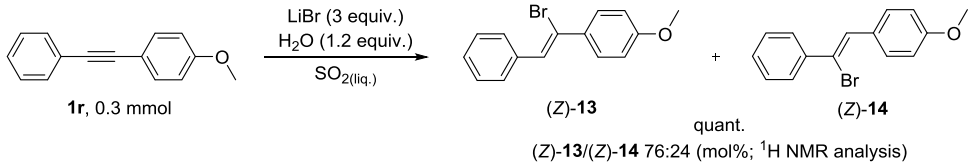
Table 6. Hydrohalogenation of Phenylpropyne (1p) in Liquid SO_2[a]



entry	MX	T (°C)	time (h)	^{1}H NMR yield of (*E*)-12 + (*Z*)-**12** (%)[b]	*E*/*Z*[c]
1	CsI	90	16	**12a**, 86	64/36
2	LiBr	105	16	**12b**, 83	75/25

[a]Reactions were carried out using **1p** (0.8−1.0 mmol) in liquid SO_2 (25 ± 5 g) in a pressure reactor. [b]Determined by ^{1}H NMR spectroscopy using diphenyl methane as an internal standard. [c]Determined by ^{1}H NMR spectroscopy.

Scheme 2. Hydrobromination of Alkyne 1r in Liquid SO_2



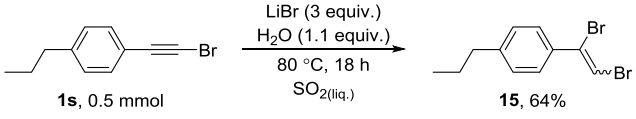
and NH_4I led to the formation of iodination products with varying conversion levels of the starting material (see Tables S13 and S14, Supporting Information). Gratifyingly, cyclopropyl acetylene (**1o**) exhibited a high reactivity, and full conversion was observed in all of the tested conditions (Tables 5 and S15). Depending on the halide ion source and the reaction conditions, a mixture of geometrical isomers of dihydrohalogenations **10** and **11** with or without desired cyclic vinyl halide **9** was obtained. In both temperature regimes (60 and 105 °C), CsI produces all possible products **9a**−**11a** (Table 5, entries 1 and 2). The reaction with NH_4I exhibited a higher temperature dependence (Table 5, entries 3 and 4). Thus, at 105 °C, NH_4I gave only the rearranged products **10a** and **11a** in 83% total yield. LiBr gave dibromides **10b** and **11b** in synthetically useful yields with average **10b**/**11b** ratio 2.3:1 in either of the tested temperature regimes (Table 5, entries 5 and 6).

Finally, we performed hydrohalogenation reactions by employing internal alkynes with at least one aromatic substituent attached to the triple bond. As expected, in the case of phenylpropyne (**1p**), C-halogen bond was formed at the benzylic position, and products **12a**,**b** were isolated as a mixture of geometrical isomers with the (*E*)-isomer being the major one (Table 6).

Hydrobromination of alkyne **1r** was (*Z*)-selective, and the formation of regioisomers (*Z*)-**13** and (*Z*)-**14** was observed (Scheme 2). Apparently, the steric effects of the substrate forbid the formation (*E*)-isomers.

1-Bromoalkyne **1s** was compatible only with our hydrobromination conditions, leading to the desired vinyl bromide **15** in good yield (Scheme 3). When iodides were used under similar reaction conditions, only the formation of a complex mixture was observed.

Scheme 3. Hydrobromination of Alkyne 1s in Liquid SO_2



In conclusion, we have discovered novel conditions for alkyne hydration and hydrohalogenation by taking advantages of liquid SO_2 as a polar solvent with Lewis acid properties that is capable of dissolving both organic and inorganic substances. As a result, a combination of $In(OTf)_3$ or $Hf(OTf)_4$ as a catalyst and liquid SO_2 as a solvent allowed us to develop effective method for the hydration of electron-rich terminal and internal aryl alkynes without the direct addition of Brønsted acid. Catalyst loading can be lowered to less than 1 mol % for alkynes containing strong electron-donating groups. It has to be mentioned that $Hf(OTf)_4$ has found an application in this chemical transformation for the first time. By employing simple reagent systems like CsI, KI, NaI, LiBr, or LiCl/H_2O as well as solo reagents like NH_4I, $MgBr_2{\cdot}6H_2O$, and $MgCl_2{\cdot}6H_2O$, we have succeeded in the hydrohalogenation of electron-rich aromatic alkynes in liquid SO_2. Most of these salts are used as halide sources in alkyne hydrohalogenation for the first time. Moreover, ammonium iodide works as both iodide and proton donor in a reaction mixture without the need for water additive. Finally, the facilitated vinyl carbenium ion formation in liquid sulfur dioxide and its quenching with nucleophiles like water or halides opens possibilities for the design of other similar transformations that would profit from the Lewis acidic and ionizing properties of liquid SO_2.

EXPERIMENTAL SECTION

General Experimental Details. Reactions at temperature above the boiling point of SO_2 (−10 °C) were carried out in a stainless steel pressure reactor. For reactions below SO_2 boiling point, a two-neck round-bottom flask equipped with a dry ice condenser was used. The solvents for reaction workup and chromatographic purification were freshly distilled prior to use. Commercially available reagents were used as received. Composition of the final reaction mixture was determined by Agilent Technologies 6890N gas chromatograph coupled with Agilent Technologies 5975B mass spectrometer (electron ionization (EI)) (for method description, see the Supporting Information). Chromatographic purification was monitored by thin-layer chromatography (TLC) on E. Merck Kieselgel 60 F_{254}, with detection by UV light or a solution of potassium permanganate as a visualizing agent. Column chromatography

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

was performed on silica gel (60 Å, 40−60 μm, ROCC). Preparative chromatography for compounds (*Z*)-**12** and (*Z*)-**13** was performed on Macherey-Nagel Sil G-25 (60 Å, 5−17 μm) plates with detection by UV light. IR spectra were recorded in KBr with Fourier transform infrared (FT-IR) PerkinElmer Spectrum BX spectrometer (4000−450 cm^{-1}). Melting point was recorded with a Fisher Digital Melting Point Analyzer model 355 apparatus. ^1H and ^{13}C NMR spectra were recorded with Bruker 300 MHz spectrometer in $CDCl_3$. Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz, respectively. The residual solvent peak is used as an internal reference (7.26 and 77.16 ppm for ^1H NMR and ^{13}C NMR, respectively). For quantitative ^1H NMR relaxation, time was increased (d_1 = 10). High-resolution mass (HRMS) (electrospray ionization (ESI)) were recorded with an Agilent 1290 Infinity series ultra-high pressure liquid chromatography connected to an Agilent 6230 time-of-flight mass spectrometer or (atmospheric pressure chemical ionization (APCI)) on 7 T solariX XR (Bruker Daltonik GmbH) Fourier transform ion cyclotron resonance mass spectrometer equipped with an APCI source.

General Procedure for Alkyne Hydration in Liquid SO_2. Alkyne (0.5−4.5 mmol), water (3 equiv), and catalyst (see Tables 2 and 3) were placed into a stainless steel reactor equipped with a glass tube and a magnetic stirring bar. The vacuum/argon cycles were performed and sulfur dioxide (25 ± 5 g) was transferred into the reactor at −78 °C by distillation. The reactor was sealed and the reaction was performed under pressure (∼8 bar) at 60 °C for 16−18 h. Then, the reactor was cooled down to room temperature and connected to either the storage cylinder of SO_2 for the solvent recycling or a trap containing aqueous $NaHCO_3$ solution for SO_2 removal. The solid residue was partitioned between dichloromethane (DCM) (10−20 mL) and water (5−15 mL). The aqueous phase was extracted with DCM (3 × 5−10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Concentration of the filtrate under reduced pressure gave a residue that was fractionated by column chromatography (EtOAc/Hex) to provide pure product. Note: for volatile hydration products **2a**, **2c**, **2n**, **2o**, and **2t**, yield was determined by quantitative ^1H NMR analysis of the reaction extract using diphenyl methane as an internal standard.

*Acetophenone (**2a**).*[19] Yield quant. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.99−7.92 (m, 2H), 7.60−7.51 (m, 1H), 7.50−7.40 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.2, 137.2, 133.2, 128.7, 128.4, 26.7. GC−MS (70 eV, EI) m/z: $[M]^+$ 120.1; t_R 6.21 min.

*1-([1,1′-Biphenyl]-4-yl)ethan-1-one (**2b**).*[19] Yield 109 mg (99%). White solid. R_f 0.29 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.04 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.66−7.59 (m, 2H), 7.52−7.44 (m, 2H), 7.44−7.37 (m, 1H), 2.64 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 197.9, 145.9, 140.0, 136.0, 129.1 (2C), 128.4, 127.4 (2C), 26.8. GC−MS (70 eV, EI) m/z: $[M]^+$ 196.1; t_R 8.40 min.

*1-(p-Tolyl)ethan-1-one (**2c**).*[19] Yield quant. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.0, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7. GC−MS (70 eV, EI) m/z: $[M]^+$ 134.2; t_R 6.65 min.

*1-(4-Ethylphenyl)ethan-1-one (**2d**).*[15] Yield 359 mg (quant.). Yellow oil. R_f 0.48 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.89 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 2.71 (q, J = 7.7 Hz, 2H), 2.58 (s, 3H), 1.26 (t, J = 7.7 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.0, 150.2, 135.0, 128.7, 128.2, 29.0, 26.6, 15.3. GC−MS (70 eV, EI) m/z: $[M]^+$ 148.1; t_R 6.95 min.

*1-(4-Propylphenyl)ethan-1-one (**2e**).*[15] Yield 348 mg (quant.). Yellow oil. R_f 0.54 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 2.56 (t, J = 7.5 Hz, 2H), 2.50 (s, 3H), 1.59 (s, J = 7.5 Hz, 2H), 0.87 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.0, 148.6, 135.1, 128.8, 128.6, 38.1, 26.6, 24.3, 13.9. GC−MS (70 eV, EI) m/z: $[M]^+$ 162.2; t_R 7.24 min.

*1-(4-Butylphenyl)ethan-1-one (**2f**).*[61] Yield 360 mg (quant.). Yellow oil. R_f 0.59 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.58 (s, 3H), 1.62 (q, J = 7.6 Hz, 2H), 1.36 (s, J = 7.6 Hz, 2H), 0.93 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.0, 148.9, 135.0, 128.7, 128.6, 35.8, 33.4, 26.6, 22.5, 14.0. GC−MS (70 eV, EI) m/z: $[M]^+$ 176.1; t_R 7.52 min.

*1-(4-(tert-Butyl)phenyl)ethan-1-one (**2g**).*[62] Yield 370 mg (quant.). Yellow oil. R_f 0.41 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 2.59 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 198.0, 156.9, 134.7, 128.4, 125.6, 35.2, 31.2, 26.7. GC−MS (70 eV, EI) m/z: $[M]^+$ 176.1; t_R 7.35 min.

*1-(4-Methoxyphenyl)ethan-1-one (**2h**).*[19] Yield 332 mg (95%). Yellowish solid. R_f 0.28 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.94 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.9, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5. GC−MS (70 eV, EI) m/z: $[M]^+$ 150.1; t_R 7.13 min.

*1-(4-Phenoxyphenyl)ethan-1-one (**2i**).*[19] Yield 346 mg (quant.). Yellowish solid. R_f 0.35 (Hex/EtOAc 9:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.94 (d, J = 8.9 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.25−7.15 (m, 1H), 7.13−7.03 (m, 2H), 7.00 (d, J = 8.9 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.9, 162.2, 155.6, 132.0, 130.7, 130.2, 124.8, 120.3, 117.4, 26.6.

*1-(4-(But-2-yn-1-yloxy)phenyl)ethan-1-one (**2j**).* Yield 81 mg (87%). Pale yellow solid. mp 61−62 °C. R_f 0.38 (Hex/EtOAc 6:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.93 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.70 (q, J = 2.3 Hz, 2H), 2.55 (s, 3H), 1.85 (t, J = 2.3 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.9, 161.8, 130.9, 130.6, 114.7, 84.6, 73.4, 56.6, 26.5, 3.8. GC−MS (70 eV, EI) m/z: $[M]^+$ 188.1; t_R 8.01 min. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{13}O_2$ 189.0910; found 189.0929. IR (FT-IR): 2240, 1680, 1275 cm^{-1}.

*1-(4-Aminophenyl)ethan-1-one (**2k**).*[63] Yield 81 mg (70%). Brownish solid. R_f 0.46 (Hex/EtOAc 1:1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 4.41−3.84 (br s, 2H), 2.50 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.6, 151.2, 130.9, 128.0, 113.9, 26.2. GC−MS (70 eV, EI) m/z: $[M]^+$ 135.1; t_R 7.31 min.

*1-(4-(Dimethylamino)phenyl)ethan-1-one (**2l**).*[64] Yield 57 mg (50%). Sulfur solid. R_f 0.46 (Hex/EtOAc 7:3). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.87 (d, J = 9.0 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 3.05 (s, 6H), 2.50 (s, 3H). ^{13}C NMR (75.5 MHz, CDCl3) δ: 196.5, 153.5, 130.6, 125.6, 110.8, 40.2, 26.1. GC−MS (70 eV, EI) m/z: $[M]^+$ 163.1; t_R 7.64 min.

*tert-Butyl (4-Acetylphenyl)carbamate (**2m**).*[65] Yield 66 mg (56%). White solid. R_f 0.53 (Hex/EtOAc 7:3). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.90 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 6.95 6.78 (br s, 1H), 2.55 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 197.1, 152.3, 143.1, 131.9, 130.0,

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

117.5, 81.4, 28.4, 26.5. GC−MS (70 eV, EI) m/z: $[M]^+$ 235.1; t_R 8.34 min.

*1-(Thiophen-3-yl)ethan-1-one (**2n**)*.[19] Yield 74%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.03 (dd, 1H, J = 2.9, 1.3 Hz, 1H), 7.53 (dd, J = 5.1, 1.3 Hz, 1H), 7.30 (dd, J = 5.1, 2.9 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 192.4, 142.7, 132.5, 127.1, 126.5, 27.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 126.0; t_R 6.13 min.

*1-Cyclopropylethan-1-one (**2o**)*.[11] Yield 79%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.23 (s, 3H), 1.98−1.88 (m, 1H), 1.06−0.98 (m, 2H), 0.91−0.84 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 209.0, 30.0, 21.1, 10.6.

*Propiophenone (**2p**)*.[19] Yield 88 mg (82%). Yellow oil. R_f 0.48 (Hex/EtOAc 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.97 (dd, J = 8.5, 1.4 Hz, 2H), 7.55 (tt, J = 7.4, 1.4 Hz, 1H), 7.50−7.40 (m, 2H), 3.01 (q, J = 7.3 Hz, 2H), 1.23 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 201.0, 137.1, 133.0, 128.7, 128.1, 31.9, 8.4. GC−MS (70 eV, EI) m/z: $[M]^+$ 134.1; t_R 6.61 min.

*1-(4-Methoxyphenyl)hexan-1-one (**2q**)*.[66] Yield 51 mg (53%). Yellow oil. R_f 0.39 (Hex/EtOAc 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.94 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.90 (t, J = 7.5 Hz, 2H), 1.79−1.65 (m, 2H), 1.41−1.29 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 199.4, 163.4, 130.4 (2C), 113.8, 55.6, 38.4, 31.8, 24.5, 22.7, 14.1. GC−MS (70 eV, EI) m/z: $[M]^+$ 206.2; t_R 8.15 min.

*1-(4-Methoxyphenyl)-2-phenylethan-1-one (**2r**)*.[67] Yield 72 mg (66%). Yellow solid. R_f 0.61 (Hex/EtOAc 7:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.00 (d, J = 8.9 Hz, 2H), 7.38−7.19 (m, 5H), 6.93 (d, J = 8.9 Hz, 2H), 4.24 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.4, 163.7, 135.1, 131.1, 129.8, 129.5, 128.8, 126.9, 113.9, 55.6, 45.4. GC−MS (70 eV, EI) m/z: $[M]^+$ 226.1; t_R 8.73 min.

*2-Bromo-1-(4-propylphenyl)ethan-1-one (**2s**)*.[62] Yield 61 mg (55%). Yellow oil. R_f 0.46 (Hex/EtOAc 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.44 (s, 2H), 2.66 (t, J = 7.5 Hz, 2H), 1.67 (s, J = 7.5 Hz, 2H), 0.95 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 191.1, 149.8, 131.8, 129.2, 129.1, 38.2, 31.1, 24.3, 13.9. GC−MS (70 eV, EI) m/z: $[M]^+$ 241.1; t_R 8.01 min.

*1-(4-Fluorophenyl)ethan-1-one (**2t**)*.[15] Yield quant. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98 (dd, J = 8.8, 5.4 Hz, 2H), 7.12 (t, J = 8.8 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 196.6, 165.9 (d, J = 255 Hz), 133.8 (d, J = 3 Hz), 131.1 (d, J = 9 Hz), 115.8 (d, J = 22 Hz), 26.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 138.1; t_R 6.03 min.

*1-(4-(Trifluoromethyl)phenyl)vinyl Trifluoromethanesulfonate (**3v**)*.[68] Yield 38 mg (45%). Yellowish oil. R_f 0.32 (Hex). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74−7.61 (m, 4H), 5.73 (d, J = 4.2 Hz, 1H), 5.52 (d, J = 4.2 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 152.1, 135.6, 132.3 (q, J = 33 Hz), 126.2 (q, J = 4 Hz), 125.8, 123.8 (q, J = 272 Hz), 118.7 (q, J = 320 Hz), 106.7. GC−MS (70 eV, EI) m/z: $[M]^+$ 320.1; t_R 6.65 min.

General Procedure for Alkyne Hydrohalogenation in Liquid SO_2. Alkyne, halide, and water (for the following halides: LiCl, LiBr, NaI, KI, CsBr, and CsI) or alkyne and halide (for the following halides: NH_4I, $MgCl_2{\cdot}6H_2O$, and $MgBr_2{\cdot}6H_2O$) were placed in a stainless steel reactor equipped with a glass tube and a magnetic stirring bar. The vacuum/argon cycles were performed, and sulfur dioxide (25 ± 5 g) was transferred into the sealed reactor at −78 °C by distillation. The reactor was sealed, and the reaction was performed under pressure at elevated temperature ($p \sim 20$ bar at 105 °C) for the time specified in Tables 5 and 6, Schemes 1−3. Then, the reactor was cooled down to room temperature and connected to either the storage cylinder of SO_2 for the solvent recycling or a trap containing aqueous $NaHCO_3$ solution for SO_2 removal. To the solid residue, ∼10 mL of DCM or chloroform was added. The resulting mixture was filtered through cotton wool or celite layer and (variations): (1) evaporated; (2) evaporated, treated with hexane and silica gel, filtered, and evaporated; (3) washed with saturated $NaHCO_3$, 10% $Na_2S_2O_3$, and brine, dried over Na_2SO_4, filtered, and evaporated; and (4) washed with saturated $NaHCO_3$, dried over Na_2SO_4, filtered, and evaporated. The obtained final residue was quantitatively analyzed by ^{1}H NMR spectroscopy using diphenyl methane or *m*-tolyl aldehyde (only for **4h** and **5h**) as an internal standard.

*(1-Iodovinyl)benzene (**4a**)*.[69] Yield 235 mg (94%; purity 96%; CsI). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60−7.45 (m, 2H), 7.40−7.27 (m, 3H), 6.48 (d, J = 1.7 Hz, 1H), 6.10 (d, J = 1.7 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 141.8, 129.0, 128.4, 128.2, 127.4, 107.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 230.0; t_R 6.93 min.

*4-(1-Iodovinyl)-1,1′-biphenyl (**4b**)*. Yield 255 mg (99%; purity 84%; CsI). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.65−7.51 (m, 6H), 7.50−7.42 (m, 2H), 7.41−7.33 (m, 1H), 6.53 (d, J = 2.1 Hz, 1H), 6.12 (d, J = 2.1 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 141.8, 140.6, 140.3, 129.0, 128.7, 127.8, 127.4, 127.2, 127.0, 107.2. GC−MS (70 eV, EI) m/z: $[M]^+$ 306.0; t_R 8.87 min. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}I$ 306.9978; found 306.9991.

*1-(1-Iodovinyl)-4-methylbenzene (**4c**)*.[69] Yield 162 mg (70%; purity 87%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H). 6.40 (d, J = 1.6 Hz, 1H), 6.01 (d, J = 1.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 139.0, 129.0, 128.1, 126.6 (2C), 107.9, 21.2. GC−MS (70 eV, EI) m/z: $[M]^+$ 244.0; t_R 7.30 min.

*1-(1-Iodovinyl)-4-propylbenzene (**4e**)*. Yield 212 mg (quant.; purity 95%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.45 (d, J = 1.7 Hz, 1H), 6.05 (d, J = 1.7 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 1.66 (s, J = 7.6 Hz, 2H), 0.96 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 143.8, 139.1, 128.4, 128.1, 126.5, 107.9, 37.7, 24.5, 13.9. GC−MS (70 eV, EI) m/z: $[M]^+$ 272.1; t_R 7.75 min. HRMS (APCI) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}I$ 273.01347; found 273.01333.

*1-Butyl-4-(1-iodovinyl)benzene (**4f**)*. Yield 167 mg (86%; purity 63%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.45 (d, J = 1.6 Hz, 1H), 6.05 (d, J = 1.6 Hz, 1H), 2.62 (t, J = 7.4 Hz, 2H), 1.61 (q, J = 7.4 Hz, 2H), 1.37 (s, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 144.1, 139.1, 128.4, 128.1, 126.6, 107.9, 35.4, 33.6, 22.5, 14.1. GC−MS (70 eV, EI) m/z: $[M]^+$ 286.1; t_R 8.01 min. HRMS (ESI) m/z: $[M + K]^+$ calcd for $C_{12}H_{15}IK$ 324.9850; found 324.9850.

*1-(1-Iodovinyl)-4-methoxybenzene (**4h**)*.[69] Yield 195 mg (82%; purity 79%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 6.37 (d, J = 1.8 Hz, 1H), 5.99 (d, J = 1.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 160.1, 134.3, 129.5, 125.7, 113.5, 107.4, 55.5. GC−MS (70 eV, EI) m/z: $[M]^+$ 260.0; t_R 7.64 min.

*1-Fluoro-4-(1-iodovinyl)benzene (**4t**)*. Yield 198 mg (91%; purity 92%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55−

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

7.44 (m, 2H), 7.05−6.95 (m, 2H), 6.41 (d, J = 1.9 Hz, 1H), 6.06 (d, J = 1.9 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 163.0 (d, J = 248 Hz), 138.1 (d, J = 3 Hz), 129.9 (d, J = 8 Hz), 127.5, 115.2 (d, J = 22 Hz), 105.8 (d, J = 2 Hz). The NMR data are not consistent with previously reported values.[70] GC−MS (70 eV, EI) m/z: $[M]^+$ 248.0; t_R 6.83 min.

*(E)-1-(1,2-Diiodovinyl)-4-(trifluoromethyl)benzene (**8**).*[71] Yield 56 mg (14%). R_f 0.69 (Hex). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.36 (s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 146.7, 130.9 (q, J = 32 Hz), 129.1, 125.7 (q, J = 4 Hz), 123.9 (q, J = 274 Hz), 93.8, 82.6. GC−MS (70 eV, EI): t_R 7.76 min, m/z 424.9 $[M]^+$.

*(1-Iodovinyl)cyclopropane (**9a**).*[72] Yield 55% (CsI); obtained mixture of **9a**, **10a**, and **11a** in 85% combined yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.07 (t, J = 1.4 Hz, 1H), 5.67 (d, J = 1.4 Hz, 1H), 1.57−1.44 (m, 1H), 0.78−0.68 (m, 2H), 0.67−0.59 (m, 2H). GC−MS (70 eV, EI) m/z: $[M]^+$ 193.9; t_R 5.06 min.

*2,5-Diiodopent-2-ene (**10a, 11a**).*[73] Yield 316 mg (83%: **10a**, 54% + **11a**, 29%; NH_4I). ^{1}H NMR (300 MHz, $CDCl_3$) δ: (**11a**): 6.12 (tq, J = 7.5, 1.6 Hz, 1H), 3.12 (t, J = 7.2 Hz, 2H), 2.65−2.56 (m, 2H), 2.41−2.34 (m, 3H). (**10a**): 5.50 (tq, J = 6.7, 1.5 Hz, 1H), 3.16 (t, J = 7.1 Hz, 2H), 2.73−2.65 (m, 2H), 2.53−2.48 (m, 3H). GC−MS (70 eV, EI) m/z: 321.8 (**10a**) and 321.9 (**11a**); t_R 7.01 (**10a**) and 7.18 (**11a**) min.

*(1-Iodoprop-1-en-1-yl)benzene (**12a**).*[74] Yield 181 mg (92%; purity 94%; CsI; $(E)/(Z)$ 64:36 mol %). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49−7.42 (m, 2H (Z)), 7.37−7.22 (m, 8H), 6.57 (q, J = 7.2 Hz, 1H (E)), 5.99 (q, J = 6.5 Hz, 1H (Z)), 1.97 (d, J = 6.5 Hz, 3H (Z)), 1.64 (d, J = 7.2 Hz, 3H (E)). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 143.3, 141.5, 137.9, 133.7, 129.0, 128.6, 128.3, 128.1, 128.0, 106.8, 95.3, 23.7, 18.0. GC−MS (70 eV, EI) m/z: $[M]^+$ 244.0; t_R 7.15 (E) and 7.31 (Z) min.

*(1-Bromovinyl)benzene (**5a**).*[32] Yield 167 mg (83%; purity 89%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64−7.56 (m, 2H), 7.41−7.29 (m, 3H), 6.13 (d, J = 2.0 Hz, 1H), 5.79 (d, J = 2.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 138.7, 131.1, 129.2, 128.4, 127.5, 117.8. GC−MS (70 eV, EI) m/z: $[M]^+$ 183.0; t_R 6.60 min.

*4-(1-Bromovinyl)-1,1′-biphenyl (**5b**).*[75] Yield 261 mg (quant.; purity 80%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.1 Hz, 2H), 7.65−7.55 (m, 4H), 7.47 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 6.19 (d, J = 1.9 Hz, 1H), 5.82 (d, J = 1.9 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 142.0, 140.3, 137.5, 130.8, 129.0, 127.9, 127.8, 127.2, 127.1, 117.7. GC−MS (70 eV, EI) m/z: $[M]^+$ 258.1; t_R 8.60 min.

*1-(1-Bromovinyl)-4-methylbenzene (**5c**).*[76] Yield 190 mg (quant.; purity 99%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.09 (d, J = 2.0 Hz, 1H), 5.75 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 139.3, 135.8, 131.2, 129.0, 127.3, 116.9, 21.3. GC−MS (70 eV, EI) m/z: $[M]^+$ 197.0; t_R 7.00 min.

*1-(1-Bromovinyl)-4-ethylbenzene (**5d**).* Yield 190 mg (quant.; purity 68%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 6.09 (d, J = 2.0 Hz, 1H), 5.74 (d, J = 2.0 Hz, 1H), 2.67 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 145.7, 136.1, 131.2, 127.9, 127.5, 117.0, 28.7, 15.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 211.0; t_R 7.22 min. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{12}Br$ 211.0117; found 211.0143.

*1-(1-Bromovinyl)-4-propylbenzene (**5e**).* Yield 185 mg (quant.; purity 90%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 2.0 Hz, 1H), 5.74 (d, J = 2.0 Hz, 1H), 2.61 (t, J = 7.5 Hz, 2H), 1.66 (s, J = 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 144.1, 131.3, 128.5, 127.3, 126.0, 116.9, 37.8, 24.5, 13.9. GC−MS (70 eV, EI) m/z: $[M]^+$ 225.1; t_R 7.51 min. HRMS (APCI) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}Br$ 225.02731; found 225.02734.

*1-(1-Bromovinyl)-4-butylbenzene (**5f**).*[77] Yield 166 mg (quant.; purity 91%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 2.0 Hz, 1H), 5.73 (d, J = 2.0 Hz, 1H), 2.63 (t, J = 7.6 Hz, 2H), 1.61 (q, J = 7.6 Hz, 2H), 1.37 (s, J = 7.6 Hz, 2H), 0.94 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 144.3, 136.1, 131.3, 128.4, 127.4, 116.9, 35.4, 33.6, 22.5, 14.1. GC−MS (70 eV, EI) m/z: $[M]^+$ 239.0; t_R 7.76 min.

*1-(1-Bromovinyl)-4-(tert-butyl)benzene (**5g**).*[78] Yield 165 mg (quant.; purity 84%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 6.10 (d, J = 2.0 Hz, 1H), 5.75 (d, J = 2.0 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 152.5, 135.9, 131.2, 127.2, 125.4, 117.0, 34.8, 31.4. GC−MS (70 eV, EI) m/z: $[M]^+$ 239.1; t_R 7.61 min.

*1-(1-Bromovinyl)-4-methoxybenzene (**5h**).*[76] Yield 150 mg (93%; purity 61%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.01 (d, J = 1.9 Hz, 1H), 5.67 (d, J = 1.9 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 160.3, 131.2, 130.8, 128.8, 116.0, 113.6, 55.5. GC−MS (70 eV, EI) m/z: $[M]^+$ 212.0; t_R 7.37 min.

*1-(1-Bromovinyl)-4-fluorobenzene (**5t**).*[75] Yield 159 mg (91%; purity 75%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64−7.50 (m, 2H), 7.10−6.96 (m, 2H), 6.05 (d, J = 2.0 Hz, 1H), 5.76 (d, J = 2.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 163.2 (d, J = 249 Hz), 134.9 (d, J = 4 Hz), 129.8, 129.3 (d, J = 9 Hz), 117.8, 115.3 (d, J = 22 Hz). GC−MS (70 eV, EI) m/z: $[M]^+$ 201.0; t_R 6.48 min.

*2,5-Dibromopent-2-ene (**10b, 11b**).*[79] Yield 230 mg (85%: **10b**, 58% + **11b**, 27%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: (**11b**): 5.86 (tq, J = 7.5, 1.5 Hz, 1H), 3.36 (t, J = 7.0 Hz, 2H), 2.64−2.54 (m, 2H), 2.27−2.22 (m, 3H). (**10b**): 5.71 (tq, J = 6.7, 1.4 Hz, 1H), 3.40 (t, J = 7.0 Hz, 2H), 2.77−2.65 (m, 2H), 2.33−2.27 (m, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: (**10b**): 125.8, 125.3, 34.9, 31.3, 29.0; (**11b**): 128.7, 122.6, 33.0, 31.1, 23.6. GC−MS (70 eV, EI): t_R 6.34 (**10b**) and 6.48 (**11b**) min, m/z 227.9 $[M]^+$.

*(1-Bromoprop-1-en-1-yl)benzene (**12b**).*[80,81] Yield 182 mg (97%; purity 86%; LiBr; $(E)/(Z)$ 75:25 mol %). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.64−7.18 (m, 10H), 6.36−6.22 (m, 2H), 1.96 (d, J = 6.6 Hz, 3H (Z)), 1.68 (d, J = 7.3 Hz, 3H (E)). GC−MS (70 eV, EI) m/z: $[M]^+$ 197.0; t_R 6.78 (E) and 6.95 (Z) min.

*(Z)-1-(1-Bromo-2-phenylvinyl)-4-methoxybenzene ((Z)-**13**).*[82] Yield 88 mg (quant.; LiBr) for a mixture of (Z)-**13** and (Z)-**14**; (Z)-**13**/(Z)-**14** 76:24 mol %. Sample for NMR analysis isolated by preparative thin-layer chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.70 (d, J = 7.4 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.14 (s, 1H), 6.91 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 160.2, 136.7, 133.7, 129.3 (2C), 128.6, 128.3, 128.0, 124.1, 113.8, 55.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 289.1; t_R 9.05 min.

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

*(Z)-1-(2-Bromo-2-phenylvinyl)-4-methoxybenzene ((Z)-**14**).*[83] Yield 88 mg (quant.; LiBr) for a mixture of (*Z*)-**13** and (*Z*)-**14**; (*Z*)-**13**/(*Z*)-**14** 76:24 mol %. Sample for NMR analysis isolated by preparative thin-layer chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.29 (d, J = 8.8 Hz, 2H), 7.18−7.08 (m, 4H), 7.03 6.95 (m, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 160.0, 136.5, 132.6, 131.9, 130.9, 128.8, 128.4, 127.5, 123.8, 114.1, 55.4. GC−MS (70 eV, EI) m/z: $[M]^+$ 289.1; t_R 8.74 min.

*1-(1,2-Dibromovinyl)-4-propylbenzene (**15**).* Yield 139 mg (97%; purity 66%; LiBr). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.76 (s, 1H), 2.61 (t, J = 7.5 Hz, 2H), 1.67 (s, J = 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 144.5, 134.4, 129.3, 128.5, 121.9, 102.5, 38.1, 24.4, 14.0. GC−MS (70 eV, EI) m/z: $[M]^+$ 304.0; t_R 8.02 min. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}Br_2$ 304.9358; found 304.9371. Configuration of the double bond is not determined.

*4-(1-Chlorovinyl)-1,1′-biphenyl (**6b**).* Yield 81% (LiCl). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.73 (d, J = 8.1 Hz, 2H), 7.66−7.55 (m, 4H), 7.47 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 5.84 (d, J = 1.7 Hz, 1H), 5.56 (d, J = 1.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 142.0, 140.3, 139.8, 135.9, 129.0, 127.8, 127.2, 127.1, 126.9, 112.6. GC−MS (70 eV, EI) m/z: $[M]^+$ 214.2; t_R 8.37 min. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}Cl$ 215.0622; found 215.0617.

*1-(1-Chlorovinyl)-4-methylbenzene (**6c**).*[84] Yield 94% (LiCl). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 5.74 (d, J = 1.4 Hz, 1H), 5.49 (d, J = 1.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 140.1, 139.3, 134.3, 129.1, 126.4, 111.9, 21.3. GC−MS (70 eV, EI) m/z: $[M]^+$ 152.1; t_R 6.63 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01630.

Description of GC−MS method used to determine the content of the reaction mixtures, detailed study on catalytic activity of Cu(II) and Ag(I) triflates, complete tables of alkyne hydrohalogenation experiments, and copies of NMR spectra, including representative spectra of quantitative NMR analysis (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: maris.turks@rtu.lv.

ORCID

Māris Turks: 0000-0001-5227-0369

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Latvian Council of Science Grant No. LZP-2018/1-0315. The authors are indebted to Professor Ivo Leito for helpful discussions on the acidity of trace amounts of water in liquid sulfur dioxide.

■ ADDITIONAL NOTE

[a]For a detailed study on the catalytic activity of Ag(I) and Cu(II) triflates in EtOAc and liquid SO_2, see Tables S1 and S2 (Supporting Information), respectively.

■ REFERENCES

(1) Hintermann, L.; Labonne, A. Catalytic Hydration of Alkynes and Its Application in Synthesis. *Synthesis* **2007**, *2007*, 1121−1150.

(2) Alonso, F.; Beletskaya, I. P.; Yus, M. Transition-Metal-Catalyzed Addition of Heteroatom-Hydrogen Bonds to Alkynes. *Chem. Rev.* **2004**, *104*, 3079−3159.

(3) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. Catalytic Markovnikov and anti-Markovnikov Functionalization of Alkenes and Alkynes: Recent Developments and Trends. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398.

(4) (a) Kutscheroff, M. Ueber eine neue Methode direkter Addition von Wasser (Hydratation) an die Kohlenwasserstoffe der Acetylenreihe. *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1540−1542. (b) Kutscheroff, M. Ueber die Einwirkung der Kohlenwasserstoffe der Acetylenreihe auf Quecksilberoxyd und dessen Salze. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 13−29.

(5) Bassetti, M.; Ciceri, S.; Lancia, F.; Pasquini, C. Hydration of Aromatic Terminal Alkynes Catalyzed by Iron(III) Sulfate Hydrate Under Chlorine-Free Conditions. *Tetrahedron Lett.* **2014**, *55*, 1608−1612.

(6) Wang, S.; Miao, C.; Wang, W.; Lei, Z.; Sun, W. A Salen−Co^{3+} Catalyst for the Hydration of Terminal Alkynes and in Tandem Catalysis with Ru−TsDPEN for the One-Pot Transformation of Alkynes into Chiral Alcohols. *ChemCatChem* **2014**, *6*, 1612−1616.

(7) Xu, C.; Du, W.; Zeng, Y.; Dai, B.; Guo, H. Reactivity Switch Enabled by Counterion: Highly Chemoselective Dimerization and Hydration of Terminal Alkynes. *Org. Lett.* **2014**, *16*, 948−951.

(8) Dong, Q.; Li, N.; Qiu, R.; Wang, J.; Guo, C.; Xu, X. Silver-Containing Microemulsion as a High-Efficient and Recyclable Catalytic System for Hydration of Alkynes. *J. Organomet. Chem.* **2015**, *799−800*, 122−127.

(9) Chen, T.; Cai, C. Catalytic hydration of Alkynes to Ketones by a Salen−Gold(III) Complex. *Catal. Commun.* **2015**, *65*, 102−104.

(10) Das, A. K.; Park, S.; Muthaiah, S.; Hong, S. H. Ligand- and Acid-Free Gold(I) Chloride Catalyzed Hydration of Terminal Alkynes. *Synlett* **2015**, *26*, 2517−2520.

(11) Li, F.; Wang, N.; Lu, L.; Zhu, G. Regioselective Hydration of Terminal Alkynes Catalyzed by a Neutral Gold(I) Complex [(IPr)AuCl] and One-Pot Synthesis of Optically Active Secondary Alcohols from Terminal Alkynes by the Combination of [(IPr)AuCl] and Cp*RhCl[(*R*,*R*)-TsDPEN]. *J. Org. Chem.* **2015**, *80*, 3538−3546.

(12) Fernández, G. A.; Chopa, A. B.; Silbestri, G. F. A Structure/Catalytic Activity Study of Gold(I)−NHC Complexes, as well as Their Recyclability and Reusability, in the Hydration of Alkynes in Aqueous Medium. *Catal. Sci. Technol.* **2016**, *6*, 1921−1929.

(13) Liu, H.; Wei, Y.; Cai, C. A Combination System of *p*-Toluenesulfonic Acid and Acetic Acid for the Hydration of Alkynes. *Synlett* **2016**, *27*, 2378−2383.

(14) Liu, W.; Wang, H.; Li, C.-J. Metal-Free Markovnikov-Type Alkyne Hydration under Mild Conditions. *Org. Lett.* **2016**, *18*, 2184−2187.

(15) Gao, Q.; Li, S.; Pan, Y.; Xu, Y.; Wang, H. The Indium-Catalysed Hydration of Alkynes Using Substoichiometric Amounts of PTSA as Additive. *Tetrahedron* **2013**, *69*, 3775−3781.

(16) Zeng, M.; Huang, R.-X.; Li, W.-Y.; Liu, X.-W.; He, F.-L.; et al. $In(OTf)_3$/Acid co-Catalyzed Hydration of 1-Haloalkynes to α-Halomethyl Ketones. *Tetrahedron* **2016**, *72*, 3818−3822.

(17) Liang, S.; Hammond, G. B.; Xu, B. Efficient Hydration of Alkynes Through Acid-Assisted Brønsted Acid Catalysis. *Chem. Commun.* **2015**, *51*, 903−906.

(18) Jha, M.; Shelke, G. M.; Pericherla, K.; Kumar, A. Microwave Assisted Copper Triflate-Catalyzed Rapid Hydration of Aryl Acetylenes. *Tetrahedron Lett.* **2014**, *55*, 4814−4816.

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

(19) Hassam, M.; Li, W. S. Copper-Catalyzed Markovnikov Hydration of Alkynes. *Tetrahedron* **2015**, *71*, 2719−2723.
(20) Das, R.; Chakraborty, D. AgOTf Catalyzed Hydration of Terminal Alkynes. *Appl. Organomet. Chem.* **2012**, *26*, 722−726.
(21) Li, W.; Zhang, J. Addition of HX Reagents to Alkenes, Alkynes, and Allenes without Transition Metal. *Comprehensive Organic Synthesis*, 2nd ed.; Knochel, P., Molander, G. A., Eds.; Elsevier: Amsterdam, 2014; Vol. *4*, pp 342−363.
(22) Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. Organic Synthesis Using Haloboration Reaction. I. A Simple and Selective Synthesis of 2-Bromo- and 2-Iodo-1-Alkenes. *Tetrahedron Lett.* **1983**, *24*, 731−734.
(23) Gao, F.; Hoveyda, A. H. α-Selective Ni-Catalyzed Hydroalumination of Aryl- and Alkyl-Substituted Terminal Alkynes: Practical Syntheses of Internal Vinyl Aluminums, Halides, or Boronates. *J. Am. Chem. Soc.* **2010**, *132*, 10961−10963.
(24) Sato, A. H.; Mihara, S.; Iwasawa, T. One-step Synthesis of (1-Iodovinyl) Arenes from Trimethylsilyl Ethynylarene Through Iodotrimethylsilane-Mediated Hydroiodation. *Tetrahedron Lett.* **2012**, *53*, 3585−3589.
(25) Kamiya, N.; Chikami, Y.; Ishii, Y. Stereoselective Synthesis of Internal Alkenyl Iodides from Alkynes via Addition of Hydrogen Iodide Generated in situ from a Chlorotrimethylsilane/Sodium Iodide/Water System. *Synlett* **1990**, *11*, 675−676.
(26) Bunrit, A.; Ruchirawat, S.; Thongsornkleeb, C. A Simple Microwave-Assisted Preparation of 2-Bromo-1-Alkenes from 1-Alkynes Using the LiBr−TMSCl−TEAB Reagent System. *Tetrahedron Lett.* **2011**, *52*, 3124−3127.
(27) Campos, P. J.; García, B.; Rodríguez, M. A. A Simple and Versatile Method for the Hydroiodination of Alkenes and Alkynes Using I_2 and Et_3SiH in the Presence of Copper(II). *Tetrahedron Lett.* **2002**, *43*, 6111−6112.
(28) Reddy, C. K.; Periasamy, M. A New, Simple Procedure for the Generation and Addition of HI to Alkenes and Alkynes Using BI_3:N,N-Diethylaniline Complex and Acetic Acid. *Tetrahedron Lett.* **1990**, *31*, 1919−1920.
(29) Kawaguchi, S. I.; Ogawa, A. Highly Selective Hydroiodation of Alkynes Using an Iodine−Hydrophosphine Binary System. *Org. Lett.* **2010**, *12*, 1893−1895.
(30) Kawaguchi, S. I.; Gonda, Y.; Masuno, H.; Vũ, H. T.; Yamaguchi, K.; Shinohara, H.; Sonoda, M.; Ogawa, A. A Convenient Hydroiodination of Alkynes Using $I_2/PPh_3/H_2O$ and its Application to the One-Pot Synthesis of Trisubstituted Alkenes via Iodoalkenes Using Pd-Catalyzed Cross-Coupling Reactions. *Tetrahedron Lett.* **2014**, *55*, 6779−6783.
(31) Bartoli, G.; Cipolletti, R.; Di Antonio, G.; Giovannini, R.; Lanari, S.; Marcolini, M.; Marcantoni, E. A Convergent Approach to (*R*)-Tiagabine by a Regio- and Stereocontrolled Hydroiodination of Alkynes. *Org. Biomol. Chem.* **2010**, *8*, 3509−3517.
(32) Dérien, S.; Klein, H.; Bruneau, C. Selective Ruthenium-Catalyzed Hydrochlorination of Alkynes: One-Step Synthesis of Vinylchlorides. *Angew. Chem., Int. Ed.* **2015**, *54*, 12112−12115.
(33) Liang, S.; Ebule, R.; Hammond, G. B.; Xu, B. A Chlorinating Reagent Yields Vinyl Chlorides with High Regioselectivity under Heterogeneous Gold Catalysis. *Org. Lett.* **2017**, *19*, 4524−4527.
(34) Müller, H. Sulfur Dioxide. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2012; Vol. *35*, pp 73−118.
(35) Burow, D. F. In *The Chemistry of Nonaqueous Solvents*; Lagowski, J. J., Ed.; Academic Press: New York, London, 1970; Vol. *3*, pp 138−185.
(36) Walden, P. Ueber die basischen Eigenschaften des Kohlenstoffs. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 2018−2031.
(37) Olah, G. A.; Donovan, D. J. Stable Carbocations. 214. Effect of Solvents of Decreasing Nucleophilicity (Sulfur Dioxide, Sulfuryl Chloride Fluoride, Sulfuryl Fluoride, and Methylene Fluoride) on the Complex Formation and Ionization of Alkyl Fluorides (Chlorides) with Antimony and Arsenic Pentafluoride. *J. Am. Chem. Soc.* **1978**, *100*, 5163−5169.
(38) Feigel, M.; Kessler, H.; Leibfritz, D.; Walter, A. Ionization of Tropylium Azide in Liquid Sulfur Dioxide and Selective Migration of the Azide Ligand in Less Polar Solvents. *J. Am. Chem. Soc.* **1979**, *101*, 1943−1950.
(39) Eisfeld, W.; Regitz, M. Energetic and Structural Aspects of the Solvation of Anions in Liquid SO_2. *J. Am. Chem. Soc.* **1996**, *118*, 11918−11926.
(40) Mayr, H.; Gorath, G.; Bauer, B. Liquid Sulfur Dioxide as a Lewis-Acidic Solvent for the Alkylation and Alkoxyalkylation of Allylsilanes. *Angew. Chem., Int. Ed.* **1994**, *33*, 788−789.
(41) Ross, J.; Percy, J. H.; Brandt, R. L.; Gebhart, A. I.; Mitchell, J. E.; Yolles, S. Liquid Sulfur Dioxide as Solvent Medium for Chemical Reactions. *Ind. Eng. Chem.* **1942**, *34*, 924−926.
(42) Tokura, N. Recent Developments in Organic Synthesis in Liquid Sulfur Dioxide. *Synthesis* **1971**, *1971*, 639−645.
(43) Chénedé, A.; Fleming, I.; Salmon, R.; West, M. C. Cationic Rearrangements Controlled by the Presence of a Silyl Group. *J. Organomet. Chem.* **2003**, *686*, 84−93.
(44) Schmidt, D.; Leutbecher, H.; Conrad, J.; Klaiber, I.; Mika, S.; Greiner, G.; Beifuss, U. Efficient Lewis Acid Mediated Epoxyolefin Cyclizations with Pyrones as Terminators in Liquid SO_2 as a Solvent. *Synlett* **2007**, *11*, 1725−1729.
(45) Posevins, D.; Suta, K.; Turks, M. Indium-Triflate-Catalyzed Ritter Reaction in Liquid Sulfur Dioxide. *Eur. J. Org. Chem.* **2016**, *2016*, 1414−1419.
(46) Luginina, J.; Uzulena, J.; Posevins, D.; Turks, M. Ring-Opening of Carbamate-Protected Aziridines and Azetidines in Liquid Sulfur Dioxide. *Eur. J. Org. Chem.* **2016**, *2016*, 1760−1771.
(47) Luginina, J.; Turks, M. Regioselective Ring Opening of *N*-H-Aziridines with Sulfur Nucleophiles in Liquid SO_2. *Synlett* **2017**, *28*, 939−943.
(48) Dzudza, A.; Marks, T. J. Efficient Intramolecular Hydroalkoxylation/Cyclization of Unactivated Alkenols Mediated by Lanthanide Triflate Ionic Liquids. *Org. Lett.* **2009**, *11*, 1523−1526.
(49) Taylor, J. G.; Whittall, N.; Hii, K. K. Copper(II)-catalysed addition of O−H bonds to norbornene. *Chem. Commun.* **2005**, 5103−5105.
(50) Blieck, R.; Bahri, J.; Taillefer, M.; Monnier, F. Copper-Catalyzed Hydroamination of Terminal Allenes. *Org. Lett.* **2016**, *18*, 1482−1485.
(51) Perego, L. A.; Blieck, R.; Groué, A.; Monnier, F.; Taillefer, M.; Ciofini, I.; Grimaud, L. Copper-Catalyzed Hydroamination of Allenes: from Mechanistic Understanding to Methodology Development. *ACS Catal.* **2017**, *7*, 4253−4264.
(52) Sarma, R.; Rajesha, N.; Prajapati, D. Indium(III) catalysed substrate selective hydrothiolation of terminal alkynes. *Chem. Commun.* **2012**, *48*, 4014−4016.
(53) Kuciński, K.; Pawluć, P.; Marciniec, B.; Hreczycho, G. Highly Selective Hydrothiolation of Unsaturated Organosilicon Compounds Catalyzed by Scandium(III) Triflate. *Chem. − Eur. J.* **2015**, *21*, 4940−4943.
(54) Hanack, M. Stabilized Vinyl Cations. *Acc. Chem. Res.* **1976**, *9*, 364−371.
(55) Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. Hydroamination and Hydroalkoxylation Catalyzed by Triflic Acid. Parallels to Reactions Initiated with Metal Triflates. *Org. Lett.* **2006**, *8*, 4179−4182.
(56) Dang, T. T.; Boeck, F.; Hintermann, L. Hidden Brønsted Acid Catalysis: Pathways of Accidental or Deliberate Generation of Triflic Acid from Metal Triflates. *J. Org. Chem.* **2011**, *76*, 9353−9361.
(57) Jin, H. J.; Kim, J. H.; Kang, E. J. Regioselective Domino Synthesis of 2-Alkylflavans via Hidden Brønsted Acid Catalysis. *Synthesis* **2017**, *49*, 3137−3144.
(58) Kuciński, K.; Hreczycho, G. S-Acetylation of Thiols Mediated by Triflic Acid: A Novel Route to Thioesters. *Org. Process Res. Dev.* **2018**, *22*, 489−493.
(59) Šolić, I.; Seankongsuk, P.; Loh, J. K.; Vilaivan, T.; Bates, R. W. Scandium as a pre-Catalyst for the Deoxygenative Allylation of Benzylic Alcohols. *Org. Biomol. Chem.* **2018**, *16*, 119−123.

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077

(60) Petruševski, V. M.; Bukleski, M.; Stojanovska, M. On the Catalyzed Disproportionation of SO_2 in Aqueous Solution of KI: A Marathon Classroom Demonstration. *J. Lab. Chem. Educ.* **2013**, *1*, 1−4.
(61) Zhou, W.-J.; Wang, K.-H.; Wang, J.-X. $Pd(PPh_3)_4$-PEG 400 Catalyzed Protocol for the Atom-Efficient Stille Cross-Coupling Reaction of Organotin with Aryl Bromides. *J. Org. Chem.* **2009**, *74*, 5599−5602.
(62) Rajbongshi, K. K.; Hazarika, D.; Phukan, P. $TsNBr_2$ Mediated Oxidative Functionalization of Alkynes. *Tetrahedron* **2016**, *72*, 4151−4158.
(63) Wang, C.; Pan, Y.; Wu, A. $InCl_3$/Al Mediated Pinacol Coupling Reactions of Aldehydes and Ketones in Aqueous Media. *Tetrahedron* **2007**, *63*, 429−434.
(64) Chen, H.; Zhong, X.; Wei, J. Stereoselective Syntheses of Fluorescent Non-Natural Aromatic Amino Acids Based on Asymmetric Michael Additions. *Molecules* **2007**, *12*, 1170−1182.
(65) Nielsen, S. D.; Smith, G.; Begtrup, M.; Kristensen, J. L. Amination of Aryl Iodides Using a Fluorous-Tagged Ammonia Equivalent. *Eur. J. Org. Chem.* **2010**, *2010*, 3704−3710.
(66) Ruan, J.; Saidi, O.; Iggo, J.; Xiao, J. Direct Acylation of Aryl Bromides with Aldehydes by Palladium Catalysis. *J. Am. Chem. Soc.* **2008**, *130*, 10510−10511.
(67) Shen, Z.-L.; Xu, X.-P.; Ji, S.-J. Brønsted Base-Catalyzed One-Pot Three-Component Biginelli-Type Reaction: An Efficient Synthesis of 4,5,6-Triaryl-3,4-dihydropyrimidin-2(1*H*)-one and Mechanistic Study. *J. Org. Chem.* **2010**, *75*, 1162−1167.
(68) Su, X.; Huang, H.; Yuan, Y.; Li, Y. Radical Desulfur-Fragmentation and Reconstruction of Enol Triflates: Facile Access to α-Trifluoromethyl Ketones. *Angew. Chem., Int. Ed.* **2017**, *56*, 1338−1341.
(69) Kawaguchi, S.; Masuno, H.; Sonoda, M.; Nomoto, A.; Ogawa, A. Highly Regioselective Hydroiodination of Terminal Alkynes and Silylalkynes with Iodine and Phosphorus Reagents Leading to Internal Iodoalkenes. *Tetrahedron* **2012**, *68*, 9818−9825.
(70) Gonzalez-de-Castro, A.; Xiao, J. Green and Efficient: Iron-Catalyzed Selective Oxidation of Olefins to Carbonyls with O_2. *J. Am. Chem. Soc.* **2015**, *137*, 8206−8218.
(71) Madabhushi, S.; Jillella, R.; Kumar, K.; Mallu, R.; Godala, K. R. A New and Efficient Method for the Synthesis of α,α-Dihaloketones by Oxyhalogenation of Alkynes Using Oxone−KX (X = Cl, Br, or I). *Tetrahedron Lett.* **2013**, *54*, 3993−3996.
(72) Cheung, L. L. W.; Yudin, A. K. Synthesis of Aminocyclobutanes through Ring Expansion of *N*-Vinyl-β-Lactams. *Org. Lett.* **2009**, *11*, 1281−1284.
(73) Takagi, R.; Yamamoto, K.; Hiraga, Y.; Kojima, S.; Abe, M. A Novel non-Metathetic Behavior of Grubbs Catalyst: Ruthenium-Mediated Intramolecular [3+2] Cycloaddition of bis-1,3-Dienes. *J. Organomet. Chem.* **2013**, *723*, 171−175.
(74) Shimizu, M.; Okura, K.; Arai, T.; Hachiya, I. Titanium Tetraiodide-promoted Tandem Prins Reaction of Alkynes with Acetals: Synthesis of (*Z*,*Z*)-1,5-Diiodo-1,3,5-triarylpenta-1,4-dienes. *Chem. Lett.* **2010**, *39*, 1052−1054.
(75) Wu, J.; Yoshikai, N. Cobalt-Catalyzed Alkenylzincation of Unfunctionalized Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 336−340.
(76) Ojha, D. P.; Prabhu, K. R. Regioselective Synthesis of Vinyl Halides, Vinyl Sulfones, and Alkynes: A Tandem Intermolecular Nucleophilic and Electrophilic Vinylation of Tosylhydrazones. *Org. Lett.* **2015**, *17*, 18−21.
(77) Zhang, Y.; Li, J.; Li, X.; He, J. Regio-Specific Polyacetylenes Synthesized from Anionic Polymerizations of Template Monomers. *Macromolecules* **2014**, *47*, 6260−6269.
(78) Chen, X.; Chen, T.; Xiang, Y.; Zhou, Y.; Han, D.; Han, L.; Yin, S. Metal-free Regioselective Hydrobromination of Alkynes Through C-H/C-Br Activation. *Tetrahedron Lett.* **2014**, *55*, 4572−4575.
(79) Von Roman, U.; Ruhdorfer, J.; Knorr, R. Alkenyl Bromides by Brominative Deoxygenation of Ketones in One or Two Steps. *Synthesis* **1993**, *1993*, 985−992.
(80) Kropp, P. J.; Crawford, S. D. Surface-Mediated Reactions. 4. Hydrohalogenation of Alkynes. *J. Org. Chem.* **1994**, *59*, 3102−3112.
(81) Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F. A Mild Synthesis of Vinyl Halides and gem-Dihalides Using Triphenyl Phosphite−Halogen-Based Reagents. *J. Org. Chem.* **2007**, *72*, 2216−2219.
(82) Chelucci, G. Stereospecific Hydrodehalogenation of Alkenyl Bromides: a New Approach to the Synthesis of (*E*)-Alkenes. *Chem. Commun.* **2014**, *50*, 4069−4072.
(83) Muthiah, C.; Kumar, K. P.; Kumaraswamy, S.; Swamy, K. C. K. An Easy Access to Trisubstituted Vinyl Chlorides and Improved Synthesis of Chloro/Bromostilbenes. *Tetrahedron* **1998**, *54*, 14315−14326.
(84) Jung, M. E.; Light, L. A. Intramolecular Diels-Alder Cycloadditions of Perchloro(allyloxy)- and Perchlorobis(allyloxy)-cyclopentadienes. *J. Org. Chem.* **1982**, *47*, 1084−1090.

DOI: 10.1021/acsomega.8b01630
ACS Omega 2018, 3, 18065−18077