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Ruthenium-catalyzed Synthesis of Aryl and Alkenyl Halides from Fluorosulfonates

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Abstract: Aryl and alkenyl halides are widely used as key intermediates in organic synthesis, particularly for the formation of organometallic reagents or as radical precursors. They are also found in pharmaceutical and agrochemical ingredients. In this work, we report the synthesis of aryl and alkenyl halides from the corresponding fluorosulfonates using commercially available ruthenium catalysts. Notably, this is the first conversion of phenols to aryl halides that is efficient with chloride, bromide, and iodide. Fluorosulfonates are readily prepared using sulfuryl fluoride (SO₂F₂) and less expensive substitutes for triflates. Although aryl fluorosulfonates and their reactions are well known, this is the first report of an efficient coupling of alkenyl fluorosulfonates. To finish, we have demonstrated, by means of representative examples, that the reaction is possible in a one-pot process, starting directly from the phenol or aldehyde.

Introduction

Sulfuryl fluoride (SO₂F₂) is a colourless, odourless gas, originally developed as a fumigant, that has gained interest as a reagent in organic chemistry, particularly in SuFEx chemistry.^[1,2] It can react with alcohols to form fluorosulfonates, convenient intermediates that can be used as triflate surrogates in coupling or substitution reactions. The formation of these fluorosulfonates is particularly attractive because it requires only a base in addition to SO₂F₂, the latter being easily removed at the end of the reaction by simply flushing with argon. This makes the reaction particularly suitable to one-pot processes. Furthermore, fluorosulfonates are more atom-economic than triflates, since they avoid the use of expensive triflic anhydride, which, moreover, is a problematic reagent in industry because it generates equimolar amounts of triflic acid and is not available on a multi-tonne scale. Interestingly, the use of aryl fluorosulfonates in coupling reactions has been particularly described with palladium or nickel, for reactions such as Suzuki-Miyaura or Buchwald-Hartwig couplings.^[2-4]

Surprisingly, the use of alkenyl fluorosulfonates, on the other hand, is not developed, and while a few descriptions of their synthesis have been reported, only one example of their use in a coupling reaction, namely a Suzuki-Miyaura reaction for which the product was obtained in a low yield and with side-products, can be found in the literature.^[5]

Aryl and alkenyl halides are versatile reagents in organic synthesis, particularly as substrates in transition metal catalysis. While the corresponding triflates or fluorosulfonates can in most cases also serve as coupling partners, they cannot however be used as precursors of polar organometallic reagents, and their use to generate radicals is very limited.^[6] Another interest of organohalides is that they are also present in pharmaceuticals and agrochemicals or in some natural products, which have been found to have anticancer or pesticidal activities for example.^[7-11] Access to aryl halides directly from phenols requires harsh conditions and the use of phosphorus reagents, which have poor functional group-tolerance (Scheme 1).^[12-14] Another possible route is *via* the formation of the corresponding triflate. Aromatic nucleophilic substitution exists with TBAB as nucleophile, but with a very limited substrate scope of electron-poor aryls.^[15] The triflate can also be used to generate a radical that is quenched with I₂, but the need for strictly airtight conditions and ultra-pure argon (> 99.999%) means that this method cannot be used for an industrial application.^[16] A much more practical method is to use palladium^[17,18] or ruthenium catalysis.^[19] Aryl fluorides are also accessible from the corresponding fluorosulfonates under metal-free conditions, but this methodology is not applicable to the other halogens.^[20]

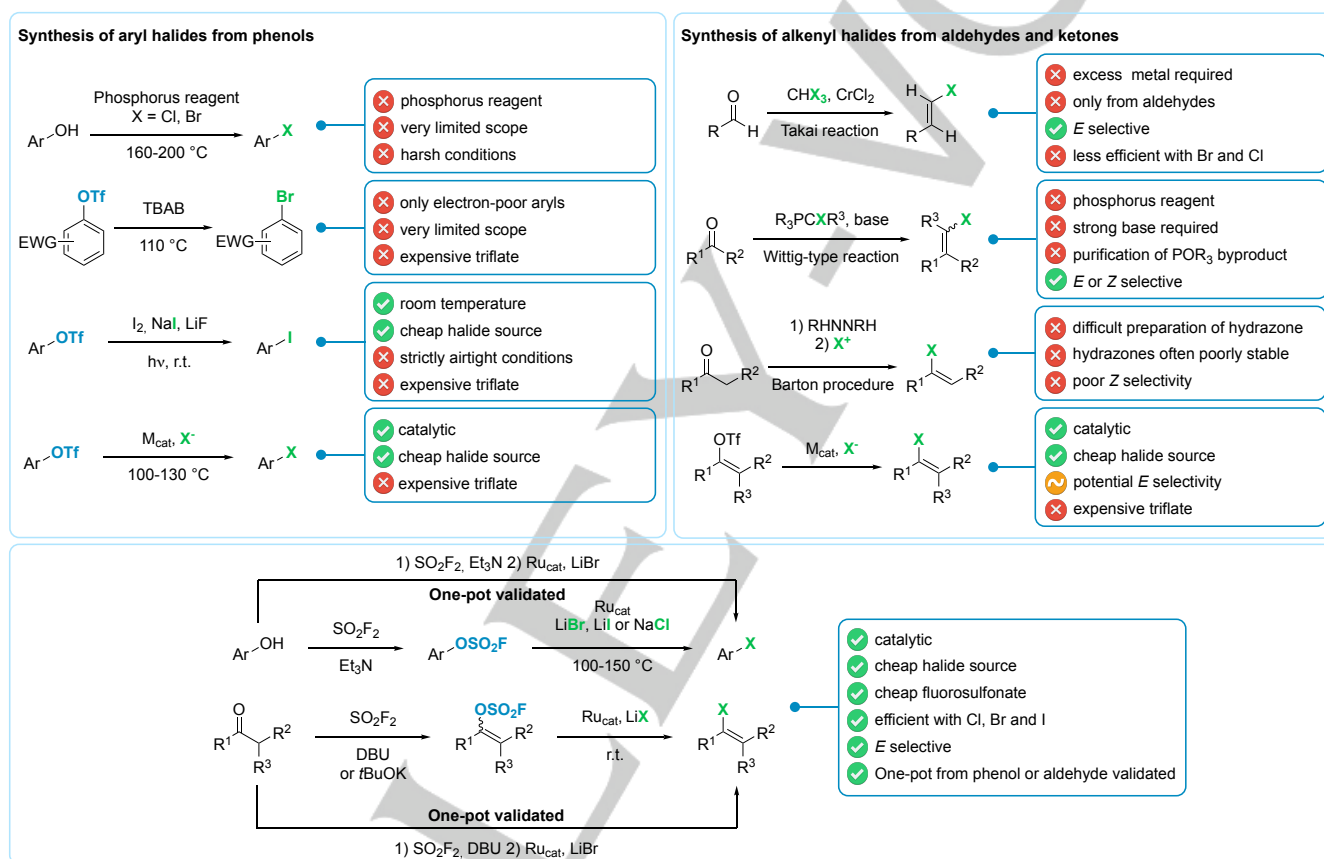
Similarly, the synthesis of alkenyl halides from aldehydes or ketones, also ubiquitous building blocks, can be achieved using several general methodologies. The Takai reaction uses diorganochromium species generated from large over-stoichiometric amounts of metals. Good *E*-selectivity can be observed only when forming alkenyl iodides.^[21,22] The Barton procedure is commonly used, *via* the formation of hydrazones,

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which are not very stable, and are often difficult to synthesize.^[23,24] One report describes a *Z*-selectivity, but in fairly low ratios for most substrates.^[25] Alternatively, phosphorus reagents can be used for this transformation in Wittig or Wittig-type reactions, but said reagents must be prepared beforehand, activated with a strong base, and release phosphine oxide as stoichiometric waste. In addition, the reaction and stereoselectivity are usually very substrate-specific.^[26–29] Another method relying on phosphorus reagents has been reported, alleviating most of these drawbacks. The active species, halogenotriphenoxyphosphonium halide, is formed *in situ* from triphenyl phosphite and chloride or bromide, and the base is only required to form the enolate intermediate. A good *Z* selectivity is reported, but only for 2 examples. However,

triphenyl phosphate is generated as a stoichiometric waste, and the method is not reported for iodine.^[30] Alkenyl halides can also be formed from the corresponding alkenyl triflates using palladium,^[17,18,31] nickel^[32,33] or ruthenium catalysis,^[19,34] but only the latter is *E/Z*-selective.

In this work, we report a method to access aryl and alkenyl halides *via* the generation of fluorosulfonates, as a cheap, atom economic and industrially compatible alternative to triflates, using commercially available ruthenium catalysts (Scheme 1, This work). To our knowledge, this work presents the first ruthenium-catalyzed coupling of fluorosulfonates and the first efficient coupling of alkenyl fluorosulfonates.



Scheme 1. Synthesis of aryl and alkenyl halides from phenols, aldehydes or triflates

Results and Discussion

ARYL HALIDES

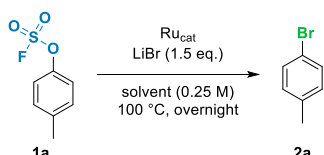
First, our efforts were focused on the halogenation of aryl fluorosulfonates, whose synthesis is well described using a base such as triethylamine.^[1] We chose as a starting point for our optimization the conditions developed by Shirakawa, Hayashi *et al.*,^[19] using a ruthenium catalyst, rather than the conditions developed by Buchwald *et al.* using a palladium catalyst,^[17] due to the much higher price of the latter. We used substrate **1a** bearing a methyl group in the *para* position, with 1.5 equivalents

of LiBr as the bromide source, in DMF, at 100 °C overnight, with different ruthenium (II) catalysts at 20 mol% loading. Catalysts bearing *p*-cymene or cyclopentadiene (Cp) ligands were not efficient for this reaction (Table 1, entries 1–2). A more electron-donating ligand, Cp* (C₅Me₅), was required for the transformation to be effective, with [Cp**RuCl*]₄ affording 9% of the desired product (entry 3) and [RuCp*(MeCN)₃]PF₆ and Cp**RuCl*(cod) both 15% (entries 4–5). Cp**RuCl*(cod) was chosen for the rest of the optimization due to its lower price. Next, different solvents were screened: carboxamide-based solvents, DMA and NMP, gave similar results compared to DMF (entries 6–7), while the cyclic ureas DMI and DMPU were the most efficient ones, with 24 and 28% yield of product, respectively. This is probably related to the

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better solubility of lithium bromide (entries 8–9) in these solvents. The catalyst loading could be successfully reduced to 10 mol% without loss of efficiency (entry 10), but further reduction led to a decrease in conversion (entry 11). The latter could be increased by raising the equivalent number of lithium bromide, with 30% obtained using 2.5 equivalents (entry 12), and 39% using 5 equivalents (entry 13). Performing the reaction at 120 °C did not affect the yield significantly (entry 14) but by further increasing the temperature to 150 °C, an NMR yield of 54% was achieved (entry 15). Finally, performing the reaction without ruthenium catalyst, no product was obtained (entry 16). Therefore, the best conditions of entry 15 were chosen (hereafter referred to as conditions A). Next, we developed a second set of milder conditions for less challenging substrates – such as most electron-poor aryl substrates, for which the oxidative addition step is more favorable, according to the analogous reaction from triflates^[19] – namely 10 mol% of [RuCp*(MeCN)₃]PF₆, 1.5 eq. of LiBr in DMPU at 100 °C overnight (conditions B; for more details, see the supporting information).

Table 1. Ruthenium-catalysed synthesis of 4-bromotoluene from *p*-tolyl fluorosulfonate.^[a]



Entry	Catalyst	Cat. load.	Solvent	Conv. ^[b]	2a ^[b]
1	[Ru(<i>p</i> -cymene)Cl ₂] ₂	20 mol%	DMF	17	-
2	[CpRu(MeCN) ₃]PF ₆	20 mol%	DMF	10	-
3	[Cp*RuCl] ₄	20 mol%	DMF	19	9
4	[RuCp*(MeCN) ₃]PF ₆	20 mol%	DMF	34	15
5	Cp*RuCl(cod)	20 mol%	DMF	37	15
6	Cp*RuCl(cod)	20 mol%	DMA	12	12
7	Cp*RuCl(cod)	20 mol%	NMP	29	19
8	Cp*RuCl(cod)	20 mol%	DMI	24	24
9	Cp*RuCl(cod)	20 mol%	DMPU	41	28
10	Cp*RuCl(cod)	10 mol%	DMPU	40	26
11	Cp*RuCl(cod)	5 mol%	DMPU	21	17
12 ^[c]	Cp*RuCl(cod)	10 mol%	DMPU	43	30
13 ^[d]	Cp*RuCl(cod)	10 mol%	DMPU	58	39
14 ^[d, e]	Cp*RuCl(cod)	10 mol%	DMPU	62	40
15 ^[d, f]	Cp*RuCl(cod)	10 mol%	DMPU	79	54
16 ^[d, f]	-	-	DMPU	59	-

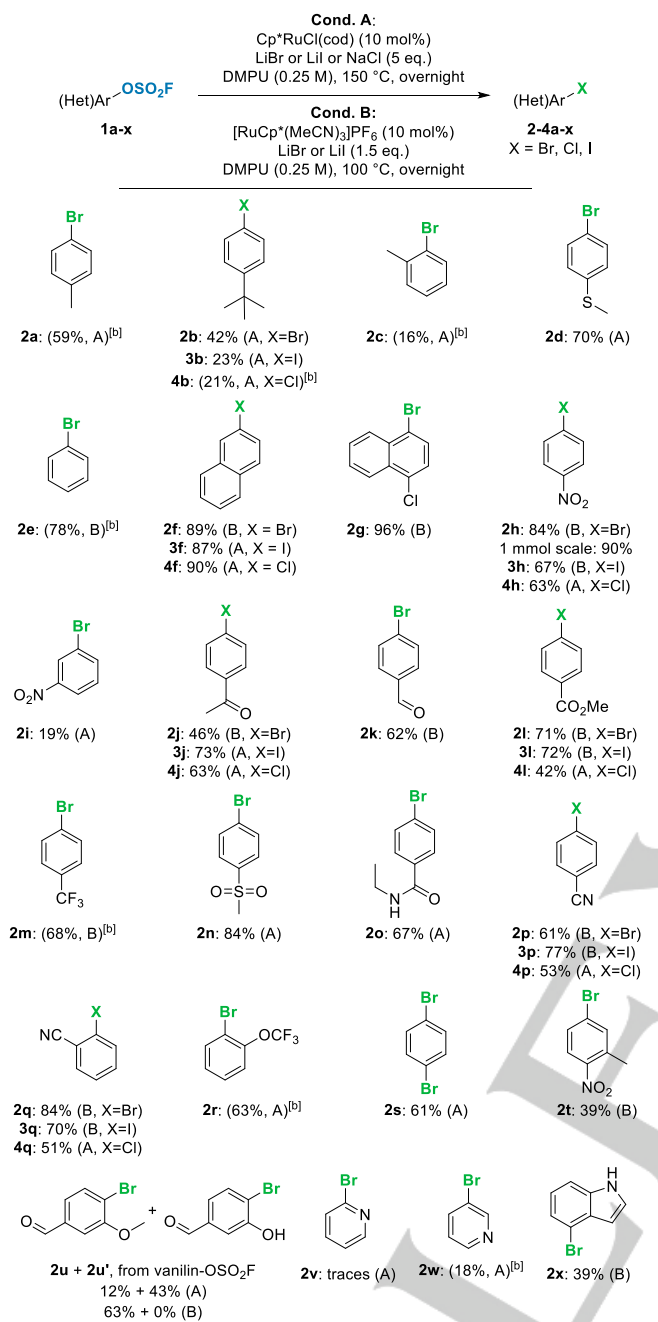
[a] Reaction conditions: **1a** (1 eq., 0.15 mmol), LiBr (1.5 eq.) and the ruthenium catalyst in 0.6 mL solvent were heated at 100 °C overnight. [b] Conversion and NMR yield determined using 1,3,5-trimethoxybenzene as an internal standard.

[c] 2.5 eq. of LiBr were used. [d] 5 eq. of LiBr were used. [e] Reaction carried out at 120 °C. [f] Reaction carried out at 150 °C.

With two sets of optimized conditions in hand, we then explored the scope of the reaction (Scheme 2). An NMR yield of 59% was obtained for the optimization substrate **1a**, bearing a methyl group in the *para* position, using conditions A. Unfortunately, the product could not be isolated due to its volatility. Compound **2b**, bearing a heavier *t*-Bu group in the *para* position, with a somewhat similar donating effect, could be isolated in 42% yield. With an *ortho*-methyl group, the conversion was reduced and only a 16% NMR yield could be obtained (**2c**). A more electron-donating thioether group was also suitable, and **2d** was obtained in 70% yield. Electron-neutral or -poor aromatics were efficiently converted under these conditions. The unsubstituted precursor **1e** gave a 78% NMR yield of **2e** under the milder reaction conditions B, and naphthalene products **2f** and **2g** were both isolated in excellent yields using the same conditions. The electron-poor product **2h**, bearing a nitro group in the *para* position, could be isolated in 84% yield, and a 90% yield was obtained on a mmol scale. With a *meta*-nitro derivative, conditions A were required, and the product was isolated in 19% yield (**2i**). Different electron-withdrawing substituents in the *para* position were also tolerated, affording the ketone, aldehyde, ester, trifluoromethyl, sulfoxide, amide, or nitrile derivatives in good to excellent yields (**2j–p**). *Ortho*-substitution was also compatible, and a good yield of 84% was obtained with a cyano group (**2q**). However, the OCF₃ moiety required harsher conditions to obtain good conversion (conditions A, 63% NMR yield, **2r**). A good yield of **2s** was obtained starting from the corresponding di-fluorosulfonate. The polysubstituted product **2t**, bearing both electron-withdrawing and electron-donating groups, was formed in moderate yields. Starting from fluorosulfonylated vaniline, conditions A led to partial demethylation of the methoxy group while conditions B gave the expected product in 63% yield (**2u** and **2u'**). Heterocyclic precursors were studied, and pyridines were found to be unsuitable for this transformation, with only trace amounts of product **2v** obtained, and 18% NMR yield for 3-pyridine **2w**. However, conditions B afforded the indole **2x** in 39% yield.

We were also able to extend this reaction to other halogens. Using lithium iodide, 23% of product **3b**, bearing an electron-donating *t*-Bu group, was obtained under conditions A. The 2-naphthyl fluorosulfonate **1f** was also a suitable substrate, and **3f** was obtained in a good yield of 87% using these same conditions A, while milder reaction conditions B had proven sufficient to achieve a similar good yield for bromide. The reaction proceeded smoothly using different electron-withdrawing groups, giving the corresponding products in good to excellent yields (**3h, j, l, p–q**). The chlorination of aryl triflates has not been previously reported using ruthenium catalysts.^[19] Starting from aryl fluorosulfonates, we found that it is less efficient compared to bromination or iodination, but the reaction was nonetheless possible using conditions A. The chloride source had to be changed to NaCl, as LiCl led to deprotection of the fluorosulfonate and obtention of the phenol as major product. A low conversion was observed for the electron-rich *t*-Bu-derivative (21% NMR yield of **4b**), whereas good yields were obtained once again with electron-poor or -neutral substrates (**4f, h, j, l, p–q**).

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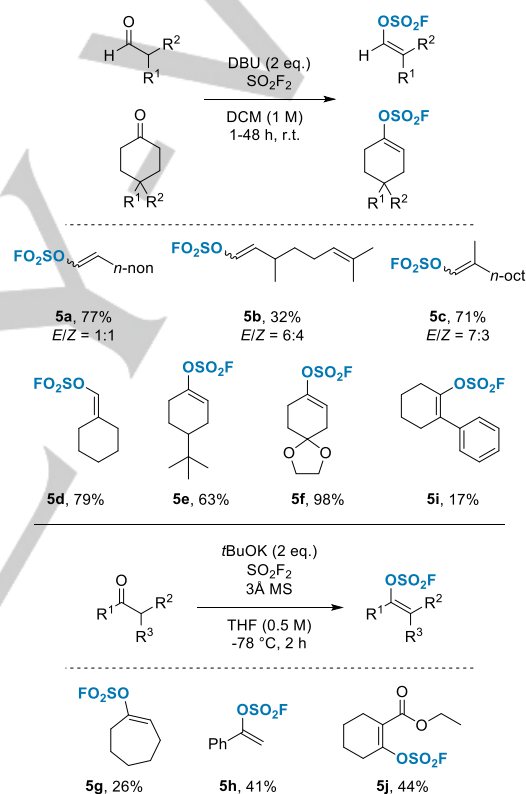
[a] Isolated yields. Reaction conditions A: **1a-x** (1 eq., 0.5 mmol), LiBr or LiCl or NaCl (5 eq.) and Cp*RuCl(cod) (10 mol%) in DMPU (0.25 M) were heated at 150 °C overnight. Reaction conditions B: **1a-x** (1 eq., 0.5 or 0.3 mmol), LiBr or LiCl (1.5 eq.) and [RuCp*(MeCN)₃]PF₆ (10 mol%) in DMPU (0.25 M) were heated at 100 °C overnight. [b] NMR yield determined using bromochloromethane as an internal standard. The product could not be isolated due to volatility and/or very low quantity obtained.

Scheme 2. Substrate scope for the synthesis of aryl bromides.^[a]

ALKENYL HALIDES

If the synthesis of aryl fluorosulfonates and their use in coupling reactions have been the subject of many publications during the last decade, alkenyl fluorosulfonates are less investigated. Only four syntheses have been reported. The first one is limited to

cyclic ketones using DBU as a base.^[5] The second one is a one-pot Swern-type oxidation starting from the corresponding alcohol followed by formation of the fluorosulfonate, to which a second base can be added to form the terminal alkyne by elimination.^[35] Unfortunately, we were not able to reproduce these results and did not observe any conversion of the starting alcohol. Furthermore, from our observations, the base used, K₂CO₃, is not strong enough to form the fluorosulfonates. Finally, we identified two methods, which, starting from ketones bearing an aromatic moiety in β position, require the use of strong bases such as LiHMDS, LDA or *t*BuOK.^[36,37] We were able to synthesize the fluorosulfonates starting from aldehydes, which has never been reported so far, with *E/Z* ratios from 3/7 to 6/4, and from diverse cyclic ketones and acetophenone (Scheme 3, for more details, see the supporting information). Regarding other acyclic ketones, the fluorosulfonates formed were very unstable and could not be isolated.



Scheme 3. Synthesis of alkenyl fluorosulfonates

Having obtained the desired alkenyl fluorosulfonates, we then studied the halogenation reaction for these substrates (Table 2). Using the conditions B described before, but this time at room temperature and for only 20 minutes, starting from fluorosulfonate **5a**, with a *E/Z* ratio of 1/1, we were pleased to observe the formation of 25% of the product **6a**, albeit with a poor *E/Z* ratio of 40/60, as well as 50% of aldehyde **6a'** formed from the decomposition of the starting material (entry 1). DCM, MeCN and DMSO as solvents gave the desired product in ratios above 96/4 in 46, 25 and 11% yield, respectively (entries 2–4). No conversion was observed with diethyl ether and toluene (entries 5–6). The best results were obtained using THF, for which a 92% conversion was attained, with an upgraded *E/Z* ratio of 91:9 and 3% of

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aldehyde (entry 7). Reducing the catalyst loading to 5 mol% slowed the reaction to 1 h but increased the *E/Z* ratio to >96/4 with full conversion and only traces of the aldehyde (entry 8). Reducing it further to 2.5 mol% had no impact on the *E/Z* ratio and only led to a decreased conversion (entry 9). Interestingly, similar high stereoselectivities in favour of the *E* isomer were observed for the same transformation using triflates. Shirakawa, Hayashi *et al.* rationalized this outcome by the formation of a 1-ruthenacyclopropene intermediate that undergoes halogenative ring-opening with substitution by the halide on the least hindered side of the double-bond of the olefin.^[19]

Table 2. Ruthenium-catalysed synthesis of 1-bromoundec-1-ene from 1-undecenyl fluorosulfonate.^[a]

				$\text{FO}_2\text{SO}-\text{CH}=\text{CH}-n\text{-non} \xrightarrow[\text{solvent (0.25 M), r.t.}]{[\text{RuCp}^*(\text{MeCN})_3]\text{PF}_6, \text{LiBr (1.5 eq.)}} \text{Br}-\text{CH}=\text{CH}-n\text{-non} + \text{O}-\text{CH}=\text{CH}-n\text{-non}$		
				5a	6a	6a'
Entry	Cat. load. (mol%)	Solvent	Time (min)	5a (%) ^[b]	6a (%) (<i>E/Z</i>) ^[b]	6a' (%) ^[b]
1	10	DMPU	20	-	25 (40:60)	50
2	10	DCM	20	27	48 (96:4)	25
3	10	MeCN	20	62	25 (1:0)	-
4	10	DMSO	20	73	11 (1:0)	5
5	10	Et ₂ O	20	98	-	2
6	10	Tol.	20	81	-	-
7	10	THF	20	-	92 (91:9)	3
8	5	THF	60	traces	96 (>96:4)	traces
9	2.5	THF	60	25	66 (>96:4)	traces

[a] Reaction conditions: **5a** (1 eq., 0.15 mmol), LiBr (1.5 eq.) and [RuCp^{*}(MeCN)₃]PF₆ in 0.6 mL solvent were left to stir for the indicated time at r.t. [b] NMR yield determined using bromochloromethane as an internal standard.

A variety of alkenyl fluorosulfonates were converted to their corresponding alkenyl halides using the optimized conditions of Table 2, entry 8. An isolated yield of 71% with an *E/Z* ratio of 97/3 could be obtained for the bromination of our model substrate **5a** (Table 3, entry 1). The scale could be increased to 1 mmol with a slightly improved yield of 75% and the same *E/Z* ratio. For the same reaction using the parent triflate, a low temperature of -20 °C was required to reach a good *E/Z* ratio, due to its slightly higher reactivity and the need to slow the reaction down.^[19] This makes fluorosulfonates, reacting under room temperature conditions, particularly interesting for this type of reaction, and for industrial applications. Substitution of LiBr by LiCl furnished the corresponding chloride **7a**. However, the catalyst loading needed to be reduced and the reaction time increased to achieve a good *E/Z* ratio. With 2.5 mol% of catalyst and 4h of reaction time, the desired product was obtained with a yield of 61% and an *E/Z* ratio of 96/4 (entry 2). With LiI, the catalyst loading needed to be further reduced to 0.5 mol%, leading after 16h of reaction to the iodinated product **8a** with a 65% yield and an *E/Z* ratio of 80/20 (entry 3). With the same catalyst loading for each halogen, products **6–8b**,

derived from citronellal, were obtained with yields of about 70% and excellent *E/Z* ratios (entries 4–6). Trisubstituted alkenes **6–8c** were obtained with lower *E/Z* ratios of 8/2 for Br and 7/3 for Cl and I and yields of about 80% (entries 7–9). In this case, the catalyst loading could not be reduced under 5 mol% due to very low conversion. The lower *E/Z* ratio can further be explained by the small difference in steric hindrance between the methyl group and the octyl chain. Trisubstituted exocyclic alkenes **6–8d** were obtained in good yields of 78% and 76% for Br and I, and a lower yield of 26% for Cl, due to lower conversion and the volatility of the product (entries 10–12). Alkenes deriving from cyclic ketones were also suitable for this reaction. These substrates are particularly interesting as only few methods to access cyclic alkenyl halides have been developed, the most common synthesis relying on the formation of an intermediate hydrazone (Barton synthesis), which is notably difficult.^[23–25] 6-Membered ring substrates **6–8e–f** were obtained in yields of about 80% for all halides (entries 13–18), while 7-membered rings **6–8g** were obtained in 37 to 48% yields (entries 19–21). Substrates **6–8h**, synthesized from acetophenone, could also be converted to the corresponding alkenyl halides in moderate yields of 12% for Br, 41% for Cl, and an NMR yield of 63% for I, the product being unstable on silica (entries 22–24). Finally, sterically hindered substrate **6i** and β-keto ester **6j** were not suitable for this reaction, and no conversion was observed (entries 25–26).

Table 3. Substrate scope for the synthesis of alkenyl halides.^[a]

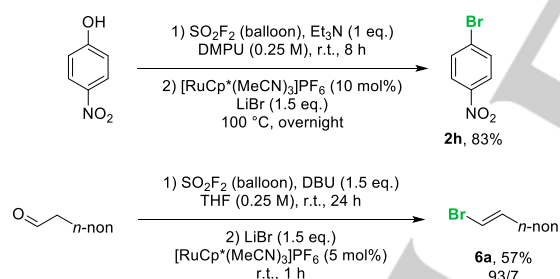
		$\text{OSO}_2\text{F}-\text{CH}=\text{CH}-\text{R}^1-\text{R}^2-\text{R}^3 \xrightarrow[\text{THF (0.25 M), 1-16 h, r.t.}]{[\text{RuCp}^*(\text{MeCN})_3]\text{PF}_6, \text{LiX (1.5 eq.)}} \text{X}-\text{CH}=\text{CH}-\text{R}^1-\text{R}^2-\text{R}^3$					
		5a-j	6-8				
Entry	ArX	X	t (h)	Cat. load. (mol%)	Yield (%)	<i>E/Z</i>	
1		6a	Br	1	5	71	97/3
					1 mmol scale:	75	97/3
2		7a	Cl	4	2.5	61	96/4
3		8a	I	16	0.5	65	8/2
4		6b	Br	1	5	71	96/4
5		7b	Cl	16	2.5	67	98/2
6		8b	I	16	0.5	67	94/4
7		6c	Br	1	5	84	8/2
8		7c	Cl	6	5	76	7/3
9		8c	I	16	5	86	7/3
10		6d	Br	2	5	78	-
11		7d	Cl	5	5	26	-
12		8d	I	5	5	76	-
13		6e	Br	1	5	79	-
14		7e	Cl	1	5	78	-

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15		8e	I	5	5	83	-
16		6f	Br	1	5	67	-
17		7f	Cl	1	5	84	-
18		8f	I	1	5	83	-
19		6g	Br	1	5	42	-
20		7g	Cl	7	5	37	-
21		8g	I	1	5	48	-
22		6h	Br	16	5	12	-
23		7h	Cl	16	5	41	-
24		8h	I	16	5	(63) ^[b]	-
25		6i	Br	24	5	0	-
26		6j	Br	24	5	0	-

[a] Isolated yields. Reaction conditions: **5a-k** (1 eq., 0.3 mmol), LiBr (1.5 eq.) and $[\text{RuCp}^*(\text{MeCN})_3]\text{PF}_6$ in 1.2 mL THF were left to stir for the indicated time at r.t. [b] Products were unstable on silica. NMR yield determined using bromochloromethane as an internal standard.

ONE-POT PROCESS



Scheme 4. One-pot synthesis.

Since the formation of fluorosulfonates only requires a base and sulfonyl fluoride, that can be easily removed by flushing argon into the reaction mixture, this transformation is very suitable for one-pot processes.^[38–40] We were able to easily convert 4-nitrophenol into the corresponding aryl halide **2h** in 83% yield by forming the fluorosulfonate in DMPU, removing the sulfonyl fluoride and adding the ruthenium catalyst and lithium bromide (Scheme 4). This traceless one-pot process, starting from the phenol, is more efficient than in two steps, for which the overall yield is 66%. Similarly, the reaction is also efficient starting from undecanal, and the desired product **6a** was obtained in 57% yield, with a slightly lower *E/Z* ratio of 93/7 than in the 2-pot sequence, the overall yield over two steps being 55%. Nicely, these two experiments validate the feasibility of this approach in a one-pot sequence.

Conclusion

In conclusion, we have developed a ruthenium-catalysed synthesis of aryl and alkenyl halides starting from aryl and alkenyl fluorosulfonates, which are readily available from inexpensive materials. The reaction is compatible with bromide, chloride and iodide, whereas previous reports for forming aryl halides from phenols were compatible with only one or two halides. Electron-poor or -neutral aryl derivatives are the most efficient for this transformation. Regarding alkenyl halides, the reaction was compatible with fluorosulfonates derived from aldehydes and cyclic ketones, and the products obtained in good to excellent *E/Z* ratio. A one-pot process was also developed starting from the phenol or the aldehyde, with yields as good as or higher than the corresponding sequential 2-step transformation. This fluorosulfonate-centered process proves advantageous when compared with the analogous triflate-based one.

Experimental Section

Caution: Sulfonyl fluoride is a toxic gas and should be used with precaution under a fumehood.

General procedure for the synthesis of the starting aryl fluorosulfonates 1a-x, adapted from the literature

In a 3-neck round-bottom flask, the phenol (1 eq.) and Et_3N (1.5 eq.) were dissolved in DCM (1 M). SO_2F_2 was bubbled via a balloon into the solution (a gas recovery balloon is installed on another neck of the flask and the gas is passed back and forth between the two balloons several times in the solution – see supporting information) under stirring, until completion of the reaction (followed by TLC). Then SO_2F_2 was flushed out with argon and water was added, and the reaction mixture acidified with concentrated HCl. The aqueous phase was washed twice with DCM, and the combined organic phases were dried over MgSO_4 , filtrated, and concentrated under reduced pressure. The obtained product was either obtained pure directly or purified over silica.

General procedures for the synthesis of aryl halides 2-4a-x

General procedure A

In a dry Schlenk tube equipped with a screw cap were added the starting fluorosulfonate 1a-x (1 eq., 0.5 mmol), the corresponding halide salt (5 eq., 2.5 mmol) and $\text{Cp}^*\text{RuCl}(\text{cod})$ (10 mol%, 0.05 mmol). Degassed DMPU (0.25 M, 2 mL) was added under argon, and the reaction mixture was left to stir at 150 °C overnight. Then, once the reaction cooled down, water was added, and the aqueous phase was washed three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. Bromochloroethane (1 eq., 32 μL) was added as internal standard to determine an NMR yield. Then, the internal standard was evaporated, and the obtained residue purified by chromatography on silica.

General procedure B

In a dry Schlenk tube equipped with a screw cap were added the starting fluorosulfonate 1a-x (1 eq., 0.5 mmol or 0.3 mmol), the corresponding halide salt (1.5 eq.) and $[\text{RuCp}^*(\text{MeCN})_3]\text{PF}_6$ (10 mol%). Degassed DMPU (0.25 M) was added under argon, and the reaction mixture was left to stir at 100 °C overnight. Then water was added, and the aqueous phase was washed three times with diethyl ether. Then, once the reaction cooled down, the combined organic phases were washed with brine, dried over

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MgSO₄, filtered, and concentrated under reduced pressure. Bromochloroethane (1 eq.) was added as internal standard to determine an NMR yield. Then, the internal standard was evaporated, and the obtained residue purified by chromatography on silica.

Procedure for the synthesis of 2h in one pot

4-Nitrophenol (1 eq., 0.5 mmol, 69.6 mg) and Et₃N (1 eq., 70 µL) were dissolved in degassed DMPU (0.25 M, 2 mL) in a dry Schlenk flask. SO₂F₂ was bubbled via a balloon into the solution, under stirring, for 8h. Then the reaction mixture was thoroughly flushed with argon to remove the SO₂F₂. LiBr (1.5 eq., 65.1 mg) and [RuCp*(MeCN)₃]PF₆ (10 mol%, 25.2 mg) were added and the reaction mixture left to stir at 100 °C overnight. Then water was added, and the aqueous phase was washed three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The obtained residue was purified by chromatography on silica (cyclohexane/EtOAc 1:0 to 9:1). Isolated yield: 83% (84.3 mg).

Note: the presence of a base is detrimental to the halogenation step, so precisely 1 equivalent needs to be used for the fluorosulfonation.

General procedures for the synthesis of the starting alkenyl fluorosulfonates 5a-j, adapted from the literature.*General procedure C*

To the aldehyde or ketone (1 eq.) in DCM (1 M) was added DBU (2 eq.) and the reaction mixture left to stir for 5 min. SO₂F₂ was bubbled via a balloon into the solution, under stirring, until completion of the reaction (followed by TLC). Then SO₂F₂ was flushed out with argon and water was added, and the reaction mixture acidified with concentrated HCl. The aqueous phase was washed twice with DCM, and the combined organic phases were dried over MgSO₄, filtered, and concentrated under reduced pressure. The obtained product was purified on silica.

General procedure D

To tBuOK (2.5 eq.) and 3 Å molecular sieves in THF (6 mL) was added the ketone (1 eq.) and the reaction mixture left to stir at r.t. for 10 min. Then, the reaction mixture was cooled to -78 °C, the headspace was evacuated until the THF began boiling and SO₂F₂ was introduced via a balloon. It condensed rapidly into the reaction mixture, as visible by the fast depleting of the balloon. The reaction mixture was left to stir at -78 °C for 2 h, after which it was left to warm to r.t. and flushed with argon to remove SO₂F₂. Then, the reaction was quenched with sat. aq. NH₄Cl. The aqueous phase was extracted with diethyl ether 3 times and the combined organic layers were washed with brine and dried over MgSO₄, filtered, and concentrated under reduced pressure. The obtained product was purified by chromatography on silica or basic alumina.

General procedure for the synthesis of alkenyl halides 6-8a-h

In a dry Schlenk tube was added the starting fluorosulfonate 5a-h (1 eq., 0.3 mmol), the corresponding lithium halide (1.5 eq.), and [RuCp*(MeCN)₃]PF₆ (0.5 to 5 mol%). Dry THF (0.25 M, 1.2 mL) was added under argon, and the reaction mixture left to stir at r.t. until complete conversion (followed by TLC). Then water was added, and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The obtained residue was purified by chromatography on silica.

Procedure for the synthesis of 6a in one pot.

Undecanal (1 eq., 0.3 mmol, 62 µL) and DBU (1.5 eq., 67 µL) were dissolved in THF (0.25 M, 1.2 mL) in a dry Schlenk tube. SO₂F₂ was bubbled via a balloon into the solution, under stirring, for 24h. Then the

reaction mixture was thoroughly flushed with argon to remove the SO₂F₂. LiBr (1.5 eq., 39.1 mg) and [RuCp*(MeCN)₃]PF₆ (5 mol%, 7.6 mg) were added and the reaction mixture left to stir at r.t. for 1h. Then water was added, and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The obtained residue was purified by chromatography on silica (pentane/Et₂O 1:0 to 9:1). Isolated yield: 56% (39.6 mg). E/Z ratio: 93/7.

Supporting Information

Additional references cited within the Supporting Information.^[41-94]

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Keywords: alkenyl halide • aryl halide • fluorosulfonate • homogeneous catalysis • ruthenium

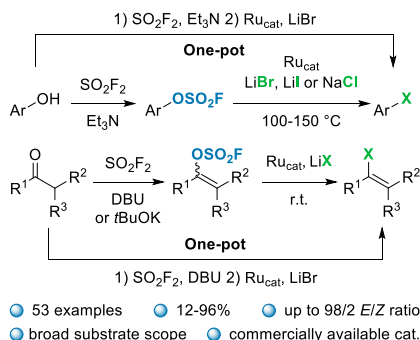
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Interest in the use of aryl fluorosulfonates in coupling reactions has increased over the past decade. Surprisingly, the use and synthesis of alkenyl fluorosulfonates is still poorly described. In this paper, we report the advantageous use of aryl and alkenyl fluorosulfonates instead of the corresponding triflates to synthesize aryl and alkenyl halides using halide salts and commercially available ruthenium catalysts.

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