



Access to Functionalized 3,5-Disubstituted 1,2-Dioxolanes under Mild Conditions through Indium(III) Chloride/Trimethylsilyl Chloride or Scandium(III) Triflate Catalysis

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Access to Functionalized 3,5-Disubstituted 1,2-Dioxolanes under Mild Conditions through Indium(III) Chloride/Trimethylsilyl Chloride or Scandium(III) Triflate Catalysis

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Abstract. Herein we report the use of catalytic amount of scandium(III) triflate or indium(III) chloride (with trimethylsilyl chloride) for the functionalization of endoperoxyacetals through Sakurai or Mukaiyama reactions. These catalysts allow milder and more practical conditions than those previously reported with improvements in scope and reproducibility. This method allows a full catalytic sequence from cyclopropanols to produce desired functionalized 1,2-dioxolanes.

Keywords: Peroxides; Peroxycarbenium; Acetal; Rare-earth; Indium

Endoperoxides are a rich source of natural or unnatural bioactive products, leading to the development of important anti-malarial drugs such as Artemisinin or Arterolane. We were involved these last years in a scientific program towards the total synthesis of mycangimycin, a fatty acid containing a 1,2-dioxolane pattern (**Figure 1**).^{[1][2]}

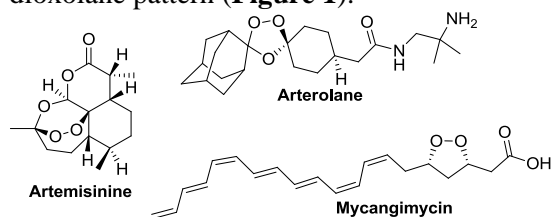
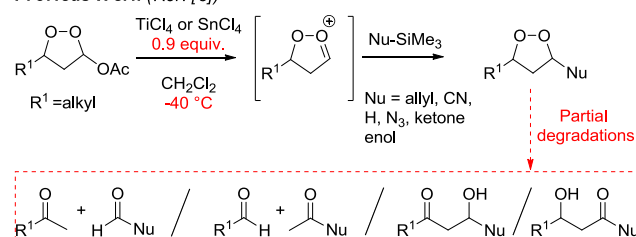


Figure 1. Artemisinin, Arterolan and Mycangimycin.

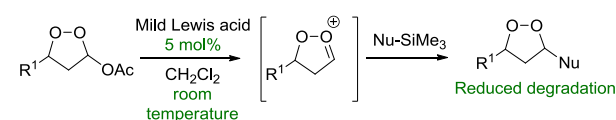
Thereafter, we described a methodology^[3] to build disubstituted 1,2-dioxolanes through Lewis acid activation of 1,2-dioxolanyl acetates with TiCl_4 or SnCl_4 at low temperature. The corresponding peroxycarbenium species^[4] was then trapped with a neutral nucleophile such as an allylsilane or silyl enol ether. We also highlighted the fact that the 1,2-dioxolane moiety undergoes two paths of degradation/rearrangement due to activation by strong Lewis acids (mainly TiCl_4), leading to lower yields but often higher diastereoselectivities.^[3] Moreover, this methodology tends to be difficult to control since a slight modification of the Lewis acid

stoichiometry can lead to more degradation products (if in excess) or a worse conversion in desired product (if in deficiency), which gives sometimes difficulties to reproduce the experiments.^[3] Thus, the utilization of a mild Lewis acid under catalytic amount at room temperature would be highly desirable to circumvent the degradations products and the utilization of sub-stoichiometric amount of Lewis acid under low temperature conditions.

Previous Work (Ref. [3])



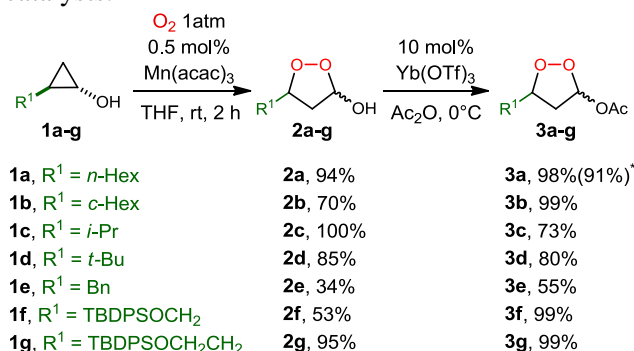
This Work



Scheme 1. Previous work about the synthesis of disubstituted 1,2-dioxolanes.

In order to prepare the dioxolanyl acetate, we transformed some cyclopropanols **1a-g** (obtained either from Kulinkovich reaction^[5] or chromium (II) mediated cyclization of β -methylene aldehydes^[6]) with two catalytic transformations. Firstly cyclopropanols **1a-g** were oxidized to peroxy-hemiacetals **2a-g** through the formation of a hydroxyl radical mediated by $\text{Mn}(\text{acac})_3$, followed by cyclopropyl opening and trapping of intermediate radical with triplet oxygen.^[7] Peroxy-hemiacetals **2a-g** were then acetylated with acetic anhydride in the presence of 10 mol% of $\text{Yb}(\text{OTf})_3$ to give acetoxyendoperoxyacetals **3a-g** in overall good yields (**Scheme 2**). Noteworthy is that only 0.5 mol% of $\text{Yb}(\text{OTf})_3$ was found, more recently, to be enough for the transformation. The use of a Lewis acid catalysed

acetylation^[8] was crucial to the success of this transformation since organic peroxides are reacting with amines, which are used in more common protocols. Both reactions are safe and multi-gram scalable and require low amounts of inexpensive catalysts.



* 0.5 mol% of Yb(OTf)₃ was used.

Scheme 2. Synthesis of 1,2-dioxolanyl acetates **3a-g**

Then, our attention focused on the functionalization of endoperoxyacetals **3a-g** under catalytic conditions. Considering the literature about catalytic Sakurai reactions combining InCl₃ and TMSCl,^[9] these reagents were chosen as a starting point. In the Sakurai reaction between peroxyacetal **3a** and allyl-trimethylsilane **5**, InCl₃ or TMSCl were alone unable to catalyse the reaction (**Table 1** entries 1 and 2). However, when the experiment was run with 10 mol% of InCl₃ and TMSCl (**Table 1** entry 3), we obtained expected product **4a** in less than 30 min. The amount of both TMSCl and InCl₃ was then reduced gradually until reaching 0.5 mol% of InCl₃ (entry 6). The less the amount of InCl₃ was used, the more the reaction time increased, but this shows the possibility to decrease sensibly the amount of catalyst (entries 5 and 6). Optimal conditions were identified for 5 mol% of InCl₃ and 2.5 equivalent of TMSCl (entry 4). This last result was comparable in term of yield and diastereoselectivity with the use of sub-stoichiometric amount of SnCl₄ at -40 °C (81% vs 80% and 70:30 vs 65:35).^[3]

Table 1. Sakurai reaction study with InCl₃/TMSCl as catalyst couple on peroxyacetal **3a**.

Entry ^[a]	Conditions	Stoichiometry (equiv)	Reaction Time	Yield ^[a]	dr ^[b] <i>trans:cis</i>
1	InCl ₃	0.1	3 h	n.r.	/
2	TMSCl	5	3 h	n.r.	/
3	InCl ₃ /TMSCl	0.1/5	25 min	63%	70:30
4	InCl₃/TMSCl	0.05/2.5	35 min	81%	67:33
5	InCl ₃ /TMSCl	0.01/2	3 h	61%	80:20

6 InCl₃/TMSCl 0.005/2 13 h 64% 80:20

^[a] Isolated yield.

^[b] Diastereomeric ratios were determined by ¹H NMR.

In parallel to our studies of InCl₃/TMSCl as a potent mild Lewis acid system, rare-earth metal triflates or more generally metallic triflate of type “M(OTf)₃” were also promising species since they were reported in catalytic version of Mukaiyama aldol reaction but also for Sakurai allylation.^[10] Thus, with these elements in hands, an investigation of metallic triflate was also conducted on peroxyacetal **3a** in a Sakurai reaction with allyltrimethylsilane **5**.

Post-transition metal triflates such as indium(III) or bismuth(III) revealed to be poorly effective as Lewis acid in our reaction (**Table 2**, entries 1 and 2). In particular, bismuth(III) led to the formation of many degradation products in a very short time, while reactions employing In(OTf)₃ proceeded slowly and extended reaction times brought many side-products without improving the yield of dioxolane **4a**. Some popular rare-earth metal triflates in catalysis were also screened at 10% mol.^[10a] Reaction employing triflates of Yb(III), Y(III), and La(III) proceeded very slowly (6–48 h) giving modest yields of compound **4a**, resulting again in a bad conversion/ degradation ratio (**Table 2**, entries 5, 6 and 7). In contrast, scandium(III) gave interesting results, comparable to those obtained with InCl₃/TMSCl (**Table 2**, entry 3). Decreasing the amount of catalyst by half did not modify the results (**Table 2**, entry 4). The improved reactivity of Sc(OTf)₃ towards other tested metal rare-earth triflates is not surprising since Sc(OTf)₃ is known to possess a higher oxophilicity.^[11]

Table 2. Sakurai reaction study with various metal (III) triflates as catalyst on peroxyacetal **3a**.

Entry ^[a]	Conditions	Stoichiometry (equiv)	Reaction Time	Yield ^[a]	dr ^[b] <i>trans:cis</i>
1	Bi(OTf) ₃	0.1	30 min	21%	80:20
2	In(OTf) ₃	0.1	60 min	31%	68:32
3	Sc(OTf) ₃	0.1	30 min	82%	67:33
4	Sc(OTf)₃	0.05	30 min	78%	67:33
5	Yb(OTf) ₃	0.1	6 h	49%	83:17
6	Y(OTf) ₃	0.1	48 h	34%	86:14
7	La(OTf) ₃	0.1	19 h	31%	78:22

^[a] Isolated yield.

^[b] Diastereomeric ratios were determined by ¹H NMR.

Because InCl₃/TMSCl and Sc(OTf)₃ exhibited similar results in term of reaction time, catalyst loading, diastereoselectivities and yields, we chose to

further study these two catalytic systems under the optimized selected conditions (**Table 1**, entry 4 and **Table 2**, entry 4). The influence of lateral chain R¹ at position 3 of 1,2-dioxolanyl acetates **3b-g** was investigated in the Sakurai reaction with allylTMS (**Table 3**). InCl₃/TMSCl and Sc(OTf)₃ behaved similarly to furnish 1,2-dioxolanes **4b-g**, giving same selectivity. Only some differences appeared on the yield with sometimes a significant improvement with InCl₃/TMSCl compared to Sc(OTf)₃ (**Table 3**, Entries 1 and 7).

When these results are compared to our previous report involving SnCl₄ or TiCl₄ as Lewis acids,^[3] these two catalytic systems gave overall slightly lower yields than sub-stoichiometric SnCl₄ but it was compensated by a higher selectivity toward *trans* product.

Table 3. Sakurai reaction with InCl₃/TMSCl or Sc(OTf)₃ as catalysts on different substrates **3b-g**.

Entry ^[a]	Substrate	Lewis acid	Product	Yield (%) ^[b] (dr <i>trans</i> : <i>cis</i>) ^[c]
1		InCl ₃ /TMSCl		81 (70:30)
2	3b	Sc(OTf) ₃	4b	71 (70:30)
3		InCl ₃ /TMSCl		42 (75:25)
4	3c	Sc(OTf) ₃	4c	58 (75:25)
5		InCl ₃ /TMSCl		70 (67:33)
6	3d	Sc(OTf) ₃	4d	80 (70:30)
7		InCl ₃ /TMSCl		78 (60:40)
8	3e	Sc(OTf) ₃	4e	58 (60:40)
9		InCl ₃ /TMSCl		70 (70:30)
10	3f	Sc(OTf) ₃	4f	67 (70:30)
11		InCl ₃ /TMSCl		53 (70:30)
	3g		4g	

^[a] Reaction conditions: **3a** (1 equiv.), InCl₃/TMSCl (5/250 mol%) or Sc(OTf)₃ (5 mol%), AllylTMS **5** (3 equiv.), 30-60 min.

^[b] Isolated yield.

^[c] Diastereomeric ratios were determined by ¹H NMR.

The nature of the nucleophile was also examined on dioxolanyl acetate **3a** for the two selected catalysts (**Table 4**). Methyl allyltrimethylsilane **6** gave product **15** with similar results for both systems (**Table 4**, entries 1-2), as well as TMS cyanide **7** and TMS azide **8** (**Table 4**, entries 3-4 and 5-6), which produced very efficiently compounds **16** and **17**. Triethylsilane **9** was able to reduce the acetal function

giving dioxolane **18**, but the yield was significantly higher with Sc(OTf)₃ (**Table 4**, entries 7-8). Mukaiyama aldol reaction was also experienced under our two selected conditions. Ketone derivatives gave contrasted results; enol ether **10** from acetophenone gave good conversion in compound **19**, in particular with Sc(OTf)₃ (entry 10) but *t*-butyl methylester derivative **11** reacted sluggishly giving poor yields (until 28 h) of *t*-butyl ketone **20** in both cases (**Table 4**, entries 11-12); this poor yield could be attributed to some steric hindrance in the nucleophile. Silyl enol ether of esters and thioesters proved to react similarly under the two tested conditions affording ester **21**, thioesters **22** and **23** in nice yields (**Table 4**, entries 13-18). Thioesters **22** and **23** are particularly interesting, since some cross coupling reactions could be applied^[12] and because of their ease of conversion into the corresponding carboxylic acid. For example, we were able to convert thioester **22** into the corresponding carboxylic acid **24** with H₂O₂ and LiOH in aqueous THF in 1h at rt in 99% yield.

Table 4. Addition of various nucleophiles to peroxyacetal **3a**^[a] under catalytic conditions.

Entry ^[a]	Nu-SiMe ₃	Lewis acid	Product	Yield (%) ^[b] (dr <i>trans</i> : <i>cis</i>) ^[c]
1		InCl ₃ /TMSCl		81 (45:55)
2	6	Sc(OTf) ₃	15	74 (50:50)
3		InCl ₃ /TMSCl		98 (50:50)
4	7	Sc(OTf) ₃	16	84 (66:33)
5		InCl ₃ /TMSCl		93 (50:50)
6	8	Sc(OTf) ₃	17	93 (50:50)
7		InCl ₃ /TMSCl		38
8	9	Sc(OTf) ₃	18	69
9		InCl ₃ /TMSCl		55 (40:60)
10	10	Sc(OTf) ₃	19	74 (50:50)
11		InCl ₃ /TMSCl		12 (65:35) ^[d]
12	11	Sc(OTf) ₃	20	33 (60:40) ^[d]
13		InCl ₃ /TMSCl		82 (45:55)
14	12	Sc(OTf) ₃	21	82 (40:60)
15		InCl ₃ /TMSCl		80 (50:50)
16	13	Sc(OTf) ₃	22	82 (50:50)
17		InCl ₃ /TMSCl		52 (50:50)
18	14	Sc(OTf) ₃	23	48 (50:50)

^[a] Reaction conditions: **3a** (1 equiv.), InCl₃/TMSCl (5/250 mol%) or Sc(OTf)₃ (5 mol%), nucleophile **6-14** (3 equiv.), 30-60 min.

^[b] Isolated yield.

^[c] Diastereomeric ratios were determined by ¹H NMR.

^[d] 20h and 28h reaction time using respectively InCl₃/TMSCl and Sc(OTf)₃.

When these results are now compared to the sub-stoichiometric utilization of SnCl₄ as a Lewis acid,^[3] it can be observed that the yields were overall similar and diastereoselectivities were slightly better towards *trans* products by using the catalytic versions. Nevertheless, there are some exceptions where strong Lewis acids are superior, such as with *t*-butyl enol ether **11**, which seemed to react better with SnCl₄ due to higher reactivity of this later.^[3] For the same reason 1-bromo- and 1-chloro-trimethylsilanes were completely inert by using our selected catalytic systems due to a decreased nucleophilicity of these allylsilanes. In contrast, InCl₃/TMSCl and Sc(OTf)₃ were far superior to SnCl₄ (and TiCl₄) in some cases. TMSCN **7** and TMSN₃ **8** gave significant higher yields with both catalytic systems. More importantly, enol ether of ester **12** and thioesters **13** and **14** were completely unreactive with SnCl₄ and TiCl₄, whereas compounds **21**, **22**, **23** were very efficiently obtained with the catalytic methods, expanding the initial scope of our reaction.

In conclusion, we developed a new catalytic protocol of functionalization for 1,2-dioxolanyl acetates, identifying two efficient systems, namely InCl₃/TMSCl and Sc(OTf)₃. Overall the use of InCl₃/TMSCl or Sc(OTf)₃ over SnCl₄ (and TiCl₄) is justified by simpler experimental procedures (room temperature *versus* -40°C, inert powders *versus* fumigating and hazardous reagents), atom economy and improvement of diastereoselectivity. Although some poorly reactive species such as deactivated allylsilanes, and hindered nucleophiles work better with SnCl₄ and TiCl₄, the two new catalytic systems also enlarge the reagents scope to ester and thioester enol ether derivatives, which makes complementary the catalytic and the stoichiometric versions of the studied transformation.

Experimental Section

General Procedure for the preparation of peroxy-hemiacetals **2a-g**:

To a solution of cyclopropanol **1a-g** (1 equiv.) in THF (1 mL/mmol), was added Mn(acac)₃ (0.5 mol%) and the reaction mixture was then stirred under an atmosphere of oxygen. After disappearance of starting material monitored on TLC (usually from 1 to 2 h), pentane was added precipitating most of the manganese salts. The solution was filtrated on a silica pad and was rinsed with Et₂O several times. Volatiles were removed under reduced pressure without heating to afford peroxy-hemiacetals **2a-g**. This procedure allows generally excellent yields with sufficiently pure materials for further utilization. In some cases, flash column chromatography might be needed, we advise to perform it in isocratic gradient as fast as possible.

General Procedure for the preparation of acetoxyendoperoxyacetal **3a-g**:

To an ice-bath cooled solution of peroxy-hemiacetal **2a-g** (1 equiv.) in anhydride acetic (2 mL/mmol) was added Yb(OTf)₃ (10 mol%, but it can be lower to 0.5 mol% such as with **3a**; most rare-earth metal triflates are usable with similar results in this reaction). Reaction was monitored by TLC and when no starting material remains (usually 30 min-1 h) the reaction was quenched by pouring the reaction mixture into a saturated solution of NaHCO₃ at 0-5 °C to be stirred 30 min at this temperature. The aqueous phase was extracted with Et₂O three times and organic layer was washed with brine and dried over MgSO₄. Volatiles were removed under reduced pressure without heating, and the residue was used in its state without further purification in case of good purity. When necessary, the residue could be purified on a silica gel flash column chromatography.

General Procedures for the preparation of functionalized 1,2-dioxolanes **4a-g** and **15-23** under catalytic conditions:

Prior to use, catalysts were dried (if soggy or old), under high vacuum (0.5 mmHg) and gentle warming with a heat-gun.

Using InCl₃ and TMSCl: To a solution of acetoxyendoperoxyacetal **3a-g** (1 equiv.) and desired nucleophile (3 equiv.) in dry DCM (4 mL/mmol) was added 5 mol% InCl₃ and TMSCl (2.5 equiv.) sequentially. After disappearance of starting material monitored on TLC (usually 1 h), the reaction mixture was poured into a saturated solution of NaHCO₃. Aqueous phase was extracted with Et₂O three times and organic layer was washed with brine and dried over MgSO₄. Volatiles were removed under reduced pressure and the crude residue was purified by silica gel flash column chromatography to afford the different 3,5-disubstituted 1,2 dioxolanes **4a-g** and **15-23**.

Using Sc(OTf)₃: To a solution of acetoxyendoperoxyacetal **3a-g** (1 equiv.) and desired nucleophile (1.5-3 equiv.) in dry DCM (4 mL/mmol) was added 5 mol% Sc(OTf)₃. After disappearance of starting material monitored on TLC (usually 1 h), the reaction mixture was poured into a saturated solution of NaHCO₃. Aqueous phase was extracted with Et₂O three times and organic layer was washed with brine and dried over MgSO₄. Volatiles were removed under reduced pressure and the crude residue was purified by silica gel flash column chromatography to afford the different 3,5-disubstituted 1,2 dioxolanes **4a-g** and **15-23**.

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