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Enantioselective Aldol Reaction with Difluoroenoxyasilanes Catalyzed by Cationic Palladium Aqua Complexes

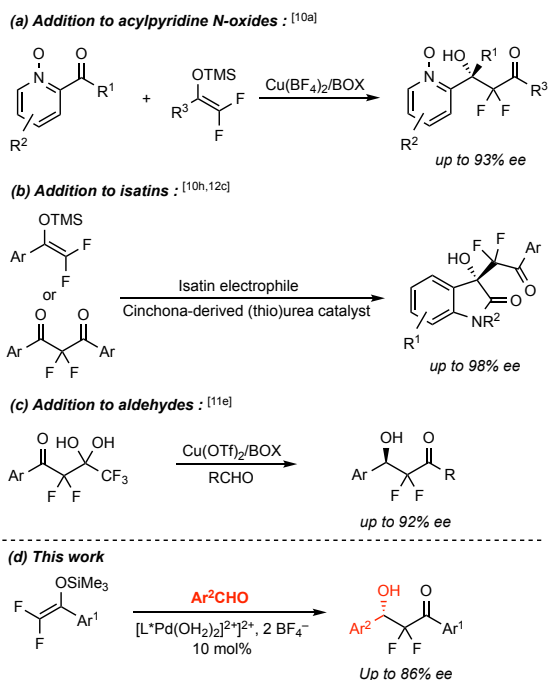
Florian Livernaux, Sidonie Laviéville, Pascale Guiffrey, Jean-Marc Campagne and Eric Leclerc*
ICGM, Université Montpellier, CNRS, ENSCM, Montpellier, France

Abstract:

The enantioselective addition of difluoroenoxyasilanes to aromatic aldehydes, catalyzed by cationic palladium aqua complexes, has been described. The reaction is operationally simple, does not require anhydrous conditions and performs at room temperature. The palladium catalysts, previously discovered and reported by Sodeoka, are easily prepared in two steps from PdCl₂(MeCN)₂. The aldol compounds were obtained in good yields and with enantiomeric ratios up to 93:7, the reaction being more efficient using electron-rich aldehydes.

Introduction

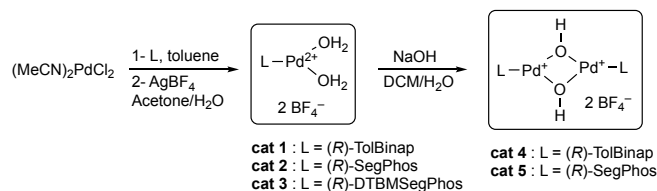
The fluorine rush that occurred in the past thirty years resulted in the very high occurrence of this element in bioactive structures, since approximately 40% of agrochemicals and 25% of the drugs released on the market feature at least one fluorine atom.[1,2] This tremendous representation finds its origin in the fascinating and unique properties of the fluorine atom (strong electronegativity combined with a small size) and of the C–F bond (very strong and short).[3] These features results in major modifications of the lipophilicity, the pKa, the metabolic stability and the binding affinities with a receptor, thus potentially improving the pharmacodynamic and pharmacokinetic properties of judiciously designed fluorinated drugs.[1,4] Such a growing importance of fluorinated molecules was therefore accompanied by a frantic research work on the development of methodologies for the preparation of a wide range of fluorinated building-blocks.[5] Trifluoromethylation,[6] difluoromethylation,[7] fluoromethylation reactions[8] and fluorination processes[9] have been thoroughly investigated. Among difluoromethylation or difluoromethylenation strategies, i.e. the direct introduction of a CF₂Y group, aldol-type reactions of difluoromethylcarbonyl compounds [Y = C(O)X] have held the attention of our research group and of many others. The synthesis of difluorinated aldol and Mannich products through Mukaiyama-type reactions from difluoroenoxyasilanes has indeed been long studied. [10] Alternative methods using more stable precursors to difluoroenolates have also been devised, such as the trifluoroacetate release strategy and other decarboxylative methods.[11,12] Our own contribution to these "non-difluoroenoxyasilane" approaches relied on one-pot strategies from CF₃TMS and acylsilanes or on the use of *trans*-difluoro-*trans*-trimethylsilylacetamides. [13] Some catalytic enantioselective additions of difluoroenolate precursors to various carbonyl-type electrophiles have been reported,[10a,10d-e,10h,11b,12a] but examples of classical aldol reaction on standard aldehydes remain scarce (scheme 1). [11e,14] We wish to report herein a novel catalytic enantioselective addition of difluoroenoxyasilanes onto aromatic aldehydes, using cationic palladium aqua complexes.



Scheme 1. Catalytic enantioselective additions of difluoroenolates to C=O electrophiles.

Results and Discussion

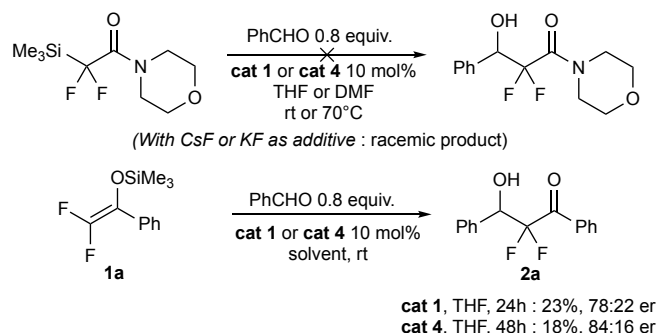
First aiming for the development of a catalytic enantioselective version of the addition of β -(trimethylsilyl)difluoroacetamides to aldehydes,[13a] we decided to examine the activity of the cationic palladium complexes developed by Sodeoka. These "diaquo" and " β -hydroxo" complexes indeed catalyzed the addition of silyl enol ethers to aldehydes and imines in a highly enantioselective manner.[15] This approach relies on the generation of a palladium enolate through activation of the O–Si bond by the H₂O ligand of the pre-catalyst and the possibility of activating the C–Si bond of β -(trimethylsilyl)difluoroacetamides was attractive. Sodeoka's catalysts were prepared according the reported procedures using either (R)-TolBINAP or (R)-DTBMSEgPhos as the chiral ligand (scheme 2).[15] It should be mentioned that the " β -hydroxo" complex could not be prepared when using (R)-DTBMSEgPhos as the ligand, the considerable steric hindrance of this bis-phosphine probably preventing the formation of a dinuclear complex.



Scheme 2. Cationic palladium complexes preparation.

These catalysts were however inactive for the addition of β -(trimethylsilyl)difluoroacetamides to aldehydes (scheme 2). Using cat 1 or cat 4, either in THF or in DMF and even upon heating, and benzaldehyde as the electrophile, no conversion to the corresponding aldol was ever observed. If the Lewis bases of an ion-pair catalysts such as TBAT were effective promoters for this reaction, the H₂O or OH[–] ligands of the cationic complexes could not trigger the C–Si bond scission and the generation of the palladium enolate. The combination of the palladium catalyst cat 1 with a mild fluoride source (CsF or KF) results in an efficient reaction but yielding a racemic product, presumably through a direct fluoride-

promoted addition as already reported.[13a] Since such a catalytic system was never applied to difluoroenoxy-silanes, the reaction of 1a with benzaldehyde was attempted under similar conditions (scheme 3). We were pleased to observe the formation of the aldol compound 2a in 23% yield after 24h of reaction (and complete consumption of 1a) and in an encouraging enantiomeric ratio (er) of 78:22, using the aqua complex cat 1 as the catalyst in THF. The η -OH complex Cat 4 induced a slower reaction but with a sensible improvement in the enantioselectivity (84:16 er).



Scheme 3. Preliminary study.

These preliminary results prompted us to begin a survey of the reaction conditions in order to improve the yields and enantioselectivity of this reaction (table 1). A first examination of the solvent influence was performed using the aqua complex cat 1 as the catalyst, demonstrating the need for a polar media since the best result was obtained in DMF (entries 1-4). It should be mentioned at that point that a mixture of 2a and of its corresponding TMS ether 2a-TMS was generally obtained after reaction, which prompted us to perform a systematic acidic hydrolysis with aq. HCl in methanol before work-up. We then tried to improve the conversion in aldehyde under the same conditions. It should be mentioned that 1a was completely consumed and that the conversion to 2a was accompanied by the formation of η , η -difluoroacetophenone, the hydrolysis product of 1a. The use of a large excess of 1a and an increase of the concentration allowed the complete conversion of the aldehyde and 2a was obtained in 68% yield and 86:14 er (entry 5). At that point, other polar solvents (DMSO, NMO and NMP) were tested under these optimized conditions, bringing no improvement compared to the result in DMF (entries 6-8). A catalyst survey was then conducted and η -OH complex Cat 4 only brought a much slower reaction with no improvement in enantioselectivity (entry 9). Using SegPhos as the ligand, the aqua complex Cat 2 led to a decreased enantioselectivity (entry 10) while η -OH complex Cat 5 once again slowed down the reaction (entry 11). The best result at that point of the study was obtained using DTBMSegPhos as the ligand since catalyst cat 3 allowed the formation of 2a in 84% yield and 87:13 er (entries 12-13).

The reaction remained a bit slow, even under improved conditions, and increasing the temperature only led to an increased hydrolysis of 1 and to a drop in enantioselectivity. We thus decided to examine the influence of additives that might promote the catalyst turnover and limit the extent of a background reaction. A protic additive appeared as an interesting option as it might help to release the palladium catalyst after addition of the palladium enolate to benzaldehyde. t-BuOH, TFE and HFIP proved to be interesting promoters of the reaction since the reaction time was shortened to 24h and gave rise to a cleaner reaction (entries 14-17). The best result was obtained with HFIP and 2a was obtained in 89% yield and 89:11 er (entry 16). This additive was tested back using η -OH complex Cat 4 as the catalyst as it gave interesting enantioselectivities in our first experiments but the enantioselectivity was still inferior to the one induced by cat 3.

It should be mentioned at that point that several control experiments were performed in order to assess the extent of a background reaction promoted either by residual impurities of the catalyst or by the additives. (ToIBINAP)PdCl₂ and AgBF₄, precursors of cat 1, were tested as catalysts for the reaction

between 1a and benzaldehyde in DMF but gave rise to only traces of 2a after 48h. However, prolonged reaction times induced a massive hydrolysis of 1a. HFIP and TFE, used as additives in the improved reaction conditions, were tested as well and promoted a complete hydrolysis of 1a, along with less than 10% of 2a. If a racemic background reaction remains a possible drawback of this catalytic system, the hydrolytic stability of 1a appears to be a much bigger issue.

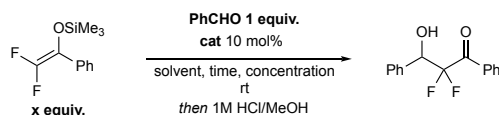


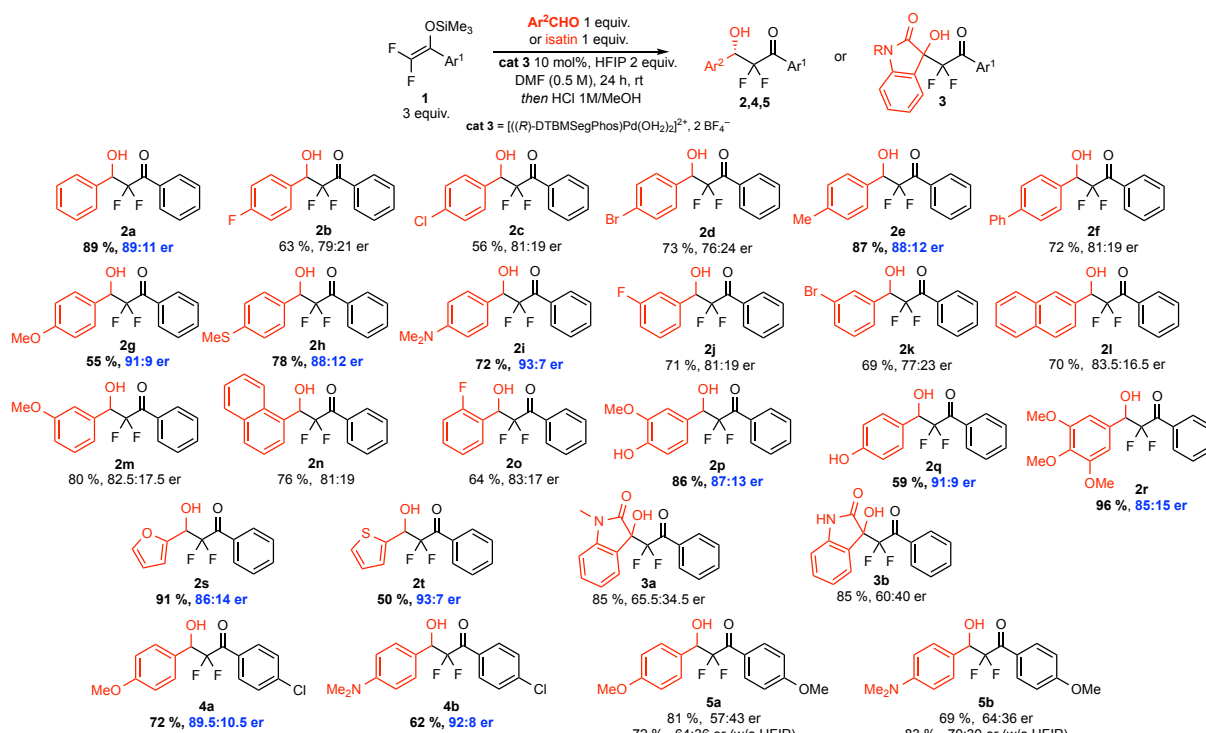
Table 1. Optimization of the Aldol Reaction. ^[a]

Entry	cat	x	solvent	time	concentration	additive	Yield (%) ^[b]	<i>er</i> ^[c]
1	cat 1	1.2	toluene	48h	0.25 M	/	/	/
2	cat 1	1.2	DCM	48h	0.25 M	/	/	/
3	cat 1	1.2	THF	24h	0.25 M	/	23	78:22
4	cat 1	1.2	DMF	24h	0.25 M	/	40	84:16
5	cat 1	3	DMF	48h	0.5 M	/	68	86:14
6	cat 1	3	DMSO	48h	0.5 M	/	33	73:27
7	cat 1	3	NMP	48h	0.5 M	/	72	79:21
8	cat 1	3	DMA	48h	0.5 M	/	80	80:20
9	cat 4	3	DMF	120h	0.25 M	/	63	84:16
10	cat 2	3	DMF	96h	0.25 M	/	80	74:26
11	cat 5	3	DMF	168h	0.25 M	/	66	85:15
12	cat 3	3	DMF	96h	0.25 M	/	83	87:13
13	cat 3	3	DMF	48h	0.5 M	/	84	87:13
14	cat 3	3	DMF	24h	0.5 M	TFE 2 equiv.	85	87:13
15	cat 3	3	DMF	24h	0.5 M	<i>t</i> -BuOH 2 equiv.	79	89:11
16	cat 3	3	DMF	24h	0.5 M	HFIP 2 equiv.	89	89:11
17	cat 4	3	DMF	24h	0.5 M	HFIP 2 equiv.	91	88:12

[a] On 0.5 mmol scale (benzaldehyde). [b] Relative to benzaldehyde. [c] Measured by chiral HPLC using a Daicel IB column eluted with *n*-hexane/*i*-PrOH 98:2.

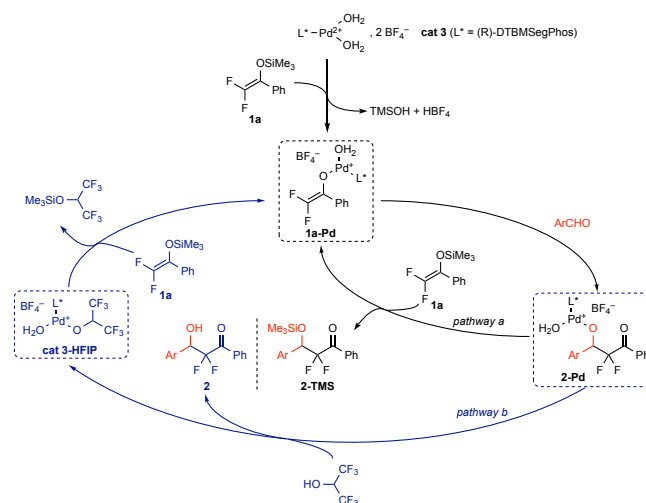
A scope of the reaction was then performed based on the improved conditions depicted in table 1, entry 16, using a panel of electron-rich and electron-poor aromatic aldehydes, isatins, as well as difluoroenoxy silanes 1b (Ar1 = 4-ClC6H4) and 1c (Ar1 = 4-MeOC6H4) (scheme 4). In contrast with Wolf's work using the trifluoroacetate release strategy, the enantioselectivity is strongly dependent on the substitution pattern of the aromatic aldehyde.[11e] The reaction is particularly efficient using electron-rich aldehydes, giving rise to the highest enantioselectivities. Indeed, the addition to benzaldehydes substituted in para position by electron-donating group (2e, 2g-i, 2r and 4a-b) or to heteroaromatic aldehydes (2s-t) provided enantiomeric ratios from 86:14 to 93:7.[16] These levels are comparable to those obtained with Wolf's method.[11e] Despite three examples below 80:20 er (2b, 2d and 2k), all other substitution patterns yield compounds with enantiomeric ratios in the 80:20 to 84:16 range, whatever the position or the EDG or EWG nature of the substituent. In contrast, the addition to a particularly electron-poor aromatic aldehyde such as para-nitrobenzaldehyde led to irreproducible results and complex reaction mixtures from which the product could only be isolated in poor yields and enantioselectivities. One remarkable feature is the tolerance of the reaction to the presence of a free hydroxy group on the aldehyde, as demonstrated by the efficient reaction on vanillin or 4-hydroxybenzaldehyde, which yielded respectively 2p and 2q with good enantioselectivities (respectively 87:13 and 91:9 er).

Reactive ketones such as isatin and N-methylisatin were also tested and led to very fast reactions but only with poor enantioselectivities (3a-b), while standard ketones such as acetophenone led to a sluggish reaction. It should be mentioned at that point that a few attempts of addition on aliphatic aldehydes, cyclohexanecarboxaldehyde, or pivalaldehyde led only to degradation products and hydrolysis of 1a. Finally, the use 1b (Ar1 = 4-ClC6H4) as the nucleophile gave results comparable to 1a (4a-b). In contrast, the more reactive and less stable enoxy silane 1c (Ar1 = 4-MeOC6H4) led to a faster reaction but compounds 5a-b were obtained in poor enantiomeric ratios despite good isolated yields. The reaction was also conducted in the absence of additive in order to circumvent a possible background reaction but this modification only slightly improved the enantioselectivity.



Scheme 4. Scope of the Aldol Reaction. Reaction conditions : Ar_2CHO (0.5 mmol), **1** (1.5 mmol), HFIP (1 mmol), **cat 3** (0.05 mmol), DMF (1 mL). The enantiomeric ratio (er) of the purified product was determined measured by chiral HPLC using a Daicel IB, IC or AS-H column eluted with *n*-hexane/*i*-PrOH 98:2, 90:10 or 80:20. *b* The absolute (*S*) configuration of **2,4** and **5** was assessed by comparison of HPLC chromatograms obtained on a Chiralcel OD column for compound **2e**, by comparison with Wolf's reported retention times for the same compound on the same column (see SI for details).[11e]

A plausible catalytic cycle is depicted in scheme 5 and is inspired from the previously reported mechanism proposals (scheme 5).[15] The generation of palladium enolate **1a**-Pd from **1a** and **cat 3**, releasing TMSOH and HBF₄, was already demonstrated by Sodeoka. After addition of this enolate to the aldehyde, the corresponding palladium alkoxide **2**-Pd can react with substrate **1a** to release the TMS-protected product **2**-TMS and regenerate the catalytic species **1a**-Pd (pathway a), which is in agreement with the presence of the TMS ether in the mixture prior to acidic hydrolysis (vide supra). However, this transfer step might be sluggish and the accelerating effect provided by HFIP could be explained by the turnover mechanism depicted in pathway b. Indeed, HFIP could act as a proton donor to release directly alcohol **2** and the catalytic species **cat 3**-HFIP, the latter being able to react with **1a** to generate a new palladium enolate **1a**-Pd and TMS-protected HFIP.



Conclusion

In summary, we have developed a robust, operationally simple, enantioselective addition of difluoroenoxy silanes to aromatic aldehydes, catalyzed by cationic palladium aqua complexes. The reaction is tolerant to protic functional groups and efficient using hydroxy-substituted benzaldehydes. The enantiomeric ratios range from 76:24 to 93:7 using aromatic aldehydes and the reaction performs best on electron-rich substrates. In contrast, poor enantioselectivities are obtained using isatins as electrophiles. Our approach is however one of the few enantioselective aldol reactions involving difluoroenolates and standard aldehydes and, as such, a complementary approach to the range of asymmetric additions of fluoroenolate-type nucleophiles to carbonyl-electrophiles.

Experimental Section

General Methods. Aldehydes are distilled prior use when relevant. Unless otherwise specified, all other commercial materials were used without further purification. Anhydrous DMF 99.8% AcroSeal® was used for the aldol reactions. Flash column chromatography was performed with the aid of a Biotage Isolera Automated Flash Chromatography System using prepacked SNAP Ultra or Sfär cartridges (10 g). Infrared spectra were recorded with a Perkin-Elmer FT-IR Spectrum 100; absorptions are given in wave numbers (cm⁻¹). Melting points were recorded on a Stuart SMP50 automatic melting point apparatus. ¹H, ¹³C and ¹⁹F spectra were recorded with a Bruker Ultra shield 400 plus. ¹H chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet at 7.26 ppm for CDCl₃ (residual CHCl₃) or to the quintuplet at 3.31 ppm for CD₃OD (undeuterated methanol).^[17] ¹³C chemical shifts are reported in ppm relative to the central line of the triplet at 77.16 ppm for CDCl₃ or to the heptuplet at 49.00 ppm for CD₃OD.^[17] ¹⁹F chemical shifts are calibrating using C₆F₆ as an external standard. The multiplicities are designated as s = singlet; d = doublet; t = triplet; q = quartet; quin = quintuplet; m = multiplet; br = broad ; app = apparatus and combinations thereof. All coupling constants (J values) are reported in Hertz (Hz). High-resolution mass spectra were obtained from the Laboratoire de Mesure Physique (Montpellier university) using a Bruker MicroTof QII. All difluoroenoxy silanes 1 were prepared according to the same

literature procedure.[18] All palladium complexes were prepared according to Sodeoka's reported methods.[15b-d] All racemic compounds were prepared from 1 and the corresponding aldehyde according to the herein reported Pd-catalyzed method but using a palladium complex made from racemic TolBINAP.[15b-d]

General Procedure for the Aldol Reaction.

To a solution of difluoroenoxy silane 1 (1.5 mmol) and aldehyde (0.5 mmol) in DMF (1 mL) were added {[DTBMSegPhosPd(OH₂)₂]²⁺,(BF₄⁻)₂} (0.075 g, 0.05 mmol) and HFIP (0.105 mL, 1.0 mmol). The vial was flushed with argon and the reaction mixture was stirred for 24h at rt. After the reaction was complete (TLC monitoring pentane/EtOAc 8:2), MeOH (2 mL) and 1N HCl (1 mL) were then added and the solution was stirred for 20 mn. The reaction mixture was poured in a separatory funnel containing saturated aqueous NaHCO₃ (20 mL) and extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with water (4 x 20 mL) and brine (10 mL), dried over sodium sulfate and evaporated under reduced pressure. The crude mixture was purified by flash chromatography using a Biotage Isolera (10 g SNAP Ultra or Sfär cartridge, EtOAc/pentane mixture) to afford the title compound. Compounds 2a, 2c-e, 2g, 2l and 2s were previously described by Wolf,[11e] while compounds 2t and 3a-b were previously described by Zhou.[10g]

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Keywords: fluorinated molecules • aldol reaction • palladium catalysis • enantioselectivity • chiral ligands

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