



HAL
open science

Calcium(II)-Catalyzed Intermolecular Hydroarylation of Deactivated Styrenes in Hexafluoroisopropanol

Chenxiao Qi, Vincent Gandon, David Leboeuf

► **To cite this version:**

Chenxiao Qi, Vincent Gandon, David Leboeuf. Calcium(II)-Catalyzed Intermolecular Hydroarylation of Deactivated Styrenes in Hexafluoroisopropanol. *Angewandte Chemie International Edition*, 2018, 57 (43), pp.14245-14249. <10.1002/anie.201809470>. <hal-01999479>

HAL Id: hal-01999479

<https://hal.science/hal-01999479v1>

Submitted on 1 Dec 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

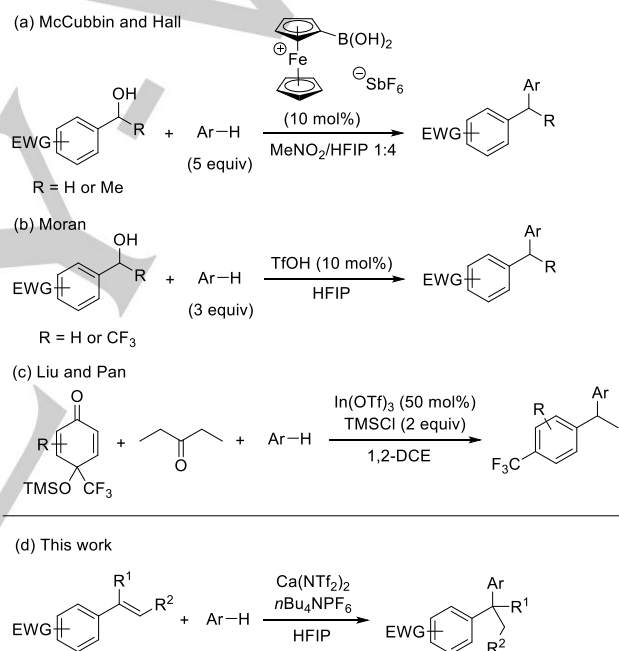
Calcium(II)-Catalyzed Intermolecular Hydroarylation of Deactivated Styrenes in Hexafluoroisopropanol

Chenxiao Qi,^[a] Vincent Gandon,^{*[a,b]} and David Leboeuf^{*[a]}

Abstract: A challenging catalytic hydroarylation of highly electron-deficient styrenes has been developed thanks to an efficient cooperation between a calcium(II) triflimide salt and hexafluoroisopropanol (HFIP). This method affords a large variety of diarylalkanes, notably diarylethanes, in good to excellent yields, while being simple to implement and tolerant to various functional groups. In addition, density functional theory (DFT) computations and deuterium labelling experiments were conducted to uncover the functioning of this promoter system.

In the last decades, diarylalkanes have attracted much attention because of their unique structural and physical properties, leading to manifold applications in medicinal chemistry, material and crop science.^[1] Currently, the hydroarylation of styrenes and the Friedel-Crafts alkylation of benzylic alcohols are among the methods of choice to synthesize diarylalkanes.^[2] However, these approaches are fraught with a major drawback: the presence of electron-donating groups or, at best, moderately electron-withdrawing groups on the aromatic ring is usually necessary to trigger the reaction, which can be overcome, in some cases, with tailor-made transition metal-based systems.^[3] As a result, the synthesis of diarylalkanes incorporating strongly electron-withdrawing groups is difficult to achieve, denying access to potentially useful compounds. In this context, only a handful of methods to generate these types of frameworks can be found in the literature, all of which bearing their own limitations.^[4-8] As an example, McCubbin and Hall reported an elegant Friedel-Crafts alkylation of deactivated benzylic alcohols featuring the use of a ferroceniumboronic acid as a catalyst (Scheme 1),^[4] while focusing mainly on the preparation of diarylmethanes. In terms of reactivity, a major advance was accomplished by the Moran group, using TfOH (Tf = trifluoromethylsulfonyl) as a catalyst in HFIP, which enables the Friedel-Crafts reaction of highly deactivated benzylic alcohols.^[5] However, their transformation could not be conducted in the presence of heteroaromatic and anisole derivatives. Another variant based on the preactivation of a quinone derivative was disclosed by Liu and Pan,^[6] but the reaction is limited to a trifluoromethyl substituent and requires a large amount of Lewis acid as a promoter. Surprisingly, a strategy relying on the activation of electron-poor styrenes has remained unprecedented, while it would have the advantage of being completely atom economical when compared to the reactions shown in Scheme 1. The lack of reactivity of electron-deficient styrenes is likely the reason why the development of such has not

been achieved so far. Recently, our group has depicted several different reactions that employ HFIP^[9,10] working hand in hand with calcium salts^[11] to enable otherwise difficult transformations that involve the activation of alcohols and alkenes.^[12] Herein, we demonstrate that the combination Ca²⁺/HFIP can be a powerful tool to promote hydroarylations featuring highly deactivated styrenes as electrophiles.^[13] The reaction proved to be general and compatible with a wide range of styrenes and aromatic nucleophiles. DFT computations and deuterium labelling experiments were also performed to address the mechanism of this new reaction.



Scheme 1. Synthesis of Diarylalkanes Bearing Strong Electron-Withdrawing Groups. EWG = electron-withdrawing group, TMS = trimethylsilyl.

We started our investigations by using a combination of Ca(NTf₂)₂/nBu₄NPF₆ (10 mol%) in HFIP as a solvent at 80 °C in order to achieve the hydroarylation of 4-(trifluoromethyl)styrene **1** with *m*-xylene **2a** (3 equiv) (Table 1). Gratifyingly, the desired product **3a** was obtained in 51% yield (Entry 1), which could then be increased to 75% with 4 equiv of **2a** (Entry 2). However, a larger proportion of **2a** (5 equiv) did not improve the yield (Entry 3). The reaction could also be performed at a lower temperature, but we observed in this case a significant drop in the yield (Entry 4). While the aforementioned reactions involved a 10 mol% catalyst loading, it is noteworthy that the reaction is still efficient in the presence of 5 mol% (Entry 5). Additional control experiments were also carried out to emphasize the role of each component (solvent, ligand on the calcium, additive and catalyst) of our system (Entries 6-9 and Supporting Information). As anticipated, little or no reaction was observed in most cases. On the other hand, the reaction could be conducted in the presence of HNTf₂ with a similar reactivity (Entry 9). However, we discarded

[a] C. Qi, Prof. V. Gandon and Dr. D. Leboeuf
Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO),
CNRS UMR 8182, Université Paris-Sud, Université Paris-Saclay,
Bâtiment 420, 91405 Orsay cedex, France.
E-mail: vincent.gandon@u-psud.fr
david.leboeuf@u-psud.fr

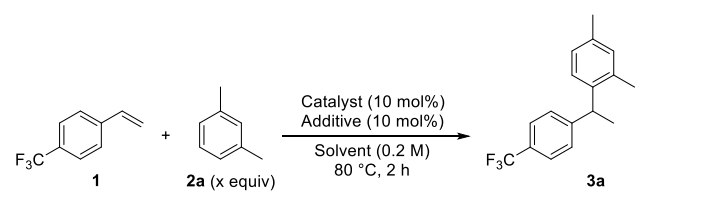
[b] Prof. V. Gandon
Laboratoire de Chimie Moléculaire (LCM), CNRS UMR 9168, Ecole
Polytechnique, Université Paris-Saclay, route de Saclay, 91128
Palaiseau cedex, France

Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

COMMUNICATION

its use as the reaction proved to be far less efficient with other substrates.^[14]

Table 1. Reaction Optimization for the Formation of Diarylethane **3a**.^[a]



Entry	Catalyst	Additive	Solvent	X	Yield 3a [%]
1	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	3	51
2	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	4	75
3	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	5	72
4 ^[b]	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	4	37
5 ^[c]	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	4	67
6	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NBF ₄	1,2-DCE	4	< 10
7	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	Toluene	4	< 10
8	Ca(NTf ₂) ₂	<i>n</i> Bu ₄ NPF ₆	MeNO ₂	4	< 10
9	HNTf ₂	<i>n</i> Bu ₄ NPF ₆	HFIP	4	72

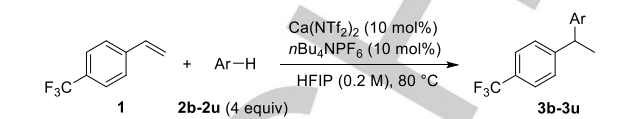
[a] Reactions performed in a sealed tube. [b] Reaction conducted at 60 °C. [c] Reaction in the presence of Ca(NTf₂)₂ (5 mol%) and *n*Bu₄NPF₆ (5 mol%). 1,2-DCE = 1,2-dichloroethane.

With the optimized reaction conditions in hand, the reactivity of a large number of arenes bearing an electron-donating group was explored in the hydroarylation of styrene **1** (Table 2). Overall, the reaction afforded the corresponding diarylethanes in good to excellent yields (up to 98%). In several cases, mixtures of regioisomers were obtained, providing preferentially the *para*-product (with the exception of phenol **2j**), which is consistent with the usual pattern of hydroarylation reactions. Increasing the steric hindrance allowed, however, to deliver the corresponding diarylethane as a single regioisomer (**3e** vs **3f** and **3g**). In the case of anisole, the reaction could even be conducted at room temperature to provide, on this occasion, the *ortho*-compound as a major product. Interestingly, combining donor substituents with moderately (Cl) and strongly electron-withdrawing (CO₂Me) groups did not preclude the reaction (**3m-3o**, **3q**). On the other hand, with less nucleophilic compounds such as benzene itself (**2h**) or bromobenzene (**2i**), the formation of the desired compound competed with the dimerization of 4-(trifluoromethyl)styrene **1**, resulting in a significant drop in yields (**3h** and **3i**). Of note, naphthalene derivatives and thiophene were also well-tolerated regarding this transformation (**3s-3u**).

The scope of deactivated styrenes was then evaluated with the presence of various electron-withdrawing groups using *m*-xylene **2a** as a model nucleophile (Table 3). Even though the hydroarylation required longer reaction times at higher temperatures, it could give rise to the desired product in good to excellent yields (up to 97%), even with strongly deactivated styrenes (**4d-4h**). In the case of **5g** and **5h**, 20 mol% of catalyst

had to be used to reach the full conversion. An interesting feature of this transformation revolved around the use of a stronger electron-withdrawing group than CF₃, such as NO₂. Indeed, styrene **4e** did not generate a dimer under the reaction conditions, so that less nucleophilic arenes such as benzene or

Table 2. Scope of Arenes **2b-2u** with **1** as an Electrophile.^[a]



3b (63%, 2 h)	3c (82%, <i>p/o</i> 7.5:1, 2 h)	3d (64%, 2 h)	3e (69%, <i>p/o</i> 5.3:1, 2 h)
3f (80%, <i>p/o</i> >20:1, 2 h)	3g (93%, <i>p/o</i> >20:1, 2 h)	3h^[b] (40%, 1 h)	3i^[b] (25%, 1 h)
3j (78%, <i>o/p</i> 8:1, 2 h)	3k (95%, <i>p/o</i> 1.1:1, 1 h) (91%, <i>p/o</i> 1:1.8, 3 h) ^[c]	3l (86%, 2 h)	3m (90%, 2 h)
3n (54%, 2 h)	3o (90%, <i>p/o</i> >20:1, 2 h)	3p (81%, <i>p/o</i> 3:1, 1 h)	3q (74%, <i>p/o</i> 3:1, 2 h)
3r (93%, 3 h)	3s (80%, <i>1/2</i> 1:1.2, 2 h)	3t (78%, 1 h)	3u (81%, <i>1/2</i> 2.4:1, 1 h)

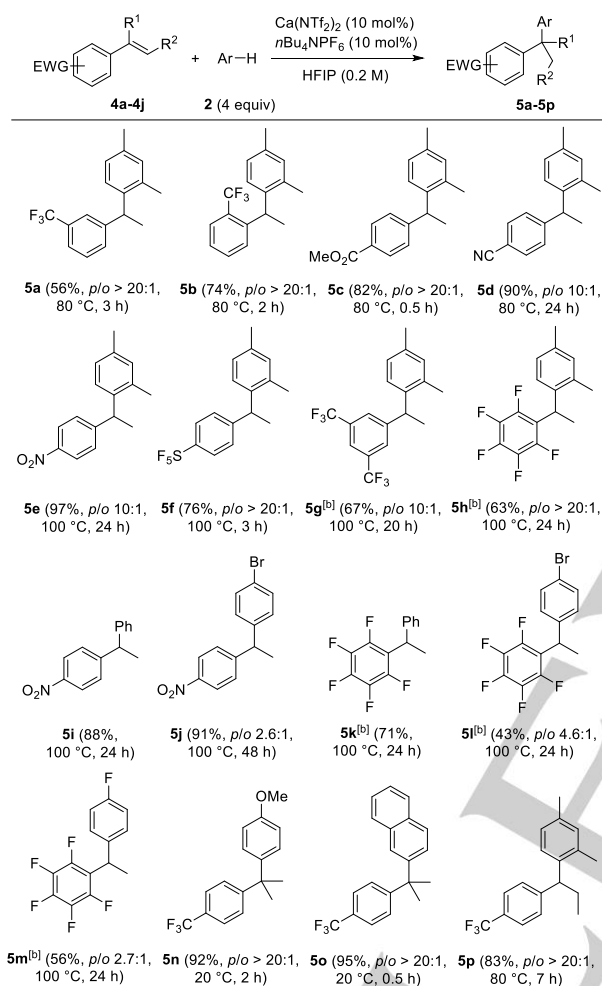
[a] Reactions performed in a sealed tube. [b] NMR yield using an external standard *p*-anisaldehyde. [c] Reaction conducted at 20 °C.

bromobenzene could also be employed to afford the corresponding diarylethanes **5i** and **5j** in excellent yields (88% and 91%, respectively). The same applied to the even more deactivated pentafluorostyrene **4h**, albeit in lower yields (**5k-5m**). The reaction was also attempted with a α -methylstyrene derivative **4i**. While the reaction was not successful with *m*-xylene **2a**, leading mainly to oligomeric products, the more nucleophilic

COMMUNICATION

anisole gave the corresponding product **5n** in 92% yield. In addition, due to the steric hindrance exhibited by the precursor, the *para*-compound could be obtained as a sole product (**5n** vs **3k** in Table 2). Interestingly, the reaction was also completely selective in the presence of naphthalene (**5o** vs **3s** in Table 2). Finally, the reaction was not limited to terminal alkenes and could provide **5l** in 83% yield for instance.

Table 3. Scope of Deactivated Styrenes **4a-4j** with **2** as an Arene Nucleophile.



[a] Reactions performed in a sealed tube. [b] Reaction in the presence of $\text{Ca}(\text{NTf}_2)_2$ (20 mol%) and $n\text{Bu}_4\text{NPF}_6$ (20 mol%).

To gain some insights into the mode of activation of electron-poor styrenes by the calcium salt in HFIP, we carried out DFT computations at the M062X/6-311+G(d,p)//M06-2X/6-31G(d) level. The values presented are Gibbs free energies at 343.15 K including solvent correction (see the Supporting Information for details). The model studied is the reaction of 4-(trifluoromethyl)styrene **1** with toluene (compound **3e**, Table 2). The addition leading to the *para* adduct is presented in Scheme 2. The *ortho* addition can be found in the Supporting Information. We started our investigations using the $\text{Ca}(\text{NTf}_2)^+$ ion as catalyst, as it is now generally accepted that the mixture of $\text{Ca}(\text{NTf}_2)_2$ and $n\text{Bu}_4\text{NPF}_6$ generates the heteroleptic $[\text{Ca}(\text{NTf}_2)]^+\text{PF}_6^-$ complex,^[15] in which the NTf_2 ligand likely remains strongly coordinated to the calcium center through its oxygen atoms.^[16] Importantly, attempts to directly activate **1** with the $\text{Ca}(\text{NTf}_2)^+$ ion failed. Then, we checked whether a calcium-coordinated HFIP molecule could become sufficiently acidic in order to transfer a proton to the alkene moiety. Thus, we introduced three molecules of HFIP in

the coordination sphere of the metal, as well as two water molecules to saturate it, while saving computer time. This model led to adduct **A**, taken as free energy reference. The proton transfer generating carbocation **B** could be modeled through TS_{AB} , lying at 22.5 kcal/mol on the potential energy surface (PES). The formation of **B** is markedly endergonic by 20.2 kcal/mol but is rapidly followed by the arene addition step, whose free energy of activation is as low as 1.7 kcal/mol from **B** (21.9 kcal/mol from the reactants). It leads to the Wheland-type intermediate **C**, lying at 13.0 kcal/mol on the PES. The deprotonation of **C** requires the rotation of the protonated toluene fragment, so that it presents its acidic proton to the NTf_2 ligand. Since the organic adduct and the calcium complex are chiral, this leads to two diastereomers **D** and **D'**, the latter being the most stable (16.5 vs 23.9 kcal/mol). The deprotonation is achieved through TS_{DE} (blue pathway) or $\text{TS}_{\text{D'E}}$ (red pathway), found at 26.0 and 18.8 kcal/mol on the PES, respectively. The relative free energies of **E** and **E'** remain positive (17.0 and 13.9 kcal/mol, respectively), but the separation of the fragments is a strongly exergonic process. It implies an internal proton transfer from the NTf_2 to the alkoxide moiety, which regenerates the active complex **F**. Overall, the formation of the hydroarylation product is exergonic by 24.1 kcal/mol. Of note, the deprotonation of the Wheland intermediate in **C** could not be modeled using the calcium alkoxide fragment. Only the NTf_2 ligand could be used as a base. A comparison with the values obtained in the *ortho* series indicates that the selection between the *para* and the *ortho* pathway is not achieved during the arene addition, but during the deprotonation step (product determining step, PDS). The best *ortho* deprotonation transition state lies at 1.1 kcal/mol higher than the *para* one (19.9 vs 18.8 kcal/mol) on the PES because of a steric clash between the *ortho* methyl and benzylic methyl substituents. These calculations corroborate the idea of hidden proton catalysis in this chemistry.^[17] The coordination of HFIP to the calcium ion increases its acidity to such an extent that it becomes able to protonate an electron-poor styrene derivative. Although this process is not energetically favorable, the acceptor properties of the NTf_2 ligand allow to go further by displacing the equilibria. Thus, the $[\text{Ca}(\text{NTf}_2)(\text{HFIP})_n]^+$ complex acts as a metal templated bifunctional organocatalyst. Besides, this mechanism was corroborated by deuterium labelling experiments (See Supporting Information for details).^[18]

In summary, we have devised a simple and efficient method for the hydroarylation of deactivated styrenes, which was hitherto unprecedented. While using a combination of a calcium salt and HFIP, good to excellent yields were observed for a vast array of electron-poor styrenes and aromatic nucleophiles, paving the way for a more extensive access to new diarylalkanes. Additionally, a series of DFT computations has been carried out to study the detailed mechanism of this transformation. To date, it represents the first example of a Lewis acid-catalyzed hydroarylation process entirely deciphered by computations, including the deprotonation step.

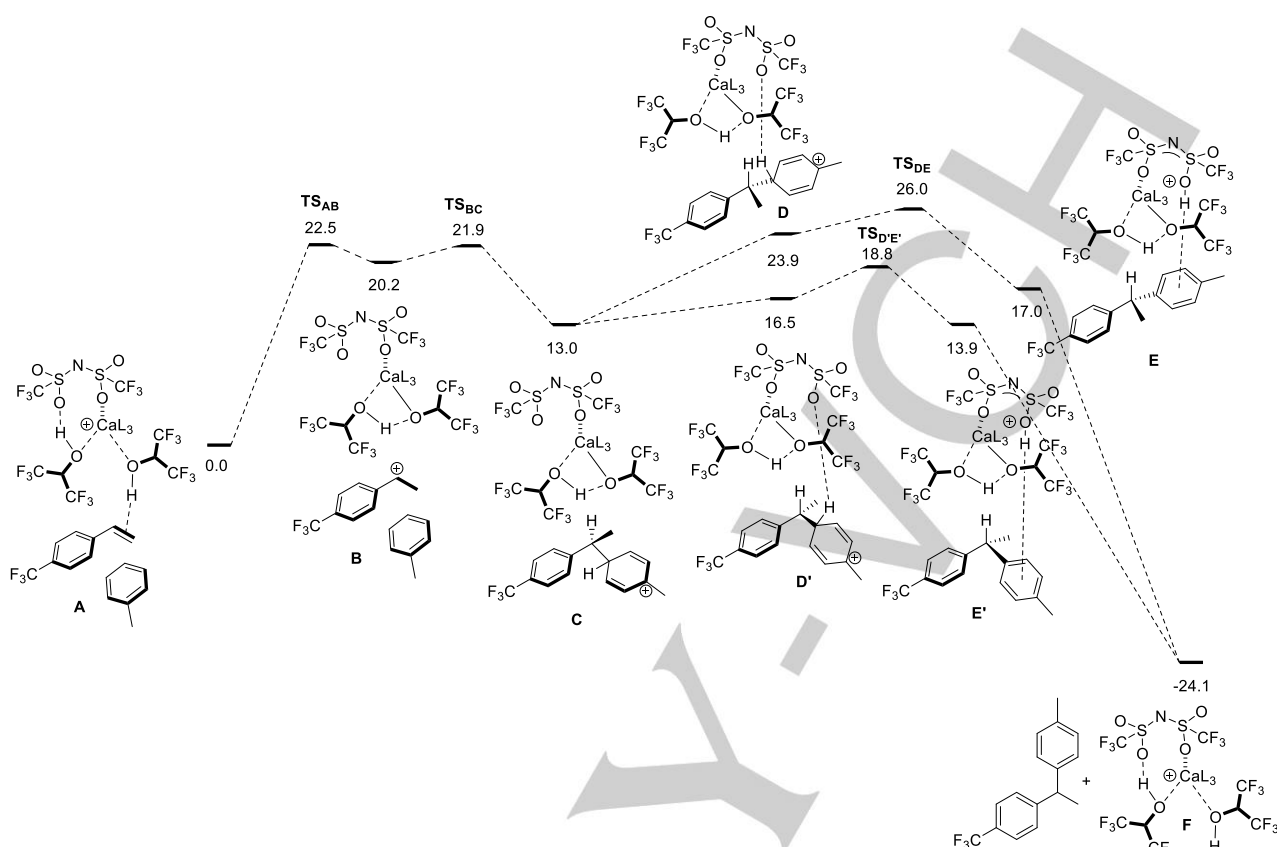
Acknowledgements

The authors are grateful for the funding support provided by the China Scholarship Council (CSC), CNRS, Université Paris-Sud, and Institut Universitaire de France (IUF) for the support of this work.

Conflict of interest

The authors declare no competing financial interest.

Keywords: Hydroarylation • calcium • hexafluoroisopropanol • diarylalkanes • DFT computations



Scheme 2. Free Energy Profile (ΔG_{343} , kcal/mol) of the Ca/HFIP-Catalyzed *para*-Addition of Toluene to 4-(Trifluoromethyl)styrene **1** ($L_3 = 1$ HFIP and 2 H_2O molecules as κ^1 -O ligands)

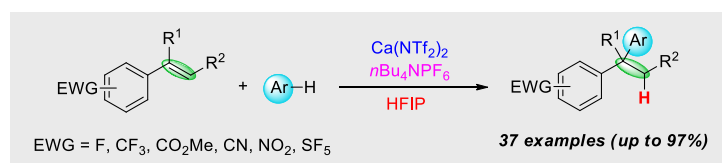
- [1] a) D. Ameen, T. J. Snape, *Med. Chem. Commun.* **2013**, *4*, 893; b) S. Mondal, G. Panda, *RSC Adv.* **2014**, *4*, 28317.
- [2] a) C. Friedel, J. M. Crafts, *J. Chem. Soc.* **1877**, *32*, 725; b) G. A. Olah, R. Krishnamurti, G. K. S. Prakash in *Friedel-Crafts Alkylation in Comprehensive Organic Synthesis*, Vol. 3 (Eds: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**; pp 293; c) M. Rueping, B. J. Nachtsheim, *Beilstein J. Org. Chem.* **2010**, *6*, No. 6; d) *Catalytic Hydroarylation of Carbon-Carbon Multiple Bonds* (Eds: L. Ackermann, B. T. Gunnoe, L. Goj Habgood), Wiley-VCH, **2018**.
- [3] For recent examples, see: a) K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao, *Angew. Chem.* **2016**, *128*, 6383; *Angew. Chem. Int. Ed.* **2016**, *55*, 6275; b) S. D. Friis, M. T. Pirnot, S. L. Buchwald, *J. Am. Chem. Soc.* **2016**, *138*, 8372; c) L.-J. Xiao, L. Cheng, W.-M. Feng, M.-L. Li, J.-H. Xie, Q.-L. Zhou, *Angew. Chem.* **2018**, *130*, 470; *Angew. Chem. Int. Ed.* **2018**, *57*, 461; d) S. Grélaud, P. Cooper, L. J. Feron, J. F. Bower, *J. Am. Chem. Soc.* **2018**, *140*, 9351. For another strategy relying on hydrogen atom transfer, see: e) S. A. Green, S. Vásquez-Céspedes, R. A. Shenvi, *J. Am. Chem. Soc.* **2018**, DOI: 10.1021/jacs.8b05868.
- [4] X. Mo, J. Yakiwchuk, J. Dansereau, J. A. McCubbin, D. G. Hall, *J. Am. Chem. Soc.* **2015**, *137*, 9694.
- [5] V. D. Vuković, E. Richmond, E. Wolf, J. Moran, *Angew. Chem.* **2017**, *129*, 3131; *Angew. Chem. Int. Ed.* **2017**, *56*, 3085.
- [6] J. Dong, S. Xin, Y. Wang, L. Pan, Q. Liu, *Chem. Commun.* **2017**, *53*, 1668.
- [7] For selected examples requiring a pre-activation, see: a) G. Schäfer, J. W. Bode, *Angew. Chem.* **2011**, *123*, 11105; *Angew. Chem. Int. Ed.* **2011**, *50*, 10913; b) J. Zhu, M. Pérez, D. W. Stephan, *Angew. Chem.* **2016**, *128*, 8588; *Angew. Chem. Int. Ed.* **2016**, *55*, 8448; c) G. Pallikonda, M. Chakravarty, *J. Org. Chem.* **2016**, *81*, 2135.
- [8] We found a single example in the literature of hydroarylation of the deactivated 4-(trifluoromethyl)styrene **1** using $FeCl_3$ as a Lewis acid (J. Kischel, I. Jovel, K. Mertins, A. Zapf, M. A. Beller, *Org. Lett.* **2006**, *8*, 19). However, this reaction requires using the nucleophile as a solvent. Besides, in our hands, these conditions proved to be inefficient with strongly deactivated styrenes. For instance, after 24 h, we obtained only 25% conversion with 4-nitrostyrene and 10% with pentafluorostyrene using *m*-xylene as a nucleophile.
- [9] For reviews on HFIP, see: a) J.-P. Bégué, D. Bonnet-Delpon, B. Crousse, *Synlett* **2004**, *18*; b) I. A. Shuklov, N. V. Dubrovina, A. Börner, *Synthesis* **2007**, 2925; c) T. Sugiishi, M. Matsugi, H. Hamamoto, H. Amii, *RSC Adv.* **2015**, *5*, 17269; d) J. Wencel-Delord, F. Colobert, *Org. Chem. Front.* **2016**, *3*, 394; e) I. Colomer, A. E. R. Chamberlain, M. B. Haughey, T. J. Donohoe, *Nat. Rev. Chem.* **2018**, *1*, 0088.
- [10] For selected examples of utilization of HFIP in synthesis, see: a) A. Berkessel, J. A. Adrio, D. Hüttenhain, J. M. Neudörfel, *J. Am. Chem. Soc.* **2006**, *128*, 8421; b) A. Berkessel, J. A. Adrio, *J. Am. Chem. Soc.* **2006**, *128*, 13412; c) H. F. Motiwala, C. Fehl, S.-W. Li, E. Hirt, P. Porubsky, J. Aubé, *J. Am. Chem. Soc.* **2013**, *135*, 9000; d) R. H. Vekariya, J. Aubé, *Org. Lett.* **2016**, *18*, 3534; e) X. Zeng, S. Liu, B. Xu, *Org. Lett.* **2016**, *18*, 4770; f) I. Colomer, R. C. Barcelos, K. E. Christensen, T. J. Donohoe, *Org. Lett.* **2016**, *18*, 5880; g) Q. Dherbassy, G. Schwertz, M. Chessé, C. K. Hazra, J. Wencel-Delord, F. Colobert, *Chem. Eur. J.* **2016**, *22*, 1735; h) T. Kamitanaka, K. Morimoto, K. Tsuboshima, D. Koseki, H. Takamuro, T. Dohi, Y. Kita, *Angew. Chem.* **2016**, *128*, 15764; *Angew. Chem. Int. Ed.* **2016**, *55*, 15535; i) I. Colomer, C. Batchelor-McAuley, B. Odell, T. J. Donohoe, R. G. Compton, *J. Am. Chem. Soc.* **2016**, *138*, 8855; j) E. Richmond, V. D. Vuković, J. Moran, *Org. Lett.* **2018**, *20*, 574; k) S. Roy, H. F. Motiwala, K. M. Koshlap, J. Aubé, *Eur. J. Org. Chem.* **2018**, 306; l) A. Bernhardt, H. Kelm, F. W. Patureau, *ChemCatChem.* **2018**, *10*, 1547; m) E. Richmond, J. Yi, V. D. Vuković, F. Sajadi, C. N. Rowley, J. Moran, *Chem. Sci.* **2018**, *9*, 6411.
- [11] For reviews on Ca(II) catalysis, see: a) J.-M. Begouin, M. Niggemann, *Chem. Eur. J.* **2013**, *19*, 8030; b) *Topics in Organometallic Chemistry*, Vol. 45 (Ed.: S. Harder), Springer, Berlin, **2013**; c) D. Leboëuf, V. Gandon, *Synthesis* **2017**, *49*, 1500.
- [12] a) D. Leboëuf, L. Marin, B. Michelet, A. Perez-Luna, R. Guillot, E. Schulz, V. Gandon, *Chem. Eur. J.* **2015**, *21*, 16165; b) L. Marin, R. Guillot, V. Gandon, E. Schulz, D. Leboëuf, *Org. Chem. Front.* **2018**, *5*, 640; c) C. Qi, V. Gandon, D. Leboëuf, *ACS Catal.* **2018**, *8*, 1734.
- [13] For an example of calcium-catalyzed hydroarylation, see: M. Niggemann, N. Bisek, *Chem. Eur. J.* **2010**, *16*, 11246. However, as stated in the introduction of this paper, the reaction is limited to styrenes bearing electron-donating or moderately withdrawing groups, while using also strong nucleophiles.

COMMUNICATION

- [14] For instance, the reaction of **1** with anisole **2k** led to a significant drop in yield (58%), when compared to the association $\text{Ca}(\text{NTf}_2)_2/n\text{Bu}_4\text{NPF}_6$ (95%) (same with a strongly deactivated styrene such as **4g**, 48% vs 63%).
- [15] a) S. Haubenreisser, M. Niggemann, *Adv. Synth. Catal.* **2011**, 353, 469;
b) J. Davies, D. Leonori, *Chem. Commun.* **2014**, 50, 15171.
- [16] L. Xue, D. D. DesMarteau, W. T. Pennington, *Solid State Sciences* **2005**, 7, 311.
- [17] a) T. T. Dang, F. Boeck, L. Hintermann, L. *J. Org. Chem.* **2011**, 76, 9353;
b) D. Munz, M. Webster-Gardiner, R. Fu, T. Strassner, W. A. Goddard, III, T. B. Gunnoe, *ACS Catal.* **2015**, 5, 769.
- [18] E. M. Simmons, J. F. Hartwig, *Angew. Chem.* **2012**, 124, 3120; *Angew. Chem. Int. Ed.* **2012**, 52, 3066.

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



Chenxiao Qi, Vincent Gandon,* and David Lebcœur*

Page No. – Page No.

Calcium(II)-Catalyzed Intermolecular Hydroarylation of Deactivated Styrenes in Hexafluoroisopropanol

A challenging catalytic hydroarylation of highly electron-deficient styrenes has been developed thanks to an efficient cooperation between a calcium(II) triflimide salt and hexafluoroisopropanol (HFIP). This method affords a large variety of diarylalkanes, notably diarylethanes, in good to excellent yields, while being simple to implement and tolerant to various functional groups. In addition, density functional theory (DFT) computations and deuterium labelling experiments were conducted to uncover the functioning of this promoter system.