OL Organic Letters

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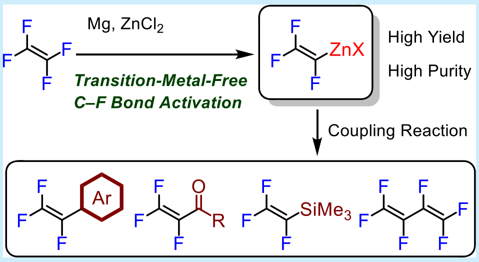
Direct Transformation of Tetrafluoroethylene to Trifluorovinylzinc via sp^2 C−F Bond Activation

Kotaro Kikushima, Yuusuke Etou, Ryohei Kamura, Ippei Takeda, Hideki Ito, Masato Ohashi, and Sensuke Ogoshi*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c03189 Read Online

ABSTRACT: Trifluorovinylzinc is a common synthetic intermediate for trifluorovinyl derivatives, including *α,β,β*-trifluorostyrenes and hexafluorobutadiene. Here, we report a novel synthetic approach for the formation of trifluorovinylzinc chloride via a C−F bond activation of tetrafluoroethylene (TFE), which is an industrially cost-effective bulk feedstock with a negligible GWP. The present system provides a practical synthetic route to various trifluorovinyl derivatives with very low energy consumption.



Trifluorovinyl compounds have attracted great attention, as they represent promising potential monomers for the synthesis of functionalized polymers with fluorinated main chains,[1] including *α,β,β*-trifluorostyrenes.[2,3] In addition, hexafluorobutadiene is the best-performing dry-etching gas with a low global warming potential (GWP),[4] which enables the fabrication of complicated networks of narrow and deep microchannels on silicon substrates for large-scale integration (LSI) chips.[5] Furthermore, the trifluorovinyl group has attracted attention as a potentially interesting fluorinated functional group for the design of drug candidates.[6]

α,β,β-Trifluorostyrene derivatives have been synthesized through the palladium-catalyzed cross-coupling of aryl halides with trifluorovinylmetal intermediates (metal = Zn,[7−9] Sn,[10] or B[11]). These intermediates have been prepared from chlorotrifluoroethylene (CTFE)[7] and 1,1,1,2-tetrafluoroethane (HFC-134a)[8,10,11] via halogen exchange or deprotonation with butyllithium generating unstable trifluorovinyllithium. However, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113, the starting material for CTFE) and HFC-134a have high GWP$_{100}$ values of 5000 and 1430, respectively. Both bromo- and iodotrifluoroethylene can be converted into the corresponding trifluorovinylzinc halides by treatment with zinc powder,[9] but these halotrifluoroethylenes are very expensive. Trifluorovinylzinc halides are also key intermediates for the synthesis of hexafluorobutadiene. The groups of Burton and Ramachandran have independently reported the synthesis of hexafluorobutadiene via the homocoupling of trifluorovinylzinc halides[12] as an alternative to the conventional multistep syntheses.[13,14] Therefore, the development of new strategies for the preparation of trifluorovinylzinc halides from environmentally benign and economical starting materials would provide a practical approach to the synthesis of the above-mentioned trifluorovinyl derivatives.

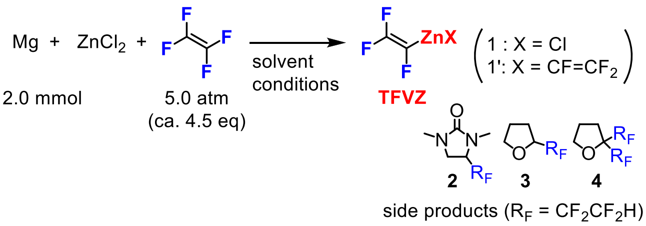
Tetrafluoroethylene (TFE) is an industrially cost-effective bulk feedstock for the production of fluorine-containing polymers that exhibits a negligible GWP.[4,15,16] TFE thus represents an ideal starting material for fluoroethylene-based compounds.,[16c17] We have demonstrated the direct transformation of TFE into *α,β,β*-trifluorostyrene derivatives via palladium-catalyzed cross-coupling reactions of TFE with arylzinc, arylboronate, and arylsilane reagents, involving C−F bond activation by a transition-metal catalyst.[17a−c,18] Our next target was the direct transformation of TFE into stable trifluorovinylzinc halides, which are common intermediates for trifluorovinyl compounds.[17d] We envisioned that the cleavage of a C−F bond could be achieved by treating TFE with a mixture of a zinc halide and an appropriate reductant to generate the corresponding trifluorovinylzinc halide. Crabtree and co-workers have reported that magnesium anthracene reacts with perfluoroarenes to generate the corresponding organomagnesium reagents, which are unstable and are subsequently converted to fluorinated benzoic acid.[19] Uneyama and Amii have demonstrated that a combination of magnesium and chlorotrimethylsilane can be used for cleavage of the C−F bond in trifluoromethyl ketones to produce the corresponding difluoro enol silyl ethers.[20] These reports prompted us to employ magnesium metal as a reductant for the C−F bond activation in TFE. Herein, we disclose a simple and cost-effective synthesis of trifluorovinylzinc chloride

Received: September 23, 2020

(TFVZ) from TFE in the presence of zinc chloride and magnesium turnings; all reagents involved are abundant and inexpensive. The resulting TFVZ was effectively converted into various trifluorovinyl derivatives, such as *α,β,β*-trifluorostyrenes, *α,β,β*-trifluoroacrylic acid derivatives, and trifluorovinylsilane. Furthermore, hexafluorobutadiene was synthesized quantitatively from the prepared TFVZ.

Exposure of a 1,3-dimethyl-2-imidazolidinone (DMI) suspension of ZnCl$_2$ and Mg turnings to a TFE atmosphere at room temperature for 6 h afforded TFVZ (**1**) in 5% yield (Table 1, run 1). In this reaction, the insertion of TFE into a C−H bond of DMI also occurred to generate **2** in 2% yield. When a mixture of ZnCl$_2$ and Mg turnings was stirred in DMI without TFE, the Mg surface and the entire suspension gradually turned black, which suggests the generation of highly activated Mg and/or Zn metal. Employing 2.0 equiv of ZnCl$_2$ improved the yield to 50% (run 2). The Knochel group has reported the convenient preparation of organozinc reagents from organohalides using a combination Mg, ZnCl$_2$, and LiCl;[21] however, in the present study, the addition of LiCl resulted in decreased yield (run 3). Conducting the reaction at 60 °C for 6 h improved the reaction yield to 74% (run 4), whereas increasing the reaction time (24 h) led to a decreased yield (run 5). In these cases, the formation of bis(trifluorovinyl)zinc (**1′**) was also observed (2%; runs 2,4, and 5) as the result of the Schlenk equilibrium. The yields listed in Table 1 represent the combined yields of TFVZ based on the trifluorovinyl moiety. Then we surveyed the effect of varying the solvent on the yield of TFVZ. The use of *N*-methylpyrrolodone (NMP) gave **1** in 11% yield, although neither *N*,*N*-dimethylacetamide (DMA) nor *N*,*N*-dimethylformamide (DMF) afforded the desired product (runs 6−8). Conversely, employing THF did not produce **1**; instead, the insertion of TFE into a C−H bond of THF proceeded to give **3** and **4** in 10% and 3% yield, respectively (run 9).

Table 1. Optimization of Reaction Conditions for Transformation of TFE into TFVZ[a]

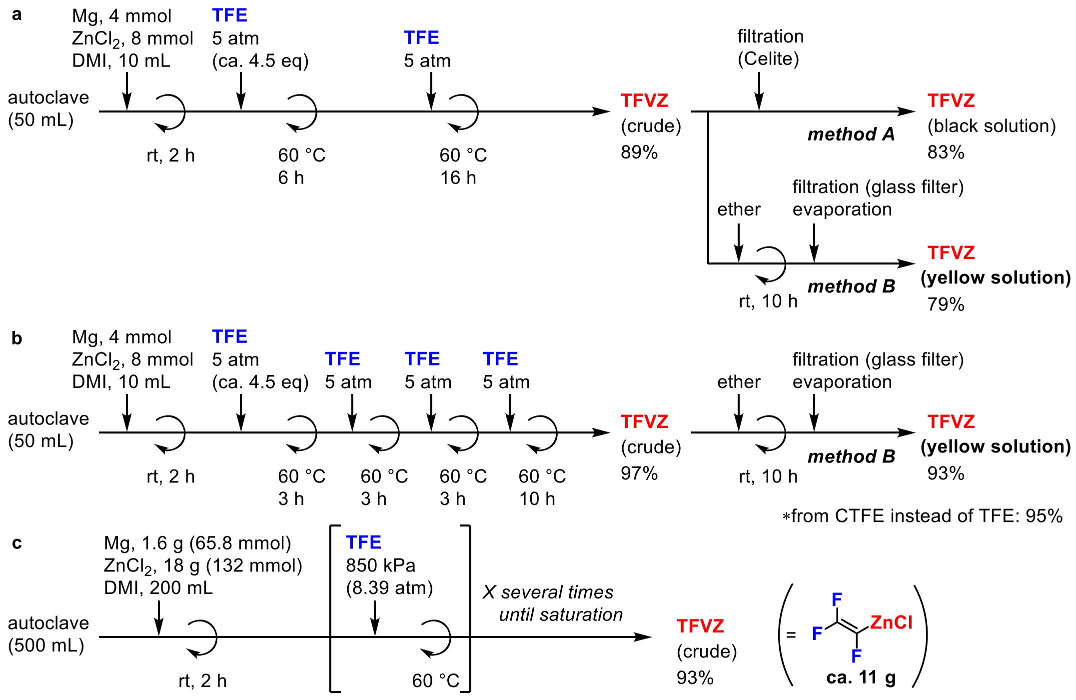


run	ZnCl$_2$ (equiv)	solvent	temp (°C)	time (h)	yield of **1** + **1′** (%)
1	1.0	DMI	rt	6	5[b]
2	2.0	DMI	rt	24	50
3[c]	2.0	DMI	rt	24	27
4	2.0	DMI	60	6	74[d]
5	2.0	DMI	60	24	62[e]
6	2.0	NMP	60	24	11
7	2.0	DMA	60	24	trace
8	2.0	DMF	60	24	0
9	2.0	THF	60	24	0[f]

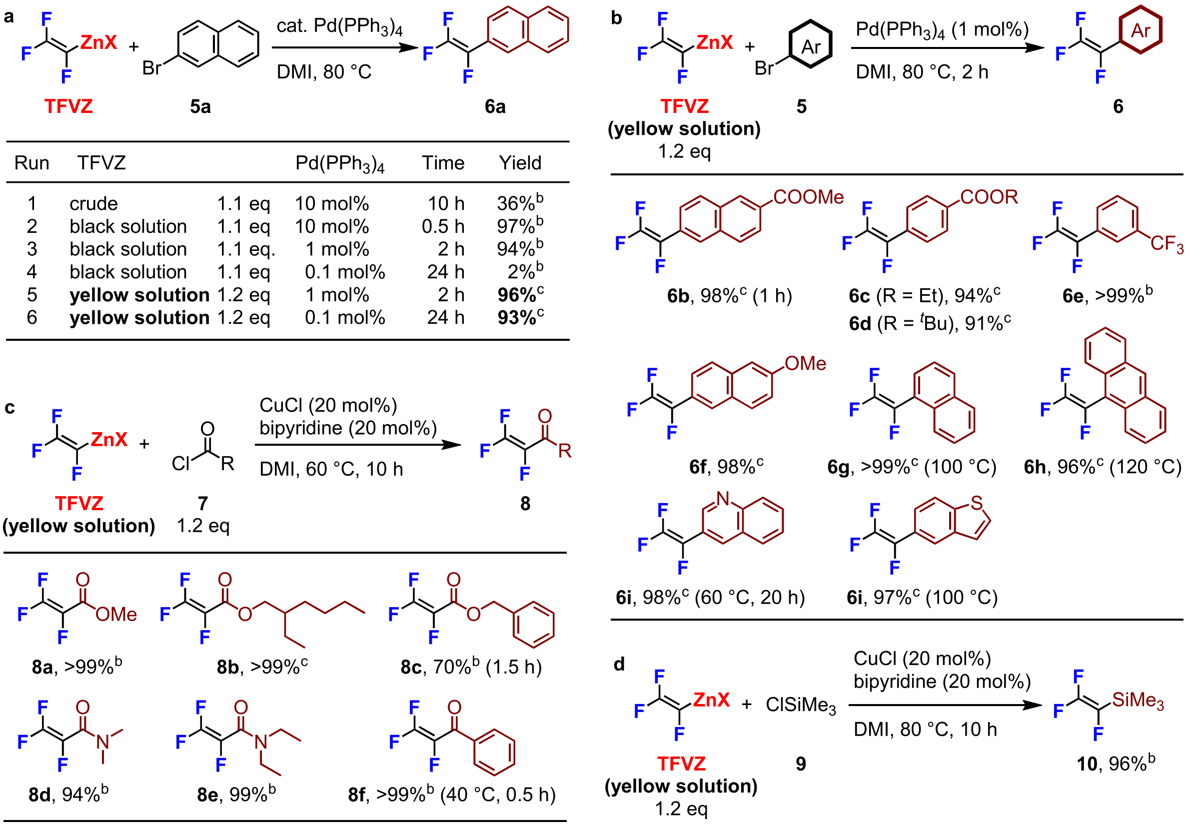
[a]Conducted in a glass autoclave reactor (55 mL). NMR yield. [b]With **2** (2%). [c]In the presence of 0.5 equiv of LiCl. [d]With **2** (4%). [e]With **2** (6%). [f]With **3** (10%) and **4** (3%).

Based on these results, we chose DMI as the optimum solvent for the direct transformation of TFE into TFVZ.[22] The reaction yield was further improved by employing a two-step procedure and maintaining a high concentration of TFE (Scheme 1a). Specifically, a mixture of Mg and ZnCl$_2$ was stirred in DMI at room temperature for 2 h, and the reactor was then pressurized with TFE. The reaction mixture was stirred at 60 °C for 6 h before the reactor was pressurized again with TFE in order to maintain a high TFE concentration. The mixture was then stirred for a further 16 h at 60 °C to afford TFVZ in 89% yield. Subsequently, we next surveyed methods to purify TFVZ in the reaction mixture, which contained

Scheme 1. Preparation and Purification of TFVZ



Scheme 2. Coupling Reactions of TFVZ to Produce Various Trifluorovinyl Monomers[a]



Run	TFVZ		Pd(PPh$_3$)$_4$	Time	Yield
1	crude	1.1 eq	10 mol%	10 h	36%^{b}
2	black solution	1.1 eq	10 mol%	0.5 h	97%^{b}
3	black solution	1.1 eq.	1 mol%	2 h	94%^{b}
4	black solution	1.1 eq	0.1 mol%	24 h	2%^{b}
5	**yellow solution**	1.2 eq	1 mol%	2 h	**96%**^{c}
6	**yellow solution**	1.2 eq	0.1 mol%	24 h	**93%**^{c}

[a]See the SI for experimental details. [b]NMR yield. [c]Isolated yield.

unreacted metal (Zn and/or Mg) as well as a substantial amount of metal halides. Filtration of the freshly prepared crude TFVZ through a Celite plug removed metal powder to furnish a black solution (Scheme 1a, method A). A ^{19}F NMR analysis of this filtrate showed that the overall TFVZ yield was 83%. A clear solution was obtained by adding diethyl ether to the crude mixture rather than filtering it directly over Celite; stirring the resulting solution for several hours at room temperature afforded a yellow solution with a gray precipitate. The insoluble material was removed by filtration through a glass filter. After concentration of the filtrate, a transparent yellow DMI solution containing 79% TFVZ was obtained (Scheme 1a, method B). This TFVZ reagent (as yellow DMI solution) could be stored without decomposition for at least three years at 25 °C under an N_2 atmosphere.

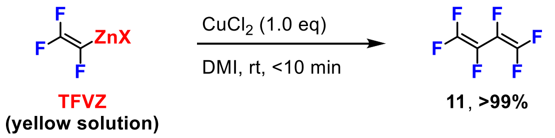
Based on these results, we attempted to further improve the reaction yield (Scheme 1b). After Mg and $ZnCl_2$ were mixed in DMI at room temperature for 2 h, the reactor was pressurized with TFE and the mixture was stirred at 60 °C. To maintain a high concentration of TFE throughout the reaction, the reactor was completely pressurized (to 5 atm) every 3 h. A ^{19}F NMR analysis of the crude mixture revealed that TFVZ was generated in 97% yield, and purification of the crude mixture via method B afforded a clear yellow DMI solution; the overall TFVZ yield after filtration was 93%. The transformation of CTFE to TFVZ was also investigated at the bench scale using the optimized conditions for TFE.[23] The reaction proceeded to produce TFVZ quantitatively; after a subsequent purification using method B a yellow solution with an overall TFVZ yield of 95% was obtained (Scheme 1b*). The transformation of TFE into TFVZ was then scaled up using 1.6 g of Mg and 18 g of $ZnCl_2$ under 850 kPa (= 8.39 atm) of TFE in a SUS 316 autoclave reactor (total volume: 500 mL) (Scheme 1c).[24] The reactor was repeatedly pressurized to 850 kPa with TFE untilno internal pressure decrease was observed. A ^{19}F NMR analysis of the resulting mixture revealed that TFVZ was generated in 93% yield (61.4 mmol, ∼11 g).

We next examined the Pd(0)-catalyzed cross-coupling reaction of the prepared TFVZ with 2-bromonaphthalene (**5a**) (Scheme 2a). Heating a suspension of freshly prepared, unpurified TFVZ (1.1 equiv) in DMI and **5a** in the presence of 10 mol % of Pd(PPh$_3$)$_4$ at 80 °C for 24 h resulted in the formation of the corresponding product (**6a**) in 36% yield (Scheme 2a, run 1). The use of the black TFVZ solution obtained from purification method A improved the reaction yield drastically to 97% within 0.5 h (run 2). The catalyst loading could be decreased to 1 mol % to obtain **6a** in 94% yield (run 3), although further decreasing the catalyst loading to 0.1 mol % reduced the reaction yield (run 4). Furthermore, the yellow TFVZ solution purified by method B showed higher reactivity (run 5). Using only 0.1 mol % of Pd(PPh$_3$)$_4$, the catalytic reaction proceeded to afford **6a** in 93% yield (run 6). With the optimized reaction conditions in hand, Pd(0)-catalyzed cross-coupling reactions of various aryl bromides with the TFVZ solution purified by method B were investigated (Scheme 2b). A bromoarene with an electron-deficient group, such as ester (**5b**, **5c** and **5d**) or trifluoromethyl (**5e**) group, produced the corresponding product (**6b**−**e**). *α*,*β*,*β*-Trifluorostyrene derivatives bearing an electron-donating group, such as a methoxy group (**6f**), was obtained in excellent yield. Although sterically hindered aryl bromides, such as 1-bromonaphthalene (**5g**) and 9-bromoanthracene (**5h**), required higher reaction temperatures, the corresponding products (**6g** and **6h**) were obtained in high yield. When the TFVZ solution purified by method A was used, the yields decreased due to the decomposition of TFVZ at high temperature. These coupling reactions could also be successfully applied to the synthesis of trifluorovinyl heteroaromatics (**6i** and **6j**).

Subsequently, we investigated the synthesis of trifluorovinyl carbonyl compounds employing the TFVZ solution obtained from purification method B (Scheme 2c). *α,β,β*-Trifluoroacrylates have been prepared via the palladium-catalyzed coupling reactions of trifluorovinylstannane with chloroformate or the reduction of 2-bromo-2,3,3,3-tetrafuoropropanoate by zinc.[25] Conversely, organozinc intermediates have not yet been employed as a trifluorovinyl source. The coupling reaction between TFVZ and methyl chloroformate (**7a**) in the presence of the catalyst $Pd(PPh_3)_4$ generated the desired product **8a**, albeit together with unidentified byproducts. When the reaction was conducted at 60 °C using CuCl and bipyridine instead of $Pd(PPh_3)_4$, **8a** was afforded as the sole product in quantitative yield. Employing chloroformates and carbamoyl chlorides produced the respective *α,β,β*-trifluoroacrylates (**8b** and **8c**) and *α,β,β*-trifluoroacrylamides (**8d** and **8e**). When benzoyl chloride was used as a coupling partner, trifluorovinyl phenyl ketone (**8f**) was obtained smoothly in quantitative yield. Furthermore, the reaction with trimethylsilyl chloride afforded trifluorovinylsilane **10**, which could be converted to other trifluorovinyl derivatives (Scheme 2d).[26]

The treatment of the TFVZ solution obtained from purification method B with a stoichiometric amount of $CuCl_2$ generated hexafluorobutadiene smoothly as the sole product in quantitative yield (Scheme 3). The previously reported methods[12] provide hexafluorobutadiene in low yield and/or together with side products such as bromo- and chlorotrifluoroethylene probably due to contamination of unpurified trifluorovinylzinc halides with metal salts generated during the preparation. In contrast, the yellow TFVZ solution prepared using our method does not contain metal salt impurities. Accordingly, side reactions were suppressed, and the desired reaction proceeded to quantitatively afford hexafluorobutadiene. The use of the black TFVZ solution (without ether treatment; Scheme 1, method A) furnished hexafluorobutadiene together with chlorotrifluoroethylene.[27]

Scheme 3. Efficient Synthesis of Hexafluorobutadiene



In conclusion, we have achieved the direct transformation of TFE into TFVZ in the presence of Mg and $ZnCl_2$ via C−F bond activation. The resulting salt impurities, including magnesium halides, were successfully removed by treatment with ether followed by filtration and concentration to afford a clear yellow solution of TFVZ in DMI. The resulting TFVZ was employed as a key intermediate to efficiently produce various trifluorovinyl derivatives including *α,β,β*-trifluorostyrenes and hexafluorobutadiene. The present findings can be expected to provide access to useful fluorine-containing chemicals from cost-effective and environmentally benign feedstocks and thus aid the development of industrial products, such as functional fluorinated polymers, LSI chips, and new drugs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03189.

Experimental procedures, characterization data, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Sensuke Ogoshi − *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan;* orcid.org/0000-0003-4188-8555; Email: ogoshi@chem.eng.osaka-u.ac.jp

Authors

Kotaro Kikushima − *College of Pharmaceutical Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*
Yuusuke Etou − *Product R&D Department Chemicals Division, Daikin Industries, Ltd., Settu, Osaka 566-8585, Japan*
Ryohei Kamura − *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
Ippei Takeda − *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
Hideki Ito − *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*
Masato Ohashi − *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan;* orcid.org/0000-0001-8718-2799

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03189

Notes

The authors declare the following competing financial interest(s): A patent application (P2016-128415A, Japan) dealing with the preparation of TFVZ and its derivatization, has been filed; K.K., Y.E., M.O., and S.O. may benefit from royalty payments.

■ ACKNOWLEDGMENTS

This research was partially supported by the JSPS in the form of Grants-in-Aid for Scientific Research (A) (16H02276 to S.O.) and (B) (16KT0057 to M.O. and 18H02014 to K.K.), a Grant-in-Aid for Young Scientists (A) (25708018 to M.O.) and (B) (16K17899 to K.K.), and a Grant-in-Aid for Scientific Research on Innovative Areas "Precisely Designed Catalysts with Customized Scaffolding" (15H05803 to S.O.).

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https://dx.doi.org/10.1021/acs.orglett.0c03189

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(24) Highly pressurized TFE can potentially explode. The scaled-up reaction was performed using the facilities at Daikin Industries, Ltd.

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