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Optimized Synthesis of a Novel 1-(trifluoroethenyl)-4-[(trifluoroethenyl)-oxy]-benzene via Palladium-Catalyzed Coupling of Arylboronic Acids with Bromotrifluoroethylene

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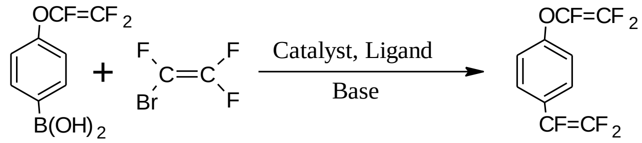
ABSTRACT

The synthesis of a novel 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene at optimized reaction conditions were described. The optimized reaction condition required only 0.25 mol% of $Pd(dba)_2$ and 0.5 mol% of $^{t-}Bu_3$-P and occurred to full conversion within 12 h at 80°C. The novel product was assayed by ^{1}H and ^{19}F NMR spectroscopy.



Keyword: Organo- fluorine, Suzuki cross-coupling reaction, Palladium, NMR

INTRODUCTION

The palladium-catalyzed Suzuki cross-coupling reaction of aryl halides with arylboronic acids is one of the most powerful tool for the construction of C – C bonds to prepare compounds trifluorostyrenes (TFS). The effect of solvent, base and catalyst loading on the coupling reaction of aryl halide with arylboronic acid were described [1-3]. TFS and its derivatives are very important to prepare monomers for fluorinated polymers, mainly due to their special structure that combines a trifluorovinyl group and a benzene ring [4, 5]. Several methods used to prepare TFS derivatives and this has proven to be the most popular in recent time [6]. In 2010, Chen, S. *et al.* reported in a patent that when 5.0 mol% of tetrakis(triphenyl)phosphane palladium(0) ($Pd(PPh_3)_4$) was first time used as the catalyst, various functionalized arylboronic acids were coupled with chlorotrifluoroethylene to give the corresponding TFS derivatives in good yields [7]. In 2012, Herein et al reported in a patent that a combination of bis(dibenzylideneactone)palladieum(0) ($Pd(dba)_2$) with tributylphosphane ($^tBu_3$-P) was used to couple bromotrifluoroethylene with a variety of arylboronic acids were good to excellent yields, with recorded only 0.2 mol % catalyst [8]. Also in 2012, Yamamoto and Yamakawa reported that when 1−3 mol% of 1,1\ bis(diphenylphosphino)ferrocene)dichloropalladium (II) ($Pd(dppf)Cl_2$) was used as the catalyst, various functionalized arylboronic acids were coupled with chlorotrifluoroethylene to give the corresponding TFS derivatives in good to excellent yields [9]. In 2012, Chunfa Xu and co-workers developed method to prepare TFS and its derivatives via palladium-catalyzed coupling of arylboronic acids with chloro- and bromotrifluoroethylene in good to excellent yields [6]. In this work is prepared a novel 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene which involves two groups of trifluoroethylene at optimized reaction conditions. This product is a good monomer which can be widely used to prepare more TFS polymers and copolymers, also at the same time it can be prepare cross linkage by perfluorocyclobuty to build high molecular weight TFS polymers. TFS polymers and copolymers found application as ionomer membranes in fuel cell separators [10].

EXPERIMENTAL

Material

4-(1,2,2-Trifluorovinyloxy)phenylboronic acid was prepared as previously described [11]. Bromotrifluoroethylene was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. The tetrakis(triphenyl)phosphane palladium(0), Bis(triphenylphosphine)palladium(II) chloride, Palladium diacetate, tri-tert-butylphosphine tetrafluoroborate were purchased from TCI (Shanghai) Development Co., Ltd.. Potassium phosphate was purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents and solvents were used as received.

Instrument

^{1}HNMR (400MHz) was recorded on a Bruker AM-400 spectrometer with $CDCl_3$ (^{1}HNMR) as internal standard. ^{19}F NMR (377 MHz) was recorded with $CDCl_3$.

General procedure

A 50 ml Schlenk-type sealed tube equipped with magnetic stirring was charged with the (trifluorovinyloxy)phenylboronic acid (5.0 mol), base (15.0 mol), catalyst (0.25 mol %), and ligand (0.5 mol %). The reaction tube was capped and then evacuated briefly under high vacuum and charged with nitrogen three times. Solvents were added, and bromotrifluoroethene was bubbled for about 5 min (saturated) under liquid nitrogen condition. Then the valve was screwed. The reaction mixture was stirred at selected temperature and time of reaction. Then reaction vessel was cooled to room temperature, and 20 ml of deionized water and 20 ml of dichloromethane were added. The organic phase was separated and washed with deionized water three times. The aqueous phase was extracted with dichloromethane three times. The organic phase was combined and dried with anhydrous magnesium sulfate, and silica gel. The mixture was evacuated under a rotary evaporator, and the resulting residue was purified by silica gel flash column chromatography using petroleum ether and remove the solvent. Finally the 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene product was dried overnight under vacuum at room temperature.

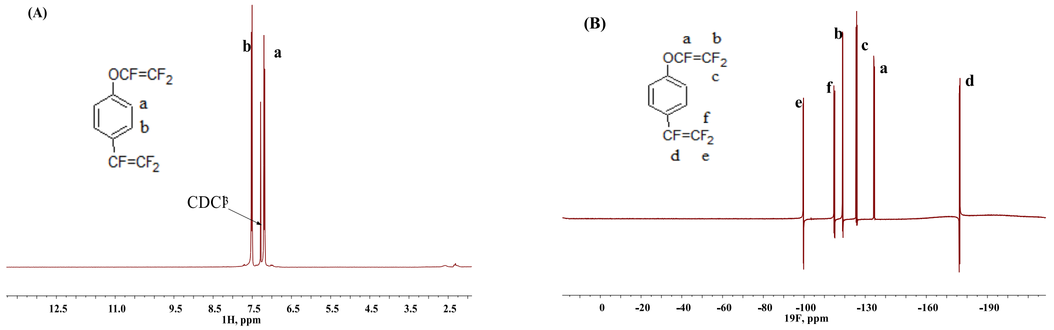


Fig 1: ^{1}H NMR (A) and ^{19}F NMR (B) spectra of 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy] – benzene.

Table 1: Catalytic and base Effect on synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]-benzene

entry	catalyst	liqand	Solvent (2/1)	base entry	temp ., ºC	time, hr	yield%
1	Pd(OAC)$_2$	$^{t-}$Bu-P	Acetone/H$_2$O	K$_3$PO$_4$	80	12	trace
2	Pd(PPh3)$_2$Cl$_2$	$^{t-}$Bu-P	Acetone/H$_2$O	K$_3$PO$_4$	80	12	Trace
3	Pd(dba)$_2$	$^{t-}$Bu-P	Acetone/H$_2$O	K$_3$PO$_4$	80	12	41.6
4.	Pd(dba)$_2$	$^{t-}$Bu-P	Acetone/H$_2$O	Cs$_2$CO$_3$	80	12	21.7
5	Pd(dba)$_2$	$^{t-}$Bu-P	Acetone/H$_2$O	Ag$_2$O/CsF	80	12	27.2

Table 2: Effect of solvent on synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene

entry	catalyst	liqand	Solvent	base entry	temp ., ºC	time, hr	yield%
1	Pd(dba)$_2$	$^{t-}$Bu-P	Acetone/H$_2$O ^{a}	K$_3$PO$_4$	80	12	41.6

2	Pd(dba)$_2$	$^{t-}$Bu-P	DMF/H_2O ^{b}	K_3PO_4	80	12	35.5
3	Pd(dba)$_2$	$^{t-}$Bu-P	DMF/Toluene/H_2O ^{c}	K_3PO_4	80	12	39.4
4.	Pd(dba)$_2$	$^{t-}$Bu-P	DMSO/Toluene/H_2O ^{c}	K_3PO_4	80	12	36.8
5	Pd(dba)$_2$	$^{t-}$Bu-P	THF/H_2O ^{b}	K_3PO_4	80	12	61.0
6	Pd(dba)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O ^{c}	K_3PO_4	80	12	75.3

The ratio of solvent a: (2/1), b: (3/1) and c: (2/2/1).

Table3: Effect of reaction temperature on synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl) - oxy] - benzene

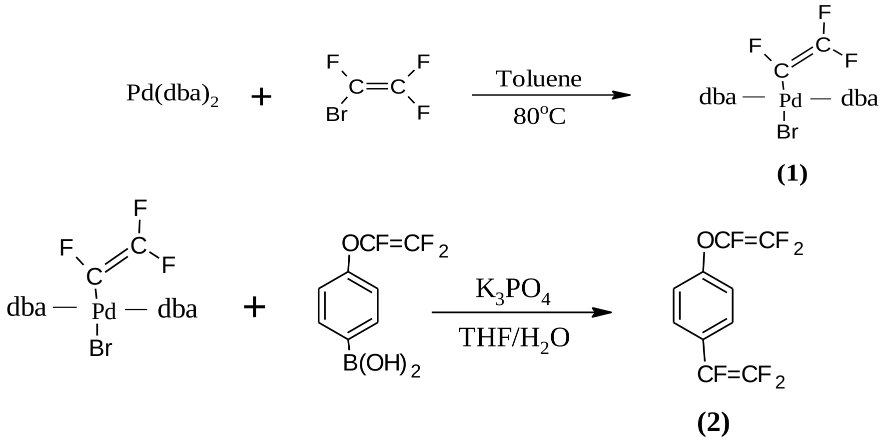
entry	catalyst	liqand	Solvent (2/2/1)	base entry	temp ., °C	time, hr	yield%
1	Pd(dba)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	rt	12	Trace
2	Pd(dba)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	60	12	71.5
3	Pd(dba)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	12	75.3
4.	Pd(dba)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	100	12	69.8

Table 4: Effect of reaction time on synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl) oxy]benzene

entry	catalyst	liqand	Solvent (2/2/1)	base entry	temp ., °C	time, hr	yield%
1	Pd(dpa)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	2	23.5
2	Pd(dpa)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	4	29.0
3	Pd(dpa)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	8	57.2
4.	Pd(dpa)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	12	75.3
5.	Pd(dpa)$_2$	$^{t-}$Bu-P	THF/Toluene/ H_2O	K_3PO_4	80	20	62.8

RESULTS AND DISCUSSION

In scheme 1, is shown the mechanism of this reaction, we began our investigation by isolation of the [(dpa)$_2$Pd(CF=CF$_2$)Br] (1) group and testing its stoichiometric reaction with arylboronic acid in the presence of base under various conditions. Heating of a mixture of Pd(dba)$_2$ with excess bromo-trifluoroethylene in toluene in a screw-caped Schlenk tube at 80 °C for 12 hr generated complex (1). Complex (1) with 1.0 equivalent of 4-(1,2,2-trifluorovinyloxy) - phenyl-boronic acid in THF/H_2O (1.0/0.5) equivalent of toluene solvent and added K_3PO_4 as the base to give 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy] benzene (2) to give colorless viscous oil; yield 75.3%.



Scheme 1: The mechanism of synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene.

In Fig. 1 A and B the product (2) was characterized by NMR spectra: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.9 Hz, 2H), δ 7.19 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -99.63, -114.81, -119.02, -125.83, -134.47, -176.26.
Shown in Table 1, the reaction of synthesis of 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]-benzene when catalyzed by $Pd(OAC)_2$ and $Pd(PPh_3)Cl_2$ a give trace products. The use $Pd(dba)_2$ a give low wt% of product with Cs_2CO_3 and Ag_2O/CSF as base but wt % of product increased about to (41.6%) with in K_3PO_4 as the base. In further search for optimal reaction conditions, we examined the solvent effect on the synthesis of product (2) catalyzed by $Pd(dba)_2$ in THF/H_2O, the yield increased to 61%. When THF/Toluene/ H_2O mixture was used, the yield increased dramatically to 74.3% but with other solvents yields dropped slightly to 35−41% as shown in Table 2. Table 3 shows the reaction temperature effect on synthesis product (2), the best temperature was 80°C. Also in Table 4, the reaction occurred to complete after 12 hr. The use of $^{t-}Bu_3P$ as the ligand was critical for the reaction.

CONCLUSION

The optimal conditions for the synthesis of a novel 1-(trifluoroethenyl)-4-[(trifluoroethenyl) oxy]benzene are: THF/Toluene/H_2O (2/2/1) as the solvent, 0.25 mol % of $Pd(dba)_2$ as the catalyst, 0.5mol % of ^{t}-Bu_3-P as the ligand, K_3PO_4 as the base at temperatutre 80°C. 74.3% conversion takes place in 12 hrs.

References:

1. **Hougham, G., et al.,** ***Fluoropolymers 1: Synthesis.*** **Kluwer academic/Plenum Publisher: New York, 1999: p. 25-50.**
2. **Punji, B., C. Ganesamoorthy, and M.S. Balakrishna,** ***Suzuki cross-coupling reactions catalyzed by palladium complex of an inexpensive phosphinite, 2-diphenylphosphinoxynaphthyl.*** **Molecular Catalysis A: Chemical, 2006. Volume 259: p. 78-83.**
3. **Kotha, S., K. Lahiri, and D. Kashinath,** ***Recent applications of the Suzuki–Miyaura cross-coupling reaction in organic synthesis.*** **Tetrahedron, 2002. 58: p. 9633-9695.**
4. **Duric, S., et al.,** ***Synthesis of Trifluorostyrene Derivatives by Palladium-Catalyzed Cross-Coupling of Lithium Trimethoxy(trifluorovinyl)borate with Aryl Bromides.*** **Chem. Eur., 2012. 18: p. 437-441.**
5. **Anilkumar, R. and D.J. Burton,** ***e-EROS Encyclopedia of Reagents for Organic Synthesis.*** **Wiley: New York, 2001: p. 1−5.**
6. **Xu, C., et al.,** ***Preparation of Trifluorostyrenes via Palladium-Catalyzed Coupling of Arylboronic Acids with Chloro- and Bromotrifluoroethylene.*** **Org. Chem. , 2012. 77: p. 10314−10320.**
7. ***Palladium complex containing trichlorethylene, synthesizing method and application of palladium complex to trifluorovinylation*****, 2012, Google Patents.**
8. **Chen, S., et al.,** ***Preparation method of trifluorostyrene compound*****, 2012, Google Patents.**
9. **Yamamoto, T. and T. Yamakawa,** ***Pd-Catalyzed Arylation of Chlorotrifluoroethylene Using Arylboronic Acids.*** **Organic Letters 2012. 14: p. 3454-3457.**
10. **Anilkumar, R. and D.J. Burton,** ***An efficient dehyrohalogenation method for the synthesis of a,b,b-trifluorostyrenes, a-chloro-b,b-difluorostyrenes and E-1-arylperfluoroalkenes.*** **Fluorine Chemistry 2005. 126: p. 1174-1184.**
11. **A. Mahajoub Imad Eldeen and Cheng Fing Ling, A** ***Novel Method for Synthesis of 4-(1,2,2-Trifluorovinyloxy)phenylboronic acid, Gezira J. of Engineering and Applied Sciences, 2016, 10(1).***
12. **Ford, L.A., D.D. DesMarteau, and D.W.S. Jr,** ***Perfluorocyclobutyl (PFCB) aromatic polyethers: Synthesis and characterization of new sulfonimide containing monomers and fluoropolymers.*** **Fluorine Chemistry 2005. 126 p. 653-660.**

الملخص

تم مناقشة تخليـق وتحديد ظروف التفاعل الامثل للمركب الجديد1−(ثلاثى فلوريد إثيل)−4−[(ثلاثى فلوريد إثيل)اوكسي] بنزين 1-(trifluoroethenyl)-4-[(trifluoroethenyl)oxy]benzene . وجد أن ظروف التفاعل الامثل تحتاج فقط الي 0.25 مول% من $Pd(dba)_2$ و 0.25 مول % من $^{t-}Bu_3$-P ليتم تحويل كامل للمتفاعلات في 12 ساعة ودرجة حرارة 80 o م. هذا المنتج الجديد تم تحديد بنيته التركيبية بواسطة الرنين المغنطيسي ^{1}H and ^{19}F NMR spectroscopy .