Journal of Fluorine Chemistry 146 (2013) 6–10

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

An efficient synthesis of perfluoroalkenylated aryl compounds via Pincer-Pd catalyzed Heck couplings

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ARTICLE INFO

Article history:
Received 10 September 2012
Received in revised form 3 December 2012
Accepted 19 December 2012
Available online 27 December 2012

Keywords:
Pincer Palladium
Fluoroalkyl-substituted ethylenes
Heck couplings
F-SPE

ABSTRACT

Heck couplings of aryl halides with fluoroalkyl-substituted ethylenes catalyzed by Pincer Palladium complex were described. A variety of fluorous ponytail-substituted aromatics were obtained with moderate to excellent yields. Moreover, the catalyst can be easily separated from the reaction mixture by F-SPE technique and reused three times without significant loss of activity.

1. Introduction

Aromatic compounds bearing long fluoroalkyl chains are widely used in fluorine chemistry and organic synthesis [1–3], which have several unique properties compared with conventional organic compounds including thermally stability, high chemical inertness and, very particularly, low solubility in a large range of common organic solvents because of low van der Waals interactions.

There is an increasing demand for effective methods to synthesize a large variety of perfluoroalkyl-substituted compounds. To our best of knowledge, only a few reports have dealt with the preparation of aromatic compounds bearing fluorous ponytails. A successful method is based on the copper-mediated cross-couplings of perfluoroalkyl iodides with aryl halides to synthesize a series of perfluoroalkylated aromatic compounds [4–6]. This method generally results in limited yields because of the formation of fluorous by-products which are difficult to remove. Ullmann-type couplings between aryl bromides or iodides and perfluoroalkyl iodides are also effective to the synthesis of these compounds, but excess copper and harsh conditions are required [7,8].

Sylvain et al. [9] have developed a new approach to yield perfluoroalkyl-substituted aromatic compounds by Heck reaction between perfluoroalkenes and arenediazonium salts in high yields. But arenediazonium salts are unstable, which should be freshly prepared before further use. Weiping Chen et al. [10] have employed the Herrmann–Beller catalyst to catalyze the Heck reaction between perfluoroalkenes and aryl halides. However, Herrmann–Beller catalyst inhibits the reactions involving aryl iodides.

Recently, Pincer complexes have become one kind of the most successful catalysts in organic synthesis [11–17]. Meanwhile, due to their unique tridentate coordination architecture, the Pincer complex is stable, highly selective, highly active to ensure high turnover numbers, and it permits low catalyst loadings and gives the possibility for fine-tuning the catalytic properties of the metal center [18].

In continuation of our studies in the research of cross-coupling reactions [19–22], herein, we report an efficient PCP-Pincer catalyst for the Heck couplings between perfluoroalkenes and aryl halides. The Pincer Palladium catalyst can be easily prepared, and the reactions of both aryl iodides and aryl bromides with perfluoroalkenes in DMF are all proceeded smoothly to generate the desired products in moderate to excellent yields. The double bond of perfluoroalkyl-substituted aromatic compounds could be further hydrogenated under standard conditions (1 mol% of Pd/C, 1 atm of H_2). Furthermore, the catalyst can be easily separated from the reaction mixture by F-SPE technique [23–26] and reused three times without significant loss of its activity.

2. Results and discussions

The procedures for the synthesis of the catalyst were shown in Scheme 1. The Pincer ligand was easily prepared using 1,3-phenylenediamine and diphenylphosphinyl chloride as raw materials with 4-dimethylamiopryidine as catalyst, and then followed by ligand substitution reactions using the Pincer ligand

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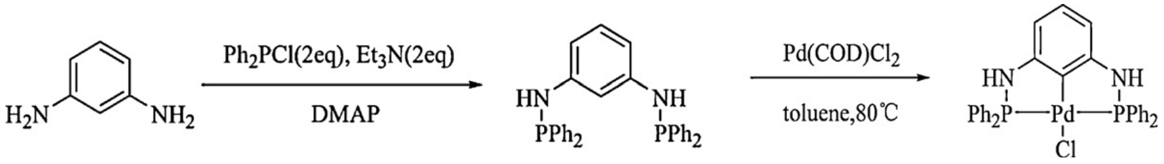
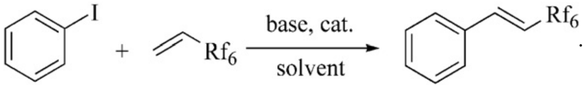
http://dx.doi.org/10.1016/j.jfluchem.2012.12.009



Scheme 1. Preparation of the Pincer-Pd complex.

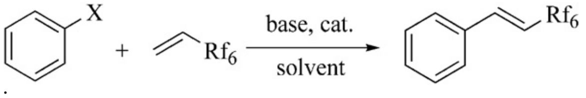
Table 1
Solvent study for the Heck reaction of iodobenzene with *1H,1H,2H-Perfluoro-1-octene*.[a]



Entry	Solvent	Base	Time (h)	Temperature (°C)	Yield (%)[b]
1[c]	EtOH:H_2O (v/v) = 1:1	K_3PO_4	24	110	80
2	H_2O	K_3PO_4	24	110	5
3	CH_3CN	K_3PO_4	24	80	None
4	DMSO	K_3PO_4	24	110	43
5[c]	H_2O	K_3PO_4	24	110	91
6	DMF	K_3PO_4	24	110	94

[a] Reaction conditions: iodobenzene (1.0 mmol), *1H,1H,2H-Perfluoro-1-octene* (1.1 mmol), base (1.0 mmol), catalyst (1 mol%), 2 mL DMF, in air.
[b] GC yield.
[c] TBAB was added.

Table 2
Time and temperature study for the Heck reaction of iodobenzene with *1H,1H,2H-Perfluoro-1-octene*.[a]



Entry	X	Base	Time (h)	Temperature (°C)	Yield (%)[b]
1	I	K_3PO_4	24	100	83
2	I	K_3PO_4	24	110	94
3	I	K_3PO_4	24	120	75
4	Br	K_3PO_4	24	130	18
5	Br	K_3PO_4	72	120	40
6	Br	K_3PO_4	72	130	52

[a] Reaction conditions: aryl halide (1.0 mmol), *1H,1H,2H-Perfluoro-1-octene* (1.1 mmol), base (1.0 mmol), catalyst (1 mol%), 2 mL DMF, in air.
[b] GC yield.

with $Pd(COD)Cl_2$ to give the catalyst in the yield of 90%, which was isolated as yellow solid [27,28].

The ligand and the catalyst were characterized by IR spectra and NMR spectra. All results were in full agreement with the proposed structure.

To evaluate the catalytic activity of the Pincer-Pd catalyst in the Heck couplings between aryl halides with fluoroalkyl-substituted ethylenes, the reaction between iodobenzene and *1H,1H,2H-Perfluoro-1-octene* in the presence of 1 mol% Pincer-Pd catalyst was chosen as a model reaction. Various factors including solvent, base, temperature and time were screened to optimize the reaction conditions. The results are summarized in Tables 1–3.

Among the different solvent tested, DMF was the most productive (Table 1, entry 6). This attributes to the good solubility of catalyst in DMF, and makes the coupling reaction in a homogeneous way. Lower catalyst activities were found in other solvents such as DMSO, CH_3CN and water (Table 1, entries 2–4). However, when tetrabutylammonium bromide (TBAB) was added as phase transfer catalyst, water proved to be effective (Table 1, entry 5).

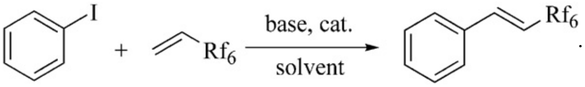
Then, we took the temperature into consideration. As illustrated in Table 2, entries 1–3, 110 °C is the best temperature for the Heck couplings between iodobenzene and *1H,1H,2H-Perfluoro-1-hexene*. The proceedings of the reactions were traced by GC, most of iodobenzene converted in 24 h. However, as for bromobenzene, the best reaction temperature is 130 °C, and the reaction time prolongs to 72 h (Table 2, entry 6).

The effect of bases was also examined for this Heck reaction. K_3PO_4 was found to be the most effective base (Table 3, entry 1). Slightly lower yields were obtained when K_2CO_3, NaOAc, and Na_2CO_3 were used as base (Table 3, entries 2, 3, and 5). When the organic bases Et_3N was used, only moderate yield was obtained (Table 3, entry 4).

The optimized conditions were applied to different aryl halides and perfluoroalkenes ($CH_2{=}CHC_4F_9$, $CH_2{=}CHC_6F_{13}$ and $CH_2{=}CHC_8F_{17}$) to survey the generality of the catalytic protocol. The results are listed in Table 4.

As can be seen from Table 4, a variety of aromatic halides underwent Heck couplings smoothly to afford a wide range of perfluoroalkenylated aromatic compounds. Aryl iodides show high activity in the couplings (Table 4, entries 1–10) which attributes to aryl iodide's high reaction activity and Pincer complex's unique tridentate coordination architecture. Only one free coordination site is available for catalysis, which implies that formation of undesirable side products arising from ligand exchange processes can be avoided [29]. It was also found that aryl iodides bearing electron-withdrawing substituent afforded the corresponding coupling product in better yields than electron-donating substituent in para

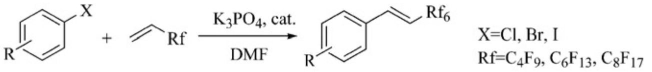
Table 3
Base study for the Heck reaction of iodobenzene with *1H,1H,2H-Perfluoro-1-octene*.[a]



Entry	Solvent	Base	Time (h)	Temperature (°C)	Yield (%)[b]
1	DMF	K_3PO_4	24	110	91
2	DMF	K_2CO_3	24	110	92
3	DMF	NaOAc	24	80	88
4	DMF	NEt_3	24	110	77
5	DMF	Na_2CO_3	24	110	90

[a] Reaction conditions: aryl halide (1.0 mmol), *1H,1H,2H-Perfluoro-1-octene* (1.1 mmol), base (1.0 mmol), catalyst (1 mol%), 2 mL DMF, in air.
[b] GC yield.

Table 4
Heck cross-coupling reactions of aryl halides with fluoroalkyl-substituted ethylenes.[a]

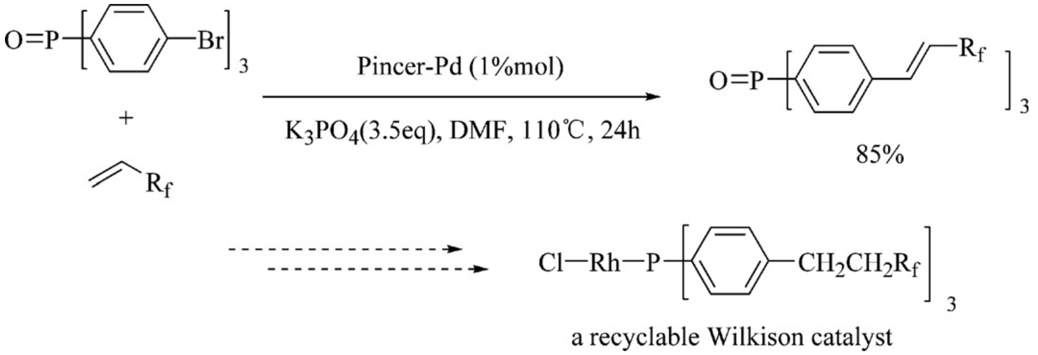


Entry	R	X	R_f	Time (h)	Temp (°C)	Yield (%)[b]	*E*/*Z*[d]
1	H	I	n-C_6F_{13}	24	110	95	90:10
2	4-OCH_3	I	n-C_6F_{13}	24	110	79	83:17
3	4-CH_3	I	n-C_6F_{13}	24	110	89	87:13
4	3-CH_3	I	n-C_6F_{13}	24	110	93	90:10
5	2-CH_3	I	n-C_6F_{13}	24	110	84	91:9
6	4-Br	I	n-C_6F_{13}	24	110	91	92:8
7	4-Cl	I	n-C_6F_{13}	24	110	93	85:15
8	4-NO_2	I	n-C_6F_{13}	24	110	10 (50[c])	–
9	H	I	n-C_4F_9	24	110	94	87:13
10	H	I	n-C_8F_{17}	24	110	90	91:9
11	H	Br	n-C_6F_{13}	72	130	61	77:23
12	4-OCH_3	Br	n-C_6F_{13}	72	130	40	94:6
13	4-NO_2	Br	n-C_6F_{13}	72	130	49 (45[c])	–
14	4-CF_3	Br	n-C_6F_{13}	48	130	79	91:9
15	2-CH_3	Br	n-C_6F_{13}	72	130	57	88:12
16	4-OCH_3	Br	n-C_8F_{17}	72	130	50	86:14
17	3-CHO	Br	n-C_6F_{13}	12	130	90	88:12
18	4-CHO	Br	n-C_6F_{13}	12	130	93	95:5
19	4-CHO	Br	n-C_4F_9	12	130	87	90:10
20	4-CHO	Br	n-C_8F_{17}	12	130	93	96:4
21	4-$COCH_3$	Br	n-C_6F_{13}	48	130	87	89:11
22	4-CHO	Cl	n-C_6F_{13}	24	135	27	84:16

[a] Aryl halides (1.0 mmol), fluoroalkyl-substituted ethylenes (1.1 mmol), base (1.0 mmol), catalyst (1 mol%) in 2 mL DMF at 110–130 °C in air.
[b] Isolated yield.
[c] Dehalogenation product.
[d] Determined by GC.

or ortho position (Table 4, entries 1–7). This electronic effect is not surprising, since the oxidative addition of the C–I bond of aryl iodides to the metal is expected to be facilitated by electron-withdrawing substituent on the aromatic ring [30]. However the nitro-substituted iodobenzene is a exception affording more dehalogenations than the aimed products (Table 4, entry 8).

As for aryl bromides, the compounds with electron-withdrawing groups, especially the bromides substituted aromatic aldehydes, reacted smoothly, while aryl bromides with electron-donating groups were less reactive (Table 4, entries 11–18), unsatisfactory yields were obtained even after prolonged reaction times to 72 h.



Scheme 2. A potential application of Pincer-Pd catalyzed Heck couplings.

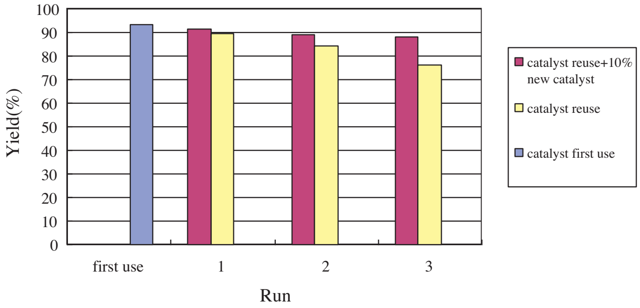


Fig. 1. Recycling experiments of the catalyst.

Regardless of aryl iodides or aryl bromides used as substrates, the stereoselectivity of the products were found, and the trans-isomers takes up 77–96%. The existing small amount cis-isomer may come from (i) post-reaction isomerization of products, leading to thermodynamically controlled mixture of isomers; (ii) isomerization of product Pd–H complex before the deprotonation takes place [31].

In addition, the coupling reaction worked equally well with both long and short fluorous olefins. Considering the electron effect, space effect and volatility of different length of fluorous tails, small difference of product yields were made (Table 4, entries 9, 10, 18–20).

We also examined whether aryl chlorides were active for the Heck reaction in our system. However, lower conversions and yields were obtained with aryl chlorides (Table 4, entry 22) just as in other cases.

To further demonstrate the potential of this methodology, fluoroalkenylated aryl phosphine oxide, a crucial intermediate en route to a recyclable wilkinson catalyst [32], was smoothly generated by the coupling of fluoroalkenyl-substituted ethylenes with tris-(4-bromo-phenyl)-phosphane oxide (Scheme 2) in the yield of 75%.

The Pincer-Pd catalyst in this system can be separated from the reaction mixture by F-SPE technique and reused several times without significant loss of activity (Fig. 1). The slight decrease of the yield may be due to the catalyst adsorption of fluorous silica gel column and the loss in separation. The addition of fresh catalyst added to each circle increased the level of conversion and the resulting yields returned to that seen in the initial experiment.

3. Conclusions

In summary, we have prepared and characterized a PCP Pincer-Pd catalyst and successfully applied it for the Heck couplings between perfluoroalkenes and aryl halides for the preparation of perfluoroalkenylated aryl compounds. The catalyst showed high catalytic activity and the corresponding coupling products were obtained in moderate to excellent yields. Moreover, the catalyst could be easily separated by F-SPE technique and reused three times without significant loss of activity. The simple procedure for catalyst preparation, high activity and reusability of the catalyst is expected to contribute to its utilization for the development of fluorine chemistry.

4. Experimental

4.1. General

All the reagents were commercially available and used without any further purification. The solvents were dried before use. IR spectra were recorded in KBr disks with a SHIMADZU IRPrestige-21 FT-IR spectrometer. GC analyses were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N_2, Injector: 300 °C, FID detection detector: initial temperature 80 °C, temperature program: 15 °C/min, final temperature 325 °C. H_2 30 mL/min, air 400 mL/min, N_2 25 mL/min). Melting points were determined uncorrected. ^{1}H NMR was recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference.

4.2. Preparation of N,N-Bis (diphenylphosphino)-1,3-benzenediamine (PCP-Pincer)

To a suspension of 1,3-diaminobenzene (2.5 g, 23 mmol) in toluene (50 mL) was added triethylamine (5.6 mL, 46 mmol), 4-dimethylamiopryidine (0.28 g, 2.3 mmol). The mixture was then cooled to 0 °C, PPh_2Cl (10.1 g, 46 mmol) was added in a dropwise fashion, the solution was warmed to room temperature and stirred at 80 °C for 12 h. After that, the solution was filtered and the solvent was removed under vacuum. The remaining yellow oil was purified by column chromatography and further purified by recrystallization (toluene:hexane (v/v) = 1:1). Yield: 8.75 g (80%). Melting point: 90–92 °C. IR (KBr); ν 3197, 3071, 1579, 1474, 1430, 1149, 1090, 978, 743, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.48–7.33 (m, 20H, PPh), 7.03 (t, J = 8.0 Hz, 1H, Ph^4), 6.74 (t, J = 2.1 Hz, 1H, Ph^{ipso}), 6.53 (d, J = 8.0 Hz, 2H, Ph^{3,5}), 4.35 (d, J = 8.2 Hz, 2H, NH), (d, J = 7.8 Hz, 1H, Ph^4), ^{13}C{1H} NMR ($CDCl_3$): δ = 147.5 (d, J = 16.5 Hz, C_{Ph}), 140.0 (d, J = 11.9 Hz, C_{PPh}), 131.1 (d, J = 20.7 Hz, C_{PPh}), 130.0 (C_{Ph}), 128.9 (C_{PPh}), 128.4 (d, J = 6.5 Hz, C_{PPh}), 107.1 (d, J = 13.8 Hz, C_{Ar}), 103.1 (t, J = 13.4 Hz, C_{Ar}).

4.3. Preparation of N,N-Bis (diphenylphosphino)-1,3-benzenediamine (PCP-Pd)

Pd(COD)Cl_2 (142 mg, 0.5 mmol) was added to a solution of PCP-Pincer (227 mg, 0.5 mmol) in toluene (10 mL), and the mixture was refluxed for 5 h, whereupon a yellow solid precipitated, which was collected on a glass frit and washed with Et_2O (10 mL ×2). Yield: 350 mg (90%). IR (KBr); ν 3211, 2588, 1599, 1542, 1454, 1434, 1386, 1102, 765, 741 cm^{-1}. ^{1}H NMR (DMSO): δ = 7.98 (s, 2H, NH), 7.90–7.82 (m, 6H, PPh), 7.55–7.40 (m, 14H, PPh), 6.70 (t, J = 7.8 Hz, 1H, Ph^4), 6.23 (d, J = 7.8 Hz, 2H, Ph^{3,5}). ^{13}C{1H} NMR (DMSO): δ = 156.7 (t, J = 14.1 Hz, C_{Ar}), 134.9 (t, J = 25.0 Hz, C_{PPh}), 131.6 (t, J = 7.8 Hz, C_{PPh}), 131.2 (C_{PPh}), 129.0 (C_{Ar}), 128.8 (t, J = 5.2 Hz, C_{PPh}), 103.0 (t, J = 10.1 Hz, C_{Ar}).

4.4. General procedures for Heck reactions using 1 mol% Pincer-Pd complex

A sealed tube was charged with aryl halide (1.0 mmol), fluoroalkyl-substituted ethylenes (1.1 mmol), K_3PO_4 (1.0 mmol), DMF (2 mL) and catalyst (1 mol% Pd), the mixture was stirred at a certain temperature for a certain time. After being cooled to room temperature, the mixture was filtered. The solvent and excess fluoroalkyl-substituted ethylenes were removed under reduced pressure and the residue was purified by F-SPE technique. Menthol and H_2O (v/v = 8:2) were used as fluorophobic elution, while H_2O were used as fluorophilic elution. The product was obtained from fluorous phase in high purity. All the products were known compounds and were identified by comparison of their physical and spectroscopic data with those of authentic samples. Characterization datas of some representative examples are given as following:

(1) (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-oct-1-enyl)-benzene (Table 4, entry 1)

Colorless oil (0.39 g, 0.93 mmol), prepared from iodobenzene (0.2 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-octene* (0.38 g, 1.1 mmol) in 93% yield according to the general procedure. ^{1}H NMR ($CDCl_3$): δ = 6.20 (dt; J = 16 Hz, 1H, CF_2–CH); 7.17 (dt; J = 16 Hz, 1H, Ar–CH); 7.36–7.60 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; J = 23 Hz; CH–CF_2); 127.8 (s; C_{Ar}); 129.2 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; $C_{Ar,\ ipso}$), 140.0 (t; J = 10 Hz; Ar–CH). ^{19}F NMR ($CDCl_3$): δ = −81.2 (t; J = 10.5 Hz, 3F); −111.5 (m; 2F); −122.0 (m; 2F); −123.2 (m; 2F); −123.6 (m; 2F); −126.6 (m; 2F).

(2) 1-(4′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (Table 4, entry 6)

White solid (0.45 g, 0.9 mmol), prepared from 1-bromo-4-iodo-benzene (0.28 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-octene* (0.38 g, 1.1 mmol) in 91% yield according to the general procedure. Melting point: 28–30 °C. ^{1}H NMR ($CDCl_3$): δ = 6.22 (dt; 1H, J = 16.1 Hz, CF_2–CH); 7.12 (dt; 1H, J = 16.1 Hz, Ar–CH); 7.36–7.57 (m; 4H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 115.0 (t; J = 23 Hz; CH–CF_2); 124.4 (s; C_{Ar}); 129.0 (s; C_{Ar}); 132.1 (s; C_{Ar}); 132.4 (s; C_{Ar}), 138.5 (t; J = 9.5 Hz; Ar–CH). ^{19}F NMR ($CDCl_3$): δ = −80.8 (t; 3F); −111.3 (m; 2F); −122.8 (m; 2F); −123.1 (m; 2F); −123.2 (m; 2F); −126.2 (m; 2F).

(3) 1-Methyl-3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-oct-1-enyl)-benzene (Table 4, entry 3)

Colorless oil (0.38 g, 0.87 mmol), prepared from 1-iodo-3-methyl-benzene (0.22 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-octene* (0.38 g, 1.1 mmol) in 89% yield according to the general procedure. ^{1}H NMR ($CDCl_3$): δ = 6.22 (dt; J = 16 Hz, 1H, CF_2–CH); 7.17 (dt; J = 16 Hz, 1H, Ar–CH); 7.23–7.34 (m; 4H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 20.3 (s; CH_3); 113.0 (t; CH–CF_2); 123.9 (s; C_{Ar}); 127.3 (s; C_{Ar}); 127.9 (s; C_{Ar}); 130.0 (s; C_{Ar}); 130.2 (s; C_{Ar}), 139.0 (t; Ar–CH). ^{19}F NMR ($CDCl_3$): δ = −80.8 (t; 3F); −111.4 (m; 2F); −121.6 (m; 2F); −123.2 (m; 4F); −126.2 (m; 2F).

(4) (3,3,4,4,5,5,6,6,6-Nonafluoro-hex-1-enyl)-benzene (Table 4, entry 9)

Colorless oil (0.3 g, 0.92 mmol), prepared from iodobenzene (0.2 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-hexene* (0.27 g, 1.1 mmol) in 92% yield according to the general procedure. ^{1}H NMR ($CDCl_3$): δ = 6.19 (dt; J = 16 Hz, 1H, CF_2–CH); 7.17 (dt; J = 16 Hz, 1H, Ar–CH); 7.30–7.60 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; CH–CF_2); 127.4 (s; C_{Ar}); 128.8 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; C_{Ar}), 140.0 (t; Ar–CH). ^{19}F NMR ($CDCl_3$): δ = −81.2 (t; Hz, 3F); −111.7 (m; 2F); −124.6 (m; 2F); −126.2 (m; 2F).

(5) (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-dec-1-enyl)-benzene (Table 4, entry 10)

Colorless oil (0.46 g, 0.88 mmol), prepared from iodobenzene (0.2 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-heptene* (0.49 g, 1.1 mmol) in 88% yield according to the general procedure. ^{1}H NMR ($CDCl_3$): δ = 6.19 (dt; J = 16 Hz, 1H, CF_2–CH); 7.17 (dt; J = 16 Hz, 1H, Ar–CH); 7.30–7.60 (m; 5H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 114.6 (t; CH–CF_2); 127.8 (s; C_{Ar}); 129.2 (s; C_{Ar}); 130.4 (s; C_{Ar}); 133.8 (s; C_{Ar}); 140.0 (t; Ar–CH). ^{19}F NMR ($CDCl_3$): δ = −81.2 (t; 3F); −111.5 (m; 2F); −122.0 (m; 2F); −122.4 (m; 4F); −123.2 (m; 2F); −123.6 (m; 2F); −126.6 (m; 2F).

(6) 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-oct-1-enyl)-4-trifluoromethyl-benzene (Table 4, entry 14)

Colorless oil (0.35 g, 0.72 mmol), prepared from 1-bromo-4-trifluoromethyl-benzene (0.23 g, 1 mmol) and *1H,1H,2H-Perfluoro-1-octene* (0.38 g, 1.1 mmol) in 72% yield according to the general procedure. ^{1}H NMR ($CDCl_3$): δ = 6.21 (dt; J = 16 Hz, 1H, CF_2–CH); 7.19 (dt; J = 16 Hz, 1H, Ar–CH); 7.30–7.60 (m; 4H, aromatic protons); ^{13}C NMR ($CDCl_3$): δ = 28.7 (s; CF_3); 114.2 (t; CH–CF_2); 120.3 (s; C_{Ar}); 128.7 (s; C_{Ar}); 137.1 (s; C_{Ar}); 137.3 (s; C_{Ar}), 148.2 (s; Ar–CF_3). ^{19}F NMR ($CDCl_3$): δ = −57.8 (t; 3F); −80.8 (t; 3F); −111.0 (m; 2F); −121.6 (m; 2F); −122.9 (m; 2F); −123.3 (m; 2F); −126.2 (m; 2F).

4.5. A typical procedure for recycle and reuse of catalyst

A sealed tube was charged with *1H,1H,2H-Perfluoro-1-octene* (1.9 g, 5.5 mmol), iodobenzene (1 g, 5.0 mmol), K_3PO_4 (1.06 g, 5.0 mmol), DMF (10 mL) and Pincer-Pd catalyst (25 mg, 1 mmol%), the mixture was stirred at 110 °C for 24 h. After being cooled to room temperature, the mixture was separated by F-SPE technique. Methanol and H_2O (v/v = 8:2) were used as fluorophobic elution, while methanol were used as fluorophilic elution. Then, the solvent of fluorophobic phase was removed, and the resulting solids were washed with Et_2O (3× 15 mL) and dried under vacuum, yellow solid (23 mg) was obtained. For the second run, fresh starting materials, the catalyst obtained and extra fresh catalyst (2.5 mg, 10%) were added to the sealed tube, and the reaction was conducted as described for the initial run. After 3 runs, the product yields are respectively 91%, 89%, 87%.

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