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Recoverable cationic Pd-catalyzed Heck reaction under thermomorphic mode

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ABSTRACT

The reaction of allylpalladium chloride dimer and 4,4'-bis(R_f CH₂OCH₂)-2,2'-bpy, **1a**–**c**, in the presence of AgOT_f resulted in the synthesis of cationic complex, [Pd(η^3 -allyl)(4,4'-bis-(R_f CH₂OCH₂)-2,2'-bpy)](OT_f), **2a**–**c** where $R_f = C_9F_{19}$ (**a**), $C_{10}F_{21}$ (**b**), $C_{11}F_{23}$ (**c**), respectively. The solubility curves of **2a**–**c** which began from virtually zero below -40 °C and increased dramatically at slightly higher temperature were quantitatively measured. Upon changing from -40-90 °C there was several orders of magnitude increase of solubility for **2a**–**c**. The cationic Pd-catalyzed Heck arylation of methyl acrylate was selected to demonstrate the feasibility of recycling usage with **2b,c** as the catalyst using DMF as the solvent at 140 °C for 3 h in each run. At the end of each cycle, the product mixtures were cooled to -30 °C, and then catalysts were recovered by decantation. The products were quantified by GC analysis or by the isolated yield. The Heck reaction of C₆H₅I with methyl acrylate could be catalyzed by **2b** with good recycling results for a total of 15 times and also with a 100% selectivity favoring the *trans* product. To our knowledge, this is the first example of cationic Pd-catalyzed Heck reaction under the thermomorphic mode.

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1. Introduction

Homogeneous catalysis offers several advantages like high efficiency, better tuning of chemoselectivity, regioselectivity and/or stereoselectivity of the catalysts [1]. However, the majority of homogeneous catalysts have not been commercialized because of its difficulty of separation from the reaction system. In other words, it is important to develop scientifically rewarding methodology that could bridge both homogeneous and heterogeneous reaction systems [2]. Thermomorphic catalysis [3-6] is one of the new approaches to solve the problems of separation and catalytic efficiency with or without the fluorous solvents. Thermomorphic catalysis has the exclusive property that the reaction mixture is homogeneous when it is heated during the reaction; and the product mixture becomes phase separated when cooled after the reaction. Bergbreiter et al. used a polymer-based thermomorphic system whose polymeric supporter was not totally dissolved at high temperature. Gladysz et al. [5,6] and Yamamoto et al. [7,8] have published the fluorinated compounds to catalyze the addition reaction of unsaturated substrates without the use of expensive fluorous solvents. Fan et al. have also reported the use of the thermomorphic system with a non-fluorous catalyst for asymmetric hydrogenation [9].

Pd-catalyzed Heck reaction has become one of the most important reactions in developing new drugs, biologically active compounds and many industrially useful chemicals or materials [10]. A number of applications have been developed in the laboratory and commercial level on this reaction. In particular, the scientist R. F. Heck won the Nobel Prize in 2010 for this important discovery sharing with E.I. Negishi and A. Suzuki reported by R.F. Service in Science [11]. So far most of the efforts in this field are to deal with the Pd catalysts, substrates, mechanisms etc. [12-15], but to develop a recyclable reaction system for the Heck reaction is still rare [16]. Previously we have reported the fluorous-ponytailed Pd complexes for the Heck arylation [17–19]. Reported here are the recyclable cationic Pd-catalyzed Heck reactions. The solubility properties of cationic Pd complexes, **2a**–**c**, are interesting and have been studied at different temperatures ranging from -40-90 °C in polar organic solvents. In addition, the catalyst 2b shows greater stability and its activity has been demonstrated by reusing up to 15 recycles with 100% selectivity to trans product.

2. Results and discussion

The solubility of cationic Pd complex $2\mathbf{a}-\mathbf{c}$ and neutral Pd complex $3\mathbf{a},\mathbf{b}$ [17–19] in DMF as a function of temperature is shown in Fig. 1. The solubility was measured by the variable temperature NMR spectrometer, where the temperatures were varied from -40-90 °C. We recorded the NMR integration of the peak of the C5(5')-protons in 2,2'-bpy and compared its value to that of the

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Fig. 1. Plot of solubility curves of $2\mathbf{a}-\mathbf{c}$ and $3\mathbf{a},\mathbf{b}$ as a function of temperature. It is note that the extent of solubility change of $2\mathbf{a}-\mathbf{c}$ with temperature is much greater than that of $3\mathbf{a},\mathbf{b}$.

peak integration of ω -proton (from terminal HCF₂ group) of the standard, HCF₂(CF₂)₃CH₂OH. It was shown that compound **2a** was slightly soluble in DMF at -30 °C, but **2b** and **2c** were totally insoluble below -30 °C. The solubility of **2a** in DMF began from virtually zero at $-30 \circ$ C, increased with the temperature from -30to 10 °C and increased remarkably at temperature >10 °C. The solubility curves of 2b and 2c, however, began from virtually zero at -20 °C and 0 °C, respectively; then increased dramatically at higher temperature (>23 °C). As shown in Fig. 1, the solubility of **2a**–**c** significantly increased with the increasing temperature from -40-90 °C while the solubility change of 2a was the greatest. Because **2a** is still slightly soluble in DMF at -30 °C, it is more difficult to work with 2a during the recycling procedures. Therefore, cationic Pd complex 2b,c was then selected as a good candidate for the subsequent catalytic experiments to examine the recyclability of Heck reactions here under fluorous biphasic system (FBS) or the thermomorphic mode.

The solubility of neutral palladium complex **3a,b** [17–19] in DMF was reported before, and was also incorporated in Fig. 1 for comparison. It was known that the solubility of **3a,b** started from virtually zero at 20 °C and then increased by several orders when temperature was raised up to 90 °C. Because of this thermomorphic property, the Heck reactions catalyzed by **3a,b** can be efficiently carried out, easily separated and recovered at room temperature for eight times [17]. It was surprising to note that the extent of solubility change of **2a–c** with temperature is at least three times greater than that of **3a,b**.

As shown in Scheme 1, the Pd-catalyzed Heck arylation of methyl acrylate with aryl iodides was selected to demonstrate the feasibility of recycling usage with **2b,c** or **3b** as the catalyst using DMF as the solvent under thermomorphic mode, at *ca.* 140–150 °C for 3–7 h varying in each run. At the end of each cycle, the product

 Table 1

 Recycling results of 2b-catalyzed Heck reaction under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	3	140	100	1000
2	3	140	100	1000
3	3	140	100	1000
4	3	140	100	1000
5	3	140	100	1000
6	3	140	100	1000
7	3	140	100	1000
8	3	140	100	1000
9	3	140	100	1000
10	3	140	100	1000
11	3	140	100	1000
12	3	140	100	1000
13	3	140	100	1000
14	3	140	100	1000
15	3	140	100	1000

Reaction conditions: DMF (5 ml); **4a** (2.54 mmol, 517.79 mg), **5b** (5.08 mmol, 437.01 mg), NEt₃ (7.61 mmol, 770.48 mg), 0.1 mol % **2b** (4.00 mg).

mixtures were cooled to below -20 °C and centrifuged, and the catalysts recovered by decantation. The recovered **2b,c** was added with DMF, substrates, and base to proceed to the next cycle. The products were quantified with GC analysis by comparison to internal standard (NMP). The results of Heck reaction exhibited a 100% selectivity favoring the trans product in just 3 h. As one example shown in Table 1, the Heck reaction of C_6H_5I (4a) with methyl acrylate (5b) could be catalyzed by 2b with good recycling results for a total of 15 times with the same trans selectivity and high TON. To our knowledge, this is the first example of fluorous cationic Pd-catalyzed Heck reaction under the thermomorphic mode with such a high yield and recyclability. Table 2 shows results of Heck reaction of 4a and 5b using neutral Pd complex 3b as a catalyst for comparison. This complex also shows 100% selectivity with high TON, but it shows less recyclability up to 8 times as compared to cationic complex 2b with extended reaction time of 6-7 h. It is well-known that Heck reaction starts with the oxidative addition of aryl halide to the active Pd catalyst center, so the oxidative addition is then favored by the electron rich Pd center. Although the Pd center in *neutral* complex **3b** is more electron rich than in *cationic* complex **2b,c**, complexes **2b** and **2c** showed the enhanced activity and recyclability than the former one, **3b**. The possible rationales are because the cationic complex **2b** or **2c** as shown in Fig. 1 demonstrates the higher degree of solubility in polar solvent due to their ionic nature which allows them for better dissociation in the solvent and better catalytic activities. This property offsets the disadvantage of electron deficiency in metal center, so cationic **2b,c** can give rise to higher activity than neutral **3b** in the overall catalytic outcomes.

The **2b**-catalyzed Heck reaction of **4a** and **5b** using very low loading of catalyst of only 0.001 mol% is shown in Table 3. It was observed that catalyst **2b** was effective at such a low amount with very high TON of 100000 in 32 h.

In addition, the cationic Pd catalyst **2b** was also studied for Heck arylation of **4a** and **5b** under fluorous biphasic system (FBS) and the results were summarized in Table 4. The catalyst could be



Scheme 1. The cationic Pd-catalyzed Heck reaction under thermomorphic mode.

Tab

 Table 2

 Recycling results of 3b-catalyzed Heck reaction under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	5	140	100	1000
2	6	140	100	1000
3	7	140	100	1000
4	7	140	100	1000
5	7	140	100	1000
6	7	140	100	1000
7	7	140	100	1000
8	7	140	100	1000

Reaction conditions: DMF (5 ml), **4a** (2.5 mmol, 610 mg), methyl acrylate **5b** (5.0 mmol, 355 mg), NEt₃ (5.0 mmol, 510 mg), 0.1 mol % **3b** (3.64 mg).

Table 3

Recycling results of 2b-catalyzed Heck reaction under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	32	140	100	100,000

Reaction conditions: DMF (5 ml); **4a** (63.45 mmol, 12.94 g), **5b** (126.80 mmol, 10.93 g), NEt₃ (190.36 mmol, 19.26 g), 0.001 mol % **2b** (1.00 mg).

successfully recycled for only 6 times, but it took a longer time to complete (i.e. 25 h for the 6th run). These results indicated that cationic Pd catalyst was more favored in thermomorphic condition than in FBS.

With electron releasing OMe substituents on iodobenzene (**4b**), excellent yields and recyclabilities could also be achieved for the **2b**-catalyzed Heck arylation of **5b** under the thermomorphic mode (Table 5). The results (see supplementary material; Table I, **2c**-catalyzed Heck arylation) of Heck reaction catalyzed by **2c** were very similar to those by **2b**, although in the case of **2c** the reaction temperature required about 10 °C higher. Overall, complex **2b,c** could be easily recovered and reused in the Pd-catalyzed Heck arylations of methyl acrylate under the thermomorphic mode. Furthermore, the results shown in Table 6 obtained from **3b**-catalyzed reaction, although it needed both higher temperature (*ca.* 10 °C higher) and longer time (mainly 7 h) to complete.

The cationic Pd complex **2b** was also found to be effective in the Heck arylation of less reactive aryl bromide under thermomorphic mode as shown in Scheme 2. Tables 7 and 8 show the results of Heck reaction of the NO₂-containing aryl bromide (**4c**) with methyl acrylate (**5b**) using tripropylamine (NPr₃) or triethylamine (NEt₃) as a base. The catalyst shows better catalytic activity using NPr₃ as a base with high TON of *ca*. 1000 and could be recycled for almost 7 times. In contrast, using NEt₃ as a base, it lowers the activity of the cationic **2b** which shows the poor recyclability as shown in Table 8.

The same effect of the base was also observed on Heck arylation of 4-bromoacetophenone (**4d**) when **2b** was used as a catalyst. As shown in Tables 9 and 10, the results from **2b**-catalyzed Heck reaction of **4d** with methyl acrylate gives rise to better recyclability

Table 4	
Recycling results of 2b -catalyzed Heck reaction under the FBS mode.	

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	3	140	100	1000
2	6.5	140	100	1000
3	10	140	100	1000
4	12	140	100	1000
5	14	140	100	1000
6	25	140	100	1000
7	27	140	36	360

Reaction conditions: DMF (3 mL), C_8F_{18} (3.00 ml), **4a** (2.54 mmol, 517.79 mg), **5b** (5.08 mmol, 437.01 mg), NEt₃ (7.61 mmol, 770.48 mg), 0.1 mol % **2b** (4.00 mg).

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Recycling results of **2b**-catalyzed Heck reaction under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield ^a (%)	TON
1	3	140	100	1000
2	3	140	100 (100)	1000
3	3	140	100	1000
4	3	140	100 (98)	1000
5	3	140	100	1000
6	3	140	100	1000
7	3	140	100 (99)	1000
8	3	140	100	1000

Reaction conditions: DMF (5 ml), 4-iodoanisol (**4b**) (2.54 mmol, 594.01 mg), **5b** (5.08 mmol, 437.01 mg), NEt₃ (7.61 mmol, 770.48 mg), 0.1 mol % **2b** (4.00 mg).

^a Isolated yields which are in good agreement with GC data are given in parentheses.

using NPr₃ as a base compared with using NEt₃. Furthermore, this cationic **2b**-catalyzed Heck reaction of aryl chloride which is known to be much difficult to react had been successfully tested one time, but the recovery and reuse of the catalyst still remained as a challenging task in this case.

However, when the neutral **3b** was used as a catalyst, the results showed the opposite base effect on catalytic activity of **3b**-catalyzed Heck reaction. Tables 11 and 12 showed the results of **3b**catalyzed Heck reaction of 4-nitrobromobenzene (**4c**) using NEt₃ or NPr₃ as a base. The **3b**-catalyzed Heck reaction showed good activities using NEt₃ as a base with almost same reactivity for 5 runs, but in contrast, when NPr₃ was used as a base, the reactivity dropped significantly after 3 cycles.

The similar trends of base effects have also been observed in the case of **3b**-catalyzed Heck reaction of 4-bromoacetophenone (**4d**). These results are listed in supplementary material (see Table II & III in Supplementary material).

The amount of residual Pd catalyst in the product solution after centrifugation from the specific run was determined by ICP-MS, the results indicating that the recovery of Pd catalyst left *ca*. 4% of the Pd catalyst in solution as shown in Table 13. The amounts of Pd recovered are 95.13, 94.33 and 97.79% for 4-2, 4-4 and 4-5, respectively. In comparison, the data from Table 14 showed the residual Pd present in the solution where neutral 3b was used. Thus, the amounts of residual Pd present from the cationic Pdcatalyzed Heck reaction were few percentages, although these numbers are higher than 0.02% which is the average amount of residual Pd present from neutral Pd-catalyzed reaction shown in Table 14. The reason why product of Heck reaction catalyzed by the cationic **2b**,**c** contained more residual Pd than that catalyzed by the neutral **3b,c** is very likely due to the good solubility of cationic Pd complexes 2b and 2c (data for 2c-catalyzed Heck reaction was shown in Table I and IV of supplementary material.) From the Fig. 1, it is known that the dissolution of cationic **2b**,**c** in DMF at $-20 \degree$ C is

Table 6
Recycling results of 3b -catalyzed Heck reaction under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield ^a (%)	TON
1	6	150	100 (100)	1000
2	7	150	100	1000
3	7	150	100	1000
4	7	150	100 (99)	1000
5	7	150	100	1000
6	7	150	100 (99)	1000
7	7	150	100	1000
8	7	150	100 (99)	1000

Reaction conditions: DMF (5 ml), 4-iodoanisol (**4b**) (2.5 mmol, 585.1 mg), **5b** (5 mmol, 355 mg), NEt₃ (5 mmol, 510 mg), 0.1 mol % **3b** (3.64 mg).

^a Isolated yields which are in good agreement with GC data are given in parentheses.



Scheme 2. Cationic/neutral Pd-catalyzed Heck reaction of aryl bromide under thermomorphic mode.

Table 7 Recycling results of 2b-catalyzed Heck reaction using NPr₃ as a base under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
		1.10	100	1000
1	3	140	100	1000
2	20	140	95	950
3	15	150	100	1000
4	15	150	98	980
5	15	150	>99	>990
6	15	150	96	960
7	15	150	99	990
8	20	150	95	950

Reaction conditions: DMF (5 ml), **4c** (2.54 mmol, 512.72 mg), **5b** (5.08 mmol, 437.01 mg), NPr₃ (7.61 mmol, 1090.89 mg), 0.1 mol % **2b** (4.00 mg).

Table 8

Recycling results of $\mathbf{2b}$ -catalyzed Heck reaction using NEt₃ as a base under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	4	140	100	1000
2	15	140	90	900
3	15	140	25	250

Reaction conditions: DMF (5 ml), **4c** (2.54 mmol, 512.72 mg), **5b** (5.08 mmol, 437.01 mg), NEt₃ (7.61 mmol, 770.48 mg), 0.1 mol % **2b** (4.00 mg).

much better than that of neutral **3b,c**, so during the work-up, more residual Pd from cationic catalyst **2b,c** could leak out to the solution than that from neutral catalyst **3b,c** when the lower temperature was difficult to maintain throughout the procedures.

3. Conclusions

In summary, the new series of cationic palladium complexes (2a-c) containing fluorous-ponytailed bipyridyl ligands were synthesized and successfully evaluated for Heck arylation under the thermomorphic mode or FBS. This type of Pd complexes shows excellent activities and reusabilities for a total of 15 recycles under thermomorphic mode [21–24]. The cationic Pd complexes 2a-c whose good thermomorphic property is attributed to their ionic nature show the even greater degree of solubility in polar solvents at high temperature than the neutral Pd complexes 3a,b. This

Table 9

Results of 2b-catalyzed Heck reaction using NPr₃ as a base under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	3	140	100	1000
2	20	140	95	950
3	15	150	100	1000
4	15	150	98	980
5	15	150	>99	>990
6	15	150	96	960
7	15	150	99	990
8	20	150	95	950

Reaction conditions: DMF (5 ml), **4d** (2.54 mmol, 505.20 mg), **5b** (5.08 mmol, 437.01 mg), NPr₃ (7.61 mmol, 1090.89 mg), 0.1 mol % **2b** (4.00 mg).

Table 10

Results of $\mathbf{2b}$ -catalyzed Heck reaction using NEt₃ as a base under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	40	150	98	980

Reaction conditions: DMF (5 ml), **4d** (2.54 mmol, 505.20 mg), methyl acrylate (**5b**) (5.08 mmol, 437.01 mg), NEt₃ (7.61 mmol, 770.48 mg), 0.1 mol % **2b** (4.00 mg).

Table 11

Recycling results of 3b-catalyzed Heck reaction using NEt₃ as a base under thermomorphic mode.

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	3	150	100	1000
2	21	150	100	1000
3	44	150	100	1000
4	35	150	100	1000
5	40	150	100	1000

Reaction conditions: DMF (5 ml), **4c** (2.74 mmol, 554.31 mg), methyl acrylate (**5b**) (5.49 mmol, 472.46 mg), NEt₃ (8.23 mmol, 832.98 mg), 0.1 mol % **3b** (4.00 mg).

unique property of complex **2b,c** gives high efficiency and good recyclability very close to ideal recoverable catalyst [25,26]. By showing homogeneous catalytic activity at the elevated temperature they can be easily recovered by freezing the solution to -20 °C (or lower) followed by decantation. For example, Heck arylation of aryl iodide with methyl acrylate was easily achieved with very high TON under thermomorphic condition. It turned out that cationic Pd complexes of this type were also the efficient catalysts for Heck arylation of less reactive aryl bromides with good activity and reusability.

4. Experimental

Table 12

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4.1. General procedures

Gas chromatographic/mass spectrometric data were obtained using an Agilent 6890 Series gas chromatograph with a series 5973 mass selective detector. The reaction was monitored with a HP 6890 GC using a 30 m \times 0.250 mm HP-1 capillary column with a 0.25 µm stationary phase film thickness. The flow rate was 1 mL/ min and splitless. Samples analyzed by fast atom bombardment (FAB) mass spectroscopy were done by the staff of the National Central University (Taiwan) mass spectrometry laboratory. Infrared

ecycling results of 3b -catalyzed	Heck	reaction	using	NPr ₃	as a	base	under	ther-
nomorphic mode.								

Run	Time (h)	Temperature (°C)	Yield (%)	TON
1	3	150	100	1000
2	35	150	86	860
3	20	150	100	1000
4	55	150	46	460

Reaction conditions: DMF (5 ml), **4c** (2.74 mmol, 554.31 mg), methyl acrylate (**5b**) (5.49 mmol, 472.5 mg), NPr₃ (8.23 mmol, 1179.38 mg), 0.1 mol % **3b** (4.00 mg).

 Table 13

 Percentage (%) of residual Pd present after 2b-catalyzed Heck reaction.

Table no Run no. ^a	Pd (in ppm) detected from ICP	Wt of the sample (mg)	Theoretical value of Pd (in ppm) before recovery	Recovery (%) ^b
4-2	27.78	473.30	570.32	95.13
4-4	32.30	474.20	569.24	94.33
4-5	22.44	265.90	1015.17	97.79

Note:

^a Taking 4–2 for example, 4-2 stands for data from Run No. 2 of Table 4.

^b Because **2c** is slightly less soluble in polar solvent than **2b** at the same temperature, the recovered Pd is higher in average percentage from **2c** case (96.99%) than that from **2b** case (95.75%). (The residual Pd data present in **2c**-catalyzed Heck reaction was shown in Table IV of supplementary material.)

Table 14

Percentage (%) of residual Pd present after **3b**-catalyzed Heck reaction.

Table No Run No.	Pd (in ppm) detected from ICP	Wt of the sample (mg)	Theoretical value of Pd (in ppm) before recovery	Recovery (%)
2-5	0.135	781	681.129	99.98
2-6	0.147	781	680.994	99.98
2-7	0.157	781	680.847	99.98

spectra were obtained on a Perkin Elmer RX I FT-IR Spectrometer. NMR spectra were recorded on Bruker AM 500 using 5 mm sample tubes. D-toluene, deuterated DMF and deuterated Me₂SO were the references for both ¹H and ¹³C NMR spectra; and Freon[®] 11 (CFCl₃) was the reference for ¹⁹F NMR spectra.

4.1.1. Starting materials

Chemicals, reagents and solvents employed were commercially available and used as received. $C_9F_{19}CH_2OH$, $C_{10}F_{21}CH_2OH$ and $C_{10}F_{23}CH_2OH$ were purchased from Aldrich and SynQuest.

4.2. Preparation of cationic Pd complexes $2\mathbf{a}-\mathbf{c}$ where $R_f = n-C_9F_{19}$ (**a**), $n-C_{10}F_{21}$ (**b**), and $n-C_{11}F_{23}$ (**c**)

As shown in Scheme 3, the reaction of allylpalladium(II) chloride dimer and AgOT_f with three highly fluorinated bipyridine derivatives, 4,4'-bis(R_f CH₂OCH₂)-2,2'-bpy (**1a**-**c**) in different reactions were charged into a round bottomed flask, and CH₂Cl₂ (3 mL) added as the solvent. The solution color changed from red to yellow after mixing for several min. The solution was further stirred at 60 °C for 24 h before the solvents and volatiles were removed under vacuum, resulted in the synthesis of cationic complex, [Pd(η^3 -allyl)(4,4'-bis-(R_f CH₂OCH₂)-2,2'-bpy)](OT_f) **2a**-**c**, as the pale yellow solid, where $R_f = n$ -C₉F₁₉ (**a**), n-C₁₀F₂₁ (**b**), n-C₁₁F₂₃ (**c**), respectively. In addition, the complex **3a**,**b**, {PdCl₂[4,4'bis-(n- R_f CH₂OCH₂)-2,2'-bpy]} where $R_f = n$ -C₉F₁₉ (**a**), n-C₁₀F₂₁ (**b**) was also synthesized by the procedure reported elsewhere [20]. The results obtained from cationic Pd complex **2a**-**c** and neutral Pd catalyst **3a,b** were also compared.

Analytical data of **2a**: Yield: 76.52%; ¹H NMR (500 MHz, *d*-DMSO, 80 °C), δ (ppm): δ 8.43 (s, 2H, H₃), 8.95 (d, 2H, ³J_{HH} = 5.3 Hz, H₆), 7.71 (d, 2H, ³J_{HH} = 5.3 Hz, H₅), 4.97 (s, 4H, bpy-CH₂), 4.39 (t, 4H, ³J_{HF} = 14.5 Hz, CH₂CF₂), 6.07 (m, 1H, allyl *H*^{central}), 4.40 (bd, 2H, allyl *H*^{syn}), 3.59 (bd, 2H, allyl *H*^{anti}); ¹⁹F NMR (470.5 MHz, *d*-DMSO, 80 °C), δ (ppm): δ -125.7, -122.9, -122.4, -121.7, -121.6, -121.5, -119.1



Scheme 3. (A) Synthesis of 2a-c; (B) Synthesis of 3a,b.

 $(-CH_2(CF_2)_8CF_3, 16F), -80.6 (t, 6F, {}^3J_{FF} = 9.7Hz, -CF_2CF_3), -77.9(3F,$ OT_f): ¹³C NMR (126 MHz, d-DMSO, 80 °C), δ (ppm): δ 71.0 (bpy-CH₂), 66.8 (CH₂CF₂), 120.3, 125.0, 151.5, 153.8, 153.9 (bpy), 100.7-148.5 $(C_{10}F_{19})$, 119.6 (s, allyl C^2), 62.3 (s, allyl $C^{1,3}$); FT-IR ν (cm⁻¹): 1617, 1561, 1454 (vbpy, m), 1266, 1211, 1152 (vCF₂ stretch, s); FAB: (M- OT_{f})⁺: C₃₅H₁₉F₃₈N₂O₂Pd, calcd *m*/*z* 1327.9, found *m*/*z* 1327.5; (M -OT_f- C₃H₅)⁺: C₃₂H₁₄F₃₈N₂O₂Pd, calcd *m*/*z* 1288.0, found *m*/*z* 1288.5.

Analytical data of 2b: Yield: 63.51%; ¹H NMR (500 MHz, d-DMSO, 80 °C), δ (ppm): δ 8.42 (s, 2H, H₃), 8.95 (d, 2H, ³ I_{HH} = 5.3 Hz, H_6), 7.71 (d, 2H, ${}^{3}J_{HH} = 5.3$ Hz, H_5), 4.97 (s, 4H, bpy-CH₂), 4.37 (t, 4H, ${}^{3}I_{HF} = 14.5 \text{ Hz}, \text{CH}_2\text{CF}_{2,}$, 6.07 (m, 1H, allyl H^{central}), 4.40 (bd, 2H, allyl H^{syn}), 3.59 (bd, 2H, allyl H^{anti}); ¹⁹F NMR (470.5 MHz, d-DMSO, 80 °C), δ (ppm): δ –125.7, –122.9, –122.4, –121.6, –121.4, –119.1 (18F, –CH₂(CF₂)₉CF₃), –80.6 (t, 6F, ³J_{FF} = 9.0 Hz, –CF₂CF₃), –77.8 (OT_f, 3F); ¹³C NMR (126 MHz, *d*-DMSO, 80 °C), δ (ppm): δ 71.0 (bpy-CH₂), 66.8 (CH₂CF₂), 120.3, 125.0, 151.5, 153.8, 153.9 (bpy), 100.7–148.5 ($C_{10}F_{21}$), 119.6 (s, allyl C^2), 62.3 (s, allyl $C^{1,3}$); FT-IR ν (cm⁻¹): 1617, 1561, 1454 (*v*bpy, m), 1266, 1211, 1152 (*v*CF₂ stretch, s); FAB: $(M-OT_f)^+$: C₃₇H₁₉F₄₂N₂O₂Pd, calcd *m*/*z* 1427.9, found *m*/*z* 1427.9; $(M-OT_{f}-C_{3}H_{5})^{+}$: $C_{34}H_{14}F_{42}N_{2}O_{2}Pd$, calcd m/z 1388.9, found *m*/*z* 1388.8.

Analytical data of 2c: Yield: 60.22%; ¹H NMR (500 MHz, d-DMSO, 80 °C), δ (ppm): δ 8.63 (s, 2H, H₃), 9.06 (d, 2H, ³J_{HH} = 5.3 Hz, H_6), 7.83 (d, 2H, ${}^{3}J_{HH} = 5.3$ Hz, H_5), 5.10 (4H, s, bpy-C H_2), 4.49 (t, 4H, ${}^{3}J_{HF} = 14.5$ Hz, $CH_{2}CF_{2}$), 6.17 (m, 1H, allyl H^{central}), 4.52 (bd, 2H, allyl H^{syn}), 3.59 (bd, 2H, allyl H^{anti}); ¹⁹F NMR (470.5 MHz, d-DMSO, 80 °C), δ (ppm): δ –126.1, –123.2, –122.6, –121.6 ~ –121.9 $(6CF_2)$, -119.7 [(-CH₂(CF₂)₁₀CF₃, 18F)], -81.4 (t, 3F, ${}^{3}J_{FF} = 9.0$ Hz, -CF₂CF₃), -78.6 (OT_f, 3F); ¹³C NMR (126 MHz, d-DMSO, 80 °C), δ (ppm): δ 72.5 (bpy-CH₂), 68.3 (CH₂CF₂), 121.6, 126.1, 153.1, 155.0, 155.4 (bpy), 101.7–119.5 (*C*₁₁F₂₃), 120.9 (s, allyl *C*²), 63.1 (s, allyl *C*^{1,3}); FT-IR ν (cm⁻¹): 1617, 1561, 1458 (ν bpy, m), 1266, 1211, 1152 (ν CF₂ stretch, s); FAB: $(M-OT_f)^+$: C₃₉H₁₉F₄₆N₂O₂Pd, calcd *m*/*z* 1527.9, found m/z 1527.9; (M-OT_f-C₃H₅)⁺: C₃₆H₁₄F₄₆N₂O₂Pd, calcd m/z1486.9, found *m*/*z* 1486.9.

4.3. Recycling studies of the Heck reaction with Pd complex **2b** (or **2c**) as a catalyst under thermomorphic mode

In a typical run, the reaction vessel was charged with DMF (5 mL), 4a-d, methyl acrylate (2 eq.), triethylamine or tripropylamine (3 eq.) and the 0.1 mol % Pd complex **2b** (about 4 mg). Then the reaction mixture was set to react at ca. 130-150 °C for 3-7 h before GC analysis. After the reaction, the product mixtures were cooled to -30 °C by the cold bath (for convenient operation, the -20 °C freezer was frequently used.) and the precipitated catalyst was centrifuged and quickly recovered by decantation at room temperature after each run. The recovered Pd catalyst was washed with 2 mL DMF (or CH₂Cl₂) 3 times before proceeding to the next cycle.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.08.028.

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