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Synthesis, characterization, and applications in Heck and Suzuki coupling reactions of amphiphilic cyclopalladated ferrocenylimines

Bing Mu,[a,b,c] Tiesheng Li,[a,b,c,*] Wenjian Xu,[a,b,c] Guoliang Zeng,[a,b,c] Pingping Liu[a,b,c] and Yangjie Wu[a,b,c,*]

[a]*Department of Chemistry, The Key Laboratory of Chemical Biology and Organic Chemistry of Henan Province, PR China*
[b]*The Key and Open Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Daxue road 75, Zhengzhou 450052, PR China*
[c]*The Key Lab of Advanced Nano-information Materials of Zhengzhou, Daxue road 75, Zhengzhou 450052, PR China*

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Abstract—A series of novel amphiphilic ferrocenylimines and their cyclopalladated complexes of general formula [Fe(η^5-C_5H_5)(η^5-$C_5H_4CR_1{=}NR_2$)] (R_1=H, R_2=$C_{12}H_{25}$-*n* **4a**, R_1=H, R_2=$C_{16}H_{33}$-*n* **4b**, R_1=CH_3, R_2=$C_{12}H_{25}$-*n* **4c**, R_1=CH_3, R_2=$C_{16}H_{33}$-*n* **4d**), [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)$CR_1{=}NR_2$]}]$_2$ (**5a–d**), [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)–$CR_1{=}NR_2$]}(PPh_3)] (**6a–d**), were prepared and characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, IR, HRMS, and elemental analysis. The crystal structures of **5c**,**d** were determined by X-ray crystallography. These amphiphilic cyclopalladated complexes are thermally stable and insensitive to oxygen and moisture. The redox properties of **4a–d**, **5a–d**, **6a–d** were also investigated using cyclic voltammetric technique. Compounds **5a–d**, **6a–d** displayed good activity in the Heck reaction of a variety of aryl halides with ethyl acrylate or styrene and the Suzuki–Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid in bulk solution. They are also suitable for formation of Langmuir–Blodgett (LB) films.

1. Introduction

Cyclopalladated compounds have been widely studied in recent decades.[1] They show important applications in organic or organometallic synthesis, in the syntheses of polynuclear organometallic complexes, in homogeneous catalysis, and in chiral recognition or discrimination.[2–5] In the past ten years, a great effort has been made in order to achieve the synthesis of palladacycles having $[C, N, X]^-$ (X=N, O, P, S) terdentate groups,[6] mainly due to the potential hemilability of the σ (Pd–X) bond in these systems.[7] By far, five-membered palladacycles with nitrogen donors have generated considerable interest because they are easily synthesized, thermally stable, insensitive to air, and high activity for various coupling reactions.[8] For example, it was reported that *ortho*-palladated imines are highly reactive in Heck reaction to afford quantitative yields and with very high TONs, and the CN-palladacycles showed impressive efficiency in Suzuki reaction by Milstein et al.[9,10] Cyclopalladated benzylamines were later studied in more detail and wider assortment including ferrocene derivatives in Heck reaction, though under more harsh conditions, and excellent yields and high TONs were recorded for the cyclopalladated complexes.[11] In our previous work, we have focused on the cyclometallation of ferrocenylimines and applications of these systems (such as compounds **1**, **2**, **3** in Scheme 1).[12] These cyclopalladated ferrocenylimines were effective catalysts for the Heck reaction, the dimerizaton of arylmercurials, and the Suzuki reaction.[13–16]

In the recent years, amphiphilic transition metal catalysts on solid substrates by Langmuir–Blodgett (LB) technique for catalytic applications inspire much interest. For instance, it was reported that amphiphilic manganese or iron porphyrins as well as rhodium complexes of 4,4-diakylbipyridines had been structured on a solid substrate leading to well-defined, supported catalytic systems by LB technique.[17–19] These results obtained with LB films have demonstrated that the catalysts' activity and selectivity were influenced by molecular order, and indicated that supporting transition metal complexes on organized LB films offered potential in the design of tailor-made catalysts.[20]

In the view of the facts and as a part of project directed toward the synthesis of amphiphilic complexes, we have now centered our attention on amphiphilic cyclopalladated

Keywords: Amphiphilic ferrocenylimines; Cyclopalladated complexes; Cyclic voltammetric techniques; Heck reaction; Suzuki–Miyaura reaction; Langmuir–Blodgett (LB) films.
* Corresponding authors. Tel./fax: +86 371 67766667; e-mail addresses: lts34@zzu.edu.cn; wyj@zzu.edu.cn

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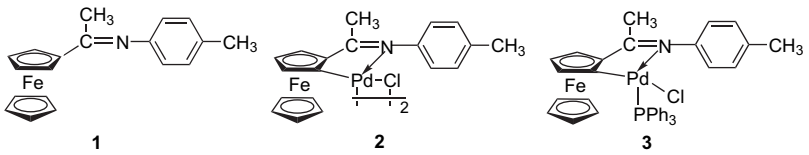


Scheme 1.

ferrocenylimines with long-chain hydrocarbon for further LB films formation.

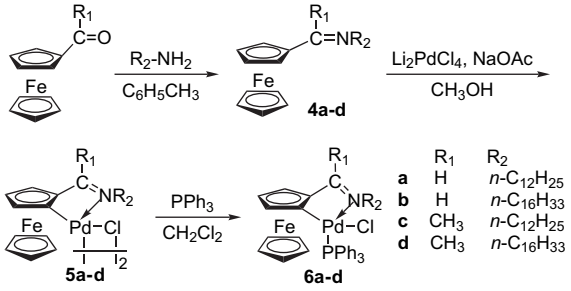
In this paper, we synthesized a series of novel long alkyl ferrocenylimines and their cyclopalladated complexes (**4a–d**, **5a–d**, **6a–d**), and undertake a broader investigation into Heck and Suzuki–Miyaura cross-coupling reactions in bulk solution as standard test reaction to probe the reactivity of **5a–d**, **6a–d** and the influence of long-chain hydrocarbon on catalytic activity. The study of their behavior at the air/water interface also was reported. We investigated primarily the catalytic application of the transferred **6d** LB films in Heck reaction.

In addition, the electrochemical properties of ferrocene derivatives[21,22] have been widely studied because ferrocene as an electrochemically active group is known to exchange electrons very quickly between the ferrocene moiety and electrode surface and behave as a reversible compound.[23] We thought it was interesting to elucidate the effect produced by the long-chain alkyl substituents at nitrogen on the electronic environment of the iron(II).

2. Results and discussion

2.1. Preparation of amphiphilic ferrocenylimines and their cyclopalladated complexes 4a–d, 5a–d, 6a–d

The synthesis of ferrocene derivatives is shown in Scheme 2. The ferrocenylimines were synthesized by the condensation of ferrocenecarbaldehyde or acetylferrocene with the corresponding amines (*n*-dodecylamine, *n*-hexadecylamine), respectively, in the presence of molecular sieves (4 Å). For the syntheses of **4c**, **4d**, large excess of amines and molecular sieves with long reaction time were needed to force the displacement of the equilibria. The difficulties of preparing **4c**, **4d** might be ascribed to the bulkier methyl substituent at the iminic carbon.[24]



Scheme 2.

Compounds **5a–d** were prepared according to the general procedure.[25] For ferrocenylimines with R=H (**4a**, **4b**), the formation of the palladacycle was achieved without precipitate, because they exhibited high solubility in methanol. A solution of chloride-bridged palladacyclic dimer (**5a–d**) were treated with 1.5 equiv of PPh_3 per palladium in CH_2Cl_2 at room temperature for 0.5 h to afford the corresponding monomeric compounds (**6a–d**) in 75–92% yields.

2.2. Characterization

All the amphiphilic complexes are thermally stable and not sensitive to air and moisture. They are highly soluble in most of the common solvents (chloroform, dichloromethane, benzene, toluene, ethyl acetate, etc.), slightly soluble in petroleum ether, hexane and alcohols, and insoluble in water.

The IR spectra of the free imines (**4a–d**) show an intense sharp band in the range of 1628–1644 cm^{-1} assigned to the stretching of the C=N bond. For the cyclopalladated complexes this band appears at lower frequencies in both families of complexes. This fact, which has been also reported for other cyclopalladation of shiff bases,[24] was attributed to a decrease in the bond order of the imine bond upon cyclopalladation. The C=N absorption of the monomeric complexes (1593–1601 cm^{-1}) is shifted to higher wave numbers in comparison to the dimeric complexes (1579–1585 cm^{-1}).

The ^1H NMR, ^{13}C NMR spectra, HRMS, and elemental analysis of **4a–d**, **5a–d**, **6a–d** were consistent with the proposed structures. For **6a–d**, the appearance of only one signal around 38 ppm in ^{31}P NMR spectra suggested the formation of a single isomer.[14]

The crystal structures of **6c** and **6d** were determined by X-ray single crystal analysis. The molecules are illustrated in Figures 1 and 2, respectively. Crystal data are listed in Table 1. Selected bond lengths (Å) and angles (°) are given in Table 2. The Pd(II) atom in every complex is in a slightly distorted square-planar environment bonded to the P, N, Cl, and C (6) atoms of ferrocenyl moiety. The deviations of the palladium from the mean plane are 0.1155 and 0.1201 Å for **6c** and **6d**, respectively. The C_5H_3 moiety and the five-membered palladacycle are approximately co-planar (dihedral angles of 3.8 (**6c**) and 5.4° (**6d**)). The two Cp rings are parallel, nearly eclipsed with tilt angles of 1.3 and 1.0° for **6c** and **6d**, respectively. The phosphine molecule and the imino nitrogen adopt a *trans* arrangement with P1Pd1N1 angle of 169.95 and 170.17° for **6c** and **6d**, respectively, possibly due to the steric bulk of the long-chain hydrocarbon.

2.3. Electrochemical behavior

To elucidate the effect produced by the long-chain alkyl substituents at nitrogen on the electronic environment of the iron(II), we studied the electrochemical properties of ferrocene derivatives.

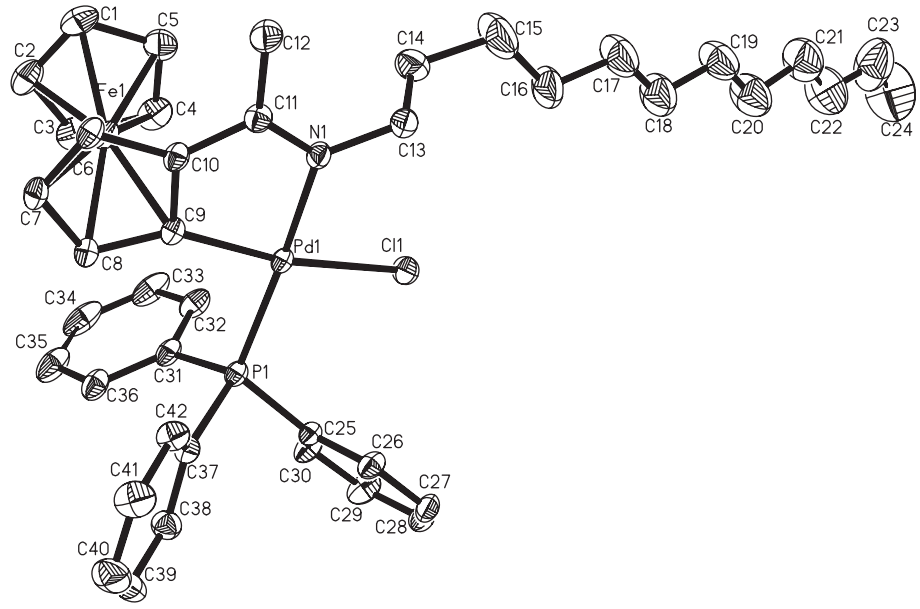


Figure 1. Molecular structure of complex **6c**·0.25C_6H_{12}. C_6H_{12} and hydrogen atoms are omitted for clarity.

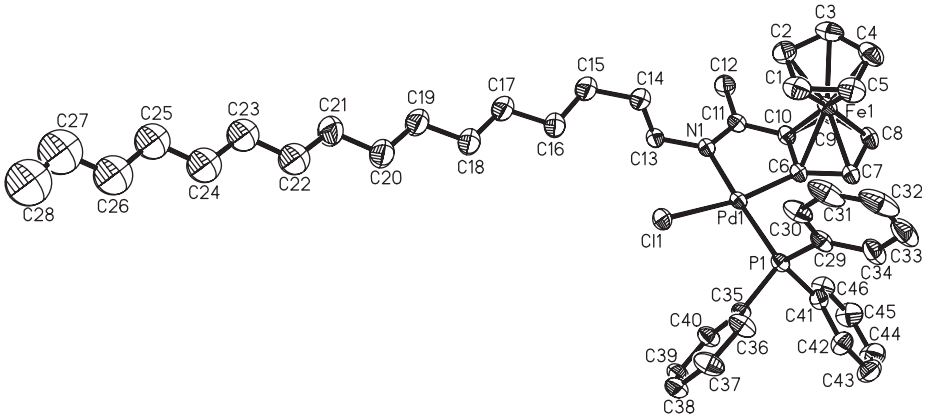


Figure 2. Molecular structure of complex **6d**·0.5C_6H_{12}. C_6H_{12} and hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data and structure refinement for **6c**, **6d**

Compound	**6c**·0.25C_6H_{12}	**6d**·0.5C_6H_{12}
Empirical formula	$C_{43.50}H_{54}ClFeNPPd$	$C_{49}H_{65}ClFeNPPd$
Formula weight	819.55	896.69
T (K)	291(2)	291(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
a (Å)	25.712(5)	28.398(6)
b (Å)	9.3761(19)	9.2385(18)
c (Å)	17.735(4)	17.775(4)
α (deg)	90	90
β (deg)	95.98(3)	93.32(3)
γ (deg)	90	90
V (Å^3)	4252.3(15)	4655.6(16)
Z	4	4
D_{calcd} (Mg/m^3)	1.280	1.279
Absorption coefficient (mm^{-1})	0.893	0.822
F(000)	1704	1880
Crystal size (mm)	0.20×0.17×0.16	0.20×0.18×0.17
Completeness to 2θ=25.00	95.3%	95.7%
Data/restraints/parameters	7131/9/437	8294/0/438
GOF (on F^2)	1.039	1.081
Final R indices $R1$, $wR2[I>2\sigma(I)]$	0.0542, 0.1461	0.0530, 0.1427
R indices (all data) $R1$, $wR2$	0.0711, 0.1565	0.0641, 0.1494

Table 2. Selected bond lengths (Å) and angles (°) for **6c**, **6d**

Compound	**6c**·0.25C_6H_{12}	**6d**·0.5C_6H_{12}
Pd(1)–C(6)	1.988(5)	1.997(4)
Pd(1)–N(1)	2.130(4)	2.134(4)
Pd(1)–P(1)	2.2407(14)	2.2432(13)
Pd(1)–Cl(1)	2.3665(15)	2.3779(13)
N(1)–C(11)	1.295(6)	1.299(5)
N(1)–C(13)	1.473(7)	1.472(6)
C(6)–Pd(1)–N(1)	80.76(19)	80.67(16)
C(6)–Pd(1)–P(1)	92.98(16)	93.13(13)
N(1)–Pd(1)–P(1)	169.95(12)	170.17(10)
C(6)–Pd(1)–Cl(1)	169.76(16)	169.38(13)
N(1)–Pd(1)–Cl(1)	93.43(12)	93.78(10)
P(1)–Pd(1)–Cl(1)	93.87(6)	93.51(5)
C(11)–N(1)–Pd(1)	114.4(4)	114.8(3)
C(13)–N(1)–Pd(1)	123.5(3)	123.4(3)

Electrochemical parameters for **4a–d**, **5a–d**, **6a–d** and related compounds were obtained one by one from cyclic voltammetric studies of freshly prepared solutions (10^{-4} M) in DMF using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. The most relevant electrochemical data

Table 3. Electrochemical data: anodic (E_{pa}) and cathodic potentials (E_{pc}), half-wave potentials E^0, and separation of the peaks (ΔE_p) for complexes (**4a–d**, **5a–d**, **6a–d**) (in mV), at a scan speed υ=50 mV s^{-1}

Compound	E_{pc}	E_{pa}	E^0	ΔE_p
Ferrocene	485	552	518.5	67
1	600	679	639.5	79
4a	593	664	628.5	71
4b	586	659	622.0	73
4c	556	628	592.0	72
4d	558	630	594.0	72
2	475	545	510	70
5a	437	508	472.0	71
5b	456	529	492.5	73
5c	435	501	468.0	66
5d	431	496	463.5	65
3	539	608	573.5	69
6a	522	589	555.5	67
6b	500	569	534.5	69
6c	490	555	522.0	65
6d	500	567	533.5	67

are summarized in Table 3. The cyclic voltammetric behavior of all the compounds showed one pair of well-defined and stable redox waves in the potential range of 0–0.9 V at the GC working electrode, which was attributed to the Fc/Fc^+ redox process. These experiments were performed at different scan rates, υ {from10 to 300 mV s^{-1}}, and in all cases, the I_{pa}/I_{pc} molar ratio was close to 1 with a linear relationship between the I_{pa} and $\upsilon^{1/2}$. All these findings were consistent with those expected for a simple and reversible one-electron transfer process.[26]

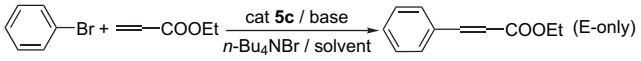
The half-wave potential E^0 of imines (**4c**, **4d**) was more cathodic than that of imines (**4a**, **4b**), suggesting that the replacement of an H by a CH_3 facilitates the oxidation of the iron(II). The variation could be related to the stronger electron donor ability of the CH_3 group.[27] For **4a** and **4b** or **4c** and **4d**, the replacement of a $-{}^nC_{12}H_{25}$ by a $-{}^nC_{16}H_{33}$ had a little influence on the E^0 values, which indicated that the two long-chain alkyl substituents at nitrogen in both cases were in the equivalent environment. For **5a–d** and **6a–d**, the E^0 values were also dependent on the nature of the substituents (R_1). Moreover, the E^0 values were almost not affected by the substituents (R_2), probably because their basicity of the nitrogen was nearly the same in both cases.[21] The E^0 values of imines (**4a–d**) were more anodic than that of cyclopalladated complexes (**5a–d**, **6a–d**), thus indicating the binding of Pd(II) to Fc facilitated the oxidation of Fe(II). Comparison of the E^0 values for dimeric and monomeric compounds revealed that dimeric complexes (**5a–d**) were less resistant to oxidation. The above findings were in good agreement with the results for related ferrocene derivations.[28] Cyclic voltammograms of di-μ-chloro-bridged derivatives (**5a–d**) exhibited only one wave thus suggesting that the two ferrocenyl units are independent of each other.[29] For the free ligand, di- and mono- nuclear complexes, the corresponding E^0 values were more cathodic than that reported for related ferrocene derivatives with R_2=phenyl group (**1**, **2**, **3**) in three families of compounds, thus indicating that the alkyl long-chain substituents at nitrogen produced a greater enhancement of the proclivity of the iron(II) to oxidation.

2.4. Heck coupling reaction

Our initial survey of solvents, including toluene, dioxane, DMA, and DMF with bromobenzene and ethyl acrylate as the coupling partners (using 0.1 mol % of **5c**, Et_3N as the base and *n*-Bu_4NBr as cocatalyst) revealed that DMF was much better than others (in Table 4, entries 1–5). The reaction carried out in the absence of *n*-Bu_4NBr is in a very low yield (entry 6). The role of *n*-Bu_4NBr probably strengthened the stabilizations of low coordinated Pd(0) species, and was as the phase transfer catalyst for the inorganic base/polar solvent/organic substrates/product phases.[30] Then screening a variety of bases (e.g., Et_3N, Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOAc, $KF{\cdot}2H_2O$, and K_3PO_4), K_3PO_4 was found to give the best result (entries 5, 7–12). Increasing the loadings of K_3PO_4 from 0.5 mmol to 1 mmol could give 100% HPLC yield (entry 13).

With the appropriate solvent (DMF), base (K_3PO_4) and cocatalyst (*n*-Bu_4NBr) in hand, the relative activities of several amphiphilic palladacycles **5a–d**, **6a–d** for bromobenzene and ethyl acrylate were studied (in Table 5, entries

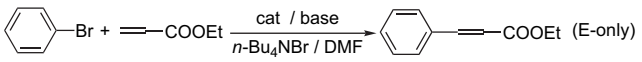
Table 4. Influence of base, solvent on the Heck coupling of bromobenzene and ethyl acrylate[a]



Entry	Base	Solvent	Yield[b] (%)	T (°C)
1	Et_3N	Dioxane	28	101
2	Et_3N	Toluene	62	115
3	Et_3N	DMA	19	140
4	Et_3N	DMA	78	160
5	Et_3N	DMF	82	140
6[c]	Et_3N	DMF	29	140
7	Na_2CO_3	DMF	55	140
8	K_2CO_3	DMF	65	140
9	Cs_2CO_3	DMF	89	140
10	NaOAc	DMF	56	140
11	$KF{\cdot}2H_2O$	DMF	59	140
12	K_3PO_4	DMF	91	140
13[d]	K_3PO_4	DMF	100	140

[a] Reaction conditions: PhBr (0.5 mmol), ethyl acrylate (2 mmol), catalyst **5c** (0.1 mol %), base (0.5 mmol), *n*-Bu_4NBr (0.5 mmol), solvent (1.5 mL), 12 h.
[b] Yield determined by HPLC, based on the product.
[c] *n*-Bu_4NBr (0 mmol).
[d] K_3PO_4 (1 mmol).

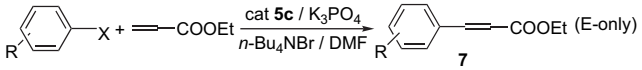
Table 5. The relative activities of several palladacycles (**5a–d**, **6a–d**) on the Heck coupling of bromobenzene and ethyl acrylate[a]

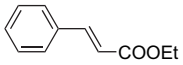
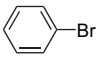
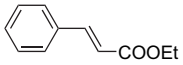
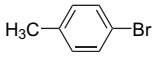
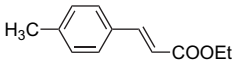
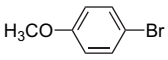
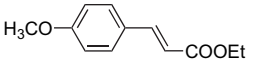
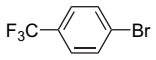
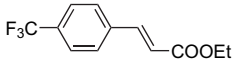
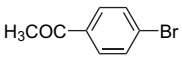
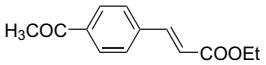
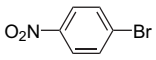
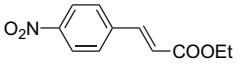
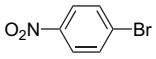
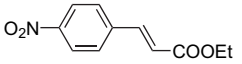
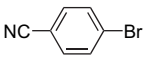
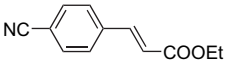
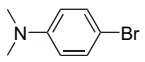
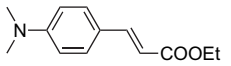
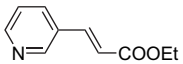
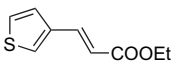
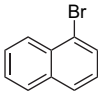
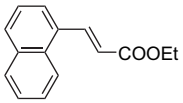
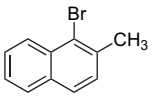
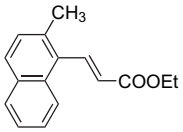
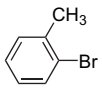
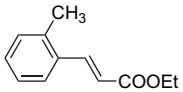
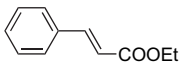
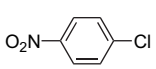
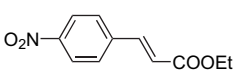
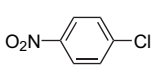
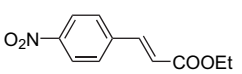


Entry	Catalyst (0.1 mol %)	Yield[b] (%)
1	**5a**	96
2	**5b**	99
3	**5c**	>99
4	**5d**	94
5	**6a**	>99
6	**6b**	>99
7	**6c**	>99
8	**6d**	>99

[a] Reaction conditions: PhBr (0.5 mmol), ethyl acrylate (2 mmol), catalyst (0.1 mol %), *n*-Bu_4NBr (0.5 mmol), K_3PO_4 (1 mmol), DMF (1.5 mL), 12 h, 140 °C.
[b] Isolated yield (average of two runs).

Table 6. Heck coupling of aryl halides with ethyl acrylate[a]

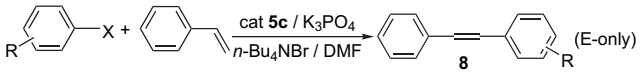


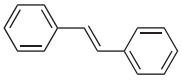
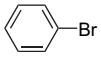
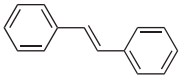
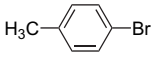
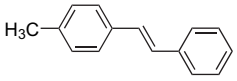
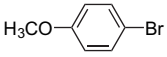
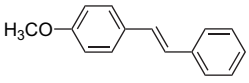
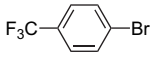
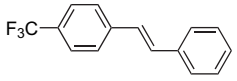
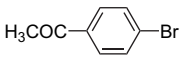
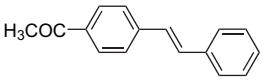
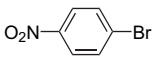
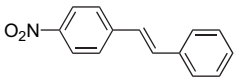
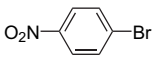
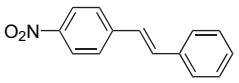
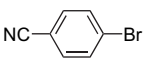
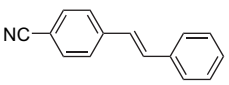
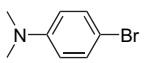
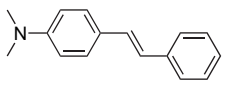
Entry	ArX	Catalyst (mol %)	*t* (h)	Base (mmol)	Product	Product	
						No.	Yield[b] (%)
1		0.0001	12	1		**7a**	99
2		0.01	12	1		**7a**	>99
3		0.1	12	1		**7b**	91
4		0.1	12	1		**7c**	95
5		0.1	12	1		**7d**	75
6		0.1	12	1		**7e**	84
7		0.1	12	1		**7f**	90
8		0.01	12	0.5		**7f**	>99
9		0.1	12	1		**7g**	88
10		0.1	24	1		**7h**	80
11		0.1	12	1		**7i**	90
12		0.1	12	1		**7j**	47
13		0.1	12	1		**7k**	96
14		0.1	24	1		**7l**	93
15		0.1	12	1		**7m**	57
16		0.1	12	1		**7a**	Trace
17		0.1	12	1		**7f**	Trace
18		0.03	12	0.5		**7f**	99

[a] Reaction conditions: aryl halide (0.5 mmol), ethyl acrylate (2.0 mmol), catalyst **5c**, *n*-Bu_4NBr (0.5 mmol), base (K_3PO_4) and DMF (1.5 mL), at 140 °C.
[b] Isolated yields (average of two experiments).

1–8). We found that **5c** and **6a–d** all exhibited higher activity with 0.1 mol % catalyst loading. However, phosphine-free cyclopalladated ferrocenylimine **5c** was more friendly to environment than others, so a wide range of electronically and structurally diverse aryl halides could be cross-coupled efficiently with ethyl acrylate or styrene by complex **5c** under these optimized reaction conditions (K_3PO_4, DMF, *n*-Bu_4NBr, 140 °C). The results are listed in Tables 6 and 7. These data suggest that styrene with aryl halides required the longer reaction time than ethyl acrylate with aryl halides. Using 10^{-4} mol % of catalyst **5c** to catalyze olefination of iodobenzene with ethyl acrylate, the high turnover number of 1 million was obtained in a ten-fold larger scale reaction (in Table 6, entry 1). The reaction of 4-methoxybromobenzene with a strongly electron-donating group and ethyl acrylate or styrene gave 95% and 91% isolated yields, respectively (in Table 6, entry 4 and in Table 7, entry 4). 3-Bromopyridine and bromonaphthalene could also proceed the cross-coupling reaction smoothly under the same reaction conditions to afford the cross-coupling products in high yields (in Table 6, entries 11, 13 and in Table 7, entries 11, 13). The sterically hindered 2-bromotoluene gave the cross-coupled product in only modest yields (in Table 6, entry 15 and in Table 7, entry 15). However, for 2-methylbromonaphthalene, prolonging the reaction time resulted in good yields (in Table 6, entry 14 and in Table 7, entry 14). For bromobenzene with ethyl acrylate or styrene, the catalyst loading could be also lowered to 10^{-2} mol % with high activity (in Table 6, entry 2 and in Table 7, entry 2). Interestingly, when the loading of K_3PO_4 was reduced, we unexpectedly found that the aryl halides with nitro group gave excellent results with catalyst loading as low as 0.01 mol % (in Table 6, entries 8, 18 and in Table 7, entries 8, 18). As for non-activated chlorobenzene, complex **5c** was nearly inactive under the similar reaction conditions. As observed above, amphiphilic cyclopalladated ferrocenylimines were efficient catalysts for the Heck coupling of aryl iodides, bromides, and electron deficient chlorides. Finally, it was worthy to note that all of these reactions studied showed high regioselectivity for *trans*-coupling, and no *cis*-product was found.

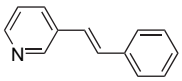
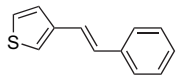
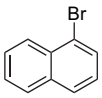
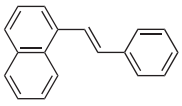
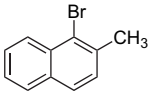
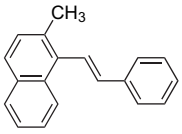
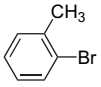
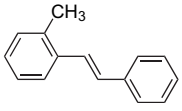
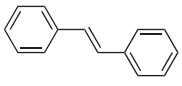
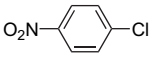
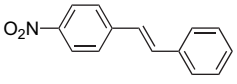
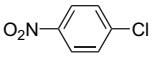
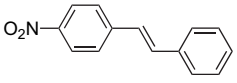
Table 7. Heck coupling of aryl halides with styrene[a]



Entry	ArX	Catalyst (mol %)	t (h)	Base (mmol)	Product	Product	
						No.	Yield[b] (%)
1		0.0001	24	1		**8a**	61
2		0.01	24	1		**8a**	91
3		0.1	24	1		**8b**	75
4		0.1	24	1		**8c**	91
5		0.1	24	1		**8d**	90
6		0.1	24	1		**8e**	54
7		0.1	24	1		**8f**	94
8		0.01	24	0.5		**8f**	94
9		0.1	24	1		**8g**	90
10		0.1	28	1		**8h**	65

(*continued*)

Table 7. (*continued*)

Entry	ArX	Catalyst (mol %)	t (h)	Base (mmol)	Product	Product	
						No.	Yield[b] (%)
11		0.1	24	1		**8i**	87
12		0.1	24	1		**8j**	58
13		0.1	24	1		**8k**	92
14		0.1	28	1		**8l**	97
15		0.1	24	1		**8m**	61
16		0.1	24	1		**8a**	Trace
17		0.1	24	1		**8f**	Trace
18		0.01	24	0.5		**8f**	68

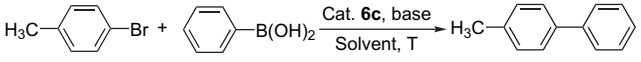
[a] Reaction conditions: aryl halide (0.5 mmol), styrene (1.5 mmol), catalyst **5c**, *n*-Bu_4NBr (0.5 mmol), base (K_3PO_4) and DMF (1.5 mL), at 140 °C.
[b] Isolated yields (average of two experiments).

2.5. Suzuki–Miyaura cross-coupling reaction

Afterwards, the Suzuki–Miyaura cross-coupling reactions of 4-bromotoluene and phenylboronic acid were carried out with various bases and solvents in the presence of 0.001 mol % of **6c** without the protection of inert gas (Table 8). It can be seen from Table 8, the reaction proceeded smoothly in toluene. Among the tested bases, $K_3PO_4\cdot 7H_2O$ was found to be the most effective base.

With the appropriate solvent (toluene) and base ($K_3PO_4\cdot 7H_2O$) in hand with 0.001 mol % catalyst loading, the relative activity of several palladacycles **5a–d**, **6c** and **6d** for the same model reaction was then studied. As shown in Table 9,

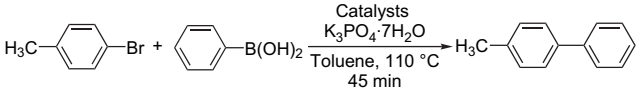
Table 8. Investigation of the Suzuki–Miyaura reaction conditions[a]



Entry	Base	Solvent	T (°C)	Yield[b] (%)
1	$K_3PO_4\cdot 7H_2O$	Dioxane	100	24
2	$K_3PO_4\cdot 7H_2O$	DMF	140	29
3	$K_3PO_4\cdot 7H_2O$	Toluene	110	98
4	K_3PO_4	Toluene	110	64
5	$KF\cdot 2H_2O$	Toluene	110	46
6	K_2CO_3	Toluene	110	76
7	NaOH	Toluene	110	73
8	NaOAc	Toluene	110	2
9	NaO^{t}Bu	Toluene	110	6

[a] Reaction conditions: 4-bromotoluene 0.5 mmol, $PhB(OH)_2$ 0.6 mmol, base 1.0 mmol, solvent 2.5 mL, 5.0×10^{-6} mmol of Pd of catalyst **6c**, reaction time is 45 min.
[b] Isolated yields based on 4-bromotoluene in two runs.

Table 9. Suzuki–Miyaura reaction: catalyst study[a]



Entry	Catalyst	Yield[b] (%)
1	**5a**	69
2	**5b**	77
3	**5c**	48
4	**5d**	62
5	**6a**	83
6	**6b**	78
7	**6c**	98
8	**6d**	68

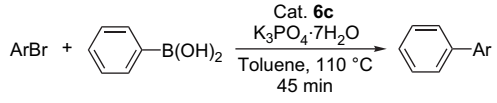
[a] Reaction conditions: 4-bromotoluene 0.5 mmol, $PhB(OH)_2$ 0.6 mmol, $K_3PO_4\cdot 7H_2O$ 1.0 mmol, Solvent 2.5 mL, 5.0×10^{-6} mmol of Pd of catalyst, reaction time is 45 min.
[b] Isolated yields based on 4-bromotoluene in two runs.

monomeric complexes **6c**, **6d** showed higher activity toward this reaction than dimeric complexes **5a–d**. In contrast, **6c** displayed the good activity between that of **5a–d**, **6a–d** (entry 7).

Under the optimized reaction conditions ($K_3PO_4 \cdot 7H_2O$, toluene, 110 °C), a variety of aryl bromides by using 0.001 mol % of **6c** could be coupled efficiently with phenylboronic acid. The results are shown in Table 10. For activated and inactivated aryl bromides, excellent yields were obtained (entries 1, 3, 4, 5). However, 4-bromotoluene with an electro-donating group also provided the biaryl product in 98% isolated yield (entry 6). For 2-bromotoluene only 40% isolated yield was obtained under the same reaction conditions (entry 8). When the catalyst loading was reduced to 0.0001 mol % for 4-nitro-bromobenzene and 4-bromotoluene, only 63% and 30% isolated yields were obtained, respectively (entries 2, 7). In a word, amphiphilic cyclopalladated ferrocenylimines were efficient catalysts for aryl bromides with phenylboronic acid.

Finally, in comparison with similar catalyst like di-μ-chloro-bridged cyclopalladated ferrocenylimine **2**,[13] and cyclopalladated ferrocenylimine triphenylphosphine complexes,[31] amphiphilic complexes **5c** and **6c** were more active for the Heck and Suzuki coupling, respectively. This could be accredited with two reasons: one was that long-chain alkyl substituents at nitrogen promoted oxidative addition of aryl halides to the Pd intermediate by making palladium more electron rich and increased the activity consequently, the other was that alkyl substituents improved the solubility of the catalysts in organic solvent.

Table 10. Suzuki coupling of aryl bromides with phenylboronic acid[a]



Entry	ArBr	Mol % of Pd	Product	Product No.	Yield[b] (%)
1	O_2N–Br	0.001	O_2N–	**9a**	97
2	O_2N–Br	0.0001	O_2N–	**9a**	63
3	H_3COC–Br	0.001	H_3COC–	**9b**	>99
4	Br	0.001		**9c**	>99
5	Br	0.001		**9d**	>99
6	H_3C–Br	0.001	H_3C–	**9e**	98
7	H_3C–Br	0.0001	H_3C–	**9e**	30
8	Br	0.001		**9f**	39
9	N–Br	0.001	N–	**9g**	72

[a] Reaction conditions: aryl bromides 0.5 mmol, $PhB(OH)_2$ 0.6 mmol, $K_3PO_4 \cdot 7H_2O$ 1.0 mmol, Solvent 2.5 mL.
[b] Isolated yields.

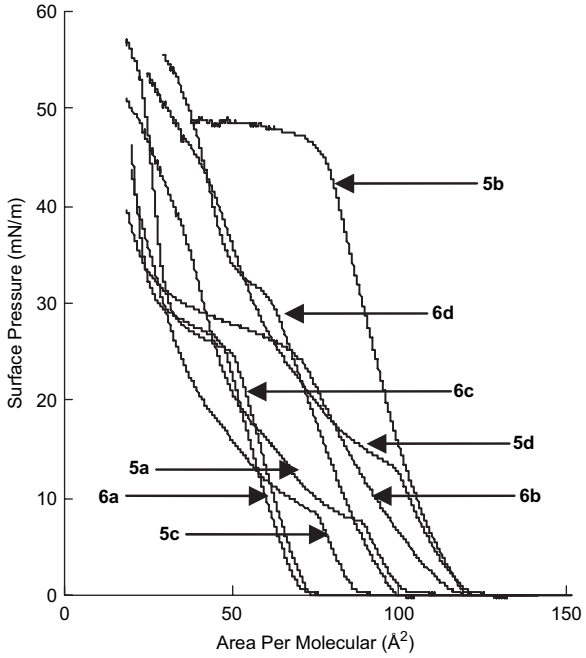


Figure 3. π–A isotherms for **5a–d**, **6a–d** on pure water subphase (compression rate: 10 mN/m).

2.6. The study on catalytic application of 6d LB films in Heck reaction

Compounds **5a–d**, **6a–d** were spread, respectively, on the water surface at room temperature to measure surface pressure (π)–area (A) isotherms (Fig. 3). The isotherms show a gradual transition, indicating a slight structure alteration in the molecules. Obviously, all the π–A isotherms have high collapse pressure, suggesting the formation of the condensed monolayers on the subphase. Take **6d** as an example, monolayer of **6d** could be transferred onto hydrophilic or hydrophobic glass slides as a Y-type films with a transfer ratio of almost unity under a surface pressure of 25 mN/m, using Langmuir–Blodgett technique. The LB films were stable, uniform and close packing of molecules.[32] We investigated primarily the catalytic activity of the transferred **6d** LB films in Heck reaction. The results indicated that **6d** LB films could not exhibit good catalytic activity, because the desorption of the films was observed when glass slides were placed in organic solvents or under heating conditions. Further experiments are currently in progress to explore milder reaction conditions in aqueous media at room temperature for the catalytic application of LB films.

3. Conclusions

We have synthesized a series of novel amphiphilic ferrocenylimines and their cyclopalladated complexes. The palladacycles are thermally stable and insensitive to oxygen and moisture. Electrochemical studies for ferrocene derivatives

indicated a simple and reversible one-electron transfer process, and the long-chain alkyl substituents at nitrogen produced a greater enhancement of the proclivity of the iron(II) to oxidation than phenyl substituents at nitrogen. Cyclopalladated complexes (**5a–d**, **6a–d**) are efficient catalysts for the Heck reaction of aryl halides with ethyl acrylate or styrene in bulk solution. Furthermore, they were also found to be very efficient for Suzuki–Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid. They are suitable for formation of Langmuir–Blodgett (LB) films.

4. Experimental

4.1. General

Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. Infrared spectra were recorded on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H, ^{13}C, and ^{31}P $\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard for ^{1}H NMR, ^{13}C NMR and 85% H_3PO_4 as external standard for ^{31}P $\{^{1}H\}$ NMR. High-resolution mass spectra were measured on a Waters Q-Tof Micro™ spectrometer. HPLC was conducted on a Waters 600 liquid chromatograph. Electrochemical experiments were carried out in DMF (HPLC grade) with CHI650A electrochemical analyzer. Solvents were dried and freshly distilled prior to use. All other chemicals were used as purchased. Elemental analyses were determined with Elementar Analysensystem GmbH (varioELIII). Measurement of surface pressure (π)–surface area (A) isotherms and the deposition of monolayer were carried out with a computer controlled Langmuir trough (KSV 5000-3). All the Heck and Suzuki reactions were accomplished without the protection of inert gas.

4.2. Preparation of the compounds

4.2.1. Preparation of [Fe(η^5-C_5H_5)(η^5-$C_5H_4CR_1$=NR_2)] (4a–d). A mixture of ferrocenecarbaldehyde or acetylferrocene (5.0 mmol) and the corresponding amine (5.01 mmol) (*n*-dodecylamine or *n*-hexadecylamine) was dissolved in 80 mL of dry toluene and refluxed on an oil bath under nitrogen atmosphere in the presence of molecular sieves (4 Å, 4.0 g). After 4–6 h, the reaction mixture was carefully filtered and the filtrate was reduced to dryness. For the syntheses of complexes (**4c**, **4d**), the reaction mixture was refluxed for two days and for every 12 h amines (0.01 mmol) and molecular sieves (0.8 g) were added (0.8 g) to force the displacement of the equilibria. Molecular sieves (4 Å) were removed by filtration, and the filtrate was reduced to dryness. All the solids were recrystallized from cold CH_3CN.

4.2.1.1. [Fe(η^5-C_5H_5)(η^5-C_5H_4CH=$NC_{12}H_{25}$)] 4a. Yield 96%, yellow solid, mp 53–54 °C; IR (KBr): 2924, 2853, 1106, 1009, 1644, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, s, H–C=N), 4.63 (2H, t, J=1.8 Hz, C_5H_4), 4.34 (2H, t, J=1.8 Hz, C_5H_4), 4.17 (5H, s, C_5H_5), 3.44 (2H, t, J=7.0 Hz, CH_2), 1.66–1.62 (2H, m, CH_2), 1.33–1.25 (18H, m, C_9H_{18}), 0.88 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 80.8, 70.2, 69.0, 68.3, 62.0, 31.9, 30.9, 29.65, 29.63, 29.61, 29.5, 29.3, 27.3, 22.7, 14.1; HRMS (positive ESI) calcd for $C_{23}H_{35}FeN$ $[M+1]^+$: 382.2197, found: 382.2190. Anal. Calcd for $C_{23}H_{35}FeN$: C, 72.43; H, 9.25; N, 3.67. Found: C, 72.21; H, 9.22; N, 3.67%.

4.2.1.2. [Fe(η^5-C_5H_5)(η^5-C_5H_4CH=$NC_{16}H_{33}$)] 4b. Yield 97%, yellow solid, mp 69–70 °C; IR (KBr): 2916, 2851, 1104, 1004, 1641, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, s, H–C=N), 4.62 (2H, t, J=1.9 Hz, C_5H_4), 4.34 (2H, t, J=1.9 Hz, C_5H_4), 4.17 (5H, s, C_5H_5), 3.44 (2H, t, J=7.4 Hz, CH_2), 1.66–1.62 (2H, m, CH_2), 1.32–1.25 (26H, m, $C_{13}H_{26}$), 0.88 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 80.8, 70.2, 69.0, 68.3, 62.0, 31.9, 30.9, 29.7, 29.65, 29.64, 29.61, 29.5, 29.3, 27.3, 22.7, 14.1; HRMS (positive ESI) calcd for $C_{27}H_{43}FeN$ $[M+1]^+$: 438.2823, found: 438.2817. Anal. Calcd for $C_{27}H_{43}FeN$: C, 74.13; H, 9.91; N, 3.20. Found: C, 74.30; H, 9.98; N, 3.44%.

4.2.1.3. [Fe(η^5-C_5H_5)(η^5-C_5H_4CMe=$NC_{12}H_{25}$)] 4c. Yield 85%, yellow solid, mp 62–64 °C; IR (KBr): 2916, 2849, 1108, 1014, 1628, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (2H, s, C_5H_4), 4.30 (2H, s, C_5H_4), 4.13 (5H, s, C_5H_5), 3.36 (2H, t, J=7.2 Hz, CH_2), 2.12 (3H, s, CH_3–C=N), 1.66–1.63 (2H, m, CH_2), 1.39–1.26 (18H, m, C_9H_{18}), 0.88 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 85.9, 69.9, 69.1, 67.6, 51.8, 31.9, 30.9, 30.8, 29.72, 29.71, 29.69, 29.67, 29.63, 29.4, 27.7, 22.7, 15.9, 14.1; HRMS (positive ESI) calcd for $C_{24}H_{37}FeN$ $[M+1]^+$: 396.2353, found: 396.2362. Anal. Calcd for $C_{24}H_{37}FeN$: C, 72.90; H, 9.43; N, 3.54. Found: C, 73.13; H, 9.34; N, 3.14%.

4.2.1.4. [Fe(η^5-C_5H_5)(η^5-C_5H_4CMe=$NC_{16}H_{33}$)] 4d. Yield 83%, yellow solid, mp 76–78 °C; IR (KBr): 2916, 2849, 1108, 1015, 1628, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (2H, s, C_5H_4), 4.31 (2H, t, J=1.4 Hz, C_5H_4), 4.13 (5H, s, C_5H_5), 3.37 (2H, t, J=7.2 Hz, CH_2), 2.12 (3H, s, CH_3–C=N), 1.66–1.63 (2H, m, CH_2), 1.37–1.26 (26H, m, $C_{13}H_{26}$), 0.88 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 85.8, 70.0, 69.1, 67.7, 51.7, 31.9, 30.8, 29.7, 29.69, 29.68, 29.63, 29.4, 27.7, 22.7, 15.9, 14.1; HRMS (positive ESI) calcd for $C_{28}H_{45}FeN$ $[M+1]^+$: 452.2979, found: 452.2989. Anal. Calcd for $C_{28}H_{45}FeN$: C, 74.48; H, 10.05; N, 3.10. Found: C, 74.46; H, 10.18; N, 3.49%.

4.2.2. Preparation of [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)CR_1=NR_2]}]$_2$ (5a–d). A solution of lithium tetrachloropalladated (II) in 10 mL of methanol (Li_2PdCl_4, 1 mmol) was added to a solution of mole equivalents of NaOAc and ferrocenylimine (**4a–d**) in 10 mL of methanol or methanol/ethyl ether=1:1, and the resulting red solution was stirred at room temperature for about 24 h. The solution (**4a** or **4b**) was reduced to dryness, and then was purified via column chromatography (CH_2Cl_2/CH_3CH_2OH=40:1 as eluent). The red oil formed was quenched by adding *n*-hexane. Evaporation of the solvent gave the remaining solid as the products. The solution (**4c** or **4d**) was carefully filtered, and then the deep red solid obtained was purified via column chromatography (CH_2Cl_2/CH_3CH_2OH=120:1 as eluent). The oil formed was quenched by adding of *n*-hexane followed by vigorous stirring produced the precipitation of

the dimeric compounds. The solvent was evaporated to give the products.

4.2.2.1. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)CH=$NC_{12}H_{25}$]}]$_2$ 5a. Yield 44%, red solid, mp 80–82 °C; IR (KBr): 2923, 2852, 1105, 1002, 1579, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, s, H–C=N), 4.79–4.77 (1H, m, C_5H_3), 4.38–4.27 (7H, m, C_5H_5, C_5H_3), 3.47–3.36 (2H, m, CH_2), 1.83–1.74 (2H, m, CH_2), 1.33–1.26 (18H, m, C_9H_{18}), 0.88 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 102.3, 86.9, 73.7, 70.7, 67.6, 65.7, 60.0, 59.1, 31.9, 30.9, 30.5, 29.64, 29.60, 29.4, 29.3, 26.8, 22.7, 14.1; HRMS (positive ESI) calcd for $C_{46}H_{68}Cl_2Fe_2N_2Pd_2$ [M−Cl]$^+$: 1007.1839, found: 1007.1835. Anal. Calcd for $C_{46}H_{68}Cl_2Fe_2N_2Pd_2\cdot 0.5C_2H_5OC_2H_5$: C, 53.30; H, 6.80; N, 2.59. Found: C, 53.78; H, 6.51; N, 2.42%.

4.2.2.2. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)CH=$NC_{16}H_{33}$]}]$_2$ 5b. Yield 65%, red solid, mp 102–103 °C; IR (KBr): 2922, 2851, 1105, 1001, 1585, 814 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (1H, s, H–C=N), 5.03 (1H, s, C_5H_3), 4.55 (1H, d, J=1.6 Hz, C_5H_3), 4.40 (1H, d, J=2.0 Hz, C_5H_3), 4.29 (5H, s, C_5H_5), 3.57–3.54 (1H, m, CH_2), 3.48–3.43 (1H, m, CH_2), 1.68–1.60 (2H, m, CH_2), 1.28–1.23 (26H, m, $C_{13}H_{26}$), 0.85 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 103.0, 87.1, 74.0, 71.0, 67.8, 65.9, 60.0, 59.2, 31.9, 31.0, 30.5, 29.7, 29.4, 26.8, 22.7, 14.1; HRMS (positive ESI) calcd for $C_{54}H_{84}Cl_2Fe_2N_2Pd_2$ [M−Cl]$^+$: 1119.3091, found: 1119.3085. Anal. Calcd for $C_{54}H_{84}Cl_2Fe_2N_2Pd_2\cdot 0.5C_2H_5OC_2H_5$: C, 56.34; H, 7.51; N, 2.35. Found: C, 56.66; H, 7.11; N, 2.01%.

4.2.2.3. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)C(CH_3)=$NC_{12}H_{25}$]}]$_2$ 5c. Yield 78%, red solid, mp 144–146 °C; IR (KBr): 2923, 2852, 1103, 1002, 1581, 812 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.99 (1H, t, J=0.9 Hz C_5H_3), 4.60 (1H, t, J=1.1 Hz, C_5H_3), 4.33 (1H, d, J=2.1 Hz, C_5H_3), 4.24 (5H, s, C_5H_5), 3.63–3.60 (1H, m, CH_2), 3.52–3.46 (1H, m, CH_2), 2.23 (3H, s, CH_3–C=N), 1.60–1.52 (2H, m, CH_2), 1.30–1.24 (18H, m, C_9H_{18}), 0.85 (3H, t, J=6.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 101.2, 91.5, 73.8, 71.3, 66.4, 65.9, 53.2, 52.4, 31.9, 31.0, 29.7, 29.69, 29.63, 29.60, 29.4, 29.37, 27.2, 22.7, 14.4, 14.1; HRMS (positive ESI) calcd for $C_{48}H_{72}Cl_2Fe_2N_2Pd_2$ [M−Cl]$^+$: 1035.2152, found: 1035.2174. Anal. Calcd for $C_{48}H_{72}Cl_2Fe_2N_2Pd_2\cdot 0.25C_6H_{12}$: C, 54.37; H, 6.91; N, 2.56. Found: C, 54.49; H, 6.65; N, 2.35%.

4.2.2.4. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)C(CH_3)=$NC_{16}H_{33}$]}]$_2$ 5d. Yield 82%, red solid, mp 139–141 °C; IR (KBr): 2921, 2850, 1103, 1001, 1579, 812 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.99 (1H, d, J=1.4 Hz, C_5H_3), 4.61 (1H, d, J=1.5 Hz, C_5H_3), 4.33 (1H, t, J=2.3 Hz, C_5H_3), 4.25 (5H, s, C_5H_5), 3.62–3.58 (1H, m, CH_2), 3.52–3.46 (1H, m, CH_2), 2.23 (3H, s, CH_3–C=N), 1.61–1.50 (2H, m, CH_2), 1.29–1.23 (26H, m, $C_{13}H_{26}$), 0.86 (3H, t, J=6.5 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 101.2, 91.4, 73.7, 71.2, 66.3, 65.8, 53.3, 52.3, 31.9, 30.9, 29.7, 29.68, 29.63, 29.60, 29.4, 27.2, 22.7, 14.4, 14.1; HRMS (positive ESI) calcd for $C_{56}H_{88}Cl_2Fe_2N_2Pd_2$ [M−Cl]$^+$: 1147.3404, found: 1147.3406. Anal. Calcd for $C_{56}H_{88}Cl_2Fe_2N_2Pd_2$: C, 56.77; H, 7.49; N, 2.36. Found: C, 57.07; H, 7.28; N, 2.16%.

4.2.3. Preparation of [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-CR_1=NR_2]}(PPh_3)] (6a–d). The solution of chloride-bridged cyclopalladated dimer (**5a–d**) (0.1 mmol) and PPh_3 (0.3 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 1 h. The solution was concentrated in vacuo and was purified via column chromatography (CH_2Cl_2/CH_3CH_2OH=120:1 as eluent). The red oil (**6a**, **6b**) was recrystallized from CH_2Cl_2/MeOH and (**6c**, **6d**) was recrystallized from CH_2Cl_2/petroleum ether.

4.2.3.1. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)CH=$NC_{12}H_{25}$]}(PPh_3)] 6a. Yield 76%, red soild, mp 54–56 °C; IR (KBr): 2922, 2851, 1101, 1000, 1601, 818, 747, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (1H, d, J=8.3 Hz, H–C=N), 7.79–7.74 (6H, m, PPh_3), 7.45–7.36 (9H, m, PPh_3), 4.36 (1H, d, J=2.4 Hz, C_5H_3), 4.02 (1H, t, J=2.2 Hz, C_5H_3), 3.96–3.89 (1H, m, CH_2), 3.86 (5H, s, C_5H_5), 3.61–3.53 (1H, m, CH_2), 3.29 (1H, d, J=2.1 Hz, C_5H_3), 1.98–1.92 (1H, m, CH_2), 1.71–1.60 (1H, m, CH_2), 1.41–1.25 (18H, m, C_9H_{18}), 0.87 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 135.0, 132.2, 131.7, 130.4, 128.1, 102.5, 87.7, 76.4, 70.0, 69.0, 66.2, 58.3, 31.9, 31.6, 29.8, 29.7, 29.68, 29.67, 29.65, 29.5, 29.4, 27.1, 22.7, 14.1; ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 38.06; HRMS (positive ESI) calcd for $C_{41}H_{49}ClFeNPPd$ [M−Cl]$^+$: 748.1987, found: 748.1992. Anal. Calcd for $C_{41}H_{49}ClFeNPPd$: C, 62.77; H, 6.30; N, 1.79. Found: C, 62.72; H, 6.33; N, 1.81%.

4.2.3.2. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)CH=$NC_{16}H_{33}$]}(PPh_3)] 6b. Yield 84%, red solid, mp 75–76 °C; IR (KBr): 2925, 2854, 1098, 999, 1601, 817, 747, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (1H, d, J=8.3 Hz, H–C=N), 7.79–7.74 (6H, m, PPh_3), 7.42–7.35 (9H, m, PPh_3), 4.36 (1H, d, J=2.2 Hz, C_5H_3), 4.02 (1H, t, J=2.2 Hz, C_5H_3), 3.95–3.89 (1H, m, CH_2), 3.85 (5H, s, C_5H_5), 3.59–3.55 (1H, m, CH_2), 3.29 (1H, d, J=1.9 Hz, C_5H_3), 1.97–1.92 (1H, m, CH_2), 1.71–1.64 (1H, m, CH_2), 1.38–1.25 (26H, m, $C_{13}H_{26}$), 0.87 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 134.9, 134.8, 132.1, 131.6, 130.3, 128.0, 102.5, 87.7, 76.4, 70.0, 69.0, 66.2, 58.2, 31.9, 31.5, 29.73, 29.71, 29.67, 29.65, 29.64, 29.62, 29.5, 29.3, 27.1, 22.7, 14.1; ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.70; HRMS (positive ESI) calcd for $C_{45}H_{57}ClFeNPPd$ [M−Cl]$^+$: 804.2612, found: 804.2650. Anal. Calcd for $C_{45}H_{57}ClFeNPPd\cdot CH_3OH$: C, 63.31; H, 7.05; N, 1.61. Found: C, 63.31; H, 6.59; N, 1.77%.

4.2.3.3. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)C(CH_3)=$NC_{12}H_{25}$]}(PPh_3)] 6c. Yield 86%, red solid, mp 157–160 °C; IR (KBr): 2922, 2852, 1097, 1000, 1594, 818, 748, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (6H, m, PPh_3), 7.38–7.34 (9H, m, PPh_3), 4.28 (1H, d, J=2.4 Hz, C_5H_3), 4.00–3.93 (2H, m, C_5H_3, CH_2), 3.77 (5H, s, C_5H_5), 3.61–3.56 (1H, m, CH_2), 3.22 (1H, d, J=2.2 Hz, C_5H_3), 2.16 (3H, s, CH_3–C=N), 1.83–1.82 (1H, m, CH_2), 1.51–1.21 (19H, m, CH_2, C_9H_{18}), 0.83 (3H, t, J=6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 135.0, 132.4, 131.9, 130.3, 128.0, 127.9, 101.3, 92.0, 76.2, 70.3, 67.8, 66.2, 51.2, 31.9, 30.3, 29.8, 29.7, 29.66, 29.63, 29.3, 27.3, 22.7, 14.5, 14.1; ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.41; HRMS (positive ESI) calcd for $C_{42}H_{51}ClFeNPPd$ [M−Cl]$^+$: 762.2143, found: 762.2163. Anal. Calcd for

$C_{42}H_{51}ClFeNPPd$: C, 63.17; H, 6.44; N, 1.75. Found: C, 63.15; H, 6.73; N, 2.22%.

4.2.3.4. [PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)C(CH_3)=$NC_{16}H_{33}$]}(PPh_3)] 6d. Yield 92%, red solid, mp 110–113 °C; IR (KBr): 2920, 2851, 1098, 1000, 1593, 819, 748, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (6H, m, PPh_3), 7.44–7.36 (9H, m, PPh_3), 4.33 (1H, s, C_5H_3), 4.03–3.99 (2H, m, C_5H_3, CH_2), 3.82 (5H, s, C_5H_5), 3.66–3.58 (1H, m, CH_2), 3.26 (1H, s, C_5H_3), 2.19 (3H, s, CH_3–C=N), 1.86–1.85 (1H, m, CH_2), 1.54–1.25 (27H, m, CH_2, $C_{13}H_{26}$), 0.88 (3H, t, J=6.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 135.0, 132.4, 131.9, 128.0, 101.5, 92.1, 76.3, 70.3, 67.8, 66.2, 51.2, 31.9, 30.9, 30.3, 29.9, 29.7, 29.69, 29.68, 29.64, 29.63, 29.4, 29.38, 27.4, 22.7, 14.5, 14.1; ^{31}P {^1H} NMR (162 MHz, $CDCl_3$) δ 37.80; HRMS (positive ESI) calcd for $C_{46}H_{59}ClFeNPPd$ $[M-Cl]^+$: 818.2769, found: 818.2772. Anal. Calcd for $C_{46}H_{59}ClFeNPPd\cdot 0.25C_6H_{12}$: C, 65.15; H, 7.14; N, 1.60. Found: C, 65.46; H, 7.33; N, 1.54%.

4.3. Electrochemical studies

Electrochemical data for compounds under study and related compounds were obtained by cyclic voltammetry under N_2 at 20 °C using DMF (HPLC grade) as solvent, and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, and CHI650A electrochemical analyzer using a conventional three-electrode system. The traditional three-electrode system consists of a saturated calomel reference electrode (SCE), a platinum wire auxiliary electrode, and a GC working electrode in 0.1 M tetrabutylammonium perchlorate DMF. All E^0 values reported were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials (E_{pa}+E_{pc})/2. Cyclic voltammograms of 10^{-4} M solutions of complexes (**4a–d**, **5a–d**, **5a–d**) in DMF were run. In these experimental conditions the standard error of the measured potentials is ±5 mV. In all experiments, the cyclic voltammograms were registered using scan rate varying from υ=10 to 300 mV s^{-1}.

4.4. General procedure for the Heck reaction of aryl halides with ethyl acrylate or styrene

Aryl halide (0.5 mmol), ethyl acrylate (2.0 mmol) or styrene (1.5 mmol) were combined with K_3PO_4 (1 mmol) and n-Bu_4NBr (0.5 mmol) in a small round-bottom flask. The catalyst was introduced as a DMF solution (0.0005 mmol mL^{-1}), and additional DMF was added to obtain a total volume of 1.5 mL. The reaction mixture was stirred at 140 °C for 12 h or 24 h, and then quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic phase was dried with $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator, the product was isolated by thin layer chromatography. The purified products were identified by ^1H NMR, ^{13}C NMR spectroscopy and melting points with the literature data.

4.5. General procedure for the Suzuki–Miyaura cross-coupling reaction of aryl halide with phenylboronic acid

Aryl halide (0.5 mmol) and phenylboronic acid (0.6 mmol) were combined with $K_3PO_4\cdot 7H_2O$ (1 mmol) in a small round-bottom flask. The catalyst was introduced as a toluene solution (0.000005 mmol mL^{-1}), and additional toluene was added to obtain a total volume of 2.5 mL. The reaction mixture was stirred at 110 °C for 45 min, and then quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic phase was dried with $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator, the product was isolated by thin layer chromatography. The purified products were identified by ^1H NMR, ^{13}C NMR spectroscopy and melting points with the literature data.

4.5.1. Compound 7a.[33] Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (1H, d, J=16.0 Hz), 7.51–7.49 (2H, m), 7.37–7.35 (3H, m), 6.43 (1H, d, J=16.0 Hz), 4.26 (2H, q, J=7.1 Hz), 1.33 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3.

4.5.2. Compound 7b.[33] Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (1H, d, J=16.0 Hz), 7.38 (2H, d, J=8.0 Hz), 7.15 (2H, d, J=7.8 Hz), 6.37 (1H, d, J=16.0 Hz), 4.24 (2H, q, J=7.1 Hz), 2.33 (3H, s, OCH_3) 1.32 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 144.4, 140.4, 131.5, 129.4, 127.8, 117.0, 60.1, 21.2, 14.1.

4.5.3. Compound 7c.[33] Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, d, J=16.0 Hz), 7.47 (2H, d, J=8.6 Hz), 6.89 (2H, d, J=8.6 Hz), 6.30 (1H, d, J=16.0 Hz), 4.25 (2H, q, J=7.1 Hz), 3.82 (3H, s), 1.33 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 161.3, 144.2, 129.6, 127.1, 115.7, 114.5, 60.2, 55.3, 14.3.

4.5.4. Compound 7d. Light yellow solid; mp 33–34 °C (lit.[34]31–33 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, d, J=16.1 Hz), 7.65–7.60 (4H, m), 6.50 (1H, d, J=16.1 Hz), 4.28 (2H, q, J=7.1 Hz), 1.35 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 143.1, 138.3, 132.3, 131.9, 128.6, 126.3, 121.3, 61.2, 14.7.

4.5.5. Compound 7e. White solid; mp 42–44 °C (lit.[34] 42–44 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (2H, d, J=7.1 Hz), 7.69 (1H, d, J=16.1 Hz), 7.61 (2H, d, J=7.3 Hz), 6.52 (1H, d, J=16.1 Hz), 4.28 (2H, q, J=7.1 Hz), 2.61 (3H, s), 1.35 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 166.5, 143.0, 138.8, 138.0, 128.9, 128.1, 120.8, 60.8, 26.7, 14.3.

4.5.6. Compound 7f. Yellow solid; mp 133–136 °C (lit.[35] 134–136 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.26–8.23 (2H, m), 7.73–7.66 (3H, m), 6.56 (1H, d, J=15.9 Hz), 4.30 (2H, q, J=7.1 Hz), 1.36 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 148.9, 142.0, 141.0, 129.0, 124.6, 123.0, 61.4, 14.7.

4.5.7. Compound 7g. White solid; mp 67–69 °C (lit.[36] 69–69.3 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.60 (5H, m), 6.52 (1H, d, J=16.0 Hz), 4.29 (2H, q, J=7.1 Hz), 1.35 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.1, 138.8, 132.6, 128.4, 121.9, 118.4, 113.4, 60.9, 14.3.

4.5.8. Compound 7h. Red solid; mp 72–73 °C (lit.[33] 77–78 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, d,

J=15.8 Hz), 7.41 (2H, d, J=8.8 Hz), 6.66 (2H, d, J=8.8 Hz), 6.21 (1H, d, J=15.8 Hz), 4.24 (2H, q, J=7.2 Hz), 3.00 (6H, s), 1.32 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 151.7, 145.1, 129.7, 122.4, 112.6, 111.9, 60.1, 40.2, 14.4.

4.5.9. Compound 7i.[37] Red liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (1H, s), 8.60 (1H, d, J=4.5 Hz), 7.85 (1H, d, J=7.8 Hz), 7.68 (1H, d, J=16.1 Hz), 7.35–7.32 (1H, m), 6.52 (1H, d, J=16.1 Hz), 4.28 (2H, q, J=7.1 Hz), 1.35 (3H, t, J=7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 150.7, 149.5, 140.6, 134.0, 130.1, 123.6, 120.3, 60.6, 14.1.

4.5.10. Compound 7j.[38] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (1H, d, J=15.9 Hz), 7.49–7.48 (1H, m), 7.34–7.27 (2H, m), 6.26 (1H, d, J=15.9 Hz), 4.25 (2H, q, J=7.1 Hz), 1.33 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 138.1, 137.6, 128.0, 127.0, 125.2, 117.9, 60.5, 14.4.

4.5.11. Compound 7k.[39] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (1H, d, J=15.8 Hz), 8.17 (1H, d, J=8.4 Hz), 7.84 (2H, t, J=6.6 Hz), 7.71 (1H, d, J=7.2 Hz), 7.54–7.41 (3H, m), 6.51 (1H, d, J=15.7 Hz), 4.30 (2H, q, J=7.2 Hz), 1.36 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 141.6, 133.7, 131.8, 131.4, 130.5, 128.8, 126.9, 126.2, 125.5, 125.0, 123.4, 121.0, 60.6, 14.4.

4.5.12. Compound 7l.[40] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, d, J=16.3 Hz), 8.03 (1H, d, J=8.4 Hz), 7.79 (1H, d, J=7.8 Hz), 7.71 (1H, d, J=8.4 Hz), 7.47–7.42 (2H, m), 7.31 (1H, d, J=8.4 Hz), 6.22 (1H, d, J=16.3 Hz), 4.32 (2H, q, J=7.1 Hz), 2.49 (3H, s), 1.37 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 142.6, 134.1, 132.1, 131.5, 130.8, 128.9, 128.6, 128.3, 126.6, 125.7, 125.2, 124.7, 60.7, 21.0, 14.4.

4.5.13. Compound 7m.[33] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (1H, d, J=15.9 Hz), 7.52 (2H, d, J=7.5 Hz), 7.24–7.15 (3H, m), 6.34 (1H, d, J=15.9 Hz), 4.25 (2H, q, J=7.1 Hz), 2.40 (3H, s), 1.32 (3H, t, J=7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 142.2, 137.6, 133.4, 130.8, 130.0, 126.4, 126.3, 119.2, 60.5, 19.8, 14.3.

4.5.14. Compound 8a. White solid; mp 122–124 °C (lit.[34] 120–122 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (4H, d, J=7.4 Hz), 7.36 (4H, t, J=7.6 Hz), 7.26 (2H, t, J=7.3 Hz), 7.11 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.71, 128.70, 127.6, 126.5.

4.5.15. Compound 8b. White solid; mp 117–119 °C (lit.[34] 121–122 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J=7.5 Hz), 7.40 (2H, d, J=8.0 Hz), 7.34 (2H, t, J=7.6 Hz), 7.23 (1H, t, J=7.2 Hz), 7.15 (2H, d, J=7.9 Hz), 7.09 (1H, d, J=16.4 Hz), 7.04 (1H, d, J=16.4 Hz), 2.35 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.6, 129.5, 128.7, 127.8, 127.5, 126.49, 126.46, 21.3.

4.5.16. Compound 8c. Light yellow solid; mp 131–134 °C (lit.[41] 132–133 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, J_1=7.5 Hz), 7.44 (2H, d, J_1=8.6 Hz), 7.33 (2H, t, J=7.6 Hz), 7.22 (1H, t, J=7.3 Hz), 7.06 (1H, d, J=16.3 Hz), 6.96 (1H, d, J=16.3 Hz), 6.89 (2H, d, J=8.7 Hz), 3.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 137.7, 130.2, 128.7, 128.3, 127.8, 127.3, 126.7, 126.3, 114.2, 55.4.

4.5.17. Compound 8d. White solid; mp 132–134 °C (lit.[34] 132–134 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (4H, s), 7.52 (2H, d, J=7.4 Hz), 7.38 (2H, t, J=7.5 Hz), 7.30 (1H, t, J=7.3 Hz), 7.18 (1H, d, J=16.2 Hz), 7.10 (1H, d, J=16.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.6, 131.2, 129.1, 128.8, 128.3, 127.1, 126.8, 126.6, 125.7, 122.9.

4.5.18. Compound 8e. Light yellow solid; mp 141–144 °C (lit.[42] 139.5–141.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (2H, d, J=8.3 Hz), 7.59–7.53 (4H, m), 7.38 (2H, t, J=7.5 Hz), 7.30 (1H, t, J=7.3 Hz), 7.23 (1H, d, J=16.5 Hz), 7.13 (1H, d, J=16.5 Hz), 2.60 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 142.0, 136.7, 136.0, 131.5, 128.9, 128.8, 128.3, 127.5, 126.9, 126.5, 26.6.

4.5.19. Compound 8f. Light yellow solid; mp 155–157 °C (lit.[43] 156–157 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (2H, d, J=8.7 Hz), 7.63 (2H, d, J=8.7 Hz), 7.55 (2H, d, J=7.4 Hz), 7.42–7.31 (3H, m), 7.27 (1H, d, J=16.3 Hz), 7.14 (1H, d, J=16.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 143.9, 136.2, 133.3, 128.9, 128.85, 127.0, 126.9, 126.3, 124.1.

4.5.20. Compound 8g. Light yellow solid; mp 114–116 °C (lit.[34] 117–119 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.52 (6H, m), 7.39 (2H, t, J=7.4 Hz), 7.32 (1H, t, J=7.2 Hz), 7.21 (1H, d, J=16.3 Hz), 7.08 (1H, d, J=16.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 136.3, 132.5, 132.4, 128.9, 128.7, 127.0, 126.9, 126.8, 119.1, 110.6.

4.5.21. Compound 8h. Red solid; mp 145–147 °C (lit.[44] 144–146 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, J=7.5 Hz), 7.41 (2H, d, J=8.7 Hz), 7.32 (2H, t, J=7.6 Hz), 7.19 (1H, t, J=7.3 Hz), 7.05 (1H, d, J=16.3 Hz), 6.91 (1H, d, J=16.3 Hz), 6.72 (2H, d, J=8.2 Hz), 2.97 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 138.6, 129.2, 129.0, 128.0, 127.1, 126.4, 124.9, 112.9, 41.0.

4.5.22. Compound 8i. Light yellow solid; mp 78–80 °C (lit.[44] 81–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (1H, s), 8.48 (1H, d, J=4.7 Hz), 7.82 (1H, d, J=8.0 Hz), 7.52 (2H, d, J=7.4 Hz), 7.39–7.26 (4H, m), 7.18 (1H, d, J=16.4 Hz), 7.06 (1H, d, J=16.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 137.1, 133.4, 133.1, 131.3, 129.2, 128.6, 127.1, 125.3, 124.0.

4.5.23. Compound 8j. Light red solid; mp 118–121 °C (lit.[45] 126–128 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, J=7.5 Hz), 7.36–7.30 (4H, m), 7.26–7.22 (2H, m), 7.12 (1H, d, J=16.3 Hz), 6.95 (1H, d, J=16.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 137.4, 128.7, 127.5, 126.3, 126.2, 125.0, 122.9, 122.4.

4.5.24. Compound 8k. White solid; mp 68–69 °C (lit.[44] 71–72 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (1H, d, J=8.0 Hz), 7.89–7.72 (4H, m), 7.60–7.28 (8H, m), 7.14 (1H, d, J=16.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 135.1, 133.8, 131.8, 131.5, 128.8, 128.7, 128.1, 127.9, 126.8, 126.2, 125.9, 125.8, 123.8, 123.7.

4.5.25. Compound 8l.[46] Light yellow solid; mp 74–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, d, J=8.7 Hz), 7.79 (1H, d, J=7.2 Hz), 7.68 (1H, d, J=8.4 Hz), 7.57 (2H, d, J=7.4 Hz), 7.46–7.27 (7H, m), 6.75 (1H, d, J=16.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.6, 133.7, 133.3, 132.3, 132.2, 128.9, 128.8, 128.1, 127.8, 127.0, 126.4, 125.9, 125.8, 125.3, 124.9, 21.0.

4.5.26. Compound 8m.[44] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, d, J=7.1 Hz), 7.49 (2H, d, J=7.6 Hz), 7.35–7.12 (7H, m), 6.97 (1H, d, J=16.1 Hz), 2.40 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.3, 135.7, 130.4, 130.0, 128.6, 127.54, 127.51, 126.5, 126.2, 125.3, 19.9.

4.5.27. Compound 9a. Light yellow solid; mp 111–113 °C (lit.[48] 111–112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (2H, d, J=8.8 Hz), 7.74 (2H, d, J=8.8 Hz), 7.63 (2H, d, J=7.0 Hz), 7.52–7.45 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

4.5.28. Compound 9b. White solid; mp 117–118 °C (lit.[49] 116–118 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (2H, d, J=8.3 Hz), 7.69–7.62 (4H, m), 7.49–7.40 (3H, m), 2.64 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.8, 139.8, 135.8, 128.9, 128.89, 128.21, 127.25, 127.20, 26.7.

4.5.29. Compound 9c. White solid; mp 69–70 °C (lit.[47] 68–71 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (4H, m), 7.45–7.42 (4H, m), 7.36–7.32 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2.

4.5.30. Compound 9d.[50] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.80 (3H, m), 7.50–7.36 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.2, 133.8, 131.6, 130.0, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.3.

4.5.31. Compound 9e. White solid; mp 43–44 °C (lit.[48] 43–44 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.56 (2H, m), 7.49 (2H, d, J=8.1 Hz), 7.42 (2H, t, J=7.5 Hz), 7.33–7.30 (1H, m), 7.24 (2H, d, J=7.9 Hz), 2.39 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0, 129.4, 128.7, 126.9, 21.1.

4.5.32. Compound 9f.[51] Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.39 (2H, m), 7.35–7.31 (3H, m), 7.26–7.23 (4H, m), 2.27 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5.

4.5.33. Compound 9g. White solid; mp 117–119 °C (lit.[49] 118–120 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.49 (4H, m), 7.41–7.37 (2H, m), 7.27–7.23 (1H, m), 6.83 (2H, d, J=8.4 Hz), 2.99 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 141.2, 129.2, 128.6, 127.7, 126.3, 126.0, 113.0, 40.7.

4.6. Structure determination

Crystals of **6c**, **6d** were obtained by recrystallization from CH_2Cl_2/petroleum ether/cyclohexane solution. Intensity data of **6c**, **6d**·C_6H_{12} were measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite monochromated Mo Kα radiation (λ=0.71073 Å) at 291(2) K. All data were corrected using $\omega-2\theta$ scan technique and corrected for Lorenz and polarization factors. The structures were solved by direct methods[52] and expanded using Fourier techniques and refined by full-matrix least-squares methods. All non-hydrogen atoms were described anisotropically, and hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN[28] crystallographic software package of Molecular Structure Corporation. Crystal data and detailed results of refinement are summarized in Table 1.

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