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Study on the Heck reaction promoted by carbene adduct of cyclopalladated ferrocenylimine and the related reaction mechanism

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ABSTRACT

Carbene adduct of cyclopalladated ferrocenylimine has been successfully applied to Heck reaction of various aryl bromides with olefins. On the basis of kinetic studies, in situ ^{13}C NMR spectra investigations and Hg poisoning experiments, it was proposed that the Heck reaction catalyzed by carbene adduct of cyclopalladated ferrocenylimine proceeded through a classical Pd(0)/Pd(II) cycle and such palladacycle was only a reservoir of the catalytically active Pd(0) species.

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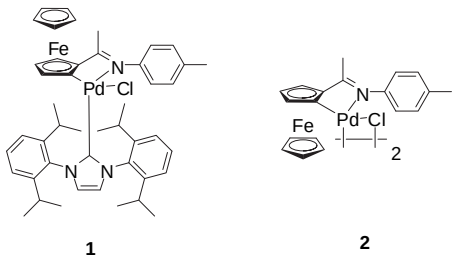
1. Introduction

The palladium-catalyzed Heck reaction (arylation of olefins with aryl halides) was discovered more than 35 years ago[1] and still remains as one of the most prominent strategies for carbon–carbon bond formation, especially in the synthesis of natural products,[2] fine chemicals and pharmaceuticals.[3] Palladacycles emerging as a new family of palladium catalysts have been widely used in the Heck reaction[4] because of their facile synthesis, thermal stability, and structural versatility.[5] Since the first application of palladacycles in the coupling reaction, the real catalytic cycle has been debated vigorously. A Pd(II)/Pd(IV) cycle was outlined by Shaw firstly.[6,7] Recently, Pd(IV) complexes were obtained by oxidation of Pd(II) with X_2 and $[Ph_2I]OTf$.[8,9] Andersson reported Heck reaction catalyzed by PCP pincer palladacycles and hypothesized a Pd(II)/Pd(IV) catalytic cycle.[10] However, there was no clear-cut experimental evidence for this hypothesis. On the other hand, it has been accepted commonly that Heck reaction promoted by palladacycle proceeds through Pd(0)/Pd(II) catalytic cycle and the palladacycle actually acted as a reservoir of the 'real catalyst'.[11] Beletskaya et al. studied a variety of SC, PC, and NC palladacycles as catalysts for Heck reaction, which results strongly supported a Pd(0)/Pd(II) catalytic cycle and the active Pd(0) species was proposed as Pd-nanoparticle.[12] Moreover, Rocaboy and Gladysz reported that cyclopalladated fluorous imines were precatalysts and released highly active soluble palladium colloids during Heck reaction based on the studies of kinetics and transmission electron microscopy (TEM).[13]

Over the past decade, part of our research effort has focused on the synthesis and applications of cyclopalladated ferrocenylimines in organic reactions.[14] Recently we synthesized the carbene adduct of cyclopalladated ferrocenylimine **1** from dimer **2** (Scheme 1), and found that complex **1** exhibited high activity in Buchwald–Hartwig amination reaction[14b], Suzuki–Miyaura et al.[14d] and Kumada et al.[14e] coupling of sterically hindered aryl chlorides, which prompted us to explore the potential application of the complex **1** in Heck reaction. Herein, we report complex **1** as a catalyst precursor for the Heck reaction of aryl bromides and investigation on the reaction mechanism through kinetic studies, in situ ^{13}C NMR spectra research and Hg poisoning experiments. It was notable that the optimized reaction conditions were applied to vinyl bromides, which were seldom used as substrates for the Heck reaction due to their less reaction activity.



1 2

Scheme 1. Carbene adduct of cyclopalladated ferrocenylimine **1** and dimer **2**.

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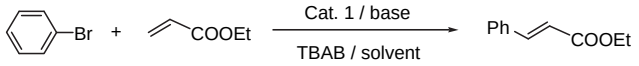
2. Results and discussion

2.1. Catalytic activity of complex 1 in Heck reaction

We initially investigated the effect of bases and solvents on Heck reaction using bromobenzene and ethyl acrylate as substrates (Table 1). K_3PO_4 was chosen as base in terms of the cost (entry 9), although Cs_2CO_3 and Et_3N also gave the excellent yields (entries 3 and 7). DMF was the best one among the solvents screened (entries 9–11).

Table 1
Effect of the bases and solvents on Heck reaction of bromobenzene with ethyl acrylate



Entry[a]	Base	Solvent	T (°C)	Yield[b] (%)
1	NaOAc	DMF	140	81
2	K_2CO_3	DMF	140	83
3	Cs_2CO_3	DMF	140	92
4	CsF	DMF	140	87
5	Na_2CO_3	DMF	140	89
6	$KF{\cdot}2H_2O$	DMF	140	70
7	Et_3N	DMF	140	94
8	KOH	DMF	140	86
9	K_3PO_4	DMF	140	>99
10	K_3PO_4	Toluene	115	67
11	K_3PO_4	1,4-dioxane	100	32

[a] Reaction conditions: bromobenzene (0.5 mmol), ethyl acrylate (0.75 mmol), cat. 1 (5.0 mmol %), TBAB (0.5 mmol), base (1 mmol), solvent (1.0 mL).
[b] Isolated yields based on bromobenzene.

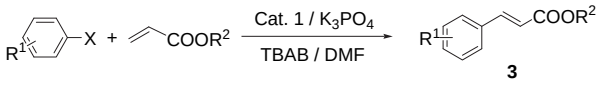
Under the optimized reaction conditions, we extended the scope of substrates (Table 2). The turnover number of $2.0X10^6$ was obtained in reaction of iodobenzene with ethyl acrylate in the presence of 0.05 mmol % complex **1** (entry 1). For activated aryl bromides and non-activated aryl bromides with electron-donating groups, excellent yields were obtained in all cases (entries 4–8). Reaction of heteroaryl bromides, *ortho*-substituted aryl bromides, 1-bromonaphthalene and activated aryl chloride also afforded the corresponding products in good to excellent yields (entries 9–14). For the reaction of bromobenzene with butyl acrylate and 2-ethylhexyl acrylate, 83% and 86% yields were obtained, respectively (entries 15 and 16).

The reaction of bromides with styrene was also investigated (Table 3). When aryl and heterocyclic bromides were used as substrates, good to excellent yields were obtained (entries 1–8). Importantly, unactivated vinyl bromides were also applied to such Heck reaction system, providing the desired double vinyl products. Reaction of 1-(2-bromovinyl)-benzene and 2-bromo-1,1-diphenylethylene with styrene afforded the products in 81% and 97% yields, respectively (entries 9 and 10). It is notable that the coupling reactions of vinyl halides with olefins have been reported rarely so far.[15] Moreover, the reaction of 2-bromo-1,1-diphenylethylene with styrene is firstly reported as we know. The reaction of bromobenzene with the pharmaceutically functional group also proceeded smoothly (entry 11). These results showed that complex **1** was highly efficient for the reaction of diverse bromides with olefins.

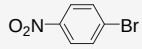
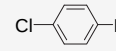
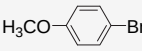
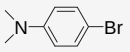
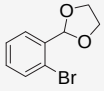
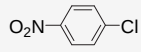
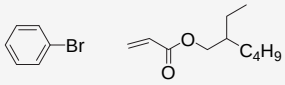
2.2. Mechanistic probes

In the reaction process, there was no visible indication of Pd black formation. The complex **1** was recovered in isolated 99% yield after aryl bromides were consumed completely, and the yield decreased dramatically when the loading of catalyst was reduced to the original amount of 1%. However, these results did not mean that complex **1** itself was the real catalyst. For exploring the mechanism of the Heck reaction promoted by cyclopalladated ferrocenylimines, we performed the experiments as follows.

Table 2
Heck reaction of aryl halides with olefins



3

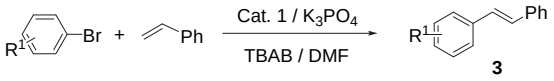
Entry[a]	Aryl halide	Olefin	Catalyst (mmol %)	Time (h)	Product	Yield[b] (%)
1		COOEt	0.05	24	**3a**	99
2		COOEt	5.0	24	**3a**	>99
3		COOEt	5.0	4	**3a**	>99
4		COOEt	1.0	2	**3b**	95
5		COOEt	1.0	2	**3c**	98
6		COOEt	5.0	4	**3d**	97
7		COOEt	5.0	5	**3e**	97
8		COOEt	5.0	5	**3f**	98
9		COOEt	5.0	4	**3g**	99
10		COOEt	5.0	4	**3h**	85
11		COOEt	5.0	4	**3i**	80
12		COOEt	5.0	5	**3j**	97
13		COOEt	5.0	4	**3k**	90
14		COOEt	100	24	**3c**	81
15		$COOC_4H_9$	5.0	4	**3l**	83
16			5.0	4	**3m**	86

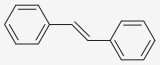
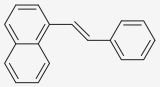
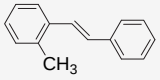
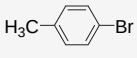
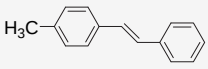
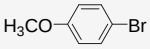
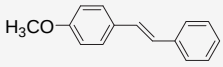
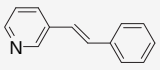
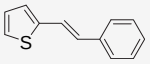
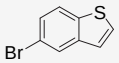
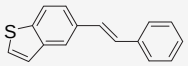
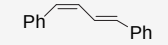
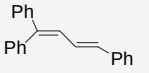
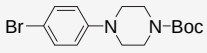
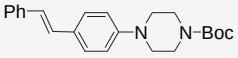
[a] Reaction conditions: aryl halide (0.5 mmol), olefin (0.75 mmol), TBAB (0.5 mmol), K_3PO_4 (1 mmol), DMF (1.0 mL), 140 °C.
[b] Isolated yields based on aryl halides in two runs.

2.3. Kinetic studies

The parallel experiments were performed using PhBr (0.5 mmol), ethyl acrylate (0.75 mmol), K_3PO_4 (1.0 mmol), TBAB (0.5 mmol), and complex **1** or dimer **2** (0.001 mmol) in DMF (5 mL). Figures 1 and 2 revealed that complex **1** showed higher activity than dimmer **2**. Conversion of 96% was achieved after 4 h for complex **1**, while only 78% conversion was obtained for dimer **2** after 25 h. Moreover, both of complex **1** and dimer **2** exhibited induction period. The induction period of complex **1** was obviously

Table 3
Heck reaction of bromides with styrene



Entry[a]	Aryl halide	Time (h)	Product	Yield[b] (%)
1		4		**3n** 96
2		4		**3o** 98
3		5		**3p** 94
4		5		**3q** 88
5		5		**3r** 80
6		5		**3s** 88
7		5		**3t** 66
8		5		**3u** 95
9		5		**3v** 81
10		5		**3w** 97
11		5		**3x** 75

[a] Reaction conditions:bromides (0.5 mmol), styrene (0.75 mmol), Cat. (5.0 mmol %), TBAB (0.5 mmol), K_3PO_4 (1 mmol), DMF (1.0 mL), 140 °C.
[b] Isolated yields based on bromides in two runs.

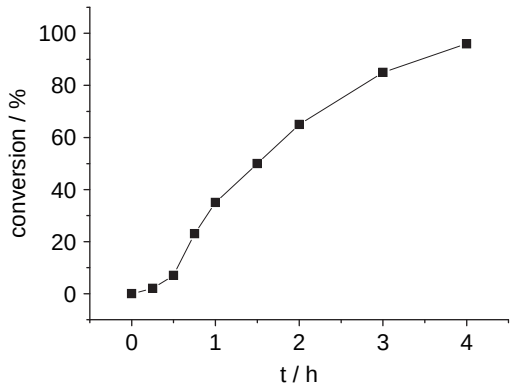


Figure 1. Conversion versus reaction time in the presence of complex **1**.

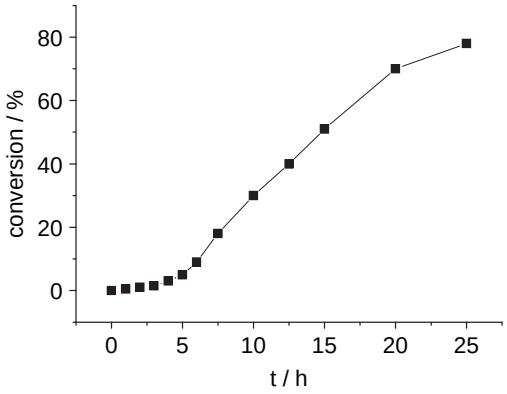


Figure 2. Conversion versus reaction time in the presence of dimer **2**.

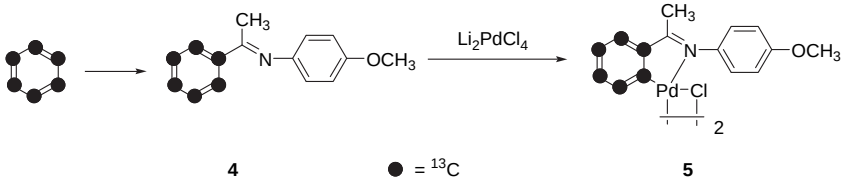
shorter (0.5 h) than that of dimer **2** (5 h). After the first catalytic cycle completed, a second catalytic cycle was conducted by directly adding the same substrates and the induction period was not observed. These results indicated that both of complex **1** and dimer **2** were catalyst precursors rather than real catalysts. NHC ligand may promote the release of 'real catalyst' species from palladacycle, and stabilize the active species under the reaction conditions to suppress the Pd black formation.

2.4. ^{13}C NMR studies

To obtain more direct information about the Pd–C bond of palladacycle in the Heck reaction, ^{13}C-enriched palladacycle **5** was synthesized (Scheme 2). We carried out similar reactions as that for kinetic study and in situ monitored by ^{13}C NMR spectra. In comparison with imine **4**, signals of the six ^{13}C-enriched carbon atoms in palladacycle **5** showed significant shifts (Fig. 3a vs 3d). Two triplets in low field disappeared when reaction time reached 10 min (Fig. 3c), and the chemical shifts did not change any more until the reaction was quenched. Moreover, the ^{13}C NMR spectrum in Figure 3c was different from that in Figure 3d. These results indicated that the Pd–C bond in palladacycle **5** cleaved during the reaction process and Pd atom was coordinated with N atom from ferrocenylimine.

2.5. Hg poisoning experiments

We also carried out the Hg poisoning experiments. The experiments were preformed using PhBr (0.5 mmol), ethyl acrylate (0.75 mmol), K_3PO_4 (1.0 mmol), TBAB (0.5 mmol), complex **1** or dimer **2** (0.001 mmol), and an excess (300 equiv to the palladacycle) of Hg(0) in DMF (5 mL). Hg(0) was added to the reaction mixture at t=0 min, and no product was observed by using complex **1** or **2**. Hg(0) was added into the reaction mixture at a certain time after a catalytically active species formed. For the reaction in the presence of complex **1**, Hg(0) was added at t=30 min and Hg(0) was added at t=7.5 h for the reaction in the presence of **2** (Fig. 4). The catalytic activity of the palladacycles was quenched instantly for both cases. These results were consistent with the above



Scheme 2. Synthesis of palladacycle **5**.

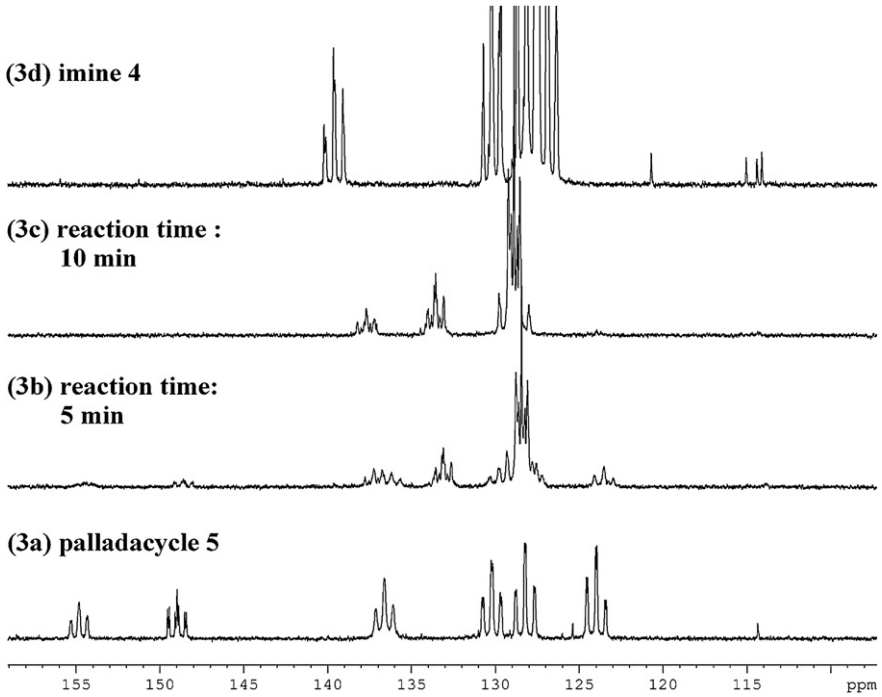


Figure 3. In situ monitoring of the Heck reaction promoted by palladacycle **5.** Reaction conditions: ethyl acrylate (0.024 mmol), 2-bromonitrobenzene (0.02 mmol), Et_3N (0.03 mmol), palladacycle **5** (0.02 mmol), and DMF (400 μL), 140 °C.

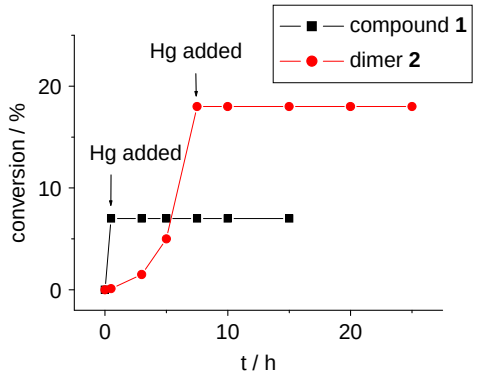


Figure 4. Conversion versus reaction time in the presence of complex **1** (Hg was added at 0.5 h) and dimer **2** (Hg was added at 7.5 h).

experiments, and further confirmed that a catalytically active Pd(0) intermediate existed during the reaction.

3. Conclusion

In summary, the carbene adduct of cyclopalladated ferrocenylimine **1** was a highly efficient precatalyst for Heck reaction of various bromides with olefins and the good to excellent yields were obtained. The kinetic studies, in situ ^{13}C NMR investigations and Hg poisoning experiments suggested that cyclopalladated ferrocenylimine was a precatalyst and Heck reaction promoted by palladacycles proceeded via a classical Pd(0)/Pd(II) cycle.

4. Experimental section

4.1. General

Melting points were measured on a XT-5 microscopic apparatus. GC analyses were performed on Agilent 4890D gas chromatograph. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. High-resolution mass spectra were measured on a Waters Q-Tof Micro spectrometer.

All solvents were purified by the standard methods. The palladacyclic dimer **2**,[16] imidazolium salt,[17] and complex **1**[14b] were prepared according to the reported procedures. Other chemicals were reagent grade and used without further purification.

4.2. General procedure for Heck reaction

A mixture of aryl halide (0.5 mmol), olefin (0.75 mmol), TBAB (0.5 mmol), K_3PO_4 (1 mmol), complex **1** (5.0 mmol %), and DMF (1.0 mL) was put into a preheated oil bath for an appropriate period of time under nitrogen. After the reaction was finished, the reaction mixture was cooled to room temperature, filtered through a short silica column and washed with ethyl acetate. Then the combined filtrates were concentrated in vacuo and the residue was purified by flash chromatography (eluent: ethylacetate/petroleum ether). The products were characterized by ^1H NMR and ^{13}C NMR. New compounds were confirmed by high-resolution mass spectra.

*4.2.1. Ethyl cinnamate (**3a**)*[18]. Light yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J=16.0 Hz, 1H), 7.53–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.44 (d, J=15.9 Hz, 1H), 4.29–4.23 (m, 2H), 1.35–1.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.5, 134.4, 130.2, 128.8, 128.0, 118.2, 60.5, 14.3.

*4.2.2. 3-(2-Nitrophenyl)-2-propenoic acid ethyl ester (**3b**)*[19]. Yellow solid, mp 41–43 °C (lit.[19] 42–43 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J=15.8 Hz, 1H), 8.05 (d, J=8.3 Hz, 1H), 7.66–7.64 (m, 2H), 7.57–7.53 (m, 1H), 6.37 (d, J=15.8 Hz, 1H), 4.32–4.27 (m, 2H), 1.37–1.33(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.8, 133.5, 130.6, 130.2, 129.1, 124.9, 123.3, 60.9, 14.2.

*4.2.3. 3-(4-Nitrophenyl)-2-propenoic acid ethyl ester (**3c**)*[20]. Yellow solid, mp 133–135 °C (lit.[20] 134–136 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 8.27–8.24 (m, 2H), 7.73–7.67 (m, 3H), 6.56 (d, J=16.0 Hz, 1H),

4.33–4.27 (m, 2H), 1.38–1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 148.4, 141.6, 140.5, 128.6, 124.2, 122.5, 61.0, 14.2.

*4.2.4. 3-(4-Chlorophenyl)-2-propenoic acid ethyl ester (**3d**)*[21]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J=16.0 Hz, 1H), 7.46–7.44 (m, 2H), 7.37–7.34 (m, 3H), 6.40 (d, J=16.1 Hz, 1H), 4.29–4.24 (m, 2H), 1.35–1.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 143.1, 136.1, 132.9, 129.2, 129.1, 118.8, 60.6, 14.3.

*4.2.5. 3-(4-Methoxyphenyl)-2-propenoic acid ethyl ester (**3e**)*[18]. Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J=16.0 Hz, 1H), 7.49–7.46 (m, 2H), 6.91–6.89 (m, 2H), 6.31 (d, J=15.9 Hz, 1H), 4.26–4.24 (m, 2H), 3.83 (s, 3H), 1.35–1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 161.3, 144.2, 129.7, 127.2, 115.7, 114.3, 55.3, 14.3.

*4.2.6. 3-[4-(Dimethylamino)phenyl]-2-propenoic acid ester (**3f**)*[18]. Yellow solid, mp 72–73 °C (lit.[18] 77–78 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J=15.8 Hz, 1H), 7.43–7.41 (m, 2H), 6.68–6.65 (m, 2H), 6.22 (d, J=15.7 Hz, 1H), 4.26–4.21 (m, 2H), 3.01 (s, 6H), 1.34–1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 151.7, 145.1, 129.7, 122.2, 112.6, 111.8, 60.0, 40.1, 14.4.

*4.2.7. 3-(Pyridin-3-yl)acrylic acid ethyl ester (**3g**)*[22]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.61–8.60 (m, 1H), 7.86–7.83 (m, 1H), 7.68 (d, J=16.1 Hz, 1H), 7.36–7.31 (m, 1H), 6.52 (d, J=16.1 Hz, 1H), 4.31–4.26 (m, 2H), 1.37–1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 150.9, 149.7, 140.8, 134.1, 130.1, 123.7, 120.4, 60.7, 14.2.

*4.2.8. 3-(2-Thienyl)acrylic acid ethyl ester (**3h**)*[23]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J=15.7 Hz, 1H), 7.36–7.35 (m, 1H), 7.27–7.23 (m, 1H), 7.05–7.03 (m, 1H), 6.23 (d, J=15.7 Hz, 1H), 4.27–4.21 (m, 2H), 1.34–1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 139.5, 137.0, 130.9, 128.4, 128.0, 117.0, 60.5, 14.3.

*4.2.9. 3-[2-(1,3-Dioxolan-2-yl)phenyl]-2-propenoic acid ethyl ester (**3i**)*[24]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J=15.9 Hz, 1H), 7.62–7.59 (m, 2H), 7.40–7.38 (m, 2H), 6.38 (d, J=15.9 Hz, 1H), 6.03 (s, 1H), 4.29–4.24 (m, 2H), 4.20–4.17 (m, 2H), 4.12–4.06 (m, 2H), 1.36–1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.7, 136.0, 133.7, 129.8, 129.4, 126.97, 126.94, 120.4, 101.9, 65.5, 65.4, 60.5, 14.3.

*4.2.10. 3-(2-Methylphenyl)-2-propenoic acid ethyl ester (**3j**)*[18]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=15.9 Hz, 1H), 7.54 (d, J=7.4 Hz, 1H), 7.26–7.24 (m, 1H), 7.21–7.18 (m, 2H), 6.36 (d, J=16.0 Hz, 1H), 4.29–4.24 (m, 2H), 2.43 (s, 3H), 1.36–1.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 142.2, 137.6, 133.4, 130.8, 130.0, 126.4, 126.3, 119.3, 60.5, 19.8, 14.3.

*4.2.11. 1-Naphthaleneacrylic acid ethyl ester (**3k**)*[25]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J=15.7 Hz, 1H), 8.18 (d, J=8.2 Hz, 1H), 7.88–7.84 (m, 2H), 7.73 (d, J=7.1 Hz, 1H), 7.56–7.46 (m, 3H), 6.52 (d, J=15.9 Hz, 1H), 4.33–4.28 (m, 2H), 1.38–1.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.5, 133.6, 131.7, 131.3, 130.4, 128.6, 126.8, 126.1, 125.4, 125.0, 123.3, 120.8, 60.5, 14.3.

*4.2.12. 3-Phenyl-2-propenoic acid butyl ester (**3l**)*[26]. Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J=16.0 Hz, 1H), 7.52–7.49 (m, 2H), 7.37–7.34 (m, 3H), 6.44 (d, J=16.0 Hz, 1H), 4.22–4.19 (m, 2H), 1.72–1.65 (m, 2H), 1.48–1.39 (m, 2H), 0.98–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.5, 134.4, 130.2, 128.9, 128.0, 118.2, 64.4, 30.8, 19.2, 13.8.

*4.2.13. 2-Ethylhexyl cinnamate (**3m**)*[27]. Yellow liquid; ^{1}H NMR (400 MHz, CDCl3) δ 7.68 (d, J=16.0 Hz, 1H), 7.55–7.52 (m, 2H), 7.40–7.38 (m, 3H), 6.45 (d, J=16.1 Hz, 1H), 4.14–4.10 (m, 2H), 1.66–1.60 (m, 1H), 1.44–1.40 (m, 2H), 1.36–1.30 (m, 6H), 0.95–0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 143.5, 133.4, 129.2, 127.8, 127.0, 117.3, 66.0, 37.8, 29.4, 28.0, 22.8, 21.9, 13.0, 10.0.

*4.2.14. 1,2-Diphenylethylene (**3n**)*[28]. White solid, mp 122–124 °C (lit.[28] 120–122 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 4H), 7.40–7.30 (m, 4H), 7.30–7.26 (m, 2H), 7.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.70, 128.67, 127.6, 126.5.

*4.2.15. 1-(2-Phenylethenyl)naphthalene (**3o**)*[28]. White solid, mp 70–71 °C (lit.[28] 71–72 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J=8.2 Hz, 1H), 7.88–7.71 (m, 4H), 7.59–7.26 (m, 8H), 7.12 (d, J=16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.0, 132.8, 130.8, 130.4, 127.8, 127.6, 127.1, 126.8, 125.7, 125.6, 125.1, 124.9, 124.8, 124.7, 122.8, 122.6.

*4.2.16. 1-Methyl-2-(2-phenylethenyl)benzene (**3p**)*[29]. Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J=7.1 Hz, 1H), 7.50 (d, J=7.8 Hz, 2H), 7.36–7.15 (m, 7H), 6.98 (d, J=16.1 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.5, 135.9, 130.5, 130.1, 128.8, 128.4, 127.7, 127.6, 126.65, 126.62, 126.56, 126.3, 125.4, 20.0.

*4.2.17. 1-Methyl-4-(2-phenylethenyl)benzene (**3q**)*[28]. White solid, mp 119–122 °C (lit.[28] 121–122 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J=8.0 Hz, 2H), 7.41 (d, J=8.0 Hz, 2H), 7.37–7.33 (m, 2H), 7.26–7.24 (m, 1H), 7.16 (d, J=8.0 Hz, 2H), 7.08–7.07 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.6, 129.4, 128.7, 128.6, 127.7, 127.4, 126.43, 126.40, 21.3.

*4.2.18. 1-Methoxy-4-(2-phenylethenyl)benzene (**3r**)*[30]. Light yellow solid, mp 131–134 °C (lit.[30] 132–133 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 4H), 7.35–7.31 (m, 2H), 7.24–7.20 (m, 1H), 7.06 (d, J=16.3 Hz, 1H), 6.96 (d, J=16.3 Hz, 1H), 6.90–6.87 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 137.7, 130.2, 128.7, 128.2, 127.8, 127.2, 126.6, 126.3, 114.2, 55.3.

*4.2.19. 3-Styrylpyridine (**3s**)*[29]. Light yellow solid, mp 80–82 °C (lit.[29] 81–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.48 (d, J=4.0 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.52 (d, J=7.5 Hz, 2H), 7.39–7.35 (m, 2H), 7.31–7.25 (m, 2H), 7.16 (d, J=16.4 Hz, 1H), 7.06 (d, J=16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 136.6, 133.0, 132.6, 130.8, 128.8, 128.2, 126.7, 124.9, 123.5.

*4.2.20. 2-Styrylthiophene (**3t**)*[31]. Light yellow solid, mp 111–112 °C (lit.[31] 110–112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2H), 7.39–7.35 (m, 2H), 7.28–7.21 (m, 3H), 7.10–7.09 (m, 1H), 7.03–7.02 (m, 1H), 6.96 (d, J=16.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.0, 128.8, 128.72, 128.69, 128.3, 127.6, 126.35, 126.31, 126.26, 126.2, 124.4, 121.8.

*4.2.21. 5-Styrylbenzothiophene (**3u**).* Light yellow solid, mp 137–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (d, J=8.4 Hz, 1H), 7.58–7.53 (m, 3H), 7.45 (d, J=5.4 Hz, 1H), 7.39–7.33 (m, 3H), 7.31–7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.9, 137.4, 133.8, 128.8, 128.7, 128.3, 127.6, 127.0, 126.5, 124.0, 122.6, 122.5, 121.9; HRMS (positive ESI) calcd for $C_{16}H_{12}S$ $[M+H]^+$: 237.0738, found: 237.0733.

*4.2.22. 1,1′-(1,3-Butadiene-1,4-diyl)bis-benzene (**3v**)*[32]. Light yellow solid, mp 151–153 °C (lit.[32] 153 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 4H), 7.35–7.31 (m, 4H), 7.25–7.23 (m, 2H), 6.98–6.94 (m, 2H), 6.69–6.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 132.8, 129.2, 128.6, 127.6, 126.4.

*4.2.23. 1,1′,1″-(1,3-Butadiene-1-yl-4-ylidene)tris-benzene (**3w**)*[33]. Light yellow solid, mp 96–97 °C (lit.[33] 96.5–97.5 °C); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.45–7.36 (m, 3H), 7.32–7.24 (m, 11H), 7.20–7.17 (m, 1H), 6.94–6.86 (m, 2H), 6.78–6.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.2, 139.7, 137.4, 133.8, 130.6, 128.5, 128.24, 128.22, 128.20, 127.6, 127.5, 127.4, 127.1, 126.4.

*4.2.24. tert-Butyl-4-(4-styrylphenyl)piperazine-1-carboxylate (**3x**).* Light yellow solid, mp 176–178 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J=7.8 Hz, 2H), 7.44 (d, J=8.7 Hz, 2H), 7.36–7.32 (m, 2H), 7.24–7.20 (m, 1H), 7.07–6.95 (m, 2H), 6.91 (d, J=8.5 Hz, 2H), 3.60–3.58 (m, 4H), 3.18–3.16 (m, 4H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 137.7, 128.6, 128.2, 127.5, 127.1, 126.2, 126.1, 116.3, 80.0, 49.0, 28.4; HRMS (positive ESI) calcd for $C_{23}H_{28}N_2O_2$ $[M+H]^+$: 365.2229, found: 365.2228.

4.3. Procedure of kinetic experiments

The parallel experiments were performed using PhBr (0.5 mmol), ethyl acrylate (0.75 mmol), K_3PO_4 (1.0 mmol), TBAB (0.5 mmol), and complex **1** or dimer **2** (0.001 mmol) in DMF (5 mL). The reactions were monitored by GC.

4.4. ^{13}C NMR experiments

*4.4.1. Procedure for preparation of imine **4** (Scheme 2).* ^{13}C-enriched hypnone (^{13}C-enriched in benzene) was prepared from ^{13}C-benzene by Friedel–Crafts acylation reaction. Then a mixture of ^{13}C-enriched hypnone (^{13}C-enriched in benzene) (2.0 mmol) and 4-methoxyaniline (2.01 mmol) was dissolved in 30 mL of dry toluene and refluxed under nitrogen atmosphere in the presence of molecular sieves (4 Å, 1.5 g). After 4 h, the reaction mixture was carefully filtered and the filtrate was reduced to dryness. The imine **4** was re-crystallized from cold CH_3OH (yield 86%, yellow solid). HRMS (positive ESI) calcd for $C_9{}^{13}C_6H_{15}NO$ $[M+H]^+$: 232.1388, found: 232.1392.

*4.4.2. Procedure for preparation of palladacycle **5**.* A solution of Li_2PdCl_4 in methanol (10 mL) was added to a solution of 1 equiv of NaOAc and imine **4**. The mixture was stirred at room temperature for 24 h, then filtrated and re-crystallized from CH_3OH. Palladacycle **5** (yellow solid) was obtained in 78% yield. HRMS (positive ESI) calcd for $C_{18}{}^{13}C_{12}H_{28}Cl_2N_2O_2Pd_2$ $[M-Cl]^+$: 742.0000, found: 742.0008.

4.4.3. Procedure of ^{13}C NMR experiments. A solution of ethyl acrylate (0.024 mmol), 2-bromonitrobenzene (0.02 mmol), Et_3N (0.03 mmol), and palladacycle **5** (0.02 mmol) in DMF (400 μL) were monitored by ^{13}C NMR when −60 °C, 25 °C, 50 °C, 80 °C, and 140 °C, respectively.

4.5. Procedure of Hg poisoning experiments

An excess (300 equiv to the palladacycle) of Hg(0) was added into the reaction mixture of PhBr (0.5 mmol), ethyl acrylate (0.75 mmol), K_3PO_4 (1.0 mmol), TBAB (0.5 mmol), and complex **1** (0.001 mmol) in DMF (5 mL) at t=0, 0.5 h, respectively.

An excess (300 equiv to the palladacycle) of Hg(0) was added into the reaction mixture of PhBr (0.5 mmol), ethyl acrylate (0.75 mmol), K_3PO_4 (1.0 mmol), TBAB (0.5 mmol), and dimer **2** (0.001 mmol) in DMF (5 mL) at t=0, 7.5 h, respectively.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.04.040.

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