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Fluorous Oxime Palladacycle: A Precatalyst for Carbon−Carbon Coupling Reactions in Aqueous and Organic Medium

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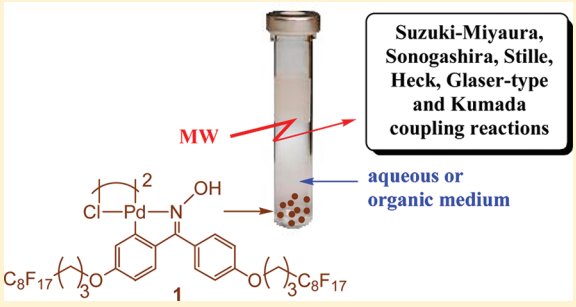
Supporting Information

ABSTRACT: To facilitate precatalyst recovery and reuse, we have developed a fluorous, oxime-based palladacycle **1** and demonstrated that it is a very efficient and versatile precatalyst for a wide range of carbon−carbon bond formation reactions (Suzuki−Miyaura, Sonogashira, Stille, Heck, Glaser-type, and Kumada) in either aqueous or organic medium under microwave irradiation. Palladacycle **1** could be recovered through F-SPE in various coupling reactions with recovery ranging from 84 to 95% for the first cycle. Inductively coupled plasma optical emission spectrometry (ICP-OES) analyses of the Pd content in the crude product from each class of transformation indicated extremely low levels of leaching and the palladacycle could be reused four to five times without significant loss of activity.



INTRODUCTION

Palladium-catalyzed carbon−carbon bond-forming reactions are one of the most important tools in organic synthesis, having found applications in the preparation of a wide spectrum of organic chemicals, materials, and natural products.[1] Over the decades, various homogeneous catalytic systems have been developed for this transformation.[2] This includes the start of the field on palladacycles as catalysts for cross-coupling reactions in 1995 when Herrmann and Beller reported that the application of cyclopalladated tri-*o*-tolylphosphane for the Pd-catalyzed Heck[3] and Suzuki[4] coupling reactions provided unparalleled turnover numbers (TONs). Since then, a wide variety of nitrogen, oxygen, phosphorus, and sulfur palladacycles with high TONs have been developed for different C−C and C-heteroatom-coupling reactions.[5]

Although homogeneous catalysts generally have a higher activity and selectivity as compared to heterogeneous catalysts, difficulties in separation and recovery of the catalyst and contamination of the products with traces of the heavy metals are common problems encountered which restrict their applications in certain industries.[6] To circumvent this problem, various new strategies for transition-metal catalysis have been developed.[7] One of these strategies involves the development of fluorous-tagged catalyst.[7e−g] Attaching fluorous groups, such as perfluorooctyl ($-C_8F_{17}$) groups to organic molecules eases the separation of the catalyst from the reaction products. In addition, fluorous tags are inert to chemical reactions and have little effect on the reactivity of the parent molecule as the electron-withdrawing fluorines are insulated from the reactive site of the parent molecule via methylene segments alone or methyl segments with heteroatoms or phenyl rings. Today, there are basically two types of fluorous catalysts. In fluorous biphasic catalysis, the catalyst contains >60% fluorine by molecular weight so as to provide good liquid/liquid separation between the organic and perfluorocarbon solvent. However the prohibitive cost of the perfluorocarbon solvents makes such catalysis impractical for industrial purposes. An alternative method involves "light fluorous" catalysts where the fluorine content is <50% by molecular weight.[7g] These catalysts can be used in conventional organic solvents, recovered and recycled by fluorous solid-phase extraction (F-SPE) with fluorous silica.[8]

Recently, we reported the synthesis of a light fluorous, oxime-based palladacycle **1** (Figure 1) and demonstrated that it

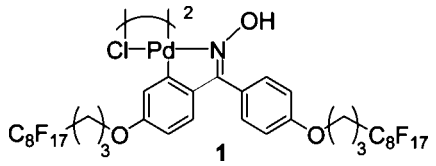


Figure 1. Oxime-derived fluorous-tagged palladacycle **1**.

is a very active precatalyst for promoting the Suzuki−Miyaura, Sonogashira and Stille coupling reactions in aqueous medium.[9] Palladacycle **1** could be used under microwave irradiation at high temperatures which shortened the reaction time significantly. It could also be recovered and recycled over five runs in a Suzuki−Miyaura reaction with very low Pd leaching (0.023−0.033 ppm over five cycles). This amount of Pd leaching is very much lower than that observed from the polymer-supported oxime-based palladacycle analogue[10] and three

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earlier reported fluorous Pd-catalysts which were applied to cross-coupling reactions in aqueous medium.[11] With these promising results in hand, we proceeded to examine the general usefulness of palladacycle **1**. Herein, we have expanded the application of palladacycle **1** to other substrates for the Suzuki-Miyaura, Sonogashira, and Stille coupling reactions and have also assessed the precatalytic activity of palladacycle **1** in the Heck and Kumada reactions.

RESULTS AND DISCUSSION

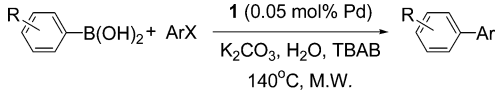
Suzuki–Miyaura Reaction. Palladium-catalyzed cross coupling reaction of aryl halides and arylboronic acids is a very versatile and widely used methodology for the construction of biaryls which are important building blocks in natural products, pharmacophores, and functional materials.[12] In our preliminary studies,[9] we have demonstrated the Suzuki–Miyaura reaction between phenylboronic acid with various aryl and benzyl halides in aqueous medium. To investigate the general usefulness of palladacycle **1** for the Suzuki–Miyaura reaction, we extended our studies to different combinations of halides and boronic acids (Tables 1 and 2). Under the optimized reaction conditions,[9] good to excellent yields of the desired products were achieved in all cases. It was also gratifying to note that our reaction protocol could be applied successfully to aryl chlorides (Table 1, entries 4 and 5) as only few recyclable catalytic systems are known to promote the Suzuki–Miyaura reaction of chloroarenes in water.[13]

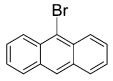
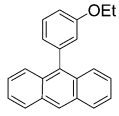
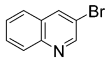
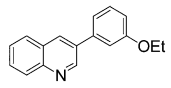
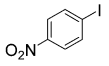
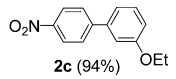
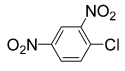
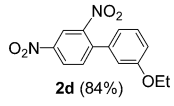
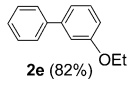
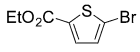
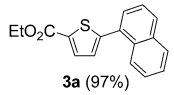
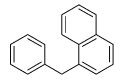
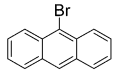
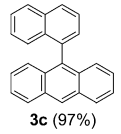
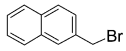
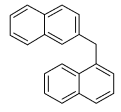
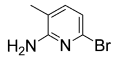
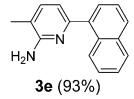
Since styrene derivatives are often used as key building blocks in the polymer industry and also for fine chemical synthesis,[15] we proceeded to examine the synthesis of styrene compounds using palladacycle **1** and trivinylboroxine-pyridine complex **4** as the representative vinylating agent. Treatment of **4** with various aryl halides under the optimized reaction condition[9] provided the styrene derivatives in good yields (Table 2, entries 1–4), indicating that palladacycle **1** is an efficient precatalyst for the installation of a terminal vinyl group.

Besides C_{sp^2}–C_{sp^2} bond formation, we have also applied palladacycle **1** to the formation of C_{sp^2}–C_{sp^3} bonds through the cross-coupling between aromatic or heteroaryl halides with trimethylboroxine (TMB) or butylboronic acid (Table 2, entries 5–10). In our initial studies, we had attempted to methylate the aromatic ring by cross-coupling aryl bromides with methylboronic acid and palladacycle **1** under the optimized reaction conditions. However, with methylboronic acid (1.5 equiv), the reaction proceeded sluggishly and the yield of the desired product obtained was much lower as compared to the yield obtained when the same equivalence of TMB was used. Increasing the amount of methylboronic acid used resulted in a higher yield of the desired product (Table 2, entry 5). Since TMB gave a better yield of the desired product and is also a cheaper reagent than methylboronic acid, it was used as the methylating agent for our Suzuki-Miyaura reaction.

Sonogashira Reaction. The Sonogashira reaction is a common reaction used for the formation of biarylacetylenes. In recent years, active research in green chemistry has resulted in numerous reports on the use of water as a cosolvent and/or the use of catalysts containing water-soluble ligands for this reaction.[17] However Sonogashira reactions in neat water and in the absence of additives[18] are rare and often low-yielding because of the poor solubility or instability of the catalysts and coupling reagents in aqueous medium.[19] In our preliminary studies, we have demonstrated that palladacycle **1** is a versatile precatalyst for the copper-free Songashira reaction between phenylacetylene and various aryl bromides and iodides in water.[9] Using the optimized reaction conditions which we have established in the previous study, we now extend the application to other terminal alkynes and aryl halides (Table 3). The results obtained show that good reactivity was preserved in both activated and nonactivated aryl halides, indicating that palladacycle **1** is an efficient precatalyst for the Sonogashira coupling reaction in aqueous medium.

Table 1. Suzuki–Miyaura Reaction of Arylboronic Acids with Various Aryl and Benzyl Halides



Entry	ArX	R	Time (min)	Product (Yield[a])
1		3-OEt	5	 **2a** (89%)
2		3-OEt	5	 **2b** (92%)
3		3-OEt	2	 **2c** (94%)
4		3-OEt	10	 **2d** (84%)
5		3-OEt	12	 **2e** (82%)
6		C_4H_4[b]	7	 **3a** (97%)
7		C_4H_4[b]	13	 **3b** (89%)[c]
8		C_4H_4[b]	12	 **3c** (97%)
9		C_4H_4[b]	7	 **3d** (95%)
10		C_4H_4[b]	18	 **3e** (93%)

[a]Isolated yield. [b]Refers to 1-naphthylboronic acid. [c]Use of TBAB is crucial for good conversion to **3b**. TBAB is known to be a phase-transfer catalyst and it also stabilizes the Pd nanoparticles so as to avoid aggregation.[14]

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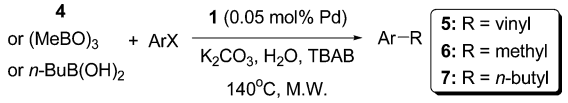
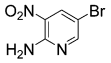
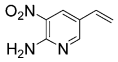
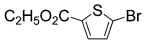
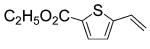
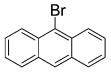
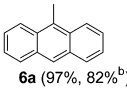
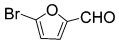
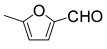
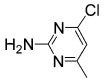
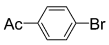
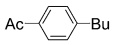
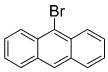
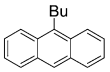
Table 2. Suzuki–Miyaura Reaction of Trivinylboroxine–Pyridine Complex 4, Trimethylboroxine, or Butylboronic Acid with Various Aryl Halides



Entry	ArX	Time (min)	Product (Yield[a])
1		12	 **5a** (99%)
2		7	 **5b** (95%)
3		15	 **5c** (86%)
4		11	 **5d** (93%)
5		12	 **6a** (97%, 82%[b])
6		16	 **6b** (82%)
7		25	 **6c** (93%)
8		38	 **6d** (85%)
9		7 (2h[b])	 **7a** (93%, 51%[c])
10		6	 **7b** (82%)

[a]Isolated yield. [b]Using 4.5 equiv of methylboronic acid instead of 1.5 equiv of TMB. [c]Using polymer-supported oxime-based palladacycle:[16] 1 mol % of Pd, K_2CO_3, H_2O, TBAB, 100 °C.

We have also investigated the possibility of recovering and recycling palladacycle **1** from the Sonogashira reaction. 4-Nitrobromobenzene and phenylacetylene were used for the model reaction under the optimized reaction conditions. In this regard, we found that over 5 runs, the time taken for the reaction to complete was 5–12 min, and compound **8k** was obtained in 89–93% yields (Table 4). In addition, ICP-OES analysis of the crude product indicated that the Pd content was very low (0.063–0.073 ppm over 5 cycles). To our knowledge, this leaching concentration is significantly lower than the amounts determined for the recyclable Pd catalysts reported earlier for the Sonogashira reaction.[11,21]

Homocoupling Reaction of Terminal Alkynes. During the optimization of the Sonogashira reaction with phenylacetylene and various aryl halides, we found that a significant amount of the homocoupled product was formed as a side-product when undegassed water was used as the solvent.[9] This prompted us to explore the use of palladacycle **1** as a precatalyst for such Glaser-type homocoupling reactions. In our initial experimentation, we used undegassed water and the optimized reaction condition for the Sonogashira reaction. However, this provided the homocoupled product in moderate yield (Table 5, entry 1). Addition of CuI as a cocatalyst not only increased the yield but also slightly reduced the reaction time. This is because CuI could aid in the formation of an activated species through its reaction with the terminal alkyne.[22] To demonstrate the generality of this reaction condition, we carried out the homocoupling reaction on other terminal alkynes which essentially gave quantitative yields for all cases (Table 5, entries 2–4).

Stille Coupling Reaction. The Stille coupling reaction is a versatile C–C bond-forming reaction between stannanes and halides because of its tolerance toward most functional groups and also because the organotin reagents are easy to make and are very stable to oxygen and moisture. In our previous studies,[9] we explored the use of palladacycle **1** as a precatalyst for the Stille reaction. As a model reaction, tributyl(4-methoxyphenyl)-stannane was coupled to various aryl halides in the presence of palladacycle **1** (0.005 mol % Pd) and tetra-*n*-butylammonium bromide (TBAB) as an additive in water and under microwave irradiation at 100 °C. The reactions occurred very rapidly and gave the products in good to excellent yields. To survey the scope of this reaction, we herein conducted the reaction using other organostannanes and aryl halides (Table 6). To our delight, the reactions occurred with ease leading to only the cross-coupled product for all cases, indicating that palladacycle **1** was generally suitable for CuI-free Stille couplings in water (CuI was demonstrated to accelerate the coupling reaction[25]).

To address the recyclability of palladacycle **1** in the Stille reaction, the leaching of the active Pd species in solution was examined for the coupling reaction of tributyl(phenyl)stannane with iodobenzene under the optimized reaction conditions. The results obtained were gratifying as the yields over five runs were quantitative and the time required for the reaction to go to completion remained short (Table 7). In addition, the Pd leaching was also very low.

Heck Reaction. Previous studies on homogeneous catalysis have shown that palladacycles, despite their high catalytic activities,[29] are not stable under the Heck reaction conditions and undergo decomposition via olefin insertion into the C–Pd bond followed by Pd(II) to Pd(0) reduction.[30] To facilitate recovery and reuse, supported palladacycles, such as the polymer-supported cyclopalladated Milstein-type imine complex (the immobilized palladacycle was reported to have completely lost its activity in the third run)[31] and the palladated Kaiser oxime resin,[32] were developed. Since palladacycle **1** has been shown to be an efficient precatalyst for the Suzuki–Miyaura, Sonogashira, Glaser-type, and Stille coupling reactions, from a practical point of view, it was important to study the scope of this palladacycle as a precatalyst in the Heck reaction.

In our initial studies, the Heck reaction was performed using *N*-vinylphthalimide and 4-methoxybromobenzene with Cy_2NMe as base, TBAB as additive, palladacycle **1** (0.5 mol % Pd) as precatalyst, DMF as solvent, and under microwave irradiation at 160 °C. This gave the *E*-configuration product **13a** in 79% yield (Table 8, entry 1). Increasing the reaction temperature to 170 and 180 °C resulted in a shortening of the reaction time (Table 8, entries 2–3). Since the product yield was higher at 170 °C, this reaction temperature was used in our subsequent studies.

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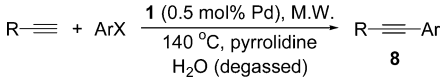
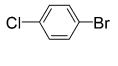
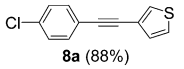
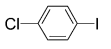
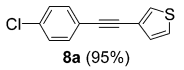
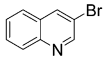
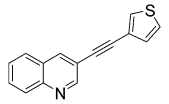
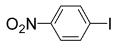
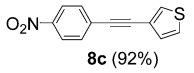
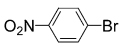
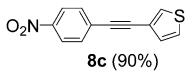
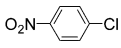
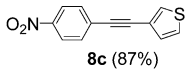
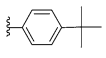
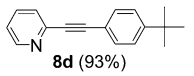
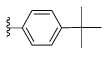
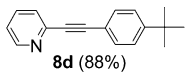
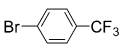
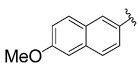
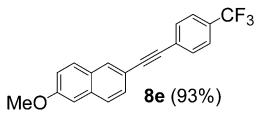
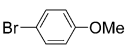
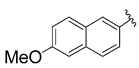
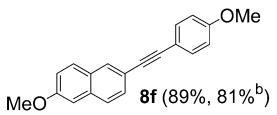
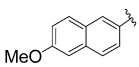
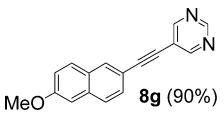
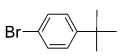
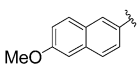
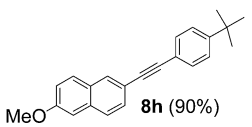
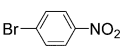
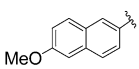
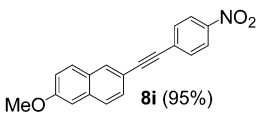
Table 3. Sonogashira Reaction Using Palladacycle 1



Entry	ArX	R	Time (min)	Product (Yield[a])
1			15	 **8a** (88%)
2			8	 **8a** (95%)
3			30	 **8b** (87%)
4			12	 **8c** (92%)
5			15	 **8c** (90%)
6			27	 **8c** (87%)
7			10	 **8d** (93%)
8			12	 **8d** (88%)
9			6	 **8e** (93%)
10			8 (4 h)[b]	 **8f** (89%, 81%[b])
11			12	 **8g** (90%)
12			7	 **8h** (90%)
13			8	 **8i** (95%)
14			15	**8i** (88%)
15			7	**8j** (93%)

[a]Isolated yield. [b]Using pincer complexes of palladium: Pd cat. (100 ppm), K_3PO_4, ethylene glycol, 140 °C.[20]

Next, we investigated the effects of bases on the reaction. In addition to Cy_2NMe, TEA and Cs_2CO_3 were examined (Table 8, entries 2, 4, and 5), and Cy_2NMe was found to be the most effective base for the reaction. The zero conversion obtained when Cs_2CO_3 was used as a base could be attributed to the insolubility of the base in DMF. Solvent was also varied and the

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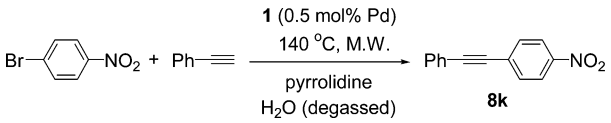
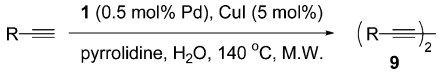
Table 4. Recycling of Palladacycle 1 in the Sonogashira Reaction

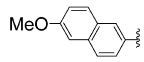
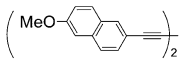
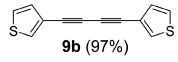
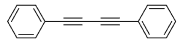
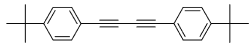


cycle	time (min)	yield[a] (%)	Pd leaching[b] (ppm)	recovered 1[c] (wt %)
1	5	93	0.067	93
2	7	93	0.063	90
3	8	91	0.065	92
4	12	89	0.069	90
5	12	89	0.073	89

[a]Isolated yield. [b]Determined by ICP-OES of the crude product. [c]Recovered via F-SPE.

Table 5. Glaser-Type Oxidative Homocoupling Using Palladacycle 1



Entry	R	Time (min)	Product (Yield[a])
1		15 (19[b])	 **9a** (88%, 68%[b])
2		12	 **9b** (97%)
3		8 (10 h[c])	 **9c** (99%, 90%[c])
4		10 (8 h[d])	 **9d** (97%, 90%[d])

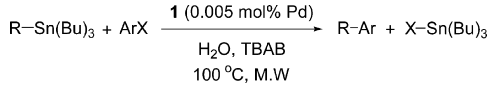
[a]Isolated yield. [b]In the absence of cocatalyst CuI. [c]Using mesoporous Pd-MCM-48: Pd catalyst (0.6 mol %), ethanol, refluxed.[23] [d]Using $PdCl_2(PPh_3)_2$ in ionic liquid: Pd catalyst (2 mol %), piperidine, 25 °C.[24]

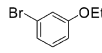
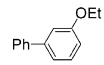
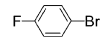
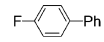
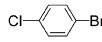
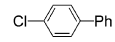
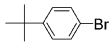
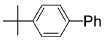
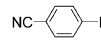
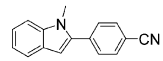
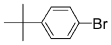
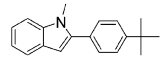
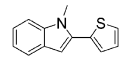
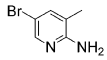
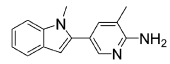
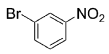
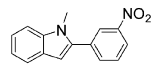
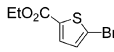
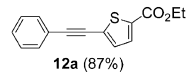
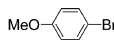
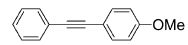
experimental data obtained (Table 8, entries 2 and 6–9) indicated that the reaction proceeded most efficiently in DMF.

Using the optimized reaction conditions, we extended the Heck reaction to both activated and deactivated aryl halides, which gave good to excellent yields of the desired product (Table 9). Comparison of palladacycle **1** with its polymer-supported and solution-phase analogues also showed that the Heck reaction with palladacycle **1** gave a higher yield of the product (Table 9, entries 3–6).

Recycling experiments for the Heck reaction were performed using iodobenzene, *N*-vinylphthalimide under the optimized reaction conditions. From the results obtained (Table 10), the reaction gave **13e** in good yields: 93% in 3 min in the first run to 90% in 30 min in the fourth run. These values are higher than those obtained via polymer-supported palladacycle[17] and with palladacycle **1**, no drastic decrease in the product yield was observed. Pd leaching was observed in the crude product but the amount of Pd leached was lower than that from the polymer-supported palladacycle[17] (Table 10, entries 1–3). The increase in reaction time and lower amount of palladacycle **1** recovered could be due to the formation of the palladium black at elevated temperature.

Table 6. Stille Coupling Reaction Using Palladacycle 1



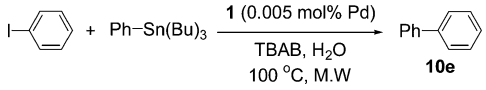
Entry	ArX	R	Time (min)	Product (Yield[a])
1		C_6H_5	4.5	 **10a** (90%)
2		C_6H_5	1	 **10b** (93%)
3		C_6H_5	1.5 (18 h)[b]	 **10c** (88%, 74%[b])
4		C_6H_5	2 (8 h)[c]	 **10d** (92%. 91%[c])
5			0.75	 **11a** (97%)
6			3	 **11b** (88%)
7			6	 **11c** (88%)
8			6	 **11d** (90%)
9			1.5	 **11e** (95%)
10			5	 **12a** (87%)
11			3.5 (24 h)[d]	 **12b** (83%, 75%[d])
12			0.58	**12c** (92%)

[a]Isolated yield. [b]Pd cat. (5 mol %), dioxane, reflux.[26] [c]Pd cat., CsF, dioxane, rt→100 °C.[27] [d]Pd cat. (0.5 mol %), DMF/H_2O (9:1), 80 °C.[28]

Encouraged by the results obtained from the Heck reaction between *N*-vinylphthalimide and the aryl halides, we proceeded to explore other coupling partners for this reaction. Previous works by Cacchi and co-workers[34] have shown that under appropriate reaction conditions and with $Pd(OAc)_2$ as catalyst, cinnamaldehydes **15** and ethyl 3-arylpropionoates **16** could be prepared from acrolein diethyl acetal **14** using the Heck reaction (Scheme 1). In our study, we initially carried out the reaction with **14** and 4-chloroiodobenzene employing the Cacchi condition (K_2CO_3 as base, tetra-*n*-butylammonium acetate (TBAA) and KCl as additives at 120 °C) with palladacycle **1** (0.5 mol % of Pd) as precatalyst. By varying the solvent, we found that the best yield for cinnamaldehyde **15a** was obtained when DMAc was used as the solvent (Table 11, entries 2, 5, and 7). Performing the reaction under microwave irradiation although gave **15a** in a similar yield, but the reaction time was very much shorter and selectivity was high (**15a**:**16a** = 97:3). Application of

dx.doi.org/10.1021/jo202482h | J. Org. Chem. 2012, 77, 2729–2742

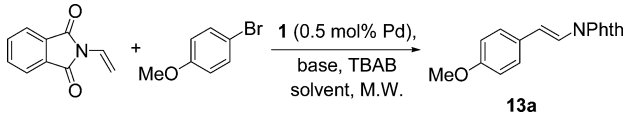
Table 7. Recycling of Palladacycle 1 in the Stille Reaction



cycle	time (min)	yield[a] (%)	Pd leaching[b] (ppm)	recovered 1[c] (wt %)
1	0.75	99	0.52	95
2	0.75	99	0.58	96
3	0.75	98	0.56	93
4	0.75	99	0.58	93
5	0.8	97	0.57	91

[a]Isolated yield. [b]Determined using the crude product, mg Pd/1 L 1% HNO_3 aqueous solution. [c]Recovered via F-SPE.

Table 8. Optimization of the Heck Reaction



entry	temp (°C)	base	solvent	time (min)	yield[a] (%)
1	160	Cy_2NMe	DMF	30	79
2	170	Cy_2NMe	DMF	20	87[b]
3	180	Cy_2NMe	DMF	10	72
4	170	TEA	DMF	20	65
5	170	Cs_2CO_3	DMF	20	0
6	120	Cy_2NMe	CH_2Cl_2	150	10
7	140	Cy_2NMe	THF	25	72
8	170	Cy_2NMe	CH_3CN	20	72
9	170	Cy_2NMe	H_2O	20	0

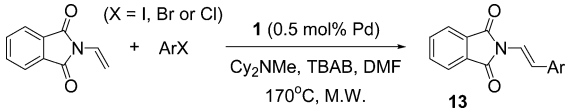
[a]Isolated yield. *E*/*Z* regioisomeric ratio is >98/2. [b]Using palladacycle **1** (2.5 mol % Pd), the isolated yield was 72%.

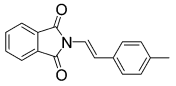
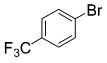
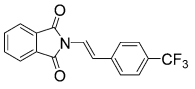
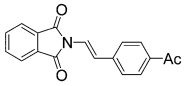
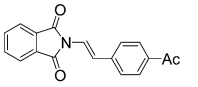
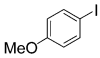
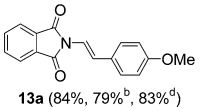
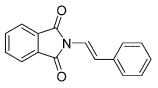
these reaction conditions to other aryl halides also proceeded well providing cinnamaldehyde **15** in good yields and high selectivity (Table 12, entries 1 and 2). For the synthesis of ethyl 3-arylpropionoates **16**, total selectivity was observed by changing the base from K_2CO_3 to Cy_2NMe and using DMAc/H_2O as solvent. This could be attributed to the similarity in shape of Cy_2NMe and triphenylphosphine which leads to the ease of its coordination with [Pd(HX)].[35a] This results in the removal of HX to form the ammonium salt, which hydrolyzes the ketene acetal into an ester.[35b] In addition, ethyl 3-arylpropionoates **16** were obtained in good yields (Table 12, entries 3–6).

For studying the recovery and reuse of palladacycle **1** in the Heck reaction, the experiments were performed using **14** and 4-chloroiodobenzene under the optimized reaction conditions. The palladacycle **1** recovered from each run (Table 13) was lower than the amount recovered from the Suzuki–Miyaura, Sonogashira, and Stille reactions. This could be due to the formation of Pd black during the reaction. It is nevertheless worth noting that the recovered palladacycle **1** showed high activity under the reaction condition and the amount of Pd leached into the solution of crude product is significantly lower than that observed from the polymer-supported palladacycle.[36]

Kumada Cross-Coupling Reaction. The Kumada cross-coupling reaction is commonly used in the industrial-scale production of styrene derivatives as it provides an economical C–C bond-forming transformation through the direct coupling between Grignard reagents and alkyl, vinyl or aryl halides.

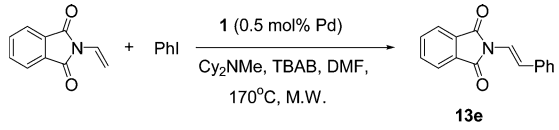
Table 9. Heck Reaction of *N*-Vinylphthalimide with Various Aryl Halides



Entry	ArX	Time (min)	Product (Yield[a])
1		20	 **13b** (81%)
2		15	 **13c** (98%)
3		25 (14 h[b])	 **13d** (91%, 68%[b])
4		25 (20[c], 24 h[d])	 **13d** (87%, 73%[c], 32%[d])
5		8 (6 h[b], 3 h[d])	 **13a** (84%, 79%[b], 83%[d])
6		3 (14 h[b])	 **13e** (93%, 86%[b])

[a]Isolated yield. *E*/*Z* regioisomeric ratio is >98/2. [b]Polymer-supported reaction condition: Cy_2NMe, TBAB, DMF, 120 °C.[33] [c]Solution-phase reaction condition: Cy_2NMe, TBAB, DMF, M.W., 140 °C.[33] [d]Solution-phase reaction condition: Cy_2NMe, TBAB, DMF, 140 °C.[33]

Table 10. Recycling Experiments: Heck Reaction of *N*-Vinylphthalimide with Iodobenzene[a]



cycle	time (min)	yield[b] (%)	Pd leaching (mg Pd/g product)[c]	recovered 1[d] (wt %)
1	3 (14 h)	93 (86)	0.24 (0.35)	70
2	10 (24 h)	93 (72)	0.24 (0.35)	75
3	20 (24 h)	92 (46)	0.18 (0.47)	60
4	30	90	<0.1	51

[a]Data within parentheses are the results obtained from *polymer-supported* reaction conditions: Pd catalyst, Cy_2NMe, TBAB, DMF at 120 °C.[17] [b]Isolated yield. [c]Determined in the crude product, mg Pd/1 L 1% HNO_3 aqueous solution. [d]Recovered via F-SPE.

Herein we report for the first time the use of an oxime-based palladacycle to catalyze the Kumada cross-coupling reaction.

Initial studies of the Kumada cross-coupling reaction between phenylmagnesium bromide (1 M) in THF and 4-bromotoluene in DMAc under microwave irradiation at 140 °C afforded 4-methylbiphenyl **17a** in only 53% yield. By screening through various solvents (Table 14, entries 1–4), we found that THF

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Scheme 1. Synthesis of Cinnamaldehydes and Ethyl 3-Arylpropionoates Using the Heck Reaction

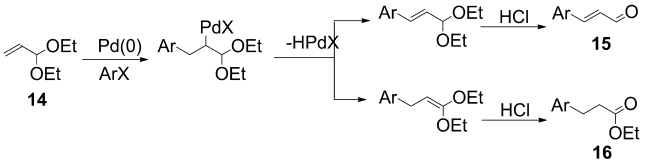
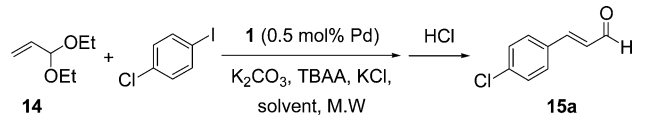


Table 11. Optimization of the Heck Coupling of 14 with 4-Chloroiodobenzene

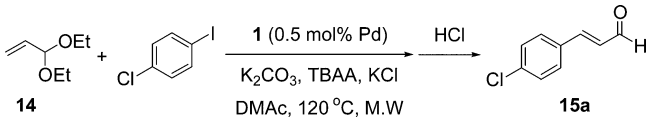


entry	temp (°C)	solvent	time (s)	yield[a] (%)
1	120	DMAc	15 min[b] (3 h[c])	82[b] (85[c])
2	120	DMAc	60	87
3	150	DMAc	10	41
4	170	DMAc	5	77
5	120	DMF	60	31
6	120	DMAc/H_2O[d]	90	39
7	100	CH_3CN	90	37

[a]Isolated yield. [b]With oil bath heating. [c]Polymer-supported reaction conditions: Pd catalyst, K_2CO_3, TBAA, KCl, DMAc, 120 °C.[36] [d]DMAc/H_2O = 4:1.

gave the best result, providing **17a** in 97% yield within 1 min. Next we varied the reaction temperature and the experimental data obtained indicated that comparable yield and reaction time could be achieved at 100 °C (Table 14, entries 5–7). Finally, we

Table 13. Recycling of Palladacycle 1 in the Heck Reaction

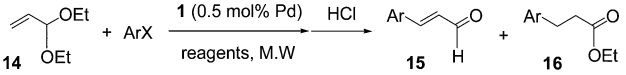


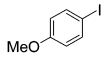
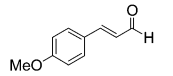
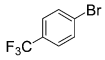
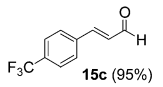
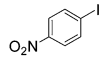
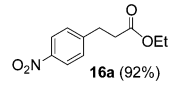
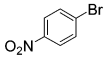
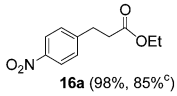
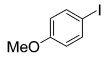
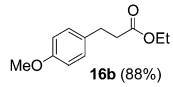
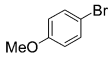
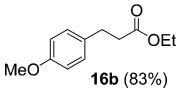
cycle	time (min)	yield[a] (%)	Pd leaching[b] (ppm)	recovered 1[c] (wt %)
1	1 (2.5 h)	92 (96)	0.067 (0.51)	84
2	3 (3.5 h)	91 (90)	0.076 (0.56)	82
3	6 (5.5 h)	87 (92)	0.048 (0.63)	65
4	10 (9 h)	85 (90)	0.004	63
5	22 (14 h)	82 (84)	0.023	63

[a]Isolated yield. [b]Determined using the crude product, mg Pd/1 L 1% HNO_3 aqueous solution. Data within parentheses are the results obtained from polymer-supported reaction conditions.[36] [c]Recovered from running through F-SPE.

explored the possibility of reducing the precatalyst loading to 0.05 mol % Pd. This afforded **17a** in 95% yield within a similar reaction time (Table 14, entry 8). However, further reduction of the precatalyst loading to 0.005 mol % Pd drastically decreased the product yield (Table 14, entry 9). Thus a precatalyst loading of 0.05 mol % Pd was used for our subsequent experiments. With the optimized reaction condition, we extended the reaction to different combinations of Grignard reagents and halides which afforded good yields of the desired product (Table 15). Finally to determine the stability of palladacycle **1** under the Kumada cross-coupling reaction conditions, we carried out the recycling experiment using bromobenzene and phenylmagnesium bromide for the model study (Table 16). Palladacycle **1** could be reused over 4 runs with yields ranging from 91 to 63%. The decreasing

Table 12. Chemoselective Synthesis of 15 and 16 Using Heck Reaction of 14 and Various Aryl Halides



Entry	ArX	Time (min)	Reagents[a]	Isomer ratio (**15**:**16**)	Product (Yield[b])
1		7 (3 h[c])	A	100:0	 **15b** (85%, 91%[c])
2		10	A	91:9	 **15c** (95%)
3		4	B	0:100	 **16a** (92%)
4		15 (3 h[c])	B	0:100	 **16a** (98%, 85%[c])
5		8	B	0:100	 **16b** (88%)
6		14	B	0:100	 **16b** (83%)

[a]A: **1** (0.5 mol % Pd), K_2CO_3, TBAA, KCl, DMAc. B: **1** (0.5 mol % Pd), Cy_2NMe, TBAB, DMAc/H_2O. [b]Isolated yield. [c]Polymer-supported reaction condition: Pd catalyst, K_2CO_3, TBAA, KCl, DMAc, 120 °C.[36]

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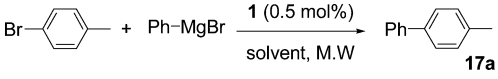
Table 14. Optimization of the Kumada Cross-Coupling Reaction



entry	temp (°C)	solvent	time (min)	yield[a] (%)
1	140	DMAc	1	53
2	140	CH_2Cl_2	1	76
3	140	THF	1	97
4	140	EtOEt	1	62
5	rt[b]	THF	8 h	53
6	reflux[b]	THF	3 h	69
7	100	THF	1 (30 min[c])	96 (93[c])
8	100[d]	THF	1.5	95
9	100[e]	THF	5	40

[a]Isolated yield. [b]Experiment was not carried out under MW conditions. [c]Experiment was not carried out under MW conditions: $Pd(OAc)_2$ (1 mol %), toluene, rt.[37] [d]Using palladacycle **1** (0.05 mol % Pd). [e]Using palladacycle **1** (0.005 mol % Pd).

yield could be attributed to the very small amounts of Pd black formed during the reaction and the comparatively higher Pd leaching. However this amount of Pd leaching is within the purity required for active pharmaceutical ingredients (2–20 ppm).[40]

CONCLUSION

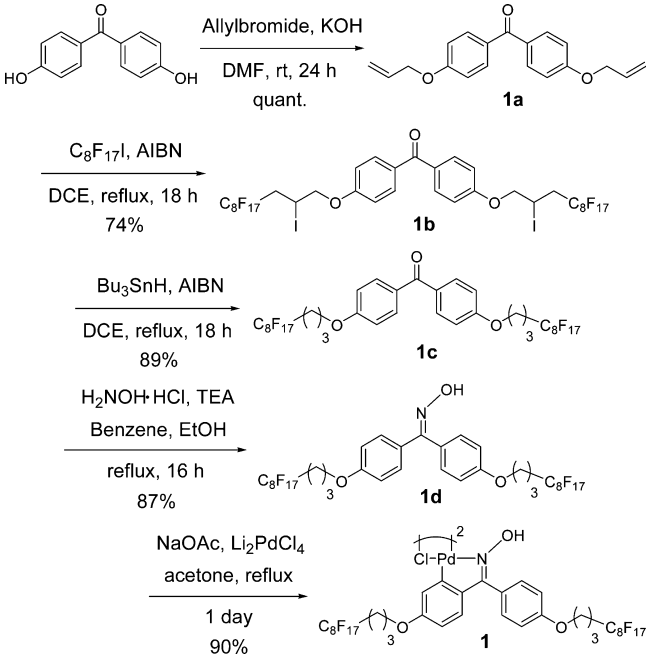
In summary, we have demonstrated that palladacycle **1** is a very versatile and efficient precatalyst which can be used in a wide variety of cross-coupling reactions (Suzuki-Miyaura, Sonogashira, Stille, Heck and Kumada), both in organic and aqueous media. The stability of palladacycle **1** is also remarkable and it could be reused four to five times without significant loss of activity. The amount of Pd leaching was also very low.

EXPERIMENTAL SECTION

All chemical reagents purchased were used without further purification. Moisture-sensitive reactions were carried out under nitrogen with commercially obtained anhydrous solvents. Analytical thin-layer chromatography (TLC) was carried out on precoated F254 silica plates and visualized with UV light or stained with the Dragendorff–Munier and Hanessian stain. Column chromatography was performed with silica (230–400 mesh). NMR spectra (^1H and ^{13}C) were recorded at 298 K. Chemical shifts are expressed in terms of δ (ppm) relative to the internal standard tetramethylsilane (TMS). Mass spectra were performed under EI mode. Microwave reactions were performed on the Biotage Initiator™ microwave synthesizer in quartz pressure tubes.

Preparation of Palladacycle 1.[9] *Bis(4-(allyloxy)phenyl)-methanone (**1a**).* To a solution of 4,4′-dihydroxybenzophenone (5.0 g, 23.3 mmol) in DMF (50 mL) were added KOH (6.5 g, 116.7 mmol) and allyl bromide (5.1 mL, 58.4 mmol). The reaction mixture was stirred at room temperature for 24 h, quenched with H_2O (10 mL), and consecutively washed with EtOAc (100 mL × 3). The organic layers were combined, washed with brine (50 mL × 3), dried over anhydrous $MgSO_4$, filtered, and concentrated. The desired product **1a** (6.77 g, 99%) was obtained as a white crystal after purification by column chromatography. ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, 8H, J = 8.9 Hz), 6.96 (d, 8H, J = 8.9 Hz), 6.06 (m, 2H), 5.44, (dd, 2H, J_1 = 17.1 Hz, J_2 = 1.3 Hz), 5.32 (dd, 2H, J_1 = 10.7 Hz, J_2 = 1.3 Hz), 4.61 (d, 4 H, J = 5.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 161.8, 132.6, 132.1, 130.8, 118.1, 114.1, 68.8. HRMS (EI): calcd for $C_{19}H_{18}O_3$ 294.1256, found 294.1259.

*Bis(4-(perfluorooctyl-2-iodopropoxy)phenyl)methanone (**1b**).* Compound **1a** (0.59 g, 2.0 mmol) was dissolved in dichloroethane



(1.2 mL), and $C_8F_{17}I$ (1.3 mL, 4.8 mmol) and AIBN (65.6 mg, 0.4 mmol) were added. The reaction flask was equipped with a condenser, and the apparatus was purged and filled with Ar, stirred at 85 °C for 18 h, and then concentrated to dryness. The desired product **1b** (2.06 g, 74%) was obtained as a pale yellow solid after purification by column chromatography. ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, 8H, J = 8.9 Hz), 6.98 (d, 8H, J = 8.9 Hz), 4.56 (q, 2H, J = 6.4 Hz), 4.38 (q, 2H, J = 5.0 Hz), 4.28 (q, 2H, J = 6.4 Hz), 3.23–3.12 (m, 2H), 2.91–2.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.1, 160.8, 132.3, 131.7, 114.3, 72.7, 37.9 (t, J = 21.0 Hz), 12.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.71 (t, 6F, J = 10.3 Hz), −113.16 to −113.59 (m, 4F), −121.49 to −121.83 (d, 12F), −122.63 (s, 4F), −123.39 (s, 4F), −126.04 (s, 4F). HRMS (ESI): calcd for $C_{35}H_{18}O_3F_{34}I_2Na$ (M + Na) 1408.8692, found 1408.8695.

*Bis(4-(perfluorooctylpropoxy)phenyl)methanone (**1c**).* Compound **1b** (20.8 g, 15.0 mmol) was dissolved in dichloroethane (80 mL), and Bu_3SnH (10.5 mL, 39.0 mmol) and AIBN (0.49 mg, 3.0 mmol) were added. The reaction flask was equipped with a condenser, and the apparatus was purged and filled with Ar. The reaction mixture was stirred at 85 °C for 18 h and then concentrated to dryness. The desired product **1c** (15.19 g, 89%) was obtained as a white solid after purification by column chromatography. ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 8H, J = 8.8 Hz), 6.96 (d, 8H, J = 8.8 Hz), 4.13 (t, 4H, J = 6.3 Hz), 2.39–2.29 (m, 4H), 2.18–2.13 (m, 4H). ^{13}C NMR (125 MHz, 50 °C, $CDCl_3$): δ 194.1, 161.9, 132.2, 131.4, 114.1, 66.7, 28.1 (t, J = 21.9 Hz), 20.7. ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.60 (t, 6F, J = 10.3 Hz), −114.73 (t, 4F, J = 14.4 Hz), −122.22 to −122.43 (d, 12F), −123.25 (s, 4F), −123.98 (s, 4F), −126.71 (s, 4F). HRMS (ESI): calcd for $C_{35}H_{20}O_3F_{34}Na$ (M + Na) 1157.0763, found 1157.0762.

*Bis(4-(perfluorooctylpropoxy)phenyl)methanone Oxime (**1d**).* To a solution of compound **1c** (1.26 g, 1.11 mmol) and triethylamine (1.7 mL, 12.5 mmol) in anhydrous EtOH (10.0 mL) and benzene (15.0 mL) was added hydroxylamine hydrochloride (575 mg, 8.28 mmol). The mixture was refluxed with a Dean–Stark apparatus for 16 h and then concentrated to dryness. Citric acid (5%) was added, and the resulting mixture was extracted with EtOAc. The organic phase was washed consecutively with 5% citric acid, 5% $NaHCO_3$, H_2O, and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The desired product **1d** (1.11 g, 87%) was obtained as a white solid after purification by column chromatography. ^1H NMR (500 MHz, acetone-d_6): δ 10.09 (s, 1H), 7.39 (d, 2H, J = 8.8 Hz), 7.33 (d, 2H, J = 8.8 Hz), 7.04 (d, 4H, J = 8.8 Hz), 6.93 (d, 4H, J = 8.8 Hz), 4.22 (t, 2H, J = 6.3 Hz), 4.17 (t, 2H, J = 5.7 Hz), 2.57–2.42 (m, 4H), 2.19–2.11

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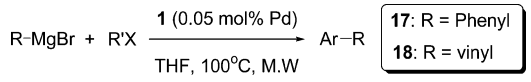
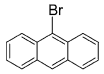
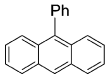
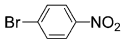
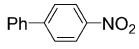
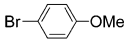
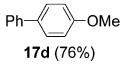
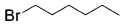
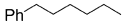
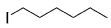
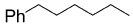
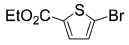
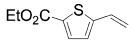
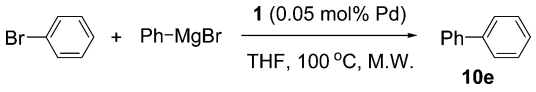
Table 15. Kumada Cross-Coupling Reaction Using Palladacycle 1



Entry	R'X	Time (min)	Product (Yield[a])
1		10	 **17b** (90%)
2		0.5 (8 h)[b]	 **10e** (98%, 90%[b])
3		2 (20 h)[c]	 **10e** (95%, 85%[c])
4		10	 **17c** (88%)
5		7	 **17d** (76%)
6		12	 **17e** (79%)
7		5	 **17e** (85%)
6		10	 **5b** (88%)
7		6	 **5d** (82%)
8		0.75	 **18** (86%)
9		1	 **18** (86%)

[a]Isolated yield. [b]Using nanosized MCM-41-supported palladium bipyridyl complex (0.05 mol % Pd), THF, 50 °C.[38] [c]Using silica-supported phosphine Pd(0) complex (1 mol % Pd), THF, 65 °C.[39]

Table 16. Recycling of Palladacycle 1 in the Kumada Cross-Coupling Reaction



cycle	time (min)	yield[a] (%)	Pd leaching[b] (ppm)	recovered 1[c] (wt %)
1	2	91	0.87	90
2	3.5	83	0.88	88
3	4.5	72	0.88	86
4	5	63	0.84	81

[a]Isolated yield. [b]Determined using the crude product, mg Pd/1 L 1% HNO_3 aqueous solution. [c]Recovered from running through F-SPE.

(m, 4H). ^{13}C NMR (125 MHz, acetone-d_6): δ 160.3, 159.7, 155.2, 132.8, 131.8, 131.3, 129.8, 127.1, 115.0, 114.7, 67.1, 67.1, 66.5, 28.5–28.1 (m), 21.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.72 (t, 6F, J = 10.3 Hz), −114.4 to −114.32 (d, 4F), −121.67 to −121.87 (d, 12F), −122.66 (s, 4F), −123.36 (s, 4F), −126.05 (s, 4F). HRMS (ESI): calcd for $C_{35}H_{22}O_3F_{34}N$ (M + H) 1150.1055; found 1150.1051.

Palladacycle (1). To a suspension of oxime **1d** (2.3 g, 2.0 mmol) in acetone (26 mL) were added anhydrous sodium acetate (0.165 g, 2.0 mmol) and Li_2PdCl_4 (0.524 g, 2.0 mmol). The mixture was stirred under reflux for 1 day, after which water (10 mL) was added and the precipitate which formed was filtered off and dried under reduced pressure over P_2O_5 to give the desired product **1** (2.33 g, 90%) as a brown solid. ^{1}H NMR (500 MHz, acetone-d_6): δ 10.9 (s, 1H), 7.49 (d, 1H, J = 2.5 Hz), 7.42 (d, 4H, J = 8.85 Hz), 7.12 (d, 4H, J = 8.85 Hz), 6.59 (d, 1H, J = 8.15 Hz), 6.49, 6.48 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.5 Hz), 4.27 (t, 2H, J = 6.3 Hz), 4.09 (t, 2H, J = 6.3 Hz), 2.57–2.41 (m, 4H), 2.19–2.07 (m, 4H). ^{13}C NMR (125 MHz, acetone-d_6): δ 163.7, 160.5, 158.0, 155.0, 137.4, 131.4, 128.0, 123.3, 121.8, 119.9, 115.1, 110.0, 67.3, 66.8, 55.4, 31.7, 28.6–28.0 (m), 21.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.64 (t, 6F, J = 10.3 Hz), −114.72 (t, 4F, J = 12.4 Hz), −122.22 to −122.43 (d, 12F), −123.25 (s, 4F), −123.95 (s, 4F), −126.71 (s, 4F). IR (KBr): v = 3429, 2961, 2762, 1578, 1246, 1206, 1025 cm^{-1}. MALDI HR: calcd for $C_{35}H_{18}O_3F_{34}NPd$ (M−H) 1287.9545, found 1287.9540.

General Procedure for the Suzuki–Miyaura Reaction of Boronic Acids and Various Halides under Microwave Heating. To a suspension of aryl halide (0.50 mmol), boronic acid/boroxine (0.75 mmol), TBAB (0.161 g, 0.50 mmol), palladacycle **1** (0.05 mol % Pd), and water (1.0 mL) in a pressure tube was added a 2 M solution of K_2CO_3 (0.5 mL). The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 140 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, poured into EtOAc (20 mL), and washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*10-(3-Ethoxyphenyl)anthracene (**2a**).* White solid. Mp: 119–120 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (s, 1H), 8.07 (d, 2H, J = 8.5 Hz), 7.78 (d, 2H, J = 14.1 Hz), 7.55–7.47 (m, 3H), 7.42–7.37 (m, 2H), 7.13–7.05 (m, 3H), 4.10 (q, 2H, J = 7.0 Hz), 1.47 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.9, 140.1, 136.9, 131.3, 130.1, 129.3, 128.3, 126.9, 126.4, 125.3, 125.1, 123.5, 117.1, 113.8, 63.4, 14.8. HRMS (EI): calcd for $C_{22}H_{18}O$ 298.1358, found 298.1357.

*3-(3-Ethoxyphenyl)quinoline (**2b**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.07 (s, 1H), 8.16 (s, 1H), 8.03 (d, 1H, J = 8.2 Hz), 7.74 (d, 1H, J = 7.9 Hz), 7.63–7.57 (m, 1H), 7.47–7.42 (m, 1H), 7.32–7.28 (m, 1H), 7.17–7.12 (m, 1H), 6.86–6.83 (m, 1H), 4.00 (q, 2H, J = 7.0 Hz), 1.35 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 149.8, 147.3, 139.2, 133.6, 133.1, 130.1, 129.3, 129.1, 127.9, 126.9, 119.6, 113.8, 63.5, 14.8. HRMS (EI): calcd for $C_{17}H_{15}ON$ 249.1154, found 249.1151.

*3-Ethoxy-4′-nitrobiphenyl (**2c**).* Yellow solid. Mp: 95–96 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.28 (d, 2H, J = 8.9 Hz), 7.72 (d, 2H, J = 8.8 Hz), 7.41–7.38 (m, 1H), 7.20–7.14 (m, 2H), 6.97 (d, 1H, J = 8.2 Hz), 4.11 (q, 2H, J = 7.0 Hz), 1.46 (t, 3H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.3, 149.1, 146.8, 142.1, 136.3, 133.1, 130.2, 126.3, 119.8, 119.5, 115.4, 114.0, 63.7, 14.7. HRMS (EI): calcd for $C_{14}H_{13}O_3N$ 243.0895, found 243.0893.

*3-Ethoxy-2′,4′-dinitrobiphenyl (**2d**).* Orange solid. Mp: 105–107 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (s, 1H), 8.45 (d, 1H, J = 8.5 Hz), 7.68 (d, 1H, J = 8.5 Hz), 7.39–7.34 (m, 1H), 7.01–6.98 (m, 1H), 6.89–6.84 (m, 2H), 4.05 (q, 2H, J = 7.0 Hz), 1.43 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.3, 149.1, 146.8, 142.1, 136.3, 133.1, 130.2, 126.3, 119.8, 119.5, 115.4, 114.0, 63.7, 14.7. HRMS (EI): calcd for $C_{14}H_{12}O_5N_2$ 288.0746, found 288.0743.

*3-Ethoxybiphenyl (**2e**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, 1H, J = 8.2 Hz), 7.49–7.41 (m, 2H), 7.39–7.37 (m, 2H), 7.23–7.18 (m, 2H), 6.95–6.92 (m,1H), 4.13 (q, 2H, J = 6.9 Hz), 1.49 (t, 3H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.3, 142.7, 141.1, 129.7, 128.7, 127.3, 127.1, 119.5, 113.5, 113.2, 63.4, 14.9. HRMS (EI): calcd for $C_{14}H_{14}O$ 198.1045, found 198.1046.

*Ethyl 5-(Naphthalen-1-yl)thiophene-2-carboxylate (**3a**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.18 (d, 1H, J = 2.6 Hz), 7.92–7.87 (m, 3H), 7.59–7.49 (m, 4H), 7.24 (d, 1H, J = 3.8 Hz), 4.41 (q, 2H, J = 7.0 Hz),

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1.42 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.3, 149.0, 133.8, 133.7, 133.4, 131.4, 131.4, 129.3, 128.4, 128.2, 128.0, 126.8, 126.2, 125.3, 125.2, 61.2, 14.4. HRMS (EI): calcd for $C_{17}H_{14}O_2S$ 282.0715, found 282.0714.

*1-Benzylnaphthalene (**3b**).* Mp: 53−55 °C (lit.[41] mp 54−57 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.73−7.66 (m, 3H), 7.57−7.55 (m, 1H), 7.38−7.11 (m, 8H), 4.06 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.0, 138.6, 133.6, 132.0, 129.0, 128.5, 128.1, 127.6, 127.6, 127.5, 127.1, 126.1, 126.0, 125.3, 42.1. HRMS (EI): calcd for $C_{17}H_{14}$ 218.1096, found 218.1093.

*10-(Naphthalen-1-yl)anthracene (**3c**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.51 (s, 1H), 8.02−7.91 (m, 4H), 7.62−7.59 (m, 2H), 7.45−7.31 (m, 4H), 6.99 (d, 1H, J = 8.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.5, 134.9, 133.7, 133.5, 131.4, 131.0, 129.1, 128.4, 128.2, 128.1, 126.9, 126.9, 126.5, 126.2, 125.9, 125.5, 125.5, 125.2. HRMS (EI): calcd for $C_{24}H_{16}$ 304.1252, found 304.1255.

*Naphthalen-1-yl(naphthalen-2-yl)methane (**3d**).* Mp: 89−90 °C (lit.[42] mp 89−91 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07 (d, 1H, J = 8.2 Hz), 7.90−7.72 (m, 5H), 7.63 (s, 1H), 7.51−7.35 (m, 4H), 4.62 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.1, 136.5, 133.9, 133.6, 132.1, 132.1, 128.6, 128.0, 127.8, 127.6, 127.5, 127.4, 127.4, 127.2, 127.0, 126.0, 125.9, 125.8, 125.6, 125.5, 125.3, 39.2. HRMS (EI): calcd for $C_{21}H_{16}$ 268.1252, found 268.1255.

*3-Methyl-6-(naphthalen-1-ylmethyl)pyridin-2-amine (**3e**).* Pale yellow solid. Mp: 156−158 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15−8.13 (m, 1H), 7.91−7.87 (m, 2H), 7.57−7.47 (m, 4H), 5.59 (s, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.2, 167.5, 163.0, 136.7, 133.8, 130.5, 129.5, 128.3, 126.8, 126.5, 126.0, 125.4, 125.1, 111.8, 24.0. HRMS (EI): calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1312.

*3-Nitro-5-vinylpyridin-2-amine (**5a**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.44 (s, 1H), 8.41 (s, 1H), 6.61 (dd, 1H, J = 17.7 Hz and 11.4 Hz), 5.71 (d, 1H, J = 17.7 Hz), 5.29 (d, 1H, J = 11.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.9, 152.6, 131.4, 131.3, 128.0, 124.4, 114.6. HRMS (EI): calcd for $C_7H_7O_2N_3$ 165.0538, found 165.0534.

*5-Vinylpyrimidine (**5b**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.10 (s, 1H), 8.76 (s, 1H), 6.66 (dd, 1H, J = 17.7 Hz and 11.4 Hz), 5.93 (d, 1H, J = 17.7 Hz), 5.51 (d, 1H, J = 11.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.6, 154.2, 130.9, 130.1, 118.6. HRMS (EI): calcd for $C_6H_6N_2$ 106.0531, found 106.0536.

*1-Nitro-3-vinylbenzene (**5c**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 8.12 (dd, J = 8.2, 1.3 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 6.79 (dd, J = 17.6, 10.9 Hz, 1H), 5.92 (d, J = 17.6 Hz, 1H), 5.47 (d, J = 10.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.61, 139.27, 134.74, 132.02, 129.41, 122.38, 120.85, 117.04. HRMS (EI): calcd for $C_8H_7NO_2$ 149.0477, found 149.0475.

*Ethyl 5-Vinylthiophene-2-carboxylate (**5d**).* Orange solid. Mp: 140−142 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, 1H, J = 3.8 Hz), 6.95 (d, 1H, J = 3.8 Hz), 6.77 (dd, 1H, J = 17 Hz and 10.7 Hz), 5.71 (d, 1H, J = 17 Hz), 5.29 (d, 1H, J = 10.7 Hz), 4.34 (q, 2H, J = 7.0 Hz), 1.47 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.2, 149.3, 133.6, 132.1, 129.5, 116.3, 61.1, 14.3. HRMS (EI): calcd for $C_9H_{10}O_2S$ 182.0402, found 182.0407.

*9-Methylanthracene (**6a**).* Mp: 78−81 °C (lit.[43] mp 79−80 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36−8.31 (m, 3H), 8.04−8.02 (m, 2H), 7.56−7.49 (m, 4H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.5, 130.1, 129.0, 128.1, 125.3, 125.2, 124.8, 124.6, 13.9. HRMS (EI): calcd for $C_{15}H_{12}$ 192.0939, found 192.0942.

*5-Methylfuran-2-carbaldehyde (**6b**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.40 (s, 1H), 7.08 (d, 1H, J = 3.8 Hz), 6.15 (d, 1H, J = 4.5 Hz), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.6, 159.5, 151.7, 123.5, 109.3, 13.7. HRMS (EI): calcd for $C_6H_6O_2$ 110.0368, found 110.0367.

*2-Methyl-1H-imidazole (**6c**).* Mp: 138−141 °C (lit.[44] mp 140−142 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 12.44 (s, 1H), 6.97 (s, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.6, 121.2, 13.7. HRMS (EI): calcd for $C_4H_6N_2$ 82.0531, found 82.0532.

*4,6-Dimethylpyrimidin-2-amine (**6d**).* Mp: 150−153 °C (lit.[45] mp 153 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.27 (s, 1H), 5.68 (s, 2H), 2.20 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.5, 163.0, 110.1, 23.4. HRMS (EI): calcd for $C_6H_9N_3$ 123.0796, found 123.0797.

*1-(4-Butylphenyl)ethanone (**7a**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, 2H, J = 8.2 Hz), 7.19 (d, 2H, J = 8.2 Hz), 2.60 (t, 2H, J = 7.6 Hz), 2.51 (s, 3H), 1.58−1.52 (m, 2H), 1.33−1.27 (m, 2H), 0.86 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.8, 148.8, 134.9, 128.6, 128.4,35.7, 33.2, 26.5, 22.3, 13.9. HRMS (EI): calcd for $C_{12}H_{16}O$ 176.1201, found 176.1203.

*10-Butylanthracene (**7b**).* Mp: 45−47 °C (lit.[46] mp 49−50 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.36−8.31 (m, 3H), 8.03−8.02 (m, 2H), 7.54−7.46 (m, 4H), 3.64 (t, 2H, J = 8.2 Hz), 1.88−1.82 (m, 2H), 1.68−1.60 (m, 2H), 1.07 (t, 3H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.4, 131.6, 129.5, 129.2, 128.6, 128.1, 125.3, 124.5, 33.5, 27.8, 23.4, 14.1. HRMS (EI): calcd for $C_{18}H_{18}$ 234.1409, found 234.1410.

General Procedure for the Sonogashira Cross-Coupling Reactions between Terminal Alkynes with Various Aryl Halides under Microwave Heating. To a suspension of aryl halide (0.50 mmol), phenylacetylene (0.75 mmol), pyrrolidine (0.161 g, 0.25 mmol), and palladacycle **1** (0.05 mol % Pd) in a pressure tube was added 1 mL of degassed water. The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 140 °C, and the reaction was monitored by TLC. When the reaction was complete, the reaction mixture was cooled to room temperature, poured into ether (20 mL), and washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*3-(2-(4-Chlorophenyl)ethynyl)thiophene (**8a**).* Mp: 102−104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57−7.50 (m, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.34−7.24 (m, 3H), 7.19 (d, J = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.2, 132.7, 130.5, 129.8, 128.9, 128.7, 125.5, 122.0, 87.8, 85.4. HRMS (EI): calcd for $C_{12}H_7ClS$ 217.9957, found 217.9955.

*3-(2-(Thiophene-3-yl)ethynyl)quinoline (**8b**).* Brown solid. Mp: 70−72 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.99 (d, J = 2.0 Hz, 1H), 8.28 (d, J = 1.8 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.73−7.68 (m, 1H), 7.63−7.53 (m, 2H), 7.35−7.33 (m, 1H), 7.28−7.23 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.0, 146.8, 138.1, 130.0, 129.8, 129.4, 129.4, 127.6, 127.3, 125.6, 121.7, 117.4, 88.9, 87.8, 86.2. HRMS (EI): calcd for $C_{15}H_9SN$ 235.0456, found 235.0455.

*3-(2-(4-Nitrophenyl)ethynyl)thiophene (**8c**).* Brown solid. Mp: 152−153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.67−7.59 (m, 3H), 7.34 (dd, J = 5.0, 2.8 Hz, 1H), 7.22 (d, J = 5.1 Hz, 1H), 1.55 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.0, 132.1, 130.3, 130.1, 129.7, 125.8, 123.6, 121.2, 89.9, 87.2. HRMS (EI): calcd for $C_{12}H_7SNO_2$ 229.0197, found 229.0197.

*2-(2-(4-tert-Butylphenyl)ethynyl)pyridine (**8d**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, J = 5.1, 1H), 7.67−7.50 (m, 3H), 7.39−7.37 (m, 2H), 7.22 - 7.19 (m, 1H), 1.32 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.3, 150.0, 143.7, 136.0, 131.8, 127.0, 125.4, 122.5, 119.2, 89.5, 88.1, 34.8, 31.1. HRMS (EI): calcd for $C_{17}H_{17}N$ 235.1361, found 235.1361.

*2-Methoxy-6-(2-(4-(trifluoromethyl)phenyl)ethynyl)naphthalene (**8e**).* Pale yellow solid. Mp: 151−153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.74−7.55 (m, 7H), 7.19 (dd, J = 9.0, 2.5 Hz, 1H), 7.13 (d, J = 2.4 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.6, 134.4, 131.7, 131.7, 129.9, 129.6, 129.4, 128.8, 128.5, 127.4, 126.9, 125.3, 125.3, 125.2, 125.2, 125.1, 122.9, 119.6, 117.4, 105.9, 92.5, 87.7, 55.3. HRMS (EI): calcd for $C_{20}H_{13}F_3O$ 326.0918, found 326.0914.

*2-Methoxy-6-(2-(4-methoxyphenyl)ethynyl)naphthalene (**8f**).* Mp: 165−166 °C (lit.[47] mp 165−167 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.70 (t, J = 8.9 Hz, 2H), 7.52 (ddd, J = 8.8, 7.6, 1.7 Hz, 3H), 7.16 (dd, J = 8.9, 2.5 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 3.93 (s, 3H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.5, 158.2, 134.0, 133.0, 130.9, 129.3, 129.0,

128.6, 126.8, 119.3, 118.5, 115.6, 114.0, 105.9, 89.0, 88.6, 55.3, 55.3. HRMS (EI): calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1151.

*5-(2-(6-Methoxynaphthalen-2-yl)ethynyl)pyrimidine (**8g**).* Yellow solid. Mp: 196−197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.87 (s, 1H), 8.00 (s, 1H), 7.72 (dd, J = 8.7, 2.3 Hz, 2H), 7.53 (dd, J = 8.5, 1.3 Hz, 1H), 7.18 (dd, J = 9.0, 2.4 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.8, 158.5, 156.5, 134.7, 131.9, 129.5, 128.6, 128.3, 127.0, 120.1, 119.7, 116.5, 105.9, 97.1, 55.3. HRMS (EI): calcd for $C_{17}H_{12}N_2O$ 260.0950, found 260.0950.

*2-(2-(4-tert-Butylphenyl)ethynyl)-6-methoxynaphthalene (**8h**).* Yellow solid. Mp: 140−142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.71 (t, J = 9.2 Hz, 2H), 7.59−7.46 (m, 3H), 7.44−7.37 (m, 2H), 7.17 (dd, J = 8.9, 2.5 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 3.93 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 151.4, 134.0, 131.3, 131.1, 129.3, 129.1, 128.5, 126.8, 125.3, 120.4, 119.3, 118.4, 89.3, 89.2, 55.3, 34.8, 31.2. HRMS (EI): calcd for $C_{23}H_{22}O$: 314.1671, found 314.1670.

*2-Methoxy-6-(2-(4-nitrophenyl)ethynyl)naphthalene (**8i**).* Mp: 128−130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 8.7 Hz, 2H), 8.00 (s, 1H), 7.72 (dd, J = 8.7, 4.1 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.54 (dd, J = 8.4, 1.4 Hz, 1H), 7.19 (dd, J = 9.1, 2.4 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.7, 146.7, 134.6, 132.1, 132.0, 130.4, 129.4, 128.7, 128.3, 127.0, 123.6, 119.7, 116.8, 105.9, 95.6, 87.3, 55.3. HRMS (EI): calcd for $C_{19}H_{13}NO_3$ 303.0895, found 303.0890.

*Ethyl 5-(2-(6-Methoxynaphthalen-2-yl)ethynyl)thiophene-2-carboxylate (**8j**).* Yellow solid. Mp: 124−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.70 (dd, J = 10.6, 6.0 Hz, 3H), 7.52 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 3.8 Hz, 1H), 7.17 (dd, J = 9.0, 2.2 Hz, 1H), 7.11 (d, J = 1.7 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 158.6, 134.5, 134.1, 133.1, 131.9, 131.6, 130.1, 129.4, 128.5, 128.4, 127.0, 119.6, 117.0, 105.9, 96.3, 81.8, 61.3, 55.3, 14.3. HRMS (EI): calcd for $C_{20}H_{16}O_3S$ 336.0820, found 336.0818.

*1-Nitro-4-(2-phenylethynyl)benzene (**8k**).* Mp: 111−112 °C (lit.[48] mp 111−113 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.64−7.53 (m, 2H), 7.52−7.35 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.9, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.0, 94.7, 87.5. HRMS (EI): calcd for $C_{14}H_9NO_2$ 223.0633, found 223.0630.

General Procedure for Glaser-Type Oxidative Homocoupling. To a suspension of the respective terminal alkyne (0.25 mmol), pyrrolidine (0.041 mL, 0.5 mmol), palladacycle **1** (0.05 mol % Pd), and CuI (5 mol %) in a pressure tube was added water (1 mL). The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 140 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, poured into ether (20 mL), and washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*1,4-Bis(6-methoxynaphthalen-2-yl)buta-1,3-diyne (**9a**).* Mp: 235−236 °C (lit.[49] mp 237−238 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 2H), 7.70 (dd, J = 12.5, 8.7 Hz, 4H), 7.52 (dd, J = 8.5, 1.4 Hz, 2H), 7.18−7.11 (m, 4H), 3.94 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.8, 134.6, 132.8, 129.4, 129.2, 128.4, 127.0, 119.6, 119.1, 105.9, 82.2, 73.9, 55.4. HRMS (EI): calcd for $C_{26}H_{18}O_2$ 362.1307, found 362.1307.

*3-(4-(Thiophene-3-yl)buta-1,3-diynyl)thiophene (**9b**).* Mp: 110−112 °C (lit.[50] mp 111.5−112.5 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.57 (m, 2H), 7.28 (dd, J = 5.0, 2.9 Hz, 2H), 7.17 (dd, J = 5.0, 1.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.2, 130.2, 125.6, 120.9, 76.5, 73.5. HRMS (EI): calcd for $C_{12}H_6S_2$ 213.9911, found 213.9908.

*1,4-Diphenylbuta-1,3-diyne (**9c**).* Mp: 83−84 °C (lit.[51] mp 85 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58−7.50 (m, 4H), 7.41−7.31 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.5, 129.2, 128.4, 121.8, 81.5, 73.9, 31.1. HRMS (EI): calcd for $C_{16}H_{10}$ 202.0783, found 202.0779.

*1,4-Bis(4-tert-butylphenyl)buta-1,3-diyne (**9d**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.3 Hz, 4H), 7.36 (d, J = 8.5 Hz, 4H), 1.33 (s, 18H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.1, 131.9, 125.3, 119.1, 83.8, 76.4, 34.8, 31.1. HRMS (EI): calcd for $C_{24}H_{26}$ 314.2035, found 314.2033.

General Procedure for the Stille Cross-Coupling Reaction between Organostannanes with Aryl Halides under Microwave Heating. To a suspension of aryl halide (0.50 mmol), boronic acid (0.75 mmol), TBAB (0.161 g, 0.25 mmol), and palladacycle **1** (0.005 mol % Pd) in a pressure tube was added 1 mL of degassed water. The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 100 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, poured into ether (20 mL), and washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*3-Ethoxybiphenyl (**10a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.27−7.19 (m, 2H), 6.96 (dd, J = 8.2, 2.4 Hz, 1H), 4.16 (q, J = 7.0 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 142.7, 141.1, 129.7, 128.7, 127.3, 127.1, 119.5, 113.5, 113.2, 63.4, 14.9. HRMS (EI): calcd for $C_{14}H_{14}O$ 198.1045, found 198.1041.

*4-Fluorobiphenyl (**10b**).* Mp: 71−72 °C (lit.[52] mp 72−73 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.52 (m, 3H), 7.52−7.41 (m, 13H), 7.39−7.29 (m, 2H), 7.17−7.10 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 128.8, 128.7, 128.6, 128.2, 127.9, 127.2, 127.0, 115.7, 115.5. HRMS (EI): calcd for $C_{12}H_9F$ 172.0688, found 172.0687.

*4-Chlorobiphenyl (**10c**).* Mp: 72−75 °C (lit.[53] mp 74−76 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58−7.46, (m, 3H), 7.44−7.42 (m, 4H), 7.39−7.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 132.7, 128.9, 128.9, 128.4, 127.9, 127.6, 127.0. HRMS (EI): calcd for $C_{12}H_9Cl$ 188.0393, found 188.0390. HRMS (EI): calcd for $C_{12}H_9Cl$ 188.0393, found 188.0391.

*4-tert-Butylbiphenyl (**10d**).* Mp: 49−51 °C (lit.[54] mp 49−50 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H), 7.56−7.54 (m, 2H), 7.49−7.42 (m, 4H), 7.34−7.33 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2, 141.0, 138.3, 136.8, 128.7, 127.0, 127.0, 126.8, 125.7, 31.3, 15.3. HRMS (EI): calcd for $C_{16}H_{18}$: 210.1409, found 210.1409.

*Biphenyl (**10e**).* Mp: 66−68 °C (lit.[55] mp 66−68 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64−7.63 (m, 4H), 7.49−7.46 (m, 4H), 7.40−7.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2, 128.7, 127.2, 127.1. HRMS (EI): calcd for $C_{12}H_{10}$ 154.0783, found 154.0785.

*4-(1-Methyl-1H-indol-2-yl)benzonitrile (**11a**).* Mp: 160−161 °C (lit.[56] mp 161−162 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 7.8 Hz, 1H), 7.36−7.28 (m, 1H), 7.20 (t, J = 7.2 Hz, 1H), 6.67 (s, 1H), 3.78 (s, 3H).). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.2, 139.0, 137.2, 132.3, 129.4, 127.6, 122.7, 120.9, 120.3, 118.7, 111.1, 109.8, 103.5, 31.4. HRMS (EI): calcd for $C_{16}H_{12}N_2$ 232.1000, found 232.1007.

*2-(4-tert-Butylphenyl)-1-methyl-1H-indole (**11b**).* Yellow solid. Mp: 115−116 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, J = 7.6 Hz, 1H), 7.51−7.45 (m, 4H), 7.36 (d, J = 8.2 Hz, 1H), 7.25−7.23 (m, 1H), 7.15−7.13 (m, 1H), 6.55 (s, 1H), 3.79 (s, 3H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.9, 141.6, 138.3, 129.9, 129.0, 128.0, 125.4, 121.5, 120.3, 119.7, 109.5, 101.3, 34.7, 31.3, 31.2. HRMS (EI): calcd for $C_{19}H_{21}N$ 263.1674, found 263.1677.

*1-Methyl-2-(thiophene-2-yl)-1H-indole (**11c**).* Mp: 59−60 °C (lit.[56] mp 58−59 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.5 Hz, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.31(d, J = 8.3 Hz, 1H), 7.23−7.20 (m, 2H), 7.12−7.06 (m, 2H), 6.64 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 134.1, 133.9, 127.6, 127.6, 126.7, 126.1, 122.0, 120.5, 120.0, 109.5, 102.7, 31.0. HRMS (EI): calcd for $C_{13}H_{11}NS$ 213.1612, found 213.1619.

*3-Methyl-5-(1-methyl-1H-indol-2-yl)pyridin-2-amine (**11d**).* Yellow solid. Mp: 115−117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.43 (s, 1H), 7.35 (d, J = 8.2 Hz, 1H),

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7.26−7.22 (m, 1H), 7.22−7.12 (m, 1H), 6.50 (s, 1H), 4.60 (br s, 2H), 3.72 (s, 3H), 2.21 (s, 3H) . ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.7, 145.9, 138.8, 138.6, 138.1, 127.9, 121.5, 120.2, 120.0, 119.6, 116.2, 109.5, 101.1, 30.9, 17.1. HRMS (EI): calcd for $C_{15}H_{15}N_3$ 237.1266, found 237.1265.

*1-Methyl-2-(3-nitrophenyl)-1H-indole (**11e**).* Mp: 152−154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (t, *J* = 1.8 Hz, 1H), 8.31−8.25 (m, 1H), 7.89−7.87 (m, 1H), 7.73−7.65 (m, 2H), 7.46−7.20 (m, 3H), 6.72 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3, 138.7, 138.6, 134.9, 134.5, 129.5, 127.6, 123.7, 122.6, 122.4, 120.9, 120.3, 109.8, 103.2, 31.3. HRMS (EI): calcd for $C_{15}H_{12}N_2O_2$ 252.0899, found 252.0895.

*Ethyl 5-(2-Phenylethynyl)thiophene-2-carboxylate (**12a**).* Brown solid. Mp: 56−58 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 4.0 Hz, 1H), 7.56−7.50 (m, 2H), 7.47−7.32 (m, 3H), 7.21 (d, *J* = 3.9 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5, 134.3, 133.4, 133.0, 131.5, 130.8, 129.0, 128.4, 122.2, 95.5, 82.0, 61.4, 14.3. HRMS (EI): calcd for $C_{15}H_{12}SO_2$ 256.0558, found 256.0555.

*1-Methoxy-4-(2-phenylethynyl)benzene (**12b**).* Mp: 59−60 °C (lit.[57] mp 57−61 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53−7.49 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 131.4, 128.3, 127.9, 123.6, 115.4, 114.0, 55.3. HRMS (EI): calcd for $C_{15}H_{12}O$ 208.0888, found 208.0887.

*4-(2-Phenylethynyl)benzonitrile (**12c**).* Mp: 109−110 °C (lit.[58] mp 110.2−111.4 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67−7.58 (m, 4H), 7.56−7.54 (m, 2H), 7.40−7.38 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.0, 132.0, 131.8, 129.1, 128.5, 128.2, 122.2, 118.5, 111.4, 93.8, 87.7. HRMS (EI): calcd for $C_{15}H_9N$ 203.0735, found 203.0733.

General Procedure for the Synthesis of (*E*)-*N*-Styrylphthalimides 13 via the Heck Reaction and under Microwave Heating. A mixture of the respective aryl halide (0.51 mmol), *N*-vinylphthalimide (87.0 mg, 0.50 mmol), Cy_2NMe (0.16 mL, 0.75 mmol), TBAB (161 mg, 0.50 mmol), and the palladacycle **1** (0.5 mol %Pd) in DMF (0.75 mL) was placed in a pressure tube. The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 170 °C, and the reaction was monitored by TLC. When the reaction was complete, the mixture was cooled to room temperature and concentrated to dryness. The crude product was separated from the palladacycle **1** using F-SPE,[8] and the desired *E*-product **13** was purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*(E)-2-(4-Methoxystyryl)isoindoline-1,3-dione (**13a**).* Mp: 162−163 °C (lit.[59] mp 164−166 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.88 (m, 2 H), 7.76−7.73 (m, 2 H), 7.60 (d, 1H, *J* = 15.1 Hz), 7.41 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 15.1 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 3.83 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 159.3, 134.4, 131.7, 128.5, 127.4, 123.6, 120.1, 115.9, 114.2, 55.3. HRMS (EI): calcd for $C_{17}H_{13}O_3N$ 279.0895, found 279.0896.

*(E)-2-(4-Methylstyryl)isoindoline-1,3-dione (**13b**).* Mp: 171−173 °C (lit.[59] mp 172−174 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.88 (m, 2 H), 7.77−7.74 (m, 2 H), 7.62 (d, *J* = 15.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 15.1 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2 H), 2.36 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 137.5, 134.5, 133.0, 131.7, 129.4, 126.1, 123.6, 120.3, 116.8, 21.2. HRMS (EI): calcd for $C_{17}H_{13}O_2N$ 263.0946, found 263.0949.

*(E)-2-[4-(Trifluoromethyl)styryl]isoindoline-1,3-dione (**13c**).* Mp: 202−204 °C (lit.[59] mp 205−207 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92−7.90 (m, 2 H), 7.79−7.77 (m, 2 H), 7.68 (d, *J* = 15.15 Hz, 1H), 7.59 (d, 2H, *J* = 8.85 Hz), 7.55 (d, 2H, *J* = 8.85 Hz), 7.43 (d, *J* = 15.15 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 139.7, 134.7, 131.6, 129.5, 126.3, 125.7 (q, *J* = 0.91 Hz), 123.8, 119.5, 118.4. HRMS (EI): calcd for $C_{17}H_{10}O_2NF_3$ 317.0664, found 317.0667.

*(E)-2-(4-Acetylstyryl)isoindoline-1,3-dione (**13d**).* Mp: 188−189 °C (lit.[59] mp 187−189 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95−7.90 (m, 4 H), 7.79−7.76 (m, 2 H), 7.69 (d, *J* = 15.1 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, 1 H, *J* = 15.1 Hz), 2.60 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 166.2, 140.9, 135.9, 134.7, 131.5, 128.9, 126.1, 123.8, 119.6, 118.6, 26.6. HRMS (EI): calcd for $C_{18}H_{13}O_3N$ 291.0895, found 291.0899.

*(E)-2-Styrylisoindoline-1,3-dione (**13e**).* Mp: 187−188 °C (lit.[59] mp 187−189 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.88 (m, 2 H), 7.77−7.74 (m, 2 H), 7.65 (d, *J* = 15.1 Hz, 1 H), 7.47 (d, *J* = 7.38 Hz, 2 H), 7.38 - 7.33 (m, 3 H), 7.28−7.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 136.0, 134.5, 131.7, 128.7, 127.6, 126.2, 123.6, 120.3, 117.6. HRMS (EI): calcd for $C_{16}H_{11}O_2N$ 249.0790, found 249.0795.

General Procedure for the Synthesis of Cinnamaldehydes 15 under Microwave Heating. A suspension of the respective aryl halide (0.25 mmol), acrolein diethyl acetal (0.06 mL, 0.38 mmol), K_2CO_3 (51.8 mg, 0.38 mmol), TBAA (151 mg, 0.50 mmol), KCl (18.8 mg, 0.25 mmol), and palladacycle **1** (0.5 mol %Pd) in DMAc (1 mL) was placed in a pressure tube. The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 120 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, and an aqueous solution of HCl (2 M, 2.5 mL) was added slowly. The mixture was stirred at room temperature for 10 min, poured into EtOAc (5 mL), and then washed successively with HCl (2 M, 5 mL) and H_2O (2 × 5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was separated from the palladacycle **1** using F-SPE and the desired cinnamaldehyde **10** was purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*4-Chlorocinnamaldehyde (**15a**).* Mp: 61−62 °C (lit.[60] mp 59−61 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.70 (d, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 15.8 Hz, 1 H), 6.69 (dd, J_1 = 15.8 Hz, J_2 = 7.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.3, 151.0, 137.3, 132.5, 129.6, 129.4, 129.0. HRMS (EI): calcd for C_9H_7OCl 166.0185, found 166.0182.

*4-Methoxycinnamaldehyde **15b**.* Mp: 56−57 °C (lit.[61] mp 57−58 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.65 (d, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 8.8 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 7.42 (d, *J* = 15.8 Hz, 1 H), 6.61 (dd, J_1 = 15.8 Hz, J_2 = 7.6 Hz, 1 H), 3.86 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.6, 152.6, 162.2, 130.3, 126.8, 114.6, 126.6, 55.4. HRMS (EI): calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0681.

*4-(Trifluoromethyl)cinnamaldehyde (**15c**).* Mp: 61−63 °C (lit.[62] mp 59−61 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.74 (d, *J* = 7.6 Hz, 1 H), 7.72−7.64 (m, 4 H), 7.50 (d, *J* = 15.8 Hz, 1 H), 6.77 (dd, J_1 = 15.8 Hz, J_2 = 7.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.1, 150.2, 137.3, 132.6 (q, *J* = 32.1 Hz), 130.5, 126.0 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.2 Hz), 128.3. HRMS (EI): calcd for $C_{10}H_7OF_3$ 200.0449, found 200.0446.

General Procedure for the Synthesis of Ethyl 3-Arylpropanoates 16 under Microwave Heating. A solution of the respective aryl halide (0.25 mmol), acrolein diethyl acetal (0.06 mL, 0.38 mmol), Cy_2NMe (0.08 mL, 0.38 mmol), TBAB (80.5 mg, 0.25 mmol), and palladacycle **1** (0.5 mol % Pd) in DMAc (1 mL) and water (0.25 mL) was placed in a pressure tube. The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 120 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, poured into EtOAc (5 mL), and washed successively with HCl (2 M, 2 × 5 mL) and H_2O (5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was separated from the palladacycle **1** using F-SPE, and the desired ethyl 3-arylpropanoate **16** was purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*Ethyl 3-(4-Nitrophenyl)propanoate (**16a**).* ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.6 Hz, 2 H), 7.35 (d, *J* = 8.6 Hz, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 3.04 (t, *J* = 7.4 Hz, 2 H), 2.65 (t, *J* = 7.6 Hz, 2 H), 1.21 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 148.3, 146.6, 129.2, 123.6, 60.6, 35.0, 30.6, 14.1. HRMS (EI): calcd for $C_{11}H_{13}O_4N$ 223.0845, found 223.0846.

*Ethyl 3-(4-Methoxyphenyl)propanoate (**16b**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.12 (q, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.58 (t, *J* = 7.7 Hz,

2H), 1.24 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 158.2, 132.3, 129.3, 113.9, 60.7, 55.2, 36.3, 30.1, 14.1. HRMS (EI): calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1097.

General Procedure for the Kumada Cross-Coupling between Grignard Reagents with Various Halides under Microwave Heating. To a solution of the respective halide (0.25 mmol) and anhydrous THF (1 mL) in a pressure tube was added palladacycle **1** (0.05 mol %) followed by 1 M Grignard reagent in THF (0.3 mL). The reaction mixture was microwave irradiated (with the heating program starting at 150 W) at 100 °C, and the reaction was monitored by TLC. When the reaction has completed, the reaction mixture was cooled to room temperature, poured into EtOAc (20 mL), and washed successively with water (3 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product obtained was purified by column chromatography. On the basis of the ^{1}H NMR, the purities of compounds were determined to be ≥96%.

*4-Methylbiphenyl (**17a**).* Mp: 45−47 °C (lit.[63] mp 43−44 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.2 Hz, 2H), 7.50−7.44 (m, 2H), 7.42−7.36 (m, 2H), 7.06 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2, 136.7, 131.2, 130.8, 128.7, 127.2, 127.1, 119.0, 20.5. HRMS (EI): calcd for $C_{13}H_{12}$ 168.0939, found 168.0937.

*10-Phenylanthracene (**17b**).* Mp: 153−155 °C (lit.[64] mp 154−155 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.08 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.68−7.54 (m, 2H), 7.53−7.46 (m, 4H), 7.41−7.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 137.0, 131.3, 131.2, 130.2, 128.3, 128.3, 127.4, 126.8, 126.5, 125.3, 125.0. HRMS (EI): calcd for $C_{20}H_{14}$ 254.1096, found 254.1093.

*4-Nitrobiphenyl (**17c**).* Mp: 106−107 °C (lit.[65] mp 108−110 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 8.8 Hz, 2H), 7.36−7.32 (m, 2H), 7.08−7.00 (m, 1H), 6.98 (d, J = 8.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3, 142.3, 132.1, 129.4, 121.6, 118.9, 118.2, 112.5. HRMS (EI): calcd for $C_{12}H_9O_2N$ 199.0633, found 199.0632.

*4-Methoxybiphenyl (**17d**).* Mp: 86−87 °C (lit.[66] mp 84−86 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66−7.60 (m, 4H), 7.52−7.47 (m, 2H), 7.41−7.36 (m, 1H), 7.06 (d, 2H, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.1, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2. HRMS (EI): calcd for $C_{13}H_{12}O$ 184.0888, found 184.0884.

*Hexylbenzene (**17e**).* ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24−7.28 (m, 2H), 7.12−7.14 (m, 3H), 2.63 (t, J = 7.6 Hz, 2H), 1.61 (m, 2H), 1.31−1.35 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 128.4, 128.2, 125.6, 36.2, 31.9, 31.5, 29.1, 22.7, 14.1. HRMS (EI): calcd for $C_{12}H_{18}$ 162.1409, found 162.1407.

*Styrene (**18**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.4 Hz, 0H), 6.78 (dd, J = 17.6, 10.9 Hz, 0H), 5.80 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.6, 136.9, 128.5,127.8, 126.2, 113.8. HRMS (EI): calcd for C_8H_8 104.0626, found 104.0626.

General Procedure for the Recycling Experiment Using F-SPE. The reaction mixture was first diluted with THF/H_2O = 8:2 and loaded into F-SPE fluorous silica. The crude product was eluted using THF/H_2O = 8:2 as eluent, and the palladacycle **1** was subsequently eluted with THF, concentrated, dried, and used for another run. For elemental analysis of Pd leaching, a solution of the crude product was concentrated and analyzed by ICP-OES. The crude product was then concentrated followed by diluting it with EtOAc (20 mL) and washed with water (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was then purified by column chromatography.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **1a−d**, **1**, **2a−e**, **3a−e**, **5a−d**, **6a−d**, **7a,b**, **8a−k**, **9a−d**, **10a−e**, **11a−e**, **12a−c**, **13a−e**, **15a−c**, **16a,b**, **17a−e**, and **18**. ^{19}F NMR spectra of compounds **1b−d** and **1**. FTIR spectrum of compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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