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N-Heterocyclic Carbene–Palladium(II)–1-Methylimidazole Complex-Catalyzed Suzuki–Miyaura Coupling of Aryl Sulfonates with Arylboronic Acids

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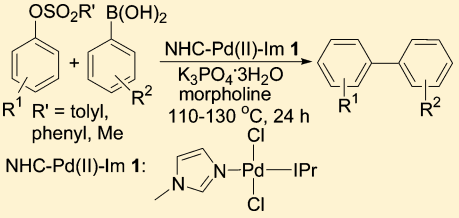
Supporting Information

ABSTRACT: A well-defined NHC–Pd(II)–Im complex **1** was found to be an effective catalyst for the Suzuki–Miyaura coupling of aryl sulfonates including tosylates and phenylsulfonates with arylboronic acids, giving the desired coupling products in good to high yields. Acceptable yields can also be achieved even by using the less reactive mesylates as the substrates. It is worthy of noting here that this is the first example of NHC–Pd(II) complex-catalyzed Suzuki–Miyaura coupling of aryl sulfonates with arylboronic acids, enriching an inexpensive, convenient, and alternative method for the synthesis of biaryl compounds.



INTRODUCTION

Transition-metal-catalyzed coupling reactions have been proven to be versatile methods for the formation of carbon–carbon bonds.[1] Among them, the Suzuki–Miyaura coupling is unarguably one of the most practical methods.[2] Among the electrophiles used in the transition-metal-catalyzed Suzuki–Miyaura coupling reactions, aryl sulfonates are a class of interesting and practical alternatives to aryl halides and triflates because they can be readily prepared from cheap, commercially available phenols and sulfonyl chlorides.[3] In addition, aryl sulfonates are more easily handled and usually less expensive than the corresponding aryl triflates. However, aryl sulfonates are generally less reactive in the metal-catalyzed coupling reactions than the corresponding aryl chlorides and triflates, and thus, much harsher reaction conditions have to be adopted accordingly.[4] For instance, to achieve an efficient Pd-catalyzed Suzuki–Miyaura coupling reaction using aryl sulfonates as the substrates, the expensive, less available, and air-sensitive sterically hindered, electron-rich phosphine ligands have to be employed to facilitate the corresponding transformations.[3a−f] In the Ni-catalyzed transformations, usually high loadings of the catalyst [1–10 mol % of Ni(0) or Ni(II)] and ancillary phosphine ligands are mandatory for the successful couplings.[3g−r] To overcome the drawbacks of using air-sensitive and cost-expensive phosphine ligands, the most straightforward way is to develop phosphine ligand-free methods. In 2011, Alonso and Nájera reported an oxime-derived palladacycle-catalyzed phosphine-free Suzuki–Miyaura coupling of aryl imidazolesulfonates with arylboronic acids and potassium aryltrifluoroborates.[5] However, this method uses the not readily available oxime palladacycle catalyst and aryl imidazolesulfonates, which were obtained by lengthy procedures. In addition, this method is only limited to the more reactive, electron-deficient aryl sulfonates such as aryl imidazolesulfonates.

On the other hand, during the past two decades, N-heterocyclic carbenes (NHCs) and their metal complexes, usually with higher air and thermal stability, have become a big challenge to phosphine–metal complexes since most phosphine ligands and their metal complexes are air-, thermal-, and/or moisture-sensitive.[6] However, in sharp contrast to the abundant reports of NHC–metal complex-catalyzed Suzuki–Miyaura coupling reactions of aryl halides,[7] their applications using aryl sulfonates as the partners are still limited and the known methods involve complicated synthetic routes for the NHC–metal catalysts.[8] Therefore, there still remains much room for improving the phosphine-free Suzuki–Miyaura coupling of aryl sulfonates with arylboronic acids, especially with respect to the easy availability of the metal complexes, stability of the ligands, high catalytic activity of the complexes, and substrate scope of the method.

Recently, we found that N-heterocyclic carbene–palladium(II)–1-methylimidazole [NHC-Pd(II)-Im] complex **1** (Figure 1), easily prepared from commercially available $PdCl_2$, 1-methylimidazole, and IPr·HCl [1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride] in a one-step process in very high yield,

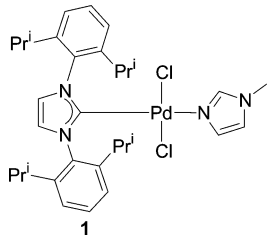


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Figure 1. NHC–Pd(II)–Im complex **1**.

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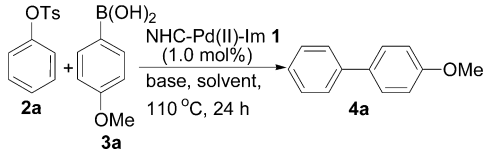
was an effective catalyst for the Suzuki−Miyaura coupling of aryl chlorides.[9] These results prompted us to further investigate its application toward the Suzuki−Miyaura coupling of more challenging substrates such as aryl sulfonates. In our continuing efforts on the development of more efficient and practical methods in the presence of this complex,[10] we report herein the first example of NHC−Pd(II) complex-catalyzed Suzuki−Miyaura coupling of aryl sulfonates including tosylates, phenylsulfonates, and even the less reactive mesylates with arylboronic acids.

RESULTS AND DISCUSSION

Initial examinations were carried out using phenyl tosylate **2a** (0.75 mmol) and 4-methoxyphenylboronic acid **3a** (0.90 mmol) as the model substrates in the presence of NHC−Pd(II)−Im complex **1** (1.0 mol %) at 110 °C for 24 h to find the most efficient base and solvent. Representative results are shown in Table 1. In the first round, dioxane was chosen as the solvent to evaluate the bases (Table 1, entries 1−4). It seems that $K_3PO_4·3H_2O$ was the best base to give the corresponding coupling product **4a** in 14% yield (Table 1, entry 2). For all other bases such as KOH, KOAc, $KF·2H_2O$, NaO^{t}Bu, and LiO^{t}Bu, only a trace of product **4a** was observed. In the second round, using $K_3PO_4·3H_2O$ as the base, a variety of solvents were tested and it was found that the solvents used significantly affected the reaction. For instance, similar yields were obtained when the reactions were performed in toluene, ^{t}BuOH, DMF, and DME (Table 1, entries 5−8). Finally, to our pleasure, the yield was dramatically increased to 92% when morpholine was chosen as the solvent (Table 1, entry 9). Further study showed that the solvent, morpholine, cannot play the role of the suitable base in this reaction, which suggests that the introduction of $K_3PO_4·3H_2O$ as the additional base is also essential (Table 1, entry 10).

Table 1. Optimization for the Reaction Conditions

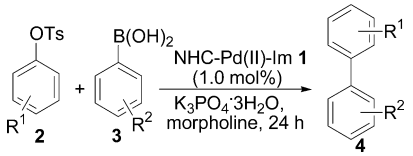


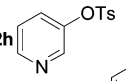
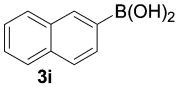
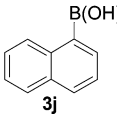
entry[a]	base	solvent	yield (%)
1	$KF·2H_2O$	dioxane	3
2	$K_3PO_4·3H_2O$	dioxane	14
3	$Na_3PO_4·12H_2O$	dioxane	7
4	KO^{t}Bu	dioxane	7
5	$K_3PO_4·3H_2O$	toluene	17
6	$K_3PO_4·3H_2O$	^{t}BuOH	17
7	$K_3PO_4·3H_2O$	DMF	18
8	$K_3PO_4·3H_2O$	DME	12
9	$K_3PO_4·3H_2O$	morpholine	92
10	*b*	morpholine	trace

[a]Unless otherwise specified, all reactions were carried out using **2a** (0.75 mmol), **3a** (0.9 mmol), base (2.5 equiv), and **1** (1.0 mol %) in solvent (2.0 mL) at 110 °C for 24h. [b]No additional base was added.

With the optimal reaction conditions in hand, we first set out to examine its generality with aryl tosylates as the electrophiles (Table 2). As can be seen from Table 2, most reactions proceeded well to give the desired products **4** in good to high yields under identical conditions. Sterically hindered substituents on the aryl tosylates have some effect on the reaction. For example, the reaction involving 2-methylphenyl tosylate **2e** gave the corresponding product **4e** only in 40% yield probably due to the steric hindrance (Table 2, entry 4). On the other hand, sterically hindered substituents on the arylboronic acids have less effect on the reactions. For example, the reactions involving 2-methylphenylboronic acid **3b** and 2-methoxyphenylboronic acid **3d** also gave products **4g** and **4i** in 80 and 82% yields, respectively (Table 2, entries 6 and 8). Reaction involving heteroaryl tosylate such as 3-pyridinyl tosylate **2h** also gave product **4r** in 81% yield (Table 2, entry 18). 2-Naphthylboronic acid **3i**, as well as 1-naphthylboronic acid **3j**, was also a suitable reaction partner (Table 2, entries 19−21).

Table 2. NHC−Pd(II)−Im Complex-1-Catalyzed Coupling of Aryl Tosylates 2 with Arylboronic Acids 3 under the Optimal Conditions



entry[a]	2 (R^1)	3 (R^2)	yield (%)
1	**2b** (4-Me)	**3a** (4-MeO)	**4b**, 81
2	**2c** (3-Me)	**3a**	**4c**, 89
3	**2d** (4-^{i}Pr)	**3a**	**4d**, 80
4	**2e** (2-Me)	**3a**	**4e**, 40
5	**2f** (4-F)	**3a**	**4f**, 94
6	**2f**	**3b** (2-Me)	**4g**, 80
7	**2f**	**3c** (4-Me)	**4h**, 95
8	**2f**	**3d** (2-OMe)	**4i**, 82
9	**2f**	**3e** (3,5-Me_2)	**4j**, 93
10	**2f**	**3f** (3-Me)	**4k**, 91
11	**2f**	**3g** (3-F)	**4l**, 86
12[b]	**2g** (4-MeO)	**3h** (H)	**4a**, 84
13[c]	**2c**	**3c**	**4m**, 85
14[c]	**2c**	**3e**	**4n**, 80
15	**2d**	**3c**	**4o**, 96
16	**2a** (H)	**3f**	**4p**, 82
17	**2a**	**3c**	**4q**, 82
18[b]	**2h** 	**3a**	**4r**, 81
19	**2a**	 **3i**	**4s**, 81
20	**2f**	**3i**	**4t**, 94
21	**2f**	 **3j**	**4u**, 85

[a]Unless otherwise specified, all reactions were carried out using **2** (0.75 mmol), **3** (0.9 mmol), $K_3PO_4·3H_2O$ (2.5 equiv), and **1** (1.0 mol %) in morpholine (2.0 mL) at 110 °C for 24 h. [b]The temperature was 130 °C. [c]The temperature was 120 °C.

Subsequently, aryl phenylsulfonates **5** were also examined under the similar reaction conditions (Table 3, entries 1−5). To our delight, all reactions took place smoothly to give the desired coupling products **4** in good to high yields at elevated temperature (120 °C). Nosylates **5c** and **5d** were labile to decompose under identical conditions, and no desired product was observed (Table 3, entries 6 and 7).

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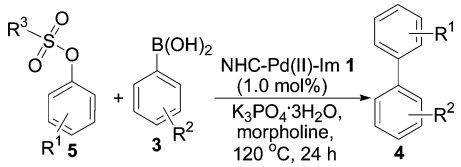
Table 3. NHC−Pd(II)−Im Complex-1-Catalyzed Coupling of Aryl Sulfonates 5 with Arylboronic Acids 3 under the Optimal Conditions

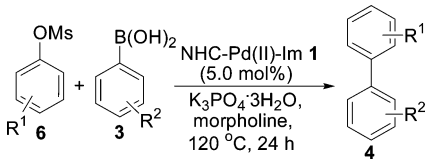


entry[a]	5 (R^1/R^3)	3 (R^2)	yield (%)
1	**5a** (4-F/Ph)	**3a** (4-MeO)	**4f**, 86
2	**5a**	**3e** (3,5-Me_2)	**4j**, 80
3	**5a**	**3k** (3-MeO)	**4v**, 80
4	**5b** (H/Ph)	**3a**	**4a**, 90
5	**5b**	**3k**	**4w**, 81
6	**5c** (4-F/3-$NO_2C_6H_4$)	**3a**	
7	**5d** (4-F/4-$NO_2C_6H_4$)	**3a**	

[a]All reactions were carried out using **5** (0.75 mmol), **3** (0.9 mmol), $K_3PO_4·3H_2O$ (2.5 equiv), and **1** (1.0 mol %) in morpholine (2.0 mL) at 120 °C for 24 h.

Except aryl tosylates and phenylsulfonates, the less reactive aryl mesylates **6** were also tested under the similar reaction conditions in order to improve the atom economy of this type of Suzuki−Miyaura coupling (Table 4). As can be seen from Table 4, by increasing the catalyst loading to 5.0 mol %, the desired coupling products **4** can also be achieved in 46−62% yields at 120 °C within 24 h.

Table 4. NHC−Pd(II)−Im Complex-1-Catalyzed Coupling of Aryl Mesylates 6 with Arylboronic Acids 3 under the Optimal Conditions

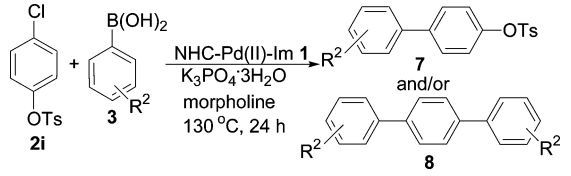


entry[a]	6 (R^1)	3 (R^2)	yield (%)
1	**6a** (4-F)	**3a** (4-MeO)	**4f**, 62
2	**6a** (4-F)	**3c** (4-Me)	**4h**, 50
3	**6a** (4-F)	**3f** (3-Me)	**4k**, 55
4	**6a** (4-F)	**3g** (3-F)	**41**, 50
5	**6a** (4-F)	**3k** (3-MeO)	**4v**, 61
6	**6b** (H)	**3f**	**4p**, 52
7	**6b**	**3c**	**4q**, 46
8	**6b**	**3a**	**4a**, 51
9	**6c** (3-F)	**3a**	**4w**, 47
10	**6d** (3-Me)	**3a**	**4c**, 47
11	**6e** (4-^{i}Pr)	**3a**	**4d**, 50

[a]All reactions were carried out using **6** (0.75 mmol), **3** (0.9 mmol), $K_3PO_4·3H_2O$ (2.5 equiv), and **1** (5.0 mol %) in morpholine (2.0 mL) at 120 °C for 24 h.

Finally, 4-chlorophenyl tosylate **2i**, as special bis-electrophiles, was also tested in this type of Suzuki−Miyaura coupling (Table 5). First, when the reaction between 4-chlorophenyl tosylate **2i** and 4-fluorophenylboronic acid **3l** was carried out under identical conditions, very low yields of both of the Cl-coupled product **7a** and the bis-coupled **8a** were observed. Second, when the reaction temperature was elevated to 130 °C,

Table 5. NHC−Pd(II)−Im Complex-1-Catalyzed Coupling of 4-Chlorophenyl Tosylate 2i



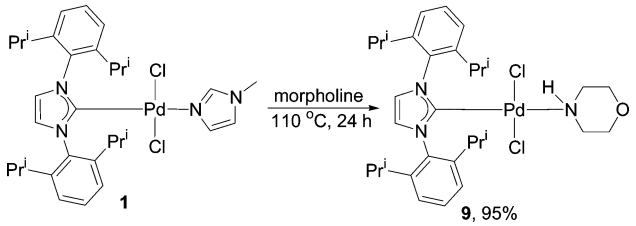
			yield (%)	
entry[a]	3 (R^2)	1 (mol %)	7	8
1	**3l** (4-F)	1.0	**7a**, 7	**8a**, 50
2	**3l**	3.0	**7a**, 6	**8a**, 66
3	**3l**	5.0		**8a**, 95
4	**3c** (4-Me)	5.0		**8b**, 83
5	**3h** (H)	5.0		**8c**, 80
6	**3f** (3-Me)	5.0		**8d**, 86
7	**3g** (3-F)	5.0		**8e**, 75

[a]All reactions were carried out using **2i** (0.75 mmol), **3** (1.8 mmol), $K_3PO_4·3H_2O$ (5.0 equiv), and **1** (1.0−5.0 mol %) in morpholine (4.0 mL) at 130 °C for 24 h.

product **8a** was obtained in 50% yield, along with **7a** in 7% yield (Table 5, entry 1). Third, when the catalyst loading was increased to 3.0 mol %, product **8a** was increased to 66% yield, along with **7a** in 6% yield (Table 5, entry 2). Finally, the best result was achieved when the catalyst loading was elevated to 5.0 mol %, giving product **8a** in 95% yield as the sole one (Table 5, entry 3). Under these optimal conditions (Table 5, entry 3), a variety of arylboronic acids were tested and all reactions gave the bis-coupled products **8** in good yields as the sole products (Table 5, entries 4−7).

As can be seen from Table 1, morpholine was found to be the only solvent for this type of Suzuki−Miyaura coupling between aryl sulfonates and arylboronic acids. So we are wondering if, in the reactions using morpholine as the solvent, the imidazole moiety may be displaced by morpholine, which will result in the real precatalyst. So in order to confirm this assumption, two control experiments were carried out. First, treatment of NHC−Pd(II)−Im complex **1** (0.2 mmol) in morpholine (2.0 mL) at 110 °C for 24 h was carried out, and complex **9** was achieved in 95% yield (Scheme 1), which may

Scheme 1. Transformtion of NHC−Pd(II)−Im Complex 1 in Morpholine



suggest that the morpholine-derived complex **9** has great stability over the 1-methylimidazole-derived complex **1** under identical conditions. The structure of complex **9** was unambiguously determined by X-ray single-crystal diffraction (see Supporting Information for the details).[11]

Subsequently, complex-**9**-catalyzed reaction between phenyl tosylate **2a** and 4-methoxyphenylboronic acid **3a** was investigated under identical conditions, and product **4a** was

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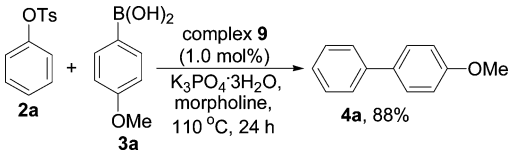
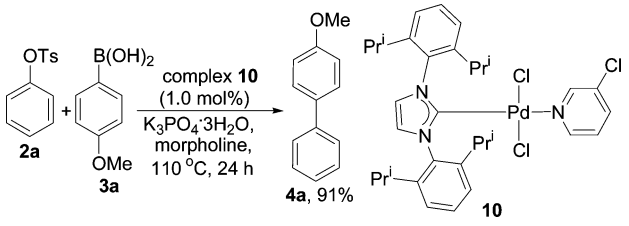
obtained in 88% yield (Scheme 2), which is comparable to the result using NHC−Pd(II)−Im complex **1** as the catalyst (Table 1, entry 9). On the basis of the results described above, we can conclude that morpholine-derived complex **9** may be the real precatalyst for this type of Suzuki−Miyaura coupling between aryl sulfonates and arylboronic acids.

Scheme 2. Complex-9-Catalyzed Reaction of 2a with 3a under Identical Conditions



In addition, a similar complex such as **10**[6e] developed by Organ's group was also investigated for the reaction between phenyl tosylate **2a** and 4-methoxyphenylboronic acid **3a** under identical conditions (Scheme 3). In this case, product **4a** was observed in 91% yield, and further investigation showed that complex **10** can also be transformed into complex **9** completely under identical conditions.

Scheme 3. Complex-10-Catalyzed Reaction of 2a with 3a under Identical Conditions



CONCLUSIONS

In conclusion, to the best of our knowledge, the results reported in this paper were the first examples of practical and easily available NHC−Pd(II) complex that can catalyze the phosphine-free Suzuki−Miyaura coupling of aryl sulfonates with arylboronic acids. By using the readily prepared NHC−Pd(II)−Im complex **1** as the catalyst, the phosphine-free Suzuki−Miyaura coupling of the easy available and advantageous aryl sulfonates with arylboronic acids can proceed efficiently to afford the target coupling products. This reaction can tolerate a broad scope of substrates. For instance, aryl and heteroaryl tosylates, aryl phenylsulfonates, sterically hindered arylboronic acids, and even the less reactive aryl mesylates can all be employed as the substrates for the reaction. These results will enrich the utilities of the NHC−Pd(II) complexes in organic synthesis. Furthermore, the control experiments showed that the real precatalyst is most possibly the NHC−Pd(II)−morpholine complex.

EXPERIMENTAL SECTION

General Remarks. Melting points are uncorrected. NMR spectra were recorded at 300/500 (for ^{1}H NMR) or 75/125 MHz (for ^{13}C NMR). ^{1}H NMR and ^{13}C NMR spectra recorded in $CDCl_3$ solutions were referenced to TMS (0.00 ppm) and the residual solvent peak (77.0 ppm), respectively. *J* values are in hertz. Organic solvents used were dried by standard methods. The mass analyzer types for the high-resolution mass spectra (HRMS) are FT-ICR (for EI) and quadrupole (for ESI). Other commercially obtained reagents were used without further purification. Flash column chromatography was performed on silica gel (300−400 mesh).

General Procedure for the NHC−Pd(II)−Im Complex-1-Catalyzed Suzuki−Miyaura Coupling of Aryl Sulfonates with Arylboronic Acids. Under N_2 atmosphere, aryl tosylates **2** (0.75 mmol), arylboronic acids **3** (0.9 mmol), NHC−Pd(II)−Im complex **1** (1.0 mol %), $K_3PO_4·3H_2O$ (2.5 equiv), and dried morpholine (2.0 mL) were successively added into a Schlenk reaction tube. The mixture was stirred vigorously at the specified temperature for 24 h. Then the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2) to give the pure products.

Compound ***4a*** *(ref 12):* a white solid (127.1 mg, 94%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.56−7.52 (m, 4H), 7.41 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 140.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

Compound ***4b*** *(ref 13):* a white solid (120.3 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.51 (d, J = 8.5, 2.0 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.5, 114.1, 55.2, 21.0.

Compound ***4c*** *(ref 14):* a pale yellow solid (131.8 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.52 (d, J = 9.0 Hz, 2H), 7.36−7.28 (m, 3H), 7.12 (d, J = 7.5 Hz, 1H), 6.96 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 140.8, 138.3, 133.9, 128.6, 128.1, 127.6, 127.4, 123.8, 114.1, 55.3, 21.5.

Compound ***4d*** *(ref 15):* a white solid (135.9 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.51 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H), 2.94 (hept, J = 7.0 Hz, 1H), 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 147.4, 138.4, 133.8, 128.0, 126.8, 126.6, 114.1, 55.3, 33.7, 24.0.

Compound ***4e*** *(ref 4e):* a colorless oil (60.0 mg, 40%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.26−7.21 (m, 6H), 6.95 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.5, 141.5, 135.4, 134.3, 130.3, 130.2, 129.9, 126.9, 125.7, 113.5, 55.2, 20.5.

Compound ***4f*** *(ref 4e):* a white solid (142.9 mg, 94%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.50−7.46 (m, 4H), 7.10 (t, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.1 (d, J_{C-F} = 243.8 Hz), 159.1, 136.9 (d, J_{C-F} = 3.0 Hz), 132.8, 128.1 (d, J_{C-F} = 8.3 Hz), 128.0, 115.5 (d, J_{C-F} = 21.0 Hz), 114.2, 55.3.

Compound ***4g*** *(ref 16):* a light yellow oil (112.1 mg, 80%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.27−7.20 (m, 6H), 7.08 (t, J = 8.7 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 243.9 Hz), 140.9, 137.8 (d, J_{C-F} = 3.5 Hz), 135.4, 130.7 (d, J_{C-F} = 7.9 Hz), 130.3, 129.8, 127.4, 125.8, 114.9 (d, J_{C-F} = 21.2 Hz), 20.4.

Compound ***4h*** *(ref 17):* a pale yellow solid (132.7 mg, 95%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.53−7.50 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.24−7.23 (m, 2H), 7.10 (t, J = 9.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 244.4 Hz), 137.4, 137.3 (d, J_{C-F} = 3.3 Hz), 137.0, 129.5, 128.4 (d, J_{C-F} = 7.9 Hz), 126.8, 115.5 (d, J_{C-F} = 21.3 Hz), 21.0.

Compound ***4i*** *(ref 17):* a pale yellow solid (124.4 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.50−7.47 (m, 2H), 7.33−7.31 (m, 2H), 7.27−6.96 (m, 4H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 244.3 Hz), 156.4, 134.4 (d, J_{C-F} = 3.4 Hz), 131.1 (d, J_{C-F} = 7.9 Hz), 130.7, 129.7, 128.7, 120.9, 114.8 (d, J_{C-F} = 21.1 Hz), 111.3, 55.5.

Compound ***4j:*** a colorless oil (139.4 mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.51 (dd, J = 8.5, 5.5 Hz, 2H), 7.15 (s, 2H), 7.09 (t, J = 8.5 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 244.4 Hz), 140.3, 138.3, 137.6 (d, J_{C-F} = 3.1 Hz), 128.9, 128.7 (d, J_{C-F} = 8.0 Hz), 125.0, 115.4 (d, J_{C-F} = 21.3 Hz), 21.4; IR (ν) 1602, 1517, 1224, 1162, 1099, 1014, 860, 830, 796, 785, 698 cm^{-1}; MS (EI, m/z) 200 [M$^+$]; HRMS (EI) calcd for $C_{14}H_{13}F$ [M]$^+$ 200.1001, found 200.1004.

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Compound ***4k*** *(ref 18):* a pale yellow oil (127.2 mg, 91%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.53 (dd, J = 9.0, 5.5 Hz, 2H), 7.35−7.30 (m, 3H), 7.16 (d, J = 6.5 Hz, 1H), 7.11 (t, J = 9.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 244.6 Hz), 140.3, 138.4, 137.5 (d, J_{C-F} = 3.3 Hz), 128.7 (d, J_{C-F} = 1.5 Hz), 128.6, 128.0, 115.5 (d, J_{C-F} = 21.3 Hz), 21.5.

Compound ***4l:*** a colorless oil (122.3 mg, 86%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.52 (dd, J = 8.5, 5.0 Hz, 2H), 7.38 (td, J = 8.0, 6.0 Hz, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.23 (dt, J = 10.0, 3.5 Hz, 1H), 7.13 (t, J = 8.5 Hz, 2H), 7.03 (td, J = 10.0, 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.4 Hz), 162.8 (d, J_{C-F} = 245.9 Hz), 142.5 (d, J_{C-F} = 7.8 Hz), 136.09 (d, J_{C-F} = 3.0 Hz), 136.07 (d, J_{C-F} =2.4 Hz), 130.3 (d, J_{C-F} = 8.5 Hz), 128.7 (d, J_{C-F} = 8.1 Hz), 122.6 (d, J_{C-F} = 2.8 Hz), 115.8 (d, J_{C-F} = 21.5 Hz), 114.0 (d, J_{C-F} = 21.0 Hz), 113.9 (d, J_{C-F} = 22.0 Hz); IR (ν) 1615, 1599, 1583, 1516, 1484, 1399, 1232, 1185, 1164, 881, 832, 780, 688 cm^{-1}; MS (EI, m/z) 190 [M$^+$]; HRMS (EI) calcd for $C_{12}H_8F_2$ [M]$^+$ 190.0594, found 190.0595.

Compound ***4m*** *(ref 19):* a colorless oil (116.1 mg, 85%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.48 (d, J = 8.1 Hz, 2H), 7.39−7.36 (m, 2H), 7.31 (td, J = 7.2, 1.2 Hz, 1H), 7.25−7.22 (m, 2H), 7.15−7.13 (m, 1H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 138.5, 138.2, 136.9, 129.4, 128.6, 127.8, 127.7, 127.0, 124.1, 21.5, 21.1.

Compound ***4n*** *(ref 20):* a colorless oil (117.2 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.37 (d, J = 7.5 Hz, 1H), 7.36 (s, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.19 (s, 2H), 7.13 (d, J = 7.5 Hz, 1H), 6.98 (s, 1H), 2.40 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 141.4, 138.1, 128.8, 128.5, 128.0, 127.8, 125.1, 124.3, 21.5, 21.4.

Compound ***4o*** *(ref 21):* a white solid (151.2 mg, 96%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.50 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.93 (hept, J = 7.0 Hz, 1H), 2.37 (s, 3H), 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 138.6, 138.3, 136.6, 129.4, 126.85, 126.83, 126.77, 33.8, 24.0, 21.1.

Compound ***4p*** *(ref 19):* a colorless oil (103.0 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.57 (d, J = 7.8 Hz, 2H) 7.44−7.37 (m, 4H), 7.31 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 7.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 141.2, 138.3, 128.7, 128.6, 127.97, 127.95, 127.2, 127.1, 124.3, 21.5.

Compound ***4q*** *(ref 19):* a white solid (103.2 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.57 (dd, J = 8.0, 1.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.00 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 138.4, 137.0, 129.5, 128.7, 126.98, 126.96, 126.9, 21.1.

Compound ***4r*** *(ref 4e):* a pale yellow solid (112.3 mg, 81%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.81 (s, 1H), 8.54 (d, J = 4.8 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.31 (dd, J = 8.1, 4.8 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 147.8, 147.7, 136.1, 133.7, 130.0, 128.1, 123.4, 114.4, 55.2.

Compound ***4s*** *(ref 19):* a white solid (123.4 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 8.04 (s, 1H), 7.92−7.86 (m, 3H), 7.85−7.71 (m, 3H), 7.52−7.46 (m, 4H), 7.39−7.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.6, 133.7, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6.

Compound ***4t*** *(ref 22):* a white solid (156.5 mg, 94%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.97 (s, 1H), 7.90−7.84 (m, 3H), 7.69−7.64 (m, 3H), 7.52−7.46 (m, 2H), 7.18−7.14 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 245.1 Hz), 137.6, 137.2 (d, J_{C-F} = 3.3 Hz), 133.6, 132.5, 128.9 (d, J_{C-F} = 8.0 Hz), 128.5, 128.1, 127.6, 126.4, 126.0, 125.6, 125.4, 115.7 (d, J_{C-F} = 21.3 Hz).

Compound ***4u*** *(ref 23):* a white solid (141.8 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.92−7.83 (m, 3H), 7.53--7.38 (m, 6H), 7.20−7.16 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 244.6 Hz), 139.2, 136.7 (d, J_{C-F} = 3.3 Hz), 133.8, 131.7, 131.6 (d, J_{C-F} = 7.9 Hz), 128.3, 127.8, 127.0, 126.1, 125.83, 125.76, 125.3, 115.2 (d, J_{C-F} = 21.1 Hz).

Compound ***4v*** *(ref 4e):* a light yellow oil (120.6 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.51 (dd, J = 8.0, 5.0 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.11−7.05 (m, 4H), 6.87 (dd, J = 8.0, 2.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 244.9 Hz), 159.9, 141.7, 137.1 (d, J_{C-F} = 3.1 Hz), 129.8, 128.7 (d, J_{C-F} = 8.0 Hz), 119.5, 115.5 (d, J_{C-F} = 21.3 Hz), 112.8, 112.5, 55.2.

Compound ***4w*** *(ref 24):* a colorless oil (112.0 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 8.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.35−7.31 (m, 2H), 7.18−7.16 (m, 1H), 7.12 (t, J = 2.0 Hz, 1H), 6.88 (dd, J = 7.5, 2.5 Hz, 1H), 3.82 (s, 3H, OMe); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 142.7, 141.0, 129.7, 128.7, 127.4, 127.1, 119.6, 112.8, 112.6, 55.2.

Compound ***7a:*** a white solid (18.1 mg, 7%); mp 121−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.74 (d, J = 8.5 Hz, 2H), 7.47 (dd, J = 8.5, 5.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.10 (t, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} = 245.6 Hz), 149.0, 145.4, 139.2, 135.9 (d, J_{C-F} = 3.3 Hz), 132.5, 129.8, 128.7 (d, J_{C-F} = 8.0 Hz), 128.5, 128.1, 122.7, 115.7 (d, J_{C-F} = 21.5 Hz), 21.7; IR (ν) 1596, 1493, 1378, 1248, 1206, 1190, 1180, 1159, 1091, 858, 826, 748, 727, 706, 677 cm^{-1}; MS (ESI) 365 [M + Na]$^+$; HRMS (ESI) calcd for $C_{19}H_{15}FO_3SNa$ [M + Na]$^+$ 365.0618, found 365.0627.

Compound ***8a*** *(ref 25):* a white solid (190.2 mg, 95%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.61 (s, 4H), 7.59 (dd, J = 8.5, 5.5 Hz, 4H), 7.14 (t, J = 8.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 245.1 Hz), 139.2, 136.7 (d, J_{C-F} = 3.3 Hz), 128.6 (d, J_{C-F} = 7.9 Hz), 127.4, 115.7 (d, J_{C-F} = 21.3 Hz).

Compound ***8b*** *(ref 26):* a white solid (160.9 mg, 83%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.64 (s, 4H), 7.54 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 137.9, 137.1, 129.5, 127.2, 126.9, 21.1.

Compound ***8c*** *(ref 26):* a white solid (138.0 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.68 (s, 4H), 7.64 (d, J = 7.0 Hz, 4H), 7.46 (t, J = 7.5 Hz, 4H), 7.36 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 140.1, 128.8, 127.5, 127.3, 127.0.

Compound ***8d*** *(ref 27):* a white solid (166.0 mg, 86%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.65 (s, 4H), 7.45−7.43 (m, 4H), 7.34 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 2.43 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 140.1, 138.4, 128.7, 128.1, 127.8, 127.4, 124.1, 21.5.

Compound ***8e*** *(ref 28):* a white solid (149.7 mg, 75%); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.62 (s, 4H), 7.38 (t, J = 5.0 Hz, 4H), 7.30 (dd, J = 9.0, 1.5 Hz, 2H), 7.05−7.01 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 244.3 Hz), 142.7 (d, J_{C-F} = 7.6 Hz), 139.3 (d, J_{C-F} = 2.1 Hz), 130.3 (d, J_{C-F} = 8.4 Hz), 127.5, 122.6 (d, J_{C-F} = 2.6 Hz), 114.2 (d, J_{C-F} = 21.1 Hz), 113.9 (d, J_{C-F} = 22.0 Hz).

Compound ***9:*** A yellow solid (124.1 mg, 95%); mp 150−151 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.50 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 4H), 7.09 (s, 2H), 3.60 (dd, J = 12.0, 3.3 Hz, 2H), 3.24 (td, J = 12.0, 2.1 Hz, 2H), 3.10−3.01 (m, 6H), 2.50−2.46 (m, 3H), 1.44 (d, J = 6.6 Hz, 12H), 1.09 (d, J = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 146.6, 135.0, 130.1, 124.8, 123.8, 67.6, 47.0, 28.7, 26.2, 23.1; IR (ν) 1727, 1698, 1464, 1345, 1234, 1208, 1116, 1098, 1012, 882, 802, 757, 742, 706 cm^{-1}; MS (ESI) 652 [M + H]$^+$; HRMS (ESI) calcd for $C_{31}H_{46}Cl_2N_3OPd$ [M + H]$^+$ 652.2053, found 652.2040.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **4**, **7a**, **8**, and **9**. X-ray data of compound **9** in CIF format. 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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(11) Crystal data of **9**: empirical formula $C_{62}H_{92}Cl_4N_6O_3Pd_2$; molecular weight = 1324.02; color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 16.4227(16) Å, b = 18.4780(19) Å, c = 25.266(3) Å, α = 90°, β = 103.557(2)°, γ = 90°, V = 7453.5(13) Å^3; space group: $P2(1)/c$; Z = 4; D_{calcd} = 1.180 g/cm^3; F_{000} = 2760; diffractometer: Rigaku AFC7R; residuals: R; Rw: 0.0581, 0.2081. CCDC-881917 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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