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Monodentate Palladium Complexes Bearing Abnormal and Normal Carbene Ligands with a Formally Identical Steric Environment

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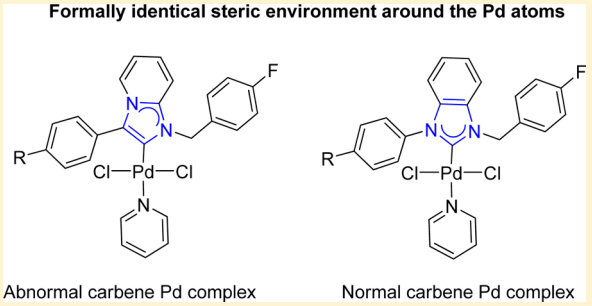
Supporting Information

ABSTRACT: We report a series of novel isomeric Pd(II) complexes with monodentate abnormal and normal carbene ligands, possessing a formally identical steric environment around the metal center. The corresponding ligand precursors were prepared via the key steps based on Pd-catalyzed direct C−H arylation between imidazo[1,2-*a*]pyridine and aryl bromides and Cu-catalyzed C−N coupling reactions between benzoimidazole and aryl bromides. The new complexes were characterized by 1D and 2D NMR spectroscopy, X-ray crystallography, and elemental analysis. The isomeric pairs of ligands show minor differences among their steric properties, which were examined by calculating their buried volume. The abnormal carbene Pd(II) complexes were found to be more efficient in catalyzing Mizoroki−Heck coupling, direct C−H arylation, and decarboxylative coupling reactions, which can be clearly attributed to a stronger electronic donating effect of the abnormal carbene ligands.

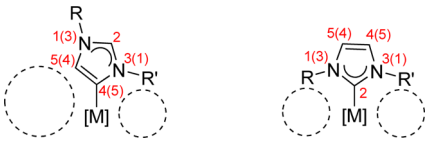


INTRODUCTION

Following the isolation and structural characterization of free carbene in a study by Arduengo,[1] *N*-heterocyclic carbene (NHC) ligands have been proven very effective in homogeneous catalysis.[2−11] An experiment unexpectedly showed that imidazole-based NHC ligands could have an alternative binding mode via C(4/5) atom, instead of the common C(2) atom in the imidazolium ring.[12−14] This variant of NHC ligands, termed "abnormal NHC ligands", has been attracting attention[15−20] because reports have shown that it is a stronger electron donor than the normal carbene ligands;[12,21−25] consequently, it exhibits better catalytic activities in reactions involving the activation of unreactive bonds as key steps.[24−28] However, metalation via C(4/5) atoms is typically accompanied by a change in the steric environment around the metal center (Chart 1), making it difficult to identify whether the enhanced catalytic activity is because of steric hindrance or owing to the intrinsic electronic property of the carbene ligand.[29] In order to obtain a rational design of precatalyst, it is desirable to develop genuine isomeric pair of abnormal and normal carbene ligands, in which the pair affords formally identical steric environment around the metal center upon binding. In this regard, Albrecht reported a unique example based on Pd complexes with bidentate abnormal and normal carbene ligands.[30] Since the use of monodentate NHC ligand, such as IMes and IPr, is more versatile in a variety of Pd-catalyzed cross-coupling reactions,[6] it is of great interest to obtain a formally and sterically identical isomeric pair based on monodentate carbene ligands. However, such isomeric pairs of Pd complexes have not yet been reported in the literature.

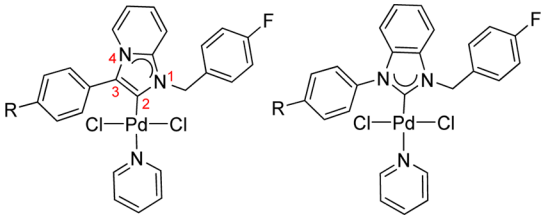
In this study, we successfully addressed the aforementioned problem by obtaining a series of novel Pd(II) dichloride complexes bearing abnormal and normal carbene ligands. They are isomeric pairs sharing formally the same steric environment around the metal centers (Chart 2). The appropriate design of

Chart 1. Metal Binding of Abnormal and Normal Carbene Ligands with Different Steric Environment around the Metal Center[a]



[a]Numbering scheme is shown in red.

Chart 2. Isomeric Normal and Abnormal Carbene Pd(II) Complexes with a Formally Identical Steric Environment around the Metal Center[a]



[a]Numbering scheme is shown in red.

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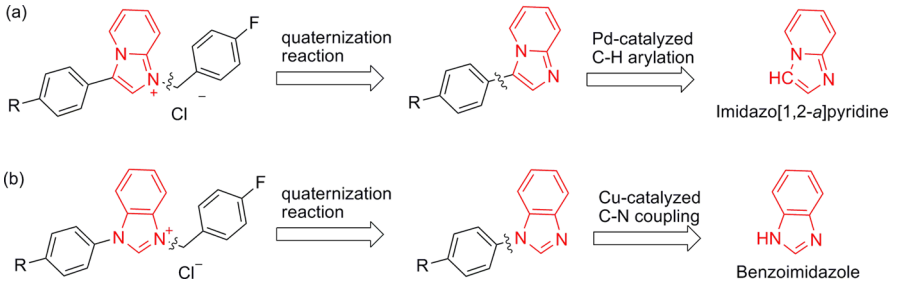
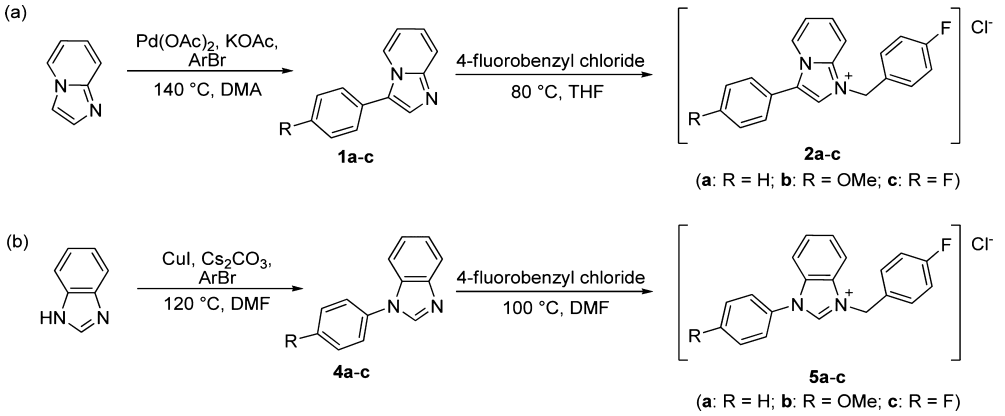
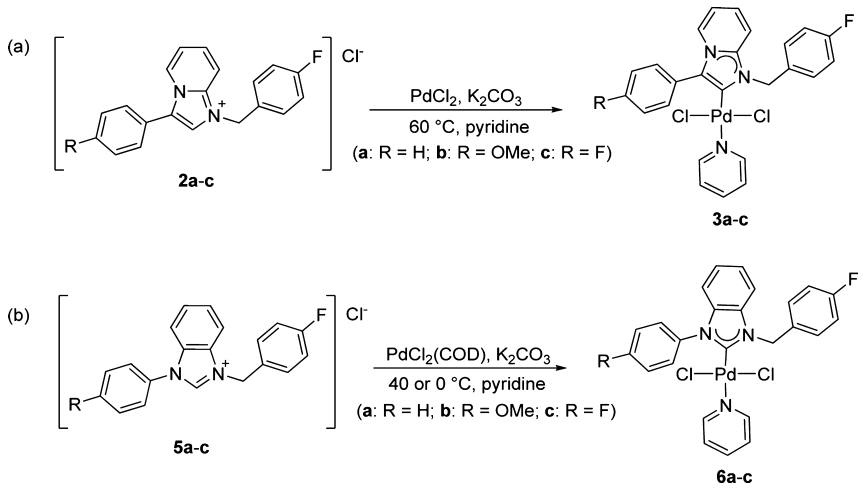
Chart 3. Retrosynthetic Analysis of the Abnormal and Normal Carbene Ligand Precursors



Scheme 1. Preparation of Abnormal and Normal Carbene Ligand Precursors



Scheme 2. Preparation of Pd Complexes with Abnormal and Normal Carbene Ligands



the isomeric ligand precursors was crucial, and on the basis of the easily available structural isomers of imidazo[1,2-*a*]pyridine and benzoimidazole (Chart 3), we were able to obtain the target ligand precursors via Pd-catalyzed direct C−H arylation reactions and Cu-catalyzed C−N coupling reactions. Our synthetic strategies also allowed a desirable, wide-ranging tunability to access ligand precursors with different electronic properties. The catalytic performances of these new abnormal carbene Pd complexes in classical and nonclassical C−C coupling reactions were compared with those of their normal carbene Pd isomers. Our findings could be unambiguously attributed to the electronic effect of the abnormal carbene ligands.

RESULTS AND DISCUSSION

Preparation of Abnormal and Normal Carbene Precursors. Carbene ligand precursors were prepared according to Scheme 1. For the abnormal carbene ligand precursors, the key intermediates **1a−c** were prepared via the Pd-catalyzed direct C−H arylation reactions of imidazo[1,2-*a*]pyridine with aryl bromides.[31] Arylation occurs regioselectively at the C(3) position, affording reasonable yields of the coupled products in the range of 60−67% yields. The abnormal carbene precursors **2a−c** were subsequently obtained by quaternization reactions of **1a−c** with 4-fluorobenzyl chloride, with 60−67% yield. Unlike the previous procedures for preparing an abnormal carbene ligand precursor with a C(2) metalation site,[32] the synthetic strategy based on Pd-catalyzed direct C−H arylation is a facile method to access ligand

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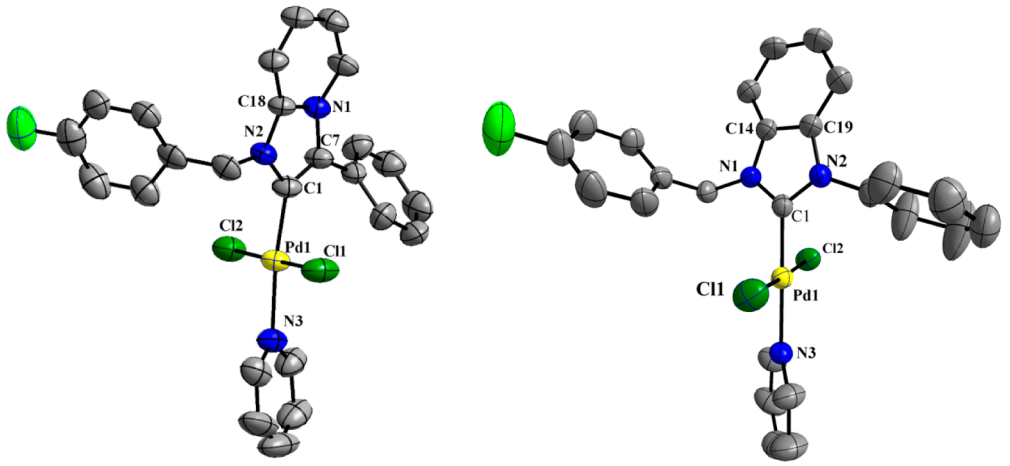

Figure 1. Molecular structures of **3a** (left) and **6a** (right) with 50% probability ellipsoids for non-H atoms. Hydrogen atoms are omitted for clarity.

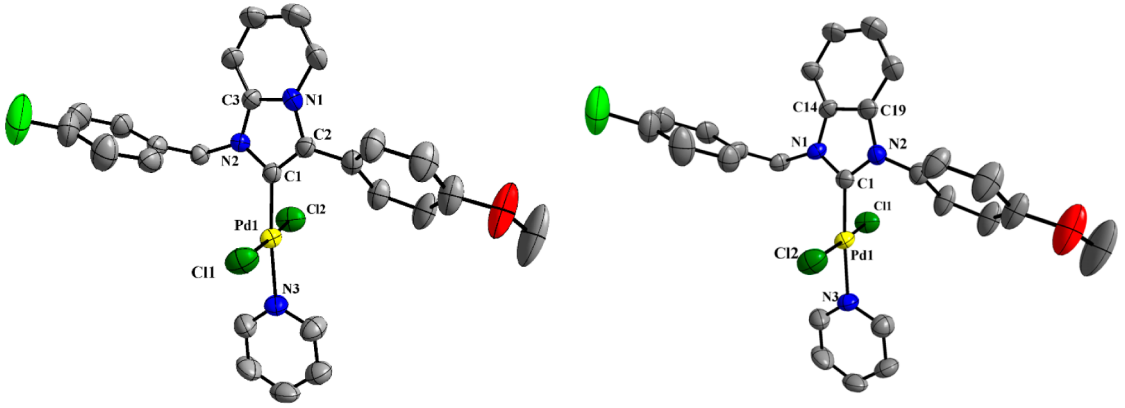

Figure 2. Molecular structures of **3b** (left) and **6b** (right) with 50% probability ellipsoids for non-H atoms. Hydrogen atoms are omitted for clarity.

precursors with different electronic property. Our method allows for the preparation of ligand precursor **2a** having a phenyl ring in the C(3) position, whereas precursors with aryl rings bearing electron-donating and -withdrawing groups (**2b** and **2c** respectively) can also be prepared straightforwardly. Notably, a study by Ghosh also reported relevant Pd complexes with abnormal carbene ligands based on imidazo[1,2-*a*]-pyridines;[33] however, in the complexes reported in that study, metalation occurred at the C(3) position of the imidazo[1,2-*a*]pyridine ring, whereas in our cases metalation took place at the C(2) position. The C*H* protons on the heteroaromatic rings in **2a**−**c** that deprotonate resonate at ca. 8.8 ppm. To unambiguously identify the NMR signal of the C(2) carbon, we conducted the HMBC experiment (**2c**), thereby establishing that the C(2) carbon and the quaternary NCN signals occurred at 124.3 and 139.0 ppm, respectively (see the Supporting Information).

In the corresponding normal carbene precursors, the *N*-arylated imidazole intermediates **4a**−**c** were prepared in good yields via the Cu-catalyzed C−N coupling reactions between benzoimidazole and aryl bromides in DMF at 120 °C.[34] Following the quaternization reactions with 4-fluorobenzyl chlorides, carbene precursors **5a**−**c** were obtained with 58−80% yields. The NC*H*N protons in **5a**−**c** that deprotonate upon metalation resonate at ca. 11.85 ppm, approximately 3 ppm more downfield compared to that of the corresponding acidic C(2)*H* proton in the abnormal carbene precursors **2a**−**c**. The corresponding NCHN carbon signals were also observed at more downfield positions compared to those of the *C*(2)H carbons in the abnormal carbene precursors (143 vs 124 ppm).

Preparation of Pd(II) Complexes with Abnormal and Normal Carbene Ligands. The abnormal Pd complexes **3a**−**c** were prepared via the reactions between the ligand precursors **2a**−**c** and $PdCl_2$ in pyridine in the presence of K_2CO_3 as base (Scheme 2). The reaction temperature was found to be crucial because excess heating above 60 °C darkened the solution, presumably because of the precipitation of Pd black. Successful formation of **3** was indicated by the disappearance of a proton signal at ca. 8.8 ppm in its NMR spectrum, with respect to that of the ligand precursor. The HMBC experiment on **3c** showed that Pd−*C* resonances in **3** appear at ca. 138 ppm (see the Supporting Information), which is downfield compared to the relevant C(3)-coordinated abnormal complexes (ca. 130 ppm).[33] These complexes were stable in solution, exhibiting good solubility in common halogenated solvents. For instance, the ^{1}H NMR spectrum for **3a** remained unchanged even when the solution was allowed to stand in air for 3 d.

Similar complexation conditions for the abnormal carbene complexes can also be applied to the preparation of the normal carbene complexes **6a**−**c**. Instead of heating at 60 °C, the reactions for **6a** and **6b** were conducted at 40 °C. For complex **6c**, it was necessary to conduct the reaction at 0 °C, because otherwise an impure sample was obtained (according to the ^{1}H NMR spectrum). In fact, in an unsuccessful attempt of the complexation reaction with the bromo analogue of **5c**, the X-ray structure of a decomposed product **6c**′ was obtained from

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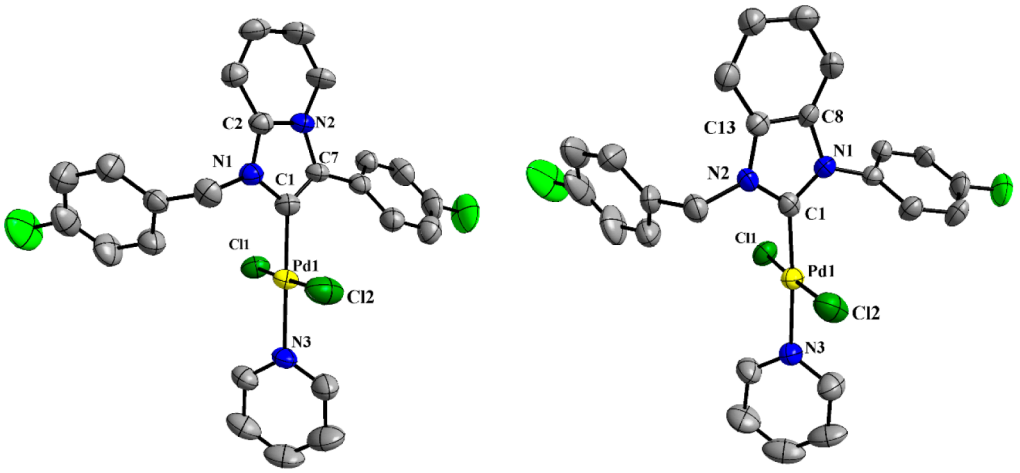

Figure 3. Molecular structures of **3c** (left) and **6c** (right) with 50% probability ellipsoids for non-H atoms. Hydrogen atoms are omitted for clarity. Only one independent molecule in the structure of **6c** was shown.

Table 1. Selected Bond Distances (Å) and Angles (°) around Pd in 3 and 6

	3a	3b	3c	6a	6b	6c
Pd–C	1.960(8)	1.960(5)	1.971(4)	1.955(4)	1.950(5)	1.964(7)
Pd–N	2.103(7)	2.094(4)	2.118(3)	2.124(3)	2.068(5)	2.095(6)
Pd–Cl1	2.298(2)	2.3028(16)	2.3221(14)	2.2981(12)	2.2989(16)	2.2868(19)
Pd–Cl2	2.309(2)	2.2913(17)	2.3061(14)	2.3060(12)	2.3037(15)	2.297(2)
C–Pd–Cl1	89.0(2)	90.84(15)	89.53(11)	90.50(12)	88.87(14)	89.20(19)
C–Pd–Cl2	89.9(2)	89.19(15)	88.61(11)	84.70(12)	90.45(14)	89.84(19)
N–Pd–Cl1	89.5(2)	89.93(13)	89.59(10)	92.99(10)	90.25(13)	90.98(17)
N–Pd–Cl2	91.8(2)	90.35(13)	92.26(10)	91.90(10)	90.54(13)	90.14(17)
C–Pd–N	173.6(3)	174.72(19)	178.91(13)	176.13(14)	176.61(19)	175.9(3)
Cl–Pd–Cl	177.96(9)	176.68(7)	178.01(4)	174.51(4)	178.00(6)	177.53(8)

the impure sample (vide infra). In general, good yields (ca. 80%) of **6a–c** were obtained. They were characterized by elemental analysis, X-ray crystallographic studies, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Their ^{1}H NMR spectra in the downfield region showed an absence of sharp signals owing to NC*H*N protons at ca. 9.4 ppm, indicating the successful formation of carbene complexes. Carbene signals (in their ^{13}C{^{1}H} NMR spectra) were observed at ca. 165 ppm, which is significantly downfield ($\Delta \approx 27$ ppm) as compared to that of the abnormal carbene complexes **3** and relevant *trans*-Pd(L)(py)Cl_2 with normal carbene ligands ($\Delta \approx 13$ ppm).[35,36] All these carbene complexes showed good solubility in halogenated solvents and appeared to be, except **6c**, stable in solution. As an example, the NMR spectrum in $CDCl_3$ for **6a** remained unchanged even after the exposure of the solution in the air for 3 d.

Structural Descriptions. In order to evaluate the difference in the structural parameters between the abnormal and normal carbene complexes, crystals of **3** and **6** were grown. The *trans* geometry of all the Pd complexes was unambiguously established via X-ray diffraction studies (Figure 1–3). Selected bond distances and angles are tabulated in Table 1. The Pd atoms in these structures adopt distorted square planar coordination geometry. Despite the fact that an abnormal carbene ligand is more electron-donating than a normal one, the structural analyses revealed that the Pd–C distances of abnormal carbene complexes were comparable to those of normal carbene complexes. For example, the Pd–C distance in abnormal carbene complex **3b** is 1.960(5) Å, which is essentially the same (within standard derivations) to that in **6b** (1.950(5) Å). The Pd–C bond lengths in the three abnormal carbene complexes are in the range of 1.960(5) to 1.971(4) Å, and they are slightly shorter than the average bond length of 1.99(3) Å (seen in 41 crystallographically determined Pd complexes with abnormal carbene ligands).[18]

It has been shown that a more useful probe to gauge the impact of an abnormal carbene ligand is to monitor its *trans* influence. The Pd–N distances in the abnormal carbene complexes **3a–c** are in the range of 2.094(4) to 2.118(3) Å, which is, however, essentially similar to that of 2.068(5) to 2.124(3) Å in the normal carbene complexes **6a–c**. Interestingly, the structure of **6a** exhibits nonclassical intramolecular hydrogen bonds between the *ortho* protons of the pyridine ligand and the coordinated chloride ions with C···Cl contact distances of 3.289(5) and 3.226(5) Å. Their contact angles are noticeably acute (ca. 117°).

Another interesting aspect of these structures is that the interplanar angles between the heterocyclic ring and the coordination plane of the metal center in the abnormal carbene complexes **3a–c** are 73.6(3)°, 77.4(1)°, and 74.9(1)°, respectively, which are smaller than those in **6a–c** (79.4(1)°, 79.9(1)°, and 82.9(2)°), indicating that the abnormal carbene ligands are more appropriately oriented for Π-back bonding.

The structure of **6c′** features a Pd atom in square coordination geometry with two *trans* bromide ligands and a normal carbene ligand. Instead of pyridine ligand, the fourth coordination site was occupied by an imidazole derivative that was formed from the cleavage of the 4-fluorobenzyl wingtip

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group in **5c** (Figure 4). The Pd−C bond length of 1.932(12) Å is the shortest among all the new structures.

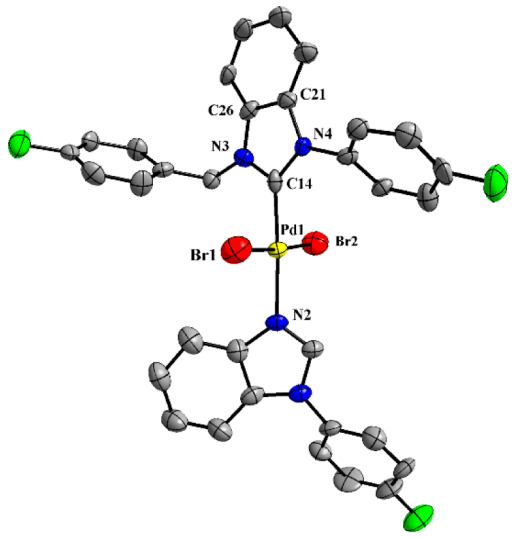
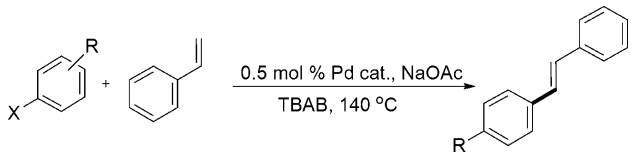


Figure 4. Molecular structures of **6c′** with 50% probability ellipsoids for non-H atoms. Hydrogen atoms are omitted for clarity. Selected bond distances: Pd1−C14, 1.932(12); Pd1−N2, 2.085(9); Pd1−Br1, 2.3972(18); Pd1−Br2, 2.4049(18) Å. Selected bond angles: C14−Pd1−N2, 175.8(4); Br1−Pd1−Br2, 174.85(7); C14−Pd1−Br1, 88.8(3); C14−Pd1−Br2, 86.9(3); N2−Pd1−Br1, 92.7(3); N2−Pd1−Br2, 91.8(3) deg.

Buried Volume of the Abnormal and Normal Carbene Ligands. Although theoretically the abnormal and normal carbene ligands should offer an identical steric environment around the metal centers, minor differences in steric properties between the isomeric pairs can still exist. In order to understand the steric properties of the new abnormal and normal carbene ligands, percent buried volumes (%V_{bur}) were calculated from the corresponding X-ray structures of Pd complexes (radius of the sphere, R = 3.5 Å; M−NHC length = 2.00 Å; Bondi radii scaled by 1.17).[37−39] As expected, the %V_{bur} values of the abnormal carbene ligands in **3a,b** (32.0 and 30.6%) were similar to those of their normal carbene counterparts in **6a,b** (31.1 and 30.9%), but surprisingly, the steric properties of the abnormal carbene ligand in **3c** and the normal carbene ligand in **6c** and **6c′** were significantly different, as indicated by the large difference in their %V_{bur} values [33.2% in **3c** vs 30.0 and 31.8% in **6c** (two independent molecules) and 31.0% in **6c′**]. The large %V_{bur} value (33.2%) implied that the abnormal carbene ligand featuring 4-fluorophenyl and 4-fluorobenzyl as wingtip groups was bulkier than expected. Notably, the large variation in the %V_{bur} values of the abnormal carbene ligands (30.6−33.2%) is in sharp contrast to the narrower range (30.9−31.1%) observed for their normal counterparts, indicating the greater sensitivity of the abnormal carbene ligands toward substituents at the *para* position of the phenyl wingtip groups. For comparison, the %V_{bur} values of IPr and 1,3-dibenzylimidazol-2-ylidene were calculated from the reported structures of Pd(NHC)(py)Cl_2[40,41] and were found to be 34.5 and 31.5%, respectively.

Catalytic Studies. The catalytic performance of the abnormal carbene Pd complexes **3a−c** in C−C coupling reactions was compared to their normal counterparts **6a−c**. The Mizoroki−Heck cross-coupling reactions between styrene and aryl halides were investigated on the basis of our previously established conditions that employ TBAB ionic liquid as solvent (Table 2).[42,43] In general, the abnormal carbene complexes delivered greater yields than the normal ones. For example, in the reaction between styrene and 4-chloroanisole, reasonable yields of coupled product were obtained (52−54%) (entries 7−9), whereas the normal carbene complexes only afforded 16−32% yields (entries 10−12). Among the abnormal carbene complexes, the more electronic rich **3b** bearing an *N*-4-methoxyphenyl group produced the best yields (entries 2 and 14). Sterically bulky aryl bromides could also be utilized to produce coupled products in good yields (entries 16−18).

Table 2. Mizoroki−Heck Cross-Coupling Reaction of Aryl Halides[a]



entry	Pd cat	R	X	product	time	yield (%)
1	**3a**	4-COMe	Cl	**7**	2	82[b]
2	**3b**	4-COMe	Cl	**7**	2	95[b]
3	**3c**	4-COMe	Cl	**7**	2	85[b]
4	**6a**	4-COMe	Cl	**7**	2	67[b]
5	**6b**	4-COMe	Cl	**7**	2	79[b]
6	**6c**	4-COMe	Cl	**7**	2	34[b]
7	**3a**	4-OMe	Cl	**8**	24	54
8	**3b**	4-OMe	Cl	**8**	24	54
9	**3c**	4-OMe	Cl	**8**	24	52
10	**6a**	4-OMe	Cl	**8**	24	32
11	**6b**	4-OMe	Cl	**8**	24	16
12	**6c**	4-OMe	Cl	**8**	24	24
13	**3a**	3-OMe	Br	**9**	24	77
14	**3b**	3-OMe	Br	**9**	24	85
15	**3c**	3-OMe	Br	**9**	24	70
16	**3a**	2-OMe	Br	**10**	24	69
17	**3b**	2-OMe	Br	**10**	24	70
18	**3c**	2-OMe	Br	**10**	24	59

[a]Reaction conditions: aryl halide (1.0 mmol), styrene (1.4 mmol), NaOAc (2.0 mmol), Pd catalyst (0.5 mol %), TBAB (2.0 g), 140 °C, 2 or 24 h, isolated yield. [b]NMR yield.

Recently, C−H arylation[44−47] has emerged as an appealing approach for the synthesis of biaryls. These nonclassical C−C coupling reactions do not require stoichiometric organometallic substrates, which can help in avoiding problems related to availability and metal waste, as well as the requirement for additional synthetic steps. The new abnormal and normal carbene complexes were tested in the direct C−H arylation reactions between imidazo[1,2-*a*]pyridine and aryl halides (Table 3). In general, the abnormal carbene complexes outperformed the corresponding normal carbenes complexes, delivering greater yields (entries 1−3 vs 4−6 and 7−9 vs 10−12). Entries 1−3 show that the abnormal carbene complex **3b** bearing the *N*-4-methoxyphenyl group exhibited better coupling activities in the direct C−H arylations, as in the case of Mizoroki−Heck cross-coupling reactions. In Scheme 1, we employed the simple $Pd(OAc)_2$ as catalyst for the direct C−H arylation to generate intermediates **1a** and **1b** with 60 and 64% yields, respectively. By employing **3b** as catalyst, these products could be obtained in improved yields of 99 and 74%

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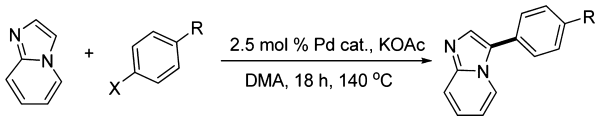
Table 3. Direct C−H Arylation Reaction[a]



entry	Pd cat	R	X	product	yield (%)
1	**3a**	OMe	Br	**1b**	68
2	**3b**	OMe	Br	**1b**	74
3	**3c**	OMe	Br	**1b**	56
4	**6a**	OMe	Br	**1b**	53
5	**6b**	OMe	Br	**1b**	66
6	**6c**	OMe	Br	**1b**	32
7	**3b**	COMe	Br	**11**	100
8	**3b**	H	Br	**1a**	99
9	**3b**	COMe	Cl	**11**	38
10	**6b**	COMe	Br	**11**	86
11	**6b**	H	Br	**1a**	85
12	**6b**	COMe	Cl	**11**	15

[a]Reaction conditions: imidazo[1,2-*a*]pyridine (1.5 mmol), aryl halide (1.0 mmol), KOAc (2.0 mmol), DMA (5 mL), Pd catalyst (2.5 mol %), 140 °C, 18 h, isolated yield.

(entries 8 and 2). Notably, these findings are in contrast with those reported by Fagnou, who showed that intramolecular direct C−H arylation with aryl chloride proceeded better with a normal carbene Pd complex than when a mixed normal/abnormal Pd complex was used.[48]

Decarboxylative coupling is an equally interesting approach for preparing heteroaromatic biaryls, because the carboxyl group can direct regioselectivity and the only waste product from the reaction is CO_2.[49−51] Decarboxylative coupling reactions between 3-(4-fluorophenyl)-5-methylisoxazole-4-carboxylic acid and aryl halides were also investigated (Table 4), on the basis of our previous established procedure.[52] Again, abnormal carbene complexes showed better yields. For example, employing **3b** as catalyst, a good yield of 72% could be obtained from 4-bromocyanobenzene (entry 3), but only a 50% yield could be obtained from **6b** (entry 7).

■ CONCLUSIONS

We prepared a series of abnormal carbene Pd complexes and their normal analogues, the first examples of isomeric pairs based on monodentate carbene systems sharing a formally identical steric environment around the Pd centers. The key steps in the preparation of the abnormal carbene ligand precursors was based on the Pd-catalyzed direct C−H arylation between imidazo[1,2-*a*]pyridine and aryl bromides, which allows ligand accessibility with wide-ranging electronic property. Minor differences exist in the steric property between abnormal and normal carbene ligands in **3c** and **6c**. Because of the minimal steric difference between the isomeric pairs as shown by the buried volume calculation, the enhanced catalytic activities exhibited by the abnormal carbene complexes in Mizoroki−Heck coupling, direct C−H coupling, and decarboxylative coupling reactions can be concluded with the stronger electron donating property of the abnormal carbene ligands. Thus the more electron-rich abnormal carbene complex **3b** excelled in all these coupling reactions.

■ EXPERIMENTAL SECTION

General Information. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with standard procedures. Starting chemicals were purchased from a commercial source and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. High-resolution mass spectroscopy (HRMS) was measured on a Finnigan/Thermo Quest MAT mass spectrometer at the National Chung Hsing University (Taiwan). Imidazo[1,2-*a*]pyridine was prepared according to the literature procedure.[53]

General Procedure of the Synthesis of 1a−c. To a 50 mL Schlenk flask was added imidazo[1,2-*a*]pyridine (3.0 g, 0.025 mol), KOAc (5.0 g, 0.050 mol) and $Pd(OAc)_2$ (0.14 g, 0.64 mmol). Degassed DMA (10 mL) and aryl bromide (0.02 mol) were also added. The mixture was allowed to heat at 140 °C for 18 h. After cooling, the solvent was removed under a vacuum. The residue was extracted with DCM. The extract was washed with water, dried over anhydrous $MgSO_4$, and filtered through a pad of Celite. The filtrate was purified by column chromatography on silica gel, using 30:70 ethyl acetate/hexane as eluent. A viscous brown liquid was obtained.

Synthesis of ***1a****.*[52] Yield: 2.48 g, 60.3%, mp = 111.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (t, J = 6.0 Hz, 1H, Ar *H*), 7.08 (t, J = 9.0 Hz, 1H, Ar *H*), 7.30−7.60 (m, 7H, imi *H*, Ar *H*), 8.20 (d, J = 9.0 Hz, 1H, Ar *H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 112.3 (*C*H), 117.7 (*C*H), 123.0 (*C*H), 124.0 (*C*H), 125.3 (quatenary *C*), 127.6 (*C*H), 127.9 (*C*H), 128.8 (quatenary *C*), 128.9 (*C*H), 131.9 (*C*H), 145.6 (quatenary *C*).

Synthesis of ***1b****.*[54] Yield: 2.97 g, 64.2%, mp = 126.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.62 (s, 3H, OCH_3), 6.53 (t, J = 9.0 Hz, 1H, Ar *H*), 6.81 (d, J = 9.0 Hz, 2H, Ar *H*), 6.93 (t, J = 9.0 Hz, 1H, Ar *H*), 7.20 (d, J = 6.0 Hz, 2H, Ar *H*), 7.41−7.74 (m, 2H, imi *H*, Ar *H*), 8.00 (d, J = 6.0 Hz, 1H, Ar *H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 54.7 (CH_3), 111.9 (*C*H), 114.0 (*C*H), 117.2 (*C*H), 120.6 (quatenary *C*), 122.6 (*C*H), 123.5 (*C*H), 124.9 (quatenary *C*), 128.9 (*C*H), 130.9 (*C*H), 144.9 (quatenary *C*), 159.0 (quatenary *C*).

Synthesis of ***1c****.*[55] Yield: 3.29 g, 66.7%, mp = 92.5 °C. ^{1}H NMR ($CDCl_3$): δ 6.74 (t, J = 6.0 Hz, 1H, Ar *H*), 7.11−7.19 (m, 3H, Ar *H*), 7.42−7.47 (m, 2H, Ar *H*), 7.59 (s, 1H, C^2*H*), 7.62 (d, J = 9.0 Hz, 2H, Ar *H*), 8.12 (d, J = 9.0 Hz, 1H, Ar *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 112.8 (*C*H), 116.3 (d, J_{CF} = 21.9 Hz, *C*H), 118.2 (*C*H), 123.1 (*C*H), 124.4 (*C*H), 124.6 (quatenary *C*), 125.2 (d, J_{CF} = 3.0 Hz, quatenary *C*), 130.1 (d, J_{CF} = 7.5 Hz, *C*H), 132.2 (*C*H), 145.9 (quatenary *C*), 162.6 (d, J_{CF} = 248.3 Hz, *C*F).

General Procedure for the Synthesis of 2a−c. A mixture of **1** (12.8 mmol) and 4-fluorobenzyl chloride (1.53 mL, 12.8 mmol) in degassed THF (25 mL) was heated at 80 °C for 24 h. After cooling, white solid was formed. The solvent was removed under a vacuum. The residual solid was thoroughly washed with ether and then dried under a vacuum. A white solid was obtained.

Synthesis of ***2a****.* Yield: 2.85 g, 66%, mp = 186 °C. HRMS (ESI; *m*/*z*): calcd for $C_{20}H_{16}ClFN_2$ 303.1292 [M − Cl]$^+$, found 303.1297. ^{1}H NMR ($CDCl_3$): δ 6.21 (s, 2H, CH_2), 6.89 (t, J = 9.0 Hz, 2H, Ar *H*), 7.37 (t, J = 6.0 Hz, 1H, Ar *H*), 7.47−7.53 (m, 5H, Ar *H*), 7.69−7.74 (m, 2H, Ar *H*), 7.91 (t, J = 9.0 Hz, 1H, Ar *H*), 8.39 (d, J = 6.0 Hz, 1H, Ar *H*), 8.80−8.83 (m, 2H, Ar *H*, C^2*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.6 (CH_2), 113.4 (*C*H), 116.0 (d, J = 21.9 Hz, *C*H), 118.1 (*C*H), 123.7 (*C*H), 124.0 (quatenary *C*), 125.4 (*C*H), 127.0 (quatenary *C*), 129.3 (*C*H), 129.8 (*C*H), 129.9 (quatenary *C*), 130.9 (*C*H), 131.2 (d, J = 8.3 Hz, *C*H), 133.9 (*C*H), 139.0 (quatenary *C*), 162.8 (d, J = 248.3 Hz, *C*F).

Synthesis of ***2b****.* Yield: 4.61 g, 73%, mp = 184.3 °C. HRMS (ESI; *m*/*z*): calcd for $C_{21}H_{18}ClFN_2O$ 333.1398 [M − Cl]$^+$, found 333.1405. ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.17 (s, 2H, CH_2), 6.90 (t, J = 6.0 Hz, 2H, Ar *H*), 7.00 (d, J = 6.0 Hz, 2H, Ar *H*), 7.37 (t, J = 6.0 Hz, 1H, Ar *H*), 7.46 (d, J = 9.0 Hz, 2H, Ar *H*), 7.68−7.73 (m, 2H, Ar *H*), 7.90 (t, J = 9.0 Hz, 1H, Ar *H*), 8.36 (d, J = 6.0 Hz, 1H, Ar *H*), 8.70 (s, 1H, C^2*H*), 8.76 (d, J = 9.0 Hz, 1H, Ar *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.4 (CH_2), 55.4 (CH_3), 133.2 (*C*H), 115.2 (*C*H), 115.6 (quatenary *C*), 115.9 (d, J = 21.1 Hz, *C*H), 117.9 (*C*H), 123.4, (*C*H), 125.4 (*C*H), 126.8 (*C*H), 129.9 (d, J = 3.8 Hz, quatenary *C*), 130.8 (*C*H), 131.1 (d,

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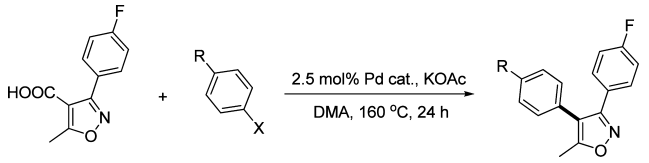
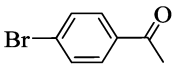
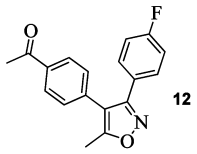
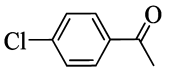
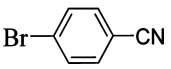
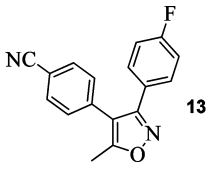
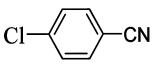
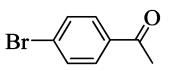
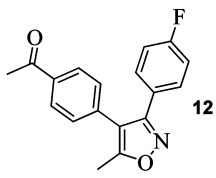
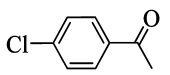
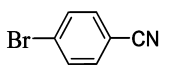
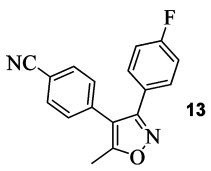
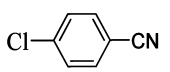
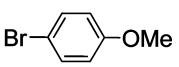
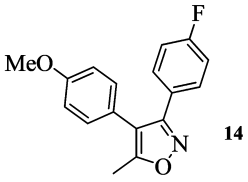
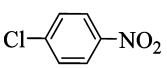
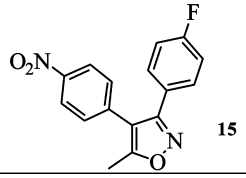
Table 4. Pd-Catalyzed Decarboxylative Coupling Reaction[a]



Entry	Pd cat.	Aryl halide	Product	Yield (%)
1	**3b**		 **12**	67
2	**3b**			23
3	**3b**		 **13**	72
4	**3b**			43
5	**6b**		 **12**	41
6	**6b**			9
7	**6b**		 **13**	50
8	**6b**			36
9	**3b**		 **14**	60
10	**3b**		 **15**	37

[a]Reaction conditions: 3-(4-fluorophenyl)-5-methylisoxazole-4-carboxylic acid (0.5 mmol), aryl halide (0.5 mmol), KOAc (1.0 mmol), dry DMA (3 mL), Pd cat. (2.5 mol %), 160 °C, 24 h, isolated yield.

J = 8.3 Hz, CH), 133.5 (quatenary *C*), 138.7 (quatenary *C*), 161.3 (quatenary *C*), 162.7 (d, *J* = 248.3 Hz, CF).

Synthesis of ***2c.*** Yield: 2.46 g, 60%, mp = 232.1−232.7 °C. HRMS (ESI; *m*/*z*): calcd for $C_{20}H_{15}ClF_2N_2$ 321.1198 $[M - Cl]^+$, found 321.1204. ^{1}H NMR ($CDCl_3$): δ 6.16 (s, 2H, CH_2), 6.91 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.21 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.40 (t, *J* = 9.0 Hz, 1H, Ar *H*), 7.58−7.73 (m, 4H, Ar *H*), 7.92 (t, *J* = 9.0 Hz, 1H, Ar *H*), 8.36 (d, *J* = 6.0 Hz, 1H, Ar *H*), 8.73 (d, *J* = 9.0 Hz, 1H, Ar *H*), 8.85 (s, 1H, C^2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 50.6 (CH_2), 113.4 (CH), 116.1 (d, *J* = 21.9 Hz, CH), 117.2 (d, *J* = 22.6 Hz, CH), 118.2 (CH), 120.0 (d, *J* = 3.7 Hz, quatenary *C*), 124.3 (C^2H), 125.5 (CH), 125.9 (quatenary *C*), 129.9 (d, *J* = 3.0 Hz, quatenary *C*), 131.3 (d, *J* = 9.8 Hz, CH), 131.8 (d, *J* = 9.1 Hz, CH), 133.9 (CH), 139.0 (NCN), 162.8 (d, *J* = 248.3 Hz, CF), 164.0 (d, *J* = 252.8 Hz, CF).

General Procedure for the Synthesis of 3a−c. Degassed pryidine (5 mL) was added to a mixture of **2** (0.59 mmol), $PdCl_2$ (0.11 g, 0.59 mmol) and K_2CO_3 (0.32 g, 2.36 mmol) in a 50 mL Schlenk flask. The solution was allowed to heat at 60 °C for 12 h. After cooling, the solvent was removed completely under a vacuum. The residual was washed with water and extracted with DCM twice. The extract was washed with water and dried over anhydrous $MgSO_4$. The solvent was then removed under a vacuum. The solid was then washed thoroughly with ether and dried under a vacuum. A brown solid was obtained.

dx.doi.org/10.1021/om4004219 | *Organometallics* XXXX, XXX, XXX−XXX

Synthesis of ***3a***. Yield: 0.26 g, 79%, mp = 220.3−222.4 °C. Anal. Calcd for $C_{25}H_{20}Cl_2FN_3Pd$: C, 53.73; H, 3.61; N, 7.52. Found: C, 53.49; H, 3.61; N, 7.29. ^{1}H NMR ($CDCl_3$): δ 6.29 (s, 2H, NCH_2Ph), 6.92−7.03 (m, 4H, Ar *H*), 7.19−7.26 (m, 2H, Ar *H*), 7.42 (t, *J* = 6.0 Hz, 2H, Ar *H*), 7.54 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.60−7.66 (m, 3H, Ar *H*), 8.09 (d, *J* = 6.0 Hz, 2H, py *H*), 8.28 (d, *J* = 6.0 Hz, 1H, py *H*), 8.88 (d, *J* = 6.0 Hz, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 53.8 (CH_2), 109.7 (*C*H), 115.0 (*C*H), 115.9 (d, J_{CF} = 21.9 Hz, *C*H), 123.1 (*C*H), 124.2 (py *C*), 126.2 (quatenary *C*), 127.5 (*C*H), 128.7 (quatenary *C*), 129.0 (*C*H), 129.1 (*C*H), 129.9 (d, J_{CF} = 8.3 Hz, *C*H), 130.5 (*C*H), 130.9 (d, J_{CF} = 3.0 Hz, quatenary *C*), 137.6 (py *C*), 138.0 (Pd*C*), 139.8 (quatenary *C*), 151.2 (py *C*), 162.5 (d, J_{CF} = 246.8 Hz, *C*F).

Synthesis of ***3b***. Yield: 0.26 g, 81%, mp = 208.6−214.3 °C. Anal. Calcd for $C_{26}H_{22}Cl_2FN_3OPd$: C, 53.04; H, 3.76; N, 7.13. Found: C, 53.32; H, 3.67; N, 7.00. ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 3H, OCH_3), 6.28 (s, 2H, NCH_2Ph), 6.91−7.08 (m, 6H, Ar *H*), 7.18−7.24 (m, 3H, Ar *H*), 7.60−7.66 (m, 3H, Ar *H*), 7.97 (d, *J* = 9.0 Hz, 2H, imipy *H*), 8.22 (d, *J* = 6.0 Hz, 1H, imipy *H*), 8.89 (d, *J* = 3.0 Hz, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 53.8 (CH_2), 55.3 (CH_3), 109.6 (*C*H), 114.6 (*C*H), 114.9 (*C*H), 115.9 (d, J_{CF} = 28.7 Hz, *C*H), 120.8 (quatenary *C*), 123.0 (*C*H), 124.1 (py *C*), 126.0 (quatenary *C*), 127.2 (*C*H), 129.9 (d, J_{CF} = 8.3 Hz, *C*H), 130.9 (d, J_{CF} = 3.7 Hz, quatenary *C*), 132.0 (*C*H), 137.1 (Pd*C*), 137.5 (py *C*), 139.5 (quatenary *C*), 151.2 (py *C*), 160.0 (quatenary *C*), 162.6 (d, J_{CF} = 246.8 Hz, *C*F).

Synthesis of ***3c***. Yield: 0.26 g, 81%, mp = 213.0−217.4 °C. Anal. Calcd for $C_{25}H_{19}Cl_2F_2N_3Pd$: C, 52.06; H, 3.32; N, 7.28. Found: C, 51.82; H, 3.47; N, 7.00. ^{1}H NMR ($CDCl_3$): δ 6.33 (s, 2H, CH_2), 7.00−7.08 (m, 3H, Ar *H*), 7.27−7.34 (m, 6H, Ar *H*), 7.69 (t, *J* = 9.0 Hz, 3H, Ar *H*), 8.10 (m, 2H, imipy *H*, py *H*), 8.25 (d, *J* = 6.0 Hz, 1H, imipy *H*), 8.92 (d, *J* = 3.0 Hz, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 53.8 (CH_2), 109.8, 115.2, 116.0 (d, J_{CF} = 24.2 Hz), 116.3 (d, J_{CF} = 21.9 Hz), 122.9, 124.2 (py *C*), 124.7, 125.0, 127.7, 130.0 (d, J_{CF} = 8.3 Hz), 130.9, 132.6 (d, J_{CF} = 8.3 Hz), 137.6 (py *C*), 138.1 (Pd*C*), 139.7, 151.1 (py *C*), 162.6 (d, J_{CF} = 248.3 Hz), 163.0 (d, J_{CF} = 248.3 Hz).

General Procedure of the Synthesis of 4a−c. Degassed DMF (10 mL) was added to a mixture of benzoimidazole (1.0 g, 8.47 mmol), Cs_2CO_3 (4.2 g, 12.74 mmol), CuI (0.24 g, 1.47 mmol), and aryl halide (6.37 mmol). The solution was allowed to heat at 120 °C for 40 h. After cooling, the solvent was removed completely under a vacuum. The residual was washed with water and extracted with DCM twice. The extract was washed with water and dried over anhydrous $MgSO_4$. The solvent was then removed under a vacuum. The solid was then washed thoroughly with ether and dried under a vacuum. The filtrate was purified by column chromatography on silica gel, using 30:70 ethyl acetate/hexane as eluent. A viscous brown liquid was obtained.

Synthesis of ***4a***.[56] Yield: 2.89 g, 88%, mp = 94.3 °C. ^{1}H NMR ($CDCl_3$): δ 7.18−7.29 (m, 2H, Ar *H*), 7.36−7.52 (m, 6H, Ar *H*), 7.79−7.82 (m, 1H, Ar *H*), 8.03 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 110.4 (*C*H), 120.5 (*C*H), 122.7 (*C*H), 123.6 (*C*H), 124.0 (*C*H), 127.9 (*C*H), 130.0 (*C*H), 133.6 (quatenary *C*), 136.3 (quatenary *C*), 142.2 (NCHN), 144.0 (quatenary *C*).

Synthesis of ***4b***.[57] Yield: 3.12 g, 82%, mp = 98.5 °C. ^{1}H NMR ($CDCl_3$): δ 3.91 (s, 3H, OCH_3), 7.10 (d, *J* = 9.0 Hz, 2H, Ar *H*), 7.28−7.37 (m, 2H, Ar *H*), 7.42−7.49 (m, 3H, Ar *H*), 7.87−7.91 (m, 1H, Ar *H*), 8.07 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.6 (CH_3), 110.2 (*C*H), 115.1 (*C*H), 120.4 (*C*H), 122.5 (*C*H), 123.4 (*C*H), 125.7 (*C*H), 129.1 (quatenary *C*), 134.2 (quatenary *C*), 142.5 (NCHN), 143.8 (quatenary *C*), 159.3 (quatenary *C*).

Synthesis of ***4c***.[58] Yield: 2.54 g, 85%, mp = 91.3 °C. ^{1}H NMR ($CDCl_3$): δ 7.16−7.27 (m, 4H, Ar *H*), 7.37−7.43 (m, 3H, Ar *H*), 7.79−7.82 (m, 1H, Ar *H*), 7.99 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 110.1 (*C*H), 116.9 (d, J_{CF} = 23.3 Hz, *C*H), 120.6 (*C*H), 122.8 (*C*H), 123.7 (*C*H), 126.0 (d, J_{CF} = 7.5 Hz, *C*H), 132.3 (quatenary *C*), 133.8 (quatenary *C*), 142.2 (NCHN), 143.8 (quatenary *C*), 161.9 (d, J_{CF} = 248.2 Hz, *C*F).

General Procedure for the Synthesis of 5a−c. A mixture of **4** (19.21 mmol) and 4-fluorobenzyl chloride (2.25 mL, 19.21 mmol) in degassed DMF (25 mL) was allowed to heat at 100 °C for 24 h. After cooling, solid was formed. The solvent was removed under a vacuum. The residual solid was thoroughly washed with ether and then dried under a vacuum. A white solid was obtained.

Synthesis of ***5a***. Yield: 3.65 g, 58%, mp = 204.2 °C. HRMS (ESI; *m*/*z*): calcd for $C_{20}H_{16}ClFN_2$ 303.1292 $[M - Cl]^+$, found 303.1298. ^{1}H NMR ($CDCl_3$): δ 6.14 (s, 2H, CH_2), 7.01 (t, *J* = 6.0 Hz, 2H, Ar *H*), 7.60−7.77 (m, 11H, Ar *H*), 11.95 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.5 (CH_2), 113.5 (*C*H), 114.0 (*C*H), 116.1 (d, J_{CF} = 21.9 Hz, *C*H), 124.6 (*C*H), 127.6 (d, J_{CF} = 7.5 Hz, *C*H), 128.9 (d, *J* = 3.0 Hz, quatenary *C*), 130.6 (*C*H), 130.9 (*C*H), 131.0 (*C*H), 131.1 (quatenary *C*), 131.1 (quatenary *C*), 132.8 (quatenary *C*), 142.6 (NCHN), 162.8 (d, *J* = 282.3 Hz, *C*F).

Synthesis of ***5b***. Yield: 4.92 g, 73%, mp = 241.2 °C. HRMS (ESI; *m*/*z*): calcd for $C_{21}H_{18}ClFN_2O$ 333.1398 $[M - Cl]^+$, found 333.1403. ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 3H, CH_3), 6.11 (s, 2H, CH_2), 6.96−7.08 (m, 4H, Ar *H*), 7.54−7.76 (m, 8H, Ar *H*), 11.85 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.6 (CH_2), 55.8 (CH_3), 113.6 (*C*H), 113.9 (*C*H), 115.7 (*C*H), 116.2 (d, *J* = 21.9 Hz, *C*H), 125.4 (*C*H), 126.2 (*C*H), 127.5 (d, *J* = 6.8 Hz, *C*H), 129.0 (d, *J* = 3.7 Hz, quatenary *C*), 130.9 (quatenary *C*), 131.0 (quatenary *C*), 131.7 (quatenary *C*), 142.8 (NCHN), 161.0 (quatenary *C*), 162.9 (d, *J* = 249.1 Hz, *C*F).

Synthesis of ***5c***. Yield: 3.25 g, 80%, mp = 220.1 °C. HRMS (ESI; *m*/*z*): calcd for $C_{20}H_{15}ClF_2N_2$ 321.1198 $[M - Cl]^+$, found 321.1204. ^{1}H NMR ($CDCl_3$): δ 6.05 (s, 2H, CH_2), 6.97 (t, *J* = 6.0 Hz, 2H, Ar *H*), 7.25 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.53−7.58 (m, 3H, Ar *H*), 7.65−7.71 (m, 3H, Ar *H*), 7.80−7.85 (m, 2H, Ar *H*), 11.79 (s, 1H, NC*H*N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 50.8 (CH_2), 113.3 (*C*H), 114.1 (*C*H), 116.2 (d, *J* = 21.9 Hz, *C*H), 117.8 (d, *J* = 21.9 Hz, *C*H), 127.0 (d, *J* = 9.0 Hz, *C*H), 127.6 (d, *J* = 12.8 Hz, *C*H), 128.9 (d, *J* = 3.8 Hz, quatenary *C*), 128.9 (d, *J* = 3.1 Hz, quatenary *C*), 130.9 (*C*H), 131.0 (*C*H), 131.1 (quatenary *C*), 131.5 (quatenary *C*), 143.2 (NCHN), 161.9 (d, *J* = 86.0 Hz, *C*F), 163.2 (d, *J* = 221.9 Hz, *C*F).

General Procedure for the Synthesis of 6a and b. Degassed pyridine (5 mL) was added to a mixture of **5** (0.59 mmol), $PdCl_2$(COD) (0.168 g, 0.59 mmol) and K_2CO_3 (0.32 g, 2.36 mmol) in a 50 mL Schlenk flask. The solution was allowed to heat at 40 °C for 12 h. After cooling, the solvent was removed completely under a vacuum. The residual was washed with water and extracted with DCM twice. The extract was washed with water and dried over anhydrous $MgSO_4$. The solvent was then removed under a vacuum. The brown solid was then washed thoroughly with ether and dried under a vacuum.

Synthesis of ***6a***. Yield: 0.27 g, 82%, mp = 221.0−213.4 °C. Anal. Calcd for $C_{25}H_{20}Cl_2FN_3Pd$: C, 53.85; H, 3.61; N, 7.54. Found: C, 53.74; H, 3.77; N, 7.56. ^{1}H NMR ($CDCl_3$): δ 6.21 (s, 2H, CH_2), 7.00 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.08−7.23 (m, 6H, Ar *H*), 7.50−7.67 (m, 6H, Ar *H*), 7.97 (d, *J* = 6.0 Hz, 2H, Ar *H*), 8.72 (d, *J* = 6.0 Hz, 2H, py *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 52.6 (CH_2), 111.2 (*C*H), 111.4 (*C*H), 115.9 (d, J_{CF} = 21.9 Hz, *C*H), 123.7 (*C*H), 124.4 (py *C*), 127.9 (*C*H), 129.5 (d, J_{CF} = 15.8 Hz, *C*H), 129.9 (*C*H), 130.1 (*C*H), 130.5 (d, J_{CF} = 3.8 Hz, quatenary *C*), 133.7 (quatenary *C*), 135.9 (quatenary *C*), 136.9 (quatenary *C*), 138.0 (py *C*), 151.1 (py *C*), 162.6 (d, J_{CF} = 246.8 Hz, *C*F), 164.7 (Pd*C*).

Synthesis of ***6b***. Yield: 0.22 g, 79%, mp = 212.7−214.7 °C. Anal. Calcd for $C_{26}H_{22}Cl_2FN_3OPd$: C, 53.04; H, 3.76; N, 7.13. Found: C, 52.58; H, 3.79; N, 7.16. ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H, CH_3), 6.20 (s, 2H, CH_2), 6.97−7.30 (m, 10H, Ar *H*), 7.60−7.66 (m, 3H, Ar *H*), 7.84 (d, *J* = 9.0 Hz, 2H, Ar *H*), 8.74−8.79 (m, 2H, Ar *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 52.5 (CH_2), 55.5 (CH_3), 111.1 (*C*H), 111.2 (*C*H), 114.6 (*C*H), 115.8 (d, J_{CF} = 21.9 Hz, *C*H), 123.6 (*C*H), 123.7 (*C*H), 124.4 (py *C*), 129.1 (*C*H), 129.5 (quatenary *C*), 130.0 (d, J_{CF} = 8.3 Hz, *C*H), 130.5 (quatenary *C*), 133.6 (quatenary *C*), 136.2 (quatenary *C*), 138.0 (py *C*), 151.1 (py *C*), 159.9 (quatenary *C*), 162.3 (d, J_{CF} = 246.8 Hz, *C*F), 164.6 (Pd*C*).

Synthesis of ***6c***. It was prepared following a procedure similar to that of **6a** and **b**, except that the reaction was conducted at 0 °C for 6 h. Yield: 0.26 g, 81%, mp = 183.2−187.1 °C. Anal. Calcd for $C_{25}H_{19}Cl_2F_2N_3Pd$: C, 52.06; H, 3.32; N, 7.28. Found: C, 51.98; H, 3.21; N, 6.88. ^{1}H NMR ($CDCl_3$): δ 6.25 (s, 2H, CH_2), 7.06 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.14−7.37 (m, 8H, Ar *H*), 7.65−7.74 (m, 3H, Ar *H*),

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7.96−8.00 (m, 2H, Ar *H*), 8.79 (d, *J* = 6.0 Hz, 2H, Ar *H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 52.7 (CH_2), 111.0 (*C*H), 111.5 (*C*H), 115.9 (d, J_{CF} = 21.9 Hz, *C*H), 116.7 (d, J_{CF} = 23.4 Hz, *C*H), 123.9 (d, J_{CF} = 4.5 Hz, quatenary *C*), 124.6 (py *C*), 130.0 (d, J_{CF} = 7.5 Hz, *C*H), 130.1 (d, J_{CF} = 8.3 Hz, *C*H), 130.5 (quatenary *C*), 132.9 (*C*H), 133.7 (quatenary *C*), 136.1 (quatenary *C*), 138.2 (py *C*), 151.1 (py *C*), 163.1 (d, J_{CF} = 247.5 Hz, *C*F), 162.9 (d, J_{CF} = 249.8 Hz, *C*F), 165.2 (Pd*C*).

Mizoroki−Heck Cross-Coupling Reactions. In a typical run, a Schlenk tube was charged with aryl halide (1.0 mmol), styrene (1.4 mmol), NaOAc (2.0 mmol), and Pd precatalyst (0.5 mol %). The flask was thoroughly degassed, added with TBAB (2.0 g), and then placed in a preheated oil bath at 140 °C. After the mixture was cooled, the mixture was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined organic portions were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed completely under a vacuum. Products were identified by comparison of NMR data with those in the literature; yields and regioselectivity were determined by integration ratio using 1,3,5-trimethoxylbenzene as internal standard or after purification with column chromatography on silica gel.

Direct C−H Arylation Reactions. Typically, a mixture of aryl halide (1.0 mmol), imidazo[1,2-*a*]pyridine (1.5 mmol), KOAc (2.0 mmol), and Pd precatalyst (2.5 mol %) was dissolved in DMA (5 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 140 °C in a preheated oil bath for 18 h. After the mixture was cooled, ethyl acetate (10 mL) was added. The solution was poured into water (50 mL) and extracted with ethyl acetate (3 × 25 mL). The combined extract was washed with brine, dried over anhydrous $MgSO_4$, and evaporated to dryness under a vacuum to give the crude product, which was purified by column chromatography. Compounds were identified by comparison of NMR data with those in the literature.

Decarboxylative Coupling Reactions. To a 50 mL flask fitted with magnetic stirrer, 3-(4-fluorophenyl)-5-methylisoxazole-4-carboxylic (0.50 mmol), aryl halide (0.50 mmol), KOAc (1.0 mmol), and Pd precatalyst (2.5 mol %) were added under nitrogen. Dry DMA (3 mL) was added to it. The reaction mixture was stirred at 160 °C for 24 h and then was allowed to cool at room temperature. After dilution with distilled water (15 mL), the solution was extracted with ethyl acetate (3 × 15 mL). The organic layer was separated and dried over anhydrous $MgSO_4$. Removal of the solvent resulted in a brownish gummy mass, which was subjected to column chromatography over silica gel using *n*-hexane and an increasing proportion of ethyl acetate as eluent. Compounds were identified by comparison of NMR data with those in the literature.

(E)-1-Acetyl-4-styrylbenzene (**7**).[59] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, 3H, CH_3), 7.08−7.19 (m, 2H, Ar *H*), 7.30 (d, *J* = 9.0 Hz, 1H, C*H*), 7.37 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.51−7.58 (m, 4H, Ar *H*), 7.94 (d, *J* = 9.0 Hz, 2H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.5 (CH_3), 126.4 (*C*H), 126.7 (*C*H), 127.3 (*C*H), 128.2 (*C*H), 128.7 (*C*H), 128.8 (*C*H), 131.3 (*C*H), 135.8 (quatenary *C*), 136.6 (quatenary *C*), 141.9 (quatenary *C*), 197.5 (*C*═O).

(E)-1-Methoxy-4-styrylbenzene (**8**).[59] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.87−6.92 (m, 2H, Ar *H*, C*H*), 6.98−7.08 (m, 2H, Ar *H*, C*H*), 7.19−7.21 (m, 1H, Ar *H*) 7.32 (t, *J* = 6.0 Hz, 2H, Ar *H*), 7.45 (t, *J* = 9.0 Hz, 4H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 55.3 (CH_3), 114.1(*C*H), 126.2 (*C*H), 126.6 (*C*H), 127.2 (*C*H), 127.7 (*C*H), 128.2 (*C*H), 128.6 (*C*H), 130.1 (quatenary *C*), 137.6 (quatenary *C*), 159.2 (quatenary *C*).

(E)-1-Methoxy-3-styrylbenzene (**9**).[60] Yellow liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H, OCH_3), 6.81 (d, *J* = 9.0 Hz, 1H, C*H*), 7.04−7.12 (m, 4H, Ar *H*), 7.25−7.37 (m, 4H, Ar *H*), 7.49 (d, *J* = 9.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 55.1 (OCH_3), 111.6 (*C*H), 113.2 (*C*H), 119.1 (*C*H), 126.4 (*C*H), 127.6 (*C*H), 128.4 (*C*H), 128.6 (*C*H), 128.9 (*C*H), 129.5 (*C*H), 137.1 (quatenary *C*), 138.6 (quatenary *C*), 159.7 (quatenary *C*).

(E)-1-Methoxy-2-styrylbenzene (**10**).[61] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H, OCH_3), 6.93 (d, *J* = 9.0 Hz, 1H, C*H*), 7.02 (t, *J* = 6.0 Hz, 1H, Ar *H*), 7.17 (d, *J* = 18 Hz, 1H, C*H*), 7.29 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.40 (t, *J* = 9.0 Hz, 2H, Ar *H*, 7.54−7.67 (m, 4H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 55.4 (CH_3), 110.8 (*C*H), 120.6 (*C*H), 123.3 (*C*H), 126.3 (*C*H), 126.5 (*C*H, quatenary *C*), 127.2 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 129.0 (*C*H), 137.8 (quatenary *C*), 156.8 (quatenary *C*).

4-Imidazo[1,2-a]pyridin-3-ylacetophenone (**11**).[52] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.60 (s, 3H, CH_3), 6.82 (t, *J* = 6.0 Hz, 1H, Ar H), 7.20 (t, *J* = 9.0 Hz, 1H, Ar *H*), 7.61−7.74 (m, 4H, Ar *H*, imi *H*), 8.04 (d, *J* = 6.0 Hz, 2H, Ar *H*), 8.35 (d, *J* = 6.0 Hz, 1H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.5 (CH_3), 113.0 (*C*H), 118.3 (*C*H), 123.2 (*C*H), 124.6 (quatenary *C*), 124.8 (*C*H), 127.1 (*C*H), 129.2 (*C*H), 133.6 (*C*H), 133.8 (quatenary *C*), 136.0 (quatenary *C*), 146.7 (quatenary *C*), 197.1 (*C*═O).

1-(4-(3-(4-Fluorophenyl)-5-methyl-isoxazol-4-yl)phenyl)-ethanone (**12**).[52] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 6.98 (t, *J* = 8.7 Hz, 2H, Ar *H*), 7.25 (d, *J* = 1.8 Hz, 2H, Ar *H*), 7.33−7.38 (m, 2H, Ar *H*), 7.94 (d, *J* = 6.6 Hz, 2H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 11.8 (CH_3), 26.7 ($COCH_3$), 114.9 (*C*H), 115.8 (d, J_{CF} = 21.9 Hz, *C*H), 124.8 (quatenary *C*), 127.5 (quatenary *C*), 128.8 (*C*H), 129.9 (*C*H), 130.5 (d, J_{CF} = 7.5 Hz, *C*H), 135.2 (quatenary *C*), 136.3 (quatenary *C*), 160.2 (quatenary *C*), 163.5 (d, J_{CF} = 249.1 Hz, *C*F), 167.3 (quatenary *C*), 197.6 (*C*O).

4-(3-(4-Fluorophenyl)-5-methylisoxazol-4-yl)benzonitrile (**13**).[52] Orange red solid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 6.98 (t, *J* = 8.7 Hz, 2H, Ar *H*), 7.23−7.33 (m, 4H, Ar *H*), 7.63 (d, *J* = 8.1 Hz, 2H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 11.8 (CH_3), 111.7 (*C*H), 114.4 (*C*H), 116.0 (d, J_{CF} = 22.6 Hz, *C*H), 118.4 (quatenary *C*), 124.5 (d, J_{CF} = 3.0 Hz, quatenary *C*), 128.0 (quatenary *C*), 130.4 (d, J_{CF} = 12.0 Hz, *C*H), 132.9 (quatenary *C*), 135.2 (quatenary *C*), 160.5 (quatenary *C*), 163.6 (d, J_{CF} = 249.1 Hz, *C*F), 167.5 (*C*N).

3-(4-Fluorophenyl)-4-(4-methoxyphenyl)-5-methylisoxazole (**14**).[52] Yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.89 (d, *J* = 6.0 Hz, 2H, Ar *H*), 6.98 (t, *J* = 9.0 Hz, 2H, Ar *H*), 7.06 (d, *J* = 9.0 Hz, 2H, Ar *H*), 7.39−7.44 (m, 2H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 11.4 (CH_3), 55.1 (OCH_3), 114.1 (*C*H), 115.1 (quatenary *C*), 115.5 (d, J_{CF} = 21.8 Hz, *C*H), 122.1 (quatenary *C*), 125.3 (d, J_{CF} = 3.0 Hz, quatenary *C*), 130.2 (d, J_{CF} = 7.5 Hz, *C*H), 130.8 (*C*H), 159.0 (quatenary *C*), 160.1 (quatenary *C*), (d, J_{CF} = 249.0 Hz, *C*F), 166.4 (quatenary *C*).

3-(4-Fluorophenyl)-5-methyl-4-(4-nitrophenyl)isoxazole (**15**). Yellow solid, mp = 118.9−119.7 °C. HRMS (EI; *m*/*z*): calcd for $C_{16}H_{11}FN_2O_3$ 298.0753, found 298.0744. ^1H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H, CH_3), 7.02 (t, *J* = 9.0 Hz, 1H, Ar *H*), 7.15 (d, *J* = 12.0 Hz, 1H, Ar *H*), 7.31−7.36 (m, 2H, Ar *H*), 7.78 (d, *J* = 9.0 Hz, 1H, Ar *H*), 8.20−8.34 (m, 3H, Ar *H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 11.8 (CH_3), 116.0 (d, *J* = 21.8 Hz, *C*H), 124.1 (*C*H), 124.3 (*C*H), 126.2 (*C*H), 128.3 (*C*H), 130.4 (d, *J* = 8.3 Hz, *C*H), 137.2 (quatenary *C*), 145.0 (quatenary *C*), 147.2 (quatenary *C*), 148.0 (quatenary *C*), 160.1 (quatenary *C*), 163.6 (d, *J* = 249.0 Hz, *C*F), 167.6 (quatenary *C*).

X-ray Diffraction Studies. Samples were collected at 150(2) K on a Bruker APEX II equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by least-squares refinement. Data collection and reduction were performed using the Bruker APEX2 and SAINT software.[36] Absorption corrections were performed using the SADABS program.[62] All the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 with the SHELXTL software package.[63] All non-H atoms were refined anisotropically. All H atoms were fixed at calculated positions and refined with the use of a riding model. Crystallographic data are given in Table S1 of the Supporting Information. CCDC files 917931 (**3a**), 917933 (**3b**), 917932 (**3c**), 917935 (**6a**), 917934 (**6b**), 917936 (**6c**), and 918254 (**6c′**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for products and crystal data (CIF). 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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