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Consecutive Aromatic Carbon–Fluorine Bond and Carbon– Hydrogen Bond Activations by Iridium Porphyrins

Bao Zhu Li,[†] Ying Ying Qian,[†] Jianwen Liu,^{*,‡} and Kin Shing Chan^{*,†}

[†]Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China [‡]National Supercomputing Center in Shenzhen, Shenzhen 518055, People's Republic of China

S Supporting Information

ABSTRACT: Consecutive aromatic C–F bond and C–H bond activations of aryl fluorides were achieved by iridium porphyrins to initially give aryl and finally fluoroaryl iridium porphyrins. The C–F bond activation product is generated first, which is the precursor for the C–H bond activation. Both experimental and theoretical results support that the C–F



bond is cleaved by iridium porphyrin anion through nucleophilic aromatic substitution, and the C–H bond cleavage is through homolytic aromatic substitution by iridium porphyrin radical followed by hydrogen atom abstraction. Moreover, the *meta*-fluorophenyl iridium porphyrin is the most thermodynamic stable regioisomers.

INTRODUCTION

Aromatic carbon–fluorine (C–F) bond is very strong (~520 kJ/mol) and thus generally thermally, photochemically, electrooxidatively, and chemically stable.^{1,2} The fundamental studies of carbon–fluorine bond activation by transition metal complexes and its application in defluorination, coordination, and organic synthesis have been extensively investigated.³ Mechanistically, the aromatic carbon–fluorine bond can be cleaved by transition metal complexes through oxidative addition, sigma-bond metathesis, nucleophilic aromatic substitution, or electron transfer.⁴

For nonperfluoroarenes, aromatic carbon–hydrogen bond activation (CHA) can compete with the C–F bond cleavage since the aromatic C–H bond is 60–100 kJ/mol weaker than the aromatic C–F bond.^{1,5} Indeed, when a hexahydride-osmium complex reacts with pentafluoroacetophenone, the ortho C–F bond is cleaved. However, the same hexahydride-osmium reacts with 2-fluoroacetophenone to cleave the ortho C–H bond.⁶ Moreover, a neutral PNP-iridium pincer dihydride complex reacts with fluorobenzene to give C–H bond cleavage products selectively.⁷

Among the C–H bond cleavage products of fluoroaryl complexes, thermal interconversions of region-isomers have been reported. Usually, the ortho-fluoro-substituted isomer is the most stable one. Milstein and co-workers have reported that a stoichiometric ratio (*o*-: *m*-: *p*- = 2:2:1) of C–H bond cleavage products is obtained in the reaction between a PNP– iridium pincer complex and fluorobenzene at 50 °C for 1 h. After being heated at 60 °C for 2 days, the mixture converts to ortho- and para- isomers with ortho- isomer as the major product.⁸ Recently, Jones and Perutz have analyzed the kinetic and thermodynamic CHA selectivity of $[(C_5R_5)Rh(PMe_3)]$ (R = H, CH₃) and Tp'Rh(CNneopentyl) (Tp' = tris(3,5-dimethylpyrazolyl)borate) complexes with aryl fluorides and found that the more *ortho*-fluoro substituent confers a more

thermodynamically stable product.⁹ The theoretically calculated relative bond dissociation energies of Rh–Ar^F bonds suggest that the *ortho*-fluorine substituent has the highest strengthening effect on the Rh–Ar^F bond.^{5a}

Our continuing interests in the aromatic C–X (X = I, Br, and Cl)¹⁰ and benzylic C–H bond¹¹ activation chemistry by group 9 transition metal porphyrin complexes have led us into the investigation of aromatic C–F and C–H bond activation of aryl fluorides. Previously, competitive aromatic C–F and C–Cl bond cleavages by iridium porphyrin complexes have been reported by the Chan group.¹² The aromatic C–F bond can be selectively cleaved with iridium porphyrin anion as the intermediate through nucleophilic aromatic substitution (Scheme 1). We now report both the scope and mechanisms

Scheme 1. Proposed Mechanism for Aromatic C–F Bond Cleavage by $Ir(ttp)^-$



for competitive aromatic C–F and C–H bond activations by iridium porphyrins and an unusual *meta*-fluorine stabilizing effect both experimentally and by density functional theory (DFT) calculations.

RESULTS AND DISCUSSION

Competitive Aromatic C–F and C–H Bond Activations. Initially, $Ir(ttp)SiEt_3$ (ttp = tetratolylporphyrinato dianion) **1a** reacted incompletely with 1,4-difluorobenzene **2d**

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at 120 °C to give mainly the CFA product **3e** (Table 1, entry 1). At 150 °C, almost all the $Ir(ttp)SiEt_3$ converted to the CFA

Table 1. Temperature Effect for the CFA and CHA of 1,4-Difluorobenzene with Ir(ttp)SiEt₃ in Benzene Solvent

					/Ir(ttp)			
$Ir(ttp)SiEt_3 + F - \swarrow F - F - F - F - F - F - F - F - F$								
1a	2d 100 ec	luiv		3e	3f			
entry	temp (°C)	time (d)	yield 1a (%)	yield 3e (%)	yield 3f (%)			
1	120	6	56	29	<5			
2^a	150	5	6	85	<5			
3^b	200	3	<5	52	8			

^{*a*}Ir(ttp)C₆H₅ **3a** was isolated in trace amount (<5%). ^{*b*}Ir(ttp)C₆H₅ **3a** was also isolated in 29% yield, which may come from the CHA of benzene solvent (Supporting Information).

product **3e** (Table 1, entry 2). At a higher temperature of 200 °C, the CHA process began to compete with the CFA process with the CHA product **3f** formed in 8% yield (Table 1, entry 3). Therefore, 200 °C was chosen to examine the competitive CFA and CHA of fluorobenzenes with Ir(ttp)SiEt₃.

In order to avoid the CHA of benzene solvent, solvent-free conditions were applied for further investigation with various fluorobenzenes. Table 2 lists the results of the CFA and CHA activations. Generally, the less fluorine-substituted fluorobenzenes reacted faster (Table 2, entries 1-4 vs entries 5-7), likely due to the higher solubility of Ir(ttp)SiEt₃ 1a in less fluorinated solvents. For mono- and difluorobenzenes 2a-2c, Ir(ttp)SiEt₃

Table 2. CFA and CHA of ArF with Ir(ttp)SiEt₃



^a3b and 3e were also isolated in trace amount (<5%) and 5% yield, respectively. ^bNo further significant consumption of $Ir(ttp)SiEt_3$ 1a.

1a was consumed completely within 4 days to give high yields of CFA and CHA products (Table 2, entries 1–3). However, the reaction times were much longer for polyfluorinated benzenes 2e-2g, and some $Ir(ttp)SiEt_3$ **1a** still remained unreacted even after 8 days (Table 2, entries 5–7).

It is interesting that for fluorobenzene 2a, the *meta*-CHA product 3d was isolated as the major one among the three regioisomeric CHA products (Table 2, entry 1), and no CHA products were observed for 1,3-difluorobenzene 2c and 1,3,5-trifluorobenzene 2e (Table 2, entries 3 and 5).

Mechanistic Study for CFA. On the basis of our previous studies,¹² the two possible mechanisms for CFA of aryl fluoride by nucleophilic aromatic substitution are (1) addition–elimination ipso-attack or (2) benzyne mechanism. The benzyne mechanism is excluded since the regiochemistry of the difluoro- and trifluorobenzene substrates was retained in the CFA products (see S1.3 of the Supporting Information). The nucleophilic aromatic substitution mechanism by ipso-attack is the most possible mechanism, which has been proposed for the CFA of fluorobenzene with iridium porphyrin anion previously (Scheme 2).¹²

Scheme 2. Proposed Mechanism for CFA of PhF by Ir(ttp)SiEt₃

$$Ir(ttp)SiEt_3 + KOH \xrightarrow{IS1} Ir(ttp)K + Et_3SiOH (i)$$

$$Ir(ttp)K + PhF \xrightarrow{IS2} Ir(ttp)Ph + KF$$
(ii)

To gain further mechanistic understanding, DFT calculations were employed. The associated reaction profile is shown in Figure 1, and the transition structures are shown in Figure 2. In



Figure 1. Reaction profiles for carbon–fluorine bond activation (CFA) by iridium(III) porphyrin. Relative total energies including zero-point vibrational energies, single point dispersion (D3) contribution, and solvation free energies are given with respect to reactants in kJ mol⁻¹.

this mechanism, $Ir(ttp)SiEt_3$ initially reacts with KOH, producing Ir(ttp)K with an energy barrier of 51 kJ/mol [Scheme 2, eq (i)]. Subsequently, Ir(ttp)K reacts with fluorobenzene to produce Ir(ttp)Ph and KF with an energy barrier of 117 kJ/mol [Scheme 2, eq (ii)]. Due to the low-energy barriers for this exothermic process, CFA readily occurs at relatively low temperature such as 150 °C, which is in good agreement with the experimental observations.

Conversion of CFA Product into CHA Product. During the reaction of $Ir(ttp)SiEt_3$ **1a** with 1,4-difluorobenzene **2d**, the CFA product of $Ir(ttp)(4-F-C_6H_4)$ **3e** was observed before the CHA product of $Ir(ttp)(2,5-F_2-C_6H_3)$ **3f** by TLC analysis.



Figure 2. Transition structures for carbon-fluorine bond activation (CFA) by iridium(III) porphyrin. Selective distances are given in angstroms. The imaginary frequencies for the transition states are given in inverse centimeters.

When the reaction was carried out in a shorter reaction time of 2 h, the CFA product **3e** was isolated in 29% yield with the CHA product **3f** formed in trace amount only (eq 1). At lower



temperature of 150 °C, the CFA product 3e was isolated in 85% yield with a trace amount of the CHA product 3f and Ir(ttp)Ph 3a (eq 2). Furthermore, the CFA product 3e converted partially to the CHA product 3f at 200 °C in 1,4-difluorobenzene (eq 3). Therefore, the CFA product is generated first, which is the precursor for the CHA product.

Mechanistic Study for CHA. In basic conditions, Ir(ttp)-SiEt₃ first converts to $Ir(ttp)^-$ (Scheme 1).¹² However, $Ir(ttp)^$ is known to be in equilibrium with Ir(ttp)H, $Ir_2(ttp)_2$, and Ir(ttp)OH under basic conditions with residual water from reagents and solvent.^{10c} Thus, there are four possible pathways with these intermediates involved for the aromatic CHA process (Scheme 3). (Pathway i) First, $Ir(ttp)^-$ cleaves the

Scheme 3. Possible CHA Mechanisms Involving One Iridium Intermediate

- (i) $lr(ttp)^{-} + PhF \longrightarrow lr(ttp)C_6H_4F + H^{-}$ (ii) $lr(ttp)H + PhF \longrightarrow lr(ttp)C_6H_4F + H_2$
- (iii) $Ir_2(ttp)_2 + PhF \longrightarrow Ir(ttp)C_6H_4F + Ir(ttp)H$ $2Ir(ttp)H \longrightarrow Ir_2(ttp)_2 + H_2$
- (iv) $Ir(ttp)OH + PhF \longrightarrow Ir(ttp)C_6H_4F + H_2O$

aromatic C–H bond to give $Ir(ttp)C_6H_4F$ and H⁻ (Scheme 3, pathway i). The nucleophilic aromatic substitution of fluorobenzene by $Ir(ttp)^-$ to give H⁻ is unlikely since H⁻ is a very poor leaving group. Moreover, $Ir(ttp)SiEt_3/KOH$ reacted with benzene solvent to give only 7% yield of Ir(ttp)Ph 3a (eq 4). Therefore, $Ir(ttp)^-$ is unlikely the direct intermediate for

$$Ir(ttp)SiEt_{3} + \underbrace{KOH (10 \text{ equiv})}_{N_{2}, 200 °C, 4 d} Ir(ttp)Ph (4)$$

$$\xrightarrow{Ir(ttp)}_{F} + \underbrace{KOH (10 \text{ equiv})}_{N_{2}, 200 °C, 4 d} Ir(ttp)Ph (5)$$

$$3a 58\%$$

$$3e$$
Recovery 32%
$$Ir(ttp)$$

$$+ \underbrace{KOH (10 \text{ equiv})}_{d_{6}} Ir(ttp)Ph + Ir(ttp)C_{6}D_{5} + PhF (6)$$

$$3a 7\% 3a' 12\% 16\%$$



CHA. (Pathway ii) The second pathway involves the metathesis of Ir(ttp)H and PhF to give $Ir(ttp)C_6H_4F$ and H_2 (Scheme 3, pathway ii). However, without base added, Ir(ttp)H reacted with PhF to give a mixture of unknowns and neither CFA nor CHA product of PhF was observed. This pathway is thus ruled out. (Pathway iii) $Ir_2(ttp)_2$ reacts with PhF to give $Ir(ttp)C_6H_4F$ and Ir(ttp)H. Ir(ttp)H, in equilibrium with $Ir_2(ttp)_2$ and H_{21} is recycled back to $Ir_2(ttp)_2$ for further reaction (Scheme 3, pathway iii). However, Ir₂(ttp)₂ reacted with PhF to give a mixture of unknowns as well. Therefore, $Ir_2(ttp)_2$ is not the intermediate for CHA of fluorobenzenes. (Pathway iv) The concerted sigma-bond metathesis between Ir(ttp)OH and PhF gives $Ir(ttp)C_6H_4F$ and H_2O (Scheme 3, pathway iv). The concerted sigma-bond metathesis between an iridium hydroxyl complex and aromatic C-H bond has been reported by Periana et al.¹³ To understand the mechanistic details, we calculated the possible reaction paths (Figure S7 of the Supporting Information). However, the calculated barrier for the direct metathesis is exceedingly high (\sim 270 kJ/mol) (Figure S7 of the Supporting Information), indicating that little reaction occurs at 200 °C.

Since all the proposed intermediates cannot react with fluorobenzene to give the CHA product directly, we carried out further experiments to find out more elaborate mechanistic possibilities. Since the CFA product can convert to the CHA product under the basic reaction conditions, the CFA product was then reacted with benzene solvent to eliminate the CFA pathway. When $Ir(ttp)(4-F-C_6H_4)$ **3e** reacted with benzene in the presence of KOH, the CHA product $Ir(ttp)C_6H_5$ **3a** was obtained in 58% yield with the recovery of **3e** in 32% yield after 4 days at 200 °C (eq 5). Furthermore, $Ir(ttp)(4-F-C_6H_4)$ **3e** reacted with benzene- d_6 to form **3a** and the CDA product **3a**', and the organic coproduct fluorobenzene **2a** was also observed by ¹H NMR in 16% yield (eq 6). Ir(ttp)Ph **3a** is formed from the CFA of fluorobenzene and CHA of benzene.

Moreover, the reaction mixture between 3e with fluorobenzene in benzene- d_6 with KOH at 200 °C for 7 days, upon cooling down at room temperature, showed a new iridium porphyrin species with the proton chemical shift at -10.94 ppm of one proton, which was assigned to the hydroxyl proton of the proposed structure of $[Ir(ttp)(4-F-C_6H_4)OH]^-$ (Figure S4 of the Supporting Information). The other symmetric proton signals further indicate the trans configuration. However, the direct sigma-bond metathesis between Ir(ttp)OH and fluorobenzene was ruled out due to high-energy barriers based on theoretical calculation. Therefore, we propose that Ir(ttp)OH is involved in the mechanism as as a precursor of Ir₂(ttp)₂ in the CHA reaction.

Since we have computed that Ir(ttp)OH does not react with fluorobenzene through a concerted sigma-bond metathesis, a radical CHA pathway can still operate. Radical substitution of benzene has been well-documented.¹⁴ In a specific example, the aromatic C–H bond of fluorobenzene can be cleaved by a methyl radical addition to fluorobenzene followed by the hydrogen atom abstraction of the cyclohexadienyl radical intermediate (Scheme 4).¹⁵ By analogy, we propose that

Scheme 4. Proposed Mechanism for the Methylation of Fluorobenzene

$$MeHgI \xrightarrow{hv} Me \bullet + HgI \bullet$$
(i)

$$\begin{array}{c} \text{Me} \\ H \end{array} \xrightarrow{\bullet} F + \text{Me} \bullet \longrightarrow CH_4 + \text{MeC}_6H_4F \quad (iii) \\ o:m:p \sim 5:3:1 \end{array}$$

Ir^{II}(ttp) radical, which can be generated from reduction of Ir(ttp)OH (Scheme 5, pathway i and ii),^{10c} can participate in the C-H bond cleavage of fluorobenzene. Scheme 5 shows the proposed mechanisms for the CHA of fluorobenzene by iridium porphyrin complexes. IrII(ttp) radical cleaves the aromatic C-H bond through homolytic aromatic substitution either followed by a hydrogen atom abstraction by Ir(ttp)OH (Scheme 5, pathway a), Ir(ttp) radical (Scheme 5, pathway b), or a hydroxyl radical (Scheme 5, pathway c). Alternatively, Ir^{II}(ttp) radical attacks fluorobenzene to give an arenium radical followed by disproportionation to give iridium fluoroaryl (Scheme 5, pathway d).¹⁴ Compared to pathways a and b, pathway c is preferred based on steric ground and instability of Ir(ttp)OH at high temperature. Pathways b and d are excluded, since the reaction of $Ir_2(ttp)_2$ with fluorobenzene in the absence of base does not give CHA products. Only mechanisms a and c can account for the CHA in the reaction of $Ir_2(ttp)_2$ with PhF in the presence of KOH (eq 7).

$$Ir_{2}(ttp)_{2} + PhF \xrightarrow{10 \text{ equiv KOH}}_{N_{2}, 200 \ ^{\circ}C, 1 \ d} + \underbrace{Ir(ttp)}_{CFA} \xrightarrow{Ir(ttp)}_{F} + \underbrace{Ir(ttp)}_{F} +$$

To further examine the possibility of the proposed radical ipso-substitution mechanism shown in Scheme 5, DFT calculations have been carried out. Due to the large scale of $Ir_2(ttp)_2$, which is out of the limitation of calculation for transition state searching, we estimated the homolysis barrier for Ir(ttp)–Ir(ttp) based on that of Rh(oep)–Rh(oep). As the known Rh(oep)–Rh(oep) bond dissociation energy is 16 kcal/

Scheme 5. Proposed Mechanisms for CHA of Fluorobenzene by Iridium Porphyrins



mol, the homolysis barrier for Ir–Ir bond in ttp was estimated around 22–23 kcal/mol in consideration of commonly accepted diffusion-controlled radical recombination barrier of 2 kcal/mol and the increased steric of ttp over oep with 2–3 kcal weaker.¹⁶ We started the calculation from the activation of PhF by the Ir(ttp)· radical. Figure 3 shows the nonconcerted mechanism of pathway *c* of Scheme 5. The activation barriers are 171, 170, and 173 kJ/mol for forming Ir(ttp)(2fluorophenyl), Ir(ttp)(3-fluorophenyl), and Ir(ttp)(4-fluoro-



Figure 3. Reaction profile for carbon-hydrogen activation by iridium(III) porphyrin. Relative total energies including zero-point vibrational energies, single point dispersion (D3) contribution and solvation free energies are given with respect to reactants in kilojoules per mol.

phenyl), respectively, and are very similar (Figure 3). The energetics are in line with the experimental reaction time. The transition state structures are also similar to each other as shown in Figure 4. The imaginary frequencies are -812, -884,



Figure 4. Transition structures for carbon–hydrogen activation iridium(III) porphyrin. Selective distances are given in angstroms. The imaginary frequencies for the transition state are given in cm^{-1} .

and -873 cm⁻¹ for associated transition state structures **TS3**, **TS4**, and **TS5**, respectively. Due to the limitation of calculation, we did not perform calculation to identify pathway a of Scheme 5, as two porphyrins in this system are comparatively large to evaluate. Though we cannot rule out this pathway completely, the large steric hindrance strongly disfavors the possibility of two iridium porphyrin species closing in non-coplanar geometry.

On the basis of the above information, the most reasonable mechanism for CHA of fluorobenzene is the iridium porphyrin radical ipso-substitution followed by a hydrogen atom abstraction by hydroxyl radical.

Meta-Fluorine Stabilizing Effect. From the reaction between $Ir(ttp)SiEt_3$ and fluorobenzene **2a**, the *meta*-CHA product **3d** was isolated as the major one among the three regioisomeric CHA products (Table 2, entry 1), which is different from the *ortho*-fluorine stabilizing effect for nonporphyrin transition metal complexes reported previously.⁹ Therefore, equilibrium experiments were then conducted with various Ir(ttp)Ar and KOH in fluorobenzene **2a** at a higher temperature of 250 °C for a longer reaction time of 30 days to find out the relative thermodynamic stability of the metal complexes (Table 3). The results show that the reactions with

 Table 3. KOH-Promoted Equilibration of Ir(ttp)Ar with

 Fluorobenzene

F _n	+ F	KOH (1) N ₂ , 250 [°]	0 equiv °C, 30	/) d F _n ∙ n	= 0, 3a	lr(ttp)
n –	0, 1 2a		Ir(tt	n p)Ar/yie	= 1, 3d, 3	3e
entry	Ir(ttp)Ar	3a	3d	3e	3d/3e	total
1	Ir(ttp)(C6H5) 3a	15	50	8	6/1	73
2	Ir(ttp)(2-F-C6H4) 3b	30	41	8	5/1	79
3	Ir(ttp)(3-F-C6H4) 3d	3	78	4	19/1	85
4	Ir(ttp)(4-F-C6H4) 3e	9	47	18	3/1	74

3a, **3b**, and **3e** have almost reached an equilibrium with the *meta*-fluorophenyl complex being the most stable isomer (Table 3, entries 1, 2, and 4).¹⁷ The slow reaction of **3d** toward equilibrium further suggests that **3d** is the most stable isomer. Density functional theory calculations confirm the experimental observations as shown in Table 4. The *meta*-

Table 4. DFT Electronic Energies, ΔE_{DFT} , Zero-Point Vibrational Energies, ΔE_{ZP} , Single-Point Dispersion Contribution (D3), $\Delta E_{\text{D}//\text{DFT}}$, Solvation Free Energies, ΔG_{S} , Total Energies at 0 K, $\Delta E_0 = \Delta E_{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta E_{\text{D}//\text{DFT}} + \Delta G_{\text{S}}$, for Ir(ttp)(C₆H₄F) Isomers^{*a*}

compounds	$\Delta E_{ m DFT}$	ΔE_{ZP}	$\Delta E_{\mathrm{D//DFT}}$	$\Delta G_{\rm S}$	ΔE_0		
$Ir(ttp)(2-F-C_6H_4)$ 3b	8	-1	-1	-1	5		
$Ir(ttp)(3-F-C_6H_4)$ 3d	0	0	0	0	0		
$Ir(ttp)(4-F-C_6H_4)$ 3e	4	0	0	1	5		
'All relative to $Ir(ttp)(3-F-C_6H_4)$ and in kJ mol ⁻¹ .							

fluorophenyl Ir(ttp) is 4 kJ/mol more stable than the parafluorophenyl complex and is 8 kJ/mol more stable than the ortho-fluorophenyl complex. Taking the zero point energies, dispersion (D3) correction and solvation free energies into consideration, meta-fluorophenyl complex is 5 kJ/mol more favorable than both ortho- and para-fluorophenyl complexes. The meta-fluorine stabilizing effect is likely caused by the electron-withdrawing property of the fluorine atom to strengthen the $Ir-C(\alpha)$ bond.^{18a} The *ortho*-fluorine destabilizing effect is reasoned to be the steric effect. Clot and coworkers systematically studied the energetics of C-H oxidative addition of benzene and fluorinated benzenes.^{18b} They fitted a linear function of the number of fluorine substituents using the change in M-C bond energy of the products with respect to different coefficients corresponding to ortho-, meta-, and parafluorine.^{18b} It was found that the values of the ortho-coefficient range from 20 to 32 kJ mol⁻¹, greatly exceeding the values for the meta- and para-coefficients $(2.0-4.5 \text{ kJ mol}^{-1})$, which indicated the steric effect was indeed an essential role for stability of these structures.

Figure 3 further shows a slightly lower energy barrier for the formation of 3d than those of 3b and 3e (1-3 kJ/mol), which indicates that the formation of 3d is not significantly favorable kinetically. However, in consideration of both thermodynamic and kinetic effect, 3d is undoubtedly confirmed as the most possible products, which is consistent with the experimental results shown in Table 3.

The lower stability of **3b** can be accounted by the crystal structure of Ir(ttp)(2-fluorophenyl) **3b** shown in Figure 5. The Ir– $C(\alpha)$ –C(F) angle [124.5 (5)°] for **3b** is significantly larger than that of Ir– $C(\alpha)$ –C(H) [113.4 (5)°] for **3d**, suggesting strong electron repulsion between *ortho*-F and the porphyrin ring due to the short distance. DFT calculations also identify this feature. The calculated $\angle C7$ –Ir–C2 for *ortho*-fluorophenyl (98.9°) is about 5° larger than that for *meta*-fluorophenyl (93.1°) and *para*-fluorophenyl (93.5°) (Table S7 of the Supporting Information). Moreover, from the optimized structures of **3b**, **3d**, and **3e** by B3LYP, the porphyrin plane of **3b** is the most distorted, indicating the largest steric effect from the *ortho*-fluorine phenyl Ir(ttp) among these three regio isomers.

Both the experimental and theoretical results show that the Ir(ttp)(3-fluorophenyl) 3d is the most stable isomer. However, the origin of the *meta*-fluorine stabilizing effect, different from



Figure 5. Molecular structure of $Ir(ttp)(2-F-C_6H_4)(H_2O)$ **3b**·H₂O (30% probability displacement ellipsoids).

the previously reported *ortho*-fluorine stabilizing effect of nonporphyrin transition metal complexes, is mainly due to the planar porphyrin ligand.⁹ Since porphyrin is planar, the *ortho*-fluorine steric effect is significant to render the complex less stable, which leads to a different relative stabilizing effect of *meta*-fluorine different from those previously reported *ortho*-fluorine stabilizing effect of nonporphyrin transition metal complexes.⁹

CONCLUSIONS

We have described a base-promoted sequential aromatic carbon–fluorine and carbon–hydrogen bond activation process with iridium porphyrin triethylsilyl. Mechanistic studies suggest that $Ir^{I}(ttp)^{-}$ cleaves the aromatic C–F bond via an ipso-substitution to give Ir(ttp) aryls, which subsequently undergoes alkaline hydrolysis to give $Ir^{II}(ttp)OH$. Reduction of $Ir^{III}(ttp)-OH$ gives $Ir^{II}(ttp)$ radical which cleaves the C–H bond through metalloradical type homolytic aromatic substitution to give iridium porphyrin aryls. Among the CHA products, the *meta*-fluoro iridium fluorophenyl is thermodynamically more stable than the ortho- and para- isomers.

EXPERIMENTAL SECTION

Computational Details. All the DFT calculations were performed using hybrid functional B3LYP¹⁹ implemented in Gaussian 09.²⁰ An effective core potential (ECP) plus DZ basis set of Lanl2dz²¹ was applied to iridium, and f-type polarization functions²² was added to increase the accuracy of energy prediction. A basis set of 6-31G(d)²³ was applied for the other elements, such as C, H, N, and F. The DFT-D3 method developed by Grimme and co-workers²⁴ was employed to calculate the dispersion correction for the optimized structures. Since most of the reactions take place in solvent, the continuum solvation model SMD²⁵ was used to take the solvent effect into account. The single point solvation free energy on the optimized structures was calculated with fluorobenzene as the solvent. Vibrational frequencies were calculated to take account of the zero-point vibrational energy (without scaling) and to identify the transition structures. All the dispersion correction energies, zero-point vibrational energies, and salvation free energies were added to the reported energy values. A stable structure was confirmed by the fact that all its vibrational frequencies were real. A transition structure was confirmed by the presence of one imaginary frequency.

General Procedure. Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Benzene used as solvent was distilled from sodium. Thin-layer chromatography was performed on precoated silica gel 60 F254 plates for thin-layer analyses for the reaction mixture. All preparation reactions were carried out in a Teflon screw-head stoppered tube heated in drilled holes in an aluminum block covered

with aluminum foil under N_2 with the temperature measured in the center small hole of the aluminum block by either a thermocouple or thermometer, and the temperature was controlled by a stirrer hot plate. For purification of iridium aryl complexes, fresh column chromatography was used and carried out in air using alumina (90 active neutral, 70–230 mesh). Ir(ttp)SiEt₃²⁶ 1a, [Ir(ttp)-Na⁺]²⁷ 1b, Ir(ttp)H²⁸ 1c were prepared according to the literature.

¹H NMR spectra were recorded on a Bruker AV400 (400 MHz). Chemical shifts were reported with reference to the residual solvent protons in C_6D_6 (δ 7.15 ppm) or in CDCl₃ (δ 7.26 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz (Hz). ¹³C NMR spectra were recorded on a Bruker 400 (100 MHz) spectrometer and referenced to CDCl₃ (δ 77.1 ppm) or CD₂Cl₂ (δ 53.8 ppm) or THF-*d*₈ (δ 67.4 ppm). ¹⁹F NMR spectra were recorded on a Varian XL-400 spectrometer at 376 MHz. Chemical shifts were referenced with the external standard fluorine in $C_6H_5CF_3$ using a sealed melting point tube and put into the NMR tube (δ = 0.00 ppm).²⁹ Coupling constants (*J*) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were performed on a Thermofinnign MAT 95 XL in FAB (using 3-nitrobenzyl alcohol (NBA) matrix and CH₂Cl₂ as the solvent) and ESI model (MeOH:CH₂Cl₂ = 1:1 as the solvent).

EXPERIMENTAL PROCEDURES

Reaction between lr(ttp)SiEt₃ 1a and 1,4-Difluorobenzenes 2d in Benzene without the Addition of KOH. Benzene (0.8 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to Ir(ttp)SiEt₃ (18.2 mg, 0.019 mmol). Then the mixture was heated at 200 °C for 3 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of Ir(ttp)SiEt₃ 1a (17.6 mg, 0.0180 mmol, 96%) was recovered.

Reaction between Ir(ttp)SiEt₃ 1a and 1,4-Difluorobenzenes 2d in Benzene with the Addition of KOH. Gererature Procedure. The reaction of $Ir(ttp)SiEt_3$ 1a with 1,4-difluorobenzene (2b) in benzene at 120 °C with the addition of 10 equiv of KOH is described as a typical example. Benzene (0.9 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to a mixture of Ir(ttp)SiEt₃ (19.6 mg, 0.020 mmol) and KOH (11.2 mg, 0.200 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 120 °C for 6 days. The crude product was purified by column chromatography, eluting with a mixture of hexane/CH₂Cl₂ (3:1) and a purple solid of Ir(ttp)SiEt₃ 1a (11.0 mg, 0.0113 mmol, 56%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)(4-F-C_6H_4)$ 3e (5.6 mg, 0.0059 mmol, 29%) was isolated. $R_f = 0.35$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C_6D_6 , 400 MHz): δ 0.92 (dd, 2 H, ⁴ J_{HF} = 6.0 Hz, J = 8.8 Hz), 2.39 (s, 12 H), 4.65 (dd, 2 H, ${}^{3}J_{HF} = 9.2$ Hz, J = 9.2 Hz), 7.21 (d, 4 H, J = 7.4 Hz), 7.33 (d, 4 H, J = 7.6 Hz), 7.91 (dd, 4 H, J = 1.6, 7.8 Hz), 8.15 (dd, 4 H, J = 1.6, 7.6 Hz), 8.82 (s, 8 H). ¹³C NMR (CDCl₃, 100 MHz): δ 21.6, 88.4, 109.8 (d, ${}^{2}J_{CF}$ = 19.5 Hz), 123.9, 127.5, 127.6, 129.1 (d, ${}^{3}J_{CF} = 6.0$ Hz), 131.5, 133.6, 134.2, 137.4, 138.7, 142.9, 157.0 (d, ${}^{1}J_{CF} = 236.2$ Hz). ${}^{19}F$ NMR (CDCl₃, 376 MHz): δ -62.36 (br, 1 F, 4-F). HRMS (FABMS): Calcd for $(C_{54}H_{40}FN_4Ir)^+$: m/z 956.2861; found m/z 956.285545. When the solvent was changed to hexane/CH2Cl2 (1:1), a purple solid of $Ir(ttp)(2,5-F_2-C_6H_3)$ 3f was isolated in trace amount (less than 5% yield). $R_f = 0.20$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C₆D₆, 400 MHz): δ 0.71 (ddd, 1 H, ${}^{3}J_{\rm HF}$ = 11.6 Hz, ${}^{4}J_{\rm HF}$ = 4.8 Hz, J = 3.2 Hz), 2.37 (s, 12 H), 4.24 (ddd, 1 H, ${}^{3}J_{HF} = 14.0$ Hz, ${}^{4}J_{HF} = 5.2$ Hz, J = 7.0 Hz), 4.79 (ddd, 1 H, ${}^{3}J_{HF} = 11.4$ Hz, ${}^{4}J_{HF} = 3.2$ Hz, J = 7.2 Hz), 7.19 (d, 4 H, J =7.6 Hz), 7.28 (d, 4 H, J = 7.6 Hz), 8.01 (dd, 4 H, J = 1.6, 7.6 Hz), 8.11 (dd, 4 H, J = 2.0, 7.6 Hz), 8.87 (s, 8 H). ¹³C NMR (CD₂Cl₂, 100 (di, $^{1}J_{CF} = 0.3$ (di, $^{2}J_{CF} = 31.9$ Hz), 107.0 (dd, $^{3}J_{CF} = 9.3$ Hz, $^{2}J_{CF} = 24.2$ Hz), 110.3 (dd, $^{3}J_{CF} = 8.9$ Hz, $^{2}J_{CF} = 31.0$ Hz), 119.6 (dd, $^{3}J_{CF} = 12.9$ Hz, $^{2}J_{CF} = 21.8$ Hz), 123.5, 127.7, 127.8, 131.6, 133.8, 134.5, 137.8, 139.0, 143.3, 152.4 (d, ${}^{1}J_{CF}$ = 236.8 Hz), 160.8 (d, ${}^{1}J_{CF}$ = 234.2). $^{19}{\rm F}$ NMR (CD₂Cl₂, 376 MHz): δ –61.40 (ddd, 1 F, $^{4}J_{\rm FH}$ = 5.3 Hz, $^{3}J_{\rm FH}$ = 11.1, 11.6 Hz, 5-F), -52.62 (ddd, ${}^{4}J_{FH}$ = 5.6, 9.4 Hz, ${}^{3}J_{FH}$ = 17.0 Hz,

2-F). HRMS (FABMS): calcd for $(C_{54}H_{39}F_2N_4Ir)^+$: m/z 974.2767; found m/z 974.276253.

Reaction between Ir(ttp)SiEt₃ 1a and 1,4-Difluorobenzenes 2d in Benzene with the Addition of 10 Equivalents of KOH at 150 °C. Benzene (0.9 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to a mixture of Ir(ttp)SiEt₃ (18.7 mg, 0.019 mmol) and KOH (10.8 mg, 0.190 mmol, 10 equiv). Then the mixture was heated at 150 °C for 5 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of Ir(ttp)SiEt₃ 1a (1.2 mg, 0.0012 mmol, 6%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)(4-F-C_6H_4)$ 3e (15.4 mg, 0.0161 mmol, 85%) and $Ir(ttp)C_6H_5$ 3a (<5%) was isolated. $Ir(ttp)C_6H_5$ 3a, $R_f = 0.35$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C₆D₆₀) 400 MHz): δ 1.10 (d, 2 H, J = 8.0 Hz), 2.39 (s, 12 H), 4.89 (t, 2 H, J = 7.2 Hz), 5.23 (t, 1 H, J = 7.2 Hz), 7.19 (d, 4 H, J = 7.6 Hz), 7.33 (d, 4 H, J = 7.6 Hz), 7.87 (dd, 4 H, J = 1.6, 7.6 Hz), 8.14 (dd, 4 H, J = 1.6, 7.6 Hz), 8.80 (s, 8 H). ¹³C NMR (CDCl₃, 100 MHz): δ 21.6, 95.2, 120.1, 123.2, 124.1, 127.5, 129.0, 131.5, 133.6, 134.2, 137.3, 138.7, 143.0. HRMS (FABMS): calcd for $(C_{54}H_{41}N_4Ir)^+$: m/z 938.2955; found m/z 938.294798. When the solvent was changed to hexane/ CH_2Cl_2 (1:1), a purple solid of $Ir(ttp)(2,5-F_2-C_6H_3)$ 3f (<5%) was isolated.

Reaction between $Ir(ttp)SiEt_3$ 1a and 1,4-Difluorobenzenes 2d in Benzene with the Addition of 10 Equivalents of KOH at 200 °C. Benzene (0.9 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to a mixture of $Ir(ttp)SiEt_3$ (18.4 mg, 0.019 mmol) and KOH (10.6 mg, 0.190 mmol, 10 equiv). Then the mixture was heated at 200 °C for 3 days. The crude product was purified by column chromatography, eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a (<5%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)(4-F-C_6H_4)$ 3e (9.4 mg, 0.0098 mmol, 52%) and $Ir(ttp)C_6H_5$ 3a (5.2 mg, 0.0055 mmol, 29%) was isolated. When the solvent was changed to hexane/CH₂Cl₂ (1:1), a purple solid of $Ir(ttp)(2,5-F_2-C_6H_3)$ 3f (1.5 mg, 0.0015 mmol, 8%) was isolated.

Reaction between lr(ttp)SiEt₃ 1a and 1,4-Difluorobenzenes 2d in Benzene- d_6 with the Addition of KOH at 200 °C. Benzene d_6 (0.9 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to a mixture of Ir(ttp)SiEt₃ (18.5 mg, 0.019 mmol) and KOH (10.6 mg, 0.190 mmol, 10 equiv). Then the mixture was heated at 200 °C for 3 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of Ir(ttp)SiEt₃ **1a** (6.4 mg, 0.0066 mmol, 34%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid mixture of Ir(ttp)(4-F-C₆H₄) **3e** (9.0 mg, 0.0094 mmol, 50%) and Ir(ttp)C₆D₅ **3a'** (1.2 mg, 0.0013 mmol, 6%) was isolated. When the solvent was changed to hexane/CH₂Cl₂ (1:1), a purple solid of Ir(ttp)(2,5-F₂-C₆H₃) **3f** (1.2 mg, 0.0012 mmol, 6%) was isolated.

Reaction between $Ir(ttp)SIEt_3$ 1a and 1,4-Difluorobenzenes 2d in Benzene with the Addition of 5 Equivalents of KOH at 150 °C. Benzene (0.8 mL) and 1,4-difluorobenzene (0.2 mL, 100 equiv) were added to a mixture of $Ir(ttp)SiEt_3$ (17.8 mg, 0.018 mmol) and KOH (5.1 mg, 0.090 mmol, 5 equiv). Then the mixture was heated at 150 °C for 5 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a (3.1 mg, 0.0032 mmol, 17%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)(4-F-C_6H_4)$ 3e (10.6 mg, 0.0111 mmol, 61%) and $Ir(ttp)C_6H_5$ 3a (<5%) was isolated. When the solvent was changed to hexane/CH₂Cl₂ (1:1), a purple solid of $Ir(ttp)(2,5-F_2-C_6H_3)$ 3f (1.9 mg, 0.0020 mmol, 11%) was isolated.

Reaction between $Ir(ttp)SiEt_3$ 1a and 1,4-Diffuorobenzenes 2d in Benzene with the Addition of 20 Equivalents of KOH at 150 °C. Benzene (0.9 mL) and 1,4-diffuorobenzene (0.2 mL, 100 equiv) were added to a mixture of $Ir(ttp)SiEt_3$ (18.6 mg, 0.019 mmol) and KOH (21.4 mg, 0.380 mmol, 20 equiv). Then the mixture was heated at 150 °C for 4 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a was recovered in trace amount (<5%). Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid of Ir(ttp)(4-F-C₆H₄) **3e** (13.5 mg, 0.0141 mmol, 74%), and Ir(ttp)C₆H₅ **3a** (<5%) was isolated. When the solvent was changed to hexane/CH₂Cl₂ (1:1), a purple solid of Ir(ttp)(2,5-F₂-C₆H₃) **3f** (<5%) was isolated.

Reaction between Ir(ttp)SiEt₃ 1a and Fluorobenzenes 2a-2g with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. Gererature Procedure. The reaction of Ir(ttp)SiEt₃ 1a with fluorobenzene (2a) at 200 °C with the addition of 10 equiv of KOH is described as a typical example. Fluorobenzene (0.9 mL, 500 equiv) was added to a mixture of Ir(ttp)SiEt₃ (18.4 mg, 0.019 mmol) and KOH (10.6 mg, 0.190 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)C_6H_5$ 3a (11.4 mg, 0.0122 mmol, 64%), $Ir(ttp)(2-F-C_6H_4)$ **3b** (<5%), Ir(ttp)(3-F-C₆H₃) 2d (3.2 mg, 0.0033 mmol, 18%), and Ir(ttp)(4-F-C₆H₄) 3e (0.9 mg, 0.0009 mmol, 5%) were isolated. Ir(ttp)(2-F- C_6H_4) 3b, $R_f = 0.35$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C_6D_6 , 400 MHz): $\delta 0.79$ (dd, 1 H, ${}^{4}J_{\rm HF}$ = 7.4 Hz, J = 7.2 Hz), 2.38 (s, 12 H), 4.44 (ddd, 1 H, ${}^{3}J_{HF}$ = 10.5 Hz, J = 1.4, 8.6 Hz), 4.79 (t, 1 H, J = 7.6 Hz), 5.09 (td, 1 H, ${}^{4}J_{HF}$ = 5.6 Hz, J = 6.2 Hz), 7.20 (d, 4 H, J = 7.6 Hz), 7.32 (d, 4 H, J = 7.6 Hz), 7.96 (dd, 4 H, J = 1.6, 7.6 Hz), 8.13 (dd, 4 H, J = 1.6, 7.6 Hz), 8.85 (s, 8 H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ 21.6, 81.7 (d, ${}^{2}J_{CF}$ = 26.6 Hz), 110.8 (d, ${}^{2}J_{CF}$ = 27.9 Hz), 119.2 (d, ${}^{4}J_{CF}$ = 2.4 Hz), 121.7 (d, ${}^{3}J_{CF} = 8.2$ Hz), 123.7, 127.7, 127.8, 131.6, 133.9, 134.0 (d, ${}^{3}J_{CF} = 11.6$ Hz), 134.5, 137.8, 139.0, 143.4, 163.9 (d, ${}^{1}J_{CF} = 240.1$ Hz). ¹⁹F NMR (CD₂Cl₂, 376 MHz): δ –45.55 (dt, 1 F, ⁴J_{FH} = 5.3 Hz, ${}^{3}J_{\rm FH}$ = 10.5 Hz, 2-F). HRMS (FABMS): calcd for $(C_{54}H_{40}FN_{4}Ir)^{+}$: m/z 956.2861; found m/z 956.284725. A single crystal for X-ray analysis was grown fron CH_2Cl_2 /hexane. $Ir(ttp)(3-F-C_6H_4)$ 3d, $R_f = 0.35$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C₆D₆, 400 MHz): δ 0.85 (d, 1 H, J = 8.4 Hz), 0.88 (ddd, 1 H, ${}^{3}J_{\text{HF}}$ = 12.0 Hz, J = 1.6, 2.0 Hz), 2.39 (s, 12 H), 4.65 (dd, 1 H, ${}^{3}J_{HF}$ = 15.2 Hz, J = 8.0 Hz), 4.94 (td, 1 H, ${}^{4}J_{HF}$ = 2.4 Hz, J = 8.4 Hz), 7.18 (d, 4 H, J = 7.6 Hz), 7.32 (d, 4 H, J = 7.6 Hz), 7.90 (dd, 4 H, J = 2.0, 7.6 Hz), 8.14 (dd, 4 H, J = 2.0, 7.8 Hz), 8.82 (s, 8 H). ¹³C NMR (CDCl₃, 100 MHz): δ 21.6, 98.2, 106.5 (d, ²J_{CF} = 20.8 Hz), 115.3 (d, ${}^{2}J_{CF}$ = 19.6 Hz), 123.1 (d, ${}^{3}J_{CF}$ = 8.0 Hz), 123.8, 124.9, 127.5, 127.6, 131.6, 133.6, 134.2, 137.4, 138.7, 142.9, 155.0 (d, ${}^{1}J_{CF}$ = 243.1 Hz). ¹⁹F NMR (C₆D₆, 376 MHz): δ -54.19 (ddd, 1 F, ⁴J_{FH} = 3.4 Hz, ${}^{3}J_{FH} = 12.0$, 15.8 Hz, 3-F). HRMS (FABMS): calcd for $(C_{54}H_{40}FN_4Ir)^+$: m/z 956.2861; found m/z 956.286859.

Reaction between Ir(ttp)SiEt₃ 1a and 1,2-Difluorobenzenes 2b with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. 1,2-Difluorobenzene (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)SiEt₃ (19.4 mg, 0.020 mmol) and KOH (11.2 mg, 0.200 mmol, 10 equiv). Then the mixture was heated at 200 °C for 2 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)(2-F-C_6H_4)$ 3b (1.1 mg, 0.0012 mmol, 6%) was isolated. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(ttp)(2,3-F_2-C_6H_3)$ 3c (17.2 mg, 0.0177 mmol, 89%) was isolated. $R_{f} = 0.25$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C₆D₆, 400 MHz): δ 0.53 (dddd, 1 H, ${}^{5}J_{\rm HF}$ = 1.4 Hz, ${}^{4}J_{\rm HF}$ = 6.8 Hz, J = 1.2, 6.8 Hz), 2.38 (s, 12 H), 4.54 (tdd, 1 H, ${}^{5}J_{HF} = 1.2$ Hz, ${}^{4}J_{HF} = 6.2$ Hz, J = 7.8 Hz), 4.93 (ddd, 1 H, ${}^{4}J_{HF} = 8.8$ Hz, ${}^{3}J_{HF} = 9.2$ Hz, J = 1.3, 7.9 Hz), 7.19 (d, 4 H, J = 7.2 Hz), 7.30 (d, 4 H, J = 7.6 Hz), 7.96 (dd, 4 H, J = 1.6, 7.6 Hz), 8.11 (dd, 4 H, J = 1.6, 8.6 Hz), 8.86 (s, 8 H). ¹³C NMR $(CD_2Cl_2, 100 \text{ MHz}): \delta 21.6, 87.5 \text{ (d, } {}^2J_{CF} = 23.6 \text{ Hz}), 108.3 \text{ (d, } {}^2J_{CF} =$ 17.3 Hz), 118.1 (dd, ${}^{3}J_{CF} = 6.6$ Hz, ${}^{4}J_{CF} = 3.1$ Hz), 123.5, 127.6, 127.8, 129.2 (dd, ${}^{3}J_{CF} = 11.0$ Hz, ${}^{4}J_{CF} = 3.2$ Hz), 131.5, 134.0, 134.4, 137.7, 139.1, 143.3, 144.7 (dd, ${}^{1}J_{CF} = 242.9$ Hz, ${}^{2}J_{CF} = 18.1$ Hz), 152.4 (dd, ${}^{1}J_{CF}$ = 239.4 Hz, ${}^{2}J_{CF}$ = 10.2 Hz). ${}^{19}F$ NMR (CD₂Cl₂, 376 MHz): δ $-79.80 \text{ (ddd, 1 F, }^{4}J_{FH} = 5.6 \text{ Hz}, \,^{3}J_{FH} = 10.0 \text{ Hz}, \,^{3}J_{FF} = 21.4 \text{ Hz}, \, 3\text{-F}),$ -73.04 (dt, 1F, ${}^{4}J_{FH} = 5.3$ Hz, ${}^{3}J_{FF} = 21.8$ Hz, 2-F). HRMS (FABMS): calcd for $(C_{54}H_{39}F_2N_4Ir)^+$: m/z 974.2767; found m/z 974.278921.

Reaction between $Ir(ttp)SiEt_3$ 1a and 1,3-Difluorobenzenes 2c with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. 1,3-Difluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)SiEt_3$ (18.8 mg, 0.019 mmol) and KOH (10.8 mg, 0.190 mmol, 10 equiv). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid of Ir(ttp)(3-F-C₆H₄) **3b** (14.6 mg, 0.0153 mmol, 80%) was isolated.

Reaction between $Ir(ttp)SiEt_3$ 1a and 1,4-Difluorobenzenes 2d with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions for Three Days. 1,4-Difluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)SiEt_3$ (18.0 mg, 0.018 mmol) and KOH (10.3 mg, 0.180 mmol, 10 equiv). Then the mixture was heated at 200 °C for 3 days. The crude product was purified by column chromatography eluting with a mixture of hexane/ CH_2Cl_2 (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a (1.7 mg, 0.0017 mmol, 10%) was recovered. Then the solvent was changed to hexane/ CH_2Cl_2 (2:1), and a purple solid of $Ir(ttp)(4-F-C_6H_4)$ 3e (8.2 mg, 0.0086 mmol, 47%) was isolated. When the solvent was changed to hexane/ CH_2Cl_2 (1:1), a purple solid of $Ir(ttp)(2,5-C_6H_3F_2)$ 3f (7.2 mg, 0.0074 mmol, 41%) was isolated.

Reaction between Ir(ttp)SiEt₃ 1a and 1,3,5-Trifluorobenzenes 2e with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. 1,3,5-Trifluorobenzene (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)SiEt₃ (20.2 mg, 0.021 mmol) and KOH (11.6 mg, 0.210 mmol, 10 equiv). Then the mixture was heated at 200 °C for 8 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of Ir(ttp)SiEt₃ 1a (15.2 mg, 0.0155 mmol, 74%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(ttp)(3,5-F_2-C_6H_3)$ 3g (4.9 mg, 0.0050 mmol, 24%) was isolated. $R_f = 0.30$ (hexane/CH₂Cl₂ = 1:1). ^TH NMR $(C_6D_6, 400 \text{ MHz})$: $\delta 0.62 \text{ (dd, 2 H, }^3J_{\text{HF}} = 9.6 \text{ Hz}, J = 2.0 \text{ Hz}), 2.39 \text{ (s,}$ 12 H), 4.69 (tt, 1 H, ${}^{3}J_{HF}$ = 9.2 Hz, J = 2.4 Hz), 7.17 (d, 4 H, J = 8.0 Hz), 7.33 (d, 4 H, J = 7.2 Hz), 7.92 (dd, 4 H, J = 1.6, 7.8 Hz), 8.13 (dd, 4 H, J = 1.6, 7.6 Hz), 8.82 (s, 8 H). The ¹³C NMR and ¹⁹F NMR spectra of 3g can not be obtained since it is insoluble in CDCl₃, $CD_2Cl_{2\ell}$ acetone- $d_{6\ell}$ and THF- d_8 . HRMS (FABMS): c for $(C_{54}H_{39}F_2N_4Ir)^+$: m/z 974.2767; found m/z 974.273442.

Reaction between Ir(ttp)SiEt₃ 1a and Pentafluorobenzene 2f with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. Pentafluorobenzene (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)SiEt₃ (18.1 mg, 0.019 mmol) and KOH (10.4 mg, 0.190 mmol, 10 equiv). Then the mixture was heated at 200 °C for 6 days. The crude product was purified by column chromatography eluting with a mixture of hexane/ CH_2Cl_2 (3:1), and a purple solid of Ir(ttp)SiEt₃ 1a (7.0 mg, 0.0072 mmol, 38%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid mixture of $Ir(ttp)(2,3,5,6-F_4-C_6H)$ 3h (1.3 mg, 0.0013 mmol, 7%) and $Ir(ttp)(C_6F_5)$ 3i (9.6 mg, 0.0093 mmol, 49%) was isolated. Ir(ttp)(2,3,5,6-F₄- C_6H) 3h was independently synthesized from Ir(ttp)H and pentafluorobenzene in the presence of KOH (as shown below). $R_f = 0.08$ (hexane/CH₂Cl₂ = 1:1). ¹H NMR (C₆D₆) 400 MHz): δ 2.36 (s, 12 H), 4.69 (tt, 1 H, ${}^{4}J_{HF}$ = 7.2 Hz, ${}^{3}J_{HF}$ = 9.4 Hz), 7.19 (dd, 8 H, J = 1.7, 8.0 Hz), 8.04-8.13 (m, 8 H [overlap with $Ir(ttp)C_6F_5$], 8.91 (s, 8 H). ¹⁹F NMR (CDCl₃, 376 MHz): δ -80.81 (ddd, 2 F, ${}^{3}J_{FH} = 10.0$ Hz, ${}^{4}J_{FF} = 9.8$ Hz, ${}^{3}J_{FF} = 22.6$ Hz, 3-F), -71. 45 (ddd, 2 F, ${}^{4}J_{FH} = 7.9$ Hz, ${}^{4}J_{FF} = 7.9$ Hz, ${}^{3}J_{FF} = 21.8$ Hz, 2-F). HRMS (FABMS): calcd for $(C_{54}H_{37}F_4N_4Ir)^+$: m/z 1010.2578; found m/z1010.280933. Ir(ttp)(C_6F_5) 3i, $R_f = 0.08$ (hexane/ $CH_2Cl_2 = 1:1$). ¹H NMR (C_6D_{61} 400 MHz): δ 2.38 (s, 12 H), 7.19 (d, 4 H, J = 7.6 Hz), 7.31 (d, 4 H, J = 7.6 Hz), 8.08 (d, 4 H, J = 7.2 Hz), 8.15 (d, 4 H, J = 7.2 Hz), 8.91 (s, 8 H). ¹³C NMR (THF-d₈, 100 MHz): δ 21.5, 123.7, 128.0, 128.2, 131.8, 134.4, 134.9, 138.1, 139.9, 144.0, 150.4-153.1 (for the C of C–F bond). $^{19}\mathrm{F}$ NMR (THF- $d_{8\prime}$ 376 MHz): δ –105.6 (t, 1 F, *J* = 19.9 Hz, 4-F), -103.2 (t, 2 F, *J* = 19.9 Hz, 3-F), -69.40 (d, 2 F, *J* = 20.3 Hz, 2-F). HRMS (FABMS): calcd for $(C_{54}H_{36}F_5N_4Ir)^+$: m/z1028.2484; found m/z 1028.251763.

Reaction between Ir(ttp)H 1c and Pentafluorobenzene 2f with the Addition of 10 Equivalents of KOH at 60 °C in Solvent-Free Conditions (Independent Synthesis of Ir(ttp)-(2,3,5,6-F₄-C₆H) 3h. Pentafluorobenzene (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)H (17.0 mg, 0.020 mmol) and KOH (11.2 mg, 0.200 mmol, 10 equiv), and the mixture was degased by the

freeze-pump-thaw method (3 cycles). Then the mixture was heated at 60 °C for 2 h. The crude product was purified by column chromatography, eluting with a mixture of hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(tp)(2,3,5,6-F_4-C_6H)$ 3h (4.2 mg, 0.0042 mmol, 21%) was isolated, with some impurities involved.



Reaction between $Ir(ttp)SiEt_3$ 1a and Hexafluorobenzenes 2g with the Addition of 10 Equivalents of KOH at 200 °C in Solvent-Free Conditions. Hexafluorobenzene (1.2 mL, 500 equiv) was added to a mixture of $Ir(ttp)SiEt_3$ (20.7 mg, 0.021 mmol) and KOH (11.9 mg, 0.210 mmol, 10 equiv). Then the mixture was heated at 200 °C for 8 days. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a (4.9 mg, 0.0050 mmol, 24%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(ttp)(C_6F_5)$ 3i (10.8 mg, 0.0105 mmol, 50%) was isolated.

Reaction between $Ir(ttp)SiEt_3$ 1a and 1,2-Difluorobenzene 2g with the Addition of 10 Equivalents of KOH at 200 °C for One Hour in Solvent-Free Conditions. 1,2-Difluorobenzene (0.9 mL, 500 equiv) was added to a mixture of $Ir(ttp)SiEt_3$ (18.6 mg, 0.019 mmol) and KOH (10.7 mg, 0.190 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 1 h. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of $Ir(ttp)SiEt_3$ 1a (17.4 mg, 0.0179 mmol, 94%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid mixture of $Ir(ttp)(2-F-C_6H_4)$ 3b (0.5 mg, 0.0005 mmol, 3%) and $Ir(ttp)(2,3-F_2-C_6H_3)$ 3c (0.5 mg, 0.0005 mmol, 3%) was isolated.

Reaction between $Ir(ttp)(2-F-C_6H_4)$ 3b and 1,2-Difluorobenzene 2b with the Addition of 10 Equivalents of KOH at 200 °C for One Day in Solvent-Free Conditions. 1,2-Difluorobenzene (0.8 mL, 500 equiv) was added to a mixture of $Ir(ttp)(2-F-C_6H_4)$ (15.9 mg, 0.017 mmol) and KOH (9.3 mg, 0.170 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 1 day. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(ttp)(2,3-F_2-C_6H_3)$ 3c (15.3 mg, 0.0157 mmol, 94%) was isolated.

Reaction between Ir(ttp)SiEt₃ 1a and 1,4-Difluorobenzenes 2d with the Addition of 10 Equivalents of KOH at 200 °C for Two Hours in Solvent-Free Conditions. 1,4-Difluorobenzene (0.9 mL, 500 equiv) was added to a mixture of Ir(ttp)SiEt₃ (17.0 mg, 0.017 mmol) and KOH (9.5 mg, 0.170 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 h. The crude product was purified by column chromatography eluting with a mixture of hexane/CH₂Cl₂ (3:1), and a purple solid of Ir(ttp)SiEt₃ 1a (10.6 mg, 0.0109 mmol, 64%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (2:1), and a purple solid of Ir(ttp)(4-F–C₆H₄) 3e (4.7 mg, 0.0049 mmol, 29%) was isolated. When the solvent was changed to hexane/CH₂Cl₂ (1:1), a purple solid of Ir(ttp)(2,5-F₂–C₆H₃) 3f (<5%) was isolated.

Reaction between $Ir(ttp)(4-F-C_6H_4)$ 3e and 1,4-Difluorobenzene 2d with the Addition of KOH. 1,4-Difluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)(4-F-C_6H_4)$ (18.9 mg, 0.020 mmol) and KOH (11.1 mg, 0.200 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 3 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)(4-F-C_6H_4)$ 3e (10.9 mg, 0.0114 mmol, 57%) was recovered. Then the solvent was changed to hexane/CH₂Cl₂ (1:1), and a purple solid of $Ir(ttp)(2,5-F_2-C_6H_3)$ 3f (5.8 mg, 0.0060 mmol, 30%) was isolated.

Reaction between Ir(ttp)SiEt₃ 1a with KOH in Benzene- d_6 in a Sealed-NMR Tube. Benzene- d_6 (0.5 mL) was added to a mixture of Ir(ttp)SiEt₃ (9.3 mg, 0.0095 mmol) and KOH (5.3 mg, 0.0950 mmol, 10 equiv) in an NMR tube with a rotaflo stopper and degassed by the freeze-pump-thaw method (3 cycles). The mixture was frozen under liquid nitrogen and then flame-sealed under vacuum. The sealed-NMR tube was heated at 200 °C and monitored by ¹H NMR spectroscopy, and the yield of product was calibrated with the internal standard residual benzene in benzene- d_6 .

Reaction between $Ir(ttp)^-Na^+$ 1b and Fluorobenzene 2a without the Addition of KOH. Fluorobenzene (1.0 mL, 500 equiv) was added to $Ir(ttp)^-Na^+$ (18.6 mg, 0.022 mmol) under N_2 , and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 120 °C for 2 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)C_6H_5$ 3a (8.2 mg, 0.0087 mmol, 40%) was isolated.

Reaction between Ir(ttp)H 1c and Fluorobenzene 2a without the Addition of KOH. Fluorobenzene (0.8 mL, 500 equiv) was added to Ir(ttp)H (15.4 mg, 0.018 mmol), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (1:1), and a purple solid mixture of unknowns (4.3 mg, ca. 28%) was isolated. No aromatic CFA or CHA product was observed.

Reaction between lr(ttp)H 1c and Fluorobenzene 2a with the Addition of KOH. Fluorobenzene (0.9 mL, 500 equiv) was added to a mixture of Ir(ttp)H (17.2 mg, 0.020 mmol) and KOH (11.2 mg, 0.200 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 1 day. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of Ir(ttp)C₆H₅ **3a** (9.4 mg, 0.0100 mmol, 50%), Ir(ttp)(2-F-C₆H₄) **3b** (1.3 mg, 0.0014 mmol, 7%), Ir(ttp)(3-F-C₆H₄) **3d** (4.2 mg, 0.0044 mmol, 22%), and Ir(ttp)(4-F-C₆H₄) **3e** (1.1 mg, 0.0012 mmol, 6%) was isolated.

Reaction between $Ir(ttp)SiEt_3$ 1a and Benzene 2h with the Addition of KOH. Benzene (0.8 mL, 500 equiv) was added to a mixture of $Ir(ttp)SiEt_3$ (17.0 mg, 0.017 mmol) and KOH (9.8 mg, 0.170 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/ CH_2Cl_2 (2:1), and a purple solid of $Ir(ttp)C_6H_5$ 3a (1.1 mg, 0.0012 mmol, 7%) was isolated.

Reaction between Ir(ttp)(4-F–C₆H₄) 3e and Benzene 2h with the Addition of KOH. Benzene (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)(4-F–C₆H₄) (21.8 mg, 0.023 mmol) and KOH (12.9 mg, 0.230 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of Ir(ttp)C₆H₅ 3a (12.5 mg, 0.0133 mmol, 58%) and Ir(ttp)(4-F–C₆H₄) 3e (7.0 mg, 0.0073 mmol, 32%) was isolated.

Reaction between $Ir(ttp)(4-F-C_6H_4)$ 3e and Benzene- d_6 2h' with the Addition of 10 equiv of KOH at 200 °C in Solvent-Free Conditions. Benzene- d_6 (0.8 mL, 500 equiv) was added to a mixture of $Ir(ttp)(4-F-C_6H_4)$ (17.6 mg, 0.018 mmol) and KOH (10.3 mg, 0.180 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/ CH_2Cl_2 (2:1), and a purple solid mixture of $Ir(ttp)(C_6H_5)$ 3a (1.2 mg, 0.0013 mmol, 7%) and $Ir(ttp)(C_6D_5)$ 3a' (2.0 mg, 0.0021 mmol, 12%) was isolated. In accordance with the ¹H NMR of the crude reaction mixture, C_6H_3F 2a was observed in 16% calibrated with the iridium porphyrin species.

Reaction between $Ir(ttp)(4-F-C_6H_4)$ 3e and Benzene 2h without the Addition of KOH. Benzene (0.8 mL, 500 equiv) was added to $Ir(ttp)(4-F-C_6H_4)$ 3e (17.5 mg, 0.018 mmol), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid of $Ir(ttp)(4-F-C_6H_4)$ 3e (16.4 mg, 0.0171 mmol, 95%) was recovered.

Reaction between Ir(ttp)(4-F–C₆H₄) 3e with KOH in Benzene-*d*₆ **in a Sealed-NMR Tube.** Benzene-*d*₆ (0.5 mL) was added to a mixture of Ir(ttp)(4-F–C₆H₄) (10.5 mg, 0.0110 mmol) and KOH (6.2 mg, 0.1100 mmol, 10 equiv) in an NMR tube with a rotaflo stopper and degassed by the freeze–pump–thaw method (3 cycles). The mixture was frozen under liquid nitrogen and then flame-sealed under vacuum. The sealed-NMR tube was heated at 200 °C and monitored by ¹H NMR spectroscopy, and the yield of product was calibrated with the internal standard residual benzene in benzene-*d*₆. After 7 days, a new species of [Ir(ttp)(4-F–C₆H₄)OH][–] was proposed to be formed. ¹H NMR (C₆D₆, 400 MHz): δ –10.94 (s, 1 H), 1.35 (d, 2 H, *J* = 4.8 Hz), 2.36 (s, 12 H), 4.73 (dd, 2 H, ³J_{HF} = 8.8 Hz, *J* = 8.8 Hz), 7.06 (d, 4 H, *J* = 7.6 Hz), 7.27 (s, 8 H), 7.59 (d, 4 H, *J* = 6.8 Hz), 8.16 (s, 8 H). HRMS (FABMS): calcd for (C₅₄H₄₁FN₄IrO)⁺ *m/z* 973.2888; found *m/z* 973.292639.

Reaction between $Ir(ttp)(C_6H_5)$ 3a and Fluorobenzene 2a with the Addition of 10 Equivalents of KOH at 250 °C for Thirty Days in Solvent-Free Conditions. Fluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)(C_6H_5)$ (19.3 mg, 0.021 mmol) and KOH (12.1 mg, 0.220 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 250 °C for 30 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)C_6H_5$ 3a (2.9 mg, 0.0031 mmol, 15%), $Ir(ttp)(3-F-C_6H_3)$ 2d (9.9 mg, 0.0103 mmol, 50%) and $Ir(ttp)(4-F-C_6H_4)$ 3e (1.6 mg, 0.0017 mmol, 8%) was isolated.

Reaction between $Ir(ttp)(2-F-C_6H_4)$ 3b and Fluorobenzene 2a with the Addition of 10 Equivalents of KOH at 250 °C for Thirty Days in Solvent-Free Conditions. Fluorobenzene (1.1 mL, 500 equiv) was added to a mixture of $Ir(ttp)(2-F-C_6H_4)$ (21.9 mg, 0.023 mmol) and KOH (12.4 mg, 0.230 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 250 °C for 30 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)C_6H_5$ 3a (6.4 mg, 0.0068 mmol, 30%), $Ir(ttp)(3-F-C_6H_3)$ 2d (9.1 mg, 0.0095 mmol, 41%) and $Ir(ttp)(4-F-C_6H_4)$ 3e (1.8 mg, 0.0019 mmol, 8%) was isolated.

Reaction between $Ir(ttp)(3-F-C_6H_4)$ 3d and Fluorobenzene 2a with the Addition of 10 equiv of KOH at 250 °C for Thirty Days in Solvent-Free Conditions. Fluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)(3-F-C_6H_4)$ (20.1 mg, 0.021 mmol) and KOH (12.1 mg, 0.220 mmol, 10 equiv), and the mixture was degassed by the freeze-pump-thaw method (3 cycles). Then the mixture was heated at 250 °C for 30 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)C_6H_5$ 3a (0.7 mg, 0.0007 mmol, 3%), $Ir(ttp)(3-F-C_6H_3)$ 2d (16.4 mg, 0.0172 mmol, 78%) and $Ir(ttp)(4-F-C_6H_4)$ 3e (0.8 mg, 0.0008 mmol, 4%) was isolated.

Reaction between lr(ttp)(4-F–C₆H₄) 3e and Fluorobenzene 2a with the Addition of 10 Equivalents of KOH at 250 °C for Thirty Days in Solvent-Free Conditions. Fluorobenzene (1.0 mL, 500 equiv) was added to a mixture of $Ir(ttp)(4-F-C_6H_4)$ (20.8 mg, 0.022 mmol) and KOH (12.3 mg, 0.220 mmol, 10 equiv), and the mixture was degassed by the freeze–pump–thaw method (3 cycles). Then the mixture was heated at 250 °C for 30 days. The crude product was purified by column chromatography on alumina eluting with a mixture of hexane/CH₂Cl₂ (2:1), and a purple solid mixture of $Ir(ttp)C_6H_5$ 3a (1.8 mg, 0.0019 mmol, 9%), $Ir(ttp)(3-F-C_6H_3)$ 2d (9.8 mg, 0.0102 mmol, 47%), and $Ir(ttp)(4-F-C_6H_4)$ 3e (3.8 mg, 0.0040 mmol, 18%) was isolated.

ASSOCIATED CONTENT

S Supporting Information

Further experimental and computational supports to main manuscript, ¹H, ¹³C, and ¹⁹F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ksc@cuhk.edu.hk.

*E-mail: liujw@nsccsz.gov.cn.

Notes

The authors declare no competing financial interest.

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