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# Steric effects on acetate-assisted cyclometallation of meta-substituted $N$-phenyl and N -benzyl imidazolium salts at $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh}) \dagger$ 

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#### Abstract

meta-Substituted $N$-phenyl, $N^{\prime}$-methyl and $N$-benzyl, $N^{\prime}$-methyl imidazolium salts undergo acetateassisted cyclometallation to provide mixtures of ortho and para substituted cyclometallated complexes. The effect of the substituents on the isomer ratios is discussed; steric effects are more important in the 6 -membered rings derived from the $N$-benzyl imidazolium salts than 5 -membered rings from the N -phenyl salts. Comparisons are made to steric effects with some other common directing groups.


## Introduction

Carboxylate-assisted cyclometallation is now a very well-established reaction both stoichiometrically and in catalysis. ${ }^{1}$ Whilst there are now hundreds of examples in catalysis there are still relatively few publications that focus on a detailed understanding of the steric and electronic influences on the cyclometallation step. Acetate assisted cyclometallation at Cp* ${ }^{*}(M=I r, R h)$ centres proceeds from $\left[M(O A c)_{2} C p^{*}\right]$ which can be accessed by the reaction of $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}$ with NaOAc. ${ }^{2}$ Cyclometallation consists of a number of steps (i) coordination of the directing group, (ii) possible anion loss, (iii) proton transfer to form coordinated carboxylic acid, (iv) substitution of carboxylic acid either by halide if stoichiometric, or by another substrate in catalysis. Recently, we described steric and electronic effects on acetate assisted cyclometallation of phenyl pyrazoles at $\mathrm{Cp}^{*} \mathrm{M}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})^{3}$ and (arene)Ru centres. ${ }^{4}$ We showed that cyclometallation is kinetically favoured at electron rich phenyl groups but thermodynamically at electron poor ones. For meta substituted substrates steric factors were particularly important in controlling the ortho/para selectivity with para isomers being favoured thermodynamically for all substituents studied except fluorine. DFT studies surprisingly showed that initial proton transfer to form ortho isomers could actually be favoured over the para isomers, even for sterically bulky substituents. However, in those cases loss of coordinated acetic acid from the ortho isomer was significantly more endergonic leading to fast reverse proton transfer, which could only

[^0]be detected by H/D exchange. The only exceptions to this were meta-fluorinated phenyl rings which always favoured the orthofluorine substituted products; a preference that is well precedented in other systems and is known as the "ortho effect". ${ }^{5}$

Jones et al. compared the effect of different directing groups phenylimines L1-R and phenylpyridines L2-R with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})$ on the regioselectivity of cyclometallation of differently meta-substituted phenyls (Scheme 1). ${ }^{6}$ We have subsequently examined related reactions with phenylpyrazoles $\mathbf{L 3}-\mathbf{R}^{3}$ and re-examined some phenylpyridines. ${ }^{7}$ In making comparisons between different directing groups it is important to bear in mind that the ortho: para ratios of the products can vary over time. Therefore, ideally, final ratios corresponding to thermodynamic ratios should be compared. Jones et al. left their reactions a set amount of time and there is no mention of whether the ratios changed over time. It should be noted that reactions at $\mathrm{Cp}^{*}$ Ir are faster and less easily reversible than those at $\mathrm{Cp}{ }^{*} \mathrm{Rh}$ and those with electron

$\mathrm{R}=\mathrm{OMe}, \mathrm{Me}, \mathrm{F}, \mathrm{COOMe}, \mathrm{CF}_{3}, \mathrm{CN}$


Scheme 1 Meta-substituted phenylimines L1-R, ${ }^{6}$ phenylpyridines L2$\mathbf{R}^{6,7}$ and phenylpyrazoles $\mathrm{L} 3-\mathbf{R}^{3}{ }^{3}$ and their products from acetate assisted cyclometallation with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{\star}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})$. ${ }^{6}$
donating substituents equilibrate faster than those with electron withdrawing substituents. ${ }^{3,6,8}$

The ortho : para ratio of products for L1-3 are shown in Table 1. As can be seen for the larger substituents $\mathrm{CF}_{3}$ and Me the para isomer is heavily favoured. With less bulky substituents ( $\mathrm{R}=\mathrm{OMe}$ ) two isomers were formed but the para-isomer was still preferred. However, for the F-substituted ligands the ortho isomer was favoured in all cases. Jones et al. suggested that the selectivity of meta-substituted phenylpyridines L2-R was slightly less than with the imines because the phenyl imines are more bulky than the corresponding pyridines. However, this seems to be mainly based on the selectivity with $\mathbf{L} 2-\mathbf{C F}_{3}$, results which we were unable to reproduce. In our study $\mathbf{L} 2-\mathbf{C F}_{3}$ gave only the para isomer for both metals.

All the ligands mentioned above cyclometallate to form five membered rings. Formation of six-membered rings by acetate assisted cyclometallation is known, though it is less facile than for five-membered rings. For example, cyclometallation of 2-phenylpyridine with $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}$ is complete within 4 hours, ${ }^{9}$ whilst the corresponding reaction of 2-benzylpyridine takes 20 hours. ${ }^{10}$ In addition, 2-phenylpyridines react with both Ir and $\mathrm{Rh},{ }^{6,9}$ whilst 2-benzylpyridine was only shown to give a complex with Ir and not Rh. ${ }^{6}$

Both five and six-membered cyclometallated ring complexes with NHCs are well known ${ }^{11}$ however in nearly all cases the phenyl that is activated has a para-substituent so only one product can be formed with the substituent meta to the metal. Here we examine acetate assisted cyclometallation of meta-substituted $N$-phenyl and $N$-benzyl imidazolium salts to consider the effect of directing group and ring size on steric effects on the cyclometallation.

## Results and discussion

To examine NHCs as donor ligands we studied cyclometallation of meta-substituted $N$-phenyl, $N^{\prime}$-methyl imidazolium salts L4-R $\left(\mathrm{R}=\mathrm{OMe}, \mathrm{F}, \mathrm{CF}_{3}, \mathrm{CN}\right)$ which were prepared as shown in Scheme 2 in high yields ( $72-98 \%$ ). L4-OMe, L4-F and L4-CN are new compounds, whilst $\mathbf{L 4}-\mathbf{C F}_{3}$ is known as the iodide salt. ${ }^{12}$

The reactions of $\mathbf{L 4}-\mathrm{R}$ with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})$ were carried out in the presence of NaOAc at $75{ }^{\circ} \mathrm{C}$ in dichloroethane; however very low conversions were observed after


Scheme 2 Preparation and NMR labelling scheme of meta-substituted $N$-phenyl, $N^{\prime}$-methyl limidazolium salts L4-R.
heating overnight. ${ }^{13}$ The reactions were repeated in the presence of $\mathrm{Et}_{4} \mathrm{NCl}^{14}$ and proceeded slowly even at room temperature and gave high conversions (Scheme 3) and the products $\mathbf{4 a} / \mathbf{b}-\mathrm{R}\left(\mathrm{R}=\mathrm{OMe}, \mathrm{CN}, \mathrm{CF}_{3}, \mathrm{~F}\right)$ were fully characterised.

Each isomer has a characteristic pattern in the ${ }^{1} \mathrm{H}$ NMR spectrum, for the para isomer $\mathrm{H}^{4}$ is a very narrow doublet and $\mathrm{H}^{2}$ shows an noe to the $\mathrm{Cp}^{*}$ signal. The reactions were repeated and monitored at room temperature ( $c a .20 \%$ conversion) and upon heating ( $50^{\circ} \mathrm{C}$ overnight) to further investigate if the ratios change and so whether selectivity is kinetic or thermodynamic (see below).

All the reactions gave a mixture of two isomers and the ratios are shown in Table 2. In no case was an intermediate non-cyclometallated complex observed. This is consistent with activation of the imidazolium CH bond being relatively slow and the cyclometallation of the phenyl being much faster. ${ }^{15}$


Scheme 3 Reactions of L4-R with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})$ and NMR labelling scheme.

Table 1 Ortho : para ratios of acetate-assisted cyclometallation of meta-substituted ligands $\mathrm{L} 1-\mathrm{R}^{6}{ }^{6} \mathrm{~L} 2-\mathrm{R}^{6,7}$ and $\mathrm{L} 3-\mathrm{R}^{3}$

|  | L1-R |  | L2-R |  | L3-R |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| R | Ir , | Rh | Ir | Rh | Ir | Rh |
| OMe | 1:1.7 | 1:1.7 | 1:2.5 ${ }^{\text {a }}$ | 1:3.0 ${ }^{\text {a }}$ | 1:1.4 | 1:3.9 |
| Me | para only | para only | para only | para only ${ }^{\text {b }}$ | 1:10 | para only |
| $\mathrm{CF}_{3}$ | para only | para only | para only ${ }^{\text {c }}$ | para only ${ }^{\text {c }}$ | para only | para only |
| F | 2.3 : 1 | 8.5 : 1 | 3.4 : 1 | 11:1 | 40:1 | 44:1 |

${ }^{a}$ Jones reported ortho : para ratios of 1:1.1 and 1:2.5 for Ir and Rh respectively but we found these changed with further heating. ${ }^{b}$ Jones reported a small amounts of a second species presumed to be the ortho isomer, ${ }^{6}$ however the selectivity with Rh is usually higher than with Ir hence it is likely that the minor species is a very small amount of an impurity. ${ }^{c}$ Jones reported ortho : para ratios of $1: 6.4$ and $1: 8.4$ for $\operatorname{Ir}$ and Rh respectively. However, we found no evidence for ortho isomers in the ${ }^{19} \mathrm{~F}$ or ${ }^{1} \mathrm{H}$ NMR spectra.

Table 2 Ortho: para ratios of acetate-assisted cyclometallation of meta-Substituted ligands L4-R in DCM/MeOH

| Entry | R | Ir |  | Rh |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
|  |  | r.t. | $50^{\circ} \mathrm{C}$ | r.t. | $50^{\circ} \mathrm{C}$ |
| 1 | $\mathrm{OMe}^{a}$ | $1: 1.5^{a}$ | $1: 3.0^{a}$ | $1: 3.0$ | $1: 3.0$ |
| 2 | CN | $1: 1.3$ | $1: 2.2$ | $1.2: 1$ | $1: 2.0$ |
| 3 | $\mathrm{CF}_{3}$ | $1: 3^{b}$ | $1:>20^{b}$ | $1: 6^{b}$ | $1:>40^{b}$ |
| 4 | F | $2.2: 1$ | $2.2: 1$ | $6.0: 1$ | $10: 1$ |

${ }^{a}$ In DCE at $50{ }^{\circ} \mathrm{C}$ after 1 hour and then after 6 hours. ${ }^{b}$ Due to the small amount of minor species present it is not possible to unambiguously identify it as the ortho isomer.

The reactions of $\mathbf{L 4}-\mathrm{R}\left(\mathrm{R}=\mathrm{OMe}, \mathrm{CN}, \mathrm{CF}_{3}\right)$ with both Ir and Rh showed that a mixture of the ortho and para-isomers was formed initially with increasing fraction of the para-isomer after heating (entries 1-3 Table 2).

This indicates that the para-isomer is thermodynamically favoured, whilst kinetically there is no clear preference for either the para or the ortho-isomers, except for $\mathrm{R}=\mathrm{CF}_{3}$ which favours the para isomer kinetically and thermodynamically. For the reactions of $\mathbf{L 4}-\mathbf{F}$ both Ir and Rh favour the ortho isomer and with Rh the selectivity increases with heating indicating that the ortho isomer is favoured thermodynamically. This preference for ortho fluorine has been observed previously. ${ }^{3,5,6}$

Overall, the steric bulk mainly controls the regioselectivities in agreement with the results observed with phenylimines, ${ }^{6}$ phenylpyridines ${ }^{6,7}$ and phenylpyrazoles. ${ }^{3}$ However, in those cases none of the ortho-isomer was observed for the reactions with $\mathrm{R}=\mathrm{CF}_{3}$, whilst it was present in substantial quantities for the reactions of $\mathbf{L 4}-\mathbf{C F}_{3}$ suggesting that there is less steric crowding at the metal centre in $\mathbf{4 a} / \mathbf{b}-\mathbf{R}$ compared to phenylimine, ${ }^{6}$ phenylpyridine, ${ }^{6,7}$ and phenylpyrazole complexes. ${ }^{3}$

To examine the effect of ring size on regioselectivity we examined cyclometallation of $N$-benzyl, $N^{\prime}$-methyl imidazolium salts L5-R ( $\mathrm{R}=\mathrm{OMe}, \mathrm{CF}_{3}, \mathrm{~F}$ ). These were prepared by reaction of N -methyl imidazole with an excess of appropriately metasubstituted benzyl chloride for 1-2 days. All three salts L5-R (R $=\mathrm{OMe}, \mathrm{CF}_{3}, \mathrm{~F}$ ) were obtained in moderate to good yields $(55-87 \%)$ and have been reported previously. ${ }^{16}$

The cyclometallated complexes $\mathbf{6 a} / \mathbf{b}-\mathbf{R}$ were prepared in a stepwise manner, transmetallation to form NHC bound complexes $\mathbf{5 a} / \mathbf{b}-\mathbf{R}$ followed by cyclometallation (Scheme 4). ${ }^{11 a}$ Thus, $\mathbf{L 5}-\mathrm{R}\left(\mathrm{R}=\mathrm{OMe}, \mathrm{CF}_{3}, \mathrm{~F}\right)$ was stirred with $\mathrm{Ag}_{2} \mathrm{O}$ in the dark for 1 hour to give a silver NHC complex. The reactions were filtered through Celite to remove the excess of Ag salts, and the resulting filtrate was reacted with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})$ (Scheme 4) which after work up gave the new complexes $\mathbf{5 a} / \mathbf{b}-\mathrm{R}\left(\mathrm{R}=\mathrm{OMe}, \mathrm{CF}_{3}, \mathrm{~F}\right)$, in moderate to excellent yields (67-92\%).

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{5 a} / \mathbf{b}-\mathbf{R}$ show two mutually coupled doublets at $\delta 5-6.5$ due to the benzylic protons showing the chiral nature of the complexes with no mirror plane. Complex 5a-OMe gave crystals suitable for X-ray diffraction and the structure is shown in Fig. 1. The orientation of the NHC ligand confirms that the benzyl protons are inequivalent and that the benzyl group has not cyclometallated.

The cyclometallated complexes $\mathbf{6 a} / \mathbf{b}-\mathbf{R}$ were prepared in good to excellent yields (68-96\%) by reaction of $5 \mathrm{a} / \mathrm{b}-\mathrm{R}(\mathrm{R}=$ $\mathrm{OMe}, \mathrm{CF}_{3}, \mathrm{~F}$ ) with NaOAc in $\mathrm{DCM}: \mathrm{MeOH}(4: 1)$ at room temperature (Scheme 4). The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{6 a / b}$-R show the mutually coupled benzylic proton doublets are closer together (between $\delta 4.5$ and 5.0) than in complexes $5 \mathbf{a} / \mathbf{b}-\mathbf{R}$. For both the OMe and $\mathrm{CF}_{3}$ substituted complexes only the para-isomer was


Fig. 1 The molecular structures of $5 \mathrm{a}-\mathrm{OMe}$ with $50 \%$ ellipsoids. H -atoms omitted for clarity. Selected bond distances $\AA \AA$; $\mathrm{Ir}-\mathrm{C}(1), 2.047$ (9), $\mathrm{Ir}-\mathrm{Cl}(1)$ 2.417(2), $\mathrm{Ir}-\mathrm{Cl}(2)$ 2.409(3).


Scheme 4 Synthesis and labelling of 6a/b-R.

Table 3 Ortho : para ratios of acetate-assisted cyclometallation of complexes $5 \mathrm{a} / \mathrm{b}-\mathrm{R}$

observed in each case; for the F-substituted products 6a/b-F a mixture of both isomers (approximately $10: 1$ ) was formed favouring the ortho isomer in each case. The reactions were repeated in $\mathrm{CDCl}_{3}$, in which they were considerably slower, to measure the initial product ratios and see if these changed over time and with heating (Table 3).

For the reactions of $\mathbf{5 a} / \mathbf{b}-\mathbf{O M e}$ (entry 1 Table 3) at low conversions ( $<20 \%$ ), the ortho and para-isomers 6a/b-OMe were observed in $1: 1$ ratio. As the time and conversion increased the ratio between the two isomers changed significantly in favour of the para-isomer for both Ir (ortho : para 1:10) and Rh which showed only traces of the ortho-isomer. These results indicate that the para-isomer is favoured thermodynamically in this case, whilst there is almost no kinetic preference for either the ortho or para isomer.

This is consistent with the isolation of only the paraisomers 6a/b-OMe from the preparative reactions in DCM : $\mathrm{MeOH}(4: 1)$. In the case of $\mathbf{5 a} / \mathbf{b}-\mathbf{C F}_{\mathbf{3}}$ all the ${ }^{1} \mathrm{H}$ NMR spectra irrespective of conversion only showed the para-isomer (as in DCM: MeOH). Based on our related work with phenylpyrazoles it is likely that formation of the ortho-isomer is significantly endergonic so is not observed. The cyclometallations of $\mathbf{5 a} / \mathbf{b}-\mathbf{F}$ led to the formation of $\mathbf{6 a / b} \mathbf{- F}$ in $10: 1$ ortho : para ratio for both Ir and Rh, (entries 5 and 6) irrespective of percentage conversion. Approximately the same ratios were formed in DCM : MeOH (4:1) after heating for $50{ }^{\circ} \mathrm{C}$ for two days. As the ratios did not change it is likely that the kinetic and thermodynamic selectivity are similar.

The reversibility of the cyclometallation of the benzyl complexes was probed by deuteration studies as in similar
studies. ${ }^{3-4,7,8 b}$ Thus, $\mathbf{5 a} / \mathbf{b}-\mathbf{O M e}$, and $\mathbf{5 b}-\mathbf{C F}_{3}$ were reacted with NaOAc in $\mathrm{CD}_{3} \mathrm{OD}$ and the percentage D -incorporation was determined by integration and the results are shown in Scheme 5. ${ }^{17}$ For 5a/b-OMe, a high d-incorporation ( $>80 \%$ ) was observed in the para isomer products, para-6a-OMe and para$\mathbf{6 b}-\mathbf{O M e}$. The formation of the deuterated products shows that formation of the ortho-isomer had occurred but was easily reversible, ultimately leading to preferential formation of the thermodynamically favoured para-isomer (a more detailed scheme showing how D incorporation occurs is in the SI). This is consistent with entries 1 and 2 in Table 3 discussed above which show that the ortho : para ratio changes over time favouring the para isomer. Note, for Rh complex 5b-OMe the reaction only reached about $55 \%$ conversion overnight and the starting complex was deuterated at sites 2 and 5 showing that formation of both isomers is reversible under these conditions. No d-incorporation was detected for the cyclometallation of $\mathbf{5 b}-\mathbf{C F}_{3}$. This result shows that either the formation of the ortho-isomer has a significantly higher activation barrier than that of the para-isomer so the para isomer is kinetically preferred and/or formation of the ortho-isomer is so easily reversible that there is no time for H/D-exchange. In addition, the lack of observation of deuterated starting material means that formation of para- $\mathbf{6 b}-\mathbf{C F}_{3}$ is exergonic so not easily reversible.

Comparing the regioselectivity of the phenyl and benzyl complexes the phenyl-NHC complexes $\mathbf{4 a} / \mathbf{b}-\mathbf{R}$ even for the largest substituent ( $\mathrm{R}=\mathrm{CF}_{3}$ ) show some ortho-isomer ( 25 and $14 \%$ for Ir and Rh respectively) and about $30 \%$ ortho-isomer was seen for $\mathrm{R}=\mathrm{OMe}$ with both metals after heating. Whereas, with the benzyl complexes $\mathbf{6 a} / \mathbf{b}-\mathbf{R}$ for $\mathrm{R}=\mathrm{CF}_{3}$ only the para


Scheme 5 Deuterium incorporation experiments with $5 a / b-O M e$ and $5 b-\mathrm{CF}_{3}$.


Fig. 2 Yaw distortion of chelating NHC complexes.
isomer is observed and for $\mathrm{R}=\mathrm{OMe}$ less than $10 \%$ of the ortho isomer is observed after heating. These results suggest a more sterically hindered metal centre for the six-membered rings leading to less of the ortho isomer. Steric distortion of bidentate NHC containing ligands has been analysed previously in terms of a "yaw"-distortion (see Fig. 2). ${ }^{18}$ A number of structures of Ir complexes have been reported for phenyl complexes ( $n=0$ ) the yaw angle varies from 9.2 to $10.2^{\circ}$ whilst the benzyl complexes $(n=1)$ the yaw angles are much less at 2.1 to $3.4^{\circ} .{ }^{18 b}$ Interestingly the lower distortion in NHC coordination in the benzyl complexes leads the ortho H to be closer to the metal M $\cdots \mathrm{H}$ distances 3.02 to $3.07 \AA$ for benzyl complexes compared to 3.21 to $3.25 \AA$ for the phenyl complexes. There are much smaller differences between 5 -membered rings with different directing groups. The observation of a second species with $\mathbf{L 4}-\mathbf{C F}_{3}$ with an NHC directing group suggests the steric hindrance is slightly less in this case than with L1-3 however it should be borne in mind that the NHC has an NMe substituent on the non-cyclometallated side, compared to a CH for the other ligands, and this may impact the overall geometry at the metal.

## Conclusions

Steric effects on C-H activation were assessed using meta-substituted $N$-phenyl and $N$-benzylimidazolium salts L4-R and L5$\mathbf{R}$ respectively. $N$-Phenyl limidazolium salts L4-R ( $\mathrm{R}=\mathrm{OMe}$, $\mathrm{CN}, \mathrm{CF}_{3}, \mathrm{~F}$ ) underwent cyclometallation easily in the presence of $\mathrm{NaOAc}^{14}$ and no intermediate non-cyclometallated NHC bound complexes were observed. The para-isomers were favoured thermodynamically over the ortho with both metals for $\mathrm{R}=\mathrm{OMe}, \mathrm{CN}$, and particularly for the more bulky $\mathrm{CF}_{3}$, whilst at shorter reaction times the selectivity was less. For L4F cyclometallation at both metals favoured the ortho isomer as has been observed in other systems.

Cyclometallation to form 6-membered rings is less favourable than 5 -membered ones hence for $N$-benzylimidazolium salts L5-R ( $\mathbf{R}=\mathbf{O M e}, \mathbf{C F} 3, \mathbf{F}$ ) intermediate non-cyclometallated NHC bound complexes 5a/b-OMe could be prepared by transmetallation and the cyclometallation studied as a separate step. Treatment of 5a/b-OMe with NaOAc resulted in formation of the ortho and para isomers of $\mathbf{6 a} / \mathbf{b}-\mathbf{O M e}$ initially ( $<20 \%$ conversion) in equal quantities. At high conversions the proportion of the ortho-isomers diminished to $<10 \%$ for Ir and none for Rh indicating a thermodynamic preference for the
para-isomer. For cyclometallation of $\mathbf{5 a} / \mathbf{b}-\mathbf{C F}_{3}$ none of the ortho-isomer could be detected even at low conversions likely due to the bulkier $\mathrm{CF}_{3}$ group. Therefore, steric effects control regioselectivity with the para-isomer being the major one for cyclometallation of $\mathbf{5 a} / \mathbf{b}-\mathbf{R}\left(\mathrm{R}=\mathrm{OMe}, \mathrm{CF}_{3}\right)$. The selectivity for the para-isomer observed in six membered ring complexes $\mathbf{6 a} / \mathbf{b}-\mathbf{R}$ is larger compared to the formation of the five-membered ring complexes $\mathbf{4 a} / \mathbf{b}-\mathbf{R}$ consistent with a more sterically hindered metal centre for the six-membered rings.

## Experimental

meta-Substituted N -phenylimidazoles were prepared according to a modified literature procedure. ${ }^{19}$ meta-Substituted arylhalide (1 eq.), imidazole ( 1.5 eq.), $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2 eq.), $\mathrm{CuO}_{2}$ ( $10 \mathrm{~mol} \%$ ) and MeCN or DMF ( $5-10 \mathrm{~mL}$ ) were added to a Schlenk flask, sealed with a screw-cap, placed under $\mathrm{N}_{2}$ atmosphere, partially evacuated, transferred to an oil bath and stirred at $100-120{ }^{\circ} \mathrm{C}$ for $1-5$ days behind a blast shield. Afterwards the reaction mixture was cooled to rt, followed by filtration through Celite. The solvent was removed by rotary evaporation and pure phenylimidazole was obtained by column chromatography. Data were in agreement with the literature. ${ }^{20}$

## General procedure for preparation of meta-substituted phenylimidazolium salts L4-R

A nitrogen flushed Schlenk flask was charged with magnetic stirrer, meta-substituted phenylimidazole (1 eq.), dry DCM ( $4-6 \mathrm{~mL}$ ), methyl trifluoromethanesulfonate ( 1.1 eq. ), capped and stirred at rt for $2-4 \mathrm{~h}$. The solvent was removed by rotary evaporation and the product was either precipitated from $\mathrm{DCM} / \mathrm{Et}_{2} \mathrm{O}$ mixture or washed with $\mathrm{Et}_{2} \mathrm{O}$ to yield imidazolium salt L4-R.

Synthesis of L4-OMe. Following the general procedure, a mixture of 1-(3-methoxyphenyl)- $1 H$-imidazole (174 mg, $1.002 \mathrm{mmol})$, dry DCM ( 4 mL ), methyl trifluoromethanesulfonate ( $0.125 \mathrm{~mL}, 181 \mathrm{mg}, 1.105 \mathrm{mmol}$ ), capped was stirred at rt for 4 h . The formed oil was washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ to yield $\mathbf{L 4}$-OMe as a colourless oil ( $244 \mathrm{mg}, 72 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta$ 3.88 (s, 3H, OMe), 3.97 (s, 3H, Me), 7.14 (m, 1H, H), 7.19-7.24 (m, $\left.2 \mathrm{H}, H^{1}, H^{4}\right), 7.51\left(\mathrm{t}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 7.57(\mathrm{t}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{5 \mathrm{~b}}\right), 7.80\left(\mathrm{t}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 9.23\left(\mathrm{~s}, 1 \mathrm{H}, H^{6}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $126 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 37.3(\mathrm{Me}), 56.8(\mathrm{OMe}), 109.0\left(C^{4}\right), 115.0\left(C^{1}\right)$, $116.7\left(C^{3}\right), 121.8(\mathrm{~d}, J=320.2 \mathrm{~Hz}$, OTf $), 122.3\left(C^{5 \mathrm{a}}\right), 125.3\left(C^{5 \mathrm{~b}}\right)$, $132.2\left(C^{2}\right), 136.6\left(C^{6}\right), 136.8,161.8 .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz , $\mathrm{CD}_{3} \mathrm{CN}$ ): $\delta-79.3$ (OTf). ESIMS: $m / z 189[\mathrm{M}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{11} \mathrm{H}_{13} \mathrm{~N}_{2} \mathrm{O}[\mathrm{M}]^{+}$189.1028, found 189.1028.

Synthesis of L4-CN. Following the general procedure, a mixture of 3 -(1H-imidazol-1-yl)benzonitrile $(253 \mathrm{mg}$, $1.497 \mathrm{mmol})$, dry DCM ( 6 mL ), methyl trifluoromethanesulfonate ( $0.19 \mathrm{~mL}, 278 \mathrm{mg}, 1.680 \mathrm{mmol}$ ) was stirred at rt for 2.5 h . The product was precipitated from $\mathrm{DCM} / \mathrm{Et}_{2} \mathrm{O}$ to yield $\mathbf{L 4} \mathbf{- C N}$ as a white solid ( $412 \mathrm{mg}, 1.237 \mathrm{mmol}, 83 \%$ ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 4.08(\mathrm{~s}, 3 \mathrm{H}, M e), 7.84\left(\mathrm{~m}, 2 \mathrm{H}, H^{4}, H^{5 \mathrm{~b}}\right)$,
7.97 (dt, $\left.J=7.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 8.05(\mathrm{ddd}, J=8.3,2.4,1.1 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{3}\right), 8.12\left(\mathrm{t}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 8.20\left(\mathrm{t}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right)$ $9.51\left(\mathrm{~s}, 1 \mathrm{H}, H^{6}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(101 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 37.2(\mathrm{Me})$, $115.6,118.3,121.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=318.7 \mathrm{~Hz}\right.$, OTf $), 123.0\left(C^{5 \mathrm{a}}\right), 126.1$ $\left(C^{5 \mathrm{~b}}\right), 127.3\left(C^{4}\right), 128.2\left(C^{3}\right), 132.9\left(C^{2}\right), 134.9\left(C^{1}\right), 137.2,137.8$ $\left(C^{6}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta-80.0$ (OTf). ESIMS: $m / z 227[\mathrm{M}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{~N}_{3}[\mathrm{M}]^{+}$184.0875, found 184.0883 .

Synthesis of $\mathbf{L 4}-\mathbf{C F}_{3}$. Following the general procedure, a mixture of 1-(3-trifluoromethylphenyl)-1H-imidazole $(213 \mathrm{mg}$, $1.007 \mathrm{mmol})$, dry DCM ( 4 mL ), methyl trifluoromethanesulfonate $(0.130 \mathrm{~mL}, 189 \mathrm{mg}, 1.150 \mathrm{mmol})$ was stirred at rt for 3 h . The product was precipitated from a $\mathrm{DCM} / \mathrm{Et}_{2} \mathrm{O}$ to yield $\mathbf{L 4}-\mathbf{C F}_{3}$ as a white solid (306 mg, 81\%). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta$ $4.06(\mathrm{~s}, 3 \mathrm{H}, M e), 7.81\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.88\left(\mathrm{~m}, 1 \mathrm{H}, H^{2}\right)$, $7.94\left(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 8.01\left(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 8.11(\mathrm{~s}$, $\left.1 \mathrm{H}, H^{4}\right), 8.15\left(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 9.55\left(\mathrm{~s}, 1 \mathrm{H}, H^{6}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (126 MHz, $\left.\mathrm{CD}_{3} \mathrm{OD}\right): \delta 37.1(\mathrm{Me}), 120.9\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.2 \mathrm{~Hz}\right.$, $\left.C^{4}\right), 121.8\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=319.2 \mathrm{~Hz}\right.$, OTf $), 123.1\left(C^{5 \mathrm{a}}\right), 124.8\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}\right.$ $\left.=272.0 \mathrm{~Hz}, C \mathrm{~F}_{3}\right), 126.0\left(C^{5 \mathrm{~b}}\right), 127.5\left(C^{1}\right), 128.1\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.0\right.$ $\left.\mathrm{Hz}, C^{3}\right), 132.8\left(C^{2}\right) 133.8\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=33.5 \mathrm{~Hz}, \mathrm{C}_{\mathrm{CF}}^{3}\right.$ ), $137.2(\mathrm{q}$, $\left.{ }^{4} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}\right), 137.9\left(C^{6}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}\left(376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta$ -80.1 (OTf), -64.3 (CF $F_{3}$ ). ESIMS: m/z 227 [M] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{~F}_{3}[\mathrm{M}]^{+}$227.0796, found 227.0796.

Synthesis of L4-F. Following the general procedure, a mixture of 1-(3-fluorophenyl)-1 H -imidazole $(166 \mathrm{mg}$, $1.022 \mathrm{mmol})$, dry DCM ( 4 mL ), methyl trifluoromethanesulfonate $(0.130 \mathrm{~mL}, 189 \mathrm{mg}, 1.150 \mathrm{mmol})$ was stirred at rt for 2.5 h . The formed oil was washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ to yield L4-F as a colourless oil (325 mg, 98\%). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CD}_{3} \mathrm{OD}\right): \delta 4.04(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 7.34$ (tdd, $J=8.4,8.4,2.4,1.0 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{3}\right), 7.57\left(\mathrm{~m}, 2 \mathrm{H}, H^{1}, H^{4}\right), 7.65\left(\mathrm{td}, J=8.3,5.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right)$, $7.76\left(\mathrm{t}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 8.05\left(\mathrm{t}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 9.47(\mathrm{~s}$, $\left.1 \mathrm{H}, H^{6}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (126 MHz, $\left.\mathrm{CD}_{3} \mathrm{OD}\right): \delta 37.1$ (Me), 111.2 $\left(\mathrm{d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=27.1 \mathrm{~Hz}, C^{4}\right), 118.2\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=21.1 \mathrm{~Hz}, C^{3}\right), 119.3(\mathrm{~d}$, $\left.{ }^{4} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{1}\right), 121.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=318.2 \mathrm{~Hz}\right.$, OTf $), 122.8\left(C^{5 \mathrm{a}}\right)$, $125.9\left(C^{5 \mathrm{~b}}\right), 133.4\left(\mathrm{~d},{ }^{3} J=9.0 \mathrm{~Hz}, C^{2}\right), 137.5\left(C^{6}\right), 137.6\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}\right.$ $=10.0 \mathrm{~Hz}), 164.5\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=249.0 \mathrm{~Hz}, C-\mathrm{F}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ (376 MHz, $\left.\mathrm{CD}_{3} \mathrm{OD}\right): \delta-111.0(F),-80.0$ (OTf). ESIMS: $m / z 177$ $[\mathrm{M}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{~F}[\mathrm{M}]^{+} 177.0828$, found 177.0832

## General procedure for cyclometallation of meta-substituted phenylimidazolium salts L4-R with $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathbf{M}=\mathrm{Ir}, \mathbf{R h})$ in DCE

$\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})(1 \mathrm{eq}),. \mathrm{NaOAc}(8 \mathrm{eq}$.$) were placed in$ an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under $\mathrm{N}_{2}$ atmosphere. DCE $(2 \mathrm{~mL})$ was added and mixture stirred for another 15 min . The appropriate imidazolium salt $\mathbf{L 4}-\mathbf{R}$ ( 2.1 eq.) and $\mathrm{Et}_{4} \mathrm{NCl}$ (2 eq.) was added, and the Schlenk flask transferred to a preheated oil bath and stirred at $50{ }^{\circ} \mathrm{C}$ for $1-2 \mathrm{~h}$, then at $70^{\circ} \mathrm{C}$ for $1-6 \mathrm{~h}$. The reaction mixture was cooled to rt with continuous stirring, diluted with DCM ( 10 mL ), filtered through Celite and solvent removed by rotary evaporation. The pure products were isolated by several precipitations from $D C M /$ hexane.

General procedure for cyclometallation of meta-substituted phenylimidazolium salts L4-R with $\left[\mathrm{MCl}_{2} \mathbf{C p}^{*}\right]_{2}(\mathbf{M}=\mathbf{I r}, \mathbf{R h})$ in DCM : MeOH
$\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})(1 \mathrm{eq} ., 0.0251 \mathrm{mmol}), \mathrm{NaOAc}(8 \mathrm{eq}$. were placed in an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under $\mathrm{N}_{2}$ atmosphere. Dry DCM ( 1.6 mL ) and $\mathrm{MeOH}(0.4 \mathrm{~mL})$ were added and the mixture stirred for another 15 min . The appropriate imidazolium salt ( 2.1 eq.) and $\mathrm{Et}_{4} \mathrm{NCl}$ (2 eq.) was added and the mixture stirred at rt overnight and then heated to $50^{\circ} \mathrm{C}$ overnight. The reactions were monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy by comparing the relative integrations of the appropriate signals $\left(\mathrm{H}^{3}\right.$ of the ortho-isomers compared to the $\mathrm{H}^{3}$ of the para-isomers).

Synthesis of $4 \mathrm{a}-\mathbf{O M e}$. Following the general procedure, a mixture of $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(20 \mathrm{mg}, 0.0251 \mathrm{mmol}), \mathrm{NaOAc}(17 \mathrm{mg}$, 0.207 mmol ), L4-OMe ( $18 \mathrm{mg}, 0.0533 \mathrm{mmol}$ ), $\mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.053 \mathrm{mmol})$, in DCE ( 2 mL ) was heated to $50^{\circ} \mathrm{C}$ for 2 h , then heated further at $70^{\circ} \mathrm{C}$ for 6 h . The product was purified by crystallisation from DCM/hexane to yield 4a-OMe (ortho: para ratio $1: 2.2$ ) as a yellow powder ( $29.9 \mathrm{mg}, 94 \%$ ). ortho-4a-OMe. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.85\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.82(\mathrm{~s}, 3 \mathrm{H}$, OMe), 3.97 (s, 3H, Me), $6.54\left(\mathrm{dd}, J=7.9,1.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 6.83$ (dd, $\left.J=7.7,1.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.93\left(\mathrm{t}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 6.95(\mathrm{~d}$, $\left.J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.31\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right)$. ESIMS: $m / z$ $513[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}]^{+}$ 515.1674, found 515.1675. para-4a-OMe. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 1.79\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.80(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 3.98(\mathrm{~s}, 3 \mathrm{H}$, $M e), 6.65\left(\mathrm{dd}, J=8.2,2.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 6.76(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{4}\right), 6.97\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.29\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right)$, $7.60\left(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $9.74\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.0(\mathrm{Me}), 55.5(\mathrm{OMe}), 90.6\left(C_{5} \mathrm{Me}_{5}\right), 98.6\left(C^{4}\right)$, $110.8\left(C^{3}\right), 114.8\left(C^{5 \mathrm{a}}\right), 121.3\left(C^{5 \mathrm{~b}}\right), 131.2,136.1\left(C^{2}\right), 146.9\left(C^{1}\right)$, 156.3, $166.6\left(C^{6}\right)$. ESIMS: $m / z 513[M-C l]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}]^{+} 515.1674$, found 515.1675.

Synthesis of $\mathbf{4 b} \mathbf{b} \mathbf{O M e}$. Following the general procedure, a mixture of $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(15 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(17 \mathrm{mg}$, 0.207 mmol ), L4-OMe ( $18 \mathrm{mg}, 0.053 \mathrm{mmol}$ ), $\mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.054 \mathrm{mmol})$, in DCE ( 2 mL ) was stirred at $50^{\circ} \mathrm{C}$ for 1 h , then at $70{ }^{\circ} \mathrm{C}$ for 6 h . The product was purified by precipitation from DCM/hexane to yield 4b-OMe (ortho: para 1:1.9 ratio) as an orange-yellow powder ( $14 \mathrm{mg}, 61 \%$ ). ortho-4b-OMe. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.68\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.83(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{OMe}), 3.97(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 6.58\left(\mathrm{dd}, J=8.0,0.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 6.78$ $\left(\mathrm{dd}, J=7.7,1.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.98\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 6.99$ $\left(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 7.37\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.9\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.0(\mathrm{Me}), 56.3(\mathrm{OMe})$, $97.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=5.2 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 104.9\left(C^{1}\right), 108.9\left(C^{3}\right), 115.9$ $\left(C^{5 \mathrm{a}}\right), 121.9\left(C^{5 \mathrm{~b}}\right), 124.0\left(C^{2}\right), 146.1,145.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=42.1 \mathrm{~Hz}\right.$, $\left.C^{4}\right)$, 156.7, $184.2\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=55.5 \mathrm{~Hz}, C^{6}\right)$. ESIMS: $m / z 425[\mathrm{M}-$ $\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+}$ 425.1100, found 425.1100. para-4b-OMe. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 1.70\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.78(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OMe}), 4.01(\mathrm{~s}, 3 \mathrm{H}$, $M e), 6.66\left(\mathrm{dd}, J=8.3,2.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 6.71(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{4}\right), 6.98\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.35\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right)$,
$7.63\left(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $9.9\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.0(\mathrm{Me}), 55.5(\mathrm{OMe}), 97.2\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=5.0 \mathrm{~Hz}\right.$, $C_{5} \mathrm{Me}_{5}$ ), $99.0\left(C^{4}\right), 110.5\left(C^{3}\right), 115.1\left(C^{5 \mathrm{a}}\right), 122.2\left(C^{5 \mathrm{~b}}\right), 137.2$ $\left(C^{2}\right), 146.1,146.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=35.7 \mathrm{~Hz}, C^{1}\right), 165.0,184.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{Rh}}\right.$ $=55.5 \mathrm{~Hz}, C^{6}$ ). ESIMS: $m / z 425$ [M-Cl] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+} 425.1100$, found 425.1100 .

Synthesis of $\mathbf{4 a - C N}$. Following the general procedure, a mixture of $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(20 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(16 \mathrm{mg}$, $0.196 \mathrm{mmol})$, L4-CN ( $18 \mathrm{mg}, 0.0526 \mathrm{mmol}$ ), $\mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.053 \mathrm{mmol})$, in DCE ( 2 mL ) was stirred at $50^{\circ} \mathrm{C}$ for 1.5 h , then heated further to $70^{\circ} \mathrm{C}$ for 1 h . The product was purified by crystallisation from DCM/hexane to yield $\mathbf{4 a}-\mathbf{C N}$ (ortho : para ratio $1: 2.0$ ) as an orange-yellow powder ( $24 \mathrm{mg}, 90 \%$ ). ortho-4a-CN. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.83\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.98$ $(\mathrm{s}, 3 \mathrm{H}, M e), 7.00\left(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 7.01(\mathrm{~d}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{5 \mathrm{~b}}\right), 7.21\left(\mathrm{dd}, J=7.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 7.33(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}$, $H^{5 \mathrm{a}}$ ), 7.37 (dd, $J=7.7,1.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}$ ), ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 9.6\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 36.8(\mathrm{Me}), 92.6\left(C_{5} \mathrm{Me}_{5}\right), 94.8,112.5\left(C^{1}\right)$, $115.6\left(C^{5 \mathrm{a}}\right), 120.3,121.6\left(C^{2}\right), 122.0\left(C^{5 \mathrm{~b}}\right), 131.2\left(C^{3}\right)$, 148.0, $151.1\left(C^{4}\right), 167.9\left(C^{6}\right)$. ESIMS: $m / z 510[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{23}{ }^{193} \mathrm{IrN}_{3}[\mathrm{M}-\mathrm{Cl}]^{+}$510.1521, found 510.1523 . ESIMS: $m / z 551[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{4}{ }^{193} \mathrm{Ir}[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$551.1787, found 551.1790. para-4a-CN. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.79\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right.$ ), $3.99(\mathrm{~s}, 3 \mathrm{H}, M e), 7.03\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.21(\mathrm{dd}, J=7.7$ $\left.\mathrm{Hz}, 1.7,1 \mathrm{H}, H^{3}\right), 7.32\left(\mathrm{~d}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 7.34(\mathrm{~d}, J=2.1 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{5 \mathrm{a}}\right), 7.88\left(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 9.7\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.0(\mathrm{Me}), 91.8\left(C_{5} \mathrm{Me}_{5}\right), 104.6,112.6$ $\left(C^{4}\right), 114.9\left(C^{5 \mathrm{a}}\right), 122.2\left(C^{5 \mathrm{~b}}\right), 122.6,129.0\left(C^{3}\right), 137.2\left(C^{2}\right)$, 147.3, $153.4\left(C^{1}\right)$, $166.2\left(C^{6}\right)$. ESIMS: $m / z 510[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{23}{ }^{193} \operatorname{IrN}_{3}[\mathrm{M}-\mathrm{Cl}]^{+}$510.1521, found 510.1523. ESIMS: $m / z 551[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{4}{ }^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$551.1787, found 551.1790.

Synthesis of $\mathbf{4 b} \mathbf{b} \mathbf{C N}$. Following the general procedure, a mixture of $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(15 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(17 \mathrm{mg}$, $0.207 \mathrm{mmol}), \mathbf{L 4}-\mathrm{CN}(18 \mathrm{mg}, 0.054 \mathrm{mmol}), \mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.054 \mathrm{mmol})$, in DCE ( 2 mL ) was stirred at $50{ }^{\circ} \mathrm{C}$ for 1.5 h , then heated to $70^{\circ} \mathrm{C}$ for 1 h . The product was purified by precipitation from DCM/hexane to yield $\mathbf{4 b - C N}$ (ortho: para ratio $1: 1.9$ ) as an orange-yellow powder ( $13 \mathrm{mg}, 58 \%$ ). ortho-4b-CN. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.75$ (s, 15H, C $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), $3.99(\mathrm{~s}, 3 \mathrm{H}$, $M e), 7.01\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.05\left(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right)$, 7.17 (dd, $\left.J=7.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 7.40\left(\mathrm{~m}, 1 \mathrm{H}, H^{3}\right), 7.41(\mathrm{~d}, J=$ $\left.2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.7$ $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.1(\mathrm{Me}), 94.0,98.8\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=4.8 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 113.1$ $\left(C^{1}\right), 116.1\left(C^{5 \mathrm{a}}\right), 122.0,123.1\left(C^{2}\right)$, $123.3\left(C^{5 \mathrm{~b}}\right), 130.7\left(C^{3}\right)$, $147.3,167.4\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=38.2 \mathrm{~Hz}, C^{4}\right), 185.1\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=54.8 \mathrm{~Hz}\right.$, $C^{6}$ ). ESIMS: $m / z 420[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{3}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+} 420.0947$, found 420.0947. ESIMS: $m / z 461[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{4}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$461.1213, found 461.1213. para-4b-CN. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.71\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $4.00(\mathrm{~s}, 3 \mathrm{H}, M e), 7.03\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.27\left(\mathrm{~m}, 1 \mathrm{H}, H^{3}\right)$, 7.27 (br.s, 1H, $H^{4}$ ), 7.41 (d, $J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}$ ), 7.94 (dd, $J=$ 8.1, $0.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}$ ), ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.8$
$\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.1(\mathrm{Me}), 98.2\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=5.6 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 105.5$, $112.8\left(C^{4}\right), 115.4\left(C^{5 \mathrm{a}}\right), 120.1,123.1\left(C^{5 \mathrm{~b}}\right), 128.0\left(C^{3}\right), 138.4\left(C^{2}\right)$, $146.6,170.3\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=35.8 \mathrm{~Hz}, C^{1}\right), 183.7\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=55.6 \mathrm{~Hz}\right.$, $C^{6}$ ). Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{3}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+} 420.0947$, found 420.0947. ESIMS: $m / z 461$ [ $\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{4}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$461.1213, found 461.1213.

Synthesis of $\mathbf{4 a - \mathbf { C F } _ { 3 }}$. Following the general procedure, a mixture of $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(20 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(17 \mathrm{mg}$, $0.207 \mathrm{mmol}), \mathbf{L 4}^{2} \mathrm{CFF}_{3}(20 \mathrm{mg}, 0.0532 \mathrm{mmol}), \mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.055 \mathrm{mmol})$, in DCE ( 2 mL ) was stirred first at rt for 24 h , then heated to $50^{\circ} \mathrm{C}$ for 1 h and then at $70^{\circ} \mathrm{C}$ for a further 1 h . The product was purified by crystallisation from DCM/ hexane to yield single regioisomer para-4- $\mathrm{CF}_{3}$ as orange crystals ( $19 \mathrm{mg}, 64 \%$ ). para-4a-CF ${ }_{3} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $1.80\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.97(\mathrm{~s}, 3 \mathrm{H}, M e), 7.02(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{5 \mathrm{~b}}\right), 7.22$ (br. d, $\left.J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 7.30(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{4}\right), 7.38\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 7.87\left(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right)$, ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.7\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $37.0(\mathrm{Me}), 91.4$ $\left(C_{5} \mathrm{Me}_{5}\right), 106.8\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz}, C^{4}\right), 114.9\left(C^{5 \mathrm{a}}\right), 121.8\left(C^{5 \mathrm{~b}}\right)$, $122.1\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=3.2 \mathrm{~Hz}, C^{3}\right), 124.4\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=31.2 \mathrm{~Hz}, C-\mathrm{CF}_{3}\right)$, $125.0\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=271.0, C F_{3}\right), 136.6\left(C^{2}\right), 146.9,148.9\left(C^{1}\right), 166.3$ $\left(C^{6}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-61.5\left(\mathrm{C}_{3}\right)$. ESIMS: $\mathrm{m} / \mathrm{z} 553$ [M - Cl] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{~F}_{3}{ }^{193} \operatorname{Ir}[\mathrm{M}-$ $\mathrm{Cl}]^{+} 553.1643$, found 553.1645 .

Synthesis of $\mathbf{4 b}-\mathbf{C F}_{3}$. Following the general procedure, a mixture of $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(20 \mathrm{mg}, 0.032 \mathrm{mmol}), \mathrm{NaOAc}(21 \mathrm{mg}$, 0.259 mmol ), $\mathrm{L} 4^{2}-\mathrm{CF}_{3}$ ( $25 \mathrm{mg}, 0.066 \mathrm{mmol}$ ), in DCE ( 2.5 mL ) was stirred first at rt for 24 h , then heated to $50^{\circ} \mathrm{C}$ for 1 h and then at $70^{\circ} \mathrm{C}$ for a further 1 h . The product was purified by crystallisation from DCM/hexane to yield para-4b-CF $\mathbf{F}_{3}$ as yellow crystals ( $25 \mathrm{mg}, 78 \%$ ).

Para-4b-CF $3 .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 1.71$ ( $\mathrm{s}, 15 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), $4.00(\mathrm{~s}, 3 \mathrm{H}, M e), 7.10\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.28(\mathrm{~d}, J$ $\left.=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 7.33\left(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 7.49(\mathrm{~d}, J=2.0$ $\left.\mathrm{Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 7.92\left(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 10.2\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.6(\mathrm{Me}), 98.5\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=\right.$ $4.8 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}$ ), $107.5\left(\mathrm{q},{ }^{3} \mathrm{~J}_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz}, C^{4}\right), 115.7\left(C^{5 \mathrm{a}}\right), 121.5$ $\left(\mathrm{q},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=2.4 \mathrm{~Hz}, C^{3}\right), 123.6\left(C^{5 \mathrm{~b}}\right), 125.4\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=31.8 \mathrm{~Hz}\right.$, $\left.C-\mathrm{CF}_{3}\right), 125.6\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=271.0, C F_{3}\right), 138.5\left(C^{2}\right), 147.1,167.1(\mathrm{~d}$, $\left.{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=36.6 \mathrm{~Hz}, C^{1}\right), 184.7\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=55.6 \mathrm{~Hz}, C^{6}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta-61.8\left(\mathrm{C}_{3}\right)$. ESIMS: $m / z 463$ [M $\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{~F}_{3}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+}$ 463.0868, found 463.0862. Anal Calcd for $\mathrm{C}_{21} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{~F}_{3} \mathrm{ClRh}$ [M]: C, 50.57 ; H, 4.65 ; N, 5.62; found C, 50.44 ; H, 4.77 ; N, $5.47 \%$.

Synthesis of 4a-F. Following the general procedure, a mixture of $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(20 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(16 \mathrm{mg}$, 0.200 mmol ), L4-F ( $18 \mathrm{mg}, 0.055 \mathrm{mmol}$ ), $\mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.055 \mathrm{mmol})$, DCE ( 2 mL ) was heated to $70{ }^{\circ} \mathrm{C}$ for 3 h . The product was purified by crystallisation from DCM/hexane to yield 4a-F (ortho : para ratio $2.1: 1$ ) as a yellow powder ( 18 mg , $67 \%$ ). ortho-4a-F. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.80(\mathrm{~d}, 15 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), $3.97(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 6.72\left(\mathrm{~m}, 1 \mathrm{H}, H^{3}\right), 6.94\left(\mathrm{~m}, 2 \mathrm{H}, H^{1}, H^{2}\right)$, $6.97\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.32\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right),{ }^{13} \mathrm{C}$ $\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.7 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $36.9(\mathrm{Me}), 91.6\left(C_{5} \mathrm{Me}_{5}\right), 106.6\left(\mathrm{~d},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=2.7 \mathrm{~Hz}, C^{1}\right), 112.1(\mathrm{~d}$,
$\left.{ }^{2} J_{\mathrm{C}-\mathrm{F}}=29.4 \mathrm{~Hz}, C^{3}\right), 115.5\left(C^{5 \mathrm{a}}\right), 121.4\left(C^{5 \mathrm{~b}}\right), 123.8\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=8.2\right.$ $\left.\mathrm{Hz}, C^{2}\right), 126.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=44.6 \mathrm{~Hz}, C^{4}\right), 148.5\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=18.3 \mathrm{~Hz}\right)$, $166.5\left(C^{6}\right), 167.8\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=235.0 \mathrm{~Hz}, C-\mathrm{F}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-94.9(F)$. ESIMS: $m / z 503[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{~F}^{193} \mathrm{Ir}[\mathrm{M}-\mathrm{Cl}]^{+}$503.1674, found 503.1676. ESIMS: $m / z 544[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{~F}^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}+\mathrm{MeCN}]^{+}$544.1740, found 544.1744. para-4a-F. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.79$ $\left(\mathrm{s}, 15 \mathrm{H}, \mathrm{C}_{5} M e_{5}\right), 3.99(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 6.78$ (ddd, $J=9.8,8.3,2.7 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{3}\right), 6.87\left(\mathrm{dd}, J=9.5,2.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 6.97(\mathrm{~d}, J=2.1 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.27\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right), 7.64(\mathrm{dd}, J=8.3,6.5 \mathrm{~Hz}$, 1H, $H^{2}$ ), ${ }^{19}{ }^{\mathrm{F}}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-122.9$ (F). ESIMS: $m / z 503[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{20} \mathrm{H}_{23}{ }^{193} \mathrm{IrN}_{2} \mathrm{~F}[\mathrm{M}-$ $\mathrm{Cl}]^{+}$503.1674, found 503.1676. ESIMS: $\mathrm{m} / \mathrm{z} 544[\mathrm{M}-\mathrm{Cl}+$ MeCN] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{~F}^{193}$ Ir $[\mathrm{M}-\mathrm{Cl}+$ $\mathrm{MeCN}]^{+} 544.1740$, found 544.1744.

Synthesis of 4b-F. Following the general procedure, a mixture of $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(15 \mathrm{mg}, 0.025 \mathrm{mmol}), \mathrm{NaOAc}(17 \mathrm{mg}$, 0.207 mmol ), L4-F ( $17 \mathrm{mg}, 0.052 \mathrm{mmol}$ ), $\mathrm{Et}_{4} \mathrm{NCl}(9 \mathrm{mg}$, $0.053 \mathrm{mmol})$, DCE ( 2 mL ) was heated to $70^{\circ} \mathrm{C}$ for 3 h . The product was purified by precipitation from DCM/hexane to yield 4b-F (ortho :para ratio $10: 1$ ) as an orange-yellow powder ( $13 \mathrm{mg}, 59 \%$ ).
Ortho-4b-F. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.75$ ( $\mathrm{s}, 15 \mathrm{H}$, $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 3.98 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ), $6.72\left(\mathrm{td}, J=8.0,1.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 6.92$ (dd, $\left.J=7.6,1.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.98\left(\mathrm{td}, J=7.8,5.4 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right)$, $6.98\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{~b}}\right), 7.39\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5 \mathrm{a}}\right),{ }^{13} \mathrm{C}$ $\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 10.0\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=1.6 \mathrm{~Hz}, \mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $37.1(\mathrm{Me}), 98.2\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=5.6 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 107.1\left(C^{1}\right), 112.3(\mathrm{~d}$, $\left.{ }^{2} J_{\mathrm{C}-\mathrm{F}}=29.4 \mathrm{~Hz}, C^{3}\right), 115.9\left(C^{5 \mathrm{a}}\right), 122.3\left(C^{5 \mathrm{~b}}\right), 124.4\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=7.9\right.$ $\left.\mathrm{Hz}, \mathrm{C}^{2}\right) 141.1\left(\mathrm{dd},{ }^{2} J_{\mathrm{C}-\mathrm{Rh}, \mathrm{C}-\mathrm{F}}=39.7,10.3 \mathrm{~Hz}, C^{4}\right), 147.9\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}\right.$ $=19.1 \mathrm{~Hz}), 168.3\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=232.9 \mathrm{~Hz}, C-\mathrm{F}\right), 183.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=\right.$ $\left.54.8 \mathrm{~Hz}, C^{6}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-93.9(F)$. ESIMS: $m / z 413[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{FRh}$ $[\mathrm{M}-\mathrm{Cl}]^{+} 413.0900$, found 413.0902.

## General procedure for preparation of meta-substituted benzylimidazolium salts L5-R

A Schlenk flask was charged with $N$-methylimidazole (1 eq.), meta-substituted benzyl chloride (1-2 eq.) and MeCN ( 5 mL ) and stirred at $55{ }^{\circ} \mathrm{C}$ for 1 day. The resulting mixture was concentrated in vacuo, the residue dissolved in DCM and washed with hexane, then the solvent removed by rotary evaporation giving pure imidazolium salt as an oil or a sticky solid.
Synthesis of L5-OMe. Following the general procedure, $N$-methylimidazole ( $250 \mathrm{mg}, 3.049 \mathrm{mmol}$ ), 3-methoxybenzyl chloride ( $373 \mathrm{mg}, 2.382 \mathrm{mmol}$ ) and MeCN ( 5 mL ) were added to a Schlenk flask and stirred at $55^{\circ} \mathrm{C}$ for 20 h . L5-OMe was obtained as a white sticky solid ( $480 \mathrm{mg}, 84 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 3.65$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OMe}$ ), 3.93 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ), 5.41 ( s , $2 \mathrm{H}, H^{1}$ ), 6.72 (dd, $\left.J=8.2,2.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 6.87(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{2}\right), 6.93$ (br. s, 1H, $H^{5}$ ), $7.12\left(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 7.41(\mathrm{~s}$, $\left.1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.56\left(\mathrm{~s}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 10.46\left(\mathrm{~s}, 1 \mathrm{H}, H^{7}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 36.1(\mathrm{Me}), 52.6\left(\mathrm{C}^{1}\right), 55.1(\mathrm{OMe}), 114.0$ $\left(C^{5}\right), 114.4\left(C^{4}\right), 120.5\left(C^{2}\right), 121.6\left(C^{6 \mathrm{a}}\right), 123.4\left(C^{6 \mathrm{~b}}\right), 130.0\left(C^{3}\right)$, $134.4\left(\mathrm{CCH}_{2}\right), 137.1\left(C^{7}\right), 159.7$ ( $C$-OMe). ESIMS: $m / z 203$ [M -
$\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{12} \mathrm{H}_{15} \mathrm{~N}_{2} \mathrm{O}[\mathrm{M}]^{+}$203.1184, found 203.1186.

Synthesis of $\mathbf{L 5}-\mathbf{C F}_{3}$. Following the general procedure, $N$-methylimidazole ( $159 \mathrm{mg}, 1.939 \mathrm{mmol}$ ), 3-trifluoromethylbenzyl chloride ( $563 \mathrm{mg}, 2.893 \mathrm{mmol}$ ) and MeCN ( 5 mL ) were added to a Schlenk flask and stirred at $55{ }^{\circ} \mathrm{C}$ for 1 day. Additional portion of 3-trifluoromethylbenzyl chloride ( $188 \mathrm{mg}, 0.965 \mathrm{mmol}$ ) was added and mixture stirred at $65{ }^{\circ} \mathrm{C}$ for 1 day. $\mathbf{L 5}-\mathbf{C F}_{3}$ was obtained as a white sticky solid ( 294 mg , $55 \%) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 3.84(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 5.59(\mathrm{~s}$, $\left.2 \mathrm{H}, H^{1}\right), 7.30\left(\mathrm{~m}, 1 \mathrm{H}, H^{3}\right), 7.38\left(\mathrm{~m}, 1 \mathrm{H}, H^{4}\right), 7.49(\mathrm{br} \mathrm{s}, 1 \mathrm{H}$, $\left.H^{6 \mathrm{~b}}\right), 7.58\left(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, H^{\mathrm{ab}}\right), 7.67\left(\mathrm{~m}, 2 \mathrm{H}, H^{2}, H^{5}\right), 10.37(\mathrm{~m}, 1 \mathrm{H}$, $\left.H^{7}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 36.0(\mathrm{Me}), 51.6\left(C^{1}\right)$, $122.0\left(C^{6 \mathrm{a}}\right), 123.2\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=273.1 \mathrm{~Hz}, C \mathrm{~F}_{3}\right), 123.5\left(C^{6 \mathrm{~b}}\right), 125.2$ $\left(C^{5}\right), 125.6\left(C^{4}\right), 129.5\left(C^{3}\right), 130.6\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=33.1 \mathrm{~Hz}, C-\mathrm{CF}_{3}\right)$, $132.2\left(C^{2}\right), 134.3\left(\mathrm{CCH}_{2}\right), 137.0\left(C^{7}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta-62.4\left(\mathrm{CF}_{3}\right)$. ESIMS: $m / z 241[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{12} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{~N}_{2}[\mathrm{M}]^{+}$241.0953, found 241.0960.

Synthesis of L5-F. Following the general procedure, $N$-methylimidazole ( $165 \mathrm{mg}, 2.010 \mathrm{mmol}$ ), 3-fluorobenzyl chloride ( $404 \mathrm{mg}, 2.793 \mathrm{mmol}$ ) and MeCN $(5 \mathrm{~mL})$ were added to a Schlenk flask and stirred at $60{ }^{\circ} \mathrm{C}$ for 24 h . L5-F was obtained as a pale yellow oil (396 mg, 87\%). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 3.96$ (s, 3H, Me), $5.48\left(\mathrm{~s}, 2 \mathrm{H}, H^{1}\right), 7.16$ (tdd, $\left.J=8.7,2.2,0.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 7.25(\mathrm{dt}, J=9.5,2.0 \mathrm{~Hz}, 1 \mathrm{H}$, $H^{5}$ ), 7.30 (br. d, $\left.J=8.3,1 \mathrm{H}, H^{3}\right), 7.47(\mathrm{td}, J=8.0,5.7 \mathrm{~Hz}, 1 \mathrm{H}$, $H^{2}$ ), $7.63\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.67\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right)$, $9.13\left(\mathrm{~s}, 1 \mathrm{H}, H^{7}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 36.8(\mathrm{Me})$, $53.4\left(C^{1}\right), 116.7\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=23.0 \mathrm{~Hz}, C^{5}\right), 117.2\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=20.7\right.$ $\left.\mathrm{Hz}, C^{4}\right), 123.8\left(C^{6 \mathrm{a}}\right), 125.5\left(C^{6 \mathrm{~b}}\right), 125.7\left(\mathrm{~d},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=3.2 \mathrm{~Hz}, C^{2}\right)$, $132.5\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=7.9 \mathrm{~Hz}, C^{3}\right), 138.0\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=7.2 \mathrm{~Hz}, C \mathrm{CH}_{2}\right)$, $138.1\left(C^{7}\right)$, $164.6\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=246.4 \mathrm{~Hz}, C-\mathrm{F}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta-113.7$ (F). ESIMS: $m / z 191[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{FN}_{2}[\mathrm{M}]^{+}$191.0985, found 191.0982.

## General procedure for complexation of meta-substituted benzylimidazolium salts L5-R with $\left[\mathbf{M C l}_{2} \mathbf{C p}\right]_{2}(\mathbf{M}=\mathbf{I r}, \mathbf{R h})$

An aluminium foil wrapped Schlenk flask was charged with a magnetic stirrer bar, the appropriate meta-substituted benzylimidazolium salt L5-R (2.1 eq.) and $\mathrm{Ag}_{2} \mathrm{O}$ (2.2 eq.), capped, purged with $\mathrm{N}_{2}$. Dry DCM $(2.5 \mathrm{~mL})$ was added and the mixture stirred at rt for 1-2 h. Then the reaction mixture was filtered through Celite and the solvent removed by rotary evaporation. The residue was re-dissolved in dry DCM $(2.5 \mathrm{~mL})$ and added to an $\mathrm{N}_{2}$ purged Schlenk flask wrapped in aluminium foil, followed by addition of $\left[\mathrm{MCl}_{2} \mathrm{Cp}^{*}\right]_{2}(\mathrm{M}=\mathrm{Ir}, \mathrm{Rh})(1 \mathrm{eq}$.$) . The reac-$ tion mixture was stirred at rt for 1-2 h, filtered through Celite, the solvent removed by rotary evaporation and the final product $\mathbf{5 a} / \mathbf{b}-\mathbf{R}$ obtained by precipitation/crystallisation from $\mathrm{DCM} / \mathrm{Et}_{2} \mathrm{O}$ or $\mathrm{DCM} /$ hexane.

Synthesis of 5a-OMe. Following the general procedure, a mixture of L5-OMe ( $58 \mathrm{mg}, 0.243 \mathrm{mmol}$ ), $\mathrm{Ag}_{2} \mathrm{O}$ ( 59 mg , $0.254 \mathrm{mmol})$, dry DCM ( 2.5 mL ), stirred at rt for 1 h , then $\left[\operatorname{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(91 \mathrm{mg}, 0.114 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ were added and the mixture was stirred for 1 h . Crystallisation from

DCM/hexane yielded 5a-OMe as yellow crystals ( 99 mg , $72 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.62$ (s, $15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}$ ), 3.78 (s, $3 \mathrm{H}, \mathrm{OMe}), 4.00(\mathrm{~s}, 3 \mathrm{H}, M e), 5.22\left(\mathrm{~d}, J=14.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right)$, $5.93\left(\mathrm{~d}, J=14.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.72\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 6.84$ (dd, $J=7.9,2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}$ ), $6.88\left(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 6.90$ $\left(\mathrm{d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 6.95\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{5}\right), 7.25(\mathrm{t}, J=$ $\left.7.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.3\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $38.7(\mathrm{Me}), 54.5\left(C^{1}\right), 55.4(\mathrm{OMe}), 88.9\left(C_{5} \mathrm{Me}_{5}\right), 113.7\left(C^{5}\right), 113.9$ $\left(C^{4}\right), 120.7\left(C^{2}\right), 121.9\left(C^{6 \mathrm{a}}\right), 123.3\left(C^{6 \mathrm{~b}}\right), 129.7\left(C^{3}\right), 138.3,156.9$ $\left(C^{7}\right)$, 159.9. ESIMS: $m / z 565$ [M -Cl$]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{29} \mathrm{~N}_{2} \mathrm{OCl}^{193} \mathrm{Ir}[\mathrm{M}-\mathrm{Cl}]^{+} 565.1598$, found 565.1591 .

Synthesis of 5b-OMe. Following the general procedure, a mixture of L5-OMe ( $51 \mathrm{mg}, 0.214 \mathrm{mmol}$ ), $\mathrm{Ag}_{2} \mathrm{O}(52 \mathrm{mg}$, $0.224 \mathrm{mmol})$, dry DCM ( 2.5 mL ), stirred at rt for 1 h , then $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(62 \mathrm{mg}, 0.100 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ were added and the mixture was stirred for 1 h . Crystallisation from DCM/hexane yielded 5b-OMe as yellow/orange crystals ( 94 mg , $92 \%) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.61\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.78(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{OMe}), 4.05(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 5.27\left(\mathrm{br} \mathrm{d}, J=14.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.03$ (br d, $\left.J=14.5 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.80\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 6.84(\mathrm{dd}$, $\left.J=8.2,2.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 6.89\left(\mathrm{br} \mathrm{d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 6.97(\mathrm{~m}, 2$ $\left.\mathrm{H}, H^{5}, H^{6 \mathrm{~b}}\right), 7.24\left(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(125 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): \delta 9.5\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 39.2(\mathrm{Me}), 54.6\left(\mathrm{C}^{1}\right), 55.3(\mathrm{OMe}), 96.2(\mathrm{~d}$, $\left.{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=6.0 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 113.7\left(C^{5}\right), 113.9\left(C^{4}\right), 120.6\left(C^{2}\right), 122.7$ $\left(C^{6 \mathrm{a}}\right), 124.1\left(C^{6 \mathrm{~b}}\right), 129.6\left(C^{3}\right), 138.2,159.9,170.3\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=56.2\right.$ $\mathrm{Hz}, C^{7}$ ). ESIMS: $m / z 475[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{29} \mathrm{~N}_{2} \mathrm{OCl}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+} 475.1023$, found 475.1016 .
Synthesis of $\mathbf{5 a - C F} \mathbf{F}_{\mathbf{3}}$. Following the general procedure, a mixture of $\mathbf{L 5}-\mathbf{C F}_{3}(52 \mathrm{mg}, 0.188 \mathrm{mmol}), \mathrm{Ag}_{2} \mathrm{O}(46 \mathrm{mg}$, $0.211 \mathrm{mmol})$, dry DCM ( 2.5 mL ), stirred at rt for 1 h , then $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(71 \mathrm{mg}, 0.089 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ were added and the mixture was stirred for 1 h . Crystallisation from DCM/hexane yielded $\mathbf{5 a - C F} \mathbf{3}_{3}$ as yellow crystals ( $81 \mathrm{mg}, 71 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 4.01(\mathrm{~s}, 3 \mathrm{H}$, $M e), 5.14$ (br d, $J=14.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}$ ), 6.23 (br d, $J=14.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{1}\right), 6.66\left(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 6.94\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right)$, $7.46\left(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 7.55$ (br. s, $1 \mathrm{H}, H^{5}$ ), 7.56 (br. d, $J=$ $7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}$ ), 7.71 (br. d, $\left.J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 9.1\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 38.7(\mathrm{Me}), 53.9\left(\mathrm{C}^{1}\right), 88.9$ $\left(C_{5} \mathrm{Me}_{5}\right), 121.6\left(C^{6 \mathrm{~b}}\right), 123.7\left(C^{6 \mathrm{a}}\right), 124.0\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=245.0 \mathrm{~Hz}\right.$, $\left.C \mathrm{~F}_{3}\right), 124.8\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{4 / 5}\right), 124.9\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz}, C^{4 /}\right.$ ${ }^{5}$ ), $129.4\left(C^{2}\right), 130.7\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=33.1 \mathrm{~Hz}, C-\mathrm{CF}_{3}\right), 132.4\left(C^{3}\right)$, 137.8, $157.3\left(C^{7}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-62.5$ $\left(\mathrm{CF}_{3}\right)$.ESIMS: m/z 603 [M - Cl] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{~F}_{3} \mathrm{Cl}^{193} \mathrm{Ir}[\mathrm{M}-\mathrm{Cl}]^{+}$603.1366, found 603.1360.
Synthesis of $\mathbf{5 b}-\mathbf{C F}_{\mathbf{3}}$. Following the general procedure, a mixture of $\mathbf{L 5}-\mathbf{C F}_{3}(53 \mathrm{mg}, 0.191 \mathrm{mmol}), \mathrm{Ag}_{2} \mathrm{O}(57 \mathrm{mg}$, $0.245 \mathrm{mmol})$, dry DCM ( 2.5 mL ), stirred at rt for 1 h , then $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(69 \mathrm{mg}, 0.112 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ were added and the mixture was stirred for 1 h . Crystallisation from $\mathrm{DCM} /$ hexane yielded $\mathbf{5 b}-\mathbf{C F}_{3}$ as yellow/orange crystals ( 89 mg , $85 \%) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.60\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right.$ ), 4.05 (s, 3H, Me), $5.17\left(\mathrm{br} \mathrm{d}, J=14.5 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.36(\mathrm{br} \mathrm{d}, J=14.5$ $\left.\mathrm{Hz}, 1 \mathrm{H}, H^{1}\right), 6.73\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.02(\mathrm{~d}, J=2.0 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.44\left(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right), 7.55\left(\mathrm{~m}, 2 \mathrm{H}, H^{4}, H^{5}\right), 7.70$ (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}$ ), ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.5$
$\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 39.3(\mathrm{Me}), 54.1\left(C^{1}\right), 96.3\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=6.0 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right)$, $125.5\left(C^{6 \mathrm{a}}\right), 123.8\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=246.0 \mathrm{~Hz}, C \mathrm{~F}_{3}\right), 124.7\left(C^{6 \mathrm{~b}}\right), 124.8$ $\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz}, C^{4 /} C^{5}\right), 125.0\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=4.0 \mathrm{~Hz} C^{4 /} C^{5}\right), 129.5$ $\left(C^{3}\right), 130.7\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=32.1 \mathrm{~Hz}, C-\mathrm{CF}_{3}\right), 132.6\left(C^{2}\right), 137.7,171.0$ $\left(\mathrm{d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=56.2 \mathrm{~Hz}, C^{7}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(376 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $-62.5\left(\mathrm{CF}_{3}\right) . \mathrm{m} / \mathrm{z} 513[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{~F}_{3} \mathrm{Cl}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+}$513.0792, found: 513.0786.

Synthesis of $5 \mathrm{a}-\mathrm{F}$. Following the general procedure, a mixture of $\mathbf{L 5 - F}(50 \mathrm{mg}, 0.218 \mathrm{mmol}), \mathrm{Ag}_{2} \mathrm{O}(50 \mathrm{mg}$, $0.216 \mathrm{mmol})$, dry DCM ( 2.5 mL ), stirred at rt for 1 h , then $\left[\mathrm{IrCl}_{2} \mathrm{Cp}^{*}\right]_{2}(79 \mathrm{mg}, 0.099 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ was added and the mixture was stirred for 1 h . Crystallisation from DCM/hexane yielded 5a-F as yellow crystals ( $86 \mathrm{mg}, 73 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 4.00(\mathrm{~s}, 3 \mathrm{H}$, $M e), 5.16\left(\mathrm{~d}, J=14.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 5.93\left(\mathrm{~d}, J=14.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right)$, $6.69\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 6.94\left(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 6.99$ $\left(\operatorname{td}, J=8.3,2.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 7.08\left(\mathrm{td}, J=9.6,2.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{5}\right)$, $7.16\left(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 7.31\left(\mathrm{~m}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 9.1\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 38.7(\mathrm{Me}), 53.9\left(C^{1}\right), 88.8$ $\left(C_{5} \mathrm{Me}_{5}\right), 114.9\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=21.1 \mathrm{~Hz}, C^{4}\right), 115.3\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=23.1 \mathrm{~Hz}\right.$, $\left.C^{5}\right), 121.7\left(C^{6 \mathrm{a}}\right), 123.5\left(C^{6 \mathrm{~b}}\right), 124.2\left(\mathrm{~d},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=2.0 \mathrm{~Hz}, C^{2}\right), 130.2$ $\left(\mathrm{d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=8.0 \mathrm{~Hz}, C^{3}\right), 139.3\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=7.0 \mathrm{~Hz}, C\right), 157.1\left(C^{7}\right)$, $162.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=247.0 \mathrm{~Hz}, C-\mathrm{F}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz , $\mathrm{CDCl}_{3}$ ): $\delta-112.4(F)$. ESIMS: $m / z 553[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{Cl}^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}]^{+} 553.1398$, found 553.1394.

Synthesis of $\mathbf{5 b}$-F. Following the general procedure, a mixture of L5-F ( $50 \mathrm{mg}, 0.221 \mathrm{mmol}$ ), $\mathrm{Ag}_{2} \mathrm{O}(52 \mathrm{mg}$, $0.223 \mathrm{mmol})$, dry $\mathrm{DCM}(2.5 \mathrm{~mL})$, stirred at rt for 1 h , then $\left[\mathrm{RhCl}_{2} \mathrm{Cp}^{*}\right]_{2}(62 \mathrm{mg}, 0.101 \mathrm{mmol})$ and dry DCM $(2.5 \mathrm{~mL})$ were added and the mixture was stirred for 1 h . Crystallisation from DCM/hexane yielded 5b-F as yellow crystals ( $67 \mathrm{mg}, 67 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.63\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 4.06(\mathrm{~s}, 3 \mathrm{H}$, $M e), 5.22\left(\mathrm{~d}, J=14.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right), 6.19\left(\mathrm{~d}, J=14.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{1}\right)$, $6.78\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.00\left(\mathrm{~m}, 2 \mathrm{H}, H^{3}, H^{6 \mathrm{~b}}\right), 7.09(\mathrm{td}, J=$ $9.6,1.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{5}$ ), $7.17\left(\mathrm{dd}, J=7.6,0.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{2}\right), 7.31(\mathrm{td}$, $\left.J=7.9,5.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 9.5$ $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 39.2(\mathrm{Me}), 54.1\left(C^{1}\right), 96.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{Rh}}=6.0 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right)$, $115.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=20.1 \mathrm{~Hz}, C^{4}\right), 115.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=22.1 \mathrm{~Hz}, C^{5}\right)$, $122.6\left(C^{6 \mathrm{a}}\right), 124.3\left(\mathrm{~d},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=2.0 \mathrm{~Hz}, C^{2}\right), 124.5\left(C^{6 \mathrm{~b}}\right), 130.3(\mathrm{~d}$, $\left.{ }^{3} J_{\mathrm{C}-\mathrm{F}}=8.0 \mathrm{~Hz}, C^{3}\right), 139.3\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=8.0 \mathrm{~Hz}, C\right), 162.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=\right.$ $250.0 \mathrm{~Hz}, C-\mathrm{F}), 170.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{Rh}}=56.2 \mathrm{~Hz}, C^{7}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}$ $\left(376 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta-112.3(F)$. ESIMS: $m / z 463[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}^{103} \mathrm{Rh}\left[\mathrm{M}-\mathrm{HCl}_{2}\right]^{+}$427.1057, found 427.1052.

## General procedure for cyclometallation of $5 \mathbf{a} / \mathbf{b}-\mathrm{R}$

An oven-dried and $\mathrm{N}_{2}$ purged Schlenk flask was charged with a magnetic stirrer bar, $\mathbf{5 a / b - R}$ ( 1 eq.), NaOAc ( 5 eq. ) and dry DCM ( 2 mL ) and $\mathrm{MeOH}(0.5 \mathrm{~mL})$ and stirred at rt for indicated time. The reaction mixture was filtered through Celite, which was washed with additional DCM ( $5-10 \mathrm{~mL}$ ), the solvent removed by rotary evaporation and the residue purified by precipitation from DCM/hexane.

Synthesis of 6a-OMe. Following the general procedure, a mixture of 5a-OMe ( $15 \mathrm{mg}, 0.025 \mathrm{mmol}$ ), NaOAc ( 8 mg , $0.098 \mathrm{mmol})$, dry DCM ( 2 mL ) and dry $\mathrm{MeOH}(0.5 \mathrm{~mL})$ was
stirred at rt overnight. Precipitation from DCM/hexane yielded regioisomer para-6a-OMe as a yellow powder ( $12 \mathrm{mg}, 84 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.68\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.75(\mathrm{~s}, 3 \mathrm{H}$, OMe), 3.92 ( $\mathrm{s}, 3 \mathrm{H}, M e$ ), $4.60\left(\mathrm{~d}, J=13.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 4.84(\mathrm{~d}, J$ $\left.=13.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right), 6.61\left(\mathrm{~d}, J=2.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{5}\right), 6.67(\mathrm{dd}, J=$ $\left.8.3,2.6 \mathrm{~Hz} 1 \mathrm{H}, H^{4}\right), 6.89\left(\mathrm{~d}, J=1.4 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 6.94(\mathrm{~d}, J=1.4$ $\mathrm{Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}$ ), 7.47 (br d, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}$ ), ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 9.4\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 36.9(\mathrm{Me}), 55.3\left(C^{1}\right), 57.1$ (OMe), $90.0\left(C_{5} \mathrm{Me}_{5}\right), 111.1\left(C^{5}\right), 113.6\left(C^{4}\right), 120.3\left(C^{6 \mathrm{a}}\right), 121.1$ $\left(C^{6 \mathrm{a}}\right), 132.5\left(C^{2}\right), 138.5,141.4\left(C^{3}\right), 155.8,157.3\left(C^{7}\right)$. ESIMS: $m / z 529[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}^{191} \mathrm{Ir}[\mathrm{M}-$ $\mathrm{Cl}^{+} 527.1808$, found 527.1804.
Synthesis of 6b-OMe. Following the general procedure, a mixture of $5 \mathbf{b b - O M e}(19 \mathrm{mg}, 0.037 \mathrm{mmol})$, NaOAc ( 12 mg , $0.146 \mathrm{mmol})$, dry DCM ( 2 mL ) and dry MeOH ( 0.5 mL ) was stirred at rt overnight. Precipitation from DCM/hexane yielded para-6b-OMe as a yellow/orange powder ( $12 \mathrm{mg}, 68 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.60\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.74(\mathrm{~s}, 3 \mathrm{H}$, OMe), $4.00(\mathrm{~s}, 3 \mathrm{H}, M e), 4.68\left(\mathrm{~d}, J=14.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 4.94(\mathrm{~d}, J$ $\left.=14.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right), 6.61\left(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}, H^{5}\right), 6.71(\mathrm{dd}, J=$ $\left.8.4,2.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 6.95\left(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.02(\mathrm{~d}, J=$ $\left.1.6 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.56\left(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.6\left(\mathrm{C}_{5} M e_{5}\right), 37.5(\mathrm{Me}), 55.3\left(C^{1}\right), 56.3$ $(\mathrm{OMe}), 97.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=5.0 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 111.6\left(C^{5}\right), 113.3\left(C^{4}\right)$, $121.4\left(C^{6 \mathrm{a}}\right), 122.0\left(C^{6 \mathrm{~b}}\right), 139.1,141.0\left(C^{3}\right), 147.8\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=32.1\right.$ $\mathrm{Hz}, C^{2}$ ), 156.1, $175.0\left(\mathrm{~d},{ }^{1} \mathrm{~J}_{\mathrm{C}-\mathrm{Rh}}=55.2 \mathrm{~Hz}, C^{7}\right)$. ESIMS: $m / z 439$ $[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+}$ 439.1257, found 439.1246 .

Synthesis of $\mathbf{6 a - \mathbf { C F } _ { 3 }}$. Following the general procedure, a mixture of $5 \mathrm{a}-\mathrm{CF}_{3}(27 \mathrm{mg}, 0.042 \mathrm{mmol})$, $\mathrm{NaOAc}(14 \mathrm{mg}$, $0.171 \mathrm{mmol})$, dry DCM ( 2 mL ) and dry MeOH ( 0.5 mL ) was stirred at rt overnight. Precipitation from DCM/hexane yielded para-6a-CF $\mathbf{3}_{3}$ as a yellow powder ( $21 \mathrm{mg}, 83 \%$ ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ): $\delta 1.68$ (s, 15H, $\mathrm{C}_{5} \mathrm{Me}_{5}$ ), 3.90 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Me}$ ), 4.72 (br d, $J=13.7 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}$ ), $4.86\left(\mathrm{br} \mathrm{d}, J=14.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right.$ ), 6.92 (br s, 1H, $H^{6 \mathrm{~b}}$ ), 6.98 (br s, $1 \mathrm{H}, H^{6 \mathrm{a}}$ ), $7.18\left(\mathrm{~m}, 2 \mathrm{H}, H^{4}, H^{5}\right.$ ), 7.75 $\left(\mathrm{m}, 1 \mathrm{H}, H^{3}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.4\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 36.9$ (Me), $55.3\left(C^{1}\right), 90.5\left(C_{5} \mathrm{Me}_{5}\right), 120.3\left(\mathrm{q},{ }^{3} \mathrm{~J}_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{4 / 5}\right), 120.4$ $\left(C^{6 \mathrm{a}}\right), 121.4\left(C^{6 \mathrm{~b}}\right), 123.6\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{4 / 5}\right), 124.1\left(\mathrm{q},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=\right.$ $31.1 \mathrm{~Hz}, C-\mathrm{CF}_{3}$ ), 125.2 ( $\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=271.1 \mathrm{~Hz}, C \mathrm{~F}_{3}$ ), $138.9,141.8$ $\left(C^{3}\right), 152.1\left(C^{2}\right), 156.6\left(C^{7}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ -61.4 (CF $F_{3}$ ). ESIMS: m/z 567 [M - Cl] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}_{3}{ }^{191} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}]^{+} 565.1574$, found 565.1576.
Synthesis of $\mathbf{6 b}-\mathbf{C F}_{3}$. Following the general procedure, a mixture of $5 \mathbf{b}-\mathrm{CF}_{3}(50 \mathrm{mg}, 0.091 \mathrm{mmol})$, NaOAc ( 30 mg , $0.366 \mathrm{mmol})$, dry DCM ( 2 mL ) and dry MeOH ( 0.5 mL ) was stirred at rt overnight. Precipitation from DCM/hexane yielded para-6b-CF $\mathbf{3}_{3}$ as a yellow/orange powder ( $40 \mathrm{mg}, 86 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.59$ (s, 15H, C ${ }_{5} \mathrm{Me}_{5}$ ), 3.97 (s, $3 \mathrm{H}, \mathrm{Me}$ ), 4.80 (d, $\left.J=14.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 4.97\left(\mathrm{~d}, J=14.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right), 6.95(\mathrm{~d}, J$ $\left.=1.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.03\left(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.16(\mathrm{br} \mathrm{s}, 1 \mathrm{H}$, $\left.H^{5}\right), 7.21\left(\mathrm{br} \mathrm{d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 7.86\left(\mathrm{br} \mathrm{d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right)$, ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 9.6\left(\mathrm{C}_{5} M e_{5}\right), 37.4(\mathrm{Me}), 56.1$ $\left(C^{1}\right), 97.4\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=5.0 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 120.6\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{5}\right)$, $121.5\left(\mathrm{q},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=3.0 \mathrm{~Hz}, C^{4}\right), 122.4\left(C^{6 \mathrm{a}}\right), 122.8\left(C^{6 \mathrm{~b}}\right), 124.4(\mathrm{q}$, $\left.{ }^{2} J_{\mathrm{C}-\mathrm{F}}=31.1 \mathrm{~Hz}, C-\mathrm{CF}_{3}\right), 125.1\left(\mathrm{q},{ }^{1} J_{\mathrm{C}-\mathrm{F}}=271.0 \mathrm{~Hz}, C \mathrm{~F}_{3}\right), 139.5$,
$141.3\left(\mathrm{q},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=2.0 \mathrm{~Hz}, C^{3}\right), 169.0\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=32.1 \mathrm{~Hz}, C^{2}\right), 174.3$ (d, $\left.{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=56.2 \mathrm{~Hz}, C^{7}\right),{ }^{19}{ }^{\mathrm{F}}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-61.5$ $\left(\mathrm{C}_{3}\right)$. ESIMS: $m / z 477$ [ $\left.\mathrm{M}-\mathrm{Cl}\right]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{22} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}_{3}{ }^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+} 477.1025$, found 477.10250.

Synthesis of 6a-F. Following the general procedure, a mixture of $5 \mathbf{a}-\mathrm{F}$ ( $30.0 \mathrm{mg}, 0.051 \mathrm{mmol}$ ), NaOAc ( 16.5 mg , $0.201 \mathrm{mmol})$, dry DCM ( 2.4 mL ) and dry MeOH ( 0.6 mL ) was stirred at rt for 2 h . Precipitation from DCM/hexane yielded 6aF (ortho : para ratio $10: 1$ ) as a yellow powder ( $27 \mathrm{mg}, 96 \%$ ). ortho-6a-F. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.73\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right)$, $3.89(\mathrm{~s}, 3 \mathrm{H}, M e), 4.71\left(\mathrm{dd}, J=13.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 4.88(\mathrm{~d}, J=$ $\left.13.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right), 6.76\left(\mathrm{~m}, 3 \mathrm{H}, H^{2}, H^{3}, H^{4}\right), 6.90(\mathrm{~d}, J=1.9 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 6.94\left(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR $(101 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): \delta 9.4\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.0(\mathrm{Me}), 57.0\left(C^{1}\right), 90.04\left(C_{5} \mathrm{Me}_{5}\right), 114.2$ $\left(\mathrm{d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=31.0 \mathrm{~Hz}, C^{4}\right), 120.3\left(C^{6 \mathrm{a}}\right), 120.6\left(\mathrm{~d},{ }^{4} J_{\mathrm{C}-\mathrm{F}}=1.6 \mathrm{~Hz}, C^{2}\right)$, $121.6\left(C^{6 \mathrm{~b}}\right), 123.8\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{C}-\mathrm{F}}=8.7 \mathrm{~Hz}, C^{3}\right), 128.0\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=38.9\right.$ $\left.\mathrm{Hz}, C^{5}\right), 141.0\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=14.3 \mathrm{~Hz}, C\right), 156.4\left(C^{7}\right), 167.2\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{F}}\right.$ $=232.9 \mathrm{~Hz}, C-F),{ }^{19} F\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-87.8(F)$. ESIMS: $m / z 517 \quad[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}^{193} \mathrm{Ir}[\mathrm{M}-\mathrm{Cl}]^{+}$517.1631, found 517.1631. para-6aF. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.66\left(\mathrm{~s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}\right), 3.91(\mathrm{~s}$, $3 \mathrm{H}, M e), 4.6\left(\mathrm{~d}, J=14.1 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{a}}\right), 4.81(\mathrm{~d}, J=13.9 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{1 \mathrm{~b}}\right), 6.71-6.74\left(\mathrm{~m}, 2 \mathrm{H}, H^{4}, H^{5}\right), 6.89\left(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right)$, $6.93\left(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.51\left(\mathrm{dd}, J=8.3,7.0 \mathrm{~Hz}, 1 \mathrm{H}, H^{3}\right)$, ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-125.3(F)$. ESIMS: $m / z 427$ $[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): ESIMS: $m / z 517$ [M - Cl] ${ }^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}^{193} \operatorname{Ir}[\mathrm{M}-\mathrm{Cl}]^{+} 517.1631$, found 517.1631.

Synthesis of 6b-F. Following the general procedure, a mixture of 5b-F ( $25.5 \mathrm{mg}, 0.051 \mathrm{mmol}$ ), NaOAc ( 16.7 mg , $0.204 \mathrm{mmol})$, dry DCM ( 2.4 mL ) and dry MeOH ( 0.6 mL ) was stirred at rt for 2 h . Precipitation from DCM/hexane yielded regioisomers 6b-F (ortho : para ratio $10: 1$ ) as a yellow powder ( $22.5 \mathrm{mg}, 96 \%$ ). ortho-6b-F. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.66$ ( $\mathrm{s}, 15 \mathrm{H}, \mathrm{C}_{5} \mathrm{Me}_{5}$ ), $3.99(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Me}), 4.71(\mathrm{dd}, J=14.2,1.0 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{1 \mathrm{a}}\right), 4.97\left(\mathrm{~d}, J=14.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 6.76\left(\mathrm{~m}, 2 \mathrm{H}, H^{2}, H^{4}\right), 6.82$ $\left(\mathrm{m}, 1 \mathrm{H}, H^{3}\right), 6.97\left(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.02(\mathrm{~d}, J=1.9 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{6 \mathrm{a}}\right),{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.7\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right), 37.8$ $(\mathrm{Me}), 56.4\left(C^{1}\right), 97.5\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=5.6 \mathrm{~Hz}, C_{5} \mathrm{Me}_{5}\right), 114.4\left(\mathrm{~d},{ }^{2} J_{\mathrm{C}-\mathrm{F}}=\right.$ $\left.31.0 \mathrm{~Hz}, C^{4}\right), 120.9\left(C^{6 \mathrm{a}}\right), 121.3\left(C^{2}\right), 122.6\left(C^{6 \mathrm{~b}}\right), 124.1\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}\right.$ $\left.=8.7 \mathrm{~Hz}, C^{3}\right), 141.60\left(\mathrm{~d},{ }^{3} J_{\mathrm{C}-\mathrm{F}}=15.1 \mathrm{~Hz}, C\right), 142.8\left(\mathrm{~m}, C^{5}\right), 166.9$ (d, $\left.{ }^{1} J_{\mathrm{C}-\mathrm{F}}=232.1 \mathrm{~Hz}, C-\mathrm{F}\right), 174.2\left(\mathrm{~d},{ }^{1} J_{\mathrm{C}-\mathrm{Rh}}=54.8 \mathrm{~Hz}, C^{7}\right),{ }^{19} \mathrm{~F}$ $\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-84.7(F) . m / z 427[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}^{103} \mathrm{Rh}[\mathrm{M}-\mathrm{Cl}]^{+}$427.1057, found 427.1049. para-6b-F. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.73$ $\left(\mathrm{s}, 15 \mathrm{H}, \mathrm{C}_{5} M e_{5}\right), 3.99(\mathrm{~s}, 3 \mathrm{H}, M e), 4.68(\mathrm{~d}, J=14.2,1.0 \mathrm{~Hz}, 1 \mathrm{H}$, $\left.H^{1 \mathrm{a}}\right), 4.92\left(\mathrm{~d}, J=14.2 \mathrm{~Hz}, 1 \mathrm{H}, H^{1 \mathrm{~b}}\right), 6.73(\mathrm{dd}, J=10.0,3.0 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{5}\right), 6.76\left(\mathrm{td}, J=9.0,2.8 \mathrm{~Hz}, 1 \mathrm{H}, H^{4}\right), 6.97(\mathrm{~d}, J=1.9 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{6 \mathrm{~b}}\right), 7.02\left(\mathrm{~d}, J=1.9 \mathrm{~Hz}, 1 \mathrm{H}, H^{6 \mathrm{a}}\right), 7.61(\mathrm{dd}, J=8.3,7.0 \mathrm{~Hz}$, $\left.1 \mathrm{H}, H^{3}\right),{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta-125.0(F)$. ESIMS: $m / z 427[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (ESI): Calcd for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{~F}^{103} \mathrm{Rh}[\mathrm{M}$ $-\mathrm{Cl}]^{+}$427.1057, found 427.1049.

## Deuteration studies

An NMR tube was charged with $\mathbf{5 a} / \mathbf{b}-\mathbf{R}(5 \mathrm{mg})$ and $\mathrm{CD}_{3} \mathrm{OD}$ $(0.5 \mathrm{~mL})$. The ${ }^{1} \mathrm{H}$ NMR spectrum was recorded and then NaOAc (4 eq.) was added. The reactions were allowed to sit at
rt overnight. The spectra in $\mathrm{CD}_{3} \mathrm{OD}$ were broad so the samples were evaporated and redissolved in $\mathrm{CDCl}_{3}$. The percentage deuteration was determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy by comparing the relative integrations for $\mathrm{H}^{3}$ and $\mathrm{H}^{5}$ for the paraisomers in the ${ }^{1} \mathrm{H}$ NMR spectra.

## Conflicts of interest

There are no conflicts to declare.

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