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Steric effects on acetate-assisted cyclometallation of *meta*-substituted *N*-phenyl and *N*-benzyl imidazolium salts at [MCl₂Cp*]₂ (M = Ir, Rh)⁺

meta-Substituted N-phenyl, N'-methyl and N-benzyl, N'-methyl imidazolium salts undergo acetate-

assisted 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.

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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 (M = Ir, Rh) centres proceeds from $[M(OAc)_2Cp*]$ which can be accessed by the reaction of [MCl₂Cp*]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 Cp*M (M = Ir, 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

be detected by H/D exchange. The only exceptions to this were *meta*-fluorinated phenyl rings which always favoured the *ortho*-fluorine 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 $[MCl_2Cp^*]_2$ (M = Ir, Rh) on the regioselectivity of cyclometallation of differently *meta*-substituted phenyls (Scheme 1).⁶ We have subsequently examined related reactions with phenylpyrazoles **L3-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 Cp*Ir are faster and less easily reversible than those at Cp*Rh and those with electron







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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 CF_3 and Me the *para* isomer is heavily favoured. With less bulky substituents (R = 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 L2-CF₃, results which we were unable to reproduce. In our study L2-CF₃ 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 [IrCl₂Cp*]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 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 known¹¹ 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'*-methyl imidazolium salts **L4-R** (R = OMe, F, CF₃, CN) which were prepared as shown in Scheme 2 in high yields (72–98%). **L4-OMe**, **L4-F** and **L4-CN** are new compounds, whilst **L4-CF**₃ is known as the iodide salt.¹²

The reactions of L4-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh) were carried out in the presence of NaOAc at 75 °C in dichloroethane; however very low conversions were observed after



Scheme 2 Preparation and NMR labelling scheme of *meta*-substituted *N*-phenyl,*N*'-methyl limidazolium salts L4-R.

heating overnight.¹³ The reactions were repeated in the presence of Et_4NCl^{14} and proceeded slowly even at room temperature and gave high conversions (Scheme 3) and the products **4a/b-R** (R = OMe, CN, CF₃, F) were fully characterised.

Each isomer has a characteristic pattern in the ¹H NMR spectrum, for the *para* isomer H⁴ is a very narrow doublet and H² shows an noe to the Cp* signal. The reactions were repeated and monitored at room temperature (*ca.* 20% conversion) and upon heating (50 °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 $[MCl_2Cp^*]_2$ (M = Ir, Rh) and NMR labelling scheme.

Table 1	Ortho: para ratios of acetate-assisted cyclometallation of meta-substituted ligands [1]-	2 ⁶ 12-R ^{6,7}	and I 3-R ³
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	L1-R		L2-R		L3-R		
R	Ir,	Rh	Ir	Rh	Ir	Rh	
OMe	1:1.7	1:1.7	$1:2.5^{a}$	$1:3.0^{a}$	1:1.4	1:3.9	
Ме	para only	<i>para</i> only	para only	para only ^b	1:10	<i>para</i> only	
CF ₃	para only	para only	para only ^c	para only ^c	<i>para</i> 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 Ir and Rh respectively. However, we found no evidence for *ortho* isomers in the ¹⁹F or ¹H NMR spectra.

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 Table 2
 Ortho:para
 ratios
 of
 acetate-assisted
 cyclometallation
 of

 meta-Substituted ligands
 L4-R
 in DCM/MeOH
 DCM/MeOH</

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

^{*a*} In DCE at 50 °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 L4-R (R = OMe, CN, CF_3) 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 $R = CF_3$ which favours the *para* isomer kinetically and thermodynamically. For the reactions of **L4-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 $R = CF_3$, whilst it was present in substantial quantities for the reactions of **L4-CF₃** suggesting that there is less steric crowding at the metal centre in **4a/b-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'*-methyl imidazolium salts **L5-R** ($R = OMe, CF_3, F$). These were prepared by reaction of *N*-methyl imidazole with an excess of appropriately *meta*-substituted benzyl chloride for 1–2 days. All three salts **L5-R** ($R = OMe, CF_3, F$) were obtained in moderate to good yields (55–87%) and have been reported previously.¹⁶

The cyclometallated complexes **6a/b-R** were prepared in a stepwise manner, transmetallation to form NHC bound complexes **5a/b-R** followed by cyclometallation (Scheme 4).^{11*a*} Thus, **L5-R** (R = OMe, CF_3 , F) was stirred with Ag₂O 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 $[MCl_2Cp^*]_2$ (M = Ir, Rh) (Scheme 4) which after work up gave the new complexes **5a/b-R** (R = OMe, CF_3 , F), in moderate to excellent yields (67–92%).

The ¹H NMR spectra of **5a/b-R** show two mutually coupled doublets at δ 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 **6a/b-R** were prepared in good to excellent yields (68–96%) by reaction of **5a/b-R** (R = OMe, CF₃, F) with NaOAc in DCM : MeOH (4 : 1) at room temperature (Scheme 4). The ¹H NMR spectra of **6a/b-R** show the mutually coupled benzylic proton doublets are closer together (between δ 4.5 and 5.0) than in complexes **5a/b-R**. For both the OMe and CF₃ substituted complexes only the *para*-isomer was



Fig. 1 The molecular structures of **5a-OMe** with 50% ellipsoids. H-atoms omitted for clarity. Selected bond distances Å; Ir-C(1), 2.047 (9), Ir-Cl(1) 2.417(2), Ir-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 5a/b-R

Entry	R Ir		Rh		
		1 day	10 days (conversion)	1 day	10 days (conversion)
1	OMe	1:1	1:10(95%)	1:1	1:>30(50%)
2	CF_3	<i>para</i> -only	para-only (33%)	<i>para</i> -only	para-only (15%)
3	F	10:1	$10:1(100)^{a}$	10:1	$9:1(100)^{a}$

"After heating in DCM/MeOH (4/1) at 50 °C for 2 days.

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 CDCl₃, 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 **5a/b-OMe** (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 *para*isomers **6a/b-OMe** from the preparative reactions in DCM:MeOH (4:1). In the case of **5a/b-CF**₃ all the ¹H 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 **5a/b-F** led to the formation of **6a/b-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 °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.^{3-4,7,8b} Thus, 5a/b-OMe, and 5b-CF₃ were reacted with NaOAc in CD₃OD and the percentage D-incorporation was determined by integration and the results are shown in Scheme 5.¹⁷ For 5a/b-OMe, a high p-incorporation (>80%) was observed in the para isomer products, para-6a-OMe and para-6b-OMe. 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 p-incorporation was detected for the cyclometallation of 5b-CF₃. 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-6b-CF₃ is exergonic so not easily reversible.

Comparing the regioselectivity of the phenyl and benzyl complexes the phenyl-NHC complexes 4a/b-R even for the largest substituent (R = CF₃) show some *ortho*-isomer (25 and 14% for Ir and Rh respectively) and about 30% *ortho*-isomer was seen for R = OMe with both metals after heating. Whereas, with the benzyl complexes 6a/b-R for R = CF₃ only the *para*



Scheme 5 Deuterium incorporation experiments with 5a/b-OMe and 5b-CF₃.



Fig. 2 Yaw distortion of chelating NHC complexes.

isomer is observed and for R = 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° whilst the benzyl complexes (n = 1) the yaw angles are much less at 2.1 to 3.4°.^{18b} Interestingly the lower distortion in NHC coordination in the benzyl complexes leads the ortho H to be closer to the metal M···H distances 3.02 to 3.07 Å for benzyl complexes compared to 3.21 to 3.25 Å for the phenyl complexes. There are much smaller differences between 5-membered rings with different directing groups. The observation of a second species with L4-CF₃ 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-R** respectively. *N*-Phenyl limidazolium salts **L4-R** (R = OMe, CN, CF₃, F) underwent cyclometallation easily in the presence of NaOAc¹⁴ and no intermediate non-cyclometallated NHC bound complexes were observed. The *para*-isomers were favoured thermodynamically over the *ortho* with both metals for R = OMe, CN, and particularly for the more bulky CF₃, whilst at shorter reaction times the selectivity was less. For **L4-F** 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 (R = OMe, CF3, 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 6a/b-OMe 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 $5a/b-CF_3$ none of the *ortho*-isomer could be detected even at low conversions likely due to the bulkier CF₃ group. Therefore, steric effects control regioselectivity with the *para*-isomer being the major one for cyclometallation of 5a/b-R (R = OMe, CF₃). The selectivity for the *para*-isomer observed in six membered ring complexes 6a/b-R is larger compared to the formation of the five-membered ring complexes 4a/b-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.), Cs_2CO_3 (2 eq.), CuO_2 (10 mol%) and MeCN or DMF (5–10 mL) were added to a Schlenk flask, sealed with a screw-cap, placed under N₂ atmosphere, partially evacuated, transferred to an oil bath and stirred at 100–120 °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 mL), methyl trifluoromethanesulfonate (1.1 eq.), capped and stirred at rt for 2–4 h. The solvent was removed by rotary evaporation and the product was either precipitated from DCM/Et₂O mixture or washed with Et₂O to yield imidazolium salt **L4-R**.

Synthesis of L4-OMe. Following the general procedure, a mixture of 1-(3-methoxyphenyl)-1H-imidazole (174)mg. 1.002 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.125 mL, 181 mg, 1.105 mmol), capped was stirred at rt for 4 h. The formed oil was washed with $Et_2O(3 \times 5 \text{ mL})$ to yield L4-OMe as a colourless oil (244 mg, 72%). ¹H NMR (400 MHz, CD₃CN): δ 3.88 (s, 3H, OMe), 3.97 (s, 3H, Me), 7.14 (m, 1H, H), 7.19-7.24 (m, 2H, H^1 , H^4), 7.51 (t, J = 8.4 Hz, 1H, H^2), 7.57 (t, J = 1.9 Hz, 1H, H^{5b}), 7.80 (t, J = 2.0 Hz, 1H, H^{5a}), 9.23 (s, 1H, H^{6}), ${}^{13}C{}^{1}H$ NMR (126 MHz, CD₃CN): δ 37.3 (*Me*), 56.8 (OMe), 109.0 (C^4), 115.0 (C^1), 116.7 (C^3), 121.8 (d, J = 320.2 Hz, OTf), 122.3 (C^{5a}), 125.3 (C^{5b}), 132.2 (C^2), 136.6 (C^6), 136.8, 161.8. ${}^{19}F_1^{(1)}H$ NMR (376 MHz, CD₃CN): δ –79.3 (OTf). ESIMS: m/z 189 [M]⁺. HRMS (ESI): Calcd for C₁₁H₁₃N₂O [M]⁺ 189.1028, found 189.1028.

Synthesis of L4-CN. Following the general procedure, a mixture of 3-(1*H*-imidazol-1-yl)benzonitrile (253 mg, 1.497 mmol), dry DCM (6 mL), methyl trifluoromethanesulfonate (0.19 mL, 278 mg, 1.680 mmol) was stirred at rt for 2.5 h. The product was precipitated from DCM/Et₂O to yield L4-CN as a white solid (412 mg, 1.237 mmol, 83%). ¹H NMR (400 MHz, CD₃OD): δ 4.08 (s, 3H, *Me*), 7.84 (m, 2H, *H*⁴, *H*^{5b}),

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7.97 (dt, J = 7.9, 1.3 Hz, 1H, H^1), 8.05 (ddd, J = 8.3, 2.4, 1.1 Hz, 1H, H^3), 8.12 (t, J = 1.8 Hz, 1H, H^{5b}), 8.20 (t, J = 1.7 Hz, 1H, H^4) 9.51 (s, 1H, H^6), $^{13}C{}^{1}H$ NMR (101 MHz, CD₃OD): δ 37.2 (*Me*), 115.6, 118.3, 121.9 (d, $^{1}J_{C-F} = 318.7$ Hz, *OTf*), 123.0 (C^{5a}), 126.1 (C^{5b}), 127.3 (C^4), 128.2 (C^3), 132.9 (C^2), 134.9 (C^1), 137.2, 137.8 (C^6), $^{19}F{}^{1}H$ NMR (376 MHz, CD₃OD): δ –80.0 (*OTf*). ESIMS: m/z 227 [M]⁺. HRMS (ESI): Calcd for C₁₁H₁₀N₃ [M]⁺ 184.0875, found 184.0883.

Synthesis of L4-CF₃. Following the general procedure, a mixture of 1-(3-trifluoromethylphenyl)-1H-imidazole (213 mg, 1.007 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.130 mL, 189 mg, 1.150 mmol) was stirred at rt for 3 h. The product was precipitated from a DCM/Et₂O to yield L4-CF₃ as a white solid (306 mg, 81%). ¹H NMR (400 MHz, CD₃OD): δ 4.06 (s, 3H, Me), 7.81 (d, J = 2.2 Hz, 1H, H^{5b}), 7.88 (m, 1H, H^{2}), 7.94 (d, J = 7.8 Hz, 1H, H^3), 8.01 (d, J = 8.2 Hz, 1H, H^1), 8.11 (s, 1H, H^4), 8.15 (d, J = 1.2 Hz, 1H, H^{5a}), 9.55 (s, 1H, H^6), ${}^{13}C{}^{1}H$ NMR (126 MHz, CD₃OD): δ 37.1 (*Me*), 120.9 (q, ${}^{3}J_{C-F}$ = 4.2 Hz, C^{4}), 121.8 (q, ${}^{1}J_{C-F}$ = 319.2 Hz, *OTf*), 123.1 (C^{5a}), 124.8 (q, ${}^{1}J_{C-F}$ = 272.0 Hz, CF_3), 126.0 (C^{5b}), 127.5 (C^1), 128.1 (q, ${}^{3}J_{C-F}$ = 4.0 Hz, C^3), 132.8 (C^2) 133.8 (q, ${}^2J_{C-F}$ = 33.5 Hz, C-CF₃), 137.2 (q, ${}^{4}J_{C-F} = 3.0 \text{ Hz}$, 137.9 (C^{6}), ${}^{19}F{}^{1}H$ NMR (376 MHz, CD₃OD): δ -80.1 (*OTf*), -64.3 (*CF*₃). ESIMS: m/z 227 [M]⁺. HRMS (ESI): Calcd for $C_{11}H_{10}N_2F_3[M]^+$ 227.0796, found 227.0796.

Synthesis of L4-F. Following the general procedure, a mixture of 1-(3-fluorophenyl)-1H-imidazole (166)mg, 1.022 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.130 mL, 189 mg, 1.150 mmol) was stirred at rt for 2.5 h. The formed oil was washed with $Et_2O(3 \times 5 mL)$ to yield L4-F as a colourless oil (325 mg, 98%). ¹H NMR (400 MHz, CD₃OD): δ 4.04 (s, 3H, *Me*), 7.34 (tdd, *J* = 8.4, 8.4, 2.4, 1.0 Hz, 1H, H^3), 7.57 (m, 2H, H^1 , H^4), 7.65 (td, J = 8.3, 5.6 Hz, 1H, H^2), 7.76 (t, J = 1.8 Hz, 1H, H^{5b}), 8.05 (t, J = 2.0 Hz, 1H, H^{5a}), 9.47 (s, 1H, H^6), ${}^{13}C{}^{1}H$ NMR (126 MHz, CD₃OD): δ 37.1 (*Me*), 111.2 (d, ${}^{2}J_{C-F} = 27.1$ Hz, C^{4}), 118.2 (d, ${}^{2}J_{C-F} = 21.1$ Hz, C^{3}), 119.3 (d, ${}^{4}J_{C-F}$ = 3.0 Hz, C^{1}), 121.9 (d, ${}^{1}J_{C-F}$ = 318.2 Hz, OTf), 122.8 (C^{5a}), 125.9 (C^{5b}), 133.4 (d, ${}^{3}J$ = 9.0 Hz, C^{2}), 137.5 (C^{6}), 137.6 (d, ${}^{3}J_{C-F}$ = 10.0 Hz), 164.5 (d, ${}^{1}J_{C-F}$ = 249.0 Hz, C-F), ${}^{19}F{}^{1}H{}$ NMR (376 MHz, CD₃OD): δ -111.0 (F), -80.0 (OTf). ESIMS: m/z 177 $[M]^+$. HRMS (ESI): Calcd for $C_{10}H_{10}N_2F[M]^+$ 177.0828, found 177.0832

General procedure for cyclometallation of *meta*-substituted phenylimidazolium salts L4-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh) in DCE

 $[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq.), NaOAc (8 eq.) were placed in an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under N₂ atmosphere. DCE (2 mL) was added and mixture stirred for another 15 min. The appropriate imidazolium salt **L4-R** (2.1 eq.) and Et₄NCl (2 eq.) was added, and the Schlenk flask transferred to a preheated oil bath and stirred at 50 °C for 1–2 h, then at 70 °C for 1–6 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 DCM/hexane. General procedure for cyclometallation of *meta*-substituted phenylimidazolium salts L4-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh) in DCM : MeOH

 $[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq., 0.0251 mmol), NaOAc (8 eq.) were placed in an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under N₂ atmosphere. Dry DCM (1.6 mL) and MeOH (0.4 mL) were added and the mixture stirred for another 15 min. The appropriate imidazolium salt (2.1 eq.) and Et₄NCl (2 eq.) was added and the mixture stirred at rt overnight and then heated to 50 °C overnight. The reactions were monitored by ¹H NMR spectroscopy by comparing the relative integrations of the appropriate signals (H³ of the *ortho*-isomers compared to the H³ of the *para*-isomers).

Synthesis of 4a-OMe. Following the general procedure, a mixture of [IrCl₂Cp*]₂ (20 mg, 0.0251 mmol), NaOAc (17 mg, 0.207 mmol), L4-OMe (18 mg, 0.0533 mmol), Et₄NCl (9 mg, 0.053 mmol), in DCE (2 mL) was heated to 50 °C for 2 h, then heated further at 70 °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 mg, 94%). ortho-4a-OMe. ¹H NMR (400 MHz, CDCl₃): δ 1.85 (s, 15H, C₅Me₅), 3.82 (s, 3H, OMe), 3.97 (s, 3H, Me), 6.54 (dd, J = 7.9, 1.1 Hz, 1H, H^3), 6.83 $(dd, J = 7.7, 1.1 Hz, 1H, H^1)$, 6.93 $(t, J = 8.3 Hz, 1H, H^2)$, 6.95 (d, J = 100 Hz)J = 2.2 Hz, 1H, H^{5b}), 7.31 (d, J = 2.2 Hz, 1H, H^{5a}). ESIMS: m/z513 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{193}Ir [M - Cl]^+$ 515.1674, found 515.1675. para-4a-OMe. ¹H NMR (400 MHz, CDCl₃): δ 1.79 (s, 15H, C₅Me₅), 3.80 (s, 3H, OMe), 3.98 (s, 3H, *Me*), 6.65 (dd, J = 8.2, 2.6 Hz, 1H, H^3), 6.76 (d, J = 2.4 Hz, 1H, H^4), 6.97 (d, J = 2.2 Hz, 1H, H^{5b}), 7.29 (d, J = 2.2 Hz, 1H, H^{5a}), 7.60 (d, J = 8.3 Hz, 1H, H^2), ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃): δ 9.74 (C_5Me_5), 37.0 (Me), 55.5 (OMe), 90.6 (C_5Me_5), 98.6 (C^4), 110.8 (C^3) , 114.8 (C^{5a}) , 121.3 (C^{5b}) , 131.2, 136.1 (C^2) , 146.9 (C^1) , 156.3, 166.6 (C^6). ESIMS: m/z 513 [M – Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{193}Ir [M - Cl]^+$ 515.1674, found 515.1675.

Synthesis of 4b-OMe. Following the general procedure, a mixture of [RhCl₂Cp*]₂ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), L4-OMe (18 mg, 0.053 mmol), Et₄NCl (9 mg, 0.054 mmol), in DCE (2 mL) was stirred at 50 °C for 1 h, then at 70 °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 mg, 61%). ortho-4b-OMe. ¹H NMR (400 MHz, CDCl₃): δ 1.68 (s, 15H, C₅Me₅), 3.83 (s, 3H, OMe), 3.97 (s, 3 H, Me), 6.58 (dd, J = 8.0, 0.9 Hz, 1H, H^3), 6.78 $(dd, J = 7.7, 1.0 Hz, 1H, H^{1}), 6.98 (d, J = 2.0 Hz, 1H, H^{5b}), 6.99$ $(t, J = 7.8 \text{ Hz}, 1\text{H}, H^2)$, 7.37 $(d, J = 2.0 \text{ Hz}, 1\text{H}, H^{5a})$, ${}^{13}\text{C}{}^{1}\text{H}$ NMR (101 MHz, CDCl₃): δ 9.9 (C₅Me₅), 37.0 (Me), 56.3 (OMe), 97.9 (d, ${}^{1}J_{C-Rh} = 5.2$ Hz, $C_{5}Me_{5}$), 104.9 (C^{1}), 108.9 (C^{3}), 115.9 (C^{5a}), 121.9 (C^{5b}), 124.0 (C^{2}), 146.1, 145.6 (d, ${}^{1}\!J_{C-Rh}$ = 42.1 Hz, C^4), 156.7, 184.2 (d, ${}^{1}J_{C-Rh}$ = 55.5 Hz, C^6). ESIMS: m/z 425 [M – Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{103}Rh [M - Cl]^+$ 425.1100, found 425.1100. para-4b-OMe. ¹H NMR (400 MHz, CDCl₃): δ 1.70 (s, 15H, C₅Me₅), 3.78 (s, 3H, OMe), 4.01 (s, 3H, *Me*), 6.66 (dd, J = 8.3, 2.6 Hz, 1H, H^3), 6.71 (d, J = 2.5 Hz, 1H, H^4), 6.98 (d, J = 2.1 Hz, 1H, H^{5b}), 7.35 (d, J = 2.0 Hz, 1H, H^{5a}),

7.63 (d, J = 8.3 Hz, 1H, H^2), ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 9.9 (C₅ Me_5), 37.0 (Me), 55.5 (OMe), 97.2 (d, ¹ $J_{C-Rh} = 5.0$ Hz, C_5Me_5), 99.0 (C^4), 110.5 (C^3), 115.1 (C^{5a}), 122.2 (C^{5b}), 137.2 (C^2), 146.1, 146.6 (d, ¹ $J_{C-Rh} = 35.7$ Hz, C^1), 165.0, 184.2 (d, $J_{C-Rh} = 55.5$ Hz, C^6). ESIMS: m/z 425 [M–Cl]⁺. HRMS (ESI): Calcd for C₂₁H₂₆N₂O¹⁰³Rh [M–Cl]⁺ 425.1100, found 425.1100.

Synthesis of 4a-CN. Following the general procedure, a mixture of [IrCl₂Cp*]₂ (20 mg, 0.025 mmol), NaOAc (16 mg, 0.196 mmol), L4-CN (18 mg, 0.0526 mmol), Et₄NCl (9 mg, 0.053 mmol), in DCE (2 mL) was stirred at 50 °C for 1.5 h, then heated further to 70 °C for 1 h. The product was purified by crystallisation from DCM/hexane to yield 4a-CN (ortho: para ratio 1:2.0) as an orange-yellow powder (24 mg, 90%). ortho-**4a-CN**. ¹H NMR (400 MHz, CDCl₃): δ 1.83 (s, 15H, C₅Me₅), 3.98 (s, 3H, Me), 7.00 (t, J = 7.8 Hz, 1H, H^2), 7.01 (d, J = 2.6 Hz, 1H, H^{5b}), 7.21 (dd, J = 7.8, 1.2 Hz, 1H, H^{1}), 7.33 (d, J = 2.2 Hz, 1H, H^{5a}), 7.37 (dd, J = 7.7, 1.2 Hz, 1H, H^{3}), ${}^{13}C{}^{1}H$ NMR (101 MHz, $CDCl_3$: δ 9.6 (C_5Me_5), 36.8 (*Me*), 92.6 (C_5Me_5), 94.8, 112.5 (C^1), 115.6 (C^{5a}) , 120.3, 121.6 (C^{2}) , 122.0 (C^{5b}) , 131.2 (C^{3}) , 148.0, 151.1 (C^4), 167.9 (C^6). ESIMS: m/z 510 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{23}^{193}IrN_3 [M - Cl]^+$ 510.1521, found 510.1523. ESIMS: m/z 551 $[M - Cl + MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4^{193}Ir [M - Cl + MeCN]^+ 551.1787$, found 551.1790. *para*-4a-CN. ¹H NMR (400 MHz, CDCl₃): δ 1.79 (s, 15H, C₅Me₅), 3.99 (s, 3H, Me), 7.03 (d, J = 2.2 Hz, 1H, H^{5b}), 7.21 (dd, J = 7.7Hz, 1.7, 1H, H^3), 7.32 (d, J = 1.7 Hz, 1H, H^4), 7.34 (d, J = 2.1 Hz, 1H, H^{5a}), 7.88 (d, J = 7.7 Hz, 1H, H^2), ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃): δ 9.7 (C₅Me₅), 37.0 (Me), 91.8 (C₅Me₅), 104.6, 112.6 (C^4) , 114.9 (C^{5a}) , 122.2 (C^{5b}) , 122.6, 129.0 (C^3) , 137.2 (C^2) , 147.3, 153.4 (C^1), 166.2 (C^6). ESIMS: m/z 510 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{23}^{193}IrN_3$ [M - Cl]⁺ 510.1521, found 510.1523. ESIMS: m/z 551 [M - Cl + MeCN]⁺. HRMS (ESI): Calcd for $C_{23}H_{26}N_4^{193}Ir [M - Cl + MeCN]^+$ 551.1787, found 551.1790.

Synthesis of 4b-CN. Following the general procedure, a mixture of [RhCl₂Cp*]₂ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), L4-CN (18 mg, 0.054 mmol), Et₄NCl (9 mg, 0.054 mmol), in DCE (2 mL) was stirred at 50 °C for 1.5 h, then heated to 70 °C for 1 h. The product was purified by precipitation from DCM/hexane to yield 4b-CN (ortho: para ratio 1:1.9) as an orange-yellow powder (13 mg, 58%). ortho-4b-CN. ¹H NMR (400 MHz, CDCl₃): δ 1.75 (s, 15H, C₅Me₅), 3.99 (s, 3H, *Me*), 7.01 (d, J = 2.2 Hz, 1H, H^{5b}), 7.05 (t, J = 7.7 Hz, 1H, H^{2}), 7.17 (dd, J = 7.8, 1.3 Hz, 1H, H^1), 7.40 (m, 1H, H^3), 7.41 (d, J =2.0 Hz, 1H, H^{5a}), ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃): δ 9.7 (C_5Me_5) , 37.1 (*Me*), 94.0, 98.8 (d, ${}^{1}J_{C-Rh} = 4.8$ Hz, C_5Me_5), 113.1 (C^{1}) , 116.1 (C^{5a}) , 122.0, 123.1 (C^{2}) , 123.3 (C^{5b}) , 130.7 (C^{3}) , 147.3, 167.4 (d, ${}^{1}J_{C-Rh}$ = 38.2 Hz, C^{4}), 185.1 (d, ${}^{1}J_{C-Rh}$ = 54.8 Hz, C^{6}). ESIMS: m/z 420 $[M - Cl]^{+}$. HRMS (ESI): Calcd for $C_{21}H_{23}N_3^{103}Rh [M - Cl]^+$ 420.0947, found 420.0947. ESIMS: m/z 461 $[M - Cl + MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4^{103}Rh [M - Cl + MeCN]^+$ 461.1213, found 461.1213. *para*-4**b**-CN. ¹H NMR (400 MHz, CDCl₃): δ 1.71 (s, 15H, C₅Me₅), 4.00 (s, 3H, Me), 7.03 (d, J = 2.2 Hz, 1H, H^{5b}), 7.27 (m, 1H, H^{3}), 7.27 (br.s, 1H, H^4), 7.41 (d, J = 2.1 Hz, 1H, H^{5a}), 7.94 (dd, J =8.1, 0.9 Hz, 1H, H^2), ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 9.8

(C₅*Me*₅), 37.1 (*Me*), 98.2 (d, ${}^{1}J_{C-Rh} = 5.6$ Hz, $C_{5}Me_{5}$), 105.5, 112.8 (C^{4}), 115.4 (C^{5a}), 120.1, 123.1 (C^{5b}), 128.0 (C^{3}), 138.4 (C^{2}), 146.6, 170.3 (d, ${}^{1}J_{C-Rh} = 35.8$ Hz, C^{1}), 183.7 (d, ${}^{1}J_{C-Rh} = 55.6$ Hz, C^{6}). Calcd for C₂₁H₂₃N₃ ¹⁰³Rh [M - Cl]⁺ 420.0947, found 420.0947. ESIMS: m/z 461 [M - Cl + MeCN]⁺. HRMS (ESI): Calcd for C₂₃H₂₆N₄ ¹⁰³Rh [M - Cl + MeCN]⁺ 461.1213, found 461.1213.

Synthesis of 4a-CF₃. Following the general procedure, a mixture of [IrCl₂Cp*]₂ (20 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), L4-CF₃ (20 mg, 0.0532 mmol), Et₄NCl (9 mg, 0.055 mmol), in DCE (2 mL) was stirred first at rt for 24 h, then heated to 50 °C for 1 h and then at 70 °C for a further 1 h. The product was purified by crystallisation from DCM/ hexane to yield single regioisomer para-4-CF₃ as orange crystals (19 mg, 64%). para-4a-CF₃. ¹H NMR (400 MHz, CDCl₃): δ 1.80 (s, 15H, C_5Me_5), 3.97 (s, 3H, Me), 7.02 (d, J = 2.2 Hz, 1H, H^{5b}), 7.22 (br. d, J = 7.8 Hz, 1H, H^{3}), 7.30 (d, J = 1.2 Hz, 1H, H^4), 7.38 (d, J = 2.2 Hz, 1H, H^{5a}), 7.87 (d, J = 7.8 Hz, 1H, H^2), ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 9.7 (C₅Me₅), 37.0 (Me), 91.4 $(C_5 \text{Me}_5)$, 106.8 (q, ${}^{3}J_{\text{C-F}}$ = 4.0 Hz, C^4), 114.9 (C^{5a}), 121.8 (C^{5b}), 122.1 (q, ${}^{3}J_{C-F} = 3.2$ Hz, C^{3}), 124.4 (q, ${}^{2}J_{C-F} = 31.2$ Hz, C-CF₃), 125.0 (q, ${}^{1}J_{C-F}$ = 271.0, CF_{3}), 136.6 (C^{2}), 146.9, 148.9 (C^{1}), 166.3 (C^{6}) , ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -61.5 (CF₃). ESIMS: m/z 553 [M – Cl]⁺. HRMS (ESI): Calcd for C₂₁H₂₃N₂F₃¹⁹³Ir [M – Cl]⁺ 553.1643, found 553.1645.

Synthesis of 4b-CF₃. Following the general procedure, a mixture of $[RhCl_2Cp^*]_2$ (20 mg, 0.032 mmol), NaOAc (21 mg, 0.259 mmol), L4-CF₃ (25 mg, 0.066 mmol), in DCE (2.5 mL) was stirred first at rt for 24 h, then heated to 50 °C for 1 h and then at 70 °C for a further 1 h. The product was purified by crystallisation from DCM/hexane to yield *para*-4b-CF₃ as yellow crystals (25 mg, 78%).

Para-4b-CF₃. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.71 (s, 15H, C₅Me₅), 4.00 (s, 3H, Me), 7.10 (d, J = 2.2 Hz, 1H, H^{5b}), 7.28 (d, J = 7.8 Hz, 1H, H^{3}), 7.33 (d, J = 1.5 Hz, 1H, H^{4}), 7.49 (d, J = 2.0 Hz, 1H, H^{5a}), 7.92 (d, J = 7.8 Hz, 1H, H^{2}), ¹³C{¹H} NMR (101 MHz, CD₂Cl₂): δ 10.2 (C₅Me₅), 37.6 (Me), 98.5 (d, ¹ $J_{C-Rh} = 4.8$ Hz, C_5 Me₅), 107.5 (q, ³ $J_{C-F} = 4.0$ Hz, C^4), 115.7 (C^{5a}), 121.5 (q, ⁴ $J_{C-F} = 2.4$ Hz, C^3), 123.6 (C^{5b}), 125.4 (q, ² $J_{C-F} = 31.8$ Hz, C-CF₃), 125.6 (q, ¹ $J_{C-F} = 271.0$, CF_3), 138.5 (C^2), 147.1, 167.1 (d, ¹ $J_{C-Rh} = 36.6$ Hz, C^1), 184.7 (d, ¹ $J_{C-Rh} = 55.6$ Hz, C^6), ¹⁹F{¹H} NMR (376 MHz, CD₂Cl₂): δ -61.8 (CF₃). ESIMS: m/z 463 [M – Cl]⁺. HRMS (ESI): Calcd for C₂₁H₂₃N₂F₃¹⁰³Rh [M – Cl]⁺ 463.0868, found 463.0862. Anal Calcd for C₂₁H₂₃N₂F₃CIRh [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 $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), NaOAc (16 mg, 0.200 mmol), L4-F (18 mg, 0.055 mmol), Et₄NCl (9 mg, 0.055 mmol), DCE (2 mL) was heated to 70 °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**. ¹H NMR (400 MHz, CDCl₃): δ 1.80 (d, 15 H, C₅*Me*₅), 3.97 (s, 3H, *Me*), 6.72 (m, 1H, *H*³), 6.94 (m, 2H, *H*¹,*H*²), 6.97 (d, *J* = 2.1 Hz, 1H, *H*^{5b}), 7.32 (d, *J* = 2.1 Hz, 1H, *H*^{5a}), ¹³C {¹H} NMR (101 MHz, CDCl₃): δ 9.9 (d, *J*_{C-F} = 2.7 Hz, C₅*Me*₅), 3.6.9 (*Me*), 91.6 (*C*₅Me₅), 106.6 (d, ⁴*J*_{C-F} = 2.7 Hz, *C*¹), 112.1 (d,

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 ${}^{2}J_{C-F}$ = 29.4 Hz, C^{3}), 115.5 (C^{5a}), 121.4 (C^{5b}), 123.8 (d, ${}^{3}J_{C-F}$ = 8.2 Hz, C^2), 126.3 (d, ${}^{2}J_{C-F}$ = 44.6 Hz, C^4), 148.5 (d, ${}^{3}J_{C-F}$ = 18.3 Hz), 166.5 (C^6), 167.8 (d, ${}^{1}J_{C-F}$ = 235.0 Hz, C-F), ${}^{19}F{}^{1}H$ NMR (376 MHz, CDCl₃): δ -94.9 (F). ESIMS: m/z 503 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{20}H_{23}N_2F^{193}Ir [M - Cl]^+$ 503.1674, found 503.1676. ESIMS: m/z 544 $[M - Cl + MeCN]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_3F^{193}Ir [M - Cl + MeCN]^+$ 544.1740, found 544.1744. *para*-4a-F. ¹H NMR (400 MHz, CDCl₃): δ 1.79 (s, 15H, C₅Me₅), 3.99 (s, 3H, Me), 6.78 (ddd, J = 9.8, 8.3, 2.7 Hz, 1H, H^3), 6.87 (dd, J = 9.5, 2.6 Hz, 1H, H^4), 6.97 (d, J = 2.1 Hz, 1H, H^{5b}), 7.27 (d, J = 2.1 Hz, 1H, H^{5a}), 7.64 (dd, J = 8.3, 6.5 Hz, 1H, H^2), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -122.9 (F). ESIMS: m/z 503 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{20}H_{23}^{-193}IrN_2F[M - M_2]^{-193}$ Cl]⁺ 503.1674, found 503.1676. ESIMS: m/z 544 [M - Cl + MeCN]⁺. HRMS (ESI): Calcd for $C_{22}H_{26}N_3F^{193}Ir$ [M – Cl + MeCN]⁺ 544.1740, found 544.1744.

Synthesis of 4b-F. Following the general procedure, a mixture of [RhCl₂Cp*]₂ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), L4-F (17 mg, 0.052 mmol), Et₄NCl (9 mg, 0.053 mmol), DCE (2 mL) was heated to 70 °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 mg, 59%).

Ortho-4b-F. ¹H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 15H, C_5Me_5 , 3.98 (s, 3H, Me), 6.72 (td, J = 8.0, 1.0 Hz, 1H, H^3), 6.92 $(dd, J = 7.6, 1.0 Hz, 1H, H^1), 6.98 (td, J = 7.8, 5.4 Hz, 1H, H^2),$ 6.98 (d, J = 2.1 Hz, 1H, H^{5b}), 7.39 (d, J = 2.1 Hz, 1H, H^{5a}), ${}^{13}C$ {¹H} NMR (101 MHz, CDCl₃): δ 10.0 (d, ¹*J*_{C-F} = 1.6 Hz, C₅*Me*₅), 37.1 (*Me*), 98.2 (d, ${}^{1}J_{C-Rh} = 5.6$ Hz, $C_{5}Me_{5}$), 107.1 (C^{1}), 112.3 (d, ${}^{2}J_{C-F} = 29.4 \text{ Hz}, C^{3}$, 115.9 (C^{5a}), 122.3 (C^{5b}), 124.4 (d, ${}^{3}J_{C-F} = 7.9$ Hz, C²) 141.1 (dd, ${}^{2}J_{C-Rh,C-F}$ = 39.7, 10.3 Hz, C⁴), 147.9 (d, ${}^{3}J_{C-F}$ = 19.1 Hz), 168.3 (d, ${}^{1}\!J_{\rm C-F}$ = 232.9 Hz, C–F), 183.9 (d, ${}^{1}\!J_{\rm C-Rh}$ = 54.8 Hz, C^6), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -93.9 (F). ESIMS: m/z 413 $[M - Cl]^+$. HRMS (ESI): Calcd for C₂₀H₂₃N₂FRh $[M - Cl]^+$ 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 °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 mg, 3.049 mmol), 3-methoxybenzyl chloride (373 mg, 2.382 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 55 °C for 20 h. L5-OMe was obtained as a white sticky solid (480 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ 3.65 (s, 3H, OMe), 3.93 (s, 3H, Me), 5.41 (s, 2H, H^1), 6.72 (dd, J = 8.2, 2.3 Hz, 1H, H^4), 6.87 (d, J = 7.6 Hz, 1H, H^2), 6.93 (br. s, 1H, H^5), 7.12 (t, J = 7.9 Hz, 1H, H^3), 7.41 (s, 1H, H^{6b}), 7.56 (s, 1H, H^{6a}), 10.46 (s, 1H, H^7), ${}^{13}C{}^{1}H$ NMR (125 MHz, CDCl₃): δ 36.1 (Me), 52.6 (C¹), 55.1 (OMe), 114.0 (C^5) , 114.4 (C^4) , 120.5 (C^2) , 121.6 (C^{6a}) , 123.4 (C^{6b}) , 130.0 (C^3) , 134.4 (CCH₂), 137.1 (C^7), 159.7 (C-OMe). ESIMS: m/z 203 [M –

Cl]⁺. HRMS (ESI): Calcd for C₁₂H₁₅N₂O [M]⁺ 203.1184, found 203.1186.

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Synthesis of L5-CF₃. Following the general procedure, N-methylimidazole (159 mg, 1.939 mmol), 3-trifluoromethylbenzyl chloride (563 mg, 2.893 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 55 °C for 1 day. Additional portion of 3-trifluoromethylbenzyl chloride (188 mg, 0.965 mmol) was added and mixture stirred at 65 °C for 1 day. L5-CF₃ was obtained as a white sticky solid (294 mg, 55%). ¹H NMR (400 MHz, CDCl₃): δ 3.84 (s, 3H, Me), 5.59 (s, 2H, H^1), 7.30 (m, 1H, H^3), 7.38 (m, 1H, H^4), 7.49 (br s, 1H, H^{6b}), 7.58 (br s, 1H, H^{ab}), 7.67 (m, 2H, H², H⁵), 10.37 (m, 1H, H^{7}), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 36.0 (*Me*), 51.6 (C^{1}), 122.0 (C^{6a}), 123.2 (q, ${}^{1}J_{C-F}$ = 273.1 Hz, CF_{3}), 123.5 (C^{6b}), 125.2 (C^5) , 125.6 (C^4) , 129.5 (C^3) , 130.6 (q, ${}^2J_{C-F} = 33.1$ Hz, C-CF₃), 132.2 (C^2), 134.3 (CCH_2), 137.0 (C^7), ¹⁹F{¹H} NMR (376 MHz, $CDCl_3$: δ -62.4 (CF₃). ESIMS: m/z 241 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{12}H_{12}F_3N_2[M]^+$ 241.0953, found 241.0960.

Synthesis of L5-F. Following the general procedure, N-methylimidazole (165 mg, 2.010 mmol), 3-fluorobenzyl chloride (404 mg, 2.793 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 60 °C for 24 h. L5-F was obtained as a pale yellow oil (396 mg, 87%). ¹H NMR (400 MHz, CD₃OD): δ 3.96 (s, 3H, Me), 5.48 (s, 2H, H¹), 7.16 $(tdd, J = 8.7, 2.2, 0.7 Hz, 1H, H^4)$, 7.25 (dt, J = 9.5, 2.0 Hz, 1H, 1H) H^{5}), 7.30 (br. d, J = 8.3, 1H, H^{3}), 7.47 (td, J = 8.0, 5.7 Hz, 1H, H^{2}), 7.63 (d, J = 2.0 Hz, 1H, H^{6b}), 7.67 (d, J = 2.0 Hz, 1H, H^{6a}), 9.13 (s, 1H, H^7), ¹³C{¹H} NMR (101 MHz, CD₃OD): δ 36.8 (*Me*), 53.4 (C^1), 116.7 (d, ${}^2J_{C-F}$ = 23.0 Hz, C^5), 117.2 (d, ${}^2J_{C-F}$ = 20.7 Hz, C^4), 123.8 (C^{6a}), 125.5 (C^{6b}), 125.7 (d, ${}^4J_{C-F}$ = 3.2 Hz, C^2), 132.5 (d, ${}^{3}J_{C-F}$ = 7.9 Hz, C^{3}), 138.0 (d, ${}^{3}J_{C-F}$ = 7.2 Hz, CCH_{2}), 138.1 (C^7), 164.6 (d, ${}^1J_{C-F}$ = 246.4 Hz, C-F). ${}^{19}F{}^{1}H$ NMR (376 MHz, CD₃OD): δ -113.7 (F). ESIMS: m/z 191 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{11}H_{12}FN_2$ [M]⁺ 191.0985, found 191.0982.

General procedure for complexation of meta-substituted benzylimidazolium salts L5-R with [MCl₂Cp*]₂ (M = Ir, Rh)

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 Ag₂O (2.2 eq.), capped, purged with N2. Dry DCM (2.5 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 mL) and added to an N2 purged Schlenk flask wrapped in aluminium foil, followed by addition of $[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq.). The reaction mixture was stirred at rt for 1-2 h, filtered through Celite, the solvent removed by rotary evaporation and the final product 5a/b-R obtained by precipitation/crystallisation from DCM/Et₂O or DCM/hexane.

Synthesis of 5a-OMe. Following the general procedure, a mixture of L5-OMe (58 mg, 0.243 mmol), Ag₂O (59 mg, 0.254 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[IrCl_2Cp^*]_2$ (91 mg, 0.114 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from

DCM/hexane yielded **5a-OMe** as yellow crystals (99 mg, 72%).¹H NMR (400 MHz, CDCl₃): δ 1.62 (s, 15H, C₅*Me*₅), 3.78 (s, 3H, O*Me*), 4.00 (s, 3H, *Me*), 5.22 (d, *J* = 14.9 Hz, 1H, *H*¹), 5.93 (d, *J* = 14.9 Hz, 1H, *H*¹), 6.72 (d, *J* = 2.2 Hz, 1H, *H*^{6a}), 6.84 (dd, *J* = 7.9, 2.2 Hz, 1H, *H*⁴), 6.88 (d, *J* = 7.6 Hz, 1H, *H*²), 6.90 (d, *J* = 2.2 Hz, 1H, *H*^{6b}), 6.95 (d, *J* = 2.2 Hz, 1H, *H*⁵), 7.25 (t, *J* = 7.9 Hz, 1H, *H*³), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.3 (C₅*Me*₅), 38.7 (*Me*), 54.5 (*C*¹), 55.4 (O*Me*), 88.9 (*C*₅Me₅), 113.7 (*C*⁵), 113.9 (*C*⁴), 120.7 (*C*²), 121.9 (*C*^{6a}), 123.3 (*C*^{6b}), 129.7 (*C*³), 138.3, 156.9 (*C*⁷), 159.9. ESIMS: *m/z* 565 [M - Cl]⁺. HRMS (ESI): Calcd for C₂₂H₂₉N₂OCl¹⁹³Ir [M - Cl]⁺ 565.1598, found 565.1591.

Synthesis of 5b-OMe. Following the general procedure, a mixture of L5-OMe (51 mg, 0.214 mmol), Ag₂O (52 mg, 0.224 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[RhCl_2Cp^*]_2$ (62 mg, 0.100 mmol) and dry DCM (2.5 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%). ¹H NMR (400 MHz, CDCl₃): δ 1.61 (s, 15H, C₅Me₅), 3.78 (s, 3H, OMe), 4.05 (s, 3 H, Me), 5.27 (br d, I = 14.7 Hz, 1H, H^{1}), 6.03 (br d, J = 14.5 Hz, 1H, H^1), 6.80 (d, J = 2.0 Hz, 1H, H^{6a}), 6.84 (dd, J = 8.2, 2.3 Hz, 1H, H^4), 6.89 (br d, J = 7.5 Hz, 1H, H^2), 6.97 (m, 2) H, H^5 , H^{6b}), 7.24 (t, J = 7.8 Hz, 1H, H^3), ${}^{13}C{}^{1}H$ NMR (125 MHz, $CDCl_3$: δ 9.5 (C_5Me_5), 39.2 (Me), 54.6 (C^1), 55.3 (OMe), 96.2 (d, ${}^{1}J_{C-Rh} = 6.0$ Hz, $C_{5}Me_{5}$), 113.7 (C^{5}), 113.9 (C^{4}), 120.6 (C^{2}), 122.7 ^a), 124.1 (C^{6b}), 129.6 (C^{3}), 138.2, 159.9, 170.3 (d, ${}^{1}J_{C-Rh} = 56.2$ Hz, C^7). ESIMS: m/z 475 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{29}N_2OCl^{103}Rh [M - Cl]^+ 475.1023$, found 475.1016.

Synthesis of 5a-CF₃. Following the general procedure, a mixture of L5-CF₃ (52 mg, 0.188 mmol), Ag₂O (46 mg, 0.211 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then [IrCl₂Cp*]₂ (71 mg, 0.089 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded 5a-CF₃ as yellow crystals (81 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ 1.63 (s, 15H, C₅Me₅), 4.01(s, 3H, *Me*), 5.14 (br d, J = 14.7 Hz, 1H, H^{1}), 6.23 (br d, J = 14.9 Hz, 1H, H^{1}), 6.66 (d, J = 2.2 Hz, 1H, H^{6a}), 6.94 (d, J = 2.0 Hz, 1H, H^{6b}), 7.46 (t, J = 7.7 Hz, 1H, H^3), 7.55 (br. s, 1H, H^5), 7.56 (br. d, J =7.8 Hz, 1H, H^4), 7.71 (br. d, J = 7.6 Hz, 1H, H^2), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.1 (C₅Me₅), 38.7 (Me), 53.9 (C¹), 88.9 $(C_5 \text{Me}_5)$, 121.6 (C^{6b}) , 123.7 (C^{6a}) , 124.0 (q, ${}^1J_{C-F}$ = 245.0 Hz, *C*F₃), 124.8 (q, ${}^{3}J_{C-F}$ = 3.0 Hz, $C^{4/5}$), 124.9 (q, ${}^{3}J_{C-F}$ = 4.0 Hz, $C^{4/5}$ ⁵), 129.4 (C^2), 130.7 (q, ${}^2J_{C-F}$ = 33.1 Hz, C-CF₃), 132.4 (C^3), 137.8, 157.3 (C^7), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -62.5 (CF_3) .ESIMS: m/z 603 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_{2}F_{3}Cl^{193}Ir [M - Cl]^{+} 603.1366$, found 603.1360.

Synthesis of 5b-CF₃. Following the general procedure, a mixture of L5-CF₃ (53 mg, 0.191 mmol), Ag₂O (57 mg, 0.245 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then [RhCl₂Cp*]₂ (69 mg, 0.112 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded 5b-CF₃ as yellow/orange crystals (89 mg, 85%). ¹H NMR (400 MHz, CDCl₃): δ 1.60 (s, 15H, C₅*Me*₅), 4.05 (s, 3H, *Me*), 5.17 (br d, *J* = 14.5 Hz, 1H, *H*¹), 6.36 (br d, *J* = 14.5 Hz, 1H, *H*¹), 6.73 (d, *J* = 2.0 Hz, 1H, *H*^{6a}), 7.02 (d, *J* = 2.0 Hz, 1H, *H*^{6b}), 7.44 (t, *J* = 8.0 Hz, 1H, *H*³), 7.55 (m, 2H, *H*⁴, *H*⁵), 7.70 (d, *J* = 7.6 Hz, 1H, *H*²), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.5

 $\begin{array}{l} ({\rm C}_5Me_5),\ 39.3\ (Me),\ 54.1\ (C^1),\ 96.3\ (d,\ ^1\!\!J_{\rm C-Rh}=6.0\ {\rm Hz},\ C_5Me_5), \\ 125.5\ (C^{6a}),\ 123.8\ (q,\ ^1\!\!J_{\rm C-F}=246.0\ {\rm Hz},\ CF_3),\ 124.7\ (C^{6b}),\ 124.8 \\ (q,\ ^3\!\!J_{\rm C-F}=4.0\ {\rm Hz},\ C^{4'}C^5),\ 125.0\ (q,\ ^3\!\!J_{\rm C-F}=4.0\ {\rm Hz}\ C^{4'}C^5),\ 129.5 \\ (C^3),\ 130.7\ (q,\ ^2\!\!J_{\rm C-F}=32.1\ {\rm Hz},\ C^{-}CF_3),\ 132.6\ (C^2),\ 137.7,\ 171.0 \\ (d,\ ^1\!\!J_{\rm C-Rh}=56.2\ {\rm Hz},\ C^7),\ ^{19}{\rm F}\{^1{\rm H}\}\ {\rm NMR}\ (376\ {\rm MHz},\ {\rm CDCl}_3);\ \delta \\ -62.5\ ({\rm CF}_3).\ m/z\ 513\ [{\rm M}\ -{\rm Cl}]^+.\ {\rm HRMS}\ ({\rm ESI}):\ {\rm Calcd}\ {\rm for} \\ {\rm C}_{22}{\rm H}_{26}{\rm N}_{2}{\rm F}_{3}{\rm Cl}^{103}{\rm Rh}\ [{\rm M}\ -{\rm Cl}]^+\ 513.0792,\ {\rm found:}\ 513.0786. \end{array}$

Synthesis of 5a-F. Following the general procedure, a mixture of L5-F (50 mg, 0.218 mmol), Ag₂O (50 mg, 0.216 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then [IrCl₂Cp*]₂ (79 mg, 0.099 mmol) and dry DCM (2.5 mL) was added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded 5a-F as yellow crystals (86 mg, 73%). ¹H NMR (400 MHz, CDCl₃): δ 1.63 (s, 15H, C₅Me₅), 4.00 (s, 3H, *Me*), 5.16 (d, J = 14.8 Hz, 1H, H^1), 5.93 (d, J = 14.8 Hz, 1H, H^1), 6.69 (d, J = 2.0 Hz, 1H, H^{6a}), 6.94 (d, J = 2.1 Hz, 1H, H^{6b}), 6.99 $(td, J = 8.3, 2.3 Hz, 1H, H^4)$, 7.08 $(td, J = 9.6, 2.1 Hz, 1H, H^5)$, 7.16 (d, J = 7.8 Hz, 1H, H^2), 7.31 (m, 1H, H^3), ${}^{13}C{}^{1}H$ NMR (125 MHz, CDCl₃): δ 9.1 (C₅Me₅), 38.7 (Me), 53.9 (C¹), 88.8 $(C_5 \text{Me}_5)$, 114.9 (d, ${}^2J_{\text{C-F}}$ = 21.1 Hz, C^4), 115.3 (d, ${}^2J_{\text{C-F}}$ = 23.1 Hz, C^{5}), 121.7 (C^{6a}), 123.5 (C^{6b}), 124.2 (d, ${}^{4}J_{C-F} = 2.0$ Hz, C^{2}), 130.2 (d, ${}^{3}J_{C-F} = 8.0$ Hz, C^{3}), 139.3 (d, ${}^{3}J_{C-F} = 7.0$ Hz, C), 157.1 (C^{7}), 162.9 (d, ${}^{1}J_{C-F}$ = 247.0 Hz, C-F), ${}^{19}F{}^{1}H{}$ NMR (376 MHz, $CDCl_3$: δ -112.4 (F). ESIMS: m/z 553 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{26}N_2Cl^{193}Ir [M - Cl]^+$ 553.1398, found 553.1394.

Synthesis of 5b-F. Following the general procedure, a mixture of L5-F (50 mg, 0.221 mmol), Ag₂O (52 mg, 0.223 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then [RhCl₂Cp*]₂ (62 mg, 0.101 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded 5b-F as yellow crystals (67 mg, 67%). ¹H NMR (400 MHz, CDCl₃): δ 1.63 (s, 15H, C₅Me₅), 4.06 (s, 3H, *Me*), 5.22 (d, J = 14.1 Hz, 1H, H^1), 6.19 (d, J = 14.1 Hz, 1H, H^1), 6.78 (d, J = 2.0 Hz, 1H, H^{6a}), 7.00 (m, 2H, H^{3} , H^{6b}), 7.09 (td, J =9.6, 1.9 Hz, 1H, H^5), 7.17 (dd, J = 7.6, 0.6 Hz, 1H, H^2), 7.31 (td, $J = 7.9, 5.9 \text{ Hz}, 1\text{H}, H^3$), ${}^{13}\text{C}{}^{1}\text{H}$ NMR (125 MHz, CDCl_3): δ 9.5 (C_5Me_5) , 39.2 (Me), 54.1 (C¹), 96.3 (d, $J_{C-Rh} = 6.0$ Hz, C_5Me_5), 115.0 (d, ${}^{2}J_{C-F}$ = 20.1 Hz, C^{4}), 115.4 (d, ${}^{2}J_{C-F}$ = 22.1 Hz, C^{5}), 122.6 (C^{6a}), 124.3 (d, ${}^{4}J_{C-F}$ = 2.0 Hz, C^{2}), 124.5 (C^{6b}), 130.3 (d, ${}^{3}J_{C-F}$ = 8.0 Hz, C^{3}), 139.3 (d, ${}^{3}J_{C-F}$ = 8.0 Hz, C), 162.9 (d, ${}^{1}J_{C-F}$ = 250.0 Hz, C-F), 170.8 (d, $J_{C-Rh} = 56.2$ Hz, C^7), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -112.3 (F). ESIMS: m/z 463 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{103}Rh [M - HCl_2]^+$ 427.1057, found 427.1052.

General procedure for cyclometallation of 5a/b-R

An oven-dried and N_2 purged Schlenk flask was charged with a magnetic stirrer bar, **5a/b-R** (1 eq.), NaOAc (5 eq.) and dry DCM (2 mL) and MeOH (0.5 mL) and stirred at rt for indicated time. The reaction mixture was filtered through Celite, which was washed with additional DCM (5–10 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 mg, 0.025 mmol), NaOAc (8 mg, 0.098 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was

stirred at rt overnight. Precipitation from DCM/hexane yielded regioisomer *para*-**6a-OMe** as a yellow powder (12 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ 1.68 (s, 15H, C₅*Me*₅), 3.75 (s, 3H, O*Me*), 3.92 (s, 3H, *Me*), 4.60 (d, *J* = 13.9 Hz, 1H, *H*^{1b}), 4.84 (d, *J* = 13.9 Hz, 1H, *H*^{1a}), 6.61 (d, *J* = 2.7 Hz, 1H, *H*⁵), 6.67 (dd, *J* = 8.3, 2.6 Hz 1H, *H*⁴), 6.89 (d, *J* = 1.4 Hz, 1H, *H*^{6b}), 6.94 (d, *J* = 1.4 Hz, 1H, *H*^{6b}), 6.94 (d, *J* = 1.4 Hz, 1H, *H*^{6a}), 7.47 (br d, *J* = 8.2 Hz, 1H, *H*³), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.4 (C₅*Me*₅), 36.9 (*Me*), 55.3 (*C*¹), 57.1 (O*Me*), 90.0 (*C*₅Me₅), 111.1 (*C*⁵), 113.6 (*C*⁴), 120.3 (*C*^{6a}), 121.1 (*C*^{6a}), 132.5 (*C*²), 138.5, 141.4 (*C*³), 155.8, 157.3 (*C*⁷). ESIMS: *m*/z 529 [M - Cl]⁺. HRMS (ESI): Calcd for C₂₂H₂₈N₂O¹⁹¹Ir [M - Cl]⁺ 527.1808, found 527.1804.

Synthesis of 6b-OMe. Following the general procedure, a mixture of 5b-OMe (19 mg, 0.037 mmol), NaOAc (12 mg, 0.146 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 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ 1.60 (s, 15H, C₅Me₅), 3.74 (s, 3H, OMe), 4.00 (s, 3H, Me), 4.68 (d, J = 14.3 Hz, 1H, H^{1b}), 4.94 (d, J= 14.3 Hz, 1H, H^{1a}), 6.61 (d, J = 2.5 Hz, 1H, H^5), 6.71 (dd, J = 8.4, 2.7 Hz, 1H, H^4), 6.95 (d, J = 1.8 Hz, 1H, H^{6b}), 7.02 (d, J =1.6 Hz, 1H, H^{6a}), 7.56 (d, J = 8.4 Hz, 1H, H^{3}), ${}^{13}C{}^{1}H$ NMR (125 MHz, CDCl₃): δ 9.6 (C₅Me₅), 37.5(Me), 55.3 (C¹), 56.3 (OMe), 97.0 (d, ${}^{1}J_{C-Rh} = 5.0$ Hz, $C_{5}Me_{5}$), 111.6 (C^{5}), 113.3 (C^{4}), 121.4 (C^{6a}), 122.0 (C^{6b}), 139.1, 141.0 (C^{3}), 147.8 (d, ${}^{1}J_{C-Rh} = 32.1$ Hz, C^2), 156.1, 175.0 (d, ${}^{1}J_{C-Rh} = 55.2$ Hz, C^7). ESIMS: m/z 439 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{28}N_2O^{103}Rh [M - Cl]^+$ 439.1257, found 439.1246.

Synthesis of 6a-CF₃. Following the general procedure, a mixture of **5a-CF**₃ (27 mg, 0.042 mmol), NaOAc (14 mg, 0.171 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was stirred at rt overnight. Precipitation from DCM/hexane yielded *para*-**6a-CF**₃ as a yellow powder (21 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ 1.68 (s, 15H, C₅*Me*₅), 3.90 (s, 3H, *Me*), 4.72 (br d, *J* = 13.7 Hz, 1H, *H*^{1b}), 4.86 (br d, *J* = 14.1 Hz, 1H, *H*^{1a}), 6.92 (br s, 1H, *H*^{6b}), 6.98 (br s, 1H, *H*^{6a}), 7.18 (m, 2H, *H*⁴, *H*⁵), 7.75 (m, 1H, *H*³), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.4 (C₅*Me*₅), 36.9 (*Me*), 55.3 (*C*¹), 90.5 (*C*₅Me₅), 120.3 (q, ³*J*_{C-F} = 3.0 Hz, *C*^{4/5}), 120.4 (*C*^{6a}), 121.4 (*C*^{6b}), 123.6 (q, ³*J*_{C-F} = 3.0 Hz, *C*^{4/5}), 124.1 (q, ²*J*_{C-F} = 31.1 Hz, *C*-CF₃), 125.2 (q, ¹*J*_{C-F} = 271.1 Hz, *C*F₃), 138.9, 141.8 (*C*³), 152.1 (*C*²), 156.6 (*C*⁷). ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ -61.4 (*CF*₃). ESIMS: *m*/*z* 567 [M - Cl]⁺. HRMS (ESI): Calcd for C₂₂H₂₅N₂F₃¹⁹¹Ir [M - Cl]⁺ 565.1574, found 565.1576.

Synthesis of 6b-CF₃. Following the general procedure, a mixture of **5b-CF**₃ (50 mg, 0.091 mmol), NaOAc (30 mg, 0.366 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was stirred at rt overnight. Precipitation from DCM/hexane yielded *para*-**6b-CF**₃ as a yellow/orange powder (40 mg, 86%). ¹H NMR (400 MHz, CDCl₃): δ 1.59 (s, 15H, C₅*Me*₅), 3.97 (s, 3H, *Me*), 4.80 (d, *J* = 14.3 Hz, 1H, *H*^(1b)), 4.97 (d, *J* = 14.3 Hz, 1H, *H*^(1a)), 6.95 (d, *J* = 1.8 Hz, 1H, *H*^{6b}), 7.03 (d, *J* = 1.8 Hz, 1H, *H*^{6a}), 7.16 (br s, 1H, *H*⁵), 7.21 (br d, *J* = 8.0 Hz, 1H, *H*⁴), 7.86 (br d, *J* = 7.8 Hz, 1H, *H*³), ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 9.6 (C₅*Me*₅), 37.4 (*Me*), 56.1 (*C*¹), 97.4 (d, ¹*J*_{C-Rh} = 5.0 Hz, *C*₅Me₅), 120.6 (q, ³*J*_{C-F} = 3.0 Hz, *C*⁵), 121.5 (q, ³*J*_{C-F} = 3.0 Hz, *C*⁴), 122.4 (*C*^{6a}), 122.8 (*C*^{6b}), 124.4 (q, ²*J*_{C-F} = 31.1 Hz, *C*-CF₃), 125.1 (q, ¹*J*_{C-F} = 271.0 Hz, *C*F₃), 139.5

141.3 (q, ${}^{4}J_{C-F} = 2.0 \text{ Hz}, C^{3}$), 169.0 (d, ${}^{1}J_{C-Rh} = 32.1 \text{ Hz}, C^{2}$), 174.3 (d, ${}^{1}J_{C-Rh} = 56.2 \text{ Hz}, C^{7}$), ${}^{19}\text{F}\{{}^{1}\text{H}\}$ NMR (376 MHz, CDCl₃): δ –61.5 (CF₃). ESIMS: m/z 477 [M – Cl]⁺. HRMS (ESI): Calcd for C₂₂H₂₅N₂F₃⁻¹⁰³Rh [M – Cl]⁺ 477.1025, found 477.10250.

Synthesis of 6a-F. Following the general procedure, a mixture of 5a-F (30.0 mg, 0.051 mmol), NaOAc (16.5 mg, 0.201 mmol), dry DCM (2.4 mL) and dry MeOH (0.6 mL) was stirred at rt for 2 h. Precipitation from DCM/hexane vielded 6a-F (ortho: para ratio 10:1) as a yellow powder (27 mg, 96%). ortho-6a-F. ¹H NMR (400 MHz, CDCl₃): δ 1.73 (s, 15H, C₅Me₅), 3.89 (s, 3H, Me), 4.71 (dd, J = 13.9, 1.3 Hz, 1H, H^{1b}), 4.88 (d, J =13.9 Hz, 1H, H^{1a}), 6.76 (m, 3H, H^2 , H^3 , H^4), 6.90 (d, J = 1.9 Hz, 1H, H^{6b}), 6.94 (d, J = 2.0 Hz, 1H, H^{6a}), ${}^{13}C{}^{1}H$ NMR (101 MHz, $CDCl_3$: δ 9.4 (C_5Me_5), 37.0 (Me), 57.0 (C^1), 90.04 (C_5Me_5), 114.2 (d, ${}^{2}J_{C-F} = 31.0 \text{ Hz}, C^{4}$), 120.3 (C^{6a}), 120.6 (d, ${}^{4}J_{C-F} = 1.6 \text{ Hz}, C^{2}$), 121.6 (C^{6b}), 123.8 (d, ${}^{3}J_{C-F}$ = 8.7 Hz, C^{3}), 128.0 (d, ${}^{2}J_{C-F}$ = 38.9 Hz, C^5), 141.0 (d, ${}^{3}J_{C-F}$ = 14.3 Hz, C), 156.4 (C^7), 167.2 (d, ${}^{1}J_{C-F}$ = 232.9 Hz, C-F), ${}^{19}F{}^{1}H{}$ NMR (376 MHz, CDCl₃): δ -87.8 (F). ESIMS: m/z 517 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{193}Ir [M - Cl]^+$ 517.1631, found 517.1631. para-6a-**F.**¹H NMR (400 MHz, CDCl₃): δ 1.66 (s, 15H, C₅Me₅), 3.91 (s, 3H, Me), 4.6 (d, J = 14.1 Hz, 1H, H^{1a}), 4.81 (d, J = 13.9 Hz, 1H, H^{1b}), 6.71–6.74 (m, 2H, H^4 , H^5), 6.89 (d, J = 1.9 Hz, 1H, H^{6b}), 6.93 (d, J = 1.9 Hz, 1H, H^{6a}), 7.51 (dd, J = 8.3, 7.0 Hz, 1H, H^{3}), ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ –125.3 (F). ESIMS: m/z 427 $[M - Cl]^+$. HRMS (ESI): ESIMS: m/z 517 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{193}$ Ir $[M - Cl]^+$ 517.1631, found 517.1631.

Synthesis of 6b-F. Following the general procedure, a mixture of 5b-F (25.5 mg, 0.051 mmol), NaOAc (16.7 mg, 0.204 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 mg, 96%). ortho-6b-F. ¹H NMR (400 MHz, $CDCl_3$): δ 1.66 (s, 15H, C₅Me₅), 3.99 (s, 3H, Me), 4.71 (dd, J = 14.2, 1.0 Hz, 1H, H^{1a}), 4.97 (d, J = 14.2 Hz, 1H, H^{1b}), 6.76 (m, 2 H, H^2 , H^4), 6.82 (m, 1H, H^3), 6.97 (d, J = 1.9 Hz, 1H, H^{6b}), 7.02 (d, J = 1.9 Hz, 1H, H^{6a}), ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃): δ 9.7 (C₅Me₅), 37.8 (*Me*), 56.4 (C^1), 97.5 (d, ${}^1J_{C-Rh}$ = 5.6 Hz, C_5Me_5), 114.4 (d, ${}^2J_{C-F}$ = 31.0 Hz, C^4), 120.9 (C^{6a}), 121.3 (C^2), 122.6 (C^{6b}), 124.1 (d, ${}^3\!J_{C-F}$ = 8.7 Hz, C^3), 141.60 (d, ${}^{3}J_{C-F}$ = 15.1 Hz, C), 142.8 (m, C^5), 166.9 (d, ${}^{1}J_{C-F} = 232.1$ Hz, C-F), 174.2 (d, ${}^{1}J_{C-Rh} = 54.8$ Hz, C⁷), ${}^{19}F$ {¹H} NMR (376 MHz, CDCl₃): δ -84.7 (F). m/z 427 [M - Cl]⁺. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{103}Rh [M - Cl]^+ 427.1057$, found 427.1049. para-6b-F. ¹H NMR (400 MHz, $CDCl_3$): δ 1.73 $(s, 15H, C_5Me_5), 3.99 (s, 3H, Me), 4.68 (d, J = 14.2, 1.0 Hz, 1H,$ H^{1a}), 4.92 (d, J = 14.2 Hz, 1H, H^{1b}), 6.73 (dd, J = 10.0, 3.0 Hz, 1H, H^5), 6.76 (td, J = 9.0, 2.8 Hz, 1H, H^4), 6.97 (d, J = 1.9 Hz, 1H, H^{6b}), 7.02 (d, J = 1.9 Hz, 1H, H^{6a}), 7.61 (dd, J = 8.3, 7.0 Hz, 1H, H^3), ${}^{19}F{}^{1}H$ NMR (376 MHz, CDCl₃): δ -125.0 (F). ESIMS: m/z 427 [M – Cl]⁺. HRMS (ESI): Calcd for C₂₁H₂₅N₂F¹⁰³Rh [M - Cl]⁺ 427.1057, found 427.1049.

Deuteration studies

An NMR tube was charged with 5a/b-R (5 mg) and CD_3OD (0.5 mL). The ¹H NMR spectrum was recorded and then NaOAc (4 eq.) was added. The reactions were allowed to sit at

rt overnight. The spectra in CD₃OD were broad so the samples were evaporated and redissolved in CDCl₃. The percentage deuteration was determined by ¹H NMR spectroscopy by comparing the relative integrations for H³ and H⁵ for the *para*-isomers in the ¹H NMR spectra.

Conflicts of interest

There are no conflicts to declare.

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