



# Enantioselective Friedel-Crafts alkylation of 1,3,5-trimethoxybenzene with *trans*- $\beta$ -nitrostyrenes catalysed by $[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(\text{H}_2\text{O})][\text{SbF}_6]_2$ (Prophos = propane-1,2-diyl-bis(diphenylphosphane))<sup>☆</sup>

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## ABSTRACT

The aqua complex  $(S_{\text{Rh}}, R_{\text{C}})\text{-}[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(\text{H}_2\text{O})][\text{SbF}_6]_2$  (Prophos = propane-1,2-diyl-bis(diphenylphosphane)) catalyses the asymmetric Friedel-Crafts (FC) alkylation of 1,3,5-trimethoxybenzene with *trans*- $\beta$ -nitrostyrenes. Only the monoalkylated adduct was obtained in all cases with enantioselectivities of up to 93/7 e.r. Solution NMR measurements have allowed us to detect and characterise catalytic intermediates such as metal-*trans*- $\beta$ -nitrostyrene and metal-*aci*-nitro complexes, as well as free *aci*-nitro compound. Based on these studies, a Michael-type Friedel-Crafts mechanism is proposed.

## 1. Introduction

The catalytic enantioselective Friedel-Crafts (FC) alkylation of aromatic substrates with electron-deficient alkenes represents an efficient method for introducing new stereogenic centres into aromatic compounds [1-4]. Since 2005, when the groups of Bandini [5], Ricci [6] and Jorgensen [7] published the first enantioselective reactions of nitroalkenes with indole catalysed by  $[\text{AlCl}(\text{Salen})]$  (Salen = *N,N*-bis(salicylidene)ethylenediamine), thioureas and bis-sulfonamides, respectively, significant progress has been made in this field. Among the metal catalysts, zinc [8-24] and copper [25-35] based compounds dominate the area, while organocatalysts such as thioureas [6,36-41] and phosphoric acids [42-46] are the most successfully employed. Among the various electrophiles used in these reactions,  $\beta$ -nitrostyrenes have attracted considerable attention. This interest stems from the pronounced electron-withdrawing nature of the nitro group and the adaptability of  $\beta$ -nitrostyrenes to be transformed into versatile organic building blocks [47]. On the other hand, heteroarenes, including derivatives of indole and pyrrole [4-7,15-21,23,24,31-35,41,44-46] as well as arene derivatives such as phenols and naphthols [36,38,39], have been found to be effective nucleophiles.

In this context, it is worth noting that the FC alkylation of various

electrophiles, especially indoles, with nitrostyrenes has become a benchmark for assessing the performance of novel catalysts. However, it is surprising that the mechanism of these reactions particularly the step that determines the enantioselectivity has not yet been fully elucidated. In particular, in the realm of transition metal-based systems, there have been mechanistic proposals where the activation of the nitroolefin occurs through a bidentate interaction [24,48]. Likewise, bifunctional mechanisms have been suggested involving the simultaneous interaction of the nitroolefin and indole with the catalyst (Fig. 1a) [16,21,23,30,31]. Furthermore, in the context of a copper-catalysed system using an imidazoline-aminophenol ligand as the chiral source, Arai *et al.* proposed a reaction mechanism in which a nitronate species plays a key role, but this species lacks experimental support (Fig. 1b) [28,33].

We have recently reported on the FC alkylation of indoles with nitrostyrenes catalysed by the rhodium complex  $[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(\text{H}_2\text{O})][\text{SbF}_6]_2$  (Prophos = propane-1,2-diyl-bis(diphenylphosphane)) (**1**) [49-51]. The detection and characterisation of intermediates such as the free *aci*-nitro compound and the *aci*-nitro complex  $[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(\text{aci-nitro})][\text{SbF}_6]_2$  depicted in Fig. 1c have played a key role in proposing a plausible mechanism for the catalytic reaction.

The excellent enantioselectivity achieved with rhodium catalyst **1** in the alkylation of indoles with nitrostyrenes inspired us to explore its

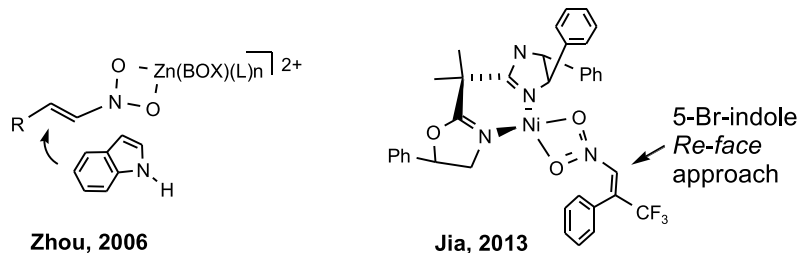
<sup>☆</sup> Electronic supplementary material available: NMR data of **3**, **5**, **6** and **8**, and HPLC chromatograms of compounds **7**.

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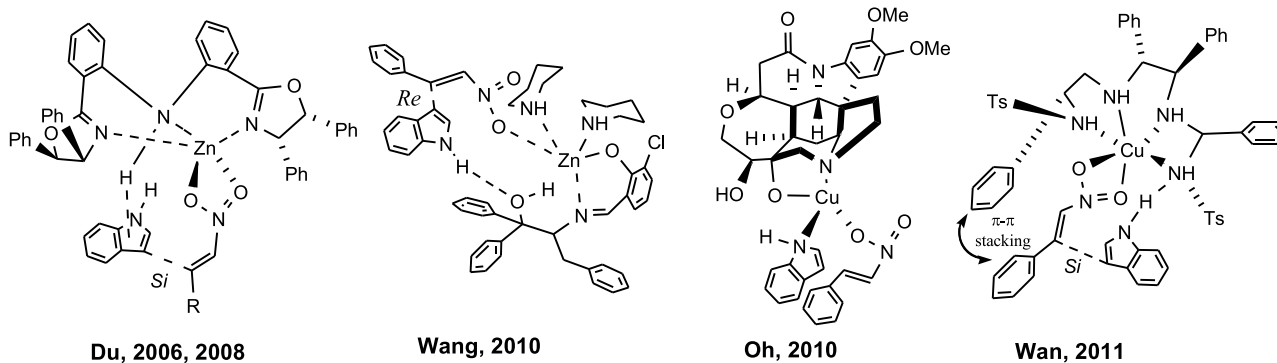
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application to the more challenging reaction between 1,3,5-trimethoxybenzene and *trans*- $\beta$ -nitrostyrenes. This work aims to demonstrate that a 1,4-Michael-type Friedel-Crafts mechanism, rather than the traditionally assumed Friedel-Crafts mechanism, is at play with aromatic substrates such as 1,3,5-trimethoxybenzene and *trans*- $\beta$ -nitrostyrenes.

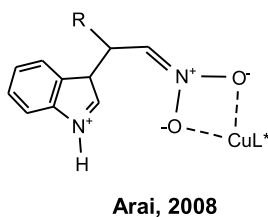
### a) Activation of nitroolefins through bidentate interaction



### Bifunctional mechanisms, interaction of both the nitroolefin and the indole



### b) Nitronate intermediate



### c) Free *aci*-nitro compound and *aci*-nitro complex intermediates

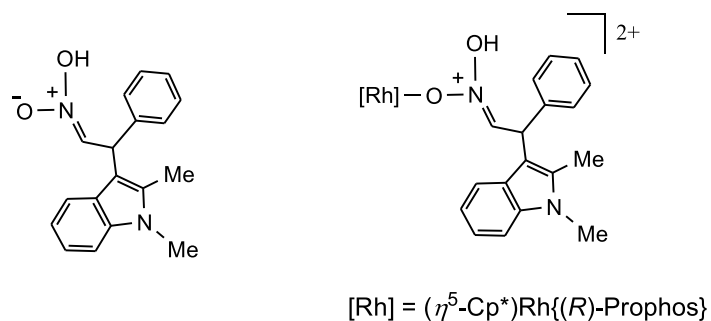


Fig. 1. Previous work on enantioselective Friedel-Crafts alkylation reactions with nitroalkenes.

## 2. Results and discussion

### 2.1. Reaction of *trans*- $\beta$ -nitrostyrenes with 1,3,5-trimethoxybenzene catalysed by the rhodium complex **1**

We have studied the reaction of 1,3,5-trimethoxybenzene (**4**) with *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene (**2a**), *trans*-2-fluoro- $\beta$ -nitrostyrene (**2b**), *trans*- $\beta$ -nitrostyrene (**2c**), and *trans*-2,4-dichloro- $\beta$ -nitrostyrene (**2d**) mediated by the previously reported [52] rhodium complex ( $S_{Rh}$ ,  $R_C$ )-[Cp\*Rh{(R)-Prophos}(H<sub>2</sub>O)][SbF<sub>6</sub>]<sub>2</sub> (**1**). In selecting the systems to be studied, we considered the results previously obtained with the related iridium catalyst. Therefore, in addition to the unsubstituted *trans*- $\beta$ -nitrostyrene (**2c**), we chose the alkenes **2b**, **2a**, and **2d**, which showed the best activity, best selectivity and worst selectivity, respectively, with the related iridium-based catalyst [53]. Table 1 collects the results obtained together with the reaction conditions employed. The results are the average of at least two comparable reaction runs. Reactions are clean with the monoalkylated adduct being the only product detected spectroscopically. Generally speaking, the rhodium catalyst **1** is more selective but less active than its iridium homologue [53] ( $S_{Ir}$ ,  $R_C$ )-[Cp\*Ir{(R)-Prophos}(H<sub>2</sub>O)][SbF<sub>6</sub>]<sub>2</sub>. The most active nitrostyrene is *trans*-2-fluoro- $\beta$ -nitrostyrene, achieving quantitative conversions in 23 h (entry 2). The results indicate that while an electron-withdrawing substituent on the phenyl ring such as fluorine leads to an improvement in the conversion, electron-donating substituents such as methoxy groups produce a decrease in the catalytic rate (entry 1). This electronic effect in *trans*-2-fluoro- $\beta$ -nitrostyrene (**2b**) and *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene (**2a**), has been attributed to the increase (**2b**) or decrease (**2a**) in its electrophilic character, making them more or less prone, respectively, to react with the aromatic substrate. However, probably due to steric factors, for the electrophile *trans*-2,4-dichloro- $\beta$ -nitrostyrene with electron-withdrawing substituents in the *ortho* and *para* positions a decrease in rate was observed (entry 4). The highest enantiomeric ratio (e.r.) = 93/7 is obtained with electrophile **2a**, which has two methoxy substituents at positions 2 and 3 of the aromatic ring (entry 1).

With the intention of shedding light on the course of the reactions, we monitored the processes by NMR spectroscopy. As a representative example, we detail below the results obtained for the catalytic reaction of *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene (**2a**) with 1,3,5-trimethoxybenzene. For the remaining substrates, detailed spectroscopic information is gathered in the Experimental Section.

#### 2.1.1. Reaction of catalyst **1** with *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene (**2a**)

The addition of 2 equivalents of **2a** to catalyst **1** results in the formation of a new compound **3a** (Scheme 1). After one hour of treatment under argon at 248 K, in the presence of 4 Å molecular sieves, the conversion to **3a** is complete. The <sup>1</sup>H and <sup>31</sup>P NMR spectra reveal that

the new complex is the result of substituting the water molecule coordinated in **1** with a molecule of **2a**. Compound **3a** is the sole phosphorous-containing compound observed in solution from 193 K up to RT and has been characterised *in situ* by comparing its spectroscopic NMR data with those previously described [53].

#### 2.1.2. Addition of 1,3,5-trimethoxybenzene to **3a**

The next step of the catalytic cycle should be the reaction of complex **3a**, in which the nitroalkane is coordinated, with the nucleophile 1,3,5-trimethoxybenzene. At this point, it should be noted that in compounds containing the Cp\*Rh{(R)-Prophos} fragment, the nucleus of the phosphorus P<sup>2</sup> (see Scheme 1) is particularly sensitive to changes in the metal coordination sphere. In the <sup>31</sup>P NMR spectra, this nucleus gives rise to a double doublet due to coupling with rhodium and P<sup>1</sup> nuclei. Therefore, the emergence of new double doublets and their evolution in the <sup>31</sup>P NMR spectra provide valuable information about the number of metal complexes present in the reaction medium as well as the progress of the reactions monitored using this technique.

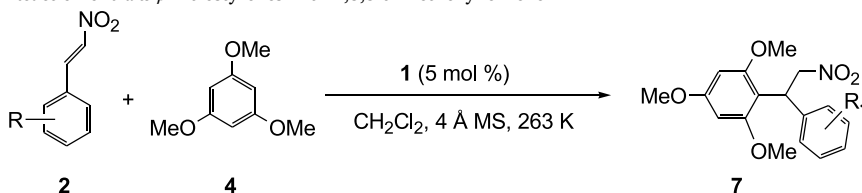
When a CD<sub>2</sub>Cl<sub>2</sub> solution of complex **3a** or a mixture of catalyst **1** and *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene, is treated with 1,3,5-trimethoxybenzene, up to three metal complexes, as well as a new organic compound, are detected by NMR spectroscopy. The sets of signals recorded in the NMR spectra indicate that the new metallic compounds are isomers of each other. The number of new compounds detected in the reaction medium and their relative concentrations depend on the initial composition of the reactant mixture, the temperature, and the reaction time. For example, if at 203 K, a solution of the compound **3a**, obtained as indicated above, is treated with 3 equiv. of 1,3,5-trimethoxybenzene in the presence of 4 Å MS, after 14 h of reaction, two new metal complexes are observed in a molar ratio of approximately 60/40 (Fig. 2).

We propose that the new metal complexes (**5a** in Scheme 2) result from a formal Michael-type Friedel-Crafts substitution, rather than the usually assumed Friedel-Crafts reaction, of the nucleophile 1,3,5-trimethoxybenzene with the electrophile *trans*-2,3-dimethoxy- $\beta$ -nitrostyrene, which is activated by coordination to the metal. The resulting *aci*-nitro compound [49-51,54] remains coordinated to the metal center. According to this proposal, these complexes exhibit a broad peak in the <sup>1</sup>H NMR spectrum at low field (9.76 and 12.02 ppm), which we attribute to the OH functionality. In addition, for one of them, it is possible to detect a new aliphatic carbon nucleus at 32.97 ppm in the <sup>13</sup>C NMR spectrum, which we assign to the stereogenic carbon atom generated by the addition reaction (C<sup>2</sup> in Scheme 2). The Experimental Section provides a more detailed description of the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of these compounds, exhibiting the expected features for the proposed structure.

On the other hand, in a reaction mixture with an initial molar ratio of **1/2a/4** = 1/2/3, after 8 days of reaction at 203 K, a third metallic isomer is observed, exhibiting spectroscopic characteristics comparable to those of the two previously mentioned counterparts (Fig. 3).

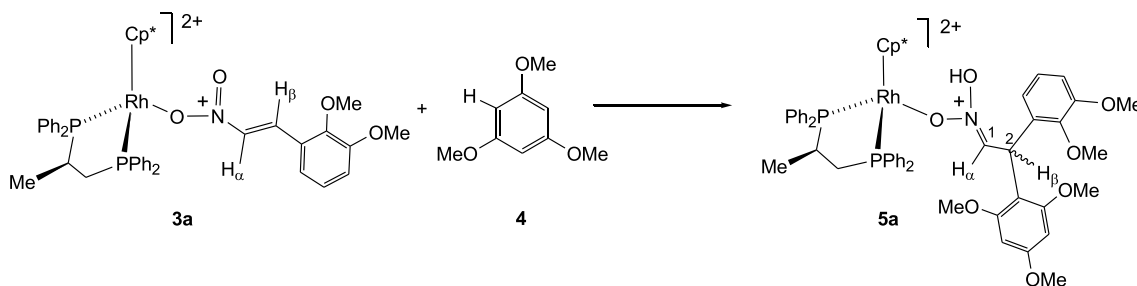
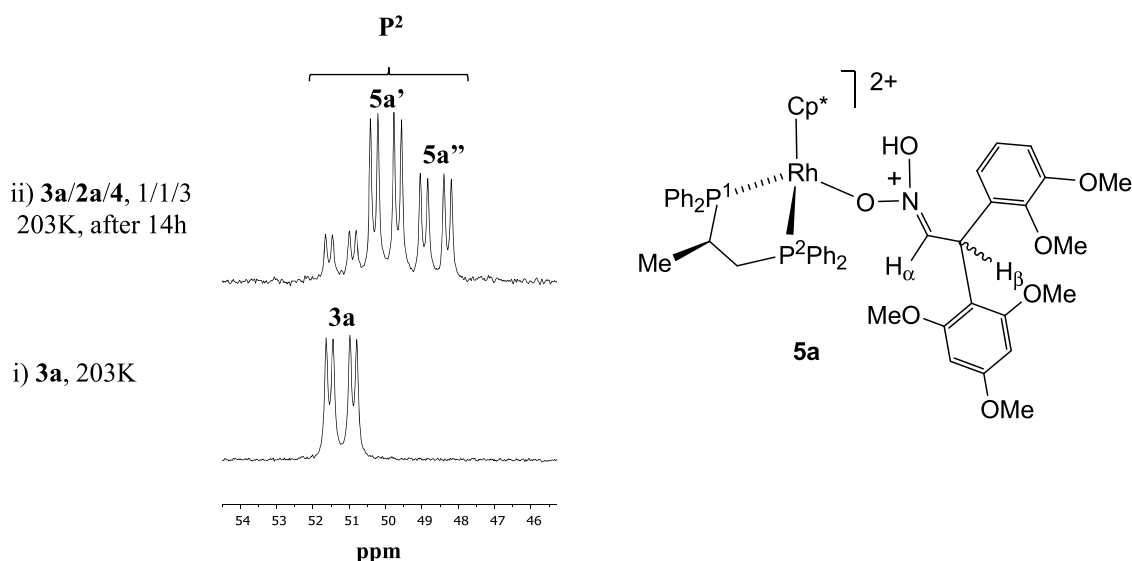
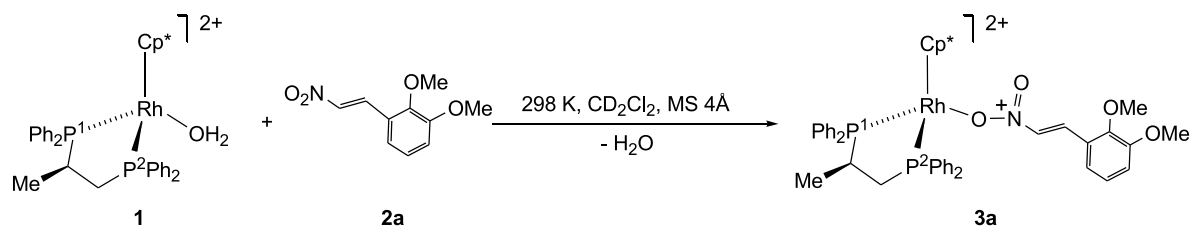
**Table 1**

Reaction of *trans*- $\beta$ -nitrostyrenes with 1,3,5-trimethoxybenzene<sup>a</sup>



Entry	R	Adduct	Reaction time	Conv. (%) <sup>b</sup>	e.r. <sup>c</sup>
1	2,3-(OMe) <sub>2</sub> ( <b>2a</b> )	<b>7a</b>	7 days	84	93/7
2	2-F ( <b>2b</b> )	<b>7b</b>	23 h	> 99	67/33
3	H ( <b>2c</b> )	<b>7c</b>	45 h	> 99	77/23
4	2,4-Cl <sub>2</sub> ( <b>2d</b> )	<b>7d</b>	4 days	83	52.5/47.5

<sup>a</sup> Reactions conditions: Catalyst (0.03 mmol), *trans*- $\beta$ -nitrostyrene (0.60 mmol), 1,3,5-trimethoxybenzene (0.60 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), 4 Å MS (100 mg). <sup>b</sup> Based on 1,3,5-trimethoxybenzene. Determined by <sup>1</sup>H NMR. <sup>c</sup> Determined by HPLC.



Separately, in the addition of 1,3,5-trimethoxybenzene to the *trans*- $\beta$ -nitrostyrene **2c** catalysed by **1** (molar ratio of **1/2c/4** = 1/10/5, in  $\text{CD}_2\text{Cl}_2$ , after 1 h at 203 K, and then, 30 min at 223 K in the presence of 4 Å MS) four metal complexes with the corresponding *aci*-nitro compound coordinated with the metal, two of which in very low abundance, are detected.

Regarding the stereochemistry of the detected metal isomers **5a**, it should be noted that these compounds contain three stereogenic centres, namely, the metal, a carbon atom of the Propfos ligand, and the  $\text{C}^2$  carbon atom to which the nucleophile has been added. Additionally, the *Z/E* isomerism around the  $\text{C}=\text{N}$  double bond of the coordinated adduct must be taken into account. In this context, it should be considered that the initial *R* configuration on the carbon of the Propfos ligand in the fragment ( $S_{\text{Rh}}, R_{\text{C}}$ )- $\text{Cp}^*\text{Rh}\{(R)\text{-Propfos}\}$  is not modified during the process since it does not participate in it. On the other hand, it is important to emphasize that no epimerization at the metal has been observed in any of the reactivity studies that we have conducted to date on compounds that contain it [49,50,55-58]. Assuming this premise, the

detected metal isomers would be diastereomers in which the carbon  $\text{C}^2$  adopts either the *R* or *S* configuration, along with those in which the arrangement around the  $\text{C}=\text{N}$  double bond is either *Z* or *E*. The analysis of molecular models of **5a** compounds suggests that *Z* isomers are likely the least abundant because, in this configuration, steric strain occurs between the *aci*-nitro coordinated group and one of the phenyl groups of the (*R*)-Propfos ligand.

As the next step in the catalytic reaction under consideration should be the replacement of the coordinated *aci*-nitro compound by a new molecule of nitroalkene (Scheme 3), we suspected that the organic compound detected in the reactions between nitroalkenes and 1,3,5-trimethoxybenzene is the free *aci*-nitro compound displaced from the metal coordination sphere. To verify this aspect and characterise this organic compound, we designed an experiment where catalyst **1** was present in sub-stoichiometric proportions. Under these conditions, it should be favoured that the catalytic cycle operates and, consequently, an increase in the concentration of the free *aci*-nitro compound. Indeed, the  $^1\text{H}$  NMR spectrum of a mixture with an initial molar ratio of **1/2a/4**

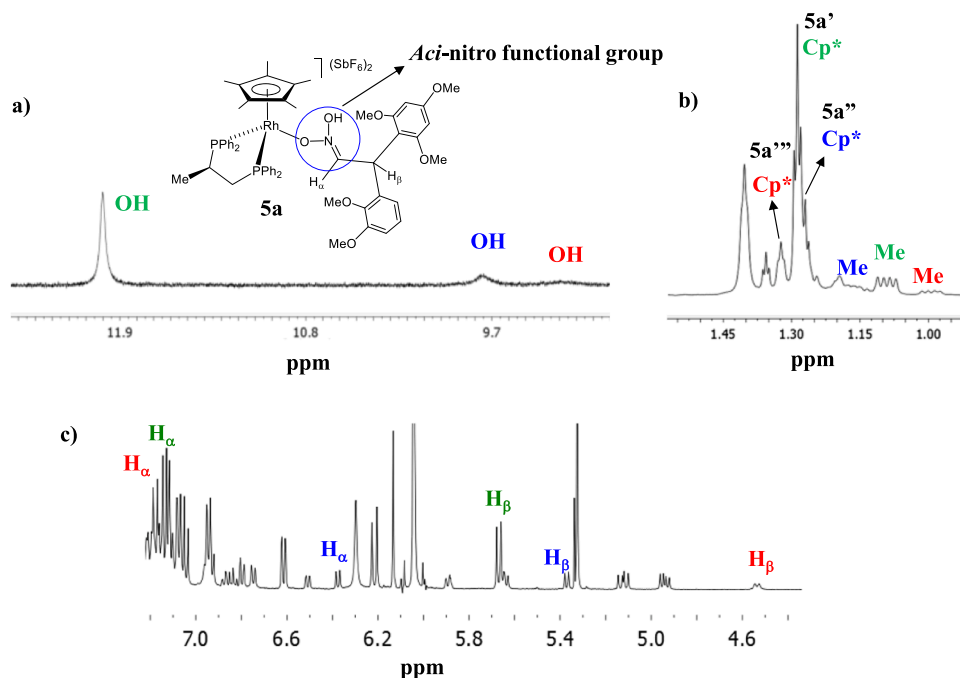
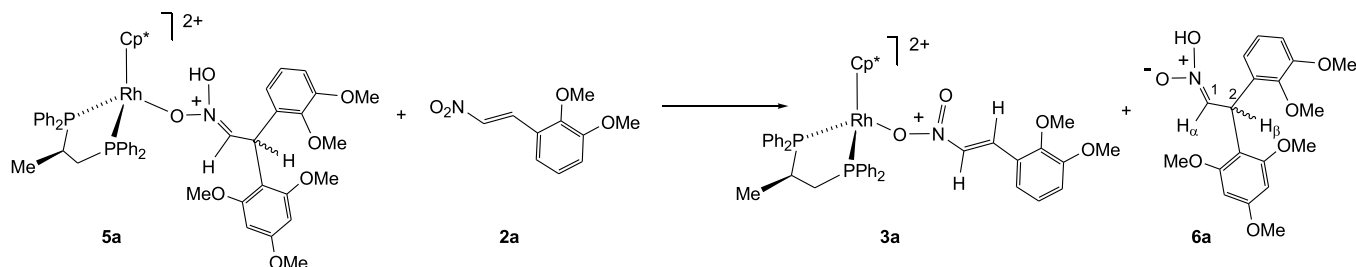


Fig. 3. Selected regions of the  $^1\text{H}$  NMR of *aci*-nitro complexes **5a**; **5a'** (green), **5a''** (blue) and **5a'''** (red labels).



Scheme 3. Substitution reaction of the coordinated *aci*-nitro compound by the nitroalkene **2a**.

= 1/25/20, dissolved in  $\text{CD}_2\text{Cl}_2$ , at 213 K, in the presence of 4 Å MS, after 16 h of reaction shows a broad peak centred at 13.36 ppm, assigned to an OH group. Furthermore, two doublets centred at 6.73 ppm ( $J = 7.8$  Hz) and 5.79 ppm ( $J = 7.4$  Hz) are observed, attributed to the  $\alpha$  and  $\beta$  protons respectively, of the *aci*-nitro compound **6a** shown in Scheme 3. Additionally, in the  $^{13}\text{C}$  NMR spectrum, two signals are recorded at 32.71 and 124.91 ppm, which we attribute to carbons 1 and 2, respectively, of this same compound (see Experimental Section and Supplementary material).

Notably, in mixtures **3a/2a/4** treated as we just mentioned, the progressive formation of the corresponding FC adduct **7a** at the expense of **6a**, most probably, through the prototropic tautomerism shown in Scheme 4 is observed. At temperatures above 243 K, the transformation of **6a** into **7a** is quantitative in a few minutes. Compound **7a** has been characterised *in situ* by comparing its spectroscopic NMR data with those previously described [53].

Finally, in some of the catalytic assays carried out, signals assignable to two metal complexes were observed, distinct from any of the metal intermediates discussed so far. Furthermore, when the catalytic reactions were carried out with a deficiency of nitroalkene, it was observed that these new complexes constituted the resting state of the catalyst. We suspected that they were the diastereomers of stoichiometry  $[\text{Cp}^*\text{Rh}\{(\text{R})\text{-Prophos}\}(7)][\text{SbF}_6]_2$  (**8**) in which the two enantiomers of the corresponding FC adduct were coordinated to the metal. The origin of these complexes could be either the displacement of ligands coordinated to the metal in the catalyst ( $\text{H}_2\text{O}$ ) or the intermediate

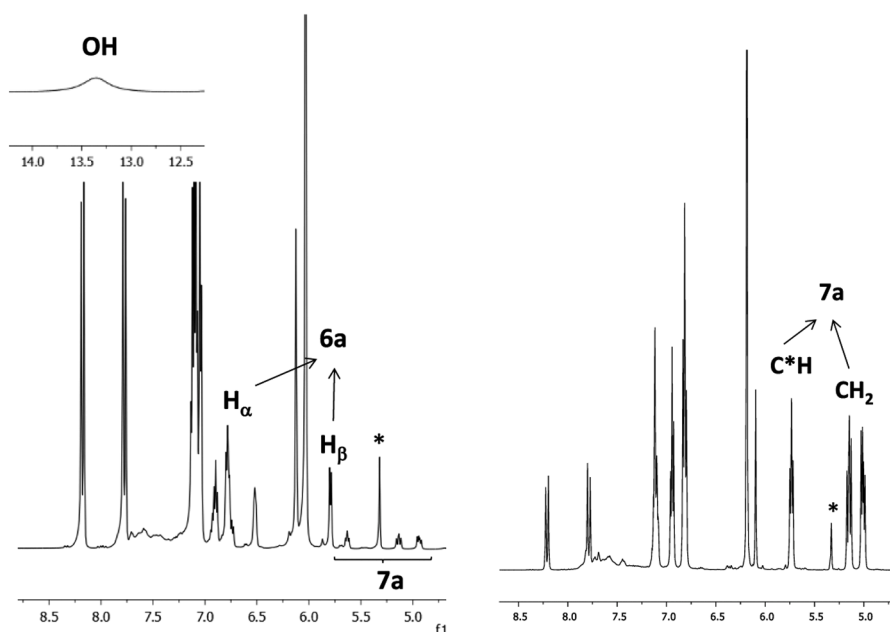
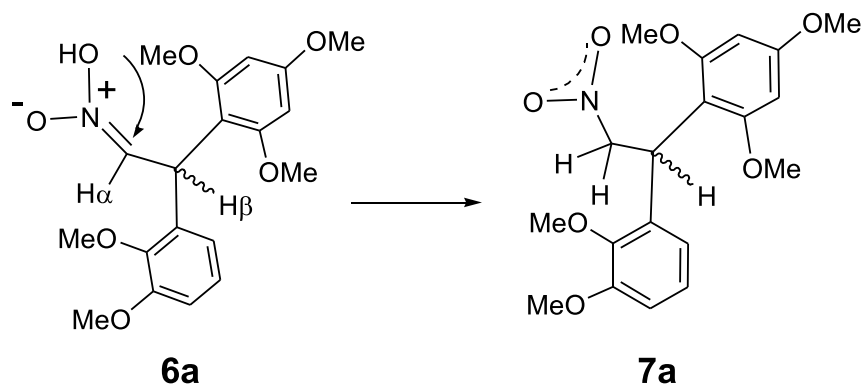
species (nitroalkene, *aci*-nitro compound) by the FC adduct formed *in situ* in the catalytic reaction itself, or the result of a 1,3-prototropism of the *aci*-nitro ligands within the corresponding *aci*-nitro complexes [49]. We propose that complex **8** can eventually slow down the process by trapping the catalyst becoming the resting state at high conversions.

To verify this hypothesis, a racemic mixture of the FC adduct **7a** was added to a  $\text{CD}_2\text{Cl}_2$  solution of catalyst **1** with a molar ratio of  $7\text{a}/1 = 1.2/1$ , in the presence of 4 Å MS. Indeed, two diastereomers, **8a'** and **8a''** (see Supplementary material), epimers at the  $\text{C}^2$  carbon of the coordinated FC adduct (Chart 1), were obtained and characterised *in situ* by NMR spectroscopy. In particular, a multiplet and a pseudotriplet in the 4.20–5.25 ppm interval of the proton NMR spectrum along with resonances around 79 ( $\text{C}^1$ ) and 32 ( $\text{C}^2$ ) ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum are indicative of the aliphatic nature that the  $\text{C}^1\text{H}_2\text{-C}^2\text{H}$  fragment should exhibit in the FC **8a** product (Chart 1).

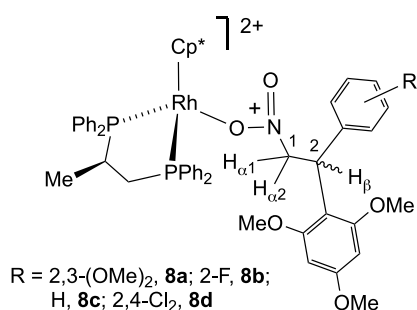
Compounds **8b-d** (Chart 1) were characterised *in situ* by NMR spectroscopy during the corresponding catalytic reaction carried out under stoichiometric conditions. Preparative and spectroscopic details are gathered in the Experimental section.

## 2.2. The catalytic cycle

From the sequential reactions discussed above, the catalytic cycle (route A) depicted in Fig. 4 could be proposed (solid lines). The coordinated water molecule in **1** is displaced by the corresponding nitrostyrene **2** to give the nitroalkene complexes **3**. Attack of 1,3,5-



**Scheme 4.** Selected regions of the  $^1\text{H}$  NMR where it is shown solution evolution of the *aci*-nitro compound **6a**.



**Chart 1.** Complexes with the FC adduct coordinated to the metal.

trimethoxybenzene **4** at the activated  $\text{C}^2$  carbon of the coordinated nitroalkene renders *aci*-nitro complexes **5**. The reaction of **5** with a further molecule of nitrostyrene **2** releases the *aci*-nitro ligand **6** and regenerates complex **3**, which restarts the cycle. Finally, the free *aci*-nitro **6** rearranges to the corresponding FC adduct **7**.

According to this cycle, the enantioselectivity-determining step would be the attack of the nucleophile **4** on the complex with the coordinated nitroalkene **3** and the  $R_{\text{C}2}/S_{\text{C}2}$  ratio measured for *aci*-nitro complexes should match the e.r. of the processes. However, e.r. higher than the measured ratios for the obtained *aci*-nitro complexes have been

obtained (Table 2, entry 1). Table 2 collects the ratio of the *aci*-nitro complexes **5** and the e.r. of FC adducts **7** achieved in the corresponding catalytic process.

In this regard, it is important to note that DFT calculations carried out for the reaction between *trans*- $\beta$ -nitrostyrenes and indoles catalysed by compound **1** establish that one of the coordinated *aci*-nitro enantiomers requires less energy to dissociate from the metal than the other [49]. If we assume that in the reaction between *trans*- $\beta$ -nitrostyrenes and 1,3,5-trimethoxybenzene, the *aci*-nitro complexes **5** behave analogously and demonstrate that the proposed cycle is reversible, a dynamic kinetic resolution will take place in the catalytic process under study. This would explain the observed e.r. values.

### 2.2.1. Reversibility of the proposed catalytic cycle

To assess the reversibility of the proposed cycle, a  $\text{CD}_2\text{Cl}_2$  solution containing catalyst **1**, *trans*-2-fluoro- $\beta$ -nitrostyrene (**2b**) and 1,3,5-trimethoxybenzene **4** in a 1/10/5 molar ratio was prepared. The mixture was allowed to react, at 193 K, until the complete consumption of electrophile **4**. At this point,  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra indicate that the predominant compounds in the mixture were the *aci*-nitro complexes **5b** and free *aci*-nitro **6b** (Fig. 5a and Chart 2). Then, the electrophile *trans*- $\beta$ -nitrostyrene **2c** was added in a molar ratio of 1/1 concerning the initially added **2b**. After 3 additional days of reaction at 213 K, compounds derived from the reaction of 1,3,5-trimethoxybenzene with

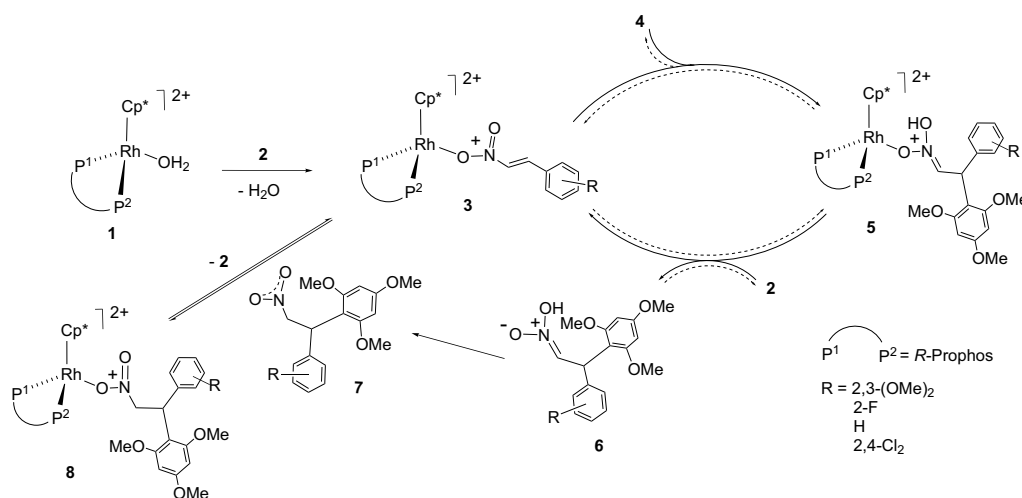


Fig. 4. Proposed catalytic cycle for the FC reaction between *trans*- $\beta$ -nitrostyrenes and 1,3,5-trimethoxybenzene.

Table 2

The molar ratio of *aci*-nitro complexes (5) and e.r. of FC adducts (7)

Entry	R	<i>Ac</i> i-nitro complexes, molar ratio <sup>a</sup> (((ratio=comcomplex	Adducts, e. r. <sup>b</sup>
1	2,3-(OMe) <sub>2</sub>	5a'/5a'', 60/40	7a, 93/7
2	2-F	5b'/5b''/5''', 85/9/6	7b, 67/33
3	H	5c'/5c''/5c'''/5c''''', 67/17/9/7	7c, 77/23
4	2,4-Cl <sub>2</sub>	5d'/5d'', 79/21	7d, 52.5/47.5

<sup>a</sup> For reaction conditions see Section 4.4. of Experimental section.

<sup>b</sup> For reaction conditions see footnote of Table 1.

*trans*- $\beta$ -nitrostyrene **2c** such as the *aci*-nitro compounds **5c**, free *aci*-nitro compound **6c** and the FC adduct **7c** (Fig. 5b and Chart 2) were spectroscopically detected in the reaction medium. When the reaction is complete, a molar ratio of **7b**/**7c** = 60/40 for the FC adducts is observed by <sup>1</sup>H NMR.

The source of 1,3,5-trimethoxybenzene, necessary for the formation of the *trans*- $\beta$ -nitrostyrene derivatives **5c**, **6c**, and **7c**, must be the pathway **6**  $\rightarrow$  **5**  $\rightarrow$  **3**, meaning the cycle shown in Fig. 4 has to be reversible (solid plus dashed lines) and, in addition, the significant formation of **6c** from **6b** suggests that the rate of the **6**  $\rightarrow$  **7** step is slower than the combined reaction rates of the steps **6**  $\rightarrow$  **5**  $\rightarrow$  **3** and **3**  $\rightarrow$  **5**  $\rightarrow$  **6** (Fig. 4). In summary, if it is assumed that enantiomers of different signs coordinated in complexes **5** have sufficiently different dissociation barriers to yield *aci*-nitro compounds **6**, a reversible catalytic cycle like the one proposed explains how the experimentally measured e.r. can be achieved.

### 3. Conclusions

The complex (*S*<sub>Rh</sub>,*R*<sub>C</sub>)-[Cp\*Rh{(R)-Prophos}(H<sub>2</sub>O)][SbF<sub>6</sub>]<sub>2</sub> (**1**) is well suited to catalyse the alkylation reaction between 1,3,5-trimethoxybenzene and *trans*- $\beta$ -nitrostyrenes. High conversions and enantioselectivities of up to 93/7 e.r. were achieved. The spectroscopic detection

and characterisation of catalytic intermediates allow us to propose a plausible reversible catalytic cycle. Notably, the achieved enantioselectivity can be explained by assuming that dynamic kinetic resolution occurs on the *aci*-nitro complex **5** within the cycle. Based on all the spectroscopic data of the metallic intermediates (nitro-, *aci*-nitro- and adduct-complexes) and the catalytic cycle, we conclude that the studied reaction of 1,3,5-trimethoxybenzene and *trans*- $\beta$ -nitrostyrenes proceeds through a Michael-type Friedel-Crafts mechanism.

## 4. Experimental section

### 4.1. General information

All solvents were treated in a PS-400-6 Innovative Technologies Solvent Purification System (SPS) and degassed before use. NMR spectra were recorded on a Bruker AV-300 (300.13 MHz), a Bruker AV-400 (400.16 MHz), or a Bruker AV-500 (500.13 MHz) spectrometer. In both <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements, the chemical shifts are expressed in ppm downfield from SiMe<sub>4</sub>. The <sup>31</sup>P NMR chemical shifts are relative to H<sub>3</sub>PO<sub>4</sub> (85%). Coupling constants (*J*) are given in Hz. COSY, NOESY, HSQC and HMBC <sup>1</sup>H-X (X = <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) correlation spectra were obtained using standard procedures. Analytical high performance liquid chromatography (HPLC) was performed on an Alliance Waters 2996 PDA detector) instrument using a chiral column Chiralpack IB (0.46 cm  $\times$  25 cm) and an IB guard (0.46  $\times$  5 cm).

### 4.2. General procedure for the FC reaction of 1,3,5-trimethoxybenzene with *trans*- $\beta$ -nitrostyrenes

Under argon, 34.2 mg (0.030 mmol) of (*S*<sub>Rh</sub>,*R*<sub>C</sub>)-[Cp\*Rh{(R)-Prophos}(H<sub>2</sub>O)][SbF<sub>6</sub>]<sub>2</sub> (**1**), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), the corresponding *trans*- $\beta$ -nitrostyrene (0.600 mmol) and 4 Å MS (100 mg) were placed in a Schlenk flask equipped with a magnetic stirrer. The resulting mixture was stirred for 20 min at 263 K and then 1,3,5-trimethoxybenzene (**4**) (100.9 mg, 0.600 mmol) was added. The reaction was monitored by thin layer chromatography. After the appropriate reaction time, the reaction was quenched by the addition of a methanol solution of [N(*n*Bu)<sub>4</sub>]Br [59]. The resulting suspension was concentrated under a vacuum until dryness. The residue was extracted with Et<sub>2</sub>O (2  $\times$  3 mL) and the resulting oil was analysed by NMR spectroscopy. The e.r. was determined by HPLC.

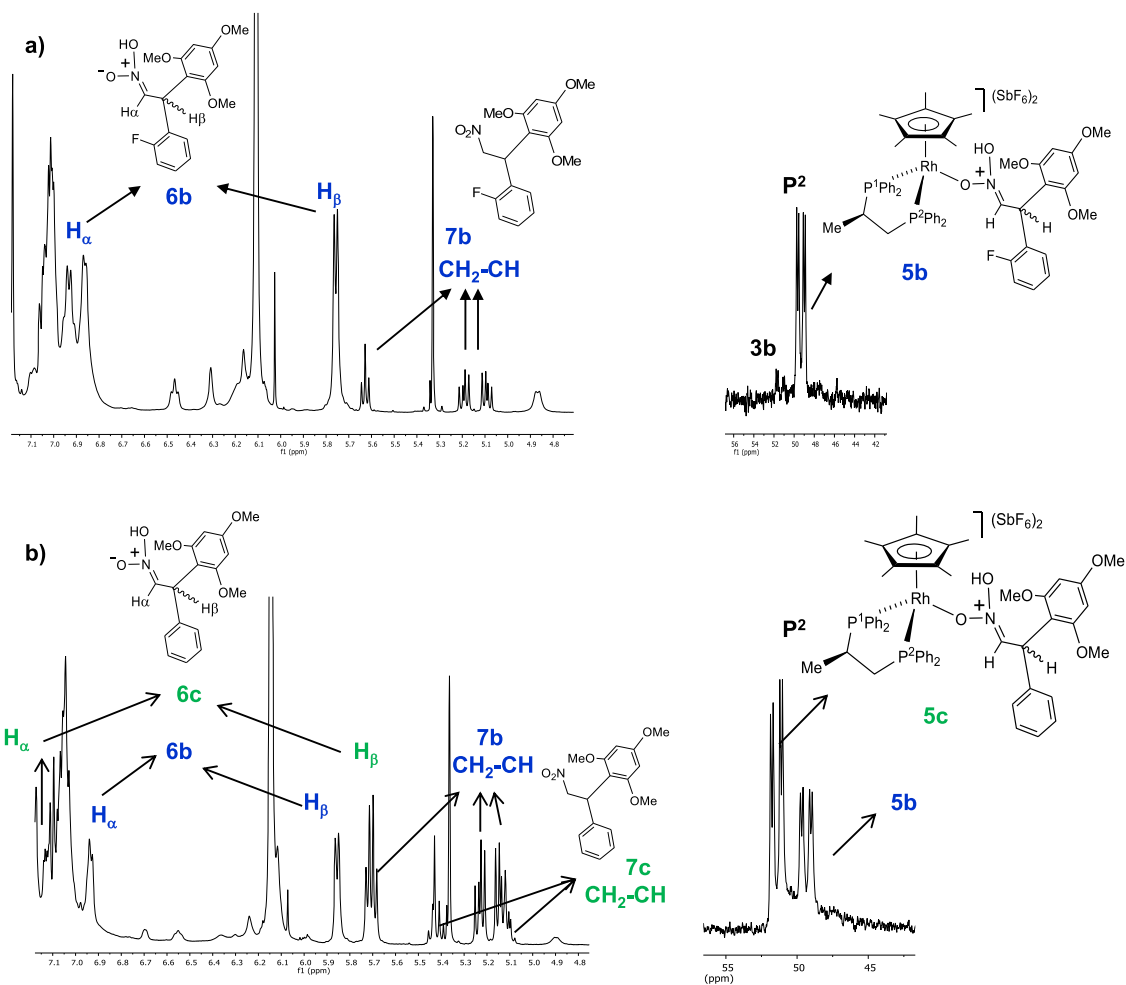


Fig. 5. Selected regions of the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of (a) mixture of 1/2b/4 and (b) mixture after adding 2c.

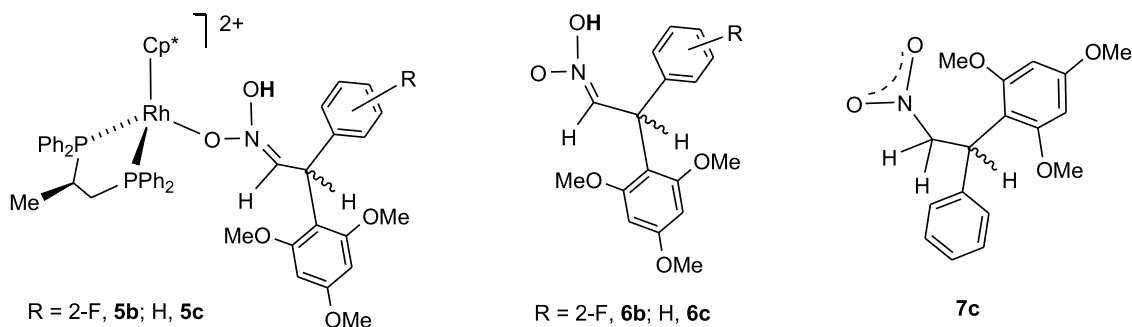
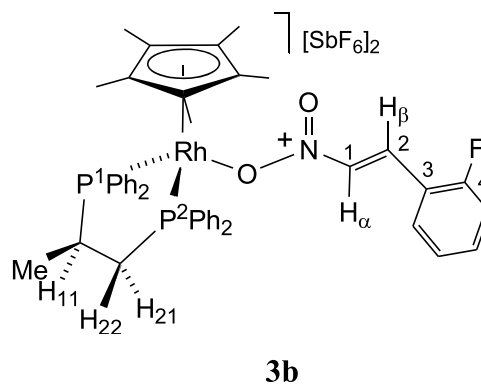


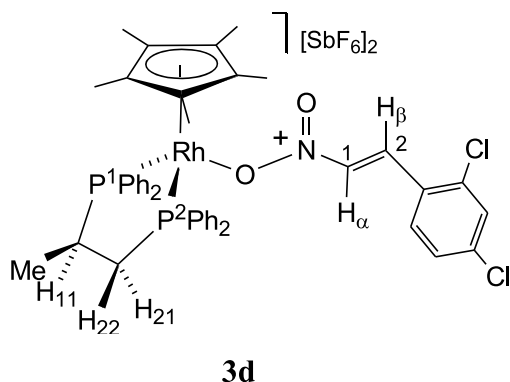
Chart 2. *Aci*-nitro complexes 5b and 5c, *aci*-nitro compounds 6b and 6c and FC adduct 7c.

#### 4.3. Characterisation of the complexes $(S_{\text{Rh}}R_{\text{C}})\text{-}[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(2)]\text{[SbF}_6\text{]}_2$ (3)

At RT, in an NMR tube, to a mixture of complex 1 (30.0 mg, 0.026 mmol), the corresponding *trans*- $\beta$ -nitrostyrene (0.056 (2a), 0.030 (2b), 0.260 (2c), 0.056 (2d) mmol),  $\text{CD}_2\text{Cl}_2$  (0.45 mL) and 4 Å MS (20 mg) were added. After 1 h under argon at 248 K, the conversion to the corresponding  $(S_{\text{Rh}}R_{\text{C}})\text{-}[\text{Cp}^*\text{Rh}\{(R)\text{-Prophos}\}(2)]\text{[SbF}_6\text{]}_2$  (3) compound was complete. Complexes 3 were characterised *in situ* by NMR spectroscopy. In some resonances of the  $^1\text{H}$  NMR spectra, the coupling constant  $J$  is not indicated because it is not discernible due to signal overlap. Complexes 3a [53] and 3c [49] have already been previously characterised.



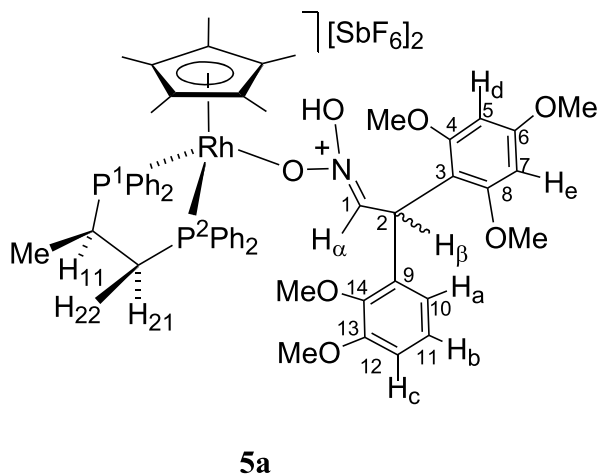
**3b**.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 7.83–7.10 (m, 24H,  $\text{H}_{\text{Ar}}$ ), 7.16 (1H,  $\text{H}_{\text{d}}$ ), 7.15 (1H,  $\text{H}_{\text{p}}$ ), 3.56 (dm,  $J$  = 53.3 Hz, 1H,  $\text{H}_{21}$ ), 3.13 (m, 1H,  $\text{H}_{11}$ ), 2.65 (t,  $J$  = 15.1 Hz, 1H,  $\text{H}_{22}$ ), 1.40 (pt,  $J$  = 3.0 Hz, 15H,  $\text{C}_5\text{Me}_5$ ), 1.26 (dd,  $J$  = 13.6 Hz,  $J$  = 6.3 Hz, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 162.66 (d,  $J(\text{F},\text{C})$  = 260.7 Hz,  $\text{C}_4$ ), 139.81 ( $\text{C}_2$ ), 135.94 ( $\text{C}_1$ ), 137.58–125.29, 116.77 (Ar), 125.37 (d,  $J$  = 39.7 Hz), 125.02 (d,  $J$  = 46.7 Hz), 123.62 (d,  $J$  = 47.1 Hz), 121.15 (d,  $J$  = 46.3 Hz) ( $\text{C}_{\text{ipso}}\text{PPh}_2$ ), 117.10 (d,  $J(\text{F},\text{C})$  = 9.8 Hz,  $\text{C}_3$ ), 107.36 ( $\text{C}_5\text{Me}_5$ ), 33.34 (d,  $J$  = 32.2 Hz,  $\text{CH}_2$ ), 31.23 (d,  $J$  = 31.1 Hz,  $\text{CMe}$ ), 15.84 (d,  $J$  = 18.2 Hz, Me), 10.12 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 75.89 (dd,  $J(\text{Rh},\text{P})$  = 130.7 Hz,  $J(\text{P},\text{P})$  = 38.1 Hz,  $\text{P}^1$ ), 51.48 (dd,  $J(\text{Rh},\text{P})$  = 133.0 Hz,  $\text{P}^2$ ).



**3d**.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 8.40–7.10 (m, 23H,  $\text{H}_{\text{Ar}}$ ), 7.61 (1H,  $\text{H}_{\text{p}}$ ), 7.18 (1H,  $\text{H}_{\text{d}}$ ), 3.62 (dt,  $J$  = 52.9 Hz, 1H,  $\text{H}_{21}$ ), 3.29 (m, 1H,  $\text{H}_{11}$ ), 2.72 (t,  $J$  = 14.6 Hz, 1H,  $\text{H}_{22}$ ), 1.38 (bs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.34 (m, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 140.17 ( $\text{C}_2$ ), 135.60 ( $\text{C}_1$ ), 141.60–125.35 (Ar), 125.75 (d,  $J$  = 50.8 Hz), 124.93 (d,  $J$  = 48.5 Hz), 123.77 (d,  $J$  = 47.3 Hz), 121.74 (d,  $J$  = 46.7 Hz), ( $\text{C}_{\text{ipso}}\text{PPh}_2$ ), 107.58 ( $\text{C}_5\text{Me}_5$ ), 34.22 (d,  $J$  = 31.7 Hz,  $\text{CH}_2$ ), 31.27 (d,  $J$  = 31.1 Hz,  $\text{CMe}$ ), 16.16 (d,  $J$  = 17.1 Hz, Me), 10.08 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121.42 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta$  = 76.42 (dd,  $J(\text{Rh},\text{P})$  = 133.7 Hz,  $J(\text{P},\text{P})$  = 37.0 Hz,  $\text{P}^1$ ), 51.96 (dd,  $J(\text{Rh},\text{P})$  = 132.8 Hz,  $\text{P}^2$ ).

#### 4.4. Characterisation of the aci-nitro complexes $[\text{Cp}^*\text{Rh}\{(\text{R})\text{-Prophos}\}(6)][\text{SbF}_6]_2$ (**5**)

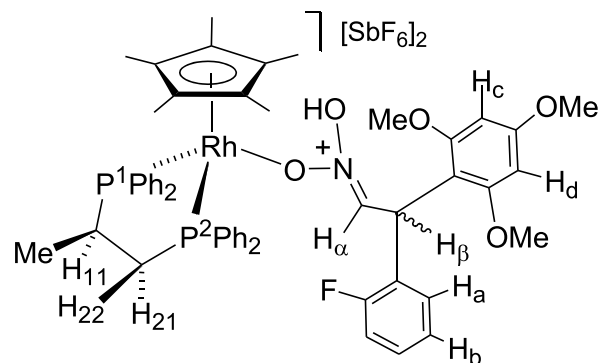
In an NMR tube at RT to a mixture of complex **1** (30.0 mg, 0.026 mmol), the corresponding *trans*- $\beta$ -nitrostyrene,  $\text{CD}_2\text{Cl}_2$  (0.45 mL) and 4 Å MS (20 mg) were added. After 10 min under argon at 213 K, **4** was added at the corresponding temperature. The reaction was monitored by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopies. The resulting complexes were characterised *in situ* by NMR spectroscopy. Some coupling constants are not given in the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra due to signal overlap. The reaction conditions are as follows: **5a**: A mixture of  $1/2\text{a}/4 = 1/2/3$ , 8 days at 203 K; **5b**: A mixture of  $1/2\text{b}/4 = 1/2/3$ , 7 h at 193 K; **5c**: A mixture of  $1/2\text{c}/4 = 1/10/5$ , 1 h at 203 K and, then, 30 min at 223 K. **5d**: A mixture of  $1/2\text{d}/4 = 1/2/3$ , 20 h at 203 K.



**5a**.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 12.02 (brs, 1H, OH), 7.22 (d,  $J$  = 10.6 Hz, 1H,  $\text{H}_{\text{d}}$ ), 7.03 (t,  $J$  = 8.1 Hz, 1H,  $\text{H}_{\text{p}}$ ), 6.93 (d,  $J$  = 8.1 Hz, 1H,  $\text{H}_{\text{c}}$ ), 6.60 (d,  $J$  = 7.0 Hz, 1H,  $\text{H}_{\text{a}}$ ), 6.29 (s, 2H,  $\text{H}_{\text{d}}$ ,  $\text{H}_{\text{e}}$ ), 5.66 (d,  $J$  = 9.3 Hz, 1H,  $\text{H}_{\text{p}}$ ), 3.7–4.1 (m, 15H,  $5 \times \text{OMe}$ ), 3.05 (brd,  $J$  = 52.4 Hz, 1H,  $\text{H}_{21}$ ), 2.90 (m, 1H,  $\text{H}_{11}$ ), 2.30 (m, 1H,  $\text{H}_{22}$ ), 1.30 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.11 (dd,  $J$  = 12.9, 6.5 Hz, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 161.62, 161.17 ( $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$ ), 151.93 ( $\text{C}_{13}$ ), 142.44 ( $\text{C}_{14}$ ), 135.41 ( $\text{C}_1$ ), 129.47 ( $\text{C}_9$ ), 126.72 ( $\text{C}_{11}$ ), 120.74 ( $\text{C}_{10}$ ), 112.21 ( $\text{C}_{12}$ ), 104.30 ( $\text{C}_5\text{Me}_5$ ), 101.84 ( $\text{C}_3$ ), 90.80 ( $\text{C}_5$ ,  $\text{C}_7$ ), 61.28–55.99 ( $5 \times \text{OMe}$ ), 32.97 ( $\text{C}_2$ ), 31.29 ( $\text{CH}_2$ ), 29.35 ( $\text{CMe}$ ), 14.43 (Me), 9.39 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 76.05 (dd,  $J(\text{Rh},\text{P})$  = 129.4 Hz,  $J(\text{P},\text{P})$  = 42.8 Hz,  $\text{P}^1$ ), 49.99 (dd,  $J(\text{Rh},\text{P})$  = 131.8 Hz,  $\text{P}^2$ ).

**5a**'.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 9.76 (brs, 1H, OH), 7.05 (1H,  $\text{H}_{\text{p}}$ ), 6.94 (1H,  $\text{H}_{\text{c}}$ ), 6.49 (d,  $J$  = 7.9 Hz, 1H,  $\text{H}_{\text{a}}$ ), 6.36 (d,  $J$  = 8.3 Hz, 1H,  $\text{H}_{\text{d}}$ ), 6.19 (s, 2H,  $\text{H}_{\text{d}}$ ,  $\text{H}_{\text{e}}$ ), 5.36 (d,  $J$  = 8.1 Hz, 1H,  $\text{H}_{\text{p}}$ ), 3.7–4.1 (m, 15H,  $5 \times \text{OMe}$ ), 3.21 (m, 1H,  $\text{H}_{21}$ ), 2.92 (m, 1H,  $\text{H}_{11}$ ), 2.32 (m, 1H,  $\text{H}_{22}$ ), 1.29 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.17 (dd,  $J$  = 13.8, 6.1 Hz, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 104.30 ( $\text{C}_5\text{Me}_5$ ), 9.39 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 75.93 ( $\text{P}^1$ ), 48.62 (dd,  $J(\text{Rh},\text{P})$  = 131.0 Hz,  $J(\text{P},\text{P})$  = 41.4 Hz,  $\text{P}^2$ ).

**5a**'''.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 9.29 (brs, 1H, OH), 7.31 (1H,  $\text{H}_{\text{d}}$ ), 6.84, 6.60 (2H,  $\text{H}_{\text{b}}$ ,  $\text{H}_{\text{c}}$ ), 5.87 (d,  $J$  = 8.2 Hz, 1H,  $\text{H}_{\text{a}}$ ), 6.22 (s, 2H,  $\text{H}_{\text{d}}$ ,  $\text{H}_{\text{e}}$ ), 4.54 (d,  $J$  = 9.4 Hz, 1H,  $\text{H}_{\text{p}}$ ), 3.7–4.1 (m, 15H,  $5 \times \text{OMe}$ ), 3.00 (m, 1H,  $\text{H}_{21}$ ), 2.90 (m, 1H,  $\text{H}_{11}$ ), 2.42 (m, 1H,  $\text{H}_{22}$ ), 1.34 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.01 (dd,  $J$  = 13.4, 6.4 Hz, 3H, Me).

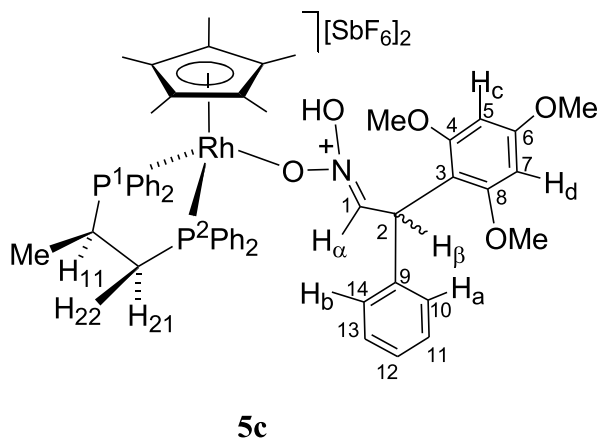


**5b**.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 9.60 (brs, 1H, OH), 7.11 (1H,  $\text{H}_{\text{d}}$ ), 6.94 (pt,  $J$  = 7.5 Hz, 1H,  $\text{H}_{\text{b}}$ ), 6.46 (pt,  $J(\text{F},\text{H})$  = 7.3 Hz, 1H,  $\text{H}_{\text{a}}$ ), 6.15, 6.30 ( $2 \times$  s, 2H,  $\text{H}_{\text{c}}$ ,  $\text{H}_{\text{d}}$ ), 4.85 (brs, 1H,  $\text{H}_{\text{p}}$ ), 3.79–3.39 (9H,  $3 \times \text{OMe}$ ), 2.91 (brd,  $J$  = 53.5 Hz, 1H,  $\text{H}_{21}$ ), 2.77 (m, 1H,  $\text{H}_{11}$ ), 2.37 (m, 1H,  $\text{H}_{22}$ ), 1.29 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 0.95 (m, 3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 162.66–157.68 ( $3 \times \text{COMe}$ ), 160.57 (CF), 128.50 ( $\text{CH}_{\text{a}}$ ), 124.37 ( $\text{CH}_{\text{b}}$ ), 115.51 ( $J$  = 21.8 Hz,  $\text{CHCF}$ ), 137.07–113.30 ( $\text{CH}_{\text{a}}$ ,  $\text{CCH}_{\text{b}}$ ,  $24\text{C}_{\text{Ar}}$ ), 103.96 ( $\text{C}_5\text{Me}_5$ ), 90.63, 90.39 ( $\text{CH}_{\text{c}}$ ,  $\text{CH}_{\text{d}}$ ), 56.72, 55.80–55.55 ( $3 \times \text{OMe}$ ), 33.40 ( $\text{CH}_2$ ), 32.72 ( $\text{CH}_{\text{p}}$ ), 29.51 ( $\text{CMe}$ ), 14.96 (Me), 9.77 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 75.25 (dd,  $J(\text{Rh},\text{P})$  = 128.4 Hz,  $J(\text{P},\text{P})$  = 40.7 Hz,  $\text{P}^1$ ), 49.23 (dd,  $J(\text{Rh},\text{P})$  = 132.0 Hz,  $\text{P}^2$ ).

**5b**'.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 8.77 (brs, 1H, OH), 7.03 (pt,  $J$  = 7.6 Hz, 1H,  $\text{H}_{\text{b}}$ ), 6.66 (pt,  $J(\text{F},\text{H})$  = 7.5 Hz, 1H,  $\text{H}_{\text{a}}$ ), 6.40–6.00 (2H,  $\text{H}_{\text{c}}$ ,  $\text{H}_{\text{d}}$ ), 5.74 (d,  $J$  = 7.7 Hz, 1H,  $\text{H}_{\text{d}}$ ), 5.60 (d,  $J$  = 7.7 Hz, 1H,  $\text{H}_{\text{p}}$ ), 3.79–3.39 (m, 9H,  $3 \times \text{OMe}$ ), 3.14 (m, 1H,  $\text{H}_{21}$ ), 2.85 (m, 1H,  $\text{H}_{11}$ ), 2.21 (m, 1H,  $\text{H}_{22}$ ), 1.26 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.20 (3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 103.73 ( $\text{C}_5\text{Me}_5$ ), 14.42 (Me), 9.14 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 75.27 ( $\text{P}^1$ ), 48.28 ( $J(\text{P},\text{P})$  = 39.4 Hz,  $\text{P}^2$ ).

**5b**'''.  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 10.18 (brs, 1H, OH), 7.01 (1H,  $\text{H}_{\text{b}}$ ), 6.72 (pt, 1H,  $J(\text{F},\text{H})$  = 8.4 Hz,  $\text{H}_{\text{a}}$ ), 6.43 (d, 1H,  $\text{H}_{\text{d}}$ ),

6.40–6.00 (2H, H<sub>c</sub>, H<sub>d</sub>), 5.78 (d,  $J = 9.1$  Hz, 1H, H<sub>β</sub>), 3.79–3.39 (m, 9H, 3 × OMe), 1.19 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 104.16$  (C<sub>5</sub>Me<sub>5</sub>), 9.06 (C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 75.27$  (P<sup>1</sup>), 49.93 ( $J(P,P) = 40.9$  Hz, P<sup>2</sup>).

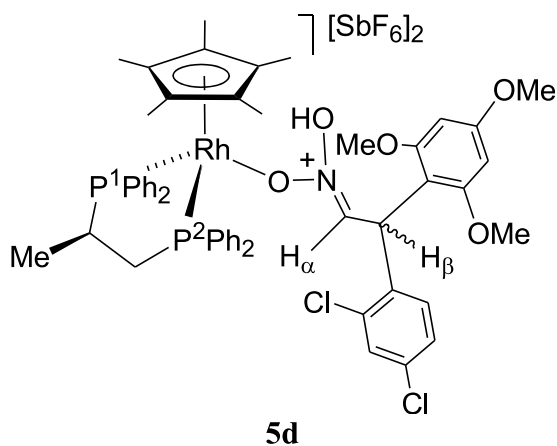


**5c**. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 9.80$  (brs, 1H, OH), 7.35 (d, 1H, H<sub>d</sub>), 6.24 (m, 2H, H<sub>a</sub>, H<sub>b</sub>), 6.20 (s, 2H, H<sub>c</sub>, H<sub>d</sub>), 4.48 (d,  $J = 9.0$  Hz, 1H, H<sub>β</sub>), 3.73 (s, 9H, 3 × OMe), 3.15 (brd, 1H, H<sub>21</sub>), 2.93 (m, 1H, H<sub>11</sub>), 2.48 (m, 1H, H<sub>22</sub>), 1.34 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.03 (dd,  $J = 13.0, 6.6$  Hz, 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 162.20$ – $155.38$  (C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>), 138.01 (C<sub>9</sub>), 134.58– $126.86$  (C<sub>1</sub>, C<sub>11</sub>–C<sub>13</sub>), 126.74 (C<sub>10</sub>, C<sub>14</sub>), 107.71 (C<sub>5</sub>Me<sub>5</sub>), 105.33 (C<sub>3</sub>), 90.73 (C<sub>5</sub>, C<sub>7</sub>), 55.97– $53.59$  (3 × OMe), 37.53 (C<sub>2</sub>), 30.50 (CH<sub>2</sub>), 29.56 (CMe), 15.38 (Me), 9.97 (C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 248 K):  $\delta = 76.20$  (P<sup>1</sup>), 51.40 (dd,  $J(Rh,P) = 131.4$  Hz,  $J(P,P) = 42.4$  Hz, P<sup>2</sup>).

**5c**'. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 9.65$  (brs, 1H, OH), 193 K), 7.35 (1H, H<sub>d</sub>), 4.79 (d,  $J = 6.3$  Hz, 1H, H<sub>β</sub>), 1.23 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 107.44$  (C<sub>5</sub>Me<sub>5</sub>), 38.76 (C<sub>2</sub>), 9.70 (C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 248 K):  $\delta = 76.20$  (P<sup>1</sup>), 51.40 (P<sup>2</sup>).

**5c**''. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 6.03$  (1H, H<sub>d</sub>), 5.79 (d,  $J = 9.1$  Hz, 1H, H<sub>β</sub>), 1.21 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 8.96$  (C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 248 K):  $\delta = 76.20$  (P<sup>1</sup>), 46.95 (dd,  $J(Rh,P) = 132.1$  Hz,  $J(P,P) = 42.5$  Hz, P<sup>2</sup>).

**5c**''. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 6.21$  (d,  $J = 7.8$  Hz, 1H, H<sub>d</sub>), 5.22 (d, 1H, H<sub>β</sub>), 1.28 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 9.06$  (C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 248 K):  $\delta = 76.20$  (P<sup>1</sup>), 49.12 (dd,  $J(Rh,P) = 129.5$  Hz,  $J(P,P) = 40.3$  Hz, P<sup>2</sup>).



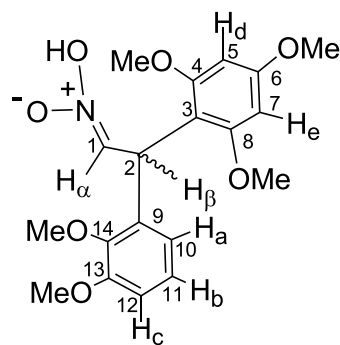
**5d**'. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 13.50$  (brs, 1H, OH), 7.12 (d,  $J = 8.4$  Hz, 1H, H<sub>d</sub>), 4.78 (d, 1H, H<sub>β</sub>), 1.21 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 75.63$  (dd,  $J(Rh,P) = 127.7$

Hz,  $J(P,P) = 40.1$  Hz, P<sup>1</sup>), 49.50 (dd,  $J(Rh,P) = 132.6$  Hz, P<sup>2</sup>).

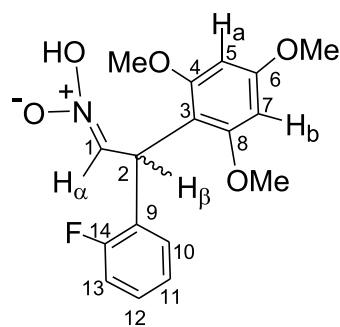
**5d**''. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 6.68$  (d,  $J = 8.2$  Hz, 1H, H<sub>d</sub>), 5.63 (d, 1H, H<sub>β</sub>), 1.25 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K):  $\delta = 76.63$  (P<sup>1</sup>), 48.06 (dd,  $J(Rh,P) = 130.5$  Hz,  $J(P,P) = 41.6$  Hz, P<sup>2</sup>).

#### 4.5. Characterisation of the aci-nitro compounds 6

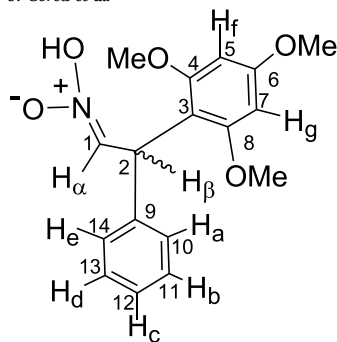
In a NMR tube at RT, a mixture of complex **1** (30.0 mg, 0.026 mmol), the corresponding *trans*- $\beta$ -nitrostyrene, CD<sub>2</sub>Cl<sub>2</sub> (0.45 mL) and 4 Å MS (20 mg) were added. After 10 min under argon at 213 K, **4** was added at the corresponding temperature. The reaction was monitored by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopies. The resulting compound was characterised *in situ* by NMR spectroscopy. The reaction conditions are as follows: **6a**: A mixture of **1/2a/4** = **1/25/20**, 16 h at 213 K. **6b**: A mixture of **1/2b/4** = **1/10/5**, 11 days at 193 K. **6c**: A mixture of **1/2c/4** = **1/10/5**, 1 h at 203 K and, then, 30 min 223 K.



**6a**. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 13.36$  (brs, 1H, OH), 6.90 (pt,  $J = 7.9$  Hz, 1H, H<sub>b</sub>), 6.77 (d,  $J = 8.5$  Hz, 1H, H<sub>c</sub>), 6.73 (d,  $J = 7.8$  Hz, 1H, H<sub>d</sub>), 6.51 (d,  $J = 5.9$  Hz, 1H, H<sub>a</sub>), 5.79 (d,  $J = 7.4$  Hz, 1H, H<sub>β</sub>), 6.13 (s, 2H, H<sub>d</sub>, H<sub>e</sub>), 3.85–3.71 (m, 15H, 5 × OMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 223 K):  $\delta = 160.62$  (C<sub>6</sub>), 158.77, 152.75 (C<sub>4</sub>, C<sub>8</sub>), 146.38 (C<sub>13</sub>), 133.18 (C<sub>14</sub>), 124.91 (C<sub>1</sub>), 124.05 (C<sub>9</sub>), 123.83 (C<sub>11</sub>), 120.29 (C<sub>10</sub>), 110.88 (C<sub>12</sub>), 106.03 (C<sub>3</sub>), 90.20 (C<sub>5</sub>, C<sub>7</sub>), 60.49–57.70 (5 × OMe), 32.71 (C<sub>2</sub>).



**6b**. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 193 K):  $\delta = 13.25$  (brs, 1H, OH), 6.88 (overlapped by H<sub>Ar</sub>, 1H, H<sub>d</sub>), 6.10 (m, 2H, H<sub>a</sub>, H<sub>b</sub>), 5.74 (d,  $J = 7.1$  Hz, 1H, H<sub>β</sub>), 3.79–3.64 (m, 9H, 3 × OMe). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 193 K):  $\delta = 161.75, 159.79, 158.40$  (C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub>), 158.61 (d,  $J(F,C) = 159.9$  Hz, C<sub>14</sub>), 134.24– $124.15$  (C<sub>10</sub>–C<sub>12</sub>), 129.37 (C<sub>1</sub>), 125.46 (C<sub>9</sub>), 115.31 (d,  $J(F,C) = 20.7$  Hz, C<sub>13</sub>), 103.50 (C<sub>3</sub>), 89.83 (C<sub>5</sub>, C<sub>7</sub>), 55.80–55.55 (3 × OMe), 31.78 (C<sub>2</sub>).

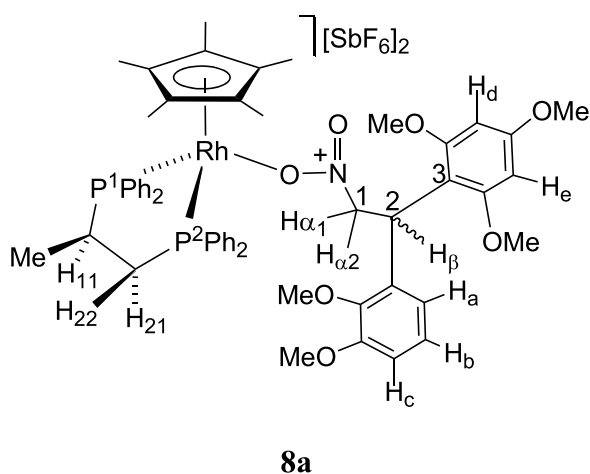
**6c**

**6c.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 223 K):  $\delta$  = 12.87 (brs, 1H, OH), 7.26–7.13 (m, 5H,  $\text{H}_\alpha$ – $\text{H}_\epsilon$ ), 7.09 (dd,  $J$  = 7.7 Hz,  $J$  = 2.8 Hz, 1H,  $\text{H}_\alpha$ ), 6.12, 6.13 (2  $\times$  s, 2H,  $\text{H}_\text{f}$ ,  $\text{H}_\text{g}$ ), 5.69 (d, 1H,  $\text{H}_\beta$ ), 3.78 (s, 9H, 3  $\times$  OMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 160.47, 158.21 ( $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$ ), 139.75 ( $\text{C}_9$ ), 127.31 ( $\text{C}_1$ ), 128.55–126.68 ( $\text{C}_{10}$ – $\text{C}_{14}$ ), 105.88 ( $\text{C}_3$ ), 89.92 ( $\text{C}_5$ ,  $\text{C}_7$ ), 55.83 (3  $\times$  OMe), 36.84 ( $\text{C}_2$ ).

#### 4.6. Characterisation of complexes $[\text{Cp}^*\text{Rh}\{\text{(R)-Prophos}\}(\mathbf{7})][\text{SbF}_6]_2$ (**8**)

**Complex 8a.** In a NMR tube, at 243 K, complex **1** (20.0 mg, 0.017 mmol), a racemic mixture [60] of **7a** (7.54 mg, 0.021 mmol), 4 Å MS (30 mg) and  $\text{CD}_2\text{Cl}_2$  (0.45 mL) were added. The resulting mixture was analysed by NMR spectroscopy at 223 K.

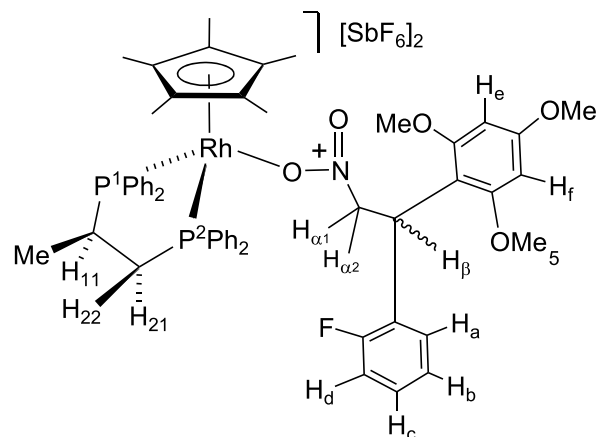
**Complexes 8b–d.** In an NMR tube, at RT, to a mixture of complex **1** (30.0 mg, 0.026 mmol), 0.052 mmol of the corresponding *trans*- $\beta$ -nitrostyrene and  $\text{CD}_2\text{Cl}_2$  (0.45 mL) 4 Å MS (30 mg) were added. After maintaining the mixture under argon for 10 min, 0.078 mmol of 1,3,5-trimethoxybenzene was added. The below reported spectroscopic data were recorded for **8b** after 20 days of reaction at 193 K, for **8c** after 1 day of reaction at 193 K and, then, 12 h at 223 K and for **8d** after 20 h of reaction at 203 K.

**8a**

**8a.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 223 K):  $\delta$  = 7.83–6.64 (m, 22H,  $\text{H}_\text{b}$ ,  $\text{H}_\text{c}$ ,  $\text{H}_{\text{Ar}}$ ), 6.05 (brs, 2H,  $\text{H}_\text{d}$ ,  $\text{H}_\text{e}$ ), 6.03 (1H,  $\text{H}_\alpha$ ), 5.25 (pt,  $J$  = 7.2 Hz, 1H,  $\text{H}_\beta$ ), 4.25 (m, 2H,  $\text{H}_{\alpha 1}$ ,  $\text{H}_{\alpha 2}$ ), 3.77–3.52 (m, 15H, 5  $\times$  OMe), 3.42 (1H,  $\text{H}_{21}$ ), 2.70 (m, 1H,  $\text{H}_{11}$ ), 2.53 (m, 1H,  $\text{H}_{22}$ ), 1.24 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.15 (3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 161.06–111.19 ( $\text{C}_{\text{Ar}}$ ), 107.94 ( $\text{C}_5\text{Me}_5$ ), 101.84 ( $\text{C}_3$ ), 119.48 ( $\text{CH}_\alpha$ ), 90.51 ( $\text{CH}_\text{d}$ ,  $\text{CH}_\text{e}$ ), 79.32 ( $\text{C}_1$ ), 60.35–54.46 (5  $\times$  OMe), 32.95 ( $\text{C}_2$ ), 33.21 ( $\text{CH}_2$ ), 31.85 (CMe), 16.21 (Me), 9.71 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 223 K):  $\delta$  = 74.74 (dd,  $J(\text{Rh},\text{P})$  = 133.43 Hz,  $J(\text{P},\text{P})$  = 38.14 Hz,  $\text{P}^1$ ), 50.22 (dd,  $J(\text{Rh},\text{P})$  = 134.83 Hz,  $\text{P}^2$ ).

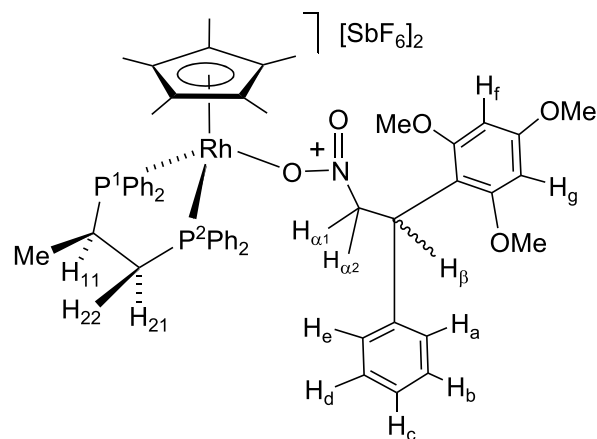
**8a.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 223 K):  $\delta$  = 7.83–6.64 (m, 22H,

$\text{H}_\text{b}$ ,  $\text{H}_\text{c}$ ,  $\text{H}_{\text{Ar}}$ ), 6.44 (d,  $J$  = 7.4 Hz, 1H,  $\text{H}_\alpha$ ), 6.05 (brs, 2H,  $\text{H}_\text{d}$ ,  $\text{H}_\text{e}$ ), 5.10 (pt,  $J$  = 7.3 Hz, 1H,  $\text{H}_\beta$ ), 4.20 (m, 2H,  $\text{H}_{\alpha 1}$ ,  $\text{H}_{\alpha 2}$ ), 3.77–3.56 (m, 15H, OMe), 3.53 (1H,  $\text{H}_{21}$ ), 3.06 (m, 1H,  $\text{H}_{11}$ ), 2.61 (m, 1H,  $\text{H}_{22}$ ), 1.22 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.24 (3H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 161.06–111.19 ( $\text{C}_{\text{Ar}}$ ), 119.62 ( $\text{CH}_\alpha$ ), 107.94 ( $\text{C}_5\text{Me}_5$ ), 90.51 ( $\text{CH}_\text{d}$ ,  $\text{CH}_\text{e}$ ), 79.51 ( $\text{C}_1$ ), 60.35–54.46 (5  $\times$  OMe), 32.41 ( $\text{C}_2$ ), 33.82 ( $\text{CH}_2$ ), 31.55 (CMe), 16.23 (Me), 9.71 ( $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 223 K):  $\delta$  = 74.74 (dd,  $J(\text{Rh},\text{P})$  = 133.43 Hz,  $J(\text{P},\text{P})$  = 38.14 Hz,  $\text{P}^1$ ), 50.95 (dd,  $J(\text{Rh},\text{P})$  = 135.17 Hz,  $\text{P}^2$ ).

**8b**

**8b.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 213 K):  $\delta$  = 7.90–6.90 (m, 23H,  $\text{H}_\text{b}$ ,  $\text{H}_\text{c}$ ,  $\text{H}_\text{d}$ ,  $\text{H}_{\text{Ar}}$ ), 6.06 (s, 2H,  $\text{H}_\text{e}$ ,  $\text{H}_\text{f}$ ), 6.93 (pt,  $J(\text{F},\text{C})$  = 7.2 Hz, 1H,  $\text{H}_\alpha$ ), 4.87 (pt,  $J$  = 7.2 Hz, 1H,  $\text{H}_\beta$ ), 4.45 (dd,  $J$  = 15.2 Hz, 1H), 4.23 (dd, 1H) ( $\text{H}_{\alpha 1}$ ,  $\text{H}_{\alpha 2}$ ), 3.90–3.50 (m, 9H, 3  $\times$  OMe), 3.50 (1H,  $\text{H}_{21}$ ), 2.96 (m, 1H,  $\text{H}_{11}$ ), 2.63 (m, 1H,  $\text{H}_{22}$ ), 1.20 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.20 (3H, Me).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 74.88 (dd,  $J(\text{Rh},\text{P})$  = 131.9 Hz,  $J(\text{P},\text{P})$  = 37.9 Hz,  $\text{P}^1$ ), 50.79 (dd,  $J(\text{Rh},\text{P})$  = 134.5 Hz,  $\text{P}^2$ ).

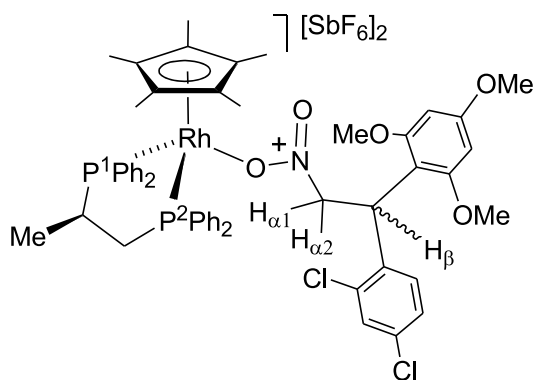
**8b.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 213 K):  $\delta$  = 7.90–6.90 (m, 23H,  $\text{H}_\text{b}$ ,  $\text{H}_\text{c}$ ,  $\text{H}_\text{d}$ ,  $\text{H}_{\text{Ar}}$ ), 6.64 (pt,  $J(\text{F},\text{C})$  = 7.0 Hz, 1H,  $\text{H}_\alpha$ ), 6.06 (s, 2H,  $\text{H}_\text{e}$ ,  $\text{H}_\text{f}$ ), 4.82 (pt,  $J$  = 7.3 Hz, 1H,  $\text{H}_\beta$ ), 4.54 (dd,  $J$  = 14.7 Hz, 1H) 4.27 (dd, 1H) ( $\text{H}_{\alpha 1}$ ,  $\text{H}_{\alpha 2}$ ), 3.90–3.50 (m, 9H, 3  $\times$  OMe), 1.20 (brs, 15H,  $\text{C}_5\text{Me}_5$ ), 1.20 (3H, Me).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{CD}_2\text{Cl}_2$ , 203 K):  $\delta$  = 74.23 (dd,  $J(\text{Rh},\text{P})$  = 129.7 Hz,  $J(\text{P},\text{P})$  = 38.8 Hz,  $\text{P}^1$ ), 50.67 (dd,  $J(\text{Rh},\text{P})$  = 134.5 Hz,  $\text{P}^2$ ).

**8c**

**8c.**  $^1\text{H}$  NMR (500.10 MHz,  $\text{CD}_2\text{Cl}_2$ , 213 K):  $\delta$  = 7.93–7.03 (m, 23H,  $\text{H}_\text{b}$ ,  $\text{H}_\text{c}$ ,  $\text{H}_\text{d}$ ,  $\text{H}_{\text{Ar}}$ ), 6.79 (d,  $J$  = 7.1 Hz 2H,  $\text{H}_\alpha$ ,  $\text{H}_\alpha$ ), 6.09 (2H,  $\text{H}_\text{f}$ ,  $\text{H}_\text{g}$ ), 5.05 (1H), 4.08 (dd,  $J$  = 14.3 Hz,  $J$  = 3.2 Hz, 1H) ( $\text{H}_{\alpha 1}$ ,  $\text{H}_{\alpha 2}$ ), 4.65 (dd,  $J$  = 9.9

Hz, 1H, H<sub>β</sub>), 3.96–3.57 (m, 9H, 3 × OMe), 3.40 (brd, *J* = 50.7 Hz, 1H, H<sub>21</sub>), 3.02 (m, 1H, H<sub>11</sub>), 2.54 (m, 1H, H<sub>22</sub>), 1.19 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>), 1.19 (3H, Me). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K): δ = 74.96 (dd, *J*(Rh,P) = 133.1 Hz, *J*(P,P) = 37.5 Hz, P<sup>1</sup>), 50.10 (dd, *J*(Rh,P) = 133.5 Hz, P<sup>2</sup>).

**8c<sup>+</sup>**. <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K): δ = 7.93–7.03 (m, 23H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>, 20H<sub>Ar</sub>), 7.00 (d, *J* = 7.5 Hz 2H, H<sub>a</sub>, H<sub>e</sub>), 5.96 (s, 2H, H<sub>f</sub>, H<sub>g</sub>), 4.83 (dd, *J* = 13.5 Hz, *J* = 9.3 Hz, 1H), 4.29 (dd, 1H), (H<sub>α1</sub> or H<sub>α2</sub>), 4.47 (dd, *J* = 9.3 Hz, *J* = 5.9 Hz, 1H, H<sub>β</sub>), 3.96–3.57 (m, 9H, 3 × OMe), 1.11 (brs, 15H, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 213 K): δ = 74.00 (dd, *J*(Rh,P) = 131.4 Hz, *J*(P,P) = 38.7 Hz, P<sup>1</sup>), 50.26 (dd, *J*(Rh,P) = 133.5 Hz, P<sup>2</sup>).



## 8d

**8d** <sup>1</sup>H NMR (500.10 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K): δ = 5.97 (d, *J* = 8.1 Hz), 5.52 (m, 1H), 5.27 (m, 1H) (H<sub>α1</sub>, H<sub>α2</sub>, H<sub>β</sub>), 1.25 (15H, C<sub>5</sub>Me<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.46 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 203 K): δ = 49.24 (P<sup>2</sup>).

## CRediT authorship contribution statement

**Jorge Cored:** Investigation, Formal analysis. **Antonio Sánchez:** Methodology, Investigation, Formal analysis. **Fernando Viguri:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ricardo Rodríguez:** Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Conceptualization. **Pilar Lamata:** Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Daniel Carmona:** Writing – original draft, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2024.123377.

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