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# Redox-responsive catalysis: fine tuning of chemoselectivity in the intramolecular reaction of diazo compounds catalysed by ferrocene-functionalised dirhodium(II) complexes

Illia Ruzhylo,<sup>a</sup> Sandrine Vincendeau,<sup>a</sup> Philippe Dauban,<sup>b</sup> Eric Manoury,<sup>a</sup> Rinaldo Poli,<sup>a,c</sup> and Agnès Labande <sup>\*a</sup>

<sup>a</sup> LCC-CNRS, Université de Toulouse, CNRS, INPT, 205 route de Narbonne, 31077 Toulouse, France  
E-mail: agnes.labande@lcc-toulouse.fr

<sup>b</sup> Université Paris-Saclay, CNRS, Institut de Chimie des Substances Naturelles, UPR 2301, 91198 Gif-sur-Yvette, France.

<sup>c</sup> Institut Universitaire de France, 1, rue Descartes, 75231 Paris, France.

A series of heteroleptic dirhodium(II) complexes (**1a-k**) of formula  $[\text{Rh}_2(\text{OAc})_3(\text{L})]$ , where L is a redox-active ferrocenecarboxylate ligand, has been evaluated in the redox-responsive, dirhodium(II)-catalysed decomposition of several diazo substrates prone to chemoselectivity issues. The influence of the counter-anion of chemically oxidised ferrocenyl-containing complexes on the chemoselectivity of the decomposition of the diazo compound **2** has been investigated with complexes **1a-d**: bulky, weakly coordinating  $\text{SbF}_6^-$  and  $\text{BArF}_4^-$  ( $[\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{4B}]^-$ ) result in a greater chemoselectivity difference between reduced and oxidised versions of the catalyst than  $\text{BF}_4^-$ . The correlation between the electronic nature of the ferrocenyl substituents and the extent of the chemoselectivity switch is not obvious, as complex **1a** with unsubstituted ferrocene gave the best results upon oxidation among complexes **1a-k**. The introduction of a saturated tether in **1j-k** drastically decreases the chemoselectivity difference between reduced and oxidized species. Finally, two additional diazo compounds with various chemoselectivity issues (**9** and **10**) were evaluated in the presence of complexes **1a** and **1a+**. $\text{SbF}_6^-$ : the decomposition of diazo complex **9**, producing an aromatic C–H insertion product **11** and a cyclopropanation product **12**, led to a 42% chemoselectivity difference between **1a** and **1a+**. $\text{SbF}_6^-$ . This demonstrates that changing the electronic properties of only one ligand on dirhodium, by oxidation of its ferrocenyl part, can have a marked influence on the reaction selectivity.

## Introduction

The design of new catalysts and the appreciation of their stereoelectronic properties is of paramount importance for the improvement of existing syntheses or to unlock new reactivities.<sup>1-5</sup> Often, only subtle variations in the coordination sphere entail important reactivity or selectivity changes.<sup>6,7</sup> In dirhodium(II) chemistry, this has been amply demonstrated by the work of Davies, who showed that the regioselectivity of carbene C–H insertion of simple alkanes could be totally changed by a steric tuning of the equatorial ligands.<sup>8-10</sup> The electronic nature of a ligand is also crucial, as it influences the electrophilicity of the rhodium centre, which can be correlated to its oxidation potential. The electronic effect on the chemo-, regio- and stereoselectivity of diazo-based reactions has been well described, particularly by Doyle and Padwa.<sup>1, 11</sup>

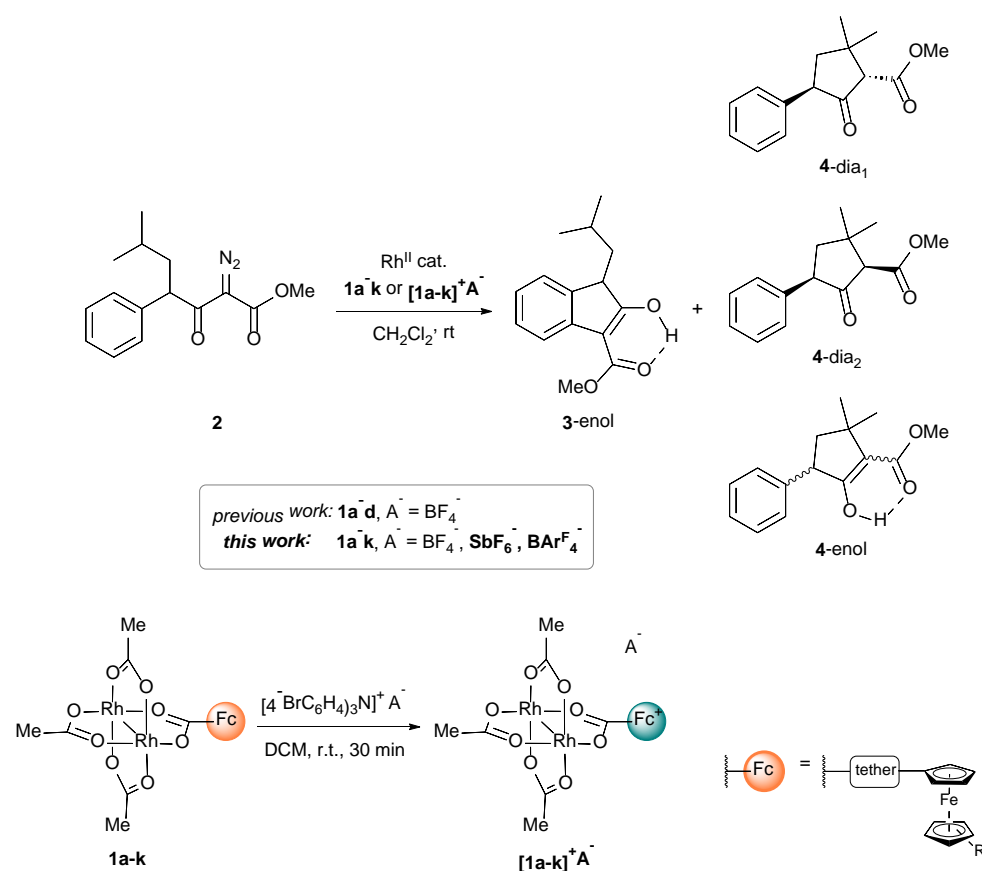
It is also known that, in catalytic processes involving cationic complexes, the nature of the anion can have a marked influence on the rate and stereoselectivity of reactions.<sup>12-22</sup> However, although numerous electrochemical studies have demonstrated that the nature of the supporting electrolyte anion has an influence on the redox behaviour of compounds bearing (several) oxidizable ferrocenyl units,<sup>23-31</sup> the influence of the anion in redox-switchable catalysis involving ferrocenyl ligands has seldom been investigated.<sup>31, 32</sup> This can be explained by the fact that most previously reported systems describe an “on-off” behaviour upon oxidation of the ferrocenyl unit, where the nature of the anion may not be crucial.<sup>32-39</sup> Among reports on redox-triggered selectivity changes,<sup>40-50</sup> mainly in the area of polymerization,<sup>42-50</sup> those using ferrocene as redox-active unit do not mention the influence of the anion of the oxidized catalyst on selectivity.<sup>41, 42, 44-46</sup> We recently demonstrated that the chemoselectivity of the dirhodium(II)-catalysed intramolecular C–H insertion of a carbene could be tuned by the oxidation state of the ferrocenyl unit in the ferrocenecarboxylate ligands (Scheme 1).<sup>51</sup> Hence, the aromatic/aliphatic C–H insertion product ratio increased as a result of ferrocene oxidation: the rhodium centre became more electrophilic, thus making the metallocarbene more reactive toward aromatic C–H bonds.

However, the selectivity changes remained modest and we wondered about the influence of the  $\text{BF}_4^-$  counter anion, which is not considered as weakly coordinating.<sup>12, 15, 52</sup> In this work, we describe our findings on the counter-anion effect on the redox-responsive chemoselectivity of dirhodium(II)-catalysed intramolecular decomposition of several acceptor-acceptor diazo substrates.

## Results and discussion

### Dirhodium(II)-catalysed decomposition of diazo compound **2**: influence of the anion and of the ferrocenyl unit

In previous work, we demonstrated that the ratio of aliphatic vs. aromatic C–H insertion products obtained by dirhodium(II)-catalysed decomposition of the acceptor-acceptor diazo compound **2** (Scheme 1) could be altered following the chemical oxidation of the ferrocenyl part of one carboxylate ligand on rhodium with  $[\text{N}(4\text{-C}_6\text{H}_4\text{Br})_3]^+\text{BF}_4^-$ .<sup>51</sup> Among the four heteroleptic ferrocenyl dirhodium(II) complexes employed, complex **1d** bearing a bulky electron-donating  $\text{Cp}^*$  substituent on the ferrocene (Figure 1) gave the greatest chemoselectivity change upon ferrocene oxidation (19% increase in aromatic C–H insertion product).

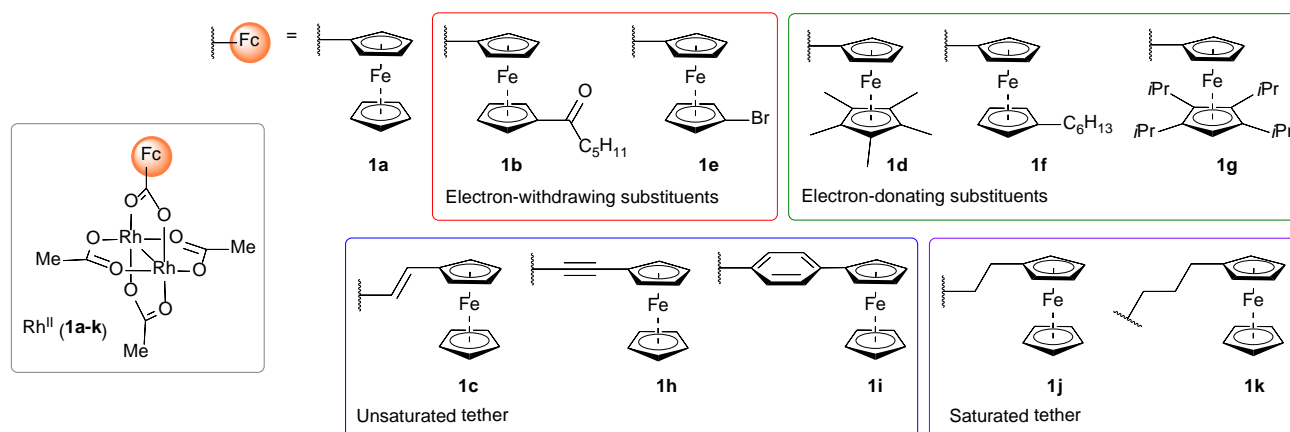


**Scheme 1.** Dirhodium(II)-catalysed, redox-responsive decomposition of diazo compound **2**.

Those results were obtained with an oxidized catalyst bearing a tetrafluoroborate anion, provided by the tris(4-bromophenyl)aminium tetrafluoroborate oxidant. However, this anion has a marked tendency to form ion pairs,<sup>15</sup> and we wondered whether its interaction with the ferrocenium moiety could reduce the ability of the latter to influence the chemoselectivity of the catalytic reaction. The oxidation of complexes **1a-d** was thus carried out with tris(4-bromophenyl)aminium salts bearing bulkier  $\text{SbF}_6^-$ <sup>53</sup> and  $\text{BARF}_4^-$  ( $[(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]^-$ ),<sup>54</sup> both known to be less prone to forming tight ion pairs (Scheme 1).

The decomposition of the diazo compound **2**<sup>51</sup> was carried out in  $\text{CH}_2\text{Cl}_2$  with complexes **1a-d** (Figure 1), in order to compare the effect of the different anions (Table 1). The reaction conditions were optimized compared to our previous work, as the diazo substrate was added in one portion instead of a slow addition by syringe pump. The catalytic loading

was also lowered to 1 mol%, and a reference experiment with  $[\text{Rh}_2(\text{OAc})_4]$  showed that these changes had no impact on either reactivity or chemoselectivity.



**Figure 1.** Heteroleptic ferrocenyl dirhodium(II) complexes **1a-k** used in this study.

**Table 1.** Anion-dependent chemoselectivity of diazo **2** decomposition with reduced and oxidized complexes **1a-d**.

Entry	Rh complex	3+4 (%) <sup>c</sup>	3:4 (+% of 3) <sup>d</sup>
1 <sup>a</sup>	<b>1a</b>	87	37:63
2 <sup>a</sup>	<b>1a</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	94	49:51 (+12%)
3 <sup>b</sup>	<b>1a</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	87	66:34 (+ 29%)
4 <sup>b</sup>	<b>1a</b> <sup>+</sup> BARF <sub>4</sub> <sup>-</sup>	91	65:35 (+ 28%)
5 <sup>a</sup>	<b>1b</b>	84	42:58
6 <sup>a</sup>	<b>1b</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	87	51:49 (+ 9%)
7 <sup>b</sup>	<b>1b</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	94	67:33 (+ 25%)
8 <sup>b</sup>	<b>1b</b> <sup>+</sup> BARF <sub>4</sub> <sup>-</sup>	92	66:34 (+ 24%)
9 <sup>a</sup>	<b>1c</b>	88	30:70
10 <sup>a</sup>	<b>1c</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	91	48:52 (+ 18%)
11 <sup>b</sup>	<b>1c</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	97	48:52 (+ 18%)
12 <sup>b</sup>	<b>1c</b> <sup>+</sup> BARF <sub>4</sub> <sup>-</sup>	95	49:51 (+ 19%)
13 <sup>a</sup>	<b>1d</b>	90	41:59
14 <sup>a</sup>	<b>1d</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	93	60:40 (+ 19%)
15 <sup>b</sup>	<b>1d</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	97	61:39 (+ 20%)
16 <sup>b</sup>	<b>1d</b> <sup>+</sup> BARF <sub>4</sub> <sup>-</sup>	96	61:39 (+ 20%)

Reagents and conditions: <sup>a</sup> diazo substrate **2** (0.2 mmol), Rh<sup>II</sup> cat. (2.5 mol%), CH<sub>2</sub>Cl<sub>2</sub> (1.5 + 1.5 mL), r.t., 3 h, ref. [9]. <sup>b</sup> diazo substrate **2** (0.2 mmol), Rh<sup>II</sup> cat. (1 mol%), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), r.t., 3 h. Oxidized species generated *in situ* by addition of 1.05 equiv. of [N(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sup>+</sup>A<sup>-</sup>. <sup>c</sup> Global isolated yield, average of two runs. <sup>d</sup> Average of two runs, determined by integration of characteristic <sup>1</sup>H NMR signals (CDCl<sub>3</sub>).

After 3 h at room temperature, all complexes - whatever the ferrocenyl ligand, its oxidation state and the nature of the anion - yielded a total conversion of the diazo substrate and very high global isolated yields. These yields are even slightly higher with **1b-d**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (entries 7, 11 and 15) and **1b-d**<sup>+</sup>BARF<sub>4</sub><sup>-</sup> (entries 8, 12 and 16), despite the use of a lower catalytic charge (1 mol%), which could be explained by their higher solubility compared to **1b-d**<sup>+</sup>BF<sub>4</sub><sup>-</sup>. Pleasingly, the results showed a clear increase in chemoselectivity difference between reduced and oxidized forms of the complexes when changing

from  $\text{BF}_4^-$  to  $\text{SbF}_6^-$  or  $\text{BAR}_4^{\text{F}_4^-}$  for complexes **1a** and **1b** (entries 2-4 and 6-8): thus a 29% increase in aromatic C–H insertion product **3** was obtained with **1a**<sup>+</sup> bearing an  $\text{SbF}_6^-$  anion, against 12% with the  $\text{BF}_4^-$  anion. However, no difference was measured upon anion change with complexes **1c** and **1d** (entries 10-12 and 14-16), despite them being the most successful ones with  $\text{BF}_4^-$ . Although the result with complex **1d** may be rationalized by the bulky character of the Cp\* moiety, which allows a better charge separation even with  $\text{BF}_4^-$  and thus a more pronounced positive charge on ferrocenium,<sup>55</sup> the same explanation cannot be invoked in the case of complex **1c** bearing an ethenyl spacer. The lack of anion effect in this case may be related to charge diffusion: the presence of a conjugated double bond makes the positive charge less pronounced on the iron centre and more evenly distributed on the unsaturated system, thus making the interaction less sensitive to the anion change. In all cases,  $\text{SbF}_6^-$  and  $\text{BAR}_4^{\text{F}_4^-}$  gave identical **3:4** ratios, which confirms that the nature of the anion is less important than its ion pair dissociating character, and that the steric effect (anion volume) is negligible.  $\text{SbF}_6^-$  was chosen as anion for the rest of the study, since the corresponding tris(4-bromophenyl)-aminium oxidant is easier to prepare than its  $\text{BAR}_4^{\text{F}_4^-}$  congener.

With this data in hand, we decided to evaluate the potential of other heteroleptic ferrocenyl dirhodium(II) complexes to induce chemoselectivity changes (Table 2). Complexes **1e-i**, previously prepared in our group,<sup>51</sup> possess ferrocenyl ligands covering a large panel of electronic and steric properties (Figure 1): **1e** bears an electron-withdrawing substituent on the second ferrocenyl Cp ring, while **1f** has a long electron-donating alkyl chain which increases its solubility in apolar solvents. Complex **1g** also bears four electron-donating groups, making it electronically similar to **1d**, but much bulkier. The influence of the spacer has been investigated further with the introduction of a triple bond (**1h**) or a phenyl ring (**1i**). Finally, in order to learn more about the nature of the electronic communication between ferrocene and rhodium, which can take place either through-bond or through-space, we designed complexes **1j** and **1k** bearing saturated two-carbon or three-carbon spacers between the ferrocene and carboxylate moieties. All reactions were stirred at room temperature for 3 h, after which the conversion of the diazo compound was consistently complete (determined by <sup>1</sup>H NMR analysis of the crude mixture).

**Table 2.** Chemoselectivity of diazo **2** decomposition with reduced and oxidised complexes **1e-k**.

Entry	Rh complex	3+4 (%) <sup>a</sup>	3:4 (+% of 3) <sup>b</sup>
1	<b>1e</b>	91	34:66
2	<b>1e</b> <sup>+</sup> $\text{SbF}_6^-$	93	56:44 (+ 18%)
3	<b>1f</b>	90	29:71
4	<b>1f</b> <sup>+</sup> $\text{SbF}_6^-$	95	56:44 (+ 27%)
5	<b>1g</b>	94	42:58
6	<b>1g</b> <sup>+</sup> $\text{SbF}_6^-$	89	60:40 (+ 18%)
7	<b>1h</b>	97	40:60
8	<b>1h</b> <sup>+</sup> $\text{SbF}_6^-$	91	53:47 (+ 13%)
9	<b>1i</b>	97	37:63
10	<b>1i</b> <sup>+</sup> $\text{SbF}_6^-$	95	50:50 (+ 13%)
11	<b>1j</b>	96	35:65
12	<b>1j</b> <sup>+</sup> $\text{SbF}_6^-$	88	39:61 (+ 4%)
13	<b>1k</b>	96	36:64
14	<b>1k</b> <sup>+</sup> $\text{SbF}_6^-$	92	32:68 (- 4%)

Reagents and conditions: diazo substrate **2** (0.2 mmol), Rh<sup>II</sup> cat. (1 mol%),  $\text{CH}_2\text{Cl}_2$  (3 mL), r.t., 3 h. Oxidized species generated *in situ* by addition of 1.1 equiv. of  $[\text{N}(4\text{-BrC}_6\text{H}_4)_3]^+\text{SbF}_6^-$ . <sup>a</sup> Global isolated yield, average of two runs. <sup>b</sup> Average of two runs, determined by integration of characteristic <sup>1</sup>H NMR signals ( $\text{CDCl}_3$ ).

The first observation that can be made from the results of this study is that the introduction of electron-withdrawing substituents yields smaller chemoselectivity changes upon oxidation relative to the unsubstituted ferrocene. Indeed, apart from **1b**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, which possesses a long acyl chain (Table 1, entry 7), a maximum increase of 18% in product **3** was obtained with **1e**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> (Table 2, entry 2). We wondered at first whether the lower solubility of this oxidized catalytic species in DCM, relative to **1b**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, could be an issue. However, a similar trend was observed with electron-donating substituents: complex **1f**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> bearing a simple alkyl chain (Table 2, entry 4, +27%) gave much better results than the more electron-donating **1d**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> and **1g**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, bearing respectively Cp\* and Cp<sup>iPr4</sup> rings (Table 1, entry 15 and Table 2, entry 6), which both show an increase in product **3** of around 20%. In this case, the solubility of the oxidized species is not a problem. The only difference between these three complexes is the increase in the ferrocene steric bulk, consistent with their gradually lower efficiency in terms of chemoselectivity difference. The change in unsaturated tether also gave contrasted results: surprisingly, switching from an ethenyl spacer (**1c**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, Table 1, entry 11) to an ethynyl spacer (**1h**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, Table 2, entry 8) made the chemoselectivity difference drop from 18% to 13%. An identical result was obtained with the complex bearing a phenyl spacer (**1i**<sup>+</sup>SbF<sub>6</sub><sup>-</sup>, Table 2, entry 10). The length of the tether and the number of bonds separating the ferrocenyl unit and the carboxylate group being the same in **1c** and **1h**, the more efficient transmission of the electronic information through the unsaturated system of **1c** may be due to a better charge delocalization upon oxidation.<sup>56, 57</sup>

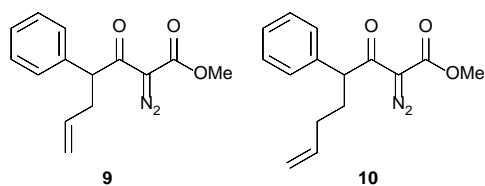
Finally, when saturated tethers were introduced between ferrocene and the carboxylate group, only very small differences were measured in the **3:4** ratio when oxidized and reduced forms of **1j** and **1k** were used (Table 2, entries 11-14). Oxidised **1k**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> produced even slightly more aliphatic C-H insertion product **4** than the reduced form (-4% **3**, Table 2, entry 14). However, the observed differences in **3:4** ratios were almost negligible, and much smaller than in the case of **1c**, **1h** and **1i**: this shows that the transmission of the electronic information mostly happens through bonds.

Surprisingly, no clear influence of the electronic properties on the results could be drawn from this study, as electron-withdrawing and electron-donating substituents showed essentially the same trend, with less interesting differences upon oxidation than for the unsubstituted ferrocene. However, introduction of long alkyl chains seems to be beneficial, whatever the electronic character of the substituent. The introduction of an unsaturated tether allows maintaining electronic communication to a certain extent, but this proved less efficient than a direct ferrocene-carboxylate linkage. Finally, the transmission of electronic information was confirmed to go through the bonds as the effect is almost suppressed in the case of saturated tethers.

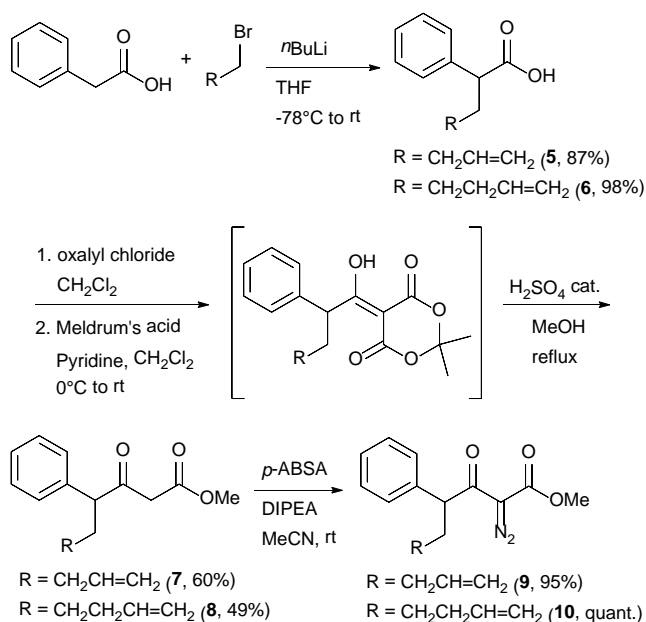
### Dirhodium(II)-catalysed decomposition of other diazo compounds

In view of these results, we decided to keep the simplest heteroleptic dirhodium(II) complex **1a**, bearing the commercially available ferrocenecarboxylic acid ligand, for the evaluation of chemoselectivity changes on diazo substrates **9** and **10**, also prone to chemoselectivity issues.

**Synthesis of diazo substrates.** We selected two additional substrates presenting different types of chemoselectivity concerns (Figure 2) for our investigation. Substrate **9** possesses a side chain with a double bond: similarly to **2**, it could give an aromatic C-H insertion product, but the double bond could also undergo cyclopropanation with the metalcarbene. The diazo compound **10**, with an additional CH<sub>2</sub> group in the side chain relative to **9**, may give rise again to an aromatic C-H insertion product, but also to a C-H insertion reaction at the allylic position, whereas the cyclopropanation reaction should be disfavoured. Indeed, intramolecular reactions of diazo substrates potentially giving bicyclo[4.1.0]heptanes were previously shown to produce very small amounts of cyclopropanes for all tested rhodium-based catalysts, whereas cyclopropanation is favoured with copper- or palladium-based catalysts.<sup>11, 58</sup>



**Figure 2.** Acceptor-acceptor diazo substrates **9** and **10** studied in this work.

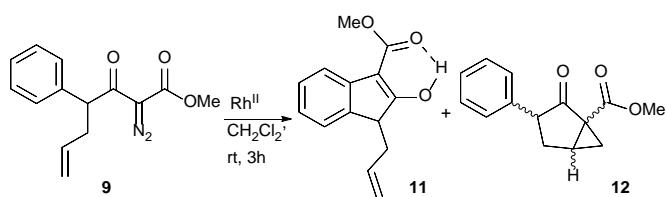


**Scheme 2.** Synthesis of diazo substrates **9** and **10**.

The syntheses of the novel diazo compounds **9** and **10** were realised in three steps (Scheme 2). First, phenylacetic acid was deprotonated in the presence of *n*BuLi and, in the presence of the adapted electrophile, gave carboxylic acids **5-6**.<sup>59-62</sup> The latter reacted with oxalyl chloride followed by Meldrum's acid to give intermediate compounds, which were treated directly with  $\text{H}_2\text{SO}_4$  and MeOH<sup>51</sup> to yield the  $\beta$ -ketoesters **7-8** (49-60% yield from **5-6**). The latter were finally treated with 4-acetamidobenzenesulfonyl azide to give the diazo substrates **9** and **10** in excellent yields (95% to quantitative). All new compounds (**7** to **10**) were fully characterized by NMR and mass spectrometry.

**Catalytic studies and selectivity issues.** The diazo substrates **9** and **10** were first decomposed in the presence of the benchmark complex  $[\text{Rh}_2(\text{OAc})_4]$  and the heteroleptic complex  $[\text{Rh}_2(\text{OAc})_3(\text{tfa})]$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. As observed with diazo substrate **2**, the conversion of substrates **9** and **10** was always complete after 3 h.  $[\text{Rh}_2(\text{OAc})_3(\text{tfa})]$ , bearing a more electron-withdrawing trifluoroacetate ligand, should be electronically closer to our heteroleptic ferrocenyl dirhodium(II) complexes **1** in their oxidized form. Indeed, an electrochemical study by Swarts *et al.* confirmed that the electron-withdrawing power of the ferrocenium moiety is similar to that of the  $\text{CF}_3$  group, albeit slightly less powerful than the latter.<sup>63</sup> It should be noted that this study was done in *n*Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte in acetonitrile, and thus on rather dissociated species, where the influence of the anion should not be significant. Ferrocene-containing heteroleptic dirhodium(II) complex **1a** was then used, both in reduced and oxidized forms. The diazo substrate **9** gave, as expected, both the aromatic C-H insertion product **11** and the cyclopropanation product **12**, the latter being obtained as a mixture of two diastereoisomers (Table 3). In the presence of  $[\text{Rh}_2(\text{OAc})_4]$ , formation of the cyclopropanation product **12** was favoured, with a 28:72 ratio (Table 3, entry 1). A marked difference was observed when the heteroleptic complex  $[\text{Rh}_2(\text{OAc})_3(\text{tfa})]$ , bearing one electron-deficient tfa ligand, was used instead: the **11:12** ratio was inverted to 67:33, clearly in favour of the aromatic C-H insertion product **11** (+39%, entry 2).

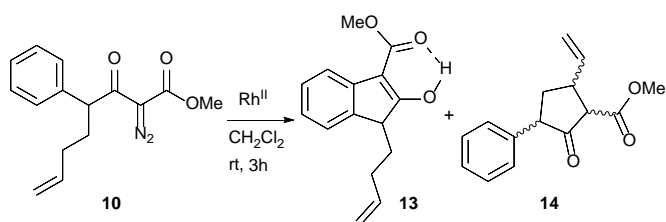
Our ferrocenyl heteroleptic complex **1a** also gave the expected products **11** and **12** in excellent overall yield, with a **11:12** ratio slightly more in favour of the cyclopropanation product **12** (entry 3). Pleasingly, oxidation of **1a** to  $\mathbf{1a}^+\text{BF}_4^-$  (entry 4) or  $\mathbf{1a}^+\text{SbF}_6^-$  (entry 5) markedly changed the **11:12** ratio, with a 30% to 42% increase of product **11**, respectively, compared to **1a**. Similarly to what was observed with diazo substrate **2**, the extent of chemoselectivity switch is more important in the case of  $\mathbf{1a}^+\text{SbF}_6^-$ , confirming the positive effect of the ion pair dissociation. This change in chemoselectivity is very similar to that observed between  $[\text{Rh}_2(\text{OAc})_4]$  and  $[\text{Rh}_2(\text{OAc})_3(\text{tfa})]$ , and is also consistent with the trend observed with substrate **2**.

**Table 3.** Rh<sup>II</sup>-catalysed decomposition of diazo substrate **9**.

Entry	Rh complex	<b>11+12</b> (%) <sup>c</sup>	<b>11:12</b> (+% of <b>11</b> ) <sup>d</sup>
1 <sup>a</sup>	[Rh <sub>2</sub> (OAc) <sub>4</sub> ]	91	28:72
2 <sup>a</sup>	[Rh <sub>2</sub> (OAc) <sub>3</sub> (tfa)]	91	67:33 (+ 39%)
3 <sup>b</sup>	<b>1a</b>	91	21:79
4 <sup>b</sup>	<b>1a</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	88	51:49 (+ 30%)
5 <sup>b</sup>	<b>1a</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	95	63:37 (+ 42%)

Reagents and conditions: diazo substrate **9** (0.15 mmol), <sup>a</sup> Rh<sup>II</sup> cat. (4 mol%), <sup>b</sup> Rh<sup>II</sup> cat. (2 mol%), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), r.t., 3 h. Oxidized species generated *in situ* by addition of 1.1 equiv. of [N(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. <sup>c</sup> Global isolated yield, average of two runs. <sup>d</sup> Average of two runs, determined by integration of characteristic <sup>1</sup>H NMR signals (CDCl<sub>3</sub>).

The catalysed decomposition of the diazo substrate **10** was investigated next (Table 4). The reaction of **10** with benchmark catalyst [Rh<sub>2</sub>(OAc)<sub>4</sub>] went smoothly and the substrate was totally consumed within 3 h. The <sup>1</sup>H NMR analysis of the crude mixture revealed a different reactivity pattern from the previous substrate: whereas the aromatic C–H insertion to cyclopropanation ratio was clearly in favour of the latter in the case of diazo compound **9**, substrate **10** led to a much greater amount of the aromatic C–H activation product **13** (Table 4, entry 1). The allylic C–H insertion product **14** was also obtained, with a *ca.* 63:37 **13:14** ratio, and indeed no cyclopropanation reaction was observed. Other products were formed in very small amounts during the reaction, but their nature was difficult to confirm. Switching to [Rh<sub>2</sub>(OAc)<sub>3</sub>(tfa)] led to a reasonable change in selectivity with a 24% increase in product **13**. Our ferrocenyl complex **1a** in its reduced form gave a similar **13:14** ratio of 61:39. However, its oxidized version gave a more modest change in selectivity than [Rh<sub>2</sub>(OAc)<sub>3</sub>(tfa)], with a 14% increase in product **13** for **1a**<sup>+</sup>BF<sub>4</sub><sup>-</sup> (entry 4). Changing the anion to **1a**<sup>+</sup>SbF<sub>6</sub><sup>-</sup> only led to a small improvement, with a 16% increase in **13** (entry 5).

**Table 4.** Rh<sup>II</sup>-catalysed decomposition of diazo substrate **10**.

Entry	Rh complex	<b>13+14</b> (%) <sup>c</sup>	<b>13:14</b> (+% of <b>13</b> ) <sup>d</sup>
1 <sup>a</sup>	[Rh <sub>2</sub> (OAc) <sub>4</sub> ]	95	63:37
2 <sup>a</sup>	[Rh <sub>2</sub> (OAc) <sub>3</sub> (tfa)]	90	87:13 (+24%)
3 <sup>b</sup>	<b>1a</b>	93	61:39
4 <sup>b</sup>	<b>1a</b> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	90	75:25 (+ 14%)
5 <sup>b</sup>	<b>1a</b> <sup>+</sup> SbF <sub>6</sub> <sup>-</sup>	95	77:23 (+ 16%)

Reagents and conditions: diazo substrate **10** (0.15 mmol), <sup>a</sup> Rh<sup>II</sup> cat. (4 mol%), <sup>b</sup> Rh<sup>II</sup> cat. (2 mol%), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), r.t., 3 h. Oxidized species generated *in situ* by addition of 1.1 equiv. of [N(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sup>+</sup>SbF<sub>6</sub><sup>-</sup>. <sup>c</sup> Global isolated yield, average of two runs. <sup>d</sup> Average of two runs, determined by integration of characteristic <sup>1</sup>H NMR signals (CDCl<sub>3</sub>).



The redox behaviour and ion-pairing thermodynamics of ferrocene in organic solvents have been studied by Yu *et al.*<sup>55</sup> In this work, it is said that “the ability to form ion pairs with ferricenium cations varies remarkably for different anions, the voltammetric responses of ferrocene (particularly the formal potential and peak shapes) would be changed consequently”. The formal redox potential of ferrocene and the electronic properties of the ferrocenyl carboxylate ligand being linked in our case, these findings support our explanation of an electronic effect for the anion-dependent chemoselectivity changes.

## Conclusions

In conclusion, we demonstrated that the nature of the anion of the oxidised catalyst is important in the field of redox-responsive catalysis, as changing the counter-anion of oxidized heteroleptic ferrocene-containing dirhodium(II) complexes from  $\text{BF}_4^-$  to  $\text{SbF}_6^-$  results in a product distribution change by 17% in favour of the aromatic C-H activation product **3** in the case of complex **1a**. No clear relationship was found between the nature of the ferrocenyl substituents and their influence on chemoselectivity: the catalysts leading to the highest redox response were complex **1a** bearing a non-substituted ferrocene and complexes **1b** and **1f** bearing, respectively, an electron-withdrawing 1'-ketoethyl and an electron-donating 1'-hexyl substituent. However, we were able to show that it is important to weaken the interaction between the ferrocenium cation and its counter-anion, and to favour a direct connexion between the ferrocene and carboxylate units, to maximise the response. We demonstrated that the electronic influence exerted by ferrocene oxidation is transmitted through the bonds, as the introduction of a saturated tether between the ferrocenyl unit and the carboxylate group suppressed almost entirely the chemoselectivity difference. Finally, we applied this concept to two new diazo substrates, with up to 42% difference in chemoselectivity observed with substrate **9**. The results show that the extent of the chemoselectivity switch not only depends on the propensity of the counter-anion to form an ion pair with ferrocenium, but also on the nature of the diazo substrate. Work is underway to study the chemoselectivity changes induced by more than one redox-active ligand on the catalyst.

## Experimental

**Warning:** diazo compounds and their relatives are reactive and potentially explosive. They should be handled with caution, in a hood and behind a blast shield whenever possible.

### Synthesis of compounds **5** and **6**

Carboxylic acids **5**<sup>59</sup> and **6**<sup>60</sup> were prepared according to previously reported procedures: to a stirred solution of phenylacetic acid (1.36 g, 10.0 mmol, 1 equiv.) in dry THF (40 mL) was added dropwise *n*-BuLi (2.5 M in hexanes, 8.5 mL, 21.0 mmol, 2.1 equiv.) at -78 °C. The reaction mixture was stirred at room temp. for 1 h and cooled to -78 °C again. The corresponding electrophile (40 mmol, 4 equiv., for **5**: allyl bromide, 3.5 mL; for **6**: 4-bromo-1-butene, 4.1 mL) was added and the reaction mixture was stirred at room temp. overnight. The reaction was then diluted with water (100 mL) and washed with Et<sub>2</sub>O (3 x 40 mL). The solution was acidified with aqueous HCl (1 M) to pH 4 and extracted with Et<sub>2</sub>O (3 x 50 mL). The combined organic layers were washed with water and saturated brine, dried (MgSO<sub>4</sub>), filtered and the solvent was removed *in vacuo* to yield the carboxylic acids as yellow viscous liquids.

2-phenylpent-4-enoic acid **5**: 1.54 g, 87 %. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34-7.27 (m, 5H, CH Ph), 5.73 (ddt, *J* = 17.0 Hz, 10.2 Hz, 6.8 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.09 (dq, *J* = 17.1 Hz, 1.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.02 (ddt, *J* = 10.2 Hz, 1.9 Hz, 1.1 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.85 (dd, *J* = 8.3 Hz, 7.2 Hz, 1H, PhCHCO<sub>2</sub>H), 2.89-2.78 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.54 (dt, *J* = 14.3 Hz, 6.8 Hz, 1.4 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>).

2-phenylhex-5-enoic acid **6**: (1.86 g, 98 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.26 (m, 5H, CH Ph), 5.77 (ddt, *J* = 16.9 Hz, 10.3 Hz, 6.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.03-5.00 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 4.99-4.97 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.59 (t, *J* = 10.2 Hz, 1H, PhCHCO<sub>2</sub>H), 2.23-2.14 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 2.06-2.00 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 1.93-1.87 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>).

### Synthesis of compounds **7** and **8**

**Representative procedure:** A solution of alkylated carboxylic acid **5** or **6** (1.0 equiv.) in dry dichloromethane (0.25 M in acid) was cooled to 0 °C and oxalyl chloride (1.1 equiv.) was added dropwise. The cooling bath was removed and the mixture was stirred at room temp. for 1.5 h. The solution was concentrated *in vacuo* and the solid residue was used without further purification. The crude acyl chloride (1.0 equiv.) was dissolved in dry dichloromethane (1.7 M in acyl

chloride), and this solution was added over 1 h to a stirred solution of Meldrum's acid (1.0 equiv.) and pyridine (2.5 equiv.) in dry dichloromethane (0.55 M in Meldrum's acid) at 0°C. The temperature was maintained at 0 °C for 1 h, then warmed to room temp. and stirred for 16 h. The reaction mixture was washed with aqueous 3 M HCl (3 x 25 mL) then water (15 mL). The phases were separated, the organic phase was dried (MgSO<sub>4</sub>), filtered and concentrated in vacuo. The crude intermediate was dissolved in methanol (12 mL) and 5 drops of conc. H<sub>2</sub>SO<sub>4</sub> were added. The mixture was heated at reflux temperature for 4 h, then the solvent was evaporated *in vacuo*.

**Compound 7.** From 2-phenylpent-4-enoic acid **5** (750 mg, 4.3 mmol). The crude residue was purified by column chromatography on silicagel (eluent: petroleum ether/EtOAc 10:1) to give **7** as a colorless oil (700 mg, 60 % yield). HRMS (DCI-CH<sub>4</sub>) m/z: [M]<sup>+</sup> calcd for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub> 232.1099, found: 232.1089.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.27 (m, 3H, CH Ph), 7.21-7.18 (m, 2H, CH Ph), 5.65 (ddt, *J* = 17.1 Hz, 10.2 Hz, 6.9 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.01 (dq, *J* = 17.1 Hz, 1.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 4.96 (ddt, *J* = 10.2 Hz, 2.0 Hz, 1.1 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.85 (t, *J* = 7.4 Hz, 1H, PhCHC(O)), 3.65+3.70 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>, enol+keto forms), 3.42 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH<sub>2</sub>CO<sub>2</sub>Me), 3.31 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH<sub>2</sub>CO<sub>2</sub>Me), 2.82 (dtt, *J* = 14.2 Hz, 7.1 Hz, 1.3 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.45 (dddd, *J* = 14.5 Hz, 8.0 Hz, 6.9 Hz, 1.3 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 201.7 (CHC(O)CH<sub>2</sub>), 167.6 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 137.4 (C<sub>quat</sub> Ph), 135.4 (CH<sub>2</sub>CH=CH<sub>2</sub>), 129.3 (*o*- or *m*-CH Ph), 128.7 (*o*- or *m*-CH Ph), 127.9 (*p*-CH Ph), 117.1 (CH<sub>2</sub>CH=CH<sub>2</sub>), 58.9 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 52.4 (CO<sub>2</sub>CH<sub>3</sub>), 48.0 (PhCHC(O)CH<sub>2</sub>), 36.3 (CH<sub>2</sub>CH=CH<sub>2</sub>).

**Compound 8.** From 2-phenylhex-5-enoic acid **6** (950 mg, 5.0 mmol). The crude residue was purified by column chromatography on silicagel (eluent: petroleum ether/EtOAc 10:1) to give **8** as a colorless oil (600 mg, 49 % yield). HRMS (DCI-CH<sub>4</sub>) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>19</sub>O<sub>3</sub> 247.1334, found: 247.1329.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 12.11 (C=C-OH, enol form), 7.37-7.27 (m, 3H, CH Ph), 7.21-7.17 (m, 2H, CH Ph), 5.82-5.69 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.07-4.95 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 3.81-3.77 (app. t, 1H, PhCHC(O)), 3.66+3.70 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>, enol+keto forms), 3.42 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH<sub>2</sub>CO<sub>2</sub>Me), 3.29 (d, AB syst., *J* = 15.5 Hz, 1H, C(O)CH<sub>2</sub>CO<sub>2</sub>Me), 2.24-2.13 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 2.00-1.92 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 1.85-1.73 (m, 1H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>).

<sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>) δ 202.3 (CHC(O)CH<sub>2</sub>), 167.7 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 137.9 (CH<sub>2</sub>CH=CH<sub>2</sub>), 137.8 (C<sub>quat</sub> Ph), 129.3 (*o*- or *m*-CH Ph), 128.7 (*o*- or *m*-CH Ph), 127.8 (*p*-CH Ph), 115.5 (CH<sub>2</sub>CH=CH<sub>2</sub>), 58.3 (CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>), 52.4 (CO<sub>2</sub>CH<sub>3</sub>), 48.0 (PhCHC(O)CH<sub>2</sub>), 31.3 (CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 30.9 (CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>).

### Synthesis of diazo compounds **9** and **10**

**Representative procedure:** Compound **7** or **8** (1.0 equiv.) was placed in dry acetonitrile (2.5 M solution) and cooled to 0°C. 4-acetobenzenesulfonyl azide (*p*-ABSA, 1.05 equiv.) was added in one go, followed by dropwise addition of *N,N*-diisopropylethylamine (DIPEA, 1.5 equiv.). The reaction mixture was warmed to room temperature and stirred for 3 h, then filtered. The precipitate was washed with dichloromethane, and the combined filtrate was concentrated in vacuo. The crude product was resolubilized in a minimum amount of DCM and filtered through a short pad of silica.

**Diazo compound 9.** From compound **7** (700 mg, 3.0 mmol). Compound **9** was obtained as a pale-yellow oil (700 mg, 95 % yield). HRMS (DCI-CH<sub>4</sub>) m/z: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> 259.1083, found: 259.1079.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.22 (m, 5H, CH Ph), 5.71 (ddt, *J* = 17.0 Hz, 10.2 Hz, 6.8 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.04 (dq, *J* = 17.2 Hz, 1.6 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 4.97 (ddt, *J* = 10.2 Hz, 2.0 Hz, 1.1 Hz, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 4.91 (dd, *J* = 8.4 Hz, 6.8 Hz, 1H, PhCHC(O)), 3.80 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 2.92-2.84 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>), 2.53-2.46 (m, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>).

<sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 192.2 (CHC(O)C(N<sub>2</sub>)), 161.5 (C(N<sub>2</sub>)CO<sub>2</sub>CH<sub>3</sub>), 138.4 (C<sub>quat</sub> Ph), 135.7 (CH<sub>2</sub>CH=CH<sub>2</sub>), 128.9 (*o*- or *m*-CH Ph), 128.7 (*o*- or *m*-CH Ph), 127.4 (*p*-CH Ph), 116.9 (CH<sub>2</sub>CH=CH<sub>2</sub>), 52.8 (PhCHC(O)C(N<sub>2</sub>)), 52.3 (CO<sub>2</sub>CH<sub>3</sub>), 37.7 (CH<sub>2</sub>CH=CH<sub>2</sub>). C(N<sub>2</sub>)CO<sub>2</sub>CH<sub>3</sub> not found.

**Diazo compound 10.** From compound **8** (600 mg, 2.44 mmol). Compound **10** was obtained as a pale-yellow oil (660 mg, quantitative yield). HRMS (DCI-CH<sub>4</sub>) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> 273.1239, found: 273.1230.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.22 (m, 5H, CH Ph), 5.78 (ddt,  $J = 16.9$  Hz, 10.2 Hz, 6.6 Hz, 1H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.02-4.95 (m, 2H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.83 (t,  $J = 7.4$  Hz, 1H,  $\text{PhCHC}(\text{O})$ ), 3.80 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 2.23-2.16 (m, 1H,  $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ), 2.03-1.97 (m, 2H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 1.93-1.84 (m, 1H,  $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ),.

$^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ )  $\delta$  192.8 ( $\text{CHC}(\text{O})\text{C}(\text{N}_2)$ ), 161.5 ( $\text{C}(\text{N}_2)\text{CO}_2\text{CH}_3$ ), 138.7 ( $\text{C}_{\text{quat}}$  Ph), 138.1 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 128.9 (*o*- or *m*-CH Ph), 128.7 (*o*- or *m*-CH Ph), 127.4 (*p*-CH Ph), 115.3 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 52.4 ( $\text{PhCHC}(\text{O})\text{C}(\text{N}_2)$ ), 52.3 ( $\text{CO}_2\text{CH}_3$ ), 32.7 ( $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ), 31.7 ( $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ).  $\text{C}(\text{N}_2)\text{CO}_2\text{CH}_3$  not found.

#### General methodology for the dirhodium(II)-catalysed decomposition of diazo substrates **2** and **9-10**:

All catalytic tests were performed twice, and the yield and product ratio are calculated as an average of these two runs.

An oven-dried Schlenk flask was charged with the dirhodium(II) catalyst (1-4 mol%) under argon. Dry  $\text{CH}_2\text{Cl}_2$  (0.75-1.5 mL) was added and a solution of the diazo substrate (0.075-0.2 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (0.75-1.5 mL) was added in one go. The reaction was stopped after 3 h and the reaction mixture was filtered through a short pad of silica, which was then washed with 10 mL of  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated *in vacuo* and the crude residue was weighed to determine the global yield and analysed by  $^1\text{H}$  NMR to determine the product ratio.

**Catalytic reactions with the oxidized dirhodium(II) complexes **1a-k<sup>+</sup>A****: An oven-dried Schlenk flask was charged with the dirhodium(II) catalyst (1-2 mol%) under argon, followed by  $\text{CH}_2\text{Cl}_2$  (0.75 mL). A solution of the  $[\text{N}(4\text{-C}_6\text{H}_4\text{Br})_3]^+\text{A}^-$  oxidant (1.1 equiv.) in dry  $\text{CH}_2\text{Cl}_2$  (0.75 mL) was added and the reaction mixture was stirred for 30 min. A solution of the diazo substrate (0.075-0.2 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (1.5 mL) was then added to the mixture. The reaction was stopped after 3 h and the reaction mixture was filtered through a short pad of silica, followed by washing with 10 mL  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated *in vacuo* and the crude residue was weighed to determine the global yield and analysed by  $^1\text{H}$  NMR to determine the product ratio.

**Decomposition of the diazo substrate **2****. The product ratio **3:4** was determined by integration of the following  $^1\text{H}$  NMR signals: **Aromatic substitution product **3****: HRMS (DCI- $\text{CH}_4$ )  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_3$  247.1334, found: 247.1339.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), enol form:  $\delta$  11.13 (s, 1H,  $\text{C}=\text{C}-\text{OH}$ ), 7.62 (app.d,  $J = 7.5$  Hz, 1H, CH Ph), 7.31-7.26 (m, 2H, CH Ph), 7.13 (td,  $J = 7.5$ , 1.2 Hz, 1H, CH Ph), 3.98 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 3.62 (t,  $J = 6.9$  Hz, 1H,  $\text{CHC}(\text{OH})=\text{C}$ ), 2.05 (app. hept.,  $J = 7.1$  Hz, 1H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 1.81 (ddd,  $J = 13.9$ , 7.0, 7.0 Hz, 1H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 1.69 (ddd,  $J = 13.8$ , 7.2, 7.2 Hz, 1H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 1.0 (d,  $J = 6.6$  Hz, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 0.99 (d,  $J = 6.6$  Hz, 3H,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ),  $\delta$  184.8 ( $\text{C}=\text{C}-\text{OH}$ ), 169.6 ( $\text{CO}_2\text{Me}$ ), 138.6, 138.4 (2 x  $\text{C}_{\text{quat}}$ , Ph), 127.1, 123.6, 123.15, 123.14 (4 x CH Ph), 103.6 ( $\text{C}=\text{C}-\text{OH}$ ), 51.5 ( $\text{CO}_2\text{CH}_3$ ), 46.4 ( $\text{CHC}(\text{OH})=\text{C}$ ), 39.7 ( $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 25.6 ( $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 22.9, 22.8 (2 x  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ).

**Aliphatic C-H activation product **4****: HRMS (DCI- $\text{CH}_4$ )  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{20}\text{O}_3$  247.1334, found: 247.1338.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), **dia **1****:  $\delta$  7.38-7.21 (m, 5H, CH Ph), 3.78 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 3.71 (m, 1H,  $\text{CH}_2\text{CHPh}$ ), 3.16 (s,  $\text{C}(\text{CH}_3)_2\text{CHCO}_2\text{Me}$ ), 2.36 (dd,  $J = 12.8$  Hz, 8.6 Hz, 1H,  $\text{CH}_2$ ), 2.05 (app. t,  $J = 12.7$  Hz, 1H,  $\text{CH}_2$ ), 1.40 (s, 3H,  $\text{CH}_3$ ), 1.21 (s, 3H,  $\text{CH}_3$ ); **dia **2****:  $\delta$  7.35-7.23 (m, 5H, CH Ph), 3.75 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 3.68 (m, 1H,  $\text{CH}_2\text{CHC}(\text{O})$ ), 3.13 (app. s,  $\text{C}(\text{CH}_3)_2\text{CHC}(\text{O})$ ), 2.51 (t,  $J = 12.7$  Hz, 1H,  $\text{CH}_2$ ), 2.25 (dd,  $J = 13.0$  Hz, 9.0 Hz, 1H,  $\text{CH}_2$ ), 1.29 (s, 3H,  $\text{CH}_3$ ), 1.25 (s, 3H,  $\text{CH}_3$ ); **enol form**:  $\delta$  7.38-7.21 (m, 5H, CH Ph), 4.05 (t,  $J = 8.8$  Hz, 1H,  $\text{CH}_2\text{CHPh}$ ), 3.84 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 2.25 (dd,  $J = 12.8$  Hz, 8.6 Hz, 1H,  $\text{CH}_2$ ), 1.76 (dd,  $J = 13.0$  Hz, 8.7 Hz, 1H,  $\text{CH}_2$ ), 1.34 (s, 3H,  $\text{CH}_3$ ), 1.26 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ), **dia **1****:  $\delta$  210.1 ( $\text{C}(\text{O})$ , ketone), 168.9 ( $\text{CO}_2\text{Me}$ ), 137.7 ( $\text{C}_{\text{quat}}$  Ph), 128.6, 128.1, 127.1 (5 x CH Ph), 66.0 ( $\text{C}(\text{CH}_3)_2\text{CHCO}_2\text{Me}$ ), 53.5 ( $\text{CH}_2\text{CHPh}$ ), 52.0 ( $\text{CO}_2\text{CH}_3$ ), 45.1 ( $\text{CH}_2\text{CHPh}$ ), 38.3 ( $\text{C}(\text{CH}_3)_2$ ), 29.5 ( $\text{C}(\text{CH}_3)_2$ ), 23.7 ( $\text{C}(\text{CH}_3)_2$ ); **dia **2****:  $\delta$  213.0 ( $\text{C}(\text{O})$ , ketone), 169.7 ( $\text{CO}_2\text{Me}$ ), 138.1 ( $\text{C}_{\text{quat}}$ , Ph), 128.6, 128.1, 127.1 (5 x CH Ph), 65.3 ( $\text{C}(\text{CH}_3)_2\text{CHCO}_2\text{Me}$ ), 54.6 ( $\text{CH}_2\text{CHPh}$ ), 52.0 ( $\text{CO}_2\text{CH}_3$ ), 44.7 ( $\text{CH}_2\text{CHPh}$ ), 38.3 ( $\text{C}(\text{CH}_3)_2$ ), 29.4 ( $\text{C}(\text{CH}_3)_2$ ), 25.1 ( $\text{C}(\text{CH}_3)_2$ ); **enol form**:  $\delta$  175.5 ( $\text{C}=\text{C}-\text{OH}$ ), 170.8 ( $\text{CO}_2\text{Me}$ ), 141.3 ( $\text{C}_{\text{quat}}$ , Ph), 128.6, 128.0, 126.9 (5 x CH Ph), 109.9 ( $\text{C}=\text{C}-\text{CO}_2\text{Me}$ ), 51.1 ( $\text{CO}_2\text{CH}_3$ ), 49.0 ( $\text{CH}_2\text{CHPh}$ ), 48.1 ( $\text{CH}_2\text{CHPh}$ ), 40.2 ( $\text{C}(\text{CH}_3)_2$ ), 29.3 ( $\text{C}(\text{CH}_3)_2$ ), 27.7 ( $\text{C}(\text{CH}_3)_2$ ).

**Decomposition of the diazo substrate **9**. Aromatic substitution product **11****: HRMS (DCI- $\text{CH}_4$ )  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_3$  230.0943, found: 230.0933.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), enol form:  $\delta$  11.06 (s, 1H,  $\text{C}=\text{C}-\text{OH}$ ), 7.61 (app. d,  $J = 7.6$  Hz, 1H, CH Ph), 7.34 (dd,  $J = 7.6$  Hz, 1.0 Hz, 1H, CH Ph), 7.32-7.25 (m, 1H, CH Ph), 7.13 (td,  $J = 7.5$ , 1.2 Hz, 1H, CH Ph), 5.69 (dddd,  $J = 17.1$  Hz, 10.1 Hz, 7.9 Hz, 6.2 Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 5.12 (dq,  $J = 17.0$  Hz, 1.7 Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 5.03 (ddt,  $J = 10.1$  Hz, 2.0 Hz, 1.1 Hz, 1H,  $\text{CH}=\text{CH}_2$ ), 3.98 (s, 3H,  $\text{CO}_2\text{CH}_3$ ), 3.65 (app. t,  $J = 6.0$  Hz, 1H,  $\text{CHC}(\text{OH})=\text{C}$ ), 2.85-2.78 (m, 1H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 2.63 (dddd,  $J = 14.3$  Hz, 7.8 Hz, 6.7 Hz, 1.1 Hz, 1H,  $\text{CH}_2\text{CH}=\text{CH}_2$ );  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ),  $\delta$  182.9 ( $\text{C}=\text{C}-\text{OH}$ ), 169.4

(CO<sub>2</sub>Me), 138.7, 137.4 (2 x C<sub>quat</sub>, Ph), 133.8 (CH=CH<sub>2</sub>), 127.3, 123.7, 123.2, 120.1 (4 x CH Ph), 117.7 (CH=CH<sub>2</sub>), 104.3 (C=C-OH), 51.5 (CO<sub>2</sub>CH<sub>3</sub>), 47.6 (CHC(OH)=C), 34.1 (CH<sub>2</sub>CH=CH<sub>2</sub>).

**Cyclopropanation product 12:** HRMS (DCI-CH<sub>4</sub>) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>20</sub>O<sub>3</sub> 230.0943, found: 230.0932. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), *dia 1 (Major)*: δ 7.36-7.19 (m, 3H, CH Ph), 7.16-7.13 (m, 2H, CH Ph), 3.79 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.45 (app. t, J = 9.6 Hz, 1H, PhCHC(O)), 2.69 (dt, J = 7.9 Hz, 5.4 Hz, 1H, CH of cyclopropane), 2.56 (dd, J = 13.3 Hz, 8.6 Hz, 1H, CH<sub>2</sub>CHC(O)), 2.43-2.36 (m, 1H, CH<sub>2</sub>CHC(O)), 2.16-2.13 (m, 1H, CH<sub>2</sub> of cyclopropane), 1.66 (t, J = 5.3 Hz, 1H, CH<sub>2</sub> of cyclopropane); *dia 2 (minor)*: δ 7.35-7.31 (m, 2H, CH Ph), 7.26-7.20 (m, 3H, CH Ph), 3.80 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.83-3.73 (m, 1H, PhCHC(O)), 2.82 (dddd, J = 13.6 Hz, 11.8 Hz, 5.9 Hz, 1.6 Hz, 1H, CH<sub>2</sub>CHC(O)), 2.63 (dt, J = 8.0 Hz, 5.7 Hz, 1H, CH of cyclopropane), 2.31 (dd, J = 5.3 Hz, 4.0 Hz, 1H, CH<sub>2</sub>CHC(O)), 2.08-2.04 (m, 1H, CH<sub>2</sub> of cyclopropane), 1.46 (t, J = 5.3 Hz, 1H, CH<sub>2</sub> of cyclopropane); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>), *dia 1 (Major)*: δ 205.7 (C(O)), 169.0 (CO<sub>2</sub>Me), 137.9 (C<sub>quat</sub>, Ph), 128.8 (o- or m-CH Ph), 128.7 (o- or m-CH Ph), 127.2 (p-CH Ph), 52.5 (CO<sub>2</sub>CH<sub>3</sub>), 49.8 (PhCHC(O)), 37.8 (C(O)CHCO<sub>2</sub>CH<sub>3</sub>), 31.4 (CH of cyclopropane), 30.99 (CH<sub>2</sub>CHC(O)), 23.1 (CH<sub>2</sub> of cyclopropane); *dia 2 (minor)*: δ 205.7 (C(O)), 168.9 (CO<sub>2</sub>Me), 138.6 (C<sub>quat</sub>, Ph), 128.7 (o- or m-CH Ph), 127.2 (o- or m-CH Ph), 127.0 (p-CH Ph), 52.7 (PhCHC(O)), 52.5 (CO<sub>2</sub>CH<sub>3</sub>), 38.5 (C(O)CHCO<sub>2</sub>CH<sub>3</sub>), 31.0 (CH of cyclopropane), 28.4 (CH<sub>2</sub>CHC(O)), 21.8 (CH<sub>2</sub> of cyclopropane).

**Decomposition of the diazo substrate 10. Aromatic substitution product 13:** HRMS (DCI-CH<sub>4</sub>) m/z: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub> 244.1099, found: 244.1086. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), enol form: δ 11.10 (s, 1H, C=C-OH), 7.61 (app. d, J = 7.6 Hz, 1H, CH Ph), 7.32-7.28 (m, 2H, CH Ph), 7.15 (td, J = 7.5, 1.2 Hz, 1H, CH Ph), 5.87-5.78 (m, 1H, CH=CH<sub>2</sub>), 5.08-5.02 (m, 1H, CH=CH<sub>2</sub>), 5.01-4.97 (m, 1H, CH=CH<sub>2</sub>), 3.99 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.66-3.62 (m, 1H, CHC(OH)=C), 2.15-2.04 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> and CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>), δ 183.7 (C=C-OH), 169.4 (CO<sub>2</sub>Me), 138.7, 137.9 (CH=CH<sub>2</sub>), 137.8 (2 x C<sub>quat</sub>, Ph), 127.2, 123.8, 122.9, 120.1 (4 x CH Ph), 115.2 (CH=CH<sub>2</sub>), 104.3 (C=C-OH), 51.5 (CO<sub>2</sub>CH<sub>3</sub>), 47.4 (CHC(OH)=C), 29.5, 29.4 (CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> and CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>).

**Allylic C-H insertion product 14:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), *dia 1 (Major)*: δ 7.39-7.35 (m, 2H, CH Ph), 7.32-7.28 (m, 1H, CH Ph), 7.22-7.20 (m, 2H, CH Ph), 5.93 (ddd, J = 17.0 Hz, 10.2 Hz, 6.8 Hz, 1H, CH=CH<sub>2</sub>), 5.27 (dt, J = 17.2 Hz, 1.3 Hz, 1H, CH=CH<sub>2</sub>), 5.19 (dt, J = 10.3 Hz, 1.2 Hz, 1H, CH=CH<sub>2</sub>), 3.82 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.65-3.58 (m, 1H, PhCHC(O)), 3.36-3.28 (m, 1H, CHCH=CH<sub>2</sub>), 3.21 (d, J = 11.7 Hz, 1H, C(O)CHCO<sub>2</sub>Me), 2.68 (ddd, J = 12.7 Hz, 8.1 Hz, 5.9 Hz, 1H, CH<sub>2</sub>CHCH=CH<sub>2</sub>), 2.03-1.93 (m, 1H, CH<sub>2</sub>CHCH=CH<sub>2</sub>); Peaks attributed to *dia 2*: 5.31-5.26, 5.24-5.21 (2x1H, CH=CH<sub>2</sub>), 3.79 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 2.61-2.51 (m, 1H, CH<sub>2</sub>CHCH=CH<sub>2</sub>); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>), *dia 1 (Major)*: δ 208.7 (C(O)), 169.1 (CO<sub>2</sub>Me), 137.8 (CH=CH<sub>2</sub>), 137.0 (C<sub>quat</sub>, Ph), 128.7, 128.1, 127.3 (CH Ph), 116.4 (CH=CH<sub>2</sub>), 61.0 (C(O)CHCO<sub>2</sub>Me), 55.7 (PhCHC(O)), 52.6 (CO<sub>2</sub>CH<sub>3</sub>), 42.5 (CHCH=CH<sub>2</sub>), 35.7 (CH<sub>2</sub>CHCH=CH<sub>2</sub>). Peaks attributed to *dia 2*: 117.6 (CH=CH<sub>2</sub>), 36.4 (CH<sub>2</sub>CHCH=CH<sub>2</sub>).

## Author Contributions

I. Ruzhylo: synthesis and general labwork, investigation, validation, writing (review); S. Vincendeau: synthesis and general labwork, validation; P. Dauban: project administration, conceptualization, writing (review); E. Manoury: conceptualization, writing (review); R. Poli: writing (review); A. Labande: funding acquisition, project administration, conceptualization, investigation, supervision, validation, writing (original draft).

## Conflicts of interest

There are no conflicts to declare.

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