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“Metal Catalysed Diboration of  $\alpha,\beta$ -  
Unsaturated Carbonyl Compounds”

By

Andrew J Cox

A thesis submitted for the degree of Master of  
Science

Department of Chemistry  
The University of Durham



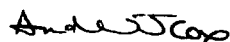
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## Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between September 2001 and September 2002, under the supervision of Dr. N.R. Cameron, Dr J.S.O. Evans and Prof. T.B. Marder. All the work is my own, unless otherwise stated, and has not been submitted previously for a degree at this or any other university.



Andrew Cox

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## Glossary

chalcone	1,3-diphenylpropenone
dimethylfumarate	but-2-enedioic acid dimethyl ester
ethylacrylate	acrylic acid ethyl ester
ethylcrotonate	but-2-enoic acid ethyl ester
methylcinnamate	3-phenyl-acrylic acid methyl ester
methylmethacrylate	2-methyl-acrylic acid methyl ester
methylvinylketone	but-3-en-2-one
norbornene	bicyclo[2.2.1]hept-2-ene
<i>trans</i> -cinnamaldehyde	3-phenylpropenal

## Abbreviations

BIAN	bis(phenylimino)acenaphthene	
BEO	<i>trans</i> -4-phenylbut-3-en-2-one	6
cat	catecholato	
CHE	2-cyclohexen-1-one	4
cod	1,5-cyclooctadiene	
cy	cyclohexyl i.e. C <sub>6</sub> H <sub>11</sub>	
dba	dibenzylideneacetone	
dcpe	1,2-dicyclohexylphosphinoethane	
dppb	1,4-diphenylphosphinobutane	
dppe	1,2-diphenylphosphinoethane	
dppf	1,1'-diphenylphosphinoferrrocene	
dppm	diphenylphosphinomethane	
dppp	1,3-diphenylphosphinopropane	
fum	dimethylfumarate	

MVK	methylvinylketone	3
NBE	norbornene	
neop	neopentyl	
pin	pinacolato	
RT	room temperature	
TCA	<i>trans</i> -cinnamaldehyde	5

**In NMR:**

s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet
dd	doublet of doublets
dt	doublet of triplets
dq	doublet of quartets

**Abstract for "Metal Catalysed Diboration of  $\alpha,\beta$ -Unsaturated Carbonyl  
Compounds"**

**by Andrew J. Cox**

This thesis describes an investigation to find an improved catalyst for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds.

Chapter 1 presents an overview of work already carried out in the area of diboration reactions of unsaturated organic molecules, particularly focusing on reactions of  $\alpha,\beta$ -unsaturated carbonyl compounds.

Chapter 2 describes the results found using a variety of Pt(0) catalysts for the diboration of various  $\alpha,\beta$ -unsaturated carbonyl compounds. These include a variety of phosphines in conjunction with Pt(NBE)<sub>3</sub>, which gave no great improvement on previously known systems, and Pt(BIAN)(fum), a diimine platinum(0) catalyst, which showed significantly improved reactivity.

Chapter 3 outlines the structural determination of products formed using Pt(BIAN)(fum) for the diboration procedure. Particularly interesting is the variance in position of diboration, i.e. 1,4 vs. 1,2 addition, depending on the electronic properties of the  $\alpha,\beta$ -unsaturated carbonyl compound.

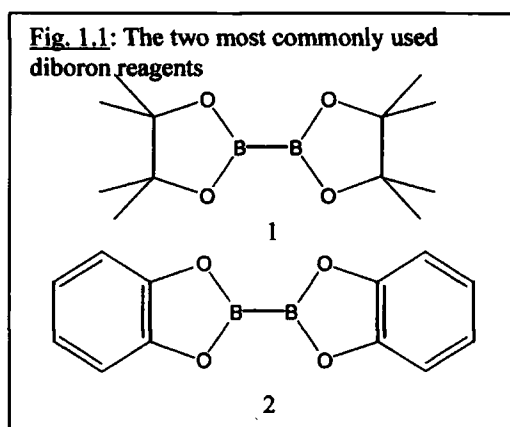
# 1. Introduction

The introduction of boron atoms into organic molecules is a valuable tool for the synthetic chemist as the carbon-boron bond can be further functionalised to form alcohols and other organic functionalities relatively simply.<sup>1</sup> The great utility of this introduction is that it allows the functionalisation of the molecule to occur at the opposite position to that usually found with organic reagents as the B-X bond which is broken is polarised differently to that usually present in a reagent used for the functionalisation of organic molecules.

Hydroboration is the process most commonly used for this. This involves cleavage of an H-B bond, which when added to an alkene adds in an anti-Markovnikov fashion. The discovery of this reaction earned Brown a Nobel Prize.<sup>2</sup> Recently, diboration has been a much investigated means of introduction of boron groups into unsaturated organic molecules.<sup>3</sup>

## 1.1. Diboration reactions

Diboration involves reaction between an unsaturated organic molecule and a molecule containing a labile B-B bond. The earliest examples of this used diboron reagents such as  $B_2Cl_4$ ; however, these molecules are unstable and difficult to prepare, consequently there are many problems associated with their use. Diboration was not a valuable process until more stable diboron reagents became available, the most widely used of which are bis(pinacolato)diboron (1) ( $B_2pin_2$ ) and bis(catecholato)diboron (2) ( $B_2cat_2$ ) (Fig. 1.1) with



other reagents now finding some use. All are based on the *bis*-boronate ester framework,  $(RO)_2B-B(OR)_2$ .

### 1.1.1. Diboration of alkenes

The first species used to diborate alkenes were of the form  $B_2X_4$  ( $X=Cl, Br, F$ ).<sup>4</sup> The reaction of  $B_2Br_4$  with ethene, for example, proceeds very quickly to give a 95 % yield of 1,2-diborated product under mild conditions. The problem with this and other reactions using this type of diborating agents is that the diboron reagents themselves are extremely unstable and so are unsuitable for general use in organic synthesis.

*Bis*-boronate esters are generally much less reactive than diboron tetrahalides, so a metal catalyst is necessary if they are to be used as diborating reagents. The first example of their use with alkenes involved a variety of rhodium based catalysts and reaction between  $B_2cat_2$  and 4-vinylanisole.<sup>5</sup> These catalysts did give the desired 1,2-diboronate ester; however, poor yields were obtained, the highest being 44 % with  $[Rh(dppb)(\eta^6\text{-catBcat})]$ . The poor yields are due to a favourable  $\beta$ -H elimination step which results in up to nine different products being formed,<sup>3b</sup> including the alkane, various monoboronate esters, other diboronate esters and even triboronate esters. As this  $\beta$ -H elimination step is so favourable with rhodium based catalysts, a new metal was sought which would avoid this problem. Gold was seen to be a good metal centre as Au(I) has low-lying d-orbitals and would favour alkyl over alkene-hydride complexes. Reaction of  $AuCl(PEt_3)/2dcpe$  with  $B_2cat_2$  and vinylanisole gave exclusively diboration; however, the relatively severe reaction conditions, long reaction time and excess of  $B_2cat_2$  needed mean this is not a particularly efficient system.<sup>5</sup>

With further study, the utility of a given catalyst for the diboration of alkenes has been found to be highly substrate dependant, with alkenes falling into two categories. These are:

1) Reactive alkenes which are terminal or strained (cyclic) internal alkenes; and 2) Unreactive unstrained internal alkenes. Catalyst development for reaction of the reactive alkenes has been much more facile and a variety of systems have been investigated. These all centre on a phosphine free platinum(0) catalyst as the lower electron density on platinum in the absence of phosphine donors inhibits  $\beta$ -H elimination to some extent.  $\text{Pt}(\text{NBE})_3$ ,<sup>6</sup>  $\text{Pt}(\text{cod})_2$ ,<sup>6</sup>  $\text{Pt}(\text{dba})_2$ <sup>7,8</sup> and  $\text{Pt}(\text{cod})\text{Cl}_2$ <sup>9</sup> have all been used as catalyst precursors with varying degrees of success.  $\text{Pt}(\text{NBE})_3$  and  $\text{Pt}(\text{cod})_2$  gave the best rates with good yields being obtained in ten minutes at ambient temperature with a range of substrates.

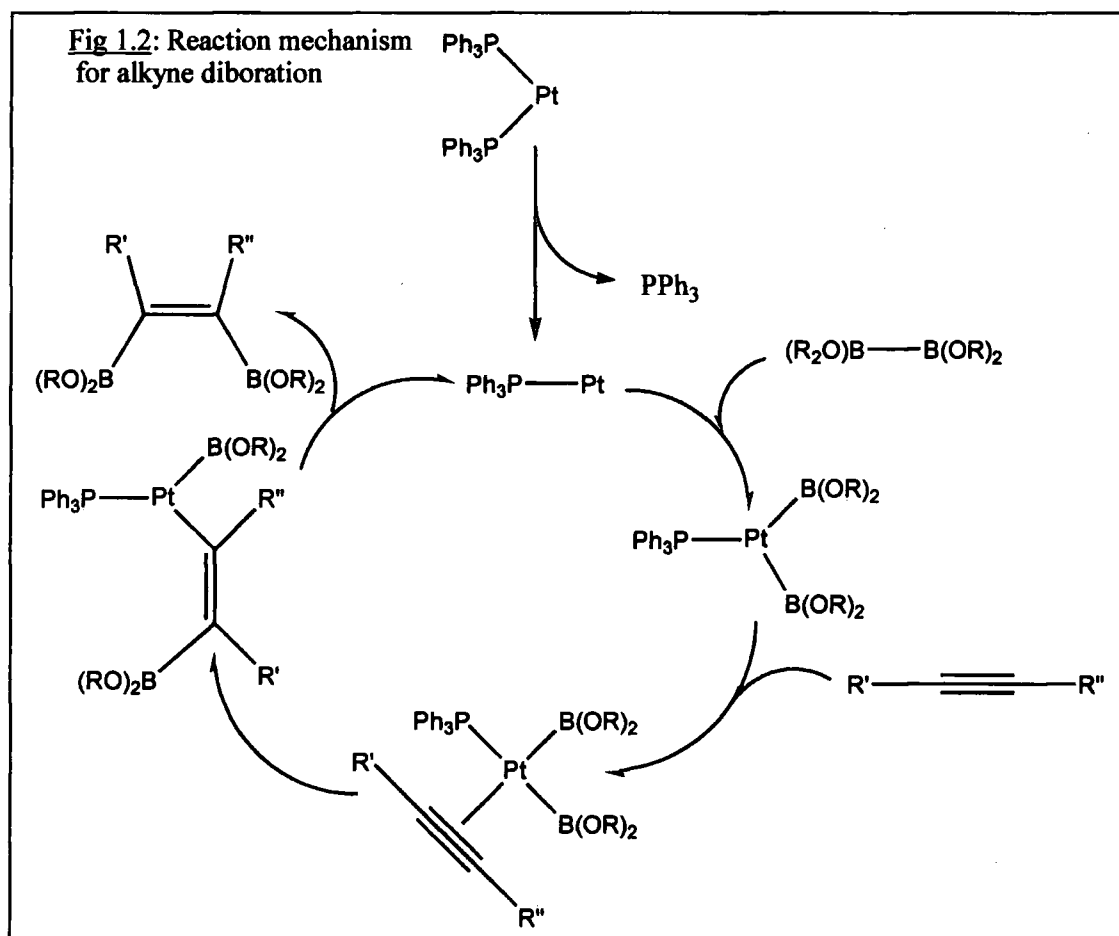
None of these platinum(0) catalysts were effective for reaction of internal, unreactive alkenes. The only catalyst capable of this reaction to date is  $(\text{dppm})\text{Rh}(\eta^6\text{-catBcat})$ <sup>10</sup> which catalyses the diboration of substrates including stilbenes and trans- $\beta$ -methylstyrene at ambient temperature and in good yields. Long reaction times are, however, necessary for these more hindered internal alkenes.

### 1.1.2. Diboration of alkynes

The first investigation of the diboration of alkynes with  $\text{B}_2\text{pin}_2$  was reported in 1993.<sup>11</sup> Various catalysts were tested which were known to be active in processes such as silyl- and stannylmetalation including  $\text{Pt}(\text{PPh}_3)_4$ ,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Pd}(\text{OAc})_2\text{-NC}$ ,  $\text{NiCl}_2\text{-dppe-DIBAL}$ ,  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{CoCl}(\text{PPh}_3)_3$ . Of these, only  $\text{Pt}(\text{PPh}_3)_4$  was found to be active. In a later study,<sup>12</sup> it was discovered that platinum(0) complexes provided the most active catalysts for the process and that  $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$  was also an effective catalyst. Platinum(II) complexes were screened, but they too were ineffective. The mechanism of the reaction was unknown; however, it was suggested that it involved the *cis* addition of the B-B bond to a " $\text{P}_2\text{Pt}$ " complex as the intermediate was isolated and characterised. It was also demonstrated that

the functionalised alkene bis(boronate) products were effective as cross-coupling reagents.<sup>13</sup>

Having identified that a platinum(0) complex was the most effective catalyst for the diboration of alkynes, further investigation was carried out into the nature of the catalyst. An improved catalyst on those mentioned above was found to be  $\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)$ .<sup>14</sup> This catalysed the diboration of various alkynes and 1,3-diynes using various diboron reagents generally within about three hours at 80°C in toluene and gave products in excellent yields. The rate of reaction was found to be highly alkyne dependant especially for terminal aryl ethynes, with electron rich alkynes reacting faster than those which are electron poor. It was also suggested that the reaction mechanism involved phosphine dissociation from the diphosphine complex and so the presence of added phosphine would



hinder the reaction. This observation was confirmed by a mechanistic study<sup>15</sup> which concluded that the rate of reaction was inversely proportional to the concentration of phosphine and also that alkyne insertion into a Pt-B bond is rate limiting. This confirms the previously postulated mechanisms (Fig. 1.2) and suggests that the optimum catalyst for this reaction is either a preformed monophosphine platinum(0) complex, or a phosphine-free platinum(0) complex with one equivalent of phosphine added.

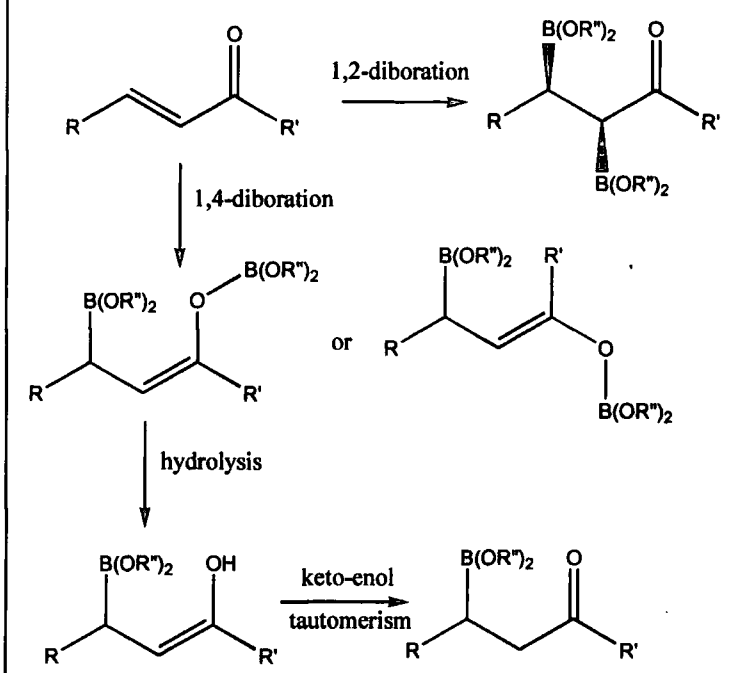
Following on from this, a further study<sup>16</sup> confirmed that 1:1 was the optimum Pt:phosphine ratio and also that in terms of rate Pt:P 1:1>1:0>1:2. This study also investigated various phosphine-free platinum sources and their catalytic activity in conjunction with a range of added phosphines. The best platinum source was found to be Pt(NBE)<sub>3</sub>, which, in a 1:1 ratio with PPh<sub>2</sub>(*o*-tol), catalysed the reaction with low catalyst loading at ambient temperature in toluene using B<sub>2</sub>pin<sub>2</sub> as the boron source. Complete reaction occurs within about one hour depending on the nature of the alkyne. PCy<sub>3</sub> was found to be the second best phosphine for the process.

### 1.1.3. Diboration of $\alpha,\beta$ -unsaturated carbonyl compounds

This section will concentrate much more than other sections on experimental details and reaction conditions in order to provide a frame of reference for comparison with results obtained for the catalysts investigated as part of this work.

The diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds has been carried out using three different metals as catalysts. Initial attempts,<sup>17</sup> as for many other diboration reactions, used a platinum catalyst, 5 mol% Pt(PPh<sub>3</sub>)<sub>2</sub>( $\mu$ -C<sub>2</sub>H<sub>4</sub>) in toluene at 80 °C for 12 hours to diborate *trans*-4-phenylbut-3-en-2-one and chalcone with B<sub>2</sub>pin<sub>2</sub> and B<sub>2</sub>cat<sub>2</sub>. With B<sub>2</sub>pin<sub>2</sub>, the 1,4-diborated product was observed by <sup>1</sup>H NMR as the *Z*-isomer; however, this diborated product was not observed with B<sub>2</sub>cat<sub>2</sub> as the diborating agent. Instead the hemi-hydrolysed

**Fig 1.3:** Possible reaction pathways for diboration reactions of  $\alpha,\beta$ -unsaturated carbonyl compounds



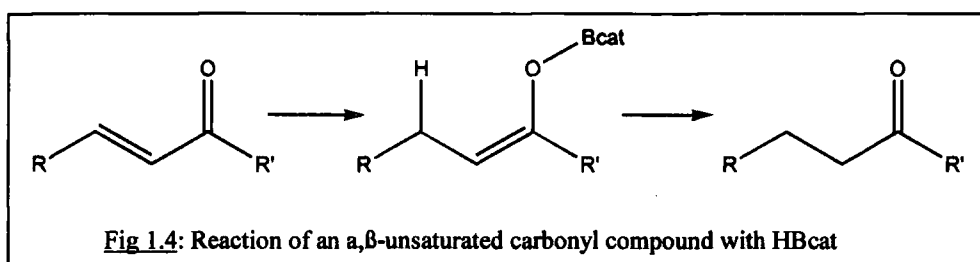
boronate ester in Fig. 1.3 was obtained suggesting that Bcat products are less stable to hydrolysis than Bpin products. This ester is different from that obtained from the hydroboration of the same substrate with HBcat.<sup>18</sup> This gives the product stereochemistry as shown in Fig 1.4.

Srebnik *et al.*<sup>19</sup> used 5 mol%

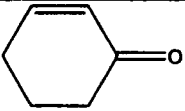
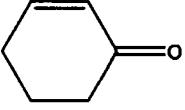
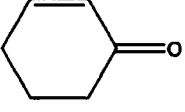
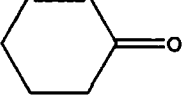
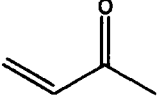
Pt(PPh<sub>3</sub>)<sub>4</sub> as a catalyst for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds with B<sub>2</sub>pin<sub>2</sub> in toluene at 110 °C for 20 hours. Yields and the substrates used are shown in Table

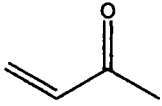
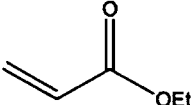
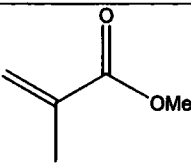
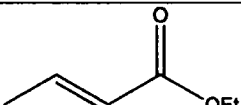
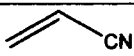
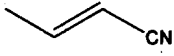
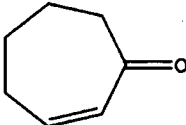
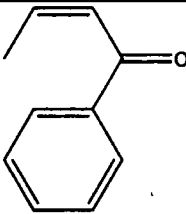
Substrate	Yield/ %
	86
	80
	79
	68

1.1. Only the hydroborated products were isolated after hydrolysis during the workup and it was not stated whether the 1,4-diborated compounds were observed as primary products. Miyaura *et al.* have investigated the use of CuX (X = Cl, I, Br, CN) and KOAc in the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>20</sup> In some experiments catalytic (10 mol% of Cu) conditions have been used, but in most cases reactions were carried out using stoichiometric amounts of copper. Only the monoboronated

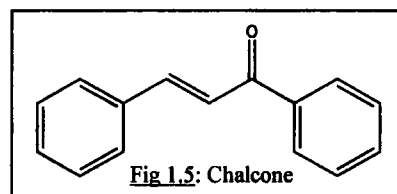


ester hydrolysis products were isolated and observed. Results and conditions are shown in Table 1.2. The reactions were investigated in some detail. It was found that reaction rates are  $\text{CuCl} > \text{CuI} > \text{CuBr} > \text{CuCN}$  and polar solvents are best:  $\text{DMF} > \text{DMSO} \gg \text{toluene} > \text{THF}$ . Smaller, more basic potassium salts were also beneficial and the addition of a salt such as LiCl improved the yields with more complicated  $\alpha,\beta$ -unsaturated carbonyl compounds. It was also postulated, although not proven, that the mechanism involved a transmetallation step of  $\text{B}_2\text{pin}_2$  to  $\text{Cu}^{\text{I}}$ , giving a Cu-Bpin complex.

<b>Table 1.2:</b> Results of diboration reactions carried out by Miyaura <i>et al.</i> <sup>20</sup>				
All reactions carried out in DMF using $\text{B}_2\text{pin}_2$ for 16 hours with the components of the 'metal mixture' in 1:1 ratios with each other.				
<u>Metal Mixture</u>	<u>Metal Conc /mol%</u>	<u>Temperature/ °C</u>	<u>Substrate</u>	<u>Yield/ %</u>
AcOK	100	RT		6
CuCl	100	RT		Trace
CuCl/AcOK	100	RT		67
CuCl/AcOK/LiCl	100	RT		68
CuCl/AcOK	100	RT		86

CuCl/AcOK	10	RT		90
CuCl/AcOK/LiCl	100	RT		59
CuCl/AcOK/LiCl	100	50		65
CuCl/AcOK/LiCl	100	50		54
CuCl/AcOK/LiCl	100	RT		57
CuCl/AcOK/LiCl	100	RT		49
CuCl/AcOK	100	RT		82
CuCl/AcOK	100	50		81

Additional work using  $\text{Cu}^{\text{I}}$  salts with various phosphines for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds was reported at about the same time by Ito *et al.*<sup>21</sup> The catalyst was investigated in detail looking at different variables using chalcone, Fig. 1.5, as the test substrate. Results again are for the formation of the hydrolysis product and are summarised in Table 1.3.

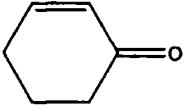
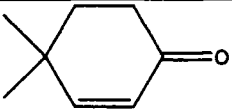
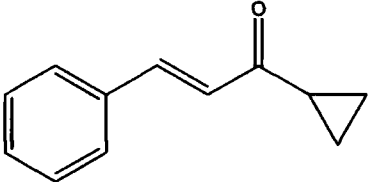
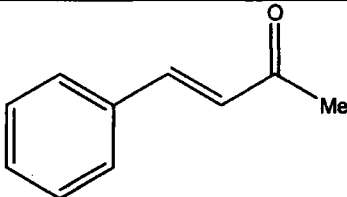
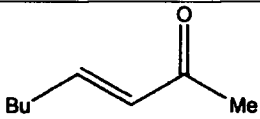
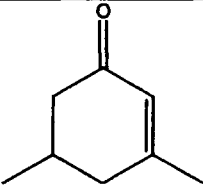


**Table 1.3:** Results of diboration reactions carried out by Ito *et al.*<sup>21</sup>

Reactions carried out with a 10 mol% catalyst loading using B<sub>2</sub>pin<sub>2</sub> as the diboron source and chalcone as a substrate with 1:1 Cu:phosphine unless otherwise stated.

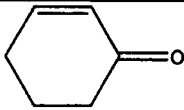
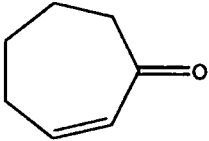
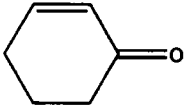
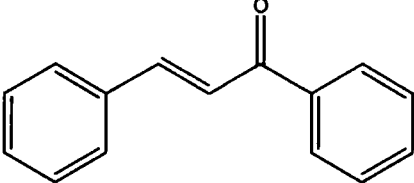
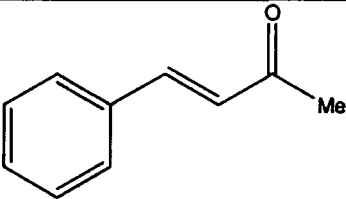
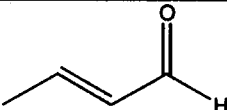
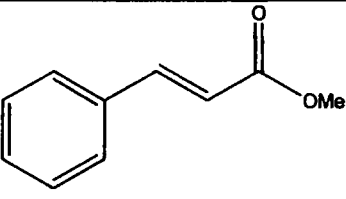
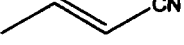
<u>Cu<sup>I</sup> source</u>	<u>Phosphine</u>	<u>Solvent</u>	<u>Temperature/ °C</u>	<u>Reaction time/ h</u>	<u>Yield/ %</u>
CuOTf	—	DMF	RT	14	0
CuOTf	PBu <sub>3</sub>	DMF	RT	10	96
CuOTf	PPh <sub>3</sub>	DMF	RT	24	50
—	PBu <sub>3</sub>	DMF	RT	24	7
—	—	DMF	RT	24	0
CuOTf	2 PBu <sub>3</sub>	DMF	RT	10	79
CuOTf	dppp	DMF	RT	13	0
CuOTf	dppp	DMF	60	12	36
CuCl	—	DMF	RT	24	0
CuCl	PBu <sub>3</sub>	DMF	RT	15	83
CuOTf	—	THF	RT	10	0
CuOTf	PBu <sub>3</sub>	THF	RT	5	77
CuOTf	PBu <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	RT	5	68
CuOTf	PBu <sub>3</sub>	toluene	RT	5	63

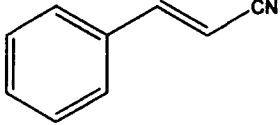
Additional substrates were then tested using the best of these catalysts systems: 10 mol% CuOTf 1:1 with PBu<sub>3</sub> in DMF. Results are shown in Table 1.4. B<sub>2</sub>pin<sub>2</sub> was used as the boron source.

<b>Table 1.4: Results of diboration reactions carried out by Ito <i>et al.</i><sup>21</sup></b>			
All reactions using 10 mol% CuOTf 1:1 with PBu <sub>3</sub> in DMF			
<u>Substrate</u>	<u>Temperature/ °C</u>	<u>Time/ h</u>	<u>Yield/ %</u>
	RT	6	87
	RT	36	67
	RT	20	71
	RT	24	72
	RT	3	82
	80	12	Trace

Two reactions were also carried out using B<sub>2</sub>cat<sub>2</sub> and the best catalyst. These were much slower and gave significantly lower yields.

The results for diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds using Wilkinson's catalyst,<sup>22</sup> Rh(PPh<sub>3</sub>)<sub>3</sub>Cl, by Kabalka *et al.* are presented in Table 1.5. Yields given are for the formation of the hydrolysis product.

<b>Table 1.5: Results of diboration reactions carried out by Kabalka <i>et al.</i><sup>22</sup></b>			
<b>Conditions: 10 mol% Rh(PPh<sub>3</sub>)<sub>3</sub>Cl in toluene at 80°C</b>			
<b>Substrate</b>	<b>Diborating agent</b>	<b>Time/ h</b>	<b>Yield/ %</b>
	B <sub>2</sub> pin <sub>2</sub>	13	78
	B <sub>2</sub> pin <sub>2</sub>	12	75
	B <sub>2</sub> neop <sub>2</sub>	12	76
	B <sub>2</sub> neop <sub>2</sub>	13	67
	B <sub>2</sub> neop <sub>2</sub>	14	64
	B <sub>2</sub> neop <sub>2</sub>	10	62
	B <sub>2</sub> neop <sub>2</sub>	14	63
	B <sub>2</sub> neop <sub>2</sub>	13	72

	$B_2neop_2$	12	65
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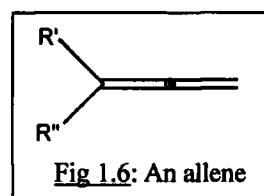
Boronate esters derived from the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds are desirable as they are useful intermediates in organic synthesis. The boronate ester formed is different from that obtained by a conventional hydroboration reaction. In contrast to diborations of purely carbon frameworked unsaturated compounds, for  $\alpha,\beta$ -unsaturated carbonyl compounds the bis-boronate ester has not been isolated due to the lability of the B-O bond, although it has been observed in solution by NMR spectroscopy. Of the reported catalytic systems, the best are based on  $Cu^I$  in conjunction with either KOAc or  $PBu_3$ ; however, high catalyst loadings were employed (10-100 mol%) to give acceptable reaction times and, in the case of some substrates, elevated temperatures were needed. Other systems, Pt and Rh catalysts, require elevated temperatures, which is not ideal.

#### 1.1.4. Diboration of dienes

The diboration of both 1,3 and 1,2 dienes has been investigated. 1,3-dienes have been found to react in two different ways with platinum(0) catalysts depending on the presence of phosphine at the catalyst centre.<sup>23</sup>  $Pt(PPh_3)_4$  was found to give clean 1,4-diboration of 1,3-dienes when reaction took place at 80 °C in toluene. When the reactants were heated in toluene at 50 °C and were in a 3:1 ratio of diene: $B_2$  compound in the presence of a phosphine free catalyst,  $Pt(dba)_2$ , a clean dimerisation and subsequent 1,8-diboration of 2-methylbuta-1,3-diene was observed. Preformed *bis*-boryl *bis*-phosphine platinum (II) complexes,  $(PPh_3)_2Pt(B(OR)_2)_2$ , were also found to be effective catalysts,<sup>24</sup> giving the 1,4-diboration product when reaction took place in toluene at 80 °C. This investigation attempted to use chiral diboron reagents to form chiral *bis*-boryl alkene compounds;

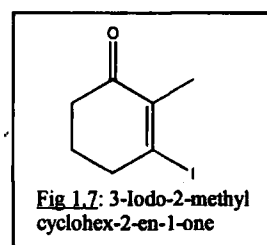
however, the asymmetric induction was ineffective. In both cases the alkene formed from the 1,4-diboration was the *Z*-isomer.

Pt(PPh<sub>3</sub>)<sub>4</sub> and Pt(dba)<sub>2</sub>/PR<sub>3</sub> have been investigated as catalysts for the diboration of 1,2-dienes, i.e. allenes.<sup>25</sup> These two catalysts were found to react at different rates and to give different regioselectivity depending on the nature of the allene. With bulky groups at R' and R'', (Fig. 1.6) both catalysts introduced the boron groups at the terminal double bond. When the bulk of the substituents was reduced, Pt(PPh<sub>3</sub>)<sub>4</sub> in toluene at 80 °C was found to introduce the



boron groups at the internal double bond, but Pt(dba)<sub>2</sub>/PCy<sub>3</sub> at 50 °C in toluene (PCy<sub>3</sub> was the most effective phosphine) diborated the terminal double bond. This varying selectivity was rationalised by the internal double bond reacting preferentially; however, with steric bulk either on the allene, or on the phosphines at the catalyst centre reaction was forced to take place at the terminal double bond.

A completely new system was recently used to diborate allenes, which involved a palladium catalyst.<sup>26</sup> This had to solve the problem of the oxidative addition of a B–B bond to a palladium(0) centre being unfavourable.<sup>27</sup> This was overcome by use of an organic iodide co-catalyst, which, it was suggested, forms a B–I bond in place of the



B–B bond, which can oxidatively add to the palladium centre and so induce the catalytic cycle. The most effective catalyst combination was 1:1 Pd(dba)<sub>2</sub> and 3-iodo-2-methylcyclohex-2-en-1-one (Fig. 1.7), which gave greater than 80 % yields in four hours in toluene at 80 °C. Interestingly, this reaction was 100 % regioselective towards the terminal double bond; less bulky substituents on the allene just resulted in a faster reaction. Various aspects of the reaction were investigated, including using palladium(II) complexes, which

were effective catalysts, and use of other organic halides. A range of organic iodides and iodine itself were effective co-catalysts, but organic bromides were ineffective.

## 1.2. Conclusion

The majority of the examples of diboration reactions of unsaturated organic molecules employ platinum(0) complexes as catalysts. The reactions have, in general, taken place at elevated temperatures; however, there are some examples of reactions at room temperature which is industrially desirable. Other catalyst centres employed include Au<sup>I</sup>, Rh<sup>I</sup>, Cu<sup>I</sup> and Pd; however, these have received less attention.  $\alpha,\beta$ -unsaturated carbonyl compounds, on which this study will concentrate, have been diborated using Pt<sup>0</sup>, Rh<sup>I</sup> and Cu<sup>I</sup>; however, there is no overall consensus at present as to the best catalyst centre for this reaction.

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## 2. Catalyst development

### 2.1 Pt(NBE)<sub>3</sub> with various phosphines

As described in Chapter 1, various different catalyst systems have the ability to diborate  $\alpha,\beta$ -unsaturated carbonyl compounds; however, there is no general consensus or understanding as to which is the best system. Pt(NBE)<sub>3</sub>/PCy<sub>3</sub> is one of the best known catalysts for the diboration of alkynes<sup>1</sup> and, in general, Pt<sup>0</sup> has been the catalyst of choice for diboration. Consequently, this system was chosen as a starting point for an investigation into improved catalysts for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds.

In the initial development stages, four substrates were used, which were chosen to represent the range of possible properties of  $\alpha,\beta$ -unsaturated carbonyl compounds. The chosen substrates were: methylvinylketone (MVK) **3**, 2-cyclohexen-1-one (CHE) **4**, *trans*-cinnamaldehyde (TCA) **5** and *trans*-4-phenylbut-3-en-2-one (BEO) **6**. In all cases, B<sub>2</sub>pin<sub>2</sub> **1** (Fig. 2.1) was used as the diborating agent.

Fig 2.1: The initial four substrates

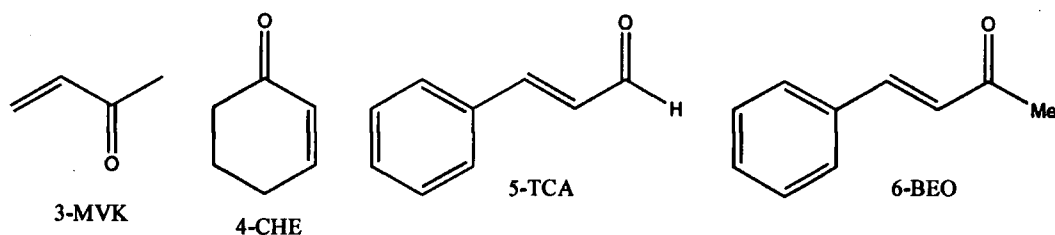


Table 2.1 shows the 'best' results already in the literature for the diboration reactions of these four substrates. Detailed in the Table are the catalyst system, general reaction conditions and the time it took to give a certain conversion.

**Table 2.1:** Best results previously reported with each substrate.

<u>Substrate</u>	<u>Best Catalyst System</u>	<u>Time/h</u>	<u>Conditions</u>	<u>% Conversion</u>
MVK	10 mol% CuCl/AcOK <sup>2</sup>	16	RT in DMF	90
CHE	10 mol% CuOTf/PBu <sub>3</sub> <sup>3</sup>	6	RT in DMF	87
TCA	5 mol% Pt(PPh <sub>3</sub> ) <sub>4</sub> <sup>4</sup>	20	110 °C in toluene	79
BEO	10 mol% CuOTf/PBu <sub>3</sub> <sup>3</sup>	24	RT in DMF	72
	or 5 mol% Pt(PPh <sub>3</sub> ) <sub>2</sub> (η-C <sub>2</sub> H <sub>4</sub> ) <sup>5</sup>	12	80 °C in toluene	100

### 2.1.1 Results

In a typical reaction, catalyst (5 μmol, 5 mol%) and B<sub>2</sub>pin<sub>2</sub> (27.93 mg, 0.11 mmol) were dissolved in solvent (2 ml) in a nitrogen filled glovebox. Substrate (0.1 mmol) was added and the reaction mixture was stirred at room temperature and monitored periodically by GC-MS.

In this section all reactions involved Pt(NBE)<sub>3</sub> and, where relevant, a 1:1 molar ratio of the mono- or bi-dentate phosphine to Pt(NBE)<sub>3</sub>. Results of reactions are outlined in Table 2.2. All products were GC-MS observed hydroborated products unless otherwise stated.

**Table 2.2:** Results of reactions using Pt(NBE)<sub>3</sub> with a variety of phosphines as catalyst

Phosphine	Substrates: Reaction times in hours for % completion shown			
	MVK	CHE	TCA	BEO
None	100 %, 1.25 h	1 %, 19 h	17 %, 19.5 h	38 %, 20 h
PCy <sub>3</sub>	100 %, 16 h	77 %, 16.5 h	100 %, 16.5 h	100 %, 17.5 h
dppm	9 %, 19 h	< 1 %, 19.5 h	1 %, 20 h	3 %, 20.5 h
dppe	3 %, 40 h	2 %, 40.5 h	6 %, 41 h	67 %, 41.5 h
dppp	< 1 %, 18 h	< 1 %, 18.5 h	0 %, 19 h	< 1 %, 19.5 h
dppb	100 %, 1 h	26 %, 93 h	30 %, 93.5 h	68 %, 94 h

dppf	100 %, 0.5 h	4 %, 40 h	8 %, 70 h	100 %, 40 h
dcpe	4 %, 45 h	0 %, 45 h	24 %, 46 h	54 %, 46.5 h

### 2.1.2 Discussion

A number of interesting conclusions can be drawn from the data in Table 2.2 when compared to that in Table 2.1.

Pt(NBE)<sub>3</sub> alone effectively catalyses the diboration of MVK, much faster than any other system, however, reaction with other substrates is not at all effective. This is a surprising result considering the general observation that ligands have been necessary to catalyse diboration reactions except in the case of alkenes. Here, however, MVK is not reacting as a simple alkene as the GC-MS trace is for a hydrolysed 1,4-diboration product *vide infra*.

Pt(NBE)<sub>3</sub>/PCy<sub>3</sub>, which is a very good catalyst for the diboration of alkynes, gives comparable catalytic activity to other known systems for the three linear substrates, but no improvement. A notable exception is reaction with CHE, which reacts much slower with this system.

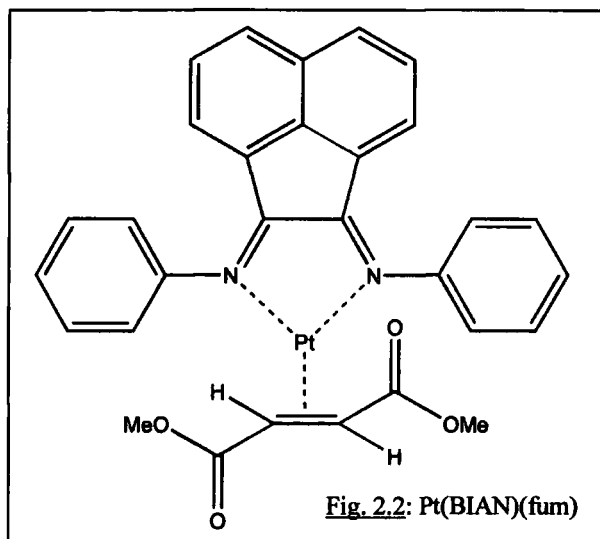
The different diphosphine catalysts have varying activity. Dppp and dppm in conjunction with Pt(NBE)<sub>3</sub> are ineffective as catalysts with no reaction, or an insignificant amount occurring within a 20 hour period. Interestingly, dppe and dcpe with Pt(NBE)<sub>3</sub> were ineffective at catalysing the reaction with MVK, CHE and TCA, but both gave significant amounts of product with BEO. This is surprising considering that MVK is the simplest and therefore generally most reactive substrate. The best results with diphosphines occurred with dppb and dppf with Pt(NBE)<sub>3</sub>. The catalysed reaction with MVK is faster than with any previously reported system and in the case of dppf/Pt(NBE)<sub>3</sub> the reaction rate with BEO was reasonably competitive with that using known systems.

In general, diphosphines with  $\text{Pt}(\text{NBE})_3$ , when they did catalyse the reaction, were effective with straight chain ketones, but did not react efficiently with the aldehyde, TCA, or the cyclic ketone, CHE. This is surprising when the general reactivity of organic substrates is considered. This must be due to a step in the catalytic cycle being unfavourable when a hydrogen rather than a carbon is  $\alpha$  to the carbonyl or an alternative reaction pathway occurs, for example a decarbonylation, which if it happened even stoichiometrically could deactivate the catalyst. It is presumed that in each case a complex was formed between the platinum centre and the phosphines as the chemistry of these systems is known. This is a good assumption as this has been observed in other cases, but also the reactivity of these mixtures bears a marked difference to that for  $\text{Pt}(\text{NBE})_3$  in the absence of phosphine. These diphosphines were chosen in order to give a variety of different chelate ring sizes and also, with dppf and dcpe, differing electronic effects of the phosphine at the metal centre.

### 2.1.3 Conclusions

To conclude, catalysts based on  $\text{Pt}(\text{NBE})_3$  with a variety of phosphines generally show little or no improvement on those already known.  $\text{Pt}(\text{NBE})_3$  with dppb and dppf and  $\text{Pt}(\text{NBE})_3$  alone gave better catalytic activity for MVK, but not with other substrates and in general reactions did not occur faster than with a known catalyst. A general order of reactivity cannot be suggested as the activity varied for each substrate. For MVK - no phosphine  $\sim$  dppb  $\sim$  dppf  $>$   $\text{PCy}_3$   $\gg$  dppm  $\sim$  dppe  $\sim$  dppp  $\sim$  dcpe; for BEO -  $\text{PCy}_3$   $>$  dppf  $>$  no phosphine  $\sim$  dppe  $\sim$  dcpe  $>$  dppb  $\gg$  dppm  $\sim$  dppp. Catalyst activity with CHE and TCA was similar and is as follows:  $\text{PCy}_3$   $\gg$  dppb  $\sim$  no phosphine  $>$  dcpe  $>$  dppe  $\sim$  dppf  $>$  dppp  $\sim$  dppm. Catalytic activity with phosphine-platinum complexes is highly substrate dependent and, although activity is better with some catalysts for certain substrates, this is not universal and these catalysts offer no significant improvement on those already known.

## 2.2 Pt(BIAN)(fum)



### 2.2.1 Results

Pt(BIAN)(fum) (Fig. 2.2) is a diimine-Pt<sup>0</sup> catalyst. Pt<sup>II</sup> diimine complexes have found a wide variety of use in C–H activation catalysis;<sup>6</sup> however, there are no reported examples of diimine Pt<sup>0</sup> complexes acting as catalysts. When tested as a catalyst for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds, Pt(BIAN)(fum) was found to be highly active and gave results with the four general substrates as outlined in Table 2.3. All results are for GC-MS observed hydrolysis products of 1,4-diborated products or 1,2-diborated products *vide infra*. A detailed discussion of the structure of products formed is provided in Chapter 3.

<u>Substrate</u>	<u>Time / h</u>	<u>% Conversion</u>
MVK	1	100
CHE	19	100
TCA	20	90
BEO	10.5	100

These results are significantly better than those for known catalysts so a wider substrate range was tested, the results of which are shown in Table 2.4.

**Table 2.4:** Further Reactions with 5 mol% Pt(BIAN)(fum) and B<sub>2</sub>pin<sub>2</sub> in THF at RT

<u>Substrate</u>	<u>Time / h</u>	<u>% Conversion</u>
Chalcone	23	91
3,5-dimethyl-2-cyclohexen-1-one	26	10
Ethylcrotonate	7	86
Methylcinnamate	27	5
3-octen-2-one	3	100
Acrylonitrile	26	23
Methylmethacrylate	19	100
Ethylacrylate	2.5	100

### 2.2.2 Discussion

Pt(BIAN)(fum) is, in the majority of cases, a better catalyst for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds than previously reported catalysts. With the three substrates, CHE, chalcone and acrylonitrile using about half the catalyst loading of previous studies gives similar conversion in approximately double the time so the catalyst activity is comparable.

Methylcinnamate seemed to give an anomalous result as the reaction barely proceeded; however, in previous work using this substrate<sup>7</sup> the reaction mixture was heated, which was not attempted in this work.

### 2.2.3 Catalyst stability

The catalytic mixture at the beginning of the reaction is a dark green solution. An interesting observation is that with more reactive substrates, such as MVK and ethylacrylate, the reaction mixture remains green, but with less reactive substrates the reaction mixture gets darker (brown or red depending on solvent). In all GC-MS studies of the reactions, the intact BIAN ligand is detectable with no evidence of ligand

diboration and the dimethylfumarate ligand is not observed either as the parent ligand or in a hydro- or diborated form. This is perhaps surprising as it is itself an  $\alpha,\beta$ -unsaturated carbonyl compound and might be expected to react.

The stability of both Pt(BIAN)(fum) and  $B_2pin_2$  to both air and moisture were investigated qualitatively by  $^1H$  and  $^{11}B$  NMR respectively. NMR spectra were recorded at  $t = 0$  and 24 hours after intentional addition of air or water. Results are shown in Table 2.5 for  $B_2pin_2$ .

	$\delta^{11}B$ before addition / ppm	$\delta^{11}B$ immediately after addition / ppm	$\delta^{11}B$ 24 h after addition / ppm
Added air	30.5	30.7	30.5
Added water	30.6	33.8	33.7

This shows that  $B_2pin_2$  is stable in the presence of air, however, in the presence of moisture it is unstable as a different, unidentified species is formed. This is possibly a  $B_2pin_2$  *aquo* complex.

Results with Pt(BIAN)(fum) are much less quantitative. By  $^1H$  NMR, Pt satellites are visible on both the alkenic and methyl peaks of the dimethylfumarate ligand at  $t = 0$ . In air, the intensity of these peaks decreased, probably due to catalyst deposition which was visible in the NMR tube as a precipitate resulting in a less concentrated sample. Interestingly, the nature of the Pt satellites around the alkene resonance did not change with time; however, around the methyl peak the satellites and the peak itself decreased in intensity and a new peak grew coincident with one of the Pt satellites. In the reaction with added water similar observations occurred, but to a greater extent. The change of the methyl resonance intensity would indicate that in the presence of water and air (probably moisture in the air) the carbonyl group of the fumarate ligand becomes less associated with the platinum centre, but the alkene still remains coordinated. In

conclusion Pt(BIAN)(fum) seems to be relatively stable in the presence of air and moisture over a short period of time, but over a longer period catalyst deposition and degradation is observed, particularly in the presence of added moisture. In solution, in the absence of air and water, the catalyst seems to be stable over a long period of time. Reaction mixtures remain in solution for periods in excess of one week and catalyst stock solutions can be used after several days and give the same results as when freshly prepared.

### 2.3 Conclusion

The diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds has been investigated using a variety of platinum based catalysts. Phosphino-platinum complexes were found to be active; however, they exhibit no real advances on known systems.

Pt(BIAN)(fum) is a superior catalyst to those already known for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds. Reactions are clean, occur in excellent yields, are relatively quick and can be performed at room temperature with low catalyst loadings.

Pt(BIAN)(fum) is stable in solution over a considerable period of time and is also relatively stable in the presence of air, but only for short periods of time. Water leads to catalyst decomposition and degradation.

### 2.4. References

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1. R. L. Thomas, F. E. S. Souza and T. B. Marder, *J. Chem. Soc., Dalton Trans.*, 2001, 1650.
  2. a) K. Takahashi, T. Ishiyama and N. Miyaura, *Chem. Lett.*, 2000, 982. b) K. Takahashi, T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2001, **625**, 47.
  3. H. Ito, H. Yamanaka, J-i. Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 2000, **41**, 6821
  4. H. A. Ali, I. Goldberg and M. Srebnik, *Organometallics*, 2001, **20**, 3962.

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5. Y. G. Lawson, M. J. G. Lesley, T. B. Marder, N. C. Norman and C. R. Rice, *Chem. Commun.*, 1997, 2051.

6. H. A. Zhong, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 2002, **124**, 1378.

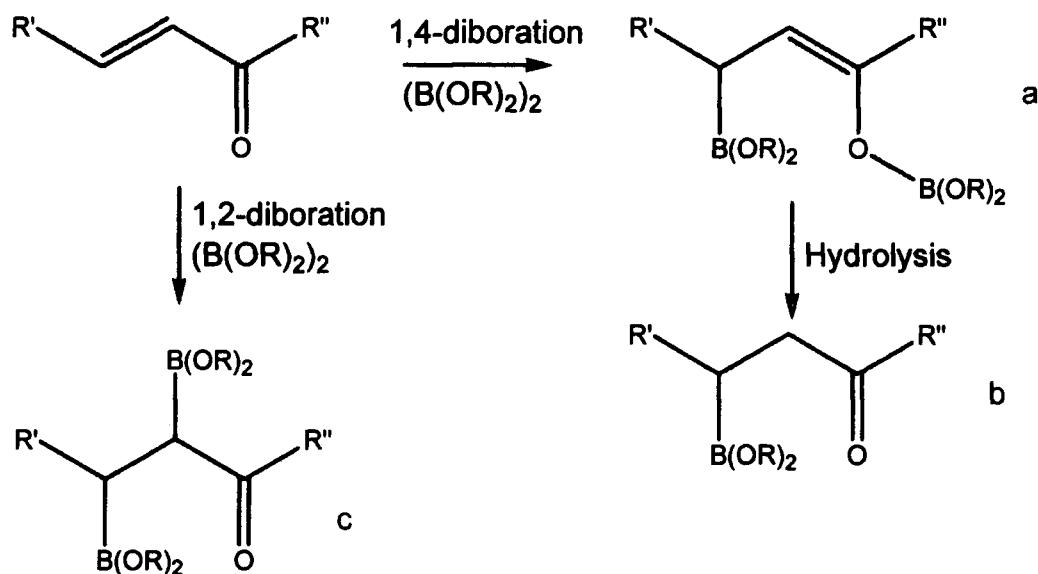
7. G. W. Kabalka, B. C. Das and S. Das, *Tetrahedron Lett.*, 2002, **43**, 2323.

### 3. Product structure determination

In order to identify the products of the reactions two techniques were used, namely GC-MS and multinuclear NMR spectroscopy. GC-MS was used as the primary tool to monitor reactions *in situ*. A total ion-chromatographic trace produces peaks when any ionised species is detected. At the same time, the mass spectrum of each species is recorded from 50–650 amu so that at a specific time the unit mass resolution spectrum of the detected species is known. This enabled products to be observed with masses consistent with either hydroboration or diboration of the starting materials along with B<sub>2</sub>pin<sub>2</sub>, residues from the ligands around the platinum centre and, in most cases, any remaining starting material. There were two major problems associated with this method of product detection. First, for  $\alpha,\beta$ -unsaturated carbonyl compounds without an electron withdrawing group attached only apparently 'hydroborated' (hydrolysed 1,4-diborated) products were observed in the GC-MS; however, this is not expected to be the initial product formed. In fact, the diborated primary products were observed by *in situ* NMR spectroscopy, *vide infra*, suggesting hydrolysis of the 1,4-diborated products must be taking place in the GC. Secondly, from the MS alone we do not know whether the isomer observed is the 1,4-diboration product (or hydrolysis product derived from it) the 1,2-diboration product or possibly even the 3,4-diboration product. These possible ambiguities meant that multinuclear NMR spectroscopy was necessary to determine the exact product structure (see fig. 3.1. for all possible products). The NMR techniques used were <sup>1</sup>H and <sup>13</sup>C 1D NMR and <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C 2D NMR spectroscopy. In the majority of cases, with the simpler substrates, only <sup>1</sup>H and <sup>1</sup>H-<sup>1</sup>H spectra were needed to determine the backbone and identify unambiguously the sites at which boron was attached, but for certain substrates <sup>13</sup>C and <sup>1</sup>H-<sup>13</sup>C spectra were also needed. In all cases it was not possible to identify the exact <sup>1</sup>H resonance of the methyl groups on the Bpin groups as an overlapping multiplet, the peaks of which could not be individually

integrated, was formed. In 2D NMR spectra there is a significant amount of  $T_1$  noise due to some instability during experiments. This is most noticeable on the strongest peaks such as the  $\text{CH}_3$ 's of Bpin, but it does not effect the overall interpretation of the spectra.

**Fig 3.1** General reaction scheme with possible products



nb Product structures are all shown in the appendix

Also, in most cases, more than one product was identified, but with both possessing the same basic structure. This is due to the presence of the  $\text{C}=\text{C}$  double bond in the products. The two different products are the kinetic and thermodynamic product. In most cases the exact stereochemistry around the double bond has not been ascertained, just the general nature of the backbone. This was not the aim of this study and the stereochemistry of the products will have to be determined in the future using further experiments such as NOE.

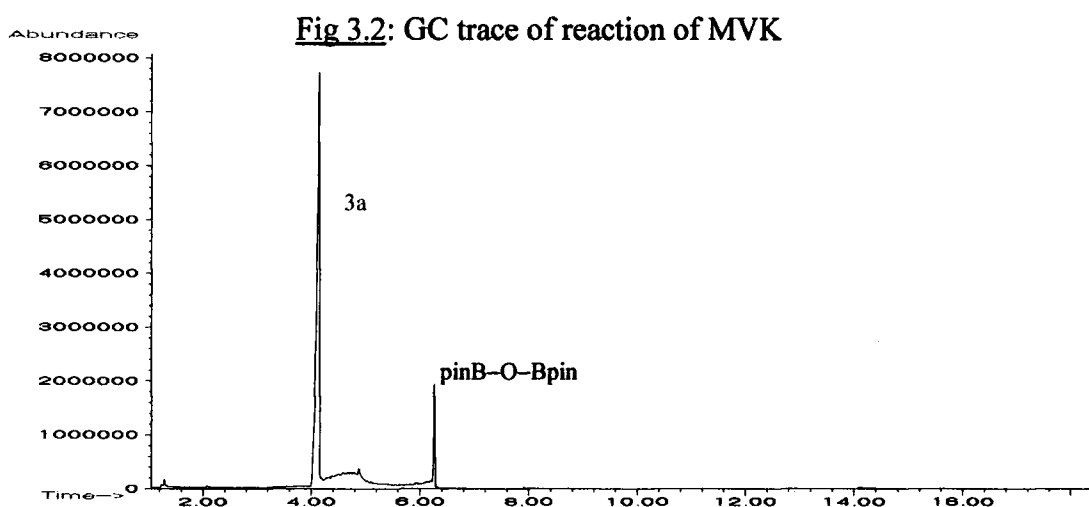
Yields quoted were determined by GC. The relative response factors in the MS of the  $\alpha,\beta$ -unsaturated carbonyl compounds, products and  $\text{B}_2\text{pin}_2$  were not determined. This means that the yields are very approximate as the mass spectrometer detector can have very different response factors for different substrates. NMR spectroscopy is a far better

technique for quantitation and this work is currently being undertaken by another student. Yields are generally quoted relative to remaining substrate; however, certain volatile substrates were not detectable using our GC conditions so the yields are relative to remaining  $B_2pin_2$ .

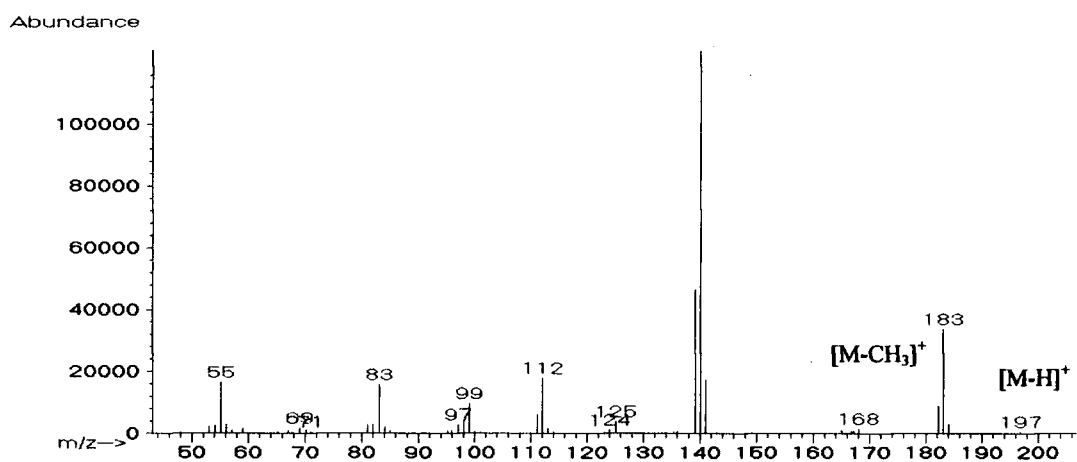
GC traces shown are representative only and are not all for the same point in a reaction. NMR's were carried out, generally after a minimum of 24 hours, but exact times are not known as it was dependent on being able to get time on the machine. pinB-O-Bpin was also observed in most GC traces as a result of the hydrolysis reaction.

### 3.1. Methylvinyl ketone

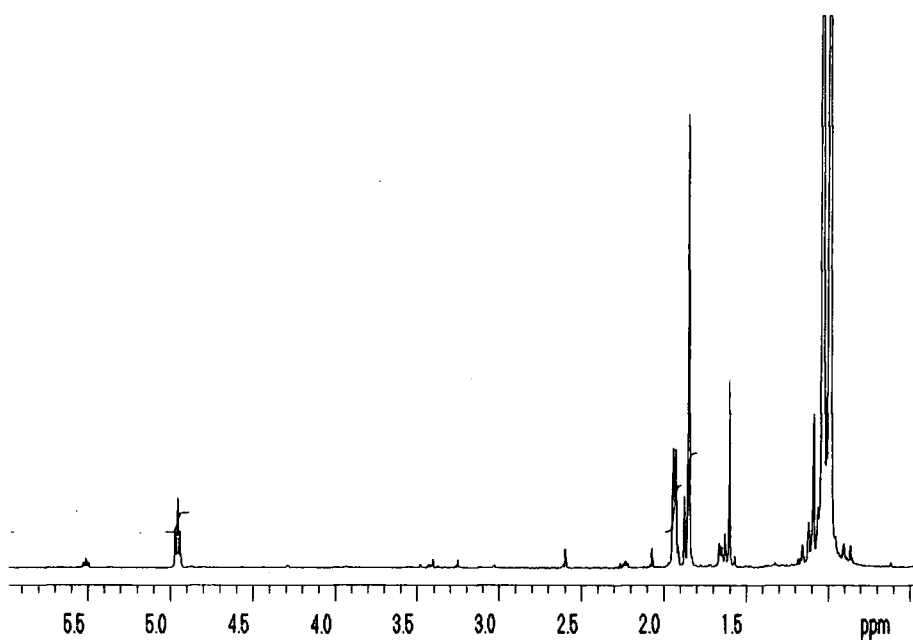
Reactions with MVK as the substrate gave an observed hydrolysed 1,4-diborated product, 3a, in the GC-MS. A typical GC with mass spectrum for the product peak is shown (Fig. 3.2 and 3.3).



**Fig 3.3:** MS of 3a



**Fig 3.4:**  $^1H$  NMR spectrum of 3b



$^1H$  NMR spectroscopy (fig 3.4) identified the 1,4-diborated product 3b. In this case 2D NMR was unnecessary as it was possible to see the product peaks growing as the starting material peaks disappeared when the reaction was monitored by  $^1H$  NMR. This is the kinetic product as another product could be seen appearing coincident with this product disappearing as time progressed in the reaction. This thermodynamic product has not been identified.

Peak / ppm	Pattern and coupling constant / Hz	Assignment
1.88	s	$\text{CH}_3-$
1.94	d, 7.5	$-\text{CH}_2\text{Bpin}$
4.96	t, 7.5	$=\text{CH}-$

### 3.2. 2-Cyclohexen-1-one

GC-MS identified in each reaction with this substrate the hydrolysed 1,4-diborated product **4a** (fig 3.5 and 3.6).

Fig 3.5: GC trace for reaction of CHE

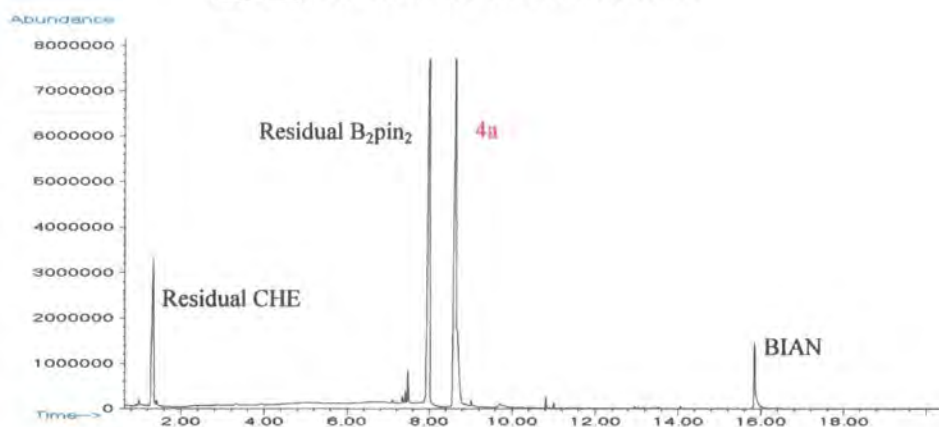
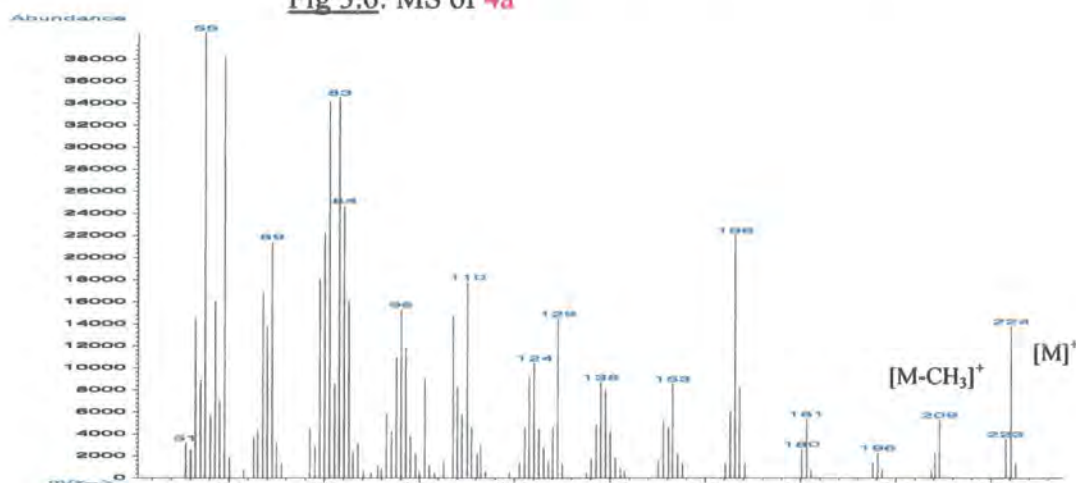
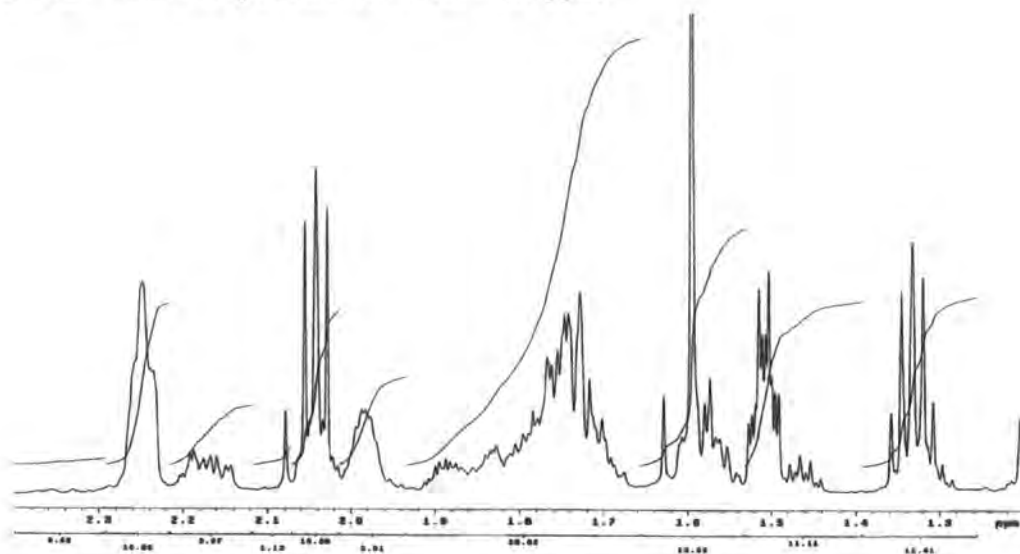


Fig 3.6: MS of **4a**

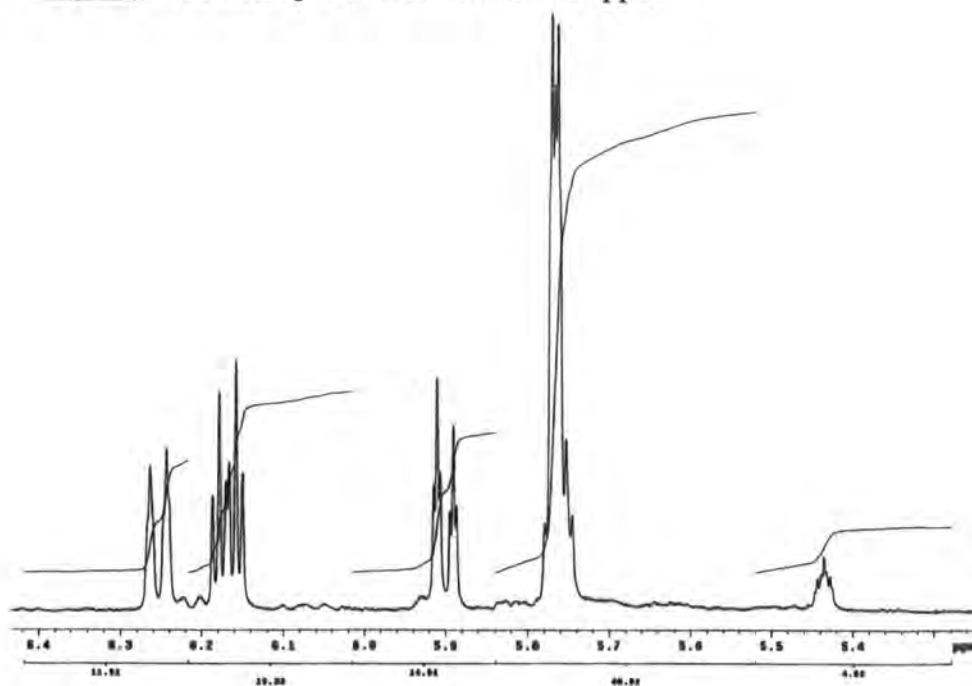


In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}-^1\text{H}$  NMR were necessary. Spectra are shown below (fig 3.7, 3.8, 3.9 and 3.10) with the peaks and correlations shown in Tables 3.2 and 3.3 and product structures (fig 3.11 and 3.12).

**Fig. 3.7:**  $^1\text{H}$  NMR spectrum of 4b 1.2 – 2.4 ppm



**Fig. 3.8:**  $^1\text{H}$  NMR spectrum of 4b 5.3 – 6.4 ppm



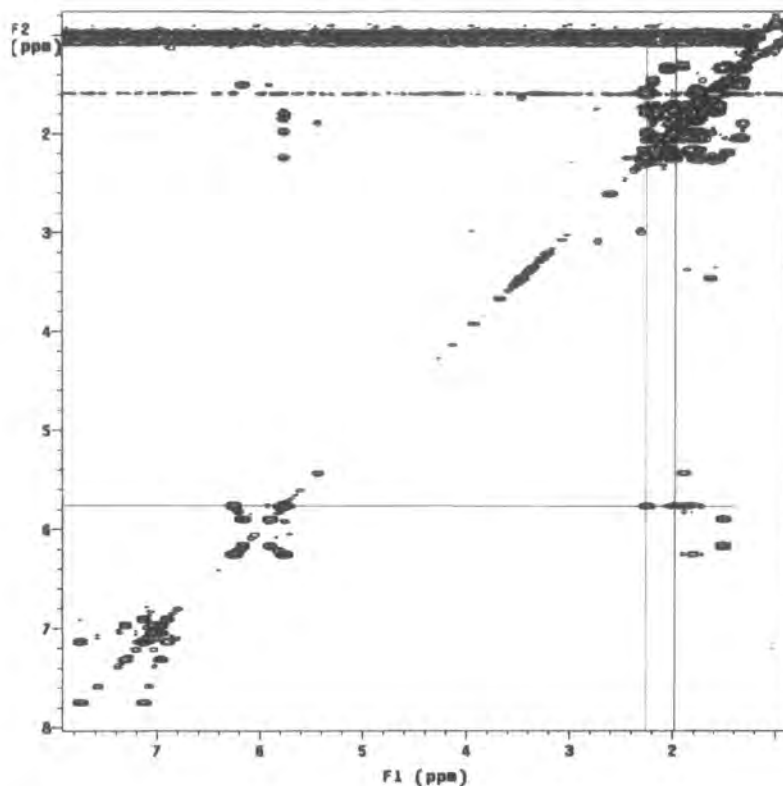


Fig 3.9: Full  $^1\text{H}$ - $^1\text{H}$  correlation spectrum for **4b**

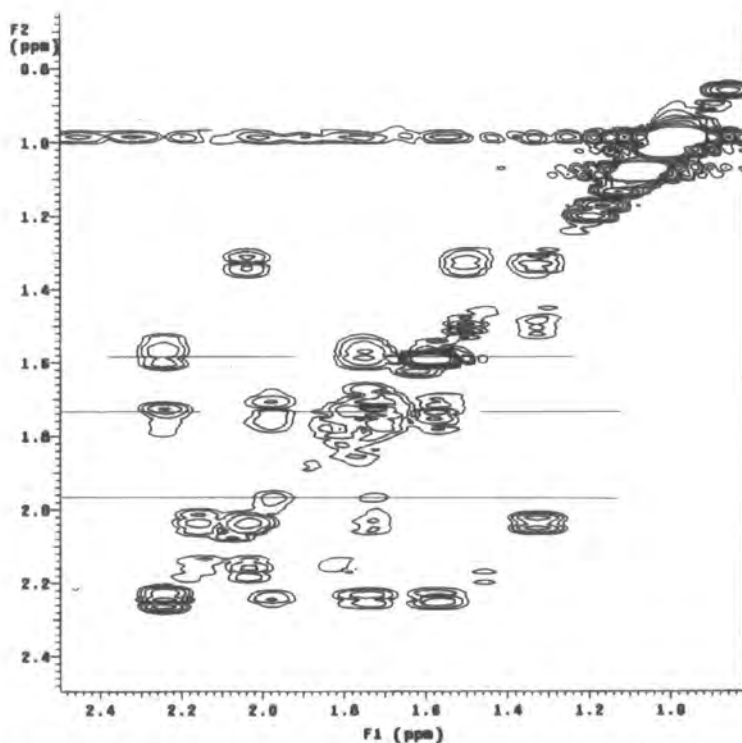
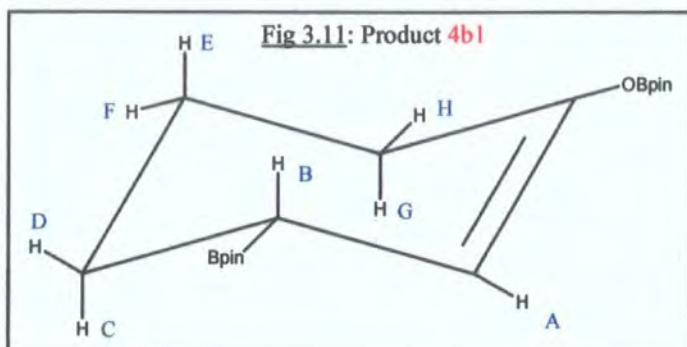


Fig 3.10:  $^1\text{H}$ - $^1\text{H}$  correlation spectrum of **4b** 0.7-2.4 ppm

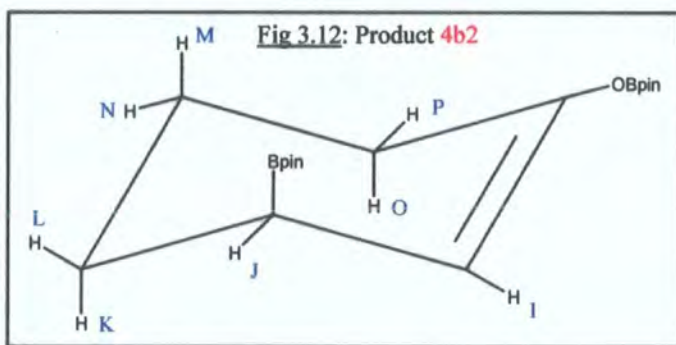
It is possible to identify for this reaction two different products resulting from the 1,4-diboration of CHE. The only difference between them is the stereochemistry about the  $-\text{CHBpin}-$  carbon. It was possible to individually identify the products **4b1** and **4b2** by

taking into account the correlations of **B** and **J**. In order to assign peaks to individual positions around the cyclohexane ring it was important to take into account that H's on the same C correlate strongly and so to do adjacent axial H's, but an equatorial H adjacent to an axial H will not correlate strongly and adjacent equatorial H's will not correlate at all.



**Table 3.2:**  $^1\text{H}$  NMR of **4b1**

<u>Peak / ppm</u>	<u>Correlation with</u>	<u>Integration in H equivalents</u>	<u>Position</u>
1.60	1.76, 2.24	1	F
1.76	1.60, 1.97, 2.24	3	E, G, H
1.97	1.76, 5.76	1	D
2.24	1.60, 1.76, 1.97, 5.76	1	C
5.76	1.97, 2.24, 6.25		B
6.25	5.76	1	A



**Table 3.3:**  $^1\text{H}$  NMR of **4b2**

<u>Peak / ppm</u>	<u>Correlation with</u>	<u>Integration in H equivalents</u>	<u>Position</u>
1.34	1.50, 2.04	1	K

1.50	1.34, 6.16	1	L
1.72	2.04	1	N
1.82	2.16	1	P
2.04	1.34, 1.72, 2.16	1	M
2.16	1.82, 2.04	1	O
5.90	1.50, 6.16	1	J
6.16	1.50, 5.90	1	I

The integration of the peak at 4.76 is approximately double that expected. The reason for this is unclear as there are no other unidentified peaks with significant intensity present in the spectrum.

### 3.3. *Trans*-cinnamaldehyde

GC-MS identified in each reaction with this substrate the hydrolysed 1,4-diborated product 5a (fig 3.13 and 3.14).

**Fig 3.13:** GC trace of a reaction of TCA

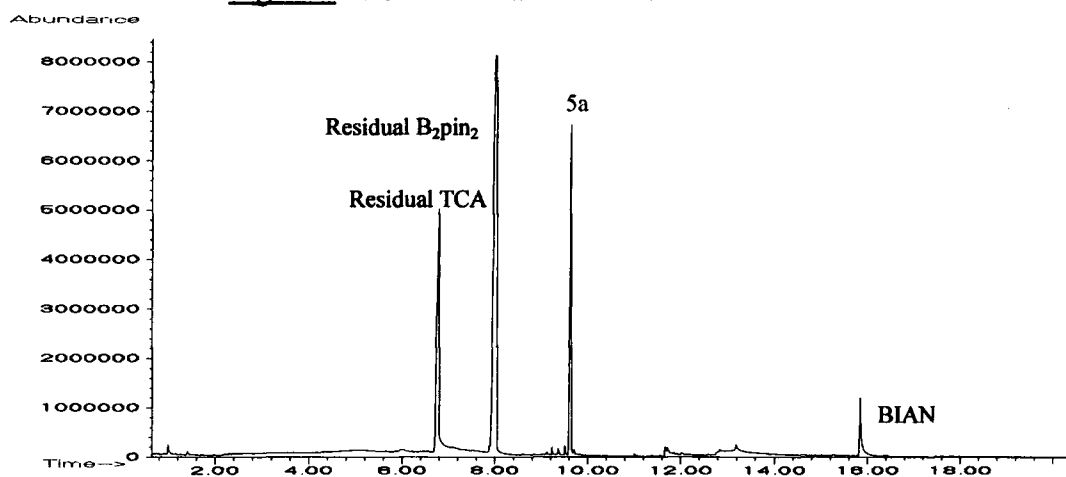
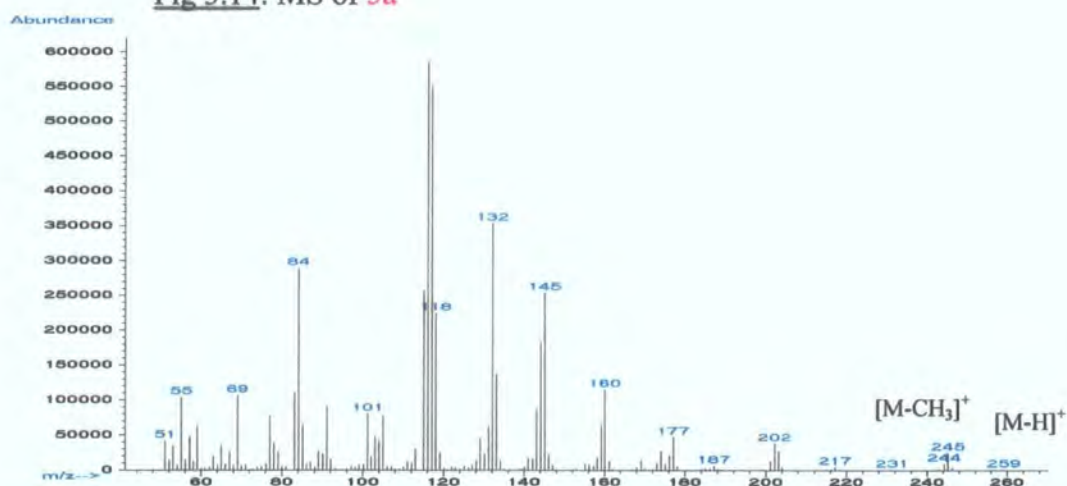


Fig 3.14: MS of 5a



In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown below (fig 3.17, 3.18 and 3.19) with the peaks and correlations shown in Table 3.4. The 1,4-diborated product 5b was identified. Both *cis* and *trans* isomers were observed and were identified.

The positions of the peaks were rationalised as, in 5b2 (fig 3.16), the *trans* isomer, the *CH*Bpin was shifted to higher frequency due to a through space interaction with the OBpin group. In both isomers the =*CH*OBpin occurs in essentially the same position as there is no major difference between the sites. In 5b2 the *-CH=* is significantly deshielded due to the influence of the OBpin *trans* to it across the double bond leading to the high frequency shift in comparison to that for 5b1 (fig 3.15).

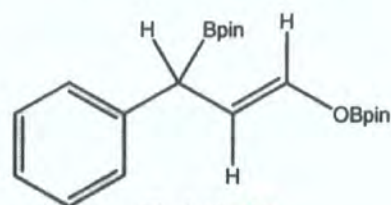


Fig 3.15: 5b1

Table 3.4:  $^1\text{H}$  NMR of 5b1

Peak/ppm	Correlation with	Pattern and Coupling Constant / Hz	Position
4.11	5.22	d, 8.5	<i>-CH</i> Bpin-
5.22	4.11, 6.84	dd, 8.5, 5.5	<i>-CH=</i>
6.84	5.22	d, 5.5	=C(OBpin) <i>H</i>

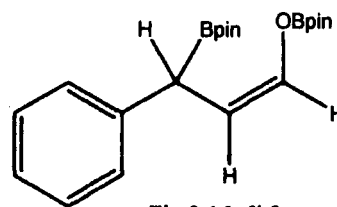
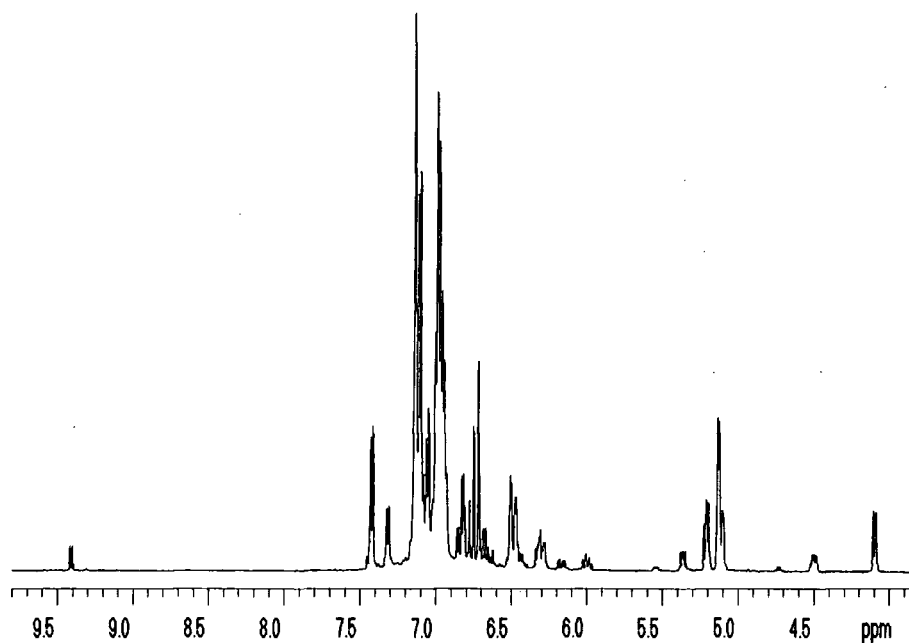


Fig 3.16: 5b2

Table 3.5: $^1\text{H}$ NMR of 5b2			
Peak/ppm	Correlation with	Pattern and Coupling Constant / Hz	Position
5.14	6.50	d, 5.5	-CHBpin-
6.50	5.14, 6.75	dd, 15.5, 5.5	-CH=
6.75	6.50	d, 15.5	=C(OBpin)H

In both cases it was not possible to identify the NMR resonances for the phenyl rings as there were no correlations observed with the -CHBpin- groups. It was also not possible to determine them by integration as they will fall in the large multiplet between 6.95 and 7.15 ppm.

Fig 3.17:  $^1\text{H}$  NMR of 5b



There was also some remaining starting material in the reaction mixture as an aldehyde  
 $^1\text{H}$  is observable at 9.4 ppm.

Fig 3.18:  $^1\text{H}$  NMR of 5b. 3.8 – 7.0 ppm

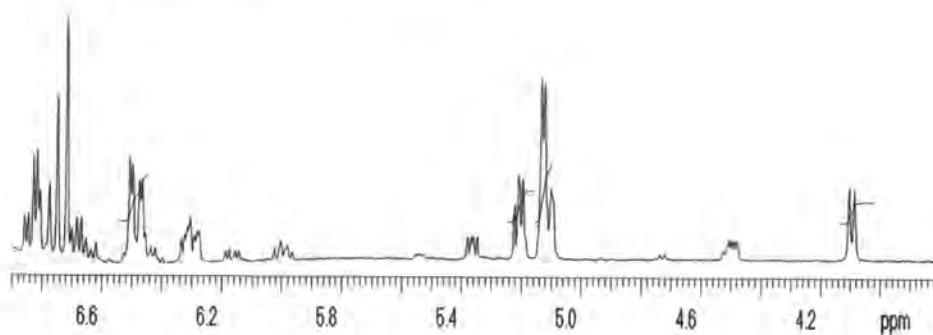
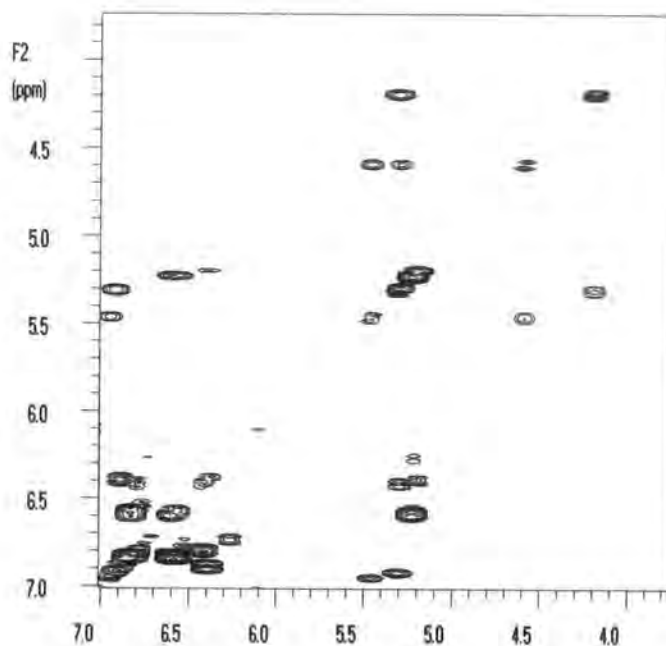


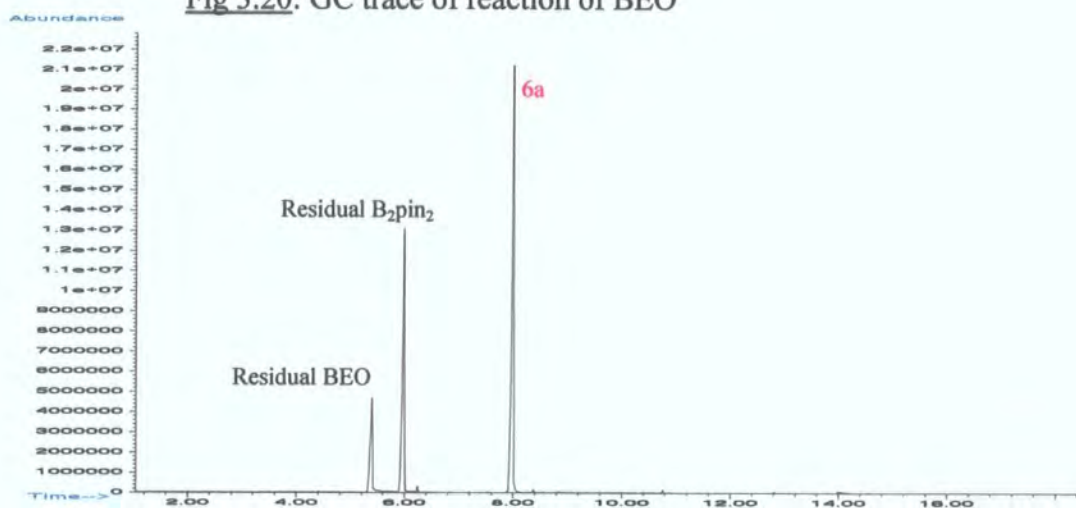
Fig 3.19:  $^1\text{H}$ - $^1\text{H}$  NMR of 5b. 3.8 – 7.0 ppm



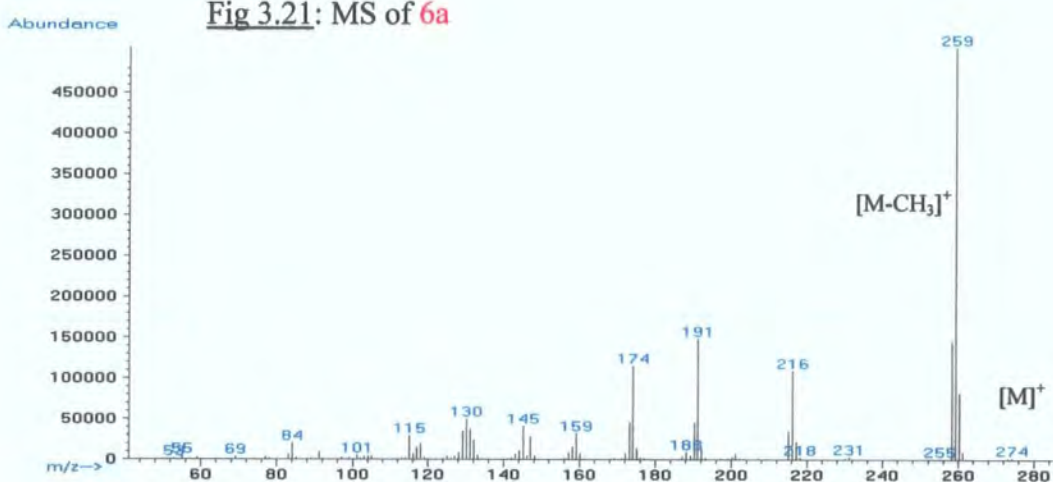
### 3.4. *Trans*-4-phenylbut-3-en-2-one

GC-MS identified in each reaction with this substrate the hydrolysed 1,4-diborated product 6a (fig 3.20 and 3.21).

**Fig 3.20:** GC trace of reaction of BEO

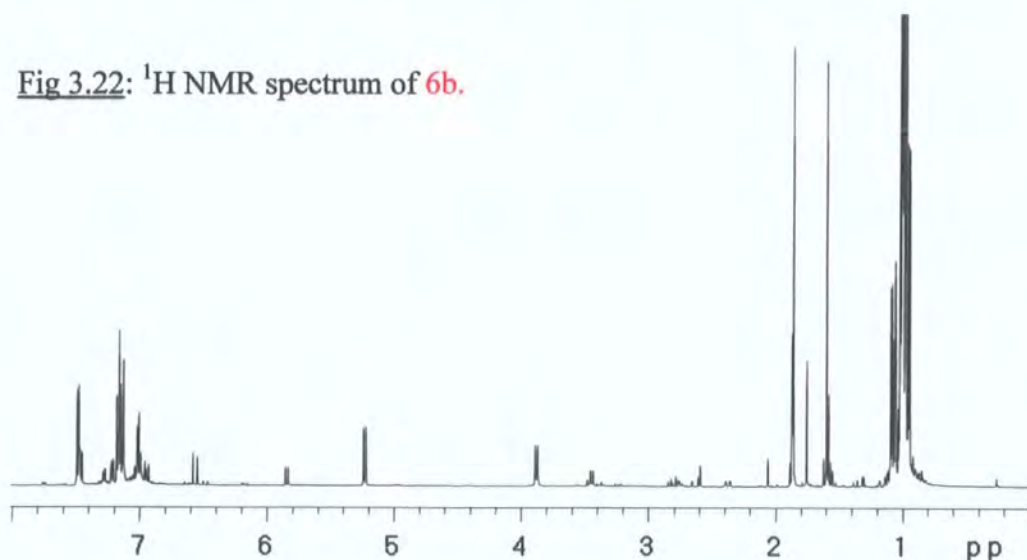


**Fig 3.21:** MS of 6a



In order to identify the product by NMR 1D <sup>1</sup>H NMR, and 2D <sup>1</sup>H-<sup>1</sup>H NMR were necessary. Spectra are shown below (fig 3.22 and 3.23) with the peaks and correlations shown in Table 3.6. The 1,4 diborated product **6b** was identified.

**Fig 3.22:** <sup>1</sup>H NMR spectrum of 6b.



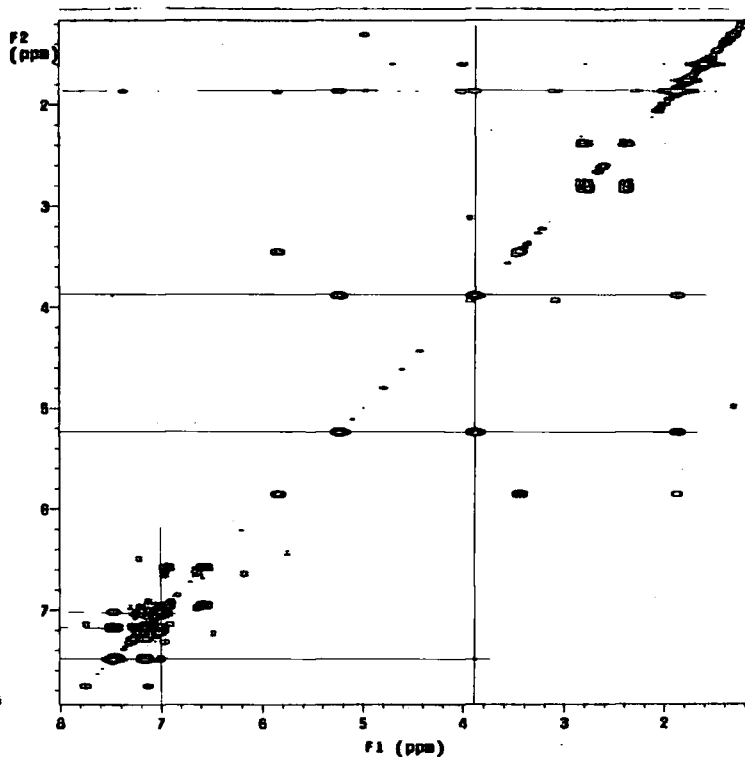


Fig 3.23:  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of 6b

Both isomers about the C=C double bond were identified; however, they were not distinguished, but could be with further experiments.

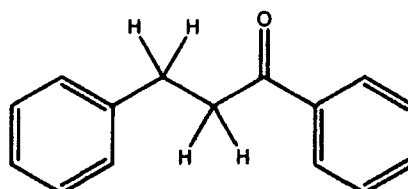
Table 3.6:  $^1\text{H}$  NMR of 6b

<u>Isomer 1:</u>			
<u>Peak/ppm</u>	<u>Correlation with</u>	<u>Pattern and Coupling Constant / Hz</u>	<u>Position</u>
1.87	3.88, 5.24	s	-CH <sub>3</sub>
3.88	1.88, 5.24, 7.48	d, 8.5	-CHBpin-
5.24	1.88, 3.88	dq, 8.5, 1.2	-CH=
7.01	7.17, 7.48	t, 7.5	<i>p</i> -C <sub>6</sub> H <sub>5</sub> -
7.17	7.01, 7.48	t (dd), 7.5	<i>m</i> -C <sub>6</sub> H <sub>5</sub> -
7.48	3.88, 7.01, 7.17	d, 7.5	<i>o</i> -C <sub>6</sub> H <sub>5</sub> -

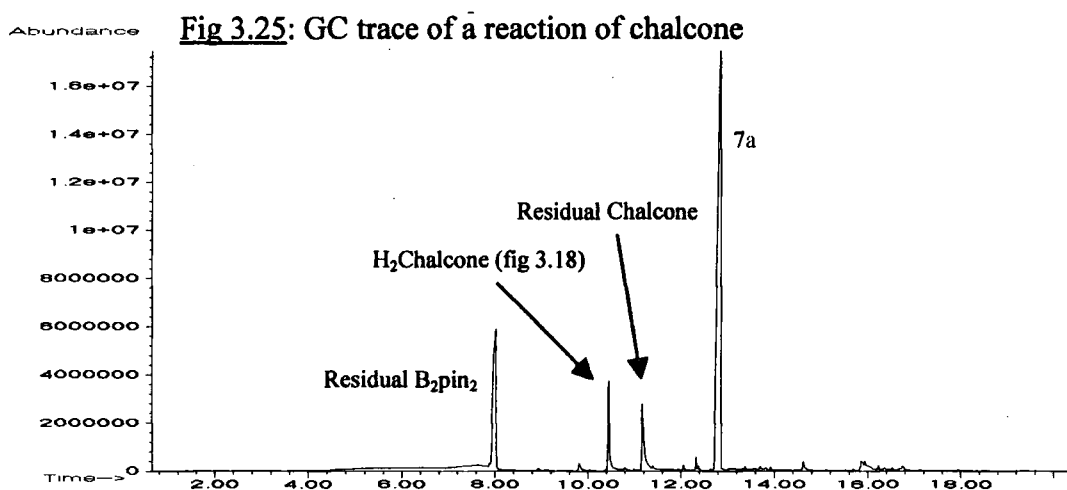
<u>Isomer 2:</u>			
<u>Peak/ppm</u>	<u>Correlation with</u>	<u>Pattern and Coupling Constant / Hz</u>	<u>Position</u>
1.88	3.45, 5.89	d, 1.0	-CH <sub>3</sub>
3.45	1.88, 5.85, 7.46	d, 10.5	-CHBpin-
5.85	1.88, 3.45	dq, 10.5, 1.0	-CH=
7.01	7.17, 7.48	? obscured by other isomer	<i>p</i> -C <sub>6</sub> H <sub>5</sub> -
7.17	7.01, 7.48	? obscured by other isomer	<i>m</i> -C <sub>6</sub> H <sub>5</sub> -
7.46	3.88, 7.01, 7.17	d, 8.5	<i>o</i> -C <sub>6</sub> H <sub>5</sub> -

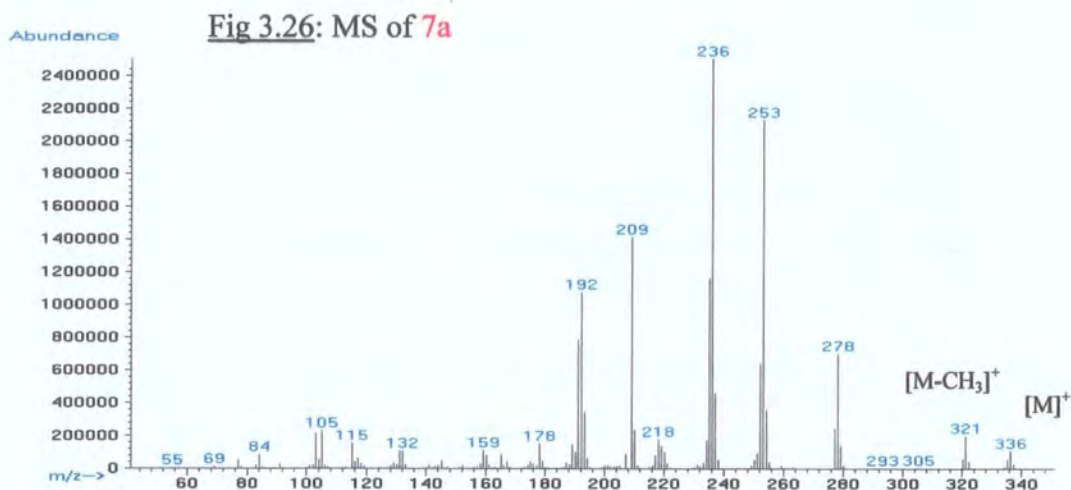
### 3.5. Chalcone

GC-MS (fig 3.25 and 3.26) identified in each reaction with this substrate the hydrolysed 1,4-diborated product 7a and also the hydrogenated product (Fig. 3.24).

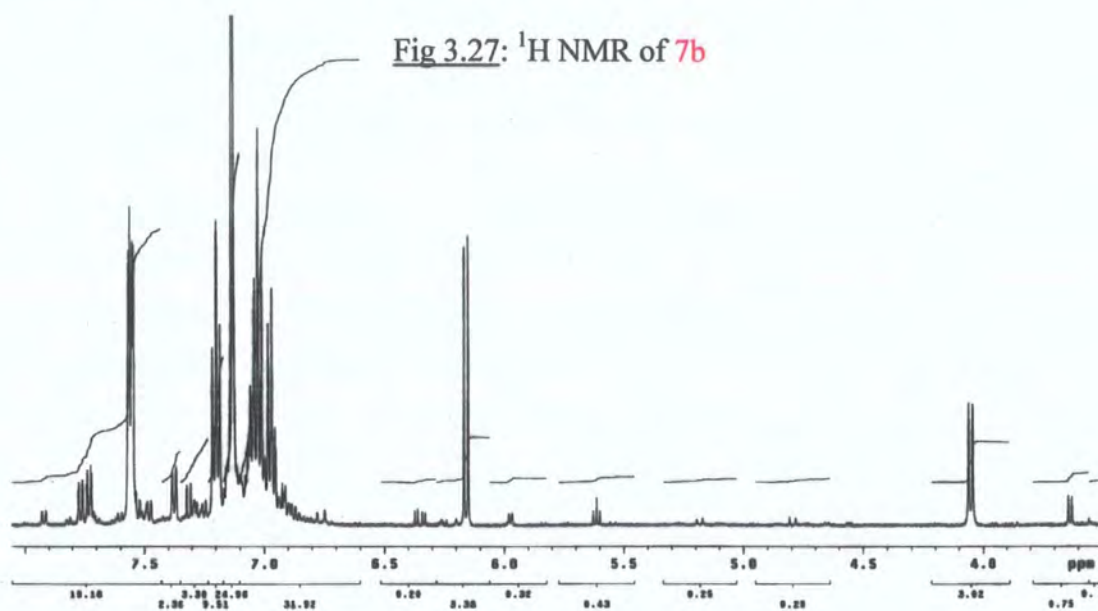


**Fig 3.24:** Hydrogenated Chalcone





In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown below (fig 3.27, 3.28 and 3.29) with the peaks and correlations shown in Table 3.7. Only one 1,4-diborated product, **7b**, was identified; however, the stereochemistry about the double bond is not known. It is likely to be the isomer shown in the products list as this isomer is less sterically hindered.



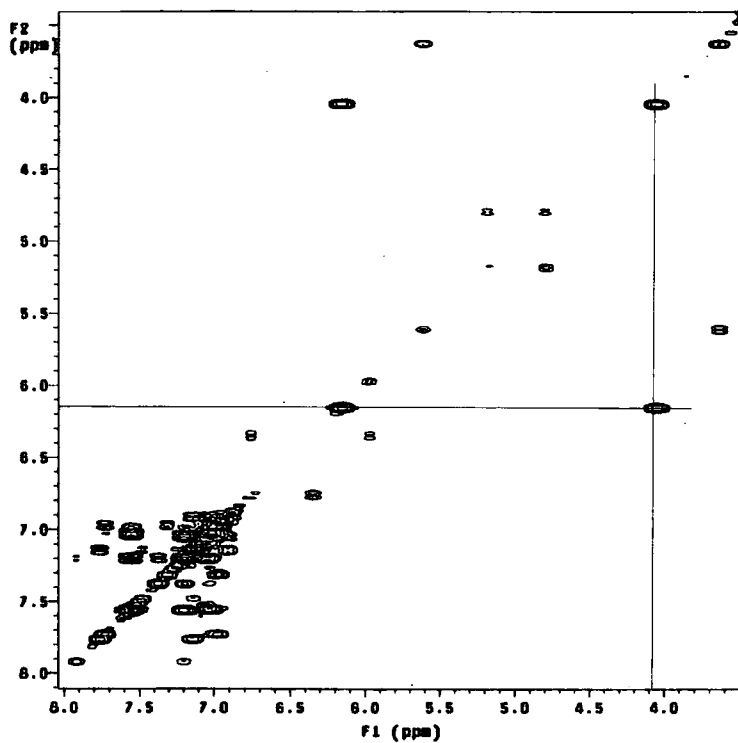


Fig 3.28:  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of 7b

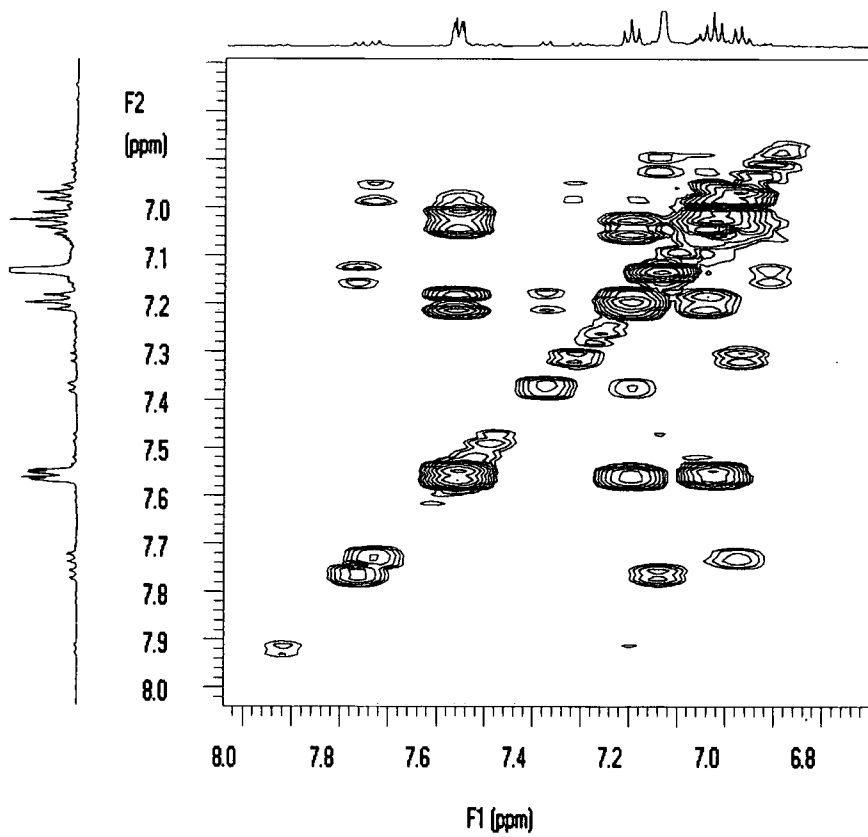


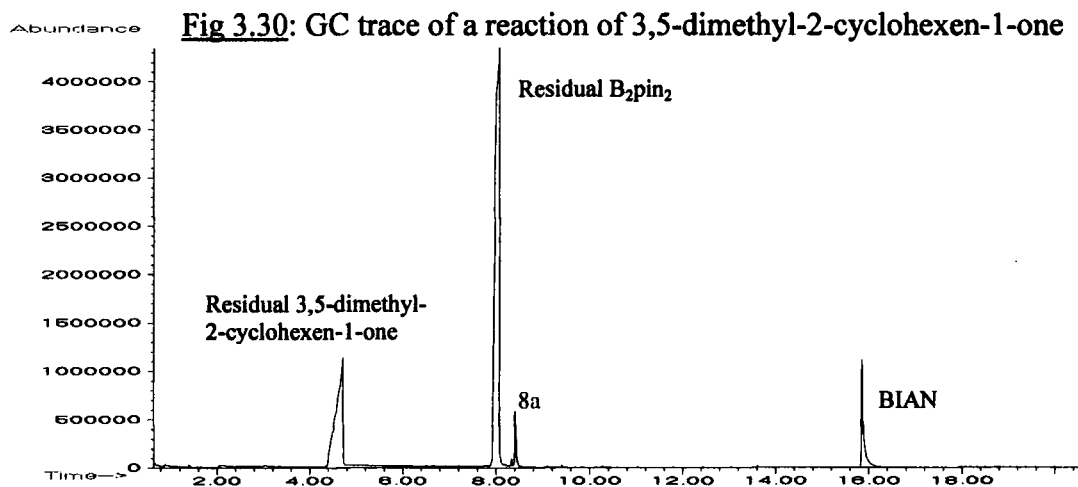
Fig 3.29:  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of 7b. 6.8-8.0 ppm

<u>Peak/ppm</u>	<u>Correlation with</u>	<u>Pattern and Coupling Constant / Hz</u>	<u>Position</u>
4.05	6.16, 7.56 (not visible above)	d, 8.5	-CHBpin-
6.16	4.05	d, 8.5	-CH=
6.97	7.14	t, 7.0	=C(OBpin)- <i>p</i> -C <sub>6</sub> H <sub>5</sub>
7.03	7.20, 7.56	m	<i>m</i> -C <sub>6</sub> H <sub>5</sub> -CHBpin
7.14	6.97, 7.75	unknown as masked by solvent peak	=C(OBpin)- <i>m</i> -C <sub>6</sub> H <sub>5</sub>
7.20	7.03, 7.56	t, 7.0	<i>p</i> -C <sub>6</sub> H <sub>5</sub> -CHBpin
7.56	4.05, 7.03, 7.20	dd, 7.0, 1.5	<i>o</i> -C <sub>6</sub> H <sub>5</sub> -CHBpin
7.75	7.14	m	=C(OBpin)- <i>o</i> -C <sub>6</sub> H <sub>5</sub>

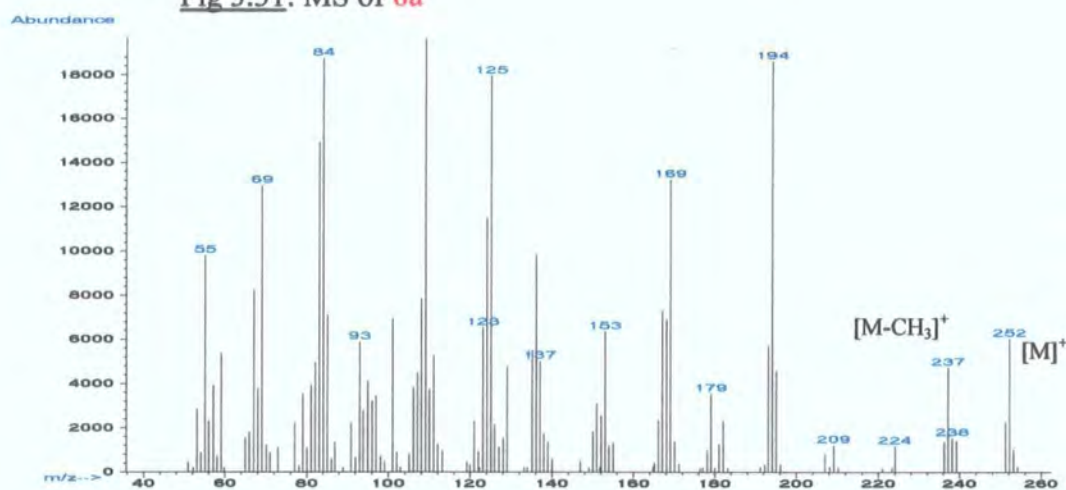
The C<sub>6</sub>H<sub>5</sub> ring attached to the CHBpin group was identified using the 2D NMR spectrum. The other phenyl group was identified using remaining peaks in the correct region of the spectrum with correct integrations.

### 3.6. 3,5-Dimethyl-2-cyclohexen-1-one

GC-MS identified in each reaction with this substrate the hydrolysed 1,4-diborated product 8a (fig 3.30 and 3.31).



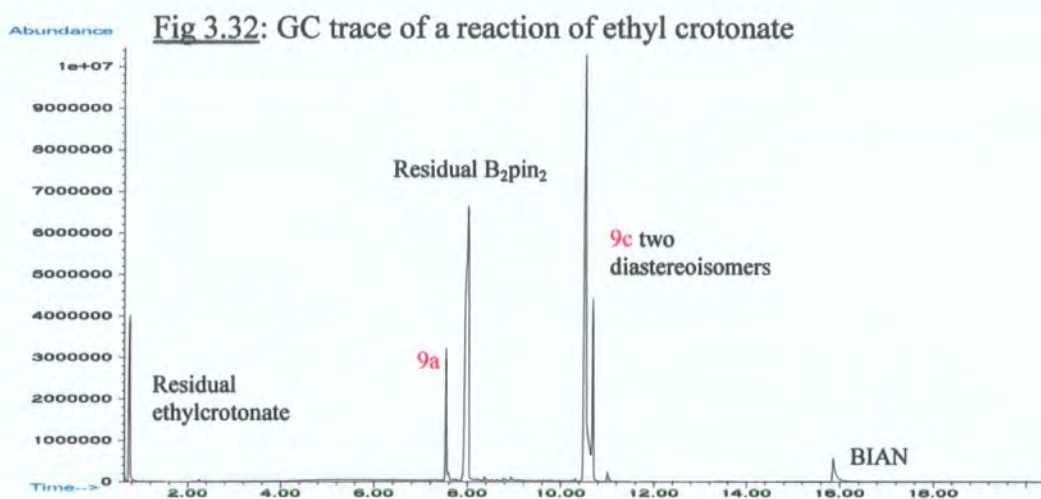
**Fig 3.31: MS of 8a**

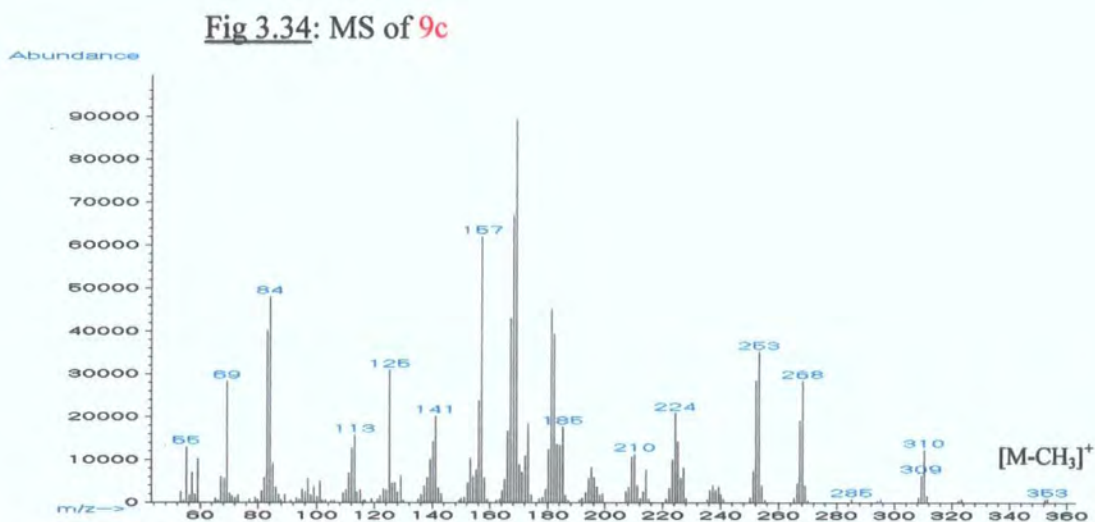
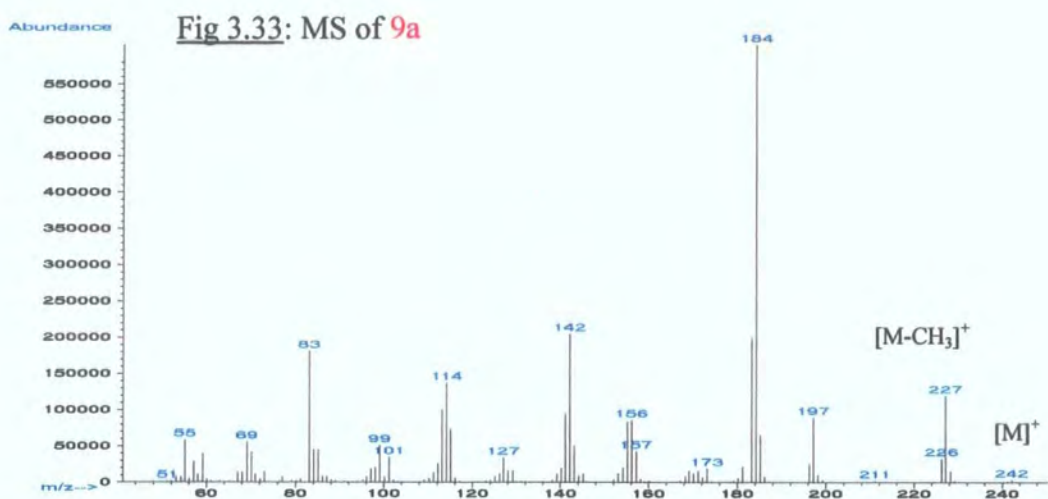


Due to the slow rate of reaction it was not possible to identify the product by NMR spectroscopy as only starting material could be observed by *in situ* NMR experiments.

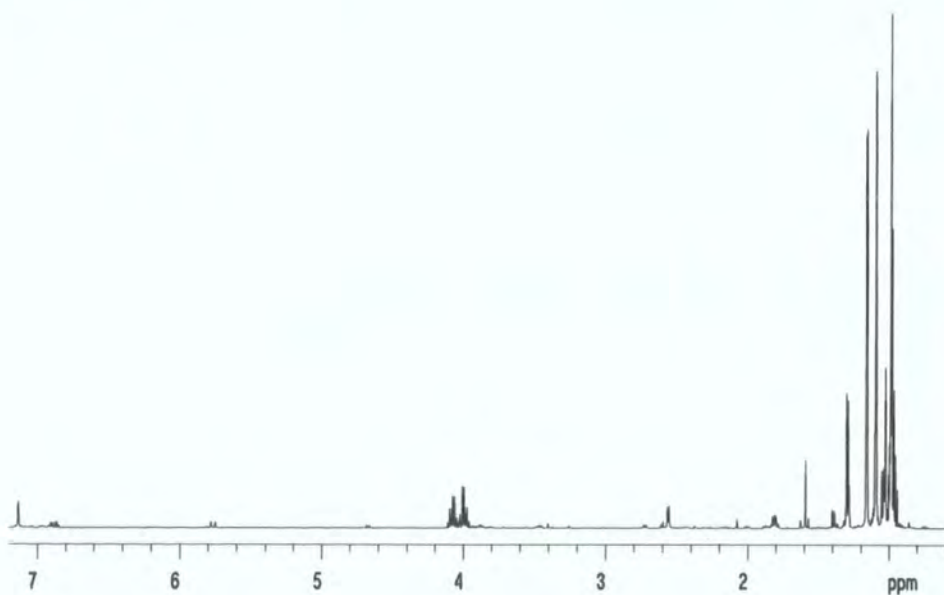
### 3.7. Ethylcrotonate

GC-MS identified in each reaction with this substrate both the hydrolysed 1,4-diborated product **9a** and the 1,2-diborated product **9c** (fig 3.32, 3.33 and 3.34).

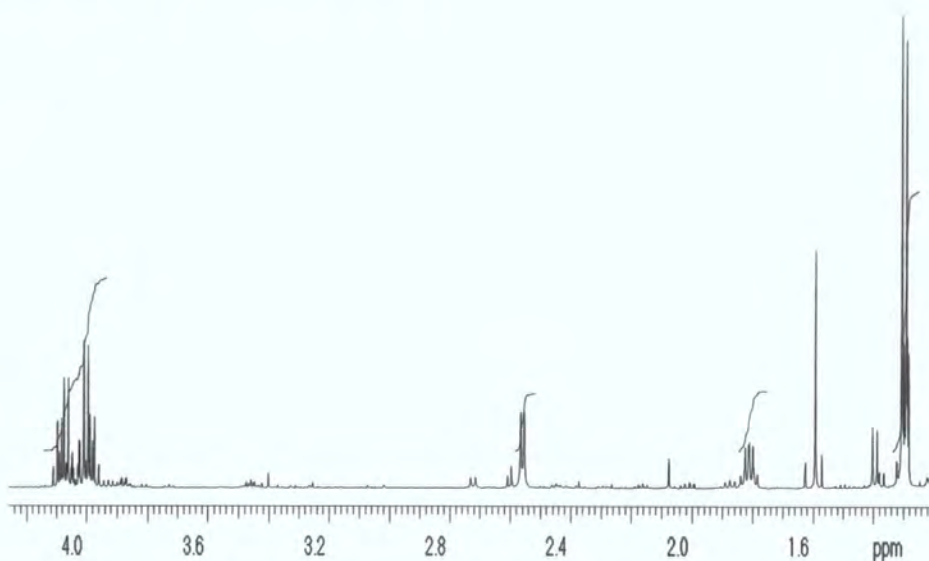




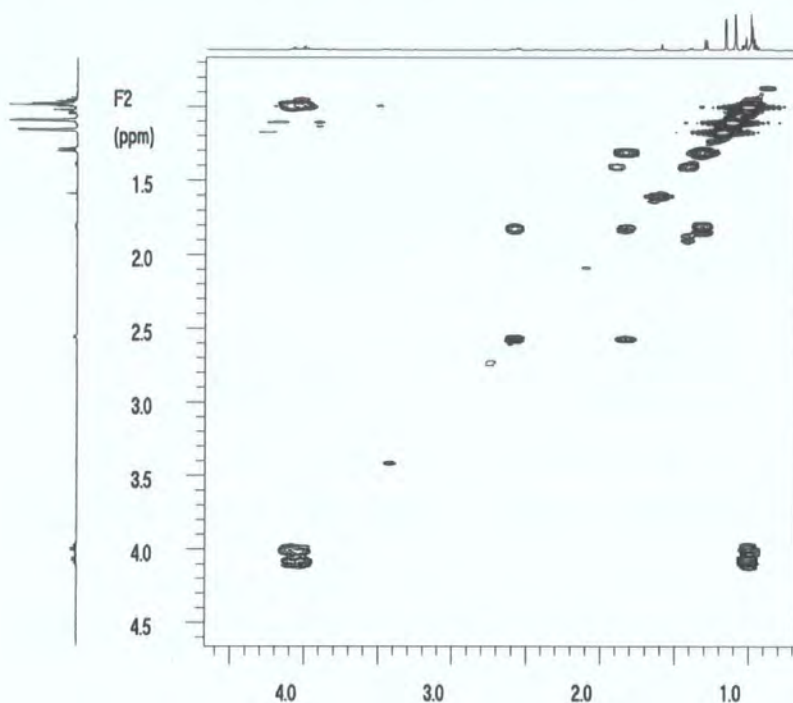
**Fig 3.35: <sup>1</sup>H NMR of 9c.**



**Fig 3.36:**  $^1\text{H}$  NMR of **9c**. 1.2 – 4.2 ppm.



**Fig 3.37:**  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of **9c**. 1.2 – 4.6 ppm



In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown above (fig 3.35, 3.36 and 3.37) with the peaks and correlations shown the Table 3.8. The 1,2-diborated product was identified. There was also some residual starting material. The AB doublet of quartets arises due to the chiral centre  $\alpha$  to the carbonyl group which makes the two H's of the  $\text{CH}_2$  group inequivalent.

<b>Table 3.8: <math>^1\text{H}</math> NMR of 9c</b>			
<b>Peak/ppm</b>	<b>Correlation with</b>	<b>Pattern and Coupling Constant / Hz</b>	<b>Position</b>
1.04	4.06	Obscured by Bpin peaks	$\text{CH}_2\text{-CH}_3$
1.32	1.83	d, 7.5	$\text{CH}_3\text{-CHBpin}$
1.83	1.32, 2.58	dq, 7.5, 5.5	$\text{CH}_3\text{-CHBpin-CHBpin}$
2.58	1.83	d, 5.9	$\text{CHBpin-CHBpin-C=O}$
4.06	1.04	AB, dq	$\text{-CH}_2\text{-CH}_3$

### 3.8. Methylcinnamate

GC-MS identified in each reaction with this substrate the hydrolysed 1,4-diborated product 10a (fig 3.38 and 3.39).

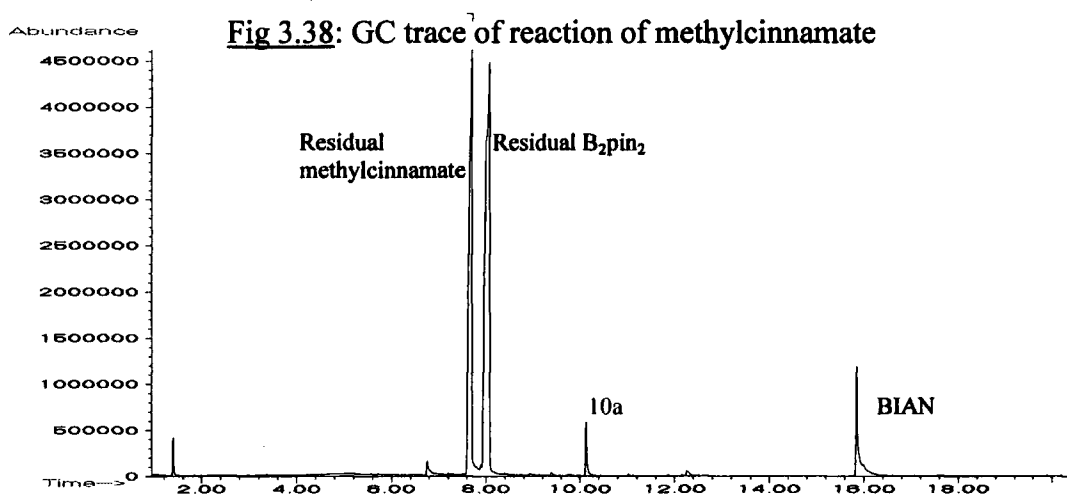
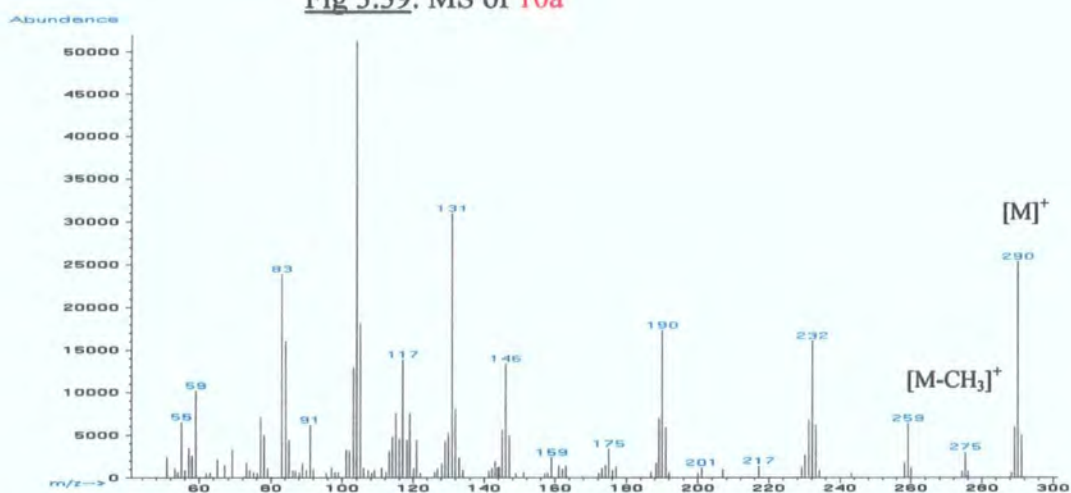


Fig 3.39: MS of 10a

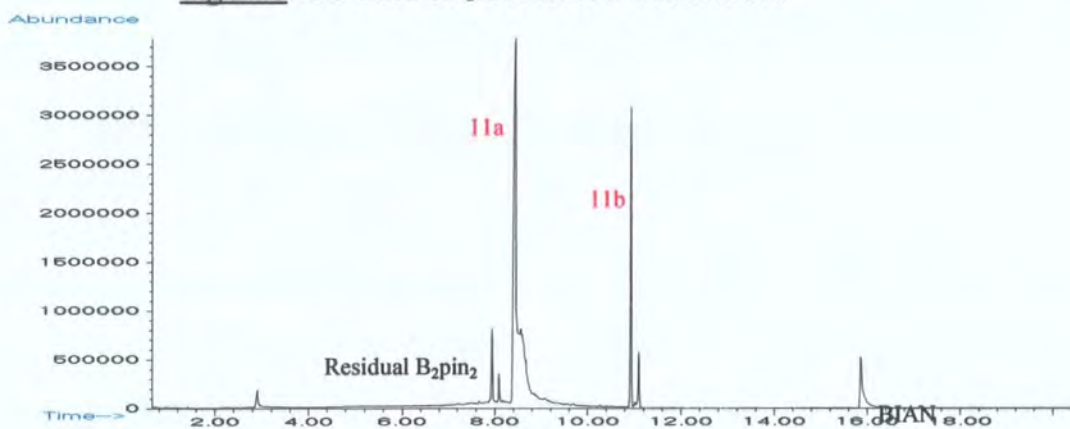


Due to the slow rate of reaction it was not possible to identify the product by NMR spectroscopy as only starting material could be observed by *in situ* NMR experiments.

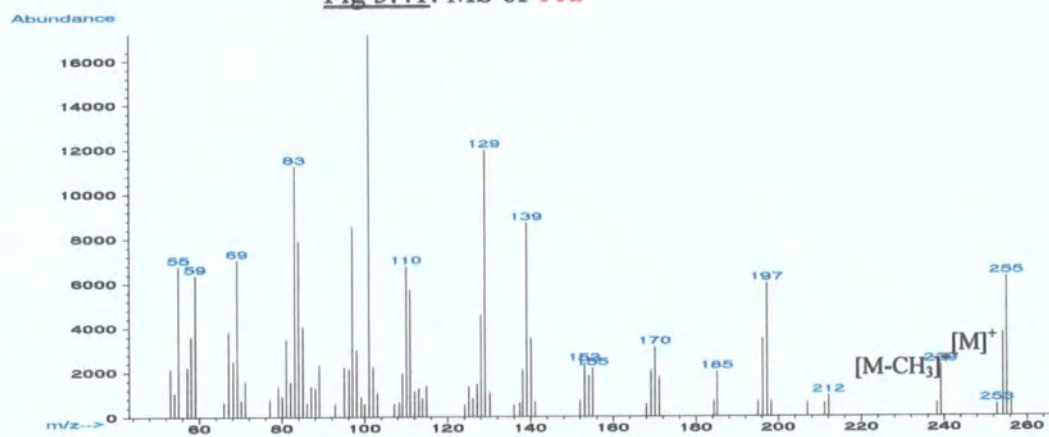
### 3.9. 3-Octen-2-one

GC-MS identified in each reaction with this substrate both the hydrolysed 1,4-diborated product **11a** and the diborated product **11b** (fig 3.40, 3.41 and 3.42).

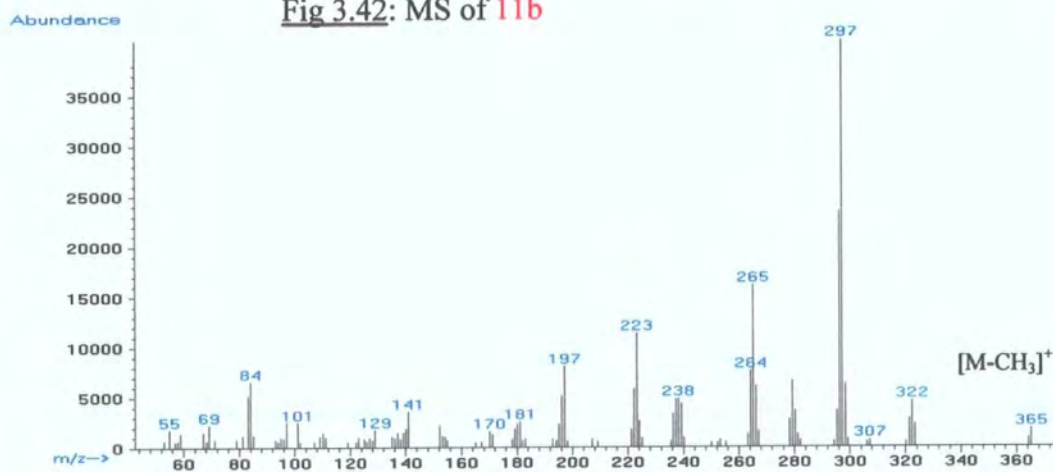
Fig 3.40: GC trace of reaction of 3-octen-2-one



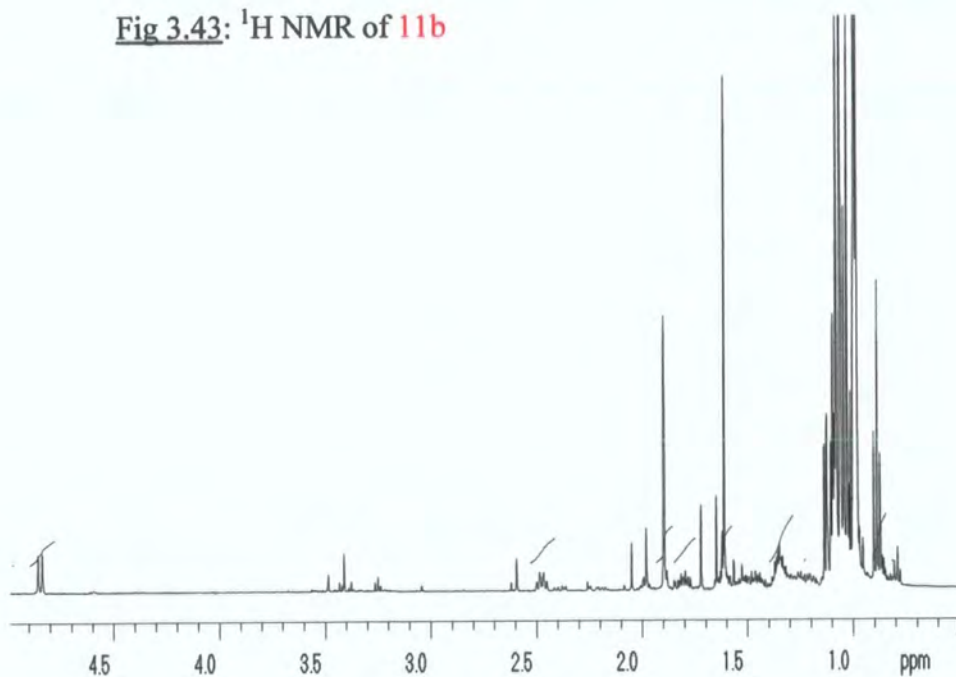
**Fig 3.41: MS of 11a**



**Fig 3.42: MS of 11b**



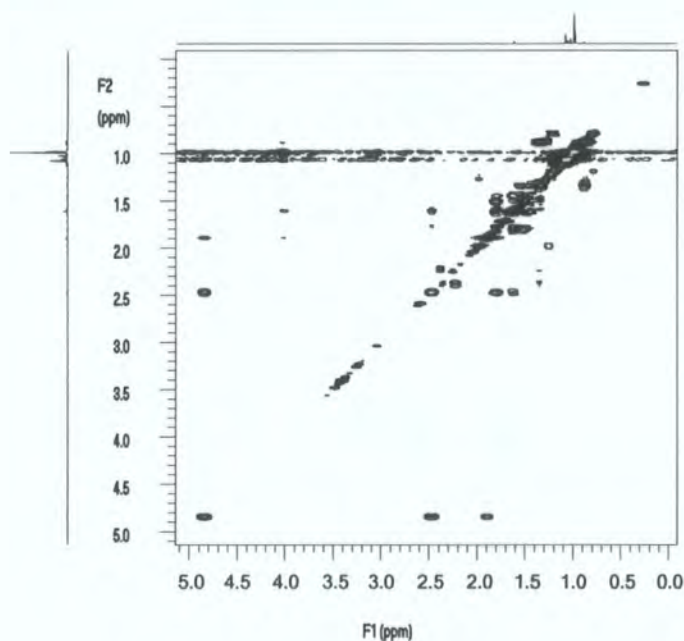
**Fig 3.43: <sup>1</sup>H NMR of 11b**



In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown (fig 3.43 and 3.44) with the peaks and correlations shown in Table 3.9. Only one 1,4-diborated product, **11b**, was identified. The isomer is unknown and both possibilities are plausible as the most stable structure.

Peak/ppm	Correlation with	Pattern and Coupling Constant / Hz	Position
0.89	1.34	t, 7.2	$\text{CH}_3\text{-CH}_2$
1.34	0.89, 1.62	m	$\text{CH}_3\text{-CH}_2\text{-}$
1.62	1.34, 1.81, 2.48	m	$\text{CH}_2\text{-CH}_2\text{-CH}_2$
1.81	1.62, 2.48	m	$\text{-CH}_2\text{-CHBpin}$
1.90	4.85	s	$\text{C(OBpin)-CH}_3$
2.48	1.62, 1.81, 4.85	q (dt), 8.2	$\text{-CHBpin-}$
4.85	1.90, 2.48	d, 9.5	$\text{-CH=}$

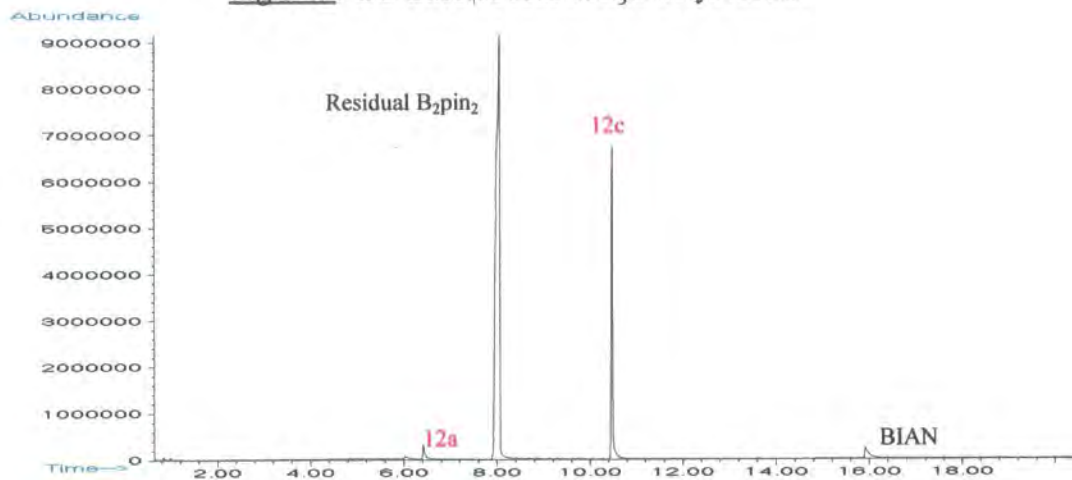
Fig 3.44:  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of **11b**



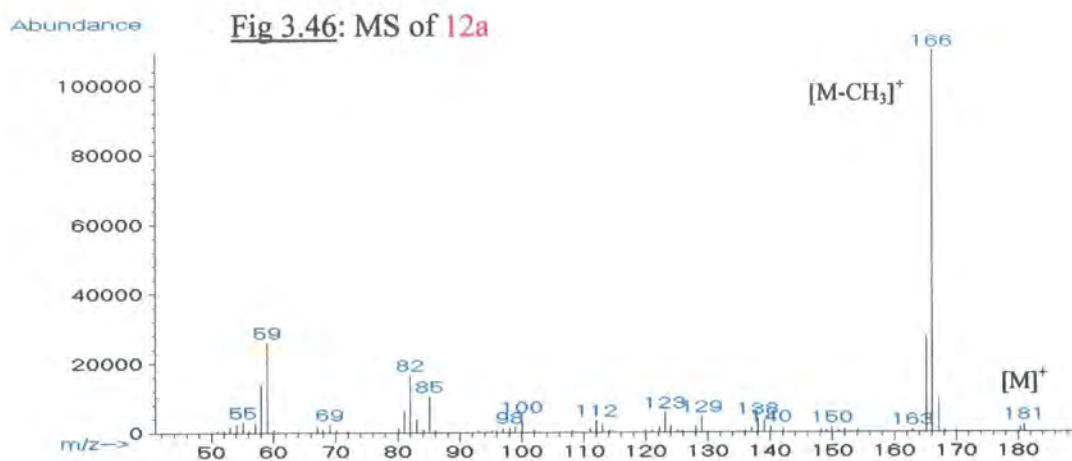
### 3.10. Acrylonitrile

GC-MS identified in each reaction with this substrate both the hydrolysed 1,4-diborated product **12a** and the diborated product **12c** (fig 3.45, 3.46 and 3.47).

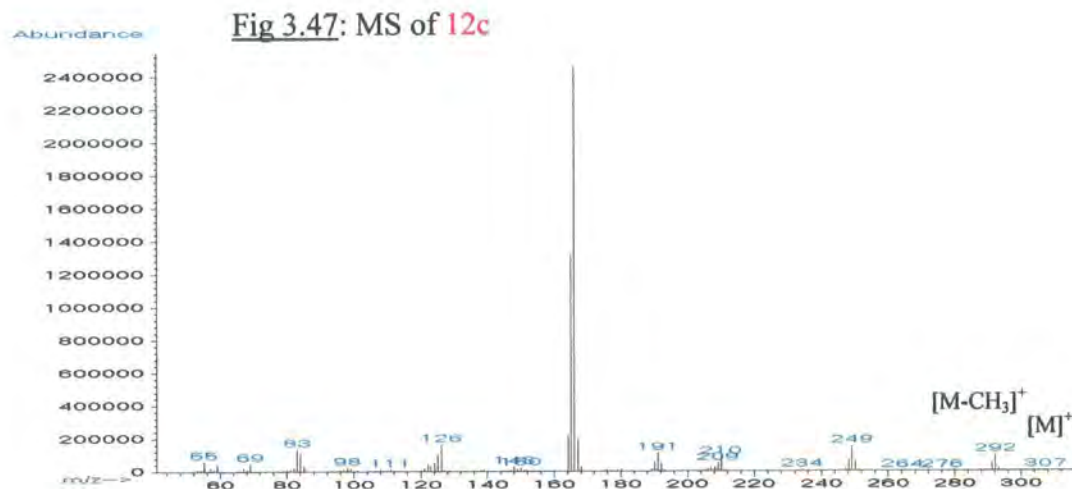
**Fig 3.45:** GC trace of reaction of acrylonitrile



**Fig 3.46:** MS of **12a**



**Fig 3.47:** MS of **12c**



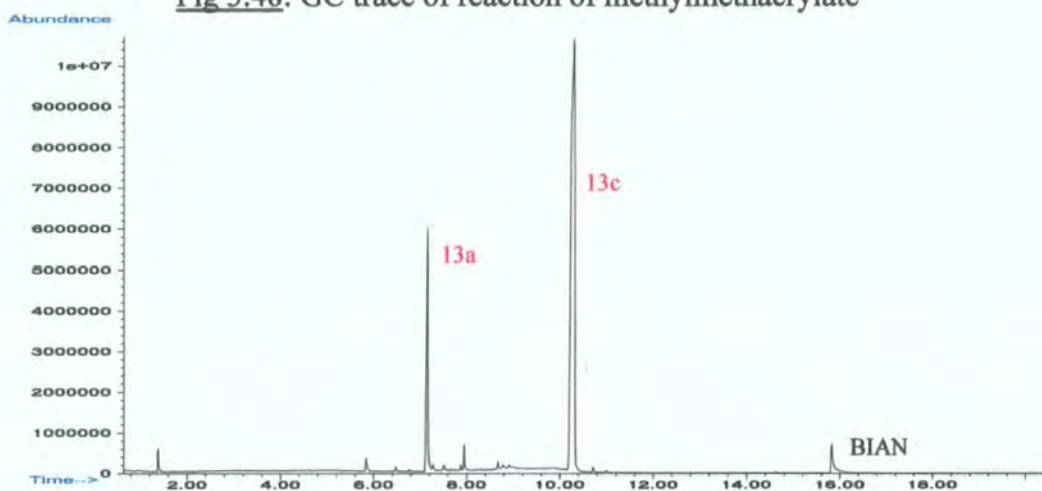
Owing to the slow rate of reaction it was not possible to identify the product by NMR spectroscopy as only starting material could be observed by *in situ* NMR experiments.

By analogy with other  $\alpha,\beta$ -unsaturated carbonyl compounds with electron-withdrawing groups attached to the carbonyl carbon it is suggested that the product **12c** is the 1,2-diborated product. Also, in the case of the possible 1,4-diborated product, **12b**, the structure is highly unusual and likely to be unstable.

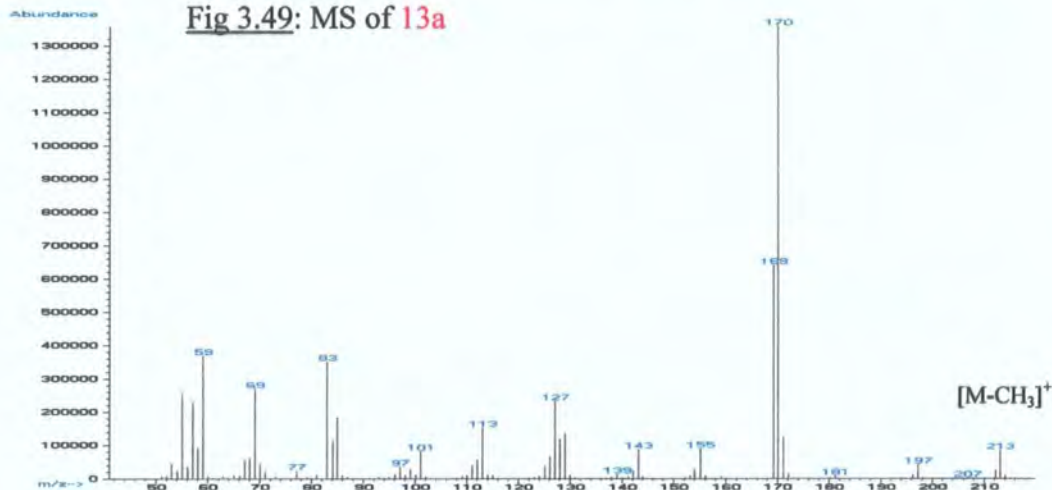
### 3.11. Methylmethacrylate

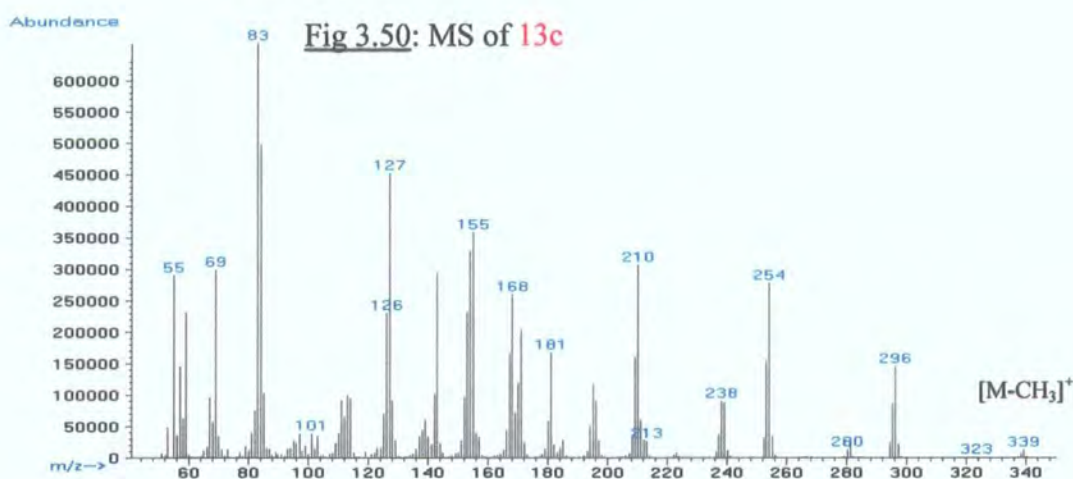
GC-MS identified in each reaction with this substrate both the hydrolysed 1,4-diborated product **13a** and the diborated product **13c** (fig 3.48, 3.49 and 3.50).

**Fig 3.48:** GC trace of reaction of methylmethacrylate



**Fig 3.49:** MS of **13a**



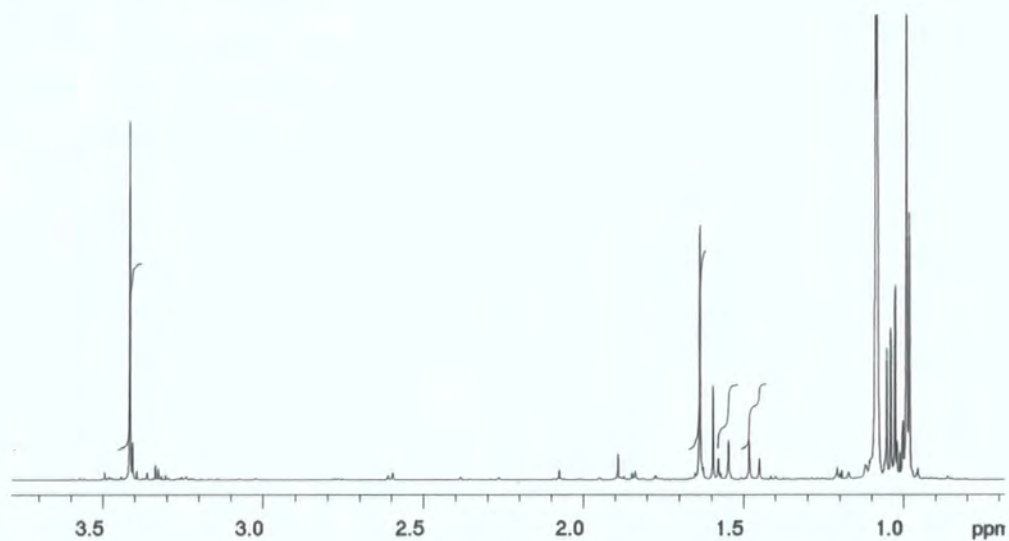


In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown below (fig 3.51 and 3.52) with the peaks and correlations shown in table 3.10. The 1,2-diborated product, **13c**, was identified. An AB doublet of doublets is observed for the  $\text{CH}_2\text{Bpin}$  group due to the adjacent chiral centre.

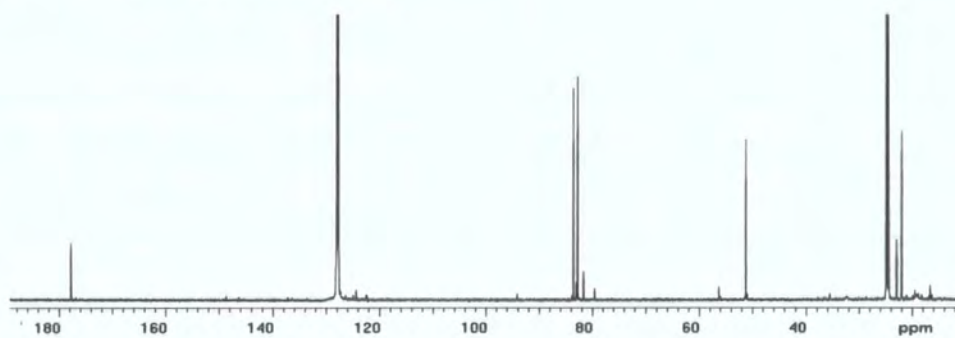
Table 3.10: NMR of **13c**

$^1\text{H}$ :			
Peak/ppm	Pattern and Coupling Constant / Hz	Correlation	Position
1.52	AB, dd	23.01	$\text{CH}_2\text{Bpin}$ -
1.64	s	22.03	$\text{CH}_3\text{-C(Bpin)(CH}_2\text{Bpin)-}$
3.42	s	51.27	$\text{CH}_3\text{-O}$
$^{13}\text{C}$ :			
22.03		1.64	$\text{CH}_3\text{-C(Bpin)(CH}_2\text{Bpin)-}$
23.01		1.52	$\text{CH}_2\text{Bpin}$ -
32	Broad	-	$(\text{CH}_3)(\text{CH}_2\text{Bpin)C(Bpin)-}$
51.25		3.42	$\text{CH}_3\text{-O}$
177.81		-	$\text{-C(=O)-}$

**Fig 3.51:**  $^1\text{H}$  NMR spectrum of **13c**.



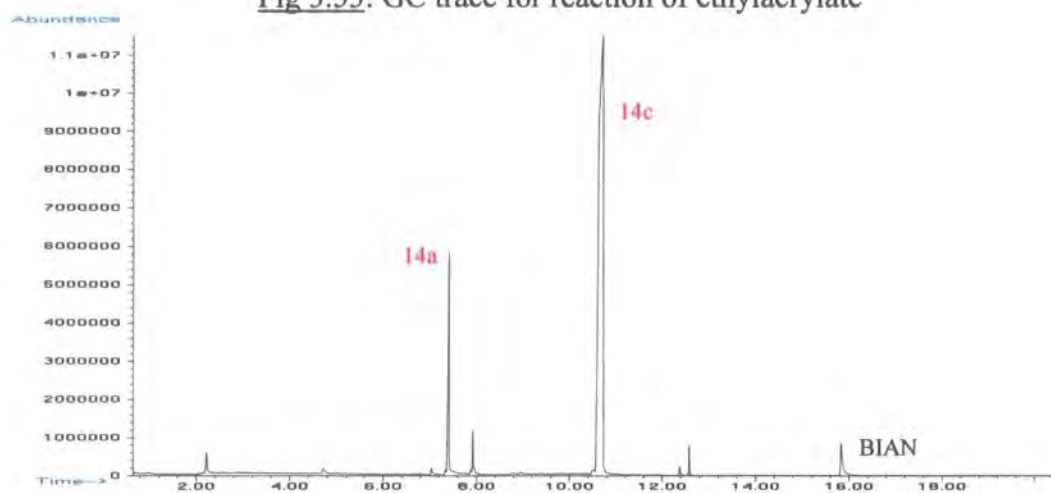
**Fig 3.52:**  $^{13}\text{C}$  NMR spectrum of **13c**.



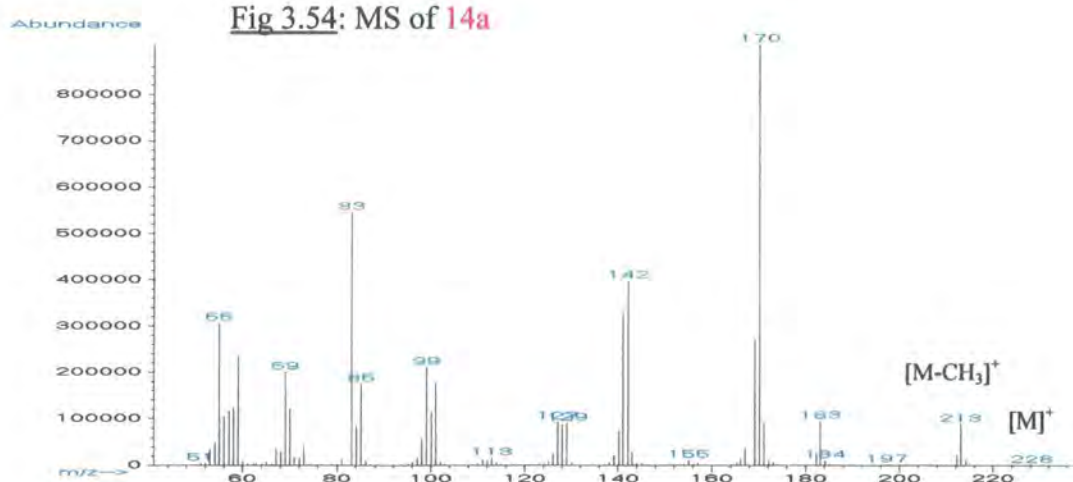
### 3.12. Ethylacrylate

GC-MS identified in each reaction with this substrate both the hydrolysed 1,4-diborated product **14a** and the diborated product **14c** (fig 3.53, 3.54 and 3.55).

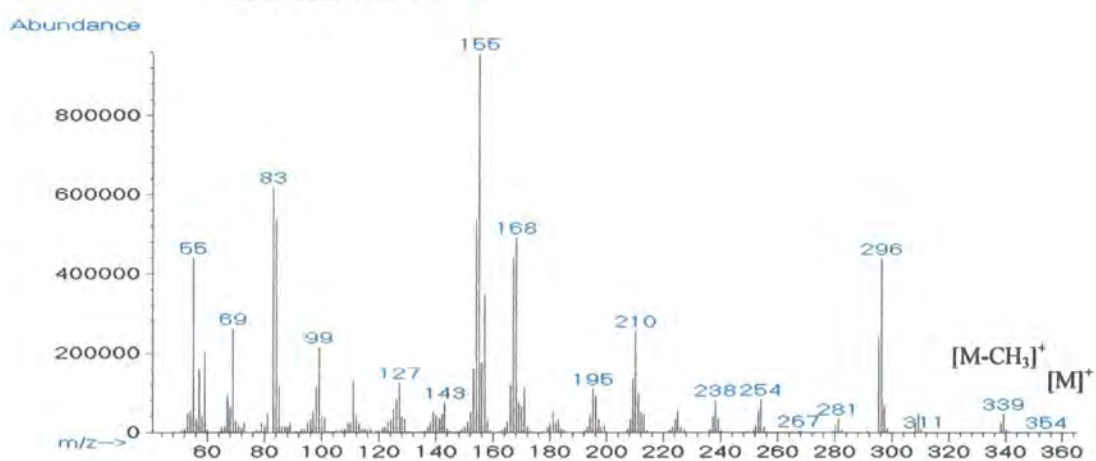
**Fig 3.53:** GC trace for reaction of ethylacrylate



**Fig 3.54:** MS of 14a



**Fig 3.55:** MS of 14c



In order to identify the product by NMR 1D  $^1\text{H}$  NMR, and 2D  $^1\text{H}$ - $^1\text{H}$  NMR were necessary. Spectra are shown below (fig 3.56, 3.57 and 3.58) with the peaks and correlations shown in the table. The 1,2-diborated product, **14c**, was identified. Again an AB pattern was observed for the  $\text{CH}_2\text{Bpin}$  group due to the adjacent chiral centre and also an AB pattern was observed for the  $\text{CH}_2$  of the ethyl group. There is also some residual starting material present.

Fig 3.56:  $^1\text{H}$  NMR spectrum of **14c**

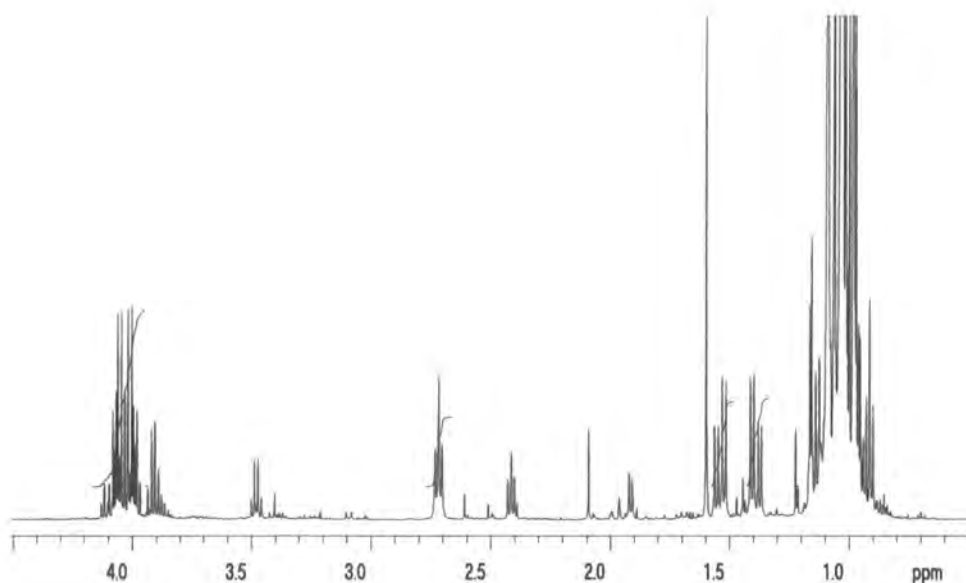


Fig 3.57:  $^1\text{H}$  NMR spectrum of **14c**. 3.80 – 4.15 ppm

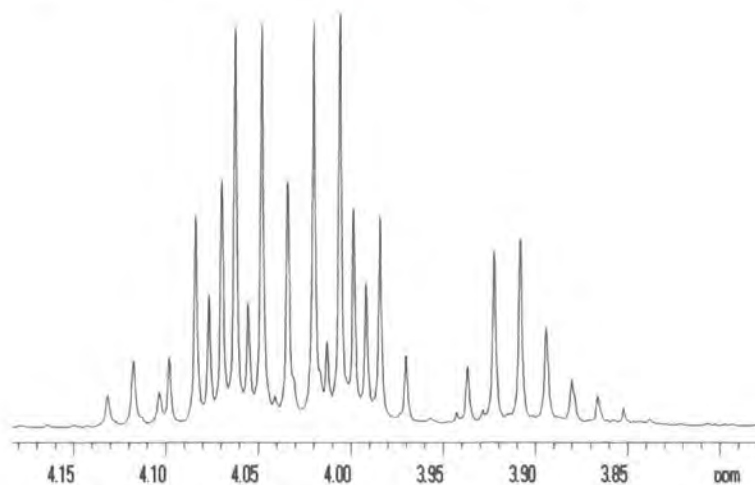


Fig 3.58:  $^1\text{H}$ - $^1\text{H}$  NMR spectrum of **14c**.

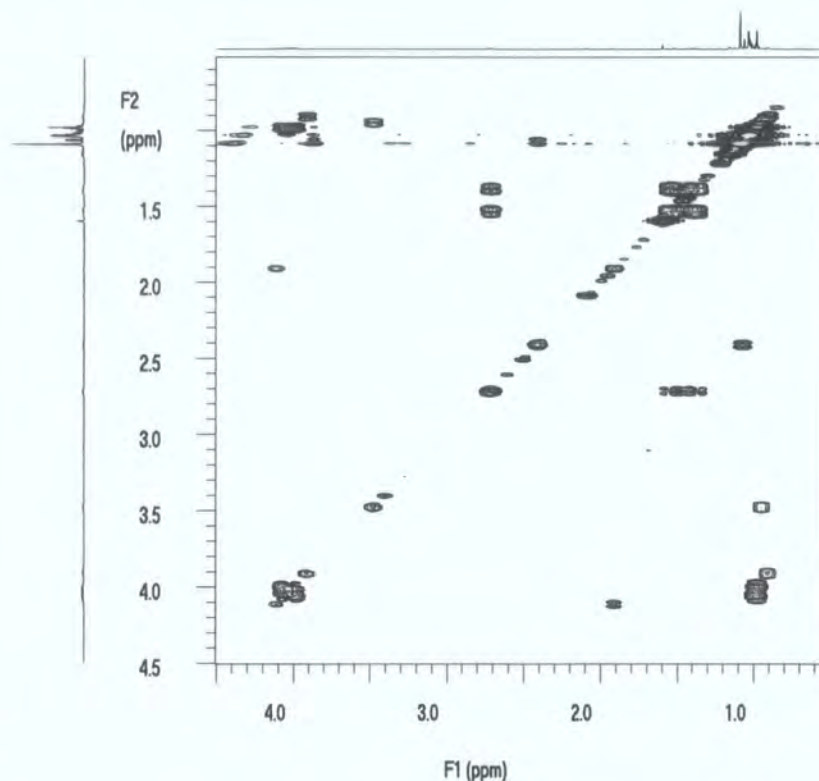


Table 3.11:  $^1\text{H}$  NMR of **14c**

Peak/ppm	Correlation with	Pattern and Coupling Constant / Hz	Position
0.99	4.03	t, 7.0	$\text{CH}_3\text{-CH}_2$
1.47	2.72	AB, dd	$\text{CH}_2\text{Bpin-}$
2.72	1.47	t, 7.5	$\text{-CHBpin-}$
4.03	0.99	AB, dq	$\text{CH}_3\text{-CH}_2\text{-O}$

### 3.13. Conclusion

Two different diborated products are observed, the position of diboration being dependant upon the electronics of the starting material. The 1,2-diborated product is formed when the  $\alpha,\beta$ -unsaturated carbonyl compounds are electron poor such as esters or nitriles. For other substrates, such as ketones and aldehydes, the 1,4-diborated product is formed.

The GC-MS observations are such because hydrolysis takes place either in the GC vials or during the injection process. It may well be that this is more likely to happen in THF as it is miscible with water and thus traces of water will react faster with products in this solvent. This process will therefore not occur in the NMR samples and so the hydrolysed 1,4-diborated products are not observed by NMR.

For reactions that give 1,2-diborated products the 1,4-diborated products are not detected in the  $^1\text{H}$  NMR spectrum. This is either because they are too small to be observed or because 1,4-diaddition does not occur in non-polar solvents such as benzene which the NMR was carried out in, whereas it does occur in THF which was the solvent used for the GC's.

## 4. Conclusion

An improved catalyst for the diboration of  $\alpha,\beta$ -unsaturated carbonyl compounds has been investigated using other diboration catalysts as a starting point. Initially  $\text{Pt}(\text{NBE})_3$  in conjunction with a variety of phosphines was investigated as a catalyst. Certain phosphines in conjunction with this platinum species were catalytically active, but no great improvement on previously reported catalysts was found.

$\text{Pt}(\text{BIAN})(\text{fum})$ , a diimine platinum(0) complex was then tested as a catalyst for the reaction and it was found to give improved activity over other catalysts at room temperature and in low catalyst concentrations. The position of diboration was found to be highly dependant upon the electronic properties of the  $\alpha,\beta$ -unsaturated carbonyl compound as those with electron withdrawing groups (i.e. esters) were found to give 1,2-diboration (i.e. the alkene C=C bond was diborated) whereas aldehydes and ketones gave 1,4 diboration products.

This catalyst suggests a new family of complexes to be investigated for their catalytic properties in diboration reactions. No optimisation has been attempted with this catalyst system and with optimisation, for which there are many possibilities, rates of reaction could potentially be significantly improved from those reported here.

## 5. Experimental

All reactions were performed under an atmosphere of dry nitrogen, in a double length glovebox (Innovative Technology Inc., System One) or in sealed GC autosampler vials which were prepared in the glovebox. Solvents were distilled under nitrogen prior to use from sodium/benzophenone (THF), calcium hydride ( $C_6D_6$ ), or dried and deoxygenated using a modified Innovative Technology Inc. SPS-solvent purification system containing activated alumina followed by an activated BASF R311 copper catalyst under argon pressure (toluene), similar to that described by Grubbs and co-workers.<sup>1</sup>

NMR spectra were recorded on Unity 300 ( $^{11}B$ ) and Inova 500 ( $^1H$ ,  $^{13}C$ ) spectrometers at the following frequencies:  $^1H$  (499.90 MHz),  $^{13}C$  (125.70 MHz),  $^{11}B$  (96.22 MHz).  $^1H$  and  $^{13}C$  were referenced to residual solvent resonances and  $^{11}B$  to an external standard ( $BF_3 \cdot OEt_2$ ). All spectra were recorded as solutions in  $C_6D_6$ . Chemical shifts are reported in ppm and coupling constants in Hz.

GC-MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5971A mass selective detector and a 7673 autosampler using a fused silica capillary column (10 m cross-linked 5 % methylphenylsilicone). The oven temperature was ramped from 70 to 270 °C at a rate of 20 °Cmin<sup>-1</sup> for experiments 1, 2 and 7 and ramped from 50 to 280 °C at a rate of 20 °Cmin<sup>-1</sup> for all other experiments. UHP grade helium was used as the carrier gas. Screw-cap autosampler vials were used, supplied by Thermoquest fitted with teflon/silicone/teflon septa and 0.25 ml micro-inserts.

The following compounds were obtained commercially: *bis*-pinacolatodiboron – Frontier Scientific; methylvinyl ketone, 2-cyclohexen-1-one, *trans*-4-phenylbut-3-en-2-one, PCy<sub>3</sub> – Aldrich; chalcone, 3,5-dimethyl-2-cyclohexen-1-one, 3-octen-2-one, methylcinnamate, ethylcrotonate, dimethylfumarate, *trans*-cinnamaldehyde – Avocado;  $C_6D_6$  – Apollo; dppm, dppe, dppp, dppb, dcpe, dppf – Strem.

The compounds  $[\text{Pt}(\text{NBE})_3]^2$  (prepared by R. L. Thomas),  $[\text{Pt}(\text{dba})_2]^3$  and  $[\text{Pt}(\text{bian})(\text{fum})]^4$  (obtained from C. J. Elsevier at the University of Amsterdam) were prepared by literature methods.

The purity of all compounds was checked prior to use by either GC-MS or NMR spectroscopy and purification as necessary was either by recrystallisation or by freeze-pump-thaw followed by trap-to-trap distillation from calcium hydride under vacuum.

Stock solutions of catalyst and  $\text{B}_2\text{pin}_2$  were made up to ensure that concentrations were constant for a given experiment and also so that concentrations were more accurate.

These solutions were used immediately to prevent any problems occurring due to instability of compounds in solution.

General Reaction procedure:

In the glovebox, catalyst (5  $\mu\text{mol}$ , 5 mol%) and  $\text{B}_2\text{pin}_2$  (27.93 mg, 0.11 mmol) were dissolved in solvent (2 ml). Substrate (0.1 mmol) was added and the reaction mixture was stirred at room temperature and monitored by GC-MS\* after set times.

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\* In all reactions involving  $\text{Pt}(\text{NBE})_3$ , as well as the reported products,  $\text{NBE}(\text{Bpin})_2$  and  $\text{NBE}(\text{H})(\text{Bpin})$  were also detectable.

## 5.1. Reactions using Pt(NBE)<sub>3</sub> as catalyst in the absence of added phosphine.

### a. MVK

To a beige solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in toluene (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred for 2 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 1.25 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: 197 M<sup>+</sup>-H, 183 M<sup>+</sup>-Me.

### b. CHE

To a beige solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in toluene (2 ml) was added CHE (9.68 μl, 0.1 mmol). The reaction was stirred for 19 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19 h GC-MS analysis indicated that reaction was 1 % complete relative to residual B<sub>2</sub>pin<sub>2</sub> and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS: M<sup>+</sup> 224, M<sup>+</sup>-Me 209.

### c. TCA

To a beige solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in toluene (2 ml) was added TCA (12.62 μl, 0.1 mmol). The reaction was stirred for 19.5 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19.5 h GC-MS analysis indicated that reaction was 17 % complete relative to residual TCA and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS: M<sup>+</sup>-Me 245.

#### **d. BEO**

To a beige solution of  $\text{Pt}(\text{NBE})_3$  (2.86 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in toluene (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 20 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 20 h GC-MS analysis indicated that reaction was 38 % complete relative to residual BEO and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS:  $\text{M}^+$ -Me 259.

### **5.2. Reactions using $\text{Pt}(\text{NBE})_3/\text{PCy}_3$ as catalyst.**

#### **a. MVK**

To a beige solution of  $\text{Pt}(\text{NBE})_3$  (2.86 mg, 5  $\mu\text{mol}$ ),  $\text{PCy}_3$  (1.40 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in toluene (2 ml) was added MVK (8.32  $\mu\text{l}$ , 0.1 mmol). The reaction was stirred for 16 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 16 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: 197  $\text{M}^+$ -H, 183  $\text{M}^+$ -Me.

#### **b. CHE**

To a beige solution of  $\text{Pt}(\text{NBE})_3$  (2.86 mg, 5  $\mu\text{mol}$ ),  $\text{PCy}_3$  (1.40 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in toluene (2 ml) was added CHE (9.68  $\mu\text{l}$ , 0.1 mmol). The reaction was stirred for 16.5 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 16.5 h GC-MS analysis indicated that reaction was 77 % complete relative to residual CHE and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS:  $\text{M}^+$  224,  $\text{M}^+$ -Me 209.

### c. TCA

To a beige solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), PCy<sub>3</sub> (1.40 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in toluene (2 ml) was added TCA (12.62 μl, 0.1 mmol). The reaction was stirred for 16.5 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 16.5 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS: M<sup>+</sup>-Me 245.

### d. BEO

To a beige solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), PCy<sub>3</sub> (1.40 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in toluene (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 17.5 h resulting in a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 17.5 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup> 274, M<sup>+</sup>-Me 259.

## 5.3. Reactions using Pt(NBE)<sub>3</sub>/dppm as catalyst.

### a. MVK

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppm (1.92 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred for 19 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19 h GC-MS analysis indicated that reaction was 9 % complete relative to residual B<sub>2</sub>pin<sub>2</sub> and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: M<sup>+</sup>-H 197, M<sup>+</sup>-Me 183.

#### **b. CHE**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppm (1.92 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68 μl, 0.1 mmol). The reaction was stirred for 19.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19.5 h GC-MS analysis indicated that the reaction was less than 1 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS: M<sup>+</sup> 224, M<sup>+</sup>-Me 209.

#### **c. TCA**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppm (1.92 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62 μl, 0.1 mmol). The reaction was stirred for 20 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 20 h GC-MS analysis indicated that reaction was 1 % complete relative to residual TCA and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS: M<sup>+</sup>-Me 245.

#### **d. BEO**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppm (1.92 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 20.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 20.5 h GC-MS analysis indicated that reaction was 3 % complete relative to residual BEO and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup>-Me 259.

## 5.4. Reactions using Pt(NBE)<sub>3</sub>/dppe as catalyst.

### a. MVK

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppe (1.99 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred for 40 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 40 h GC-MS analysis indicated that reaction was 3 % complete relative to residual B<sub>2</sub>pin<sub>2</sub> and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: M<sup>+</sup>-Me 183.

### b. CHE

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppe (1.99 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68 μl, 0.1 mmol). The reaction was stirred for 40.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 40.5 h GC-MS analysis indicated that the reaction was 2 % complete relative to residual CHE and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS: M<sup>+</sup> 224, M<sup>+</sup>-Me 209.

### c. TCA

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppe (1.99 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62 μl, 0.1 mmol). The reaction was stirred for 41 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 41 h GC-MS analysis indicated that reaction was 6 % complete relative to residual TCA and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS: M<sup>+</sup>-Me 245.

#### **d. BEO**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppe (1.99 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 41.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 41.5 h GC-MS analysis indicated that reaction was 67 % complete relative to residual BEO and peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup> 274, M<sup>+</sup>-Me 259.

### **5.5. Reactions using Pt(NBE)<sub>3</sub>/dppp as catalyst.**

#### **a. MVK**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppp (2.06 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred for 18 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 18 h GC-MS analysis indicated that reaction was less than 1 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: M<sup>+</sup>-Me 183.

#### **b. CHE**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppp (2.06 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68 μl, 0.1 mmol). The reaction was stirred for 18.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 18.5 h GC-MS analysis indicated that the reaction was less than 1 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS: M<sup>+</sup> 224, M<sup>+</sup>-Me 209.

### c. TCA

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppp (2.06 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62 μl, 0.1 mmol). The reaction was stirred for 19 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19 h GC-MS analysis indicated that no reaction had occurred.

### d. BEO

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppp (2.06 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 19.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 19.5 h GC-MS analysis indicated that reaction was less than 1 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup>-Me 259.

## 5.6. Reactions using Pt(NBE)<sub>3</sub>/dppb as catalyst.

### a. MVK

To an orange/brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppb (2.13 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 1 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: M<sup>+</sup>-Me 183.

### b. CHE

To an orange/brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dppb (2.13 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68 μl, 0.1 mmol).

The reaction was stirred for 93 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 93 h GC-MS analysis indicated that the reaction was 26 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a, but also a peak was observed consistent with hydrogenated CHE, 16 %, with  $M^+$  98, relative to residual CHE. MS:  $M^+$  224,  $M^+$ -Me 209.

#### c. TCA

To an orange/ brown solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppb (2.13 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62  $\mu$ l, 0.1 mmol). The reaction was stirred for 93.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 93.5 h GC-MS analysis indicated that the reaction was 30 % complete relative to residual TCA. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS:  $M^+$ -H 259,  $M^+$ -Me 245.

#### d. BEO

To an orange/brown solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppb (2.13 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 94 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 94 h GC-MS analysis indicated that reaction was 68 % complete relative to residual BEO. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS:  $M^+$  274,  $M^+$ -Me 259.

### 5.7. Reactions using $Pt(NBE)_3$ /dppf as catalyst.

#### a. MVK

To a yellow solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppf (2.77 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32  $\mu$ l, 0.1 mmol). The

reaction was stirred giving a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 0.5 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS:  $M^+$  198,  $M^+$ -Me 183.

#### **b. CHE**

To a yellow solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppf (2.77 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68  $\mu$ l, 0.1 mmol). The reaction was stirred for 40 h giving a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 40 h GC-MS analysis indicated that the reaction was 4 % complete to residual  $B_2pin_2$ . Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 4a. MS:  $M^+$  224,  $M^+$ -Me 209.

#### **c. TCA**

To a yellow solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppf (2.77 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62  $\mu$ l, 0.1 mmol). The reaction was stirred for 70 h giving a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 70 h GC-MS analysis indicated that the reaction was 8 % complete relative to residual TCA. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS:  $M^+$ -Me 245.

#### **d. BEO**

To a yellow solution of  $Pt(NBE)_3$  (2.86 mg, 5  $\mu$ mol), dppf (2.77 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 40 h giving a brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After

40 h GC-MS analysis indicated that reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS:  $M^+$  274,  $M^+$ -Me 259.

### **5.8. Reactions using Pt(NBE)<sub>3</sub>/dcpe as catalyst.**

#### **a. MVK**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5  $\mu$ mol), dcpe (2.11 mg, 5  $\mu$ mol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32  $\mu$ l, 0.1 mmol). The reaction was stirred giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 45 h GC-MS analysis indicated that reaction was 4 % complete relative to residual B<sub>2</sub>pin<sub>2</sub>. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS:  $M^+$ -Me 183.

#### **b. CHE**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5  $\mu$ mol), dcpe (2.11 mg, 5  $\mu$ mol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68  $\mu$ l, 0.1 mmol). The reaction was stirred for 45 h and monitored by GC-MS. After 45 h GC-MS analysis indicated that no reaction had taken place.

#### **c. TCA**

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5  $\mu$ mol), dcpe (2.11 mg, 5  $\mu$ mol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62  $\mu$ l, 0.1 mmol). The reaction was stirred for 46 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 46 h GC-MS analysis indicated that the reaction was 24 % complete relative to residual TCA. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 5a. MS:  $M^+$ -Me 245.

#### d. BEO

To a brown solution of Pt(NBE)<sub>3</sub> (2.86 mg, 5 μmol), dcpe (2.11 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred for 46.5 h giving a dark brown solution. Aliquots (0.2 ml) were removed periodically, transferred to GC-MS autosampler vials and examined by GC-MS. After 46.5 h GC-MS analysis indicated that reaction was 54 % complete relative to residual BEO. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup> 274, M<sup>+</sup>-Me 259.

### 5.9. Reactions using Pt(BIAN)(fum) as catalyst

#### a. MVK

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added MVK (8.32 μl, 0.1 mmol). The reaction was stirred, giving a green solution which was monitored by GC-MS. GC-MS indicated that after 1 h reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 3a. MS: M<sup>+</sup> 198, M<sup>+</sup>-Me 183.

The same reaction was carried out in C<sub>6</sub>D<sub>6</sub> and product 3b was identified by <sup>1</sup>H NMR spectroscopy (1D and 2D).

NMR: <sup>1</sup>H δ 0.9-1.1 (m, CH<sub>3</sub> of Bpins), 1.88 (s, CH<sub>3</sub>C(OBpin)=CH-CH<sub>2</sub>Bpin), 1.94 (d, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, CH<sub>3</sub>C(OBpin)=CH-CH<sub>2</sub>Bpin), 4.96 (t, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, CH<sub>3</sub>C(OBpin)=CH-CH<sub>2</sub>Bpin).

#### b. CHE

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5 μmol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added CHE (9.68 μl, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 19 h reaction was 100 % complete. Peaks were observed in the total ion

chromatogram which had mass spectra consistent with formation of **4a**. MS:  $M^+$  224,  $M^+$ -Me 209.

The same reaction was carried out in  $C_6D_6$  and two products **4b1** and **4b2** were identified by  $^1H$  NMR spectroscopy (1D and 2D).

**4b1**: NMR:  $^1H$   $\delta$  0.9-1.1 (m,  $CH_3$  of Bpins), 1.60 (m, 1H, F), 1.76 (m, 3H, E G H), 1.97 (m, 1H, D), 2.24 (m, 1H, C), 5.76 (m, 1H, B), 6.25 (d,  $^3J_{H-H} = 10$  Hz, 1H, A).

**4b2**: NMR:  $^1H$   $\delta$  1.0 (m,  $CH_3$  of Bpin), 1.34 (m, 1H, K), 1.50 (m, 1H, L), 1.72 (m, 1H, N), 1.82 (m, 1H, P), 2.04 (m, 1H, M), 2.16 (m, 1H, O), 5.90 (dt,  $^3J_{H-H} =$  Hz  $^3J_{H-H} =$  Hz, 1H, J), 6.16 (dt,  $^3J_{H-H} =$  Hz  $^3J_{H-H} =$  Hz, 1H, I).

### c. TCA

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added TCA (12.62  $\mu$ l, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 20 h reaction was 90 % complete relative to residual TCA. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **5a**. MS:  $M^+$ -H 259,  $M^+$ -Me 245.

The same reaction was carried out in  $C_6D_6$  and two products **5b1** and **5b2** were identified by  $^1H$  NMR spectroscopy (1D and 2D).

**5b1**: NMR:  $^1H$   $\delta$  0.9-1.1 (m,  $CH_3$  of Bpins), 4.11 (d,  $^3J_{H-H} = 8.5$  Hz, Ph-CHBpin-CH=C(OBpin)H), 5.22 (dd,  $^3J_{H-H} = 8.5$  Hz,  $^3J_{H-H} = 5.5$  Hz, Ph-CHBpin-CH=C(OBpin)H), 6.84 (d,  $^3J_{H-H} = 5.5$  Hz, Ph-CHBpin-CH=C(OBpin)H).

**5b2**: NMR:  $^1H$   $\delta$  0.9-1.1 (m,  $CH_3$  of Bpins), 5.14 (d,  $^3J_{H-H} = 5.5$  Hz, Ph-CHBpin-CH=C(OBpin)H), 6.50 (dd,  $^3J_{H-H} = 15.5$  Hz,  $^3J_{H-H} = 5.5$  Hz, Ph-CHBpin-CH=C(OBpin)H), 6.75 (d,  $^3J_{H-H} = 15.5$  Hz, Ph-CHBpin-CH=C(OBpin)H).

#### d. BEO

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added BEO (14 mg, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 10.5 h reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 6a. MS: M<sup>+</sup> 274 , M<sup>+</sup>-Me 259.

The same reaction was carried out in C<sub>6</sub>D<sub>6</sub> and two isomers of product 6b were identified by <sup>1</sup>H NMR spectroscopy (1D and 2D), but the individual peaks were not attributed to either isomer.

Isomer 1: NMR: <sup>1</sup>H  $\delta$  0.9-1.1 (m, CH<sub>3</sub> of Bpins), 1.87 (s, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 3.88 (d, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 5.24 (dq, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.2 Hz, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.01 (t, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, *p*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.17 (t (dd), <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, *m*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.49 (d, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, *o*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>).

Isomer 2: NMR: <sup>1</sup>H  $\delta$  0.9-1.1 (m, CH<sub>3</sub> of Bpins), 1.88 (d, <sup>3</sup>J<sub>H-H</sub> = 1.0 Hz, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 3.45 (d, <sup>3</sup>J<sub>H-H</sub> = 10.5 Hz, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 5.85 (dq, <sup>3</sup>J<sub>H-H</sub> = 10.5 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.0 Hz, PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.01 (*p*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.17 (*m*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>), 7.46 (d, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, *o*-PhCH(Bpin)CH=C(OBpin)CH<sub>3</sub>).

#### e. Chalcone

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and B<sub>2</sub>pin<sub>2</sub> (0.11 mmol, 27.93 mg) in THF (2 ml) was added chalcone (21 mg, 0.1 mmol). The reaction was

stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 23 h reaction was 91 % complete relative to residual chalcone. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 7a and hydrogenated chalcone. MS: 7a  $M^+$  336,  $M^+$ -Me 321;  $H_2$  prod  $M^+$  210.

The same reaction was carried out in  $C_6D_6$  and product 7b was identified by  $^1H$  NMR spectroscopy (1D and 2D).

NMR:  $^1H$   $\delta$  0.9-1.1 (m,  $CH_3$  of Bpins), 4.05 (d,  $^3J_{H-H} = 8.5$  Hz, Ph-CHBpin-CH=C(OBpin)-Ph), 6.16 (d,  $^3J_{H-H} = 8.5$  Hz, Ph-CHBpin-CH=C(OBpin)-Ph), 6.97 (t,  $^3J_{H-H} = 7.0$  Hz, Ph-CHBpin-CH=C(OBpin)-*p*- $C_6H_5$ ), 7.03 (m, *m*- $C_6H_5$ -CHBpin-CH=C(OBpin)-Ph), 7.14 (Ph-CHBpin-CH=C(OBpin)-*m*- $C_6H_5$ ), 7.20 (t,  $^3J_{H-H} = 7.0$  Hz, *p*- $C_6H_5$ -CHBpin-CH=C(OBpin)-Ph), 7.56 (dd,  $^3J_{H-H} = 7.0$  Hz,  $^4J_{H-H} = 1.5$  Hz, *o*- $C_6H_5$ -CHBpin-CH=C(OBpin)-Ph), 7.75 (m, Ph-CHBpin-CH=C(OBpin)-*o*- $C_6H_5$ ).

### f. 3,5-dimethyl-2-cyclohexen-1-one

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added 3,5-dimethyl-2-cyclohexen-1-one (14.10  $\mu$ l, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 26 h reaction was 10 % complete relative to residual 3,5-dimethyl-2-cyclohexen-1-one. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 8a. MS:  $M^+$  252,  $M^+$ -Me 237.

### g. Ethylcrotonate

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added ethylcrotonate (12.43  $\mu$ l, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 7 h reaction was 86 % complete relative to residual ethyl crotonate.

Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **9a** (12 %) and **9c** (88 %). MS: **9a**  $M^+$  242,  $M^+$ -Me 227; **9c**  $M^+$ -Me 353.

The same reaction was carried out in  $C_6D_6$  and product **9c** was identified by  $^1H$  NMR spectroscopy (1D and 2D).

NMR:  $^1H$   $\delta$  0.9-1.1 (m,  $CH_3$  of Bpins), 1.04 ( $CH_3$ -CHBpin-CHBpin-C(=O)-O- $CH_2$ - $CH_3$ ), 1.32 (d,  $^3J_{H-H} = 7.5$  Hz,  $CH_3$ -CHBpin-CHBpin-C(=O)-O- $CH_2$ - $CH_3$ ), 1.83 (dd,  $^3J_{H-H} = 7.5$  Hz,  $^3J_{H-H} = 5.5$  Hz,  $CH_3$ -CHBpin-CHBpin-C(=O)-O- $CH_2$ - $CH_3$ ), 2.58 (d,  $^3J_{H-H} = 5.9$  Hz,  $CH_3$ -CHBpin-CHBpin-C(=O)-O- $CH_2$ - $CH_3$ ), 4.01 4.10 (AB dq,  $^2J_{H-H} = 10.5$  Hz,  $^3J_{H-H} = 7.0$  Hz,  $CH_3$ -CHBpin-CHBpin-C(=O)-O- $CH_2$ - $CH_3$ )

#### **h. Methylcinnamate**

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added methylcinnamate (16 mg, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 27 h reaction was 5 % complete relative to residual methylcinnamate. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **10a**. MS:  $M^+$  290,  $M^+$ -Me 275.

#### **i. 3-octen-2-one**

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu$ mol) and  $B_2pin_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added 3-octen-2-one (14.51  $\mu$ l, 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 3 h reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **11a** and **11b**. MS: **11a**  $M^+$  254,  $M^+$ -Me 239; **11b**  $M^+$ -Me 365.

The same reaction was carried out in  $C_6D_6$  and product **11b** was identified by  $^1H$  NMR spectroscopy (1D and 2D).

NMR:  $^1\text{H}$   $\delta$  0.89 (t,  $^3J_{\text{H-H}} = 7.2$  Hz,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHBpin-CH=C(OBpin)-CH}_3$ ), 0.9-1.1 (m,  $\text{CH}_3$  of Bpins), 1.34 (m,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHBpin-CH=C(OBpin)-CH}_3$ ), 1.62 (m,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHBpin-CH=C(OBpin)-CH}_3$ ), 1.81 (m,  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CHBpin-CH=C(OBpin)-CH}_3$ ), 1.90 (s,  $\text{Bu-CHBpin-CH=C(OBpin)-CH}_3$ ), 2.48 (apparent q (dt),  $^3J_{\text{H-H}} = 8.2$  Hz,  $\text{Bu-CHBpin-CH=C(OBpin)-CH}_3$ ), 4.85 (d,  $^3J_{\text{H-H}} = 9.5$  Hz,  $\text{Bu-CHBpin-CH=C(OBpin)-CH}_3$ ).

#### j. Acrylonitrile

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added acrylonitrile (6.58  $\mu\text{l}$ , 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 26 h reaction was 23 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **12a** (7 %) and **12c** (93 %). MS: **12a**  $\text{M}^+$  181,  $\text{M}^+$ -Me 166; **12c**  $\text{M}^+$  307,  $\text{M}^+$ -Me 292.

#### k. Methylmethacrylate

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added methylmethacrylate (10.70  $\mu\text{l}$ , 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 19 h reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of **13a** and **13c**. MS: **13a**  $\text{M}^+$ -Me 213; **13c**  $\text{M}^+$ -Me 339.

The same reaction was carried out in  $\text{C}_6\text{D}_6$  and product **13c** was identified by  $^1\text{H}$  and  $^{13}\text{C}$  1D NMR spectroscopy and  $^1\text{H}$ - $^{13}\text{C}$  2D NMR spectroscopy.

NMR:  $^1\text{H}$   $\delta$  0.9-1.1 (m,  $\text{CH}_3$  of Bpins), 1.47 1.56 (AB dd, 2H,  $^3J_{\text{H-H}} = 15.5$  Hz,  $\text{CH}_2\text{Bpin-}$ ), 1.64 (s, 3H,  $\text{CH}_3\text{-C(Bpin)(CH}_2\text{Bpin-)}$ ), 3.42 (s, 3H,  $\text{CH}_3\text{-O}$ ).  $^{13}\text{C}$   $\delta$  22.03 ( $\text{CH}_3\text{-C(Bpin)(CH}_2\text{Bpin-)}$ ), 23.01 ( $\text{CH}_2\text{Bpin-}$ ), 51.25 ( $\text{CH}_3\text{-O}$ ), 82.79 83.59 ( $(\text{CH}_3)(\text{CH}_2\text{Bpin)CBpin-}$ ), 177.81 ( $\text{-C(=O)-}$ ).

## I. Ethylacrylate

To a dark green solution of Pt(BIAN)(fum) (3.36 mg, 5  $\mu\text{mol}$ ) and  $\text{B}_2\text{pin}_2$  (0.11 mmol, 27.93 mg) in THF (2 ml) was added ethylacrylate (10.84  $\mu\text{l}$ , 0.1 mmol). The reaction was stirred, giving a red/brown solution which was monitored by GC-MS. GC-MS indicated that after 2.5 h reaction was 100 % complete. Peaks were observed in the total ion chromatogram which had mass spectra consistent with formation of 14a and 14c. MS: 14a  $\text{M}^+\text{-Me}$  213; 14c  $\text{M}^+\text{-Me}$  339.

The same reaction was carried out in  $\text{C}_6\text{D}_6$  and product 14c was identified by  $^1\text{H}$  NMR spectroscopy (1D and 2D).

NMR:  $^1\text{H}$   $\delta$  0.99 (t,  $^3\text{J}_{\text{H-H}} = 7.0$  Hz,  $\text{CH}_3\text{-CH}_2$ ), 1.0-1.1 (m,  $\text{CH}_3$  of Bpins), 1.39 1.54 (AB dd,  $^2\text{J}_{\text{H-H}} = 16.0$  Hz,  $^3\text{J}_{\text{H-H}} = 7.5$  Hz,  $\text{CH}_2\text{Bpin-}$ ), 2.72 (t,  $^3\text{J}_{\text{H-H}} = 7.5$  Hz,  $-\text{CHBpin-}$ ), 4.01 4.05 (AB dq,  $^2\text{J}_{\text{H-H}} = 10.5$  Hz,  $^3\text{J}_{\text{H-H}} = 7.0$  Hz,  $\text{CH}_3\text{-CH}_2\text{-O}$ ).

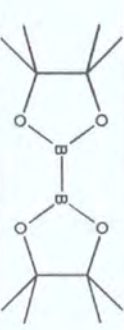
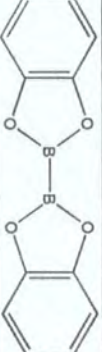
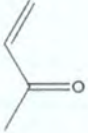
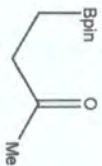
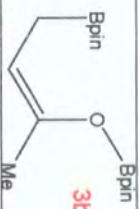

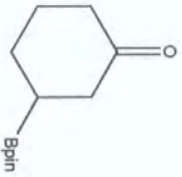

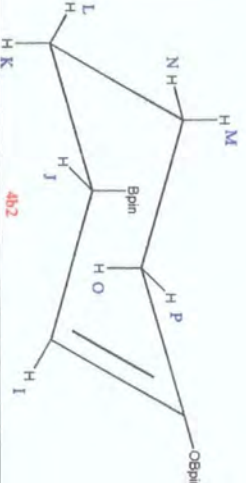
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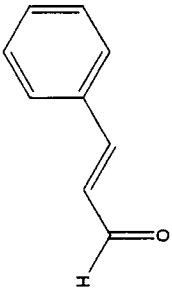
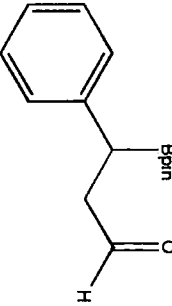
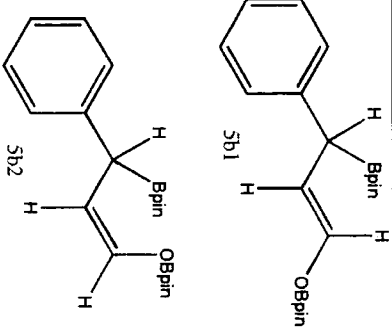
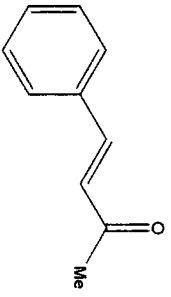
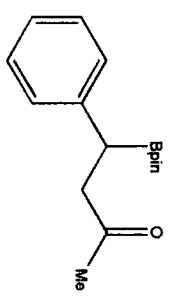
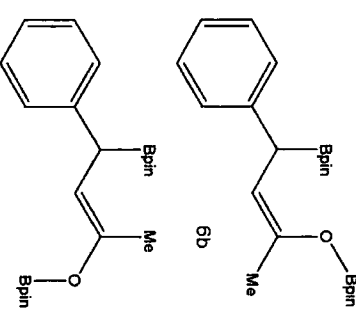
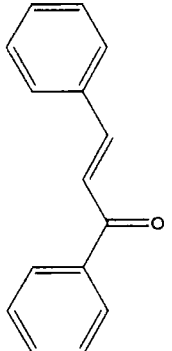
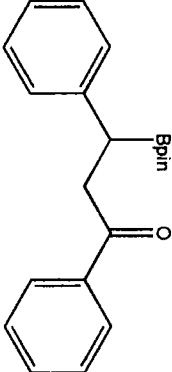
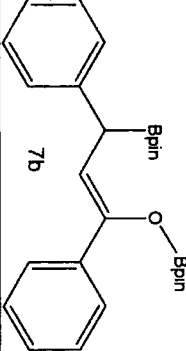
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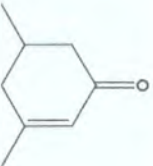
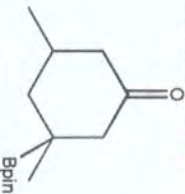
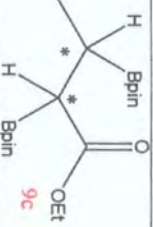
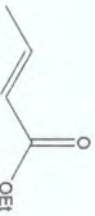
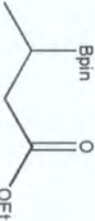
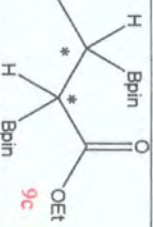
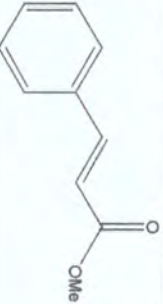
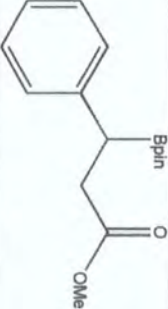
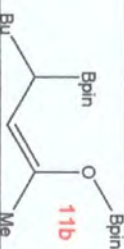
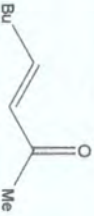
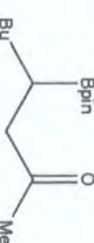
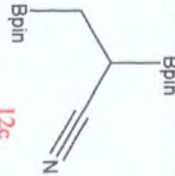

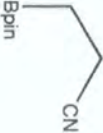
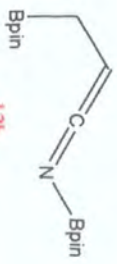
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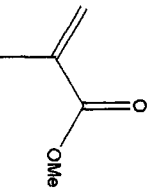
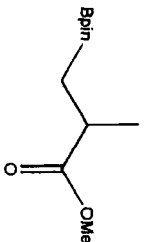
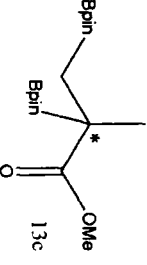
## Appendix: Substrates and Products

Nb **Xb** = 1,4-diborated product, **Xc** = 1,2-diborated product

Substrate Name	Number	Substrate Structure <b>X</b>	Hydrolysed 1,4-diborated Product <b>Xa</b>	Diborated Product
bis(pinacolato)diboron (B <sub>2</sub> pin <sub>2</sub> )	1			
biscatecholodiboron (B <sub>2</sub> cat <sub>2</sub> )	2			
Methyl vinyl ketone (MVK)	3			
2-cyclohexen-1-one (CHE)	4			
				

<u>Substrate Name</u>	<u>Number</u>	<u>Substrate Structure X</u>	<u>Hydrolysed 1,4-diborated Product Xa</u>	<u>Diborated Product</u>
<i>trans</i> -cinnamaldehyde (TCA)	5			
<i>trans</i> -4-phenylbut-3-en-2-one (BEO)	6			
Chalcone	7			

Substrate Name	Number	Substrate Structure X	Hydrolysed 1,4-diborated Product Xa	Diborated Product
3,5-dimethyl-2-cyclohexen-1-one	8			
Ethylcrotonate	9			
Methylcinnamate	10			
3-octen-2-one	11			
Acrylonitrile	12			

<u>Substrate Name</u>	<u>Number</u>	<u>Substrate Structure X</u>	<u>Hydrolysed 1,4-diborated Product Xa</u>	<u>Diborated Product</u>
Methylmethacrylate	13			
Ethylacrylate	14	