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Auxiliary Accelerated Reactions: Towards the Use of Catalytic Chiral Auxiliaries.

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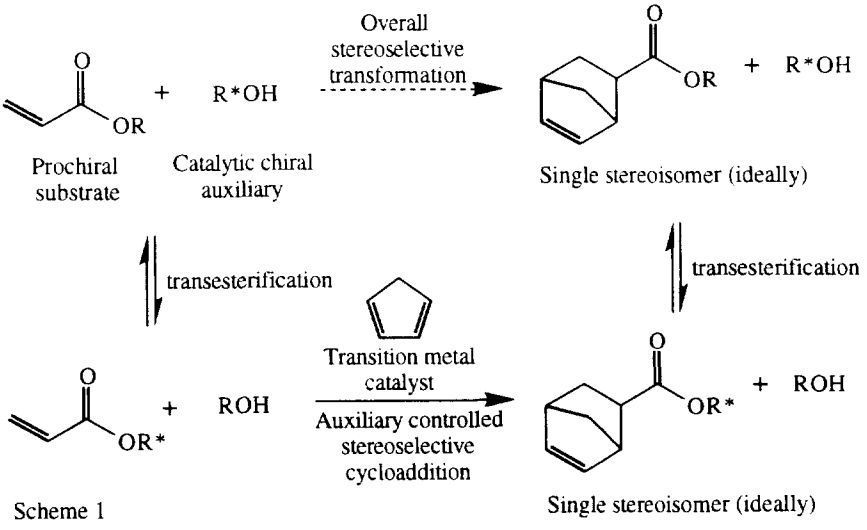
Abstract: In competition experiments, the acceleration of reactivity of alkenes tethered to pyridyl groups compared with the corresponding alkenes tethered to phenyl groups in the presence of transition metals was demonstrated for two reaction types: Diels-Alder cycloaddition of enoate esters and catalytic hydrogenation of allylic and homoallylic ethers. The rate accelerations observed are of crucial importance in the development of a new concept for asymmetric catalysis: chiral auxiliaries which can function in a catalytic manner.

The use of enantiomerically pure auxiliaries in asymmetric synthesis to control the stereochemical outcome of reactions, although of fundamental importance and of widespread usage in synthesis, suffers important drawbacks in terms of synthetic efficiency; namely that the attachment and detachment of the auxiliary incorporates two extra steps into the synthetic sequence and that a stoichiometric amount of the auxiliary relative to the substrate is required.

In order to try to overcome these deficiencies, we envisaged the use of a chiral auxiliary in a catalytic manner, whereby the attachment and detachment of the auxiliary would occur in one pot *via* a reversible reaction such as transesterification or transacetalisation.

A generalised catalytic cycle for Diels-Alder cycloaddition of enoate esters is shown in Scheme 1. It should be noted that this kind of catalytic cycle could, in principle, be applied to many other reactions.



Scheme 1

In order for the above catalytic cycle to function successfully, we were able to identify three major criteria which needed to be satisfied:

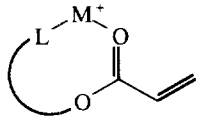
(i) The auxiliary bound cycloaddition should be highly stereoselective.
(ii) Equilibrium attachment/detachment conditions for the auxiliary must be maintained throughout the catalytic cycle.
(iii) The catalytic auxiliary bound substrate should react very much more quickly than the unbound substrate when both are present in the reaction mixture. If this were not the case, the achiral substrate would react competitively, significantly lowering the level of asymmetric induction.

This paper details the successful application of one of these principles, namely the issue of rate enhancement of auxiliary bound substrates, and our progress towards the goal of catalytic chiral auxiliaries.

RESULTS AND DISCUSSION

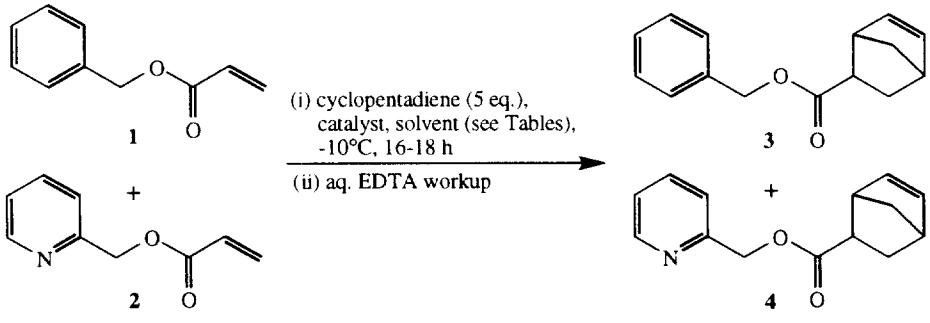
Our approach towards accelerated reactions by potential chiral auxiliaries was based on our anticipation that an auxiliary containing a donor atom, such as the 2-pyridyl group, would bind to a suitable transition-metal species and accelerate reaction at a double bond *via* chelation, as shown in Figure 1.[2] Initially the Diels-Alder cycloaddition of enoate esters was chosen for study since the reaction is known to be catalysed by a wide variety of Lewis acidic transition-metal promoters[3] and because the issue of acceleration and selectivity enhancement is a topic of considerable current interest in synthesis.[4]

Figure 1 : Auxiliary Acceleration *via* Chelate Delivery of a Transition-Metal Promoter



L = donor atom
M = transition-metal

Competition experiments between equimolar quantities of benzyl propenoate **1** and (2-pyridyl)methyl propenoate **2** in the presence of transition metal promoters known for their affinity for nitrogen[5] were carried out over a period of 16-18 h using cyclopentadiene as diene.[6] A temperature of -10°C was chosen as the optimum for these studies since at room temperature the non-selective cycloaddition in the absence of transition metal (which would obviously lower the level of rate discrimination observed) was too fast, giving an overall conversion level of 21% after 18 h in dichloromethane. At temperatures below -10°C the rates of metal-promoted reaction were found to be too slow, giving mainly starting materials after 18 h.



A range of transition metal species known for their high affinity for nitrogen was examined to try to enhance the reactivity of **2** *via* a chelation effect (Figure 1) in competition experiments in dichloromethane. The

results of these studies are shown in Table 1, and raised several interesting points. In the absence of a transition metal promoter, both substrates were found to react at the same rate which was gratifying since this meant that any subsequent rate accelerations observed would be due to the metal reagent employed. However the 9% conversion observed for both substrates (entry 1) did indicate that this small background reaction would slightly lower the levels of rate discrimination between **1** and **2** in metal promoted reactions.

The best levels of rate enhancement of **2** over **1** were found using copper (II) triflate[7,8] and zinc (II) triflate, although less impressive results were obtained using other transition metal promoters. Magnesium bromide etherate enhanced the reactivity of both **1** and **2** without significant rate discrimination, as expected for a Lewis acid with a high affinity for oxygen donors.

Copper(II) and zinc (II) triflate both accelerate the Diels-Alder reaction for the (2-pyridyl)methyl substrate but have virtually no effect on the benzyl substrate. This demonstrates that the auxiliary is able to modify the rate of reaction

Table 1:Effect of metal catalyst on Diels-Alder competition reactions between **1** and **2**

Catalyst	% Conversion (Ph)	% Conversion (Py)
None	9.0	9.0
$Cu(OTf)_2$	**10.5**	**75.9**
$Zn(OTf)_2$	**9.6**	**58.7**
HgI_2	9.0	9.0
$AgBF_4$	12.9	38.7
$FeCl_3$	44.3	62.6
$Ni(NO_3)_2.6H2O$	13.2	14.4
$MgBr_2.OEt_2$	59.1	69.0

All above reactions carried out in dichloromethane at -10°C over a period of 16-18 hrs.
In each case, the *endo* isomer was formed predominantly for both cycloadducts.

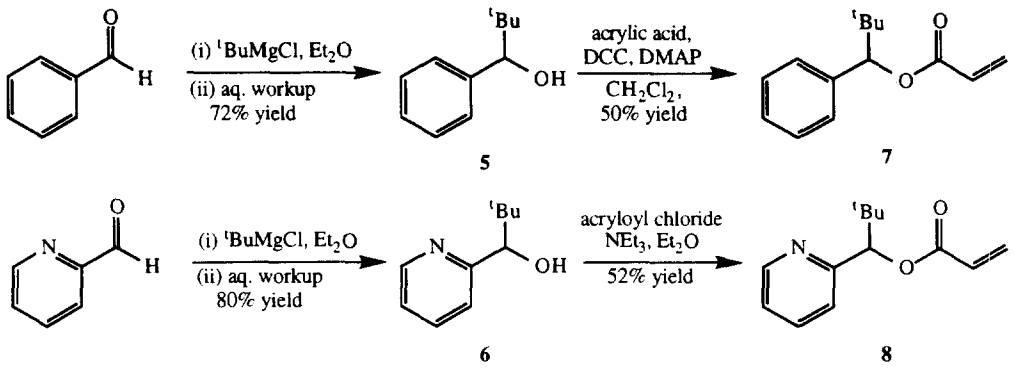
The solvent effect on competition reactions was examined, since it was anticipated that a more co-ordinating solvent than dichloromethane would compete with benzyl propenoate **1** for binding sites at copper, thereby enhancing the rate discrimination between **1** and **2**. The results of this study are shown in Table 2, which indicates that, in fact, the highest difference in reactivity was observed in dichloromethane and more co-ordinating solvents do not enhance the rate discrimination between **1** and **2**.

Table 2:Solvent effect on Diels-Alder competition reactions between **1** and **2**.

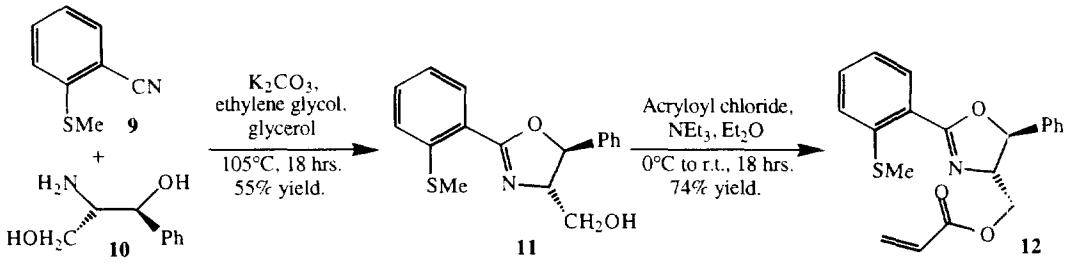
Solvent	% Conversion (Ph)	% Conversion (Py)
CH_2Cl_2	10.5	75.9
Et_2O	44.6	75.3
THF	6.9	41.8
Me_2CO	8.1	43.9
MeOH	17.4	32.1

All above reactions carried out using copper (II) triflate as catalyst at -10°C over a period of 16-18 hrs.
In each case, the *endo* isomer was formed predominantly for both cycloadducts.

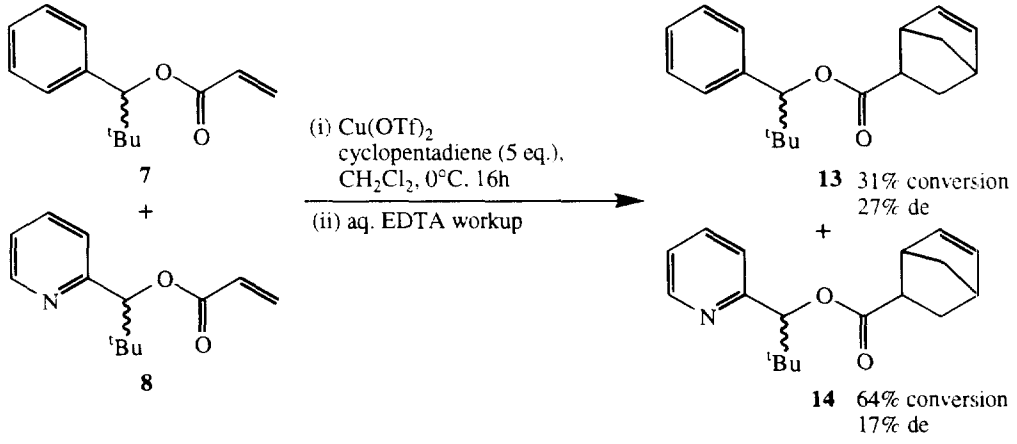
Extension of this work to potential chiral auxiliaries was undertaken. The preparation of α-^{t}butylbenzyl propenoate **7** and α-^{t}butylpicolyl propenoate **8**[9] (as racemic mixtures) was accomplished in two steps, as shown.

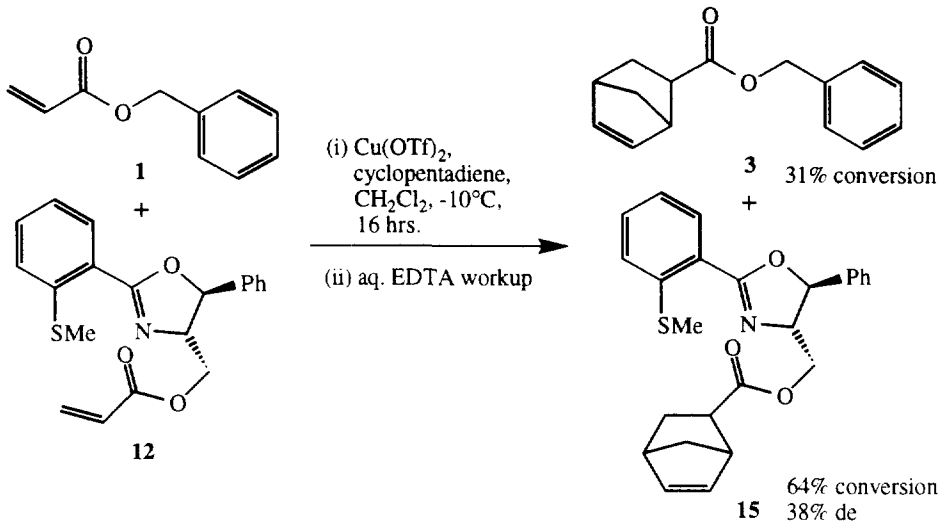


A chiral auxiliary based on an optically pure oxazoline was also envisaged and the chiral enoate ester **12** prepared in two steps, from nitrile **9** and aminodiol **10** using standard methodology.[10]



Competition experiments of the type described above using substrates **7** and **8** and between substrates **1** and **12** (equimolar quantities) gave the following results:

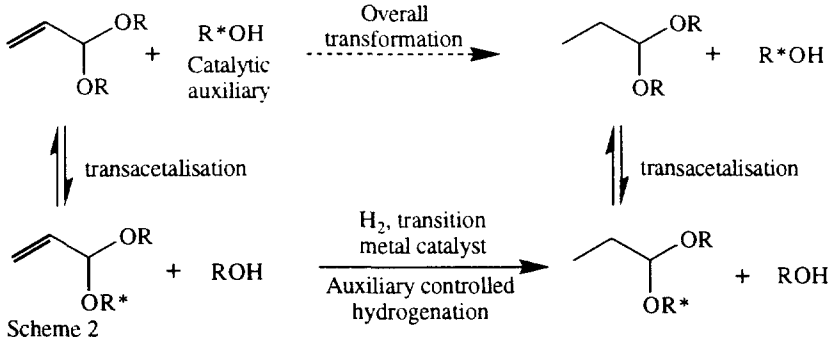




Thus, chiral pyridyl and oxazolinyl auxiliary bound substrates **8** and **12** show moderate rate enhancements over the corresponding phenyl substrates **7** and **1**. Modest levels of diastereoselectivity were observed for cycloaddition involving chiral auxiliaries and in all cases predominantly *endo* cycloadducts were formed.

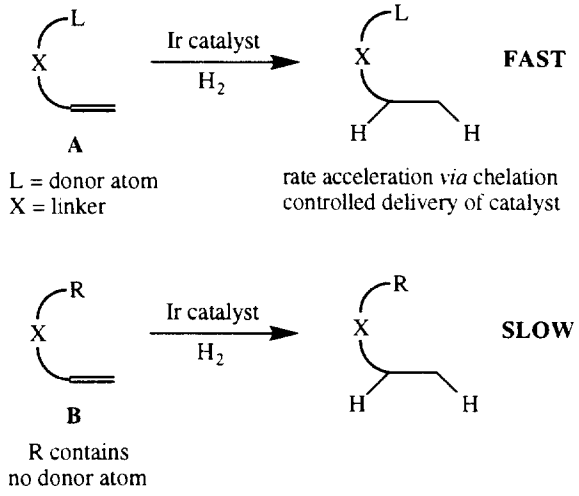
Although copper (II) catalysed transesterifications are known,[11] we observed no ester scrambling (benzyl / picolyl transesterification) for achiral or chiral auxiliaries under the transition metal promoted rate discrimination conditions. Indeed, it was found that mixing benzyl propenoate **1** and 2-(hydroxymethyl)-pyridine in equimolar quantities with copper (II) triflate in dichloromethane gave no transesterification (formation of picolyl propenoate **2**) at room temperature.

Although the principle of transition metal promoted rate enhancement of auxiliary bound substrates containing a nitrogen donor atom in the presence of substrates containing no such donor atom in competition experiments has now been demonstrated with a fair degree of success, rate discrimination levels were not yet high enough to apply the pyridyl and oxazolinyl groups described as potential catalytic auxiliaries. One fundamental problem in this context with using the Diels-Alder cycloaddition was the low reactivity of both substrates at the same rate in the absence of transition metal promoters (Table 1), contributing a significant background rate of non-discriminatory cycloaddition. At this point, it was decided to change the process examined to transition metal catalysed homogenous hydrogenation and the intended attachment / detachment of the auxiliary equilibrium process from transesterification to transacetalisation. A catalytic cycle of the type shown below (Scheme 2) was envisaged, initially for an achiral auxiliary.



Scheme 2

Initial studies in this area were concentrated on the hydrogenation of allylic ethers.[12] Cationic iridium complexes such as $[Ir(COD)(P(c\text{-}C_6H_{11})_3(Py)]PF_6$ (Crabtree catalyst) have been shown to be highly efficient homogenous hydrogenation catalysts.[13] In a similar manner to the above cycloaddition studies, we were interested in the possibility that auxiliaries containing a nitrogen donor atom (as a pyridine ring) capable of chelation might be able to react more quickly in the presence of Crabtree catalyst than the corresponding auxiliaries containing no such donor atom in competition experiments.[14] It was anticipated that substrates of type **A** would react more quickly in the presence of iridium than substrates of type **B** in competition studies (Scheme 3).

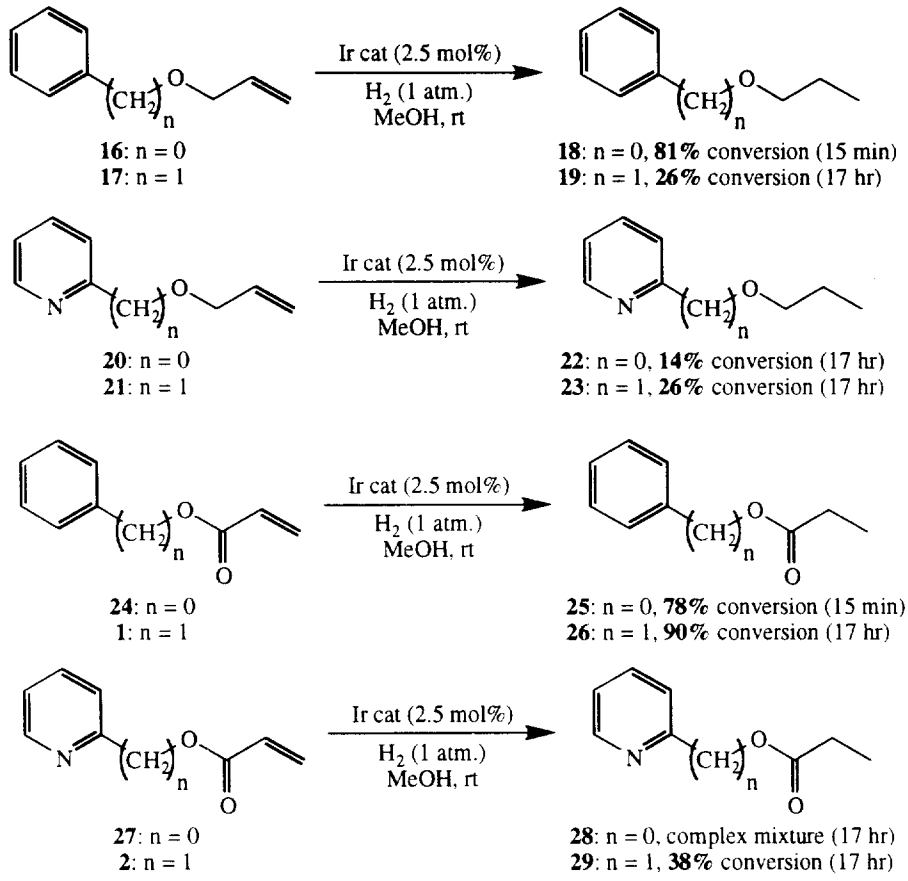


Scheme 3

Rate studies on individual substrates (the more usual non-competitive mode of reaction) gave interesting, if not entirely surprising, results. We found that allyl phenyl ether **16**, which is not capable of chelation, underwent iridium catalysed hydrogenation in methanol in high conversion within 15 minutes at room temperature. Although methanol is known to lower the activity of the catalyst by competitive binding to iridium,[15] we found that for our studies involving allylic ethers conversion levels in methanol were as high, and often higher, than those in dichloromethane, the solvent usually recommended for this type of reaction. In contrast, allyl benzyl ether **17**[16] reacted much more slowly under identical conditions, giving a lower level of conversion even after 17 hours. Presumably the greater Lewis basicity of the oxygen atom in **13** which can poison the iridium catalyst is the reason for this difference in reactivity.

Interestingly 2-allyloxypyridine **20**[17] reacted much more slowly than the corresponding phenyl substrate **16**, giving lower levels of conversion after a much longer reaction time. Again, the presence of a co-ordinating group, in this case pyridyl nitrogen, is dramatically lowering the reactivity of the substrate (presumably by inhibiting catalyst turnover). Allyl picolyl ether **21**[16] reacted at about the same rate as allyl benzyl ether **17**. The corresponding reaction using $[Rh(COD)(Ph_2P(CH_2)_4PPh_2]^+BF_4^-$ in dichloromethane gave fairly low levels of conversion for substrates **16** and **20**.

The reactivity of the related enoate esters (non-competitive) was also examined. Phenyl and benzyl acrylates **24** and **1** underwent rapid iridium catalysed hydrogenation whereas picolyl acrylate **2** was much less reactive under the same conditions. Pyridyl acrylate **27** was found to be unstable in the presence of iridium (or rhodium) catalyst.



Investigation of the relative reactivity of phenyl and 2-pyridyl substrates in competition reactions revealed some surprising results (Table 3).

In all the competitive hydrogenation studies shown in Table 3, the 2-pyridyl-based (Py) substrates reacted more quickly than the phenyl-based (Ph) substrates.

Particularly noteworthy are the results for the competitive hydrogenation between allyl phenyl ether **16** and 2-allyloxypyridine **20**. In the independent studies, the phenyl substrate **16** was found to be more than 100X more reactive than pyridyl substrate **20**. In contrast, the results from competitive studies under the same conditions revealed that the pyridyl substrate **20** was now more than 10X more reactive than compound **16**. The phenyl ether **16** was found to undergo a dramatic deceleration of reactivity in the presence of the 2-pyridyl substrate **20**, whilst the reactivity of **20** was not greatly affected by the presence of **16**. The greater reactivity of **20** over **16** in competition reactions was as expected as described in Scheme 3, demonstrating the principle of auxiliary accelerated reactions. Competition reactions between allyl benzyl and allyl picolyl ethers **17** and **21** did not give much rate acceleration, and the results for the corresponding esters **1** and **2** revealed that the reactivity of benzyl acrylate **2** was greatly reduced by the presence of picolyl acrylate **27**.

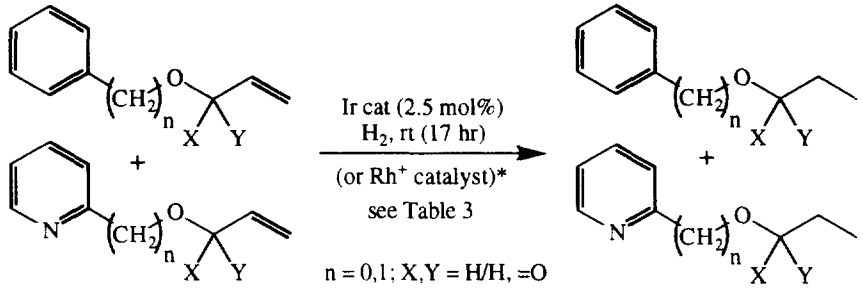
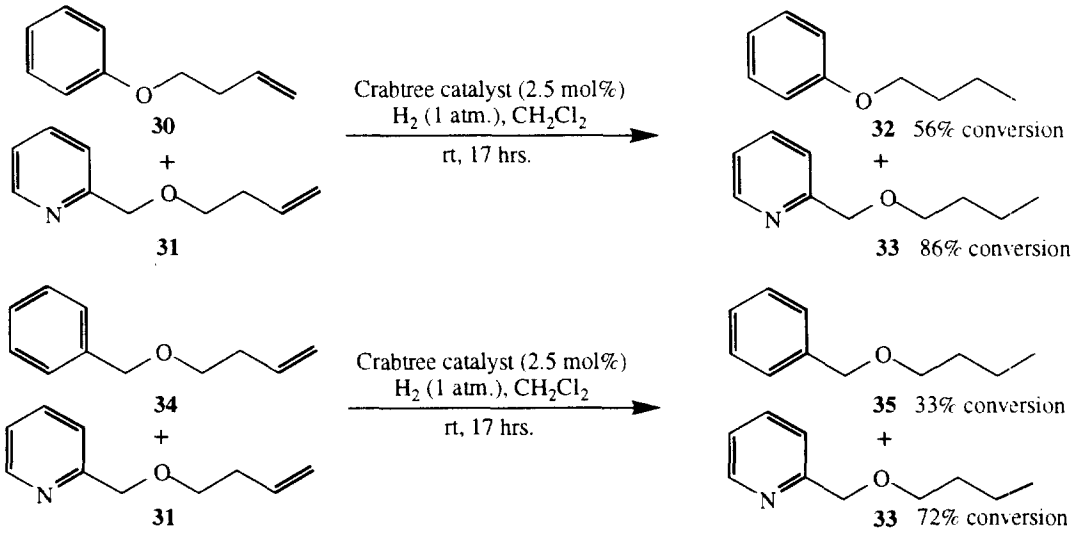


Table 3. Competitive hydrogenation studies

Substrates	Products	Catalyst	H_2 (atm)	Solvent	Conversion / % (Ph)	Conversion / % (Py)
16 + 20	**18 + 22**	Ir	1.0	MeOH	**2**	**26**
16 + 20	**18 + 22**	Ir	1.0	CH_2Cl_2	**0.8**	**7**
16 + 20	**18 + 22**	Ir	2.7	MeOH	47	85
16 + 20	**18 + 22**	Ir	4.4	CH_2Cl_2	15	49
16 + 20	**18 + 22**	Rh*	4.4	CH_2Cl_2	4	19
17 + 21	**19 + 23**	Ir	4.4	MeOH	16	24
24 + 27	**25**	Ir	4.4	MeOH or CH_2Cl_2	–	Decomp.
1 + 2	**26 + 29**	Ir	2.0	MeOH	25	33

All reactions were run at r.t. for 17 hr. *Rh catalyst = $[Rh(COD)(Ph_2P(CH_2)_4PPh_2)]^+BF_4^-$

The rate differences between phenyl- and 2-pyridyl-based homoallylic ethers for catalytic hydrogenation were also investigated. Dichloromethane was found to be the best solvent for these substrates for hydrogenation using Crabtree catalyst. Competitive hydrogenations between 4-(phenyloxy)-1-butene **30**[18] and 4-(picolyloxy)-1-butene **31**[19] and between 4-(benzyloxy)-1-butene **34**[19] and **31** gave the following results.



In both of the above cases, substrate **31** reacted more quickly than the phenyl or benzyl substrate **30** or **34**, although the levels of rate discrimination are not so great as to be applicable to the type of catalytic auxiliary system outlined in Scheme 2. Nevertheless, we have now established methods for auxiliary acceleration, and future research will be directed towards the development of a catalytic cycle using acetals as substrates.[20]

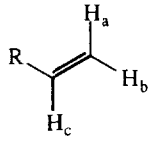
Summary

The principle of rate acceleration in transition metal competition experiments for substrates containing a nitrogen donor atom *via* a chelation effect (as described in Figures 1 and 2) over substrates without a donor atom has been demonstrated for two reaction types: the Diels-Alder cycloaddition of enoate esters and the catalytic hydrogenation of allyl and homoallyl ethers. These observations represent an important advance towards the principle of catalytic chiral auxiliaries, a new concept on organic synthesis and our eventual goal.

EXPERIMENTAL SECTION

General Experimental

General experimental procedures, including equipment used and solvent purification have been described elsewhere.[21] Acetone was distilled from calcium chloride before use. Methanol was distilled from magnesium turnings and iodine. ^{1}H nmr nomenclature for alkenes is as indicated.



Benzyl propenoate (1). Triethylamine (6.73mL, 48.3mmol) was added to a solution of benzyl alcohol (5.00mL, 48.3mmol) in dry diethyl ether (40mL) under nitrogen with stirring at room temperature. Acryloyl chloride (4.01mL, 48.3mmol) was then added dropwise at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for a further two hours then poured into water (30mL). The ether layer was washed with saturated aqueous sodium bicarbonate solution (2 x 30mL) and the aqueous layers extracted using ether (3 x 50mL). The combined organic layers were dried over magnesium sulfate, and the solvent removed *in vacuo*. Purification by flash chromatography (10% ether/light petroleum) gave the title compound **1** (4.082g, 52%) as an oil. Found M$^+$, 162.0683. $C_{10}H_{10}O_2$ requires M$^+$, 162.0681. ν_{max} / cm^{-1} 3100-2950 (C-H), 1725 (C=O), 1635, 1407, 1270, 1178 (C-O), 1049, 995, 810, 755 and 698. δ_H (250 MHz, $CDCl_3$) 5.20 (2H, s, PhC**H$_2$**O), 5.84 (1H, dd, J = 1.6, 10.4 Hz, **H$_b$**), 6.16 (1H, dd, J = 10.4, 17.2 Hz, **H$_c$**), 6.45 (1H, dd, J = 1.6, 17.2 Hz, **H$_a$**), 7.35 (5H, m, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 66.24 (PhCH$_2$O), 128.20 (**C**H), 128.30 (**C**H), 128.52 (**C**H), 130.98 (CH$_2$=CH), 135.89 (Ar**C**), 165.88 (**C**=O). *m/z* (EI) 162 (M+, 7%), 105 (70), 91 (100), 77 (28), 55 (32).

(2-Pyridyl)methyl propenoate (2) Triethylamine (4.33mL, 31.1mmol) was added to a solution of 2-pyridylcarbinol (3.00mL, 31.3mmol) in dry diethyl ether (40mL) under nitrogen with stirring at room temperature. Acryloyl chloride (2.53mL, 31.2mmol) was then added dropwise at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for a further two hours then poured into water (30mL). The ether layer was washed with saturated aqueous sodium bicarbonate solution (2 x 30mL) and the

aqueous layers extracted using ether (3 x 50mL). The combined organic layers were dried over magnesium sulfate, and the solvent removed *in vacuo*. Purification by flash chromatography (100% ether) gave the title compound **2** (3.193g, 63%) as an oil. Found M^+, 163.0619. $C_9H_9NO_2$ requires M^+, 163. 0633. ν_{max} / cm^{-1} 3100-2950 (C-H), 1727 (C=O), 1635 (C=C), 1594, 1573, 1477, 1439, 1407, 1272, 1151 (C-O), 1050, 984, 809 and 755. δ_H (250 MHz, $CDCL_3$) 5.32 (2H, s, Py**CH$_2$**O), 5.89 (1H, dd, J = 1.5, 10.4 Hz, **H$_b$**), 6.23 (1H, dd, J = 10.4, 17.4 Hz, **H$_c$**), 6.50 (1H, dd, J = 1.5, 17.4 Hz, **H$_a$**), 7.22 (1H, m, Ar**H**), 7.37 (1H, d, J = 7.8 Hz, Ar**H**), 7.71 (1H, m, Ar**H**), 8.60 (1H, m, Ar**H**). δC (62.5 MHz, $CDCl_3$) 66.55 (Py**C**H$_2$O), 121.47 (**C**H), 122.65 (**C**H), 127.63 (**C**H), 131.23 (**C**H$_2$=CH), 136.56 (**C**H), 149.19 (**C**H), 155.52 (Ar**C**), 165.44 (**C**=O). *m/z* (EI) 164 (M^++1, 8%), 135 (5), 118 (5), 108 (100), 92 (26), 79 (21), 65 (23), 55 (71).

General Procedure for Transition Metal Promoted Competitive Diels-Alder Cycloadditions

To a solution of an equimolar mixture of benzyl propenoate **1** and (2-pyridyl)methyl propenoate **2** (0.5mmol) in the appropriate solvent at the room temperature was added the transition metal promoter (0.5mmol). After stirring at room temperature for 15mins., the reaction mixture was cooled to -10°C and cyclopentadiene monomer (freshly 'cracked' by distillation through a Vigreux column) (2.5mmol, 5 eq.) added. The reaction mixture was then stirred at the appropriate temperature for 16-18 hours. Removal of solvent *in vacuo* and 'filtration' through a pad of silica (100% diethyl ether) afforded a mixture of starting materials and products which were then analysed by gas chromatography (BP1 column from SGE) after calibration with standards. Oven temperature : 100°C for starting materials: 150°C for cycloadducts.

***Endo* (2-carbobenzyloxy)bicyclo[2.2.1]hept-2-ene (3)** Found M^+, 228.1151. $C_{15}H_{16}O_2$ requires M^+, 228.1150. ν_{max} / cm^{-1} 3100-2850 (C-H), 1735 (C=O), 1594, 1573, 1476, 1336, 1183 (C-O), 1110, 1027 and 699. δ_H (250 MHz, $CDCl_3$) 1.28 (1H, d, J = 7.8 Hz, one of **CH$_2$**-7), 1.42 (1H, m, one of **CH$_2$**), 1.47 (1H, m, one of **CH$_2$**), 1.90 (1H, m, one of **CH$_2$**), 2.92 (1H, broad s, bridgehead **H**), 3.00 (1H, m, **CH**-6), 3.24 (1H, broad s, bridgehead **H**), 5.08 (2H, s, Ph**CH$_2$**O), 5.88 (1H, dd, J = 2.9, 5.7 Hz, alkene **H**), 6.19 (1H, dd, J = 2.9, 5.7 Hz, alkene **H**), 7.35 (5H, m, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 29.19 (**C**H$_2$-7), 42.53 (**C**H), 43.32 (**C**H), 45.75 (**C**H), 49.57 (**C**H$_2$-6), 65.93 (Ph**C**H$_2$O), 127.99 (**C**H), 128.43 (**C**H), 132.26 (**C**H), 136.53 (Ar**C**), 137.72 (**C**H), 174.60 (**C**=O). *m/z* (EI) 228 (M^+, 3%), 163 (3), 156 (8), 137 (5), 117 (3), 91 (100), 77 (10), 66 (88), 55 (23).

***Endo* (2-carbopicolyloxy)bicyclo[2.2.1]hept-6-ene (4)** Found M^+, 229.1102. $C_{14}H_{15}NO_2$ requires M^+, 229.1103. ν_{max} / cm^{-1} 3100-2850 (C-H), 1737 (C=O), 1594, 1575, 1482, 1377, 1172 (C-O), 1112, 753 and 699. δ_H (250 MHz, $CDCl_3$) 1.22 (1H, m, one of **CH$_2$**-7), 1.43 (1H, m, one of **CH$_2$**), 1.49 (1H, m, one of **CH$_2$**), 1.93 (1H, m, one of **CH$_2$**), 2.91 (1H, broad s, bridgehead **H**), 3.06 (1H, m, **CH**-6), 3.26 (1H, broad s, bridgehead **H**), 5.17 (2H, s, Py**CH$_2$**O), 5.91 (1H, dd, J = 2.9, 5.6 Hz, alkene **H**), 6.19 (1H, dd, J = 2.9, 5.6 Hz, alkene **H**), 7.21 (1H, m, Ar**H**), 7.32 (1H, d, J = 7.8 Hz, Ar**H**), 7.68 (1H, m, Ar**H**), 8.57 (1H, m, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 29.19 (**C**H$_2$-7), 42.35 (**C**H), 43.17 (**C**H), 45.59 (**C**H), 49.43 (**C**H$_2$-6), 66.30 (Ph**C**H$_2$O), 121.40 (**C**H), 122.57 (**C**H), 132.09 (**C**H), 136.55 (**C**H), 137.61 (**C**H), 149.07 (**C**H), 155.97 (Ar**C**), 174.06 (**C**=O). *m/z* (EI) 230 (M^++1, 30%), 200 (17), 164 (84), 108 (62), 92 (75), 66 (100), 55 (63), 39 (53).

(2,2-Dimethyl-1-phenylpropyl)propenoate (7). Acrylic acid (0.67mL, 9.73mmol) and 4-dimethylaminopyridine (0.131g, 1.07mmol) were added to a solution of ^{t}butylbenzyl alcohol (1.759g, 10.71mmol) in dichloromethane (25mL) at room temperature under N_2 with stirring. 1,3-

Dicyclohexylcarbodiimide (2.209g, 10.71mmol) was then added to the reaction mixture at 0°C. After stirring for 5 mins. at 0°C the mixture was allowed to warm to room temperature and stirred for a further 21 hrs., after which time the urea by-product was filtered off and the residue washed with further dichloromethane (50mL). The filtrate was washed with 5% acetic acid solution (2x30mL) and water (30mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. The crude product was purified by flash chromatography (10% ether/light petroleum) to give the title compound **7** (1.070g, 50%) as an oil. Found M^+, 236.1651. $C_{10}H_{10}O_2 + NH_4^+$ requires M^+, 236.1651. ν_{max} / cm^{-1} 3100-2900 (C-H), 1728 (C=O), 1633 (C=C), 1480, 1464, 1395, 1188 (C-O), 1048, 983, 808, 738 and 702. δ_H (250 MHz, $CDCl_3$) 0.95 (9H, s, $(\mathbf{CH_3})_3C$), 5.56 (1H, s, $\mathbf{CH}$-^{t}Bu), 5.85 (1H, dd, J = 1.6, 10.4 Hz, $\mathbf{H_b}$), 6.17 (1H, dd, J = 10.4, 17.4 Hz, $\mathbf{H_c}$), 6.45 (1H, dd, J = 1.6, 17.4 Hz, $\mathbf{H_a}$), 7.28 (5H, m, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 26.01 ($(\mathbf{C}H_3)_3C$), 35.14 ($\mathbf{C}(CH_3)_3$), 82.91 ($\mathbf{C}$H-^{t}Bu), 127.50 (**C**H), 127.56 (**C**H), 127.67 (**C**H), 128.75 (**C**H), 130.43 ($\mathbf{C}H_2$=CH), 138.32 (Ar**C**), 165.16 (**C**=O). *m/z* (EI) 218 (M^+, 1%), 161 (24), 131 (8), 117 (8), 105 (14), 91 (11), 77 (10), 55 (100).

(2,2-Dimethyl-1-(2-pyridyl)propyl)propenoate (8). Triethylamine (0.88mL, 6.30mmol) was added to a solution of α-^{t}butylpicolyl alcohol (0.946g, 5.73mmol) in dry diethyl ether (15mL) under nitrogen with stirring at room temperature. Acryloyl chloride (0.52mL, 6.30mmol) was then added dropwise at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for a further 30 mins. then poured into water (10mL). The ether layer was washed with saturated aqueous sodium bicarbonate solution (10mL) and the aqueous layers extracted using ether (3 x 20mL). The combined organic layers were dried over magnesium sulfate, and the solvent removed *in vacuo*. Purification by flash chromatography (60% ether/light petroleum) gave the title compound **8** (0.659g, 52%) as an oil. Found M^+, 220.1338. $C_{10}H_{10}O_2$ requires MH^+, 220.1338. δ_H (250 MHz, $CDCl_3$) 1.00 (9H, s, $(\mathbf{CH_3})_3C$), 5.61 (1H, s, $\mathbf{CH}$-^{t}Bu), 5.86 (1H, dd, J = 1.7, 10.3 Hz, $\mathbf{H_b}$), 6.24 (1H, dd, J = 10.3, 17.3 Hz, $\mathbf{H_c}$), 6.46 (1H, dd, J = 1.7, 17.3 Hz, $\mathbf{H_a}$), 7.18 (1H, m, Ar**H**), 7.27 (1H, d, J = 5.7 Hz, Ar**H**), 7.64 (1H, m, Ar**H**), 8.58 (1H, d, J = 5.0 Hz, Ar**H**). *m/z* (EI) 219 (M+, not observed), 163 (16), 148 (4), 132 (11), 108 (100), 93 (17), 78 (15), 55 (52).

2-((2'-Methylthio)phenyl)-4-methylhydroxy-5-phenyloxazoline (11). To a suspension of (1S, 2S)-(+)-2-amino-1-phenyl-1,3-propanediol (3.167g, 18.6mmol) and potassium carbonate (0.616g, 4.45mmol) in a mixture of ethylene glycol (10mL) and glycerol (5.5mL) was added 2-(methylthio)benzonitrile (3.392g, 18.6mmol) under nitrogen with stirring at room temperature. The reaction mixture was heated at 110°C for 17 h. with stirring. The mixture was allowed to cool to room temperature then water (50mL) added. The product was extracted using chloroform (3 x 100mL), dried over magnesium sulfate and the solvent removed *in vacuo*. Purification by column chromatography (80% ether/light petroleum) gave the title compound (2.764g, 55%) as a colourless solid. Found: C, 68.14; H, 5.67; N, 4.26. $C_{17}H_{17}NO_2S$ requires C, 68.20; H, 5.72; N, 4.68%. M.p. 69.5-72.0°C. Found M^+, 299.0963. $C_{17}H_{17}NO_2S$ requires M^+, 299.0980. $[\alpha]_D^{25}$ +12.5° (c=0.40, $CHCl_3$). ν_{max} / cm^{-1} 3500-3200 (O-H), 3100-2920 (C-H), 1636 (C=N), 1314, 1040, 1030, 734 and 722. δ_H (250 MHz, $CDCl_3$) 2.49 (3H, s, $\mathbf{CH_3}$S), 3.77 (1H, dd, J = 3.6, 11.6 Hz, one of $\mathbf{CH_2}$-OH), 4.11 (1H, dd, J = 3.5, 11.6 Hz, one of $\mathbf{CH_2}$-OH), 4.41 (1H, dt, J = 3.5, 7.4 Hz, **CH**-4), 5.48 (1H, d, J = 7.4 Hz, **CH**-5), 7.32 (8H, m, Ar**H**), 7.88 (1H, d, J = 7.7 Hz, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 16.01 (CH_3S), 63.90 (CH_2-OH), 77.35 (**C**H-4), 82.19 (**C**H-5), 123.77 (Ar**C**H), 124.62 (Ar**C**H), 124.93 (Ar**C**H), 125.73 (Ar**C**H), 128.29 (Ar**C**H), 128.81 (Ar**C**H), 130.19 (Ar**C**H), 131.20 (Ar**C**H), 140.56 (Ar**C**), 140.95 (Ar**C**), 151.97 (Ar**C**), 163.61 (**C**-2). *m/z* (EI) 299 (M^+, 23%), 284 (23), 166 (27), 151 (100), 149 (37), 91 (73), 77 (48).

2-((2'-Methylthio)phenyl)-5-phenyloxazolinyl-4-methylpropenoate (12).

Triethylamine (0.85mL, 6.09mmol) was added to a solution of 2-((2'-methylthio)phenyl)-4-methylhydroxy-5-phenyloxazoline () (1.824g, 6.09mmol) in dry diethyl ether (70mL) under nitrogen with stirring at room temperature. Acryloyl chloride (0.51mL, 6.09mmol) was then added dropwise at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for a further two hours then poured into water (50mL). The ether layer was washed with saturated aqueous sodium bicarbonate solution (30mL) and the aqueous layer extracted using chloroform (3 x 100mL). The combined organic layers were dried over magnesium sulfate, and the solvent removed *in vacuo*. Purification by flash chromatography (60% ether/light petroleum) gave the title compound **12** (1.601g, 74%) as an oil. Found M^+, 353.1103. $C_{20}H_{19}NO_3S$ requires M^+, 353.1086. $[\alpha]_D^{25}$ +16.0° (c=6.00, $CHCl_3$). ν_{max} / cm^{-1} 3100-2920 (C-H), 1712 (C=O), 1277, 1216, 758 and 669. δ_H (250 MHz, $CDCl_3$) 2.46 (3H, s, $\mathbf{CH_3}$S), 4.44 (1H, m, C**H**-4), 4.58 (2H, m, $\mathbf{CH_2}$), 5.41 (1H, d, J = 6.2 Hz, C**H**-5), 5.84 (1H, dd, J = 1.5, 10.3 Hz, $\mathbf{H_b}$), 6.15 (1H, dd, J = 10.3, 17.5 Hz, $\mathbf{H_c}$), 6.42 (1H, dd, J = 1.5, 17.5 Hz, $\mathbf{H_a}$), 7.16-7.44 (8H, m, Ar**H**), 7.91 (1H, d, J = 7.8 Hz, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 15.59 ($\mathbf{CH_3}$S), 55.59 (**C**H-4), 62.08 ($\mathbf{CH_2}$-O), 75.27 (**C**H-5), 123.81 (**C**H), 124.36 (**C**H), 126.83 ($\mathbf{CH_2}$=CH), 126.99 (**C**H), 128.56 (**C**H), 128.67 (**C**H), 128.88 (Ar**C**), 130.60 (**C**H), 131.99 (**C**H), 132.90 (**C**H), 136.95 (Ar**C**), 143.20 (Ar**C**), 165.93 (**C**-2) *m/z* (EI) 353 (M^+, 1%), 184 (21), 169 (33), 166 (27), 136 (100), 108 (65), 77 (30).

Endo (2,2-Dimethyl-1-phenylpropyloxy)bicyclo[2.2.1]hept-6-ene (13) δ_H (250 MHz, $CDCl_3$) 0.96 (9H, s $(\mathbf{CH_3})_3$C), 1.32 (1H, m, one of $\mathbf{CH_2}$), 1.45 (1H, m, one of $\mathbf{CH_2}$), 1.50 (1H, m, one of $\mathbf{CH_2}$), 1.94 (1H, m, one of $\mathbf{CH_2}$), 2.92 (1H, broad, s, bridgehead **H**), 3.04 (1H, m, C**H**-C(O)), 3.32 (1H, broad s, bridgehad **H**), 5.46 (1H, s, C**H**-^{t}Bu), 5.96 (1H, dd, J = 2.8, 5.7 Hz, alkene **H**), 6.22 (1H, dd, J = 3.1, 5.7 Hz, alkene **H**), 7.29 (5H, m, Ar**H**).

Endo (2,2-Dimethyl-1-(2'-pyridyl)propyloxy)bicyclo[2.2.1]hept-6-ene (14) δ_H (250 MHz, $CDCl_3$) 0.99 (9H, s, $(\mathbf{CH_3})_3$C), 1.32 (1H, m, one of $\mathbf{CH_2}$), 1.45 (2H, m, $\mathbf{CH_2}$) 1.91 (1H, m, one of $\mathbf{CH_2}$), 2.90 (1H, broad s, bridgehead **H**), 3.06 (1H, m, C**H**-C(O)), 3.35 (1H, broad s, bridgehead **H**), 5.48 (1H, s, C**H**-^{t}Bu), 5.93 (1H, dd, J = 2.9, 5.7 Hz, alkene **H**), 6.17 (1H, dd, J = 3.0, 5.7 Hz, alkene **H**), 7.16 (1H, m, Ar**H**), 7.27 (1H, m, Ar**H**), 7.65 (1H, m, Ar**H**), 8.57 (1H, m, Ar**H**).

***Endo*-[2-carbo(2-((2'-Methylthio)phenyl)-5-phenyloxazolinyl-4-methyloxy)]-bicyclo[2.2.1]hept-6-ene (15)**. ν_{max} / cm^{-1} 3100-2920 (C-H), 1739 (C=O), 1645, 1436, 1336, 1271, 1175 (C-O), 1039, 736 and 700. δ_H (250 MHz, $CDCl_3$) 1.23 (1H, d, J = 7.0 Hz, one of $\mathbf{CH_2}$-7), 1.39 (1H, m, one of $\mathbf{CH_2}$), 1.45 (1H, m, one of $\mathbf{CH_2}$), 1.89 (1H, m, one of $\mathbf{CH_2}$), 2.46 (3H, s, $\mathbf{CH_3}$S), 2.87 (1H, broad s, bridgehead **H**), 2.96 (1H, m, C**H**-2), 3.18 (1H, broad s, bridgehead **H**), 4.30 (1H, dd, J = 5.6, 10.9 Hz, one of $\mathbf{CH_2}$-O), 4.44 (1H, dd, J = 3.9, 10.9 Hz, one of $\mathbf{CH_2}$-O), 4.50 (1H, m, $\mathbf{CHCH_2}$O), 5.38 (1H, d, J = 6.3 Hz, C**H**-Ph), 5.91 (1H, m, alkene **H**), 6.12 (1H, m, alkene **H**), 7.13-7.41 (8H, m, Ar**H**), 7.92 (1H, d, J = 7.0 Hz, Ar**H**). δ_C (62.5 MHz, $CDCl_3$) 15.74 ($\mathbf{CH_3}$S), 29.10 ($\mathbf{CH_2}$-7), 42.36 (**C**H), 43.21 (**C**H), 45.60 (**C**H), 49.52 ($\mathbf{CH_2}$-3), 65.20 ($\mathbf{CH_2}$-O), 74.46 ($\mathbf{CHCH_2}$O), 82.63 (**C**H-Ph), 123.51 (**C**H), 124.31 (**C**H), 125.57 (**C**H), 128.34 (**C**H), 128.75 (**C**H), 130.34 (**C**H), 131.22 (**C**H), 132.28 (**C**H), 135.75 (Ar**C**), 137.71 (**C**H), 140.23 (Ar**C**), 141.33 (Ar**C**), 163.45 (**C**=N), 174.52 (**C**=O)

Allyl (2-pyridyl) ether (20). Sodium (1.04g, 45.2mmol) was added to allyl alcohol (10.0mL, 147mmol) at room temperature with stirring. When all traces of sodium had reacted (ca. one hour) 2-bromopyridine (2.16mL, 22.6mmol) was added with stirring. The reaction mixture was heated at 115°C for 18h. then allowed to cool and water (20mL) added. The product was extracted using ether (3x20mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flask chromatography (10% ether/light petroleum) gave the title compound **20** (1.578g, 52%) as a volatile oil with a pungent odour. ν_{max} / cm^{-1} 3100-2870 (C-H), 1650, 1597, 1571, 1475, 1425, 1287, 1008, 927, 779, 737 and 617. δ_H (250 MHz, $CDCL_3$) 4.85 (2H, m, CH_2O), 5.26 (1H, dd, J = 1.6, 10.5 Hz, H_b), 5.40 (1H, dd, J = 1.6, 17.2 Hz, H_a), 6.10 (1H, m, H_c), 6.76 (1H, d, J = 8.4 Hz, ArH), 6.86 (1H, m, ArH), 7.57 (1H, m, ArH), 8.15 (1H, d, J = 5.0 Hz, ArH). δC (62.5 MHz, $CDCl_3$) 66.28 (CH_2O), 111.06 (CH), 116.65 (CH), 117.19 (CH_2=CH), 133.52 (CH), 138.43 (CH), 146.72 (CH), 163.33 (ArC).

Allyl benzyl ether (17). Sodium hydride (1.28g of a 60% dispersion in mineral oil, 31.89mmol) was added portionwise to a solution of benzyl alcohol (3.00mL, 28.99mmol) in DMF (10mL) at 0°C under N_2 with stirring (CAUTION! Vigorous evolution of H_2). After the initial exothermic reaction had subsided, allyl bromide (2.51mL, 28.99mmol) was added dropwise at 0°C with stirring. After stirring at 0°C for one hour, the mixture was allowed to warm to room temperature and stirred for a further 24h. The reaction mixture was then poured into water (100mL), and the product extracted using ether (3x100mL). The ether fractions were then washed with saturated sodium bicarbonate (100mL), brine (100mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*, to give the title compound **17** (2.79g, 65%) as an oil. ν_{max} / cm^{-1} 3100-2850 (C-H), 1723 (C=C), 1590, 1570, 1493, 1454, 1272, 1070, 991, 749 and 699. δ_H (250 MHz, $CDCL_3$) 4.08 (2H, m, OCH_2CH), 4.58 (2H, s, $PhCH_2O$), 5.26 (1H, dd, J = 1.7, 10.1 Hz, H_b), 5.37 (1H, dd, J = 1.7, 17.1 Hz, H_a), 6.01 (1H, m, H_c), 7.37 (5H, m, ArH). δC (62.5 MHz, $CDCl_3$) 71.08 (CH_2), 72.04 (CH_2), 117.13 (CH_2=CH), 127.56 (CH), 127.70 (CH), 128.37 (CH), 134.65 (CH), 138.19 (ArC).

Allyl picolyl ether (21). Sodium hydride (2.25g of a 60% dispersion in mineral oil), 56.05mmol) was added portionwise to a solution of 2-pyridylcarbinol (4.16mL, 43.11mmol) in DMF (25mL) at 0°C under N_2 with stirring (CAUTION! Vigorous evolution of H_2). After the initial exothermic reaction had subsided, allyl bromide (3.70mL, 43.11mmol) was added dropwise at 0°C with stirring. After stirring at 0°C for one hour, the mixture was allowed to warm to room temperature and stirred for a further 24h. The reaction mixture was then poured into water (150mL), and the product extracted using ether (3x150mL). The ether fractions were then washed with saturated sodium bicarbonate (150mL), brine (150mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*, to give the title compound **21** (5.322g, 83%) as an oil. ν_{max} / cm^{-1} 3100-2850 (C-H), 1680, 1591, 1572, 1476, 1436, 1107 (C-O), 1086, 994 and 927. δ_H (250 MHz, $CDCL_3$) 4.13 (2H, m, OCH_2CH), 4.65 (2H, s, $PhCH_2O$), 5.23 (1H, dd, J = 1.6, 10.2 Hz, H_b), 5.35 (1H, dd, J = 1.6, 17.1 Hz, H_a), 5.98 (1H, m, H_c), 7.20 (1H, m, ArH), 7.46 (1H, d, J = 7.8 Hz, ArH), 7.69 (1H, m, ArH), 8.56 (1H, m, ArH). δC (62.5 MHz, $CDCl_3$) 71.55 (CH_2), 72.71 (CH_2), 117.01 (CH_2=CH), 121.03 (CH), 122.03 (CH), 134.18 (CH), 136.31 (CH), 148.79 (ArCH), 158.30 (ArC).

4-Phenoxy-1-butene (30). Sodium hydroxide (0.546g, 13.66mmol) was dissolved in ethanol (25mL) with stirring (requires gentle warming). Phenol (1.071g, 11.4mmol) was then added followed by 4-bromo-1-butene (1.16mL, 11.4mmol) dropwise at room temperature with stirring. The reaction mixture was then heated under reflux for 21hrs. The ethanol was then removed *in vacuo* and the crude product taken up in ether (40mL) and washed with brine (25mL). The aqueous layer was extracted using ether (3x40mL) and

the combined organic layers dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash chromatography (5% ether/light petroleum) gave the title compound **30** (0.885g, 52%) as an oil. ν_{max} / cm^{-1} 3100-2850 (C-H), 1643 (C=C), 1601, 1587, 1497, 1471, 1080 (C-O), 991 and 918. δ_H (250 MHz, $CDCL_3$) 2.55 (2H, q, J = 6.7 Hz, CH_2CH_2CH), 4.02 (2H, t, J = 6.7 Hz, OCH_2CH_2), 5.11 (1H, dd, J = 1.4, 10.9 Hz, H_b), 5.17 (1H, dd, J = 1.4, 17.6 Hz, H_a), 5.90 (1H, m, H_c), 6.92 (3H, m, ArH), 7.27 (2H, m, ArH). δC (62.5 MHz, $CDCl_3$) 33.68 (CH_2CH_2CH), 67.06 (OCH_2CH_2), 114.56 (CH), 116.97 (CH_2=CH), 120.66 (CH), 129.43 (CH), 134.50 (CH), 159.03 (ArC).

4-(Benzyloxy)but-1-ene (34). Sodium hydride (0.933g of a 60% dispersion in mineral oil), 23.32mmol) was added portionwise to a solution of 3-buten-1-ol (1.82mL, 21.20mmol) in THF (25mL) at 0°C under N_2 with stirring (CAUTION! Vigorous evolution of H_2). After the initial exothermic reaction had subsided, benzyl bromide (2.77mL, 23.32mmol) was added dropwise at 0°C with stirring. After stirring at 0°C for one hour, the mixture was allowed to warm to room temperature and stirred for a further 16hrs. Brine (15mL) was then added and the product extracted using ether (3x25mL). The ether fractions were then dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash chromatography (5% ether/light petroleum) gave the title compound **34** (3.416g, 99%) as an oil. ν_{max} / cm^{-1} 3100-2850 (C-H), 1722, 1642, 1597, 1575, 1496, 1454, 1362, 1274, 1101 (C-O), 995, 914, 736 and 697. δ_H (250 MHz, $CDCL_3$) 2.38 (2H, q, J = 6.8 Hz, CH_2CH_2CH), 3.53 (2H, t, J = 6.8 Hz, OCH_2CH_2), 4.52 (2H, s, $PhCH_2O$), 5.05 (1H, dd, J = 1.2, 10.1 Hz, H_b), 5.11 (1H, dd, J = 1.2, 17.1 Hz, H_a), 5.83 (1H, m, H_c), 7.31 (5H, m, ArH). δC (62.5 MHz, $CDCl_3$) 34.17 (CH_2CH_2CH), 69.53 (OCH_2CH_2), 72.81 ($PhCH_2O$), 116.28 (CH_2=CH), 127.45 (CH), 127.55 (CH), 128.27 (CH), 135.19 (CH), 138.15 (ArC).

4-(Picolyloxy)-1-butene (31). 3-Buten-1-ol (1.15mL, 13.4mmol) was added to a mixture of potassium hydride (1.29g, 32.2mmol) and THF (30mL) at 0°C with stirring. The mixture was stirred at 0°C for 30mins. then picolyl chloride hydrochloride salt (2.198g, 13.4mmol) was added portionwise. The reaction mixture was heated at reflux for 24h. then allowed to cool and brine (25mL) added. The crude product was extracted using ether (3x30mL), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Purification by flash chromatography (40% ether/light petroleum) gave the title compound **31** (1.491g, 68%) as an oil. ν_{max} / cm^{-1} 3100-2850 (C-H), 1720, 1642, 1591, 1572, 1476, 1436, 1282, 1125 (C-O), 994 and 759. δ_H (250 MHz, $CDCL_3$) 2.43 (2H, m, CH_2CH_2CH), 3.63 (2H, t, J = 6.8 Hz, OCH_2CH_2), 4.65 (2H, s, $PhCH_2O$), 5.07 (1H, dd, J = 1.7, 10.2 Hz, H_b), 5.12 (1H, dd, J = 1.7, 17.2 Hz, H_a), 5.86 (1H, m, H_c), 7.19 (1H, m, ArH), 7.44 (1H, d, J = 7.8 Hz, ArH), 7.69 (1H, m, ArH), 8.55 (1H, d, J = 4.9 Hz, ArH). δC (62.5 MHz, $CDCl_3$) 34.00 (CH_2CH_2CH), 70.12 (OCH_2CH_2), 73.51 ($PhCH_2O$), 116.29 (CH_2=CH), 121.05 (CH), 122.05 (CH), 134.90 (CH), 135.05 (CH), 148.77 (ArCH), 158.52 (ArC).

General procedure for catalytic hydrogenation

To a solution of allyl/homoallyl ether (0.2mmol) in the appropriate solvent (2mL) was added the Crabtree catalyst ($5x10^{-3}$mmol) at room temperature with stirring. The solution was then subjected to hydrogenation (1 atm.) for 17 hrs. The crude product was passed through a pad of flash silica (10% MeOH/ether) to remove metal catalyst then the solvent removed *in vacuo*. The level of conversion was determined by ^1H nmr integration. The ^1H nmr data for the hydrogenation products are listed below.

General procedure for competitive catalytic hydrogenations

To an equimolar mixture of phenyl and pyridyl substrates (0.2mmol) in the appropriate solvent (2mL) was added the transition metal catalyst ($5x10^{-3}$mmol) at room temperature with stirring. The solution was then subjected to hydrogenation at the appropriate pressure for 17 hrs. The crude product was then passed through a pad of flash silica (10% MeOH/ether) to remove metal catalyst then the solvent removed *in vacuo*. The starting material and product distribution was determined by ^{1}H nmr integration. The ^{1}H nmr data for the hydrogenation products are listed below.

^{n}Propyl phenyl ether (18) δ_H (250 MHz, $CDCl_3$) 1.04 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.81 (2H, sextet, J = 7.0 Hz, $CH_3CH_2CH_2$), 3.92 (2H, t, J = 6.6 Hz, $CH_3CH_2CH_2$), 6.92 (3H, m, ArH), 7.27 (2H, m, ArH).

^{n}Propyl (2-pyridyl) ether (22) δ_H (250 MHz, $CDCl_3$) 1.03 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.79 (2H, sextet, J = 7.1 Hz, $CH_3CH_2CH_2$), 4.24 (2H, t, J = 6.7 Hz, $CH_3CH_2CH_2$), 6.72 (1H, m, ArH), 6.83 (1H, m, ArH), 7.55 (1H, m, ArH), 8.14 (1H, m, ArH).

^{n}Propyl benzyl ether (19) δ_H (250 MHz, $CDCl_3$) 0.94 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.64 (2H, sextet, J = 7.0 Hz, $CH_3CH_2CH_2$), 3.43 (2H, t, J = 6.6 Hz, $CH_3CH_2CH_2$), 4.50 (2H, s, $PhCH_2O$), 7.29 (5H, m, ArH).

^{n}Propyl picolyl ether (23) δ_H (250 MHz, $CDCl_3$) 0.96 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.60 (2H, sextet, J = 7.4 Hz, $CH_3CH_2CH_2$), 3.52 (2H, t, J = 6.7 Hz, $CH_3CH_2CH_2$), 4.63 (2H, s, $PyCH_2O$), 7.17 (1H, m, ArH), 7.45 (1H, m, ArH), 7.69 (1H, m, ArH), 8.54 (1H, m, ArH).

Phenyl propanoate (25) δ_H (250 MHz, $CDCl_3$) 1.26 (3H, t, J = 7.6 Hz, CH_3CH_2), 2.59 (2H, q, J = 7.6 Hz, CH_3CH_2), 7.32 (5H, m, ArH).

Benzyl propanoate (26) δ_H (250 MHz, $CDCl_3$) 1.16 (3H, t, J = 7.5 Hz, CH_3CH_2), 2.39 (2H, q, J = 7.5 Hz, CH_3CH_2), 5.12 (2H, s, $PhCH_2O$), 7.35 (5H, m, ArH).

(2-Pyridyl)methyl propanoate (29) δ_H (250 MHz, $CDCl_3$), 1.19 (3H, t, J = 7.4 Hz, CH_3CH_2), 2.45 (2H, q, J = 7.4 Hz, CH_3CH_2), 5.23 (2H, s, $PyCH_2O$), 7.20 (1H, m, ArH), 7.35 (1H, m, ArH), 7.71 (1H, m, ArH), 8.56 (1H, m, ArH).

^{n}Butyl phenyl ether (32) δ_H (250 MHz, $CDCl_3$) 0.97 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.51 (2H, sextet, J = 7.4 Hz, $CH_3CH_2CH_2$), 1.75 (2H, m, $CH_2CH_2CH_2$), 3.96 (2H, t, J = 6.5 Hz, CH_2CH_2O), 6.91 (3H, m, ArH), 7.27 (2H, m, ArH).

^{n}Butyl picolyl ether (33) δ_H (250 MHz, $CDCl_3$) 0.93 (3H, t, J = 7.3 Hz, CH_3CH_2), 1.42 (2H, sextet, J = 7.3 Hz, $CH_3CH_2CH_2$), 1.63 (2H, m, $CH_2CH_2CH_2$), 3.56 (2H, t, J = 6.5 Hz, CH_2CH_2O), 4.63 (2H, s, $PyCH_2O$), 7.31 (1H, m, ArH), 7.81 (1H, m, ArH), 8.39 (1H, m, ArH), 8.68 (1H, m, ArH).

^{n}Butyl benzyl ether (35) δ_H (250 MHz, $CDCl_3$) 0.92 (3H, t, J = 7.4 Hz, CH_3CH_2), 1.40 (2H, m, $CH_3CH_2CH_2$), 1.59 (2H, m, $CH_2CH_2CH_2$), 3.48 (2H, t, J = 6.5 Hz, CH_2CH_2O), 4.50 (2H, s, $PhCH_2O$), 7.34 (5H, m, ArH).

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