Iridium-Catalysed Allylic Substitution: Stereochemical Aspects and Isolation of Ir^{III} Complexes Related to the Catalytic Cycle

Björn Bartels,[a] Cristina García-Yebra,[a] Frank Rominger,[a] and Günter Helmchen*[a]

Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

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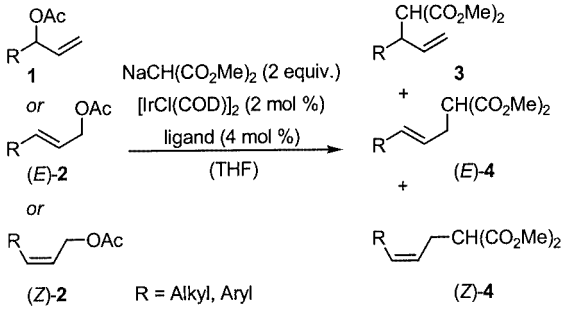
Ir-catalysed allylic alkylations of enantiomerically enriched monosubstituted allylic acetates proceed with up to 87% retention of configuration using $P(OPh)_3$ as ligand. High regio- and enantioselectivity of up to 86% *ee* in asymmetric allylic alkylations of achiral or racemic substrates is achieved with monodentate phosphorus amidites as ligands. Lithium *N*-tosylbenzylamide was identified as a suitable nucleophile for allylic aminations. Of particular importance is the use of lithium chloride as an additive, generally leading to increased enantioselectivities. Two (π-allyl)Ir^{III} complexes were characterised by X-ray crystal structure analysis and spectroscopic data.

Introduction

Asymmetric transition-metal-catalysed allylic substitution is a useful reaction in organic synthesis.[1] The selectivity of this reaction is a function of many factors, for example the metal ion, ligands, nucleophile and substituents of the allyl system. Over the last few years, work has been directed at finding catalysts that favour the formation of branched, chiral products **3** in the substitution of monosubstituted allylic substrates **1** and (*E*)-**2** (Scheme 1). With palladium complexes this is so far only possible for special cases.[2] With Mo- or W-based catalysts, branched products are generally preferred, with higher levels of both regio- and enantioselectivity reported for substrates with R = aryl.[3] It is assumed that in these cases the reactions proceed via π-allyl complexes, which can isomerize[3d] via π−σ−π rearrangement or related processes in such a way that memory of the chiral sense of the stereogenic centre in the branched substrate **1** is lost during the reaction.



Scheme 1. General scheme for the Ir^{I}-catalysed allylic alkylation of monosubstituted allylic acetates

Substitutions catalysed by Rh, Fe or Ru complexes differ from the above as they generally proceed for branched substrates **1** with a high degree of conservation of enantiomeric excess (*cee*). It has been proposed that these reactions proceed via σ-allyl or π-allyl complexes, which isomerize slowly.[4] As a consequence, from enantiomerically enriched substrates **1**, even with achiral ligands enantiomerically enriched products **3** are obtained via reactions proceeding with double inversion.

Not many examples of Ir^{I}-catalysed allylic substitutions have been published so far. In the last few years, it has been shown that catalysts prepared by combining $[IrCl(COD)]_2$ with a strong π-acceptor ligand — for example triphenylphosphite — in situ give rise to excellent regioselectivities in favour of the branched product **3** for both aryl- and alkyl-substituted allylic substrates.[5] In 1997, we described the first enantioselective Ir^{I}-catalysed allylic alkylations of aryl-allyl acetates (*E*)-**2**, which gave high levels of regio- and enantioselectivity in favour of product **3** when the bidentate phosphinooxazoline **L1** (Figure 1) was used as the chiral ligand.[6] Better results were later achieved with monodentate chiral strong π-acceptor ligands.[7] Thus, branched products **3** are obtained in Ir^{I}-catalysed allylic alkylations of both monoaryl- and monoalkylallyl acetates, (*rac*)-**1** and (*E*)-**2**, with ligands such as phosphites and phosphorus amidites [(*R*)-**L2**]. It was also found that Ir^{I}-catalysed allylic alkylations of enantiomerically enriched acetates **1** with achiral ligands occurred with a noticeable "memory effect", i.e. partial conservation of the enantiomeric purity of the starting substrates. For example, a sample of (*R*)-**1** with 91% *ee* furnished (*R*)-**3** with 51% *ee* [R = $(CH_2)_2Ph$].[7a]

[a] Organisch-chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) +49-6221/544-205
E-mail: en4@popix.urz.uni-heidelberg.de

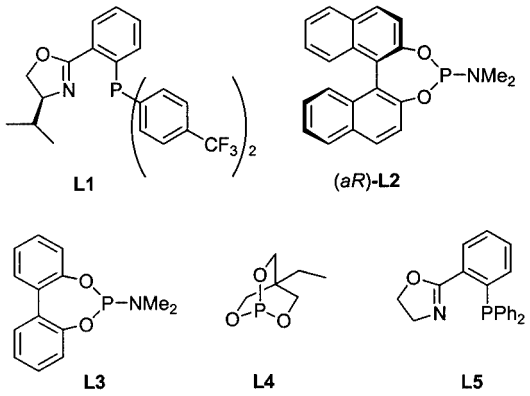


Figure 1. Ligands used in Ir^{I}-catalysed substitutions

This observation led us to consider the formation of π- as well as (σ-allyl)Ir^{III} complexes as intermediates, which undergo slow isomerization.[4d,8]

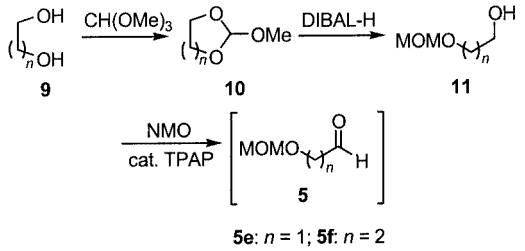
Herein we present a full account of our studies concerning the various factors affecting the course of the Ir^{I}-catalysed allylic alkylation and amination as well as the isolation and full characterization of Ir^{III} complexes related to the proposed intermediate species, in order to contribute to the elucidation of the still unclear mechanisms of these processes.

Results and Discussion

Synthesis of Allylic Substrates

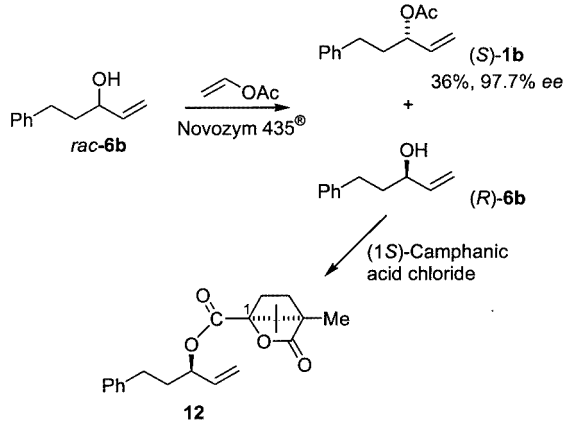
The branched substrates **1** were prepared by reaction of aldehydes **5** with vinylmagnesium bromide and esterification of the resulting alcohols **6**. The linear substrates (*E*)-**2** were obtained by Wittig−Horner−Emmons olefination to give the (*E*)-α,β-unsaturated ester **7** which, after reduction to alcohols **8** and esterification, gave the acetates (*E*)-**2** (Scheme 2).

Substrates **1e**,**f** and (*E*)-**2f** were prepared in a similar way; the requisite aldehydes[9] were not commercially available and were prepared according to the procedure described in Scheme 3, involving formation of the orthoester **10** by reaction of diol **9** with trimethyl orthoformate, reduction of the orthoester with DIBAL-H[10] and, finally, oxidation of the resulting alcohol **11** with NMO/TPAP.[11]



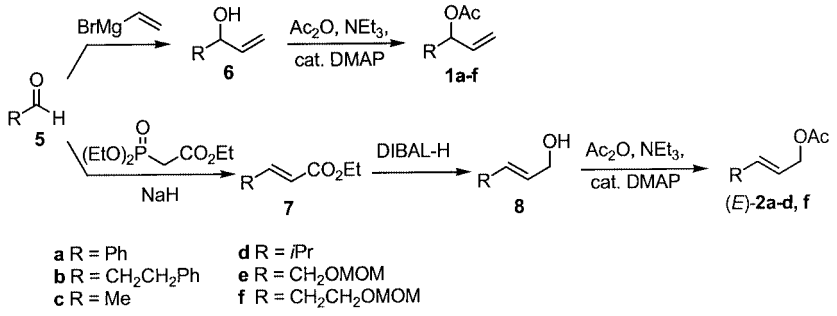
Scheme 3. Synthesis of aldehydes **5**; TPAP: (nPr_4N)[RuO_4]; MOM: methoxymethyl; DMAP: 4-dimethylaminopyridine; NMO: *N*-methylmorpholine *N*-oxide

Enantiomerically pure substrates **1a−c** were prepared either by esterification of commercially available enantiomerically pure alcohols (**6a** and **6c**) or by enzyme (Novozym 435®) catalysed kinetic resolution of *rac*-**6b** with vinyl acetate (**1b**) (Scheme 4).[12] The absolute configuration of (*R*)-**6b** was confirmed by X-ray crystal analysis of the corresponding ester **12** of (1*S*)-camphanic acid (Figure 2).



Scheme 4. Kinetic resolution of the alcohol **6b** by enzyme-catalysed esterification and confirmation of the absolute configuration of the products

Substrates (*Z*)-**2** were prepared as described in Scheme 5. (*Z*)-**2e** was obtained from the commercially available (*Z*)-2-buten-1,4-diol (**13**) via reaction with trimethyl orthoformate, reduction of the resulting orthoester **14**, and subsequent esterification.[10] The synthesis of the homologous alkene (*Z*)-**2f** was performed starting from 3-butyn-1-ol (**16**)



Scheme 2. Synthesis of substrates **1** and (*E*)-**2**; DIBAL-H: Diisobutylaluminium hydride; DMAP: 4-dimethylaminopyridine

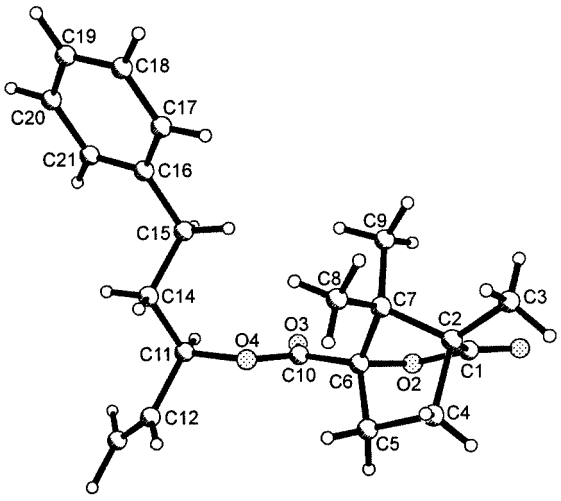
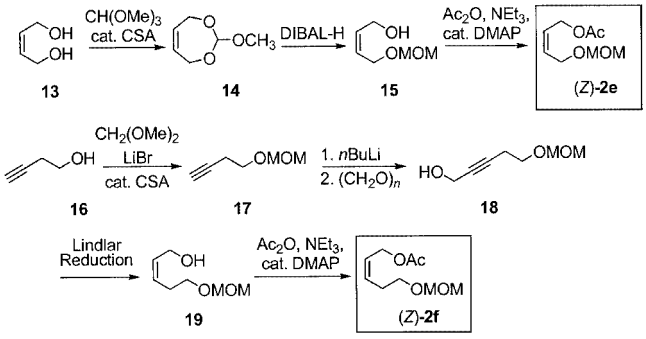


Figure 2. Crystal structure of ester **12** prepared by reaction of the enantiomerically pure alcohol (*R*)-**6b** with (1*S*)-camphanic acid chloride



Scheme 5. Synthesis of substrates (*Z*)-**2e** and (*Z*)-**2f** (CSA: camphorsulfonic acid)

which, after a three-step sequence, afforded the (*Z*)-alkene **19**, which was then esterified to give acetate (*Z*)-**2f**.[13]

Factors Affecting the Rate and Regioselectivity of Ir^I-Catalysed Allylic Alkylation

Allylic alkylations of aryl- and alkyl-substituted allyl acetates **1** and (*E*)-**2** catalysed by $[IrCl(COD)]_2$ and combinations of this complex with PPh_3 or the strong π-acceptor ligand $P(OPh)_3$ were initially investigated. The results are summarized in Table 1.

Concerning the rate of the reaction, the allylic alkylation of linear substrate (*E*)-**2a** was slightly slower than that of the isomeric branched substrate **1a** when $[IrCl(COD)]_2$ without additional ligand was used as catalyst (Table 1, entries 2 and 5). Differences in reaction rates between branched and linear substrates have been observed for the Rh^I-catalysed reaction and they have been attributed to a S_N2' mechanism operating in the oxidative addition step.[4d]

While the combination of $[IrCl(COD)]_2$ with PPh_3 led to slow reactions and low degrees of regioselectivity (entries 6, 9 and 13), the π-acceptor ligand $P(OPh)_3$ gave rise to the shortest reaction times along with optimal yields and regioselectivities in favour of the branched product **3** (entries 1, 4, 7 and 11).[5a][5b] Furthermore, a 1:1 ratio of $P(OPh)_3$ and

Table 1. Allylic alkylation of acetates **1** and (*E*)-**2** catalysed by Ir^I complexes according to Scheme 1[a]

Entry	Substrate	Ligand	L/Ir	*T* [°C]	Time [h]	Yield [%][b] **3** and (*E*)-**4**	Ratio[c] **3**:(*E*)-**4**
1	**1a**	$P(OPh)_3$	1:1	25	3	99	98:2
2	**1a**	–	0	25	3	98	98:2
3	**1a**	PPh_3	1:1	25	3	15	98:2
4	(*E*)-**2a**	$P(OPh)_3$	1:1	25	3	98	98:2
5	(*E*)-**2a**	–	0	65	24	89	32:68
6	(*E*)-**2a**	PPh_3	1:1	65	24	58	64:36
7	**1b**	$P(OPh)_3$	1:1	25	3	99	95:5
8	**1b**	–	0	25	3	66	89:11
9	**1b**	PPh_3	1:1	25	3	0	–
10	**1b**	PPh_3	1:1	55	22	60	83:17
11	(*E*)-**2b**	$P(OPh)_3$	1:1	25	3	99	95:5
12	(*E*)-**2b**	–	0	25	3	0	–
13	(*E*)-**2b**	PPh_3	1:1	25	3	0	–
14	**1b**	$P(OPh)_3$	2:1	25	18	90	95:5

[a] All reactions were carried out in THF on a 0.5 mmol scale (0.125 M) with 2 equiv. of $NaCH(CO_2Me)_2$ and 2 mol % of $[IrCl(COD)]_2$. [b] Isolated yields are given. [c] Determined by GC/MS.

Ir^I gave the best results (compare entries 7 and 14). In this respect, it is significant that only one complex is formed by reaction of $[IrCl(COD)]_2$ with two equivalents ($L/Ir^I = 1:1$) of $P(OPh)_3$ (^{31}P NMR: $\delta = 86.77$ ppm),[14] while an excess of ligand gives rise to the formation of additional species.[5b]

It is also remarkable that while the regioselectivities obtained from the reaction of the branched substrates are generally high, the linear substrates give rise to lower degrees of regioselectivity, with PPh_3 showing a particularly strong "memory effect" (entries 6 and 10).

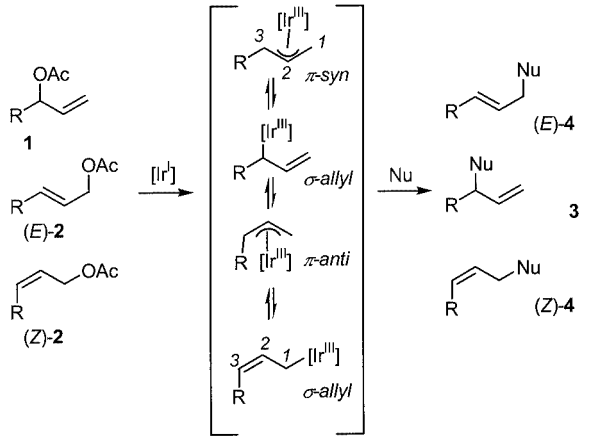
It has been reported that the geometry of the double bond of the linear substrates is also a factor determining the regioselectivity of Ir^I-catalysed allylic substitutions.[15] Using substrates **1e**, **1f** and **2f** (Scheme 1), the dependence on the geometry of the double bond in combination with the influence of σ-acceptor substituents in the substrate was studied. The results (Table 2) clearly show that the allylic alkylations of (*Z*)-**2e** and (*Z*)-**2f** preferentially yield (*Z*)-**4e** and (*Z*)-**4f** as products, respectively. It is also remarkable that the (*Z*)-substrates react distinctly faster than the (*E*)-substrates. Furthermore, it is apparent from Table 1 and 2 that regioselectivity (**3**:**4**) is a function of the substituent at the allylic moiety, giving rise to the order Ph > $(CH_2)_2$Ph > $(CH_2)_2$OMOM > CH_2OMOM, reflecting the ability of the substituent to stabilize a positive charge.

Some of the results described above contribute to the understanding of the mechanism of the Ir^I-catalysed allylic alkylation. Generally, the following steps are to be considered: a) oxidative addition of the substrate to the metal centre and formation of π- and/or σ-allyl complexes, b) isomerization of the intermediates via π–σ–π rearrangement or similar processes, and c) attack of a nucleophile (Scheme 6). If π-allyl complexes are the product determining intermediates, it is expected that cationic character favours attack at the substituted allylic terminus. It is, therefore, clear that the rate and regioselectivity of the nucleo-

Table 2. Influence of the configuration of the double bond of the substrates on the regioselectivity of the substitution[a]

Entry	Substrate	R	*T* [°C]	Time [h]	Yield [%]	Ratio[b] **3**:**4**	*E*/*Z* in **4**[b]
1	**1e**	CH_2OMOM	25	18	91	77:23	99:1
2	(*Z*)-**2e**	CH_2OMOM	24	4	65	0:100	8:92
3	**1f**	CH_2CH_2OMOM	25	18	94	93:7	99:1
4	(*E*)-**2f**	CH_2CH_2OMOM	25	18	95	97:3	99:1
5	(*Z*)-**2f**	CH_2CH_2OMOM	25	4	80	12:88	1:99

[a] All reactions were carried out in THF on a 0.5 mmol scale (0.125 M) with 2 equiv. of $NaCH(CO_2Me)_2$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % $P(OPh)_3$. [b] Determined by GC/MS.



Scheme 6. Ir^I-catalysed allylic substitution of substrates **1** and **2** via σ- and π-allyl intermediates

philic attack would be higher with π-acceptor ligands such as $P(OPh)_3$ and olefins (such as COD) than with σ-donor ligands such as PPh_3.[16] It has been argued that nucleophilic attack on analogous Rh^{III} complexes is determined by the location of the acceptor ligand in the *trans* position to the higher substituted allyl terminus.[17] This argument neglects the fact that due to the strong *trans* influence of both an allyl and a phosphorus-based ligand, these ligands strongly prefer a mutual *cis* disposition. Furthermore, there is no marked influence of the steric bulk of the phosphorus ligand on the regioselectivity.[5b]

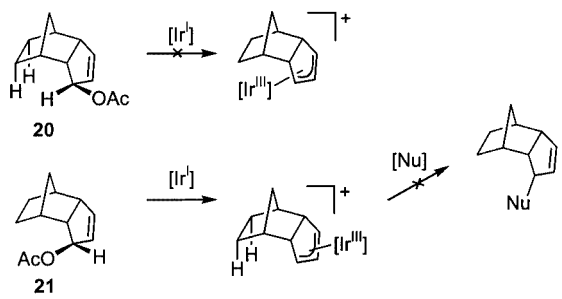
The fact that no (*Z*)-products were obtained from (*E*)-substrates while these are the major products in the allylic alkylation of (*Z*)-substrates is highly significant and is also found in the reaction catalysed by Fe complexes.[4b] As (*E*)-substrates would form *syn* π-allyl intermediates and (*Z*)-substrates *anti* π-allyl intermediates, these results clearly show that the *syn*-*anti* isomerization between these species is a slow process (Scheme 6). Considering a generally close analogy of Ir^I- and Rh^I-catalysed allylic substitutions, it is of interest to note that reactions of isolated *anti* (π-allyl)Rh^{III} complexes with carbon nucleophiles occur at the less substituted terminus of the allylic moiety, giving rise exclusively to the formation of (*Z*)-olefin complexes.[18] On the other hand, there are no facts which would rule out a reaction course via σ-complexes.

Steric Course of the Substitution and Memory Effects

It has already been reported that Rh^I- and Ir^I-catalysed allylic substitutions show a noticeable "memory effect",[4d,7a,19] i.e. enantiomerically enriched branched substrates **1** yield substitution products with retention of configuration and partial conservation of enantiomeric purity. Rather than aiming at high degrees of conservation we were interested in finding conditions that would maximally erode enantiomeric purity in order to achieve asymmetric induction via dynamic kinetic resolution. To this end, the influence of reaction conditions, such as concentration of the nucleophile, temperature, influence of additives and ligand, were studied in allylic alkylations of enantiomerically enriched acetates **1** using $[IrCl(COD)]_2$ combined in situ with achiral ligands $P(OPh)_3$ and **L3**−**L5** as catalysts. The results are summarized in Table 3.

The results allow the following conclusions: (a) phosphorus amidite **L3** gives rise to maximal erosion of enantiomeric purity (entries 7 and 8); (b) the highest degree of conservation of enantiomeric purity is induced by $[IrCl(COD)]_2$ without additional ligand (entry 11); (c) surprisingly, there is almost no influence of the concentration of the nucleophile (cf. entries 1 and 2). It was expected that an increase would lead to a higher degree of conservation of enantiomeric purity because of acceleration of the nucleophilic attack relative to isomerization of allyl complexes; (d) halide ions are known to accelerate the isomerization of allyl complexes via σ-allyl complexes.[20] Indeed, addition of LiCl induces an enhanced degree of racemisation (entries 5, 6 and 8), (e) finally, increase of the reaction temperature also favours racemisation (entry 6).

Concerning the steric course of the process, it was of interest to establish whether the Ir^I-catalysed reactions proceed with double inversion or retention. To this end, reactions with substrates **20** and **21** were investigated (Scheme 7).[21] These substrates do not allow a double inversion process because in **20** oxidative addition to Ir^I and in **21** nucleophilic attack at the (allyl)Ir^{III} intermediate are both prevented by steric hindrance. Indeed, no reaction occurred under reaction conditions typical for allylic alkylations.[22] Control experiments showed that under the same conditions the reaction of $NaCH(CO_2Me)_2$ with cyclopentenyl acetate proceeds to completion. These results demonstrate that the Ir^I-catalysed allylic alkylation proceeds via a double inversion process.



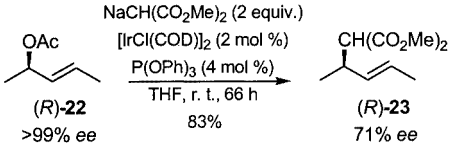
Scheme 7. Ir^I-catalysed allylic substitutions

Table 3. Influence of ligand, reaction conditions and addition of lithium chloride on allylic substitutions of substrates **1a**−**1c**[a]

Entry	Substrate	*ee* [%] of **1** (*conf.*)	Ligand	Time [h]	c_{Nu} [M]	Additive (equiv.)	Yield [%]	Ratio **3**:(*E*)-**4**[b]	*ee* [%][b] (*conf.*)	*cee* [%][c]
1	**1b**	95 (*R*)	$P(OPh)_3$	3	0.250	–	95	95:5	54 (*R*)	57
2[d]	**1b**	95 (*R*)	$P(OPh)_3$	3	0.125	–	79	96:4	60 (*R*)	63
3[d]	**1b**	98 (*S*)	$P(OPh)_3$	3	0.125	–	98	96:4	65 (*S*)	66
4	**1b**	91 (*R*)	$P(OPh)_3$	3	0.250	–	97	95:5	51 (*R*)	56
5	**1b**	91 (*R*)	$P(OPh)_3$	3	0.250	LiCl (1.0)	71	93:7	49 (*R*)	54
6[e]	**1b**	98 (*S*)	$P(OPh)_3$	3	0.250	LiCl (1.0)	91	91:9	38 (*S*)	39
7	**1b**	91 (*R*)	**L3**	3	0.250	–	98	99:1	39 (*R*)	43
8	**1b**	91 (*R*)	**L3**	3	0.250	LiCl (1.0)	61	79:21	34 (*R*)	37
9	**1b**	98 (*S*)	**L4**	18	0.250	–	99	84:16	70 (*S*)	71
10	**1b**	91 (*R*)	**L5**	3	0.250	–	93	53:47	66 (*R*)	73
11	**1b**	98 (*S*)	–	18	0.250	–	67	91:9	85 (*S*)	87
12	**1a**	94 (*R*)	$P(OPh)_3$	3	0.250	–	98	95:5	56 (*S*)	60
13	**1c**	99.8 (*R*)	$P(OPh)_3$	3	0.250	–	91	95:5	85 (*R*)	85

[a] All reactions were carried out in THF at a 0.5 mmol scale (0.125 M) with 2 mol % $[IrCl(COD)]_2$ and 4 mol % ligand, at room temperature. [b] Determined by HPLC (entries 1−12) or GC (entry 13). [c] Retention or *cee* (conservation of enantiomeric excess) is defined as [*ee*(product)/*ee*(substrate)]×100. [d] Ratio substrate/nucleophile 1:1. [e] Temperature: 50 °C.

To gain further insight, the alkylation of the symmetrically substituted acetate **22** was studied (Scheme 8).[7a] In this reaction enantiomerically pure (*R*)-**22** gave the product (*R*)-**23** with 71% *ee*.



Scheme 8. Allylic substitution using a substrate with a potentially symmetric (π-allyl)Ir^{III} intermediate

This result rules out the intermediacy of a symmetric (π-allyl)Ir^{III} complex or a fast dynamic equilibrium between isomeric complexes, as is typical in palladium chemistry. Possible intermediates (Figure 3) are a σ-complex **A**, formed by direct oxidative addition with inversion, or a corresponding π-complex **B** with a nonsymmetric ligand sphere. A third type of intermediate conceivable is a *nondynamic* (σ+π)-allyl complex **C** formed by S_N2' attack of an Ir^I species. Complexes of this type have been proposed for Rh^I-catalysed allylic substitutions which proceed with almost complete conservation of enantiomeric purity.[4d] In principle, proposals **B** and **C** are identical as they are simply different ways of describing a nonsymmetric π-allyl complex. Assessing such intermediates is fairly straightforward

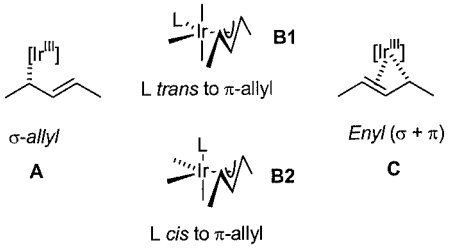


Figure 3. Possible intermediates in the allylic substitution of acetate (*R*)-**22**

for tetracoordinate planar Pd complexes.[23] However, for octahedral Ir^{III} or Rh^{III} complexes the *trans* disposition of an allyl and a phosphorus ligand, i.e. **B1**, is destabilised by their strong *trans* influence.[24] A complex **B2** with *cis* disposition of these ligands is expected to be more stable. Rescue of the argument, i.e. control of the substitution via the trans effect operating in **B1**, would require further assumption of a dynamic system with strong *kinetic* preference for attack of a nucleophile at the *trans* complex **B1**.

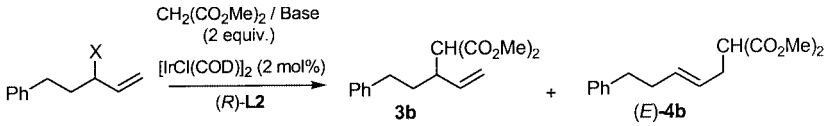
Also conceivable is a reaction via a (π-allyl)metal complex with *syn-anti* configuration of the allyl ligand. According to precedents in Pd-catalysed allylic substitutions, such a complex might react preferentially at the terminus carrying the *anti* substituent.[25] In view of the results for the Ir^I-catalysed allylic substitution of monosubstituted (*Z*)-substrates (vide infra), i.e. preferential formation of linear product, this possibility appears unlikely.[15]

Asymmetric Catalysis

The results in Table 3 show that isomerization among the various intermediate species is fastest with phosphorus amidites as ligands and, therefore, these appeared particularly suited for asymmetric Ir^I-catalysed allylic substitutions. In preliminary experiments we found that branched substrates yield higher degrees of enantio- as well as regioselectivity than linear substrates. Accordingly, reactions with branched substrates were studied preferentially. Using (*R*)-**L2** as the chiral ligand, the dependence of the enantioselectivity on the reaction conditions and substrate structure were investigated. These results are displayed in Table 4.

The ratio of ligand to iridium is an important parameter. In analogy to the earlier finding (Table 1), a 1:1 ratio was optimal (compare entries 2−4). In view of the previous discussion concerning allylic intermediates it is significant that a decrease of temperature leads to a lowering of enantioselectivity (cf. entries 2, 5 and 6). This is probably caused by a slow isomerization of intermediary allyl complexes. A further aspect to take into account is the influence of the

Table 4. Variation of reaction parameters in asymmetric allylic alkylations using (*R*)-**L2** as chiral ligand[a]



1b, X = OAc
24b, X = Cl
25b, X = OCO_2Et
26b, X = $PO(OEt)_2$

Entry	X	Solvent	Base	Ratio P/Ir	Additive[b]	*T*	Time	Yield [%][c]	**3**:(*E*)-**4**[d]	*ee* of **3** [%] (*R*)[e]
1	OAc	THF	NaH	0	–	room temp.	3 h	66	89:11	–
2	OAc	THF	NaH	1	–	room temp.	3 h	92	99:1	69
3	OAc	THF	NaH	2	–	room temp.	3 h	66	99:1	68
4	OAc	THF	NaH	4	–	room temp.	3 h	5	–[f]	–[f]
5	OAc	THF	NaH	1	–	0 °C	6 h	74	99:1	47
6	OAc	THF	NaH	1	–	65 °C	1 h	98	98:2	68
7	Cl	THF	NaH	1	–	room temp.	3 h	88	60:40	0
8	OCO_2Et	THF	NaH	1	–	room temp.	3 h	47	85:15	25
9	$OPO(OEt)_2$	THF	NaH	1	–	room temp.	3 h	41	82:18	0
10	OAc	ether	NaH	1	–	room temp.	3 d	65	99:1	25
11	OAc	toluene	NaH	1	–	room temp.	3 d	91	98:2	0
12	OAc	CH_2Cl_2	NaH	1	–	room temp.	3 d	10	99:1	53
13	OAc	THF	*n*BuLi[g]	1	–	room temp.	3 h	30	98:2	60
14	OAc	THF	*n*BuLi	1	$ZnCl_2$	room temp.	7 d	91	86:14	3
15	OAc	THF	Cs_2CO_3[h]	1	–	room temp.	3 h	76	99:1	29
16	OAc	THF	BSA[i]	1	–	room temp.	5 d	13	–[f]	20
17	OAc	THF	NaH	1	NMe_4Br	room temp.	3 h	95	99:1	49
18	OAc	THF	NaH	1	$N(nBu)_4Cl$	room temp.	3 h	15	99:1	25
19	OAc	THF	NaH	1	LiF	room temp.	3 h	99	99:1	58
20	OAc	THF	NaH	1	LiCl	room temp.	3 h	83	99:1	86
21	OAc	THF	NaH	1	LiCl	50 °C	3 h	97	99:1	80
22	OAc	THF	NaH	1	LiBr	room temp.	3 h	69	98:2	83

[a] Nucleophiles were prepared by treatment of $CH_2(CO_2Me)_2$ with base over a period of 30 min at room temperature in THF. [b] One equivalent (relative to substrate) of additive was added before the nucleophile. [c] Isolated yields. [d] Determined by GC/MS. [e] Determined by HPLC. [f] Not determined. [g] The nucleophile was generated by addition of *n*BuLi at −78 °C and keeping the reaction mixture at room temperature for 30 min. [h] The nucleophile was generated by reacting the base with dimethyl malonate in THF for 30 min at reflux temperature. [i] BSA = *N*,*O*-bis(trimethylsilyl)acetamide; KOAc (catalytic quantity) was added to start the reaction.

leaving group on rate, regio- and enantioselectivity (cf. entries 2, 7−9). Substrates with better leaving groups than acetate give rise to very low selectivities. As of now, the best results are obtained with acetates. Of the solvents used, tetrahydrofuran was found to be the most suitable (entries 2, 10−12).

Variation of the cation (entries 13−17) did not lead to an improvement of the enantioselectivity. This was surprising because an improvement had been achieved previously with zinc derivatives in a closely related reaction.[7b] In contrast, addition of *anhydrous* lithium bromide or lithium chloride resulted in an improved regio- and enantioselectivity (up to 86% *ee*) (entries 20−22).

Using the reaction conditions optimized for **1b**, allylic substitutions with a set of systematically varied substrates were investigated (Table 5). In every case addition of LiCl led to markedly improved enantioselectivities; this is probably due to an acceleration of the isomerization of the intermediary allyl complexes. A most surprising result was the low enantioselectivity obtained with the phenyl derivative **1a**. It is quite clear that further progress in this area will depend on establishing conditions for further enhanced rates of isomerization of allylic intermediates.

Ir^I-Catalysed Allylic Amination

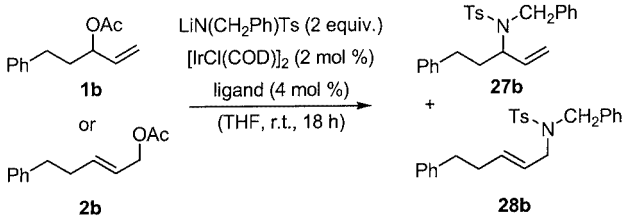
Ir^I-Catalysed allylic aminations have so far only been described for amines as nucleophiles.[15] These reactions require polar solvents and/or high concentration and relatively high temperature. We have now found that lithium *N*-tosylbenzyl amide, already successfully employed in Rh^I-catalysed allylic aminations,[19a,26] reacts under the conditions typical for malonates (Scheme 9). Some preliminary results obtained in allylic aminations of both branched and linear substrates with this nucleophile are presented here (Table 6). With triphenylphosphite as ligand, only moderate yields and regioselectivities were obtained in the amination of substrate **1b** (entry 1). With the chiral phosphorus amidite (*R*)-**L2** as ligand (entries 2−3) yield (up to 97%) and regioselectivity (up to 99:1) were improved for the branched

Table 5. Asymmetric allylic substitutions with substrates **1a**−**f** using (*aR*)-**L2** as chiral ligand[a]

Entry	Substrate	R	Additive[b]	Time [h]	Yield [%]	Ratio[c] **3**:(*E*)-**4**	*ee* [%][d] (*config.*)
1	**1c**	Me	−	3	99	95:5	31 (*R*)
2	**1c**	Me	LiCl	3	99	94:6	57 (*R*)
3	**1a**	Ph	−	3	98	98:2	8 (*S*)
4	**1a**	Ph	LiCl	3	97	98:2	4 (*R*)
5	**1b**	CH_2CH_2Ph	−	3	92	98:2	69 (*R*)
6	**1b**	CH_2CH_2Ph	LiCl	3	83	99:1	86 (*R*)
7	**1d**	*i*Pr	−	48	41	99:1	66 (*R*)
8	**1d**	*i*Pr	LiCl	48	31	99:1	74 (*R*)
9	**1e**	CH_2OMOM	−	3	93	94:6	49 (*R*)
10	**1e**	CH_2OMOM	LiCl	3	90	95:5	78 (*R*)
11	**1f**	CH_2CH_2OMOM	−	3	94	99:1	31 (*R*)
12	**1f**	CH_2CH_2OMOM	LiCl	3	78	98:2	70 (*R*)

[a] All reactions were carried out in THF at 25 °C on a 0.5 mmol scale [0.125 M] with 2 equiv. $NaCH(CO_2Me)_2$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % (*R*)-**L2**; a general procedure (II) for the Ir^I-catalysed allylic alkylation is described in the Exp. Sect. (see below). [b] One equivalent (relative to substrate) of additive was added before addition of the nucleophile. [c] Determined by GC/MS. [d] Determined by HPLC or GC (for details see Exp. Sect.).

product **27b**. Further work is required in order to improve the enantioselectivity of this reaction.



Scheme 9. Ir^I-catalysed allylic amination of (*rac*)-**1b** and (*E*)-**2b**

Table 6. Ir-catalysed allylic amination of acetates **1b** and (*E*)-**2b**[a]

Entry	Substrate	Ligand	Yield [%]	Ratio **27**:**28**[b]	*ee* [%][b] (*config.*)
1	**1b**	$P(OPh)_3$	47	77:23	−
2	**1b**	(*R*)-**L2**	97	99:1	11 (*S*)
3	(*E*)-**2b**	(*R*)-**L2**	47	85:15	13 (*S*)

[a] The reaction was carried out on a 0.5 mmol scale in THF (0.1 M) (18 h, room temp.), with 2 equiv. of $LiN(CH_2Ph)Ts$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % ligand. [b] Determined by HPLC.

Characterization of Ir^I and Ir^{III} Complexes Related to the Catalytic Cycle

Both Ir^I- and σ- or (π-allyl)Ir^{III} complexes are expected to participate in the catalytic process. Therefore, the isolation and structural characterization of such complexes is of great interest. We have prepared a variety of these compounds by stoichiometric reactions of the type comprising the catalytic cycle.

A Chiral Ir^I Complex Containing a Chiral Phosphorus Amidite

Reaction of ligand **L** with complex $[IrCl(COD)]_2$ proceeds with cleavage of the chloride bridges to give monomeric complexes of the type [IrCl(COD)L].[27] Thus, with the chiral ligand (*R*)-**L2**, the complex [IrCl(COD){(*R*)-**L2**}] (**29**) was prepared and fully characterised by NMR spectroscopy and X-ray diffraction. The crystal structure of **29** together with a selection of bond lengths is shown in Figure 4.

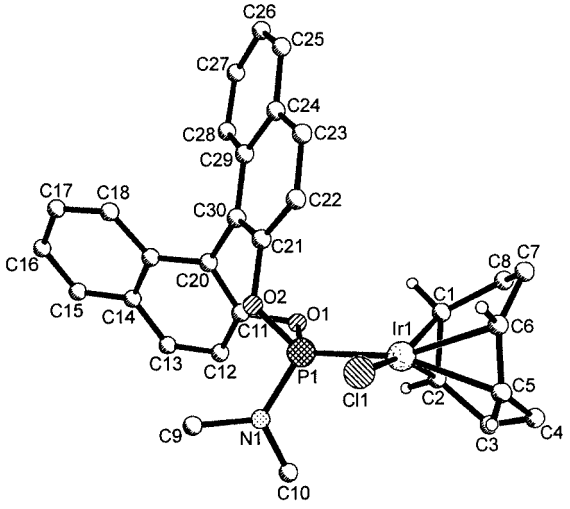


Figure 4. X-ray structure of complex **29**; selected bond lengths (Å): Ir(1)−C(1) 2.114(6), Ir(1)−C(2) 2.118(6), Ir(1)−C(5) 2.222(5), Ir(1)−C(6) 2.222(5), Ir(1)−P(1) 2.2363(13), Ir(1)−Cl(1) 2.358(1), C(1)−C(2) 1.434(8), C(5)−C(6) 1.371(8)

As expected, the coordinated double bond [C(1)-C(2)] *trans* to the chloro ligand is noticeably longer than that [C(5)-C(6)] *trans* to the phosphorus due to the greater *trans* influence of the phosphorus ligand, which is translated into a weakening of the Ir−C(5,6) bonds and a stronger C(5)-C(6) double bond character.

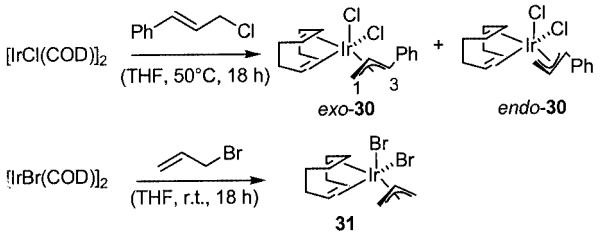
Preparation of (π-Allyl)Ir^{III} Complexes

Oxidative addition is a necessary step in the catalytic process. Therefore, we attempted to generate the corresponding (allyl)Ir^{III} intermediates by direct reaction of al-

lyl acetates with the Ir^I precursors $[IrCl(COD)]_2$ or complexes [IrCl(COD)(L)]. Surprisingly, despite long reaction times and a large excess of the allyl acetate, the expected oxidative addition reaction, which proceeds readily in palladium chemistry,[1c] did not take place here.

We observed that addition of the nucleophile $NaCH(CO_2Me)_2$ to a solution of the catalyst generally produced a change of colour from pale orange to pale yellow. This seemed to indicate that the true catalyst is produced by reaction with the nucleophile. Accordingly, the stoichiometric reaction of $[IrCl(COD)P(OPh)_3]$,[14] formed by treatment of $[IrCl(COD)]_2$ with triphenylphosphite (1:2), with $NaCH(CO_2Me)_2$ (1 equiv.) was explored. The $^{31}P\{^1H\}$ NMR spectrum of the mixture, recorded in $[D_8]$THF after one hour at room temperature, showed a singlet (δ = 86.3 ppm), corresponding to the initial complex, and two sets of doublets of which one (δ = 124.5 and 81.4 ppm, $^3J_{P,P}$ = 74 Hz) was identified as belonging to the previously reported orthometallation product $[Ir\{\eta^2\text{-}(P,C)\text{-}P(OC_6H_4)(OPh)_2\}(COD)\{P(OPh)_3\}]$.[14] The second set of doublets (δ = 104.3 and 85.1 ppm, $^3J_{P,P}$ = 43 Hz) indicates coordination of two equivalents of ligand per metal centre. Attempts to isolate and characterise this complex were unsuccessful.

Next, the oxidative addition of allyl halides to $[IrCl(COD)]_2$ was studied. The reaction of (*E*)-cinnamyl chloride with $[IrCl(COD)]_2$ and allyl bromide with $[IrBr(COD)]_2$ gave complexes **30** and **31**, respectively, in up to 80% yield (Scheme 10).[28] In the presence of phosphorus-derived ligands such as $P(OPh)_3$ or $P(C_6F_5)_3$ the same compounds were formed, which demonstrates the very strong coordination of COD. Complexes **30** and **31** were fully characterised by spectroscopic methods and X-ray diffraction.



Scheme 10. Oxidative addition of allyl halides to Ir^I complexes

X-ray Crystal Structures of (π-Allyl)Ir^{III} Complexes 30 and 31

Complexes **30** and **31** gave yellow single crystals from dichloromethane/diethyl ether solutions.

The crystal of complex **30** (Figure 5) contains a ca. 1:1 mixture of *endo* and *exo* isomers.[29] As a consequence, the structural data of the allyl moieties are of low precision. The configuration of the complex is as expected on the basis of *trans* influences of the ligands. The *syn* configuration of the allyl ligands is typical for aryl-allyl ligands.

The allyl ligand of complex **31** was found to be in the *exo* disposition. The Ir(1)−C(10) bond [2.321(8) Å] is longer than the Ir(1)−C(12) bond [2.176(8) Å] due to the *trans* influence of the COD double bond C(1)−C(2) (Figure 6). Concerning the bond lengths within the allyl moiety, it is remarkable that the C(10)−C(11) bond [1.36(1) Å] is considerably shorter than the C(11)−C(12) bond [1.46(1) Å], i.e. the allyl ligand is highly unsymmetrical and distorted towards a σ-complex.

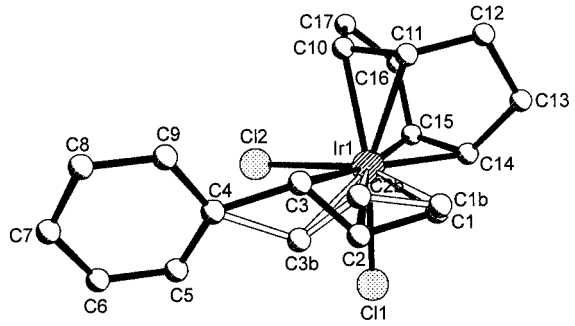


Figure 5. Crystal structure of complex **30**; selected bond lengths (Å) with estimated standard deviations: Ir(1)−C(1)/C(1B) 2.11(3)/2.31(5), Ir(1)−C(2)/C(2B) 2.24(2)/2.31(2), Ir(1)−C(3)/C(3B) 2.45(1)/2.48(1), C(1)−C(2) = 1.44(1), C(1B)−C(2B) 1.44(2), C(2)−C(3) 1.35(1), C(2B)−C(3B) 1.34(2)

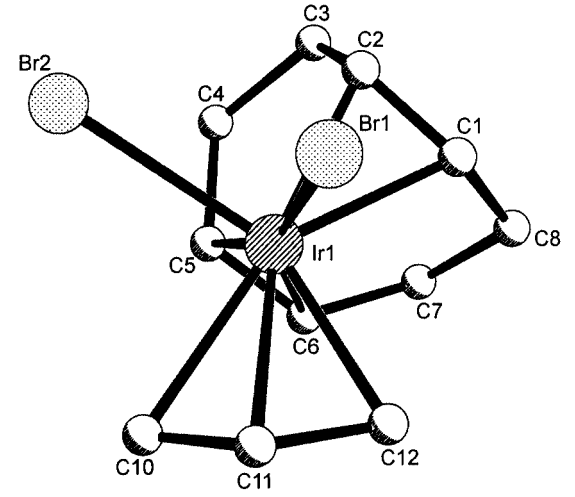


Figure 6. Crystal structure of complex **31**; selected bond lengths (Å) with estimated standard deviations: Ir(1)−C(10) 2.321(8), Ir(1)−C(11) 2.241(9), Ir(1)−C(12) 2.176(8), C(10)−C(11) 1.36(1), C(11)−C(12) 1.46(1), C(1)−C(2) 1.39(1), C(3)−C(4) 1.53(1), C(5)−C(6) 1.38(1), C(7)−C(8) 1.53(1)

Asymmetry in π-allyl systems as a consequence of either an asymmetric set of ligands or an asymmetric substitution pattern of the allyl group is quite common for Ir[30] or Mo[31] complexes and distinctly more pronounced than in Pd complexes.[32] For example, Fryzuk et al. have found a situation similar to that of **30** for the (π-allyl)Ir^{III} complexes $[Ir(\eta^3\text{-}CH_2CHCHMe)(H)\{N(SiMe_2CH_2PPh_2)_2\}]$ and $[Ir(\eta^3\text{-}CH_2CHCHCN)(H)\{N(SiMe_2CH_2PPh_2)_2\}]$, which display σ-character for the substituted allylic carbon and double bond character for the $CHCH_2$ moiety. The authors describe this situation as a $\sigma\text{-}\pi^2$-type allyl ligand.[30d] Many additional examples of such ligands have been

reported.[8e,30b−30d,31] Obviously, the previously discussed "enyl (σ+π)" species proposed as intermediates in Rh^{I}-catalysed allylic substitutions (cf. Scheme 8) belong to this type.[4d]

NMR Spectroscopic Study of (π-Allyl)Ir^{III} Complexes

(π-Allyl)Ir^{III} complexes generally show slow isomerisation compared to π-allyl complexes of the first and second row late transition metals such as Ni, Pd, Fe, Ru and Co.[8,30] In contrast, complexes **30** and **31** display broad peaks in their ^{1}H NMR spectra at room temperature, indicating that dynamic processes are taking place.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **30** at temperatures in the range −60 to −40 °C show a 2:1 ratio of two species which, on the basis of the proton coupling constants, are the *syn*-π-allyl complexes found in the crystal structure (cf. Scheme 10). The ^{1}H NMR spectrum of **30** at 50 °C shows one set of signals as a consequence of fast equilibration; coalescence was found at ca. 0 °C.

For both isomers of complex **30**, the resonances of the allylic protons appear in the range δ = 4−6.5 ppm (^{1}H NMR spectrum at −60 °C). The *syn*-configuration of the allyl ligand is apparent from the values of the coupling constant ($^3J_{2,3}$ = 14 Hz) for both isomers, indicating the *anti*-disposition of 3-H (for numbering see Scheme 10). An unusual feature is a marked downfield shift of 3-H for the minor (δ = 6.33 ppm) relative to the major isomer (δ = 4.93 ppm).

The ^{13}C{^{1}H} NMR spectroscopic data (recorded at −60 °C) were analysed with the help of HMQC and HMBC experiments. Resonances at δ = 40.9 and 42.6 ppm for the methylene carbon atoms (C-1) of the major and minor isomer, respectively, are characteristic of the CH_2 group of (π-allyl)Ir^{III} systems; σ-bound allylic CH_2 groups typically appear in the range δ = 0−25 ppm. Resonances at δ = 110.6 and 102.2 ppm for C-2 of the major and minor isomer, respectively, are also in the range typical for π systems; σ systems display values greater than δ = 130 ppm. The resonances for the substituted carbon (-*C*HPh) appear at δ = 111 and 123 ppm for the major and minor isomers, respectively. The latter value is unusually low compared to other (η^3-$CH_2CHCHPh$)Ir^{III} or (η^3-$CH_2CHCHPh$)Pd complexes.[8d,33]

The rate of interconversion of the isomers of **30** was determined as follows. By recording ^{1}H-^{1}H EXSY spectra at varied mixing times (t_m) at −40 °C, the magnetisation transfer between chosen atoms present in both isomers, denoted as **A** (minor isomer) and **B**, was measured (Figure 7).[34] From the 2D NMR spectra a correlation between the allylic protons in the isomers was chosen to perform the calculations. Applying Equation (1) (I_{ii}, I_{ij} integral values of diagonal and cross-peaks, respectively, X_i molar fraction)[35] to the data summarised in Table 7 a value of k = 4 Hz at −40 °C was determined for the rate constant.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of complex **31** measured at −60 °C show two isomeric species in a 9:1 ratio; these are probably the *endo* and *exo* isomers in analogy to

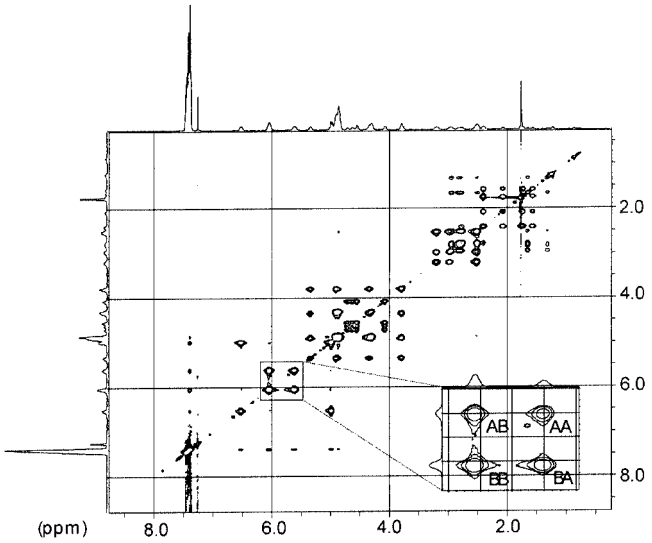


Figure 7. ^{1}H,^{1}H EXSY spectrum of complex **30** recorded at −40 °C ($CDCl_3$, 500.13 MHz); cross peaks chosen for the calculations are enlarged; A and B denote the minor and major isomer, respectively

Table 7. ^{1}H,^{1}H EXSY data for the determination of the isomerisation rate constant k [a]

t_m [ms]	X_A [b]	X_B [b]	I_{AA}	I_{BB}	I_{AB}	I_{BA}	r	k [s^{-1}]
25	0.43	0.57	1.00	1.77	0.065	0.069	23.74	3.37
50	0.42	0.58	1.00	1.88	0.150	0.147	10.32	3.89
100	0.41	0.59	1.00	2.08	0.309	0.302	5.16	3.92

[a] Measured at −40 °C in $CDCl_3$. [b] The molar fraction X_i is given by the formula $X_A = \sqrt{I_{AA}} / \left(\sqrt{I_{AA}} + \sqrt{I_{BB}}\right)$

complex **30**. Coalescence was found at ca. 50 °C. The ^{1}H NMR resonances are found in the expected range. In the ^{13}C{^{1}H} NMR spectrum (−60 °C), one of the CH_2 groups shows resonances in the expected range (δ = 44.6 and 44.9 ppm) while the other appears at unusually low field (δ = 79.7 and 89.6 ppm), for the major and minor isomer, respectively. The latter values are very unusual for (π-allyl)Ir^{III} complexes,[8a−8d,30c,36] although values at similarly low field are known for (π-allyl)Pd complexes.[33] Similar to complex **30**, the resonances of C-2 appear at fairly low field, δ = 114.5 and 107.9 ppm for the minor and major isomer, respectively.

$$k = \frac{1}{t_m} \cdot \ln\frac{r+1}{r-1} \qquad r = \frac{4X_A X_B \cdot \left(I_{AA} + I_{BB}\right)}{\left(I_{AB} + I_{BA}\right) - \left(X_A - X_B\right)^2} \tag{1}$$

Activity of Complex 30 in Stoichiometric Reactions with Nucleophiles and in Catalysis

The low-temperature stoichiometric reaction of complex **30** with dimethyl 2-sodiomalonate as nucleophile in the presence of chiral ligand (*R*)-**L2** was investigated. The ^{1}H and ^{31}P NMR spectra of the reaction mixture, recorded at −60 °C, show fast formation of the branched substitution

product **3a** and the complex {IrCl(COD)[(*R*)-**L2**]} (**29**) in a 1:1 ratio. After workup compound **29** was isolated in 32% yield and **3a** in 64% yield. A GC and HPLC investigation revealed that **3a** had been formed with 99% regioselectivity and 0% *ee*. The lack of enantioselectivity shows that nucleophilic attack at the allyl ligand is faster than coordination of the chiral ligand by displacement of a COD double bond.

Complexes **30** and **31** were found to possess catalytic activity. For example, allylic alkylations of substrates **1** and (*E*)-**2** with $NaCH(CO_2Me)_2$ gave very similar results with catalyst **30**/(*R*)-**L2** (4 mol %) and catalyst $[IrCl(COD)]_2$/(*R*)-**L2** (see Table 8). In agreement with the results obtained in the stoichiometric reaction described above, small amounts of racemic **3a** (HPLC) were formed in allylic alkylations of substrates **1b** and (*E*)-**2b** upon catalysis with **30**/(*R*)-**L2** as a consequence of attack of the nucleophile at the allyl ligand present in complex **30**. In this reaction, complex **29** is also formed, which acts as the catalyst of the process.

Table 8. Allylic alkylations of substrates **1** and (*E*)-**2** catalysed by mixtures of **30** and **L2** or [IrCl(COD)**L2**] (**29**)[a]

Entry	Substrate	Catalyst[b]	Time [h]	Yield [%] **3** and **4**	Ratio **3**:**4**	*ee* [%] of **3** (config.)[c]
1	**1a**	**30/L2** [1:1]	18	85	98:2	9 (*S*)
2	**1a**	[IrCl(COD)**L2**]	3	98	92:8	8 (*S*)
3	(*E*)-**2a**	**30/L2** [1:1]	18	38	95:5	34 (*R*)
4	(*E*)-**2a**	[IrCl(COD)**L2**]	3	99	98:2	37 (*R*)
5[d]	**1b**	**30/L2** [1:1]	3	80	99:1	67 (*R*)
6	**1b**	[IrCl(COD)**L2**]	3	92	98:2	69 (*R*)
7[d]	(*E*)-**2b**	**30/L2** [1:1]	18	12	50:50	40 (*R*)
8	(*E*)-**2b**	[IrCl(COD)**L2**]	3	54	95:5	43 (*R*)

All the reactions were performed at 25 °C in THF with 0.5 mmol of allyl substrate [0.125 M], 1 mmol of $NaCH(CO_2Me)_2$ and 4 mol % of [Ir]. [b] When catalyst [IrCl(COD)**L2**] was used, this was formed in situ by reaction of $[IrCl(COD)]_2$ (2 mol %) with (*R*)-**L2** (4 mol %). [c] Determined by HPLC. [d] Small quantities of **3a** were also formed.

Conclusions

Our results demonstrate that it is possible to achieve modest to high levels of enantioselectivity in Ir^I-catalysed asymmetric alkylations of monoalkylallyl acetates. Presently it is necessary to use racemic, branched allylic derivatives as substrates. Further progress will probably be achieved on the basis of more detailed mechanistic investigations. In particular, further investigations of the structure and dynamic properties of (allyl)Ir^{III} complexes are required.

Experimental Section

General: All reactions were carried out using dry solvents under an argon atmosphere. TLC: Macherey & Nagel Polygram Sil G/UV precoated sheets, treatment with I_2 or aqueous $KMnO_4$ solution for visualization of spots. Column chromatography: Fluka silica gel, grade 60 (0.04−0.063 mm). ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker DRX 200, DRX 300 or DRX 500 instruments. ^1H NMR chemical shifts are relative to residual non-deuterated solvent in $CDCl_3$ (δ = 7.26 ppm) or CD_2Cl_2 (δ = 5.32 ppm). ^{13}C NMR shifts are given relative to the solvents $CDCl_3$ (δ = 77.0 ppm) and CD_2Cl_2 (δ = 53.8 ppm) and ^{31}P NMR shifts are relative to 85% H_3PO_4 (δ = 0.00 ppm). MS: JEOL, JMS-700. FAB: JEOL, JMS-700; matrix: 4-nitrobenzyl alcohol (NBA) or 4-nitrophenyl octyl ether (NPOE). Optical rotation: Perkin−Elmer P 241. GC: Hewlett Packard HP 5890 with Chiraldex γ-CD TA column (30 m × 0.25 mm). GC/MS: Hewlett Packard HP 5890/7972 instrument with a HP 5 column (crosslinked methylsilicon, 25 m × 0.2 mm, helium). HPLC: Hewlett Packard HP 1090 with DAICEL Chiralcel ODH column (25 cm × 0.46 cm) in combination with DAICEL Chiralcel ODH precolumn (5 cm × 0.46 cm). Elemental analyses: Microanalytical laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. The compounds (*aR*)-**L2**,[37] **L5**[38] and $[IrCl(COD)]_2$,[39] were prepared according to published procedures. The allylic esters were prepared by reaction of the corresponding alcohols with acetic anhydride [**1a**,[40] **1b**,[41] **1c**,[42] **1d**,[43] (*E*)-**2a**,[40] (*E*)-**2b**,[44] (*E*)-**2c**,[42]], methyl chloroformate (**25b**)[45] or diethyl chlorophosphate (**26b**). Compounds **3a**,[40] **3c**,[4d,42] **6b**,[12a] **7b**−**8b**,[46] **8d**,[47] **7a**,[48] **7c**−**7f**,[48] **20**−**21**,[21a] and **23**[4d] have been described and characterised previously. The enantiomerically pure allylic acetates (*S*)-**1b**,[12a] (*R*)-**1b**,[12a,49] and **22**[50] were obtained by enzyme-catalysed partial esterification of the corresponding racemic alcohols. Compounds **14** and **15**,[10] and **18**[13] were prepared according to previously published methods. 1-(*S*)-Phenylpropen-2-ol [(*S*)-**6a**], (*R*)-buten-2-ol [(*R*)-**6c**], tetra(*n*-propyl)ammonium perruthenate (TPAP), $[P(NMe_2)_3]$ and **L4** are commercially available.

General Procedure I. Acetylation of the Alcohols: A solution of the alcohol (10 mmol), DMAP (12 mg, 0.10 mmol) and NEt_3 (4.2 mL, 30 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C. Freshly distilled Ac_2O (1.9 mL, 20 mmol) was added dropwise and the mixture was stirred for 18 h at room temperature. Water (20 mL) was then added and the aqueous layer extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with satd. NH_4Cl solution (20 mL), dried (Na_2SO_4) and concentrated in vacuo. Products were purified by flash chromatography.

1-Methoxymethoxymethylallyl Acetate (1e): Crude **1e** was prepared according to general procedure I from alcohol **6e** (740 mg, 5.6 mmol) and was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 8:1). Yield: 58% (570 mg). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.10 (s, 3 H, $COCH_3$), 3.36 (s, 3 H, CH_3OCH_2), 3.63−3.67 [m, 2 H, $CH_2CH(OAc)$], 4.63 (s, 2 H, OCH_2O), 5.26 [ddd, $^2J_{H,H}$ = 1.1, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 10.7 Hz, 1 H, *syn*-(=CH_2)], 5.34 [ddd, $^2J_{H,H}$ = 1.1, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 17.3 Hz, 1 H, *anti*-(=CH_2)], 5.44−5.48 [m, 1 H, CH(OAc)], 5.83 (ddd, $^3J_{H,H}$ = 6.3, $^3J_{H,H}$ = 10.7, $^3J_{H,H}$ = 17.3 Hz, 1 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.9 ($COCH_3$), 55.1 (CH_3OCH_2), 68.4 [CH_2CH(OAc)], 73.0 [CH(OAc)], 96.2 (OCH_2O), 117.9 (=CH_2), 133.0 (=CH), 170.0 (C=O) ppm. MS (CI, isobutane): *m*/*z* (%) = 175 (10) [M^+ + 1], 143 (90) [M^+ − OCH_3], 113 (100) [M^+ − OMOM]. HRMS (EI) for $C_7H_{11}O_3$ [M^+ − OCH_3]: calcd. 143.0708; found 143.0685.

1-(2-Methoxymethoxyethyl)allyl Acetate (1f): Crude **1f** was prepared according to general procedure I from alcohol **6f** (1.5 g, 10.3 mmol) and purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 6:1). Yield: 86% (1.7 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.85−1.99 [m, 2 H, CH_2CH(OAc)], 2.07 (s, 3 H, CH_3CO), 3.35 (s, 3 H, CH_3OCH_2), 3.56 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, MOMOCH_2), 4.60 (s, 2 H,

CH_3OCH_2), 5.19 [ddd, $^2J_{H,H}$ = 1.1, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 10.5 Hz, 1 H, *syn*−(=CH_2)], 5.27 [ddd, $^2J_{H,H}$ = 1.1, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 17.2 Hz, 1 H, *anti*−(=CH_2)], 5.80 (ddd, $^3J_{H,H}$ = 6.5, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 17.2 Hz, 1 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 21.0 (COCH_3), 34.1 [CH_2CH(OAc)], 55.0 (CH_3OCH_2), 63.4 (MOMOCH_2), 71.8 [CH(OAc)], 96.3 ($CH_3OCH_2OCH_2$), 116.7 (=CH_2), 136.0 (=CH), 170.0 (C=O) ppm. $C_9H_{16}O_4$ (188.22): calcd. C 57.43, H 8.57; found C 57.23, H 8.58.

5-Phenylpent-2-enyl Acetate [(*E*)-2b]: Crude **2b** was prepared according to general procedure I from alcohol **8b** (6.0 g, 37.0 mmol) and purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 97:3). Yield: 83% (6.3 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.08 (s, 3 H, $COCH_3$), 2.41 (dt, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 8.1 Hz, 2 H, $PhCH_2CH_2$), 2.74 (br. t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $PhCH_2$), 4.54 (dd, $^4J_{H,H}$ = 0.9, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH_2OAc), 5.58−5.89 (m, 2 H, =CH), 7.19−7.34 (m, 5 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.8 (COCH_3), 33.9 (CH_2), 35.2 (CH_2), 64.1 (CH_2OAc), 124.4 (=$CHCH_2OAc$), 126.1 (Ph), 128.2 (Ph), 128.3 (Ph), 135.2 (CH=$CHCH_2OAc$), 141.4 (Ph), 170.6 (C=O) ppm. $C_{13}H_{16}O_2$ (204.27): calcd. C 76.44, H 7.90; found C 76.26, H 7.85.

4-Methylpent-2-enyl Acetate [(*E*)-2d]: Crude **2d** was prepared according to general procedure I from alcohol **8d** (4.6 g, 46.5 mmol) and purified by flash chromatography (silica gel, petroleum ether/diethyl ether 95:5). Yield: 89% (5.9 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.00 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 2.06 (s, 3 H, $COCH_3$), 2.31 [br. sext., $^3J_{H,H}$ = 7.0 Hz, 1 H, $CH(CH_3)_2$], 4.50 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH_2OAc), 5.50 (ddt, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 15.5 Hz, 1 H, =$CHCH_2OAc$), 5.74 (ddt, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 6.2, $^3J_{H,H}$ = 15.5 Hz, 1 H, CH=$CHCH_2OAc$) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 21.0 (COCH_3), 22.0 (two CH_3), 30.7 [$CH(CH_3)_2$], 65.4 (CH_2OAc), 120.9 ($CHCH_2OAc$), 143.2 (CH=$CHCH_2OAc$), 170.9 (C=O) ppm. $C_8H_{14}O_2$ (142.20): calcd. C 67.57, H 9.92; found C 67.69, H 10.07.

(*E*)-5-Methoxymethoxypent-2-enyl Acetate [(*E*)-2f]: Crude (*E*)-**2f** was prepared according to general procedure I from alcohol **8f** (1.2 g, 8.2 mmol) and purified by flash column chromatography (silica gel, petroleum ether/diethyl ether 5:1). Colourless oil. Yield: 97% (1.5 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.06 (s, 3 H, $COCH_3$), 2.37 (dt, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 12.1 Hz, 2 H, MOMOCH_2CH_2), 3.35 (s, 3 H, CH_3O), 3.58 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, $MOMOCH_2$), 4.51 (dd, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 6.2 Hz, 2 H, CH_2OAc), 4.62 (s, 2 H, CH_3OCH_2), 5.61−5.72 (m, 1 H, CH), 5.74−5.85 (m, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.8 (COCH_3), 32.5 ($MOMOCH_2CH_2$), 55.0 (CH_3O), 64.8 (MOMOCH_2 or CH_2OAc), 66.6 (MOMOCH_2 or CH_2OAc), 96.2 (CH_3OCH_2), 125.7 (CH), 132.2 (CH), 170.6 (C=O) ppm. $C_9H_{16}O_4$ (188.22): calcd. C 57.43, H 8.57; found C 57.21, H 8.56.

(*Z*)-4-Methoxymethoxybut-2-enyl Acetate [(*Z*)-2e]: Crude (*Z*)-**2e** was prepared from alcohol **15** (6.8 g, 51.8 mmol) according to general procedure I and purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 6:1). Colourless oil. Yield: 69% (6.2 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.03 (s, 3 H, CH_3CO), 3.30 (s, 3 H, OCH_3), 4.14 (d, $^3J_{H,H}$ = 5.7 Hz, 2 H, MOMOCH_2), 4.60 (s, 2 H, CH_3OCH_2), 4.63 (d, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2OAc), 5.62−5.80 (m, 2 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.7 (CH_3CO), 55.2 (OCH_3), 60.1 (CH_2OAc), 62.6 (MOMOCH_2), 95.6 (CH_3OCH_2), 126.7, 130.2 (=CH), 170.7 (C=O) ppm. MS (EI): *m*/*z* (%) = 174 (1) [M^+], 129 (8) [$M^+ - CH_2OCH_3$], 99 (6) [$M^+ - CH_2OCH_3 - CH_2O$], 85 (32) [$M^+ - CH_2OCH_3 - CO_2$], 45 (100) [$CH_2OCH_3^+$]. HRMS (EI) - for $C_6H_9O_3$ [$M^+ - CH_2OCH_3$]: calcd. 129.0552; found 129.0557.

(*Z*)-5-Methoxymethoxypent-2-enyl Acetate [(*Z*)-2f]: Crude (*Z*)-**2f** was prepared from alcohol **19** (5.0 g, 34.2 mmol) according to general procedure I and purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 9:1). Colourless oil. Yield: 77% (4.9 g). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.03 (s, 3 H, CH_3CO), 2.38 (dt, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 6.6 Hz, 2 H, MOMOCH_2CH_2), 3.32 (s, 3 H, OCH_3), 3.53 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, MOMOCH_2), 4.58 (s, 2 H, CH_3OCH_2), 4.60 (d, $^3J_{H,H}$ = 5.6 Hz, 2 H, CH_2OAc), 5.52−5.76 (m, 2 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 20.9 (CH_3CO), 28.1 (MOMOCH_2CH_2), 55.1 (OCH_3), 60.2 (CH_2OAc), 66.8 (MOMOCH_2), 96.3 (CH_3OCH_2), 125.4, 131.1 (=CH), 170.8 (C=O) ppm. $C_9H_{16}O_4$ (188.22): calcd. C 57.43, H 8.57; found C 57.27, H 8.72.

General Procedure II. Ir^I-Catalysed Allylic Alkylation: A solution of $[IrCl(COD)]_2$ (6.7 mg, 0.01 mmol) in THF (2 mL) was treated with substrate (0.5 mmol) and then ligand (0.02 mmol). The resulting solution was stirred for 5 min. If the reaction was run with additive, this was added now (0.5 mmol) and the solution stirred for a further 5 min. After that, a freshly prepared solution of dimethyl 2-sodiomalonate, prepared by suspending sodium hydride (24 mg, 1.0 mmol) in THF (2 mL) and dropwise addition of dimethyl malonate (115 μL, 1.0 mmol), was added. The mixture was stirred under the stated reaction conditions, then water (4 mL) was added and the mixture extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with a satd. NH_4Cl solution (10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash column chromatography to give substitution products **3** and **4** as colourless oils.

2-(1-Phenethylallyl) Dimethylmalonate (3b): Compound **3b** was obtained by allylic alkylation of substrate **1b** (535 mg, 2.6 mmol) according to general procedure II [ligand: $P(OPh)_3$, reaction time: 3 h, room temperature]. After purification (silica gel, petroleum ether/ethyl acetate 97:3), a 95:5 mixture of **3b** and **4b** was obtained. Yield: 91% (650 mg). $[\alpha]_D^{20}$ = 11.4 (*c* = 0.63, $CHCl_3$) for **3b** with 93% *ee* (*R*). HPLC: DAICEL Chiralcel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL·min^{-1}, eluent: *n*-hexane/*i*PrOH (99.5:0.5); **3b**: t_R(*R*) = 32.2 min, t_R(*S*) = 34.3 min; (*E*)-**4b**: t_R = 49.6 min. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.57−1.88 (m, 2 H, $PhCH_2CH_2$), 2.46−2.77 (m, 2 H, $PhCH_2$), 2.84 (dddd, $^4J_{H,H}$ = 3.7, $^3J_{H,H}$ = 9.0, $^3J_{H,H}$ = 9.5, $^3J_{H,H}$ = 9.3 Hz, 1 H, $CHCH$=CH_2), 3.44 [d, $^3J_{H,H}$ = 9.0 Hz, 1 H, $CH(CO_2CH_3)_2$], 3.69 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 5.11−5.20 (m, 2 H, =CH_2), 5.73 (ddd, $^3J_{H,H}$ = 9.3, $^3J_{H,H}$ = 10.7, $^3J_{H,H}$ = 16.6 Hz, 1 H, CH=CH_2), 7.13−7.31 (m, 5 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 33.2 ($PhCH_2CH_2$), 33.9 ($PhCH_2$), 43.7 ($CHCH$=CH_2), 52.1 (CH_3), 52.2 (CH_3), 56.7 [$CH(CO_2CH_3)_2$], 117.9 (=CH_2), 125.8 (Ph), 128.2 (Ph), 128.3 (Ph), 137.6 (CH=CH_2), 141.6 (Ph), 168.3 (C=O), 168.5 (C=O) ppm. $C_{16}H_{20}O_4$ (276.33): calcd. C 69.55, H 7.30; found C 69.34, H 7.33.

2-(1-Isopropylallyl) Dimethylmalonate (3d): Ester **3d** was prepared by allylic alkylation of substrate **1d** (850 mg, 6.0 mmol) according to general procedure II [ligand: $P(OPh)_3$, reaction time: 5 days, room temperature]. After purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 98:2), a 93:7 mixture of **3d** and **4d** was obtained. Yield: 69% (890 mg). $[\alpha]_D^{20}$ = 0.07 (*c* = 0.54, $CHCl_3$) for **3d** with 66% *ee* (*R*). GC: Chiraldex γ-CD TA column, length: 30 m, 100 kPa helium, 50→100 °C at 1 °C·min^{-1}, then 20 min at 100 °C; **3d**: t_R(*R*) = 44.8 min, t_R(*S*) = 46.3 min; (*E*)-**4d**: t_R = 56.7 min. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 0.82

(d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.89 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.71 [dqq, $^3J_{H,H}$ = 5.2, $^3J_{H,H}$ = 7.0, $^3J_{H,H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$], 2.64 (ddd, $^3J_{H,H}$ = 5.2, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 9.9 Hz, 1 H, C*H*CH=CH_2), 3.56 [d, $^3J_{H,H}$ = 9.6 Hz, 1 H, C*H*(CO_2CH_3)$_2$], 3.67 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 5.05 [dd, $^2J_{H,H}$ = 1.8, $^3J_{H,H}$ = 16.9 Hz, 1 H, *anti*-(=CH_2)], 5.10 [dd, $^2J_{H,H}$ = 1.8, $^3J_{H,H}$ = 10.1 Hz, 1 H, *syn*-(=CH_2)], 5.67 (ddd, $^3J_{H,H}$ = 9.9, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 16.9 Hz, 1 H, C*H*=CH_2) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 17.5 (CH_3), 21.2 (CH_3), 29.0 [*C*H(CH_3)$_2$], 50.3 (*C*HCH=CH_2), 52.2 (OCH_3), 52.4 (OCH_3), 54.9 [*C*H(CO_2CH_3)$_2$], 118.6 (=CH_2), 134.8 (*C*H=CH_2), 168.7 (C=O), 169.0 (C=O) ppm. $C_{11}H_{18}O_4$ (214.26): calcd. C 61.66, H 8.47; found C 61.47, H 8.43.

2-[1-Methoxymethoxymethylallyl] Dimethylmalonate (3e): Ester **3e** was obtained by allylic alkylation of substrate **1e** (43 mg, 0.25 mmol) according to general procedure II [ligand: $P(OPh)_3$, reaction time: 18 h, room temperature]. After purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1), a 77:23 mixture of **3e** and **4e** was obtained. Yield: 91% (56 mg). $[\alpha]_D^{24}$ = 23.3 (*c* = 0.69, $CHCl_3$) for **3e** with 78% *ee* (*R*). GC: Chiraldex γ-CD TA column, length: 30 m, 100 kPa helium, 50→100 °C at 10 °C·min^{-1}, then 60 min at 100 °C; **3e**: t_R(*R*) = 54.1 min, t_R(*S*) = 55.8 min; (*E*)-**4e**: t_R = 63.5 min. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 3.06−3.23 [m, 1 H, C*H*(CH=CH_2)] 3.32 (s, 3 H, C*H*$_3$OCH$_2$), 3.59 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, MOMOC*H*$_2$), 3.61 (d, $^3J_{H,H}$ = 5.5 Hz, 1 H, MOMOC*H*$_2$), 3.68 [d, $^3J_{H,H}$ = 8.1 Hz, 1 H, C*H*(CO_2Me)$_2$], 3.70 (s, 3 H, Me), 3.73 (s, 3 H, Me), 4.57 (s, 2 H, CH_3OCH_2), 5.11−5.21 (m, 2 H, =CH_2), 5.84 (ddd, $^3J_{H,H}$ = 8.8, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 17.3 Hz, 1 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 43.8 [*C*H(CH=CH_2)], 52.3 (Me), 52.5 (Me), 53.1 [*C*H(CO_2Me)$_2$], 55.3 (*C*H$_3$OCH$_2$), 68.4 (MOMO*C*H$_2$), 96.5 (CH_3OCH_2), 118.2 (=CH_2), 135.3 (=CH), 166.9 (C=O), 168.7 (C=O) ppm. $C_{11}H_{18}O_6$ (246.26): calcd. C 53.65, H 7.37; found C 53.37, H 7.23.

2-[1-(2-Methoxymethoxyethyl)allyl] Dimethylmalonate (3f): Ester **3f** was obtained by allylic alkylation of substrate **1f** (94 mg, 0.5 mmol) according to general procedure II [ligand: $P(OPh)_3$, reaction time: 18 h, room temperature]. After purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1), a 93:7 mixture of **3f** and **4f** was obtained. Yield: 94% (122 mg). $[\alpha]_D^{24}$ = −1.4 (*c* = 0.76, $CHCl_3$) for **3f** with 70% *ee* (*R*). HPLC: DAICEL Chiralcel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL·min^{-1}, eluent: *n*-hexane/*i*PrOH (95:5); **3f**: t_R(*R*) = 23.2 min, t_R(*S*) = 24.6 min; (*E*)-**4f**: t_R = 28.9 min. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.54−1.66 (m, 1 H, MOMOCH$_2$C*H*$_2$), 1.76−1.87 (m, 1 H, MOMOCH$_2$C*H*$_2$), 2.94−2.97 [m, 1 H, C*H*(CH=CH_2)], 3.45 [d, $^3J_{H,H}$ = 8.4 Hz, 1 H, C*H*(CO_2Me)$_2$], 3.39−3.58 (m, 2 H, MOMOC*H*$_2$), 3.70 (s, 3 H, Me), 3.75 (s, 3 H, Me), 4.56−4.61 (m, 2 H, =CH_2), 5.69 (ddd, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 9.6, $^3J_{H,H}$ = 16.9 Hz, 1 H, =CH), 3.34 (s, 3 H, C*H*$_3$OCH$_2$) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 32.1 (MOMOCH$_2$*C*H$_2$), 41.1 [*C*H(CH=CH_2)], 52.4 (Me), 52.6 (Me), 55.2 (*C*H$_3$OCH$_2$), 56.6 [*C*H(CO_2Me)$_2$], 65.1 (MOMO*C*H$_2$), 96.4 (CH_3OCH_2), 118.0 (=CH_2), 137.3 (=CH), 168.4 (C=O), 168.6 (C=O) ppm. $C_{12}H_{20}O_6$ (260.29): calcd. C 55.37, H 7.74; found C 55.28, H 7.63.

(*Z*)-[2-(4-Methoxymethoxybut-2-enyl)] Dimethylmalonate [(*Z*)-4e]: Ester (*Z*)-**4e** was obtained by allylic alkylation of substrate (*Z*)-**2e** (87 mg, 0.5 mmol) according to general procedure II [ligand: $P(OPh)_3$, reaction time: 4 h, room temperature]. After purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1) an 8:92 mixture of (*E*)-**4e** and (*Z*)-**4e** was obtained. Yield: 65% (80 mg). GC/MS (*Z*)-**4e**: t_R = 12.79 min; (*E*)-**4e**: t_R = 12.85 min. **(*Z*)-4:** ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.65 [dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 7.4 Hz, 2 H, C*H*$_2$CH(CO_2Me)$_2$], 3.34 (s, 3 H, C*H*$_3$OCH$_2$), 3.40 [t, $^3J_{H,H}$ = 7.4 Hz, 1 H, C*H*(CO_2Me)$_2$], 3.70 (s, 6 H, CO_2CH_3), 4.11 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, MOMOC*H*$_2$), 4.59 (s, 2 H, CH_3OCH_2), 5.40−5.72 (m, 2 H, C*H*=C*H*) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 25 °C): δ = 26.4 [*C*H$_2$CH(CO_2Me)$_2$], 51.3 [*C*H(CO_2Me)$_2$], 52.5 (CO_2CH_3), 55.1 (*C*H$_3$OCH$_2$), 62.6 (MOMO*C*H$_2$), 95.7 (CH_3OCH_2), 128.2 (=CH), 129.0 (=CH), 169.1 (2s, C=O) ppm. HRMS (EI) for $C_{10}H_{15}O_5$ [M^+ − OCH_3]: calcd. 215.0919; found 215.0892.

(*Z*)-[2-(5-Methoxymethoxypent-2-enyl)] Dimethylmalonate [(*Z*)-4f]. Ester (*Z*)-**4f** was obtained by allylic alkylation of substrate (*Z*)-**2f** (752 mg, 4.0 mmol) according to the general method II [ligand: $P(OPh)_3$, reaction time: 4 h, room temperature]. After purification (silica gel, petroleum ether/ethyl acetate 9:1), a 6:1 mixture of (*Z*)-**4f** and **3f** was obtained. Yield: 80% (830 mg). GC/MS (*Z*)-**4f**: t_R = 13.33 min. ^1H NMR (200.13 MHz, $CDCl_3$, 25 °C): δ = 2.31 (dt, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 6.6 Hz, 2 H, MOMOCH$_2$C*H*$_2$), 2.61 [dd, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*$_2$CH(CO_2Me)$_2$], 3.29 (s, 3 H, C*H*$_3$OCH$_2$), 3.32−3.39 [m, 1 H, C*H*(CO_2Me)$_2$], 3.48 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, MOMOC*H*$_2$), 3.68 (s, 6 H, CH_3), 4.56 (s, 2 H, CH_3OCH_2), 5.27−5.53 (m, 2 H, C*H*=C*H*) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 25 °C): δ = 26.7 [*C*H$_2$CH(CO_2Me)$_2$], 27.7 (MOMOCH$_2$*C*H$_2$), 51.5 [*C*H(CO_2Me)$_2$], 52.3 (CH_3), 56.4 (*C*H$_3$OCH$_2$), 66.9 (MOMO*C*H$_2$), 96.2 (CH_3OCH_2), 126.5 (=CH), 129.1 (=CH), 169.2 (C=O) ppm. $C_{12}H_{20}O_6$ (260.29): calcd. C 55.37, H 7.74; found C 55.22, H 7.85.

1-Methoxymethoxybut-3-en-2-ol (6e): This compound was prepared via intermediates (see Schemes 2 and 3) that were not fully characterised.

11e: A solution of 2-methoxy-1,3-dioxolane (**10e**) (30.0 g, 0.288 mol) in 250 mL of dichloromethane was cooled to −70 °C. Then, a pre-cooled (−70 °C) solution of DIBAL-H in hexane (346 mL, 0.346 mol) was added dropwise and the reaction mixture was stirred for 90 min at −70 °C. Thereafter, the temperature was allowed to rise slowly to 0 °C and water (20 mL) was added. The resulting precipitate was dissolved by addition of aqueous NaOH (20%, 300 mL) and the resulting solution was extracted with dichloromethane (4 × 50 mL). The combined organic layers were washed with satd. NaCl solution (2 × 80 mL), dried (Na_2SO_4) and concentrated in vacuo to give an oil which was distilled [65 °C (10 Torr)] to give **11e**. Yield: 51% (15.2 g).[51] ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 1 H, OH), 3.38 (s, 3 H, C*H*$_3$OCH$_2$), 3.67 (m, 2 H, C*H*$_2$OH or MOMOC*H*$_2$), 3.73 (m, 2 H, C*H*$_2$OH or MOMOC*H*$_2$), 4.66 (s, 2 H, CH_3OCH_2) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 55.1 (*C*H$_3$OCH$_2$), 61.9, 70.1 (*C*H$_2$OH and MOMO*C*H$_2$), 96.3 (CH_3OCH_2) ppm.

6e: A mixture of **11e** (4.00 g, 37.7 mmol), NMO (6.63 g, 56.6 mmol), activated molecular sieves (4 Å) (18.86 g) and dichloromethane (75 mL) was cooled to 0 °C, then TPAP (0.132 g, 0.38 mmol) was added slowly and the mixture stirred for 30 min. After stirring for a further 2 h at room temperature the mixture was filtered through a short silica column. The filtrate containing the aldehyde **5e**,[52] was concentrated in vacuo and the residue was used immediately for the next step.

A solution of aldehyde **5e** (8 mL, 37.7 mmol) in THF (50 mL) was added dropwise to a pre-cooled (0 °C) solution of vinylmagnesium bromide in THF (1.0 M, 41.5 mL, 41.5 mmol). The resulting mixture was stirred for 1 h at 0 °C and 18 h at room temperature. Then,

water (ca. 50 mL) was added dropwise and the resulting precipitate was dissolved by addition of 2 N HCl. The solution was extracted with diethyl ether (4 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried (Na_2SO_4) and concentrated in vacuo to give a yellow oil which was subjected to flash column chromatography (silica gel, petroleum ether/ethyl acetate 1:1). Yield: 10% (500 mg over 2 steps). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.85 (s, 1 H, OH), 3.39 (s, 3 H, CH_3O), 3.47 [dd, $^3J_{H,H}$ = 7.4, $^2J_{H,H}$ = 10.6 Hz, 1 H, CH_2CH(OH)], 3.67 (dd, $^3J_{H,H}$ = 3.2, $^2J_{H,H}$ = 10.6 Hz, 1 H, CH_2CH(OH)], 4.29−4.34 [m, 1 H, CH(OH)], 4.67 (s, 2 H, CH_3OCH_2), 5.22 [d, $^3J_{H,H}$ = 10.6 Hz, 1 H, *syn*−(=CH_2)], 5.29 (d, $^3J_{H,H}$ = 17.3 Hz, 1 H, *anti*−(=CH_2)], 5.86 (ddd, $^3J_{H,H}$ = 5.5, $^3J_{H,H}$ = 10.6, $^3J_{H,H}$ = 17.3 Hz, 1 H, =CH) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 55.3 (CH_3O), 71.4 [CH(OH)], 72.5 [CH_2CH(OH)], 96.8 [CH_3OCH_2)], 116.3 (=CH), 136.4 (=CH_2) ppm. MS (CI, isobutane): *m*/*z* (%) = 133 (15) [M^+ + 1].

5-Methoxymethoxypent-1-en-3-ol (6f): This compound was prepared via intermediates (see Schemes 2 and 3) that were not fully characterised.

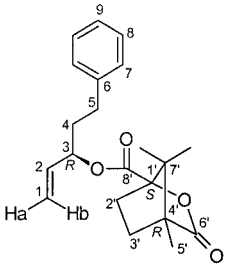
10f: Trimethyl orthoformate (151 mL, 1.38 mol) was dropwise added to a stirred solution of diol **9f** (50.0 mL, 0.69 mol) and camphorsulfonic acid monohydrate (1.73 g, 6.91 mmol) in dichloromethane (300 mL), and the mixture was stirred for 20 h at room temperature. The solvent was then removed under reduced pressure and the residue distilled to give **10f** (b.p. 148−152 °C) as a colourless oil.[53] Yield: 45% (37.02 g). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.71−1.73 (m, 2 H, CH_2CH$_2$O), 3.36 (s, 3 H, CH_3O), 3.74−3.77 (m, 2 H, CH_2CH_2O), 4.13−4.15 (m, 2 H, CH_2CH_2O), 5.18 [s, 1 H, CH(OCH$_3$)] ppm. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 24.7 (CH_2CH_2O), 52.5 (CH_3), 61.7 (CH_2CH_2O), 110.2 (OCHO) ppm

11f: Treatment of **10f** (15 g, 0.127 mol) with DIBAL-H (153 mL, 1 M in hexane, 0.153 mol) in 200 mL dichloromethane, according to the procedure described above for **11e**, gave crude monoester **11f**, which was purified by distillation (85−87 °C, 10 Torr) as a colourless oil.[54] Yield: 40% (6.16 g). ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C): δ = 1.83 (tt, $^3J_{H,H}$ = 6.0, $^3J_{H,H}$ = 6.0 Hz, 2 H, CH_2CH$_2$OH), 2.41 (s, 1 H, OH), 3.34 (s, 3 H, CH_3O), 3.70 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, MOMOCH_2 or CH_2OH), 3.74 (t, $^3J_{H,H}$ = 5.9 Hz, 2 H, MOMOCH_2 or CH_2OH), 4.60 (s, 2 H, OCH_2O) ppm. ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$, 25 °C): δ = 32.1 (CH_2CH_2OH), 55.2 (CH_3O), 61.0, 66.1 (CH_2OH and MOMOCH$_2$), 96.4 (OCH$_2$O) ppm

6f: Monoester **11f** (4.9 g, 41.37 mmol) was transformed into aldehyde **5f** and this reacted in situ with vinylmagnesium bromide (1 M in THF, 45.8 mmol), by following an analogous procedure to the one described above for the preparation of **6e**.[55] After purification by flash column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) **6f** was obtained as an oil. Yield: 29% over 2 steps (17.5 g). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.74−1.91 [m, 2 H, CH_2CH(OH)], 2.32 (s, 1 H, OH), 3.37 (s, 3 H, CH_3O), 3.60−3.80 (m, 2 H, MOMOCH_2), 4.31−4.36 [m, 1 H, CH(OH)], 4.62 (s, 2 H, CH_3OCH_2), 5.13 [ddd, $^2J_{H,H}$ = 1.4, $^4J_{H,H}$ = 1.4, $^3J_{H,H}$ = 10.5 Hz, 1 H, *syn*-(=CH_2)], 5.28 [ddd, $^2J_{H,H}$ = 1.4, $^4J_{H,H}$ = 1.4, $^3J_{H,H}$ = 17.2 Hz, 1 H, *anti*-(=CH_2)], 5.89 (ddd, $^3J_{H,H}$ = 5.6, $^3J_{H,H}$ = 10.5, $^3J_{H,H}$ = 17.2 Hz, 1 H, =CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz, 25 °C): δ = 36.3 [CH_2CH(OH)], 55.4 (CH_3O), 65.5 (MOMOCH$_2$), 71.6 [CH(OH)], 96.5 (CH_3OCH_2), 114.6 (=CH_2), 140.5 (=CH) ppm. MS (CI, isobutane): *m*/*z* (%) = 147 (100) [M^+ + 1], 129 (40) [M^+ + 1 − H_2O].

(*E*)-5-Methoxymethoxypent-2-en-1-ol (8f): A solution of ester **7f** (2.7 g, 14.4 mmol) in diethyl ether (50 mL) was cooled to −70 °C and DIBAL-H (31.6 mL of 1.0 M solution in hexane, 31.6 mmol) was slowly added via a dropping funnel. After stirring for 3.5 h at −70 °C, water (10 mL) was added dropwise and the solution was allowed to warm to room temperature. Additional water (10 mL) was added and the resulting precipitate was dissolved with 2 N HCl solution (ca. 90 mL). The mixture was extracted with diethyl ether (4 × 20 mL), the combined organic layers washed (2 × 30 mL satd. NH_4Cl solution), dried (Na_2SO_4) and concentrated in vacuo to give a colourless oil which was subjected to flash column chromatography (silica gel, diethyl ether/petroleum ether) to give **8f** with >95% purity (GC/MS). Yield: 66% (1.4 g, 9.5 mmol). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.56 (s, 1 H, OH), 2.31−2.42 (m, 2 H, MOMOCH_2CH_2), 3.36 (s, 3 H, CH_3O), 3.59 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, MOMOCH_2), 4.02−4.13 (m, 2 H, CH_2OH), 4.63 (s, 2 H, CH_3OCH_2), 5.71−5.77 (m, 2 H, =CH) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 32.6 (MOMOCH_2CH_2), 55.2 (CH_3O), 63.7, 67.1 (CH_2OH and MOMOCH$_2$), 96.4 (CH_3OCH_2), 129.3, 131.1 (both =CH) ppm. MS (EI): *m*/*z* (%) = 145 (1) [M^+ − H], 129 (1) [M^+ − OH], 115 (10) [M^+ − OCH_3], 45 (100) [$H_3COCH_2^+$]. HRMS (EI) for $C_8H_{14}O_2$ [M^+ − (O=CH_2)]: calcd. 116.0837; found 116.0837.

(*R*)-5-Phenyl-1-penten-3-yl (1*S*,4*R*)-4,7,7-Trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (12): (*R*)-5-phenyl-1-penten-3-ol [(*R*)-**6b**)] (0.50 g, 3.1 mmol) (prepared by enzyme-catalysed kinetic resolution of *rac*-**6b**)[12a] followed by 864 μL (6.2 mmol) of triethylamine were added dropwise to a cooled (0 °C) solution of (1*S*)-camphanic acid chloride (671 mg, 3.1 mmol) in anhydrous dichloromethane (10 mL). The solution was stirred at room temperature for 18 h and left to stand for 7 days. Colourless crystals precipitated from the mixture, were filtered off and washed with diethyl ether. The combined filtrates were concentrated in vacuo to give crude **12**. Crystals suitable for X-ray diffraction were obtained by recrystallization from ethyl acetate. Yield: 84% (890 mg). M. p. 55−58 °C.



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^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 0.98 (s, 3 H, 7′-CH_3), 1.07 (s, 3 H, 7′-CH_3), 1.12 (s, 3 H, 5′-H), 1.71 (ddd, $^3J_{3'a,2'a}$ = 4.4, $^2J_{3'a,3'b}$ = 9.6, $^3J_{3'a,2'b}$ = 13.6 Hz, 1 H, 3′-Ha), 1.87−2.15 (m, 4 H, 4-H, 3′-Hb, 2′-Ha), 2.44 (ddd, $^3J_{2'b,3'b}$ = 4.4, $^2J_{2'b,2'a}$ = 10.7, $^3J_{2'b,3'a}$ = 13.6 Hz, 1 H, 2′-Hb), 2.67 (ddd, $^3J_{5,4a}$ = 3.3, $^3J_{5,3}$ = 6.6, $^3J_{5,4b}$ = 9.6 Hz, 2 H, 5-H), 5.25 (ddd, $^2J_{1a,1b}$ = 1.1, $^4J_{1a,3}$ = 1.1, $^3J_{1a,2}$ = 10.5 Hz, 1 H, 1-Ha), 5.32 (ddd, $^2J_{1b,1a}$ = 1.1, $^4J_{1b,3}$ = 1.1, $^3J_{1b,2}$ = 17.1 Hz, 1 H, 1-Hb), 5.36−5.45 (m, 1 H, 3-H), 5.83 (ddd, $^3J_{2,3}$ = 6.6, $^3J_{2,1a}$ = 10.5, $^3J_{2,1b}$ = 17.1 Hz, 1 H, 2-H), 7.13−7.32 (m, 5 H, *arom.* H) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 9.66 (C-5′), 16.80 (7′-CH_3), 28.95 (C-3′), 30.73 (C-4′), 31.31 (C-5), 35.75 (C-4), 54.19, 54.82 (C-4′ and C-7′), 75.82 (C-3), 91.05 (C-1′), 118.16 (C-2), 126.11 (C-9), 128.32, 128.49 (C-7 and C-8), 135.51 (C-1), 140.87 (C-6), 166.81 (C-8′), 178.21 (C-6′) ppm. MS (FAB): *m*/*z* (%) = 343 (42) [M^+ + 1], 199 (46) [{M^+ + 1} −

($PhCH_2CH_2$) − (CH-CH=CH_2)], 181 (36) [{M^+ + 1} − ($PhCH_2CH_2$) − (CHO)-CH=CH_2)], 153 (60) [{M^+ + 1} − ($PhCH_2CH_2$) − CH(OCO) − ($CHCH_2$)]. $C_{21}H_{26}O_4$ (342.44): calcd. C 73.66, H 7.65; found C 73.49, H 7.64.

(*Z*)-5-Methoxymethoxypent-2-en-1-ol (19): A mixture of Lindlar catalyst (1.2 g), quinoline (0.33 mL, 357 mg, 2.77 mmol), alcohol **18** (5.9 g, 40.1 mmol) and methanol (340 mL) was stirred under a H_2 atmosphere for 15 hours at room temperature. The catalyst was removed by filtration through celite and the brown filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) to afford a colourless oil. Yield: 69% (4.1 g). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.32 (ddt, $^4J_{H,H}$ = 1.5, $^3J_{H,H}$ = 6.2, $^3J_{H,H}$ = 6.2 Hz, 2 H, MOMOCH$_2$CH_2), 2.68 (br. s, 1 H, OH), 3.29 (s, 3 H, OCH_3), 3.50 (t, $^3J_{H,H}$ = 6.2 Hz, 2 H, MOMOCH_2), 4.09 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, CH_2OH), 4.55 (s, 2 H, CH_3OCH_2), 5.46−5.57 (m, 1 H, =CH), 5.62−5.77 (m, 1 H, =CH) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 27.8 (MOMOCH$_2$CH_2), 55.1 (OCH_3), 57.8 (CH_2OH), 66.5 (MOMOCH_2), 96.2 (CH_3OCH_2), 128.8, 130.9 (= CH) ppm.

5-Phenyl-1-penten-3-yl Diethylphosphonate (26b): A solution of alcohol **6b** (2.0 g, 12.3 mmol) in THF (40 mL) was cooled to −78 °C and *n*BuLi (13 mL, 1.6 M in hexane, 20.9 mmol) was added slowly with a syringe. After stirring for 30 min at −78 °C, diethyl chlorophosphate (5.35 mL, 6.36 g, 36.9 mmol) was added. The mixture was stirred for 18 h, while the temperature was allowed to slowly rise from −78 °C to 25 °C. Then, water (40 mL) was added and the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with satd. NaCl solution (50 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) to give **26b** as a yellow oil. Yield: 64% (2.3 g). ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.32 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.33 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.87−2.14 (m, 2 H, CH_2CH), 2.65−2.74 (m, 2 H, PhCH_2), 4.10 (br. q, $^3J_{H,H}$ = 6.6 Hz, 4 H, OCH_2), 4.74−4.85 [m, 1 H, CHO-P(O)(OEt)$_2$], 5.25 (d, $^3J_{H,H}$ = 10.3 Hz, 1 H, =CH_2), 5.34 (d, $^3J_{H,H}$ = 17.3 Hz, 1 H, =CH_2), 5.88 (ddd, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 10.3, $^3J_{H,H}$ = 17.3 Hz, 1 H, =CH), 7.15−7.35 (m, 5 H, Ph) ppm. ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 16.1 (2 CH_3), 31.0 (CH_2CHOR), 37.5 (PhCH_2), 63.7 (2 OCH_2), 79.2 (CHOR), 117.5 (=CH_2), 126.0 (Ph), 128.4 (Ph), 128.4 (Ph), 136.7 (=CH), 141.3 (Ph) ppm. ^{31}P NMR (121.49 MHz, $CDCl_3$, 25 °C): δ = −1.40 ppm. HRMS (FAB) for $C_{14}H_{24}O_4P$ [M^+ + 1]: calcd. 299.1412; found 299.1440.

***N*-Benzyl-4-methyl-*N*-(1-phenethylallyl) Benzenesulfonamide (27b):** An LHMDS solution (4.0 mL, 1.0 M in THF, 4.0 mmol) was added to a solution of *N*-tosylbenzylamine (1.1 g, 4.2 mmol) in THF (12 mL). The mixture was stirred for 30 min at room temperature and then added to a substrate/catalyst solution prepared as follows: $[IrCl(COD)]_2$ (26.8 mg, 0.04 mmol) was dissolved in THF (4 mL) and substrate **1b** (2.0 mmol) and then triphenylphosphite (21.7 μL, 0.08 mmol) were added. The reaction mixture was stirred for 18 h at room temperature and then, treated with water (20 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with satd. $NaHCO_3$ (1 × 50 mL) and satd. NaCl solutions (1 × 50 mL) and dried over Na_2SO_4. After removal of the solvent in vacuo a yellow oil was obtained which was subjected to flash column chromatography (silica gel, petroleum ether/ethyl acetate 97:3) to give a 79:21 mixture of **27b** and **28b**. Yield: 47% (382 mg), colourless oil. $[\alpha]_D^{24}$ = 7.55 (*c* = 0.58, $CHCl_3$) for **27b** with 11% *ee* (*S*). HPLC: DAICEL Chiralcel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL min^{-1}, eluent: *n*-hexane/*i*PrOH (95:5); **27b**: t_R(*S*) = 23.8 min, t_R(*R*) = 27.9 min; (*E*)-**28b**: t_R = 38.2 min.

27b: ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.53−1.75 (m, 2 H, PhCH$_2$CH_2), 2.44 (s, 3 H, CH_3), 2.43−2.53 (m, 2 H, PhCH_2), 4.10 (d, $^2J_{H,H}$ = 15.4 Hz, 1 H, PhCH_2N), 4.37 (ddd, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 7.7 Hz, 1 H, CHN), 4.60 (d, $^2J_{H,H}$ = 15.4 Hz, 1 H, PhCH_2N), 4.99 [ddd, $^4J_{H,H}$ = 1.1, $^2J_{H,H}$ = 1.5, $^3J_{H,H}$ = 17.3 Hz, 1 H, *anti*-(=CH_2)], 5.10 [ddd, $^4J_{H,H}$ = 1.1, $^2J_{H,H}$ = 1.5, $^3J_{H,H}$ = 10.7 Hz, 1 H, *syn*-(=CH_2)], 5.47 (ddd, $^3J_{H,H}$ = 6.6, $^3J_{H,H}$ = 10.7, $^3J_{H,H}$ = 17.3 Hz, 1 H, CH= CH_2), 6.78−6.84 (m, 2 H, *arom.* H), 7.08−7.21 (m, 3 H, *arom.* H), 7.24−7.35 (m, 5 H, *arom.* H), 7.38−7.45 (m, 2 H, *arom.* H), 7.70 [d, $^3J_{H,H}$ = 8.7 Hz, 2 H, *m*-(1-SO_2-4-Me-C_6H_4)] ppm. ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 21.5 (CH_3), 32.6 (Ph*C*H$_2$), 34.1 (PhCH$_2$*C*H$_2$), 48.2 (Ph*C*H$_2$N), 60.3 [*C*H(NTs)(Bzl)], 118.6 (=CH_2), 125.7, 127.3, 127.5, 128.2, 128.3, 128.5, 128.6, 129.6 (all CH *arom.*), 135.8 (*C*H=CH_2), 138.1, 138.1, 141.6, 143.1 (s, all C *arom.*) ppm. MS (FAB): *m*/*z* (%) = 406 (60) [M^+ + H], 300 (100) [M^+ − PhCH$_2$CH$_2$], 262 (99) [M^+ − Ts]. $C_{25}H_{27}NO_2S$ (405.55): calcd. C 74.04, H 6.71, N 3.45, S 7.91; found C 74.03, H 6.74, N 3.51, S 7.76.

(5,7-Dioxa-6-phosphadibenzo[a,c]cyclohepten-6-yl)dimethylamine (L3): A mixture of 2,2′-dihydroxybiphenyl (1.00 g, 5.4 mmol), NH_4Cl (8.0 mg, 0.1 mmol) and [P(NMe_2)$_3$] (976 μL, 5.4 mmol) and toluene (15 mL) was stirred for 18 h at 80 °C and then concentrated in vacuo to give a yellow oil which was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate 98:2). Colourless oil. Yield: 29% (400 mg). ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 2.66 (d, $^3J_{H,P}$ = 9.4 Hz, 6 H, CH_3), 7.18 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *arom.* H), 7.22−7.26 (m, 2 H, *arom.* H), 7.32−7.37 (m, 2 H, *arom.* H), 7.46 (br. d, $^3J_{H,H}$ = 8.0 Hz, 2 H, *arom.* H) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, 25 °C): δ = 35.9 (d, $^2J_{P,C}$ = 10.7 Hz, CH_3), 121.9 (*arom.* C), 124.5 (*arom.* C), 129.2 (*arom.* C), 129.6 (*arom.* C), 131.1 (d, $^2J_{P,C}$ = 2.8 Hz, *arom.* C), 151.5 (*arom.* C) ppm. ^{31}P NMR (202.46 MHz, $CDCl_3$, 25 °C): δ = 149.74 (s) ppm. $C_{14}H_{14}NO_2P$ (259.24): calcd. C 64.86, H 5.44, N 5.40, P 11.95; found C 64.95, H 5.37, N 5.45, P 11.91.

[IrCl(η^4-1,5-COD){(a*R*)-L2}] (29): THF (4 mL) was added to a mixture of $[IrCl(COD)]_2$ (20 mg, 0.03 mmol) and phosphorus amidite (*R*)-**L2** (21.3 mg, 0.06 mmol) at room temperature. Formation of complex **29** was observed by ^{1}H and ^{31}P NMR spectroscopy within 10 min. Recrystallization from diethyl ether furnished orange crystals of **29**. Yield: 90% (37.5 mg). ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 1.22−1.44 (m, 2 H, CH_2-COD), 1.74−1.84 (m, 2 H, CH_2-COD), 1.81−1.91 (m, 2 H, CH_2-COD), 1.93−2.04 (m, 1 H, CH_2-COD) 2.09−2.19 (m, 1 H, CH_2-COD), 2.20−2.30 (m, 1 H, CH-COD), 2.45−2.52 (m, 1 H, CH-COD), 2.79 (d, $^3J_{P,H}$ = 10.7 Hz, 6 H, CH_3), 3.35−3.42 (m, 1 H, CH-COD), 5.30−5.45 (m, 1 H, CH-COD), 7.27 (dd, $^3J_{H,H}$ = 8.4, $^3J_{H,H}$ = 8.7 Hz, 2 H, CH *arom.*), 7.30 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, CH *arom.*), 7.32 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, CH *arom.*) 7.42 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, CH *arom.*), 7.39−7.47 (m, 2 H, CH *arom.*), 7.89 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH *arom.*), 7.91 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, CH *arom.*) 7.95 (d, $^3J_{H,H}$ = 8.35 Hz, 2 H, CH *arom.*), 8.01 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, CH *arom.*) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 29.7 (d, $^4J_{P,C}$ = 1.9 Hz, CH_2-COD), 29.0 (d, $^4J_{P,C}$ = 2.8 Hz, CH_2-COD), 32.5 (d, $^4J_{P,C}$ = 2.8 Hz, CH_2-COD), 34.2 (d, $^4J_{P,C}$ = 3.8 Hz, CH_2-COD), 38.2 (d, $^3J_{P,C}$ = 10.36 Hz, CH_3), 52.2 (d, $^3J_{P,C}$ = 1.9 Hz, CH-COD), 55.3 (d, $^3J_{P,C}$ = 1.88 Hz, CH-COD), 102.7 (d, $^3J_{P,C}$ = 17.9 Hz, CH-COD), 103.22 (d, $^3J_{P,C}$ = 19.1 Hz, CH-COD), 121.1 (*C*H *arom.*), 122.1 (d, $^4J_{C,P}$ = 1.88 Hz, *C*-*arom.*), 122.9 (d, $^4J_{C,P}$ = 2.86 Hz, *C*-*arom.*), 123.9 (d, $^4J_{C,P}$ = 2.83 Hz, *C*H-*arom.*), 125.2,

126.1, 126.5, 126.8, 127.1, 128.3, 128.4, 129.9, 130.3 (s, all CH *arom.*), 131.0, 131.6 (both s, *C-arom.*), 132.2 (d, $^3J_{C,P}$ = 1.88 Hz, *C-arom.*), 132.5 (s, *C-arom.*), 148.4 (d, $^2J_{C,P}$ = 4.7 Hz, O*C-arom.*), 149.5 (d, $^2J_{C,P}$ = 12.9 Hz, O*C-arom.*) ppm. ^{31}P NMR (202.46 MHz, $CDCl_3$, 25 °C): δ = 116.3 (s) ppm. $C_{30}H_{30}ClIrNO_2P$ (694.4): calcd. C 51.79, H 4.35, N 2.01, P 4.46; found C 52.01, H 4.47, N 2.06, P 4.40.

[Ir(η^3-CH$_2$CHCHPh)(Cl)$_2$(η^4-1,5-COD)] (30): Cinnamyl chloride (83 μL, 91 mg, 0.596 mmol) was added to a solution of $[IrCl(COD)]_2$ (100 mg, 0.149 mmol) in THF (2 mL) and the mixture stirred for 18 h at 50 °C. A yellow precipitate of **30** was formed, which was isolated by filtration, washed with hexane and dried in vacuo. Yield: 82% (119.3 mg). A 2:1 mixture of two isomers was observed in solution at between −60 and −40 °C.

Major isomer: ^{1}H NMR (300.13 MHz, CD_2Cl_2, −60 °C): δ = 1.45−1.65 (m, 1 H, CH_2-COD), 1.65−1.83 (m, 1 H, CH_2-COD), 2.25−2.55 (m, 3 H, CH_2-COD), 2.60−3.00 (m, 2 H, CH_2-COD), 2.95−3.15 (m, 1 H, CH_2-COD), 3.72 3.87 (m, 1 H, CH-COD), 4.07 [d, $^3J_{H,H}$ = 8.8 Hz, 1 H, *anti*-(*allyl* CH_2)], 4.45 [d, $^3J_{H,H}$ = 6.8 Hz, 1 H, *syn*-(*allyl* CH_2)], 4.59−4.86 (m, 3 H, CH-COD), 4.93 [d, $^3J_{H,H}$ = 14.0 Hz, 1 H, *anti*-(*allyl* C*H*Ph)], 6.06 (ddd, $^3J_{H,H}$ = 6.8, $^3J_{H,H}$ = 8.8, $^3J_{H,H}$ = 14.0 Hz, 1 H, *allyl* CH), 7.20−7.90 (m, 5 H, -C_6H_5) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, −60 °C): δ = 26.6 (CH_2-COD), 28.6 (CH_2-COD), 35.5 (CH_2-COD), 37.6 (CH_2-COD), 40.9 (*allyl* CH_2), 81.9 (CH-COD), 83.0 (CH-COD), 92.7 (CH-COD), 93.3 (CH-COD), 110.6 (*allyl* CH), 111.1 (*allyl C*HPh), 129.0, 130.3, (C_6H_5), 134.8 (C_{ipso}-C_6H_5) ppm.

Minor isomer: ^{1}H NMR (300.13 MHz, CD_2Cl_2, −60 °C): δ = 1.26−1.36 (m, 1 H, CH_2-COD), 1.45−1.65 (m, 1 H, CH_2-COD), 1.93−2.10 (m, 1 H, CH_2-COD), 2.25−2.55 (m, 2 H, CH_2-COD), 2.60−3.00 (m, 3 H, CH_2-COD), 4.13−4.26 (m, 1 H, CH-COD), 4.31−4.55 (m, 2 H, CH-COD and *allyl* CH_2), 4.59−4.86 (m, 2 H, CH-COD and *allyl* CH_2), 5.22−5.32 (m, 1 H, CH-COD), 5.55−5.74 (m, 1 H, *allyl* CH), 6.33 [d, $^3J_{H,H}$ = 14.1 Hz, 1 H, *anti*-(*allyl* C*H*Ph)], 7.20−7.90 (m, 5 H, -C_6H_5) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, −60 °C): δ = 27.0 (CH_2-COD), 28.8 (CH_2-COD), 33.6 (CH_2-COD), 37.9 (CH_2-COD), 42.6 (*allyl* CH_2), 80.8 (CH-COD), 81.7(CH-COD) 89.4 (CH-COD), 92.6 (CH- COD), 102.2 (*allyl* CH), 123.0 (*allyl C*HPh), 128.5, 128.9, 130.8 (C_6H_5), 147.6 (C_{ipso}-C_6H_5) ppm. $C_{17}H_{21}Cl_2Ir$ (488.52): calcd. C 41.80, H 4.34; found C 41.84, H 4.37.

[Ir(Br)$_2$(η^3-C$_3$H$_5$)(η^4-1,5-COD)] (31). Method A: A solution of $[IrCl(COD)]_2$ (50 mg, 0.07 mmol) and allyl bromide (28.6 μL, 36.0 mg, 0.3 mmol) in THF (1 mL) was stirred for 18 h at 50 °C. A yellow precipitate of **31** formed which was washed with diethyl ether and recrystallised from dichloromethane/pentane. Yield: 81% (60 mg).

Method B: $[IrCl(COD)]_2$ (150 mg, 0.2 mmol) was treated with an excess of *anhydrous* LiBr (155.1 mg, 1.8 mmol) in acetone (15 mL). After stirring for 18 h, the solvent was removed under vacuum and the product $[IrBr(COD)]_2$ extracted three times with dichloromethane. Removal of the solvent gave an orange oil which was further treated with allyl bromide (57 μL, 79.8 mg, 0.7 mmol). After 18 h, a crystalline yellow precipitate had formed, which was isolated by filtration and washed with diethyl ether. Yield: 66% (145 mg). NMR spectroscopy at −60 °C showed a 9:1 mixture of two isomers.

Major isomer: ^{1}H NMR (500.13 MHz, CD_2Cl_2, −60 °C): δ = 1.46−1.59 (m, 1 H, CH_2-COD), 1.75−1.88 (m, 1 H, CH_2-COD), 2.23−2.35 (m, 1 H, CH_2-COD), 2.40−2.50 (m, 1 H, CH_2-COD), 2.50−2.61 (m, 1 H, CH_2-COD), 2.60−2.72 (m, 1 H, CH_2-COD), 3.00−3.10 (m, 1 H, CH_2-COD), 3.12 [d, $^3J_{H,H}$ = 13.3 Hz, 1 H, *anti*-(*allyl* CH_2)], 3.22−3.34 (m, 1 H, CH_2-COD), 3.33−3.41 (m, 1 H, CH-COD), 3.83 [d, $^3J_{H,H}$ = 10.0 Hz, 1 H, *anti*-(*allyl* CH_2)], 4.48 [d, $^3J_{H,H}$ = 6.7 Hz, 1 H, *syn*-(*allyl* CH_2)], 4.75−4.84 (m, 1 H, CH-COD), 4.93 [d, $^3J_{H,H}$ = 8.7 Hz, 1 H, *syn*-(*allyl* CH_2)], 4.95−5.03 (m, 1 H, CH-COD), 5.10−5.17 (m, 1 H, CH-COD), 5.74−5.87 (m, 1H. *allyl* CH) ppm. ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2, −60 °C): δ = 26.4, 27.2, 36.4, 37.1 (all CH_2-COD), 44.6 (*allyl* CH_2), 83.2, 85.5 (both CH-COD), 79.7 (*allyl* CH_2), 91.8, 92.7 (both CH-COD), 114.5 (*allyl* CH) ppm.

Table 9. Crystal data and details of the structure refinement for compounds **12**, **29**, **30**, and **31**

Compound	**12**	**29**	**30**	**31**
Empirical formula	$C_{21}H_{26}O_4$	$C_{30}H_{30}ClIrNO_2P$	$C_{17}H_{21}Cl_2Ir$	$C_{11}H_{17}Br_2Ir$
Molecular weight [g·mol^{-1}]	342.42	695.17	488.44	501.27
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_1/n$	$Pna2_1$
Z	2	4	4	4
a [Å]	7.6989(3)	11.9440(1)	6.8597(1)	15.6809(3)
b [Å]	12.4705(5)	14.2192(1)	20.9350(3)	7.4221(1)
c [Å]	10.0936(4)	15.2164(2)	11.1414(2)	10.5656(2)
β [deg.]	99.888(1)	−	97.724(1)	−
Volume [Å^3]	954.68(7)	2584.26(4)	1585.48(4)	1229.68(4)
Absorption coefficient [mm^{-1}]	0.08	5.36	8.75	17.32
Max. and min. transmission	1.07 and 0.80	0.80 and 0.46	0.67 and 0.58	0.77 and 0.41
Crystal size [mm^3]	.64 × .13 × .13	.22 × .12 × .05	.14 × .08 × .06	.50 × .04 × .02
Theta range [deg.]	2.0 to 25.0	2.0 to 27.5	2.0 to 25.6	2.6 to 27.5
Reflections collected	8026	27013	11653	11961
Independent reflections	3350 (R_{int} = 0.052)	5926 (R_{int} = 0.075)	2761 (R_{int} = 0.034)	2816 (R_{int} = 0.066)
Observed reflections [$I > 2\sigma(I)$]	2568	5087	2301	2494
Refined parameters	330	343	209	154
Goodness-of-fit on F^2	1.06	0.99	1.09	1.00
Final $R1$ index [$I > 2\sigma(I)$]	0.043	0.030	0.023	0.027
Final $wR2$ index [$I > 2\sigma(I)$]	0.086	0.050	0.048	0.058
Absolute structure parameter	−1.4(12)	−0.018(6)	−	0.015(15)
Largest diff. peak/hole [e Å^{-3}]	0.15/−0.17	0.93/−0.72	0.60/−0.74	1.03/−1.23

Minor isomer: ^{1}H NMR (500.13 MHz, CD_2Cl_2, −60 °C): δ = 1.09−1.20 (m, 1 H, CH_2-COD), 1.57−1.67 (m, 1 H, CH_2-COD), 2.11−2.20 (m, 1 H, CH_2-COD), 2.24−2.35 (m, 1 H, CH_2-COD), 2.40−2.50 (m, 1 H, CH_2-COD), 2.69−2.79 (m, 1 H, CH_2-COD), 2.93−3.00 (m, 1 H, CH_2-COD), 3.00−3.10 (m, 1 H, CH_2-COD), 4.23−4.30 (m, 1 H, CH-COD), 4.62−4.70 (m, 3 H, CH-COD and *allyl* CH_2), 4.75−4.84 (m, 1 H, CH-COD), 4.90−4.97 (m, 1 H, *allyl* CH), 5.20−5.30 (m, 2 H, *allyl* CH_2), 5.58−5.63 (m, 1 H, CH-COD) ppm. $^{13}C\{^1H\}$ NMR (125.76 MHz, CD_2Cl_2, −60 °C): δ = 26.7, 27.2, 35.3, 37.7 (all CH_2-COD), 44.9 (*allyl* CH_2), 83.6, 85.4, 87.1 (all CH-COD), 89.6 (*allyl* CH_2), 93.9 (both CH-COD), 107.9 (*allyl* CH) ppm. $C_{11}H_{17}Br_2Ir$ (501.28): calcd. C 26.36, H 3.42; found C 26.30, H 3.56.

Stoichiometric Reaction of Complex 30 with Dimethyl 2-Sodiomalonate in the Presence of (*R*)-L2: A 0.24 M solution of $NaCH(CO_2Me)_2$ (0.4 mL, 0.1 mmol) in THF was syringed into a Schlenk tube and the solvent was removed under vacuum. To the residual white solid were added complex **30** (49.9 mg, 0.1 mmol) and the stoichiometric quantity of ligand (*R*)-**L2** (36.2 mg, 0.1 mmol), then $[D_8]THF/CD_2Cl_2$ (2:1; 1.5 mL) was added at −78 °C. The mixture was stirred for a few minutes at this temperature to give a clear light yellow solution that was transferred into a pre-cooled (−60 °C) NMR tube. The ^{1}H and ^{31}P NMR spectra of this solution, recorded at −60 °C, showed complete reaction to give exclusively a 1:1 mixture of *rac*-**3a** and complex **29** which were separated by flash column chromatography (silica gel, hexane/diethyl ether 9:1). Yield: 64% (16 mg) of **3a** (purity > 99% by GCMS) and 32% (22.6 mg) of **29** as orange crystals.

X-ray Crystallographic Studies: Crystals of compound **12** were obtained as needles by slow evaporation of solvent from a saturated solution in ethyl acetate. Single crystals of complex **29** were grown as orange needles by slow concentration of a saturated solution in diethyl ether. Single crystals of complexes **30** and **31** were grown, both as yellow needles, by slow diffusion of diethyl ether into a saturated solution in dichloromethane.

The measurements were made on a Bruker SMART-CCD diffractometer with graphite monochromated Mo-K_α radiation (0.71073 Å) at 200 K. Frames corresponding to a sphere of data were collected. 20 s exposures of 0.3 degree scans in omega were taken. An absorption correction was applied using SADABS (G. M. Sheldrick, SADABS, Bruker AXS, Inc.: Madison, WI, 1996) based on the laue symmetry of the reciprocal space. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters, most hydrogen atoms could be located in the Fourier map, in **12** all hydrogens were refined isotropically, in **29** and **30** only the allylic hydrogens and the olefinic hydrogens of the COD were refined isotropically, in **30** the allylic hydrogens were not included in the structure model due to the disorder, all the rest of the hydrogen atoms was taken into account at calculated positions. The full-matrix least-squares refinement against F^2 converged. All calculations were performed using the SHELXTL crystallographic software package of Bruker (G. M. Sheldrick, SHELXTL V5.10, Bruker AXS, Inc.: Madison, WI, 1997). For details and crystal data see Table 9.
CCDC-181254 (**12**), -181255 (**29**), -181256 (**30**) and -181257 (**31**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk)

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