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Regiocontrol and Stereoselectivity in Tungsten-Bipyridine Catalysed Allylic Alkylation

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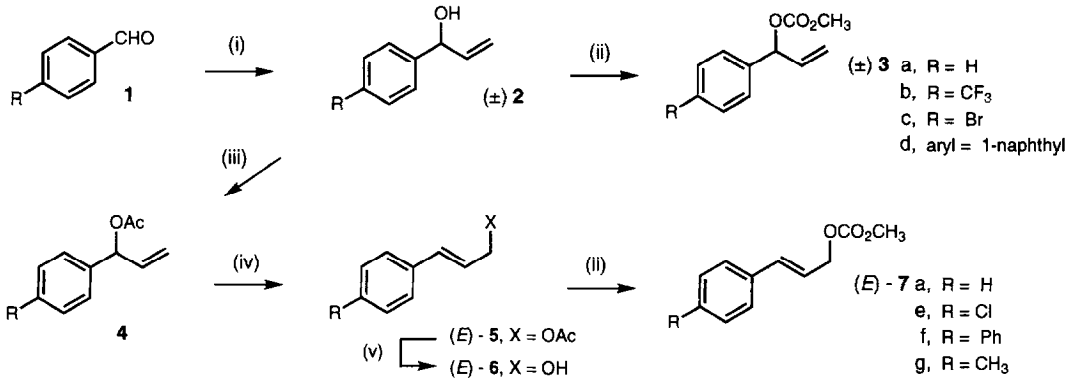
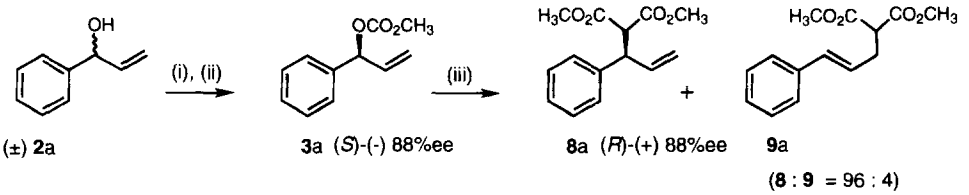
Abstract: Tungsten-bipyridine complexes, generated *in situ*, catalyse the allylic alkylation of isocinnamyl methyl carbonate by dimethyl sodiomalonate [$NaCH(CO_2CH_3)_2$] with complete *syn*-stereoselectivity. When *para* substituted aryl-allyl methyl carbonates are employed, the regioselectivity correlates with Swain-Lupton parameters. Cross-over experiments demonstrate that the reactions do not procede *via* the conventional [M^0] —› [M^{II} allyl]$^+$ —› [M^0 allyl-Nu] catalytic cycle.

We recently reported the enantioselective allylic alkylation (up to 96% ee) of (*E*)-aryl-allyl diethyl phosphates[1], catalysed by tungsten complexes bearing phosphino-aryl oxazoline ligands[2,3] - the first asymmetric variant of the pioneering work of Trost and Hung.[4] During the course of this work we observed that although the prochiral carbonate (*E*)-**7a** could be alkylated enantioselectively, regio-isomeric and racemic carbonate (±)-**3a** could not.[1] Since the conventional mechanism for metal-catalysed allylic substitution suggests that both substrates should converge on the same set of catalytic intermediates, this result was unexpected. Consequently, we have further explored the factors controlling selectivity in tungsten-catalysed allylic alkylation. Here we report on the stereo- and regioselectivity of the addition of [$NaCH(CO_2CH_3)_2$] to *para*-substituted aryl-allyl methyl carbonates **3**a-d and (*E*)-**7**a,e-g - synthesised as shown in Scheme 1, employing the procedure of Overman and Knoll[5] for a highly *E*-selective Pd-catalysed isomerisation of (±)-**4** to (*E*)-**5**.



Scheme 1 - **(i)** CH_2=$CHMgCl$, THF, 0 °C, 1 h, 46-80 % **(ii)** MeOCOCl, C_5H_5N, CH_2Cl_2, refl. 18 h, 67-97% **(iii)** Ac_2O, Et_3N, CH_2Cl_2, cat. DMAP, 25 °C, 3 h, 96% **(iv)** [$PdCl_2(CH_3CN)_2$] 1 mol%, THF, 25 °C, 14 h, 68-97% **(v)** K_2CO_3, MeOH, 25 °C, 6 h, 76-82 %.

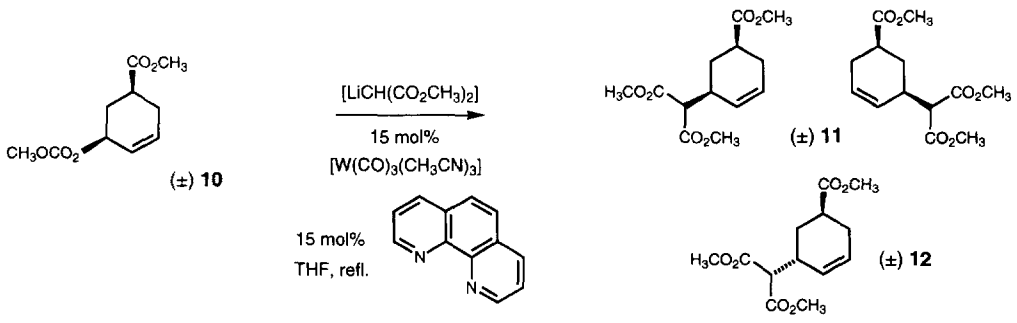
In initial experiments we examined the stereochemical consequences of alkylating the chiral phenyl-allyl carbonate **3a** and employed the achiral tungsten-bipyridine catalyst generated *in situ* by mixing equimolar quantities of $[W(CO)_3(CH_3CN)_3]$ and 2,2'-bipyridine.



Scheme 2 - **(i)** (+) L-DIPT (1.2 eq.), $Ti(iOPr)_4$ (1.0 eq.), CH_2Cl_2, 4Å MS, -25 °C, 0.6 eq. TBHP, 3 d, 37 % **(ii)** MeOCOCl, C_5H_5N, CH_2Cl_2, refl. 18 h, 67 % **(iii)** $NaCH(CO_2CH_3)_2$ (4.6 eq.), $[W(CO)_3(CH_3CN)_3]$ 15 mol %, 2,2'-bipyridine 15 mol %, THF, 60 °C, 11h, 84 %.

An optically enriched sample of 1-phenyl allyl alcohol (*S*)-(−)-**2a**, obtained by Sharpless-Katsuki epoxidation[6] of the racemate (0.6 eq. TBHP), was converted to the corresponding methyl carbonate **3a** (88% ee (*S*)-(−)).[6,7] Reaction of (*S*)-(−)-**3a** with $[NaCH(CO_2CH_3)_2]$, in the presence of the W-bipyridine catalyst, afforded **8a** and **9a**, with 96% regioselectivity[8] for **8a** (Scheme 2).

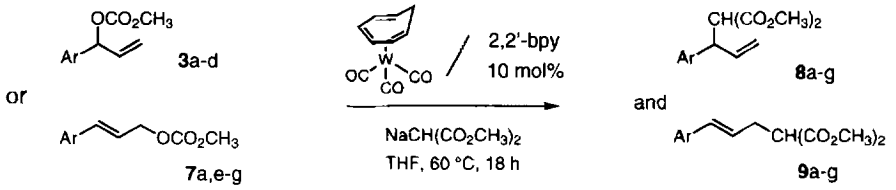
The enantiomeric excess of **8a** was 88% (*R*)-(+), the result of substitution of methyl carbonate by dimethyl malonate with complete *syn*-stereoselectivity - the absolute configuration being assigned by degradation of **8a** to dimethyl phenyl succinate.[9] Although the complete stereocontrol [(*S*)-(−)-**3a** —> (*R*)-(+)-**8a**] is unexpected, the *syn*-selectivity is consistent with the earlier observations of Trost and Hung on the W-phenanthroline catalysed *syn* substitution of (±)-carbonate **10** (Scheme 3). In their example however, *racemic* (±)-**10** precluded the potential for monitoring epimerisation, e.g. *via* an η^1-η^3-η^1 mechanism. Furthermore, the *syn*-selectivity was not complete (ca. 9 : 1 **11** / **12**; a competing uncatalysed process was not ruled out).[4a]



Scheme 3 - *syn*-Selective W-catalysed allylic alkylation[4a]

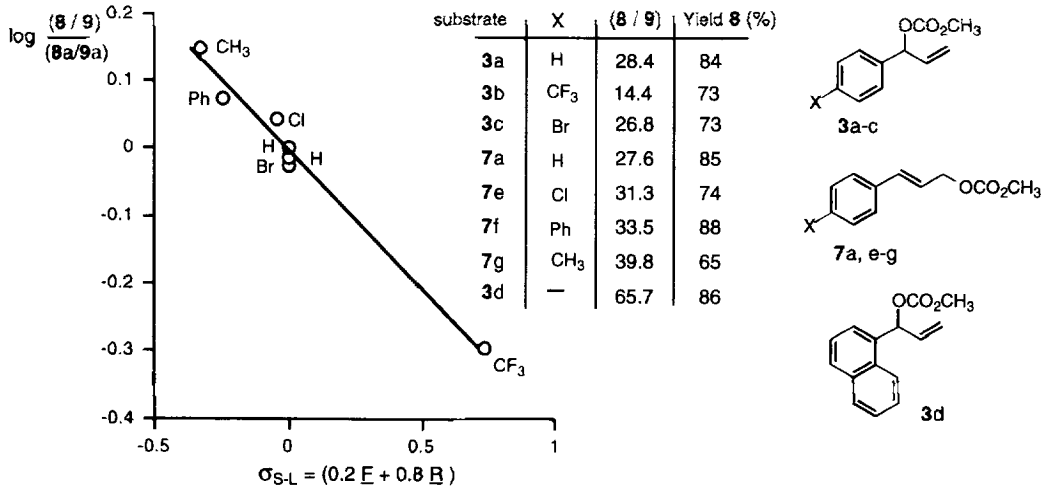
We subsequently found that $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (C_7H_8 = cycloheptatriene)[2,10] is a more convenient catalyst precursor than $[W(CO)_3(CH_3CN)_3]$, since the former is air-stable, readily soluble in THF, sublimable and has a long shelf-life. The regio- and stereoselectivity obtained with this catalyst system was identical to that

with $[W(CO)_3(CH_3CN)_3]$. Using $[W(CO)_3(\eta^6\text{-}C_7H_8)]$, we examined the regioselectivity of W-bipyridine catalysed allylic substitution of secondary (±)-**3** and primary (*E*)-**7** aryl-allyl methyl carbonates (Scheme 4).



Scheme 4.

In these experiments $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (10 mol%) was treated with 2,2'-bipyridine (60 °C, 15 min) and then $[NaCH(CO_2CH_3)_2]$ (2.0 eq., 60 °C, 10 min) prior to adding the allylic electrophile [(±)-**3**a-d or (*E*)-**7**a, e-g]. After 18 h, the reactions were quenched (NH_4Cl aq.) and the regioselectivities (**8** / **9**) determined by GC. Subsequent chromatography (silica-gel) afforded analytically pure **8**a-g.

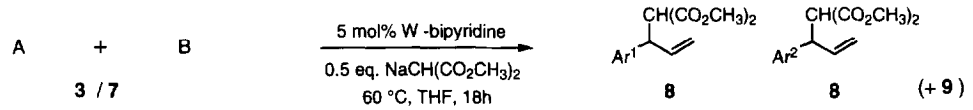


substrate	X	(8 / 9)	Yield 8 (%)
3a	H	28.4	84
3b	CF_3	14.4	73
3c	Br	26.8	73
7a	H	27.6	85
7e	Cl	31.3	74
7f	Ph	33.5	88
7g	CH_3	39.8	65
3d	—	65.7	86

Fig. 1 - Hammett correlation of regioselectivity (**8** / **9**) of W-bpy catalysed allylic alkylation (Scheme 4).

With the two regioisomeric unsubstituted phenyl-allyl systems **3**a and **7**a, the regioselectivity for (±)-**8**a (96.6 and 96.5% respectively) was essentially independent of the location of nucleofuge - suggesting a common intermediate (Figure 1). For all the substrates examined, there was no obvious correlation between regioselectivity and steric effects - although the α-naphthyl-allyl (**3**d) did yield 98.5% regioselectivity for the branched isomer (±)-**8**d. The regioselectivities of the *para* substituted series [(±)-**3**a-c, and (*E*)-**7**a,e-g] correlate (r^2 = 0.98) with Swain-Lupton[11] parameters ($\sigma_{S\text{-}L}$). The large resonance contribution to $\sigma_{S\text{-}L}$ (80% R) and negative ρ value (-2.5) is consistent with the correlation of regioselectivity against charge location made by Trost and Hung [4b] using INDO and MNDO calculations of polyene type allylic cations and also the recent report by Frisell and Åkermark[12] on the regioselectivities and rates of allylic alkylations catalysed by tungsten complexes bearing 4,7-substituted 1,10-phenanthroline ligands.

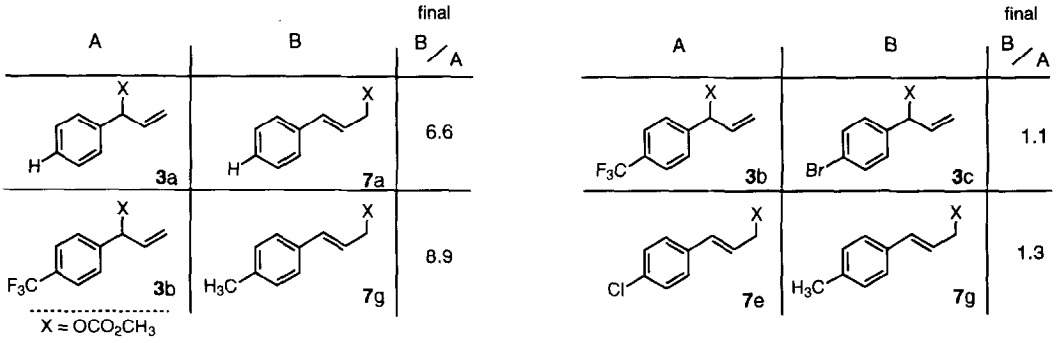
In further experiments, pairs of aryl-allyl methyl carbonates (A and B) were allowed to compete for a limiting quantity of nucleophile (Scheme 5).



Scheme 5.

The location of the nucleofuge and nature of the *para*-aryl substituent were found to control relative reactivities (Table 1). Thus when $Ar^1 = Ar^2 = Ph$, benzylic **3a** was consumed over six-fold more efficiently than linear **7a**; with **3b** (*p*-CF_3-C_6H_4-) and **7g** (*p*-Me-C_6H_4-) the factor was 8.9 (Table 1, left) - paralleling the regioselective ionisation of allylic dicarbonates noted by Trost, Tometzki and Hung.[4d] For substrates with the same allylic geometry (Table 1, right), the influence of the *para* substituent was low but consistent: the electrophile bearing the more electron withdrawing *para* substituent was consumed more efficiently.

Table 1. Final ratios (**B / A**) of pairs (**A** and **B**) of allylic substrates **3**a-c, **7**a,e,g after competition for a limiting quantity of nucleophile in the presence of 5 mol % W-bpy catalyst (Scheme 5).



Late transition metals (e.g. Pd, Ni or Pt) are generally accepted to catalyse allylic alkylations[13] *via* oxidative addition of the allylic electrophile to a low-valent metal complex [e.g. M(0) —› M(II)(allyl)X] followed by attack of the nucleophile (directly on the allyl or internally with subsequent M —› C migration) thus yielding the allylic substitution product and regenerating the catalytically active M(0) species (Figure 2).

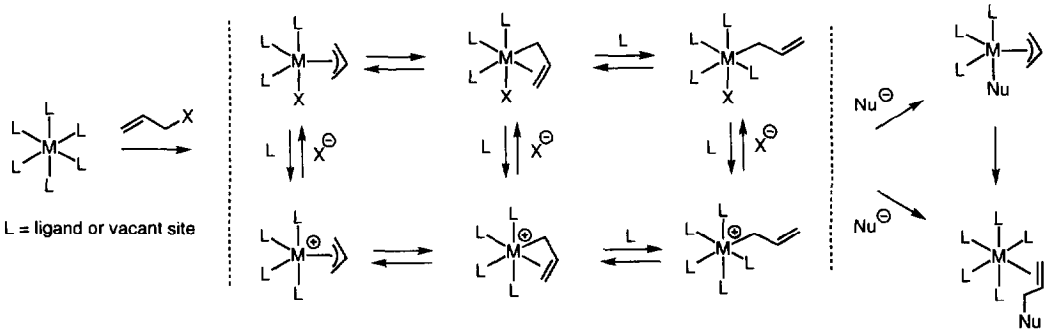
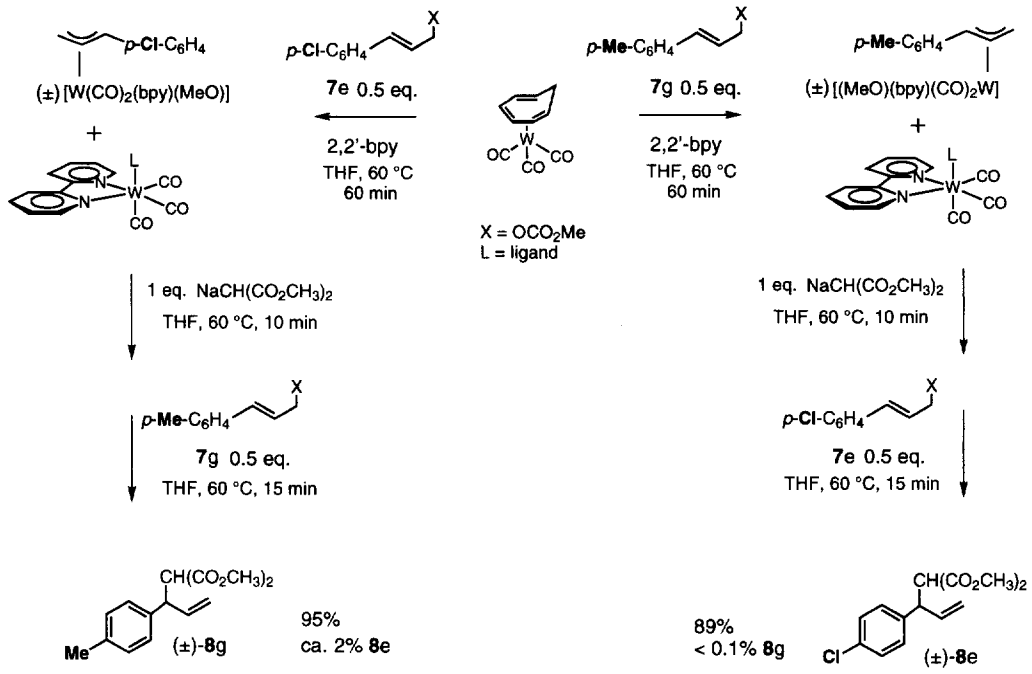


Fig. 2 - A conventional mechanism for metal-catalysed allylic substitution.

W(0) complexes of the type $[W(CO)_3L_3]$ (L = e.g. N, P or C=C ligand) react readily with allylic electrophiles e.g. C_3H_5Cl to yield, after loss of CO, the corresponding W(II)-allyl species $[W(CO)_2(\eta^3\text{-}C_3H_5)L_2X]$. Accordingly, reaction of 0.5 eq. **7e** (*p*-Cl-C_6H_4-) with $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ and 2,2'-bipyridine afforded a deep red solution - presumably containing the W(II)-allyl complex (±)-$[W(CO)_2(\eta^3\text{-}C_9H_9Cl)(bipy)(MeO)]$,[14] together with $[W(CO)_3(\eta^2\text{-}C_7H_8)(bipy)]$. No residual **7e** was detected by TLC (Scheme 6 - left).



Scheme 6.

However, addition of $[NaCH(CO_2CH_3)_2]$ and then the less reactive electrophile **7g** (*p*-Me-C_6H_4-) afforded a crude product containing **8g** (*p*-Me-C_6H_4-) (isolated in 95% yield) with ca. 2% **8e** (*p*-Cl-C_6H_4-) (GC-MS / NMR). The same experiment was repeated (Scheme 4 - right), reversing the order of **7e** and **7g** and in this case **8e** (89%) and ≤ 0.1% **8g** (*p*-Me-C_6H_4) was isolated. Taken together with earlier observations[4,1,2] these results further reinforce the conclusion that the conventional mechanism is not operative in W-catalysed allylic alkylations. Mechanistic and synthetic studies on related catalyses are in train.

Acknowledgements. This work was carried out in the laboratories of Prof. Andreas Pfaltz, University of Basel. G. C. L.-J. thanks the Royal Society (London) for a post-doctoral fellowship (1992-94) and Prof. Andreas Pfaltz for an ongoing and stimulating collaboration. We thank the Swiss National Science Foundation for financial support.

EXPERIMENTAL

General Solvents and reagents were purified by standard procedures. Aromatic aldehydes were purchased from *Fluka AG* and used as received. $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ was prepared as described in ref. 2; $Na[CH(CO_2CH_3)_2]$ was prepared as a powder - as described in ref. 13e. When appropriate, reactions were carried out under Ar using Schlenk techniques. NMR spectra: *Varian Gemini 300*; chemical shifts δ (ppm) are referenced to residual $CHCl_3$ (7.27 ppm, ^1H, 300 MHz) and to $CDCl_3$ (77.0 ppm, ^{13}C, 75 MHz). Mass spectra: *Varian MAT 212*; GC-MS: *Hewlett Packard 5971 Series Mass Detector* (EI) coupled with *Hewlett Packard 5890 Series II Gas Chromatograph*, FID-Detector. HPLC: *Daicel Chiralcel OJ* column (25 x 0.46 cm) with pre-column (5.0 cm), detecting at 220 nm. Optical rotations: *Perkin Elmer 141* polarimeter (*c* in g/100 ml, $CHCl_3$, 23°, estimated accuracy ±5 %). Flash column chromatography (FC): *Chemie Uetikon C560* silica gel (35 - 70 mm). TLC: 0.25 mm, *Merck* silica gel 60 F254 visualising at 254 nm or with 2 % $KMnO_4$ solution.

1-Aryl-allyl alcohols (2a-g)

1-phenyl-prop-2-en-1-ol (**2a**) Vinyl magnesium chloride (27.2 ml of a 15% solution in THF, 42.3 mmol) was slowly added to an ice-cold solution of benzaldehyde (5.0 g, 47.2 mmol) in 30 ml THF. After one hour, the reaction was quenched with 50 mL ice-cold NH_4Cl (50% sat. aq. soln.). The two phase mixture was three times extracted with *tert*-butyl methyl ether. The combined organic extracts were dried over $MgSO_4$ then concentrated *in vacuo*. The yellow-orange crude product was purified by Kugelrohr distillation (36 mbar, oven T = 170 °C) to afford **2a** as a colourless oil 5.36g (84.8%).

(*S*)-(-)-1-phenyl-prop-2-en-1-ol (*S*)-(-)-(**2a**) (+)-(L)-Diisopropyl tartrate (1.71 g, 7.29 mmol), (±)-(**2a**) (815 mg, 6.08 mmol) and 4Å molecular sieves (400 mg), in CH_2Cl_2 (30 mL) at -25 °C was treated with $Ti(^iPrO)_4$ (1.73 g, 6.08 mmol), stirred for 30 min, then treated with 1.05 mL of a 3M solution of *tert*-butyl hydroperoxide in *iso*-octane, resulting in a pale yellow solution. After stirring for 3 d at -25 °C, the reaction mixture was warmed to -10 °C and added to 100 mL of an aqueous solution containing $FeSO_4 \cdot 9H_2O$ (33 g) and citric acid (11 g). After stirring for 30 min, the mixture was warmed to 25 °C, filtered through a pad of Celite and extracted with 2 x 50 mL portions of Et_2O. The combined organic extracts were then treated at 0 °C with 10 mL of an aqueous solution containing NaCl (0.5 g) and NaOH (3g) with vigorous stirring for 3 h. The organic phase was separated, and the aqueous phase further extracted with 2 x 50 mL portions of Et_2O. The combined organic extracts were dried (Na_2SO_4) and evaporated to afford a yellow oil (1.19g) that was distilled (22 mmHg, kugelrohr oven T = 170 °C) and the resulting pale yellow oil (475 mg) purified by chromatography on silica-gel (20 x 3 cm, hexane / ethyl acetate 5:1) to afford (*S*)-(-)-**2a** as a colourless oil, 297.8 mg, 37%). $[\alpha]_D$ = -2.5 (c = 0.93, $CHCl_3$, 24 °C); lit[7] (S)-(-) ≥ 95% ee: $[\alpha]_D$ = -1.3 (c = 1.74, $CHCl_3$, 25 °C). $C_9H_{10}O$ 134.18 req. C 80.56 H 7.51 found C 79.93 H 7.42%. ^1H NMR ($CDCl_3$) 2.18 (*br s*, 1H, OH), 5.24 (*m*, 2H, C(1)H, C(3)H); 5.36 (*dd*, *J* = 17.5, 1.6, 1H, C(3)H); 6.06 (*ddd*, *J* = 17.5, 10.1, 5.6, 1H, C(2)H); 7.35 (*m*, 5H, arom. H). ^{13}C NMR ($CDCl_3$) 75.9 (C(1)); 115.7 (C(3)); 126.9, 128.3, 129.1 (arom. C); 140.8 (C(3)); 143.2 (arom. C). MS (EI) 134 (46, M+), 115 (46), 105 (53), 92 (100), 78 (65).

1-(4'-Trifluoromethylphenyl)-prop-2-en-1-ol (**2b**) Colourless oil, 824 mg (66 %). $C_{10}H_9F_3O$ 202.18 req. C 59.4 H 4.49 found C 59.3 H 4.64% IR (NaCl) 3599*s*, 3409*brs*, 3087*m*, 3026*w*, 3013*s*, 2986*m*, 2876*m*, 1642*m*, 1619*s*, 1587*w*, 1418*s*, 1335*s*, 1240*s*, 1107*s*, 1069*s*, 1016*s*, 989*s*, 932*s*, 850*s*. ^1H NMR ($CDCl_3$) 2.16 (*s*, 1H, OH); 5.25 (*m*, 2H, C(1)H, C(3)H); 5.38 (*d*, *J* = 17.1, 1H, C(3)H); 6.02 (*ddd*, *J* = 17.1, 10.2, 6.4, 1H, C(2)H); 7.50 (*d*, *J* = 8.6, 2H, arom. H); 7.62 (*m*, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 74.9 (C(1)); 116.2 (C(3)); 125.5, 126.6, 129.9 (arom. C); 139.7 (C(2)); 146.4 (arom. C). MS 202 (21, M+), 201 (14), 183 (19), 173 (47), 160 (46), 145 (37), 133 (100), 127 (978), 115 (22), 95 (8.5), 91 (12), 77 (16), 57 (8), 55 (34). TLC R_f = 0.29 (hexane /*tert*-butyl methyl ether 2:1).

1-(4'-Bromophenyl)-prop-2-en-1-ol (**2c**) Colourless oil, 560 mg (46%). C_9H_9BrO 213.07 req. C 50.7 H 4.26 found C 50.7 H 4.32% IR ($CHCl_3$) 3595*m*, 3385*br s*, 3086*w*, 3011*s*, 2872*w*, 1642*w*, 1592*m*, 1486*s*, 1402*s*, 1270*w*, 1232*w*, 1224*w*, 1185*w*, 1100*m*, 1072*m*, 1032*m*, 1008*s*, 989*s*, 930*s*, 835*m*, 815*m*. ^1H NMR ($CDCl_3$) 2.10 (*d*, *J* = 3.3, 1H, OH); 5.16 (*m*, 1H, C(1)H); 5.21 (*d*, *J* = 10.3, 1H, C(3)H); 5.34 (*d*, *J* = 17.1, 1H, C(3)H); 6.00 (*ddd*, *J* = 17.1, 10.3, 6.1, 1H, C(2)H); 7.25 (*d*, *J* = 8.4, 2H, arom. H); 7.48 (*d*, *J* = 8.4, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 74.8 (C(1)); 115.7 (C(3)); 121.6, 128.1, 131.6 (arom. C); 139.9 (C(2)); 141.5 (arom. C). MS(EI) 213 (35.7, M+), 211 (36), 187 (14), 185 (46), 171 (13), 157 (25), 133 (100), 115 (30), 105 (22), 91 (7), 77 (61), 63 (9), 55 (34). TLC R_f = 0.34 (hexane /*tert*-butyl methyl ether 2:1).

1-(1'-Naphthyl)-prop-2-en-1-ol (**2d**) Colourless oil, 3.59g (61%). $C_{13}H_{12}O$ 184.24 req. C 84.8 H 6.57 found C 84.4 H 6.89%. IR (NaCl) 3599*m*, 3419*w*, 3053*w*, 3020*s*, 3013*s*, 1640*w*, 1598*w*, 1511*m*, 1409*w*,

1396*w*, 1349*w*, 1228*m*, 1165*w*, 1117*w*, 1051*w*, 989*m*, 929*m*. ^{1}H NMR ($CDCl_3$) 2.06 (*d*, *J* = 4.2, 1H, OH); 5.30 (*d*, *J* = 10.4, 1H, C(3)H); 5.47 (*d*, *J* = 17.2, 1H, C(3)H); 5.97 (*m*, 1H, C(1)H); 6.27 (*ddd*, *J* = 17.2, 10.4, 5.4, 1H, C(2)H); 7.53 (*m*, 3H, arom. H); 7.64 (*d*, *J* = 6.7, 1H, arom. H); 7.82 (*d*, *J* = 8.2, 1H, arom, H); 7.89 (*m*, 1H, arom. H); 8.21 (*d*, *J* = 9.3, 1H, arom, H). ^{13}C NMR ($CDCl_3$) 72.2 (C(1)); 115.6 (C(3)); 123.7, 123.9 , 125.4, 125.6, 126.0, 128.5, 128.8, 130.6, 133.9, 138.0 (arom. C); 139.6 (C(2)). MS(EI) 184 (63, M+), 165 (44), 155 (23), 141 (32), 129 (100), 115 (8), 102 (6), 77 (13), 63 (11), 55 (19). TLC R_f = 0.13 (hexane */tert*-butyl methyl ether 5:1).

1-(4'-Chlorophenyl)-prop-2-en-1-ol (**2e**) Colourless oil, 4.8 g (80%). C_9H_9ClO 168.61 req. C 64.1 H 5.38 found C 64.0 H 5.59%. IR (NaCl) 3598*s*, 3405*brs*, 3086*m*, 3026*m*, 3011*s*, 2872*m*, 1640*m*, 1597*m*, 1491*s*, 1409*s*, 1365*m*, 1293*m*, 1272*m*, 1228*s*, 1185*m*, 1090*s*, 1030*s*, 1010*s*, 985*s*, 925*s*, 840*s*, 829*s*. ^{1}H NMR ($CDCl_3$) 2.17 (*br s*, 1H, OH); 5.18 (*br d*, *J* = 6.1, 1H, C(1)H)); 5.21 (*d*, *J* = 10.3, 1H, C(3)H)); (5.35 (*d*, *J* = 17.1, 1H, C(3)H)); 6.01 (*ddd*, *J* = 17.1, 10.3, 6.1, 1H, C(2)H); 7.25-7.40 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 74.7 (C(1)), 115.7 (C(3)), 127.8, 128.7, 133.5 (arom. C); 139.9 (C(2)); 141.0 (arom. C). MS (EI) 168 (39, M+), 139 (44), 141 (40), 133 (100), 115 (27), 103 (14), 91 (13), 77 (93), 55 (54). TLC R_f = 0.30 (hexane */tert*-butyl methyl ether. 2:1).

1-(4'-Biphenyl)-prop-2-en-1-ol (**2f**) Colourless solid, 4.2g (73%). $C_{15}H_{14}O$ 210.28 req. C 85.7 H 6.71 found C 85.3 H 6.80%. Mp. 55-56°C. IR ($CHCl_3$) 3600*m*, 3415*w* br, 3063*w*, 3028*m*, 3013*s*, 2871*w*, 1640*w*, 1600*w*, 1486*s*, 1449*w*, 1410*m*, 1364*w*, 1299*w*, 1279*w*, 1228*m*, 1219*s*, 1208*m*, 1179*w*, 1105*w*, 1075*w*, 1008*m*, 989*m*, 925m, 840*m*. ^{1}H NMR ($CDCl_3$) 2.15 (*d*, *J* = 3.6, 1H, OH); 5.26 (*m*, 2H, C(1)H, C(3)H); 5.42 (*d*, *J* = 17.1, 1H, C(3)H); 6.12 (*ddd*, *J* = 17.1, 10.2, 6.1, 1H, C(2)H); 7.38 (*m*, 1H, arom. H); 7.46 (*m*, 4H, arom. H); 7.62 (*m*, 4H, arom. H).^{13}C NMR ($CDCl_3$) 75.2 (C(1)); 115.3 (C(3)); 126.8, 127.2, 127.4, 128.8 (arom. C); 140.2 (C(2)); 140.8, 140.9, 141.7 (arom. C). MS 210 (100, M+), 181 (26), 167 (33), 155 (67), 133 (20), 115 (10), 77 (24), 55 (29). TLC R_f = 0.11 (hexane */tert*-butyl methyl ether. 5:1).

1-(4'-Methylphenyl)-prop-2-en-1-ol (**2g**) Colourless oil, 5.19g (84%). $C_{10}H_{12}O$ 148.20 req. C 81.0 H 8.16% found C 81.0 H 8.22%. IR (NaCl) 3600*m*, 3420*w*, 3024*m*, 3013*s*, 2924*w*, 2867*w*, 1641*w*, 1613*w*, 1513*m*, 1410*w*, 1367*w*, 1302*w*, 1277*w*, 1228*m*, 1205*s*, 1177*w*, 1106*w*, 1019*m*, 989 *m*, 928*s*. ^{1}H NMR ($CDCl_3$) 1.98 (*s*, 1H, OH); 2.35 (*s*, 3H, CH_3); 5.19 (*m*, 2H, C(1)H, C(3)H); 5.35 (*d*, *J* = 17.1, 1H, C(3)H); 6.06 (*ddd*, *J* = 17.1, 10.2, 6.1, 1H, C(3)H); 7.16 (*d*, *J* = 8.0, 2H; arom. H); 7.27 (*d*, *J* = 8.0, 2H; arom. H). ^{13}C NMR ($CDCl_3$) 21.7 (CH_3); 75.7 (C(1)); 115.4 (C(3)); 126.9, 129.8, 138.0, 140.4 (arom. C); 141.0 (C(2)). MS (EI) 148 (58, M+), 133 (100), 119 (42), 115 (24), 105 (28), 93 (37), 91 (76), 77 (33), 65 (20), 55 (27), 41 (23). TLC R_f = 0.31 (hexane */tert*-butyl methyl ether. 2:1).

1-Aryl-allyl carbonates (**3**a-d)

(*S*)-(-)-1-phenyl-prop-2-enyl methyl carbonate (*S*)-(-)-(**3a**) A solution of (*S*)-(-)-1-phenyl-prop-2-en-1-ol (*S*)-(-)-(**2a**) (1.0g, 7.45 mmol) in 10 ml CH_2Cl_2 was treated with pyridine (5 ml) and cooled to 0°C. With stirring, methyl chloroformate (1.25 ml, 17.0 mmol) was added dropwise and then the reaction refluxed for 18 h. After quenching with NH_4Cl (50% sat. aq., 10 ml) the mixture was extracted three times with CH_2Cl_2 (15 ml portions), the combined extracts washed with NaCl (sat. aq.) and then dried (Na_2SO_4). Evaporation of the solvent afforded an oil that was purified by chromatography on silica-gel (43 x 3.5 cm, hexane */tert*-butyl methyl ether 10:1), then distilled (0.1 mBar, kugelrohr oven T = 90 °C) to afford (*S*)-(-)-(**3a**) as a colourless oil, 0.96g (67%). $[\alpha]_D$ = -42.0 (c = 0.92, $CHCl_3$, 24 °C), 88% ee HPLC (OJ column, 220 nm, 0.5 ml/min 93% hexane / 7% iPrOH; t_R = 32.8 (S) and 37.6 (R) min). $C_{11}H_{12}O_3$ 192.21 req. C 68.7 H 6.29 % found C 68.7 H 6.26%. ^{1}H NMR ($CDCl_3$) 3.78 (*s*, 3H, CH_3); 5.33 (*m*, 2H, C(3)H_2); 6.04 (*m*, 1H, C(2)H); 6.09 (*m*, 1H, C(1)H); 7.32-7.39 (*m*, 5H, arom. H). ^{13}C NMR ($CDCl_3$) 54.8 (CH_3); 80.2 (C(1)); 117.4 (C(3)); 127.0, 128.4, 128.6 (arom. C); 135.7 (C(2)); 138.2 (arom. C); 155.0 (C=O). MS (EI) 192 (18, M+), 147 (10), 133 (5), 116 (100), 105 (14), 91 (20), 77 (21).

1-(4'-Trifluoromethylphenyl)-prop-2-enyl methyl carbonate (**3b**) Colourless oil, 0.86g (88%). $C_{12}H_{11}F_3O_3$ 260.21 req. C 55.4 H 4.26 foundC 55.4 H 4.29%. IR (NaCl) 3026*m*, 3017*m*, 2958*m*, 2854*w*, 1749*s*, 1644*w*, 1621*m*, 1587*w*, 1443*s*, 1420*m*, 1327*s*, 1277*s*, 1169*s*, 1131*s*, 1067*s*, 1019*s*, 980*s*, 943*s*, 840*m*. ^{1}H NMR ($CDCl_3$) 3.80 (*s*, 3H, CH_3); 5.33 (*d*, *J* = 10.3, 1H, C(3)H); 5.38 (*d*, *J* = 17.8, 1H, C(3)H); 6.00 (*ddd*, *J* = 17.8, 10.3, 6.0, 1H, C(2)H); 6.13 (*d*, *J* = 6.0, 1H, C(1)H); 7.50 (*d*, *J* = 8.6, 2H, arom. H); 7.64 (*d*, *J* = 8.6, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 55.0 (CH_3); 79.4 (C(1)); 118.4 (C(3)); 125.6, 127.3 (arom. C); 130.6 (*q*, *J* = 32.3, arom. C); 135.1 (C(2)), 142.3 (arom. C), 154.9 (C=O); (CF_3 not located). MS (EI) 260 (M+, 11), 241 (12), 228 (2), 215 (16), 201 (9), 185 (58), 165 (35), 147 (29), 133 (14), 115 (100), 95 (5), 89 (4), 77 (9), 59 (25), 45 (2). TLC R_f = 0.27 (hexane / ethyl acetate 10:1).

1-(4'-Bromophenyl)-prop-2-enyl methyl carbonate (**3c**) Colourless oil, 0.53g (83%). $C_{11}H_{11}BrO_3$ 271.11 req. C 48.7 H 4.09% found C 48.7 H 4.15%. IR (NaCl) 3091*m*, 3028*s*, 3003*s*, 2957*s*, 2854*w*, 1757*s*,

1643*m*, 1593*m*, 1489*s*, 1442*s*, 1413*m*, 1254*s*, 1179*m*, 1153*w*, 1105*m*, 1072*s*, 1012*s*, 940*s*, 855*s*, 825*s*. ^{1}H NMR ($CDCl_3$) 3.78 (*s*, 3H, CH_3); 5.32 (*m*, 2H, C(3)H_2); 6.00 (*m*, 2H, C(1)H, C(2)H); 7.25 (*d*, *J* = 8.2, 2H, arom H); 7.50 (*d*, *J* = 8.2, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 54.4 (CH_3); 79.0 (C(1)), 117.5 (C(3)), 122.0, 128.3, 131.3 (arom. C); 134.8 (C(2)); 136.9 (arom. C); 154.4 (C=O). MS (EI) 272 (M+, 28), 270 (28), 227 (4), 225 (4), 196 (48), 194 (48), 157 (5), 155 (5), 147 (6), 115 (100), 104 (9), 89 (10), 77 (8), 59 (17), 50 (7). TLC Rf = 0.24 (hexane / ethyl acetate 10:1).

1-(1'-Naphthyl)-prop-2-enyl methyl carbonate (**3d**) Colourless oil, 0.76g (72%). $C_{15}H_{14}O_3$ 242.27 req. C 74.4 H 5.82 found C 74.4 H 5.86%. IR (NaCl) 3021*s*, 3001*s*, 2958*s*, 2854*w*, 1732*s*, 1642*m*, 1599*m*, 1512*s*, 1443*s*, 1440*m*, 1397*m*, 1379*m*, 1360*m*, 1335*s*, 1297*s*, 1201*m*, 1170*s*, 1113*m*, 1084*m*, 1055*w*, 1036*m*, 1018*m*, 945*s*. ^{1}H NMR ($CDCl_3$) 3.81 (*s*, 3H, CH_3); 5.34 (*d*, *J* = 10.6, 1H, C(3)H); 5.40 (*d*, *J* = 17.3, 1H, C(3)H); 6.24 (*ddd*, *J* = 17.3, 10.6, 5.5, 1H, C(2)H); 6.83 (*d*, *J* = 5.5, 1H, C(1)H); 7.53 (*m*, 3H, arom. H); 7.64 (*d*, *J* = 6.6, 1H, arom. H); 7.86 (*d*, *J* = 9.7, 1H, arom. H); 7.89 (*d*, *J* = 7.6, 1H, arom. H). ^{13}C NMR ($CDCl_3$) 54.5 (CH_3); 77.4 (C(1)); 117.4 (C(3)); 123.3, 124.9, 125.0, 125.4, 126.0, 128.4, 128.8, 130.1, 133.5 (arom. C); 135.0 (C(2)); 154.7 (C=O). MS (EI) (242 (M+, 15), 183 (1), 165 (100), 152 (15), 139 (3), 127 (9), 115 (4), 82 (7), 77 (3), 59 (5), 44 (3). TLC R_f = 0.24 (hexane */tert*-butyl methyl ether 10:1).

1-Aryl-allyl acetates (**4**e-g)

1-(4'-Chlorophenyl)-prop-2-enyl acetate (**4e**) A solution of 1-(4'-chlorophenyl)-prop-2-en-1-ol (**2e**) (4.51 g, 26.7 mmol), Et_3N (5.54 g, 54.7 mmol) and 4-dimethylaminopyridine (0.109 g, 0.892 mmol) in 50 ml CH_2Cl_2 at 0 °C was slowly treated with a solution of Ac_2O (3.94 g, 38.6 mmol) in 5 ml CH_2Cl_2 and then allowed to warm to 25 °C over a period of 3 h. After quenching with 50 mL ice-cold NH_4Cl (50% sat. aq. soln.), the two phase mixture was three times extracted with CH_2Cl_2. The combined organic extracts were washed with 50 ml portions of sat. aq. NH_4Cl, sat. aq. NaCl and sat. aq. $NaHCO_3$ before being dried over $MgSO_4$ and then concentrated *in vacuo*. Chromatography on silica-gel (44 x 5.5 cm, hexane */tert*-butyl methyl ether 10:1) afforded (**4e**) as a colourless oil, 5.40 g (96%). $C_{11}H_{11}ClO_2$ 210.66 req. C 62.7 H 5.26 found C 62.6 H 5.35%. IR (NaCl) 3091*w*, 3018*m*, 3030*m*, 3009*m*, 2938*w*, 1736*s*, 1643*m*, 1598*m*, 1492*s*, 1411*m*, 1371*s*, 1248*s*, 1198*m*, 1178*w*, 1091*s*, 1015*s*, 983*s*, 939*s*, 845*m*, 820*s*. ^{1}H NMR ($CDCl_3$) 2.12 (*s*, 3H, CH_3), 5.27 (*d*, *J* = 10.4, 1H, C(3)H); 5.29 (*d*, *J* = 17.2, 1H, C(3)H); 5.98 (*ddd*, *J* = 17.2, 10.4, 5.8, 1H, C(2)H); 6.23 (*d*, *J* = 5.8, 1H, C(1)H); 7.29 (*d*, *J* = 10.9, 2H, arom. H); 7.34 (*d*, *J* = 10.9, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 21.2 (CH_3); 75.5 (C(1)); 117.4 (C(3)); 128.6, 128.8, 134.0 (arom. C), 135.9 (C(2)), 137.5 (arom. C); 169.9 (C=O). MS (EI) 210 (2, M+), 170 (21), 168 (64), 150 (12), 115 (100), 103 (5), 89 (8), 77 (10), 63 (7), 55 (8), 43 (99). TLC R_f = 0.27 (hexane */tert*-butyl methyl ether 10:1).

1-(4'-Biphenyl)-prop-2-enyl acetate (**4f**) Colourless oil, 4.62g (95%). $C_{17}H_{16}O_2$ 252.31 req. C 80.9 H 6.39 found C 80.5 H 6.61%. IR (NaCl) 3092*w*, 3026*s*, 2948*w*, 1733*s*, 1654*m*, 1600*w*, 1558*w*, 1519*w*, 1486*s*, 1449*m*, 1409*m*, 1381*m*, 1363*m*, 1295*w*, 1231*s*, 1217*s*, 1201*w*, 1101*w*, 1075*m*, 1024*s*, 969*s*. ^{1}H NMR ($CDCl_3$) 2.14 (*s*, 3H, CH_3); 5.29 (*d*, *J* = 10.4, 1H, C(3)H); 5.35 (*d*, *J* = 17.2, 1H, C(3)H); 6.06 (*ddd*, *J* = 17.2, 10.4, 5.8, 1H, C(2)H); 6.32 (*d*, *J* = 5.8, 1H, C(1)H); 7.37 (*m*, 1H, arom. H); 7.45 (*m*, 4H, arom. H); 7.59 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 21.3 (CH_3); 76.1 (C(1)); 117.1 (C(3)); 127.2, 127.4, 127.5, 127.7, 128.9 (arom. C); 136.3 (C(2)); 138.0, 140.7, 141.2 (arom. C); 170.1 (C=O). MS (EI) 252 (18, M+), 210 (100), 192 (84), 178 (39), 165 (26), 152 (25), 133 (3), 115 (16), 94 (3), 82 (4), 77 (7), 55 (8), 43 (35). TLC R_f = 0.24 (hexane */tert*-butyl methyl ether 10:1).

1-(4'-Methylphenyl)-prop-2-enyl acetate (**4g**) Colourless oil, 6.2g (96%) $C_{12}H_{14}O_2$ 190.24 req. C 75.8 H 7.42 found C 75.9 H 7.49%. IR (NaCl) 3092*w*, 3026*s*, 3013*s*, 2925*m*, 2865*w*, 1737*s*, 1644*m*, 1615*w*, 1578*w*, 1515*s*, 1410*m*, 1371*s*, 1246*s*, 1182*m*, 1111*m*, 1094*m*, 1019*s*, 985*s*, 937*s*, 855*w*, 825*s*. ^{1}H NMR ($CDCl_3$) 2.10 (*s*, 3H, CH_3); 2.35 (*s*, 3H, Ar-CH_3); 5.24 (*d*, *J* = 10.4, 1H, C(3)H); 5.29 (*d*, *J* = 17.3, 1H, C(3)H); 6.01 (*ddd*, *J* = 17.3, 10.4, 5.8, 1H, C(2)H); 6.24 (*d*, *J* = 5.8, 1H, C(1)H); 7.17 (*d*, *J* = 8.1, 2H, arom. H); 7.26 (*d*, *J* = 8.1, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 21.1, 21.2 (CH_3); 76.0 (C(1)); 116.6 (C(1)); 127.1, 129.2, 135.9 (arom. C); 136.4 (C(2)); 137.9 (arom. C); 169.9 (C=O). MS 190 (4, M+), 148 (100), 129 (60), 115 (79), 91 (40), 65 (12), 43 (26). TLC R_f = 0.32 (hexane */tert*-butyl methyl ether 10:1).

Pd-catalysed rearrangement[5] of 1-aryl-allyl acetates (**4**e-g) **to (*E*)-1-aryl-allyl acetates** (**5**e-g)

(*E*)-3-(4'-Chlorophenyl)-prop-2-enyl acetate (**5e**) A solution of 1-(4'-chlorphenyl)-prop-2-enyl acetate (**4e**) (5.03 g, 23.9 mmol) in 240 ml THF was treated with $[PdCl_2(CH_3CN)_2]$ (62.0 mg, 0.239 mmol, 1 mol%). After stirring for 14 h at 25 °C, the THF was removed *in vacuo* and the crude product purified by chromatography on silica-gel (43 x 5.5 cm, hexane */tert*-butyl methyl ether 20:1).to afford (**5e**) as a colourless oil, 4.68 g (93%). $C_{11}H_{11}ClO_2$ 210.66 req. C 62.7 H 5.26 found C 62.3 H 5.30%. IR ($CHCl_3$) 3026*m*, 3013*w*, 2949*w* , 1735*s*, 1658*w*, 1594*w*, 1492*s*, 1445*w*, 1406*w*, 1381*m*, 1363*m*, 1250*s*, 1232*s*, 1093*s*, 1025*m*, 1005*m*, 968*s*. ^{1}H NMR ($CDCl_3$) 2.08 (*s*, 3H, CH_3); 4.69 (*dd*, *J* = 6.4, 1.3, 2H, C(1)H_2); 6.23 (*dt*, *J*

= 15.9, 6.4, 1H, C(2)H); 6.57 (*dt*, *J* = 15.9, 1.3, 1H, C(3)H); 7.27 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 20.8 (CH_3); 64.6 (C(1)); 123.8 (C(2)); 127.7, 128.0 (arom. C), 132.6 (C(3)); 1343.6, 134.6 (arom. C), 170.52 (C=O). MS (EI) 212 (10), 210 (29, M+), 168 (37), 151 (20), 139 (15), 133 (16), 117 (33), 115 (100), 103 (2), 89 (9), 77 (12), 63 (7), 51 (5), 43 (43). TLC R_f = 0.15 (hexane /*tert*-butyl methyl ether 20:1).

(*E*)-3-(4'-Biphenyl)-prop-2-enyl acetate (**5f**) Yellow crystals (from hexane /*tert*-butyl methyl ether), 3.14g (68%). $C_{17}H_{16}O_2$ 252.31 req. C 80.9 H 6.39 found C 80.6 H 6.59%. Mp. 100-101°C. IR ($CHCl_3$) 3026*s*, 3014*s*, 2948*w*, 2880*w*, 1733*s*, 1654*w*, 1600*w*, 1558*w*, 1519*w*, 1487*s*, 1448*m*, 1409*m*, 1381*m*, 1362*s*, 1250*s*, 1232*s*, 1201*w*, 1101*w*, 1075*m*, 1024*s*, 968*s*, 860*s*. ^{1}H NMR ($CDCl_3$) 2.13 (*s*, 3H, CH_3); 4.78 (*dd*, *J* = 6.5, 1.3, 2H, C(1)H_2); 6.35 (*dt*, *J* = 15.9, 6.5, 1H, C(2)H); 6.71 (*dt*, *J* = 15.9, 1.3, 1H, C(3)H); 7.37 (*m*, 1H, arom. H); 7.47 (*m*, 4H, arom. H); 7.61 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 21.0 (CH_3); 65.1 (C(1)); 123.2 (C(2)); 126.9, 127.0, 127.2, 127.4, 128.8 (arom. C); 133.8 (C(3)); 135.2, 140.5, 140.8 (arom. C); 170.8 (C=O). MS (EI) 252 (87, M+), 210 (55), 191 (45), 178 (52), 165 (37), 152 (20), 115 (21), 77 (11), 63 (7), 51 (8), 43 (100). TLC R_f = 0.23 (hexane /*tert*-butyl methyl ether 10:1).

(*E*)-3-(4'-Methylphenyl)-prop-2-enyl acetate (**5g**) Colourless oil, 4.75g (97%). $C_{12}H_{14}O_2$ 190.24 req. C 75.8 H 7.42 O 16.8 found C 75.1 H 7.47 O 16.8% IR (NaCl) 3024*s*, 3012*s*, 2948*w*, 1732*s*, 1656*w*, 1613*w*, 1513*m*, 1446*w*, 1381*m*, 1362*m*, 1295*w*, 1256*s*, 1228*s*, 1182*w*, 1072*w*, 1025*m*, 967*m*, 840*w*. ^{1}H NMR ($CDCl_3$) 2.11 (*s*, 3H, CH_3); 2.35 (*s*, 3H, Ar-CH_3); 4.73 (*d*, *J* = 6.5, 2H, C(1)H_2); 6.25 (*dt*, *J* = 15.9, 6.5, 1H, C(2)H); 6.64 (*d*, *J* = 15.9, 1H, C(3)H); 7.14 (*d*, *J* = 8.0, 2H, arom. H); 7.30 (*d*, *J* = 8.0, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 20.9 (Ar-CH_3); 21.1 (CH_3); 65.1 (C(1)); 122.0 (C(2)); 126.5, 129.2, 133.4 (arom. C), 134.2 (C(3)); 137.9 (arom. C); 170.7 (C=O). MS (EI) 190 (64, M+), 148 (53), 115 (100), 91 (55), 65 (12), 43 (42). TLC R_f = 0.27 (hexane /*tert*-butyl methyl ether 9:1).

(*E*)-1-Aryl-allyl alcohols (**6**e-g)

(*E*)-3-(4'-Chlorophenyl)-prop-2-en-1-ol (**6e**) A solution of (*E*)-3-(4'-chlorophenyl)-prop-2-enyl acetate (**5e**) (4.44 g, 21.1 mmol) in 100 ml methanol was treated with K_2CO_3 (1.0 g, 7.2 mmol) and the resulting suspension stirred for 6 h at 25 °C. After removing the volatiles *in vacuo*, the yellow residue was dissolved in *tert*-butyl methyl ether and washed with water. The combined aqueous washings were back-extracted with *tert*-butyl methyl ether and the combined organic phases dried over $MgSO_4$. The solvent was removed *in vacuo* to afford a yellow solid that was twice re-crystallised from *tert*-butyl methyl ether / hexane to afford (**6e**) as a yellow crystalline solid, 2.69g (76%). C_9H_9ClO 168.62 req. C 64.1 H 5.38 found C 63.9 H 5.50%. Mp. 55-56 °C. IR ($CHCl_3$) 3607*m*, 3415*br*, 3043*s*, 3024*s*, 2926*w*, 2871*w*, 1654*w*, 1594*m*, 1491*s*, 1452*w*, 1405*m*, 1381*m*, 1296*w*, 1260*w*, 1179*w*, 1089*s*, 1012*s*, 969*s*, 845*m*, 830*m*. ^{1}H NMR ($CDCl_3$) 1.96 (*bt*, *J* = 5.0, 1H, OH); 4.32 (*dd*, *J* = 5.5, 5.0, 2H, C(1)H_2); 6.32 (*dt*, *J* = 15.9, 5.5, 1H, C(2)H); 6.56 (*d*, *J* = 15.9, 1H, C(3)H); 7.28 (*s*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 63.4 (C(1)); 127.6 (C(2)); 128.7, 129.1 (arom. C); 129.7 (C(1)), 133.2, 135.1 (arom. C). MS (EI) 170 (30), 168 (88, M+), 151 (9), 149 (17), 133 (85), 125 (100), 115 (75), 103 (54), 91 (44), 89 (21), 77 (44), 63 (16), 55 (24). TLC R_f = 0.18 (hexane / ethyl acetate 2:1).

(*E*)-3-(4'-Biphenyl)-prop-2-en-1-ol (**6f**) Yellow crystals, 2.08g (82%). Mp. 159-160°C IR ($CHCl_3$) 3606*m*, 3418*mbr*, 3029*m*, 3013*s*, 2928*w*, 2871*w*, 1673*m*, 1600*m*, 1518*w*, 1487*s*, 1409*w*, 1409*m*, 1380*m*, 1224*s*, 1186*w*, 1112*w*, 1085*m*, 1007*s*, 970*s*, 840*w*. ^{1}H NMR ($CDCl_3$) 4.37 (*dd*, *J* = 5.7, 1.4, 2H, C(1)H_2); 6.43 (*dt*, *J* = 15.9, 5.7, 1H, C(2)H); 6.67 (*dd*, *J* = 15.9, 1.4, 1H, C(3)H); 7.36 (*m*, 1H, arom. H); 7.47 (*m*, 4H, arom. H); 7.58 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 63.6 (C(1)); 126.7, 127.1 (arom. C); 127.2 (C(2)); 128.4, 128.6 (arom. C); 130.5 (C(1)); 135.5, 140.3, 140.4 (arom. C). MS (EI) 210 (M+, 81), 191 (8), 178 (18), 167 (100), 154 (38), 115 (8), 77 (7), 55 (7). TLC R_f = 0.02 (hexane /*t*-Butyl-methyl-ether 1:1).

(*E*)-3-(4'-Methylphenyl)-prop-2-en-1-ol (**6g**) Yellow crystals, 2.83g (81%). $C_{10}H_{12}O$ 148.2 req. C 81.0 H 8.16 found 80.6 H 8.22%. Mp. 52-53°C IR ($CHCl_3$) 3606*m*, 3429*brm*, 3026*m*, 3011*s*, 2924*m*, 2869*m*, 1654*w*, 1612*w*, 1570*w*, 1512*s*, 1453*m*, 1410*m*, 1380*s*, 1293*w*, 1181*m*, 1086*s*, 1002*s*, 969*s*, 850*m*, 830*m*. ^{1}H NMR ($CDCl_3$) 1.95 (*s*, 1H, OH); 2.36 (*s*, 3H, CH_3); 4.31 (*d*, *J* = 5.8, 2H, C(1)H_2); 6.32 (*dt*, *J* = 15.9, 5.8, 1H, C(2)H); 6.59 (*d*, *J* = 15.9, 1H, C(3)H); 7.14 (*d*, *J* = 8.0, 2H, arom. H); 7.30 (*d*, *J* = 8.0, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 20.8 (CH_3); 63.3 (C(1)); 126.0 (arom. C); 127.0(C(2)); 128.9 (arom. C); 130.7 (C(3)); 133.5, 137.1 (arom. C). MS (EI) 148 (98, M+), 133 (38), 119 (23), 115 (80), 105 (100), 92 (70), 91 (79), 77 (27), 74 (49), 65 (18), 55 (18), 41 (3). TLC R_f = 0.33 (hexane /*t*-Butyl-methyl-ether 1:1).

(*E*)-3-Aryl-allyl methyl carbonates (**7**a, e-g) - following the procedure described for **3**a-d.

(*E*)-3-Phenyl-prop-2-enyl methyl carbonate (**7a**) Colourless oil, 21.0g (80%). IR (NaCl) 3027*w*, 2956*w*, 1749*s*, 1448*m*, 1380*w*, 1266*s*, 1121*w*, 948*m*. ^{1}H NMR ($CDCl_3$) 3.80 (*s*, 3H, CH_3); 4.79 (*d*, *J* = 6.4, 2H, C(1)H_2); 6.30 (*dt*, *J* = 15.9, 6.4, 1H, C(2)H); 6.69 (*d*, *J* = 15.9, 1H, C(3)H); 7.32 (*m*, 5H, arom. H). ^{13}C

NMR ($CDCl_3$) 55.0 (OCH3); 68.5 (C(1)); 122.5 (C(2)); 126.7, 128.2, 128.6 (arom. C), 134.8 (C(3)); 136.0 (arom. C); 155.5 (C=O). TLC R_f 0.5 (hexane / ethyl acetate 4:1).
(*E*)-3-(4'-Chlorophenyl)-prop-2-enyl methylcarbonate (**7e**) Colourless solid, 1.06 g (97%). $C_{11}H_{11}ClO_3$ 226.65 req. C 58.3 H 4.89 found C 58.3 H 4.92%. Mp. 46-47°C. IR ($CHCl_3$) 3026*s*, 3013*m*, 2958*m*, 2858*w*, 1737*s*, 1659*w*, 1594*m*, 1491*s*, 1443*s*, 1407*m*, 1378*m*, 1256*s*, 1177*w*, 1120*m*, 1093*s*, 1013*m*, 968*s*, 946*s*, 855*m*, 835*m*, 800*m*. ^1H NMR ($CDCl_3$) 3.81 (*s*, 3H, CH_3); 4.78 (*dd*, *J* = 6.4, 1.4, 2H, C(1)H_2); 6.27 (*dt*, *J* = 15.9, 6.4, 1H, C(2)H); 6.64 (*dt*, *J* = 15.9, 1.3, 1H, C(3)H); 7.31 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 54.9 (CH_3); 68.2 (C(1)); 123.2 (C(2)); 127.9, 128.8 (arom. C); 133.4 (C(3)); 133.9, 134.6 (arom. C); 155.8 (C=O). MS (EI) 226 (M^+, 23), 167 (17), 151 (39), 139 (15), 115 (100), 103 (16), 77 (8), 59 (14), 51 (5). TLC R_f = 0.13 (hexane */tert*-butyl methyl ether 10:1).

(*E*)-3-(4'-Biphenyl)-prop-2-enyl methyl carbonate (**7f**) Yellow solid, 0.78g (76%). $C_{17}H_{16}O_3$ 268.31 req. C 76.1 H. 6.01 found C 76.1 H. 6.11%. Mp. 121-122°C. IR ($CHCl_3$) 3026*s*, 3013*m*, 2958*m*, 2857*w*, 1747*s*, 1654*w*, 1599*w*, 1519*w*, 1486*s*, 1443*s*, 1409*w*, 1378*m*, 1268*s*, 1121*m*, 1076*w*, 1038*w*, 1007*m*, 969*s*, 949*s*, 850*m*. ^1H NMR ($CDCl_3$) 3.83 (*s*, 3H, CH_3); 4.83 (*dd*, *J* = 6.4, 1.3, 2H, C(1)H_2); 6.35 (*dt*, *J* = 15.9, 6.4, 1H, C(2)H); 6.74 (*dt*, *J* = 15.9, 1.3, 1H, C(3)H); 7.36 (*m*, 1H, arom. H); 7.45 (*m*, 4H, arom. H); 7.60 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 54.9 (CH_3); 68.5 (C(1)); 122.5 (C(2)); 127.0, 127.2, 127.4, 127.5, 128.9 (arom. C); 134.4 (C(3)); 135.1, 140.6, 141.0 (arom. C); 155.8 (C=O). MS (EI) 268 (M^+, 100), 209 (34), 192 (90), 178 (55), 165 (35), 152 (16), 115 (22) 77 (8), 59 (12), 51 (6). TLC R_f = 0.65 (hexane */tert*-butyl methyl ether 1:1).

(*E*)-3-(4-Methylphenyl)-prop-2-enyl methyl carbonate (**7g**) Colourless solid, 1.08g (94 %). $C_{12}H_{14}O_3$ 206.24 req. C 69.9 H 6.84 found C 70.1 H 6.82%. Mp. 47-48°C. IR ($CHCl_3$) 3026*m*, 3013*m*, 1747*s*, 1611*w*, 1513*m*, 1443*s*, 1378*m*, 1298*s*, 1270*s*, 1182*w*, 1121*w*, 969*m*, 944*m*. ^1H NMR ($CDCl_3$) 2.35 (*s*, 3H, CH_3); 3.81 (*s*, 3H, CH_3O); 4.79 (*dd*, *J* = 6.0, 1.0, 2H, C(1)H_2); 6.26 (*dt*, *J* = 15.9, 6.6, 1H, C(2)H); 6,67 (*dt*, *J* = 15.9, 1.0, 1H, C(3)H); 7.14 (*d*, *J* = 8.0, 2H, arom. H); 7.30 (*d*, *J* = 8.0, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 21.2 (Ar-CH_3); 54.7 (CH_3O); 68.5 (C(1)); 121.3 (C(2)); 126.6, 129.3, 133.3 (arom. C); 134.8 (C(3)); 138.1 (arom. C); 155.7 (C=O). MS (EI) 206 (M+, 58), 147 (44), 131 (100), 119 (41), 115 (95), 103 (8), 91 (43), 77 (12), 59 (14) 51 (11). TLC R_f = 0.26 (hexane */tert*-butyl methyl ether 10:1).

Tungsten-catalysed allylic substitution of (3a-d) and (7a,f-g): preparation of (8a-g).

(*R*)-(+)-Dimethyl 3-phenyl-1-butene-4,4-dicarboxylate (*R*)-(+)-**8a** An orange-red solution of [$W(CO)_3(\eta^6$-C_7H_8)] (9.33 mg, 25.9 µmol) and 2,2'-bipyridine (4.97 mg, 31.9 µmol) in 4 ml degassed, argon-saturated THF was heated to 60 °C for 15 min resulting in a homogenous brown-black solution. After cooling to 25 °C, dimethyl sodiomalonate (81.9 mg, 0.531 mmol) was added and the suspension stirred vigorously at 60°C for 10 min. The resulting grey-black solution was cooled to 25 °C and combined with 88% ee (*S*)-(-)-1-phenyl-prop-2-enyl methyl carbonate (*S*)-(-)-(**3a**) (50.0 mg , 0.260 mmol). After heating to 60 °C for 18 h, the deep red homogeneous solution was quenched with NH_4Cl (50% sat. aq., 5 ml) and the mixture extracted three times with CH_2Cl_2 (15 ml portions). The combined extracts were dried (Na_2SO_4) and then filtered through a short plug of silica-gel before analysis of the products by GC. Evaporation of the solvent afforded an oil that was purified by chromatography on silica-gel (20 x 2 cm, hexane / ethyl acetate 9:1) to afford (*R*)-(+)-**8a** as colourless oil, 54.0mg (84%). $C_{14}H_{16}O_4$ 248.28 req. C 67.7 H 6.50 found C 68.1 H 6.54%. $[\alpha]_D$ = +31.3 (c = 0.97, $CHCl_3$, 24 °C). 88% ee HPLC (OJ column, 220 nm, 0.5 ml/min 93% hexane / 7% iPrOH; t_R = 45.5 (S) and 51.0 (R) min). IR (NaCl) 3030*w*, 2953*m*, 2844*w*, 1759*s*, 1739*s*, 1638*w*, 1601*w*, 1493*w*, 1453*m*, 1434*s*, 1318*m*, 1263*s*, 1197*s*, 1197*s*, 1163*s*, 1027*m*, 922*w*. ^1H NMR ($CDCl_3$) 3.50 (*s*, 3H, CH_3); 3.75 (*s*, 3H, CH_3); 3.88 (*d*, *J* = 11.0, 1H, C(4)H); 4.10 (*dd*, *J* = 8.1, 11.0, 1H, C(3)H); 5.09 (*d*, *J* = 10.2, 1H, C(1)H); 5.13 (*d*, *J* = 17.1, 1H, C(1)H); 6.0 (*ddd*, *J* = 17.1, 10.2, 8.1, 1H, C(2)H); 7.27 (*m*, 5H, arom. H). ^{13}C NMR ($CDCl_3$) 49.8 (C(4)); 52.5, 52.7 (CH_3), 57.5 (C(3)); 116.6 (C(1)); 127.1, 127.9, 128.6 (arom. C); 137.8 (C(2)); 139.9 (arom. C); 167.7, 168.2 (C=O). MS (EI) 248 (1, M+), 217 (1), 189 (100), 173 (3), 156 (18), 129 (38), 117 (74), 103 (6), 91 (14), 77 (9), 65 (4), 59 (9). TLC R_f = 0.41 (hexane / ethyl acetate 4:1).

Dimethyl 3-(4'-trifluoromethylphenyl)-1-butene-4,4-dicarboxylate (**8b**) Colourless oil, 55.0mg (73%). $C_{15}H_{15}F_3O_4$ 316.28 req. 57.0 H 4.78 found 57.3 H 4.90%. IR 3086*w*, 3026*s*, 3013*m*, 2955 *s*, 2846*w*, 1752 *s*, 1639 *m*, 1618*s*, 1586*m*, 1436*s*, 1416*s*, 1318*s*, 1265*s*, 1126*s*, 1069*s*, 988*m*. ^1H NMR ($CDCl_3$) 3.52 (*s*, 3H, CH_3); 3.76 (*s*, 3H, CH_3); 3.90 (*d*, *J* = 11.0, 1H, C(4)H); 4.19 (*dd*, *J* = 8.2, 11.0, 1H, C(3)H); 5.13 (*d*, *J* = 10.0, 1H, C(1)H); 5.14 (*d*, *J* = 17.3, 1H, C(1)H); 5.97 (*ddd*, *J* = 17.3, 10.0, 8.2, 1H, C(2)H); 7.36 (*d*, *J* = 8.0, 2H, arom. H); 7.57 (*d*, *J* = 8.0, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 49.4 (C(4)); 52.6, 52.7 (CH_3); 57.0 (C(3)); 117.6 (C(1)); 125.6, 128.4 (arom. C); 136.9 (C(2)); 144.2 (arom. C); 167.6, 167.9 (C=O). MS (EI) 297 (27), 257 (100), 224 (27), 197 (30), 185 (50), 165 (28), 128 (16), 115 (18), 101 (4), 75 (11), 59 (27), 44 (6). TLC R_f = 0.16 (hexane / ethyl acetate 6:1).

Dimethyl 3-(4'-bromophenyl)-1-butene-4,4-dicarboxylate (**8c**) Colourless oil, 51.1mg (73%). $C_{14}H_{15}BrO_4$ 327.17 req. C 51.4 H 4.62 found C 51.3 H 4.67%. IR(NaCl) 3086*w*, 3026*s*, 3015*s*, 2955*s*, 2845*w*, 1746*s*, 1639*m*, 1591*w*, 1483*w*, 1436*s*, 1405*m*, 1313*s*, 1264*s*, 1166*s*, 1125*m*, 1074*s*, 1026*m*, 1011*s*, 988*m*. ^{1}H NMR ($CDCl_3$) 3.52 (*s*, 3H, CH_3); 3.74 (*s*, 3H, CH_3); 3.82 (*d*, *J* = 11.0, 1H, C(4)H); 4.06 (*dd*, *J* = 8.0, 11.0, 1H, C(3)H); 5.10 (*d*, *J* = 10.2, 1H, C(1)H); 5.11 (*d*, *J* = 17.1, 1H, C(1)H); 5.95 (*ddd*, *J* = 17.1, 10.2, 8.0, 1H, C(2)H); 7.11 (*d*, *J* = 8.4, 2H, arom. H); 7.43 (*d*, *J* = 8.4, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 49.1 (C(4)); 52.6, 52.7 (CH_3)); 57.1 (C(3)); 117.1 (C(1)); 121.1, 129.7, 131.8 (arom. C), 137.2 (C(2)); 139.1 (arom. C), 167.6, 168.0 (C=O). MS (EI) 328 (M+, 3), 326 (3), 269 (97), 267 (100), 236 (12), 234 (11), 197 (20), 195 (20), 187 (3), 155 (21), 128 (32), 116 (95), 102 (10), 75 (6), 59 (12), 51 (5). TLC = 0.34 (hexane / ethyl acetate 4:1).

Dimethyl 3-(1'-naphthyl)-1-butene-4,4-dicarboxylate (**8d**) Colourless oil 55.0mg (86%). $C_{18}H_{18}O_4$ 298.34 req. C 72.5 H 6.08 found C 72.3 H 6.14%. IR (NaCl) 3026*m*, 3021*s*, 3016*s*, 2954*w*, 1745*s*, 1735*s*, 1637*w*, 1599*w*, 1511*w*, 1436*m*, 1396*w*, 1260*m*, 1231*m*, 1165*m*, 1026*w*, 989*w*. ^{1}H NMR ($CDCl_3$) 3.39 (*s*, 3H, CH_3); 3.79 (*s*, 3H, 2 x CH_3); 4.17 (*d*, *J* = 10.9, 1H, C(4)H); 5.04 (*dd*, *J* = 8.1, 10.9, 1H, C(3)H); 5.11 (*d*, *J* = 10.2, 1H, C(1)H); 5.17 (*d*, *J* = 17.1, 1H, C(1)H); 6.09 (*ddd*, *J* = 17.1, 10.2, 8.1, 1H, C(2)H); 7.47 (*m*, 4H, arom. H); 7.75 (*d*, *J* = 7.7, 1H, arom. H); 7.85 (*d*, *J* = 7.9, 1H, arom. H); 8.25 (*d*, *J* = 8.5, 1H, arom. H). ^{13}C NMR ($CDCl_3$) 44.2 (C(4)); 52.5, 52.7 (CH_3), 57.0 (C(3)); 117.1 (C(1)); 123.3, 124.4, 125.3, 125.7, 126.3, 127.8, 128.9, 131.4, 134.1, 136.2 (arom. C), 137.7 (C(2)); 167.9, 168.5 (C=O). MS (EI) 298 (M+, 8), 267 (1), 238 (4), 235 (3), 207 (6), 179 (21), 167 (100), 152 (28), 133 (3), 115 (3), 89 (2), 69 (2), 59 (4). TLC R_f = 0.30 (hexane / ethyl acetate 4:1).

Dimethyl 3-(4'-chlorophenyl)-1-butene-4,4-dicarboxylate (**8e**) Colourless oil, 54.0 mg (74%). $C_{14}H_{15}ClO_4$ 282.72 req. C 59.5 H 5.35 found C 59.6 H 5.41%. IR (NaCl) 3030*m*, 3018*s*, 3010*w*, 2955*m*, 1735*s*, 1638*m*, 1492*s*, 1436*s*, 1408*m*, 1314*s*, 1263*s*, 1198*s*, 1166*s*, 1125*m*, 1092*s*, 1026*m*, 1015*s*, 988*m*, 929*m*. ^{1}H NMR ($CDCl_3$) 3.52 (*s*, 3H, CH_3); 3.75 (*s*, 3H, CH_3); 3.82 (*d*, *J* = 10.9, 1H, C(4)H); 4.10 (*dd*, *J* = 10.9, 8.0, C(3)H); 5.10 (*d*, *J* = 10.3, 1H, C(1)H); 5.11 (*d*, *J* = 16.0, 1H, C(1)H); 5.95 (*ddd*, *J* = 16.0, 10.3, 8.0, 1H, C(2)H); 71.7 (*d*, *J* = 8.5, 2H, arom. H); 7.28 (*d*, *J* = 8.5, 2H, arom. H). ^{13}C NMR ($CDCl_3$) 49.0 (C(4)); 52.6, 52.7 (CH_3); 57.2 (C(3)); 117.1 (C(1)); 128.9, 129.4, 133.0 (arom. C); 137.3 (C(2)); 138.5 (arom. C); 167.7, 168.3 (C=O). MS (EI) 282 (M+, 2), 225 (33), 223 (100), 191 (16), 163 (19), 151 (56), 128 (19), 115 (42), 102 (5), 89 (4), 75 (6), 59 (9). TLC R_f = 0.29 (hexane / ethyl acetate 4:1).

Dimethyl 3-(4'-biphenyl)-1-butene-4,4-dicarboxylate (**8f**) Colourless oil, 54.0mg (88%). $C_{20}H_{20}O_4$ 324.38req. C 74.0 H 6.21 found C 73.6 H 6.25%. IR (NaCl) 3024*s*, 3016*s*, 2955*m*, 1756*s*, 1735*s*, 1638*w*, 1486*m*, 1449*w*, 1436*s*, 1320*m*, 1263*s*, 1228*s*, 1166*m*. ^{1}H NMR ($CDCl_3$) 3.54 (*s*, 3H, CH_3); 3.77 (*s*, 3H, CH_3); 3.92 (*d*, *J* = 11.0, 1H, C(4)H); 4.18 (*dd*, *J* = 11.0, 8.2, 1H, C(3)H); 5.12 (*d*, *J* = 10.4, 1H, C(1)H); 5.17 (*d*, *J* = 17.2, 1H, C(1)H); 6.04 (*ddd*, *J* = 17.2, 10.4, 8.2, 1H, C(2)H); 7.33 (*m*, 3H, arom. H); 7.43 (*m*, 2H, arom. H); 7.56 (*m*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 49.4 (C(4)); 52.5, 52.7 (CH_3O); 57.3 (C(3)); 116.8 (C(1)); 127.0, 127.3, 127.4, 128.3, 128.8 (arom. C); 137.7 (C(2)); 139.1, 140.0, 140.7 (arom. C); 167.9, 168.2 (C=O). MS (EI) 324 (33, M+), 293 (1), 265 (100), 233 (14), 205 (24), 193 (66), 178 (80), 165 (27), 152 (11), 115 (11), 102 (3), 91 (6), 59 (10), 51 (3). TLC R_f = 0.21 (hexane / ethyl acetate 5:1).

Dimethyl 3-(4'-methylphenyl)-1-butene-4,4-dicarboxylate (**8g**) Colourless oil, 44.0mg (65%). $C_{15}H_{15}O_4$ 262.30 req. C 68.7 H 6.92 found C 68.7 H 6.96%. IR (NaCl) 3085*w* , 3034*s*, 3007*s*, 2954*s*, 2925*m*, 1736*s*, 1638*m*, 1513*s*, 1435*s*, 1320*s*, 1265*s*, 1193*s*, 1165*s*, 1024*m*, 989*m*. ^{1}H NMR ($CDCl_3$) 2.31 (*s*, 3H, Ar-CH_3); 3.52 (*s*, 3H, CH_3O); 3.74 (*s*, 3H, CH_3O); 3.86 (*d*, *J* = 11.0, 1H, C(4)H); 4.08 (*dd*, *J* = 11.0, 8.2, 1H, C(3)H); 5.07 (*d*, *J* = 9.4, 1H, C(1)H); 5.11 (*d*, *J* = 17.0, 1H, C(1)H); 5.98 (*ddd*, *J* = 17.0, 9.4, 8.2, 1H, C(2)H); 7.11 (*s*, 4H, arom. H). ^{13}C NMR ($CDCl_3$) 21.1 (CH_3); 49.4 (C(2)); 52.4, 52.6 (CH_3O); 57.4 (C(3)), 116.4 (C(1)), 127.7, 129.4, 136.7, 136.9 (arom. C); 138.0 (C(2)); 167.9, 168.3 (C=O). MS (EI) 262 (M+, 5), 244 (1), 231 (1), 203 (100), 171 (19), 143 (29), 131 (73), 115 (25), 103 (3), 91 (21), 77 (4), 65 (4), 59 (7). TLC R_f = 0.31 (hexane / ethyl acetate 4:1).

Assignment of absolute configuration of (**8a**) *via* : [(*S*)-(-)-(**8a**) —> (*S*)-(+)-(**13**) —> (*S*)-(+)-(**14**)]
(*S*)-(+)-Methyl 3-phenyl-pent-4-enoate (*S*)-(+)-(**13**) A solution of (*S*)-(-)-dimethyl 3-phenyl-1-butene-4,4-dicarboxylate (*S*)-(-)-(**8a**) (38 % ee) (100 mg, 0.403 mmol), H_2O (36 mg) and NaCl (67 mg) in DMSO (0.5 mL) was sealed at 2 x 10^{-2} mmHg in an ampoule. The ampoule was heated to 180 °C for 6 h, cooled to 25 °C and then carefully opened. The volatiles were removed under high vacuum, the residue extracted with a mixture of hexane / ethyl acetate (9:1) and then applied to silica-gel (25 x 2.5 cm). Elution with hexane / ethyl acetate (9:1) afforded (*S*)-(+)-(**13**) as a colourless oil, 47 mg (61%). $C_{12}H_{14}O_2$ 190.24 req. C 75.8 H 7.42 found C 75.4 H 7.21%. $[\alpha]_D$ = +3.7 (c = 1.07, $CHCl_3$, 24 °C) IR (NaCl) 3062*w*, 3028*w*, 2951*w*, 1740*s*, 1638*w*, 1601*w*, 1493*w*, 1458*w*, 1436*m*, 1361*w*, 1258*m*, 1195*w*, 1164*m*, 1077*w*, 994*w*, 920*w*, 759*w*, 701*m*. ^{1}H NMR ($CDCl_3$) 2.75 (*m*, 2H, C(2)H_2); 3.63 (*s*, 3H, CH_3O); 3.88 (*m*, 1H, C(3)H); 5.46 (*m*, 2H, C(5)H_2);

5.99 (*m*, 1H, C(4)H); 7.2-7.35 (*m*, 5H, arom. H). ^{13}C NMR ($CDCl_3$) 40.1 (C(2)); 45.6 (CH_3); 51.6 (C(3)); 114.8 (C(5)); 126.8, 127.5, 128.6 (arom. C); 140.2 (C(4)); 142.5 (arom. C); 172.3 (C=O). MS(EI) 190 (36, M^+), 158 (6), 147 (7), 130 (91), 117 (100), 115 (81), 103 (9), 91 (41), 77 (15), 65 (9).

(*S*)-(+)-dimethyl phenyl succinate (*S*)-(+)-(**14**) A solution of (*S*)-(+)-methyl 3-phenyl-pent-4-enoate (*S*)-(+)-(**13**) (40 mg, 0.21 mmol) in C_6H_6 (10 mL) was percolated through a column of $KMnO_4$ on silica-gel (ca. 25% w/w) and then the column washed (C_6H_6, 4mL) and dried (N_2). Elution with H_2O (30 mL) into a mixture of $Na_2S_2O_5$ (5g) and HCl (1M aq.) afforded a colourless solution that was extracted with 5 x 10 mL CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and evaporated. The residue was dissolved in a mixture of MeOH (2 mL) and toluene (5 mL) and stirred at RT for 2 h. Addition of Me_3SiCHN_2 (0.5 mL of a 2.0 M solution in hexane) resulted in a yellow solution and vigorous N_2 evolution. Excess Me_3SiCHN_2 was quenched with a few drops of AcOH and then the mixture evaporated. The residue was purified by chromatography on silica-gel (2.5 x 15 cm, hexane / ethyl acetate 9:1) to afford (*S*)-(+)-(**14**) as a pale yellow oil, 36.8 mg (79%). $C_{12}H_{14}O_4$ 222.24 req. C 64.9 H 6.35 found C 64.9 H 6.26%. $[\alpha]_D$ = +50.7 (c = 0.95, $CHCl_3$, 24 °C), 38% ee HPLC (OJ column, 220 nm, 0.5 ml/min 85% hexane / 15% iPrOH; t_R = 40.7 (S) and 50.7 (R) min). IR (NaCl) 3064*w*, 3031*w*, 2954*m*, 2847*w*, 1738*s*, 1603*w*, 1584*w*, 1497*m*, 1455*m*, 1437*s*, 1411*w*, 1336*m*, 1296*m*, 1253*s*, 1232*s*, 1198*s*, 1163*s*, 1073*w*, 1006*m*, 967*w*, 913*w*, 859*w*, 844*w*, 779*w*, 736*w*, 700*m*. ^{1}H NMR ($CDCl_3$) 2.65 (*dd*, *J* = 17.1, 5.3, 1H, C(3)H); 3.22 (*dd*, *J* = 17.1, 10.2, 1H, C(3)H); 3.69 (*s*, 6H, 2 x CH_3); 4.10 (*dd*, *J* = 10.2, 5.3, 1H, C(2)H); 7.27-7.34 (*m*, 5H, arom. H). ^{13}C NMR ($CDCl_3$) 37.7 (C(3)); 47.1 (C(2)); 51.9, 52.4 (CH_3); 127.7, 127.8, 128.9, 137.7 (arom. C); 172.0, 173.5 (C=O). MS(CI) 240 (64), 223 (100, MH^+), 208 (29), 190 (8), 121 (7). TLC R_f 0.12 (hexane / ethyl acetate 9:1).

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8. Under identical conditions, with $[Pd(PPh_3)_4]$ as catalyst the regioselectivity is reversed (**8a** : **9a** = 6 : 94).
9. 38% ee (*S*)-(-)-**8a** Was converted to 38% ee (*S*)-(+)-dimethyl phenyl succinnate (**14**) - see experimental section. The reported specific rotation for **8a** is low: 97 % ee (*S*)(-) (**3a**) $[\alpha]_D$ -24 (c = 0.12, CHCl3, 21 °C); Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organometal. Chem.*, **1990**, 383, 161-177.
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14. $MeOCO_2^-$ is assumed to decarboxylate (—> CO_2 + MeO^-). $[W(CO)_4(bipy)]$ was also isolated after work-up and identified by ^{1}H NMR, IR and elemental analysis. Other organic products resulting from side reactions were identified - these will be reported elsewhere.

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