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Reaction of α,β-unsaturated Fischer carbene complexes with allyl alkoxide

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Abstract—Optically enriched homo-binuclear Fischer chromium carbene complexes with planar chiral arene chromium complexes gave α-allyl β-arylpropionates up to 97% ee by reaction with allyl alkoxide and subsequent photo-oxidative demetalation. The chiral hetero-binuclear tungsten carbene complexes afforded *anti* α-allyl β-hydroxy β-arylpropionates as a major product up to 92/8 dr by the same reaction sequence. High diastereoselectivity in these reactions is contributed to the planar chirality of the arene chromium complex, even though the reaction was carried out under vigorous basic media. The reaction products, α-allyl β-arylpropionates were derived by 1,3-$M(CO)_5$ shift and subsequent [3,3]-sigmatropic rearrangement. Also, the corresponding chromium-uncomplexed α,β-unsaturated Fischer carbene complexes afforded α-allyl β-arylpropionates under the same conditions. Formation of β-allyl β-arylpropionates via 1,2-$M(CO)_5$ shift followed by [3,4]-sigmatropic rearrangement was not observed in both reactions of chromium-coordinated and the corresponding chromium-uncoordinated α,β-unsaturated Fischer carbene complexes with allyl alkoxide in the presence of base.

1. Introduction

Fischer carbene complexes are one of the most versatile organometallic reagents for organic synthesis,[1] and a number of novel reactions using Fischer carbene complexes have been reported.[2] For instance, α,β-unsaturated Fischer carbene complexes are significant for organic synthesis such as Michael addition reaction,[3] [3+2]-, [4+2]- and [3+2+1]-cycloaddition reactions.[4–6] Furthermore, optically active Fischer carbene complexes have attracted increasing attention as powerful tool of asymmetric reaction, and various chiral carbene complexes have been developed to date. Most of these chiral α,β-unsaturated Fischer carbene complexes have chiral alcohols or amines at the carbene carbon atom as a stabilizing substituent (type I) due to their easy preparation (Fig. 1). On the other hand, there are few examples of the other type of chiral α,β-unsaturated Fischer carbene complexes, in which a chiral auxiliary is directly attached to the α,β-unsaturated bond.[7] As a synthetic development of the planar chiral arene chromium complexes, we have investigated asymmetric reaction of optically pure α,β-unsaturated Fischer carbene complexes with planar chirality (Type II, R*=$ArCr(CO)_3$). We expected that these type of chiral Fischer carbene complexes would become promising chiral reagents, since a reactive site is located closely to the chiral auxiliary. Moreover, these binuclear chiral complexes would be expected to develop interesting asymmetric reactions based on the combined nature of two metallic moieties. However, to best of our knowledge, there is no report on asymmetric reactions utilizing α,β-unsaturated binuclear Fischer carbene complexes[8] with a planar chiral transition metal π-complex. Herein, we wish to report asymmetric reaction utilizing planar chiral binuclear Fischer carbene complexes with allyl alkoxides.[9]

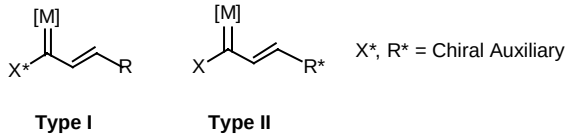

Figure 1. Chiral α,β-unsaturated Fischer carbene complexes.

2. Results and discussion

Barluenga et al. reported[10] that aryl α,β-unsaturated Fischer carbene complexes **1** were treated with allyl alcohol in the

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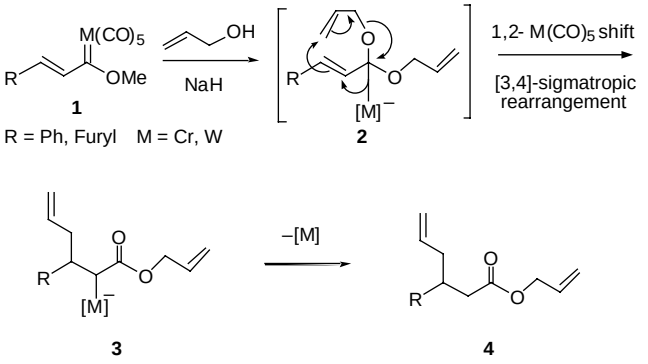
presence of a base to give β-allyl β-arylpropionate **4** via concerted 1,2-$M(CO)_5$ shift followed by [3,4]-sigmatropic rearrangement (Scheme 1). The allyl group was introduced at the β-carbon to the ester carbonyl group. Therefore, β-allyl β-arylpropionates **4** would be expected to obtained as optically active compounds by utilizing α,β-unsaturated binuclear Fischer carbene complexes with planar chiral arene chromium complex as a chiral auxiliary.

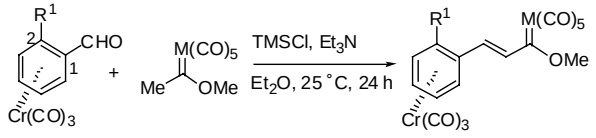


Scheme 1. [3,4]-Sigmatropic rearrangement promoted by [1,2]-metal shift reported by Barluenga.

2.1. Synthesis of α,β-unsaturated binuclear Fischer carbene complexes

Chiral binuclear α,β-unsaturated Fischer carbene complexes **7** as starting materials were easily prepared by aldol condensation of planar chiral *o*-substituted benzaldehyde chromium complexes **5** with methylmethoxycarbene complexes **6** in the presence of triethylamine and trimethylsilyl chloride in reasonable yields (Table 1).[11] The geometry of the double bond of complexes **7** was determined as (*E*)-configuration by ^{1}H NMR.

Table 1. Preparation of chiral α,β-unsaturated binuclear Fischer carbene complexes[a]



5 **6** **7**

Entry	Compound	M	R^1	Yield **7** (%)
1	**7a**	Cr	H	55
2	**7b**	Cr	OMe	74
3	**7c**	Cr	Me	60
4	**7d**	Cr	OPr-*i*	31
5	**7e**	W	H	40
6	**7f**	W	OMe	59
7	**7g**	W	Me	65
8	**7h**	W	OPr-*i*	30

[a] Planar chiral (1*R*,2*S*)-enantiomer was used as starting materials in this study.

2.2. Reactions of binuclear Fischer carbene complexes with allyl alkoxides

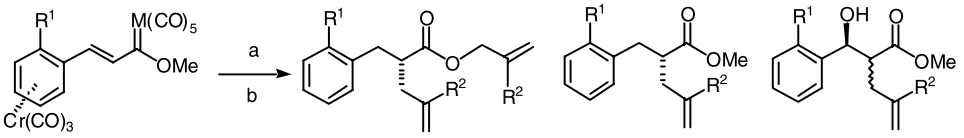
Since we have chiral binuclear α,β-unsaturated Fischer carbene complexes in hand, we examined an asymmetric version of [3,4]-sigmatropic rearrangement reaction of these chiral binuclear α,β-unsaturated Fischer carbene complexes with allyl alkoxides. Initially, we studied the synthesis of β-allyl β-phenyl propionate **4** (R=Ph) by using nonchiral binuclear Fischer carbene complex **7a** according to Barluenga's conditions. A reaction was carried out by stirring a solution of the binuclear carbene complex **7a** and allyl alcohol in the presence of NaH under inert gas in a balloon, and subsequently exposed to sunlight. Surprisingly, α-allyl β-phenyl propionate **8a** was obtained in 75% yield without formation of β-allyl β-phenyl propionate **4** (R=Ph) (Table 2, entry 1). Thus, the allyl group was regioselectively introduced at the α position to the ester group. The structure of α-allyl β-phenyl propionate **8a** was absolutely confirmed by comparison with both authentic samples **8a** and **4** (R=Ph).[12] Both compounds **4** and **8a** could be cleanly distinguished by ^{1}H NMR spectra. The formation of α-allyl β-phenyl propionate **8a** is in sharp contrast to Barluenga's report, in which the allyl group was introduced at the β-position.

We initially imagined that the distinct difference of two reaction pathways of α,β-unsaturated Fischer carbene complexes with allyl alkoxide might be attributed to the strong electron-withdrawing ability of the tricarbonylchromium fragment. Hence, we examined the reaction of α,β-unsaturated chromium carbene complex **11** having *p*-nitrophenyl group with allyl alkoxide. However, only ester exchange product **12** was obtained (Scheme 2). Thus, the electronic effect of the arene ring of α,β-unsaturated binuclear Fischer carbene complexes does not seem to control the two reaction pathways. Surprisingly, the tricarbonylchromium-uncomplexed α,β-unsaturated Fischer carbene complex **1** (R=Ph, M=Cr) gave only α-allyl β-phenyl propionate **8a** in 68% yield without detection of β-allyl β-phenyl propionate **4** (R=Ph) by the reaction with allyl alkoxide under identical conditions with Barluenga's report. In this way, we obtained only α-allyl β-phenyl propionate by reaction with allyl alkoxide in both cases of α,β-unsaturated Fischer carbene complex **1** and the corresponding tricarbonylchromium coordinated α,β-unsaturated Fischer carbene complex **7**. Consequently, we concluded that the structural assignment of the reaction products is wrong in Barluenga's report.[10]

We next extended this interesting reaction to the asymmetric synthesis of α-allyl β-phenyl propionate by using planar chiral binuclear carbene complexes. When enantiomerically pure binuclear Fischer carbene complex **7b** ($[\alpha]_D^{24}$ −3400 (*c* 0.001, $CHCl_3$)), derived from a planar chiral (−)-(*R*)-*o*-methoxybenzaldehyde chromium complex, was reacted with allyl alkoxide at 25 °C, α-allyl β-(*o*-methoxyphenyl)propionate (**8b**) ($[\alpha]_D^{23}$ −25.2 (*c* 0.09, $CHCl_3$)) was obtained in 68% yield with 95% ee[13] (entry 2). Expectedly, the α-allyl phenyl propionate **8b** was obtained with high ee despite severe basic conditions.

The absolute stereochemistry of the compound **8b** was determined as (*R*)-configuration by comparison of an optical rotation of authentic (*S*)-configurated allyl 2-allyl *o*-methoxyphenylpropionate (**15**) ($[\alpha]_D^{23}$ +27.1 (*c* 0.38, $CHCl_3$)) prepared from Evans' oxazolidone derivative **13** (Scheme 3).[14]

Table 2. Reaction of binuclear carbene complexes **7** with allyl alcohols[a]



7 **8** **9** **10**

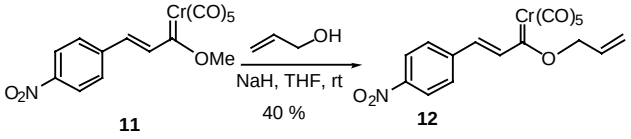
7a; R^1 = H, M = Cr
7b; R^1 = OMe, M = Cr
7c; R^1 =Me, M = Cr
7d; R^1 = OPr-*i*, M = Cr
7e; R^1 = H, M = W
7f; R^1 = OMe, M = W
7g; R^1 = Me, M = W
7h; R^1 = OPr-*i*, M = W

Alphabetical numbering for compounds **8**, **9** and **10** is as follows;
a: R^1 = R^2 = H; **b:** R^1 = OMe, R^2 = H; **c:** R^1 = OMe, R^2 = Me;
d: R^1 = Me, R^2 = H; **e:** R^1 = OPr-*i*, R^2 = H

Entry	Complex	Temperature (°C)[b]	Yield **8** (%)	Yield **9** (%)	Yield **10** (%)	ee (%) of **8** or **9**[c]	*anti*/*syn* Ratio of **10**[d]
1	**7a**	25	**8a** (75)	—	—	—	—
2	**7b**	25	**8b** (68)	—	—	95	—
3	**7b**	0	—	**9b** (40)	**10b** (40)	97	78/22
4	**7b**	25	**8c** (85)	—	—	72	—
5	**7b**	0	—	—	**10c** (45)	—	83/17
6	**7c**	25	**8d** (83)	—	—	77	—
7	**7c**	0	—	**9d** (55)	**10d** (40)	93	83/17
8	**7c**	−30	—	**9d** (33)	**10d** (30)	97	80/20
9	**7d**	0	—	**9e** (10)	**10e** (51)	—	85/15
10	**7e**	25	—	**9a** (10)	**10a** (71)	—	63/37
11	**7e**	−30	—	—	**10a** (75)	—	92/8
12	**7f**	−30	—	—	**10b** (65)	—	92/8
13	**7g**	−30	—	—	**10d** (70)	—	92/8
14	**7h**	−30	—	—	**10e** (31)	—	75/25

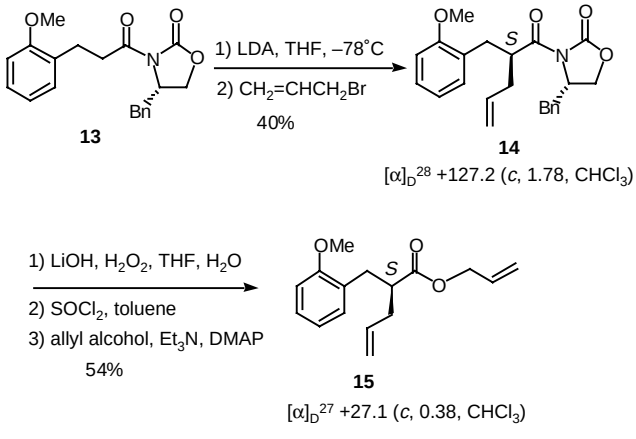
[a] Reagents and conditions: (a)  , NaH, THF, under inert gas in ballon; (b) *hν* air, ether

[b] Reaction time; 30 min for the reaction at 25 °C: 1.5 h for the reaction at 0 or −30 °C.
[c] Determined by chiral HPLC.
[d] Determined by integration of representative signals by ^{1}H NMR of the crude product.



11 **12**

Scheme 2. Reaction of electron deficient mononuclear carbene complex with allyl alkoxide.



13 **14**

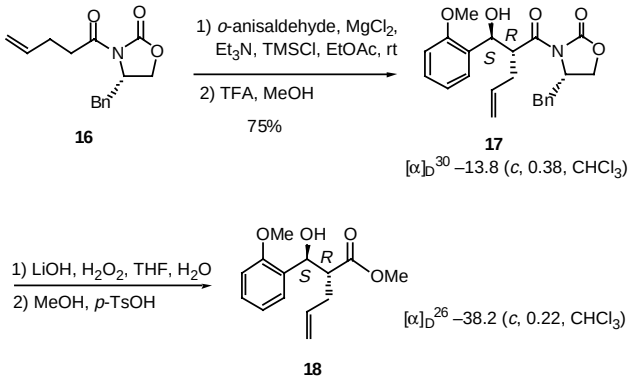
$[\alpha]_D^{28}$ +127.2 (*c*, 1.78, $CHCl_3$)

15

$[\alpha]_D^{27}$ +27.1 (*c*, 0.38, $CHCl_3$)

Scheme 3. Absolute configuration of α-allyl β-(2-methoxyphenyl) propionate.

When the reaction was performed at 0 °C, the corresponding α-allyl methyl ester **9b** was obtained in 40% yield with 97% ee along with formation of α-allyl β-hydroxy ester **10b** as an easily separable diastereomeric mixture in 40% yield (entry 3). The stereochemistry of the major α-allyl β-hydroxy ester **10b** ($[\alpha]_D^{30}$ −36.0 (*c* 0.23, $CHCl_3$)) was determined to possess the *anti* (2*R*,3*S*)-configuration by comparison with authentic compound. The authentic methyl 2(*R*)-allyl-3(*S*)-hydroxy-3(*o*-methoxyphenyl)propionate (**18**) was prepared by *anti* selective aldol reaction of chiral oxazoline derivative **16** according to the reported procedure[15] (Scheme 4).



16 **17**

$[\alpha]_D^{30}$ –13.8 (*c*, 0.38, $CHCl_3$)

18

$[\alpha]_D^{26}$ –38.2 (*c*, 0.22, $CHCl_3$)

Scheme 4. Absolute configuration of α-allyl-β-hydroxy ester.

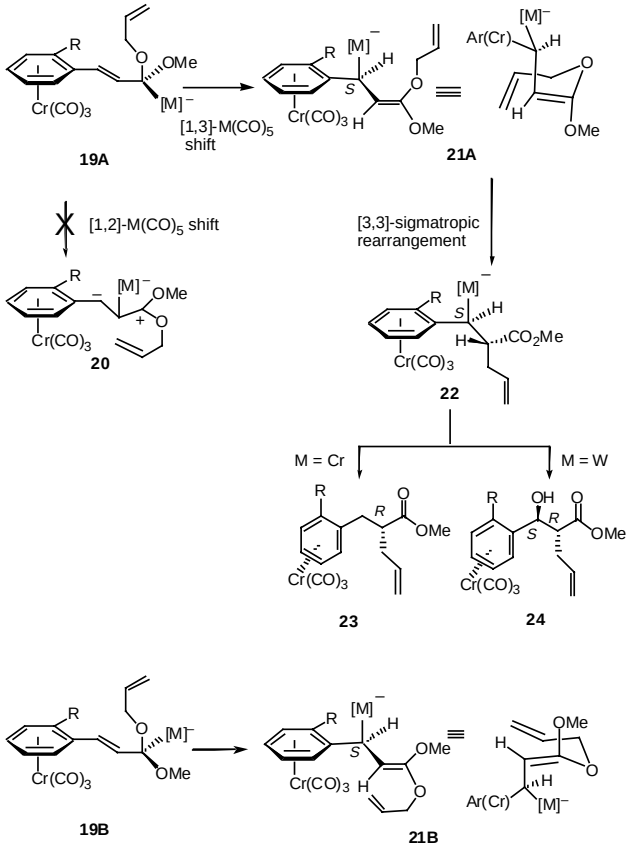
Similarly, with 2-methyl-2-propen-1-ol at 25 °C, the corresponding β-allyl β-arylpropionate **8c** was obtained in 85% yield with 72% ee (Table 2, entry 4). On reaction of **7b** with 2-methyl-2-propen-1-ol at 0 °C, the corresponding α-allyl-β-hydroxy ester **10c** was only obtained with 83/17 dr (entry 5). Similarly, with *o*-methyl substituted-arene chromium complex **7c**, the reaction products were controlled by reaction temperature. Thus, α-allyl-β-hydroxy ester **8d** was obtained at 25 °C (entry 6), while the corresponding α-allyl methyl ester **9d** and diastereomeric α-allyl-β-hydroxy ester **10d** were obtained at lower reaction temperature (entries 7 and 8). The optical yield of **9d** increased to 97% ee in the reaction at −30 °C (entry 8). When the *ortho* substituent of the arene chromium complex was changed to an isopropoxy group, aldol type product **10e** was obtained as a major product in 51% yield with 85/15 dr (entry 9). In this way, binuclear α,β-unsaturated chromium carbene complexes with planar chiral arene chromium complex were reacted with allyl alcohols in the presence of a base to give [3,3]-sigmatropic rearrangement products, α-allyl *o*-substituted phenyl propionate esters, with high ee without formation of β-allyl β-arylpropionates. Furthermore, when the reaction was performed at lower temperature under longer reaction time, methyl α-allyl β-hydroxy-β-arylpropionates **10**, were obtained with high *anti* selectivity in moderate yield. Thus, the coordination of the tricarbonylchromium fragment to the arene ring of α,β-unsaturated Fischer carbene complexes gave optically active α-allyl β-arylpropionates and α-allyl β-aryl β-hydroxy-propionates, respectively, with high selectivity by reaction with allyl alkoxides depending on the reaction temperature.

To further pursue this unique reaction, we next turned our attention to the reaction of hetero-binuclear tungsten carbene complexes having planar chiral arene chromium complexes with allyl alkoxides. A hetero-binuclear tungsten carbene complex **7e** was reacted with allyl alkoxide to give [3,3]-sigmatropic rearranged products, **9a** and **10a**. In analogy with α,β-unsaturated chromium carbene complex **1** (M=Cr), the corresponding tungsten carbene complex **1** (R=Ph, M=W) gave still α-allyl β-phenyl propionate in 55% yield without detection of β-allyl β-phenyl propionate reported by Barluenga.[10] Thus, α,β-unsaturated chromium or tungsten carbene complexes afforded always α-allyl propionates via metal 1,3-shift and subsequent [3,3]-sigmatropic rearrangement by reaction with allyl alkoxides, regardless of the coordination of the tricarbonylchromium fragment to the arene ring. In the case of binuclear tungsten carbene complex, methyl α-allyl-β-hydroxy-β-aryl propionate **10a** was predominantly obtained even at room temperature (entry 10). The aldol type product **10a** was obtained as sole product with higher diastereoselectivity at lower reaction temperature (entry 11). Similarly, optically active tungsten carbene complexes with planar chiral arene chromium complexes **7f**, **7g** gave the corresponding α-allyl-β-aryl-β-hydroxypropionates **10b**, **10d** in good yields with high diastereoselectivity by reaction with allyl alkoxide at −30 °C (entries 12 and 13). Compared with homo-binuclear chromium complexes, the hetero-binuclear tungsten carbene complexes having planar chiral arene chromium complex gave predominantly *anti* α-allyl-β-hydroxy-β-arylpropionates as major reaction product with high selectivity in spite of vigorous basic conditions. With a sterically bulky *ortho* isopropoxy substituent of the arene chromium complex, diastereomeric ratio decreased to 75/25 (entry 14).

A clarification of origin of the benzylic oxygen of α-allyl-β-hydroxy-β-arylpropionates **10** in the reaction of the binuclear carbene complexes **7** is significant for the reaction mechanism. Although the reaction was carried out under an inert atmosphere in a balloon, trace amounts of oxygen might be present in the solvent and/or inert gas. Therefore, the reaction mixture of **7g**, allyl alcohol and NaH in dry THF was carefully degassed by an inert gas/freeze/vacuum technique, and the reaction was carried out in a well-degassed glove box. Consequently, it was found that the aldol-type product **10d** decreased to 15% yield, and the α-allyl product **9d** was obtained in 50% yield. This result indicates obviously that the benzylic hydroxy group was introduced from oxygen in the solvent and/or inert gas. The oxygenated product **10** in the reaction with hetero-binuclear tungsten carbene complexes was obtained with higher yield than the reaction with chromium complexes.

3. Reaction mechanism

On the basis of these results, we propose the reaction mechanism of α,β-unsaturated binuclear Fischer carbene complexes with allyl alkoxide in Scheme 5. Nucleophilc addition of allyl alkoxide at the metal carbene fragment of



Scheme 5. Proposed mechanism.

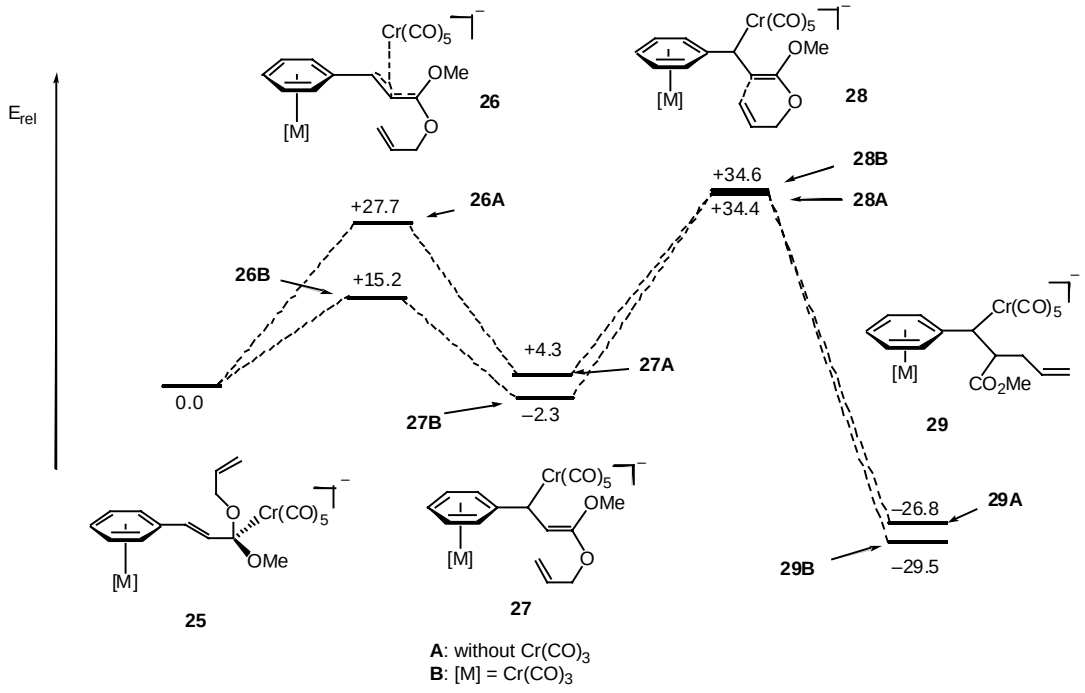


Figure 2. Ab initio calculation.

α,β-unsaturated Fischer carbene complex **7** is initiated to give tetrahedral intermediates **19A** and **19B**. A tetrahedral intermediate **19A** would be formed by the addition to *s-transoid* configurated carbene carbon of the complex **7**, and another intermediate **19B** is formed from *s-cisoid* conformer of the complex **7**. Generally, [1,2]-$M(CO)_5$ shift[16] in α,β-unsaturated Fischer carbene complexes is a concerted process accompanied with sigmatropic rearrangement. The products derived from this process were not observed in the reaction of α,β-unsaturated carbene complexes **1** and **7** with allyl alkoxides. The formation of (*R*)-configurated α-allyl arylpropionates **8**, **9** and **10** would be explained by 1,3-metal shift[17] followed by [3,3]-sigmatropic rearrangement reaction. 1,3-Metal shift from the tetrahedral intermediate **19A** generates an intermediate **21** with *anti* conformation between the tricarbonylchromium fragment and the pentacarbonylmetal group due to steric repulsion. Consequently, benzylic position of the resulting σ-allyl chromium complex **21** is *S*-configuration. Subsequent [3,3]-sigmatropic rearrangement produces α-allyl β-aryl propionate complex **22** with (*R*)-configuration at the α-position via 6-membered chair form **21A**. Furthermore, in the case of the chromium carbene complexes, protonation and the following reductive elimination of the intermediate **22** occur to give complex **23** as the major product. On the other hand, with tungsten carbene complexes, the anionic tungsten species is easily trapped with oxygen followed by reductive elimination to give *anti* aldol type products **24**. Similarly, the intermediate **19B** affords α-allyl β-aryl propionate complex **22** via [3,3]-sigmatropic rearrangement from the transition state **21B**.

4. Computational studies

We, furthermore, studied ab initio calculation in this unique 1,3-metal shift process of α,β-unsaturated unsaturated Fischer carbene complex (Fig. 2).[18,19] The complex **26A** and **26B** were transition states for the 1,3-metal shift step of tetrahedral non-chromium coordinated intermediate **25A** and the corresponding $Cr(CO)_3$-complexed intermediate **25B**. Activation energies for the 1,3-metal shift step are 27.7 and 15.2 kcal mol^{-1}, respectively.[20] On the other hand, the structures **27A** and **27B** are the 1,3-metal shifted stable intermediate of **25A** and **25B**. The corresponding chromium-coordinated intermediate **27B** is 6.6 kcal mol^{-1} more stable than non-chromium complexed intermediate **27A**. Following [3,3]-sigmatropic rearrangement takes place with exothermicity of almost same energy in both $Cr(CO)_3$-complexed and non-complexed intermediates to give rearranged products **29A** and **29B**. In contrast, we could not find out the transition state structures for concerted 1,2-metal shift and 3,4 sigmatropic rearrangemet giving β-allyl arylpropionate. Theoretical study also supports that 1,3-metal shift process in the reaction of α,β-unsaturated Fischer carbene complexes with allyl alkoxides is favorable reaction path than 1,2-metal shift.

5. Conclusions

The binuclear α,β-unsaturated carbene complexes with arene chromium complex afforded α-allyl β-arylpropionates and *anti* α-allyl-β-hydroxy-β-arylpropionates as optically enriched compounds via 1,3-$M(CO)_5$ shift and [3,3]-sigmatropic rearrangement. The corresponding α,β-unsaturated carbene complexes without tricarbonylchromium coordination gave also α-allyl β-aryl propionate without detection of β-allyl β-aryl propionate under the same reaction conditions.

6. Experimental

6.1. General

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using inert gas/vacuum double manifold techniques. All NMR spectra were recorded in $CDCl_3$ or acetone-d_6 solvent with tetramethylsilane as an internal reference. Mass spectra were determined with EI or FAB mode. Optical rotations were obtained at wavelength 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 5 mL. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use.

6.2. General procedure for preparation of binuclear α,β-unsaturated Fischer carbene complexes

Binuclear Fischer carbene complexes were prepared by reported procedure.[8a,11] To an equimolar solution of pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) (1 mmol) and the corresponding benzaldehyde chromium complex in anhydrous Et_2O (0.1 M) was added Et_3N (4 mmol) at room temperature. Then, TMSCl (3 mmol) was added dropwise at the same temperature, and the reaction mixture was stirred until disappearance of the starting material. The solvent was removed in vacuo and the residue was purified by silica gel chromatography.

6.2.1. Binuclear carbene complex 7a. Mp 116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (3H, s), 5.69 (2H, t, J=6.0 Hz), 5.89 (1H, t, J=6.0 Hz), 6.20 (2H, d, J=6.0 Hz), 6.79 (1H, d, J=15.6 Hz), 7.98 (1H, d, J=15.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 66.68, 90.74, 93.43, 94.08, 98.33, 125.36, 138.67, 216.39, 224.28, 231.58, 332.02; IR ($CHCl_3$) 3034, 2957, 2058, 2000, 1586, 1453, 1225, 986 cm^{-1}. Anal. Calcd for $C_{18}H_{10}O_9Cr_2$: C, 45.59; H, 2.13. Found: C, 45.64; H, 2.41.

6.2.2. Binuclear carbene complex 7b. $[\alpha]_D^{24}$ −3400 (*c* 0.001, $CHCl_3$); mp 88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (3H, s), 4.82 (3H, s), 4.99 (1H, t, J=6.3 Hz), 5.10 (1H, d, J=6.3 Hz), 5.72 (1H, t, J=6.3 Hz), 5.94 (1H, d, J=6.3 Hz), 6.94 (1H, d, J=15.3 Hz), 7.78 (1H, d, J=15.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.06, 66.56, 73.22, 84.87, 88.73, 93.39, 93.97, 122.39, 138.73, 143.65, 211.55, 216.60, 231.93, 331.83; IR ($CHCl_3$) 2957, 2058, 2000, 1580, 1464, 1213, 992 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_{10}Cr_2$: C, 45.25; H, 2.40. Found: C, 45.51; H, 2.41.

6.2.3. Binuclear carbene complex 7c. $[\alpha]_D^{24}$ −5600 (*c* 0.001, $CHCl_3$); mp 95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 4.83 (3H, s), 5.14 (1H, d, J=6.3 Hz), 5.25 (1H, t, J=6.3 Hz), 5.58 (1H, t, J=6.3 Hz), 5.79 (1H, d, J=6.3 Hz), 6.79 (1H, d, J=15.2 Hz), 7.68 (1H, d, J=15.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.39, 66.56, 88.92, 92.19, 92.63, 94.46, 98.00, 111.28, 124.60, 139.66, 216.49, 224.27, 232.05, 332.38; IR ($CHCl_3$) 3032, 2959, 2058, 2000, 1580, 1451, 1225, 992 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_9Cr_2$: C, 46.74; H, 2.48. Found: C, 46.48; H, 2.43.

6.2.4. Binuclear carbene complex 7d. $[\alpha]_D^{24}$ −2400 (*c* 0.001, $CHCl_3$); mp 112 °C; ^{1}H NMR (500 MHz, acetone-d_6) δ 1.42–1.48 (6H, m), 4.72–4.75 (1H, m), 4.81 (3H, s), 5.29 (1H, t, J=6.4 Hz), 5.69 (1H, d, J=6.9 Hz), 6.13 (1H, t, J=6.4 Hz), 6.48 (1H, d, J=6.9 Hz), 7.41 (1H, d, J=15.6 Hz), 7.97 (1H, d, J=15.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.78, 22.41, 66.38, 72.93, 74.94, 84.43, 94.42, 94.60, 125.26, 138.78, 142.87, 216.67, 232.15, 245.56, 332.18; IR ($CHCl_3$) 2986, 2056, 2000, 1580, 1454, 1252, 992 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O_{10}Cr_2$: C, 47.38; H, 3.03. Found: C, 47.57; H, 2.86.

6.2.5. Binuclear carbene complex 7e. Mp 117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (3H, s), 5.68 (2H, t, J=6.3 Hz), 5.90 (1H, t, J=6.3 Hz), 6.21 (2H, d, J=6.3 Hz), 6.97 (1H, d, J=15.5 Hz), 7.95 (1H, d, J=15.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 59.87, 90.24, 93.24, 93.90, 98.08, 113.36, 148.91, 197.22, 231.53, 233.37, 305.15; IR ($CHCl_3$) 2953, 2067, 2000, 1586, 1451, 1215, 988 cm^{-1}. Anal. Calcd for $C_{18}H_{10}O_9CrW$: C, 35.67; H, 1.66. Found: C, 35.71; H, 1.88.

6.2.6. Binuclear carbene complex 7f. $[\alpha]_D^{24}$ −4000 (*c* 0.001, $CHCl_3$); mp 148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 4.64 (3H, s), 5.14 (1H, d, J=6.6 Hz), 5.24 (1H, t, J=6.2 Hz), 5.59 (1H, t, J=6.2 Hz), 5.80 (1H, d, J=6.6 Hz), 7.07 (1H, d, J=15.3 Hz), 7.58 (1H, d, J=15.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.09, 69.09, 73.23, 84.89, 88.62, 93.28, 94.00, 127.49, 142.65, 143.49, 197.43, 203.93, 231.90, 305.60; IR ($CHCl_3$) 3032, 2951, 2066, 2000, 1580, 1464, 1252, 995 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_{10}CrW$: C, 35.87; H, 1.90. Found: C, 35.82; H, 1.93.

6.2.7. Binuclear carbene complex 7g. $[\alpha]_D^{24}$ −3800 (*c* 0.001, $CHCl_3$); mp 145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (3H, s), 4.64 (3H, s), 5.14 (1H, d, J=6.6 Hz), 5.24 (1H, t, J=6.3 Hz), 5.59 (1H, t, J=6.3 Hz), 5.80 (1H, d, J=6.6 Hz), 7.07 (1H, d, J=15.3 Hz), 7.58 (1H, d, J=15.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.45, 69.19, 88.84, 92.04, 92.57, 94.49, 97.74, 111.11, 129.64, 143.69, 197.31, 203.67, 231.97, 305.87; IR ($CHCl_3$) 3032, 2953, 2073, 2000, 1580, 1449, 1219, 995 cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_9CrW$: C, 36.80; H, 1.95. Found: C, 36.70; H, 2.03.

6.2.8. Binuclear carbene complex 7h. $[\alpha]_D^{23}$ −2600 (*c* 0.001, $CHCl_3$); mp 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (3H, d, J=6.0 Hz), 1.49 (3H, d, J=6.0 Hz), 4.48 (1H, sep, J=6.0 Hz), 4.63 (3H, s), 4.94 (1H, t, J=6.5 Hz), 5.10 (1H, d, J=6.5 Hz), 5.74 (1H, t, J=6.5 Hz), 5.92 (1H, d, J=6.5 Hz), 7.28 (1H, d, J=15.6 Hz), 7.66 (1H, d, J=15.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.80, 22.43, 69.02, 72.98, 74.89, 84.43, 88.06, 94.26, 130.85, 142.56, 142.73, 197.48, 203.88, 232.12, 306.23; IR ($CHCl_3$) 3025, 2988, 2066, 1971, 1941, 1578, 1452, 1219 cm^{-1}; MS (relative intensity) *m*/*z*, 664 (M^+, 5), 167 (30), 149 (100), 81 (41); HRMS calcd for $C_{21}H_{16}O_{10}CrW$ 663.9658, found 663.9651.

6.3. General procedure for stereoselective [3,3]-sigmatropic reactions utilizing binuclear Fischer carbene complexes

A solution of complex **7** (0.082 mmol) in dry THF (2.0 mL) was added dropwise to a solution of NaH (66 mg, 60% in oil, 1.6 mmol) in allyl alcohol (2.0 mL) under argon. The solution immediately turned from dark purple to yellow.

The reaction mixture was stirred and quenched with aqueous NH_4Cl. The resulting mixture was extracted with EtOAc and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and filtered and concentrated under reduced pressure. The yellow residue was pushed a plug of silica gel with EtOAc, and all yellow bands were collected. Without further purification, the crude reaction mixture was diluted with ether (5.0 mL) and was exposed to sunlight until yellow solution became colorless. The precipitate was filtered off, and the solution was evaporated under reduced pressure and purified by silica gel chromatography to give a demetallated product.

6.3.1. Allyl 2-allyl-3-phenylpropionate (8a). (Lit. Ref. 21) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26–2.42 (2H, m), 2.76–2.81 (2H, m), 2.93–2.98 (1H, m), 4.50 (2H, dd, J=6.0, 1.4 Hz), 5.03–5.09 (2H, m), 5.15–5.22 (2H, m), 5.72–5.83 (2H, m), 7.15–7.28 (5H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.01, 37.75, 47.23, 64.95, 117.18, 118.08, 126.35, 128.37, 128.93, 132.13, 135.05, 139.06, 174.49.

6.3.2. (−)-(*R*)-Allyl 2-allyl-3-(2-methoxyphenyl)propionate (8b). $[\alpha]_D^{23}$ −25.2 (*c* 0.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25–2.30 (1H, m), 2.36–2.42 (1H, m), 2.86–2.91(3H, m), 3.82 (3H, s), 4.49 (2H, ddd, J=4.6, 3.3, 1.4 Hz), 5.02–5.09 (2H, m), 5.14–5.22 (2H, m), 5.73–5.83 (2H, m), 6.82–6.86 (2H, m), 7.09 (1H, dd, J=7.3, 1.8 Hz), 7.19 (1H, dt, J=7.3, 1.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 32.84, 36.29, 45.17, 55.16, 64.77, 110.19, 116.75, 117.81, 120.24, 127.44, 127.71, 130.79, 132.33, 135.42, 157.59, 174.89; IR ($CHCl_3$) 3013, 2942, 1728, 1495, 1466, 1246, 1163, 922, 742 cm^{-1}; MS (relative intensity) (FAB) *m/z*, 260 (M^+, 44), 203 (32), 121 (100), 91 (31); HRMS calcd for $C_{16}H_{20}O_3$ 260.1412, found 260.1416. HPLC conditions; Chiralcel OD; hexane/2-propanol=100:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 14.3 min, 16.9 min: **8b**, 16.9 min.

6.3.3. (−)-(*R*)-2-Methylpropenyl 2-(2-methylpropenyl)-3-(2-methoxyphenyl)propionate (8c). $[\alpha]_D^{27}$ −50.0 (*c* 0.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (3H, s), 1.74 (3H, s), 2.21 (1H, dd, J=14.2, 6.4 Hz), 2.43 (1H, dd, J=14.2, 8.7 Hz), 2.81 (1H, dd, J=13.3, 8.7 Hz), 2.89 (1H, dd, J=13.3, 6.4 Hz), 3.01–3.07 (1H, m), 3.82 (3H, s), 4.37 (2H, s), 4.76 (2H, d, J=6.0 Hz), 4.84 (2H, s), 6.82–6.85 (2H, m), 7.09 (1H, d, J=7.3 Hz), 7.18 (1H, t, J=7.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.40, 22.16, 33.32, 40.75, 43.96, 55.19, 67.50, 110.19, 112.17, 112.82, 120.31, 127.56, 127.70, 130.73, 140.06, 143.02, 157.59, 175.30; IR ($CHCl_3$) 3000, 2920, 1724, 1648, 1491, 1460, 1240, 1160, 899, 739 cm^{-1}; MS (relative intensity) *m/z*, 288 (M^+, 25), 232 (38), 187 (36), 161 (48), 121 (100), 91 (64), 55 (12); HRMS calcd for $C_{18}H_{24}O_3$ 288.1726, found 288.1723. HPLC conditions; Chiralcel OD; hexane/2-propanol=20:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 5.2 min, 6.3 min: **8c**, 6.3 min.

6.3.4. (−)-(*R*)-Allyl 2-allyl-3-(2-methylphenyl)propionate (8d). $[\alpha]_D^{26}$ −17.7 (*c* 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27–2.32 (4H, m), 2.41–2.47 (1H, m), 2.74–2.82 (2H, m), 2.92–2.97 (1H, m), 4.50 (2H, d, J=5.5 Hz), 5.04–5.22 (4H, m), 5.73–5.83 (2H, m), 7.10–7.13 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.41, 35.32, 45.89, 64.96, 117.20, 118.05, 125.85, 126.50, 129.58, 130.34, 132.16, 135.11, 136.18, 137.29, 174.67; IR ($CHCl_3$) 3013, 2930, 1730, 1495, 1456, 1229, 1165, 924, 741 cm^{-1}; MS (relative intensity) *m/z*, 244 (M^+, 4), 203 (20), 157 (53), 105 (100), 121 (100), 91 (14); HRMS calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1459. HPLC conditions; Chiralcel OD; hexane/2-propanol=20:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 4.1 min, 4.7 min: **8d**, 4.1 min.

6.3.5. Methyl 2-allyl-3-phenylpropionate (9a). (Lit. Ref. 22) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26–2.40 (2H, m), 2.73–2.81 (2H, m), 2.91–2.99 (1H, m), 3.59 (s, 3H), 5.01–5.09 (2H, m), 5.70–5.80 (1H, m), 7.13–7.29 (5H, m); IR (neat) 3018, 2961, 1722, 1212.

6.3.6. (−)-(*R*)-Methyl 2-allyl-3-(2-methoxyphenyl)-propionate (9b). $[\alpha]_D^{27}$ −53.6 (*c* 0.056, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24–2.40 (2H, m), 2.82–2.88 (3H, m), 3.58 (3H, s), 3.82 (3H, s), 5.00–5.08 (2H, m), 5.72–5.80 (1H, m), 6.82–6.87 (2H, m), 7.08 (1H, dd, J=7.8, 1.4 Hz), 7.19 (1H, dt, J=7.8, 1.4 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 32.85, 36.31, 45.26, 51.25, 55,20, 110.12, 116.54, 120.15, 127.58, 130.56, 135.35, 157.42, 175.48; IR ($CHCl_3$) 3013, 2953, 1728, 1601, 1494, 1466, 1439 cm^{-1}; MS (relative intensity) *m/z*, 234 (M^+, 25), 116 (37), 121 (100), 91 (68); HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1256. HPLC conditions; Chiralcel OD; hexane/2-propanol=9:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 6.4 min, 7.2 min: **9b**, 7.2 min.

6.3.7. (+)-(*R*)-Methyl 2-(2-methylpropenyl)-3-(2-methoxyphenyl)propionate (9c). $[\alpha]_D^{30}$ +24.0 (*c* 0.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) 1.72 (3H, s), 2.14–2.21(1H, m), 2.35–2.44 (1H, m), 2.73–2.93 (2H, m), 2.96–3.02 (1H, m), 3.54 (3H, s), 3.81 (3H, s), 4.74 (2H, d, J=7.2 Hz), 6.82 (1H, d, J=7.8 Hz), 6.84 (1H, t, J=7.8 Hz), 7.07 (1H, dd, J=7.8, 1.7 Hz), 7.18 (1H, dt, J=7.8, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 22.17, 33.27, 40.72, 43.99, 51.27, 55.20, 110.14, 111.99, 120.20, 127.52, 127.62, 130.56, 143.00, 157.44, 175.89; IR ($CHCl_3$) 3379, 2928, 1728, 1601, 1464, 1217 cm^{-1}; MS (relative intensity) *m/z*, 248 (M^+, 18), 217 (13), 192 (96), 161 (100), 121 (86), 91 (65); HRMS calcd for $C_{15}H_{20}O_3$ 248.1413, found 248.1417. HPLC conditions; Chiralcel OD; hexane/2-propanol=20:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 6.7 min, 12.0 min: **9c**, 12.0 min.

6.3.8. (−)-(*R*)-Methyl 2-allyl-3-(2-methylphenyl)propionate (9d). $[\alpha]_D^{20}$ −62.5 (*c* 0.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23–2.31 (1H, m), 2.31 (3H, s), 2.34–2.46 (1H, m), 2.70–2.80 (1H, m), 2.78 (1H, dd, J=7.9, 20.4 Hz), 2.94 (1H, dd, J=7.9, 13.3 Hz), 3.59 (3H, s), 5.02–5.10 (2H, m), 5.70–5.80 (1H, m), 7.08–7.14 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.45, 29.76, 35.23, 36.36, 45.95, 51.46, 117.06, 125.80, 126.45, 129.43, 130.28, 135.08, 137.26, 175.37; IR ($CHCl_3$) 3027, 3013, 2928, 1730, 1213 cm^{-1}; MS (relative intensity) *m/z*, 218 (M^+, 28), 177 (32), 159 (25), 158 (89), 145 (54), 113 (48), 106

(28), 105 (100); HRMS calcd for $C_{14}H_{18}O_2$ 218.1310, found 218.1310. HPLC conditions; Chiralcel OD; hexane/2-propanol = 100:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 7.5 min, 9.1 min: **9d**, 7.5 min.

6.3.9. (−)-(*R*)-Methyl 2-allyl-3-(2-isopropoxyphenyl)-propionate (9e). $[\alpha]_D^{26}$ −29.6 (*c* 0.054, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.25–1.30 (6H, m), 2.17–2.32 (2H, m), 2.77–2.80 (2H, m), 3.51 (3H, s), 4.44–4.52 (1H, m), 4.92–5.19 (3H, m), 5.13–5.68 (1H, m), 6.73–7.10 (4H, m); IR ($CHCl_3$) 3373, 2983, 1728, 1601, 1454 cm^{-1}; MS (relative intensity) *m/z*, 262 (M^+, 18), 188 (24), 147 (29), 146 (100), 107 (40); HRMS calcd for $C_{16}H_{22}O_3$ 262.1569, found 262.1570.

6.3.10. Methyl 2-allyl-3-hydroxy-3-phenylpropionate (10a). (Lit. Ref. 23) ^1H NMR (500 MHz, $CDCl_3$) δ 2.11–2.17 (1H, m), 2.25–2.31 (1H, m), 2.84–2.88 (2H, m), 3.69 (3H, s), 4.83 (1H, dd, *J* = 7.8, 5.0 Hz), 5.00–5.04 (2H, m), 5.64–5.72 (1H, m), 7.29–7.38 (5H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 33.75, 51.71, 52.77, 74.85, 117.33, 126.41, 128.13, 128.57, 134.30, 141.63, 174.96.

6.3.11. (−)-(2*R*,3*S*)-Methyl 2-allyl-3-hydroxy-3-(2-methoxyphenyl)propionate (10b). $[\alpha]_D^{30}$ −36.0 (*c* 0.23, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 2.09–2.14 (1H, m), 2.32–2.38 (1H, m), 3.04 (1H, ddd, *J* = 12.8, 7.3, 5.0 Hz), 3.34 (1H, d, *J* = 9.2 Hz), 3.66 (3H, s), 3.86 (3H, s), 4.97–5.04 (3H, m), 5.65–5.73 (1H, m), 6.89 (1H, d, *J* = 8.7 Hz), 6.96 (1H, t, *J* = 7.3 Hz), 7.26–7.28 (2H, m); IR ($CHCl_3$) 3555, 2953, 1730, 1641, 1215 cm^{-1}; MS (relative intensity) *m/z*, 250 (M^+, 2), 138 (10), 137 (100), 135 (19), 107 (21); HRMS calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1171. HPLC conditions; Chiralcel OD; hexane/2-propanol = 9:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 10.2 min, 11.1 min: **10b**, 10.2 min.

6.3.12. (−)-(2*R*,3*S*)-Methyl 2-(2-methylpropenyl)-3-hydroxy-3-(2-methoxyphenyl)propionate (10c). $[\alpha]_D^{30}$ −34.3 (*c* 0.07, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.61 (3H, s), 1.95–2.01 (1H, m), 2.29–2.37 (1H, m), 3.01–3.16 (1H, m), 3.32 (1H, d, *J* = 9.1 Hz), 3.55 (3H, s), 3.79 (3H, s), 4.66 (2H, d, *J* = 1.0 Hz), 4.91 (1H, dd, *J* = 9.1, 7.0 Hz), 6.79–6.91 (2H, m), 7.17–7.22 (2H, m); IR ($CHCl_3$) 3013, 2957, 1730, 1240, 1215 cm^{-1}; MS (relative intensity) *m/z*, 264 (M^+, 1), 208 (22), 137 (100), 135 (23), 107 (41); HRMS calcd for $C_{15}H_{20}O_4$ 264.1361, found 264.1360. HPLC conditions; Chiralcel OD; hexane/2-propanol = 9:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 6.3 min, 7.0 min: **10c**, 6.3 min.

6.3.13. (−)-(2*R*,3*S*)-Methyl 2-allyl-3-hydroxy-3-(2-methylphenyl)propionate (10d). $[\alpha]_D^{27}$ −40.2 (*c* 0.48, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 2.09–2.15 (1H, m), 2.32–2.37 (4H, m), 2.82 (1H, d, *J* = 5.5 Hz), 2.87–2.92 (1H, m), 3.68 (3H, s), 4.99–5.10 (3H, m), 5.63–5.71 (1H, m), 7.14–7.38 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.33, 33.61, 51.68, 52.24, 71.08, 117.29, 125.85, 126.39, 127.77, 130.59, 134.37, 135.22, 139.67, 175.07; IR ($CHCl_3$) 3470, 3081, 3013, 2953, 1723, 1644, 1441 cm^{-1}; MS (relative intensity) *m/z*, 234 (M^+, 2), 157 (10), 121 (100), 114 (91), 93 (66); HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1251.

6.3.14. (−)-(2*R*,3*S*)-Methyl 2-allyl-3-hydroxy-3-(2-isopropoxyphenyl)propionate (10e). $[\alpha]_D^{27}$ −34.8 (*c* 0.48, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.36 (3H, d, *J* = 6.1 Hz), 1.39 (3H, d, *J* = 6.1 Hz), 2.12 (1H, quin, *J* = 7.2 Hz), 2.34 (1H, quin, *J* = 7.2 Hz), 3.06 (1H, ddd, *J* = 9.2, 7.2, 6.1 Hz), 3.44–3.54 (1H, m), 3.65 (3H, s), 4.64 (1H, sep, *J* = 6.1 Hz), 4.94–5.05 (3H, m), 5.65–5.75 (1H, m), 6.87 (1H, d, *J* = 7.9 Hz), 6.91 (1H, t, *J* = 7.9 Hz), 7.20–7.26 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.07, 22.29, 34.17, 51.56, 69.84, 72.27, 112.33, 116.74, 120.28, 128.11, 128.59, 129.99, 134.81, 154.52, 174.94; IR ($CHCl_3$) 3366, 3025, 3013, 1730, 1601, 1238 cm^{-1}; MS (relative intensity) *m/z*, 278 (M^+, 2), 165 (43), 149 (8), 123 (100), 121 (15); HRMS calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1514. HPLC conditions; Chiralcel OD; hexane/2-propanol = 9:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 6.1 min, 7.5 min: **10e**, 6.1 min.

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References and notes

1. Some selected reviews: (a) Doyle, M. P. In Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Comprehensive Organometallic Chemistry II; Pergamon: New York, 1995; Vol. 12, pp 387–420. (b) Wulff, W. D. In Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Comprehensive Organometallic Chemistry II; Pergamon: New York, 1995; Vol. 12, pp 469–547. (c) Hegedus, L. S. In Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Comprehensive Organometallic Chemistry II; Pergamon: New York, 1995; Vol. 12, pp 549–600. (d) *Metal Carbons in Organic Synthesis*; Dötz, K.-H., Ed.; Topics in Organometallic Chemistry; Springer: Berlin, 2004; Vol. 13. (e) Bertrand, G. (Guest Ed.); *J. Organomet. Chem.* **2001**, *617/618*, 3–754.
2. Some selected references: (a) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518–519. (b) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814–5815. (c) Barluenga, J.; López, L. A.; Löber, O.; Tomás, M.; García-Granda, S.; Alvarez-Rúa, C.; Borge, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3392–3394. (d) Barluenga, J.; Aznar, F.; Palomero, M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4346–4348. (e) Barluenga, J.; Aznar, F.; Gutiérrez, I.; Martín, A.; García-Granda, S.; Llorca-Baragaño, M. A. *J. Am. Chem. Soc.* **2000**, *122*, 1314–1324. (f) Barluenga, J.; Ballesteros, A.; Santamaría, J.; Bernardo de la Rúa, R.; Rubio, E.; Tomás, M. *J. Am. Chem. Soc.* **2000**, *122*, 12874–12875. (g) Barluenga, J.; Rodríguez, F.; Fañanás, F. J.; Rubio, E. *Angew. Chem., Int. Ed.* **1999**, *38*, 3084–3086.
3. Some selected references for Michael reactions: (a) Barluenga, J.; Montserrat, J. M.; Flórez, J.; García-Granda, S.; Martin, E.

Chem. Eur. J. **1995**, *1*, 236–242. (b) Barluenga, J.; Montserrat, J. M.; Flórez, J.; García-Granda, S.; Martín, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *23*, 1392–1394. (c) Barluenga, J.; Bernad, P. L., Jr.,; Concellón, J. M.; Piñera-Nicolás, A.; García-Granda, S. *J. Org. Chem.* **1997**, *62*, 6870–6875. (d) Ezquerra, J.; Pedregal, C.; Merino, I.; Flórez, J.; Barluenga, J.; García-Granda, S.; Llorca, M.-A. *J. Org. Chem.* **1999**, *64*, 6554–6565. (e) Shi, Y.; Wulff, W. D.; Yap, G. P. A.; Rheingold, A. L. *Chem. Commun.* **1996**, 2601–2602.

4. Some selected references for [3+2]-cycloaddition: (a) Barluenga, J.; Fernández-Marí, F.; Viado, A. L.; Aguilar, E.; Olano, B.; García-Granda, S.; Moya-Rubiera, C. *Chem. Eur. J.* **1999**, *5*, 883–896. (b) Kagoshima, H.; Okamura, T.; Akiyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 7182–7183. (c) Merino, I.; Laxmi, Y. R. S.; Flórez, J.; Barluenga, J. *J. Org. Chem.* **2002**, *67*, 648–655.
5. Some selected references for [4+2]-cycloaddition: (a) Powers, T. S.; Jiang, W.; Su, J.; Wulff, W. D.; Waltermire, B. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 6438–6439. (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. (c) Hsung, R. P.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6449–6450. (d) Beddoes, R. L.; King, J. D.; Quayle, P. *Tetrahedron Lett.* **1995**, *36*, 3027–3028. (e) Hsung, R. P.; Wulff, W. D.; Challener, C. A. *Synthesis* **1996**, 773–789.
6. Some selected references for [3+2+1]-cycloaddition: (a) Quinn, J. F.; Powers, T. S.; Wulff, W. D.; YAP, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4945–4947. (b) Dötz, K. H.; Stinner, C.; Nieger, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2535–2536. (c) Bao, J.; Wulff, W. D.; Fumo, M. J.; Grant, E. B.; Heller, D. P.; Whitcomb, M. C.; Yeung, S.-M. *J. Am. Chem. Soc.* **1996**, *118*, 2166–2181.
7. (a) Vorogushin, A. V.; Wulff, W. D.; Hansen, H.-J. *J. Am. Chem. Soc.* **2002**, *124*, 6512–6513. (b) Dötz, K. H.; Jäkel, C.; Hasse, W.-C. *J. Organomet. Chem.* **2001**, *617–618*, 119–132. (c) Janes, E.; Dötz, K. H. *J. Organomet. Chem.* **2001**, *622*, 251–258.
8. Some selected α,β-unsaturated binuclear Fischer carbene complexes with arene tricarbonylchromium complex or ferrocene: (a) Sierra, M. A.; del Amo, J. C.; Mancheño, M. J.; Gómez-Gallego, M. *J. Am. Chem. Soc.* **2001**, *123*, 851–861. (b) Barluenga, J.; López, S.; Trabanco, A. A.; Fernández-Acebes, A.; Flórez, J. *J. Am. Chem. Soc.* **2000**, *122*, 8145–8154. (c) Barluenga, J.; Fernández-Acebes, A.; Trabanco, A. A.; Flórez, J. *J. Am. Chem. Soc.* **1997**, *119*, 7591–7592.
9. A preliminary report: Kamikawa, K.; Tachibana, A.; Shimizu, Y.; Uchida, K.; Furusyo, M.; Uemura, M. *Org. Lett.* **2004**, *6*, 4307–4310.
10. Barluenga, J.; Rubio, E.; López-Pelegrín, J. A.; Tomás, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1091–1093.
11. Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 537–540 and Ref. 8a.
12. Authentic samples **4** (R=Ph) and **8a** were prepared by allyl esterification of 3-phenyl-hex-5-enoic acid and LDA-mediated α-allylation of β-phenyl propionate, respectively. 3-Phenyl-hex-5-enoic acid; Majetich, G.; Casares, A. M.; Chapman, D.; Behnke, M. *Tetrahedron Lett.* **1983**, *24*, 1909–1912.
13. Enantiomeric excess was determined by chiral HPLC with Chiralcel OD; hexane/2-propanol=100:1; flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm, retention time, racemate, 14.3 min, 16.9 min: **8b**, 16.9 min.
14. Evans, D. A.; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737–1739.
15. Evans, D. A.; Tedrow, J. S.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2002**, *124*, 392–393.
16. (a) Dötz, K. H.; Christoffers, C.; Knochel, P. *J. Organomet. Chem.* **1995**, *489*, C84–C86. (b) Iwasawa, N.; Ochiai, T.; Maeyama, K. *J. Org. Chem.* **1998**, *63*, 3164–3165. (c) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Chem. Soc.* **1997**, *119*, 1486–1487. (d) Iwasawa, N.; Ochiai, T.; Maeyama, K. *Organometallics* **1997**, *16*, 5137–5139. (e) Barluenga, J.; Trabanco, A. A.; Flórez, J.; Gracía-Granda, S.; LLlorca, M.-A. *J. Am. Chem. Soc.* **1998**, *120*, 12129–12130. (f) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. L.; García-Granda, S.; Priede, M. P. *J. Am. Chem. Soc.* **1999**, *121*, 3065–3071.
17. (a) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198. (b) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701. (c) Maxey, C. T.; Sleiman, H. F.; Massey, S. T.; McElwee-White, L. *J. Am. Chem. Soc.* **1992**, *114*, 5153–5160. (d) Fischer, H.; Schlageter, A.; Bidell, W.; Früh, A. *Organometallics* **1991**, *10*, 389–391.
18. All calculations were performed with Gaussian 98: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A. 5; Gaussian, Inc.: Pittsburgh, PA, 1998.
19. Geometry optimizations for Cr complexes **25–29** were carried out with RHF level theory on using 3-21G(d) basis sets.
20. Total energies of compounds **25A** and **25B** were −2245.7650 H and −3620.2431 H, respectively. Relative energies were including zero point energy correction.
21. Zou, X.-W.; Lu, T.-M.; Song, J.; Wu, F.-H.; Shen, Y.-J. *Huadong Ligong Daxue Xuebao* **2003**, *29*, 210–213.
22. Kim, D. H.; Li, Z.-H.; Lee, S. S.; Park, J.-Il.; Chung, S. J. *Bioorg. Med. Chem.* **1998**, *6*, 239–249.
23. (a) Hart, D. J.; Krishnamurthy, R. *J. Org. Chem.* **1992**, *57*, 4457–4470. (b) Urabe, H.; Takeda, T.; Hideura, D.; Sato, F. *J. Am. Chem. Soc.* **1997**, *119*, 11295–11305.