DOI: 10.1002/cjoc.201200410

Kinetic Resolution of Aryl Alkenylcarbinols Catalyzed by Fc-PIP†

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An effective kinetic resolution of a variety of aryl alkenylcarbinols catalyzed by nonenzymatic acyl transfer catalyst **Fc-PIP** was developed, affording corresponding unreacted alcohols in good to excellent *ee* value up to 99% and with selectivity factors up to 24.

Keywords kinetic resolution, acyl transfer, **Fc-PIP**

Introduction

Chiral allylic alcohols are among the most versatile synthetic intermediates.[1] Catalytic enantioselective synthesis of these chiral building blocks currently relies on three main methods: the kinetic resolution (KR) of corresponding racemic allylic alcohols through asymmetric epoxidation[2a-2d] or acylative transformation,[2e-2g] asymmetric addition of alkenylzinc reagents to carbonyl compounds,[3] and asymmetric Baylis-Hillman reaction.[4]

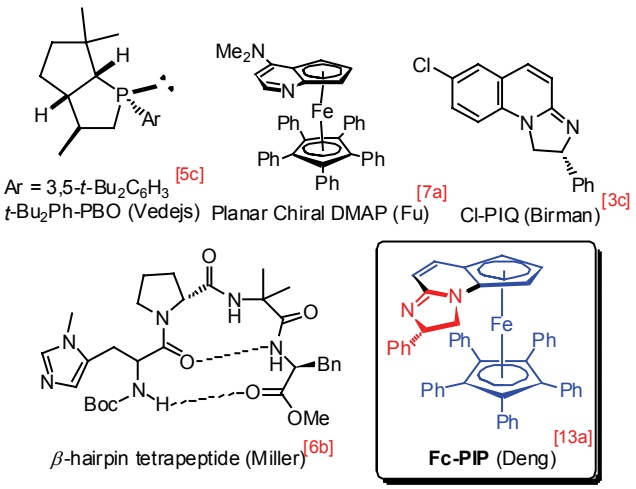

Figure 1 Representative nonenzymatic acyl transfer catalysts.

Since the pioneering works of Vedejs and co-workers in asymmetric acylation of secondary alcohols by nonenzymatic catalysts,[5a,5b] significant progress has been made in the development of nonenzymatic nucleophilic catalysts for the kinetic resolution of secondary alcohols.[5-9] To date, mainly four families of active catalyst scaffolds, including cyclic phosphines by Vedejs,[5] *N*-methyl imidazole (NMI)[6] by Miller and Ishihara, 4-(dimethylamino)-pyridine (DMAP)[7] by Fu, Fuji and Spivey *et. al.*, and 2,3-dihydroimidazopyridine (benzothiazole) derivatives[8] by Birman *et al.* incorporated with a variety of chiral elements, have been developed (Figure 1). A range of secondary alcohols, including aryl alkyl carbinols,[3b-3d,6c,7a,8a,8b] allylic alcohols[3] and propargylic alcohols,[10] have been kinetically resolved using aforementioned nucleophilic catalysts with good to excellent stereoselectivities.

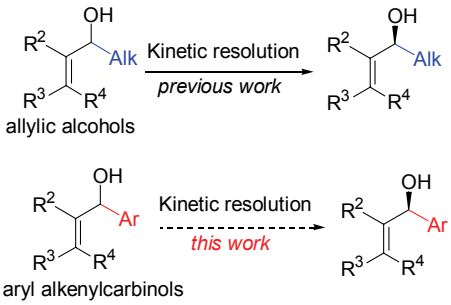

Figure 2 The KR of different type of allylic alcohols

While the origin of enantioselectivity of nonenzymatic KR has still not been elucidated unambiguously, it is generally accepted that π-cation and π-stacking interactions between the arene ring π-electrons of substrates and acylated catalysts play an important role in the process of chiral recognition.[5d,7d,8c,11] Aryl alkenylcarbinols (Figure 2), which bear two sp^2-hybridized substituents, have received relatively little attention in the field of asymmetric nonenzymatic acyl transforma-

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Received April 28, 2012; accepted June 4, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200410 or from the author.
† Dedicated to Professor Jun Zhou on the occasion of his 80th birthday.

tion presumably due to its difficulty in distinguishing the π-cation and π-stacking interactions arised from both aryl or alkenyl substituents of aryl alkenylcarbinols. As a consequence, the KR of aryl alkenylcarbinols remains a great challenging task. It is notable that all the enantioenriched allylic alcohols **1**, which bear a simple alkyl (not EWG group) group as R^2, can not be prepared directly through asymmetric Baylis-Hillman reaction.

The only report that described the KR of aryl alkenylcarbinols is the Connon's KR of Baylis-Hillman adducts using chiral DMAP derivatives.[12] However, the stereoselectivities in this case were found to be very disappointing. Only one substrate was resolved with a synthetically acceptable selectivity factor S=13.1, and the others were less than 4. In addition, the reaction normally requires long reaction times (24 h) and low temperature (−78 ℃).

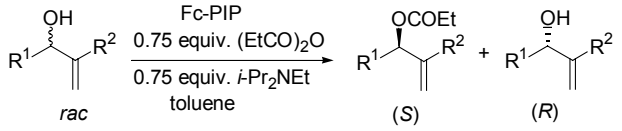
Recently, we have developed a ferrocene-based acyl transfer catalyst (**Fc-PIP**), which proved to be particularly-effective in the KR of aryl alkylcarbinols (S up to 1892)[13a] and bulky (hetero)aryl alkylcarbinols[13b] affording the unreacted alcohols with more than 99% *ee* and good yields for all substrates. In this paper, we extended our catalytic system to the KR of a range of challenging aryl alkenylcarbinol substrates, and moderate to good selectivity factors were observed (up to 24) with the enantiomeric excess up to 99% for corresponding unreacted alcohols at reasonable yileds.

Results and Discussion

Initial investigation was carried out by chosing **1b**, **1c** and **1j** as model substrates using 2 mol% of **Fc-PIP** in toluene at 0 ℃, providing the selectivity factor S=5.6, 5.5, 10.5 respectively (Table 1, Entries 1, 3, 6). Surprisingly, further screening of the reaction conditions revealed that selectivity factor was not improved regardless of lowering the reaction temperature to −20 ℃ or increasing the catalyst loading to 5 mol% (Table 1, Entrries 2, 4, 7, 8). Therefore, 2 mol% of **Fc-PIP** in toluene at 0 ℃ was established as the optimal KR condition for our further study.

With the optimized reaction condition, the generality and substrate scope were then examined. It was found that **Fc-PIP** can catalyze the kinetic resolution of all tried aryl alkenylcarbinols with moderate to good selectivities (Table 2). In contrast to aryl alkylcarbinols that the selectivity factor increases as the size of alkyl group increases, for the case of aryl alkenylcarbinols, the selectivity factor decreases as the substituent R^2 increases (Table 2, Entries 1—3). To our delight, carbinols **1d** and **1e** in which a *ortho*-methyl group are attached to the phenyl ring gave good selectivity factors up to 24 affording corresponding unreacted alcohol with enantiomeric excess up to 99% (Table 2, Entries 4 and 5). The presence of both electron-withdrawing and -donating groups led to a slightly improved selectivity factors (Table 2, Entries 6—8). Furthermore, naphthyl alkenylcarbinols **1j**—**1l** also showed good selectivities (Table 2, Entries 9—12) probably due to the reinforcement of π-stacking interactions between aryl of substrate and acylated catalyst, especially for 1-naphthyl substrates **1k** and **1l**, the selectivity factor was found to be as high as the that of carbinols with *ortho*-methyl group **1d** and **1e** presumably due to the similar *ortho*-steric hinderence (Entries 11, 12 vs. Entries 4, 5). The alcohol **1m** containing

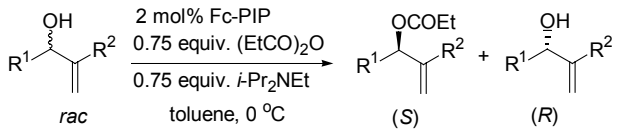
Table 1 Optimization of reaction conditions



Entry	R^1	R^2	t/h	ee_E[d]/%	ee_A[e]/%	C_{HPLC}[f]/%	S[f]
1	Ph (**1b**)[a]	Me	7	53.2	55.6	51.1	5.6
2	Ph (**1b**)[b]	Me	3.5	51.3	71.2	58.1	6.4
3	Ph (**1c**)[a]	Et	8.5	47.0	69.7	59.7	5.5
4	Ph (**1c**)[b]	Et	4	45.1	76.6	62.9	5.8
5	Ph (**1c**)[c]	Et	14	63.8	51.9	55.1	5.9
6	2-Naphthyl (**1j**)[a]	Et	8	51.0	95.0	65.1	10.5
7	2-Naphthyl (**1j**)[b]	Et	4	50.6	95.4	65.3	10.6
8	2-Naphthyl (**1j**)[c]	Et	12	61.9	86.4	58.3	11.4

[a] Reaction was run at 0 ℃ using 2 mol% **Fc-PIP**. [b] Reaction was run at 0 ℃ using 5 mol% **Fc-PIP**. [c] Reaction was run at −20 ℃ using 5 mol% **Fc-PIP**. [d] *ee* value of the ester products. [e] *ee* value of the unreacted alcohols. [f] Calculated from the *ee*s of the esters and the unreacted alcohols.

Table 2 The kinetic resolution of aryl alkenylcarbinols catalyzed by **Fc-PIP**



Entry	R^1	R^2	t/h	ee_E[a]/%	ee_A[b]/%	C_{HPLC}[c]/%	S[c]
1	Ph (**1a**)	H	8	61.7	76.6	55.4	10.0
2	Ph (**1b**)	Me	7	53.2	55.6	51.1	5.6
3	Ph (**1c**)	Et	8.5	47.0	69.7	59.7	5.5
4	*o*-MePh (**1d**)	Me	13	60.4	99.7	62.3	24.0
5	*o*-MePh (**1e**)	Et	13	63.1	99.3	61.1	23.0
6	*p*-MePh (**1f**)	Me	12	59.5	86.2	59.2	11.0
7	*p*-ClPh (**1g**)	Me	12	43.4	95.7	68.8	9.0
8	*m*-BrPh (**1h**)	Me	10	42.5	80.9	65.6	6.0
9	2-Naphthyl (**1i**)	Me	9.5	56.0	91.8	62.1	11.0
10	2-Naphthyl (**1j**)	Et	8	51.0	95.0	65.1	10.5
11	1-Naphthyl (**1k**)	Me	8	60.9	99.3	62.0	21.4
12	1-Naphthyl (**1l**)	Et	6.5	55.7	99.2	64.0	18.0
13	Thienyl (**1m**)	Me	5.5	30.0	30.5	50.4	3.0

[a] *ee* value of the ester products. [b] *ee* value of the unreacted alcohols. [c] Calculated from the *ee*s of the esters and the unreacted alcohols.

a heteroaromatic ring displayed lower selectivity factor than that of phenyl alkenylcarbinols (Table 2, Entry 13, S=3).

According to the π-stacking model proposed by Birman and the exlusive stacked transition state in our catalytic system proposed previously,[13] aryl alkenylcarbinols are believed to approach the acylated catalyst also via π-cation and π-stacking interactions, however with competition between aryl and alkenyl group of the substrate due to their sp^2 π-electron properties. The moderate to good selectivity factors imply that our **Fc-PIP** can discriminate the aforementioned competition of two π-stacking interactions effectively in the KR of aryl alkenylcarbinols (Figure 3).

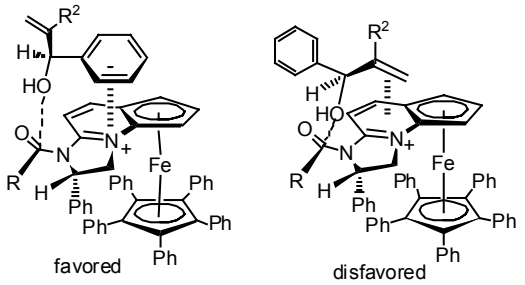


Figure 3 Proposed transition state models.

Conclusions

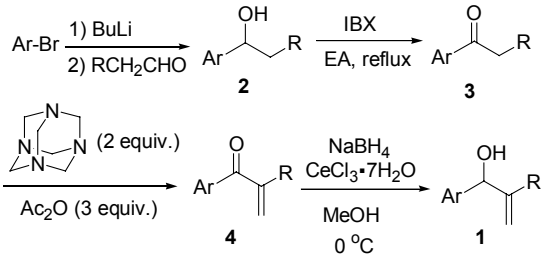
In summary, we have developed an efficient KR of a series of aryl alkenylcarbinols catalyzed by **Fc-PIP**, providing moderate to good selectivity factors up to 24 and excellent enantiomeric excess of corresponding unreacted alcohols over 99%. It is noteworthy that it is the first example for aryl alkenylcarbiols to give S value over 20 by using nonenzymatic catalyst, which would be of great benefit for the synthesis of a wide range of chiral aryl alkenylcarbiols with excellent optical purity. Further application of new type of substrates for the KR using **Fc-PIP** is still in the progress in our laboratory.

Experimental

General information

THF and toluene were distilled from sodium prior to use, *n*-BuLi was available from Aldrich. The substrates used in the kinetic resolution experiments were prepared according to the literature procedures.[14,15] ^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-d_3. Chemical shifts are reported with the internal TMS signal at δ 0.0 as a standard. ^{13}C NMR spectra were recorded on a Bruker DPX 100 MHz spectrometer in chloroform-d_3. Chemical shifts are reported with the internal chloroform signal at δ 77.0 as a standand. Methods used for kinetic resolution experiments, determination of *ee*'s and calculation of conversions and selectivities were adopted from previously published work.[8a] Enatiomeric ratios were determined by HPLC, using a chiralpak OD-H, AS-H or OJ-H column with hexane and *i*-propanol as mobile phase at a flow rate of 1 mL/min and UV detection at 254 or 220 nm.

Preparation of racemic aryl alkenylcarbinols and spectral data for new substrates



The aryl alkyl ketones **3** were prepared according to literature's procedure, then substrates **1** could be obtained through α-methylenation and Luche reduction as follows:

Under nitrogen, **3** (21.4 mmol, 1.0 equiv.), hexamethylenetetramine (6.0 g, 42.8 mmol, 2.0 equiv.) and acetic anhydride (6.07 mL, 64.2 mmol, 3.0 equiv.) were added to a 50-mL Schlenk flask. After stirring at 80 ℃ for 5 h, the reaction mixture was cooled to 25 ℃ and quenched into a stirred mixture of methylene chloride and sodium hydroxide (20 mL of 2 mol•L^{-1} solution). The organic layer was separated and washed with aqueous HCl (10 mL of 1 mol•L^{-1} solution). The combined organic layer was concentrated on a rotary evaporator to afford the crude product which was sufficiently pure for subsequent experiment. The resulting colorless oil residue was dissolved in methanol (50 mL) and cooled to 0 ℃, then treated with $CeCl_3$•$7H_2O$ (7.45 g, 20.0 mmol, 1.0 equiv.). After stirring at 0 ℃ for a few minutes, $NaBH_4$ (757 mg, 20.0 mmol, 1.0 equiv.) was added in several portions during 15 min. After the reduction reaction was completed, it was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the water layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated on a rotary evaporator, and this crude product was then purified by flash chromatography on silica gel (petroleum/EtOAc=10/1, V/V) to afford pure carbinols **1b**—**1m**.

Substrate **1a** was prepared according to literature[16] via Grignard reaction of benzaldehyde with vinyl magnesium bromide.

Compouds **1b**, **1c**, **1f**—**1i**, **1k** and **1m** are previously reported.[17]

2-Methyl-1-(*o*-tolyl)prop-2-en-1-ol (1d) Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44—7.42 (m, 1H), 7.23—7.13 (m, 3H), 5.31 (d, J=3.6 Hz, 1H), 5.12 (s, 1H), 5.00—4.98 (m, 1H), 2.35 (s, 3H), 1.87 (d, J=3.9 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.0, 139.9, 135.8, 130.5, 127.5, 126.3, 126.1, 111.9, 74.3, 19.2, 18.9; IR (film) v: 3141, 2982, 1672, 1481,

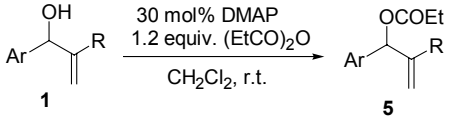
1387, 1020, 901, 762 cm^{-1}. HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1052.

2-Methylene-1-(*o*-tolyl)butan-1-ol (1e) Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42—7.40 (m, 1H), 7.23—7.12 (m, 3H), 5.36 (d, J=4.0 Hz, 1H), 5.15—5.14 (m, 1H), 5.01 (s, 1H), 2.34 (s, 1H), 2.06—1.84 (m, 1H), 1.01 (t, J=7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9, 140.3, 135.9, 130.4, 127.4, 126.5, 126.1, 109.7, 73.7, 25.0, 19.2, 12.2; IR (film) v: 3140, 2993, 1649, 1472, 1022, 902, 742 cm^{-1}. HRMS calcd for $C_{12}H_{16}O$ 176.1201, found 176.1202.

2-Methylene-1-(naphthalen-2-yl)butan-1-ol (1j) Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.83—7.79 (m, 4H), 7.49—7.43 (m, 3H), 5.32 (s, 2H), 5.02 (s, 1H), 2.11 (s, 1H), 2.04—1.83 (m, 2H), 0.99 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.5, 139.8, 133.3, 133.1, 128.2, 128.1, 127.8, 126.2, 126.0, 125.6, 124.8, 109.2, 77.6, 24.5, 12.1; IR (film) v: 3145, 2992, 1655, 1469, 1379, 1283, 1024, 901, 820 cm^{-1}. HRMS calcd for $C_{15}H_{16}O$ 212.1201, found 212.1205.

2-Methylene-1-(naphthalen-1-yl)butan-1-ol (1l) Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.17—8.15 (m, 1H), 7.87—7.85 (m, 1H), 7.79 (d, J=8.2 Hz, 1H), 7.60 (d, J=7.0 Hz, 1H), 7.52—7.44 (m, 3H), 5.87 (d, J=4.0 Hz, 1H), 5.31 (s, 1H), 5.10 (s, 1H), 2.10 (s, 1H), 2.03—2.01 (m, 1H), 1.92—1.90 (m, 1H), 1.01 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.3, 138.0, 134.1, 131.6, 129.0, 128.5, 126.2, 125.7, 125.6, 124.9, 124.3, 110.3, 74.1, 25.5, 12.3; IR (film) v: 3142, 2991, 1661, 1473, 1398, 1001, 901, 791 cm^{-1}. HRMS calcd for $C_{15}H_{16}O$ 212.1201, found 212.1201.

General procedure for the synthesis of corresponding racemic esters



1 5

A solution of aryl alkenylcarbinols **1** (1.01 mmol) in 5 mL of CH_2Cl_2 was treated with DMAP (37.1 mg, 30% mmol) at room temperature. Then the reaction mixture was treated with propionyl anhydride (0.17 mL, 1.31 mmol). After completion of the reaction, the solvent was removed on a rotary evaporator and the residue was purified by flash chromatography on silica gel (petroleum/EtOAc=10/1, *V*/*V*), to afford racemic esters **5**.

2-Methyl-1-phenylallyl propionate (5b) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35—7.28 (m, 5H), 6.18 (s, 1H), 5.11 (s, 1H), 4.97 (s, 1H), 2.41 (q, J=7.6 Hz, 2H), 1.64 (s, 3H), 1.16 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 143.3, 138.7, 128.4, 128.0, 127.1, 112.4, 78.2, 27.8, 18.9, 9.1; IR (film) v: 2997, 1742, 1463, 1182, 1091, 1019, 902, 763, 700 cm^{-1}. HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1154.

2-Methylene-1-phenylbutyl propionate (5c) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34—7.30 (m, 5H), 6.22 (s, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 2.41 (q, J=7.6 Hz, 2H), 1.95 (q, J=7.2 Hz, 2H), 1.16 (t, J=7.5 Hz, 3H), 1.01 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 149.0, 138.9, 128.4, 128.0, 127.3, 110.0, 77.8, 27.8, 25.0, 11.9, 9.1; IR (film) v: 2991, 1739, 1462, 1181, 1090, 1011, 901, 778, 700 cm^{-1}. HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1310.

2-Methyl-1-(*o*-tolyl)allyl propionate (5d) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35—7.33 (m, 1H), 7.21—7.13 (m, 3H), 6.38 (s, 1H), 4.98 (d, J=1.1 Hz, 2H), 2.43—2.36 (m, 5H), 1.68 (s, 3H), 1.15 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 142.6, 136.7, 136.3, 130.5, 127.9, 127.0, 126.0, 112.9, 75.0, 27.8, 19.4, 19.3, 9.1; IR (film) v: 2996, 1740, 1471, 1378, 1180, 1090, 1013, 902, 766 cm^{-1}. HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1308.

2-Methylene-1-(*o*-tolyl)butyl propionate (5e) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (m, 1H), 7.20—7.13 (m, 3H), 6.43 (s, 1H), 5.00 (d, J=5.7 Hz, 2H), 2.43—2.37 (m, 5H), 1.99 (q, J=7.3 Hz, 2H), 1.15 (t, J=7.6 Hz, 3H), 1.04 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 148.5, 136.9, 136.3, 130.5, 128.0, 127.2, 126.0, 110.8, 74.5, 27.8, 25.5, 19.3, 12.0, 9.2; IR (film) v: 2991, 1738, 1472, 1368, 1180, 1081, 1009, 902, 773 cm^{-1}. HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1465.

2-Methyl-1-(*p*-tolyl)allyl propionate (5f) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, J=8.1 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 6.14 (s, 1H), 5.10 (s, 1H), 4.95 (m, 1H), 2.42—2.36 (m, 2H), 2.33 (s, 3H), 1.64 (s, 3H), 1.15 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 143.4, 137.8, 135.6, 129.1, 127.1, 112.1, 78.1, 27.9, 21.2, 19.0, 9.1; IR (film) v: 2997, 1735, 1462, 1180, 1087, 1015, 906, 804 cm^{-1}. HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1310.

1-(4-Chlorophenyl)-2-methylallyl propionate (5g) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32—7.26 (m, 4H), 6.14 (s, 1H), 5.10 (s, 1H), 4.99—4.97 (m, 1H), 2.46—2.33 (m, 2H), 1.63 (s, 3H), 1.16 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 142.7, 137.1, 133.8, 128.5, 128.4, 112.9, 77.4, 27.7, 18.7, 9.0; IR (film) v: 2992, 1735, 1481, 1173, 1090, 1009, 902, 801 cm^{-1}; HRMS calcd for $C_{13}H_{15}ClO_2$ 238.0761, found 238.0762.

1-(3-Bromophenyl)-2-methylallyl propionate (5h) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42—7.40 (m, 1H), 7.35—7.33 (m, 1H), 7.20—7.18 (m, 1H), 7.13—7.11 (m, 1H), 6.05 (s, 1H), 5.04 (d, J=0.7 Hz, 1H), 4.91 (d, J=0.7 Hz, 1H), 2.37—2.31 (m, 2H), 1.55 (s, 3H), 1.08 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 142.6, 141.0, 131.1, 130.0, 125.7, 122.6, 113.3, 77.4, 27.8, 18.7, 9.1; IR (film) v: 2996, 1742, 1418, 1183, 1079, 1027, 906, 790, 701 cm^{-1}; HRMS calcd for $C_{13}H_{15}BrO_2$ 282.0255, found 282.0252.

2-Methyl-1-(naphthalen-2-yl)allyl propionate (5i) ^1H NMR (400 MHz, $CDCl_3$) δ: 7.82 (s, 4H), 7.49—7.44 (m, 3H), 6.35 (s, 1H), 5.19 (s, 1H), 5.02 (s, 1H), 2.44 (q, J=7.7 Hz, 2H), 1.67 (s, 3H), 1.18 (t, J=7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 143.2, 136.0, 133.2, 128.3, 128.2, 127.8, 126.4, 126.3, 126.3, 124.9, 112.7, 78.3, 27.9, 19.1, 9.2; IR (film) v: 2995, 1746,

1469, 1370, 1181, 1086, 1023, 901, 815, 762 cm^{-1}. HRMS calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1308.

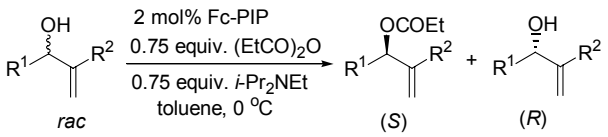
2-Methylene-1-(naphthalen-2-yl)butylpropionate (5j) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81—7.79 (m, 4H), 7.47—7.44 (m, 3H), 6.40 (s, 4H), 5.23 (s, 3H), 5.03 (s, 1H), 2.45—2.39 (m, 2H), 1.97 (q, J=7.1 Hz, 2H), 1.16 (t, J=7.6 Hz, 3H), 1.01 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 149.0, 136.2, 133.2 (d), 128.3, 128.1, 127.7, 126.6, 126.3, 126.2, 125.1, 110.2, 77.9, 27.9, 25.2, 12.0, 9.2; IR (film) v: 2994, 1747, 1471, 1369, 1188, 1091, 1017, 901, 818, 753 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1464.

2-Methyl-1-(naphthalen-1-yl)allyl propionate (5k) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J=8.0 Hz, 1H), 7.84 (dd, J=16.7, 7.9 Hz, 2H), 7.58 (d, J=7.1 Hz, 1H), 7.53—7.44 (m, 3H), 6.93 (s, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 2.48—2.37 (m, 2H), 1.70 (s, 3H), 1.16 (t, J=7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 143.0, 134.0 (d), 131.3, 129.0, 128.9, 126.4, 125.8, 125.3, 123.9, 113.3, 75.3, 27.9, 19.9, 9.2; IR (film) v: 2995, 1731, 1468, 1357, 1186, 1086, 1028, 907, 800, 790 cm^{-1}. HRMS calcd for $C_{17}H_{18}O_2$ 254.1307, found 254.1309.

2-Methylene-1-(naphthalen-1-yl)butyl propionate (5l) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J=8.1 Hz, 1H), 7.84 (dd, J=17.0, 7.9 Hz, 2H), 7.57 (d, J=7.1 Hz, 1H), 7.53—7.43 (m, 3H), 6.98 (s, 1H), 5.14 (s, 1H), 5.10 (s, 1H), 2.47—2.36 (m, 2H), 2.01 (q, J=7.3 Hz, 2H), 1.16 (t, J=7.5 Hz, 3H), 1.04 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 148.9, 134.3, 134.1, 131.5, 129.1, 128.9, 126.4, 126.0, 125.8, 125.3, 123.9, 111.1, 74.7, 27.9, 26.0, 12.2, 9.3; IR (film) v: 2991, 1739, 1468, 1371, 1190, 1093, 1009, 910, 801, 789 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1466.

2-Methyl-1-(thiophen-2-yl)allyl propionate (5m) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (m, 1H), 7.03—7.01 (m, 2H), 6.66 (s, 1H), 4.64 (s, 2H), 2.39 (q, J=7.6 Hz, 2H), 2.01 (s, 3H), 1.17 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 140.0, 130.9, 127.7, 126.9, 125.4, 121.6, 70.0, 27.6, 16.3, 9.2; IR (film) v: 2995, 1732, 1470, 1181, 1089, 1009, 867, 701 cm^{-1}. HRMS calcd for $C_{11}H_{14}O_2S$ 210.0715, found 210.0718.

General procedure for the kinetic resolution of aryl alkenylcarbinols



0.008 mmol of catalyst, 0.4 mmol of secondary alcohol, toluene (1 mL) and 0.3 mmol of *N*,*N*-diisopropyl ethylamine (0.052 mL) were added in turn to a 10-mL flask in a 0 ℃ ice bath, resulting in a red-orange solution. After stirring at 0 ℃ for 5 min, the reaction mixture was treated with 0.3 mmol of propionyl anhydride (0.039 mL), resulting in a green solution. Then the reaction mixture was strirred at 0 ℃ for a specified period of time, at the end of which it was quenched by rapid addition of 0.5 mL of methanol. The solution was allowed to warm up to room temperature and stirred until the solution color turned to red-orange again. The solvent was removed *in vacuo*, and the residue was chromatographed (5%—10% EtOAc/petroleum, *V*/*V*) to separate the ester from the unreacted alcohol.

The enantiomeric excess values of the esters **5** were determined according to corresponding alcohols after hydrolysis (2 mL of 2 mol•L^{-1} KOH in methanol, at room temperature). The conversions and selectivities were caculated as $C_{HPLC}=ee_A/(ee_E+ee_A)$, $S=\ln((1-C_{HPLC})\cdot(1-ee_A))/\ln((1-C_{HPLC})(1+ee_A))$ from previously published work.[8a]

The absolute configurations of the unreacted alcohols were assigned by comparison of the sign of optical rotation of **1c** and **1k** with literature data.[17c]

Methods used to assay enantiometric excess of corresponding unreacted alcohols are as follows:

1a: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=40/1, *V*/*V*, 1.0 mL/min) major: t_R=13.88 min, minor: t_R=18.77 min.

1b: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=33.96 min, minor: t_R=38.57 min.

1c: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=33.09 min, minor: t_R=37.32 min.

1d: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=29.53 min, minor: t_R=36.13 min.

1e: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=26.66 min, minor: t_R=32.37 min.

1f: HPLC (Daicel CHIRALCEL AS-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=14.67 min, minor: t_R=17.74 min.

1g: HPLC (Daicel CHIRALCEL AS-H, Hexane/isopropanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=19.71 min, minor: t_R=22.52 min.

1h: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=60/1, *V*/*V*, 1.0 mL/min) major: t_R=15.42 min, minor: t_R=18.84 min.

1i: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=40/1, *V*/*V*, 1.0 mL/min) major: t_R=26.86 min, minor: t_R=31.07 min.

1j: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=40/1, *V*/*V*, 1.0 mL/min) major: t_R=25.62 min, minor: t_R=29.48 min.

1k: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=40/1, *V*/*V*, 1.0 mL/min) major: t_R=26.23 min, minor: t_R=58.05 min.

1l: HPLC (Daicel CHIRALCEL OD-H, Hexane/isopropanol=40/1, *V*/*V*, 1.0 mL/min) major: t_R=21.67 min, minor: t_R=42.38 min.

1m: HPLC (Daicel CHIRALCEL OJ-H, Hexane/iso-

propanol=99.5/0.5, *V*/*V*, 1.0 mL/min) major: t_R=43.07 min, minor: t_R=47.41 min.

Acknowledgement

This work was financially supported by the Fundamental Research Funds for the Central Universities, the Natural Science Foundation of China (Nos. 20972047, 21172068), the 'Shu Guang' project of Shanghai Municipal Education Commission, Shanghai Education Development Foundation (No. 09SG28), and the Shanghai Committee of Science and Technology (No. 11DZ2260600).

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