Tetrahedron 68 (2012) 1988–1991

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A catalytic asymmetric approach to C_1-chiral 3-methylene-indan-1-ols

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ARTICLE INFO

Article history:
Received 28 October 2011
Received in revised form 15 December 2011
Accepted 15 December 2011
Available online 21 December 2011

Keywords:
Asymmetric allylation
Heck reaction
Sakurai reaction
(*R*)-BINAP
Sequential catalysis

ABSTRACT

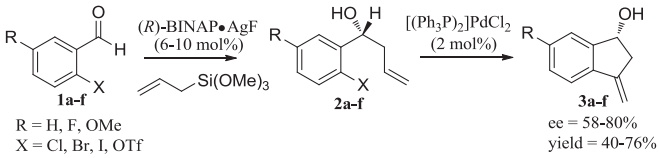
A sequential (*R*)-BINAP·Ag^{I}F (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) (6–10 mol %), and $(Ph_3P)_2Pd^{II}Cl_2$ (bis(triphenylphosphine)palladium(II) dichloride) (2 mol %) catalyzed asymmetric Sakurai–Hosomi–Yamamoto allylation/Mizoroki–Heck reaction that affords C_1-chiral 3-methylene-indan-1-ols with enantiomeric excess (ee) up to 80% is reported. Notably, this protocol allows for the use of various *o*-substituted benzaldehydes and allyltrimethoxysilane. It was also discovered that the presence of electron-rich groups had no effect on the enantioselectivity of the reaction, whereas electron-withdrawing groups lead to erosion in product ee.

1. Introduction

Both the Lewis acid-catalyzed Sakurai–Hosomi allylation and palladium-catalyzed Mizoroki–Heck cross-coupling reactions represent two of the most powerful and widely utilized C–C bond forming reactions in the field of synthesis at this time. Moreover, with the ever increasing demand for highly-optically enriched materials, such as agrochemicals and chiral pharmaceuticals, it is noteworthy that asymmetric versions of the Heck and Sakurai reactions have also been developed.

As for the above advancements, the (*R*)- and (*S*)-BINAP·Ag^{I}F catalyzed asymmetric Sakurai–Hosomi–Yamamoto allylation reaction is considered by many as being one of the most effective means for preparing chiral homoallylic alcohols.[1] It is also noteworthy that a number of other synthetically useful procedures for carrying out the catalytic enantioselective allylation of carbonyls have been reported, including those by Demark, Schaus, and Keck.[2–4] Likewise, the asymmetric Mizoroki–Heck reaction has been well studied over the last three decades and notably several methodologies for constructing chiral quaternary centers have been developed.[5]

Accordingly, we were attracted by the potential development of an annulative Ag^{I}F and $Pd^{II}Cl_2$-catalyzed asymmetric Sakurai–Hosomi/Mizoroki–Heck reaction sequence for the synthesis of enantioenriched C_1-chiral 3-methylene-indan-1-ol products **3a** (Scheme 1). At this time we are unaware of a previous catalytic asymmetric Sakurai–Hosomi/Mizoroki–Heck reaction sequence. After acceptance of this work it was brought to our attention that Schütte et. al. have reported both a racemic and, most recently, an enantioselective palladium-catalyzed domino Sakurai-type allylstannylation-Heck reaction sequence.[14] Although, of mention is that several tandem reactions involving a Sakurai reaction are known.[6] It is also noteworthy, that the chiral indanol products of this procedure are key substructures within a number of biologically active compounds. For instance, the A and B rings of Anisatin, a biologically active component of fruit obtained from the Japanese star anise, are derived from a chiral indanol template. Recent syntheses of Anisatin have hinged upon the use of a chiral indanols.[7] Moreover, in 2006 Smith et al. disclosed the use of a cyclic carbamate substituted indane motif as a side chain of HIV-1 protease inhibitors.[8] Likewise, alkylidene indanes have been employed in diversity oriented synthesis (DOS) as published by Kesavan et al. in 2007.[9] Chiral indanols have also been used to prepare dopamine reuptake blockers for the treatment of cocaine abuse.[10]



Scheme 1. Synthesis of C_1-chiral 3-methylene-indan-1-ols derivatives via a sequential (*R*)-BINAP·Ag^{I}F catalyzed allylation/$(Ph_3P)_2Pd^{II}Cl_2$ Heck alkenylation reaction.

The hypothesis at the outset of this work was that a sequential, or possibly concurrent, pair of catalytic reaction cycles akin to that shown in Scheme 2 would provide routine accesses to optically enriched products, such as **3a**–**f**. As for the mechanistic elements of this

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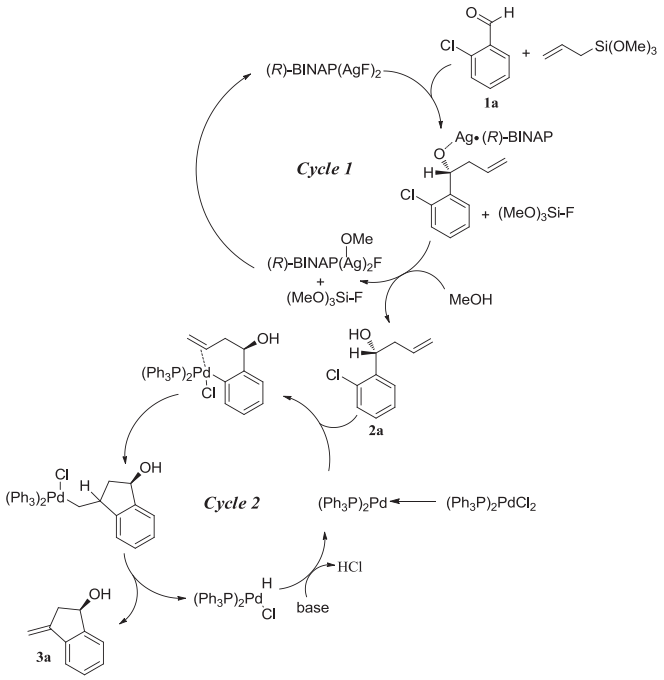
doi:10.1016/j.tet.2011.12.040



Scheme 2. Proposed catalytic cycle for formation of C_1-chiral 3-methylene-indan-1-ols.

catalytic event, Cycle 1 corresponds to a Sakurai–Hosomi–Yamamoto allylation that establishes C_1-chirality via the formation of homoallylic alcohol **2a**. In Cycle 2 **2a** undergoes a 5-*exo*-*trig* ring closing Mizoroki–Heck reaction to afford enantioenriched **3a**.

With this mechanistic proposal in mind, a one-pot concurrent tandem catalysis (CTC) reaction using 2-chlorobenzaldehyde (**1a**) (1.0 equiv), allyltrimethoxysilane (1.8 equiv), and (*R*)-BINAP·$Ag^{I}F$ (6–10 mol %) and $(Ph_3P)_2Pd^{II}Cl_2$ (2 mol %) in MeOH was attempted that only afforded an intractable mixture of products.[11]

Nevertheless, we felt confident that our envisioned reaction sequence could be achieved. As such, a subsequent reaction utilizing sequential tandem catalysis (STC) conditions afforded the targeted C_1-chiral indanol product **3a** with moderate ee=68% in 45% yield (Table 1, entry 1).

Having found this to be the optimal set of reaction conditions we then set out to explore the substrate scope of this reaction. The more sterically demanding and electron-deficient substrate *o*-bromodobenzaldehyde (**1b**) resulted in the formation of **2b** in slightly higher ee than **2a** (Table 1, entry 2 vs 1). This result was unexpected, as in general, marked erosion in enantioselectivity is observed when *o*-substituted arylaldehyde are used in catalytic asymmetric allylations.[12] The sterically more demanding *o*-iodobenzaldehyde substrate **1c** was then reacted, which afforded the desired indanol **3a** with even higher ee (Table 1, entry 3). In order to explore this trend further we tested the sterically demanding *o*-trifluromethylsulfonylated substrate **1d**. Under these reaction conditions no reaction occurred and only starting material and decomposition products were obtained (Table 1, entry 4). Further exploration of the reaction scope demonstrated that electron-rich 2-bromo-5-methoxyaldehdye **1e** afforded **3e** of comparable ee to **3a** (Table 1, entry 5). In contrast, the use of the electron-deficient 2-bromo-5-fluoroaldehdye **1f** resulted in a dramatic decrease in product ee (Table 1, entry 6).

As a working model we propose transition state **TS1** (Fig. 1, X=Cl, Br, I) to account for the increase in product ee as a function of halogen size (see entries 1–3, Table 1). **TS1** not only accounts for the increase in product ee observed herein, but also offers a rational for the enantioselectivity in the Sakurai–Hosomi–Yamamoto allylation reaction. This last point is noteworthy as the precise mechanism for the asymmetric (*R*)- or (*S*)-BINAP·$Ag^{I}F$ Sakurai–Hosomi–Yamamoto allylation reaction is poorly understood at this time.

TS1 possesses four energetically favorable binding interactions, which reduce to (1) a bifurcated mode (Modes 1 and 2) of aldehyde activation, (2) a conformational reinforcing aldehyde based C–H···F interaction (Mode 3), and (3) an aryl C–X···Ag (X=Cl, Br, I) agostic interaction or Ag···halogen coordination (Mode 4) (Fig. 1). Based upon this model it is surmised that the greater level of enantioselectivity found with increasing *o*-aryl halogen size originates from the better donor–acceptor coordinating ability of larger halogens with silver (i.e., mode 4). The strengthening of this C–X···Ag interaction with growing halogen size results in better (*re*)-stereofacial selectivity in the following order I>Br>Cl, as a result of increasing transition state stabilization. It is presumed that other non-stereoselective modes of addition do not appreciably benefit from this interaction.

In summary, we have reported a dual metal-catalyzed methodology for the synthesis of enantioenriched C_1-chiral 3-methylene-indan-1-ols (ee≤80%) that hinges upon the sequential use of a Yamamoto's asymmetric Sakurai–Hosomi allylation reaction and a Mizoroki–Heck reaction. Notably, this procedure benefits from the use of various *o*-substituted arylaldehydes, allyltrimethoxysilane, and catalytic amounts of (*R*)-BINAP·$Ag^{I}F$ (6–10 mol %) and $(Ph_3P)_2Pd^{II}Cl_2$ (2 mol %). Ongoing efforts in our group are focusing upon the extension of this approach for the construction of C_1-chiral 3-methylene-indan-1-ols into an operationally simpler concurrent tandem catalytic (CTC) process. The development of a sequential tandem catalyzed (STC), solid support, variant of this reaction is currently under investigation.

2. Experimental

2.1. General

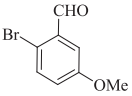
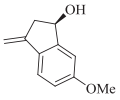
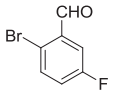
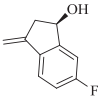
Materials were obtained from commercial suppliers (Sigma–Aldrich)and were used without further purification. DMF (dimethylformamide) was distilled under reduced pressure. All reactions were performed under an inert atmosphere. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F_{254}, EMD Merck. Flash column chromatography was performed over Silicycle ultrapure silica gel (230–400 mesh). NMR spectra were obtained with a Bruker DPX-300 (^{1}H 300 MHz, ^{13}C 75.5 MHz) in $CDCl_3$. The chemical shifts are reported as δ values (ppm) relative to tetramethylsilane. Enantiomeric excess were measured on an Agilent 1100 series high pressure liquid chromatography (HPLC) with (OD-H) column. Mass spectra were obtained on an MSI/Kratos concept IS Mass spectrometer.

2.2. Synthesis

The typical procedure for the asymmetric allylation of an aldehyde with allyltrimethoxysilane and (*R*)-BINAP·AgF as catalyst.

2.2.1. Synthesis of (R)-1-(2-bromophenyl)-3-buten-1-ol, ***2b*** *(Table 1, entry 2).* A mixture of AgF (32.9 mg, 0.26 mmol) and (*R*)-BINAP·AgF (99.6 mg, 0.16 mmol) was dissolved in anhydrous methanol (3 ml) under nitrogen atmosphere with exclusion of direct light, and it was stirred at room temperature for 10 min. To the resulting solution were added dropwise 2-bromobenzaldehyde (264 μL, 2.6 mmol) and allyltrimethoxysilane (791 μL, 4.7 mmol) at −20 °C. The mixture was stirred for 4 h at this temperature, and then treated with a mixture of 1 N HCl (13 ml) and solid KF (1.3 g) at room temperature for 30 min. The resulting precipitate was filtered off, dried over Na_2SO_4, and concentrated in vacuo. The residual crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:6) as eluent to afford the chiral

Table 1
Sequential (*R*)-BINAP·Ag^{I}F catalyzed allylation[a]/$(Ph_3P)_2Pd^{II}Cl_2$ Heck alkenylation[b] reaction of functionally different electrophilic aldehyde

Entry	Substrate	Step 1		Step 2				
		Intermediate	Yield[b] (%)	*T* (°C)	*t* (h)	Product	Yield[c] (%)	ee[d] (%)
1	 **1a**	**2a**	91	100	48	 **3a**	0	—[e]
				130	24		45	68
2	 **1b**	**2b**	80	100	24	**3a**	73	75
3	 **1c**	**2c**	81	100	12	**3a**	64	80
4	 **1d**	**2d**	0				—	—
5	 **1e**	**2e**	64	100	24	 **3e**	76	74
6	 **1f**	**2f**	67	100	48	 **3f**	0	—
				130	24		40	58

Reaction conditions:
[a] (*R*)-BINAP·Ag^{I}F (6–10 mol %), MeOH, −20 °C, 4 h.
[b] $(Ph_3P)_2Pd^{II}Cl_2$ (2 mol %), DMF.
[c] Yields of isolated products after flash chromatography.
[d] Enantiomeric excess was determined by HPLC analysis (OD-H).
[e] (—) Not applicable.

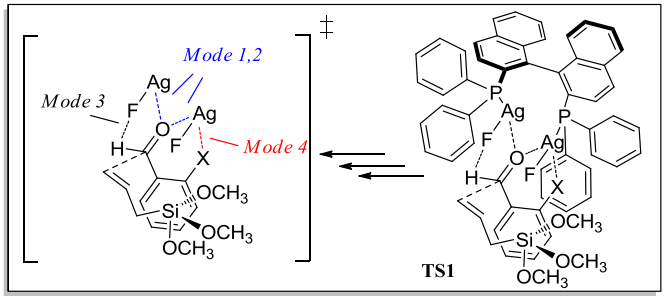


Fig. 1. Proposed transition state model **TS1**.

homoallylic alcohol (469 mg, 2 mmol, 80% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.35–2.43 (m, 1H), 2.62–2.65 (m, 2H), 5.12 (dd, *J*=8.5, 3.8 Hz, 1H), 5.21–5.25 (m, 2H), 5.85–5.91 (m, 1H), 7.14 (td, *J*=7.3, 1.8 Hz, 1H), 7.35 (td, *J*=7.6, 1.0 Hz, 1H), 7.52–7.59 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=42.1, 71.8, 118.7, 121.8, 127.3, 127.7, 128.8, 132.6, 134.3, 142.7; MS (EI) *m*/*z* 226 (M^+); HRMS (EI): *m*/*z* calcd for $C_{10}H_{11}BrO$ (^{79}Br) (M^+): 225.9993; found: 225.9989. Based upon the work of Hall et al.[13] we assigned the absolute configuration of the chiral homoallylic alcohol (*R*)-**2b** [entry 2, Table 1: $[\alpha]_D^{20}$ +38.2 (*c* 3.7, $CHCl_3$)] as (*R*)-configuration. Previously, Hall reported that chiral homoallylic alcohol (*R*)-**2b** had an optical rotation of $[\alpha]_D^{25}$ +50.71 (*c* 1.61, $CHCl_3$). The absolute configurations of the remaining chiral homoallylic alcohols (i.e., (*R*)-**2a**, (*R*)-**2c**–**f**) reported in the present submission were assumed to be the same as (*R*)-**2b**.

2.2.2. (R)-1-(2-Chlorophenyl)-3-buten-1-ol, ***2a*** *(in Table 1, entry 1).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.30 (br, 1H), 2.40–2.45 (m, 1H), 2.61–2.69 (m, 1H), 5.21–5.82 (m, 3H), 5.82–5.96 (m, 1H), 7.20–7.25 (m, 3H), 7.35 (dd, *J*=7.8, 1.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=42.0, 69.6, 118.5, 127.0, 127.1, 128.4, 129.3, 131.7, 134.3, 141.3; MS (EI) *m*/*z* 182 (M^+); HRMS (EI): *m*/*z* calcd for $C_{10}H_{11}ClO$ (M^+): 182.0498; found: 182.0495; $[\alpha]_D^{20}$ +78.8 (*c* 1.9, $CHCl_3$).

2.2.3. (R)-1-(2-Iodophenyl)-3-buten-1-ol, ***2c*** *(in Table 1, entry 3).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.28–2.35 (m, 2H), 2.38–2.66 (m, 1H), 4.94 (dd, *J*=8.6, 3.7 Hz, 1H), 5.19–5.26 (m, 1H), 5.87–5.93 (m, 1H), 6.70 (td, *J*=7.5, 1.5 Hz, 1H), 7.37 (td, *J*=7.6, 0.5 Hz, 1H), 7.54 (dd, *J*=8.1, 0.9 Hz, 1H), 7.82 (dd, *J*=7.8, 0.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=42.3, 76.3, 97.5, 118.6, 127.1, 128.5, 129.2, 134.3, 139.3, 145.6; MS (EI) *m*/*z* 274 (M^+); HRMS (EI): *m*/*z* calcd for $C_{10}H_{11}IO$ (M^+): 273.9855; found: 273.9849; $[\alpha]_D^{20}$ +54.8 (*c* 1.6, $CHCl_3$).

2.2.4. (R)-1-(2-Bromo-5-methoxyphenyl)-3-buten-1-ol, ***2e*** *(in Table 1, entry 5).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37–2.39 (m, 2H), 2.62–2.68 (m, 1H), 3.83 (s, 3H), 5.04–5.08 (m, 1H), 5.19–5.25 (m,

2H), 5.84–5.97 (m, 1H), 7.71 (dd, J=8.9, 3.1 Hz, 1H), 7.14 (d, J=3.0 Hz, 1H). 7.27 (d, J=8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=42.0, 55.5, 71.9, 112.0, 114.9, 118.5, 133.2, 134.3, 143.9, 145.1, 159.2; MS (EI) m/z 256 (M^+); HRMS (EI): m/z calcd for $C_{11}H_{13}BrO_2$ (^{79}Br) (M^+): 256.0099; found: 256.0101; $[\alpha]_D^{20}$ +2.3 (c 2, $CHCl_3$).

2.2.5. (R)-1-(2-Bromo-5-fluorophenyl) -3-buten-1-ol, ***2f*** *(in Table 1, entry 6).* ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.31–2.40 (m, 2H), 2.60–2.67 (m, 1H), 5.02–5.07 (m, 1H), 5.19–5.24 (m, 2H), 5.83–5.90 (m, 1H), 6.88 (td, J=8.1, 3.1 Hz, 1H), 7.31 (dd, J=9.7, 3.0 Hz, 1H). 7.47 (dd, J=8.7, 5.3 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=42.0, 71.7, 114.6, 116.2, 119.2, 133.9, 145.2, 145.3, 160.8, 164.1; MS (EI) m/z 244 (M^+); HRMS (EI): m/z calcd for $C_{10}H_{10}BrFO$ (^{79}Br) (M^+): 243.9899; found: 243.9899; $[\alpha]_D^{20}$ +65.6 (c 0.7, $CHCl_3$).

2.3. Typical procedure for alkenylation of chiral homoallylic alcohol with catalytic amount of $(Ph_3P)_2Pd^{II}Cl_2$

2.3.1. Synthesis of (R)-3-methylene-2,3-dihydro-1H-inden-1-ol, ***3a*** *(in Table 1, entry 2).* To a mixture of (*R*)-1-(2-bromophenyl)-3-buten-1-ol (385.9 mg, 1.7 mmol), bis(triphenylphosphine)palladium(II) chloride (23.8 mg, 0.034 mmol), potassium carbonate (469.9 mg, 3.4 mmol), and DMF (3 ml) were added under a nitrogen atmosphere followed by 2 drops of hydrazine monohydrate by syringe. The mixture was heated at 100 °C for 24 h. The resulting mixture was filtered off and it was diluted with ether and washed with water. The ether layer was dried over Na_2SO_4 and concentrated. The residual crude product was purified by column chromatography on silica gel with pentane/ether (1:4) as the eluent to afford the chiral (*R*)-3-methylene-2,3-dihydro-1*H*-inden-1-ol (180 mg, 1.2 mmol, 73% yield) as a colorless oil. ^{1}H NMR: (300 MHz, $CDCl_3$): δ=1.82 (d, J=7.3 Hz, 1H), 2.66–2.73 (m, 1H), 3.18–3.28 (m, 1H), 5.12 (t, J=1.9 Hz, 1H), 5.27–5.34 (m, 1H), 5.55 (t, J=2.3 Hz, 1H), 7.28–7.38 (m, 2H), 7.49–7.57 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 42.4, 73.1, 104.1, 120.6, 125.2, 128.6, 128.9, 140.2, 146.5, 147.1; MS (EI) m/z 146 (M^+); HRMS (EI): m/z calcd for $C_{10}H_{10}O$ (M^+): 146.0732; found: 146.0730; $[\alpha]^{20}$ −6.7 (c 0.4, $CHCl_3$), $[\alpha]^{20}$ −8.8 (c 0.5, $CHCl_3$), $[\alpha]_D^{20}$ −10.5 (c 0.5, $CHCl_3$) for intermediate **2a**, **2b**, and **2c**, respectively. The enantioselectivity was determined by HPLC analysis on a chiral column (OD-H, hexane/^{i}PrOH 95:5, flow rate 1.0 mL min^{-1}) to be 68%: t_{minor}=9.33 min (*S*), t_{major}=10.40 min (*R*), 75%: t_{minor}=9.29 min (*S*), t_{major}=10.49 min (*R*), 80% t_{minor}=9.36 min (*S*), t_{major}=10.43 min (*R*) for intermediate **2a**, **2b**, and **2c**, respectively.

2.3.2. (R)-6-Methoxy-3-methylene-2,3-dihydro-1H-inden-1-ol, ***3e*** *(in Table 1, entry 5).* ^{1}H NMR: (300 MHz, $CDCl_3$): δ=1.79 (d, J=7.9 Hz, 1H), 2.65–2.72 (m, 1H), 3.19–3.27 (m, 1H), 3.83 (s, 3H), 4.98 (t, J=1.8 Hz, 1H), 5.22–5.28 (m, 1H), 5.37 (t, J=2.3 Hz, 1H), 6.93 (dd, J=8.5, 2.3 Hz, 1H), 7.00 (d, J=2.0 Hz, 1H), 7.45 (d, J=8.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 43.0, 55.5, 73.3, 101.9, 108.6, 116.3, 121.7, 133.0, 145.7, 148.6, 160.6; MS (EI) m/z 176 (M^+); HRMS (EI): m/z calcd for $C_{11}H_{12}O_2$ (M^+): 176.0837; found: 176.0835; $[\alpha]_D^{20}$ −42.7 (c 0.9, $CHCl_3$); The enantioselectivity was determined by HPLC analysis on a chiral column (OD-H, hexane/^{i}PrOH 95:5, flow rate 1.0 mL min^{-1}) to be 74%: t_{minor}=11.81 min (*S*), t_{major}=13.56 min (*R*).

2.3.3. (R)-6-Fluoro-3-methylene-2,3-dihydro-1H-inden-1-ol, ***3f*** *(in Table 1, entry 6).* ^{1}H NMR: (300 MHz, $CDCl_3$): δ=2.62–2.68 (m, 2H), 3.14–3.22 (m, 1H), 5.05 (br, 1H), 5.19 (br, 1H), 5.43 (br, 1H), 7.02–7.13 (m, 2H), 7.45 (dd, J=8.3, 4.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 42.9, 73.0, 103.9, 111.7, 116.3, 122.2, 136.3, 145.3, 149.1, 161.9; MS (EI) m/z 164 (M^+); HRMS (EI): m/z calcd for $C_{10}H_9FO$ (M^+): 164.0637; found: 164.0633; $[\alpha]_D^{20}$ −2.9 (c 1, $CHCl_3$); The enantioselectivity was determined by HPLC analysis on a chiral column (OD-H, hexane/^{i}PrOH 95:5, flow rate 1.0 mL min^{-1}) to be 58%: t_{minor}=7.55 min (*S*), t_{major}=8.22 min (*R*).

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding of this research. We thank Dr. Costa Metallinos and Dr. Paul Zelisko of Brock University for use of equipment and helpful suggestions.

References and notes

1. Asakawa, K.; Matsumoto, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3701–3703.
2. Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763–2793.
3. Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679–8682.
4. Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467–8468.
5. Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945–2963.
6. For select examples, see (a) Stevens, B. D.; Nelson, S. G. *J. Org. Chem.* **2005**, *70*, 4375–4379; (b) Tietze, L. F.; Rischer, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1221–1222.
7. Loh, T.-P.; Hu, Q.-Y. *Org. Lett.* **2001**, *3*, 279–281.
8. Smith, A. B., III; Charnley, A. K.; Harada, H.; Beiger, J. J.; Cantin, L.-D.; Kenesky, S.; Hirschmann, R.; Munshi, S.; Olsen, D. B.; Stahlhut, M. W.; Schleifb, W. A.; Kuo, L. C. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 859–863.
9. Kesavan, S.; Panek, J. S.; Porco, J. A., Jr. *Org. Lett.* **2007**, *9*, 5203–5206.
10. Mark Froimowitz, M.; Wu, K.-M.; Moussa, A.; Haidar, R. M.; Jurayj, J.; George, C.; Gardner, E. *J. Med. Chem.* **2000**, *43*, 4981–4992.
11. Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001–1020.
12. As noted, the catalytic enantioselective allylation of *o*-substituted aldehydes generally results in reduced product stereoselectives. This fact may be readily appreciated by a detailed inspection of a recent review, see: (a) Yus, M.; Gonzalez-Gomez, J. C.; Foubelo, F. *Chem. Rev.* **2011**, *111*, 7774–7854 For recent papers, see: (b) Haddad, T. D.; Hirayama, L. C.; Singaram, B. *J. Org. Chem.* **2010**, *75*, 642–649; (c) Hrdina, R.; Valterova, I.; Hodacova, J.; Cisarova, I.; Kotora, M. *Adv. Synth. Catal.* **2007**, *349*, 822–826.
13. Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481–8490.
14. (a) Cvengroš, J.; Schütte, J.; Schlörer, N.; Neudörfl, J.; Schmalz, H.-G. *Angew. Chem.* **2009**, *121*, 6264–6267; (b) Schütte, J.; Ye, S.; Schmalz, H.-G. *Synlett* **2011**, *18*, 2725–2729.