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Indium hydride catalyzed chemo- and diastereoselective reductive aldol reactions

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ABSTRACT

The reductive aldol reaction of enones has been established catalyzed by Br_2InOMe (cat.)–$MePhSiH_2$ system where Br_2InH acted as an active catalytic species. Addition of 1.0 equivalent of MeOH was essential for catalytic turnover. The system, Br_2InOMe(cat.)–$MePhSiH_2$–MeOH, provided highly chemo- and diastereoselective reductive aldol reaction of enones with functionalized substrates such as α-bromo carbonyls, α-keto esters and α-alkoxy ketones.

1. Introduction

The reductive aldol reaction of enones with aldehydes promoted by metal hydrides is a valuable method for obtaining β-hydroxyketones in one-pot synthesis [1]. To date, metal-catalyzed reductive aldol reaction of enones has been investigated [2]. We have previously reported that dibromoindium hydride (Br_2InH) as stoichiometric metal hydride promoted reductive aldol reaction of enones with aldehydes [3]. Moreover, catalytic generation of indium hydride species was successful by $InBr_3$(cat.)–Et_3SiH [4a] and $In(OAc)_3$(cat.)–$PhSiH_3$ systems [4b]. Although $InBr_3$(cat.)–Et_3SiH underwent highly diastereoselective reactions [4a], functionalized substrates were not applicable because of accompanying an acidic by-product Et_3SiBr in the transmetallation. We have developed a mild method for generating Br_2InH by using Br_2InOMe instead of $InBr_3$ and applied to radical cyclization of functionalized substrates [5]. We report here the catalytic reductive aldol reaction of enones by Br_2InOMe(cat.)–hydrosilane system, and accomplished high chemo- and diastereoselectivities (Scheme 1).

2. Results and discussion

To optimization of conditions for the indium-catalyzed reductive aldol reaction, initially, we performed the simple example of 1-phenyl-2-buten-1-one (**1**) with cyclohexanone (**2a**) in the presence of a catalytic amount of Br_2InOMe and stoichiometric $MePhSiH_2$ (Table 1). Without additives, no aldol product **3a** was obtained at rt for 3 h (entry 1). When MeOH was used as an additive, product **3a** was obtained (entry 2). However, undesirable side product, 1-phenyl-butan-1-one, was formed by conjugate reduction of 1 in 84% yield. The reaction at lower temperature provided a maximum yield of **3a** (52%) (entry 3). Yields were not satisfactory when H_2O or ^{i}PrOH was used in place of MeOH (entries 4 and 5). The use of Ph_2SiH_2 as a hydride source slightly decreased the yield of **3a** (entry 6). $PhSiH_3$ and Et_3SiH were not effective as stoichiometric reductants (entries 7 and 8).

A plausible catalytic cycle is shown in Scheme 2. Initially, Br_2InH is formed by the transmetallation of Br_2InOMe with $MePhSiH_2$. Br_2InH undergoes conjugate reduction to enone **1** to give indium enolate **A** [6]. In this step, Br_2InH could reduce ketone **2a**. The conditions at 0 °C allows the predominant reduction of enone **1**. Next, generated indium enolate **A** reacts with ketone **2a** to form indium aldolate **B**. In the final step, aldolate **B** is protonated by MeOH, and aldol product **3a** is obtained with regeneration of Br_2InOMe. We assume that this is the rate determining step. The choice of additive is important. Thus MeO group has effects on both steps of trapping of indium aldolate **B** and of generation of Br_2InH. Using ^{i}PrOH instead of MeOH does not promote protonation of indium aldolate and generation of Br_2InH due to less acidity and generation of sterically hindered indium alkoxide compared with MeOH.

We next tried to use functionalized substrates. In the reaction with α-bromo alkylaldehyde **2b**, desired product **3b** was obtained

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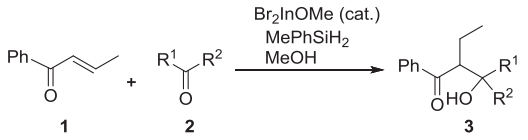


Scheme 1. Reductive aldol reaction of enones.

in 40% yield (Scheme 3). Noteworthy is high diastereoselectivity of the reaction *via* Zimmerman–Traxler six-membered transition state **C** [7]. Previously reported system, $InBr_3$(cat.)–Et_3SiH, resulted in low yield. Thus in the generation of Br_2InH, $InBr_3$(cat.)–Et_3SiH system [4a] accompanied acidic Et_3SiBr which would decompose functionalized compounds, **2b** and **3b**. In contrast, starting from Br_2InOMe–$MePhSiH_2$ accompanied silyl methoxide as a mild and neutral by-product.

The reactions using other functionalized ketones are summarized in Table 2. The highly chemoselective reaction was also applicable to α-bromo acetophenone (**2c**) (entry 2). The presented reductive aldol reaction has limited application for simple ketone such as acetophenone. However, dehalogenation of product **3c** afforded adduct **4** which corresponds to the product using acetophenone (Scheme 4).

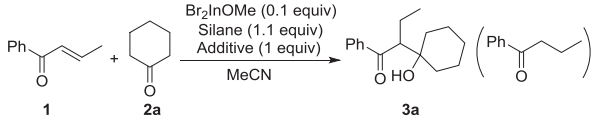
Functionalized ketones such as α-keto esters, **2d** and **2e**, were also reactive to give products, **3d** and **3e**, respectively (entries 2 and 3). No by-products derived from the reduction of **2d** and **2e** were obtained. Noteworthy is high diastereoselectivities of these reactions which could be rationalized by bicyclic transition state **D** as shown in Scheme 5.

The use of α-methoxy acetophenone **2f** also underwent highly diastereoselective reaction where OMe group acts as coordinating group to indium (entry 4). The reaction with benzoin methyl ether (**2g**) gave diastereoselective product **3g** with three contiguous stereogenic centers (entry 5). In this reaction, among possible chelated cyclic transition states, an excellent stereocontrol was achieved through **E** as sterically least hindered cyclic transition state (Scheme 6).

3. Conclusions

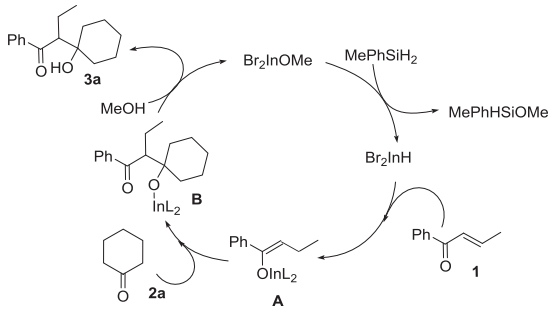
We have established that $MePhSiH_2$ and MeOH promoted reductive aldol reaction of enones in the presence of a catalytic amount of dibromoindium methoxide (Br_2InOMe). Br_2InH acted as an active catalytic species. The reactions were performed only using main group metals and any expensive transition metals were not required. Highly chemo- and diastereoselective aldol products were obtained in the case using α-halo ketones, α-keto esters and α-alkoxy ketones. We are now enlarging the scope of substrates.

Table 1
Optimization of reductive aldol reaction of enone **1** with **2a**.[a]



Entry	Silane	Conditions	Additive	**3a** Yield%[b]
1	$MePhSiH_2$	rt, 3 h	None	Trace (5)
2	$MePhSiH_2$	rt, 3 h	MeOH	12 (84)
3	$MePhSiH_2$	0 °C, 24 h	MeOH	52 (37)
4	$MePhSiH_2$	0 °C, 24 h	H_2O	Trace (15)
5	$MePhSiH_2$	0 °C, 24 h	^{i}PrOH	Trace (14)
6	Ph_2SiH_2	0 °C, 24 h	MeOH	37 (26)
7	$PhSiH_3$	0 °C, 24 h	MeOH	10 (72)
8	Et_3SiH	0 °C, 24 h	MeOH	Trace (trace)

[a] Conditions: Br_2InOMe (0.1 mmol), silane (1.1 mmol), additive (1.0 mmol), **1** (1 mmol), **2a** (1 mmol), MeCN (1 mL).
[b] Yields of 1-phenyl-butan-1-one in parentheses.



Scheme 2. Plausible catalytic cycle.

4. Experimental

4.1. General experimental methods

To a dry nitrogen-filled 10-mL round-bottomed flask containing $InBr_3$ (0.1 mmol) in MeCN (1 mL) was added NaOMe (0.12 mmol) at rt. The mixture was stirred at room temperature for 30 min. To the solution were added $MePhSiH_2$ (1.1 mmol), enones **1** (1 mmol), carbonyl **2** (1 mmol) and MeOH (1 mmol) and the resulting mixture was stirred at 0 °C for 24 h. After quenching with saturated NaCl (aq) (2 mL), the reaction mixture was extracted with ether (10 mL × 2). The combined organic layer was dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography eluting with hexane/EtOAc. Indium and silane residue were removed by this treatment. The crude product was then purified by flash column chromatography eluted by hexane/EtOAC with gradation mode changing from 9/1 to 3/7. The desired product was obtained at hexane/EtOAC = 7:3.

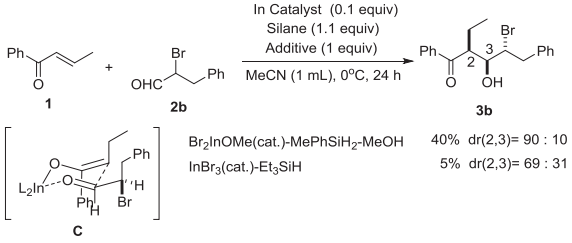
4.1.1. 2-(1′-Hydroxy-cyclohexyl)-1-phenyl-butan-1-one (**3a**)

The NMR data well agree with the reported data in Ref. [2i].

Colorless liquid. IR (neat) 3493 cm^{-1} (OH), 1659 cm^{-1} (C=O). MS (EI, 70 eV) *m*/*z* 246 (M^+, 5), 105 (PhCO, 100), 77 (Ph, 28). HRMS calcd for $C_{16}H_{22}O_2$: 246.1620, found: *m*/*z* 246.1614 (EI, M^+, −0.6 mmu). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00–7.98 (m, 2H, Ph(*o*)), 7.62–7.57 (m, 1H, Ph(*p*)), 7.51–7.47 (m, 2H, Ph(*m*)), 3.51 (dd, *J* = 4.3 and 9.9 Hz, 1H, C=OCH), 3.47 (s, 1H, OH), 1.93–1.18 (m, 12H, CH_2Me, cyclohexyl CH_2), 0.83 (t, *J* = 7.48 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.6, 138.9, 133.4, 128.7, 128.2, 73.0, 54.7, 37.7, 35.2, 25.7, 21.8, 21.7, 20.9, 12.7.

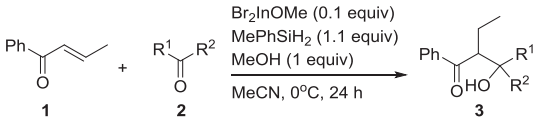
4.1.2. 4-Bromo-2-ethyl-3-hydroxy-1, 5-diphenyl-pentan-1-one (**3b**)

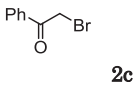
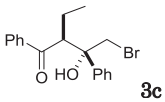
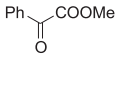
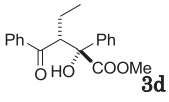
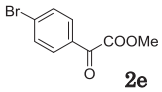
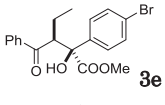
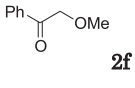
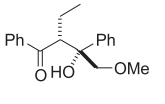
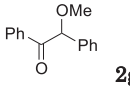
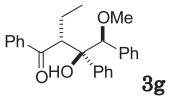
Pale yellow liquid. IR (neat) 3444 cm^{-1} (OH), 1651 cm^{-1} (C=O). MS (CI, 200 eV) *m*/*z* 362 (M^+ + 1, 20.38). HRMS calcd for



Scheme 3. The reaction of **1** with α-bromo alkylaldehyde (**2b**).

Table 2
Reductive aldol reaction of enone **1** with functionalized ketones **2**.[a]



Entry	Ketone **2**	Product **3**	Yield% (dr)
1	 **2c**	 **3c**	64 (99:1)
2	 **2d**	 **3d**	71 (>99:1)
3	 **2e**	 **3e**	60 (85:15)
4	 **2f**	 **3f**	61 (>99:1)
5	 **2g**	 **3g**	72 (96:4)

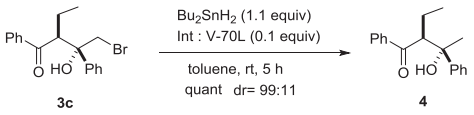
[a] Conditions: Br_2InOMe (0.1 mmol), $MePhSiH_2$ (1.1 mmol), MeOH (1.0 mmol), **1** (1 mmol), **2** (1 mmol), MeCN (1 mL).

$C_{19}H_{21}BrO_2$: 361.2728, found: *m/z* 361.0799 (CI, $M^+ + 1$, −0.4 mmu). Major isomer (2*S**,3*S**,4*R**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 7.2 Hz, 2H, 1-Ph(*o*)), 7.60 (d, J = 7.2 Hz, 1H, 1-Ph(*p*)), 7.48 (t, J = 7.2 Hz, 2H, 1-Ph(*m*)), 7.36–7.21 (m, 5H, 5-Ph), 4.46 (d, J = 9.4 Hz, 1H, OH), 4.17 (ddd, J = 2.9, 7.0 and 10.4 Hz, 1H, CHEt), 4.03 (ddd, J = 2.9, 8.9 and 12.3 Hz, 1H, CHBr), 3.96 (ddd, J = 2.9, 9.4 and 12.3 Hz, 1H, CHOH), 3.73 (dd, J = 2.9 and 14.7 Hz, 1H, CH_2Ph), 3.08 (dd, J = 8.9 and 14.7 Hz, 1H, CH_2Ph), 1.90–1.83 (m, 2H, CH_2Me), 1.00 (t, J = 7.5 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.1, 138.1, 136.8, 134.0, 129.6, 128.8, 128.7, 128.2, 126.6, 75.8, 59.1, 47.4, 40.9, 24.4, 12.2. Minor isomer (2*S**,3*R**,4*R**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 7.2 Hz, 2H, 1-Ph(*o*)), 7.65–7.21 (m, 8H, 1-Ph(*p*), 1-Ph(*m*), 5-Ph(*o*), 5-Ph(*m*) and 5-Ph(*p*)), 4.43 (ddd, J = 1.7, 7.5 and 7.7 Hz, 1H, CHBr), 4.00 (brs, 1H, OH), 3.93 (dd, J = 1.7 and 8.0 Hz, 1H, CHOH), 3.84 (ddd, J = 4.8, 8.0 and 8.0 Hz, 1H, CHEt), 3.38 (dd, J = 7.5 and 14.2 Hz, 1H, CH_2Ph), 3.26 (dd, J = 7.7 and 14.3 Hz, 1H, CH_2Ph), 1.77–1.51 (m, 2H, CH_2Me), 0.75 (t, J = 7.7 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.3, 137.9, 133.5, 129.1, 128.7, 128.5, 128.4, 126.9, 125.2, 72.5, 63.4, 52.7, 42.8, 23.3, 11.0.

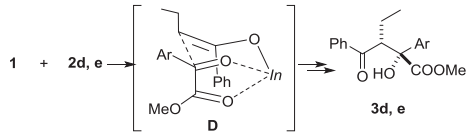
4.1.3. (2R,3R*)-4-Bromo-2-ethyl-3-hydroxy-1, 3-diphenyl-butan-1-one (**3c**)*

The NMR data well agree with the reported data in Ref. [2i].

Colorless liquid. IR (neat) 3433 cm^{-1} (OH), 1655 cm^{-1} (C=O). MS (CI, 200 eV) *m/z* 347 ($M^+ + 1$, 4), 199 (M^+ − $PhCOCH_2CH_2CH_3$, 20), 149 (100), 105 (PhCO, 18). HRMS calcd for $C_{18}H_{19}BrO_2$: 346.0568, found: *m/z* 347.0650 (CI, $M^+ + 1$, +0.3 mmu). Major isomer (2*R**,3*R**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03–8.00 (m, 2H, 1-Ph(*o*)), 7.64–7.60 (m, 1H, 1-Ph(*p*)), 7.57–7.54 (m, 2H, 3-Ph(*o*)), 7.50–7.48 (m, 2H, 1-Ph(*m*)), 7.39–7.35 (m, 2H, 3-Ph(*m*)), 7.30–7.28 (m, 1H, 3-Ph(*p*)), 4.81 (s, 1H, OH), 4.13 (dd, J = 3.6 and 10.1 Hz, 1H, CHEt), 3.76 (d, J = 10.6 Hz, 1H, CH_2Br), 3.56 (d, J = 10.6 Hz, 1H, CH_2Br), 1.82 (qdd, J = 7.4 and 10.1 and 13.7 Hz, 1H, CH_2Me), 1.54 (qdd, J = 3.6 and 7.7 and 13.7 Hz, 1H, CH_2Me), 0.68 (t, J = 7.4 and 7.7 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.2, 142.0, 137.9, 134.0, 128.8, 128.5, 128.1, 127.4, 125.5, 77.5, 52.7, 42.3, 23.2, 12.4. Minor isomer (2*S**,3*R**) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, J = 7.4 Hz, 2H, 1-Ph(*o*)), 7.55–7.52 (m, 1H, 1-Ph(*p*)), 7.46–7.39 (m, 4H, 1-Ph(*m*) and 3-Ph(*o*)), 7.26–7.22 (m, 2H, 3-Ph(*m*)), 7.18–7.14 (m, 1H, 3-Ph(*p*)), 4.39 (s, 1H, OH), 4.17 (dd, J = 3.8 and 10.6 Hz, 1H, CHEt), 3.97 (d, J = 10.6 Hz, 1H, CH_2Br), 3.91 (d, J = 10.6 Hz, 1H, CH_2Br), 2.00 (qdd, J = 7.2 and 10.6 and 13.7 Hz, 1H, CH_2Me), 1.85 (qdd, J = 3.8 and 7.7 and 13.7 Hz, 1H, CH_2Me), 0.84 (dd, J = 7.2 and 7.7 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 205.7, 143.5, 138.4, 133.4, 128.5, 128.3, 128.0, 127.4, 125.8, 77.3, 53.5, 40.4, 21.5, 12.6.



Scheme 4. Dehalogenation of **3c**.



Scheme 5. Plausible mechanism through chelated cyclic transition state.

4.1.4. (2R,3R*)-3-Benzoyl-2-hydroxy-2-phenyl-pentanoic acid methyl ester (**3d**)*

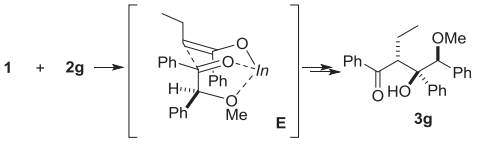
The NMR data well agree with the reported data in Ref. [2i].

White solid. Mp 73 °C. IR (KBr) 3409 cm^{-1} (OH), 1720 cm^{-1} (C=O), 1650 cm^{-1} (C=O). MS (CI, 200 eV) *m/z* 313 ($M^+ + 1$, 100), 165 (58), 149 (84). HRMS calcd for $C_{19}H_{20}O_4$: 312.1362, found: *m/z* 313.1444 (CI, $M^+ + 1$, +0.4 mmu). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07–8.05 (m, 2H, COPh(*o*)), 7.71–7.69 (m, 2H, 2-Ph(*o*)), 7.64–7.59 (m, 1H, COPh(*p*)), 7.53–7.39 (m, 4H, 2-Ph(*m*) and COPh(*m*)), 7.35–7.31 (m, 1H, 2-Ph(*p*)), 5.36 (s, 1H, OH), 4.31 (dd, J = 4.8 and 8.2 Hz, 1H, CHEt), 3.55 (s, 3H, OMe), 1.66–1.50 (m, 2H, CH_2Me), 0.61 (t, J = 7.7 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.3, 174.8, 139.0, 137.2, 133.7, 128.6, 128.5, 128.3, 127.9, 125.0, 81.0, 53.5, 52.7, 21.0, 12.5.

4.1.5. (2R,3R*)-3-Benzoyl-2-(4′-bromo-phenyl)-2-hydroxy-pentanoic acid methyl ester (**3e**)*

The NMR data well agree with the reported data in Ref. [2i].

White solid. Mp 112 °C, recrystallization from hexane/Et_2O. IR (KBr) 3444 cm^{-1} (OH), 1723 cm^{-1} (C=O), 1659 cm^{-1} (C=O). MS (CI, 200 eV) *m/z* 391 ($M^+ + 1$, 20), 243 (30), 149 (84). HRMS calcd for $C_{19}H_{19}BrO_4$: 390.0467, found: *m/z* 391.0543 (CI, $M^+ + 1$, −0.2 mmu). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.6 Hz, 2H, COPh(*o*)), 7.66–7.47 (m, 7H, COPh(*m*) and COPh(*p*) and 2-Ph(*o*) and 2-Ph(*m*)), 5.37 (s, 1H, OH), 4.25 (dd, J = 4.8 and 8.2 Hz, 1H, CHEt), 3.57 (s, 3H, OMe), 1.67–1.58 (m, 1H, CH_2Me), 1.54–1.44 (m, 1H, CH_2Me), 0.63 (t, J = 7.4 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.0, 174.5, 138.2, 137.2, 133.9, 131.6, 128.7, 128.6, 127.0, 122.2, 80.8, 53.4, 53.0, 21.0, 12.6.



Scheme 6. Control of diastereoselectivity of three contiguous stereogenic centers.

4.1.6. (2R,3R*)-2-Ethyl-3-hydroxy-4-methoxy-1,3-diphenyl-butan-1-one (**3f**)*

The NMR data well agree with the reported data in Ref. [2i].

White solid. Mp 72 °C. IR (KBr) 3444 cm^{-1} (OH), 1658 cm^{-1} (C=O). MS (CI, 200 eV) *m/z* 299 ($M^+ + 1$, 1.7), 151 (100), 149 (44). HRMS calcd for $C_{19}H_{22}O_3$: 298.1569, found: *m/z* 299.1648 (CI, $M^+ + 1$, +0.1 mmu). Anal. calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43, found: C, 76.49; H, 7.41. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, $J = 8.2$ Hz, 2H, 1-Ph(*o*)), 7.63–7.59 (m, 3H, 1-Ph(*p*) and 3-Ph(*o*)), 7.52 (t, $J = 8.2$ Hz, 2H, 1-Ph(*m*)), 7.38 (t, $J = 7.2$ Hz, 2H, 3-Ph(*m*)), 7.30 (d, $J = 7.2$ Hz, 1H, 3-Ph(*p*)), 4.79 (s, 1H, OH), 3.99 (dd, $J = 3.6$ and 10.8 Hz, 1H, CHEt), 3.48 (d, $J = 9.4$ Hz, 1H, CH_2OMe), 3.37 (d, $J = 9.4$ Hz, 1H, CH_2OMe), 2.97 (s, 3H, OMe), 1.83–1.77 (m, 1H, CH_2Me), 1.35–1.29 (m, 1H, CH_2Me), 0.65 (t, $J = 7.4$ Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.6, 143.1, 138.9, 133.2, 128.6, 128.2, 128.1, 127.0, 125.3, 80.4, 78.2, 58.6, 51.8, 22.3, 12.3.

4.1.7. (2R,3R*,4S*)-2-Ethyl-3-hydroxy-4-methoxy-1,3,4-triphenyl-butan-1-one (**3g**)*

The NMR data well agree with the reported data in Ref. [2i].

White solid. Mp 141 °C, recrystallization from hexane/Et_2O. IR (KBr) 3346 cm^{-1} (OH), 1647 cm^{-1} (C=O). MS (CI, 200 eV) *m/z* 375 ($M^+ + 1$, 6), 227 (100), 195 (81), 149 (97). HRMS calcd for $C_{25}H_{26}O_3$: 374.4721, found: *m/z* 375.1953 (CI, $M^+ + 1$, −0.8 mmu). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (d, $J = 6.7$ Hz, 2H, 1-Ph(*o*)), 7.63–7.54 (m, 3H, arom), 7.35–7.30 (m, 2H, arom), 7.24–7.21 (m, 2H, arom), 7.17–7.13 (m, 1H, arom), 7.07–6.98 (m, 3H, arom), 6.85–6.86 (m, 2H, arom), 5.18 (s, 1H, OH), 4.28 (s, 1H, CHOMe), 4.08 (dd, $J = 3.3$ and 11.1 Hz, 1H, CHEt), 2.54 (s, 3H, OMe), 1.83 (qdd, $J = 7.4$ and 11.1 and 13.5 Hz, 1H, CH_2Me), 1.26 (qdd, $J = 3.3$ and 7.4 and 13.5 Hz, 1H, CH_2Me), 0.67 (t, $J = 7.4$ Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 205.6, 142.1, 139.1, 136.3, 132.7, 128.7, 128.6, 127.8, 127.7, 127.1, 126.8, 126.6, 125.5, 90.7, 83.0, 56.0, 51.6, 23.3, 12.0.

*4.1.8. Dehalogenation of **3c** and determination of stereochemistry major isomer **4***

The column chromatography purification of the reaction mixture of **1** with **2c** afforded major isomer **3c**. The radical dehalogenation of **3c** (major isomer) with Bu_2SnH_2 in the presence of V-70 [8] as initiator at rt for 5 h afforded the aldol product **4** which did not agree with reported values of *threo* isomer [9]. Hence major isomer is determined as *erythro* isomer.

4.1.9. (2S,3S*)-2-Ethyl-3-hydroxy-1,3-diphenyl-1-butan-1-one (**4**)*

Colorless liquid. IR (neat) 3474 cm^{-1} (OH), 1655 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07–8.04 (m, 2H, 1-Ph(*o*)), 7.67–7.63 (m, 1H, arom), 7.57–7.52 (m, 4H, arom), 7.39–7.36 (m, 2H, arom), 7.28–7.24 (m, 1H, arom), 4.50 (s, 1H, OH), 3.83 (dd, $J = 3.6$ and 10.3 Hz, 1H, CHEt), 1.92–1.76 (m, 1H, CH_2Me), 1.45 (s, 1H, Me), 1.40–1.30 (m, 1H, CH_2Me), 0.64 (t, $J = 7.4$ Hz, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 208.7, 146.1, 138.6, 133.8, 128.8, 128.4, 128.1, 126.5, 124.8, 75.6, 55.8, 30.4, 22.4, 12.5.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.083.

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