

Remarkable Dependence of Diastereoselectivity on Anhydrous or Aqueous Solvent in the Indium Hydride Promoted Reductive Aldol Reaction of α,β -Unsaturated Ketones

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Abstract: Dichloroindium hydride generated by the transmetallation between tributyltin hydride and indium trichloride predominantly reduced α,β -unsaturated ketones (enones) with 1,4-selectivity even in the presence of aldehydes. Under anhydrous conditions, the successive aldol reaction between the resulting enolates and the remaining aldehydes proceeded with high *anti*-selectivity. The stereochemistry was dramatically reversed to be *syn*-selective by the use of water and methanol as an additive and solvent, respectively.

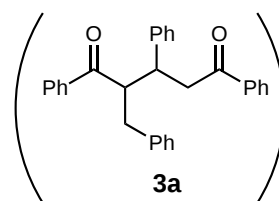
Keywords: aldol reaction; diastereoselectivity; hydrides; indium; water chemistry

The potential of indium compounds in the field of organic syntheses has been intensively studied in this decade.^[1] Although several indium hydrides such as $\text{LiPh}_n\text{InH}_{4-n}$ ($n = 0 - 2$),^[2] $\text{InH}_3[\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})]$, and $\text{InH}_3[\text{P}(\text{C}_6\text{H}_{11})_3]$ ^[3] have been reported, the synthetic use of indium hydrides remains to be explored. We have recently demonstrated that dichloroindium hydride (Cl_2InH) was generated by the transmetallation between tri-*n*-butyltin hydride (Bu_3SnH) and indium trichloride (InCl_3),^[4] and that the hydride has accomplished the reduction of acid chlorides to aldehydes and dehalogenation of alkyl bromides.^[5] During further study of the reduction of α,β -unsaturated ketones (enones), we discovered a three-component synthesis of aldols (reductive aldol reaction) from Cl_2InH , enones, and aldehydes, in which a predominant 1,4-reduction of enones by Cl_2InH is followed by the aldol reaction between the resulting enolates and the remaining aldehydes. Noteworthy is that, in the reductive aldol reaction, both *anti*- and *syn*-selective aldol reactions were effected by the use of THF and an aqueous solvent, respectively.

Table 1 shows the results of the reduction of enones **1** with indium hydride generated from Bu_3SnH and InCl_3 .

Table 1. Effect of solvents on the selective 1,4-reduction of α,β -unsaturated ketones (enones) **1** with indium hydride.^[a]

$\text{R}^1-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{R}^2 \xrightarrow[\text{Solvent, } -78^\circ\text{C to rt, 1 h}]{\text{InCl}_3, \text{Bu}_3\text{SnH}} \text{R}^1-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(\text{R}^2)-\text{R}^2$				
Entry	R ¹	R ²	Solvent	Yield of 2 (%) ^[b]
1	Ph	Ph (1a)	THF	66 (33)
2 ^[c]	Ph	Ph (1a)	THF	59 (34)
3 ^[d]	Ph	Ph (1a)	THF	12
4 ^[e]	Ph	Ph (1a)	THF	3
5	Ph	Ph (1a)	MeCN	32
6	Ph	Ph (1a)	CH_2Cl_2	34 (13)
7	Ph	Ph (1a)	MeOH	97
8	Ph	Ph (1a)	<i>i</i> -PrOH	85
9	Ph	Ph (1a)	THF/H ₂ O (9/1)	77
10	Ph	Ph (1a)	H ₂ O	15
11	Ph	Me (1b)	MeOH	97
12	Ph	<i>t</i> -Bu (1c)	MeOH	99
13	Me	Ph (1d)	MeOH	28 ^[f]
14	<i>t</i> -Bu	Ph (1e)	MeOH	66 ^[g]



^[a] InCl_3 1 mmol, Bu_3SnH 1 mmol, **1** 1 mmol, solvent 1 mL.

^[b] Values in parentheses are yields of dimerization product **3a**.

^[c] Galvinoxyl (0.1 mmol) was added.

^[d] AlCl_3 was used instead of InCl_3 .

^[e] $\text{BF}_3 \cdot \text{OEt}_2$ was used instead of InCl_3 .

^[f] 1,2-Reduction product was accompanied (4%).

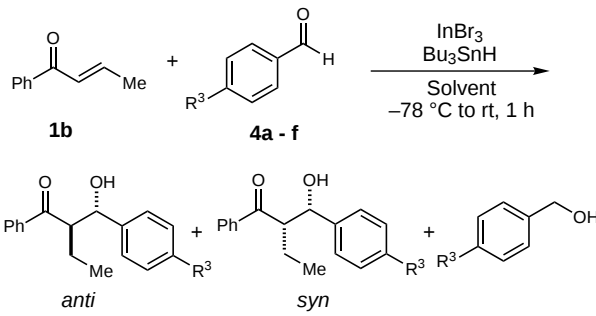
^[g] 1,2-Reduction product was accompanied (8%).

When anhydrous THF was used as solvent, the 1,4-reduction product **2a** was obtained in 66% yield from chalcone (**1a**), accompanied by the dimerization prod-

uct **3a** in 33% yield (entry 1). The formation of **3a** indicates that the generation of the indium enolate is followed by the Michael addition to residual **1a**. The low effect of galvinoxyl suggests that no radical process is involved in this reaction (entry 2). Other group 13 element halides such as AlCl_3 and $\text{BF}_3 \cdot \text{OEt}_2$ show less effects (entries 3 and 4). Employment of solvents such as MeCN and CH_2Cl_2 resulted in considerably lower yields (entries 5 and 6). However, when MeOH and *i*-PrOH were used, the 1,4-reduced product **2a** was obtained in good to excellent yields without accompanying **3a** (entries 7 and 8). These results indicate that indium hydride has considerably stability for alcohols and that the resulting indium enolate is smoothly protonated by the alcohol solvents. The addition of small amounts of water to THF (THF/ H_2O = 9/1) also induced the selective formation of **2a** (entry 9). Using water as a solvent did not give a satisfying result (entry 10), perhaps because of the insolubility of the substrates. In MeOH, enones bearing a benzoyl moiety **1a**, **1b**, and **1c** were reduced to provide the corresponding ketones in quantitative yields (entries 7, 11, and 12). In contrast, the reduction of aliphatic ketones **1d** and **1e** resulted in lower yields along with slight amounts of the 1,2-reduction products (entries 13 and 14).

In the next stage, we could fortunately accomplish a reductive aldol reaction of enones as shown in Table 2. In general, the reductive aldol reaction using the three components metal hydrides, enones, and aldehydes has been a difficult issue^[6] because an aldehyde is more susceptible than an enone to conventional metal hydrides. When the reduction of enone **1b** was performed in the presence of *p*-anisaldehyde (**4a**), the aldol product **5a** was obtained in 64% yield with high *anti*-selectivity (*syn:anti* = 9:91), in spite of the accompanying reduction of aldehyde **4a** in 14% yield (Table 2 entry 1). The predominant formation of the aldol adduct **5a** indicates that indium hydride reacts with enone **1b** in preference to aldehyde **4a**, and that the generated indium enolate reacts with **4a** smoothly. When InBr_3 was used instead of InCl_3 , the yield of **5a** was increased to 79% yield (entry 2). Moreover, the use of a small excess amount of enones and indium hydride achieved a high yield (86%) and *anti*-diastereoselectivity (96%) of **5a** (entry 3). To our knowledge, this is the highest *anti*-selectivity reported so far. To our surprise, even when MeOH was used as a solvent, the aldol reaction effectively proceeded without decomposition of the intermediate enolate (entry 4). The aldol reaction of the indium enolate apparently took place much faster than protonolysis (alcoholysis) by MeOH. Moreover, of particular interest is that the obtained aldol product was solely the *syn*-isomer, which was completely opposite to the *anti*-selective reaction in THF under anhydrous conditions. When aqueous THF (THF/ H_2O = 9/1) was used, a high *syn*-selectivity was also obtained (entry 5). Various aromatic aldehydes **4** were applicable for the formation

Table 2. Stereoselective reductive aldol reactions of **1b** with **4** by using indium hydride.^[a]



Entry	R^3	4	Solvent	Yield [%]		
				5	<i>syn:anti</i>	6
1 ^[b]	MeO	4a	THF	64 (5a)	9:91	14
2 ^[c]	MeO	4a	THF	79 (5a)	14:86	12
3	MeO	4a	THF	86 (5a)	4:96	6
4	MeO	4a	MeOH	69 (5a)	> 99: > 1	19
5	MeO	4a	THF/ H_2O (9/1)	79 (5a)	94:6	13
6	Me	4b	THF	89 (5b)	4:96	11
7	Me	4b	THF/ H_2O (9/1)	77 (5b)	95:5	18
8	Ph	4c	THF	85 (5c)	5:95	14
9	Ph	4c	THF/ H_2O (9/1)	71 (5c)	93:7	29
10	H	4d	THF	87 (5d)	10:90	11
11	H	4d	THF/ H_2O (9/1)	76 (5d)	91:9	19
12	Cl	4e	THF	83 (5e)	7:97	16
13	Cl	4e	THF/ H_2O (9/1)	68 (5e)	85:15	32
14	Cl	4e	MeOH	68 (5e)	90:10	22
15	NO_2	4f	THF	70 (5f)	14:86	16
16	NO_2	4f	THF/ H_2O (9/1)	44 (5f)	63:37	56

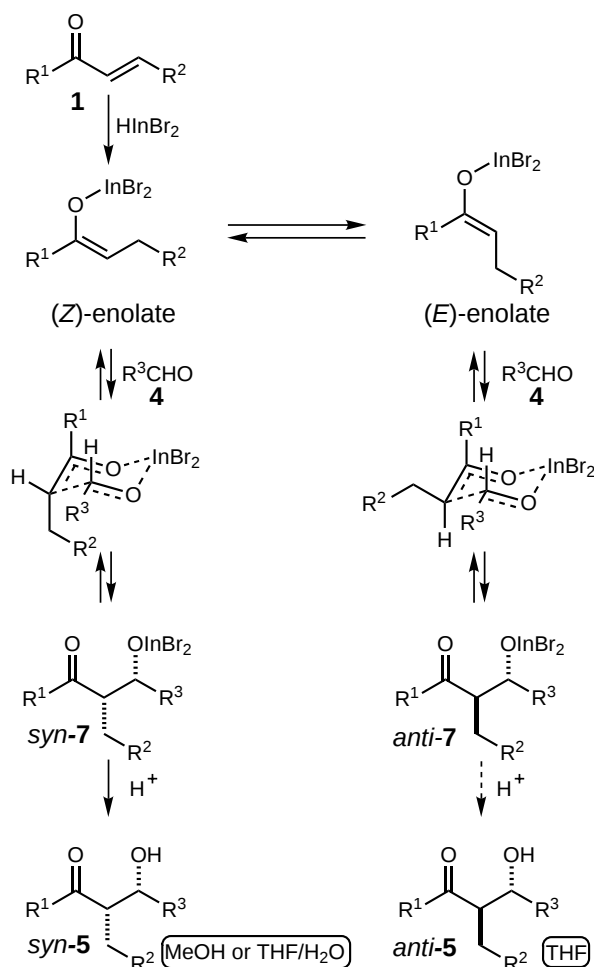
^[a] InBr_3 1.2 mmol, Bu_3SnH 1.2 mmol, **1b** 1.5 mmol, **4** 1 mmol, solvent 2 mL.

^[b] InCl_3 1 mmol, Bu_3SnH 1 mmol, **1b** 1 mmol, **4** 1 mmol, solvent 2 mL.

^[c] InBr_3 1 mmol, Bu_3SnH 1 mmol, **1b** 1 mmol, **4** 1 mmol, solvent 2 mL.

of aldol adducts **5** (entries 6 – 16). In these cases, the stereochemistry of *syn*- and *anti*-selectivities in **5** could be controlled by the choice of solvents, THF and aqueous solvent. In the case of using *p*-nitrobenzaldehyde (**4f**) under aqueous conditions, the yield and selectivity of **5f** are not favorable (entry 16). Moreover, an aliphatic aldehyde is not applicable. This is a limitation of our method at this stage.

Although the mechanism for the presented diastereoselective aldol reaction is not clear as yet, a tentative path is illustrated in Scheme 1. When Br_2InH is treated with the mixture of enone and aldehyde, selective 1,4-reduction of the enone occurs without the reduction of the aldehyde. The (*Z*)-enolate is generated initially because of the preferred 1,4-addition of indium hydride to the *s-cis* form of enone **1**,^[7] and the enolate reacts with aldehyde, giving the *syn*-indium aldolate *syn*-**7** by way of a Zimmerman–Traxler six-membered transition



Scheme 1. Plausible reaction path.

state.^[8] In MeOH or aqueous THF (THF/H₂O = 9/1), *syn*-7 is immediately protonated to give the *syn*-aldol product *syn*-5. On the other hand, in anhydrous THF, the retro aldol reaction from *syn*-7 takes place to give *anti*-aldolate *anti*-7 in which the transformation is controlled thermodynamically.^[9] The resulting aldolate *anti*-7 is hydrolyzed by water in after treatment to produce the *anti*-aldol product *anti*-5.

In conclusion, dichloroindium hydride (Cl_2InH) facilitates the reductive aldol reaction of enones. Noteworthy is that *syn*- and *anti*-selective aldol reactions were accomplished in high levels by anhydrous and aqueous solvents, respectively. The *anti*-selectivity (96%) obtained is the highest one so far reported. In addition, the first example of the reductive aldol reaction in aqueous media is presented.

Experimental Section

General Remarks

IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All the ¹H and ¹³C NMR spectra were recorded with a JEOL JNM-GSX-270 (270 and 67.9 MHz, respectively) in deuteriochloroform (CDCl_3) containing 0.03% (w/v) of tetramethylsilane as internal standard. Mass spectra were recorded on a JEOL JMS-DS-303. Column chromatography was performed using Fuji Davison silica gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel.

Tri-*n*-butyltin hydride (*n*-Bu₃SnH) was prepared by the reduction of tri-*n*-butyltin chloride (*n*-Bu₃SnCl) with LiAlH₄. Commercially available InCl₃ was used without further purification. All aldehydes were purchased and purified by usual methods. THF was freshly distilled from sodium benzophenone ketyl. All reactions were carried out under a dry nitrogen atmosphere.

Representative Procedure for the 1,4-Reduction of Enones

A mixture of InCl₃ (0.221 g, 1 mmol) and Bu₃SnH (0.291 g, 1 mmol) in MeOH (1 mL) was stirred at -78°C for 5 min to generate dichloroindium hydride. Chalcone **1a** (0.208 g, 1 mmol) was added at this temperature and the reaction mixture was warmed up to room temperature for 1 h. After adding aqueous ammonium fluoride, the volume was extracted with ether (50 mL $\times$ 2). The combined extract was dried over anhydrous MgSO₄ and concentrated. The residue was subjected to column chromatography eluting with hexane-EtOAc (9:1) to give product **2a**; yield: 97%. Further purification was performed by silica gel TLC with hexane-Et₂O (9:1).

Representative Procedure for the Reductive Aldol Reaction

A mixture of InBr₃ (0.426 g, 1.2 mmol) and Bu₃SnH (0.349 g, 1.2 mmol) in THF (2 mL) was stirred at -78°C for 5 min to generate dichloroindium hydride. Enone **1b** (0.219 g, 1.5 mmol), and aldehyde **4a** (0.136 g, 1 mmol) were successively added and the reaction mixture was warmed up to room temperature for 1 h. After then, similar treatments as above were done. Column chromatography eluting with hexane-EtOAc (8:2) gave a mixture of **5a** (86%, *syn:anti* = 4:96) and **6a** (6%). The product ratio was determined by ¹H NMR spectroscopy. Further purification was performed by silica gel TLC with hexane-Et₂O (8:2).

threo-2-(Hydroxy-4'-methoxyphenylmethyl)-1-phenylbutan-1-one (anti-5a): IR(neat): $\nu = 3494, 1666\text{ cm}^{-1}$; ¹H NMR (CDCl_3 , 270 MHz): $\delta = 0.78$ (t, $J = 7.81\text{ Hz}$, 3H), 1.38–1.78 (m, 2H), 2.94 (d, $J = 4.88\text{ Hz}$, 1H), 3.79 (s, 3H), 3.69–3.83 (m, 1H), 4.98 (dd, $J = 4.88$ and 7.81 Hz , 1H), 6.82–6.93 (m, 2H), 7.24–7.60 (m, 5H), 7.92–7.98 (m, 2H); ¹³C NMR (CDCl_3 , 67.9 MHz): $\delta = 11.6, 23.6, 54.4, 55.3, 75.4, 113.8, 127.6, 128.3, 128.6, 133.2, 134.8, 138.3, 159.2, 205.7$; MS: $m/z = 284$ (0.2), 255 (0.5), 148 (51), 135 (78), 120 (9), 105 (100), 92 (8), 77 (49); HRMS: calcd. for C₁₈H₂₀O₃: 284.1413; found: 284.1409.

erythro-2-(Hydroxy-4'-methoxyphenylmethyl)-1-phenylbutan-1-one (syn-5a): IR(neat): $\nu = 3494, 1666 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.79$ (t, $J = 7.81 \text{ Hz}$, 3H), 1.70–2.03 (m, 2H), 3.05 (br, 1H), 3.77 (s, 3H), 3.66–3.83 (m, 1H), 5.03 (dd, $J = 4.40 \text{ Hz}$, 1H), 6.77–6.86 (m, 2H), 7.24–7.60 (m, 5H), 7.84–7.90 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 12.1, 20.7, 54.2, 55.2, 73.5, 113.6, 127.3, 128.3, 128.6, 133.3, 134.2, 137.5, 158.9, 205.2$; MS: $m/z = 284$ (10), 255 (11), 148 (94), 135 (100), 120 (9), 105 (99), 92 (9), 77 (54); HRMS: calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_3$: 284.1413; found: 284.1414.

threo-2-(Hydroxy-4'-methylphenylmethyl)-1-phenylbutan-1-one (anti-5b): IR(neat): $\nu = 3463, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.79$ (t, $J = 7.33 \text{ Hz}$, 3H), 1.41–1.80 (m, 2H), 2.32 (s, 3H), 2.93 (d, $J = 4.88 \text{ Hz}$, 1H), 3.69–3.83 (m, 1H), 4.98 (dd, $J = 4.88$ and 7.33 Hz , 1H), 7.08–7.33 (m, 4H), 7.40–7.60 (m, 3H), 7.90–7.98 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 11.6, 21.1, 23.7, 54.3, 75.6, 126.4, 128.3, 128.6, 129.1, 133.1, 137.5, 138.3, 139.7, 205.6$; MS: $m/z = 268$ (18), 250 (5), 239 (25), 148 (100), 133 (47), 119 (35), 105 (70), 91 (33), 77 (34); HRMS: calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: 268.1463; found: 268.1457.

erythro-2-(Hydroxy-4'-methylphenylmethyl)-1-phenylbutan-1-one (syn-5b): IR(neat): $\nu = 3463, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.79$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.63–2.03 (m, 2H), 2.30 (s, 3H), 3.14 (d, $J = 1.46 \text{ Hz}$, 1H), 3.68–3.81 (m, 1H), 5.06 (dd, $J = 1.46$ and 3.90 Hz , 1H), 7.08–7.32 (m, 4H), 7.40–7.60 (m, 3H), 7.86–7.94 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 12.1, 20.4, 21.1, 54.1, 73.6, 126.1, 128.3, 128.6, 128.9, 133.3, 137.0, 137.4, 139.0, 205.3$; MS: $m/z = 268$ (18), 250 (7), 239 (38), 148 (100), 133 (52), 119 (48), 105 (81), 91 (41), 77 (41); HRMS: calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: 268.1463; found: 268.1464.

threo-2-(Hydroxy-4'-phenylphenylmethyl)-1-phenylbutan-1-one (anti-5c): IR(neat): $\nu = 3475, 1677 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.84$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.50–1.86 (m, 2H), 3.12 (d, $J = 5.37 \text{ Hz}$, 1H), 3.76–3.87 (m, 1H), 5.08 (dd, $J = 7.32$ and 5.37 Hz , 1H), 7.23–7.61 (m, 12H), 7.91–7.98 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 11.6, 23.7, 54.2, 75.4, 126.8, 127.0, 127.2, 127.3, 128.3, 128.6, 128.8, 131.2, 138.2, 140.6, 140.7, 141.8, 205.6$; MS: $m/z = 330$ (4), 301 (7), 182 (100), 148 (69), 133 (27), 120 (7), 105 (75), 90 (5), 77 (36); HRMS: calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_2$: 330.1620; found: 330.1613.

erythro-2-(Hydroxy-4'-phenylphenylmethyl)-1-phenylbutan-1-one (syn-5c): IR(neat): $\nu = 3460, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.81$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.70–2.08 (m, 2H), 3.26 (d, $J = 1.95 \text{ Hz}$, 1H), 3.74–3.83 (m, 1H), 5.14 (dd, $J = 1.95$ and 4.39 Hz , 1H), 7.23–7.61 (m, 12H), 7.88–7.95 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 12.1, 20.5, 54.0, 73.5, 126.6, 126.8, 127.0, 127.2, 128.3, 128.6, 128.7, 133.4, 137.4, 140.3, 140.8, 141.1, 205.3$; MS: $m/z = 330$ (3), 301 (5), 182 (100), 148 (51), 133 (23), 120 (6), 105 (63), 90 (5), 77 (32); HRMS: calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_2$: 330.1620; found: 330.1634.

threo-2-(Hydroxy-4'-chlorophenylmethyl)-1-phenylbutan-1-one (anti-5e): IR(neat): $\nu = 3433, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.83$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.48–1.79 (m, 2H), 3.29 (d, $J = 5.86 \text{ Hz}$, 1H), 3.64–3.79 (m, 1H), 5.00 (dd, $J = 6.35$ and 5.86 Hz , 1H), 7.23–7.36 (m, 4H), 7.40–7.63 (m, 3H), 7.84–7.94 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 11.7, 23.7, 54.1, 74.8, 127.7, 128.2, 128.5, 128.6, 133.4, 137.9, 141.3, 205.5$; MS: $m/z = 288$ (15), 270 (7), 259 (34), 148 (100), 139 (42), 133 (62), 111 (20), 105 (83), 91 (5), 77 (52); HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{ClO}_2$: 288.0917; found: 288.0918.

erythro-2-(Hydroxy-4'-chlorophenylmethyl)-1-phenylbutan-1-one (syn-5e): IR(neat): $\nu = 3433, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$

(CDCl_3 , 270 MHz): $\delta = 0.78$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.63–2.00 (m, 2H), 3.36 (d, $J = 1.95 \text{ Hz}$, 1H), 3.64–3.72 (m, 1H), 5.07 (dd, $J = 4.40$ and 1.95 Hz , 1H), 7.23–7.37 (m, 4H), 7.40–7.63 (m, 3H), 7.86–7.93 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 12.2, 20.4, 53.8, 73.0, 127.6, 128.3, 128.4, 128.8, 133.1, 133.6, 137.2, 140.5, 205.2$; MS: $m/z = 288$ (15), 270 (9), 259 (52), 148 (100), 139 (51), 133 (66), 111 (23), 105 (89), 91 (5), 77 (55); HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{ClO}_2$: 288.0917; found: 288.0916.

threo-2-(Hydroxy-4'-nitrophenylmethyl)-1-phenylbutan-1-one (anti-5f): IR(neat): $\nu = 3433, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.92$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.64–1.89 (m, 2H), 3.69–3.85 (m, 1H), 3.82 (d, $J = 6.84 \text{ Hz}$, 1H), 5.14 (dd, $J = 6.35$ and 6.84 Hz , 1H), 7.38–7.65 (m, 5H), 7.80–7.88 (m, 2H), 8.12–8.20 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 11.8, 23.8, 53.5, 74.3, 123.6, 127.0, 128.2, 128.8, 133.8, 137.3, 147.3, 150.3, 205.2$; MS: $m/z = 299$ (5), 270 (13), 177 (13), 148 (100), 133 (42), 120 (6), 105 (85), 91 (3), 77 (34); HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{ClO}_2$: 299.1157; found: 299.1158.

erythro-2-(Hydroxy-4'-nitrophenylmethyl)-1-phenylbutan-1-one (syn-5f): IR(neat): $\nu = 3437, 1674 \text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 0.77$ (t, $J = 7.32 \text{ Hz}$, 3H), 1.61–2.00 (m, 2H), 3.69 (d, $J = 1.46 \text{ Hz}$, 1H), 3.69–3.84 (m, 1H), 5.21 (dd, $J = 3.42$ and 1.46 Hz , 1H), 7.38–7.69 (m, 5H), 7.78–7.99 (m, 2H), 8.10–8.26 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 67.9 MHz): $\delta = 12.2, 20.3, 53.3, 72.8, 123.5, 127.1, 128.4, 128.9, 133.9, 136.8, 147.2, 149.5, 204.9$; MS: $m/z = 299$ (6), 270 (23), 177 (6), 148 (100), 133 (50), 120 (7), 105 (89), 91 (4), 77 (40); HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{ClO}_2$: 299.1158; found: 299.1155.

CAS Registry Nos.: 1,3-diphenylpropan-1-one (**2a**), [1083-30-3]; 1-phenylbutan-1-one (**2b**), [495-40-9]; 4,4-dimethyl-1-phenylpentan-1-one (**2c**), [37608-93-8]; 4-phenylbutan-2-one (**2d**), [2550-26-7]; 4,4-dimethyl-1-phenylpentan-3-one (**2e**), [5195-24-4]; 2-benzyl-1,3,5-triphenylpentane-1,5-dione (**3a**), [38335-02-3]; 2-(hydroxyphenylmethyl)-1-phenylbutan-1-one (**5d**), [60669-63-8].

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References and Notes

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