Samarium(II) diiodide-mediated intermolecular aldol type reactions of phenacyl bromides with carbonyl compounds

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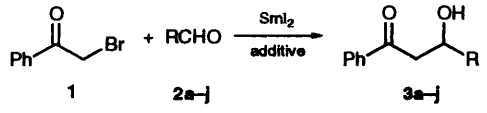
Intermolecular aldol type reactions of phenacyl bromides with various carbonyl compounds mediated by samarium(II) diiodide afford β-hydroxy ketones in moderate to good yields. The addition of *N,N,N',N'*-tetramethylethylenediamine or diethylaluminium chloride resulted in better yields in some reactions.

Samarium(II) diiodide (SmI_2) is an essential reagent in organic synthesis,[1] and many practical reactions using it as a powerful one-electron reducing agent have been developed.[2] It is known that the intermolecular Reformatsky type reaction of α-halogeno ketones with carbonyl compounds is a method for the preparation of β-hydroxy ketones.[3] For example, the cross-aldol reaction, which is based on the generation of an aluminium enolate by the coupling of Et_2AlCl and metallic zinc, was reported by Nozaki and co-workers.[4] This group also developed the $Bu_3SnAlEt_2$- or $Bu_3PbAlEt_2$-mediated Reformatsky type reactions of α-halogeno ketones or α-halogeno esters with carbonyl compounds.[5] Reaction of metallic tin with α-halogeno ketones gave the tin(II) enolates, which when treated with carbonyl compounds gave β-hydroxy ketones in good yields.[6] The stereoselective cross-aldol type condensation in aqueous media was reported to be promoted by metallic zinc or tin.[7] A hexabutyldistannane-promoted Reformatsky type reaction of α-iodo ketones with aldehydes was described by Shibata *et al.*[8] Kagan *et al.* reported the SmI_2-mediated intermolecular aldol type reactions of α-halogeno esters with cyclohexanone.[1] Although the intramolecular coupling of α-halogeno ketones with carbonyl compounds has been reported,[9] little is known about the intermolecular SmI_2-mediated Reformatsky type reaction of these compounds, with the exception of the intermolecular coupling between α-halogeno ketones and aldehydes with electron-withdrawing groups to give α,β-enones in good yields.[10] Interestingly, it was stated that the corresponding aldols could not be obtained.[10]

In this paper, we report the SmI_2-mediated intermolecular aldol type reaction between phenacyl bromides and carbonyl compounds in the presence of suitable additives, such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and diethylaluminium chloride (Et_2AlCl).

First, the reaction of phenacyl bromide **1** with benzaldehyde **2a** was examined under a variety of conditions (see entries 1–8 in Table 1 and Scheme 1). Under the conditions of entry 7 in Table 1, the corresponding aldol **3a** was obtained in an acceptable yield but no α,β-enones were obtained. These results are in contrast to those of Zhang.[10]



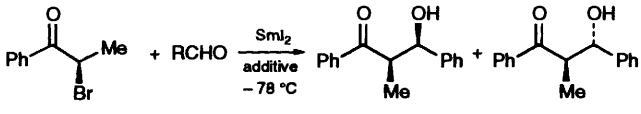
1 **2a–j** **3a–j**

a	R = Ph	**f**	R = 3-$MeOC_6H_4$
b	R = 2-ClC_6H_4	**g**	R = 4-$MeOC_6H_4$
c	R = 4-ClC_6H_4	**h**	R = 4-$O_2NC_6H_4$
d	R = 4-HOC_6H_4	**i**	R = *c*-C_6H_{11}
e	R = 2-$MeOC_6H_4$	**j**	R = $[CH_2]_6Me$

Scheme 1

We then allowed the phenacyl bromide **1** to react with the aldehydes **2b–j**, the results for which reactions are shown in entries 9–28 (Table 1). Although in the reactions of the *ortho*-substituted benzaldehydes with phenacyl bromide **1**, addition of Et_2AlCl had no effect with *meta*- and *para*-substituted benzaldehydes it improved the product yields slightly (entries 9–24, Table 1). It is noteworthy that not only could the benzaldehyde **2d** having a phenolic hydroxy group be used in this reaction (entries 15 and 16, Table 1), but aldehydes such as cyclohexanecarbaldehyde **2i** and octanal **2j** reacted with phenacyl bromide **1** in a satisfactory manner (entries 25–28, Table 1).

The SmI_2-mediated aldol type reaction of 2-bromo-1-phenylpropanone **4** with benzaldehyde **2a** proceeded smoothly to give the β-hydroxy ketones **5**[12] in good yields with moderate stereoselectivity (Scheme 2 and Table 2).



4 **2a** **5a** **5b**

Scheme 2

Next, we allowed acetophenone **6** and octan-2-one **7** to react with phenacyl bromide **1** under a variety of conditions (Table 3). Although the presence of TMEDA or Et_2AlCl were essential to initiate the coupling, no reaction occurring in their absence, other Lewis acids were ineffective. The correlation of the amount of Lewis acid and the yield of compound **9**[13] in the reactions of octan-2-one **7** with phenacyl bromide **1** is shown in Table 4. The addition of 2 equiv. Et_2AlCl to a carbonyl substrate was found to be optimal.

6 R = Ph
7 R = $[CH_2]_5Me$

8 R = Ph
9 R = $[CH_2]_5Me$

The reaction of 2-bromo-1-phenylpropanone **4** with octan-2-one **7** gave a mixture of diastereoisomers **10** (Table 5) in the presence of Et_2AlCl.

Table 1 SmI_2-mediated aldol type reactions of phenacyl bromide **1** with aldehydes **2a–j**

Entry	Aldehyde	Method[a]	Temp. (°C)	Additive[b]	Product (yield %)[c]
1	**2a**	A	0	—	**3a**[11] (31)
2	**2a**	A	0	HMPA	**3a**[11] (51)
3	**2a**	A	r.t.	—	complex mixture
4	**2a**	B	0	—	**3a**[11] (55)
5	**2a**	B	−78	—	**3a**[11] (69)
6	**2a**	B	0	TMEDA	complex mixture
7	**2a**	B	−78	Et_2AlCl	**3a**[11] (75)
8	**2a**	B	−78	Et_2AlCl	**3a**[11] (57)
9	**2b**	B	0	—	**3b** (89)
10	**2b**	B	−78	—	**3b** (85)
11	**2b**	B	0	Et_2AlCl	**3b** (52)
12	**2b**	B	−78	Et_2AlCl	**3b** (58)
13	**2c**	B	−78	—	**3c**[12] (46)
14	**2c**	B	−78	Et_2AlCl	**3c**[12] (54)
15	**2d**	B	−78	—	**3d** (62)
16	**2d**	B	−78	Et_2AlCl[d]	**3d** (80)
17	**2e**	B	−78	—	**3e** (66)
18	**2e**	B	−78	Et_2AlCl	**3e** (60)
19	**2f**	B	−78	—	**3f** (61)
20	**2f**	B	−78	Et_2AlCl	**3f** (70)
21	**2g**	B	−78	—	**3g**[12] (77)
22	**2g**	B	−78	Et_2AlCl	**3g**[12] (77)
23	**2h**	B	−78	—	**3h**[13] (58)
24	**2h**	B	−78	Et_2AlCl	**3h**[13] (38)
25	**2i**	B	−78	—	**3i**[14] (82)
26	**2i**	B	−78	Et_2AlCl	**3i**[14] (64)
27	**2j**	B	−78	—	**3j**[15] (50)
28	**2j**	B	−78	Et_2AlCl	**3j**[15] (84)

[a] Method A (Grignard type addition), Method B (Barbier type addition); see Experimental section. [b] HMPA = hexamethylphosphoramide; TMEDA = *N,N,N',N'*-tetramethylethylenediamine. [c] Isolated yields. [d] Ratio Et_2AlCl:aldehyde = 4:1.

Table 2 Reactions of 2-bromo-1-phenylpropanone **4** with benzaldehyde **2a**[a]

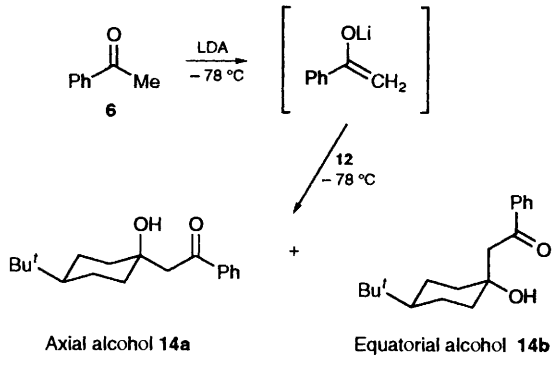
Entry	Additive	Ratio of diastereoisomers[b] **5a** (2*R*,3*S*) : **5b** (2*R*,3*R*)		Total yield (%)[c] of **5**[17]
1	—	23	77	69
2	TMEDA	33	67	60
3	Et_2AlCl	28	72	81
4	MAD[d]	46	54	98

[a] Method B was used. [b] The product ratio was determined by ^1H NMR. [c] Isolated yields. [d] MAD = methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide).[16]

Further, the reactions of cyclic ketones **11** and **12** with phenacyl bromide **1** were examined (Table 6). When 4-*tert*-butylcyclohexanone **12** was used in this reaction, the corresponding axial and equatorial alcohols **14a** and **14b**, were obtained in good yields. Interestingly, the opposite stereoselectivity was observed on changing the additive (entries 4 and 5, Table 6). Thus, the Reformatsky type reactions gave predominantly the axial alcohol in the presence of TMEDA, but the equatorial alcohol in the presence of Et_2AlCl. The relative configurations of the alcohols were established by an alternative synthesis (Scheme 3).

Finally, the structure of the axial alcohol **14a** was proven by X-ray crystallography.† The ORTEP representation of this compound is shown in Fig. 1.

† Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For full details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.



Scheme 3

In conclusion, in the presence of suitable additives, the SmI_2-mediated aldol type reactions between phenacyl bromides and carbonyl compounds proceeded to give the corresponding aldols in good yields. Although, in general, treatment of benzaldehyde derivatives with SmI_2 gives the corresponding pinacol coupling products, this did not occur in our work. Further work is in progress regarding the limitations of these reactions.

Experimental

Melting points were obtained on a Yamagimoto melting point apparatus (Yamagimoto Co., Ltd) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Gemini-300 spectrometer as solutions in $CDCl_3$. Medium-pressure column chromatography was conducted using a UVILOG 5III spectrophotometer as UV detector (Oyo Bunko Kiki Co., Ltd, Tokyo) and Kieselgel 60 (Merck AG, Darmstadt) as the packing material. Other

Table 3 Reaction of phenacyl bromide **1** with acetophenone **6** or octan-2-one **7** using SmI_2

Entry	Ketone	Method	Additive	Temp. (°C)	Product (yield %)[a]
1	**6**	A	—	0	N.R.
2	**6**	B	—	0	N.R.
3	**6**	B	HMPA	r.t.	complex mixture
4	**6**	B	TMEDA	0	N.R.
5	**6**	B	Et_2AlCl	0	N.R.
6	**6**	B	ZnCl	0	**8**[12] (21)
7	**6**	B	$TiCl_4$	0	trace
8	**6**	A	Et_2AlCl	0	trace
9	**6**	B	Et_2AlCl	−78 then 0	**8**[12] (50)
10	**7**	B	—	−78 then 0	**9** (12)[b]
11	**7**	B	$EtAlCl_2$	−78 then 0	N.R.
12	**7**	B	Et_2AlCl	−78 then 0	**9** (73)

[a] Isolated yields; N.R. = no reaction. [b] The yield was estimated by HPLC.

Table 4 Effect of the amount of Et_2AlCl on the yield of **9**[a]

Entry	Amount of Et_2AlCl[b]	Yield of **9**[c]
1	0	12
2	0.2	26
3	0.5	30
4	1.0	34
5	2.0	73
6	4.0	70

[a] Method B was employed. [b] Equiv., relative to ketone. [c] The yields were determined by HPLC.

Table 5 Reaction of octan-2-one **7** with 2-bromo-1-phenylpropanone **4**[a]

Entry	Additive	Temp. (°C)	Total yield (%) of **10**[b,c]
1	—	−78 then 0	69 (1:1.1)
2	Et_2AlCl	−78 then 0	81 (1:1.1)

[a] Method B was used. [b] Isolated yields. [c] The product ratio was determined by ^1H NMR.

Table 6 Reactions of cyclic ketones **11** and **12** with phenacyl bromide **1**[a]

Entry	Cyclic ketone	Additive	Product (yield %)
1	**11**	—	**13**[4] (47)
2	**11**	TMEDA	**13**[4] (94)
3	**12**	—	unseparable mixture
4	**12**	TMEDA	**14** (85) (axial:equatorial = 96:4)[b]
5	**12**	Et_2AlCl	**14** (98) (axial:equatorial = 29:71)[b]

[a] Method B was employed. [b] The ratio was determined on basis of isolated yields.

spectral data were obtained using the following instruments. IR: Japan Spectroscopic Co., A-100 spectrometer; MS: Hitachi M-80b spectrometer (Hitachi Co., Ltd) or VG Auto Spec (Fisons Co., Ltd); High-resolution MS: VG Auto Spec (Fisons Co., Ltd); X-ray structure determination: Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation.

Reactions of phenacyl bromides with carbonyl compounds in the presence of SmI_2

Method A, Grignard type method. Under an argon atmosphere, a solution of SmI_2 in THF (0.1 mol dm^{-3}; 10.5 cm^3, 1.05 mmol) was added to a solution of an α-halogeno ketone (0.5 mmol) in THF (5 cm^3) at the temperature shown in the tables. A suitable additive was added before the addition of SmI_2, if necessary. After the reaction mixture had been stirred for 10 min, a solution of a carbonyl compound (0.5 mmol) in THF (5 cm^3) was added dropwise and the resulting solution was stirred for 1 h at the specified temperature, 10% HCl was added to the resulting solution, which was then diluted with Et_2O (20 cm^3). The organic layer was separated and subsequently washed with sat. aqueous NaCl (15 cm^3), 8% aqueous $Na_2S_2O_3$ (15 cm^3) and sat. aqueous NaCl (15 cm^3). The organic phase was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to give a residue, which was purified with PTLC (preparative thin layer chromatography) or MPLC (medium pressure liquid chromatography) to afford the pure β-hydroxy ketone.

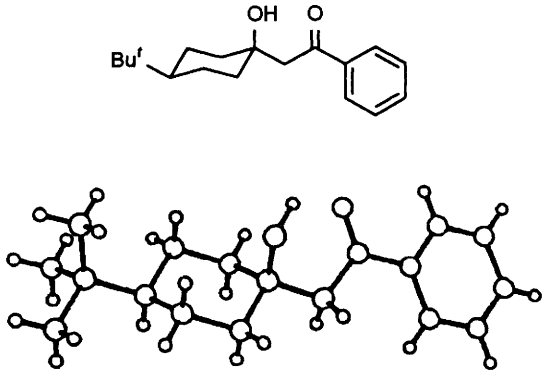


Fig. 1 ORTEP representation of compound **14a**

Method B, Barbier type method. Under an argon atmosphere, a solution of SmI_2 in THF (0.1 mol dm^{-3}; 10.5 cm^3, 1.05 mmol) was added to a solution of an α-halogeno ketone (0.5 mmol) in THF (10 cm^3) and a carbonyl compound (0.5 mmol) at the temperature shown in the tables. A suitable additive was added before the addition of SmI_2, if necessary. After the reaction mixture had been stirred for 1 h at the specified temperature, 10% HCl was added to the resulting solution, which was then diluted with Et_2O (20 cm^3). The organic layer was separated and subsequently washed with sat. aqueous NaCl (15 cm^3), 8% aqueous $Na_2S_2O_3$ (15 cm^3) and sat. aqueous NaCl (15 cm^3). The organic phase was dried (Na_2SO_4) and evaporated under reduced pressure to give a residue, which was purified with PTLC or MPLC to afford the pure β-hydroxy ketone.

3-(*o*-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one 3b. Colourless crystals, mp 80–81 °C (hexane–CH_2Cl_2) (Found: C, 69.0; H, 5.0. $C_{15}H_{13}O_2Cl$ requires C, 69.10; H, 5.03%); ν_{max}/cm^{-1} 3540 (OH) and 1660 (C=O); δ_H(300 MHz; $CDCl_3$) 3.16 (1 H, dd, *J* 18 and 9.5), 3.58 (1 H, dd, *J* 18 and 2), 3.85 (1 H, d, *J* 2.8), 5.70 (1 H, d, *J* 9.5), 7.25 (1 H, m), 7.35 (2 H,

m), 7.48 (2 H, m), 7.61 (1 H, m), 7.73 (1 H, d, *J* 8) and 7.97 (2 H, dd, *J* 8 and 1); δ_C(75 MHz; $CDCl_3$) 46.93, 68.43, 99.66, 112.66, 128.85, 129.79, 130.18, 130.32, 130.93, 135.34, 138.00, 141.89 and 201.94; *m/z* 260 (M^+).

3-Hydroxy-3-(*p*-hydroxyphenyl)-1-phenylpropan-1-one 3d. Colourless needles, mp 119–120 °C (Pr^i_2O) (Found: C, 74.3; H, 5.85. $C_{15}H_{14}O_3$ requires C, 74.36; H, 5.83%); ν_{max}/cm^{-1} 3375 (OH) and 1670 (C=O); δ_H(300 MHz; $CDCl_3$) 3.37 (2 H, d, *J* 6), 3.62 (1 H, br s), 5.22 (1 H, br s), 5.29 (1 H, t, *J* 6), 6.82 (2 H, d, *J* 9), 7.31 (2 H, d, *J* 9), 7.50 (2 H, m), 7.60 (1 H, m) and 7.97 (2 H, d, *J* 8); δ_C(75 MHz; $CDCl_3$) 48.74, 71.43, 117.03, 128.89, 129.77, 130.31, 135.30, 136.47, 138.11, 156.88 and 202.04; *m/z* 260 (M^+), 224 ($M^+ - H_2O$).

3-Hydroxy-3-(*o*-methoxyphenyl)-1-phenylpropan-1-one 3e. Colourless viscous oil (Found: C, 75.15; H, 6.4. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.38%); ν_{max}/cm^{-1} 3500 (OH) and 1680 (C=O); δ_H(300 MHz; $CDCl_3$) 3.26 (1 H, dd, *J* 17 and 9), 3.53 (1 H, dd, *J* 17 and 4), 3.67 (1 H, d, *J* 4), 3.86 (3 H, s), 5.62 (1 H, dt, *J* 9 and 4), 6.91 (1 H, d, *J* 8), 7.03 (1 H, m), 7.29 (1 H, m), 7.47 (2 H, m), 7.58 (2 H, m) and 7.98 (2 H, d, *J* 7); δ_C(75 MHz; $CDCl_3$) 45.71, 55.17, 65.47, 110.10, 120.77, 126.38, 128.09, 128.24, 128.51, 131.05, 133.31, 136.66, 155.60 and 200.42; *m/z* 256 (M^+).

3-Hydroxy-3-(*m*-methoxyphenyl)-1-phenylpropan-1-one 3f. Colourless viscous oil (Found: C, 75.25; H, 6.3. $C_{16}H_{16}O_3$ requires C, 74.98; H, 6.29%); ν_{max}/cm^{-1} 3500 (OH) and 1680 (C=O); δ_H(300 MHz; $CDCl_3$) 3.37 (2 H, d, *J* 6), 3.55 (1 H, d, *J* 3), 3.83 (3 H, s), 5.33 (1 H, dt, *J* 6 and 3), 6.84 (1 H, m), 7.00 (2 H, m), 7.29 (2 H, t, *J* 7.8), 7.47 (2 H, t, *J* 7.5), 7.59 (1 H, m) and 7.96 (1 H, d, *J* 8); δ_C(75 MHz; $CDCl_3$) 48.99, 56.86, 71.53, 112.78, 114.82, 119.57, 120.75, 130.30, 131.20, 135.26, 138.12, 146.22, 161.43 and 201.76; *m/z* 256 (M^+).

3-Hydroxy-3-methyl-1-phenylnonan-1-one 9. Colourless oil (Found: M, 230.167 313. $C_{16}H_{24}O_2$ requires *M*, 230.167 066); ν_{max}/cm^{-1} 3520 (OH) and 1680 (C=O); δ_H(300 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7), 1.63–1.25 (13 H, m), 3.11 (1 H, d, *J* 15), 3.17 (1 H, d, *J* 15), 4.11 (1 H, s), 7.48 (2 H, m), 7.57 (1 H, t, *J* 7) and 7.95 (2 H, d, *J* 8); δ_C(75 MHz; $CDCl_3$) 15.66, 24.17, 29.18, 30.57, 31.11, 33.26, 43.14, 122.05, 129.75, 130.00, 133.81 and 162.24; *m/z* 230 ($M^+ - H_2O$).

3-Hydroxy-2,3-dimethyl-1-phenylnonan-1-one 10. Colourless oil (Found: M – H_2O, 244.184 542. $C_{17}H_{26}O_2 - H_2O$ requires *M* – H_2O, 244.182 716); ν_{max}/cm^{-1} 3500 (OH) and 1670 (C=O); δ_H(300 MHz; $CDCl_3$) 0.81 (1.5 H, t, *J* 7), 0.90 (1.5 H, t, *J* 7), 1.21 (16 H, m), 3.56 (1 H, m), 3.80 (0.5 H, s), 3.99 (0.5 H, s), 7.50 (3 H, m) and 7.61 (2 H, t, *J* 7); δ_C(75 MHz; $CDCl_3$) 14.36, 14.80, 15.58, 15.68, 24.06, 24.22, 25.23, 25.27, 25.83, 27.89, 31.29, 31.49, 33.23, 33.42, 41.03, 43.83, 47.49, 47.77, 75.08, 75.65, 129.88, 129.91, 130.38, 135.13, 135.18, 138.42, 138.45, 209.22 and 209.29; *m/z* 244 ($M^+ - H_2O$).

2-(*cis*-4-*tert*-Butyl-1-hydroxycyclohexyl)-1-phenylethan-1-one 14a. Colourless crystals, mp 125–127 °C (Found: C, 78.8; H, 9.65. $C_{18}H_{26}O_2$ requires C, 78.79; H, 9.55%); ν_{max}/cm^{-1} 3540 (OH) and 1670 (C=O); δ_H(300 MHz; $CDCl_3$) 0.88 (9 H, s), 1.26 (1 H, m), 1.26–1.61 (6 H, m), 1.94 (2 H, m), 3.08 (2 H, s), 3.78 (1 H, br s), 7.48 (2 H, m), 7.59 (1 H, m) and 7.95 (2 H, d, *J* 8); δ_C(75 MHz; $CDCl_3$) 23.77, 29.19, 34.04, 39.64, 49.55, 50.82, 71.83, 129.68, 130.24, 135.09, 139.06 and 203.38; *m/z* 274 (M^+).

2-(*trans*-4-*tert*-Butyl-1-hydroxycyclohexyl)-1-phenylethan-1-one 14b. Colourless crystals, mp 67–68 °C (Found: C, 78.8; H, 9.6. $C_{18}H_{26}O_2$ requires C, 78.79; H, 9.55%); ν_{max}/cm^{-1} 3525 (OH) and 1670 (C=O); δ_H(300 MHz; $CDCl_3$) 0.86 (9 H, s), 1.07 (3 H, m), 1.52 (2 H, m), 1.72 (2 H, m), 1.97 (2 H, m), 3.22 (2 H, s), 4.73 (1 H, br s), 7.49 (2 H, m), 7.60 (1 H, m) and 7.97 (2 H, d, *J* 8); δ_C(75 MHz; $CDCl_3$) 26.07, 29.18, 33.83, 40.14, 44.07, 49.01, 73.38, 129.65, 130.32, 135.20, 139.10 and 203.56; *m/z* 256 ($M^+ - H_2O$).

Reaction of acetophenone 6 with 4-*tert*-butylcyclohexanone 12

To a THF solution (5 cm^3) of LDA, prepared from 1.6 mol dm^{-3} BuLi (0.68 cm^3, 1.1 mmol) and diisopropylamine (0.14 cm^3, 1 mmol) at −78 °C, acetophenone **6** (0.12 g, 1 mmol) in dry THF (5 cm^3) was added dropwise. The resulting solution was stirred at −78 °C for 20 min. To this solution, 4-*tert*-butylcyclohexanone **12** (0.15 g, 1 mmol) in dry THF (5 cm^3) was added and the mixture was stirred at this temperature for 2 h. After the solution had been diluted with Et_2O (20 cm^3), sat. aqueous NH_4Cl (10 cm^3) was added. The aqueous phase was extracted with Et_2O (20 cm^3 × 2). The combined organic layers were washed with sat. aqueous NaCl (20 cm^3 × 3), dried (Na_2SO_4) and evaporated under reduced pressure to afford a crude oil, which was purified with PTLC to afford the corresponding coupling products **14a**, **b** (0.11 g, 42%) (ratio **14a**:**14b** = 77:23).

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