Cross-coupling reaction of alcohols for carbon–carbon bond formation using pincer-type NHC/palladium catalysts†

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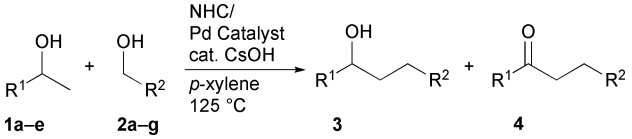
A cross-coupling reaction of different alcohols was achieved using a pincer-type NHC/PdBr complex as the catalyst precursor, and the reaction, under either Ar or H_2 gas, displayed a broad substrate scope with respect to both primary and secondary alcohol components, with high alcohol product selectivity.

Introduction

In an effort to minimize salt waste by-products in the field of carbon–carbon bond-forming reactions, transition metal-catalyzed direct coupling between two different alcohols was recently reconsidered.[1] The homo-coupling of primary alcohols, where two different carbon atoms are coupled, was first recognized as the Guerbet reaction, which was discovered around 1900[2] using heterogeneous transition metal catalysts at a high pressure/temperature (~220 °C) in the presence of excess alkali metal hydroxides or alkoxides. A stepwise process, involving a dehydrogenation/aldol condensation/hydrogenation sequence, was proposed. Thus far, the most frequently used metal sources are Ir[3,4,5] or Ru,[6,7,8] which showed a high reactivity with subtle modification from original conditions; however, the reaction frequently utilized a stoichiometric amount of alkaline metal base (1–3 equiv. with respect to one of the two alcohols), with some exceptions.[3] In contrast, heterogeneous[9,10,11] and homogeneous[10,11] Pd complexes were tested earlier and more recently, but showed scant catalytic activity or were limited to a special case, such as those in which MeOH, *n*-PrOH and *n*-BuOH were coupled using 1 equiv. of base at a high temperature (200 °C)[10,11] and pressure (30 atm).[11] Recently, heterogeneous Pd/AlO(OH) catalysts,[12] Pd-NP (nanoparticles)/viologen[13] and Ni-NPs[14] were examined for ketone–alcohol coupling, allowing ketones to become major products. Here, the carbonyl functionality remained intact and thus the corresponding secondary alcohols were rarely produced. Even though a PdH species was supposedly generated during the dehydrogenation from alcohols, the reduction of ketone carbonyls was highly unlikely owing to the relative inertness of the PdH species towards the C=O double bonds.[15] The Ag/Al_2O_3 system was very recently highlighted in the selective synthesis of the corresponding ketones, but not the alcohols, by alcohol–alcohol coupling.[16] We report here that pincer-type *N*-heterocyclic carbene (NHC)/Pd complexes[17,18] are effective catalyst precursors in the presence of alkaline metal base for the selective formation of alcohols within a range of alcohol–alcohol coupling reactions (Scheme 1).



1b: R^1= -C_6H_5; **2a**: R^2 = C_6H_5; **2b**: R^2 = *p*-MeO(C_6H_4)-
1c: R^1 = *p*-MeO(C_6H_4)- **2c**: R^2 = *p*-Me(C_6H_4)-; **2d**: R^2 = 2-furfuryl
1d: R^1 = -$(CH_2)_2(C_6H_5)$ **2e**: R^2 = thiophenyl; **2f**: R^2 = -$(CH_2)_2$Me
1e: R^1 = -C_6H_{11} **2g**: R^2 = -$(CH_2)_6$Me

Scheme 1 General: NHC/Pd-catalyzed cross-coupling of alcohols.

Results and discussion

We first chose secondary alcohol **1a** as a model substrate, since a considerable amount of ketone **4aa** was generated as a side product using Ir[4] or Ru[6] complexes. Treatment of secondary (2°) alcohol **1a** (2 mmol) with primary (1°) alcohol **2a** (1 mmol) in *p*-xylene (1 mL) at 125 °C for 12 h in the presence of $Pd_2(dba)_3$ (1 mol%), ligand precursor **5a** (2 mol%) and CsOH (40 mol%), afforded, after the mixture was purified by column chromatography on silica gel, coupling product alcohol **3aa** in an isolated yield of 47% (Table 1, entry 2). Formation of ketone **4aa** was undetected (<1%) by ^{1}H NMR analysis. Scant reactivity was observed (entry 1) when either one of these three species, $Pd_2(dba)_3$, **5a**, or the base, was lacking. The **1a** : **2a** ratio of 2 : 1 proved to be the best mixing ratio, as the 1 : 1 ratio gave the product in a lower yield (76%) and selectivity (entry 7). The NHC/PdBr complex **7**[18] was also synthesized in a separate experiment, and it was examined whether this species is the most responsible for the catalytic cycle (entry 3). As expected, the reaction completed under otherwise identical conditions to give product **3aa** in near quantitative yield in the presence of not more than 4 mol% of **7** (entry 4). In this case, homo-coupling of **1a** was not detected. Doubling the molar amount of **7** (or $Pd_2(dba)_3$ and **5a**) from 2 to 4 mol% ensured the best smooth conversion (entries 3 and 4; entries 2 and 7). Other alkaline metal hydroxides were totally unsatisfactory to give ketone **4aa** as the major product (entries 8–10). The solvent screening with $Pd_2(dba)_3$ (2 mol%)/**5a** (4 mol%) (an initial concentration of Pd: 0.04 M; 125 °C, 24 h) suggested that polar solvents including DMSO, DMF and 1,4-dioxane were not promising (**3aa**: 0–20%). When we used ligand

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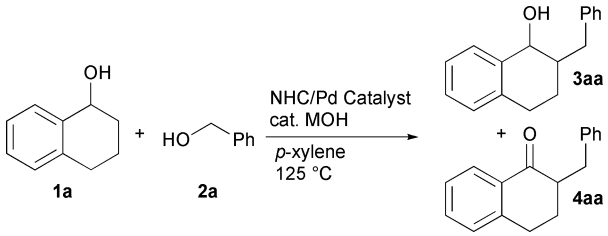
† Electronic supplementary information (ESI) available: General experimental information, synthetic procedure for NHC precursors and spectral data of new and known compounds. See DOI: 10.1039/b914618k

Table 1 NHC/Pd complex-catalyzed coupling between secondary (2°) alcohol **1a** and primary (1°) alcohol **2a** (2 : 1 ratio) to give **3aa** + **4aa**[a]



Entry	Catalyst precursors (mol%)	Base (MOH) (mol%)[b]	Yield (%)[c]	**3aa** : **4aa**[d]
1	$Pd_2(dba)_3$ (1)	CsOH (40)	7	99 : 1
2	$Pd_2(dba)_3$ (1), **5a** (2)	CsOH (40)	47	99 : 1
3	**7** (2)	CsOH (40)	47	99 : 1
4	**7** (4)	CsOH (40)	97	18 : 1
5	$Pd_2(dba)_3$ (1.5), **5a** (3)	CsOH (40)	78	38 : 1
6	$Pd_2(dba)_3$ (2), **5a** (4)	CsOH (20)	80	1.8 : 1
7	$Pd_2(dba)_3$ (2), **5a** (4)	CsOH (40)	99 (76)[e]	13 : 1 (2.5 : 1)[e]
8	$Pd_2(dba)_3$ (2), **5a** (4)	KOH (40)	87	0.67 : 1
9	$Pd_2(dba)_3$ (2), **5a** (4)	NaOH (40)	79	0.65 : 1
10	$Pd_2(dba)_3$ (2), **5a** (4)	LiOH (40)	68	0.28 : 1
11	$Pd_2(dba)_3$ (2), **5b** (4)	CsOH (40)	97	5.5 : 1
12	$Pd_2(dba)_3$ (2), **5c** (4)	CsOH (40)	89	4.6 : 1
13	$Pd_2(dba)_3$ (2), **5d** (4)	CsOH (40)	99	4.5 : 1

[a] $Pd_2(dba)_3$: ligand precursor : 2° alcohol **1a** : 1° alcohol **2a** = 0.01–0.02 : 0.02–0.04 : 2 : 1. Conditions: 125 °C, 12 h in anhydrous *p*-xylene under argon (initial concentration of Pd: 0.02–0.04 M). Diastereoselectivity was consistently *ca.* 1 : 1. [b] With respect to **2a**. [c] Of isolated, purified products based on the conversion (%) of **2a**. [d] Determined by ^{1}H NMR. [e] 1 equiv. of **1a** was used.

5b in place of **5a**, the reaction was less selective, suggesting that it could be controlled by precise adjustment of electronic and steric environments around inner and outer spheres of the Pd center. Other NHC precursors **5c** or **5d** additionally tested so far also did not improve the productivity but lowered the selectivity (**3aa** : **4aa** = 4.5 : 1–5.5 : 1) (entries 11–13).

Although NHC/PdBr complex **7** (Fig. 1) was able to be synthesized according to literature procedure,[18] for a practical reason we utilized the general procedure for further screening, in which $Pd_2(dba)_3$ and NHC precursor **5a** were mixed just before running the coupling reaction. Subsequently, the substrate scope was investigated under optimal conditions ($Pd_2(dba)_3$ (2.5 mol%); **5a** (5 mol%) in *p*-xylene; 125 °C for 12–24 h).

Table 2 summarizes representative examples of cross-coupling between 1° and 2° alcohols. The combinations of benzylic alcohol derivatives were well suited for this general procedure (entries 1–3), and the product alcohols were produced selectively and in good to excellent yields in many cases. Although alcohols were consistently the major products, a substantial amount of ketone was generated in some cases. For instance, when we used aliphatic alcohols as 1° alcohol counterparts (entries 7–12), selectivities and/or conversions were rather lower under argon atmosphere (entries 4, 8, 11, 13 and 16); in sharp contrast, under H_2 gas (1 atm), productivities and/or selectivities were reasonably increased (entries 5, 9, 12, 14 and 17). In some cases, the use of NHC precursor **6** was better suited for reactivity (entries 8, 11, 15 and 16), and the combination with KO*t*-Bu was more favorable (entries 15–17). In the other cases, conversion of 1° alcohols was satisfactory using NaOH in place of CsOH (entries 7 and 8, and

Table 2 NHC/Pd complex-catalyzed cross-coupling reaction of secondary (2°) and primary (1°) alcohols **1** and **2** (2 : 1 ratio)[a]

Entry	2° Alcohol **1**	1° Alcohol **2**	Base	Main product	Yield (%) (**3** : **4**)[b]
1	**1b**	**2a**	CsOH	**3ba**	97 (48 : 1)
2	**1b**	**2b**	CsOH	**3bb**	99 (21 : 1)
3	**1b**	**2c**	CsOH	**3bc**	99 (24 : 1)
4	**1b**	**2d**	CsOH	**3bd**	55 (4.0 : 1)
5	**1b**	**2d**	CsOH	**3bd**	82 (15 : 1)[d]
6	**1b**	**2e**	NaOH	**3be**	26 (>99 : 1)
7	**1b**	**2f**	CsOH	**3bf**	26 (3.3 : 1)
8	**1b**	**2f**	NaOH	**3bf**	78 (3.3 : 1)[c]
9	**1b**	**2f**	NaOH	**3bf**	92 (9.2 : 1)[c,d]
10	**1b**	**2g**	CsOH	**3bg**	50 (6.0 : 1)
11	**1b**	**2g**	NaOH	**3bg**	78 (3.3 : 1)[c]
12	**1b**	**2g**	NaOH	**3bg**	99 (9.0 : 1)[c,d]
13	**1c**	**2a**	CsOH	**3ca**	94 (3.6 : 1)
14	**1c**	**2a**	CsOH	**3ca**	95 (4.3 : 1)[d]
15	**1d**	**2a**	KO*t*-Bu	**3da**	50 (>99 : 1)[c]
16	**1e**	**2a**	KO*t*-Bu	**3ea**	73 (1.6 : 1)[c]
17	**1e**	**2a**	KO*t*-Bu	**3ea**	81 (2.7 : 1)[c,d]

[a] $Pd_2(dba)_3$: **5a** : base : **1** : **2** = 0.025 : 0.05 : 0.4 : 2 : 1. Conditions: 125 °C, 12–24 h in anhydrous *p*-xylene under argon (initial concentration of Pd: 0.05 M). [b] Of isolated, purified products **3** and **4** (Fig. 2 and 3) based on the conversion (%) of **2**. The ratio **3** and **4** was determined by ^{1}H NMR. [c] 5 mol% of **6** was used instead of **5a**. [d] Reactions were performed under 1 atm pressure of H_2.

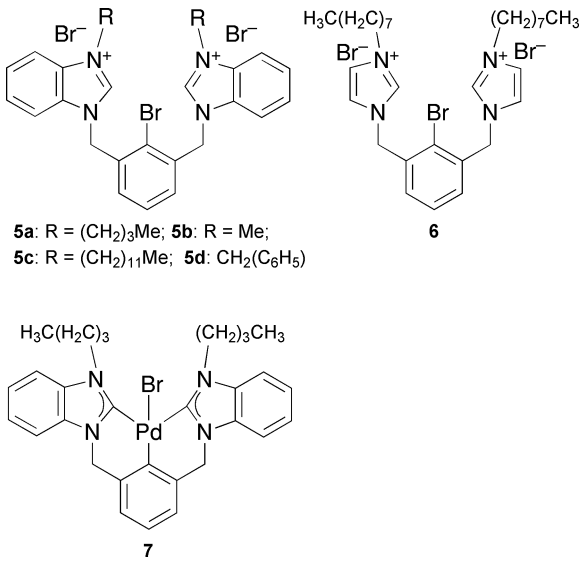


Fig. 1 NHC precursors **5a–d** and **6**; NHC/PdBr complex **7**.

10 and 11), so that the reactivity and selectivity strongly depended on structure of substrates, as well as NHC ligands and alkaline metals.

Coupling between 2° alcohols was also successful without purging H_2 (1 atm), which is one of the advantages overriding other methods previously reported.[1,3–12] Thus, optically pure (*S*)-**1b** (>98% ee) was utilized to see whether the present catalysis is supportive of the conventional mechanistic model (Scheme 2). We identified little preservation of chirality in **8**, so that a main process supported the redox/acid–base cooperative mechanism (Fig. 4), although other pathways could not be fully ruled out.

Based on this working hypothesis, several issues were to be addressed in the present coupling, which consisted of two different

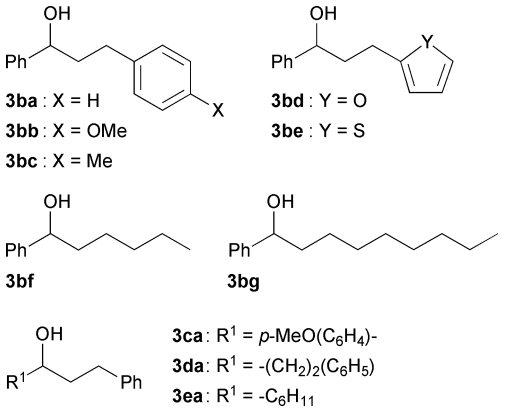


Fig. 2 A series of product alcohols **3**.

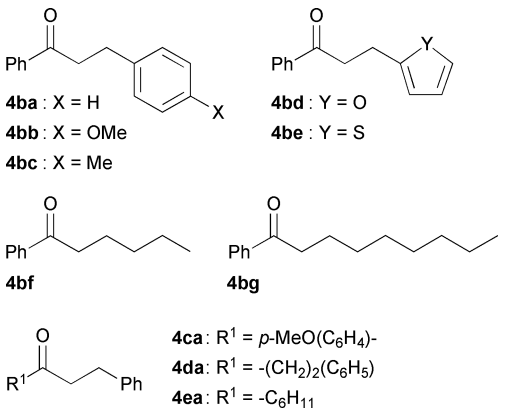
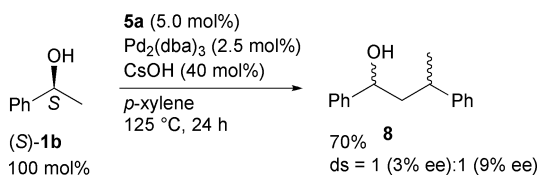


Fig. 3 A series of product ketones **4**.



Scheme 2 Coupling reaction between 2° alcohols. The yield of **8** was calculated based on the conversion (%) of (*S*)-**1b**.

hydrogen sources: one is a 1° alcohol and the other is a 2° alcohol. Why were 2 molar amounts of 2° over 1° alcohols required to ensure high yields of product alcohols as well as high alcohol selectivity in products? Why were C=O bonds reduced in the catalysis, likely by involving the PdH species? To get further insight into these mechanistic aspects, we carried out a set of experiments separately. The results are summarized in eqn (1)–(4), from which several characteristic features are discussed. (i) The mechanistic scenario shown in Fig. 4 was further supported, since a coupling to give alcohol **3ba** proceeded whether the ketone and aldehyde, or the corresponding 2° and 1° alcohols, were used as starting materials (eqn (1) and (2)); (ii) not only 2° alcohol **1b**, but also 1° alcohol **2a** can promote the reduction of C=C bonds of *trans*-chalcone (**9**), in which both L_nPd–OCHR(Ph)- and L_nPdH-like species may have chance to participate (eqn (3) and (4)). The former Pd-alkoxide, while might being in an equilibrium with L_nPdH-like species, probably was involved in the Meerwein–Ponndorf–Verley (MPV)-type reduction; (iii) in contrast, 2° alcohol **1b** seems to be the only species that is most responsible for smooth hydrogen

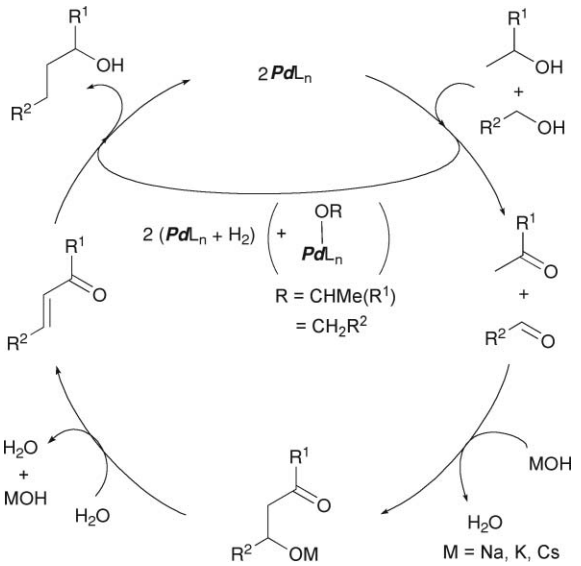
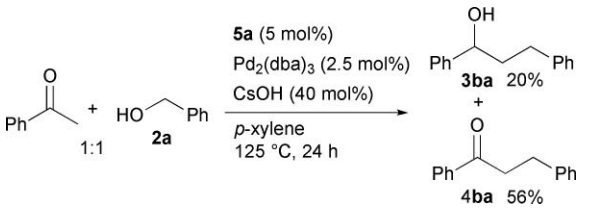
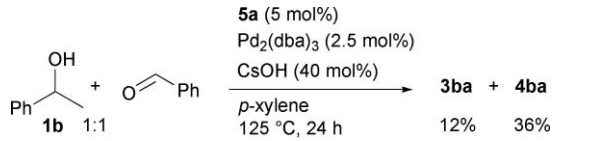


Fig. 4 Simplified plausible mechanism.

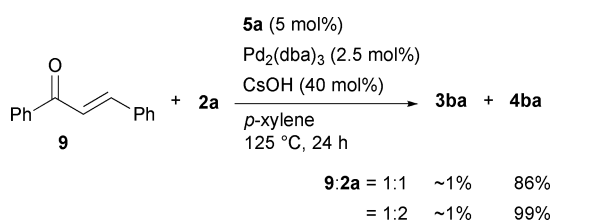
transfer upon reduction of product ketone **4ba** leading to **3ba** (eqn (3) and (4)), so that L_nPd–OCH(R)(Ph) might prevail over L_nPdH-like species for the reduction of the ketone carbonyl; (iv) to summarize the points so far, 2° alcohol **1b** has two important roles: one is for providing a partial structure of **3ba** and **4ba**, and the other is for smooth reduction of the C=O, so that an excess amount of **1b** was necessary for both a higher productivity and alcohol selectivity; otherwise an equilibrium between **3ba** and **4ba**, involving $L_nPd(OR)$-promoted hydrogen (H_2) transfer, would reach an apparent static point, eventually giving a mixture of **3ba** and **4ba** in a lower selectivity (Table 1, entry 7); (v) these speculations have some relevance to a notable effect of H_2, which helps enhancing high alcohol selectivity in some examples (Table 2, entries 5, 9 and 12), although the way of additional H_2 to participate in this multi-steps sequence, redox and acid–base cooperative reactions, should be far more complicated than would be expected.



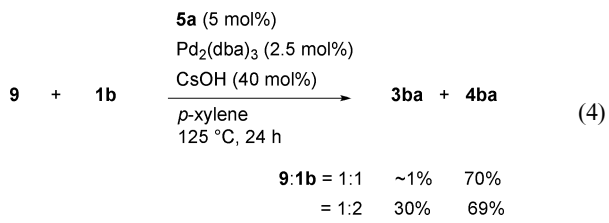
(1)



(2)



(3)



(4)

Conclusions

We have demonstrated that Pd-catalysts, derived from pincer-type NHCs, were useful for the cross-coupling reaction of two different alcohols in the absence or in the presence of H_2, which was complementary to related methods.[3–11] To the best of our knowledge, this is essentially the first successful example showing a wider substrate scope in the coupling reaction of alcohols *via* Pd-catalysis. No more than 40 mol% of base was required without any extra additives including olefinic substrates.[3,7] The reaction was selective, providing the corresponding alcohols in good to high yields, especially under the conditions of an H_2 atmosphere. The search for the mechanistic aspects, including the *ab initio* calculation, of the present catalysis is now under way in our laboratories.

Experimental

General

All reactions were carried out under either argon or H_2 atmosphere and in dried glassware by means of standard Schlenk techniques unless otherwise noted. All reagents were purchased from Aldrich, Wako, TCI or Kanto and used without further purification, except for benzyl alcohol, which was simply distilled under reduced pressure. Column chromatography was performed using silica gel (silica gel 60, 230-400 mesh, Merck). TLC was performed using pre-coated silica gel plates (silica gel 60 F_{254}, Merck) and products were observed under UV light or with phosphomolybdic acid reagent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-600 spectrometer, operating in $CDCl_3$ at 600 MHz. Chemical shifts and coupling constants are presented in ppm (δ) relative to tetramethylsilane (TMS) and Hz, respectively. High resolution mass spectra were obtained on JEOL JMS-700. Chiral high performance liquid chromatography analysis was conducted using Shimadzu LC-10AD coupled with photo diode array-detector SPD-M20A and chiral column of CHIRALCEL OD-H (Daicel chemical industries, LTD.). Alcohols **3aa**,[6,19] **3ba**,[6,19] **3bb**,[4] **3bc**,[4] **3bd**,[7,20] **3bf**,[4] **3bg**,[4] **3ca**[6] and **3ea**,[21] as well as ketones **4aa**,[22] **4ba**,[23] **4bb**,[24] **4bd**,[24] **4bf**,[4] **4ca**[25] and **4ea**,[26] are all known compounds, and their ^{1}H and ^{13}C NMR data measured this time, as well as synthetic procedures and full spectral or analytical data for NHC precursors **5a–d** and **6** are presented in the ESI† (scans of raw ^{1}H and ^{13}C NMR spectral charts are also available).

Representative procedure for the alcohol–alcohol coupling under Ar (1 atm)

To a degassed, and argon-filled suspension of $Pd_2(dba)_3$ (18 mg, 0.02 mmol) in anhydrous *p*-xylene (1.0 mL) was added **5a** (40 mg, 0.04 mmol), **1a** (294 mg, 2 mmol), **2a** (108 mg, 1 mmol) and CsOH (60 mg, 0.4 mmol) at 25 °C, and the mixture was immediately stirred at 125 °C for 24 h. The mixture was cooled down to 25 °C and was directly purified by column chromatography on silica gel (EtOAc–*n*-hexane = from 1 : 100 to 1 : 30) to give alcohol **3aa** and ketone **4aa** in a ratio of 13 : 1 (236 mg, 99% yield). The structure and diastereoselectivity were determined by comparing with the data in literatures (also see the ESI†).[6]

Representative procedure for the alcohol–alcohol coupling under H_2 (1 atm)

To a 30 mL flask stoppered by a Young's stopcock was added $Pd_2(dba)_3$ (22.5 mg, 0.025 mmol), **6** (35 mg, 0.05 mmol), **1b** (244 mg, 2 mmol), **2f** (74 mg, 1 mmol), NaOH (16 mg, 0.4 mmol) and anhydrous *p*-xylene (1.0 mL) at 25 °C. The flask was degassed and subsequently filled with H_2, and was stoppered again by a Young's stopcock to make a closed system. The resulting suspension was immediately heated and stirred at 125 °C for 24 h. The mixture was cooled down to 25 °C and was directly purified by column chromatography on silica gel (EtOAc–*n*-hexane = from 1 : 100 to 1 : 30) to give alcohol **3bf** and ketone **4bf** in a ratio of 9.2 : 1 (92% ^{1}H NMR total yield, using 1,1,2,2-tetrachloroethane as an internal standard).

1-Phenyl-3-thiophenylpropan-1-ol (3be). Yield (57 mg, 26%). IR (ATR): ν/cm^{-1} = 3388, 2920, 1721, 1492, 1451, 1276, 1056, 914, 849, 752, 694. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.35–7.25 (m, 5H), 7.09 (d, J = 4.1 Hz, 1H), 6.90 (dd, J = 5.2 Hz, 3.4 Hz, 1H), 6.78 (t, J = 1.7 Hz, 1H), 4.68 (t, J = 5.9 Hz, 1H), 2.95–2.85 (m, 2H), 2.18–2.12 (m, 1H), 2.07–2.02 (m, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 144.9, 144.7, 128.9, 128.0, 127.1, 126.2, 124.6, 123.4, 73.8, 41.0, 26.5. HRMS (EI) Calcd for $C_{13}H_{14}OS$ (M^+): 218.0765. Found m/z = 218.0756.

1,5-Diphenylpentan-3-ol (3da). Yield (120 mg, 50%). IR (ATR): ν/cm^{-1} = 3364, 3024, 2919, 1602, 1595, 1454, 1029, 911, 743, 696. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.29–7.26 (m, 4H), 7.19–7.17 (m, 6H), 3.68–3.65 (m, 1H), 2.81–2.76 (m, 2H), 2.69–2.64 (m, 2H), 1.85–1.74 (m, 4H), 1.44 (s, 1H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 142.4 (2C), 128.8 (8C), 126.2 (2C), 71.2, 39.5, 32.4. HRMS (EI) Calcd for $C_{17}H_{22}$ (M^+–H_2O): 222.1408. Found m/z = 222.1406.

3-(4-Methylphenyl)-1-phenylpropan-1-one (4bc). Yield (8.9 mg, 4%). IR (ATR): ν/cm^{-1} = 2922, 1683, 1596, 1514, 1447, 1360, 1290, 1202, 972, 808, 741, 688. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.97 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 3.28 (t, J = 7.9 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 199.7, 138.7, 137.3, 136.1, 133.5, 129.7, 129.1, 128.8, 128.5, 41.0, 30.2, 21.5. HRMS (FAB) Calcd for $C_{16}H_{16}O$ (M^+): 224.1201. Found m/z = 224.1200.

1-Phenyl-3-thiophenylpropan-1-one (4be). Yield (~1%). IR (ATR): ν/cm^{-1} = 3103, 2922, 1682, 1594, 1446, 1363, 1207, 971, 852, 748, 707, 692. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.97 (d, J = 8.3 Hz, 2H), 7.57 (t, J = 7.6, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.13–7.12 (m, 1H), 6.93–6.91 (m, 1H), 6.87 (t, J = 1.4 Hz, 1H), 3.38–3.35 (m, 2H), 3.32–3.29 (m, 2H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 198.9, 144.2, 137.1, 133.5, 129.0, 128.4, 127.2, 125.0, 123.7, 40.9, 24.5. HRMS (FAB) Calcd for $C_{13}H_{12}OS$ (M^+): 216.0609. Found m/z = 216.0607.

1-Phenyldecan-1-one (4bg). Yield (23 mg, 10%). IR (KBr): ν/cm^{-1} = 2918, 2846, 1686, 1596, 1473, 1447, 1375, 1256, 1220, 1193, 970, 733, 688. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.96 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 1.76–1.71 (m, 2H), 1.39–1.28 (m, 12H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 201.0, 137.5, 133.2, 128.9, 128.4, 39.0, 32.2, 29.7, 24.7, 23.0, 14.4. HRMS (EI) Calcd for $C_{16}H_{24}O$ (M^+): 232.1827. Found m/z = 232.1818.

1,3-Diphenyl-3-methylpropan-1-ol (8) (*cis* and *trans*).

Diastereomer. Yield (158 mg, 70% (for two diastereomers)). IR (ATR): ν/cm^{-1} = 3401, 3025, 2956, 1492, 1452, 1069, 1021, 762, 697. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.33–7.29 (m, 4H), 7.25–7.20 (m, 6H), 4.41–4.39 (m, 1H), 3.05–2.99 (m, 1H), 2.06–2.01 (m, 1H), 1.94–1.90 (m, 1H), 1.78 (d, J = 3.4 Hz, 1H), 1.28 (d, J = 6.8 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 146.9, 145.5, 128.9, 128.8, 127.8, 127.5, 126.5, 126.0, 72.6, 48.0, 37.0, 23.4.

Another diastereomer. IR (ATR): ν/cm^{-1} = 3357, 3026, 2925, 1602, 1492, 1452, 1051, 1015, 908, 760, 697. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.36–7.19 (m, 10H), 4.58–4.56 (m, 1H), 2.76–2.70 (m, 1H), 2.21–2.16 (m, 1H), 1.97–1.92 (m, 1H), 1.71 (d, J = 2.8 Hz, 1H), 1.27 (d, J = 6.9 Hz, 3H). ^{13}C NMR (600 MHz, $CDCl_3$) δ (ppm): 147.3, 144.9, 128.7, 128.1, 127.4, 126.5, 73.3, 47.6, 37.0, 22.9. HRMS (EI) Calcd for $C_{16}H_{18}O$ (M^+, two diastereomers): 226.1358. Found m/z = 226.1361. The chiral HPLC analytical data for **8** were obtained using *i*-PrOH/hexane (2.5/97.5) as eluent at a flow rate of 1.0 mL min^{-1}. Column: OD-H, t_R = 10.7 min and 11.9 min for the two enantiomers of either *cis* or *trans* isomer; 14.8 min and 15.5 min for the two enantiomers of either *cis* or *trans* isomer.

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Notes and references

1 Recent review: G. Guillena, D. J. Ramón and M. Yus, *Angew. Chem., Int. Ed.*, 2007, **46**, 2358–2364; M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, **349**, 1555–1575.
2 M. C. R. Guerbet, *Acad. Sci.*, 1909, **49**, 129–132.
3 Ir catalyst: T. Matsu-ura, S. Sakaguchi, Y. Obora and Y. Ishii, *J. Org. Chem.*, 2006, **71**, 8306–8308.
4 Ir catalyst: K.-i. Fujita, C. Asai, T. Yamaguchi, F. Hanasaka and R. Yamaguchi, *Org. Lett.*, 2005, **7**, 4017–4019.
5 Ir catalysts: A. P. da Costa, M. Viciano, M. Sanaú, S. Merino, J. Tejeda, E. Peris and B. Royo, *Organometallics*, 2008, **27**, 1305–1309. Related coupling: K. Taguchi, H. Nakagawa, T. Hirabayashi, S. Sakaguchi and Y. Ishii, *J. Am. Chem. Soc.*, 2004, **126**, 72–73; C. Löfberg, R. Grigg, M. A. Whittaker, A. Keep and A. Drrick, *J. Org. Chem.*, 2006, **71**, 8023–8027.
6 Ru catalyst: C. S. Cho, B. T. Kim, H.-S. Kim, T.-J. Kim and S. C. Shim, *Organometallics*, 2003, **22**, 3608–3610.
7 R. Martínez, D. J. Ramón and M. Yus, *Tetrahedron*, 2006, **62**, 8982–8987.
8 Ru catalysts: G. R. A. Adair and J. M. J. Williams, *Tetrahedron Lett.*, 2005, **46**, 8233–8235; M. Viciano, M. Sanaú and E. Peris, *Organometallics*, 2007, **26**, 6050–6054; A. Prades, M. Viciano, M. Sanaú and E. Peris, *Organometallics*, 2008, **27**, 4254–4259; Ru and Ir catalysts:; D. Gnanamgari, C. H. Leung, N. D. Schley, S. T. Hilton and R. H. Crabtree, *Org. Biomol. Chem.*, 2008, **6**, 4442–4445; D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**, 321–325; related examples: C. S. Cho, B. T. Kim, T.-J. Kim and S. C. Shim, *Tetrahedron Lett.*, 2002, **43**, 7987–7989; K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 5662–5663; R. Martínez, D. J. Ramón and M. Yus, *Tetrahedron*, 2006, **62**, 8988–9001; P. A. Slatford, M. K. Whittlesey and J. M. J. Williams, *Tetrahedron Lett.*, 2006, **47**, 6787–6789; G. Onodera, Y. Nishibayashi and S. Uemura, *Angew. Chem., Int. Ed.*, 2006, **45**, 3819–3822.
9 G. Gregorio, G. F. Pregaglia and R. Ugo, *J. Organomet. Chem.*, 1972, **37**, 385–387.
10 C. Carlini, A. Macinai, A. M. R. Galletti and G. Sbrana, *J. Mol. Catal. A: Chem.*, 2004, **212**, 65–70.
11 C. Carlini, M. D. Girolamo, A. Macinai, M. Marchionna, M. Noviello, A. M. R. Galletti and G. Sbrana, *J. Mol. Catal. A: Chem.*, 2003, **204–205**, 721–728.
12 C. S. Cho, *J. Mol. Catal. A: Chem.*, 2005, **240**, 55–60; M. S. Kwon, N. Kim, S. H. Seo, I. S. Park, R. K. Cheedrala and J. Park, *Angew. Chem., Int. Ed.*, 2005, **44**, 6913–6915.
13 Y. M. A. Yamada and Y. Uozumi, *Org. Lett.*, 2006, **8**, 1375–1378; Y. M. A. Yamada and Y. Uozumi, *Tetrahedron*, 2007, **63**, 8492–8498.
14 F. Alonso, P. Riente and M. Yus, *Eur. J. Org. Chem.*, 2008, 4908–4914.
15 V. V. Grushin, *Chem. Rev.*, 1996, **96**, 2011–2033; J. Muzart, *Tetrahedron*, 2003, **59**, 5789–5816; J. A. Mueller, C. P. Goller and M. S. Sigman, *J. Am. Chem. Soc.*, 2004, **126**, 9724–9734; Y. Uozumi and R. Nakao, *Angew. Chem., Int. Ed.*, 2003, **42**, 194–197.
16 K.-i. Shimizu, R. Sato and A. Satsuma, *Angew. Chem., Int. Ed.*, 2009, **48**, 3982–3986.
17 E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239–2246; R. J. Rubio, G. T. S. Andavan, E. B. Bauer, T. K. Hollis, J. Cho, F. S. Tham and B. Donnadieu, *J. Organomet. Chem.*, 2005, **690**, 5353–5364; J. R. Miecznikowski, S. Gründemann, M. Albrecht, C. Mégret, E. Clot, J. W. Faller, O. Eisenstein and R. H. Crabtree, *Dalton Trans.*, 2003, 831–838; S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller and R. H. Crabtree, *Organometallics*, 2001, **20**, 5485–5488.
18 F. E. Hahn, M. C. Jahnke and T. Pape, *Organometallics*, 2007, **26**, 150–154; F. E. Hahn, M. C. Jahnke, V. G.-Benitez, D. M.-Morales and T. Pape, *Organometallics*, 2005, **24**, 6458–6463.
19 C. Thorey, S. Bouquillon, A. Helimi, F. Hénin and J. Muzart, *Eur. J. Org. Chem.*, 2002, 2151–2159.
20 B. C. Ranu and S. Samanta, *Tetrahedron*, 2003, **59**, 7901–7906.
21 Z.-L. Shen, Y.-L. Yeo and T.-P. Loh, *J. Org. Chem.*, 2008, **73**, 3922–3924.
22 E. Fillion, D. Fishlock, A. Wilsily and J. M. Goll, *J. Org. Chem.*, 2005, **70**, 1316–1327.
23 T. Kawakami, M. Miyatake, I. Shibata and A. Baba, *J. Org. Chem.*, 1996, **61**, 376–379.
24 C. S. Cho and S. C. Shim, *J. Organomet. Chem.*, 2006, **691**, 4329–4332.
25 O. Chuzel, A. Roesch, J.-P. Genet and S. Darses, *J. Org. Chem.*, 2008, **73**, 7800–7802.
26 A. R. Katritzky, G. Zhang and J. Jiang, *J. Org. Chem.*, 1995, **60**, 7605–7611.

