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Ruthenium Phosphine-Pyridone Catalyzed Cross Coupling of Alcohols to form α -Alkylated Ketones

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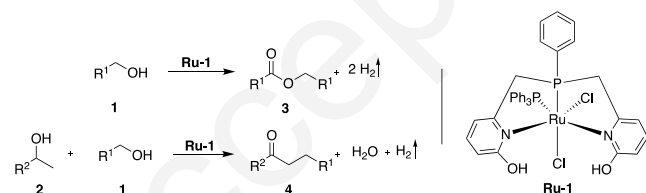
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The aspiration for development of highly selective and atom efficient catalytic transformations is currently compelling scientists around the world.¹ Development of “hydrogen auto-transfer process” is one of the most important milestones in this line.² Application of this technique for the synthesis of biologically as well as synthetically important molecules like α -alkylated ketones³ is a proper demonstration of its excellent utility. Unlike conventional methods using hazardous halide reagents, “hydrogen borrowing methodology” offers a greener path by using readily available alcohols as alkylating agents and generates water as the only byproduct. Thus, during the last decade, a number of catalytic systems based on ruthenium,⁴ osmium,⁴ iridium,⁵ palladium,⁶ rhodium,⁷ iron,⁸ cobalt,⁹ and copper¹⁰ catalysts have been developed for the synthesis of α -alkylated ketones which utilize primary alcohols for α -alkylation of ketones.

More recently, this transformation has been realized via direct dehydrogenative and dehydrative coupling of primary and secondary alcohols. Heterogeneous¹¹ as well as homogeneous systems based on iridium,¹² rhodium,⁷ and ruthenium^{12d,13} catalysts have been reported. Despite significant success, these systems have limitations. In most cases, high catalyst loading, stoichiometric amount of base, excess amount of primary alcohol or additional additives are required. Therefore, we now report a catalytic system based on our recently developed ruthenium phosphine-pyridone complex,^{14a} which overcomes these issues.

Our group recently disclosed a series of new proton responsive bi- and tri-dentate phosphine pyridon-e/-ate ligands. The corresponding transition metal complexes have shown impressive reactivity for alcohol dehydrogenation and selective formation of acetals or esters.¹⁴ Observing the efficiency of **Ru-1** in dehydrogenative coupling of primary alcohols, we envisaged the formation of corresponding α -alkylated ketone when a secondary alcohol is introduced in the system via dehydrogenative cross coupling of the two alcohols (Scheme 1).

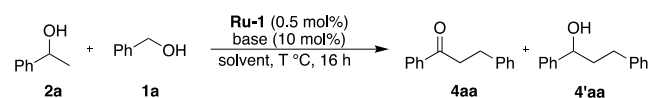
Scheme 1. Cross Coupling of Alcohols in the Presence of Ru-1 Precatalyst



Thus, benzyl alcohol (**1a**) and 1-phenylethanol (**2a**) were selected as benchmark substrates. Reaction of **1a** (0.5 mmol) and **2a** (0.5 mmol) in presence of **Ru-1** (0.5 mol%) and NaOH (10 mol%) at 150 °C for 16 h resulted in complete conversion of starting materials affording selective formation of the corresponding α -alkylated ketone **4aa** with an isolated yield of 85% (Table 1, entry 1). Encouraged by the result, we further studied the effect of other parameters. Interestingly, we observed lower temperature favored hydrogen borrowing yielding the corresponding alcohol **4'aa** as the major product (Table 1, entries 2,3).^{15,16} Screening of solvents showed toluene as the best suitable solvent (Table 1, entries 1, 4–6). Both NaOH and KO^tBu efficiently performed the reaction with almost equal selectivity (Table 1, entries 1,7). Other inorganic bases proved to be comparatively inefficient for this transformation (Table 1, entries 8–10). The reaction without metal catalyst in the presence of catalytic amount of base showed that only hydrogen borrowing occurred with incomplete conversion whereas no conversion was observed in the absence of base highlighting the cru-

cial role of the catalyst toward dehydrogenative coupling process (Table 1, entries 11,12).¹⁷ Taken together, these results demonstrate the tunable formation of the corresponding ketone or alcohol by simple modification of the reaction conditions.

Table 1. Optimization of Reaction Conditions^a


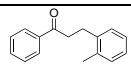

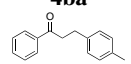

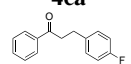

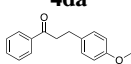

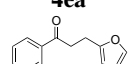

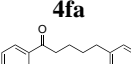

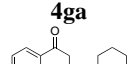

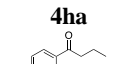

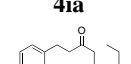
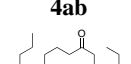

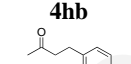


Entry	Solvent	T (°C)	Base	Conv. ^b	Ratio ^b 4aa:4'aa
1 ^c	Toluene	150	NaOH	100	92(85):8
2	Toluene	100	NaOH	100	6:94
3	Toluene	120	NaOH	100	15:85
4	<i>p</i> -xylene	150	NaOH	100	24:76
5	<i>t</i> AmOH	150	NaOH	100	70:30
6	Neat	150	NaOH	100	35:65
7	Toluene	150	KO ^t Bu	100	90:10
8	Toluene	150	KOH	100	85:15
9	Toluene	150	K ₂ CO ₃	72	66:34
10	Toluene	150	Cs ₂ CO ₃	81	74:26
11	Toluene	150	-	0	-
12 ^d	Toluene	150	NaOH	15	0:100

^aConditions: Benzyl alcohol (0.5 mmol), 1-phenylethanol (0.5 mmol), **Ru-1** (0.5 mol%), base (10 mol%), solvent (1.0 mL) under argon atmosphere for 16 h. ^bConversions and ratios were determined by GC and ¹H NMR analyses. ^cIsolated yield in parentheses. ^dReaction was performed without catalyst.

With the optimized reaction conditions in hand, we further explored the scope of the reaction. 1-Phenylethanol reacted smoothly with various benzylic alcohols to give excellent isolated yields irrespective of the electronic nature of their substituents (Table 2, entries 1–4). Hetero-aromatic alcohol like furan-2-ylmethanol also could react satisfactorily (Table 2, entry 5). Surprisingly, aliphatic primary alcohols which are known for their enolizable nature under dehydrogenative conditions reacted easily to furnish the corresponding α -alkylated ketones with very good yields (Table 2, entries 6,7). More interestingly, light alcohols like ethanol could be employed as alkylating agents with good yield (Table 2, entry 8). Noteworthy that aliphatic secondary alcohols like 2-octanol and isopropanol were also suitable coupling partners under the present conditions to provide fair to very good yields of the corresponding ketones (Table 2, entries 9–11). To the best of our knowledge, the use of *iso*-propanol in such transformation has been limited to redox neutral processes with moderate selectivities.^{16e,20}

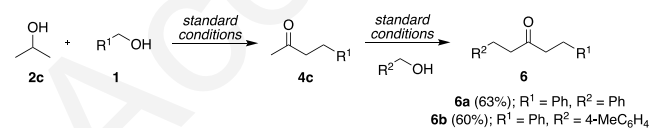
Table 2. Scope of the Reaction

Entry	Alcohol 1	Alcohol 2	Product	Yield ^b (%) ^c
1	 1b	2a	 4ba	89(5)
2	 1c	2a	 4ca	81(9)
3	 1d	2a	 4da	83(10)
4	 1e	2a	 4ea	88(3)
5	 1f	2a	 4fa	75(13)
6	 1g	2a	 4ga	83(11)
7	 1h	2a	 4ha	82(6)
8 ^{d,e}	 1i	2a	 4ia	75(10)
9	1a	 2b	 4ab	82(12)
10	1h	2b	 4hb	65(15)
11 ^f	1a	 2c	 4ac	78(7)

^aConditions: **1** (0.5 mmol), **2** (0.5 mmol), **Ru-1** (0.5 mol%), NaOH (10 mol%), toluene (1.0 mL) at 150 °C under argon atmosphere for 16–24 h. ^bIsolated yields of the ketones **4**. ^cNumbers in parentheses show yield of the corresponding alcohol **4**. ^dKO^tBu was used instead of NaOH. ^e**1i** (15 mmol) was used. ^f**2c** (10 mmol) was used.

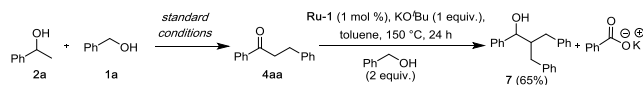
After establishing the generality of the reaction, we further investigated the possibility of double alkylation in a single pot through the sequential addition of primary alcohols to isopropanol. The resulting doubly alkylated products were isolated in fair yields (Scheme 2).

Scheme 2. Double Alkylation in a Single-pot through Sequential Addition of Alcohols



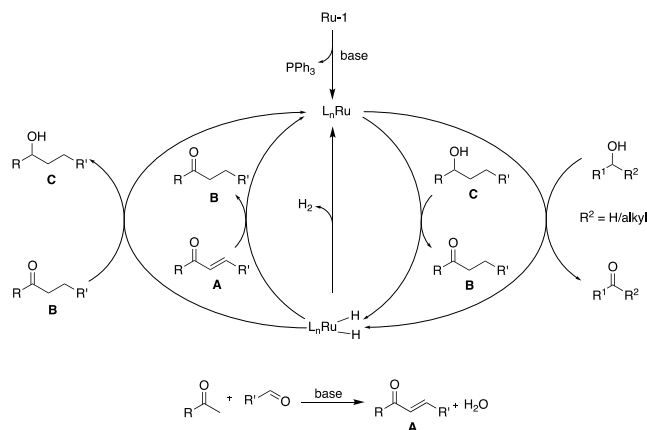
Additionally, when we tried to further alkylate an α -position which is already alkylated using a relatively stronger base KO^tBu, the corresponding dialkylated alcohol was obtained with 65% isolated yield (Scheme 3) along with the formation of potassium benzoate. In this case, reduction of the keto group occurred due to hydrogen transfer from the excess of benzyl alcohol acting both as a source of electrophile and hydrogen donor.

Scheme 3. α,α Dialkylation in a One-pot Process.



Monitoring the reaction in GC and NMR revealed that alcohol **4'aa** was initially formed as major product in the reaction which gradually undergoes dehydrogenation to provide the α -alkylated ketone **4aa**. In order to get a better insight of the reaction mechanism, the reaction was performed in *toluene-d8*. ^{31}P NMR showed that PPh_3 was decoordinated at the beginning of the reaction. With the advancement of the reaction, ^1H NMR revealed two doublets resonating at -6.4 ($J_{\text{P-H}} = 23.6$ Hz) and -6.5 ppm ($J_{\text{P-H}} = 21.2$ Hz) which indicated the presence of a ruthenium dihydride species.

Scheme 4. Plausible Mechanism for Cross Coupling of Primary and Secondary Alcohols



Although, insufficient data exist at present to describe a detailed mechanism, from the above observations, a possible mechanism of this transformation can be proposed. As delineated in Scheme 4, decoordination of PPh_3 in the presence of base generates the catalytically active intermediate L_nRu . Transfer of hydrogen from alcohol generates ruthenium dihydride intermediate L_nRuH_2 . The resulting aldehyde and ketone can condense in the presence of base to generate the α,β -unsaturated ketone **A**. **A** can be hydrogenated in two steps to generate the β -alkylated alcohol **C** by ruthenium dihydride complex during the course of the reaction.¹⁸ Finally, **C** undergoes ruthenium assisted dehydrogenation leading to the α -alkylated ketone **B**. L_nRu is regenerated from L_nRuH_2 by release of H_2 molecule.

In conclusion, we have demonstrated a simple, efficient and highly selective synthesis of α -alkylated ketones by the direct dehydrogenative coupling of primary and secondary alcohols which precludes the use of stoichiometric amount of base or any other additives. This reaction is catalyzed by a novel, air stable ruthenium phosphine pyridonate complex. Detailed mechanistic studies to unveil the catalytic potential of **Ru-1** and related complexes are under way. Pivotal results like the use of ethanol as alkylating agent reveals the plausible utilization of the presented protocol toward the synthesis of higher ranked alcohols like butanol. Also, the sequential addition of alkylating agents to isopropanol disclosed a very convenient path to aliphatic ketones in which the carbonyl group can be tailored to a desired position by appropriate selection of the alkylating alcohols.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out under an inert argon atmosphere with standard schlenk techniques. Solvents were degassed and stored in argon atmosphere before use. Reagents were used as received without further purification, unless otherwise stated. Toluene and THF were dried over Braun MB-SPS-800 solvent purification system. Technical grade petroleum ether and ethyl acetate were used for column chromatography. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). ^1H NMR spectra were recorded using a Bruker Avance^{III} 300 and 400 MHz NMR spectrometers. All ^1H -NMR data are reported in δ units, parts per million (ppm) and were calibrated relative to the reported residual solvent signals in the corresponding deuterated solvents. All ^{13}C -NMR and ^{31}P -NMR data are reported in ppm and were recorded with ^1H decoupling. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, br = broad, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF mass spectrometer using ESI-TOF (electrospray ionization time of flight).

Complex $[\text{Ru}(\text{P}(\text{NOH})_2)_2\text{Cl}_2(\text{PPh}_3)]$ (**Ru-1**) was synthesized according to the reported procedure.^{14a}

General Procedure for Cross Coupling of Alcohols (Table 2). A clean Schlenk tube was charged with complex Ru-1 (0.0025 mmol, 0.5 mol%) in degassed toluene (1.0 mL). NaOH (0.05 mmol, 10 mol%) was added to this opaque yellow solution. After stirring for 5 minutes, secondary alcohol (0.5 mmol) was mixed followed by the addition of the required primary alcohol (0.5 mmol). This reaction mixture was stirred in a preheated oil bath at 150 °C for 16–24 h. The reaction was monitored by TLC and GC. After the completion of the reaction, the reaction mixture was cooled to room temperature and solvent was evaporated. The crude reaction mixture was purified by silica gel column chromatography using petroleum ether and ethyl acetate mixture as eluent to get the desired ketone.

1,3-Diphenylpropan-1-one (4aa).^{19a} 16 h of reaction; White solid; Eluent: PE/EA = 9/1; 85% yield (89 mg); ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.38–7.24 (m, 5H), 3.35 (t, *J* = 7.7 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 199.2, 141.4, 136.9, 133.1, 128.7, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

1-Phenyl-3-(o-tolyl)propan-1-one (4ba).^{19b} 16 h of reaction; White solid; Eluent: PE/EA = 9/1; 89% yield (100 mg); ¹H NMR (400 MHz, CDCl₃): 8.06–8.02 (m, 2H), 7.65–7.59 (m, 1H), 7.54–7.49 (m, 2H), 7.28–7.15 (m, 4H), 3.34–3.29 (m, 2H), 3.16–3.11 (m, 2H), 2.43 (s, CH₃); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 199.3, 139.4, 136.9, 136.0, 133.1, 130.4, 128.8, 128.6, 128.1, 126.4, 126.2, 39.1, 27.5, 19.4.

1-Phenyl-3-(p-tolyl)propan-1-one (4ca).^{19c} 16 h of reaction; White solid; Eluent: PE/EA = 9/1; 81% yield (91 mg); ¹H NMR (300 MHz, CDCl₃): δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.25–7.18 (m, 4H), 3.35 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 199.3, 138.2, 136.9, 135.6, 133.0, 129.2, 128.6, 128.3, 128.1, 40.6, 29.7, 21.0.

3-(4-Fluorophenyl)-1-phenylpropan-1-one (4da).^{11a} 18 h of reaction; White solid; Eluent: PE/EA = 9/1; 83% yield (95 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J*₁ = 8.3 Hz, *J*₂ = 5.6 Hz, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 199.0, 161.4 (d, ¹J_{C-F} = 243.7 Hz), 137.0 (d, ⁴J_{C-F} = 3.2 Hz), 136.8, 133.1, 129.9 (d, ³J_{C-F} = 7.8 Hz), 128.6, 128.0, 115.2 (d, ²J_{C-F} = 21.1 Hz), 40.4, 29.3.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (4ea).^{19c} 16 h of reaction; White solid; Eluent: PE/EA = 9/1; 88% yield (106 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.8 (s, 3H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 199.4, 158.1, 137.0, 133.4, 133.1, 129.4, 128.7, 128.1, 114.0, 55.4, 40.8, 29.4.

3-(Furan-2-yl)-1-phenylpropan-1-one (4fa).^{19c} 20 h of reaction; Pale yellow oil; Eluent: PE/EA = 9/1; 75% yield (75 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.99–7.97 (m, 2H), 7.59–7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 1.7 Hz, 1H), 6.29 (dd, *J*₁ = 3.1 Hz, *J*₂ = 1.9 Hz, 2H), 6.06–6.05 (m, 2H), 3.34 (t, *J* = 7.4 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 198.8, 154.9, 141.2, 136.8, 133.3, 128.7, 128.1, 110.4, 105.4, 37.4, 22.6.

1,5-Diphenylpentan-1-one (4ga).^{19d} 18 h of reaction; Colourless oil; Eluent: PE/EA = 9/1; 83% yield (99 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.97–7.95 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32–7.28 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 3H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.86–1.69 (m, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 200.3, 142.3, 137.1, 133.0, 128.7, 128.5, 128.4, 128.1, 125.8, 38.5, 35.9, 31.2, 24.1.

1-Phenyldecan-1-one (4ha).^{19e} 16 h of reaction; Colourless oil; Eluent: PE/EA = 9/1; 82% yield (95 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.95 (dt, *J*₁ = 7.1 Hz, *J*₂ = 1.3 Hz, 2H), 7.55–7.50 (m, 1H), 7.46–7.40 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.73 (qu, *J* = 7.4 Hz, 2H), 1.27 (br, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 200.5, 137.2, 132.8, 128.6, 128.1, 38.6, 31.9, 29.6, 29.5, 29.4, 29.4, 24.4, 22.7, 14.2.

1-Phenylbutan-1-one (4ia).^{19f} KO^tBu was used instead of NaOH; 24 h of reaction; Colourless oil; Eluent: PE/EA = 9/1; 75% yield (56 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.97–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.77 (sextet, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 200.6, 137.2, 133.0, 128.7, 128.2, 40.7, 17.9, 14.0.

1-Phenylnonan-3-one (4ab).^{5e} 24 h of reaction; Colourless oil; Eluent: PE/EA = 24/1; 82% yield (89 mg); ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.28 (m, 2H), 7.22–7.19 (m, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.54 (qu, *J* = 8.0 Hz, 2H), 1.28 (br, 6H), 0.90 (t, *J* = 6.9 Hz, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 210.3, 141.3, 128.5, 128.4, 126.1, 44.3, 43.1, 31.7, 29.9, 29.0, 23.8, 22.6, 14.1.

Hexadecan-7-one (4hb).^{6a} 24 h of reaction; Colourless oil; Eluent: PE/EA = 24/1; 65% yield (78 mg); ¹H NMR (400 MHz, CDCl₃): δ 2.36 (t, *J* = 7.4 Hz, 4H), 1.54 (qu, *J* = 7.2 Hz, 4H), 1.24 (br, 18H), 0.86 (t, *J* = 6.8 Hz, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 211.7, 42.9, 32.0, 31.7, 29.6, 29.6, 29.4, 29.1, 24.0, 24.0, 22.8, 22.6, 14.2, 14.1.

4-Phenylbutan-2-one (**4ac**).^{19g} 24 h of reaction; Colourless oil; Eluent: PE/EA = 9/1; 78% yield (58 mg); ¹H NMR (300 MHz, CDCl₃): δ 7.31–7.26 (m, 2H), 7.21–7.17 (m, 3H), 2.93–2.86 (m, 2H), 2.80–2.73 (m, 2H), 2.14 (s, 3H); ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 208.0, 141.1, 128.6, 128.4, 126.2, 45.3, 30.2, 29.8.

General Procedure for Cross Coupling of Alcohols (Scheme 2,3).

1,5-Diphenylpentan-3-one (**6a**).^{19g} 2-Propanol (1mL) and benzyl alcohol (0.5 mmol) was reacted in presence of complex **Ru-1** (0.5 mol%) and NaOH (10 mol%) in toluene at 150 °C for 24 h under argon atmosphere. Then the generated extra acetone was removed from the reaction medium by applying vacuum. Further the reaction mixture was reloaded with benzyl alcohol (0.5 mmol), **Ru-1** (0.5 mol%) and NaOH (10 mol%). Then the reaction mixture was heated at 150 °C for 24 h. After it was cooled to room temperature. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 63% yield (75 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.27 (m, 4H), 7.23–7.17 (m, 6H), 2.91 (t, *J* = 7.6 Hz, 4H), 2.73 (t, *J* = 7.6 Hz, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 209.2, 141.1, 128.6, 128.4, 126.2, 44.6, 29.8.

1-Phenyl-5-(*p*-tolyl)pentan-3-one (**6b**).^{19h} 2-Propanol (1mL) and benzyl alcohol (0.5 mmol) was reacted in presence of complex **Ru-1** (0.5 mol%) and NaOH (10 mol%) in toluene at 150 °C for 24 h under argon atmosphere. Then the generated extra acetone was removed from the reaction medium by applying vacuum. Further to the reaction mixture 4-methylbenzyl alcohol (0.5 mmol) was reloaded with **Ru-1** (0.5 mol%) and NaOH (10 mol%). Then the reaction mixture was heated at 150 °C for 24 h. After it was cooled to room temperature. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a colourless oil with 60% yield (76 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.25–7.19 (m, 3H), 7.11 (q, *J* = 8.1 Hz, 4H), 2.91 (dt, *J*₁ = 14.4 Hz, *J* = 7.6 Hz, 4H), 2.76–2.70 (m, 4H), 2.35 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 209.2, 141.1, 138.0, 135.6, 129.2, 128.6, 128.4, 128.3, 126.2, 44.7, 44.6, 29.8, 29.4, 21.1.

2-benzyl-1,3-diphenylpropan-1-ol (**7**): Benzyl alcohol (0.5 mmol) and 1-phenyl ethanol (0.5 mmol) was reacted in presence of complex **Ru-1** (0.5 mol%) and NaOH (10 mol%) in toluene at 150 °C for 16 h under argon atmosphere. Further to the reaction mixture benzyl alcohol (1.0 mmol) was added along with **Ru-1** (1.0 mol%) and KO^tBu (2.0 mmol). Then the reaction mixture was heated at 150 °C for 24 h. After it was cooled to room temperature and the solvent was removed by vacuum. Then water (2.0 mL) was added to the reaction mixture and the organic products are extracted with DCM (2*2 mL). The DCM layer was dried over dry MgSO₄ and filtered. Solvent was removed under vacuum. Purification by silica gel column chromatography (pet. ether : EtOAc = 9 : 1) afforded the product as a white solid with 65% yield (98 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.24 (m, 9H), 7.20–7.13 (m, 4H), 7.10–7.08 (m, 2H), 4.71 (d, *J* = 3.8 Hz, 1H), 2.78–2.53 (m, 4H), 2.41–2.33 (m, 1H), 1.84 (br, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ 143.6, 141.0, 141.0, 129.4, 129.2, 128.5, 128.4, 128.4, 127.3, 126.2, 126.0, 126.0, 73.8, 49.6, 36.2, 34.2. HRMS: *m/z* calcd for C₂₂H₄₄O 325.1563 [M+Na]⁺, found 325.1562.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

¹H and ¹³C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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