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Iridium(I) Catalyzed Alkylation Reactions to form α-Alkylated Ketones

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Supporting Information

ABSTRACT: A highly effective and green procedure for the formation of α-alkylated ketones has been disclosed via the reaction of primary alcohols with secondary alcohols and ketones by using [IrCl(COD)(NHC)] complexes as a catalyst. Various α-alkylated ketones were obtained in high yields from the alkylation of alcohol with alcohol and ketone with alcohol through a borrowing hydrogen reaction by using 0.05-0.5 mol% iridium(I), catalytic amount of KOH (5-10 mol%) as the base under air atmosphere and within very short reaction times.

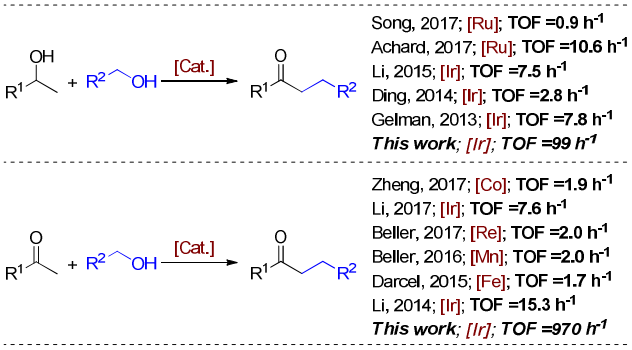
INTRODUCTION

Transition metal (TM) catalyzed carbon–carbon bond formation has become an important synthetic method in organic chemistry to synthesize functionalized molecules.[1] Among the numerous protocols, alkylation represents a class of the most important reactions for this transformation. Traditionally, mutagenic alkyl halides have been employed as alkylating reagents with equivalent or excess amount of strong base which generates a stoichiometric amount of salts as waste. Considering the demand of environmentally benign processes, the use of alcohols as inexpensive and greener alkylating agents via TM catalyzed hydrogen autotransfer (HA) process, also designated borrowing hydrogen (BH) methodology, has attracted great attention.[2] In this context, α–alkylation of ketones with primary alcohols based on the HA procedure to prepare biologically and synthetically important α–alkylated ketones using various transition metal complexes such as Mn,[3] Re,[4] Fe,[5] Ru,[6] Co,[7] Rh,[8] Ir[9] and Pd[10] and catalyst free conditions[11] have been reported. More recently, α–alkylated ketones have been synthesized by direct dehydrogenative coupling of primary alcohols with secondary alcohols using heterogeneous[12] and homogeneous Ru,[13,6c] Rh[8b] and Ir[9e,13c,14] catalysts. In most cases, a stoichiometric amount of base, a high catalyst loading, or prolonged reaction times are needed. Catalytic activities of recently reported various complexes in such reactions to give α–alkylated ketones are listed in Scheme 1. Although considerable improvement has been made in this field, the final turnover frequencies (TOF) of these catalysts are still significantly low. Therefore, it is essential to develop more effective and sustainable processes for this reaction with a greater TOF and low amount of base.

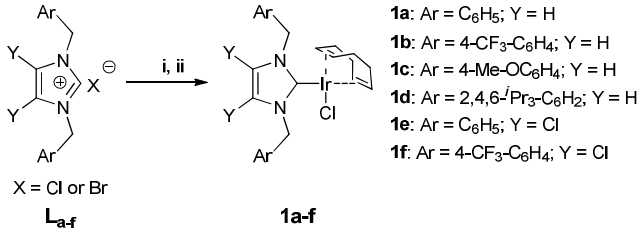
Ir-NHC (NHC = *N*-heterocyclic carbene) complexes have revealed a wealth of catalytic reactions. Among them, transfer hydrogenation (TH), a process that transfers hydrogen from 2-propanol to an unsaturated molecule in combination with a strong base, have received a great deal of attention in the past decade.[15] These iridium complexes have great advantages including their remarkable tunable character, the ease of synthesis and the high stability. We recently reported a series of Ir^{I}–NHC complexes and the application of these complexes as the catalysts for hydrogen transfer reactions. These complexes have exhibited very high catalytic activities in these transformations and it was found that the electronic and steric character of the NHC ligand perform a critical function for the catalytic activity.[16] In addition, similar complexes have found application in the dehydrogenation of alcohols and selective formation of β–alkylated secondary alcohols from coupling of primary and secondary.[17] During the course of our continuing work on Ir^{I}–NHC catalyzed acceptorless dehydrogenation of alcohols, we reasonably envisioned that these complexes might be used as the catalyst for cross–coupling of primary alcohols with secondary alcohols and also with ketones to give α–alkylated ketones.

In this study, we compare catalytic activities of a series of [IrCl(COD)(NHC)] (COD = cyclooctadiene) complexes (**1a-f**) (Scheme 2) and report a remarkably active catalytic system for the reaction of primary alcohols with secondary alcohols and also with ketones to give α–alkylated ketones by using 0.05-0.1 equiv. KOH under air with the highest TOF ever reported. Notably, this system overcomes all the following limitations for the reaction: including (1) the use of a stoichiometric amount or expensive bases, (2) high catalyst loading, (3) an excess amount of primary alcohol or any other additives, (4) very long reaction times, (5) inert reaction conditions.

Scheme 1. Recent Examples of Catalysts for C–C Bond Formation Reactions to form α-Alkylated Ketones.



Scheme 2. Preparation of Ir^{I}–NHC Complexes 1a-f Studied in This Work.



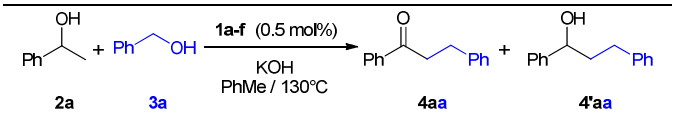
Reaction conditions: i) Ag_2O (0.5 equiv.), CH_2Cl_2, RT, 1 h.
ii) $[IrCl(COD)]_2$ (0.5 equiv.), CH_2Cl_2, RT, 12 h.

RESULTS AND DISCUSSION

Based on our previous experience on [IrCl(COD)(NHC)] catalyzed TH reactions,[16] we decided to prepare a set of [IrCl(COD)(NHC)] complexes (**1a-f**) having electron deficient and electron withdrawing benzyl substituents as wingtip on the nitrogen atom of imidazole or 4,5-dichloroimidazole (Scheme 2). All the new complexes were prepared in high yields as air- and moisture-stable yellow solids and were characterized by NMR spectroscopy and HRMS analysis.

To probe the potential of these Ir^{I}-NHC catalysts for the reaction of primary alcohols with secondary alcohols, 1-phenylethanol (**2a**) and benzyl alcohol (**3a**) were selected as benchmark substrates (Table 1). In the presence of **1a-f** as the catalyst (0.5 mol%) and KOH (10 mol%), the reaction was carried out in toluene (2 mL) at 130 ºC under air for 1 h (entries 1–6). All the reactions resulted in complete conversion of substrates and complex **1f**, which bore a 1,3-bis(4-trifluorobenzyl)-4,5-dichloroimidazol-2-ylidene ligand, provided the highest selectivity to ketone product **4aa** (entry 6) while more electron deficient complex **1d**, which is one of the most active NHC–based catalysts for the transfer hydrogenation of carbonyl compounds,[16b] affording selective formation of alcohol product **4′aa** (entry 4). Clearly, the electronic character of the NHC ligand is important for the selectivity. Increasing the reaction time to 2 h led to increase of the corresponding α–alkylated ketone (**4aa**:**4′aa** ratio 93:7) (entry 7). The reaction conducted under an argon atmosphere was also resulted in complete conversion of starting alcohols and afforded the **4aa** selectively (entry 8). Other strong bases such as KO^{t}Bu and NaOH resulted with slightly lower selectivity for the formation of **4aa** (entries 9 and 10). Reducing the amount of KOH from 0.1 equiv. to 0.05 equiv. lowered the selectivity of **4aa** to 73:27 (entry 11). Additional experiments were carried out in the absence of KOH or Ir^{I}-NHC catalyst and no product formation was observed (entries 12 and 13). However, with $[IrCl(COD)]_2$ and 0.1 equiv. of KOH, only 12% conversion was observed, which indicates the critical role of the NHC ligand (entry 14).

Table 1. Optimization of Reaction Conditions[a]



2a 3a 4aa 4′aa

entry	cat.	base	time (h)	conv.[b] (%)	ratio[c] 4aa:4′aa
1	**1a**	KOH	1	100	45:55
2	**1b**	KOH	1	100	62:38
3	**1c**	KOH	1	100	44:56
4	**1d**	KOH	1	100	15:85
5	**1e**	KOH	1	100	60:40
6	**1f**	KOH	1	100	68:32
7	**1f**	KOH	2	100	93:7
8[d]	**1f**	KOH	2	100	91:9
9	**1f**	KO^{t}Bu	2	100	90:10
10	**1f**	NaOH	2	100	86:14
11[e]	**1f**	KOH	2	100	73:27
12	**1f**	–	2	0	–
13	–	KOH	2	0	–
14	**$[IrCl(COD)]_2$**	KOH	2	12	30:70

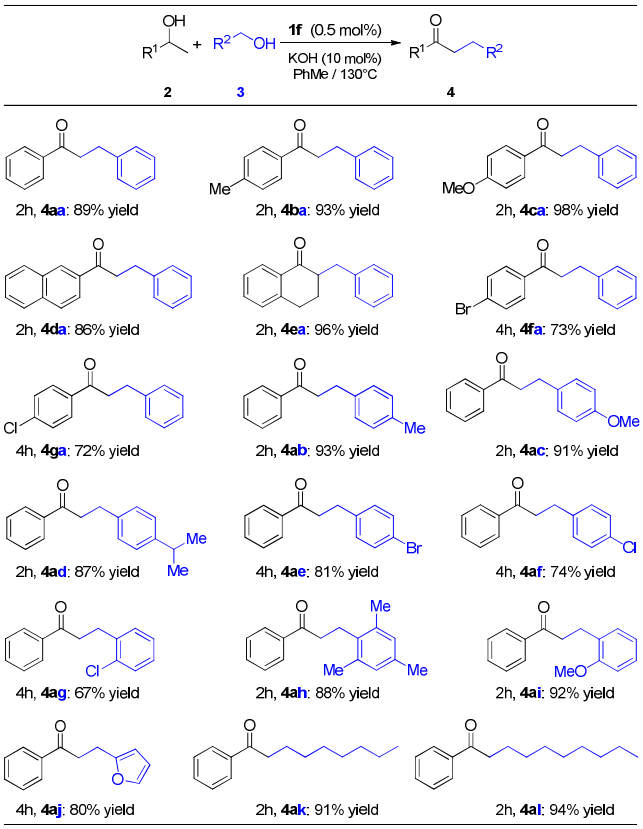
[a]Reaction Conditions: **2a** (1.0 mmol), **3a** (1.0 mmol), **1a-f** (0.5 mol%), base (10 mol%), toluene (2.0 mL), 130 ºC, under air. [b]GC conversion. [c]Ratios were determined by ^{1}H NMR analyses. [d]Reaction was performed under an argon atmosphere. [e]KOH (5 mol%).

To examine the scope of the reaction, various secondary and primary alcohols were reacted under the optimized conditions (Scheme 3). All reactions resulted in complete conversion of starting materials affording selective formation of the corresponding ketone **4**. Various electron–rich or electron–deficient 1-arylethanols (**2a**–**g**) were effectively transformed into the corresponding ketones (**4aa**–**4ga**) in high isolated yields by using **1f** (0.5 mol%) as the catalyst. Reactions of electron–rich substituted 1-phenylethanols (**2b,c**) afforded the desired products **4ba** and **4ca** in 93 and 98% yields respectively. Furthermore, 1-(2-naphthyl)ethanol (**2d**) and α–tetralol (**2e**) gave the corresponding ketones **4da** and **4ea** in 86 and 96% yields, respectively. In the case of halogenated 1-phenylethanols **2f** and **2g** longer reaction time (4 h) required to obtain good selectivity and desired products **4fa** and **4ga** were obtained in 73 and 72%. This result is consistent with our previous observations on iridium–catalyzed acceptorless dehydrogenative oxidation of secondary alcohols, where we found that dehydrogenation of electron–deficient secondary alcohols were more difficult.[18] We also investigated the reactions with respect to primary alcohols. Transformation of 1-phenylethanol with various primary alcohols including electron–donating (**3b**–**d**), electron–withdrawing (**3e** and **3f**), more sterically hindered (**3g**–**i**), heteroaromatic (**3j**) and aliphatic (**3k** and **3l**) gave the corresponding ketones **4ab**–**4al** in 67–94% isolated yield within 2–4 h.

After studying the iridium–catalyzed reaction of primary alcohols with secondary alcohols to give α–alkylated ketones, we focused our interest on α–alkylation of ketones with primary alcohols, a processes using HA methodology.[3-11] Our initial investigation focused on the α–alkylation of acetophenone (**5a**) (1.0 mmol) with **3a** (1.0 mmol) in the presence of a very low amount **1f** (0.05 mol%) as catalyst and KOH (5.0 mol %) at 130 °C and this reaction resulted in complete conversion of substrates affording formation of **4aa** with an isolated yield of 91% within 2 h (Scheme 4). Encouraged by the result, we further expanded the reaction generality with respect to methyl ketones (**5b**–**g**) (Scheme 4). Methyl ketones with different electronic nature all reacted with benzyl alcohol (**3a**) affording the corresponding ketones **4ba**–**4ga** with excellent isolated yields (86–97%). Next, we examined the scope of α–alkylation of ketones with respect to primary alcohols. Acetophenone (**4a**) reacted smoothly with a variety of primary alcohols (**3b**–**l**) to give excellent isolated yields (81–96%) of α–

alkylated ketones (**4ab**–**4al**) irrespective of the electronic and steric nature of primary alcohol within 2 h. Comparing the results in Scheme 3 with those in Scheme 4 shows that the *α*–alkylation of ketones is considerably easier than the direct dehydrogenative coupling of primary alcohols with secondary alcohols to produce **4**, requiring lower catalyst and base loadings.

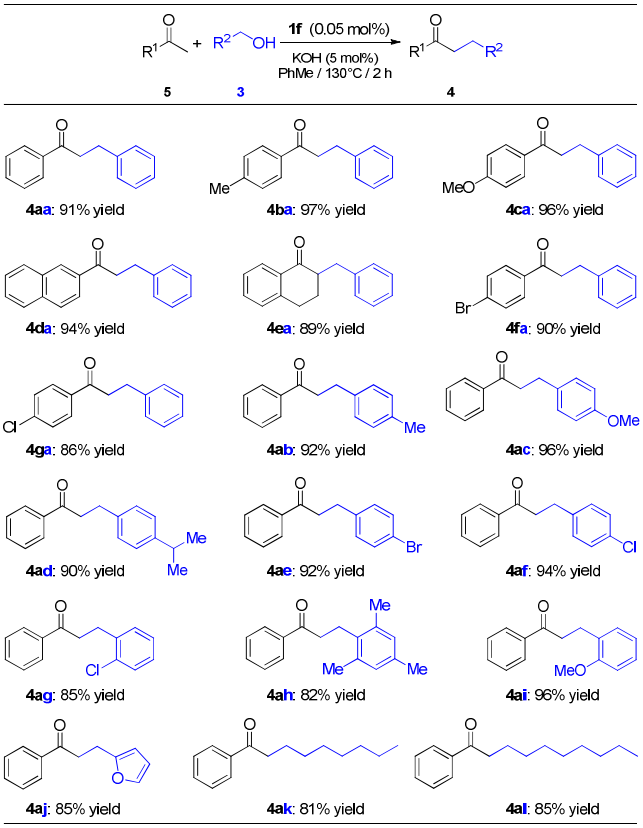
Scheme 3. Scope of Dehydrogenative Coupling of Primary and Secondary Alcohols Catalyzed by Complex 1f[a]



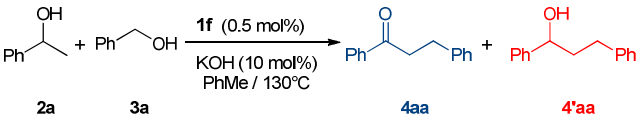
[a]Reaction Conditions: Secondary alcohol (1.0 mmol), primary alcohol (1.0 mmol), **1f** (0.5 mol%), base (10 mol%), toluene (2.0 mL), 130 ºC, under air. Isolated yields.

Monitoring the time profile of the direct dehydrogenative coupling of **2a** with **3a** revealed that the reaction is very fast and results in complete conversion of substrates to **4aa** and **4′aa** with a ratio of 49:51 within 12.5 minutes (Figure 1). Then, initially formed **4′aa** gradually undergoes dehydrogenation to form **4aa**. From the above observations, a plausible mechanism for this reaction can be proposed as shown in Scheme 5.[13a,14a] The mechanism involves decoordination of Cl in the presence of KOH to generate $[Ir(COD)(NHC)]^+$ intermediate. Then, dehydrogenation of **2** and **3** generates transient iridium–hydride.[17b] The resulting ketone (**5**) and aldehyde (**3′**) may give the *α,β*–unsaturated ketone in the presence of base. This enone can be reduced to afford the **4′** and **4** by iridium–hydride. Last of all, in the presence of catalyst, dehydrogenation of **4′** gives the desired product **4**. To gain further insight into the reaction mechanism, the reaction of **2a** and **3a** in toluene-d_8 was monitored by ^{1}H NMR spectroscopy. During the reaction ^{1}H NMR revealed two singlets in the hydridic region resonating at −9.34 and −10.87 ppm and persisted throughout the reaction which indicated the presence of iridium hydride species.

Scheme 4. Scope of α–Alkylation of Ketones with Primary Alcohols Catalyzed by Complex 1f[a]



[a]Reaction Conditions: Ketone (1.0 mmol), primary alcohol (1.0 mmol), **1f** (0.05 mol%), base (5.0 mol%), toluene (1.0 mL), 130 ºC, under air. Isolated yields.



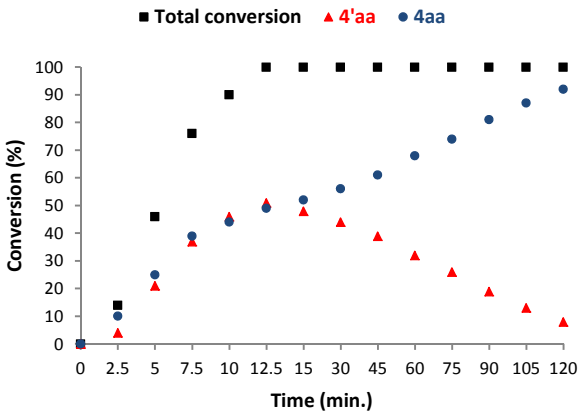
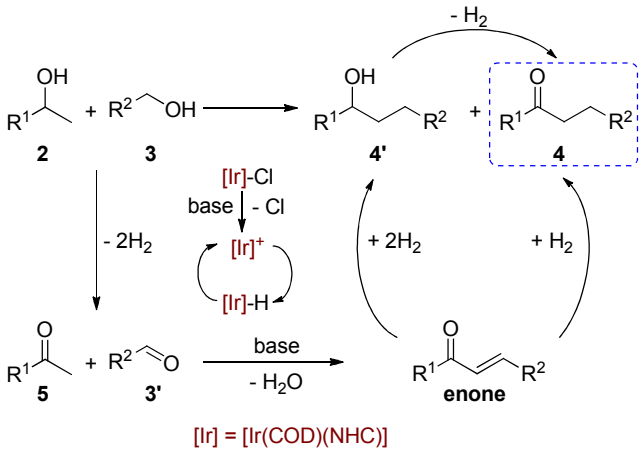


Figure 1. Time course of the direct dehydrogenative coupling of benzyl alcohol with 1-phenylethanol. Reaction Conditions: **2a** (1.0 mmol), **3a** (1.0 mmol), **1f** (0.5 mol%), KOH (10 mol%),

toluene (2.0 mL), 130 ºC, under air. Conversions and ratios were determined by ^{1}H NMR analyses.

Scheme 5. Plausible Reaction Mechanism.



CONCLUSIONS

In conclusion, we have synthesized a series of easily tunable [IrCl(COD)(NHC)] complexes having electron deficient and electron withdrawing benzyl substituents as wingtip on the nitrogen atom of imidazole or 4,5-dichloroimidazole. The complex **1f** proved that it is a general and highly effective catalyst for the direct dehydrogenative cross–coupling reactions under air atmosphere within very short reaction times. Importantly, this catalytic system revealed exceptionally high TOFs (up to 98 h^{-1} for reaction of secondary alcohols with primary alcohols and up to 970 h^{-1} for α–alkylation of ketones with primary alcohols). To the best of our knowledge, these TOF values are the highest among all the reported transition metal complexes for these transformations.

EXPERIMENTAL SECTION

Experimental Details. Experiments involving air or moisture sensitive reagents were performed under an atmosphere of dry argon using standard Schlenk techniques. Unless otherwise specified, all reagents were obtained commercially and used without further purification. $[IrCl(COD)]_2$ was prepared according to the published procedure.[19] Imidazolium salts $\mathbf{L_{a\text{-}c}}$[18], $\mathbf{L_d}$[16b], $\mathbf{L_e}$[20] and complexes **1a**[21] and **1d**[16b] were synthesized according to published procedure and the physical properties and spectroscopic data of the obtained compound are in accordance with previous reports. NMR spectra were recorded on Varian AS 400 Mercury NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ = 0 ppm) or $CDCl_3$ (δ = 7.26 ppm for ^{1}H and δ = 77.0 ppm for ^{13}C NMR). Melting points measured on Gallenkamp electrothermal melting point apparatus without correction. HRMS were carried out on Agilent 6530 Accurate-Mass Q-TOF mass spectrometer at Atatürk University East Anatolia High Technology Application and Research Center. Gas chromatography (GC) analysis was performed on an Agilent 6890N gas chromatograph with a HP-5 Agilent 19091J-413 column.

Synthesis of imiazolium salt $\mathbf{L_f}$. A mixture of 4,5-dichloro-1-*H*-imidazole (685 mg, 5.0 mmol) and K_2CO_3 (760 g, 11 mmol) was suspended in CH_3CN (10 mL) and stirred at ambient temperature for 1 h. 4-(Trifluoromethyl)benzyl bromide (1.20 g, 5 mmol) was then added to the suspension. The reaction mixture was stirred under reflux conditions for 2 h. The solution was filtered-off and the solvent was removed under reduced pressure. To the resulting crude product second portion of 4-(Trifluoromethyl)benzyl bromide (1.20 g, 5 mmol) was added and stirred at 160 ºC for 1 h. The colorless mixture first melted and then solidified. The resulting solid dissolved in MeOH (5 mL) and Et_2O (30 mL) was added. The colorless solid that separated out was filtered and washed with Et_2O (2×20 mL) and dried under reduced pressure (2.44 g, 91%). M.p. = 205 ºC. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, 25ºC, ppm): δ = 9.95 (s, 1 H, NC*H*N$^+$), 7.75 (dd, J = 8.0 Hz, 8 H, Ar-*H*), 5.71 (s, 4 H, NCH_2Ar). ^{13}C NMR (100.6 MHz, DMSO-d_6, TMS): δ = 137.8 (d, J = 6.0 Hz, NCHN$^+$), 129.8 (q, J(C,F) = 31.8 Hz), 129.6 (Ar-*C*), 125.9 (q, J(C,F) = 3.6 Hz), 124.4 (q, J(C,F) = 272.4 Hz), 119.9 (N*C*=*C*N), 51.4 (N*C*H_2Ar). ^{19}F NMR (376 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = – 61.3. HRMS (APCI) *m/z*: [M–Br]$^+$ Calcd for $C_{19}H_{13}BrCl_2F_6N_2$ 453.0360; Found: 453.0351.

Synthesis of Ir^I–NHC complexes used in this study. Under an argon atmosphere, a mixture of $\mathbf{L_{a\text{-}f}}$ (0.5 mmol) and Ag_2O (58 mg, 0.25 mmol) was suspended in degassed CH_2Cl_2 (10 mL) and stirred at ambient temperature for 1 h shielded from light. $[IrCl(COD)]_2$ (168 mg, 0.25 mmol) was then added to the suspension and the reaction mixture was stirred at ambient temperature for more 12 h. The resulting suspension was filtered over Celite®. The remaining solid was washed with CH_2Cl_2 (2×5 mL) and the solvent of the filtrate was evaporated. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure complex as a yellow solid. Complexes **1b**, **1c**, **1e** and **1f** are new compounds and spectroscopic data are given below.

*Complex **1b***. Yield: 85%, 305 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 7.64 (d, 4 H, J = 8.0 Hz, Ar-*H*), 7.52 (d, 4 H, J = 8.0 Hz, Ar-*H*), 6.71 (s, 2 H, NC*H*=C*H*N), 6.01 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 5.58 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 4.69 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.90 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.21-2.08 (m, 4 H, COD-CH_2), 1.78-1.72 (m, 2 H, COD-CH_2), 1.62-1.56 (m, 2 H, COD-CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 182.1 (Ir-$C_{carbene}$), 140.1 (Ar-*C*), 130.5 (d, J(C,F) = 32.0 Hz), 128.4 (Ar-*C*), 125.9 (q, J(C,F) = 4.0 Hz), 123.9 (d, J(C,F) = 271.0 Hz), 120.8 (NHC=*C*HN), 86.1 (COD-C*H*), 53.8 (NCH_2Ar), 52.2 (COD-C*H*), 33.5 (COD-*C*H_2), 29.9 (COD-CH_2). ^{19}F NMR (376 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = – 62.7. Anal. Calcd for $C_{27}H_{26}ClF_6IrN_2$: C, 45.03; H, 3.64; N, 3.89. Found: C, 44.98; H, 3.66; N, 3.88. HRMS (APCI) *m/z*: [M–Cl+H]$^+$ Calcd for $C_{27}H_{27}F_6IrN_2$ 684.1684 (59.5%); Found 684.1718.

*Complex **1c***. Yield: 81%, 262 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 7.32 (d, 4 H, J = 8.4 Hz, Ar-*H*), 6.89 (d, 4 H, J = 8.4 Hz, Ar-*H*), 6.62 (s, 2 H, NC*H*=C*H*N), 5.75 (d, J = 14.4 Hz, 2 H, NCH_2Ar), 5.46 (d, J = 14.4 Hz, 2 H, NCH_2Ar), 4.66 (t, J = 2.6 Hz, 2 H, COD-C*H*), 3.79 (s, 6 H, OCH_3), 2.99 (t, J = 2.6 Hz, 2 H, COD-C*H*), 2.21-2.16 (m, 4 H, COD-CH_2), 1.76-1.68 (m, 2 H, COD-CH_2), 1.64-1.57 (m, 2 H, COD-CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 180.3 (Ir-$C_{carbene}$), 159.5 (Ar-*C*), 129.7 (Ar-*C*), 128.3 (Ar-*C*), 120.1 (NHC=*C*HN), 114.2 (Ar-*C*), 84.7 (COD-C*H*), 55.3 (O*C*H_3), 53.4 (NCH_2Ar), 51.8 (COD-C*H*), 33.6 (COD-*C*H_2), 29.5 (COD-CH_2). Anal. Calcd for $C_{27}H_{32}ClIrN_2O_2$: C, 50.34; H, 5.01; N, 4.35. Found: C, 50.41; H, 5.02; N, 4.31. HRMS (APCI) *m/z*: [M–Cl]$^+$ Calcd for $C_{27}H_{32}IrN_2O_2$ 609.2093; Found: 609.2094.

*Complex **1e***. Yield: 89%, 292 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 7.38-7.29 (m, 10 H, Ar-*H*), 5.83 (dd, J = 15.6 Hz, 4 H, NCH_2Ar), 4.71 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.69 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.17-2.08 (m, 2 H, COD-CH_2), 1.93-1.84 (m, 2 H, COD-CH_2), 1.71-1.64 (m, 2 H, COD-CH_2), 1.47-1.40 (m, 2 H, COD-CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 182.7 (Ir-$C_{carbene}$), 135.5 (N*C*=*C*N), 128.7 (Ar-*C*), 127.9 (Ar-*C*), 127.2 (Ar-*C*), 116.8 (Ar-*C*), 86.7 (COD-C*H*), 53.6 (NCH_2Ar), 53.2 (COD-C*H*), 33.3 (COD-*C*H_2), 29.2 (COD-CH_2). Anal. Calcd for $C_{25}H_{26}Cl_3IrN_2$: C, 45.98; H, 4.01; N, 4.29. Found: C, 46.07; H, 3.97; N, 4.27. HRMS (APCI) *m/z*: [M–Cl]$^+$ Calcd for $C_{25}H_{26}Cl_2IrN_2$ 617.1102; Found: 617.1096.

*Complex **1f***. Yield: 90%, 356 mg. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 7.65 (d, 4 H, J = 8.0 Hz, Ar-*H*), 7.55 (d, 4 H, J = 8.0 Hz, Ar-*H*), 6.07 (d, J = 15.6 Hz, 2 H, NCH_2Ar), 5.72 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 4.75 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.67 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.18-2.09 (m, 2 H, COD-CH_2), 1.99-1.90 (m, 2 H, COD-CH_2), 1.77-1.69 (m, 2 H, COD-CH_2), 1.56-1.49 (m, 2 H, COD-CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = 182.3 (Ir-$C_{carbene}$), 139.1 (Ar-*C*), 130.4 (q, J(C,F) = 32.7 Hz), 127.7 (Ar-*C*), 125.8 (q, J(C,F) = 3.6 Hz), 123.9 (d, J(C,F) = 269.1 Hz),

116.9 (N*C*≡*C*N), 87.9 (COD-C*H*), 53.3 (NCH_2Ar), 53.1 (COD-C*H*), 33.3 (COD-*C*H_2), 29.2 (COD-CH_2). ^{19}F NMR (376 MHz, $CDCl_3$, TMS, 25ºC, ppm): δ = – 62.7. Anal. Calcd for $C_{27}H_{24}Cl_3F_6IrN_2$: C, 41.10; H, 3.07; N, 3.55. Found: C, 41.04; H, 3.04; N, 3.51. HRMS (APCI) *m/z*: $[M–Cl]^+$ Calcd for $C_{27}H_{24}Cl_2F_6IrN_2$753.0850; Found: 753.0841.

General procedure for the dehydrogenative coupling of secondary alcohols with primary alcohols to give *α*-alkylated ketones. In a 20 mL reaction tube (1 cm × 20 cm) with a condenser were added KOH (5.6 mg, 0.1 mmol, 0.1 equiv.) secondary alcohol (1.0 mmol), primary alcohol (1.0 mmol) and a solution of complex **1** (0.005 mmol, 0.5 mol%) in toluene (2.0 mL) under air atmosphere. The reaction mixture was vigorously stirred (1200 rpm) under reflux in a preheated oil bath at 130 ºC for 2–4 h. Then the reaction mixture was cooled to ambient temperature and a 10 μL solution was syringed out for GC analysis. The solvent was evaporated and the crude product was submitted for NMR analysis to calculate the conversion and product selectivity (**4**:**4′**). All the crude products were combined after analysis and purified by silica gel column chromatography using hexane and ethyl acetate (9:1) mixture as eluent to afford the desired ketone.

General procedure for the *α*-alkylation of ketones with primary alcohols to give *α*-alkylated ketones. In a 20 mL reaction tube (1 cm × 20 cm) with a condenser were added KOH (2.8 mg, 0.05 mmol, 0.05 equiv.) ketone (1.0 mmol), primary alcohol (1.0 mmol) and a solution of complex **1** (0.0005 mmol, 0.05 mol%) in toluene (1.0 mL) under air atmosphere. The reaction mixture was vigorously stirred (1200 rpm) under reflux in a preheated oil bath at 130 ºC for 2–4 h. Then the reaction mixture was cooled to ambient temperature and a 10 μL solution was syringed out for GC analysis. The solvent was evaporated and the crude product was submitted for NMR analysis to calculate the conversion. All the crude products were combined after analysis and purified by silica gel column chromatography using hexane and ethyl acetate (9:1) mixture as eluent to afford the desired ketone.

*1,3-Diphenylpropan-1-one (**4aa**).*[5,6f,7,14a,22] White solid; 89% yield (187 mg) for Scheme 3 and 91% yield (191 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.98 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.34-7.21 (m, 5H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.1, 141.3, 136.9, 133.0, 128.6, 128.6, 128.5, 128.0, 126.1, 40.4, 30.2.

*3-Phenyl-1-(p-tolyl)propan-1-one (**4ba**).*[14a,23] White solid; 93% yield (209 mg) for Scheme 3 and 97% yield (218 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.89 (d, *J* = 8.0 Hz, 2H), 7.34-7.23 (m, 7H), 3.29 (t, *J* = 7.4 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.8, 143.8, 141.4, 134.5, 129.3, 128.5, 128.4, 128.2, 126.1, 40.3, 30.3, 21.6.

*1-(4-Methoxyphenyl)-3-phenylpropan-1-one (**4ca**).*[3,7,14a,24] White solid; 98% yield (235 mg) for Scheme 3 and 96% yield (231 mg) for Scheme 4.. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 8.8 Hz, 2H), 7.32-7.19 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (t, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.8, 163.4, 141.5, 130.3, 130.0, 128.5, 128.4, 126.1, 113.7, 55.4, 40.1, 30.3.

*1-(Naphthalen-2-yl)-3-phenylpropan-1-one (**4da**).*[5,7,14a,25] White solid; 86% yield (224 mg) for Scheme 3 and 94% yield (245 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.47 (s, 1H), 8.06 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 7.2 Hz, 2H), 7.63-7.53 (m, 2H), 7.37-7.29 (m, 4H), 7.27-7.20 (m, 1H), 3.45 (t, *J* = 7.6 Hz, 2H), 3.16 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.1, 141.4, 135.6, 134.2, 132.5, 129.6, 129.5, 129.1, 128.6, 128.5, 128.4, 128.4, 127.7, 126.7, 126.2, 123.8, 40.5, 30.3.

*2-Benzyl-3,4-dihydronaphthalen-1-one (**4ea**).*[5,7,11,14a] Yellow oil; 96% yield (227 mg) for Scheme 3 and 89% yield (210 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.11 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.35-7.22 (m, 7H), 3.52 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 2.99-2.88 (m, 2H), 2.81-2.65 (m, 2H), 2.16-2.09 (m, 1H), 1.86-1.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 144.0, 140.0, 133.3, 132.5, 129.3, 128.7, 128.4, 127.5, 126.6, 126.1, 49.5, 35.7, 28.6, 27.7.

*1-(4-Bromophenyl)-3-phenylpropan-1-one (**4fa**).*[5,7,14a,26] White solid; 73% yield (211 mg) for Scheme 3 and 90% yield (260 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.81 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.32-7.21 (m, 5H), 3.26 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.1, 141.0, 135.6, 131.9, 129.6, 128.6, 128.4, 128.2, 126.2, 40.4, 30.1.

*1-(4-Chlorophenyl)-3-phenylpropan-1-one (**4ga**).*[5,7,14a,27] White solid; 72% yield (176 mg) for Scheme 3 and 86% yield (210 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.89 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.32-7.19 (m, 5H), 3.27 (t, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 197.9, 141.1, 139.5, 135.2, 129.4, 129.0, 128.9, 128.6, 128.5, 128.4, 126.2, 40.4, 30.1.

*1-Phenyl-3-(p-tolyl)propan-1-one (**4ab**).*[6f,7,9d] White solid; 93% yield (209 mg) for Scheme 3 and 92% yield (206 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.99 (d, *J* = 8.0 Hz, 2H), 7.56 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.49-7.45 (m, 2H), 7.19-7.13 (m, 4H), 3.30 (t, *J* = 7.6 Hz, 2H), 3.07 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 138.2, 137.0, 135.6, 133.0, 129.2, 128.6, 128.3, 128.1, 40.6, 29.8, 21.0.

*3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**4ac**).*[6,7,9,12] White solid; 91% yield (219 mg) for Scheme 3 and 96% yield (231 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.97 (d, *J* = 8.0 Hz, 2H), 7.56 (tt, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 9.2 Hz, 2H), 3.79 (s, 3H), 3.28 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 158.0, 136.9, 133.3, 132.9, 129.3, 128.6, 128.0, 113.9, 55.3, 40.7, 29.3.

*3-(4-Isopropylphenyl)-1-phenylpropan-1-one (**4ad**).*[12b,14a] Colorless oil; 87% yield (220 mg) for Scheme 3 and 90% yield (227 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.01 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.26-7.21 (m, *5*H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.98-2.91 (m, 1H), 1.31 (d, *J* = 6.8 Hz, 6H), ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.3, 146.7, 138.6, 137.0, 133.0, 128.6, 128.4, 128.1, 126.6, 40.6, 33.8, 29.8, 24.1.

*3-(4-Bromophenyl)-1-phenylpropan-1-one (**4ae**).*[7,9d,14a,28] White solid; 81% yield (234 mg) for Scheme 3 and 92% yield (266 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 7.4 Hz, 2H), 3.03 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.7, 140.2, 136.7, 133.1, 131.5, 130.2, 128.6, 127.9, 119.8, 40.0, 29.4.

*3-(4-Chlorophenyl)-1-phenylpropan-1-one (**4af**).*[7,9d,14a,27] White solid; 74% yield (181 mg) for Scheme 3 and 94% yield (230 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.28 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.7, 139.7, 136.7, 133.1, 131.8, 129.8, 128.6, 128.5, 127.9, 40.09, 29.38.

*3-(2-Chlorophenyl)-1-phenylpropan-1-one (**4ag**).*[9c] White solid; 67% yield (164 mg) for Scheme 3 and 85% yield (208 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.97 (d, *J* = 8.0 Hz, 2H), 7.56 (tt, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.37-7.30 (m, 2H), 7.22-7.14 (m, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 3.18 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.9, 138.8, 136.8, 133.9, 133.1, 130.8, 129.6, 128.6, 128.0, 127.7, 126.7, 38.4, 28.3.

*3-(2,4,6-Trimethylphenyl)-1-phenylpropan-1-one (**4ah**).*[29] White solid; 88% yield (222 mg) for Scheme 3 and 82% yield (207 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.96 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.88 (s, 2H), 3.14-3.02 (m, 4H), 2.32 (s, 6H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.5, 136.9, 136.1, 135.5, 134.8, 133.1, 129.1, 128.7, 128.1, 38.0, 23.8, 20.9, 19.8.

*3-(2-Methoxyphenyl)-1-phenylpropan-1-one (**4ai**).*[3,7] White solid; 92% yield (221 mg) for Scheme 3 and 96% yield (231 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.99 (t, *J* = 6.8 Hz,

2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.24-7.20 (m, 2H), 6.93-6.86 (m, 2H), 3.84 (s, 3H), 3.28 (t, *J* = 7.8 Hz, 2H), 3.07 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 199.9, 157.5, 137.0, 132.9, 130.2, 129.6, 128.5, 128.1, 127.5, 120.6, 110.3, 55.2, 38.9, 25.7.

*3-(Furan-2-yl)-1-phenylpropan-1-one (**4aj**).*[6f,14a] Yellow oil; 80% yield (160 mg) for Scheme 3 and 85% yield (170 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.98 (d, *J* = 7.2 Hz, 2H), 7.57 (tt, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 1H), 7.46 (t, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 1.6 Hz, 1H), 6.28 (dd, J_1 = 3.0 Hz, J_2 = 1.8 Hz, 1H), 6.05 (d, *J* = 3.2 Hz, 1H), 3.34 (t, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 198.6, 154.7, 141.1, 136.8, 133.1, 128.6, 128.0, 110.2, 105.3, 36.9, 22.5.

*1-Phenylnonan-1-one (**4ak**).*[30] Colorless oil; 91% yield (199 mg) for Scheme 3 and 81% yield (177 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.77-1.69 (m, 2H), 1.39-1.27 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 200.5, 137.1, 132.7, 128.5, 128.0, 38.6, 31.8, 29.4, 29.4, 29.1, 24.4, 22.6, 14.0.

*1-Phenyldecan-1-one (**4al**).*[7,14a,31] Colorless oil; 94% yield (218 mg) for Scheme 3 and 85% yield (198 mg) for Scheme 4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.95 (d, *J* = 8.8 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.77-1.70 (m, 2H), 1.40-1.27 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 200.4, 137.1, 132.8, 128.5, 128.0, 38.6, 31.9, 29.5, 29.4, 29.4, 29.3, 24.4, 22.6, 14.1.

ASSOCIATED CONTENT

Supporting Information

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

Traces of ^{1}H, ^{13}C NMR and HRMS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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