Pd(II)-catalyzed Denitrogenative & Desulfinative Addition of Arylsulfonyl Hydrazides with Nitriles

Mengting Meng, Liangfeng Yang, Kai Cheng, and Chenze Qi

Just Accepted

Pd(II)-catalyzed Denitrogenative & Desulfinative Addition of Arylsulfonyl Hydrazides with Nitriles

Mengting Meng, Liangfeng Yang, Kai Cheng* and Chenze Qi

Zhejiang Key Laboratory of Alternative Technologies for Fine Chemicals Process, Shaoxing University, 312000, Shaoxing, People's Republic of China, chengkai@usx.edu.cn. Fax:+86-575-88345682; Tel: +86-575-88345682.
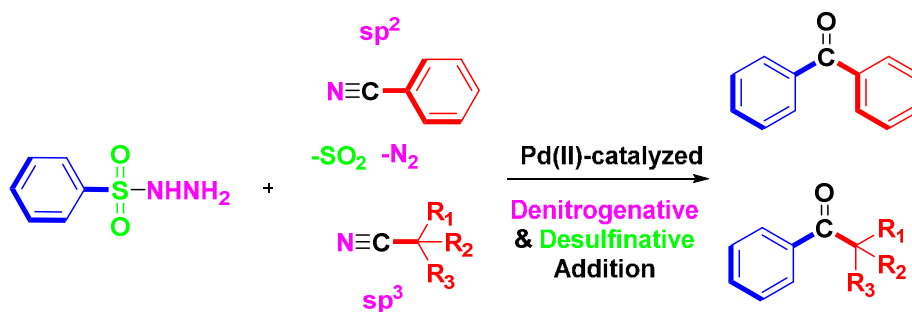
Abstracts

A Pd(II)-catalyzed denitrogenative & desulfinative addition of arylsulfonyl hydrazides with nitriles has been successfully achieved under mild conditions. This transformation is a new method for the addition reaction to nitriles with arylsulfonyl hydrazides as arylating agent, thus providing an alternative synthesis of aryl ketones. The reported addition reaction is tolerant to many common functional groups, and work well in the presence of electron-donating and electron-withdrawing substituents. Notably, the reported denitrogenative & desulfinative addition was also be appropriate for alkyl nitriles, making this newly developed transformation attractive.

Keywords: denitrogenative & desulfinative addition, arylsulfonyl hydrazides,

Pd(II)-catalyzed, addition with nitriles, synthesis of aryl ketones

Introduction

The aryl ketone moiety is one of the most fundamental and common building blocks occurring in many pharmaceuticals, fragrances, natural products and synthetic biologically active molecules.[1] Aryl ketones are widely regarded as a privileged skeleton with broad pharmaceutical activities, including neuroprotective drug (Nizofenone), antiarrhythmic (Pitofenone), hypolipidemic (Fenofibrate), antitussive (Morclofone), uricosuric (Benzarone, Tienilic acid), anxiolytic (Indiplon), anti-inflammatory (Suprofen, Ketorolac), NSAID (Amtolmetin guacil), antiseptic (Pyoluteorin), antihelmintic (Flubendazole), antineoplastic (Nocodazole), phosphodiesterase inhibitor (Piroximone), anticancer (ITE) and antitumor (Topsentin).(Scheme 1)
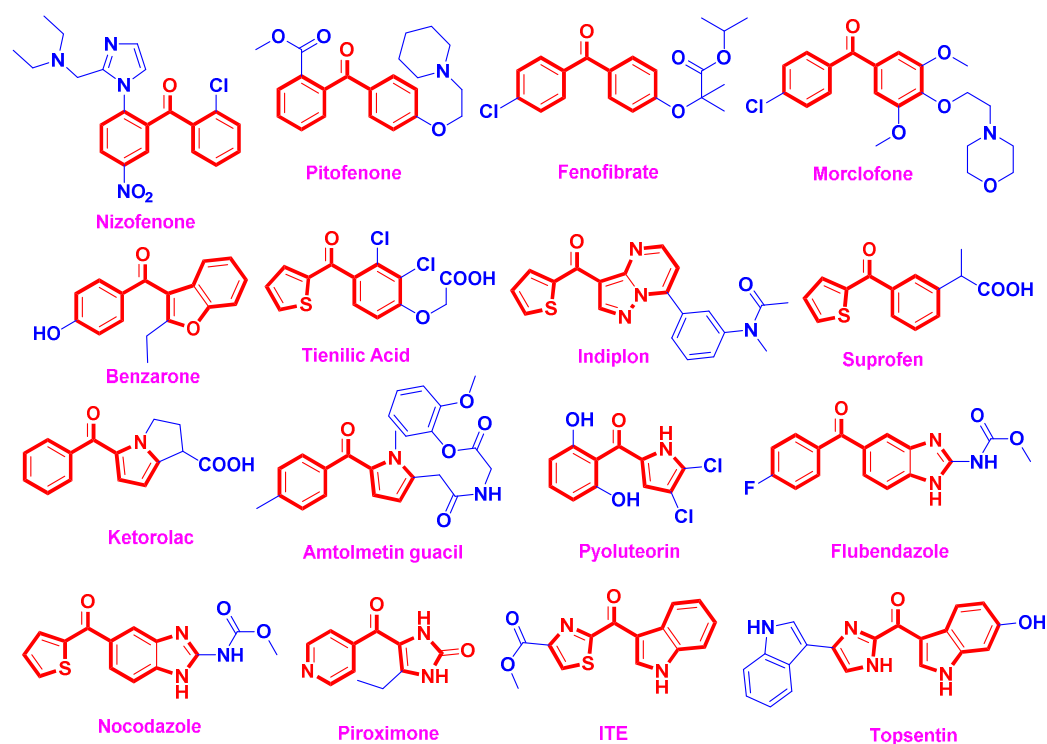
Scheme 1 Arylketone Skeletons in Drug Molecule

Classical routes to synthesize aryl ketones mainly rely on the Friedel–Crafts acylation of

aromatic compounds in the presence of strong Lewis acids such as corrosive $AlCl_3$, although the reaction sometimes fails with electron-deficient arenes and suffer from low functional group tolerance generally yields the desired products as isomeric mixtures.[2] The reactions of stoichiometric organometallic compounds with acid chlorides, or Weinreb amides are also popular and well-known for the preparation of ketones, provides us with an protocol for the synthesis of aryl ketones.[3] However, the poor functional group tolerance and strict handling requirement of the organometallic reagents limits their applications and thus there is a need for cleaner, milder and catalytic alternatives.[4] Consequently, it continues to inspire the development of methods for the construction of this structural element. During the last decade, transition metal catalysts have been utilized for the synthesis of many compounds, and transition-metal-catalyzed reactions provide many opportunities for the synthesis of aryl ketones.[5]

Nitriles are normally very stable and widely commercially available. On the other hand, transformations of nitriles play an important role in both the laboratory and industry due to their well-recognized chemical versatility. The nucleophilic addition of organometallic reagents to nitriles is an old and well-known reaction for ketone preparation. However, the nitrile group is generally inert in organometallic reactions, and thus acetonitriles or benzonitriles usually participate as solvents or ligands in transition-metal-catalyzed coupling reactions.[6] Among them, it is an attractive and useful synthetic method for preparing aryl ketones from aryl halides and nitriles through selective addition and subsequent in situ hydrolysis. In recent years, the transition-metal-catalyzed addition reaction has resulted in great progress in the synthesis of aryl ketones from nitriles. The addition of arylpalladium species to the cyano group, pioneered by the Larock group[7] and elegantly employed in recent years,[8] provided a conceptual basis for this

palladium-catalyzed approach.

Arylsulfonyl hydrazides are multipurpose and readily accessible intermediates in organic synthesis, which are more air-stable than sulfonyl chlorides, can be synthesized directly from the reaction of hydrazine hydrates with arylsulfonyl chloride.[9] In general, they exist as solids that are noncorrosive, compatible with water, and free of unpleasant odor. The electrophiles avoid the production of undesired halide-containing byproducts and hence are more environmentally desirable. Arylsulfonyl hydrazides are good cross-coupling partners for ready generation of reactive diazo compounds,[10] as sulfonyl sources in organic synthesis.[11] Arylsulfonyl hydrazides can also react with carbon nucleophilic reagents by I_2 to form various C–S bonds as sulfenylation reagents.[12] Recently, these compounds have also successfully been used as aryl sources via desulfitation–denitrogenation have also been used in desulfinative cross-coupling reactions.[13] Desulfinative reactions not only produce sulfur dioxide as their main byproduct, but the loss of gaseous SO_2 is also the main driving force of desulfinative processes.[14] In order to achieve greener, more sustainable chemistry, this gas should not be wasted but rather recycled, possibly as the feedstock for another process.[15]

Nowadays, arylsulfonyl hydrazides have been acted as arylating agents under desulfinative processes (Scheme 2), mostly by direct C-H arylation of heteroarenes[16] (such as benzoxazole, indole, indolizine, caffeine), and cross-coupling reaction[17] (such as Sonogashira, Suzuki, Hiyama, Heck, iodination and homocoupling). However, the desulfinative addition with arylsulfonyl hydrazides was under development. The only example was reported by Deng et al.[18] for desulfinative conjugate addition of unsaturated carbonyl compounds. In continuing with our interest in desulfinative coupling and addition with nitriles,[19] herein we reported the first example

of desulfinative addition of nitriles with arylsulfonyl hydrazides with good to excellent efficiency.

Both aryl and alkyl nitriles could afford corresponding aryl ketones in high yields.
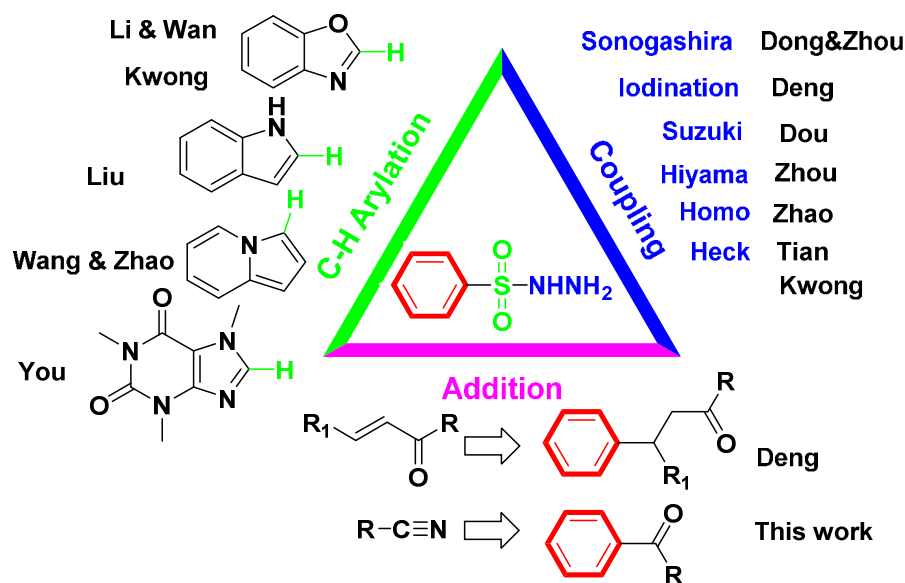
Scheme 2 Pd-catalyzed denitrogenative & desulfinative reaction of arylsulfonyl hydrazides

Results and Discussion

Our studies commenced by evaluating the feasibility of the desulfinative addition reaction with the investigation of reaction parameters with phenylsulfonyl hydrazides and benzonitrile in the presence of active cationic Pd(II) species. The use of Pd(OAc)$_2$ was explored in DMSO with 1 equiv H$_2$O at 80°C under air in the presence of various ligands used previously in analogous Pd-catalyzed transformations (Table 1). Unsurprisingly, the phosphine ligands (PPh$_3$, dppf, BINAP), which has been recognized as a weakly coordinating promoter in desulfinative reaction, failed to generate the desired product (Table 1, **1a-1c**). To our delight, 62% yield of the desired desulfinative addition product was found using 3 mol% of tetramethylethane-1,2-diamine (TMEDA) as ligand (Table 1, **1d**). A series of diamine ligands, including 1,2-diamine, 1,2-diphenylethane-1,2-diamine and benzene-1,2-diamine, was subsequently tested, and each of these catalysts was less effective than TMEDA (Table 1, **1e-1g**).

4,4,4',4'-Tetramethyl-4,4',5,5'-tetrahydro-2,2'-bioxazole was ineffective to this transformation

(Table 1, **1h**). To our delight, the application of bpy ligand (2,2'-bipyridine) increased the yields

to 71% (Table 1, **1i**). A screen of various phen-type ligands, such as 1,10-phenanthroline (phen),

4,7-dimethoxy-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline,

4,7-dichloro-1,10-phenanthroline and 2,2'-biquinoline (bq), revealed bq was the best choice (Table

1, **1j-1n**). In genaral, the use of a ligand is essential to obtain synthetically useful yield of biphenyl

ketone from the desulfinative addition reaction. Additionally, no desired product is obtained in the

absence of any ligands.

Table 1 Ligand selection of the desulfinative addition reaction [a]
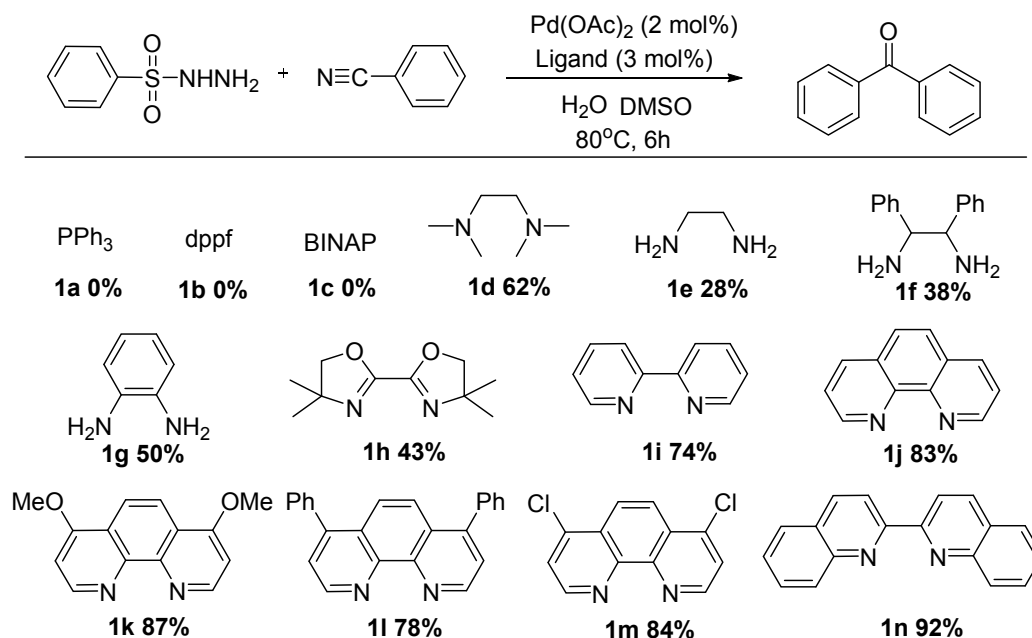
PPh$_3$	dppf	BINAP	1d 62%	1e 28%	1f 38%
1a 0%	**1b 0%**	**1c 0%**	**1d 62%**	**1e 28%**	**1f 38%**

1g 50%   1h 43%   1i 74%   1j 83%

1k 87%   1l 78%   1m 84%   1n 92%

[a] Reaction conditions: phenylsulfonyl hydrazide (1.1 mmol), benzonitrile (1.0 mmol), Pd(OAc)$_2$ (2 mol%),

ligand (3 mol%), H$_2$O (2.0 mmol), DMSO (2 mL), 80 ^{o}C, 6 h. Isolated yields.

Encouraged by the aforementioned results, other reaction conditions were investigated,

including the choice of catalyst and solvent. The results are summarized in Table 2. We initially

examined palladium, ruthenium, and rhodium catalysts, respectively, using phenylsulfonyl

hydrazide and benzonitrile as our standard substrates and bq as the ligand. The reactions were

carried out in DMSO with 1 equiv H_2O at 80 °C for 6 h. It was shown that Rh and Ru complex are

not effective for this reaction (Table 2, entries 1 and 2). The reaction failed to proceed in the

absence of palladium catalyst (Table 1, entry 3), suggesting that palladium catalyst is very crucial

for the formation of benzophenone compound. As detailed in Table 2, the optimal conditions for

the desulfinative addition can be applied toward the use of other palladium catalysts. Application

of Pd(dba)$_2$ as a catalyst yielded traces of desired product (Table 2, entry 4). It was observed that

most of the Pd(II) catalysts could successfully promote the reaction (Table 2, entries 5−12).

Therefore, PdCl$_2$, PdBr$_2$ and PdI$_2$ in combination with bq was applied affording benzophenone in

yields varying between 72% and 82% (Table 2, entries 5-7). It should be noted that Pd(TFA)$_2$ and

Pd(OTf)$_2$ were less effective than Pd(OAc)$_2$ for this reaction (Table 2, entries 8−10). Among the

Pd(II) catalysts tested, Pd(OAc)$_2$ was the most effective affording the addition product in 92%

yield (Table 2, entry 10). The introduction of various palladium with nitrogen ligands

(Pd(CH$_3$CN)$_2$Cl$_2$ and Pd(PhCN)$_2$Cl$_2$) didn't increased the yields (Table 2, entries 11−12). Various

solvents were screened, and the results revealed that aprotic solvent is the better choice for the

reaction (Table 2, entries 13−15). Although many traditional solvents have been tested, no better

results were obtained (Table 2, entries 16−18). Only a trace amount of product was detected with

other solvent, such as EA, hexane and DCM (Table 2, entries 19−21). Unfortunately, the desired

product was not obtained in water (Table 2, entry 22). Moreover, the yield was slightly decreased

when the reaction was performed in DMSO with a lower or higher amount of additional water

(Table 2, entries 23−24). Among these, DMSO was determined optimum, and benzophenone was

isolated in 92% yield.

Table 2 Desulfinative addition of phenylsulfonyl hydrazides with benzonitrile with various catalysts in various solvents [a]
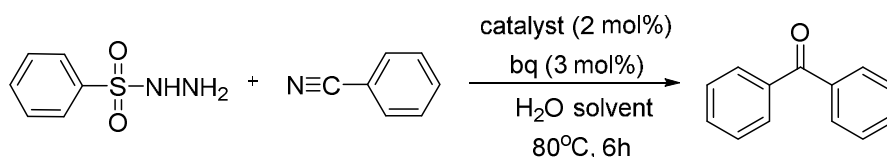
entry	catalyst (in DMSO)	yield (%) [b]	entry	Solvent (with Pd(OAc)$_2$)	yield (%) [c]
1	RuCl$_2$(PPh$_3$)$_3$	-	13	DMF	88
2	RhCl(PPh$_3$)$_3$	-	14	DMA	81
3	-	-	15	acetone	73
4	Pd(dba)$_2$	<5	16	1,4-dioxane	53
5	PdCl$_2$	77	17	THF	45
6	PdBr$_2$	82	18	DME	60
7	PdI$_2$	72	19	EA	<5
8	Pd(TFA)$_2$	81	20	hexane	<5
9	Pd(OTs)$_2$	86	21	DCM	<5
10	Pd(OAc)$_2$	92	22	H$_2$O	-
11	Pd(CH$_3$CN)$_2$Cl$_2$	83	23	DMSO	77 [d]
12	Pd(PhCN)$_2$Cl$_2$	78	24	DMSO	84 [e]

[a] Reaction conditions: phenylsulfonyl hydrazide (1.1 mmol), benzonitrile (1.0 mmol), bq (3 mol%), 80 °C, 6 h. Isolated yields. [b] catalyst (2 mol%), H$_2$O (2.0 mmol), DMSO (2 mL). [c] Pd(OAc)$_2$ (2 mol%), H$_2$O (2.0 mmol), solvent (2 mL). [d] Pd(OAc)$_2$ (2 mol%), H$_2$O (1.0 mmol), DMSO (2 mL). [e] Isolated yields. Pd(OAc)$_2$

(2 mol%), H$_2$O (4.0 mmol), DMSO (2 mL).

Furthermore, considerable efforts have been made to test the substrate scope of this reaction under the optimized reaction conditions. We applied this catalytic system to various arylsulfonyl hydrazides with benzonitrile, and this reaction showed good compatibility with different groups on aryl rings (Table 3). Electron-rich, electron-neutral, and electron-deficient arylsulfonyl hydrazides afford the desired products in modest to good yields (Table 3, **3a-3e**). The transformation is compatible with a number of synthetically versatile functional groups including methoxy, fluoro, nitro, and trifluoromethyl. Position varied methyl and chloro phenylsulfonyl hydrazides with *para*-, *meta*- and *ortho*-substitution also couple with benzonitrile to afford the corresponding diaryl ketone products in good yields (Table 3, **3f-3k**). In general, the efficiency of these reactions is attenuated relative to those with high steric hindrance. Treatment of highly steric hindrance permethyl phenylsulfonyl hydrazides also provided the desired product in 73% yield (Table 3, **3l**). Notably, when the *p*-bromo phenylsulfonyl hydrazides is used, corresponding desulfinative addition product is obtained in high yield, suggesting that the bromide leaving group in the electrophile could survived and the relative reactivity toward desulfinative addition over traditional coupling methods (Table 3, **3m**). Heteroaryl-substituted sulfonyl hydrazides led to a slightly lower yield of the desired products (Table 3, **3n-3o**).

Table 3 Scope of desulfinative addition with various arylsulfonyl hydrazides [a]
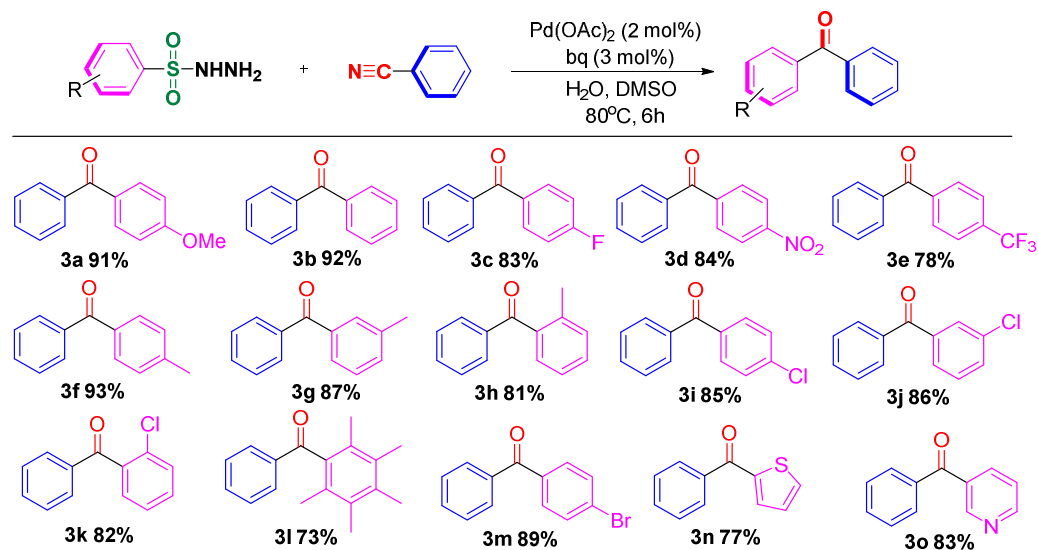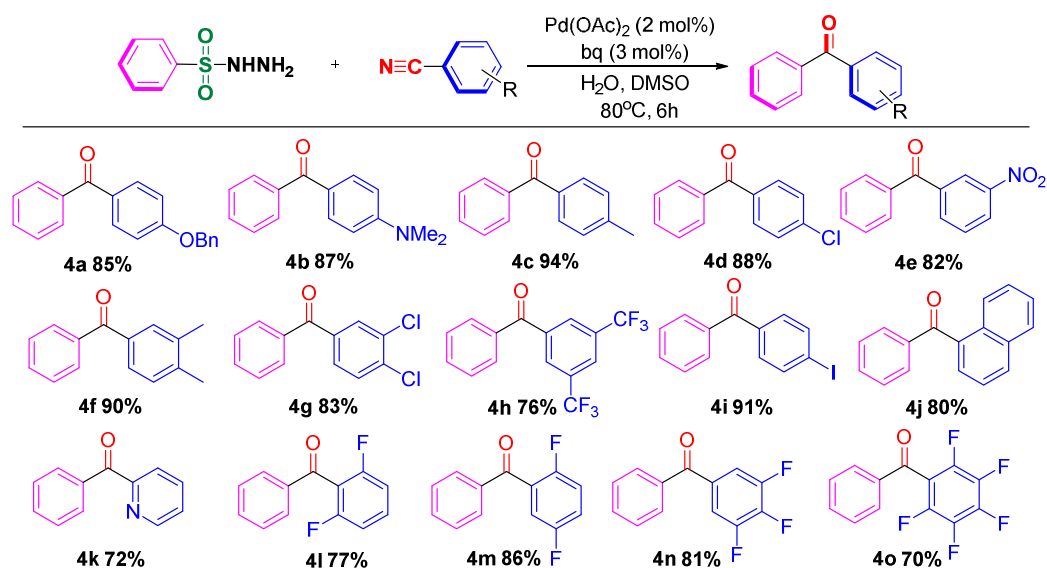
^a Reaction conditions: arylsulfonyl hydrazide (1.1 mmol), benzonitrile (1.0 mmol), Pd(OAc)$_2$ (2 mol%), bq (3 mol%), H$_2$O (2.0 mmol), DMSO (2 mL), 80 °C, 6 h. Isolated yields.

Having explored the preliminary scope for the desulfinative addition of various arylsulfonyl hydrazide, we next examined the reaction of phenylsulfonyl hydrazide with other aryl nitriles (Table 4). Electron-deficient, electron-rich, and moderately electron-deficient aryl nitriles couple with phenylsulfonyl hydrazide to afford the products in good to excellent yields (Table 4, **4a-4e**). In addition, *ortho*- and *meta*-substituted aryl nitriles could also be well tolerated, generating the desired coupling products in moderate to good yields (Table 4, **4f-4g**). *meta*-Trifluoromethyl disubstituted benzonitrile also participate effectively in this desulfinative reaction (Table 4, **4h**). The tolerance of the iodo group is especially significant, as successive functional-group transformations are hopeful (Table 4, **4i**). Notably, the naphthalene nitrile also underwent Pd-catalyzed addition method, as did reactions of heteroaromatic nitrile was also proceeded smoothly (Table 4, **4j-4k**). The reaction of multiple fluoro substituted benzonitriles with phenylsulfonyl hydrazide was next examined. Both 2,6-difluoro and 2,5-difluoro benzonitriles

couple with phenylsulfonyl hydrazide to afford the desired products with comparable efficiencies (Table 4, **4l-4m**). However, the efficiency of the reactions using the perfluoro benzonitriles is lower than that with trifluoro substituted and difluoro substituted substrates (Table 4, **4n-4o**).

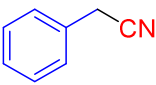**Table 4** Scope of desulfinative addition with various aryl nitriles [a]

4a 85% 4b 87% 4c 94% 4d 88% 4e 82%

4f 90% 4g 83% 4h 76% 4i 91% 4j 80%

4k 72% 4l 77% 4m 86% 4n 81% 4o 70%
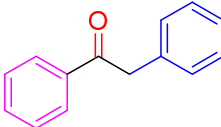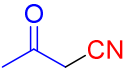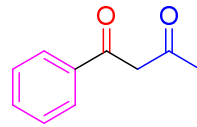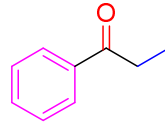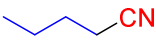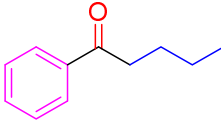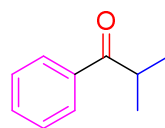
[a] Reaction conditions: phenylsulfonyl hydrazide (1.1 mmol), aryl nitrile (1.0 mmol), Pd(OAc)$_2$ (2 mol%), bq (3 mol%), H$_2$O (2.0 mmol), DMSO (2 mL), 80 °C, 6 h. Isolated yields.

Inspired by the above excellent results, we set out to explore the desulfinative addition of alkyl nitriles. We begin our research by investigating the reaction of phenyl sulfonyl hydrazides with 2-phenylacetonitrile in DMSO with H$_2$O by using Pd(OAc)$_2$ as catalyst and the desired product was obtained in 33% yield. In order to improve the reaction yield, we attempted to optimized the catalysts, ligands, solvents to enhance the reaction efficiency. Thus, we finished the optimization of this challenging reaction with Pd(OAc)$_2$/phen catalysts and H$_2$O additive, in DMF solvents at 100 °C (Table 5, entry 1). Table 5 illustrates a preliminary scope for the reaction of various alkyl nitriles with phenylsulfonyl hydrazide. Importantly, 87% yield of product is obtained with

3-oxobutanenitrile under the reaction conditions (Table 5, entry 2). Structurally varied alkyl

nitriles were couple with phenylsulfonyl hydrazide to afford the corresponding aryl ketone

products in modest to good yields (Table 5, entries 3-6). The reactions of the branched substituted

nitriles with phenylsulfonyl hydrazide were also explored and compared to the analogous

reactions with linear alkyl nitriles. Notably, for substituent, the yield was slightly enhanced with

gradually increasing the size of the substituent from Et, *n*-Bu to i-Pr and finally to cyclopentyl.

Table 5 Scope of desulfinative addition of phenylsulfonyl hydrazides with various   alkyl nitriles

a

entry	alkyl nitrile	product	yield (%) [b]
1			90
2			87
3			75
4			82
5			79

6
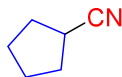
83
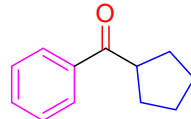
The subsequent solvent examination showed that a recent yield was observed without additional solvent (DMF). The *p*-toluenesulfonyl hydrazide coupling using CH$_3$CN (2 mL) as the solvent affords product *p*-tolylethanone (96%) in higher yield than product (71%) using CH$_3$CN (2 equiv) in DMF. Under the optimized reaction conditions, the scope of substituted arylsulfonyl hydrazides was examined with Pd(OAc)$_2$/phen catalysts and H$_2$O (2 equiv) in CH$_3$CN (Table 6). Functional groups such as ethoxy, methoxy, nitro and fluoro were well tolerated under the optimal reaction conditions (Table 6, **6a–6p**). Notably, reaction with arylsulfonylhydrazide bearing NMe$_2$ and SMe group can also proceed smoothly to give the desired product in 85% and 87% yield and are not affected by the N/S atom (Table 6, **6d–6e**). It was found that arylsulfonyl hydrazides possessing either electron-rich or electron-deficient groups at the *o*-, *m*- or *p*-position proceeded efficiently to afford corresponding aryl ethanone in good to excellent yields (Table 6, **6f–6p**). Furthermore, cyano phenylsulfonyl hydrazide can also be a partner in the reaction to afford *p*-cyano-phenyl ethanone, with the cyano group untouched (Table 6, **6j**). It should be noted that cleavage of C-halogen bond was not observed during the reaction process (Table 6, **6q–6s**). The substrate scope of various steric hindered *ortho*-functionalized aryl sulfonyl hydrazides were explored, only with slightly decrease of efficiency (Table 6, **6m, 6p, 6s**). When mesitylene sulfonyl hydrazides reacted with acetonitrile, slightly lower yields were obtained probably due to the steric effect of the substituents (Table 6, **6i**). In addition, 2-naphthyl substituted sulfonyl hydrazides was also

tested in the reaction and afforded the desired product 3af in 80% yield (Table 6, **6t**).

Table 6 Scope of desulfinative addition of various arylsulfonyl hydrazides with acetonitrile [a]
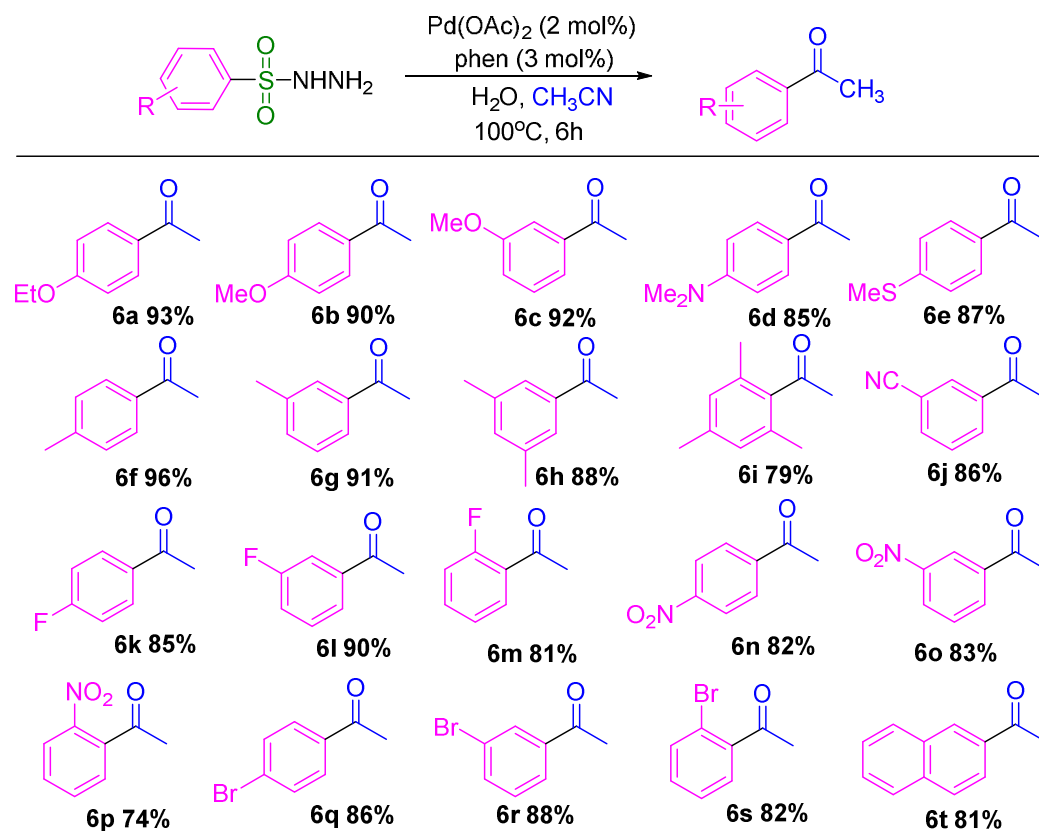
In order to understand the mechanism of the reaction, a series of control experiments were

carried out (Scheme 3). When the reaction was carried out under a nitrogen atmosphere, the

corresponding benzophenone was obtained in 82% yield (Scheme 3, Eq 1, **A**), which indicated

that the reaction didn't required the presence of oxygen. Only 12% yield of desired product was

detected under typical procedure without 2 equiv water (Scheme 3, Eq 1, **B**). Also, the product

formation was completely suppressed upon the addition of the 4A molecular sieve to the reaction

(Scheme 3, Eq 1, **C**). The ^{18}O-labeling experiment was also performed to get more insights into

this reaction process (Scheme 3, Eq 1, **D**), indicating that the oxygen atom in the ketone molecule

was derived from H_2O. Furthermore, when 4-cyano phenylsulfonyl hydrazides was reacted with

benzonitrile or acetonitrile under the optimal conditions, the cross-coupling products

4-benzoylbenzonitrile and 4-acetylbenzonitrile were isolated, respectively without concomitant

formation of 4-(4-(sulfonyl)benzoyl)benzonitrile analogue as the product (Scheme 3, Eq 2 and Eq

3). No homo-coupling products of 4-cyano phenylsulfonyl hydrazides were detected by GC−MS

further. The phthalonitrile and isophthalonitrile substrates can be elaborated using myriad known

transformations of excessive phenylsulfonyl hydrazides for the synthesis of diverse dibenzoyl

motifs (Scheme 3, Eq 4). Another application of the presented desulfinative addition is its

potential for combination with Pd-catalyzed Suzuki–Miyaura cross-coupling to synthesize

(4-biphenylyl) (phenyl) methanone (Scheme 3, Eq 5). The Pd-catalyzed desulfinative addition of

4-iodobenzonitrile with phenylsulfonyl hydrazides, followed by consecutive Suzuki

cross-coupling by the addition of $PhB(OH)_2$, provides the 4-biphenylyl-benzophenone in the yield

of 83%. This approach has great potential in combination of Pd-catalyzed

addition/Suzuki-coupling by the sequential addition of reagents. Finally, the desulfinative addition

of both aryl nitriles and alkyl nitriles were scalable on gram scale, which showed the potential of

our palladium-catalyzed methods in the industrial application (Scheme 3, Eq 6 and Eq 7).
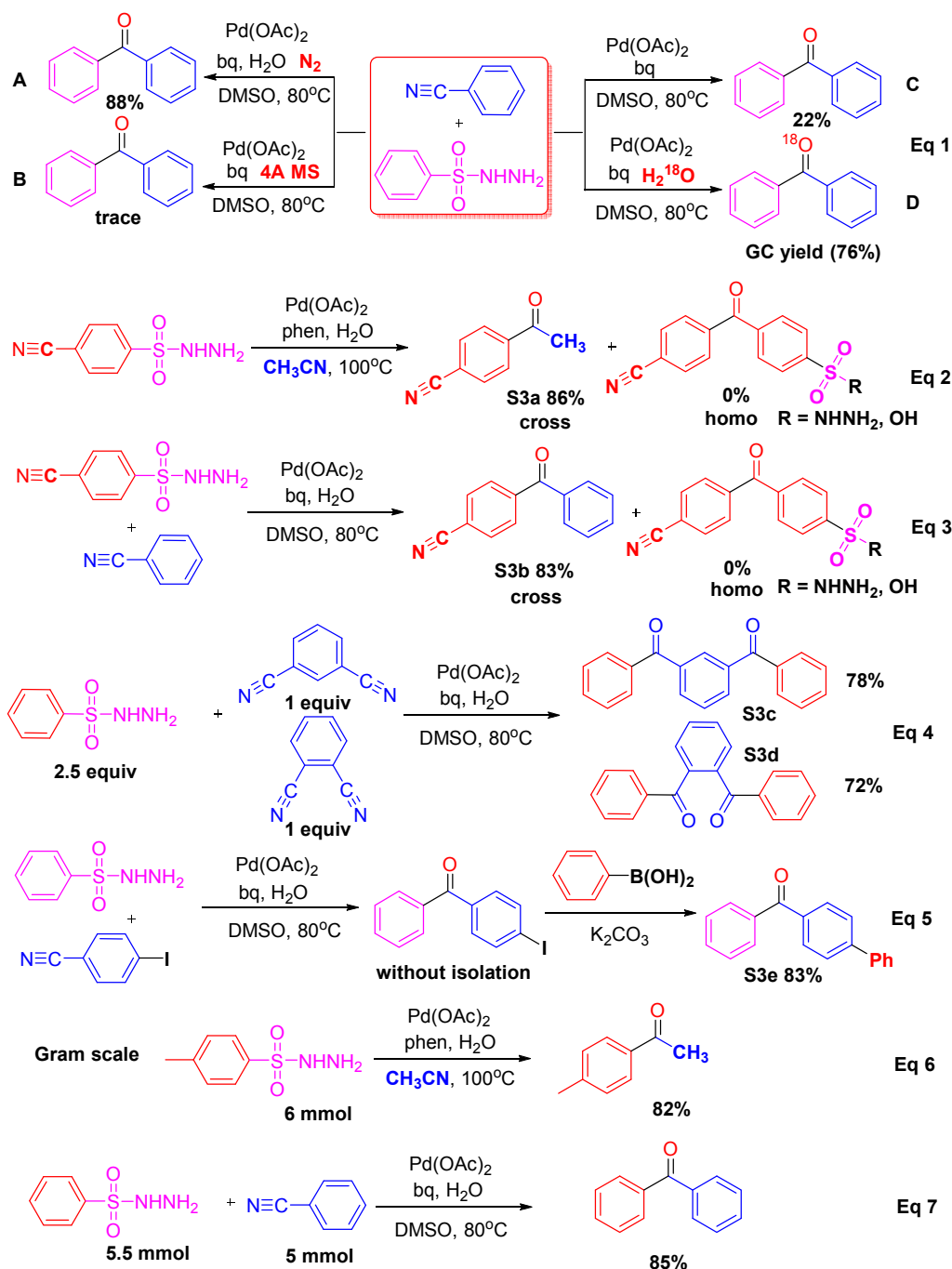
Scheme 3 Control experiments and further application

Although the mechanistic details are yet to be ascertained, we propose a plausible catalytic

cycle for the palladium-catalyzed addition reaction of arylsulfonyl hydrazides with nitriles via

direct desulfitative and denitrificative coupling in the presence of bq is shown in Scheme 4.

Starting with the ligand coordinated Pd(II)-complex, it is converted to Pd(II) species **A** and HOAc

by deprotonation with arylsulfonyl hydrazide. Intermediate **A** undergoes β-hydride elimination to

generated (arylsulfonyl)diazene and release HPdOAc at the same time. Subsequent displacement

of Pd(OAc)$_2$ with (arylsulfonyl)diazene providing reactive Pd(II) intermediate **B**, arylpalladium(II)

intermediate **C** is formed through successive liberation of N$_2$ and SO$_2$ gas. The coordination of the

nitrile group with complex **C** to form Pd(II) complex **D**, which is probably a fast process given the

excess of nitrile. After 1,2-carbopalladation of the nitrile to form ketimine complex **E**, protonation

of the ketimine **E** by the HOAc afforded the free ketimine and a regenerated ligand coordinated

Pd(OAc)$_2$ to complete the catalytic cycle. Finally, the formation of desired ketone product could

be achieved via the hydrolysis of the ketimine moiety. Additional water was enough for

hydrolysis.
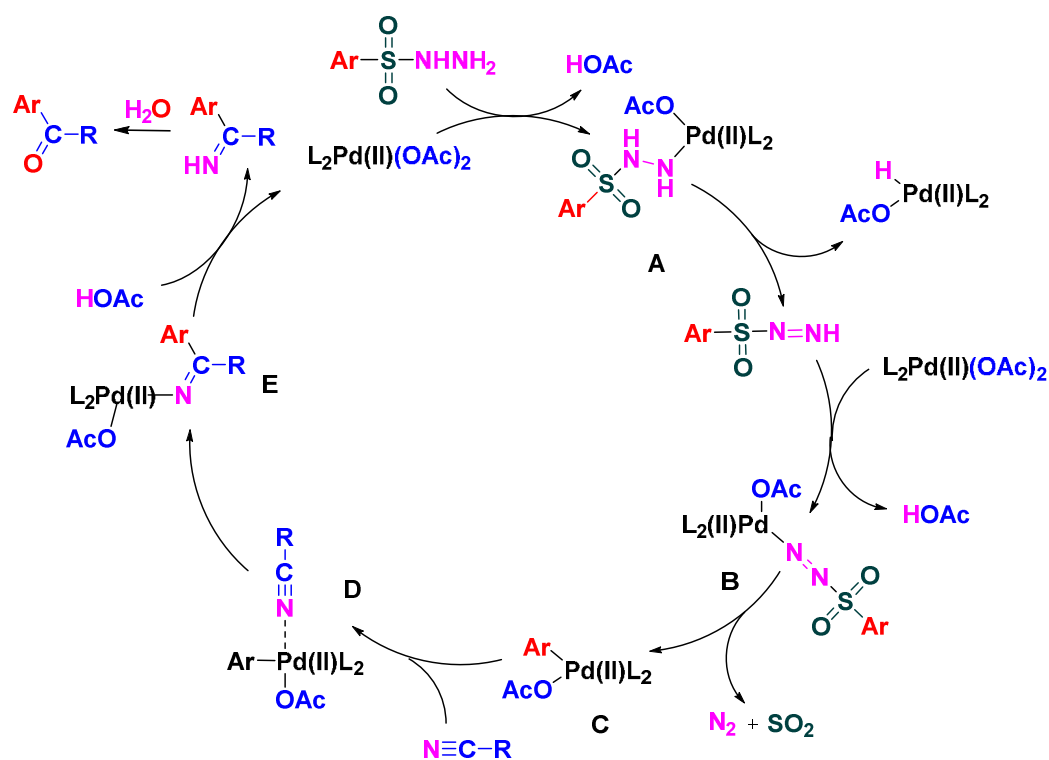
Scheme 4 Possible Mechanism

Conclusion

We have developed a novel, highly efficient and air-stable method for the construction of aryl ketone derivatives by the palladium catalyzed addition of arylsulfonyl hydrazides with nitriles in good yields with high selectivities under aerobic and aqueous conditions. This denitrogenative & desulfinative reaction proceeds with $Pd(OAc)_2$/N-ligand catalysis with a broad scope of substrates, and a series of aryl nitriles and alkyl nitriles can be utilized in this reaction. With the reaction, a wide range of diaryl ketones and aryl alkyl ketones are synthesized in good to excellent yields.

Experimental Section

General

Reagents and solvents were used as it is obtained from commercial vendors. Products were purified by column chromatography on silica gel (300–400 mesh) (ethyl acetate / petroleum ether = v/v). ^{1}H and ^{13}C NMR spectra were obtained on Bruker–400 MHz spectrometers using tetramethylsilane as internal standard in $CDCl_3$. Chemical shifts of ^{1}H NMR and ^{13}C NMR are reported as δ values relative to TMS and $CDCl_3$ respectively. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad resonances (br). HRMS (EI) data were collected on High Resolution mass spectrometer (ion trap).

General experimental procedure for synthesis of aryl ketones

A mixture of phenylsulfonyl hydrazides (1.1 mmol), nitriles (1.0 mmol), $Pd(OAc)_2$ (2 mol%), bq (3 mol%) was stirred in DMSO (2 mL) and H_2O (2 mmol) at 80°C for 6 hours at ambient atmosphere. The reaction mixture was extracted by Et_2O (5 mL) for three times. And then the

organic phase was combined and evaporated under reduced pressure. The residue was purified on

a silica gel (300-400 mesh) column to afford the desired product (with petroleum and ethyl

acetate).

4-Methoxy-benzophenone (3a) White solid (E/P = 1/15), 192.9 mg (91%), m.p. 59–60 $^{\circ}$C. [1]H

NMR (400 MHz, CDCl$_3$, TMS) δ 7.83 (d, J = 8.4 Hz, 2 H), 7.75 (t, J = 7.6 Hz, 2 H), 7.56 (t, J

= 7.6 Hz, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 6.95 (d, J = 8.4 Hz, 2 H), 3.88 (s, 3 H). ^{13}C NMR

(100 MHz, CDCl$_3$) δ 195.6, 163.2, 138.3, 132.6, 132.0, 130.1, 129.8, 128.2, 113.6, 55.5. HRMS

(EI) Calcd for C$_{14}$H$_{12}$O$_2$ (M$^+$) 212.0837, Found 212.0843.

Benzophenone (3b) White solid (E/P = 1/20), 167.4 mg (92%), m.p. 46–48 $^{\circ}$C. ^{1}H NMR (400

MHz, CDCl$_3$, TMS) δ 7.80 (d, J = 8.4 Hz, 4 H), 7.58 (t, J = 7.6 Hz, 2 H), 7.47 (t, J = 8.0 Hz, 4

H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.9, 137.6, 132.4, 130.1, 128.3. HRMS (EI) Calcd for

C$_{13}$H$_{10}$O (M$^+$) 182.0732, Found 182.0738.

4-Fluorobenzophenone (3c) White solid (E/P = 1/20), 166.1 mg (83%), m.p. 45–46 $^{\circ}$C. ^{1}H NMR

(400 MHz, CDCl$_3$, TMS) δ 7.86 (dd, J_1 = 8.4 Hz, J_2 = 5.0 Hz, 2 H), 7.78 (d, J = 7.2 Hz, 2 H),

7.57 (t, J = 7.2 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 7.16 (t, J = 8.4 Hz, 2 H). ^{13}C NMR (100

MHz, CDCl$_3$) δ 195.3, 165.8 (d, J = 252 Hz), 137.5, 133.8 (d, J = 3.1 Hz), 132.7 (d, J = 9.0 Hz),

132.5, 129.9, 128.4, 115.5 (d, J = 21.5 Hz). HRMS (EI) Calcd for C$_{13}$H$_9$FO (M$^+$) 200.0637, Found

200.0638.

4-Nitrobenzophenone (3d) Light yellow solid (E/P = 1/3), 190.7 mg (84%), m.p. 141–143 $^{\circ}$C. [1]H

NMR (400 MHz, CDCl$_3$, TMS) δ 8.34 (d, J = 8.4 Hz, 2 H), 7.94 (d, J = 8.4 Hz, 2 H), 7.81 (d,

J = 7.2 Hz, 2 H), 7.67 (t, J = 7.6 Hz, 1 H), 7.53 (t, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz,

CDCl$_3$) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7, 130.1, 128.7, 123.5. HRMS (EI) Calcd for

$C_{13}H_9NO_3$ (M$^+$) 227.0582, Found 227.0586.

4-Trifluoromethyl-benzophenone (3e) White solid (E/P = 1/3), 195.1 mg (78%), m.p. 117–118

^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.89 (d, J = 8.0 Hz, 2 H), 7.81 (d, J = 7.2 Hz, 2 H),

7.75 (d, J = 8.4 Hz, 2 H), 7.63 (t, J = 7.6 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100

MHz, CDCl$_3$) δ 195.6, 140.7, 136.7, 133.7 (dd, J_1 = 64.6 Hz, J_2 = 32.6 Hz), 133.1, 130.2 (d, J =

3.8 Hz), 128.5, 125.4 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz), 123.7 (d, J = 271.2 Hz). HRMS (EI) Calcd

for $C_{14}H_9F_3O$ (M$^+$) 250.0605, Found 250.0602.

4-Methylbenzophenone (3f, 4c) White solid (E/P = 1/20), 182.3 mg (93%) for 3f and 184.3 mg

(94%) for 4c, m.p. 55–56 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.80 (d, J = 6.8 Hz, 2 H),

7.74 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 8.0 Hz, 1 H), 7.48 (t, J = 7.2 Hz, 2 H), 7.29 (d, J = 8.0

Hz, 2 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.5, 143.3, 138.0, 134.9, 132.2, 130.3,

130.0, 129.0, 128.2, 21.7. HRMS (EI) Calcd for $C_{14}H_{12}O$ (M$^+$) 196.0888, Found 196.0893.

3-Methyl-benzophenone (3g) Colorless oil (E/P = 1/15), 170.5 mg (87%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.80 (d, J = 7.2 Hz, 2 H), 7.63 (s, 1 H), 7.58 (d, J = 7.2 Hz, 2 H), 7.49 (t, J =

7.6 Hz, 2 H), 7.33-7.41 (m, 2 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.1, 138.2,

137.7, 137.6, 133.3, 132.4, 130.5, 130.1, 128.3, 128.1, 127.4, 21.4. HRMS (EI) Calcd for $C_{14}H_{12}O$

(M$^+$) 196.0888, Found 196.0883.

2-Methylbenzophenone (3h) Colorless oil (E/P = 1/20), 158.8 mg (81%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.81 (d, J = 8.4 Hz, 2 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H),

7.41 (t, J = 7.2 Hz, 1 H), 7.24-7.34 (m, 3 H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ

198.7, 138.6, 137.7, 136.8, 133.1, 131.0, 130.2, 130.1, 128.52, 128.47, 125.2, 20.0. HRMS (EI)

Calcd for $C_{14}H_{12}O$ (M$^+$) 196.0888, Found 196.0882.

4-Chloro-benzophenone (3i, 4d) White solid (E/P = 1/15), 183.7 mg (85%) for 3i and 190.1 mg (88%) for 4d, m.p. 75–76 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.77 (t, J = 7.2 Hz, 4 H), 7.60 (t, J = 7.2 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 7.46 (d, J = 8.8 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.6, 138.9, 137.2, 135.8, 132.7, 131.5, 130.0, 128.7, 128.4. HRMS (EI) Calcd for C$_{13}$H$_9$ClO (M$^+$) 216.0342, Found 216.0347.

3-Chloro-benzophenone (3j) White solid (E/P = 1/15), 185.8 mg (86%), m.p. 83–85 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.79 (d, J = 6.8 Hz, 2 H), 7.78 (s, 1 H), 7.67 (d, J = 6.8 Hz, 1 H), 7.62 (t, J = 7.2 Hz, 1 H), 7.56 (d, J = 8.0 Hz, 1 H), 7.50 (t, J = 7.6 Hz, 2 H), 7.42 (t, J = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.3, 139.2, 136.9, 134.6, 132.9, 132.4, 130.1, 129.9, 129.7, 128.5, 128.2. HRMS (EI) Calcd for C$_{13}$H$_9$ClO (M$^+$) 216.0342, Found 216.0335.

2-Chlorobenzophenone (3k) White solid (E/P = 1/20), 177.1 mg (82%), m.p. 43–45 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.81 (d, J = 8.4 Hz, 2 H), 7.60 (t, J = 7.6 Hz, 1 H), 7.41-7.49 (m, 4 H), 7.36-7.39 (m, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.3, 138.6, 136.5, 133.7, 131.3, 131.2, 130.1, 129.1, 128.6, 126.7. HRMS (EI) Calcd for C$_{13}$H$_9$ClO (M$^+$) 216.0342, Found 216.0340.

2,3,4,5,6-Pentamethyl-benzophenone (3l) White solid (E/P = 1/20), 184.0 mg (73%), m.p. 136–137 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.83 (d, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 2.28 (s, 3 H), 2.21 (s, 6 H), 2.02 (s, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.0, 137.7, 135.6, 133.4, 132.9, 129.6, 129.0, 128.7, 17.6, 16.8, 16.0. HRMS (EI) Calcd for C$_{18}$H$_{20}$O (M$^+$) 252.1514, Found 252.1516.

4-Bromobenzophenone (3m) White solid (E/P = 1/15), 231.4 mg (89%), m.p. 80–82 °C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.77 (d, J = 8.4 Hz, 2 H), 7.58-7.69 (m, 5 H), 7.49 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.7, 137.1, 136.3, 132.7, 131.63, 131.61, 130.0,

128.5, 127.6. HRMS (EI) Calcd for $C_{13}H_9BrO$ (M^+) 259.9837, Found 259.9832.

2-Benzoylthiophene (3n) White solid (E/P = 1/20), 144.8 mg (77%), m.p. 53–54 ^{o}C. ^{1}H NMR

(400 MHz, CDCl$_3$, TMS) δ 7.86 (d, J = 7.2 Hz, 2 H), 7.72 (d, J = 4.8 Hz, 1 H), 7.64 (d, J =

3.6 Hz, 1 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.48 (t, J = 7.2 Hz, 2 H), 7.16 (t, J = 4.4 Hz, 1 H). ^{13}C

NMR (100 MHz, CDCl$_3$) δ 188.2, 143.6, 138.2, 134.9, 134.2, 132.3, 129.2, 128.4, 128.0. HRMS

(EI) Calcd for $C_{11}H_8OS$ (M^+) 188.0296, Found 188.0299.

3-Benzoylpyridine (3o) White solid (E/P = 1/15), 152.7 mg (83%), m.p. 40–42 ^{o}C. ^{1}H NMR (400

MHz, CDCl$_3$, TMS) δ 8.99 (s, 1 H), 8.81 (d, J = 7.6 Hz, 1 H), 8.12 (d, J = 8.0 Hz, 1 H), 7.82

(d, J = 8.4 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.44-7.54 (m, 3 H). ^{13}C NMR (100 MHz,

CDCl$_3$) δ 195.0, 152.8, 150.9, 137.2, 136.6, 133.2, 133.1, 130.0, 128.6, 123.4. HRMS m/z (ESI)

calcd for $C_{12}H_{10}NO$ [M+H]$^+$ 184.0757, found 184.0750.

4-Benzyloxy-benzophenone (4a) White solid (E/P = 1/20), 244.8 mg (85%), m.p. 83–85 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 7.82 (d, J = 8.4 Hz, 2 H), 7.75 (t, J = 7.2 Hz, 2 H), 7.55 (t, J

= 7.6 Hz, 1 H), 7.32-7.48 (m, 7 H), 7.03 (d, J = 8.8 Hz, 2 H), 5.14 (s, 2 H). ^{13}C NMR (100

MHz, CDCl$_3$) δ 195.5, 162.4, 138.3, 136.2, 132.6, 131.9, 130.4, 129.8, 128.7, 128.3, 128.2, 127.5,

114.4, 70.2. HRMS (EI) Calcd for $C_{20}H_{16}O_2$ (M^+) 288.1150, Found 288.1143.

4-(Dimethylamino)benzophenone (4b) White solid (E/P = 1/5), 196.6 mg (87%), m.p. 92-94 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.80 (d, J = 9.2 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H), 7.52

(t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 6.66 (d, J = 7.6 Hz, 2 H), 3.06 (s, 6 H). ^{13}C

NMR (100 MHz, CDCl$_3$) δ 195.2, 153.3, 139.3, 132.8, 131.2, 129.5, 128.0, 124.7, 110.5, 40.1.

HRMS m/z (ESI) calcd for $C_{15}H_{16}NO$ [M+H]$^+$ 226.1226, found 226.1223.

3-Nitrobenzophenone (4e) Light yellow solid (E/P = 1/5), 186.2 mg (82%), m.p. 96–97 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 8.62 (s, 1 H), 8.45 (d, J = 8.0 Hz, 1 H), 8.14 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 7.2 Hz, 2 H), 7.72 (t, J = 7.6 Hz, 1 H), 7.66 (t, J = 7.6 Hz, 1 H), 7.54 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.2, 148.1, 139.0, 136.3, 135.5, 133.4, 130.0, 129.7, 128.8, 126.7, 124.7. HRMS (EI) Calcd for C$_{13}$H$_9$NO$_3$ (M$^+$) 227.0582, Found 227.0586.

3,4-Dimethylbenzophenone (4f) White solid (E/P = 1/20), 188.9 mg (90%), m.p. 47–48 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.80 (d, J = 8.0 Hz, 2 H), 7.64 (s, 1 H), 7.53-7.61 (m, 2 H), 7.49 (t, J = 7.6 Hz, 2 H), 7.24 (t, J = 8.0 Hz, 1 H), 2.36 (s, 3 H), 2.34 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.7, 142.0, 138.1, 136.8, 135.3, 132.1, 131.2, 130.0, 129.5, 128.2, 128.1, 20.0, 19.8. HRMS (EI) Calcd for C$_{15}$H$_{14}$O (M$^+$) 210.1045, Found 210.1040.

3,4-Dichlorobenzophenone (4g) White solid (E/P = 1/20), 207.5 mg (83%), m.p. 103–104 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.90 (s, 1 H), 7.77 (d, J = 6.8 Hz, 2 H), 7.64 (t, J = 8.0 Hz, 2 H), 7.58 (d, J = 8.0 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.2, 137.2, 137.0, 136.7, 133.0, 131.8, 130.5, 129.9, 129.1, 128.6. HRMS (EI) Calcd for C$_{13}$H$_8$Cl$_2$O (M$^+$) 249.9952, Found 249.9956.

3,5-Bis(trifluoromethyl)benzophenone (4h) White solid (E/P = 1/10), 241.7 mg (76%), m.p. 108–110 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.24 (s, 2 H), 8.10 (s, 1 H), 7.79 (d, J = 7.6 Hz, 2 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.56 (d, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.6, 139.4, 135.9, 133.6, 132.0 (dd, J_1 = 67.2 Hz, J_2 = 33.6 Hz), 130.0, 129.8 (d, J = 2.1 Hz), 128.9 125.6 (t, J = 3.9 Hz), 124.3, 121.5 (q, J = 271 Hz). HRMS (EI) Calcd for C$_{15}$H$_8$F$_6$O (M$^+$) 318.0479, Found 318.0481.

4-Iodobenzophenone (4i) White solid (E/P = 1/20), 280.3 mg (91%), m.p. 101–103 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.84 (d, J = 8.4 Hz, 2 H), 7.77 (d, J_1 = 7.6 Hz, 2 H), 7.60 (t, J =

7.2 Hz, 1 H), 7.46-7.53 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.9, 137.6, 137.1, 136.9,

132.7, 131.5, 130.0, 128.4, 100.2. HRMS (EI) Calcd for C$_{13}$H$_9$IO (M$^+$) 307.9698, Found

307.9692.

1-Naphthyl-benzophenone (4j) White solid (E/P = 1/15), 186.5 mg (80%), m.p. 76–78 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 8.10 (d, J = 7.6 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 7.91 (d,

J = 7.2 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.42-7.61 (m, 7 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ

198.1, 138.3, 136.3, 133.7, 133.3, 131.3, 131.0, 130.5, 128.48, 128.45, 127.8, 127.3, 126.5, 125.7,

124.4. HRMS m/z (ESI) calcd for C$_{17}$H$_{13}$O [M+H]$^+$ 233.0961, found 233.0961.

2-Benzoylpyridine (4k) White solid (E/P = 1/15), 131.8 mg (72%), m.p. 42–43 ^{o}C. ^{1}H NMR

(400 MHz, CDCl$_3$, TMS) δ 8.72 (d, J = 4.8 Hz, 1 H), 8.02-8.08 (m, 3 H), 7.89 (t, J = 7.6 Hz, 1

H), 7.59 (d, J = 7.2 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.1,

155.1, 148.6, 137.1, 136.3, 133.0, 131.0, 128.2, 126.2, 124.6. HRMS (EI) Calcd for C$_{12}$H$_9$NO (M$^+$)

183.0684, Found 183.0683.

2,6-Difluorobenzophenone (4l) White solid (E/P = 1/10), 167.9 mg (77%), m.p. 134–136 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 7.80 (d, J = 8.4 Hz, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.52 (t, J

= 7.6 Hz, 2 H), 7.31 (dt, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2 H), 7.05 (tt, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 193.9, 162.6 (dd, J_1 = 250 Hz, J_2 = 11.6 Hz), 140.6 (t, J = 7.2

Hz), 136.4, 133.2, 130.0, 128.6, 112.9 (dd, J_1 = 18.3 Hz, J_2 = 7.4 Hz), 107.7 (t, J = 25.1 Hz).

HRMS (EI) Calcd for C$_{13}$H$_8$F$_2$O (M$^+$) 218.0543, Found 218.0549.

2,5-Difluorobenzophenone (4m) White solid (E/P = 1/10), 187.5 mg (86%), m.p. 99–100 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 7.84 (d, J = 8.4 Hz, 2 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.48 (d,

J = 7.6 Hz, 2 H), 7.19-7.28 (m, 2 H), 7.11-7.17 (m, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ

192.1, 159.7, 157.2 (d, J = 252 Hz), 136.8, 133.8, 129.8, 128.6, 128.1 (dd, J_1 = 17.2 Hz, J_2 = 6.4 Hz), 119.7 (dd, J_1 = 23.6 Hz, J_2 = 8.6 Hz), 117.8 (dd, J_1 = 24.8 Hz, J_2 = 8.0 Hz), 117.0 (dd, J_1 = 18.4 Hz, J_2 = 7.2 Hz). HRMS (EI) Calcd for $C_{13}H_8F_2O$ (M^+) 218.0543, Found 218.0548.

3,4,5-Trifluorobenzophenone (4n) White solid (E/P = 1/10), 191.2 mg (81%), m.p. 121–123 ^{o}C.

^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.78 (d, J = 7.2 Hz, 2 H), 7.66 (t, J = 7.6 Hz, 1 H), 7.54 (t, J = 8.0 Hz, 2 H), 7.50 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.9, 152.2 (dd, J_1 = 41.2 Hz, J_2 = 12 Hz), 149.7 (dd, J_1 = 40.8 Hz, J_2 = 14 Hz), 144.0 (t, J = 62.4 Hz), 141.4 (t, J = 61.6 Hz), 136.2, 133.1, 129.8, 128.6, 114.6 (dd, J_1 = 64 Hz, J_2 = 24.8 Hz). HRMS (EI) Calcd for $C_{13}H_7F_3O$ (M^+) 236.0449, Found 236.0438.

2,3,4,5,6-Perfluoro-benzophenone (4o) White solid (E/P = 1/15), 190.4 mg (70%), m.p. 36–37 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.86 (d, J = 7.6 Hz, 2 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.54 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 185.2, 135.9, 135.1, 129.7, 129.1. HRMS (EI) Calcd for $C_{13}H_5F_5O$ (M^+) 272.0261, Found 272.0265.

1,2-Diphenylethanone (T5-1) White solid (E/P = 1/20), 177.3 mg (90%), m.p. 55–57 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.01 (d, J = 7.8 Hz, 2 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.22-7.34 (m, 5 H), 4.28 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.6, 136.6, 134.6, 133.2, 129.5, 128.70, 128.67, 128.64, 126.9, 45.5. HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ [M+H]$^+$ 197.0961, found 197.0962.

Benzoylacetone (T5-2) Colorless oil (E/P = 1/30), 141.8 mg (87%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.87 (d, J = 7.2 Hz, 2 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.2 Hz, 2 H), 6.17 (s, 2 H), 2.19 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 193.8, 183.3, 134.9, 132.3, 128.8, 128.6, 127.0, 96.7, 25.8. HRMS m/z (ESI) calcd for $C_{10}H_{11}O_2$ [M+H]$^+$ 163.0754, found 163.0749.

Propiophenone (T5-3) Colorless oil (E/P = 1/50), 101.2 mg (75%). ^{1}H NMR (400 MHz, CDCl$_3$,

TMS) δ 7.90 (d, J = 7.6 Hz, 2 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.38 (t, J = 7.6 Hz, 2 H), 2.93 (q,

J = 7.2 Hz, 2 H), 1.15 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.6, 136.9, 132.8,

128.5, 127.9, 31.7, 8.2. HRMS m/z (ESI) calcd for C$_9$H$_{11}$O [M+H]$^+$ 135.0804, found 135.0802.

Pentanophenone (T5-4) Colorless oil (E/P = 1/50), 133.7 mg (82%). ^{1}H NMR (400 MHz, CDCl$_3$,

TMS) δ 7.94 (d, J = 7.2 Hz, 2 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 2 H), 2.95 (t, J

= 7.6 Hz, 2 H), 1.67-1.75 (m, 2 H), 1.37-1.43 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H). ^{13}C NMR

(100 MHz, CDCl$_3$) δ 200.5, 137.1, 132.8, 128.5, 128.0, 38.3, 26.5, 22.5, 13.9. HRMS m/z (ESI)

calcd for C$_{11}$H$_{15}$O [M+H]$^+$ 163.1117, found 163.1109.

Isobutyrophenone (T5-5) Colorless oil (E/P = 1/50), 117.7 mg (79%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.95 (d, J = 7.6 Hz, 2 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.2 Hz, 2 H),

3.55 (m, 1 H), 1.21 (d, J = 6.8 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 204.4, 136.2, 132.8,

128.6, 128.3, 35.3, 19.1. HRMS m/z (ESI) calcd for C$_{10}$H$_{13}$O [M+H]$^+$ 149.0961, found 149.0957.

Cyclopentyl(phenyl)methanone (T5-6) Colorless oil (E/P = 1/50), 145.3 mg (83%). ^{1}H NMR

(400 MHz, CDCl$_3$, TMS) δ 7.97 (d, J = 7.2 Hz, 2 H), 7.53 (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.2

Hz, 2 H), 3.66-3.75 (m, 1 H), 1.86-1.94 (m, 4 H), 1.60-1.77 (m, 4 H). ^{13}C NMR (100 MHz,

CDCl$_3$) δ 202.8, 136.9, 132.7, 128.5, 128.4, 46.3, 30.0, 26.3. HRMS m/z (ESI) calcd for C$_{12}$H$_{15}$O

[M+H]$^+$ 175.1117, found 175.1109.

4'-Ethoxyacetophenone (6a) Colorless oil (E/P = 1/30), 152.5 mg (93%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.79 (d, J = 8.8 Hz, 2 H), 6.77 (d, J = 8.8 Hz, 2 H), 3.94 (q, J = 7.2 Hz, 2 H),

2.41 (s, 3 H), 1.30 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.5, 162.8, 130.4,

130.0, 114.0, 63.6, 26.1, 14.6. HRMS (EI) Calcd for C$_{10}$H$_{12}$O$_2$ (M$^+$) 164.0837, Found 164.0833.

4'-Methoxyacetophenone (6b) Colorless oil (E/P = 1/30), 135.0 mg (90%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.86 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 8.8 Hz, 2 H), 3.78 (s, 3 H), 2.48 (s, 3

H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.7, 163.4, 130.5, 130.2, 113.6, 55.4, 26.3. HRMS (EI)

Calcd for C$_9$H$_{10}$O$_2$ (M$^+$) 150.0681, Found 150.0689.

3'-Methoxyacetophenone (6c) Colorless oil (E/P = 1/30), 138.1 mg (92%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.38 (d, J = 7.6 Hz, 1 H), 7.33 (s, 1 H), 7.21 (t, J = 8.0 Hz, 1 H), 6.96 (d, J =

7.2 Hz, 1 H), 3.68 (s, 3 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.6, 159.7, 138.3,

129.5, 120.9, 119.3, 112.3, 55.2, 26.5. HRMS (EI) Calcd for C$_9$H$_{10}$O$_2$ (M$^+$) 150.0681, Found

150.0677.

4'-Dimethylaminoacetophenone (6d) Colorless oil (E/P = 1/20), 138.6 mg (85%). ^{1}H NMR (400

MHz, CDCl$_3$, TMS) δ 7.86 (d, J = 8.4 Hz, 2 H), 6.63 (d, J = 8.0 Hz, 2 H), 3.03 (s, 6 H), 2.50

(s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.4, 153.4, 130.5, 125.3, 110.6, 40.0, 26.0. HRMS

(EI) Calcd for C$_{10}$H$_{13}$NO (M$^+$) 163.0997, Found 163.0991.

4'-Methylthioacetophenone (6e) Colorless oil (E/P = 1/30), 144.4 mg (87%). ^{1}H NMR (400

MHz, CDCl$_3$, TMS) δ 7.82 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 2.52 (s, 3 H), 2.47

(s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.1, 145.9, 133.4, 128.7, 124.9, 26.4, 14.7. HRMS

(EI) Calcd for C$_9$H$_{10}$OS (M$^+$) 166.0452, Found 166.0460.

4'-Methylacetophenone (6f) Colorless oil (E/P = 1/30), 128.6 mg (96%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.76 (d, J = 6.8 Hz, 2 H), 7.14 (d, J = 7.2 Hz, 2 H), 2.45 (s, 3 H), 2.30 (s, 3

H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.6, 143.7, 134.6, 129.2, 128.4, 26.4, 21.5. HRMS (EI)

Calcd for C$_9$H$_{10}$O (M$^+$) 134.0732, Found 134.0728.

3'-Methylacetophenone (6g) Colorless oil (E/P = 1/30), 152.5 mg (93%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.76 (s, 1 H), 7.74 (d, J = 7.2 Hz, 2 H), 7.36 (d, J = 7.6 Hz, 1 H), 7.33 (t, J = 7.2 Hz, 1 H), 2.57 (s, 3 H), 2.40 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.3, 138.3, 137.1, 133.9, 128.8, 128.4, 125.6, 26.7, 21.3. HRMS (EI) Calcd for C$_9$H$_{10}$O (M$^+$) 134.0732, Found 134.0739.

3', 5'-Dimethylacetophenone (6h) Colorless oil (E/P = 1/30), 130.2 mg (93%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.55 (s, 2 H), 7.17 (s, 1 H), 2.55 (s, 3 H), 2.34 (s, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.5, 138.1, 137.2, 134.7, 126.2, 26.7, 21.2. HRMS (EI) Calcd for C$_{10}$H$_{12}$O (M$^+$) 148.0888, Found 148.0895.

2', 4', 6'-Trimethylacetophenone (6i) Colorless oil (E/P = 1/30), 128.0 mg (79%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 6.82 (s, 2 H), 2.43 (s, 3 H), 2.27 (s, 3 H), 2.21 (s, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 208.1, 140.0, 138.1, 132.2, 128.5, 32.1, 21.0, 19.0. HRMS (EI) Calcd for C$_{11}$H$_{14}$O (M$^+$) 162.1045, Found 162.1052.

3'-Cyanoacetophenone (6j) Colorless oil (E/P = 1/30), 124.7 mg (86%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.21 (s, 1 H), 8.16 (d, J = 7.6 Hz, 2 H), 7.82 (d, J = 6.8 Hz, 1 H), 7.61 (t, J = 8.0 Hz, 1 H), 2.62 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.9, 137.7, 136.0, 132.3, 132.0, 129.7, 117.9, 113.1, 26.6. HRMS (EI) Calcd for C$_9$H$_7$NO (M$^+$) 145.0528, Found 145.0522.

4'-Fluoroacetophenone (6k) Colorless oil (E/P = 1/30), 117.3 mg (85%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.81 (d, J = 8.4 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 2 H), 2.41 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.2, 165.5 (d, J = 251.8 Hz), 133.5 (d, J = 2.8 Hz), 130.8 (d, J = 9.1 Hz), 115.4 (d, J = 22.4 Hz), 26.2. HRMS (EI) Calcd for C$_8$H$_7$FO (M$^+$) 138.0481, Found 138.0486.

3'-Fluoroacetophenone (6l) Colorless oil (E/P = 1/30), 124.2 mg (90%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.69 (d, J = 8.0 Hz, 1 H), 7.58 (d, J = 9.6 Hz, 1 H), 7.37-7.43 (m, 1 H),

7.18-7.24 (m, 1 H), 2.55 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.7 (d, J = 2.5 Hz), 162.8

(d, J = 246.0 Hz), 139.1 (d, J = 5.2 Hz), 130.2 (d, J = 7.4 Hz), 124.1 (d, J = 5.2 Hz), 120.0 (d, J =

21.4 Hz), 114.8 (d, J = 22.2 Hz), 26.6. HRMS (EI) Calcd for C$_8$H$_7$FO (M$^+$) 138.0481, Found

138.0489.

2'-Fluoroacetophenone (6m) Colorless oil (E/P = 1/30), 111.8 mg (81%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.79 (t, J = 8.0 Hz, 1 H), 7.44 (q, J = 6.4 Hz, 1 H), 7.79 (t, J = 7.6 Hz, 1 H),

7.05 (t, J = 9.6 Hz, 1 H), 2.55 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.6 (d, J = 3.0 Hz),

162.1 (d, J = 252.6 Hz), 134.6 (d, J = 8.6 Hz), 130.5 (d, J = 2.6 Hz), 125.6 (d, J = 2.7 Hz), 124.3

(d, J = 3.9 Hz), 116.6 (d, J = 23.7 Hz), 31.2 (d, J = 6.7 Hz). HRMS (EI) Calcd for C$_8$H$_7$FO (M$^+$)

138.0481, Found 138.0474.

4'-Nitroacetophenone (6n) Colorless oil (E/P = 1/15), 135.3 mg (82%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 8.24 (d, J = 8.8 Hz, 2 H), 8.08 (d, J = 8.4 Hz, 2 H), 2.65 (s, 3 H). ^{13}C NMR

(100 MHz, CDCl$_3$) δ 196.4, 150.3, 141.4, 129.3, 123.8, 26.9. HRMS (EI) Calcd for C$_8$H$_7$NO$_3$

(M$^+$) 165.0426, Found 165.0421.

3'-Nitroacetophenone (6o) Colorless oil (E/P = 1/15), 137.0 mg (83%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 8.69 (s, 1 H), 8.35 (d, J = 7.2 Hz, 1 H), 8.26 (d, J = 8.4 Hz, 1 H), 7.67 (t, J =

8.0 Hz, 1 H), 2.66 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.7, 148.3, 138.2, 133.9, 130.0,

127.3, 123.1, 26.7. HRMS (EI) Calcd for C$_8$H$_7$NO$_3$ (M$^+$) 165.0426, Found 165.0429.

2'-Nitroacetophenone (6p) Colorless oil (E/P = 1/15), 122.1 mg (74%). ^{1}H NMR (400 MHz,

CDCl$_3$, TMS) δ 7.95 (d, J = 8.0 Hz, 1 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.53 (t, J = 8.0 Hz, 1 H),

7.40 (d, J = 7.6 Hz, 1 H), 2.66 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.9, 145.8, 137.5,

134.3, 130.8, 127.4, 124.2, 29.9. HRMS (EI) Calcd for C$_8$H$_7$NO$_3$ (M$^+$) 165.0426, Found 165.0420.

4'-Bromoacetophenone (6q) Colorless oil (E/P = 1/30), 170.3 mg (86%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.69 (d, J = 8.8 Hz, 2 H), 7.46 (d, J = 8.4 Hz, 2 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.8, 135.7, 131.8, 129.8, 128.1, 26.5. HRMS (EI) Calcd for C$_8$H$_7$BrO (M$^+$) 197.9680, Found 197.9687.

3'-Bromoacetophenone (6r) Colorless oil (E/P = 1/30), 174.2 mg (88%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.83 (s, 1 H), 7.64 (d, J = 7.6 Hz, 1 H), 7.43 (d, J = 9.2 Hz, 1 H), 7.12 (t, J = 8.0 Hz, 1 H), 2.37 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.1, 138.6, 135.7, 131.0, 130.1, 126.8, 122.7, 26.4. HRMS (EI) Calcd for C$_8$H$_7$BrO (M$^+$) 197.9680, Found 197.9681.

2'-Bromoacetophenone (6s) Colorless oil (E/P = 1/30), 162.5 mg (82%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.55 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 7.2 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.24 (d, J = 7.6 Hz, 1 H), 2.57 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.2, 141.3, 133.8, 131.8, 128.9, 127.5, 118.8, 30.3. HRMS (EI) Calcd for C$_8$H$_7$BrO (M$^+$) 197.9680, Found 197.9675.

2-Acetylnaphthalene (6t) Colorless oil (E/P = 1/30), 137.7mg (81%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.33 (s, 1 H), 7.95 (d, J = 8.8 Hz, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 2 H), 7.51 (d, J = 6.8 Hz, 1 H), 7.46 (d, J = 6.8 Hz, 1 H), 2.61 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 197.9, 135.5, 134.4, 132.4, 130.2, 129.5, 128.4, 128.3, 127.7, 126.7, 123.8, 26.6. HRMS (EI) Calcd for C$_{12}$H$_{10}$O (M$^+$) 170.0732, Found 170.0741.

(55) 4'-Cyanoacetophenone (S3a) Colorless oil (E/P = 1/30), 124.7 mg (86%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 8.02 (d, J = 8.8 Hz, 2 H), 7.75 (d, J = 8.8 Hz, 2 H), 2.62 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.6, 139.9, 132.5, 128.7, 117.9, 116.3, 26.8. HRMS (EI) Calcd for C$_9$H$_7$NO (M$^+$) 145.0528, Found 145.0522.

4-Cyanobenzophenone (S3b) White solid (E/P = 1/20), 171.8 mg (83%), m.p. 115–117 ^{o}C. ^{1}H

NMR (400 MHz, CDCl$_3$, TMS) δ 7.88 (t, J = 8.0 Hz, 2 H), 7.77-7.80 (m, 4 H), 7.64 (t, J = 7.6

Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.0, 141.2, 136.3, 133.3,

132.2, 130.3, 130.1, 128.7, 118.0, 115.7. HRMS (EI) Calcd for C$_{14}$H$_9$NO (M$^+$) 207.0684, Found

207.0689.

Phthalonitrile (S3c) White solid (E/P = 1/15), 223.1 mg (78%), m.p. 100–101 ^{o}C. ^{1}H NMR (400

MHz, CDCl$_3$, TMS) δ 8.20 (s, 1 H), 8.03 (d, J = 7.6 Hz, 2 H), 7.83 (d, J = 7.6 Hz, 4 H), 7.62

(dd, J = 16.8, 8.0 Hz, 3 H), 7.50 (t, J = 7.6 Hz, 4 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.9,

137.8, 137.0, 133.6, 132.9, 131.3, 130.1, 128.6, 128.5. HRMS (EI) Calcd for C$_{20}$H$_{14}$O$_2$ (M$^+$)

286.0994, Found 286.0985.

Isophthalonitrile (S3d) White solid (E/P = 1/15), 205.9 mg (72%), m.p. 159–161 ^{o}C. ^{1}H NMR

(400 MHz, CDCl$_3$, TMS) δ 7.71 (d, J = 7.2 Hz, 4 H), 7.63 (s, 4 H), 7.52 (d, J = 7.2 Hz, 2 H),

7.38 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.6, 140.0, 137.2, 133.1, 130.4,

129.9, 129.7, 128.4. HRMS (EI) Calcd for C$_{20}$H$_{14}$O$_2$ (M$^+$) 286.0994, Found 286.0999.

(59) 4-biphenylyl-benzophenone (S3e) White solid (E/P = 1/20), 214.2 mg (83%), m.p. 101–103

^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ 7.88 (d, J = 8.4 Hz, 2 H), 7.83 (d, J = 7.2 Hz, 2 H),

7.69 (d, J = 8.0 Hz, 2 H), 7.63 (d, J = 7.2 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.47 (dd, J_1 =

15.2 Hz, J_2 = 7.6 Hz, 4 H), 7.39 (t, J = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.4,

145.2, 140.0, 137.8, 136.2, 132.4, 130.8, 130.1, 129.0, 128.4, 128.3, 127.4, 127.0. HRMS (EI)

Calcd for C$_{19}$H$_{14}$O (M$^+$) 258.1045, Found 258.1042.

Acknowledgements

■ ASSOCIATED CONTENT

Supporting Information

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

Copies of ^{1}HNMR and ^{13}CNMR Spectrum (PDF)

References

1. For reviews, see: (a) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling reactions*, John Wiley & Sons, Weinheim, Germany, 2nd edn, **2004**. (b) Surburg, H.; Panten, J. *Common Fragrance and Flavor Materials*, Wiley-VCH, Weinheim, 5th edn, **2006**.

2. (a) Sartori, G.; Maggi, R. *Advances in Friedel–Crafts Acylation Reactions: Catalytic and Green Process*, CRC Press, Florida, **2010**. (b) Olah, G. A. *Friedel–Crafts Chemistry*, Wiley, New York, **1973**.

3. (a) Shirley, D. A. *Org. React*. **1954**, *8*, 28. (b) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett*. **1981**, *22*, 3815.

4. For reviews, see: (a) Roman, B. I.; Kimpe, N. D.; Stevens, C. V. *Chem. Rev*. **2010**, *110*, 5914. (b) Otera, J. *Modern Carbonyl Chemistry*, Wiley-VCH, Weinheim, **2001**.

5. (a) Zhou, Q.; Wei, S.; Han, W. *J. Org. Chem*. **2014**, *79*, 1454. (b) Cheng, K.; Zhao, B.; Qi, C. *RSC Adv*. **2014**, *4*, 48698. (c) Goossen, L. J.; Ghosh, K. *Angew. Chem*., *Int. Ed*. **2001**, *40*, 3458. (d) Li, M.; Wang, C.; Ge, H. *Org. Lett*. **2011**, *13*, 2062. (e) Wu, H.; Xu, B.; Li, Y.; Hong, F.; Zhu, D.; Jian, J.; Pu, X.; Zeng, Z. *J. Org. Chem*. **2016**, *81*, 2987. (f) Demkiw, K.; Araki, H.; Elliott, E. L.; Franklin, C. L.; Fukuzumi, Y.; Hicks, F.; Hosoi, K.; Hukui, T.; Ishimaru, Y.; Brien, E. O.; Omori, Y.; Mineno, M.; Mizufune, H.; Sawada, N.; Sawai, Y.; Zhu, L. *J. Org. Chem*. **2016**, *81*, 3447. (g)

Zhao, M. –N.; Ran, L.; Chen, M.; Ren, Z. –H.; Wang, Y. –Y.; Guan, Z. –H. *ACS Catal.* **2015**, *5*, 1210. (h) Meng, M.; Wang, G.; Yang, L.; Cheng, K.; Qi, C. *Adv. Synth. Catal.*, 10.1002/adsc.201701469.

6. (a) Rach, S. F.; Kühn, F. E. *Chem. Rev.* **2009**, *109*, 2061. (b) Fleming, F. F.; Wang, Q. Z. *Chem. Rev.* **2003**, *103*, 2035. (c) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.

7. (a) Larock, R. C.; Tian, Q.; Pletnv, A. A. *J. Am. Chem. Soc.* **1999**, *121*, 3238. (b) Pletnv, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 9276. (c) Tian, Q.; Pletnv, A. A.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 339. (d) Pletnv, A. A.; Larock, R. C. *Tetrahedron Lett.* **2002**, *43*, 2133. (e) Pletnv, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 9428. (f) Zhou, C.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 2302. (g) Zhou, C.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3551.

8. (a) Xia, G.; Han, X.; Lu, X. *Adv. Synth. Catal.* **2012**, *354*, 2701. (b) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229. (c) Hsieh, J.-C.; Chen, Y.-C.; Cheng, A.; Tseng, H.-C. *Org. Lett.* **2012**, *14*, 1282. (d) Shimizu, H.; Murakami, M. *Chem. Commun.* **2007**, 2855. (e) Yu, J.; Li, J.; Cui, M.; Wu, Y. *Synlett.* **2007**, 3063. (f) Tsui, G. C.; Glenadel, Q.; Lau, C.; Lautens, M. *Org. Lett.* **2011**, *13*, 208. (g) Wong, Y. C.; Parthasarathy, K.; Cheng, C.–H. *Org. Lett.* **2010**, *12*, 1736. (h) Wang, X.; Huang, Y.; Xu, Y.; Tang, X.; Wu, W.; Jiang, H. *J. Org. Chem.* **2017**, *82*, 2211 and references cited therein.

9. (a) Friedman, L.; Litle, R. L.; Reichle, W. R. *Org. Synth.* **1960**, *40*, 93. (b) Myers, A. G.; Zheng, B.; Movassaghi, M. *J. Org. Chem.* **1997**, *62*, 7507. (c) Shapiro, R. H. *Org. React.* **1976**, *23*, 405. (d) Hutchins, R. O.; Hutchins, M. K. In: Trost B. M, Fleming I, eds. *Comprehensive Organic Synthesis*, Vol. 8. Oxford, U.K.: Pergamon Press; **1991**, 327. (e) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486. (f) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560.

10. For selected reviews, see: (a) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (b) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486.

11. (a) Yang, F.; Tian, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 4929. (b) Yang, X.; Yan, R. *Org. Biomol. Chem.* **2017**, *15*, 3571. (c) Wang, T.; Yang, F.; Tian, S. *Adv. Synth. Catal.* **2015**, *357*, 928. (d) Rahaman, R.; Devi, N.; Sarmaa, K.; Barman, P. *RSC Adv.* **2016**, *6*, 10873. (e) Yang, F.; Wang, F.; Wang, T.; Wang, Y.; Tian, S. *Chem. Commun.* **2014**, *50*, 2111. (f) Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 4202. (g) Bagdi, A. K.; Mitra, S.; Ghosh, M.; Hajra, A. *Org. Biomol. Chem.* **2015**, *13*, 3314. (h) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. *J. Org. Chem.* **2015**, *80*, 4697. (i) Rahaman, R.; Barman, P. *Synlett.* **2017**, *28*, 684.

12. Dong, D.-Q.; Hao, S.-H.; Yang, D.-S.; Li, L.-X.; Wang, Z.-L. *Eur. J. Org. Chem.* **2017**, 6576

13. Yuan, K.; Soulé, J.-F.; Doucet, H. *ACS Catal.* **2015**, *5*, 978.

14. O'Connor Sraj, L.; Khairallah, G. N.; da Silva, G.; O'Hair, R. A. J. *Organometallics* **2012**, *31*, 1801.

15. Ortgies, D. H.; Hassanpour, A.; Chen, F.; Woo, S.; Forgione, P. *Eur. J. Org. Chem.* **2016**, 408.

16. (a) Yu, X.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2012**, *10*, 7479. (b) Liu, B.; Li, J.; Song, F.; You, J. *Chem. Eur. J.* **2012**, *18*, 10830. (c) Yuen, O. Y.; So, C. M.; Wong, W. T.; Kwong, F. Y. *Synlett* **2012**, *23*, 2714. (d) Liu, C.; Ding, L.; Guo, G.; Liu, W.; Yang, F.-L. *Org. Biomol. Chem.* **2016**, *14*, 2824. (e) Wang, C.; Jia, H.; Li, Z.; Zhang, H.; Zhao, B. *RSC Adv.* **2016**, *6*, 21814.

17. (a) Yang, F.-L.; Ma, X.-T.; Tian, S.-K. *Chem. Eur. J.* **2012**, *18*, 1582. (b) Liu, S.; Chen, J.; Zhang, R.; Zhao, F.; Deng, G. J. *Asian J. Org. Chem.* **2014**, *3*, 1150. (c) Zhang, W.; Zhao, B.; Li, K. *J. Chem. Res.* **2013**, 674. (d) Zhong, S.; Sun, C.; Dou, S.; Liu, W. *RSC Adv.* **2015**, *5*, 27029. (e) Qian, L.–W.; Sun, M.; Dong, J.; Xu, Q.; Zhou, Y.; Yin, S. F. *J. Org. Chem.* **2017**, *82*, 6764. (f)

Miao, H.; Wang, F.; Zhou, S.; Zhang, G.; Li, Y. *Org. Biomol. Chem.* **2015**, *13*, 4647. (g) Yuen, O.

Y.; So, C. M.; Kwong, F. Y. *RSC Adv.*, **2016**, *6*, 27584.

18. Chen, W.; Chen, H.; Xiao, F.; Deng, G. J. *Org. Biomol. Chem.* **2013**, *11*, 4295.

19. (a) Cheng, K.; Hu, S.; Zhao, B.; Zhang, X.-M.; Qi, C. *J. Org. Chem.* **2013**, *78*, 5022. (b)

Cheng, K.; Yu, H.-Z.; Zhao, B.; Hu, S.; Zhang, X.-M.; Qi, C. *RSC Adv.* **2014**, *4*, 57923. (c) Cheng,

K.; Wang, G.; Meng, M.; Qi, C. *Org. Chem. Front.*, **2017**, *4*, 398.