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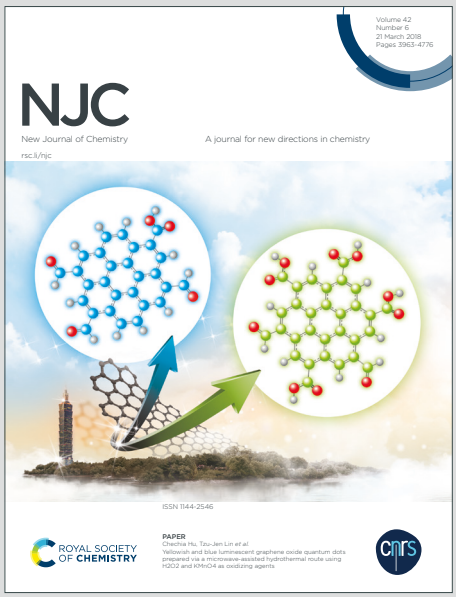

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ARTICLE

Nickel-catalyzed regioselective C–H acylation of chelating arenes: new catalytic system for C–C bond formation via a radical process and its mechanism explorations

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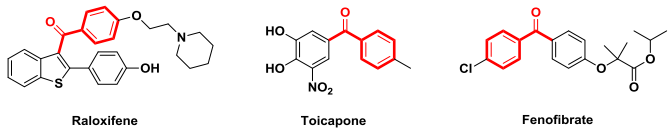
An unprecedented acylation at the *ortho* C-H bond of chelating arenes via Ni(II)-catalyzed cross dehydrogenative coupling strategy has been developed here. This new procedure exhibits an excellent regioselectivity and accomplished with good functional group tolerance. This discovery could be of great importance on the C-H acylation reactions of chelating arenes without any extraneous directing group and the application of nickel-catalyzed C-H activations. Mechanistic investigations into the reaction process are also described.

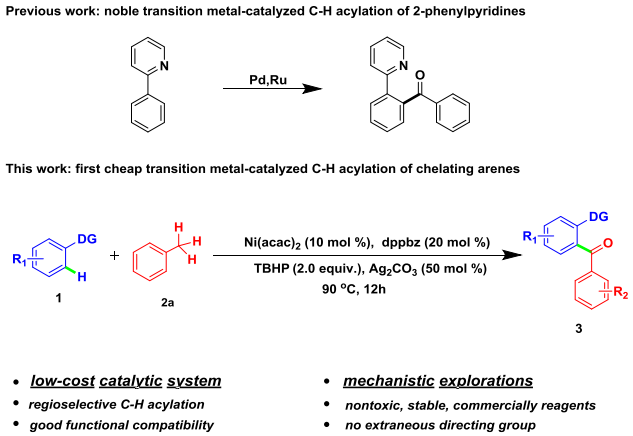
Introduction

The synthesis of aryl ketones plays a very important role in modern organic chemistry due to the widespread application of functionalized carbonyl compounds in natural products, drug compounds, functional materials and disease treatment[1]. For examples (Scheme 1, **1**, **2** and **3**), Raloxifene **1** (a seletive estrogen), Toicapone **2** (for the treatment of Parkinson's disease), Fenofibrate **3** (for the treatment of hypercholesterolemia).



Scheme 1. Examples of drugs containing benzophenones.

Over the past decade, transition metal-catalyzed C–H bond activation has become one of the most facile and powerful tools to construct C–C bonds.[2] Among a series of reliable C–H activation procedures, the directing group (DG) assisted C–H bond activation has received significant attention. In the regard of acylation in chelating arenes with DG, catalytic systems of transition metals including Pd and Ru catalyzed C–H acylation in chelating arenes have been well established.[3,4] Representative examples include the first acylation of *ortho*-C–H bonds developed by Cheng's group in 2009,[3a] who discovered that *ortho*-C–H bonds of 2-arylpyridines could be directly acylated under palladium catalysis system using aldehydes as acylation reagents in the presence of air. Then, Wu[3h] and co-workers described a facile and efficient protocol for palladium-catalyzed ortho-acylation of 2-aryl pyridines. The reported procedure utilized arylmethyl amines as the new, cheap and readily available acylation reagent and exhibited high regioselectivity for 2-aryl pyridines. Furthermore, a general and selective ruthenium-catalyzed acylation with carbon monoxide of (hetero)arenes bearing *ortho*-directing groups was provided by Beller's team[3k], opening up new possibilities for the first ruthenium catalyzed carbonylative C-C bond formation by directed C H functionalization. All the previous developed methodologies were regioselective and tolerated good functional compatibility. However, they were generally limited by the high-cost of noble metal catalyst, by efficiency, or by the use of poisonous reagents. Apart from these, there is still a need for complementary methods to attain a broader utility of this transformation.



Scheme 2. Previous strategies for C-H acylation in chelating arenes.

Very recently, nickel[5] has displayed its superiority in C–H activation of chelating arenes due to the abundance, low-cost, environmental friendliness and good catalytic activity. Our group[5a] has developed a nickel-catalyzed cross-

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dehydrogenative coupling of α-C(sp^3)–H bonds in N-methylamides with C(sp^3)–H bonds in cyclic alkanes to form C–C bonds. So we next consider whether the low-cost catalytic systems could be used in acylation of chelating arenes with DG in order to make the introduction of acyl group more efficiently and cheaply.

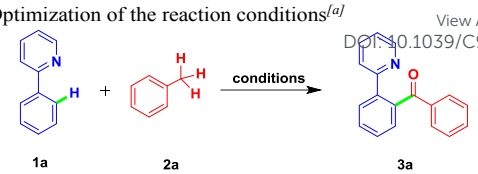
Inspired by these, we herein demonstrated the first example of nickel-catalyzed regioselective C–H acylation of chelating arenes by using toluene derivatives as the acylation reagent. Compared with previous research studies, our transformation (1) is the first cheap transition-metal catalyzed C-H acylation of chelating arenes; (2) explores the reaction process; (3) achieves regioselective C–H acylation; (4) employs low toxic, stable, commercially available toluene derivatives, thus avoiding the harm of high toxicity to human body; (5) tolerates a variety of functional groups; (6) does not require an extraneous directing group to be used, thus avoiding the preparation of raw materials and waste of resources.

Results and discussion

As indicated in Table 1, we started our model study by investigating the direct C-H acylation of 2-phenylpyridine **1a** with tert-Butyl hydroperoxide (TBHP) as the oxidant in the presence of $Ni(acac)_2$/$MePh_2P$ and Ag_2O in toluene (Table 1). Initially, a number of Ni catalysts were surveyed, including $Ni(acac)_2$, $Ni(OAc)_2$, $Ni(OTf)_2$ and $NiCl_2$ (Table 1, entries 1-4). The results showed that $Ni(acac)_2$ displayed the highest catalytic activity for this process and the anion bound to nickel plays a critical role in the catalysis system (entry 1). Next, the choice of ligands was made; dppbz (entries 5–16) proved to be more suitable to the activation of the catalyst. Thereafter, replacement of TBHP with other peroxides, such as Di-t-butyl peroxide (DTBP) and Dicumyl peroxide (DCP) fails to give better results (entries 17-18). In addition, we are also interested in the influence of different Ag salts on the yield (entries 19–20), we found that the reaction could proceed well by using Ag_2CO_3 and generate the acylation product in 89% yield. Unfortunately, when we changed the additive from Ag salts to $K_2S_2O_8$ or Oxone, the acylation reaction could not proceed well (entries 21–22). Moreover, optimizations in various solvents were conducted (entries 23-24), with toluene proving the most suitable for this transformation. Finally, we have made experiments with lower catalyst and ligand loading (entry 25-26). Good results have also been achieved (entry 25)

With the optimized reaction conditions in hand, the acylation of various chelating arenes by toluene were tested. As shown in Table 2, a wide range of functional groups on the phenyl ring of the 2-arylpyridines were compatible under this procedure and the reaction efficiency was not sensitive to the electronic property of the substituents, as both electron-donating groups (**3b**) and electron-withdrawing groups at para position on the phenyl ring could be tolerated well (**3c-3e**). Next, substrates with a Br group on the phenyl ring at the *meta*-position and a methyl group on the pyridine ring at the 3-position were investigated, furnishing (**3f**) and (**3g**) in 70% and 75% yield respectively, thus indicating high steric tolerance

Table 1. Optimization of the reaction conditions[a]



1a 2a 3a

Entry	Cat.	Ligand	Oxidant	Additive	3a(%)[b]
1	$Ni(acac)_2$	$MePh_2P$	TBHP	Ag_2O	57
2	$Ni(OAc)_2$	$MePh_2P$	TBHP	Ag_2O	10
3	$Ni(OTf)_2$	$MePh_2P$	TBHP	Ag_2O	39
4	$NiCl_2$	$MePh_2P$	TBHP	Ag_2O	trace
5	$Ni(acac)_2$	PCy_3	TBHP	Ag_2O	30
6	$Ni(acac)_2$	L_0	TBHP	Ag_2O	29
7	$Ni(acac)_2$	PPh_3	TBHP	Ag_2O	21
8	$Ni(acac)_2$	dppe	TBHP	Ag_2O	50
9	$Ni(acac)_2$	dppbz	TBHP	Ag_2O	78
10	$Ni(acac)_2$	dtbpy	TBHP	Ag_2O	33
11	$Ni(acac)_2$	bpy	TBHP	Ag_2O	15
12	$Ni(acac)_2$	phen	TBHP	Ag_2O	34
13	$Ni(acac)_2$	TMEDA	TBHP	Ag_2O	13
14	$Ni(acac)_2$	BINAP	TBHP	Ag_2O	43
15	$Ni(acac)_2$	DME	TBHP	Ag_2O	0
16	$Ni(acac)_2$	BDMAE	TBHP	Ag_2O	trace
17	$Ni(acac)_2$	dppbz	DTBP	Ag_2O	50
18	$Ni(acac)_2$	dppbz	DCP	Ag_2O	36
19	$Ni(acac)_2$	dppbz	TBHP	$AgSbF_6$	47
20	**$Ni(acac)_2$**	**dppbz**	**TBHP**	**Ag_2CO_3**	**89**
21	$Ni(acac)_2$	dppbz	TBHP	$K_2S_2O_8$	46
22	$Ni(acac)_2$	dppbz	TBHP	Oxone	51
23[c]	$Ni(acac)_2$	dppbz	TBHP	Ag_2CO_3	59
24[d]	$Ni(acac)_2$	dppbz	TBHP	Ag_2CO_3	37
25[e]	**$Ni(acac)_2$**	**dpppz**	**TBHP**	**Ag_2CO_3**	**88**
26[f]	$Ni(acac)_2$	dpppz	TBHP	Ag_2CO_3	52

[a]Reaction condition: **1a** (0.5 mmol), cat. (20 mol %), ligand (40 mol %), oxidant (2.0 equiv.), additive (50 mol %), toluene (1 mL), 90 °C, 12h. [b]Isolated yield. [c] toluene (5.0 equiv.), DMSO (1 mL). [d] toluene (5.0 equiv.), PhCl (1 mL). Dppbz = 1,2-bis(diphenylphosphino)benzene, BDMAE=bis(2-dimethylaminoethyl)ether, L_0=1,2-bis(dimethylphosphino)benzene. [e] cat. (10 mol %), ligand (20 mol %). [f] cat. (5 mol %), ligand (10 mol %).

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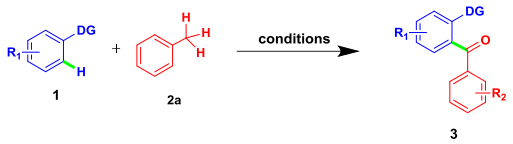
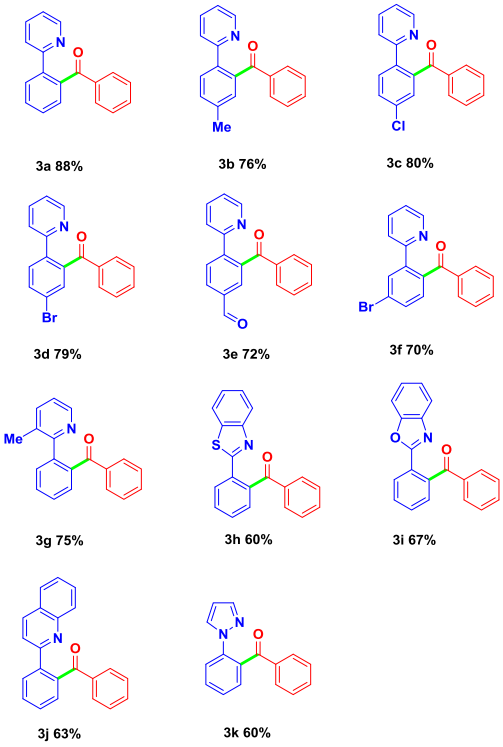
of this catalytic system. To our delight, the arene ring can also be extended to thiazole ring (**3h**), oxazole ring (**3i**), quinoline (**3j**) and pyrazole (**3k**). They underwent the reaction to give good yields of the corresponding products, which further expanded the substrate scope.

Table 2. Screening of substrate scope in the acylation reaction of substituted chelating arenes.[a]





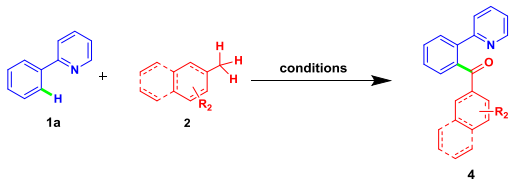
[a]Reaction condition: **1** (0.5 mmol), cat. (10 mol %), ligand (20 mol %), oxidant (2.0 equiv.), additive (50 mol %), toluene (1 mL), 90 °C, 12h.

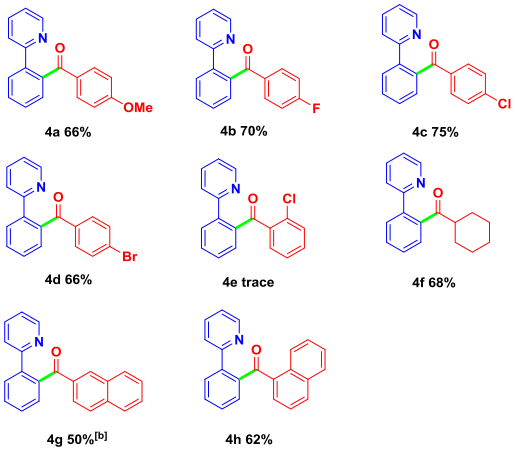
Encouraged by the above results, we investigated the tolerance of this catalysis system for toluene derivatives (Table 3). Gratifyingly, these transformations showed excellent tolerance for various toluenes bearing donating as well as withdrawing groups (**4a-4d**). Furthermore, methylcyclohexane and methylnaphthalenes also reacted with **1a** to afford corresponding products in good yields (**4f-4h**). Unfortunately, *ortho*-substituted toluene such as 1-chloro-2-methylbenzene (**4e**) can't couple with **1a** well in this procedure and this might be due to steric effect.

To gain more understanding of this reaction mechanism, some control experiments were carried out. As is shown in Scheme 3, we added 4 equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), BHT (butylated hydroxytoluene) or 1,1-diphenylethene to the acylation reaction as a radical scavenger and the coupling process was completely inhibited (determined by GC-MS), indicating that the acylation might proceed through a radical pathway.

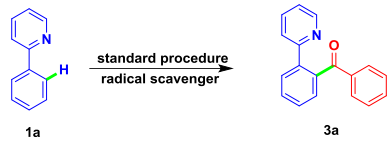
Subsequently, other experiments were also conducted (Scheme 4). When the acylation reaction was run without $Ni(acac)_2$, no *ortho* product was obtained, suggesting that the catalyst is critical for this

Table 3. Representative examples in the acylation reaction of chelating arenes with toluene derivatives.





[a]Reaction condition: **1a** (0.5 mmol), cat. (10 mol %), ligand (20 mol %), oxidant (2.0 equiv.), additive (50 mol %), toluene derivatives (1 mL), 90 °C, 12h. [b]2-methylnaphthalene (5.0 equiv.), DMSO (1 mL) .



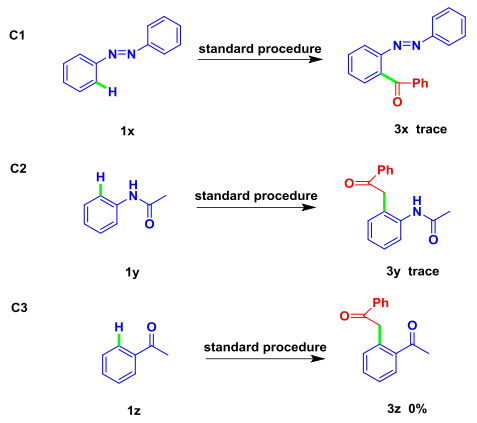
A1	*TEMPO (4equiv.)*	3a, 0%	GC-MS
A2	*BHT (4equiv.)*	3a, 0%	GC-MS
A3	*1,1-diphenylethene (4equiv.)*	3a, 0%	GC-MS

Scheme 3. Control experiments.

B1	X=metal	3a, 0%	GC-MS	B2	X=ligand	3a, 17%	GC-MS
B3	X=TBHP	3a, 0%	GC-MS	B4	X=TBHP	toluene to benzaldehyde 3a, 0%	GC-MS
B5	$X=Ag_2CO_3$	3a, 11%	GC-MS				

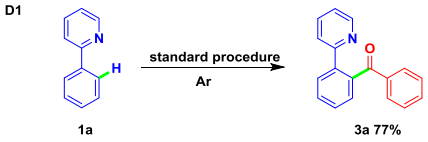
Scheme 4. Control experiments.

transformation (Scheme 4, B1). In addition, the procedure did not proceed well under ligand-free condition (determined by GC-MS), indicating that the procedure is very dependent on dppbz (Scheme 4, B2). Moreover, when 2-phenylprydine treated with benzaldehyde in the absence of TBHP, we failed to get the desired product (Scheme 4, B3 and B4). The results showed that the TBHP may have two different effects, oxidizing toluene and promoting the formation of radicals. It should be noted that this reaction could not proceed smoothly when we removed Ag_2CO_3 (Scheme 4, B5).



Scheme 5. Control experiments.

In order to further explore the reaction process, more necessary control experiments were made in Scheme 5 and Scheme 6. When we replaced **1a** with (E)-1,2-diphenyldiazene, N-phenylacetamide or acetophenone under optimal conditions, this reaction did not proceeded well (determined by GC-MS), showing that the nitrogenous heterocyclic is very critical to this transformation (Scheme 5 C1, C2 and C3). Notablely, this procedure under argon resulted in no significant decrease of the yield (Scheme 6 D1), suggesting that this procedure was not essential to oxygen. Finally, the GC-MS analysis of the aliquots taken during an ongoing reaction of **1a** with toluene showed the presence of benzaldehyde.



Scheme 6. Control experiments.

Conclusions

In summary, the first example of nickel(II) catalyzed regioselective C–H acylation of chelating arenes by using toluene derivatives as the acylation reagent has been developed. This procedure features low-cost, excellent regioselectivity, avoiding of the harm of high toxicity to human body, avoiding of the preparation of raw materials, a broad range of substrates and mechanistic explorations into the reaction process. This discovery could be of great significance on expanding the field of nickel-catalyzed C-H functionalizations and provides an important complement to C-H acylation reactions. Further studies in our laboratory are devoted to developing a milder method and performing a more detailed mechanistic investigation

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Experimental

General experimental method

All compounds are characterized by ^{1}H NMR, ^{13}C NMR and MS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm.GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413:30 m × 320 μm × 0.25 μm, H, FID detection). GC-MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). High resolution mass spectral data were acquired on Agilent Technologies Accurate-Mass Q TQF LC/MS 6520 operated by China Pharmaceutical University.

General procedure for C–H acylation of chelating arenes: To a mixture of 2-phenylpyridine (0.5 mmol) **1a**, $Ni(acac)_2$ (10 mol %), dppbz (20 mol %), TBHP (2.0 equiv.), Ag_2CO_3 (50 mol %) and toluene derivatives (1mL) were added in a reaction tube. The reaction mixture was stirred at 90°C for 12h. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired products **3**.

The rest products were prepared by a similar procedure.

phenyl(2-(pyridin-2-yl)phenyl)methanone (3a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3a** as white solid (113.96mg, 88%)[3f]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.74 – 7.69 (m, 2H), 7.65 – 7.58 (m, 3H), 7.54 – 7.50 (m, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.10 – 7.04 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.7, 147.9, 138.4, 136.8, 135.6, 133.3, 132.3, 131.4, 129.3, 128.5, 128.1, 127.9, 127.7, 127.1, 121.9, 121.1. GC-MS (EI) m/z: 259.

(5-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methanone (3b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3b** as white solid (103.74mg, 76%)[3i]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.73 (dd, *J* = 7.8, 2.9 Hz, 3H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 (s, 2H), 7.31 (dt, *J* = 8.2, 4.1 Hz, 2H), 7.03 (dt, *J* = 7.5, 3.6 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.7, 148.9, 139.5, 138.8, 138.0, 136.4, 132.2, 130.9, 129.7, 129.6, 129.4, 128.6, 128.0, 122.5, 121.7, 21.2. GC-MS (EI) m/z: 273.

(5-chloro-2-(pyridin-2-yl)phenyl)(phenyl)methanone (3c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3c** as white solid (117.20mg, 80%)[3i]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.64 (d, *J* = 5.9 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.09 (dd, *J* = 7.6, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.1, 155.6, 149.0, 140.9, 137.8, 137.2, 136.7, 134.9, 133.5, 132.8, 130.1, 129.5, 129.1, 128.2, 122.8, 122.4. GC-MS (EI) m/z: 293.

(5-bromo-2-(pyridin-2-yl)phenyl)(phenyl)methanone (3d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3d** as white solid (133.12mg, 79%)[3i]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 4.8 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.79 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.72 (dd, *J* = 4.0, 2.1 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.55 – 7.50 (m, 2H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.10 (ddd, *J* = 7.7, 4.9, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.3, 155.6, 149.0, 141.1, 138.2, 136.7, 133.6, 133.2, 132.8, 131.9, 130.4, 129.5, 128.5, 128.2, 122.7, 122.4. GC-MS (EI) m/z: 337.

3-benzoyl-4-(pyridin-2-yl)benzaldehyde (3e): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3e** as white solid (103.32mg, 72%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 8.45 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.18 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.08 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.69 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.48 (td, *J* = 7.3, 1.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.15 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.2, 155.4, 149.2, 144.8, 137.3, 136.8, 136.0, 132.8, 130.7, 130.6, 130.1, 129.6, 129.5, 128.5, 128.3, 123.0, 122.9. GC-MS (EI) m/z: 287. HRMS (ESI) m/z: calculated for $[C_{19}H_{13}NO_2 + H]^+$ 288.1025, found 288.1029.

(4-bromo-2-(pyridin-2-yl)phenyl)(phenyl)methanone (3f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3f** as white solid (117.95mg, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.99 – 7.95 (m, 1H), 7.75 – 7.67 (m, 3H), 7.63 (t, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 – 7.29 (m, 2H), 7.09 (dd, *J* = 7.3, 3.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.3, 149.2, 141.5, 138.3, 137.5, 136.6, 132.6, 131.8, 131.6, 130.7, 129.4, 128.2, 128.2, 124.5, 122.8, 122.5. GC-MS (EI) m/z: 337. HRMS (ESI) m/z: calculated for $[C_{18}H_{12}BrNO + H]^+$ 338.0181, found 338.0183.

(2-(3-methylpyridin-2-yl)phenyl)(phenyl)methanone (3g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3g** as white solid (102.38mg, 75%)[6q]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 4.9 Hz, 1H), 8.14 – 8.07 (m, 1H), 7.75 – 7.71 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.10 (dd, *J* = 7.7, 4.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.3, 145.8, 137.6, 133.1, 132.5, 132.1, 130.6, 130.4, 130.0, 129.9, 129.8, 129.6, 128.3, 128.0, 127.9, 122.5, 19.5. GC-MS (EI) m/z: 273.

(2-(benzo[d]thiazol-2-yl)phenyl)(phenyl)methanone (3h): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3h** as white solid (94.50mg, 60%)[6r]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.1 Hz, 1H), 7.99 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 1.4 Hz, 3H), 7.69 – 7.64 (m, 2H), 7.60 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.36 – 7.33 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.6, 165.4, 153.3, 139.7, 137.8, 135.3, 133.8, 132.7, 132.0, 129.7, 129.3, 128.9, 128.5, 128.3, 126.2, 125.4, 123.4, 121.4. GC-MS (EI) m/z: 315.

(2-(benzo[d]oxazol-2-yl)phenyl)(phenyl)methanone (3i): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3i** as white solid (100.17mg, 67%)[6s]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.85 (d, *J* = 7.1 Hz, 2H), 7.72 (td, *J* = 7.3, 1.6 Hz, 2H), 7.69 – 7.64 (m, 2H), 7.59 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.42 – 7.39 (m, 2H), 7.30 – 7.28 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.1, 150.6, 141.6, 140.1, 137.3, 133.1, 131.1, 130.2, 130.0, 129.5, 129.3, 128.6, 128.4, 125.3, 124.5, 120.3, 110.5, 100.0. GC-MS (EI) m/z: 299.

phenyl(2-(quinolin-2-yl)phenyl)methanone (3j): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3j** as white solid (97.34mg, 63%)[6t]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.73 (td, *J* = 8.4, 2.6 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.2, 140.3, 139.4, 138.2, 136.8, 133.7, 132.2, 130.2, 130.2, 129.7, 129.5, 129.3, 129.1, 128.9, 128.5, 128.0, 127.3, 126.6, 126.6, 120.1. GC-MS (EI) m/z: 309.

(2-(1H-pyrazol-1-yl)phenyl)(phenyl)methanone (3k): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **3k** as white solid (74.40mg, 60%)[6u]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 3.1 Hz, 2H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.54 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 6.23 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.9, 141.2, 136.7, 133.9, 133.0, 131.3, 130.2, 129.8, 129.1, 128.5, 128.2, 127.6, 123.4, 107.7. GC-MS (EI) m/z: 248.

(4-methoxyphenyl)(2-(pyridin-2-yl)phenyl)methanone (4a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4a** as white solid (95.37mg, 66%)[3f]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 4.1 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.66 – 7.63 (m, 1H), 7.56 (d, *J* = 4.1 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.1, 156.9, 148.9, 136.6, 132.3, 132.0, 130.7, 130.1, 129.1, 128.9, 128.6, 123.3, 122.1, 122.0, 113.7, 113.4, 55.4. GC-MS (EI) m/z: 289.

(4-fluorophenyl)(2-(pyridin-2-yl)phenyl)methanone (4b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4b** as white solid (96.95mg, 70%)[6v]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 4.5 Hz, 1H), 8.19 – 8.16 (m, 2H), 7.82 (d, *J* = 7.7 Hz,

1H), 7.75 (d, *J* = 3.2 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.60 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.98 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5, 167.3, 165.3, 132.9, 132.8, 132.1, 130.5, 129.0, 128.9, 125.7, 123.0, 122.3, 115.8, 115.6, 115.3, 115.2, 100.0. GC-MS (EI) m/z: 277.

(4-chlorophenyl)(2-(pyridin-2-yl)phenyl)methanone (4c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4c** as white solid (109.88mg, 75%)[3f]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 4.6 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 3H), 7.61 – 7.57 (m, 3H), 7.30 – 7.24 (m, 3H), 7.09 (dd, *J* = 7.5, 4.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.4, 148.9, 139.1, 138.6, 136.6, 136.4, 130.7, 130.7, 130.4, 129.0, 128.8, 128.6, 128.6 , 128.4, 122.5, 122.2. GC-MS (EI) m/z: 293.

(4-bromophenyl)(2-(pyridin-2-yl)phenyl)methanone (4d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4d** as white solid (111.21mg, 66%)[3a]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 4.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (td, *J* = 7.5, 2.2 Hz, 2H), 7.58 (td, *J* = 7.6, 6.7, 2.5 Hz, 5H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 7.5, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.3, 148.9, 139.3, 139.1, 136.8, 136.7, 131.4, 130.8, 130.4, 129.0, 128.9, 128.8, 128.6, 127.3, 122.4, 122.2. GC-MS (EI) m/z: 337.

cyclohexyl(2-(pyridin-2-yl)phenyl)methanone (4f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4f** as white solid (90.10 mg, 68%)[6w]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.34 – 7.27 (m, 1H), 2.41 – 2.32 (m, 1H), 2.27 (td, *J* = 11.5, 9.8, 5.8 Hz, 1H), 1.98 (dd, *J* = 13.3, 3.9 Hz, 1H), 1.78 – 1.74 (m, 2H), 1.64 – 1.54 (m, 1H), 1.51 – 1.48 (m, 1H), 1.43 – 1.39 (m, 1H), 1.34 – 1.30 (m, 1H), 1.24 – 1.16 (m, 1H), 1.05 – 1.00 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.1, 149.2, 141.2, 140.0, 136.9, 129.9, 128.7, 128.7, 128.1, 122.4, 122.3, 100.0, 50.7, 42.9, 29.1, 25.9. GC-MS (EI) m/z: 265.

naphthalen-2-yl(2-(pyridin-2-yl)phenyl)methanone (4g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4g** as white solid (77.25 mg, 50%)[3i]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 – 8.38 (m, 1H), 8.15 (m, 1H), 8.05 – 7.94 (m, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.86 – 7.80 (m, 3H), 7.74 – 7.69 (m, 1H), 7.64 (ddt, *J* = 11.8, 7.7, 3.2 Hz, 4H), 7.60 – 7.56 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.2, 135.2, 132.3, 131.9, 131.5, 131.4, 130.4, 129.5, 129.1, 129.0, 128.5, 128.3, 128.2, 128.1, 127.8, 127.7, 126.7, 126.5, 125.5, 124.8, 122.7, 122.2. GC-MS (EI) m/z: 309.

naphthalen-1-yl(2-(pyridin-2-yl)phenyl)methanone (4h): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) to give **4h** as white solid (95.79 mg, 62%)[3a]. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.13 (d, *J* = 8.7 Hz, 2H), 8.92 (d, *J* = 8.6 Hz, 1H), 8.45 (dd, *J* = 7.3, 1.5 Hz, 2H), 8.29 – 8.23 (m, 1H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.83 – 7.80 (m, 2H), 7.77 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.62 (dd, *J* = 8.0, 6.8 Hz, 3H), 7.56 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.22 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.85 (ddd, *J* = 6.8, 4.9, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.7, 157.1, 148.8, 136.3, 134.4, 134.0, 132.4, 131.6, 130.8, 130.3, 129.9, 129.1, 128.7, 128.6, 128.0, 127.7, 126.3, 126.0, 124.6, 123.9, 122.7, 121.6. GC-MS (EI) m/z: 309.

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Conflicts of interest

There are no conflicts to declare.

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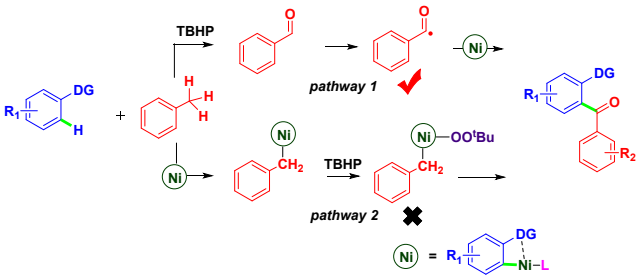

low-cost catalytic system

Graphical abstract