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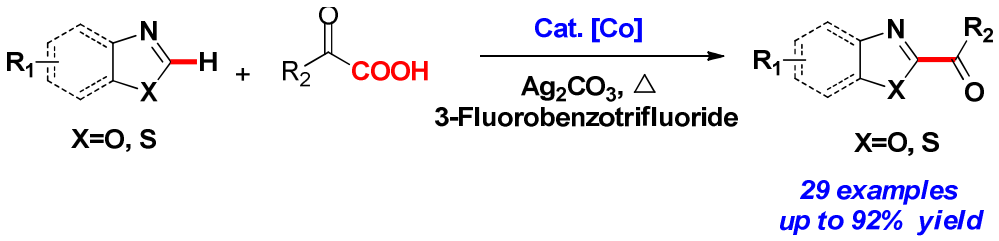
Cobalt-Catalyzed Decarboxylative 2-Benzoylation of Oxazoles and Thiazoles with α-Oxocarboxylic Acids

Ke Yang,[†,§] Xinyong Chen,[†,§] Yuqi Wang,[†] Wanqing Li,[†] Adnan A. Kadi,[‡] Hoong-Kun Fun,[‡] Hao Sun,[†,*] Yan Zhang,[†,‡] Guigen Li,[†,*] and Hongjian Lu[†,*]

[†] Institute of Chemistry & BioMedical Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[‡] Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, Riyadh 11451, Saudi Arabia

Graphical Abstract



Abstract Cobalt-catalyzed decarboxylative cross-coupling of oxazoles and thiazoles with α-oxocarboxylic acids was developed through an sp^2 C−H bond functionalization process. This work represents the first example of cobalt-catalyzed decarboxylative C−H bond functionalization, and provides an efficient mean of building some important bioactive heteroaryl ketone derivatives.

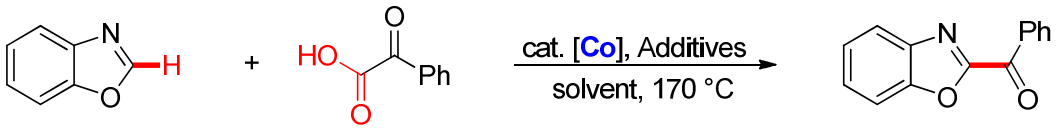
Transition-metal catalyzed C−H functionalization process allows simplification and abbreviation of synthetic procedures, and is one of the most powerful and facile methods with which to construct complex molecules in synthetic organic and medicinal chemistry.[1] Recently, cobalt-catalyzed C−H functionalization has met with success due to its economy, low toxicity and interesting reaction modes.[2,3] Many C−C[4] and C−heteroatom[5] bond-forming reactions have been achieved by this method since the first example of cobalt-catalyzed chelation-assisted C−H functionalization process was reported by Murahashi.[4x] Due to their value in synthetic chemistry, C−C bond-forming reactions have attracted significant attention, and various reagents including *N*-tosylhydrazones, *N*-cyanosuccinimide, alkyl and aryl halides, sulfamates, aziridines, alkenes and alkynes have been utilized as coupling partners.[2,4] In the meanwhile, transition-metal catalyzed decarboxylative cross-coupling reactions of (hetero)arenes with carboxylic acids through sp^2 C−H bond functionalization have also received attention because of the low cost, stability, and general availability of carboxylic acids, one of the coupling partners.[6] Since 2008,[7m] Pd complexes have been recognized as most efficient catalysts in decarboxylative C−H functionalization for the construction of versatile C−C bonds.[7-9] Other transition-metal complexes, including Rh, Ag, Cu and Ni complexes have very recently emerged as efficient catalysts,[10] but no decarboxylative C−H functionalization processes through cobalt catalysis have been reported to date.

2-Substituted oxazoles and thiazoles, present in many medicinally active compounds with a diverse array of biological activities, medicines and functional materials.[11] Previous methods to direct synthesis of 2-substituted oxazoles and thiazoles relies primarily on transition-metal catalyzed direct C-2 functionalizations of oxazoles and thiazoles.[4r,7h,10a,10b,12] Although many transition-metal catalyzed direct C-2 functionalizations have been reported, the success of direct C-2 acylation is still rare.[10a,12f,12m] To continue our efforts on cobalt-catalyzed C−H functionalization[5e,5j] and metal-catalyzed decarboxylative acylation of oxazoles,[10a] we disclose the cobalt-catalyzed 2-benzoylation of oxazoles and thiazoles with α-oxocarboxylic acids through an sp^2 C−H bond functionalization reaction. This

process represents the first example of decarboxylative cross-couplings *via* an sp^2 C–H functionalization process with cobalt catalysis.

Initially, we examined the decarboxylative cross-coupling of benzoxazole (**1a**) and 2-oxo-2-phenylacetic acid (**2a**) with $CoCl_2$ in the presence of Ag_2CO_3 at 170 °C. After extensive screening of solvents, 3-fluorobenzotrifluoride (3-F-$C_6H_4CF_3$) was found to be optimal, and with this solvent, the desired product benzo[*d*]oxazol-2-yl(phenyl)-methanone (**3a**) was obtained in 72% yield (**Table 1**, entries 1-6). Subsequently, various cobalt catalysts were examined and we found that the reaction could be effectively catalyzed by a variety of cobalt(II) complexes, including $Co(OAc)_2{\cdot}4H_2O$, $CoSO_4{\cdot}7H_2O$, $Co(acac)_2$, $CoCO_3{\cdot}\ H_2O$ and $Co(ClO_4)_2{\cdot}6H_2O$ (entries 7-12). Cobalt(III) species, such as $Co(acac)_3$ and $Co(bpy)_3(ClO_4)_3$ were also found to catalyze the reaction, albeit in low yield (entries 13 and 14). These investigations identified $Co(ClO_4)_2{\cdot}6H_2O$ as the most efficient catalyst, which provided the desired product **3a** in 92% isolated yield. Additionally, we found that replacement of Ag_2CO_3 with other oxidants, such as $K_2S_2O_8$, AgOAc or Ag_2O, produced low yield of the desired product **3a** (entries 15-17). Finally, in the absence of the Co catalyst, only a trace amount of product **3a** was formed (entry 18).

Table 1. Optimization of reaction conditions.[a]



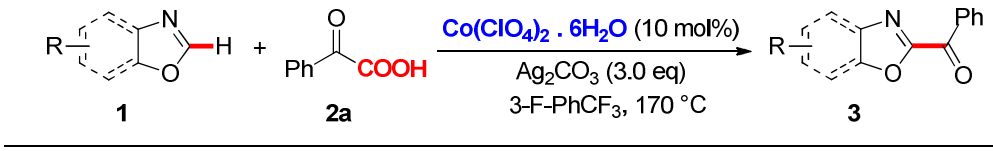
1a + **2a** → **3a**

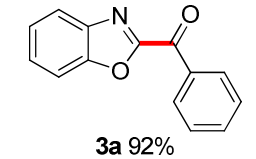
Entry	Co source (mol%)	Additives	Solvent	Yield (%)[b]
1	$CoCl_2$	Ag_2CO_3	C_6H_6	30
2	$CoCl_2$	Ag_2CO_3	$C_6H_5CH_3$	29
3	$CoCl_2$	Ag_2CO_3	C_6H_5F	29
4	$CoCl_2$	Ag_2CO_3	C_6H_5Cl	< 5
5	$CoCl_2$	Ag_2CO_3	$C_6H_5CF_3$	60
6	$CoCl_2$	Ag_2CO_3	3-F-$C_6H_4CF_3$	72
7	$CoCl_2 \cdot 6H_2O$	Ag_2CO_3	3-F-$C_6H_4CF_3$	70
8	$Co(OAc)_2 \cdot 4H_2O$	Ag_2CO_3	3-F-$C_6H_4CF_3$	45[c]
9	$CoCO_3{\cdot}\ H_2O$	Ag_2CO_3	3-F-$C_6H_4CF_3$	61
10	$CoSO_4 \cdot 7H_2O$	Ag_2CO_3	3-F-$C_6H_4CF_3$	10

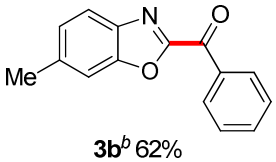
11	$Co(acac)_2$	Ag_2CO_3	3-F-$C_6H_4CF_3$	18
12	**$Co(ClO_4)_2 \cdot 6H_2O$**	**Ag_2CO_3**	**3-F-$C_6H_4CF_3$**	**95(92)**[d]
13	$Co(acac)_3$	Ag_2CO_3	3-F-$C_6H_4CF_3$	20
14	$Co(bpy)_3(ClO_4)_3$	Ag_2CO_3	3-F-$C_6H_4CF_3$	25
15	$Co(ClO_4)_2 \cdot 6H_2O$	$K_2S_2O_8$	3-F-$C_6H_4CF_3$	9
16	$Co(ClO_4)_2 \cdot 6H_2O$	AgOAc	3-F-$C_6H_4CF_3$	< 5
17	$Co(ClO_4)_2 \cdot 6H_2O$	Ag_2O	3-F-$C_6H_4CF_3$	23
18	-	Ag_2CO_3	3-F-$C_6H_4CF_3$	< 5

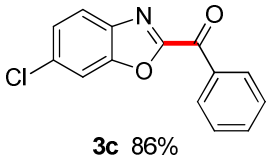
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Co source (10 mol%), Additives (0.6 mmol), 2 mL of solvent, 170 °C, 24 h. [b] Yields are based on 1a, determined by crude ^{1}H NMR using dibromomethane as the internal standard. [c] 35% of **1a** isolated. [d] Isolated yield.

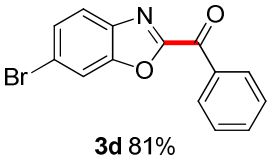
Table 2. Scope of oxazole derivatives.[a]

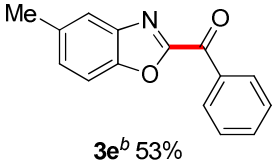


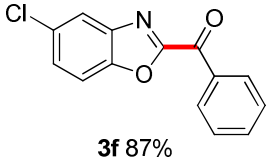

3a 92%

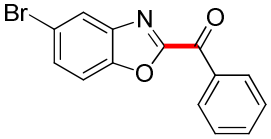

3b[b] 62%

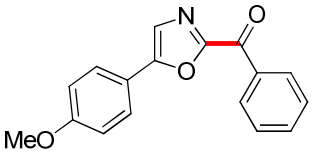

3c 86%

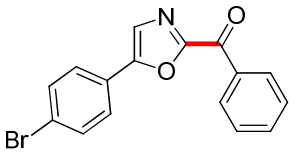

3d 81%

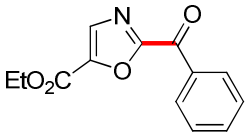

3e[b] 53%

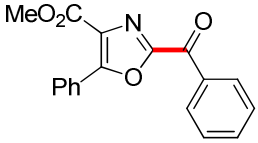

3f 87%


3g 91%


3h[b] 80%

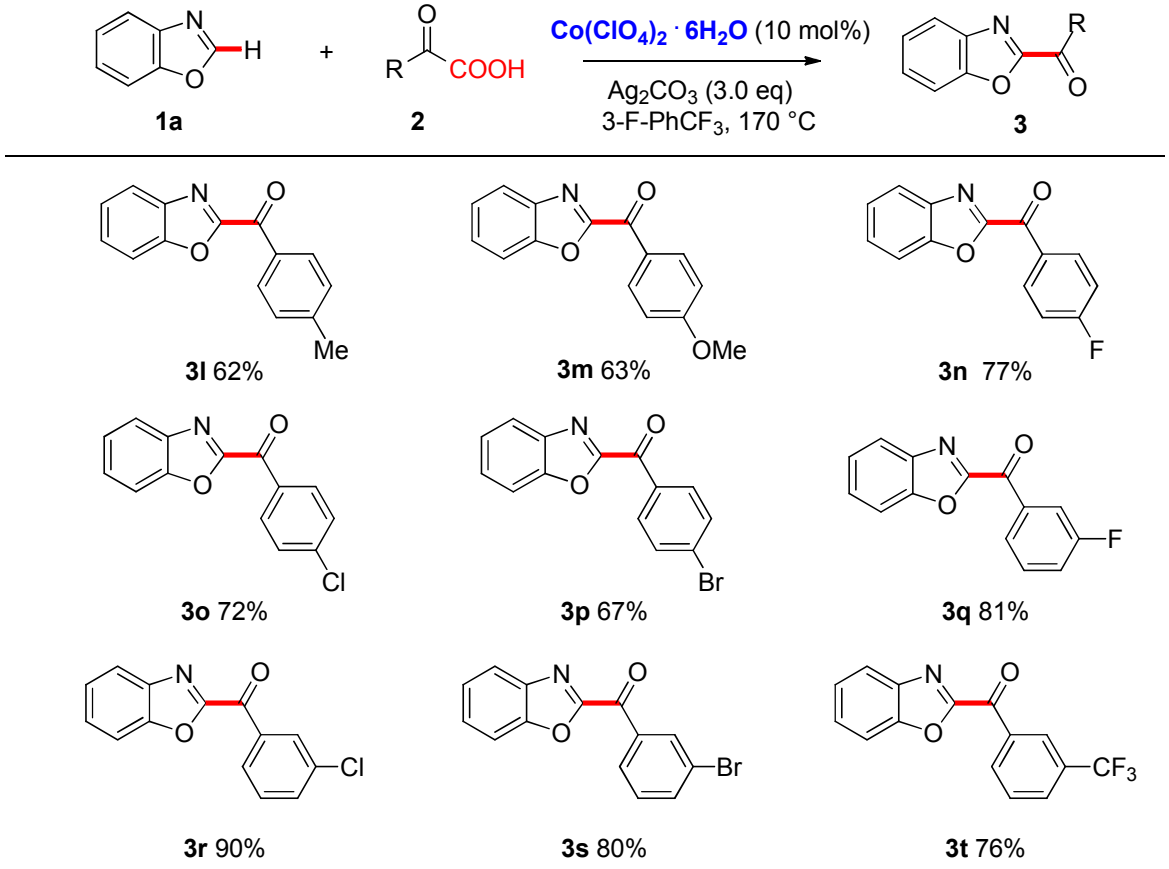

3i 82%


3j 62%


3k 56%

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (10 mol%), Ag_2CO_3 (3.0 eq), 3-fluorobenzotrifluoride (2 mL), 170 °C, 24 h. Isolated yields. [b] 36 h.

Table 3. Scope of α-oxocarboxylic acids.[a]



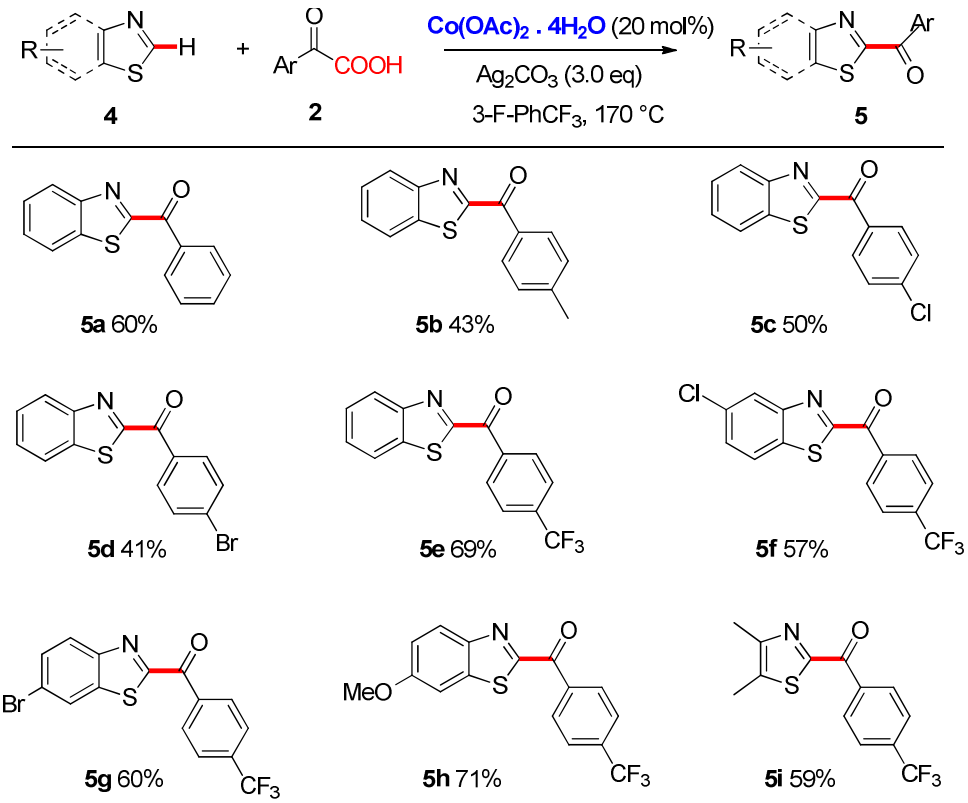
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (10 mol%), Ag_2CO_3 (3.0 eq), 3-fluorobenzotrifluoride (2 mL), 170 °C, 24 h. Isolated yields.

With the optimum conditions defined, we explored the scope of the oxazole substrates. The current catalytic system proceeds smoothly to provide 2-acylated substituted oxazoles in good yield (**Table 2**). Both electron-donating (Me) and electron-withdrawing groups (Cl and Br) on the phenyl ring of benzoxazole are tolerated (**3b-g**), and this provides more options for further potential transformations. Furthermore, both mono- and di-substituted oxazoles were effective coupling partners, and the desired products were isolated in good yield (**3h-k**). Next, the substrate scope study of α-oxocarboxylic acids was also examined. As shown in **Table 3**, *para*- or *meta*-substituted phenylglyoxylic acids, with either

an electron-donating or an electron-withdrawing group on the phenyl ring were good substrates in the coupling reaction (**3l**–**3t**). In addition, we found that there were no desired products formed when *ortho*-chloro-substituted phenylglyoxylic acid, 4-methyl-2-oxopentanoic acid or 2-cyclopropyl-2-oxoacetic acid were used as the coupling reagents.

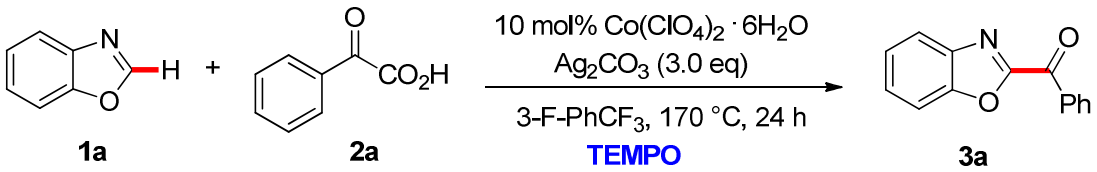
We also explored the substrate scope of thiazoles and α-oxocarboxylic acids in the presence of cobalt catalysts. In the reaction of benzothiazole **4a** with 2-oxo-2-phenylacetic acid (**2a**) under standard conditions, 31% yield of the desired product **5a** was formed and 37% of **4a** was recovered. Obvious decomposition was observed, probably due to the oxidative property of $Co(ClO_4)_2 \cdot 6H_2O$. Rescreening of the cobalt catalysts identified $Co(OAc)_2 \cdot 4H_2O$ as the optimal catalyst in the presence of Ag_2CO_3 and 3-fluorobenzotrifluoride at 170 °C (**Table 4**). Various α-oxocarboxylic acids **2** and thiazoles **4** were well tolerated under these reaction conditions, providing the desired products in moderate to good yield (**5a**-**5i**).

Table 4. Scope of thiazoles and α-oxocarboxylic acids.[a]



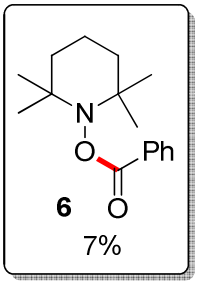
[a] Reaction conditions: **4** (0.2 mmol), **2** (0.6 mmol), $Co(OAc)_2 \cdot 4H_2O$ (20 mol%), Ag_2CO_3 (3.0 eq), 3-fluorobenzotrifluoride (2 mL), 170 °C, 24 h. Isolated yields.

Scheme 1. Radical trapping experiments

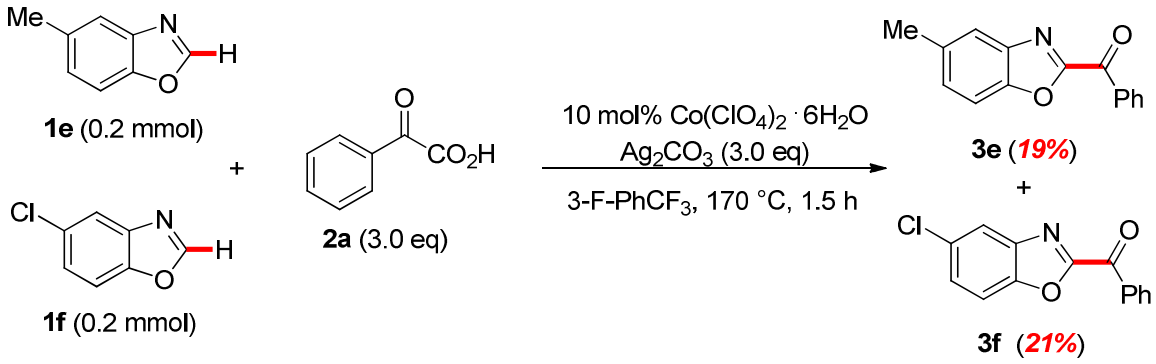


		3a
entry 1	No TEMPO	95% (44%[a])
entry 2	TEMPO (1.0 eq)	41% (11%[a])
entry 3	TEMPO (2.0 eq)	12% (< 5%[a])
entry 4	TEMPO (3.0 eq)	0% (0%[a])

a: The reaction was performed for 1 h.



Scheme 2. Intermolecular competition experiment

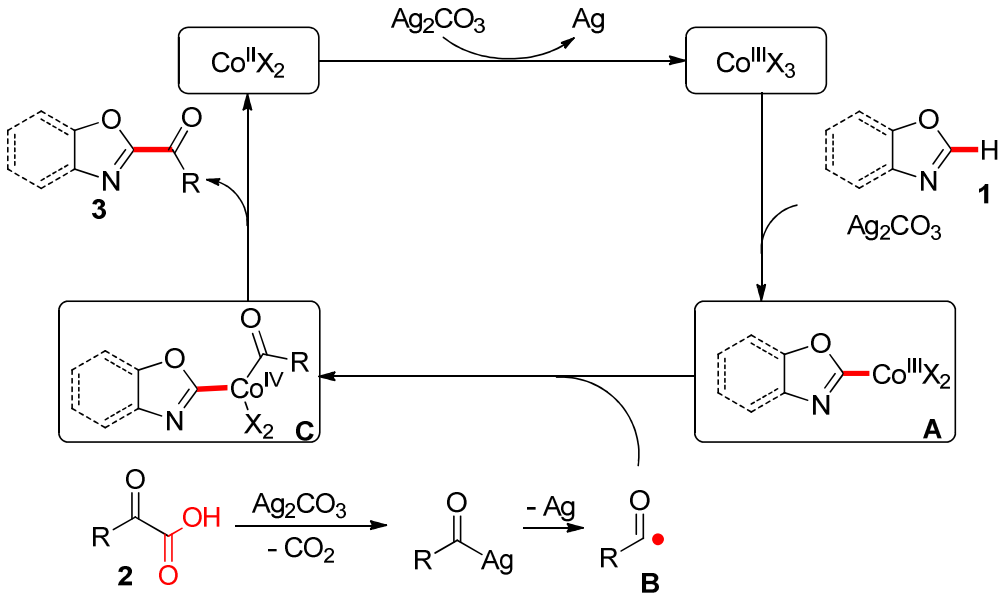


To gain insight into the reaction mechanism, some preliminary experiments were performed as depicted in Schemes 1 and 2. It was found that the addition of TEMPO resulted in the decreased yield of this reaction (**Scheme 1**, entries 1-4) and the formation of 2,2,6,6-tetramethylpiperidin-1-yl benzoate **6** (7% isolated yield) when 3 equivalent TEMPO was added (entry 4), suggesting that a radical mechanism may be implicated in the reaction. Intermolecular competition experiments between **1e** and **1f** revealed that the reaction can reach in proximity reaction rate with electron-deficient or electron-rich

arene as the substrate (**Scheme 2**). To gain further insight into the reaction mechanism, especially the rate-determining step for the transformation, deuterium-labeling experiments were carried out (**Schemes S1** and **S2** in **SI**). Significant primary kinetic isotope effects were observed in a parallel experiment (**Scheme S1**). Meanwhile, the intermolecular H/D exchange between D-benzoxazole [D]-**1a** and 2-oxo-2-phenylacetic acid **2a** was also observed (**Scheme S2**). These results suggest that the C−H bond cleavage of benzoxazoles is rate-limiting in the process. In addition, cobalt(III) compounds were found to be able to catalyze the reaction under the oxidative reaction conditions (entries 13 and 14, **Table 1**), which illustrates that Co(III) species may involve in the C−H bond cleavage step.

Although the mechanism of the reaction remains unclear, the following Co(III/IV/II) catalytic cycle (**Scheme 3**) has been proposed on the basis of the results above and previous reports.[5b] Ag_2CO_3 may oxidize the Co^{II} catalyst to the Co^{III} species, which reacts with oxazole (**1**) in the presence of Ag_2CO_3 to give the Co^{III} intermediate **A**. Subsequent addition of the acyl radical species **B**, which could be formed by the oxidation of α–oxocarboxylic acid (**2**) in the presence of Ag_2CO_3,[13] may produce cobalt(IV) species **C**. Reductive elimination of the species **C** leads to the desired product **3** and regenerating the Co^{II} catalyst thus completing the catalytic cycle. However, a catalytic cycle involving Co(II/III/I) oxidation states can not be excluded at the present stage.[4, 5, 13]

Scheme 3. A possible catalytic cycle



In summary, we have developed an efficient cobalt(II)-catalyzed direct decarboxylative 2-benzoylation of oxazole and thiazole derivatives through an sp^2 C−H bond functionalization process. This transformation is the first example of a decarboxylative C−H functionalization reaction with cobalt catalysis, and provides an efficient complementary approach to important bioactive heteroaryl ketone derivatives.

EXPERIMENTAL SECTION

General. All the solvents and commercially available reagents were purchased from commercial sources and used directly. Thin layer chromatography (TLC) was performed on plates (silica gel) and visualized by fluorescence quenching under UV light. Column chromatography was performed on silica gel (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on 400 MHz and 100 MHz spectrometer. ^{1}H NMR data were reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data were reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Mass (HRMS) analysis was obtained using TOF LC/MS system with Electrospray Ionization (ESI).

Materials. Azoles (**1a**, **1b**, **1e**, **1f**, **1j)**, α-oxocarboxylic acids (**2a**) and thiazoles (**4**) were purchased from commercial sources and used directly (**1c**, **1d**, **1g**) were prepared from condensation of the corresponding 2-aminophenol and triethyl orthoformate according to the reported procedure.[14] Azoles(**1h**, **1i**) were prepared from *p*-toluenesulfonylmethylisocyanide and the corresponding benzaldehyde in methanol according to the reported procedure.[15] Azoles(**1k**) were prepared from methyl 2-isocyanoacetate and the corresponding anhydride in THF according to the reported procedure.[16] Other α-oxocarboxylic acids were prepared from oxidation of corresponding methyl ketones with SeO_2 according to the reported procedure.[17]

General procedures for the synthesis of product 3. A 35 mL oven-dried pressure tube was charged with oxazoles **1** (0.2 mmol), α-oxocarboxylic acid **2** (0.6 mmol), $Co(ClO_4)_2 \cdot 6H_2O$ (7.3 mg, 0.02 mmol), Ag_2CO_3 (165.4 mg, 0.6 mmol) and 3-F-$PhCF_3$ (2.0 mL). The tube was then sealed and stirred vigorously at 170 ˚C for 24 h. After cooling to room temperature, the reaction mixture was diluted with DCM (20 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel (1% ethyl acetate in petroleum ether, v/v) to yield the desired products **3**.

*Benzo[d]oxazol-2-yl(phenyl)methanone (**3a**)* : white solid, 41.0 mg, yield: 92% (known compound[7o,18]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.63 – 7.58 (m, 3H), 7.52 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 157.1, 150.4, 140.8, 135.0, 134.4, 131.03, 128.7, 128.5, 125. 8, 122.4, 111.9.

*(6-Methylbenzo[d]oxazol-2-yl)(phenyl)methanone (**3b**)* : white solid, 29.4 mg, yield: 62% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8. 0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.53 (s, 1H), 7.32 (d, J = 8.4 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 156.8, 150.8, 139.6, 138.7, 135.1, 134.2, 131.0, 128.6, 127.4, 121.8, 111.8,

22.2.

(6-Chlorobenzo[d]oxazol-2-yl)(phenyl)methanone ***(3c)*** : white solid, 44.3 mg, yield: 86% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.8 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.61 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.5, 150.6, 139.5, 134.8, 134.6, 134.4, 131.0, 128.7, 126.8, 123.0, 112.4.

(6-Bromobenzo[d]oxazol-2-yl)(phenyl)methanone ***(3d)*** : white solid, 49.0 mg, yield: 81% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.55 (m, 2H), 7.92 (d, J = 1.6 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.65 – 7.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 157.3, 150.8, 139.9, 134.8, 134.5, 131.0, 129.5, 128.7, 123.4, 121.9, 115.3.

(5-Methylbenzo[d]oxazol-2-yl)(phenyl)methanone ***(3e)*** : white solid, 25.0 mg, yield: 53% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.0 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.60 (t, J = 7.6 Hz, 3H), 7.39 (d, J = 8.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 157.3, 148.7, 141.0, 135.8, 135.1, 134.2, 131.0, 129.9, 128.6, 121.9, 111.2, 21.6.

(5-Chlorobenzo[d]oxazol-2-yl)(phenyl)methanone ***(3f)*** : white solid, 44.8 mg, yield: 87% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 – 8.55 (m, 2H), 7.96 (d, J = 2.0 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.61 (t, J = 7.6 Hz, 2H), 7.55 (dd, J = 8.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 158.1, 149.0, 141.7, 134.7, 134.6, 131.3, 131.0, 128.9, 128.7, 122.1, 112.7.

(5-Bromobenzo[d]oxazol-2-yl)(phenyl)methanone ***(3g)*** : white solid, 55.0 mg, yield: 91% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 7.6 Hz, 2H), 8.13 (s, 1H), 7.76 – 7.68 (m, 2H), 7.65 – 7.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.8, 149.4, 142.2, 134.7, 134.6, 131.6, 131.0, 128.7, 125.2, 118.5, 113.2.

(5-(4-Methoxyphenyl)oxazol-2-yl)(phenyl)methanone ***(3h)*** : white solid, 44.6 mg, yield: 80% (known compound[18]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.47 (m, 2H), 7.81 – 7.79 (m, 2H), 7.66 (d, J = 7.2

Hz, 1H), 7.58 – 7.53(m, 3H), 7.02 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 161.0, 156.6, 154.4, 135.5, 133.7, 130.7, 128.4, 127.1, 122.6, 119.4, 114.6, 55.6.

(5-(4-Bromophenyl)oxazol-2-yl)(phenyl)methanone ***(3i)*** : white solid, 53.8 mg, yield: 82% (known compound[19]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.71 – 7.64 (m, 4H), 7.57 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 157.1, 153.2, 135.2, 133.9, 132.4, 130.8, 128.5, 126.8, 125.6, 124.3, 124.3.

Ethyl 2-benzoyloxazole-5-carboxylate ***(3j)*** : white solid, 30.0 mg, yield: 62% (known compound[19]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.45 (m, 2H), 7.99 (s, 1H), 7.72 – 7.68 (m, 1H), 7.59 – 7.55 (m, 2H), 4.48 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 158.2, 157.2, 144.1, 134.5, 134.5, 134.4, 130.9, 128.7, 62.3, 14.2.

Methyl 2-benzoyl-5-phenyloxazole-4-carboxylat ***e*** *(**3k**)* : yellow solid, 34.4 mg, yield: 56% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.6 Hz, 2H), 8.24 (d, J = 3.6 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.61 – 7.55 (m, 5H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 162.1, 157.5, 154.8, 134.7, 134.3, 131.5, 131.0, 129.1, 128.7, 128.6, 128.0, 125.9, 52.7.

Benzo[d]oxazol-2-yl(p-tolyl)methanone ***(3l)*** : white solid, 29.4 mg, yield: 62% (known compound[7o]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 2H), 7.98 (d, J =8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.52 – 7.48 (m, 1H), 7.40 (d, J = 8.0 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 157.3, 150.4, 145.6, 140.8, 132.5, 131.2, 129.4, 128.3, 125.7, 122.3, 111.9, 21.9.

Benzo[d]oxazol-2-yl(4-methoxyphenyl)methanone ***(3m)*** : white solid, 31.9 mg, yield: 63% (known compound[7o]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.51 – 7.48 (m, 1H), 7.07 (d, J = 8.0 Hz, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 164.7, 157.4, 150.3, 140.8, 133.6, 128.2, 128.0, 125.6, 122.2, 114.0, 111.8, 55.6.

Benzo[d]oxazol-2-yl(4-fluorophenyl)methanone ***(3n)*** : white solid, 37.0 mg, yield: 77% (known compound[7o]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.67 (m, 2H), 7.98 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.62 – 7.50 (m, 2H), 7.31 – 7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 166.6 (d, J = 256.0 Hz), 156.9, 150.4, 140.7, 134.0 (d, J = 9.6 Hz), 131.4 (d, J = 2.9 Hz), 128.6, 125.8, 122.4, 115.9 (d, J = 21.9 Hz), 111.9.

Benzo[d]oxazol-2-yl(4-chlorophenyl)methanone ***(3o)*** : white solid, 37.0 mg, yield: 72% (known compound[19]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.56 (m, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.61 – 7.55 (m, 3H), 7.53 – 7.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 156.8, 150.4, 141.1, 140.7, 133.3, 132.5, 129.0, 128.7, 125.9, 122.4, 111.9.

Benzo[d]oxazol-2-yl(4-bromophenyl)methanone ***(3p)*** : white solid, 40.5 mg, yield: 67% (known compound[7o]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.49 (m, 2H), 7.97 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 3H), 7.61 – 7.57 (m, 1H), 7.51 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 156.8, 150.4, 140.7, 133.7, 132.5, 132.0, 130.0, 128.7, 125.9, 122.5, 111.9.

Benzo[d]oxazol-2-yl(3-fluorophenyl)methanone ***(3q)*** : white solid, 39.0 mg, yield: 81% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.42 (m, 1H), 8.36 – 8.32 (m, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.54 – 7.50 (m, 1H), 7.45 – 7.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1 (d, J = 2.0 Hz), 162.6 (d, J = 246.0 Hz), 156.8, 150.5, 140.7, 136.8 (d, J = 7.1 Hz), 130.3 (d, J = 7.7 Hz), 128.7, 126.9 (d, J = 3.1 Hz), 125.9, 122.5, 121.4 (d, J = 21.4 Hz), 117.8 (d, J = 23.5 Hz), 111.9.

Benzo[d]oxazol-2-yl(3-chlorophenyl)methanone ***(3r)*** : white solid, 46.2 mg, yield: 90% (known compound[19]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (t, J = 2.0 Hz, 1H), 8.54 – 8.51 (m, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.63 – 7.57 (m, 1H), 7.55 – 7.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 156.7, 150.5, 140.7, 136.4, 134.9, 134.2, 130.9, 123.0, 129.2, 128.8,

125.9, 122.6, 111.9.

*Benzo[d]oxazol-2-yl(3-bromophenyl)methanone (**3s**)* : white solid, 40.0 mg, yield: 80% (known compound[18]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (t, J = 2.0 Hz, 1H), 8.59 – 8.57 (m, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 156.6, 150.5, 140.7, 137.1, 136.6, 133.8, 130.2, 129.7, 128.8, 125.9, 122.8, 122.6, 111.9.

*Benzo[d]oxazol-2-yl(3-(trifluoromethyl)phenyl)methanone (**3t**)* : white solid, 44.2 mg, yield: 76% (known compound[7a]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 – 8.84 (m, 2H), 8.01 – 7.96 (m, 2H), 7.77 – 7.74 (m, 2H), 7.64 – 7.60 (m, 1H), 7.55 – 7.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 156.6, 150.5, 140.7, 135.5, 134.3, 131.4 (q, J = 33.0 Hz), 130.6 (q, J = 3.5 Hz), 129.3, 128.9, 127.9 (q, J = 3.9 Hz), 126.0, 122.6, 123.7 (q, J = 274.0 Hz), 112.0.

General procedures for the synthesis of product 5. A 35 mL oven-dried pressure tube was charged with thiazoles **4** (0.2 mmol), α-oxocarboxylic acid **2** (0.6 mmol), $Co(OAc)_2 \cdot 4H_2O$ (7.6 mg, 0.04 mmol), Ag_2CO_3 (165.4 mg, 0.6 mmol) and 3-F-PhCF_3 (2.0 mL). The tube was then sealed and stirred vigorously at 170 ˚C for 24h. After cooling to room temperature, the reaction mixture was diluted with DCM (20 mL), filtered through a pad of Celite, and the filtrate was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel (gradient eluent of 1% ethyl acetate in petroleum ether, v/v) to yield the desired products **5.**

*Benzo[d]thiazol-2-yl(phenyl)methanone (**5a**)* : yellow solid, 28.7 mg, yield: 60% (known compound[19]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.57 (m, 2H), 8.29 – 8.27 (m, 1H), 8.07 – 8.04 (m, 1H), 7.72 – 7.69 (m, 1H), 7.64 – 7.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 167.1, 153.9, 137.0, 135.0, 134.0, 131.3, 128.6, 127.7, 127.0, 125.8, 122.2.

*Benzo[d]thiazol-2-yl(p-tolyl)methanone (**5b**)* : yellow solid, m.p.: 89-90 ^{o}C, 21.8 mg, yield: 43% ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 7.6 Hz, 2H), 8.27 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.39 (d, J = 7.2 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 167.5, 153.9, 145.0, 137.0, 132.4, 131.4, 129.3, 127.5, 126.9, 125.7, 122.2, 21.9. IR (neat) v 3004, 2916, 1637, 1566, 1318, 1273, 1183, 1116, 889, 833, 764, 705 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{12}NOS$ $(M+H)^+$: 254.0634, found: 254.0628.

*Benzo[d]thiazol-2-yl(4-chlorophenyl)methanone (**5c**)* : yellow solid, m.p.: 91-92 ^{o}C, 27.4 mg, yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.57 (m, 2H), 8.28 – 8.26 (m, 1H), 8.06 – 8.04 (m, 1H), 7.65 – 7.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 166.8, 153.8, 140.6, 137.1, 133.3, 132.7, 128.9, 127.8, 127.1, 125.8, 122.2. IR (neat) v 3005, 2316, 1638, 1585, 1320, 1275, 1175, 1117, 891, 835, 764, 708 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{14}H_9ClNOS$ $(M+H)^+$: 274.0088, found: 274.0077.

*Benzo[d]thiazol-2-yl(4-bromophenyl)methanone (**5d**)* : yellow solid, m.p.: 90-91 ^{o}C, 26.0 mg, yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 2H), 8.27 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.65 – 7.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 166.8, 153.8, 137.1, 133.7, 132.8, 131.9, 129.5, 127.8, 127.1, 125.8, 122.2. IR (neat) v 3010, 2987, 1639, 1581, 1394, 1275, 1173, 1115, 891, 835, 749, 710 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{14}H_9BrNOS$ $(M+H)^+$: 317.9583, found: 317.9568.

*Benzo[d]thiazol-2-yl(4-(trifluoromethyl)phenyl)methanone (**5e**)* : yellow solid, m.p.: 95-96 ^{o}C, 42.3 mg, yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 8.0 Hz, 2H), 8.28 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.66 – 7.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 166.3, 153.8, 137.8, 137.1, 134.9 (q, J = 32.7 Hz), 131.6, 128.1, 127.2, 125.9, 125.56 (q, J = 3.7 Hz), 126.3 (q, J = 272.0 Hz), 122.3. IR (neat) v 3061, 3004, 1655, 1486, 1320, 1275, 1170, 1154, 893, 852, 715, 706 cm^{-1}.HRMS (ESI, *m/z*): calcd. for $C_{15}H_9F_3NOS$ $(M+H)^+$: 308.0351, found: 308.0337.

*(5-Chlorobenzo[d]thiazol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**5f**)* : yellow solid, m.p.: 135-136

°C, 38.4 mg, yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 9.2 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 2.4 Hz, 1H), 7.23 (dd, J = 9.2, 2.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 163.7, 160.1, 148.5, 139.3, 138.1, 134.8 (q, J = 32.2 Hz), 131.4, 126.6, 125.4 (q, J = 3.7 Hz), 123.7 (q, J = 274.2 Hz), 118.0, 103.4, 55.9. IR (neat) v 3005, 2989, 1646, 1538, 1327, 1275, 1169, 1118, 897, 858, 763, 705 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{11}F_3NO_2S$ $(M+H)^+$: 338.0457, found: 338.0443.

*(6-Bromobenzo[d]thiazol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**5g**)* : yellow solid, m.p.: 104-105 °C, 41.0 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 1.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.58 (dd, J = 8.4, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 168.0, 154.5, 137.5, 135.3, 135.1 (q, J= 32.8 Hz), 133.3, 131.6, 128.7, 125.5 (q, J = 3.7 Hz), 125.4, 123.1, 123.6 (q, J= 271.0 Hz). IR (neat) v = 3005, 2989, 1650, 1583, 1325, 1275, 1170, 1129, 892, 839, 765, 704 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_8ClF_3NOS$ $(M+H)^+$: 341.9962, found: 341.9948.

*(6-Methoxybenzo[d]thiazol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**5h**)* : yellow solid, m.p.: 97-99 °C, 54.8 mg, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.0 Hz, 2H), 8.21 (s, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.73 (dd, J = 8.8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184. 1, 166.7, 152.6, 138.6, 137.5, 135.0 (q, J = 32.7 Hz), 131.5, 131.0, 126.9, 125.5 (q, J = 3.7 Hz), 123.6 (q, J= 272.3 Hz), 124.9, 122.5. IR (neat) v 3005, 2989, 1643, 1495, 1325, 1275, 1174, 1110, 865, 830, 765, 704 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_8BrF_3NOS$ $(M+H)^+$: 385.9457, found: 385.9440.

*(4,5-Dimethylthiazol-2-yl)(4-(trifluoromethyl)phenyl)methanone (**5i**)* : yellow oil, 33.6 mg, yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 2.51 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 161.7, 152.2, 138.4, 136.9, 134.3 (q, J = 32.7 Hz), 131.3, 125.2 (q, J = 3.7 Hz), 123.7 (q, J = 271.0 Hz), 15.1, 12.0. IR (neat) v3002, 2913, 1623, 1564, 1324, 1260, 1171, 1115, 918, 806, 750, 702 cm^{-1}.HRMS (ESI, *m/z*): calcd. for $C_{13}H_{10}F_3NOS$ $(M+H)^+$:

286.0508, found: 286.0513.

2,2,6,6-Tetramethylpiperidin-1-yl benzoate ***(6)*** : white soild, 10.9 mg, yield: 7 % (3eq.TEMPO for 1h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.04 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 1.89 – 1.44 (m, 6H), 1.30 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 132.8, 129.8, 129.6, 128.5, 60.4, 39.1, 32.0, 20.9, 17.0. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{24}NO_2$ $(M+H)^+$: 262.1802, found: 262.1788.

ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of the desired product. Deuterium labeling studies.

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AUTHOR INFORMATION

Corresponding Authors

*E-mail: haosun@nju.edu.cn,

*E-mail: guigenli@nju.edu.cn,

*E-mail: hongjianlu@nju.edu.cn

Author contributions

§ These individuals contributed equally to this research**.**

Notes

The authors declare no competing financial interest.

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