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Nickel-catalyzed cross-coupling of β-carbonyl alkenyl pivalates with arylzinc chlorides

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The nickel-catalyzed cross-coupling reaction of β-carbonyl alkenyl pivalates with arylzinc reagents generates 3-aryl-substituted α,β-unsaturated carbonyl compounds via C-O bond cleavage. The reaction features mild reaction conditions, a wide scope of substrates, and good functional group tolerance.

Introduction

α,β-Unsaturated carbonyl compounds are widely existed in natural and bioactive molecules.[1] They were also used in the synthesis of pharmaceuticals, natural products, pesticides, and other useful materials.[1,2] A range of classical methods such as Wittig reaction,[3] Peterson olefination,[4] Horner-Wadsworth-Emmons reaction[5] and Claisen-Schmidt condensation[6] have been used to synthesize the compounds. In recent years, transition-metal-catalyzed reactions such as cross couplings as versatile and highly effective synthetic methods were developed to prepare the compounds or perform functionalization of α,β-unsaturated carbonyl compounds.[7-9] For example, Bethi and Fernandes carried out one-pot synthesis of α,β-unsaturated methyl ketones from homoallyl alcohols by sequential $PdCl_2/CrO_3$-promoted Wacker process followed by an acid-mediated dehydration reaction.[7a] Cheng and co-workers developed a palladium-catalyzed dehydrogenative coupling reaction of saturated carbonyl compounds with aryl halides to prepare highly substituted α,β-unsaturated carbonyl compounds.[7b] Li et al. reported Ru-catalyzed selective synthesis of (*E*)-2-arylcinnamaldehydes from (*E*)-β-bromostyrenes and aryl aldehydes.[7c] Shi et al. reported β-alkylation of α,β-unsaturated ketones or esters via Fe-catalyzed cross-coupling of alkenyl pivalates with alkyl Grignard reagents.[8b] In view of the importance of α,β-unsaturated carbonyl compounds and inspired by the reported syhthetic methods, we initiated a study of nickel-catalyzed cross-coupling of β-carbonyl alkenyl pivalates with arylzinc reagents. Herein we report the results.

Results and discussion

To screen catalysts, solvents, and other reaction conditions, reaction of 4-oxopent-2-en-2-yl pivalate (**1a**) with *p*-MeC_6H_4ZnCl (**2**) was chosen as the model reaction. It has been reported that nickel can effectively catalyze C-O bond activation.[10] Hence we chose nickel complexes as pre-catalysts in this study. $Ni(PCy_3)_2Cl_2$ was first tested and it led to 74% product yield when the reaction was run in THF at 30 °C for 24 h (Table 1, entry 1). Next, we examined the reaction in different solvents including Et_2O, dioxane, toluene, THF/NMP, THF/DMF and THF/DMA and found that toluene and 3:1 THF/NMP were also suitable solvents for this transformation besides THF (Table 1, entries 2–9). However, further tests showed that THF and toluene did not suit for a wide scope of substrates. Hence other condition screening was performed in a 3:1 THF/NMP mixture. Other nickel complexes including $Ni(dppp)Cl_2$, $Ni(PPh_3)_2Cl_2$, $Ni(DME)Cl_2$, and a combination of $Ni(DME)Cl_2$ and TMEDA were tested and each of them was demonstrated to be less effective than $Ni(PCy_3)_2Cl_2$ (Table 1, entries 10–13). Increasing or decreasing loading amount of $Ni(PCy_3)_2Cl_2$ resulted in yield decrease (Table 1, entries 14 and 15). In above reactions, the zinc reagent was prepared by reaction of *p*-MeC_6H_4MgBr with an equimolar amount of $ZnCl_2$ in the presence of 2 equiv. of LiCl. In the absence of a LiCl additive the coupling reaction gave 51% product yield. If the zinc reagent was prepared from *p*-MeC_6H_4Li and $ZnCl_2$, the coupling reaction afforded only trace amount of desired product (Table 1, entries 16 and 17). These experimental facts showed that both Li^+ and Mg^{2+} ions played important roles in the catalytic transformation. It has been reported that action of ArZnX with MgX_2 led to formation of ionic zincates which have higher reactivity than ArZnX.[11] The role of LiX may involve increasing the solubility of the zinc reagents through forming a trimetallic adduct and producing reactive zincates.[12] The temperature effect was next tested. The reaction in THF/NMP at 40 °C gave a little lower yield and at 25 °C and 20 °C gave comparable yields to that at 30 °C. When the reaction was run

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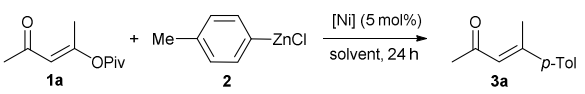
Table 1 Screening of catalyst and optimization of reaction conditions[a]



1a 2 3a

Entry	Catalyst	Solvent	T (°C)	Yield(%)[b]
1	$Ni(PCy_3)_2Cl_2$	THF	30	74
2	$Ni(PCy_3)_2Cl_2$	Et_2O	30	53
3	$Ni(PCy_3)_2Cl_2$	dioxane	30	40
4	$Ni(PCy_3)_2Cl_2$	toluene	30	78
5	$Ni(PCy_3)_2Cl_2$	THF/NMP (1:1)	30	69
6	$Ni(PCy_3)_2Cl_2$	THF/NMP (2:1)	30	72
7	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	30	76
8	$Ni(PCy_3)_2Cl_2$	THF/DMF (3:1)	30	54
9	$Ni(PCy_3)_2Cl_2$	THF/DMA (3:1)	30	45
10	Ni(dppp)Cl_2	THF/NMP (3:1)	30	69
11	$Ni(PPh_3)_2Cl_2$	THF/NMP (3:1)	30	66
12	Ni(DME)Cl_2	THF/NMP (3:1)	30	69
13[c]	Ni(DME)Cl_2	THF/NMP (3:1)	30	69
14[d]	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	30	69
15[e]	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	30	64
16[f]	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	30	51
17[g]	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	30	trace
18	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	40	67
19	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	25	74
20	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	20	73
21	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	10	49
22[h]	$Ni(PCy_3)_2Cl_2$	THF/NMP (3:1)	25	60

[a] The reactions were carried out on a 0.3 mmol scale, 1.5 equiv. of *p*-MeC_6H_4ZnCl and 2 cm^3 of solvent were employed. Unless otherwise specified, *p*-MeC_6H_4ZnCl was prepared from *p*-MeC_6H_4MgBr and 1 equiv. of $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] Isolated yield. [c] 7.5 mol% of TMEDA was employed as the ligand. [d] 2.5 mol% $Ni(PCy_3)_2Cl_2$ was employed. [e] 7.5 mol% $Ni(PCy_3)_2Cl_2$ was employed. [f] *p*-MeC_6H_4ZnCl was prepared from *p*-MeC_6H_4MgBr and 1 equiv. of $ZnCl_2$. [g] *p*-MeC_6H_4ZnCl was prepared from *p*-MeC_6H_4Li and 1 equiv. of $ZnCl_2$. [h] The reaction time was 12 h.

at 10 °C, the product yield markedly reduced (Table 1, entries 18-21). We also noticed that shortening reaction time led to the yield decrease (Table 1, entry 22). Finally, the reaction mixture obtained under the optimized conditions was examined using GC-MS to identify the by-products. The homocoupling species of the zinc reagent, 4,4'-dimethylbiphenyl, was a main by-product. Small amounts of 4,5-dimethylocta-3,5-diene-2,7-dione and 4,4-di-*p*-tolylpentan-2-one were also observed. The former was the homocoupling species of **1a** and the latter probably resulted from conjugate addition of **3a** with the zinc reagent.

Next, the substrate scope of the cross-coupling reaction was examined. The reactions in THF often led to slightly lower yields than those in THF/NMP (3:1) mixture in a series of tests. Toluene only suited as the reaction solvent for partial substrates. Hence next tests were mostly carried out in a 3:1 mixture of THF and NMP. We have demonstrated that 4-oxopent-2-en-2-yl pivalate (**1a**) reacted with *p*-MeC_6H_4ZnCl to afford a cross-coupling product in good yield (Table 1). Further test showed that other electron-rich zinc reagents including *p*-$Me_2NC_6H_4ZnCl$ and *p*-$MeOC_6H_4ZnCl$ also reacted smoothly with **1a** to give corresponding cross-coupling product in good yields (Table 2, entries 1 and 2). Electron-poor arylzinc chloride, *p*-$CF_3C_6H_4ZnCl$, reacted with **1a** under standard conditions to form desired product in 52% yield. Elevated reaction temperature resulted in a slight yield increase (59%) (Table 2, entry 3). The relatively low yield was ascribed to the weak nucleophilic power of *p*-$CF_3C_6H_4ZnCl$. Reaction of *o*-MeC_6H_4ZnCl with **1a** afforded 4-*o*-tolylpent-3-en-2-one in 89% yield, including 55% of (*E*)-isomer and 34% of (*Z*)-isomer which can be separated by column chromotography (Table 2, entry 4). It seems that the steric hindrance of the *o*-tolyl group did not affect the reactivity of the zinc reagent and *o*-MeC_6H_4ZnCl even led to higher product yield than *p*-MeC_6H_4ZnCl. This is probably because steric hindrance of the *o*-tolyl group prevented the homo-coupling side reaction of the zinc reagent. 2-Thienylzinc chloride as a representative of heteroarylzinc reagent was demonstrated to react with **1a** under standard conditions, giving 4-(thiophen-2-yl)pent-3-en-2-one in 58% yield (Table 2, entry 5). 4-Oxo-4-phenylbut-2-en-2-yl pivalate (**1b**) exhibited higher reactivity than **1a** when it reacted with either electron-rich or electron-poor arylzinc reagents, giving corresponding cross-coupling products in 71-90% yields (Table 2, entries 6-9). The high reactivity of **1b** probably results from the existence of an extended π-conjugated system. 3-Oxocyclopent-1-enyl pivalate (**1c**) displayed a comparable reactivity to **1a**. Its reaction with *p*-$Me_2NC_6H_4ZnCl$, *p*-$MeOC_6H_4ZnCl$, and *p*-MeC_6H_4ZnCl, respectively, resulted in desired products in 75-88% yields (Table 2, entries 10-12). *p*-$CF_3C_6H_4ZnCl$ still showed relatively low reactivity in the reaction with **1c**, leading to the cross-coupling product in 50% yield (Table 2, entry 13). 2-Furylzinc chloride was demonstrated to react with **1c** to afford 3-(furan-2-yl)cyclopent-2-enone in 45% yield (Table 2, entry 14). Reaction of 2-thienylzinc chloride with **1c** formed desired product in 89% yield (Table 2, entry 15), which was much higher than that obtained from its reaction with **1a**. We noticed that the reaction of *p*-MeC_6H_4ZnCl, *p*-$CF_3C_6H_4ZnCl$, and 2-thienylzinc chloride with **1c** proceeded better in toluene than in a 3:1 mixture of THF and NMP, and the reaction of *p*-$CF_3C_6H_4ZnCl$, 2-furylzinc chloride, and 2-thienylzinc chloride required a higher reaction temperature (50 °C) to achieve the optimal results. Ethyl 3-(pivaloyloxy)but-2-enoate (**1d**) exhibited higher reactivity than **1a**. In most reactions tested its reactivity was comparable to that of **1b**. For example, reaction of **1d** with *p*-$Me_2NC_6H_4ZnCl$, *p*-$MeOC_6H_4ZnCl$, *p*-MeC_6H_4ZnCl, and *p*-$CF_3C_6H_4ZnCl$, respectively, gave comparable yields of desired products to corresponding those in the reaction of **1b** (Table 2, entries 16-19). Reaction of **1d** with *o*-MeC_6H_4ZnCl generated ethyl 3-*o*-tolylbut-2-enoate in 92% yield (Table 2, entry 20), which is consistent with the result in the reaction of **1a** with *o*-MeC_6H_4ZnCl. Compound **1d** also reacted smoothly with 2-furylzinc chloride and 2-thienylzinc chloride at 50 °C to afford the desired products in 69% and 82% yields, respectively (Table 2, entries 21 and 22). Ethyl 2-(pivaloyloxy)cyclohex-1-ene-1-carboxylate (**1e**) showed a lower reactivity than **1d**. It exhibited a similar reactivity to **1a** when *p*-$MeOC_6H_4ZnCl$ and *p*-MeC_6H_4ZnCl were employed as the nucleophilic reagents (Table 2, entries 23 and 24). However, reaction of **1e** with *p*-$Me_2NC_6H_4ZnCl$ under standard conditions

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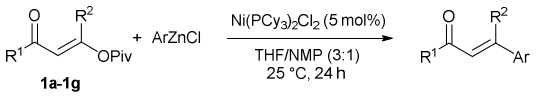
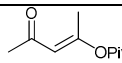
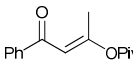
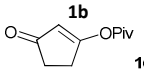
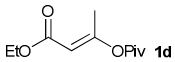
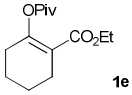
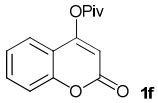
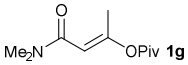
Table 2 Cross-coupling of β-carbonyl alkenyl pivalates with arylzinc chlorides[a]



1a-1g

Entry	Alkenyl-OPiv	Ar	Yield (%)[b]
1	 **1a**	*p*-$Me_2NC_6H_4$	84
2	**1a**	*p*-$MeOC_6H_4$	77
3	**1a**	*p*-$CF_3C_6H_4$	52 (59[c])
4	**1a**	*o*-MeC_6H_4	89[d]
5	**1a**	2-thienyl	58
6	 **1b**	*p*-$Me_2NC_6H_4$	86
7	**1b**	*p*-$MeOC_6H_4$	90
8	**1b**	*p*-MeC_6H_4	89
9	**1b**	*p*-$CF_3C_6H_4$	71[c]
10	 **1c**	*p*-$Me_2NC_6H_4$	88
11	**1c**	*p*-$MeOC_6H_4$	82
12	**1c**	*p*-MeC_6H_4	75[e]
13	**1c**	*p*-$CF_3C_6H_4$	50[c,e]
14	**1c**	2-furyl	45[c]
15	**1c**	2-thienyl	89[c,e]
16	 **1d**	*p*-$Me_2NC_6H_4$	93
17	**1d**	*p*-$MeOC_6H_4$	83
18	**1d**	*p*-MeC_6H_4	85
19	**1d**	*p*-$CF_3C_6H_4$	74[c]
20	**1d**	*o*-MeC_6H_4	92
21	**1d**	2-furyl	69[c]
22	**1d**	2-thienyl	82[c]
23	 **1e**	*p*-$MeOC_6H_4$	77
24	**1e**	*p*-MeC_6H_4	74
25	**1e**	*p*-$Me_2NC_6H_4$	54 (61[c])
26	 **1f**	*p*-$Me_2NC_6H_4$	88
27	**1f**	*p*-$MeOC_6H_4$	78
28	**1f**	*p*-MeC_6H_4	70
29	**1f**	*p*-$CF_3C_6H_4$	73[c]
30	**1f**	2-furyl	55
31	**1f**	2-thienyl	69[c]
32	 **1g**	*p*-$Me_2NC_6H_4$	99[f]
33	**1g**	*p*-$MeOC_6H_4$	99[f]
34	**1g**	*p*-MeC_6H_4	90[f]

[a] Unless otherwise specified, the reactions were carried out on a 0.3 mmol scale according to the conditions indicated by above equation, 1.5 equiv. of arylzinc chlorides and 2 cm^3 solvent were employed. *p*-RC_6H_4ZnCl was prepared from *p*-RC_6H_4MgBr and 1 equiv. of $ZnCl_2$ in the presence of 2 equiv. of LiCl; 2-furylzinc chloride and 2-thienylzinc chloride were prepared by reaction of 2-furyllithium or 2-thienyllithium with 1 equiv. of $ZnCl_2$ in the presence of 1 equiv. of LiCl and 1 equiv. of $MgBr_2$. [b] Isolated yield. [c] The reaction was run at 50 °C. [d] The product includes 55% (*E*)-4-(*o*-tolyl)pent-3-en-2-one and 34% (*Z*)-4-(*o*-tolyl)pent-3-en-2-one. [e] Toluene was used as the reaction solvent. [f] A mixture of *Z* and *E* isomers was obtained.

resulted in relatively low yield (54%) for unclear reasons. Elevating the reaction temperature (50 °C) led to only small increase of the product yield (Table 2, entry 25). 2-Oxo-2H-chromen-4-yl pivalate (**1f**) as a lactone derivative displayed a similar reactivity to 1a when it reacted with electron-rich zinc reagents including *p*-$Me_2NC_6H_4ZnCl$, *p*-$MeOC_6H_4ZnCl$ and *p*-MeC_6H_4ZnCl and showed a little higher reactivity than 1a when it reacted with the electron-poor zinc reagent, *p*-$CF_3C_6H_4ZnCl$, and heteroaryl- zinc reagent, 2-thienylzinc chloride (Table 2, entries 26-31). The lower reactivity of both **1e** and **1f** than **1d** was probably because the former ones have larger steric hindrance. 4-(Dimethylamino)-4-oxobut-2-en-2-yl pivalate (**1g**) exhibited excellent reactivity. Its reaction with *p*-$Me_2NC_6H_4ZnCl$ and *p*-$MeOC_6H_4ZnCl$ gave desired products in quantitative yields, and with *p*-MeC_6H_4ZnCl afforded the cross-coupling product in 90% yield (Table 2, entries 32-34). In addition, each reaction of **1g** tested gave a mixture of *Z*- and *E*-isomers of the cross-coupling products.

The $Ni(PCy_3)_2Cl_2$-catalyzed reaction of 4-oxopent-2-en-2-yl pivalate with *p*-MeC_6H_4ZnCl was not affected by 1,1-diphenylethene additive. The reaction run under the optimized conditions in the presence of 1,1-diphenylethene (1 equiv.) gave the desired product in 74% yield. This ruled out the possibility of a radical process. Reaction of 4-oxopent-2-en-2-yl pivalate with *p*-MeC_6H_4ZnCl could not occur in the absence of $Ni(PCy_3)_2Cl_2$, which means that a direct nucleophilic substitution was impossible. When a combination of $Ni(COD)_2$ (5 mol%) and PCy_3 (10 mol%) was employed to replace $Ni(PCy_3)_2Cl_2$ as the catalyst, the reaction afforded cross-coupling product in 75% yield. This experimental fact showed that the catalytically active species might be a Ni(0) complex. Based on the above experimental results and the reported mechanism of nickel-catalyzed cross-coupling reaction,[9a,9c] a possible catalytic cycle is outlined in Scheme 1 (catalytic cycle **I**). Thus, reaction of $Ni(PCy_3)_2Cl_2$ with arylzinc chloride generates $L_2Ni(0)$ (**A**) which is active catalyst. Oxidative addition of β-carbonyl alkenyl pivalate to $L_2Ni(0)$ forms $L_2Ni(OPiv)(C(Me)=CHC(O)R)$ (**B**). Substitution of OPiv from the metal center in complex **B** by the arylzinc reagent results in $L_2Ni(Ar)(C(Me)=CHC(O)R)$ (**C**). The intermediate **C** undergoes reductive elimination to give cross-coupling product and regenerate $L_2Ni(0)$. In the process a (*E*)-isomeric product should be formed from (*E*)-β-carbonyl alkenyl pivalate. However, in the reactions of **1a** with *o*-MeC_6H_4ZnCl as well as **1g** with various zinc reagents, a mixture of (*Z*)- and (*E*)-isomers was obtained in each case. The ^1H NMR spectra of starting material **1a**, and the products (*Z*)- and (*E*)-4-(*o*-tolyl)pent-3-en-2-one showed that they were stable in $CDCl_3$ solution in 37 hours, no isomerized species being observed in each case (see figures S1-S3 in the ESI). GC monitoring of the reaction process also showed that (1) no isomerized species of compound **1a** was detected; (2) both (*Z*)- and (*E*)-4-(*o*-tolyl)pent-3-en-2-one appeared in the early stage of the reaction, and the ratio of the (*Z*)- and (*E*)-isomers was approximately constant as the reaction progress (see figures S7-S10 in the ESI). These results imply that a competitive reaction process might be existed. This process is also nickel-catalyzed because the cross-coupling

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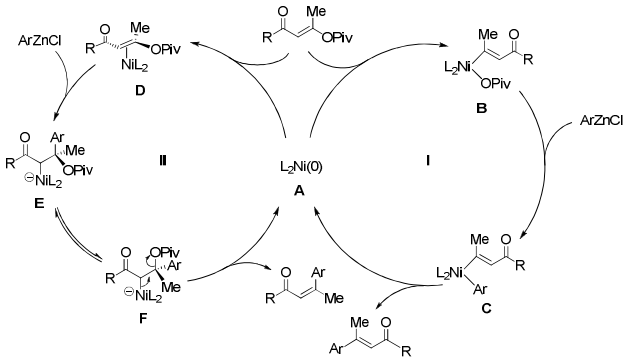
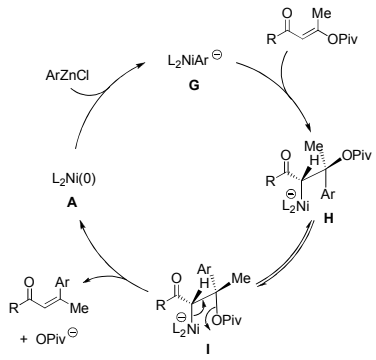


Scheme 1 Proposed catalytic cycle.

reaction cannot occur in the absence of a nickel catalyst. The competitive catalytic cycle is proposed in Scheme 1 (cycle **II**). In this cycle, interaction of $L_2Ni(0)$ with (*E*)-β-carbonyl alkenyl pivalate forms a alkene-nickel coordination complex **D**. Addition of ArZnCl to the C-C double bond of **D** from the opposite side of the L_2Ni unit generates the intermediate **E**.[13,14] **E** can convert to conformation **F** in which the OPiv group and the NiL_2 moiety are *anti*-periplanar. *Anti*-elimination of $OPiv^-$ and NiL_2 from **F** results in (*Z*)-RC(O)CH=C(Me)Ar.[14] However, we cannot rule out another pathway to generate (*Z*)-isomer as shown in Scheme 2. Thus, interaction of ArZnCl with $L_2Ni(0)$ forms an ate complex L_2NiAr^- (**G**). *Syn* insertion of the C-C double bond of (*E*)-β-carbonyl alkenyl pivalate into the Ni-C_{Ar} bond of the ate complex forms the intermediate **H**. Bond rotation of **H** results in **I**. *Syn*-elimination of $OPiv^-$ and NiL_2 from **I** produces (*Z*)-RC(O)CH=C(Me)Ar.



Scheme 2 Another possible pathway to generate (*Z*)-isomer.

Conclusions

We have performed a nickel-catalyzed cross-coupling of β-carbonyl alkenyl pivalates with arylzinc chlorides under mild reaction conditions. β-Arylated α,β-unsaturated ketones, esters, and amides were synthesized via the reaction. Both acyclic and cyclic β-carbonyl alkenyl pivalates were suitable for this transformation. Electron-rich and electron-poor arylzinc chlorides, 2-furylzinc chloride and 2-thienylzinc chloride can be employed as the nucleophilic reagents. Due to easy preparation of β-carbonyl alkenyl carboxylates from 1,3-dicarbonyl compounds, this approach provides a convenient route to synthesize β-aryl-substituted α,β-unsaturated carbonyl compounds from widely available 1,3-dicarbonyl compounds. Studies are in progress to expand the scope of the reaction to alkyl- and alkenylzinc reagents.

Experimental

All air or moisture-sensitive manipulations were performed under nitrogen using standard Schlenk techniques. Toluene, THF and Et_2O were purified by JC Meyer Phoenix Solvent Systems. 1,4-Dioxane was distilled over sodium under nitrogen. NMP, DMF and DMA were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. Ethyl 2-(pivaloyloxy)cyclohex-1-ene-1-carboxylate (**1e**) and 2-oxo-2*H*-chromen-4-yl pivalate (**1f**) were prepared according to literature procedures.[8b] Other β-carbonyl alkenyl pivalates were prepared by similar method. Grignard reagents[15] and lithium reagents[16] were prepared according to reported methods. Arylzinc chlorides were prepared from $ZnCl_2$ and an equiv. of ArMgBr in the presence of 2 equiv of LiCl. 2-Furylzinc chloride and 2-thiophenylzinc chloride were prepared by reaction of 2-furyllithium or 2-thiophenyllithium with an equiv. of $ZnCl_2$ in the presence of 1 equiv. of LiCl and 1 equiv. $MgBr_2$. Other solvents and chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a Bruker av400 NMR spectrometer at ambient temperature. The chemical shifts of ^1H NMR spectra were referenced to TMS, and the chemical shifts of ^{13}C NMR spectra were referenced to internal solvent resonances. High-resolution mass spectra (HR-MS) were acquired on a Thermo Fisher LTQ Orbitrap XL mass spectrometer in ESI mode using an Orbitrap mass analyzer.

Synthesis of β-carbonyl alkenyl pivalates

(*E*)-4-oxopent-2-en-2-yl pivalate (1a). Pivaloyl chloride (45 mmol) was added dropwise to a stirred solution of 2,4-pentanedione (30 mmol) and NEt_3 (60 mmol) in dry CH_2Cl_2 (30 cm^3) at 0 °C. The solution was stirred at room temperature for 6 h. The resulting mixture was successively washed with water (20 cm^3) and saturated NH_4Cl solution (20 cm^3), dried over anhydrous Na_2SO_4, and evaporated to dryness by rotary evaporation. The residue was purified by column chromatography (eluted with 100:1 petroleum ether/EtOAc) to yield (*E*)-4-oxopent-2-en-2-yl pivalate as a light yellow oil, yield 2.27 g (41%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 2.22 (s, 3H), 2.30 (d, *J* = 0.7 Hz, 3H), 6.04 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.60, 27.04, 32.26, 39.26, 116.32, 163.30, 176.10, 197.53. HR-MS: m/z 207.09880 $[M+Na]^+$; calcd for $C_{10}H_{16}O_3Na$, 207.09917.

The same procedure as for (*E*)-4-oxopent-2-en-2-yl pivalate was used to prepare other β-carbonyl alkenyl pivalates.

(*E*)-4-oxo-4-phenylbut-2-en-2-yl pivalate (1b). Eluent: petroleum ether/EtOAc (40:1 v/v). Yellow oil, yield 0.67 g (54%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 2.39 (s, 3H), 6.75 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H),

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7.90–7.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.03, 27.10, 39.35, 113.47, 128.27, 128.69, 132.92, 138.83, 164.50, 176.14, 190.51. HR-MS: m/z 269.11412 $[M+Na]^+$; calcd for $C_{15}H_{18}O_3Na$, 269.11482.

3-oxocyclopent-1-en-1-yl pivalate (1c). Eluent: petroleum ether/EtOAc (20:1 v/v). Light yellow solid, yield 1.50 g (82%); mp 41-43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 2.43–2.51 (m, 2H) , 2.72–2.82 (m, 2H), 6.19–6.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 26.88, 28.76, 33.37, 39.72, 116.44, 174.10, 180.17, 206.98. HR-MS: m/z 183.10204 $[M+H]^+$; calcd for $C_{10}H_{15}O_3$, 183.10157.

ethyl (*E*)-3-(pivaloyloxy)but-2-enoate (1d).[17] Eluent: petroleum ether/EtOAc (200:1 v/v). Colorless oil, yield 1.94 g (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.33 (d, *J* = 0.8 Hz, 3H), 4.18 (q, *J* = 7.1 Hz, 2H), 5.63 (q, *J* = 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.32, 17.05, 25.99, 38.15, 59.21, 108.94, 163.48, 165.08, 174.95.

(*E*)-4-(dimethylamino)-4-oxobut-2-en-2-yl pivalate (1g). Eluent: petroleum ether/EtOAc (3:1 v/v). Light yellow oil, yield 0.586 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 9H), 1.99 (d, *J* = 0.8 Hz, 3H), 2.92 (s, 3H), 3.01 (s, 3H), 5.68 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 20.12, 26.81, 34.48, 37.67, 38.82, 110.38, 152.04, 165.05, 175.62. HR-MS: m/z 214.14430 $[M+H]^+$; calcd for $C_{11}H_{20}NO_3$, 214.14377.

General procedure for the cross-coupling of β-carbonyl alkenyl pivalate with arylzinc chlorides.

A Schlenk tube was charged with β-carbonyl alkenyl pivalate (0.3 mmol), NMP (0.5 cm^3), and $Ni(PCy_3)_2Cl_2$ (0.015 mmol). To the stirred mixture was added dropwise ArZnCl solution (1.5 cm^3, 0.3 M solution in THF, 0.45 mmol) by syringe. The reaction mixture was stirred at 25 °C for 24 h. Then 30% NH_4Cl solution (15 cm^3) was added. The mixture was extracted with ethyl acetate (3×10 cm^3). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography on silica gel.

(*E*)-4-(*p*-tolyl)pent-3-en-2-one.[18] Eluent: petroleum ether/EtOAc (100:1 v/v). Light yellow oil, yield 38.6 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.37 (s, 3H), 2.53 (d, *J* = 1.0 Hz, 3H), 6.51 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.30, 21.31, 32.36, 123.80, 126.49, 129.33, 139.42, 139.54, 153.94, 199.06.

(*E*)-4-(4-(dimethylamino)phenyl)pent-3-en-2-one. Eluent: petroleum ether/EtOAc (60:1 v/v). Yellow solid, yield 51.5 mg (84%); mp 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.54 (d, *J* = 0.8 Hz, 3H), 3.00 (s, 6H), 6.52 (s, 1H), 6. 68 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.20, 32.43, 55.51, 114.02, 122.98, 128.03, 134.63, 153.51, 160.69, 199.00. HR-MS: m/z 204.13882 $[M+H]^+$; calcd for $C_{13}H_{18}NO$, 204.13829.

(*E*)-4-(4-methoxyphenyl)pent-3-en-2-one.[19,20] Eluent: petroleum ether/EtOAc (100:1 v/v). Light yellow solid, yield 44 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.53 (d, *J* = 1.1 Hz, 3H), 3.84 (s, 3H), 6.50 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.19, 32.42, 55.49, 114.01, 122.96, 128.02, 134.62, 153.49, 160.68, 198.98.

(*E*)-4-(4-(trifluoromethyl)phenyl)pent-3-en-2-one.[20,21] Eluent: petroleum ether/EtOAc (100:1 v/v). Light yellow oil, yield 40.5 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.54 (s, 3H), 6.52 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.43, 32.35, 124.07 (q, *J* = 273.1 Hz), 125.62 (q, *J* = 3.8 Hz), 126.02, 126.95, 130.94 (q, *J* = 32.7 Hz), 146.22, 152.16, 198.84.

(*E*)-4-(*o*-tolyl)pent-3-en-2-one. Eluent: petroleum ether /EtOAc (100:1 v/v). Light yellow oil, yield 29 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.29 (s, 3H), 2.41 (d, *J* = 1.4 Hz, 3H), 6.16 (q, *J* = 1.3 Hz, 1H), 7.07 (d, *J* = 7.1 Hz, 1H), 7.15–7.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.89, 21.35, 32.20, 125.86, 126.73, 127.19, 127.83, 130.56, 134.02, 144.19, 156.76, 199.10.

(*Z*)-4-(*o*-tolyl)pent-3-en-2-one. Eluent: petroleum ether /EtOAc (100:1 v/v). Light yellow oil, yield 18 mg (34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (s, 3H), 2.13 (d, *J* = 1.4 Hz, 3H), 2.24 (s, 3H), 6.20 (q, *J* = 1.4 Hz, 1H), 6.98–7.03 (m, 1H), 7.17–7.25 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 19.22, 27.58, 29.66, 126.22, 126.61, 127.92, 129.50, 130.45, 133.62, 141.04, 154.26, 199.31. HR-MS: m/z 175.11154 $[M+H]^+$; calcd for $C_{12}H_{16}O$, 175.11174.

(*E*)-4-(thiophen-2-yl)pent-3-en-2-one.[20] Eluent: petroleum ether/EtOAc (100:1 v/v). Yellow oil, yield 28.8 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.57 (s, 3H), 6.64 (s, 1H), 7.03–7.09 (m, 1H), 7.34 (d, *J* = 5.1 Hz, 1H), 7.36 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 17.74, 32.44, 121.50, 127.43, 127.59, 128.24, 145.92, 146.23, 198.53.

(*E*)-3-(4-(dimethylamino)phenyl)-1-phenylbut-2-en-1-one. Eluent: petroleum ether/EtOAc (30:1 v/v). Yellow solid, yield 68.6 mg (86%); mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (s, 3H), 3.03 (s, 6H), 6.73 (d, *J* = 8.9 Hz, 2H), 7.20 (s, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.39, 40.39, 111.89, 118.05, 127.91, 128.24, 128.54, 129.55, 132.14, 140.44, 151.42, 156.00, 191.73. HR-MS: m/z 266.15475 $[M+H]^+$; calcd for $C_{18}H_{20}NO$, 266.15394.

(*E*)-(4-methoxyphenyl)-1-phenylbut-2-en-1-one.[22] Eluent: petroleum ether/EtOAc (40:1 v/v). Light yellow oil, yield 69 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (d, *J* = 1.0 Hz, 3H), 3.86 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.15–7.19 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.51–7.60 (m, 3H), 7.96–8.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.78, 55.49, 114.05, 120.42, 128.03, 128.31, 128.61, 132.47, 134.93, 139.78, 154.97, 160.71, 191.85.

(*E*)-1-phenyl-3-(*p*-tolyl)but-2-en-1-one.[22] Eluent: petroleum ether/EtOAc (40:1 v/v). Yellow oil, yield 63 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 2.60 (d, *J* = 1.1 Hz, 3H), 7.15–7.19 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7. 43–7. 51 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.96–8.03 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.92, 21.38, 121.42, 126.56, 128.38, 128.65, 129.44, 132.58, 139.51, 139.64, 139.93, 155.33, 192.01.

(*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-one. Eluent: petroleum ether/EtOAc (40:1 v/v). Yellow oil, yield 62 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58 (d, *J* = 1.1 Hz, 3H),

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7.14–7.19 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7. 64–7. 71 (m, 4H), 7.98–8.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 18.97, 123.87, 124.11 (q, *J* = 273.2 Hz), 125.73 (q, *J* = 3.7 Hz), 126.97, 128.47, 128.80, 131.00 (q, *J* = 32.7 Hz), 133.02, 139.01, 146.43, 153.10, 191.86. HR-MS: m/z 291.09991 $[M+H]^+$; calcd for $C_{17}H_{14}F_3O$, 291.09913.

3-(4-(dimethylamino)phenyl)cyclopent-2-en-1-one.[9a] Eluent: petroleum ether/EtOAc (5:1 v/v). White solid, yield 53.2 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51–2.58 (m, 2H), 2.97–3.03 (m, 2H), 3.05 (s, 6H), 6.40 (s, 1H), 6.70 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.50, 35.25, 40.18, 111.52, 121.51, 122.98, 128.67, 152.38, 174.67, 209.51.

3-(4-methoxyphenyl)cyclopent-2-en-1-one.[9a,23] Eluent: petroleum ether/EtOAc (10:1 v/v). Light yellow solid, yield 46.2 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53–2.62 (m, 2H), 2.98–3.06 (m, 2H), 3.87 (s, 3H), 6.48 (t, *J* = 1.5 Hz, 1H), 6.97 (d, *J* = 8.8, Hz, 2H), 7.63 (d, *J* = 8.8, Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.71, 35.34, 55.56, 114.37, 125.59, 126.82, 128.72, 162.20, 173.77, 209.47.

3-(*p*-tolyl)cyclopent-2-en-1-one.[9a] Eluent: petroleum ether /EtOAc (10:1 v/v). White solid, yield 39 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.53–2.61 (m, 2H), 2.98–3.08 (m, 2H), 6.54 (t, *J* = 1.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.65, 28.70, 35.34, 126.72, 126.91, 129.72, 131.41, 141.95, 174.16, 209.57.

3-(4-(trifluoromethyl)phenyl)cyclopent-2-en-1-one.[9b] Eluent: petroleum ether/EtOAc (10:1 v/v). White solid, yield 33.8 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.58–2.68 (m, 2H), 3.03–3.13 (m, 2H), 6.65 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 28.82, 35.44, 123.81 (q, *J* = 273.4 Hz), 126.03 (q, *J* = 3.7 Hz), 127.18, 129.52, 132.73 (q, *J* = 32.8 Hz), 137.50, 171.94, 208.98.

3-(furan-2-yl)cyclopent-2-en-1-one.[23] Eluent: petroleum ether/EtOAc (10:1 v/v). Yellow solid, yield 20 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46–2.61 (m, 2H) , 2.88–3.02 (m, 2H), 6.40 (s, 1H), 6.55 (d, *J* = 1.6 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 7.60 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 27.21, 34.68, 112.54, 113.73, 124.81, 145.79, 150.59, 161.50, 208.85.

3-(thiophen-2-yl)cyclopent-2-en-1-one.[23] Eluent: petroleum ether/EtOAc (10:1 v/v). White solid, yield 43.8 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49–2.65 (m, 2H), 2.97–3.11 (m, 2H), 6.36 (s, 1H), 7.14 (dd, *J* = 4.0, 4.8 Hz, 1H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.54 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 29.39, 35.13, 125.88, 128.44, 128.61, 130.34, 138.73, 166.71, 208.61.

ethyl (*E*)-3-(4-(dimethylamino)phenyl)but-2-enoate.[24] Eluent: petroleum ether/EtOAc (60:1 v/v). White solid, yield 65 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.57 (s, 3H), 2.99 (s, 6H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.12 (s, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.56, 17.32, 40.39, 59.64, 111.83, 112.89, 127.54, 129.09, 151.20, 155.45, 167.64.

ethyl (*E*)-(4-methoxyphenyl)but-2-enoate.[24] Eluent: petroleum ether/EtOAc (200:1 v/v). Colorless oil, yield 54.9 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.56 (d, *J* = 1.2 Hz, 3H), 3.83 (s, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.08–6.13 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.50, 17.78, 55.46, 59.85, 113.93, 115.43, 127.79, 134.44, 155.01, 160.53, 167.22.

ethyl (*E*)-3-(*p*-tolyl)but-2-enoate.[21] Eluent: petroleum ether /EtOAc (200:1 v/v). Colorless oil, yield 52 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.36 (s, 3H), 2.57 (d, *J* = 1.2 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 6.10–6.15 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.48, 17.92, 21.30, 59.88, 116.39, 126.33, 129.30, 139.24, 155.53, 167.12.

ethyl 3-(4-(trifluoromethyl)phenyl)but-2-enoate.[21,24] Eluent: petroleum ether/EtOAc (200:1 v/v). Colorless oil, (*E*)/(*Z*) ratio 45:1, yield 57.7 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (t, *J* = 7.1 Hz, 3H), 2.58 (d, *J* = 1.3 Hz, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 6.11–6.18 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.42, 18.07, 60.25, 119.08, 124.09 (q, *J* = 273.4 Hz), 125.60 (q, *J* = 3.7 Hz), 126.80, 130.91 (q, *J* = 32.8 Hz), 145.92, 153.91, 166.55.

ethyl (*E*)-3-(*o*-tolyl) but-2-enoate. Eluent: petroleum ether/EtOAc (200:1 v/v). Colorless oil, yield 56.5 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.29 (s, 3H), 2.45 (d, *J* = 1.1 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 5.72–5.79 (m, 1H), 7.07 (d, *J* = 7.1 Hz, 1H), 7.12–7.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.44, 19.83, 20.92, 59.94, 119.51, 125.83, 127.19, 127.79, 130.50, 133.98, 144.02, 158.38, 166.79.

ethyl (*E*)-3-(furan-2-yl)but-2-enoate.[21] Eluent: petroleum ether/EtOAc (200:1 v/v). Yellow oil, yield 37.6 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 2.46 (d, *J* = 1.1 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.35–6.39 (m, 1H), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.64 (d, *J* = 3.4 Hz, 1H), 7.44 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 14.49, 14.86, 59.91, 111.36, 112.10, 112.61, 142.24, 144.00, 154.52, 167.34.

ethyl (*E*)-3-(thiophen-2-yl)but-2-enoate.[21] Eluent: petroleum ether/EtOAc (200:1 v/v). Yellow oil, yield 48 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.32 (t, *J* = 7.1 Hz, 2H), 2.61 (d, *J* = 1.0 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 1H), 6.22–6.29 (m, 1H), 7.05 (t, *J* = 4.4 Hz, 1H), δ 7.32 (d, *J* = 4.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ14.49, 17.43, 60.01, 114.41, 126.83, 127.19, 128.06, 145.72, 147.92, 166.90.

ethyl 4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate.[25] Eluent: petroleum ether/EtOAc (100:1 v/v). Colorless oil, yield 60 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.66–1.80 (m, 4H), 2.32–2.47 (m, 4H), 3.80 (s, 3H), 3.91 (q, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.85, 22.08, 22.68, 26.90, 32.62, 55.36, 60.16, 113.47, 127.92, 128.16, 135.87, 144.82, 158.82, 170.51.

ethyl 4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate. Eluent: petroleum ether/EtOAc (100:1 v/v). Light yellow oil, yield 54.5 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, *J* = 7.1 Hz, 3H), 1.66–1.80 (m, 4H), 2.33 (s, 1H), 2.34–2.46 (m, 4H), 3.89 (q, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), δ 7.11 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.74, 21.28, 22.09, 22.66, 26.80, 32.70, 60.14, 126.86, 127.92, 128.76, 136.71, 140.63, 145.55, 170.30. HR-MS: m/z 245.15282 $[M+H]^+$; calcd for $C_{16}H_{21}O_2$, 245.15361.

ethyl 4'-(dimethylamino)-3,4,5,6-tetrahydro-[1,1'-

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biphenyl]-2-carboxylate. Eluent: petroleum ether/EtOAc (60:1 v/v). Light yellow oil, yield 44 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.1 Hz, 3H), 1.64–1.81 (m, 4H), 2.32–2.46 (m, 4H), 2.93 (s, 6H), 3.94 (q, *J* = 7.1 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 13.97, 22.17, 22.80, 27.10, 32.27, 40.75, 60.13, 112.15, 127.03, 127.91, 131.38, 144.96, 149.96, 171.10. HR-MS: m/z 274.17941 $[M+H]^+$; calcd for $C_{17}H_{24}NO_2$, 274.18016.

4-(4-(dimethylamino)phenyl)-2*H*-chromen-2-one.[9d] Eluent: petroleum ether/EtOAc (30:1 v/v). Yellow solid, yield 70.2 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (s, 6H), 6.34 (s, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.20–7.26 (m, 1H), 7.39 (d, *J* = 8.9 Hz, 3H), 7.49–7.57 (m, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 31.10, 40.39, 112.02, 113.48, 117.46, 119.47, 122.51, 124.01, 127.38, 129.97, 131.65, 151.48, 154.48, 155.91, 161.49.

4-(4-methoxyphenyl)-2*H*-chromen-2-one.[9e] Eluent: petroleum ether/EtOAc (60:1 v/v). White solid, yield 59 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 6.36 (s, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.20–7.26 (m, 1H), 7.37–7.45 (m, 3H), 7.51–7.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ55.57, 114.42, 114.71, 117.45, 119.22, 124.21, 127.13, 127.52, 130.07, 131.93, 154.32, 155.45, 160.92, 161.06.

4-(*p*-tolyl)-2*H*-chromen-2-one.[9e] Eluent: petroleum ether/EtOAc (60:1 v/v). White solid, yield 50 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 6.37 (s, 1H), 7.20–7.25 (m, 1H), 7.30–7.39 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.51–7.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 21.51, 115.02, 117.44, 119.21, 124.23, 127.18, 128.53, 129.68, 131.96, 132.43, 140.03, 154.32, 155.87, 161.02.

4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one.[9e] Eluent: petroleum ether/EtOAc (60:1 v/v). White solid, yield 63.3 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (s, 1H), 7.22–7.31 (m, 1H), 7.39 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.55–7.63 (m, 3H), 7.82 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 115.93, 117.66, 118.61, 123.88 (q, *J* = 273.3 Hz), 124.57, 126.09 (q, *J* = 3.7 Hz), 126.70, 129.04, 131.95 (q, *J* = 32.9 Hz), 132.48, 138.85, 154.29, 160.39.

4-(furan-2-yl)-2*H*-chromen-2-one.[9d] Eluent: petroleum ether/EtOAc (60:1 v/v). Yellow solid, yield 35.1 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.69 (s, 1H), 7.06 (d, *J* = 3.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.71 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ111.65, 112.51, 114.59, 116.60, 117.65, 124.44, 126.46, 131.98, 142.05, 145.41, 148.52, 154.37, 161.02.

4-(thiophen-2-yl)-2*H*-chromen-2-one.[9d] Eluent: petroleum ether/EtOAc (60:1 v/v). Yellow solid, yield 47.5 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (s, 1H), 7.24 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.28–7.35 (m, 1H), 7.38–7.47 (m, 2H), 7.54–7.64 (m, 2H), 7.94 (dd, *J* = 8.0, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ115.21, 117.62, 118.40, 124.46, 126.75, 128.27, 128.66, 129.49, 132.26, 136.02, 148.12, 154.29, 160.57.

3-(4-(dimethylamino)phenyl)-N,N-dimethylbut-2-enamide. Eluent: petroleum ether/EtOAc (5:1 v/v). Light yellow oil, (*E*)/(*Z*) ratio 10:1, yield 70 mg (99%). The NMR spectroscopic data for the major isomer are given. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (s, 3H), 2.64 (s, 3H), 2.84 (s, 3H), 2.96 (s, 6H), 5.78 (s, 1H), 6.64 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.10, 34.40, 37.81, 40.39, 111.77, 118.47, 127.83, 128.02, 142.28, 150.19, 170.04. HR-MS: m/z 233.16545 $[M+H]^+$; calcd for $C_{14}H_{20}N_2O$, 233.16484.

3-(4-methoxyphenyl)-N,N-dimethylbut-2-enamide.[26] Eluent: petroleum ether/EtOAc (5:1 v/v). Colorless oil, (*E*)/(*Z*) ratio 4:1, yield 66 mg (99%). The NMR spectroscopic data for the major isomer are given. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (s, 3H), 2.65 (s, 3H), 2.82 (s, 3H), 3.81 (s, 3H), 5.88 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 24.29, 34.35, 37.72, 55.24, 113.58, 119.96, 128.28, 132.52, 142.05, 159.36, 169.43.

N,N-dimethyl-3-(*p*-tolyl)but-2-enamide. Eluent: petroleum ether/EtOAc (5:1 v/v). Light yellow oil, (*E*)/(*Z*) ratio 2:1, yield 54.6 mg (90%). The NMR spectroscopic data for the major isomer are given. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (d, *J* = 1.3 Hz, 3H), 2.34 (s, 3H), 2.64 (s, 3H), 2.81 (s, 3H), 5.91 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ21.24, 24.32, 34.36, 37.72, 120.37, 126.84, 128.95, 137.25, 137.85, 142.63, 169.30. HR-MS: m/z 204.13870 $[M+H]^+$; calcd for $C_{13}H_{18}NO$, 204.13829.

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Graphical abstract

Nickel-catalyzed cross-coupling of β-carbonyl alkenyl pivalates with arylzinc chlorides

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Reaction of β-carbonyl alkenyl pivalates with arylzinc reagents was carried out via nickel-catalyzed C-O bond cleavage, forming 3-aryl-substituted α,β-unsaturated carbonyl compounds in mederate to excellent yields.