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可见光诱导镍催化烯烃还原 Heck 反应

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摘要 使用温和的有机还原剂汉斯酯代替传统金属还原剂或负氢试剂, 发展了一种有效的可见光驱动下过渡金属镍催化的烯烃还原 Heck 反应. 在无需外源光氧化还原催化剂的条件下, 成功实现了芳基卤化物与丙烯酸酯类型底物的还原氢芳基化反应. 该反应条件简单、温和, 官能团兼容性好, 为烯烃还原 Heck 反应提供了一种互补的催化策略.
关键词 镍; 还原 Heck 反应; 可见光; 有机还原剂; 烯烃

Photoinduced Nickel-Catalyzed Reductive Heck Reaction

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Abstract An efficient visible-light induced nickel-catalyzed reductive Heck reaction of alkenes by using mild organic reductant Hantzsch ester (HEH) instead of traditional metal reductants or hydride reagents was developed. The reductive hydroarylation of acrylates with aryl halides was successfully achieved without requiring exogenous photoredox catalysts. This reaction is highlighted by the simple and mild conditions, good functional group tolerance, thus providing a complementary approach for alkenes reductive Heck reaction.
Keywords nickel; reductive Heck reaction; visible light; organic reductant; alkene

1 Introduction

Reductive Heck reactions have emerged as a powerful tool for efficient construction of saturated C—C bonds,[1] which enable cross-coupling between aryl (pseudo)halides and alkenes followed by protonation or coupling with a hydride, while avoiding the use of highly reactive and air-sensitive organometallics. To this end, palladium-catalyzed reductive Heck reactions including asymmetric versions have been widely developed.[2] Unlike palladium, nickel is an earth-abundant, extremely cheap transition metal, which is more electropositive than palladium. In Heck reactions, the migration insertion of Ni^{II} species to alkenes is more favorable than Pd, while *β*-hydride elimination of alkyl nickel species is calculated to have higher barriers than Pd.[3] Thus, nickel has also been viewed as an efficient catalyst for reductive Heck reaction.[4] Recent progress has been achieved in the field of nickel-catalyzed reductive Heck cyclization.[5] And very recently, Zhou and co-workers[6] reported the first example of asymmetric intermolecular reductive Heck reaction by nickel catalysis. Despite of a progress achieved, the reductive Heck reactions require elevated temperatures and stoichiometric amounts of metal reductant such as Mn or Zn (Scheme 1, a), which results in a large disposal of metal waste and a high risk in practical synthesis. Therefore, further exploration of reductive Heck reaction under mild conditions without requirement of metallic reductants is highly desirable.

Compared to metal reductants, organic reductants are mild, cheap, and user environmentally friendly.[7] Taking advantage of photoexcited chemistry, a sort of organic reductants could be applied in metal-catalyzed reductive cross-coupling reactions to replace traditional metal reductants,[8] while the application in reductive Heck reaction remains underdeveloped. In this regard, our group has developed several examples of photo-assisted nickel-catalyzed reductive cross-coupling in the aid of organic reductant, such as tertiary amine or Hantzsch ester (HEH).[9] Previously, we reported a photo-induced nickel-catalyzed reductive acyl-coupling without photoredox catalyst by using HEH as a potent organic reductant.[9c] Recently, Yang and co-workers[10] reported a photoexcited Ni^{II}-aryl complex-mediated Giese addition of aryl radicals to alkenes enabled by nickel/photoredox dual catalysis, in which HEH was used as reductant. Inspired by these works, we envisioned

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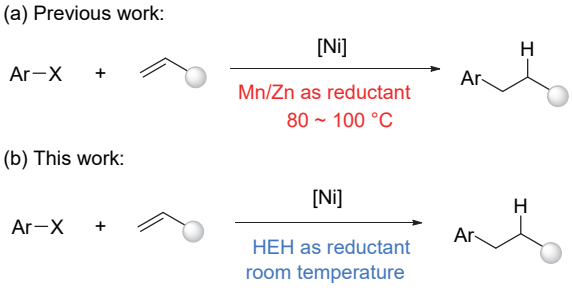
that the excited-state of HEH* [E_{ox}(HEH$^{\bullet+}$/HEH*)＝－2.28 V vs. SCE][11] could potentially reduce Ni(II) [E_{red}(Ni^{II}/Ni^{0})＝－1.2 V vs. SCE][12] back to Ni(0) to furnish the catalytic cycle, meanwhile the protons releasing from HEH during the reductive process could protonate alkyl Ni(II) species to afford hydroarylation products. Herein, we reported the first photo-induced nickel-catalyzed reductive Heck arylation of alkenes in the presence of HEH as organic reductant under extremely mild conditions (Scheme 1, b). HEH was identified as a unique bifunctional reagent which serves as a reductant and proton source. This method obviates the use of metal-based reductants and provides a complementary approach for reductive Heck reaction.



Scheme 1 Ni-Catalyzed reductive Heck reaction

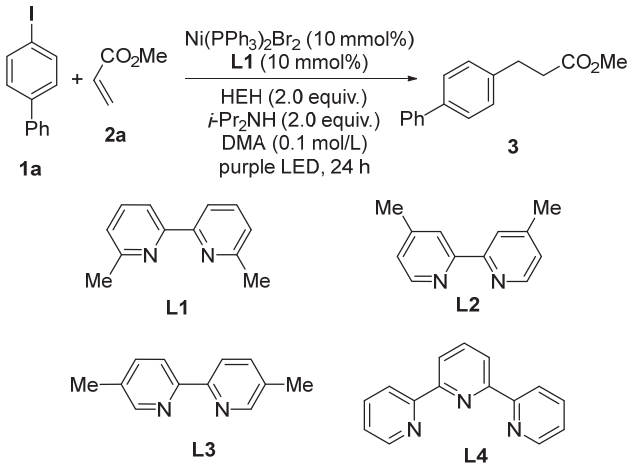
2 Results and discussion

4-Iodo-1,1'-biphenyl (**1a**) and methyl acrylate (**2a**) were chosen as model substrate to test the hypothesis. To our delight, after a detailed survey of reaction conditions, the reductive Heck product **3** could be detected in 78% GC yield when performing the reaction in the presence of $Ni(PPh_3)_2Br_2$ as catalyst, 6,6'-dmbpy (**L1**) as ligand, Hantzsch ester (HEH) as organic reductant, *i*-Pr_2NH as base, in dimethyl adipate (DMA) under 1.5 W purple LED irradiation for 24 h (Table 1, Entry 1). Nickel catalyst has an important effect on the reactivity. Replacing $Ni(PPh_3)_2Br_2$ to other nickel sources led to decreased yields (Entries 2, 3). Interestingly, the direct use of Ni^0 precatalyst such as $Ni(cod)_2$ could also give 65% yield (Entry 3). Ligand screening showed that the bipyridyl ligand bearing di-*ortho*-methyl substituents is critical to the reaction as moving methyl group to *para* or *meta* position resulted in very low efficiency (Entries 4, 5). The use of terpyridyl ligand **L4** largely decreased the reactivity (Entry 6). The survey of different solvents indicated that *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) were all inferior to the reaction (Entries 7～9). The purple light was important for the reaction process as using 456 nm blue LED irradiation led to no reaction (Entry 10). Control experiments suggested that nickel, ligand, purple light, and base were all indispensable for the reductive Heck reaction (Entry 11).

With the optimized reaction conditions in hand, we started to examine the substrate scope. First, the substrate scope of electron-deficient alkenes was investigated (Table 2). Acrylates bearing methyl (**3**), ethyl (**4**), isopropyl (**5**), *tert*-butyl (**6**), benzyl (**7**), isobutyl (**8**) and cyclohexyl (**9**) substituent reacted smoothly, affording the corresponding products in good yields (66%～80% isolated yields). Besides, phenyl acrylate (**10**), allyl acrylate (**11**), and 2-methoxyethyl acrylate (**12**) were all valid substrates. Gratifyingly, methyl methacrylate reacted as well (**13**). Moreover, acrylonitrile (**14**) was also proven to be a valid substrate for the nickel-catalyzed reductive Heck reaction. While acrylamides reacted with largely decreased yields. Unfortunately, acrolein, *α*,*β*-unsaturated ketones, *β*-substituted or *α*,*β*-disubstituted acrylates were incompatible to the standard conditions.

Next, the scope generality of aryl halides was investigated (Table 3). Aryl iodides with different electronic and steric natures of substituents have no significant influence on the reactivity. Aryl iodides irrespective of *para*, *meta*, or *ortho* substituents all successfully engaged in the reaction. Not only electron-withdrawing groups but also electron-donating groups were reacted smoothly, affording desired products in moderate to good yields (**15**～**23**). The reaction tolerated a variety of functional groups, such as CF_3 (**15**), OCF_3 (**18**), fluoride (**19**, **23**), chloride (**20**), thioether (**21**), and *tert*-butyldimethylsilyl ether (OTBS) (**22**).

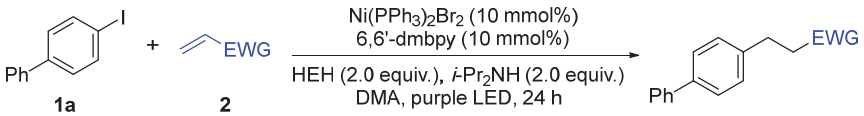
Table 1 Optimization of the reaction conditions[a]

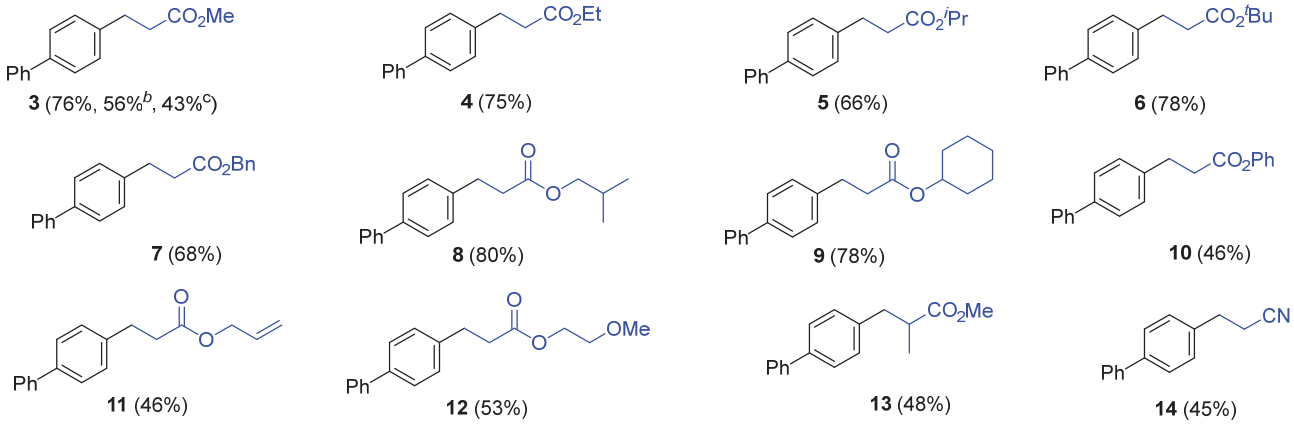


Entry	Deviation from the standard condition	Yield[b]/%
1	None	78
2	$NiBr_2$	22
3	$Ni(cod)_2$	65
4	**L2**	Trace
5	**L3**	16
6	**L4**	30
7	DMF	57
8	DMSO	24
9	THF	Trace
10	456 nm blue LED	0
11	No Ni, ligand, HEH, base, or light	0

[a] Unless otherwise noted, the reaction was carried out at 0.1 mmol scale with **1a** (0.1 mmol), **2a** (0.2 mmol); [b] Yields were determined by GC with *n*-tridecane as an internal standard.

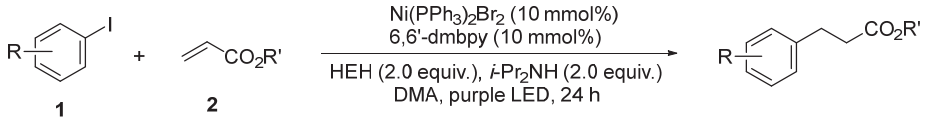
Table 2 Substrate scope of alkenes[a]

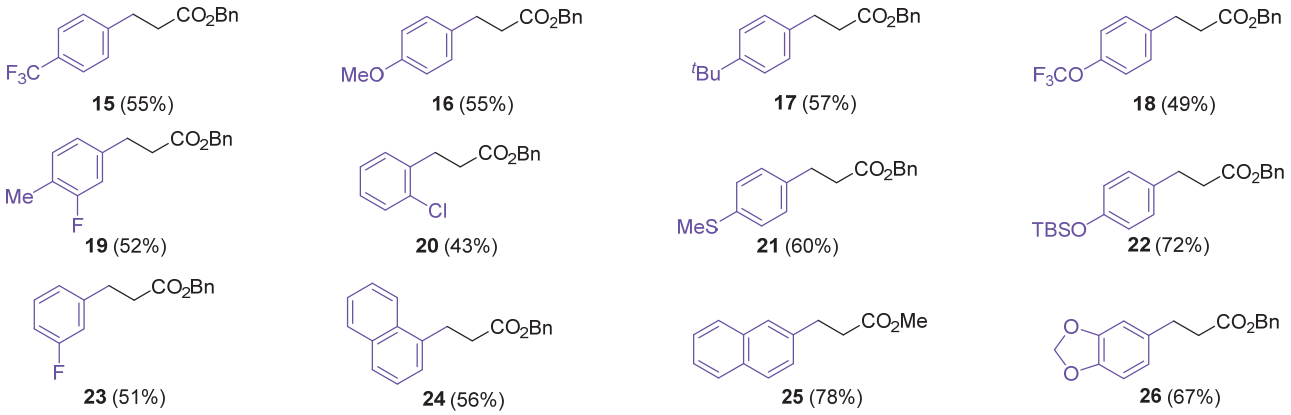




[a] All reactions were carried out at 0.2 mmol scale with **1a** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv). Isolated yields were provided. [b] Aryl bromide was used. [c] Aryl triflate was used.

Table 3 Substrate scope of aryl halides[a]



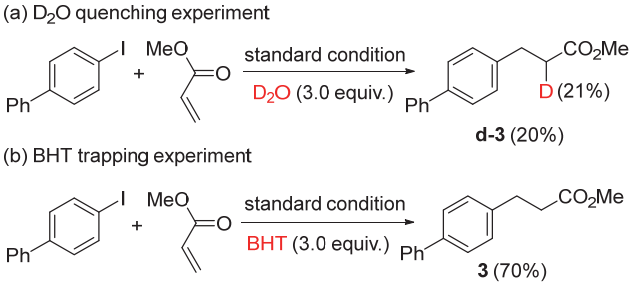


[a] All reactions were carried out at 0.2 mmol scale with **1** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv). Isolated yields were provided.

Besides of phenyl iodides, 1-iodonaphthalene and 2-iodonaphthalene were proven to be suitable substrates (**24**, **25**). Presumably due to the steric hindrance effect, *ortho*-substituted aryl iodides provided generally lower reactivity (**20** and **24**). Gratifyingly, heteroaryl halide, such as 5-iodobenzo[*d*][1,3]dioxole (**26**) was also successfully participated in the reaction to give the expected product in good yield. Besides of aryl iodides, aryl bromides and aryl triflates were valid substrates.

In order to give an insight into the mechanism, the related mechanistic experiments were carried out. when D_2O was added, 20% yield of deuterated reductive Heck product **d-3** was isolated with 21% deuterium incorporation (Scheme 2). The low deuterium incorporation might be contributed to the competitive protonation by HE. This result indicated the formation of C—Ni bond adjacent to the ester group by reductive Heck reaction of **1a** and **2a**. Moreover, the radical-trapping experiment was performed with butylated hydroxytoluene (BHT) as a radical inhibitor, while the reaction still proceeded smoothly without detection of aryl radical-trapped adducts by HRMS (Scheme 2), suggesting that the radical pathway was most unlikely involved. The Stern-Volmer quenching experiments were performed and the results revealed that the oxidative quenching of the excited state of HEH* by nickel catalyst was existed in the reaction system, suggesting a single electron-transfer (SET) between HEH* and Ni^{II} (Figure 1).

Based on the experimental results, a plausible mechanism was proposed in Scheme 3. The ground-state of HEH



Scheme 2 D_2O quenching experiment and BHT trapping experiment

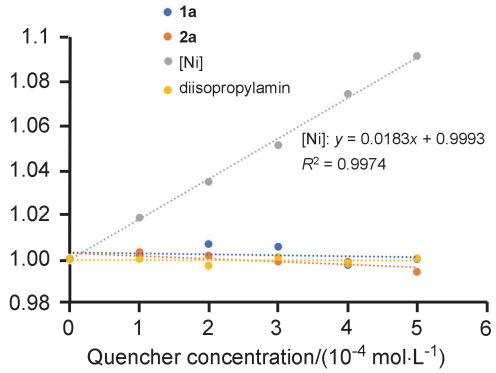
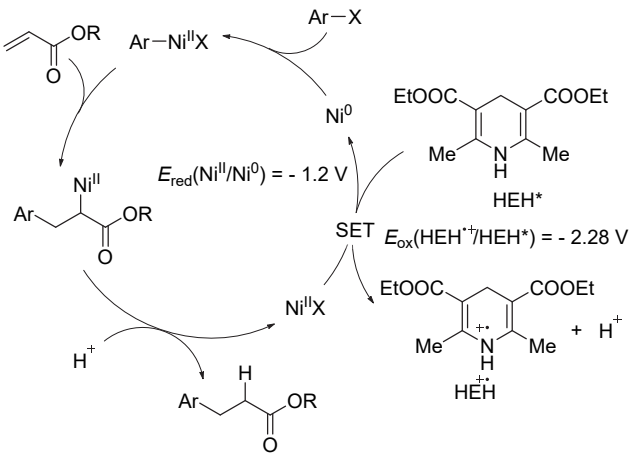


Figure 1 Stern-Volmer quenching experiment

was irradiated by purple light to reach its excited state HEH*, which is a strong reductant that can potentially reduce Ni^{II} to Ni^0. Then Ni^0 undergoes oxidative addition with aryl halide to get aryl-Ni^{II} species, followed by migration insertion of alkenes to form α-carbonyl Ni^{II} species. Final single electron reduction of the resulting Ni^{II} by HEH* regenerates Ni^0 to complete the catalytic cycle.



Scheme 3 Proposed mechanism

3 Conclusions

In summary, a photo-induced nickel-catalyzed reductive Heck reaction of aryl halides with electron-deficient alkenes under very mild conditions was developed. Hantzsch ester (HEH) was disclosed as a mild organic reductant to replace traditionally used metal reductants for reductive Heck reaction. The photoexcited state of HEH* possessing strong reductive potential can reduce Ni^{II} back to Ni^0 to furnish the catalytic cycle. The reaction shows relatively broad scope of aryl halides and tolerates a variety of functional groups.

4 Experimental section

4.1 General Information

The HRMS analyses were performed on a BRUKER FT-ICR-MS SolariX 7T instrument with ESI mode. GC analyses were performed on a Shimadzu GC 2010 Pro instrument with *n*-tridecane as an internal standard to calculate GC yields. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AV600 and Bruker AV400 instruments, respectively. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200～300 mesh silica gels using the indicated solvents.

4.2 Experimental method

The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar was added aryl halides (0.20 mmol, 1.0 equiv.), Hantzsch ester (0.40 mmol, 2.0 equiv.), 6,6'-dmbpy (20 μmol, 0.10 equiv.) and $Ni(PPh_3)_2Br_2$ (20 μmol, 0.10 equiv.). Then, DMA (0.10 mol/L, 2.0 mL), *i*-Pr_2NH (0.40 mmol, 2.0 equiv.) and alkenes (0.40 mmol, 2.0 equiv.) were added. The vial was sealed and removed from the glovebox, then irradiated with a 1.5 W purple LED lamp (at approximately 1.0 cm away from the light source) with cooling from a fan for 24 h. The reaction was quenched by H_2O, and extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. Then the residue was purified by flash chromatography (petroleum ether/ethyl acetate, V∶V=100∶1～50∶1) to give the corresponding product.

Methyl 3-([1,1'-biphenyl]-4-yl)propanoate (**3**): 36.5 mg, 76% yield, colorless oil. ^1H NMR (600 MHz, Chloroform-*d*) δ: 7.60～7.59 (m, 2H), 7.55～7.54 (m, 2H), 7.46～7.43 (m, 2H), 7.36～7.34 (m, 1H), 7.30～7.29 (m, 2H), 3.71 (s, 3H), 3.02 (t, J=8.0 Hz, 2H), 2.70 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 173.44, 141.03, 139.72, 139.37, 128.85, 128.82, 127.36, 127.24, 127.11, 51.76, 35.74, 30.67; HRMS (ESI) calcd for $C_{16}H_{17}O_2$ $(M+H)^+$ 241.1223, found 241.1225.

Ethyl 3-([1,1'-biphenyl]-4-yl)propanoate (**4**): 38.1 mg, 75% yield, colorless oil. ^1H NMR (400 MHz, Chloroform-*d*) δ: 7.65～7.63 (m, 2H), 7.60～7.58 (m, 2H), 7.51～7.47 (m, 2H), 7.41～7.37 (m, 1H), 7.35～7.33 (m, 2H), 4.21 (q, J=7.2 Hz, 2H), 3.06 (t, J=8.0 Hz, 2H), 2.72 (t, J=8.0 Hz, 2H), 1.31 (t, J=7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ: 172.95, 141.02, 139.76, 139.28, 128.81 (2C), 127.28, 127.19, 127.06, 60.52, 35.94, 30.67, 14.30; HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$ $(M+Na)^+$ 277.1199, found 277.1208.

Isopropyl 3-([1,1'-biphenyl]-4-yl)propanoate (**5**): 35.4 mg, 66% yield, colorless oil. ^1H NMR (600 MHz, Chloroform-*d*) δ: 7.64～7.63 (m, 2H), 7.59～7.57 (m, 2H),

7.49～7.47 (m, 2H), 7.38～7.37 (m, 1H), 7.34～7.33 (m, 2H), 5.10～5.06 (m, 1H), 3.05 (t, J=8.0 Hz, 2H), 2.69 (t, J=8.0 Hz, 2H), 1.28～1.27 (m, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.51, 141.05, 139.81, 139.25, 128.85, 128.82, 127.26, 127.19, 127.08, 67.84, 36.26, 30.75, 21.92; HRMS (ESI) calcd for $C_{18}H_{20}O_2Na$ $(M+Na)^+$ 291.1356, found 291.1355.

tert-Butyl 3-([1,1'-biphenyl]-4-yl)propanoate (**6**): 44.0 mg, 78% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.63～7.61 (m, 2H), 7.57～7.56 (m, 2H), 7.49～7.45 (m, 2H), 7.39～7.36 (m, 1H), 7.33～7.31 (m, 2H), 3.00 (t, J=8.0 Hz, 2H), 2.62 (t, J=8.0 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.38, 141.12 140.02, 139.20, 128.88, 128.84, 127.24, 127.20, 127.11, 80.52, 37.14, 30.87, 28.21; HRMS (ESI) calcd for $C_{19}H_{23}O_2$ $(M+H)^+$ 283.1693, found 283.1687.

Benzyl 3-([1,1'-biphenyl]-4-yl)propanoate (**7**): 43.0 mg, 68% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.64～7.62 (m, 2H), 7.58～7.56 (m, 2H), 7.50～7.46 (m, 2H), 7.42～7.35 (m, 6H), 7.32～7.30 (m, 2H), 5.18 (s, 2H), 3.07 (t, J=8.0 Hz, 2H), 2.78 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.77, 141.01, 139.58, 139.32, 136.00, 128.83 (2C), 128.64, 128.32 (2C), 127.31, 127.22, 127.08, 66.40, 35.91, 30.67; HRMS (ESI) calcd for $C_{22}H_{21}O_2$ $(M+H)^+$ 317.1356, found 317.1345.

Isobutyl 3-([1,1'-biphenyl]-4-yl)propanoate (**8**): 45.1 mg, 80% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.64～7.63 (m, 2H), 7.59～7.58 (m, 2H), 7.50～7.47 (m, 2H), 7.40～7.38 (m, 1H), 7.35～7.34 (m, 2H), 3.93 (d, J=6.5 Hz, 2H), 3.07 (t, J=8.0 Hz, 2H), 2.74 (t, J=8.0 Hz, 2H), 2.01～1.94 (m, 1H), 0.98 (d, J=6.5 Hz, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 173.04, 141.05, 139.74, 139.30, 128.82, 128.80, 127.30, 127.19, 127.08, 70.71, 35.93, 30.74, 27.79, 19.15; HRMS (ESI) calcd for $C_{19}H_{22}O_2Na$ $(M+Na)^+$ 305.1512, found 305.1522.

Cyclohexyl 3-([1,1'-biphenyl]-4-yl)propanoate (**9**): 48.1 mg, 78% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.65～7.63 (m, 2H), 7.59～7.58 (m, 2H), 7.50～7.47 (m, 2H), 7.40～7.37 (m, 1H), 7.35～7.34 (m, 2H), 4.86～4.84 (m, 1H), 3.06 (t, J=8.0 Hz, 2H), 2.71 (t, J=8.0 Hz, 2H), 1.88～1.87 (m, 2H), 1.77～1.76 (m, 2H), 1.60～1.58 (m, 1H), 1.47～1.40 (m, 4H), 1.34～1.30 (m, 1H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.42, 141.04, 139.80, 139.22, 128.81, 128.79, 127.23, 127.15, 127.05, 72.76, 36.25, 31.68, 30.77, 25.45, 23.79; HRMS (ESI) calcd for $C_{21}H_{25}O_2$ $(M+H)^+$ 309.1849, found 309.1850.

Phenyl 3-([1,1'-biphenyl]-4-yl)propanoate (**10**): 27.8 mg, 46% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.64～7.63 (m, 2H), 7.61～7.59 (m, 2H), 7.49～7.47 (m, 2H), 7.42～7.38 (m, 5H), 7.27～7.25 (m, 1H), 7.08～7.06 (m, 2H), 3.16 (t, J=8.0 Hz, 2H), 2.97 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 171.54, 150.78, 141.03, 139.56, 139.35, 129.55, 128.99, 128.90, 127.46, 127.31, 127.16, 125.96, 121.67, 36.08, 30.71; HRMS (ESI) calcd for $C_{21}H_{19}O_2$ $(M+H)^+$ 303.1380, found 303.1395.

Allyl 3-([1,1'-biphenyl]-4-yl)propanoate (**11**): 24.5 mg, 46% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.61～7.60 (m, 2H), 7.56～7.55 (m, 2H), 7.47～7.45 (m, 2H), 7.37～7.35 (m, 1H), 7.32～7.29 (m, 2H), 5.96～5.91 (m, 1H), 5.34～5.25 (m, 2H), 4.63～4.62 (m, 2H), 3.04 (t, J=8.0 Hz, 2H), 2.74 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.69, 141.08, 139.69, 139.41, 132.28, 128.88 (2C), 127.39, 127.27, 127.15, 118.42, 65.34, 35.93, 30.70; HRMS (ESI) calcd for $C_{18}H_{18}O_2Na$ $(M+Na)^+$ 289.1199, found 289.1187.

2-Methoxyethyl 3-([1,1'-biphenyl]-4-yl)propanoate (**12**): 30.1 mg, 53% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.63～7.61 (m, 2H), 7.57～7.56 (m, 2H), 7.48～7.46 (m, 2H), 7.38～7.36 (m, 1H), 7.33～7.32 (m, 2H), 4.30～4.24 (m, 2H), 3.62～3.61 (m, 2H), 3.41 (s, 3 H), 3.05 (t, J=8.0 Hz, 2H), 2.77 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.95, 141.00, 139.64, 139.29, 128.83, 128.81, 127.29, 127.19, 127.06, 70.53, 63.61, 59.04, 35.73, 30.59; HRMS (ESI) calcd for $C_{18}H_{21}O_3$ $(M+H)^+$ 285.1485, found 285.1496.

Methyl 3-([1,1'-biphenyl]-4-yl)-2-methylpropanoate (**13**): 24.4 mg, 48% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.62～7.61 (m, 2H), 7.56～7.55 (m, 2H), 7.48～7.45 (m, 2H), 7.38～7.35 (m, 1H), 7.28～7.27 (m, 2H), 3.70 (s, 3H), 3.13～3.09 (m, 1H), 2.85～2.79 (m, 1H), 2.77～2.74 (m, 1H), 1.24～1.23 (m, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 176.67, 141.05, 139.36, 138.59, 129.50, 128.86, 127.24, 127.21, 127.11, 51.75, 41.52, 39.45, 16.96; HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$ $(M+Na)^+$ 277.1199, found 277.1209.

3-([1,1'-Biphenyl]-4-yl)propanenitrile (**14**): 18.6 mg, 45% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.57～7.53 (m, 4H), 7.44～7.40 (m, 2H), 7.34～7.31 (m, 1H), 7.28～7.26 (m, 2H), 2.94 (t, J=8.0 Hz, 2H), 2.59 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 140.61, 140.16, 137.12, 128.84, 128.75, 127.56, 127.40, 127.04, 119.22, 31.17, 19.28; HRMS (ESI) calcd for $C_{15}H_{13}NNa$ $(M+Na)^+$ 230.0940, found 230.0943.

Benzyl 3-(4-(trifluoromethyl)phenyl)propanoate (**15**): 33.9 mg, 55% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.56～7.35 (m, 2H), 7.39～7.36 (m, 3H), 7.33～7.32 (m, 4H), 5.15 (s, 2H), 3.06 (t, J=8.0 Hz, 2H), 2.74 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ: 172.37, 144.57, 135.86, 128.80, 128.69, 128.67 (q, $J_{C\text{-}F}$=33.2 Hz), 128.44, 128.40, 125.54 (q, $J_{C\text{-}F}$=4.5 Hz), 124.38 (q, $J_{C\text{-}F}$=271.8 Hz), 66.56, 35.50, 30.79; ^{19}F NMR (565 MHz, Chloroform-*d*)) δ: −62.35 ; HRMS (ESI) calcd for $C_{17}H_{15}F_3O_2Na$ $(M+Na)^+$ 331.0916, found 331.0933.

Benzyl 3-(4-methoxyphenyl)propanoate (**16**): 29.7 mg, 55% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ: 7.40～7.34 (m, 5H), 7.15～7.14 (m, 2H), 6.86～6.85 (m, 2H), 5.15 (s, 2H), 3.82 (s, 3H), 2.96 (t, J=8.0 Hz, 2H), 2.70 (t, J=8.0 Hz, 2H); ^{13}C NMR (151 MHz,

Chloroform-*d*) *δ*: 172.89, 158.18, 136.06, 132.56, 129.36, 128.63, 128.31, 128.29, 114.00, 66.33, 55.33, 36.30, 30.21; HRMS (ESI) calcd for $C_{17}H_{19}O_3$ $(M+H)^+$ 271.1329, found 271.1333.

Benzyl 3-(4-(*tert*-butyl)phenyl)propanoate (**17**): 33.8 mg, 57% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.44～7.39 (m, 7H), 7.23～7.21 (m, 2H), 5.21 (s, 2H), 3.05 (t, *J*=8.0 Hz, 2H), 2.77 (t, *J*=8.0 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.91, 149.12, 137.41, 136.06, 128.61, 128.30, 128.26, 128.04, 125.46, 66.32, 35.94, 34.44, 31.47, 30.48; HRMS (ESI) calcd for $C_{20}H_{25}O_2$ $(M+H)^+$ 297.1849, found 297.1858.

Benzyl 3-(4-(trifluoromethoxy)phenyl)propanoate (**18**): 31.8 mg, 49% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.39～7.33 (m, 5H), 7.24～7.22 (m, 2H), 7.15～7.14 (m, 2H), 5.15 (s, 2H), 3.01 (t, *J*=8.0 Hz, 2H), 2.72 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.52, 147.84, 139.23, 135.92, 129.76, 128.69, 128.42, 128.40, 121.16, 120.62 (q, J_{C-F}=256.7 Hz), 66.52, 35.80, 30.32; ^{19}F NMR (565 MHz, Chloroform-*d*) *δ*: −57.89; HRMS (ESI) calcd for $C_{17}H_{16}F_3O_3$ $(M+H)^+$ 325.1049, found 325.1065.

Benzyl 3-(3-fluoro-4-methylphenyl)propanoate (**19**): 28.3 mg, 52% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.41～7.36 (m, 5H), 7.13～7.11 (m, 1H), 6.91～6.89 (m, 2H), 5.17 (s, 2H), 2.98 (t, *J*=8.0 Hz, 2H), 2.72 (t, *J*=8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.55, 161.33 (d, J_{C-F}=244.6 Hz), 140.10 (d, J_{C-F}=6.0 Hz), 135.96, 131.45 (d, J_{C-F}=5.4 Hz), 128.62, 128.32, 128.25, 123.71 (d, J_{C-F}=3.0 Hz), 122.58 (d, J_{C-F}=18.1 Hz), 114.99 (d, J_{C-F}=22.6Hz), 66.40, 35.74, 30.37, 14.22 (d, J_{C-F}=3.0 Hz); ^{19}F NMR (565 MHz, Chloroform-*d*) *δ*: −117.63; HRMS (ESI) calcd for $C_{17}H_{17}FO_2Na$ $(M+Na)^+$ 295.1105, found 295.1101.

Benzyl 3-(2-chlorophenyl)propanoate (**20**): 23.6 mg, 43% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.40～7.35 (m, 6H), 7.26 ～7.25 (m, 1H), 7.20～7.19 (m, 2H), 5.16 (s, 2H), 3.13 (t, *J*=8.0 Hz, 2H), 2.75 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.63, 138.06, 136.00, 134.07, 130.60, 129.68, 128.67, 128.34 (2C), 127.98, 127.02, 66.45, 34.06, 29.05; HRMS (ESI) calcd for $C_{16}H_{16}ClO_2$ $(M+H)^+$ 275.0833, found 275.0833.

Benzyl 3-(4-(methylthio)phenyl)propanoate (**21**): 34.3 mg, 60% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.41～7.33 (m, 5H), 7.23～7.21 (m, 2H), 7.16～7.14 (m, 2H), 5.15 (s, 2H), 2.97 (t, *J*=8.0 Hz, 2H), 2.70 (t, *J*=8.0 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.69, 137.48, 136.07, 135.96, 128.94, 128.63, 128.30 (2C), 127.16, 66.37, 35.92, 30.48, 16.22; HRMS (ESI) calcd for $C_{17}H_{19}O_2S$ $(M+H)^+$ 287.1100, found 287.1124.

Benzyl 3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)propanoate (**22**): 53.3 mg, 72% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.39～7.34 (m, 5H), 7.07～7.05 (m, 2H), 6.78～6.76 (m, 2H), 5.14 (s, 2H), 2.93 (t, *J*=8.0 Hz, 2H), 2.68 (t, *J*=8.0 Hz, 2H), 1.01 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.99, 154.15, 136.09, 133.20, 139.31, 128.68, 128.34 (2C), 120.14, 66.37, 36.31, 30.32, 25.82, 18.32, −4.30; HRMS (ESI) calcd for $C_{22}H_{31}O_3Si$ $(M+H)^+$ 371.2037, found 371.2016.

Benzyl 3-(3-fluorophenyl)propanoate (**23**): 26.3 mg, 51% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.40～7.35 (m, 5H), 7.29～7.25 (m, 1H), 7.01～7.00 (m, 1H), 6.95～6.93 (m, 2H), 5.16 (s, 2H), 3.01 (t, *J*=8.0 Hz, 2H), 2.73 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.48, 162.99 (d, J_{C-F}=246.1 Hz), 143.02 (d, J_{C-F}=8.5 Hz), 135.91, 120.3 (d, J_{C-F}=8.5 Hz), 128.66, 128.36, 128.34, 124.05 (d, J_{C-F}=3.0 Hz), 115.32 (d, J_{C-F}=21.4 Hz), 113.28 (d, J_{C-F}=21.4 Hz), 66.48, 35.60, 30.69; ^{19}F NMR (565 MHz, Chloroform-*d*) *δ*: −113.34; HRMS (ESI) calcd for $C_{16}H_{15}FO_2Na$ $(M+Na)^+$ 281.0948, found 281.0955.

Benzyl 3-(naphthalen-1-yl)propanoate (**24**): 32.5 mg, 56% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 8.14～8.12 (m, 1H), 7.96～7.95 (m, 1H), 7.83～7.82 (m, 1H), 7.63～7.56 (m, 2H), 7.49～7.41 (m, 7H), 5.25 (s, 2H), 3.55 (t, *J*=8.0 Hz, 2H), 2.92 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.85, 136.43, 135.97, 133.93, 131.65, 128.93, 128.60, 128.27 (2 C), 127.20, 126.13, 126.01, 125.65, 125.62, 123.43, 66.38, 35.20, 28.13; HRMS (ESI) calcd for $C_{20}H_{18}O_2Na$ $(M+Na)^+$ 313.1199, found 313.1208.

Methyl 3-(naphthalen-2-yl)propanoate (**25**): 33.4 mg, 78% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.87～7.83 (m, 3H), 7.70～7.70 (m, 1H), 7.53～7.47 (m, 2H), 7.40～7.38 (m, 1H), 3.73 (s, 3H), 3.18 (t, *J*=8.0 Hz, 2H), 2.78 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 173.39, 138.08, 133.67, 132.24, 128.21, 127.70, 127.59, 127.03, 126.53, 126.10, 125.47, 51.71, 35.68, 31.16; HRMS (ESI) calcd for $C_{14}H_{15}O_2$ $(M+H)^+$ 215.1067, found 215.1070.

Benzyl 3-(benzo[*d*][1,3]dioxol-5-yl)propanoate (**26**): 38.1 mg, 67% yield, colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) *δ*: 7.40～7.35 (m, 5H), 6.76～6.67 (m, 3H), 5.94 (s, 2H), 5.16 (s, 2H), 2.93 (t, *J*=8.0 Hz, 2H), 2.68 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) *δ*: 172.68, 147.70, 146.02, 135.99, 134.25, 128.60, 128.28 (2C), 121.19, 108.86, 108.30, 100.88, 66.32, 36.25, 30.76; HRMS (ESI) calcd for $C_{17}H_{16}O_4Na$ $(M+Na)^+$ 307.0941, found 307.0943.

Supporting Information Tables of condition optimization, procedure for control experiments, UV-Vis absorption spectroscopic measurements, ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of all products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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