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Catalytic Cascade Access to Biaryl-2-Methyl Acetates from Pyruvate *O*-Arylmethyl Ketoximes *via* the Palladium-Catalyzed C(sp^2)–H Bond Arylation and C–O Bond Solvolysis

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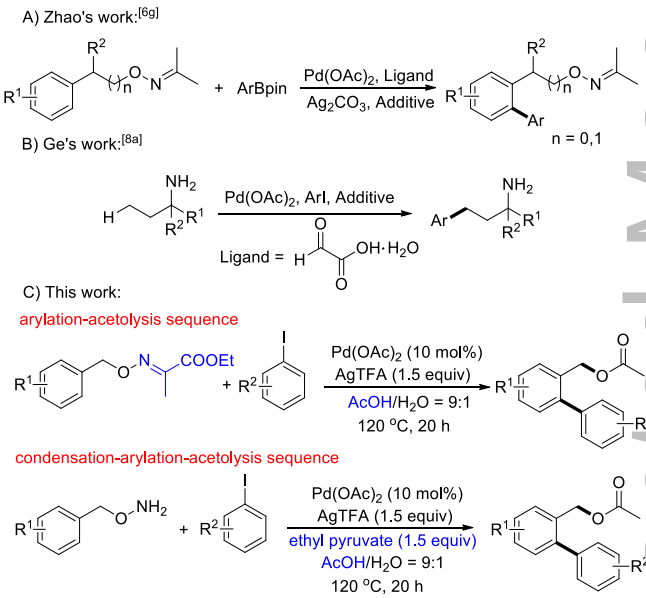
Abstract. A catalytic cascade has been developed for the synthesis of biaryl-2-methyl acetates *via* a palladium-catalyzed *ortho*-C(sp^2)–H bond arylation of pyruvate *O*-arylmethyl ketoximes with aryl iodides followed by a solvolysis, in which the pyruvic ketoxime ester as a new auxiliary is employed to direct the C(sp^2)–H bond activation. The straightforward treatment of *O*-arylmethyl hydroxylamines and ethyl pyruvate with aryl iodides also provides the target products in a one-pot fashion. Furthermore, the new palladacycle intermediate is unambiguously confirmed by single-crystal X-ray diffraction analysis. A plausible reaction pathway is proposed for the Pd-catalyzed arylation-acetolysis sequence.

Keywords: arylation; biaryl-2-methyl acetates; C(sp^2)–H bond activation; pyruvate ketoximes; solvolysis

Introduction

Biaryl motifs are broadly distributed in numerous bioactive molecules, natural products, agrochemicals, pharmaceuticals, and organic functional materials.[1] Over the past few decades, transition-metal-catalyzed cross-couplings of arenes with aryl halides, arylsilanes, arylboron reagents or other arylmetallic reagents[2] have been exploited to assemble myriads of the molecular architectures. However, these methods usually require prefunctionalized or electronically biased substrates. For the sake of step-economy, significant efforts have been devoted to directing inert C–H bond activation/functionalization.[3] In particular, heteroarenes[3,4] or functionalities[3,5] directed arylations have been proved to be powerful strategies to furnish aromatic C–C bond formations.



Scheme 1. Previous related works and present work.

In addition to *N*-heterocyclic directing groups, oxime functionality has been applied in C–H bond activation enabling diversiform transformations such as acetoxylation, acylation, olefination, amidation, iodination and (hetero)arylation.[6] These C–C as well as C–X (X = O, N, I) bonds were effectively built *via* either *endo*- or *exo*-type cyclometalation (π-bond of the directing group inside or outside the metallocycle). In this context, with the aid of exogenous ligand, Zhao's group recently achieved a Pd^{II}/Pd^{0}-catalyzed *ortho*-arylation with arylboronic esters as arylating reagents, directed by simple acetoxime *via* an *exo*-type activation (Scheme 1A).[6g] This work provides a concise two-step access to 2-aryl substituted arylmethyl alcohols through arylation and Ni-

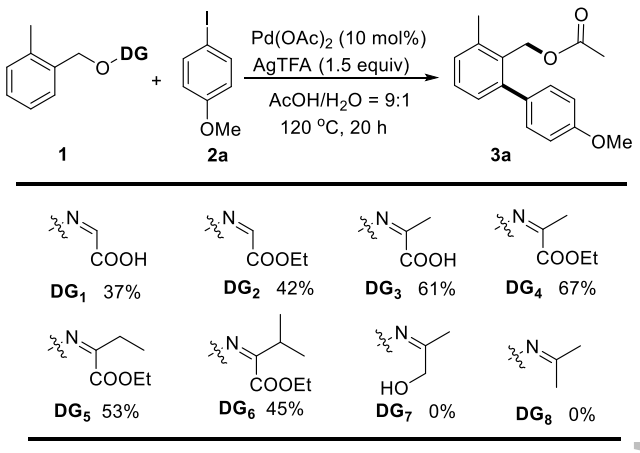
catalyzed hydrogenation reduction. In fact, the biaryl-2-methyl alcohol scaffolds frequently appear in various bioactive molecules, for example, HNF-4α modulators, CaSR antagonists, VEGF receptor inhibitors, etc.[7] More recently, Ge's group reported an *exo*-type directed site-selective C(sp^3)−H arylation of primary aliphatic amines using glyoxylic acid as a transient imine-carboxylic *N,O*-bidentate directing group (Scheme 1B).[8a] Most recently, a powerful 2,2-dimethyl aminooxyacetic acid auxiliary was disclosed by Yu's group to enable an *endo*-type Pd-catalyzed C(sp^3)−H (hetero)arylation,[8b] demonstrating the outstanding directing ability of oxime in concert with another weak dentate.

Nevertheless, compared to developed pyridine-based auxiliaries,[3d,e] simple functionality-based bidentates[8,9] deserve to pay more attention. Herein, we report a new Pd^{II}/Pd^{IV}-catalyzed *ortho*-C(sp^2)–H arylation of masked arylmethyl alcohols followed by a benzylic C–O bond solvolysis to straightforwardly prepare biaryl-2-methyl acetates in a one-pot fashion. The simple bidentate oxime-ester functions as a directing group for the arylation, and a chelating agent for the solvolysis. The activation mode of pyruvic ketoxime ester directing group *via* oxime-carbonylic *N,O*-bidentate chelation is revealed by single-crystal X-ray diffraction analysis, and a plausible reaction pathway is depicted based on a set of rational mechanistic surveys.

Results and Discussion

Our initial efforts aimed at evaluating the different types of *O*-arylmethyl oxime bidentate directing groups for the arylation without exogenous ligand (Scheme 2). The reaction was carried out in the presence of substrate **1** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), 1-iodo-4-methoxybenzene **2a** (1.2 equiv), AgTFA (1.5 equiv) in AcOH/H_2O (9:1, v/v, 2.5 mL) at 120 °C. Unexpectedly, biaryl-2-methyl acetate **3a** was obtained at the end of all effective reactions. Presumably, a nucleophilic C–O bond acetolysis proceeded following the directed C(sp^2)–H arylation.[10] Ge's directing group of glyoxylic acid aldoxime (**DG_1**)[8a] firstly afforded the arylation-acetolysis product **3a** in 37% yield. Furthermore, ethyl glyoxylate aldoxime (**DG_2**) delivered a better yield of 42%. The outcomes were further increased to 61% and 67% by installing pyruvic ketoxime (**DG_3**) and pyruvic ketoxime ester (**DG_4**), respectively. However, bulkier ketoxime ester directing groups (**DG_5** and **DG_6**) significantly reduced the yields. In contrast, the alcohol-assisted ketoxime (**DG_7**) and monodentate acetoxime (**DG_8**) failed to deliver any anticipated product **3a**, where only slight acetolysis of starting ketoxime substrates were detected along with a small amount of homocoupling of **2a**. In the end, pyruvic ketoxime ester (**DG_4**) was selected as the optimal directing group for further investigations.

Scheme 2. Screening of directing groups.[a,b]



[a] *Reaction conditions:* **1** (0.3 mmol), **2a** (84.2 mg, 0.36 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), AgTFA (99.2 mg, 0.45 mmol), AcOH/H_2O (9:1, v/v, 2.5 mL), 120 °C, 20 h.
[b] Isolated yields.

We turned our attention to investigating main reaction parameters (Table 1). The desired product **3a** was obtained with up to 81% yield upon increasing **2a** to 3.0 equiv (entries **1**−**4**). But, further increasing **2a** did not lead to a higher yield (entry **5**). Based on entry **4**, we conducted an intensive survey of Pd catalysts. $Pd(PPh_3)_2Cl_2$ was inefficient (entry **6**) while $PdCl_2$ and $Pd(CH_3CN)_2Cl_2$ resulted in inferior efficiencies (entries **7** and **8**). Albeit a similar outcome with $Pd(TFA)_2$ (entry **9**), $Pd(OAc)_2$ was chosen as the suitable catalyst in light of its lowe cost. Moreover, AgTFA was identified as the best additive among the tested silver salts (entries **10**−**12**). In addition, the yield of **3a** dramatically diminished to 10% in the absence of water (entry **13**). However increasing the amount of water in the mixed solvent was detrimental (entries **14**−**16**). Finally, it was demonstrated that 120 °C was an optimal temperature for the process (entries **17**−**19**). Thus, we established entry **4** as the standard reaction conditions.

With the optimized reaction conditions, we then explored the scope of aryl iodides. As shown in Scheme 3, various electronically and sterically biased aryl iodides with OMe, Me, CH_2OH, F, Cl, Br, I, CF_3 or COOMe groups were suitable substrates (**3a**−**n**). Generally, the partners with electron-donating groups at *para*- and *meta*-positions gave higher yields of 75–83% (**3a**, **b** and **3h**−**j**). Interestingly, 3-iodobenzyl alcohol underwent an additional esterification giving a biarylmethyl diacetate compound **3j**. As for the aryl iodides containing electron-withdrawing groups at *para*- and *meta*-positions, the relatively lower yields of 62–69% were obtained (**3c**−**f** and **3k**−**m**), but the *para*-methoxycarbonyl substituted partner delivered a better yield of 73% (**3g**).[11] It should be noted that the -F, -Cl, -Br, -I, -CH_2OCOMe and -COOMe groups add flexibility to further elaborate the biaryl-2-methyl acetate products. It appears that steric effect

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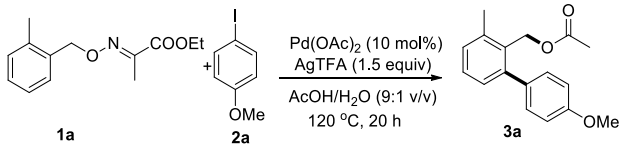
Table 1. Investigations of the reaction parameters.[a]



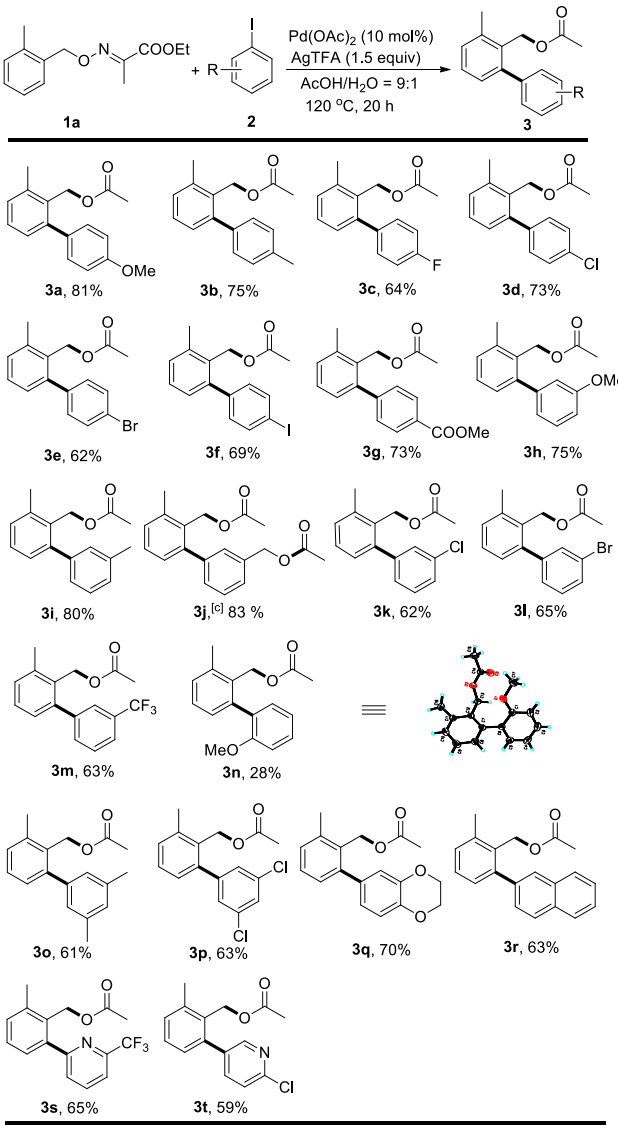
1a 2a 3a

Entry	Mainly deviation from the "primary conditions"	Yield[b]
1	None	67%
2	**2a** (2.0 equiv)	71%
3	**2a** (2.5 equiv)	77%
4	**2a (3.0 equiv)**	**81%**
5	**2a** (3.5 equiv)	80%
6	$Pd(PPh_3)_2Cl_2$ instead of $Pd(OAc)_2$	0%
7	$PdCl_2$ instead of $Pd(OAc)_2$	23%
8	$Pd(CH_3CN)_2Cl_2$ instead of $Pd(OAc)_2$	38%
9	$Pd(TFA)_2$ instead of $Pd(OAc)_2$	79%
10	Ag_3PO_4 instead of AgTFA	15%
11	AgOAc instead of AgTFA	33%
12	Ag_2CO_3 instead of AgTFA	61%
13	AcOH	10%
14	AcOH/H_2O (2:1)	35%
15	AcOH/H_2O (4:1)	41%
16	AcOH/H_2O (6:1)	53%
17	90 °C	63%
18	110 °C	74%
19	130 °C	79%

[a] *Reaction conditions:* **1a** (70.5 mg, 0.3 mmol), **2a** (210.6 mg, 0.90 mmol, except otherwise specified), $Pd(OAc)_2$ (6.7 mg, 10 mol%), AgTFA (99.2 mg, 0.45 mmol), AcOH/H_2O (9:1, v/v, 2.5 mL), 120 °C, 20 h.
[b] Isolated yields.

plays a significant role. Low yield (**3n**) or no product was observed for the *ortho*-substituted reactants. Likely, the larger steric congestion around palladacyclic intermediates would block oxidative addition or reductive elimination step.[12] The disubstituted and fused *O*-heterocyclic aryl iodides, as well as condensed arene 2-iodonaphthalene were also effective to afford the arylmethyl acetates in moderate yields (**3o**–**r**). Less strongly coordinating 2-substituted pyridyl worked well to offer the *N*-heteroarylated products in moderate yields (**3s** and **t**), suggesting the *ortho*-steric effect against the coordination of pyridine with Pd. Functional groups such as ether, arylmethyl acetate, halogen, methoxycarbonyl, 1,4-dioxane and pyridyl were well-tolerated under the reaction conditions. Finally, the NMR-based geometrical configuration of **3n** was further confirmed by single-crystal X-ray diffraction (Scheme 3, see ESI).[13]

Scheme 3. Scope of aryl iodides.[a,b]



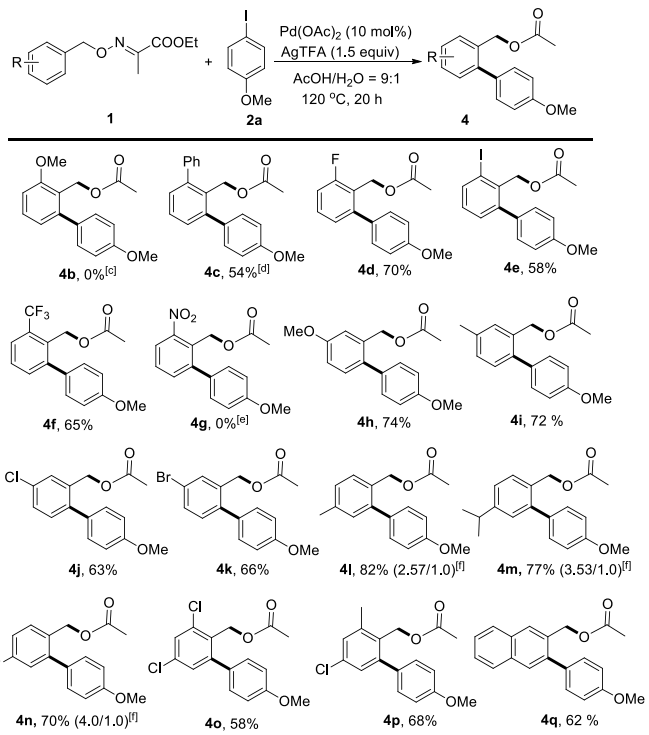
[a] *Reaction conditions*: **1a** (70.6 mg, 0.3 mmol), **2** (0.90 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), AgTFA (99.2 mg, 0.45 mmol), AcOH/H_2O (9:1, v/v, 2.5 mL), 120 °C, 20 h.
[b] Isolated yields.
[c] The product of arylation-acetolysis and additional esterification.

Next, different pyruvic *O*-arylmethyl ketoxime esters were surveyed (Scheme 4). Similarly, wide functional group tolerance was observed including Me, OMe, *i*-Pr, Ph, F, Cl, Br, I, and CF_3 groups (**3a**, **4c**–**f** and **h**–**p**). The substrates bearing electron-donating groups furnished the corresponding biaryl-2-methyl acetates in good yields of 72–82% (**3a**, **4h**, **i**, **l** and **m**). Slightly lower yields were observed for the substrates with electron-withdrawing groups (**4d**–**f**, **j**, **k**, **n** and **o**). As for strongly coordinating -OMe and -NO_2 groups,[6d,k,l,8b] their *ortho*-substituted *O*-arylmethyl ketoximes underwent a solvolysis to exclusively offer the non-arylated arylmethyl acetates (**4b**' and **g**').[14] It is likely that -OMe and -NO_2 might coordinate with the Pd center along with the ketoxime ester directing group, bringing about a larger molecular distortion and ring strain.

Consequently, the tri-dentate chelation would impede potential arylation and impair the stability of benzylic C–O bond, leading to the exclusive acetolysis.[14] Other *ortho*-systems were amenable to the approach delivering desired products in moderate yields of 54–70% (**4c**–**f**). It should be pointed out that sterically crowded terphenyl **4c** offered a relatively lower yield of 54%, accompanying with 2-phenylbenzyl acetate **6a** (see Scheme 5) as a by-product of direct acetolysis therein.

With respect to the *meta*-substituted *O*-arylmethyl ketoximes, the pivotal arylation appropriately took place at less sterically hindered positions (**4g**–**k**).[15] As for *para*-substituted substrates (**4l**–**n**), the corresponding diarylated acetates were also observed. Besides, the method was applicable for disubstituted masked arylmethyl alcohols in moderate yields (**4o** and **p**). Furthermore, the condensed arene turned out to be a feasible substrate for the arylation at less hindered position (**4q**).

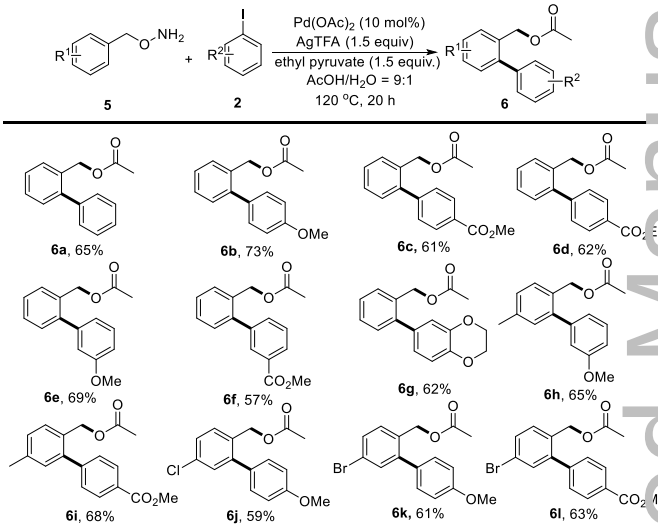
Scheme 4. Scope of pyruvic *O*-arylmethyl ketoxime esters.[a,b]



[a] *Reaction conditions*: **1** (0.3 mmol), **2a** (210.6 mg, 0.90 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), AgTFA (99.2 mg, 0.45 mmol), $AcOH/H_2O$ (9:1, v/v, 2.5 mL), 120 °C, 20 h.
[b] Isolated yields.
[c] The product of direct acetolysis observed in 91% yield, see Ref.14a and ESI.
[d] The by-product of direct acetolysis observed in 21% yield, see **6a** in Scheme 5.
[e] The product of direct acetolysis observed in 87% yield, see Ref.14b and ESI.
[f] Ratio of *mono/di*.

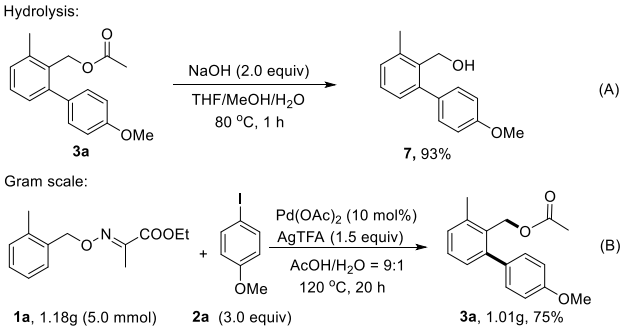
We demonstrated that the cascade of condensation, arylation, and acetolysis could be accomplished in a one-pot fashion by using *O*-arylmethyl hydroxylamines and ethyl pyruvate as starting materials (Scheme 5). Owing to the strong coordinating ability and reactivity, free *O*-arylmethyl hydroxylamines often interfere with the reactive reagents and catalysts.[6m] With the slightly modified protocol (1.5 equiv ethyl pyruvate and other identical conditions), these unsubstituted and *para*-substituted free amines were subjected to the one-pot procedure with various aryl iodides to generate the desired products in moderate to good yields of 57–73% (**6a**–**l**). Furthermore, it is noteworthy that only monoarylated acetates were obtained without diarylated products. We speculated that the excessive ethyl pyruvate served as an exogenous ligand coordinating with Pd to inhibit the potential secondary activation/oxidative addition. With the help of arylation-derived *ortho*-steric hindrance and auxiliary chelation, such additional chelation further impairs the stability of benzylic C–O bond.

Scheme 5. One-pot synthesis of biaryl-2-methyl acetates from *O*-arylmethyl hydroxylamines.[a,b]



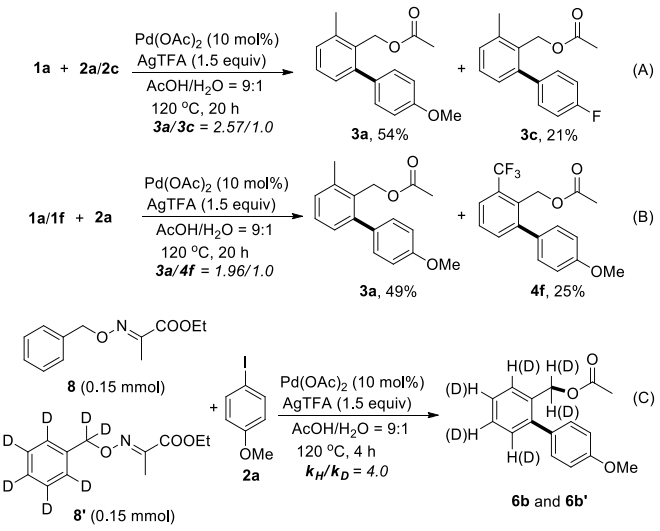
[a] *Reaction conditions*: **5** (0.3 mmol), **2** (0.90 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), AgTFA (99.2 mg, 0.45 mmol), ethyl pyruvate (52.2 mg, 0.45 mmol), $AcOH/H_2O$ (9:1, v/v, 2.5 mL), 120 °C, 20 h.
[b] Isolated yields.

The strategy can be expediently adopted to prepare synthetically valuable 2-aryl substituted arylmethyl alcohols (Scheme 6A). Subjecting the acetate **3a** and NaOH to a mixed solvent of $THF/MeOH/H_2O$ afforded biaryl alcohol **7** in 93% yield without the need for a column-chromatographic purification (see ESI). Thus, as an alternative to the laborious hydrogenation,[6g] this enabled a rapid access to biaryl-2-methyl alcohols. In addition, the reaction on gram scale has also been examined in good yield (Scheme 6B).



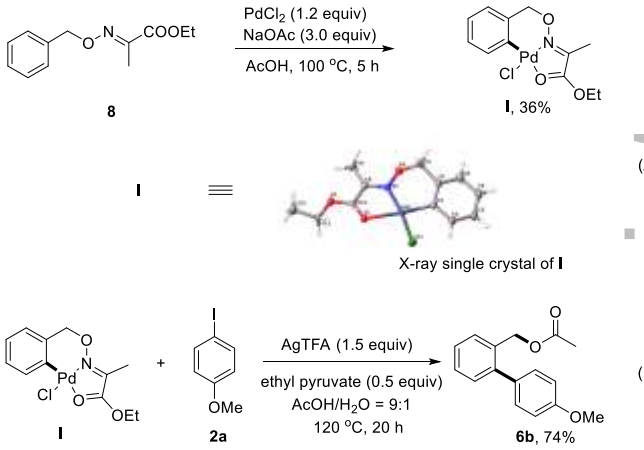
Scheme 6. Convenient access to 2-aryl substituted arylmethyl alcohol and a gram scale reaction.

To gain insight into the reaction mechanism of the arylation, the intermolecular competition experiments were firstly carried out to probe the electronic effect. The treatment of a mixture of electronically biased iodides **2a** and **2c** (1:1 equiv) with ketoxime ester **1a** generated the products **3a** and **3c** with the ratio of 2.57/1.0 (Scheme 7A, see ESI). It was found that the electron-rich **2a** predominantly coupled with the substrate **1a**, suggesting that electron-donating group substituted aryl iodides would facilitate the transformation.[12,16] In addition, the competition process of **1a** and **1f** gave a similar result that the electron-rich ketoxime ester **1a** was preferred to yield **3a** as a major product (Scheme 7B, see ESI). At last, a deuterium labeling isotope experiment was carried out to probe the kinetics of Pd^{II}/Pd^{IV}-catalyzed C(sp^2)−H arylation (Scheme 7C). The intermolecular competition reactions between **8** and **8´** (**8**-d_7) with **2a** in one vessel clearly revealed a primary kinetic isotopic effect (k_H/k_D = 4.0; see ESI). The result indicates that the C(sp^2)−H bond cleavage/carbopalladation might be involved in the rate-limiting step.



Scheme 7. Intermolecular kinetic competition experiments.

We successfully obtained a crystallizable palladacycle **I** from $PdCl_2$ and pyruvate *O*-benzyl ketoxime **8**.[17] The structure of **I** was unambiguously confirmed by single-crystal X-ray diffraction analysis to reveal an activation mode referring to five-membered oxime-carbonylic *N*,*O*-bidentate chelation with six-membered *exo*-carbopalladation (5,6-fused metallocycle mode, Scheme 8A, see ESI)[13]. Accordingly, the palladacycle favorably converted into the desired arylated benzyl acetate **6b** in 74% yield in the absence of $Pd(OAc)_2$ (Scheme 8B). Therefore, the cyclopalladated **I** was suggested as a key intermediate engaged in the process. The present work represents a new example of *N*,*O*-bidentate activation.

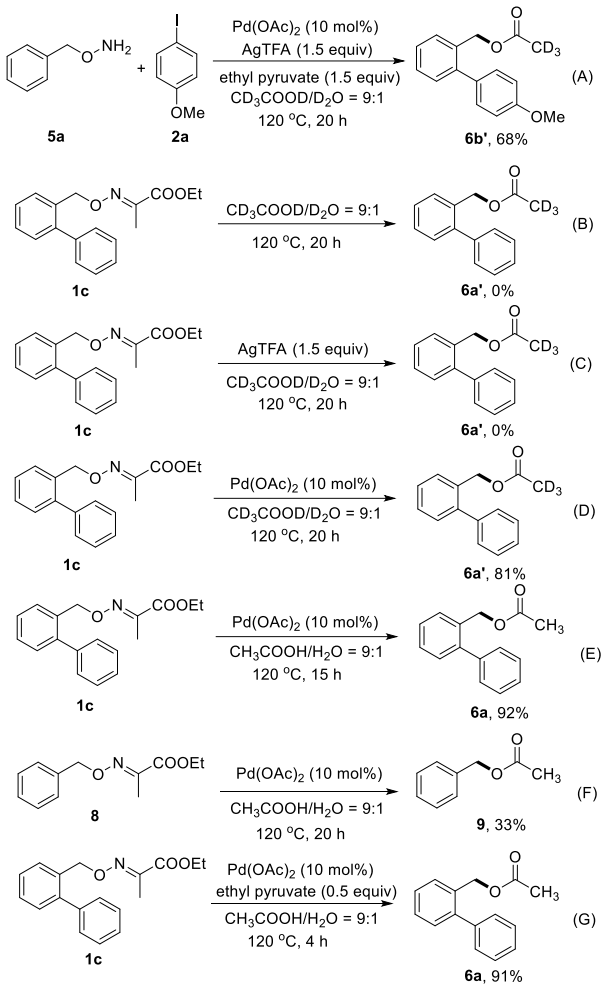


Scheme 8. Preparation and arylation-solvolysis of the palladacycle **I**.

We implemented a set of control experiments to detect the influences on acetolysis (Scheme 9). Firstly, subjecting *O*-benzyl hydroxylamine **5a**, iodide **2a**, and ethyl pyruvate to the one-pot protocol with CD_3COOD/D_2O (9:1, v/v) as a solvent, 2-arylbenzyl deuterated acetate **6b'** was obtained as the desired product (Scheme 9A). This suggests that a nucleophilic solvolysis of the benzylic C−O bond with acetic acid indeed occurs[10] after arylation. Secondly, without the metal salt, the solvolysis of biaryl pyruvate ketoxime **1c** failed to provide any deuterated acetate **6a'** (Scheme 9B), and the stoichiometric AgTFA was proved to be completely ineffective (Scheme 9C). However, introducing a catalytic amount of $Pd(OAc)_2$ into the system strikingly gave the deuterated **6a'** in 81% yield (Scheme 9D), or acetate product **6a** in 92% yield (Scheme 9E). These facts undoubtedly revealed a dual role of Pd catalyst, directing proximal C(sp^2)−H bond activation and facilitating benzylic C−O bond solvolysis.

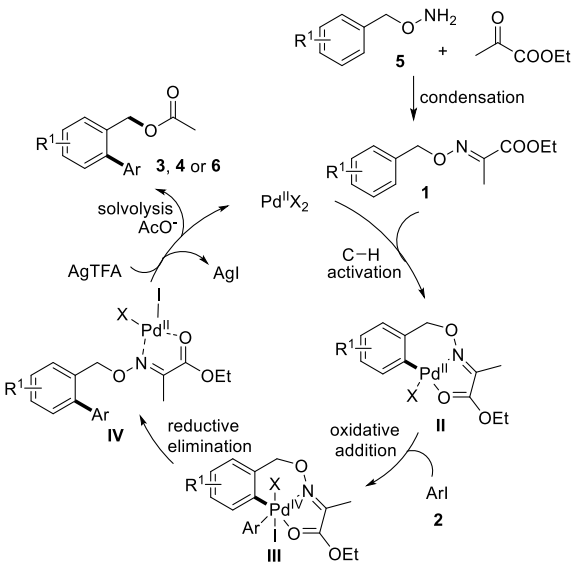
On the other hand, the influence of *ortho*-aryl hindrance on the acetolysis was further investigated. Compared to biaryl pyruvate ketoxime **1c** (Scheme 9E), the solvolysis of *O*-benzyl ketoxime **8** was considerably more sluggish to deliver only 33% yield of acetate product (Scheme 9F). In this regard, it was revealed that the arylation-derived *ortho*-hindrance can result in a more accessible acetolysis. Meanwhile, we considered that the use of 3 equiv of ArI greatly enhances Pd-catalyzed arylation, accordingly promoting the subsequent acetolysis. Finally, the control experiment showed that the excessive ethyl pyruvate can serve as an exogenetic ligand to

promote the solvolysis (Scheme 9G). These synergistic effects of ethyl pyruvate coordination, arylation-derived *ortho*-hindrance, and intrinsic auxiliary chelation significantly accelerate the Pd-catalyzed acetolysis with severely aggravated molecular distortion.



Scheme 9. Control experiments.

On the basis of experimental investigations and the well-documented reports,[8,10,18] a plausible reaction pathway involving Pd^{II}/Pd^{IV} catalytic cycle is proposed for the cascade process (Scheme 10). Pyruvate ketoxime **1** firstly coordinates with Pd^{II} to form the palladated bicyclic intermediate **II** *via* a five-membered chelation and an *exo*-type six-membered concerted metallation–deprotonation (CMD).[19,20] Then, the key Pd^{IV} species **III** is generated through the oxidative addition of palladacycle **II** with aryl iodide. The highly active hexa-coordinated Pd^{IV} adduct **III** undergoes a following reductive elimination to furnish the Pd^{II} pincer-type complex **IV**. Finally, the complex **IV** is followed by a nucleophilic acetolysis and iodide abstraction[20] to release the arylated arylmethyl acetate **3**, **4** or **6**, and regenerate the Pd^{II} catalyst. The complex **IV** may be further chelated by excessive ethyl pyruvate through ligand exchange, to drastically accelerate the solvolysis (Scheme 5).



Scheme 10. Plausible reaction pathway.

Conclusion

In summary, we have developed an efficient cascade for synthesis of biaryl-2-methyl acetates *via* Pd-catalyzed *ortho*-C(sp^2)–H arylation and acetolysis. With the cost-effective ethyl pyruvate as a directing group, structurally diverse masked arylmethyl alcohols (**1** and **5**) can be arylated on the aromatic ring and acetoxylated at the benzyl position in one-pot fashion. The *exo*-six-membered palladacycle with five-membered *N*,*O*-bidentate chelation is unambiguously confirmed by single-crystal X-ray diffraction analysis. We have also conducted a series of mechanistic studies depicting a plausible reaction pathway. Further related studies are underway in our laboratory.

Experimental Section

Unless otherwise indicated, all reagents were obtained from commercial sources and used as received without further purification. All reactions were carried out in an oven-dried glass sealed tube and monitored by thin layer chromatography (TLC, pre-coated silica gel plates containing HF254). All solvents were only dried over 4 Å molecular sieves. Reaction products were purified *via* column chromatography on silica gel (300–400 mesh). Melting points were determined using open capillaries and uncorrected. NMR spectra were determined on Bruker AV400 in $CDCl_3$ with TMS as internal standard for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz), respectively. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer or Micromass GCTTM gas chromatograph-mass spectrometer.

Procedure for the Synthesis of Biaryl-2-Methyl Acetates (3, 4) from Pyruvate *O*-Arylmethyl Ketoximes
A mixture of substrate **1** (0.3 mmol), **2** (0.9 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), AgTFA (99.2 mg, 0.45 mmol), and $AcOH/H_2O$ (9:1, v/v, 2.5 mL) was stirred in a glass sealed-tube at room temperature for 30 min, then the mixture was heated to 120 °C for 20 h. Upon completion of the reaction, the mixture was cooled to room temperature and added dropwise into a saturated $NaHCO_3$ solution (25 mL). The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layer was dried over anhydrous $MgSO_4$. Finally, the solution was

concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 40:1) to supply the desired product **3** or **4**.

(4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3a): yellow oil, 65.7 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (t, J = 7.6 Hz, 1H), 7.26−7.22 (m, 3H), 7.16 (d, J = 7.6 Hz, 1H), 6.94 (dt, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 2H), 5.03 (s, 2H), 3.85 (s, 3H), 2.42 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.9, 158.9, 143.8, 138.9, 133.4, 131.0, 130.3 (2C), 129.5, 128.5, 128.3, 113.6 (2C), 62.4, 55.3, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1254.

(3,4'-dimethyl-[1,1'-biphenyl]-2-yl)methyl acetate (3b): yellow oil, 57.2 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 (t, J = 7.2 Hz, 1H), 7.30−7.28 (m, 1H), 7.29−7.26 (m, 4H), 7.22 (d, J = 7.6 Hz, 1H), 5.08 (s, 2H), 2.48 (s, 3H), 2.45 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 144.2, 138.9, 138.1, 136.9, 131.0, 129.5, 129.1 (2C), 128.9 (2C), 128.5, 128.2, 62.4, 21.2, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_2$: 254.1307, found 254.1308.

(4'-fluoro-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3c): yellow oil, 49.6 mg (64%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (s, 1H), 7.19 (d, J = 3.6 Hz, 1H), 7.17−7.15 (m, 2H), 7.05 (d, J = 7.6 Hz, 1H), 7.00 (t, J = 8.8 Hz, 2H), 4.91 (s, 2H), 2.34 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 162.2 (d, $^1J_{CF}$ = 244.8 Hz), 143.1, 139.0, 137.0 (d, $^4J_{CF}$ = 3.3 Hz), 131.1, 130.8 (d, $^3J_{CF}$ = 8.0 Hz, 2C), 129.9, 128.6, 128.2, 115.1 (d, $^2J_{CF}$ = 21.3 Hz, 2C), 62.1, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2F$:258.1056, found 258.1054.

(4'-chloro-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3d): yellow oil, 60.2 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.17 (s, 2H), 7.15 (s, 1H), 7.04 (d, J = 7.6 Hz, 1H), 4.90 (s, 2H), 2.34 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 142.9, 139.5, 139.1, 133.4, 131.0, 130.6 (2C), 130.1, 128.7, 128.3 (2C), 128.0, 62.1, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2{}^{35}Cl$: 274.0761, found 274.0762.

(4'-bromo-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3e): yellow oil, 59.4 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 6.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 7.2 Hz, 1H), 4.90 (s, 2H), 2.34 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 142.9, 140.0, 139.1, 131.3 (2C), 130.9 (2C), 130.1, 128.8, 128.7, 127.9, 121.6, 62.1, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2{}^{81}Br$: 320.0235, found 320.0238.

(4'-iodo-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3f): yellow solid, m.p. 78–80 °C, 75.8 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.65 (d, J = 8.4 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 6.4 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 4.90 (s, 2H), 2.33 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 142.9, 140.6, 139.1, 137.3 (2C), 131.2 (2C), 130.8, 130.1, 128.7, 127.9, 93.2, 62.1, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2{}^{127}I$: 366.0117, found 366.0115.

Methyl 2'-(acetoxymethyl)-3'-methyl-[1,1'-biphenyl]-4-carboxylate (3g): yellow oil, 65.3 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.99 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 6.4 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 4.89 (s, 2H), 3.85 (s, 3H), 2.34 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 166.9, 145.8, 143.1, 139.1, 130.9, 130.3, 129.4 (2C), 129.3 (2C), 129.0, 128.7, 127.8, 62.0, 52.2, 20.8, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{18}H_{18}O_4$: 298.1205, found 298.1204.

(3'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3h): yellow oil, 60.8 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 6.4 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.83−6.81 (m, 1H), 6.81−6.79 (m, 1H), 6.78 (t, J = 1.6 Hz, 1H), 4.94 (s, 2H), 3.73 (s, 3H), 2.33 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 159.3, 144.0, 142.4, 139.0, 130.9, 129.8, 129.2, 128.6, 128.0, 121.7, 114.9, 112.9, 62.3, 55.2, 20.9, 19.4; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1254.

(3,3'-dimethyl-[1,1'-biphenyl]-2-yl)methyl acetate (3i): yellow oil, 61.0 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (q, J = 7.2 Hz, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 5.01 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 144.3, 141.0, 138.9, 137.7, 130.9, 130.1, 129.6, 128.5, 128.1, 128.02, 127.96, 126.3, 62.3, 21.5, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_2$: 254.1307, found 254.1306.

(3'-acetoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3j): yellow oil, 77.7 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40 (t, J = 7.2 Hz, 1H), 7.36 (s, 1H), 7.31 (s, 2H), 7.26 (s, 2H), 7.16 (d, J = 7.6 Hz, 1H), 5.13 (s, 2H), 4.98 (s, 2H), 2.42 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.92, 170.86, 143.7, 141.4, 139.0, 136.6, 135.8, 130.9, 129.9, 129.1, 128.6, 128.4, 128.1, 127.2, 66.2, 62.2, 21.0, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{19}H_{20}O_4$: 312.1263, found 312.1262.

(3'-chloro-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3k): yellow oil, 51.1 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33 (s, 1H), 7.32 (s, 1H), 7.32 (d, J = 1.2 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1H), 7.20−7.17 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 4.97 (s, 2H), 2.42 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 142.8, 142.8, 139.1, 134.0, 130.9, 130.2, 129.5, 129.4, 128.7, 127.9, 127.4, 127.4, 62.0, 20.9, 19.6, HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2{}^{35}Cl$: 274.0761, found 274. 0759.

(3'-bromo-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3l): yellow oil, 62.2 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42−7.39 (m, 2H), 7.23 (t, J = 8.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.17−7.14 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H), 4.89 (s, 2H), 2.34 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 143.1, 142.7, 139.1, 132.4, 130.9, 130.3, 130.2, 129.7, 128.7, 127.9, 127.8, 122.2, 62.0, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_2{}^{79}Br$: 318.0255, found 318.0253.

(3-methyl-3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl acetate (3m): yellow solid, m.p. 48–50 °C, 58.3 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (s, 2H), 7.56−7.51 (m, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 6.8 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 4.94 (s, 2H), 2.45 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 142.7, 141.8, 139.2, 132.4, 131.0, 130.6, 130.3, 128.8, 128.7, 128.0, 126.2 (q, $^3J_{CF}$ = 3.8 Hz), 124.1 (q, $^2J_{CF}$ = 3.7 Hz), 124.1 (q, $^1J_{CF}$ = 270.8 Hz), 62.0, 20.7, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{15}O_2F_3$: 308.1024, found 308.1023.

(2'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3n): yellow solid, m.p. 82–84 °C, 22.7 mg (28%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.25 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.07 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 4.99 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 12.0 Hz, 1H), 3.64 (s, 3H), 2.33 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.9, 156.4, 140.0, 138.3, 132.1, 131.3, 129.9, 129.7, 129.0, 128.5, 128.4, 120.4, 110.6, 62.6, 55.4, 20.8, 19.7; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1254.

(3,3',5'-trimethyl-[1,1'-biphenyl]-2-yl)methyl acetate (3o): yellow oil, 49.1 mg (61%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 6.84 (s, 2H), 4.93 (s, 2H), 2.34 (s, 3H), 2.26 (s, 6H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 144.4, 140.9, 138.8, 137.5 (2C), 130.9, 129.5, 128.8, 128.5, 128.0, 127.1 (2C), 62.4, 21.4 (2C), 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{18}H_{20}O_2$: 268.1463, found 268.1462.

(3',5'-dichloro-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (3p): yellow oil, 58.4 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (t, J = 2.0 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 1.6 Hz, 2H), 7.03 (d, J = 6.8 Hz, 1H), 4.87 (s, 2H), 2.35 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 169.7, 142.9, 140.5, 138.2, 133.6 (2C), 129.9, 129.6, 127.7, 126.8 (2C), 126.6, 126.4, 60.7, 19.8, 18.5; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{14}O_2{}^{35}Cl$: 308.0371, found 308.0373.

2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-6-methylbenzyl acetate (3q): yellow oil, 62.6 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 6.69 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 4.95 (s, 2H), 4.20 (s, 4H), 2.32 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.0, 143.7, 143.1, 143.0, 138.9, 134.4, 131.0, 129.5, 128.5, 128.1, 122.4, 118.2, 116.9, 64.4 (2C), 62.4, 20.9, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{18}H_{18}O_4$: 298.1205, found 298.1204.

2-methyl-6-(naphthalen-2-yl)benzyl acetate (3r): yellow oil, 54.9 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.76 (d, J = 8.4 Hz, 2H), 7.72 (t, J = 5.2 Hz, 1H), 7.68 (s, 1H), 7.40 (t, J = 4.4 Hz, 2H), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 2H), 4.96 (s, 2H), 2.35 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 144.2, 139.1, 138.6, 133.2, 132.5, 131.2, 129.9, 128.7, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 126.4, 126.1, 62.4, 20.9, 19.7; HRMS (EI): *m/z* [M^+] calcd. for $C_{20}H_{18}O_2$: 290.1307, found 290.1304.

2-methyl-6-(6-(trifluoromethyl)pyridin-2-yl)benzyl acetate (3s): yellow solid, m.p. 75–77 °C, 60.3 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.8 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.24–7.20 (m, 2H), 5.03 (s, 2H), 2.37 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.9, 160.1, 147.6 (q, $^2J_{CF}$ = 34.4 Hz), 140.8, 139.7, 137.9, 131.7, 131.4, 128.8, 128.0, 126.8, 121.5 (q, $^1J_{CF}$ = 272.7 Hz), 118.6 (q, $^3J_{CF}$ = 2.7 Hz), 61.6, 20.7, 19.5; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{14}NO_2F_3$: 309.0977, found 309.0979.

2-(6-chloropyridin-3-yl)-6-methylbenzyl acetate (3t): yellow oil, 48.8 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.29 (d, J = 2.4 Hz, 1H), 7.55 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.30 (t, J = 8.0 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 4.88 (s, 2H), 2.36 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 150.5, 149.6, 139.5, 139.3, 139.0, 135.6, 131.3, 130.9, 129.0, 128.1, 123.7, 61.7, 20.8, 19.6; HRMS (EI): *m/z* [M^+] calcd. for $C_{15}H_{14}NO_2{}^{35}Cl$: 275.0713, found 275.0712.

2-methoxybenzyl acetate (4b'): yellow oil, 49.2 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.32 (t, J = 8.0 Hz, 2H), 6.96 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.17 (s, 2H), 3.85 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.1, 157.5, 129.8, 129.6, 124.2, 120.4, 110.5, 61.8, 55.4, 21.1; HRMS (EI): *m/z* [M^+] calcd. for $C_{10}H_{12}O_3$: 180.0786, found 180.0785.

(4-methoxy-[1,1',3',1''-terphenyl]-2'-yl)methyl acetate (4c): yellow solid, m.p. 56–58 °C, 53.8 mg (54%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 4.0 Hz, 1H), 7.29 (s, 3H), 7.28 (d, J = 1.2 Hz, 1H), 7.23 (s, 1H), 7.22 (s, 1H), 7.21 (s, 1H), 7.20 (s, 1H), 6.85 (d, J = 8.8 Hz, 2H), 4.73 (s, 2H), 3.75 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.2, 159.0, 144.6, 144.3, 141.1, 133.3, 130.5, 130.4 (2C), 129.8, 129.3, 129.2 (2C), 128.4, 128.1 (2C), 127.4, 113.6 (2C), 62.7, 55.3, 20.8; HRMS (EI): *m/z* [M^+] calcd. for $C_{22}H_{20}O_3$: 332.1412, found 332.1411.

(3-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4d): yellow oil, 57.6 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 (dd, J_1 = 80 Hz, J_2 = 2.0 Hz, 1H), 7.17 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 4.97 (s, 2H), 3.76 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 162.3 (d, $^1J_{CF}$ = 247.8 Hz), 159.3, 145.3 (d, $^3J_{CF}$ = 3.2 Hz), 132.6 (d, $^4J_{CF}$ = 2.6 Hz), 130.3 (2C), 130.0 (d, $^3J_{CF}$ = 9.4 Hz), 125.9 (d, $^4J_{CF}$ = 3.1 Hz), 120.6 (d, $^2J_{CF}$ = 14.4 Hz), 114.1 (d, $^2J_{CF}$ = 22.2 Hz), 113.8 (2C), 58.4 (d, $^3J_{CF}$ = 4.8 Hz), 55.3, 20.9; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}O_3F$: 274.1005, found 274.1006.

(3-iodo-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4e): yellow oil, 66.5 mg (58%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86 (t, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.29 (s, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 5.05 (s, 2H), 3.85 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 159.0, 142.1, 139.0, 133.3, 132.8, 130.2 (2C), 129.6, 128.3, 127.3, 113.7 (2C), 64.5, 55.3, 21.0; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}{}^{127}IO_3$: 382.0066, found 382.0067.

(4'-methoxy-3-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl acetate (4f): yellow oil, 63.2 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.72 (t, J = 4.4 Hz, 1H), 7.50 (d, J = 4.4 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 5.07 (s, 2H), 3.86 (s, 3H) , 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.2, 159.3, 146.0, 134.3, 131.8, 131.1, 130.8, 130.3 (2C), 128.6, 125.4, 124.2 (q, $^1J_{CF}$ = 272.7 Hz), 113.7 (2C), 60.7, 55.3, 20.8; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{15}O_3F_3$: 324.0973, found 324.0975.

2-nitrobenzyl acetate (4g'): yellow oil, 50.9 mg (87%), ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.11 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 5.52 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.4, 147.5, 133.8, 132.1, 129.0, 128.8, 125.1, 63.0, 20.8; HRMS (EI): *m/z* [M-NO_2]$^+$ calcd. for $C_9H_9O_2$: 149.0603, found 149.0599.

(4,4'-dimethoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4h): yellow oil, 63.6 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 5.6 Hz, 2H), 7.20 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 2.8 Hz, 1H), 5.01 (s, 2H), 3.85 (s, 3H) , 3.84 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 158.8 (2C), 134.51, 134.49, 132.5, 131.4, 130.4 (2C), 114.7, 113.73, 113.67 (2C), 64.6, 55.4, 55.3, 21.1; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_4$: 286.1205, found 286.1204.

(4'-methoxy-4-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (4i): yellow oil, 58.4 mg (72%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20 (s, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.10 (s, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.93 (s, 2H), 3.75 (s, 3H), 2.31 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 158.9, 139.3, 137.1, 133.0, 132.7, 130.4, 130.32 (2C), 130.30, 129.2, 113.7 (2C), 64.2, 55.3, 21.1 (2C); HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1257.

(4-chloro-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4j): yellow oil, 54.9 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, J = 2.0 Hz, 1H), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.14 (d, J = 3.6 Hz, 1H), 7.11 (d, J = 2.8 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.91 (s, 2H), 3.76 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 159.2, 140.2, 135.2, 133.1, 131.6, 131.5,

130.2 (2C), 129.0, 128.2, 113.9 (2C), 63.8, 55.3, 20.9; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{16}H_{15}O_3{}^{35}Cl$: 290.0710, found 290.0714.

(4-bromo-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4k): yellow oil, 66.4 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (d, J = 2.0 Hz, 1H), 7.48 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 5.00 (s, 2H), 3.85 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 159.2, 140.7, 135.5, 131.95, 131.86, 131.5, 131.2, 130.1 (2C), 121.2, 113.9 (2C), 63.7, 55.3, 21.0; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{16}H_{15}O_3{}^{79}Br$: 324.0205, found 324.0204.

(4'-methoxy-5-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (4l): yellow oil, 47.8 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.8 Hz, 1H), 7.03 (s, 1H), 6.85 (d, J = 8.8 Hz, 2H), 4.91 (s, 2H), 3.75 (s, 3H), 2.28 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.9, 158.9, 142.1, 138.2, 132.9, 131.1, 130.3, 130.2 (2C), 129.9, 128.0, 113.6 (2C), 64.5, 55.3, 21.2, 21.1; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1258.

(4,4''-dimethoxy-5'-methyl-[1,1':3',1''-terphenyl]-2'-yl)methyl acetate (4l'): yellow solid, m.p. 68–70 °C, 26.0 mg (23%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (d, J = 8.4 Hz, 4H), 7.12 (s, 2H), 6.92 (d, J = 8.4 Hz, 4H), 4.77 (s, 2H), 3.84 (s, 6H), 2.40 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.3, 158.9 (2C), 144.3 (2C), 138.2, 133.5 (2C), 130.30 (4C), 130.25 (2C), 127.7, 113.5 (4C), 62.7, 55.3 (2C), 29.7, 20.9; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{24}H_{24}O_4$: 376.1675, found 376.1672.

(5-isopropyl-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4m): yellow oil, 53.7 mg (60%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.23 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 5.01 (s, 2H), 3.86 (s, 3H), 2.98−2.90 (m, 1H), 2.06 (s, 3H), 1.27 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.9, 158.9, 149.2, 142.2, 133.1, 130.6, 130.3 (2C), 129.9, 128.5, 125.4, 113.6 (2C), 64.5, 55.3, 33.9, 24.0 (2C), 21.1; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{19}H_{22}O_3$: 298.1569, found 298.1570.

(5'-isopropyl-4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)methyl acetate (4m'): yellow oil, 20.6 mg (17 %); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40 (d, J = 8.0 Hz, 2H), 7.29 (s, 2H), 7.23 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 7.16 (d, J = 1.6 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 5.01 (s, 2H), 3.86 (s, 6H), 2.98−2.90 (m, 1H), 2.06 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 159.1, 144.5, 133.9 (2C), 130.6 (4C), 127.9 (2C), 116.2 (2C), 115.0 (2C), 113.7 (4C), 63.1, 55.5 (2C), 34.2, 24.1 (2C), 21.1; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{26}H_{28}O_4$: 404.1988, found 404.1989.

(5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4n): yellow oil, 46.1 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 1H), 7.18 (d, J = 8.8 Hz, 2H), 6.97 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.92 (dd, J_1 = 9.6 Hz, J_2 = 2.4 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 4.91 (s, 2H), 3.77 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 162.3 (d, $^1J_{CF}$ = 246.3 Hz), 159.3, 144.4 (d, $^3J_{CF}$ = 8.0 Hz), 131.8 (d, $^3J_{CF}$ = 8.6 Hz), 131.7 (d, $^4J_{CF}$ = 1.7 Hz), 130.1 (2C), 129.3 (d, $^4J_{CF}$ = 3.1 Hz), 117.0 (d, $^2J_{CF}$ = 21.3 Hz), 114.1 (d, $^2J_{CF}$ = 21.0 Hz), 113.8 (2C), 63.9, 55.3, 21.0; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{16}H_{15}O_3F$: 274.1005, found 274.1004.

(5'-fluoro-4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)methyl acetate (4n'): yellow solid, m.p. 60–62 °C, 16.0 mg (14%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 9.2 Hz, 2H), 6.94 (d, J = 8.8 Hz, 4H), 4.74 (s, 2H), 3.85 (s, 6H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.2, 161.7 (d, $^1J_{CF}$ = 247.6 Hz), 159.3 (2C), 146.7 (d, $^3J_{CF}$ = 8.5 Hz, 2C), 132.4 (d, $^4J_{CF}$ = 1.8 Hz, 2C), 130.2 (4C), 126.8 (d, $^4J_{CF}$ = 3.1 Hz), 116.1 (d, $^2J_{CF}$ = 20.8 Hz, 2C), 113.6 (4C), 62.3, 55.3 (2C), 20.9; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{23}H_{21}O_4F$: 380.1424, found 380.1429.

(3,5-dichloro-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (4o): yellow oil, 56.6 mg (58%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (d, J = 2.0 Hz, 1H), 7.23 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.03 (s, 2H), 3.85 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.5, 159.6, 146.6, 137.2, 134.7, 131.0, 130.1 (2C), 129.6, 129.1, 128.3, 113.9 (2C), 61.6, 55.4, 20.8; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{16}H_{14}O_3{}^{35}Cl_2$: 324.0320, found 324.0321.

(5-chloro-4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)methyl acetate (4p): yellow oil, 62.2 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.22−1.19 (m, 3H),7.15 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 4.97 (s, 2H), 3.85 (s, 3H), 2.39 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 159.2, 145.4, 140.9, 134.0, 132.1, 130.2 (2C), 129.7, 129.2, 128.0, 113.7 (2C), 61.7, 55.3, 20.9, 19.6; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{17}H_{17}O_3{}^{35}Cl$: 304.0866, found 304.0862.

(3-(4-methoxyphenyl)naphthalen-2-yl)methyl acetate (4q): yellow oil, 57.0 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.96 (s, 1H), 7.89 (d, J = 4.8 Hz, 1H), 7.83 (d, J = 4.8 Hz, 1H), 7.75 (s, 1H), 7.51 (d, J = 4.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 5.19 (s, 2H), 3.88 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 169.7, 158.0, 138.7, 132.0, 131.7, 131.3, 130.8, 129.3 (2C), 128.1, 127.7, 126.7, 126.6, 125.6, 125.1, 112.6 (2C), 63.8, 54.3, 20.0; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{20}H_{18}O_3$: 306.1256, found 306.1255.

Procedure for the One-pot Synthesis of Biaryl-2-methyl Acetates (6) from *O*-Arylmethyl Hydroxylamines

A mixture of *O*-arylmethyl hydroxylamines **5** (0.3 mmol), **2** (0.9 mmol), $Pd(OAc)_2$ (6.7 mg , 0.03 mmol), AgTFA (99.2 mg, 0.45 mmol), ethyl pyruvate (52.3 mg, 0.45 mmol), and $AcOH/H_2O$ (9:1, v/v, 2.5 mL) was stirred in a glass sealed-tube at room temperature for 30 min, then the mixture was heated to 120 °C for 20 h. Upon completion of the reaction, the mixture was cooled to room temperature and added dropwise into a saturated $NaHCO_3$ solution (25 mL). The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layer was dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 40:1) to supply the desired product **6**.

[1,1'-biphenyl]-2-ylmethyl acetate (6a): yellow oil, 44.1 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.51 (dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.40−7.38 (m, 2H), 7.38−7.35 (m, 2H), 7.34 (d, J = 1.6 Hz, 1H), 7.32 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 5.05 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 142.4, 140.4, 133.2, 130.2, 129.6, 129.1, 128.6, 128.32, 128.29, 128.2, 127.6, 127.4, 64.4, 21.0; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{15}H_{14}O_2$: 226.0994, found 226.0993.

(4'-methoxy-[1,1'-biphenyl]-2-yl)methyl acetate (6b): yellow oil, 56.1 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49−7.46 (m, 1H), 7.36 (t, J = 3.6 Hz, 2H), 7.30 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 5.04 (s, 2H), 3.85 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 159.0, 142.1, 133.3, 132.8, 130.4, 130.3 (2C), 129.6, 128.3, 127.3, 113.7 (2C), 64.6, 55.3, 21.1; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{16}H_{18}O_3$: 256.1099, found 256.1100.

Methyl 2′-(acetoxylmethyl)-[1,1′-biphenyl]-4-carboxylate (6c): yellow oil, 52.0 mg (61%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.10 (d, J = 8.4 Hz, 2H),

7.51(dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 1H), 7.43 (d, J = 2.4 Hz, 2H), 7.41 (t, J = 2.0 Hz, 2H), 7.30 (dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 1H), 5.01 (s, 2H), 3.95 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.5, 166.8, 145.1, 141.3, 137.8, 133.0, 129.9, 129.8, 129.4 (2C), 129.1 (2C), 128.4, 128.1, 64.1, 52.1, 20.8; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{16}O_4$: 284.1049, found 284.1046.

Ethyl 2´-(acetoxylmethyl)-[1,1´-biphenyl]-4-carboxylate (6d): yellow oil, 55.5 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.10 (d, J = 8.4 Hz, 2H), 7.51 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H), 7.43 (d, J = 1.6 Hz, 2H), 7.41 (t, J = 3.2 Hz, 2H), 7.30 (dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 1H), 5.01 (s, 2H), 4.41 (q, J = 7.2 Hz, 2H), 2.04 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 166.4, 145.0, 141.4, 133.1, 130.0, 129.9, 129.52, 129.50 (2C), 129.2 (2C), 128.5, 128.2, 64.2, 61.1, 20.9, 14.4; HRMS (EI): *m/z* [M^+] calcd. for $C_{18}H_{18}O_4$: 298.1205, found 298.1204.

(3´-Methoxy-[1,1´-biphenyl]-2-yl)methyl acetate (6e): yellow oil, 53.1 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 1H), 7.40−7.37 (m, 2H), 7.34 (d, J = 6.0 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.90 (dd, J_1 = 4.0 Hz, J_2 = 2.0 Hz, 2H), 5.05 (s, 2H), 3.83 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 159.3, 142.2, 141.6, 133.1, 130.0, 129.5, 129.1, 128.2, 127.5, 121.5, 114.7, 112.9, 64.3, 55.1, 20.9; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{16}O_3$: 256.1099, found 256.1098.

Methyl 2´-(acetoxylmethyl)-[1,1´-biphenyl]-3-carboxylate (6f): yellow oil, 48.6 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06 (d, J = 1.6 Hz, 1H), 8.04 (d, J = 1.2 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.50 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 7.41 (dd, J_1 = 4.8 Hz, J_2 = 4.0 Hz, 2H), 7.31 (t, J = 3.6 Hz, 1H), 4.98 (s, 2H), 3.92 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 166.9, 141.5, 140.6, 133.5, 133.2, 130.4, 130.20, 130.15, 130.1, 128.60, 128.58, 128.4, 128.0, 64.4, 52.2, 20.9; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{16}O_4$: 284.1049, found 284.1048.

2-(2,3-*2H*-benzo[*b*][1,4]dioxin-6-yl)benzyl acetate (6g): yellow oil, 52.9 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.47 (t, J = 4.4 Hz, 1H), 7.36 (t, J = 4.4 Hz, 2H), 7.28 (dd, J_1 = 7.2 Hz, J_2 = 3.6 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 1.6 Hz, 1H), 6.80 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 5.05 (s, 2H), 4.30 (s, 4H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 143.15, 143.05, 141.9, 133.7, 133,2, 130.2, 129.6, 128.3, 127.4, 122.3, 118.1, 117.0, 64.5, 64.423, 64.418, 21,1; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{16}O_4$: 284.1049, found 284.1050.

(5-Methyl-3´-methoxy-[1,1´-biphenyl]-2-yl)methyl acetate (6h): yellow oil, 52.7 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.15 (s, 1H), 6.92 (s, 1H), 6.91−6.89 (m, 2H), 5.01 (s, 2H), 3.83 (s, 3H), 2.39 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.8, 159.3, 142.3, 141.9, 138.2, 130.8, 130.2, 129.9, 129.2, 128.4, 121.6, 114.8, 112.9, 64.4, 55.2, 21.2, 21.1; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{18}O_3$: 270.1256, found 270.1255.

Methyl 5´-methyl-2´-(acetoxylmethyl)-[1,1´-biphenyl]-4-carboxylate (6i): yellow oil, 60.9 mg (68%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.08 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.12 (s, 1H), 4.97 (s, 2H), 3.95 (s, 3H), 2.40 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 167.0, 145.3, 141.4, 138.5, 130.7, 130.2, 130.1, 129.5 (2C), 129.2 (2C), 129.0, 128.9, 64.2, 52.2, 21.2, 21.0; HRMS (EI): *m/z* [M^+] calcd. for $C_{18}H_{18}O_4$: 298.1205, found 298.1204.

(5-Chloro-4´-methoxy-[1,1´-biphenyl]-2-yl)methyl acetate (6j): yellow oil, 51.5 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.41 (d, J = 8.4 Hz, 1H), 7.32 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H), 7.24 (dt, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 2H), 6.95(dt, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 2H), 4.99 (s, 2H), 3.85 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.7, 159.3, 143.7, 133.9, 131.9, 131.4, 131.0, 130.2, 130.1 (2C), 127.3, 113.8 (2C), 63.8, 55.3, 21.0; HRMS (EI): *m/z* [M^+] $C_{16}H_{15}ClO_3$: 290.0710, found 290.0708.

(5-Bromo-4´-methoxy-[1,1´-biphenyl]-2-yl)methyl acetate (6k): yellow oil, 61.3 mg (61%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40 (s, 1H), 7.37 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.89 (s, 2H), 3.77 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.6, 159.3, 144.0, 133.1, 132.4, 131.3, 131.1, 130.3, 130.1 (2C), 122.1, 113.8 (2C), 63.8, 55.3, 21.0; HRMS (EI): *m/z* [M^+] calcd. for $C_{16}H_{15}{}^{81}BrO_3$: 336.0184, found 336.0190.

Methyl 2'-(acetoxymethyl)-5'-bromo-[1,1'-biphenyl]-4-carboxylate (6l): yellow oil, 68.6 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.10 (d, J = 8.4 Hz, 2H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 8.0 Hz , 2H), 7.37 (s, 1H), 4.94 (s, 2H), 3.95 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.5, 166.7, 143.6, 143.2, 132.7, 132.3, 131.4, 131.2, 129.7 (2C), 129.1 (2C), 122.4, 63.5, 52.3, 20.9; HRMS (EI): *m/z* [M^+] calcd. for $C_{17}H_{15}O_4{}^{81}Br$: 364.0133, found 364.0132.

Supporting Information Available: Experimental details for Scheme 6–9; copies of ^{1}H NMR, ^{13}C NMR spectral, HRMS and crystallographic data for **3n** and **I**.

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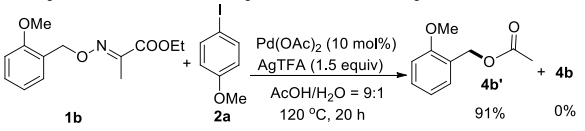
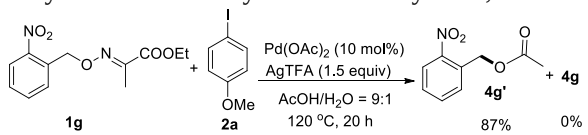
[13] The X-ray crystal structures of compound **3n** and **I** are also available from CCDC 1815998 and CCDC 1554822, respectively, which can be obtained free of charge *via* www.ccdc.cam.ac.uk

[14] a) Herein, the product of direct acetolysis **4b'** was only detected in 91% yield without arylation, see ESI;



10.1002/adsc.201800216

b) Herein, the product of direct acetolysis **4g'** was only detected in 87% yield without arylation, see ESI.



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FULL PAPER

Catalytic Cascade Access to Biaryl-2-Methyl Acetates from Pyruvate *O*-Arylmethyl Ketoximes *via* the Palladium-Catalyzed C(sp^2)–H Bond Arylation and C–O Bond Solvolysis

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