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Cationic Palladium-Catalyzed [5 + 2] Annulation of 2-Acylmethoxyarylboronic Acids and Allenoates: Synthesis of 1-Benzoxepine Derivatives

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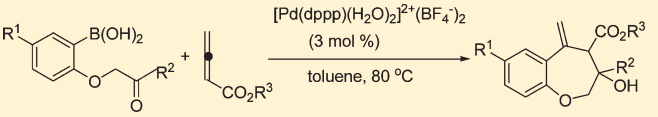
Supporting Information

ABSTRACT: The 1-benzoxepine derivatives were synthesized conveniently by cationic palladium-catalyzed [5 + 2] annulation reaction of 2-acylmethoxyarylboronic acids with allenoates in high yields. This annulation involves the intramolecular nucleophilic addition to ketones without the formation of π-allylpalladium species.



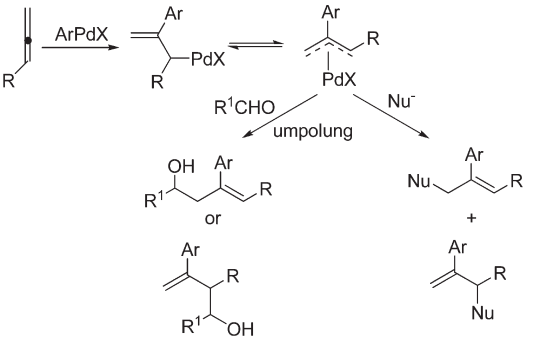
Transition-metal-catalyzed reactions of allenes have attracted increasing interest during the last two decades due to the existence of two orthogonal π-bonds.[1−5] Various kinds of reactions using organoboronic acids and transition metals have been developed to construct carbon−carbon bonds.[6,7]

Transition-metal-catalyzed reactions of organometallic reagents provide powerful approaches toward the synthesis of useful organic compounds. Special attention was concentrated to palladium-based catalysts as it provides the versatile possibilities for the carbon−carbon bond formation.[8−11] Recently, our group and others have developed a series of addition reactions of arylboronic acids to carbon−heteroatom multiple bonds catalyzed by Pd(II) species.[12−22] In all of these systems, Pd(II) species were used as the catalyst without the use of any redox system that is indispensable in many Pd(0)-catalyzed reactions. Among the Pd(II) catalysts, cationic Pd(II) complexes have great advantages in exhibiting high reactivity in the transmetalation step due to the following reasons: (1) vacant coordination site for substrates or reagents; (2) higher Lewis acidity.[23]

The benzoxepine moiety is an important structural unit in many natural products,[24−26] biologically active molecules,[25] and natural herbicides.[27] The simple and efficient synthesis of benzoxepine derivatives is attractive in synthetic organic chemistry and medicinal chemistry.[28−30] Our group previously developed the synthesis of 1-benzoxepines by cationic palladium complex $[Pd(dppp)(H_2O)_2]^{2+}(TfO^-)_2$ catalyzed tandem cyclization of 2-aroylmethoxyarylboronic acids and alkynes involving the addition of vinylpalladium species to ketones.[17] Inspired by this reaction, we set out to investigate the tandem reaction of 2-acylmethoxyarylboronic acids and allenes.

According to the literature, an allene can insert rapidly into a palladium−carbon bond, generated from oxidative addition of an organic halide to the palladium catalyst or transmetalation process, to give π-allylpalladium species (Scheme 1).[31−33] It is widely accepted that a π-allylpalladium complex is electrophilic and will react with nucleophiles.[34] In the previous reports of Pd-catalyzed allylation of the carbonyl groups, a process called "umpolung" was generally used to change the electrophilicity of the π-allylpalladium species by adding low-valent metals or some reducing agents, making the addition reaction possible.[35−42] Unfortunately, this umpolung process is not suitable for the Pd(II)-catalyzed reactions because Pd(0) will be formed in the presence of reducing agents, making the regeneration of the Pd(II) catalyst impossible. Malinakova realized the intermolecular three-component coupling of an arylboronic acid with allenes and aldehydes using a particular β-pinene-derived π-allylpalladium dimer as the catalyst, suggesting that η^1-allylpalladium species was formed which can act as a nucleophile.[43] We recently reported the cationic palladium complex catalyzed diastereo- and enantioselective tandem annulation of 2-formylphenylboronic acids with substituted allenoates

Scheme 1. Reaction of the π−Allylpalladium Complex



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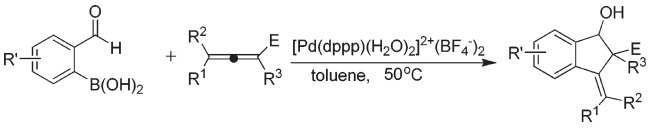
Scheme 2. Tandem Annulation Reaction of the 2-Formylphenylboronic Acids with Substituted Allenoates

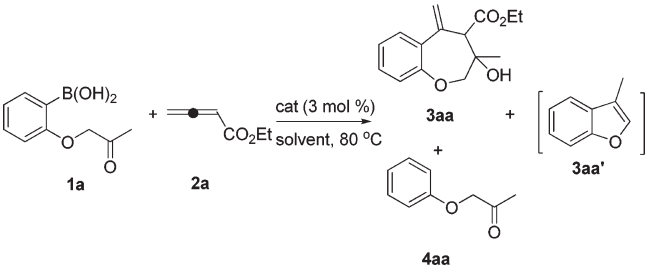


involving the intramolecular nucleophilic addition without the formation of π-allylpalladium species, which solved the problems mentioned above (Scheme 2).[19] Herein, we report a new, efficient method to synthesize the 1-benzoxepine derivatives by cationic palladium complex $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ catalyzed tandem cyclization of 2-acylmethoxyarylboronic acids and allenoates.

We initiated our studies by investigating the tandem annulation reaction of 2-acylmethoxyarylboronic acid **1a** with allenoate **2a** under a variety of conditions. A reaction conducted in dioxane at 80 °C catalyzed by $[Pd(dppp)(H_2O)_2]^{2+}(TfO^-)_2$ led to the formation of the intramolecular cyclization product **3aa′** in 73% yield (Table 1, entry 1). By changing the solvent to toluene, the reaction gave a complex mixture of products. Gratifyingly, the desired product **3aa** could be obtained in 87% yield within 25 min when the reaction was conducted in toluene under 80 °C in the presence of $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ as a catalyst (Table 1, entry 3). Various cationic palladium complexes were evaluated in order to improve the yield of the desired product **3aa** and prevent the formation of deboronated product. The cationic palladium complex with SbF_6^- as the counteranion could not furnish the tandem annulation reaction (Table 1, entry 4). Therefore, the counteranions of cationic palladium catalysts are particularly important in this reaction. The difference of the reactivity is probably due to their coordinating ability to the transition metals, and BF_4^- is less coordinating than TfO^-.[44] Thus, the cationic palladium complex $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ has more vacant sites for coordinating with the substrates to accelerate the process. At present, the reason for poor performance of SbF_6^- cannot be explained. Meanwhile, it should be noted that the ligand of the cationic palladium has an obvious effect on the reaction. When $[Pd(dppe)(H_2O)_2]^{2+}(BF_4^-)_2$ and $[Pd(bpy)(H_2O)_2]^{2+}(BF_4^-)_2$ were used as the catalyst, the reactions were inhibited (Table 1, entries 5 and 6). Furthermore, the [5 + 2] annulation was not catalyzed by $Pd(OAc)_2$/dppp or $Pd(TFA)_2$/dppp under the same reaction conditions. The reaction was also affected by the solvent. While toluene led to the best result, the reaction was complicated in THF or dioxane, and large amounts of deboronated product **4aa** were obtained when using DCE as the solvent (Table 1, entries 9−13). When the mixture was lowered to room temperature, the reaction was totally inhibited, even after extending the time to 3 days (Table 1, entry 7). Increasing the ratio of substrates to 2:1 did not play a pronounced role in this tandem cyclization (Table 1, entry 8).

Additives are well-known to play an important role in the transmetalation between arylboronic acids and palladium.[45] Therefore, we examined the base effect on this tandem annulation reaction. Adding K_3PO_4 (2 equiv) and H_2O (2 equiv) resulted in complicated reaction, and none of the annulation product was obtained (Table 2, entries 1 and 2). The addition of Amberlite IRA-400 (OH) could completely suppress the formation of the undesired product **4aa**, but the yield of **3aa** was low (Table 2, entry 5) as compared with the condition without adding any additive (Table 1, entry 3). On the basis of the above

Table 1. Optimization of the Tandem Annulation Reaction Conditions[a]



entry	catalyst (3 mol %)	solvent	t (h)	yield (%)[b] 3aa	4aa
1	$[Pd(dppp)(H_2O)_2]^{2+}(TfO^-)_2$	dioxane	0.5	**3aa′**(73)[c]	–
2	$[Pd(dppp)(H_2O)_2]^{2+}(TfO^-)_2$	toluene	0.5	complex mixture	
3	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	toluene	0.4	87	trace
4	$[Pd(dppp)(H_2O)_2]^{2+}(SbF_6^-)_2$	toluene	1	–	–
5	$[Pd(dppe)(H_2O)_2]^{2+}(BF_4^-)_2$	toluene	12	trace	–
6	$[Pd(bpy)(H_2O)_2]^{2+}(BF_4^-)_2$	toluene	12	NR	
7[d]	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	toluene	72	trace	–
8[e]	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	toluene	0.4	84	trace
9	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	THF	1	complex mixture	
10	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	DCE	12	–	70
11	$[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$	dioxane	0.5	complex mixture	
12	$Pd(OAc)_2$/dppp	toluene	12	NR	
13	$Pd(TFA)_2$/dppp	toluene	15	NR	

[a] Reaction conditions: **1a** (0.18 mmol), **2a** (0.15 mmol), and catalyst (3 mol %) were stirred at 80 °C. [b] Cited yields refer to pure product after column chromatography. [c] **3aa′** was the product of intramolecular cyclization. [d] The reaction was stirred at room temperature. [e] The ratio of substrates was increased to 2:1.

investigation, the optimal condition for this tandem annulation reaction was as follows: $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ (3 mol %), arylboronic acid **1a** (1.2 equiv), and allenoate **2a** (1 equiv) in toluene at 80 °C.

With the optimized reaction conditions in hand, a number of other readily available arylboronic acids including relatively electron-rich and electron-poor substrates were allowed to react with the allenoate **2a**. As summarized in Table 3, the corresponding annulation products **3** were obtained in moderate to good yields with excellent diastereoselectivities (Table 3, entries 1−4). When aromatic ketone **1e** or **1f** reacted with allenoate **2a**, moderate amounts of the corresponding products were isolated (Table 3, entries 5 and 6). When the naphthylboronic acid **1g** was subjected to reaction conditions, only the deboronated product **4ga** was formed. The *tert*-butyl-substituted ketone **1h** (Figure 1) did not give the corresponding annulation product presumably due to the high steric hindrance. When the boronic acid **1i** bearing a cyclic ketone moiety was treated with **2a** in the presence of $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ (3 mol %) in toluene at 80 °C, a tricyclic product **3ia** was formed in relatively low yield and the intramolecular cyclization−dehydration product **5ia** was obtained in moderate yield (Scheme 3). The scope of the tandem annulation with regard to the allenoate was also investigated. A number of allenoates could react with boronic acid **1a** smoothly to yield the expected products **3** in good to excellent yields

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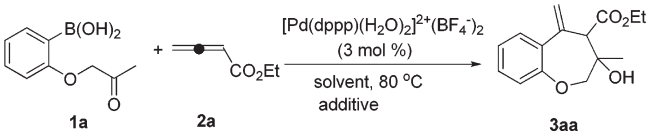
Table 2. Effect of the Additive[a]



entry	solvent	additive (equiv)	t (h)	yield (%)[b]
1	toluene	K_3PO_4 (2), H_2O (2)	12	complex mixture
2	dioxane	K_3PO_4 (2), H_2O (2)	12	complex mixture
3	toluene	K_3PO_4 (2)	10	complex mixture
4	toluene	$Ba(OH)_2$ (2)	12	complex mixture
5	toluene	Amberlite IRA-400 (OH) (1.5)	0.5	58
6	DCE	Amberlite IRA-400 (OH) (1.5)	10	NR
7	dioxane	Amberlite IRA-400 (OH) (1.5)	10	complex mixture
8	DME	Amberlite IRA-400 (OH) (1.5)	10	NR

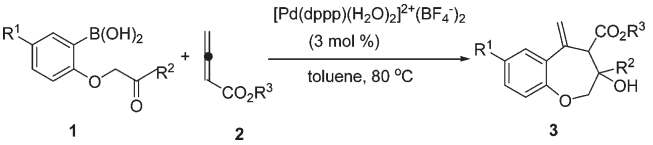
[a] Reaction conditions: **1a** (0.18 mmol), **2a** (0.15 mmol), and catalyst (3 mol %) were stirred at 80 °C. [b] Cited yields refer to pure product after column chromatography.

(Table 3, entries 7−11). All of the reactions listed in Table 3 proceeded with excellent diastereoselectivities, giving **3** as the only cyclization products. However, the multiply substituted allenoates (not shown) could not finish the annulation reaction, and the substrate scope was limited. In order to achieve the synthesis of molecules with large rings, the reactions of substrates **1j**−**1l** with allenoate **2a** under the optimal conditions were also tested, but all of them resulted in the recovery of the starting materials (Figure 1).

Subsequently, our attention turned to the asymmetric version of the reaction. Initially, using the $Pd^{2+}(CH_3CN)_4(BF_4^-)_2$ combined with various chiral ligands (such as chiral diphosphine or monophosphine ligands) as the catalyst, the (2*S*,4*S*)-bis-(diphenylphosphinyl)pentane ((2*S*,4*S*)-bdpp) was found to be superior, providing the expected product in 81% yield, but the enantioselectivity was poor. In addition, we also optimized this asymmetric reaction by employing chiral palladium catalysts $\{Pd[(R)\text{-binap}](H_2O)_2\}^{2+}(TfO^-)_2$ and $\{Pd[(S,S)\text{-bdpp}](H_2O)_2\}^{2+}(BF_4^-)_2$, but only the latter catalyzed formation of the product, which was formed in 72% yield with very low enantiomeric excess value.

The proposed [5 + 2] annulation reaction mechanism is described in Scheme 4. The palladium complex **A** would generate the Pd hydroxo complex **C**, which is supposed to be the active catalytic species[10,46−48] and enables smooth transmetalation with the substrate **1** without any assistance of bases.[23,48] Meanwhile, the allenoate will coordinate to the palladium center to give intermediate **D**. Then, η^1-allylpalladium complex **E** is formed when the allenoate is inserted into the palladium−carbon bond. While the substrates with oxygen linkage lead to successful reactions, the substrate with carbon linkage (**1j**) does not provide the desired product, a result that may be explained by the coordination of the oxygen atom with cationic palladium, which makes the intermediate **E** more stable, leading the successful reactions. High Lewis acidity of cationic palladium species **E** may activate the carbonyl group by coordination, and the high nucleophilic property of cationic η^1-allylpalladium complex **E** may result in intramolecular 1,2-addition to furnish the seven-membered ring intermediate **F**. The subsequent protonation of **F** by $B(OH)_3$ or boronic acid would afford product **3** and

Table 3. Substrate Scope for $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ Catalyzed [5 + 2] Annulation of 2-Acylmethoxyarylboronic Acids with Allenoates[a]



entry	substrate **1** (R^1, R^2)	allenoates (R^3)	yield (%)[b]
1	R^1 = H, R^2 = Me (**1a**)	Et (**2a**)	**3aa** (87)
2	R^1 = Me, R^2 = Me (**1b**)	Et (**2a**)	**3ba** (72)
3	R^1 = ^{t}Bu, R^2 = Me (**1c**)	Et (**2a**)	**3ca** (80)
4	R^1 = Cl, R^2 = Me (**1d**)	Et (**2a**)	**3da** (64)
5	R^1 = H, R^2 = Ph (**1e**)	Et (**2a**)	**3ea** (34)
6	R^1 = H, R^2 = *p*-$OMeC_6H_4$ (**1f**)	Et (**2a**)	**3fa** (49)
7	**1a**	Me (**2b**)	**3ab** (93)
8	**1a**	^{i}Pr (**2c**)	**3ac** (87)
9	**1a**	^{n}Bu (**2d**)	**3ad** (83)
10	**1a**	Bn (**2e**)	**3ae** (80)
11	**1a**	Ph (**2f**)	**3af** (87)

[a] Reaction conditions: **1a** (0.18 mmol), **2a** (0.15 mmol) and catalyst (3 mol %) were stirred at 80 °C using toluene (2 mL) as the solvent. [b] Cited yields refer to pure product after column chromatography with dr >99.9%.

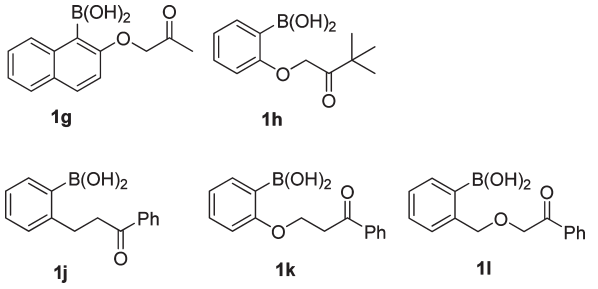
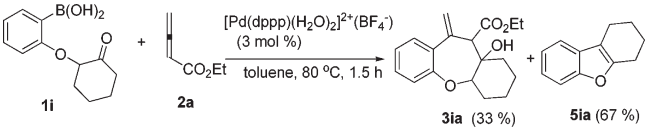


Figure 1. Limitation of the substrates.

Scheme 3. Reaction of 1i and Allenoate 2a



regenerate the catalytically active species **C** to complete the catalytic cycle. From the structure of the product **3** of this reaction, it is worth noting that the more stable η^3-allyl complex cannot be formed immediately due to the orthogonal orbitals of the allene. The η^1-allyl complex lacking the conjugation with other double bond is always formed first, and then η^3-coordination forms after a rotation around the σ-C−C bond.[2] The highly active cationic η^1-allylpalladium complex will react with the carbonyl group immediately once it was formed without the formation of the η^3-allyl complex.[49] The success for the tandem cyclization of allenes without the use of "umpolung" reagents showed the advantage of the use of cationic palladium complex as

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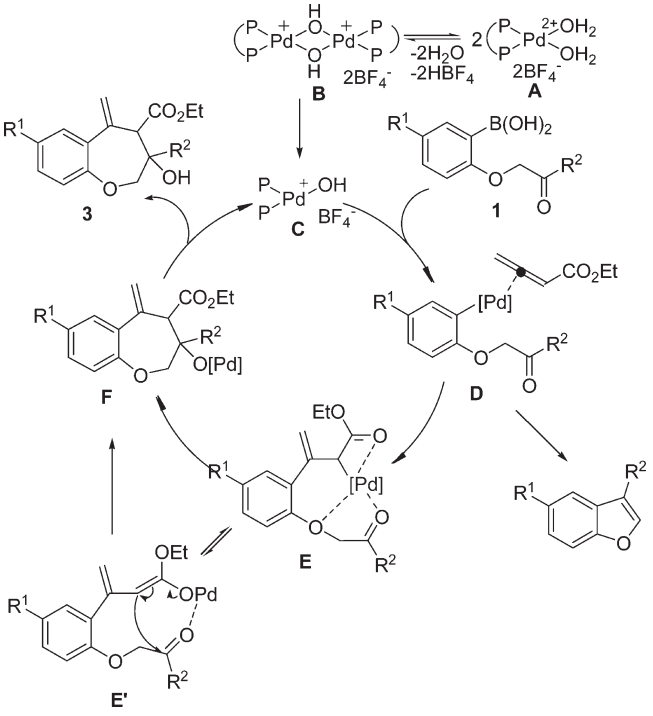
Scheme 4. Proposed Mechanism of the Tandem Reaction



a catalyst for allenes. On the other hand, another pathway involving the reaction of the palladium enolate intermediate **E′** formed from the η^1-allylpalladium species **E** with the carbonyl group could not be excluded. In addition, it is supposed that the tunable role of allenes may arise from the stronger affinity of the palladium complex with the carbon−carbon double bond rather than with the intramolecular carbonyl group in intermediate **D**, facilitating the insertion of allenes into the carbon−palladium bond to form intermediate **E**. Therefore, the intramolecular addition product could be suppressed.

In summary, we have uncovered a new and highly efficient way to achieve the synthesis of benzoxepine derivatives from 2-acyl-methoxyarylboronic acids and allenoates in the presence of a catalytic amount of $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$. The use of cationic palladium species is crucial for this reaction. This tandem annulation involves the intramolecular nucleophilic addition of η^1-allylpalladium species to ketones, and no redox reagent for the catalytic system is involved. Current studies are aimed at the asymmetric version of this reaction.

EXPERIMENTAL SECTION

General. All solvents were dried and distilled before use according to the standard procedures. All melting points were uncorrected. The cationic palladium complexes $[Pd(dppp)(H_2O)_2]^{2+}(TfO^-)_2$,[48] $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$,[19] $[Pd(dppp)(H_2O)_2]^{2+}(SbF_6^-)_2$,[19] $\{Pd[(R)\text{-binap}](H_2O)_2\}^{2+}(TfO^-)_2$,[50] and $\{Pd[(S,S)\text{-bdpp}](H_2O)_2\}^{2+}(BF_4^-)_2$[20] were synthesized following the literature procedure. The boronic acids **1e**, **1f**, and **1j**−**1l** were all synthesized according to the published procedures.[12] Amberlite IRA 400 (Cl) were purchased from Lancaster. Before use, they were treated with NaOH solution (2 N), then washed with water until neutrality and filtered under vacuum.

Experimental Procedure for Synthesis of Substrates. *Typical Procedure for the Preparation of* ***1a****:* K_2CO_3 (3.036 g, 22 mmol) was added to a solution of 1-bromopropan-2-one (3.0 g, 22 mmol) and 2-iodophenol (4.845 g, 22 mmol) in acetone (13 mL), and the resulting mixture was heated under reflux for 4 h. The mixture was then allowed to cool to room temperature and poured into water (100 mL). The precipitate was collected by filtration to afford crude product 1-(2-iodophenoxy)-propan-2-one, which was used for the next step without purification. The crude product was added to a stirred solution of benzene (150 mL), ethylene glycol (5.5 g, 89 mmol), and *p*-toluenesulfonic acid (120 mg, 0.66 mmol), fitted with a water trap and refluxed overnight. The reaction mixture was cooled and washed with saturated solution of $NaHCO_3$ (20 mL) and NaCl (20 mL). The organic portion was dried with Na_2SO_4, concentrated in vacuo, and the residue was purified by flash column chromatography to obtain the product 2-(2-iodophenoxymethyl)-2-methyl-1,3-dioxolane (6.687 g, 64% for two steps). To 17.6 mmol of compound 2-(2-iodophenoxymethyl)-2-methyl-1,3-dioxolane dissolved in the mixture of Et_2O (30 mL) and THF (60 mL) in a flame-dried 250 mL round-bottom flask was added at −78 °C 13.1 mL (21 mmol) of a 1.6 M solution of *n*-BuLi in hexanes. The mixture was stirred at −78 °C for 20 min followed by addition of 4 mL (35 mmol) of $B(OMe)_3$ in one portion via syringes. The resulting mixture was allowed to stir at −78 °C for 0.5 h, warmed to ambient temperature, and stirred for further 2 h. Twenty milliliters of aq 1 N HCl was added, and the mixture was stirred for an additional 0.5 h. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 30 mL). The organic layers were combined, washed with water, 10% aqueous $Na_2S_2O_3$, then brine, dried with Na_2SO_4, and concentrated. The crude product was added to MeOH (20 mL) plus 2 mL of 8 N H_2SO_4, and the mixture was allowed to stand at room temperature overnight. After dilution with water and being extracted with EtOAc (2 × 20 mL), the organic layers were combined, dried with Na_2SO_4, and concentrated. The pure compound **1a** (2.591 g, 55% for two steps) was obtained by recrystillization in a mixture of EtOAc/petroleum ether.

Substrate ***1a****:* white solid; yield 55%; mp 129−130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89−7.87 (m, 1H), 7.46−7.40 (m, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 4.79−4.74 (m, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 204.2, 162.3, 136.0, 132.0, 121.1, 111.9, 72.5, 26.0; IR (KBr) ν 3337 (br), 1732, 1604 cm^{-1}; MS (70 eV, EI) m/z (%) 194 (M^+), 151, 121, 107, 43 (100). Anal. Calcd for $C_9H_{11}BO_4$: C, 55.72; H, 5.72. Found: C, 55.66; H, 5.73.

Substrate ***1b****:* white solid; yield 45%; mp 129−130 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 (s, 2H), 7.46 (s, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 4.88 (s, 2H), 2.23 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 204.2, 160.3, 136.5, 132.3, 129.5, 111.8, 72.7, 25.9, 20.1; IR (KBr) ν 3425 (br), 1732, 1608 cm^{-1}; MS (70 eV, EI) m/z (%) 208 (M^+), 165, 121 (100), 91. Anal. Calcd for $C_{10}H_{13}BO_4$: C, 57.74; H, 6.30. Found: C, 57.78; H, 6.32.

Substrate ***1c****:* white solid; yield 74%; mp 122−123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 2.4 Hz, 1H), 7.43 (dd, J = 2.4 and 8.4 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 4.72 (s, 2H), 2.23 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.8, 160.5, 144.6, 134.0, 129.4, 110.8, 72.9, 34.1, 31.4, 25.9; IR (KBr) ν 3444, 3469, 2963, 1726, 1067 cm^{-1}; MS (70 eV, EI) m/z (%) 252 (M^+ + 2), 235, 206, 191 (100), 135. Anal. Calcd for $C_{13}H_{19}BO_4$: C, 62.43; H, 7.66. Found: C, 62.16; H, 7.89.

Substrate ***1d****:* white solid; yield 63%; mp 140−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (br, 2H), 7.60 (d, J = 2.7 Hz, 1H), 7.45−7.41 (m, 1H), 6.98 (d, J = 8.7 Hz, 1H), 4.93 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.0, 160.8, 134.9, 131.3, 125.1, 114.0, 72.9, 26.0; IR (KBr) ν 3423, 3320, 1731, 1484 cm^{-1}; MS (70 eV, EI) m/z (%) 228 (M^+), 210, 168, 155, 43 (100). Anal. Calcd for $C_9H_{10}ClBO_4$: C, 47.32; H, 4.41. Found: C, 47.35; H, 4.26.

Substrate ***1g****:* white solid; yield 50%; mp 122−123 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.38 (br, 2H), 7.86−7.79 (m, 3H), 7.46 (t, J = 6.9 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 9.0 Hz, 1H), 4.84 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 205.9, 157.5, 135.8,

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129.6, 128.8, 127.9, 127.5, 126.0, 123.4, 114.5, 73.7, 26.5; IR (KBr) ν 3383, 3290, 1733, 1620, 1509 cm^{-1}; MS (70 eV, EI) m/z (%) 244 (M^+), 182 (100), 153, 115. Anal. Calcd for $C_{13}H_{13}BO_4$: C, 63.98; H, 5.37. Found: C, 63.90; H, 5.33.

Substrate ***1h:*** white solid; yield 25%; mp 123−125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 1H), 7.43−7.38 (m, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 4.92 (s, 2H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 162.8, 137.2, 132.5, 121.9, 111.3, 68.5, 42.7, 26.2; IR (KBr) ν 3351 (br), 1720, 1608, 1579, 1455, 749 cm^{-1}; MS (70 eV, EI) m/z (%) 218 ($M^+ - H_2O$), 192, 174, 159, 131, 77, 57 (100); HRMS calcd for $C_{12}H_{15}BO_3$ ($M^+ - H_2O$) 218.1114, found 218.1117.

Substrate ***1i:*** white solid; yield 51%; mp 103−105 °C (lit.[12] 103 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, J = 1.8 and 7.5 Hz, 1H), 7.41−7.34 (m, 1H), 7.06−7.01 (m, 1H), 6.89 (s, 2H), 6.79 (d, J = 8.1 Hz, 1H), 4.82−4.76 (m, 1H), 2.69−2.60 (m, 2H), 2.47−2.41 (m, 1H), 2.17−2.04 (m, 2H), 1.89−1.71 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.5, 162.5, 137.2, 132.4, 121.8, 111.9, 81.8, 40.7, 34.7, 27.4, 23.6; IR (KBr) ν 3378 (br), 2955, 1722, 1600, 774 cm^{-1}; MS (70 eV, EI) m/z (%) 234 (M^+), 138, 120 (100), 96.

Experimental Procedure for $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ *Catalyzed Synthesis of 1-Benzoxepine Derivatives (****3****).* A dried schenk tube was charged with **1a** (35 mg, 0.18 mmol), **2a** (16.8 mg, 0.15 mmol), and 2 mL of toluene. $[Pd(dppp)(H_2O)_2]^{2+}(BF_4^-)_2$ (3.3 mg, 3 mol %) was then added to the mixture, and the solution was stirred at 80 °C. The progress of the reaction was monitored by TLC (EtOAc/petroleum ether = 1:4). Upon completion, the solution was purified by flash column chromatography (pure petroleum ether, then ethyl acetate/petroleum ether = 1:4) to obtain the product **3aa**.

Compound ***3aa:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.31 (m, 1H), 7.20−7.16 (m, 1H), 7.00−6.91 (m, 2H), 5.48 (s, 1H), 5.21 (s, 1H), 4.80 (s, 1H), 4.16−4.02 (m, 2H), 3.99−3.94 (m, 2H), 3.63 (s, 1H), 1.47 (s, 3H), 1.17−1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 157.6, 140.9, 129.9, 129.4, 129.0, 122.6, 119.7, 115.8, 78.8, 73.5, 61.2, 57.0, 25.6, 13.8; IR (neat) ν 3491 (br), 3068, 2978, 2935, 1711, 1603, 1570, 759 cm^{-1}; MS (m/z, EI) 262 (M^+), 244, 216 (100), 189, 145, 115, 91, 43; HRMS-EI calcd for $C_{15}H_{18}O_4$ (M^+) 262.1203, found 262.1205.

Compound ***3ba:*** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 2.0 Hz, 1H), 6.99−6.97 (m, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.47 (s, 1H), 5.19 (s, 1H), 4.74 (s, 1H), 4.19−4.09 (m, 2H), 3.98−3.91 (m, 2H), 3.61 (s, 1H), 2.29 (s, 3H), 1.46 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 155.6, 141.0, 131.9, 129.7, 129.6, 119.5, 115.6, 78.7, 73.4, 61.1, 57.1, 25.7, 20.5, 13.8; IR (neat) ν 3489 (br), 2978, 2934, 1710, 1631, 1035, 734 cm^{-1}; MS (70 eV, EI) m/z (%) 276 (M^+), 230, 175, 159 (100), 115, 91, 43; HRMS calcd for $C_{16}H_{20}O_4$ (M^+) 276.1352, found 276.1362.

Compound ***3ca:*** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 2.1 Hz, 1H), 7.22 (dd, J = 8.4 and 1.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 5.47 (s, 1H), 5.22 (s, 1H), 4.80 (s, 1H), 4.15−4.11 (m, 2H), 3.97−3.92 (m, 2H), 3.63 (s, 1H), 1.46 (s, 3H), 1.31 (s, 9H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 155.4, 145.3, 141.5, 129.2, 126.2, 126.0, 119.3, 115.8, 78.7, 73.5, 61.1, 57.2, 34.2, 31.4, 25.6, 13.9; IR (neat) ν 3494 (br), 2964, 2872, 1712, 1035 cm^{-1}; MS (70 eV, EI) m/z (%) 318 (M^+), 303, 272, 245, 229 (100), 187, 173; HRMS calcd for $C_{19}H_{26}O_4$ (M^+) 318.1827, found 318.1831.

Compound ***3da:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 2.4 Hz, 1H), 7.15 (dd, J = 8.7 and 2.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 5.49 (s, 1H), 5.25 (s, 1H), 4.78 (s, 1H), 4.21−4.10 (m, 2H), 3.96 (s, 2H), 3.60 (s, 1H), 1.46 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 156.3, 139.9, 131.4, 128.9, 128.8, 127.5, 121.2, 116.9, 78.8, 73.3, 61.3, 56.8, 25.6, 13.8; IR (neat) ν 3492 (br), 2980, 2939, 1712, 1478, 1032, 824 cm^{-1}; MS (70 eV, EI) m/z (%) 296 (M^+), 278, 250, 223, 179, 165, 115, 43 (100); HRMS calcd for $C_{15}H_{17}ClO_4$ (M^+) 296.0820, found 296.0815.

Compound ***3ea:*** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 5.7 Hz, 2H), 7.43−7.35 (m, 3H), 7.31−7.29 (m, 1H), 7.25−7.21 (m, 1H), 7.06−7.04 (m, 1H), 7.02−7.00 (m, 1H), 5.64 (s, 1H), 5.32 (s, 1H), 5.19 (s, 1H), 4.32 (s, 1H), 4.23−4.15 (m, 2H), 4.03 (q, J = 7.2 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 157.9, 144.6, 140.0, 129.1, 128.9, 128.4, 128.2, 127.5, 125.1, 122.7, 119.9, 115.2, 79.9, 76.5, 61.2, 55.7, 13.7; IR (neat) ν 3473 (br), 2980, 1709, 1603, 1482, 764 cm^{-1}; MS (70 eV, EI) m/z (%) 324 (M^+), 306, 278, 145, 105 (100); HRMS calcd for $C_{20}H_{20}O_4$ (M^+) 324.1364, found 324.1362.

Compound ***3fa:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.22 (t, J = 8.1 Hz, 1H), 7.06−6.97 (m, 2H), 6.91 (d, J = 8.4 Hz, 2H), 5.63 (s, 1H), 5.31 (s, 1H), 5.17 (s, 1H), 4.28 (s, 1H), 4.22−4.11 (m, 2H), 4.05 (q, J = 7.2 Hz, 2H), 3.80 (s, 3H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 158.9, 157.9, 140.1, 136.8, 130.3, 129.0, 128.9, 126.3, 122.6, 119.9, 115.0, 113.6, 80.1, 76.3, 61.1, 55.7, 55.2, 13.7; IR (neat) ν 3480 (br), 2980, 2937, 1709, 1610, 1512, 1184, 733 cm^{-1}; MS (70 eV, EI) m/z (%) 354 (M^+), 337, 308, 150, 135 (100), 121,107; HRMS calcd for $C_{21}H_{22}O_5$ (M^+) 354.1470, found 354.1467.

Compound ***3ia:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.34 (m, 1H), 7.20−7.15 (m, 1H), 6.99−6.92 (m, 2H), 5.52 (s, 1H), 5.14 (s, 1H), 4.47 (s, 1H), 4.22−4.16 (m, 2H), 3.98 (s, 1H), 3.59 (s, 1H), 1.84−1.57 (m, 8H), 1.27 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 158.1, 140.0, 130.2, 128.8, 128.7, 121.9, 119.7, 112.9, 81.2, 73.8, 61.2, 56.5, 34.2, 27.7, 20.8, 20.0, 13.9; IR (neat) ν 3485 (br), 2936, 1708, 1479, 1450, 1019, 755 cm^{-1}; MS (70 eV, EI) m/z (%) 302 (M^+), 284, 229, 171, 160 (100), 131; HRMS calcd for $C_{18}H_{22}O_4$ (M^+) 302.1516, found 302.1518.

Compound ***3ab:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.30 (m, 1H), 7.21−7.16 (m, 1H), 7.02−6.91 (m, 2H), 5.49 (s, 1H), 5.20 (s, 1H), 4.61 (s, 1H), 4.03−3.93 (m, 2H), 3.69−3.66 (m, 4H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 157.6, 140.7, 129.8, 129.2, 129.1, 122.7, 119.8, 115.7, 78.6, 73.4, 56.8, 52.2, 25.8; IR (neat) ν 3501 (br), 2975, 2955, 1716, 1603, 1483, 1207, 734 cm^{-1}; MS (70 eV, EI) m/z (%) 248 (M^+), 230, 216, 145 (100), 131, 115, 43; HRMS calcd for $C_{14}H_{16}O_4$ (M^+) 248.1049, found 248.1048.

Compound ***3ac:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.30 (m, 1H), 7.20−7.15 (m, 1H), 7.01−6.90 (m, 2H), 5.48 (s, 1H), 5.21 (s, 1H), 5.02−4.98 (m, 2H), 3.99−3.94 (m, 2H), 3.59 (s, 1H), 1.46 (s, 3H), 1.21 (d, J = 6.6 Hz, 3H), 1.05 (d, J = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 157.6, 141.1, 129.9, 129.6, 129.0, 122.5, 119.7, 115.9, 78.9, 73.5, 68.8, 57.2, 25.5, 21.6, 21.1; IR (neat) ν 2982, 2938, 1706, 1630, 1483, 1220, 1106 cm^{-1}; MS (70 eV, EI) m/z (%) 276 (M^+), 258, 216, 173, 145, 131, 91, 45 (100); HRMS calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1364.

Compound ***3ad:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.22 (m, 1H), 7.13−7.07 (m, 1H), 6.94−6.83 (m, 2H), 5.41 (s, 1H), 5.13 (s, 1H), 4.76 (s, 1H), 4.03−3.95 (m, 2H), 3.92−3.86 (m, 2H), 3.56 (s, 1H), 1.45−1.39 (m, 5H), 1.23−1.15 (m, 2H), 0.82 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 157.6, 140.9, 129.9, 129.4, 129.0, 122.6, 119.8, 115.8, 78.8, 73.4, 65.0, 57.0, 30.3, 25.7, 18.9, 13.5; IR (neat) ν 3492, 2963, 1710, 1631, 1604, 1483, 1218, 759 cm^{-1}; MS (70 eV, EI) m/z (%) 290 (M^+), 272, 232, 216, 173, 161, 145 (100), 131, 115; HRMS calcd for $C_{17}H_{22}O_4$ (M^+) 290.1518, found 290.1520.

Compound ***3ae:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.14 (m, 7H), 6.98−6.90 (m, 2H), 5.46 (s, 1H), 5.17 (s, 1H), 5.09 (s, 2H), 4.69 (s, 1H), 4.03−3.93 (m, 2H), 3.69 (s, 1H), 1.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 157.6, 140.6, 135.1, 129.7, 129.4, 129.1, 128.4, 128.3, 128.1, 122.7, 119.8, 116.1, 78.8, 73.5, 66.9, 57.1, 25.6; IR (neat) ν 3500, 3066, 1716, 1483, 910, 734 cm^{-1}; MS (70 eV, EI) m/z (%) 324 (M^+), 233, 216, 173, 145, 91 (100); HRMS calcd for $C_{20}H_{20}O_4$ (M^+) 324.1362, found 324.1364.

Compound ***3af:*** oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.20 (m, 5H), 7.06−6.96 (m, 2H), 6.86−6.83 (m, 2H), 5.59 (s, 1H), 5.36 (s, 1H),

4.51 (s, 1H), 4.06−4.04 (m, 2H), 3.91 (s, 1H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 157.6, 150.0, 140.8, 129.6, 129.5, 129.4, 129.3, 126.2, 122.8, 121.2, 120.0, 116.7, 78.8, 73.7, 57.8, 25.4; IR (neat) ν 3529, 2979, 1744, 1633, 1602, 1484, 1199, 734 cm^{-1}; MS (70 eV, EI) m/z (%) 310 (M^+), 230, 216, 173 (100), 161, 145, 131, 115; HRMS calcd for $C_{19}H_{18}O_4$ (M^+) 310.1205, found 310.1204.

Compound ***5ia****:* oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.36 (m, 2H), 7.21−7.16 (m, 2H), 2.74−2.70 (m, 2H), 2.63−2.58 (m, 2H), 1.96−1.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 153.9, 128.8, 122.9, 122.0, 118.3, 112.8, 110.7, 23.4, 22.9, 22.6, 20.4; IR (neat) ν 2934, 2847, 1477, 1454, 743 cm^{-1}; MS (70 eV, EI) m/z (%) 172 (M^+), 144 (100), 128, 115; HRMS calcd for $C_{12}H_{12}O$ (M^+) 172.0892, found 172.0888.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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