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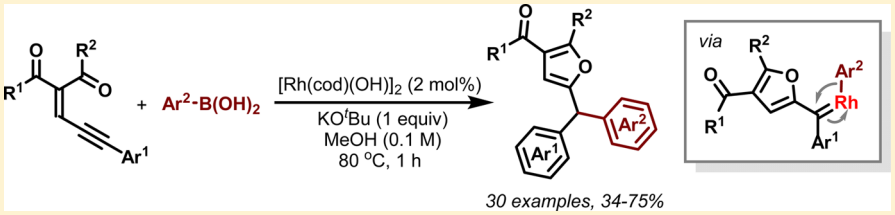
Rh(I)-Catalyzed Coupling of Conjugated Enynones with Arylboronic Acids: Synthesis of Furyl-Containing Triarylmethanes

Ying Xia, Li Chen, Peiyuan Qu, Guojing Ji, Sheng Feng, Qing Xiao, Yan Zhang, and Jianbo Wang*

Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

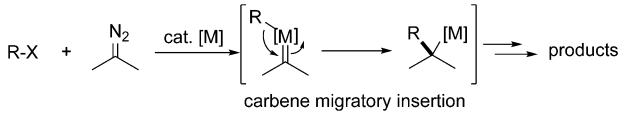
Supporting Information



ABSTRACT: Conjugated enynones can be used as carbene precursors to couple with arylboronic acids in the presence of Rh(I) catalyst. This reaction shows good functional compatibility, and a range of furyl-containing triarylmethanes can be smoothly synthesized from easily available starting materials under mild reaction conditions. Mechanistically, the formation of Rh(I) (2-furyl)carbene species and the subsequent carbene migratory insertion are proposed as the key steps in this reaction.

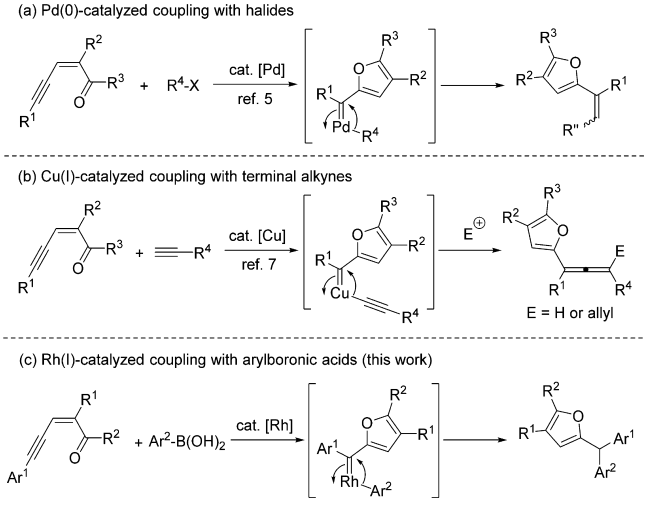
Transition metal-catalyzed carbene-based cross-coupling reactions have achieved significant development over the past decade.[1] This type of coupling reaction features the carbene migratory insertion process, which is the key step for the formation of carbon−carbon bonds. Numerous methodologies have been developed based on this concept, providing unique approaches for carbon−carbon bond formation. Diazo compounds,[2] including those generated from *N*-tosylhydrazones, are the common carbene precursors that have been explored in this type of coupling reaction (Scheme 1).

Scheme 1. Catalytic Carbene Coupling Reactions Using Diazo Compounds as Carbene Precursors



Apart from diazo compounds, extensive studies on transition metal-catalyzed reactions of conjugated enynones have established that conjugated enynones can be severed as precursors of furyl-substituted metal carbene intermediates in various transformations.[3,4] We have first demonstrated conjugated enynones as carbene precursors in Pd-catalyzed carbene coupling reactions, providing a general method to synthesize 2-alkenyl-substituted furan derivatives (Scheme 2a).[5] DFT calculations have indicated that Pd(II) (2-furyl)carbene formation and subsequent carbene migratory insertion are involved in this coupling reaction. Subsequently, we have developed the palladium-catalyzed oxidative coupling of conjugated enynones with aryl, alkenyl boronic acids, and terminal alkynes, affording furyl-substituted olefins, dienes, and

Scheme 2. Transition Metal-Catalyzed Carbene Coupling Reactions Using Conjugated Enynones as the Carbene Precursors



enynes, respectively.[6] In addition, we have also achieved the Cu(I)-catalyzed coupling reaction of conjugated enynones with terminal alkynes in which furyl-substituted allenes could be obtained in high efficiency (Scheme 2b).[7] Meanwhile, we and others have demonstrated that Rh(I) complexes are also efficient catalysts for carbene-based coupling reactions.[8] As a

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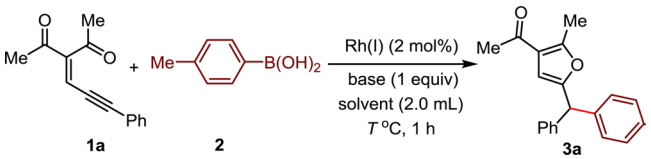
continuation of our interest in carbene-based coupling reactions, we have conceived that conjugated enynones may be served as carbene precursors to participate in the cross-coupling with aryl boronic acids in Rh(I)-catalyzed reactions. Herein we report the investigation along this line. The reaction developed in this study represents a general method for the synthesis of furyl-containing triarylmethanes (Scheme 2c).[9]

At the beginning of this investigation, we employed enynone **1a** and *p*-tolylboronic acid **2** as the substrates to optimize this reaction (Table 1). First, we used $[Rh(cod)OH]_2$ as the catalyst

Table 1. Optimization of the Reaction Conditions[a]



entry	Rh(I)	solvent	base	T (°C)	yield (%)[b]
1	$[Rh(cod)OH]_2$	1,4-dioxane	KO^{t}Bu	60	<10
2	$[Rh(cod)OH]_2$	MeCN	KO^{t}Bu	60	trace
3	$[Rh(cod)OH]_2$	toluene	KO^{t}Bu	60	0
4	$[Rh(cod)OH]_2$	THF	KO^{t}Bu	60	0
5	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	60	40
6	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	40	trace
7	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	80	64
8	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	90	63
9	$[Rh(cod)OH]_2$	MeOH	LiO^{t}Bu	80	63
10	$[Rh(cod)OH]_2$	MeOH	NaO^{t}Bu	80	53
11	$[Rh(cod)OH]_2$	MeOH	KOH	80	61
12	$[Rh(cod)OH]_2$	MeOH	Cs_2CO_3	80	42
13	$[Rh(cod)Cl]_2$	MeOH	KO^{t}Bu	80	58
14	$[Rh(CO)_2Cl]_2$	MeOH	KO^{t}Bu	80	trace
15	$[Rh(coe)_2Cl]_2$	MeOH	KO^{t}Bu	80	32
16	$Rh(PPh_3)_3Cl$	MeOH	KO^{t}Bu	80	trace
17[c]	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	80	63
18[d]	$[Rh(cod)OH]_2$	MeOH	KO^{t}Bu	80	70
19[d,e]		MeOH	KO^{t}Bu	80	trace

[a]If not otherwise noted, the reaction was carried out with **1a** (0.20 mmol) and **2** (0.20 mmol) in the presence of 2 mol % Rh(I) catalyst in 2.0 mL of solvent for 1 h. [b]All of the yields refer to products by silica gel column chromatography. [c]The ratio of **1a**:**2** is 1:1.2. [d]The ratio of **1a**:**2** is 1.2:1. [e]In the absence of $[Rh(cod)OH]_2$.

and KO^{t}Bu as the base, and a series of solvents were explored (entries 1−5). We found that only protic solvent MeOH could provide target product **3a** in moderate yield (entry 5), and other solvents led to no or trace product. It was found that the reaction temperature had a large influence on this transformation (entries 6−8). Lowering the temperature to 40 °C resulted in the formation of a trace amount of product along with the decomposition of enynone **1a** (entry 6). The suitable temperature for this reaction is 80 °C, and the yield can reach 64% under such conditions (entry 7). Apart from KO^{t}Bu, other bases gave similar or lower yields (entries 9−12).[10] Next, we further screened the Rh(I) sources and found that other Rh(I) catalysts were less effective than $[Rh(cod)OH]_2$ for this reaction (entries 13−16). In addition, through slightly adjusting the ratio of the two substrates, we could improve the yield up to 70% (entries 17 and 18). Finally, a control experiment revealed that the Rh(I) catalyst was crucial for this transformation (entry 19).

With the optimized reaction conditions in hand, we then examined the scope of this reaction. A series of conjugated enynones were subjected to the reaction with *p*-tolylboronic acid **2** under the optimized conditions, and the corresponding furyl-containing triarylmethanes were obtained in 40−75% yields (Scheme 3). As compared to enynone **1a**, enynones **1b**−**f**, which are derived from unsymmetrical 1,3-dicarbonyl compounds, were synthesized as 1:1 mixtures of E/Z isomers.[11] Interestingly, in all of the cases with E/Z mixtures of conjugated enones subjected to the Rh(I)-catalyzed reactions, single products through cyclization of the ketone carbonyl oxygen were obtained exclusively. We have previously observed the same phenomenon in Pd-catalyzed reactions.[5,6]

The slightly lower yields in the cases of **3d** and **e** might be attributed to the instability of the ester moiety in such reaction conditions. The aryl group adjacent to the alkyne moiety was then examined (**3g**−**o**). The substituents on the para (**3g**−**l**)- or meta (**3m** and **n**)-position of the aryl ring showed marginal impact on this reaction. It is noteworthy that halogen substituents, especially iodo, are fully tolerated in this reaction, which is beneficial for further transformations through transition metal-catalyzed cross-coupling reactions (**3j** and **k**). Finally, the enynone bearing heteroaryl moiety was also found to be a suitable substrate for this Rh(I)-catalyzed transformation, affording two heteroaryl-containing triarylmethanes in acceptable yields (**3o**). It should be noted that the aryl group adjacent to the alkyne moiety on enynones was crucial for this reaction, as enynone **1p** that contains an aliphatic substituent only afforded a trace amount of the desired product along with decomposition of the starting materials.

We further investigated the scope of aryl boronic acids. Thus, a variety of arylboronic acids (**2a**−**o**) were tested to react with enynone **1a** under the standard reaction conditions.[12] The corresponding products of furyl-containing triarylmethanes were obtained in 34−74% yields (Scheme 4). It was observed that the position of the substituents on the arylboronic acids had a marginal influence on the reaction (**4a**−**l**). Ortho-substituted boronic acid could also participate in this transformation smoothly (**4l**). For product **4a**, X-ray crystallography was obtained, thus unambiguously confirming the structure of the products. Notably, sensitive functional groups, including chloride (**4d**), bromide (**4e** and **j**), ester (**4f**), ketone (**4g**), and a vinyl group (**4h**), are all compatible with this reaction. Naphthyl boronic acid also reacted with enynone **1a** smoothly (**4m**). In addition, the reaction conditions were also tolerated with heteroaryl boronic acids, albeit with diminished yields (**4n** and **o**).

On the basis of previously reported similar reactions with palladium catalysts,[5−7] a plausible reaction mechanism was proposed for this Rh(I)-catalyzed coupling reaction (Scheme 5). First, dedimerization of $[Rh(cod)OH]_2$ produces an active monomeric rhodium species **A**, which may undergo transmetalation with arylboronic acid **2** to generate arylrhodium intermediate **B** with the aid of the base KO^{t}Bu.[13] Then, arylrhodium intermediate **B** coordinates with alkyne moiety of the enynone substrate to afford complex **C**, followed by a 5-exo-dig cyclization process to generate Rh(I) (2-furyl)carbene species **D**, which is similar to our previously reported Pd(II)- or Cu(I)-catalyzed reactions.[5−7] Subsequently, migratory insertion of the aryl group to the carbenic leads to the formation of triarylmethyl rhodium intermediate **E**.[8] Finally, the protonation of **E** by MeOH affords product **3a** and regenerates the Rh(I) catalyst (path a).

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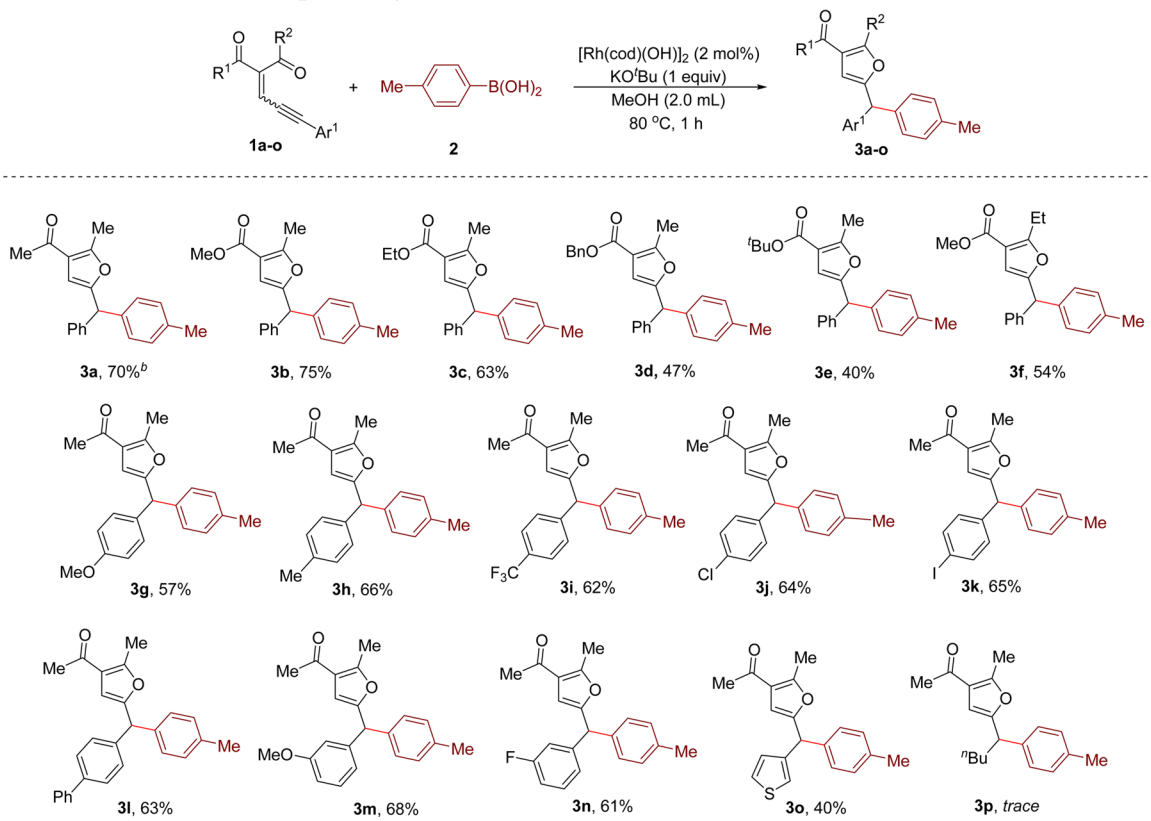
Scheme 3. Reaction Scope of Enynones[a]



[a]Unless otherwise noted, the reaction was carried out with **1a–o** (0.24 mmol), **2** (0.20 mmol), $[Rh(cod)(OH)]_2$ (2 mol %), and KO^{t}Bu (0.20 mmol) in 2.0 mL of MeOH at 80 °C for 1 h. [b]Yields of products were isolated by silica gel column chromatography.

On the other hand, a mechanism that does not involve a rhodium carbene intermediate is also possible (path b). In this case, arylrhodium intermediate **B** may undergo a 1,6-addition to conjugated enynone and generate allene-substituted rhodium enolate species **F**.[14] Then, intramolecular nucleophilic attack of enolate oxygen to the allene moiety generates triarylmethyl rhodium intermediate **E**. Further studies are required to unambiguously distinguish these two mechanisms.

In conclusion, we have developed a Rh(I)-catalyzed coupling reaction of conjugated enynones with arylboronic acids. This reaction provides a novel approach for the synthesis of furyl-containing triarylmethanes from easily available starting materials with good functional group compatibility. The mechanism of this novel transformation most likely involves the Rh(I) (2-furyl)carbene formation/migration insertion sequence or the 1,6-addition/cyclization sequence.

EXPERIMENTAL SECTION

General Methods. All of the rhodium-catalyzed reactions were performed under nitrogen atmosphere in a flame-dried reaction tube. All solvents were distilled under nitrogen atmosphere prior to use. Toluene, 1,4-dioxane, and THF were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN and MeOH were dried over CaH_2. For chromatography, 200–300 mesh silica gel was employed. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C{1H}NMR spectra are reported relative to the chemical shift of tetramethylsilane (TMS); chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. The conjugated ene-yne-ketones were prepared according to literature procedures.[5−7,11] Other materials were obtained from commercial suppliers and used without further purification.

General Procedure for Rh(I)-Catalyzed Coupling Reactions of Conjugated Enynones with Arylboronic Acids. Under a nitrogen atmosphere, $[Rh(cod)OH]_2$ (1.8 mg, 0.004 mmol, 2 mol %), enynone (0.24 mmol, 1.2 equiv), arylboronic acid (0.20 mmol), and KO^{t}Bu (22 mg, 0.20 mmol) were successively added to a flame-dried 10 mL Schlenk tube. The reaction tube was degassed three times with nitrogen, and dry MeOH (2.0 mL) was added using a syringe. The reaction was immediately immersed in an 80 °C oil bath with stirring for 1 h, it was then cooled to room temperature and filtered through a short plug of silica gel with ethyl acetate (10 mL) as the eluent. The solvent was then removed in vacuo to leave a crude mixture, which was purified by silica gel column chromatography to afford pure product. (Notice: The reaction gave a trace amount of product along with the decomposition of enynones when the temperature was below 40 °C. Thus, when the solvent was added, *the reaction tube was immediately immersed in the 80 °C oil bath*; otherwise, the yield would decrease approximately 10–15%.)

*1-(2-Methyl-5-(phenyl(p-tolyl)methyl)furan-3-yl)ethanone (**3a**).* Yield 70% (42.7 mg); yellow solid, mp 85–87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.22 (m, 3H), 7.17–7.11 (m, 4H), 7.06–7.04 (m, 2H), 6.09 (s, 1H), 5.34 (s, 1H), 2.53 (s, 3H), 2.33–2.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.0, 154.9, 141.3, 138.1, 136.5, 129.2, 128.6, 128.5, 128.5, 126.8, 122.0, 108.8, 50.2, 29.1, 21.0, 14.4; HRMS (ESI, m/z) calcd for $C_{21}H_{21}O_2$ $[M + H]^+$ 305.1536, found 305.1533; LRMS (EI, m/z) 304 (M^+, 100), 289 (31), 261 (31), 227 (50), 213 (25); IR (film) 701, 744, 1228, 1566, 1677, 2925 cm^{-1}.

*Methyl-2-methyl-5-(phenyl(p-tolyl)methyl)furan-3-carboxylate (**3b**).* Yield 75% (48.0 mg); white solid, mp 58–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.21 (m, 3H), 7.16–7.04 (m, 6H), 6.12 (s, 1H), 5.33 (s, 1H), 3.76 (s, 3H), 2.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 158.8, 155.0, 141.3, 138.1, 136.5, 129.2, 128.6,

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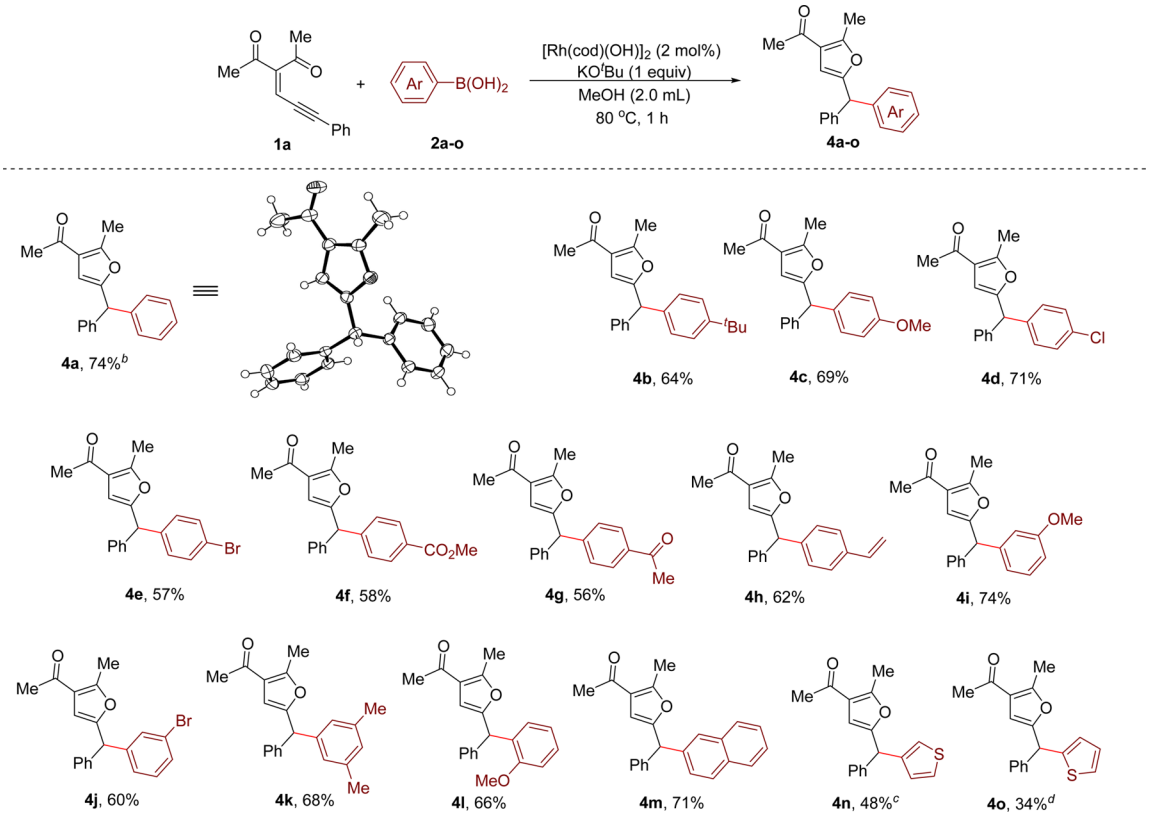
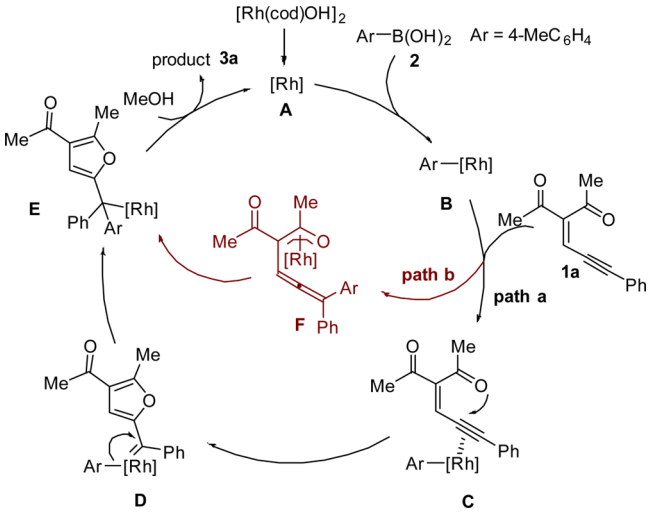
Scheme 4. Reaction Scope of Aryl Boronic Acids[a]



[a]Unless otherwise noted, the reaction was carried out with **1a–o** (0.20 mmol), **2** (0.24 mmol), $[Rh(cod)(OH)]_2$ (2 mol %), and KO^{t}Bu (0.20 mmol) in 2.0 mL of MeOH at 80 °C for 1 h. [b]All of the yields refer to the isolated products by silica gel column chromatography. [c]The ratio of **1a**:**2n** is 1:1.5. [d]The ratio of **1a**:**2o** is 1:1.5. For the X-ray structure of **4a**, the thermal ellipsoids were shown at 30% probability.

Scheme 5. Proposed Reaction Mechanism



128.5, 128.5, 126.8, 113.6, 109.0, 51.1, 50.2, 21.0, 13.8; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485, found 321.1491; LRMS (EI, *m*/*z*) 320 (M^+, 100), 305 (50), 288 (30), 245 (63), 229 (30); IR (film) 700, 778, 1085, 1227, 1718, 2951 cm^{-1}.

Ethyl-2-methyl-5-(phenyl(p-tolyl)methyl)furan-3-carboxylate (***3c***). Yield 63% (42.1 mg); white solid, mp 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 3H), 7.17–7.04 (6H), 6.13 (s, 1H), 5.33 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 2.32 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 158.7, 154.8, 141.4, 138.2, 136.4, 129.2, 128.6, 128.5, 128.5, 126.8, 113.9, 109.0, 60.0, 50.3, 21.0, 14.4, 13.8; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}O_3$ $[M + H]^+$ 335.1642, found 335.1639; LRMS (EI, *m*/*z*) 334 (M^+, 100), 305 (40), 257 (40), 245 (53), 165 (47); IR (film) 700, 736, 1081, 1227, 1714, 2923 cm^{-1}.

Benzyl-2-methyl-5-(phenyl(p-tolyl)methyl)furan-3-carboxylate (***3d***). Yield 47% (37.1 mg); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 8H), 7.16–7.03 (m, 6H), 6.17 (s, 1H), 5.32 (s, 1H), 5.26 (s, 2H), 2.52 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 159.0, 155.0, 141.3, 138.1, 136.5, 136.2, 129.2, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 126.8, 113.7, 109.0, 65.8, 50.2, 21.0, 13.9; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{25}O_3$ $[M + H]^+$ 397.1798, found 397.1810; LRMS (EI, *m*/*z*) 396 (M^+, 69), 305 (60), 119 (22), 105 (23), 91 (100); IR (film) 698, 799, 1071, 1225, 1716, 2924 cm^{-1}.

tert-Butyl-2-methyl-5-(phenyl(p-tolyl)methyl)furan-3-carboxylate (***3e***). Yield 40% (28.9 mg); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 3H), 7.17–7.04 (m, 6H), 6.10 (s, 1H), 5.32 (s, 1H), 2.49 (s, 3H), 2.32 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 157.9, 154.4, 141.5, 138.3, 136.4, 129.2, 128.6, 128.6, 128.4, 126.7, 115.4, 109.3, 80.4, 50.3, 28.3, 21.0, 13.9; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{26}NaO_3$ $[M + Na]^+$ 385.1774, found 385.1784; LRMS (EI, *m*/*z*) 362 (M^+, 100), 306 (76), 228 (76), 245 (60), 229 (87); IR (film) 700, 1082, 1161, 1230, 1708, 2926 cm^{-1}.

Methyl-2-ethyl-5-(phenyl(p-tolyl)methyl)furan-3-carboxylate (***3f***). Yield 54% (36.3 mg); white solid, mp 54–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.20 (m, 3H), 7.15–7.03 (m, 6H), 6.11 (s, 1H), 5.34 (s, 1H), 3.76 (s, 3H), 2.96 (q, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.18 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 163.8, 154.8, 141.5, 138.3, 136.4, 129.2, 128.6, 128.5, 128.4, 126.7, 112.6, 109.0, 51.1, 50.2, 21.1, 21.0, 12.4; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}O_3$ $[M + H]^+$ 335.1642, found 335.1648; LRMS (EI, *m*/*z*) 334 (M^+, 100), 319 (49), 257 (54), 245 (46), 205 (41); IR (film) 700, 1039, 1089, 1228, 1717, 2949 cm^{-1}.

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*1-(5-((4-Methoxyphenyl)(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3g**).* Yield 57% (38.0 mg); white solid; mp 84−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.03 (m, 6H), 6.85−6.83 (m, 2H), 6.09 (s, 1H), 5.29 (s, 1H), 3.78 (s, 3H), 2.53 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.4, 157.9, 155.2, 138.4, 136.4, 133.4, 129.6, 129.2, 128.4, 121.9, 113.9, 108.6, 55.2, 49.4, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}O_3$ $[M + H]^+$ 335.1642, found 335.1646; LRMS (EI, *m*/*z*) 334 (M^+, 100), 319 (25), 291 (30), 243 (45), 227 (17); IR (film) 810, 1228, 1249, 1510, 1676, 2922 cm^{-1}.

*1-(5-(Di-p-tolylmethyl)-2-methylfuran-3-yl)ethanone (**3h**).* Yield 66% (51.2 mg); yellow solid; mp 78−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12−7.04 (m, 8H), 6.08 (s, 1H), 5.30 (s, 1H), 2.53 (s, 3H), 2.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 157.9, 155.1, 138.3, 136.4, 129.2, 128.5, 122.0, 108.6, 49.8, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}O_2$ $[M + H]^+$ 319.1693, found 319.1694; LRMS (EI, *m*/*z*) 318 (M^+, 100), 303 (60), 275 (36), 227 (64), 165 (19); IR (film) 765, 808, 1227, 1565, 1677, 2922 cm^{-1}.

*1-(2-Methyl-5-(p-tolyl(4-(trifluoromethyl)phenyl)methyl)furan-3-yl)ethanone (**3i**).* Yield 62% (46.4 mg); white solid; mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2, 2H), 7.28 (d, *J* = 8.1, 2H), 7.14 (d, *J* = 8.0, 2H), 7.04 (d, *J* = 8.0, 2H), 6.11 (s, 1H), 5.39 (s, 1H), 2.54 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 158.2, 153.8, 145.4, 137.2, 137.0, 129.4, 129.2 (q, *J* = 32.5 Hz), 129.0, 128.5, 125.5 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 272.1 Hz), 122.1, 109.1, 50.0, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{20}F_3O_2$ $[M + H]^+$ 373.1410, found 373.1412; LRMS (EI, *m*/*z*) 372 (M^+, 100), 357 (35), 329 (35), 281 (21), 227 (54); IR (film) 734, 1068, 1125, 1164, 1325, 1678 cm^{-1}.

*1-(5-((4-Chlorophenyl)(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3j**).* Yield 64% (43.2 mg); yellow solid; mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.25 (m, 2H), 7.14−7.02 (m, 6H), 6.08 (s, 1H), 5.31 (s, 1H), 2.53 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.1, 154.3, 139.8, 137.6, 136.8, 132.7, 129.9, 129.3, 128.6, 128.4, 122.0, 108.9, 49.6, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}ClO_2$ $[M + H]^+$ 339.1146, found 339.1149; LRMS (EI, *m*/*z*) 338 (M^+, 100), 323 (38), 295 (34), 247 (28), 227 (43); IR (film) 733, 803, 1228, 1565, 1677, 2922 cm^{-1}.

*1-(5-((4-Iodophenyl)(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3k**).* Yield 65% (56.0 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.13−7.11 (m, 2H), 7.03−7.02 (m, 2H), 6.91−6.89 (m, 2H), 6.08 (s, 1H), 5.28 (s, 1H), 2.53 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 158.1, 154.2, 141.0, 137.6, 137.4, 136.8, 130.6, 129.3, 128.4, 122.0, 108.9, 92.4, 49.7, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}IO_2$ $[M + H]^+$ 431.0502, found 431.0512; LRMS (EI, *m*/*z*) 430 (M^+, 100), 415 (21), 387 (21), 303 (20), 227 (36); IR (film) 733, 801, 1007, 1228, 1676, 2923 cm^{-1}.

*1-(5-([1,1′-Biphenyl]-4-yl(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3l**).* Yield 63% (47.9 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.52 (m, 4H), 7.43−7.40 (m, 2H), 7.34−7.30 (m, 1H), 7.24−7.22 (m, 2H), 7.15−7.08 (m, 4H), 6.14 (s, 1H), 5.38 (s, 1H), 2.55 (s, 3H), 2.33 (s, s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.0, 154.8, 140.7, 140.4, 139.8, 138.0, 136.6, 129.3, 129.0, 128.7, 128.5, 127.2, 127.0, 122.0, 108.8, 49.9, 29.1, 21.0, 14.5; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{25}O_2$ $[M + H]^+$ 381.1849, found 381.1861; LRMS (EI, *m*/*z*) 380 (M^+, 100), 365 (25), 337 (25), 289 (29), 227 (23); IR (film) 698, 732, 757, 1227, 1565, 1676 cm^{-1}.

*1-(5-((3-Methoxyphenyl)(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3m**).* Yield 68% (45.4 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.20 (m, 1H), 7.13−7.05 (m, 4H), 6.80−6.71 (m, 3H), 6.10 (s, 1H), 5.31 (s, 1H), 3.75 (s, 3H), 2.53 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.7, 157.9, 154.7, 142.8, 137.9, 136.6, 129.5, 129.2, 128.5, 122.0, 121.1, 114.8, 111.8, 108.8, 55.1, 50.2, 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}O_3$ $[M + H]^+$ 335.1642, found 335.1645; LRMS (EI, *m*/*z*) 334 (M^+, 100), 319 (24), 291 (27), 249 (25), 227 (52); IR (film) 732, 768, 1228, 1263, 1676, 2922 cm^{-1}.

*1-(5-((3-Fluorophenyl)(p-tolyl)methyl)-2-methylfuran-3-yl)-ethanone (**3n**).* Yield 61% (39.3 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 1H), 7.14−7.04 (m, 4H), 6.96−6.91 (m, 2H), 6.86 (d, *J* = 10.0 Hz, 1H), 6.11 (s, 1H), 5.33 (s, 1H), 2.54 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 162.92 (d, *J* = 246.0 Hz), 158.1, 154.2, 143.8 (d, *J* = 6.8 Hz), 137.4, 136.9, 129.9 (d, *J* = 8.3 Hz), 129.4, 128.5, 124.3 (d, *J* = 2.8 Hz), 122.0, 115.6 (d, *J* = 22.0 Hz), 113.8 (d, *J* = 21.2 Hz), 108.9, 49.9 (d, *J* = 1.25 Hz), 29.1, 21.0, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{20}FO_2$ $[M + H]^+$ 323.1442, found 323.1445; LRMS (EI, *m*/*z*) 322 (M^+, 100), 307 (34), 279 (31), 227 (60), 183 (24); IR (film) 772, 785, 1228, 1566, 1677, 2921 cm^{-1}.

*1-(2-Methyl-5-(thiophen-3-yl(p-tolyl)methyl)furan-3-yl)ethanone (**3o**).* Yield 40% (24.8 mg); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.26 (m, 1H), 7.14−7.08 (m, 4H), 6.93−6.88 (m, 2H), 6.15 (s, 1H), 5.36 (s, 1H), 2.54 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 157.8, 154.7, 142.0, 137.9, 136.7, 129.3, 128.2, 128.0, 125.8, 122.4, 122.0, 108.0, 45.8, 29.1, 21.0, 14.5; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{19}O_2S$ $[M + H]^+$ 311.1100, found 311.1099; LRMS (EI, *m*/*z*) 310 (M^+, 100), 295 (29), 267 (29), 219 (44), 207 (76); IR (film) 742, 762, 1228, 1566, 1677, 2924 cm^{-1}.

*1-(5-Benzhydryl-2-methylfuran-3-yl)ethanone (**4a**).* Yield 71% (41.1 mg); brown solid; mp 119−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.23 (m, 6H), 7.17−7.16 (m, 4H), 6.09 (s, 1H), 5.38 (s, 1H), 2.54 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.0, 154.6, 141.0, 128.6, 128.5, 126.9, 122.0, 108.9, 50.6, 29.1, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{19}O_2$ $[M + H]^+$ 291.1380, found 291.1376; LRMS (EI, *m*/*z*) 290 (M^+, 100), 247 (29), 229 (17), 213 (71), 165 (21); IR (film) 705, 738, 755, 1229, 1671, 2926 cm^{-1}.

*1-(5-((4-tert-Butylphenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4b**).* Yield 64% (44.4 mg); white solid; mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.22 (m, 5H), 7.19−7.17 (m, 2H), 7.09−7.08 (m, 2H), 6.11 (s, 1H), 5.35 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 157.9, 154.9, 149.7, 141.3, 137.9, 128.6, 128.5, 128.2, 126.8, 125.4, 122.0, 108.7, 50.2, 34.4, 31.3, 29.1, 14.5; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{27}O_2$ $[M + H]^+$ 347.2006, found 347.2008; LRMS (EI, *m*/*z*) 346 (M^+, 98), 331 (23), 289 (100), 269 (38), 213 (23); IR (film) 702, 736, 1228, 1566, 1677, 2962 cm^{-1}.

*1-(5-((4-Methoxyphenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4c**).* Yield 69% (44.2 mg); yellow solid; mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.22 (m, 3H), 7.16−7.14 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.08 (s, 1H), 5.33 (s, 1H), 3.78 (s, 3H), 3.53 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.5, 157.9, 155.0, 141.4, 133.2, 129.6, 128.5, 128.5, 126.8, 122.0, 113.9, 108.7, 55.2, 49.8, 29.1, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485, found 321.1486; LRMS (EI, *m*/*z*) 320 (M^+, 100), 289 (23), 277 (31), 243 (73), 213 (16); IR (film) 702, 734, 1250, 1511, 1676, 2970 cm^{-1}.

*1-(5-((4-Chlorophenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4d**).* Yield 71% (46.1 mg); yellow solid; mp 91−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.25 (m, 5H), 7.15−7.08 (m, 4H), 6.09 (s, 1H), 5.35 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.1, 154.1, 140.5, 139.6, 132.8, 130.0, 128.7, 128.6, 128.6, 127.1, 122.0, 109.0, 49.9, 29.1, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{18}ClO_2$ $[M + H]^+$ 325.0990, found 325.0993; LRMS (EI, *m*/*z*) 324 (M^+, 100), 281 (35), 247 (44), 213 (39), 165 (28); IR (film) 701, 753, 1227, 1491, 1677, 2927 cm^{-1}.

*1-(5-((4-Bromophenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4e**).* Yield 57% (42.1 mg); white solid; mp 111−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.34−7.25 (m, 3H), 7.14 (d, *J* = 7.1 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.09 (s, 1H), 5.33 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 158.1, 154.0, 140.4, 140.1, 131.7, 130.4, 128.7, 128.6, 127.2, 122.0, 120.9, 109.1, 50.0, 29.1, 14.4; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{18}{}^{79}BrO_2$ $[M + H]^+$ 369.0485, found 369.0493; LRMS (EI, *m*/*z*) 370 (M^+ for ^{81}Br, 100), 368 (M^+ for ^{79}Br, 96), 325 (35), 293 (42), 213 (62), 165 (46); IR (film) 701, 1011, 1227, 1487, 1676, 2927 cm^{-1}.

*Methyl-4-((4-acetyl-5-methylfuran-2-yl)(phenyl)methyl)benzoate (**4f**).* Yield 58% (40.6 mg); yellow solid; mp 71−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.25−7.26 (m, 5H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.10 (s, 1H), 5.43 (s, 1H), 3.90 (s, 3H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 166.8, 158.2, 153.8, 146.2, 140.2, 129.8, 128.9, 128.7, 128.7, 128.6, 127.2, 122.0,

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109.2, 52.0, 50.5, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{22}H_{21}O_4$ $[M + H]^+$ 349.1434, found 349.1439; LRMS (EI, m/z) 348 (M^+, 100), 333 (28), 289 (28), 271 (29), 213 (40); IR (film) 703, 734, 1279, 1677, 1723, 2925 cm^{-1}.

*1-(4-((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)phenyl)-ethanone (**4g**).* Yield 56% (37.0 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3, 2H), 7.35−7.26 (m, 5H), 7.17−7.15 (m, 2H), 6.12 (s, 1H), 5.44 (s, 1H), 2.59 (s, 3H), 2.55 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 194.0, 158.2, 153.7, 146.4, 140.2, 135.9, 128.9, 128.7, 128.6, 128.6, 127.3, 122.1, 109.2, 50.5, 29.1, 26.6, 14.4; HRMS (ESI, m/z) calcd for $C_{22}H_{21}O_3$ $[M + H]^+$ 333.1485, found 333.1485; LRMS (EI, m/z) 332 (M^+, 100), 289 (48), 255 (28), 213 (44), 165 (24); IR (film) 702, 799, 1228, 1267, 1681, 2925 cm^{-1}.

*1-(2-Methyl-5-(phenyl(4-vinylphenyl)methyl)furan-3-yl)ethanone (**4h**).* Yield 62% (39.4 mg); brown solid; mp 77−80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.23 (m, 5H), 7.17−7.12 (m, 4H), 6.69 (dd, J = 10.9, 17.6 Hz, 1H), 6.10 (s, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.37 (s, 1H), 5.23 (d, J = 10.9 Hz, 1H), 2.54 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.0, 154.5, 140.9, 140.6, 136.3, 130.9, 128.8, 128.6, 128.7, 127.0, 126.4, 122.0, 113.8, 108.9, 50.3, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{22}H_{21}O_2$ $[M + H]^+$ 317.1536, found 317.1538; LRMS (EI, m/z) 316 (M^+, 100), 273 (32), 255 (21), 239 (47), 213 (24); IR (film) 702, 747, 1228, 1566, 1677, 2923 cm^{-1}.

*1-(5-((3-Methoxyphenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4i**).* Yield 74% (47.4 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.16 (m, 6H), 7.81−7.62 (m, 3H), 6.11 (s, 1H), 5.35 (s, 1H), 3.75 (s, 3H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.7, 158.0, 154.5, 142.6, 140.9, 129.5, 128.6, 128.5, 127.0, 122.0, 121.1, 114.9, 111.8, 108.9, 55.1, 50.5, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485, found 321.1486; LRMS (EI, m/z) 320 (M^+, 100), 277 (31), 243 (31), 235 (23), 213 (35); IR (film) 703, 734, 1228, 1566, 1676, 2926 cm^{-1}.

*1-(5-((3-Bromophenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4j**).* Yield 60% (44.1 mg); white solid; mp 83−85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.25 (m, 5H), 7.20−7.10 (m, 4H), 6.11 (s, 1H), 5.34 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 158.2, 153.8, 143.4, 140.2, 131.6, 130.1, 130.1, 128.7, 128.6, 127.3, 127.2, 122.7, 122.0, 109.1, 50.2, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{20}H_{18}{}^{79}BrO_2$ $[M + H]^+$ 369.0485, found 369.0492; LRMS (EI, m/z) 370 (M^+ for ^{81}Br, 100), 368 (M^+ for ^{79}Br, 99), 325 (30), 291 (30), 213 (86), 165 (30); IR (film) 702, 732, 909, 1566, 1676, 2924 cm^{-1}.

*1-(5-((3,5-Dimethylphenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4k**).* Yield 68% (43.4 mg); yellow solid; mp 98−100 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.26−7.22 (m, 1H), 7.18−7.16 (m, 2H), 6.89 (s, 1H), 6.78 (s, 2H), 6.09 (s, 1H), 5.30 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 157.9, 154.9, 141.2, 140.9, 138.0, 128.6, 128.5, 126.8, 126.4, 122.0, 108.7, 50.5, 29.1, 21.3, 14.4; HRMS (ESI, m/z) calcd for $C_{22}H_{23}O_2$ $[M + H]^+$ 319.1693, found 319.1696; LRMS (EI, m/z) 318 (M^+, 100), 303 (38), 275 (26), 241 (38), 213 (26); IR (film) 703, 731, 910, 1566, 1676, 2921 cm^{-1}.

*1-(5-((2-Methoxyphenyl)(phenyl)methyl)-2-methylfuran-3-yl)-ethanone (**4l**).* Yield 66% (42.5 mg); white solid; mp 98−101 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.20 (m, 4H), 7.17−7.15 (m, 2H), 6.99−6.97 (m, 1H), 6.92−6.87 (m, 2H), 6.04 (s, 1H), 5.82 (s, 1H), 3.76 (s, 3H), 2.53 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 157.8, 156.7, 154.8, 141.0, 129.6, 129.4, 128.7, 128.3, 128.1, 126.6, 122.0, 120.4, 110.7, 108.7, 55.5, 43.2, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{21}H_{21}O_3$ $[M + H]^+$ 321.1485, found 321.1487; LRMS (EI, m/z) 320 (M^+, 100), 277 (38), 235 (22), 165 (19), 91 (18); IR (film) 701, 732, 753, 1245, 1676, 2929 cm^{-1}.

*1-(2-Methyl-5-(naphthalen-2-yl(phenyl)methyl)furan-3-yl)-ethanone (**4m**).* Yield 71% (48.1 mg); yellow solid; mp 98−100 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.72 (m, 3H), 7.56 (s, 1H), 7.46−7.44 (m, 2H), 7.34−7.20 (m, 6H), 6.12 (s, 1H), 5.55 (s, 1H), 2.55 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 158.1, 154.6, 140.9, 138.6, 133.4, 132.4, 128.8, 128.6, 128.2, 127.8, 127.6, 127.2, 127.0, 126.1, 125.9, 122.0, 109.1, 50.7, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{24}H_{21}O_2$ $[M + H]^+$ 341.1536, found 341.1538; LRMS (EI, m/z) 340 (M^+, 100), 297 (19), 279 (17), 263 (35), 213 (19); IR (film) 702, 732, 1227, 1565, 1676, 3058 cm^{-1}.

*1-(2-Methyl-5-(phenyl(thiophen-3-yl)methyl)furan-3-yl)ethanone (**4n**).* Yield 48% (28.7 mg); yellow solid; mp 116−117 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.19 (m, 6H), 6.93−6.89 (m, 2H), 6.16 (s, 1H), 5.40 (s, 1H), 2.54 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 157.9, 154.4, 141.7, 140.8, 128.6, 128.3, 128.0, 127.0, 125.8, 122.5, 122.0, 108.1, 46.2, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{18}H_{17}O_2S$ $[M + H]^+$ 297.0944, found 297.0943; LRMS (EI, m/z) 296 (M^+, 100), 253 (23), 235 (12), 219 (46), 211 (12); IR (film) 705, 746, 1228, 1565, 1669, 2926 cm^{-1}.

*1-(2-Methyl-5-(phenyl(thiophen-2-yl)methyl)furan-3-yl)ethanone (**4o**).* Yield 34% (20.0 mg); yellow solid; mp 69−72 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.22 (m, 6H), 6.96−6.94 (m, 1H), 6.80−6.79 (m, 1H), 6.25 (s, 1H), 5.57 (s, 1H), 2.55 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.0, 154.0, 144.4, 140.8, 128.6, 128.2, 127.4, 126.7, 126.0, 124.8, 122.0, 108.3, 45.9, 29.1, 14.4; HRMS (ESI, m/z) calcd for $C_{18}H_{17}O_2S$ $[M + H]^+$ 297.0944, found 297.0943; LRMS (EI, m/z) 296 (M^+, 100), 253 (29), 235 (7), 219 (46), 211 (7); IR (film) 701, 744, 1228, 1566, 1677, 2925 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00730.

X-ray crystallographic data (CIF) for product **4a** (CIF)

Copies of ^1H and ^{13}C spectra for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wangjb@pku.edu.cn.

Notes

The authors declare no competing financial interest.

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