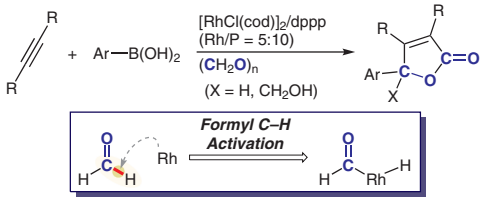
Synthesis T. Morimoto et al. Special Topic

Rhodium(I)-Catalyzed CO-Gas-Free Arylative Dual-Carbonylation of Alkynes with Arylboronic Acids via the Formyl C–H Activation of Formaldehyde

Tsumoru Morimoto[*a]
Chuang Wang[a]
Hiroki Tanimoto[b]
Levent Artok[c]
Kiyomi Kakiuchi[a]

[a] Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science and Technology (NAIST), Ikoma, Nara 630-0192, Japan
morimoto@ms.naist.jp
[b] Academic Assembly, Faculty of Pharmaceutical Sciences, University of Toyama, 2630 Sugitani, Toyama 930-0194, Japan
[c] Department of Chemistry, Faculty of Science, Izmir Institute of Technology, Urla 35430, Izmir, Turkey

Published as part of the Special Topic *Bond Activation – in Honor of Prof. Shinji Murai*

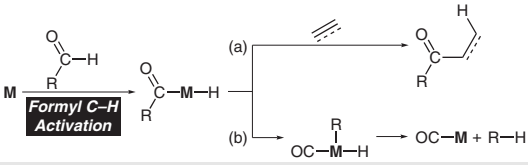


Received: 12.03.2021
Accepted after revision: 29.03.2021
Published online: 29.03.2021
DOI: 10.1055/a-1468-8377; Art ID: ss-2021-f0130-st

Abstract The rhodium(I)-catalyzed reaction of alkynes with arylboronic acids in the presence of formaldehyde results in a CO-gas-free arylative dual-carbonylation to produce γ-butenolide derivatives. The simultaneous loading of phosphine-ligated and phosphine-free rhodium(I) complexes is required for efficient catalysis. The former complex catalyzes the abstraction of a carbonyl moiety from formaldehyde through the activation of its formyl C–H bond (decarbonylation) and the latter catalyzes the subsequent dual-incorporation of the resulting carbonyl unit (carbonylation). The use of larger amounts of the phosphine-ligated rhodium(I) complex generates more carbonyl units, leading to the formation γ-butenolides via the dual-incorporation of the carbonyl unit.

Key words C–H activation, decarbonylation, rhodium, formaldehyde, γ-butenolides, alkynes, arylboronic acids

Transition-metal complexes, especially those of late-transition metals, activate the formyl C–H bond of an aldehyde which is then cleaved to form an acyl-metal-hydride species (RCO-M-H) (Scheme 1). This type of activation represents a new synthetic transformation that is different from the conventional mode, which leads to the creation of a new C–C bond between the highly electron-deficient carbonyl carbon of an aldehyde and the electron-rich carbon of a nucleophile. The addition of an acyl-metal-hydride species to an unsaturated bond, such as an alkene or an alkyne, leads to hydroacylation and the production of ketones (Scheme 1, a).[1] Furthermore, the acyl group of the acyl-metal-hydride species undergoes migratory extrusion (α-elimination), followed by the reductive elimination of the organic group (R) and the hydride (H) to give a metal carbonyl species (aldehyde decarbonylation) (Scheme 1, b).[2] This reaction has mainly been used in the multi-step synthesis of complex organic compounds to remove an unnecessary carbonyl unit from the final product after carbonyl-based chemical transformations.[3]



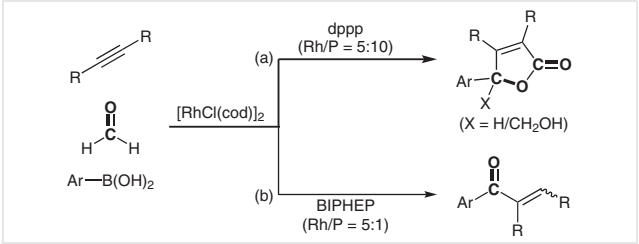
Scheme 1 Transition-metal complexes activate formyl C–H bonds of aldehydes

In the last two decades, new chemical reactions have been developed in which the carbonyl units generated in the reaction system by decarbonylation via activation of the formyl C–H bond of the aldehyde are utilized as a carbonyl source, leading to carbonylation without the direct need for carbon monoxide (transfer carbonylation).[4] Since our report of the first example of a transfer carbonylation in which aldehydes are used as a carbonyl source,[5] we have given priority to focus on transfer carbonylation reactions in which the decarbonylation of aldehydes and the insertion of the resulting carbonyl moiety into a substrate (carbonylation) are catalyzed by a separate transition-metal complex, respectively, in an attempt to expand the application of the method.[6] Among these types of reactions, we focused on carbonylation reactions that are catalyzed by a phosphine-free rhodium(I) complex, proceeding by a transfer carbonylation method using aldehydes, because such complexes can catalyze various carbonylative transformation reactions

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

and are unique to rhodium catalysis.[7] Rhodium complexes that contain phosphine ligands are generally more effective for the decarbonylation of aldehydes.[2a–e] Therefore, it would appear that the nature of highly active catalysts are in conflict with one another when the transfer carbonylation strategy is applied to phosphine-free rhodium(I)-catalyzed carbonylation reactions. The key to solving this problem was the simultaneous use of both phosphine-ligated and phosphine-free rhodium species in the same reaction. These two different types of complexes effectively catalyze decarbonylation and carbonylation processes without interfering with each other, thus resulting in an overall highly efficient carbonylation transfer.[6a,6c–g]

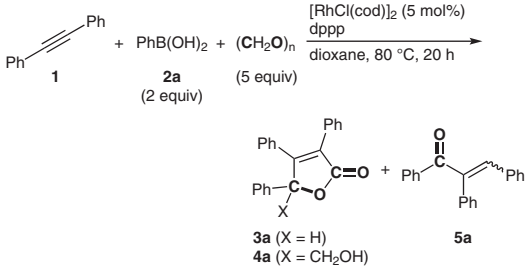
Herein we report on the catalytic transfer carbonylative synthesis of γ-butenolides from alkynes and arylboronic acids using formaldehyde as the carbonyl source via activation of its formyl C–H bond by a rhodium(I) complex (Scheme 2, a). We previously reported that a lower molar ratio of the rhodium(I) center and the phosphorous atom than that used in the present catalysis produces a different transfer carbonylation product, namely α,β-unsaturated enones from the combination of the same substrate (alkynes), the reaction partner (an arylboronic acid), and the carbonyl source (formaldehyde) (Scheme 2, b).[6c] Thus, a higher molar ratio of the rhodium(I) center and the phosphorous atom leads to an increased formation of a phosphine-ligated rhodium(I) complex, resulting in an increase in the in situ generation of the carbonyl unit via the activation of the formyl C–H bond of formaldehyde. As a result, it permits two carbonyl moieties to be incorporated into one alkyne to give γ-butenolide derivatives. γ-Butenolides and their corresponding saturated analogues are important frameworks that are commonly found in natural products, in particular, biologically active compounds.[8] The present method provides an accessible route to such derivatives using readily available starting materials.



Scheme 2 Phosphine-ligated and phosphine-free Rh(I)-catalyzed carbonylation reactions using formaldehyde as the carbonyl source

We first examined the reaction of diphenylacetylene (**1**) with phenylboronic acid (**2a**) and paraformaldehyde under the rhodium(I) catalytic conditions, which consist of $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) and dppp[9] (Table 1). The reaction of **1** with **2a** and paraformaldehyde in the presence of a catalytic amount of only $[RhCl(cod)]_2$ resulted in the hydrobenzoylation via the mono-insertion of a carbonyl moiety to give the enone **5a** in 32% (entry 1). As the amount of added dppp was increased from 0 mol% to 10 mol% with 5 mol% of $[RhCl(cod)]_2$, the use of 10 mol% of dppp led to the formation of the γ-butenolides **3a** and **4a** in 64% yield, both of which were formed via the dual-insertion of the carbonyl moiety (entries 2–5). Based on previous reports that, under phosphine-free rhodium(I) catalyst conditions, a low pressure of carbon monoxide gives the monocarbonyl insertion product **5a**, and when pressurized carbon monoxide is used, the dual-carbonyl insertion product **3a** is formed;[10] these results indicate that an increase in the amount of dppp results in an increase in the amount of carbonyl moiety that is generated through the formyl C–H activation of formaldehyde, leading to an increase in the formation of the γ-butenolide framework. On the contrary, when the amount of dppp was further increased (12 mol% and 20 mol%), the formation of γ-butenolides decreased (entries 6 and 7). Under conditions utilizing 5 mol% of $[RhCl(cod)]_2$ and 10 mol% of dppp, the decarbonylation of formaldehyde and the dual-insertion of the resulting carbonyl moiety are the most cooperative.

Table 1 Effect of dppp on the Rhodium(I)-Catalyzed Reaction of **1a** with **2a** Using $(CH_2O)_n$[a]



Entry	Dppp (mol%)	Yield (%)[b]	
		3a + **4a** (**3a**/**4a**)	**5a**
1	0	0	32
2	2	6 (1:5)	45
3	5	29 (4:25)	13
4	8	49 (7:42)	21
5	10	64 (8:56)	5
6	12	17 (3:14)	3
7	20	0	0

[a] Reaction conditions: **1** (1 mmol), **2a** (2 mmol), paraformaldehyde (5 mmol), dppp, $[RhCl(cod)]_2$ (5 mol%), dioxane (1 mL), 80 °C, 20 h.
[b] Isolated yield.

Under catalytic conditions consisting of 5 mol% of $[RhCl(cod)]_2$ and 10 mol% of diphosphine, the effect of other diphosphines on the product distribution was investigated. The use of dppp was found to be effective in the following catalytic systems: BIPHEP, 16% (**3a**/**4a** = 3%/13%) and 4% (**5a**); BINAP, 9% (**3a**/**4a** = 1%/8%) and 5% (**5a**); dppf, 8% (**3a**/**4a**

= 1%/7%) and 3% (**5a**); dppb, 7% (**3a**/**4a** = 1%/6%) and 5% (**5a**).[9] When a rhodium(I)-alkene complex, such as $[RhCl(cod)]_2$, was mixed with a phosphine such that the ratio of the rhodium(I) center to the phosphine atom is 1:1, the addition of biaryl diphosphines such as BIPHEP or BINAP led to the in situ generation of $[RhCl(P{-}P)]_2$,[11] with no remaining phosphine-free rhodium(I) species; while in the case of the other diphosphines that were examined (dppf, dppb, and dppp), four phosphorus atoms at most can coordinate to one rhodium(I) center, leading to the partial formation of $RhCl(P{-}P)_2$.[12] As a result, the loaded rhodium(I) is divided into the diphosphine-ligated species and the intact form. In fact, in a mixture of $[RhCl(C_2H_4)_2]_2$[13] and dppp in a molar ratio of 1:2 in $CDCl_3$, two types of phosphine-ligated rhodium species were formed, which can be assigned to $RhCl(dppp)_2$ at 8.3 ppm and $[RhCl(dppp)]_2$ at 33.9 ppm in a molar ratio of 8.00:4.83 (Figure 1).[14] It is known that such complexes, $RhCl(dppp)_2$ and $[RhCl(dppp)]_2$, show catalytic activity for the decarbonylation of aldehydes.[15] In addition, the fact that there is no remaining dppp at –17.2 ppm (based on ^{31}P NMR observations) and that $RhCl(dppp)_2$ is predominantly formed indicates that intact $[RhCl(C_2H_4)_2]_2$ is present in the reaction mixture, i.e., dppp-ligated rhodium(I) complexes and a dppp-free rhodium(I) species are simultaneously involved in the catalysis. It therefore follows that these complexes would be involved in the decarbonylation of formaldehyde and the arylative dual-carbonylation processes, respectively.

A plausible reaction pathway for the present reactions is shown in Scheme 3. As in our previous report,[6a,6c–g] the addition of dppp, the amount of which cannot be equivalent to that of all of the loaded rhodium metal, leads to the partial formation of some dppp-ligated Rh(I) complexes, along with intact $[RhCl(cod)]_2$. The former dppp-ligated Rh(I) species functions to mainly decarbonylate formaldehyde via activation of the formyl C–H bond of formaldehyde to generate the carbonyl unit and hydrogen (Cycle I), while the latter predominantly catalyzes the actual arylative carbonylation process. Thus, Rh(I)–OH (**A**) generated in situ from Rh(I)–Cl and H_2O is transmetalated with $PhB(OH)_2$ to generate Rh(I)–Ph (**B**). The carbonyl unit from the decarbonylation process that is catalyzed by the phosphine-ligated Rh(I) complex is transferred to **B** [the formation of Ph–Rh–CO (**C**)], which is followed by the migratory insertion of CO into the Ph–Rh bond in **C** to yield the PhCO–Rh intermediate (**D**). The subsequent benzoylrhodation to alkyne **1** in a *syn*-manner, followed by protonation of the formed vinylrhodium **E**, produces the primary enone product (*E*)-**5a**, along with the regeneration of **A**. (*E*)-**5a** isomerizes to give an equilibrium mixture of (*E*)- and (*Z*)-**5a** under the rhodium(I)-catalytic conditions in the presence of an acidic arylboronic acid.[6c] Furthermore, when a larger amount of dppp is added, this results in the generation of more carbonyl units. The second carbonyl unit from Cycle I is then inserted into the Rh(I)–carbon bond in **E** to form the complex **F**, followed by ring-closure to yield the σ-furanonyl-Rh(I) complex **G**. This step corresponds to the step leading to the formation of the γ-butenolide framework. Finally, the displacement of Rh(I) from the cyclic complex by reacting with a proton or formaldehyde leads to the formation of the γ-butenolide derivatives **3a** and **4a** via protonation and a vinylogous aldol reaction[16] (Cycle II).

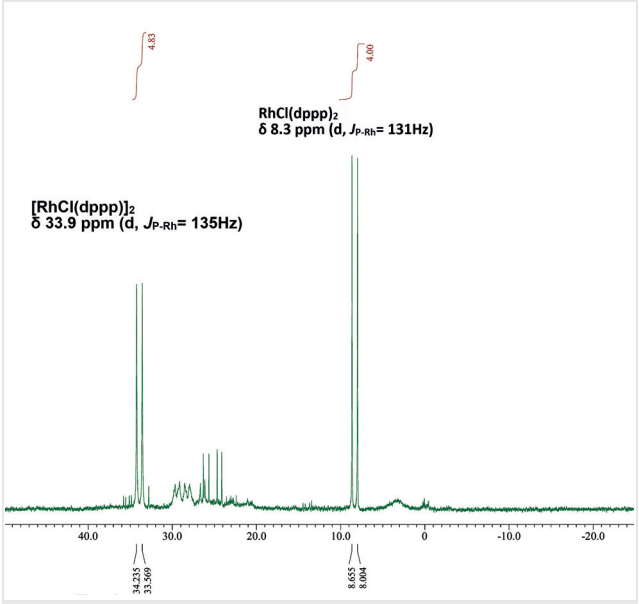
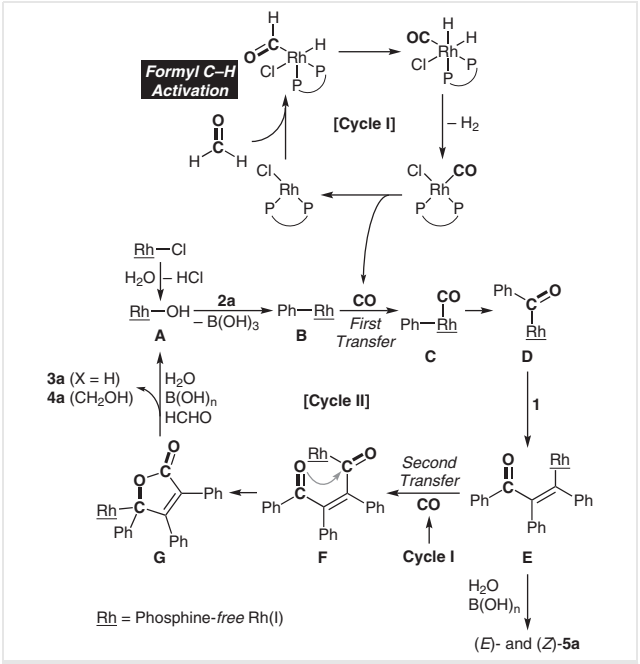


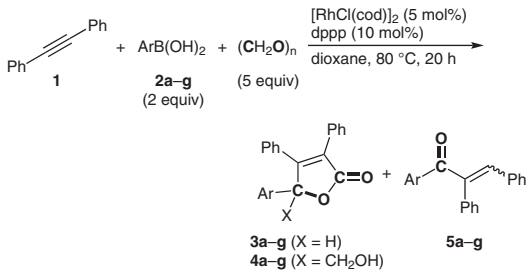
Figure 1 ^{31}P NMR spectrum of a mixture of $[RhCl(cod)]_2$ and dppp in a molar ratio of 1:2



Scheme 3 A plausible reaction pathway

With the above-mentioned standard conditions in hand, the scope of arylboronic acids in the reaction with **1** was next investigated (Table 2). Electronic properties of reactants have a strong effect on the dual-incorporation process. Thus, reactions of arylboronic acids possessing an electron-donating group at the *para*-position of the aromatic ring, such as *p*-methoxyphenylboronic acid (**2b**) and *p*-methylphenylboronic acid (**2c**), afforded the corresponding dual-carbonylative products **3b**/**4b** and **3c**/**4c** in 77% and 71% total yields (entries 1 and 2). On the contrary, the introduction of an electron-withdrawing group to the arylboronic acid (*p*-Cl: **2d**, *p*-CF_3: **2e**) resulted in a decrease in the yields of the dual-carbonylated products **3d**/**4d** (58%) and **3e**/**4e** (48%), while the yields of the mono-carbonylated products **5d** and **5e** were slightly increased (entries 4 and 5). As the substituent (OMe) on the aromatic ring of the arylboronic acid was shifted from the *p*- (**2b**) to the *m*- (**2f**) and *o*-positions (**2g**), the yield of the arylative dual-carbonylated products (**3b**/**4b**, **3f**/**4f**, and **3g**/**4g**) decreased, and small amounts of the arylative mono-carbonylated products **5b**, **5f**, and **5g** were formed (entries 1, 6 and 7).

Table 2 Reaction of **1a** with Various Arylboronic Acids **2** Using $(CH_2O)_n$[a]

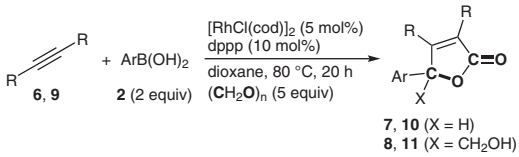


Entry	Arylboronic acid **2**	Yield (%)[b] **3** + **4** (**3**/**4**)	**5**
1	4-$MeOC_6H_4$ (**2b**)	77 [**3b** (10)/**4b** (67)]	**5b** (4)
2	4-MeC_6H_4 (**2c**)	71 [**3c** (11)/**4c** (60)]	**5c** (5)
3	C_6H_5 (**2a**)	64 [**3a** (8)/**4a** (56)]	**5a** (5)
4	4-ClC_6H_4 (**2d**)	58 [**3d** (9)/**4d** (49)]	**5d** (8)
5	4-$F_3CC_6H_4$ (**2e**)	48 [**3e** (7)/**4e** (41)]	**5e** (9)
6	3-$MeOC_6H_4$ (**2f**)	63 [**3f** (10)/**4f** (53)]	**5f** (5)
7	2-$MeOC_6H_4$ (**2g**)	16 [**3g** (12)/**4g** (4)]	**5g** (1)

[a] Reaction conditions: **1** (1 mmol), **2** (2 mmol), paraformaldehyde (5 mmol), $[RhCl(cod)]_2$ (5 mol%), dppp (10 mol%), dioxane (1 mL), 80 °C, 20 h.
[b] Isolated yield.

The results obtained from the reactions of other internal alkynes under the present arylative dual-carbonylation reaction conditions are summarized in Table 3. The reactions of diphenylacetylene derivatives **6** and **9** with *p*-$MeOC_6H_4B(OH)_2$ (**2b**) gave the corresponding butenolides **7b**/**8b** and **10b**/**11b** in 68% and 63% total yields, respectively (entries 1 and 4). The reactions of **6** or **9** with various *para*-substituted arylboronic acids **2** showed the same tendency for the production of γ-butenolides **7**, **8**, **10** and **11** as that observed for entries 1, 3 and 5 in Table 2. Thus, a more electron-donating substituent (OMe) led to the formation of higher yields of the γ-butenolides **7**, **8**, **10** and **11** (entries 1–6).

Table 3 Reactions of Various Alkynes with **2** Using $(CH_2O)_n$[a]



Entry	Alkyne (R)	Arylboronic acid (**2**)	Yield (%)[b] γ-Butenolides (X = H/CH_2OH)
1	4-$MeOC_6H_4$ (**6**)	4-$MeOC_6H_4$ (**2b**)	68 [**7b** (13)/**8b** (55)]
2	**6**	C_6H_5 (**2a**)	60 [**7a** (11)/**8a** (49)]
3	**6**	4-$CF_3C_6H_4$ (**2e**)	46 [**7e** (11)/**8e** (35)]
4	4-$F_3CC_6H_4$ (**9**)	**2b**	63 [**10b** (6)/**11b** (57)]
5	**9**	**2a**	47 [**10a** (5)/**11a** (42)]
6	**9**	**2e**	26 [**10e** (0)/**11e** (26)]

[a] Reaction conditions: alkyne (1 mmol), **2** (2 mmol), paraformaldehyde (5 mmol), $[RhCl(cod)]_2$ (5 mol%), dppp (10 mol%), dioxane (1 mL), 80 °C, 20 h.
[b] Isolated yield.

In conclusion, we have reported herein on the rhodium(I)-catalyzed reaction of alkynes with arylboronic acids in the presence of formaldehyde, resulting in a CO-gas-free arylative dual-carbonylation to yield γ-butenolide derivatives. The simultaneous loading of phosphine-ligated and phosphine-free rhodium(I) complexes is required for efficient catalysis and thus higher yields. The former complex catalyzes the abstraction of a carbonyl moiety from formaldehyde through the activation of its formyl C–H bond (decarbonylation) and the latter catalyzes the subsequent incorporation of the resulting carbonyl unit (arylative dual-carbonylation). The use of larger amounts of the phosphine-ligated rhodium(I) complex generates more carbonyl units, thus leading to the formation γ-butenolides via the incorporation of two carbonyl units. The present method provides an accessible route to these types of derivatives using readily available starting materials.

All reactions were carried out in dried glassware under a nitrogen atmosphere using anhydrous solvents, unless stated otherwise. $[RhCl(cod)]_2$ was prepared using a previously reported method.[17] 1,3-Bis(diphenylphosphino)propane (dppp), 1,3-bis(diphenylphosphino)butane (dppb), 1,1′-ferrocenediyl-bis(diphenylphosphine) (dppf), 2,2′-bis(diphenylphosphino)biphenyl (BIPHEP), and 2,2′-bis(diphen-

ylphosphino)-1,1′-binaphthyl (BINAP) were purchased from Strem Chemicals, Inc., and used directly without further purification. 1,2-Diphenylethyne (**1**) and phosphine ligands were purchased from Tokyo Chemical Industry Co., Ltd. and used directly without further purification. Arylboronic acids **2** were purchased from Wako Pure Chemical Industries, Ltd., and were used directly without further purification. Paraformaldehyde was purchased from Wako Pure Chemical Industries, Ltd. and dried over P_2O_5 under vacuum prior to use. Anhydrous 1,4-dioxane was purchased from Wako Pure Chemical Industries, Ltd., and was further dried over 4 Å molecular sieves and degassed by freeze–pump–thaw cycles (3 times), and then stored in a glove box. 1,2-Bis(4-methoxyphenyl)ethyne (**6**) and 1,2-bis[4-(trifluoromethyl)phenyl]ethyne (**9**) were synthesized from commercially available starting materials according to the reported methods.[2c]

Reactions were monitored by TLC (Merck TLC Silicagel 60 F254). Cerium phosphomolybdate solution and iodine were used to enable visualization of samples. Merck Silica gel 60 was used for flash column chromatography. Melting points were obtained using a Yanaco MP-500D apparatus. Infrared (IR) absorption spectra were measured using a JASCO FT/IR-4200 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using a JEOL JNM-ECX500 spectrometer (^{1}H NMR: 500 MHz, ^{13}C NMR: 126 MHz). The chemical shift values were adjusted based on the chloroform solvent peak (^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.0 ppm) as the internal standard. Multiplicities are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (complex multiplet). Mass spectrometry (MS) was performed using a JEOL JMS-700 Mstation [EI (70 eV)]. HRMS was accomplished with a JEOL LMS-700 MStation. X-ray crystallography was performed using a Rigaku R-AXIS RAPID/S imaging plate diffractometer.

Catalytic Reactions; General Procedure

In a 10 mL screw-capped vial were placed $[RhCl(cod)]_2$ (24.6 mg, 0.05 mmol), dppp (41.4 mg, 0.1 mmol), alkyne **1** (1 mmol), arylboronic acid **2** (2 mmol), paraformaldehyde (150.2 mg, 5 mmol), and 1,4-dioxane (1 mL). The mixture was degassed by three freeze-pump-thaw cycles and then the vial was sealed under N_2. The mixture was stirred at 80 °C for 20 h, cooled to room temperature and then transferred to a 50 mL flask using ethyl acetate (10 mL) and treated with 8 g of activated aluminum oxide (Al_2O_3) with stirring for 1 h. The reaction mixture was filtered through a short pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel.

3,4,5-Triphenylfuran-2(5*H*)-one (3a) (Table 1, Entry 5)[10]

Yield: 25.0 mg (8.0%); white solid; mp 124.0–125.2 °C; R_f = 0.47 (hexane/EtOAc, 2:1).

IR (KBr): 2923, 2853, 1752 (C=O), 1012, 963, 745, 695 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.27 (s, 1 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.31–7.37 (m, 9 H), 7.47–7.48 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 83.7, 126.8, 127.4, 127.6, 128.1, 128.3, 128.5, 128.7, 128.9, 129.1, 129.2, 129.4, 129.7, 129.9, 131.0, 134.7, 159.3, 172.5.

MS (EI): *m*/*z* (%) = 312 (21) [M$^+$], 284 (3), 265 (7), 252 (6), 239 (5), 207 (12), 178 (100), 152 (20), 105 (42), 77 (51), 51 (26).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{16}O_2$: 312.1150; found: 312.1152.

Crystallographic data for **3a** (CCDC 1002969): $C_{22}H_{16}O_2$, Mr = 312.37, colorless block, 0.120 × 0.070 × 0.030 mm, monoclinic, primitive, *a* = 10.6542(9) Å, *b* = 8.8328(7) Å, *c* = 17.640(2) Å, *β* = 96.005(3)°, *V* = 1650.9(2) Å^3, *Z* = 4, ρ_c = 1.257 g/cm^3, *μ* = 0.794 cm^{-1}, *T* = 123 K, *λ* = 0.71075 Å, 15833 reflections, 3373 unique [*R*(int) = 0.0429], final *GoF* = 1.077, R_1 = 0.0471 ([*I* > 2.00σ(*I*)]), wR_2 = 0.1080 (all data).

5-(Hydroxymethyl)-3,4,5-triphenylfuran-2(5*H*)-one (4a) (Table 1, Entry 5)

Yield: 191.7 mg (56%); white solid; mp 143.1–144.6 °C; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (KBr): 3449, 3058, 2925, 1752 (C=O), 1409, 1445, 1178, 1005, 749, 696 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (s, 1 H), 4.27 (s, 2 H), 6.92 (d, *J* = 7.0 Hz, 2 H), 7.19–7.39 (m, 13 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 64.0, 90.9, 125.7, 128.1, 128.3, 128.5, 128.6, 129.2, 131.7, 135.0, 162.6, 172.5.

MS (EI): *m*/*z* (%) = 342 (5) [M$^+$], 312 (63), 311 (60), 284 (3), 265 (7), 252 (6), 207 (40), 179 (50), 178 (49), 152 (6), 105 (100), 77 (35), 51 (4).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{23}H_{18}O_3$: 342.1256; found: 342.1254.

Crystallographic data for **4a** (CCDC 1002983): $C_{23}H_{18}O_3$, Mr = 342.39, colorless block, 0.170 × 0.110 × 0.030 mm, orthorhombic, primitive, *a* = 24.4574(5) Å, *b* = 15.1514(3) Å, *c* = 10.3240(2) Å, *V* = 3825.7(2) Å^3, *Z* = 8, ρ_c = 1.189 g/cm^3, *μ* = 0.779 cm^{-1}, *T* = 123 K, *λ* = 0.71075 Å, 52627 reflections, 6977 unique [*R*(int) = 0.0823], final *GoF* = 1.077, R_1 = 0.0542 ([*I* > 2.00σ(*I*)]), wR_2 = 0.1427 (all data).

(*E*)-1,2,3-Triphenyl-2-propen-1-one [(*E*)-5a] (Table 1, Entry 5)[6c]

Yield: 5.3 mg (1.9%); white solid; mp 100.1–101.2 °C; R_f = 0.14 (hexane/EtOAc, 30:1).

IR (KBr): 3047, 3021, 1644 (C=O), 1595, 1576, 1444, 1250 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 7.5 Hz, 2 H), 7.16–7.23 (m, 4 H), 7.27–7.29 (m, 2 H), 7.33–7.36 (m, 3 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.54 (t, *J* = 7.0 Hz, 1 H), 7.86 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.9, 128.2, 128.3, 128.8, 128.9, 129.6, 129.8, 130.3, 132.1, 134.7, 136.5, 138.1, 140.2, 140.7, 197.6.

MS (EI): *m*/*z* (%) = 284 (87) [M$^+$], 283 (33), 207 (13), 206 (20), 180 (10), 179 (60), 178 (82), 167 (32), 152 (15), 105 (100), 77 (60), 51 (14).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{21}H_{16}O$: 284.1201; found: 284.1200.

(*Z*)-1,2,3-Triphenyl-2-propen-1-one [(*Z*)-5a] (Table 1, Entry 5)[6c]

Yield: 9.5 mg (3.1%); white solid; mp 85.0–86.7 °C; R_f = 0.20 (hexane/EtOAc, 30:1).

IR (KBr): 3057, 3025, 2924, 2359, 1666 (C=O), 1596, 1579, 1448, 1224 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.21 (m, 4 H), 7.29–7.32 (m, 3 H), 7.34–7.38 (m, 4 H), 7.46–7.50 (m, 3 H), 7.99 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.3, 128.0, 128.1, 128.4, 128.71, 128.75, 128.8, 129.6, 130.0, 133.6, 135.3, 136.2, 137.9, 140.7, 199.3.

MS (EI): *m*/*z* (%) = 284 (100) [M$^+$], 283 (21), 206 (12), 179 (35), 178 (53), 167 (18), 105 (82), 77 (42), 60 (11), 57 (15), 55 (11).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{21}H_{16}O$: 284.1201; found: 284.1201.

3,4-Diphenyl-5-(4-methoxyphenyl)furan-2(5*H*)-one (3b) (Table 2, Entry 1)[10]

Yield: 34.2 mg (10%); white solid; mp 112.0–113.1 °C; R_f = 0.39 (hexane/EtOAc, 2:1).

IR (KBr): 2921, 2851, 1750 (C=O), 1608, 1514, 1457, 1158 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 3 H), 6.23 (s, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 7.11 (d, *J* = 7.0 Hz, 2 H), 7.21–7.27 (m, 5 H), 7.34–7.37 (m, 3 H), 7.46–7.48 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.1, 83.3, 114.2, 126.5, 126.7, 128.3, 128.5, 128.6, 128.7, 129.0, 129.3, 129.7, 129.8, 131.1, 159.2, 160.2, 172.5.

MS (EI): *m*/*z* (%) = 342 (55) [M^+], 314 (3), 285 (7), 252 (11), 237 (11), 207 (15), 178 (80), 135 (100), 126 (6), 77 (13), 57 (8).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{23}H_{18}O_3$: 342.1256; found: 342.1255.

3,4-Diphenyl-5-(hydroxymethyl)-5-(4-methoxyphenyl)furan-2(5*H*)-one (4b) (Table 2, Entry 1)

Yield: 249.5 mg (67%); white solid; mp 164.6–165.8 °C; R_f = 0.20 (hexane/EtOAc, 2:1).

IR (KBr): 3449, 3057, 3020, 2933, 2837, 1752 (C=O), 1609, 1513, 1255, 833, 760, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.47–2.49 (m, 1 H), 3.81 (s, 3 H), 4.20–4.24 (m, 2 H), 6.86 (d, *J* = 6.0 Hz, 2 H), 6.92 (d, *J* = 6.5 Hz, 2 H), 7.13 (d, *J* = 6.5 Hz, 2 H), 7.23–7.40 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.1, 63.8, 90.8, 113.9, 126.8, 127.1, 127.6, 128.0, 128.3, 128.5, 129.0, 129.1, 129.4, 131.7, 159.6, 162.7, 172.6.

MS (EI): *m*/*z* (%) = 372 (8) [M^+], 312 (3), 311 (2), 281 (1), 237 (2), 207 (4), 178 (5), 135 (12), 83 (100), 69 (6), 59 (7).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{24}H_{20}O_4$: 372.1362; found: 372.1363.

(*E*)-2,3-Diphenyl-1-(4-methoxyphenyl)-2-propen-1-one [(*E*)-5b] (Table 2, Entry 1)[6c]

Yield: 3.3 mg (1.0%); colorless oil; R_f = 0.18 (hexane/EtOAc, 20:1).

IR (neat): 3056, 2931, 2838, 1646 (C=O), 1599, 1574, 1312, 1508, 1253, 1166, 1027 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 6.92 (d, *J* = 8.5 Hz, 2 H), 7.11 (d, *J* = 7.5 Hz, 2 H), 7.14 (s, 1 H), 7.15–7.24 (m, 3 H), 7.27–7.37 (m, 5 H), 7.90 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 113.6, 127.9, 128.2, 128.6, 128.8, 129.5, 130.2, 130.4, 132.3, 135.0, 136.8, 137.8, 141.0, 163.1, 196.3.

MS (EI): *m*/*z* (%) = 316 (21) [M + 2$^+$], 315 (70) [M + 1$^+$], 314 (96) [M^+], 286 (25), 236 (22), 221 (17), 198 (18), 197 (63), 179 (57), 178 (76), 177 (37), 176 (48), 152 (33), 151 (22), 149 (34), 136 (56), 135 (100), 107 (50), 92 (53), 86 (60), 84 (71), 77 (65), 57 (52).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{22}H_{18}O_2$: 314.1307; found: 314.1305.

(*Z*)-2,3-Diphenyl-1-(4-methoxyphenyl)-2-propen-1-one [(*Z*)-5b] (Table 2, Entry 1)[6c]

Yield: 9.4 mg (3.0%); white solid; mp 88.5–89.9 °C; R_f = 0.18 (hexane/EtOAc, 20:1).

IR (KBr): 3056, 3026, 2932, 2839, 1658 (C=O), 1652, 1595, 1575, 1508, 1258, 1235, 1164 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.83 (d, *J* = 8.5 Hz, 2 H), 7.13–7.22 (m, 4 H), 7.27–7.36 (m, 5 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.97 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 114.0, 126.2, 127.9, 128.1, 128.4, 128.8, 129.4, 129.5, 132.0, 135.4, 138.1, 140.9, 163.9, 197.8.

MS (EI): *m*/*z* (%) = 316 (27) [M + 2$^+$], 315 (68) [M + 1$^+$], 314 (100) [M^+], 286 (38), 236 (21), 198 (21), 197 (62), 179 (55), 178 (68), 177 (47), 176 (52), 152 (41), 136 (56), 135 (100), 107 (52), 92 (57), 85 (31), 83 (47), 77 (60), 64 (26), 51 (23).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{22}H_{18}O_2$: 314.1307; found: 314.1308.

3,4-Diphenyl-5-(4-methylphenyl)furan-2(5*H*)-one (3c) (Table 2, Entry 2)[10]

Yield: 35.9 mg (11%); white solid; mp 119.0–120.2 °C; R_f = 0.47 (hexane/EtOAc, 2:1).

IR (KBr): 3055, 2923, 2853, 1752 (C=O), 1598, 1445, 963, 695 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 6.23 (s, 1 H), 7.10–7.48 (m, 14 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 83.6, 127.6, 128.3, 128.5, 128.6, 128.8, 129.4, 129.6, 129.8, 131.1, 131.6, 139.3, 159.3, 172.6.

MS (EI): *m*/*z* (%) = 326 (35) [M^+], 298 (3), 269 (5), 252 (7), 221 (11), 207 (32), 178 (100), 176 (30), 152 (20), 119 (65), 91 (35), 57 (10).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{23}H_{18}O_2$: 326.1307; found: 326.1306.

3,4-Diphenyl-5-hydroxymethyl-5-(4-methylphenyl)furan-2(5*H*)-one (4c) (Table 2, Entry 2)

Yield: 213.8 mg (60%); white solid; mp 158.8–160.0 °C; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (KBr): 3435, 3057, 3024, 2923, 2876, 1752 (C=O), 1513, 1444, 1180, 1007, 819, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.54–2.56 (m, 1 H), 4.20–4.25 (m, 2 H), 6.93 (d, *J* = 7.0 Hz, 2 H), 7.11 (dd, *J* = 30.5, 8.5 Hz, 4 H), 7.22–7.39 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8, 63.7, 90.7, 125.4, 127.4, 127.8, 128.1, 128.3, 128.9, 129.0, 129.2, 131.5, 131.7, 138.3, 162.4, 172.3.

MS (EI): *m*/*z* (%) = 356 (8) [M^+], 325 (95), 323 (8), 298 (11), 265 (12), 252 (11), 221 (21), 207 (55), 179 (70), 178 (69), 152 (13), 119 (100), 91 (60), 65 (14), 57 (12).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{24}H_{20}O_3$: 356.1412; found: 356.1412.

(*E*)-2,3-Diphenyl-1-(4-methylphenyl)-2-propen-1-one [(*E*)-5c] (Table 2, Entry 2)[6c]

Yield: 4.0 mg (1.3%); white solid; mp 88.1–89.3 °C; R_f = 0.14 (hexane/EtOAc, 30:1).

IR (KBr): 3044, 1644 (C=O), 1605, 1494, 1448, 1381, 1318, 1264, 1181, 1064 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.09 (d, *J* = 6.5 Hz, 2 H), 7.15–7.37 (m, 11 H), 7.79 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 127.8, 128.2, 128.75, 128.73, 129.0, 129.6, 130.0, 130.2, 134.9, 135.3, 136.6, 139.1, 140.9, 143.0, 197.3.

MS (EI): *m*/*z* (%) = 299 (53) [M + 1$^+$], 298 (71) [M^+], 297 (25), 236 (35), 221 (43), 220 (40), 182 (27), 181 (61), 180 (26), 179 (63), 178 (87), 177 (52), 176 (51), 152 (62), 151 (53), 119 (100).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{22}H_{18}O$: 298.1358; found: 298.1357.

(*Z*)-2,3-Diphenyl-1-(4-Methylphenyl)-2-propen-1-one [(*Z*)-5c] (Table 2, Entry 2)[6c]

Yield: 11.0 mg (3.7%); colorless oil; R_f = 0.18 (hexane/EtOAc, 30:1).

IR (neat): 3056, 3025, 1663 (C=O), 1605, 1492, 1448, 1227, 1174 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33 (s, 3 H), 7.12–7.21 (m, 6 H), 7.26–7.36 (m, 5 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.89 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 126.3, 127.9, 128.1, 128.4, 128.8, 129.5, 129.7, 129.9, 133.9, 135.4, 138.1, 140.9, 144.6, 199.0.

MS (EI): *m*/*z* (%) = 299 (12) [M + 1$^+$], 298 (52) [M$^+$], 179 (12), 178 (28), 119 (100), 91 (39), 65 (13).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{18}O$: 298.1358; found: 298.1357.

5-(4-Chlorophenyl)-3,4-diphenylfuran-2(5*H*)-one (3d) (Table 2, Entry 4)[10]

Yield: 31.2 mg (9%); white solid; mp 132.0–133.2 °C; R_f = 0.47 (hexane/EtOAc, 2:1).

IR (KBr): 2923, 2853, 1752 (C=O), 1598, 1445, 1156, 963, 852 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.25 (s, 1 H), 7.09–7.48 (m, 14 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.8, 128.2, 128.6, 128.8, 128.9, 129.2, 129.3, 129.5, 130.1, 130.8, 133.2, 135.2, 159.0, 172.3.

MS (EI): *m*/*z* (%) = 346 (35) [M$^+$], 318 (3), 265 (11), 241 (7), 208 (4), 207 (32), 178 (100), 176 (32), 139 (42), 111 (22), 77 (15), 75 (14), 51 (12).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{15}ClO_2$: 346.0761; found: 346.0761.

5-(4-Chlorophenyl)-3,4-diphenyl-5-(hydroxymethyl)furan-2(5*H*)-one (4d) (Table 2, Entry 4)

Yield: 184.7 mg (49%); white solid; mp 155.1–157.0 °C; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (KBr): 3434, 3056, 3024, 2925, 2876, 1755 (C=O), 1492, 1176, 1005, 696 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (t, *J* = 7.0 Hz, 1 H), 4.20–4.22 (m, 2 H), 6.93 (d, *J* = 7.0 Hz, 2 H), 7.11 (d, *J* = 8.5 Hz, 2 H), 7.22–7.38 (m, 10 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 63.8, 90.6, 127.1, 127.9, 128.0, 128.2, 128.6, 128.7, 129.1, 131.4, 133.6, 134.6, 162.3, 172.3.

MS (EI): *m*/*z* (%) = 376 (3) [M$^+$], 346 (65), 345 (35), 312 (25), 283 (6), 265 (8), 241 (6), 207 (50), 179 (70), 178 (50), 139 (43), 105 (23), 83 (100), 69 (20), 57 (13).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{23}H_{17}ClO_3$: 376.0866; found: 376.0871.

(*E*)-1-(4-Chlorophenyl)-2,3-diphenyl-2-propen-1-one [(*E*)-5d] (Table 2, Entry 4)[6c]

Yield: 9.3 mg (2.9%); white solid; mp 89.3–90.1 °C; R_f = 0.26 (hexane/EtOAc, 20:1).

IR (KBr): 3054, 3025, 1647 (C=O), 1592, 1443, 1257, 1087, 1013 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 7.0 Hz, 2 H), 7.19 (t, *J* = 7.5 Hz, 2 H), 7.20–7.27 (m, 4 H), 7.31–7.37 (m, 3 H), 7.40 (d, *J* = 7.5 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 128.0, 128.3, 128.6, 128.8, 129.1, 129.6, 130.4, 131.1, 134.6, 136.2, 136.4, 138.5, 140.2, 140.4, 196.3.

MS (EI): *m*/*z* (%) = 321 (10) [M + 3$^+$], 320 (48) [M + 2$^+$], 319 (44) [M + 1$^+$], 318 (M$^+$, 100), 317 (37), 283 (57), 201 (12), 180 (12), 179 (72), 178 (79), 177 (13), 176 (16), 152 (14), 141 (24), 139 (77), 111 (19).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{21}H_{15}ClO$: 318.0811; found: 318.0810.

(*Z*)-1-(4-Chlorophenyl)-2,3-diphenyl-2-propen-1-one [(*Z*)-5d] (Table 2, Entry 4)[6c]

Yield: 174 mg (5.4%); white solid; mp 104.3–105.6 °C; R_f = 0.31 (hexane/EtOAc, 20:1).

IR (neat): 3082, 3057, 3023, 1663 (C=O), 1596, 1584, 1494, 1450, 1401, 1223, 1176, 1090, 1011 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.21 (m, 4 H), 7.24–7.37 (m, 7 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 126.3, 128.2, 128.3, 128.5, 128.8, 128.9, 129.1, 130.4, 131.0, 134.7, 135.2, 137.7, 140.1, 140.3, 198.1.

MS (EI): *m*/*z* (%) = 321 (10) [M + 3$^+$], 320 (44) [M + 2$^+$], 319 (42) [M + 1$^+$], 318 (100) [M$^+$], 317 (32), 283 (47), 206 (12), 179 (38), 178 (48), 139 (50), 111 (16).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{21}H_{15}ClO$: 318.0811; found: 318.0810.

3,4-Diphenyl-5-[4-(trifluoromethyl)phenyl]furan-2(5*H*)-one (3e) (Table 2, Entry 5)[10]

Yield: 26.6 mg (7%); white solid; mp 132.6–133.7 °C; R_f = 0.47 (hexane/EtOAc, 2:1).

IR (neat): 3059, 2924, 2853, 1758 (C=O), 1446, 1325, 1068, 850 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.33 (s, 1 H), 7.12 (d, *J* = 7.5 Hz, 2 H), 7.23–7.48 (m, 10 H), 7.58 (d, *J* = 7.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.6, 122.6, 125.8, 125.9 (*tet*), 127.0, 127.8, 128.2, 128.6, 128.9, 129.1, 129.3, 129.4, 130.2, 130.7, 131.5, 138.8, 158.9, 172.1.

MS (EI): *m*/*z* (%) = 380 (30) [M$^+$], 361 (3), 352 (2), 275 (5), 208 (8), 207 (60), 179 (100), 178 (53), 145 (7), 126 (4), 105 (5), 77 (4), 51 (3).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{23}H_{15}F_3O_2$: 380.1024; found: 380.1024.

3,4-Diphenyl-5-hydroxymethyl-5-[4-(trifluoromethyl)phenyl]-furan-2(5*H*)-one (4e) (Table 2, Entry 5)

Yield: 168.3 mg (41%); white solid; mp 143.7–145.2 °C; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (KBr): 3434, 3056, 3024, 2925, 2876, 1758 (C=O), 1326, 1170, 1005, 843 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.57 (dd, *J* = 9.0, 6.0 Hz, 1 H), 4.20–4.30 (m, 2 H), 6.95 (d, *J* = 7.5 Hz, 2 H), 7.22–7.40 (m, 10 H), 7.58 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 64.0, 90.8, 123.7 (q, $^1J_{C-F}$ = 270.6 Hz), 125.4 (q, $^3J_{C-F}$ = 3.6 Hz), 126.1, 126.9, 128.1, 128.2, 128.3, 128.6, 128.9, 129.1, 129.4, 130.7 (q, $^2J_{C-F}$ = 32.1 Hz), 131.3, 139.2, 162.0, 172.3.

MS (EI): *m*/*z* (%) = 410 (3) [M$^+$], 380 (35), 379 (20), 352 (4), 281 (2), 265 (4), 235 (15), 207 (12), 173 (62), 145 (27), 126 (5), 105 (6), 83 (100), 69 (15), 60 (10).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{24}H_{17}F_3O_3$: 410.1130; found: 410.1130.

(*E*)-2,3-Diphenyl-1-[4-(trifluoromethyl)phenyl]-2-propen-1-one [(*E*)-5e] (Table 2, Entry 5)[6c]

Yield: 13.0 mg (3.7%); white solid; mp 116.1–117.2 °C; R_f = 0.17 (hexane/EtOAc, 30:1).

IR (KBr): 3052, 1650 (C=O), 1493, 1443, 1405, 1332, 1255, 1167, 1142, 1108, 1069, 1016 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.0 Hz, 2 H), 7.16–7.21 (m, 2 H), 7.22–7.28 (m, 4 H), 7.33–7.40 (m, 3 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.7 (q, $^1J_{C-F}$ = 273 Hz), 125.3 (q, $^3J_{C-F}$ = 1.5 Hz), 128.2, 128.3, 128.8, 128.9, 129.4, 129.6, 129.8, 130.5, 133.3 (q, $^2J_{C-F}$ = 32.6 Hz), 134.4, 135.9, 140.3, 141.5, 141.9, 196.4.

MS (EI): *m*/*z* (%) = 353 (11) [M + 1$^+$], 352 (36) [M$^+$], 351 (11), 341 (11), 295 (12), 257 (13), 256 (16), 255 (12), 237 (15), 236 (32), 221 (26), 180 (19), 179 (71), 178 (86), 177 (22), 176 (21), 173 (45), 152 (38), 149 (31), 145 (51), 137 (71), 136 (49), 127 (53), 123 (50), 121 (52), 109 (53), 95 (100), 82 (85), 57 (80).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{15}F_3O$: 352.1075; found: 352.1072.

(*Z*)-2,3-Diphenyl-1-[4-(trifluoromethyl)phenyl]-2-propen-1-one [(*Z*)-5e] (Table 2, Entry 5)[6c]

Yield: 18.7 mg (5.3%); white solid; mp 105.3–107.2 °C; R_f = 0.26 (hexane/EtOAc, 30:1).

IR (KBr): 3069, 1672 (C=O), 1580, 1497, 1450, 1412, 1325, 1228, 1170, 1124, 1067, 1015 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.22 (m, 3 H), 7.24–7.28 (m, 3 H), 7.29–7.39 (m, 3 H), 7.44 (d, *J* = 7.5 Hz, 2 H), 7.61 (d, *J* = 8.5 Hz, 2 H), 8.07 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.5 (q, $^1J_{C-F}$ = 273 Hz), 125.8 (q, $^3J_{C-F}$ = 3.8 Hz), 126.4, 128.4, 128.5, 128.6, 128.8, 129.0, 129.9, 131.0, 134.6 (q, $^2J_{C-F}$ = 32.6 Hz), 135.1, 137.5, 138.9, 140.2, 198.3.

MS (EI): *m*/*z* (%) = 353 (15) [M + 1$^+$], 352 (57) [M$^+$], 351 (21), 219 (10), 207 (12), 181 (12), 180 (16), 179 (95), 178 (100), 177 (43), 176 (35), 175 (11), 174 (11), 173 (63), 152 (26), 151 (19), 146 (11), 145 (67), 133 (40), 131 (21), 126 (15), 125 (16), 121 (11), 119 (21), 103 (28), 102 (22), 101 (24), 95 (20), 89 (45), 88 (42), 87 (43), 77 (25), 75 (35), 73 (41), 72 (20), 69 (41), 59 (41), 58 (36), 57 (29).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{15}F_3O$: 352.1075; found: 352.1076.

3,4-Diphenyl-5-(3-methoxyphenyl)furan-2(5*H*)-one (3f) (Table 2, Entry 6)[10]

Yield: 35.6 mg (10%); colorless liquid; R_f = 0.42 (hexane/EtOAc, 2:1).

IR (neat): 2921, 2851, 1755 (C=O), 1599, 1450, 1165 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 (s, 3 H), 6.15 (s, 1 H), 6.73–7.39 (m, 14 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 70.6, 83.5, 113.2, 114.6, 120.0, 127.5, 128.3, 128.5, 128.7, 129.0, 129.4, 129.8, 136.2, 159.2, 159.8, 172.4.

MS (EI): *m*/*z* (%) = 342 (25) [M$^+$], 314 (3), 285 (4), 252 (11), 237 (7), 207 (18), 178 (100), 152 (25), 135 (28), 107 (26), 77 (33), 57 (43).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{23}H_{18}O_3$: 342.1256; found: 342.1256.

3,4-Diphenyl-5-(hydroxymethyl)-5-(3-methoxyphenyl)furan-2(5*H*)-one (4f) (Table 2, Entry 6)

Yield: 196.3 g (53%); colorless liquid; R_f = 0.26 (hexane/EtOAc, 2:1).

IR (neat): 3433, 3056, 3022, 2933, 2837, 1752 (C=O), 1600, 1490, 1264, 1007, 786 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.49 (t, *J* = 7.0 Hz, 1 H), 3.71 (s, 3 H), 4.24 (d, *J* = 6.0 Hz, 2 H), 6.72–6.76 (m, 2 H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1 H), 6.97 (d, *J* = 7.0 Hz, 2 H), 7.22–7.39 (m, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 64.1, 90.9, 111.4, 114.2, 118.0, 127.9, 128.1, 128.4, 128.5, 128.7, 129.1, 129.2, 129.3, 131.8, 136.6, 159.5, 162.4, 172.4.

MS (EI): *m*/*z* (%) = 372 (3) [M$^+$], 342 (50), 341 (38), 314 (5), 252 (8), 207 (22), 178 (100), 135 (88), 107 (30), 77 (38), 57 (18).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{24}H_{20}O_4$: 372.1362; found: 372.1366.

(*E*)-2,3-Diphenyl-1-(3-methoxyphenyl)-2-propen-1-one [(*E*)-5f] (Table 2, Entry 6)[6c]

Yield: 4.6 mg (1.5%); white solid; mp 88.4–89.5 °C; R_f = 0.27 (hexane/EtOAc, 10:1).

IR (KBr): 3057, 2923, 2852, 2362, 1653 (C=O), 1597, 1495, 1443, 1269 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 7.06–7.10 (m, 3 H), 7.16–7.23 (m, 3 H), 7.25–7.29 (m, 3 H), 7.32–7.38 (m, 5 H), 7.44 (d, *J* = 7.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 114.1, 118.6, 122.5, 126.3, 127.9, 128.2, 128.8, 128.9, 129.2, 129.6, 130.3, 134.7, 136.4, 139.4, 140.1, 140.7, 159.5, 197.3.

MS (EI): *m*/*z* (%) = 315 (13) [M + 1$^+$], 314 (59) [M$^+$], 197 (40), 179 (32), 178 (65), 177 (11), 176 (13), 152 (16), 136 (22), 135 (100), 108 (19), 107 (83), 92 (51), 86 (48), 84 (73), 77 (90), 69 (40).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{18}O_2$: 314.1307; found: 314.1307.

(*Z*)-2,3-Diphenyl-1-(3-methoxyphenyl)-2-propen-1-one [(*Z*)-5f] (Table 2, Entry 6)[6c]

Yield: 12.0 mg (3.8%); white solid; mp 71.2–72.8 °C; R_f = 0.29 (hexane/EtOAc, 10:1).

IR (KBr): 3056, 3024, 2938, 2835, 1666 (C=O), 1594, 1580, 1484, 1429, 1261, 1037 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 7.01–7.05 (m, 1 H), 7.14–7.25 (m, 5 H), 7.27–7.37 (m, 5 H), 7.46 (d, *J* = 7.5 Hz, 2 H), 7.53–7.57 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 113.0, 120.4, 122.8, 126.3, 128.0, 128.1, 128.4, 128.8, 129.7, 130.0, 135.3, 137.6, 137.9, 140.8, 159.8, 199.1.

MS (EI): *m*/*z* (%) = 315 (40) [M + 1$^+$], 314 (100) [M$^+$], 286 (18), 236 (14), 198 (15), 197 (95), 180 (13), 179 (94), 178 (96), 177 (40), 176 (47), 166 (10), 152 (47), 151 (25), 150 (10), 136 (37), 135 (98), 126 (14), 108 (25), 107 (95), 102 (20), 92 (94), 77 (95), 69 (73).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{22}H_{18}O_2$: 314.1307; found: 314.1310.

3,4-Diphenyl-5-(2-methoxyphenyl)furan-2(5*H*)-one (3g) (Table 2, Entry 7)[10]

Yield: 40.1 mg (12%); colorless liquid; R_f = 0.43 (hexane/EtOAc, 2:1).

IR (neat): 2921, 2851, 1752 (C=O), 1690, 1657, 1158 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 6.73 (s, 1 H), 6.80–7.40 (m, 14 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.6, 70.6, 111.2, 120.9, 122.9, 126.1, 127.5, 128.5, 128.7, 129.0, 129.3, 129.4, 156.1, 159.6, 173.0.

MS (EI): *m*/*z* (%) = 342 (13) [M$^+$], 314 (3), 281 (2), 252 (4), 236 (20), 207 (8), 178 (80), 152 (22), 135 (23), 105 (13), 83 (100), 77 (33), 51 (31).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{23}H_{18}O_2$: 342.1256; found: 342.1254.

3,4-Diphenyl-5-hydroxymethyl-5-(2-methoxyphenyl)furan-2(5*H*)-one (4g) (Table 2, Entry 7)

Yield: 16.4 mg (4%); white solid; mp 62.5–63.9 °C; R_f = 0.20 (hexane/EtOAc, 2:1).

IR (KBr): 3409, 2917, 2849, 1744 (C=O), 1598, 1180, 1076, 751 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (t, *J* = 7.5 Hz, 1 H), 3.51 (s, 3 H), 4.19–4.35 (m, 2 H), 6.78 (d, *J* = 5.0 Hz, 2 H), 6.84 (d, *J* = 10.0 Hz, 1 H), 6.91 (m, 1 H), 7.12–7.33 (m, 10 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 64.3, 89.6, 112.0, 120.8, 122.4, 128.0, 128.2, 128.3, 128.6, 128.7, 129.0, 129.2, 129.4, 130.6, 132.2, 158.3, 160.6, 172.7.

MS (EI): *m*/*z* (%) = 372 (1) [M^+], 342 (21), 341 (28), 314 (4), 252 (8), 207 (8), 178 (80), 135 (56), 107 (13), 83 (100), 57 (45).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{24}H_{20}O_4$: 372.1362; found: 372.1371.

2,3-Diphenyl-1-(2-methoxyphenyl)-2-propen-1-one [(*E*)- and (*Z*)-5g] (Table 2, Entry 7)[6c]

Yield: 4.1 mg (1.3%); colorless oil; R_f = 0.21; (hexane/EtOAc, 10:1).

^1H NMR (500 MHz, $CDCl_3$): δ = 3.74 (s, 3 H, *E*-isomer), 3.76 (s, 3 H, *Z*-isomer).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 55.6, 111.2, 111.9, 120.3, 120.5, 127.7, 128.1, 128.4, 128.5, 128.9, 129.3, 130.0, 130.6, 131.5, 132.0, 134.6, 150.0, 136.0, 136.1, 138.2, 141.7, 142.2, 144.3, 157.0, 159.4, 197.6, 198.0.

(*Z*)-2,3-Diphenyl-1-(2-methoxyphenyl)-2-propen-1-one [(*Z*)-5g] (Table 2, Entry 7)[6c]

Yield: 2.8 mg (0.9%); white solid; mp 91.4–92.5 °C; R_f = 0.21; (hexane/EtOAc, 10:1).

IR (KBr): 3021, 1650 (C=O), 1595, 1483, 1285, 1248, 1213, 1162, 1021, 757, 727, 694, 673, 566, 523, 514 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = 7.0 Hz, 1 H), 7.00 (s, 1 H), 6.82 (d, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = 7.0 Hz, 2 H), 7.14–7.33 (m, 5 H), 7.39 (t, *J* = 7.0 Hz, 1 H), 7.43–7.45 (m, 2 H), 7.85 (d, *J* = 9.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 111.9, 120.3, 126.8, 127.6, 127.8, 128.2, 128.5, 128.8, 132.0, 134.5, 136.0, 138.2, 144.3, 159.4, 197.6.

MS (EI): *m*/*z* (%) = 316 (3) [M + 2^+], 315 (23) [M + 1^+], 314 (94) [M^+], 178 (22), 135 (100), 92 (13), 77 (20), 51 (4).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{22}H_{18}O_2$: 314.1307; found: 314.1305.

3,4-Bis(4-methoxyphenyl)-5-phenylfuran-2(5*H*)-one (7a) (Table 3, Entry 2)[10]

Yield: 42.1 mg (11%); colorless liquid; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (neat): 2933, 2837, 1750 (C=O), 1605, 1517, 1253, 1025, 835 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 3.84 (s, 3 H), 6.21 (s, 1 H), 6.72 (d, *J* = 9.5 Hz, 2 H), 6.91 (d, *J* = 8.5 Hz, 2 H), 7.11 (d, *J* = 9.0 Hz, 2 H), 7.29–7.34 (m, 5 H), 7.45 (d, *J* = 9.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.16, 55.21, 83.4, 114.0, 122.4, 123.4, 124.9, 127.7, 128.9, 129.3, 129.9, 130.7, 135.3, 157.4, 159.8, 160.6, 173.0.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{24}H_{20}NaO_4$: 395.1259; found: 395.1259.

3,4-Bis(4-methoxyphenyl)-5-hydroxymethyl-5-phenylfuran-2(5*H*)-one (8a) (Table 3, Entry 2)

Yield: 196.4 mg (49%); colorless liquid; R_f = 0.14 (hexane/EtOAc, 2:1).

IR (neat): 3451, 2934, 2837, 1751 (C=O), 1606, 1516, 1251, 1175, 828 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.52 (br, 1 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 4.19–4.29 (m, 2 H), 6.76–7.34 (m, 13 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.2, 31.7, 55.1, 64.0, 69.7, 90.8, 113.6, 114.2, 122.1, 124.0, 125.9, 126.8, 128.6, 128.7, 129.9, 130.0, 130.6, 135.6, 159.6, 160.1, 160.7, 173.0.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{25}H_{22}NaO_5$: 425.1365; found: 425.1365.

3,4,5-Tris(4-methoxyphenyl)furan-2(5*H*)-one (7b) (Table 3, Entry 1)[10]

Yield: 53.1 mg (13%); colorless liquid; R_f = 0.19 (hexane/EtOAc, 2:1).

IR (neat): 3003, 2933, 2837, 1747 (C=O), 1606, 1513, 1457, 1252, 1177, 1029, 833 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H), 6.18 (s, 1 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.84 (d, *J* = 9.0 Hz, 2 H), 6.91 (d, *J* = 9.0 Hz, 2 H), 7.10 (d, *J* = 9.0 Hz, 2 H), 7.22 (d, *J* = 9.0 Hz, 2 H), 7.44 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.13, 55.17, 55.2, 83.1, 114.0, 114.1, 114.2, 122.5, 122.7, 124.0, 127.2, 127.5, 128.7, 129.1, 129.7, 130.0, 130.2, 130.7, 131.1, 149.9, 157.6, 160.1, 160.5, 172.4.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{25}H_{22}NaO_5$: 425.1365; found: 425.1365.

5-(Hydroxymethyl)-3,4,5-tris(4-methoxyphenyl)furan-2(5*H*)-one (8b) (Table 3, Entry 1)

Yield: 238.7 mg (55%); colorless liquid; R_f = 0.11 (hexane/EtOAc, 2:1).

IR (neat): 3451, 2958, 2934, 2837, 1747 (C=O), 1607, 1513, 1253, 1175, 1031, 833 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.35–2.37 (m, 1 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 3.82 (s, 3 H), 4.14–4.27 (m, 2 H), 6.78 (d, *J* = 9.0 Hz, 4 H), 6.86–6.88 (m, 4 H), 7.18 (d, *J* = 9.0 Hz, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.02, 55.06, 55.14, 64.0, 90.4, 113.5, 113.9, 114.0, 122.1, 123.2, 123.9, 126.4, 127.2, 127.3, 129.9, 130.5, 159.4, 159.6, 160.0, 160.5, 172.8.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{26}H_{24}NaO_5$: 455.1471; found: 455.1471.

3,4-Bis(4-methoxyphenyl)-5-[4-(trifluoromethyl)phenyl]furan-2(5*H*)-one (7e) (Table 3, Entry 3)[10]

Yield: 48.0 mg (11%); colorless liquid; R_f = 0.28 (hexane/EtOAc, 2:1).

IR (neat): 2916, 1752 (C=O), 1606, 1507, 1254, 1124, 834 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 3.81 (s, 3 H), 6.28 (s, 1 H), 6.72 (d, *J* = 8.5 Hz, 2 H), 6.89 (d, *J* = 9.0 Hz, 2 H), 7.09 (d, *J* = 9.0 Hz, 2 H), 7.40–7.43 (m, 4 H), 7.56 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.2, 55.3, 82.3, 114.1, 114.3, 122.0, 123.0, 125.1, 125.9 (q, J_{C-F} = 3.5 Hz), 128.0, 129.8, 130.7, 139.4, 157.0, 160.8, 172.7.

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{25}H_{19}F_3NaO_4$: 463.1133; found: 463.1133.

3,4-Bis(4-methoxyphenyl)-5-hydroxymethyl-5-[4-(trifluoromethyl)phenyl]furan-2(5*H*)-one (8e) (Table 3, Entry 3)

Yield: 166.1 mg (35%); colorless liquid; R_f = 0.14 (hexane/EtOAc, 2:1).

IR (neat): 2916, 1752 (C=O), 1606, 1507, 1254, 1124, 834 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (t, *J* = 10.0 Hz, 1 H), 3.77 (s, 3 H), 3.82 (s, 3 H), 4.24 (d, *J* = 6.5 Hz, 2 H), 6.77 (d, *J* = 9.0 Hz, 2 H), 6.84–6.89 (m, 4 H), 7.33–7.36 (m, 4 H), 7.59 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.1, 55.2, 64.3, 90.4, 113.6, 114.4, 121.6, 123.7 (q, $^1J_{C-F}$ = 270.6 Hz), 124.8, 125.4 (q, $^3J_{C-F}$ = 3.6 Hz), 126.3, 127.1, 129.8, 130.5, 135.7 (q, $^2J_{C-F}$ = 32.6 Hz), 139.7, 159.6, 160.2, 172.5.

HRMS (ESI): *m*/*z* [M + Na $^+$] calcd for $C_{26}H_{21}F_3NaO_5$: 493.1239; found: 493.1239.

3,4-Bis[4-(trifluoromethyl)phenyl]-5-phenylfuran-2(5*H*)-one (10a) (Table 3, Entry 5)[10]

Yield: 23.8 mg (5%); colorless liquid; R_f = 0.42 (hexane/EtOAc, 2:1).

IR (neat): 2920, 1763 (C=O), 1324, 1168, 1128, 1018 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.28 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.36–7.54 (m, 6 H), 7.58 (d, *J* = 8.0 Hz, 3 H), 7.64 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 69.6, 83.9, 125.7 (q, J_{C-F} = 3.5 Hz), 126.0 (q, J_{C-F} = 3.5 Hz), 127.5, 128.6, 128.9, 129.1, 129.2, 129.7, 129.8, 136.0, 158.8, 171.4.

MS (EI): *m*/*z* (%) = 448 (32) [M$^+$], 447 (8), 343 (6), 314 (35), 295 (9), 210 (18), 173 (100), 134 (79), 105 (97), 77 (30).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{24}H_{14}F_6O_2$: 448.0898; found: 448.0897.

3,4-Bis[4-(trifluoromethyl)phenyl]-5-hydroxymethyl-5-phenylfuran-2(5*H*)-one (11a) (Table 3, Entry 5)

Yield: 199.5 mg (42%); colorless liquid; R_f = 0.33 (hexane/EtOAc, 2:1).

IR (neat): 3403, 3081, 2920, 1753 (C=O), 1617, 1328, 1166, 1123, 826 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.54 (dd, *J* = 8.5, 5.0 Hz, 1 H), 4.26 (qd, *J* = 21.0, 12.5, 9.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.15–7.17 (m, 2 H), 7.36–7.40 (m, 3 H), 7.49 (dd, *J* = 24.0, 8.0 Hz, 4 H), 7.59 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 63.6, 91.4, 123.6 (q, $^1J_{C-F}$ = 270.0 Hz), 123.7 (q, $^1J_{C-F}$ = 271.3 Hz), 125.3 (q, $^3J_{C-F}$ = 3.8 Hz), 125.5, 125.9 (q, $^3J_{C-F}$ = 3.6 Hz), 127.9, 128.8, 129.0, 129.3, 129.5, 130.7 (q, $^2J_{C-F}$ = 31.3 Hz), 131.6 (q, $^2J_{C-F}$ = 32.5 Hz), 132.4, 134.0, 134.9, 162.9, 171.7.

HRMS (ESI): *m*/*z* [M + Na $^+$] calcd for $C_{25}H_{16}F_6NaO_3$: 501.0901; found: 501.0901.

3,4-Bis[4-(trifluoromethyl)phenyl]-5-(4-methoxyphenyl)furan-2(5*H*)-one (10b) (Table 3, Entry 4)[10]

Yield: 28.2 mg (6%); colorless liquid; R_f = 0.36 (hexane/EtOAc, 2:1).

IR (neat): 3059, 2925, 2853, 1757 (C=O), 1612, 1548, 1324, 1168, 1068 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.25 (s, 1 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 7.19 (t, *J* = 9.0 Hz, 4 H), 7.51 (d, *J* = 5.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 10.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 63.6, 91.2, 114.3, 123.6 (q, $^1J_{C-F}$ = 270.6 Hz), 123.7 (q, $^1J_{C-F}$ = 270.5 Hz), 125.3 (q, $^3J_{C-F}$ = 3.6 Hz), 125.672, 126.6 (q, $^3J_{C-F}$ = 3.6 Hz), 127.0, 127.7, 128.8, 129.5, 130.7 (q, $^2J_{C-F}$ = 32.3 Hz), 131.3 (q, 2JC–F = 32.1 Hz), 131.7, 132.5, 135, 160.1, 162.9, 171.7

MS (EI): *m*/*z* (%) = 478 (45) [M$^+$], 459 (8), 421 (6), 314 (35), 295 (8), 246 (4), 225 (3), 135 (100), 71(13).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{25}H_{16}F_6O_3$: 478.1004; found: 478.1004.

3,4-Bis[4-(trifluoromethyl)phenyl]-5-hydroxymethyl-5-(4-methoxyphenyl)furan-2(5*H*)-one (11b) (Table 3, Entry 5)

Yield: 291.8 mg (57%); white solid; mp 80.5–81.7 °C; R_f = 0.22 (hexane/EtOAc, 2:1).

IR (KBr): 3434, 2916, 1757 (C=O), 1613, 1514, 1325, 1257, 828 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.63 (br, 1 H), 3.83 (s, 3 H), 4.16–4.28 (m, 2 H), 6.89 (d, *J* = 9.5 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 7.49 (dd, *J* = 21.5, 8.5 Hz, 4 H), 7.58 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 63.6, 91.2, 114.3, 123.9 (q, $^1J_{C-F}$ = 272.5 Hz), 124.0 (q, $^1J_{C-F}$ = 271.3 Hz), 125.3 (q, $^3J_{C-F}$ = 3.8 Hz), 125.7, 125.8 (q, $^3J_{C-F}$ = 3.8 Hz), 127.0, 128.0, 128.8, 129.5, 131.0 (q, $^2J_{C-F}$ = 32.5 Hz), 131.6 (q, $^2J_{C-F}$ = 32.5 Hz), 131.7, 132.5, 135.0, 160.1, 162.9, 171.7.

MS (EI): *m*/*z* (%) = 508 (1) [M$^+$], 478 (100), 477 (90), 421 (13), 320 (5), 314 (72), 246 (8), 225 (6), 176 (3), 135 (100), 57 (19).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{26}H_{18}F_6O_4$: 508.1109; found: 508.1109.

5-(Hydroxymethyl)-3,4,5-tris[4-(trifluoromethyl)phenyl]furan-2(5*H*)-one (11e) (Table 3, Entry 6)

Yield: 142.1 mg (26%); white solid; mp 71.3–72.5 °C; R_f = 0.33 (hexane/EtOAc, 2:1).

IR (KBr): 3448, 2936, 1760 (C=O), 1617, 1327, 1123, 1069, 844 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.88 (br, 1 H), 4.25 (qd, *J* = 17.5, 12.5, 5.0 Hz, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 7.26–7.27 (m, 2 H), 7.47 (dd, *J* = 32.5, 8.5 Hz, 4 H), 7.63 (dd, *J* = 14.5, 8.0 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 63.8, 91.2, 122.4 (q, $^1J_{C-F}$ = 271.3 Hz), 122.46 (q, $^1J_{C-F}$ = 271.3 Hz), 122.51 (q, $^1J_{C-F}$ = 270.9 Hz), 125.2 (q, $^3J_{C-F}$ = 3.8 Hz), 125.8 (q, $^3J_{C-F}$ = 3.6 Hz), 125.8, 126.1 (q, $^3J_{C-F}$ = 3.5 Hz), 128.3, 128.7, 129.4, 129.3, 129.5, 130.6 (q, $^2J_{C-F}$ = 32.5 Hz), 131.1 (q, $^2J_{C-F}$ = 27.5 Hz), 131.6 (q, $^2J_{C-F}$ = 30.0 Hz), 131.9, 132.0, 134.4, 138.1, 162.2, 171.4.

MS (EI): *m*/*z* (%) = 546 (4) [M$^+$], 516 (90), 497 (20), 315 (100), 314 (25), 246 (12), 173 (61), 145 (17), 115 (3), 91 (2).

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{26}H_{15}F_9O_3$: 546.0877; found: 546.0877.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

We wish to thank Ms. Yoshiko Nishikawa and Ms. Mieko Yamagaki, and Mr. Shouhei Katao for assistance in obtaining HRMS and X-ray crystallographic data, respectively.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1468-8377.

References

(1) For recent reviews on hydroacylation, see: (a) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725. (b) Leung, J. C.; Krische, M. J. *Chem. Sci.* **2012**, *3*, 2202. (c) Yang, L.; Huang, H. *Catal. Sci. Technol.* **2012**, *2*, 1099.

(2) (a) First report, stoichiometric reaction, Rh: Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1965**, 3969. For catalytic Rh reactions, see: (b) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083. (c) Kreis, M.; Palmelund, A.; Bunch, L.; Madsen, R. *Adv. Synth. Catal.* **2006**, *348*, 2148. (d) Fessard, T. C.; Andrews, S. P.; Motoyoshi, H.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 9331. (e) Fristrup, P.; Kreis, M.; Palmelund, A.; Norrby, P.-O.; Madsen, R. *J. Am. Chem. Soc.* **2008**, *130*, 5206. (f) Catalytic, Ir: Iwai, T.; Fujihara, T.; Tsuji, Y. *Chem. Commun.* **2008**, 6215. (g) Catalytic, Pd: Modak, A.; Deb, A.; Patra, T.; Rana, T.; Maity, S.; Maiti, D. *Chem. Commun.* **2012**, *48*, 4253.

(3) For a selected paper on the utilization of the decarbonylation in a total synthesis, see: Zhang, H.; Padwa, A. *Tetrahedron Lett.* **2006**, *47*, 3905.

(4) For reviews on the CO-gas-free carbonylation reaction including the use of aldehydes as a carbonyl source, see: (a) Morimoto, T.; Kakiuchi, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 5580. (b) Wu, L.; Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 6310. (c) Gautam, P.; Bhanage, B. M. *Catal. Sci. Technol.* **2015**, *5*, 4663. (d) Cao, J.; Zheng, Z.-J.; Xu, Z.; Xu, L. W. *Coord. Chem. Rev.* **2017**, *336*, 43. (e) Gorbunov, D. N.; Nenasheva, M. V.; Kardasheva, Y. S.; Karakhanov, E. A. *Russ. Chem. Bull.* **2020**, *69*, 625.

(5) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **2002**, *124*, 3806.

(6) (a) Morimoto, T.; Yamazaki, K.; Hirano, A.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K.; Harada, Y.; Fukumoto, Y.; Chatani, N.; Nishioka, T. *Org. Lett.* **2009**, *11*, 1777. (b) Makado, G.; Morimoto, T.; Sugimoto, Y.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K. *Adv. Synth. Catal.* **2010**, *352*, 299. (c) Wang, C.; Morimoto, T.; Kaneshiro, H.; Tanimoto, H.; Nishiyama, Y.; Kakiuchi, K.; Artok, L. *Synlett* **2014**, *25*, 1155. (d) Furusawa, T.; Morimoto, T.; Ikeda, K.; Tanimoto, H.; Nishiyama, Y.; Kakiuchi, K.; Jeong, N. *Tetrahedron* **2015**, *71*, 875. (e) Furusawa, T.; Morimoto, T.; Nishiyama, Y.; Tanimoto, H.; Kakiuchi, K. *Chem. Asian J.* **2016**, *11*, 2312. (f) Furusawa, T.; Tanimoto, H.; Nishiyama, Y.; Morimoto, T.; Kakiuchi, K. *Adv. Synth. Catal.* **2017**, *359*, 240. (g) Furusawa, T.; Tanimoto, H.; Nishiyama, Y.; Morimoto, T.; Kakiuchi, K. *Chem. Lett.* **2017**, *46*, 926. (h) Pan, J.; Morimoto, T.; Kobayashi, H.; Tanimoto, H.; Kakiuchi, K. *Heterocycles* **2019**, *98*, 519. (i) Morimoto, T.; Yamashita, M.; Tomiie, A.; Tanimoto, H.; Kakiuchi, K. *Chem. Asian J.* **2020**, *15*, 473.

(7) For books on rhodium-catalyzed reactions in organic synthesis, see: (a) *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, **2005**. (b) *Rhodium Catalysis in Organic Synthesis*; Tanaka, K., Ed.; Wiley-VCH: Weinheim, **2019**.

(8) (a) Laduwahetty, T. *Contemp. Org. Synth.* **1995**, *2*, 133. (b) Collins, I. *Contemp. Org. Synth.* **1996**, *3*, 295. (c) Collins, I. *Contemp. Org. Synth.* **1997**, *4*, 281.

(9) Abbreviations: cod = 1,5-cyclooctadiene, dppp = 1,3-bis(diphenylphosphino)propane, BIPHEP = 2,2′-bis(diphenylphosphino)biphenyl, BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, dppf = 1,1′-ferrocenediyl-bis(diphenylphosphine), dppb = 1,3-bis(diphenylphosphino)butane.

(10) (a) Aksin, Ö.; Dege, N.; Artok, L.; Türkmen, H.; Çetinkaya, B. *Chem. Commun.* **2006**, 3187. (b) Kuş, M.; Aksin, Ö.; Ziyanak, F.; Artok, L. *Synlett* **2008**, 2587. (c) Artok, L.; Kuş, M.; Aksin-Artok, Ö.; Dege, N. F.; Özkilinç, F. Y. *Tetrahedron* **2009**, *65*, 9125.

(11) Bunten, K. A.; Farrar, D. H.; Poë, A. J.; Lough, A. *Organometallics* **2002**, *21*, 3344.

(12) James, B. R.; Mahajan, D. *Can. J. Chem.* **1977**, *57*, 180.

(13) $[RhCl(C_2H_4)_2]_2$ instead of $[RhCl(cod)]_2$ also catalyzed the reaction of **1** with **2a** in the presence of formaldehyde under the above standard conditions to give **3a** and **4a** in 64% yield (**3a**, 11%; **4a**, 53%) along with **5a** in 6% yield.

(14) The ^{31}P NMR spectrum shows that some signals for small amounts of P are also observed in the area of 20–30 ppm, which are split by coupling with a rhodium nucleus. Thus, other dppp-ligated rhodium(I) species are also present in the mixture.

(15) For $RhCl(dppp)_2$, see: (a) Shibata, T.; Toshida, N.; Takagi, K. *Org. Lett.* **2002**, *4*, 1619. (b) Shibata, T.; Toshida, N.; Takagi, K. *J. Org. Chem.* **2002**, *67*, 7446. (c) For $[RhCl(dppp)]_2$, see reference 2e.

(16) For a representative review on vinylogous aldol reactions, see: Casiraghi, G.; Zanardi, F.; Appendino, G.; Rassu, G. *Chem. Rev.* **2000**, *100*, 1929.

(17) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.