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PREPARATION OF FURANS BY PALLADIUM-CATALYZED REACTION OF ACYLCHROMATES AND PROPARGYLIC TOSYLATES

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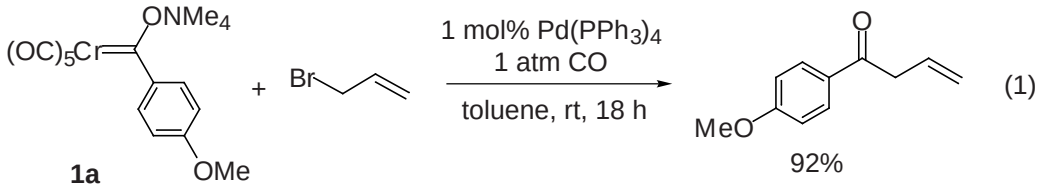
Abstract - Substituted furans are prepared by the palladium-catalyzed reaction of propargylic tosylates with acylchromates. The reaction is initiated by the oxidative additiion of propagylic tosylates to palladium(0) complexes to give 1,2-propadienylpalladium(II) complexes, which in turn react with acylchromates to form 1,2-propadienyl ketones. Then 1,2-propadienyl ketones are transformed to furans by the action of *in situ* generated $Cr(CO)_5$.

Propargyl- and 1,2-propadienyl-transition metal complexes are recognized as analogues of allylic metals,[1] and a variety of palladium-catalyzed coupling reactions have been reported by employing propargylic halides and esters. For example, in Suzuki, Stille, and Negishi couplings, these metal complexes are utilized to introduce 1,2-propadienyl or propargyl group.[2] We previously reported that acylchromate complexes are utilized as good acyl donors in the palladium-catalyzed coupling reactions.[3,4] That is, when a mixture of acylchromate (**1a**) and allyl bromide is treated with 1 mol% of $Pd(PPh_3)_4$ under 1 atm of CO, allyl ketone is obtained as shown in Eq. 1.[3]



Dedicated to Professor Yuichi Kanaoka on the occasion of his 75th birthday.

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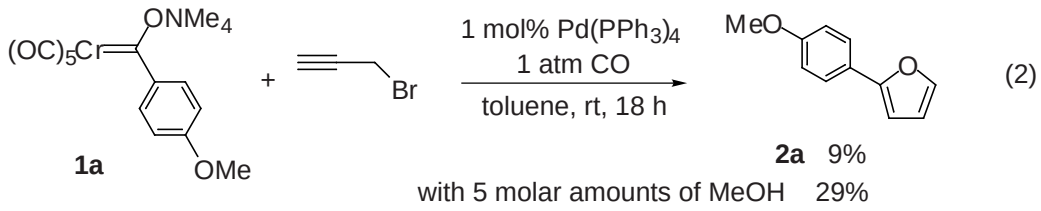
Result and Discussion

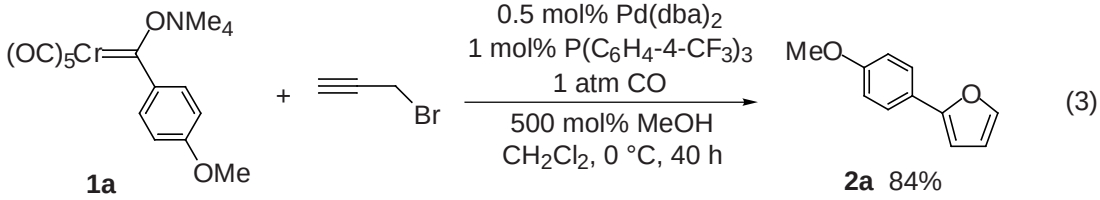
Reaction of propargyl bromide and tetramethylammonium pentacarbonyl(4-methoxybenzoyl)-chromate (1a)

Based on the above allyl ketone formation, we then examined the reaction of propargyl bromide with the expectation of the formation of propargyl and/or 1,2-propadienyl ketone. When a toluene solution of tetramethylammonium pentacarbonyl(4-methoxybenzoyl)chromate (**1a**) and propargyl bromide was treated with 1 mol% $Pd(PPh_3)_4$, however, the expected ketones were not detected and 2-(4-methoxyphenyl)furan (**2a**) was obtained in 9% yield (Eq. 2). The yield of the furan (**2a**) was increased to 29% by the addition of 5 molar amounts of methanol.



(2)

After screening the reaction conditions, furan (**2a**) was obtained in 84% yield by the treatment of **1a** with 1.5 molar amounts of propargyl bromide, 0.5 mol% bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$), 1 mol% tris(4-trifluoromethylphenyl)phosphine, and 5 molar amounts of methanol at 0 ˚C in dichloro-methane under 1 atm of CO atmosphere (Eq. 3).

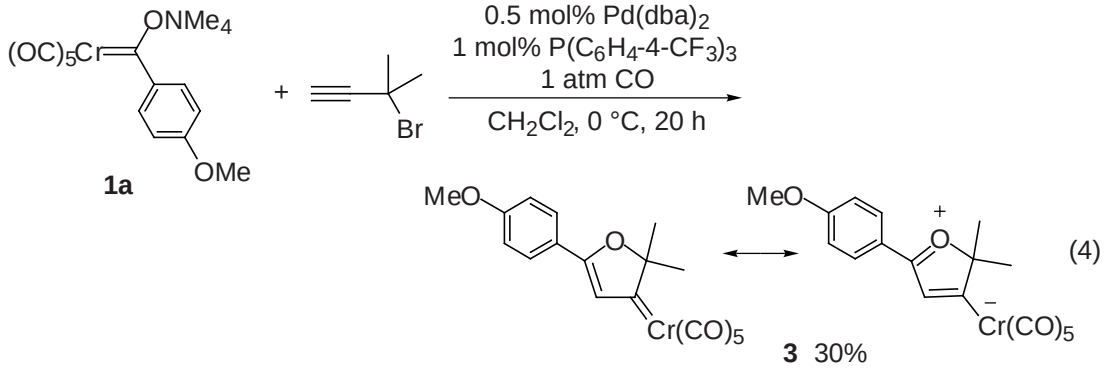


(3)

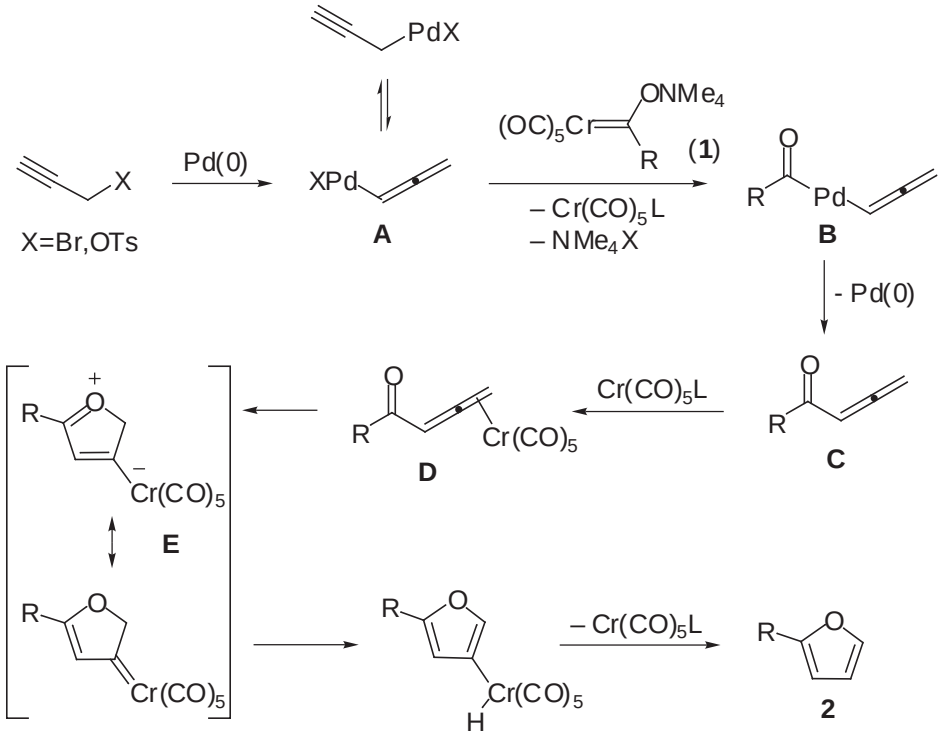
Mechanistic study of the formation of furan (2a)

When α,α-disubstituted propargyl bromide such as 3-bromo-3-methylbutyne was reacted with **1a** under the same conditions, furan was not formed but chromium carbene complex (**3**)[5] was isolated in 30% yield. Although chromium(0) dialkylcarbene complexes are generally unstable, the carbene complex (**3**) was stable enough to be isolated due to the stabilization by the conjugation with the oxygen atom. The chemical shift of ^{13}C NMR spectrum at the carbene carbon (δ = 306.1 ppm in CD_2Cl_2) indicates that the complex (**3**) has rather zwitter ionic character as compared with the corresponding Fischer-type carbene complex $(CO)_5Cr=C(OMe)(C_6H_4\text{-}4\text{-}OMe)$; δ = 340.5 ppm in $CDCl_3$[6] and acylchromate Me_4N $(CO)_5Cr$-

C(=O)(C_6H_4-4-OMe); δ = 295.6 ppm in CD_2Cl_2 (Eq. 4).



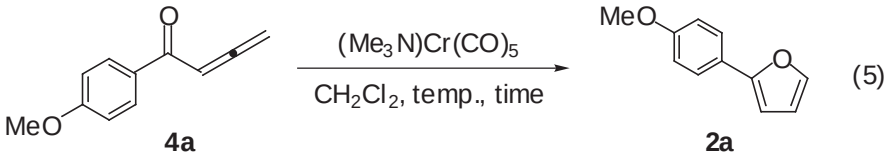
The formation of the above carbene complex revealed the route of the furan formation as dipicted in Scheme 1. To 1,2-propadienylpalladium(II) complex (**A**) generated by the oxidative addition of propargyl bromide to Pd(0) catalyst,[1] acyl transfer occurs from acylchromate (**1**) to give acyl(1,2-propadienyl)palladium(II) species (**B**) with the formation of $Cr(CO)_5$.[3] The reductive elimination of 1,2-propadienyl ketone (**C**) from **B** regenerates the Pd(0) catalyst. The released coordinatively unsaturated chromium complex, $Cr(CO)_5$, makes a π-complex (**D**) with 1,2-propadienyl ketone (**C**), and nucleophilic attack of the carbonyl oxygen to the Cr-coordinating alkenyl moiety affords a chromium



Scheme 1. Plausible mechanism of formation of furan (**2**)

carbene complex (**E**).[7-9] 1,3-Hydrogen shift[10] from the β-methylene group to the chromium center results in the formation of furan (**2**) and $Cr(CO)_5$, which is finally trapped with atmospheric carbon monoxide to give $Cr(CO)_6$. In the reaction of α,α-disubstituted propargyl bromide in Eq. 4, the reaction stopped at the stage of **E**, because there is no hydrogen for the 1,3-shift. Although the role of methanol is not clear yet, it can be considered that methanol might protonate the anionic chromium center of **E** to facilitate the 1,3-hydrogen shift.

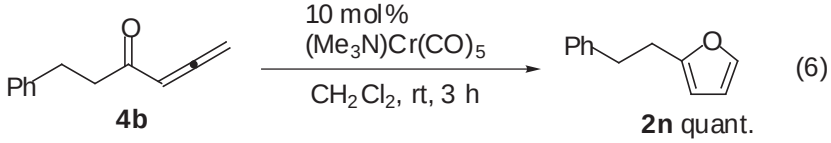
To prove the transformation of 1,2-propadienyl ketone (**C**) to furan (**2**) was examined the cyclization of 1,2-propadienyl ketone with pentacarbonylchromium, $Cr(CO)_5$. As it is known that pentacarbonyl-(trimethylamine)chromium(0), $(Me_3N)Cr(CO)_5$, exists in equilibrium with $Cr(CO)_5$ and trimethylamine in appropriate solvents,[11] the transformation of 4-methoxyphenyl 1,2-propadienyl ketone (**4a**) to furan (**2a**) was examined in the presence of $(Me_3N)Cr(CO)_5$. In fact, furan (**2a**) was obtained in good yield irrespective of the amount of $(Me_3N)Cr(CO)_5$ (Table 1). In addition, phenethyl 1,2-propadienyl ketone (**4b**) also cyclized to give furan (**2n**) quantitatively (Eq. 6). Thus the coordinatively unsaturated chromium complex functions as a good catalyst in the transformation of 1,2-propadienyl ketones to furans.[8,9]



4a **2a** (5)

Table 1. Cyclization of 4-methoxyphenyl-1,2-propadienylketone (**4a**)

entry	$(Me_3N)Cr(CO)_5$ / mol%	temp.	time	yield / %
1	100	0 ˚C	30 h	85
2	10	0 ˚C	20 h	85
3	10	rt	14 h	85



4b **2n** quant. (6)

Reaction of propargylic bromides with acylchromates

The reactions of some propargylic bromides with acylchromates were examined as listed in Table 2. The combination of aroylchromates bearing electron donating group with propargyl bromide or α-substituted propargylic bromides was suitable to form furans (entries 1,2,5, and 6), whereas the corresponding furans were obtained in poor yields when aroylchromates bearing electron withdrawing group and alkanoylchromate were employed (entries 3 and 4). The reaction of γ-subsutituted propargyl bromides

also afforded the furans (**2**) and the regioisomers (**5**) in poor total yield (entries 7 and 8). The regioisomer (**5**) seemed to be obtained *via* propargylpalladium(II) intermediate, which is known to be formed reversibly from 1,2-propadienylpalladium(II) (**A**) in Scheme 1.[1]

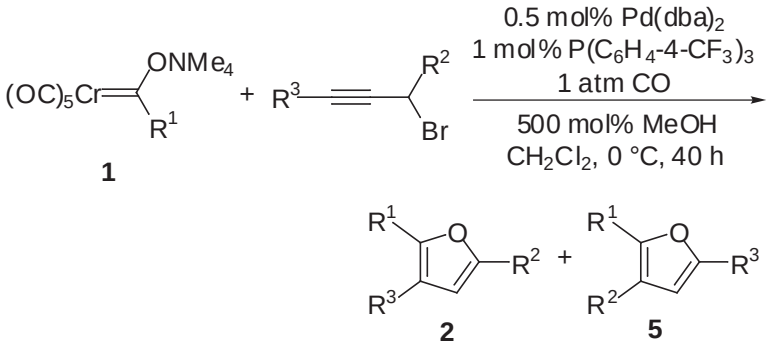


Table 2. Reaction with propargylic bromide[a)]

entry	R^1	R^2	R^3	yield / % **2**	**5**
1[b)]	4-$MeOC_6H_4$	H	H	84 (**2a**)	
2	Ph	H	H	74 (**2b**)	
3	4-$CF_3C_6H_4$	H	H	32 (**2c**)	
4[c)]	*n*-Bu	H	H	47 (**2d**)	
5	4-$MeOC_6H_4$	Me	H	78 (**2e**)	0
6	4-$MeOC_6H_4$	*n*-Bu	H	73 (**2f**)	0
7[d)]	4-$MeOC_6H_4$	H	Me	16 (**2g**)	1 (**5g**)
8[d)]	4-$MeOC_6H_4$	H	Ph	16 (**2h**)	<1 (**5h**)

a) 1.5 Molar amounts of propargylic bromide was used.
b) In the absence of MeOH, **2a** was obtained in 64% yield.
c) Determined by ^{1}H NMR spectral analysis.
d) The mixture of **2** and **5** was isolated.
The yields of **2** and **5** were determined by ^{1}H NMR spectral analysis.

Reaction of propargylic tosylates with acylchromates

Since propargyl bromides did not exhibit a wide applicability to the furan synthesis, various propargyl derivatives were screened as shown in Table 3. Propargyl acetate and carbamate were not active and recovered at 0 ˚C (entries 3 and 4), and the reactions of propargyl chloride, trifluoroacetate, and diethylphosphate gave only a small amount of furan (**2a**) as entries 2, 5, and 6. By the use of propargyl tosylate, furan (**2a**) was obtained in 74% yield (entry 7). In this case, triphenylphosphine was found as a good ligand, and the yield of furan (**2a**) was increased to 95% (entry 9). In the reaction of propargyl tosylate the addition of methanol exhibited no effect in the product yield (entry 8). It could be considered that 1,3-hydrogen shift might be promoted by *in situ* generated tetramethylammonium tosylate.[10]

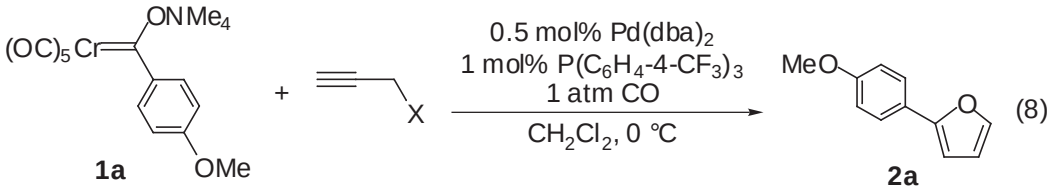


Table 3. Investigation of propargyl derivatives[a)]

entry	X	yield/%
1	Br[b)]	84
2	Cl	24
3	OAc	0
4	OCO_2Me	0
5	$OCOCF_3$	8
6	$OPO(OEt)_2$	4
7	OTs	74
8	OTs[b)]	70
9	OTs[c)]	95

a) 1.5 Molar amounts of propargyl derivatives were used.
b) 500 mol% MeOH was added.
c) 1.2 Molar amounts of propargyl tosylate and PPh_3 as a ligand were used.

In the group 6 acyl metal complexes such as Cr, Mo, W, furan (**2a**) was formed in high yield only when acylchromate (**1a**) was employed (Table 4, entries 1-3). Various aroylchromates reacted smoothly with propargyl tosylate and alkanoylchromate also gave 2-butylfuran in a moderate yield (entries 4-10). 2,5-Disubstituted furans (**2**) were produced regioselectively without forming 2,3-disubstituted isomers by the reaction of α-substituted propargyl tosylates (entries 11 and 12). Based on the equilibrium of 1,2-propadienyl and propargyl palladium intermediates, this particular regioselectivity is well explained by the formation of less hindered 3-substituted 1,2-propadienyl intermediate rather than α-substituted propargyl intermediate.[1] In contrast, two regioisomers were formed in rather low yields by the reaction of γ-subsutituted propargyl tosylates (entries 13 and 14).

Conclusion

Various substituted furans are synthesized by the reaction of acylchromates with propargylic tosylates in the presence of a palladium catalyst. It was also noted that the coordinatively unsaturated chromium complex, $Cr(CO)_5$, catalyzes the cyclization of 1,2-propadienyl ketones to furans effectively. Thus, acylchromate acts as $Cr(CO)_5$ sources as well as good acyl donors to palladium(II) intermediates.

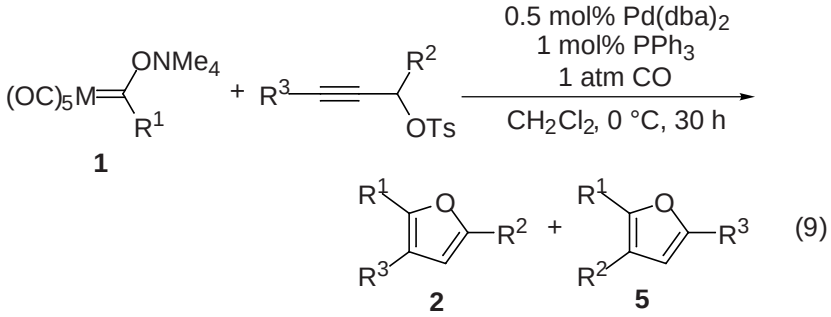


Table 4. Reaction with propargylic tosylate[a)]

entry	M	R^1	R^2	R^3	yield / % **2**	**5**
1	Cr	4-$MeOC_6H_4$	H	H	95	
2	Mo	4-$MeOC_6H_4$	H	H	10	
3	W	4-$MeOC_6H_4$	H	H	30	
4	Cr	4-$Me_2NC_6H_4$	H	H	87 (**2i**)	
5	Cr	2-$MeOC_6H_4$	H	H	86 (**2j**)	
6	Cr	4-$CH_3C_6H_4$	H	H	85 (**2k**)	
7	Cr	Ph	H	H	85	
8	Cr	4-BrC_6H_4	H	H	65 (**2l**)	
9	Cr	4-$CF_3C_6H_4$	H	H	63	
10[b)]	Cr	*n*-Bu	H	H	59	
11	Cr	4-$MeOC_6H_4$	Me	H	96	0
12	Cr	4-$MeOC_6H_4$	*n*-C_5H_{11}	H	91 (**2m**)	0
13[c)]	Cr	4-$MeOC_6H_4$	H	Me	17	18
14[c)]	Cr	4-$MeOC_6H_4$	H	Ph	33	10

a) 1.2 Molar amounts of propargylic tosylate was used.
b) Determined by ^{1}H NMR spectral analysis.
c) The mixture of **2** and **5** was isolated.
The yields of **2** and **5** were determined by ^{1}H NMR spectral analysis.

EXPERIMENTAL

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DRX 500 spectrometer in $CDCl_3$ or CD_2Cl_2 solutions using $CHCl_3$ (for ^{1}H, δ = 7.24 ppm), $CDCl_3$ (for ^{13}C, δ = 77.00 ppm), CH_2Cl_2 (for ^{1}H, δ = 5.32 ppm) and CD_2Cl_2 (for ^{13}C, δ = 53.20 ppm) as internal standards. IR spectra were recorded on Horiba FT 300-S spectrophotometer. HRMS spectra were obtained with JEOL JMS-SX102A mass spectrometer at an ionization energy of 70 eV. The melting points were uncorrected. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo. TLC was carried out on a silica gel (Wakogel B-5F). Dichloromethane was distilled from P_2O_5, then from CaH_2, and dried over MS 4A. Methanol was distilled from magnesium methoxide, and dried over MS 3A. Bis(dibenzylideneacetone)-

palladium(0) ($Pd(dba)_2$) was purchased from Tokyo Kasei Kogyo Co., Ltd. Phosphines were purchased from Tokyo Kasei Kogyo Co., Ltd. or Strem Chemicals Inc. and recrystallized from ethanol. Pentacarbonyl(trimethylamine)chlomium(0) was prepared according to the literature procedure.[11] Ammonium cerium(IV) nitrate (CAN) was purchased from Aldrich Chemical Co., Inc. 1-Bromo-2-propyne and 1-bromo-2-butyne were purchased from Tokyo Kasei Kogyo Co., Ltd. or Aldrich Chemical Co., Inc. and distilled from CaH_2. The other propargylic bromides,[12] propargylic tosylates,[13] propargyl acetate,[14] propargyl trifluoroacetate,[15] propargyl carbamate,[16] and diethyl propargylphosphate[17] were prepared from the corresponding propargylic alcohols according to the literature procedures. 1,2-Propadienyl ketones were prepared according to the literature procedure.[9]

General Procedure for Preparation of Tetramethylammonium Pentacarbonylacylchromates

Acylchromates were prepared by the procedure described by E. O. Fischer.[18] To a solution of 4-bromoanisole (19.25 g, 102.9 mmol) in ether (100 mL), *n*-butyllithium (66.0 mL, 1.56 M in hexane, 102.9 mmol) was added at – 78 ˚C under argon atmosphere, then the solution warmed gradually to 0 ˚C. To a slurry of chromium hexacarbonyl (22.02 g, 100.1 mmol) in ether (2.0 L) the solution of the aryl lithium was slowly added at 0 ˚C. After the resulting brown solution was stirred at 0 ˚C for 2 h, the solvent was removed under reduced pressure. The residue was desolved in degassed water (300 mL), and was quickly filtered through Celite into a degassed water solution (35 mL) of tetramethylammonium bromide (16.53 g, 107.3 mmol). The precipitate was filtered, and dried *in vacuo* to give **1a** (34.78 g, 87%).

Typical Procedure for Reaction of Acylchromates and Propargylic Bromides

All the reactions were carried out under 1 atm of CO by using balloon. To a solution of tetrametyl-ammonium pentacarbonyl(4-methoxybenzoyl)chromate (**1a**) (80.7 mg, 0.201 mmol), propargyl bromide (35.3 mg, 0.297 mmol) and methanol (41 μL, 1.01 mmol) in dichloromethane (3 mL) was added a solution of tris(4-trifluoromethylphenyl)phosphine (1.00 mg, 2.14 μmol) and bis(dibenzylideneacetone)-palladium(0) (0.595 mg, 1.03 μmol) in dichloromethane (2 mL). The mixture was stirred for 40 h at 0 ˚C. After the mixture was filtered through Celite, the solvent was removed *in vacuo*. The crude materials were purified by TLC (silica gel, hexane : ethyl acetate = 9 : 1) to give 2-(4-methoxyphenyl)-furan (**2a**) (29.5 mg, 84%) as colorless crystals.

Typical Procedure for Reaction of Acylchromates and Propargylic Tosylates

All the reactions were carried out under 1 atm of CO by using balloon. To a solution of tetrametyl-ammonium pentacarbonyl(4-methoxybenzoyl)chromate (**1a**) (79.6 mg, 0.198 mmol) and propargyl tosylate (49.2 mg, 0.234 mmol) in dichloromethane (3 mL) was added a solution of triphenylphosphine

(0.532 mg, 2.03 μmol) and bis(dibenzylideneacetone)palladium(0) (0.568 mg, 0.988 μmol) in dichloromethane (2 mL). The mixture was stirred for 30 h at 0 ˚C. The mixture was filtered through Celite, concentrated, and purified by TLC (silica gel, hexane : ethyl acetate = 9 : 1), which afforded 2-(4-methoxyphenyl)furan (**2a**) (32.8 mg, 95%) as colorless crystals.

Typical Procedure for the Cyclization of 1,2-Propadienyl Ketone

Pentacarbonyl(trimethylamine)chromium(0) (6.4 mg, 25.5 μmol) added to a solution of phenethyl-1,2-propadienyl ketone (**4b**) (42.9 mg, 0.249 mmol) in dichloromethane (2 mL). After the mixture was stirred for 3 h at rt under argon atomosphere, the solvent was removed *in vacuo*, and the crude materials were purified by TLC (silica gel, hexane : ethyl acetate = 19 : 1) to give 2-phenethylfuran (**2n**) (42.9 mg, 100%) as a colorless oil.

Procedure for the Reaction of 3-Bromo-3-methylbutyne and Acylchromate (1a)

The reaction was carried out under 1 atm of CO by using balloon. To a solution of tetramethyl-ammonium pentacarbonyl(4-methoxybenzoyl)chromate (**1a**) (456.1 mg, 1.14 mmol), 3-bromo-3-methylbutyne (252.6 mg, 1.72 mmol) in dichloromethane (15 mL) was added a solution of tris(4-trifluoromethylphenyl)phosphine (5.4 mg, 11.6 μmol) and bis(dibenzylideneacetone)palladium(0) (3.3 mg, 5.74 μmol) in dichloromethane (10 mL). The mixture was stirred for 20 h at 0 ˚C. After the removal of the solvent *in vacuo* under argon atomosphere, the residue was purified by column chromatography (silica gel, hexane : ethyl acetate = 9 : 1) at 0 ˚C under argon atomosphere to give pentacarbonyl(2,2-dimethyl-4-(4-methoxyphenyl)-3-oxa-4-cyclopentylidene)chromium(0) (**3**) (134.6 mg, 30%) as a purple oil.

Spectral Data

2-(4-Methoxyphenyl)furan (2a)[19]: Colorless crystals; mp 53 ˚C (hexane) (lit., 52 - 53 ˚C (MeOH)); IR (KBr) 1483, 1248, 1028, 833, 800, 631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.82 (3H, s), 6.43 (1H, dd, *J* = 1.6, 3.2 Hz), 6.50 (1H, d, *J* = 3.2 Hz), 6.91 (2H, d, *J* = 7.8 Hz), 7.41 (1H, d, *J* = 1.6 Hz), 7.59 (2H, d, *J* = 7.8 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 55.3, 103.3, 111.4, 114.1, 124.1, 125.2, 141.3, 154.0, 159.0 ppm.

2-Phenylfuran (2b)[19]: Colorless oil; IR (neat) 1606, 1506, 760, 733, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.39 (1H, dd, *J* = 1.4, 3.0 Hz), 6.57 (1H, d, *J* = 3.0 Hz), 7.17 (1H, t, *J* = 7.3 Hz), 7.30 (2H, dt, *J* = 7.3, 7.3 Hz), 7.39 (1H, d, *J* = 1.4 Hz), 7.59 (2H, d, *J* = 7.3 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 104.9, 111.6, 123.8, 127.3, 128.6, 130.9, 142.0, 154.0 ppm.

2-(4-Trifuluoromethylphenyl)furan (2c)[20]: Colorless crystals; mp 88 - 89 ˚C (hexane); IR (KBr) 1479, 846, 810, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.43 (1H, dd, *J* = 1.1, 3.2 Hz), 6.69 (1H, d, *J* = 3.2 Hz), 7.44 (1H, d, *J* = 1.1 Hz), 7.69 (2H, d, *J* = 7.9 Hz), 7.94 (2H, d, *J* = 7.9 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ =

106.9, 111.9, 123.7, 124.1 (q, J_{CF} = 270.3 Hz), 125.7 (q, J_{CF} = 3.8 Hz), 128.9 (q, J_{CF} = 32.1 Hz), 133.9, 143.1, 152.5 ppm; Anal. Calcd for $C_{11}H_7OF_3$: C, 62.27; H, 3.33. Found: C, 62.08; H, 3.59.

2-*n*-Butylfuran (2d)[21]: Furan (**2d**) was not isolated; ^{1}H NMR ($CDCl_3$) δ = 0.88 (3H, t, *J* = 7.6 Hz), 1.25 (2H, tq, *J* = 7.6, 7.6 Hz), 1.55 (2H, tt, *J* = 7.3, 7.6 Hz), 2.55 (2H, t, *J* = 7.3 Hz), 5.89 (1H, dd, *J* = 0.8, 2.4 Hz), 6.20 (1H, d, *J* = 2.4 Hz), 7.22 (1H, d, *J* = 0.8 Hz) ppm.

2-(4-Methoxyphenyl)-5-methylfuran (2e)[22]: Furan (**2e**) and furan (**5g**) were identical; Colorless crystals; mp 38 ˚C (hexane) (lit., 38 - 40 ˚C (ether – haxane)); IR (KBr) 1500, 1249, 1020, 833, 787 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.34 (3H, s), 3.81 (3H, s), 6.00 (1H, d, *J* = 3.0 Hz), 6.37 (1H, d, *J* = 3.0 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 7.54 (2H, d, *J* = 8.4 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 13.7, 55.3, 104.2, 107.5, 114.0, 124.4, 124.7, 151.1, 152.3, 158.6 ppm.

2-Butyl-5-(4-methoxyphenyl)furan (2f): Colorless oil; IR (neat) 1579, 1456, 1249, 1031, 831, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.94 (3H, t, *J* = 7.0 Hz), 1.39 (2H, tq, *J* = 7.3, 7.0 Hz), 1.66 (2H, tt, *J* = 7.0, 7.3 Hz), 2.66 (2H, t, *J* = 7.0 Hz), 3.80 (3H, s), 6.01 (1H, d, *J* = 2.4 Hz), 6.39 (1H, d, *J* = 2.4 Hz), 6.89 (2H, d, *J* = 8.6 Hz), 7.55 (2H, d, *J* = 8.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 13.9, 22.3, 27.8, 30.2, 55.3, 104.0, 106.6, 114.0, 124.4, 124.7, 152.1, 155.7, 158.5 ppm; Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.17; H, 8.05.

2-(4-Methoxyphenyl)-3-methylfuran (2g): Furan (**2g**) was not separated from furan (**2e**). The yield was determined by ^{1}H NMR spectral analysis; IR (KBr) 1498, 1249, 1035, 955, 887, 793 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.23 (3H, s), 3.82 (3H, s), 6.29 (1H, d, *J* = 1.6 Hz), 6.93 (2H, d, *J* = 8.6 Hz), 7.32 (1H, d, *J* = 1.6 Hz), 7.53 (2H, d, *J* = 8.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 11.7, 55.3, 114.0, 114.6, 114.9, 124.8, 126.8, 140.1, 148.7, 158.4 ppm.

2-(4-Methoxyphenyl)-3-phenylfuran (2h): Furan (**2h**) was not separated from furan (**5h**). The yield was determined by ^{1}H NMR spectral analysis; IR (KBr) 1570, 1483, 1253, 1024, 943, 891, 833 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.73 (3H, s), 6.47 (1H, d, *J* = 1.6 Hz), 6.76 (2H, d, *J* = 7.8 Hz), 7.20 - 7.55 (8H, m) ppm; ^{13}C NMR ($CDCl_3$) δ = 55.2, 113.7, 113.8, 120.8, 124.0, 126.9, 127.8, 128.6, 128.6, 134.4, 141.0, 148.6, 159.0 ppm.

2-(4-*N*,*N*-Dimethylaminophenyl)furan (2i)[23]: Colorless crystals; mp 66 - 67 ˚C (hexane) (lit., 66 - 67 ˚C); IR (KBr) 1487, 1360, 822, 781, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.97 (6H, s), 6.42 (1H, d, *J* = 1.1 Hz), 6.73 (2H, d, *J* = 8.9 Hz), 7.38 (1H, d, *J* = 1.1 Hz), 7.54 (2H, d, *J* = 8.9 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 40.5, 102.0, 111.4, 112.4, 119.9, 125.0, 140.7, 149.9, 154.9 ppm.

2-(2-Methoxyphenyl)furan (2j): Colorless oil; IR (neat) 1489, 1245, 1025, 902, 813, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.86 (3H, s), 6.41 (1H, dd, *J* = 1.6, 3.2 Hz), 6.87 (1H, d, *J* = 3.2 Hz), 6.89 (1H, dd, *J* =

0.8, 7.8 Hz), 6.94 (1H, ddd, *J* = 0.8, 7.6, 7.8 Hz), 7.17 (1H, ddd, *J* = 1.6, 7.8, 7.8 Hz), 7.38 (1H, d, J = 1.6 Hz), 7.77 (1H, dd, *J* = 1.6, 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 55.2, 113.7, 120.4, 124.0, 126.9, 127.8, 128.6, 134.5, 141.0, 148.6, 159.0 ppm; Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.88; H, 5.85.

2-(4-Methylphenyl)furan (2k)[18]: Colorless oil; IR (neat) 1558, 1484, 819, 794, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.35 (3H, s), 6.44 (1H, dd, *J* = 1.6, 3.2 Hz), 6.57 (1H, d, *J* = 3.2 Hz), 7.17 (2H, d, *J* = 7.8 Hz), 7.43 (1H, d, *J* = 1.6 Hz), 7.56 (2H, d, *J* = 7.8 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 21.2, 104.2, 111.5, 123.8, 128.2, 129.3, 137.1, 141.6, 154.2 ppm.

2-(4-Bromophenyl)furan (2l)[24]: Colorless crystals; mp 85 ˚C (hexane) (lit., 85 - 86 ˚C); IR (KBr) 1495, 829, 806, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 6.46 (1H, d, *J* = 3.2 Hz), 6.63 (2H, d, *J* = 8.6 Hz), 7.42 - 7.55 (5H, m) ppm; ^{13}C NMR ($CDCl_3$) δ = 105.5, 111.8, 121.1, 125.3, 129.8, 131.8, 142.4, 152.9 ppm.

2-(4-Methoxyphenyl)-5-pentylfuran (2m)[25]: Colorless crystals; mp 129 ˚C (hexane) (lit., 129 - 131 ˚C); IR (KBr) 1579, 1500, 1250, 1032, 831, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.90 (3H, t, *J* = 6.8 Hz), 1.34 - 1.36 (4H, m), 1.76 (2H, m), 2.65 (2H, t, *J* = 7.6 Hz), 3.81 (3H, s), 6.01 (1H, d, *J* = 3.0 Hz), 6.39 (1H, d, *J* = 3.0 Hz), 6.89 (2H, d, *J* = 8.6 Hz), 7.55 (2H, d, *J* = 8.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 14.0, 22.4, 27.8, 28.1, 31.4, 55.3, 104.0, 106.6, 114.0, 124.5, 124.7, 152.1, 155.7, 158.6 ppm.

2-Phenethylfuran (2n)[26]: Colorless oil; IR (neat) 1601, 1506, 1012, 926, 833, 798 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.91 (4H, s like), 5.96 (1H, d, *J* = 3.0 Hz), 6.27 (1H, dd, *J* = 2.2, 3.0 Hz), 7.16 - 7.32 (6H, m) ppm; ^{13}C NMR ($CDCl_3$) δ = 29.9, 34.4, 105.1, 110.1, 126.0, 128.3, 140.8, 141.2, 155.3 ppm; Anal. Calcd for $C_{12}H_{12}O$: C, 83.45; H, 7.16. Found: C, 83.69; H, 7.02.

Pentacarbonyl(2,2-dimethyl-4-(4-methoxyphenyl)-3-oxa-4-cyclopentylidene)chromium(0) (3): purple oil; IR (neat): 2046, 1968, 1940 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ = 1.87 (6H, s), 3.98 (3H, s), 7.11 (2H, d, *J* = 7.9 Hz), 7.80 (1H, s), 8.09 (2H, d, *J* = 7.9 Hz) ppm; ^{13}C NMR (CD_2Cl_2) δ = 23.7, 29.6, 55.8, 91.9, 115.1, 130.4, 133.3, 165.9, 167.4, 176.4, 218.5, 226.7, 306.1 ppm; HR-FABMS Calcd for $C_{18}H_{14}O_7Cr$+H, 395.0223. Found: *m/z* 395.0232.

4-Methoxyphenyl 1,2-Propadienyl Ketone (4a)[9]: Yellow crystals; mp 52.5 - 53.0 ˚C (dichloro-methane – hexane) (lit., 52.5 - 53.5 ˚C); ^{1}H NMR ($CDCl_3$) δ = 3.85 (3H, s), 5.22 (2H, d, *J* = 6.5 Hz), 6.42 (1H, t, *J* = 6.5 Hz), 6.91 (2H, d, *J* = 8.6 Hz), 7.90 (2H, d, *J* = 8.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 55.5, 79.0, 92.9, 113.6, 125.3, 130.4, 131.0, 163.4, 216.5 ppm.

Phenethyl 1,2-Propadienyl Ketone (4b)[27]: Colorless oil; ^{1}H NMR ($CDCl_3$) δ = 2.91 (4H, s like), 5.19 (2H, d, *J* = 6.5 Hz), 5.78 (1H, t, *J* = 6.5 Hz), 7.17 - 7.29 (5H, m) ppm; ^{13}C NMR ($CDCl_3$) δ = 30.3, 40.8,

79.5, 96.6, 126.1, 128.3, 128.4, 141.0, 199.6, 216.7 ppm.

2-(4-Methoxyphenyl)-5-methylfuran (5g): Furan (**5g**) and furan (**2e**) were identical.

2-(4-Methoxyphenyl)-5-phenylfuran (5h)[28]: Furan (**5h**) was not separated from furan (**2h**). The yield was determined by ^{1}H NMR spectral analysis; IR (KBr) 1599, 1498, 1254, 1022, 835, 787, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 3.75 (3H, s), 6.52 (1H, d, *J* = 2.2 Hz), 6.63 (1H, d, *J* = 2.2 Hz), 6.87 (2H, d, *J* = 8.9 Hz), 7.16 - 7.45 (5H, m) 7.60 (2H, d, *J* = 8.9 Hz), 7.65 (2H, d, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ = 55.3, 105.6, 107.2, 114.2, 123.5, 123.9, 125.2, 127.1, 128.6, 128.7, 130.9, 153.4, 159.1 ppm.

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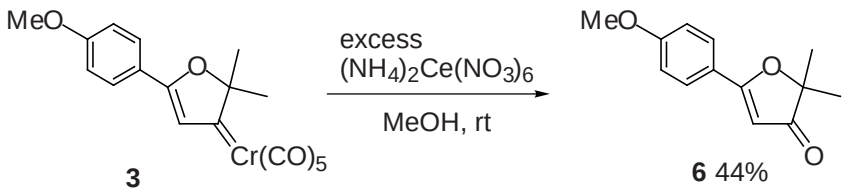

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