Studies on the Chemistry of Manganese Tricarbonyl Cations of Phenol and Cresols

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Treatment of (arene)tricarbonylmanganese cations (arene = phenol, cresol) with nucleophiles affords η^5-cyclohexadienyl complexes that can be demetalated to give *ortho*-substituted phenols. Acylation of the phenolic oxygen in the η^5-cyclohexadienyl complexes obtained from phenol, followed by treatment with acid, gives manganese tricarbonyl cations with coordinated monosubstituted arenes. Reaction of η^5-cyclohexadienyl complexes derived from *ortho*- and *para*-cresol with acid gives *meta*-substituted toluene manganese tricarbonyl cations, and those derived from *meta*-cresol give *ortho*- and/or *para*-substituted toluene manganese complexes depending upon the nucleophiles.

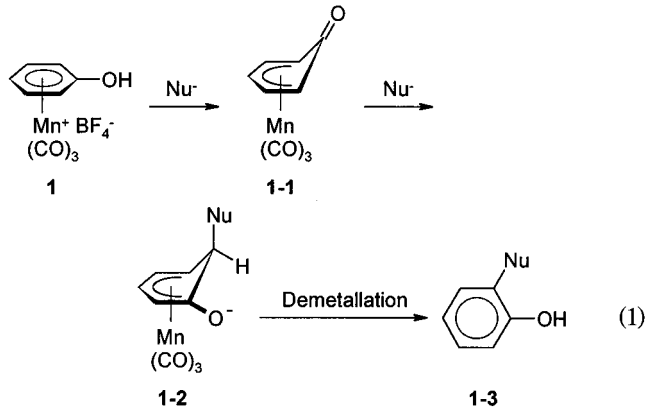
Introduction

The use of transition metal compounds in organic synthesis is useful[1] because it can provide pathways for reactions that are impossible or difficult to achieve by conventional synthetic methods. Synthetic applications of arene transition metal complexes have evolved rapidly over the last two decades.[2] The use of (arene)$Mn(CO)_3^+$ complexes in organic synthesis, however, has remained relatively undeveloped compared to those of chromium and iron derivatives.[3]

Manganese complexes of phenol are known,[4] but their chemistry is not well developed. Several years ago,[5] we reported the complex $[(\eta^6\text{-}C_6H_5OH)Mn(CO)_3]BF_4$ (**1**) and its use in the synthesis of doubly functionalized cyclohexadienyl manganese tricarbonyl complexes. We recently reinitiated the study of **1** and the cresol complexes $[(\eta^6\text{-}o\text{-cresol})Mn(CO)_3]BF_4$ (**2**), $[(\eta^6\text{-}p\text{-cresol})Mn(CO)_3]BF_4$ (**3**), and $[(\eta^6\text{-}m\text{-cresol})Mn(CO)_3]BF_4$ (**4**). We have demonstrated the use of **3** in the preparation of planar chiral [(1,3-disubstituted arene)$Mn(CO)_3$]BF_4.[6] Herein we report a new route for the formation of *ortho*-substituted phenols and manganese tricarbonyl cations of monosubstituted arenes and *ortho*-, *meta*-, and *para*-substituted toluenes. Recently, Rose et al. reported[7] the preparation of disubstituted arene manganese tricarbonyl cations by the Stille coupling reaction between (η^5-halogencyclohexadienyl)$Mn(CO)_3$ and $ArSnBu_3$ in the presence of $Pd_2(dba)_3$ and $AsPh_3$ in DMF.

Results and Discussion

Synthesis of *Ortho*-Substituted Phenols via Nucleophilic Addition to $[(\eta^6\text{-}C_6H_5OH)Mn(CO)_3]BF_4$. We found that nucleophilic addition of RMgBr or RLi to **1** followed by demetalation led to the isolation of exclusively *ortho*-alkylated phenols. Thus, treatment of **1** with 2.4 equiv of nucleophile in THF at 0 °C for 30 min gave adducts **1-2** (eq 1).



(1)

The first step is deprotonation of **1** to yield the oxocyclohexadienyl manganese complex **1-1**. The acidity

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Table 1. Yields of *Ortho*-Substituted Phenols from Reaction of 1

entry	Nu	yield (%)	demet. cond.
1	MeMgBr	51[a]	Me_3NO
2	EtMgBr	42[a]	Me_3NO
3	PhMgBr	83[b]	MnO_2
4	*n*-BuLi	75[b]	Me_3NO
5	*t*-BuLi	58[b]	Me_3NO
6	c-HexMgCl	80[b]	Me_3NO
7	$C_5H_5FeC_5H_4Li$	21[b]	$(H_2N)_2C(=O)/H_2O_2$
8	4-$CF_3C_6H_4MgBr$	58[b]	$(H_2N)_2C(=O)/H_2O_2$

[a] Yield by GC. [b] Isolated yield.

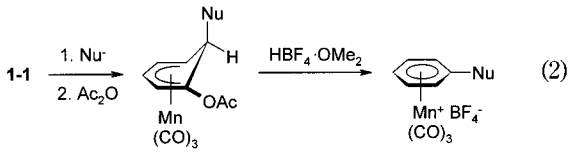
of phenol coordinated to $Mn(CO)_3^+$ is known to be enhanced.[5] Complex **1-1** reacts further with the remaining nucleophile to afford **1-2**. The nucleophile was found to attack only at a terminal position of **1-1**. Formation of **1-2** from **1** can be carried out stepwise or via a one-pot reaction. Although complex **1-2** could be isolated in a protonated form, it was found that crude **1-2** can be reacted directly with a demetalating agent to afford **1-3**. The demetalating agents trimethylamine *N*-oxide (TMANO),[8] MnO_2,[9] and $(H_2N)_2C(=O)\cdot H_2O_2$ [10] in acetonitrile were used. The demetalation reaction was performed under basic conditions; under acidic conditions, satisfactory yields were not obtained.

Table 1 gives the yields of the products. In the case of entries 1 and 2, phenol was detected as one of the side products, thus accounting for the modest yields (51% and 42%, respectively). When the nucleophile was phenyl, butyl, and cyclohexyl (entries 3, 4, and 6), the yields were high (75−83%). The present method can be extended to prepare 2-ferrocenylphenol (entry 7), although in low yield. In this case, neither TMANO nor MnO_2 was an effective demetalating agent, but $(H_2N)_2C(=O)\cdot H_2O_2$ was found to be partially successful as a demetalating agent. Entry 8 shows the general usefulness of $(H_2N)_2C(=O)\cdot H_2O_2$ in the synthesis of aromatic substituted phenols, even though the yield may not be high.

Generally, aromatic substituted phenols can be prepared by a metal-mediated coupling reaction with an aryl halide.[11] Usually the scope of the reaction is limited by the formation of homocoupled byproducts. Lourak et al.[12] have shown that all three possible coupling products are obtained in the synthesis of 2-(4-trifluoromethylphenyl)phenol. This presents both a low yield and a separation problem. By comparison, entry 8 in Table 1 shows that the *ortho*-substituted phenol was obtained as the sole product in 58% yield, suggesting that this reaction may be of general utility.

Ortho-functionalized phenols are common in natural products and serve as industrial intermediates in the synthesis of agrochemicals and polymers. Thus, there have been many reports on the selective *ortho*-alkylation of phenol.[13] The present study provides a new methodology of the synthesis of *ortho*-alkylated phenols in reasonable to high yields. This method is conceptually quite different from the well-known electrophilic substitution or rearrangements. In this way, the present study complements known synthetic methods.

Synthesis of [(Nu-C_6H_5)$Mn(CO)_3$]BF_4 from [(phenol)$Mn(CO)_3$]BF_4. Complexes **1-2′** have a carboxylate group as a substituent, which is a good leaving group in the presence of acid. Thus, treatment of **1-2′** (Nu = $CF_3C_6H_4$, $MeOC_6H_4$) with HBF_4 afforded [(Nu-C_6H_5)-$Mn(CO)_3$]BF_4 (eq 2).



1-2′ **1-4** (2)

Nu⁻		yield(%)		yield(%)
p-$CF_3C_6H_4MgBr$	**1-2′-1**	85	**1-4-1**	31
p-$MeOC_6H_4MgBr$	**1-2′-2**	79	**1-4-2**	47

New [(monosubstituted arene)$Mn(CO)_3$]BF_4 derivatives **1-4-1** (Nu = *p*-$CF_3C_6H_4$) and **1-4−2** (Nu = *p*-$MeOC_6H_4$) were obtained in useful yields by this methodology. Several synthetic methods have been reported for the coordination of arenes to the $Mn(CO)_3^+$ moiety.[14] However, compounds **1-4-1** and **1-4-2** are not easily obtained by the conventional synthetic methods due to low regioselectivity when the relevant biphenyl is reacted with a $Mn(CO)_3^+$ source.[14] Thus, the present method will be quite useful for the regioselective synthesis of biphenyl and related manganese complexes.

Synthesis of [(*meta*-substituted toluene)$Mn(CO)_3$]-BF_4 Complexes from [(*o*-cresol)$Mn(CO)_3$]BF_4 (2) and [(*p*-cresol)$Mn(CO)_3$]BF_4 (3). Tricarbonylmanganese complex (**2**) was synthesized by the reaction of *o*-cresol with $Mn(CO)_5BF_4$ or with [(naphthalene)Mn-$(CO)_3$]BF_4 in dichloromethane. Treatment of **2** with *t*-BuOK in THF led to the isolation of oxocyclohexadienylmanganese complex **2-1** (eq 3).

Nucleophilic addition to **2-1** followed by an addition of an electrophile led to the isolation of **2-2**, showing that a nucleophile attacks the terminal position of the dienyl group containing no substituent. Successive reactions of **2-1** with a nucleophile (Nu^-) and acetic anhydride gave **2-2-1**−**2-2-6** in relatively high yields. The nucleophiles were 4-trifluoromethylphenyl, phenyl, cyclohexyl, *tert*-butyl, *n*-butyl, and methyl. The lowest yield (50%) was obtained when the nucleophile was MeMgBr. Treatment of **2-2** with HBF_4 in dichloromethane led to the isolation of [(*meta*-substituted arene)$Mn(CO)_3$]BF_4 (**2-3**) in 52−76% yields.

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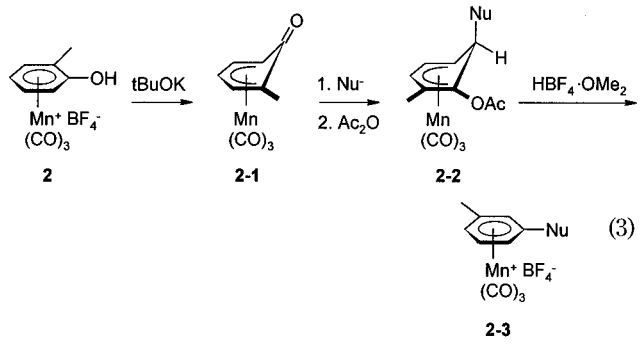
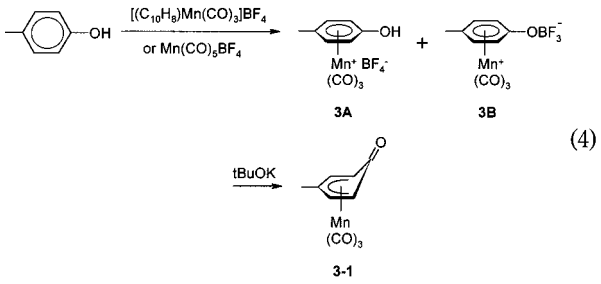


Nu⁻		yield(%)		yield(%)
p-$CF_3C_6H_4MgBr$	**2-2-1**	85	**2-3-1**	76
C_6H_5MgBr	**2-2-2**	83	**2-3-2**	56
c-HexMgCl	**2-2-3**	70	**2-3-3**	70
tBuLi	**2-2-4**	76	**2-3-4**	61
nBuLi	**2-2-5**	85	**2-3-5**	52
MeMgBr	**2-2-6**	50	**2-3-6**	67

It was expected that (*p*-cresol)manganese tricarbonyl complex (**3**) would be synthesized in the same manner as [(*o*-cresol)$Mn(CO)_3$]BF_4 (**2**). Thus, $Mn(CO)_5BF_4$ or [(naphthalene)$Mn(CO)_3$]BF_4 in dichloromethane was heated with *p*-cresol (eq 4).



However, after the reaction, the ^1H NMR of the product in CD_3NO_2 shows two sets of arene protons (δ 6.64 (d, J = 7.3 Hz, 2 H), 6.01 (d, J = 7.3 Hz, 2 H), 2.36 (s, 3 H); 6.53 (d, J = 7.4 Hz, 2 H), 5.85 (d, J = 7.4 Hz, 2 H), 2.32 (s, 3 H) ppm). The ratio of the two sets of resonances was dependent upon the preparation method. When $Mn(CO)_5BF_4$ was used, the ratio was 1.7:1. When [(naphthalene)$Mn(CO)_3$]BF_4 was used, the ratio was 3.4:1. When the product was deprotoneated by *t*-BuOK in THF, compound **3-1** was obtained as the sole product in 78% yields. These observations suggest that there are two isomeric forms of **3** in CD_3NO_2. Maitlis et al. reported[15] the hydrogen-bonded dimeric phenol complex [{MCp*}$_2${η^6-PhO-H$\cdots$O(η^6-Ph)}][PF_6]$_3$ from the reaction of phenol and [MCp*(acetone)$_3$][PF_6]$_2$ (M = Rh, Ir). The dimeric compounds were easily deprotonated to the corresponding η^5-oxocyclohexadienyl complexes [MCp*(η^5-C_6H_5O)]PF_6. The situation seems to be quite similar to ours; even the details are not the same. Thus, we envisioned that a monomeric (η^6-phenol complex) and a dimeric ({η^6-PhO-H$\cdots$O(η^6-Ph)} complex) species coexisted in the solution. Diffusion of a nitromethane solution of the product prepared by using $Mn(CO)_5BF_4$ into diethyl ether yielded single crystals suitable for an X-ray study. Figure 1 shows the ORTEP drawing of the crystal. Contrary to our expectation, the BF_3-substituted phenoxide compound **3B** was obtained instead of a dimeric compound. Due to the difficulty in the purification, we failed to completely characterize the other compound. However, we could easily assign the other to **3A** when we compared with **1A** and **2A**. Thus, instead of two isomeric forms, two different compounds, **3A** and **3B**, were obtained. Selected bond lengths and angles are given in Table 3. Compound **3B** is found to be an eclipsed conformation. The bond distance between boron and oxygen is 1.498(4) Å, which is longer than that (av 1.468 Å) in BO_4^- and that (1.367 Å) in X_2−BOX.[16] The average C−C bond distance in the coordinated arene ring is 1.409 Å. The metal−carbon distances in the coordinated arene ring show a pattern in which the metal atom is significantly closer to C3−C5 than others. Other numerical parameters of **3B** are similar to those of other (arene)$Mn(CO)_3^+$ cations.[17] When we took a ^1H NMR of the crystal used for X-ray diffraction, the ^1H NMR peaks (δ 6.53 (d) and 5.85 (d)) were consistent with one of two sets of arene protons mentioned above. Thus, we can assign the lower-field peaks to **3A** and the higher-field peaks to **3B**. Compound **3B** is a zwitterionic complex and insoluble in diethyl ether. In the same way as in the synthesis of **2-2**, treatment of **3-1** with *t*-BuLi followed by the addition of acetic anhydride gave **3-2-1** in 86% yield (eq 5).

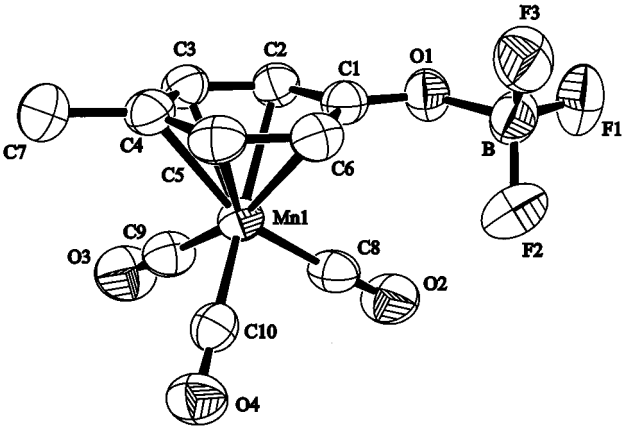
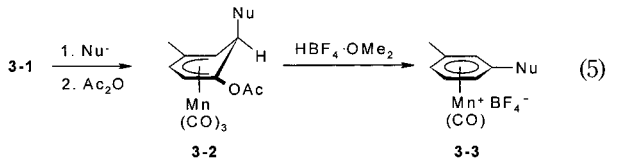


Figure 1. ORTEP drawing of **3B** (50% probability ellipsoids).



Nu		yield(%)		yield(%)
tBuLi	**3-2-1**	86	**3-3-1**	44
PhMgBr	**3-2-2**	88	**3-3-2**	76
2-thienylLi	**3-2-3**	56	**3-3-3**	26

No isomeric compounds were observed. In the same way, compounds **3-2-2** and **3-2-3** were obtained in 88% and 56% yield, respectively. Treatment of **3-2-1** with

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Table 2. Crystal Data and Structure Refinement for 3B, 4-3-2, and 5-3

	3B	4-3-2	5-3
empirical formula	$C_{10}H_7BF_3MnO_4$	$C_{16}H_{12}BF_4MnO_3$	$C_{19}H_{18}BF_4MnO_3$
fw	313.91	394.01	436.08
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a, Å	7.7887(2)	10.9259(3)	10.5925(2)
b, Å	13.1980(4)	12.0340(3)	11.8344(3)
c, Å	11.2573(4)	13.0645(4)	15.5621(4)
α, deg	90	90	90
β, deg	90.843(1)	104.592(1)	96.581(1)
γ, deg	90	90	90
volume, Å^3	1157.07(6)	1662.34(8)	1937.95(8)
Z	4	4	4
d(calcd), Mg/m^3	1.802	1.574	1.495
θ range, deg	2.38−27.47	1.61−27.51	2.17−27.45
no. tot. collection	4681	6716	7797
no. unique data	2644	3807	4425
no. params refined	624	792	888
$R_1[I>2\sigma(I)]$	0.0373	0.0610	0.0891
$wR_2[I>2\sigma(I)]$	0.1063	0.1622	0.2474
R_1(all data)	0.0506	0.134	0.1209
wR_2(all data)	0.1208	0.2089	0.2791
gof	1.179	0.968	1.073

Table 3. Selected Bond Distances (Å) and Angles (deg) for 3B, 4-3-2, and 5-3

		3B			
Mn(1)−C(1)	2.317(3)	Mn(1)−C(2)	2.197(2)	Mn(1)−C(3)	2.171(3)
Mn(1)−C(4)	2.203(2)	Mn(1)−C(5)	2.165(2)	Mn(1)−C(6)	2.210(2)
Mn(1)−C(8)	1.825(3)	Mn(1)−C(9)	1.807(3)	Mn(1)−C(10)	1.826(3)
B−O(1)	1.498(4)	O(1)−C(1)	1.309(3)		
C(7)−C(4)−Mn(1)	130.54(19)			C(1)−O(1)−B	124.0(2)
O(1)−C(1)−Mn(1)	132.05(18)			F(2)−B−F(1)	110.8(3)
F(2)−B−O(1)	110.1(2)				
		4-3-2			
Mn−C(1)	2.234(4)	Mn−C(2)	2.204(4)	Mn−C(3)	2.162(4)
Mn−C(4)	2.174(5)	Mn−C(5)	2.165(4)	Mn−C(6)	2.183(4)
Mn−C(14)	1.821(6)	Mn−C(15)	1.809(6)	Mn−C(16)	1.814(5)
C(1)−C(8)	1.491(6)	C(2)−C(7)	1.510(5)		
C(7)−C(2)−Mn	128.5(3)			C(8)−C(1)−Mn	131.3(3)
		5-3			
Mn−C(1)	2.256(4)	Mn−C(2)	2.201(4)	Mn−C(3)	2.168(4)
Mn−C(4)	2.220(4)	Mn−C(5)	2.168(4)	Mn−C(6)	2.199(4)
Mn−C(17)	1.813(6)	Mn−C(18)	1.832(5)	Mn−C(19)	1.823(5)
C(1)−C(7)	1.487(6)	C(4)−C(13)	1.535(6)		
C(7)−C(1)−Mn	131.1(3)			C(13)−C(4)−Mn	133.5(3)

HBF_4·OMe_2 in dichloromethane led to the isolation of [(3-*tert*-butyltoluene)Mn(CO)$_3$]BF_4 (**3-3-1**) in 44% yield.

The ^{1}H NMR of **3-3-1** was the same as that of **2-3-4**. In the same way, [(3-phenyltoluene)Mn(CO)$_3$]BF_4 (**3-3-2** = **2-3-2**) and [(3-thiopenyltoluene)Mn(CO)$_3$]BF_4 (**3-3-3**) were prepared in 76% and 26% yield, respectively, from **3-2-2** and **3-2-3**.

In organic syntheses, there are few direct methods for the synthesis of *meta*-substituted toluenes. Thus, [(*m*-substituted toluene)Mn(CO)$_3$]BF_4 complexes are rare, and their chemistry is not well developed. Thus, the present method is complementary to the well-known synthetic methods and can provide a new methodology for the synthesis of *meta*-substituted toluenes starting from *o*-cresol or *p*-cresol.

Reactions of [(*m*-cresol)Mn(CO)$_3$]BF_4 (4): Synthesis of [(*o*- *or* *p*-substituted toluene)Mn(CO)$_3$]BF_4. We attempted to synthesize tricarbonyl(*m*-cresol)-manganese complex (**4**) in the same way as the synthesis of [(*o*-cresol)Mn(CO)$_3$]BF_4 (**2**). However, as in the case of **3**, the ^{1}H NMR of the product in CD_3NO_2 shows two sets of arene protons in the ratio 2.5:1 (δ 6.74 (br), 5.93−5.65 (m); 6.61 (t), 5.81−5.78 (m), 5.70 (d)). Purification gave an analytically pure compound that was assigned as **4B** from elemental analysis data and proton NMR. This allowed assignment of the lower-field peaks to **4A** and the high-field peaks to **4B** as **3A** and **3B** (eq 6).

Deprotonation of a mixture of **4A** and **4B** by *t*-BuOK gave **4-1** in 72% yield. When **4-1** was treated with *t*-BuLi and acetic anhydride, two isomeric forms (**a** and **b**) of **4-2-1** were obtained in 84% yield in a ratio of 6:1 (eq 7).

The two isomeric forms **a** and **b** were assigned by the inspection of the ^{1}H NMR spectrum. Treatment of **4-1** with PhMgBr and acetic anhydride gave **4-2-2 a** and **b** in 94% yield with a ratio 1:6. When the nucleophile was MeMgBr, the ratio **a** to **b** was 1.1:1 and with *p*-$MeOC_6H_4MgBr$ the **b** isomer was obtained exclusively. Thus, the ratio of **a** to **b** is sensitive to the nature of the nucleophile. In the case of *t*-BuLi and MeMgBr, the

(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

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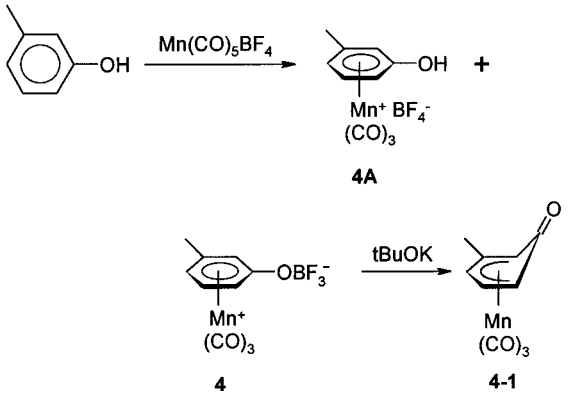
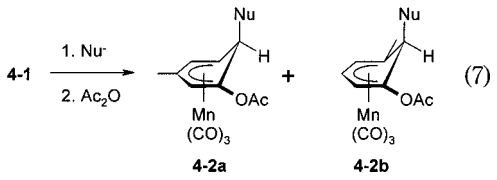


(6)

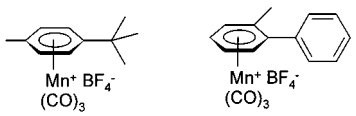


(7)

Nu	4-2a : 4-2b
tBu-i	6 : 1
PhMgBr	1 : 6
MeMgBr	1.1 : 1
p-$MeOC_6H_4MgBr$	0 : 1

results can be explained by steric effects. However, with PhMgBr and *p*-$MeOC_6H_4MgBr$, the situation is not simple. We envision that the electronic effect of PhMgBr and *p*-$MeOC_6H_4MgBr$ may play an important role in the distribution of products.

To obtain cationic complexes, compounds **4-2-1** and **4-2-2** were treated with HBF_4 in dichloromethane. Recrystallization of the reaction products in nitromethane/diethyl ether gave **4-3-1a** and **4-3-2b** in 50% and 40% yield, respectively.



4-3-1a **4-3-2b**

According to the ^1H NMR spectrum of **4-3-1**, only the *para*-substituted toluene manganese complex **4-3-1a** existed. Thus, during recrystallization, the *ortho*-substituted toluene complex is removed. On the contrary, the ^1H NMR spectrum of **4-3-2** shows only the *ortho*-substituted toluene manganese complex **4-3-2b**. The formation of **4-3-2b** was verified by an X-ray crystal structure determination of the product (Figure 2). Selected bond distances and angles of **4-3-2b** are given in Table 3. **4-3-2b** adopts a staggered conformation. The metal−carbon distances in the coordinated arene ring show a pattern in which the metal atom is significantly closer to C3−C5 than others. The torsion angle between the phenyl ring and the coordinated arene is 49.1°. Other numerical parameters of **4-3-2b** are similar to those of other (arene)$Mn(CO)_3^+$ cations.[17]

Reactions of [(*m*-*tert*-butylphenol)$Mn(CO)_3$]BF_4 (5): Synthesis of [(1-*t*-Bu-4-Ph-C_6H_4)$Mn(CO)_3$]BF_4. As an extension of the chemistry described above, [(*m*-

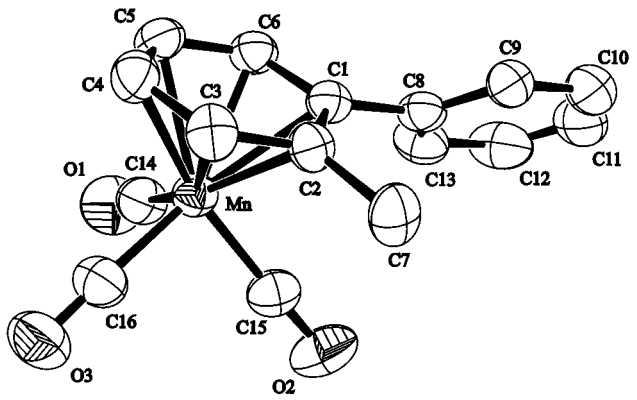


Figure 2. ORTEP drawing of **4-3-2** (50% probability ellipsoids).

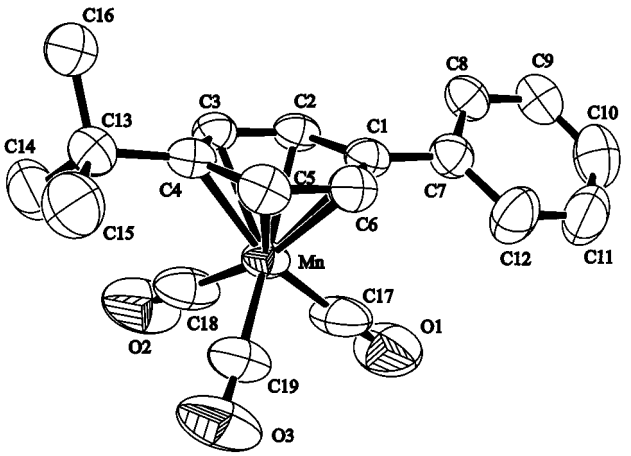
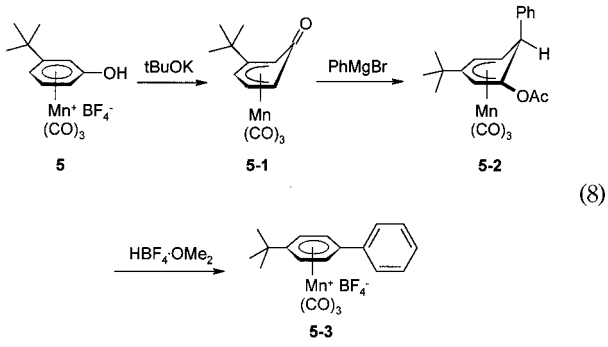


Figure 3. ORTEP drawing of **5-3** (50% probability ellipsoids).

tert-butylphenol)$Mn(CO)_3$]BF_4 (**5**) was synthesized by the reaction of *m*-*tert*-butylphenol with $Mn(CO)_5BF_4$. As expected, the steric effect of the *tert*-butyl group affects the regioselectvity of nucleophilic addition. Thus, treatment of **5-1** with PhMgBr followed by acetic anhydride afforded **5-2** as the sole product (eq 8).



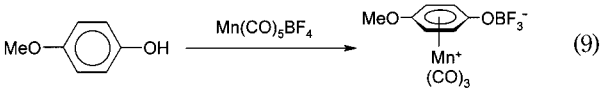
(8)

Acid treatment of **5-2** gave **5-3** in 80% yield. The structure of **5-3** was confirmed by an X-ray diffraction study (Figure 3). Selected bond distances and angles are given in Table 3. Complex **5-3** adopts an eclipsed conformation, with the average C−C bond distance in the coordinated arene ring being 1.409 Å. The metal−carbon distances in the coordinated arene ring show a pattern in which the metal atom is significantly closer to C3−C5 than the others. The torsion angle between the phenyl ring and the coordinated arene is 30.5°.

Other numerical parameters of **5-3** are similar to those of other (arene)$Mn(CO)_3^+$ cations.[17]

Factors Affecting the Formation of Complex(es) Type A and/or B. As mentioned above, Maitlis et al.[15] reported the hydrogen-bonded dimeric phenol complex $[\{MCp^*\}_2\{\eta^6\text{-PhO-H}\cdots\text{O}(\eta^6\text{-Ph})\}][PF_6]_3$ from the reaction of phenol and $[MCp^*(acetone)_3][PF_6]_2$ (M = Rh, Ir). Sweigart et al. reported[18] the η^6-hydroquinone and catechol complexes of manganese tricarbonyl. According to the X-ray structure of $[(\eta^6\text{-hydroquinone})Mn(CO)_3]_2(SiF_6)$, −OH substitutents are strongly bonded to the fluorine atoms in the SiF_6^{2-} anion. On the basis of these published reports, we did not expect the formation of the BF_3-substituted phenoxide manganese tricarbonyl complex **B** in the reaction of $Mn(CO)_5BF_4$ with *m*- and *p*-cresol.

Steric and electronic factors due to substituent(s) on the arene affect the ratio of **A** to **B**. In the case of phenol, complex **A** was the sole product. It can be expected that the introduction of a methyl group to arene would increase the nucleophilicity of the hydroxy group in reacting with BF_4. However, in the case of *o*-cresol, complex **A** was obtained perhaps due to the steric hindrance of methyl group. With *m*- or *p*-cresol, a mixture of **A** and **B** was obtained. With *m*-*tert*-butylphenol, complex **A** was exclusively obtained presumably due to the steric hindrance of the *tert*-butyl group. These observations suggest that the proportion of **B** could be increased provided a stronger electron donor was introduced instead of a methyl group. In agreement with this view, the use of *p*-methoxyphenol as an arene source was found to afford complex **6B** as the sole product (eq 9).



(9)

6B

The ratio **A**:**B** was also dependent upon the synthetic methods, e.g., the source of manganese carbonyls and the synthetic procedure. Compared to the case of $Mn(CO)_5BF_4$ as the source of manganese carbonyls, the use of $[(C_{10}H_8)Mn(CO)_3]BF_4$ increased the portion of **A**. Treatment of *p*-cresol with $AgBF_4$ for 7 h and then with $Mn(CO)_5Br$ exclusively yielded **B** in 65% yield. These observations suggested that complex **B** would be obtained as a major compound provided the reaction between cresol and BF_4^- anion took place before the formation of complex **A**.

In conclusion, we have demonstrated the usefulness of cationic manganese tricarbonyl complexes of phenol and cresols in the preparation of *ortho*-substituted phenols. Also presented are related procedures for the synthesis of manganese tricarbonyl complexes of monosubstituted arene and *ortho*-, *meta*-, and *para*-substituted toluenes. The general methodology described may have significant applications in organic and organometallic synthesis.

Experimental Section

General. All reactions were conducted under nitrogen using standard Schlenk-type flasks. Workup procedures were done in air. All solvents were dried and distilled according to standard methods before use. THF was freshly distilled from sodium benzophenone ketyl prior to use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. IR spectra were obtained in solution or measured as films on NaCl by evaporation of solvent. Mass spectra were recorded with a VG ZAB-E double-focusing mass spectrometer.

Compounds **1-1**, **1-3-1**−**1-3-6**, and **1-3-8** were known compounds.[12,19] Formation of these compounds was verified by comparing GC retention times, NMR, or high-resolution mass spectra.

Synthesis of 1-3-1−**1-3-8. (a) A Typical Procedure for Demetalation Using TMANO.** To a solution of **1** (0.30 g, 0.94 mmol) in 15 mL of THF at 0 °C was added dropwise cyclohexylmagnesium chloride (2.4 equiv, 2.25 mmol, 1.1 mL of 2 M solution in diethyl ether). After the solution was stirred for 30 min, water (4 or 5 drops) was added to the reaction mixture to quench any excess nucleophile. Removal of the solvent by rotary evaporator gave a brownish yellow powder. The powder was dissolved in 15 mL of acetonitrile, and dried TMANO (3.6 equiv, 3.25 mmol) was added. The resulting solution was stirred for 12 h at 40 °C, and the reaction mixture extracted with excess diethyl ether and 1 M HCl. The ether extracts were dried over anhydrous $MgSO_4$ and evaporated to give a yellow residue. Purification by chromatography on a silica gel column eluting with ether/hexane (v/v, 1:20) gave 0.132 g of the product **1-3-6** (80%) (entry 6 in Table 1).

(b) A Typical Procedure for Demetalation Using $(H_2N)_2C(=O)/H_2O_2$. Ferrocenyllithium (0.80 mmol, in situ generated from ferrocene and *t*-BuLi) was added to the solution of **1** (0.25 g, 0.78 mmol) in 15 mL of THF at 0 °C. $(H_2N)_2C(=O)/H_2O_2$ (1.5 equiv) was poured into the above solution, and the resulting solution was stirred for 12 h at 60 °C. After purification by chromatography on a silica gel column eluting with ether/hexane (v/v, 1:20), the product **1-3-7** was obtained in 21% yield (45 mg). **1-3-7** (entry 7 in Table 1): ^{1}H NMR ($CDCl_3$) δ 7.23−7.20 (m, 2 H), 7.17 (s, OH), 6.96 (d, J = 8.34 Hz, 1 H), 6.85 (t, J = 7.38 Hz, 1 H), 4.52 (t, J = 1.83 Hz, 2 H), 4.42 (t, J = 1.86 Hz, 2 H), 4.25 (s, Cp) ppm; ^{13}C NMR ($CDCl_3$) 153.4, 131.0, 129.4, 128.3, 127.8, 122.8, 120.2, 115.7, 69.5, 69.1, 67.4 ppm; HRMS (M^+) calcd 278.0394, obsd 278.0399.

Synthesis of 1-2′-1. To a solution of **1-1** (0.46 g, 2.0 mmol) in THF (10 mL) at −78 °C was added 3.0 mmol of *p*-$CF_3C_6H_4$-MgBr (generated from 4-bromobenzotrifluoride and magnesium turnings in ether). The solution was stirred at −78 °C for 2 h, and acetic anhydride (0.56 mL, 6.0 mmol) was added. After the solution was stirred for 30 min at room temperature, it was quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether. Chromatography on a silica gel column eluting with hexane and diethyl ether (v/v, 10:1) gave 0.73 g (85%) of the product. ^{1}H NMR ($CDCl_3$): δ 7.48 (d, J = 8.2 Hz, 2 H), 7.08 (d, J = 7.9 Hz, 2 H), 5.62 (t, J = 5.9 Hz, 1 H), 5.29 (d, J = 5.5 Hz, 1 H), 4.87 (t, J = 6.1 Hz, 1 H), 4.54 (d, J = 6.6 Hz, 1 H), 3.62 (t, J = 6.3 Hz, 1 H), 2.07 (s, 3 H) ppm. IR (Et_2O): ν_{CO} 2020, 1944 cm^{-1}. ^{13}C NMR ($CDCl_3$): 221.8, 168.5, 147.3, 129.3, 126.4, 125.5, 121.5, 100.8, 93.9, 89.5, 72.4, 58.7, 46.0, 21.3 ppm. HRMS (M^+): calcd 420.0017, obsd 420.0020.

1-2′-2. Yield: 79%. ^{1}H NMR ($CDCl_3$): δ 6.88 (d, J = 8.6 Hz, 2 H), 6.74 (d, J = 8.6 Hz, 2 H), 5.59 (t, J = 4.9 Hz, 1 H), 5.22 (d, J = 5.8 Hz, 1 H), 4.84 (t, J = 6.1 Hz, 1 H), 4.40 (d, J = 6.2 Hz, 1 H), 3.74 (s, 3 H), 3.65 (t, J = 6.2 Hz, 1 H), 2.05 (s, 3 H) ppm. IR (Et_2O): ν_{CO} 2016, 1939 cm^{-1}. ^{13}C NMR ($CDCl_3$): 222.2, 168.9, 159.3, 137.3, 127.7, 114.0, 103.5, 94.1, 89.5, 72.3, 61.3, 55.6, 46.2, 21.8 ppm. HRMS (M^+): calcd 382.0249, obsd 382.0250.

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(19) Dewar, M. J. C.; Puttnam, N. A. *J. Chem. Soc.* **1959**, 4080. Kolka, A. J. *J. Org. Chem.* **1957**, *22*, 642. The Aldrich Library of ^{13}C and ^{1}H FT NMR spectra: 1(2)245(A) and 1(2)317(A).

Synthesis of 1-4-1. To a solution of **1-2′-1** (0.25 g, 0.59 mmol) in 10 mL of CH_2Cl_2 was added HBF_4·OEt_2 (0.11 mL, 1.5 equiv) at −78 °C. After the solution was stirred for 2 h, K_2CO_3 (0.25 g, 3 equiv) was added to the solution. The resulting solution was allowed to warm to room temperature. Nitromethane (1−2 mL) was added to dissolve the salt, and the solution was filtered over Celite. Excess diethyl ether (50 mL) was added to the filtrate to precipitate **1-4-1** (80 mg, 31%). ^{1}H NMR ($CDCl_3$): δ 8.29 (d, J = 8.3 Hz, 2 H), 8.01 (d, J = 8.3 Hz, 2 H), 7.41 (d, J = 6.7 Hz, 2 H), 7.23 (t, J = 6.9 Hz, 2 H), 6.96 (t, J = 6.6 Hz, 1 H) ppm. IR (CH_3NO_2): ν_{CO} 2072, 2024 cm^{-1}. Anal. Calcd for $C_{16}H_9BF_7MnO_3$: C, 42.86; H, 2.02. Found: C, 43.14; H, 1.96.

1-4-2. Yield: 47%. ^{1}H NMR ($CDCl_3$): δ 8.03 (d, J = 8.8 Hz, 2 H), 7.25−7.18 (m, 6 H), 6.75 (t, J = 6.0 Hz, 1H), 3.93 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2072, 2024 cm^{-1}. Anal. Calcd for $C_{18}H_{15}MnO_6$: C, 46.83; H, 2.95. Found: C, 46.54; H, 2.91.

Synthesis of [(*o*-cresol)Mn(CO)$_3$]BF$_4$ (2). *o*-Cresol (2.3 mL, 22.0 mmol) was added to a solution of $Mn(CO)_5BF_4$ in 50 mL of CH_2Cl_2 (generated by the reaction of $Mn(CO)_5Br$ (3.0 g, 11.0 mmol) and $AgBF_4$ (2.4 g, 12.0 mmol) in CH_2Cl_2). The resulting solution was heated at reflux for 12 h. Evaporation followed by recrystallization in dichloromethane/diethyl ether gave **2** in 82% yield (3.0 g). ^{1}H NMR (CD_3NO_2): δ 6.94 (d, J = 5.2 Hz, 1 H), 6.76 (t, J = 6.7 Hz, 1 H), 6.16 (d, J = 7.8 Hz, 1 H), 5.99 (t, J = 5.7 Hz, 1 H), 2.30 (s, 3 H) ppm. IR (CH_2Cl_2): ν_{CO} 2060, 1997 cm^{-1}. Anal. Calcd for $C_{10}H_8BF_4MnO_4$: C, 35.97; H, 2.41. Found: C, 36.14; H, 2.35.

Synthesis of 2-1. To a solution of **2** (1.0 g, 3.6 mmol) in 20 mL of THF was added *t*-BuOK (0.40 g, 3.6 mmol) in THF. The solution was stirred for 1 h. Evaporation followed by chromatography on a silica gel column eluting with ethyl acetate gave **2-1** in 99% yield (0.88 g). ^{1}H NMR ($CDCl_3$): δ 5.96 (d, J = 5.5 Hz, 1 H), 5.86 (t, J = 6.6 Hz, 1 H), 5.18 (t, J = 5.7 Hz, 1 H), 4.86 (d, J = 7.2 Hz, 1H), 2.03 (s, 3 H) ppm. IR (CH_2Cl_2): ν_{CO} 2040, 1966 cm^{-1}. Anal. Calcd for $C_{10}H_7MnO_4$: C, 48.81; H, 2.87. Found: C, 48.56; H, 2.95.

Synthesis of 2-2-1−2-2-7. Typical Procedures. To a solution of **2-1** (0.30 g, 1.2 mmol) in 20 mL of THF was added nucleophile (2.4 mmol) at 0 °C. After the solution was stirred at 0 °C for 1 h, acetic anhydride (1.0 mL, 10.5 mmol) was added to the solution. The solution was allowed to warm to room temperature and stirred at room temperature for 1 h. Excess diethyl ether (50 mL) and water (30 mL) were added to quench the reaction, and the ether layer was separated, evaporated to dryness, and chromatographed on a silica gel column eluting with ethyl acetate and hexane (v/v, 1:20). Removal of the solvent gave the product **2-2**.

2-2-1. Yield: 85%. ^{1}H NMR ($CDCl_3$): δ 7.48 (d, J = 8.1 Hz, 2 H), 7.01 (d, J = 8.0 Hz, 2 H), 5.55 (d, J = 5.1 Hz, 1 H), 4.81 (dd, J = 5.2, 7.0 Hz, 1 H), 4.70 (d, J = 6.3 Hz, 1 H), 3.62 (dd, J = 6.4, 7.1 Hz, 1 H), 2.09 (s, 3 H), 1.98 (s, 3 H) ppm. IR (CH_2Cl_2): ν_{CO} 2016, 1931, 1748 cm^{-1}. Anal. Calcd for $C_{19}H_{14}F_3MnO_5$: C, 52.55; H, 3.25. Found: C, 52.78; H, 3.25.

2-2-2. Yield: 83%. ^{1}H NMR ($CDCl_3$): δ 7.22−7.17 (m, 3 H), 6.89 (d, J = 9.2 Hz, 2 H), 5.52 (d, J = 5.1 Hz, 1 H), 4.79 (dd, J = 5.1, 7.2 Hz, 1 H), 4.65 (d, J = 6.3 Hz, 1 H), 3.67 (dd, J = 6.4, 7.2 Hz, 1 H), 2.08 (s, 3 H), 1.99 (s, 3 H) ppm. IR (CH_2Cl_2): ν_{CO} 2012, 1938, 1746 cm^{-1}. Anal. Calcd for $C_{18}H_{15}MnO_5$: C, 59.03; H, 4.13. Found: C, 59.00; H, 4.17.

2-2-3. Yield: 70%. ^{1}H NMR ($CDCl_3$): δ 5.40 (d, J = 5.0 Hz, 1 H), 4.66 (dd, J = 5.0, 6.7 Hz, 1 H), 3.37 (dd, J = 5.8, 7.5 Hz, 1 H), 3.30 (t, J = 5.8 Hz, 1 H), 2.10 (s, 3 H), 1.90 (s, 3 H), 1.63−0.62 (m, 11 H) ppm. IR (CH_2Cl_2): ν_{CO} 2016, 1936, 1748 cm^{-1}. Anal. Calcd for $C_{18}H_{21}MnO_5$: C, 58.07; H, 5.69. Found: C, 58.21; H, 5.78.

2-2-4. Yield: 76%. ^{1}H NMR ($CDCl_3$): δ 5.36 (d, J = 5.0 Hz, 1 H), 4.70 (dd, J = 5.0, 7.2 Hz, 1 H), 3.54 (d, J = 6.3 Hz, 1 H), 3.38 (dd, J = 6.6, 7.2 Hz, 1 H), 2.08 (s, 3 H), 1.93 (s, 3 H), 0.60 (s, 9 H) ppm. IR (CH_2Cl_2): ν_{CO} 2020, 1940, 1765 cm^{-1}. Anal. Calcd for $C_{16}H_{19}MnO_5$: C, 55.50; H, 5.53. Found: C, 55.65; H, 5.40.

2-2-5. Yield: 85%. ^{1}H NMR ($CDCl_3$): δ 5.46 (d, J = 5.0 Hz, 1 H), 4.65 (dd, J = 5.1, 7.1 Hz, 1 H), 3.40 (dd, J = 6.1, 7.3 Hz, 1 H), 3.21−3.18 (m, 1 H), 2.12 (s, 3 H), 1.85 (s, 3 H), 0.97−0.86 (m, 6 H), 0.80 (t, 7.0 Hz, 3 H) ppm. IR (CH_2Cl_2): ν_{CO} 2016, 1941, 1763 cm^{-1}. Anal. Calcd for $C_{16}H_{19}MnO_5$: C, 55.50; H, 5.53. Found: C, 55.59; H, 5.73.

2-2-6. Yield: 50%. ^{1}H NMR ($CDCl_3$): δ 5.49 (d, J = 5.1 Hz, 1 H), 4.63 (dd, J = 5.1, 7.0 Hz, 1 H), 3.36 (dd, J = 5.9, 7.5 Hz, 1 H), 3.22−3.17 (m, 1 H), 2.13 (s, 3 H), 1.85 (s, 3 H), 0.54 (d, J = 6.4 Hz, 3H) ppm. IR (CH_2Cl_2): ν_{CO} 2016, 1934, 1761 cm^{-1}. Anal. Calcd for $C_{13}H_{13}MnO_5$: C, 51.33; H, 4.31. Found: C, 51.62; H, 4.41.

Synthesis of 2-3-1−2-3-6. To a solution of **2-2** in (0.5 mmol) in 5 mL of CH_2Cl_2 was added 3 equiv of HBF_4·OMe_2. After the solution was stirred for 1.5 h, 4 equiv of K_2CO_3 was added to the reaction mixture. Filtration through Celite followed by recrystallization in dichloromethane/diethyl ether gave the product **2-3**.

2-3-1. Yield: 76%. ^{1}H NMR (acetone-d_6): δ 8.32 (d, J = 8.1 Hz, 2 H), 8.00 (d, J = 8.1 Hz, 2 H), 7.28 (s, 1 H), 7.24 (t, J = 6.6 Hz, 1 H), 7.17 (d, J = 6.6 Hz, 1 H), 6.74 (d, J = 6.25 Hz, 1 H), 2.77 (s, 3 H) ppm. IR: ν_{CO} 2072, 2012 cm^{-1}. Anal. Calcd for $C_{17}H_{11}BF_7MnO_3$: C, 44.20; H, 2.40. Found: C, 43.99; H, 2.36.

2-3-2. Yield: 56%. ^{1}H NMR (CD_3NO_2): δ 7.91 (d, J = 6.4 Hz, 2 H), 7.67 (br, 3 H), 6.94 (t, J = 6.4 Hz, 1 H), 6.79 (m, 2 H), 6.36 (d, J = 5.9 Hz, 1 H), 2.68 (s, 3 H) ppm. IR: ν_{CO} 2080, 2016 cm^{-1}. Anal. Calcd for $C_{16}H_{12}BF_4MnO_3$: C, 48.77; H, 3.07. Found: C, 48.48; H, 3.05.

2-3-3. Yield: 70%. ^{1}H NMR (acetone-d_6): δ 6.91 (t, J = 6.5 Hz, 1 H), 6.71 (s, 1 H), 6.64 (d, J = 8.5 Hz, 1H), 6.61(d, J = 7.7 Hz, 1H), 2.73 (t, J = 11.6 Hz, 1 H), 2.60 (s, 3 H), 2.05 (m, 2 H), 1.90 (d, J = 11.0 Hz, 2 H), 1.76 (d, J = 12.8 Hz, 1 H), 1.61−1.45 (m, 4 H), 1.25 (m, 1 H) ppm. IR: ν_{CO} 2080, 2016 cm^{-1}. Anal. Calcd for $C_{16}H_{18}BF_4MnO_3$: C, 48.04; H, 4.54. Found: C, 48.07; H, 4.54.

2-3-4. Yield: 61%. ^{1}H NMR (CD_3NO_2): δ 6.59−6.55 (m, 3 H), 6.46 (d, J = 5.1 Hz, 1 H), 2.54 (s, 3 H), 1.47 (s, 9 H) ppm. IR: ν_{CO} 2072, 2012 cm^{-1}. Anal. Calcd for $C_{14}H_{16}BF_4MnO_3$: C, 44.96; H, 4.31. Found: C, 44.96; H, 4.33.

2-3-5. Yield: 52%. ^{1}H NMR (acetone-d_6): δ 6.99 (t, J = 6.6 Hz, 1 H), 6.63 (s, 1 H), 6.54 (d, J = 6.4 Hz, 2 H), 2.84 (m, 2 H), 2.61 (s, 3 H), 1.76 (m, 2 H), 1.49 (m, 2 H), 0.95 (t, J = 7.3 Hz, 3 H) ppm. IR: ν_{CO} 2082, 2016 cm^{-1}. Anal. Calcd for $C_{14}H_{16}BF_4MnO_3$: C, 44.96; H, 4.31. Found: C, 45.12; H, 4.33.

2-3-6. Yield: 67%. ^{1}H NMR (acetone-d_6): δ 6.96 (t, J = 6.6 Hz, 1 H), 6.59 (s, 1 H), 6.48 (d, J = 6.5 Hz, 2 H), 2.60 (s, 6 H) ppm. IR: ν_{CO} 2080, 2016 cm^{-1}. Anal. Calcd for $C_{11}H_{10}BF_4MnO_3$: C, 39.80; H, 3.04. Found: C, 39.76; H, 2.98.

Synthesis of a Mixture of 3A and 3B. Method A. *p*-Cresol (0.82 mL, 7.8 mmol) was added to the solution of $Mn(CO)_5BF_4$ in 20 mL of CH_2Cl_2 (generated by the reaction of $Mn(CO)_5Br$ (1.4 g, 5.1 mmol) and $AgBF_4$ (1.1 g, 5.7 mmol) in CH_2Cl_2). The resulting solution was heated at reflux for 5 h. After the solution was cooled to room temperature, nitromethane (2−3 mL) was added to dissolve salts. Filtration followed by recrystallization with diethyl ether gave a mixture of **3A** and **3B** in a ratio 1.7:1 (1.35 g). IR (CH_3NO_2): ν_{CO} 2064, 2006 cm^{-1}. ^{1}H NMR (CD_3NO_2) of **3A**: δ 6.64 (d, J = 7.2 Hz, 2 H), 6.01 (d, J = 7.3 Hz, 2 H), 2.36 (s, 3 H) ppm. ^{1}H NMR (CD_3NO_2) of **3B**: δ 6.53 (d, J = 7.5 Hz, 2 H), 5.85 (d, J = 7.4 Hz, 2 H), 2.32 (s, 3 H) ppm. Anal. Calcd for $C_{10}H_7BF_3MnO_4$ (**3B**): C, 38.26; H, 2.25. Found: C, 38.03; H, 2.22.

Method B. $[(C_{10}H_8)Mn(CO)_3]BF_4$ was used instead of $Mn(CO)_5Br$, and a mixture of **3A** and **3B** was obtained in a ratio 3.4:1.

Method C. A solution of *p*-cresol (0.20 mL, 2.0 mmol) and $AgBF_4$ (0.39 g, 2.0 mmol) in 15 mL of CH_2Cl_2 was heated at

reflux for 7 h. To the solution was added $Mn(CO)_5Br$ (0.54 g, 2.0 mmol). The reaction mixture was heated at reflux for 12 h. Filtration and recrystallization gave 0.41 g (65%) of **3B** only.

Synthesis of 3-1. To the solution of a mixture of **3A** and **3B** (0.61 g, 1.8 mmol) in 15 mL of THF at −78 °C was added *t*-BuOK (0.26 g, 2.3 mmol). The solution was allowed to warm to room temperature for 1 h. After the solution was filtered over Celite, the filtrate was chromatographed on a silica gel column eluting with ethyl acetate and acetone (v/v, 1:2). Removal of the solvent gave **3-1** in 74% yield (0.34 g). ^{1}H NMR ($CDCl_3$): δ 5.93 (br, 2 H), 4.81 (br, 2 H), 2.30 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2036, 1966 cm^{-1}. Anal. Calcd for $C_{10}H_7MnO_4$: C, 48.81; H, 2.87. Found: C, 48.35; H, 2.85.

Synthesis of 3-2-1. To the solution of **3-1** (0.35 g, 1.4 mmol) in 15 mL of THF at −78 °C was added *t*-BuLi (1.7 mL, 2.9 mmol). The solution was stirred at −78 °C for 20 min and allowed to warm to room temperature for 1 h. To the resulting solution was added acetic anhydride (0.45 mL, 4.8 mmol). After the solution was stirred for 30 min, the solution was quenched with aqueous NH_4Cl solution (30 mL) and diethyl ether (50 mL). The ether layer was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v, 20:1). Yield: 86% (0.43 g). ^{1}H NMR ($CDCl_3$): δ 5.29 (d, J = 5.1 Hz, 1 H), 5.18 (d, J = 5.8 Hz, 1 H), 3.23 (s, 2 H), 2.06 (s, 3 H), 1.88 (s, 3 H), 0.61 (s, 9 H) ppm. IR (Et_2O): ν_{CO} 2012, 1924 cm^{-1}. Anal. Calcd for $C_{16}H_{19}MnO_5$: C, 55.50; H, 5.53. Found: C, 55.79; H, 5.61.

3-2-2. Yield: 88% (1.06 g). ^{1}H NMR ($CDCl_3$): δ 7.23 (m, 3 H), 6.92 (d, J = 6.9 Hz, 2 H), 5.46 (d, J = 4.5 Hz, 1 H), 5.20 (d, J = 5.5 Hz, 1 H), 4.46 (d, J = 5.4 Hz, 1 H), 3.55 (d, J = 4.8 Hz, 1 H), 2.05 (s, 3 H), 1.92 (s, 3 H) ppm. IR (Et_2O): ν_{CO} 2016, 1929 cm^{-1}. Anal. Calcd for $C_{18}H_{15}MnO_5$: C, 59.03; H, 4.13. Found: C, 58.80; H, 4.14.

3-2-3. Yield: 0.25 g (56%). ^{1}H NMR ($CDCl_3$): δ 7.00 (d, J = 4.4 Hz, 1 H), 6.75 (dd, J = 3.5, 4.7 Hz, 1 H), 6.50 (d, J = 3.3 Hz, 1 H), 5.45 (d, J = 3.1 Hz, 1 H), 5.07 (d, J = 4.5 Hz, 1 H), 4.54 (d, J = 6.1 Hz, 1 H), 3.52 (d, J = 5.0 Hz, 1 H), 1.99 (s, 3 H), 1.87 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 221.09, 168.52, 126.52, 125.87, 124.33, 123.09, 109.12, 102.16, 87.16, 73.81, 60.62, 42.34, 21.96, 21.37 ppm. IR (Et_2O): ν_{CO} 2016, 1930 cm^{-1}. HRMS (M^+) calcd 371.9864, obsd 371.9866.

Synthesis of 3-3-1. To the solution of **3-2-1** (0.93 g, 1.2 mmol) in 10 mL of CH_2Cl_2 at −78 °C was added $HBF_4{\cdot}OMe_2$ (0.22 mL, 1.8 mmol). After the solution was stirred for 2 h, K_2CO_3 (0.66 g, 4.8 mmol) was added to the solution. The resulting solution was allowed to warm to room temperature. Nitromethane (1−2 mL) was added to dissolve the salt, and the solution was filtered over Celite. Excess diethyl ether (50 mL) was added to the filtrate to precipitate **3-3-1** in 44% yield (0.20 g). The ^{1}H NMR of **3-3-1** was the same as that of **2-3-4**.

3-3-2. Yield: 76% (0.75 g). The ^{1}H NMR of **3-3-2** was the same as that of **2-3-2**.

3-3-3. Yield: 26%. ^{1}H NMR (CD_3NO_2): δ 7.92 (d, J = 3.8 Hz, 1 H), 7.86 (d, J = 3.9 Hz, 1 H), 7.31 (dd, J = 3.82, 3.86 Hz, 1 H), 6.90 (t, J = 6.7 Hz, 1 H), 6.70 (s, 1 H), 6.65 (d, J = 6.7 Hz, 1 H), 6.22 (d, J = 6.8 Hz, 1 H), 2.64 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2068, 2014 cm^{-1}. Anal. Calcd for $C_{14}H_{10}BF_4MnO_3S$: C, 42.04; H, 2.52; S, 8.01. Found: C, 41.96; H, 2.48; S, 8.29.

Synthesis of a Mixture of 4A and 4B. The same procedure as the synthesis of a mixture of **3A** and **3B** was applied except with *m*-cresol instead of *p*-cresol. After the reaction, a mixture of **4A** and **4B** was obtained in a ratio 5:2.

4-B. ^{1}H NMR (CD_3NO_2): δ 6.65 (t, J = 6.7 Hz, 1 H), 5.81−5.78 (m, 2 H), 5.70 (d, J = 6.3 Hz, 1 H), 2.30 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2064, 2004 cm^{-1}. Anal. Calcd for $C_{10}H_8BF_4MnO_4$: C, 38.26; H, 2.25. Found: C, 38.67; H, 2.40.

Synthesis of 4-1. Yield: 63%. ^{1}H NMR (acetone-d_6): δ 6.31 (br, 1 H), 5.59 (br, 1 H), 4.80 (br, 1 H), 4.73 (s, 1 H), 2.23 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2036, 1965 cm^{-1}. Anal. Calcd for $C_{10}H_7MnO_4$: C, 48.81; H, 2.87. Found: C, 49.09; H, 2.89.

Synthesis of 4-2-1. To the solution of **4-1** (0.47 g, 1.9 mmol) in 15 mL of THF at −78 °C was added *t*-BuLi (2.3 mL in 1.7 M pentane, 3.9 mmol). The solution was stirred at −78 °C for 2 h. To the resulting solution was added acetic anhydride (0.45 mL, 4.8 mmol). After the solution was allowed to warm to room temperature, the solution was quenched with aqueous NH_4Cl solution (30 mL) and diethyl ether (50 mL). The ether layer was dried over anhydrous $MgSO_4$, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v, 20:1). Yield: 84% (0.57 g). ^{1}H NMR (acetone-d_6) of **a**: δ 5.44 (s, 1 H), 5.06 (d, J = 7.2 Hz, 1 H), 3.44 (t, J = 6.8 Hz, 1 H), 3.26 (d, J = 5.5 Hz, 1 H), 2.48 (s, 3 H), 2.05 (s, 3 H), 0.64 (s, 9 H) ppm. ^{1}H NMR (acetone-d_6) of **b**: δ 5.57 (t, J = 5.5 Hz, 1 H), 5.38 (d, J = 5.9 Hz, 1 H), 4.86 (d, J = 4.8 Hz, 1 H), 3.44 (s, 1 H), 2.00 (s, 3 H), 1.85 (s, 3 H), 0.72 (s, 9 H) ppm. IR (Et_2O): ν_{CO} 2012, 1927 cm^{-1}. Anal. Calcd for $C_{16}H_{19}MnO_5$: C, 55.50; H, 5.53. Found: C, 55.79; H, 5.61.

4-2-2. Yield: 94%. ^{1}H NMR ($CDCl_3$) of **a**-isomer: δ 7.96 (d, J = 7.4 Hz, 2 H), 7.47 (m, 3 H), 5.32 (s, 1 H), 4.88 (d, J = 6.8 Hz, 1 H), 4.10 (t, J = 6.1 Hz, 1 H), 3.56 (d, J = 6.9 Hz, 1 H), 2.61 (s, 3 H), 1.58 (s, 3 H) ppm. ^{1}H NMR ($CDCl_3$) of **b**-isomer: δ 7.23 (m, 3 H), 6.95 (d, J = 5.7 Hz, 2 H), 5.50 (t, J = 5.1 Hz, 1 H), 5.19 (d, J = 5.2 Hz, 1 H), 4.63 (d, J = 4.3 Hz, 1 H), 4.46 (s, 1 H), 2.04 (s, 3 H), 1.71 (s, 3 H) ppm. IR (Et_2O): ν_{CO} 2010, 1930 cm^{-1}. Anal. Calcd for $C_{18}H_{15}MnO_5$: C, 59.03; H, 4.13. Found: C, 58.61; H, 4.05.

4-2-3. Yield: 69%. ^{1}H NMR ($CDCl_3$) of **a**-isomer: δ 5.08 (s, 1 H), 4.71 (d, J = 7.1 Hz, 1 H), 3.30 (t, J = 6.5 Hz, 1 H), 3.12−3.05 (m, 1 H), 2.50 (s, 3 H), 2.11 (s, 3 H), 0.53 (d, J = 6.4 Hz, 3 H) ppm. ^{1}H NMR ($CDCl_3$) of **b**-isomer: δ 5.45 (t, J = 5.3 Hz, 1 H), 4.98 (d, J = 5.6 Hz, 1 H), 4.43 (d, J = 5.0 Hz, 1 H), 3.19 (d, J = 6.3 Hz, 1 H), 2.11 (s, 3 H), 1.73 (s, 3 H), 0.58 (d, J = 6.4 Hz, 3 H) ppm. IR (Et_2O): ν_{CO} 2010, 1936 cm^{-1}. Anal. Calcd for $C_{13}H_{13}MnO_5$: C, 51.33; H, 4.31. Found: C, 51.56; H, 4.34.

4-2-4. Yield: 85%. ^{1}H NMR ($CDCl_3$): δ 6.96 (d, J = 8.7 Hz, 2 H), 6.79 (d, J = 8.8 Hz, 2 H), 5.78 (t, J = 5.3 Hz, 1 H), 5.34 (d, J = 5.3 Hz, 1 H), 4.93 (d, J = 5.2 Hz, 1 H), 4.40 (s, 1 H), 3.74 (s, 3 H), 2.02 (s, 3 H), 1.71 (s, 3 H) ppm. IR (Et_2O): ν_{CO} 2010, 1938 cm^{-1}. Anal. Calcd for $C_{19}H_{17}MnO_6$: C, 57.59; H, 4.32. Found: C, 57.93; H, 4.42.

4-3-1. The same procedure as the synthesis of **3-3** was applied. Yield: 50%. ^{1}H NMR (CD_3NO_2): δ 6.85 (d, J = 7.1 Hz, 2 H), 6.27 (d, J = 7.1 Hz, 2 H), 2.55 (s, 3 H), 1.45 (s, 9 H) ppm. IR (CH_3NO_2): ν_{CO} 2068, 2012 cm^{-1}. Anal. Calcd for $C_{14}H_{16}BF_4MnO_3$: C, 44.96; H, 4.31. Found: C, 45.08; H, 4.43.

4-3-2. Yield: 40%. ^{1}H NMR (CD_3NO_2): δ 7.61 (m, 5 H), 6.79 (m, 2 H), 6.55 (m, 2 H), 2.53 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2070, 2014 cm^{-1}. Anal. Calcd for $C_{16}H_{12}BF_4MnO_3$: C, 48.77; H, 3.07. Found: C, 48.78; H, 3.10.

Synthesis of 5. It was prepared by method A of the synthesis of **3**. Yield: 69%. ^{1}H NMR (acetone-d_6): δ 6.89 (t, J = 6.7 Hz, 1 H), 6.11 (d, J = 6.7 Hz, 1 H), 6.05 (s, 1 H), 6.04 (d, J = 7.7 Hz, 1 H), 1.49 (s, 9 H) ppm. IR (CH_3NO_2): ν_{CO} 2060, 2000 cm^{-1}. Anal. Calcd for $C_{10}H_7BF_3MnO_5$: C, 36.41; H, 2.14. Found: C, 36.47; H, 2.17.

5-1. The same procedure as the synthesis of **3-1** was applied. Yield: 97%. ^{1}H NMR ($CDCl_3$): δ 5.99 (br s, 1 H), 5.30 (br s, 1 H), 5.04 (br s, 1 H), 4.85 (br s, 1 H), 1.32 (s, 9 H) ppm. IR (CH_3NO_2): ν_{CO} 2036, 1966 cm^{-1}. Anal. Calcd for $C_{13}H_{13}MnO_4$: C, 54.18; H, 4.55. Found: C, 54.00; H, 4.79.

5-2. The same procedure as the synthesis of **3-2-2** was applied. Yield: 65%. ^{1}H NMR ($CDCl_3$): δ 7.20 (m, 3 H), 6.94 (d, J = 6.3 Hz, 2 H), 5.31 (s, 1 H), 4.91 (d, J = 7.3 Hz, 1 H), 4.51 (d, J = 5.9 Hz, 1 H), 3.57 (t, J = 6.9 Hz, 1 H), 2.05 (s, 3 H), 1.49 (s, 9 H) ppm. IR (Et_2O): ν_{CO} 2008, 1918 cm^{-1}. Anal. Calcd for $C_{21}H_{21}MnO_5$: C, 61.77; H, 5.18. Found: C, 61.89; H, 5.31.

5-3. The same procedure as the synthesis of **3-3** was applied. Yield: 80%. ^{1}H NMR (acetone-d_6): δ 8.09 (d, J = 7.9 Hz, 2 H), 7.69 (m, 3 H), 7.42 (d, J = 7.4 Hz, 2 H), 7.14 (d, J = 7.4 Hz, 2

H), 1.56 (s, 9 H) ppm. IR (CH_3NO_2): ν_{CO} 2064, 2000 cm^{-1}. Anal. Calcd for $C_{19}H_{18}BF_4MnO_3$: C, 52.33; H, 4.16. Found: C, 52.23; H, 4.20.

Synthesis of 6. The same procedure as the synthesis of a mixture of **3A** and **3B** was applied except with *p*-methoxyphenol instead of *p*-cresol. Only isomer **B** was obtained. ^1H (CD_3NO_2): δ 6.25 (d, $J = 7.8$ Hz, 2 H), 6.07 (d, $J = 7.7$ Hz, 2 H), 3.93 (s, 3 H) ppm. IR (CH_3NO_2): ν_{CO} 2064, 2004 cm^{-1}. Anal. Calcd for $C_{13}H_{14}BF_4MnO_4$: C, 41.53; H, 3.75. Found: C, 41.88; H, 3.81.

X-ray Data Collection, Structure Determination, and Refinement for Compounds 3B, 4-3-2, and 5-3. Crystal data, details of the data collection, and refinement parameters are listed in Table 2. Selected bond distances and angles are given in Table 3.

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Supporting Information Available: Tables giving atomic positions, anisotropic thermal parameters, and bond lengths and angles for **3B** and **4-3-2**. This material is available free of charge via the Internet at http://pubs.acs.org. Structure factor tables are available from the authors.

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