A Combined Experimental−Theoretical Study on the Lithiation/Electrophilic Quench Sequence of (η^5-Cyclohexadienyl)Mn(CO)$_3$ Complexes

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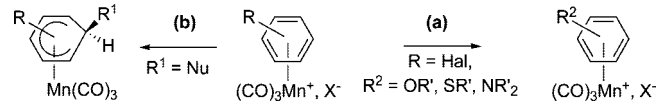
An easy and versatile functionalization of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes by a lithiation/electrophilic quench sequence is described. Using TMSCl as a model electrophile, the reactivity of the series of substrates **1**–**5** was studied. In addition to the regiochemistry control by *ortho*-directing groups, such as OMe or Cl, the results suggest a strong influence of the Mn(CO)$_3$ tripod conformation on the regioselectivity of the lithiation. In order to gain a better understanding of the reactivity features of the cyclohexadienyl ligand in the η^5 complex, a theoretical investigation was undertaken. It indicates that the regioselectivity relies mainly on the intrinsic stabilities of the deprotonated intermediates, the species lithiated at C^2, eclipsed by a Mn−CO bond, being the most stable one. The synthetic methodology was finally successfully extended to a representative range of electrophiles, giving access in good to excellent yields to η^5 derivatives substituted by various heteroatoms (iodine, sulfur, or stannyl groups) or functions, such as ketone, ester, amide, or alcohols, α to the π system.

Introduction

The coordination of a transition metal to an arene modifies the reactivity of the arene ligand in several distinct ways. Among them, the increased acidity of the ring protons, which strongly facilitates direct proton abstraction from the arene, is remarkable. The first lithiation of the arene in an (η^6-arene)Cr(CO)$_3$ complex was reported in 1968,[1] and since then, this reaction has seen extensive development and has been the subject of several reviews.[2] Very surprisingly, no report exists on isoelectronic tricarbonylmanganese complexes, although these have become increasingly important in organometallic and organic syntheses.[3] The lithiation is only known in the close family of (η^5-cyclopentadienyl)Mn(CO)$_3$ complexes, namely, the cymantrene derivatives,[4] where this reaction has found significant applications.[5] The reactivity features of the (η^6-arene)tricarbonylmanganese complexes are the following: *ipso* chloride substitution allows a clean nucleophile introduction (Scheme 1, path a), but such a strategy is restricted to amino, oxo, and thio nucleophiles, thus limiting its scope.[6]

Scheme 1. Reactivity Features of the (η^6-Arene)-tricarbonylmanganese Complexes



All the attempts we made to functionalize an η^6 complex by any other direct route, such as palladium-catalyzed cross-couplings[7] or lithiation, failed. One major limitation in the chemistry of such cationic complexes is the poor solubility of most of them in the usual organic solvents; in order to circumvent this problem, we developed an anion-exchange procedure giving access to tetraarylborate salts.[8] These new substrates are soluble in reaction solvents such as THF and can be purified by chromatography; nevertheless, the nature of the counteranion does not contribute to their reactivity. Finally, the

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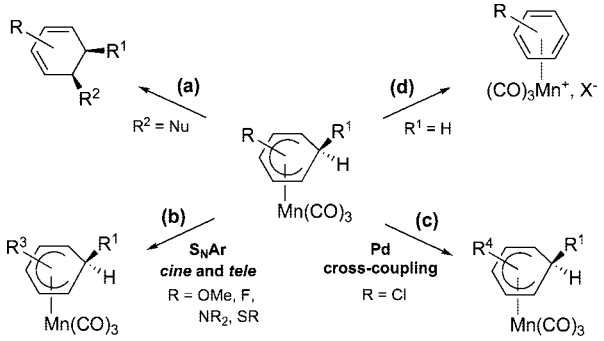
Scheme 2. Reactivity Features of the (η^5-Cyclohexadienyl)-tricarbonylmanganese Complexes



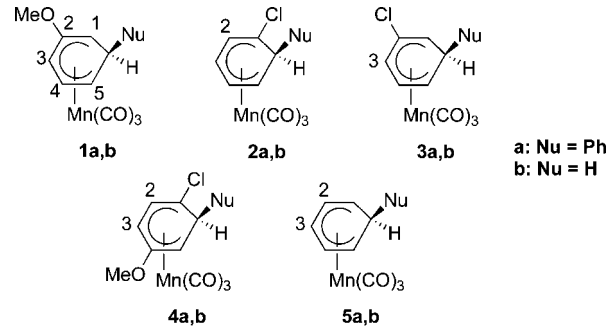


Figure 1. η^5-Cyclohexadienyl)Mn(CO)$_3$ complexes used as substrates in this study.

most useful reaction for the cationic η^6 complexes is the nucleophilic addition (Scheme 1, path b).[9] Indeed, the increased electrophilic character of these cationic complexes, compared to neutral ones, allows the arene to be attacked by a broad range of nucleophiles, leading to neutral and stable (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes, which have become increasingly attractive, in the past decade, to establish efficient functionalization pathways.

The (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes proved to be useful synthetic intermediates,[3,10] which could lead, after nucleophilic addition, to the corresponding dienes (Scheme 2, path a) with total control of the stereochemistry.[10a−c] In the specific case of the (η^5-oxocyclohexadienyl)Mn(CO)$_3$ complexes, the addition of a nucleophile allowed the synthesis of disubstituted η^5 derivatives.[10d−f] Thus, a chemistry at the η^5 system without loss of the metal was developed. The first *cine* and *tele* nucleophilic substitutions of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes (Scheme 2, path b) were developed in 1996 by treatment with hydrides and a proton source,[11] and their mechanism is very close to the *cine* and *tele* S$_N$Ar described for (η^6-arene)Cr(CO)$_3$ complexes.[3d] The discovery of Pd cross-coupling reactions in the η^5-cyclohexadienyl manganese series[12a] enables easy access to a large variety of substituted η^5 complexes, bearing double or triple bonds, aryl or keto groups linked to the π system (Scheme 2, path c).[12b,c] Moreover, this procedure represents an indirect functionalization pathway for (η^6-arene)tricarbonylmanganese complexes, via a rearomatization step (Scheme 2, path d), applicable to substrates bearing an *exo* hydrogen on the sp^3 carbon. This work established that the presence of the tricarbonyl-Mn fragment dramatically activates the carbon−halogen bonds in η^5-cyclohexadienyl Mn complexes in the same way as the tricarbonyl-Cr entity does in η^6-arene Cr complexes for which Pd-catalyzed reactions are well-documented for many years.[13] Based on similar reactivity properties between the η^5-cyclohexadienyl Mn and η^6-arene Cr series, our present work reports the conditions of lithiation of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes and provides a new strategy further extending the scope of applications of the organomanganese family. Part of this work was the subject of a preliminary communication.[14]

Results and Discussion

Lithiation Conditions Depending on the Structure of the Substrates. The (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes **1**–**5** (Figure 1) used as starting materials in this work were readily obtained by nucleophilic addition of phenylmagnesium chloride[15] or hydride[11,16] onto the corresponding [(η^6-arene)-Mn(CO)$_3$]$^+$ complexes. Chloro- and/or methoxy-substituted arenes were chosen for their good *ortho*-directing properties, due either to inductive electron-withdrawing effect (Cl) or to lithium coordination (OMe), as demonstrated in the lithiation of (η^6-arene)Cr(CO)$_3$ complexes.[2] Nucleophilic addition to the cationic manganese complex of chlorobenzene led to a mixture of two regioisomers, **2** and **3**.[11,16] In contrast, due to the strong mesomeric donor effect of the methoxy group in the anisole or *para*-chloroanisole, complexes **1a**,**b** and **4a**,**b** were isolated as the sole (**4a**,**b**) or the major (**1a**,**b**) products after regioselective addition of the nucleophile to the corresponding η^6 complexes. Complexes **5a**,**b**, without any substituent on the cyclohexadienyl ring, were also prepared from the cationic [(η^6-benzene)Mn-(CO)$_3$]$^+$ complex.

The lithiation/electrophilic quench of these complexes was effected by reaction with *n*-butyllithium (*n*BuLi) at −78 °C, followed by the addition of the electrophile at the same temperature. Trimethylsilylchloride (TMSCl) was chosen as the reference electrophile. The experimental conditions were optimized to achieve the complete conversion of each substrate.

These reactions give efficient access to the silylated products with yields ranging from 62 to 88% and a high degree of regiocontrol (Table 1). Although an excess of lithiated base (1.4 to 2 equiv) is necessary for complete conversion of the various substrates, the formation of bis-silylated products resulting from

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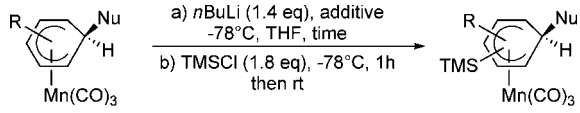
Table 1. Silylation Conditions for Complexes 1–5



1-5 **6-10**

entry	substrate	time	additive	product	position	yield[a] (%)
1[b]	**1a**	1 h	TMEDA	**6a**	C^3	86
2	**1b**	1 h	TMEDA	**6b**	C^3	66
3[b]	**2a**	1 h	none	**7a**	C^2	62
4[b]	**3a**	1 h	none	**8a**	C^3	81
5[b]	**4a**	15 min	none	**9a** + **9′a**	$C^2 + C^{3c}$	88
6	**4a**[d]	1 h	none	**9a** + **9′a**	$C^2 + C^{3e}$	82
7	**4b**	15 min	none	**9b** + **9′b**	$C^2 + C^{3f}$	75
8	**5a**[g]	2 h	TMEDA	**10a** + **10′a**	$C^2 + C^{3h}$	66

[a] Isolated yield, unless otherwise specified. [b] Reference 14. [c] Ratio = 90:10 determined by ^{1}H NMR analysis of the crude mixture. [d] LDA instead of *n*BuLi. [e] Ratio = 75:25. [f] Ratio = 60:40. [g] 2 equiv of *n*BuLi and TMEDA, 2.5 equiv of TMSCl. [h] Ratio = 80:20.

a double deprotonation has never been observed.[17] The efficiency of the cyclohexadienyl lithiation, based on the use of *n*BuLi at −78 °C, is in sharp contrast with the nucleophilic addition of methyl- or aryl-lithium reagents to a carbonyl Mn ligand at higher temperature, leading first to acylmetalate species, then to the corresponding carbene complexes after an alkylation step.[18]

For complexes **1**–**4**, substituted by *ortho*-directing groups, NMR characterization of products **6**–**9** confirmed that the trimethylsilyl group is, in all cases, located *ortho* to the Cl or OMe substituent.[19] When a chlorine atom is present on the complex (Table 1, entries 3–7), no competing halogen−lithium exchange was observed, similarly to what has already been noticed for chloro-substituted (η^6-arene) metal complexes.[2d,20] In order to determine the most efficient procedure, we tested the lithiation of complex **4a**, the *para*-chloroanisole derivative, with the milder base lithium diisopropylamide (LDA) (Table 1, entry 6). We were pleased to observe that LDA is able to deprotonate the metal-coordinated cyclohexadienyl moiety. However, whereas the reaction time was 15 min in the case of *n*BuLi (Table 1, entry 5), 1 h was required for a complete conversion to give the silylated derivatives in 82% yield. The lithiation/electrophilic quench sequence was also tested in Et_2O, instead of THF. The lithiation step is nevertheless slower in this solvent; longer reaction times were therefore needed, leading to partial degradation of the lithiated species.

We can compare the substituent effects on the reactivity from the series of complexes **1**–**5**: complexes **a**, bearing a phenyl group on the *exo* position, give the silylated products with better overall yields than the corresponding complexes **b**, with an *exo* hydrogen on C^6. These latter ones seem more sensitive to degradation during the lithiation step, which therefore needs to be carefully monitored. This was clearly observed for substrates **2b**, **3b**, and **5b**, for which poor yields were obtained and were not optimized. The 2-methoxy derivative **1a**, which gives the 3-trimethylsilylated complex **6a** (Table 1, entry 1), is less reactive than the chloro-substituted ones **2a** and **3a**, which afford the 2- and the 3-trimethylsilylated complexes **7a** and **8a** (Table 1, entries 3 and 4): thus, in the case of **1a**, addition of tetramethylethylenediamine (TMEDA) was needed to ensure complete conversion of the substrate. Complex **4a** appears to be the most reactive η^5-cyclohexadienyl complex, probably due to a synergic effect of the two activating groups: the reaction required only 15 min at −78 °C without TMEDA for complete conversion of this substrate (Table 1, entry 5). When both the C^1 and C^3 positions are available adjacent to the C^2 substituent, as in **1a** or **3a**, the competition between C^1 and C^3 is fully controlled for *selective lithiation at the C³ position* (Table 1, entries 1 and 4). Furthermore, when two *ortho*-directing groups are present as in **4a**, there is a substantial preference for lithiation at C^2, *ortho* to the chlorine atom (Table 1, entries 5 and 6).

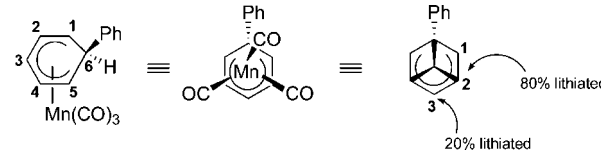


Figure 2. Regioselective lithiation of (η^5-6-phenylcyclohexadienyl)$Mn(CO)_3$ complex **5a**.

Theoretical Investigation on the Lithiation of Substrates 5. It is important to highlight that the lithiation is still efficient without any activating group on the substrate. Indeed, the cyclohexadienyl complex **5a** has been silylated in 66% yield (Table 1, entry 8), although stronger conditions were required: reaction with 2 equiv of *n*BuLi and TMEDA for 2 h before addition of the electrophile. Two regioisomers, resulting from the lithiation at $C^{2,4}$ or at C^3, were isolated in a 80:20 ratio, respectively; again, no lithiation was observed on the $C^{1,5}$ positions of the cyclohexadienyl (Figure 2). This selectivity should arise from the greater sp^2 character of the $C^{2,4}$ and C^3 carbon atoms with respect to the $C^{1,5}$ carbons, the five C−H bonds of the metal-complexed cyclohexadienyl being not equivalent toward deprotonation.

Furthermore, conformational effects might be put forward to explain the high selectivity for the lithiation at the $C^{2,4}$ positions; it is indeed well-known that, in all the structures of η^5 complexes described in the literature, the $Mn(CO)_3$ tripod adopts a conformation eclipsing the C^2, C^4, and C^6 carbons,[12a] as justified from a molecular orbital point of view.[21] A similar tripod conformation was also obtained from geometry optimization for isoelectronic and isostructural tricarbonylchromium[22] and tricarbonyliron[23] analogues. A computational study was performed on complex **5b** starting from the opposite conformation, in which the C^6 center is *anti*-eclipsed with respect to the CO ligands. This structure is found to be a transition state (TS) connecting two eclipsed structures. The associated rotational barrier is 9.9 kcal/mol, which is consistent with a slow rotation movement and is marginally higher that the value reported in

(17) Multiple metalated species can indeed be generated if more than one equivalent of base is employed in the lithiation of (η^6-arene)$Cr(CO)_3$ complexes: Gibson, S. E.; Steed, J. W.; Sur, S. *J. Chem. Soc., Perkin Trans.1* **2001**, 636, and references therein.

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Table 2. Energies (kcal/mol) with Respect to the Most Stable Regioisomer (for definition of $L_{H\text{-}Me}$, see text)

entry				
1	**5a**$^-$ (R = Ph)	5.1	0.0	3.2
2	**5b**$^-$ (R = H)	4.8	0.0	3.0
3	**X** = $LiL_{H\text{-}Me}$	3.0	0.0	1.4
4	**X** = SiH_3	0.9	2.7	0.0
5	$C_6H_6^{2-}$	0.8	0.0	4.1

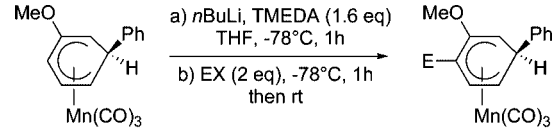
the literature[22] for the anionic (η^5-cyclohexadienyl)Cr(CO)$_3$ complex. This represents, to the best of our knowledge the first computational study dealing with (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes since the work by R. Hoffmann et al.[24] They reported on the charge densities of the π system carbons calculated for the cyclohexadienyl anion as well as the (η^5-cyclohexadienyl)Mn(CO)$_3$ complex in the course of a study dealing with the origin of the geometrical deformation of the cyclohexadienyl ring upon complexation.

Conformational effects have already been observed for the lithiation of the (η^6-dimethylaniline)Cr(CO)$_3$ complex, giving the *meta* substitution as the major product, whereas the lithiation of the uncomplexed dimethylaniline is selective of the *ortho* position.[25] The authors have proposed that the chelation of the alkyllithium base by the oxygen of a CO ligand could be at the origin of this unusual selectivity. In the cyclohexadienyl complexes **5a**,**b**, such a coordination between *n*BuLi and a carbonyl ligand could also be involved in the selective lithiation at C^{2,4} carbons. It is nevertheless not the only regiodirector effect that can be proposed for this system due to the inequivalence of the five hydrogen atoms. Deprotonation and lithiation of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes **5a** and **5b** were thus computationally examined in detail in order to determine the origin of the experimentally observed regioselectivity. The species deprotonated in position C^2 (Table 2, entries 1 and 2) are found to be the most stable in both cases. No major effect of the phenyl substituent in position C^6 could be observed: the unsubstituted **5b** was thus used as a model in the following study in order to limit the computational cost. Rotational barriers for the species deprotonated in C^1, C^2, and C^3 are respectively 8.8, 9.9, and 6.0 kcal/mol, indicating that the conformational preference of the complex is not affected upon deprotonation, whatever the deprotonation site is. This is consistent with the fact that deprotonation alters the σ skeleton of the cyclohexadienyl ligand, whereas coordination to the metal relies on the π orbitals.

The study of the relative stability of the lithiated form of **5b** was then undertaken in order to examine the effect of the counterion coordination on the relative stabilities of the deprotonated species. It is well-known that the structure of lithiated compounds in solution most often involves aggregation, so that the species computed in this case are not exactly portraying the species present in solution. It can nevertheless be assumed that the relative stability of the regioisomers in the monomeric species is similar to that in the aggregated form. However, the sole replacement of the hydrogen by a naked Li appears to be a too rough modeling. Indeed, geometry optimizations lead to strongly distorted species since, in the absence of any explicit solvent representation, the lithium cation is seaking to complete its coordination sphere. It thus builds chemically unrelevant interactions with its neighbors, namely, the CO ligands (Figure 3). A chemical model of TMEDA was thus coordinated to the lithium cation in order to get closer to the experimental system. It leads to a tricoordinated lithium, which is consistent with recent theoretical data[26] for this cation in the presence of steric hindrance. For the sake of computational cost, the methyl groups were replaced by H substituents, and ethylenediamine (referred as $L_{H\text{-}H}$ = $H_2N\text{-}C_2H_4\text{-}NH_2$) was used. Nevertheless the obtained structures using this model are still not satisfying since H-bonds are being built during the optimization process between the amine groups of $L_{H\text{-}H}$ and the carbonyl ligands, interactions that are not relevant since the hydrogens are modeling Me groups (Figure 3). The most suitable model was finally the dimethylethylenediamine ligand, $L_{H\text{-}Me}$ = $MeHN\text{-}C_2H_4\text{-}NHMe$, the methyl being added only on the *endo* side of the molecule, in order to avoid any H bonds with the CO ligands (Figure 3).

The lithium sphere being completed with $L_{H\text{-}Me}$ in the lithiated form of **5b**, the lithiated species at C^2 is found to be the most stable regioisomer (Table 2, entry 3). It thus appears that the preference for position C^2 obtained in the anionic species (Table 2, entry 2) is maintained even when the negative charge is

Table 3. Functionalization of 1a by Various Electrophiles



entry	EX	E−	product	yield[a] (%)
1[b]	MeI	Me−	**11a**	82
2	CD_3OD	D−	**12a**	96
3[b]	nBu$_3$SnCl	nBu$_3$Sn−	**13a**	87
4[b]	$I(CH_2)_2I$	I−	**14a**	95
5[b]	$ClCO_2Et$	EtO_2C−	**15a**	72
6	$ClC(O)N(Me)_2$	$Me_2N(O)C$−	**16a**	50[c]

[a] Isolated yield, unless otherwise specified. [b] Reference 14. [c] 2.5 equiv of EX and 2.5 h at −78 °C before warming at rt.

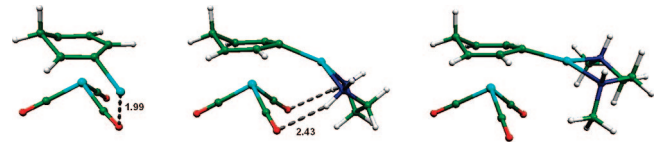


Figure 3. Representation of the lithiated species in position C^2 (left) and C^3 (center and right): Li^+ cation alone (left), Li^+ cation coordinated to $L_{H\text{-}H}$ (see text for notation, center), and the retained model of a Li^+ cation coordinated to $L_{H\text{-}Me}$ (right). Distances of the undesired interactions are given in Å.

(24) Hoffmann, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.
(25) (a) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2560. (b) Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 955.
(26) See for recent examples: (a) De la Lande, A.; Fressigné, C.; Gérard, H.; Maddaluno, J.; Parisel, O. *Chem. Eur. J.* **2007**, *13*, 3459. (b) Pratt, L. M.; Truhlar, D. G.; Cramer, C. J.; Kass, S. R.; Thompson, J. D.; Xidos, J. D. *J. Org. Chem.* **2007**, *72*, 2962, and references therein.

stabilized by coordination to a lithium center. The experimentally observed preference for functionalization at C^2 can thus be fully justified on the basis of the stability of the intermediate carbolithiated moiety, stability that is found to be similar to that of the carbanionic complex. Moreover, the stability of the final silylated product cannot be at the origin of the experimentally observed 80:20 ratio for C^2:C^3. Indeed, computations on the SiH_3 addition products (Table 2, entry 4), models for the $SiMe_3$ complexes experimentally obtained, gave the C^3-functionalized species as the most stable and therefore the major product.

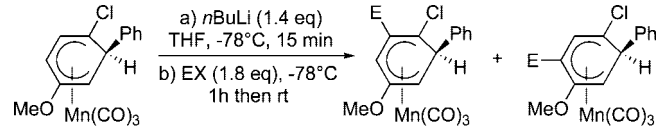
In addition to the preference for position C^2, the results of the computations are also in line with the reactivity of position C^3, for which the carbolithiated species is found to be only 1.4 kcal/mol above the reference. This is fully in line with the experimental observation for the formation of 20% of **10′a** (Table 1, entry 8), the regioisomer substituted at position C^3. On the other side, the species lithiated at position C^1 is significantly higher in energy (Table 2, entry 3) and is therefore not expected to be formed. In order to bring forward the role played by the $Mn(CO)_3$ tripod on the regioselectivity, we examined the deprotonation of a "virtual" unbound anionic cyclohexadienyl ligand, $C_6H_6^{2-}$ (Table 2, entry 5); such a comparison with an uncoordinated ligand has also proven its usefulness in the computational studies of aryl[27] or benzyl[28] anions, radicals, and cations of (η^6-arene)$Cr(CO)_3$ complexes in order to understand their chemical properties. The results show that positions C^1 and C^2 are very close in energy, whereas position C^3 is much more destabilized. This is in sharp contrast with the complexed analogue **5b**$^-$ (Table 2, entry 2) and thus with the experimental results. In conclusion, whereas a slight preference for position C^2 is intrinsic to the cyclohexadienyl ligand, the strong destabilization of position C^1, and thus the regioselectivity of the lithiation, is thermodynamically due to its coordination to the $Mn(CO)_3^+$ moiety. In these conditions, the strong conformational preference of the $Mn(CO)_3^+$ moiety is likely to play an important role in the selectivity of the reaction.

Extension to a Wide Range of Electrophiles. Having investigated Me_3SiCl as an electrophile for functionalization of various η^5 complexes, we carried out further investigations using a large panel of electrophiles, complexes **1a** (Table 4) and **4a** (Table 5) being chosen as model substrates. The results established the general applicability of the lithiation/electrophilic quench sequence, which led to a large variety of derivatives in moderate to excellent yields (50 to 95%). Most of the functional groups presented in Tables 4 and 5 are incompatible with the arene complexation procedures[29] and therefore need to be introduced subsequently by efficient synthetic procedures.

This reaction is efficient not only to label the cyclohexadienyl ring by a deuterium (Table 3, entry 2) but also to introduce alkyl groups (Tables 3 and 4, entry 1) and thioether (Table 4, entry 5), ketone (Table 4, entry 4), and ester (Table 3, entry 5; Table 4, entry 3) functions. An amide derivative (Table 3, entry 6) was also prepared, but in a relatively lower yield, using a carbamoyl chloride as the electrophile. In an earlier study, we already introduced ketone, ester, and amide groups on (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes by using the C−Cl reactivity toward Pd-catalyzed coupling reactions under a CO atmosphere.[12a] In the present work, the procedure does not affect the substituents of the starting material, and consequently, when a chlorine atom is present as in **2**, **3**, or **4**, it remains available for a subsequent functionalization. This new approach is therefore complementary to the Pd-catalyzed method published in this series a few years ago. More strategically important products were formed by reaction with tributyltin chloride and 1,2-diiodoethane, introducing tributylstannyl (complexes **13a** and **23**–**23′a**) and iodo (complexes **14a** and **22**–**22′a**) groups in high yields (86–95%). Monocrystals of complex **14a** were readily obtained and the corresponding crystal structure was previously described.[14] The synthesis of the boronated η^5 complex **18a** was also attempted (Table 4, entry 2); although the expected product was formed with a good conversion (70%) in the crude mixture, we failed to isolate it in a pure form. As far as further transformations are concerned, such functionalized complexes could be involved in halogen−metal or metal−metal exchange[30] and also in palladium cross-coupling procedures. Indeed, the methodology previously developed in our group allowed efficient functionalization at the C^1 and C^2 positions of the cyclohexadienyl ring. Thanks to the lithiation/electrophilic quench sequence, new precursors bearing suitable functions at C^3 can now be synthesized.

The regioselectivity of the lithiation/electrophilic quench process for the *para*-chloroanisole derivatives **4a**,**b** deserves much more comment. Indeed, as two *ortho*-directing groups are

Table 4. Functionalization of 4a by Various Electrophiles

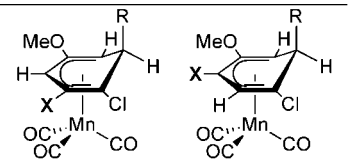


4a **17a-23a** **17′a-23′a**

entry	EX	E−	product	yield[a] (%)	C^2:C^3[b]
1	MeI	Me−	**17a**	80	100:0
2	(−C(Me)$_2$O)$_2$B-O*i*Pr	(−C(Me)$_2$O)$_2$B-	**18a**	70[c]	100:0
3	$ClCO_2Et$	EtO_2C−	**19a** + **19′a**	84	80:20
4	$(CH_3)_3COCl$	$(CH_3)_3CO$−	**20a** + **20′a**	86	74:26
5	PhS-SPh	PhS−	**21a** + **21′a**	73	65:35
6	$I(CH_2)_2I$	I−	**22a** + **22′a**	86	62:38
7	*n*Bu_3SnCl	*n*Bu_3Sn−	**23a** + **23′a**	86	57:43

[a] Isolated yield, unless otherwise specified. [b] Determined by ^1H NMR analysis of the crude mixture. [c] Conversion, determined by ^1H NMR analysis of the crude mixture.

Table 5. Energies (kcal/mol) with Respect to the Most Stable Regioisomers (for definition of $L_{H\text{-}Me}$, see text)



entry			
1	X = ⊖	1.4	0.0
2	X = $LiL_{H\text{-}Me}$	0.0	2.6
3	X = $Li(OMe_2)_2$	0.0	1.6

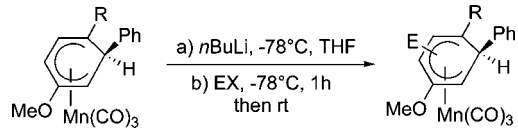
(27) Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904.

(28) Merlic, C. A.; Walsh, J. C.; Tantillo, D. J.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3596.

(29) Jackson, J. D.; Villa, S. J.; Bacon, D. S.; Pike, R. D.; Carpenter, G. B. *Organometallics* **1994**, *13*, 3972.

(30) See for example: Ariffin, A.; Blake, A. J.; Ewin, R. A.; Li, W.-S.; Simpkins, N. S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3177.

Table 6. Selective Access to Variously Substituted (η^5-hydroxymethylcyclohexadienyl)Mn(CO)$_3$ Complexes



entry	substrate	R−	EX	E−	product	yield[a] (%)	C^2:C^3[b]
1[c]	**1a**	H−	Ph_2CO	$Ph_2C(OH)$−	**24a**	83	C^3 only
2	**1a**	H−	PhCHO	PhCH(OH)−	**25a**[d]	93	C^3 only
3	**4a**	Cl−	Ph_2CO	$Ph_2C(OH)$−	**26a** + **26′a**	64	60:40
4	**4a**	Cl−	PhCHO	PhCH(OH)−	**27a** + **27′a**[e]	87	66:34
5	**4a**	Cl−	$(CH_3)_2CO$	$(CH_3)_2C(OH)$−	**28a** + **28′a**	31[f]	65:35

[a] Isolated yield, unless otherwise specified. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] Reference 14. [d] Four diastereoisomers (2 pairs of enantiomers) in a 56:44 ratio. [e] Four diastereoisomers (2 pairs of enantiomers) in a 52:48 ratio for **27a**, a 75:25 ratio for **27′a**. [f] Conversion of 46% determined by ^{1}H NMR analysis of the crude mixture.

present, two regioisomers are isolated from the lithiation either *ortho* to the methoxy group or *ortho* to the chlorine atom. We have not been able to separate all the regioisomers by chromatography on silica gel, depending on the polarity of the resulting η^5 complexes. The different results are summarized in Table 1 (entries 5–7) and in Table 4. The first comment is that there is a substantial preference for the functionalization at C^2, *ortho* to the chlorine atom. From Table 4, it also clearly appears that the regioselectivity is highly dependent on the electrophile introduced. While a unique regioisomer is isolated using iodomethane (C^2:C^3 = 100:0; Table 4, entry 1), two regioisomers are obtained in C^2:C^3 ratios varying from 90:10 for Me_3SiCl (Table 1, entry 5) to 57:43 for tributyltin chloride (Table 4, entry 7). This variation according to the electrophile suggests that the regioselectivity is not fully determined at the end of the deprotonation step; depending on the electrophilic quench kinetics, an isomerization of the lithiated η^5 anion might occur. Equilibration processes have also been observed with lithiated (η^6-arene)Cr(CO)$_3$[31] and have for instance been put forward to explain the erosion of the ee observed in the enantioselective lithiation of anisole-type arene chromium complexes.[31c] We led several nonconclusive attempts to get more information about the isomerization process involved in the lithiated (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes. For instance, allowing the temperature to increase before the electrophile addition led to the degradation of the lithiated species instead of their expected thermodynamic equilibration.[31a,b] A second reported strategy to demonstrate the occurrence of an anion equilibration consists in submitting a stannylated substrate to a metal−metal exchange with *n*BuLi and then determining its stability after quenching with an electrophile such as TMSCl.[31c] Unfortunately, in our case, we could not separate the stannylated regioisomers **23a**−**23′a** in order to obtain a pure substrate.[32]

Theoretical investigations within the stability of the *para*-chloroanisole derivatives evidence the greater complexity of the regioselectivity issue in this system. The C^2 deprotonated species without any countercation Li^+ is found to be disfavored by 1.4 kcal/mol with respect to the C^3 one (Table 5, entry 1), whereas it was favored by 3.0 kcal/mol in the unsubstituted species (Table 2, entry 2). The potential for lithium coordination to OMe is therefore not the only origin of its *ortho*-directing properties. This could be explained by simple inductive attractor effects on the σ skeleton localized minus charge: indeed, the methoxy group electronegativity (3.7)[33a] is higher than the chloride one (2.8).[33b]

In contrast, the C^2-lithiated form, stabilized by coordination of the Li cation to $MeNHCH_2CH_2NHMe$ ($L_{H\text{-}Me}$) as in the case of the unsubstituted η^5 complex computations (Table 2, entry 3), was found to be the most stable by 2.6 kcal/mol (Table 5, entry 2). The C^2-substituted form is also found to be the most stable when the lithium is coordinated to two additional dimethyl ether molecules in order to model solvation. It highlights the strong impact of the lithium chelation at the anionic center on the regiochemical outcome of the reaction for this specific substrate. In this connection, the stability of the species will most probably be altered by other factors, among which aggregation but also chelation to the electrophile. A close examination of the mechanisms of both lithiation and electrophilic quench, and especially of the regiochemical stability of the lithiated intermediates in the presence of the electrophile, is thus necessary, and a thorough study will be published in due time.

Application: Synthesis of Unprecedented Alcohol Derivatives and Indirect Functionalization of η^6 Complexes. Having in hand an efficient and general substitution pathway, we turned our attention to η^5 manganese complexes substituted by an alcohol group, α to the π-system. Such complexes cannot be prepared from the corresponding cationic complexes, the benzylic alcohol function being indeed incompatible with the complexation procedures. For this reason, the first example was only recently reported in our group[34] and was obtained by hydride reduction of a keto-substituted η^5 complex prepared by a palladium-catalyzed carbonylative coupling. In comparison, the lithiation/electrophilic quench sequence offers a one-pot access to alcohol derivatives, provided that an aldehyde or a ketone is employed as the electrophile. We therefore undertook the synthesis of variously substituted (η^5-hydroxymethylcyclohexadienyl)Mn(CO)$_3$ complexes, starting from either **1a** or **4a** and following the previously optimized experimental conditions. Benzophenone, benzaldehyde, and acetone were chosen as the electrophiles.

The expected alcohol derivatives were isolated in good to excellent yields, except for **28a**−**28′a** (Table 6, entry 5), for which the poor conversion could be explained by a competitive

(31) (a) Treichel, P. M.; Kirss, R. U. *Organometallics* **1987**, *6*, 249. (b) Schmalz, H.-G.; Volk, T.; Bernicke, D.; Huneck, S. *Tetrahedron* **1997**, *53*, 9219. (c) Ewin, R. A.; MacLeod, A. M.; Price, D. A.; Simpkins, N. S.; Watt, A. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 401.

(32) The metal−metal exchange was nevertheless attempted on the mixture of the two stannylated regioisomers (C^2:C^3 = 55:45), giving a new ratio C^2:C^3 = 82:18.

(33) (a) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182, and references therein. (b) Alred, A. L.; Rochov, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

(34) Eloi, A.; Rose-Munch, F.; Jonathan, D.; Tranchier, J.-P.; Rose, E. *Organometallics* **2006**, *25*, 4554.

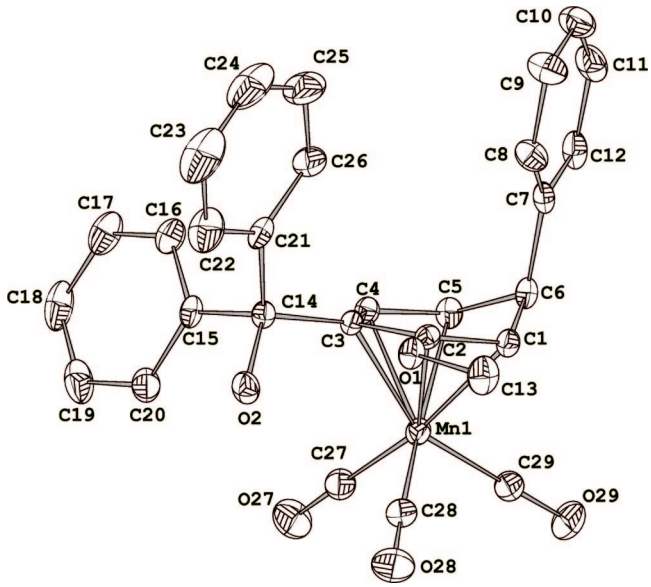


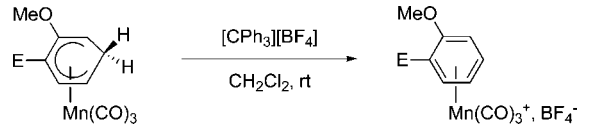
Figure 4. Molecular structure of complex **24a** with thermal ellipsoids at the 30% probability level. All H atoms are omitted for clarity. Selected bond lengths (Å): Mn−C[1] 2.223(2), Mn−C[2] 2.1979(18), Mn−C[3] 2.1628(18), Mn−C[4] 2.149(2), Mn−C[5] 2.241(2), C[3]−C[14] 1.545(3), C[14]−O[2] 1.438(2).

acetone enolization, giving back the substrate **4a**. When benzaldehyde was used as the electrophile, a new stereogenic center was created during the addition of the lithiated anion. Although prepared as racemic mixtures, the substrates **1a** and **4a** indeed present a planar chirality. Four diastereoisomers (two pairs of enantiomers) were therefore obtained and the diastereoisomeric ratios determined by ^{1}H NMR analysis of the crude mixtures. The facial stereodiscrimination of the benzaldehyde C=O bond by the planar chiral anion is not efficient for **25a** (dr = 56:44) and **27a** (dr = 52:48) and is really limited for **27′a** (dr = 75:25); this lack of diastereoselectivity has been observed previously in a similar experiment using a planar chiral (η^6-lithio-arene)Cr(CO)$_3$ complex.[31c]

Pleasingly, monocrystals of complex **24a** were readily obtained to provide a crystal structure of an alcohol-substituted (η^5-cyclohexadienyl)Mn(CO)$_3$ complex.[35] The ORTEP view is presented in Figure 4 as well as some selected bonds. The diphenylhydroxymethyl group is located adjacent to the methoxy group, the distance between the two oxygens O[1] and O[2] being 2.733 Å, suitable for the establishment of a hydrogen bond between these two functions. The single C[14]−O[2] bond presents a 1.438(2) Å bond length value very similar to the one (1.398(7) Å) found in the structure of the η^5 complex containing an alcohol function α to the C[1] carbon.[34] The two phenyl groups are oriented in order to minimize the steric hindrance. The η^5 structure has not been modified by the functionalization, with five coplanar sp^2 carbons, while the remaining sp^3 carbon is located 38° above this plane. The conformation of the Mn(CO)$_3$ tripod is in agreement with what is usually observed,[12a] the sp^3 C[6] carbon being eclipsed by one Mn−CO bond.

(35) Crystal data for **24a**: $C_{29}H_{23}MnO_5$, M = 506.43, yellow crystals, T = 250 K, monoclinic, space group $P2_1/c$, a = 12.864(3), b = 11.6069(18), c = 17.1408(8) Å, V = 2533.4(7) Å^3, Z = 4, ρ_{calcd} = 1.328 g·cm^{-3}, $2\theta_{max}$ = 64°, μ(Mo Kα) = 5.574 cm^{-1}, 8783 independent reflections, R = 0.0303, wR = 0.0307. The structure was solved by direct methods using SHELXS86 and refined with full-matrix least-squares technique on F using the CRYSTALS programs. CCDC-650517 and the supporting information contain the supplementary crystallographic data for this paper.

Table 7. Synthesis of Functionalized (η^6-Arene)Mn(CO)$_3^+$ Complexes by Rearomatization



entry	substrate	E−	product	yield[a] (%)
1	**6b**	−SiMe$_3$	**29**	78
2	**30b**	−I	**31**	76

[a] Isolated yield, unless otherwise specified.

This novel family of metal-complexed benzylic alcohols could exhibit a rich and varied chemistry, which is currently under investigation.

The straightforward access to a large panel of functionalized η^5 manganese derivatives opens numerous perspectives for the chemistry of tricarbonylmanganese complexes. Among them, the indirect functionalization of the cationic (η^6-arene)Mn(CO)$_3^+$ complexes is especially attractive. Indeed, as mentioned before, most of the functionalized cationic complexes are difficult or impossible to prepare by direct complexation. Taking advantage of the rearomatization procedure by *exo*-hydride abstraction[6a] already successfully exploited in the group,[12a] we have applied it to two new η^5 complexes, **6b** and **30b** (Table 7), the latter one being synthesized in 61% yield by lithiation of **4b** followed by an electrophilic quench with diiodoethane; the corresponding η^6 cationic complexes **29** and **31** were isolated in 78 and 76% yield, respectively.

Whereas (η^6-chloroarene)Mn(CO)$_3^+$ and their corresponding η^5complexes have been well-documented for many years, only two syntheses[6a,29] of a bromo derivative are mentioned in the literature to our knowledge, leading to a mixture, difficult to purify, of the expected (η^6-bromobenzene)Mn(CO)$_3^+$ complex either with a dehalogenated derivative, the (η^6-benzene)Mn(CO)$_3^+$,[6a] or with Mn(CO)$_6^+$.[29] As for an iodo-substituted complex, nothing has been reported up to now.[36] The nucleophilic addition/lithiation/electrophilic quench/rearomatization sequence represents therefore the only alternative to efficiently prepare the halogeno manganese η^6 derivatives.

Conclusion

We successfully developed a highly efficient and versatile strategy for easy functionalization of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes through a lithiation/electrophilic quench sequence. The electrophiles examined (methyl iodide, diphenyldisulfide, tributylstannyl chloride, ethyl chloroformiate, pivaloyl chloride, ...) all gave good to excellent yields of the corresponding substituted η^5 complexes. Using benzophenone or benzaldehyde as electrophiles led to the formation, also in very good yields, of η^5 complexes substituted by alcohol functions. In all cases the reaction occurred at the π system, *ortho* to the directing groups, when OMe or Cl is present, and no functionalization was detected at the extremity positions C[1] and C[5] of the cyclohexadienyl moiety. Theoretical investigations performed on η^5 complexes without any substituent on the conjugated system provided a particularly well-suited example of the fruitful interplay between theory and experiment. Indeed, they highlighted the major role of the Mn(CO)$_3$ tripod on the

(36) The complexation of iodobenzene, according to the chlorobenzene complexation procedure, was unsuccessful in our hands: Chavarot, M.; Rose-Munch, F.; Rose, E., unpublished results.

regioselectivity of the lithiation/electrophilic quench sequence which is mainly governed by the stability of the deprotonated species on the C^2 carbon eclipsed by a Mn−CO bond. On the other hand, the origins of the reaction regioselectivity on the *para*-chloroanisole derivatives are less obvious; preliminary theoretical studies showed that it cannot be anymore explained by the sole thermodynamic properties of the deprotonated species.

This new reaction, together with the Pd-catalyzed cross-couplings that we developed a few years ago, sheds new light on the applications of (η^5-cyclohexadienyl)Mn(CO)$_3$ complexes in organic and organometallic syntheses.

Experimental Section

Computational Details. Full geometry optimizations were systematically conducted with no symmetry restraints using the Gaussian 03 program[37] within the framework of the density functional theory (DFT) using the hybrid B3LYP exchange−correlation functional[38–40] and the 6-31+G** basis set for all atoms. This level of theory has been widely used in modeling arene-Cr(CO)$_3$ complexes and has proved to give good results from both geometrical[41] and energetic basis.[22] NMR chemical shift computations were carried out using the standard Gaussian03 procedure. Evaluation of chemical shifts using such gas-phase modeling should be taken cautiously since long-range environment effects are known to play an essential role in chemical shifts. Nevertheless, since the present study is only concerned with trends in series of highly analogous compounds, we believe the results remain reliable.

General Procedures. All reactions were routinely performed under a dry nitrogen atmosphere using standard Schlenk techniques. THF was dried over sodium benzophenone ketyl and distilled. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled over KOH and stored under nitrogen over 4 Å molecular sieves. Acetone and benzaldehyde were distilled over K_2CO_3. NMR spectra were recorded on a Bruker ARX 200 MHz or Avance 400 MHz spectrometer. Infrared spectra were measured on a Bruker Tensor 27 spectrometer. Elemental analyses were performed by the Service Central d'Analyze du CNRS. Mass spectra were performed for MALDI-TOF by the Plate-Forme Spectrométrie de Masse et Protéomique (IFR83, UPMC), for ES-MS by the Groupe de Spectrométrie de Masse (UMR 7613, UPMC), and for the EI-MS by the Service de Spectrométrie de Masse de l'ENS (Chemistry Dpt, Paris).

Complexes **1a**,[15] **1b**,[11] **2a**,[16] **2b**,[11] **3a**,[16] **3b**,[11] **4a**,[12a] **4b**,[11] and **5a**[15] were synthesized according to procedures previously described in the literature.

Typical Procedure for the Lithiation/Electrophilic Quench Sequence. A solution of (η^5-cyclohexadienyl)Mn(CO)$_3$ complex (0.5 mmol) and freshly distilled TMEDA (0 to 2 equiv; see Table 1) in 5 mL of THF was cooled to −78 °C. A solution of *n*-BuLi (1.6 M in hexanes; 1.4 to 2 equiv; see Table 1) was slowly added. The mixture was stirred for 15 min to 2 h (see Table 1) at −78 °C before the addition of the electrophile (1.6 to 2.5 equiv; see Table 1). The mixture was stirred for another hour at −78 °C before warming to room temperature and quenching by addition of H_2O. After extraction of the mixture by Et_2O, the combined organic layers were washed with a saturated aqueous NaCl solution and dried over $MgSO_4$. After concentration *in vacuo*, the crude mixture was purified by flash chromatography on silica gel to afford the pure functionalized η^5-cyclohexadienyl complex.

6a (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.45 (s, 9H, $SiMe_3$), 3.38 (s, 3H, OCH_3), 3.50 (m, 2H, H^1 and H^5), 3.97 (t_{app}, J = 6.0 Hz, 1H, H^6), 4.86 (d, J = 6.4 Hz, 1H, H^4), 6.89–6.92 (m, 2H, H^{Ph}), 7.12–7.27 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.2 ($SiMe_3$), 42.9 (C^6), 44.2 (C^1), 54.4 (OCH_3), 61.9 (C^5), 74.7 (C^3), 97.3 (C^4), 125.9 (CH^{Ph}), 127.1 (CH^{Ph}), 128.8 (CH^{Ph}), 146.6 (C^2 or C^{Ph}), 148.0 (C^2 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1913, 2007 (CO (Mn)). HRMS (EI, positive mode): *m/z* calcd for $C_{19}H_{21}MnO_4Si$, 396.0590; found, 396.0599 (M^+).

6b (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.41 (s, 9H, $SiMe_3$), 2.19 (d, J = 12.6 Hz, 1H, H^{6exo}), 2.73–3.01 (m, 3H, H^1, H^5 and H^{6endo}), 3.29 (s, 3H, OCH_3), 4.75 (d, J = 7.2 Hz, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.5 ($SiMe_3$), 27.1 (C^6), 36.5 (C^1), 54.2 (OCH_3), 54.8 (C^5), 75.1 (C^3), 99.3 (C^4), 147.4 (C^2), 220.6 (CO (Mn)). IR (neat):$\tilde{\nu}$ (cm^{-1}) 1910, 2005 (CO (Mn)). HRMS (MALDI TOF, positive mode): *m/z* calcd for $C_{13}H_{16}MnO_4Si$, 319.0198; found, 319.0117 (M + H^+).

7a (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.35 (s, 9H, $SiMe_3$), 3.75 (ddd, J = 7.0, 6.3, 1.5 Hz, 1H, H^5), 4.21 (d, J = 6.3 Hz, 1H, H^6), 4.88 (dd, J = 7.0, 5.2 Hz, 1H, H^4), 5.55 (dd, J = 5.2, 1.5 Hz, 1H, H^3), 6.96–7.00 (m, 2H, H^{Ph}), 7.21–7.26 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) −0.1 ($SiMe_3$), 52.2 (C^6), 60.7 (C^5), 80.6 (C^3), 86.8 (C^1), 95.7 (C^4), 103.5 (C^2), 126.4 (CH^{Ph}), 127.8 (CH^{Ph}), 128.6 (CH^{Ph}), 144.5 (C^{Ph}), 222.2 (CO (Mn)). IR (neat): $\tilde{\nu}$(cm^{-1}) 1920, 2011 (CO (Mn)). HRMS (EI, positive mode): *m/z* calcd for $C_{18}H_{18}ClMnO_3Si$, 400.0094; found, 400.0060 (M^+).

8a (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.52 (s, 9H, $SiMe_3$), 3.60 (ddd, J = 7.3, 5.9, 2.0 Hz, 1H, H^5), 3.86 (dd, J = 5.9, 2.0 Hz, 1H, H^1), 3.96 (t_{app}, J = 5.9 Hz, 1H, H^6), 4.75 (d, J = 7.3 Hz, 1H, H^4), 6.88–6.94 (m, 2H, H^{Ph}), 7.15–7.32 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.6 ($SiMe_3$), 43.3 (C^6), 62.1 (C^5), 64.0 (C^1), 83.9 (C^3), 97.2 (C^4), 121.1 (C^2), 126.0 (CH^{Ph}), 127.5 (CH^{Ph}), 128.9 (CH^{Ph}), 146.8 (C^{Ph}), 222.0 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1923, 2014 (CO (Mn)). Anal. Calcd: C, 53.94; H, 4.53. Found: C, 53.89; H, 4.65.

Lithiation of 4a (overall yield: 88%; **9a** partly isolated pure; **9′a** isolated as a mixture with **9a**).

9a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.37 (s, 9H, $SiMe_3$), 3.45 (s, 3H, OCH_3), 3.67 (dd, J = 6.5, 3.0 Hz, 1H, H^5), 4.28 (d, J = 6.5 Hz, 1H, H^6), 5.46 (d, J = 3.0 Hz, 1H, H^3), 6.95–7.00 (m, 2H, H^{Ph}), 7.16–7.37 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) −0.1 ($SiMe_3$), 46.7 (C^5), 54.7 (C^6 or OCH_3), 54.9 (C^6 or OCH_3), 69.3 (C^3), 85.2 (C^1), 99.2 (C^2), 126.3 (CH^{Ph}), 127.8 (CH^{Ph}), 128.7 (CH^{Ph}), 142.5 (C^4 or C^{Ph}), 144.7 (C^4 or C^{Ph}), 221.9 (CO (Mn)). IR (neat): $\tilde{\nu}$(cm^{-1}) 1923, 2013 (CO(Mn)). Anal. Calcd: C, 52.97; H, 4.68. Found: C, 52.92; H, 4.82.

9′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.42 (s, 9H, $SiMe_3$), 3.36 (s, 3H, OCH_3), 3.61 (d, J = 6.4 Hz, 1H, H^5), 4.30 (dd, J = 6.4, 1.4 Hz, 1H, H^6), 5.04 (d, J = 1.4 Hz, 1H, H^2), 6.96–7.00 (m, 2H, H^{Ph}), 7.23–7.28 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.1 ($SiMe_3$), 45.6 (C^5), 52.6 (C^6), 54.9 (OCH_3), 71.9 (C^3), 83.5 (C^1), 96.6 (C^2), 126.5 (CH^{Ph}), 128.0 (CH^{Ph}), 128.8 (CH^{Ph}),

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144.2 (C^4 or C^{Ph}), 145.0 (C^4 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1921, 2012 (CO (Mn)).

Lithiation of 4b (overall yield: 75%).

9b (49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.38 (s, 9H, $SiMe_3$), 2,76 (d, J = 12.0 Hz, 1H, H^{6exo}), 3.14 (m, 2H, H^{6endo} and H^5), 3.43 (s, 3H, OCH_3), 5.52 (d, J = 2.5 Hz, 1H, H^3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.0 ($SiMe_3$), 39.3 (C^5), 39.8 (C^6), 54.8 (OMe), 69.6 (C^3), 79.2 (C^1), 100.8 (C^2), 143.5 (C^4), 222.1 (CO (Mn)). IR (neat): $\tilde{\nu}$(cm^{-1}) 1918, 2010 (CO (Mn)).

9′b (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.41 (s, 9H, $SiMe_3$), 2,72 (d, J = 11.8 Hz, 1H, H^{6exo}), 3.16 (m, 2H, H^{6endo} and H^5), 3.30 (s, 3H, OMe), 5.02 (s, 1H, H^2). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.4 ($SiMe_3$), 37.2 (C^6), 38.8 (C^5), 54.8 (OMe), 72.2 (C^1 or C^3), 76.9 (C^1 or C^3), 98.4 (C^2), 145.9 (C^4). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1919, 2011 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{13}H_{16}ClMnO_4Si$, 353.9887; found, 353.9894 (M^+).

10 (66%; mixture of the two regioisomers). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1908, 2002 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{18}H_{19}MnO_3Si$, 366.0484; found, 366.0474 (M^+).

10a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.20 (s, 9H, $SiMe_3$), 3.38 (m, 1H, H^1), 3.62 (m, 1H, H^5), 3.80 (t_{app}, J = 6.0 Hz, 1H, H^6), 4.96 (dd, J = 7.0, 5.0 Hz, 1H, H^4), 5.65 (ddd, J = 5.0, 1.2, 1.2 Hz, 1H, H^3), 6.91–6.94 (m, 2H, H^{Ph}), 7.13–7.24 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) –1.9 ($SiMe_3$), 39.9 (C^6), 59.5 (C^1 or C^5), 59.6 (C^1 or C^5), 83.8 (C^3), 97.6 (C^4), 106.2 (C^2), 125.9 (CH^{Ph}), 126.9 (CH^{Ph}), 128.6 (CH^{Ph}), 148.2 (C^{Ph}), 223.4 (CO (Mn)).

10′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.38 (s, 9H, $SiMe_3$), 3.62 (m, 2H, $H^{1,5}$), 3.80 (t, J = 6.0 Hz, 1H, H^6), 4.84 (d, J = 7.2 Hz, 2H, $H^{2,4}$), 6.91–6.94 (m, 2H, H^{Ph}), 7.13–7.24 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) −0.6 ($SiMe_3$), 40.1 (C^6), 62.1 ($C^{1,5}$), 85.9 (C^3), 99.6 ($C^{2,4}$), 126.1 (CH^{Ph}), 127.2 (CH^{Ph}), 128.7 (CH^{Ph}), 147.7 (C^{Ph}), 223.4 (CO (Mn)).

11a (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.48 (s, 3H, Me), 3.22 (ddd, J = 7.1, 6.1, 1.7 Hz, 1H, H^5), 3.38 (dd, J = 6.1, 1.7 Hz, 1H, H^1), 3.44 (s, 3H, OCH_3), 3.87 (t_{app}, J = 6.1 Hz, 1H, H^6), 5.06 (d, J = 7.1 Hz, 1H, H^4), 6.91 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.16 (t, J = 7.5 Hz, 1H, H^{Ph}), 7.24 (t_{app}, J = 7.5 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 16.0 (CH_3), 40.8 (C^1), 43.0 (C^6), 54.6 (C^5 or OCH_3), 54.7 (C^5 or OCH_3), 85.2 (C^3), 96.2 (C^4), 125.5 (CH^{Ph}), 127.0 (CH^{Ph}), 128.7 (CH^{Ph}), 142.6 (C^2 or C^{Ph}), 147.9 (C^2 or C^{Ph}), 223.2 (CO (Mn)). IR (neat): $\tilde{\nu}$(cm^{-1}) 1901, 2003 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{17}H_{15}MnO_4$, 338.0351; found, 338.0363 (M^+).

12a (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.37–3.43 (m, 2H, H^1 and H^5), 3.51 (s, 3H, OCH_3), 3.93 (t_{app}, J = 6.1 Hz, 1H, H^6), 4.97 (d, J = 7.3 Hz, 1H, H^4), 6.94 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.15 (t, J = 7.5 Hz, 1H, H^{Ph}), 7.23 (t_{app}, J = 7.5 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 42.3 (C^6), 43.8 (C^1), 54.6 (OCH_3), 58.3 (C^5), 67.7 (t, J^{CD} = 27 Hz, C^3), 93.0 (C^4), 125.6 (CH^{Ph}), 127.0 (CH^{Ph}), 128.7 (CH^{Ph}), 143.3 (C^2 or C^{Ph}), 147.7 (C^2 or C^{Ph}), 222.9 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1895, 2001 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{16}H_{12}DMnO_4$, 325.0257; found, 396.0243 (M^+).

13a (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.93 (t, J = 7.3 Hz, 9H, $n$$Bu_3Sn$), 1.13–1.22 (m, 6H, $n$$Bu_3Sn$), 1.35–1.45 (m, 6H, $n$$Bu_3Sn$), 1.60–1.69 (m, 6H, $n$$Bu_3Sn$), 3.34 (s, 3H, OCH_3), 3.50 (m, 2H, H^1 and H^5), 3.97 (t_{app}, J = 6.0 Hz, 1H, H^6), 4.79 (d, J = 7.1 Hz, 1H, H^4), 6.95 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.16 (t, J = 7.5 Hz, 1H, H^{Ph}), 7.24 (t_{app}, J = 7.5 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.1 ($n$$Bu_3Sn$), 14.1 ($n$$Bu_3Sn$), 27.7 ($n$$Bu_3Sn$), 29.4 ($n$$Bu_3Sn$), 42.9 ($C^6$), 44.3 ($C^1$), 54.4 ($OCH_3$), 61.9 ($C^5$), 73.4 ($C^3$), 98.6 ($C^4$), 125.9 ($CH^{Ph}$), 127.0 ($CH^{Ph}$), 128.7 ($CH^{Ph}$), 146.0 ($C^2$ or C^{Ph}), 148.1 (C^2 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1912, 2009 (CO (Mn)). HRMS (MALDI TOF, positive mode): m/z calcd for $C_{28}H_{40}MnO_4Sn$, 613.1329; found, 613.0836 (M + H^+).

14a (95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.29 (m, 1H, H^5), 3.47 (dd, J = 6.0, 2.0 Hz, 1H, H^1), 3.49 (s, 3H, OCH_3), 3.89 (t_{app}, J = 6.0 Hz, 1H, H^6), 5.45 (d, J = 7.3 Hz, 1H, H^4), 6.89 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.19 (t, J = 7.5 Hz, 1H, H^{Ph}), 7.26 (t_{app}, J = 7.5 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 39.5 (C^3), 40.9 (C^1), 42.4 (C^6), 55.7 (OCH_3), 58.9 (C^5), 101.9 (C^4), 125.5 (CH^{Ph}), 127.3 (CH^{Ph}), 128.9 (CH^{Ph}), 142.1 (C^2 or C^{Ph}), 147.0 (C^2 or C^{Ph}), 222.2 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1912, 2009 (CO (Mn)). Anal. Calcd: C, 42.69; H, 2.69. Found: C, 42.65; H, 2.66.

15a (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38 (t_{app}, J = 7.1 Hz, 3H, CH_3), 3.49 (s, 3H, OCH_3), 3.52 (dd, J = 6.1, 1.6 Hz, 1H, H^1), 3.64 (m, 1H, H^5), 3.97 (t_{app}, J = 6.1 Hz, 1H, H^6), 4.33–4.48 (m, 2H, CH_2), 5.73 (d, J = 7.6 Hz, 1H, H^4), 6.93 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.17 (t, J = 7.5 Hz, 1H, H^{Ph}), 7.24 (t_{app}, J = 7.5 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.5 (CH_3), 41.9 (C^6), 44.3 (C^1), 55.3 (OCH_3), 61.5 (CH_2), 62.2 (C^5), 73.4 (C^3), 96.0 (C^4), 125.7 (CH^{Ph}), 127.4 (CH^{Ph}), 128.9 (CH^{Ph}), 144.1 (C^2 or C^{Ph}), 147.0 (C^2 or C^{Ph}), 167.7 (CO_2Et). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1725 (CO (CO_2Et)), 1920, 2015 (CO (Mn)). HRMS (MALDI TOF, positive mode): m/z calcd for $C_{19}H_{17}MnNaO_6$, 419.030; found, 418.994 (M + Na^+).

16a (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.03 (s, 3H, CH_3), 3.11 (s, 3H, CH_3), 3.34 (m, 2H, H^1 and H^5), 3.45 (s, 3H, OCH_3), 3.90 (t_{app}, J = 6.0 Hz, 1H, H^6), 5.43 (d, J = 7.0 Hz, 1H, H^4), 6.92 (d, J = 7.2 Hz, 2H, H^{Ph}), 7.13 (t, J = 7.2 Hz, 1H, H^{Ph}), 7.22 (t_{app}, J = 7.2 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 36.2 (CH_3), 38.2 (C^1), 38.9 (CH_3), 41.2 (C^6), 54.6 (C^5), 54.9 (OCH_3), 89.3 (C^3), 95.9 (C^4), 125.1 (CH^{Ph}), 127.0 (CH^{Ph}), 128.8 (CH^{Ph}), 141.4 (C^2 or C^{Ph}), 147.6 (C^2 or C^{Ph}), 166.5 (C(O)NMe_2). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1639 (CO (C(O)NMe_2)), 1921, 2014 (CO (Mn)). HRMS (electrospray): m/z calcd for $C_{19}H_{19}MnNO_5$, 396.0638; found, 396.0645 (M + H^+).

17a (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.22 (s, 3H, CH_3), 3.48 (s, 3H, OCH_3), 3.59 (dd, J = 6.5, 2.8 Hz, 1H, H^5), 4.36 (d, J = 6.5 Hz, 1H, H^6), 5.59 (d, J = 2.8 Hz, 1H, H^3), 6.97–6.99 (m, 2H, H^{Ph}), 7.20–7.30 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.3 (CH_3), 45.5 (C^5), 53.7 (C^6), 55.0 (OCH_3), 67.8 (C^3), 81.0 (C^1), 105.7 (C^2), 126.2 (CH^{Ph}), 127.7 (CH^{Ph}), 128.8 (CH^{Ph}), 141.0 (C^4 or C^{Ph}), 144.4 (C^4 or C^{Ph}), 221.7 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1917, 2011 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{17}H_{14}ClMnO_4$, 371.9961; found, 371.9951 (M^+).

19 (overall yield: 84%).

19a (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.37 (t, J = 7.1 Hz, 3H, CH_3), 3.52 (s, 3H, OCH_3), 3.60 (dd, J = 6.6, 2.8 Hz, 1H, H^5), 4.3 (m, 3H, H^6 and CH_2), 5.99 (d, J = 2.8 Hz, 1H, H^3), 7.00 (m, 2H, H^{Ph}), 7.19–7.28 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.3 (CH_3), 45.3 (C^5), 53.7 (C^6), 55.3 (OCH_3), 63.1 (CH_2), 66.2 (C^3), 76.1 (C^1), 97.4 (C^2), 126.1 (CH^{Ph}), 127.9 (CH^{Ph}), 128.9 (CH^{Ph}), 140.0 (C^4 or C^{Ph}), 143.7 (C^4 or C^{Ph}), 165.6 (CO_2Et), 221.0 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1734 (CO (CO_2Et)), 1931, 2019 (CO (Mn)). Anal. Calcd: C, 52.98; H, 3.74. Found: C, 52.93; H, 3.86.

19′a (15%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.40 (t, J = 7.2 Hz, 3H, CH_3), 3.49 (s, 3H, OCH_3), 3.65 (d, J = 6.6 Hz, 1H, H^5), 4.32 (dd, J = 6.6, 1.7 Hz, 1H, H^6), 4.42 (m, 2H, CH_2), 5.96 (d, J = 1.7 Hz, 1H, H^2), 7.00 (m, 2H, H^{Ph}), 7.23–7.27 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.5 (CH_3), 45.4 (C^5), 51.9 (C^6), 55.9 (OCH_3), 61.9 (CH_2), 70.0 (C^1 or C^3), 83.3 (C^1 or C^3), 94.9 (C^2), 126.4 (CH^{Ph}), 128.3 (CH^{Ph}), 129.1 (CH^{Ph}), 142.8 (C^4 or C^{Ph}), 143.5 (C^4 or C^{Ph}), 166.9 (CO_2Et). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1729 (CO (CO_2Et)), 1937, 2023 (CO (Mn)).

20 (86%; mixture of the two regioisomers). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1710 (CO (COtBu)), 1930, 2019 (CO (Mn)). HRMS (EI, positive mode): m/z calcd for $C_{21}H_{20}ClMnO_5$, 442.0380; found, 442.0392 (M^+).

20a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.01 (s, 9H, *t*Bu), 3.47 (dd, J = 6.3 Hz, J = 2.8 Hz, 1H, H^5), 3.61 (s, 3H, OCH_3), 4.41 (d, J = 6.3 Hz, 1H, H^6), 5.54 (d, J = 2.8 Hz, 1H, H^3), 7.08–7.11 (m, 2H, H^{Ph}), 7.26–7.34 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.5 (C(CH_3)$_3$), 43.0 (C^5), 46.2 (C(CH$_3$)$_3$), 53.3 (C^6), 55.3 (OCH_3), 64.6 (C^3), 76.2 (C^1), 116.7 (C^2), 126.9 (CH^{Ph}), 128.2 (CH^{Ph}), 128.7 (CH^{Ph}), 138.6 (C^4 or C^{Ph}), 142.1 (C^4 or C^{Ph}), 205.2 (*CO*tBu), 221.3 (CO (Mn)).

20′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.37 (s, 9H, *t*Bu), 3.45 (s, 3H, OCH_3), 3.54 (d, J = 6.8 Hz, 1H, H^5), 4.34 (dd, J = 6.8, 1.5 Hz, 1H, H^6), 5.43 (d, J = 1.5 Hz, 1H, H^2), 7.08–7.11 (m, 2H, H^{Ph}), 7.26–7.34 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.5 (C(CH_3)$_3$), 41.3 (C^5), 45.9 (C(CH$_3$)$_3$), 51.6 (C^6), 55.3 (OCH_3), 76.9 (C^1), 90.5 (C^3), 94.2 (C^2), 126.0 (CH^{Ph}), 128.0 (CH^{Ph}), 128.9 (CH^{Ph}), 139.8 (C^4 or C^{Ph}), 143.6 (C^4 or C^{Ph}), 207.6 (*CO*tBu).

21 (overall yield: 73%; **21a** partly isolated pure; **21′a** isolated as a mixture with **21a**).

21a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.34 (s, 3H, OCH_3), 3.56 (dd, J = 6.6, 2.3 Hz, 1H, H^5), 4.42 (d, J = 6.6 Hz, 1H, H^6), 5.20 (d, J = 2.3 Hz, 1H, H^3), 6.99 (d, J = 7.3 Hz, 2H, H^{Ph}), 7.22–7.31 (m, 3H, H^{Ph}), 7.44–7.49 (m, 3H, H^{Ph}), 7.61 (d, J = 7.3 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 45.7 (C^5), 54.1 (C^6), 55.0 (OCH_3), 65.9 (C^3), 76.4 (C^1), 115.5 (C^2), 126.2 (CH^{Ph}), 127.8 (CH^{Ph}), 128.9 (CH^{Ph}), 129.6 (C^{Ph}), 130.3 (2 x CH^{Ph}), 135.7 (CH^{Ph}), 140.0 (C^4 or C^{Ph}), 143.6 (C^4 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1922, 2013 (CO (Mn)). HRMS (EI, positive mode): *m*/*z* calcd for $C_{22}H_{16}ClMnO_4S$, 465.9838; found, 465.9835 (M$^+$).

21′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.46 (s, 3H, OCH_3), 3.64 (d, J = 6.6 Hz, 1H, H^5), 4.35 (dd, J = 6.6, 1.8 Hz, 1H, H^6), 5.60 (d, J = 1.8 Hz, 1H, H^2), 6.94–6.97 (m, 2H, H^{Ph}), 7.23–7.26 (m, 3H, H^{Ph}), 7.27–7.33 (m, 3H, H^{Ph}), 7.47–7.49 (m, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 43.4 (C^5), 52.2 (C^6), 55.8 (OCH_3), 78.1 (C^1 or C^3), 80.3 (C^1 or C^3), 100.6 (C^2), 126.2 (CH^{Ph}), 127.4 (CH^{Ph}), 128.1 (CH^{Ph}), 128.9 (CH^{Ph}), 129.5 (CH^{Ph}), 129.6 (CH^{Ph}), 138.0 (C^{Ph}), 143.1 (C^4 or C^{Ph}), 143.5 (C^4 or C^{Ph}).

22 (83%; mixture of the two regioisomers). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1927, 2016 (CO (Mn)). HRMS (EI, positive mode): *m*/*z* calcd for $C_{16}H_{11}ClMnO_4$, 483.8771; found, 483.8759 (M$^+$).

22a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.48 (s, 3H, OCH_3), 3.66 (dd, J = 6.6, 2.8 Hz, 1H, H^5), 4.53 (d, J = 6.6 Hz, 1H, H^6), 6.16 (d, J = 2.8 Hz, 1H, H^3), 6.94–6.97 (m, 2H, H^{Ph}), 7.22–7.31 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 46.1 (C^5), 53.7 (C^6), 55.4 (OCH_3), 75.5 (C^2), 76.2 (C^3), 79.9 or 82.4 (C^1), 126.2 (CH^{Ph}), 128.0 (CH^{Ph}), 129.0 (CH^{Ph}), 140.2 (C^4 or C^{Ph}), 143.6 (C^4 or C^{Ph}), 221.3 (CO (Mn)).

22′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.47 (s, 3H, OCH_3), 3.61 (d, J = 6.6 Hz, 1H, H^5), 4.26 (dd, J = 6.6, 1.8 Hz, 1H, H^6), 5.71 (d, J = 1.8 Hz, 1H, H^2), 6.94–6.97 (m, 2H, H^{Ph}), 7.22–7.31 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 34.9 (C^3), 41.8 (C^5), 52.4 (C^6), 56.2 (OCH_3), 79.9 or 82.4 (C^1), 100.8 (C^2), 126.2 (CH^{Ph}), 128.2 (CH^{Ph}), 129.1 (CH^{Ph}), 140.7 (C^4 or C^{Ph}), 143.3 (C^4 or C^{Ph}), 221.3 (CO (Mn)).

23 (86%; mixture of the two regioisomers). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1921, 2010 (CO (Mn)). HRMS (EI, positive mode): *m*/*z* calcd for $C_{28}H_{38}ClMnO_4$, 648.0861; found, 648.0837 (M$^+$).

23a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.87 (t, J = 7.3 Hz, 9H, *n*Bu$_3$Sn), 1.11–1.67 (m, 18H, *n*Bu$_3$Sn), 3.49 (s, 3H, OCH_3), 3.60 (dd, J = 6.6, 2.8 Hz, 1H, H^5), 4.32 (d, J = 6.6 Hz, 1H, H^6), 5.40 (d, J = 2.8 Hz, 1H, H^3), 6.99–7.03 (m, 2H, H^{Ph}), 7.17–7.28 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 12.0 (*n*Bu$_3$Sn), 13.9 (*n*Bu$_3$Sn), 27.6 (*n*Bu$_3$Sn), 29.0 (*n*Bu$_3$Sn), 46.1 (C^5), 52.7 (C^6), 54.9 (OCH_3), 70.9 (C^3), 83.5 (C^1), 103.0 (C^2), 126.5 (CH^{Ph}), 127.7 (CH^{Ph}), 128.6 (CH^{Ph}), 144.3 (C^4 or C^{Ph}), 144.5 (C^4 or C^{Ph}), 222.2 (CO (Mn)).

23′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.93 (t, J = 7.3 Hz, 9H, *n*Bu$_3$Sn), 1.11–1.67 (m, 18H, *n*Bu$_3$Sn), 3.32 (s, 3H, OCH_3), 3.65 (d, J = 6.3 Hz, 1H, H^5), 4.32 (dd, J = 6.3, 1.8 Hz, 1H, H^6), 4.98 (d, J = 1.8 Hz, 1H, H^2), 6.99–7.03 (m, 2H, H^{Ph}), 7.17–7.28 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.3 (*n*Bu$_3$Sn), 14.0 (*n*Bu$_3$Sn), 27.7 (*n*Bu$_3$Sn), 29.4 (*n*Bu$_3$Sn), 45.8 (C^5), 54.1 (C^6), 55.0 (OCH_3), 70.5 (C^3), 87.8 (C^1), 98.1 (C^2), 126.5 (CH^{Ph}), 127.8 (CH^{Ph}), 128.7 (CH^{Ph}), 143.8 (C^4), 144.5 (C^{Ph}), 222.2 (CO (Mn)).

24a (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.16 (m, 1H, H^5), 3.37 (s, 3H, OCH_3), 3.51 (dd, J = 6.3, 1.5 Hz, 1H, H^1), 3,99 (t$_{app}$, J = 6.3 Hz, 1H, H^6), 4.20 (d, J = 7.3 Hz, 1H, H^4), 4.97 (s, 1H, OH), 7.00 (d, J = 7.5 Hz, 2H, H^{Ph}), 7.21 (t, J = 7.5 Hz, 2H, H^{Ph}), 7.26–7.38 (m, 7H, H^{Ph}), 7.43–7.50 (m, 4H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 40.8 (C^6), 41.8 (C^1), 53.3 (C^5), 55.6 (OCH_3), 80.3 (C(OH)Ph$_2$), 95.7 (C^4), 100.5 (C^3), 125.2 (CH^{Ph}), 126.9 (CH^{Ph}), 127.5 (CH^{Ph}), 127.9 (CH^{Ph}), 128.0 (CH^{Ph}), 128.6 (CH^{Ph}), 128.7 (CH^{Ph}), 141.3 (C^2 or C^{Ph}), 143.3 (C^2 or C^{Ph}), 147.4 (C^2 or C^{Ph}), 147.7 (C^2 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1919, 2011 (CO (Mn)). Anal. Calcd: C, 68.78; H, 4.58. Found: C, 68.99; H, 4.40.

25a (overall yield: 93%).

25a-dia1 (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.41 (d, J = 2.6 Hz, 1H, OH), 3.29–3.36 (m, 2H, H^1 and H^5), 3.39 (s, 3H, OCH_3), 3,85 (t$_{app}$, J = 5.8 Hz, 1H, H^6), 5.36 (d, J = 7.4 Hz, 1H, H^4), 6.34 (d, J = 2.6 Hz, 1H, C*H*(OH)Ph), 6.64 (d, J = 7.1 Hz, 2H, H^{Ph}), 7.03–7.08 (m, 3H, H^{Ph}), 7.35–7.43 (m, 3H, H^{Ph}), 7.61 (d, J = 7.3 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 41.8 (C^1), 43.0 (C^6), 54.8 (OCH_3), 57.0 (C^5), 69.6 (*C*H(OH)Ph), 90.1 (C^4), 94.5 (C^3), 125.9 (CH^{Ph}), 126.6 (CH^{Ph}), 127.1 (CH^{Ph}), 128.2 (CH^{Ph}), 128.6 (CH^{Ph}), 128.9 (CH^{Ph}), 141.1 (C^2 or C^{Ph}), 143.3 (C^2 or C^{Ph}), 147.2 (C^2 or C^{Ph}), 223.1 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1916, 2008 (CO (Mn)).

25a-dia2 (48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.19–3.24 (m, 2H, H^5 and OH), 3.44 (d, J = 6.1 Hz, 1H, H^1), 3.47 (s, 3H, OCH_3), 3,88 (t$_{app}$, J = 6.1 Hz, 1H, H^6), 4.71 (d, J = 7.5 Hz, 1H, H^4), 6.30 (d, J = 4.8 Hz, 1H, C*H*(OH)Ph), 6.95 (d, J = 7.6 Hz, 2H, H^{Ph}), 7.17–7.27 (m, 3H, H^{Ph}), 7.33–7.44 (m, 3H, H^{Ph}), 7.65 (d, J = 7.4 Hz, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 42.7 (C^1), 42.9 (C^6), 55.0 (OCH_3), 56.6 (C^5), 72.2 (*C*H(OH)Ph), 93.0 (C^3), 93.1 (C^4), 125.9 (CH^{Ph}), 127.3 (CH^{Ph}), 128.2 (CH^{Ph}), 128.6 (CH^{Ph}), 128.9 (CH^{Ph}), 141.2 (C^2 or C^{Ph}), 141.8 (C^2 or C^{Ph}), 147.4 (C^2 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1911, 2008 (CO (Mn)). HRMS (electrospray): *m*/*z* calcd for $C_{23}H_{19}MnNaO_5$, 453.0505; found, 453.0542 (M + Na$^+$).

26 (overall yield: 64%).

26a (44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.47 (s, 3H, OCH_3), 3.50 (dd, J = 6.3, 2.8 Hz, 1H, H^5), 4.04 (s, 1H, OH), 4.42 (d, J = 6.3 Hz, 1H, H^6), 5.01 (d, J = 2.8 Hz, 1H, H^3), 6.80 (m, 4H, H^{Ph}), 7.05 (m, 3H, H^{Ph}), 7.32–7.38 (m, 6H, H^{Ph}), 7.47 (m, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 43.2 (C^5), 54.8 (C^6 or OCH_3), 55.0 (C^6 or OCH_3), 71.4 (C^3), 76.8 (C^1), 80.9 (C(OH)Ph$_2$), 118.7 (C^2), 126.9 (CH^{Ph}), 127.1 (CH^{Ph}), 127.3 (CH^{Ph}), 128.0 (CH^{Ph}), 128.1 (CH^{Ph}), 128.2 (CH^{Ph}), 128.7 (CH^{Ph}), 128.8 (CH^{Ph}), 139.3 (C^4 or C^{Ph}), 141.6 (C^4 or C^{Ph}), 142.1 (C^4 or C^{Ph}), 145.5 (C^4 or C^{Ph}), 221.5 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1928, 2016 (CO (Mn)). HRMS (electrospray): *m*/*z* calcd for $C_{29}H_{22}ClMnNaO_5$, 563.0428; found, 563.0417 (M + Na$^+$).

26′a (20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.35 (s, 3H, OCH_3), 3.64 (d, J = 6.8 Hz, 1H, H^5), 4.42 (dd, J = 6.8, 1.8 Hz, 1H, H^6), 4.48 (d, J = 1.8 Hz, 1H, H^2), 4.83 (s, 1H, OH), 7.10 (m, 2H, H^{Ph}), 7.25 (m, 2H, H^{Ph}), 7.29–7.39 (m, 7H, H^{Ph}), 7.49–7.51 (m, 4H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 43.3 (C^5), 51.1 (C^6), 56.2 (OCH_3), 75.7 (C^1), 80.2 (C(OH)Ph$_2$), 95.4 (C^2), 97.2 (C^3), 126.0 (CH^{Ph}), 127.8 (CH^{Ph}), 128.0 (CH^{Ph}), 128.2 (CH^{Ph}), 128.4 (CH^{Ph}), 128.5 (CH^{Ph}), 128.9 (CH^{Ph}), 139.9 (C^4 or C^{Ph}), 142.6 (C^4 or C^{Ph}), 143.8 (C^4 or C^{Ph}), 146.7 (C^4 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1930, 2017 (CO (Mn)). Anal. Calcd: C, 64.40; H, 4.10. Found: C, 64.38; H, 4.21.

27 (overall yield: 87%).

27a-dia 1 (mixture with **27′a-dia 1**). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.15 (d, $J = 4.8$ Hz, 1H, OH), 3.33 (s, 3H, OCH_3), 3.69 (dd, $J = 6.6$, 2.8 Hz, 1H, H^5), 4.36 (d, $J = 6.6$ Hz, 1H, H^6), 5.15 (d, $J = 2.8$ Hz, 1H, H^3), 5.58 (d, $J = 4.8$ Hz, 1H, C*H*(OH)Ph), 7.04–7.66 (m, 10H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 47.6 (C^5), 54.4 (C^6 or OCH_3), 55.0 (C^6 or OCH_3), 67.6 (C^3), 74.9 (*C*H(OH)Ph), 76.5 (C^1), 111.1 (C^2), 126.4 (CH^{Ph}), 128.0 (CH^{Ph}), 128.4 (CH^{Ph}), 128.9 (CH^{Ph}), 129.0 (CH^{Ph}), 129.1 (CH^{Ph}), 139.5 (C^4 or C^{Ph}), 143.0 (C^4 or C^{Ph}), 143.6 (C^4 or C^{Ph}), 221.5 (CO (Mn)).

27′a-dia 1 (mixture with **27a-dia 1**). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) $\delta = 2.37$ (d, $J = 3.0$ Hz, 1H, OH), 3.39 (s, 3H, OCH_3), 3.51 (d, $J = 6.5$ Hz, 1H, H^5), 4.20 (dd, $J = 6.5$, 1.8 Hz, 1H, H^6), 5.66 (d, $J = 1.8$ Hz, 1H, H^2), 6.27 (d, $J = 3.0$ Hz, 1H, C*H*(OH)Ph), 6.67 (m, 2H, H^{Ph}), 7.04–7.66 (m, 8H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 43.3 (C^5), 53.0 (C^6), 55.3 (OCH_3), 69.4 (*C*H(OH)Ph), 79.4 (C^1), 89.6 (C^2), 90.9 (C^3), 126.5 (CH^{Ph}), 127.9 (CH^{Ph}), 128.6 (CH^{Ph}), 128.8 (CH^{Ph}), 129.1 (CH^{Ph}), 140.0 (C^4 or C^{Ph}), 143.5 (C^4 or C^{Ph}), 145.2 (C^4 or C^{Ph}), 221.5 (CO (Mn)).

27a-dia 2 (28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.42 (d, $J = 3.5$ Hz, 1H, OH), 3.54 (s, 3H, OCH_3), 3.64 (dd, $J = 6.5$ Hz, 3.0 Hz, 1H, H^5), 4.26 (d, $J = 6.5$ Hz, 1H, H^6), 5.55 (d, $J = 3.5$ Hz, 1H, C*H*(OH)Ph), 6.14 (d, $J = 3.0$ Hz, 1H, H^3), 6.53 (m, 2H, H^{Ph}), 6.93–7.46 (m, 8H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 45.7 (C^5), 53.6 (C^6), 55.2 (OCH_3), 63.0 (C^3), 72.4 (*C*H(OH)Ph), 75.5 (C^1), 111.5 (C^2), 125.9 (CH^{Ph}), 127.3 (CH^{Ph}), 127.5 (CH^{Ph}), 128.5 (CH^{Ph}), 128.9 (CH^{Ph}), 140.8 (C^4 or C^{Ph}), 141.1 (C^4 or C^{Ph}), 143.6 (C^4 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1924, 2014 (CO (Mn)). HRMS (electrospray): *m*/*z* calcd for $C_{23}H_{18}ClMnNaO_5$, 487.0115; found, 487.0107 ($M + Na^+$).

27′a-dia 2 (23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.00 (d, $J = 4.7$ Hz, 1H, OH), 3.48 (s, 3H, OCH_3), 3.60 (d, $J = 6.6$ Hz, 1H, H^5), 4.23 (dd, $J = 6.6$, 1.6 Hz, 1H, H^6), 4.95 (d, $J = 1.6$ Hz, 1H, H^2), 6.28 (d, $J = 4.7$ Hz, 1H, C*H*(OH)Ph), 7.00 (m, 2H, H^{Ph}), 7.21–7.28 (m, 3H, H^{Ph}), 7.36–7.49 (m, 3H, H^{Ph}), 7.64 (m, 2H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) $\delta = 44.2$ (C^5), 52.9 (C^6), 55.5 (OCH_3), 71.7 (*C*H(OH)Ph), 78.9 (C^1), 89.8 (C^3), 92.4 (C^2), 126.5 (CH^{Ph}), 127.2 (CH^{Ph}), 128.1 (CH^{Ph}), 128.6 (CH^{Ph}), 128.8 (CH^{Ph}), 129.0 (CH^{Ph}), 140.3 (C^4 or C^{Ph}), 140.6 (C^4 or C^{Ph}), 143.7 (C^4 or C^{Ph}). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1922, 2011 (CO (Mn)). HRMS (electrospray): *m*/*z* calcd for $C_{23}H_{18}ClMnNaO_5$, 487.0115; found, 487.0106 ($M + Na^+$).

28 (overall yield: 31%; **28a** partly isolated pure; **28′a** isolated as a mixture with **28a**).

28a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.55 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 2.94 (s, 1H, OH), 3.49 (s, 3H, OCH_3), 3.61 (dd, $J = 6.5$, 2.7 Hz, 1H, H^5), 4.23 (d, $J = 6.5$ Hz, 1H, H^6), 5.85 (d, $J = 2.7$ Hz, 1H, H^3), 6.98–7.02 (m, 2H, H^{Ph}), 7.21–7.26 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 28.6 (CH_3), 30.1 (CH_3), 46.0 (C^5), 55.1 (OCH_3), 55.8 (C^6), 65.9 (C^3), 72.7 ($C(CH_3)_2OH$), 76.1 (C^1), 115.3 (C^2), 126.5 (CH^{Ph}), 128.1 (CH^{Ph}), 128.7 (CH^{Ph}), 139.8 (C^4 or C^{Ph}), 144.0 (C^4 or C^{Ph}), 221.6 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1920, 2012 (CO (Mn)). HRMS (electrospray): *m*/*z* calcd for $C_{19}H_{18}ClMnNaO_5$, 439.0115; found, 439.0107 ($M + Na^+$).

28′a. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.77 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 3.13 (s, 1H, OH), 3.46 (s, 3H, OCH_3), 3.53 (d, $J = 6.7$ Hz, 1H, H^5), 4.25 (dd, $J = 6.7$, 1.6 Hz, 1H, H^6), 5.53 (d, $J = 1.6$ Hz, 1H, H^2), 6.98–7.02 (m, 2H, H^{Ph}), 7.22–7.31 (m, 3H, H^{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.7 (CH_3), 32.7 (CH_3), 43.3 (C^5), 52.7 (C^6), 55.4 (OCH_3), 71.5 ($C(CH_3)_2OH$), 78.9 (C^1), 91.8 (C^2), 95.1 (C^3), 126.3 (CH^{Ph}), 128.1 (CH^{Ph}), 128.9 (CH^{Ph}), 139.2 (C^4 or C^{Ph}), 143.7 (C^4 or C^{Ph}).

30b (61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.17 (d, $J = 11.9$ Hz, 1H, H^{6exo}), 2.65–2.88 (m, 3H, H^{6endo}, H^5 and H^1), 3.42 (s, 3H, OCH_3), 5.34 (d, $J = 7.3$ Hz, 1H, H^4). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 0.5 ($SiMe_3$), 27.0 (C^6), 33.0 (C^1), 40.3 (C^3), 52.1 (C^5), 55.6 (OCH_3), 103.6 (C^4), 142.9 (C^2). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1924, 2012 (CO (Mn)).

Typical Rearomatization Procedure. A solution of triphenylcarbenium tetrafluoroborate (0.70 mmol, 3 equiv) in CH_2Cl_2 (4 mL) was added to a solution of η^5 complex (0.23 mmol, 1 equiv) in CH_2Cl_2 (5 mL). After stirring at room temperature for 1.5 h, 50 mL of freshly distilled Et_2O was added to induce precipitation of the expected cationic η^6 complex. The resulting yellow powder was isolated by filtration and washed with Et_2O.

29 (78%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) 0.53 (s, 9H, $SiMe_3$), 4.30 (s, 3H, OCH_3), 6.26 (ddd, $J = 6.3$, 6.3, 0.8 Hz, 1H, H^4), 6.54 (dd, $J = 7.6$, 0.8 Hz, 1H, H^6), 7.12 (dd, $J = 6.3$, 1.5 Hz, 1H, H^3), 7.37 (ddd, $J = 7.6$, 6.3, 1.5 Hz, 1H, H^5). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ (ppm) -0.5 ($SiMe_3$), 59.5 (OCH_3), 81.1 (C^6), 90.8 (C^4), 95.6 (C^2), 108.6 (C^5), 112.8 (C^3), 155.8 (C^1), 217.7 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 2002, 2068 (CO (Mn)). HRMS (MALDI TOF, positive mode): *m*/*z* calcd for $C_{13}H_{16}MnO_4Si$, 319.0198; found, 319.0215 ($M - BF_4^-$).

31 (76%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ (ppm) 4.33 (s, 3H, OMe), 6.23 (dt_{app}, $J = 6.6$, 1.0 Hz, 1H, H^5), 6.67 (dd, $J = 7.1$, 1.0 Hz, 1H, H^3), 7.17 (dt_{app}, $J = 7.1$, 1.3 Hz, 1H, H^4), 7.69 (dd, $J = 6.6$, 1.3 Hz, 1H, H^6). ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ (ppm) 60.8 (OMe), 81.2 (C^3), 92.9 (C^5), 106.0 (C^4), 115.6 (C^6), 149.5 (C^1 or C^2), 150.8 (C^2 or C^1), 217.3 (CO (Mn)). IR (neat): $\tilde{\nu}$ (cm^{-1}) 1991, 2067 (CO (Mn)). HRMS (FAB, positive mode): *m*/*z* calcd for $C_{10}H_7IMnO_4$, 372.8770; found, 372.8778 ($M - BF_4^-$).

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Supporting Information Available: Full experimental procedures, ^{13}C NMR spectra of all new compounds, and crystal data for **24a**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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