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Pentamethylcyclopentadienide in organic synthesis: nucleophilic addition of lithium pentamethylcyclopentadienide to carbonyl compounds and carbon–carbon bond cleavage of the adducts yielding the parent carbonyl compounds

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Abstract—Lithium pentamethylcyclopentadienide (C_5Me_5Li, Cp*Li) reacted with aromatic aldehyde to provide the corresponding carbinol in excellent yield. The carbinol returns to the parent aldehyde and pentamethylcyclopentadiene upon exposure to acid or due to heating. Chlorodimethylaluminum is essential as an additive to attain the nucleophilic addition of Cp*Li to aliphatic aldehyde. The carbinol derived from aliphatic aldehyde returns to the parent aldehyde and pentamethylcyclopentadiene by the action of a catalytic amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The reversible addition/elimination of the Cp* group can represent a protection of aldehyde. Mechanistic details of the carbon–carbon bond cleavage are also disclosed.
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1. Introduction

Pentamethylcyclopentadienide ($Me_5C_5^-$, Cp^{*-}) is an extremely important ligand in transition metal chemistry because of its unique structure and electronic property.[1,2] Cp^{*-} serves as a ligand of transition metal catalysts in organic synthesis. However, there are few reports to use Cp^{*-} by itself as a reagent in organic synthesis.[3] We have been exploring the utility of Cp^{*-} as a reagent in organic synthesis,[4] and here we report the full details of reversible addition/elimination of the Cp* group to carbonyl, which can represent a protection of a carbonyl group.

2. Results and discussions

2.1. Addition of Cp^{*-} to aromatic aldehydes and its reverse process

Treatment of *p*-bromobenzaldehyde (**1a**, 2.0 mmol) with Cp*Li (2.4 mmol, derived from ^{n}BuLi and pentamethylcyclopentadiene, Cp*H) in THF at −20 °C for 1 h provided the corresponding adduct **2a** in 95% isolated yield (Table 1, entry 1, from **1** to **2**).[5] Reactions at higher temperatures such as 0 °C resulted in the concurrence of a side reaction, that is, Meerwein–Ponndrof–Verley

Table 1. Formally reversible addition of Cp*Li to aromatic aldehydes

Entry	Ar	From **1** to **2** (%)[a]	From **2** to **1** (%)[b]
1	*p*-BrC_6H_4 (**a**)	95	92
2	2-$C_{10}H_7$ (**b**)	88	87
3	*p*-PhC(=O)C_6H_4 (**c**)	85	87
4	*p*-MeOC(=O)C_6H_4 (**d**)	87	91
5	*p*-NCC_6H_4 (**e**)	95	79
6	*p*-$BuOC_6H_4$ (**f**)	98	87
7	*p*-^{i}PrC(=O)C_6H_4 (**g**)	84	93
8	*o*-$MeOC_6H_4$ (**h**)	97	69

[a] Conditions: 1.2 equiv CpLi, THF, −20 °C, 1 h; then quenching with water.
[b] Conditions: 0.10 equiv trichloroacetic acid, dichloromethane, 25–30 °C, 0.25–1.5 h.

Keywords: Pentamethylcyclopentadiene; Nucleophilic addition; Carbon–carbon bond cleavage; Protection; Carbonyl compounds.
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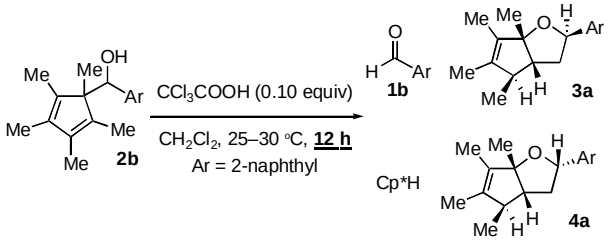
reduction/Oppenauer oxidation, to yield *p*-bromobenzyl alcohol and *p*-Br–$C_6H_4C(=O)Cp^*$. Use of methylmagnesium bromide instead of ^{n}BuLi also enhanced the reduction/oxidation side reaction. The attempted nucleophilic addition reaction led to no or little conversion under Cs_2CO_3/DMSO, $KN(SiMe_3)_2$/THF, or $NaN(SiMe_3)_2$/THF deprotonation conditions. Replacement of LiCp* with lithium cyclopentadienide led to the formation of the corresponding fulvene by facile dehydration.[6]

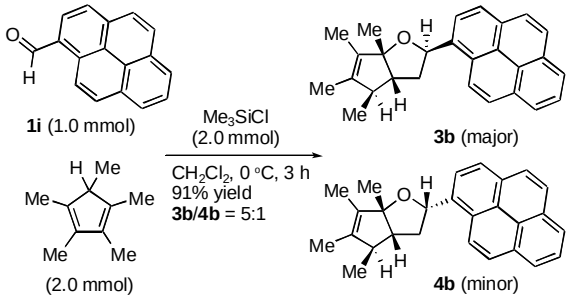
A variety of aromatic aldehydes were subjected to the nucleophilic addition of Cp*Li (Table 1, from **1** to **2**). The reaction was so chemoselective that keto (entries 3 and 7), ester (entry 4), and cyano (entry 5) moieties survived during the reaction. Sterically demanding *ortho*-substitution did not interfere with the reaction (entry 8). In contrast to the reactions with **1c** and **1g**, enolization of *p*-formylacetophenone was inevitable, furnishing the expected adduct in less than 30% yield.

Carbinols **2** were sensitive to acids. Specifically, acid-induced carbon–carbon bond cleavage took place to afford the parent aldehydes and Cp*H.[7,8] Carbinol **2a** was exposed to 10 mol% of trichloroacetic acid in dichloromethane at 25–30 °C for 1.5 h to provide **1a** in 92% isolated yield (entry 1, from **2** to **1**). It is worth noting that quantitative recovery of Cp*H upon the cleavage is advantageous since Cp*H is expensive. Other acids such as trifluoroacetic acid, camphorsulfonic acid monohydrate, *p*-toluenesulfonic acid monohydrate also promoted the carbon–carbon bond cleavage under the otherwise same reaction conditions, although the yields of **1a** were lower by ca. 20% because of several unidentified byproducts (vide infra). Acetic acid is too weak to cleave the carbon–carbon bond at a satisfactory rate. Silica gel in dichloromethane did not work at all. In polar coordinating solvents such as THF and methanol, acid-catalyzed cleavage was not observed. Under the standard reaction conditions, all the carbinols **2** returned to the parent aldehydes (Table 1, from **2** to **1**).

The progress of the acid-induced cleavage should be monitored by thin-layer chromatography. When the reaction was performed for an unnecessarily long time or with a too strong acid, the reactions yielded more complex mixtures. For instance, the reaction of **2b** with trichloroacetic acid overnight gave not only **1b** and Cp*H but also **3a** and **4a** (Eq. 1, yields undetermined). The formations of **3a** and **4a** are unusual, and the exact structures of **3a** and **4a** were not determined even with the aid of two-dimensional NMR technique. Alternatively, compounds **3b** and **4b**, the analogues of **3a** and **4a**, could be prepared by the reaction of **1i** and Cp*H in the presence of chlorotrimethylsilane (Eq. 2). Luckily the structures of **3b** and **4b** were fully determined by X-ray crystallographic analysis (Fig. 1)[9] as well as by ^{1}H, ^{13}C NMR, DEPT, and COSY spectra. The products **3b** and **4b** are epimers, with respect to the location of the pyrenyl ring. Other acids such as trichloroacetic acid also mediated the same transformation, while the yields of **3b** and **4b** were low. The mechanism for the formation of **3b** and **4b** is unclear.

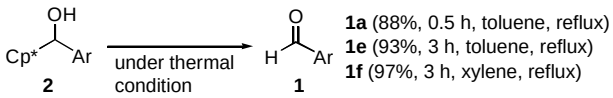


(1)



(2)

A similar carbon–carbon bond cleavage was observed in the absence of acid, which can avoid the careful monitoring. Boiling **2a** and **2e** in toluene furnished aldehydes **1a** and **1e** in 88 and 93% yields, respectively (Eq. 3). Electron-rich carbinol **2f** required a higher temperature to return efficiently to **1f** in boiling xylene. Complete conversion of **2f** in refluxing toluene took more than 20 h, albeit the yield was quantitative.



(3)

The lithium alkoxides of **2** can be trapped with *N*-trimethylsilylimidazole (Scheme 1). Trimethylsilylimidazole is the best reagent for the trapping. Chlorotrimethylsilane, trimethylsilyl triflate, and other *N*-silylimidazoles were less effective. Interestingly, the silyl ethers **2-Si** could return to **1** with the aid of tetrabutylammonium fluoride. The generation of **1** did not go to completion in some cases. However, treatment of the crude mixture of **1** and **2** with trichloroacetic acid afforded **1** in reasonable overall yield.

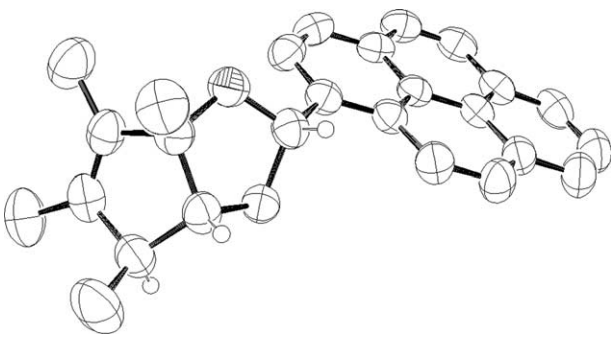
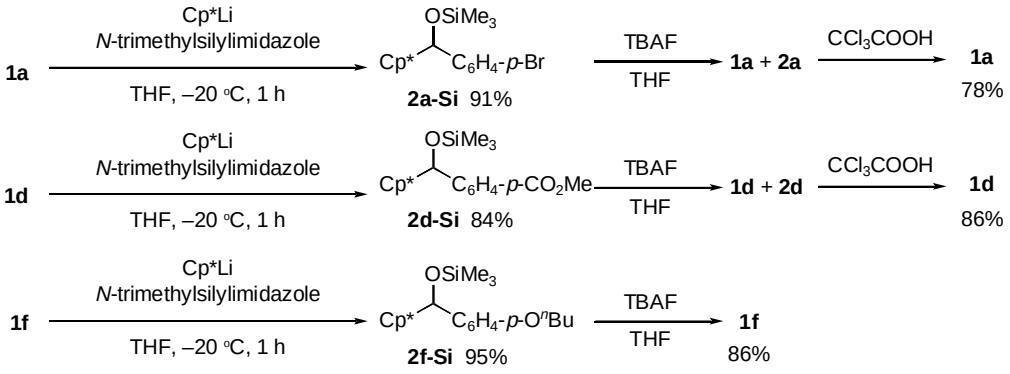
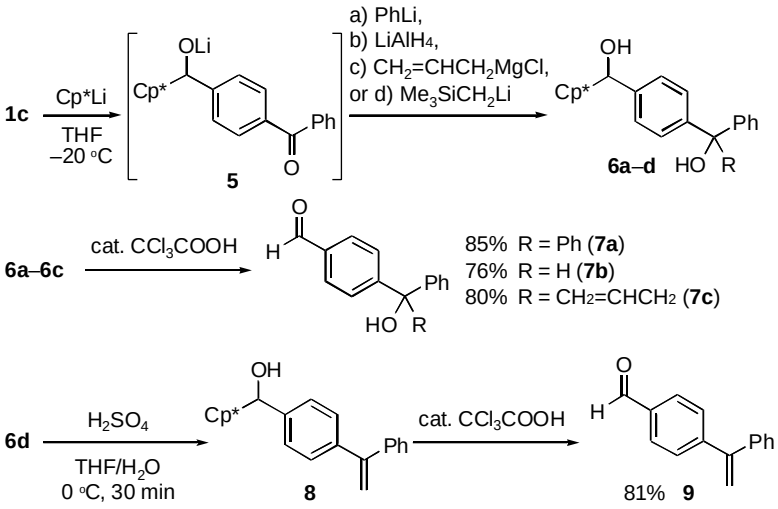


Figure 1. ORTEP drawing of **4b**. Thermal ellipsoids are 50% probability level. Three hydrogen atoms are shown for convenience.



Scheme 1.



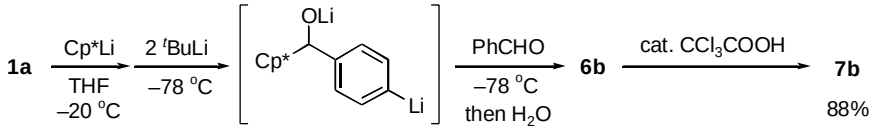
Scheme 2.

The utility of the Cp* group as a protective group is outlined in Scheme 2. After Cp* had masked the aldehyde moiety of **1c** in situ, the keto group was subjected to nucleophilic addition reaction with phenyllithium to afford diol **6a**. The crude oil was exposed to the acidic conditions to produce hydroxy aldehyde **7a** in 85% overall yield. Chemoselective reduction and allylation provided **7b** and **7c**, respectively.[10,11] Attempted Wittig reaction of **5** with $CH_2{=}PPh_3$ failed, and the methylenation of the aldehyde moiety that must be masked was partly observed. Alternatively, addition of trimethylsilylmethyllithium to **5** followed by acid-catalyzed olefination in aqueous THF yielded carbinol **8**. Treatment of **8** under the deprotection conditions afforded **9** in 81% overall yield. All the procedures proceeded so cleanly that no purification of the intermediates such as **6** and **8** was necessary.

The protective method allowed for preparation of a formyl-substituted phenyllithium equivalent (Scheme 3). Nucleophilic addition of Cp*Li to **1a** followed by bromine–lithium exchange furnished the corresponding aryllithium. The lithium reagent could be trapped with benzaldehyde to yield crude diol **6b**. Subsequent removal of Cp*H afforded **7b** in 88% overall yield.

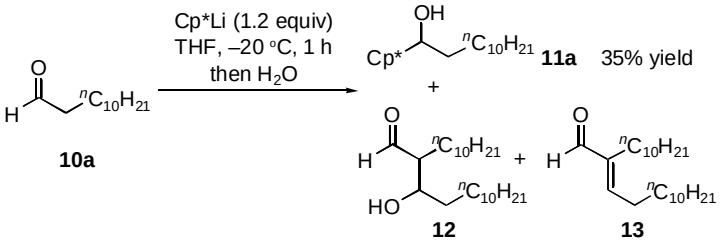
2.2. Addition of Cp^{*-} to aliphatic aldehyde and ketone with the aid of chlorodimethylaluminum and its reverse process

The reaction of Cp*Li with aliphatic aldehyde failed to yield a satisfactory amount of the corresponding adduct. For instance, treatment of dodecanal (**10a**) with Cp*Li afforded the corresponding adduct **11a** in only 35% yield (Eq. 4). The byproducts mainly comprised β-hydroxy aldehyde **12** and



Scheme 3.

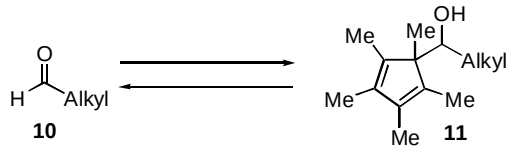
α,β-unsaturated aldehyde **13**, which means that Cp*Li served as a base to generate the lithium enolate of **10a**. Many additives were thus screened, and we found that chlorodimethylaluminum promotes the addition of Cp^{*-} to aliphatic aldehydes.



(4)

Chlorodimethylaluminum (6.0 mmol) was added to a suspension of Cp*Li (6.0 mmol) in THF at −20 °C. Aldehyde **10a** (5.0 mmol) was then added, and the mixture was stirred at −20 °C for 1 h. Extractive workup followed by silica gel column purification provided alcohol **11a** in 92% yield (Table 2, entry 1, from **10** to **11**). Trace amounts of **12** and **13** were detected in the crude oil. The role of chlorodimethylaluminum is unclear. No visible or spectroscopic changes of significance were observed. Chlorodimethylaluminum can activate the carbonyl group as a Lewis acid. Alternatively, Me_2Cp^*Al reagent may be formed via transmetallation and can effect the selective nucleophilic attack. Other Lewis acids including chlorotrimethylsilane, triethylaluminum, and magnesium dibromide were much less effective than chlorodimethylaluminum. Titanium tetraisopropoxide similarly assisted the addition reaction (81% yield).

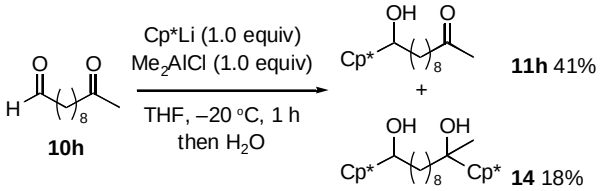
Table 2. Formally reversible addition of Cp*Li to aliphatic aldehydes



Entry	Alkyl	From **10** to **11** (%)[a]	From **11** to **10** (%)[b]
1	$CH_3(CH_2)_{10}$ (**a**)	92	92 (12 h)
2	$PhCH_2CH_2$ (**b**)	94	80 (12 h)
3[c]	$^cC_6H_{11}$ (**c**)	97	82 (24 h)[d]
4	$^tC_4H_9$ (**d**)	<10	—
5	$NC(CH_2)_5$ (**e**)	89	75 (24 h)
6	$Cl(CH_2)_9$ (**f**)	93	95 (12 h)
7	$CH_3OC(=O)(CH_2)_4$ (**g**)	82	81 (36 h)

[a] Conditions: 1.2 equiv Cp*Li, 1.2 equiv Me_2AlCl, THF, −20 °C, 1 h; then quenching with water.
[b] Conditions: 0.01 equiv DDQ, toluene, reflux. The reaction time of each run is in parentheses.
[c] To complete the reaction, 1.5 equiv of Cp*Li and Me_2AlCl were used.
[d] Isolated as 1-cyclohexylpentanol after treatment of the crude oil with *n*-butyllithium because cyclohexanecarbaldehyde is volatile.

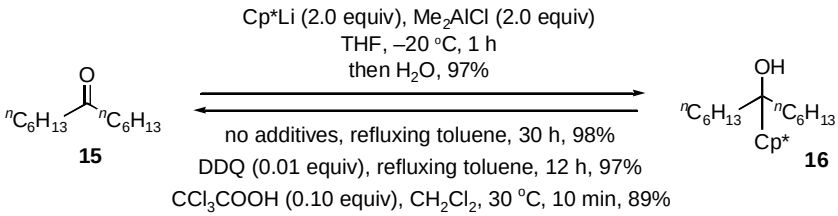
The nucleophilic addition is applicable to a wide range of aliphatic aldehydes (Table 1, from **10** to **11**). Whereas the reaction of cyclohexanecarbaldehyde (**10c**) cleanly provided **11c**, sterically congested pivalaldehyde (**10d**) resisted the reaction. The reaction was chemoselective enough to leave cyano, chloro, and ester moieties untouched (entries 5–7). The reactions with catalytic amounts of chlorodimethylaluminum did not go to completion and gave rise to ca. 80% conversion. Unfortunately, the reaction with keto aldehyde **10h** exhibited unsatisfactory chemoselectivity (Eq. 5).



(5)

Removal of the Cp* group of **11**, which corresponds to regeneration of **10**, can represent a protective method of aliphatic aldehydes. Contrary to the instability of aromatic carbinols **2** under the acidic or thermal conditions, carbinols **11** were stable toward acids or at high temperature. By extensive screening of reaction conditions, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), proved to induce smooth carbon–carbon bond cleavage to produce the parent aldehyde **10** and Cp*H. Treatment of **11a** with 1 mol% of DDQ in boiling toluene for 12 h furnished **10a** in 92% isolated yield (entry 1, from **11** to **10**), with quantitative generation of Cp*H. With the aid of DDQ, all the carbinols **11** returned to the original aldehydes (Table 1, from **11** to **10**). Carbinols **11e** and **11g** with polar cyano and ester moieties were transformed more slowly to **10e** and **10g**, respectively. The bulkier cyclohexyl group of **11c** also retarded the reaction. Other organic oxidants such as chloranil, 2,3-dichlorobenzoquinone, trityl tetrafluoroborate ($Ph_3C^+BF_4^-$) also facilitated the removal albeit the efficiency was much lower.

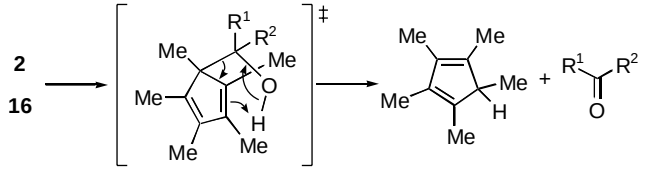
Chlorodimethylaluminum also promoted the addition onto dihexyl ketone (**15**) (Eq. 6). Without the additive, enolization of **15** predominated and none of **16** was obtained. Interestingly, boiling **16** in toluene for 30 h yielded **15** and Cp*H quantitatively. It is worth noting that DDQ accelerated the transformation (reflux, 12 h). A catalytic amount of trichloroacetic acid also effected the degradation of **16** into **15** and Cp*H.



(6)

2.3. Mechanisms of the carbon–carbon bond cleavage

A concerted retro-carbonyl-ene mechanism can rationalize the fragmentation reaction under the thermal cleavage conditions (Scheme 4).[12] Generally, thermal retro-carbonyl-ene reactions require higher temperature, most of which were performed in a gas phase.[12e] The reaction temperatures used herein are low as being temperatures for retro-carbonyl-ene reactions.



Scheme 4.

To clarify the origin of the facile retro-carbonyl-ene process, we set up five simplified models, Eqs. A–E, and performed ab initio calculations. The energy profile of the model reactions is shown in Figure 2. The activation barrier of the retro-carbonyl-ene reaction from **Adduct A** to **Products A** was calculated to be 29.25 kcal/mol. The higher barrier of 33.18 kcal/mol in Eq. B suggests that the methyl group at the 1 position of Cp* plays an important role to enhance the carbon–carbon bond cleavage. The removal of the cyclopentadienyl group, without any methyl groups on the cyclopentadiene ring, should go over the higher barrier (35.97 kcal/mol) from **Adduct C** to **Products C** (Eq. C). The steric hindrance of the Cp* group thus contributes to the facile retro-carbonyl-ene reaction. In addition, the conjugated diene system of Cp* proved to be much more important than the steric factor, by comparison of the activation barriers of Eqs. A, D, and E. The activation barriers of Eqs. D and E, wherein pentamethylcyclopentenes liberate, are calculated to be higher than that of Eq. A by ca. 10 kcal/mol. The characteristic features of the Cp* group, that is, its steric bulkiness and conjugated diene system, allows for the retro-carbonyl-ene reaction at a low temperature. It is worth noting that the activation barrier of the retro-carbonyl-ene reaction of 2-methyl-4-penten-2-ol was calculated to be 35.40 kcal/mol at the B3LYP/6-311+G**//RHF/6-311+G** levels of theory.[13]

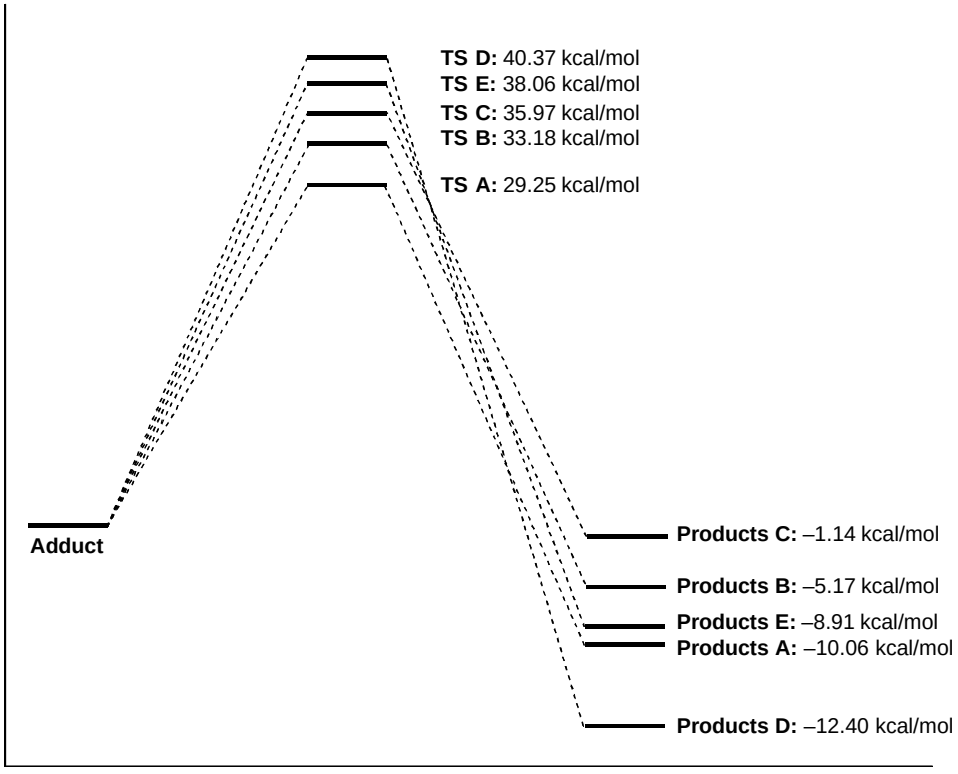
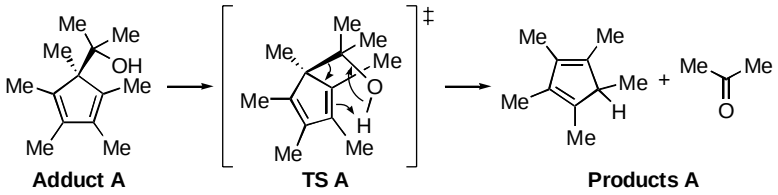
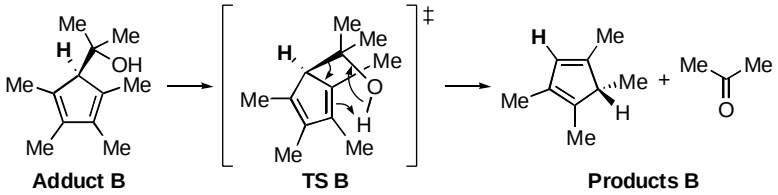


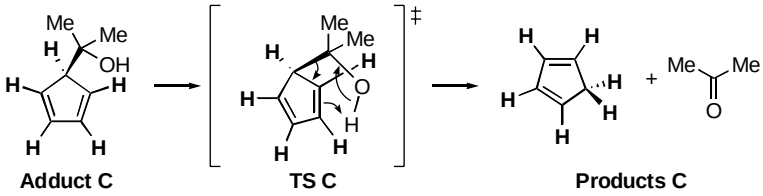
Figure 2. Calculated energy profile for Eqs. A–E at the B3LYP/6-311+G**//RHF/6-311+G** levels of theory.



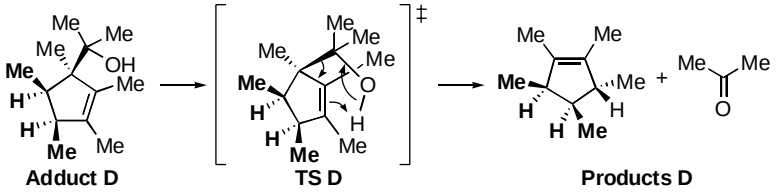
(A)



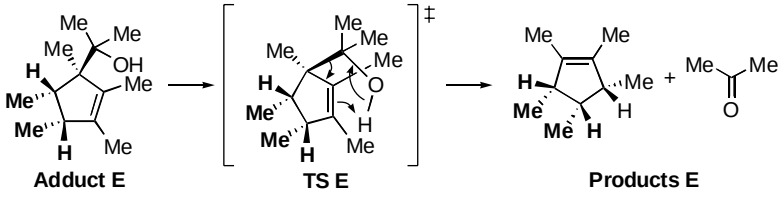
(B)



(C)

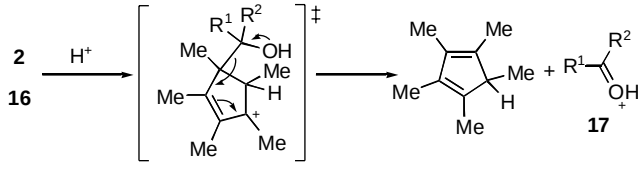


(D)



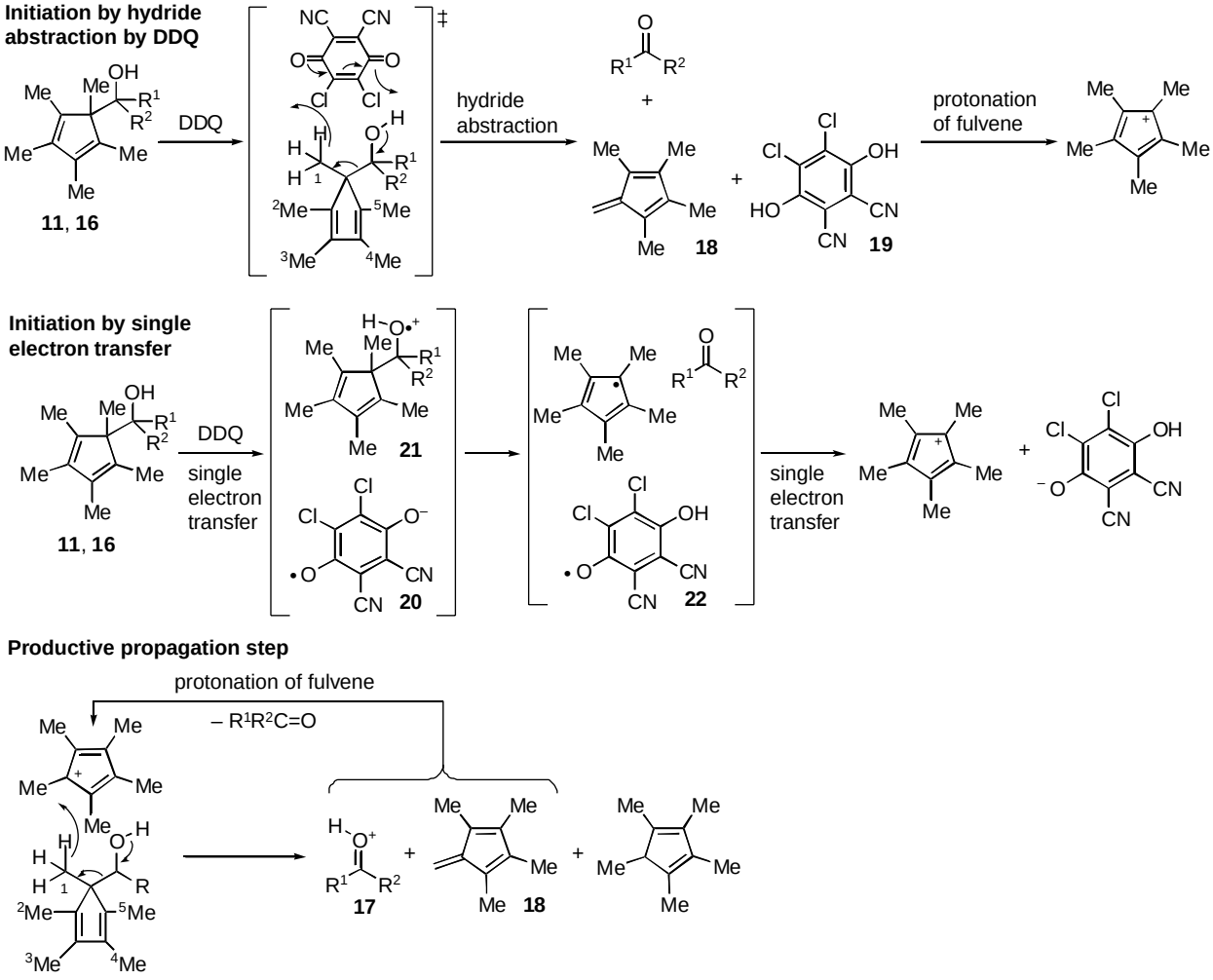
(E)

Under the acid-catalyzed conditions, protonation at the Cp* group would facilitate the carbon–carbon bond cleavage (Scheme 5). The Cp* group would be more easily protonated than the hydroxy group.[14] As described, the acid-catalyzed cleavage did not take place in a coordinating solvent. A coordinating solvent would interfere with the protonation of the Cp* group. Solvents of less coordinating nature such as dichloromethane facilitated the protonation. The protonation would promote release of the steric hindrance and recovery of a stabilized conjugated diene and result in carbon–carbon bond cleavage to form Cp*H and oxonium cation **17**.



Scheme 5.

While the mechanism of the DDQ-promoted cleavage is not clear, we are tempted to propose the two possible mechanisms (Scheme 6). One mechanism begins with hydride abstraction by DDQ, a strong hydride acceptor.[15] DDQ would abstract the hydride at the 1-methyl group of the Cp* group,[16] which generates the original carbonyl compound, tetramethylfulvene (**18**), and **19**. Protonation of **18** with **19** would yield unstable pentamethylcyclopentadienyl cation (Cp^{*+}).[17] The cyclic 4π-electronic cation Cp^{*+} would be a hydride acceptor efficient enough to abstract hydride from $Cp^*R^1R^2COH$ to produce oxonium cation **17**, **18**, and Cp*H. Protonation of the fulvene **18** with the oxonium cation **17** again generates Cp^{*+} to complete the catalytic cycle. An alternative scenario involves single electron transfer.[18] Single electron transfer from $Cp^*R^1R^2COH$ to DDQ generates radical anion **20** and radical cation **21**. The cation **21** undergoes fragmentation into pentamethylcyclopentadienyl radical (Cp*·) and the original carbonyl compound. Cp*· would be oxidized by **22** to form Cp^{*+}. The cation Cp^{*+} takes part in the same catalytic cycle in the hydride abstraction mechanism. It is noteworthy that no deuterium incorporation was observed in the cleavage reaction in toluene-d_8, which eliminates the possibility of hydrogen abstraction of the possible radical intermediates from solvent.



Scheme 6.

The hydroxy group of **11** plays a key role in the carbon–carbon bond cleavage process. Additional polar groups such as cyano and ester groups in **11e** and **11g** would prevent the weak interaction between the hydroxy group and electron deficient species such as DDQ and Cp^{*+}. The bulkier cyclohexyl group of **11c** hampered the access of the electron deficient species to the hydroxy group of **11c**. Namely, rate-determining hydride abstraction or single electron transfer would be retarded. It is worth noting that the silyl ether of **11b** completely resisted the cleavage upon treatment with DDQ in boiling toluene.

3. Conclusion

Pentamethylcyclopentadienide has now participated in organic synthesis as a new 'reagent'. The protection of an aldehyde moiety with Cp* emerges by utilizing the facile cleavage of the Cp^{*}–CR^1R^2OH bond. The cleavage is due to the unique nature of Cp* group.

4. Experimental

4.1. Instrumental

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken on Varian Mercury 300 spectrometers and were recorded in C_6D_6. Chemical shifts (δ) are in parts per million relative to benzene at 7.16 ppm for ^1H and at 128.0 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

4.2. Material

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aldehydes were purified by distillation or recrystallization prior to use. 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene

was purchased from TCI. THF (dehydrated, stabilizer free) was purchased from Kanto Chemical Co., stored under nitrogen, and used without distillation. Dichloromethane was dried over molecular sieves 3 Å. Trichloroacetic acid was diluted with dichloromethane to prepare a 0.1 M solution. *n*-Butyllithium, *t*-butyllithium, trimethylsilylmethyllithium were purchased from Nacalai Tesque, Kanto Chemical, and Aldrich, respectively. DDQ was purchased from Wako Pure Chemical Co. Chlorodimethylaluminum was purchased from Kanto Chemical. All reactions were carried out under argon atmosphere.

4.3. Theoretical calculations

All the calculations were performed by using Spartan'04.[19] All the structures were optimized at the HF/6-311+G** level of theory. Single point calculations of the total energies were performed at the B3LYP/6-311+G** at the HF/6-311+G** optimized geometries. The transition states obtained gave proper single imaginary frequencies.

5. Experimental

5.1. General procedure for nucleophilic addition of Cp*Li to aromatic aldehydes (Table 1)

A solution of ^{n}BuLi in hexane (1.6 M, 1.57 mL, 2.4 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.42 mL, 2.6 mmol) in THF (20 mL) at −78 °C. The mixture was stirred for 30 min at room temperature to provide a white suspension of pentamethylcyclopentadienyllithium. To the resulting mixture, a solution of 4-bromobenzaldehyde (**1a**, 370 mg, 2.0 mmol) in THF (3.0 mmol) was added at −20 °C, and the reaction mixture was stirred for 1 h at −20 °C. After quenching the reaction with water, the mixture was extracted with hexane–ethyl acetate (10/1, 20 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. Purification by chromatography on silica gel afforded **2a** (609.1 mg, 1.90 mmol) in 95% yield.

5.2. Acid-induced cleavage reaction (Table 1)

A solution of trichloroacetic acid in CH_2Cl_2 (0.1 M, 0.50 mL, 0.05 mmol) was added to a solution of **2a** (160.4 mg, 0.50 mmol) in CH_2Cl_2 (3.0 mL) at room temperature. The mixture was stirred for 90 min at 28 °C. After quenching the reaction with saturated aqueous $NaHCO_3$, the mixture was extracted with hexane–ethyl acetate (10/1, 20 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. Silica gel column purification provided 4-bromobenzaldehyde (**1a** 84.8 mg, 0.458 mmol) in 92% yield.

5.3. Acid-mediated coupling of pyrenecarbaldehyde with Cp*H (Eq. 2)

A mixture of 1-pyrenecarbaldehyde (**1i**, 230 mg, 1.0 mmol) and Cp*H (0.31 mL, 2.0 mmol) was dissolved in dichloromethane (1.0 mL). Chlorotrimethylsilane (0.26 mL, 2.0 mmol) was added dropwise at 0 °C. After the mixture was stirred for 4 h at 0 °C, the reaction was quenched with sodium hydrogencarbonate solution. Work-up followed by silica gel column purification provided **3b** and **4b** in 91% combined yield (330 mg, 0.91 mmol) in a ratio of 5:1.

5.4. Thermal cleavage reaction (Eq. 3)

Carbinol **2a** (643.7 mg, 2.0 mmol) was dissolved in toluene (10 mL). After the solution was stirred at 110 °C for 0.5 h, the solvent was removed under reduced pressure. Purification of the residue by chromatography on silica gel gave 4-bromobenzaldehyde (**1a**, 324.1 mg, 1.75 mmol) in 88% yield.

5.5. Synthesis of 2-Si (Scheme 1)

Butyllithium in hexane (1.6 M, 7.4 mL, 12 mmol) was added dropwise to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (2.0 mL, 13 mmol) in THF (100 mL) at −20 °C. The resulting suspension was stirred for 30 min. A solution of 4-bromobenzaldehyde (1.85 g, 10 mmol) in THF (10 mL) was added to the suspension. The reaction mixture was stirred at −20 °C for 1 h. *N*-Trimethylsilylimidazole (1.9 mL, 13 mmol) was then added at −20 °C, and the resulting mixture was stirred for 1 h at the same temperature. After the reaction was terminated by an addition of water, the organic layer was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo to give a crude oil. The oil was purified by column chromatography (Wakogel C-200, pretreated with Et_3N in hexane and eluted with hexane) to afford **2a-Si** (3.60 g, 9.1 mmol, 91%).

5.6. Regeneration of 1f from 2f-Si

A solution of tetrabutylammonium fluoride in THF (1.0 M, 0.60 mL, 0.60 mmol) was added to a solution of **2f-Si** (193 mg, 0.50 mmol) in THF (3.3 mL) at 0 °C. The resulting solution was stirred for 1 h at room temperature. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a crude oil. Chromatographic purification on silica gel (Wakogel C-200, hexane/ethyl acetate=20:1) furnished **1f** (76.5 mg, 0.43 mmol, 86%).

5.7. From 2a-Si to 1a

Tetrabutylammonium fluoride (1.0 M THF solution, 0.60 mL, 0.60 mmol) was added to a solution of **2a-Si** (197 mg, 0.50 mmol) in THF (1.7 mL) at 0 °C. The resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic parts were washed with brine, dried, and concentrated in vacuo to give a crude oil. Trichloroacetic acid in dichloromethane (0.1 M, 0.5 mL, 0.05 mmol) was added to the crude oil in dichloromethane (3.3 mL) at 30 °C. After 1 h, the reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Silica gel column

chromatography (Wakogel C-200, hexane/ethyl acetate = 20:1) yielded 72.1 mg of **1a** (0.39 mmol, 78%).

5.8. From 2d-Si to 1d

Tetrabutylammonium fluoride (1.0 M THF solution, 0.60 mL, 0.60 mmol) was added to a solution of **2d-Si** (186 mg, 0.50 mmol) in THF (1.7 mL) at 0 °C. The resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Trichloroacetic acid (0.1 M in dichloromethane, 0.5 mL, 0.05 mmol) was added to the crude oil in dichloromethane (3.3 mL) at 30 °C and the mixture was stirred for 1 h. Additional trichloroacetic acid in dichloromethane (0.1 M, 0.5 mL, 0.05 mmol) was added to the reaction mixture, and the reaction mixture was stirred for another 30 min. After being quenched with saturated $NaHCO_3$ solution, the mixture was extracted with ethyl acetate. Usual workup followed by purification on silica gel (Wakogel C-200, hexane/ethyl acetate = 10:1) provided **1d** (70.7 mg, 0.43 mmol, 86%).

5.9. Synthesis of 7a from 1c (Scheme 2)

Butyllithium (1.6 M hexane solution, 0.39 mL, 0.60 mmol) was added to a solution of Cp^*H (0.11 mL, 0.65 mmol) in THF (5 mL) at −78 °C under argon. By removing a dry ice/acetone bath, the resulting mixture was allowed to warm to room temperature. After being stirred at room temperature for 30 min, the mixture was cooled to −20 °C. Keto aldehyde **1c** (105 mg, 0.50 mmol in 1.5 mL of THF) was then added. The mixture was stirred for 1 h at the same temperature. The reaction mixture was then cooled to −78 °C. Phenyllithium (0.77 mL, 0.75 mmol, 0.98 M in cyclohexane/ether, Kanto Chemical Co.) was added and the whole mixture was stirred for 20 min. Water (10 mL) was added at −78 °C to quench the reaction. Extractive workup afforded a crude oil of **6a**. Trichloroacetic acid in dichloromethane (0.1 M, 0.5 mL, 0.05 mmol) was added to the crude oil in dichloromethane (3 mL) under argon at 25–30 °C, and the resulting solution was stirred for 1 h. After being quenched with saturated $NaHCO_3$ solution, the mixture was extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous sodium sulfate. Evaporation followed by silica gel column purification (hexane/ethyl acetate = 3:1) yielded 123 mg of **7a** (0.427 mmol, 85% overall yield).

5.10. Synthesis of 7b from 1c (Scheme 2)

Butyllithium (1.6 M hexane solution, 0.75 mL, 1.2 mmol) was added to a solution of Cp^*H (0.21 mL, 1.3 mmol) in THF (10 mL) at −20 °C. After being stirred for 30 min, keto aldehyde **1c** (210 mg, 1.0 mmol in 3.0 mL of THF) was then added. The mixture was stirred for 1 h at the same temperature. The reaction mixture was then cooled to −78 °C. Lithium aluminum hydride (57 mg, 1.5 mmol) was added in one portion. The whole mixture was stirred for 1 h at 0 °C. Water (10 mL) was added to quench the reaction. Extractive workup gave a crude oil of **6b**. Trichloroacetic acid in dichloromethane (0.1 M, 1.0 mL, 0.1 mmol) was added to a solution of **6b** in dichloromethane (6.7 mL) under argon at 25–30 °C, and the resulting solution was stirred for 1 h. After being quenched with saturated $NaHCO_3$ solution, the mixture was extracted with ethyl acetate (20 mL×3). Removal of volatiles followed by silica gel column purification (hexane/ethyl acetate = 2:1) yielded 136 mg of **7b** (0.76 mmol, 76% overall yield).

5.11. Synthesis of 7c from 1c (Scheme 2)

After similar treatment of **1c** (0.50 mmol-scale) with Cp^*Li at −20 °C, allylmagnesium chloride (0.92 M ethereal solution, 1.1 mL, 1.0 mmol) was added to the reaction flask at −20 °C. The whole mixture was stirred for 1 h. Quenching with water (10 mL) followed by extractive workup gave a crude oil of **6c**. Trichloroacetic acid in dichloromethane (0.1 M, 1.0 mL, 0.1 mmol) was added to a solution of **6c** in dichloromethane (5 mL) under argon at 25–30 °C, and the resulting solution was stirred for 45 min. After the reaction was quenched with saturated $NaHCO_3$ solution, extraction, evaporation, and purification on silica gel (hexane/ethyl acetate = 5:1) furnished 101 mg of **7c** (0.402 mmol, 80% overall yield).

5.12. Synthesis of 9 from 1c (Scheme 2)

The reaction started from 0.50 mmol of **1c**. Trimethylsilylmethyllithium (0.66 M pentane solution, 1.5 mL, 1.0 mmol) was added at −78 °C to **5** prepared in the method described above. The resulting mixture was stirred for 30 min. Quenching with water (10 mL) followed by extraction with ethyl acetate gave **6d**. Under air, 2.0 M aqueous sulfuric acid (1.0 mL) was added to a solution of crude **6d** in THF–H_2O (4.0 mL/1.0 mL) at 0 °C. The mixture was stirred for 30 min at the same temperature. After addition of aqueous $NaHCO_3$, extraction with ethyl acetate and evaporation under reduced pressure afforded crude **8**, clean formation of which NMR analysis revealed. Trichloroacetic acid in dichloromethane (0.1 M, 0.5 mL, 0.05 mmol) was added to a solution of **8** in dichloromethane (3 mL) under argon at 25–30 °C, and the resulting solution was stirred for 30 min. After the reaction was quenched with saturated $NaHCO_3$ solution, extraction, evaporation, and purification on silica gel (hexane/ethyl acetate = 10:1) furnished 84.3 mg of **9** (0.405 mmol, 81% overall yield).

5.13. Synthesis of 7b from 1a (Scheme 3)

Butyllithium (1.6 M hexane solution, 0.75 mL, 1.2 mmol) was added to a solution of Cp^*H (0.21 mL, 1.3 mmol) in THF (10 mL) at −78 °C, and the resulting mixture was allowed to warm to room temperature. After being stirred for 30 min, the mixture was cooled to −20 °C. Bromo aldehyde **1a** (186 mg, 1.0 mmol in 1.5 mL of THF) was then added and the mixture was stirred for 1 h at the same temperature. The reaction mixture was then cooled to −78 °C and *t*-butyllithium in pentane (1.56 M, 1.4 mL, 2.2 mmol) was added. After 40 min, benzaldehyde (0.16 mL, 1.6 mL) was added and the whole mixture was stirred for an additional 40 min at −78 °C. Water (10 mL) was added to quench the reaction. Extractive workup gave a crude oil of **6b**. Trichloroacetic acid in dichloromethane (0.1 M, 1.0 mL, 0.1 mmol) was added to a solution of **6b** in

dichloromethane (4 mL) under argon at 25–30 °C, and the resulting solution was stirred for 30 min. Workup as above followed by silica gel column purification (hexane/ethyl acetate=2:1) yielded 187 mg of **7b** (0.88 mmol, 88% overall yield).

5.14. General procedure for nucleophilic addition of Cp*Li to aliphatic aldehydes (Table 2)

A solution of ^{n}BuLi in hexane (1.6 M, 3.8 mL, 6.0 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.95 mL, 6.5 mmol) in THF (50 mL) at −20 °C. The mixture was stirred for 30 min at the same temperature to provide a white suspension of pentamethylcyclopentadienyllithium. Chlorodimethylaluminum in hexane (1.0 M, 6.0 mL, 6.0 mmol) was added to the resulting mixture, and the reaction mixture was stirred for 30 min at −20 °C. After an addition of dodecanal (**10a**, 1.1 mL, 5.0 mmol), the mixture was stirred for an additional 1 h at −20 °C. After being stirred for 1 h, the reaction was quenched with water, and the mixture was extracted with ethyl acetate three times. The combined organic parts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (Wakogel C-200, hexane/ethyl acetate=10:1) to afford **11a** (1.47 g, 92%).

5.15. General procedure of DDQ-induced cleavage (Table 2)

A solution of **11a** (321 mg, 1.0 mmol) in toluene (1.0 mL) was added to a solution of DDQ (2 mg, 0.01 mmol) in toluene (19 mL). The mixture was warmed up to 110 °C and stirred for 12 h. After the reaction was terminated by an addition of water, the organic layer was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude oil obtained was subjected to silica gel column purification (Wakogel C-200, hexane/ethyl acetate=10:1) to afford **10a** (170 mg, 0.92 mmol, 92%).

5.16. Preparation of 10-chlorodecanal

To a solution of pyridinium chlorochromate (3.9 g, 18 mmol) and silica gel (Silica Gel 60, spherical, neutrality, Nacalai Tesque, 3.9 g) in CH_2Cl_2 (60 mL) was added a solution of 10-chloro-1-decanol (2.4 mL, 12 mmol) for 12 h at room temperature. The resulting mixture was filtered through a pad of Celite 545 and the organic layer was concentrated in vacuo to give a crude oil. The crude product was chromatographed on silica gel (Wakogel C-200, hexane/ethyl acetate=30:1) to afford the title compound (1.7 g, 74%). *10-Chlorodecanal* (**10f**). IR (neat) 650, 723, 1356, 1466, 1726, 2719, 2930, 3429 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24–1.82 (m, 14H), 2.92 (td, J=7.2, 1.8 Hz, 2H), 3.53 (t, J=6.6 Hz, 2H), 9.76 (t, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.00, 26.79, 28.76, 29.07, 29.20 (×2), 32.56, 43.87, 45.15, 202.95. HRMS CI [M+H$^+$] 191.1203. Calcd for $C_{10}H_{20}ClO$: 191.1202.

5.17. Characterization data

5.17.1. (4-Bromophenyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methanol (2a). IR (neat) 3458, 2856, 1657, 1591, 1487, 1445, 1379, 1072, 1009, 812, 773, 719, 659, 607 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.08 (s, 3H), 1.35–1.42 (m, 1H), 1.43 (s, 3H), 1.49 (s, 3H), 1.52 (s, 3H), 1.95 (s, 3H), 4.31 (d, J=3.0 Hz, 1H), 6.87 (d, J=8.0 Hz, 2H), 7.22 (d, J=8.0 Hz, 2H); ^{13}C NMR (C_6D_6) δ 10.77, 10.82, 11.27, 12.07, 18.09, 61.34, 77.78, 121.02, 128.59, 130.08, 136.40, 136.54, 137.66, 139.28, 140.89. Found: C, 63.58; H, 6.86%. Calcd for $C_{17}H_{21}BrO$: C, 63.56; H, 6.59%.

5.17.2. (2-Naphthyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methanol (2b). IR (neat) 3444, 3057, 2856, 1654, 1600, 1508, 1444, 1379, 1033, 858, 815, 748, 686, 478 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.22 (s, 3H), 1.42 (d, J=1.0 Hz, 3H), 1.50 (d, J=1.0 Hz, 3H), 1.59–1.61 (m, 1H), 1.62 (s, 3H), 2.07 (s, 3H), 4.68 (d, J=3.0 Hz, 1H), 7.20–7.28 (m, 2H), 7.37 (dd, J=1.5, 8.5 Hz, 1H), 7.57 (d, J=8.5 Hz, 1H), 7.62 (d, J=8.0 Hz, 1H), 7.67–7.70 (m, 2H); ^{13}C NMR (C_6D_6) δ 10.83, 10.85, 11.50, 12.09, 18.44, 61.50, 78.50, 125.68, 125.81, 125.87, 126.47, 127.86, 127.91, 128.29, 133.21, 133.36, 136.28, 136.40, 138.19, 139.65, 139.68. Found: C, 85.98; H, 8.34%. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27%.

5.17.3. {4-[(Hydroxy)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methyl]phenyl}(phenyl)methanone (2c). IR (Nujol) 3438, 1639, 1604, 1317, 1280, 1147, 1035, 943, 704 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.14 (s, 3H), 1.47 (s, 3H), 1.51 (s, 3H), 1.58 (s, 3H), 1.40–1.80 (br s, 1H), 2.00 (s, 3H), 4.47 (s, 1H), 7.05–7.20 (m, 5H), 7.68–7.74 (m, 4H); ^{13}C NMR (C_6D_6) δ 10.79, 10.86, 11.34, 12.11, 18.15, 61.26, 78.05, 126.70, 128.26, 128.99, 130.08, 131.83, 136.38, 136.64, 136.70, 137.70, 138.61, 139.45, 146.49, 195.63. Found: C, 82.97; H, 7.58%. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56%. Mp 89–90 °C.

5.17.4. Methyl 4-[(hydroxy)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methyl]benzoate (2d). IR (Nujol) 3521, 1706, 1608, 1438, 1282, 1109, 1049, 1018, 763, 711 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.26 (d, J=4.0 Hz, 3H), 1.35–1.55 (br s, 1H), 1.43 (s, 3H), 1.47 (s, 3H), 1.57 (s, 3H), 1.99 (s, 3H), 3.46 (s, 3H), 4.41–4.45 (m, 1H), 7.15–7.18 (m, 2H), 8.04–8.09 (m, 2H); ^{13}C NMR (C_6D_6) δ 10.73, 10.79, 11.26, 12.12, 18.07, 51.41, 61.18, 78.07, 126.79, 128.42, 129.46, 136.35, 136.61, 137.59, 139.39, 147.09, 166.72. Found: C, 75.82; H, 8.16%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. Mp 91–92 °C.

5.17.5. 4-[(Hydroxy)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methyl]benzonitrile (2e). IR (Nujol) 3488, 2220, 1606, 1313, 1201, 1037, 819, 775, 875, 609 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.03 (s, 3H), 1.27 (s, 1H), 1.40 (d, J=1.5 Hz, 3H), 1.42 (d, J=1.5 Hz, 3H), 1.46 (s, 3H), 1.90 (s, 3H), 4.21 (d, J=8.5 Hz, 1H), 6.85 (d, J=8.5 Hz, 2H), 6.98 (d, J=8.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 10.64, 10.73, 11.14, 12.01, 17.79, 60.99, 77.63, 111.20, 119.07, 117.08, 130.40, 136.53, 136.88, 137.17, 139.09, 146.56. Found: C, 80.79; H, 8.16%. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92%. Mp 99–100 °C.

5.17.6. (4-Buthoxyphenyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methanol (2f). IR (neat) 3469, 2931, 1612, 1512, 1446, 1244, 1174, 1029, 821, 603 cm^{-1}; ^1H NMR (C_6D_6) δ 0.80 (t, J=7.5 Hz, 3H), 1.22 (s, 3H), 1.20–1.30 (m, 1H), 1.30 (dq, J=7.5, 7.5 Hz, 2H), 1.51 (s, 3H), 1.54 (dd, J=7.5, 7.5 Hz, 2H), 1.59 (s, 3H), 1.67 (s, 3H), 2.07 (s, 3H), 3.59 (t, J=7.5 Hz, 2H), 4.56 (d, J=3.0 Hz, 1H), 6.77 (d, J=3.5 Hz, 2H), 7.15 (d, J=3.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 10.94 (C×2), 11.41, 12.24, 13.95, 18.58, 19.49, 31.64, 61.45, 67.35, 78.35, 113.18, 128.29, 134.08, 135.98, 136.07, 138.46, 139.74, 158.78. Found: C, 79.91; H, 9.68%. Calcd for $C_{21}H_{30}$: C, 80.21; H, 9.62%.

5.17.7. 1-{4-[(Hydroxy)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methyl]phenyl}-2-methyl-1-propanone (2g). IR (neat) 3492, 2872, 1682, 1606, 1382, 1228, 981, 823, 759, 704 cm^{-1}; ^1H NMR (C_6D_6) δ 1.06 (d, J=7.0 Hz, 6H), 1.14 (s, 3H), 1.43 (d, J=3.0 Hz, 1H), 1.46 (s, 3H), 1.50 (s, 3H), 1.60 (s, 3H), 2.02 (s, 3H), 3.11 (septet, J=7.0 Hz, 1H), 4.46 (d, J=3.0 Hz, 1H), 7.18 (d, J=8.5 Hz, 2H), 7.81 (d, J=8.5 Hz, 2H); ^{13}C NMR (C_6D_6) δ 10.78, 10.85, 11.27, 12.39, 18.31, 19.21, 19.28, 35.26, 61.29, 78.14, 126.94, 127.10, 134.98, 136.10, 136.41, 137.72, 139.64, 147.46, 203.68. Found: C, 80.71; H, 8.94%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 8.78%.

5.17.8. (2-Methoxyphenyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methanol (2h). IR (neat) 3469, 2925, 1600, 1587, 1490, 1400, 1240, 1033, 752, 607 cm^{-1}; ^1H NMR (C_6D_6) δ 1.30 (s, 3H), 1.57 (d, J=1.0 Hz, 3H), 1.67 (d, J=1.0 Hz, 3H), 1.74 (s, 3H), 1.84 (d, J=4.5 Hz, 1H), 2.08 (s, 3H), 3.26 (s, 3H), 5.39 (d, J=4.5 Hz, 1H), 6.47 (d, J=7.5 Hz, 1H), 6.85 (dd, J=7.5, 7.5 Hz, 1H), 7.03 (dd, J=7.5, 7.5 Hz, 1H), 7.46 (d, J=7.5 Hz, 1H); ^{13}C NMR (C_6D_6) δ 11.04 (C×2), 11.54, 12.08, 18.82, 54.55, 61.89, 71.90, 109.88, 120.02, 128.13, 128.87, 130.65, 135.56, 135.77, 139.49, 140.40, 157.03. Found: C, 79.16; H, 9.02%. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%.

5.17.9. (4-Bromophenyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)(trimethylsiloxy)methane (2a-Si). IR (neat) 841, 889, 1076, 1250, 1377, 1458, 1655, 2924 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01 (s, 9H), 1.11 (s, 3H), 1.44 (br s, 3H), 1.48 (br s, 3H), 1.79 (s, 3H), 1.93 (s, 3H), 4.56 (s, 1H), 6.83–6.88 (m, 2H), 7.15–7.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.08, 10.52, 10.64, 10.91, 12.60, 18.07, 60.74, 79.40, 120.02, 127.72, 129.08, 135.77, 136.05, 136.83, 139.29, 140.76. Found: C, 60.84; H, 7.33%. Calcd for $C_{20}H_{29}BrOSi$: C, 61.06; H, 7.43%.

5.17.10. Methyl 4-[(trimethylsiloxy)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methyl]benzoate (2d-Si). IR (neat) 619, 710, 764, 841, 1076, 1279, 1437, 1611, 1728, 1931, 2957 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01 (s, 9H), 1.13 (s, 3H), 1.40 (br s, 3H), 1.43 (br s, 3H), 1.81 (s, 3H), 1.94 (s, 3H), 3.87 (s, 3H), 4.65 (s, 1H), 7.02–7.07 (m, 2H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.11, 10.46, 10.60, 10.94, 12.59, 18.03, 51.87, 60.83, 79.62, 125.96, 127.47, 128.16, 135.75, 136.16, 136.70, 139.30, 147.14, 167.40. Found: C, 70.97; H, 8.49%. Calcd for $C_{22}H_{32}O_3Si$: C, 70.92; H, 8.66%.

5.17.11. (4-Butoxyphenyl)(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)(trimethylsiloxy)methane (2f-Si). IR (neat) 619, 750, 841, 891, 1070, 1173, 1250, 1512, 1612, 2959 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.02 (s, 9H), 0.96 (t, J=7.2 Hz, 3H), 1.11 (s, 3H), 1.40–1.52 (m, 8H), 1.67–1.78 (m, 5H), 1.94 (s, 3H), 3.88 (t, J=6.6 Hz, 2H), 4.56 (s, 1H), 6.56–6.62 (m, 2H), 6.83–6.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.02, 10.59, 10.66, 10.90, 12.67, 13.92, 18.24, 19.26, 31.42, 60.96, 67.44, 79.84, 112.03, 127.11, 133.92, 135.39, 135.41, 137.40, 139.59, 157.58. Found: C, 74.30; H, 9.83%. Calcd for $C_{24}H_{38}O_2Si$: C, 74.55; H, 9.91%.

Compound **3b**: IR (neat) 839, 1074 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, J=7.0 Hz, 3H), 1.61 (s, 3H), 1.72 (br s, 3H), 1.74 (br s, 3H), 2.20–2.31 (m, 3H), 2.51 (distorted q, 1H), 5.97 (dd, J=5.5, 10.0 Hz, 1H), 7.96–8.09 (m, 4H), 8.14–8.17 (m, 3H), 8.26–8.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 9.73, 12.46, 20.35, 25.07, 43.45, 50.54, 54.79, 75.93, 95.96, 122.93, 123.21, 124.71, 124.75, 124.84, 124.92, 125.09, 125.66, 126.80, 127.10, 127.51, 127.83, 130.39, 130.65, 131.30, 132.51, 135.62, 138.74. Found: C, 88.18; H, 7.21%. Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15%. Mp 131.2–132.4 °C.

Compound **4b**: IR (Nujol) 852, 1076 cm^{-1}; ^1H NMR (500 MHz, ppm, $CDCl_3$) δ 1.11 (d, J=7.0 Hz, 3H), 1.56 (s, 3H), 1.63 (br s, 3H), 1.67–1.74 (m, 1H), 1.87 (br s, 3H), 2.24 (distorted q, 1H), 2.36 (m, 1H), 2.90 (m, 1H), 5.97 (dd, J=5.5, 10.5 Hz, 1H), 7.96–8.09 (m, 4H), 8.14–8.17 (m, 3H), 8.21 (d, J=7.5 Hz, 1H), 8.29 (d, J=9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.79, 12.53, 19.63, 25.45, 44.55, 47.99, 56.03, 77.65, 96.41, 122.82, 123.11, 124.69, 124.75, 124.92, 124.95, 125.10, 125.72, 126.75, 127.06, 127.51, 127.60, 130.33, 130.67, 131.37, 134.56, 135.19, 136.51. Found: C, 88.49; H, 7.14%. Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15%. Mp 159.4–160.8 °C.

5.17.12. 4-[(Hydroxy)(diphenyl)methyl]benzaldehyde (7a)[20] and 4-[(hydroxy)(phenyl)methyl]benzaldehyde (7b) .[21] The title compounds are found in the literature.

5.17.13. 4-(1-Hydroxy-1-phenyl-3-butenyl)benzaldehyde (7c). IR (neat) 3477, 3060, 2839, 1699, 1606, 1573, 1446, 1213, 1174, 1062, 991, 825, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.69 (s, 1H), 3.07 (dd, J=7.2, 14.1 Hz, 1H), 3.15 (dd, J=7.2, 14.1 Hz, 1H), 5.19–5.30 (m, 2H), 5.58–5.73 (m, 1H), 7.22–7.28 (m, 2H), 7.31–7.36 (m, 2H), 7.44–7.49 (m, 2H), 7.62–7.66 (m, 2H), 7.81–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 46.34, 76.81, 121.18, 125.88, 126.56, 127.32, 128.44, 129.68, 132.62, 134.94, 145.53, 153.28, 191.92. Found: C, 80.69; H, 6.55%. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39%.

5.17.14. 4-(1-Phenylethenyl)benzaldehyde (9). IR (neat) 3028, 2829, 2734, 1697, 1604, 1566, 1211, 1168, 840, 779, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58 (d, J=1.0 Hz, 1H), 5.59 (d, J=1.0 Hz, 1H), 7.30–7.38 (m, 5H), 7.51 (d, J=8.0 Hz, 2H), 7.86 (d, J=8.0 Hz, 2H), 10.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 116.48, 128.08, 128.16, 128.35, 128.79, 129.66, 135.59, 140.53, 147.59, 149.12, 191.80. Found: C, 86.28; H, 5.81%. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81%.

5.17.15. 1-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl)-1-dodecanol (11a). IR (neat) 1013, 1379, 1445, 1657, 2924, 3483 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, $J=6.6$ Hz, 3H), 1.02 (s, 3H), 1.05–1.53 (m, 21H), 1.70 (s, 3H), 1.76 (br s, 6H), 1.79 (s, 3H), 3.54 (dt, $J=7.2$, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.93 (×2), 11.05, 11.40, 14.12, 18.21, 22.69, 27.25, 29.34, 29.63 (×2), 29.65, 29.69, 29.71, 31.56, 31.91, 60.34, 75.96, 135.12, 135.33, 138.69, 139.87. Found: C, 82.05; H, 12.67%. Calcd for $C_{22}H_{40}O$: C, 82.43; H, 12.58%.

5.17.16. 1-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl)-3-phenyl-1-propanol (11b). IR (neat) 700, 1030, 1454, 2920, 3483 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.34–1.47 (m, 3H), 1.59 (s, 3H), 1.74 (br s, 6H), 1.80 (s, 3H), 2.54 (dt, $J=13.8$, 7.8 Hz, 1H), 2.82 (dt, $J=13.8$, 7.8 Hz, 1H), 3.48–3.62 (m, 1H), 7.10–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.84, 11.07, 11.20, 11.62, 18.30, 33.44, 33.50, 60.27, 75.21, 125.57, 128.16 (×2), 128.41 (×2), 135.12, 135.28, 138.44, 139.59, 142.32. Found: C, 84.59; H, 9.97%. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69%.

5.17.17. 1-Cyclohexyl-1-(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)methanol (11c). IR (neat) 974, 1379, 1448, 1655, 2922, 3504 cm^{-1}; ^1H NMR (C_6D_6) δ 0.99–1.58 (m, 15H), 1.66 (s, 3H), 1.71 (br s, 6H), 2.04 (s, 3H), 3.35 (d, $J=5.1$ Hz, 1H); ^{13}C NMR (C_6D_6) δ 10.87, 11.35, 11.51, 13.41, 21.32, 27.14, 27.18, 27.61, 27.87, 33.37, 40.86, 61.04, 81.52, 134.81, 134.90, 140.13, 142.13. Found: C, 82.10; H, 11.53%. Calcd for $C_{17}H_{28}O$: C, 82.10; H, 11.36%.

5.17.18. 7-Hydroxy-7-(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)heptanenitrile (11e). IR (neat) 1059, 1379, 1445, 1657, 2247, 2932, 3520 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 3H), 1.10–1.67 (m, 9H), 1.70 (s, 3H), 1.76 (br s, 6H), 1.79 (s, 3H), 2.32 (t, $J=7.2$ Hz, 2H), 3.53 (dt, $J=7.5$, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.93, 10.94, 11.07, 11.37, 17.08, 18.14, 25.38, 26.43, 28.67, 31.14, 60.27, 75.77, 119.85, 135.33, 135.58, 138.46, 139.69. HRMS FAB [$M+H^+$] 261.2094. Calcd for $C_{17}H_{28}NO$: 261.2093.

5.17.19. 10-Chloro-1-(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)-1-decanol (11f). IR (neat) 1036, 1379, 1447, 2926, 3449 cm^{-1}; ^1H NMR (C_6D_6) δ 0.97–1.66 (m, 20H), 1.70 (s, 3H), 1.71 (s, 3H), 1.73 (s, 3H), 1.97 (s, 3H), 3.11 (t, $J=6.9$ Hz, 2H), 3.45–3.55 (m, 1H); ^{13}C NMR (C_6D_6) δ 10.62, 10.97, 11.13, 12.14, 18.75, 27.04, 27.51, 29.08, 29.74, 29.98, 30.03, 31.88, 32.81, 44.93, 60.80, 75.99, 134.97, 135.07, 139.21, 140.91. HRMS FAB [$M+H^+$] Found: 326.2376. Calcd for $C_{20}H_{36}ClO$: 326.2376.

5.17.20. Methyl 6-hydroxy-6-(1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl)hexanoate (11g). IR (Nujol) 1377, 1462, 1724, 2361, 2853, 3520 cm^{-1}; ^1H NMR (C_6D_6) δ 1.05 (s, 3H), 1.07–1.60 (m, 7H), 1.64 (s, 3H), 1.69 (s, 3H), 1.71 (s, 3H), 1.94 (s, 3H), 2.07 (t, $J=7.2$ Hz, 2H), 3.33 (s, 3H), 3.37–3.45 (m, 1H); ^{13}C NMR (C_6D_6) δ 10.55, 10.94, 11.10, 12.10, 18.70, 25.05, 26.75, 31.29, 34.09, 50.88, 60.71, 75.53, 134.93, 135.04, 139.14, 140.87, 173.41. Found: C, 72.52; H, 10.11%. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06%. Mp 63–65 °C.

5.17.21. 7-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl)-7-tridecanol (16). IR (neat) 523, 621, 725, 935, 1036, 1136, 1379, 1456, 1653, 1715, 2926, 3508 cm^{-1}; ^1H NMR (C_6D_6) δ 0.91 (t, $J=6.3$ Hz, 6H), 0.97 (s, 1H), 1.18 (s, 3H), 1.20–1.64 (m, 20H), 1.74 (s, 6H), 1.98 (s, 6H); ^{13}C NMR (C_6D_6) δ 11.23 (×2), 13.94 (×2), 14.30 (×2), 17.03, 23.02 (×2), 24.63 (×2), 30.61 (×2), 32.23 (×2), 37.12 (×2), 64.38, 77.62, 135.51 (×2), 141.69 (×2). HRMS FAB [M−OH] Found: 317.3203. Calcd for $C_{23}H_{41}$: 317.3210.

5.17.22. 1-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl)-3-phenyl-1-(trimethylsilyloxy)propane (the trimethylsilyl ether of 11b). IR (neat) 511, 698, 748, 866, 1059, 1250, 1447, 1605, 1657, 1938, 2957 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 0.24 (s, 9H), 1.12 (s, 3H), 1.43–1.51 (m, 1H), 1.54–1.62 (m, 4H), 1.67 (s, 3H), 1.70 (s, 3H), 2.06 (s, 3H), 2.49 (ddd, $J=13.5$, 10.0, 7.0 Hz, 1H), 2.80 (ddd, $J=13.5$, 10.5, 5.0 Hz, 1H), 3.80 (dd, $J=8.0$, 2.5 Hz, 1H), 6.99–7.03 (m, 1H), 7.07–7.13 (m, 4H); ^{13}C NMR (C_6D_6, 126 MHz) δ 0.96 (×3), 10.16, 10.92, 11.07, 12.49, 20.25, 33.78, 34.98, 60.90, 77.39, 125.96, 128.62 (×2), 128.70 (×2), 134.88, 134.93, 139.19, 141.50, 142.93. Found: C, 77.38; H, 10.18%. Calcd for $C_{22}H_{34}Si$: C, 77.13; H, 10.00%.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.01.097. Supplementary data including the coordinates of the atoms obtained by the ab initio calculations can be found online alongside the electronic version of the manuscript.

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