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A convenient synthesis of bromopentaarylcyclopentadienes containing methyl or fluorine substituents

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Abstract

The ketones $C_5(3,5\text{-}C_6H_3Me_2)_4(O)$ (**5b**) and $C_5\text{-}2,5(3,5\text{-}C_6H_3Me_2)_2(C_6H_5)_2(O)$ (**5c**) were prepared and characterized. The pentaarylcyclopentadienols $C_5(C_6H_5)_4(Ar')(OH)$ ($Ar' = 3,5\text{-}C_6H_3Me_2$, **6a3**; $Ar' = 2,4,6\text{-}C_6H_2Me_3$, **6a5**; $Ar' = 3\text{-}C_6H_4F$, **6a6**; $Ar' = 3,5\text{-}C_6H_3F_2$, **6a7**), $C_5(3,5\text{-}C_6H_3Me_2)_4(Ar')(OH)$ ($Ar' = 3\text{-}C_5H_4Me$, **6b2**; $3,5\text{-}C_5H_3Me_2$, **6b3**; $3,6\text{-}C_5H_3Me_2$, **6b4**; $2,4,6\text{-}C_5H_2Me_3$, **6b5**; $Ar' = 3\text{-}C_6H_4F$, **6a6**; $Ar' = 3,5\text{-}C_6H_3F_2$, **6a7**; $Ar' = 2,6\text{-}C_6H_3F_2$, **6a8**) were obtained by reaction of the corresponding Ar′Li with the ketones $C_5(C_6H_5)_4(O)$ (**5a**), or $C_5(3,5\text{-}C_6H_3Me_2)_4(O)$ (**5b**). The synthesis and characterization of the bromopentaarylcyclopentadienes $C_5(C_6H_5)_4(Ar')(Br)$ ($Ar' = 3,5\text{-}C_6H_3Me_2$, **7a3**; $Ar' = 2,4,6\text{-}C_6H_2Me_3$, **7a5**) and $C_5(3,5\text{-}C_6H_3Me_2)_4(Ar')(Br)$ ($Ar' = 3\text{-}C_5H_4Me$, **7b2**; $3,5\text{-}C_5H_3Me_2$, **7b3**; $3,6\text{-}C_5H_3Me_2$, **7b4**; $2,4,6\text{-}C_5H_2Me_3$, **7b5**; $Ar' = 3\text{-}C_6H_4F$, **7a6**; $Ar' = 3,5\text{-}C_6H_3F_2$, **7a7**; $Ar' = 2,6\text{-}C_6H_3F_2$, **7a8**) containing methyl groups or fluorine atoms on the Ar′ rings are reported. The bromopentaarylcyclopentadienes are isolated as a 1:2:2 mixture of three isomers when Ar and Ar′ are different, except when the latter substituent bears two fluorine or two methyl groups in the *ortho* positions. In these cases the reaction is regiospecific and provides a unique isomer with the di-*ortho*-substituted arene located in the β-position with respect to the carbon bearing the bromine atom.

Keywords: Bromopentaarylcyclopentadienes; Methyl and fluorine substituents; Regiospecific reactions

1. Introduction

Since the discovery of ferrocene in 1951 [1,2], the cyclopentadienyl ligand has played a major role in the development of organometallic chemistry. Over the years peralkylcyclopentadienyl ligands have become popular as chemists appreciated the positive effects of the alkyl groups on their solubility, steric protection and electron releasing ability. At the same time complexes containing perarylcyclopentadienyl ligands have been described [3–12]. However, the interest in these compounds was lowered by their poor solubility in most organic solvents and the lack of convenient ^{1}H-NMR probes. In this respect, it was shown that the replacement of the phenyl groups on the C_5 ring by five *p*-tolyl groups significantly increases the solubility and provides a ^{1}H-NMR signature [13].

The development of bulky and electron withdrawing pentaarylcyclopentadienyl ligands can be useful in organometallic chemistry not only for stabilizing anionic and radical complexes but also for designing donor–acceptor organometallic molecular devices that display preferential one-way electron transfer, acting as rectifiers [14]. For this reason, we prepared a series of iron complexes containing pentaarylcyclopentadienyl ligands with methyl or fluorine substituents in the *ortho* or *meta* positions of the C_6 rings. The ultimate goal of this project is the preparation of metal complexes with (i) better solubility, fine tuning of the (ii) steric and (iii) electronic environment of the metal center, and (iv) stabilization of transient radicals. In this first paper, we report the synthesis of several bromopentaarylcyclopentadienes, which constitute a convenient entry to the iron complexes (Scheme 1). We prepared two families of bromo derivatives that contain four equivalent arene rings $\{C_5Ar_4Ar'Br$ ($Ar = C_6H_5$, series **a**; $Ar = C_5(3,5\text{-}C_6H_3Me_2)_4Ar$, series **b**)$\}$.[1] The fifth arene contains ei-

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[1] In the compounds' numbers, the letter references to the series a or b and the last digit indicate the substitution of Ar′ as shown in Scheme 1.

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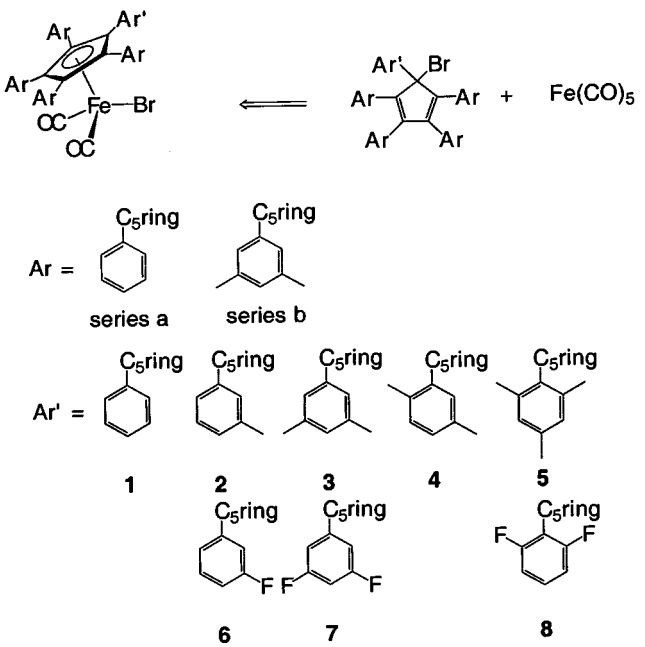
ther 0, 1, 2, or 3 methyl substituents or 0, 1, or 2 fluorine atoms.

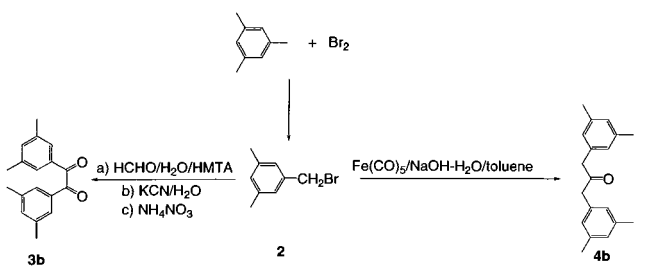
2. Results and discussion

2.1. Preparation of the methyl-substituted tetraphenylcyclopentadienones *5b* and *5c*

The synthesis of tetraphenylcyclopentadienone (**5a**) is easily achieved from commercially available compounds [15], whereas access to its homologues containing two methyl groups in the *meta* positions of 2 or 4 phenyl rings requires the preparation of 3,5,3′5′-tetramethylbenzil (**3b**) and 1,3-bis(3,5-dimethylphenyl)-propanone (**4b**). As depicted in Scheme 2, both derivatives can be easily prepared from mesitylene (**1**) as a unique and cheap precursor. Treatment of **1** with bromine vapor at 140°C according to the Kadesh–Shacklett procedure yielded 3,5-dimethylbenzyl bromide (**2**) (87%) [16,17]. Following well-described



Scheme 1.



Scheme 2.

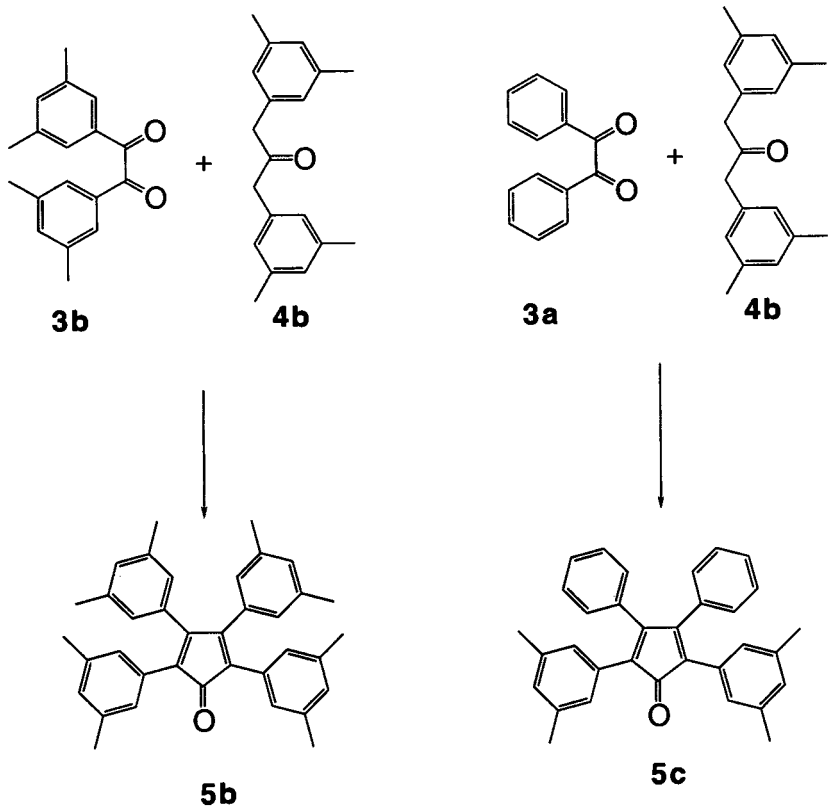
procedures, **2** was successively transformed into 3,5-dimethylbenzaldehyde, 3,5-dimethylbenzoin and **3b** in 70% overall yield (m.p. 139–140°C, literature value 139.5°C) [16]. On the other hand, **4b** was obtained by reacting **2** with iron pentacarbonyl in an alkaline water–toluene bilayer using the phase transfer catalysis technique (67%; m.p. 50°C, literature from Beilstein data base, 53°C) [18–20].

Condensation of the organic derivatives **3b** and **4b** in alkaline conditions affords the tetrakis(3,5-dimethylphenyl)cyclopentadienone **5b** (Scheme 3). Similarly, reaction of **3a** with 1,3-bis(3,5-dimethylphenyl)propanone (**4b**) provided 2,5-bis(3,5-dimethylphenyl)-3,4-diphenylcyclopentadienone (**5c**). Both ketones are obtained pure as purple solids after chromatography on silica gel with moderate yields of 75 and 60%, respectively. Surprisingly, no mention of the ketones **5b** and **5c** was found in the literature. These ketones are fairly soluble in most organic solvents and were fully characterized (see Section 4). Despite its easy access, the ketone **5c** was not used in the following project.

2.2. Preparation of substituted pentaarylcyclopentadienols (*6*)

The non-substituted pentaphenylcyclopentadienol $(C_6H_5)_5C_5OH$ (**6a1**) has been obtained by addition of the phenyl Grignard reagent to **5a** [3,21]. Compound **6a3** can also be prepared by this way. However, Ar′MgBr did not react with **5b** when one or two *ortho* positions of Ar′ are substituted by methyl or fluorine groups; in these cases the starting ketones were almost quantitatively recovered. For this reason, the fifth aryl group was systematically introduced onto the C_5 ring by treatment of the tetraarylcyclopentadienones **5a** and **5b** with the corresponding lithium-aryl reagents Ar′Li in THF (Scheme 4). The corresponding pentaarylcyclopentadienols (**6**) were isolated as pale yellow powders in moderate to good yields (42–80%). It was observed that the yields decrease with the number of methyl or fluorine groups on the *ortho* positions of the incoming arene. The new methyl-substituted pentaarylcyclopentadienols (**6a3**, **6a5**, **6b2**–**6b5**) were isolated as light yellow powders after recrystallization and fully characterized by the usual spectroscopic techniques and elemental analysis (see Section 4).

Aryl groups containing fluorine atoms were also introduced onto the tetraphenyl ketones **5a** and **5b** by using the corresponding aryl lithium reagent. Introduction of the 3-fluorophenyl and 2,6-difluorophenyl substituents did not require special attention and the alcohols **6a8**, **6b6**, and **6b8** were readily obtained. The preparation of **6a7** and **6b7** was less easy. Indeed, addition of *n*-butyllithium to 1-bromo-3,5-difluorobenzene resulted in a competitive abstraction of the bromine and *p*-hydrogen as previously reported

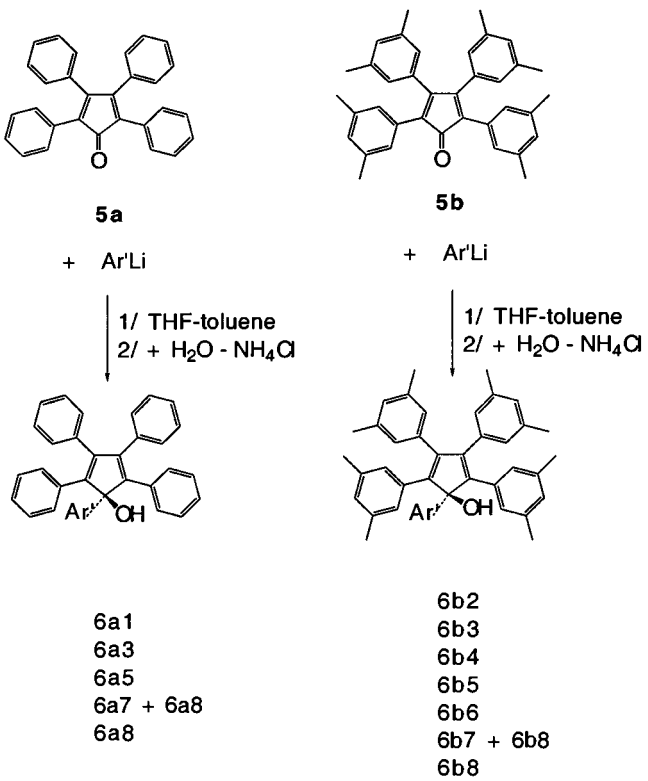


Scheme 3.

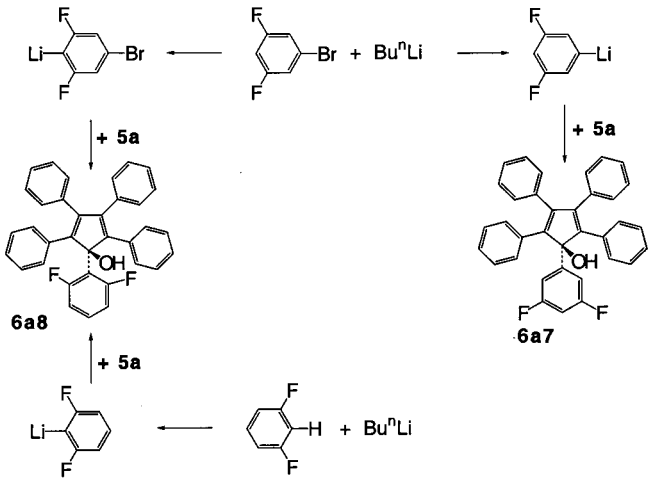
(Scheme 5) [22,23]. Condensation of the resulting aryllithium reagent with ketones **5a** and **5b** produced a mixture of **6a7–6a9** (or **6b7–6b9**). When the reaction was carried out with an excess of *n*-butyllithium (4 equivalents), the formation of the undesired bromine-containing compounds **6a9** and **6b9** was not observed (traces of **6a9** or **6b9** were only detected by mass spectroscopy). It is likely that the bromine versus lithium exchange converted them into **6a8** and **6b8**, respectively.

As a result, the alcohols **6a7** could not be easily obtained in the pure form. The crude product was a mixture of **6a7** and **6a8**, the ratio of which was not reproducible from one preparation to another. In one experiment, for purposes of characterization, purification of **6b7** was achieved by chromatography on silica followed by recrystallization from ethanol. In all other cases, the mixture of alcohols was converted into the corresponding bromoarylcyclopentadienes and the separation was achieved at this stage.

In these two series of alcohols, the *ortho* and *meta* positions are equivalent for all the phenyl rings except for those bearing two methyl or two fluorine substituents on the two *ortho* positions. Thus, in alcohols **6a3**, **6b3**, **6a7**, and **6b7** the methyl and fluorine substituents on the Ar′ ring are equivalent. In contrast, the ^{1}H-NMR spectrum of the compounds **6a5** and **6b5**



Scheme 4.



Scheme 5.

display two different resonances for the methyl groups (δ, 2.18, 2.41 and 2.00, 2.49, for **6a5** and **6b5**, respectively). The hydrogen atoms on the *meta* and *meta′* positions of the phenyl bound to the sp^3 carbon of the cyclopentadienyl ring are also non-equivalent as clearly seen in the ^{1}H-NMR spectra of **6b5** (δ, 6.67, 6.74 ppm). In the ^{19}F-NMR spectra of **6a7** and **6b7**, a unique resonance is observed for the fluorine atoms (δ -109.79 and -110.47 ppm, respectively), whereas the ^{19}F-NMR spectra of both the alcohols **6a8** and **6b8** show AB systems (**6a8**, δ -107.87, -115.59 ppm, $^4J_{F-F} = 5.5$ Hz, and **6b8**, δ -107.92, -115.61 ppm, $^4J_{F-F} = 5.8$ Hz). Moreover, the ^{1}H and ^{19}F-NMR spectra of **6a8** and **6b8** reveal a coupling between the proton of the hydroxy group and one *ortho* fluorine ($J_{F-H} =$ 10.3 and 8.5 Hz, respectively), indicating the existence of a F···H bond.

In the case of **6a8** a variable temperature ^{1}H-NMR experiment carried out in toluene clearly showed a doublet for the resonance of the proton of the hydroxyl group at 298 K ($J_{H-F} = 7.4$ Hz). Up to 330 K, this signal appeared increasingly broader, and an unresolved massif was observed at 347 K. A similar $\{^1H\}^{19}$F-NMR experiment allowed observation of the signal at δ -107.87, which corresponds to the fluorine atom involved in the F···H bond moved upfield by 50 Hz when the temperature increased from 298 to 347 K. Upon warming, the position of the signal at δ -115.59 remained unchanged. These data indicate that in these alcohols the conformation of the *ortho*-fluorinated aromatic ring strongly favors the hydrogen bonding between the fluorine and the hydroxylic proton.

2.3. Preparation of the substituted bromopentaarylcyclopentadienes 7

The C_5Ph_5Br derivative (**7a1**) was previously prepared by reacting **6a1** with gaseous HBr in toluene or aqueous HBr in acetic acid [24,25]. Surprisingly, these reactions became very sluggish with the methyl-substituted alcohols of the **6b** series. Except for the preparation of **7a3**, the substitution of the hydroxy group by a bromide was achieved using the $SOBr_2$–pyridine system (Scheme 6) [26].

This reagent allowed conversion of the pentaarylcyclopentadienols into the corresponding bromo derivatives with fair yields, whatever the number of methyl or fluorine substituents on the arene rings. When the Ar and Ar′ groups are different, three different isomers for the bromopentaarylcyclopendienes are expected. This is exactly what was found in the case for the compounds **7a3**, **7a7**, **7b2**, **7b4**, **7b6**, and **7b7**. The bromo derivatives were each isolated as a mixture of the three possible positional isomers in the statistical 1:2:2 ratio [24]. The assignment of the ^{1}H- and ^{13}C-NMR spectra was not straightforward for these mixtures of isomers. For this reason, the characterization of these bromo derivatives **7** was mainly achieved on the basis of elemental analysis and the presence of three ^{13}C-NMR resonances corresponding to the carbons of the C_5 ring bound to the bromine atoms. In the case of **7b3**, the presence of five equivalent 3,5-dimethylphenyl substituents eliminates the problem of isomers and full characterization was achieved.

Interestingly, for the compounds **7a5**, **7a8**, **7b5**, and **7b8** the presence of two methyl or two fluorine substituents on the two *ortho* positions of Ar′ rendered the reaction fully specific and a single isomer was obtained in a yield of 90%. However, the ^{1}H- and ^{13}C-NMR spectra clearly show that all the hydrogen and carbon atoms of these molecules are non-equivalent. This observation indicates that the carbon atom bound to the halide should be chiral and as a consequence, this carbon does not bear the di-*ortho*-substituted Ar′ group. In particular, for each of these four compounds, the five resonances corresponding to the carbon atoms of the C_5 ring were observed in the ^{13}C-NMR spectra. The structure given in Scheme 6 can be established on the basis of the ^{13}C-NMR data. Indeed, assuming that (i) the two higher field ^{13}C resonances of the diene pattern could be assigned to the two carbon atoms in the α and α' positions with respect to the carbon bearing the bromine (i.e. **7a5**, δ 147.8 and 150.3 ppm) [27],[2] and (ii) considering that these carbon resonances appeared as a pseudotriplet (i.e. **7a5**, $^3J_{C-H} = 3$ Hz), it could be concluded that the arene bearing the *ortho* substituents is bound to a carbon in a β-position (i.e.

[2] Surprisingly, the ^{13}C-NMR spectra for the pentaphenylcyclopentadienol and bromopentaphenylcyclopentadiene were not reported. Similarly, ^{13}C data were not reported for *cis*-2,3-diphenylbromopropene [30]. Few ^{13}C-NMR data are available for related compounds, most of them can be obtained at the Spectral Data Base System (SDBS).

7a5, δ 142.6 and 143.1 ppm). Accordingly, the carbon resonance at δ 142.6 is a sharp singlet and corresponds to the carbon of the cyclopentadiene bearing the di-*ortho* subsituted arene. As a result, the bromine is on the less sterically hindered position. The same effect on the regioselectivity was observed when the two *ortho* hydrogen atoms were replaced by either the methyl or fluorine groups, whereas the replacement of only one of these hydrogen atoms remained without any effect (**7b4**). These observations suggest steric control of the reaction by bulky *ortho* groups. Indeed, despite similar van der Waals radii for hydrogen (1.135 Å) and fluorine (1.293 Å) atoms [28], the presence of eight electrons in the valence shell of fluorine makes the steric effect of this atom much closer to that of a methyl group than that of an hydrogen atom [28]. Moreover, the steric effect of the fluorine atom is probably enhanced in such a reaction by the anionic nature of the incoming group.

3. Conclusions

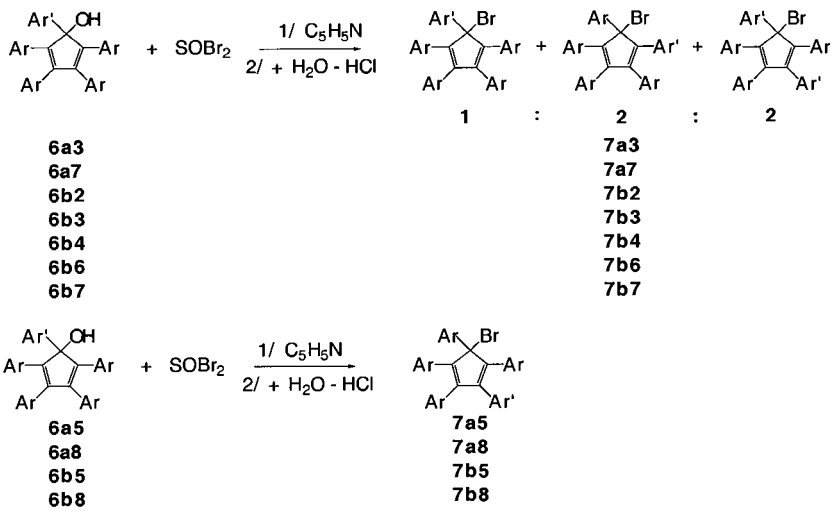
The procedures for the preparation of bromopentaarylcyclopentadienes described here allow facile access to the C_5Ar_4Ar' ligand precursors containing from two to eleven methyl groups on the phenyl rings. It is also possible to prepare bromopentaarylcyclopentadienes containing one or two fluorines on a single phenyl substituent. In following papers, we will report the reaction of $C_5Ar_4Ar'Br$ with iron carbonyl, which is formally an oxidative addition (Scheme 1). We found that the difference in reactivity between ligands containing methyl groups on the *ortho* and *meta* positions provides insights on the mechanism of this reaction. On the other hand, in the case of $C_5(3,5\text{-}C_6H_3Me_2)_5$, which possesses a higher symmetry, we are currently examining the relative arrangement of the 3,5-dimethylphenyl groups around the C_5 ring and the possible interactions between the phenyl substituents and the other ligands bound to the metal in the series of iron piano stool compounds.

4. Experimental

4.1. General data

Reagent grade tetrahydrofuran (THF), pentane, diethyl ether, toluene, and mesitylene were predried and distilled over sodium benzophenoneketyl prior to use. Benzil, diphenylacetone and bromoaryl compounds (Aldrich or Acros) were used as received. Deuterated solvents (Merck) were used as received, except $CDCl_3$, which was previously treated with P_2O_5, and then Na_2CO_3, and stored on basic alumina under argon. NMR measurements were performed on a Bruker AC300P instrument; chemical shifts are referenced to external standards (TMS for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F). FTIR spectra were recorded on a Bruker IFS28 spectrometer. Mass spectra were performed at the CRMPO (Rennes) using a Varian MAT 311 spectrometer for EI spectra and a Micromass ZABSpec TOF spectrometer for FAB mass spectra in a matrix of *m*-nitrobenzyl alcohol. Elemental analyses were performed at the Service Central d'Analyses, USR CNRS 59, at Lyon-Vernaison.

Tetrakis(3,5-dimethylphenyl)cyclopentadienone (**5b**). In a two-necked flask, equipped with a reflux condenser, a septum, and a magnetic stirrer, were placed **3b** (11.5 g, 0.043 mol), **4b** (11.5 g, 0.043 mol), and 200 ml of dried ethanol. The mixture was heated to dissolve the solid reagents; then benzyltrimethylammonium hydroxide (40 wt% in methanol, 19 ml, 0.043 mol) was added by syringe, and refluxing was continued for 15



Scheme 6.

min. Compound **5b** formed as a deep violet precipitate. The mixture was cooled to −20°C, and **5b** was isolated by filtration. Purification achieved on a silica gel column (pentane–diethyl ether 9:1) provided 2.65 g of **5b** (75%); m.p. 192°C. EIMS: Found, 496.2774. Calc. for $C_{37}H_{36}O$ ($M^{\bullet+}$) 496.2766. IR (CH_2Cl_2, cm^{-1}) 1707 (CO), 1601 (Ph). ^{1}H-NMR (300 MHz, $CDCl_3$) 2.10 (s, 12H, Me), 2.19 (s, 12H, Me), 6.51 (br s, 4H, Ph), 6.83 (s, 4H, Ph), 6.88 (s, 4H, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.2 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 4.9$ Hz, Me), 21.4 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 4.9$ Hz, Me), 124.7 (st, $^3J_{C-H} = 4$ Hz, *C*=C), 127.2 (dm, $^1J_{C-H} = 158$, $^3J_{C-H} = 5.2$ Hz, *o*-$C_6H_3Me_2$), 127.9 (dm, $^1J_{C-H} = 159$, $^3J_{C-H} = 5.4$ Hz, *o*-$C_6H_3Me_2$), 129.0 (dm, $^1J_{C-H} = 154$, $^2J_{C-H} = 4.9$ Hz, *p*-$C_6H_3Me_2$), 129.8 (dm, $^1J_{C-H} = 154$ $^2J_{C-H} = 4.9$ Hz, *p*-$C_6H_3Me_2$), 130.9 (s, *ipso*-$C_6H_3Me_2$), 133.2 (s, *ipso*-$C_6H_3Me_2$), 136.9 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 137.1 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 154.8 (t, $^3J_{C-H} = 4$ Hz, C=*C*), 201.3 (t, $^4J_{C-H} = 6.5$ Hz, CO).

2,5-Bis(3,5-dimethylphenyl)-3,4-diphenylcyclopentadienone (**5c**). According to the procedure described for **5b**, **5c** was prepared from **3a** (2.10 g, 0.010 mol) and **4b** (2.66 g, 0.010 mol). Compound **5c** was obtained as a purple powder (2.65 g, 0.006 mol, 60%), m.p. 202°C. Anal. Found: C, 90.05; H, 6.19. Calc. for $C_{33}H_{28}O$: C, 89.96; H, 6.41%. IR (CH_2Cl_2, cm^{-1}) 1708 (CO), 1601 (Ph). ^{1}H-NMR (300 MHz, $CDCl_3$) 2.21 (s, 12H, Me), 6.88 (s, 2H, *o*-$C_6H_3Me_2$), 6.94–6.97 (m, 2H, *o*-Ph), 7.15–7.25 (m, 12H, other Ph). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.4 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, Me), 125.5 (s, C=C), 127.9 (d, $^1J_{C-H} = 161$ Hz, *o*-$C_6H_3Me_2$), 128.0 (dm, $^1J_{C-H} = 161$ Hz, *o*-Ph), 128.4 (dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 6$ Hz, *m*-Ph), 129.3 (d, $^1J_{C-H} = 160$ Hz, *p*-$C_6H_3Me_2$), 129.4 (dt, $^1J_{C-H} = 160$, $^2J_{C-H} = 6$ Hz, *p*-Ph), 130.6 (s, *ipso*-$C_6H_3Me_2$), 133.4 (t, $^3J_{C-H} = 7$ Hz, *ipso*-Ph), 137.3 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 154.2 (t, $^3J_{C-H} = 4$ Hz, C=C), 200.8 (t, $^4J_{C-H} = 6$ Hz, CO).

4.2. General procedure for substituted-pentaarylcyclopentadienols (6)

The Ar′Li derivatives were prepared according to Brandsma and Verkruijsse [29]. They were obtained by reacting a THF solution (10 ml, −80°C) of the corresponding bromoaryl derivative (3.0 mmol) with one equivalent of *n*-BuLi (1.6 M in hexane, 1.87 ml). In the particular cases of **6a7** and **6b7** an excess of *n*-BuLi (4 equivalents) was used to react the bromo-3,5-difluorobenzene (see text). All the reactions were carried out by mixing a 20 ml toluene solution of tetraarylcyclopentadienone (2.0 mmol, **5a** 0.769 g or **5b** 0.993 g) and the solution of Ar′Li at −80°C. After completion, the mixture was allowed to warm up to 20°C, and hydrolyzed with 10 ml of a saturated solution of NH_4Cl. The resulting two-layer solution was poured in water (0.5 l) and extracted with diethyl ether (3 × 50 ml). The ethereal extracts were washed with water, and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave pale yellow powders. Further recrystallization of the crude solids from ethanol (20 ml) afforded analytically pure compounds.

6a3. 0.690 g, 1.4 mmol, 70%, m.p. 135°C. Anal. Found: C, 90.66; H, 6.23. Calc. for $C_{37}H_{30}O$: C, 90.58; H, 6.16%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.26 (s, 6H, Me), 2.42 (s, 1H, OH), 6.82 (s, 2H, *o*-$C_6H_3Me_2$), 7.00–7.15 (m, 21H, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.9 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, Me), 90.4 (s, C–OH), 123.1 (dq, $^1J_{C-H} = 157$, $^3J_{C-H} = 5$ Hz, *o*-$C_6H_3Me_2$), 127.2 (dt, $^1J_{C-H} = 160$, $^3J_{C-H} = 7$ Hz, *p*-Ph), 127.3 (dt, $^1J_{C-H} = 160$, $^3J_{C-H} = 7$ Hz, *p*-Ph), 127.9 (dm, $^1J_{C-H} = 160$ Hz, *p*-Ph), 128.1 (dm, $^1J_{C-H} = 160$ Hz, *p*-Ph), 128.9 (dm, $^1J_{C-H} = 160$ Hz, *p*-$C_6H_3Me_2$), 129.8 (dm, $^1J_{C-H} = 160$ Hz, *m*-Ph), 130.2 (dm, $^1J_{C-H} = 160$ Hz, *m*-Ph), 134.3 (m, *ipso*-Ph), 135.5 (m, *ipso*-Ph), 137.7 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 140.1 (s, *ipso*-$C_6H_3Me_2$), 142.4 (s, C=C), 148.3 (s, C=C).

6a5. The reaction of mesityl-lithium and **5a** afforded a mixture containing **6a5** and the corresponding mesityltetraphenylcyclopentadiene with unreacted **5a**. Several crystallizations from ethanol and washings allowed isolation of the fairly insoluble **6a5**, which was isolated as a pure sample with final yields of 20–25%. For further synthesis, this purification was omitted, and crude **6a5** was converted into **7a5** without purification. The latter compound is easily purified by chromatography; m.p. 150°C. ^{1}H-NMR (300 MHz, $CDCl_3$, 30°C) 2.18 (s, 3H, Me), 2.29 (s, 1H, OH), 2.41 (s, 3H, Me), 2.44 (s, 3H, Me), 6.7–7.5 (m, 22H, Ph and Mes). ^{13}C-NMR (75 MHz, $CDCl_3$, 30°C) 20.6 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, *p*-Me), 21.1 (qd, $^1J_{C-H} = 126$, $^3J_{C-H} = 6$ Hz, *o*-Me), 25.6 (qd, $^1J_{C-H} = 126$, $^3J_{C-H}$ 5 = Hz, *o*-Me), 93.6 (s, *C*–OH), 127.0 (dt, $^1J_{C-H} = 163$, $^3J_{C-H} = 7$ Hz, *p*-C_6H_5), 127.1 (dt, $^1J_{C-H} = 163$, $^3J_{C-H} = 7$ Hz, *p*-C_6H_5), 127.8 (dm, $^1J_{C-H} = 160$ Hz, *p*-C_6H_5), 128.0 (dm, $^1J_{C-H} = 160$ Hz, *o*-C_6H_5), 129.5 (dm, $^1J_{C-H} = 160$ Hz, *m*-C_6H_5), 129.7 (dm, $^1J_{C-H} = 160$ Hz, *m*-C_6H_5), 131.0 (dm, $^1J_{C-H} = 155$ Hz, *m*-$C_6H_2Me_3$), 132.6 (mm, *ipso*-$C_6H_2Me_3$), 132.9 (dm, $^1J_{C-H} = 155$ Hz, *m*-$C_6H_2Me_3$), 134.5 (t, $^3J_{C-H} = 6$ Hz, *ipso*-C_6H_5), 135.1 (q, $^2J_{C-H} = 5$ Hz, $C_6H_2Me_3$), 135.4 (t, $^3J_{C-H} = 6$ Hz, *ipso*-C_6H_5), 135.8 (sq, $^2J_{C-H} = 6$ Hz, $C_6H_2Me_3$), 139.3 (q, $^2J_{C-H} = 5$ Hz, $C_6H_2Me_3$), 142.2 (s, C=C), 147.5 (s, C=C).

6a7. Several recrystallizations allowed isolation of a pure sample for analysis (0.400g, 0.8 mmol, 40%). For further synthesis of **7a7** the crude compound was used (m.p. 135°C). FABHRMS: Found, 498.1796. Calc. for [$C_{35}H_{24}F_2O^{\bullet+}$] ([$M^{\bullet+}$]), 498.1795. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.52 (s, 1H, OH), 6.6–7.3 (m, 23H, phenyls), ^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$) −109.79.

6a8. 0.690 g, 1.4 mmol, 70%; m.p. 135°C. EIMS: Found, 498.1803. Calc. for [$C_{35}H_{24}F_2O^{\bullet+}$] ([$M^{\bullet+}$]), 498.1795. ^{1}H-NMR (300 MHz,$CDCl_3$) 3.42 (d, J_{F-H} = 10.3 Hz, OH), 6.6–7.3 (M, 23H). ^{19}F-NMR (282 MHz, $CDCl_3$) − 107.87 (d, $^4J_{F-F}$ = 5.5 Hz), − 115.59 (dd, $^4J_{F-F}$ = 5.5, $^1J_{F-H}$ = 10.3 Hz, F···HO). ^{13}C-NMR (75 MHz, $CDCl_3$) 89.4 (s, *C*–OH), 112.5, 112.9 (ddd, $^1J_{C-H}$ = 158, $^2J_{C-F}$ = 84, $^4J_{C-F}$ 3.7 Hz, *m*-$C_6H_3F_2$), 117.2 (m, *m*-$C_6H_3F_2$), 127.2, 127.3 (dt, $^1J_{C-H}$ = 158, $^3J_{C-H}$ = 7 Hz, *p*-Ph), 127.9 (dm, $^1J_{C-H}$ = 160 Hz, Ph), 128.1 (dm, $^1J_{C-H}$ = 160 Hz, Ph), 128.8 (dt, $^1J_{C-H}$ = 163, $^3J_{C-F}$ = 11 Hz, *p*-$C_6H_3F_2$), 129.5 (dm, $^1J_{C-H}$ = 158 Hz, Ph), 129.9 (dm, $^1J_{C-H}$ = 158 Hz, Ph), 134.2 (m, *ipso*-Ph), 135.2 (m, *ipso*-Ph), 143.2 (s, C=C), 144.9 (s, C=C), 159.1 (ddm, $^1J_{C-F}$ = 251, $^3J_{C-F}$ = 7 Hz, C–F), 163.5 (ddm, $^1J_{C-F}$ = 248, $^3J_{C-F}$ = 7 Hz, C–F).

6b2. 0.948 g, 1.6 mmol, 80%; m.p. 160°C. Anal. Found: C, 89.36; H, 7.62; Calc. for $C_{44}H_{44}O$: C, 89.75; H, 7.53%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.04 (s, 12H, CH_3), 2.11 (s, 12H, CH_3), 2.32 (s, 3H, CH_3), 2.43 (s, 1H, OH), 6.62 (s, 4H, *o*-$C_6H_3Me_2$), 6.66 (s, 4H, *o*-$C_6H_3Me_2$), 6.69 (s, 2H, *p*-$C_6H_3Me_2$), 6.76 (s, 2H, *p*-$C_6H_3Me_2$), 6.69 (d, 1H, $^3J_{H-H}$ = 7,5 Hz, *o*-C_6H_4Me), 7.17 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, *o*-C_6H_4Me), 7.36 (d, 1H, $^3J_{H-H}$ = 8.0 Hz, *o*-C_6H_4Me), 7.42 (s, 1H, *o*-C_6H_4Me). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.3 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C_6H_3*Me*$_2$), 21.4 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C_6H_3*Me*$_2$), 21.9 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C(OH)(C_6H_3*Me*), 90.1 (s, *C*(OH), 122.4 (dt, $^1J_{C-H}$ = 160, $^3J_{C-H}$ = 7 Hz, *o*-C_6H_4Me), 126.2 (dq, $^1J_{C-H}$ = 160, $^3J_{C-H}$ = 7 Hz, *o*-$C_6H_3Me_2$), 127.4 (dq, $^1J_{C-H}$ = 158, $^3J_{C-H}$ = 6 Hz, *o*-$C_6H_3Me_2$), 127.5 (dm, $^1J_{C-H}$ = 160 Hz, *p*-C_6H_4Me), 127.8 (dq, $^1J_{C-H}$ = 163, $^3J_{C-H}$ = 6 Hz, *o*′-C_6H_4Me), 128.2 (d, $^1J_{C-H}$ = 160 Hz, *m*-C_6H_4Me), 128.4 (dm, $^1J_{C-H}$ = 154 Hz, *p*-$C_6H_3Me_2$), 128.5 (dm, $^1J_{C-H}$ = 154 Hz, *p*-$C_6H_3Me_2$), 134.0 (s, *m*-$C_6H_3Me_2$), 135.5 (s, *ipso*-$C_6H_3Me_2$), 136.6 (q, $^2J_{C-H}$ = 5 Hz, *m*-$C_6H_3Me_2$), 136.8 (q, $^2J_{C-H}$ = 5 Hz, *m*-$C_6H_3Me_2$), 137.6 (q, $^2J_{C-H}$ = 6, $^3J_{C-H}$ = 6 Hz, *m*-C_6H_4Me), 140.8 (d, $^3J_{C-H}$ = 8 Hz, *ipso*-C_6H_4Me), 142.9 (t, $^3J_{C-H}$ = 4 Hz, C=C), 147.3 (s, C=C).

6b3. 0.760 g, 1.26 mmol, 63%;. m.p. 190°C. Anal. Found: C, 89.29; H, 7.80. Calc. for $C_{45}H_{46}O$: C, 89.66, H, 7.69%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.05 (s, 12H, C_6H_3*Me*$_2$), 2.12 (s, 12H, C_6H_3*Me*$_2$), 2.28 (s, 6H, C_6H_3*Me*$_2$), 2.41 (s, 1H, OH), 6.63 (d, $^4J_{H-H}$ = 6 Hz, 4H, $C_6H_3Me_2$), 6.68 (s, 4H, $C_6H_3Me_2$), 6.76 (s, 2H, $C_6H_3Me_2$), 6.82 (s, 1H, $C_6H_3Me_2$), 7.19 (s, 2H, $C_6H_3Me_2$). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.3 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 4 Hz, C_6H_3*Me*$_2$), 21.4 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 4 Hz, C_6H_3*Me*$_2$), 21.7 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 4 Hz, C(OH)C_6H_3*Me*$_2$), 90.1 (s, *C*(OH)$C_6H_3Me_2$), 123.2 (dq, $^1J_{C-H}$ = 157, $^3J_{C-H}$ = 5 Hz, C(OH)*o*-$C_6H_3Me_2$), 127.4 (dq, $^1J_{C-H}$ = 158, $^3J_{C-H}$ = 5 Hz, C=C*o*-$C_6H_3Me_2$), 127.8 (dq, $^1J_{C-H}$ = 157, $^3J_{C-H}$ = 5 Hz, C=C*o*-$C_6H_3Me_2$), 128.3 (dm, $^1J_{C-H}$ = 149, $^3J_{C-H}$ = 5 Hz, *p*-$C_6H_3Me_2$), 128.4 (dm, $^1J_{C-H}$ = 149, $^3J_{C-H}$ = 5 Hz, *p*-C(OH)$C_6H_3Me_2$), 128.5 (dm, $^1J_{C-H}$ = 149, $^3J_{C-H}$ = 5 Hz, *p*-$C_6H_3Me_2$), 134.0 (s, *ipso*-$C_6H_3Me_2$), 135.6 (s, *ipso*-$C_6H_3Me_2$), 136.6 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 136.8 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 137.4 (q, $^2J_{C-H}$ = 6 Hz, *m*-C(OH)$C_6H_3Me_2$), 140.5 (s, *ipso*-C(OH)$C_6H_3Me_2$), 142.8 (t, $^3J_{C-H}$ = 3.5 Hz, C=C), 147.2 (t, $^3J_{C-H}$ = 3.5 Hz, C=*C*).

6b4. 0.750 g, 1.24 mmol, 62%; m.p. 220°C. FABHRMS: Found, 602.3549. Calc. for [$C_{45}H_{46}O^{\bullet+}$] ([$M^{\bullet+}$]): 602.3549. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.00 (s, 12H, Me), 2.09 (s, 12H, Me), 2.29 (s, 3H, Me), 2.39 (s, 4H, Me, OH), 6.55 (s, 4H, *o*-$C_6H_3Me_2$), 6.59 (s, 4H, *o*-$C_6H_3Me_2$), 6.65 (s, 2H, *p*-$C_6H_3Me_2$), 6.76 (s, 2H, *p*-$C_6H_3Me_2$), 6.90 (m, 2H, *m*-,*p*-$C_6H_3Me_2$), 7.19 (s, 1H, *o*-$C_6H_3Me_2$). ^{13}C-NMR (75 MHz, $CDCl_3$) 19.3 (qd, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C_6H_3*Me*$_2$), 21.2 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C_6H_3*Me*$_2$), 21.3 (qt, $^1J_{C-H}$ = 126, $^3J_{C-H}$ = 5 Hz, C_6H_3*Me*$_2$), 89.6 (s, *C*–OH), 127.4 (dm, $^1J_{C-H}$ = 162 Hz, *o*-$C_6H_3Me_2$), 127.6 (dm, $^1J_{C-H}$ = 162 Hz, *o*-$C_6H_3Me_2$, *m*-$C_6H_3Me_2$), 128.4 (dm, $^1J_{C-H}$ = 162 Hz, *p*-$C_6H_3Me_2$), 128.5 (dm, $^1J_{C-H}$ = 162 Hz, *p*-$C_6H_3Me_2$), 128.7 (dm, $^1J_{C-H}$ = 162 Hz, *p*-$C_6H_3Me_2$), 131.3 (dq, $^1J_{C-H}$ = 156, $^3J_{C-H}$ = 5 Hz, *o*-$C_6H_3Me_2$), 131.4 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 134.0 (s, *ipso*-$C_6H_3Me_2$), 134.9 (m, J_{C-H} = 6 Hz, *o*-$C_6H_3Me_2$), 135.6 (s, *ipso*-$C_6H_3Me_2$), 136.5 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 136.8 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 138.5 (m, *ipso*-$C_6H_3Me_2$), 143.8 (t, $^3J_{C-H}$ = 3 Hz, C=C), 144.6 (s, C=C).

6b5. 0.650 g, 1.05 mmol, 52%; m.p. 254°C. Anal. Found: C, 89.20; H, 7.92. Calc. for $C_{46}H_{48}O$: C, 89.56; H, 7.84%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.02 (s, 12H, C_6H_3*Me*$_2$), 2.08 (s, 12H, C_6H_3*Me*$_2$), 2.19 (s, 3H, *p*-$C_6H_2Me_3$), 2.22 (s, 1H, OH), 2.00 (s, 3H, *o*-$C_6H_2Me_3$), 2.49 (s, 3H, *o*′-$C_6H_2Me_3$), 6.55 (s, 4H, *o*-$C_6H_3Me_2$), 6.63 (s, 4H, *o*-$C_6H_3Me_2$), 6.67 (s, 3H, *p*-$C_6H_3Me_2$, *m*-$C_6H_2Me_3$), 6.74 (s, 3H, *p*-$C_6H_3Me_2$, *m*-$C_6H_2Me_3$). ^{13}C-NMR (75 MHz, $CDCl_3$) 20.5 (qt, $^1J_{C-H}$ = 126 Hz, *p*-C_6H_2*Me*$_3$), 21, 15 (qd, $^1J_{C-H}$ = 126 Hz, *o*-C_6H_2*Me*$_3$), 21.2 (qt, $^1J_{C-H}$ = 126 Hz, *o*-C_6H_3*Me*$_2$), 21.3 (qt, $^1J_{C-H}$ = 126 Hz, C_6H_3*Me*$_2$), 25.6 (qd, $^1J_{C-H}$ = 128 Hz, *o*′-C_6H_2*Me*$_3$), 93.4 (s, C(OH)), 127.3 (dq, $^1J_{C-H}$ = 155, $^2J_{C-H}$ = 6 Hz, *o*-$C_6H_3Me_2$), 127.4 (dq, $^1J_{C-H}$ = 155, $^2J_{C-H}$ = 6 Hz, *o*-$C_6H_3Me_2$), 128.3 (dm, $^1J_{C-H}$ = 155 Hz, *p*-$C_6H_3Me_2$), 128.4 (dm, $^1J_{C-H}$ = 155 Hz, *p*-$C_6H_3Me_2$), 131.0 (dm, $^1J_{C-H}$ = 155 Hz, *m*-$C_6H_2Me_3$), 132.5 (dm, $^1J_{C-H}$ = 155 Hz, *m*′-$C_6H_2Me_3$), 133.9 (m, *ipso*-$C_6H_2Me_3$), 134.3 (s, *ipso*-$C_6H_3Me_2$), 135.2 (q, $^2J_{C-H}$ = 6 Hz, *o*′-$C_6H_2Me_3$), 135.4 (q, $^2J_{C-H}$ = 6 Hz, *p*-$C_6H_2Me_3$), 135.5 (s, *ipso*-$C_6H_3Me_2$), 136.5 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 136.8 (q, $^2J_{C-H}$ = 6 Hz, *m*-$C_6H_3Me_2$), 139.2 (q, $^2J_{C-H}$ = 6 Hz, *o*-$C_6H_2Me_3$), 142.5 (t, $^3J_{C-H}$ 3.5 Hz, C=C), 146.5 (t, $^3J_{C-H}$ 3.5 Hz, C=C).

6b6. 0.710 g, 1.2 mmol, 60%; m.p. 200°C. EIMS: Found, 592.3162. Calc. for [$C_{43}H_{41}OF^{\bullet+}$] ([$M^{\bullet+}$])

592.3141. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.04 (s, 12H, $C_6H_3Me_2$), 2.10 (s, 12H, $C_6H_3Me_2$), 2.45 (s, 1H, OH), 6.59 (s, 4H, *o*-$C_6H_3Me_2$), 6.64 (s, 4H, *o*-$C_6H_3Me_2$), 6.69 (s, 2H, *p*-$C_6H_3Me_2$), 6.76 (s, 2H, *p*-$C_6H_3Me_2$), 6.92 (m, 1H, C_6H_4F), 7.30–7.50 (m, 3H, C_6H_4F). ^{19}F-NMR (282 MHz, $CDCl_3$) 113.86 (M), ^{13}C-NMR (75 MHz, $CDCl_3$), 21.3 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, $C_6H_3Me_2$), 21.4 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, $C_6H_3Me_2$), 89.9 (s, *C*(OH)(C_6H_4F)), 112.8 (ddt, $^1J_{C-H} = 162$, $^2J_{C-F} = 23$, $^3J_{C-H} = 5$ Hz, *p*-C_6H_4F), 113.7 (ddt, $^1J_{C-H} = 161$, $^2J_{C-F} = 21$, $^3J_{C-H} = 4$ Hz, *o*-C_6H_4F), 121.1 (dt, $^1J_{C-H} = 160$, $^3J_{C-H} = 7$ Hz, *o*-C_6H_4F), 127.5 (dq, $^1J_{C-H} = 157$, $^3J_{C-H} = 6$ Hz, *o*-$C_6H_3Me_2$), 128.0 (dq, $^1J_{C-H} = 157$, $^3J_{C-H} = 6$ Hz, *o*-$C_6H_3Me_2$), 128.8 (dm, $^1J_{C-H} = 154$, $^3J_{C-H} = 5$ Hz, *p*-$C_6H_3Me_2$), 128.9 (dm, $^1J_{C-H} = 154$, $^3J_{C-H} = 5$ Hz, *p*-$C_6H_3Me_2$), 129.5 (dd, $^1J_{C-H} = 160$, $^3J_{C-F} = 9$ Hz, *m*-C_6H_4F), 133.9 (s, *ipso*-$C_6H_3Me_2$), 135.4 (s, *ipso*-$C_6H_3Me_2$), 136.9 (q, $^4J_{C-H} = 6$, *ipso*-$C_6H_3Me_2$), 137.0 (q, $^4J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 143.3 (t, $^3J_{C-H} = 4$ Hz, C=C), 144.5 (dd, $3J_{C-H} = 7$, $^3J_{C-F} = 7$ Hz, *ipso*-C_6H_4F), 147.2 (t, $^3J_{C-H} = 4$ Hz, C=C), 163.4 (dm,.$^1J_{C-F} = 244$, $^3J_{C-H} = 5$ Hz, *m*-C_6H_4F).

6b7. 0.240 g, 0.8 mmol, 40%; m.p. 185°C. FABHRMS: Found, 610.3038. Calc. for [$C_{43}H_{40}OF_2^{\bullet+}$] ([$M^{\bullet+}$]) 610.3047. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.06 (s, 12H, $C_6H_3Me_2$), 2.10 (s, 12H, Me), 2.46 (s, 1H, OH), 6.57 (m, 4H, *o*-$C_6H_3Me_2$), 6.59 (dt, 1H, $^3J_{F-H} = 9$, $^4J_{H-H} = 2.4$ Hz, *p*-$C_6H_3F_2$), 6.64 (m, 4H, *o*-$C_6H_3Me_2$), 6.71 (m, 2H, *p*-$C_6H_3Me_2$), 6.77 (m, 2H, *p*-$C_6H_3Me_2$), 7.11 (dt, 2H, $^3J_{F-H} = 9$, $^4J_{H-H}$ 2.4 Hz, *o*-$C_6H_3F_2$). ^{19}F-NMR (282 MHz, $CDCl_3$) −110.47 (t, $^3J_{F-H}$ 8.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.2 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, $C_6H_3Me_2$), 21.4 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 5$ Hz, $C_6H_3Me_2$), 89.6 (s, *C*(OH)($C_6H_3F_2$)), 102.2 (dtt, $^1J_{C-H} = 166$, $^2J_{C-F} = 26$, $^3J_{C-H} = 4$ Hz, *p*-$C_6H_3F_2$), 108.5 (dtd, $^1J_{C-H} = 165$, $^3J_{C-H} = 6$, $^2J_{C-F} = 25$ Hz, *o*-$C_6H_3F_2$), 127.3 (dq, $^1J_{C-H} = 158$, $^3J_{C-H} = 6$ Hz, *o*-$C_6H_3Me_2$), 127.8 (dq, $^1J_{C-H} = 163$, $^3J_{C-H} = 6$ Hz, *o*-$C_6H_3Me_2$), 128.7 (dm, $^1J_{C-H} = 155$, $^3J_{C-H} = 5$ Hz, *p*-$C_6H_3Me_2$), 128.9 (dm, $^1J_{C-H} = 155$, $^3J_{C-H} = 5$ Hz, *p*-$C_6H_3Me_2$), 133.4 (s, *ipso*-$C_6H_3Me_2$), 135.0 (s, *ipso*-$C_6H_3Me_2$), 137.0 (q, $^2J_{C-H} = 5$ Hz, *m*-$C_6H_3Me_2$-all), 143.6 (t, $^3J_{C-H} = 4$ Hz, *C*=C), 146.5.(s, C=*C*), 146.3 (d, $^3J_{C-F} = 8$ Hz, *ipso*-$C_6H_3F_2$), 163.3 (dtd,.$^1J_{C-F} = 247$, $^2J_{C-H} = 5$, $^3J_{C-F} = 12$ Hz, *m*-$C_6H_3F_2$).

6b8. (0.950 g, 1.55 mmol, 77%). m.p. 205°C. Anal. Found: C, 84.33; H, 6.72. Calc. for $C_{43}H_{40}OF_2$: C, 84.56; H, 6.60. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.06 (s, 12H, Me), 2.09 (s, 12H, Me), 3.24 (d, $J_{H-F} = 8.5$ Hz, 1H, OH), 6.60 (s, 4H, *o*-$C_6H_3Me_2$), 6.71 (s, 2H, *p*-$C_6H_3Me_2$), 6.73 (s, 2H, *p*-$C_6H_3Me_2$), 6.76 (s, 4H, *o*-$C_6H_3Me_2$), 6.78 (m, 2H, *m*-$C_6H_3F_2$), 7.11 (m, 1H, *p*-$C_6H_3F_2$). {^{1}H}^{19}F-NMR (282 MHz, $CDCl_3$) −107.92 (d, $^4J_{F-F} = 5.8$ Hz, 1F), −115.61 (d, $^4J_{F-F} = 5.8$ Hz, 1F). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.2 (qm, $^1J_{C-H} = 126$ Hz, Me), 21.3 (qm, $^1J_{C-H} = 126$ Hz, Me), 89.2 (s, C–OH), 112.2, 112.6 (2 dddm, $^1J_{C-H} = 160$, $^2J_{C-F} = 62$, $^4J_{C-F}$ 3.7 Hz, *m*-$C_6H_3F_2$), 117.9 (m, *ipso*-$C_6H_3F_2$), 127.1, 127.6 (2 dm, $^1J_{C-H} = 160$ Hz, *o*-$C_6H_3Me_2$), 128.2 (dm, $^1J_{C-H} = 160$ Hz, *p*-$C_6H_3F_2$), 128.4, 128.7 (2 dm, $^1J_{C-H} = 160$ Hz, *p*-$C_6H_3Me_2$), 134.1, 135.4 (2 s, *ipso*-$C_6H_3Me_2$), 136.7, 136.9 (2 q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 143.4, 144.0 (2s, C=C), 159.2, 163.6 (2dd = 251, $^3J_{C-F}$ 7.3 Hz, C–F).

4.3. Procedures for substituted-bromopentaarylcyclopentadienes (7)

Method A: The alcohol **6a3** (1.7 g, 3.47 mmol) was dissolved in toluene (20 ml) at 70°C in the presence of an excess of gaseous HBr. After stirring the solution for 10 h, the solvent was removed under vacuum. Purification of the solid residue was achieved by chromatography on neutral alumina with CH_2Cl_2–hexane (1:3) as eluent. Slow removal of the solvent resulted in crystallization of **7a3**, which was isolated as an orange powder in 68% yield (1.4 g, 2.5 mmol). Anal. Found: C, 80.42, H 5.36. Calc. for $C_{37}H_{29}Br$: C, 80.28; H, 5.28%. ^{13}C-NMR (75 MHz, CD_3COCD_3) 77.8, 77.9 (4/1; C–Br).

Method B: In a Schlenk tube, 2 mmol of the pentaarylcyclopentadienols **6a5** (1.008 g), **6a7** (0.998 g), **6a8** (0.998 g), **6b2** (1.178 g), **6b3** (1.205 g), **6b4** (1.205 g), **6b5** (1.235 g), **6b6** (1.185 g), **6b7** (1.220 g), and **6b8** (1.222 g) were dissolved in diethyl ether (50 ml) or in a mixture of diethyl ether–THF (2:1, 50 ml), and the solution was cooled to −10°C. Then pyridine (2.20 mmol, 180 μl) and thionyl bromide (2.20 mmol, 171 μl) were added successively. After the temperature rose to 20°C, the mixture was hydrolyzed with aqueous HCl (1.0 N, 50 ml). After extraction of the organics with diethyl ether, the ethereal solution was washed with water to neutrality and dried over magnesium sulfate. Removal of the solvent yielded the bromo derivatives as orange powders, which were purified by recrystallization from CH_2Cl_2–hexane (1:4) or chromatographed on silica (hexane–diethyl ether 9:1).

7a5. 0.75 g, 44% from cyclopentadienone **5a**; m.p. 85°C. EIMS: Found, 566.1592. Calc. for [$C_{38}H_{31}^{79}Br^{\bullet+}$] [$M^{\bullet+}$], 566.1609. ^{1}H-NMR (300 MHz, CD_3COCD_3) 2.16 (s, 3H, Me), 2.20 (s, 3H, Me), 2.21 (s, 3H, Me), 6.60–7;70 (m, 22H, Ph and Mes). ^{13}C-NMR (75 MHz, CD_3COCD_3) 20.2 (qd, $^1J_{C-H} = 125$, $^3J_{C-H} = 6$ Hz, *o*-Me), 21.2 (qm, $^1J_{C-H} = 125$ Hz, *o*′, *p*-Me), 77.2 (t, $^3J_{C-H} = 4$ Hz, *C*–Br), 128.1, 128.3, 128.4 (3 d, $^1J_{C-H} = 160$ Hz, *m*,*p*-Ph), 128.9, 129.1 (2 dm, $^1J_{C-H} = 161$ Hz, *m*-Mes), 129.3, 129.4, 130.2, 131.6 (4 d, $^1J_{C-H} = 160$ Hz, *o*-Ph), 132.7 (s, *ipso*-Mes), 134.7, 135.0, 135.5 (3 dd, $^1J_{C-H} = 160$, $^3J_{C-H} = 6$ Hz, *ipso*-Ph), 136.6 (q, $^3J_{C-H} = 6$ Hz, *C*–Me), 137.1 (d, $^3J_{C-H} = 6$ Hz, *ipso*-Ph), 137.2, 138.0 (2 q, $^3J_{C-H} = 6$ Hz, *C*–Me), 142.6 (s, *C*–Mes), 143.1, 147.8, 150.0 (3 d, $^3J_{C-H} = 3$ Hz, *C*–Ph).

7a7. 0.360 g,.65 mmol, 32% from **5a**. Anal. Found: C, 74.59; H, 4.14. Calc. for $C_{35}H_{23}BrF_2$: C, 74.87; H, 4.13%. ^{19}F-NMR (282 MHz, $CDCl_3$) −110.67, −111.20 (2:3).

7a8. 1.00 g, 1.8 mmol, 90%; m.p. 180°C. EIMS: Found, 560.0941. Calc. for $[C_{35}H_{23}^{79}BrF_2^{\bullet+}]$ ($[M^{\bullet+}]$) 560.0952. ^{19}F-NMR (282 MHz, CD_3COCD_3). −110.49 (d, 1F, $^4J_{F-F} = 5$ Hz), −110.98 (d, 1F, $^4J_{F-F} = 5$ Hz). $\{^1H\}^{13}$C-NMR (75 MHz, CD_3COCD_3) 76.5(s, CBr), 112.1, 112.2 (2dd, $^2J_{C-F} = 22$, $^4J_{C-F} = 4$ Hz, *m*-$C_6H_3F_2$), 113.5 (t, $^2J_{C-F} = 22$ Hz, *ipso*-$C_6H_3F_2$), 128.2 (Ph), 128;3 (Ph), 128.4 (Ph), 128.5 (Ph), 128.8 (s, C=*C*($C_6H_3F_2$)), 128.9 (Ph), 129.2 (Ph), 129.6 (Ph), 129.7 (Ph), 129.9 (Ph), 131.0 (Ph), 131.6 (t, $^3J_{C-F} = 10$ Hz, *p*-$C_6H_3F_2$), 134.5, 134.7, 135.4, 135.9 (4 s, *ipso*-Ph), 142.5, 149.1, 153.6 (3 s, C=*C*(Ph)), 161.0, 161.4 (2 dd, $^1J_{C-F} = 247$, $^3J_{C-F} = 7$ Hz, *o*-$C_6H_3F_2$).

7b2. 1.18 g, 1.90 mmol, 95%. Anal. Found: C, 80.65; H, 6.85. Calc. for $C_{44}H_{43}Br$: C, 81.09; H 6.65%. ^{13}C-NMR (75 MHz, CD_3COCD_3) 78.1 (br s, C–Br).

7b3. 1.23 g, 1.9 mmol, 95%. Anal. Found: C, 81.20; H, 6.73. Calc. for $C_{45}H_{45}Br$: C, 81.19; H 6.81%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.04 (s, 12H, $C_6H_3Me_2$), 2.08 (s, 12H, $C_6H_3Me_2$), 2.25 (s, 6H, C(Br)($C_6H_3Me_2$), 6.55 (s, 4H, *o*-$C_6H_3Me_2$), 6.59 (s, 4H, *o*-$C_6H_3Me_2$), 6.69 (s, 2H, *p*-$C_6H_3Me_2$), 6.73 (s, 2H, *p*-$C_6H_3Me_2$), 6.85 (s, 1H, *p*-C(Br)$C_6H_3Me_2$), 7.18 (s, 2H, *o*-C(Br)$C_6H_3Me_2$). ^{13}C-NMR (75 MHz, CD_3COCD_3) 21.2 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 6$ Hz, $C_6H_3Me_2$), 21.3 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 6$ Hz, $C_6H_3Me_2$), 21.5 (qt, $^1J_{C-H} = 126$, $^3J_{C-H} = 6$ Hz, C(Br)$C_6H_3Me_2$)), 77.3 (s, *C*(Br)), 125.6 (dq, $^1J_{C-H} = 159$, $^3J_{C-H} = 5$ Hz, *o*-C(Br)$C_6H_3Me_2$), 127.9 (dq, $^1J_{C-H} = 158$, $^3J_{C-H} = 5$ Hz, *o*-$C_6H_3Me_2$), 128.4 (dm + dq, $^1J_{C-H} = 158$ Hz, *o*-, *p*-$C_6H_3Me_2$), 128.5 (dm, $^1J_{C-H} = 158$ Hz, *p*-$C_6H_3Me_2$), 129.2 (dm, $^1J_{C-H} = 158$ Hz, *p*-C(Br)$C_6H_3Me_2$), 134.1 (s, *ipso*-$C_6H_3Me_2$), 135.1 (s, *ipso*-$C_6H_3Me_2$), 136.0 (s, *ipso*-C(Br)$C_6H_3Me_2$), 136.1 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 136.5 (q, $^2J_{C-H} = 6$ Hz, *m*-$C_6H_3Me_2$), 137.4 (q, $^2J_{C-H} = 6$ Hz, *m*-C(Br)$C_6H_3Me_2$), 141.8 (t, $^3J_{C-H} = 6$ Hz, *C*=C), 147.4 (t, $^3J_{C-H} = 6$ Hz, C=*C*).

7b4. 0.800 g, 1.2 mmol, 60%. Anal. Found: C, 80.88; H, 6.90. Calc. for $C_{45}H_{45}Br$: C, 81.19; H, 6.81%.^{13}C-NMR (75 MHz, CD_3COCD_3) 77.7 (*C*–Br).

7b5. 1.23 g, 1.8 mmol, 90%; m.p. 210°C. Anal. Found: C, 81.46; H, 7.02. Calc. for $C_{46}H_{47}Br$: C, 81.28; H, 6.97%. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.03 (s, 12H, 4 Me), 2.06 (s, 6H, 2Me), 2.15 (s, 6H, 2Me), 2.24 (s, 3H, 1Me), 2.26 (s, 6H, 2Me), 6.50–7.10 (m, 14H, Ph). ^{13}C-NMR (75 MHz, $CDCl_3$). 20.0, 20.8 (2 qd, $^1J_{C-H} = 126$, $^3J_{C-H}$ 4.9 Hz, *o*-mes), 21.1, 21.2, 21.3, 21.45, 21.5 (5 qt, $^1J_{C-H} = 126$, $^3J_{C-H}$ 4.9 Hz, other Me), 76.7 (t, $^3J_{C-H} = 5$ Hz, C–Br; 125.6, 128.0, 128.2, 128.4, 128.5, 129.2 (6dm, $^1J_{C-H} = 160$ Hz, *p*-$C_6H_3Me_2$ and *m*-$C_6H_2Me_3$), 126.7, 127.3, 128.6, 128.7 (4dq, $^1J_{C-H} = 160$, $^3J_{C-H} = 6$ Hz, *o*-$C_6H_3Me_2$), 132.7 (m, *ipso*-$C_6H_2Me_3$), 133.8, 134.2, 134.6, 136.6 (4s, *ipso*-$C_6H_3Me_2$), 135.6, 136.1, 136.28, 136.32, 136.4, 136.65, 137;5 (7q, $^3J_{C-H} = 6$ Hz, *C*–Me), 141.4, = 146, 148.6 (3t, $^3J_{C-H} = 4$ Hz, *C*–$C_6H_3Me_2$), 141.6 (s, *C*–$C_6H_2Me_3$).

7b6. 1.19 g, 1.8 mmol, 90%. Anal. Found: C, 78.67; H, 6.41. Calc. for $C_{43}H_{40}BrF$: C, 78.77; H, 6.15%. ^{13}C-NMR (75 MHz, CD_3COCD_3) 77.0, 77.6, 77.8 (s, *C*–Br, 1:2:2).

7b7. 0.470 g,.7 mmol, 40% from **5b**. ^{19}F-NMR (282 MHz, $CDCl_3$) −111.44, −111.79 (s, 2:3 ratio) ^{13}C-NMR (75 MHz, CD_3COCD_3) 77.2, 77.6 (s, *C*–Br, 2:3). FABHRMS: Found 672.2197. Calc. for $[C_{43}H_{39}F_2^{79}Br]^{\bullet+}$ ($[M^{\bullet+}]$) 672.2203.

7b8. 1.21 g, 1.8 mmol, 90% from **6b8**. m.p. 120°C. Anal. Found: C, 76.75; H, 5.78. Calc. for $C_{43}H_{49}BrF_2$: C, 76.66; H, 5.84%. FABHRMS: Found, 672.2206. Calc. for $[C_{43}H_{39}^{79}BrF_2^{\bullet+}]$ ($[M^{\bullet+}]$), 672.2203 . ^{19}F-NMR (282 MHz, CD_3COCD_3) −110.50 (1F, $^4J_{F-F}$ 5.5 Hz), −111.21 (1F, $^4J_{F-F}$ 5.5 Hz). ^{13}C-NMR (75 MHz, CD_3COCD_3) 21.2 (qm, $^1J_{C-H} = 127$ Hz, Me), 21.3 (qm, $^1J_{C-H} = 127$ Hz, Me), 21.5 (qm, $^1J_{C-H} = 127$ Hz, Me), 76.9 (t, $^3J_{C-H} = 5$ Hz, C–Br), 111.9, 112.0 (2ddd, $^1J_{C-H} = 160$, $^2J_{C-F} = 22$, $^4J_{C-F} = 3$ Hz, *m*-$C_6H_3F_2$), 114.2 (tt, $^2J_{C-F} = 21$, $^4J_{C-F} = 5$ Hz, *ipso*-$C_6H_3F_2$), 126.2, 127.4, 127.8 (3dq, $^1J_{C-H} = 159$, $^3J_{C-H} = 5$ Hz, *o*-$C_6H_3Me_2$), 128.7 (s, C=*C*($C_6H_3F_2$)), 129.0 (dq, $^1J_{C-H} = 159$, $^3J_{C-H} = 5$ Hz, *o*-$C_6H_3Me_2$), 129.0 (4dq, $^1J_{C-H} = 159$, $^3J_{C-H} = 5$ Hz, *o*-$C_6H_3Me_2$), 129.2, 129.8, 130.1, 130.3 (4dm, $^1J_{C-H} = 159$ Hz, *p*-$C_6H_3Me_2$), 131.3 (dt, $^1J_{C-H} = 166$, $^3J_{C-F} = 10$ Hz, *p*-$C_6H_3F_2$), 134.5, 134.6, 135.5, 136.0 (4s, *ipso*-$C_6H_3Me_2$), 137.1, 137.4, 137;9, 138.7 (4q, $^2J_{C-H} = 5$ Hz, *m*-$C_6H_3Me_2$), 141.9, 148.7, 153.2 (3t, $^3J_{C-H} = 4$ Hz, C=*C*($C_6H_3Me_2$)), 161.1, 161.6 (2ddm, $^1J_{C-F} = 247$, $^3J_{C-F} = 7$ Hz, *o*-$C_6H_3F_2$).

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