Synthesis of Hindered and Functionalized 1-CF_3 Substituted Olefins via a Carbolithiation−Elimination−Metalation Cascade

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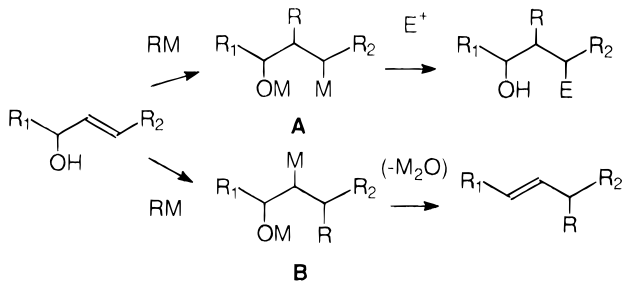
Addition of organolithium reagents to trifluoromethyl enol ethers **1a**−**d** and thio enol ethers **2a** provided stereoselectively the corresponding trisubstituted fluoroalkenes **3a**−**d** in 70−90% yields. The products could themselves react with organolithium reagents and undergo a vinyl metalation providing, after trapping with an electrophile, tetrasubstituted olefins in excellent yields and with stereoselectivity. This method can be applied to other fluoroalkyl enol ethers (Rf = C_2F_5). The product, tetrasubstituted olefin, can be obtained directly from enol ether with 2 equiv of reagent through a carbolithiation−elimination−metalation cascade.

The addition of organometallic reagents to alkenes is of considerable interest, in particular for the construction of stereogenic centers.[1] Alkenes are activated toward carbometalation by the presence of a π-acceptor substituent on the double bond and/or a heteroatom in the allylic position.[2]

In the case of allylic alcohols, since earlier reported papers,[3] great effort has been focused on the achievement of stereocontrol in the reaction and, more recently, on enantioselective carbometalation.[4,5] In most cases, the addition of the organic moiety of the organometallic reagent occurs at the olefinic carbon closest to the alcohol to give the dimetallic species **A**, which can be subsequently trapped with an electrophile. However, depending on the substitution pattern of the olefin, and on the structure of the organometallic agents, the addition can take place to the Cβ carbon, leading to the dimetallic species **B**, which readily undergoes an elimination process (Scheme 1).[6]

Scheme 1



Terminal CF_3-substituted olefins[7] and thioenol ethers[7a] have been shown to react with organolithium reagents through this latter addition−elimination process providing *gem*-difluoroalkenes (Scheme 2). In this reaction, one fluorine atom of the CF_3-group acts as an allylic leaving group as in the S_N2' reaction of allylic alcohols, and a cyclic mechanism involving concerted C−C bond forming and C−F bond breaking has been proposed.

Scheme 2

R_1 = PhS, H, Ph

We reported in a preliminary communication that nonterminal CF_3-substituted enol and thioenol ethers, conjugated with unsaturation in the β-position, also undergo addition of organolithium reagents but with the opposite regioselectivity to that of CF_3-substituted terminal olefins.[8] In this paper, we detail our work on the reactivity of organolithium reagents with different types of nonterminal CF_3-substituted vinylic compounds.

Results and Discussion

Enol and Thioenol Ethers 1 and 2. The treatment of enol ethers *(Z)*-**1a**−**c** and the thioenol ether *(Z)*-**2a**,[9] with 1.1 equiv of *tert*-butyllithium reagent at −78 °C in diethyl ether or tetrahydrofuran and warming up to 0 °C, resulted in the stereoselective formation of trifluoromethyl alkenes (*E*)-**3a-c**, and (*E*)-**3a**, respectively, in excellent yields (Scheme 3, Table 1). The *E* configuration of alkenes **3** was demonstrated by NOE experiments. For example, after complete assignment of protons by COSY,

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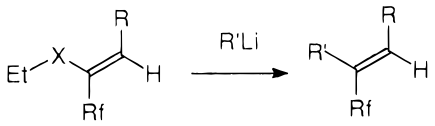
Scheme 3



Rf=CF_3,	Rf=CF_3
1a X=O, R=Ph	**3a** R'=*t*-Bu, **4a** R'=*n*-Bu, **5a** R'=Ph
1b X=O, R=CH=CHPh	**3b** R'=*t*-Bu
1c X=O, R=pMeOPh	**3c** R'=*t*-Bu
1d X=O, R=CH_2CH_2Ph	**3d** R'=*t*-Bu
2a X=S, R=Ph	**3a** R'=*t*-Bu
Rf=C_2F_5,	Rf=C_2F_5
6a X=O, R=Ph	**7a** R'=*t*-Bu

Table 1. Reaction of Vinyl Ethers with Organolithium Reagents

vinyl ether	R′Li[a]	product (% yield)
1a	*t*-BuLi	**3a** (92)
	n-BuLi	**4a** (96)
	PhLi	**5a** (92)
1b	*t*-BuLi	**3b** (80)
1c	*t*-BuLi	**3c** (70)
1d	*t*-BuLi	**3d** (0)[b]
2a	*t*-BuLi	**3a** (80)
6a	*t*-BuLi	**7a** (82)

[a] 1.1 equiv of R′Li from −78 to 0 °C. [b] Starting material recovered even with an excess of *t*-BuLi and in the presence of TMEDA.

heteronuclear multiple-quantum coherence (hmqc), and heteronuclear multiple bond coherence (hmbc) experiments, irradiation of the *tert*-butyl group resulted in a 8% enhancement of *ortho* aromatic protons. The reaction was also successful when the phenyl group was replaced by another conjugated substituent, such as a styryl group (**1b**), but failed in the case of an alkyl substituent (**1d**). This reaction can be applied to other fluoroalkyl compounds: under the same conditions, enol ether **6a** (Rf = C_2F_5) led to the olefin **7a** in a 82% yield. Other organolithium reagents such as *n*-butyllithium, and the less reactive phenyllithium, also provided the corresponding trisubstituted alkenes **4a** and **5a** from **1a**. However, thioenol ether **2a** was found to be unreactive toward phenyllithium. The stereochemistry of **4a** was assigned by analogy of NMR data with those of **3a** (δ^{19}F and $^3J_{CF}$).[10] The particular steric strain in **5a** did not allow such an analogy. This *E* configuration was unambiguously assigned by the observation of a hetero NOE $\{^{19}F\},^1H$ effect (9%) between CF_3 and the ethylenic proton, which are exceptionally close (2 Å), as shown by already described X-ray data.[11]

The reaction is formally a substitution of an ethoxy or ethylthio group by an alkyl group. Such pseudosubstitutions are unusual for an alkoxy group[12,13] but are well documented for the reactions of organolithium reagents with *gem*-difluoroalkenes[14] and perfluoroalkenes,[15] in which a fluorine atom is the leaving group. These reactions are in sharp contrast to vinylic substitutions

Figure 1.

of halides, which take place only with electron-deficient olefins, where a good leaving group is β to an electron-withdrawing substituent.[16] Since in reactions of ethylenic compounds with organolithium reagents, metalation of the double bond can compete with carbometalation, the formation of alkenes **3** could be envisaged through the formation of a vinyl anion followed by elimination of lithium ethoxide, leading to the corresponding alkynes, and a further stereoselective carbolithiation. Such a process which requires 2 equiv of organolithium reagent has been ruled out.

Formation of **3**−**5** and **7** can therefore be explained by the addition of the organolithium reagent to the double bond to form the intermediate **C,** followed by elimination of lithium ethoxide (Figure 1). Compared with terminal olefins, the displacement of the ethoxy group instead of the fluorine atom is determined by the regioselectivity of the initial addition of the reagent to the double bond, which seems to be directed by the stabilizing β-substituent. Assuming that this elimination is likely *anti*, the carbolithiation of enol and thioenol ethers is *cis*, leading to the *syn* intermediate **C**, which eliminates into the (*E*)-olefins **3**−**5** and **7**.

All our attempts to trap the postulated lithiated intermediate **C** by performing the reaction in the presence of trimethylsilyl chloride and by adding a chelating agent such as *N*,*N*,*N*′,*N*′-tetramethylethylene diamine (TMEDA) failed, indicating that the elimination of lithium ethoxide is instantaneous, even at −78 °C.

Olefins 3. We envisaged that CF_3-substituted olefins **3** could themselves undergo a further carbolithiation which, in the case of the same regioselectivity as for terminal CF_3-substituted olefins, would provide *gem*-difluoroalkenes or, in the case of the opposite regioselectivity as from enol ethers, would lead to a lithiated intermediate **D** (Figure 1). In the absence of leaving group, **D** could be trapped by an electrophile.

The olefin **3a** was first treated in THF with 1 equiv of *n*-butyllithium or *tert*-butyllithium, from −78 to 0 °C, and the solution was quenched with one equiv of propanal. A mixture of the allylic alcohol **8a** and starting material (10/90) was obtained, indicating that a vinylic metalation occurred from **3a** instead of the expected addition (Scheme 4). Neither difluoroalkene nor product resulting from the lithiated species **D** could be detected. This lack of reactivity indicates that the stabilization of the lithium species by a conjugated group is not the only condition for the carbolithiation to occur. The presence of a good leaving group β to the metalated carbon is also a driving force. The reaction was then performed in hexane at room temperature in the presence of 1 equiv of TMEDA and 1 equiv of *tert*-butyllithium, and the resulting orange-

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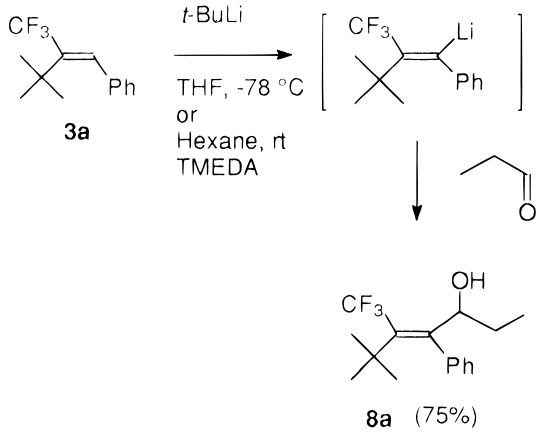
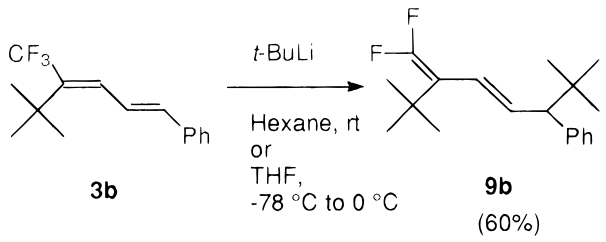
Scheme 4



Scheme 5



red solution was again quenched with one equiv of propanal. It is possible to perform this reaction in a one-pot process from **1a**. The allylic alcohol **8a** was thus obtained in a 75% yield in the first case and 53% in the second case. This last yield has not been optimized. Surprisingly, when performed with **3b**, this reaction in THF or in hexane using TMEDA did not result in a vinyl metalation but again in an addition, which, after the subsequent fluoride elimination, provided a *gem*-difluoroalkene (Scheme 5). ^{13}C NMR spectrum exhibits C−F coupling constants for all of the four ethylenic carbons, indicating that the double bonds are conjugated. The structure of **9b** was confirmed by C−H (hmbc) and H−F correlations. In particular, a correlation is observed between the aromatic protons and a saturated carbon. The organic moiety of the reagent was therefore introduced on the Cδ carbon. Thus the addition to the nonhindered α,β-disubstituted double bond of the styryl substituent of **3b** is more favored than metalation of the trisubstituted double bond.

Conclusion

We have demonstrated that the course of the reaction of nonterminal CF_3-substituted vinylic compounds with organolithium reagents is strongly dependent on the substitution pattern. From enol and thioenol ethers, providing a conjugated substituent is present in the β-position, a stereoselective carbolithiation occurs. An instantaneous stereoselective elimination of lithium ethoxide/thioethoxide provided *E*-trisubstituted fluoroolefins in high yields, with the introduction of the organic moiety of the reagent on the carbon initially bearing the ethoxy/thioethoxy group. This reaction offers an alternative route to the Wittig reaction between a trifluoromethyl ketone and an ylide which generally provides the opposite stereoisomer.[17] Furthermore, it allows a route to sterically hindered (fluoroalkyl)alkenes, the access to which through a Wittig reaction is limited by the preparation of hindered fluoroalkyl ketones.[18] From these trisubstituted fluoroolefins, a further treatment with organolithium reagent leads either to a vinyl anion, which can be trapped, or to a second addition, depending on the β-substituent.

Experimental Section

The compounds **1a**, **1c**, **1d**, and **6a** were described in ref 9.

Reaction of Organolithium Reagent with Enol and Thioenol Ether: General Procedure. To a solution of the enol ethers **1** and **6** or the thioenol ether **2** (1 mmol) in diethyl ether (10 mL) at −78 °C was added RLi (1 mol equiv). The solution was stirred for a further 15 min at −78 °C and then allowed to warm to 0 °C over 1 h. The resulting brown reaction mixture was then poured into a saturated ammonium chloride solution (10 mL) and extracted with diether ether (3 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to give a brown oil which was purified by chromatography on silica gel (eluent: pentane/Et_2O 95/5) to the pure compounds **3**−**5** and **7**.

1-((*E*)-3,3-Dimethyl-2-(trifluoromethyl)-1-butenyl)benzene (3a). Enol ether **1a** (0.216 g, 1 mmol) in Et_2O (10 mL), treated with *tert*-butyllithium (0.8 mL of a 1.5 M solution in hexanes), afforded, after work up and purification, **3a** (0.210 g, 92%): IR (neat) 1645 cm^{-1}; ^{19}F NMR δ −60.3; ^1H NMR δ 1.1 (s, 9 H), 7.15 (m, 2H, ortho), 7.3 (m, 4 H, C=CH and Ph); ^{13}C NMR δ 31.3, 35.0, 125.1 (q, $^1J_{CF}$ = 277 Hz), 127.0 (*para*); 127.5 (*ortho*), 127.9, 133.5 (q, $^3J_{CF}$ = 8.3 Hz), 137.3, 138.2 (q, $^2J_{CF}$ = 24.2 Hz). Anal. Calcd for $C_{13}H_{15}F_3$: C, 68.4; H, 6.6. Found: C, 68.2; H, 6.75.

The same reaction performed between thioenol ether **2a** (0.232 g, 1 mmol) in Et_2O (10 mL) and *tert*-butyllithium (0.8 mL of a 1.5 M solution in hexanes) afforded, after work up and purification, **3a** (0.183 g, 80%).

1-((*Z*)-2-(Ethylsulfanyl)-3,3,3-trifluoro-l-propenyl)benzene (2a): IR (neat) 1616 cm^{-1}; ^{19}F NMR δ −64.8; ^1H NMR δ 1.1 (t, ^3J = 7.4 Hz, 3H), 2.7 (q, ^3J = 7.4 Hz, 2H), 7.25−7.7 (1H vinyl and Ph); ^{13}C NMR δ 14.4, 28.5, 123.5 (q, $^1J_{CF}$ = 273.7 Hz), 123.6 (q, $^2J_{CF}$ = 31.3 Hz), 128.4, 129.6, 130.5, 139.4. Anal. Calcd for $C_{11}H_{11}SF_3$: C, 56.9; H, 4.7. Found: C, 56.6; H, 4.9.

1-((*E*)-2-(Trifluoromethyl)-1-hexenyl)benzene (4a). Enol ether **1a** (0.216 g, 1 mmol) in Et_2O (10 mL), treated with *n*-butyllithium (0.48 mL of a 2.5 M solution in hexanes), afforded, after work up and purification, **4a** (0.220 g, 96%): IR (neat) 1640 cm^{-1}; ^{19}F NMR δ −66.9; ^1H NMR δ 0.9 (t, J = 7 Hz, 3 H), 1.3−1.44 (m, 2 H), 1.54−1.70 (m, 2 H), 2.44 (m, 2 H), 7.1 (1 H, C=CH), 7.4 (m, 5 H, C_6H_5); ^{13}C NMR δ 13.7, 22.7, 26.1, 30.7, 124.9 (q, $^1J_{CF}$ = 274 Hz), 127.1, 128.4, 128.8, 130.8, 131.5 (q, $^2J_{CF}$ = 35.9 Hz), 131.9, (q, $^3J_{CF}$ = 6.4 Hz), 134.8. Anal. Calcd for $C_{13}H_{15}F_3$: C, 68.4; H, 6.6. Found: C, 68.6; H, 6.8.

The same reaction performed between thioenol ether **2a** (0.232 g, 1 mmol) in Et_2O (10 mL) and *n*-butyllithium (0.48 mL of a 2.5 M solution in hexanes) at −78 °C afforded, after work up and purification, **4a** (0.182g, 80%).

(*E*)-3,3,3-Trifluoro-1,2-diphenyl-1-propene (5a). Enol ether **1a** (0.216 g, 1 mmol) in Et_2O (10 mL), treated with phenyllithium (0.6 mL of a 2 M solution in Et_2O) afforded, after work up and purification, **5a** (0.220 g, 92%): mp 62 °C (lit.[11] recrystallization from MeOH, mp 61.5−62 °C); IR (neat) 1649 cm^{-1}; ^{19}F NMR δ −66.0; ^1H NMR δ 7.0−7.6 (m, 11H, C=CH and Ph); ^{13}C NMR δ 122.0 (q, $^1J_{CF}$ = 274 Hz), 127.3, 127.4, 128.4, 128.7, 128.8, 128.9, 129.0, 129.1, 129.6, 130.0, 130.2, 130.5 (q, $^2J_{CF}$ = 28.6 Hz), 132.7 (q, $^3J_{CF}$ = 6.8 Hz), 141.4. Anal. Calcd for $C_{15}H_{11}F_3$: C, 72.6; H, 4.4. Found: C, 73.8; H, 4.8.

1-((1*E*,3*Z*,*E*)-4-Ethoxy-5,5,5-trifluoro-1,3-pentadienyl)benzene (1b). A 5 g portion of enol ether **1b** was prepared according to ref 9 and was obtained from 17.9 g of (*E*)-3-phenylprop-2-enephosphonium salt, 1.1 g of NaH and 4.7 g of

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ethyl trifluoroacetate in a 60% yield of a *Z*/*E* mixture (90/10): IR (neat) 1650, 1619 cm^{-1}; ^{19}F NMR δ −65.3 *(E)*, −68.9 *(Z)*; ^1H NMR δ 1.3/1.31 (*Z*) (t, 3 H, ^3J = 7 Hz), 3.8/3.9 (*Z*) (q, 2 H, J = 7 Hz), 5.75/6.25 (*Z*) (d, ^3J = 10.9 Hz, =CH), 6.4/6.6 (*Z*) (d, ^3J = 15.8 Hz, =CH), 6.85 (dd, ^3J = 10.9 Hz, ^3J = 15.8 Hz, =CHC*H*=CH), 7.2 (5H); ^{13}C NMR δ 14.4/15.5 (*Z*), 64.9 *(Z)*/ 70.6 , 108.5, 118.7, 119.0 (q, $^3J_{CF}$ = 4.2 Hz), 120.2, 122.0 (q, $^1J_{CF}$ = 275 Hz), 126.5, 127.0, 128.6, 129.6, 136.6, 142.5 *(Z)*/ 143.2 (q, $^2J_{CF}$ = 29.3). Anal. Calcd for $C_{13}H_{13}OF_3$: C, 64.46; H, 5.37. Found: C, 64.57; H, 5.44.

1-((1*E*,3*E*)-5,5-Dimethyl-4-(trifluoromethyl)-1,3-hexadienyl)benzene (3b). Enol ether **1b** (0.242 g, 1 mmol) in Et_2O (10 mL), treated with *tert*-butyllithium (0.8 mL of a 1.5 M solution in hexanes) at −78 °C, afforded, after work up and purification, **3b** (0.203 g, 80%): IR (neat) 1631, 1606 cm^{-1}; ^{19}F NMR δ −60.3, −54.0 (*1E,3Z*, 5%); ^1H NMR δ 1.48 (s, 9 H), 6.80 (m, 2 H), 7.6 (m, 6 H, C=CH and Ph); ^{13}C NMR δ 31.5, 34.3, 125.4 (q, $^1J_{CF}$ = 274 Hz), 127.1, 128.9, 132.1 (q, $^3J_{CF}$ = 8 Hz), 135.7 (q, $^2J_{CF}$ = 29.8 Hz), 136.6, 139.4. Anal. Calcd for $C_{15}H_{17}F_3$: C, 70.9; H, 6.7. Found: C, 70.7; H, 6.9.

1-((*E*)-3,3-Dimethyl-2-(trifluoromethyl)-1-butenyl)-4-methoxy)benzene (3c). Enol ether **1c** (0.246 g, 1 mmol) in Et_2O (10 mL), treated with *tert*-butyllithium (0.8 mL of a 1.5 M solution in hexanes) at −78 °C, afforded, after work up and purification, **3c** (0.210 g, 70%): IR (neat) 1640 cm^{-1}; ^{19}F NMR δ −60.0; ^1H NMR δ 1.0 (s, 9 H), 3.8 (s, 3H), 6.7−7.3 (m, 5 H, C=CH and Ph); ^{13}C NMR δ 31.4, 35.0, 55.3, 110.1, 125.2 (q, $^1J_{CF}$ = 278 Hz), 126.7, 127.4, 132.0, 133.4 (q, $^3J_{CF}$ = 8 Hz), 138.6 (q, $^2J_{CF}$ = 23 Hz). Anal. Calcd for $C_{14}H_{17}OF_3$: C, 65.11; H, 6.59. Found: C, 64.92; H, 6.6.

1-((*E*)-2-*tert*-Butyl-3,3,4,4,4-pentafluoro-1-butenyl)benzene (7a). Enol ether **6a** (0.266 g, 1 mmol) in Et_2O (10 mL), treated with *tert*-butyllithium (0.8 mL of a 1.5 M solution in hexanes), afforded, after work up and purification, **7a** (0.228 g, 82%): IR (neat) 1645 cm^{-1}; ^{19}F NMR δ −82.0 (CF_3), −104.1 (CF_2); ^1H NMR δ 1.0 (s, 9 H), 7.1−7.4 (m, 6H, C=CH and Ph); ^{13}C NMR δ 31.6, 37.0, 126.9, 127.3, 127.8, 136.5 (qt, $^3J_{CF}$ = 10 Hz, $^4J_{CF}$ = 2 Hz), 138.9 (t, $^2J_{CF}$ = 20 Hz), *C*F_2 and *C*F_3 not observed. Anal. Calcd for $C_{14}H_{15}F_5$: C, 60.4; H, 5.4. Found: C, 60.5; H, 5.7.

(*Z*)-1-Ethyl-4,4-dimethyl-2-phenyl-3-(trifluoromethyl)-2-pentenyl Alcohol (8a). A solution of **3a** (0.228 g, 1mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.234 g, 1 mmol) in hexane (10 mL) was treated with *tert*-butyllithium (0.6 mL of a 1.5 M solution in hexanes) at room temperature. After 5 min, a red color appeared, propanaldehyde (58 mg, 1 mmol) was added, and the solution was stirred for 30 min. The mixture was quenched by ammonium chloride and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to give a yellow oil which was purified by chromatography on silica gel (eluent: pentane/Et_2O 90:10) to the pure compound **8a** (0.213 g, 75%).

One-Pot Process. A solution of **1a** (0.216 g, 1 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.234 g, 1 mmol) in hexane (10 mL) was treated with 2 equiv of *tert*-butyllithium (1.2 mL of a 1.5 M solution in hexanes) at room temperature. After 5 min, a red color appeared, propanaldehyde (58 mg, 1 mmol) was added, the solution was stirred for 30 min. Workup afforded a mixture (80/20) of **8a** and **1a**. After purification, pure **8a** was obtained (0.151 g, 53%). The yield has not been optimized: IR (CCl_4) 3640 cm^{-1}, 1635 cm^{-1}; ^{19}F NMR δ −48.9 (s); ^1H NMR δ 0.8 (t, J = 6 Hz, CH_3), 0.9 (s, 9 H,), 1.5 (m, 2 H, CH_2), 4.6 (1H, C*H*OH), 6.9−7.2 (m, 5 H, Ph); ^{13}C NMR δ 10.2, 28.9, 31.5, 37.2, 73.1 (q, $^4J_{CF}$ = 4.6 Hz, *C*HOH), 125.5 (q, $^1J_{CF}$ = 282 Hz), 126.9, 127.0, 127.1, 129.7, 130.6, 135.2 (q, $^2J_{CF}$ = 23.5 Hz) 136.6, 149.2 (q, $^3J_{CF}$ = 2.9 Hz). Anal. Calcd for $C_{16}H_{21}F_3O$: C, 67.13; H, 7.34. Found: C, 67.30; H, 7.35.

1-((2*E*)-1,4-Di-*tert*-butyl-5,5-difluoro-2,4-pentadienyl)-benzene (9b). A solution of **3b** (0.254 g, 1mmol) in THF (10 mL) was treated with *tert*-butyllithium (0.66 mL of a 1.5 M solution in hexanes) at −78 °C. The solution was stirred for 15 min at −78 °C and then warmed to room temperature. The mixture was quenched with ammonium chloride and extracted with dichloromethane (3 × 25 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated to give a yellow oil which was purified by chromatography on silica gel (pentane) to give the pure compound **9b** (0.175g, 60%): IR (neat) 1649, 1602 cm^{-1}; ^{19}F NMR δ −88.2 (dd, $^2J_{FF}$ = 49.6 Hz, $^4J_{FH}$ = 7.6 Hz, 1F), −89.9 (dd, $^2J_{FF}$ = 49.6 Hz, $^5J_{FH}$ = 2.2Hz, 1F); ^1H NMR δ 0.87 (s, 9H, 3 × CH_3), 1.06 (d, $^5J_{HF}$ = 2 Hz, 9H, 3 × CH_3), 3.03 (d, ^3J = 9.9 Hz, 1H, C*H*Ph), 5.6 (dd, ^3J = 15.4 Hz, $^4J_{HF}$ = 7.6 Hz, 1H, C*H*=CHCHPh), 6.11 (ddd, ^3J = 15.4 Hz, ^3J = 9.9Hz, $^5J_{HF}$ = 2.2 Hz, 1H, CH=C*H*CHPh), 7.2 (m, 5H); ^{13}C NMR δ 28.0, 29.6 (dd, $^4J_{CF}$ = 4.3 Hz, $^4J_{CF}$ = 1.9 Hz, 3 × CH_3), 32.0, 34.2, 60.5, 98.4 (dd, $^2J_{CF}$ = 14.9 Hz, $^2J_{CF}$ = 11.2 Hz), 122.3 (dd, $^3J_{CF}$ = 5.2 Hz, $^3J_{CF}$ = 1.7 Hz), 125.9, 127.6, 129.1, 135.8 (dd, $^4J_{CF}$ = 5.8 Hz, $^4J_{CF}$ = 2.5 Hz), 142.6, 153.2 (dd, $^1J_{CF}$ = 285.7 Hz, $^1J_{CF}$ = 286.3 Hz). Anal. Calcd for $C_{19}H_{26}F_2$: C, 78.1; H, 8.9. Found: C, 78.2; H, 8.96.

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