

The chemistry of poly(trifluoromethyl)benzenes.

Part II. Reactions of 1,2,3,5-tetrakis(trifluoromethyl)benzene with organolithium compounds

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Abstract

1,2,3,5-Tetrakis(trifluoromethyl)benzene reacts with phenyl-lithium or t-butyl-lithium to give mixtures of de-aromatised products, derivatives of 2,5- and 2,4-cyclohexadiene-1-ylidene of molecular composition $C_{10}H_2F_{10}Ph_2$, $C_{10}H_2F_9Ph_3$, $C_{10}H_2F_{10}Bu_2$ and $C_{10}H_3F_{10}Bu$. The X-ray crystal structure of the triphenyl derivative has been obtained. The 1H , ^{19}F and ^{13}C NMR data provide a satisfactory proof for the structures of the other compounds.

Introduction

In a preceding paper [1], the reactions of 1,2,4,5-tetrakis(trifluoromethyl)benzene with a number of organolithium reagents have been reported. These reactions proceeded in unusual ways and instead of the expected tetrakis(trifluoromethyl)phenyl-lithium, led to de-aromatised products, i.e. derivatives of 2,5-cyclohexadiene-1-ylidene.



R = n-Bu, tert-Bu, Ph

Recently, we have found that 1,2,3,5-tetrakis(trifluoromethyl)benzene (**1**) displays a similar type of reactivity. The relevant results are described in the present paper.

Results and discussion

As for 1,2,4,5-tetrakis(trifluoromethyl)benzene [1], attempted lithiation of the isomeric compound 1,2,3,5-tetrakis(trifluoromethyl)benzene (**1**) with

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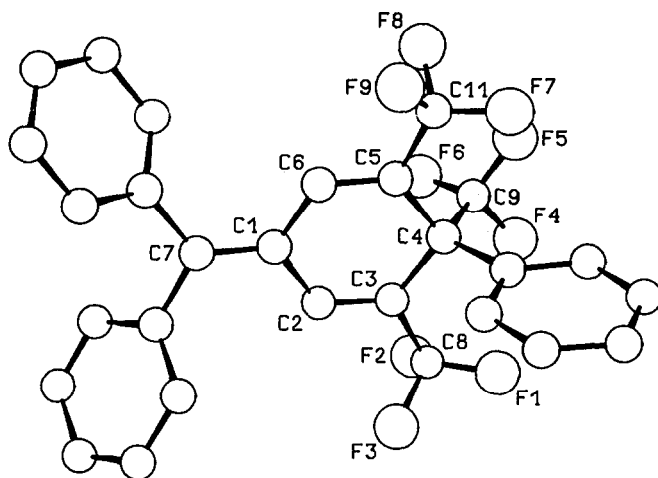
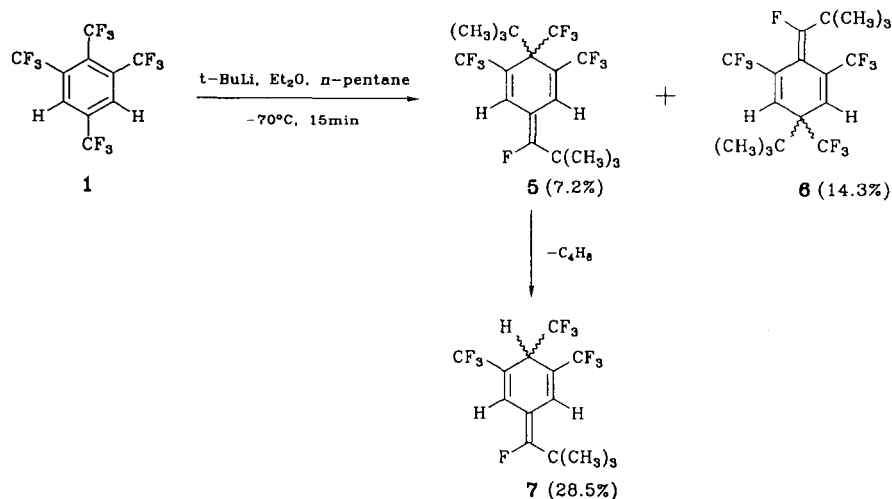


Fig. 1. X-Ray molecular structure of 4,7,7-triphenyl-3,4,5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**3**). Hydrogen atoms and double bonds are not shown.

other new compounds were elucidated from their ^1H , ^{19}F (Fig. 2) and ^{13}C NMR (see Experimental) data in conjunction with the crystal structure of compound **3**.

Analysis of the previously reported [1] and the present NMR data for trifluoromethyl-substituted cyclohexadiene-1-ylidenes has shown that signals of the ring protons located between two CF_3 groups characteristically appear at about 6.5 ppm, while those neighbouring only one CF_3 group appear at about 7.5 ppm. A high-field signal (4.20 ppm) in the ^1H NMR spectrum of compound **7** indicates that the corresponding proton is bound to an sp^3 carbon atom. The ^1H NMR spectra of all the compounds investigated exhibit

TABLE 1

Atomic coordinates for structure **3**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B_{eq}</i>
F(1)	4840(2)	3623(3)	831(3)	6.5(2)
F(2)	4306(4)	2631(3)	1255(5)	8.6(4)
F(3)	4115(3)	3053(4)	−21(5)	8.7(3)
F(4)	5790(3)	2988(3)	1917(3)	6.9(2)
F(5)	6851(3)	2580(3)	1643(3)	7.3(2)
F(6)	5967(3)	1807(3)	1675(3)	7.2(2)
F(7)	7572(2)	2736(3)	112(3)	6.2(2)
F(8)	7603(3)	1582(4)	462(6)	9.2(3)
F(9)	7578(3)	1886(5)	−862(5)	8.1(5)
C(1)	5453(4)	1282(4)	−708(5)	3.8(3)
C(2)	4989(4)	1826(4)	−277(5)	4.0(3)
C(3)	5216(4)	2414(4)	201(5)	3.8(3)
C(4)	6015(4)	2597(4)	382(4)	4.0(2)
C(5)	6485(4)	2012(4)	−107(5)	3.7(3)
C(6)	6222(5)	1433(4)	−580(5)	4.5(3)
C(7)	5202(4)	719(4)	−1238(4)	3.8(3)
C(8)	4641(5)	2941(5)	589(7)	6.0(4)
C(9)	6170(5)	2489(5)	1401(5)	5.4(3)
C(10)	6193(4)	3398(4)	41(4)	3.6(2)
C(11)	7290(5)	2096(5)	−119(7)	5.8(4)
C(12)	5668(4)	94(4)	−1586(5)	3.8(2)
C(13)	4426(5)	681(4)	−1505(4)	4.0(2)
C(14)	4085(5)	1302(5)	−1896(5)	5.0(3)
C(15)	3362(6)	1252(6)	−2178(5)	6.1(3)
C(16)	2979(5)	598(8)	−2051(6)	6.5(4)
C(17)	3309(6)	−23(6)	−1600(7)	6.6(4)
C(18)	4027(5)	17(5)	−1390(5)	5.1(3)
C(19)	6488(4)	3996(4)	523(5)	5.0(3)
C(20)	6611(5)	4692(5)	116(6)	6.3(3)
C(21)	6441(6)	4822(5)	−755(7)	6.7(4)
C(22)	6170(5)	4233(6)	−1217(6)	6.7(4)
C(23)	6039(4)	3538(4)	−849(5)	5.0(3)
C(24)	6160(5)	−296(4)	−1066(5)	5.4(3)
C(25)	6582(5)	−878(5)	−1402(7)	6.9(3)
C(26)	6501(6)	−1089(5)	−2283(8)	6.9(4)
C(27)	6016(6)	−726(6)	−2799(6)	7.1(4)
C(28)	5590(5)	−139(5)	−2488(5)	5.7(3)

signals corresponding to phenyl and *t*-butyl groups of the expected intensities. The characteristic feature of the ^{19}F NMR spectra is a long-range coupling ($^5J=6.1\text{--}8.0$ Hz) between the neighbouring trifluoromethyl groups in compounds **3**, **4**, **5** and **7**, and between the vinylic fluorine and one of the CF_3 groups ($^5J=30.5$ and 41 Hz) in compounds **2** and **6**. No couplings were observed between vinylic fluorine and the ring protons in compounds **5** and **7**. The ^{13}C NMR spectra of compounds **2–7** are fully consistent with the proposed structures.

TABLE 2

Bond lengths for structure 3

Bond	Distance (Å)	Bond	Distance (Å)
C(8)–F(1)	1.30(1)	C(12)–C(7)	1.49(1)
C(8)–F(2)	1.29(1)	C(13)–C(7)	1.49(1)
C(8)–F(3)	1.35(1)	C(19)–C(10)	1.39(1)
C(9)–F(4)	1.36(1)	C(23)–C(10)	1.39(1)
C(9)–F(5)	1.32(1)	C(24)–C(12)	1.38(1)
C(9)–F(6)	1.32(1)	C(28)–C(12)	1.42(1)
C(11)–F(7)	1.29(1)	C(14)–C(13)	1.39(1)
C(11)–F(8)	1.38(1)	C(18)–C(13)	1.39(1)
C(11)–F(9)	1.29(1)	C(15)–C(14)	1.40(1)
C(2)–C(1)	1.44(1)	C(16)–C(15)	1.36(2)
C(6)–C(1)	1.46(1)	C(17)–C(16)	1.38(2)
C(7)–C(1)	1.35(1)	C(18)–C(17)	1.39(1)
C(3)–C(2)	1.32(1)	C(20)–C(19)	1.38(1)
C(4)–C(3)	1.53(1)	C(21)–C(20)	1.36(1)
C(8)–C(3)	1.52(1)	C(22)–C(21)	1.34(1)
C(5)–C(4)	1.53(1)	C(23)–C(22)	1.36(1)
C(9)–C(4)	1.56(1)	C(25)–C(24)	1.38(1)
C(10)–C(4)	1.53(1)	C(26)–C(25)	1.38(2)
C(6)–C(5)	1.33(1)	C(27)–C(26)	1.34(2)
C(11)–C(5)	1.49(1)	C(28)–C(27)	1.38(1)

Experimental

The ^1H , ^{19}F and ^{13}C NMR spectra were recorded via a Varian 200 Mz spectrometer in CDCl_3 solutions; chemical shifts are in ppm from internal TMS for the proton and carbon nuclei (positive downfield) and from internal CFCl_3 for the fluorine nuclei (positive upfield).

The X-ray structural analysis of compound 3 was obtained with a Syntex P2₁ diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation (0.71069 Å). The cell constants were obtained from a least-squares refinement on the setting angles of 25 reflections. The data were collected with the $\omega/2\theta$ scan technique up to $2\theta_{\text{max}} = 50^\circ$.

Crystal data: $\text{C}_{28}\text{H}_{17}\text{F}_9$, $M = 524.42$, orthorhombic; space group $Pbca$; $a = 18.47(1)$, $b = 17.54(1)$, $c = 14.978(8)$ Å, $V = 4850.2(7)$ Å³; $Z = 8$; $F(000) = 2128$; $D_x = 1.44$ g cm⁻³; $\mu(\text{MoK}\alpha) = 0.89$ mm⁻¹.

A total of 2709 reflections were collected of which 2047 were unique; 1959 reflections were found to be $I > 2\sigma_I$. Lorentz and polarisation corrections were applied to the data. No absorption correction was applied at the measurement stage.

The phase problem was solved by direct methods [2]. A total of 37 atoms were located in an E-map. Initially, the positional parameters and individual isotropic temperature factors of all non-hydrogen atoms were refined to $R = 0.165$ [3].

TABLE 3

Bond angles for structure **3**

Bonds	Angle (°)	Bonds	Angle (°)
F(1)–C(8)–F(2)	107.8(8)	C(4)–C(5)–C(6)	124.0(7)
F(1)–C(8)–F(3)	105.0(7)	C(4)–C(5)–C(11)	120.3(7)
F(1)–C(8)–C(3)	117.8(7)	C(5)–C(4)–C(9)	106.4(6)
F(2)–C(8)–F(3)	103.9(8)	C(5)–C(4)–C(10)	109.5(6)
F(2)–C(8)–C(3)	111.9(7)	C(9)–C(4)–C(10)	113.4(6)
F(3)–C(8)–C(3)	109.4(8)	C(4)–C(10)–C(19)	127.3(6)
F(4)–C(9)–F(5)	104.9(6)	C(4)–C(10)–C(23)	116.1(6)
F(4)–C(9)–F(6)	105.1(6)	C(6)–C(5)–C(11)	115.6(7)
F(4)–C(9)–C(4)	112.4(7)	C(7)–C(12)–C(24)	123.3(7)
F(5)–C(9)–F(6)	107.2(7)	C(7)–C(12)–C(28)	119.2(7)
F(5)–C(9)–C(4)	115.4(7)	C(12)–C(7)–C(13)	115.4(6)
F(6)–C(9)–C(4)	111.2(6)	C(7)–C(13)–C(14)	121.0(7)
F(7)–C(11)–F(8)	103.4(8)	C(7)–C(13)–C(18)	121.0(7)
F(7)–C(11)–F(9)	108.4(8)	C(10)–C(19)–C(20)	120.2(7)
F(7)–C(11)–C(5)	119.1(7)	C(19)–C(10)–C(23)	116.6(6)
F(8)–C(11)–F(9)	100.7(8)	C(10)–C(23)–C(22)	120.8(7)
F(8)–C(11)–C(5)	110.2(7)	C(12)–C(24)–C(25)	122.2(8)
F(9)–C(11)–C(5)	113.2(8)	C(24)–C(12)–C(28)	117.5(7)
C(1)–C(2)–C(3)	124.9(7)	C(12)–C(28)–C(27)	118.7(8)
C(2)–C(1)–C(6)	113.7(6)	C(13)–C(14)–C(15)	120.7(8)
C(2)–C(1)–C(7)	123.1(7)	C(14)–C(13)–C(18)	118.0(8)
C(1)–C(6)–C(5)	124.4(7)	C(13)–C(18)–C(17)	120.9(8)
C(6)–C(1)–C(7)	123.0(7)	C(14)–C(15)–C(16)	120.3(9)
C(1)–C(7)–C(12)	123.1(7)	C(15)–C(16)–C(17)	119.7(9)
C(1)–C(7)–C(13)	121.4(7)	C(16)–C(17)–C(18)	120.4(9)
C(2)–C(3)–C(4)	124.3(7)	C(19)–C(20)–C(21)	122.2(8)
C(2)–C(3)–C(8)	117.3(7)	C(20)–C(21)–C(22)	116.9(9)
C(3)–C(4)–C(5)	108.7(6)	C(21)–C(22)–C(23)	123.2(9)
C(3)–C(4)–C(9)	108.8(6)	C(24)–C(25)–C(26)	119.1(9)
C(3)–C(4)–C(10)	109.9(6)	C(25)–C(26)–C(27)	119.7(9)
C(4)–C(3)–C(8)	118.4(6)	C(26)–C(27)–C(28)	122.7(9)

The positions of the hydrogen atoms bonded to carbon atoms were generated from assumed geometries and added with isotropic temperature factors to the set of atomic parameters. The refinement of atomic positional and thermal anisotropic parameters (isotropic for H) was performed by the least-squares full-matrix procedure using SHELX-76. The final value of R was 0.0829 unit weight. The highest peak in the final difference map was $0.27 \text{ e } \text{\AA}^{-3}$.

The refined positional parameters for the non-H atoms of **3**, together with their B_{eq} values, are given in Table 1, and bond lengths and bond angles in Tables 2 and 3.

1,2,3,5-Tetrakis(trifluoromethyl)benzene (**1**) was prepared from mesitylene in three steps: trifluoromethylation of mesitylene with a carbon tetrachloride/hydrogen fluoride mixture at 95°C [4], oxidation of 2,5,6-trimethyl-

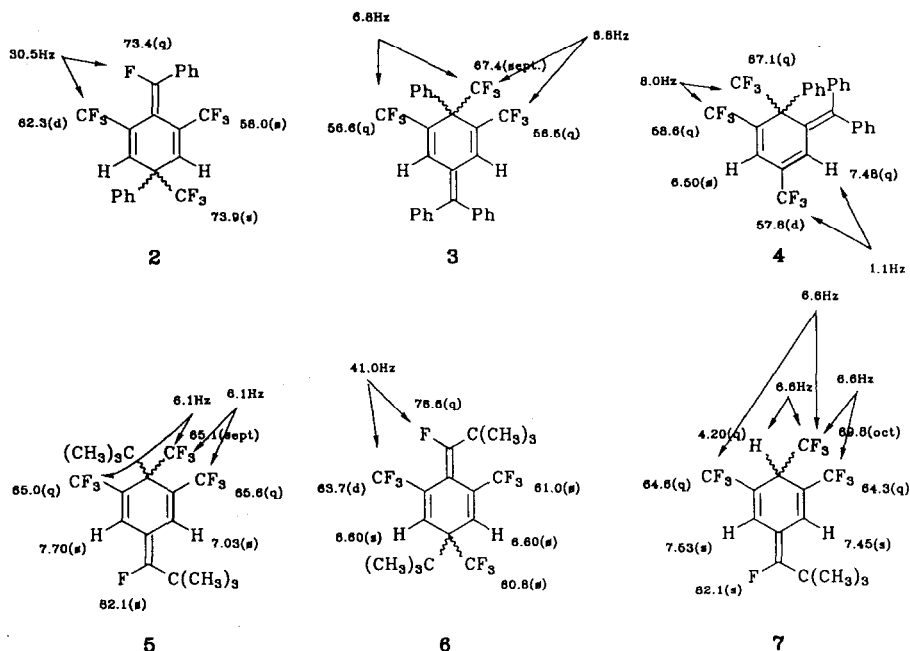


Fig. 2. ^1H and ^{19}F NMR data for compounds 2–7. Chemical shifts are in ppm from internal TMS for the proton nuclei (positive downfield) and from internal CFCl_3 for the fluorine nuclei (positive upfield). (The ring proton signals of compounds 2 and 3 overlap with those of the phenyl groups.)

trifluoromethylbenzene with nitric acid at 180 °C followed by refluxing with aqueous potassium permanganate [5] and fluorination of the resultant trifluoromethyltrimesic acid with sulphur tetrafluoride in an excess of hydrogen fluoride at 250 °C for 20 h. Steam distillation and recrystallisation of the crude product from *n*-pentane gave compound 1 (25% yield) of 99.5% purity (GLC estimate) as white crystals, m.p. 49–50 °C (lit. value [6], m.p. 49.5–50 °C).

Phenyl-lithium was freshly prepared according to a known procedure by refluxing a mixture of benzene, *n*-butyl-lithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in a 4:1:1 molar ratio [7]. *t*-Butyl-lithium was a commercial 1.4 M solution in *n*-pentane.

General procedure

All reactions were conducted under an atmosphere of dry argon.

Phenyl-lithium (6 mmol, in a benzene/hexane solution) or *t*-butyl-lithium (6 mmol, 4.7 ml of a 1.4 M solution in *n*-pentane) was added with a syringe via a rubber septum to a precooled (–78 °C) stirred solution of 1,2,3,5-tetrakis(trifluoromethyl)benzene (1) (1.2 g, 3 mmol) in diethyl ether (20 ml), at such a rate as to keep the temperature below –65 °C. The reactions

were highly exothermic. After addition was complete, stirring was maintained at -70°C for 15 min, and then the reaction was quenched by careful addition of a solution of acetic acid (1 ml) in tetrahydrofuran (3 ml). After warming up to ambient temperature, the solution was poured into water (100 ml) and extracted with diethyl ether (3×10 ml). The combined extracts were dried (MgSO_4), the solvent was removed under vacuum, and the brownish residue obtained was subjected to chromatographic separation on silica gel (230–400 mesh, 1:100 by weight) using *n*-hexane as the eluent. ^1H and ^{19}F NMR spectra are given in Fig. 2.

7-Fluoro-4,7-diphenyl-2,4,6-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**2**): colourless liquid. ^{13}C NMR δ : 160.4 (d, C-7, $^1J(\text{C}-\text{F}) = 271$ Hz); 134.9 and 132.8 (m, C-3 and C-5); 128–132 (C-2, C-6 and C-arom.); 122.2 and 125.0 (q, CF_3 , $^1J(\text{C}-\text{F}) = 268$ and 273 Hz); 120.9 (qd, CF_3 , $^1J(\text{C}-\text{F}) = 275$ Hz, $^4J(\text{C}-\text{F}) = 5$ Hz); 103.6 (d, C-1, $^2J(\text{C}-\text{F}) = 26.5$ Hz); 53.9 (q, C-4, $^2J(\text{C}-\text{F}) = 27.5$ Hz) ppm.

4,7,7-Triphenyl-3,4,5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**3**): pale-yellow crystals (from CHCl_3), m.p. $145\text{--}147^{\circ}\text{C}$ (uncorrected, decomp.). ^{13}C NMR δ : 154.7 (s, C-7); 134.5 (q, C-2 and C-6, $^3J(\text{C}-\text{F}) = 5.4$ Hz); 139.3 (C-arom.); 127–131 (C-3, C-5 and C-arom.); 124.2 (q, CF_3 , $^1J(\text{C}-\text{F}) = 235$ Hz); 123.2 (q, 2CF_3 , $^1J(\text{C}-\text{F}) = 275$ Hz); 123.9 (s, C-1); 55.8 (q, C-4, $^2J(\text{C}-\text{F}) = 28$ Hz) ppm.

6,7,7-Triphenyl-3,5,6-tris(trifluoromethyl)-2,4-cyclohexadiene-1-ylidene (**4**): yellow oil. ^{13}C NMR δ : 153.5 (s, C-7); 141.0 (C-arom.); 138.5 (q, C-2, $^3J(\text{C}-\text{F}) = 6$ Hz); 135.2 (q, C-4, $^3J(\text{C}-\text{F}) = 4.2$ Hz); 127–131 (C-3, C-5 and C-arom.); 124.2, 123.0 and 122.1 (q, CF_3 , $^1J(\text{C}-\text{F}) = 283$, 275 and 276 Hz); 122.5 (s, C-1); 54.2 (q, C-6, $^2J(\text{C}-\text{F}) = 27.3$ Hz) ppm.

7-Fluoro-4,7-bis(*t*-butyl)-3,4,5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**5**): colourless liquid. ^{13}C NMR δ : 171.0 (d, C-7, $^1J(\text{C}-\text{F}) = 280$ Hz); 130.7 and 130.0 (m, C-2 and C-6); 105.1 (d, C-1, $^2J(\text{C}-\text{F}) = 23$ Hz); 42.3 (s, $\text{C}(\text{CH}_3)_3$); 38.0 (d, $\text{C}(\text{CH}_3)_3$, $^2J(\text{C}-\text{F}) = 25$ Hz); 29.7 (s, CH_3); 28.2 (d, CH_3 , $^3J(\text{C}-\text{F}) = 4.6$ Hz) ppm. Signals for the ring carbons C-3, C-4, C-5 and of the CF_3 groups were too weak to be recognised.

7-Fluoro-4,7-bis(*t*-butyl)-2,4,6-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**6**): colourless liquid. ^{13}C NMR δ : 169.9 (d, C-7, $^1J(\text{C}-\text{F}) = 279$ Hz); 132.6 and 133.1 (m, C-3 and C-5); 125.7, 123.3 and 121.9 (q, CF_3 , $^1J(\text{C}-\text{F}) = 272$, 273.5 and 276.5 Hz); 105.7 (d, C-1, $^2J(\text{C}-\text{F}) = 24.5$ Hz); 56.7 (q, C-4, $^2J(\text{C}-\text{F}) = 24$ Hz); 42.9 (s, $\text{C}(\text{CH}_3)_3$); 37.6 (d, $\text{C}(\text{CH}_3)_3$, $^2J(\text{C}-\text{F}) = 24$ Hz); 29.2 (d, CH_3 , $^3J(\text{C}-\text{F}) = 5.8$ Hz); 27.9 (s, CH_3) ppm. Signals for the ring carbons C-2 and C-6 were too weak to be recognised.

7-Fluoro-7-(*t*-butyl)-3,4,5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**7**): colourless liquid. ^{13}C NMR δ : 174.2 (d, C-7, $^1J(\text{C}-\text{F}) = 284$ Hz); 130.8 and 130.4 (m, C-2 and C-6); 124.0, 122.5 and 122.4 (q, CF_3 , $^1J(\text{C}-\text{F}) = 283.8$ and 272.2 Hz); 121.3 and 121.2 (q, C-3 and C-5, $^2J(\text{C}-\text{F}) = 32.8$ Hz); 109.7 (d, C-1, $^2J(\text{C}-\text{F}) = 22.4$ Hz); 39.1 (q, C-4, $^2J(\text{C}-\text{F}) = 32.6$ Hz); 37.9 (d, $\text{C}(\text{CH}_3)_3$, $^2J(\text{C}-\text{F}) = 23.0$ Hz); 28.7 (d, CH_3 , $^3J(\text{C}-\text{F}) = 4.6$ Hz) ppm.

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