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Title: Unusual Photocyclization of Perfluoro *cis*-1,2-Dimethyl-1,3-Butadienyl Benzenes as a means to Synthesize Partially Fluorinated Naphthalenes



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Graphical Abstract



Graphical Abstract Synopsis

The preparation of perfluoro *cis*-1,2-dimethyl butadienyl copper reagent and subsequent coupling with aryl iodides is described. Photocyclization of the corresponding butadienyl benzenes give novel naphthalene derivatives and 1,4-dihydronaphthalenes. Additionally, naphthalene derivatives are prepared by treatment of 1,4-dihydronaphthalenes with DABCO.

Research Highlights

- 1. The preparation of perfluoro *cis*-1,2-dimethyl butadienyl copper reagent.
- 2. Preparation of perfluoro *cis*-1,2-dimethyl butadienyl benzenes from copper reagent and aryl iodides.
- 3. Photocyclization to give novel naphthalene derivatives and 1,4dihydronaphthalenes.
- 4. Naphthalene derivative prepared by treatment of 1,4-dihydronaphthalene with DABCO.

Unusual Photocyclization of Perfluoro *cis*-1,2-Dimethyl-1,3-Butadienyl Benzenes as a means to Synthesize Partially Fluorinated Naphthalenes.

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Abstract:

Photoirradiation of the titled compounds perfluoro-*cis*-1,2-dimethyl-butadienyl benzenes (**1**), which were prepared in several steps from perfluorovinyl bromide, results in the formation of the corresponding novel naphthalene derivatives and 1,4-dihydronaphthalenes. Isolated 1,1,2-trifluoro-3,4-bis(trifluoromethyl)-1,4-dihydronaphthalene (**3a**) could be converted into 1,2-bistrifluoromethyl-3,4-difluoronaphthalene (**2a**) by base treatment (DABCO); however, **3a** did not lead to **2a** by photoreaction, suggesting **3a** was not a possible photochemical precursor. Competitive photoreaction studies suggest that varying the substituent on benzene ring (*e.g.* methyl or trifluoromethyl) does not significantly affect the reaction rate. Presently, this reaction mechanism is not yet clearly understood.

Keyword: Photocyclization, perfluoro-*cis*-1,2-dimethyl-butadienylbenzene, 1,2-difluoro-3,4-bis(trifluoromethyl)naphthalene, photoelimination of HF, and 1,1,2-trifluoro-3,4-bis(trifluoromethyl)-1,4-dihydronaphthalene.

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1. Introduction

We have reported that trifluoromethylcopper [1], F-vinyl copper [2,3], and F-

acetylenic copper [4] reagents could be readily obtained *via* copper(I) halide

metathesis reaction of the corresponding cadmium or zinc reagent (Eq. 1). These

reagents have found extensive utility in preparative organofluorine chemistry [5]. Terminal F-vinyl copper reagents added to perfluoroalkynes can give extended dienyl copper reagents, which could be functionalized *via* coupling reactions (Eq. 2) [6, 7]. The reaction of F-dienyl copper reagents with aryl halides generates coupled products (Eq. 3) [6, 7, 8, 9]. We focused on perfluoro *cis*-1,2-dimethyl butadienyl benzenes (**1**) which could be readily prepared from perfluoro-1,3-butadienyl copper (**6**) reagents (Scheme 1).



Scheme 1. Synthesis of perfluoro *cis*-1,2-dimethyl butadienyl benzenes (1)



2. Results and Discussion

Preparation of **1** was carried out by the method [6] shown in Table 1. These transformations were carried out by the one-pot reaction under N₂ atmosphere. Conversion of **5** to **6** was done at room temperature and the yield was calculated by ¹⁹F-NMR spectroscopy using an internal trifluoromethyl benzene standard. In the conversion of **6** to **1**, a variety of functionalized aryl iodides were added (mole ratio

0.70 equivalent) to the copper reagent **6** and reaction mixtures were heated at 80-90 °C overnight. After reaction, compounds of general structure **1** were isolated by silica gel chromatography. The resultant benzenes **1** in hexane were photolyzed using a Rayonet reactor at 254nm in a quartz tube at 30-40 °C under degassed conditions (Scheme 2).

Table 1. Preparation of perfluoro-cis-1,2-dimethyl-butadienyl benzenes 1



Entry	Aryl Iodide	1	Yield ^a
1a		F ₃ C CF ₃ F F F	76%
1b	F ₃ C	F_3C F_3C F_3C F_5C F_5 F_5	83%
1c	H ₃ CO	H ₃ CO F F F F	87%
1d	CI		86%
1e	Me	F ₃ C CF ₃ F F Me F	91%



^aIsolated yields based on aryl-iodide

Scheme 2. Synthesis of 1,1,2-trifluoro-3,4-bis(trifluoromethyl)-1,4-

dihydronaphthalene (3) and 1,2-bistrifluoromethyl-3,4-difluoronaphthalene (2)



In the case of p-substituted perfluoro *cis*-1,2-dimethyl butadienyl benzenes **1a-d**, photolysis of **1** leads to the unusual intramolecular cyclization and two principal products are obtained (Table 2). In these reactions, the 1,4dihydronaphthalene derivatives **3a-d** were the minor photocyclization products. The predominant naphthalene derivatives **2a-d** were obtained after photocyclization accompanied by photoelimination of HF.





а	F ₃ C	46 (65)	19 (29)	(6)
	F F			
b	F ₃ C	53 (64)	26 (29)	(7)
	F ₃ C F F			
С	F ₃ C	50 (59)	24(25)	(16)
	H ₃ CO F F			
d	F ₃ C	59 (67)	14 (27)	(6)
	CI F F		2	

^aIsolated yields (GC yields)

The formation of naphthalene derivatives **2a-d** and 1,4-dihydronaphthalenes **3a-d** were confirmed *via* GC-MS and NMR spectra analysis of isolated compounds (Table 3 and 4).

Table 3. Selected NMR data of isolated *p*-naphthalene compounds **2a-d**.



Entry		ppm						
¹⁹ F-NMR	Z	F ^a (3F)	F ^b (3F)	- F ^c (1F)	F ^d (1F)	J_{ab}	$J_{ m bc}$	$J_{\rm cd}$
2a	Н	-51.4(q)	-54.1(qd)	-138.7(qd)	-142.6(d)	17	34	17
2b	CF_3	-51.4(q)	-54.4(qd)	-139.6(qd)	-136.4(d)	16	34	17
2c	OCH ₃	-51.3(q)	-53.7(qd)	-142.2(qd)	-140.3(d)	16	32	16
2d	Cl	-51.5(q)	-54.2(qd)	-140.1(qd)	-138.2(d)	16	32	18
			ppm				Hz	
¹ H-NMR	Z	H^{1}	H ²	H ³	H^4		$J_{1,2}$	

2a	Н		7.7-8.2 (4H)						
2b	CF_3	7.9 (1H, d)	8.5 (1H, d)	-	8.5	(1H, s)		8	
2c	OCH_3	7.1 (1H, d)	8.0 (1H, d)	-	7.1	(1H, s)		8	
2d	Cl	8.2 (1H, d)	8.5 (1H, d)	-	8.0	(1H, s)		9	
			ppm				Hz		
¹³ C-NMR	Z	C^1	C ³	C^4	${}^{2}J_{1,F}$	1J _{3,F}	${}^{2}J_{3,F}$	1J _{4,F}	${}^{2}J_{4,F}$
2a	Н	123.7(q)	144.3(dd)	148.8(dd)	34	258	14	255	14
2b	CF_3	126.6(q)	148.8(dd)	144.7(dd)	39	263	14	262	14
2c	OCH_3	123.3(q)	144.3(dd)	147.1(dd)	36	257	14	256	14
2d	Cl	124.1(q)	147.3(dd)	144.6(dd)	32	261	14	259	14

Table 4. Selected NMR data of isolated 1,4-dihydronaphthalene compounds **3a-d**.



Entry				ppr	n			I	Hz
¹⁹ F-NMR	Z	Fa (3F)	F ^b (3F)	F ^c (1F)) F ^d (1)	F) F ^e	(1F)	$J_{a,H5}$	$J_{\rm cd}$
3a	Η	-60.7(d)	-69.6(s)	-114.9(r	n) -85.3(d	dd) -101	.3(dd)	7	304
3b	CF_3	-60.8(d)	-69.3(s)	-114.2(r	n) -85.5(d	dd) -101	.3(dd)	7	306
3c	OCH_3	-60.7(d)	-69.9(s)	-115.6(r	n) -85.4(o	dd) -101	.3(dd)	6	304
3d	Cl	-60.8(d)	-69.6(s)	-114.7(r	n) -85.5(d	dd) -101	.3(dd)	6	304
				ppm				Hz	
¹ H-NMR	Z	H^{1}		H ² H ³	H^4	H^5		J _{1,2}	J _{1,Fa}
3a	Н		7.9	-7.5(4H)		4.6(1H	, q)	-	7
3b	CF_3	7.7 (1H,	d) 7.9(1H, d) -	8.1 (1H, s) 4.6(1H	, q)	8	7
3c	OCH_3	7.1 (1H,	d) 7.4 ((1H, d) -	7.3 (1H, s) 4.5(1H	, q)	9	6
3d	Cl	7.4 (1H,	d) 7.6 ([1H, d) -	7.8 (1H, s) 4.5(1H	, q)	8	6
				ppm				Hz	
¹³ C-NMR	Z	C1	C ²	C ³	C^4	C ⁵	${}^{2}J_{1,F}$	${}^{1}J_{3,F}$	${}^{1}J_{4,F}$
3a	Η	43.7(q)	111.1(m)	156.7(dt)	109.9(td)	131.0(t)	31	294	236
3b	CF_3	43.8(q)	111.1(m)	156.4(dt)	109.3(td)	132.1(t)	31	294	235
3c	OCH_3	43.2(q)	111.1(m)	156.7(dt)	109.7(td)	132.2(t)	31	294	239
3d	Cl	43.7(q)	111.1(m)	156.7(dt)	109.4(td)	133.4(t)	31	294	239

The ¹⁹F-NMR spectrum of the naphthalene derivatives showed the resonance of the two fluorines and two trifluoromethyl groups instead of the three vinyl fluorines and two trifluoromethyl groups which were observed in the staring compounds **1a-d.** The coupling patterns of the two aryl fluorines (doublet, *J* = 16-18 Hz and quartet-doublet, *J* = 32-34, 16-18 Hz) and the two trifluoromethyl groups

(quartet, *J* = 16-17 Hz, and doublet-quartet, *J* = 32-34, 16-17 Hz) supported these naphthalene structures (Table 3).

In contrast, ¹⁹F-NMR spectra of 1,4-dihydronaphthalene derivatives **3a-d** exhibited a fluorine, difluoromethylene, and two trifluoromethyl groups (Table 4). Splitting of methylene H5 into a quartet (${}^{3}J_{H5,F} = 6-7$ Hz) in the ¹H-NMR spectrum and splitting of C1 (${}^{2}J_{C1,F} = 31$ Hz) in the ¹³C-NMR spectrum supports the assigned structures. The existence of three (**3b-d**) or four (**3a**) aromatic protons, excluding H5 (since no structures could be written without breaking aromaticity), provides further support.

To our knowledge, only two examples of photocyclizations which are accompanied by HF photoelimination have been reported. Although the reaction mechanism are not clearly understood, Fokin and coworkers [10] found that Nmethyl-2,3,4,5-tetrafluoro diphenyl amine was converted to 2,3,4-trifluoro-9-methyl carbazole with HF photoelimination. Mallory [11] also found that 1fluoro[5]helicenes proceed through HF photoelimination in their conversion to benzo[ghi]perylene. An NMR study of this compound was independently carried out by Gorsane [12].

The treatment of isolated **3a** with 1,4-diazabicyclo[2.2.2]octane base (DABCO), resulted in the naphthalene derivative **2a** (Scheme 3). Photolysis of **3a**, however, does not afford **2a**, implicating an intermediate other than **3a** as the photochemical precursor to **2a**.

Scheme 3. HF elimination of 3a to 2a with use of DABCO



The photolysis of 1,4-bis(perfluoro cis-1,2-dimethyl-1,3-butadienyl) benzene **1f** leads to multiple products. Among them, two major products, anthracene (**7**) and phenanthrene (**8**) could be isolated (Scheme 4). In this reaction, phenanthrene **8** is the favored product, although for reasons unclear. In conjunction with various analytical data (*e.g.* NMR), X-ray crystal analysis data (Fig. 1) also assisted in the assignment of chemical structures. From X-ray analysis, phenanthrene derivative **8** has a twisted structure (twisted angle of **8** is 27° between ring A and C), while anthracene derivative **7** has a planar structure [13].

Scheme 4. Photolysis of 1f to lead 7 and 8.



Figure 1. Crystal Sturture of a) 7 and b) 8.



Photolysis of *m*-methyl substituted benzene **1e** was carried out under similar conditions and generates four major products (Scheme 5). The obtained products could not be completely separated due to extremely close boiling points and similar TLC behavior. However, the naphthalene derivatives and **1**,4-dihydronaphthalene derivatives could be separated as mixtures of **2e/2e'** and **3e/3e'**.





From the NMR spectrum and GC yields, the mixture of naphthalene derivatives **2e/2e'** consisted of 40% **2e** and 60% **2e'**. Having similar ¹⁹F-NMR spectra (Table 5), compounds **2e** and **2e'** were differentiated on the basis of the respective H4 coupling patterns in the ¹H-NMR. For the methyl H4 protons, compound **2e'** exhibited a singlet, while the **2e** methyl 4H protons were split into a doublet by the adjacent Fd ($J_{H4-Fd} = 8$ Hz).

$\begin{array}{c c c c c c c } & 2e' & 2e' \\ \hline Entry & ppm & Hz \\ \hline 1^{9}F-NMR & F^{a}\left(3F\right) & F^{b}\left(3F\right) & F^{c}\left(1F\right) & F^{d}\left(1F\right) & J_{bc} & J_{cd} \\ \hline 2e & -51.4(m) & -54.2(m) & -143.0(qd) & -129.7(bs) & 34 & 14 \\ \hline 2e' & -51.4(m) & -54.0(m) & -144.1(qd) & -139.2(d) & 34 & 18 \\ \hline 2e' & -51.4(m) & -54.0(m) & -144.1(qd) & -139.2(d) & 34 & 18 \\ \hline 1H-NMR & H^{1-3} & Pm & Hz \\ \hline 1H-NMR & H^{1-3} & H^{4} & J_{4,Fd} \\ \hline 2e & 7.4-7.9\left(3H,m\right) & 2.8\left(d\right) & 8 \\ \hline 2e' & 7.4-7.9\left(3H,m\right) & 2.8\left(d\right) & 0 \\ \hline \end{array}$		H ² H ² H ³ CH ₃	CF ^a CF ^b F ^c	$H_{3}C^{4}$ $H_{3}C^{4}$ H^{1} H^{2} H^{2} H^{3} H^{4}	CF ₃ ^b CF ₃ ^b F ^d		
$\begin{array}{c c c c c c c c c } & & & & & & & & & & & & & & & & & & &$		20	e	2e'			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Entry			ppm		H	z
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	¹⁹ F-NMR	F ^a (3F)	F ^b (3F)	F ^c (1F)	F ^d (1F)	Jbc	Jcd
2e' -51.4(m) -54.0(m) -144.1(qd) -139.2(d) 34 18 ppm ppm Hz Hz	2e	-51.4(m)	-54.2(m)	-143.0(qd)	-129.7(bs)	34	14
ppm Hz ¹ H-NMR H ¹⁻³ H ⁴ J _{4,Fd} 2e 7.4-7.9 (3H, m) 2.8 (d) 8 2e' 7.4-7.9 (3H, m) 2.8 (d) 0	2e'	-51.4(m)	-54.0(m)	-144.1(qd)	-139.2(d)	34	18
¹ H-NMR H ¹⁻³ H ⁴ J _{4,Fd} 2e 7.4-7.9 (3H, m) 2.8 (d) 8 2e' 7.4-7.9 (3H, m) 2.8 (d) 0				ppm		H	łz
2e 7.4-7.9 (3H, m) 2.8 (d) 8 2e' 7.4-7.9 (3H, m) 2.8 (d) 0	¹ H-NMR	H ¹⁻³		H^4		J_4	l,Fd
2e' 7.4-7.9 (3H, m) 2.8 (d) 0	2e	7.4-7.9 (3H, m))	2.8 (d)			8
	2e'	7.4-7.9 (3H, m))	2.8 (d)			0

Table 5. NMR data of m-naphthalene mixtures 2e and 2e'.

Lack of diagnostic difference in the NMR spectra prevented the direct assignment of either **3e** or **3e'** as the major component in the observed **3/7** ratio. However, a mixture of the **3e/3e'** was converted to a **3/7** mixture of the **2e/2e'** by treatment with diazabicycloundecene (DBU) in CDCl₃ (Scheme 6). The ¹⁹F-NMR spectrum of the reaction mixture was consistent with the structures **2e** and **2e'**. Thus, the conversion of **1**,4-dihydronaphthalene derivatives to the naphthalene derivatives provided the structural confirmation and facilitated determination of the **3e/3e'** ratio (Table 6).

Table 6. NMR data of 1,4-dihydronaphthalene mixtures 3e and 3e'.

	$H^{1} H^{5} CF_{3}^{*} H_{3}C^{4} H^{5} CF_{3}^{*} H_{3}C^{4} CF_{3}^{*} CF$			
Entry	ppm		Hz	
¹⁹ F-NMR	F ^a (3F) or F ^b (3F) F ^c (1F) F ^d (1F) or F ^e (1F)	Jcd	J_{ce}	$J_{ m de}$

3e	-60.9(m)	-69.9(s)	-115.4(m)	-93.8(dd)	-95.8(dd)	22	14	309
3e'	-60.9(m)	-69.6(s)	-115.1(m)	-84.9(dd)	-101.1(dd)	23	13	303
			ppm				Hz	
¹ H-NMR	H1-3		H^4		H ⁵			
3e	7.3-7.7(3H, m)		2.6 (1H, m)		4.5 (1H, m)			
3e'	7.3-7.7(3H, m)		2.	4 (1H, s)	4.4 (1H, m)			

Scheme 6. Conversion of the mixture 3e/3e' into 2e/2e'.

3e (0.3) + **3e'** (0.7) DBU, CDCl₃, RT **2e** (0.3) + **2e'** (0.7)

To probe the photoreaction mechanism, we initially hypothesized the involvement of electrophilic attack on the benzene ring and that this step might be slowest and rate determining. As a consequence, we expect that reaction rates would be sensitive to the nature of the substituent on the benzene ring. That is, electron-donating groups should enhance reaction rate through stabilization of the intermediate cation while electron-withdrawing groups slow the reaction rate through destabilization. Competitive photoreaction studies were carried out between several perfluoro *cis*-1,2-dimethyl butadienyl benzenes **1**. Direct competition between non-substituted benzene **1a** and *m*-methyl-substituted benzene **1e**, however resulted in little difference in reaction rate, suggesting that the methyl inductive effect contributed insignificantly to the reaction rate. Similarly, competition between *p*-trifluoromethyl-substituted benzene **1b** and nonsubstituted **1a** resulted in no significant decrease in reaction rate. The failure of both *p*-trifluoromethyl **1b** and *m*-methyl **1e** to significantly influence reaction rate was inconsistent with a mechanism in which electrophilic attack was rate

determining. Additional detailed studies are required to elucidate other mechanistic pathways (*i.e.* radical).

Figure 2. Competitive photolysis of 1a (dash, ---) and 1e (m-CH₃, solid, -).



Figure 3. Competitive photolysis of 1a (dash, ---) and 1b (p-CF₃, solid, -).



3. Experimental

3.1 General experimental procedures

Routine ¹⁹F-NMR spectra were recorded on a JEOL FX90Q Spectrometer

(83.81 MHz) and high-resolution data was obtained on a Bruker AC-300

Spectrometer (282.41 MHz). Chemical shifts have been reported in ppm relative to

internal CFCl₃. Spectra of reaction mixtures were obtained in the ⁷Li external lock

mode. Quantitative determinations were carried out by integration relative to internal benzotrifluoride. Routine ¹H-NMR (300.17 MHz) spectra and highresolution data were generally obtained on a Bruker AC-300 Spectrometer. Unless noted otherwise, CDCl₃ was used as the NMR lock solvent. Chemical shifts have been reported in ppm relative to internal TMS. High resolution {¹H} ¹³C NMR spectra were recorded on a Bruker AC-300 Spectrometer (75.48 MHz). Chemical shifts have been reported in ppm relative to internal TMS. High-resolution mass spectra were obtained by the University of Iowa High Resolution Mass Spectrometry Facility. Photolysis experiments were preformed in a Rayonet Reactor with 254nm bulbs. Analytical GLPC were performed on a Hewlett–Packard Model 5890 equipped with a thermal conductivity detector and 3393A integrator. The column was packed with 5% OV-101 on chromo- sorb P. UV measurements (hexane) were made with a Hewlett-Packard 8452A diode array spectrophotometer. All boiling points were determined during fractional distillation using a partial immersion thermometer and are uncorrected. 4 Å molecular sieves (Fisher) were activated by heating under vacuum (300 °C at 0.5 mm Hg) overnight. DMF was dried overnight over CaH₂ and then distilled at reduced pressure. Silica gel was purchased from EM Science (Silica Gel 60, particle sized 0.063-0.200 µm, 70-230 Mesh, ASTM). CuBr was purified by the method reported by Morken [14]. Hexafluorobutyne can be prepared by the zinc dehalogenation of $CF_3CCl_2CCl_2CF_3$ or purchased from PCR Specialty Chemicals. Bromotrifluoroethylene (Halocarbon), DBU, DABCO, and substituted aryl iodides were obtained from commercial sources and used without further purification.

3.2 Activation of Zinc Powder

Zinc powder (70 g) was suspended in 200 mL of water and 3 mL of conc. HCl was added dropwise. After stirring for 15 min, the precipitate was washed with water (3 x 500 mL). The zinc powder was then dried under vacuum for 3 h.

3.3 Preparation of CF₂=CFCu (5),

An oven-dried one-liter 3-necked flask, equipped with a dry ice/IPA condenser, N_2 inlet, septum port, and magnetic stirring bar, was charged with activated Zn powder (19 g, 290 mmol) and dry DMF (300 mL). Then trifluorobromoethylene (16 g, 100 mmol) was then slowly added into this solution. The resultant mixture was gently heated with a heat gun until an exothermic reaction (50-60 °C) occurred. Additional trifluorobromoethylene (32 g, 200 mmol) was then condensed into the solution, maintaining the internal temperature for an additional 3 h, and then unreacted olefin was removed by vacuum. The NMR yield of CF₂=CFZnBr was 62%. A 1000 mL two-necked flask, equipped with dry ice-IPA condenser, N₂ inlet, and septum port was charged with CuBr (29.4 g, 192 mmol). To this flask, the CF₂=CFZnBr/DMF solution (0.62 M, 300 mL, 186 mmol) was transferred by syringe. The reaction mixture was stirred for 20 min at room temperature and then check by ¹⁹F NMR to verify formation of the copper reagent [15]. CF₂=CFZnBr: ¹⁹F NMR (83.9 MHz, JEOL FX-90Q, DMF) -94.7 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fa), -128.9 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fb), -193.3 ppm (dd, 1F, C<u>F</u>=CF₂, Fc), (*J*_{ab} = 93 Hz, *J*_{ac} = 34 Hz, *J*_{bc} = 105 Hz). CF2=CFCu: ¹⁹F NMR (83.9 MHz, JEOL FX-90Q, DMF) -96.1 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fa), -131.3 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fb), -182.8 ppm (dd, 1F, C<u>F</u>=CF₂, Fc), (J_{ab} = 100 Hz, J_{ac} = 32 Hz, J_{bc} = 100 Hz).

3.4 Preparation of $CF_2=CF-C(CF_3)=C(CCF_3)Cu$ (6),

F-2-butyne (33.0 g, 206 mmol) was slowly condensed into the above copper DMF solution of **5** at 0 °C. The reaction mixture was stirred for 3 h at room temperature. The NMR yield (based on CF₂=CFZnBr) was quantitative. ¹⁹F NMR (83.9 MHz, JEOL FX-90Q, DMF) -53.5 ppm (bs, 3F, C<u>F</u>₃, Fa), -58.2 ppm (q, 3F, C<u>F</u>₃, Fb), -102.5 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fc), -115.8 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fd), -158.5 ppm (dd, 1F, C<u>F</u>=CF₂, Fe), (*J*_{cd} = 73 Hz, *J*_{ce} = 28 Hz, *J*_{de} = 117 Hz).

3.5 Preparation of Z-1,1,2,5,5,5-hexafluoro-4-aryl-3-trifluoromethyl-1,3pentadiene derivatives (**1a-f**).

A 250 mL two-necked flask, equipped with magnetic stirrer and septum port was charged with copper compound **6** (42 mL, 26 mmol). Then aryl iodine (18 mmol) was added at once and the solution was heated with an oil bath to 70-80°C and stirred for 16 h under N₂. The cooled reaction mixture was poured into water (50 mL) and ether (100 mL). The ether layer was washed with water (2 x 50 mL) and dried over anhydrous MgSO₄. After filtration, a rotary evaporator removed the solvent. The crude mixture was purified *via* silica gel (70-230 mesh) chromatography (hexane). Yields are also shown in Table 1.

1a: Yield 5.8 g (76%); GLPC purity 97%; ¹⁹F NMR (CDCl₃) -59.6 ppm (q, 3F, -C<u>F</u>₃, Fa), -60.3 ppm (q, 3F, -C<u>F</u>₃, Fb), -99.1 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fc), -111.9 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fd), -165.4 ppm (dd, 1F, -C<u>F</u>=CF₂, Fe), (J_{ab} = 13 Hz, J_{cd} = 61 Hz, J_{ce} = 32 Hz, J_{de} = 117 Hz); ¹H NMR (CDCl₃) 7.2-7.4 ppm (m, 5H); ¹³C {¹H} NMR (CDCl₃) 153.2 ppm (dd, -CF=<u>C</u>F₂, ¹ J_{CF} = 294 Hz, 280 Hz, ² J_{CF} = 46 Hz), 148.3 ppm (q, ϕ -<u>C</u>(CF₃)=C, ² J_{CF} = 32 Hz), 131.9 ppm (s), 130.8 ppm (s), 129.1 ppm (s), 128.1 ppm (s), 126.2 ppm (m, -C(CF₃)=<u>C</u>(CF₃)-CF), 122.4 ppm (ddd, -<u>C</u>F=CF₂, ¹ J_{CF} = 236 Hz, ² J_{CF} = 54 Hz, 24 Hz), 121.1 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 275 Hz), 120.9 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 275 Hz); GC-MS 320 (M⁺,

13), 300 (M⁺-HF, 17), 281 (13), 251 (100), 231 (42), 201 (83), 182 (74), 151 (37); HRMS ($C_{12}H_5F_9$, calculated: 320.0248, observed: 320.0244); UV (cyclohexane) c = 3.29x10⁻⁴, λ max = 206 nm (A = 1.910, ε = 5800), λ = 230 nm (A = 1.360, ε = 4100), 257 nm (A = 1.550, ε = 4700), 280 nm (A = 1.650, ε = 5000); FT-IR (cm⁻¹, CCl₄) 3080 (w, C-H), 1795 (s, -CF=CF₂), 1630 (m), 1446 (s), 1321 (s), 1291 (s), 1238 (s), 1214 (s), 1195 (s) 1182 (s), 1172 (s), 1132 (s), 871 (m), 843 (m), 710 (m).

1b: Yield 83%; GLPC purity 97%; ¹⁹F NMR (CDCl₃) -59.7 ppm (q, 3F, -C<u>F</u>₃, Fa), -60.1 ppm (q, 3F, -C<u>F</u>₃, Fb), -63.7 ppm (s, 3F, φ-C<u>F</u>₃, Fc), -97.0 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fd), -111.0 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fe), -165.9 ppm (dd, 1F, -C<u>F</u>=CF₂, Ff), (*J*_{ab} = 13 Hz, *J*_{de} = 59 Hz, *J*_{df} = 32 Hz, *J*_{ef} = 118 Hz); ¹H NMR (CDCl₃) 7.7 ppm (d, 2H, ³*J*_{HH} = 8 Hz) 7.4 ppm (d, 2H, ³*J*_{HH} = 8 Hz); ¹³C {¹H} NMR (CDCl₃) 152.7 ppm (ddd, -CF=<u>C</u>F₂, ^{*I*}*J*_{CF} = 294 Hz, 280 Hz, ²*J*_{CF} = 45 Hz), 146.1 ppm (m, φ-<u>C</u>(CF₃)=C), 138.1 ppm (s), 134.8 ppm (s), 132.7 ppm (q, -<u>C</u>(CF₃), ²*J*_{CF} = 33 Hz), 127.4 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 266 Hz), 125.9 ppm (s), 123.5 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 272 Hz), 121.5 ppm (m, -<u>C</u>F=CF₂), 120.7 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 266 Hz); GC-MS 388 (M⁺, 5), 369 (M⁺-F, 16), 319 (70), 299 (34), 269 (77), 250 (100), 219 (59), 200 (71) HRMS (C₁₃H₄F₁₂, calculated: 388.0121, observed: 388.0121); UV (cyclohexane) c = 1.93x10⁻⁴, λmax = 212 nm (A = 1.244, ε = 6400), λ = 244 nm (A = 0.607, ε = 3100), 268 nm (A = 0.560, ε = 2900); FT-IR (cm⁻¹, CCl₄) 1795 (s, -CF=CF₂), 1730 (m, C=C), 1500 (w), 1440 (w), 1324 (s) 1292 (s), 1241 (s), 1214 (s), 1178 (s), 1174 (s), 1078 (m), 723 (m).

1c: Yield 87%; GLPC purity 96%; ¹⁹F NMR (CDCl₃) -59.5 ppm (q, 3F, -C<u>F</u>₃, Fa), -60.4 ppm (q, 3F, -C<u>F</u>₃, Fb), -99.5 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fc), -112.3 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fd), -164.9 ppm (dd, 1F, -C<u>F</u>=CF₂, Fe), (*J*_{ab} = 12 Hz, *J*_{cd} = 61 Hz, *J*_{ce} = 32 Hz, *J*_{de} = 117 Hz); ¹H NMR (CDCl₃) 7.2 ppm (d, 2H), 6.9 ppm (d, 2H), 3.8 ppm (s, 3H); ¹³C {¹H} NMR (CDCl₃) 161.8 (s), 153.2 ppm (ddd, -CF=<u>C</u>F₂, ¹*J*_{CF} = 294 Hz, 280 Hz, ²*J*_{CF} = 46 Hz), 148.8 ppm (q, ϕ -<u>C</u>(CF₃)=C, ²*J*_{CF} = 34 Hz), 129.9 ppm (s), 125.2 ppm (m, -C(CF₃)=<u>C</u>(CF₃)-CF), 124.0 ppm (s), 123.0 ppm (ddd, -<u>C</u>F=CF₂, ¹*J*_{CF} = 236 Hz, ²*J*_{CF} = 55 Hz, 26 Hz), 121.2 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 274 Hz), 121.0 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 275 Hz), 114.5 ppm (s), 55.3 ppm (s); GC-MS 351 (M⁺+1, 17), 332 (M⁺-F, 9), 282 (100), 231 (30), 212 (19), 169 (24); HRMS (C₁₃H₇F₉O, calculated: 350.0353, observed: 350.0346); UV (cyclohexane) c = 3.86x10⁻⁴, λmax = 226 nm (A = 2.267, ε = 5000), λ = 310 nm (A = 1.143, ε = 3000); FT-IR (cm⁻¹, CCl₄) 3010 (m), 2962 (m), 2938 (m), 2912(m), 2842 (m), 1787 (s, -CF=CF₂), 1609 (s, C=C), 1513 (s), 1464 (m), 1443 (s), 1419 (s), 1351 (s), 1320 (s), 1290 (s), 1256 (s), 1239 (s), 1214 (s), 1194 (s), 1173 (s), 1132 (s), 874 (s), 828 (s).

1d: Yield 86%; GLPC purity 98%; ¹⁹F NMR (CDCl₃) -59.6 ppm (q, 3F, -C<u>F</u>₃, Fa), -60.3 ppm (q, 3F, -C<u>F</u>₃, Fb), -98.1 ppm (dd, 1F, *cis*-CF=C<u>F</u>₂, Fc), -111.5 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fd), -165.6 ppm (dd, 1F, -C<u>F</u>=CF₂, Fe), (J_{ab} = 13 Hz, J_{cd} = 61 Hz, J_{ce} = 32 Hz, J_{de} = 118 Hz); ¹H NMR (CDCl₃) 7.4 ppm (d, 2H, ³ J_{HH} = 8 Hz), 7.2 ppm (d, 2H, ³ J_{HH} = 8 Hz); ¹³C {¹H} NMR (CDCl₃) 153.1 ppm (ddd, -CF=<u>C</u>F₂, ¹ J_{CF} = 295 Hz, 280 Hz, ² J_{CF} = 46 Hz), 147.2 ppm (q, φ -<u>C</u>(CF₃)=C, ² J_{CF} = 34 Hz), 137.5 ppm (s), 130.2 ppm (s), 129.8 ppm (s), 129.6 ppm (s), 126.3 ppm (m, -C(CF₃)=<u>C</u>(CF₃)-CF), 122.2 ppm (ddd, -<u>C</u>F=CF₂, ¹ J_{CF} = 238 Hz, ² J_{CF} = 53 Hz, 26 Hz), 120.8 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 275 Hz), 120.8 ppm (two

peak overlapping, q, -<u>C</u>F₃, ¹*J*_{CF} = 275 Hz); GC-MS 356 (M⁺+2, 6), 354 (M⁺, 16), 319 (M⁺-Cl, 97), 287 (23), 285 (78), 269 (78), 250 (100), 235 (41), 200 (50); HRMS (C₁₂H₄F₉Cl, calculated: 353.9858, observed: 353.9854); UV (cyclohexane) c = 4.24x10⁻⁴, λ max = 220 nm (A = 1.526, ε = 3600), λ = 258 nm (A = 0.587, ε = 1380), λ = 284 nm (A = 0.568, ε = 1340); FT-IR (cm⁻¹, CCl₄) 1780 (s, -CF=CF₂), 1620 (w), 1595 (m), 1492 (m), 1351 (s), 1320 (s), 1291 (s), 1285 (s), 1266 (s), 1241 (s), 1233 (s), 1222 (s), 1212 (s), 1192 (s), 1182 (s), 1176 (s), 1163 (s), 1152 (s), 1134 (s), 1095 (s), 1019 (m), 872 (m), 820 (m).

1e: Yield 91%; GLPC purity 96%; ¹⁹F NMR (CDCl₃) -59.6 ppm (q, 3F, -C<u>F</u>₃, Fa), -60.4 ppm (q, 3F, -CF₃, Fb), -99.4 ppm (dd, 1F, *cis*-CF=CF₂, Fc), -112.1 ppm (dd, 1F, *trans*- $CF=CF_2$, Fd), -165.1 ppm (dd, 1F, -CF=CF₂, Fe), (J_{ab} = 13 Hz, J_{cd} = 62 Hz, J_{ce} = 32 Hz, J_{de} = 117 Hz); ¹H NMR (CDCl₃) 7.1-7.3 ppm (m, 4H), 2.4 ppm (s, 3H); ¹³C {¹H} NMR $(CDCl_3)$ 153.5 ppm (ddd, -CF=<u>C</u>F₂, ¹/_{CF} = 294 Hz, 280 Hz, ²/_{CF} = 48 Hz), 148.7 ppm (q, ϕ -C(CF₃)=C, ²/_{CF} = 34 Hz), 139.3 ppm (s), 132.0 ppm (s), 131.6 ppm (s), 129.0 ppm (s), 128.7 ppm (s), 126.7 ppm (m, -C(CF₃)=<u>C(CF₃)-CF</u>), 125.3 ppm (s), 122.5 ppm $(ddd, -CF = CF_2, ^1/_{CF} = 240 \text{ Hz}, ^2/_{CF} = 55 \text{ Hz}, 26 \text{ Hz}), 121.2 \text{ ppm} (q, -CF_3, ^1/_{CF} = 276 \text{ Hz}),$ 121.0 ppm (q, $-CF_3$, $^1J_{CF}$ = 276 Hz), 21.4 ppm (s); GC-MS 334 (M⁺, 21), 295 (9), 265 (100), 245 (26), 215 (72), 196 (46), 146 (26); HRMS (C₁₃H₇F₉, calculated: 334.0404, observed: 334.0396); UV (cyclohexane) $c = 2.54 \times 10^{-4}$, $\lambda max = 206 \text{ nm}$ (A = 0.587, $\varepsilon =$ 2310), $\lambda = 268$ nm (A = 0.026, $\varepsilon = 100$); FT-IR (cm⁻¹, CCl₄) 3042 (w), 3031 (w), 2960 (w, C-H), 2928 (w, C-H), 1789 (s, -CF=CF₂), 1606 (w), 1487 (m), 1353 (m), 1319 (s), 1294 (s), 1289 (s), 1251 (s), 1244 (s), 1230 (s), 1225 (s), 1219 (s), 1213 (s), 1210 (s), 1201 (s), 1190 (s), 1181 (s), 1172 (s), 1166 (s), 1162 (s), 1132 (s), 848 (m), 723 (m), 621 (m).

1f: Yield 52%; mp 141-142 °C; ¹⁹F NMR (376 MHz, JEOL GX-400, CDCl₃) -60.2 ppm (qm, 3F, -C<u>F</u>₃, Fa), -60.5 ppm (qm, 3F, -C<u>F</u>₃, Fb), -98.6 ppm (ddm, 1F, *cis*-CF=C<u>F</u>₂, Fc), -111.6 ppm (dd, 1F, *trans*-CF=C<u>F</u>₂, Fd), -166.6 ppm (ddm, 1F, -C<u>F</u>=CF₂, Fe), (*J*_{ab} = 13 Hz, *J*_{cd} = 59 Hz, *J*_{ce} = 33 Hz, *J*_{de} = 117 Hz); ¹H NMR (400 MHz, JEOL GX-400, CDCl₃) 7.4 ppm (s, 4H); ¹³C {¹H} NMR (100 MHz, JEOL GX-400, CDCl₃) 152.6 ppm (ddd, -CF=<u>C</u>F₂, ¹*J*_{CF} = 297 Hz, 281 Hz, ²*J*_{CF} = 46 Hz), 146.2 ppm (qm, ϕ -<u>C</u>(CF₃)=C, ²*J*_{CF} = 34 Hz), 133.5 ppm (s), 128.3 ppm (s), 126.3 ppm (m, -C(CF₃)=<u>C</u>(CF₃)-CF), 121.7 ppm (ddd, -<u>C</u>F=CF₂, ¹*J*_{CF} = 236 Hz, ²*J*_{CF} = 54 Hz, 24 Hz), 120.3 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 269 Hz), 120.1 ppm (q, -<u>C</u>F₃, ¹*J*_{CF} = 269 Hz);GC-MS 562 (M⁺, 3), 493 (26), 423 (20), 355 (40), 305 (42), 250 (42), 69 (CF₃, 100); HRMS (C₁₈H₄F₁₈, calculated: 562.0026, observed: 562.0027); UV (cyclohexane) c = 1.78x10⁻⁴, λmax = 216 nm (A = 1.784, ε = 10000), λ = 254 nm (A = 1.554, ε = 8700), λ = 272 nm (A = 1.526, ε = 8600); FT-IR (cm⁻¹, CCl₄) 1790 (m, -CF=CF₂), 1324 (s), 1292 (s), 1267 (s), 1239 (s), 1217 (s), 1194 (s), 1177 (s), 1134 (s), 867 (w), 721 (w), 715 (w).

3.6 Preparation of 1,2-difluoro-3,4-bis(trifluoromethyl)naphthalene (**2a-e**), 1,1,2-

trifluoro-3,4-bis(trifluoromethyl)-1,4-dihydronaphthalene (**3a-e**), anthracene (**7**) and

phenanthrene (8) via photocyclization.

Compound **1** (1.0g) was dissolved in hexane (10 mL) in a Rotaflo quartz tube.

After freezing this solution in liq. N₂, the tube was degassed by a vacuum pump.

Then the solution was thawed and placed in the photoreactor (254 nm). After

reaction the solvent was evaporated and the obtained residue was purified via silica

gel (70-230 mesh) chromatography (hexane) to yield 2 and 3. Yields are shown in

Table 2.

2a: Yield 430 mg (46%); mp 141-142 °C; ¹⁹F NMR (CDCl₃) -50.6 ppm (q, 3F, -C(C<u>F₃</u>)=C(CF₃)-CF=, Fa), -53.3 ppm (dq, 3F, -C(CF₃)=C(C<u>F₃</u>)-CF=, Fb), -138.5 ppm (d, 1F, -C(CF₃)-CF=C<u>F</u>-, Fc), -143.5 ppm (dq, 1F, -C(CF₃)-C<u>F</u>=CF-, Fd), (J_{ab} = 17 Hz, J_{bd} = 33 Hz, J_{cd} = 18 Hz); ¹H NMR (CDCl₃) 8.3-7.7 ppm (m, 4H); ¹³C {¹H} NMR (acetone-d₆) 148.9 ppm (dd, -<u>C</u>F=CF-, ¹ J_{CF} = 258 Hz, ² J_{CF} = 14 Hz), 144.4 ppm (dd, -CF=<u>C</u>F-, ¹ J_{CF} = 255 Hz, ² J_{CF} = 14 Hz), 131.2 ppm (s), 130.3 ppm (s), 128.1 ppm (bs), 126.6 ppm (m), 125.5 ppm (m), 124.0 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 276 Hz), 123.7 ppm (qm, -<u>C</u>(CF₃), ² J_{CF} = 34 Hz), 123.1 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 277 Hz), 121.1 ppm (bs); GC-MS 301 (M⁺+1, 12), 300 (M⁺, 100), 423 (28), 250 (100), 231 (40), 211 (12); HRMS (C₁₂H₄F₈, calculated: 300.0185, observed: 300.0193); UV (cyclohexane) c = 6.83x10⁻⁵, λ max = 228 nm (A = 2.966, ε = 43400), λ = 281 nm (A = 0.4177, ε = 6100), λ = 334 nm (A = 0.2945, ε = 4300); FT-IR (cm⁻¹, CCl₄) 1650 (m), 1616 (m), 1467 (m), 1402 (s), 1379 (s), 1315 (s), 1237 (s), 1211 (s), 1176 (s), 1141 (s), 952 (w).

2b: Yield 53%; GLPC purity 97%; ¹⁹F NMR (CDCl₃) -51.4 ppm (q, 3F, -C(C<u>F</u>₃)=C(CF₃)-CF=, Fa), -54.4 ppm (dq, 3F, -C(CF₃)=C(C<u>F</u>₃)-CF=, Fb), -64.2 ppm (s, 3F, -C<u>F</u>₃, Fc) -136.4 ppm (d, 1F, -C(CF₃)-CF=C<u>F</u>-, Fd), -139.6 ppm (dq, 1F, -C(CF₃)-C<u>F</u>=CF-, Fe), (J_{ab} = 16 Hz, J_{be} = 32 Hz, J_{de} = 17 Hz); ¹H NMR (CDCl₃) 8.5 ppm (s, 1H), 8.4 ppm (d, 1H, ³J_{HH} = 8 Hz), 7.9 ppm (d, 1H, ³J_{HH} = 8 Hz); ¹³C {¹H} NMR (CDCl₃) 148.9 ppm (dd, -<u>C</u>F=CF-, ¹J_{CF} = 263 Hz, ²J_{CF} = 14 Hz), 144.7 ppm (dd, -CF=<u>C</u>F-, ¹J_{CF} = 262 Hz, ²J_{CF} = 14 Hz), 132.1 ppm (q, -<u>C</u>(CF₃), ²J_{CF} = 34 Hz), 128.8 ppm (s), 127.9 ppm (m), 126.6 ppm (qm, -<u>C</u>(CF₃)=C(CF₃)-CF=, ²J_{CF} = 39 Hz), 125.5 ppm (d, -CF=<u>C</u>F-, ²J_{CF} = 14 Hz), 124.7 ppm (s), 123.5 ppm (q, -<u>C</u>F₃, ¹J_{CF} = 273 Hz), 122.8 ppm (q, -<u>C</u>F₃, ¹J_{CF} = 274 Hz), 121.6 ppm (q, -<u>C</u>F₃, ¹J_{CF} = 277 Hz), 118.6 ppm (q, -C(CF₃)=C(CF₃)-<u>C</u>, ³J_{CF} = 5 Hz); GC-MS 368 (M⁺, 92), 349 (M⁺-F, 44), 318 (38), 299 (100), 249 (33), 229 (21), 211 (25); HRMS (C₁₃H₃F₁₁, calculated: 368.0059, observed: 368.0059); UV (cyclohexane) c = 2.98x10⁻⁵, λ max = 224 nm (A = 2.091, ε = 70200), λ = 276 nm (A = 0.1920, ε = 6400), λ = 336 nm (A = 0.1374, ε = 4600); FT-IR (cm⁻¹, CCl₄) 3100 (w), 1680 (m), 1648 (s), 1631 (s), 1434 (s), 1393 (s), 1327 (s), 1291 (s), 1232 (s), 1208 (s), 1177 (s), 1145 (s), 1125 (s), 1074 (s), 1027 (s), 902 (s), 861 (s), 855 (m), 697 (m).

2c: Yield 50%; GLPC purity 98%; ¹⁹F NMR (CDCl₃) -51.3 ppm (q, 3F, -C(C<u>F</u>₃)=C(CF₃)-CF=, Fa), -53.7 ppm (dq, 3F, -C(CF₃)=C(C<u>F</u>₃)-CF=, Fb), -140.3 ppm (d, 1F, -C(CF₃)-CF=C<u>F</u>-, Fc), -142.2 ppm (dq, 1F, -C(CF₃)-C<u>F</u>=CF-, Fd), (J_{ab} = 16 Hz, J_{bd} = 32 Hz, J_{cd} = 16 Hz); ¹H NMR (CDCl₃) 8.0 ppm (d, 1H), 7.1 ppm (m, 2H), 3.9 ppm (s, 3H); ¹³C {¹H} NMR (CDCl₃) 160.6 ppm (s),147.1 ppm (dd, -<u>C</u>F=CF-, ¹ J_{CF} = 257 Hz, ² J_{CF} = 14 Hz), 144.3 ppm (dd, -CF=<u>C</u>F-, ¹ J_{CF} = 256 Hz, ² J_{CF} = 14 Hz), 128.1 ppm (m), 127.9 ppm (s), 124.0 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 276 Hz), 123.3 ppm (q, <u>C</u>-C(CF₃)=C(CF₃)-, ² J_{CF} = 36 Hz), 123.0 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 276 Hz), 122.9 ppm (s), 122.3 ppm (s), 117.1 ppm (m), 97.6 ppm (q, ⁴ J_{CF} = 6 Hz), 55.8 ppm (s); GC-MS 331 (M⁺+1, 11), 330 (M⁺, 100), 311 (M⁺-F, 21), 287 (30), 268 (10), 237 (13), 218 (30); HRMS (C₁₃H₆F₈O, calculated: 330.0291, observed: 330.0280); UV (cyclohexane) c = 4.48x10⁻⁵, λ max = 245 nm (A = 2.426, ε = 54000), λ = 304 nm (A = 0.3141, ε = 7000); FT-IR (cm⁻¹, CCl₄) 2970 (w), 2940 (w), 1720 (w), 1620 (m), 1485 (m), 1312 (s), 1300 (s), 1279 (s), 1258 (s), 1245 (s), 1231 (s), 1222 (s), 1205 (s), 1171 (s), 1141 (m), 879 (m).

2d: Yield 59%; GLPC purity >99%; ¹⁹F NMR (CDCl₃) -51.4 ppm (q, 3F, -C(C<u>F</u>₃)=C(CF₃)-CF=, Fa), -54.2 ppm (dq, 3F, -C(CF₃)=C(C<u>F</u>₃)-CF=, Fb), -138.2 ppm (d, 1F, -C(CF₃)-CF=CF-, Fc), -140.1 ppm (dq, 1F, -C(CF₃)-C<u>F</u>=CF-, Fd), (J_{ab} = 16 Hz, J_{bd} = 32 Hz, J_{cd} = 18 Hz); ¹H NMR (CDCl₃) 8.2 ppm (dm, 1H, ³ J_{HH} = 9 Hz), 8.0 ppm (s, 1H), 7.5 ppm (dm, 1H, ³ J_{HH} = 9 Hz); ¹³C {¹H} NMR (CDCl₃) 147.3 ppm (dd, -<u>C</u>F=CF-, ¹ J_{CF} = 261 Hz, ² J_{CF} = 14 Hz), 144.6 ppm (dd, -CF=<u>C</u>F-, ¹ J_{CF} = 259 Hz, ² J_{CF} = 14 Hz), 137.1 ppm (s), 130.0 ppm (s), 128.0 ppm (s), 126.1 ppm (d, <u>C</u>-CF=CF-, ² J_{CF} = 12 Hz), 125.7 ppm (s), 124.1 ppm (m), 122.3 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 277Hz), 121.9 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 277 Hz), 120.6 ppm (m), 119.4 ppm (m); GC-MS 336 (M⁺+2, 43), 334 (M⁺, 100), 315 (M⁺⁻F, 22), 299 (23), 284 (20), 265 (31); HRMS (C₁₂H₃F₈³⁵Cl, calculated: 333.9796, observed: 333.9797); UV (cyclohexane) c = 3.29x10⁻⁵, λ max = 236 nm (A = 1.427, ε = 43400), λ = 290 nm (A = 0.1561, ε = 4700), λ = 336 nm (A = 0.0566, ε = 1700); FT-IR (cm⁻¹, CCl₄) 2990 (w), 2880 (w), 1790 (w), 1641 (m), 1615 (m), 1609 (w), 1495 (m), 1463 (m), 1455 (m), 1433 (m), 1386 (m), 1322 (m), 1297 (s), 1269 (s), 1205 (s), 1193 (s), 1178 (s), 1143 (s), 1027 (m), 858 (m), 821 (m).

2e: GLPC Yield 25%; ¹⁹F NMR (CDCl₃) -51.4 ppm (m, 3F, $-C(CF_3)=C(CF_3)-CF=$, Fa), -54.2 ppm (m, 3F, $-C(CF_3)=C(CF_3)-CF=$, Fb), -129.7 ppm (m, 1F, $-C(CF_3)-CF=CF-$, Fd), -143.0 ppm (dq, 1F, $-C(CF_3)-CF=CF-$, Fc), ($J_{bc} = 34$ Hz, $J_{cd} = 14$ Hz); ¹H NMR (CDCl₃) 7.9-7.4 ppm (m, 3H), 2.8 ppm (d, 3H, ⁵ $J_{HF} = 8$ Hz); GC-MS 315 (M⁺+1, 13), 314 (M⁺, 100), 295 (27), 263 (12), 245 (99), 224 (28), 175 (27).

2e': GLPC Yield 36%; ¹⁹F NMR (CDCl₃) -51.4 ppm (m, 3F, -C(C<u>F₃</u>)=C(CF₃)-CF=, Fa), -54.0 ppm (m, 3F, -C(CF₃)=C(C<u>F₃</u>)-CF=, Fb), -139.2 ppm (d, 1F, -C(CF₃)-CF=C<u>F</u>-, Fc), -144.1 ppm (dq, 1F, -C(CF₃)-C<u>F</u>=CF-, Fd), (*J*_{bd} = 34 Hz, *J*_{cd} = 18 Hz); ¹H NMR (CDCl₃) 7.9-7.4 ppm (m, 3H), 2.5 ppm (s, 3H); GC-MS 315 (M++1, 13), 314 (M+, 100), 295 (M+-F, 27), 263 (13), 245 (98), 224 (32), 175 (18).

3a: Yield 190 mg (19%); GLPC purity 99%; ¹⁹F NMR (CDCl₃) -60.7 ppm (m, 3F, -CH(CE₃)-C(CF₃)=, Fa), -69.6 ppm (s, 3F, -CH(CF₃)-C(C<u>F₃</u>)=CF-, Fb), -85.3 ppm (dd, 1F, =CF-<u>F</u>₂-, Fc), -101.3 ppm (dd, 1F, =CF-<u>F</u>₂-, Fd), -114.9 ppm (m, 1F, =C<u>F</u>-CF₂-, Fe), (J_{cd} = 304 Hz, J_{ce} = 30 Hz, J_{de} = 13 Hz); ¹H NMR (CDCl₃) 7.9-7.5 ppm (m, 4H), 4.6 ppm (qm, 1H, -C<u>H</u>(CF₃)-, ³ J_{HF} = 7 Hz); ¹³C {¹H} NMR (CDCl₃) 156.7 ppm (dt, =<u>C</u>F-CF₂-, $^{1}J_{CF}$ = 294 Hz, ² J_{CF} = 29 Hz), 131.6 ppm (s) 131.0 ppm (t, <u>C</u>-CF₂-CF₌, ² J_{CF} = 24 Hz), 130.3 ppm (s), 129.6 ppm (s), 127.4 ppm (s), 126.2 ppm (s), 124.1 ppm (q, -<u>C</u>F₃, $^{1}J_{CF}$ = 277 Hz), 121.8 ppm (q, -<u>C</u>F₃, $^{1}J_{CF}$ = 272 Hz), 111.1 ppm (q, -CH(CF₃)-<u>C</u>(CF₃)=CF-, ² $^{2}J_{CF}$ = 30 Hz), 109.9 ppm (ddd, =CF-<u>C</u>F₂-, $^{1}J_{CF}$ = 239 Hz, 236 Hz, $^{2}J_{CF}$ = 23 Hz), 43.7 ppm (q, -<u>C</u>H(CF₃)-, $^{2}J_{CF}$ = 31 Hz); GC-MS 320 (M⁺, 13), 301 (8), 251 (100), 232 (24), 201 (63), 182 (63); HRMS (C₁₂H₅F₉, calculated: 320.0248, observed: 320.0249); UV (cyclohexane) c = 3.28x10⁻⁴, λ max = 216 nm (A = 1.565, ε = 4800), λ = 272 nm (A = 0.2328, ε = 710); FT-IR (cm⁻¹, CCl₄) 2828 (w, C-H), 2853 (w), 1721 (m), 1461 (w), 1392 (m), 1315 (s), 1303 (s), 1260 (s), 1244 (s), 1184 (s), 1162 (s), 1138 (s), 1118 (s), 1059 (m), 992 (m), 658 (m).

3b: Yield 26%; GLPC purity 95%; ¹⁹F NMR (CDCl₃) -60.7 ppm (m, 3F, -CH(CF₃)-C(CF₃)=, Fa), -63.7 ppm (s, 3F, -CH(CF₃)-C(CF₃)=CF-, Fb), -69.2 ppm (s, 3F, -CF₃, Fc), -85.4 ppm (dd, 1F, =CF-F₂-, Fd), -101.6 ppm (dd, 1F, =CF-F₂-, Fe), -114.1 ppm (m, 1F, $=CE-CF_2$, Ff), ($J_{aH} = 7 Hz$, $J_{de} = 306 Hz$, $J_{df} = 13 Hz$, $J_{ef} = 21 Hz$); ¹H NMR (CDCl₃) 8.1 ppm (s, 1H), 7.9 ppm (d, 1H, ${}^{3}I_{HH}$ = 7 Hz), 7.7 ppm (d 1H, ${}^{3}I_{HH}$ = 7 Hz), 4.6 ppm (q, 1H, $-CH(CF_3)$, ${}^{3}/_{HF} = 7$ Hz); ${}^{13}C$ { ^{1}H } NMR (CDCl₃) 156.4 ppm (dt, =<u>C</u>F-CF₂-, ${}^{1}/_{CF} = 294$ Hz, ${}^{2}I_{CF} = 27 \text{ Hz}$, 133.3 ppm (q, -<u>C</u>(CF₃), ${}^{2}I_{CF} = 34 \text{ Hz}$), 132.1 ppm (t, <u>C</u>-CF₂-CF=, ${}^{2}I_{CF} = 21$ Hz), 131.1 ppm (s), 130.5 ppm (s), 128.4 ppm (s), 123.8 ppm (q, $-CF_3$, $^1J_{CF} = 272$ Hz), 123.6 ppm (q, $-\underline{C}F_3$, $^1J_{CF}$ = 277 Hz), 123.6 ppm (s), 121.3 ppm (q, $-\underline{C}F_3$, $^1J_{CF}$ = 284 Hz), 111.1 ppm (m, -CH(CF₃)-<u>C</u>(CF₃)=CF-), 109.3 ppm (ddd, =CF-<u>C</u>F₂-, ¹/_{CF} = 238 Hz, 235 Hz, ${}^{2}/_{CF}$ = 23 Hz), 43.8 ppm (q, $-\underline{C}$ H(CF₃)-, ${}^{2}/_{CF}$ = 31 Hz); GC-MS 388 (M⁺, 8), 369 (M⁺-F, 14), 319 (100), 300 (20), 269 (61), 265 (61), 200 (26); HRMS (C₁₃H₄F₁₂, calculated: 388.0121, observed: 388.0118); UV (cyclohexane) $c = 2.58 \times 10^{-4}$, $\lambda max = 226 \text{ nm}$ (A = 0.893, ε = 3500), λ = 338 nm (A = 0.075, ε = 290); FT-IR (cm⁻¹, CCl₄) 1720 (w), 1443 (w), 1388 (w), 1343 (w), 1316 (m), 1282 (m), 1246 (s), 1232 (s), 1198 (s), 1186 (s), 1165 (s), 1146 (s), 1124 (m), 1095 (m), 1067 (w), 911 (w).

3c: Yield 24%; GLPC purity 95%; ¹⁹F NMR (CDCl₃) -60.7 ppm (m, 3F, -CH(C<u>F</u>₃)-C(CF₃)=, Fa), -69.9 ppm (s, 3F, -CH(CF₃)-C(C<u>F</u>₃)=CF-, Fb), -85.4 ppm (dd, 1F, =CF-<u>F</u>₂-, Fc), -101.4 ppm (dd, 1F, =CF-<u>F</u>₂-, Fd), -115.5 ppm (m, 1F, =C<u>F</u>-CF₂-, Fe), (J_{cd} = 304 Hz, J_{ce} = 23 Hz, J_{de} = 14 Hz); ¹H NMR (CDCl₃) 7.4 ppm (d, 1H, ³ J_{HH} = 9 Hz), 7.3 ppm (s), 7.1 ppm (d, 1H, ³ J_{HH} = 9 Hz) 4.5 ppm (qm, 1H, -C<u>H</u>(CF₃)-, ³ J_{HF} = 7 Hz), 3.9 ppm (s, 3H); ¹³C {¹H} NMR (CDCl₃) 161.2 ppm (s),156.8 ppm (dt, =<u>C</u>F-CF₂-, ¹ J_{CF} = 293 Hz, ² J_{CF} = 29=8 Hz), 132.2 ppm (t, <u>C</u>-CF₂-CF=, ² J_{CF} = 24 Hz), 131.0 ppm (s), 124.0 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 282 Hz), 121.3 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 275 Hz), 119.3 ppm (bs), 118.9 ppm (s), 109.7 ppm (m), 110.2 ppm (m), 109.7 ppm (ddd, =CF-<u>C</u>F₂-, ¹ J_{CF} = 239 Hz, 236 Hz, ² J_{CF} = 24 Hz), 55.8 ppm (s), 43.3 ppm (q, -<u>C</u>H(CF₃)-, ² J_{CF} = 31 Hz); GC-MS 350 (M⁺, 22), 331

(M⁺-F, 9), 281 (100), 231 (23), 212 (40), 169 (32); HRMS (C₁₃H₇F₉O, calculated: 350.0353, observed: 350.0358); UV (cyclohexane) c = 3.14×10^{-4} , $\lambda max = 212 \text{ nm}$ (A = 1.038, $\varepsilon = 3300$), $\lambda = 242 \text{ nm}$ (A = 0.625, $\varepsilon = 2000$), $\lambda = 334 \text{ nm}$ (A = 0.468, $\varepsilon = 1500$); FT-IR (cm⁻¹, CCl₄) 2959 (w), 2930 (w), 1723 (m), 1682 (m), 1656 (m), 1649 (m), 1636 (m), 1624 (m), 1594 (m), 1550 (m), 1449 (m), 1410 (s), 1340 (m), 1306 (m), 1274 (m), 1264 (m), 1231 (m), 1210 (s), 1202 (s), 1192 (s), 1168 (s), 1148 (s), 1003 (w), 908 (m).

3d: Yield 14%; GLPC purity 95%; ¹⁹F NMR (CDCl₃) -60.8 ppm (m, 3F, -CH(CF₃)-C(CF₃)=, Fa), -69.5 ppm (s, 3F, -CH(CF₃)-C(CF₃)=CF-, Fb), -85.5 ppm (dd, 1F, =CF-F₂-, Fc), -101.5 ppm (dd, 1F, =CF-<u>F</u>₂-, Fd), -114.7 ppm (m, 1F, =C<u>F</u>-CF₂-, Fe), (*J*_{FH} = 6 Hz, *J*_{cd} = 305 Hz, *J*_{ce} = 23 Hz, *J*_{de} = 14 Hz); ¹H NMR (CDCl₃) 7.8 ppm (m, 1H), 7.6 ppm (dm, 1H, 3 /_{HH} = 8 Hz), 7.4 ppm (d, 1H, 3 /_{HH} = 8 Hz), 4.5 ppm (q, 1H, -C<u>H</u>(CF₃)-, 3 /_{HF} = 6 Hz); ¹³C {¹H} NMR (CDCl₃) 156.7 ppm (dt, =<u>C</u>F-CF₂-, ¹ J_{CF} = 294 Hz, ² J_{CF} = 28 Hz), 137.3 ppm (s), 133.4 ppm (t, C-CF₂-CF=, ${}^{2}/_{CF}$ = 28 Hz), 132.2 ppm (s), 131.2 ppm (s), 126.8 ppm (m), 126.0 ppm (s), 124.0 ppm (q, $-CF_3$, $^1J_{CF} = 274$ Hz), 121.3 ppm (q, $-CF_3$, $^1J_{CF} =$ 274 Hz), 111.1 ppm (m), 109.4 ppm (ddd, =CF- \underline{CF}_2 -, $\frac{1}{CF}$ = 240 Hz, 239 Hz, $\frac{2}{CF}$ = 24 Hz), 43.7 ppm (q, $-CH(CF_3)$ -, ${}^{2}/_{CF}$ = 31 Hz); GC-MS 354 (M⁺, 15), 335 (M⁺-F, 7), 287 (41), 285 (100), 250 (22), 235 (44), 216 (54); HRMS (C₁₂H₄F₉³⁵Cl, calculated: 353.9858, observed: 353.9844); UV (cyclohexane) $c = 3.53 \times 10^{-4}$, $\lambda max = 220 \text{ nm}$ (A = 2.013, ε = 5700), λ = 272 nm (A = 0.172, ε = 500), λ = 282 nm (A = 0.163, ε = 460); FT-IR (cm⁻¹, CCl₄) 1710 (m), 1492 (w), 1430 (w), 1382 (m), 1316 (m), 1299 (m), 1278 (m), 1244 (s), 1232 (s), 1204 (s), 1196 (s), 1186 (s), 1165 (s), 1142 (s), 1122 (s), 1110 (s), 1065 (s), 855 (m).

3e: GLPC Yield 7%; ¹⁹F NMR (CDCl₃) -60.9 ppm (m, 3F, -C<u>F</u>₃, Fa), -69.9 ppm (s, 3F, -C<u>F</u>₃, Fb), -93.8 ppm (dd, 1F, =CF-<u>F</u>₂-, Fc), -95.8 ppm (dd, 1F, =CF-<u>F</u>₂-, Fd), -115.4 ppm (m, 1F, =C<u>F</u>-CF₂-, Fe), (*J*_{cd} = 309 Hz, *J*_{ce} = 22 Hz, *J*_{de} = 14 Hz); ¹H NMR (CDCl₃) 7.7-7.3 ppm (m, 3H), 4.5 ppm (m, 1H) 2.6 ppm (m, 3H); GC-MS 334 (M⁺, 58), 315 (M⁺-F, 18), 283 (60), 265 (100), 245 (26), 215 (27), 196 (81).

3e': GLPC Yield 18%; ¹⁹F NMR (CDCl₃) -60.9 ppm (m, 3F, -C<u>F</u>₃, Fa), -69.6 ppm (s, 3F, -C<u>F</u>₃, Fb), -84.9 ppm (dd, 1F, =CF-<u>F</u>₂-, Fc), -101.1 ppm (dd, 1F, =CF-<u>F</u>₂-, Fd), -115.1 ppm (m, 1F, =C<u>F</u>-CF₂-, Fe), (*J*_{ae} = 13 Hz, *J*_{cd} = 303 Hz, *J*_{ce} = 23 Hz); ¹H NMR (CDCl₃) 7.7-7.3 ppm (m, 3H), 4.5 ppm (m, 1H), 2.4 ppm (m, 3H); GC-MS 334 (M⁺, 24), 265 (100), 246 (14), 215 (48), 196 (29), 146 (15).

7: Yield 7%; mp 155-156 °C; ¹⁹F NMR (acetone-d₆) -51.7 ppm (q, 6F, -C(C<u>F</u>₃)=C(CF₃)-CF=, Fa), -54.6 ppm (dq, 6F, -C(CF₃)=C(C<u>F</u>₃)-CF=, Fb), -136.1 ppm (d, 2F, =C(CF₃)-CF=C<u>F</u>-, Fc), -140.3 ppm (qd, 2F, =C(CF₃)-C<u>F</u>=CF-, Fd), (J_{ab} = 16 Hz, J_{bd} = 32 Hz, , J_{cd} = 15 Hz); ¹H NMR (acetone-d₆) 9.3 ppm (s, 2H); ¹³C {¹H} NMR (acetone-d₆) 149.0 ppm (dd, -<u>C</u>F=CF-, ¹ J_{CF} = 262 Hz, ² J_{CF} = 14 Hz), 144.1 ppm (dd, -CF=<u>C</u>F-, ¹ J_{CF} = 257 Hz, ² J_{CF} = 14 Hz), 126.2 ppm (s), 125.3 ppm (d, <u>C</u>-CF=CF-, ² J_{CF} = 13 Hz), 124.8 ppm (m), 123.7 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 271 Hz), 122.4 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 276 Hz), 120.6 ppm (s); GC-MS 523 (M⁺+1, 17), 522 (M⁺, 100), 503 (M⁺-F, 33), 472 (25), 453 (42), 315 (25); HRMS (C₁₈H₂F₁₆, calculated: 521.9901, observed: 521.9924); UV (cyclohexane) c = 5.42x10⁻

⁵, $\lambda \max = 260 \text{ nm}$ (A = 2.80, $\varepsilon = 51700$), $\lambda = 205 \text{ nm}$ (A = 1.48, $\varepsilon = 27300$), $\lambda = 400 \text{ nm}$ (A = 0.190, $\varepsilon = 3500$), $\lambda = 430 \text{ nm}$ (A = 0.230, $\varepsilon = 4250$); FT-IR (cm⁻¹, CCl₄) 1631 (m), 1549 (w), 1455 (m), 1441 (w), 1430 (w), 1385 (m), 1372 (m), 1360 (m), 1329 (s), 1294 (s), 1261 (s), 1232 (s), 1182 (s), 1146 (s), 1058 (w), 934 (w).

8: Yield 28%; mp 129-130 °C; ¹⁹F NMR (CDCl₃) -50.0 ppm (q, 6F, -C(C<u>F</u>₃)=C(CF₃)-CF=, Fa), -54.5 ppm (dq, 6F, -C(CF₃)=C(C<u>F</u>₃)-CF=, Fb), -115.7 ppm (bs, 2F, -C(CF₃)-CF=C<u>F</u>-, Fc), -134.2 ppm (qm, 2F, -C(CF₃)-C<u>F</u>=CF-, Fd), (J_{ab} = 16 Hz, J_{bd} = 34 Hz); ¹H NMR (CDCl₃) 8.2 ppm (s, 2H); ¹³C {¹H} NMR (CDCl₃) 150.1 ppm (dd, -<u>C</u>F=CF-, ¹ J_{CF} = 267 Hz, ² J_{CF} = 15 Hz), 147.6 ppm (dm, -CF=<u>C</u>F-, ¹ J_{CF} = 265 Hz), 128.2 ppm (s), 125.7 ppm (m), 124.5 ppm (dm, <u>C</u>-CF=CF-, ² J_{CF} = 31 Hz), 123.8 ppm (m), 122.7 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 276 Hz), 122.6 ppm (m, ² J_{CF} = 33 Hz), 121.5 ppm (q, -<u>C</u>F₃, ¹ J_{CF} = 275 Hz), 118.4 ppm (bs); GC-MS 523 (M⁺+1, 18), 522 (M⁺, 100), 503 (M⁺-F, 30), 472 (27), 453 (33), 315 (13); HRMS (C₁₈H₂F₁₆, calculated: 521.9901, observed: 521.9879); UV (cyclohexane) c = 5.43x10⁻⁵, λmax = 260 nm (A = 2.17, ε = 40000), λ = 205 nm (A = 1.68, ε = 310), λ = 300 nm (A = 0.415, ε = 7650), λ = 310 nm (A = 0.415, ε = 7650); FT-IR (cm⁻¹, CCl₄) 1600 (w), 1493 (w), 1454 (w), 1434 (m), 1416 (m), 1352 (m), 1334 (m), 1292 (m), 1274 (m), 1250 (w), 1221 (s), 1200 (s), 1178 (s), 1145 (s), 1080 (w), 1010 (w), 902 (w), 871 (w).

3.7 Conversion of **3a** into **2a** (NMR tube scale).

The isolated **3a** (60 mg, 0.20 mmol) was dissolved with CDCl₃ (1.0 mL) and DABCO (30 mg, 0.27 mmol) was added. After 30 min at room temperature, the reaction mixture was checked by ¹⁹F-NMR. Spectral data matched well with that obtained for the previously isolated **2a**. The conversion was quantitative. Additionally, the isolated **3a** (100 mg) was dissolved in hexane (1.0 mL) and this solution was put into the photoreactor using the same method as in *3.6*. After 2 days, no photoconversion to **2a** was observed.

3.8 Conversion of **3e/3e'** into **2e/2e'** (NMR tube scale).

The mixture of **3e/3e'** (80 mg, 0.20 mmol) was dissolved with CDCl₃ (1.0 mL) and DBU (35 mg, 0.23 mmol) was added. After 30 min at room temperature, the

reaction mixture was checked by ¹⁹F-NMR. This spectrum coincided with a previously isolated mixture of **2e/2e'**.

4. Conclusion

In conclusion, readily prepared perfluoro *cis*-1,2-dimethyl butadienyl benzenes (**1**) underwent photocyclization to yield novel naphthalene and 1,4dihydronaphthalene derivatives. The isolated 1,4-dihydronaphthalene could be converted to their respective naphthalenes by base treatment but not photochemically. Competitive photochemical reactions indicate that varying the benzene substituent did not significantly affect reaction rate, suggesting that the mechanism does not involve electrophilic attack on the benzene as the ratedetermining step.

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