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			76%
1b			83%
1c			87%
1d			86%
1e			91%

1f

52%

^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 1,4-dihydronaphthalene derivatives **3a-d** were the minor photocyclization products. The predominant naphthalene derivatives **2a-d** were obtained after photocyclization accompanied by photoelimination of HF.

Table 2. Photoreaction of *p*-substituted perfluoro-*cis*-1,2-dimethyl-butadienyl benzenes **1a-d**.

Entry 1	2a-d	Yield ^a (%) 3a-d	unknown

a		46 (65)	19 (29)	(6)
b		53 (64)	26 (29)	(7)
c		50 (59)	24(25)	(16)
d		59 (67)	14 (27)	(6)

^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**.

<p style="text-align: center;">2a-d</p>								
Entry	Z	F ^a (3F)	F ^b (3F)	F ^c (1F)	F ^d (1F)	<i>J</i> _{ab}	<i>J</i> _{bc}	<i>J</i> _{cd}
2a	H	-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								
¹ H-NMR	Z	H ¹	H ²	H ³	H ⁴	Hz		
						<i>J</i> _{1,2}		

2a	H		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}	¹ J _{3,F}	² J _{3,F}	¹ J _{4,F}	² J _{4,F}
2a	H	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		ppm					Hz	
¹⁹ F-NMR	Z	F ^a (3F)	F ^b (3F)	F ^c (1F)	F ^d (1F)	F ^e (1F)	J _{a,H5}	J _{cd}
3a	H	-60.7(d)	-69.6(s)	-114.9(m)	-85.3(dd)	-101.3(dd)	7	304
3b	CF ₃	-60.8(d)	-69.3(s)	-114.2(m)	-85.5(dd)	-101.3(dd)	7	306
3c	OCH ₃	-60.7(d)	-69.9(s)	-115.6(m)	-85.4(dd)	-101.3(dd)	6	304
3d	Cl	-60.8(d)	-69.6(s)	-114.7(m)	-85.5(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	H		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	C ¹	C ²	C ³	C ⁴	C ⁵	² J _{1,F}	¹ J _{3,F}	¹ J _{4,F}
3a	H	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 starting 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, ^{19}F -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 ($^3J_{\text{H5,F}} = 6$ - 7 Hz) in the ^1H -NMR spectrum and splitting of C1 ($^2J_{\text{C1,F}} = 31$ Hz) in the ^{13}C -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 N-methyl-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 1-fluoro[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'**.

Scheme 5. Photoreaction of *m*-CH₃ substituted **1e**.

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).

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

2e		2e'				
Entry	ppm				Hz	
¹⁹ F-NMR	F ^a (3F)	F ^b (3F)	F ^c (1F)	F ^d (1F)	J _{bc}	J _{cd}
2e	-51.4(m)	-54.2(m)	-143.0(qd)	-129.7(bs)	34	14
2e'	-51.4(m)	-54.0(m)	-144.1(qd)	-139.2(d)	34	18
		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	

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'**.

3e		3e'			
Entry		ppm		Hz	
¹⁹ F-NMR	F ^a (3F) or F ^b (3F)	F ^c (1F)	F ^d (1F) or F ^e (1F)	J _{cd}	J _{ce}
				J _{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	H ¹⁻³		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'**.

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 non-substituted **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 high-resolution data were generally obtained on a Bruker AC-300 Spectrometer. Unless noted otherwise, CDCl_3 was used as the NMR lock solvent. Chemical shifts have been reported in ppm relative to internal TMS. High resolution $\{^1\text{H}\} \text{ }^{13}\text{C}$ 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 CaH_2 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 $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{CF}_3$ 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 $\text{CF}_2=\text{CFCu}$ (**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 $\text{CF}_2=\text{CFZnBr}$ was 62%. A 1000 mL two-necked flask, equipped with dry ice-IPA condenser, N_2 inlet, and septum port was charged with CuBr (29.4 g, 192 mmol). To this flask, the $\text{CF}_2=\text{CFZnBr}$ /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 ^{19}F NMR to verify formation of the copper reagent [15]. $\text{CF}_2=\text{CFZnBr}$: ^{19}F NMR (83.9 MHz, JEOL FX-90Q, DMF) -94.7 ppm (dd, 1F, *cis*- $\text{CF}=\text{CF}_2$, Fa), -128.9 ppm (dd, 1F, *trans*- $\text{CF}=\text{CF}_2$, Fb), -193.3 ppm (dd, 1F, $\text{CF}=\text{CF}_2$, Fc), ($J_{\text{ab}} = 93$ Hz, $J_{\text{ac}} = 34$ Hz, $J_{\text{bc}} = 105$ Hz). $\text{CF}_2=\text{CFCu}$: ^{19}F NMR (83.9 MHz, JEOL FX-90Q, DMF) -96.1 ppm (dd, 1F, *cis*- $\text{CF}=\text{CF}_2$, Fa), -131.3 ppm (dd, 1F, *trans*- $\text{CF}=\text{CF}_2$, Fb), -182.8 ppm (dd, 1F, $\text{CF}=\text{CF}_2$, Fc), ($J_{\text{ab}} = 100$ Hz, $J_{\text{ac}} = 32$ Hz, $J_{\text{bc}} = 100$ Hz).

3.4 Preparation of $\text{CF}_2=\text{CF}-\text{C}(\text{CF}_3)=\text{C}(\text{CCF}_3)\text{Cu}$ (**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 $\text{CF}_2=\text{CFZnBr}$) was quantitative. ^{19}F NMR (83.9 MHz, JEOL FX-90Q, DMF) -53.5 ppm (bs, 3F, CF_3 , Fa), -58.2 ppm (q, 3F, CF_3 , Fb), -102.5 ppm (dd, 1F, *cis*- $\text{CF}=\text{CF}_2$, Fc), -115.8 ppm (dd, 1F, *trans*- $\text{CF}=\text{CF}_2$, Fd), -158.5 ppm (dd, 1F, $\text{CF}=\text{CF}_2$, Fe), ($J_{\text{cd}} = 73$ Hz, $J_{\text{ce}} = 28$ Hz, $J_{\text{de}} = 117$ Hz).

3.5 Preparation of *Z*-1,1,2,5,5,5-hexafluoro-4-aryl-3-trifluoromethyl-1,3-pentadiene 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 N_2 . 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 MgSO_4 . 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%; ^{19}F NMR (CDCl_3) -59.6 ppm (q, 3F, CF_3 , Fa), -60.3 ppm (q, 3F, CF_3 , Fb), -99.1 ppm (dd, 1F, *cis*- $\text{CF}=\text{CF}_2$, Fc), -111.9 ppm (dd, 1F, *trans*- $\text{CF}=\text{CF}_2$, Fd), -165.4 ppm (dd, 1F, $\text{CF}=\text{CF}_2$, Fe), ($J_{\text{ab}} = 13$ Hz, $J_{\text{cd}} = 61$ Hz, $J_{\text{ce}} = 32$ Hz, $J_{\text{de}} = 117$ Hz); ^1H NMR (CDCl_3) 7.2-7.4 ppm (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) 153.2 ppm (ddd, $\text{CF}=\text{CF}_2$, $^1J_{\text{CF}} = 294$ Hz, 280 Hz, $^2J_{\text{CF}} = 46$ Hz), 148.3 ppm (q, $\phi-\text{C}(\text{CF}_3)=\text{C}$, $^2J_{\text{CF}} = 32$ Hz), 131.9 ppm (s), 130.8 ppm (s), 129.1 ppm (s), 128.1 ppm (s), 126.2 ppm (m, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}$), 122.4 ppm (ddd, $\text{CF}=\text{CF}_2$, $^1J_{\text{CF}} = 236$ Hz, $^2J_{\text{CF}} = 54$ Hz, 24 Hz), 121.1 ppm (q, CF_3 , $^1J_{\text{CF}} = 275$ Hz), 120.9 ppm (q, CF_3 , $^1J_{\text{CF}} = 275$ 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) $c = 3.29 \times 10^{-4}$, $\lambda_{\max} = 206$ nm ($A = 1.910$, $\epsilon = 5800$), $\lambda = 230$ nm ($A = 1.360$, $\epsilon = 4100$), 257 nm ($A = 1.550$, $\epsilon = 4700$), 280 nm ($A = 1.650$, $\epsilon = 5000$); FT-IR (cm^{-1} , CCl_4) 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 ($CDCl_3$) -59.7 ppm (q, 3F, -CF₃, Fa), -60.1 ppm (q, 3F, -CF₃, Fb), -63.7 ppm (s, 3F, ϕ -CF₃, Fc), -97.0 ppm (dd, 1F, *cis*-CF=CF₂, Fd), -111.0 ppm (dd, 1F, *trans*-CF=CF₂, Fe), -165.9 ppm (dd, 1F, -CF=CF₂, Ff), ($J_{ab} = 13$ Hz, $J_{de} = 59$ Hz, $J_{df} = 32$ Hz, $J_{ef} = 118$ Hz); ¹H NMR ($CDCl_3$) 7.7 ppm (d, 2H, ³ $J_{HH} = 8$ Hz) 7.4 ppm (d, 2H, ³ $J_{HH} = 8$ Hz); ¹³C {¹H} NMR ($CDCl_3$) 152.7 ppm (ddd, -CF=CF₂, ¹ $J_{CF} = 294$ Hz, 280 Hz, ² $J_{CF} = 45$ Hz), 146.1 ppm (m, ϕ -C(CF₃)=C), 138.1 ppm (s), 134.8 ppm (s), 132.7 ppm (q, -C(CF₃), ² $J_{CF} = 33$ Hz), 127.4 ppm (q, -CF₃, ¹ $J_{CF} = 266$ Hz), 125.9 ppm (s), 123.5 ppm (q, -CF₃, ¹ $J_{CF} = 272$ Hz), 121.5 ppm (m, -CF=CF₂), 120.7 ppm (q, -CF₃, 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 ($C_{13}H_4F_{12}$, calculated: 388.0121, observed: 388.0121); UV (cyclohexane) $c = 1.93 \times 10^{-4}$, $\lambda_{\max} = 212$ nm ($A = 1.244$, $\epsilon = 6400$), $\lambda = 244$ nm ($A = 0.607$, $\epsilon = 3100$), 268 nm ($A = 0.560$, $\epsilon = 2900$); FT-IR (cm^{-1} , CCl_4) 1795 (s, -CF=CF₂), 1730 (m, C=C), 1500 (w), 1440 (w), 1324 (s), 1292 (s), 1241 (s), 1214 (s), 1194 (s), 1178 (s), 1144 (s), 1078 (m), 723 (m).

1c: Yield 87%; GLPC purity 96%; ¹⁹F NMR ($CDCl_3$) -59.5 ppm (q, 3F, -CF₃, Fa), -60.4 ppm (q, 3F, -CF₃, Fb), -99.5 ppm (dd, 1F, *cis*-CF=CF₂, Fc), -112.3 ppm (dd, 1F, *trans*-CF=CF₂, Fd), -164.9 ppm (dd, 1F, -CF=CF₂, Fe), ($J_{ab} = 12$ Hz, $J_{cd} = 61$ Hz, $J_{ce} = 32$ Hz, $J_{de} = 117$ Hz); ¹H NMR ($CDCl_3$) 7.2 ppm (d, 2H), 6.9 ppm (d, 2H), 3.8 ppm (s, 3H); ¹³C {¹H} NMR ($CDCl_3$) 161.8 (s), 153.2 ppm (ddd, -CF=CF₂, ¹ $J_{CF} = 294$ Hz, 280 Hz, ² $J_{CF} = 46$ Hz), 148.8 ppm (q, ϕ -C(CF₃)=C, ² $J_{CF} = 34$ Hz), 129.9 ppm (s), 125.2 ppm (m, -C(CF₃)=C(CF₃)-CF), 124.0 ppm (s), 123.0 ppm (ddd, -CF=CF₂, ¹ $J_{CF} = 236$ Hz, ² $J_{CF} = 55$ Hz, 26 Hz), 121.2 ppm (q, -CF₃, ¹ $J_{CF} = 274$ Hz), 121.0 ppm (q, -CF₃, 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 ($C_{13}H_7F_9O$, calculated: 350.0353, observed: 350.0346); UV (cyclohexane) $c = 3.86 \times 10^{-4}$, $\lambda_{\max} = 226$ nm ($A = 2.267$, $\epsilon = 5000$), $\lambda = 310$ nm ($A = 1.143$, $\epsilon = 3000$); FT-IR (cm^{-1} , CCl_4) 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 ($CDCl_3$) -59.6 ppm (q, 3F, -CF₃, Fa), -60.3 ppm (q, 3F, -CF₃, Fb), -98.1 ppm (dd, 1F, *cis*-CF=CF₂, Fc), -111.5 ppm (dd, 1F, *trans*-CF=CF₂, Fd), -165.6 ppm (dd, 1F, -CF=CF₂, Fe), ($J_{ab} = 13$ Hz, $J_{cd} = 61$ Hz, $J_{ce} = 32$ Hz, $J_{de} = 118$ Hz); ¹H NMR ($CDCl_3$) 7.4 ppm (d, 2H, ³ $J_{HH} = 8$ Hz), 7.2 ppm (d, 2H, ³ $J_{HH} = 8$ Hz); ¹³C {¹H} NMR ($CDCl_3$) 153.1 ppm (ddd, -CF=CF₂, ¹ $J_{CF} = 295$ Hz, 280 Hz, ² $J_{CF} = 46$ Hz), 147.2 ppm (q, ϕ -C(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)=C(CF₃)-CF), 122.2 ppm (ddd, -CF=CF₂, ¹ $J_{CF} = 238$ Hz, ² $J_{CF} = 53$ Hz, 26 Hz), 120.8 ppm (q, -CF₃, ¹ $J_{CF} = 275$ Hz), 120.8 ppm (two

peak overlapping, q, $-\underline{\text{CF}}_3$, $^1J_{\text{CF}} = 275$ Hz); GC-MS 356 ($\text{M}^+ + 2$, 6), 354 (M^+ , 16), 319 ($\text{M}^+ - \text{Cl}$, 97), 287 (23), 285 (78), 269 (78), 250 (100), 235 (41), 200 (50); HRMS ($\text{C}_{12}\text{H}_4\text{F}_9\text{Cl}$, calculated: 353.9858, observed: 353.9854); UV (cyclohexane) $c = 4.24 \times 10^{-4}$, $\lambda_{\text{max}} = 220$ nm ($A = 1.526$, $\epsilon = 3600$), $\lambda = 258$ nm ($A = 0.587$, $\epsilon = 1380$), $\lambda = 284$ nm ($A = 0.568$, $\epsilon = 1340$); FT-IR (cm^{-1} , CCl_4) 1780 (s, $-\text{CF}=\text{CF}_2$), 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%; ^{19}F NMR (CDCl_3) -59.6 ppm (q, 3F, $-\underline{\text{CF}}_3$, Fa), -60.4 ppm (q, 3F, $-\underline{\text{CF}}_3$, Fb), -99.4 ppm (dd, 1F, *cis*- $\text{CF}=\underline{\text{CF}}_2$, Fc), -112.1 ppm (dd, 1F, *trans*- $\text{CF}=\underline{\text{CF}}_2$, Fd), -165.1 ppm (dd, 1F, $-\underline{\text{CF}}=\text{CF}_2$, Fe), ($J_{\text{ab}} = 13$ Hz, $J_{\text{cd}} = 62$ Hz, $J_{\text{ce}} = 32$ Hz, $J_{\text{de}} = 117$ Hz); ^1H NMR (CDCl_3) 7.1-7.3 ppm (m, 4H), 2.4 ppm (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) 153.5 ppm (ddd, $-\text{CF}=\underline{\text{CF}}_2$, $^1J_{\text{CF}} = 294$ Hz, 280 Hz, $^2J_{\text{CF}} = 48$ Hz), 148.7 ppm (q, $\phi-\underline{\text{C}}(\text{CF}_3)=\text{C}$, $^2J_{\text{CF}} = 34$ 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, $-\text{C}(\text{CF}_3)=\underline{\text{C}}(\text{CF}_3)-\text{CF}$), 125.3 ppm (s), 122.5 ppm (ddd, $-\underline{\text{CF}}=\text{CF}_2$, $^1J_{\text{CF}} = 240$ Hz, $^2J_{\text{CF}} = 55$ Hz, 26 Hz), 121.2 ppm (q, $-\underline{\text{CF}}_3$, $^1J_{\text{CF}} = 276$ Hz), 121.0 ppm (q, $-\underline{\text{CF}}_3$, $^1J_{\text{CF}} = 276$ Hz), 21.4 ppm (s); GC-MS 334 (M^+ , 21), 295 (9), 265 (100), 245 (26), 215 (72), 196 (46), 146 (26); HRMS ($\text{C}_{13}\text{H}_7\text{F}_9$, calculated: 334.0404, observed: 334.0396); UV (cyclohexane) $c = 2.54 \times 10^{-4}$, $\lambda_{\text{max}} = 206$ nm ($A = 0.587$, $\epsilon = 2310$), $\lambda = 268$ nm ($A = 0.026$, $\epsilon = 100$); FT-IR (cm^{-1} , CCl_4) 3042 (w), 3031 (w), 2960 (w, C-H), 2928 (w, C-H), 1789 (s, $-\text{CF}=\text{CF}_2$), 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; ^{19}F NMR (376 MHz, JEOL GX-400, CDCl_3) -60.2 ppm (qm, 3F, $-\underline{\text{CF}}_3$, Fa), -60.5 ppm (qm, 3F, $-\underline{\text{CF}}_3$, Fb), -98.6 ppm (ddm, 1F, *cis*- $\text{CF}=\underline{\text{CF}}_2$, Fc), -111.6 ppm (dd, 1F, *trans*- $\text{CF}=\underline{\text{CF}}_2$, Fd), -166.6 ppm (ddm, 1F, $-\underline{\text{CF}}=\text{CF}_2$, Fe), ($J_{\text{ab}} = 13$ Hz, $J_{\text{cd}} = 59$ Hz, $J_{\text{ce}} = 33$ Hz, $J_{\text{de}} = 117$ Hz); ^1H NMR (400 MHz, JEOL GX-400, CDCl_3) 7.4 ppm (s, 4H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, JEOL GX-400, CDCl_3) 152.6 ppm (ddd, $-\text{CF}=\underline{\text{CF}}_2$, $^1J_{\text{CF}} = 297$ Hz, 281 Hz, $^2J_{\text{CF}} = 46$ Hz), 146.2 ppm (qm, $\phi-\underline{\text{C}}(\text{CF}_3)=\text{C}$, $^2J_{\text{CF}} = 34$ Hz), 133.5 ppm (s), 128.3 ppm (s), 126.3 ppm (m, $-\text{C}(\text{CF}_3)=\underline{\text{C}}(\text{CF}_3)-\text{CF}$), 121.7 ppm (ddd, $-\underline{\text{CF}}=\text{CF}_2$, $^1J_{\text{CF}} = 236$ Hz, $^2J_{\text{CF}} = 54$ Hz, 24 Hz), 120.3 ppm (q, $-\underline{\text{CF}}_3$, $^1J_{\text{CF}} = 269$ Hz), 120.1 ppm (q, $-\underline{\text{CF}}_3$, $^1J_{\text{CF}} = 269$ Hz); GC-MS 562 (M^+ , 3), 493 (26), 423 (20), 355 (40), 305 (42), 250 (42), 69 (CF_3 , 100); HRMS ($\text{C}_{18}\text{H}_4\text{F}_{18}$, calculated: 562.0026, observed: 562.0027); UV (cyclohexane) $c = 1.78 \times 10^{-4}$, $\lambda_{\text{max}} = 216$ nm ($A = 1.784$, $\epsilon = 10000$), $\lambda = 254$ nm ($A = 1.554$, $\epsilon = 8700$), $\lambda = 272$ nm ($A = 1.526$, $\epsilon = 8600$); FT-IR (cm^{-1} , CCl_4) 1790 (m, $-\text{CF}=\text{CF}_2$), 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(CF₃)=C(CF₃)-CF=, Fa), -53.3 ppm (dq, 3F, -C(CF₃)=C(CF₃)-CF=, Fb), -138.5 ppm (d, 1F, -C(CF₃)-CF=CF-, Fc), -143.5 ppm (dq, 1F, -C(CF₃)-CF=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, -CF=CF-, ¹*J*_{CF} = 258 Hz, ²*J*_{CF} = 14 Hz), 144.4 ppm (dd, -CF=CF-, 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, -CF₃, ¹*J*_{CF} = 276 Hz), 123.7 ppm (qm, -C(CF₃), ²*J*_{CF} = 34 Hz), 123.1 ppm (q, -CF₃, 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(CF₃)=C(CF₃)-CF=, Fa), -54.4 ppm (dq, 3F, -C(CF₃)=C(CF₃)-CF=, Fb), -64.2 ppm (s, 3F, -CF₃, Fc) -136.4 ppm (d, 1F, -C(CF₃)-CF=CF-, Fd), -139.6 ppm (dq, 1F, -C(CF₃)-CF=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, ³*J*_{HH} = 8 Hz), 7.9 ppm (d, 1H, ³*J*_{HH} = 8 Hz); ¹³C {¹H} NMR (CDCl₃) 148.9 ppm (dd, -CF=CF-, ¹*J*_{CF} = 263 Hz, ²*J*_{CF} = 14 Hz), 144.7 ppm (dd, -CF=CF-, ¹*J*_{CF} = 262 Hz, ²*J*_{CF} = 14 Hz), 132.1 ppm (q, -C(CF₃), ²*J*_{CF} = 34 Hz), 128.8 ppm (s), 127.9 ppm (m), 126.6 ppm (qm, -C(CF₃)=C(CF₃)-CF=, ²*J*_{CF} = 39 Hz), 125.5 ppm (d, -CF=CF-C-, ²*J*_{CF} = 14 Hz), 124.7 ppm (s), 123.5 ppm (q, -CF₃, ¹*J*_{CF} = 273 Hz), 122.8 ppm (q, -CF₃, ¹*J*_{CF} = 274 Hz), 121.6 ppm (q, -CF₃, ¹*J*_{CF} = 277 Hz), 118.6 ppm (q, -C(CF₃)=C(CF₃)-C-, ³*J*_{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%; ^{19}F NMR (CDCl_3) -51.3 ppm (q, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fa), -53.7 ppm (dq, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fb), -140.3 ppm (d, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fc), -142.2 ppm (dq, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fd), ($J_{ab} = 16 \text{ Hz}, J_{bd} = 32 \text{ Hz}, J_{cd} = 16 \text{ Hz}$); ^1H NMR (CDCl_3) 8.0 ppm (d, 1H), 7.1 ppm (m, 2H), 3.9 ppm (s, 3H); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) 160.6 ppm (s), 147.1 ppm (dd, $-\text{CF}=\text{CF}-$, $^1J_{\text{CF}} = 257 \text{ Hz}, ^2J_{\text{CF}} = 14 \text{ Hz}$), 144.3 ppm (dd, $-\text{CF}=\text{CF}-$, $^1J_{\text{CF}} = 256 \text{ Hz}, ^2J_{\text{CF}} = 14 \text{ Hz}$), 128.1 ppm (m), 127.9 ppm (s), 124.0 ppm (q, $-\text{CF}_3$, $^1J_{\text{CF}} = 276 \text{ Hz}$), 123.3 ppm (q, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-$, $^2J_{\text{CF}} = 36 \text{ Hz}$), 123.0 ppm (q, $-\text{CF}_3$, $^1J_{\text{CF}} = 276 \text{ Hz}$), 122.9 ppm (s), 122.3 ppm (s), 117.1 ppm (m), 97.6 ppm (q, $^4J_{\text{CF}} = 6 \text{ Hz}$), 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 ($\text{C}_{13}\text{H}_6\text{F}_8\text{O}$, calculated: 330.0291, observed: 330.0280); UV (cyclohexane) $c = 4.48 \times 10^{-5}$, $\lambda_{\text{max}} = 245 \text{ nm}$ ($A = 2.426$, $\epsilon = 54000$), $\lambda = 304 \text{ nm}$ ($A = 0.3141$, $\epsilon = 7000$); FT-IR (cm^{-1} , CCl_4) 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%; ^{19}F NMR (CDCl_3) -51.4 ppm (q, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fa), -54.2 ppm (dq, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fb), -138.2 ppm (d, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fc), -140.1 ppm (dq, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fd), ($J_{ab} = 16 \text{ Hz}, J_{bd} = 32 \text{ Hz}, J_{cd} = 18 \text{ Hz}$); ^1H NMR (CDCl_3) 8.2 ppm (dm, 1H, $^3J_{\text{HH}} = 9 \text{ Hz}$), 8.0 ppm (s, 1H), 7.5 ppm (dm, 1H, $^3J_{\text{HH}} = 9 \text{ Hz}$); ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) 147.3 ppm (dd, $-\text{CF}=\text{CF}-$, $^1J_{\text{CF}} = 261 \text{ Hz}, ^2J_{\text{CF}} = 14 \text{ Hz}$), 144.6 ppm (dd, $-\text{CF}=\text{CF}-$, $^1J_{\text{CF}} = 259 \text{ Hz}, ^2J_{\text{CF}} = 14 \text{ Hz}$), 137.1 ppm (s), 130.0 ppm (s), 128.0 ppm (s), 126.1 ppm (d, $-\text{CF}=\text{CF}-$, $^2J_{\text{CF}} = 12 \text{ Hz}$), 125.7 ppm (s), 124.1 ppm (m), 122.3 ppm (q, $-\text{CF}_3$, $^1J_{\text{CF}} = 277 \text{ Hz}$), 121.9 ppm (q, $-\text{CF}_3$, $^1J_{\text{CF}} = 277 \text{ Hz}$), 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 ($\text{C}_{12}\text{H}_3\text{F}_8^{35}\text{Cl}$, calculated: 333.9796, observed: 333.9797); UV (cyclohexane) $c = 3.29 \times 10^{-5}$, $\lambda_{\text{max}} = 236 \text{ nm}$ ($A = 1.427$, $\epsilon = 43400$), $\lambda = 290 \text{ nm}$ ($A = 0.1561$, $\epsilon = 4700$), $\lambda = 336 \text{ nm}$ ($A = 0.0566$, $\epsilon = 1700$); FT-IR (cm^{-1} , CCl_4) 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%; ^{19}F NMR (CDCl_3) -51.4 ppm (m, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fa), -54.2 ppm (m, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fb), -129.7 ppm (m, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fd), -143.0 ppm (dq, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fc), ($J_{bc} = 34 \text{ Hz}, J_{cd} = 14 \text{ Hz}$); ^1H NMR (CDCl_3) 7.9-7.4 ppm (m, 3H), 2.8 ppm (d, 3H, $^5J_{\text{HF}} = 8 \text{ Hz}$); GC-MS 315 (M^++1 , 13), 314 (M^+ , 100), 295 (27), 263 (12), 245 (99), 224 (28), 175 (27).

2e': GLPC Yield 36%;

^{19}F NMR (CDCl_3) -51.4 ppm (m, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fa), -54.0 ppm (m, 3F, $-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-\text{CF}=$, Fb), -139.2 ppm (d, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fc), -144.1 ppm (dq, 1F, $-\text{C}(\text{CF}_3)-\text{CF}=\text{CF}-$, Fd), ($J_{bd} = 34 \text{ Hz}, J_{cd} = 18 \text{ Hz}$); ^1H NMR (CDCl_3) 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%; ^{19}F NMR (CDCl_3) -60.7 ppm (m, 3F, -CH(CF_3)-C(CF_3)=, Fa), -69.6 ppm (s, 3F, -CH(CF_3)-C(CF_3)=CF-, Fb), -85.3 ppm (dd, 1F, =CF-F₂-, Fc), -101.3 ppm (dd, 1F, =CF-F₂-, Fd), -114.9 ppm (m, 1F, =CF-CF₂-, Fe), ($J_{\text{cd}} = 304$ Hz, $J_{\text{ce}} = 30$ Hz, $J_{\text{de}} = 13$ Hz); ^1H NMR (CDCl_3) 7.9-7.5 ppm (m, 4H), 4.6 ppm (qm, 1H, -CH(CF_3)-, $^3J_{\text{HF}} = 7$ Hz); ^{13}C { ^1H } NMR (CDCl_3) 156.7 ppm (dt, =CF-CF₂-, $^1J_{\text{CF}} = 294$ Hz, $^2J_{\text{CF}} = 29$ Hz), 131.6 ppm (s), 131.0 ppm (t, C-CF₂-CF=, $^2J_{\text{CF}} = 24$ Hz), 130.3 ppm (s), 129.6 ppm (s), 127.4 ppm (s), 126.2 ppm (s), 124.1 ppm (q, -CF₃, $^1J_{\text{CF}} = 277$ Hz), 121.8 ppm (q, -CF₃, $^1J_{\text{CF}} = 272$ Hz), 111.1 ppm (q, -CH(CF_3)-C(CF_3)=CF-, $^2J_{\text{CF}} = 30$ Hz), 109.9 ppm (ddd, =CF-CF₂-, $^1J_{\text{CF}} = 239$ Hz, 236 Hz, $^2J_{\text{CF}} = 23$ Hz), 43.7 ppm (q, -CH(CF_3)-, $^2J_{\text{CF}} = 31$ Hz); GC-MS 320 (M^+ , 13), 301 (8), 251 (100), 232 (24), 201 (63), 182 (63); HRMS ($\text{C}_{12}\text{H}_5\text{F}_9$, calculated: 320.0248, observed: 320.0249); UV (cyclohexane) $c = 3.28 \times 10^{-4}$, $\lambda_{\text{max}} = 216$ nm ($A = 1.565$, $\epsilon = 4800$), $\lambda = 272$ nm ($A = 0.2328$, $\epsilon = 710$); FT-IR (cm^{-1} , CCl_4) 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%; ^{19}F NMR (CDCl_3) -60.7 ppm (m, 3F, -CH(CF_3)-C(CF_3)=, Fa), -63.7 ppm (s, 3F, -CH(CF_3)-C(CF_3)=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, =CF-CF₂-, Ff), ($J_{\text{ah}} = 7$ Hz, $J_{\text{de}} = 306$ Hz, $J_{\text{df}} = 13$ Hz, $J_{\text{ef}} = 21$ Hz); ^1H NMR (CDCl_3) 8.1 ppm (s, 1H), 7.9 ppm (d, 1H, $^3J_{\text{HH}} = 7$ Hz), 7.7 ppm (d, 1H, $^3J_{\text{HH}} = 7$ Hz), 4.6 ppm (q, 1H, -CH(CF_3)-, $^3J_{\text{HF}} = 7$ Hz); ^{13}C { ^1H } NMR (CDCl_3) 156.4 ppm (dt, =CF-CF₂-, $^1J_{\text{CF}} = 294$ Hz, $^2J_{\text{CF}} = 27$ Hz), 133.3 ppm (q, -C(CF_3), $^2J_{\text{CF}} = 34$ Hz), 132.1 ppm (t, C-CF₂-CF=, $^2J_{\text{CF}} = 21$ Hz), 131.1 ppm (s), 130.5 ppm (s), 128.4 ppm (s), 123.8 ppm (q, -CF₃, $^1J_{\text{CF}} = 272$ Hz), 123.6 ppm (q, -CF₃, $^1J_{\text{CF}} = 277$ Hz), 123.6 ppm (s), 121.3 ppm (q, -CF₃, $^1J_{\text{CF}} = 284$ Hz), 111.1 ppm (m, -CH(CF_3)-C(CF_3)=CF-), 109.3 ppm (ddd, =CF-CF₂-, $^1J_{\text{CF}} = 238$ Hz, 235 Hz, $^2J_{\text{CF}} = 23$ Hz), 43.8 ppm (q, -CH(CF_3)-, $^2J_{\text{CF}} = 31$ Hz); GC-MS 388 (M^+ , 8), 369 ($M^+ - F$, 14), 319 (100), 300 (20), 269 (61), 265 (61), 200 (26); HRMS ($\text{C}_{13}\text{H}_4\text{F}_{12}$, calculated: 388.0121, observed: 388.0118); UV (cyclohexane) $c = 2.58 \times 10^{-4}$, $\lambda_{\text{max}} = 226$ nm ($A = 0.893$, $\epsilon = 3500$), $\lambda = 338$ nm ($A = 0.075$, $\epsilon = 290$); FT-IR (cm^{-1} , CCl_4) 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%; ^{19}F NMR (CDCl_3) -60.7 ppm (m, 3F, -CH(CF_3)-C(CF_3)=, Fa), -69.9 ppm (s, 3F, -CH(CF_3)-C(CF_3)=CF-, Fb), -85.4 ppm (dd, 1F, =CF-F₂-, Fc), -101.4 ppm (dd, 1F, =CF-F₂-, Fd), -115.5 ppm (m, 1F, =CF-CF₂-, Fe), ($J_{\text{cd}} = 304$ Hz, $J_{\text{ce}} = 23$ Hz, $J_{\text{de}} = 14$ Hz); ^1H NMR (CDCl_3) 7.4 ppm (d, 1H, $^3J_{\text{HH}} = 9$ Hz), 7.3 ppm (s), 7.1 ppm (d, 1H, $^3J_{\text{HH}} = 9$ Hz), 4.5 ppm (qm, 1H, -CH(CF_3)-, $^3J_{\text{HF}} = 7$ Hz), 3.9 ppm (s, 3H); ^{13}C { ^1H } NMR (CDCl_3) 161.2 ppm (s), 156.8 ppm (dt, =CF-CF₂-, $^1J_{\text{CF}} = 293$ Hz, $^2J_{\text{CF}} = 29 = 8$ Hz), 132.2 ppm (t, C-CF₂-CF=, $^2J_{\text{CF}} = 24$ Hz), 131.0 ppm (s), 124.0 ppm (q, -CF₃, $^1J_{\text{CF}} = 282$ Hz), 121.3 ppm (q, -CF₃, $^1J_{\text{CF}} = 275$ Hz), 119.3 ppm (bs), 118.9 ppm (s), 109.7 ppm (m), 110.2 ppm (m), 109.7 ppm (ddd, =CF-CF₂-, $^1J_{\text{CF}} = 239$ Hz, 236 Hz, $^2J_{\text{CF}} = 24$ Hz), 55.8 ppm (s), 43.3 ppm (q, -CH(CF_3)-, $^2J_{\text{CF}} = 31$ 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) $c = 3.14 \times 10^{-4}$, $\lambda_{\text{max}} = 212$ nm ($A = 1.038$, $\epsilon = 3300$), $\lambda = 242$ nm ($A = 0.625$, $\epsilon = 2000$), $\lambda = 334$ nm ($A = 0.468$, $\epsilon = 1500$); 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-E₂-, Fc), -101.5 ppm (dd, 1F, =CF-E₂-, Fd), -114.7 ppm (m, 1F, =CF-CF₂-, Fe), ($J_{\text{FH}} = 6$ Hz, $J_{\text{cd}} = 305$ Hz, $J_{\text{ce}} = 23$ Hz, $J_{\text{de}} = 14$ Hz); ¹H NMR (CDCl₃) 7.8 ppm (m, 1H), 7.6 ppm (dm, 1H, $^3J_{\text{HH}} = 8$ Hz), 7.4 ppm (d, 1H, $^3J_{\text{HH}} = 8$ Hz), 4.5 ppm (q, 1H, -CH(CF₃)-, $^3J_{\text{HF}} = 6$ Hz); ¹³C {¹H} NMR (CDCl₃) 156.7 ppm (dt, =CF-CF₂-, $^1J_{\text{CF}} = 294$ Hz, $^2J_{\text{CF}} = 28$ Hz), 137.3 ppm (s), 133.4 ppm (t, C-CF₂-CF=, $^2J_{\text{CF}} = 28$ Hz), 132.2 ppm (s), 131.2 ppm (s), 126.8 ppm (m), 126.0 ppm (s), 124.0 ppm (q, -CF₃, $^1J_{\text{CF}} = 274$ Hz), 121.3 ppm (q, -CF₃, $^1J_{\text{CF}} = 274$ Hz), 111.1 ppm (m), 109.4 ppm (ddd, =CF-CF₂-, $^1J_{\text{CF}} = 240$ Hz, 239 Hz, $^2J_{\text{CF}} = 24$ Hz), 43.7 ppm (q, -CH(CF₃)-, $^2J_{\text{CF}} = 31$ 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) $c = 3.53 \times 10^{-4}$, $\lambda_{\text{max}} = 220$ nm ($A = 2.013$, $\epsilon = 5700$), $\lambda = 272$ nm ($A = 0.172$, $\epsilon = 500$), $\lambda = 282$ nm ($A = 0.163$, $\epsilon = 460$); 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, -CF₃, Fa), -69.9 ppm (s, 3F, -CF₃, Fb), -93.8 ppm (dd, 1F, =CF-E₂-, Fc), -95.8 ppm (dd, 1F, =CF-E₂-, Fd), -115.4 ppm (m, 1F, =CF-CF₂-, Fe), ($J_{\text{cd}} = 309$ Hz, $J_{\text{ce}} = 22$ Hz, $J_{\text{de}} = 14$ 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, -CF₃, Fa), -69.6 ppm (s, 3F, -CF₃, Fb), -84.9 ppm (dd, 1F, =CF-E₂-, Fc), -101.1 ppm (dd, 1F, =CF-E₂-, Fd), -115.1 ppm (m, 1F, =CF-CF₂-, Fe), ($J_{\text{ae}} = 13$ Hz, $J_{\text{cd}} = 303$ Hz, $J_{\text{ce}} = 23$ 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(CF₃)=C(CF₃)-CF=, Fa), -54.6 ppm (dq, 6F, -C(CF₃)=C(CF₃)-CF=, Fb), -136.1 ppm (d, 2F, =C(CF₃)-CF=CF-, Fc), -140.3 ppm (qd, 2F, =C(CF₃)-CF=CF-, Fd), ($J_{\text{ab}} = 16$ Hz, $J_{\text{bd}} = 32$ Hz, $J_{\text{cd}} = 15$ Hz); ¹H NMR (acetone-d₆) 9.3 ppm (s, 2H); ¹³C {¹H} NMR (acetone-d₆) 149.0 ppm (dd, -CF=CF-, $^1J_{\text{CF}} = 262$ Hz, $^2J_{\text{CF}} = 14$ Hz), 144.1 ppm (dd, -CF=CF-, $^1J_{\text{CF}} = 257$ Hz, $^2J_{\text{CF}} = 14$ Hz), 126.2 ppm (s), 125.3 ppm (d, C-CF=CF-, $^2J_{\text{CF}} = 13$ Hz), 124.8 ppm (m), 123.7 ppm (q, -CF₃, $^1J_{\text{CF}} = 271$ Hz), 122.4 ppm (q, -CF₃, $^1J_{\text{CF}} = 276$ 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) $c = 5.42 \times 10^{-4}$.

⁵, $\lambda_{\text{max}} = 260 \text{ nm}$ ($A = 2.80$, $\epsilon = 51700$), $\lambda = 205 \text{ nm}$ ($A = 1.48$, $\epsilon = 27300$), $\lambda = 400 \text{ nm}$ ($A = 0.190$, $\epsilon = 3500$), $\lambda = 430 \text{ nm}$ ($A = 0.230$, $\epsilon = 4250$); FT-IR (cm^{-1} , CCl_4) 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 (CDCl_3) -50.0 ppm (q, 6F, -C(CF₃)=C(CF₃)-CF=, Fa), -54.5 ppm (dq, 6F, -C(CF₃)=C(CF₃)-CF=, Fb), -115.7 ppm (bs, 2F, -C(CF₃)-CF=CF-, Fc), -134.2 ppm (qm, 2F, -C(CF₃)-CF=CF-, Fd), ($J_{\text{ab}} = 16 \text{ Hz}$, $J_{\text{bd}} = 34 \text{ Hz}$); ¹H NMR (CDCl_3) 8.2 ppm (s, 2H); ¹³C {¹H} NMR (CDCl_3) 150.1 ppm (dd, -CF=CF-, $^1J_{\text{CF}} = 267 \text{ Hz}$, $^2J_{\text{CF}} = 15 \text{ Hz}$), 147.6 ppm (dm, -CF=CF-, $^1J_{\text{CF}} = 265 \text{ Hz}$), 128.2 ppm (s), 125.7 ppm (m), 124.5 ppm (dm, CF=CF-, $^2J_{\text{CF}} = 31 \text{ Hz}$), 123.8 ppm (m), 122.7 ppm (q, -CF₃, $^1J_{\text{CF}} = 276 \text{ Hz}$), 122.6 ppm (m, $^2J_{\text{CF}} = 33 \text{ Hz}$), 121.5 ppm (q, -CF₃, $^1J_{\text{CF}} = 275 \text{ Hz}$), 118.4 ppm (bs); GC-MS 523 (M^{++1} , 18), 522 (M^+ , 100), 503 ($\text{M}^+\text{-F}$, 30), 472 (27), 453 (33), 315 (13); HRMS ($\text{C}_{18}\text{H}_2\text{F}_{16}$, calculated: 521.9901, observed: 521.9879); UV (cyclohexane) $c = 5.43 \times 10^{-5}$, $\lambda_{\text{max}} = 260 \text{ nm}$ ($A = 2.17$, $\epsilon = 40000$), $\lambda = 205 \text{ nm}$ ($A = 1.68$, $\epsilon = 310$), $\lambda = 300 \text{ nm}$ ($A = 0.415$, $\epsilon = 7650$), $\lambda = 310 \text{ nm}$ ($A = 0.415$, $\epsilon = 7650$); FT-IR (cm^{-1} , CCl_4) 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 CDCl_3 (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 CDCl_3 (1.0 mL) and DBU (35 mg, 0.23 mmol) was added. After 30 min at room temperature, the

reaction mixture was checked by ^{19}F -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 1,4-dihydronaphthalene 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 rate-determining step.

5. Acknowledgement

We wish to thank the National Science Foundation and the Air Force Office of Scientific Research for support of this work. M. Y. wishes to thank Nitto Denko Co., Ltd. (Japan) for the release time to pursue this research. D. J. wishes to thank Michael Sinnwell for help with manuscript preparation.

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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.

Graphical Abstract