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Reaction of octafluorocyclopentene with various carbon nucleophiles

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Abstract

The treatment of octafluorocyclopentene with organolithium reagents gave the corresponding symmetrical disubstituted perfluorocyclopentenes in good to high yields. The reaction with Grignard reagents led to the monosubstituted perfluorocyclopentenes, which were subjected to the further nucleophilic substitution reaction using another Grignard or aryllithium reagents, unsymmetrical disubstituted perfluorocyclopentenes being obtained in high yields.

Keywords: Octafluorocyclopentene; Nucleophilic substitution; Carbon nucleophiles; Organolithium reagents; Grignard reagents; Monosubstituted perfluorocyclopentene; Symmetrical disubstituted perfluorocyclopentene; Unsymmetrical disubstituted perfluorocyclopentene

1. Introduction

Incorporation of fluorine(s) into organic molecules often changes their structure, stability, reactivity, and biological activity, and thereby frequently leads to the discovery of novel and potent applications in various domains from liquid crystalline materials to biologically active substances, peptide isosteres, or enzyme inhibitors [1]. Consequently, a wide variety of methods have hitherto been developed for the preparation of various types of fluorine-incorporated compounds [2].

Out of such compounds, organic molecules containing a perfluorocyclopentene (**1**) backbone are recently recognized as one of the most attractive materials for the applications to optoelectronic devices, etc. (Scheme 1) [3].

A nucleophilic substitution reaction of octafluorocyclopentene (**2**) would provide a promising entry to the synthesis of such molecules. However, very little attention has been paid to the nucleophilic substitution reactions of **2** with *carbon nucleophiles* thus far [4], though many studies have been made on the reaction of **2** with *hetero nucleophiles*, such as phenoxide [5], aryl or alkyl thiolate [6], primary or secondary amines [7], and so on [8].

Herein we disclose the results of our systematic studies on the nucleophilic substitution reactions of **2** with representative carbon nucleophiles, such as organolithium and Grignard reagents.

2. Results and discussion

2.1. The reaction of octafluorocyclopentene (2) with various organolithium reagents

Initially, the reaction of **2** with 1.1 equiv. of phenyllithium (**3a**) was run at −78 °C for 2 h, mono- and disubstituted products **4a** and **5a** being obtained in only 27% combined yield in a ratio of ca. 1:5 (Table 1, entry 1). Although the prolonged reaction time (6 h) did not lead to a remarkable change of the yield (entry 2), the use of 2.2 equiv. of the nucleophile resulted in significant improvement, **5a** being afforded in 56% yield as a sole product and any trace of **4a** being not detected. With these reaction conditions, various organolithium reagents **3** were applied for the reaction as shown in entries 4–7. Neither an electron-donating nor an electron-withdrawing group on an aromatic ring of aryllithium reagents affected the efficiency of the reaction at all (entries 4 and 5). Butyllithium could also participate nicely in this type of nucleophilic

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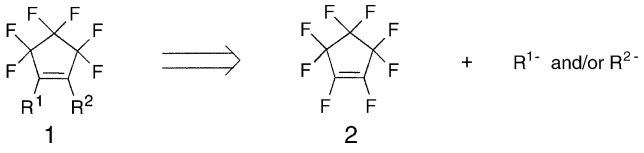


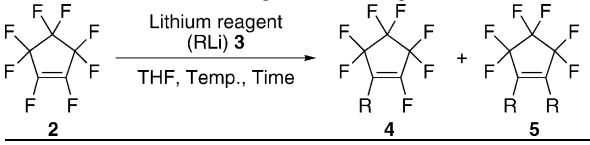
Scheme 1.

substitution reaction (entry 6), but the vinyllithium reagent **3e** was very reluctant to the reaction, affording **4e** in only 21% yield (entry 7). When 6.6 equiv. of **3e** was used, the disubstituted product **5e** was given in 75% yield, together with 18% of the monosubstituted cyclopentene **4e** (entry 9). As can be seen in entries 11–19, various lithium acetylides were found to be good nucleophiles leading to the corresponding disubstituted cyclopentenes **5** in good yields without any trace of monosubstituted ones **4**. Thus, 2.2 equiv. of acetylides derived from phenylacetylene, 4-methoxyphenylacetylene, propargyl alcohol, enyne, and so on, readily reacted with **2** at room temperature for 2 h to afford the corresponding substituted products **5** in 52–66% yields as a sole product. In the case of the reaction with trimethylsilylacetylide **3h**, it was crucial to carry out the reaction at −10 °C for 20 h, not room temperature (entries 14 and 15).

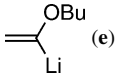
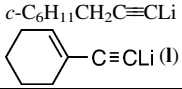
2.2. The reaction of octafluorocyclopentene (2) with various Grignard reagents

We next examined the nucleophilic substitution reaction of **2** with various Grignard reagents **6**, as summarized in Table 2. The treatment of **2** with 1.1 equiv. of phenylmagnesium bromide (**6a**) at room temperature for 6 h gave the monosubstituted cyclopentene **4a** in only 29% yield as a sole product (entry 1). In sharp contrast to the reaction with organolithium reagents, no disubstituted product **5a** was observed. Even the use of 2.2 equiv. of **6a** did not lead to a dramatical change in the yield (entry 2). Prolonged reaction time, on the other hand, caused the increase of the yield from 35% to 55% (entry 3). However, the use of 4.4 equiv. of **6a** afforded a mixture of mono- and di-substituted cyclopentene in a ratio of ca. 2:1 (entry 4). As shown in entries 6 and 9, the reaction of **2** with 2.2 equiv. of 4-methoxyphenylmagnesium bromide (**6m**) or 4-methylphenylmagnesium bromide (**6b**) at room temperature proceeded smoothly to provide the monosubstituted product **4m** or **4b** in 82% or 71% yield, respectively. These results may primarily be ascribed to higher reactivity of the Grignard reagents than that of **6a**, due to an electron-donating group (MeO or Me) on the aromatic ring in R. It was found that increasing the amount of Grignard reagent caused a preferential formation of **5**.

Table 1
Reaction of **2** with various organolithium reagents

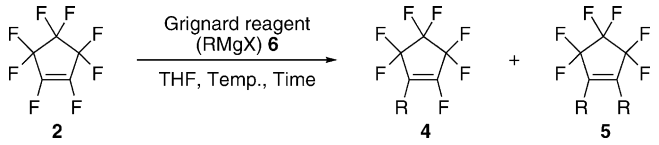


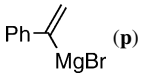
2 **4** **5**

Entry	Organolithium reagent	Equiv. of organolithium reagent	Temperature (°C)	Time/h	Yield%[a] of **4**	Yield%[a] of **5**
1[b]		1.1	−78	2	5	22
2[b]	PhLi (**a**)	1.1	−78	6	6	27
3		2.2	−78	2	Trace	56
4	4-MeC_6H_4Li (**b**)	2.2	−78	2	Trace	61
5	4-$F_3CC_6H_4Li$ (**c**)	2.2	−78	2	Trace	68 (54)
6	*n*-BuLi (**d**)	2.2	−78	2	Trace	58
7		2.2	−78	2	21	0
8	 (**e**)	4.4	−78	2	26	16
9		6.6	−78	2	18	75 (40)
10		6.6	−78	6	10	62
11	PhC≡CLi (**f**)	2.2	r.t.	2	0	64
12		2.2	r.t.	6	0	66 (64)
13	4-$MeOC_6H_4C$≡CLi (**g**)	2.2	r.t.	2	0	Quant. (76)
14[b]	TMSC≡CLi (**h**)	2.2	r.t.	2	0	24
15		2.2	−10	20	0	52 (50)
16	$TBSOCH_2C$≡CLi (**i**)	2.2	r.t.	2	0	57 (57)
17	*n*-C_3H_7C≡CLi (**j**)	2.2	r.t.	2	0	61 (60)
18	*c*-$C_6H_{11}CH_2C$≡CLi (**k**)	2.2	r.t.	2	0	56 (37)
19	 (**l**)	2.2	r.t.	2	0	65 (54)

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] The unreacted starting material was detected in the reaction mixture.

Table 2
Reaction of **2** with various Grignard reagents



Entry	Grignard reagent	Equiv. of Grignard reagent	Temp (°C)	Time (h)	Yield%[a] of **4**	Yield%[a] of **5**
1[b]		1.1	r.t.	6	29	0
2[b]	PhMgBr (**a**)	2.2	r.t.	6	35	Trace
3[b]		2.2	r.t.	20	55	6
4		4.4	r.t.	20	42	23
5		4.4	refl.	6	15	Trace
6	4-$MeOC_6H_4MgBr$ (**m**)	2.2	r.t.	6	82	0
7		4.4	refl.	6	30	46
8		6.6	refl.	6	0	69 (58)
9	4-MeC_6H_4MgBr (**b**)	2.2	r.t.	20	71	Trace
10		4.4	refl.	6	0	46
11[b]	4-$(CH_2{=}CH)C_6H_4MgBr$ (**n**)	2.2	r.t.	20	60 (47)	Trace
12		4.4	refl.	6	21	Trace
13[b]	4-$F_3CC_6H_4MgBr$ (**c**)	2.2	r.t.	6	0	0
14[b]		4.4	refl.	6	0	0
15	*n*-BuMgCl (**d**)	1.1	r.t.	20	21	6
16		2.2	r.t.	20	6	57
17[b]	*c*-$C_6H_{11}MgBr$(**o**)	2.2	r.t.	20	17	0
18		4.4	refl.	6	18	0
19[b]	 (**p**)	2.2	r.t.	20	0	0
20		4.4	refl.	6	Trace	0
21[b]	PhC≡CMgCl (**f**)	2.2	r.t.	2	0	53
22[b]		2.2	r.t.	20	0	68

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] The unreacted starting material was detected in the reaction mixture.

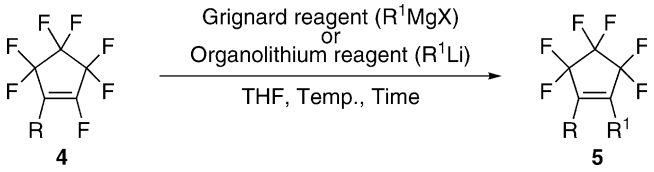
Thus, when 6.6 equiv. of **6m** or 4.4 equiv. of **6b** was used, **5m** or **5b** was given in 69% or 46% yield, respectively (entries 8 and 10). The reaction of **2** with 2.2 equiv. of 4-vinylphenylmagnesium bromide (**6n**) at room temperature afforded the monosubstituted cyclopentene **4n** in 60% yield (entry 11). The reaction of **2** with 4-trifluoromethylphenylmagnesium bromide (**6c**) did not produce the corresponding substituted product **4c** at all (entries 13 and 14), these facts being attributable to the reduced reactivity of **6c** due to an electron-withdrawing group (CF_3) on the aromatic ring in R. As shown in entries 15–22, aliphatic Grignard reagents were found to be poor nucleophiles. Cyclohexyl- (**6o**) or vinylmagnesium bromide (**6p**) did not give the products **4** and/or **5** in satisfactory yields, though the reaction of **2** with 2.2 equiv. of *n*-butyl- (**6d**) or alkynylmagnesium chloride (**6f**) proceeded smoothly to give the corresponding disubstituted product **5d** or **5f** in 57% or 68% yield, respectively.

2.3. Synthesis of the unsymmetrical disubstituted cyclopentenes 5

Finally, we attempted the nucleophilic substitution reaction of monosusbstituted cyclopentenes **4** with Grignard or organolithium reagents. The results are summarized in Table 3.

As shown in entries 1–4, 4-methoxyphenylmagnesium bromide (**6m**) was not so efficient to the reaction with monosubstituted cyclopentene **4a**. Even though the amount of Grignard reagent, the reaction temperature and the prolonged reaction time were increased, the results were all fruitless. However, *n*-butylmagnesium chloride (**6d**) reacted with **4a** very smoothly to afford the unsymmetrical disubstituted cyclopentene **5a** in high yields. It should be noted that the nucleophilic substitution reaction of **4a** or **4n** with organolithium reagents **3a–c** took place effectively even at −78 °C for 2 h, giving the corresponding

Table 3
Synthesis of unsymmetrical disubstituted perfluorocyclopentene



4 5

Entry	R	Nucleophile	Equiv. of nucleophile	Temperature (°C)	Time (h)	Yield%[a] of **5**	Recovery%[a] of **4**
1			2.2	r.t.	20	33	45
2	Ph (**a**)	4-$MeOC_6H_4MgBr$ (**6m**)	2.2	refl.	6	28	19
3			4.4	r.t.	20	7	19
4			4.4	refl.	6	2	25
5	Ph (**a**)	*n*-BuMgCl (**6d**)	2.2	r.t.	20	86 (83)	0
6	4-$MeOC_6H_4$ (**m**)	*n*-BuMgCl (**6d**)	2.2	r.t.	20	89 (85)	0
7	Ph (**a**)	4-MeC_6H_4Li (**3b**)	2.2	−78	2	71	0
8	Ph (**a**)	4-$F_3CC_6H_4Li$ (**3c**)	2.2	−78	2	89 (60)	0
9	4-$(CH_2{=}CH)C_6H_4$ (**n**)	PhLi (**3a**)	2.2	−78	2	61 (40)	0

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.

unsymmetrical disubstituted cyclopentenes **5** in good to high yields.

3. Conclusion

In summary, we have demonstrated the nucleophilic substitution reaction of octafluorocyclopentene (**2**) with various carbon nucleophiles, such as organolithium and Grignard reagents. The organolithium reagents, generally highly reactive, gave rise to the symmetrical disubstituted products **5** by using 2.2 equiv. of the reagents. In sharp contrast, the Grignard reagents, not so reactive as the corresponding organolithium reagents, produced the monosubstituted products **4** in good to high yields as a sole product. Thus obtained monosubstituted cyclopentenes **4** underwent further nucleophilic substitution reaction with aliphatic Grignard reagents or organolithium reagents to afford the unsymmetrical disubstituted cyclopentenes **5** in high yields.

4. Experimental

4.1. General

All reactions were carried out in an oven-dried glassware under an atmosphere of argon, and all the reagents and anhydrous solvents were commercially available. The reagents were used without further purification or, if necessary, purified by distillation on appropriate drying agents. Melting points were recorded on a Shimadzu MM-2 type instrument at atmospheric pressure. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 spectrometer operating at 500.13 and 125.75 MHz, respectively. $CDCl_3$ was used as solvent in all NMR measurements and chemical shifts were recorded in ppm relative to internal tetramethylsilane. ^{19}F NMR spectra were measured for $CDCl_3$ solutions with a JEOL JNM-EX90A spectrometer operating at 84.10 MHz. All ^{19}F chemical shifts were reported in ppm relative to trichlorofluoromethane ($CFCl_3$) as an internal standard. IR spectra were determined with a Shimadzu FT-IR 8200 PC spectrophotometer. High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer. Column chromatography was carried out on silica gel (Wako gel C-200) and TLC analysis was performed on silica gel TLC plates (Merck, Silica gel 60 F_{254}).

4.2. Typical procedure for the synthesis of 1,2-diphenyl-3,3,4,4,5,5-hexafluorocyclopentene (*5a*) by using phenyllithium

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 2.2 equiv. of phenyllithium in diethyl ether. To this solution was slowly added 0.212 g (1.0 mmol) of **2** in THF (1 mL) via a syringe at −78 °C. After being stirred for 2 h at −78 °C, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL), followed by extraction with ether (20 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane yielded pure product, 1,2-diphenyl-3,3,4,4,5,5-hexafluorocyclopentene (**5a**).

4.2.1. 1,2-Diphenyl-3,3,4,4,5,5-hexafluorocyclopentene (*5a*)

m.p.: 75–77 °C; ^1H NMR ($CDCl_3$) $\delta = 7.31$–7.47 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 111.19$ (tquint., $J = 245.6$, 21.9 Hz), 116.53 (tt, $J = 264.3$, 31.3 Hz), 127.78, 128.86,

129.28, 130.26, 139.40–140.10 (m); ^{19}F NMR ($CDCl_3$) $\delta = -132.22$ (tt, $J = 5.5, 5.5$ Hz, 2F), -110.97 (t, $J = 5.5$ Hz, 4F); IR (KBr) 3089 (w), 2962 (w), 1492 (m), 1118 (vs), 1080 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 329.0767. Calcd. for $C_{17}H_6F_6O$: 329.0765.

*4.2.2. 1,2-Bis(4-methylphenyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5b**)*

m.p.: 62–64 °C; ^{1}H NMR ($CDCl_3$) $\delta = 2.34$ (s, 6H), 7.13 (ABq, $J = 8.0$ Hz, 4H), 7.22 (ABq, $J = 8.0$ Hz, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 21.39$, 111.17 (tquint., $J = 270.4$, 25.2 Hz), 116.57 (tt, $J = 256.1$, 24.3 Hz), 124.99, 129.16, 129.57, 138.50–139.50 (m), 140.50; ^{19}F NMR ($CDCl_3$) $\delta = -132.31$ to -132.24 (m, 2F), -111.00 to -110.90 (m, 4F); IR (KBr) 3309 (m), 2661 (m), 1612 (m), 1261 (s), 1195 (s) cm^{-1}; HRMS (FAB). Found: *m/z* 356.1000. Calcd. for $C_{19}H_{14}F_6$: 356.1000.

*4.2.3. 1,2-Bis(4-trifluoromethylphenyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5c**)*

m.p.: 93–95 °C; ^{1}H NMR ($CDCl_3$) $\delta = 7.48$ (ABq, $J = 8.3$ Hz, 2H), 7.66 (ABq, $J = 8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 111.09$ (tquint., $J = 261.4$, 34.9 Hz), 116.4 (tt, $J = 258.1$, 23.8 Hz), 123.52 (q, $J = 272.5$ Hz), 126.15 (q, $J = 3.6$ Hz), 129.76, 130.84, 132.72 (q, $J = 33.0$ Hz), 139.52–140.65 (m); ^{19}F NMR ($CDCl_3$) $\delta = -132.40$ to -131.90 (m, 2F), -111.04 (t, $J = 5.6$ Hz, 4F), -63.80 (s, 6F); IR (KBr) 1620 (m), 1330 (vs), 1288 (s), 1164 (s), 1064 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 464.0435. Calcd. for $C_{19}H_8F_{12}$: 464.0434.

*4.3. Typical procedure for the synthesis of 1,2-bis(1-butoxyvinyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5e**)*

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 6.6 equiv. of 1-butoxyvinyllithium in THF. To this solution was slowly added 0.767 g (6.6 mmol) of tetramethylenediamine at 0 °C. The whole was stirred for 10 min at 0 °C and then cooled to −78 °C. To the solution was slowly added 0.212 g (1.0 mmol) of **2** in THF (1 mL) via a syringe at −78 °C. After stirring for 2 h at −78 °C, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL). The resultant mixture was extracted with ether (20 mL × 5) and the organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator under reduced pressure. Column chromatography of the residue using hexane gave pure product, 1,2-bis(1-butoxyvinyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5e**).

*4.3.1. 1,2-Bis(1-butoxyvinyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5e**)*

^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (t, $J = 7.4$ Hz, 3H), 1.42 (tq, $J = 7.6, 7.6$ Hz, 2H), 1.66 (tt, $J = 7.2, 7.2$ Hz, 2H), 3.72 (t, $J = 6.4$ Hz, 2H), 4.50 (d, $J = 3.2$ Hz, ^{1}H), 4.59 (d, $J = 3.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 13.71$, 19.21, 30.76, 67.74, 91.05, 110.01 (tt, $J = 271.5, 25.3$ Hz), 115.45 (ttt, $J = 263.1, 26.3, 2.3$ Hz), 136.45–137.30 (m), 150.09; ^{19}F NMR ($CDCl_3$) $\delta = -132.30$ (tt, $J = 4.8, 4.8$ Hz, 2F), -111.82 (t, $J = 4.8$ Hz, 4F); IR (neat) 2962 (s), 1614 (s), 1309 (vs), 1276 (vs), 1143 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 372.1519. Calcd. for $C_{17}H_{22}F_6O_2$: 372.1524.

*4.4. Typical procedure for the synthesis of 1,2-bis(phenylethynyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5f**) by using lithium phenylacetylide*

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 0.247 g (2.42 mmol) of ethynylbenzene in THF (4.4 mL). To this solution was dropwise added a solution of *n*-butyllithium in hexane (2.2 mmol) via a syringe at 0 °C and the whole was stirred for 30 min at 0 °C. To the resulting solution was slowly added 0.212 g (1.0 mmol) of **2** in THF (1 mL) via a syringe at −78 °C. After being stirred for 2 h at room temperature, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL), followed by extraction with ether (20 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane as eluent yielded pure product, 1,2-bis(phenylethynyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5f**). The synthesis of **5h** and **5i** was made as follows. To a solution of the corresponding terminal alkyne in THF was dropwise added a solution of *n*-butyllithium in hexane at −78 °C via a syringe. After stirring at −78 °C for 30 min, a solution of **2** in THF was added slowly via a syringe at −78 °C. The reaction mixture was stirred at −10 °C for 20 h (for **5h**) or at room temerature for 2 h (for **5i**).

*4.4.1. 1,2-Bis(phenylethynyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5f**)*

m.p.: 32–34 °C; ^{1}H NMR ($CDCl_3$) $\delta = 7.40$–7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) $\delta = 78.02$, 106.94, 111.03 (tquint., $J = 272.9$, 23.9 Hz), 114.61 (tt, $J = 259.0$, 23.9 Hz), 120.65, 128.71, 130.72, 132.47, one peak cannot be analyzed for overlapping a carbon of phenyl group; ^{19}F NMR ($CDCl_3$) $\delta = -131.73$ (tt, $J = 4.4, 4.4$ Hz, 2F), -111.38 (t, $J = 5.5$ Hz, 4F); IR (KBr) 2214 (vs), 1492 (s), 1323 (vs), 1276 (vs), 1145 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 376.0681. Calcd. for $C_{21}H_{10}F_6$: 376.0687.

*4.4.2. 1,2-Bis(4-metoxyphenylethynyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5g**)*

m.p.: 107–109 °C; ^{1}H NMR ($CDCl_3$) $\delta = 3.85$ (s, 3H), 6.92 (ABq, $J = 8.8$ Hz, 2H), 7.54 (ABq, $J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 55.31$, 77.72, 107.33, 111.05 (tquint., $J = 272.2$, 25.0 Hz), 112.69, 114.39, 114.64 (tt, $J = 266.6$,

26.1 Hz), 127.00–127.85 (m), 134.23, 161.52; ^{19}F NMR ($CDCl_3$) δ = −131.82 (tt, J =4.5, 4.5 Hz, 2F), −111.31 (t, J = 4.5 Hz, 4F); IR (KBr) 2906 (w), 2202 (vs), 1508 (vs), 1315 (s), 1296 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 436.0900. Calcd. for $C_{23}H_{14}F_6O_2$: 436.0898.

*4.4.3. 1,2-Bis[(trimethylsilyl)ethynyl]-3,3,4,4,5, 5-hexafluorocyclopentene (**5h**)*

^{1}H NMR ($CDCl_3$) δ = 0.28 (s, 18H); ^{13}C NMR ($CDCl_3$) δ = −0.70, 91.51, 110.86 (tquint., J = 272.9, 23.9 Hz), 114.26 (tt, J = 259.0, 25.2 Hz), 115.80, 129.50–130.50 (m); ^{19}F NMR ($CDCl_3$) δ = −132.11 (tt, J = 4.4, 4.4 Hz, 2F), −112.05 (t, J = 5.5 Hz, 4F); IR (neat) 2966 (m), 2360 (w), 1353 (s), 1280 (vs), 1161 (s) cm^{-1}; HRMS (EI). Found: *m/z* 368.0848. Calcd. for $C_{15}H_{18}F_6Si_2$: 368.0851.

*4.4.4. 1,2-Bis[3-(t-butyldimethylsilyloxy)propyn-1-yl]-3,3,4,4,5,5-hexafluorocyclopentene (**5i**)*

^{1}H NMR ($CDCl_3$) δ = 0.15 (s, 12H), 0.92 (s, 18H), 4.58 (s, 4H); ^{13}C NMR ($CDCl_3$) δ = −5.23, 18.19, 25.65, 52.06, 72.91, 110.68 (tquint., J = 271.6, 25.2 Hz), 114.38 (tt, J = 259.0, 23.9 Hz), 105.85, 128.50–129.50 (m); ^{19}F NMR ($CDCl_3$) δ = −132.00 (tt, J = 4.4, 4.4 Hz, 2F), −111.82 (t, J = 4.4 Hz, 4F); IR (neat) 2958 (s), 2233 (m), 1334 (s), 1257 (s), 1199 (s) cm^{-1}; HRMS (FAB). Found: *m/z* 513.2087. Calcd. for $C_{23}H_{35}F_6O_2Si_2$: 513.2080.

*4.4.5. 1,2-Di(1-pentynyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5j**)*

^{1}H NMR ($CDCl_3$) δ = 1.06 (t, J = 7.5 Hz, 6H), 1.66 (tq, J = 7.5, 7.5 Hz, 4H), 2.49 (t, J = 7.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ = 13.20, 21.42, 21.94, 69.80, 108.87, 110.93 (tquint., J = 271.6, 26.4 Hz), 114.62 (tt, J = 257.8, 23.9 Hz), 128.55–129.25 (m); ^{19}F NMR ($CDCl_3$) δ = −132.05 (tt, J = 4.4, 4.4 Hz, 2F), −112.12 (t, J = 4.4 Hz, 4F); IR (neat) 2970 (s), 2229 (s), 1384 (s), 1276 (vs), 1134 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 308.1000. Calcd. for $C_{15}H_{14}F_6$: 308.1000.

*4.4.6. 1,2-Bis(3-cyclohexyl-1-propynyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5k**)*

^{1}H NMR ($CDCl_3$) δ = 1.01–1.11 (m, 4H), 1.13–1.20 (m, 2H), 1.22–1.32 (m, 4H), 1.55–1.64 (m, 2H), 1.65–1.71 (m, 2H), 1.72–1.78 (m, 4H), 1.81–1.87 (m, 4H), 2.40 (d, J = 6.6Hz, 4H); ^{13}C NMR ($CDCl_3$) δ = 26.08, 26.09, 27.76, 32.61, 37.00, 70.60, 108.09, 110.94 (tquint., J = 272.2, 24.3 Hz), 114.62 (tt, J = 257.9, 24.1 Hz), 128.55–129.25 (m); ^{19}F NMR ($CDCl_3$) δ = −131.98 (tt, J = 4.5, 4.5 Hz, 2F), −112.04 (t, J = 4.5 Hz, 4F); IR (neat) 2927 (vs), 2229 (s), 1450 (s), 1388 (s), 1278 (vs), 1136 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 416.1936. Calcd. for $C_{23}H_{26}F_6$: 416.1939.

*4.4.7. 1,2-Bis(1-cyclohexenylethynyl)3,3,4,4,5, 5-hexafluorocyclopentene (**5l**)*

m.p.: 42–44 °C; ^{1}H NMR ($CDCl_3$) δ = 1.60–1.73 (m, 8H), 2.15–2.25 (m, 8H), 6.42–6.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 21.12, 21.96, 26.10, 28.43, 76.10, 108.64, 111.00 (tquint., J = 272.2, 24.0 Hz), 114.56 (tt, J = 257.9, 24.0 Hz), 119.81, 127.42–128.05 (m), 141.28; ^{19}F NMR ($CDCl_3$) δ = −131.95 (tt, J = 4.5, 4.5 Hz, 2F), −111.64 (t, J = 4.5 Hz, 4F); IR (KBr) 2935 (s), 2181 (vs), 1618 (s), 1436 (s), 1313 (vs), 1191 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 384.1310. Calcd. for $C_{21}H_{18}F_6$: 384.1313.

*4.5. Typical procedure for the synthesis of 1-(4-methoxyphenyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4m**)*

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 2.2 equiv. of 4-methoxyphenylmagnesium bromide in THF. To this solution was slowly added 0.212 g (1.0 mmol) of **2** in THF (1 mL) via a syringe at 0 °C. After being stirred for 20 h at room temperature, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL). The resultant mixture was extracted with ether (20 mL × 5) and the organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator under reduced pressure. Column chromatography of the residue using hexane gave pure product, 1-(4-methoxyphenyl)-2,3,3,4,4,5,5- heptafluorocyclopentene (**4m**).

*4.5.1. 1-(4-Methoxyphenyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4m**)*

^{1}H NMR ($CDCl_3$) δ = 3.87 (s, 3H), 7.00 (ABq, J = 9.0 Hz, 2H), 7.71 (ABq, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 55.28, 110.02 (tquint.d, J = 274.1, 23.9, 5.0 Hz), 111.05 (tq, J = 256.5, 25.1 Hz), 114.70, 116.07 (br s), 118.18 (td, J = 22.6, 8.8 Hz), 121.76 (tt, J = 25.1, 5.0 Hz), 130.52 (d, J = 6.3 Hz), 147.75–151.25 (dm, J = 300.5 Hz), 161.90; ^{19}F NMR ($CDCl_3$) δ = −134.85 to −133.80 (m, 1F), −130.56 (br s, 2F), −118.23 (s, 1F), −118.05 (s, 1F), −108.48 (s, 1F), −108.34 (s, 1F); IR (neat) 2846 (w), 2372 (m), 1612 (s), 1377 (vs), 1272 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 300.0380. Calcd. for $C_{12}H_7F_7O$: 300.0385.

*4.5.2. 1-Phenyl-2,3,3,4,4,5,5-heptafluorocyclopentene (**4a**)*

^{1}H NMR ($CDCl_3$) δ = 7.49–7.52 (m, 3H), 7.71–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 110.18 (tquint.d, J = 273.8, 24.9, 4.8 Hz), 111.08 (tq, J = 256.9, 23.2 Hz), 116.16 (tdt, J = 259.2, 10.8, 2.2 Hz), 122.19 (tt, J = 25.3, 6.1 Hz), 123.90 (d, J = 3.7 Hz), 128.77 (d, J = 5.8 Hz), 129.26, 131.46, 149.75–153.00 (dm, J = 303.4 Hz); ^{19}F NMR ($CDCl_3$) δ = −132.00 to −131.10 (m, 1F), −130.71 (br s, 2F), −118.86 (s, 1F), −118.68 (s, 1F), −108.40 (s, 1F), −108.26 (s, 1F); IR (neat) 3066 (w), 2927 (w), 1685 (m), 1380 (vs), 1265 (s) cm^{-1}; HRMS (EI). Found: *m/z* 270.0277. Calcd. for $C_{11}H_5F_7$: 270.0279.

*4.5.3. 1-(4-Methylphenyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4b**)*

^{1}H NMR ($CDCl_3$) δ = 2.43 (s, 3H), 7.31 (ABq, J = 8.0 Hz, 2H), 7.64 (ABq, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 21.49, 110.94 (tquint. d, J = 256.5, 23.9, 5.0 Hz), 116.16 (tq, J = 237.7, 28.9 Hz), 120.90, 122.05 (tt, J = 25.1, 5.0 Hz), 128.62, 128.66, 129.97, 142.13, 148.50–152.50 (m); ^{19}F NMR ($CDCl_3$) δ = −133.10 to −132.10 (m, 1F), −130.74 (br s, 2F), −118.70 (s, 1F), −118.52 (s, 1F), −108.55 (s, 1F), −108.42 (s, 1F); IR (neat) 2927 (w), 2360 (m), 1685 (m), 1380 (vs), 1265 (vs), 1145 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 284.0433. Calcd. for $C_{12}H_7F_7$: 284.0436.

*4.5.4. 1-(4-Vinylphenyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4n**)*

^{1}H NMR ($CDCl_3$) δ = 5.42 (d, J = 10.5 Hz, 1H), 5.88 (d, J = 17.5 Hz, 1H), 6.74 (dd, J = 17.5, 10.5 Hz, 1H), 7.52 (ABq, J = 8.3 Hz, 2H), 7.70 (ABq, J = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 109.98 (tquint.d, J = 272.9, 23.9, 6.3 Hz), 110.91 (tq, J = 256.6, 22.6 Hz), 116.01 (tdt, J = 262.8, 11.3, 2.5 Hz), 116.71, 121.74 (tt, J = 25.2, 6.3 Hz), 122.88, 126.90, 128.96 (d, J = 6.3 Hz), 135.63, 140.59, 150.92 (dm, J = 299.3 Hz); ^{19}F NMR ($CDCl_3$) δ = −132.00∼−131.10 (m, 1F), −130.66 (br s, 2F), −118.65 (s, 1F), −118.47 (s, 1F), −108.34 (s, 1F), −108.21 (s, 1F); IR (neat) 3097 (w), 1681 (m), 1380 (vs), 1265 (s), 1145 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 296.0435. Calcd. for $C_{13}H_7F_7$: 296.0436.

*4.5.5. 1-Cyclohexyl-2,3,3,4,4,5,5-heptafluorocyclopentene (**4o**)*

^{1}H NMR ($CDCl_3$) δ = 0.85–1.40 (m, 6H), 1.50–1.90 (m, 5H); ^{19}F NMR ($CDCl_3$) δ = −134.40 to −133.20 (m, 1F), −131.00 (br s, 2F), −119.57 (s, 1F), −119.38 (s, 1F), −109.83 (s, 1F), −109.70 (s, 1F); IR (neat) 2922 (vs), 2851 (vs), 1448 (m), 1387 (m), 1153 (s) cm^{-1}; HRMS (FAB). Found: *m/z* 276.0740. Calcd. for $C_{11}H_{11}F_7$: 276.0749.

*4.6. Typical procedure for the synthesis of 1,2-bis(4-methoxyphenyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5m**) by using 4-methoxyphenylmagnesium bromide*

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 6.6 equiv. of 4-methoxyphenylmagnesium bromide in THF. To this solution was slowly added 0.212 g (1.0 mmol) of **2** in THF (1 mL) via a syringe at 0 °C. After being stirred for 6 h at reflux temperature, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL), followed by extraction with ether (20 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (2:1) as eluent yielded pure product, 1,2-bis(4-methoxyphenyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5m**).

*4.6.1. 1,2-Bis(4-methoxyphenyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5m**)*

m.p.: 86–88 °C; ^{1}H NMR ($CDCl_3$) δ = 3.75 (s, 6H), 6.82 (ABq, J = 8.5 Hz, 2H), 7.29 (ABq, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 55.07, 111.22 (tquint., J = 270.6, 25.3 Hz), 114.35, 116.72 (tt, J = 255.7, 23.6 Hz), 120.11, 130.86, 137.45–138.10 (m), 161.02; ^{19}F NMR ($CDCl_3$) δ = −132.10 (s, 2F), −110.70 (s, 4F); IR (KBr) 3008 (w), 2842 (m), 1612 (vs), 1519 (vs), 1257 (vs), 1026 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 388.0901. Calcd. for $C_{19}H_{14}F_6O_2$: 388.0898.

*4.6.2. 1,2-Dibutyl-3,3,4,4,5,5-hexafluorocyclopentene (**5d**)*

^{1}H NMR ($CDCl_3$) δ = 0.94 (t, J = 7.0 Hz, 6H), 1.37 (tq, J = 7.5, 7.5 Hz, 4H), 1.53 (tt, J = 7.5, 7.5 Hz, 4H), 2.30 (t, J = 8.0 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ = 13.65, 22.77, 23.59, 29.92, 111.04 (tquint., J = 271.6, 25.1 Hz), 117.17 (tt, J = 254.0, 23.9 Hz), 141.25–142.00 (m); ^{19}F NMR ($CDCl_3$) δ = −133.5 to −132.9 (m, 2F), −112.9 to −113.4 (m, 4F); IR (KBr) 2962 (vs), 2873 (s), 1666 (s), 1342 (vs), 1284 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 288.1314. Calcd. for $C_{13}H_{18}F_6$: 288.1313.

*4.7. Typical procedure for the synthesis of 1-butyl-2-(4-methoxyphenyl)-3,3,4,4,5,5-hexafluorocyclopentene (**5am**)*

A 50 mL three-necked round-bottomed flask quipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 2.2 equiv. of butylmagnesium chloride in THF. To this solution was slowly added 0.301 g (1.0 mmol) of **4m** in THF (1 mL) via a syringe at 0 °C. After being stirred for 20 h at room temperature, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL). The resultant mixture was extracted with ether (20 mL × 5) and the organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator under reduced pressure. Column chromatography of the residue using hexane/benzene (5:1) gave pure product, 1-butyl-2-(4-methoxyphenyl)-3,3,4,4,5,5- hexafluorocyclopentene (**5am**).

*4.7.1. 1-(4-Methoxyphenyl)-2-phenyl-3,3,4,4,5,5-hexafluorocyclopentene (**5am**)*

^{1}H NMR ($CDCl_3$) δ = 3.80 (s, 3H), 6.82 (ABq, J = 8.8 Hz, 2H), 7.27 (ABq, J = 8.8 Hz, 2H), 7.31–7.42 (m, 5H); ^{19}F NMR ($CDCl_3$) δ = −132.15 (tt, J = 4.4, 4.4 Hz, 2F), −111.20 to −110.45 (m, 4F); IR (neat) 3062 (w), 2842 (m), 1515 (s), 1396 (s), 1257 (vs), 1029 (s) cm^{-1}; HRMS (FAB). Found: *m/z* 358.0797. Calcd. for $C_{18}H_{12}F_6O$: 358.0792.

*4.7.2. 1-Butyl-2-phenyl-3,3,4,4,5,5-hexafluorocyclopentene (**5ad**)*

^{1}H NMR ($CDCl_3$) δ = 0.84 (t, J = 10.0 Hz, 3H), 1.28 (tq, J = 7.5, 7.5 Hz, 2H), 1.54 (tt, J = 7.5, 7.5 Hz, 2H), 2.40 (t,

J = 7.0 Hz, 2H), 7.36–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 13.41, 22.64, 24.25, 29.68, 111.27 (tquint., J = 270.6, 25.4 Hz), 116.54, 116.72 (tt, J = 256.4, 24.3 Hz), 117.19 (tt, J = 255.6, 23.9 Hz), 127.90, 128.67, 128.89, 130.03, 139.96–141.11 (m), 142.70–143.70 (m); ^{19}F NMR ($CDCl_3$) δ = −133.20 to −132.40 (m, 2F), −113.18 (br s, 2F), −111.05 (br s, 2F); IR (neat) 2962 (s), 2873 (m), 1342 (s), 1284 (vs), 1099 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 308.1001. Calcd. for $C_{15}H_{14}F_6$: 308.1000.

*4.7.3. 1-Butyl-2-(4-methoxyphenyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5md**)*

^{1}H NMR ($CDCl_3$) δ = 0.90 (t, J = 7.0 Hz, 3H), 1.35 (tq, J = 7.5, 7.5 Hz, 2H), 1.60 (tt, J = 7.5, 7.5 Hz, 2H), 2.46 (br s, 2H), 3.87 (s, 3H), 7.02 (ABq, J = 8.5 Hz, 2H), 7.37 (ABq, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 13.44, 22.69, 24.31, 29.67, 55.18, 111.22 (tquint., J = 266.6, 25.2 Hz), 114.35, 116.68 (tt, J = 255.3, 22.6 Hz), 117.27 (tt, J = 255.3, 22.6 Hz), 119.95, 130.15, 139.75–140.30 (m), 141.27–142.20 (m), 160.96; ^{19}F NMR ($CDCl_3$) δ = −132.86 (tt, J = 4.4 Hz, 2F), −112.98 (br s, 2F), −111.05 (br s, 2F); IR (neat) 2962 (s), 1612 (vs), 1515 (vs), 1342 (s), 1276 (vs), 1188 (vs) cm^{-1}; HRMS (FAB). Found: *m/z* 338.1097. Calcd. for $C_{16}H_{16}F_6O$: 338.1105.

*4.8. Typical procedure for the synthesis of 1-(4-methylphenyl)-2-phenyl-3,3,4,4,5,5-hexafluorocyclopentene (**5ab**)*

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of 2.2 equiv. of 4-methylphenyllithium in diethyl ether. To this solution was slowly added 0.284 g (1.0 mmol) of **4b** in THF (1 mL) via a syringe at −78 °C. After being stirred for 2 h at −78 °C, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride (30 mL), followed by extraction with ether (20 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (5:1) as eluent yielded pure product, 1-(4-methylphenyl)-2-phenyl-3,3,4,4,5,5-hexafluorocyclopentene (**5ab**).

*4.8.1. 1-(4-Methylphenyl)-2-phenyl-3,3,4,4,5, 5-hexaflurocyclopentene (**5ab**)*

^{1}H NMR ($CDCl_3$) δ = 2.31 (s, 3H), 7.10 (ABq, J = 8.0 Hz, 2H), 7.21 (ABq, J = 8.0 Hz, 2H), 7.31–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 21.36, 111.23 (tquint., J = 270.7, 25.4 Hz), 116.55 (tt, J = 253.8, 23.3 Hz), 116.62 (tt, J = 259.7, 21.0 Hz), 124.76, 126.82, 128.08, 128.88, 129.29, 129.61, 130.16, 138.55–139.25 (m), 139.45–140.15 (m), 140.73; ^{19}F NMR ($CDCl_3$) δ = −132.18 (tt, J = 4.4, 4.4 Hz, 2F), −111.15 to −110.55 (m, 4F); IR (neat) 3062 (w), 1608 (m), 1342 (s), 1284 (vs), 1195 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 342.0851. Calcd for $C_{18}H_{12}F_6$: 342.0843.

*4.8.2. 1-(4-Trifluoromethylphenyl)-2-phenyl-3,3,4,4,5, 5-hexafluorocyclopentene (**5ac**)*

^{1}H NMR ($CDCl_3$) δ = 7.32–7.45 (m, 5H), 7.48 (ABq, J = 8.2 Hz, 2H), 7.62 (ABq, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 111.09 (tquint., J = 271.2, 25.1 Hz), 116.24 (tt, J = 254.0, 24.1 Hz), 116.34 (tt, J = 256.7, 23.8 Hz), 123.58 (q, J = 272.5 Hz), 125.91 (q, J = 3.5 Hz), 127.13, 129.12, 129.22, 129.80, 130.75, 131.51, 132.18 (q, J = 33.0 Hz), 137.85–138.65 (m), 141.20–141.85 (m); ^{19}F NMR ($CDCl_3$) δ = −132.15 (tt, J = 5.5, 5.5 Hz, 2F), −111.45 to −111.00 (m, 2F), −110.95 to −110.55 (m, 2F), −63.64 (s, 3F); IR (neat) 3066 (w), 1620 (w), 1326 (vs), 1130 (vs), 1068 (vs) cm^{-1}; HRMS (EI). Found: *m/z* 396.0566. Calcd. for $C_{18}H_9F_9$: 396.0561.

*4.8.3. 1-Phenyl-2-(4-vinylphenyl)-3,3,4,4,5, 5-hexafluorocyclopentene (**5na**)*

^{1}H NMR ($CDCl_3$) δ = 5.32 (d, J = 11.0 Hz, 1H), 5.78 (d, J = 17.5 Hz, 1H), 6.67 (dd, J = 17.5, 11.0 Hz, 1H), 7.26–7.45 (m, 5H); ^{19}F NMR ($CDCl_3$) δ = −132.18 (tt, J = 5.5, 5.5 Hz, 2F), −111.10 to −110.60 (m, 4F); IR (neat) 3313 (m), 1666 (m), 1342 (s), 1261 (vs), 1195 (vs) (m) cm^{-1}; HRMS (EI). Found: *m/z* 354.0844. Calcd. for $C_{19}H_{12}F_6$: 354.0844.

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References

[1] (a) J.T. Welch, S. Eswarakrishnan, Fluorine in Bioorganic Chemistry, Wiley, New York, 1991;
(b) I. Ojima, J.R. McCarthy, J.T. Welch, Biomedical Frontiers of Fluorine Chemistry, American Chemical Society, Washington, DC, 1996;
(c) T. Hiyama, Organofluorine Compounds, Chemistry and Applications, Springer, New York, 2000;
(d) B.E. Smart, Chem. Rev. 96 (1996) 1555–1823.

[2] (a) V.A. Soloshonok, Enantiocontrolled Synthesis of Fluoro-organic Compounds, Wiley, New York, 1999;
(b) T. Kitazume, T. Yamazaki, Experimental Methods in Organic Fluorine Chemistry, Kodansha (1998);
(c) X. Qiu, W. Meng, F. Qing, Tetrahedron 60 (2004) 6711–6745;
(d) K. Mikami, Y. Itoh, M. Yamanaka, Chem. Rev. 104 (2004) 1–16;
(e) J. Ichikawa, Y. Wada, M. Fujiwara, K. Sakoda, Synthesis (2002) 1917–1936.

[3] (a) M. Irie, K. Sakemura, M. Okinaka, K. Uchida, J. Org. Chem. 60 (1995) 8305–8309;
(b) M. Takeshita, M. Irie, Tetrahedron Lett. 40 (1999) 1345–1348;
(c) J.P. Malval, I. Gosse, J.P. Morand, R. Lapouyade, J. Am. Chem. Soc. 124 (2002) 904–905;
(d) T. Kaieda, S. Kobatake, H. Miyasaka, M. Murakami, N. Iwai, Y. Nagata, A. Itaya, M. Irie, J. Am. Chem. Soc. 124 (2002) 2015–2024;
(e) A. Peters, C. Vitols, R. McDonald, N.R. Branda, Org. Lett. 5 (2003) 1183–1185;
(f) S. Yamamoto, K. Matsuda, M. Irie, Org. Lett. 5 (2003) 1769–1772;

(g) K. Yagi, M. Irie, Chem. Lett. 32 (2003) 848–849;
(h) K. Morimitsu, S. Kobatake, S. Nakamura, M. Irie, Chem. Lett. 32 (2003) 858–859.

[4] (a) J.D. Park, R. Sullivan, R.J. Mcmurtry, Tetrahedron Lett. 2 (1967) 173–176;
(b) J.D. Park, C.D. Bertino, B.T. Nakata, J. Org. Chem. 34 (1969) 1490–1492.

[5] (a) R.F. Stochel, M.T. Beachem, F.H. Megson, J. Org. Chem. 30 (1965) 1629–1632;
(b) K. Ralf, N. Michael, Japanese Patent Appl. 72,939 (1994).;
(c) R.F. Stockel, M.T. Beachem, F.H. Megson, Can. J. Chem. 42 (1964) 2880–2883;
(d) P.E. Lindner, D.M. Lemal, J. Org. Chem. 61 (1996) 5109–5115;
(e) A.E. Bayliff, M.R. Bryce, R.D. Chambers, J. Chem. Soc., Perkin Trans. 1 (1987) 763–767.

[6] (a) M. Matsui, M. Tsuge, K. Funabiki, K. Shibata, H. Muramatsu, K. Hirota, M. Hosoda, K. Tai, H. Shiozaki, M. Kim, K. Nakatsu, J. Fluorine Chem. 97 (1999) 207–212;
(b) Q. Mir, J.M. Shreeve, J. Fluorine Chem. 68 (1994) 269–275.

[7] (a) E.T. McBee, J.J. Turner, C.J. Morton, A.P. Stefani, J. Org. Chem. 30 (1965) 3698–3705;
(b) Q. Mir, C. Guo, R.L. Kirchmeier, J.M. Shreeve, J. Org. Chem. 59 (1994) 173–177;
(c) W.R. Cullen, P.S. Dhaliwal, Can. J. Chem. 45 (1967) 719–724.

[8] (a) D. Su, C. Guo, D. Willett, B. Scott, R.L. Kirchmeier, J.M. Shreeve, J. Am. Chem. Soc. 112 (1990) 3152–3155;
(b) R.F. Stockel, Can. J. Chem. 46 (1968) 2625–2628;
(c) A.W. Frank, J. Org. Chem. 31 (1966) 917–921;
(d) A. Matsui, H. Muramatsu, K. Inukai, Nippon Kagaku Kaishi (1972) 602–608.