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Tetrahedron 64 (2008) 4215–4223
Tetrahedron
www.elsevier.com/locate/tet

Preparation of perfluorocyclopentenylmetal species and their cross-coupling reaction with electrophiles—Remarkable accesses to versatile perfluorocyclopentene derivatives

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Received 20 December 2007; received in revised form 26 February 2008; accepted 27 February 2008
Available online 29 February 2008

Abstract

On treating perfluorocyclopentene with bis(tributylstannyl)cyanocuprate in THF at −78 °C for 1 h, perfluorocyclopentenylstannane was obtained in good yield. The reaction of the fluorinated vinylstannane with *n*-BuLi in THF at −78 °C for 1 h, followed by addition of carbonyl compounds, gave the corresponding allyl alcohols in good yields. On the other hand, Pd(0)-catalyzed cross-coupling reaction of perfluorocyclopentenylstannane with benzyl chloroformate in THF at reflux temperature for 2 h proceeded smoothly to form the decarbonated coupling product in high yield.

Keywords: Perfluorinated vinylstannane; Sn−Li exchange reaction; Perfluoroallyl alcohols; Stille-type coupling reaction

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]

Among such compounds, organic molecules containing a perfluorocyclopentene backbone have recently been recognized as one of the most attractive units for the applications to optoelectronic devices, etc.[3] Addition−elimination reactions of perfluorocyclopentene (**1**) with nucleophiles would provide a promising entry to the preparation of various perfluorocyclopentene derivatives.[4–7] Very recently, we reported that the reaction of **1** with various nucleophiles, such as Grignard reagents and organolithium reagents, took place smoothly to give the corresponding mono- (**2**) and/or di-substituted perfluorocyclopentenes (**3**) in good yields.[8] Moreover, a large excess amount of stabilized carbanions, such as diethyl sodiomalonate and triphenylphosphonium methylide, also underwent continuous addition−elimination/1,4-HF elimination/1,6-conjugate addition sequence, leading to 1,3-disubstituted products **4** in excellent yields (Scheme 1).[9]

The reaction of perfluorocyclopenten-1-ylmetal species with various *electrophiles* would also bring about a new and complementary entry to the synthetic methods for various types of perfluorocyclopentene derivatives, since little attention has been paid to this subject thus far. Herein, we wish to disclose a first preparation of perfluorocyclopent-1-enylstannane (**5-Sn**) and the cross-coupling reaction with various electrophiles (Scheme 2).

2. Results and discussion

2.1. Preparation of perfluorocyclopent-1-enylstannane (5-Sn)

Initially, we examined the preparation of perfluorocyclopenten-1-ylstannane **5-Sn** through the reaction of perfluorocyclopentene

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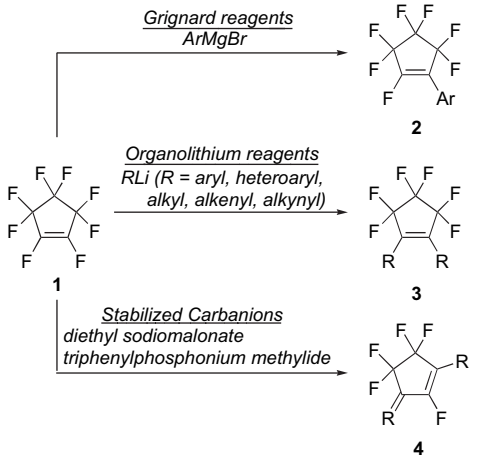
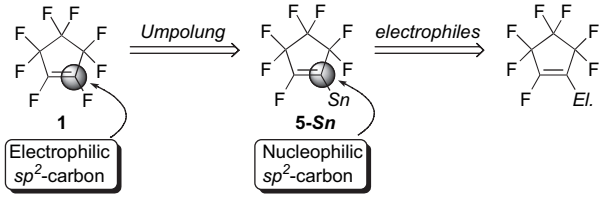
0040-4020/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.02.089



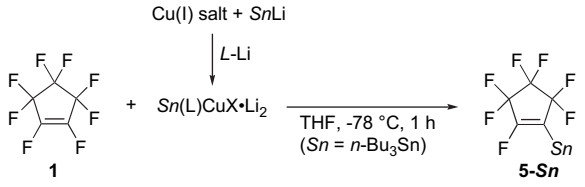
Scheme 1. Previous research outline.



Scheme 2. Intended research outline.

(**1**) with tributylstannyllithium.[10] Thus, the treatment of 1.0 equiv of **1** with 2.2 equiv of tributylstannyllithium in THF at −78 °C for 2 h led to a complex mixture, no desired product being obtained (Table 1, entry 1).

Table 1
Preparation of perfluorocyclopent-1-enylstannane (**5-Sn**)



Entry	Cu(I) salt	L	Equiv of **1**	Equiv of cuprate	Yield[a]/% of **5-Sn**
1[b]	None	*n*-Bu_3Sn	1.0	—	—
2	CuBr	*n*-Bu_3Sn	1.0	1.1	9
3	CuI	*n*-Bu_3Sn	1.0	1.1	7
4	CuCN	*n*-Bu_3Sn	1.0	1.1	34
5	CuCN	*n*-Bu_3Sn	1.0	2.2	49
6[c]	CuCN	None	1.0	2.2	38
7	CuCN	Me	1.0	2.2	12
8	CuCN	2-Thienyl	1.0	2.2	18
9	CuCN	*n*-Bu_3Sn	3.0	1.0	52
10[d]	CuCN	*n*-Bu_3Sn	3.0	1.0	35
11[e]	CuCN	*n*-Bu_3Sn	3.0	1.0	15

[a] Determined by ^{19}F NMR.
[b] Reaction of **1** with 2.2 equiv of *n*-Bu_3SnLi in THF at −78 °C for 1 h was carried out.
[c] Lower-ordered cyanocuprate (*n*-$Bu_3SnCuCN\cdot Li$) was used.
[d] Carried out at −50 °C for 1 h.
[e] Carried out at −78 °C for 15 h.

Addition of copper(I) salt, such as CuBr and CuI, did not also give satisfactory results. However, changing copper(I) salt from CuBr and CuI to CuCN significantly improved the yield, the desired vinylstannane **5-Sn** being obtained in 34% yield (entries 2–4). As shown in entry 5, when 2.2 equiv of bis(tributylstannyl)cyanocuprate[11] was used, the reaction proceeded smoothly to provide the corresponding **5-Sn** in 49% yield. The use of methyl or 2-thienyl group as a dummy ligand[12] was not effective, **5-Sn** was given in only 12 or 18% yield, respectively (entries 7 and 8). The reaction of an excess amount of **1** (3.0 equiv) with 1.0 equiv of bis(tributylstannyl)-cyanocuprate took place effectively to give the corresponding vinylstannane **5-Sn** in 52% yield (entry 9). It was found that the reaction at −50 °C for 1 h or at −78 °C for 15 h appreciably decreased the yield of **5-Sn** (entries 10 and 11). Although the vinylstannane **5-Sn** could not be obtained in an analytically pure form, due to the contaminated tetrabutyltin, we found that the contamination did not lead to a significant decrease of the yields of the coupling products.

3. Coupling reaction with various electrophiles

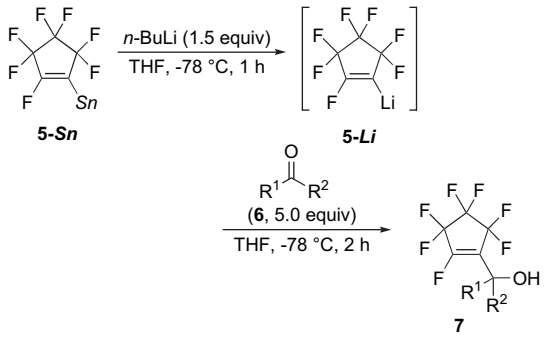
3.1. Coupling reaction with aldehydes or ketones through Sn–Li exchange reaction

With the fluorinated vinylstannane **5-Sn** in hand, our attention was directed toward the coupling reaction of **5-Sn** with various electrophiles. Thus, the treatment of **5-Sn** with 1.5 equiv of butyllithium in THF at −78 °C for 1 h, followed by the addition of carbonyl compounds, led to the corresponding allylic alcohols. The results are tabulated in Table 2.

The reaction of **5-Li** with 2.0 equiv of benzaldehyde (**6a**) in THF at −78 °C for 2 h did not give a satisfactory result, the corresponding allyl alcohol **7a** being obtained in only 25% yield (entry 1). When 5.0 equiv of **6a** was used, the yield of **7a** significantly increased to 88% (entry 2). As shown in entry 3, aromatic aldehyde having an electron-donating group at *p*-position in benzene ring, like 4-methylbenzaldehyde (**6b**), could participate in the coupling reaction. In the case of 4-chlorobenzaldehyde (**6c**) or cinnamaldehyde (**6f**), the yield of **7c** or **7f** was decreased to 62 or 41% yield. Additionally, aliphatic aldehydes, such as 3-phenylpropionaldehyde (**6d**) and cyclohexanecarboxaldehyde (**6e**), were found to be much less reactive in this coupling reaction, while the addition of $BF_3\cdot OEt_2$ was very effective, leading to the corresponding allylic alcohol **7d** or **7e** in 34–85% yield as shown in entries 5, 7, 9, and 11. As described in entries 12–16, various ketones, such as acetophenone (**6g**), 4-methylacetophenone (**6h**), 4-chloroacetophenone (**6i**), and benzylideneacetone (**6j**), were also found to be good electrophiles, the corresponding allylic alcohols **7g**, **7h**, **7i**, and **7j** being obtained in 60–78% yields. In Table 2, the difficulty of the separation between the coupling product and carbonyl compound by silica gel column chromatography resulted in the low isolated yield.

The coupling reaction with other electrophiles,[13] such as acyl chloride, chloroformate, and *N*-tosyl benzaldimine, were

Table 2
Cross-coupling reaction of **5-Sn** with carbonyl compounds through Sn–Li exchange reaction



Entry	R^1	R^2		Yield[a]/% of **7**
1[b]	Ph	H	(**a**)	25
2	Ph	H	(**a**)	88 (61)
3	4-MeC_6H_4	H	(**b**)	82 (60)
4	4-ClC_6H_4	H	(**c**)	62
5[c]	4-ClC_6H_4	H	(**c**)	85 (78)
6	$PhCH_2CH_2$	H	(**d**)	Trace
7[c]	$PhCH_2CH_2$	H	(**d**)	34
8	Cy	H	(**e**)	Trace
9[c]	Cy	H	(**e**)	49 (18)
10	(*E*)-PhCH=CH	H	(**f**)	41
11[c]	(*E*)-PhCH=CH	H	(**f**)	72 (55)
12	Ph	Me	(**g**)	78 (49)
13	4-MeC_6H_4	Me	(**h**)	60 (35)
14[c]	4-MeC_6H_4	Me	(**h**)	72 (42)
15[c]	4-ClC_6H_4	Me	(**i**)	72 (50)
16[c]	(*E*)-PhCH=CH	Me	(**j**)	67

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] With 2.0 equiv of aldehyde.
[c] $BF_3{\cdot}OEt_2$ was employed as Lewis acid.

examined. However, any trace of the corresponding coupling products were not detected at all in all cases.

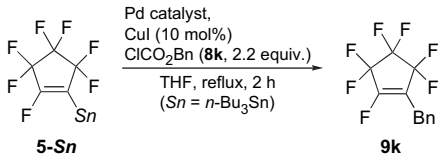
3.2. *Pd(0)-catalyzed cross-coupling of **5-Sn** with chloroformates*

We next attempted the Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloroformate **8k**.[14] Initial studies were started from the coupling reaction conditions reported previously[14a] (entry 1, Table 3). Thus, the coupling reaction of **5-Sn** with **8k** in the presence of 5 mol % of $Cl_2Pd(PPh_3)_2$ and 10 mol % of CuCN in toluene at 80 °C for 2 h was conducted. However, no coupling product was obtained at all. Then, we reexamined the coupling reaction of **5-Sn** with **8k** in detail.

In entries 2–7, various phosphine ligands, such as $(o\text{-Tol})_3P$, Cy_3P, $n\text{-}Bu_3P$, and $t\text{-}Bu_3P$, were carefully examined, however, no trace of the desired coupling product was detected. Interestingly, the use of $(EtO)_3P$ or $(2\text{-furyl})_3P$ as a ligand caused a small amount of formation of decarbonated product, i.e., 1-benzylperfluorocyclopentene (**9k**), together with 60 or 38% recovery of the starting material, respectively.

Changing the phosphine ligand from the above monodentate ligands to a bidentate ligand, 1,1′-bis(diphenylphosphino)ferrocene (dppf) improved the yield of **9k**. Other bidentate ligand,

Table 3
Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloroformate (**8k**)

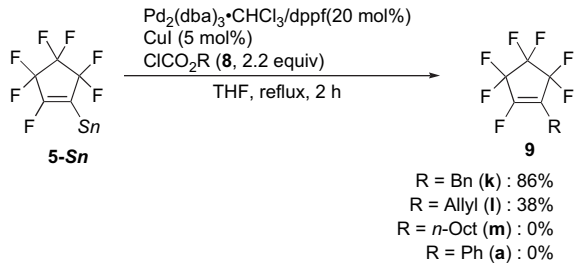


Entry	Pd catalyst (mol %)	Yield[a]/% of **9k**	Recovery[a]/% of **5-Sn**
1[b]	$Cl_2Pd(PPh_3)_2$ (5)	0	68
2	$1/2Pd_2(dba)_3{\cdot}CHCl_3$ (5)	0	87
3[c]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2Ph_3P$ (5)	Trace	37
4[c]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2(o\text{-Tol})_3P$ (5)	0	58
5[c]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2Cy_3P$ (5)	0	Trace
6[c]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2n\text{-}Bu_3P$ (5)	0	4
7[c]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2t\text{-}Bu_3P$ (5)	0	26
8	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2(EtO)_3P$ (5)	6	60
9	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+$2(2\text{-furyl})_3P$ (5)	13	38
10	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppe (5)	0	57
11	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (5)	38	40
12[c,d]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (5)	4	0
13[c,e]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (5)	7	0
14[c,f]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (5)	45	0
15	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (20)	87	0
16[g]	$1/2Pd_2(dba)_3{\cdot}CHCl_3$+dppf (20)	86	0

[a] Determined by ^{19}F NMR.
[b] Carried out in the presence of CuCN in toluene at 80 °C for 2 h.
[c] Unknown product was obtained.
[d] CuBr was employed as Cu(I) salt.
[e] CuCN was employed as Cu(I) salt.
[f] Carried out for 20 h.
[g] With 5 mol % of CuI.

like 1,1′-bis(diphenylphosphino)ethane (dppe), did not lead to a satisfactory result. As shown in entries 12 and 13, it was found that CuBr and CuCN were less efficient and that CuI was the additive of choice. Increasing the amount of catalyst from 5 to 20 mol % caused a significant improvement of the yield (entry 15). Thus, when the coupling reaction in the presence of 20 mol % of palladium catalyst and 10 mol % of CuI in THF at reflux temperature for 2 h was performed, **9k** was obtained in 87% yield. The coupling reaction in the presence of 5 mol % of CuI also proceeded smoothly to give the corresponding **9k** in 86% yield (entry 16).

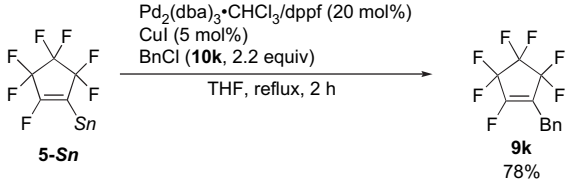
Subsequently, the coupling reaction of **5-Sn** with commercially available chloroformates **8** using the above optimum reaction conditions (entry 16 in Table 3) was carried out, as shown in Scheme 3.



Scheme 3. Cross-coupling reaction of **5-Sn** with various chloroformates.

The coupling reaction with allyl chloroforomate (**8l**) took place to form the corresponding 1-allylperfluorocyclopentene (**9l**), though the yield was unsatisfactory. Other chloroformates (*n*-alkyl or aryl chloroformates, **8m** and **8a**) could not participate in the coupling reaction at all.

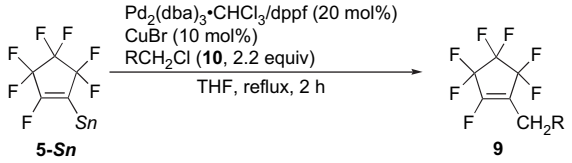
We next attempted the Stille-type cross-coupling reaction of **5-Sn** with other halides such as benzoyl chloride and aryl or alkyl halides under the same conditions. Thus, the cross-coupling reaction of **5-Sn** with benzoyl chloride, iodobenzene or β-phenethyl bromide in the presence of 10 mol % of $Pd_2(dba)_3 \cdot CHCl_3$, 20 mol % of dppf, and 5 mol % of CuI in THF at reflux temperature for 2 h did not lead to satisfactory results, while the use of benzyl bromide[15] as a halide was so effective for the coupling reaction, affording the corresponding coupling product **9k**, quantitatively. It was found, moreover, that the corresponding chloride **10k** could also be applied to the coupling reaction, **9k** being obtained in 78% yield (Scheme 4).



Scheme 4. Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloride (**10k**).

Then, our interest was directed toward the Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with various benzyl-type chlorides **10**. The results are summarized in Table 4.

Table 4
Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl-type chlorides **10**



Entry	R	Yield[a]/% of **9**	Recovery[a]/% of **5-Sn**
1[b]	Ph (**k**)	78	18
2[c]	Ph (**k**)	85	12
3	Ph (**k**)	90 (41)	9
4	4-$MeOC_6H_4$ (**n**)	95 (39)	0
5	4-MeC_6H_4 (**o**)	97 (60)	0
6	4-NCC_6H_4 (**p**)	55	Trace
7	2-Furyl (**q**)	63	0
8	2-Thienyl (**r**)	70	0
9[d]	(*E*)-PhCH=CH (**s**)	48	10
10[e]	(*E*)-PhCH=CH (**s**)	75 (52)	0
11	PhC≡CH (**t**)	85 (45)	0

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[b] CuI (5 mol %) was employed.
[c] CuI (10 mol %) was employed.
[d] Unknown product was obtained in 20% yield.
[e] The corresponding bromide was used.

As shown in entries 2 and 3, when 10 mol % of CuI or CuBr was employed in the coupling reaction with benzyl chloride (**10k**), a slight increase of the yield was observed, **9k** being obtained in 85 or 90% yield, respectively. Benzyl-type chlorides having an electron-donating group at *p*-position in benzene ring, e.g., 4-methoxybenzyl chloride (**10n**) or 4-methylbenzyl chloride (**10o**), also participated in the coupling reaction, leading to the corresponding benzylated product **9n** or **9o** in 95 or 93% yield, respectively (entries 4 and 5). On the other hand, the reaction with 4-cyanobenzyl chloride (**10p**) was slightly sluggish, the corresponding **9p** being obtained in 55% yield. As shown in entries 7 and 8, 2-(chloromethyl)furan (**10q**) or -thiophene (**10r**) also participated well in the coupling reaction, giving rise to the corresponding coupling product **9q** or **9r** in 63 or 66% yield, respectively. (*E*)-Cinnamyl chloride (**10s**) was not effective for the coupling reaction, but the use of the corresponding bromide facilitated the coupling reaction, affording the coupling product **9s** in 75% yield (entries 9 and 10). The coupling reaction with 3-phenyl-2-propyn-1-yl chloride (**10t**) also took place smoothly to give the coupling product **9t** in 85% yield. The volatility of the products given in Table 4 causes the decrease of the isolated yields.

On the basis of the results that the Pd(0)-catalyzed cross-coupling reaction with benzyl chloroformate or benzyl chloride afforded the same product, 1-benzylperfluorocyclopentene **9k** in similar yields, both reactions may proceed via a common benzylpalladium complex **Int-B**. Therefore, the following reaction mechanism may be proposed as shown in Scheme 5. Thus, the coupling reaction presumably proceeds via the following steps: (1) oxidative addition of C–Cl bond in chloroformate to Pd(0) (**Int-A**), (2) formation of benzylpalladium chloride (**Int-B**) via evolution of CO_2, which is also formed from benzyl chloride and palladium catalyst, (3) transmetallation of vinyl copper species **5-Cu**, which is formed by treatment of **5-Sn** with copper(I) salt, leading to **Int-C**, (4) reductive elimination to give the coupling product **9k** and regeneration of Pd(0).

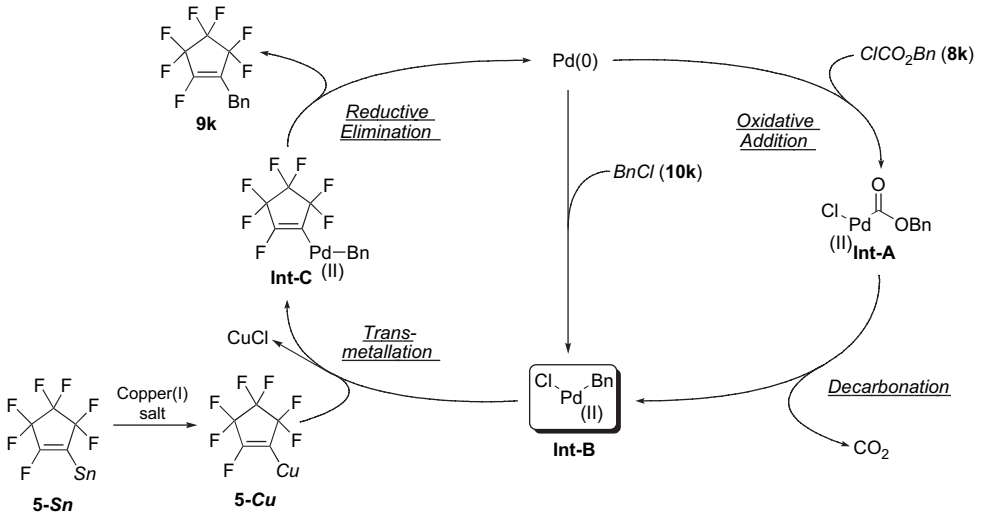
4. Conclusion

In conclusion, we discovered perfluorocyclopent-1-enylstannane (**5-Sn**) as a new perfluorinated vinylmetal species. Treatment of the perfluorinated vinylstannane **5-Sn** with *n*-BuLi in THF at −78 °C, followed by addition of aromatic aldehydes or ketones in the presence of $BF_3 \cdot OEt_2$ at −78 °C, afforded the corresponding secondary or tertiary allyl alcohols in good yields, respectively. The Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloroformate (**8k**) in the presence of 20 mol % of $Pd_2(dba)_3 \cdot CHCl_3$/dppf and 5 mol % of CuI in THF at reflux temperature for 2 h proceeded smoothly to form the decarbonated coupling product in high yield. We also found that the Pd(0) catalyst, i.e., $Pd_2(dba)_3 \cdot CHCl_3$/dppf, also facilitated the coupling reaction of **5-Sn** with various benzyl-type chlorides, leading to the coupling products in good yields.

5. Experimental

5.1. Measurements and materials

^1H and ^{13}C NMR spectra were recorded with a Bruker DRX-500 (500.13 MHz for ^1H and 125.75 MHz for ^{13}C)



Scheme 5. Proposed reaction mechanism for Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with **8k** or **10k**.

spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane as an internal reference. A JEOL JNM-AL400 (376.05 MHz) spectrometer was used to record ^{19}F NMR spectra in $CDCl_3$ using $CFCl_3$ as an internal standard. Infrared spectra (IR) were determined in a liquid film or KBr disk method with an FT/IR-4100 (JASCO) instrument. High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer.

Anhydrous tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries, Ltd. *n*-BuLi (a 1.6 M hexane solution) was commercially available from Wako Pure Chemical Industries, Ltd. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. All reactions were carried out under an atmosphere of argon. Thin layer chromatography (TLC) was done with Merck silica gel $60F_{254}$ plates and column chromatography was carried out with Wako gel C-200.

5.2. Preparation of tributyl(perfluorocyclopent-1-enyl)stannane (*5-Sn*)

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 suspension of 0.045 g (0.5 mmol) of CuCN in THF (1 mL). To the suspension was slowly added a THF solution of 1.0 mmol of tributylstannyllithium (0.75 mL), prepared from bis(tributylstannane) and *n*-BuLi in THF at 0 °C for 0.5 h, via a syringe at −78 °C. The whole mixture was stirred at −50 °C for 10 min, and to the resulting solution was slowly added 0.318 g (1.5 mmol) of perfluorocyclopentene **1** in THF (2 mL) via a syringe at −78 °C. After being stirred for 1 h at −78 °C, the reaction mixture was poured into a saturated aqueous NH_4Cl (30 mL), followed by extraction with Et_2O (20 mL×5). The organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography of the residue using hexane yielded 1-(tributylstannyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**5-Sn**), as contaminated by ca. 40 wt % of tetrabutyltin.

5.2.1. 1-(Tributylstannyl)-2,3,4,4,5,5-heptafluorocyclopentene (*5-Sn*)

^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.3 Hz, 9H), 1.1−1.2 (m, 6H), 1.3−1.4 (m, 6H), 1.5−1.6 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 10.62, 13.48, 27.01, 28.56, 111.21 (tq, J=261.8, 25.8 Hz), 111.27 (tquint.d, J=276.8, 24.5, 1.9 Hz), 119.32 (tddt, J=252.9, 46.2, 45.7, 4.3 Hz), 126.25 (dtquint., J=35.8, 35.8, 4.3 Hz), 162.0−165.3 (dm, J=285.0 Hz); ^{19}F NMR ($CDCl_3$) δ −129.38 (s, 2F), −119.18 (br s, 1F), −119.14 (br s, 1F), −117.8 to −117.7 (m, 1F), −100.3 to −100.2 (m, 2F); IR (neat) 2961, 2857, 1655, 1466, 1355, 958 cm^{-1}; HRMS (FAB) found: *m/z* 482.1015, calcd for (M^+) $C_{17}H_{27}F_7Sn$: 482.1023.

5.3. Typical procedure for the coupling reaction of *5-Sn* with benzaldehyde through Sn−Li exchange reaction

A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with 40 wt % solution of **5-Sn** (0.241 g, 0.2 mmol) in THF (1 mL). To this solution was slowly added a 1.6 M hexane solution of *n*-BuLi (0.19 mL, 0.3 mmol) via a syringe at −78 °C. The whole mixture was stirred at the same temperature for 1 h. After being stirred at −78 °C for 1 h, the reaction mixture was treated with 0.106 g (1.0 mmol) of benzaldehyde at −78 °C for 1 h. After stirring for 1 h, the reaction mixture was poured into ice-cooled saturated aqueous NH_4Cl (30 mL), followed by extraction with Et_2O (30 mL×3). The organic layers were washed with 5% aqueous KF solution, and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography of the residue using hexane/ethyl acetate (12:1) yielded pure 1-phenyl-(2,3,3,4,4,5,5-heptafluorocyclopenten-1-yl)methanol (**7a**, 0.033 g, 61%). The coupling product **7j** could not be separated as a pure product.

5.3.1. (2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)phenylmethanol (*7a*)

^1H NMR ($CDCl_3$) δ 2.81 (d, J=4.3 Hz, 1H), 5.69 (br s, 1H), 7.3−7.4 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 67.54, 110.03 (tquint.d,

J=274.4, 23.9, 4.1 Hz), 110.63 (tq, J=259.5, 24.0 Hz), 115.29 (ttdt, J=258.7, 24.8, 10.7, 2.5 Hz), 125.23 (tt, J=24.8, 5.8 Hz), 126.14, 129.14, 129.26, 138.42, 150.7–154.7 (dm, J=298.4 Hz); ^{19}F NMR ($CDCl_3$) δ −131.49 (dd, J=239.2, 4.9 Hz, 1F), −130.43 (d, J=239.2 Hz, 1F), −128.9 to −128.6 (m, 1F), −120.79 (dd, J=261.0, 14.7 Hz, 1F), −118.57 (dd, J=261.0, 14.7 Hz, 1F), −110.43 (dd, J=258.3, 12.0 Hz, 1F), −107.50 (dd, J=258.3, 12.0 Hz, 1F); IR (neat) 3376, 3070, 1709, 1456, 1385, 1204, 1155 cm^{-1}; HRMS (EI) found: m/z 300.0388, calcd for (M^+) $C_{12}H_7F_7O$: 300.0385.

5.3.2. (2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-4-methylphenylmethanol (**7b**)

^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 2.46 (d, J=4.8 Hz, 1H), 5.68 (br s, 1H), 7.22 (AB q, J=8.0 Hz, 2H), 7.30 (AB q, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.17, 67.62, 110.00 (tquint.d, J=273.6, 21.5, 3.3 Hz), 110.63 (tqd, J=282.7, 24.0, 2.4 Hz), 115.29 (ttd, J=260.4, 29.7, 7.4 Hz), 125.40 (td, J=29.7, 5.8 Hz), 126.13, 129.83, 135.55, 139.35, 150.7–154.6 (dm, J=294.3 Hz); ^{19}F NMR ($CDCl_3$) δ −131.48 (dd, J=239.2, 4.9 Hz, 1F), −130.13 (d, J=239.2 Hz, 1F), −129.2 to −128.9 (m, 1F), −120.79 (dd, J=263.2, 14.7 Hz, 1F), −118.51 (dd, J=263.2, 14.7 Hz, 1F), −110.48 (dd, J=256.9, 12.0 Hz, 1F), −107.55 (dd, J=256.9, 12.0 Hz, 1F); IR (neat) 3323, 2928, 1708, 1330, 1275, 1156, 1083 cm^{-1}; HRMS (FAB) found: m/z 314.0548, calcd for (M^+) $C_{13}H_9F_7O$: 314.0542.

5.3.3. 4-Chlorophenyl-(2,3,3,4,4,5,5-heptafluorocyclopenten-1-yl)methanol (**7c**)

^{1}H NMR ($CDCl_3$) δ 2.50 (br s, 1H), 5.73 (br s, 1H), 7.35–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 66.72, 110.07 (tquint.d, J=276.1, 24.0, 4.9 Hz), 110.52 (tqd, J=259.5, 22.4, 4.1 Hz), 115.24 (ttd, J=258.7, 28.0, 9.9 Hz), 124.78 (tt, J=23.3, 5.8 Hz), 127.47, 129.35, 135.20, 136.82, 151.0–154.9 (dm, J=299.3 Hz); ^{19}F NMR ($CDCl_3$) δ −131.47 (dd, J=239.2, 4.9 Hz, 1F), −130.41 (d, J=239.2 Hz, 1F), −128.3 to −128.1 (m, 1F), −120.81 (dd, J=261.3, 14.7 Hz, 1F), −118.62 (dd, J=261.3, 14.7 Hz, 1F), −110.39 (dd, J=258.7, 9.8 Hz, 1F), −107.37 (dd, J=258.7, 9.8 Hz, 1F); IR (neat) 3401, 2928, 1708, 1494, 1301, 1205, 1159, 1085 cm^{-1}; HRMS (FAB) found: m/z 333.9987, calcd for (M+H) $C_{12}H_6ClF_7O$: 333.9995.

5.3.4. 1-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)phenylpropan-1-ol (**7d**)

^{1}H NMR ($CDCl_3$) δ 2.05–2.30 (m, 3H), 2.70–2.90 (m, 2H), 4.68 (br s, 1H), 7.18–7.38 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −131.43 (d, J=239.2 Hz, 1F), −130.52 (d, J=239.2 Hz, 1F), −129.7 to −129.5 (m, 1F), −120.60 (dd, J=243.7, 14.7 Hz, 1F), −118.93 (dd, J=243.7, 14.7 Hz, 1F), −110.13 (dd, J=256.1, 9.8 Hz, 1F), −107.94 (dd, J=256.1, 9.8 Hz, 1F); IR (neat) 3424, 3030, 2930, 1709, 1497, 1455, 1372, 1276, 1157, 1121 cm^{-1}; HRMS (FAB) found: m/z 328.0710, calcd for (M^+) $C_{14}H_{11}F_7O$: 328.0698.

5.3.5. Cyclohexyl-(2,3,3,4,4,5,5-heptafluorocylopenten-1-yl)methanol (**7e**)

^{1}H NMR ($CDCl_3$) δ 1.04–1.35 (m, 5H), 1.45–2.02 (m, 7H), 4.38 (br s, 1H); ^{19}F NMR ($CDCl_3$) δ −131.76 (dd, J=239.2, 4.9 Hz, 1F), −130.31 (d, J=239.2 Hz, 1F), −129.4 to −129.2 (m, 1F), −121.12 (dd, J=261.3, 12.0 Hz, 1F), −118.27 (dd, J=261.3, 12.0 Hz, 1F), −111.28 (dd, J=263.6, 4.9 Hz, 1F), −106.58 (dd, J=263.6, 4.9 Hz, 1F); IR (neat) 3423, 2933, 1708, 1422, 1330, 1271, 1158, 1122 cm^{-1}; HRMS (FAB) found: m/z 307.0931, calcd for (M+H) $C_{12}H_{14}F_7O$: 307.0934.

5.3.6. 1-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-3-phenyl-2-propen-1-ol (**7f**)

^{1}H NMR ($CDCl_3$) δ 2.34 (br s, 1H), 5.34 (d, J=6.8 Hz, 1H), 6.32 (dd, J=15.0, 6.8 Hz, 1H), 6.77 (d, J=15.0 Hz, 1H), 7.30–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 66.15, 110.09 (tquint.d, J=275.3, 240, 3.3 Hz), 110.61 (tqd, J=258.6, 23.1, 2.5 Hz), 115.44 (ttdt, J=258.7, 24.8, 9.1, 2.5 Hz), 124.25 (tt, J=28.1, 5.8 Hz), 124.86, 126.92, 128.77, 128.83, 134.36, 135.19, 151.0–155.0 (dm, J=299.2 Hz); ^{19}F NMR ($CDCl_3$) δ −131.33 (d, J=239.2 Hz, 1F), −130.36 (d, J=239.2 Hz, 1F), −129.1 to −128.7 (m, 1F), −120.63 (dd, J=258.7, 14.7 Hz, 1F), −118.74 (dd, J=258.7, 14.7 Hz, 1F), −110.13 (dd, J=256.1, 9.8 Hz, 1F), −107.76 (dd, J=256.1, 9.8 Hz, 1F); IR (neat) 3389, 3031, 2928, 1709, 1495, 1386, 1303, 1205, 1157, 1079 cm^{-1}; HRMS (FAB) found: m/z (M^+) 326.0544, calcd for $C_{14}H_9F_7O$: 326.0542.

5.3.7. 1-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-1-phenylethanol (**7g**)

^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3H), 2.51 (br s, 1H), 7.34–7.48 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.91, 73.39, 109.95 (tquint.d, J=274.4, 26.4, 4.9 Hz), 110.49 (tqd, J=258.7, 25.6, 1.6 Hz), 115.6 (ttd, J=260.3, 24.0, 9.9 Hz), 124.54, 128.57, 128.89, 133.15, 150.2–154.3 (dm, J=297.5 Hz); ^{19}F NMR ($CDCl_3$) δ −131.86 (d, J=239.2 Hz, 1F), −130.91 (d, J=239.2 Hz, 1F), −126.4 to −126.2 (m, 1F), −120.78 (dd, J=256.1, 12.0 Hz, 1F), −119.15 (dd, J=256.5, 12.0 Hz, 1F), −108.71 (dd, J=256.5, 12.0 Hz, 1F), −106.26 (dd, J=256.5, 12.0 Hz, 1F); IR (neat) 3454, 2992, 1696, 1389, 1372, 1280, 1203, 1153, 1052 cm^{-1}; HRMS (EI) found: m/z 314.0547, calcd for (M^+) $C_{13}H_9F_7O$: 314.0542.

5.3.8. 1-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-1-(4-methylphenyl)ethanol (**7h**)

^{1}H NMR ($CDCl_3$) δ 1.93 (s, 3H), 2.47 (s, 3H), 2.42 (br s, 1H), 7.21 (AB q, J=8.0 Hz, 2H), 7.33 (AB q, J=8.0 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −131.82 (d, J=242.5 Hz, 1F), −130.61 (d, J=242.5 Hz, 1F), −126.7 to −126.4 (m, 1F), −120.67 (dd, J=256.1, 12.0 Hz, 1F), −119.21 (dd, J=256.1, 12.0 Hz, 1F), −108.59 (dd, J=28.7, 12.0 Hz, 1F), −106.46 (dd, J=258.7, 12.0 Hz, 1F); IR (neat) 3636, 1696, 1388, 1333, 1280, 1203, 1155, 1051 cm^{-1}; HRMS (FAB) found: m/z 328.0706, calcd for (M^+) $C_{14}H_{11}F_7O$: 328.0698.

*5.3.9. 1-(4-Chlorophenyl)-1-(2,3,3,4,4,5,5-heptafluorocyclopenten-1-yl)ethanol (**7i**)*

^{1}H NMR ($CDCl_3$) δ 1.93 (s, 3H), 2.67 (br s, 1H), 7.34–7.43 (m, 4H); ^{19}F NMR ($CDCl_3$) δ −131.96 (dd, J=239.1, 4.9 Hz, 1F), −130.89 (dd, J=239.1, 4.9 Hz, 1F), −126.0 to −125.8 (m, 1F), −120.95 (dd, J=253.8, 14.7 Hz, 1F), −119.07 (dd, J=253.8, 14.7 Hz, 1F), −108.91 (dd, J=258.3, 12.4 Hz, 1F), −106.00 (dd, J=258.3, 12.4 Hz, 1F); IR (neat) 3465, 2931, 1697, 1492, 1389, 1284, 1204, 1155 cm^{-1}; HRMS (FAB) found: m/z (M^+) 348.0161, calcd for $C_{13}H_8ClF_7$: 348.0152.

*5.3.10. 1-(2,3,3,4,4,5,5-Heptafluorocyclopenten-1-yl)-1-methyl-3-phenyl-2-propen-1-ol (**7j**)*

^{1}H NMR ($CDCl_3$) δ 1.77 (s, 3H), 2.42 (br s, 1H), 6.36 (d, J=16.0 Hz, 1H), 6.73 (d, J=16.0 Hz, 1H), 7.25–7.41 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −131.09 (br s, 2F), −126.79 to −126.65 (m, 1F), −120.15 (dd, J=261.0, 17.3 Hz, 1F), −119.42 (dd, J=261.0, 17.3 Hz, 1F), −107.82 (dd, J=258.7, 12.4 Hz, 1F), 107.05 (dd, J=258.7, 12.4 Hz, 1F).

*5.4. Typical procedure for Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloroformate*

A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a solution of 10 mol % of $Pd_2(dba)_3\cdot CHCl_3$ (0.021 g, 0.02 mmol), 20 mol % of dppf (0.022 g, 0.04 mmol), benzyl chloroformate (**8k**, 0.075 g, 0.44 mmol), 5 mol % of CuI (0.002 g, 0.01 mmol) in THF. To the solution was slowly added 0.241 g of 1-(tributylstannyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**5-Sn**, 0.2 mmol, 40 wt % solution) in THF (1 mL) via a syringe at 0 °C. The whole mixture was stirred at reflux temperature for 2 h. After stirring for 2 h, the reaction mixture was filtered on Celite and concentrated in vacuo. Column chromatography of the residue using pentane gave pure product, 1-benzyl-2,3,3,4,4,5,5-heptafluorocyclopentene **9k**. The allylated product **9l** could not be isolated as a pure product due to the low boiling point and volatility. ^{19}F NMR of **9l** was as follows: δ ($CDCl_3$) −134.25 to −134.22 (m, 1F), −130.65 (br s, 2F), −119.38 (br s, 2F), −111.33 (br s, 2F).

*5.4.1. 1-Benzyl-2,3,3,4,4,5,5-heptafluorocyclopentene (**9k**)*

^{1}H NMR ($CDCl_3$) δ 3.68 (s, 2H), 7.25–7.29 (m, 2H), 7.28–7.30 (m, 1H), 7.35–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.13, 110.34 (tquint.d, J=274.8, 24.5, 4.4 Hz), 110.96 (tq, J=259.2, 23.3 Hz), 115.65 (ttd, J=261.3, 9.9, 3.5 Hz), 123.60 (ttd, J=25.9, 5.7, 5.7 Hz), 127.62, 128.70, 129.04, 134.05, 152.0–154.9 (dm, J=299.7 Hz); ^{19}F NMR ($CDCl_3$) δ −133.8 to −133.7 (m, 1F), −130.59 (s, 2F), −119.3 (s, 1F), −119.2 (s, 1F), −111.1 (s, 1F), −111.0 (s, 1F); IR (neat) 3036, 2931, 1716, 1605, 1497, 1456, 1383, 1151, 755 cm^{-1}; HRMS (FAB) found: m/z 284.0425, calcd for (M^+) $C_{12}H_7F_7$: 284.0436.

*5.5. Typical procedure for Pd(0)-catalyzed cross-coupling reaction of **5-Sn** with benzyl chloride*

A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum, and an inlet tube for argon was charged with a solution of 10 mol % of $Pd_2(dba)_3\cdot CHCl_3$ (0.021 g, 0.02 mmol), 20 mol % of dppf (0.022 g, 0.04 mmol), benzyl chloride (**10k**, 0.056 g, 0.44 mmol), 10 mol % of CuBr (0.003 g, 0.02 mmol) in THF. To the solution was slowly added 0.2 mmol of 1-(tributylstannyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**5-Sn**) in THF (1 mL) via a syringe at 0 °C. The whole mixture was stirred at reflux temperature for 2 h. After stirring for 2 h, the resultant mixture was filtered on Celite and concentrated in vacuo. Column chromatography of the residue using pentane gave pure product, 1-benzyl-2,3,3,4,4,5,5-heptafluorocyclopentene **9k** (0.023 g, 41%). The products **9q** and **9r** could not be isolated as a pure product due to their low boiling point and volatility.

*5.5.1. 1-(4-Methoxybenzyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9n**)*

^{1}H NMR ($CDCl_3$) δ 3.62 (br s, 2H), 3.80 (s, 3H), 6.87 (AB q, J=8.6 Hz, 2H), 7.14 (AB q, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.37, 55.25, 110.19 (tquint.d, J=278.0, 24.1, 4.8 Hz), 110.83 (tt, J=258.4, 22.9 Hz), 114.379, 115.54 (ttdt, J=282.3, 24.7, 10.9, 2.8 Hz), 123.80 (tq, J=26.3, 6.0 Hz), 125.819, 129.761, 151.5–155.5 (dm, J=295.5 Hz), 159.90; ^{19}F NMR ($CDCl_3$) δ −134.4 to −134.3 (m, 1F), −130.60 (s, 2F), −119.247 (br s, 1F), −119.217 (br s, 1F), −111.090 (br s, 1F), −111.064 (br s, 1F); IR (neat) 3004, 2937, 2840, 1714, 1613, 1515, 1382, 1252, 1202, 1150 cm^{-1}; HRMS (FAB) found: m/z (M^+) 314.0548, calcd for $C_{13}H_9F_7O$: 314.0542.

*5.5.2. 1-(4-Methylbenzyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9o**)*

^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3H), 3.64 (br s, 2H), 7.11 (AB q, J=8.0 Hz, 2H), 7.15 (AB q, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.03, 26.78, 110.21 (tquint.d, J=275.2, 25.6, 4.9 Hz), 110.94 (tqd, J=258.6, 22.4, 1.6 Hz), 115.54 (ttdt, J=260.3, 24.0, 11.5, 3.3 Hz), 123.69 (tq, J=26.4, 5.8 Hz), 128.54, 129.68, 130.87, 137.33, 151.1–155.2 (dm, J=293.5 Hz); ^{19}F NMR ($CDCl_3$) δ −134.1 to −134.0 (m, 1F), −130.60 (s, 2F), −119.28 (br s, 1F), −119.24 (br s, 1F), −111.08 (br s, 1F), −111.05 (br s, 1F); IR (neat) 2927, 1715, 1517, 1382, 1326, 1289, 1203, 1152 cm^{-1}; HRMS (EI) found: m/z (M^+) 298.0598, calcd for $C_{13}H_9F_7$: 298.0592.

*5.5.3. 1-(4-Cyanobenzyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9p**)*

^{1}H NMR ($CDCl_3$) δ 4.60 (br s, 2H), 7.50 (AB q, J=8.0 Hz, 2H), 7.66 (AB q, J=8.0 Hz, 2H); ^{19}F NMR ($CDCl_3$) δ −132.0 to −131.9 (m, 1F), −130.49 (s, 2F), −119.31 (br s, 1F), −119.27 (br s, 1F), −110.82 (br s, 1F), −110.79 (br s, 1F); IR (neat) 2944, 2254, 2232, 1383, 1267, 1154 cm^{-1}; HRMS (FAB) found: m/z (M+H) 310.0485, calcd for $C_{13}H_7F_7N$: 310.0467.

*5.5.4. 1-(2-Furyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9q**)*

^{1}H NMR ($CDCl_3$) δ 3.72 (br s, 2H), 6.19 (d, J=2.8 Hz, 1H), 6.33 (dd, J=2.8, 2.4 Hz, 1H), 7.37 (d, J=2.4 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −134.8 to −132.8 (m, 1F), −130.67 (s, 2F), −119.55 (br s, 1F), −119.51 (br s 1F), −111.97 (br s, 1F), −111.94 (br s, 1F); HRMS (EI) found: m/z (M^+) 274.0218, calcd for $C_{10}H_5F_7O$: 274.0229.

*5.5.5. 1-(2-Thienyl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9r**)*

^{1}H NMR ($CDCl_3$) δ 3.89 (br s, 2H), 6.91−6.94 (m, 1H), 6.97 (dd, J=5.6, 3.2 Hz, 1H), 7.23 (dd, J=5.2, 1.2 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −132.8 to −132.5 (m, 1F), −130.67 (s, 2F), −119.51 (br s, 1F), −119.47 (br s, 1F), −111.33 (br s, 1F), −111.30 (br s, 1F); HRMS (EI) found: m/z (M^+) 289.9994, calcd for $C_{10}H_5F_7S$: 290.0000.

*5.5.6. 1-((E)-3-Phenyl-2-propen-1-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9s**)*

^{1}H NMR ($CDCl_3$) δ 3.28 (d, J=5.2 Hz, 2H), 6.13 (dt, J=15.6, 5.2 Hz, 1H), 6.57 (d, J=15.6 Hz, 1H), 7.23−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.81, 110.18 (tquint.d, J=275.2, 25.6, 4.9 Hz), 110.82 (tqd, J=258.7, 24.8, 1.7 Hz), 115.60 (tqt, J=260.3, 10.8, 2.5 Hz), 120.65, 122.78 (tq, J=25.6, 5.8 Hz), 126.38, 128.03, 128.66, 134.43, 136.13, 151.2−155.5 (dm, J=307.4 Hz); ^{19}F NMR ($CDCl_3$) δ −134.1 to −133.5 (m, 1F), −130.50 (s, 2F), −119.25 (br s, 1F), −119.21 (br s, 1F), −111.16 (br s, 1F), −111.13 (br s, 1F); IR (neat) 3030, 1715, 1449, 1384, 1298, 1203, 1151, 1118 cm^{-1}; HRMS (FAB) found: m/z (M^+) 310.0587, calcd for $C_{14}H_9F_7$: 310.0592.

*5.5.7. 1-(3-Phenyl-2-propyn-1-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**9t**)*

^{1}H NMR ($CDCl_3$) δ 5.44 (s, 2H), 7.25−7.28 (m, 2H), 7.30−7.40 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 80.49, 94.43, 94.45, 110.08 (tquint.d, J=274.5, 24.0, 5.0 Hz), 110.63 (tqd, J=258.7, 22.3, 2.5 Hz), 115.03 (ttdt, J=259.6, 24.0, 7.4, 3.2 Hz), 119.61 (tq, J=24.0, 4.2 Hz), 127.11, 128.36, 128.77, 131.76, 149.5−153.5 (dm, J=300.0 Hz); ^{19}F NMR ($CDCl_3$) δ −130.80 (s, 2F), −125.1 to −124.7 (m, 1F), −119.04 (br s, 1F), −119.00 (br s, 1F), −109.94 (br s, 1F), −109.91 (br s, 1F); IR (neat) 3064, 1925, 1682, 1451, 1384, 1203, 1151, 997 cm^{-1}; HRMS (EI) found: m/z (M^+) 308.0431, calcd for $C_{14}H_7F_7$: 308.0436.

Acknowledgements

The authors are grateful to Zeon Corporation for supplying the starting material, perfluorocyclopentene (**1**).

References and notes

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